# Supporting information

# Regio-, diastereo- and enantioselectivity in the photocatalytic generation of carbanions via hydrogen atom transfer and reductive radical-polar crossover

Sascha Grotjahn,[a] Lea Müller,[a] Aryaman Pattanaik,[a] Alexander Falk, [b] Giorgia Barison, [c] Jonathan O. Bauer, [b] Julia Rehbein,[a] Ruth M. Gschwind,[a] and Burkhard König*[a]

[a] S. Grotjahn, A. Pattanaik, L. Müller, Prof. Dr. J. Rehbein, Prof. Dr. R. M. Gschwind, Prof. Dr. B. König
Faculty of Chemistry and Pharmacy, Institute of Organic Chemistry
University of Regensburg
Universitätsstraße 31, 93053 Regensburg, Germany
E-mail: burkhard.koenig@ur.de

[b] A. Falk, PD Dr. J. O. Bauer
Faculty of Chemistry and Pharmacy, Institute of Inorganic Chemistry
University of Regensburg
Universitätsstraße 31, 93053 Regensburg, Germany

[c] Giorgia Barison
Department of Chemical Sciences
University of Padova
Via Marzolo 1, 35131 Padova, Italy

# Table of content

# 1 General Information

All reactions were conducted in dried and deoxygenated solvents unless otherwise stated. Ethyl acetate and petroleum ether (PE) for column chromatography and recrystallization were distilled prior to use. Commercially available starting materials were used as received.

### NMR Analysis

NMR-spectra were recorded using a Bruker Avance 400 or Bruker Avance III HD 400 (400 MHz for $^1$H, 101 MHz for $^{13}$C, 376 MHz for $^{19}$F, 79 MHz for $^{29}$Si) at a temperature of 298 K. Chemical shifts are reported in ppm on the $\delta$ scale with the solvent residual signal internal standard wherever possible. Abbreviations for the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. Spectra were analyzed using Topspin 4.3.0. The degree of mono-deuteration of slightly overlapping signals was determined *via* deconvolution using the mldcon -pp function of Topspin 4.3.0.

### Thin Layer Chromatography

With silica gel pre-coated aluminum sheets (Machery-Nagel, silica gel 60 G/UV254, 0.2 mm) were used for thin layer chromatography. Visualization of the separated compounds was achieved by UV-light (254 nm and 365 nm) and by staining with potassium permanganate.

### High Resolution Mass Spectrometry

HRMS were measured at the Central Analytical Laboratory of the University of Regensburg on an Agilent Q-TOF 6540 UHD and a Jeol AccuTOF GCX instrument.

### Elemental Analysis

Elemental analyses were performed on a Vario MICRO cube apparatus.

### Single-Crystal X-Ray Diffraction Analysis

The crystals were selected and measured on a SuperNova Dualflex diffractometer equipped with a TitanS2 detector. Data collection and reduction were performed with CrysAlisPro {Version 1.171.43.36a}.[1] An analytical numeric absorption correction using a multifaceted crystal model, based on expressions derived by Clark and Reid.[2] A numerical absorption correction based on Gaussian integration over a multifaceted crystal model, and an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was applied. Using Olex2,[3] the structures were solved with ShelXT[4] and a least-square refinement on $F^2$ was carried out with ShelXL.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. Hydrogen atoms on sulfur atoms were located from the difference Fourier map and refined without restraints. The figures in the Supporting Information were created with Olex2.[3]

## Chiral HPLC analysis

Chiral HPLC analysis was performed using a CHIRALPAK® AD-3 column (250x 4.6 mm, 3 µm) and CHIRALCEL® OD-H column (250x 4.6 mm, 5 µm) on an Agilent 1260 Infinity II system with photodiode array detector. Enantiomeric excess of benzochromane derivative **5b** was determined at a wavelength of 220 nm. Additionally, absorption at 200 nm, 250 nm and 280 nm was measured to verify the results.

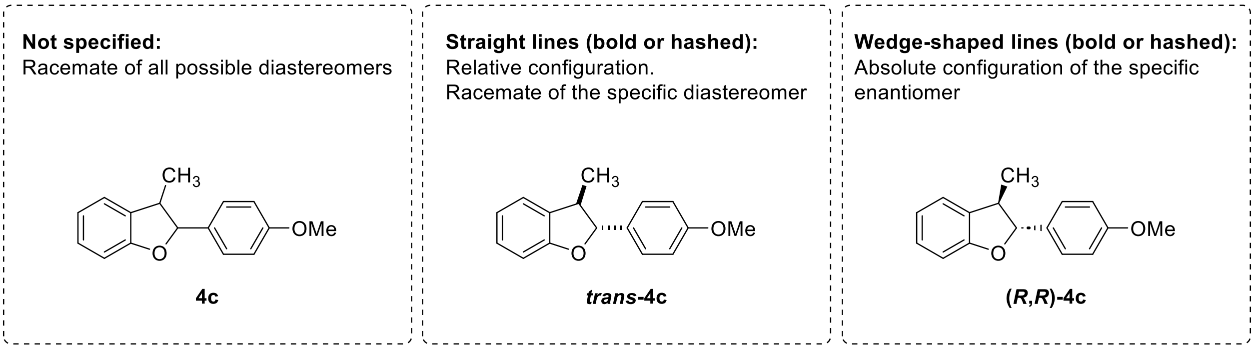
## Graphical representation of stereochemical configuration

Stereochemistry in molecular structures is represented according to IUPAC recommendations.[6]

No stereochemistry specified: The structure or name refers to a mixture of all possible diastereomers in a racemic mixture or is mentioned as a general comment true for any possible stereoisomer. If relevant, the diastereomeric ratio is mentioned separately.

Straight bold or hashed lines: The structure refers to a specific diastereomer as a racemate.

Wedge-shaped lines: The structure refers to a specific enantiomer. Bold wedged bonds point from the stereocenter to above the plain and hashed wedged bonds point from the stereocenter to below the plain. The directionality is from the narrow end representing the atom in plain for both, the bold and the hashed bond.



**Not specified:**
Racemate of all possible diastereomers

**4c**

**Straight lines (bold or hashed):**
Relative configuration.
Racemate of the specific diastereomer

***trans*-4c**

**Wedge-shaped lines (bold or hashed):**
Absolute configuration of the specific enantiomer

**(*R*,*R*)-4c**

**Figure S1.** Graphical representation of stereochemistry as used in this work.

# 2 Photoreactor setups

## Small scale room temperature photoreactions

Room temperature photoreactions were performed in the reactor depicted in Figure S2. Reagents were placed in 6 mL crimp-capped vials. The vials fit into a cooling block kept at 20 °C by a thermostat. The vials were irradiated from below *via* OSRAM Oslon SSL 80 LT-1960 royal-blue LEDs ($\lambda_{max}$ = 440 nm). Stirring was achieved *via* a magnetic stirrer placed below the reactor. Although the emission maximum is reported at 451 nm by the supplier, it was determined to be at 440 nm with a range of approximately 400 – 500 nm.

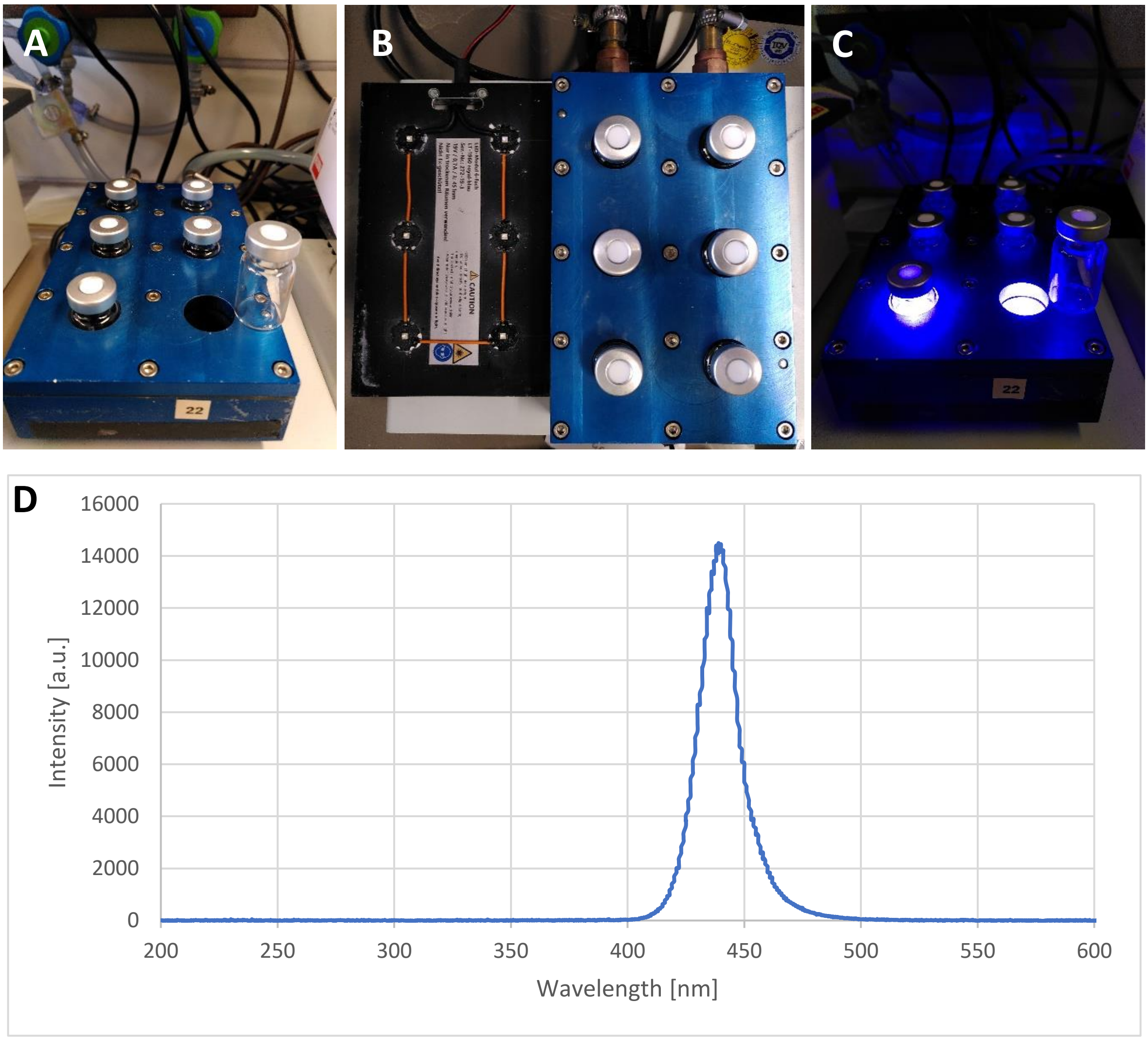


**Figure S2.** Photoreactor setup for small scale reactions. A: Cooling block front view; B: Cooling block and LED module top view; C: Photoreactor setup in operation; D: Emission spectrum of the LEDs.

## Large scale room temperature photoreactions

Large scale room temperature photoreactions were performed in the reactor depicted in Figure S3. All reagents and the solvent were put into the reaction flask together with a stirring bar. Reaction mixtures were degassed by purging with nitrogen gas via a cannula for 20 minutes. Reactions were irradiated by 24 LEDs ($\lambda_{max}$ = 455 nm). The temperature was controlled via a cold finger connected to a thermostat.

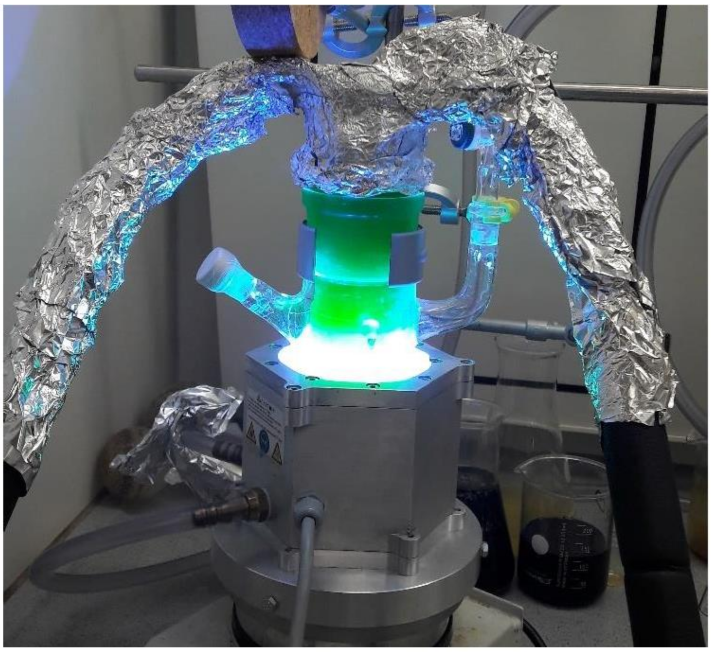


**Figure S3.** Large scale reactor. The green cooling liquid (ethylene glycol/$H_2O$ 1:1) can be seen inside the cold finger.

## Low temperature photoreactions

Low temperature photoreactions were performed in a TAK120 LC photoreactor from HK-Testsysteme GmbH. Temperature was measured via a sensor inside the reaction vials and thus corresponds to the actual reaction temperature. Reactions were irradiated by blue LEDs with an emission maximum at 441 nm at an optical power of 2.5 W/vial.

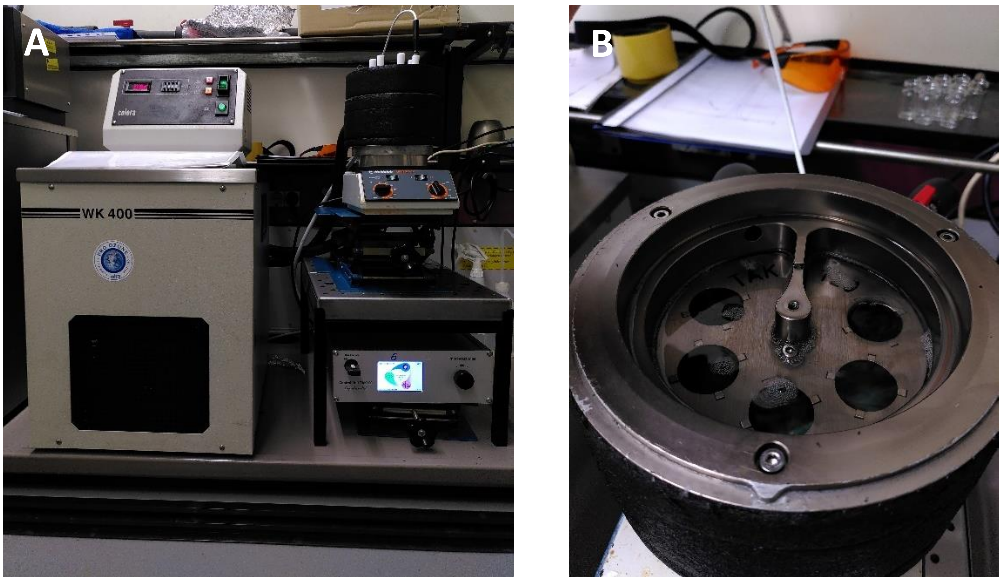


**Figure S4.** Low temperature photoreactor setup. A: complete setup with cryostat, photoreactor and control unit; B: Liquid cooled reactor compartment.

# 3 Synthetic procedures

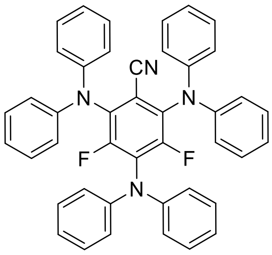
## 3.1 Synthesis of photocatalysts

### General procedure A: Synthesis of literature known cyanobenzene-based photocatalysts

Derived from literature procedure.[7]

Carbazole or diphenylamine (1.1 equiv. per substituted fluorine) is dissolved in anhydrous THF (0.14 M based on the fluorinated benzonitrile derivative). A solution of sodium bis(trimethylsilyl)amide (NaHMDS; 2 M in THF) is added via cannula while cooling in an ice bath. The solution is stirred at room temperature for 30 min. The fluorinated benzonitrile derivative is dissolved in a few mL THF and added dropwise. The reaction mixture is stirred for 24 h at 60 °C. The solvent is removed under reduced pressure and the residue suspended in diethyl ether. The solid is filtered and washed with diethyl ether (40 mL per mmol product). The solid is extracted with chloroform until the extract is almost colorless (roughly 70 mL per mmol product). The solvent is removed under reduced pressure and washed with a 9:1 mixture of hexane/acetone by volume (5 mL per mmol product) and hexane (5 mL per mmol product). The product is dried under high vacuum.

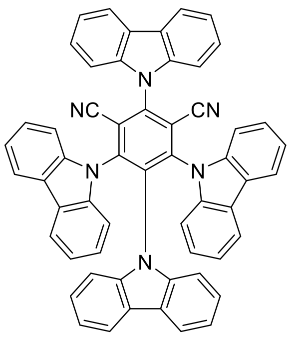
### 3DPA2FBN (1a)



Synthesized according to general procedure A on 1.5 mmol scale from pentafluorobenzonitrile (290 mg, 1.5 mmol) and diphenylamine (838 mg, 4.95 mmol, 3.3 equiv.). The product was obtained as a bright yellow powder (731 mg, 1.24 mmol, 76%). The $^1$H and $^{19}$F NMR spectra are in accordance with literature.[8]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.28 – 7.21 (m, 12+1 H, overlapping with solvent residual signal), 7.07 – 6.93 (m, 18H). **$^{19}$F-NMR (377 MHz, CDCl$_3$):** δ [ppm] = -120.73 (s).

### 2,4,5,6-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, 1b)



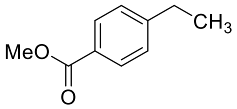
Synthesized according to general procedure A on 5 mmol scale (1.00 g, 5.0 mmol) and carbazole (3.69 g, 4.4 mmol, 4.4 equiv.). The product was obtained as a bright yellow powder (3.20 g, 4.06 mmol, 81%). The $^1$H-NMR spectrum is in accordance with literature. The 4CzIPN used in this work has been synthesized for a previous project.[9] The same batch was used in this work.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.23 (d, *J* = 7.7 Hz, 2H), 7.76 – 7.66 (m, 8H), 7.53 – 7.46 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.13 – 7.04 (m, 8H), 6.87 – 6.79 (m, 4H), 6.67 – 6.60 (m, 2H).

## 3.2 Synthesis of substrates for C-H activation

Note: Synthesis of dihydrobenzofuran derivatives, including the corresponding intermediate carboxylic acids and secondary alcohols, is described in section 5. Other substrates for C-H activation not mentioned in this section were used as received from commercial suppliers.

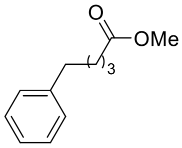
### Methyl 4-ethylbenzoate (2i)



4-Ethylbenzoic acid (1.5 g, 10 mmol) was dissolved in 10 mL methanol. Concentrated sulfuric acid (1.07 mL, 20 mmol, 2 equiv.) were added dropwise and the solution stirred at room temperature for 2 h. The solution was diluted with 50 mL EtOAc, washed with water, saturated aqueous $K_2CO_3$ solution, and brine. The solvent was removed under reduced pressure to yield clean product without further purification (1.61 g, 9.89 mmol, 98%). The NMR spectra are in accordance with literature.[10]

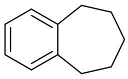
**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.02 – 7.92 (m, 2H), 7.31 – 7.23 (m, 2H), 3.92 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.61 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 167.3, 149.8, 129.8, 128.0, 127.7, 52.0, 29.0, 15.3.

## Methyl 5-phenylpentanoate (2s)



Ester **2s** was synthesized for a previous project. The same batch was used in this work.[11]

## 6,7,8,9-Tetrahydro-5*H*-benzo[7]annulene (3c)

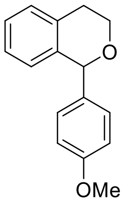


Synthesized according to literature procedure.[12]

6,7,8,9-Tetrahydro-5*H*-benzo[7]annulen-5-one (985 mg, 6.16 mmol, 1 equiv.) was dissolved in 10 mL trifluoroacetic acid. Triethylsilane (1.88 mL, 9.24 mmol, 1.5 equiv.) was added dropwise and the solution stirred at 60 °C overnight. Most of the trifluoroacetic acid was removed under reduced pressure, the residue poured onto ice, exctracted with EtOAc, the organic phase washed with water and brine, dried over $Na_2SO_4$, the solvent removed under reduced pressure, and the crude product purified via column chromatography (PE) to give the product as a colorless liquid. The yield was not determined. The $^1$H NMR spectrum is in accordance with literature.[12]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.12 – 7.06 (m, 4H), 2.83 – 2.75 (m, 4H), 1.88 – 1.79 (m, 2H), 1.70 – 1.59 (m, 4H).

## 1-(4-Methoxyphenyl)isochromane (5b)



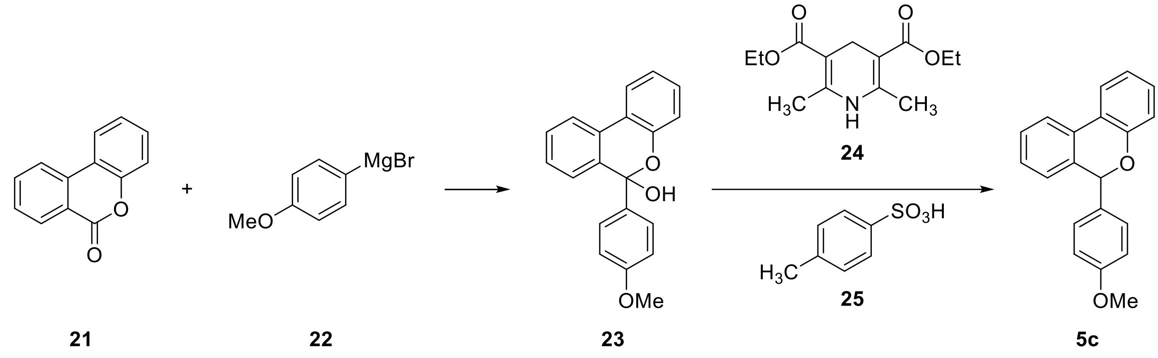
Synthesized according to literature procedure.[13]

Isochromane (2.0 mL, 15.9 mmol, 1 equiv.) and anisole (10 mL, 95.4 mmol, 6 equiv.) were mixed. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 3.97 g, 17.49 mmol, 1.1 equiv.) and $CuCl_2$ (214 mg, 9.5 mmol, 10 mol%) were added and the suspension stirred for 36 h at 100 °C. The solution was filtered, and the product purified via column chromatography (0→10% EtOAc in PE). Recrystallization from EtOAc/*n*-hexane yielded the product as colorless needles (2.39 g, 63%).

The $^1$H NMR spectrum is in accordance with literature.[13]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.25 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 7.12 – 7.05 (m, 1H), 6.90 – 6.85 (m, 2H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.70 (s, 1H), 4.18 (ddd, *J* = 11.3, 5.5, 3.9 Hz, 1H), 3.92 (ddd, *J* = 11.4, 9.4, 4.0 Hz, 1H), 3.81 (s, 3H), 3.19 – 3.06 (m, 1H), 2.81 (dt, *J* = 16.3, 3.9 Hz, 1H).

## 6-(4-Methoxyphenyl)-6*H*-benzo[*c*]chromen-6-ol (5c)



Synthesized according to literature procedure.[14]

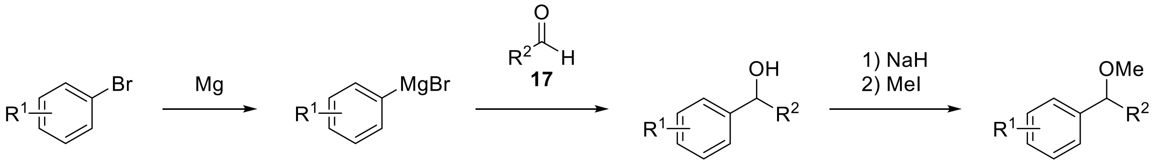
Step 1: A Grignard-solution was prepared from 4-bromo anisole (608 mg, 3.25 mmol, 1.3 equiv.) and activated magnesium turnings (91 mg, 3.75 mmol, 1.3 equiv.) in 3.25 mL THF. 6*H*-Benzo[*c*]chromen-6-one (**21**, 491 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 5 mL THF and the solution cooled to -78 °C. The Grignard solution was added dropwise, and the cooling bath removed. The solution was stirred for 2 h at room temperature, quenched with saturated aqueous $NH_4Cl$ solution, extracted with EtOAc, the organic phase washed with brine, dried over $Na_2SO_4$, the solvent removed under reduced pressure, and the crude product purified via column chromatography (10→20% EtOAc in PE) to yield the intermediate **23** as a slightly yellow solid (614 mg, 2.02 mmol, 81%).

Step 2: 6-(4-Methoxyphenyl)-6*H*-benzo[*c*]chromen-6-ol (**23**, 380 mg, 1.25 mmol, 1 equiv.), Hantz´sch ester (**24**, 380 mg, 1.5 mmol, 1.2 equiv.) and *p*-toluenesulfonic acid (**25**, 43 mg, 250 µmol, 20 mol%) were dissolved in 5 mL DCM and the solution stirred at room temperature for 1 h. The Solution was then diluted with EtOAc (50 mL), washed with saturated aqueous $K_2CO_3$ solution and brine, dried over $Na_2SO_4$, the solvent removed under reduced pressure and the crude product purified via column chromatography (0→20% EtOAc in PE) to yield the product as slightly yellow solid (350 mg, 1.21 mmol, 97%).

The NMR spectra are in accordance with literature.[14]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.82 – 7.72 (m, 2H), 7.44 – 7.37 (m, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.17 (m, 2H), 7.04 (td, *J* = 7.5, 1.1 Hz, 1H), 6.98 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.92 – 6.85 (m, 3H), 6.14 (s, 1H), 3.80 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.8, 153.8, 134.3, 131.9, 130.2, 129.71, 129.66, 128.5, 127.7, 126.4, 123.2, 122.9. 122.20, 122.16, 118.1, 114.0, 79.5, 55.4.

## Synthesis of benzyl alcohol methyl ethers



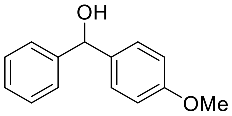
## General procedure B: Synthesis of benzyl alcohols

A 1 M or 1.5 M (specified in the specific reaction procedures) solution of the respective aryl bromide (**26**, 1 equiv.) in THF is prepared. A small portion of the solution is added to activated magnesium turnings (1.1 equiv.) to just cover the magnesium. A grain of iodine is added, and the solution heated with a heat gun until boiling without stirring. The start of the reaction is evident by fading of the color. The heating is stopped, and the remaining solution added dropwise while stirring to keep the reaction gently refluxing. After addition of all aryl bromide stirring is continued until the solution has cooled to room temperature. The respective aldehyde (**17**, 1.2 equiv.) is dissolved in a small amount of THF (solid aldehydes) or added directly to the Grignard solution (liquid aldehydes) at room temperature. The solution is stirred at room temperature for 2 h, quenched with saturated aqueous $NH_4Cl$ solution, extracted with EtOAc, the organic phase washed with 1 M HCl, water and brine, dried over $Na_2SO_4$, and the solvent removed under reduced pressure. The crude alcohol is purified via column chromatography with appropriate mixtures of EtOAc/PE. The products were then methylated according to general procedure C.

### General procedure C: Synthesis of benzyl alcohol methyl ethers

Sodium hydride (2 equiv.) is suspended in THF. A solution of secondary alcohol (obtained according to general procedure B or if available from a commercial supplier) in THF is added slowly while stirring and cooling in an ice bath. The suspension is then stirred at room temperature until the hydrogen evolution stops (1-2 h). Methyl iodide (1.5 equiv.) is added, and the reaction mixture stirred at room temperature for 2 h. Saturated aqueous $NH_4Cl$ solution is then added, the mixture extracted with EtOAc, the organic phase washed with water and brine, dried over $Na_2SO_4$ and the solvent evaporated under reduced pressure. The crude product is purified via column chromatography with appropriate mixtures of EtOAc/PE.

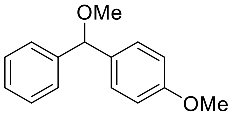
### (4-Methoxyphenyl)(phenyl)methanol (18m)



Synthesized according to general procedure B from 4-bromoanisole (16.5 mmol scale) and benzaldehyde. The Grignard solution was prepared as a stock solution on 150 mmol scale (1.5 M) and 11 mL (16.5 mmol) were used for this reaction. The product was obtained as a colorless solid (2.64 g, 12.32 mmol, 75%). The NMR spectra are in accordance with literature.[15]

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.40 – 7.24 (m, 7H), 6.90 – 6.84 (m, 2H), 5.80 (s, 1H), 3.79 (s, 3H), 2.25 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 159.2, 144.1, 136.3, 128.6, 128.0, 127.5, 126.5, 114.0, 75.9, 55.4.

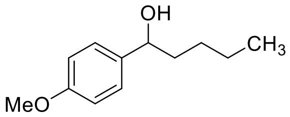
### 1-Methoxy-4-(methoxy(phenyl)methyl)benzene (7a)



Synthesized according to general procedure C from alcohol **18m** (536 mg, 2.5 mmol). The product was obtained as colorless liquid (454 mg, 1.99 mmol, 80%). The NMR spectra are in accordance with literature.[16]

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.37 – 7.30 (m, 4H), 7.29 – 7.12 (m, 3H), 6.89 – 6.84 (m, 2H), 5.21 (s, 1H), 3.78 (s, 3H), 3.37 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 159.1, 142.5, 134.4, 128.5, 128.4, 127.5, 126.9, 113.9, 85.1, 57.0, 55.4.

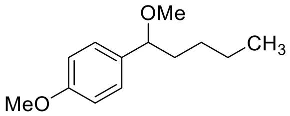
### 1-(4-Methoxyphenyl)pentan-1-ol (18n)



Synthesized according to general procedure B from 4-bromoanisole (16.5 mmol scale) and *n*-pentanal. The Grignard solution was prepared as a stock solution on 150 mmol scale (1.5 M) and 11 mL (16.5 mmol) were used for this reaction. The product was obtained as a colorless solid (2.64 g, 12.32 mmol, 75%). The NMR spectra are in accordance with literature.[17]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.31 – 7.22 (m, 2H), 6.91 – 6.84 (m, 2H), 4.60 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 1.89 – 1.75 (m, 2H), 1.74 – 1.62 (m, 1H), 1.42 – 1.28 (m, 3H), 1.28 – 1.14 (m, 1H), 0.88 (t, *J* = 7.1 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.1, 137.2, 127.3, 113.9, 55.4, 38.8, 28.2, 22.7, 14.1.

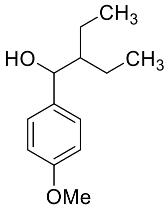
### 1-Methoxy-4-(1-methoxypentyl)benzene (7c)



Synthesized according to general procedure C from alcohol **18n** (2.5 mmol). The product was obtained as colorless liquid (450 mg, 2.16 mmol, 86%). The NMR spectra are in accordance with literature.[18]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.24 – 7.16 (m, 2H), 6.93 (m, 2H), 4.02 (t, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 3.17 (s, 3H), 1.87 – 1.74 (m, 1H), 1.66 – 1.54 (m, 1H), 1.40 – 1.24 (m, 3H), 1.24 – 1.13 (m, 1H), 0.86 (t, *J* = 7.1 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.1, 134.7, 128.0, 113.8, 83.8, 56.5, 55.4, 37.9, 28.2, 22.8, 14.1.

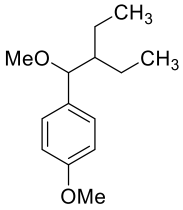
### 2-Ethyl-1-(4-methoxyphenyl)butan-1-ol (18o)



Synthesized according to general procedure B from 4-bromoanisole (33.0 mmol) and 2-ethyl butanal. The Grignard solution was prepared as a stock solution on 150 mmol scale (1.5 M) and 22 mL (16.5 mmol) were used for this reaction. The product was obtained as a colorless liquid (4.10 g, 19.68 mmol, 60%). The NMR spectra are in accordance with literature.[19]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.27 – 7.20 (m, 2H), 6.90 – 6.84 (m, 2H), 4.55 (d, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 1.79 (s, 1H), 1.60 – 1.38 (m, 3H), 1.33 – 1.21 (m, 1H), 1.20 – 1.07 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 158.9, 136.3, 127.8, 113.7, 75.7, 55.3, 47.8, 21.7, 20.8, 11.3, 10.9.

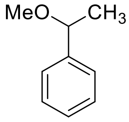
## 1-(2-Ethyl-1-methoxybutyl)-4-methoxybenzene (7d)



Synthesized according to general procedure C from alcohol **18o** (2.5 mmol). The product was obtained as colorless liquid (400 mg, 1.80 mmol, 74%).

**TLC:** $R_f$ = 0.41 (hexanes/EtOAc 20:1). **$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.22 – 7.13 (m, 2H), 6.92 – 6.83 (m, 2H), 3.93 (d, *J* = 6.9 Hz, 1H), 3.81 (s, 3H), 3.16 (s, 3H), 1.59 – 1.39 (m, 3H), 1.31 – 1.18 (m, 1H), 1.13 – 0.99 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 159.0, 133.5, 128.7, 113.6, 85.5, 56.8, 55.3, 47.3, 21.6, 21.1, 11.2, 10.9. **HRMS (EI+):** exact mass calcd for $C_{14}H_{22}O_2^+$ $[M]^+$: m/z = 222.16143, found: 222.16178.

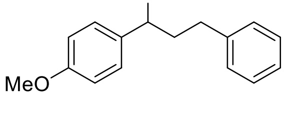
## (1-Methoxyethyl)benzene (7e)



Synthesized according to general procedure C from commercially available 1-phenylethanol (12.28 mmol). The product was obtained as colorless liquid. The yield was not determined. The $^1$H NMR spectrum is in accordance with literature.[20]

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.38 – 7.25 (m, 5H), 4.30 (q, *J* = 6.5 Hz, 1H), 3.23 (s, 3H), 1.44 (d, *J* = 6.5 Hz, 3H).

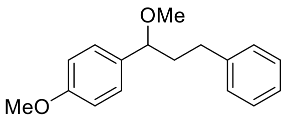
## 1-(4-Methoxyphenyl)-2-phenylpropan-1-ol (18p)



Synthesized according to general procedure B from 4-bromoanisole (33.0 mmol scale) and 2-phenylethanal. The Grignard solution was prepared as a stock solution on 150 mmol scale (1.5 M) and 22 mL (16.5 mmol) were used for this reaction. The product was obtained as a colorless liquid (3.80 g, 15.68 mmol, 48%). The NMR spectra are in accordance with literature.[21]

**TLC:** $R_f$ = 0.38 (hexanes/EtOAc 5:1). **$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.32 – 7.26 (m, 4H), 7.23 – 7.17 (m, 3H), 6.02 – 6.87 (m, 2H), 4.64 (t, *J* = 6.6 Hz, 1H), 3.82 (s, 3H), 2.79 – 2.60 (m, 2H), 2.21 – 2.08 (m, 1H), 2.08 – 1.95 (m, 1H), 1.89 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 159.2, 142.0, 136.8, 128.6, 128.5, 127.3, 125.9, 114.0, 73.6, 55.4, 40.5, 32.2.

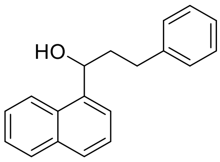
### 1-Methoxy-4-(1-methoxy-3-phenylpropyl)benzene (7f)



Synthesized according to general procedure C from alcohol **18p** (606 mg, 2.5 mmol). The product was obtained as a colorless liquid (480 mg, 1.87 mmol, 75%).

**TLC:** $R_f$ = 0.28 (hexanes/EtOAc 20:1). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.37 – 7.31 (m, 2H), 7.30 – 7.20 (m, 5H), 6.98 – 6.92 (m, 2H), 4.10 (dd, *J* = 7.6, 5.8 Hz, 1H), 3.87 (s, 3H), 3.25 (s, 3H), 2.82 – 2.63 (m, 2H), 2.27 – 2.13 (m, 1H), 2.04 – 1.91 (m, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.2, 142.1, 134.2, 128.6, 128.4, 128.1, 125.9, 113.9, 82.7, 56.5, 55.4, 39.7, 32.2. **HRMS (EI+):** exact mass calcd for $C_{17}H_{20}O_2^+$ [M]$^+$: m/z = 256.14578, found: 256.14529.

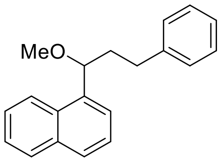
### 1-(Naphthalen-1-yl)-3-phenylpropan-1-ol (18q)



Synthesized according to general procedure B from 1-bromonaphthalene (49.0 mmol scale) and 2-phenylethanal. The Grignard solution was prepared as a stock solution on 150 mmol scale (1 M) and 49.0 mL (49.0 mmol) were used for this reaction. The product was obtained as a colorless liquid (4.2 g, 16.01 mmol, 33%). The NMR spectra are in accordance with literature.[22]

**TLC:** $R_f$ = 0.49 (hexanes/EtOAc 5:1). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.96 – 7.85 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.36 – 7.28 (m, 2H), 7.28 – 7.20 (m, 2H), 5.47 (dd, *J* = 7.4, 5.1 Hz, 1H), 2.96 – 2.79 (m, 2H), 2.33 – 2.18 (m, 2H), 2.05 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 141.9, 140.4, 133.9, 130.4, 129.0, 128.7, 128.1, 126.1, 126.0, 125.7, 125.6, 123.2, 122.9, 70.5, 39.8, 32.5.

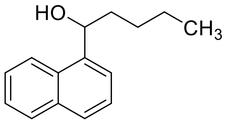
### 1-(1-Methoxy-3-phenylpropyl)naphthalene (7h)



Synthesized according to general procedure C from alcohol **18q** (656 mg, 2.5 mmol). The product was obtained as slightly yellow liquid (314 mg, 1.14 mmol, 45%).

**TLC:** $R_f$ = 0.40 (hexanes/EtOAc 20:1). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.96 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 6.4 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.33 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.84 (dd, *J* = 8.4, 4.3 Hz, 1H), 3.31 (s, 3H), 2.92 – 2.73 (m, 2H), 2.32 – 2.11 (m, 2H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 142.0, 137.9, 134.1, 131.2, 129.0, 128.8, 128.5, 128.0, 125.98, 125.96, 125.6, 124.0, 123.4, 80.7, 57.0, 39.3, 32.5. **HRMS (EI+):** exact mass calcd for $C_{20}H_{20}O^+$ [M]$^+$: m/z = 267.15087, found: 267.15078.

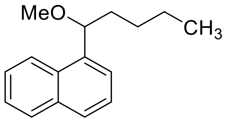
### 1-(Naphthalen-1-yl)pentan-1-ol (18r)



Synthesized according to general procedure B from 1-bromonaphthalene (49.0 mmol scale) and pentanal. The Grignard solution was prepared as a stock solution on 150 mmol scale (1 M) and 49.0 mL (49.0 mmol) were used for this reaction. The product was obtained as a colorless liquid (6.00 g, 28.00 mmol, 57%). The NMR spectra are in accordance with literature.[23]

**TLC:** $R_f$ = 0.56 (hexanes/EtOAc 5:1). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.16 – 8.09 (m, 1H), 7.91 – 7.84 (m, 1H), 7.78 (d, $J$ = 8.20 Hz, 1H), 7.65 (d, $J$ = 6.9 Hz, 1H), 7.56 – 7.44 (m, 3H), 5.47 (dd, $J$ = 7.7, 4.8 Hz, 1H), 2.03 – 1.86 (m, 3H), 1.62 – 1.29 (m, 4H), 0.92 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 140.8, 134.0, 130.6, 129.0, 128.0, 126.1, 125.63, 125.59, 123.3, 122.9, 71.5, 38.2, 28.6, 22.8, 14.2.

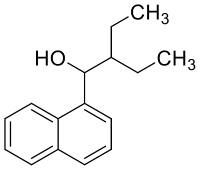
### 1-(1-Methoxypentyl)naphthalene (7i)



Synthesized according to general procedure C from alcohol **18r** (536 mg, 2.5 mmol). The product was obtained as slightly yellow liquid (430 mg, 1.88 mmol, 75%) in low purity.

**TLC:** $R_f$ = 0.48 (hexanes/EtOAc 20:1). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.26 – 8.15 (m, 1H), 7.92 – 7.87 (m, 1H), 7.79 (d, $J$ = 7.7 Hz, 1H), 7.58 – 7.45 (m, 4H), 4.87 (dd, $J$ = 7.5, 5.4 Hz, 1H), 3.29 (s, 3H), 2.01 – 1.83 (m, 2H), 1.43 – 1.27 (m, 4H), 0.89 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 138.2, 134.1, 131.3, 129.0, 127.9, 125.9, 125.55, 125.53, 123.6, 82.1, 57.0, 37.6, 28.7, 22.8, 14.2. **HRMS (EI+):** exact mass calcd for $C_{16}H_{20}O^+$ [M]$^+$: m/z = 228.15087, found: 228.15082.

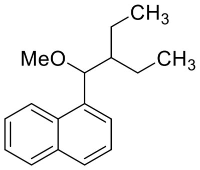
### 2-Ethyl-1-(naphthalen-1-yl)butan-1-ol (18s)



Synthesized according to general procedure B from 1-bromonaphthalene (49.0 mmol scale) and 2-ethylbutanal. The Grignard solution was prepared as a stock solution on 150 mmol scale (1 M) and 49.0 mL (49.0 mmol) were used for this reaction. The product was obtained as a colorless liquid (4.20 g, 18.39 mmol, 54%). The NMR spectra are in accordance with literature.[24]

**TLC:** $R_f$ = 0.63 (hexanes/EtOAc 5:1). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.15 – 8.08 (m, 1H), 7.92 – 7.86 (m, 1H), 7.28 (d, $J$ = 8.2 Hz, 1H), 7.64 (d, $J$ = 7.1 Hz, 1H), 7.55 – 7.44 (m, 3H), 5.49 (d, $J$ = 5.7 Hz, 1H), 1.89 (s, 1H), 1.87 – 1.79 (m, 1H), 1.66 – 1.29 (m, 4H), 0.99 (t, $J$ = 7.4 Hz, 3H), 0.83 (t, $J$ = 7.5 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 139.9, 134.0, 130.8, 129.1, 127.8, 125.9, 125.5, 125.4, 124.2, 123.5, 72.5, 46.7, 22.9, 20.5, 11.8, 11.2.

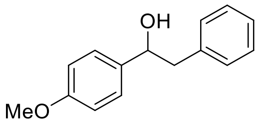
## 1-(2-Ethyl-1-methoxybutyl)naphthalene (7j)



Synthesized according to general procedure C from alcohol **18s** (571 mg, 2.5 mmol). The product was obtained as a slightly yellow liquid (494 mg, 2.04 mmol, 82%) in moderate purity.

**TLC:** $R_f$ = 0.53 (hexanes/EtOAc 20:1). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.24 – 8.13 (m ,1H), 7.93 – 7.83 (m, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.42 (m, 4H), 4.82 (d, *J* = 6.2 Hz, 1H), 3.24 (s, 3H), 1.87 – 1.74 (m, 1H), 1.62 – 1.45 (m, 2H), 1.41 – 1.20 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 137.1, 134.1, 131.8, 129.0, 127.8, 125.7, 125.4, 125.3, 123.8, 83.4, 57.4, 46.6, 22.6, 21.0, 11.7, 11.0. **HRMS (EI+):** exact mass calcd for $C_{17}H_{22}O^+$ $[M]^+$: m/z = 242.16652, found: 242.16596.

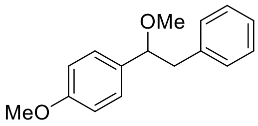
## 1-(4-Methoxyphenyl)-2-phenylethan-1-ol (18t)



Synthesized according to general procedure B from anisaldehyde (1.22 mL, 10 mmol, 1 equiv.) and benzylmagnesium bromide (7.5 mL, 2 M in THF, 15 mmol, 1.5 equiv.). The product was obtained as a colorless solid (1.72 g, 7.5 mmol, 75%). The NMR spectra are in accordance with literature.[25]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.34 – 7.23 (m, 5H), 7.22 – 7.17 (m, 2H), 6.92 – 6.86 (m, 2H), 4.89 – 4.80 (m, 1H), 3.82 (s, 3H), 3.02 (d, *J* = 6.8 Hz, 2H), 2.05 (d, *J* = 2.6 Hz, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.1, 138.3, 136.1, 129.6, 128.5, 127.3, 126.6, 113.9, 75.1, 55.4, 46.1.

## 1-Methoxy-4-(1-methoxy-2-phenylethyl)benzene (7k)



Synthesized according to general procedure C from alcohol **18t** (571 mg, 2.5 mmol). The product was obtained as a slightly yellow liquid (628 mg, 2.75 mmol, 79%). The $^1$H NMR spectrum is in accordance with literature.[26]

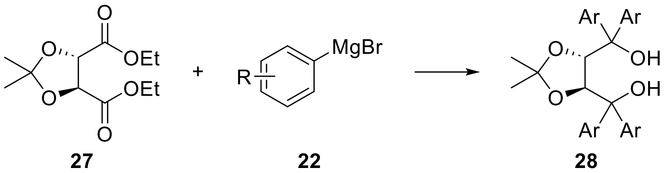
**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.39 – 7.24 (m, 5H), 7.24 – 7.19 (m, 2H), 7.01 – 6.95 (m, 2H), 4.40 (t, *J* = 6.7 Hz, 1H), 3.93 (s, 3H), 3.29 (s, 3H), 3.25 (dd, *J* = 13.7, 7.4 Hz, 1H), 3.00 (dd, *J* = 13.7, 6.1 Hz, 1H) .

## 3.3 Synthesis of chiral silane thiols

### 3.3.1 Synthesis of tartaric acid based chiral silane thiols

### 3.3.1.1 Synthesis of TADDOL derivatives

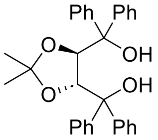
### General procedure D: Synthesis of TADDOL derivatives



A Grignard reagent is prepared by dropwise addition of a 1 M solution of the corresponding aryl bromide (5 – 6 equiv. with respect to ester **27**) in THF to activated magnesium turnings. First, enough of the solution is added to cover the magnesium. A small grain of iodine is added, and the solution heated without stirring until it starts boiling. The heating is stopped and checked if the reaction started, visible from immediate fading of the iodine color. If not, the heating procedure is repeated until reaction is observed. Once the reaction has started, the remaining aryl bromide solution is added dropwise under stirring to keep the reaction gently boiling. After complete addition, the mixture is further stirred until it has reached room temperature.

Diethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (**27**) is dissolved in a few milliliters (the exact amount does not influence the reaction) and added dropwise to the Grignard reagent (strongly exothermic reaction). The reaction mixture is stirred at room temperature for at least 2 h, usually overnight. The reaction is quenched by addition of at least twice the volume of saturated aqueous $NH_4Cl$ solution, extracted with ethyl acetate, washed with water and brine, dried over $Na_2SO_4$, and the solvent removed under reduced pressure. The crude product is purified by dissolving it in a small amount of DCM and addition of *n*-hexane until the solution starts to become cloudy. Cooling at -18 °C overnight completes the crystallization. If the product contains some sticky residues after the first crystallization an additional recrystallization yields the clean product.

### ((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) ((*R*,*R*)-28a)

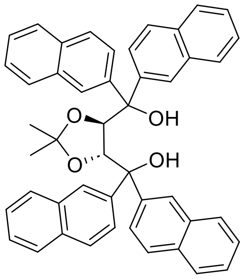


Synthesized according to general procedure D on 6 mmol scale.

The compound was obtained as colorless crystalline solid (2.39 g, 5.12 mmol, 85%). 6.0 mmol scale. The enantiomer **(*S*,*S*)-28a** was also synthesized on 6 mmol scale and obtained as colorless crystalline solid (2.19 g, 4.69 mmol, 78%). The $^1$H NMR spectra are in accordance with literature.[27]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.56 – 7.50 (m, 4H), 7.37 – 7.22 (m, 16H+2H solvent residual signal), 4.61 (s, 2H), 3.85 (s, 2H), 1.04 (s, 6H).

### ((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(di(naphthalen-2-yl)methanol) ((*R*,*R*)-28b)

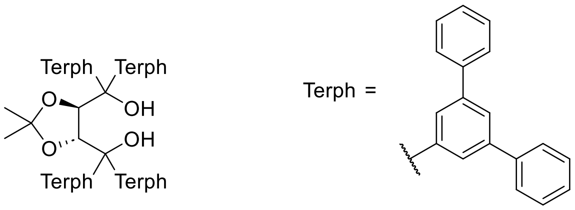


Synthesized according to general procedure D on 6.09 mmol scale.

The compound was obtained as colorless crystalline solid (2.70 g, 4.05 mmol, 66%). The $^{1}$H NMR spectrum is in accordance with literature.[28]

**$^{1}$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.20 (s, 2H), 7.94 (d, *J* = 1.2 Hz, 2H), 7.92 – 7.84 (m, 4H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.76 – 7.64 (m, 6H), 7.56 – 7.47 (m, 6H), 7.47 – 7.38 (m, 4H), 7.28 – 7.22 (m, 2H), 4.99 (s, 2H), 4.31 (s, 2H), 1.19 (s, 6H).

### ((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(di([1,1':3',1''-terphenyl]-5'-yl)methanol) ((*R*,*R*)-28c)



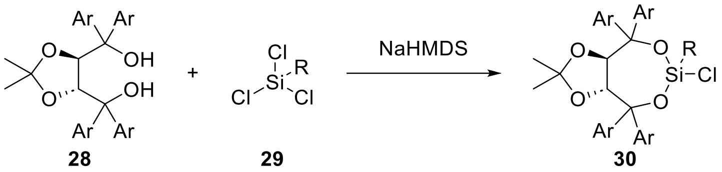
Synthesized according to general procedure D on 934 µmol scale. **28c** is literature known as an intermediate and no NMR spectra were reported.[29–31]

The compound was obtained as colorless crystalline solid (629 mg, 585 µmol, 64%). The enantiomer **(*S*,*S*)-28c** was synthesized on 6 mmol scale and obtained as colorless crystalline solid (4.78 g, 4.45 mmol, 74%).

**$^{1}$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.94 (d, *J* = 1.6 Hz, 4H), 7.80 (t, *J* = 1.6 Hz, 2H), 7.73 (d, *J* = 1.6 Hz, 4H), 7.69 – 7.64 (m, 10H), 7.53 – 7.49 (m, 8H), 7.44 – 7.29 (m, 24H), 5.08 (s, 2H), 4.20 (broad s, 2H), 1.10 (s, 6H). **$^{13}$C{$^{1}$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 146.8, 143.9, 141.7, 141.3, 141.2, 141.0, 128.94, 128.89, 127.52, 127.50, 127.4, 126.5, 125.9, 125.58, 125.55, 110.22, 81.8, 78.7, 27.5.

### 3.3.1.2 Synthesis of TADDOL-silyl chlorides (30)

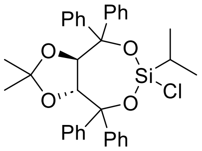
### General procedure E: Synthesis of TADDOL-silyl chlorides



TADDOL-silyl chlorides (**30**) were synthesized by a modified literature procedure.[32]

The TADDOL derivative (**28**) is dissolved in toluene (0.2 M) and NaHMDS (2 M in THF, 2.1 equiv.) is added slowly at 0 °C. The solution is stirred for 1 h at 0 °C and trichlorosilane derivative (**29**) is added at 0 °C. The solution is stirred at room temperature for at least 1 h, usually overnight. Longer stirring (tested up to 4 d) does not influence the reaction outcome. Within seconds after addition of the trichlorosilane the reaction mixture turns into a gel. The Solvent is removed under reduced pressure, the residue extracted with boiling *n*-hexane and filtered. The solvent is removed under reduced pressure and the crude product purified via recrystallization from *n*-hexane. The formation of a gel is not reported in the literature procedure. Also, the literature procedure states that sodium chloride should precipitate and can be filtered off. However, this did not happen in any of the reactions attempted. Still, the reactions proceed quantitatively with losses in yield attributed only to the workup. No side products containing the TADDOL part are observed in the crude NMR. In the literature report the crude product was used without further purification. It is also not required for synthesis of the corresponding silane thiols. However, as purification of silane thiols **10** synthesized in the last step is difficult it is recommended to recrystallize silyl chlorides before use.

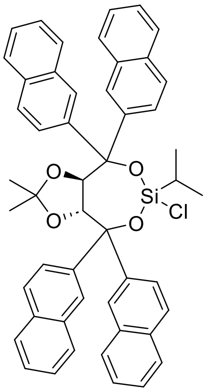
### (3a*R*,8a*R*)-6-Chloro-6-isopropyl-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*R*,*R*)-30a)



Synthesized according to general procedure E from TADDOL (2.5 g, 5.36 mmol) and $^{i}$PrSiCl$_3$. The product was obtained as colorless, crystalline solid (2.6 g, 4.55 mmol, 85%). The enantiomer **(*S*,*S*)-30a** was synthesized from (*S*,*S*)-TADDOL (1.10 g, 2.36 mmol) and obtained as a colorless, crystalline solid (1.03g, 1.80 mmol, 76%). The NMR spectra are in accordance with literature.[32]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.62 – 7.49 (m, 4H), 7.41 – 7.14 (m, 16H), 5.17 (d, *J* = 7.3 Hz, 1H), 5.11 (d, *J* = 7.2 Hz, 1H), 1.16 – 1.02 (m, 1H), 1.02 – 0.90 (m, 6H), 0.56 (s, 3H), 0.52 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.0, 145.9, 142.1, 142.0, 129.6, 129.0, 128.2, 128.0, 127.7, 127.6, 127.29, 127.25, 127.18, 127.1, 114.2, 85.1, 83.0, 80.96, 80.91, 27.2, 16.3, 16.2. **HRMS (EI+):** exact mass calcd for $C_{34}H_{35}ClO_4Si^+$ $[M]^+$: m/z = 570.19877, found: 570.19773.

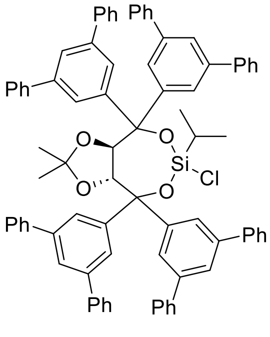
### (3a*R*,8a*R*)-6-chloro-6-isopropyl-2,2-dimethyl-4,4,8,8-tetra(naphthalen-2-yl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*R*,*R*)-30b)



Synthesized according to general procedure E from TADDOL derivative **(*R*,*R*)-28b** (1.33 g, 2.0 mmol) and isopropyltrichlorosilane. The product was obtained as a colorless, crystalline solid (1.40 g, 1.81 mmol, 91%).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.30 – 8.22 (m, 3H), 8.09 (s, 1H), 8.00 – 7.94 (m, 2H), 7.94 – 7.74 (m, 8H), 7.68 (dd, *J* = 8.7, 4.3 Hz, 2H), 7.63 – 7.47 (m, 10H), 7.43 (dt, *J* = 8.7, 1.9 Hz, 2H), 5.55 (d, *J* = 7.3 Hz, 1H), 5.49 (d, J = 7.2 Hz, 1H), 1.34 – 1.22 (m, 1H + 1H overlap with traces of hexane), 1.13 (t, *J* = 7.81 Hz, 6H), 0.68 (s, 3H), 0.61 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 144.1, 143.0, 139.6, 139.4, 132.98, 132.95, 132.94, 132.70, 132.67, 132.61, 131.1, 128.96, 128.95, 128.91, 128.73, 128.80, 128.24, 128.14,128.03, 128.01, 127.7, 127.6, 127.5, 127.3, 126.42, 126.39, 126.36, 126.27, 126.25, 126.23, 126.22, 126.17, 126.04, 125.99, 125.89, 125.2, 124.9, 114.4, 85.5, 83.2, 81.5, 81.4, 27.5, 27.4, 16.5, 16.4, 16.3. **HRMS (FD+):** exact mass calcd for $C_{50}H_{43}ClO_4Si^+$ $[M]^+$: m/z = 770.26137, found: 770.26037.

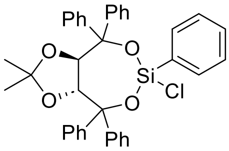
### (3a*R*,8a*R*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-chloro-6-isopropyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*R*,*R*)-30c)



Synthesized according to general procedure E from TADDOL derivative **(*R*,*R*)-28c** (538 mg, 500 µmol) and isopropyltrichlorosilane. The product was obtained as a colorless, crystalline solid (480 mg, 407 µmol, 81%). The enantiomer **(*S*,*S*)-30d** was synthesized from TADDOL derivative **(*S*,*S*)-28c** (1.04 g, 870 µmol) and obtained as a colorless, crystalline solid (622 mg, 527 µmol, 54%).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.98 (s, 4H), 7.89 – 7.74 (m, 9H), 7.72 – 7.62 (m, 17H), 7.50 – 7.33 (m, 27H), 5.69 (d, *J* = 7.2 Hz, 1H), 5.63 (d, *J* = 7.2 Hz, 1H), 1.40 – 1.30 (m, 1H + 2H overlap with residual n-hexane), 1.17 (t, *J* = 8.1 Hz, 6H), 0.77 (s, 3H), 0.68 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.8, 146.6, 143.0, 142.9, 141.7, 141.6, 141.54, 141.46, 141.35, 141.26, 141.25, 140.7, 140.5, 129.01, 128.97, 128.92, 127.59, 127.52, 127.46, 127.43, 127.40, 127.31, 127.27, 126.9, 126.1, 126.0, 125.6, 125.4, 125.2, 114.6, 85.6, 83.4, 81.1, 81.0, 27.5, 27.3, 22.8, 16.42, 16.37, 16.32. **HRMS (FD+):** exact mass calcd for $C_{82}H_{67}ClO_4Si^+$ $[M]^+$: m/z = 1178.44917, found: 1178.44611.

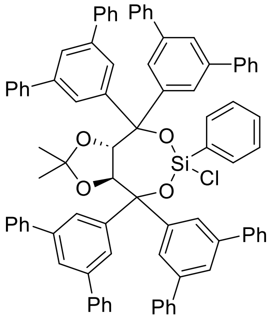
## (3a*R*,8a*R*)-6-Chloro-2,2-dimethyl-4,4,6,8,8-pentaphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*R*,*R*)-30d)



Synthesized according to general procedure E from **(*R*,*R*)-28a** (1.63 g, 3.5 mmol) and phenyltrichlorosilane. The product was obtained as a colorless, crystalline solid (1.95 g, 3.22 mmol, 92%). The enantiomer **(*S*,*S*)-30d** was synthesized from **(*S*,*S*)-28a** (467 mg, 1.00 mmol) and obtained as a colorless, crystalline solid (498 mg, 823 µmol, 82%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.70 – 7.63 (m, 2H), 7.62 – 7.52 (m, 4H), 7.52 – 7.21 (m, 19H), 5.33 (d, *J* = 7.2 Hz, 1H), 5.23 (d, *J* = 7.2 Hz, 1H), 0.67 (s, 3H), 0.58 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 146.4, 145.7, 141.82, 141.79, 134.0, 131.3, 131.2, 129.6, 129.1, 128.13, 128.05, 127.75, 127.72, 127.39, 127.36, 127.34, 127.19, 127.16, 114.2, 85.7, 83.8, 81.2, 81.0, 27.2, 27.1.

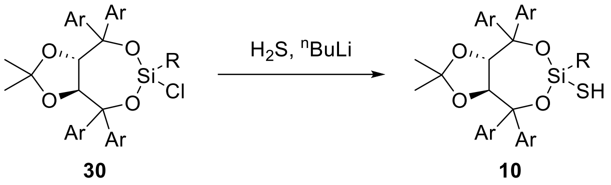
## (3a*S*,8a*S*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-chloro-2,2-dimethyl-6-phenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*S*,*S*)-30e)



Synthesized according to general procedure E from TADDOL derivative **(*S*,*S*)-28c**, (500 mg, 465 µmol) and phenyltrichlorosilane. The product was obtained as a colorless, solid (320 mg, 264 µmol, 57%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 8.07 – 8.00 (m, 2H), 7.95 – 7.89 (m, 4H), 7.87 – 7.83 (m, 2H), 7.81 – 7.73 (m, 6H), 7.72 – 7.66 (m, 8H), 7.62 – 7.57 (m, 4H), 7.53 – 7.48 (m, 4H), 7.48 – 7.29 (m, 30H), 5.81 (d, *J* = 7.3 Hz, 1H), 5.69 (d, *J* = 7.3 Hz, 1H), 0.79 (s, 3H), 0.73 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 147.0, 146.4, 142.5, 141.7, 141.6, 141.5, 141.30, 141.27, 141.2, 140.7, 140.6, 134.0, 131.5, 131.0, 128.98, 128.93, 128.89, 128.2, 127.54, 127.48, 127.4, 127.3, 127.2, 127.0, 126.2, 126.0, 125.5, 125.43, 125.39, 125.3, 114.7, 85.9, 84.4, 81.6, 81.2, 27.4, 27.4. **HRMS (FD+):** exact mass calcd for $C_{85}H_{65}ClO_4Si^+$ $[M]^+$: m/z = 1212.4335, found: 1212.4443.

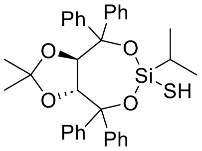
## General Procedure F: Synthesis of TADDOL-silane thiols (10)



A septum capped Schlenk flask connected to a hydrogen sulfide gas cylinder is charged with THF (20 mL per mmol chlorosilane). A second inlet for nitrogen is connected to avoid negative pressure in the apparatus and to remove excess $H_2S$ after the reaction. A subsequent gas-washing bottle with aqueous NaOH solution is used for binding excess hydrogen sulfide. The reaction flask is cooled in liquid nitrogen until the THF has frozen. A slow flow of $H_2S$ is started until an excess of $H_2S$ has condensed into the flask. The liquid nitrogen is exchanged by a -78 °C cooling bath to melt the THF and $H_2S$. At -78 °C *n*-BuLi (4 equiv., 2 M in THF) is added dropwise and the solution warmed to 0 °C within 1 h. The solution is cooled to -78 °C again and the chlorosilane **30**, dissolved in a few milliliters of THF is added. The solution is warmed to room temperature within 1-2 h. The reaction flask is purged with nitrogen for a few hours (or overnight) to remove most of the hydrogen sulfide (this step is not necessary but reduced the amount of $H_2S$ released). The solvent is then removed under reduced pressure and the residue extracted with boiling *n*-hexane. The solvent is removed under reduced pressure to yield the product in sufficient purity.

If necessary, column chromatography (10% EtOAc in petrol ether) can be used. However, slow hydrolysis to the corresponding silanol is observed on silica which causes some product loss.

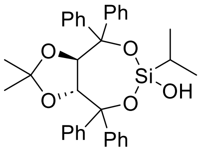
## (3a*R*,8a*R*)-6-isopropyl-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*R*,*R*)-10a)



Synthesized according to general procedure F from chlorosilane **(*R*,*R*)-30a** (1.20 g, 2.10 mmol). The product was obtained as a colorless foam (1.09 g, 1.92 mmol, 91%).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.61 – 7.54 (m, 4H), 7.42 – 7.17 (m, 16H), 5.27 (d, *J* = 7.3 Hz, 1H), 5.12 (d, *J* = 7.3 Hz, 1H), 1.06 – 0.88 (m, 7H), 0.59 (s, 3H), 0.48 (s, 3H), -0.20 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.3, 146.4, 142.53, 142.46, 129.6, 129.1, 128.3, 128.1, 127.7, 127.6, 127.4, 127.25, 127.22, 127.20, 127.1, 114.1, 84.8, 82.6, 81.1, 81.0, 27.2, 27.1, 17.7, 16.5, 16.4. **HRMS (FD+):** exact mass calcd for $C_{34}H_{36}O_4SSi^+$ [M]$^+$: m/z = 568.20981, found: 568.20892.

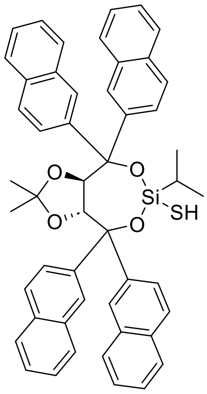
### (3a*R*,8a*R*)-6-Isopropyl-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*R*,*R*)-31a)



Obtained as side product in the synthesis of **(*R*,*R*)-10a** in trace amounts.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.68 – 7.57 (m, 4H) 7.45 – 7.18 (m, 16H), 5.12 + 5.10 (d, *J* = 7.6 Hz + d, *J* = 7.6 Hz, 2H), 1.86 (s, 1H), 1.01 – 0.88 (m, 7H), 0.65 (s, 3H), 0.49 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.63, 147.56, 142.8, 142.5, 129.4, 129.0, 128.5, 128.0, 127.7, 127.4, 127.3, 127.13, 127.10, 127.04, 126.99, 126.8, 113.7, 83.1, 81.4, 81.4, 81.1, 27.3, 26.9, 16.6, 12.3. **HRMS (FD+):** exact mass calcd for $C_{34}H_{36}O_5Si^+$ [M]$^+$: m/z = 552.23265, found: 552.23170.

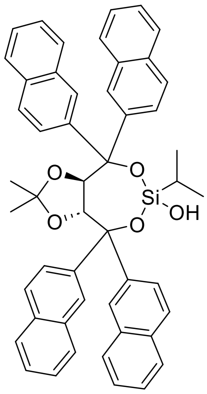
### (3a*R*,8a*R*)-6-Isopropyl-2,2-dimethyl-4,4,8,8-tetra(naphthalen-2-yl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*R*,*R*)-10b)



Synthesized according to general procedure F on 200 µmol scale from **(*R*,*R*)-30b** (154 mg, 200 µmol). The product was obtained as a colorless foam (98.0 mg, 127 µmol, 64%).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.34 (d, *J* = 1.2 Hz, 1H), 8.32 (d, *J* = 1.08 Hz, 1H), 8.30 (d, *J* = 0.96, 1H), 8.17 (d, *J* = 1.0 Hz, 1H), 8.04 – 7.98 (m, 2H), 7.98 – 7.93 (m, 1H), 7.93 – 7.82 (m, 7H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.67 – 7.61 (m, 2H), 7.61 – 7.46 (m, 10H), 5.70 (d, *J* = 7.3 Hz, 1H), 5.55 (d, *J* = 7.3 Hz, 1H), 1.25 – 1.19 (m, 1H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 3H), 0.75 (s, 3H), 0.61 (s, 3H), -0.02 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 144.3, 143.4, 139.93, 139.92, 133.04, 132.96, 132.92, 132.70, 132.65, 132.63, 131.0, 128.97, 128.91, 128.84, 128.75, 128.69, 128.29, 128.01, 127.99, 127.75, 127.70, 127.58, 127.51, 127.3, 126.5, 126.4, 126.33, 126.27, 126.21, 126.16, 125.95, 125.87, 125.5, 124.9, 114.3, 85.2, 82.8, 81.6, 81.5, 27.5, 27.4, 17.8, 16.7, 16.5. **HRMS (FD+):** exact mass calcd for $C_{50}H_{44}O_4SSi^+$ [M]$^+$: m/z = 768.27241, found: 768.27431.

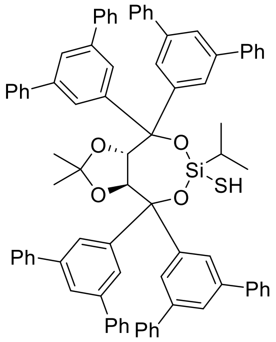
### (3a*R*,8a*R*)-6-Isopropyl-2,2-dimethyl-4,4,8,8-tetra(naphthalen-2-yl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*R*,*R*)-31b)



Obtained as side product in the synthesis of **(*R*,*R*)-10b** as a colorless foam (14 mg, 18.6 µmol, 9%).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 8.23 (d, *J* = 1.2 Hz, 1H), 8.21 (d, *J* = 1.1 Hz, 1H), 8.19 (d, *J* = 1.0 Hz, 1H), 8.08 (d, *J* = 1.1 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.88 – 7.73 (m, 8H), 7.66 – 7.56 (m, 4H), 7.55 – 7.36 (m, 10H), 5.42 (s, 2H), 1.94 (s, 1H), 1.10 – 0.99 (m, 7H), 0.68 (s, 3H), 0.50 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 143.70, 143.67, 139.3, 139.0, 132.1, 131.97, 131.94, 131.87, 131.71, 131.67, 131.63, 127.96, 127.93, 127.8, 127.7, 127.5, 127.3, 126.9, 126.80, 126.75, 126.70, 126.6, 126.5, 126.3, 125.6, 125.4, 125.33, 125.28, 125.2, 125.1, 125.0, 124.9., 124.8, 124.7, 123.9, 123.8, 113.0, 82.5, 80.8, 80.7, 80.6, 26.6, 26.2, 16.0, 15.9, 11.4. **HRMS (FD+):** exact mass calcd for $C_{50}H_{44}O_5Si^+$ [M]$^+$: m/z = 752.29548, found: 752.29673.

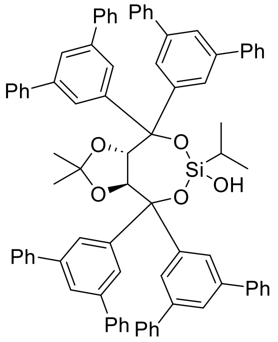
### (3a*S*,8a*S*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-isopropyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*S*,*S*)-10c)



Synthesized according to general procedure F from **(*S*,*S*)-30c** (472 mg, 400 µmol). The product was obtained as a colorless foam (183 mg, 155 µmol, 39%). The enantiomer **(*R*,*R*)-10c** was synthesized from **(*R*,*R*)-30c** (354 mg, 300 µmol) and obtained as a colorless foam (249 mg, 211 µmol, 70%).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.99 (d, *J* = 1.6 Hz, 2H), 7.97 (d, *J* = 1.6 Hz, 2H), 7.89 (d, *J* = 1.5 Hz, 2H), 7.87 – 7.83 (m, 3H), 7.81 – 7.76 (m, 3H), 7.74 – 7.62 (m, 16H), 7.49 – 7.33 (m, 25+1H), 5.82 (d, *J* = 7.3 Hz, 1H), 5.61 (d, *J* = 7.2 Hz, 1H), 1.18 – 1.13 (m, 6H), 1.02 – 0.92 (m, 1H), 0.03 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 148.1, 147.2, 143.4, 143.3, 141.8, 141.5, 141.41, 141.36, 141.33, 141.30, 140.63, 140.56, 128.99, 128.97, 127.53, 127.51, 127.49, 127.45, 127.41, 127.35, 127.28, 127.0, 126.1, 125.9, 125.5, 125.30, 125.25, 114.5, 85.3, 83.0, 81.3, 81.2, 27.6, 27.2, 17.9, 16.6, 16.5. **HRMS (FD+):** exact mass calcd for $C_{37}H_{34}O_4SSi^+$ [M]$^+$: m/z = 1176.4602, found: 1176.4630.

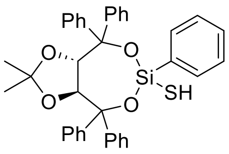
## (3a*S*,8a*S*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-isopropyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*S*,*S*)-31c)



Obtained as side product in the synthesis of **(*S*,*S*)-10c** as a colorless foam (38 mg, 32.7 µmol, 8%).

**$^{1}$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.97 (d, *J* = 1.6 Hz, 2H), 7.93 (d, *J* = 1.6 Hz, 2H), 7.83 – 7.76 (m, 4H), 7.74 – 7.70 (m, 4H), 7.66 – 7.56 (m, 16H), 7.44 – 7.27 (m, 24H), 5.57 (d, *J* = 7.4 Hz, 1H), 5.50 (d, *J* = 7.4 Hz, 1H), 1.22 (s, 1H), 1.12 – 1.04 (m, 7H), 0.74 (s, 3H), 0.57 (m, 3H). **$^{13}$C{$^{1}$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 148.5, 148.4, 143.7, 143.4, 141.9, 141.49, 141.47, 141.45, 141.2, 140.6, 140.5, 129.00, 128.99, 128.96, 128.92, 127.6, 127.47, 127.43, 127.36, 127.28, 126.99, 125.96, 125.7, 125.4, 125.3, 124.8, 114.2, 83.5, 81.9, 81.42, 81.39, 27.6, 27.1, 17.0, 16.9, 12.4. **HRMS (FD+):** exact mass calcd for $C_{82}H_{68}O_5Si^+$ $[M]^+$: m/z = 1160.4836, found: 1160.48628.

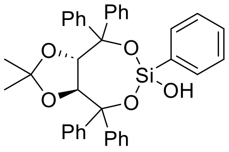
## (3a*S*,8a*S*)-2,2-Dimethyl-4,4,6,8,8-pentaphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*S*,*S*)-10d)



Synthesized according to general procedure F from chlorosilane **(*S*,*S*)-30d** (60.5 mg, 100 µmol). The product was purified via column chromatography (0→10% EtOAc in PE) and obtained as a colorless foam (39.0 mg, 64.7 µmol, 65%). The enantiomer **(*R*,*R*)-10d** was synthesized from **(*R*,*R*)-30d** (454 mg, 750 µmol) and obtained as a colorless foam (365 mg, 605 µmol, 81%).

**$^{1}$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.68 – 7.63 (m, 2H), 7.57 – 7.51 (m, 4H), 7.51 – 7.46 (m, 2H), 7.42 – 7.36 (m, 3H), 7.36 – 7.18 (m, 14H), 5.38 (d, *J* = 7.3 Hz, 1H), 5.21 (d, *J* = 7.3 Hz, 1H), 0.67 (s, 3H), 0.50 (s, 3H), 0.10 (s, 1H). **$^{13}$C{$^{1}$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 146.6, 146.2, 142.4, 142.1, 134.1, 134.0, 130.9, 129.6, 129.2, 128.4, 128.0, 127.92, 127.85, 127.60, 127.52, 127.42, 127. 31, 127.27, 127.19, 127.14, 114.1, 85.3, 83.3, 81.3, 81.2, 27.3, 27.0. **HRMS (FD+):** exact mass calcd for $C_{37}H_{34}O_4SSi^+$ $[M]^+$: m/z = 602.19416, found: 602.19556.

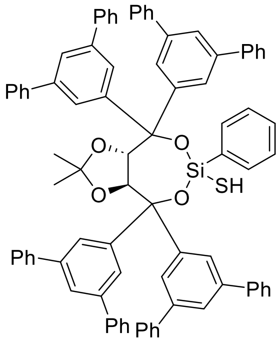
### (3a*S*,8a*S*)-2,2-dimethyl-4,4,6,8,8-pentaphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*S*,*S*)-31d)



Obtained as side product in the synthesis of **(*S*,*S*)-10d** as a colorless foam (9 mg, 15.3 µmol, 15%) in low purity.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.71 – 7.66 (m, 2H), 7.57 – 7.51 (m, 4H), 7.50 – 7.45 (m, 2H), 7.42 – 7.36 (m, 3H), 7.35 – 7.18 (m, 14H + 11H overlap with solvent residual signal), 5.23 (d, *J* = 7.44 Hz, 1H), 5.18 (d, *J* = 7.4 Hz, 1H), 0.69 (s, 3H), 0.50 (s, 3H). The O-H proton is not visible, potentially due to overlap/exchange with residual $H_2O$. **HRMS (FD+):** exact mass calcd for $C_{37}H_{34}O_5Si^+$ [M]$^+$: m/z = 586.21700, found: 586.21567.

### (3a*S*,8a*S*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-2,2-dimethyl-6-phenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*S*,*S*)-10e)



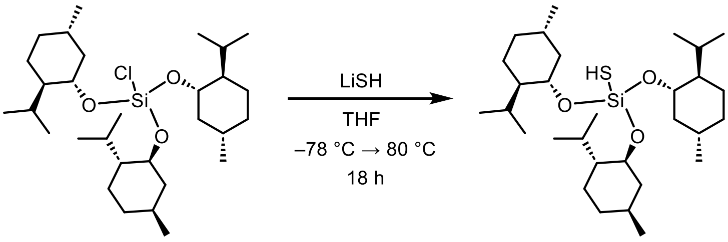
Synthesized according to general procedure F from chlorosilane **(*S*,*S*)-30e** (243 mg, 200 µmol). The product was obtained as a colorless foam (138 mg, 114 µmol, 57%). The compound could not be fully separated from the corresponding silanol and was used as a mixture.

Silane thiol **(*S*,*S*)-10e**: **HRMS (FD+):** exact mass calcd for $C_{85}H_{66}O_4SSi^+$ [M]$^+$: m/z = 1210.4446, found: 1210.4271.

Silanol **(*S*,*S*)-31e**: **HRMS (FD+):** exact mass calcd for $C_{85}H_{66}O_5Si^+$ [M]$^+$: m/z = 1194.4674, found: 1194.4474.

### 3.3.2 Synthesis of menthol-based chiral silane thiol

### Tris((1*S*,2*R*,5*S*)-menthoxy)silane thiol (11)



**32** **11**

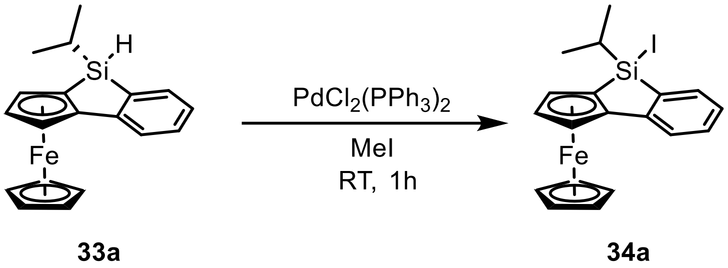
First, $H_2S$ (52.07 mL of a 1 M solution in THF, 52.07 mmol, 1.2 equiv) was diluted in 100 mL of THF and cooled to -78°C. Then *n*-Butyllithium (18.23 mL, 2.5 M in hexane, 45.57 mmol, 1.05 equiv) was added dropwise. The reaction mixture was stirred in the cooling bath until it reached a temperature of 0 °C, then it was cooled to -78 °C again. Next trimenthoxy(chloro)silane[33] (**32**, 22.97 g, 43.40 mmol, 1 equiv.) was added. The reaction was allowed to stir for 18 h at room temperature and then 18 h at 80 °C. The reaction mixture was then checked by NMR analysis, and since no complete conversion was observed another portion of LiSH (26.4 mmol, 1.6 equiv.) in situ prepared in the aforementioned manner was added. The reaction mixture was then stirred for 72 h at room temperature. Afterwards all volatiles were removed *in vacuo* and the oily suspension extracted with 50 mL of hot toluene. The cloudy suspension was filtered using a P3-Frit with added celite and silica. After removal of all volatiles in vacuo silane thiol **11** was obtained as a slightly yellow oil (20.8 g, 39.5 mmol, 91%).

**$^1$H NMR (400 MHz, $C_6D_6$):** δ [ppm] = 4.10 – 3.83 (m, 3H), 2.69 – 2.23 (m, 6H), 1.66 1.45 (m, 6H), 1.44 – 1.19 (m, 9H), 1.12 - 65 (m, 33H), 0.19 (s, 1H, S*H*). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 74.4 (s, *C*H), 50.2 (s, *C*H), 45.3 (s, *C*$H_2$), 34.7 (s, *C*$H_2$), 31.9 (s, *C*H), 25.8 (s, *C*H), 23.1 (s, *C*$H_2$), 22.4 (s, *C*$H_3$), 21.5 (s, *C*$H_3$), 16.3 (s, *C*$H_3$). **$^{29}$Si{$^1$H} NMR (79 MHz, $C_6D_6$):** δ [ppm] = -59.2 (*Si*–SH). **CHN Analysis:** Calcd for $C_{30}H_{58}O_3SSi$: C, 68.38; H, 11.10. Found: C, 68.69; H, 10.72.

### 3.3.3 Synthesis of silicon-chiral silane thiols

Reactions were performed in an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated at 600 °C prior to use. Dichloromethane (DCM), *n*-hexane, *n*-pentane, tetrahydrofuran (THF), and toluene were dried and degassed with an MBraun SP800 solvent purification system. ($^{R}$*Si*, *S*$_P$)-8,8 isopropyl(hydrido)benzosilolo[2,3-*a*]ferrocene and ($^{R}$*Si*,-*S*$_P$)-8,8-cyclohexyl(hydrido)benzosilolo[2,3-a]ferrocene were prepared according to literature procedures.[34] A stock solution of hydrogen sulfide in THF was prepared by saturating THF with gaseous hydrogen sulfide and checking the concentration by NMR with 1,3,5-trimethoxybenzene as internal standard. $C_6D_6$ and $CD_2Cl_2$ used for NMR spectroscopy were dried over 3 Å molecular sieves and degassed by a standard freeze-pump-thaw procedure.

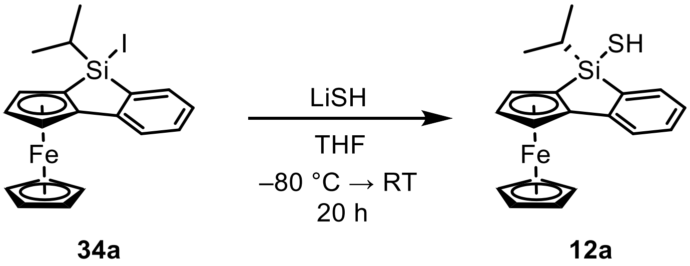
### 8,8-Isopropyl(iodo)benzosilolo[2,3-a]ferrocene (34a)



Prepared according to a modified literature procedure.[35]

First ($^{R}$*Si*, *S*$_P$)-8,8-isopropyl(hydrido)benzosilolo[2,3-a]ferrocene[34] (150 mg, 0.45 mmol, 1 equiv.) was combined with bis(triphenylphosphine)palladium(II) dichloride (15.84 mg, 0.022 mmol, 0.05 equiv.) in a flame dried Schlenk flask. The mixture was then dissolved in methyl iodide (0.5 mL, 8.13 mmol, 18 equiv.) and stirred for 1 h at room temperature. Afterwards all volatiles were removed *in vacuo*. The remaining red solid was immediately used in the next reaction step without further purification.

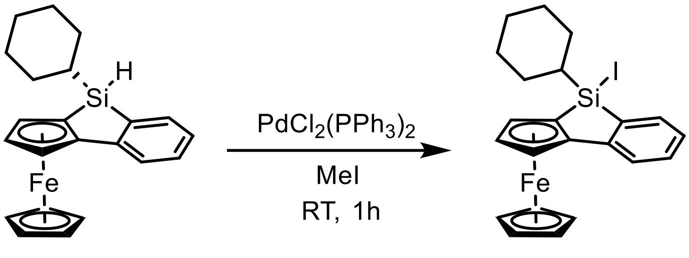
### 12a



First $H_2S$ (8.99 mL, 0.5 M in THF, 4.5 mmol, 10 equiv.) was cooled to -80 °C and then *n*-butyllithium (0.9 mL, 2.5 M in hexane, 2.25 mmol, 5 equiv.) was added, and the mixture stirred for 20 min. In a separate Schlenk flask 8,8-isopropyl(iodo)benzosilolo[2,3-a]ferrocene[34] (**34a**, 206 mg, 0.445 mmol, 1 equiv.) was dissolved in 10 mL of THF and added to the cooled mixture. The reaction mixture was allowed to slowly warm up in the cooling bath, and then stirred for 20 h at room temperature. Next all volatiles were removed *in vacuo* and the black green residue suspended with 5 mL of hot hexane and filtered using a teflon cannula. The filtrate was concentrated *in vacuo* and purified by thin-layer chromatography (hexane, $R_f$ = 0.4). Silane thiol **12a** was obtained as a red powder (53.0 mg, 145 µmol, 32%, *d.r.* = 14:1). Crystals of the major diastereomer suitable for single-crystal X-ray diffraction analysis were obtained from a concentrated *n*-pentane solution at -30°C. The absolute configuration was determined as ($^{S}$*Si*, *S*$_{P}$).

**$^{1}$H NMR (400 MHz, $C_6D_6$):** δ [ppm] = 7.51 (d, *J* = 7.17 Hz, 1H), 7.23 – 7.12 (m, 2H, overlapping with solvent residual signal), 7.03 (td, *J* = 7.1, 1.5 Hz, 1H), 4.59 – 4.56 (m, 1H), 4.35 (t, *J* = 2.28 Hz, 1H), 4.30 – 4.27 (m, 1H), 3.83 (s, 5H), 1.57 – 1.46 (m, 1H, 0verlap with minor diastereomer), 1.37 (d, *J* = 7.1 Hz, 3H), 1.35 (d, *J* = 7.3 Hz, 3H), -0.19 (s, 1H). **$^{13}$C{$^{1}$H} NMR (101 MHz, $C_6D_6$):** δ [ppm] = 147.8, 140.0, 133.7, 130.7, 126.3, 121.4, 96.3, 74.4, 71.2, 71.0, 70.5 (probably diastereomer), 70.4, 64.9, 17.8, 17.7, 16.3. **$^{29}$Si{$^{1}$H} NMR (79 MHz, $C_6D_6$):** δ [ppm] = 9.5. **CHN Analysis:** Calcd for $C_{19}H_{20}FeSSi$: C, 62.6; H, 5.5. Found: C, 62.92; H, 5.80.

## 8,8-Cyclohexyl(iodo)benzosilolo[2,3-a]ferrocene (34b)

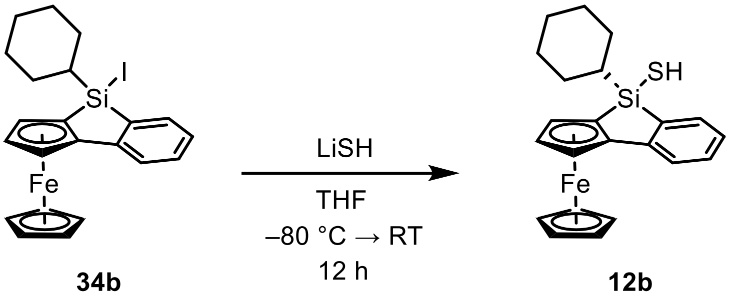


**33b** **34b**

Prepared according to a modified literature procedure.[35]

First ($^{R}$*Si*, *S*$_{P}$)-8,8-cyclohexyl(hydrido)benzosilolo[2,3-a]ferrocene[34] (**33b**, 140 mg, 375 µmol, 1 equiv.) was combined with bis(triphenylphosphine)palladium(II) dichloride (13.2 mg, 18.0 µmol, 5 mol%) in a flame dried Schlenk flask. The mixture was then dissolved in methyl iodide (0.42 mL, 6.77 mmol, 18 equiv.) and stirred for 1 h at room temperature. Afterwards all volatiles were removed in vacuo. The remaining red solid was immediately used in the next reaction step without further purification.

## 12b



**34b** **12b**

First, $H_2S$ (11.24 mL of a 0.5 M solution in THF, 5.62 mmol, 20 equiv.) was cooled to -80 °C and then *n*-butyllithium (1.12 mL of a 2.5 M solution in *n*-hexane, 2.81 mmol, 10 equiv.) was added and the mixture stirred for 20 min. In a separate schlenk flask 8,8-cyclohexyl(iodo)benzosilolo[2,3-a]ferrocene (**34b**, 140 mg, 280 µmol, 1 equiv.) was dissolved in 10 mL of THF and added to the cooled mixture. The reaction mixture was allowed to slowly warm up to room temperature in the cooling bath, and then stirred for 12 h at room temperature. Next, all volatiles were removed *in vacuo*, the residue suspended with 5 mL of hot *n*-hexane, and filtered using a teflon cannula. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from the filtrate at -30°C. The product was isolated via filtration and dried in vacuo to yield the product as an orange, crystalline solid (83 mg, 205 µmol, 73%, *d.r.* = 17:1). Crystals of the major diastereomer suitable for single-crystal X-ray diffraction analysis were obtained from a concentrated *n*-pentane solution at -30°C. The absolute configuration was determined as ($^{S}Si$, $S_P$).

**$^1$H NMR (400 MHz, $C_6D_6$):** δ [ppm] = 7.53 – 7.49 (m, 1H), 7.23 – 7.18 (m, 1H), 7.04 (td, J = 7.2, 1.4 Hz, 1H), 4.58 (dd, J = 2.3, 0.7 Hz, 1H), 4.26 (t, J = 2.3 Hz, 1H), 4.31 (dd, J = 2.2, 0.6 Hz, 1H), 3.87 (s, 5H), 2.25 – 2.11 (m, 2H), 1.84 – 1.62 (m, 5H), 1.51 – 1.41 (m, 1H), 1.33 – 1.22 (m, 3H), -0.13 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, $C_6D_6$):** δ [ppm] = 147.8, 140.1, 133.9, 130.7, 126.3, 121.5, 96.4, 74.3, 71.3, 71.2, 40.4, 70.1 (probably diastereomer), 64.8, 28.1, 28.00, 27.98, 27.87, 27.6, 26.9. **$^{29}$Si{$^1$H} NMR (79 MHz, $C_6D_6$):** δ [ppm] = 6.0 (s, *Si*–SH). **CHN Analysis:** Calcd for $C_{22}H_{24}FeSSi$: C, 65.34; H, 5.98. Found: C, 65.81; H, 6.35.

# 4 Deuteration via benzylic C-H activation

## General procedure G: Benzylic deuteration

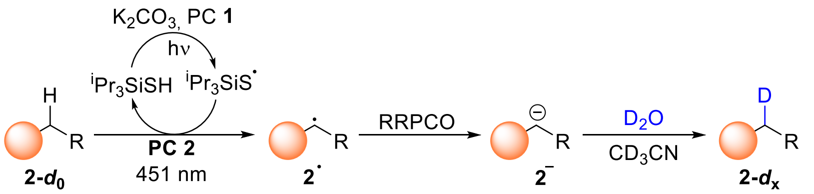
Carbanion generation from benzylic C-H bonds was done according to a slightly modified previous report on benzylic C-H activation:[36]

Benzylic substrate (1 equiv., 100 µmol per mL solvent), $K_2CO_3$ (10 mol%) and photocatalyst 3DPA2FBN (**1a**, 3 mol%) are placed in a 6 mL crimp capped vial with a stirring bar and closed. The vial is evacuated and backfilled with nitrogen 3 times via cannula. HAT-catalyst ($^iPr_3SiSH$ unless otherwise noted, 10 mol%), $D_2O$ (10 equiv.), and solvent ($CH_3CN$ or $CD_3CN$) are added via syringe. Solid reaction partners are added before closing the vial and liquids via syringe after closing the vial. The reaction mixture is degassed by 3 cycles of freeze-pump-thaw and irradiated by blue light (LEDs; $\lambda_{max}$ = 440 nm) for the time specified. Reactions were generally irradiated overnight (16 h) to ensure maximum deuterium incorporation unless otherwise noted. However, for synthetic applications the optimal reaction time is expected to vary depending on the substrate and higher yields are expected at shorter reaction times. The optimal compromise between yield and degree of deuteration also depends on the specific application.

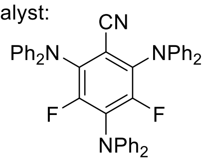
For isolation the reaction mixture is diluted with water, extracted with *n*-pentane, and dried over $Na_2SO_4$. The solvent is removed under reduced pressure. Crude compounds are purified via column chromatography with appropriate mixtures of EtOAc/PE.

For determination of deuteration degrees the reactions were conducted on 100 µmol scale in 1 mL $CD_3CN$. 1,1,2,2-Tetrachloroethane was added as NMR standard after the reaction to estimate the yield. For reactions where aliquots were taken at different time points the residual solvent signal was used as internal standard. To note, benzylic carbanions generated in this work are highly basic and most of them are expected to or have been shown to deprotonate acetonitrile which can potentially influence the residual solvent signal. However, it has been demonstrated previously that in the presence of at least 5 equivalents of $H_2O/D_2O$ solvent deprotonation is outcompeted and the residual solvent remains constant.[11]

## 4.1 Extended substrate scope of benzylic deuteration

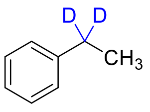


Photocatalyst:

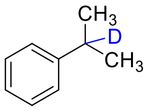


**3DPA2FBN (1)**

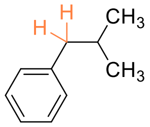
**Acyclic alkyl arenes**



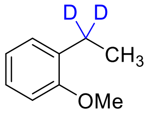
**2a-$d_2$**
86% D (80%)



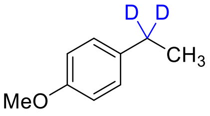
**2b-$d_1$**
87% D (>95%)



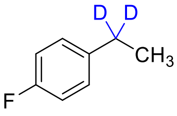
**2c**
No conversion



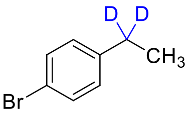
**2d-$d_2$**
87% D (>95%)



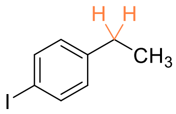
**2e-$d_2$**
84% D (>95%)



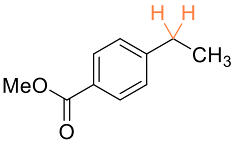
**2f-$d_2$**
65% D (>95%)



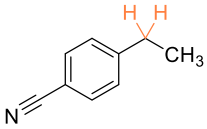
**2g-$d_2$**
86% D (>95%)



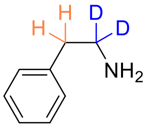
**2h**
No conversion.



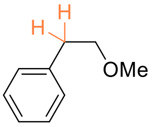
**2i**
10% D, (>95%)



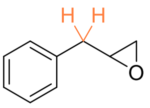
**2j**
No conversion



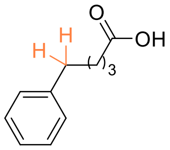
**2k-$d_2$**
68% D (>95%)



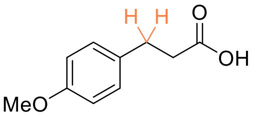
**2l**
No conversion



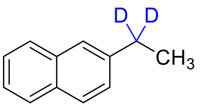
**2m**
no conversion



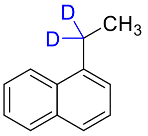
**2n**
No conversion



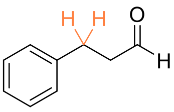
**2o**
No conversion



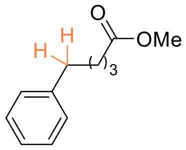
**2p-$d_2$**
47% D (>95%)



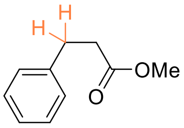
**2q-$d_2$**
16% D (>95%)



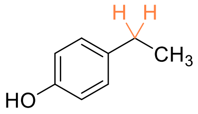
**2r**
Decomposition



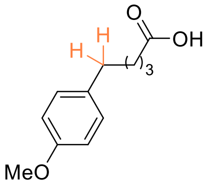
**2s**
69% D (>95%)



**2t**
No conversion

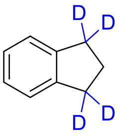


**2u**
no conversion

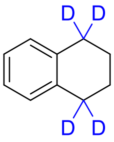


**2v**
No conversion

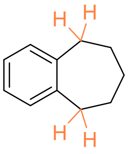
**Cyclic alkyl arenes**



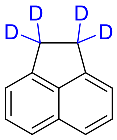
**3a-$d_4$**
40% D (>95%)



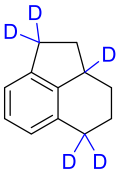
**3b-$d_4$**
>95% D (>95%)



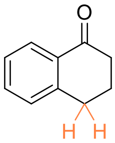
**3c**
No conversion



**3d-$d_4$**
87% D (>95%)

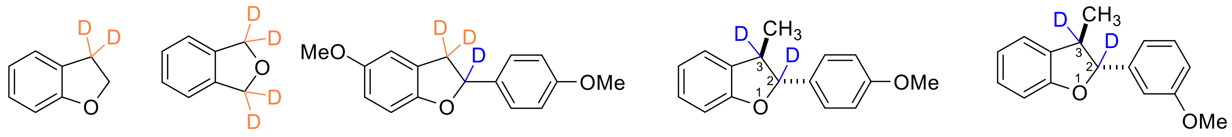


**3e-$d_5$**
52% D



**3f**
<10% D (76%)

**Benzofurans and isochromanes**



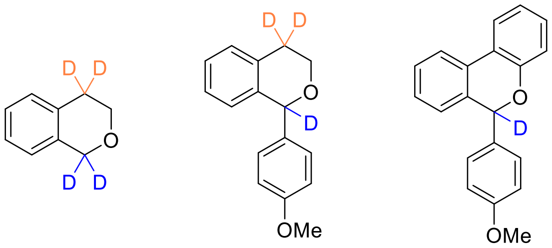
**4a**
No conversion

**4e**
No conversion

**4b-*d*$_1$**
1 h: 83% D (65%)

**4c-*d*$_2$**
3 h: (70%)
pos. 2: 93% D
pos. 3: 61% D

**4d-*d*$_2$**
3 h: (89%)
pos. 2: 69% D
pos. 3: 37% D

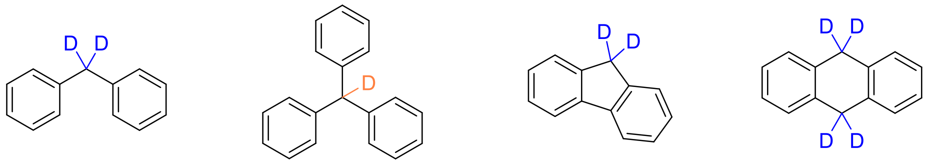


**5a-*d*$_2$**
>95% D (56%)

**5b-*d*$_1$**
6h >95% D (63%)

**5c-d$_1$**
1h: 94% D, (>95%)

**Hydrocarbons with doubly or triply benzylic positions**



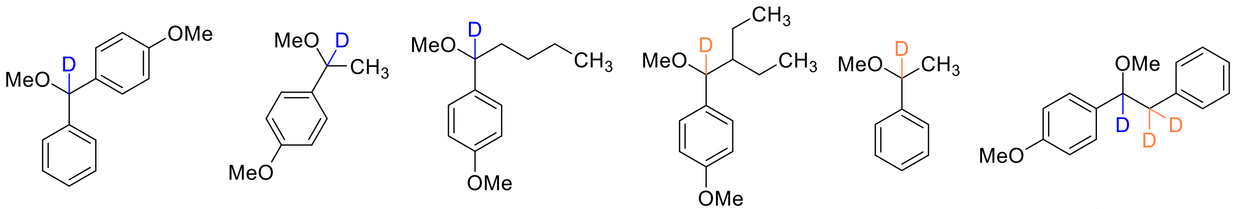
**6a-*d*$_2$**
76% D (>95%)

**6b**
No conversion

**6c-*d*$_2$**
61% D (>95%)

**6d-*d*$_4$**
83% D (72%)

**Benzyl ethers**



**7a-*d*$_1$**
93% D (91%)

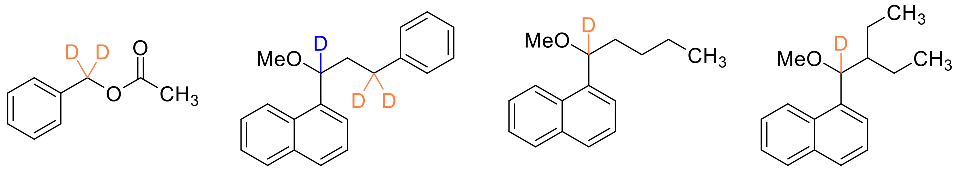
**7b-*d*$_1$**
56% D (81%)

**7c-*d*$_1$**
73% D (55%)

**7d**
No conversion

**7e**
No conversion

**7f-*d*$_1$**
68% (n.d.)



**7g**
No conversion

**7h-*d*$_1$**
35% D (n.d.)

**7i**
No conversion

**7j**
No conversion

**Scheme S1.** Extended substrate scope for benzylic deuteration via a HAT/RRPCO/deuteration sequence. Reaction conditions according to general procedure G. Positions deuterated to notable extent are marked in blue, positions not deuterated to notable extent are marked in orange. NMR yield in parentheses. Photocatalyst 1 is not stable under irradiation and a photocyclization product is likely the active catalyst. For details see section 8.

## 4.2 Computational investigations

The trends in reactivity according to Scheme S1 follow C-H bond dissociation energies (BDE) only to some extent. For a more quantitative overview and to separate steric and electronic effects, density functional theory (DFT) calculations were performed. All the optimization and frequency calculations were performed on the r$^2$SCAN-3c [37–41] level of theory as implemented in the quantum chemical software ORCA version 5.0.4.[42–45] Fully optimized structures were characterized to be either local minima or saddle points of first order, i.e. transition state structures by the number of imaginary frequencies. Minimum energy structures feature zero imaginary frequencies, whereas transition states have exactly one. The correct minimum energy pathways associated with the respective imaginary frequency of a given transition state structure was traced by an IRC calculation in the back- and forward direction. Energy values were derived from frequency analysis using the harmonic oscillator approach and include zero-point energy (ZPE) correction. Values of enthalpy (*H*) and Gibb's free energy (*G*) are unscaled and are report for standard conditions if not stated otherwise.

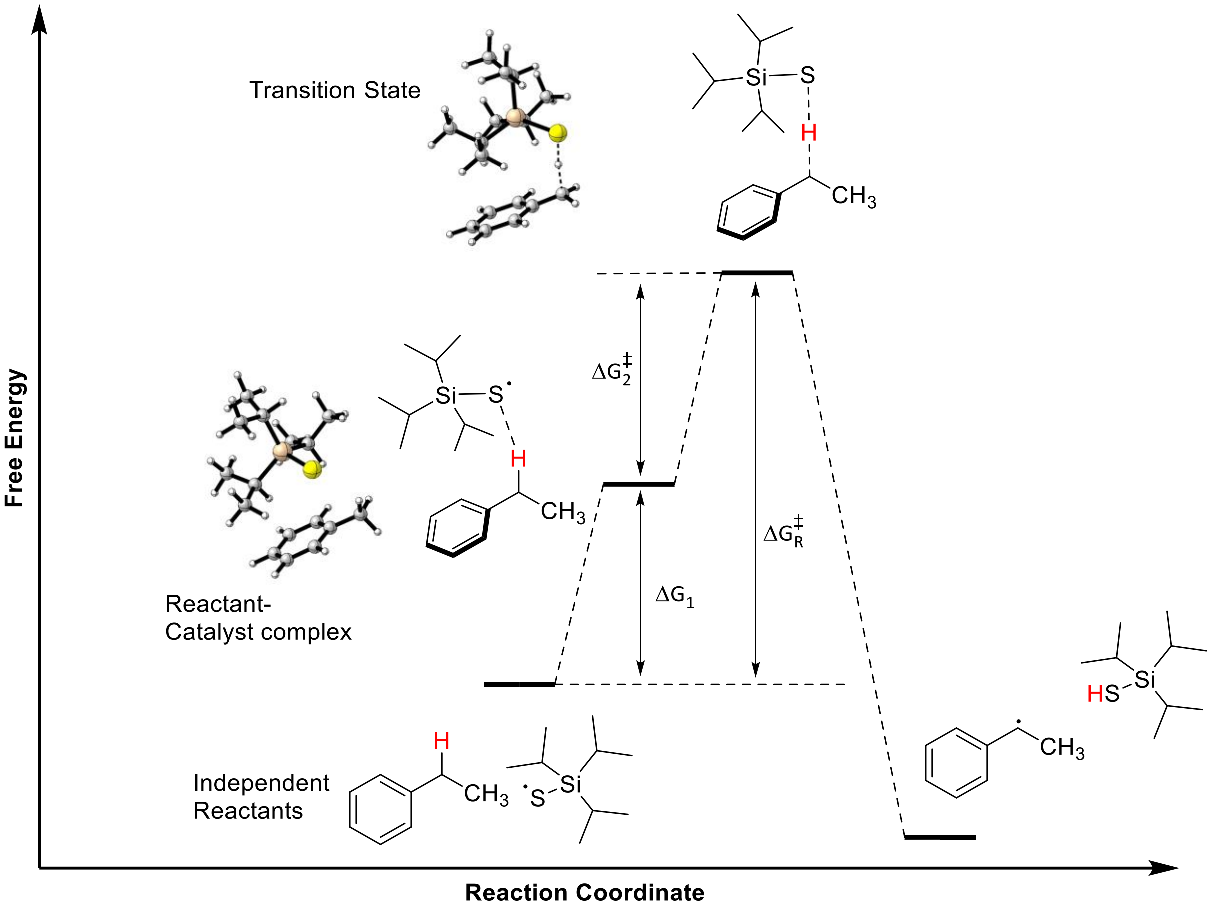


**Figure S5.** Reaction free energy profile.

To establish a trend for benzylic C-H activation, the hydrogen atom transfer (HAT) reaction barriers were calculated for a selection of substrates. To obtain the optimized reactant-catalyst pre-TS complex, the appropriate IRC end point was optimized, and the local minima were confirmed by all positive frequencies.

For a HAT process to be thermodynamically favored, the C-H bond dissociation energy (BDE) of the substrate must be lower than that of the X-H bond (S-H, in this case) of the catalyst. The BDEs were calculated by taking the difference of free energy of dissociated species (radical and hydrogen atom) and the substrate. The free energies according to Figure S5 and BDEs are tabulated in Tables S1.

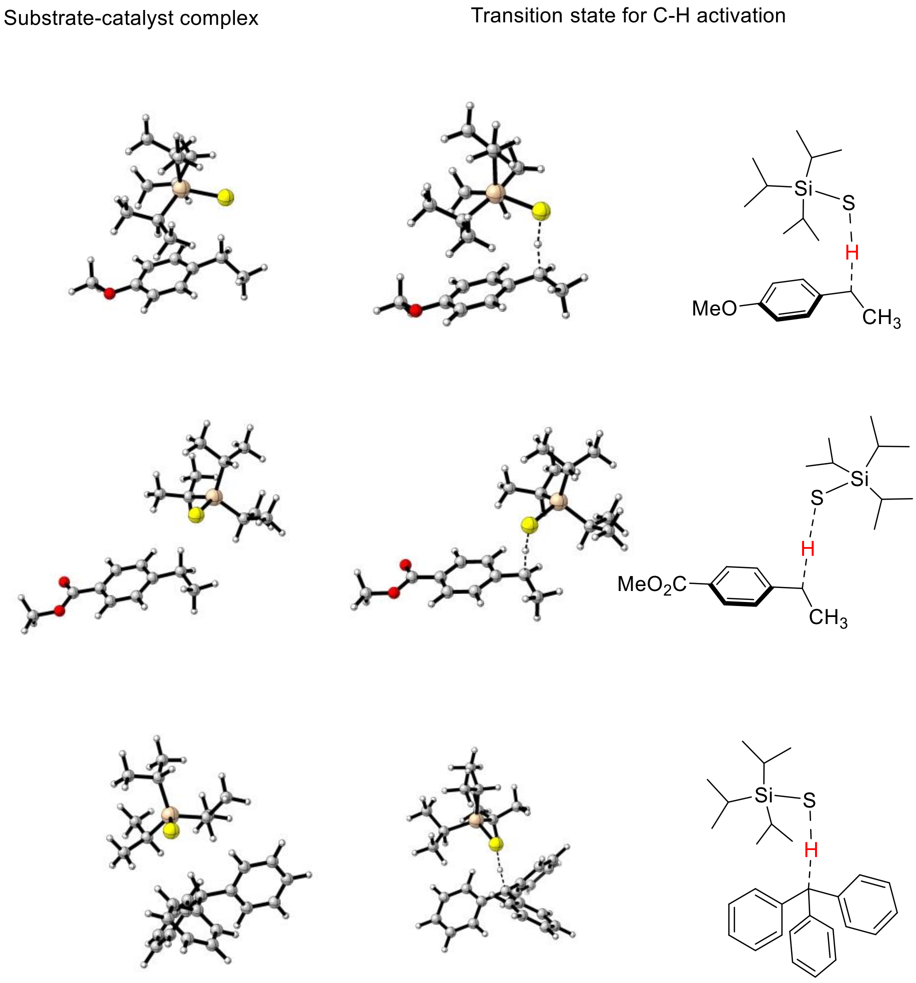
**Table S1.** Free energies of reactant-catalyst-complexes and transition states for the HAT-step relative to the substrates and bond dissociation energies (BDE) of the respective benzylic C-H bonds.

| Substrates | $\Delta G_1$ (kcal/mol) | $\Delta G_2^\ddagger$ (kcal/mol) | $\Delta G_R^\ddagger$ (kcal/mol) | BDE (kcal/mol) | Reactive |
|---|---|---|---|---|---|
| **$^iPr_3SiSH$** | | | | 84.56 | Catalyst |
| **toluene** | 5.51 | 6.71 | 12.22 | 83.81 | No |
| **2a** | 5.78 | 2.90 | 8.68 | 79.62 | Yes |
| **2b** | | | | 79.63 | Yes |
| **2c** | 5.91 | 4.34 | 10.25 | 82.30 | No |
| **2e** | 6.66 | 1.82 | 8.48 | 80.29 | Yes |
| **2i** | 8.09 | 2.66 | 10.75 | 78.93 | No |
| **3b** | 5.19 | 2.59 | 7.78 | 79.09 | Yes |
| **3c** | 5.67 | 2.51 | 8.19 | 80.78 | No |
| **6b** | 7.37 | -0.05 | 7.32 | 71.07 | No |
| **7b** | 6.30 | 0.31 | 6.61 | 76.67 | Yes |
| **7e** | 6.38 | 1.08 | 7.45 | 75.98 | No |

It is evident that the trends in BDE only reflect the reactivity of the substrates to some extent. Toluene, **2c**, and **3c** have the highest BDEs and are unreactive towards HAT. However, triphenylmethane (**6b**) and benzyl ether **7e** have the lowest BDE of all substrates calculated but are also unreactive. The transition state energy reflects the trend in BDEs for the substrates with high BDEs and in addition identified ester substituted substrate **2i** as kinetically unfavored for HAT despite its rather low BDE. A possible explanation will be discussed later.

Substrates **2a** and **2b** are reactive towards benzylic HAT while **2c** with an isopropyl group adjacent to the benzylic position did not give any conversion. The low reactivity of **2c** is reflected in the high BDE and transition state energy. The high BDE suggests that the steric bulk of the isopropyl group interferes with stabilization of the radical due to steric hindrance in the preferred orientation for stabilization of the unpaired electron by the π-system.

The role of steric effects is further highlighted by the non-reactivity of triphenylmethane (**6b**) despite having the lowest BDE. The free-energy difference between the reactant-catalyst complex and that of independent reactants ($\Delta G_1$) is the second highest calculated after the also unreactive ester substituted substrate **2i**. This suggests that destabilization of the substrate-catalyst-complex can prevent HAT even if the abstraction step itself is thermodynamically feasible. The optimized structures for substrate-catalyst-complexes and transition states suggest the preferred orientation of the triisopropylsilyl moiety is face-to-face above the aromatic system for all substrates with no substituents or electron donating substituents on the arene while this orientation is unfavored for electron poor substrate **2i**. Thus, dispersion interactions between electron rich π-systems and the triisopropylsilyl group might be necessary for HAT to be feasible. These interactions are prevented by electron withdrawing groups or by steric hindrance in the case of triphenylmethane (**6b**) where the tilted phenyl groups block access to the π-system. Optimized structures of substrate-catalyst-complexes and transition states for a representative selection of substrates is depicted in Figure S6. Electronically similar substrates prefer similar orientation compared to the examples depicted in Figure S6.



Attractive interactions between triisopropylsilyl group and π-system stabilize substrate-catalyst complex and transition state

Lack of attractive interactions between triisopropylsilyl group and π-system destabilize substrate-catalyst complex and transition state

Tilted phenyl groups prevent interaction between triisopropylsilyl group and π-system

**Figure S6.** Substrate-catalyst-complexes and transition states for a selection of substrates.

Another interesting observation is the effect of ring sizes. While the six-membered substrate **3b** undergoes efficient deuteration in the benzylic positions, benzylic positions in the seven-membered ring system of **3c** do not. The reason for this anomaly might be attributed to the steric hindrance offered by the 1,4-H interaction in the benzylic position (Figure S7). The calculated BDE of **3c** is also slightly higher compared to **3b** (80.78 vs. 79.09 kcal/mol) which suggests less stabilization of the unpaired electron in the seven-membered ring compared to the 6-membered ring.

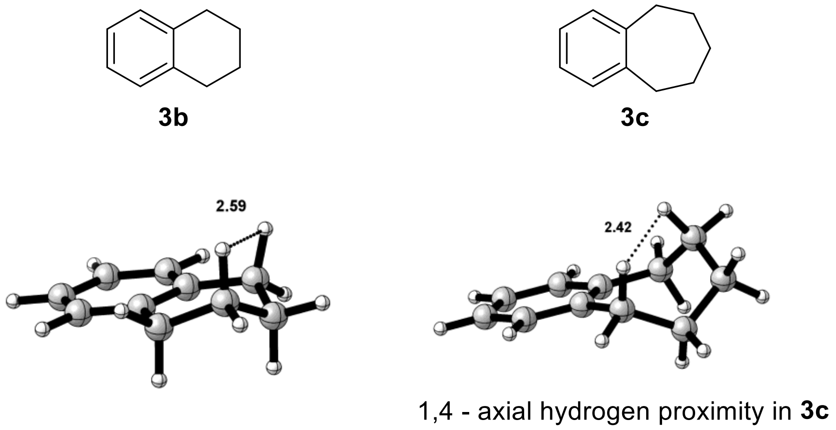
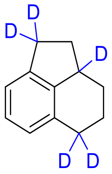


**Figure S7.** Inherent steric interactions in **3b** and **3c**.

Considering all these factors, it is sufficient to conclude that the BDEs are not the only determining factor in the initial HAT process and steric and electronic effects stabilizing or destabilizing the reactant complex play a definitive role in the reactivity of substrates towards C-H abstraction.

## 4.3 Isolated deuterated compounds

### 1,2,2a,3,4,5-Hexahydroacenaphthylene-1,1,2a,5,5-*d*$_5$ (3e-*d*$_5$)



Synthesized according to general procedure G from hexahydroacenaphthylene (190 mg, 6x 200 µmol) in $CH_3CN$. The product was obtained as a colorless liquid (86.8 mg, 538 µmol, 45%).

NMR spectra are in accordance with the non-deuterated compound. Most signals in the $^{13}C$ are doubled and multiple multiplets from coupling to deuterium are visible. Due to the presence of different diastereomers and compounds with different degree of deuteration no assignment to the individual benzylic positions has been made. According to the $^{13}C$ NMR the benzylic methine C-H is almost fully deuterated while the methylene C-H bonds are moderately deuterated.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.19 – 7.05 (m, 2H), 6.97 (d, *J* = 6.9 Hz, 1H), 2.99 – 2.66 (m, 2.39H, corresponds to 52% deuteration), 2.42 – 2.30 (m, 1H), 2.24 – 2.06 (m, 2H), 1.90 – 1.75 (m, 1H), 1.66 – 1.54 (m, 1H), 1.28 (t, *J* = 12.6 Hz, 1H).

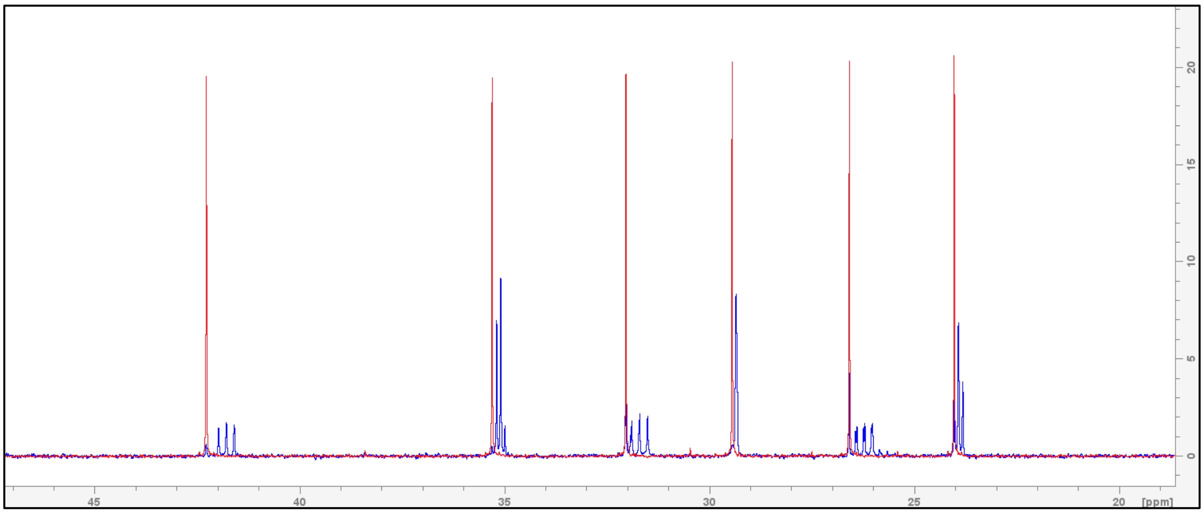
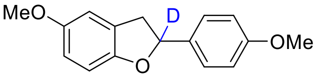


**Figure S8.** Superimposed aliphatic region of the $^1$H NMR spectra of deuterated **3e** (blue) and **3e-*d*$_0$** (red). The full NMR spectrum can be found in section 11.2.

### 5-Methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-2-*d* (Corsifuran A-*d*$_1$, 4b-*d*$_1$)

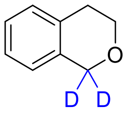


Synthesized according to general procedure G. The reaction was set up at 200 µmol scale in 2 mL $CD_3CN$ and 500 µL aliquots removed for NMR analysis before irradiation and after 1 h of irradiation. The remaining solution after 1 h of irradiation was treated according to general procedure G for isolation. The product was obtained as colorless solid (15.0 mg, 58.3 µmol, 58%).

The NMR spectra are in accordance with the non-deuterated compound **4b** with differences only in the benzylic position and adjacent positions as expected.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.37 – 7.31 (m, 2H), 6.93 – 6.88 (m, 2H), 6.79 (d, *J* = 2.44 Hz, 1H), 6.75 (d, *J* = 8.60 Hz, 1H), 6.70 (dd, *J* = 8.64, 2.60 Hz, 1H), 5.69 (t, *J* = 8.80 Hz, 0.11H, corresponds to 89% deuteration), 3.81 (s, 3H), 3.77 (s, 3H), 3.54 (d, *J* = 15.73 Hz, 1H), 3.19 (d, *J* = 15.69 Hz, 1H) **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.6, 154.4, 153.9, 134.0, 127.8, 127.4, 144.1, 133.1, 111.3, 109.3, 84.3 (residual **4b-*d*$_0$**) 83.9 (t, $J_{C,D}$ = 23.0 Hz), 56.4, 55.4, 38.7. **HRMS (EI+):** exact mass calcd for $C_{16}H_{15}O_3D^+$ [M]$^+$: m/z = 257.11567, found: 257.11565.

## Isochromane-1,1-*d*$_2$ (5a-*d*$_2$)

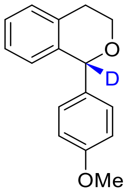


Synthesized according to general procedure G from isochromane (53.7 mg, 2x 200 µmol) in CH$_3$CN. The product was obtained as a colorless liquid (26.0 mg, 191 µmol, 48%). Due to its volatility the compound was not dried under high vacuum and some petrol ether remained in the product.

NMR spectra are in accordance with literature[46] and the NMR spectra of the non-deuterated compound **5a** with differences only in the benzylic position as expected.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.20 – 7.09 (m, 3H), 7.02 – 6.94 (m, 1H), 4.76 (s, 0.05H, corresponds to 98% deuteration), 3.98 (t, *J* = 5.7 Hz, 2H), 2.87 (t, *J* = 5.7 Hz, 2H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 134.9, 133.4, 129.0, 126.5, 126.1, 124.6, 67.4 (quint, $J_{C,D}$ = 21.9 Hz, almost lost in the noise), 65.5, 28.5. **HRMS (EI+):** exact mass calcd for $C_9H_8OD_2^+$ [M]$^+$: m/z = 136.08517, found: 136.08471.

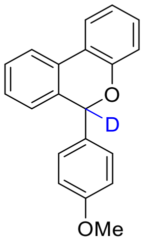
## (*R*)-1-(4-Methoxyphenyl)isochromane-1-*d* (5b-*d*$_1$)



Synthesized according to general procedure G from isochromane derivative **5b** (48.06 mg, 200 µmol) in CD$_3$CN with chiral HAT-catalyst **(*S,S*)-10c**. 500 µL of the solution were removed before irradiation for NMR analysis. The remaining solution (150 µmol substrate in 1.5 mL CD$_3$CN) was irradiated for 16 h at -17 °C and the product isolated according to general procedure G. The product was obtained as a colorless liquid (29.71 mg, 123 µmol, 82%, 32% *ee*). The enantiomeric excess was determined by chiral HPLC on a CHIRALPAK® AD-3 column ($^i$PrOH/*n*-hexane 10:1, flow rate 0.8 mL/min). $t_{minor}$ = 7.284 min, $t_{major}$ = 8.365 min. The absolute configuration of the (*S*)-enantiomer was determined by chiral HPLC on a CHIRALCEL® OD-H column. Racemic **5b-*d*$_1$** was synthesized using triisopropylsilane thiol as HAT catalyst but not isolated. The NMR spectra are in accordance with those of the non-deuterated compound **5b** with differences only in the benzylic position as expected. Compound **5b-*d*$_1$** is mentioned in the literature but was not characterized.[47]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 7.11 – 7.05 (m, 1H), 6.91 – 6.85 (m, 2H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.70 (s, 0.12H, corresponds to 88% deuteration), 4.22 – 4.13 (m, 1H), 3.97 – 3.87 (m, 1H), 3.81 (s, 3H), 3.19 – 3.06 (m, 1H), 2.81 (dt, *J* = 16.3, 3.6 Hz, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.6, 137.7, 134.6, 124.1, 130.3, 128.8, 127.1, 126.7, 126.0, 113.9, 78.8 (t, $J_{C,D}$ = 21.4 Hz), 63.8, 55.4, 29.0.

## 6-(4-methoxyphenyl)-6*H*-benzo[*c*]chromene-6-*d* (5c-*d*$_1$)

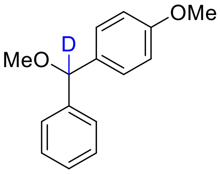


Synthesized according to general procedure G from isochromane derivative **5c** (57.7 mg, 200 µmol) in $CD_3CN$. The product was obtained as a colorless solid (49.1 mg, 170 µmol, 85%).

The NMR spectra are in accordance with those of the non-deuterated compound **5c** with differences only in the benzylic position as expected.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.83 – 7.73 (m, 2H), 7.41 (td, *J* = 7.6, 1.17 Hz, 1H), 7.35 – 7.19 (m, 4H), 7.05 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.00, (dd, *J* = 8.1, 1.0 Hz, 1H), 6.93 – 6.86 (m, 3H), 6.15 (s, 0.06H, corresponds to 96% deuteration). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 159.8, 159.7, 134.3, 134.2, 131.9, 131.8, 130.2, 129.7, 129.6, 128.5, 127.7, 126.4, 123.2, 122.9, 122.2, 122.1, 118.0, 114.0, 79.0 (t, $J_{C,D}$ = 22.38 Hz), 55.4.

## 1-Methoxy-4-(methoxy(phenyl)methyl-*d*)benzene (7a-*d*$_1$)

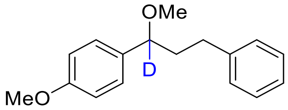


Synthesized according to general procedure G from benzyl ether **7a** (22.8 mg, 100 µmol) with chiral HAT-catalyst **(*S*,*S*)-10c** in 1 mL $CD_3CN$. The product was obtained as a colorless liquid (19.0 mg, 82.9 µmol, 83%).

The NMR spectra are in accordance with those of the non-deuterated compound **7a** with differences only in the benzylic position as expected.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.38 – 7.31 (m, 4H), 7.29 – 7.23 (m, 3H), 6.89 – 6.84 (m, 2H), 5.21 (s, 0.04H, corresponds to 96% deuteration), 3.78 (s, 3H), 3.37 (s, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 159.1, 142.4, 134.4, 128.5, 128.4, 127.5, 127.0, 113.9, 85.1 (residual **5c-*d*$_0$**), 84.6 (t, $J_{C,D}$ = 21.5 Hz), 57.0, 55.4.

### 1-Methoxy-4-(1-methoxy-3-phenylpropyl-1-*d*)benzene (7f-*d*$_1$)

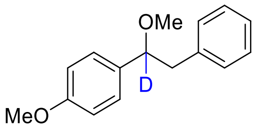


Synthesized according to general procedure G from benzyl ether **7f** (25.6 mg, 100 µmol) with chiral HAT-catalyst **(*S,S*)-10c** in 1 mL $CD_3CN$. The product was obtained as a colorless liquid (21.0 mg, 81.6 µmol, 81%).

NMR spectra are in accordance with those of the non-deuterated compound **7f** with differences only in the benzylic position and adjacent position as expected and some small shifts for some of the signals in the $^{13}C$ NMR. Due to the only moderate deuteration degree signals for both, the deuterated and non-deuterated compound are visible with similar intensity.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.31 – 7.24 (m, 2H + 1H solvent residual signal), 7.24 – 7.15 (m, 5H), 6.92 – 6.87 (m, 2H), 4.03 (dd, *J* = 7.7, 5.7 Hz, 0.52H, corresponds to 48% deuteration), 3.82 (s, 3H), 3.19 (s, 3H), 2.76 – 2.55 (m, 2H), 2.19 – 2.07 (m, 1H), 1.97 – 1.86 (m, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.2, 142.1, 134.23 (**7f-*d*$_0$**), 134.17, 128.6, 128.5, 128.1, 125.9, 113.9, 82.7 (**7f-*d*$_0$**), 82.2 (t, $J_{C,D}$ = 21.7 Hz), 56.8, 56.5 (**7f-*d*$_0$**), 56.4, 55.4, 39.7 (**7f-*d*$_0$**), 39.6, 32.18 (residual **7f-*d*$_0$**), 32.15.

### 1-Methoxy-4-(1-methoxy-2-phenylethyl-1-*d*)benzene (7k-*d*$_1$)

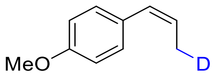


Synthesized according to general procedure G from benzyl ether **7k** (24.2 mg, 100 µmol) with chiral HAT-catalyst **(*S,S*)-10c** in 1 mL $CD_3CN$. The product was obtained as a colorless liquid (18.1 mg, 74.4 µmol, 74%).

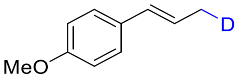
NMR spectra are in accordance with those of the non-deuterated compound **7k** with differences only in the benzylic position and adjacent positions as expected.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.25 – 7.12 (m, 5H), 7.12 – 7.07 (m, 2H), 6.88 – 6.83 (m, 2H), 4.28 (t, *J* = 6.7 Hz, 0.12H, corresponds to 88% deuteration), 3.81 (s, 3H), 3.17 (s, 3H), 3.12 (d, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 13.7 Hz, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.2, 138.7, 133.7, 129.6, 128.2, 128.1, 126.2, 113.8, 84.6 (**7k-*d*$_0$**), 84.3 (t, J = 21.7 Hz), 56.6, 55.4, 44.8.

### 1-Methoxy-4-(prop-1-en-1-yl-3-*d*)benzene (9-*d*$_1$, mixture of (*E*)- and (*Z*) isomer)



***Z*-9**



***E*-9**

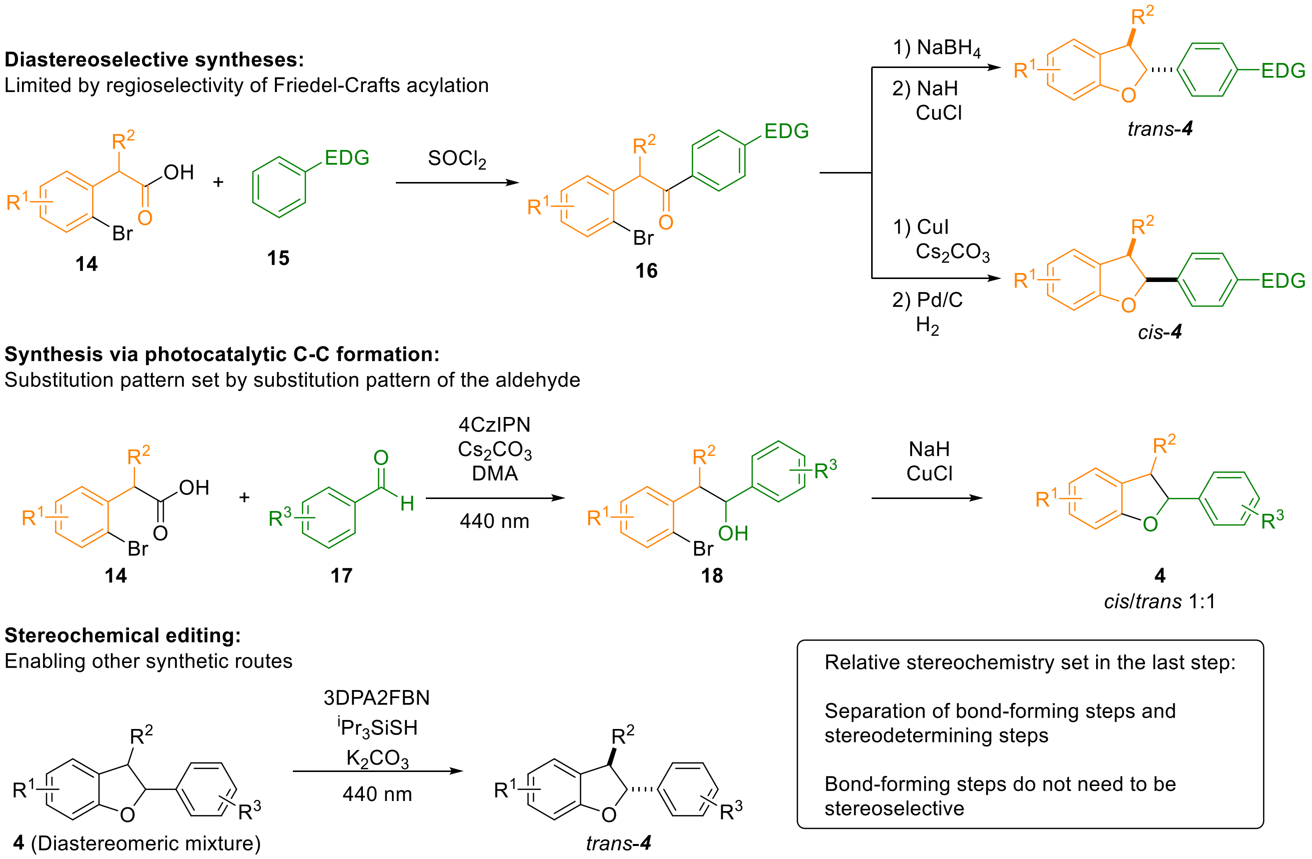
Synthesized according to general procedure G from 1-allyl-4-methoxybenzene (**8**, 59.3 mg, 400 µmol) in 4 mL $CD_3CN$. The product was obtained as a colorless liquid (41.0 mg, 275 µmol, 69%, *Z*/*E* = 3:1, >90% mono-deuteration). The crude product had a *Z*/*E* ratio of 4:1.

The NMR spectra of **(*Z*)-9** are in accordance with literature reports of the non-deuterated compound with differences only in the allylic position and adjacent vinylic position as expected.[48] **(*E*)-9-*d*$_1$** was compared to commercially available **(*E*)-9-*d*$_0$** and the NMR-spectra also match except for differences in the allylic position and adjacent vinylic position as expected. Following NMR-data refers to the (*Z*)-isomer.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.19 – 7.14 (m, 2H, overlap with **(*E*)-9**), 6.84 – 6.78 (m, 2H), 6.33 – 6.27 (m, 1H), overlap with **(*E*)-9**), 5.68 – 5.56 (m, 1H), 3.74 (s, 3H), 1.84 – 1.71 (m, 2.47H, overlap with **(*E*)-9**, corresponds to >90% mono-deuteration). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 158.2, 130.5, 130.1, 129.4, 125.2, 113.7, 55.4, 14.5 (t, $J_{C,D}$ = 19.4 Hz).

# 5 Application of benzofuran isomerization via a photocatalytic HAT/RRPCO/protonation sequence

The dihydrobenzofuran scaffold is a common motif in natural products and different synthetic methods have been reported for their synthesis.[49] A straightforward synthesis of 2,3-dihydrobenzofurans (**4**) starts from phenylacetic acid derivatives and electron rich benzenes. After Friedel-Crafts acylation a divergent synthesis gives the *cis*- or the *trans*-dihydrobenzofurans. However, the substitution pattern on the pendent aryl group is limited by the directing effect of the substituents. Based on previous reports on photocatalytic Barbier and Grignard-like reactions we developed a method for a synthesis of 2,3-dihydrobenzofurans by decarboxylative C-C coupling between bromophenylacetic acids and aromatic aldehydes.



Relative stereochemistry set in the last step:

Separation of bond-forming steps and stereodetermining steps

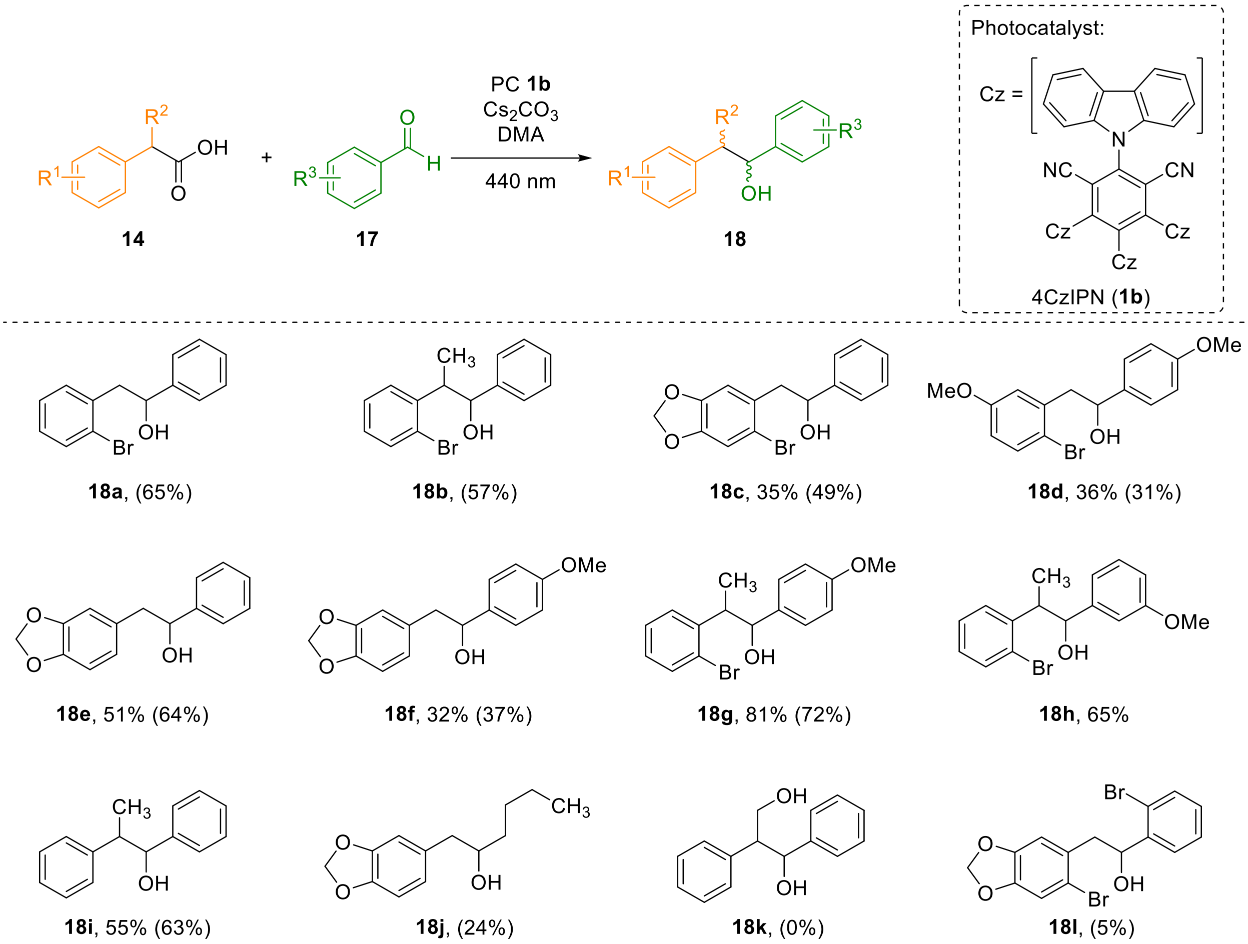
Bond-forming steps do not need to be stereoselective

**Scheme S2.** Synthetic routes to dihydrobenzofurans.

In contrast to the non-photocatalytic pathways, the photocatalytic C-C coupling lacks diastereoselectivity and the dihydrobenzofurans are obtained in a 1:1 diastereomeric mixture if a methyl group is present on the 3-position. Other substituents at this position have not been tested but it is expected that diastereoselectivity is also low. By subjecting the mixture of diastereomers to reaction conditions for isomerization via a HAT/RRPCO/protonation sequence the *trans*-isomer is obtained selectively. In total, the sequence based on non-diastereoselective photocatalytic C-C coupling and late stage stereochemical editing is short, provides the *trans*-2,3-dihydrobenzofurans with high atom economy and access to substitution patterns not obtainable by Friedel-Crafts acylation. This is demonstrated on the example of a diastereomeric mixture of meta-substituted dihydrobenzofuran **4d** synthesized in this section which is converted to pure ***trans*-4d** in section 6.

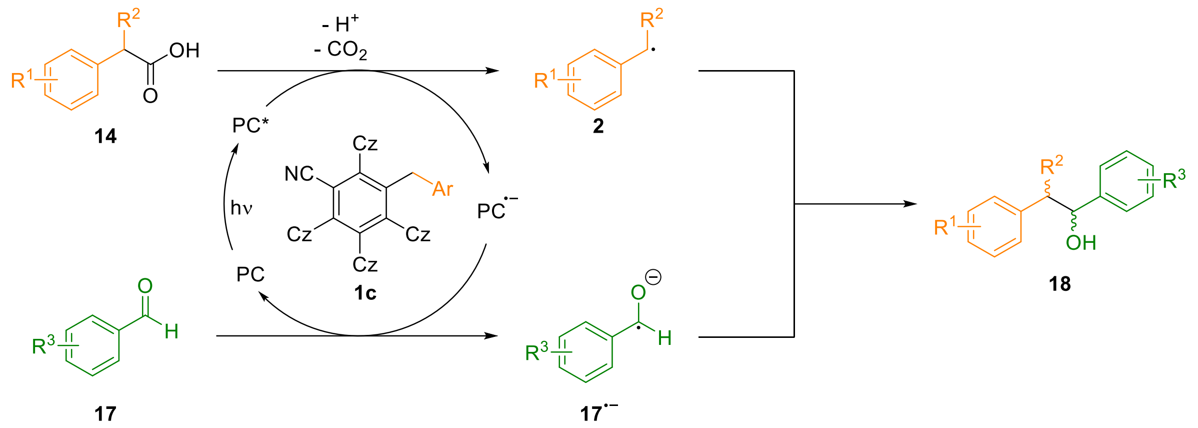
## 5.1 Synthesis of 1,2-diarylethanol derivatives

1,2-Diarylethanols were synthesized according to general procedure H via a previously published method[50] and obtained in moderate yields. However, no optimization of the reaction conditions for the specific substrates was conducted. 4CzIPN acts only as precursor of the active catalyst which is generated in situ via a photosubstitution[9] with the respective carboxylic acid substrate. Thus, the active catalyst is different for each substrate.



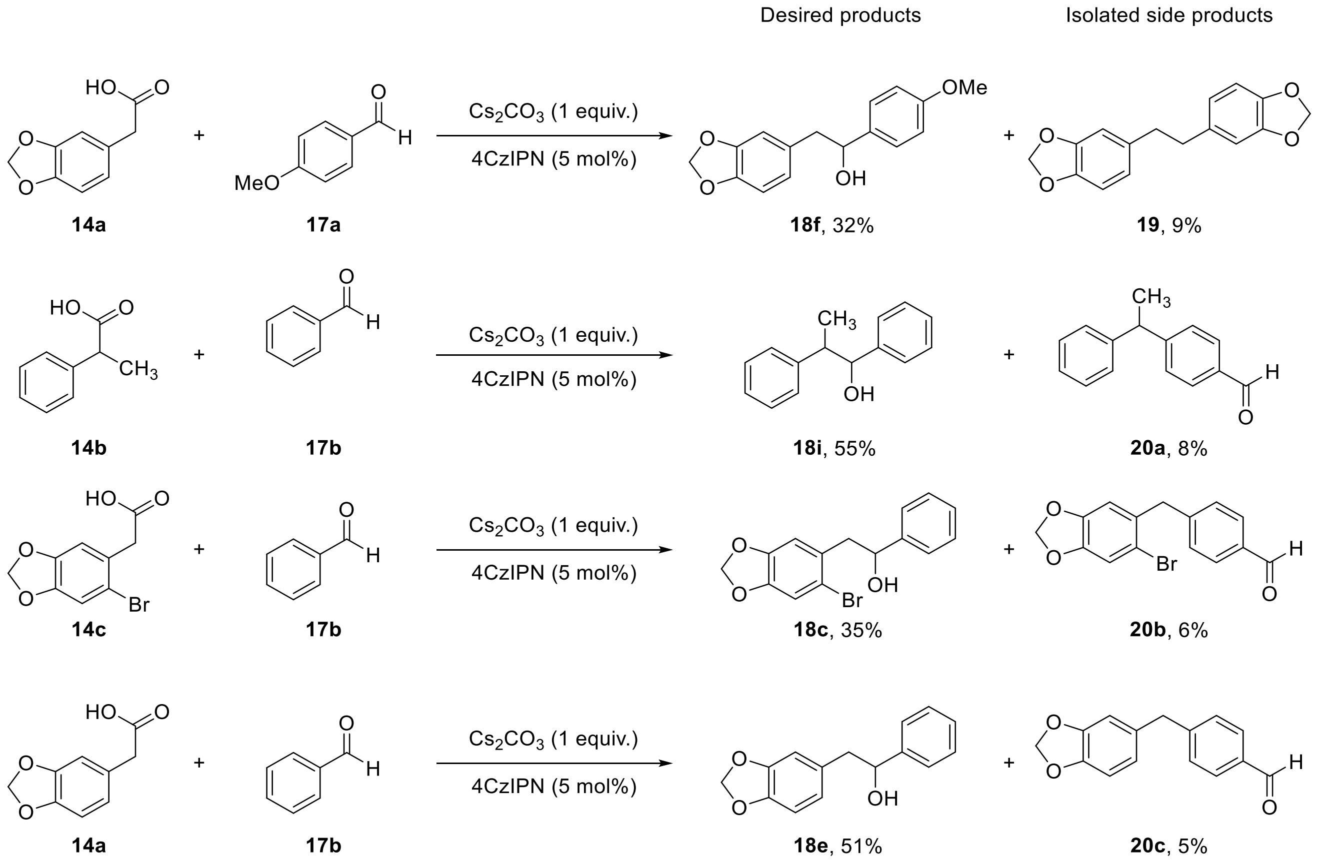
**Scheme S3.** Photocatalytic synthesis of 1,2-diarylethanols (**18**). Isolated yields where isolated, NMR yields in parentheses, determined via $^1$H NMR spectroscopy with 1,4-dicyanobenzene (0.25 equiv.) as internal standard for a separate reaction (150 µmol scale in 2 mL MeCN). Compounds **18b**, **18g**, **18h** and **18i** were formed as diastereomeric mixtures (*d.r.* = 1:1). Isolated diastereomeric ratios vary slightly mostly due to moderate separation of diastereomers during column chromatography.

With aromatic aldehydes the reaction likely proceeds via radical-radical coupling according to Scheme S4 as has been proposed previously.[50]



**Scheme S4.** Proposed reaction mechanism for coupling of phenylacetic acids with aromatic aldehydes. The active photocatalyst is formed in situ via a photosubstitution reaction between 4CzIPN (**1b**) and the corresponding carboxylic acid.[9]

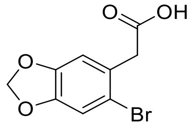
The proposed mechanism is supported by the observation that the reaction is insensitive to addition of water and by the observed side products **19** and **20**. Dimerization of the benzyl radicals to bibenzyl **19** and benzyl substitution in the 4-position of the aromatic aldehydes are observed in low but notable yield. Isolated products and side products are summarized in Scheme S5.



**Scheme S5.** Reactions scaled up for isolation of products where side products were isolated. Isolated yields.

## Synthesis of carboxylic acids (14)

### 2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)acetic acid (14c)

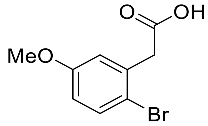


Synthesized according to literature procedure.[51]

Carboxylic acid **14a** (1.80 g, 10 mmol, 1 equiv.) was dissolved in 10 mL $CHCl_3$. Bromine (615 µL, 12 mmol, 1.2 equiv.) was added dropwise and the solution stirred for 2 h at room temperature. The reaction was quenched with saturated aqueous sodium thiosulfate solution, the organic phase extracted with 3 M aqueous NaOH solution (3x 10 mL) and the combined aqueous phases washed with $Et_2O$. The aqueous phase was then acidified with concentrated HCl to a pH of approximately 2. The suspension was extracted with $Et_2O$ (3x 20 mL), the organic phase washed with water and brine, dried over $Na_2SO_4$, and the solvent removed under reduced pressure to yield the product as colorless solid (1.80 g, 6.95 mmol, 69%). The $^1H$ NMR is in accordance with literature.[51]

**$^1H$ NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.03 (s, 1H), 6.78 (s, 1H), 5.98 (s, 2H), 3.75 (s, 2H).

### 2-(2-Bromo-5-methoxyphenyl)acetic acid (14d)

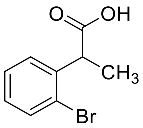


Synthesized according to literature procedure.[51]

3-Methoxyphenylacetic acid (1.16 g, 7.0 mmol, 1 equiv.) was dissolved in 10 mL $CHCl_3$. Bromine (430 µL, 8.4 mmol, 1.2 equiv.) was added dropwise and the solution stirred for 2 h at room temperature. The reaction was quenched with saturated aqueous sodium thiosulfate solution, the organic phase extracted with 3 M aqueous NaOH solution (3x 10 mL) and the combined aqueous phases washed with $Et_2O$. The aqueous phase was then acidified with concentrated HCl to a pH of approximately 2. The suspension was extracted with $Et_2O$ (3x 20 mL), the organic phase washed with water and brine, dried over $Na_2SO_4$, and the solvent removed under reduced pressure to yield the product as colorless solid (1.55 g, 6.32 mmol, 90%). The $^1H$ NMR is in accordance with literature.[52]

**$^1H$ NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.46 (d, *J* = 8.8 Hz, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 6.73 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.80 (s, 2H), 3.78 (s, 3H).

### 2-(2-Bromophenyl)propanoic acid (14e)



Synthesized according to literature procedure.[53]

Diisopropylamine (1.49 mL, 10.45 mmol, 2.1 equiv.) was dissolved in 5 mL THF. *n*-BuLi (1.6 M in *n*-hexane, 6.59 mL, 10.54 mmol, 2.1 equiv.) was added at -78 °C and the solution stirred for 30 min at -78 °C. Bromophenylacetic acid (5.02 mmol, 1.08 mmol, 1 equiv.) dissolved in 2 mL THF was added at -78 °C, the solution warmed to 0 °C and stirred for 60 min. Iodomethane (331 µL, 5.32 mmol, 1.06 equiv.) was added and the solution stirred at room temperature overnight. The reaction was quenched with $H_2O$ (0.2 mL) and concentrated under reduced pressure. The residue was dissolved in 10 mL $H_2O$, acidified to pH 1 and extracted with $Et_2O$. The solvent was removed under reduced pressure and the crude product recrystallized from EtOAc to yield the product as a colorless, crystalline solid (538 mg, 2.35 mmol, 47%). The $^1$H NMR is in accordance with literature.[53]

**$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] =7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.35 (dt, *J* = 7.3, 1.8 Hz, 1H), 7.31 (td, *J* = 7.4, 1.0 Hz, 1H), 7.17 – 7.09 (m, 1H), 4.29 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.3 Hz, 3H).

### General procedure H: Benzylation of aromatic aldehydes to secondary alcohols

According to previously reported procedure.[50] Phenylacetic acid derivative (**14**, 75 µmol per mL solvent, 1 equiv.), aldehyde (3 equiv.), cesium carbonate (1 equiv.) and 4CzIPN (**1b**, 5 mol%) are added to a crimp-capped vial with septum. DMA (1 mL per 75 µmol of carboxylic acid) is added via syringe. The vials are degassed by three cycles of freeze-pump-thaw and irradiated with blue LEDs ($\lambda_{max}$ = 440 nm) overnight at room temperature.

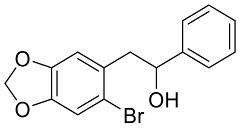
For isolation:

Multiple reactions on 300 µmol scale are combined, diluted with ethyl acetate, washed with water and brine, dried over $Na_2SO_4$, and the solvent removed under reduced pressure. The crude product is purified via column chromatography (0→25% EtOAc in PE).

### General procedure I: Large scale benzylation of aromatic aldehydes to secondary alcohols

Carboxylic acid (**14**, 4.5 mmol), cesium carbonate (1.47 g, 4.5 mmol, 1 equiv.), and 4CzIPN (**1b**, 177.5 mg, 225 µmol, 5 mol%) are added to a reaction flask under nitrogen atmosphere. Dry DMA (60 mL) and aldehyde (**17**, 13.5 mmol, 3 equiv.) are added, and the solution degassed by purging with nitrogen for 20 min. The solution is irradiated in the reactor depicted in Figure S3 for 5 h at room temperature. Isolation according to general procedure H.

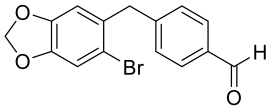
### 2-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-1-phenylethan-1-ol (18c)



Secondary alcohol **18c** was synthesized according to general procedure H from 2-(6-bromobenzo[*d*][1,3]dioxol-5-yl)acetic acid and benzaldehyde on 2.4 mmol scale (8x 300 µmol). The product was obtained as a colorless solid (273 mg, 850 µmol, 35%).

**Melting point:** $T_m$ = 98 °C. **TLC:** $R_f$ = 0.50 (20% EA in PE). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.43 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 2.03 (m, 1H), 6.70 (s, 1H), 5.95 (d, *J* = 1.4 Hz, 1H), 5.94 (d, *J* = 1.4 Hz, 1H), 4.97 (dd, *J* = 8.8, 4.3 Hz, 1H), 3.11 (dd, *J* = 13.9, 4.3 Hz, 1H), 2.98 (dd, *J* = 13.9, 8.9 Hz, 1H), 1.83 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.4, 144.0, 130.8, 128.6, 127.8, 125.8, 115.1, 112.9, 111.7, 101.8, 73.9, 46.1. **HRMS (EI+):** exact mass calcd for $C_{15}H_{13}BrO_3$ $[M]^+$: m/z = 320.00426, found: 320.00415.

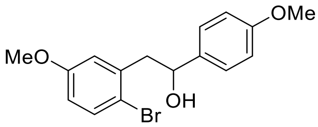
### 4-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)benzaldehyde (20b)



Compund **20b** was obtained as a side product of secondary alcohol **18c** as a yellow liquid in low purity (42 mg, 0.1 mmol, 6%).

**TLC:** $R_f$ = 0.53 (20% EA in PE). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 9.97 (s, 1H), 7.83 – 7.78 (m, 2H), 7.36 – 7.31 (m, 2H), 7.04 (s, 1H), 6.64 (s, 1H), 5.96 (s, 2H), 4.10 (s, 2H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 191.9, 147.6, 147.3, 147.1, 134.8, 132.0, 130.0, 129.4, 115.0, 112.9, 110.7, 101.8, 41.8. **HRMS (EI+):** exact mass calcd for $C_{15}H_{11}BrO_3$ $[M]^+$: m/z = 317.98861, found: 317.98791.

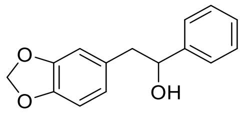
### 2-(2-Bromo-5-methoxyphenyl)-1-(4-methoxyphenyl)ethan-1-ol (18d)



Secondary alcohol **18d** was synthesized according to general procedure I from carboxylic acid (**14d**) and aldehyde **17a** at 4.5 mmol scale. The product was obtained as a slightly yellow colored solid as a 1:1 mixture of diastereomers (545 mg, 1.62 mmol, 36%). The cooling system failed during the reaction which might be responsible for the low yield. The $^1$H and $^{13}$C NMR spectra are in accordance with literature.[52]

**Melting point:** $T_m$ = 72 °C **TLC:** $R_f$ = 0.53 (20% EtOAc in PE). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.44 (d, *J* = 8.7 Hz, 1H), 7.35 – 7.28 (m, 2H), 6.92 – 6.85 (m, 2H), 6.72 (d, *J* = 3.0 Hz, 1H), 6.66 (dd, *J* = 8.9, 3.2 Hz, 1H), 4.96 (dd, *J* = 8.6, 4.6 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.13 (dd, *J* = 13.7, 4.78 Hz, 1H), 3.04 (dd, *J* = 13.7, 8.6 Hz, 1H) 2.03 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.2, 158.8, 138.8, 136.1, 133.4, 127.1, 117.5, 115.3, 114.3, 113.9, 73.1, 55.5, 55.4, 46.4. **HRMS (EI+):** exact mass calcd for $C_{16}H_{17}BrNaO_3$ $[M+Na]^+$: m/z = 359.0253, found: 359.0254.

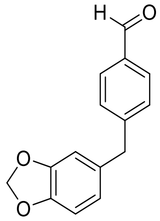
### 2-(Benzo[*d*][1,3]dioxol-5-yl)-1-phenylethan-1-ol (18e)



Secondary alcohol **18e** was synthesized according to general procedure H from carboxylic acid **14a** and benzaldehyde (**17b**) on 2.1 mmol scale (7x 300 µmol). The product was obtained as a colorless solid (260 mg, 1.07 mmol, 51%). The NMR spectra are in accordance with literature.[54]

**Melting point:** $T_m$ = 98 °C. **TLC:** $R_f$ = 0.38 (20% EtOAc in PE). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.35 (d, *J* = 4.3 Hz, 4H), 7.31 – 7.26 (m, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 1.5 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.93 (s, 2H), 4.4 (dd, *J* = 8.49, 4.9 Hz, 1 H), 2.96 (dd, *J* = 13.8, 4.9 Hz, 1H), 2.90(dd, *J* = 13.8, 8.4 Hz, 1H), 1.96 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.8, 146.4, 143.8, 131.8, 128.6, 127.8, 126.0, 122.6, 109.9, 108.4, 101.0, 75.5, 45.9. **HRMS (EI+):** exact mass calcd for $C_{15}H_{14}O_3$ $[M]^+$: m/z = 242.09375, found: 242.09360.

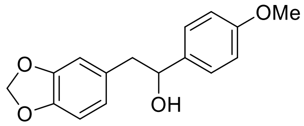
### 4-(Benzo[*d*][1,3]dioxol-5-ylmethyl)benzaldehyde (20c)



Compound **20c** was isolated as a side product in the synthesis of secondary alcohol **18e** as a yellow liquid (27 mg, 112 µmol, 5%).

**TLC:** $R_f$ = 0.53 (20% EtOAc in PE). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 9.97 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.68 – 6.62 (m, 2H), 5.92 (s, 2H), 3.96 (s, 2H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.4, 144.0, 130.8, 128.6, 127.8, 125.8, 115.1, 112.9, 111.7, 101.8, 73.9, 46.1. **HRMS (EI+):** exact mass calcd for $C_{15}H_{12}O_3$ $[M]^+$: m/z = 240.07810, found: 240.07816.

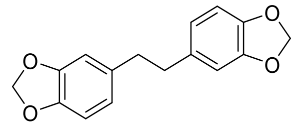
### 2-(Benzo[*d*][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)ethan-1-ol (18f)



Secondary alcohol **18f** was synthesized according to general procedure H from carboxylic acid **14a** and aldehyde **17a** on 1.2 mmol scale (4x 300 µmol). The product was obtained as a colorless solid (104 mg, 382 µmol, 32%).

**Melting point:** $T_m$ = 99 °C. TLC: $R_f$ = 0.25 (20% EtOAc in PE). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 7.27 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 1.0 Hz, 1 H), 6.66 – 6.60 (m, 1H), 5.93 (s, 2H), 4.79 (dd, *J* = 7.1, 6.0 Hz, 1H), 3.81 (s, 3H), 2.97 – 2.85 (m, 2H), 1.93 (s, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.2, 147.8, 146.4, 136.0, 132.0, 127.3, 122.6, 113.9, 109.9, 108.4, 101.0, 75.1, 55.4, 45.8. **HRMS (EI+):** exact mass calcd for $C_{16}H_{16}NaO_4$ $[M+Na]^+$: m/z = 295.0941, found: 295.0945.

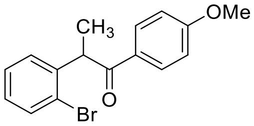
## 1,2-Bis(benzo[*d*][1,3]dioxol-5-yl)ethane (19)



Bibenzyl **19** was obtained as a side product of secondary alcohol **18f** as colorless needles. The NMR spectra are in accordance with literature.[55]

**TLC:** $R_f$ = 0.63 (20% EtOAc in PE). **$^1$H NMR (400 MHz, CDCl$_3$):** δ [ppm] = 6.72 (d, *J* = 7.8 Hz, 2H), 6.66 (d, 1.6 Hz, 2H), 6.60 (dd, *J* = 7.9, 1.7 Hz, 2H), 5.92 (s, 4H), 2.79 (s, 4H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 147.6, 145.8, 135.6, 121.3, 109.1, 108.3, 100.1, 38.3.

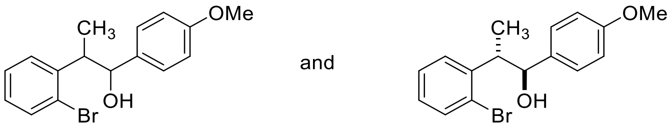
## 2-(2-Bromophenyl)-1-(4-methoxyphenyl)propan-1-one (16a)



2-Bromophenylacetic acid (**14e**) (8.79 g, 38.38 mmol, 1 equiv.) was refluxed in 2.8 mL thionyl chloride for 30 min. The excess SOCl$_2$ was then evaporated under reduced pressure and the residue redissolved in 70 mL DCM, cooled to 0 °C, and anisole (4.17 mL, 38.38 mmol, 1.0 equiv.) was added. AlCl$_3$ (5.12 g, 38.38 mmol, 1.0 equiv.) was added in small portions, and stirred for 30 min at room temperature. The reaction mixture was then poured onto ice and extracted with DCM. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The crude product was purified via column chromatography (10→50% EtOAc in PE) to give the product as a light orange solid (9.39 g, 29.43 mmol, 86%). The $^1$H NMR spectrum is in accordance with Literature.[56]

**$^1$H NMR (400 MHz, CDCl3):** δ [ppm] = 7.96 – 7.87 (m, 2H), 7.59 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.22 – 7.11 (m, 2H), 7.09 – 7.02 (m, 1H), 6.90 – 6.83 (m, 2H), 5.05 (q, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 3H).

## 2-(2-Bromophenyl)-1-(4-methoxyphenyl)propan-1-ol (18g)



Diastereomeric mixture:

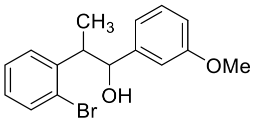
Secondary alcohol **18g** was synthesized according to general procedure H from carboxylic acid **14b** and aldehyde **17a** on 1.2 mmol scale (4x 300 µmol). The product was obtained as a colorless oil as a 1:0.77 mixture of diastereomers not fully separated from aldehyde **17a** (313 mg, 974 µmol, 81%) and used as a mixture for the synthesis of dihydrobenzofuran **4c**.

### *trans*-18g

Ketone **16a** (400 mg, 1.25 mmol, 1 equiv.) was dissolved in 4 mL EtOH, NaBH$_4$ (95.0 mg, 2.50 mmol, 2 equiv.) was added, and the mixture stirred for 2 h at room temperature. The reaction was then quenched by slow addition of 1 M HCl, extracted with EtOAc, the organic phase washed with H$_2$O and brine, dried over Na$_2$SO$_4$, and the crude product purified via column chromatography (5→20% EtOAc in PE) to give the product as a colorless solid (337 mg, 1.05 mmol, 84%).

**$^1$H NMR (400 MHz, CDCl3):** δ [ppm] = 7.62 – 7.60 (m, 1H), 7.33 – 7.23 (m, 4H), 7.15 – 7.06 (m, 1H), 6.92 – 6.85 (m, 2H), 4.77 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.81 (s, 3H), 1.03 (d, *J* = 7.0 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$):** δ [ppm] = 159.5, 143.0, 134.5, 133.2, 128.4, 128.1, 127.9, 113.8, 78.6, 55.4, 17.7.

## 2-(2-Bromophenyl)-1-(3-methoxyphenyl)propan-1-ol (18h)

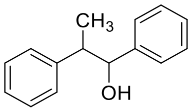


*cis*/*trans* = 1:1.5

Secondary alcohol **18h** was synthesized according to general procedure H from carboxylic acid **14b** and aldehyde **17c** on 2.1 mmol scale (7x 300 µmol). The product was obtained as a colorless oil as a mixture of diastereomers (441 mg, 1.37 mmol, 65%, *d.r.* = 1:1.5).

**$^1$H NMR (diastereomeric mixture) (400 MHz, CDCl3):** δ [ppm] = 7.61 – 7.54 (m, 2.8H), 7.38 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.34 – 7.28 (m, 5.2H), 7.25 – 7.22 (m, 1.5H), 7.13 – 7.06 (m, 3H), 7.03 – 6.99 (m, 2H), 6.94 – 6.89 (m, 1.7H), 6.89 – 6.83 (m, 3.6H), 6.82 – 6.77 (m, 1H), 4.97 (d, *J* = 4.0 Hz, 1H), 4.79 (d, *J* = 8.3 Hz, 1.5H), 3.81 + 3.80 (2x s, 8.1H), 3.76 – 3.63 (m, 3.1H), 1.84 + 1.73 (2x s, 2.7H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 4.5H). **$^{13}$C{$^1$H} NMR (diastereomeric mixture) (101 MHz, CDCl$_3$):** δ [ppm] = 159.7, 159.6, 144.8, 144.0, 143.1, 142.8, 133.2, 133.1, 129.4, 129.3, 129.2, 128.4, 128.2, 127.8, 127.6, 126.1, 125.1, 119.6, 118.5, 113.8, 113.6, 112.9, 112.6, 111.6, 55.4, 45.2, 17.7, 13.1. **HRMS (+APCI):** exact mass calcd for $C_{16}H_{21}BrNO_2$ $[M+NH_4]^+$: m/z = 338.0750, found: 338.0752 and 338.0748.

## 1,2-Diphenylpropan-1-ol (18i)

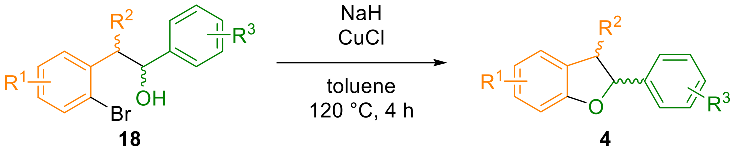


Secondary alcohol **18i** was synthesized according to general procedure I from 2-phenylpropanoic acid and 4-methoxybenzaldehyde (**17a**) on 4.50 mmol scale. The product was obtained as a slightly yellow colored viscous liquid as a 1:1 mixture of diastereomers (561 mg, 2.64 mmol, 59%). The $^1$H NMR spectrum is in accordance with literature.[25] The corresponding *p*-benzylated benzaldehyde was obtained as an additional fraction but was not fully separated from alcohol **18i**. Purification of the side product was not attempted.

**TLC:** $R_f$ = 0.53 (20% EtOAc in PE**)**. **$^1$H NMR (mixture of diastereomers) (400 MHz, CDCl$_3$):** δ [ppm] = 7.41 – 7.13 (m, 20H), 4.82 (d, *J* = 5.8 Hz, 1H), 4.67 (d, *J* = 8.7 Hz, 1H), 3.17 – 8.08 (m, 1H), 3.08 – 2.99 (m, 1H), 1.88 (s, 2H), 1.33 (d, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 7.1 Hz, 3H).

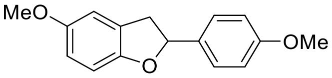
## 5.2 Synthesis of dihydrobenzofurans

### General procedure J: Cyclization of secondary alcohols (18) to dihydrobenzofurans (4)



According to literature procedure.[52] Secondary alcohol (1 equiv.) and NaH (60% dispersion in mineral oil; pre-washed with *n*-hexane; 1.25 equiv.) are added to a crimp vial and dissolved in toluene. The solution is stirred for 1 h at room temperature. CuCl (5 mol%), suspended in toluene, and ethyl acetate (1 µL) are added, and the mixture stirred at 120 °C for 4 h. The solution is diluted with ethyl acetate (20 mL), washed with water (3 x 15 mL) and brine (15 mL), dried over $Na_2SO_4$ and the solvent removed under reduced pressure. The crude product is purified via column chromatography (0→15% EtOAc in PE).

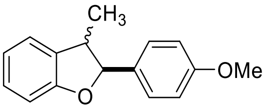
### 5-Methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (Corsifuran A, 4b)



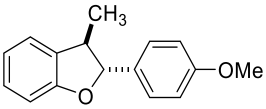
Synthesized according to general procedure J with secondary alcohol **18d** (303.5 mg, 900 µmol). Dihydrobenzofuran **4b** was obtained as colorless, crystalline solid (160 mg, 624.3 µmol, 69%). The compound is known as natural product Corsifuran A and the NMR spectra are in accordance with literature.[52]

**Melting point:** $T_m$ = 83 °C. **TLC:** $R_f$ = 0.58 (20% EA in PE). **$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.39 – 7.28 (m, 2H), 6.95 – 6.84 (m, 2H), 6.82 – 6.64 (m, 3H), 5.68 (t, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.55 (dd, *J* = 15.79, 9.18 Hz, 1H), 3.20 (dd, *J* = 15.77, 8.44 Hz, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 159.6, 154.4, 153.9, 134.1, 127.8, 127.4, 114.1, 113.1, 111.3, 109.3, 84.3, 56.2, 55.4, 38.8.

### *trans*-2-(4-Methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (4c)



and



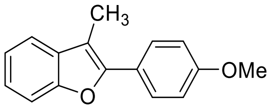
Synthesized according to general procedure J with a diastereomeric mixture of ***cis*-18g** and ***trans*-18g** and in a separate batch with pure ***trans*-18g** obtained in the non-photocatalytic synthesis. The NMR spectra are in accordance with literature.[57,58]

With a diastereomeric mixture (1:0.71) of secondary alcohol **18g** (161 mg, 500 µmol). Dihydrobenzofuran **4c** was obtained as yellow liquid (96 mg, 400 µmol, 80%) as a mixture of both diastereomers (1:0.77).

With ***trans*-18g** (360 mg, 1.12 mmol, *trans*/*cis* >9:1). ***trans*-4c** was obtained as a yellow liquid (221 mg, 920 µmol, 82%).

***trans*-4c**: **$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.41 – 7.35 (m, 2H), 7.22 – 7.13 (m, 2H), 6.96 – 6.90 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 9.0 Hz, 1H), 3.83 (s, 3H), 3.45 (quintet, *J* = 7.3 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H).

## 2-(4-Methoxyphenyl)-3-methylbenzofuran (35)

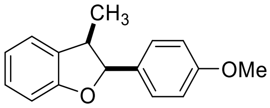


Synthesized according to literature procedure.[59]

A mixture of secondary alcohol **18g** (711 mg, 2.23 mmol), $Cs_2CO_3$ (1.54 g, 4.73 mmol, 2.2 equiv.), and CuI (212 mg, 1.11 mmol, 0.5 equiv.) in dry DMF (10 mL) was stirred at 105 °C for 48 h. After cooling to room temperature, water (50 mL) was added directly to the reaction mixture over 15 minutes and the resulting orange slurry was extracted with EtOAc (3× 30 mL), the organic phases were combined, dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The crude product was purified via column chromatography (10% EtOAc in PE) to give benzofuran **35** as yellow oil (481 mg, 2.02 mmol, 68%). The $^1$H NMR spectrum is in accordance with literature.[59]

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ(ppm) = 7.79 – 7.71 (m, 2H), 7.55 – 7.44 (m, 2H), 7.31 – 7.21 (m, 2H+overlap with solvent residual signal), 7.06 – 6.98 (m, 2H), 3.87 (s, 3H), 2.45 (s, 3H).

## *cis*-2-(4-Methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (*cis*-4c)



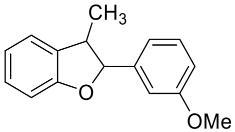
***cis*-4c** was synthesized by hydrogenation of the corresponding benzofuran **35**.

Benzofuran **35** (0.57 g, 2.38 mmol, 1 equiv.) was dissolved in a mixture of 5 mL isopropanol and 15 mL ethanol and added to Palladium on activated charcoal (252 mg, 0.24 mmol, 10 mol%) in an autoclave reactor. The setup was charged with 50 bar hydrogen gas and stirred at room temperature for 72 h. The mixture was then filtered through celite, the solvent evaporated, and the product separated from unreacted starting material by column chromatography (toluene/petrol ether, 5:1). The product was obtained as yellow oil (0.21 g, 0.87 mmol, 31%) with a *d.r.* of 6.5:1. The use of a toluene/PE mixture for column chromatography was necessary due to the poor separation of product and starting material with EtOAC/PE mixtures.

The $^1$H NMR spectrum is in accordance with literature.[58]

**$^1$H-NMR (300 MHz, $CDCl_3$):** δ(ppm) = 7.25 – 7.20 (m, 2H), 7.19 – 7.12 (m, 2H), 6.94 – 6.85 (m, 4H), 5.77 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.66 (quint, *J* = 7.7 Hz, 1H), 0.83 (d, *J* = 7.1, 3H).

## 2-(3-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (4d)



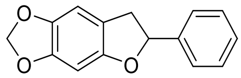
*cis*/*trans* = 1:1.5

Synthesized according to general procedure J from **18h** (*cis*/*trans* = 1:1.5) on 1.37 mmol scale.

The product was obtained as a yellow liquid with the same diastereomeric ratio as the starting material (282 mg, 1.17 mmol, 86%, *cis*/*trans* = 1:1.5). *cis*/*trans* isomerization to convert the diastereomeric mixture of **4d** to pure ***trans*-4d** is explained in section 6.

**$^1$H NMR (diastereomeric mixture) (400 MHz, $CDCl_3$):** δ(ppm) = 7.30 (q, *J* = 7.9 Hz, 3H), 7.22 – 7.13 (m, 5.4H), 7.04 – 6.98 (m, 2H), 6.96 – 6.83 (m, 10H), 5.79 (d, *J* = 8.7 Hz, 1H), 5.15 (d, *J* = 8.7, 1.5H), 3.82 + 3.81 (2x s, 8.2H), 3.69 (p, *J*=7.6 Hz, 1H), 3.45 (p, *J* = 7.3 Hz, 1.6H), 1.45 (d, *J* = 6.8, 4.7H), 0.85 (d, *J* = 7.2 Hz, 3H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)**: δ(ppm) = 160.0, 159.7, 159.3, 159.2, 142.7, 139.8, 132.9, 132.0, 129.8, 129.4, 128.4, 128.3, 124.5, 123.8, 120.98, 120.92, 118.9, 118.5, 113.9, 113.1, 112.1, 111.6, 109.7, 109.6, 92.4, 87.7, 55.41, 55.36, 45.7, 41.0, 18.3, 17.1. **HRMS (EI+):** exact mass calcd for $C_{15}H_{12}O_3$ [M+]: m/z = 240.11448, found: 240.11475 and 240.11473.

## 6-Phenyl-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran (4e)



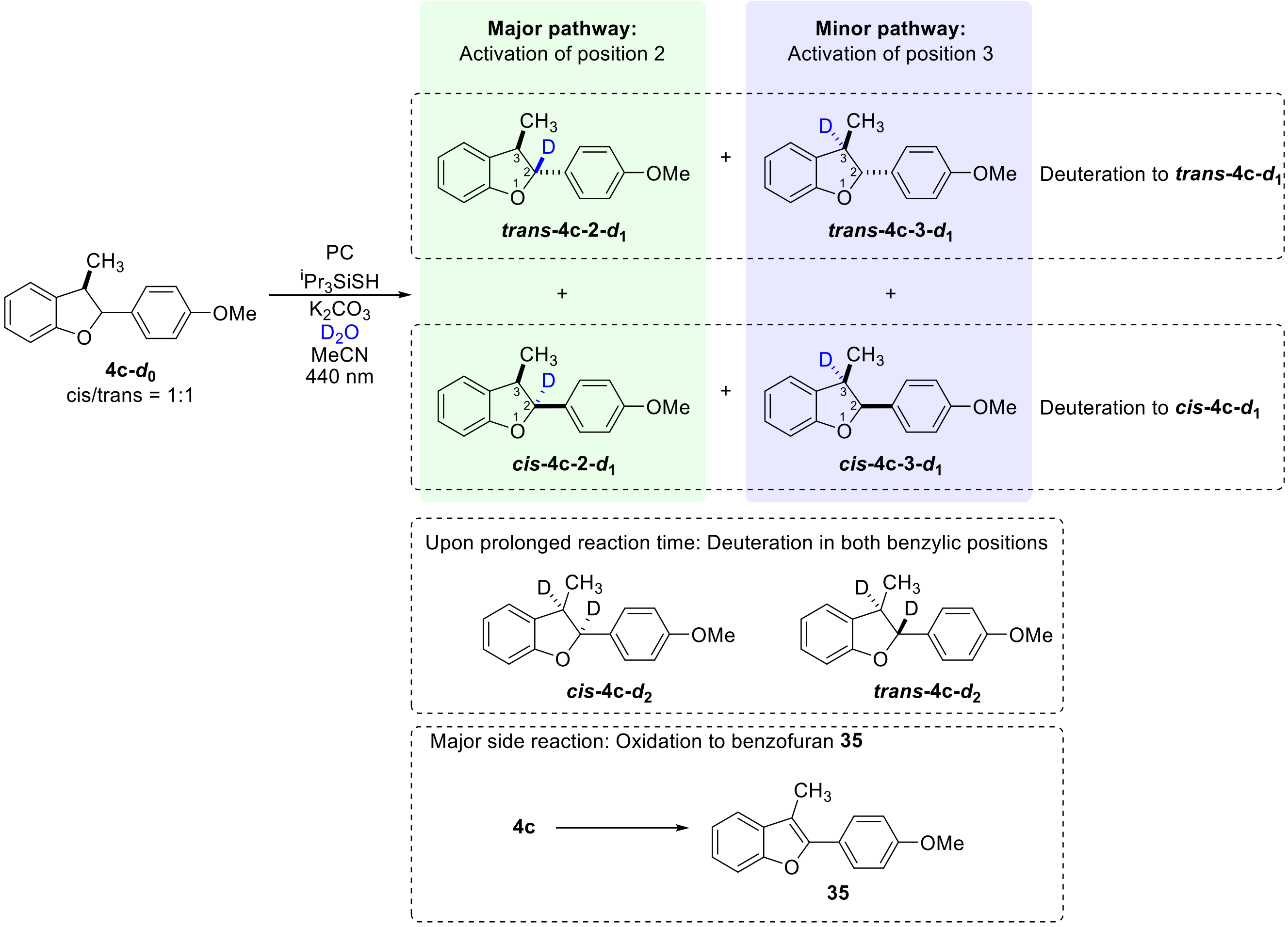
Synthesized according to general procedure J with secondary alcohol **18c** (96.35 mg, 300 µmol). Dihydrobenzofuran **4e** was obtained as a colorless liquid (55 mg, 229 µmol, 76%).

**TLC:** *$R_f$* = 0.68 (20% EA in PE). **$^1$H NMR (400 MHz, $CDCl_3$):** δ [ppm] = 7.43 – 7.29 (m, 5H), 6.66 (s, 1H), 6.47 (s, 1H), 5.91 (dd, *J* = 4.0, 1.3 Hz, 2H), 5.75 (t, *J* = 8.8 Hz, 1H), 3.53 (dd, *J* = 15.2, 9.5 Hz, 1H), 3.13 (dd, *J* = 15.1, 8.2 Hz, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$):** δ [ppm] = 154.3, 147.5, 142.0, 141.8, 128.7, 128.2, 125.9, 117.3, 105.1, 101.2, 93.2, 85.0, 38.6. **HRMS (EI+):** exact mass calcd for $C_{15}H_{12}O_3$: m/z = 240.07810, found: 240.07825[M+].

# 6 Kinetic studies for dihydrobenzofuran *cis/trans* isomerization and deuteration

Isomerizations and deuterium labelling of dihydrobenzofuran derivatives was conducted according to general procedure G. 50 µL aliquots were removed from the reaction mixtures and diluted with 550 µL $CDCl_3$ or $CD_3CN$. Yields were determined via NMR with 1,1,2,2-tetrachloroethane or the residual solvent signal as standard. The methyl group at the 3-position was used to determine yield and *cis/trans* ratios. Deuteration degrees were determined by comparison of the integrals for the benzylic hydrogens with the integrals for the methyl group in the 3-position.

The assignments of the signals and the procedure for determination of deuteration degrees is demonstrated exemplarily for deuteration of a 1:1 mixture of ***trans*-4c-*d*₀** and **cis-4c-*d*₀**.



**Scheme S6.** A 1:1 mixture of ***cis*-4c-*d*₀** and ***trans*-4c-*d*₀** initially generates monodeuterated products ***cis*-4c-2-*d*₁**, *trans*-**4c-2-*d*₁**, ***cis*-4c-3-*d*₁**, and ***trans*-4c-3-*d*₁**. With prolonged reaction time, the doubly deuterated products ***cis*-4c-*d*₂** and ***trans*-4c-*d*₂** form. Product loss occurs predominantly due to oxidation of dihydrobenzofuran **4c** to the corresponding benzofuran **35**.

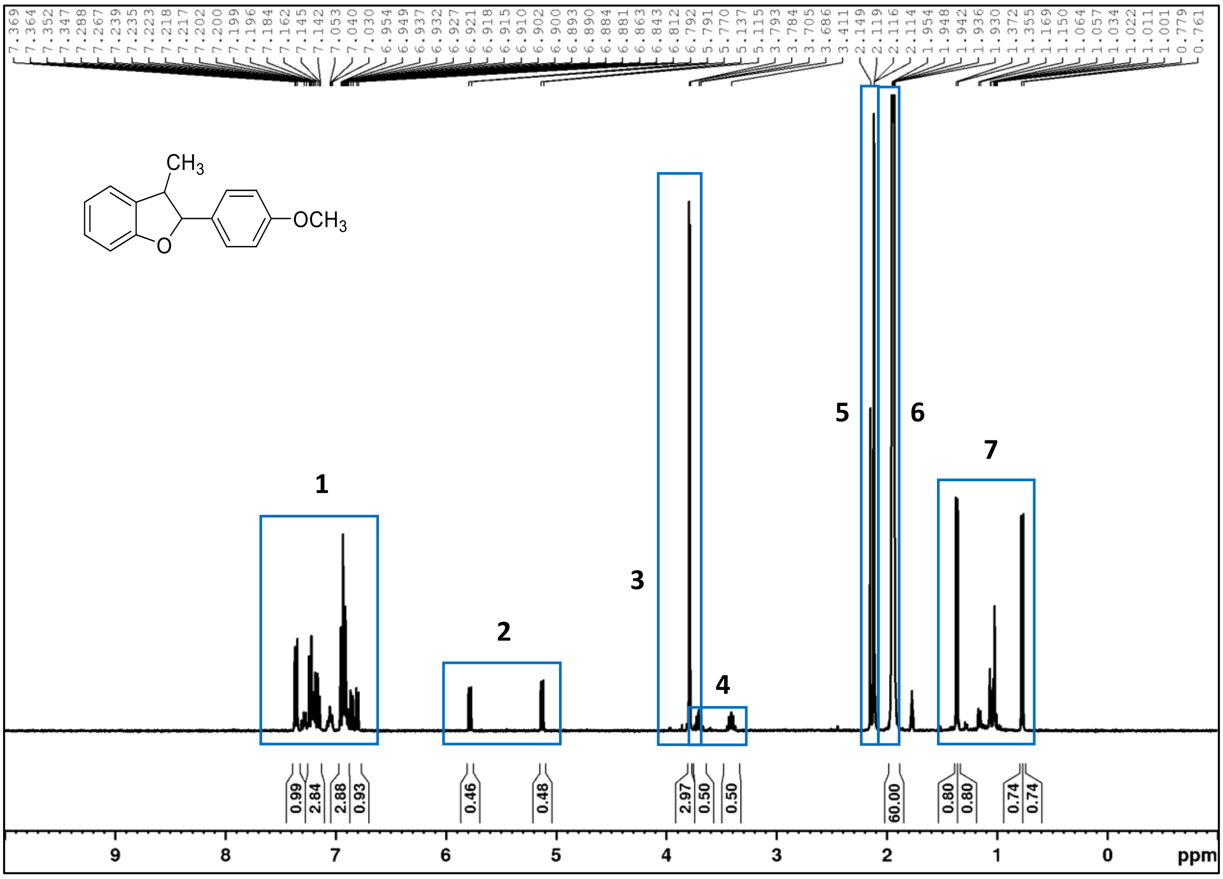


**Figure S9.** 1:1 mixture of ***trans*-4c-*d*$_0$** and ***cis*-4c-*d*$_0$**. The individual areas relevant for determination of yields and deuteration degrees are depicted individually in Figures S10 – S13.

Area 1: The aromatic region is crowded and due to overlaps between the diastereomers, photocatalyst, and side products it is less suited for analysis than other areas.

Area 2: This area contains the benzylic hydrogens of position 2. *cis*- and *trans*-isomer are well separated, and the area is free of other signals that might interfere. These signals were used to determine the deuteration degrees in the 2-position by comparison of the respective integral with the integral of the methyl group of the 2-position (area 7). Changes in area 2 during the reaction are depicted in Figure S10.

Area 3: Methoxy groups. The signals for both diastereomers are overlapping. Thus, they are less suited for analysis than other areas. The signal for the methoxy group of side product **35** also appears in this area. Changes in area 3 during the reaction are depicted in Figure S11.

Area 4: This area contains the benzylic hydrogens in position 3 and was used to determine the deuteration degree in position 3, where possible. The diastereomers are well separated, but in some reactions side products and impurities are interfering, especially when the respective signals are of low intensity due to high degree of deuteration. Deuteration in the 3-position can also be determined from the methyl group in position 3 (area 7). Changes in area 4 during the reaction are depicted in Figure S12.

Area 5: Residual $H_2O$, and HDO. The intensity increases with reaction progress, as abstracted H-atoms end up in the deuteron reservoir ($D_2O$). As these signals do not belong to the molecules of interest, no information was extracted from this are.

Area 6: The solvent residual signal (residual acetonitrile-*d*$_2$) was used as internal standard.

Area 7: Methyl groups in position 3. The signals for both diastereomers are well separated and, thus, were used to determine the relative concentration of ***cis*-4c** and ***trans*-4c**. Upon H-D exchange in position 3, the doublet changes to a broadened singlet, as expected. Deuteration in position 3 can be estimated from these signals and gives results consistent with those obtained from the integrals for the protons in the 3-position. Changes in area 7 during the reaction are depicted in Figure S13.

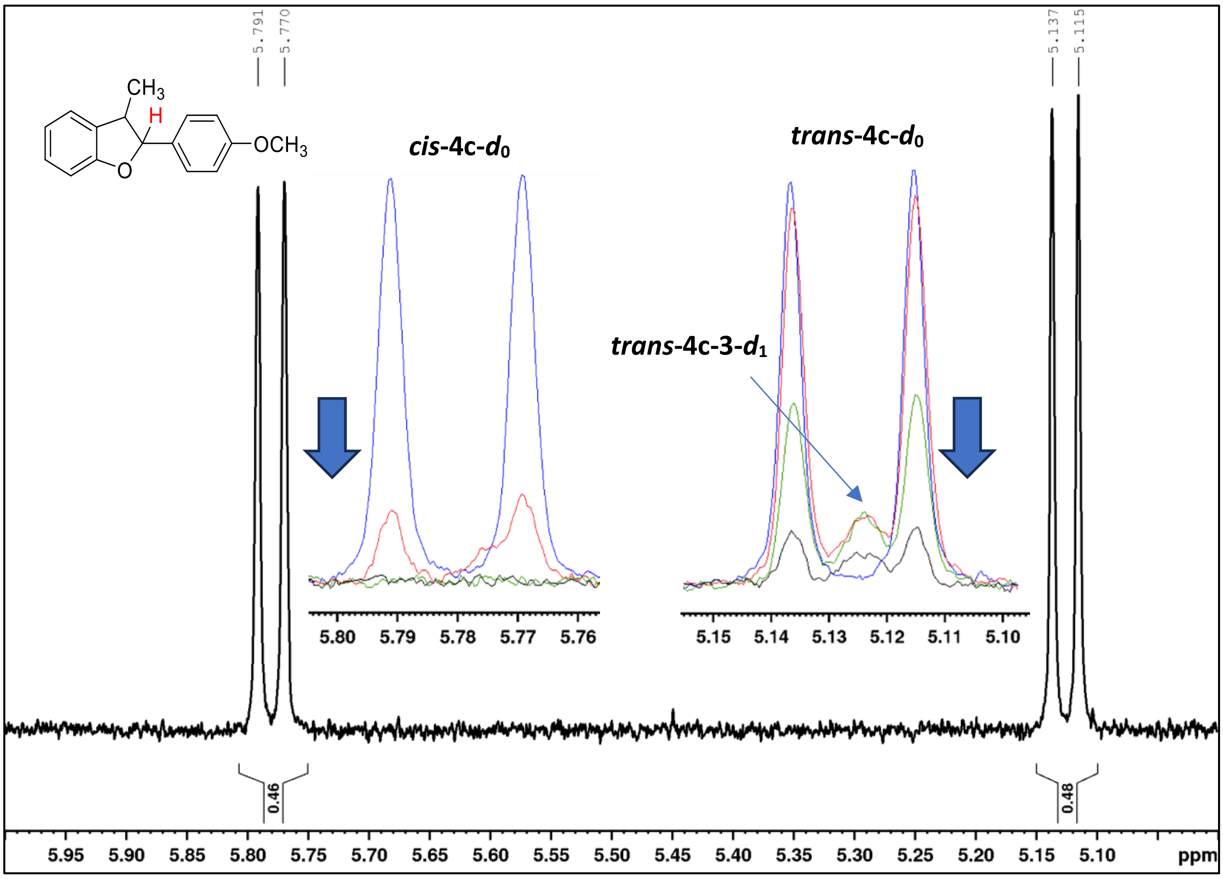


**Figure S10.** Area 2 during the HAT/RRPCO/deuteration reaction, starting with a 1:1 mixture of ***cis*-4c-*d*$_0$** and ***trans*-4c-*d*$_0$**, (Scheme S6). The large spectrum shows the $^1$H NMR spectrum before irradiation. Inserted superimposed spectra were measured at t = 0 min (blue), 10 min (red), 80 min (green), and 350 min (black). The fast consumption of the *cis*-isomer is evident by the strong decrease in signal intensity within the first minutes of irradiation. C-H activation in the 3-position can be seen by the initial appearance of a new singlet for ***trans*-4c-3-*d*$_1$** at 5.124 ppm which later decreased again upon deuteration to ***trans*-4c-*d*$_2$**. As this signal grows substantially slower than the signal for ***cis*-4c-*d*$_0$** decreases, it is evident that C-H activation in the 2-position is faster than C-H activation in the 3-position.

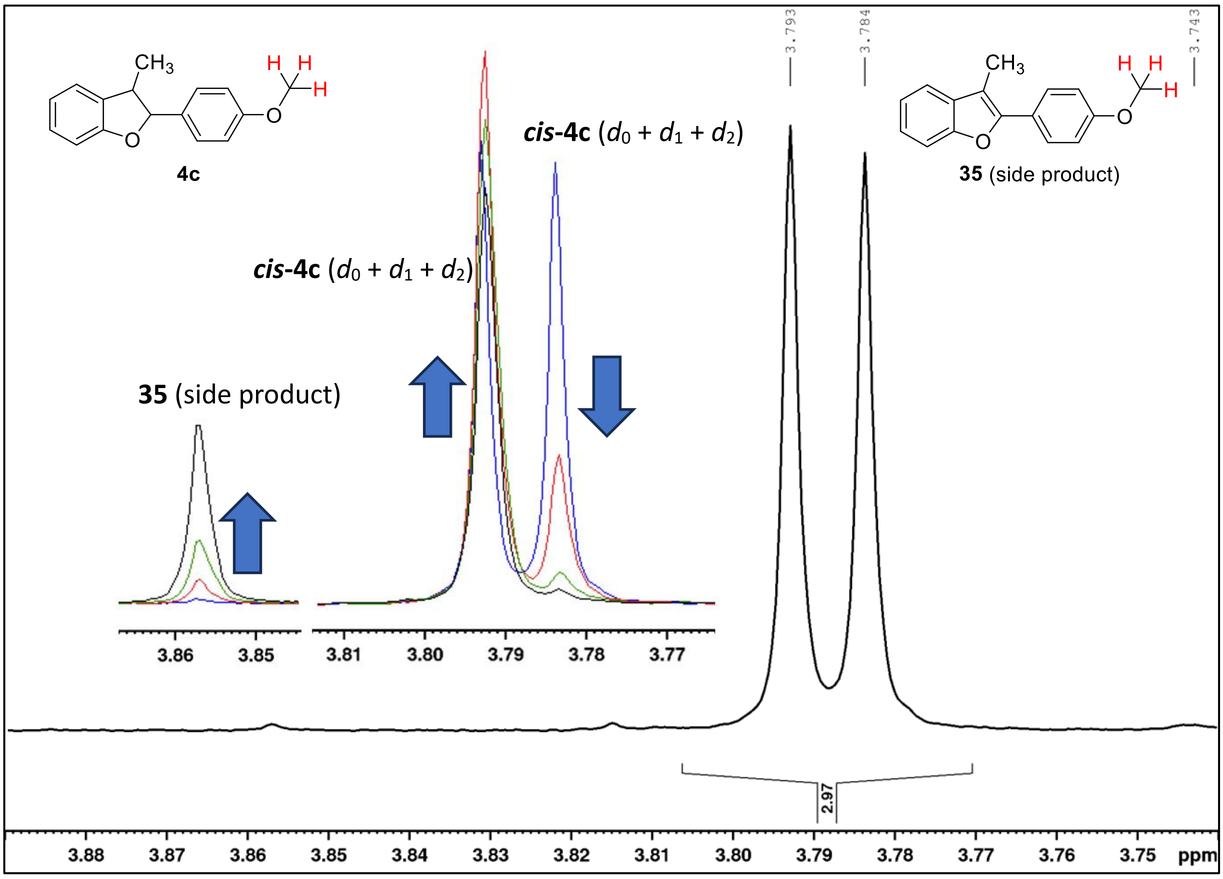


**Figure S11.** Area 3 during the HAT/RRPCO/deuteration reaction, starting with a 1:1 mixture of ***cis*-4c-*d*$_0$** and ***trans*-4c-*d*$_0$**, (Scheme S6). The large spectrum shows the $^1$H NMR spectrum before irradiation. Inserted superimposed spectra were measured at t = 0 min (blue), 10 min (red), 80 min (green), and 350 min (black). The concentration of the cis isomer decreases within minutes of irradiation (signal at 3.78 ppm) while the concentration of the trans isomer increases (signal at 3.79 ppm). Upon prolonged reaction time, the concentration of ***trans*-4c** also decreases, mostly due to formation of the oxidation product benzofuran **35**. This is evident by the appearance of a singlet at 3.86 ppm. The corresponding methyl group in position 3 of benzofuran **35** appears at 2.45 ppm. The $^1$H NMR spectrum of benzofuran **35** in $CD_3CN$ can be found in section 11.3.

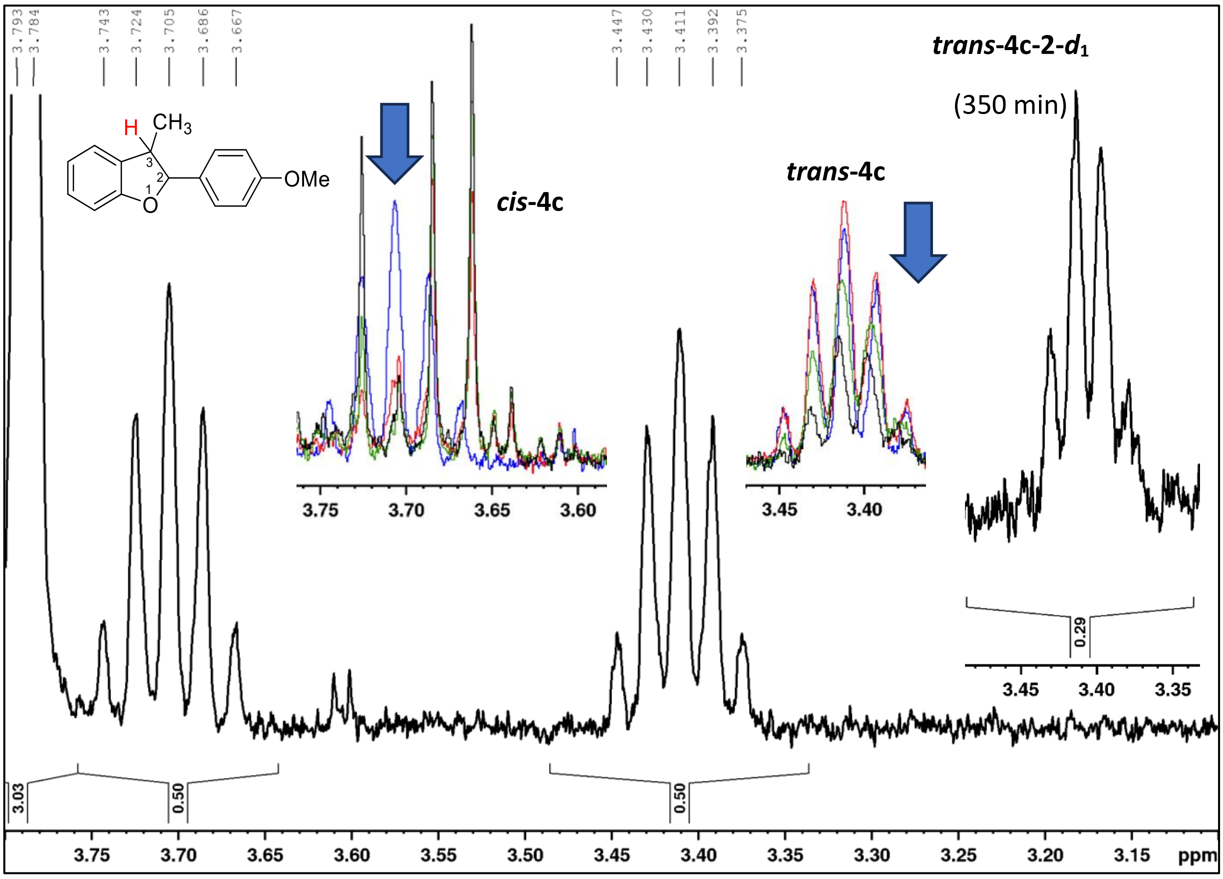


**Figure S12.** Area 4 during the HAT/RRPCO/deuteration reaction, starting with a 1:1 mixture of ***cis*-4c-*d*$_0$** and ***trans*-4c-*d*$_0$**, (Scheme S6). The large spectrum shows the $^1$H NMR spectrum before irradiation. Inserted superimposed spectra were measured at t = 0 min (blue), 10 min (red), 80 min (green), and 350 min (black). The signal of ***cis*-4c** decreases within minutes of irradiation, while the signal for trans-4c first increases slightly (due to *cis*/*trans* isomerization) and then decreases slowly, demonstrating an increasing degree of deuteration in the 3-position. The multiplet structure for the *trans*-isomer changes from a quintet to a quartet upon deuteration in the adjacent 2-position (inserted black spectrum, measured at 350 min). Additional signals for side products appear in the range of 3.60 – 3.75 ppm over the course of the reaction and overlap with ***cis*-4c**, thus, making this signal not suited for determination of the deuteration degree in the 3-position of ***cis*-4c**. The deuteration degree in the 3-position of ***trans*-4c** was determined by comparison of the integral for the benzylic hydrogen atom with the methyl group in the 3-position. The integral for the methyl signal of ***trans*-4c** at 350 min is 1.73. With an integral for the proton in the 3-position of 0.29 a deuteration degree of 50% is obtained. This is in agreement with the deuteration degree as determined solely from the methyl group (48%, see Figure S13).

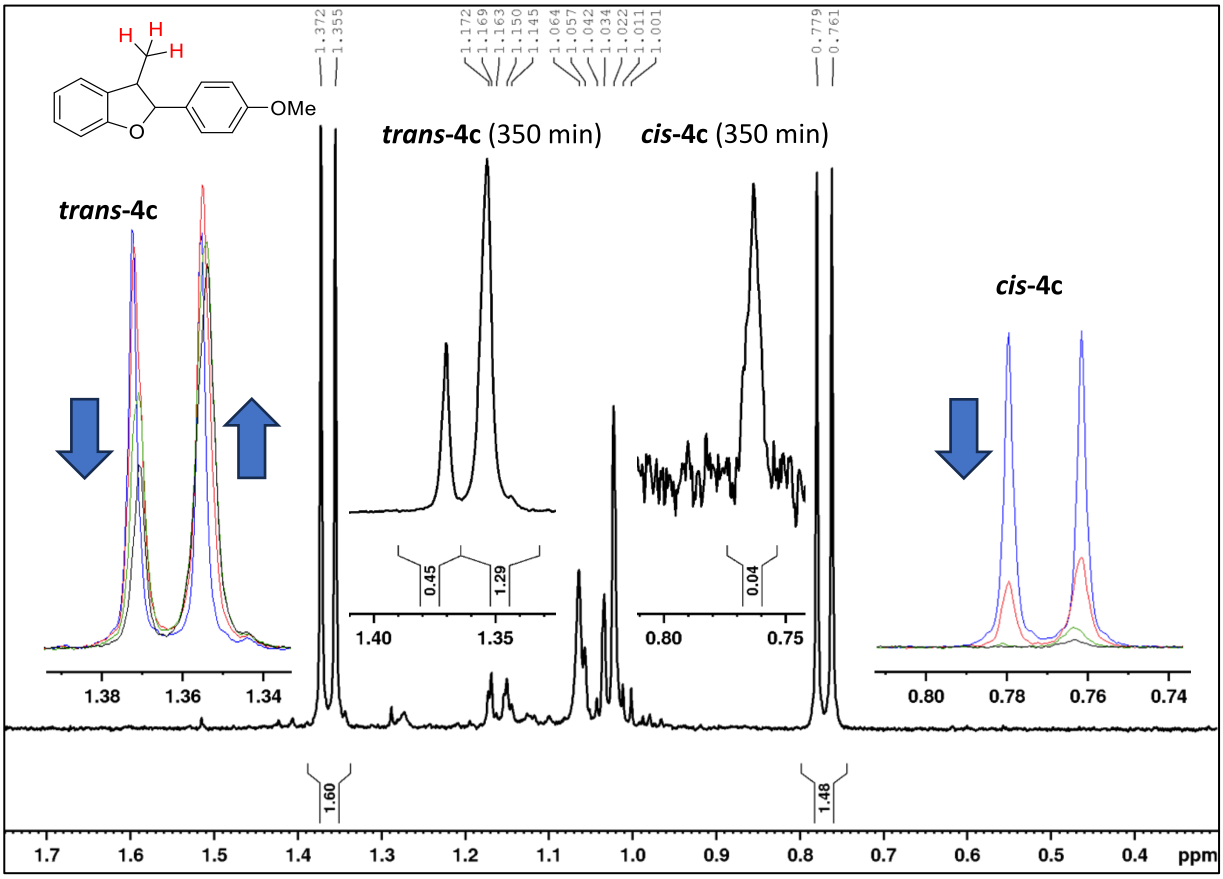
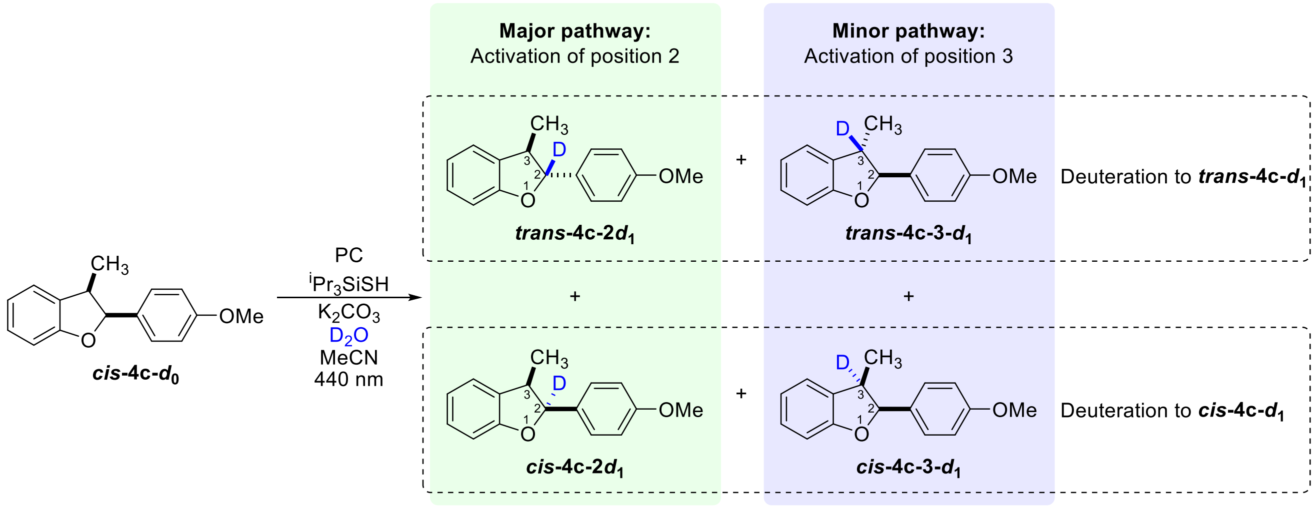


**Figure S13.** Area 7 during the HAT/RRPCO/deuteration reaction, starting with a 1:1 mixture of **_cis_-4c-$d_0$** and **_trans_-4c-$d_0$**, (Scheme S6). The large spectrum shows the $^1$H NMR spectrum before irradiation. Inserted superimposed spectra were measured at t = 0 min (blue), 10 min (red), 80 min (green), and 350 min (black). Inserted black spectra show the respective methyl-signal after 350 min of irradiation. The methyl groups of **_trans_-4c-$d_0$** and **_cis_-4c-$d_0$** give a doublet at 1.36 ppm ($J$ = 6.8 Hz, **_trans_-4c-$d_0$**) and 0.77 ppm ($J$ = 7.2 Hz, **_cis_-4c-$d_0$**) which, upon deuteration in the 3-position, change to a singlet at 1.35 ppm (**_trans_-4c-3-$d_1$** and **_trans_-4c-$d_2$**) and 0.76 ppm (**_cis_-4c-3-$d_1$** and **_cis_-4c-$d_2$**). The deuteration degree in the 3-position was determined by comparison of the integral for the proton in the 2-position with the integral for the methyl group in the 3-position (Figure S12) and additionally from the coupling pattern of the methyl signal to verify the deuteration degrees determined by either method. The deuteration degree in the 3-position at 350 min as determined solely from the methyl signal is (1.29 – 0.45)/(1.29 + 0.45) = 48%. The deuteration degree in the 3-position at 350 min as determined from the signal for the benzylic hydrogen is 50%. Thus, both methods give similar results.

## Kinetics with *cis*-4c



**Scheme S7**. Deuteration of ***cis*-4c-*d*$_0$** gives ***trans*-4c-2-*d*$_1$, *trans*-4c-3-*d*$_1$, *cis*-4c-2-*d*$_1$,** and ***cis*-4c-3-*d*$_1$**. With increasing reaction progress, the corresponding species with deuteration in both benzylic positions (***cis*-4c-*d*$_2$ and *trans*-4c-*d*$_2$**) are also formed. Product losses can be attributed predominantly to oxidation of dihydrobenzofuran **4c** to the corresponding benzofuran **35** (Scheme S6).

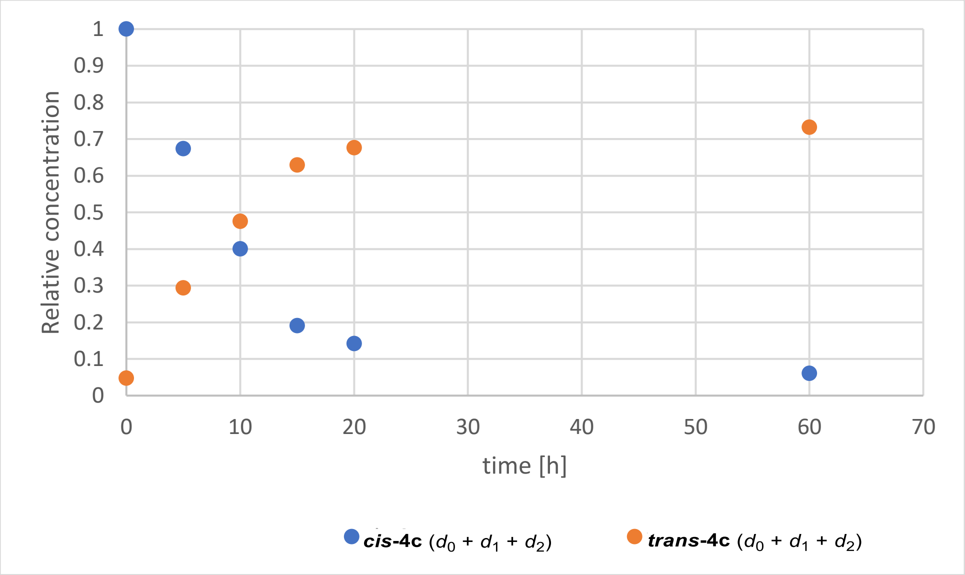


**Figure S14.** Relative concentrations of ***cis*-4c** (sum of ***cis*-4c-*d*$_0$**, ***cis*-4c-2-*d*$_1$**, ***cis*-4c-3-*d*$_1$**, and ***cis*-4c-*d*$_2$**) and ***trans*-4c** (sum of ***trans*-4c-*d*$_0$**, ***trans*-4c-2-*d*$_1$**, ***trans*-4c-3-*d*$_1$**, and ***trans*-4c-*d*$_2$**) starting from ***cis*-4c-*d*$_0$**.

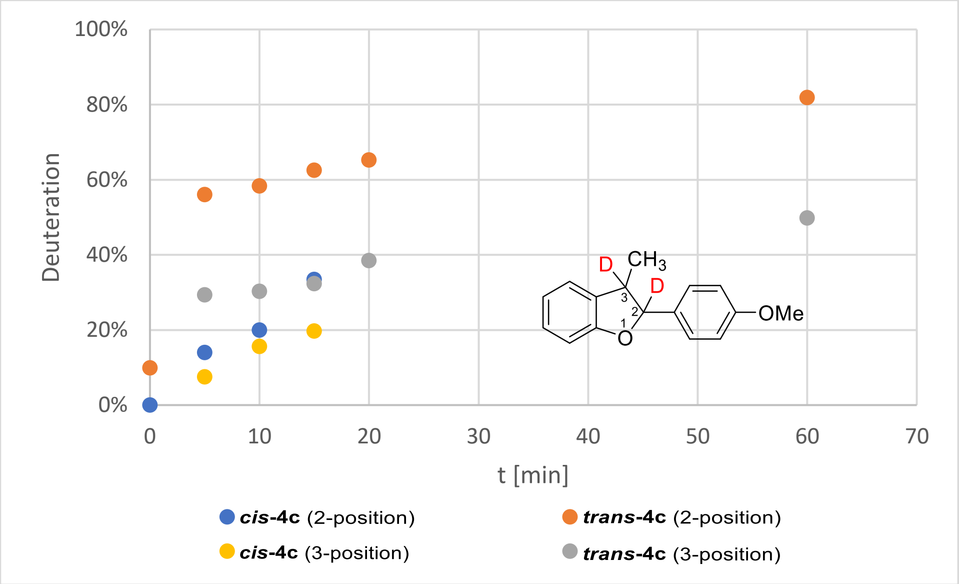


**Figure S15.** Deuteration degrees of ***cis*-4c** and ***trans*-4c** in the 2-position and 3-position, starting from ***cis*-4c-$d_0$**. Due to the low concentration and fast deuteration of ***cis*-4c**, deuteration degrees of ***cis*-4c** could not be determined after 15 min. The deuteration of ***trans*-4c** in the 2-position during the first minutes of the reaction is almost twice as high as in the 3-position. This demonstrates a 2.0-fold preference for activation of the 2-position over the 3-position in ***cis*-4c** which is similar to the 2.4-fold preference for activation of the 2-position over the 3-position in ***trans*-4c** (see Figure S20). The values for regioselectivity are under the assumption that protonation of the carbanion in the 2-position and in the 3-position has a similar *cis*/*trans*-selectivity.

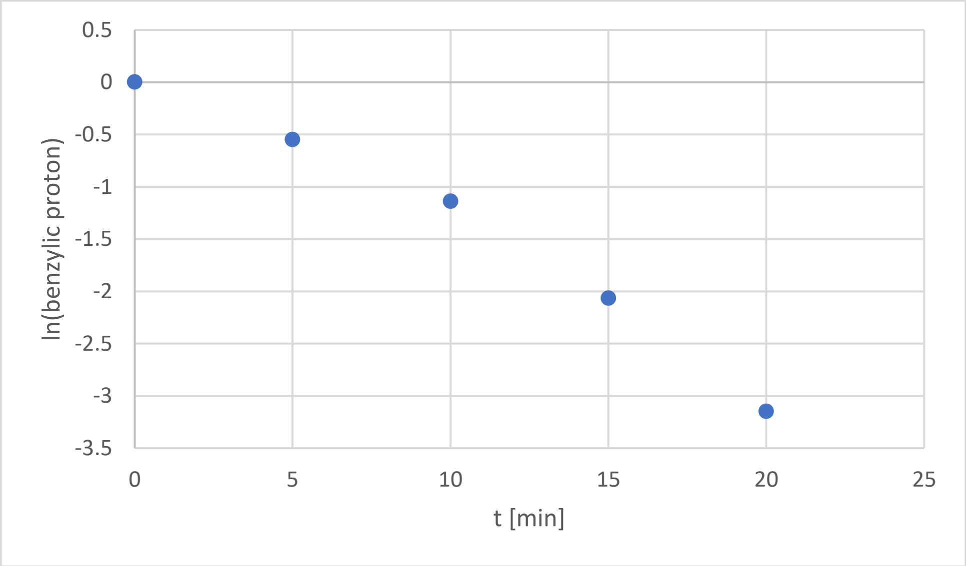


**Figure S16.** Natural logarithm of the integral for the proton in 2-position of ***cis*-4c**. Deuteration of the substrate can be approximated by a first order kinetic with a rate constant of $1.6*10^{-1}$ min$^{-1}$. Small deviations from a first order kinetic are expected because ***cis*-4c-$d_1$** and ***trans*-4c-$d_1$** are also activated under the reaction conditions and constantly regenerate small amounts of ***cis*-4c-$d_0$**. Conversion of ***cis*-4c-$d_0$** includes the reactions giving ***cis*-4c-2-$d_1$**, ***trans*-4c-2-$d_1$**, and ***trans*-4c-3-$d_1$**.

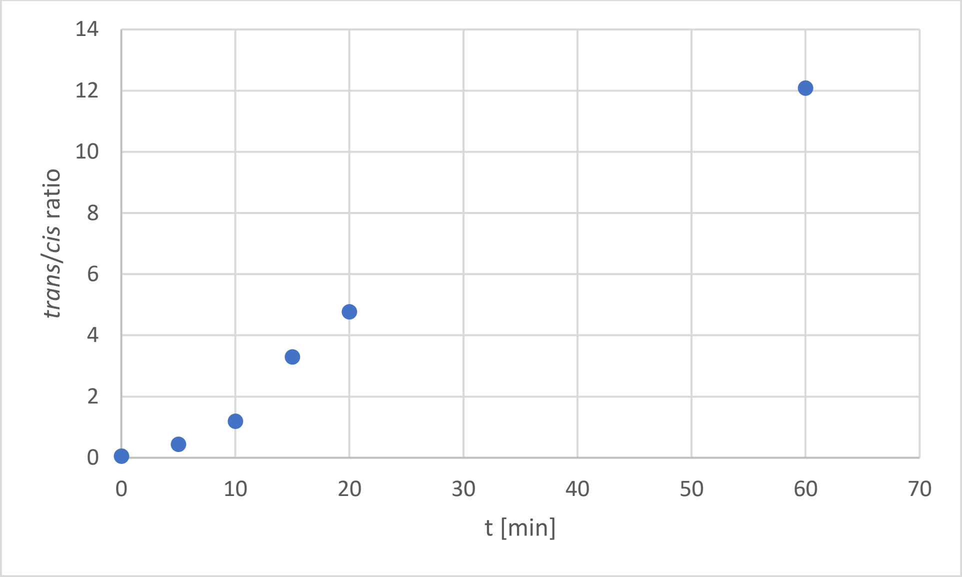
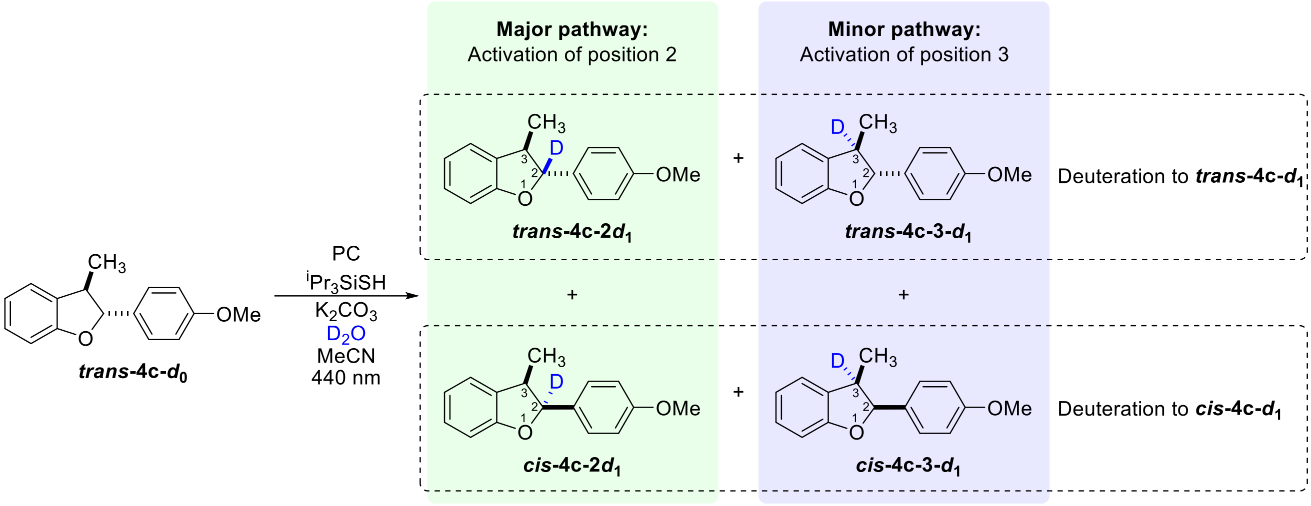


**Figure S17.** Ratio of ***trans/cis*-4c** during the reaction including all deuterated and non-deuterated species.

## Kinetics with *trans*-4c



**Scheme S8.** Deuteration of ***trans*-4c-$d_0$** gives ***trans*-4c-2-$d_1$, *trans*-4c-3-$d_1$**, ***cis*-4c-2-$d_1$,** and ***cis*-4c-3-$d_1$**. With increasing reaction progress, the corresponding species with deuteration in both benzylic positions (***cis*-4c-$d_2$ and *trans*-4c-$d_2$**) are also formed. Product losses can be attributed predominantly to oxidation of dihydrobenzofuran **4c** to the corresponding benzofuran **35** (Scheme S6).

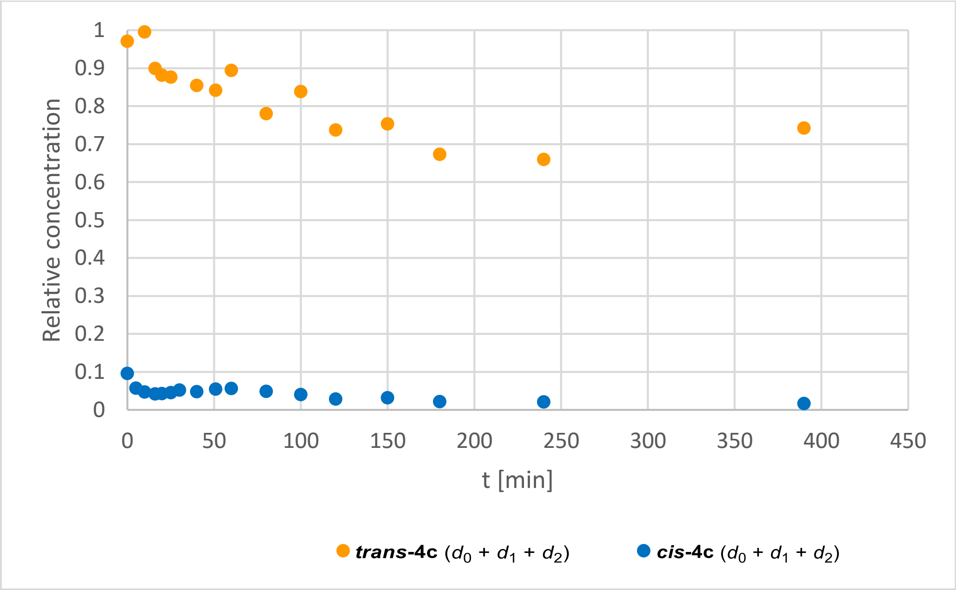


**Figure S18.** Relative concentrations of ***cis*-4c** (sum of ***cis*-4c-$d_0$**, ***cis*-4c-2-$d_1$**, ***cis*-4c-3-$d_1$**, and ***cis*-4c-$d_2$**) and ***trans*-4c** (sum of ***trans*-4c-$d_0$**, ***trans*-4c-2-$d_1$**, ***trans*-4c-3-$d_1$**, and ***trans*-4c-$d_2$**) starting from ***trans*-4c-$d_0$** (*d.r.* = 10:1).

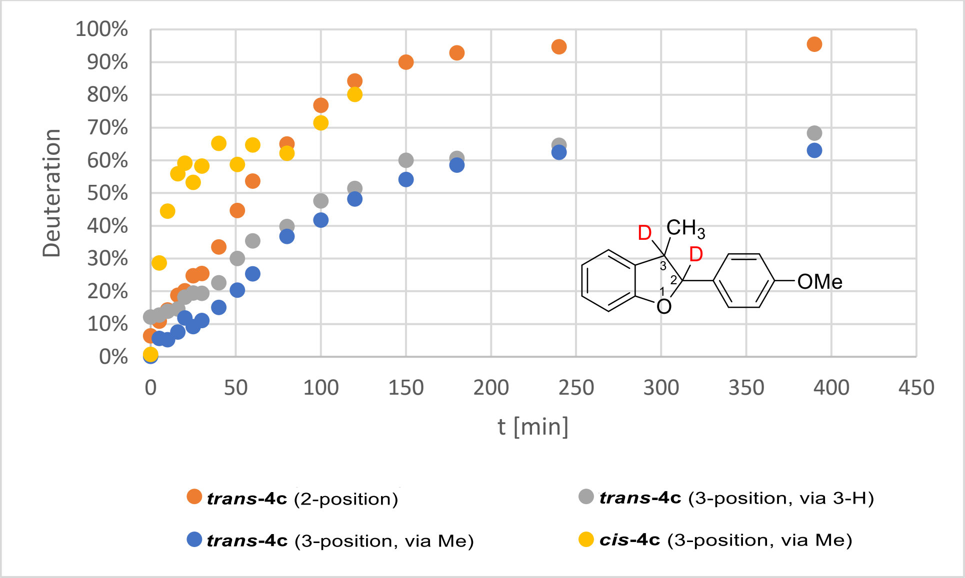


**Figure S19.** Deuteration degrees in the benzylic positions of **4c**, starting from ***trans*-4c-$d_0$**. Due to the constantly low concentration of ***cis*-4c** and fast deuteration, its deuteration degree in the 2-position could not be determined. The deuteration degree of cis-4c in the 3-position was determined from the signal for the methyl group in the 3-position until the signal intensity became too low (after 120 min). The deuteration degree of ***trans*-4c** in the 3-position was determined from the integral for the proton in the 3-position by comparison with the integral for the methyl group in the 3-position (***trans*-4c** (3-position, via 3-H)), and additionally, from the signal for the methyl group in the 3-position (***trans*-4c** (3-position, via Me)). The initial fast increase in deuteration degree of ***cis*-4c** in the 3-position is explained by the high reactivity of residual ***cis*-4c** in both benzylic positions.

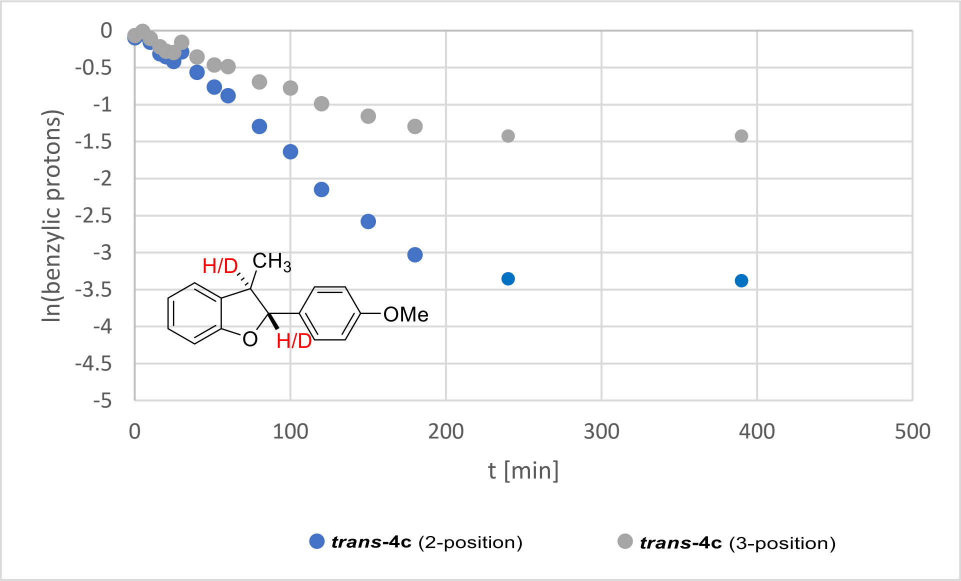


**Figure S20.** Natural logarithm of the signal intensities of the benzylic protons of ***trans*-4c**. C-H activation of the substrate can be approximated by a first order kinetic with a rate constant of $1.7*10^{-2}$ min$^{-1}$ for deuteration of the 2-position and a rate constant of $7.2*10^{-3}$ for deuteration of the 3-position. Small deviations from a first order kinetic are expected because ***cis*-4c-$d_1$** and ***trans*-4c-$d_1$** are also activated under the reaction conditions and constantly regenerate small amounts of ***trans*-4c-$d_0$**. After 180 minutes, almost the final deuteration degrees are reached (Figure S19). Thus, data points after 180 min (green and orange) were excluded from approximation of the rate constant.

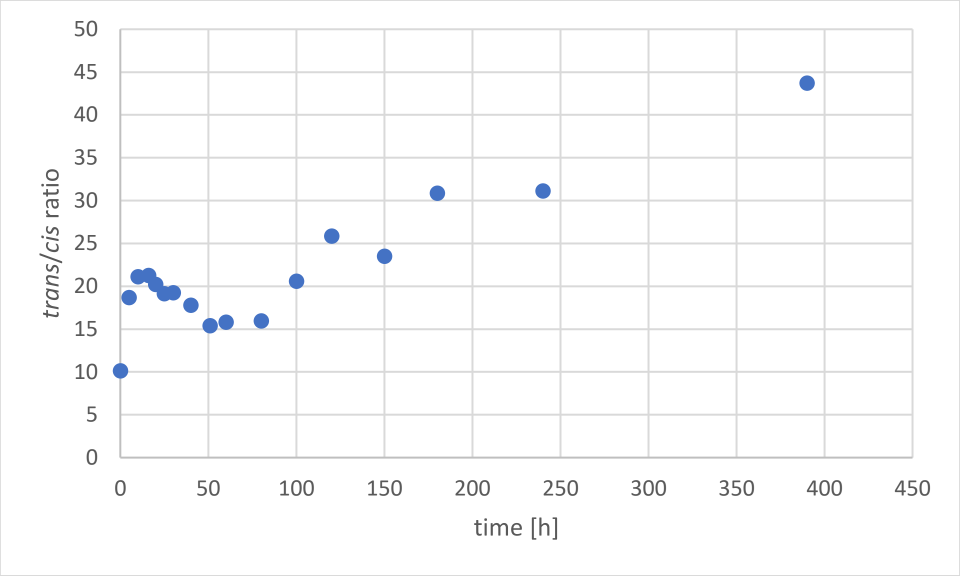
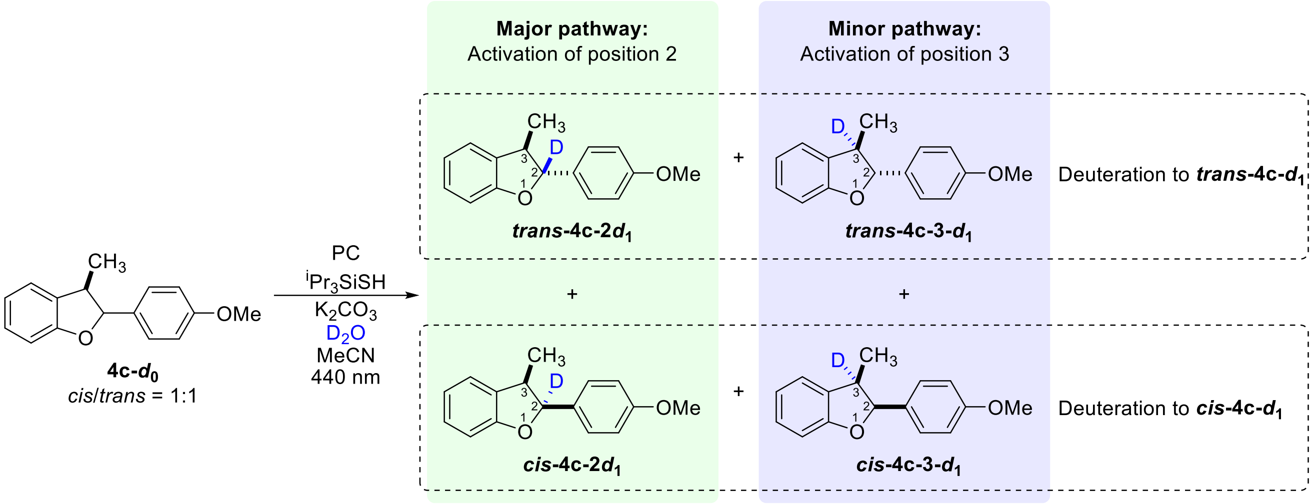


**Figure S21.** Ratio of ***trans/cis*-4c** during the reaction including all deuterated and non-deuterated species. The initial rapid increase in *trans/cis* ratio followed by a slight decrease is likely due to a kinetic isotope effect leading to faster C-H abstraction compared to C-D abstraction and, thus, a change in relative activation rates upon increasing deuteration degree of ***cis*-4c**. Kinetic isotope effects under identical reaction conditions have been reported previously for ethyl anisole.[11]

## Kinetics with a diastereomeric mixture of cis/*trans*-4c



**Scheme S9.** Deuteration of a 1:1 mixture of ***cis*-4c-$d_0$** and ***trans*-4c-$d_0$** gives ***trans*-4c-2-$d_1$**, ***trans*-4c-3-$d_1$**, ***cis*-4c-2-$d_1$**, and ***cis*-4c-3-$d_1$**. With increasing reaction progress, the corresponding species with deuteration in both benzylic positions (***cis*-4c-$d_2$** and ***trans*-4c-$d_2$**) are also formed. Product losses can be attributed predominantly to oxidation of dihydrobenzofuran **4c** to the corresponding benzofuran **35** (Scheme S6).

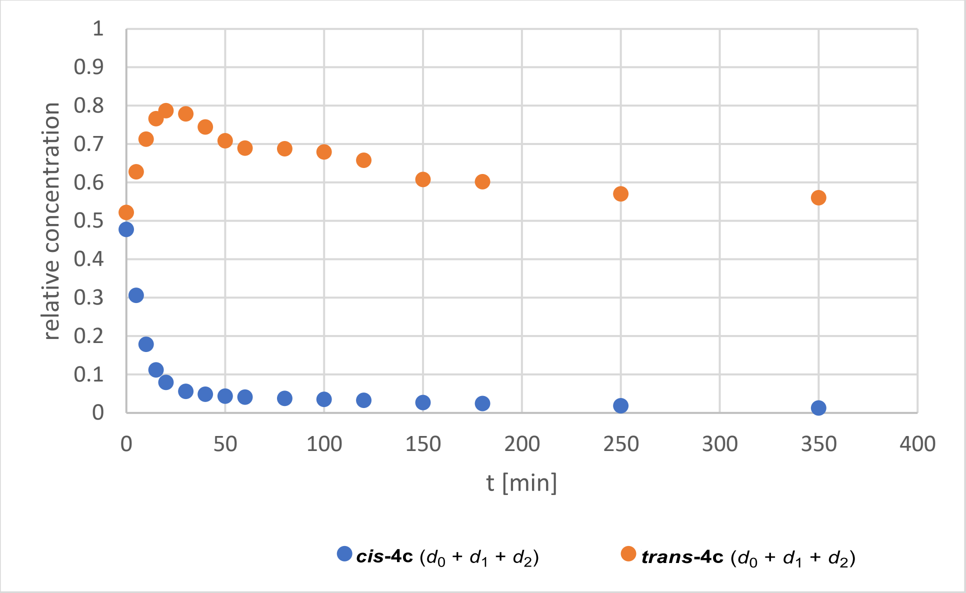


**Figure S22.** Relative concentrations of ***cis*-4c** (sum of ***cis*-4c-*d*₀**, ***cis*-4c-2-*d*₁**, ***cis*-4c-3-*d*₁**, and ***cis*-4c-*d*₂**) and ***trans*-4c** (sum of ***trans*-4c-*d*₀**, ***trans*-4c-2-*d*₁**, ***trans*-4c-3-*d*₁**, and ***trans*-4c-*d*₂**) starting from a 1:1 mixture of ***cis*-4c-*d*₀** and ***trans*-4c-*d*₀**. Determined from the methyl group in the 3-position.

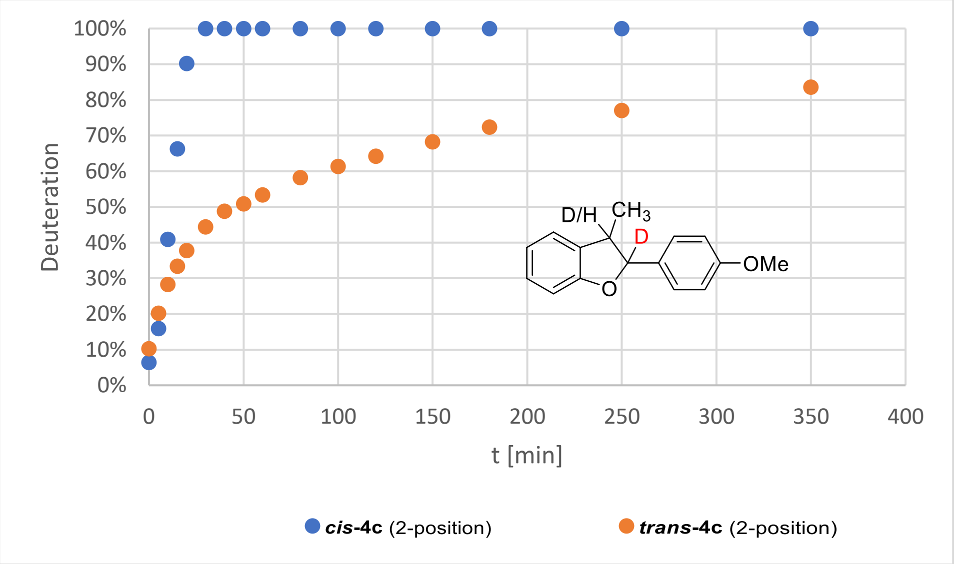


**Figure S23.** Deuteration degrees in the 2-position. After 20 minutes, the signal for ***cis*-4c-*d*₀** is not distinguishable from the noise anymore. The actual degree of deuteration is likely between 95-100%. The deuteration degree was determined by comparison of the integral for the proton in the 2-position with the integral of the methyl group in the 3-position. Deuteration in the 3-position was also observed and is depicted in Figure S24.

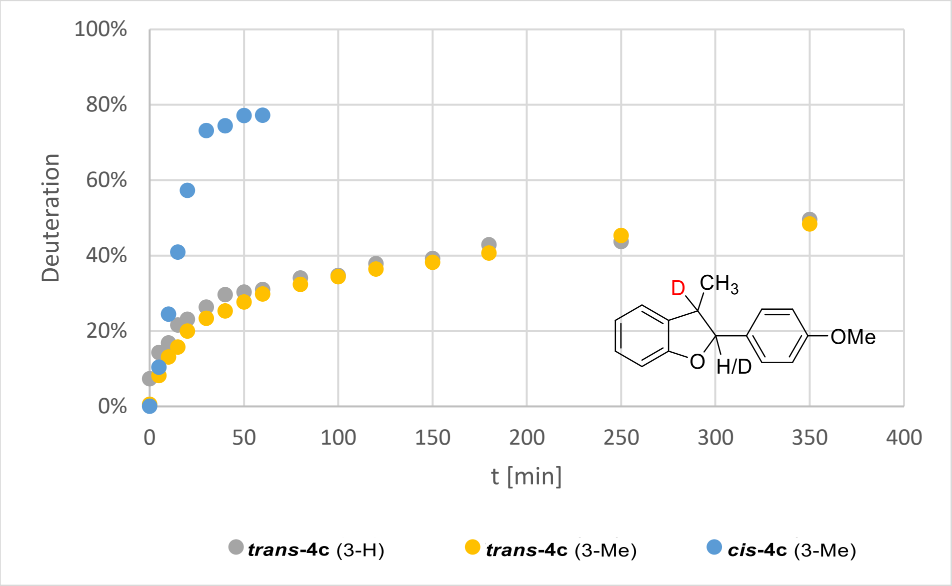


**Figure S24.** Deuteration degrees in the 3-position. After 60 minutes, the signal for ***cis*-4c-*d*$_0$** is not distinguishable from the noise anymore. Deuteration in the 3-position of ***cis*-4c** was determined from the signal for the methyl group in the 3-position (***cis*-4c** (3-Me)). Deuteration in the 3-position of ***trans*-4c** was additionally determined by comparison of the integral for the proton in the 3-position (***trans*-4c** (3-H)). Both methods give similar results.

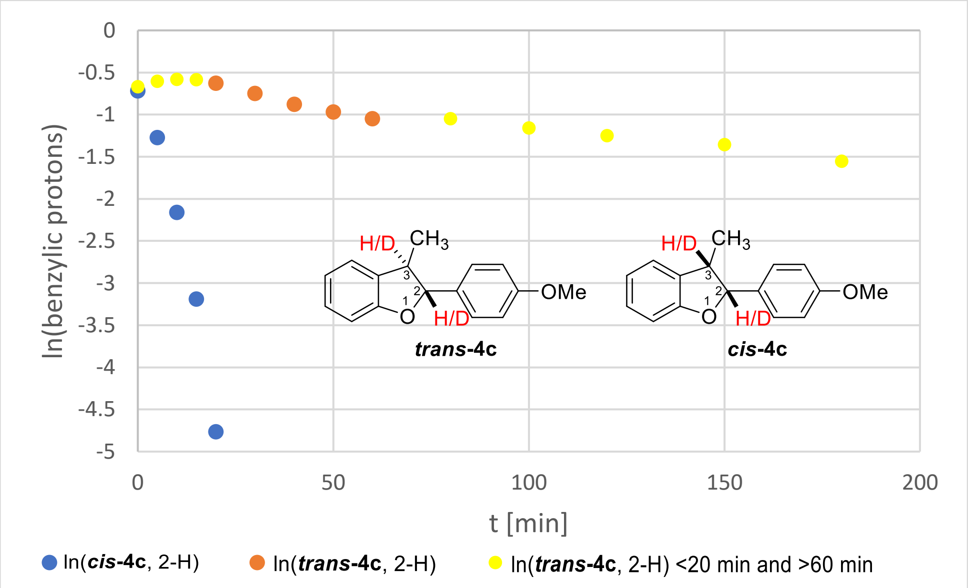


**Figure S25.** Natural logarithm of the integrals for the benzylic protons in the 2-position of ***cis*-4c** and ***trans*-4c** (see Figure S9, area 2). Deuteration in the 2-position can be approximated by a first order kinetic with rate constants of $2.0*10^{-1}$ min$^{-1}$ for ***cis*-4c** and $1.1*10^{-2}$ min$^{-1}$ for ***trans*-4c**. Deuteration of ***trans*-4c** can be separated into 3 parts: <20 min mostly ***cis*-4c** is activated and isomerized to ***trans*-4c** due to the higher reactivity of ***cis*-4c**. The slight initial increase in signal intensity for the proton in 2-position of ***trans*-4c** is explained by the activation of ***cis*-4c-*d*$_0$** in the 3-position, generating **trans-4c-3-*d*$_1$** which still contains a proton in the 2-position. Additionallly, the presence of residual protons (residual $H_2O$, abstracted H-atoms, silane thiol) can protonate a small fraction of the intermediate carbanions in the isomerization of ***cis*-4-*d*$_0$** to give some ***trans*-4c-*d*$_0$**. Between 20 – 60 min, the predominant reaction is deuteration in the 2-position of ***trans*-4c** (***trans*-4c-*d*$_0$** and ***trans*-4c-3-*d*$_1$**) (orange) until C-D activation of the 2-position of ***trans*-4c-2-*d*$_1$** and ***trans*-4c-*d*$_2$** becomes more dominant due to high degree of overall deuteration. Thus, the middle part was used for an approximation of the rate constant for C-H activation in the 2-position of ***trans*-4c** in the mixture.

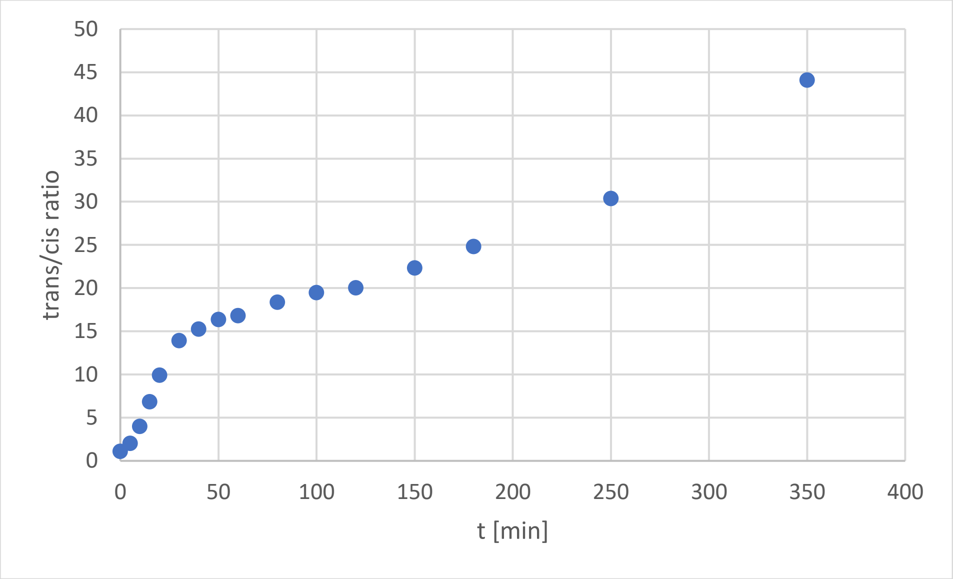


**Figure S26.** Ratio of ***trans/cis*-4c** during the reaction including all deuterated and non-deuterated species. The *trans*/*cis* ratio increases quickly until ***cis*-4c-*d*$_0$** is consumed (see Figure S17). As C-H activation of ***cis*-4c-*d*$_0$** is likely faster than C-D activation of ***cis*-4c-*d*$_1$** due to a primary kinetic isotope effect the increase in *trans*/*cis* ratio in the intermediate part of the experiment is slower. With increasing deuteration of ***trans*-4c** its activation slows down and the relative reaction rate for activation of ***cis*-4c** over ***trans*-4c** increases again.

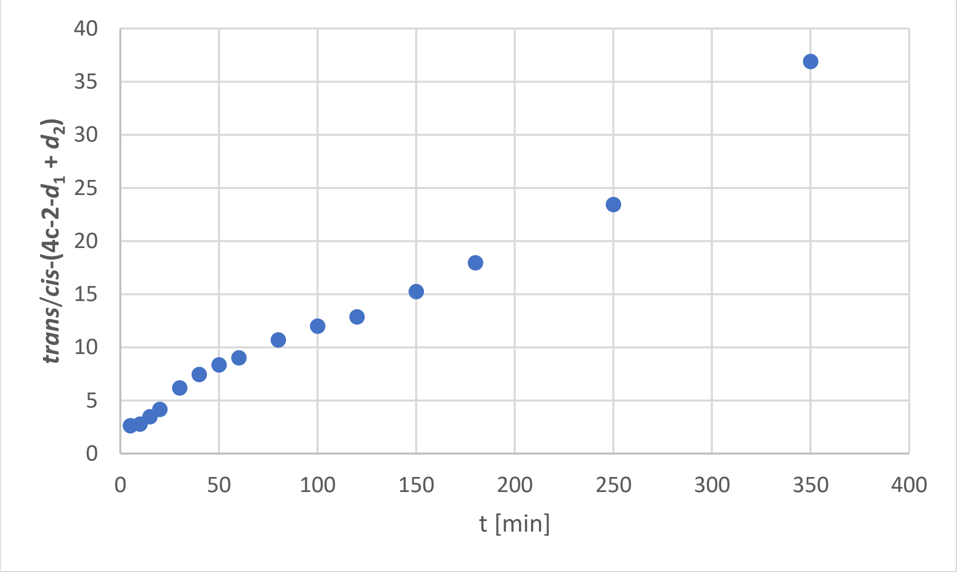
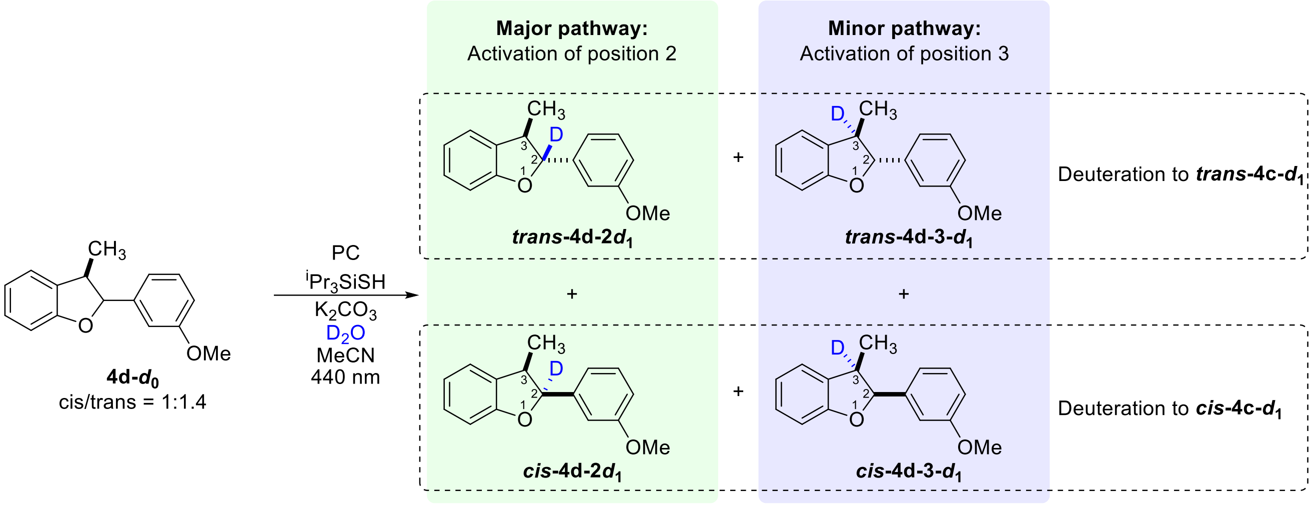


**Figure S27.** Ratio of (***trans*-4c-2-*d*$_1$** + ***trans*-4c-*d*$_2$**)/(***cis*-4c-2-*d*$_1$** + ***cis*-4c-*d*$_2$**) during the reaction. The products deuterated in the 2-position have only a low *trans*/*cis* ratio of 1:2.6 after 5 minutes of reaction which increases 14-fold over 350 minutes. This demonstrates that the *cis*/*trans*-isomerization is kinetically driven in the C-H abstraction step and only a small part of the selectivity arises from selective protonation/deuteration.

## Kinetics with a diastereomeric mixture of cis/*trans*-4d



**Scheme S10.** Deuteration of a 1:1.4 mixture of ***cis*-4d-*d*₀** and ***trans*-4d-*d*₀** gives ***trans*-4d-2-*d*₁, *trans*-4d-3-*d*₁, *cis*-4d-2-*d*₁,** and ***cis*-4d-3-*d*₁.** With increasing reaction progress, the corresponding species with deuteration in both benzylic positions (***cis*-4d-*d*₂ and *trans*-4d-*d*₂**) are also formed. Product losses can be attributed predominantly to oxidation of dihydrobenzofuran **4c** to the corresponding benzofuran as observed for substrate **4c** (Scheme S6).

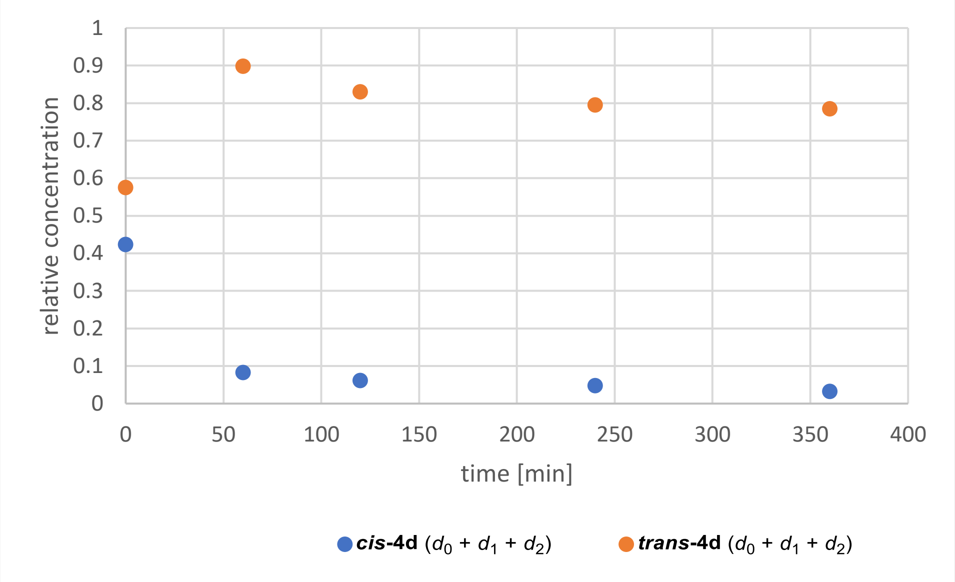


**Figure S 28.** Relative concentrations of ***cis*-4d** (sum of ***cis*-4d-*d*₀**, ***cis*-4d-2-*d*₁**, ***cis*-4d-3-*d*₁**, and ***cis*-4d-*d*₂**) and ***trans*-4d** (sum of ***trans*-4d-*d*₀**, ***trans*-4d-2-*d*₁**, ***trans*-4d-3-*d*₁**, and ***trans*-4d-*d*₂**) starting from a 1:1.4 mixture of ***cis*-4d-*d*₀** and ***trans*-4d-*d*₀**. Determined from the integral for the methyl group in the 3-position.

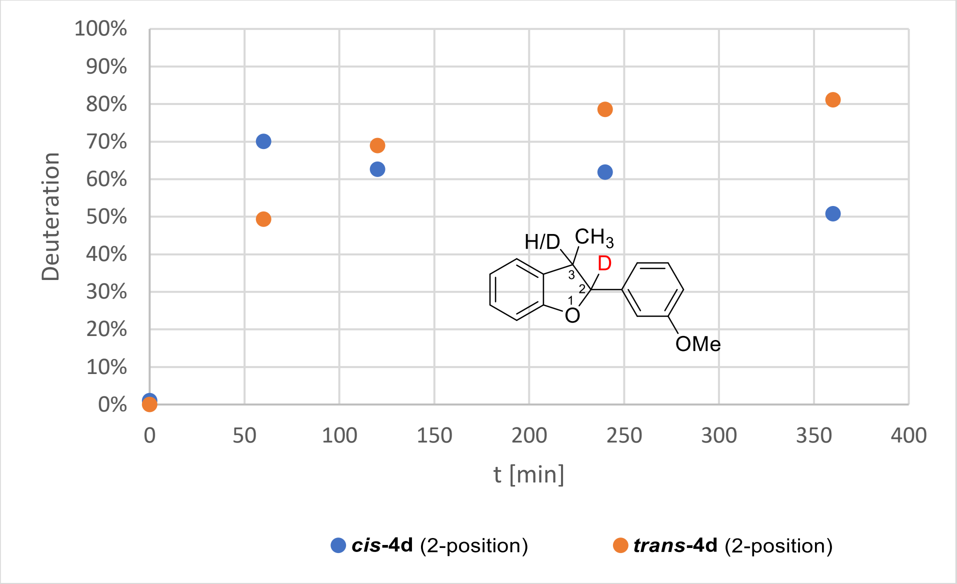


**Figure S29.** Deuteration degrees in the 2-position of **4d**. Determined from comparison of the integral for the proton in the 2-position with the methyl group in the 3-position.

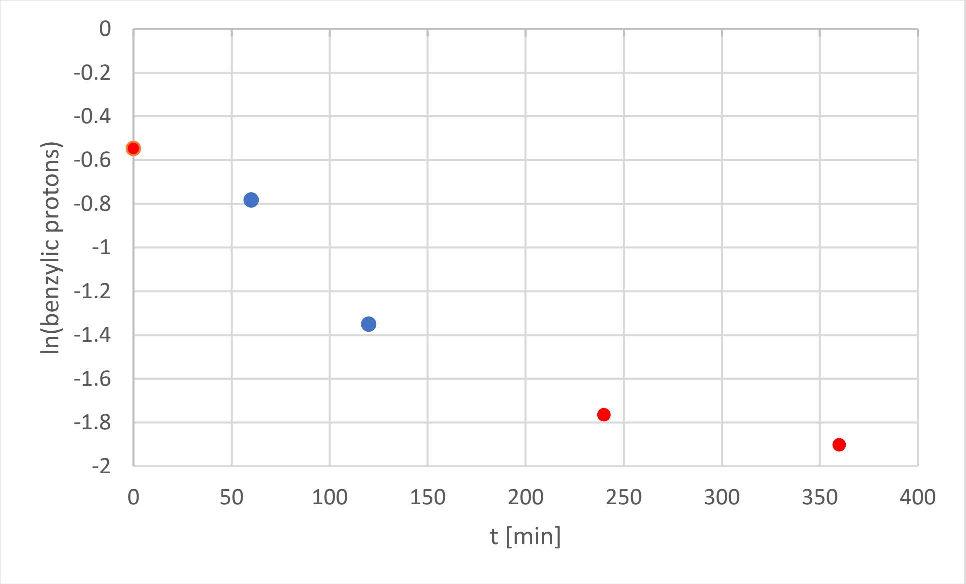


**Figure S30.** Natural logarithm of the integral for the benzylic proton in the 2-position of ***trans*-4d**. As only few data points have been collected, no exact rate constant can be extracted. Most of the *cis*/*trans*-isomerization is completed within 60 minutes and high deuteration of ***trans*-4d** is reached within 120 minutes (see Figures 22 and 23). Thus, the rate constant for C-H activation of the 2-position of ***trans*-4d** can be roughly approximated by the slope between 60 – 120 min with $1.0*10^{-2}$ $min^{-1}$ which is close to the 4-substituted derivative ***trans*-4c-*d*₀** ($1.1*10^{-2}$, see Figure S25). Only deuteration in the 2-position was considered.

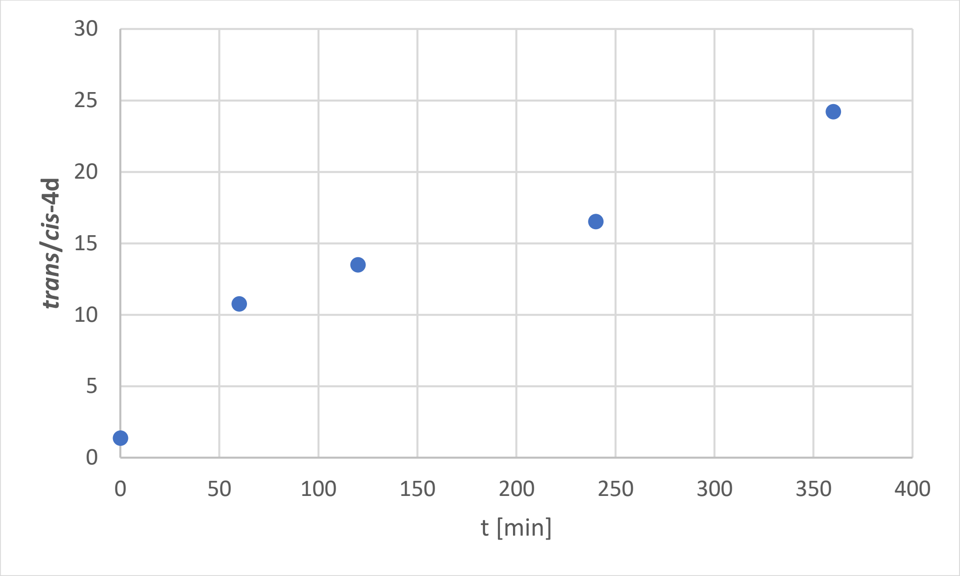


**Figure S31.** Ratio of ***trans*-4d/*cis*-4d** during the reaction including all deuterated and non-deuterated species.

The influence of the d1 time in the $^1$H NMR experiments was tested on the example of compound **4d**. The difference in integrals of the signals for the hydrogen at the 2-position and the methyl group at the 3-position were chosen as reference points and calibrated on 1,1,2,2-tetrachloroethane added as internal standard. As can be seen in Table S2 the difference in integrals with longer d1 time is small and the default d1 time of 2 s is sufficient for estimation of yield and deuteration degrees.

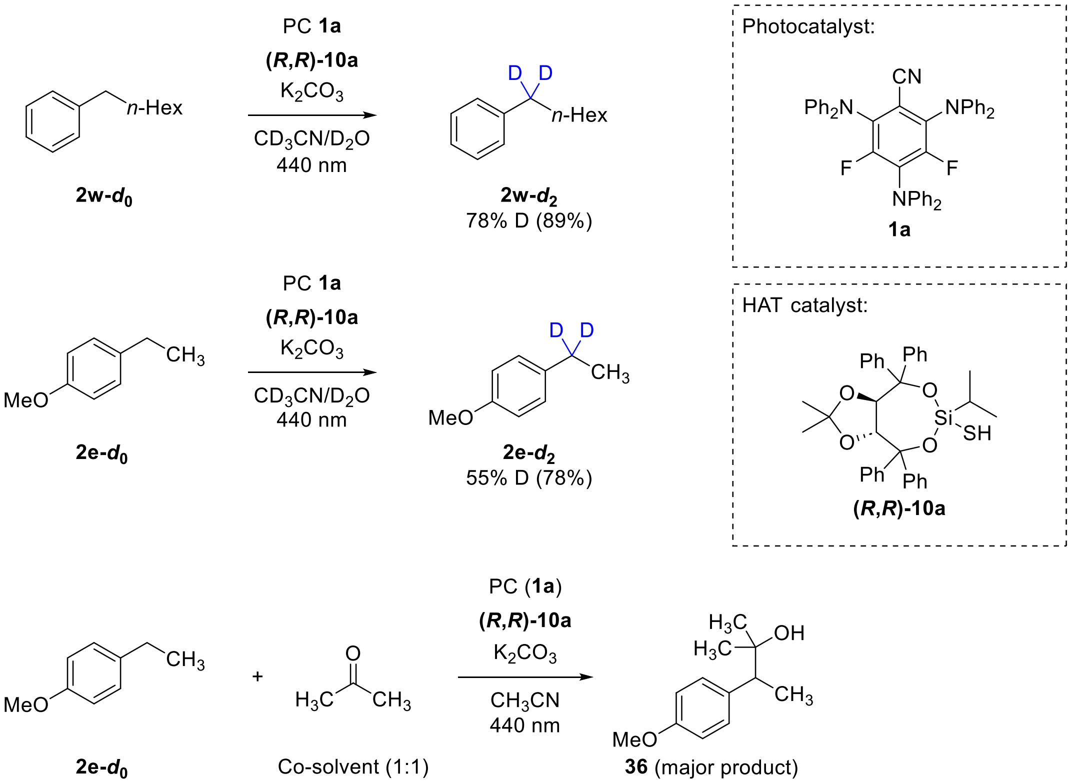
**Table S2.** Difference in integrals in dependence to the d1 time, relative to d1 = 2 s.

| **d1 [s]** | ***cis*-H (0 h)** | ***trans*-H (0 h)** | ***trans*-Me (0 h)** | ***trans*-H (1 h)** | ***trans*-Me (1 h)** |
|---|---|---|---|---|---|
| **2** | 0% | 0% | 0% | 0% | 0% |
| **5** | 6% | -2% | -4% | -6% | -6% |
| **20** | 2% | -2% | -10% | -5% | -11% |

# 7 Deracemization via enantioselective HAT with chiral silane thiols

## 7.1 TADDOL-derived silane thiols as HAT reagents and their stability

Initial test to evaluate whether TADDOL-derived chiral silane thiols are capable of catalyzing carbanion generation via a HAT/RRPCO sequence were conducted with heptyl benzene (**2w**) and ethyl anisole (**2e**). Both substrates reacted cleanly with good deuterium incorporation into the benzylic position under the reaction conditions of general procedure G with chiral HAT-catalyst **(*R*,*R*)-10a** as depicted in Scheme S11.



**Scheme S11.** Chiral silane thiol **(*R*,*R*)-10a** is an efficient HAT catalyst for photocatalytic generation of benzyl carbanions. Deuteration was used as mechanistic probe. NMR yield in parentheses. Nucleophilic addition product **36** was synthesized previously.[36]

The hydrolytic stability of HAT catalyst **10a** is sufficient for use under standard reaction conditions for benzylic deuteration according to general procedure G. After 16 h of irradiation 42% of the initial catalyst are still present in the deuteration of ethyl anisole (**2e**). 53% of the corresponding silanol were detected. In the deuteration of heptyl benzene (**2w**) 24% of the silane thiol remained after 16 h of irradiation together with 42% silanol.

No decomposition of silane thiols **10** was observed during storing at ambient conditions under air for up to 2 years. The corresponding chlorosilanes in solid form can also be stored at ambient conditions without notable decomposition. However, in solution hydrolysis to the silanols occurs within hours in the presence of water. The difference in chemical shifts between both methine protons of the TADDOL backbone is substantially smaller in the silanols compared to the corresponding chlorosilanes and even larger in silane thiols for all TADDOL-based silicon compounds synthesized in this work. The lack of other signals in the range of 5 – 6 ppm makes these protons most suitable for following the fate of these silicon compounds during reactions. A comparison of the signals for the methine protons of chlorosilane **30d**, silane thiol **10d** and silanol **31d** is depicted in Figure S32.

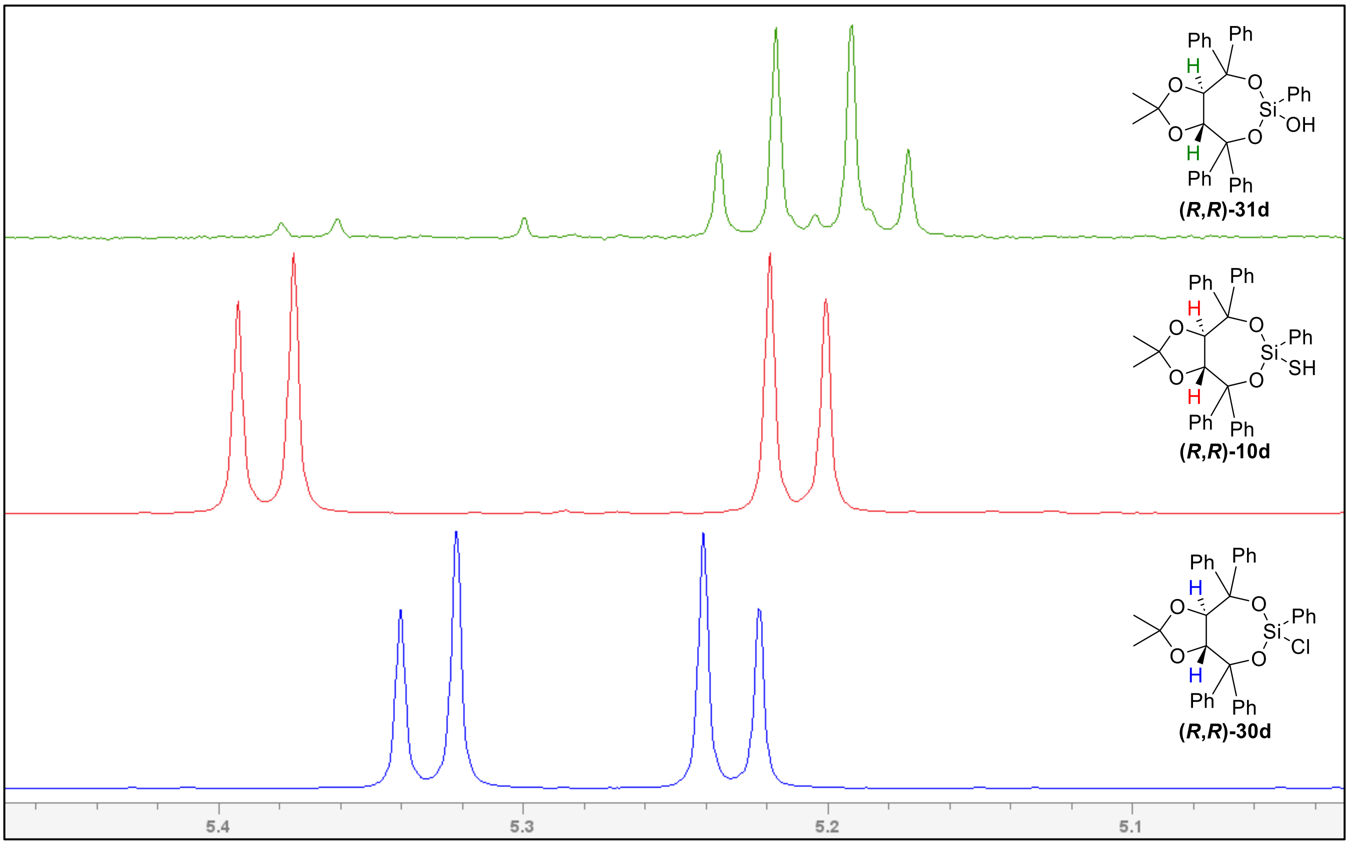


**Figure S32.** Comparison of the methine protons of TADDOL-based silicon compounds **31d**, **10d,** and **30d**. Only the section of the $^1$H NMR spectra showing the methine protons of the TADDOL backbone are depicted. The respective compounds have been isolated and fully characterized in section 3.3. 400 MHz, $CDCl_3$. Chemical shifts in $CD_3CN$ differ only slightly and follow the same trend.

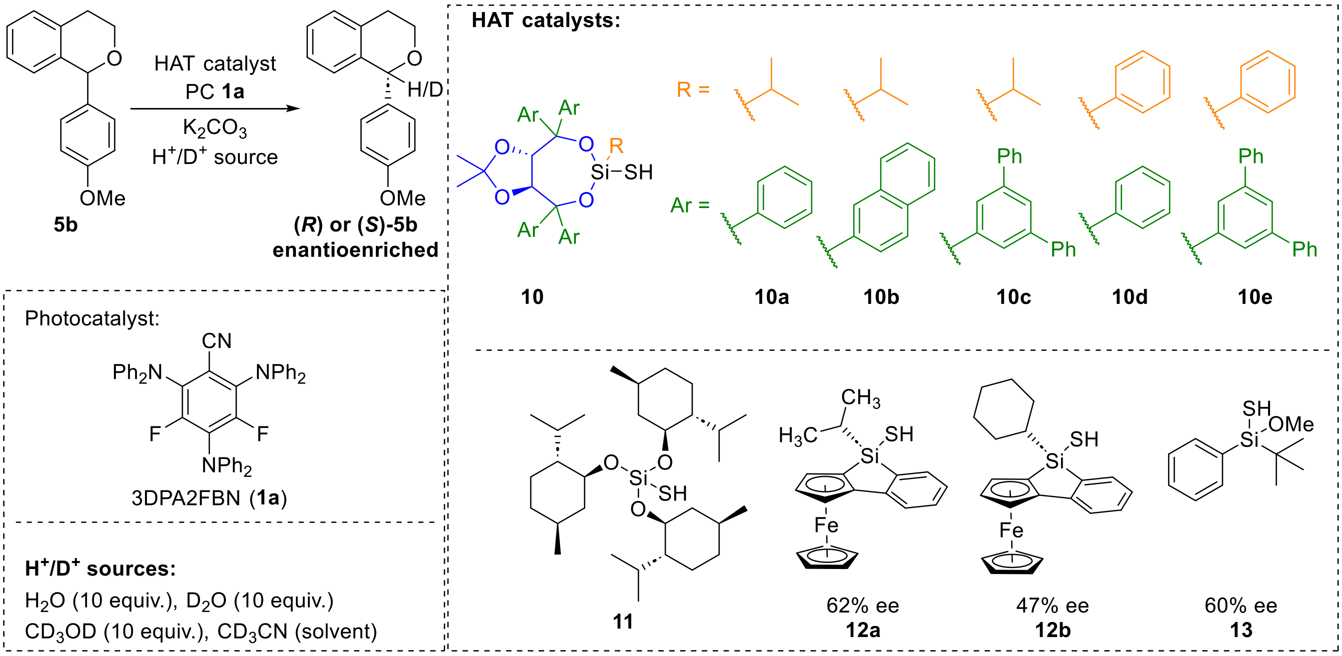
## 7.2 Deracemization with chiral HAT-reagents

Deracemizations were performed according to general procedure G for benzylic deuteration. Deuteration was used as mechanistic probe to confirm benzylic C-H activation and evaluate the efficiency of the HAT catalysts. For easy determination of NMR yield and deuteration degrees reactions were performed in $CD_3CN$ and the solvent residual signal used as internal standard. Under anhydrous conditions proton/deuteron-abstraction from the solvent by highly basic carbanions and reprotonation can change the deuteration degree of the solvent as reported previously.[11] Solvent deprotonation is outcompeted in the presence of 10 equivalents (corresponds to a concentration of 1 mol/L) $D_2O/H_2O$ and thus the residual solvent signal can be used as internal standard under the reaction conditions.

To minimize errors in the determination of the enantiomeric excess due to impurities, compounds subjected to chiral HPLC analysis were purified via preparative TLC.

An initial screening of chiral compounds of Scheme S1 with TADDOL-based silane thiols **7a**, **7b**, and **7c** gave a notable enantiomeric excess only for isochromane derivative **5b**. The enantiomers of acyclic benzyl ethers (**7a**, **7b**, **7c**) did not fully separate on the chiral HPLC and low selectivity might have been overlooked. However, separation was sufficient to exclude moderate enantioselectivity. Benzochromene derivative **5c** and dihydrobenzofuran derivative **4b** showed good separation on the chiral HPLC but did not give any enantiomeric excess. Thus, isochromane derivative **5b** was chosen as model substrate for the optimization depicted in Table 1 of the main text and the subsequent paragraphs refer to reactions using **5b** as substrate.

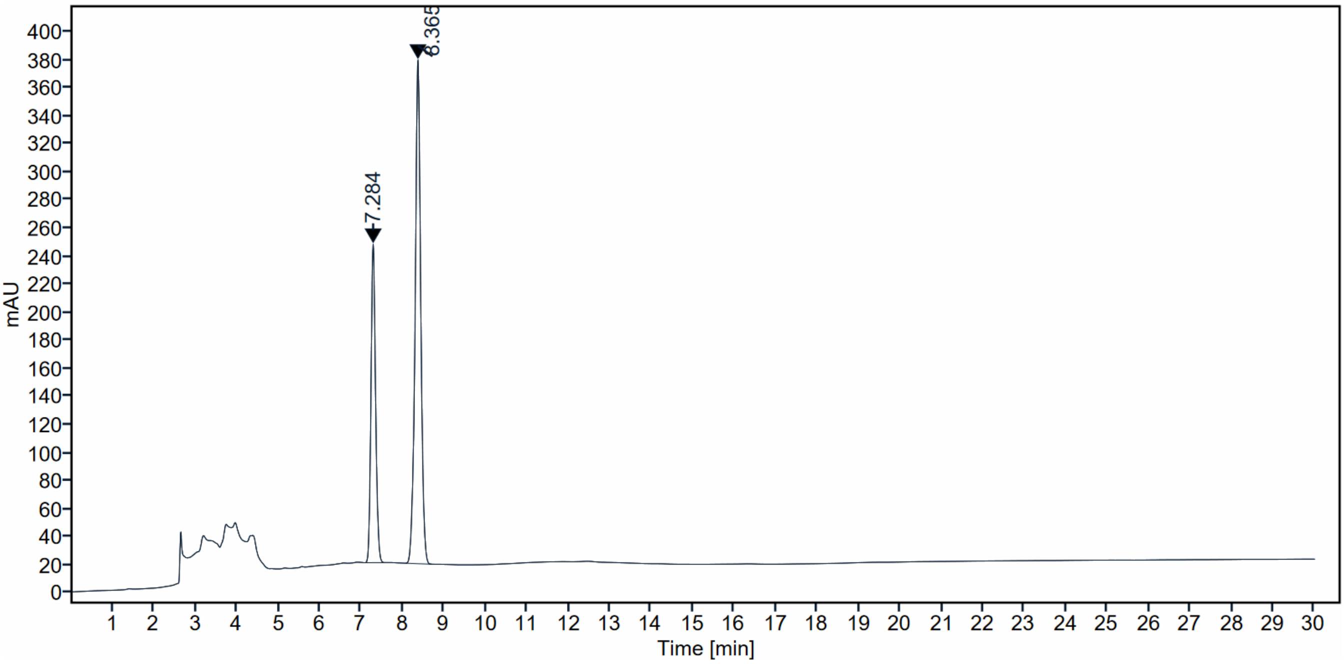
**Table S3.** Deracemization of isochromane derivative **5b** via a HAT/RRPCO/protonation sequence.



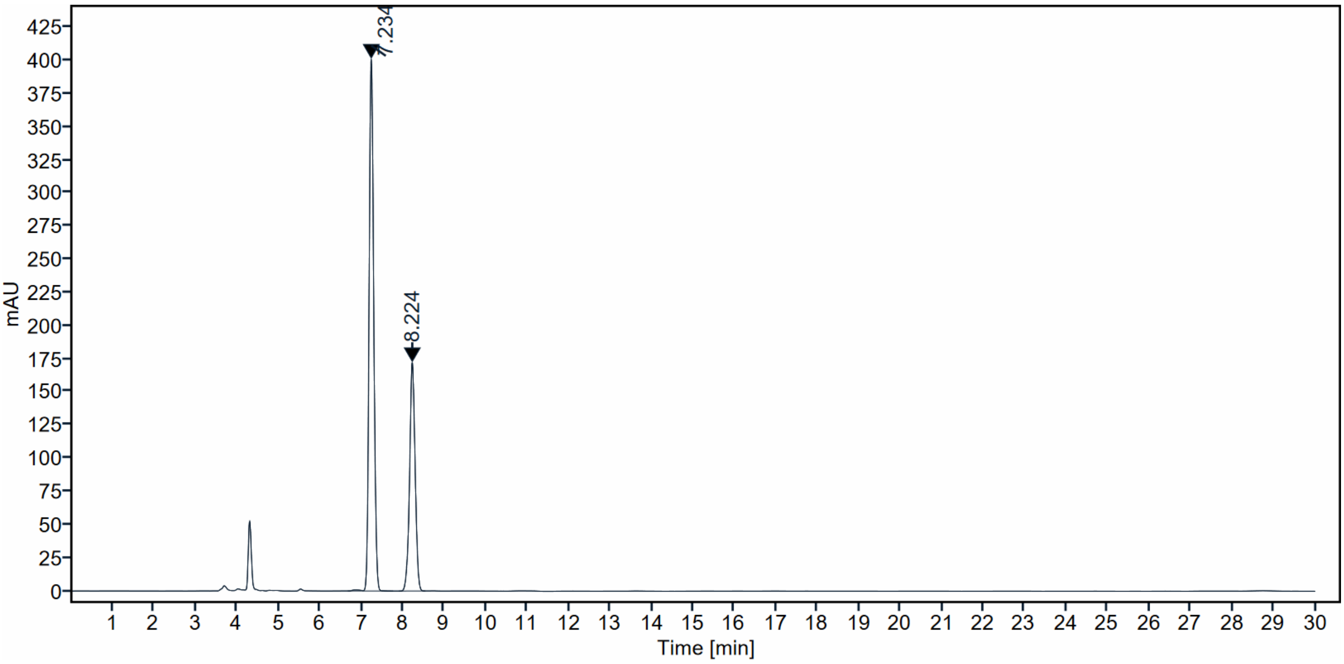
| Entry | HAT catalyst | T | $H^+/D^+$ | time [h] | *ee* | Config. | deuteration | yield |
|---|---|---|---|---|---|---|---|---|
| **1** | **(*R*,*R*)-10a** | rt | $H_2O$ | 6 h | 4% | (*R*) | - | 65%[a] |
| **2** | **(*R*,*R*)-10a** | -17 °C | $CD_3OD$ | 6 h | 6% | (*R*) | 78% | 81%[a] |
| **3** | **(*R*,*R*)-10a** | -17 °C | - | 6 h | 7% | (*R*) | 89% | 77%[a] |
| **4** | **(*R*,*R*)-10b** | -17 °C | $D_2O$ | 6 h | 3% | (*R*) | 79% | 78%[a]/94%[b] |
| **5** | **(*R*,*R*)-10b** | -17 °C | $H_2O$ | 6 h | 2% | (*R*) | - | 75%[a] |
| **6** | **(*R*,*R*)-10c** | -17 °C | $D_2O$ | 6 h | -19% | (*S*) | 69% | 87%[a]/89%[b] |
| **7** | **(*R*,*R*)-10c** | -17 °C | $H_2O$ | 6 h | -13% | (*S*) | - | 85%[a] |
| **8** | **(*R*,*R*)-10a** | -17 °C | $D_2O$ | 16 h | 7% | (*R*) | 93% | n.d. |
| **9** | **(*R*,*R*)-10c** | -17 °C | $D_2O$ | 16 h | -32% | (*S*) | 90 | 79%[a] |
| **10** | **(*R*,*R*)-10c** | -17 °C | - | 16 h | -25% | (*S*) | 60% | 77%[a] |
| **11** | **(*R*,*R*)-10d** | -17 °C | $D_2O$ | 16 h | 13% | (*R*) | 96% | n.d. |
| **12** | **(*S*,*S*)-10d** | -17 °C | $D_2O$ | 16 h | -11% | (*S*) | 93% | 87%[a] |
| **13** | **(*S*,*S*)-10e** | -17 °C | $D_2O$ | 16 h | 14% | (*R*) | 93% | 64%[a] |
| **14** | **(*S*,*S*)-10c** | -17 °C | $D_2O$ | 16 h | 32% | (*R*) | 88% | 82%[a]/>95%[b] |
| **15** | **(*S*,*S*)-10c** | -17 °C | $D_2O$ | 24 h | 33% | (*R*) | 92% | n.d. |
| **16** | **(*S*,*S*)-10c** | -17 °C | $D_2O$/acetone | 16 h | 37% | (*R*) | 91% | 40%[a] |
| **17** | **13** | -17 °C | - | 16 h | 10% | (*R*) | 76% | 66%[b] |
| **18** | **13** | -17 °C | $D_2O$ | 16 h | 12% | (*R*) | 96% | 44%[b] |
| **19** | **11** | -17 °C | $D_2O$ | 16 h | 1% | (*R*) | 91% | 82%[a] |
| **20** | **12a** | -17 °C | $D_2O$ | 16 h | - | - | <5% | No conversion |

Reactions were performed according to general procedure G. [a]Isolated yield; [b]NMR yield with solvent residual signal as internal standard. The absolute configuration of the major product was determined via chiral HPLC analysis and comparison with literature data.[60]

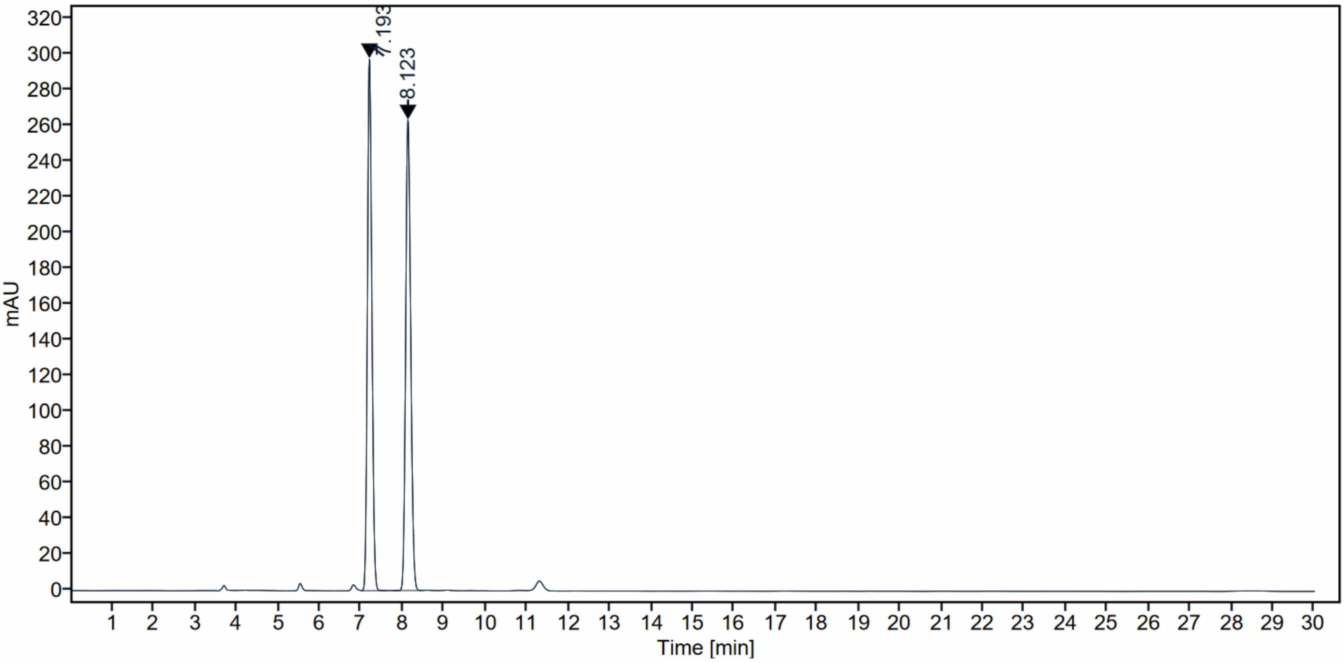
Entry 14:



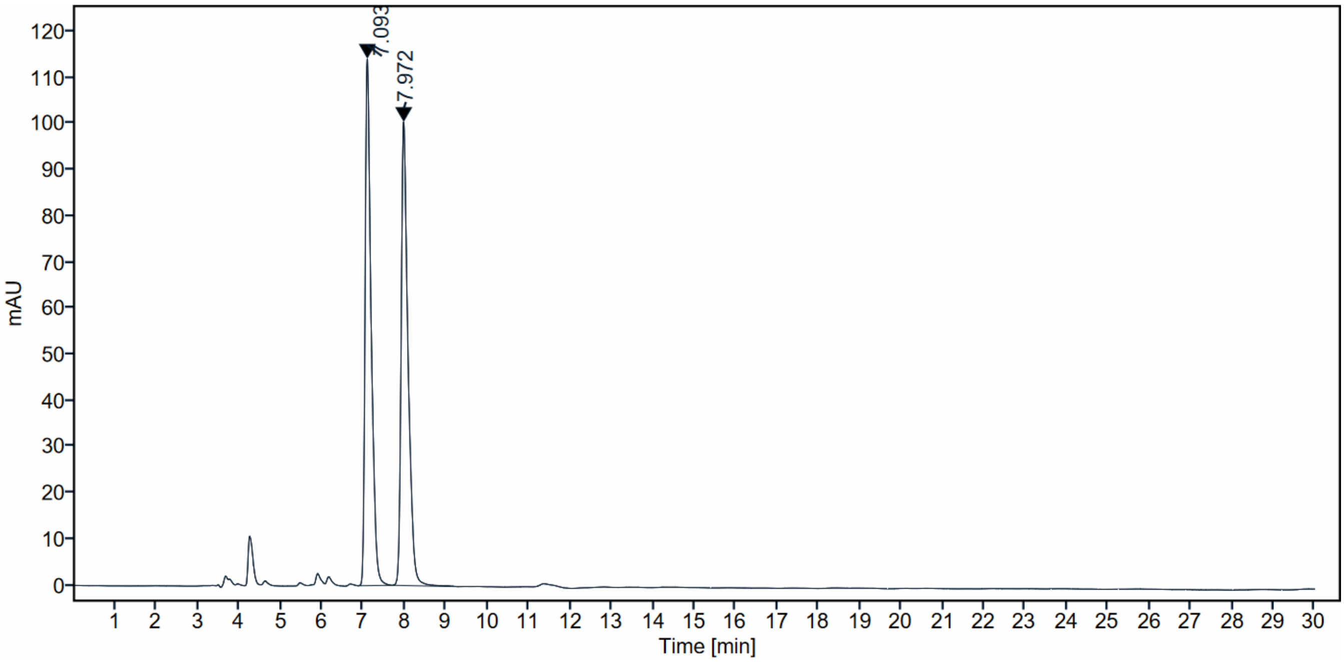
Entry 9:



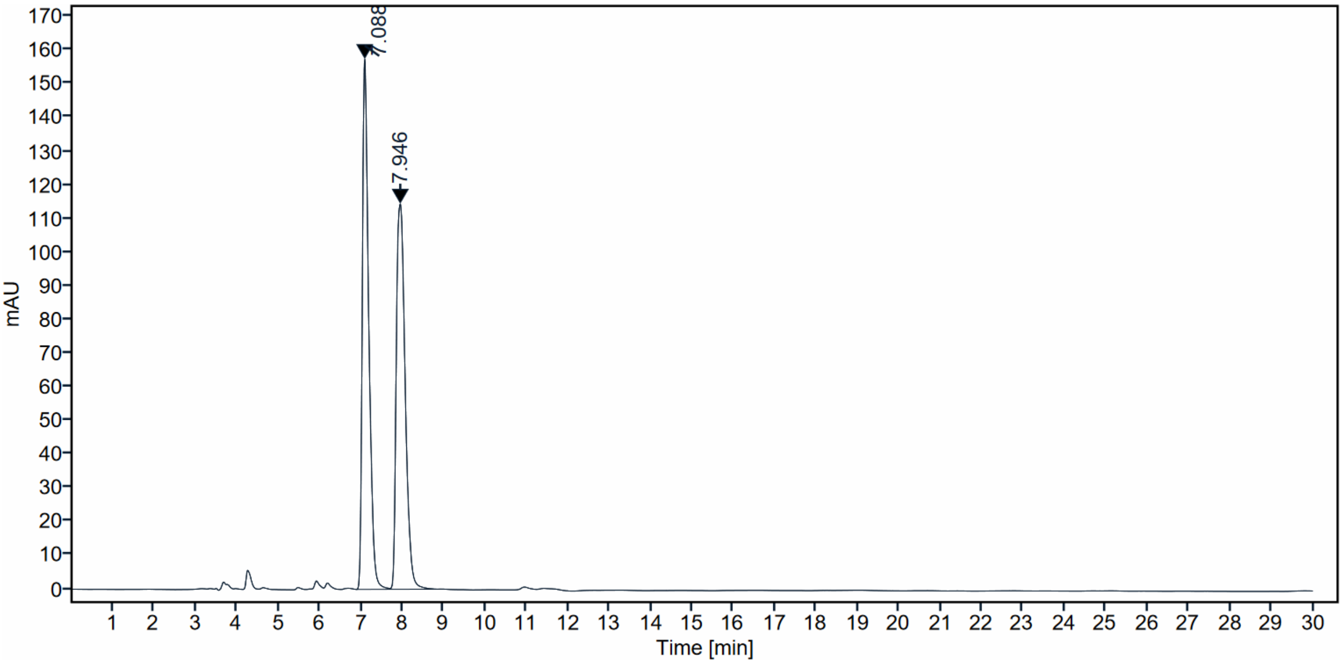
Racemic **5b-*d*$_0$**:



Racemic **5b-*d*$_1$**:



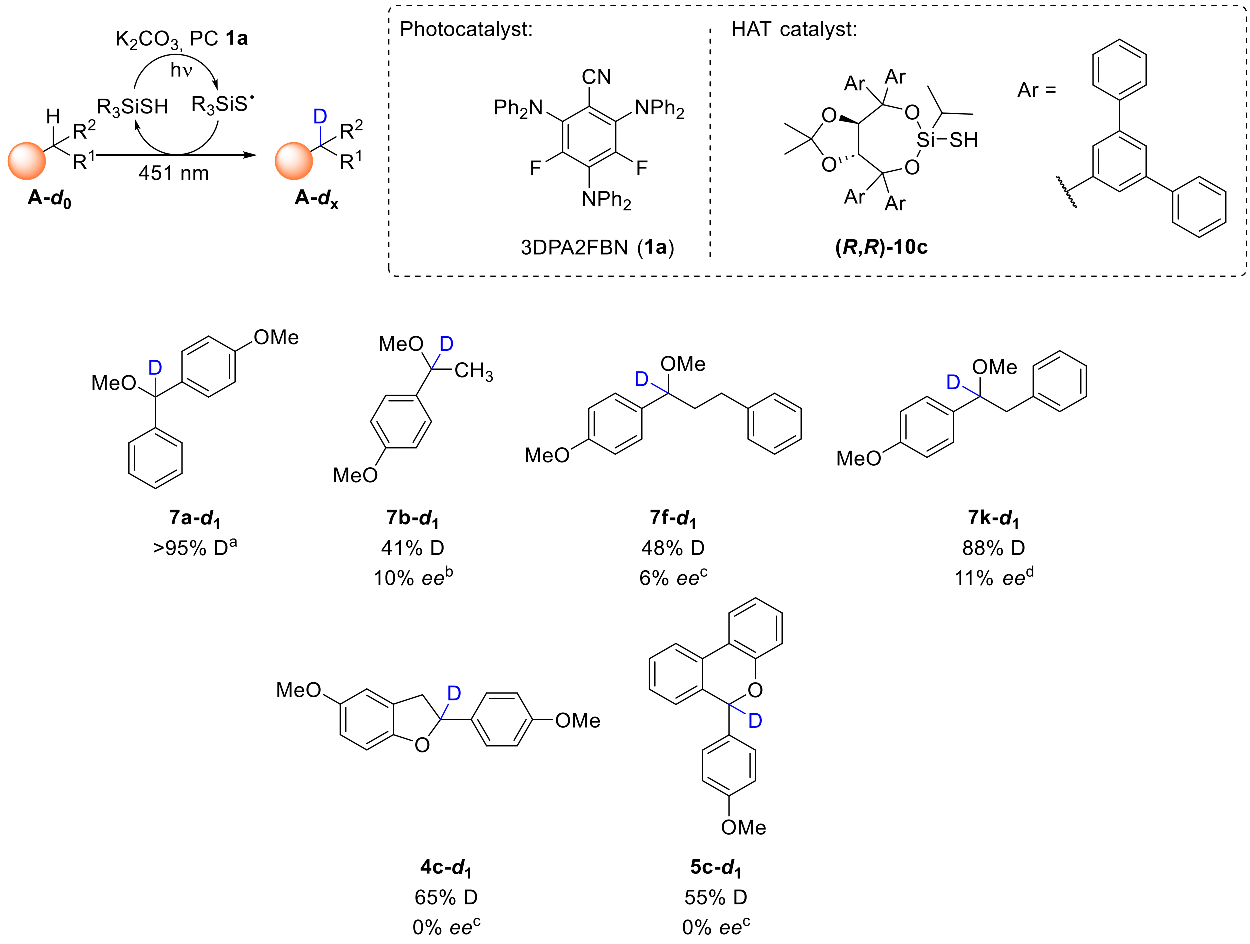
1:1 mixture of racemic **5b-$d_0$** and **5b-$d_1$**



It is worth mentioning that **(*R*)-5b-$d_0$** and **(*R*)-5b-$d_1$** have slightly different retention times. At moderate deuteration degrees this leads to a slight broadening of the respective signal.

## 7.3 Unsuccessful substrates

Substrates depicted in Scheme S12 were tested under the optimized reaction conditions (Table S3, entry 14). However, only low or no enantiomeric excess (*ee*) was observed, or enantiomers were not sufficiently separable to determine the *ee*.



**7a-*d*$_1$**
>95% D[a]

**7b-*d*$_1$**
41% D
10% *ee*[b]

**7f-*d*$_1$**
48% D
6% *ee*[c]

**7k-*d*$_1$**
88% D
11% *ee*[d]

**4c-*d*$_1$**
65% D
0% *ee*[c]

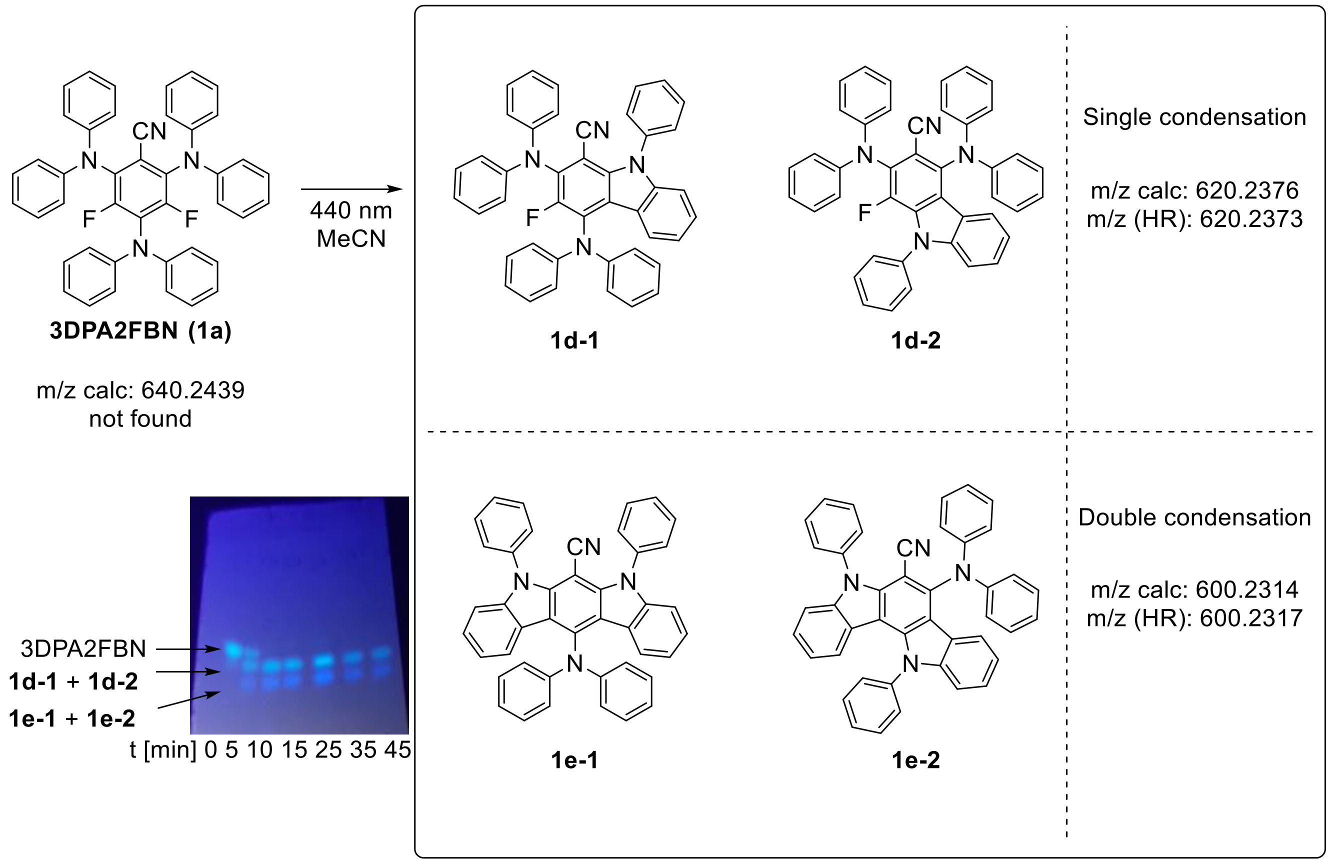
**5c-*d*$_1$**
55% D
0% *ee*[c]

**Scheme S12.** Substrates tested for deracemization where only small or no enantiomeric excess was observed. [a]Poor separation of enantiomers; *ee* could not be determined. [b]Moderate separation of enantiomers; *ee* is only a crude estimate. [c]Enantiomers sufficiently separated. [d]Impurity overlapping with major enantiomer; *ee* is only a crude estimate.

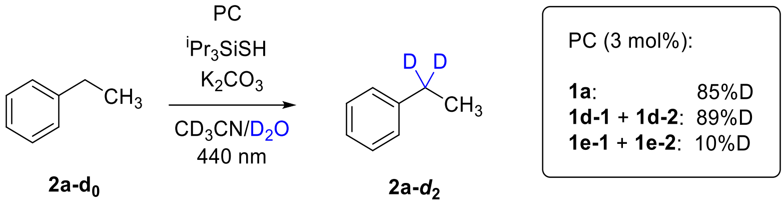
The lower enantiomeric excess of the compounds depicted in Scheme S12 compared to isochromane derivative **5b** might be explained by the higher flexibility (**7a**, **7b**, **7f**, **7k**), smaller steric difference between the substituents at the stereocenter and decreased reactivity (**7b**, **7f**, **5c**). However, this is only speculation, and there is not sufficient data to draw such conclusions at the current state.

## 8 In situ generation of the active photocatalyst by photocyclization of 3DPA2FBN (1a)

The photocatalyst 3DPA2FBN (**1a**) used in this work is not stable under irradiation. Under the reaction conditions for benzylic C-H activation it is converted within minutes. Multiple products were observed but could not be fully separated by column chromatography. These products arise from an intramolecular condensation of one or two of the diphenylamino groups onto the cyanobenzene core as has been reported for a similar photocatalyst.[61] Two products formed by condensation of one diphenylamino group (**1d-1** and **1d-2**) and two products in which two diphenylamino groups are condensed onto the acceptor part (**1e-1** and **1e-2**) were identified by high resolution mass spectrometry and partially isolated in a separate batch where only 3DPA2FBN (**1a**) was irradiated in MeCN. The isomers were not separable via column chromatography but a fraction containing a mixture of **1d-1** and **1d-2** and a fraction containing a mixture of **1e-1** and **1e-2** were obtained.



**Scheme S13.** Photocatalyst 3DPA2FBN (**1a**) undergoes intramolecular condensation under irradiation.



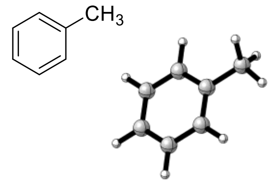
**Scheme S14.** The mixture of **1d-1** and **1d-2** is similarly active compared to 3DPA2FBN (**1a**) in photocatalytic deuteration of ethyl benzene (**2a**). The mixture of **1e-1** and **1e-2** is almost inactive.

The mixture of **1d-1** and **1d-2** performed similar to pure 3DPA2FBN (**a1**) while the mixture of **1e-1** and **1e-2** was almost inactive. Thus, **1d-1**, **1d-2**, or likely both, are catalytically active and as most of the conversion in the reactions presented in this work occurs long after full photocondensation of 3DPA2FBN (**1a**), these photocondensation products should not be seen as decomposition products, but they are the actual photocatalysts in the reactions and probably also in most other reactions where 3DPA2FBN (**1a**) is used. When using the mixture of **1d-1** and **1d-2** as photocatalyst, **1e-1** and/or **1e-2** are observed after the reaction. However, even after 16 h of irradiation **1d-1**/**1d-2** is still present, similar to when 3DPA2FBN is used as catalyst. Thus, 3DPA2FBN (**1a**) can be used as pre-catalyst.

# 9 Optimized cartesian coordinates and thermodynamic data

## Toluene

**Substrate**

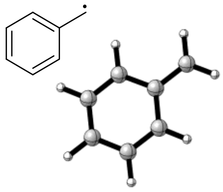


G: -271.38903891 Eh
H: -271.35376477 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.38784481547119 | -1.32301983790344 | 0.32765563708489 |
| C | 3.02359237360718 | -0.28837550479583 | 1.18096150471360 |
| C | 2.77343766662251 | 0.99600754601848 | 0.68732961085250 |
| C | 2.89843750132878 | 1.21388540287309 | -0.68516001516021 |
| C | 3.26335612346781 | 0.17988408617984 | -1.54396092869601 |
| C | 3.50933673783775 | -1.09254458599621 | -1.04079146405051 |
| H | 3.57731818602162 | -2.31387333532258 | 0.73114733074215 |
| H | 2.93041172286472 | -0.47625209902995 | 2.24860334657928 |
| C | 2.38305814715681 | 2.10917542460885 | 1.62228732574337 |
| H | 3.35466150600551 | 0.37130611316951 | -2.60949698147357 |
| H | 3.79328936102206 | -1.90049284014914 | -1.70869311945747 |
| H | 1.48585575475855 | 1.84746424549715 | 2.19401486726823 |
| H | 3.18083624692708 | 2.31278342522841 | 2.34579404795084 |
| H | 2.17923386774684 | 3.03451187590931 | 1.07721033201043 |
| H | 2.70756398916160 | 2.20602108371251 | -1.08748849410751 |

**Benzyl radical**



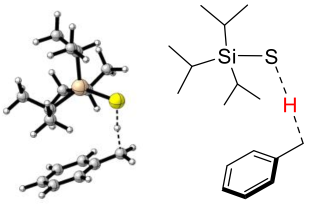
G: -270.75820463 Eh
H: -270.72187962 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.71310428901446 | -1.31490218394319 | -0.05490376270108 |
| C | 3.20693983597211 | -0.61847344793215 | 1.02537255384290 |
| C | 2.73247938823078 | 0.71462333042110 | 0.88014600163171 |
| C | 2.80086210175170 | 1.29693244334582 | -0.41581337016017 |
| C | 3.30949753883101 | 0.58923643648768 | -1.48757803241513 |
| C | 3.76967459175946 | -0.72055613021753 | -1.31945609522200 |
| H | 4.06983924758549 | -2.33229491591556 | 0.07942929922528 |
| H | 3.16573860356866 | -1.08544666624680 | 2.00604768218542 |
| C | 2.21647989968816 | 1.42785048959587 | 1.97335934503146 |
| H | 3.35197917441023 | 1.05432773173312 | -2.46852479049912 |
| H | 4.16830279823108 | -1.27227562740349 | -2.16517223878051 |

| | | | |
|---|---|---|---|
| H | 2.16700400059385 | 0.97777050958905 | 2.95889357556623 |
| H | 1.85610777364212 | 2.44401726394142 | 1.85574861206009 |
| H | 2.44482069672087 | 2.31481573654464 | -0.55228895976507 |

**HAT transition state toluene**



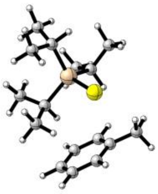
G: -1314.28009906 Eh
H: -1314.20699697 Eh
Charge: 0
Multiplicity: 2

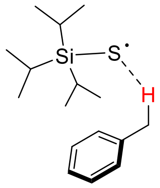
Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.71003528091204 | -1.31520870242546 | -0.05393963021528 |
| C | 3.16125575120387 | -0.63237526465333 | 1.01783785658399 |
| C | 2.66584417929403 | 0.67957064720528 | 0.86233235581105 |
| C | 2.75908622333959 | 1.27867325447170 | -0.41235403959020 |
| C | 3.31237261763523 | 0.59184379346421 | -1.48012068803248 |
| C | 3.78376058701512 | -0.71102853398669 | -1.31001428294172 |
| H | 4.08051080652014 | -2.32686870385356 | 0.08370320581707 |
| H | 3.09342755402647 | -1.11007710321132 | 1.99178789879193 |
| C | 2.02676752208954 | 1.35691709113606 | 1.96034282528548 |
| H | 3.37869218785871 | 1.07018591101054 | -2.45308110695351 |
| H | 4.21077689894244 | -1.25013009613915 | -2.15021527394085 |
| S | -0.78521602510736 | 0.44444291162933 | 2.25706342405348 |
| Si | -1.23704021315136 | 0.07137783600295 | 0.16840492606790 |
| C | -0.88424641365147 | 1.71748705467704 | -0.73451951073145 |
| H | 0.07239878404849 | 2.03841182322882 | -0.29357851554161 |
| H | 0.66380363830374 | 0.89207303285453 | 2.01252601862576 |
| C | -3.10051944003661 | -0.33944614703239 | 0.18829731017943 |
| H | -3.54336470388447 | 0.48083609302372 | 0.77485410162283 |
| C | -0.12480952035602 | -1.31826872611320 | -0.52527546526204 |
| H | 0.82594056123768 | -0.81198290713884 | -0.75733209854366 |
| C | -3.76282166513851 | -0.32697639570136 | -1.19877411181201 |
| H | -4.84793515720047 | -0.46244747738115 | -1.09940302490426 |
| H | -3.59897639906980 | 0.61260017441095 | -1.73515433303304 |
| H | -3.39201627897139 | -1.13962288275159 | -1.83147560659465 |
| C | -3.41028910901392 | -1.65540615457127 | 0.91673391051570 |
| H | -2.95872130296487 | -1.69045769531471 | 1.91348355315853 |
| H | -4.49415974904324 | -1.78770766523063 | 1.03033120571802 |
| H | -3.03662256730634 | -2.51543327568864 | 0.34930841238259 |
| C | -1.92297479504327 | 2.79207837281302 | -0.38519912685991 |
| H | -2.04706466916386 | 2.89024641678331 | 0.69844671498492 |
| H | -1.61958667467456 | 3.76973055452108 | -0.78187427954858 |
| H | -2.90322078906218 | 2.55824855115973 | -0.81574295897690 |
| C | -0.66780482646713 | 1.61537537860272 | -2.25010493705043 |
| H | -1.56700866629866 | 1.26506261559412 | -2.76987894657786 |
| H | -0.41669235909208 | 2.59948189484911 | -2.66844779576705 |
| H | 0.15165809925828 | 0.93227312275343 | -2.49835226981820 |
| C | -0.65557158825312 | -1.93012088954985 | -1.83284772149495 |
| H | 0.10253249555697 | -2.58664504529307 | -2.27978308047687 |
| H | -1.54248156005688 | -2.54513727240321 | -1.64351865679924 |
| H | -0.92545945402633 | -1.17911713588000 | -2.58171071561391 |
| C | 0.18271699407101 | -2.43641828251480 | 0.48009482362920 |

| | | | |
|---|---|---|---|
| H | -0.71982060165620 | -3.00487920968772 | 0.73149164482407 |
| H | 0.91049354271228 | -3.13992080699710 | 0.05397096617817 |
| H | 0.59039991790101 | -2.04264620296831 | 1.41453054158309 |
| H | 2.27865744858439 | 1.02756871700765 | 2.96761440616824 |
| H | 1.83986824192659 | 2.42495350153489 | 1.85890140959937 |
| H | 2.39577119625261 | 2.29369582775319 | -0.55032433450003 |

**Reactant complex toluene**





G: -1314.29079371 Eh
H: -1314.21445853 Eh
Charge: 0
Multiplicity: 2

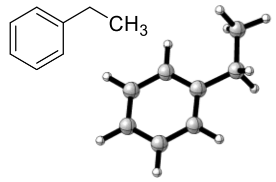
Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.39092108540905 | -1.32089673194552 | 0.32861311914585 |
| C | 3.01573942239370 | -0.28837287175066 | 1.18040120596520 |
| C | 2.76818180492921 | 0.99729646370877 | 0.68685784310065 |
| C | 2.89136114943918 | 1.21259491399870 | -0.68727752260081 |
| C | 3.26047169399301 | 0.17909030605022 | -1.54553978393741 |
| C | 3.51559554907309 | -1.09145865166262 | -1.03994440679457 |
| H | 3.57953546004799 | -2.31147906251955 | 0.73314831856528 |
| H | 2.91288272083897 | -0.47596610268030 | 2.24692860509011 |
| C | 2.38729774949950 | 2.11011321270341 | 1.62361202737788 |
| H | 3.35152702737798 | 0.36991039838097 | -2.61139059689571 |
| H | 3.80762579444574 | -1.89818401218927 | -1.70604480144465 |
| S | -0.91413252339903 | -0.14020459040103 | 2.34278782357870 |
| Si | -1.34866296727384 | -0.11324517805652 | 0.23585492409179 |
| C | -0.87394675491637 | 1.61382551780468 | -0.41507796413474 |
| H | 0.09746718991969 | 1.79090624459890 | 0.06945175322348 |
| H | 1.48966758450219 | 1.84663243907360 | 2.19549084403910 |
| C | -3.21123677445260 | -0.48583814835444 | 0.03922179759347 |
| H | -3.69500804342101 | 0.22639489028224 | 0.72670310139968 |
| C | -0.17256262022659 | -1.42920649615740 | -0.51837664654646 |
| H | 0.77156359830023 | -0.87247852325287 | -0.61847281078465 |
| C | -3.77169408613767 | -0.22222956308235 | -1.36710481173211 |
| H | -4.85487510804381 | -0.40080322584386 | -1.38008499011399 |
| H | -3.60712791207446 | 0.80810205805049 | -1.69595255751402 |
| H | -3.32533682650650 | -0.88697270373124 | -2.11371897594183 |
| C | -3.56710191705912 | -1.90082511950332 | 0.51422709422648 |
| H | -3.17140976817700 | -2.10380318445368 | 1.51458667533192 |
| H | -4.65603986123325 | -2.03460929583741 | 0.54654203107282 |
| H | -3.16791989222808 | -2.65920344046617 | -0.16899356326746 |
| C | -1.84740314205038 | 2.69018842414779 | 0.08430845089342 |
| H | -1.95581324752889 | 2.66197543382911 | 1.17482465389087 |
| H | -1.49295405814897 | 3.69227035643781 | -0.18938183451185 |
| H | -2.84535746247341 | 2.56830789451058 | -0.35276796134716 |
| C | -0.64910397140652 | 1.71549944490427 | -1.92912049080723 |
| H | -1.55663362626291 | 1.49479420138355 | -2.50228902888252 |
| H | -0.33790778152734 | 2.73433974773780 | -2.19656514984792 |
| H | 0.13997125387156 | 1.03536792576836 | -2.26641752232507 |
| C | -0.62389508493274 | -1.87014514862619 | -1.91768871740386 |
| H | 0.17314558724523 | -2.46220880081607 | -2.38795228743892 |

| | | | |
|---|---|---|---|
| H | -1.51389422590963 | -2.50668571108667 | -1.86636396473927 |
| H | -0.84570776891307 | -1.03175431428224 | -2.58474144051656 |
| C | 0.09222597364241 | -2.65450435736866 | 0.36345228137918 |
| H | -0.82694836241323 | -3.21478941642839 | 0.56569167003963 |
| H | 0.79255608599163 | -3.33255697307579 | -0.14222691811508 |
| H | 0.53057542293923 | -2.37491395926311 | 1.32629310067459 |
| H | 3.19019737002311 | 2.30417552014477 | 2.34408508186418 |
| H | 2.19041030763703 | 3.03917503256380 | 1.08112674076822 |
| H | 2.69681947412277 | 2.20385213954527 | -1.09065284310097 |

## 2a

**Substrate 2a**

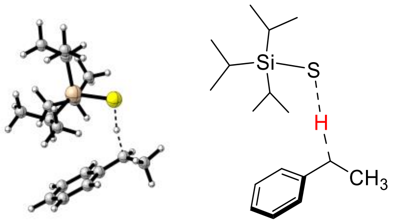


G: -310.66138785 Eh
H: -310.62191776 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.54746406868165 | -1.29050026529371 | -0.26553538075926 |
| C | 3.17842837049373 | -0.61165757216360 | 0.89501548553773 |
| C | 2.77594890696199 | 0.72311335738409 | 0.84547092559511 |
| C | 2.75508880231854 | 1.36035991319515 | -0.40072929692965 |
| C | 3.12078060691567 | 0.68743707519816 | -1.55891799002333 |
| C | 3.52014360623219 | -0.64607994409720 | -1.49589862327968 |
| H | 3.85882230033266 | -2.32956253215633 | -0.20277663599866 |
| H | 3.21014138314032 | -1.13557353546177 | 1.84518681857874 |
| C | 2.35499204833855 | 1.50043568619910 | 2.07425102655896 |
| H | 3.09710460885453 | 1.20450905206139 | -2.51421953468658 |
| H | 3.80913332732501 | -1.17509434784312 | -2.39936196616907 |
| H | 1.29328863362768 | 1.76448382408941 | 1.96755796014730 |
| H | 2.89572675726226 | 2.45641720309033 | 2.07510768118662 |
| H | 2.44586359686725 | 2.40238428295390 | -0.45821406264020 |
| C | 2.56565772684560 | 0.80159484452075 | 3.41316375383948 |
| H | 2.26832665481159 | 1.45990437988468 | 4.23488594877007 |
| H | 1.96840906691923 | -0.11288265009772 | 3.49072749693477 |
| H | 3.61692353407155 | 0.53305422853649 | 3.56280539333764 |

**HAT transition state 2a**

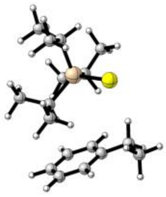


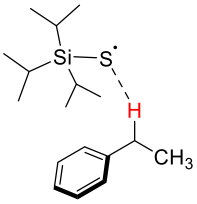
G: -1353.55808959 Eh
H: -1353.48162363 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.70440007517578 | -1.29576733481958 | -0.18769152985394 |
| C | 3.17942935305140 | -0.69847670310383 | 0.94798371811833 |
| C | 2.68583481074008 | 0.61972715223671 | 0.90597343002510 |
| C | 2.75826167484397 | 1.31360342989474 | -0.31937331838020 |
| C | 3.28307273066335 | 0.71307337183357 | -1.45197523859644 |
| C | 3.75317929221829 | -0.59940207450700 | -1.39463714633367 |
| H | 4.07502777342400 | -2.31547555127297 | -0.13546798396881 |
| H | 3.13817619671437 | -1.25988219086863 | 1.87549837627392 |
| C | 2.06555005070352 | 1.25230789310711 | 2.05938333379291 |
| H | 3.32929706863303 | 1.26756819431300 | -2.38488511109753 |
| H | 4.15993928070679 | -1.07337617710891 | -2.28289136502844 |
| S | -0.79407431686401 | 0.53599646109538 | 2.22726284441011 |
| Si | -1.24208548380988 | 0.10055361119753 | 0.15233982872868 |
| C | -0.88750053357966 | 1.71266286928240 | -0.80800593812055 |
| H | 0.07306063080453 | 2.04229302107188 | -0.38207029341621 |
| H | 0.71192612041584 | 0.90123072703816 | 1.99447843812479 |
| C | -3.10606685456526 | -0.31097639722376 | 0.18223476445367 |
| H | -3.55034538116915 | 0.52312527526933 | 0.74789616966743 |
| C | -0.12833678793385 | -1.31116283526533 | -0.49242516088931 |
| H | 0.82045890948869 | -0.81057252039431 | -0.74452811636775 |
| C | -3.76738375880939 | -0.33335609519890 | -1.20533994854675 |
| H | -4.85141674086773 | -0.47619732945931 | -1.10401805791202 |
| H | -3.61105120315344 | 0.59665148597607 | -1.76009602713211 |
| H | -3.38874024903583 | -1.15540496444837 | -1.82118248429812 |
| C | -3.41497638961158 | -1.60841443559240 | 0.94335744508773 |
| H | -2.96267336713367 | -1.61779069624341 | 1.94030427444350 |
| H | -4.49878305376313 | -1.73828518311631 | 1.06062123283952 |
| H | -3.04137201406245 | -2.48235399318880 | 0.39752605612999 |
| C | -1.91909904160666 | 2.80359092457896 | -0.49026059895735 |
| H | -2.03772168991614 | 2.93834948030423 | 0.59005266922514 |
| H | -1.61258687088754 | 3.76605725427072 | -0.92039601456094 |
| H | -2.90252148163578 | 2.56077567759982 | -0.90852814208141 |
| C | -0.67843875876941 | 1.55773457317295 | -2.32007387216965 |
| H | -1.58078380358186 | 1.19202635588737 | -2.82370968174988 |
| H | -0.42622404331531 | 2.52611745094510 | -2.77300038744008 |
| H | 0.13834165241255 | 0.86454944578338 | -2.54822912289817 |
| C | -0.65746054021889 | -1.97269709387429 | -1.77630695376079 |
| H | 0.10168015029645 | -2.64519893467515 | -2.19705152957514 |
| H | -1.54479326970247 | -2.58038188859336 | -1.56621281130089 |
| H | -0.92570143423415 | -1.25032245300319 | -2.55328526060912 |
| C | 0.18189615755505 | -2.39001233725367 | 0.55384216613581 |
| H | -0.71928735713726 | -2.95165276028092 | 0.82474131315307 |
| H | 0.91383241415797 | -3.10619102843097 | 0.15692151104197 |
| H | 0.58484403813892 | -1.95989292888011 | 1.47447569185753 |
| H | 1.93267275992408 | 2.33195516356796 | 1.95033094235748 |
| H | 2.39813452837522 | 2.33820822351108 | -0.36759471334611 |
| C | 2.38548094852426 | 0.79647696960237 | 3.45892247519597 |
| H | 1.78300417138416 | 1.34627495099888 | 4.18663698065793 |
| H | 2.17927423696867 | -0.26869229045936 | 3.59992704376869 |
| H | 3.44531398004354 | 0.96990458472415 | 3.68704053290204 |

**Reactant complex 2a**





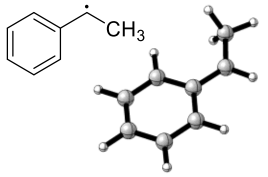
G: -1353.56272452 Eh
H: -1353.48364268 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.54782882640275 | -1.28995581318780 | -0.26473883553245 |
| C | 3.19213953308648 | -0.60633360734624 | 0.89662159328581 |
| C | 2.78923751329521 | 0.72889090124901 | 0.84760248724780 |
| C | 2.76872327259452 | 1.36513122317148 | -0.40017845494057 |
| C | 3.12015854894952 | 0.68716203281729 | -1.56034681052919 |
| C | 3.50783624373025 | -0.65031400772237 | -1.49790273927677 |
| H | 3.85501101761878 | -2.33022257036555 | -0.20133874007707 |
| H | 3.22518938578195 | -1.12845240226371 | 1.84746062167046 |
| C | 2.35786658011461 | 1.49907259625993 | 2.07473515921264 |
| H | 3.09371524668644 | 1.20343318522252 | -2.51607332189946 |
| H | 3.78298926730387 | -1.18408561045775 | -2.40291175738879 |
| S | -1.20198771942364 | 0.40670974747760 | 2.33506381565750 |
| Si | -1.36999427170204 | 0.04602492266063 | 0.22401003815095 |
| C | -0.93413919551027 | 1.68714704818027 | -0.65006134054833 |
| H | -0.00209060188623 | 1.98657077399018 | -0.14468619600804 |
| H | 1.28901340629544 | 1.74617760123846 | 1.96789217526198 |
| C | -3.23894485389754 | -0.39208309505283 | 0.04243165424390 |
| H | -3.76293287864701 | 0.41176925617200 | 0.57924011661202 |
| C | -0.16835276711370 | -1.32821581134812 | -0.33378349094453 |
| H | 0.77083296832915 | -0.78211765574446 | -0.51445710200845 |
| C | -3.70805276526888 | -0.36426619575245 | -1.41949954663779 |
| H | -4.78976631573203 | -0.55056733522828 | -1.46009197079375 |
| H | -3.52507807360332 | 0.60006300286200 | -1.90138418664398 |
| H | -3.22144388986764 | -1.13892351772630 | -2.01953107716544 |
| C | -3.59638650534253 | -1.72804610372358 | 0.70595218259279 |
| H | -3.31221523507874 | -1.75218707324821 | 1.76208603948014 |
| H | -4.67744987448170 | -1.90726373441963 | 0.63790745458765 |
| H | -3.09809342971663 | -2.56648613206400 | 0.20695648819507 |
| C | -1.97641703966443 | 2.77966076741376 | -0.38452236826722 |
| H | -2.17942831479624 | 2.88812209850337 | 0.68618971466219 |
| H | -1.62591102606708 | 3.74917890691315 | -0.76112602042843 |
| H | -2.92588023658596 | 2.56124951796592 | -0.88697408901408 |
| C | -0.60977957670071 | 1.55886350779609 | -2.14497561324581 |
| H | -1.47676005099069 | 1.22816469200168 | -2.72776015944065 |
| H | -0.30043508920869 | 2.53202941004259 | -2.54922553299699 |
| H | 0.20893379351265 | 0.85466871767007 | -2.32356254880373 |
| C | -0.56937060513538 | -2.00517247479238 | -1.65398097817636 |
| H | 0.24751790810008 | -2.64914393364395 | -2.00471744594034 |
| H | -1.45065231011668 | -2.64241857207822 | -1.52017083016826 |
| H | -0.79097001645180 | -1.29107623300185 | -2.45317522982182 |
| C | 0.11532717003956 | -2.38814509888683 | 0.73685985635299 |
| H | -0.78754321755665 | -2.95452980550329 | 0.99286371605177 |
| H | 0.86474905709285 | -3.10170437927060 | 0.36970462266666 |
| H | 0.49210548235195 | -1.94147552506809 | 1.66078434924807 |
| H | 2.88006743152330 | 2.46538633030926 | 2.07712654800541 |

|  |  |  |  |
|---|---|---|---|
| H | 2.47081790999675 | 2.41060547404522 | -0.45880297559352 |
| C | 2.56463445198531 | 0.79936927980168 | 3.41305783400588 |
| H | 2.24871600435859 | 1.45264350851268 | 4.23153090134127 |
| H | 1.97096084052294 | -0.11817047932465 | 3.48187747190667 |
| H | 3.61733893930073 | 0.54200611333607 | 3.57290789731474 |

**Radical 2a**



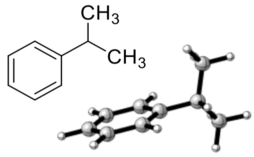
G: -310.03723847 Eh
H: -309.99676631 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

|  |  |  |  |
|---|---|---|---|
| C | 3.77723687743787 | -1.26354677638206 | -0.16940657175165 |
| C | 3.33242381108650 | -0.63212714111580 | 0.97849053301379 |
| C | 2.81492218510958 | 0.69013232514793 | 0.92981826708766 |
| C | 2.77586872567426 | 1.32878093567465 | -0.33925691443188 |
| C | 3.22308314553367 | 0.68744082422714 | -1.47778195501847 |
| C | 3.72814408179146 | -0.61467423952793 | -1.40534843145629 |
| H | 4.16887914279067 | -2.27525663829901 | -0.10741580553206 |
| H | 3.37877517463591 | -1.15349906351928 | 1.92979475194795 |
| C | 2.35165247787560 | 1.36353259118610 | 2.08116053322555 |
| H | 3.18172689466087 | 1.19872601329512 | -2.43557371823930 |
| H | 4.07905051347871 | -1.11679055822025 | -2.30164849164973 |
| H | 1.97156913079800 | 2.37398220091275 | 1.95242519965029 |
| H | 2.38384267787160 | 2.34102087296181 | -0.40205313338036 |
| C | 2.35356763253227 | 0.77505967302327 | 3.45086567231282 |
| H | 1.94361067267133 | 1.47433820111618 | 4.18282725659867 |
| H | 1.75747367891298 | -0.14690194588706 | 3.50035159379401 |
| H | 3.36773862713870 | 0.50625272540644 | 3.77826171382899 |

# 2b

**Substrate 2b**



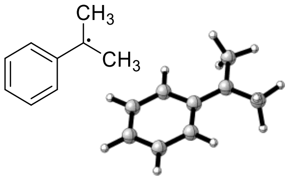
G: -349.93794805 Eh
H: -349.89549105 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

|  |  |  |  |
|---|---|---|---|
| C | 4.10448601204513 | -0.89282278220611 | -0.28116416107275 |
| C | 3.80157079992375 | -0.12308438468997 | 0.83605648889947 |
| C | 2.82620135908205 | 0.87730563503864 | 0.77619239326912 |
| C | 2.16583693513961 | 1.08358864238810 | -0.43569875517411 |

| | | | |
|---|---|---|---|
| C | 2.46591357289632 | 0.31559390915725 | -1.55794067905880 |
| C | 3.43707744662920 | -0.67659541838882 | -1.48434601569478 |
| H | 4.86496824479651 | -1.66591646581350 | -0.21338546162190 |
| H | 4.33260378004349 | -0.30563260765781 | 1.76711648261035 |
| C | 2.49377173492558 | 1.71869083294193 | 1.99201831816413 |
| H | 1.93860938270362 | 0.49404881249094 | -2.49098092917997 |
| H | 3.67343149845487 | -1.27818701398274 | -2.35719671124498 |
| H | 1.69741088229874 | 2.41512756929135 | 1.69468502729115 |
| H | 1.40465289458069 | 1.85809944869722 | -0.50065658452075 |
| C | 1.95865751898505 | 0.85751159823657 | 3.14355589406344 |
| H | 1.65657783422128 | 1.48655955024173 | 3.98824179322685 |
| H | 1.09399891134607 | 0.26704821601645 | 2.82475303031849 |
| H | 2.72611757393346 | 0.16276839607793 | 3.50243388918629 |
| C | 3.70032605323939 | 2.55163361509519 | 2.44452459891869 |
| H | 4.08083171541699 | 3.17043868765328 | 1.62585311466804 |
| H | 3.42541124049836 | 3.20875586638112 | 3.27707583577793 |
| H | 4.51758930883978 | 1.90578052303123 | 2.78491790117408 |

**Radical 2b**



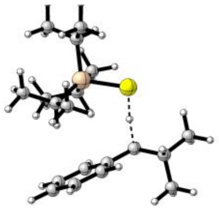
G: -349.31376769 Eh
H: -349.27135215 Eh
Charge: 0
Multiplicity: 2

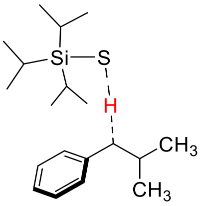
Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.77230389149377 | -1.26167714340567 | -0.14284914386730 |
| C | 3.31784125984625 | -0.60065911667605 | 0.98407726345405 |
| C | 2.80394699001066 | 0.72250618326905 | 0.90873937717233 |
| C | 2.78140936202204 | 1.32751369896113 | -0.37702834992476 |
| C | 3.23890636324167 | 0.65570808022000 | -1.49653534270838 |
| C | 3.73887305497345 | -0.64377672975195 | -1.39446380283067 |
| H | 4.15933391783965 | -2.27281903689593 | -0.04976171041139 |
| H | 3.35668104354165 | -1.10679482847331 | 1.94304446986592 |
| C | 2.33479309680952 | 1.40868393619122 | 2.06534407064296 |
| H | 3.20735425743786 | 1.14781159893180 | -2.46492469773165 |
| H | 4.09683082440555 | -1.16641702699108 | -2.27613657917232 |
| H | 2.39851016993927 | 2.33658851610010 | -0.48907963169409 |
| C | 2.37126599412513 | 0.74680782578090 | 3.40920466071484 |
| H | 1.97042202296515 | 1.40290201312326 | 4.18501919106906 |
| H | 1.78491257489308 | -0.18234712922082 | 3.42521650347486 |
| H | 3.39393998010382 | 0.47227399144088 | 3.70324883908840 |
| C | 1.80037961090898 | 2.80423443318540 | 1.95723050189662 |
| H | 2.54929436642138 | 3.49978343811363 | 1.55386622840697 |
| H | 0.93235867648688 | 2.86022942700319 | 1.28567982437519 |
| H | 1.48769624253423 | 3.18555131909426 | 2.93174640817935 |

## 2c

**HAT transition state 2c**





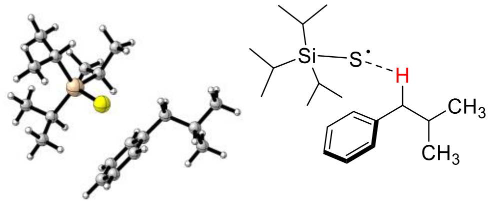
G: -1432.10773530 Eh
H: -1432.02617819 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.58633812423323 | -1.48259060841991 | 0.01442955573347 |
| C | 3.04645509608613 | -0.78823559038129 | 1.08546624831933 |
| C | 2.63743135077569 | 0.55192548725323 | 0.94404557035395 |
| C | 2.79371884573540 | 1.16015892990479 | -0.31720537680668 |
| C | 3.33509945347555 | 0.46280910065048 | -1.38604093896647 |
| C | 3.73086913408092 | -0.86496807517940 | -1.22771717483946 |
| H | 3.88775645759276 | -2.51817516676244 | 0.14320853225704 |
| H | 2.92168138409594 | -1.28955495170556 | 2.04058711376821 |
| C | 2.01825577297325 | 1.28490875953751 | 2.03722397776529 |
| H | 3.45063070952300 | 0.95421069101206 | -2.34787457131690 |
| H | 4.14906907071645 | -1.41439037046240 | -2.06581047374631 |
| S | -0.73144659310585 | 0.18468607251543 | 2.26335409899094 |
| Si | -1.21809806218099 | -0.01998154426071 | 0.16104691856783 |
| C | -0.83256901592884 | 1.67875416794819 | -0.62628072339588 |
| H | 0.13626634745027 | 1.94732274133491 | -0.17916984323503 |
| H | 0.68600934764738 | 0.78371605373178 | 2.04913728282092 |
| C | -3.09407328448729 | -0.37413554342733 | 0.17402087334558 |
| H | -3.50504815321337 | 0.42391442897345 | 0.81190700534651 |
| C | -0.15923265479865 | -1.38833396663554 | -0.64786081987328 |
| H | 0.80852846112193 | -0.89797597144376 | -0.84185307092762 |
| C | -3.76791691396591 | -0.26220880643826 | -1.20234927164382 |
| H | -4.85614005282533 | -0.36678950183166 | -1.09900177550707 |
| H | -3.57709683629975 | 0.69998049714964 | -1.68727366235264 |
| H | -3.43046826218190 | -1.05025095548508 | -1.88280812463206 |
| C | -3.43902239218478 | -1.71947234994756 | 0.82931753849442 |
| H | -2.98478423297149 | -1.82360693794665 | 1.82022549437524 |
| H | -4.52578119520950 | -1.82701071627420 | 0.94212596816102 |
| H | -3.09251328098914 | -2.55684070968499 | 0.21293579985474 |
| C | -1.84257730317477 | 2.74963175585686 | -0.19198568003042 |
| H | -1.95676455080399 | 2.77277500676755 | 0.89697872469782 |
| H | -1.51877378442886 | 3.74563292298914 | -0.52120727933945 |
| H | -2.83122075265496 | 2.56950716097641 | -0.62923043511422 |
| C | -0.63527149279469 | 1.67530265613733 | -2.14783805043937 |
| H | -1.54761062033540 | 1.38103737225494 | -2.67934734690963 |
| H | -0.36607082325280 | 2.67982486352896 | -2.50135270514133 |
| H | 0.16553707662860 | 0.99233371787441 | -2.45123290475917 |
| C | -0.71288408130848 | -1.87933873996898 | -1.99650300927446 |
| H | 0.02334228873396 | -2.52132329034257 | -2.49792030020656 |
| H | -1.61628248523815 | -2.48176449046631 | -1.84924605046662 |
| H | -0.96407437657739 | -1.06565671984901 | -2.68374365926638 |
| C | 0.11131497175751 | -2.59330648008595 | 0.26376881612943 |
| H | -0.80795889617599 | -3.15570060456232 | 0.46279177179457 |
| H | 0.82100971002595 | -3.27975113362383 | -0.21718958931558 |

|  |  |  |  |
|---|---|---|---|
| H | 0.52571231241535 | -2.29044688230716 | 1.22875222803912 |
| H | 1.81668032143993 | 2.33689582342603 | 1.80818288048089 |
| H | 2.49176628561076 | 2.19666687929863 | -0.44584358618401 |
| C | 2.41954359530895 | 1.04187093020843 | 3.47958176590414 |
| H | 2.23036257494856 | -0.01218189085841 | 3.72923778924804 |
| C | 3.92214034780830 | 1.31933108768163 | 3.65862531303458 |
| H | 4.21630151849065 | 1.14789437899614 | 4.69990570941979 |
| H | 4.52984112316191 | 0.67702631808405 | 3.01469686371620 |
| H | 4.15066528272009 | 2.36214931860312 | 3.40978516374194 |
| C | 1.59809770093604 | 1.91416853976217 | 4.43059192774445 |
| H | 0.52527165591066 | 1.72998658323198 | 4.32307569485692 |
| H | 1.87650875408616 | 1.71632301643266 | 5.47051746199288 |
| H | 1.78407302159697 | 2.97639173622935 | 4.23016833473514 |

**Reactant complex 2c**



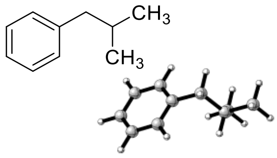
G: -1432.11465988 Eh
H: -1432.03055130 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

|  |  |  |  |
|---|---|---|---|
| C | 2.76463955817292 | -1.90023500804874 | 1.16720472406513 |
| C | 2.34426838119815 | -0.83197842025459 | 1.95824534799479 |
| C | 2.43343232425273 | 0.48759940296355 | 1.49287983053384 |
| C | 2.95690063302755 | 0.70415675798558 | 0.21763239680058 |
| C | 3.37942088186117 | -0.36096305354851 | -0.57408631521854 |
| C | 3.28235825054150 | -1.66770731892201 | -0.10206458251284 |
| H | 2.67945395256171 | -2.91468350733250 | 1.54589392383421 |
| H | 1.96570323870278 | -1.01902732520369 | 2.95964056791314 |
| C | 1.99116911175886 | 1.62809078470176 | 2.36810297104521 |
| H | 3.78207610469826 | -0.16974845819591 | -1.56509985193760 |
| H | 3.60359740141587 | -2.49913993137196 | -0.72257275182705 |
| S | -0.75138571260879 | -1.19257742670522 | 1.90327371585708 |
| Si | -1.26968402001327 | -0.54207980621230 | -0.08043057142059 |
| C | -0.74153207667216 | 1.28516540917678 | -0.22788928578247 |
| H | 0.28476750383558 | 1.26349560667168 | 0.16713382107706 |
| H | 1.00370006378927 | 1.39228143883844 | 2.78711633604112 |
| C | -3.18312342943522 | -0.73332930390174 | -0.08471398949540 |
| H | -3.50549716362345 | -0.23491337148435 | 0.84165559665479 |
| C | -0.35913683665965 | -1.59255339739167 | -1.39086039222552 |
| H | 0.62905413148771 | -1.10899595014237 | -1.46358233835934 |
| C | -3.85843280900580 | -0.00958944884274 | -1.25973718083944 |
| H | -4.94969129773533 | -0.09039384225094 | -1.16536254095750 |
| H | -3.61190305733259 | 1.05531011623484 | -1.29406819784070 |
| H | -3.58231276966731 | -0.45003091682161 | -2.22281293908488 |
| C | -3.63502676510991 | -2.19833421816597 | -0.01765952551905 |
| H | -3.18291135942604 | -2.72986167821700 | 0.82503743975553 |
| H | -4.72640554262889 | -2.25616431350486 | 0.08719851046261 |
| H | -3.37026237843315 | -2.73812878884662 | -0.93389519005575 |
| C | -1.56652964569690 | 2.19690462516045 | 0.68845315738021 |
| H | -1.60614360062704 | 1.80656597848336 | 1.71119331902641 |
| H | -1.12947536393766 | 3.20327559520468 | 0.72932131605079 |

| | | | |
|---|---|---|---|
| H | -2.59663687933736 | 2.30564456328081 | 0.32942870195662 |
| C | -0.65704319106761 | 1.84444445444041 | -1.65465860101354 |
| H | -1.63110230686692 | 1.85203302095004 | -2.15671417782393 |
| H | -0.29628746825285 | 2.88149286734878 | -1.63342958539169 |
| H | 0.03740615802541 | 1.26997509018090 | -2.27660902257409 |
| C | -1.01787274550405 | -1.53835123619605 | -2.77921099088079 |
| H | -0.36812324074897 | -2.01264105753091 | -3.52624934568421 |
| H | -1.96565465720401 | -2.08822332176992 | -2.78291557487448 |
| H | -1.22308857962891 | -0.51885609447634 | -3.12012105999291 |
| C | -0.12375771446034 | -3.05137366474242 | -0.97935924113137 |
| H | -1.06893522428924 | -3.59504089290252 | -0.87035251183398 |
| H | 0.46886972707278 | -3.56954901259530 | -1.74526942551422 |
| H | 0.40594211620273 | -3.12152031267788 | -0.02638249159852 |
| H | 1.87315255557234 | 2.53634112614670 | 1.76042905947870 |
| H | 3.03227388646805 | 1.72162058139275 | -0.16017828462181 |
| C | 2.96671214554991 | 1.93445335790991 | 3.52352684776033 |
| H | 3.07259691302139 | 1.01710660988701 | 4.12214165901971 |
| C | 4.34716512158262 | 2.32719831109847 | 2.99811538420847 |
| H | 5.03365761092911 | 2.54249529598143 | 3.82379064740587 |
| H | 4.78705778735756 | 1.53175833024776 | 2.38812396777423 |
| H | 4.27739050869807 | 3.22886069262080 | 2.37601134776042 |
| C | 2.38734977800712 | 3.03073550384040 | 4.41784365885934 |
| H | 1.40684368295318 | 2.74651182357246 | 4.81481022845630 |
| H | 3.04997857259081 | 3.23943451808474 | 5.26447637237655 |
| H | 2.26440129541394 | 3.96296928378004 | 3.85263460016725 |

**Substrate 2c**



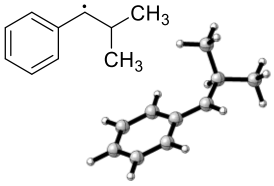
G: -389.21353649 Eh
H: -389.16834094 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 2.76012690902100 | -1.89888351809006 | 1.16807295922618 |
| C | 2.32228199984229 | -0.83782990210042 | 1.95262765278375 |
| C | 2.41682703996543 | 0.48034148341347 | 1.49681364828535 |
| C | 2.95891116055414 | 0.70607562125211 | 0.23029420481445 |
| C | 3.39833981876520 | -0.35285246346266 | -0.55952159911986 |
| C | 3.30137358933535 | -1.65957642578183 | -0.09261293697408 |
| H | 2.67431348689530 | -2.91661617586620 | 1.53867542776915 |
| H | 1.89482282464248 | -1.03325689987000 | 2.93408617806437 |
| C | 1.97830792592652 | 1.62195507887828 | 2.37524472378766 |
| H | 3.81534430031906 | -0.15599872152808 | -1.54331018453978 |
| H | 3.64134243196354 | -2.48742704188380 | -0.70801597250939 |
| H | 0.99747844538879 | 1.39173215544711 | 2.81269622417062 |
| H | 1.85025055895614 | 2.52825654639235 | 1.76749795664988 |
| H | 3.03892772280909 | 1.72581067441742 | -0.13979354217946 |
| C | 2.96684239298122 | 1.93322888377819 | 3.51886226072408 |
| H | 3.08131811052305 | 1.01662471903110 | 4.11732118937694 |
| C | 4.34121137282794 | 2.32448243947491 | 2.97639924363675 |
| H | 5.03731251089419 | 2.54081629769030 | 3.79378029846898 |
| H | 4.77242523764112 | 1.52751707192265 | 2.36262475136068 |

|  |  |  |  |
|---|---|---|---|
| H | 4.26456552769706 | 3.22503452391142 | 2.35345842925488 |
| C | 2.40092217017378 | 3.03216484627684 | 4.41884818108814 |
| H | 1.42563989499516 | 2.75085292353029 | 4.83121645098273 |
| H | 3.07536755461793 | 3.24223297215966 | 5.25580208567133 |
| H | 2.27104801326422 | 3.96344691100694 | 3.85355036920665 |

**Radical 2c**



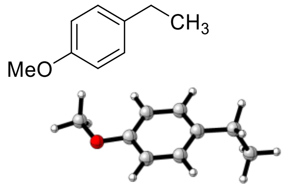
G: -388.58510972 Eh
H: -388.53921505 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

|  |  |  |  |
|---|---|---|---|
| C | 3.62865570333547 | -1.45190628333155 | -0.01946617960679 |
| C | 3.28361889685867 | -0.68471354497953 | 1.07836139145029 |
| C | 2.82320917914247 | 0.65176224854963 | 0.92155562410646 |
| C | 2.73775447769086 | 1.15540817245337 | -0.40641582308974 |
| C | 3.08355035575547 | 0.37816829446347 | -1.49384705509340 |
| C | 3.53303395434221 | -0.93380847521096 | -1.31322738681183 |
| H | 3.97870939635146 | -2.46998037449612 | 0.12837930412585 |
| H | 3.36923688078682 | -1.11075332722512 | 2.07310575266162 |
| C | 2.46190005736109 | 1.47369935934740 | 2.00994333387035 |
| H | 3.00600297587649 | 0.78993989154039 | -2.49632687773854 |
| H | 3.80505902471418 | -1.54334653909909 | -2.16934124915309 |
| H | 2.14915970495479 | 2.49320183518043 | 1.78396285044487 |
| H | 2.38959924761745 | 2.17476268553028 | -0.55445914413606 |
| C | 2.53746801429095 | 1.09133300930778 | 3.45495692457873 |
| H | 2.29032914792913 | 0.02465438935758 | 3.55717376352077 |
| C | 3.96554357393661 | 1.29617787861310 | 3.99742028966679 |
| H | 4.02891260585224 | 0.98713051865554 | 5.04724202669544 |
| H | 4.69580226258202 | 0.72045867343520 | 3.42045797214622 |
| H | 4.24711690194351 | 2.35342402608207 | 3.93498611749983 |
| C | 1.52861243585344 | 1.89151333398660 | 4.28469956340927 |
| H | 0.50651827693831 | 1.73429365670550 | 3.92562030376388 |
| H | 1.57070397767381 | 1.59940395676902 | 5.33922956948689 |
| H | 1.74817348821252 | 2.96434229436501 | 4.22477240820216 |

## 2e

**Substrate 2e**

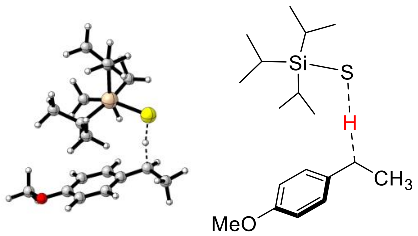


G: -425.13871708 Eh
H: -425.09334334 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.20965683830274 | -1.53290730214255 | -0.33538506483382 |
| C | 2.67088831499158 | -0.99092013610526 | 0.81924066865247 |
| C | 2.44926474189281 | 0.38548758569590 | 0.94676920318485 |
| C | 2.79037566413627 | 1.19775365402086 | -0.13059238555016 |
| C | 3.33495263486661 | 0.67517819125164 | -1.30378817229929 |
| C | 3.54649809659955 | -0.69954286281326 | -1.40625858407283 |
| H | 3.37427265355400 | -2.60145134751708 | -0.43360727729432 |
| H | 2.41031031423609 | -1.65284633369655 | 1.64270380271954 |
| C | 1.91129895513052 | 0.96711426436571 | 2.22905985909257 |
| H | 3.57974093628775 | 1.34575301688257 | -2.11938461441074 |
| H | 1.15494226378844 | 0.29235961820822 | 2.64950080619616 |
| H | 1.40284338521858 | 1.91509396754573 | 2.01520519496326 |
| H | 2.62682583709910 | 2.27131612606039 | -0.06265933660382 |
| C | 3.01596929816922 | 1.20370490044653 | 3.26742075508549 |
| H | 2.60731040790552 | 1.62330766815867 | 4.19296854806623 |
| H | 3.52559628973910 | 0.26592491329360 | 3.51255765159468 |
| H | 3.76893427598697 | 1.89697435200721 | 2.87809588442638 |
| O | 4.06807229991170 | -1.32660489448200 | -2.50256057888975 |
| C | 4.42245447603662 | -0.51478742413527 | -3.61501891098509 |
| H | 5.19802990892778 | 0.21617473366696 | -3.34786305101329 |
| H | 4.81502793947364 | -1.19726507309972 | -4.37083905050952 |
| H | 3.54878946774524 | 0.01323638238770 | -4.02143334751900 |

**HAT transition state 2e**



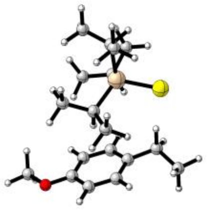
G: -1468.03575054 Eh
H: -1467.95420525 Eh
Charge: 0
Multiplicity: 2

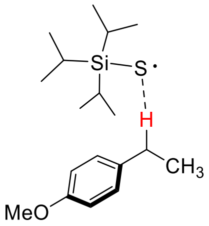
Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.68424142566162 | -1.33235557259861 | -0.09406546132908 |
| C | 3.16458773032282 | -0.72606545361370 | 1.02924682337702 |
| C | 2.67605176674937 | 0.59847063569015 | 0.99038735756423 |

| | | | |
|---|---|---|---|
| C | 2.76175172855968 | 1.27977017606392 | -0.23830228389559 |
| C | 3.27789056928942 | 0.68230037342903 | -1.37750077821326 |
| C | 3.73463883747722 | -0.63935074084358 | -1.31185862289361 |
| H | 4.05239483420628 | -2.35303969741589 | -0.06268902878362 |
| H | 3.12100610025679 | -1.28884679164453 | 1.95581399609702 |
| C | 2.04282645970118 | 1.22895021380218 | 2.13163004807969 |
| H | 3.32163793341793 | 1.24795049469394 | -2.30093946380659 |
| S | -0.83978334426254 | 0.54268020062885 | 2.24728530651766 |
| Si | -1.24014647539191 | 0.11090249850103 | 0.16678409382880 |
| C | -0.85581059949668 | 1.72191810500576 | -0.78757473238734 |
| H | 0.09253142117540 | 2.05003480123627 | -0.33409074867061 |
| H | 0.67816668537680 | 0.89351323951240 | 2.04538766403057 |
| C | -3.10540224234511 | -0.29587227279312 | 0.13865271970941 |
| H | -3.56316496824312 | 0.53810867250095 | 0.69371818466712 |
| C | -0.11411590249484 | -1.30218737905058 | -0.45663503553750 |
| H | 0.84190009585964 | -0.80162361159397 | -0.67950397704869 |
| C | -3.72869468567655 | -0.31478032258210 | -1.26624995002326 |
| H | -4.81509720608313 | -0.45839200204945 | -1.19532136929483 |
| H | -3.55755361391003 | 0.61678946857674 | -1.81415602688414 |
| H | -3.33279410873197 | -1.13500701203978 | -1.87362081050120 |
| C | -3.43850127884955 | -1.59355551777707 | 0.88915625176611 |
| H | -3.01164013512525 | -1.60530710326405 | 1.89720110316124 |
| H | -4.52541847397837 | -1.72041176802445 | 0.97845600292909 |
| H | -3.05365584420484 | -2.46789708997971 | 0.35162175851294 |
| C | -1.89293278836324 | 2.81559072088755 | -0.49862416858376 |
| H | -2.03955669899237 | 2.95011195882687 | 0.57829999686882 |
| H | -1.57295406644744 | 3.77760645939820 | -0.92015635666203 |
| H | -2.86567232377721 | 2.57518804761768 | -0.94255666648230 |
| C | -0.60496807904503 | 1.56704077820171 | -2.29309696368411 |
| H | -1.49336473218238 | 1.20208754330305 | -2.82148597402825 |
| H | -0.33869263475424 | 2.53484125334677 | -2.73983144590196 |
| H | 0.21667137164044 | 0.87160882357669 | -2.49695460193208 |
| C | -0.60811290025114 | -1.95938088668125 | -1.75638466257102 |
| H | 0.16137169927137 | -2.63181105564906 | -2.15863589142656 |
| H | -1.50117838623975 | -2.56669922028463 | -1.57101061870643 |
| H | -0.85681494485370 | -1.23471882012019 | -2.53787137992579 |
| C | 0.16578256170904 | -2.38499314007999 | 0.59403912030590 |
| H | -0.74384107534918 | -2.94525672207024 | 0.83830641584800 |
| H | 0.90752229377991 | -3.10127397228736 | 0.21582583568587 |
| H | 0.54315520988255 | -1.95744100687023 | 1.52671396901747 |
| H | 1.92276059578468 | 2.31062222508536 | 2.02782289132007 |
| H | 2.41163277046249 | 2.30722047677344 | -0.29672590160187 |
| C | 2.33040706065846 | 0.75986288671737 | 3.53453486208236 |
| H | 1.71709215665953 | 1.30921947208525 | 4.25367380671851 |
| H | 2.10863975565914 | -0.30399350681122 | 3.66331673831429 |
| H | 3.38646099391557 | 0.91954085996893 | 3.78929263447055 |
| O | 4.24612080849124 | -1.33258453693833 | -2.36188705379969 |
| C | 4.28008246054822 | -0.68553134408800 | -3.63229638420397 |
| H | 4.92433182303337 | 0.20309607576125 | -3.61022064338667 |
| H | 4.69602506010685 | -1.41689737320908 | -4.32659823140661 |
| H | 3.27115896939258 | -0.40253917083117 | -3.96013504730030 |

**Reactant complex 2e**





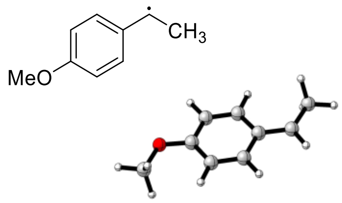
G: -1468.03864815 Eh
H: -1467.95455259 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.67556997031381 | -1.33302820296820 | -0.20272749024836 |
| C | 3.19812771203766 | -0.72969122484679 | 0.94659217523806 |
| C | 2.73604811978151 | 0.59440103383602 | 0.93966939497045 |
| C | 2.80186083467033 | 1.29302076417486 | -0.26789410992421 |
| C | 3.27462630373301 | 0.70575951146296 | -1.43725654112858 |
| C | 3.70522189798297 | -0.62295186792246 | -1.40824668221755 |
| H | 4.02518157805878 | -2.36073807863186 | -0.19510875331352 |
| H | 3.16864760767901 | -1.30843114260328 | 1.86440304621048 |
| C | 2.10281200098974 | 1.22756051948851 | 2.14325781614736 |
| H | 3.30186537261838 | 1.28837260069723 | -2.35079451782110 |
| S | -1.29093270523767 | 0.50692761565122 | 2.34808629233708 |
| Si | -1.39208880521795 | 0.09512080141588 | 0.24167939504059 |
| C | -0.90239118524109 | 1.71526577954138 | -0.64683472130603 |
| H | -0.00239798684437 | 2.03195235133076 | -0.09539750594417 |
| H | 1.01015430857766 | 1.00161241171833 | 2.11269444799095 |
| C | -3.24757857055893 | -0.33267294182035 | -0.02104356259396 |
| H | -3.78424300206277 | 0.49304822294778 | 0.46918071009310 |
| C | -0.17496897051042 | -1.29381219419893 | -0.25346707957363 |
| H | 0.77216444824127 | -0.75892884796702 | -0.42591935646556 |
| C | -3.66732129946368 | -0.35041615768862 | -1.49828517997198 |
| H | -4.75093399403767 | -0.51381880576675 | -1.57268952978351 |
| H | -3.44414817054795 | 0.59014194005845 | -2.01020349783996 |
| H | -3.17851205701498 | -1.15779337488683 | -2.05170510147996 |
| C | -3.64960478106087 | -1.64055459130319 | 0.67422233336420 |
| H | -3.40493039754481 | -1.62948786132689 | 1.74072057907692 |
| H | -4.72960759674485 | -1.81050121918226 | 0.57294949284590 |
| H | -3.14290385432877 | -2.50215532517407 | 0.22496174393168 |
| C | -1.95841797713756 | 2.81253247096030 | -0.46755153414188 |
| H | -2.22363151456449 | 2.94276001994429 | 0.58689914100877 |
| H | -1.58716141708293 | 3.77456914341888 | -0.84402326886003 |
| H | -2.87660493775846 | 2.58117965741879 | -1.01997570042718 |
| C | -0.49771042867410 | 1.55238808218535 | -2.11818741392975 |
| H | -1.33372057756086 | 1.20862330850319 | -2.73776387077538 |
| H | -0.16509928807523 | 2.51506786631371 | -2.52995697560988 |
| H | 0.32687877226465 | 0.84159420946502 | -2.23707985982777 |
| C | -0.54276546131796 | -2.00590636334118 | -1.56508569388107 |
| H | 0.27756335654220 | -2.66575021123562 | -1.87677996775214 |
| H | -1.43234854896082 | -2.63282028607701 | -1.43790978564189 |
| H | -0.73922723983228 | -1.31185543212347 | -2.38847737247493 |
| C | 0.07844951063618 | -2.32528758444431 | 0.85237224674958 |
| H | -0.83111330724253 | -2.88811294625540 | 1.09231743597226 |
| H | 0.84326899900313 | -3.04453843923511 | 0.53042207098317 |
| H | 0.41808510159355 | -1.85207611859752 | 1.77796411351396 |

| | | | |
|---|---|---|---|
| H | 2.16571221096266 | 2.31905629719494 | 2.05535040760067 |
| H | 2.46240198635132 | 2.32584775626734 | -0.30351698669190 |
| C | 2.62655627274644 | 0.77279227432900 | 3.50219008539371 |
| H | 2.14190543250670 | 1.34005934543787 | 4.30193084682917 |
| H | 2.41521075348050 | -0.28502727368605 | 3.68435591526005 |
| H | 3.70906382763110 | 0.92295903397249 | 3.57724549056226 |
| O | 4.17227552036292 | -1.30913548108345 | -2.48734256039029 |
| C | 4.17796161027296 | -0.63789451638223 | -3.74389579160332 |
| H | 4.84168077260240 | 0.23684497410171 | -3.72730740119767 |
| H | 4.55387774753039 | -1.36297208418230 | -4.46727583546483 |
| H | 3.16529167400258 | -0.32536386293609 | -4.03218794383915 |

**Radical 2e**



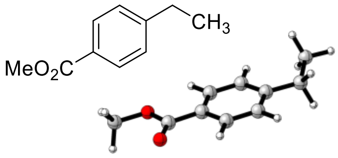
G: -424.51348316 Eh
H: -424.46730210 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.77278257757204 | -1.28809016450591 | -0.07438833446974 |
| C | 3.30862464820923 | -0.65926483540590 | 1.05925860714800 |
| C | 2.79918131271839 | 0.66935254732811 | 1.01649325001798 |
| C | 2.79609110268435 | 1.30723827050982 | -0.25028814008188 |
| C | 3.26124860249095 | 0.67977843441689 | -1.39259034848014 |
| C | 3.75502117624248 | -0.62848019824688 | -1.31196034919450 |
| H | 4.16040671905565 | -2.30163509671568 | -0.03492019218947 |
| H | 3.33339108264203 | -1.19237510060129 | 2.00477178807896 |
| C | 2.31737980528396 | 1.33524707869083 | 2.16214400145551 |
| H | 3.23634884973228 | 1.21201211904420 | -2.33673076883302 |
| H | 1.94644962175455 | 2.34922620614714 | 2.03641569871463 |
| H | 2.41436105036944 | 2.32266744197954 | -0.32241128071483 |
| C | 2.28797457194000 | 0.73144549115705 | 3.52573209696942 |
| H | 1.86379639447109 | 1.42480483880808 | 4.25558004785720 |
| H | 1.68796687687654 | -0.18921715164340 | 3.55575165911609 |
| H | 3.29383601060079 | 0.45735583301985 | 3.87511529375510 |
| O | 4.23750378888407 | -1.34435096023507 | -2.36915459041586 |
| C | 4.24317790489365 | -0.71315519333228 | -3.64450789063069 |
| H | 4.86886268180440 | 0.18970564047164 | -3.64216056796834 |
| H | 4.66536603663799 | -1.44314868377434 | -4.33720635227635 |
| H | 3.22601644513608 | -0.45236672711242 | -3.96715446785808 |

## 2i

**Substrate 2i**

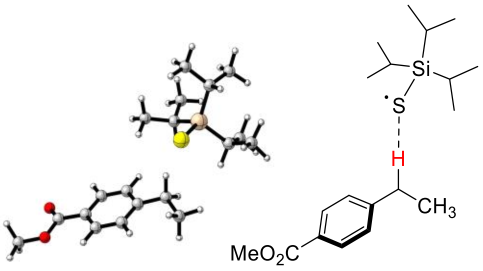


G: -538.47850054 Eh
H: -538.42857252 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.64356037615759 | -0.63437546984722 | -0.95065498930405 |
| C | 2.90658198516688 | -0.63430120774387 | 0.22840328008546 |
| C | 2.61402032973534 | 0.55747356934218 | 0.89411765368909 |
| C | 3.08515494308838 | 1.75608890363203 | 0.34211026085997 |
| C | 3.81755467177228 | 1.76663362080371 | -0.83174845879189 |
| C | 4.10471327221040 | 0.56682184722876 | -1.49126550153967 |
| H | 3.86299366131795 | -1.56984602701586 | -1.45315327277023 |
| H | 2.56249602962060 | -1.58125950188349 | 0.63142924958645 |
| C | 1.80151989076992 | 0.60478458796592 | 2.16825642439338 |
| H | 4.18326376799838 | 2.69587614586672 | -1.25713228697273 |
| H | 0.83551960627073 | 1.07828978398825 | 1.94048933077955 |
| H | 2.30428902791502 | 1.28798258789993 | 2.86551831083685 |
| H | 2.87021566222717 | 2.69460422779799 | 0.84876074872451 |
| C | 1.55830471033135 | -0.73416343280975 | 2.85732585227609 |
| H | 1.02195641528777 | -0.58277135563370 | 3.79864473683014 |
| H | 0.95390998872271 | -1.40620443733983 | 2.23969996575144 |
| H | 2.50168927261415 | -1.24110501610869 | 3.08643805827083 |
| C | 4.89670996694171 | 0.63192110485421 | -2.74272725180743 |
| O | 5.31551470252565 | 1.65574903747814 | -3.24110984795193 |
| O | 5.10809547924268 | -0.59277051987563 | -3.28239341861025 |
| C | 5.87576242488291 | -0.58999180077789 | -4.50112277331305 |
| H | 5.95246946758237 | -1.63606437722233 | -4.79949449153237 |
| H | 5.36775459564404 | -0.00398888483519 | -5.27235339688318 |
| H | 6.86792775197401 | -0.16371638576439 | -4.32725818260698 |

**Reactant complex 2i**



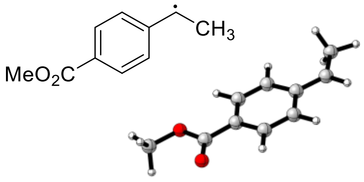
G: -1581.37614270 Eh
H: -1581.28565596 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.64715015370377 | -0.63759222851886 | -0.95099939149564 |
| C | 2.91015107353106 | -0.64017748429451 | 0.22704878180326 |

| | | | |
|---|---|---|---|
| C | 2.62266236317573 | 0.55121495782944 | 0.89725579613706 |
| C | 3.09790414228375 | 1.75141931281270 | 0.34986032185916 |
| C | 3.82820681540994 | 1.76415634030544 | -0.82463312919613 |
| C | 4.11039012010616 | 0.56517039679261 | -1.48803400301104 |
| H | 3.86429942246052 | -1.57148820389759 | -1.45731820596210 |
| H | 2.56033432294039 | -1.58605561964365 | 0.62750680779260 |
| C | 1.80552524113634 | 0.59679334270090 | 2.16099423686211 |
| H | 4.19566504230809 | 2.69348664990361 | -1.24818679028504 |
| S | -1.68025513345327 | 1.09930078760647 | 2.08816199864307 |
| Si | -1.32900249131842 | 3.02067403051047 | 2.98062219827569 |
| C | -0.60813314094661 | 2.72074564044527 | 4.72269612575909 |
| H | 0.21596699156623 | 2.01047761832812 | 4.54299348223539 |
| H | 0.82611797751230 | 1.04523612481440 | 1.90510332358945 |
| C | -3.10100686432417 | 3.76983901687091 | 3.04325645093080 |
| H | -3.71904198576515 | 2.96775806087647 | 3.47306556454092 |
| C | -0.07843367133650 | 4.02341651378769 | 1.93296677380445 |
| H | 0.89970922126544 | 3.68492751830450 | 2.31619777484367 |
| C | -3.21008469554103 | 4.98804686994401 | 3.97261659412585 |
| H | -4.24990123189583 | 5.34073829652495 | 3.99276715500047 |
| H | -2.92538291045272 | 4.75552331300784 | 5.00227839673749 |
| H | -2.59052629424986 | 5.82247060078696 | 3.63002436475630 |
| C | -3.64939130877646 | 4.09442447914312 | 1.64734975758477 |
| H | -3.59933431635740 | 3.23336914082141 | 0.97438247851696 |
| H | -4.69765597610146 | 4.41233607094788 | 1.71812619101621 |
| H | -3.09455855215924 | 4.91644485615497 | 1.18173245326221 |
| C | -1.62049393862659 | 2.02450982023224 | 5.64141855358815 |
| H | -2.04024363998596 | 1.12936300242572 | 5.17053498333076 |
| H | -1.14505831364309 | 1.72036435297835 | 6.58252756386980 |
| H | -2.45179340094275 | 2.69108214111347 | 5.89922927721026 |
| C | 0.01263134528679 | 3.95161524102214 | 5.40176444961872 |
| H | -0.72504423402484 | 4.74086674793222 | 5.58199318184893 |
| H | 0.43368402307849 | 3.67326645931808 | 6.37653424293214 |
| H | 0.82495936469337 | 4.38147911271258 | 4.80686648630122 |
| C | -0.16966644785488 | 5.53954137697296 | 2.17318395328955 |
| H | 0.66876424184428 | 6.05106166832441 | 1.68334501578407 |
| H | -1.09006078594154 | 5.94980477570847 | 1.74397614467110 |
| H | -0.14706203966401 | 5.80908634110471 | 3.23355140633152 |
| C | -0.12760874930647 | 3.72510301417509 | 0.42912255258117 |
| H | -1.10111400041973 | 3.99382522601711 | 0.00463537435322 |
| H | 0.63678093450144 | 4.30887969750168 | -0.10031288750911 |
| H | 0.03745548839225 | 2.66690682426655 | 0.20967167763252 |
| H | 2.27382493037101 | 1.31114608049540 | 2.85107442916400 |
| H | 2.88488592654492 | 2.68830697015645 | 0.86022787490336 |
| C | 1.56029205499114 | -0.72991053592450 | 2.86822441524704 |
| H | 0.99530115610394 | -0.56358461155155 | 3.79003663601489 |
| H | 0.97106732062699 | -1.41358067576170 | 2.24950620436504 |
| H | 2.50338525966412 | -1.22342529362605 | 3.12689830091219 |
| C | 4.89911891674705 | 0.63258560481987 | -2.74190450025735 |
| O | 5.31742338325826 | 1.65777258877946 | -3.23787855067565 |
| O | 5.10699570896686 | -0.59043308994691 | -3.28512273734713 |
| C | 5.86887881010689 | -0.58577927737691 | -4.50771609964399 |
| H | 5.94266855562443 | -1.63122352255611 | -4.80884217167105 |
| H | 5.35743929512287 | 0.00262307004429 | -5.27480308437623 |
| H | 6.86229192131561 | -0.16099256725447 | -4.33751712279838 |

**Radical 2i**

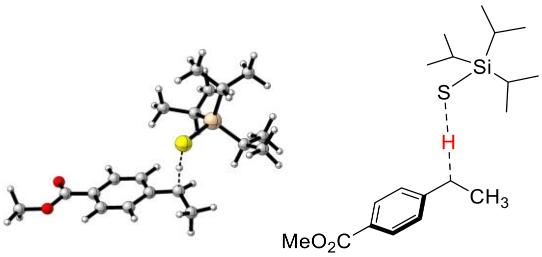


G: -537.85543685 Eh
H: -537.80467051 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.47586137314385 | -0.63637130949531 | -0.79501256943916 |
| C | 2.88286575271996 | -0.64033235594162 | 0.44954287660178 |
| C | 2.71407033104394 | 0.56434268617102 | 1.18689718238975 |
| C | 3.18214451250898 | 1.76809978833491 | 0.58825360874269 |
| C | 3.77213978537705 | 1.76573274664762 | -0.65378922550121 |
| C | 3.92888492084433 | 0.56439770077223 | -1.36666960787608 |
| H | 3.59571906465764 | -1.56495855818381 | -1.34195355126504 |
| H | 2.53980886589808 | -1.57927350304736 | 0.87293237624899 |
| C | 2.11134758318865 | 0.59265234165626 | 2.45821802818126 |
| H | 4.12721024325479 | 2.68547532933544 | -1.10775070059296 |
| H | 2.02770110591414 | 1.55918026532767 | 2.94946332429874 |
| H | 3.06519430701980 | 2.70196335432617 | 1.13218206559686 |
| C | 1.58651401531741 | -0.60827987439329 | 3.16727507384994 |
| H | 1.14676064124154 | -0.33881207991868 | 4.12969974550424 |
| H | 0.81512727813096 | -1.12328887668264 | 2.57874416847556 |
| H | 2.37755104043088 | -1.34710401145768 | 3.35668112699123 |
| C | 4.56820363641542 | 0.62488920506829 | -2.69610677424469 |
| O | 4.96864902374981 | 1.64279473256735 | -3.22457503000709 |
| O | 4.66445333923220 | -0.59678764240188 | -3.27897677728658 |
| C | 5.27982123613795 | -0.59541182986315 | -4.58051412562618 |
| H | 5.27912573126189 | -1.63671465819836 | -4.90451954819671 |
| H | 4.70664888915632 | 0.02578809893414 | -5.27481035846717 |
| H | 6.30171905335437 | -0.20985949955731 | -4.52102276837820 |

**HAT transition state 2i**



G: -1581.37189598 Eh
H: -1581.28480824 Eh
Charge: 0
Multiplicity: 2

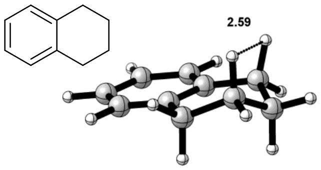
Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.33058202009007 | -0.61266418866089 | -0.86745366273698 |
| C | 2.67960929942224 | -0.60734073114941 | 0.35299501621062 |
| C | 2.56219053183593 | 0.57849034254396 | 1.10390289665966 |
| C | 3.11063885888605 | 1.76203716235647 | 0.56706240635395 |
| C | 3.75819330306012 | 1.75880609748281 | -0.65138297196713 |

| | | | |
|---|---|---|---|
| C | 3.87803048579162 | 0.56953639979013 | -1.38204301268982 |
| H | 3.41949357454689 | -1.53405423865653 | -1.43180485634428 |
| H | 2.25960633527274 | -1.53199385278627 | 0.73514428758184 |
| C | 1.86490583087234 | 0.62554139042446 | 2.37642822670823 |
| H | 4.18637117486312 | 2.66731473584865 | -1.06259624610557 |
| S | -0.97937855214366 | 1.14261608480206 | 1.80693338412723 |
| Si | -1.05107578971810 | 3.04463998342291 | 2.83800213042035 |
| C | -0.47417731810723 | 2.71228702060222 | 4.62925910525608 |
| H | 0.43094016034107 | 2.09713951450589 | 4.49606054697044 |
| H | 0.55857787580850 | 0.93015063245172 | 2.02909850079497 |
| C | -2.89529452934601 | 3.52309198454433 | 2.75323830571473 |
| H | -3.41328769904745 | 2.61566798128517 | 3.10211416685131 |
| C | 0.14710680347159 | 4.28304319401833 | 2.00705721695748 |
| H | 1.12903115941199 | 4.04238236521517 | 2.45223143600284 |
| C | -3.30045199136134 | 4.67327486576672 | 3.68812331969696 |
| H | -4.38607881325171 | 4.83056297725469 | 3.64189944110467 |
| H | -3.04404489042696 | 4.47337895750300 | 4.73276770295350 |
| H | -2.82434526825609 | 5.61643444775949 | 3.40164359072825 |
| C | -3.36490522851828 | 3.80359578426256 | 1.31783378649560 |
| H | -3.10216782724776 | 2.99082816807860 | 0.63320143137742 |
| H | -4.45447692501618 | 3.93322582201703 | 1.28816372920672 |
| H | -2.91875460839475 | 4.72601243268079 | 0.92853013661206 |
| C | -1.48841204313414 | 1.85817917160484 | 5.40240933982077 |
| H | -1.77232026917924 | 0.96298997688514 | 4.83885785924412 |
| H | -1.07247260285647 | 1.53675070211072 | 6.36604998432001 |
| H | -2.40273114849540 | 2.42293415988543 | 5.61799232696948 |
| C | -0.06050878297066 | 3.95101095472260 | 5.43661364393229 |
| H | -0.89903133283793 | 4.64034941604709 | 5.58597540697145 |
| H | 0.29652059453920 | 3.65650796240752 | 6.43223589198913 |
| H | 0.74680281959774 | 4.50818648227306 | 4.95040944779350 |
| C | -0.16713543523405 | 5.75093977554944 | 2.34429056945973 |
| H | 0.63692299703605 | 6.40726530859338 | 1.98716120825530 |
| H | -1.08833954720005 | 6.07123813775902 | 1.84530098135419 |
| H | -0.29034856315116 | 5.93027661224557 | 3.41670808607767 |
| C | 0.27105029343169 | 4.11531218339553 | 0.48616766442988 |
| H | -0.67333887166278 | 4.35647350649851 | -0.01416756819730 |
| H | 1.03723446300774 | 4.79348484064064 | 0.08687499667517 |
| H | 0.53359372149683 | 3.09262478826388 | 0.20340660939340 |
| H | 2.07908425076692 | 1.53056697252778 | 2.95176524203560 |
| H | 3.01813059357461 | 2.68812193695369 | 1.12905810536210 |
| C | 1.66649021222616 | -0.61567250345669 | 3.20619533300750 |
| H | 1.08057785591909 | -0.38735380068357 | 4.10042771658477 |
| H | 1.13175782370842 | -1.39542140902933 | 2.65614145413199 |
| H | 2.63493940208620 | -1.02625147044357 | 3.52085008390728 |
| C | 4.59130227304881 | 0.62090341696270 | -2.68028362443372 |
| O | 5.07780178812972 | 1.62493227306568 | -3.15712166312300 |
| O | 4.64482214245067 | -0.58922519461209 | -3.28423873570652 |
| C | 5.32787636205427 | -0.60116805119535 | -4.55310427785959 |
| H | 5.28316761516687 | -1.63458427275280 | -4.89786513694964 |
| H | 4.82829792964331 | 0.06549237876528 | -5.26163497393790 |
| H | 6.36554648599877 | -0.27790758834829 | -4.43120198644890 |

## 3b

### Reactant complex 3b

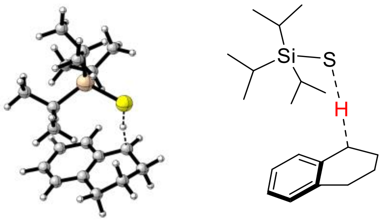


G: -388.03635104 Eh
H: -387.99522205 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.46612038868204 | -1.37863269194440 | -0.09015380324987 |
| C | 3.11072997670188 | -0.62322235206071 | 1.03185335939811 |
| C | 2.72471841970933 | 0.71292315863507 | 0.85848539962412 |
| C | 2.70683598810431 | 1.25267498498659 | -0.43156084880065 |
| C | 3.06131689452929 | 0.49452186830877 | -1.53841310476308 |
| C | 3.44465167105927 | -0.83358301772992 | -1.36620525175742 |
| H | 3.76421960468461 | -2.41627393629187 | 0.04802037199251 |
| C | 2.30488073885078 | 1.57256550224837 | 2.03086783162427 |
| H | 3.04105055135602 | 0.93600648084817 | -2.53070288127013 |
| H | 3.72387439618255 | -1.44033902414076 | -2.22285397568041 |
| H | 1.20734551180410 | 1.65445852670788 | 2.02979014184376 |
| H | 2.68540511579389 | 2.59171217036398 | 1.88863810114024 |
| H | 2.40820123556494 | 2.29108180419774 | -0.56271234635195 |
| C | 2.75958821694849 | 1.01030596587942 | 3.37611254858066 |
| H | 3.84746549918575 | 1.12805748600914 | 3.47948579639557 |
| H | 2.29656072502534 | 1.57492771489962 | 4.19383513173910 |
| C | 3.17684918453705 | -1.25594090207302 | 2.40486465069843 |
| H | 4.23266011958189 | -1.32223065391516 | 2.70852992547846 |
| H | 2.81305334461547 | -2.28933926254333 | 2.34666077471781 |
| C | 2.40417977023085 | -0.47247093600152 | 3.46446378303547 |
| H | 2.62803353488444 | -0.87124162657179 | 4.46083192078109 |
| H | 1.32396011196771 | -0.59563525981228 | 3.30360847482390 |

### HAT transition state 3b



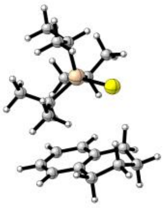
G: -1430.93450164 Eh
H: -1430.85677123 Eh
Charge: 0
Multiplicity: 2

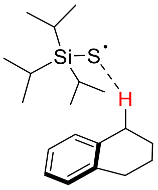
Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.75553637578805 | -1.33146418309637 | -0.01542339666250 |
| C | 3.23296118078829 | -0.68413396487279 | 1.10077394188525 |
| C | 2.65889778348071 | 0.59941740759955 | 0.94025754417891 |
| C | 2.67757947501418 | 1.20200657025054 | -0.33405225273648 |
| C | 3.21279225372093 | 0.54723754055796 | -1.42844257546451 |

|  |  |  |  |
|---|---|---|---|
| C | 3.74117237672243 | -0.73599997841915 | -1.27326231400020 |
| H | 4.18727873617334 | -2.32291169099107 | 0.10468881175218 |
| C | 2.01818173786296 | 1.26498996693197 | 2.05942268257075 |
| H | 3.21721772080431 | 1.02756748797525 | -2.40249309064166 |
| H | 4.14948830255145 | -1.26568944474235 | -2.12894913587329 |
| S | -0.85420856383440 | 0.54963184582071 | 2.17360120842469 |
| Si | -1.29190436187332 | 0.12880332853654 | 0.09465178507101 |
| C | -0.95103134004733 | 1.75657482064561 | -0.84601037263725 |
| H | 0.00191779369229 | 2.09291261351923 | -0.40895215282201 |
| H | 0.66867813571079 | 0.91266144858949 | 1.97221671917966 |
| C | -3.15529087498528 | -0.28962430201906 | 0.11981186766671 |
| H | -3.60072634762864 | 0.53725273273676 | 0.69508072951676 |
| C | -0.17860925902215 | -1.27282827781269 | -0.57551037062664 |
| H | 0.77147585267053 | -0.77183048657490 | -0.81879744784353 |
| C | -3.81927045870443 | -0.29834907062855 | -1.26663871198260 |
| H | -4.90411920883283 | -0.43411648828856 | -1.16407969070928 |
| H | -3.65752822924372 | 0.63357428409008 | -1.81661140590364 |
| H | -3.44789230433561 | -1.11935107487434 | -1.88810075556984 |
| C | -3.46122623380545 | -1.59576555220936 | 0.86699033101716 |
| H | -3.00715611629590 | -1.61499638268220 | 1.86295231025623 |
| H | -4.54468029794547 | -1.72864123704235 | 0.98454035101638 |
| H | -3.08726761353294 | -2.46302912277659 | 0.31076789339682 |
| C | -1.99553792231577 | 2.83242409025261 | -0.51835772844414 |
| H | -2.12002048778546 | 2.95091875297676 | 0.56323936818945 |
| H | -1.69617796137982 | 3.80375332951116 | -0.93330775783691 |
| H | -2.97467048831066 | 2.58638234303167 | -0.94452780536407 |
| C | -0.73181995081208 | 1.62627587680369 | -2.35880991112787 |
| H | -1.62881090991814 | 1.26231574668501 | -2.87312082737082 |
| H | -0.48361190421691 | 2.60295374945561 | -2.79586802441657 |
| H | 0.09039401659029 | 0.94133168404199 | -2.59267026156152 |
| C | -0.71395720237581 | -1.90657719484319 | -1.87099622346657 |
| H | 0.04368613775962 | -2.56885779848765 | -2.31018949339914 |
| H | -1.59931708790187 | -2.51980161741168 | -1.66888894272416 |
| H | -0.98760496166030 | -1.16815726701285 | -2.63081675818949 |
| C | 0.13297426498968 | -2.37511820867588 | 0.44519611378450 |
| H | -0.76903460377738 | -2.93321307595729 | 0.72037041914328 |
| H | 0.85236687229818 | -3.09018572913510 | 0.02380060709662 |
| H | 0.55623140194516 | -1.96605100608390 | 1.36541438214497 |
| H | 1.88502688967735 | 2.34395096639085 | 1.94556807212319 |
| H | 2.26154725817770 | 2.19979002027044 | -0.44839910907670 |
| C | 2.33946693952240 | 0.77718266741163 | 3.44988187436315 |
| H | 3.32294301682067 | 1.17718832876378 | 3.74593993006444 |
| H | 1.60835381089986 | 1.17338243790016 | 4.16429102992470 |
| C | 3.34487323317998 | -1.31471587044006 | 2.46827040075035 |
| H | 4.37279178981168 | -1.14950804854701 | 2.82712552439055 |
| H | 3.22565101510138 | -2.40140316120391 | 2.37971020857147 |
| C | 2.35997043144414 | -0.75032903866070 | 3.49200386129871 |
| H | 2.62512146871510 | -1.10071233533536 | 4.49568575602999 |
| H | 1.34741688862820 | -1.11454875192414 | 3.28138784264352 |

**Reactant complex 3b**





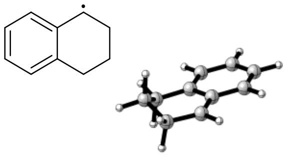
G: -1430.93862421 Eh
H: -1430.85893141 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.45833802078900 | -1.38049711366299 | -0.09112712353472 |
| C | 3.10786688963754 | -0.62382201307592 | 1.03125575175992 |
| C | 2.72667962696791 | 0.71496807733639 | 0.85860847646108 |
| C | 2.72219070682307 | 1.25755663349344 | -0.43113230074465 |
| C | 3.07191317275302 | 0.49749103134201 | -1.53902152644862 |
| C | 3.43888324299493 | -0.83567426235731 | -1.36812004032243 |
| H | 3.74833215132598 | -2.42035723477858 | 0.04710624226203 |
| C | 2.29704002466331 | 1.56741812663683 | 2.02931134121072 |
| H | 3.06123351857598 | 0.94199005315484 | -2.53022896793588 |
| H | 3.71189860122055 | -1.44450579558528 | -2.22533842444474 |
| S | -1.30018399276747 | 0.23545154623014 | 2.32727783036712 |
| Si | -1.42803128411403 | -0.00192661276585 | 0.19513080372264 |
| C | -0.97493050679758 | 1.67986386814704 | -0.58338780111835 |
| H | -0.05255790681957 | 1.95011955952736 | -0.04439394310686 |
| H | 1.19486915787445 | 1.62466718111102 | 2.03681853680167 |
| C | -3.29153091586776 | -0.43136877499416 | -0.04703497152643 |
| H | -3.82998949827726 | 0.33641907891069 | 0.52728353559111 |
| C | -0.21435554298947 | -1.34930840709975 | -0.40289406693123 |
| H | 0.73250311525447 | -0.79777634793211 | -0.51239743394248 |
| C | -3.73329468123979 | -0.31504457024565 | -1.51361622027381 |
| H | -4.81318229810768 | -0.50166379483102 | -1.58721669207743 |
| H | -3.54440716247725 | 0.67770183583428 | -1.93079068526877 |
| H | -3.23153646854899 | -1.05038014957345 | -2.14984800129615 |
| C | -3.65740358288268 | -1.80595964874942 | 0.52638737473478 |
| H | -3.37462182753689 | -1.90163440350862 | 1.57874381889090 |
| H | -4.73931669301618 | -1.97420950780823 | 0.44534045474651 |
| H | -3.16297372908444 | -2.61168830484450 | -0.02747225485162 |
| C | -2.02000905419244 | 2.75822970726713 | -0.27130555511774 |
| H | -2.23959811140665 | 2.80501010916819 | 0.80079616651563 |
| H | -1.66201960567245 | 3.74733943343823 | -0.58450584928735 |
| H | -2.96167820162827 | 2.57200059025717 | -0.80064815161640 |
| C | -0.62570651815513 | 1.64313287845291 | -2.07768439863708 |
| H | -1.48488131181939 | 1.35705848019222 | -2.69474220611832 |
| H | -0.30178358398071 | 2.63669659425084 | -2.41521108653431 |
| H | 0.19007945536767 | 0.94383194965397 | -2.28590471787391 |
| C | -0.57341603551732 | -1.93152712622270 | -1.77923140975365 |
| H | 0.26014820564391 | -2.54058949758046 | -2.15269957408896 |
| H | -1.45022063750379 | -2.58588867895790 | -1.71494358389869 |
| H | -0.78182333130322 | -1.16422554195873 | -2.53110100769690 |
| C | 0.02403046225041 | -2.48283561398278 | 0.60057724895527 |
| H | -0.88626549685163 | -3.06939957145247 | 0.76945689028328 |
| H | 0.79508271055673 | -3.16526943764323 | 0.21865011252687 |
| H | 0.35129605182521 | -2.10498141279118 | 1.57254812157241 |
| H | 2.65121384146251 | 2.59568619974038 | 1.88434388890525 |
| H | 2.43769048518274 | 2.29991755108236 | -0.56294015357223 |

| | | | |
|---|---|---|---|
| C | 2.75900978907745 | 1.01345479598618 | 3.37463306043929 |
| H | 3.84617253475895 | 1.14290704318944 | 3.47602446952966 |
| H | 2.28902538623954 | 1.57574782549435 | 4.18949128512442 |
| C | 3.17557115953538 | -1.25650047404676 | 2.40348785229392 |
| H | 4.23366986610426 | -1.32943749994959 | 2.69786816274490 |
| H | 2.80521630509607 | -2.28759466715809 | 2.34460222072653 |
| C | 2.41456719667714 | -0.47072379562069 | 3.46912542186863 |
| H | 2.64930138724333 | -0.86659284492464 | 4.46403474291828 |
| H | 1.33101830654350 | -0.59577421134235 | 3.32464351513278 |

**Radical 3b**



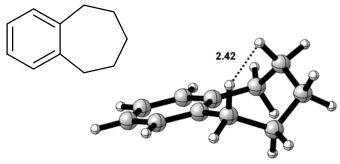
G: -387.41303038 Eh
H: -387.37131685 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.73776726214516 | -1.35389680071434 | -0.01792775397365 |
| C | 3.32859014152122 | -0.66470744573149 | 1.11229245434055 |
| C | 2.79889739637665 | 0.65598728971963 | 0.97668949146887 |
| C | 2.72962461396546 | 1.22089414320402 | -0.32536334448769 |
| C | 3.15194595074574 | 0.51498417828961 | -1.43368854467268 |
| C | 3.65704697015360 | -0.78137395639731 | -1.28934836252848 |
| H | 4.13347899312150 | -2.36160638601813 | 0.09255696252063 |
| C | 2.36096851607928 | 1.37126921850152 | 2.10704248409906 |
| H | 3.08776349457178 | 0.96570141775612 | -2.42008499135429 |
| H | 3.98345225219129 | -1.34184435434535 | -2.16006381232132 |
| H | 2.01973671019331 | 2.39585502896235 | 1.97774269472315 |
| H | 2.32989010229343 | 2.22611677778959 | -0.43554050695318 |
| C | 2.35190005080925 | 0.77178955886286 | 3.47427723544730 |
| H | 3.24287325052697 | 1.10592531609818 | 4.03460146635061 |
| H | 1.49102103462496 | 1.14509398341066 | 4.04402995043686 |
| C | 3.45181052355986 | -1.25766005253188 | 2.49154634157489 |
| H | 4.42525647622756 | -0.97027532438614 | 2.91975146016273 |
| H | 3.44959941411517 | -2.35208959478191 | 2.42929853748428 |
| C | 2.34037276972615 | -0.75836560654421 | 3.41590830466436 |
| H | 2.45859063028789 | -1.17995711152066 | 4.42049747028930 |
| H | 1.37068079676373 | -1.09693876962311 | 3.02823408272867 |

## 3c

**Substrate 3c**

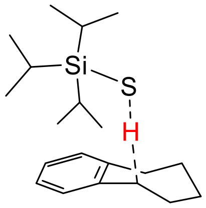


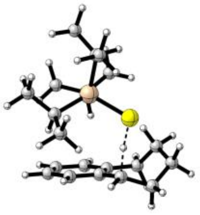
G: -427.30124139 Eh
H: -427.25775319 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | -2.22159368938972 | -2.89555574330983 | -0.53817445387430 |
| C | -1.17745040069888 | -2.91913646801800 | 0.37875028777921 |
| C | -0.77173957152894 | -1.73297904608154 | 0.97454835166533 |
| C | -1.38313457576201 | -0.50609179240142 | 0.68897875362098 |
| C | -2.44395870683117 | -0.48293391427358 | -0.23692071733309 |
| C | -2.83980648872174 | -1.68769811411401 | -0.83044113561266 |
| H | -2.55664397084203 | -3.80988422187195 | -1.01941377325105 |
| H | -0.67824366471177 | -3.85170868632236 | 0.62559467606036 |
| H | 0.05123913970415 | -1.74967099366845 | 1.68596622398346 |
| H | -3.66303989839233 | -1.67028325744508 | -1.54156601805333 |
| C | -3.20231555974076 | 0.76901027872517 | -0.63771932562020 |
| H | -4.18271261128426 | 0.45008054337056 | -1.00929391267282 |
| H | -2.70439661368105 | 1.24674134612472 | -1.49540877643573 |
| C | -0.84324814485303 | 0.71969800741770 | 1.40327823124663 |
| H | -1.39653646294390 | 0.87874566184084 | 2.34148060029798 |
| H | 0.18519730948535 | 0.49156411374560 | 1.70533264683452 |
| C | -3.39614636315743 | 1.80430434279919 | 0.47565022813049 |
| H | -4.29398125077677 | 2.39917886678465 | 0.26858565544135 |
| H | -3.59244935298894 | 1.27516945224299 | 1.41718452877565 |
| C | -0.85362281938106 | 2.01512722206837 | 0.58426682880503 |
| H | -0.06910734587421 | 2.68653335936404 | 0.95397967993790 |
| H | -0.58588748215863 | 1.77703446232405 | -0.45321424206686 |
| C | -2.19878802140254 | 2.74590736793708 | 0.63297375504183 |
| H | -2.22380429059995 | 3.50497369677474 | -0.16021638274696 |
| H | -2.28849295346836 | 3.28628899598651 | 1.58472582004627 |

**HAT transition state 3c**



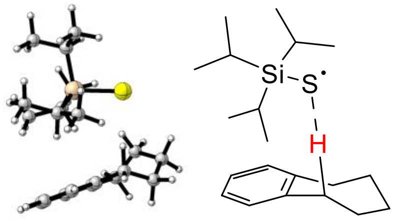


G: -1470.19873587
H: -1470.11898801
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | -1.66250201940223 | -3.09597931781947 | -0.69956614146967 |
| C | -0.82155372800592 | -2.97123773855372 | 0.40431545422937 |
| C | -0.45753087959424 | -1.71050508487708 | 0.83885849261083 |
| C | -0.91570532729188 | -0.53633894366059 | 0.20196583824628 |
| C | -1.76615966166916 | -0.66859700543100 | -0.92907439746423 |
| C | -2.11601650455405 | -1.95195865482054 | -1.34879059141502 |
| H | -1.96627739283007 | -4.07707449094925 | -1.05238945698826 |
| H | -0.45315239649168 | -3.85339277260996 | 0.91986549716878 |
| H | 0.19915363431578 | -1.60562589873032 | 1.69937675787215 |
| H | -2.77389316880004 | -2.05644042562629 | -2.20835618246738 |
| C | -2.33513151898901 | 0.51280475770953 | -1.68071878167281 |
| H | -3.13163039671350 | 0.13678146183890 | -2.33182903021283 |
| H | -1.57390136228539 | 0.93215432152937 | -2.35564142108553 |
| C | -0.51561416180061 | 0.73141543413556 | 0.79344788987606 |
| H | -1.45800569322262 | 0.99492234967069 | 1.81413039823985 |
| H | 0.32535418302510 | 0.61654065407026 | 1.48222001057061 |
| C | -2.88942508898143 | 1.62259731292507 | -0.77539605864232 |
| H | -3.70124316960119 | 2.14606493281450 | -1.29420943835725 |
| H | -3.33890727632938 | 1.16311396684426 | 0.11300220974129 |
| C | -0.47521397198472 | 2.01816977869530 | 0.00114063255461 |
| H | 0.12224495160684 | 2.75151179771136 | 0.55363160487908 |
| H | 0.07844288834924 | 1.81236953568718 | -0.92773269119225 |
| C | -1.83559412876698 | 2.64331607150839 | -0.34452215799007 |
| H | -1.67682585606971 | 3.37752745881908 | -1.14490586100596 |
| H | -2.21223599476991 | 3.19405744767882 | 0.52459211740930 |
| S | -2.34352554703915 | 1.50202021914826 | 3.00273933328354 |
| Si | -3.19695355082387 | -0.39040439976789 | 3.62814929387454 |
| C | -4.08701014474823 | -1.14798424405130 | 2.12034406149388 |
| C | -4.42617510246895 | 0.16962440521599 | 4.97993032089443 |
| C | -1.84884292857108 | -1.60565259490289 | 4.22847902552932 |
| H | -3.35010290627409 | -1.04552231345866 | 1.30814545380917 |
| C | -5.33064802178849 | -0.34125127748201 | 1.72327741410089 |
| C | -4.40933714117848 | -2.64561731717270 | 2.22781670295544 |
| H | -4.99861371561039 | 0.97027024022962 | 4.48537924496328 |
| C | -5.43008149225951 | -0.90623070445233 | 5.42240551909793 |
| C | -3.72509560543643 | 0.78615745468463 | 6.19968978143181 |
| H | -1.54488647168284 | -2.12960464445076 | 3.30839290625104 |
| C | -2.38614526450123 | -2.66599652284890 | 5.20400838744313 |
| C | -0.60250572347075 | -0.93181191086338 | 4.81525705887380 |
| H | -5.11615824901220 | 0.73127553758331 | 1.66159362773685 |
| H | -5.71111022841441 | -0.66752999891490 | 0.74621876007322 |
| H | -6.14120777958233 | -0.47574052696325 | 2.44915594573235 |
| H | -5.12858727754176 | -2.85746520085732 | 3.02769874461467 |
| H | -4.85143966714426 | -3.00501586812207 | 1.28905369387912 |
| H | -3.51171580689534 | -3.24495287298143 | 2.41309614115765 |
| H | -6.18051463113615 | -0.46777015454421 | 6.09355890724902 |
| H | -5.96626851717553 | -1.35118194214677 | 4.57884040735483 |
| H | -4.94092088514071 | -1.71705356311253 | 5.97117139718936 |
| H | -3.03779712702657 | 1.58905804686481 | 5.91473053846358 |
| H | -4.46181601910100 | 1.20295636803389 | 6.89893795688320 |
| H | -3.14833739382478 | 0.03225855692947 | 6.74805057439871 |
| H | -1.62579591220284 | -3.43594934425647 | 5.39024207962886 |
| H | -2.63433712823770 | -2.21819570478559 | 6.17255814705503 |
| H | -3.28304351197423 | -3.16998899775688 | 4.83025852857579 |
| H | -0.84260752081623 | -0.37614292255763 | 5.72897978856478 |
| H | 0.15581758417098 | -1.68308192147144 | 5.07461857270781 |
| H | -0.15896987223468 | -0.21498042932875 | 4.11778600129824 |

**Reactant Complex 3c**



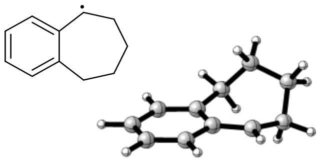
G: -1470.20273502
H: -1470.12051340
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | -1.70590084565954 | -3.20075589185695 | -0.69546112277351 |
| C | -0.77749836376262 | -3.08895299190985 | 0.33328956497307 |
| C | -0.38818733055409 | -1.82674400954021 | 0.75848400693230 |
| C | -0.90411722565503 | -0.65467880045069 | 0.18981426278139 |
| C | -1.83437328051280 | -0.76804289236441 | -0.86432384919482 |
| C | -2.21727037284002 | -2.04900835452922 | -1.27874784445858 |
| H | -2.03141236161450 | -4.17724396213816 | -1.04244833272902 |
| H | -0.35737709564662 | -3.97568441943202 | 0.79928896855245 |
| H | 0.34364084250496 | -1.73567237962793 | 1.55861566656960 |
| H | -2.94347768867724 | -2.13900972033330 | -2.08366535116680 |
| C | -2.45604752406477 | 0.41318416681697 | -1.58437255074075 |
| H | -3.37942918988993 | 0.05573601647145 | -2.05422364485118 |
| H | -1.80306435943555 | 0.71929989379579 | -2.41614186430687 |
| C | -0.44285175158395 | 0.65826224734359 | 0.77420441573398 |
| H | -1.16419337676048 | 0.97899559707815 | 1.55689913040149 |
| H | 0.49545763026182 | 0.47834409437500 | 1.31084926101496 |
| C | -2.77227532436540 | 1.63341131460940 | -0.71202103310953 |
| H | -3.58837133500299 | 2.20329822964581 | -1.17249592315605 |
| H | -3.15637545767942 | 1.29663664468845 | 0.25898664595751 |
| C | -0.26927391157906 | 1.81187393898916 | -0.21860332627271 |
| H | 0.47107335452404 | 2.51846099647208 | 0.17442410855695 |
| H | 0.15364357280332 | 1.41158102351681 | -1.14965184858552 |
| C | -1.57345781785842 | 2.56294067391559 | -0.50400067908269 |
| H | -1.43482072288824 | 3.19357388017703 | -1.39215057181328 |
| H | -1.79385356887772 | 3.23797326881109 | 0.33311592267532 |
| S | -2.68182635103547 | 1.77963954118106 | 3.32002697467540 |
| Si | -3.33239463252215 | -0.22765399712595 | 3.74466615056831 |
| C | -4.13849213469114 | -0.91210309993842 | 2.16030167614538 |
| C | -4.60455726354624 | 0.06116618333498 | 5.15878051867052 |
| C | -1.84415308309907 | -1.32984847933205 | 4.21577150017948 |
| H | -3.38961626821842 | -0.68120643461496 | 1.38606827667469 |
| C | -5.42480698904572 | -0.16142265793465 | 1.79499709319528 |
| C | -4.34140589850395 | -2.43389142228575 | 2.12383658770378 |
| H | -5.25198866063315 | 0.86769323060050 | 4.78394716224544 |
| C | -5.49299492851482 | -1.16351668134964 | 5.42447874368960 |
| C | -3.94201299754222 | 0.54694968041500 | 6.45475744263440 |
| H | -1.49090905432705 | -1.68437792299999 | 3.23384188900015 |
| C | -2.23781958473444 | -2.56678547991279 | 5.03933633692757 |
| C | -0.68493578574127 | -0.58781488726883 | 4.89105938109157 |
| H | -5.27644839083677 | 0.92402524426117 | 1.80794908151708 |
| H | -5.76278817016468 | -0.44289084644653 | 0.78906477330920 |
| H | -6.24006020405229 | -0.39707790977420 | 2.48946323775962 |
| H | -5.03878189967849 | -2.77795979593132 | 2.89610615843279 |
| H | -4.75461453835657 | -2.73251184395708 | 1.15166829458183 |

| | | | |
|---|---|---|---|
| H | -3.39673343616386 | -2.97258305716665 | 2.24865450109685 |
| H | -6.23963694070661 | -0.91677261378513 | 6.19116819270162 |
| H | -6.03532960142937 | -1.48902906167881 | 4.53236315677920 |
| H | -4.91356499158743 | -2.01419272240916 | 5.79606898205991 |
| H | -3.32658711543532 | 1.43686861485068 | 6.29292713735439 |
| H | -4.70620412978035 | 0.79091806270089 | 7.20431686124478 |
| H | -3.30062322116054 | -0.22857095978464 | 6.88813082569790 |
| H | -1.38311188316717 | -3.25017760957491 | 5.12602987789893 |
| H | -2.53009553721955 | -2.28675507083693 | 6.05742476368158 |
| H | -3.06541785084148 | -3.12891589588697 | 4.59577847150659 |
| H | -0.98529814508490 | -0.17107886624194 | 5.85920577180033 |
| H | 0.15202900001525 | -1.27521264879737 | 5.07299969629603 |
| H | -0.32315339046857 | 0.24542694030559 | 4.28203785864476 |

**Radical 3c**



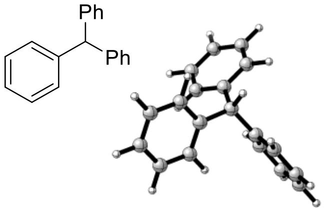
G: -426.67523491 Eh
H: -426.63105786 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | -2.31448106877636 | -2.89486648528740 | -0.42264882514651 |
| C | -1.33437476976072 | -2.90259521770710 | 0.57197540868736 |
| C | -0.87287799506612 | -1.70928159874444 | 1.08669585861565 |
| C | -1.35447761265852 | -0.45104708447108 | 0.62732946731664 |
| C | -2.38823273003035 | -0.45649349946384 | -0.36520918489628 |
| C | -2.83150760911311 | -1.67655728991224 | -0.86224008340044 |
| H | -2.68773573492403 | -3.82624907238503 | -0.83721942519829 |
| H | -0.93445269746893 | -3.84331103155517 | 0.93964278634251 |
| H | -0.10213481143366 | -1.71248112650883 | 1.85356272502793 |
| H | -3.62329651822211 | -1.67677477770908 | -1.60835461374095 |
| C | -3.08516513787168 | 0.80907809261076 | -0.81384404904695 |
| H | -3.98835075270842 | 0.51448659218645 | -1.35915528492413 |
| H | -2.47083923522795 | 1.36555299582695 | -1.53588104535121 |
| C | -0.77370896954680 | 0.72008769157825 | 1.16723684943684 |
| H | -0.05822059681441 | 0.57699090662271 | 1.97417418399866 |
| C | -3.46997635722586 | 1.72899306496086 | 0.35863486294042 |
| H | -4.36570658372867 | 2.30424121332011 | 0.09593944687958 |
| H | -3.74603407679665 | 1.09622278404149 | 1.21074725732177 |
| C | -0.94260289136690 | 2.10062102339533 | 0.62308532369387 |
| H | -0.22198375074819 | 2.77152962718034 | 1.10294375455509 |
| H | -0.67994673627442 | 2.09409014770549 | -0.44519051342306 |
| C | -2.35494491343737 | 2.69891091062872 | 0.77020540448946 |
| H | -2.40199134267956 | 3.60600916896278 | 0.15304090122376 |
| H | -2.51281818811917 | 3.01569432472401 | 1.80812367459826 |

## 6b

**Substrate 6b**

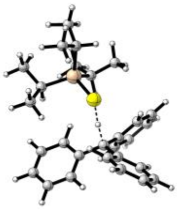


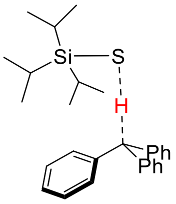
G: -733.23136565 Eh
H: -733.17423835 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 4.85872331486194 | -0.92430842774806 | 0.44287999715938 |
| C | 4.12652370210167 | -0.18131617527540 | 1.36636283375515 |
| C | 2.87536202503477 | 0.33327479815306 | 1.02891058397284 |
| C | 2.36964326267232 | 0.08589186825793 | -0.25025417038925 |
| C | 3.09656668367833 | -0.65779933814838 | -1.17150474968819 |
| C | 4.34736079074540 | -1.16575335049210 | -0.82724726889082 |
| H | 5.83162955770621 | -1.31905590427565 | 0.72200308712836 |
| H | 4.52779630035841 | -0.00371753102468 | 2.36013338235927 |
| C | 2.06218752767907 | 1.19197924538680 | 1.98812196858779 |
| H | 2.68617799444215 | -0.84383360352224 | -2.16007411058421 |
| H | 4.91645220998912 | -1.74968585327622 | -1.54481802725617 |
| H | 1.01271892318405 | 0.88458854205660 | 1.86627223897952 |
| H | 1.39791014702667 | 0.49128433971433 | -0.52470751801152 |
| C | 2.41985469324023 | 0.93190205263438 | 3.44507937298195 |
| C | 1.94984899630672 | -0.23203862091721 | 4.05933679747893 |
| C | 3.23657560175094 | 1.79321942227862 | 4.17655147911617 |
| C | 2.28744192269712 | -0.52936095122490 | 5.37388131418969 |
| H | 1.31896992075104 | -0.91435844989574 | 3.49329219824809 |
| C | 3.57959080108368 | 1.49510442548561 | 5.49337997436014 |
| H | 3.60118290449761 | 2.70640592192788 | 3.71436111321088 |
| C | 3.10667850424123 | 0.33502630939482 | 6.09663736709294 |
| H | 1.90922544966416 | -1.43636976598919 | 5.83708818729541 |
| H | 4.21618480343666 | 2.17723714196939 | 6.04992202583107 |
| H | 3.37017213223836 | 0.10618220430676 | 7.12519048596387 |
| C | 2.11969918512016 | 2.67190602345951 | 1.63433696970000 |
| C | 1.09818454560214 | 3.51314782572439 | 2.08468927909818 |
| C | 3.17551370432664 | 3.22710731372613 | 0.91294936395065 |
| C | 1.13021335355151 | 4.87668887822695 | 1.82122849274305 |
| H | 0.27452384491020 | 3.09011102953153 | 2.65629027858427 |
| C | 3.21170125874772 | 4.59525715669596 | 0.65107687869545 |
| H | 3.97213355891740 | 2.58517325768904 | 0.54719586906906 |
| C | 2.19101096993962 | 5.42403233200298 | 1.10260820859300 |
| H | 0.32513799989108 | 5.51447088574864 | 2.17527796067495 |
| H | 4.04145246650632 | 5.01169562976336 | 0.08681179005681 |
| H | 2.21757994309931 | 6.48953036765508 | 0.89342934594325 |

**HAT transition state 6b**





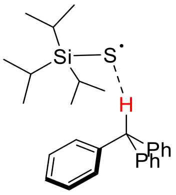
G: -1776.13023535 Eh
H: -1776.03842838 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 4.70492451728519 | -1.43946547290042 | 0.73837356482507 |
| C | 4.01886179906325 | -0.60156842924899 | 1.61070746448473 |
| C | 2.98214017749356 | 0.21829884640446 | 1.14602764805881 |
| C | 2.65813501906328 | 0.16823930062670 | -0.21834973069536 |
| C | 3.33709686347036 | -0.67235628788822 | -1.08556308205961 |
| C | 4.36561346541034 | -1.48437488614015 | -0.60994138245875 |
| H | 5.51236824065927 | -2.05962028272756 | 1.11704097499565 |
| H | 4.29841548623329 | -0.56911572174720 | 2.65864304948721 |
| C | 2.21154602814253 | 1.12721974571012 | 2.04500790489034 |
| H | 3.05901495326878 | -0.70277151973245 | -2.13538370487568 |
| H | 4.89775039731912 | -2.14602934173658 | -1.28711069188056 |
| S | -0.57267663209503 | 0.07757662011184 | 2.04976915422228 |
| Si | -1.36140174195963 | 0.16883248389719 | 0.04277151720978 |
| C | -1.06148454313982 | 1.93517809291409 | -0.62393858966505 |
| H | -0.01640680475936 | 2.15941610833463 | -0.35439965108285 |
| H | 0.99225446113610 | 0.66721155518007 | 1.91830260710851 |
| C | -3.22636646878682 | -0.15190027696837 | 0.34795129033893 |
| H | -3.48046424757108 | 0.57447605155296 | 1.13532756747559 |
| C | -0.53343214456776 | -1.11431847110184 | -1.11496100507182 |
| H | 0.33010234654563 | -0.58408335215899 | -1.54499795604634 |
| C | -4.13739777083239 | 0.13684963245907 | -0.85539623149167 |
| H | -5.19049632427665 | 0.05535781947931 | -0.55456785299393 |
| H | -3.99129069810626 | 1.14212410427692 | -1.26153182929781 |
| H | -3.97729710411600 | -0.57755714143088 | -1.66847967632352 |
| C | -3.50274405480734 | -1.55604847123179 | 0.90531518322360 |
| H | -2.90755457712325 | -1.76639759718266 | 1.79953799530878 |
| H | -4.56297069165246 | -1.66237976208677 | 1.17032101381453 |
| H | -3.27521447415427 | -2.33016428452342 | 0.16348837186311 |
| C | -1.93290420006382 | 2.97032759879467 | 0.10089763227501 |
| H | -1.86038744571543 | 2.86413925231231 | 1.18846701333566 |
| H | -1.61838253133698 | 3.98917769804145 | -0.15914862395201 |
| H | -2.98849187219321 | 2.87012838383976 | -0.17664365595951 |
| C | -1.17903040178435 | 2.08135742472636 | -2.14815684402512 |
| H | -2.19535533427175 | 1.87219839774161 | -2.50094589047873 |
| H | -0.93404870073919 | 3.10713799872824 | -2.45349295305126 |
| H | -0.49851088121561 | 1.40880422647284 | -2.68161534679975 |
| C | -1.42725962390618 | -1.54006912277510 | -2.29138891275002 |
| H | -0.85514485234431 | -2.15194398855696 | -3.00109497460327 |
| H | -2.26879193415748 | -2.15032660255453 | -1.94666407882863 |
| H | -1.83658808247800 | -0.68800513660671 | -2.84388624846726 |
| C | 0.00880119279155 | -2.34949804081038 | -0.38502841950030 |
| H | -0.79832394441554 | -2.91114392433683 | 0.09924272444527 |
| H | 0.50759056004229 | -3.02433252612706 | -1.09371500726300 |
| H | 0.72803168267934 | -2.07608869566178 | 0.39178550439281 |
| H | 1.85608517432460 | 0.79820202409438 | -0.59285427314020 |

| | | | |
|---|---|---|---|
| C | 2.42979707292774 | 0.94768476606628 | 3.51511205163450 |
| C | 2.13734436374658 | -0.28473811223395 | 4.11797580191910 |
| C | 2.94221991013644 | 1.97837500431834 | 4.31161151130513 |
| C | 2.35745381492167 | -0.48007848543878 | 5.47354860124826 |
| H | 1.71955249311337 | -1.08494908379921 | 3.51288574217064 |
| C | 3.17128888215278 | 1.77647592259055 | 5.66828951636035 |
| H | 3.17670017389070 | 2.93747866818537 | 3.86022302140441 |
| C | 2.87744157105922 | 0.55002940894922 | 6.25531993603775 |
| H | 2.11437518582114 | -1.43757083695193 | 5.92505042754104 |
| H | 3.58155357566401 | 2.58351743360629 | 6.26858474969581 |
| H | 3.04830857065709 | 0.39702474654722 | 7.31700380030731 |
| C | 2.06596019852954 | 2.54561796871687 | 1.59093355060820 |
| C | 1.03254093998045 | 3.33019571957599 | 2.12384013146401 |
| C | 2.94518290556843 | 3.13077780892133 | 0.67195141808138 |
| C | 0.87737250292302 | 4.65370061523435 | 1.74072096645972 |
| H | 0.33780515654091 | 2.87677594898195 | 2.82586991287399 |
| C | 2.79089749556475 | 4.46051080191877 | 0.29371293236203 |
| H | 3.76246204682009 | 2.54399395703637 | 0.26434328535538 |
| C | 1.75485500076791 | 5.22508015447596 | 0.82039048767169 |
| H | 0.06132265348766 | 5.24034629631140 | 2.15282560219486 |
| H | 3.48801971432086 | 4.90104304677243 | -0.41338126354567 |
| H | 1.63135548904716 | 6.26094822075179 | 0.51783524785643 |

**Reactant complex 6b**



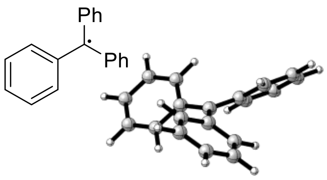
G: -1776.13016202 Eh
H: -1776.03759999 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 4.60615007539011 | -1.34497413661156 | 0.52267098938977 |
| C | 3.91231032571699 | -0.56739120109624 | 1.44761439578876 |
| C | 2.93434854358377 | 0.33465075324564 | 1.02655943131722 |
| C | 2.67204776066903 | 0.44041343301939 | -0.34499302882856 |
| C | 3.35874806948968 | -0.33638988665504 | -1.26711503417579 |
| C | 4.33108163308429 | -1.23701761335447 | -0.83517733645035 |
| H | 5.36575641014184 | -2.03927049041684 | 0.87051158053781 |
| H | 4.13465399599195 | -0.66262598382001 | 2.50574442948750 |
| C | 2.12189532351163 | 1.17648197067738 | 1.99795024064077 |
| H | 3.13635317315852 | -0.23961505940349 | -2.32636368746793 |
| H | 4.87060925999315 | -1.84643659994236 | -1.55438121237981 |
| S | -1.22194339923988 | 0.14918924853784 | 2.25815469511375 |
| Si | -1.63930968529302 | 0.10893232879452 | 0.15109039226264 |
| C | -1.22193730703053 | 1.84041215260714 | -0.53552237556961 |
| H | -0.22416120272573 | 2.04823704925041 | -0.11526157804253 |
| H | 1.07019604995914 | 0.81781950447598 | 1.90356050813708 |
| C | -3.53242502519852 | -0.24357206628886 | 0.14193241724995 |
| H | -3.94537013841116 | 0.49325373345203 | 0.84627940427537 |
| C | -0.57389642646539 | -1.19961810360743 | -0.74960091721433 |
| H | 0.32345219161001 | -0.63595104461114 | -1.04802778479882 |
| C | -4.18902463636467 | -0.00008034973833 | -1.22454629642199 |
| H | -5.27532799823367 | -0.13743501814072 | -1.13889312188229 |

| | | | |
|---|---|---|---|
| H | -4.01699726064801 | 1.01391214161454 | -1.59657842400503 |
| H | -3.83107687927569 | -0.70322316909084 | -1.98226114587906 |
| C | -3.86498648573059 | -1.64592609118119 | 0.66939980135367 |
| H | -3.45782355458240 | -1.81453892977680 | 1.67084469432372 |
| H | -4.95282039190077 | -1.78715674345232 | 0.71447483650219 |
| H | -3.46448324064487 | -2.42611907395635 | 0.01254475101793 |
| C | -2.16249257268943 | 2.92348475785286 | 0.00475893373015 |
| H | -2.24680809616645 | 2.87202710585299 | 1.09562250431482 |
| H | -1.78988653435519 | 3.92213137111057 | -0.25700296449844 |
| H | -3.17050532986750 | 2.82707031204076 | -0.41569479790481 |
| C | -1.09463705575843 | 1.91315287716722 | -2.06380077872853 |
| H | -2.04855687282616 | 1.71570297525996 | -2.56566341696311 |
| H | -0.76811054112264 | 2.91586613141016 | -2.36846654895960 |
| H | -0.36110730945553 | 1.19786778174168 | -2.45130823062777 |
| C | -1.21497054772895 | -1.73653958901970 | -2.03942254868111 |
| H | -0.49404535172215 | -2.35740566920803 | -2.58695863735531 |
| H | -2.08330146503304 | -2.36812780438127 | -1.82281324575580 |
| H | -1.54230443574416 | -0.93903569171294 | -2.71475926477099 |
| C | -0.10487853307019 | -2.35535346103826 | 0.14142096674267 |
| H | -0.95138110834943 | -2.93469236890588 | 0.52818422964581 |
| H | 0.53768183017233 | -3.03789623148514 | -0.42976534183172 |
| H | 0.46362672405707 | -1.99535829639230 | 1.00376013768951 |
| H | 1.92550759374924 | 1.15187184475121 | -0.68958862967359 |
| C | 2.49969951591985 | 0.95238527598269 | 3.45216806474632 |
| C | 1.95302637981635 | -0.12754181583326 | 4.14846291061396 |
| C | 3.42387150800585 | 1.77337502315846 | 4.09986116261103 |
| C | 2.32546811079276 | -0.38587555454508 | 5.46280744082878 |
| H | 1.22466070917879 | -0.76634851875530 | 3.65344222928696 |
| C | 3.80064002319381 | 1.51323141182378 | 5.41405229865919 |
| H | 3.84690635631046 | 2.62367169691340 | 3.57231423254438 |
| C | 3.25338679662702 | 0.43368656837023 | 6.10008000743829 |
| H | 1.88472778571594 | -1.22563140798256 | 5.99252228696069 |
| H | 4.52021606361924 | 2.16235832147102 | 5.90512113500986 |
| H | 3.54191063879644 | 0.23616337858865 | 7.12847400906933 |
| C | 2.08088902208761 | 2.65187469444085 | 1.63953609202287 |
| C | 0.96742781472243 | 3.40726469939146 | 2.01746187607078 |
| C | 3.13827420307789 | 3.29067890011958 | 0.98928442955552 |
| C | 0.90689935597534 | 4.76805681618323 | 1.74415642243296 |
| H | 0.13915431911133 | 2.91266359614707 | 2.52122507087112 |
| C | 3.08154585363600 | 4.65593206126076 | 0.72138181138640 |
| H | 4.00887886272597 | 2.71454801115816 | 0.68722314270367 |
| C | 1.96543241684738 | 5.39799744866864 | 1.09351143241929 |
| H | 0.02865231938283 | 5.33743804024661 | 2.03537638475057 |
| H | 3.91298820339288 | 5.13923729960666 | 0.21598703757997 |
| H | 1.91761490612237 | 6.46093650304518 | 0.87525466250756 |

**Radical 6b**



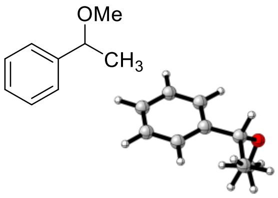
G: -732.62082919 Eh
H: -732.56394671 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 4.69755299805550 | -1.55894451143441 | 0.67815643787244 |
| C | 4.24671800789685 | -0.59637980044069 | 1.56800011584402 |
| C | 3.25428773030329 | 0.33390566678830 | 1.19322041490598 |
| C | 2.73599903750353 | 0.24437128301995 | -0.11602740979577 |
| C | 3.18466525586730 | -0.72635652583982 | -0.99804735628030 |
| C | 4.16954717925837 | -1.63358240294761 | -0.60998249740535 |
| H | 5.47461534793337 | -2.25247817668388 | 0.98735032367565 |
| H | 4.67750704869766 | -0.53544512341189 | 2.56299831379516 |
| C | 2.78323712807873 | 1.34829951940794 | 2.12397205725839 |
| H | 2.75628691401954 | -0.78327171274796 | -1.99488530322254 |
| H | 4.52168381312474 | -2.39080731925839 | -1.30411738794579 |
| H | 1.95545211610995 | 0.93445510189633 | -0.42232994142217 |
| C | 2.71133035482410 | 1.05231236414513 | 3.54728205925356 |
| C | 2.38774857314490 | -0.24053427140529 | 4.00991634595413 |
| C | 2.96267503778456 | 2.04858193740362 | 4.51401166472465 |
| C | 2.31520625085747 | -0.51736048892472 | 5.36630727201023 |
| H | 2.16842318424257 | -1.01965002342783 | 3.28586777033776 |
| C | 2.89798243809184 | 1.76290723469896 | 5.86899414641076 |
| H | 3.23511219018663 | 3.04667947820231 | 4.18396494156174 |
| C | 2.57180710352541 | 0.47985694928101 | 6.30609090137559 |
| H | 2.04690049107742 | -1.51745198083877 | 5.69531153143736 |
| H | 3.11291309856709 | 2.54461829237019 | 6.59230039550988 |
| H | 2.51786119385427 | 0.25952867768929 | 7.36808193874938 |
| C | 2.38311058395356 | 2.65845861252313 | 1.63326770859744 |
| C | 1.33946566865341 | 3.38130989436599 | 2.24871863112516 |
| C | 3.02422513483444 | 3.25185153291268 | 0.52538204646101 |
| C | 0.95687209604222 | 4.62711462110616 | 1.77643035777306 |
| H | 0.81529412620504 | 2.93715524811760 | 3.08968562836318 |
| C | 2.64306333657382 | 4.50228726188657 | 0.06385772553243 |
| H | 3.84533807959812 | 2.72602422979894 | 0.04725709834794 |
| C | 1.60603932280097 | 5.19856927980608 | 0.68298117686260 |
| H | 0.13855641189577 | 5.15476652218385 | 2.25844764623798 |
| H | 3.16521733024835 | 4.94349080703019 | -0.78060487761104 |
| H | 1.30708861618917 | 6.17633294272701 | 0.31711595370547 |

# 7e

**Substrate 7e**



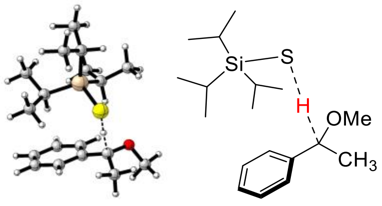
G: -425.13006083 Eh
H: -425.08511788 Eh
Charge: 0
Multiplicity: 1

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.91776976572963 | -1.07821009039483 | -0.19934622381537 |
| C | 3.41811972281591 | -0.48076107326763 | 0.95738138902428 |
| C | 2.68007779669252 | 0.69987667814496 | 0.88623027730675 |
| C | 2.45281507762636 | 1.27210619938699 | -0.37023124694324 |
| C | 2.95128120664421 | 0.68049017748257 | -1.52286892206942 |
| C | 3.68716795112323 | -0.50059310433765 | -1.44135627816649 |

| | | | |
|---|---|---|---|
| H | 4.49123588320436 | -1.99792604234755 | -0.12446065086263 |
| H | 3.61235393147822 | -0.94876396379311 | 1.91732959421520 |
| C | 2.10204503978110 | 1.40005079923819 | 2.10817629476916 |
| H | 2.76466420638512 | 1.13930911672055 | -2.48985904014636 |
| H | 4.07709899371227 | -0.96570203603577 | -2.34218981359272 |
| H | 1.00727666105454 | 1.38140638456267 | 2.01061563721412 |
| H | 1.88872755001091 | 2.19928083533924 | -0.42949544021810 |
| C | 2.46442804492047 | 0.76665776045110 | 3.44598650755230 |
| H | 2.05950767104640 | 1.38184852003478 | 4.25477045600520 |
| H | 2.02837559162741 | -0.23391786766263 | 3.52651581696633 |
| H | 3.54626054637990 | 0.67679688459047 | 3.58562190014326 |
| O | 2.39704700656838 | 2.80579801436248 | 2.07606911206721 |
| C | 3.77946838866522 | 3.11941653321254 | 2.19115939664626 |
| H | 4.38645112448637 | 2.57223917357207 | 1.45474221752954 |
| H | 3.86900477087525 | 4.19131724862673 | 1.99745427530240 |
| H | 4.16669306917218 | 2.91236185211380 | 3.19927074107232 |

**HAT transition state 7e**



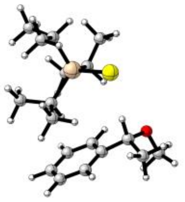
G: -1468.02872302 Eh
H: -1467.94692873 Eh
Charge: 0
Multiplicity: 2

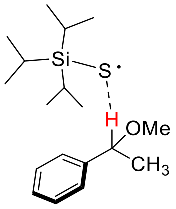
Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.62732635038837 | -1.43734840884081 | 0.06025064061677 |
| C | 3.05950773345751 | -0.73697810046529 | 1.11415665589896 |
| C | 2.66361199364154 | 0.60145609143391 | 0.95420627028084 |
| C | 2.85264362144258 | 1.20983772918847 | -0.29813770773504 |
| C | 3.42407880593272 | 0.50428976124383 | -1.34773216443975 |
| C | 3.81056990600026 | -0.82334981002198 | -1.17717187874295 |
| H | 3.91979395825915 | -2.47370441364245 | 0.20203416817550 |
| H | 2.90533618495164 | -1.24118613496728 | 2.06251002738576 |
| C | 1.99612306260784 | 1.33218385694514 | 2.05084798306979 |
| H | 3.56503033002914 | 0.99245904382377 | -2.30790865497038 |
| H | 4.24946119273990 | -1.37633957326515 | -2.00230522402869 |
| S | -0.68887942011554 | 0.14833278806313 | 2.29842526352630 |
| Si | -1.19366588452167 | -0.02031054574686 | 0.19836424301787 |
| C | -0.81186925904357 | 1.68537487087382 | -0.57011940150691 |
| H | 0.16825493041933 | 1.94515361960801 | -0.14501251081329 |
| H | 0.75043937662594 | 0.79506105975926 | 2.04625377764312 |
| C | -3.06918357918928 | -0.38381849108878 | 0.21991197568687 |
| H | -3.47623263509605 | 0.39105462244400 | 0.88798129207794 |
| C | -0.13850904572385 | -1.37665602641772 | -0.63982964333528 |
| H | 0.82563464820852 | -0.88014661174046 | -0.83871766337089 |
| C | -3.75781237766976 | -0.22862081916347 | -1.14478884177710 |
| H | -4.84294271169768 | -0.35870585733190 | -1.03667868238848 |
| H | -3.58940137218490 | 0.75726188409182 | -1.58827109777844 |
| H | -3.41135818830007 | -0.98004383779249 | -1.86130781582851 |
| C | -3.40074898683486 | -1.75141944062201 | 0.83453223695095 |
| H | -2.93133212501639 | -1.88726363859178 | 1.81453774605660 |
| H | -4.48548440032046 | -1.86641433844498 | 0.95963834381856 |
| H | -3.06129654626953 | -2.56683016384248 | 0.18549641383170 |

| | | | |
|---|---|---|---|
| C | -1.79822675159968 | 2.75865546332280 | -0.09039149729278 |
| H | -1.87481290839664 | 2.76764799412309 | 1.00182703563030 |
| H | -1.47104494247350 | 3.75530293579172 | -0.41401589329314 |
| H | -2.80261742122906 | 2.59697348819527 | -0.49890763174791 |
| C | -0.65753480292094 | 1.70284615331259 | -2.09682591218225 |
| H | -1.58305514527727 | 1.41657485893303 | -2.60971314666851 |
| H | -0.39692630891757 | 2.71272223626089 | -2.44163147784397 |
| H | 0.13567037324887 | 1.02577455230242 | -2.43227180441743 |
| C | -0.70563954721563 | -1.85243598459861 | -1.98835886862890 |
| H | 0.02390568560562 | -2.49109777012585 | -2.50377985216541 |
| H | -1.60937433914929 | -2.45390225753900 | -1.83902516745869 |
| H | -0.96102509472803 | -1.03071311409037 | -2.66425125949685 |
| C | 0.14746021232110 | -2.59290485547209 | 0.25177556550946 |
| H | -0.76679742903585 | -3.16367564720525 | 0.45033940571207 |
| H | 0.85753348107825 | -3.26828210531721 | -0.24433608250834 |
| H | 0.56667403191183 | -2.30093026718856 | 1.21804934228388 |
| H | 2.54294130543235 | 2.24009939047505 | -0.43646459878326 |
| C | 2.39180145507253 | 1.03784419065468 | 3.47976050626031 |
| H | 1.76902993840407 | 1.62459841649715 | 4.16108506046475 |
| H | 2.23031460931584 | -0.01638333604454 | 3.71429049641023 |
| H | 3.44857753561972 | 1.27023027149923 | 3.66061189160356 |
| O | 1.73050211467035 | 2.66922992878866 | 1.76239512662562 |
| C | 2.71284392209396 | 3.60975378060323 | 2.20742042140922 |
| H | 3.70915750871534 | 3.35028756736029 | 1.82155644151458 |
| H | 2.40776513453582 | 4.57755923602213 | 1.80406593846876 |
| H | 2.75105556019695 | 3.67492438794996 | 3.30184739927291 |

**Reactant complex 7e**





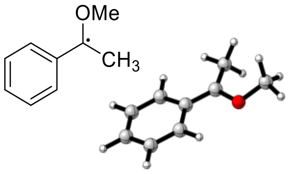
G: -1468.03043804 Eh
H: -1467.94657950 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.69762123618153 | -1.24569507510909 | -0.25499133457196 |
| C | 3.26413850561699 | -0.62759027607498 | 0.91536411738311 |
| C | 2.75729374664204 | 0.67359901408555 | 0.89079737442083 |
| C | 2.71590960470578 | 1.34885155303679 | -0.33357600278859 |
| C | 3.15638050264314 | 0.73632165363632 | -1.50087540518467 |
| C | 3.64255924865861 | -0.56850624242964 | -1.46819305100657 |
| H | 4.08143512746374 | -2.26141049891064 | -0.21549674478613 |
| H | 3.30839996930400 | -1.17779020130048 | 1.84986309916127 |
| C | 2.15641350145270 | 1.32957720578667 | 2.12509087704185 |
| H | 3.11529652828157 | 1.27831275345231 | -2.44190829228158 |
| H | 3.98109086512717 | -1.05051012912712 | -2.38081448011507 |
| S | -1.57235627988564 | 0.38920264719861 | 2.42896339358147 |
| Si | -1.59071947976490 | 0.03418840296741 | 0.30767808034247 |
| C | -1.17476972616765 | 1.78356434766819 | -0.38699535699142 |
| H | -0.33377512116503 | 2.14355808875176 | 0.22417698866857 |
| H | 1.07303245712694 | 1.12900825923669 | 2.09032050129537 |
| C | -3.36621585804777 | -0.50426049162024 | -0.13881064483230 |
| H | -3.99010872066771 | 0.25404938036345 | 0.35885504428519 |

| | | | |
|---|---|---|---|
| C | -0.21778524998390 | -1.19597341360067 | -0.18404539348307 |
| H | 0.68332838509290 | -0.56710369052794 | -0.25093337293475 |
| C | -3.71114425276018 | -0.49323166872922 | -1.63435683222049 |
| H | -4.76824237232877 | -0.75458791396281 | -1.77619247929379 |
| H | -3.55519933034013 | 0.48837356255583 | -2.09230211068459 |
| H | -3.11901281705294 | -1.22193475559684 | -2.19639575153576 |
| C | -3.70430902342334 | -1.86667094055579 | 0.48578365500587 |
| H | -3.51904672267134 | -1.87702830457434 | 1.56568775516620 |
| H | -4.76168974682047 | -2.11336121868091 | 0.32464584176181 |
| H | -3.11085124299674 | -2.67071529698857 | 0.03569543331854 |
| C | -2.34131565913541 | 2.76420290550729 | -0.22304348434627 |
| H | -2.66161439515445 | 2.84529424705465 | 0.81994037606057 |
| H | -2.04743797074325 | 3.76407035621787 | -0.56741459443737 |
| H | -3.20984367127940 | 2.45816410126120 | -0.81728613435120 |
| C | -0.69190419428947 | 1.71952540118399 | -1.84306182302243 |
| H | -1.46988059213026 | 1.34929509588619 | -2.51970804250239 |
| H | -0.41805972206813 | 2.72789595200610 | -2.18218654053538 |
| H | 0.19176289625387 | 1.08477895091488 | -1.95679274766860 |
| C | -0.42803614746744 | -1.85191758440841 | -1.55755696467675 |
| H | 0.47379587349926 | -2.40704051265421 | -1.84700863483640 |
| H | -1.25716065813301 | -2.56824840842309 | -1.53227424442373 |
| H | -0.63596808506179 | -1.12727943863839 | -2.35112849264807 |
| C | 0.05603675659138 | -2.27151200258023 | 0.87646675579177 |
| H | -0.80828484160443 | -2.93253493008422 | 1.01195164052168 |
| H | 0.90629281962996 | -2.89533339447328 | 0.57121824720872 |
| H | 0.29229965523506 | -1.82790935262588 | 1.84842448320103 |
| H | 2.32728203413108 | 2.36285995569477 | -0.35739308321926 |
| C | 2.67047525287907 | 0.78264014277346 | 3.45293498649509 |
| H | 2.28490734803876 | 1.40299008567030 | 4.26731710653465 |
| H | 2.30186855054801 | -0.23473956640229 | 3.61251164741606 |
| H | 3.76423096803446 | 0.76334681433527 | 3.50239340087492 |
| O | 2.23360384144595 | 2.75675092458686 | 2.04977856017753 |
| C | 3.54869465003421 | 3.27985888806465 | 2.19668086972019 |
| H | 4.26314742746988 | 2.79023671877870 | 1.51809199814271 |
| H | 3.49028018739119 | 4.34190985100005 | 1.94460650296659 |
| H | 3.91380668462480 | 3.18305786050224 | 3.22901149807801 |

**Radical 7e**



G: -424.51170810 Eh
H: -424.46551442 Eh
Charge: 0
Multiplicity: 2

Optimized cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 3.48628859925683 | -1.57844482476505 | -0.01094059382660 |
| C | 3.21383290514395 | -0.74955250100066 | 1.06131602657074 |
| C | 2.99375944131567 | 0.64343080421683 | 0.87584583545881 |
| C | 3.06190577736999 | 1.13685316228085 | -0.45871067286592 |
| C | 3.33289512244751 | 0.29117286284466 | -1.51713460559315 |
| C | 3.54952510238630 | -1.07390524679014 | -1.31212612726565 |
| H | 3.65093464621160 | -2.63776844506887 | 0.16686208791356 |
| H | 3.17025125580768 | -1.18415867195447 | 2.05387822670270 |

| | | | |
|---|---|---|---|
| C | 2.71731307879253 | 1.51970695218349 | 1.95367202171453 |
| H | 3.37850139705182 | 0.69913850357985 | -2.52348895797663 |
| H | 3.76287869655341 | -1.73159568828799 | -2.14877085817481 |
| H | 2.89903019586603 | 2.19305788137261 | -0.63609872109269 |
| C | 2.58128052143396 | 1.13913901856409 | 3.38677820772401 |
| H | 1.55509795751951 | 1.30263776680964 | 3.74658594217522 |
| H | 2.81877245773722 | 0.08726785301755 | 3.53711391834115 |
| H | 3.24765426530885 | 1.71859709212440 | 4.03799554636026 |
| O | 2.42172142163178 | 2.80887747537189 | 1.58940563807524 |
| C | 2.55972614031258 | 3.83675426981028 | 2.56676147441113 |
| H | 3.59125578501216 | 3.89532169905149 | 2.93900643536922 |
| H | 2.31010667876276 | 4.76826466366521 | 2.05511388486563 |
| H | 1.87411276407784 | 3.69959283297432 | 3.41197194111322 |

# 10 Single-Crystal X-Ray Diffraction Analysis

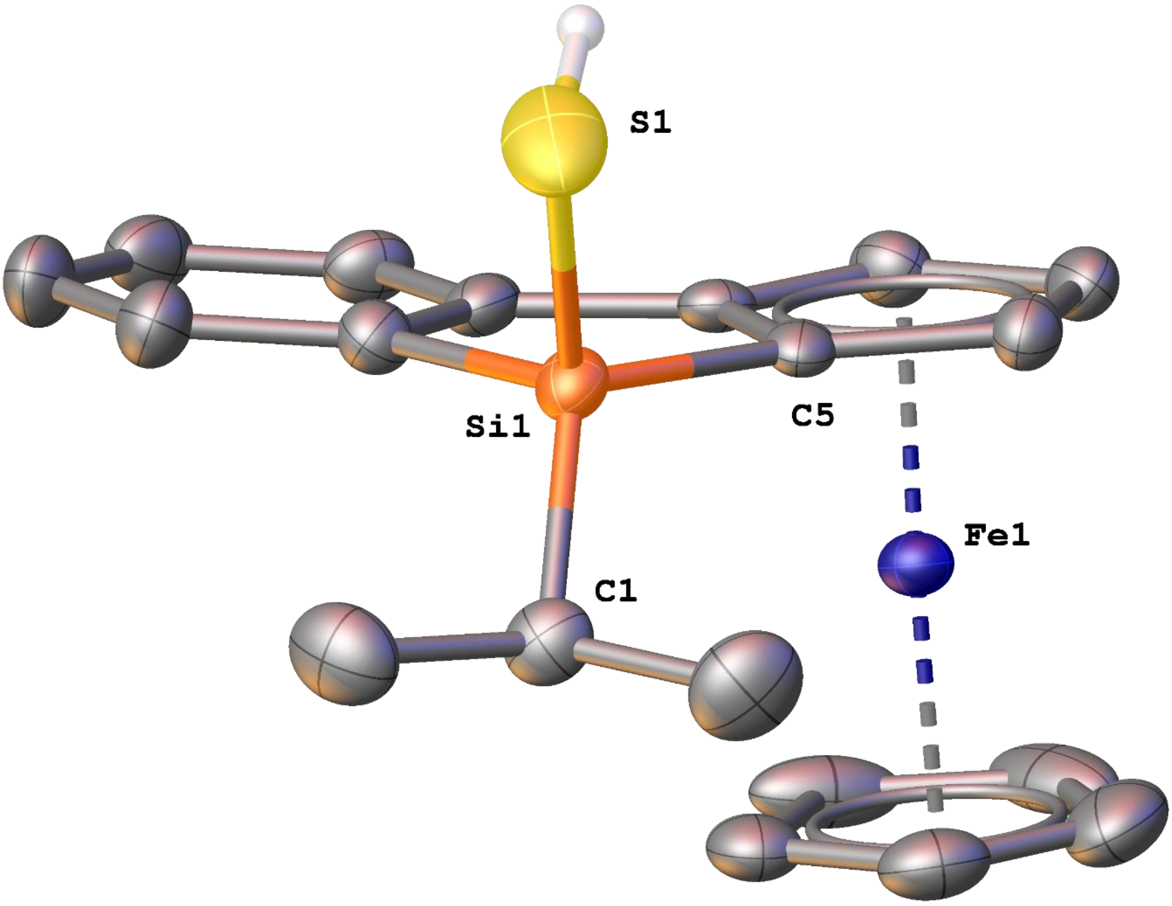
Compound **12a**: The asymmetric unit contains one molecule.

Compound **12b**: The asymmetric unit contains one molecule.

| **Compound** | **12a** | **12b** |
|---|---|---|
| Data Set (internal naming) | **AF246** | **AF250new_commented12b** |
| CCDC Number | 2354889 | 2354890 |
| Formula | $C_{19}H_{20}FeSSi$ | $C_{22}H_{24}FeSSi$ |
| $\rho_{calc.}$ / g·cm$^{-3}$ | 1.403 | 1.413 |
| $\mu$/mm$^{-1}$ | 8.731 | 7.984 |
| Formula Weight | 364.35 | 404.41 |
| Color | clear intense orange | clear intense orange |
| Shape | plate | irregular |
| Size/mm$^3$ | 0.38 x 0.22 x 0.1 | 0.3 x 0.2 x 0.17 |
| *T*/K | 12.98(10) | 123.00(10) |
| Crystal System | orthorhombic | orthorhombic |
| Space Group | $P2_12_12_1$ | $P2_12_12_1$ |
| *a*/Å | 7.5566(2) | 8.348990(2) |
| *b*/Å | 13.3052(3) | 12.90523(2) |
| *c*/Å | 17.1617(4) | 17.6385(3) |
| α/° | 90 | 90 |
| β/° | 90 | 90 |
| γ/° | 90 | 90 |
| V/Å$^3$ | 1725.47(7) | 1900.458(6) |
| *Z* | 4 | 4 |
| *Z'* | 1 | 1 |
| Wavelength/Å | 1.54184 | 1.54184 |
| Radiation Type | Cu $K_\alpha$ | Cu $K_\alpha$ |
| $2_{\Theta min}$/° | 8.408 | 8.49 |
| $2_{\Theta max}$/° | 133.746 | 133.788 |
| Measured Refl. | 15492 | 1733445 |
| Independent Refl. | 3049 | 3366 |
| $R_{int}$ | 0.0866 | 0.071224 |
| Parameters | 205 | 226 |
| Restraints | 0 | 910 |
| Largest Peak | 0.50 | 0.790 |
| Deepest Hole | -0.79 | -0.935 |
| GooF | 1.031 | 1.03254 |
| $wR_2$ (all data) | 0.1217 | 0.158447 |
| $wR_2$ | 0.1175 | 0.155114 |
| $R_1$ (all data) | 0.0538 | 0.0603588 |
| $R_1$ | 0.0475 | 0.057259 |

**12a**

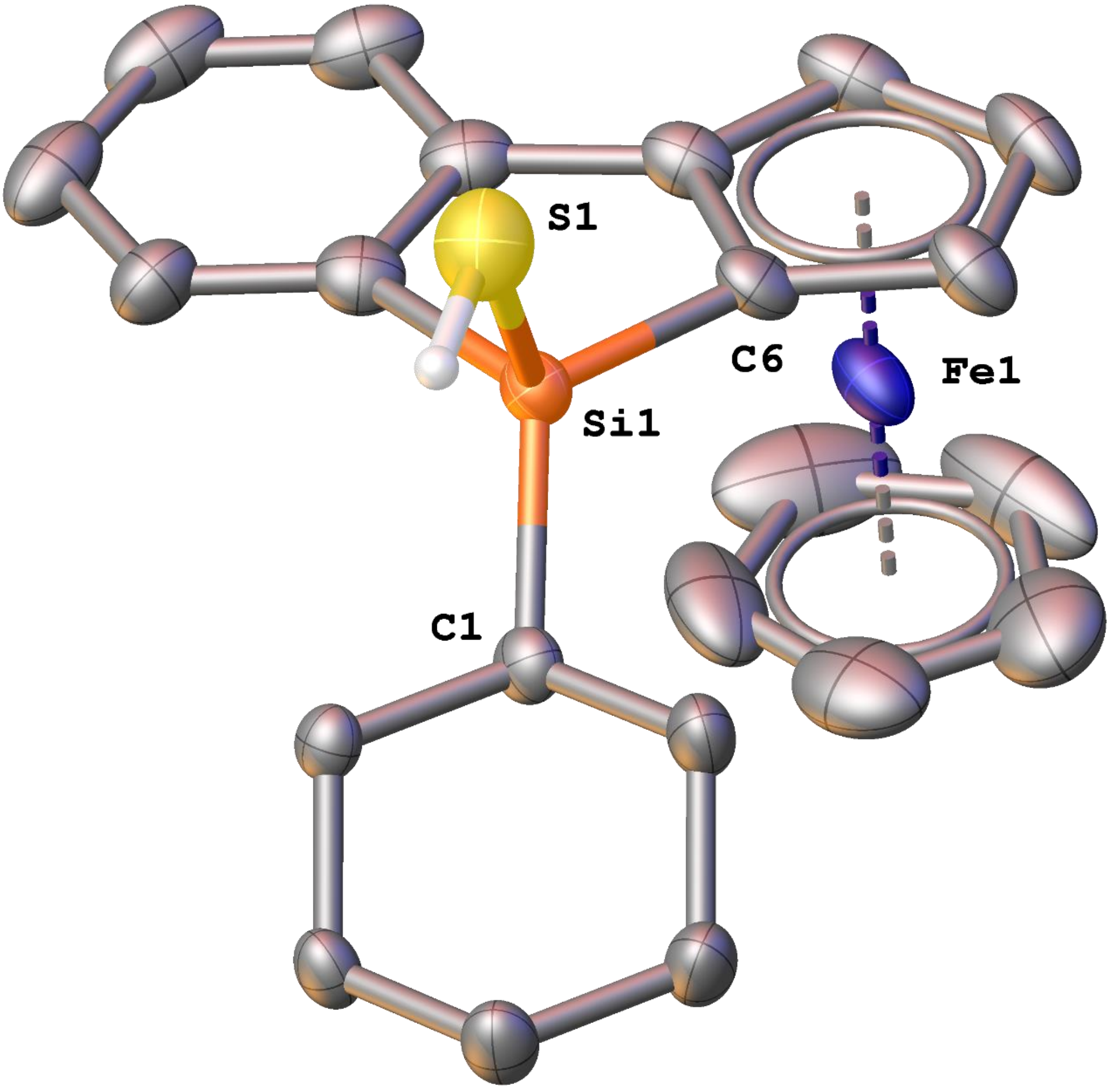
Hydrogen atoms except S–H are omitted for clarity.



| **Selected Bond Lengths in Å** | | **Selected Bond Angles in °** | |
|---|---|---|---|
| **Si(1)–S(1)** | 2.122(2) | **C(1)–Si(1)–S(1)** | 105.9(2) |
| **Si(1)–C(1)** | 1.868(6) | **C(1)–Si(1)–C(5)** | 118.4(3) |
| **Si(1)–C(5)** | 1.857(6) | **S(1)–Si(1)–C(5)** | 112.72(17) |

**12b**

Hydrogen atoms except S–H are omitted for clarity.



| Selected Bond Lengths in Å | | Selected Bond Angles in ° | |
|---|---|---|---|
| **Si(1)–S(1)** | 2.132(3) | **C(1)–Si(1)–S(1)** | 109.2(2) |
| **Si(1)–C(1)** | 1.865(7) | **C(1)–Si(1)–C(6)** | 117.2(3) |
| **Si(1)–C(6)** | 1.846(7) | **S(1)–Si(1)–C(6)** | 111.4(2) |

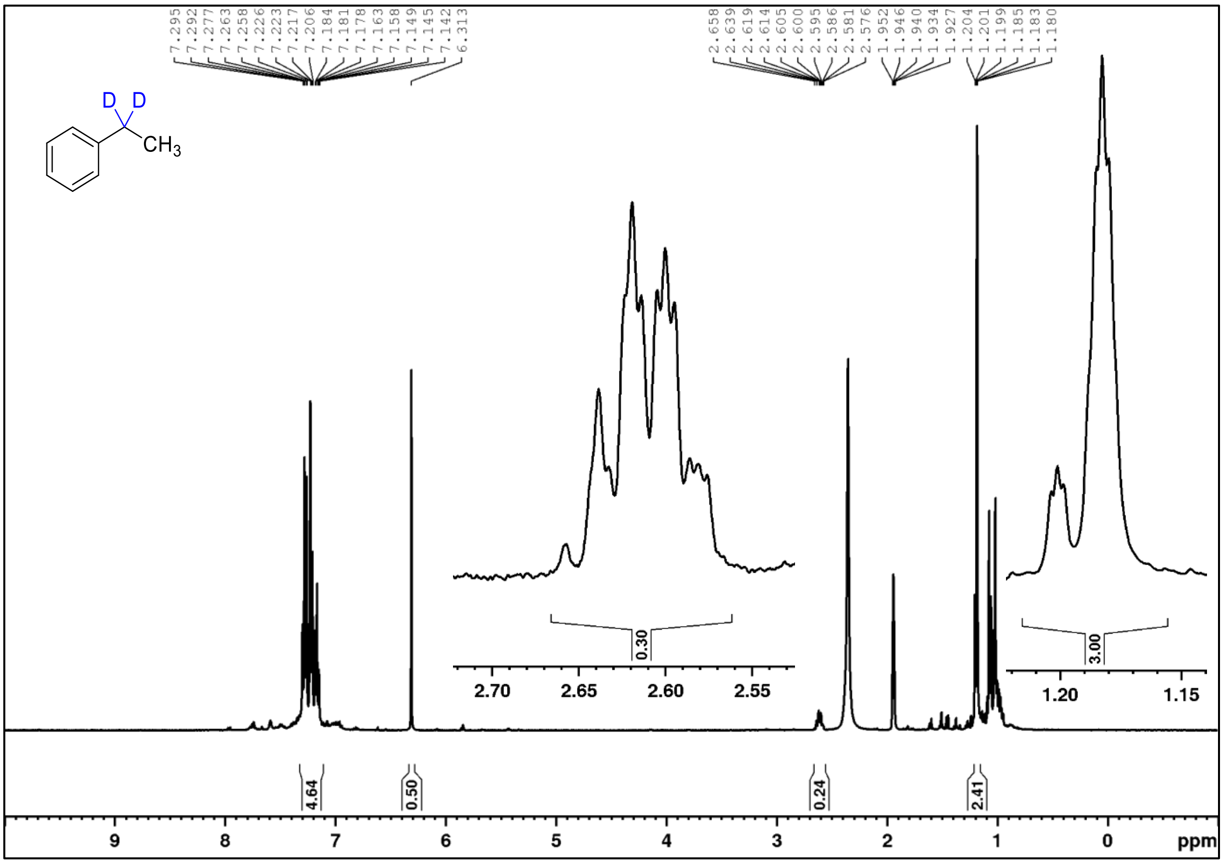
# 11 NMR spectra

## 11.1 NMR spectra of crude reaction mixtures for determination of deuteration degrees

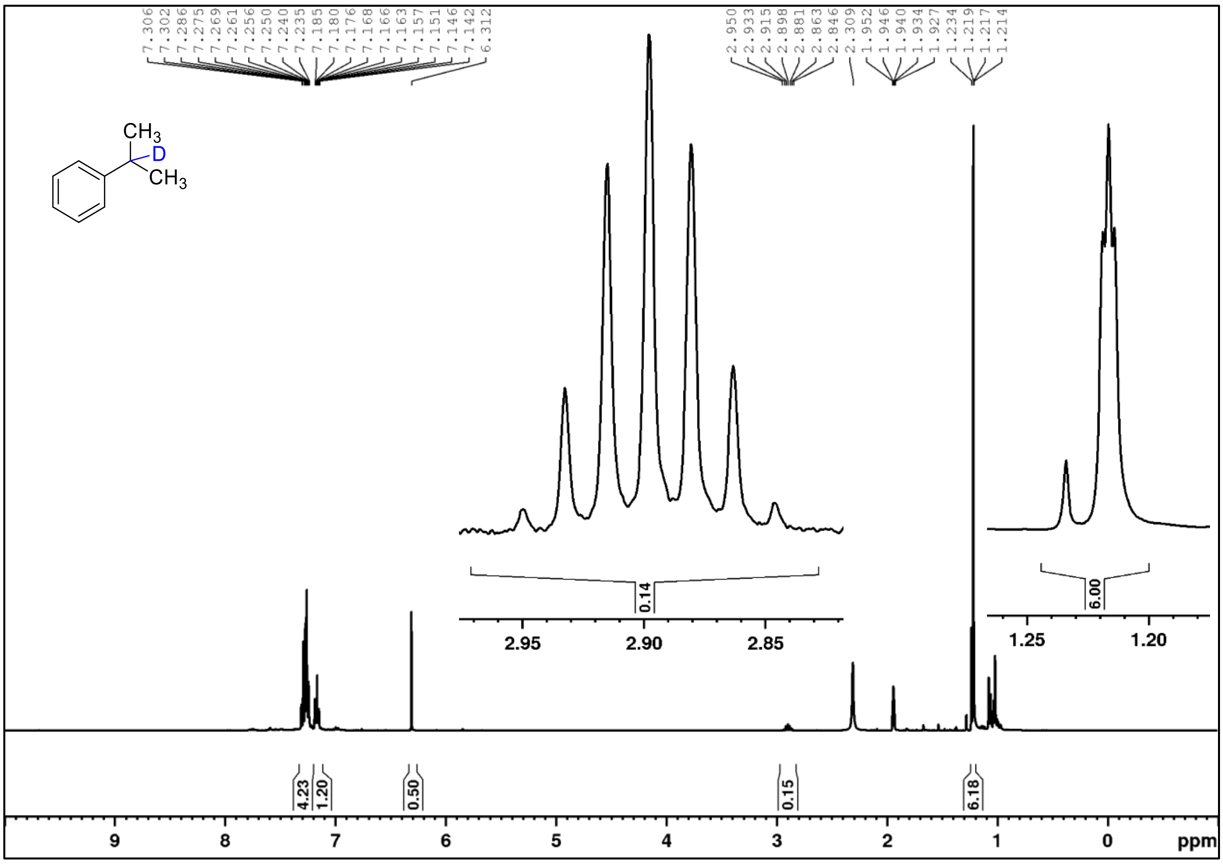
NMR spectra were recorded with 1,1,2,2-tetrachloroethane or the $CD_3CN$ residual signal as standard for integration. The large spectra are calibrated with respect to the standard. Inserted individual peaks are added for the benzylic positions and neighboring positions influenced by the deuteration. These are calibrated on a well separated reference proton in the molecule for determination of the deuteration degrees.

**2a-*d*₂**

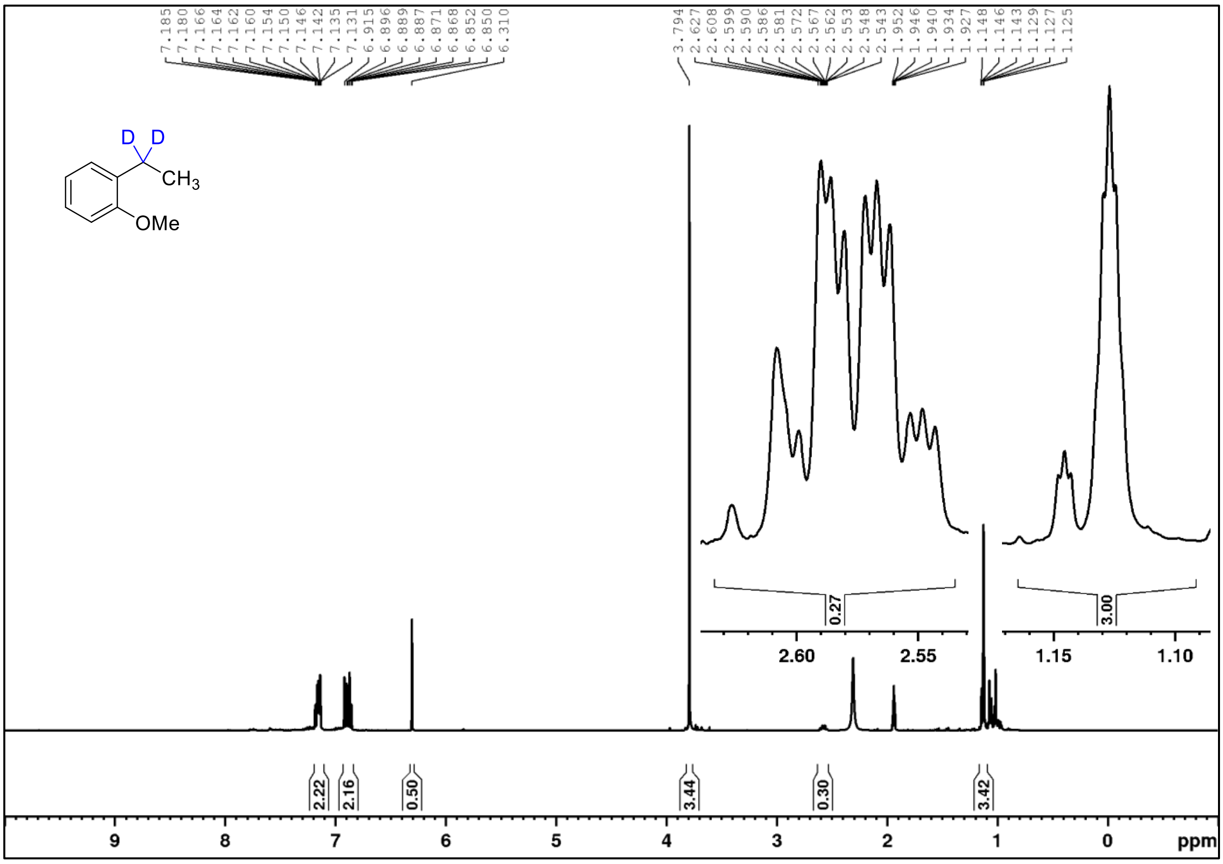
$^1H$ NMR (400 MHz, $CD_3CN$)



**2b-$d_1$** $^1$H NMR (400 MHz, $CD_3CN$)

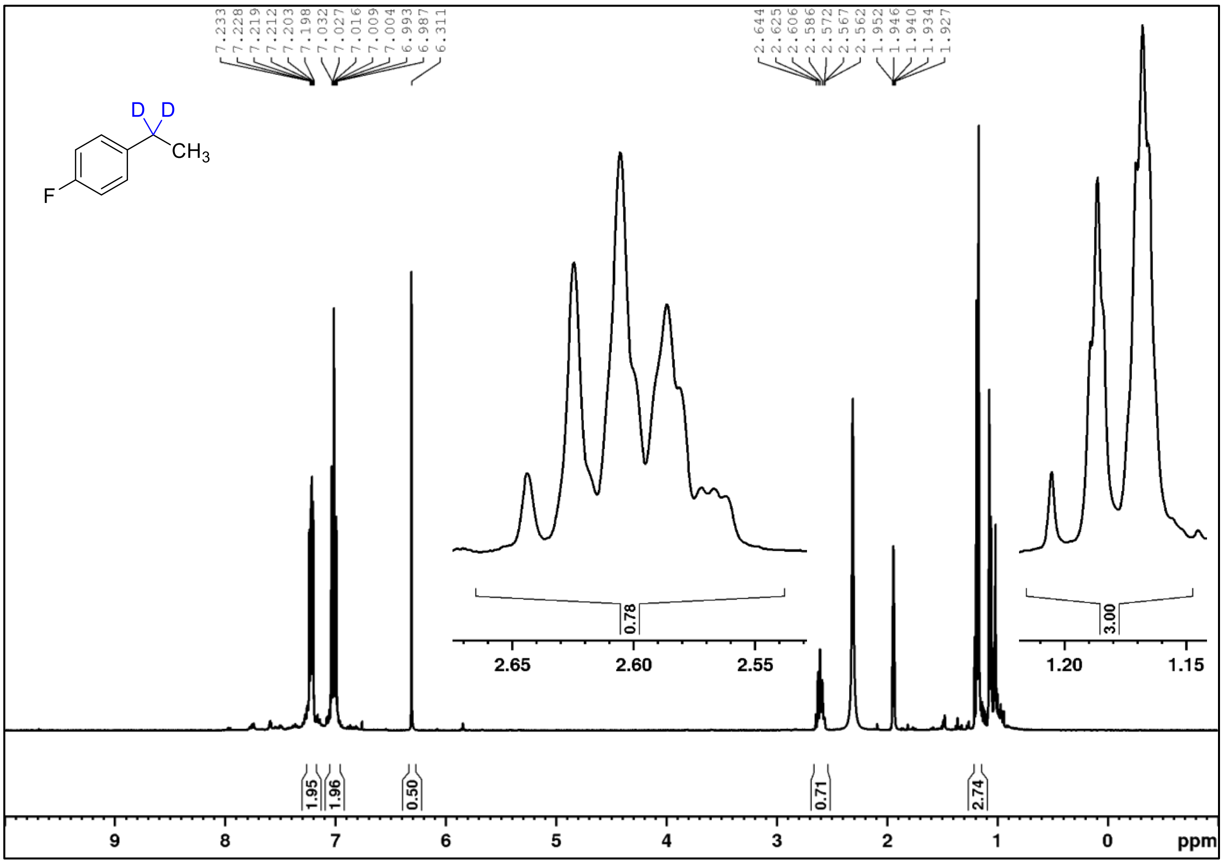


**2d-$d_2$** $^1$H NMR (400 MHz, $CD_3CN$)



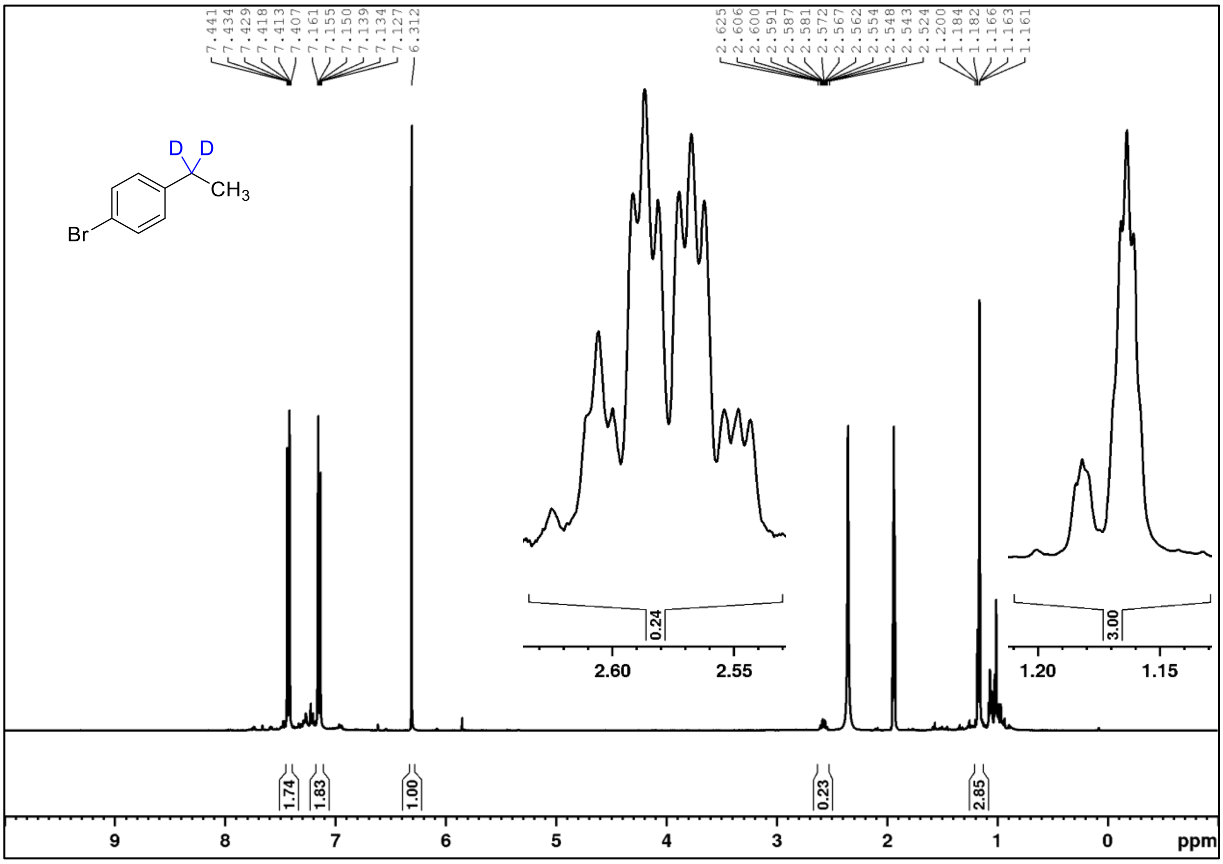
**2f-$d_2$**

$^1$H NMR (400 MHz, $CD_3CN$)



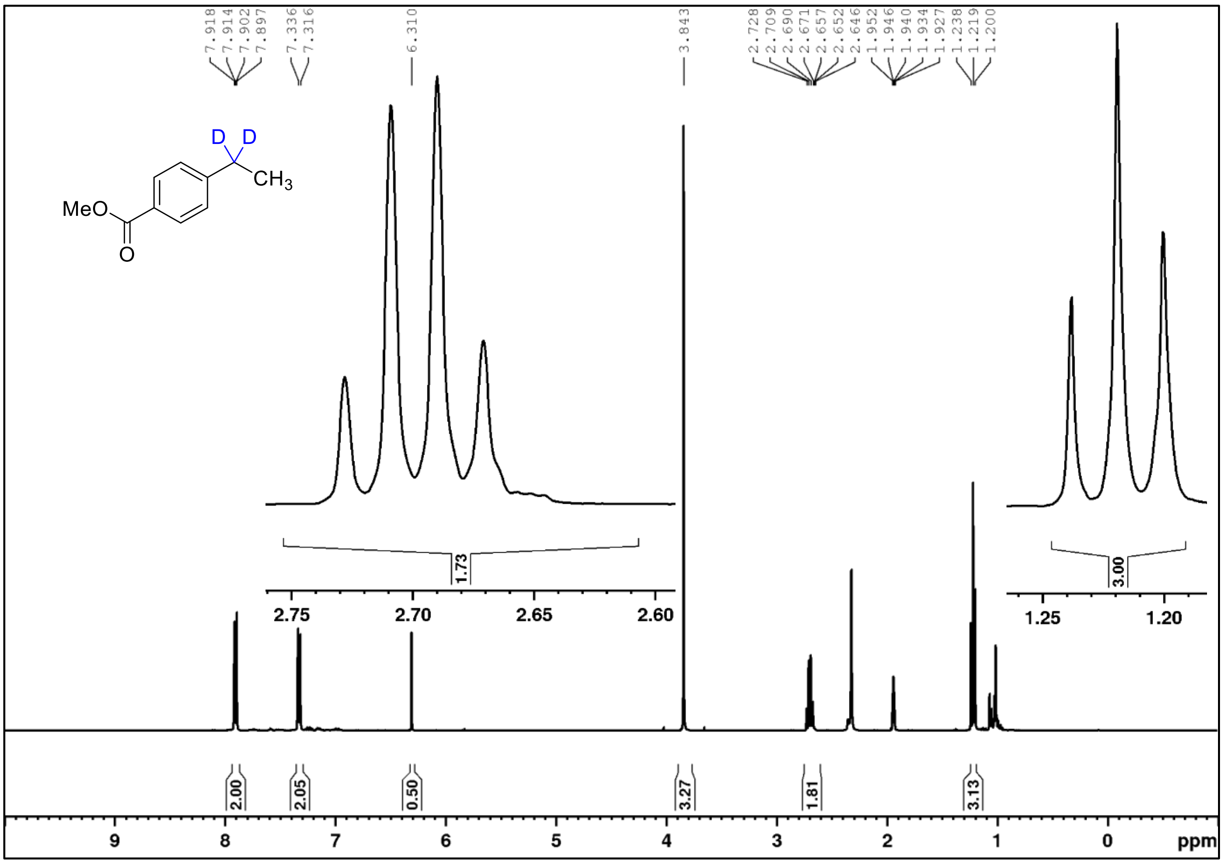
**2g-$d_2$**

$^1$H NMR (400 MHz, $CD_3CN$)



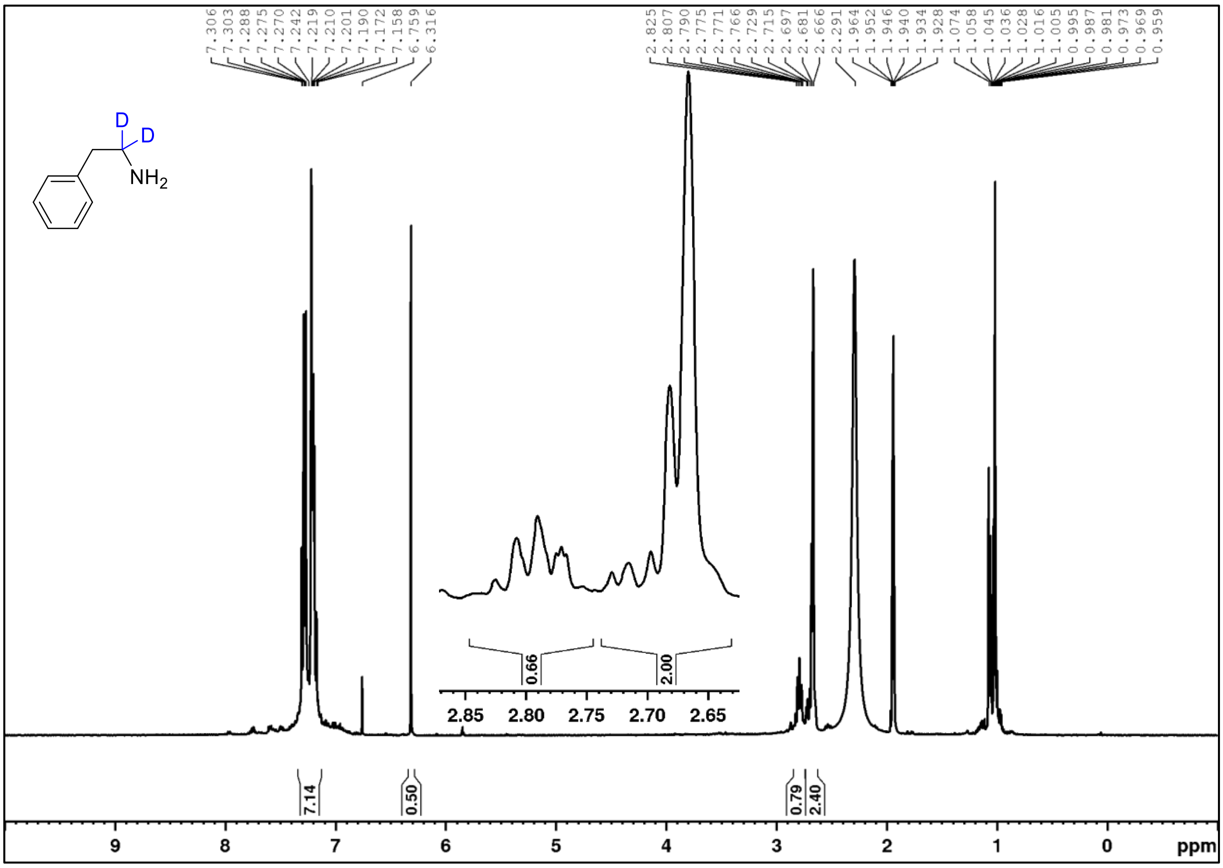
**2i-*d*₂**

$^{1}$H NMR (400 MHz, CD$_3$CN)

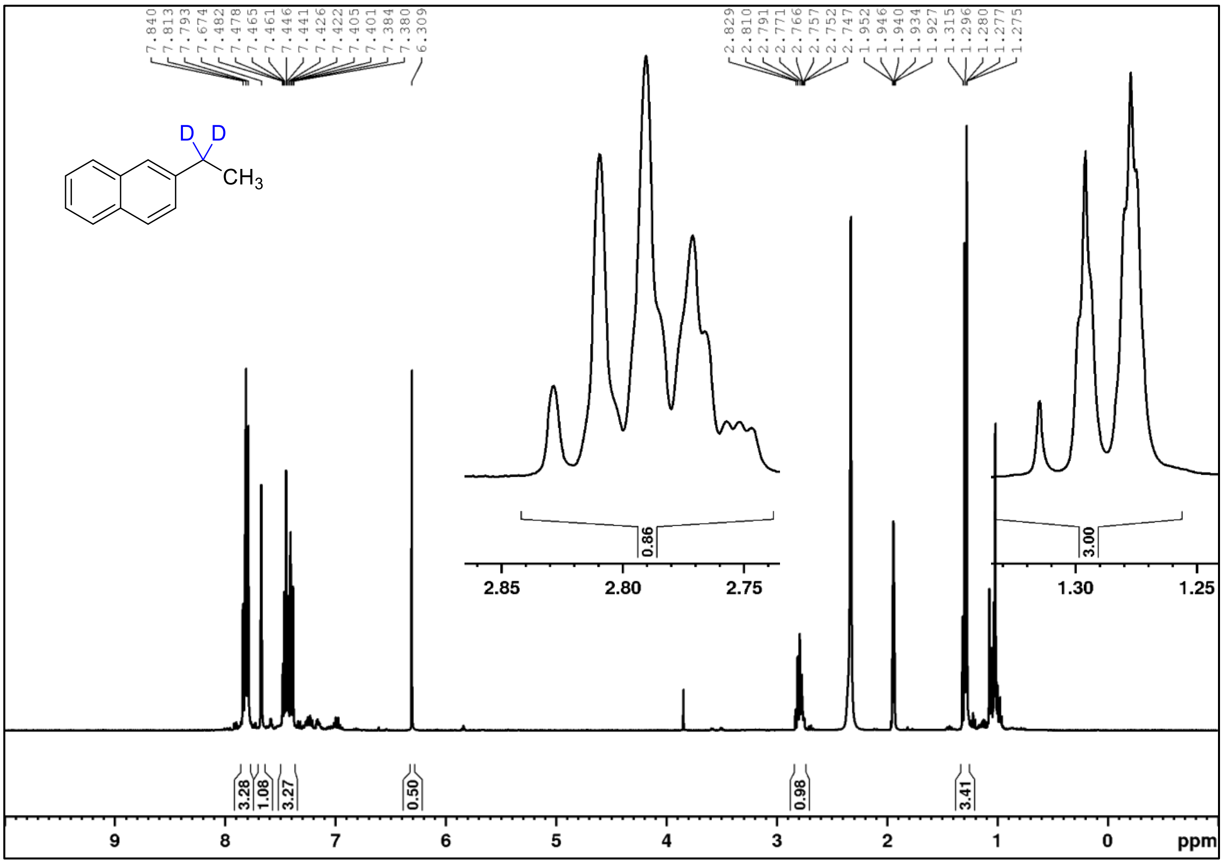


**2k-*d*₂**

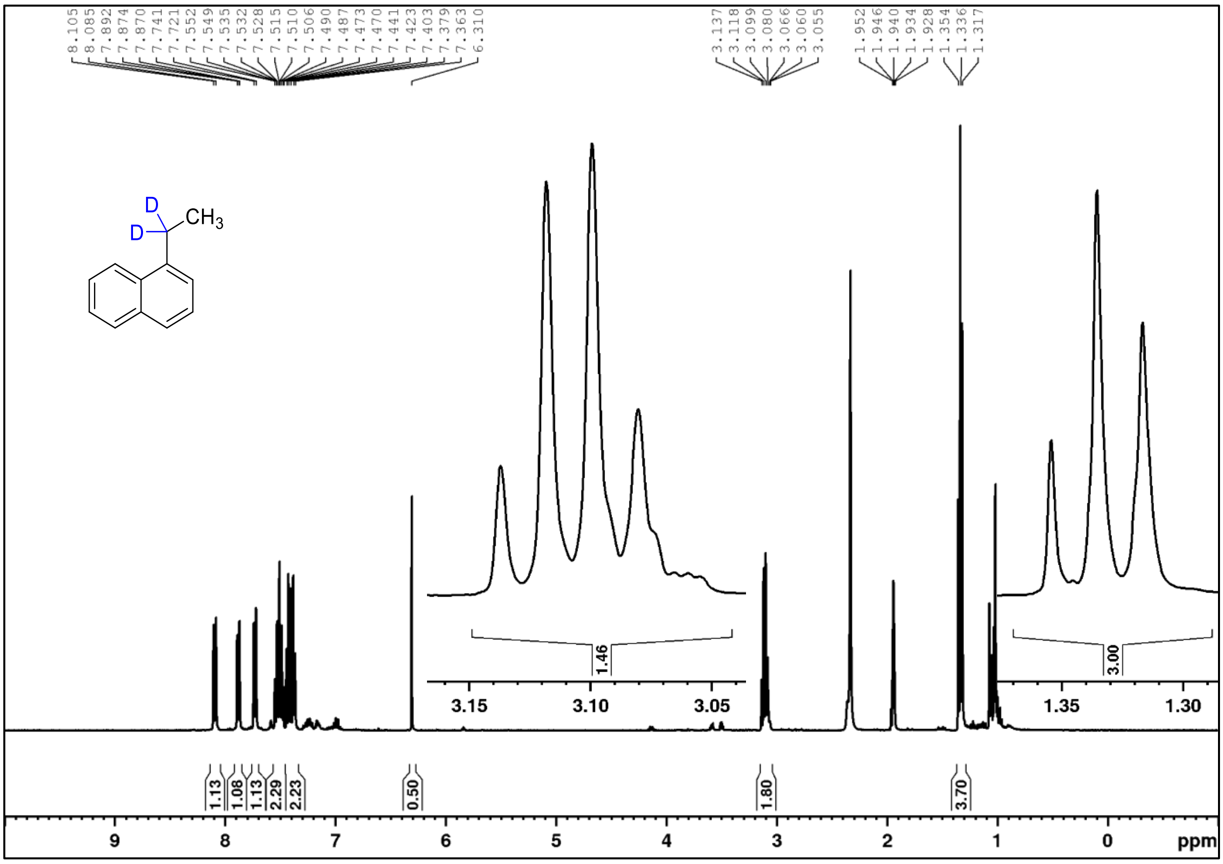
$^{1}$H NMR (400 MHz, CD$_3$CN)



**2p-$d_2$** $^1$H NMR (400 MHz, CD$_3$CN)

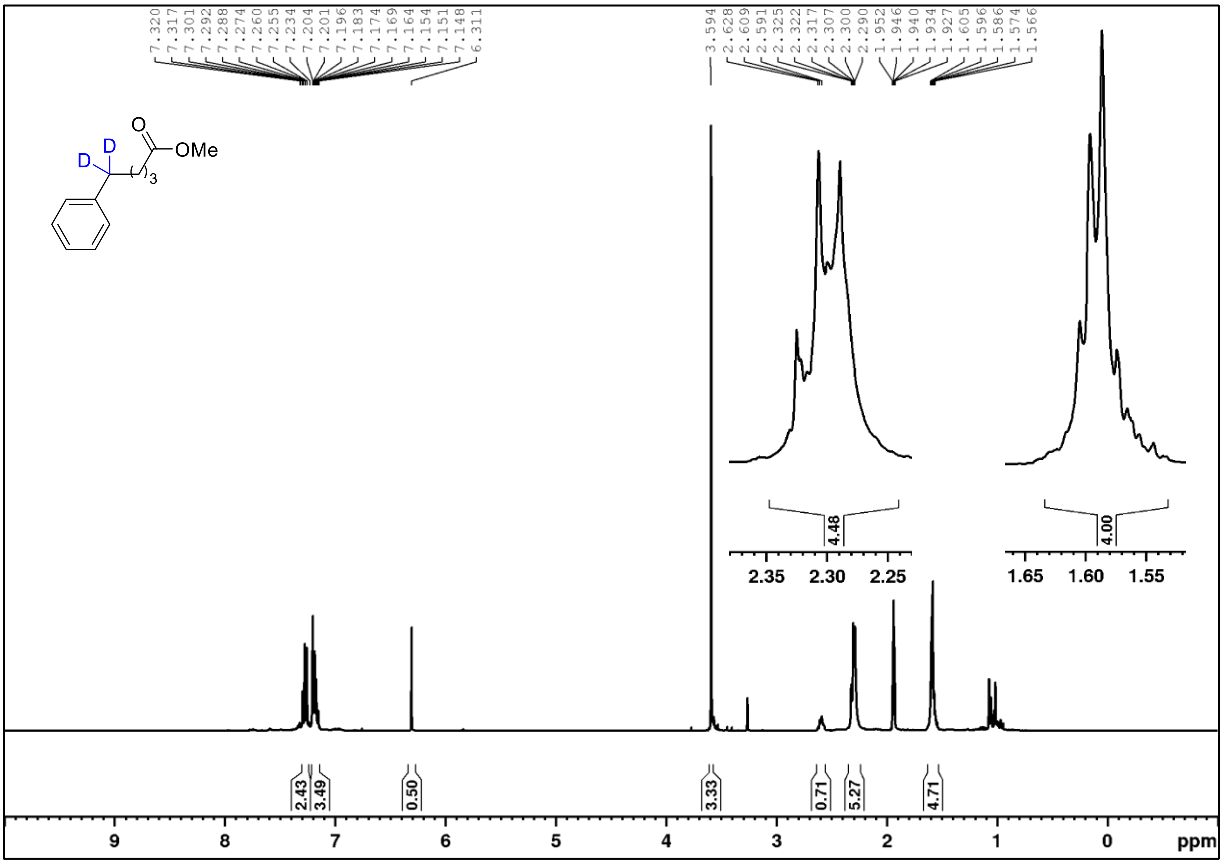


**2q-$d_2$** $^1$H NMR (400 MHz, CD$_3$CN)



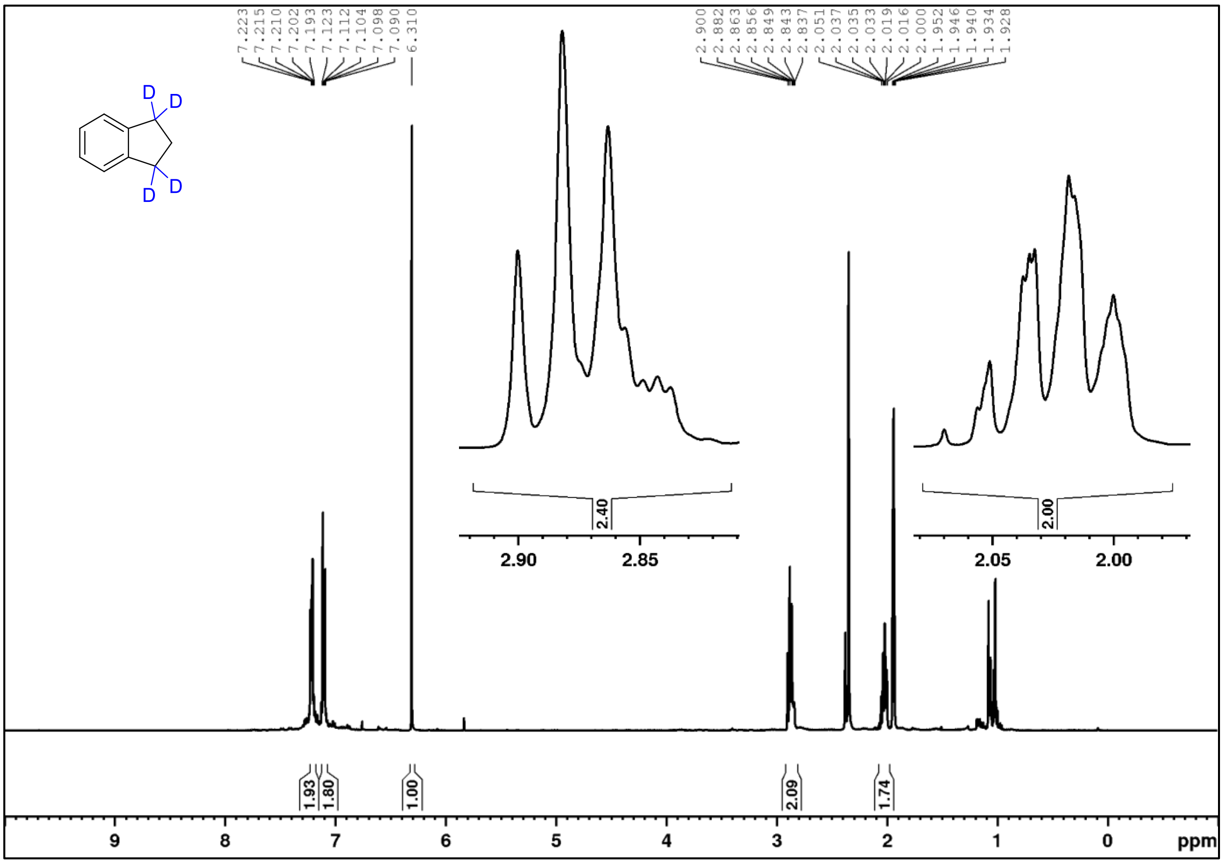
**2s-$d_2$**

$^1$H NMR (400 MHz, $CD_3CN$)

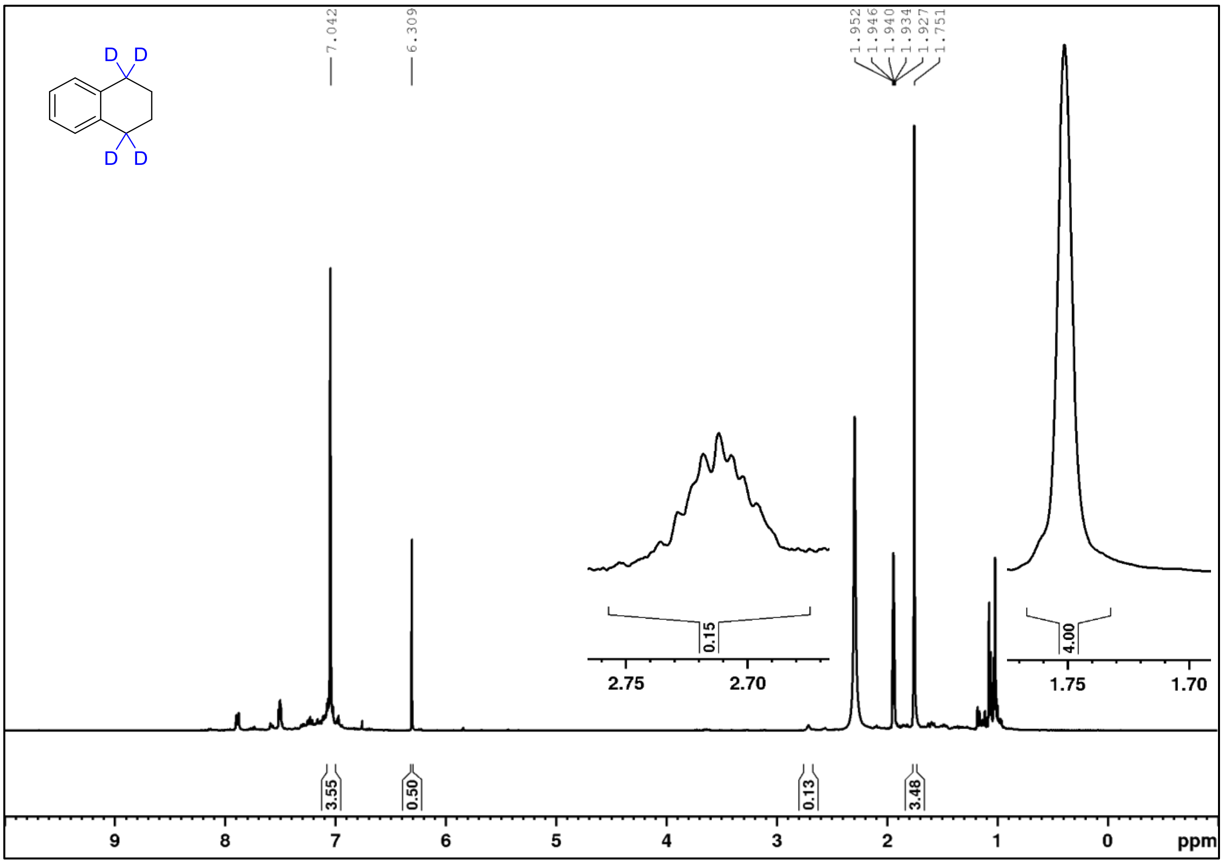


**3a-$d_4$**

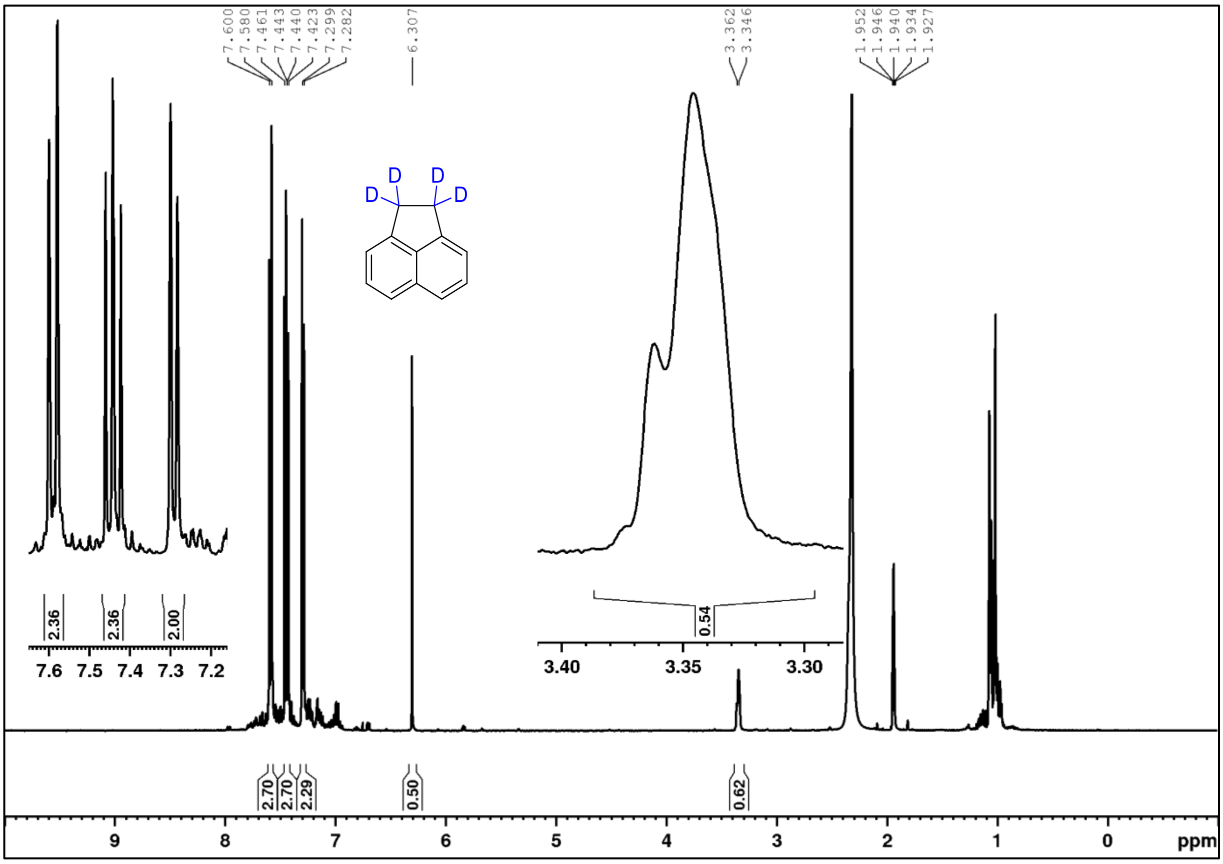
$^1$H NMR (400 MHz, $CD_3CN$)



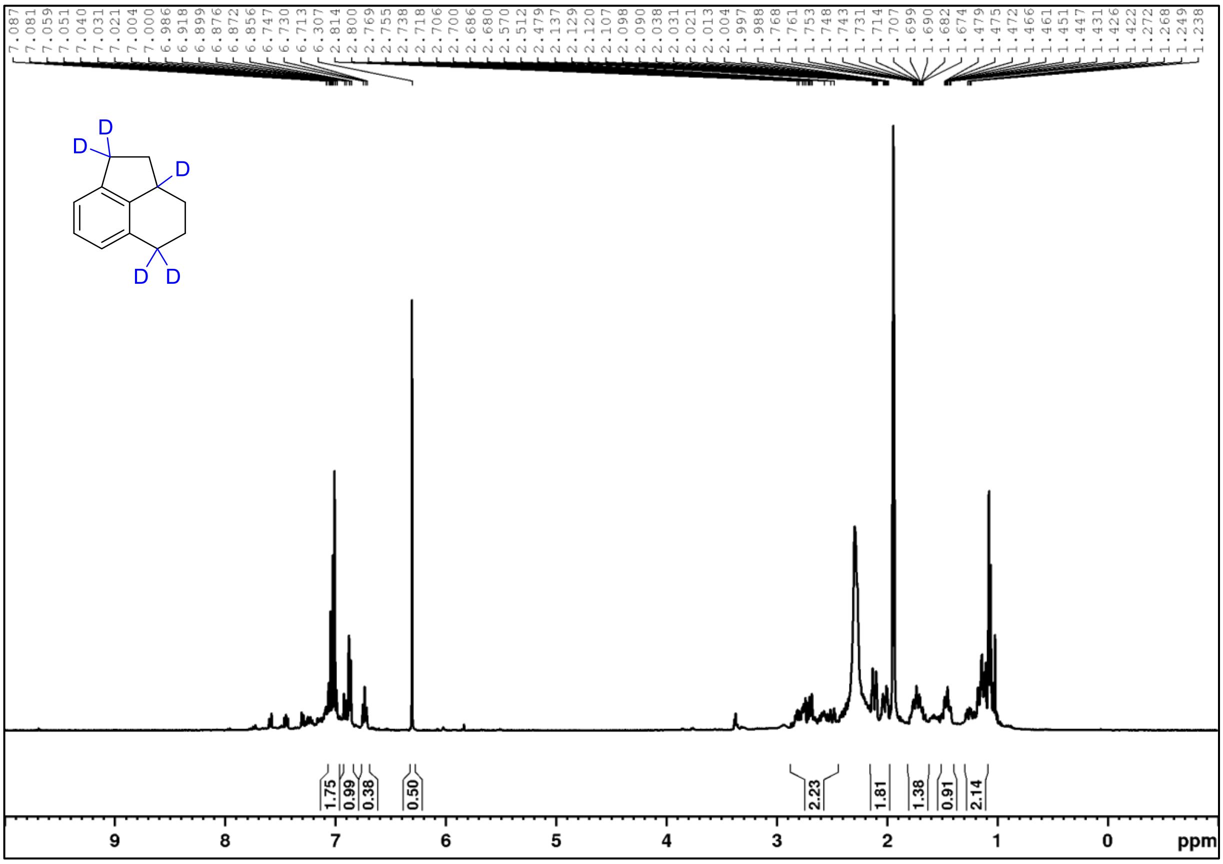
**3b-$d_4$** $^1$H NMR (400 MHz, $CD_3CN$)



**3d-$d_4$** $^1$H NMR (400 MHz, $CD_3CN$)

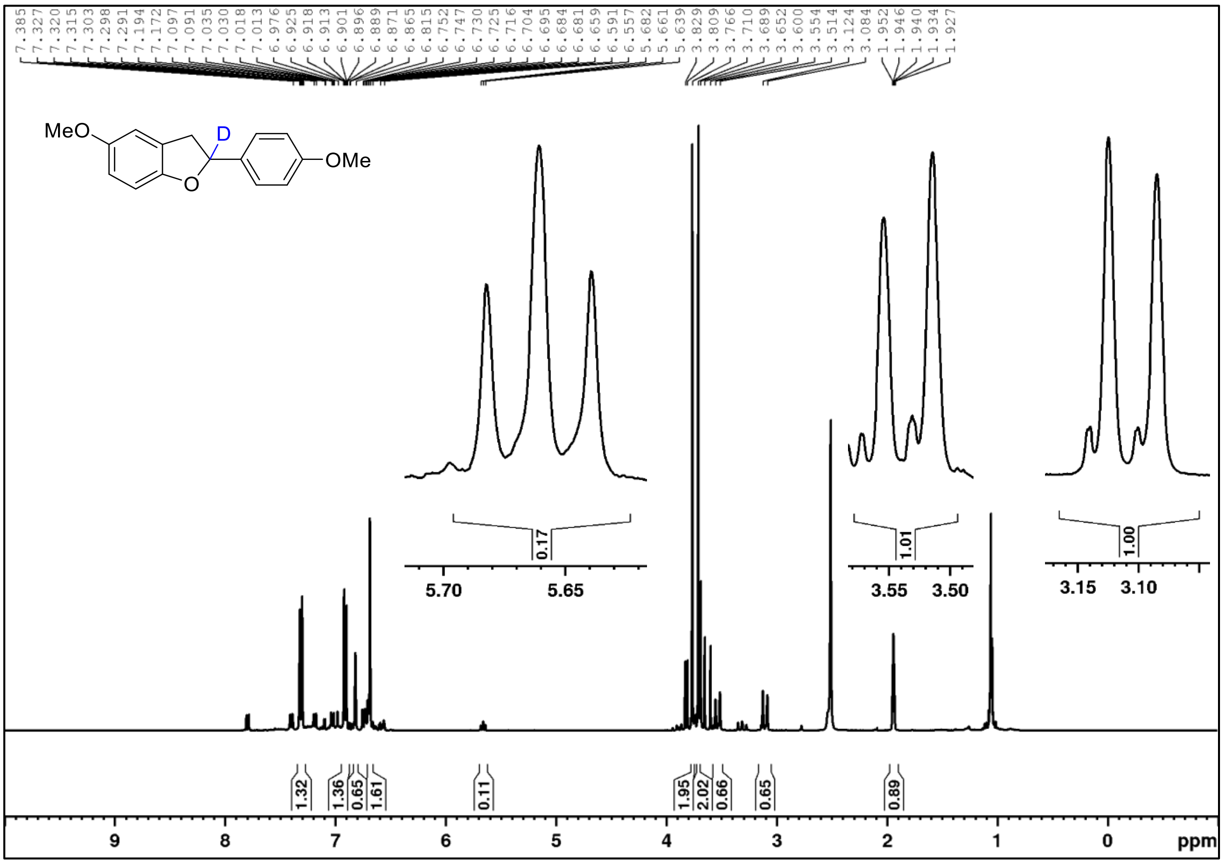


**3e-*d*$_5$** $^1$H NMR (400 MHz, $CD_3CN$)



$^1$H and $^{13}$C NMR of this compound can be found in section 11.2.

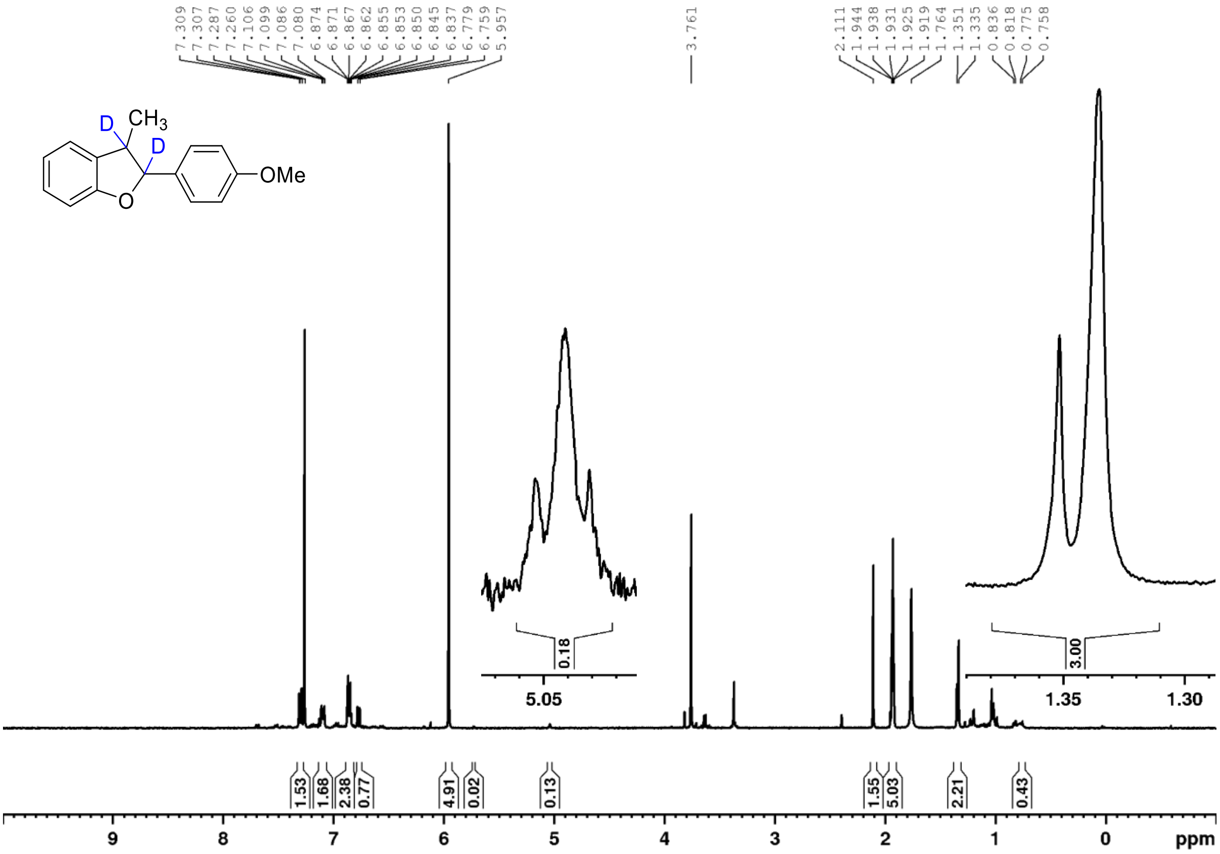
**4b-$d_1$** $^1$H NMR (400 MHz, $CD_3CN$)



NMR spectra of the isolated compound can be found in section 11.2.

**4c-$d_2$**

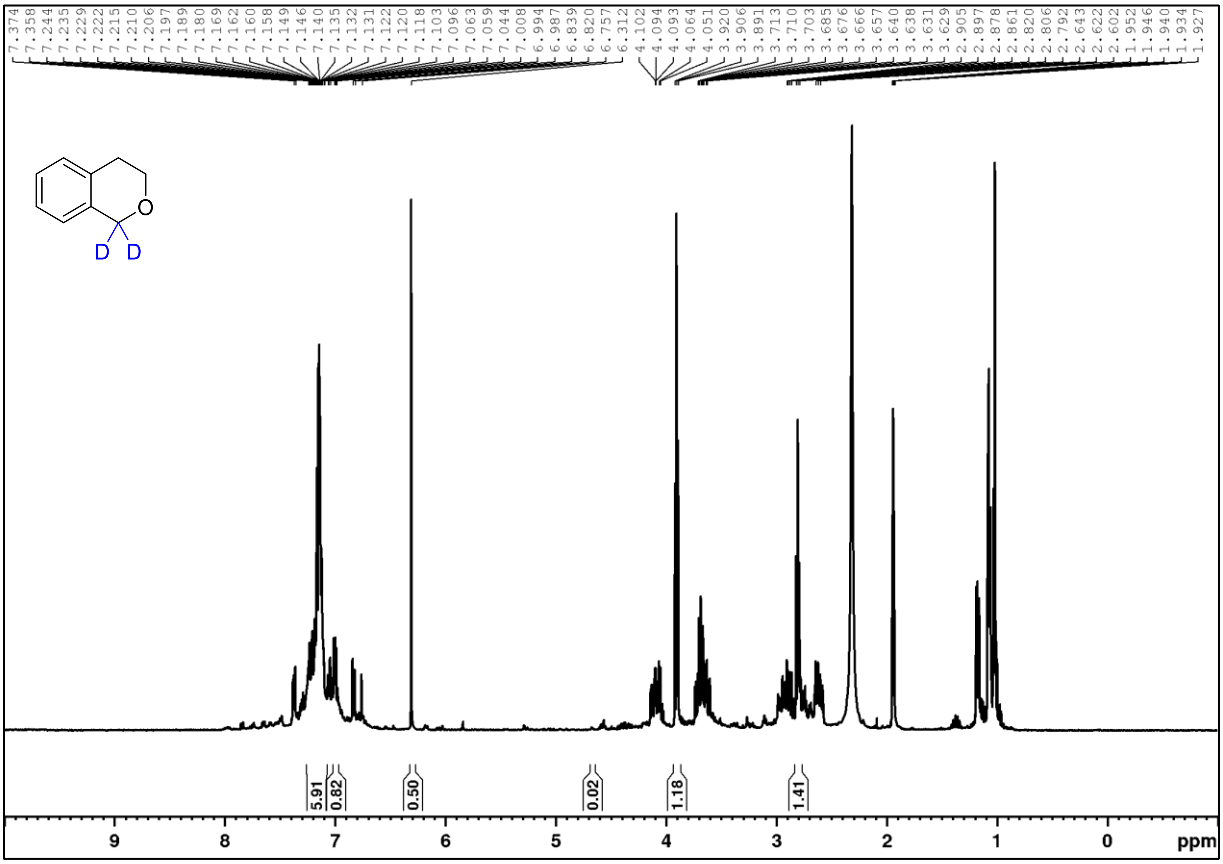
$^1$H NMR (400 MHz, CD$_3$CN)



This $^1$H NMR spectrum was part of the respective kinetics experiment in section 6. A 50 µL aliquot was taken after 1 h of irradiation and diluted with 500 µL CDCl$_3$. 1,1,2,2-tetrachloroethane was added as internal standard but the solvent residual signal of CD$_3$CN turned out to be more consistent.

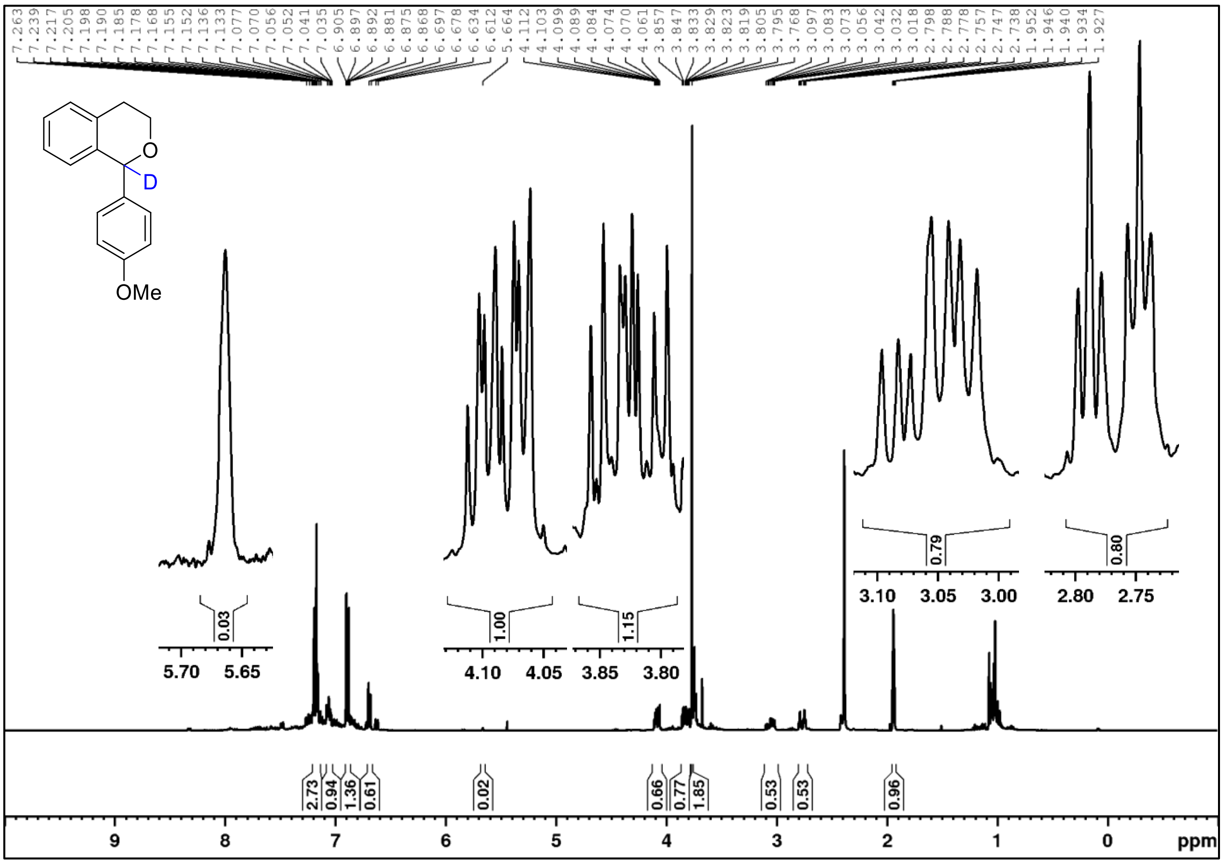
**5a-$d_2$**

$^1$H NMR (400 MHz, CD$_3$CN)



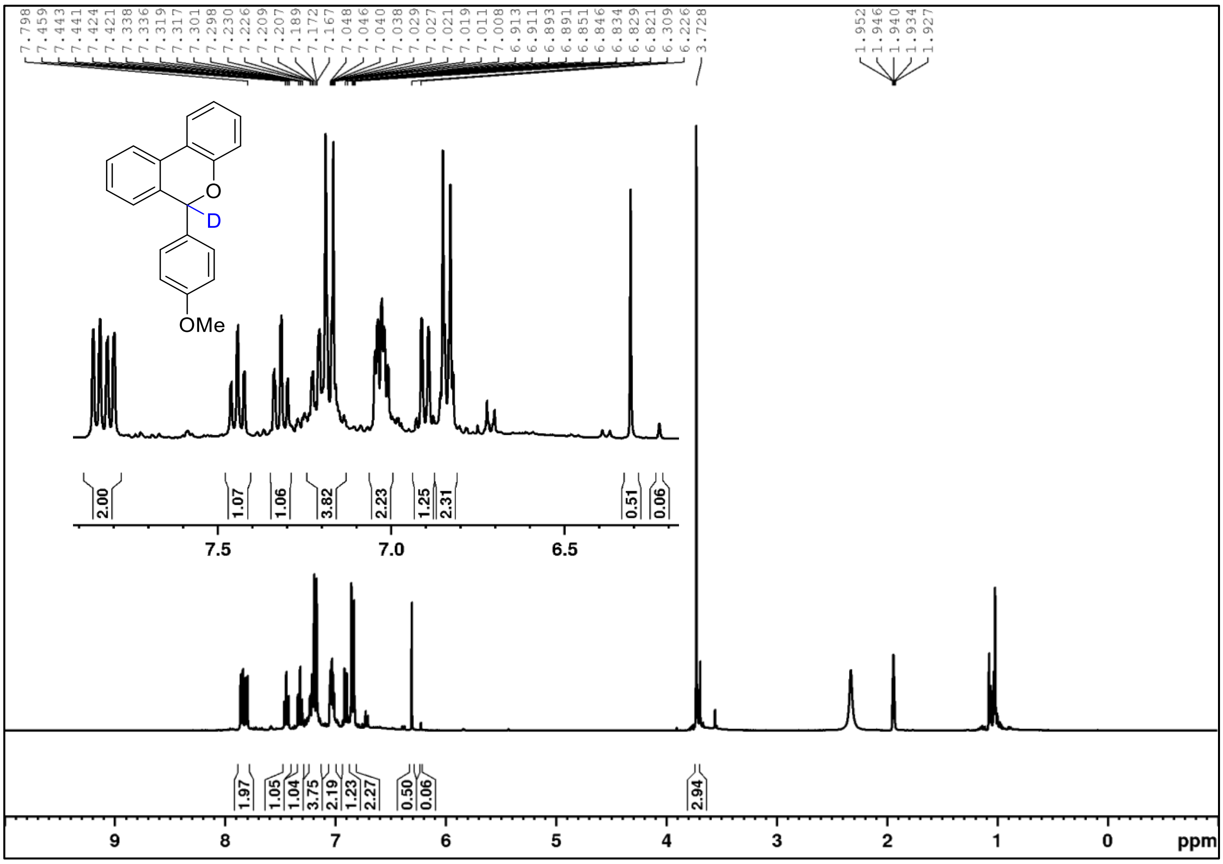
For spectra of the isolated compound see section 11.2.

**5b-$d_1$** $^1$H NMR (400 MHz, CD$_3$CN)



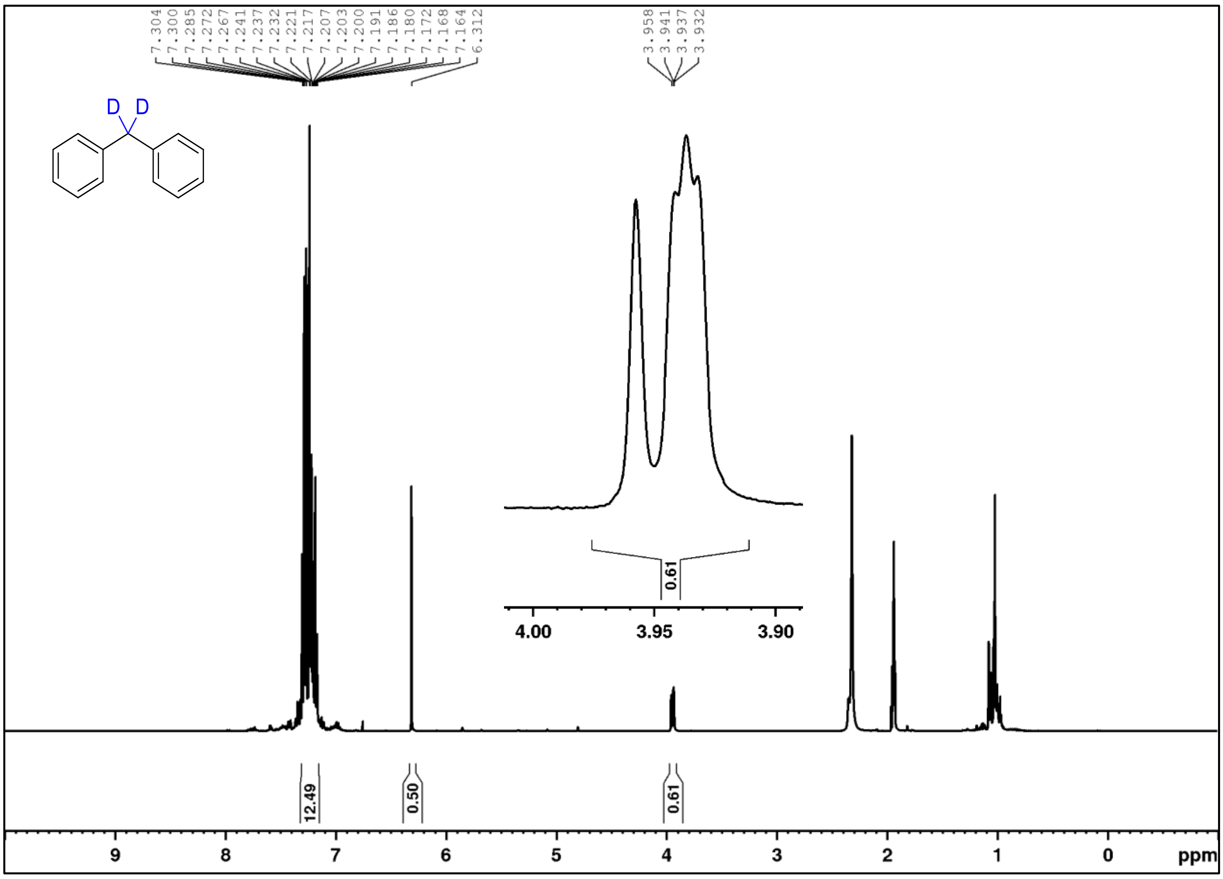
The solvent residual signal was used as internal standard. For spectra of the isolated compound see section 11.2.

**5c-$d_1$** $^1$H NMR (400 MHz, $CD_3CN$)

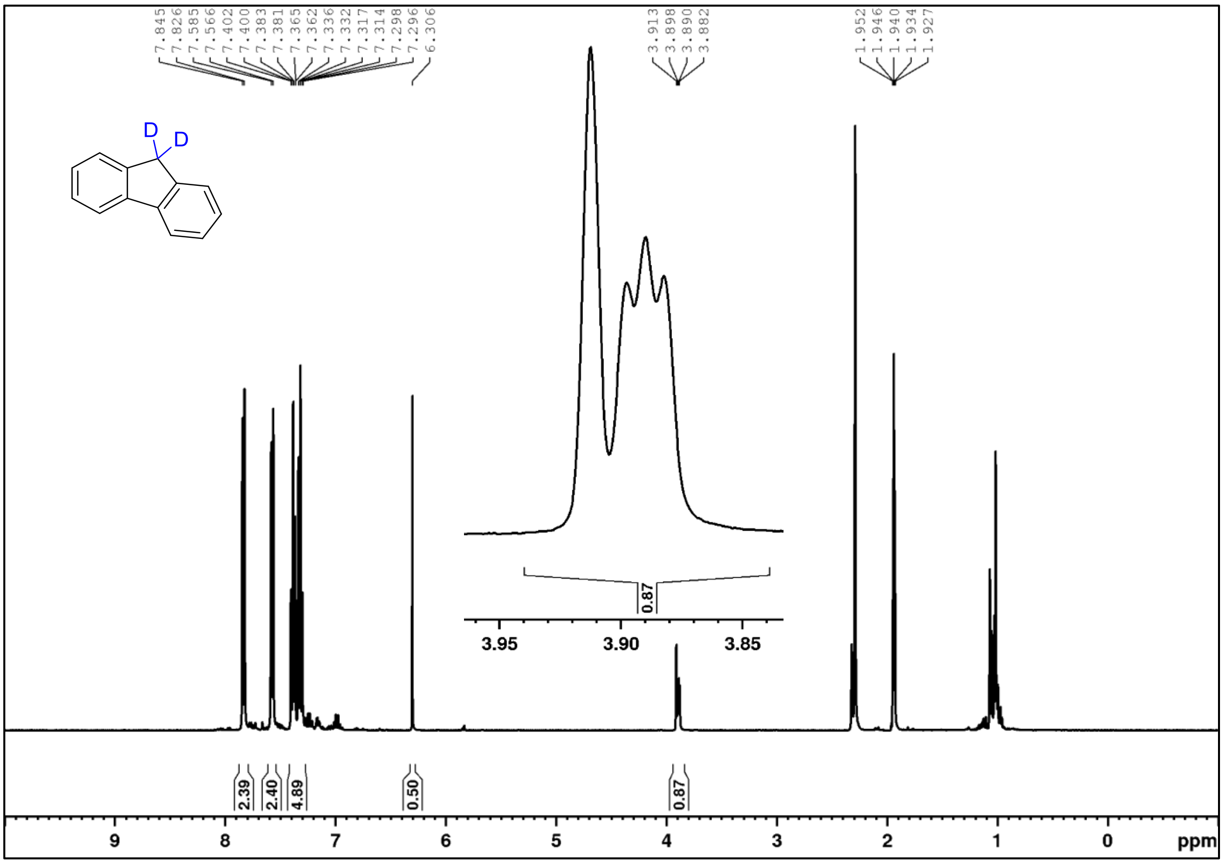


For spectra of the isolated compound see section 11.2.

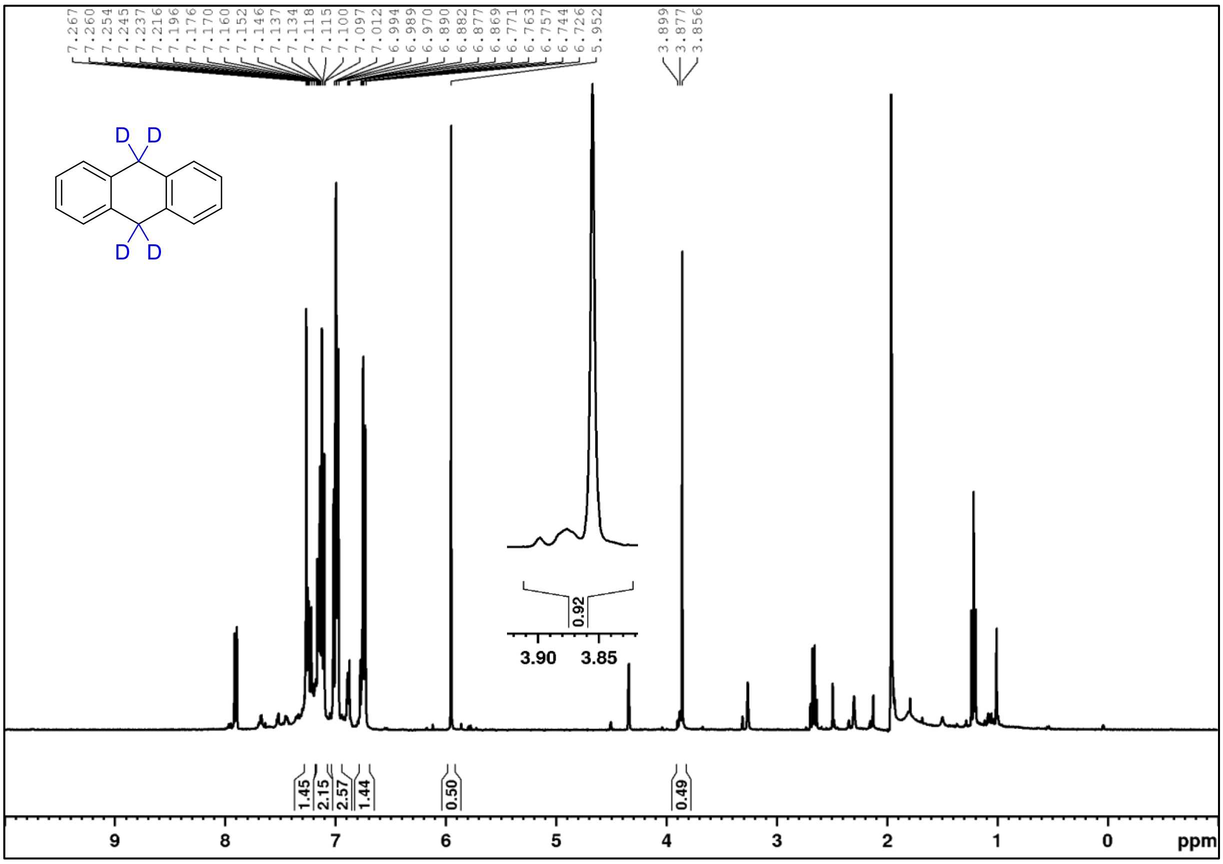
**6a-$d_2$** $^1$H NMR (400 MHz, $CD_3CN$)



**6c-$d_2$** $^1$H NMR (400 MHz, $CD_3CN$)

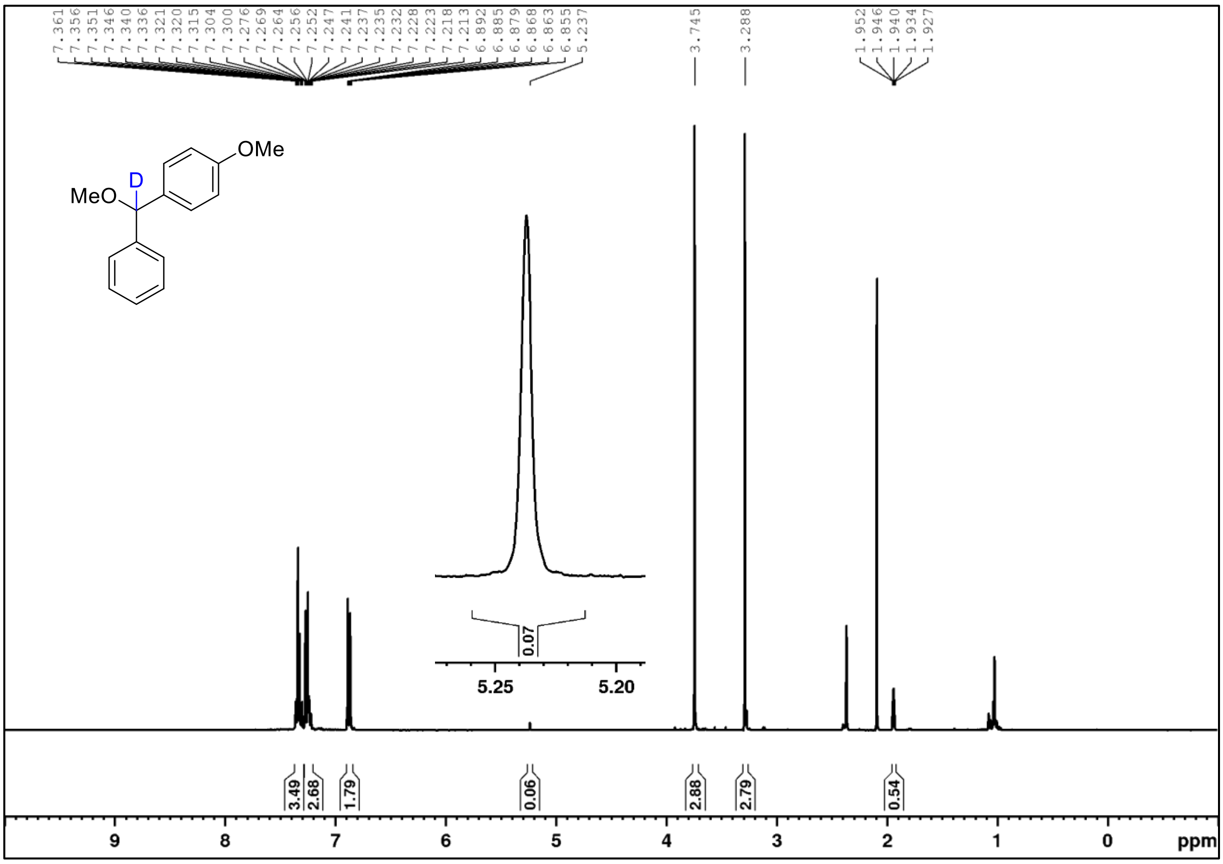


**6d-$d_4$** $^1$H NMR (400 MHz, CDCl$_3$)



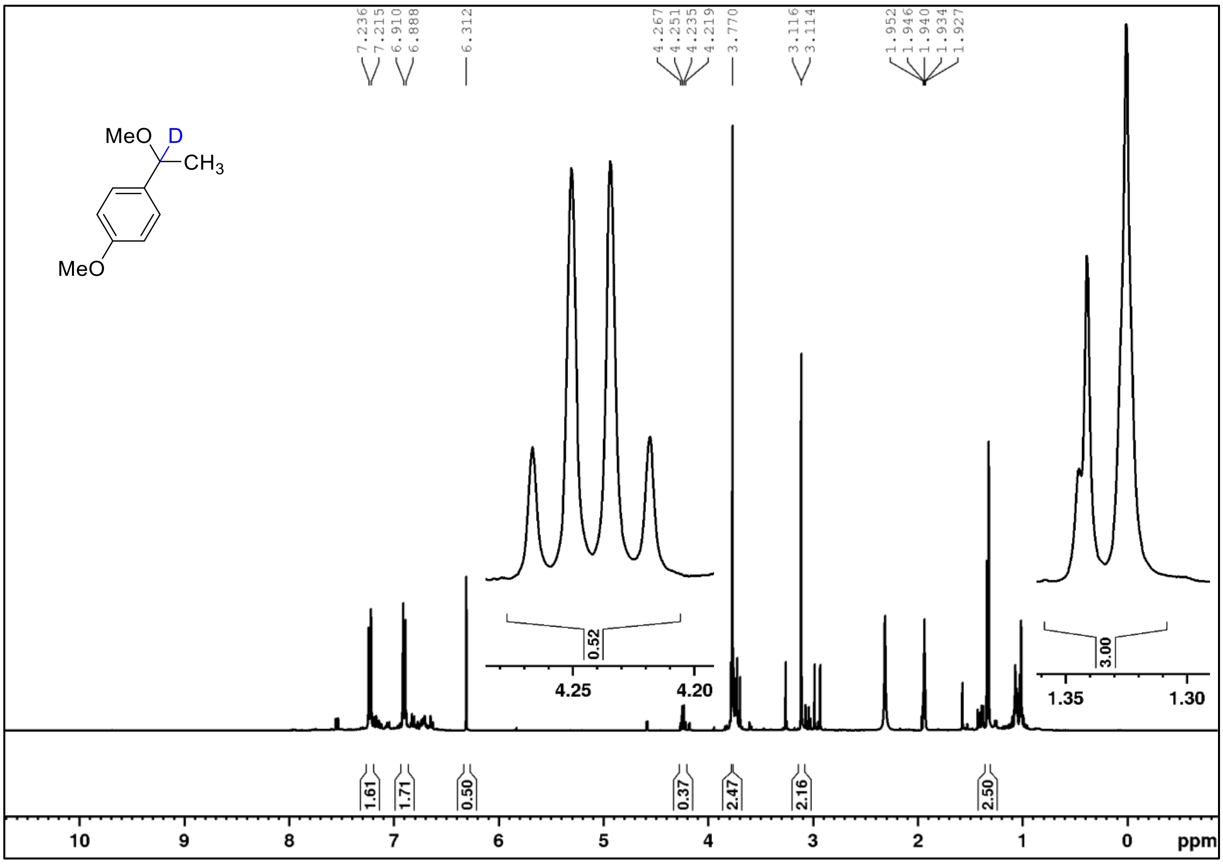
Due to low solubility of compound **6d** in CD$_3$CN the solvent was removed under reduced pressure and the crude product redissolved in CDCl$_3$ with 1,1,2,2-tetrachloroethane as internal standard.

**7a-*d*$_1$** $^1$H NMR (400 MHz, $CD_3CN$)



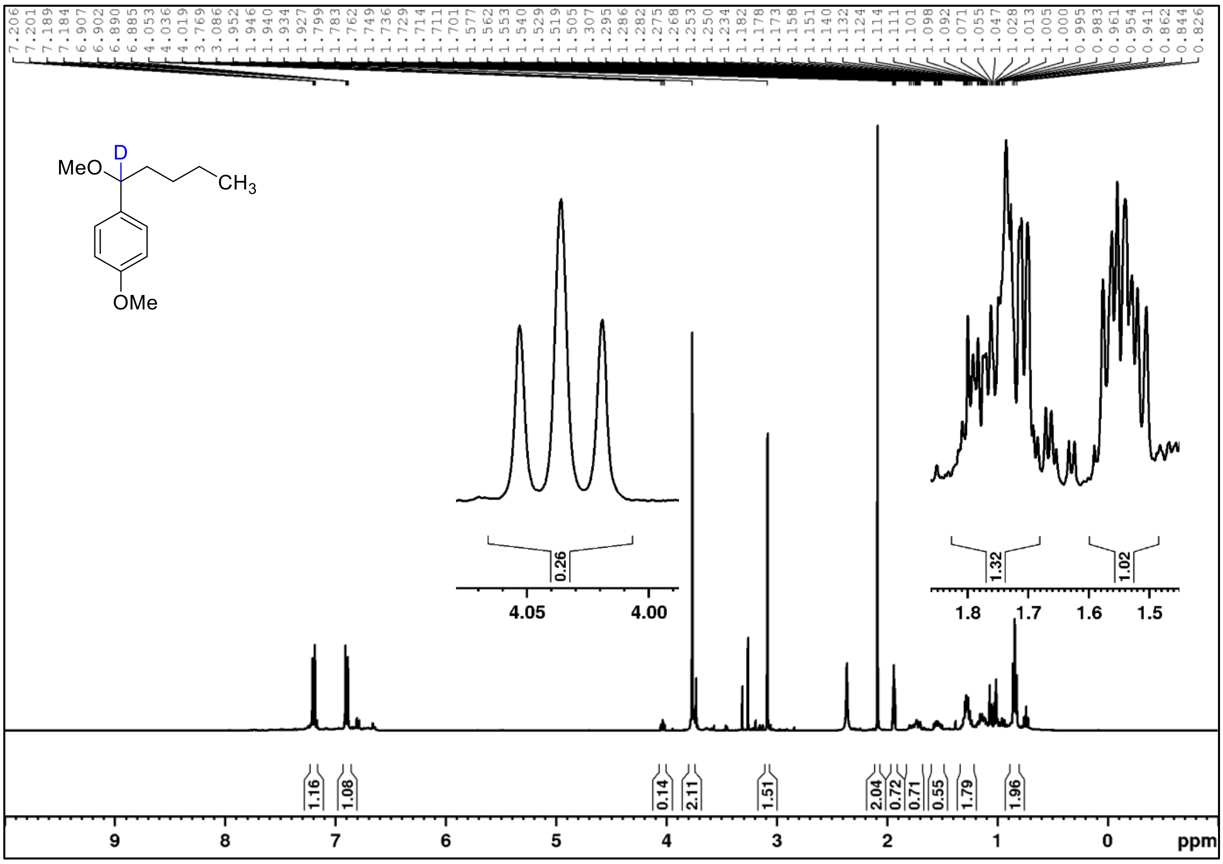
The solvent residual signal was used as internal standard. For spectra of the isolated compound see section 11.2.

**7b-$d_1$** $^1$H NMR (400 MHz, $CD_3CN$)



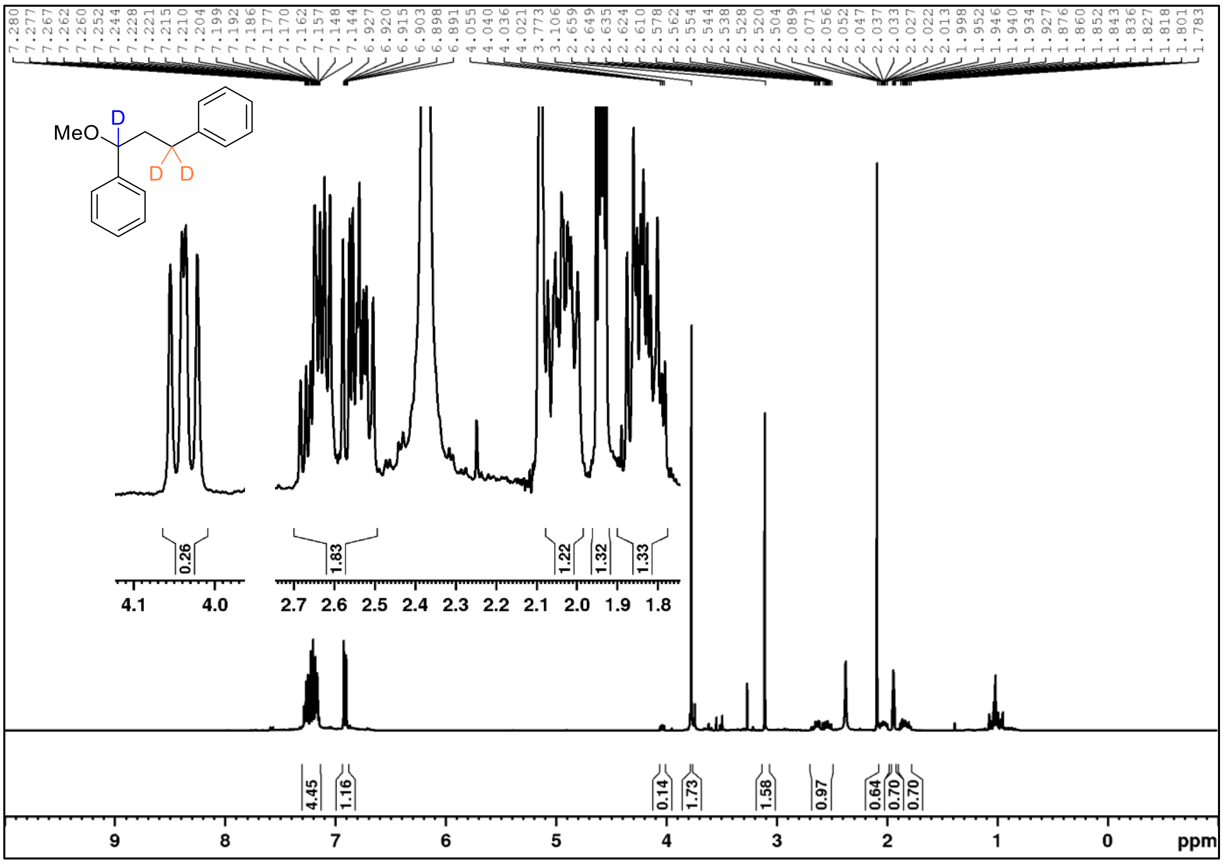
For spectra of the isolated compound see section 11.2.

**7c-*d*$_1$** $^1$H NMR (400 MHz, $CD_3CN$)



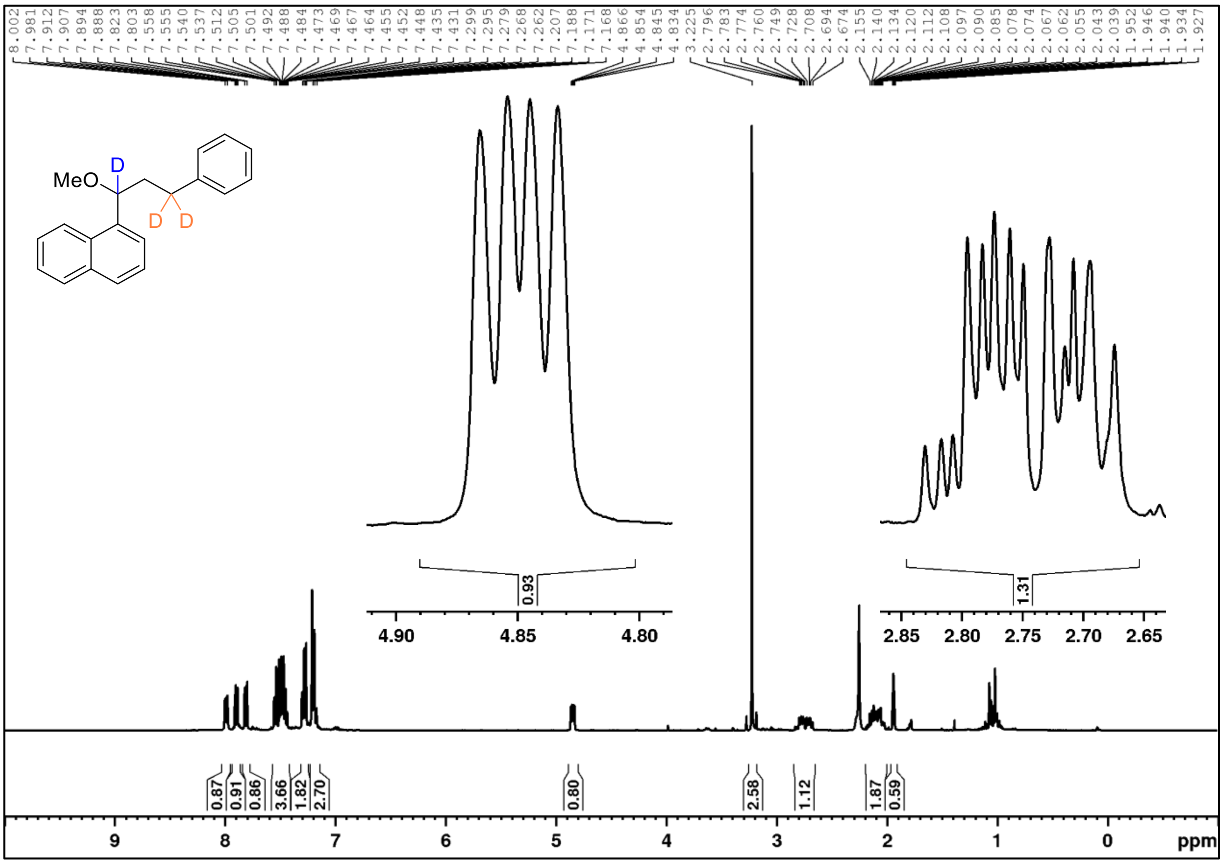
The solvent residual signal was used as internal standard.

**7f-$d_1$** $^1$H NMR (400 MHz, $CD_3CN$)



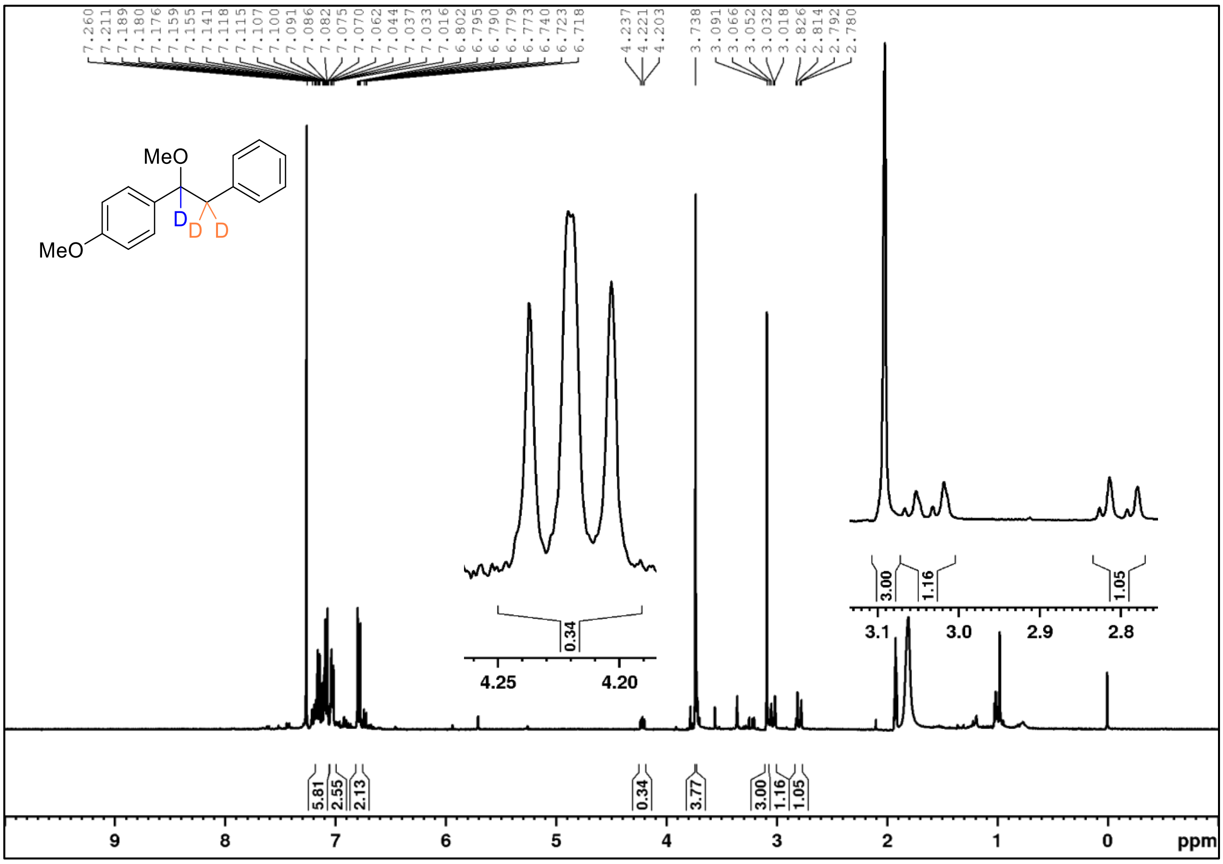
The solvent residual signal was used as internal standard. For spectra of the isolated compound see section 11.2.

**7i-$d_1$** $^1$H NMR (400 MHz, $CD_3CN$)



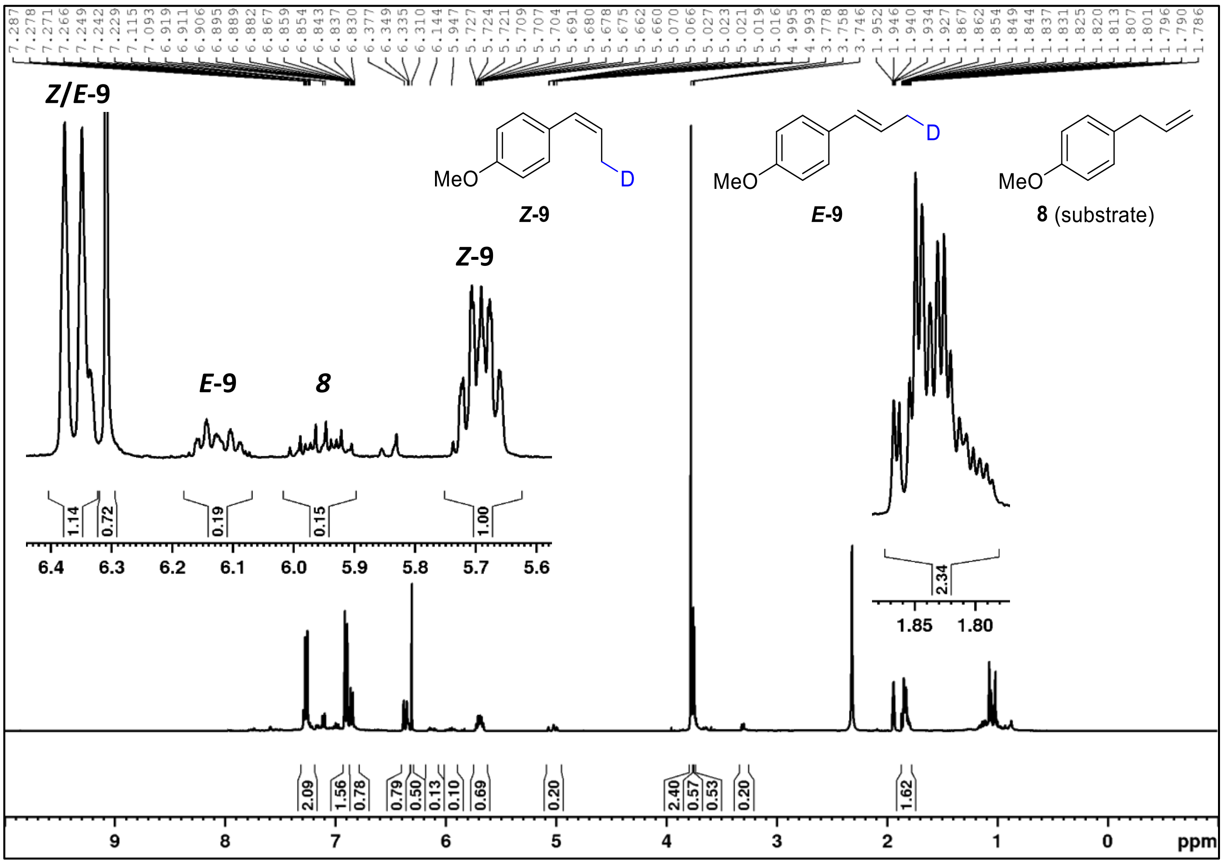
The solvent residual signal was used as internal standard.

**7k-*d*$_1$** $^1$H NMR (400 MHz, CDCl$_3$)



Crude product redissolved in CDCl$_3$ after evaporation of the solvent CH$_3$CN. The yield was not determined.

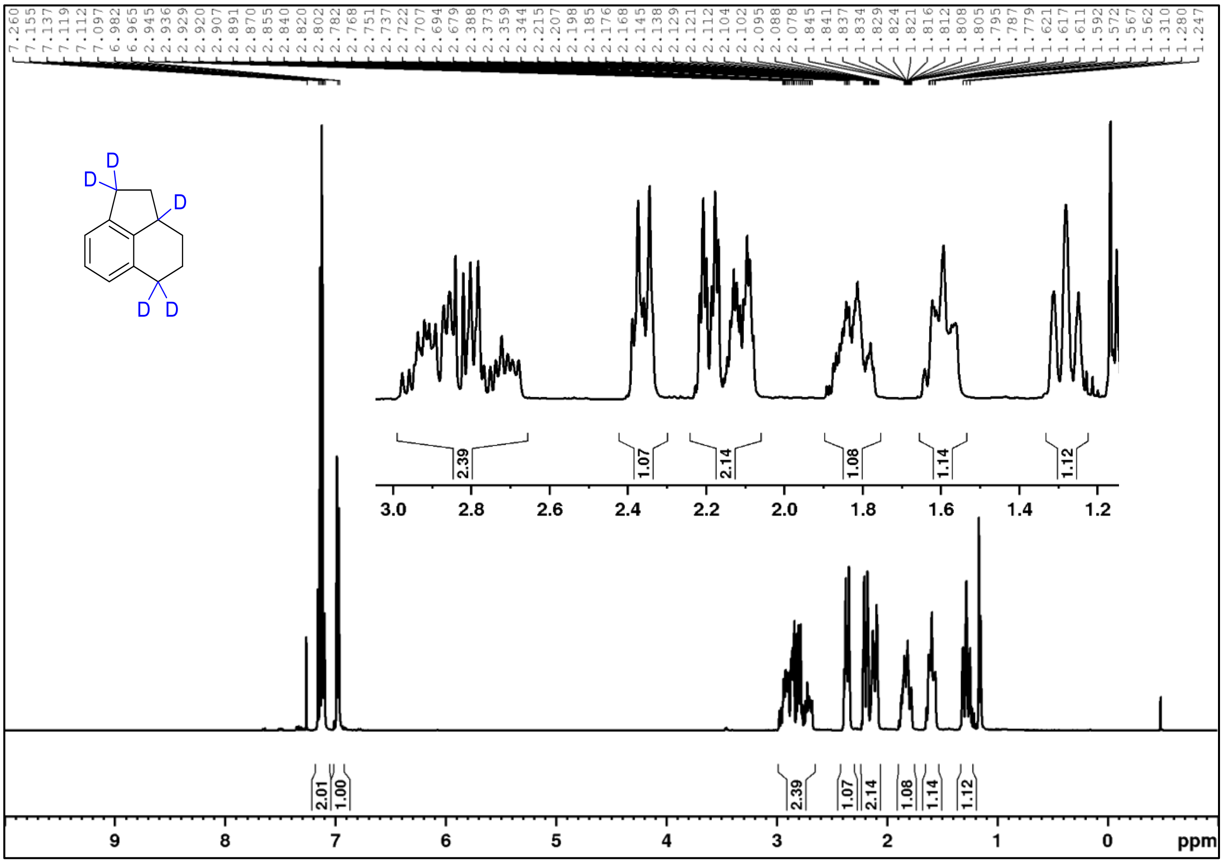
**9 (*Z*/*E* = 5:1)** $^1$H NMR (400 MHz, CD$_3$CN)



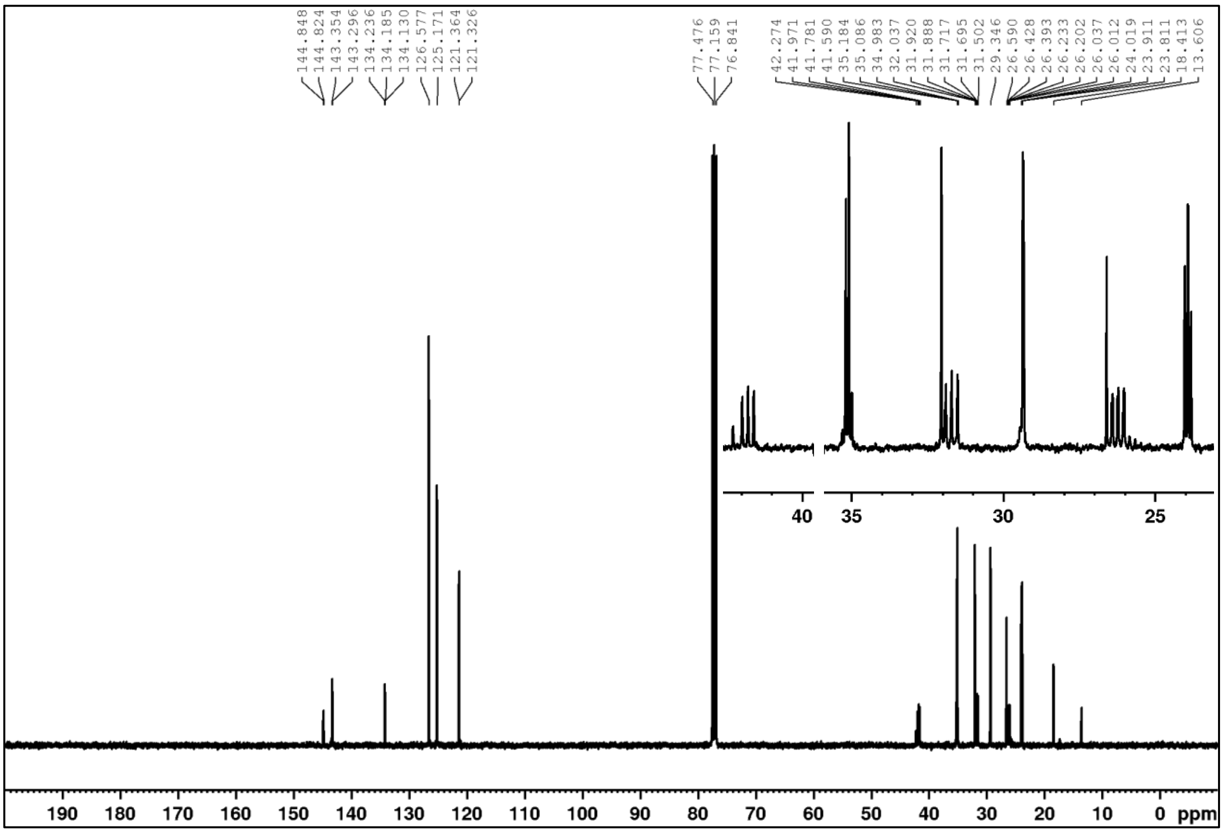
## 11.2 NMR-spectra of isolated deuterated compounds

**1,2,2a,3,4,5-hexahydroacenaphthylene-1,1,2a,5,5-$d_5$ (3e-$d_5$)**

$^1$H NMR (400 MHz, CDCl$_3$)

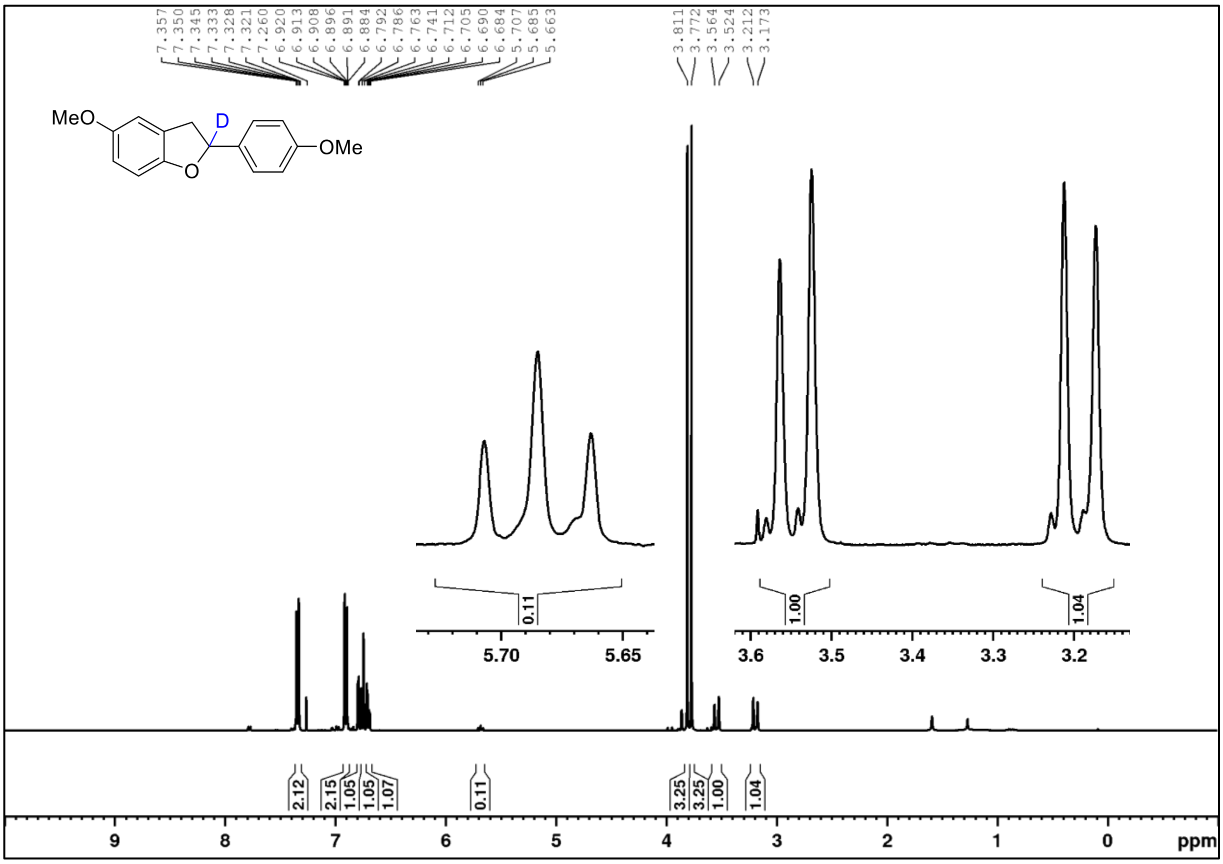


$^{13}$C NMR (101 MHz, CDCl$_3$)

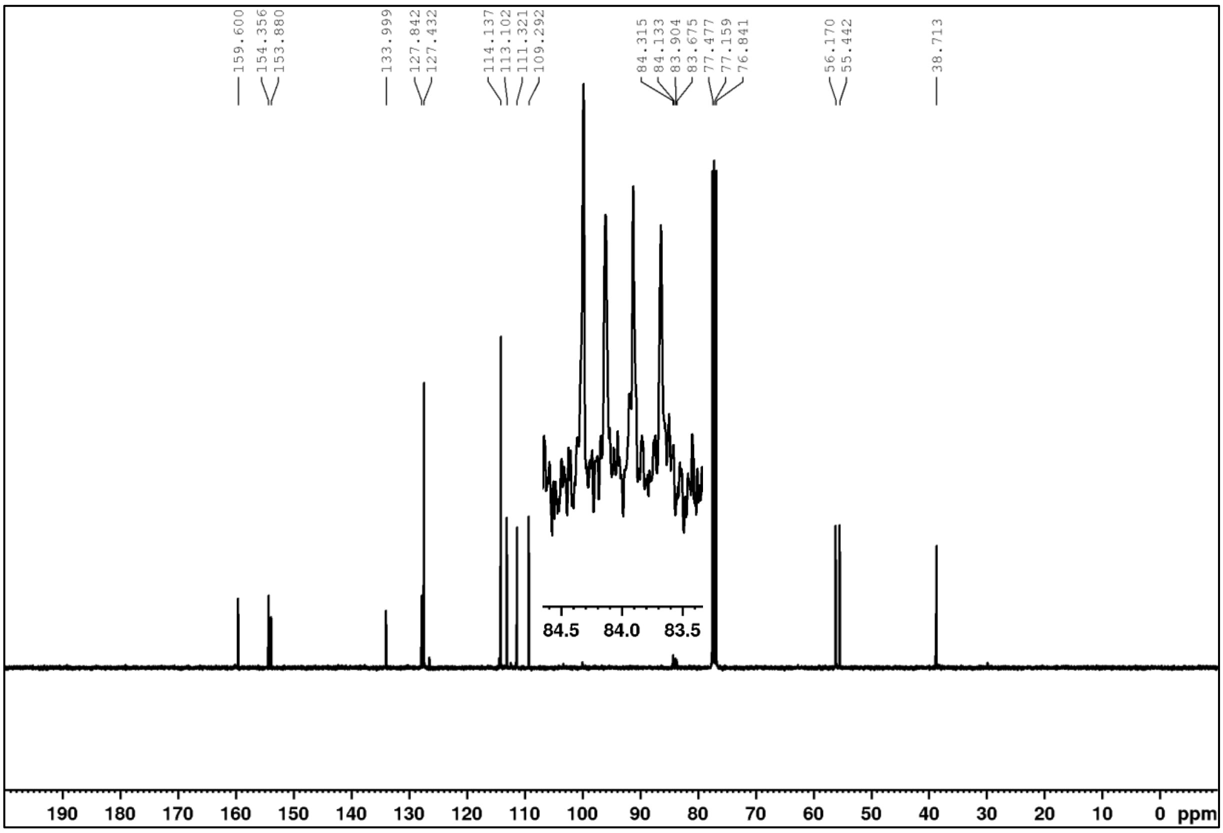


**5-Methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-2-*d* (4b-*d*$_1$)**

$^1$H NMR (400 MHz, CDCl$_3$)

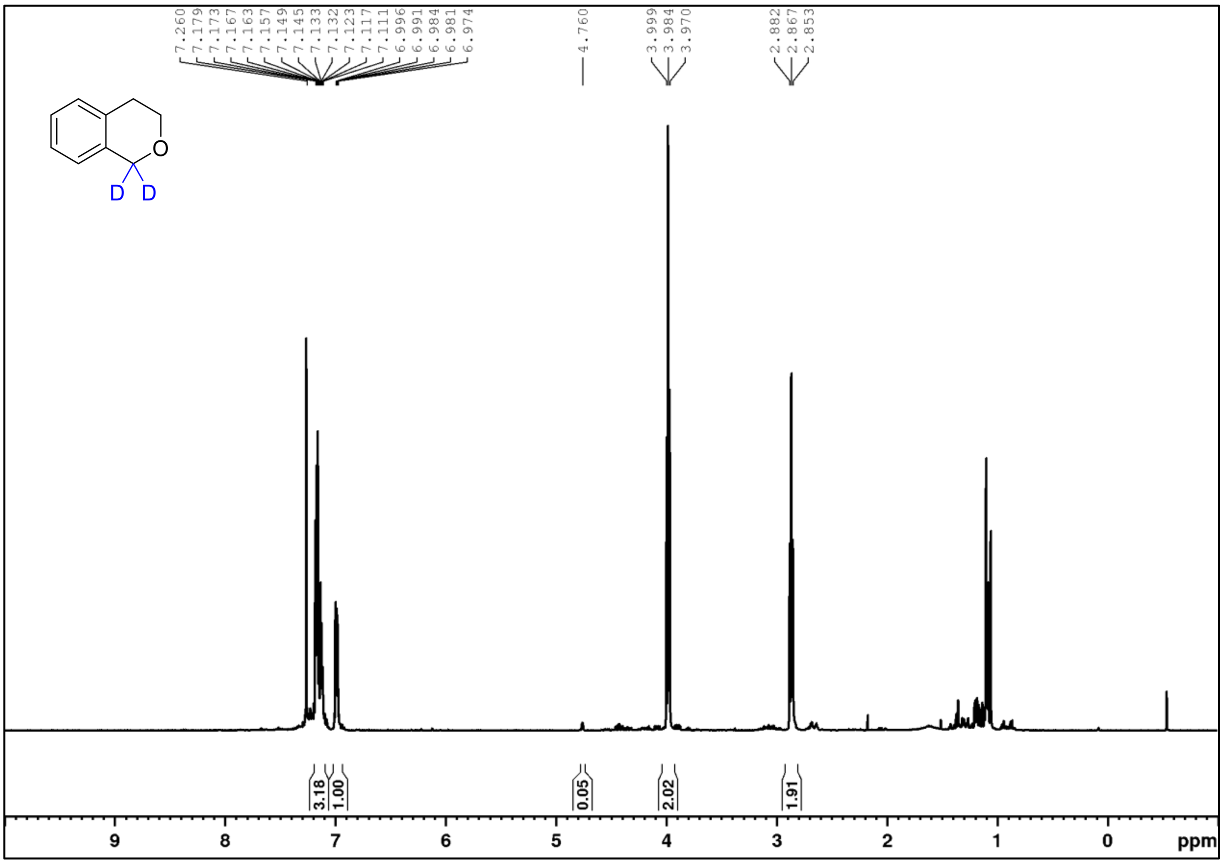


$^{13}$C NMR (101 MHz, CDCl$_3$)

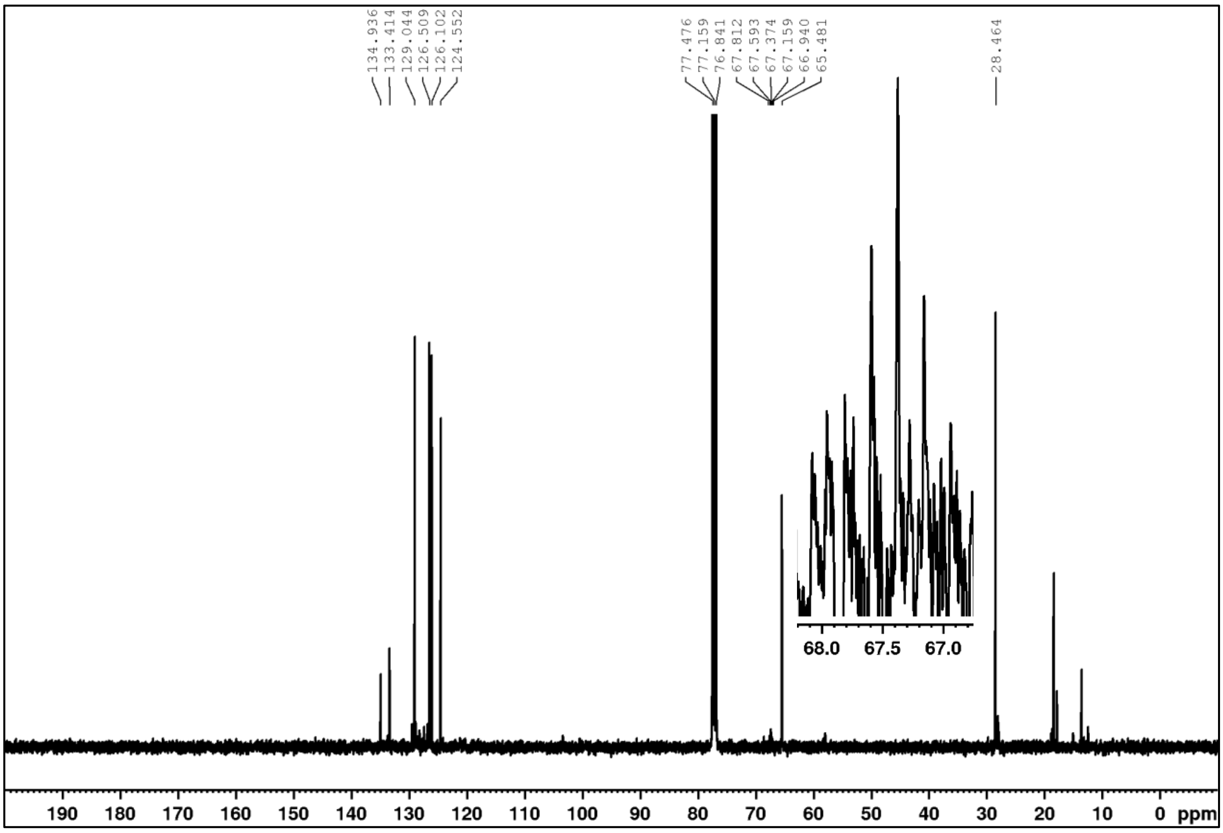


**Isochromane-1,1-$d_2$ (5a-$d_2$)**

$^1$H NMR (400 MHz, $CDCl_3$)

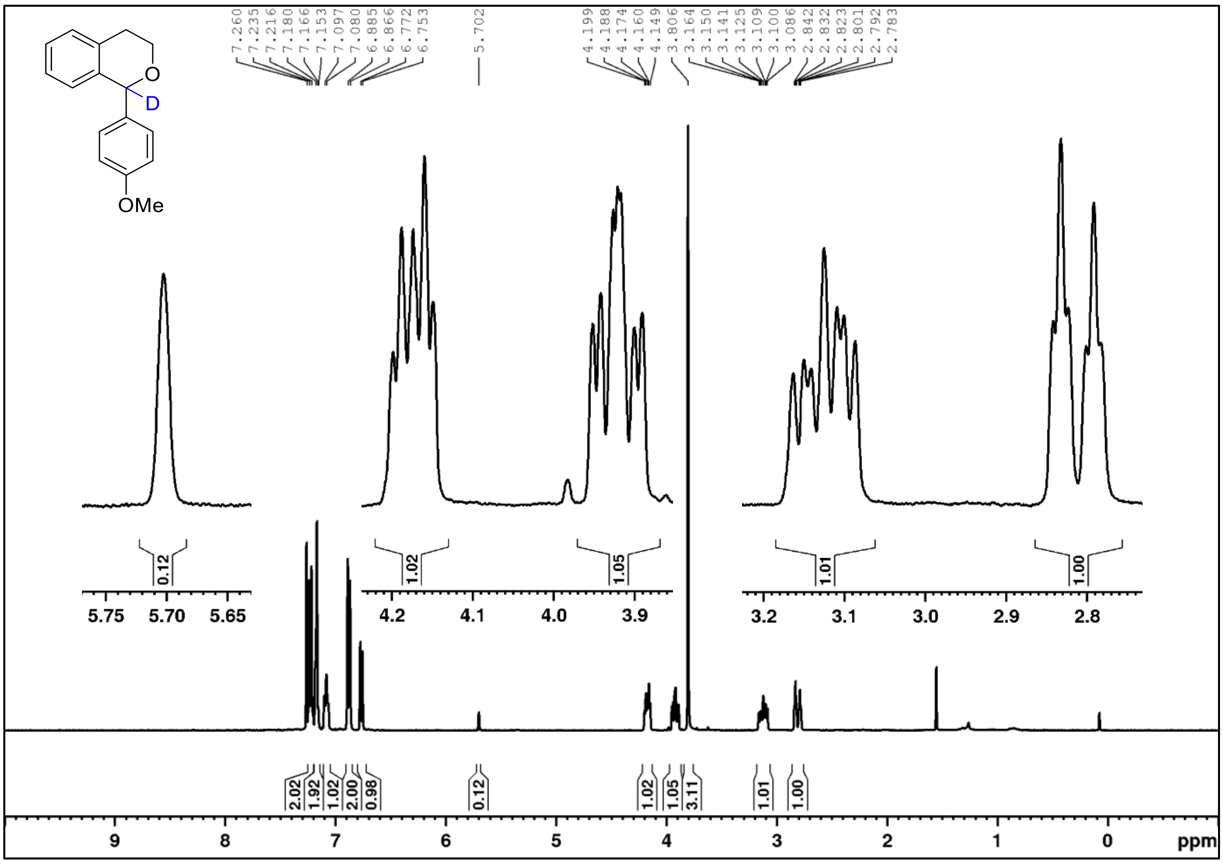


$^{13}$C NMR (101 MHz, $CDCl_3$)

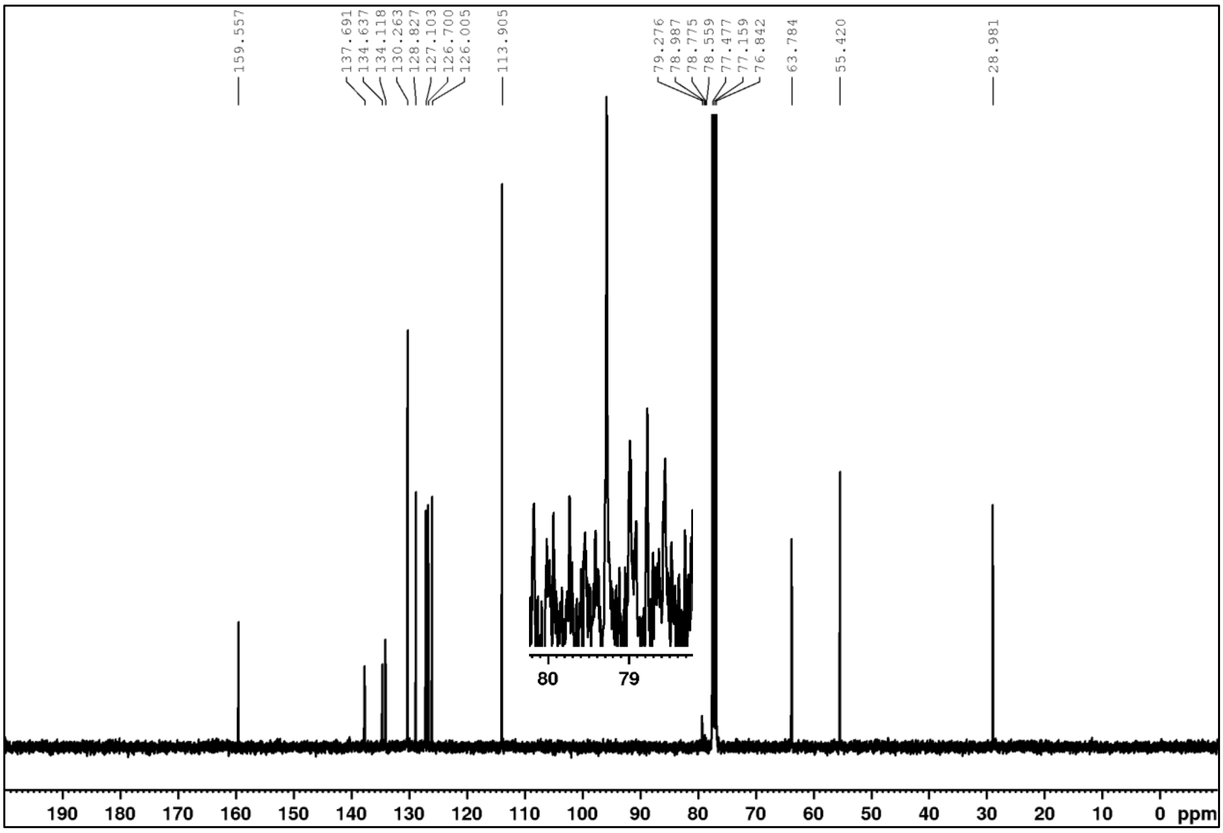


**1-(4-methoxyphenyl)isochromane-1-*d* (5b-$d_1$)**

$^1$H NMR (400 MHz, CDCl$_3$)

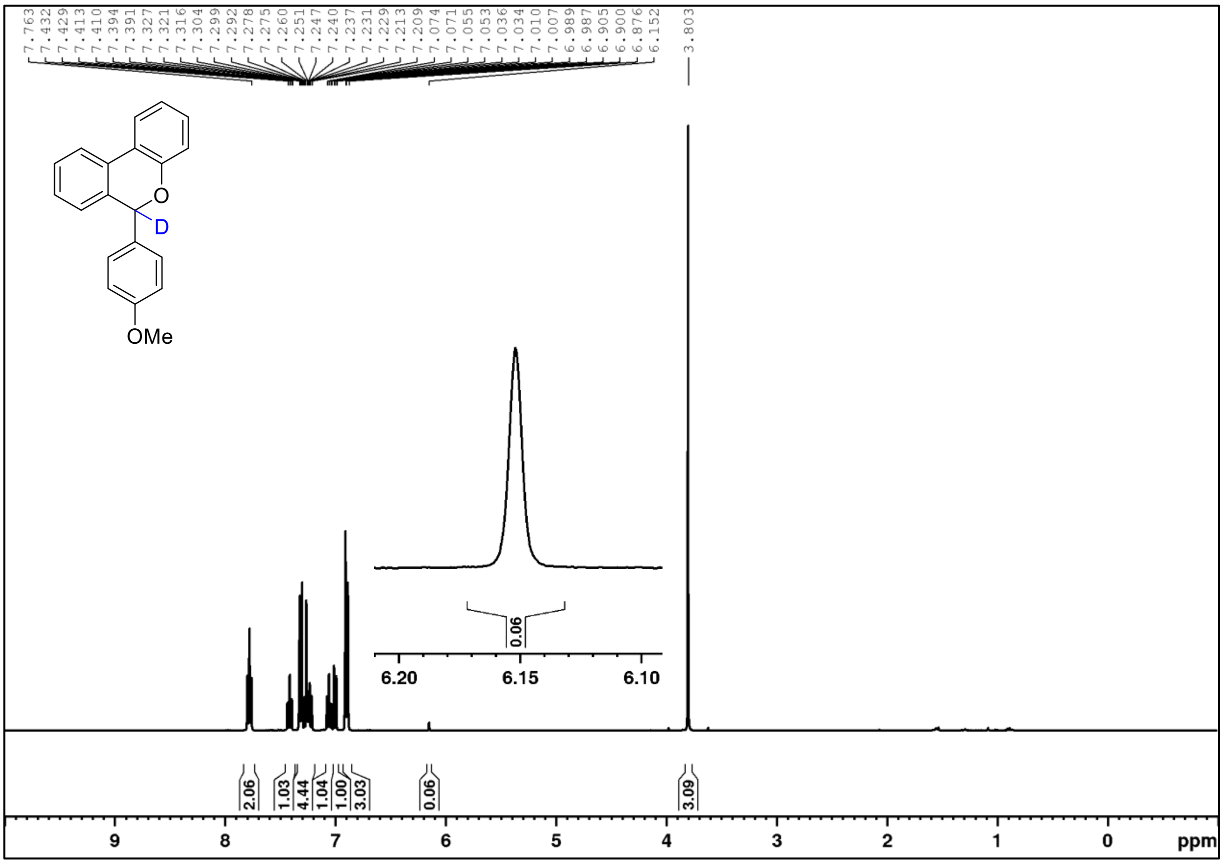


$^{13}$C NMR (101 MHz, CDCl$_3$)

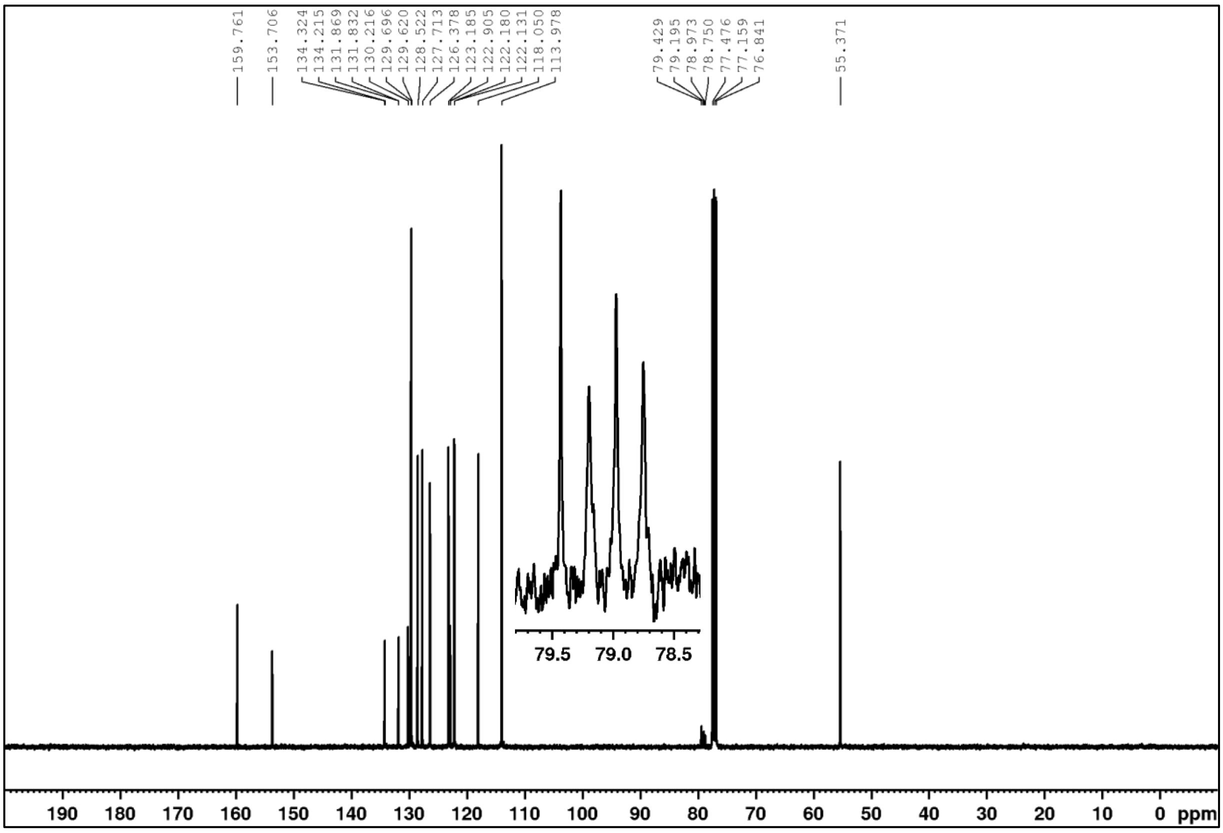


**6-(4-methoxyphenyl)-6H-benzo[c]chromene-6-*d* (5c-$d_1$)**

$^1$H NMR (400 MHz, $CDCl_3$)

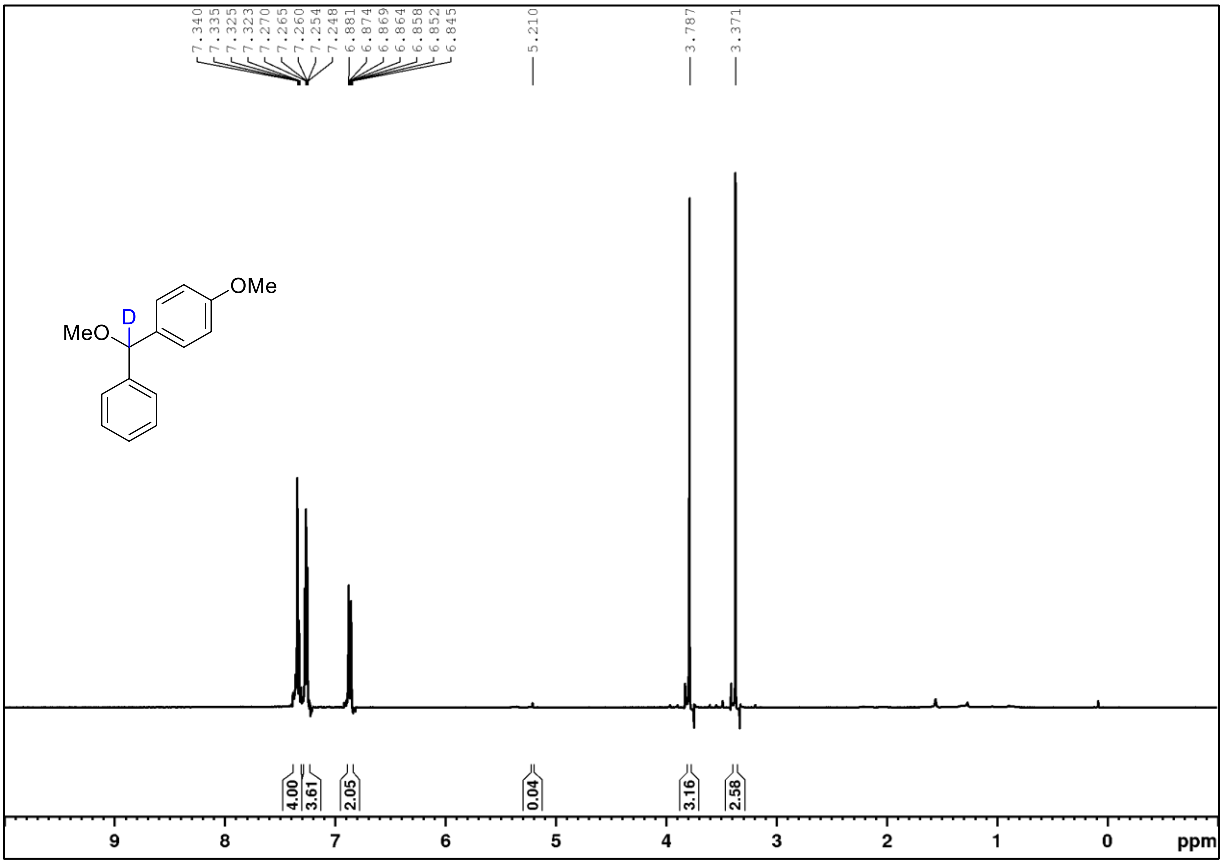


$^{13}$C NMR (101 MHz, $CDCl_3$)

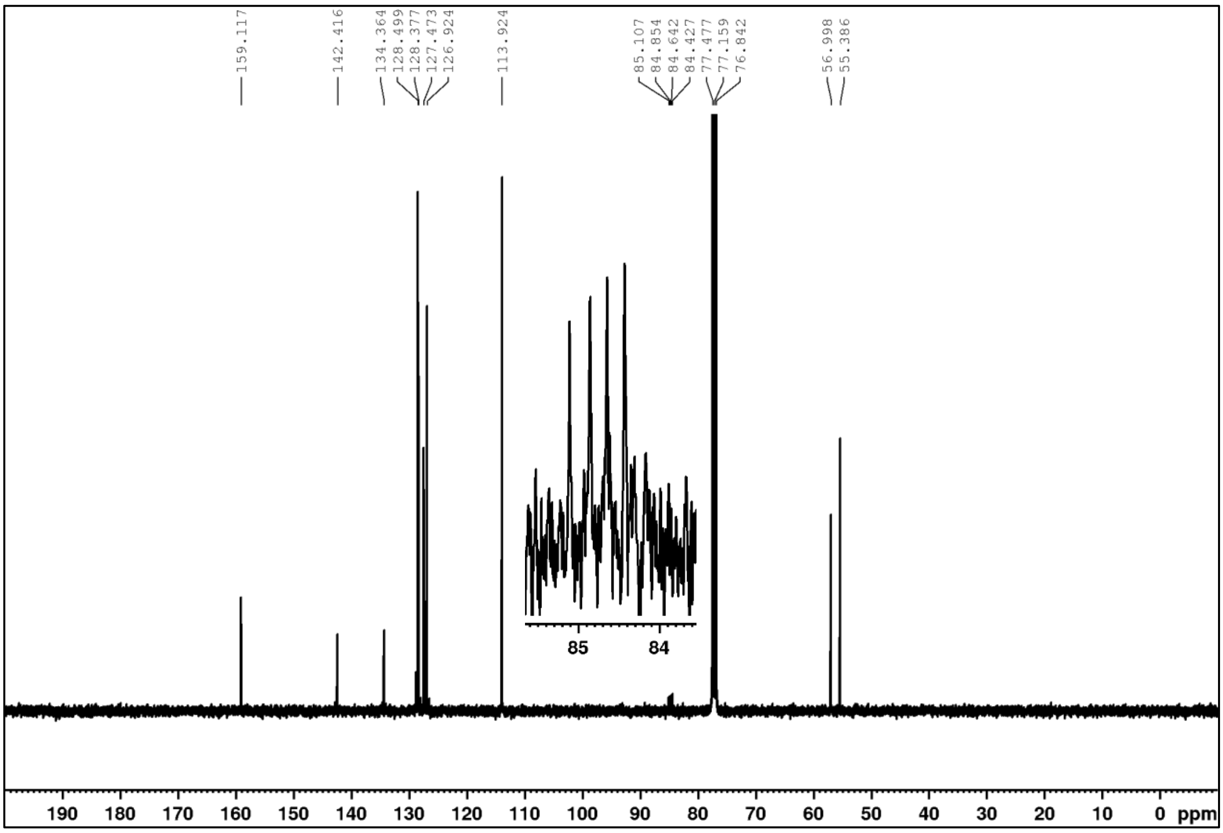


**1-Methoxy-4-(methoxy(phenyl)methyl-*d*)benzene (7a-$d_1$)**

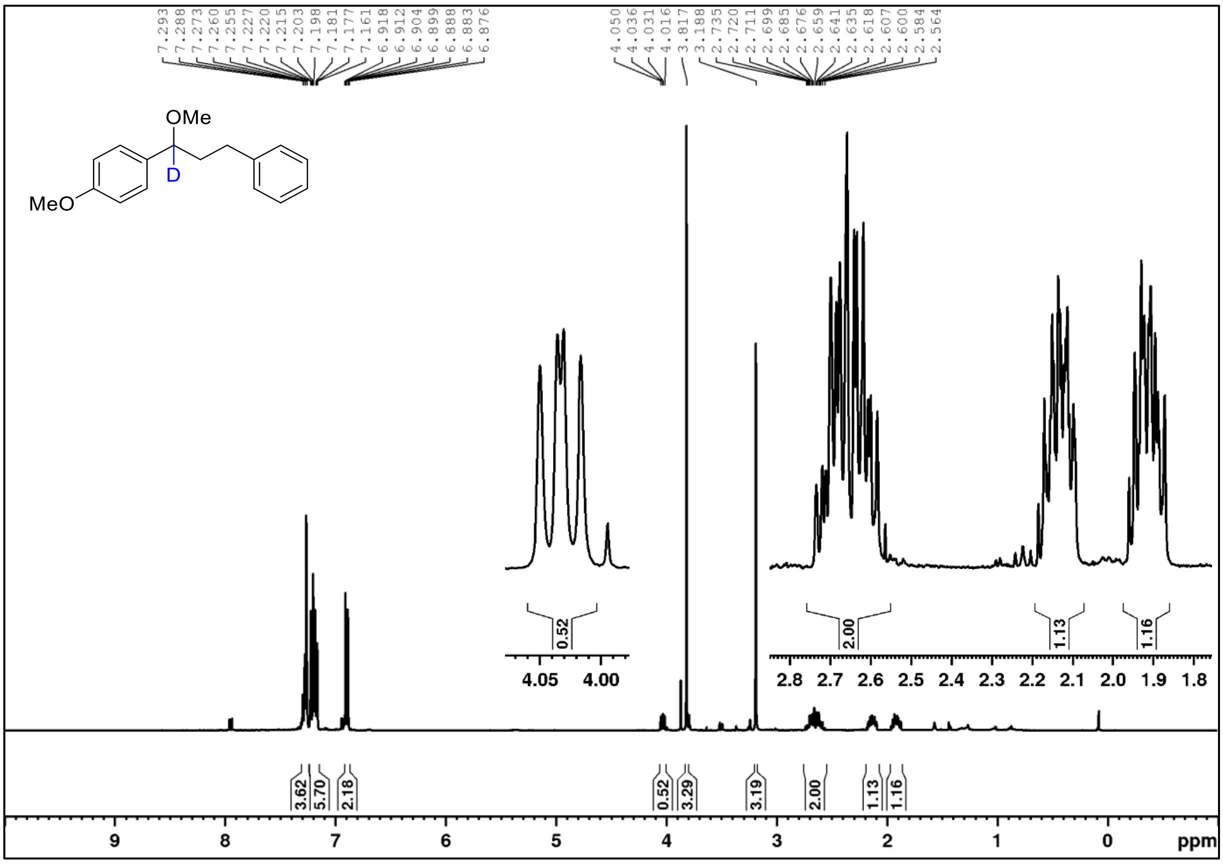
$^1$H NMR (400 MHz, CDCl$_3$)



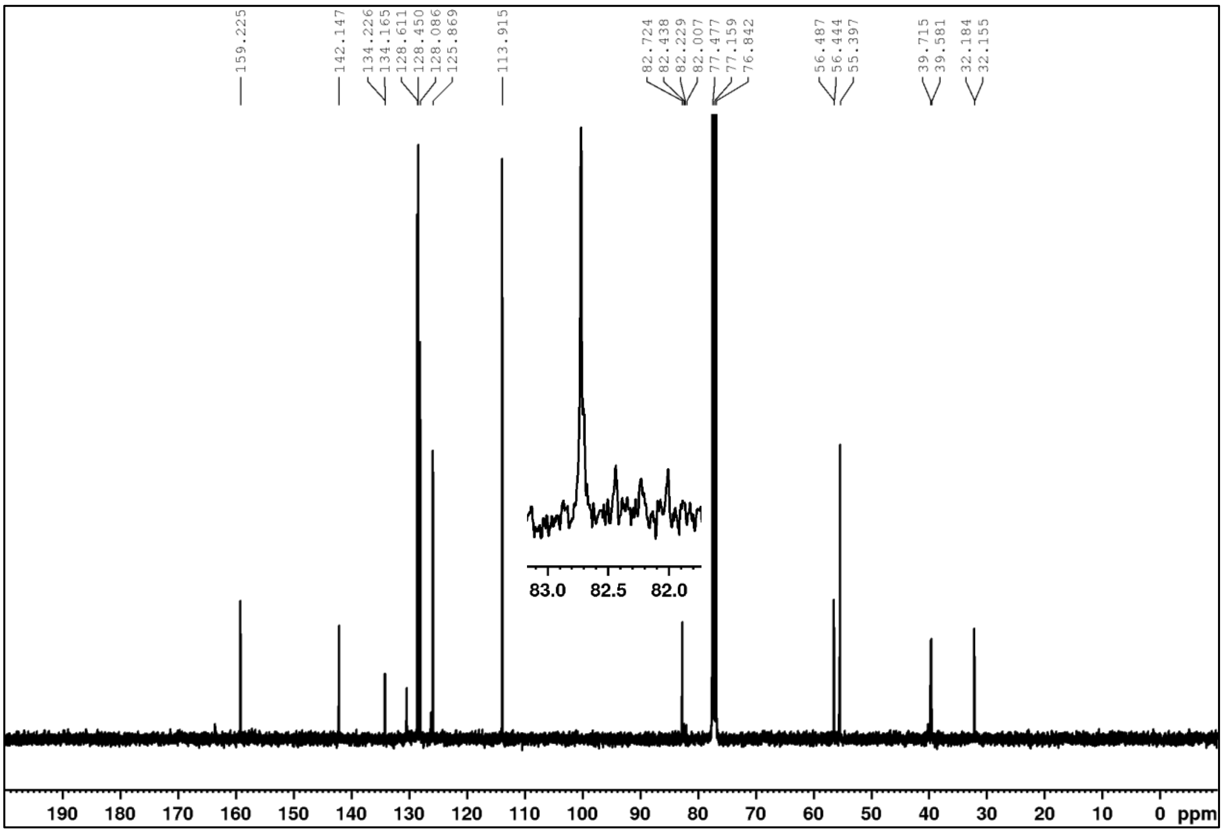
$^{13}$C NMR (101 MHz, CDCl$_3$)



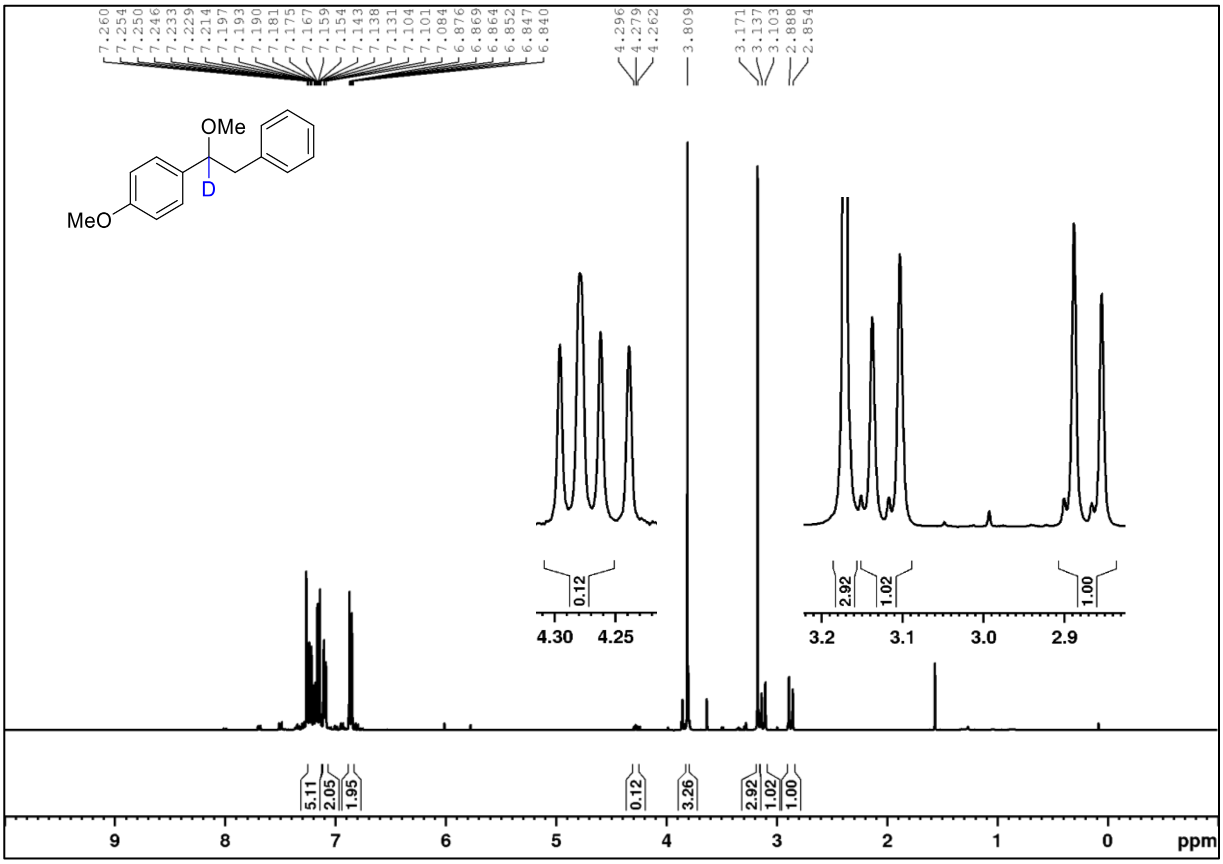
**1-Methoxy-4-(1-methoxy-3-phenylpropyl-1-*d*)benzene (7f-*d*$_1$)** $^1$H NMR (400 MHz, CDCl$_3$)



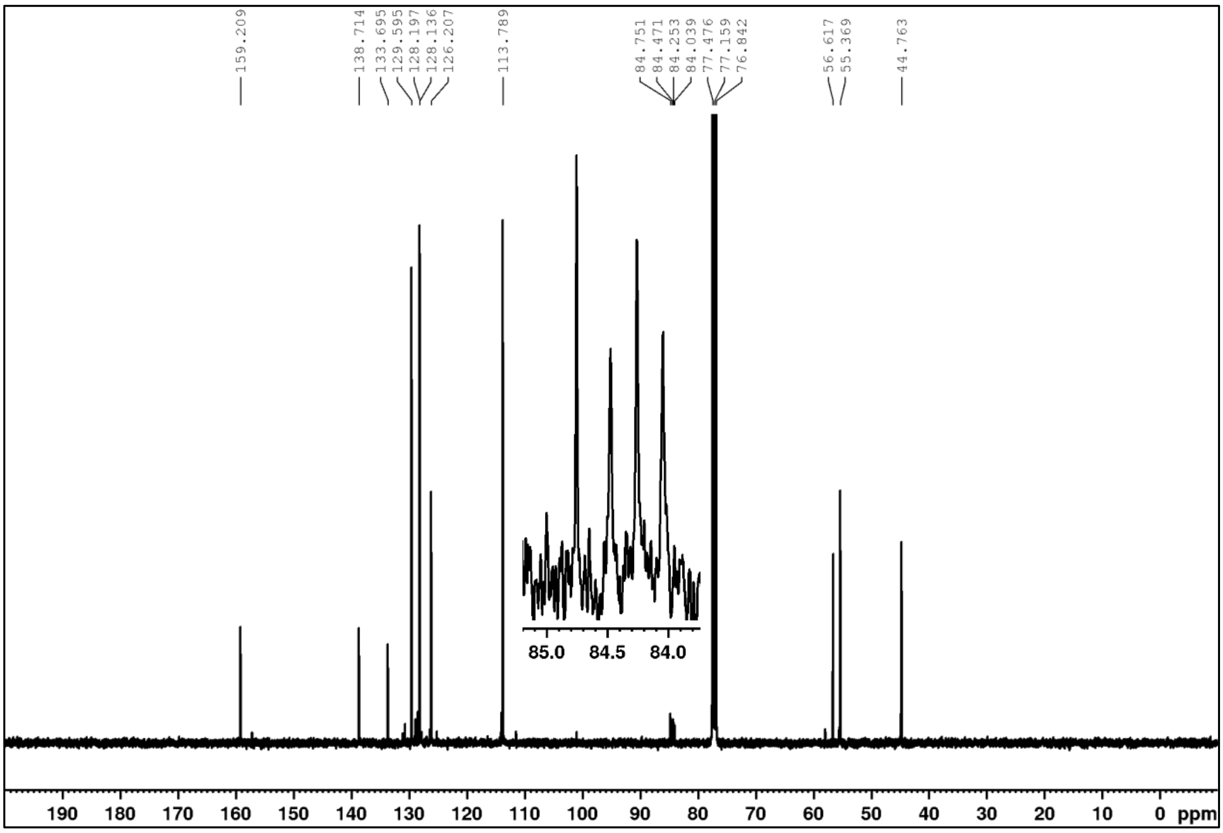
$^{13}$C NMR (101 MHz, CDCl$_3$)



**1-Methoxy-4-(1-methoxy-2-phenylethyl-1-*d*)benzene (7k-$d_1$)** $^1$H NMR (400 MHz, CDCl$_3$)

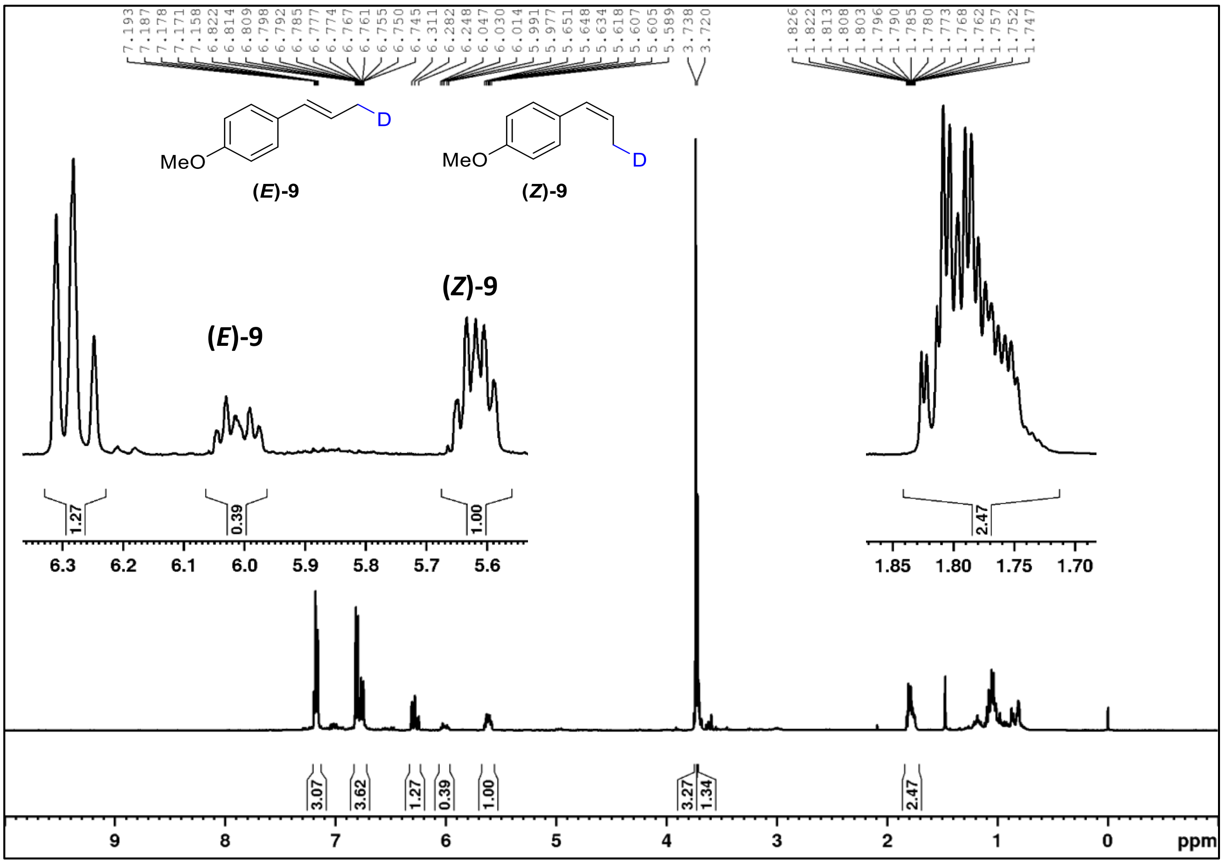


$^{13}$C NMR (101 MHz, CDCl$_3$)

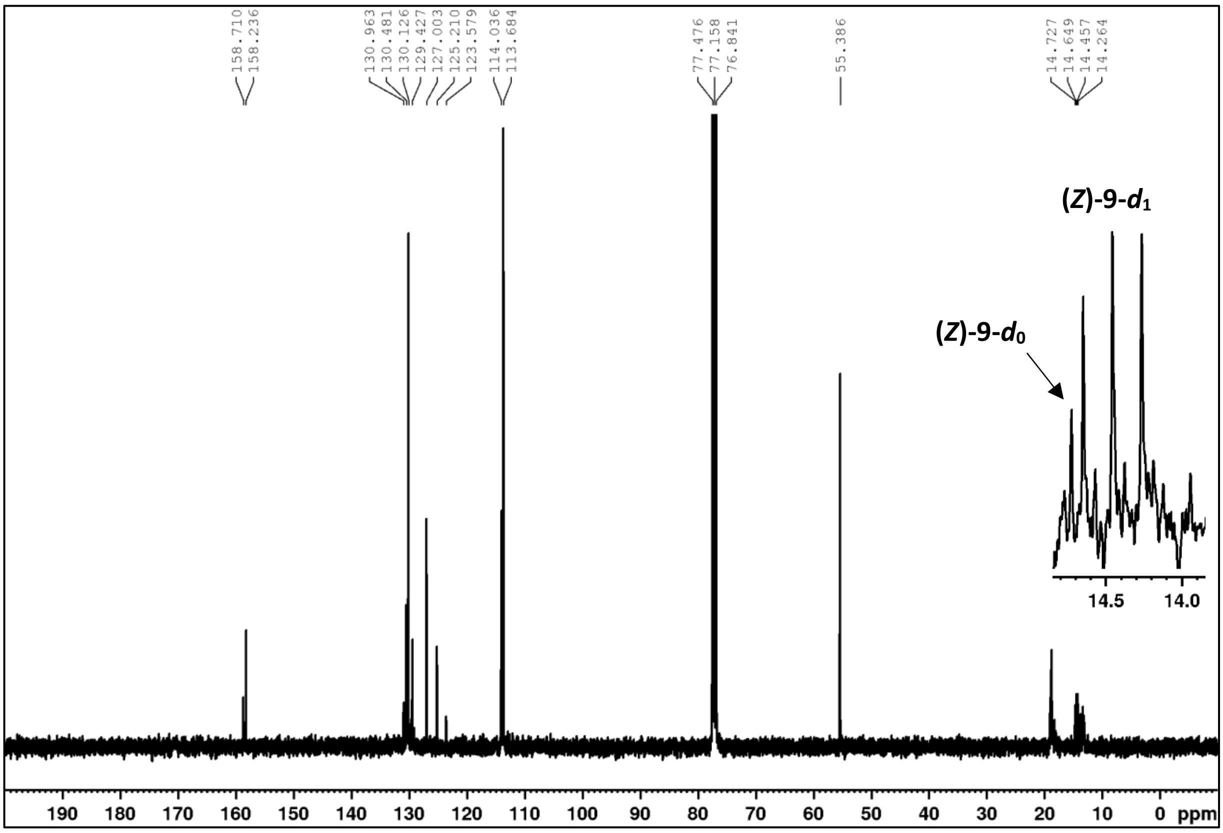


**1-Methoxy-4-(prop-1-en-1-yl-3-d)benzene (9, *Z*/*E* = 3:1)**

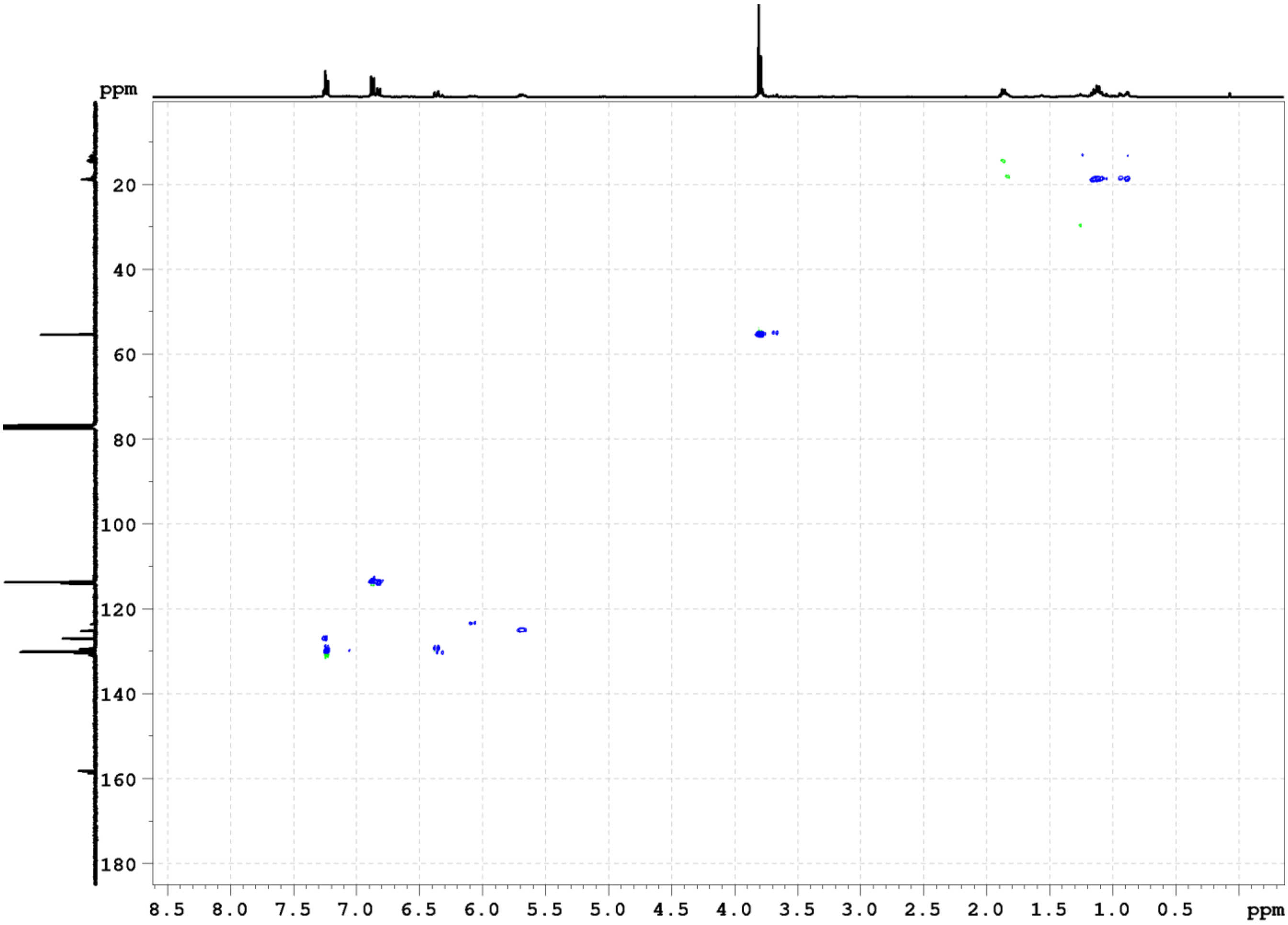
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (101 MHz, CDCl$_3$)



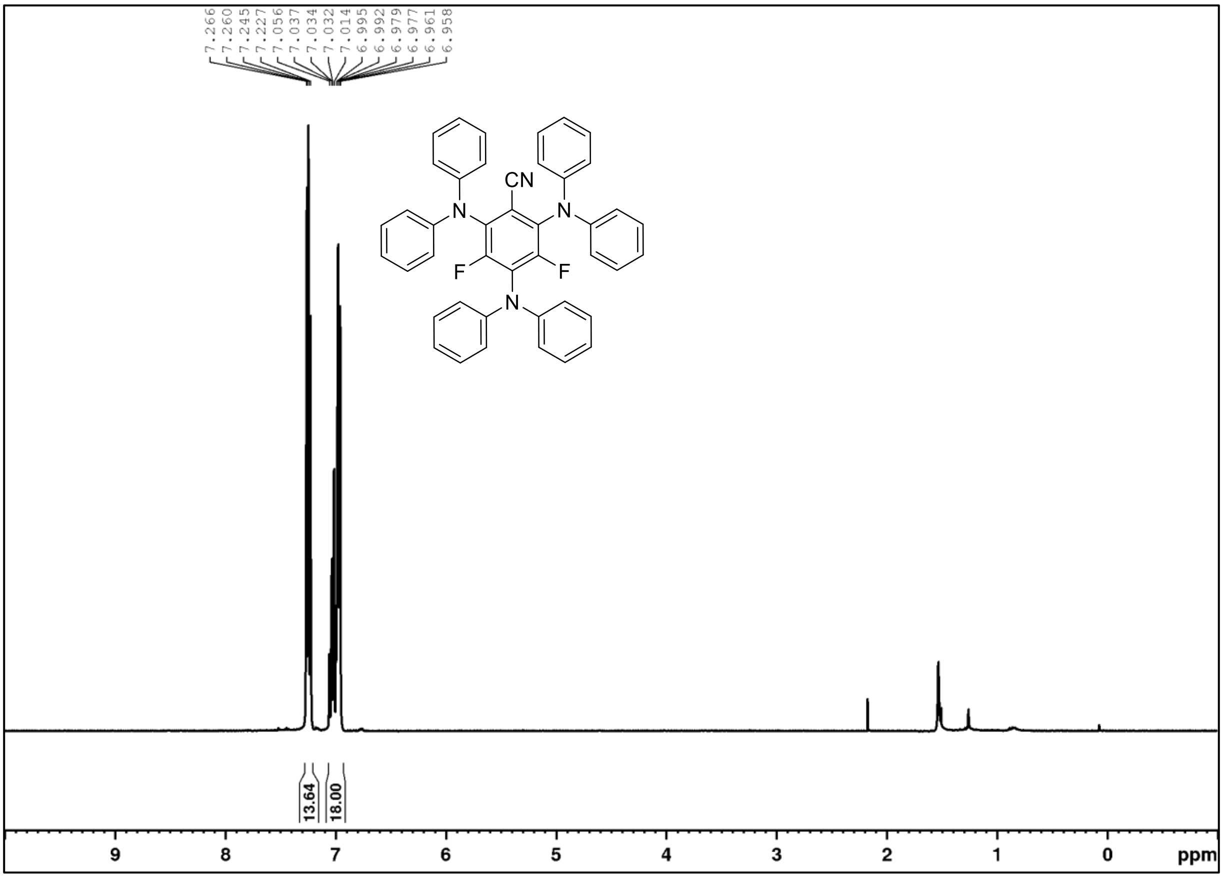
HSQC (CDCl₃)


ppm
20
40
60
80
100
120
140
160
180
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

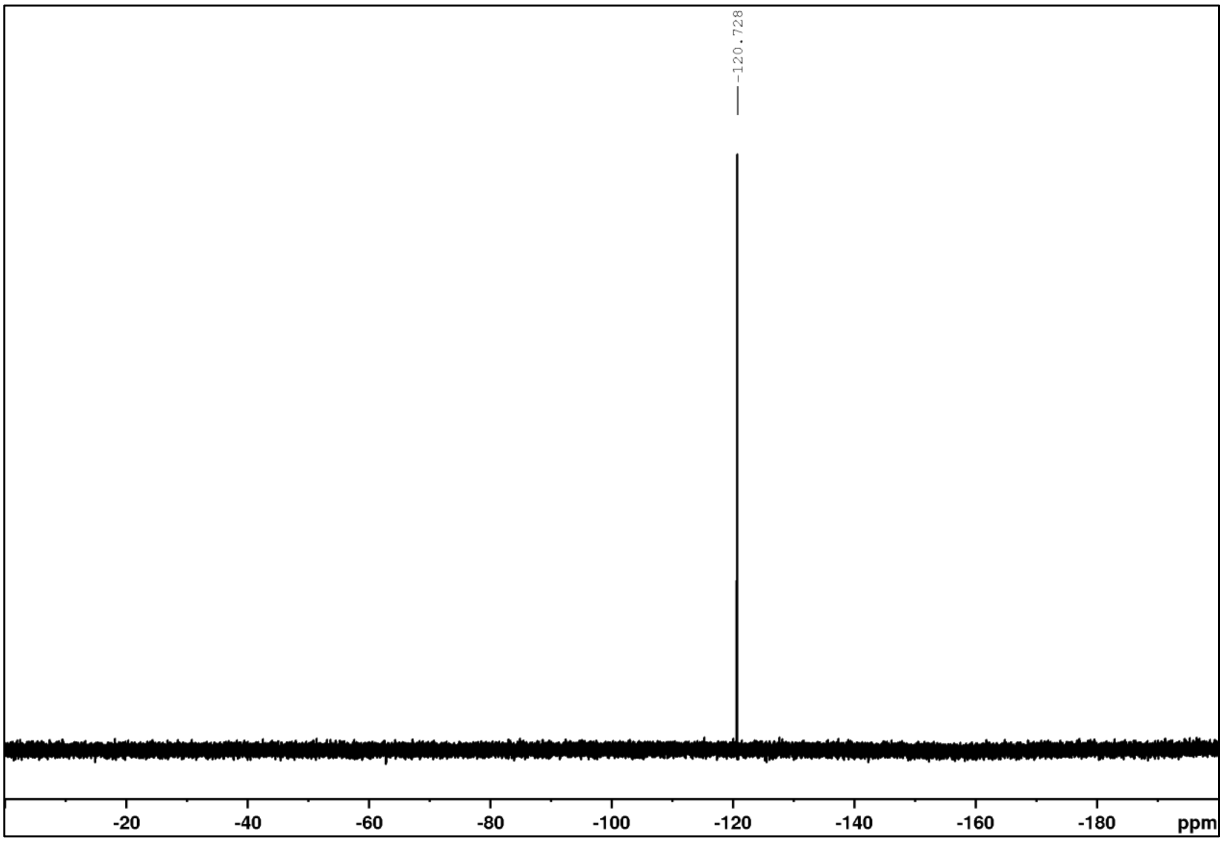
## 11.3 NMR spectra of other isolated compounds

**2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (3DPA2FBN; 1a)**

$^1$H NMR (400 MHz, $CDCl_3$)

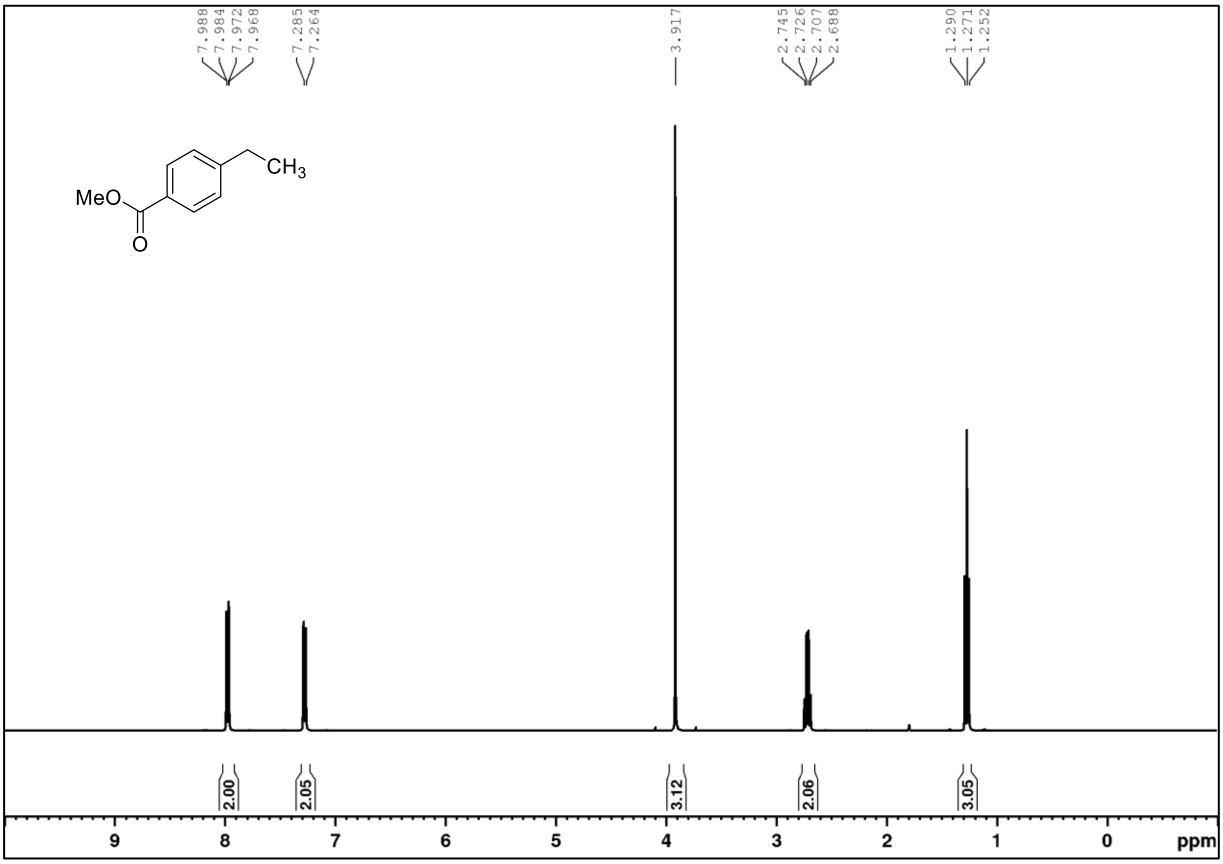


$^{19}$F NMR (377 MHz, $CDCl_3$)

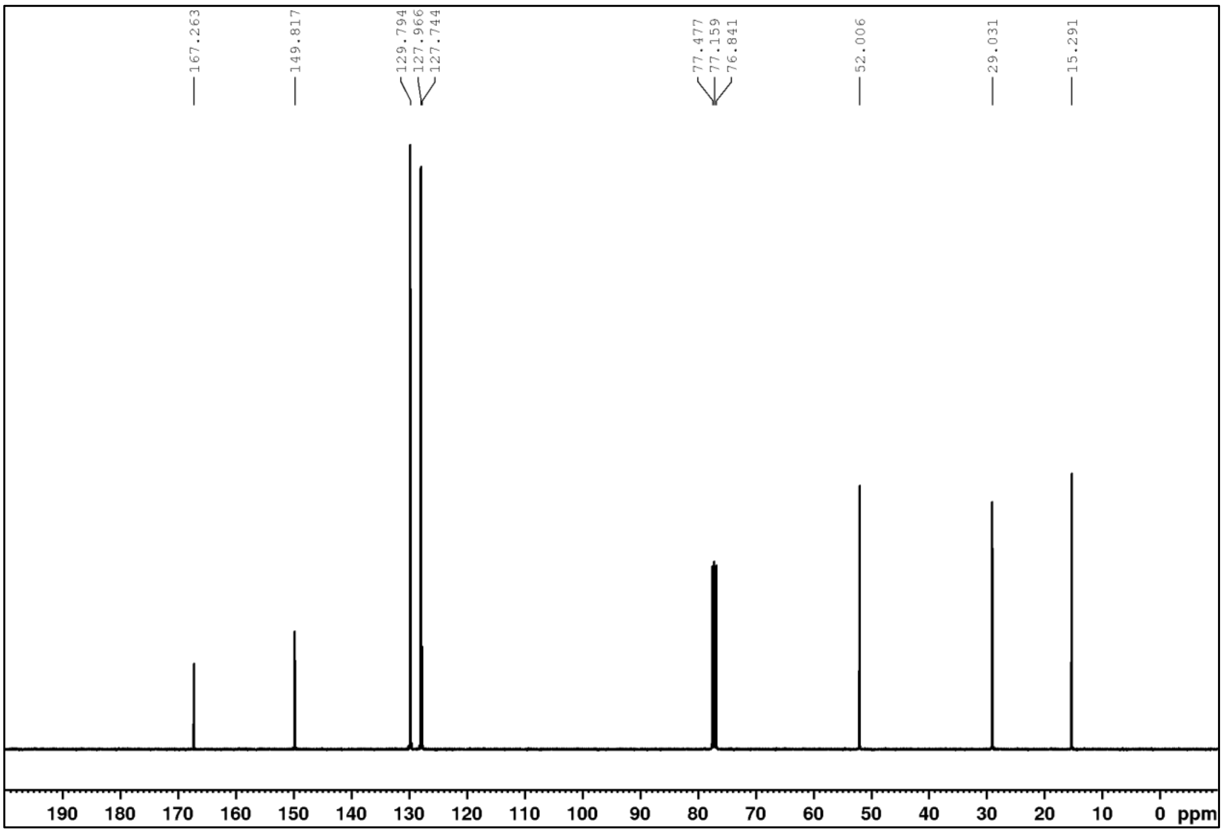


**Methyl 4-ethylbenzoate (2i)**

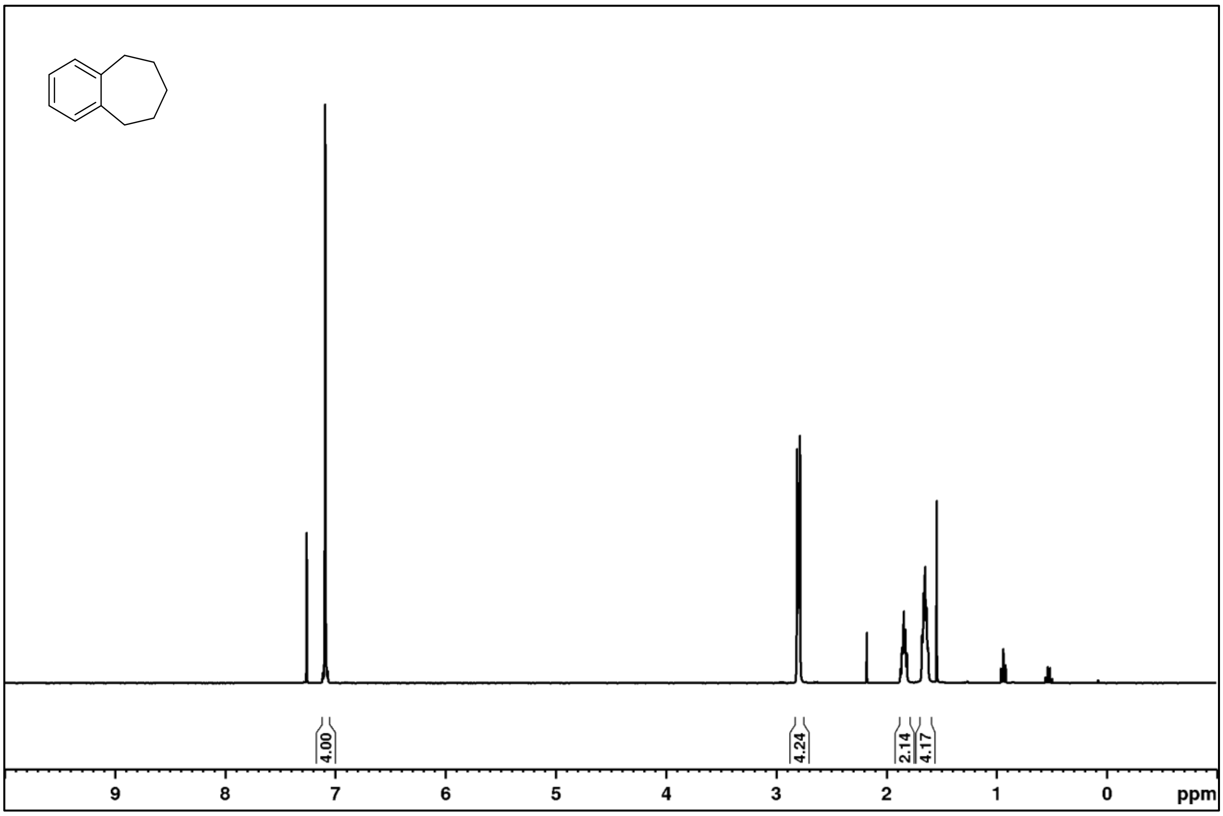
$^{1}H$ NMR (400 MHz, $CDCl_3$)



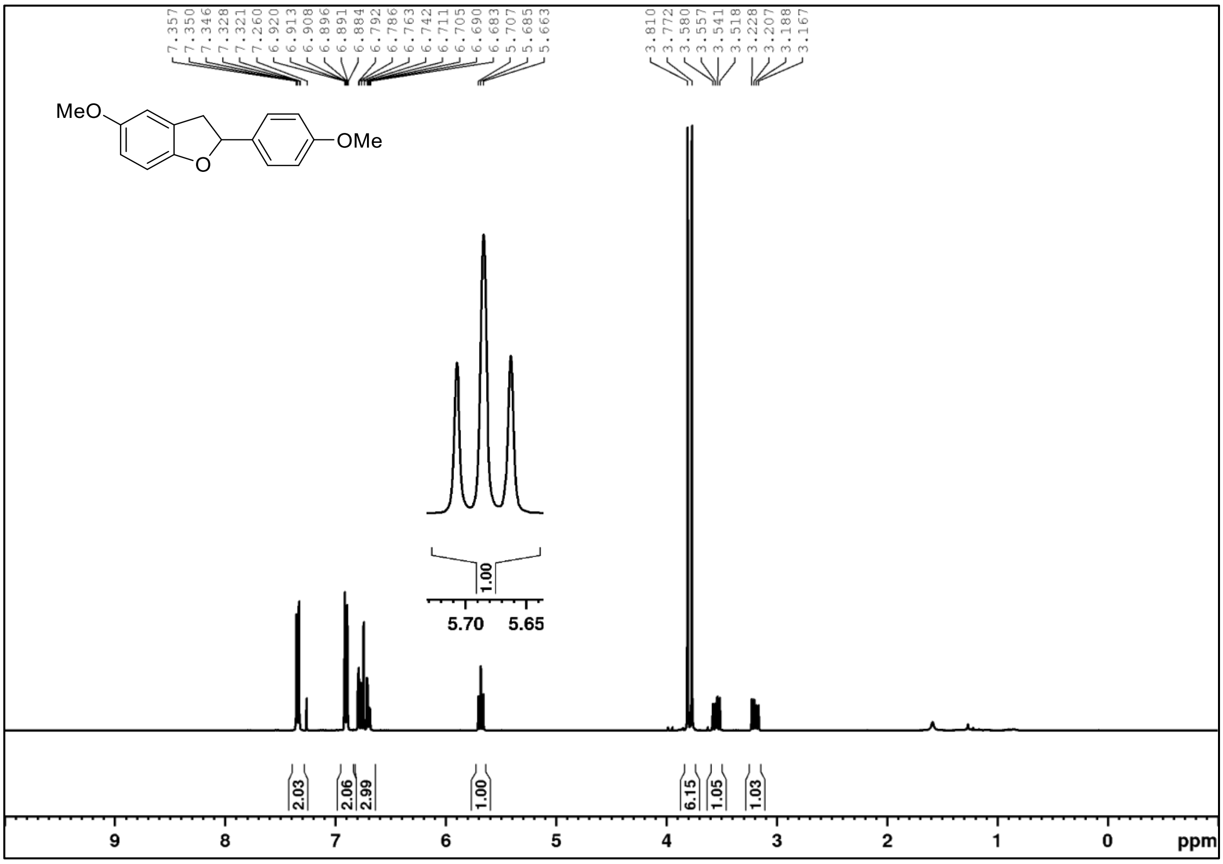
$^{13}C$ NMR (101 MHz, $CDCl_3$)



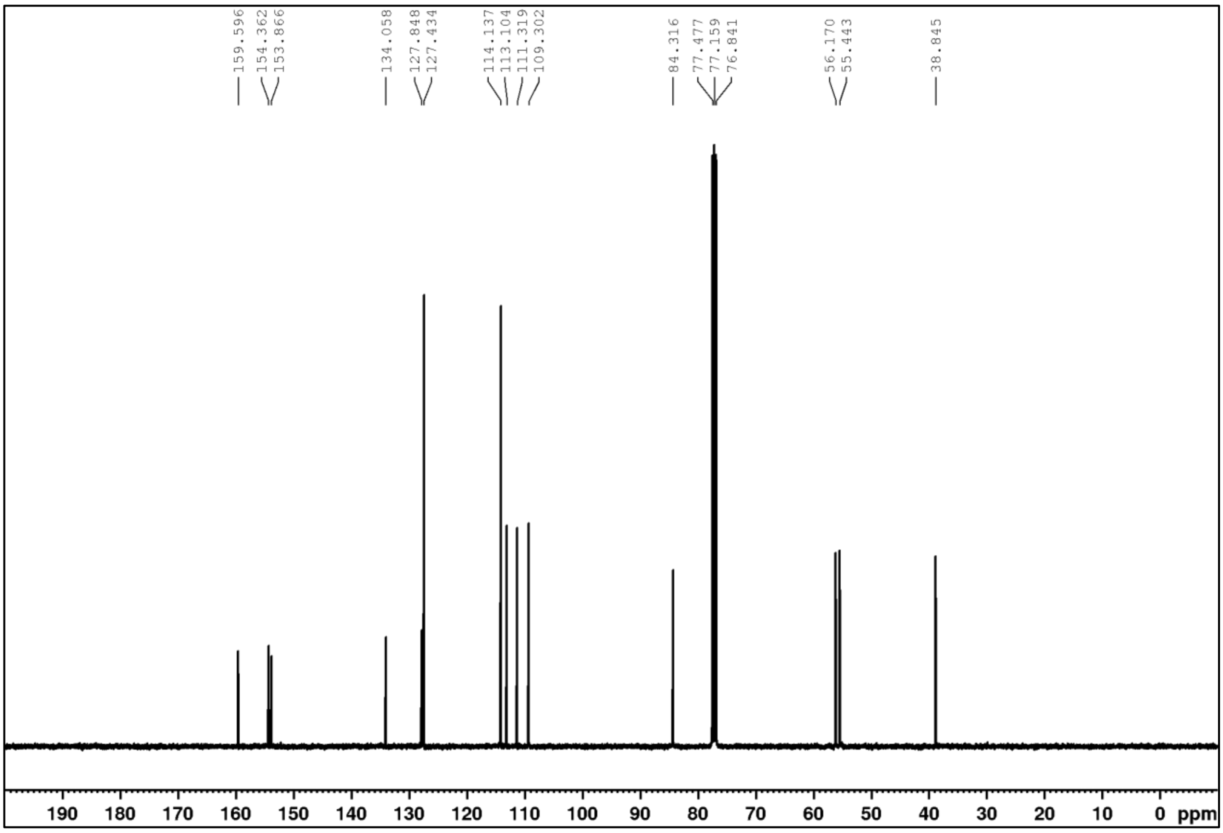
**6,7,8,9-Tetrahydro-5*H*-benzo[7]annulene (3c)** $^{1}$H NMR (400 MHz, CDCl$_3$)



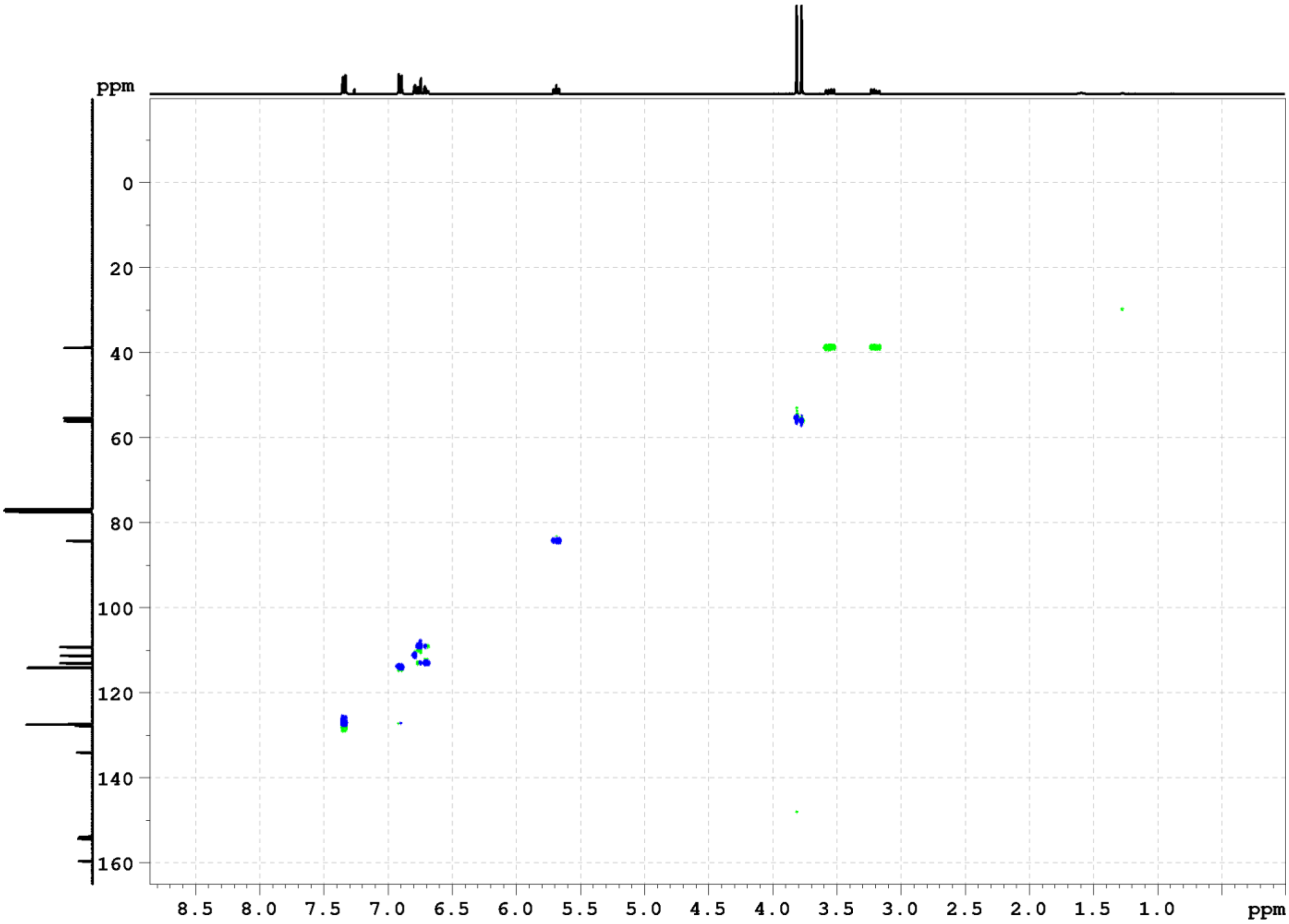
**5-Methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (Corsifuran A, 4b)** $^{1}$H NMR (400 MHz, CDCl$_3$)



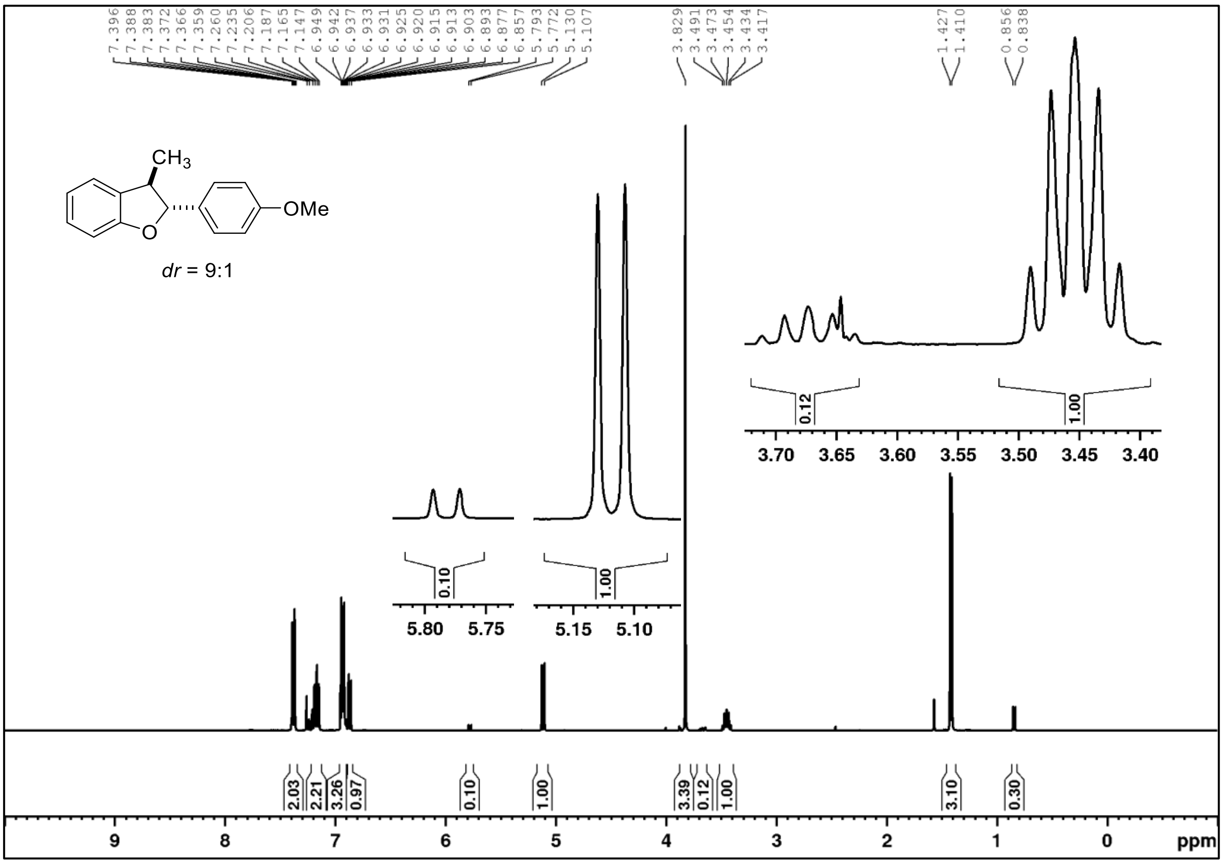
$^{13}$C NMR (101 MHz, CDCl$_3$)



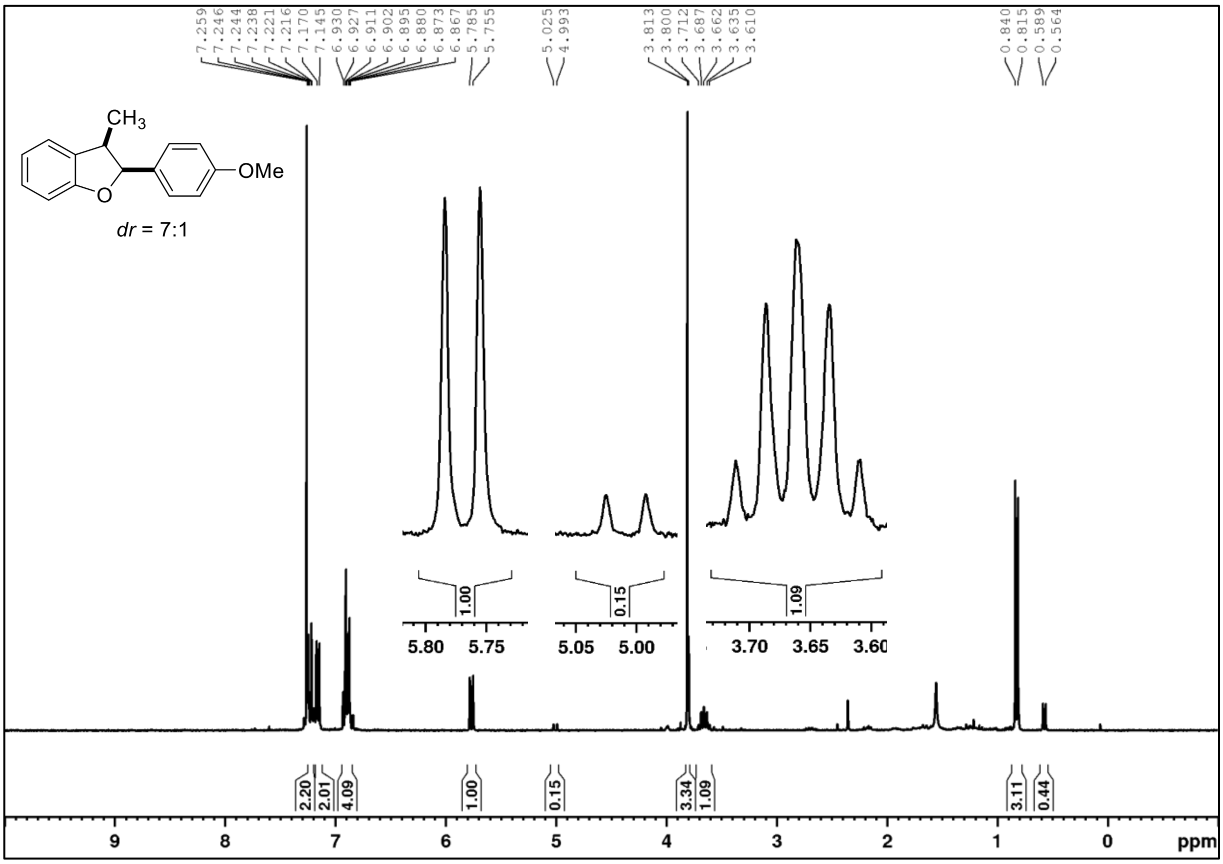
HSQC (CDCl$_3$)



***trans*-2-(4-Methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (*trans*-4c)** $^1$H NMR (400 MHz, $CDCl_3$)

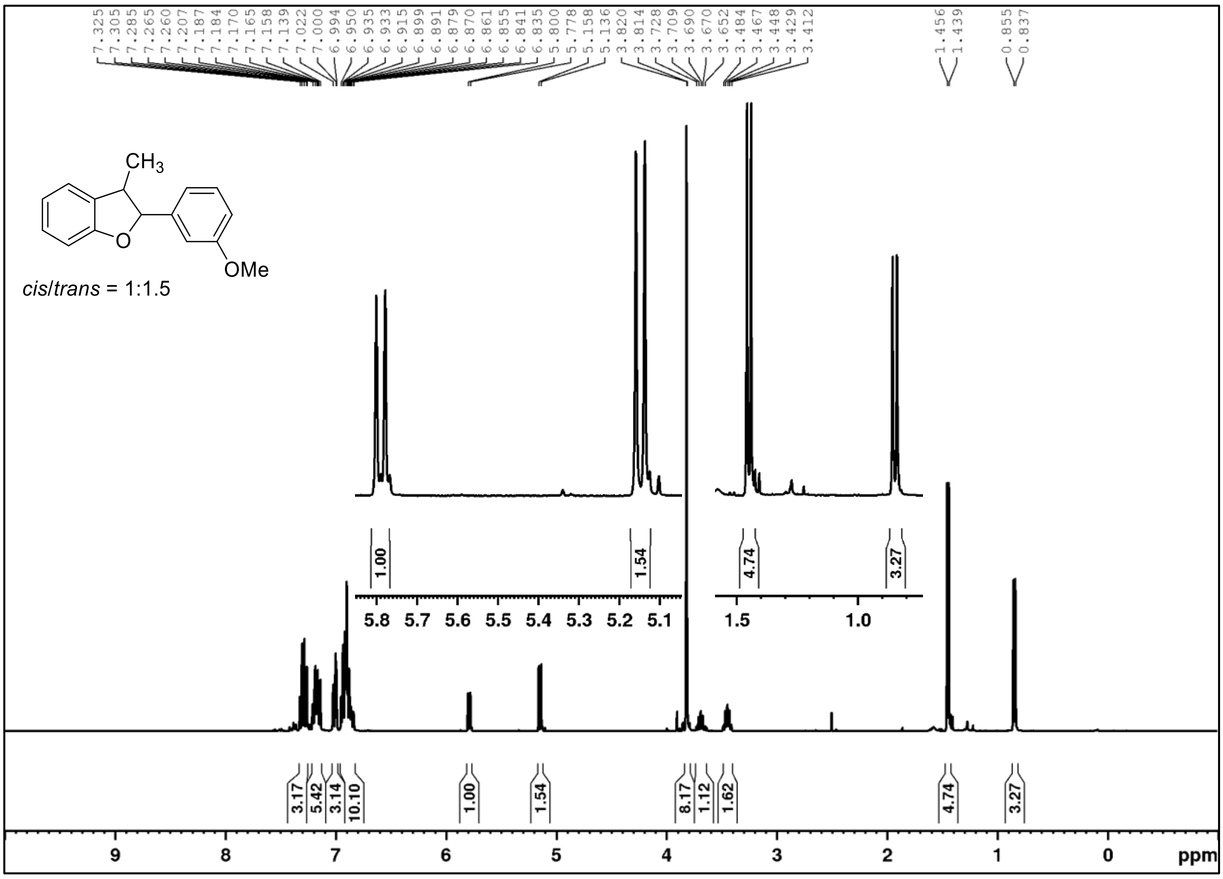


***cis*-2-(4-Methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (*cis*-4c)** $^1$H NMR (400 MHz, $CDCl_3$)

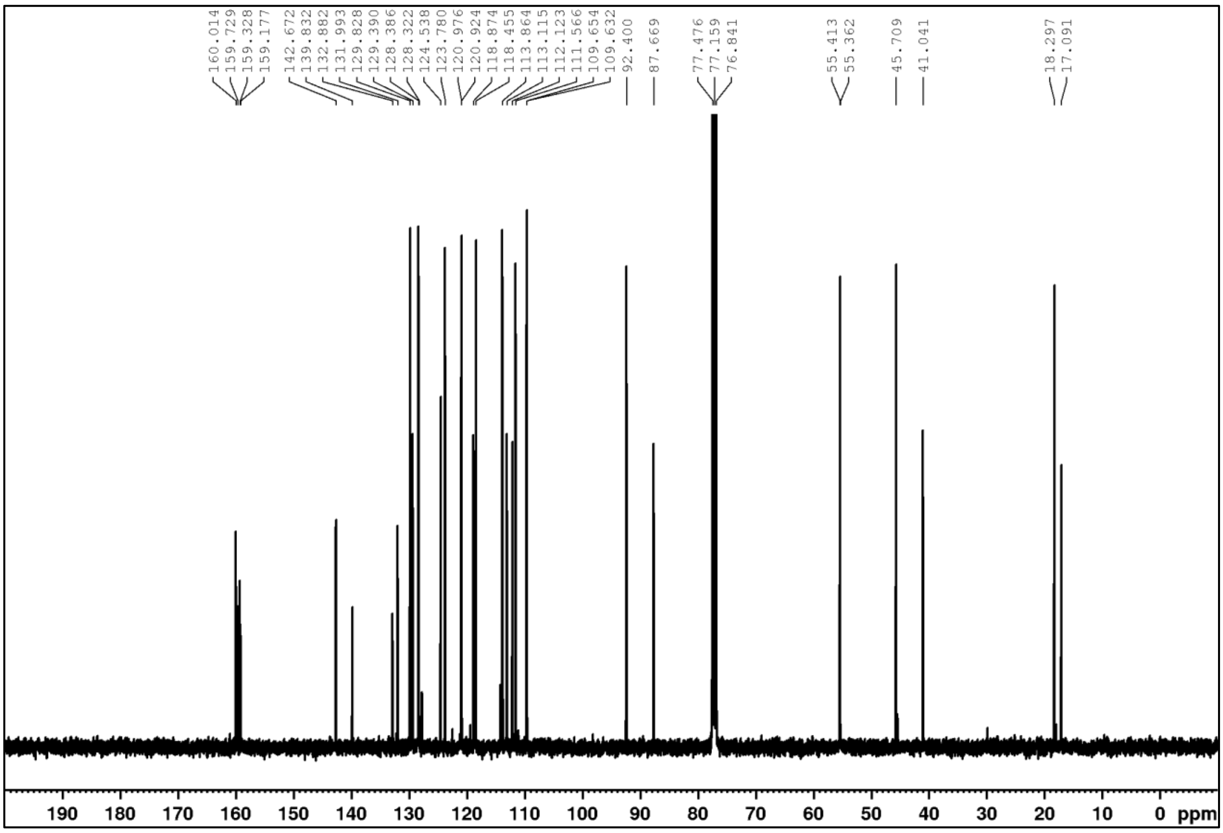


**2-(3-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (4d)**

$^1$H NMR (400 MHz, CDCl$_3$)

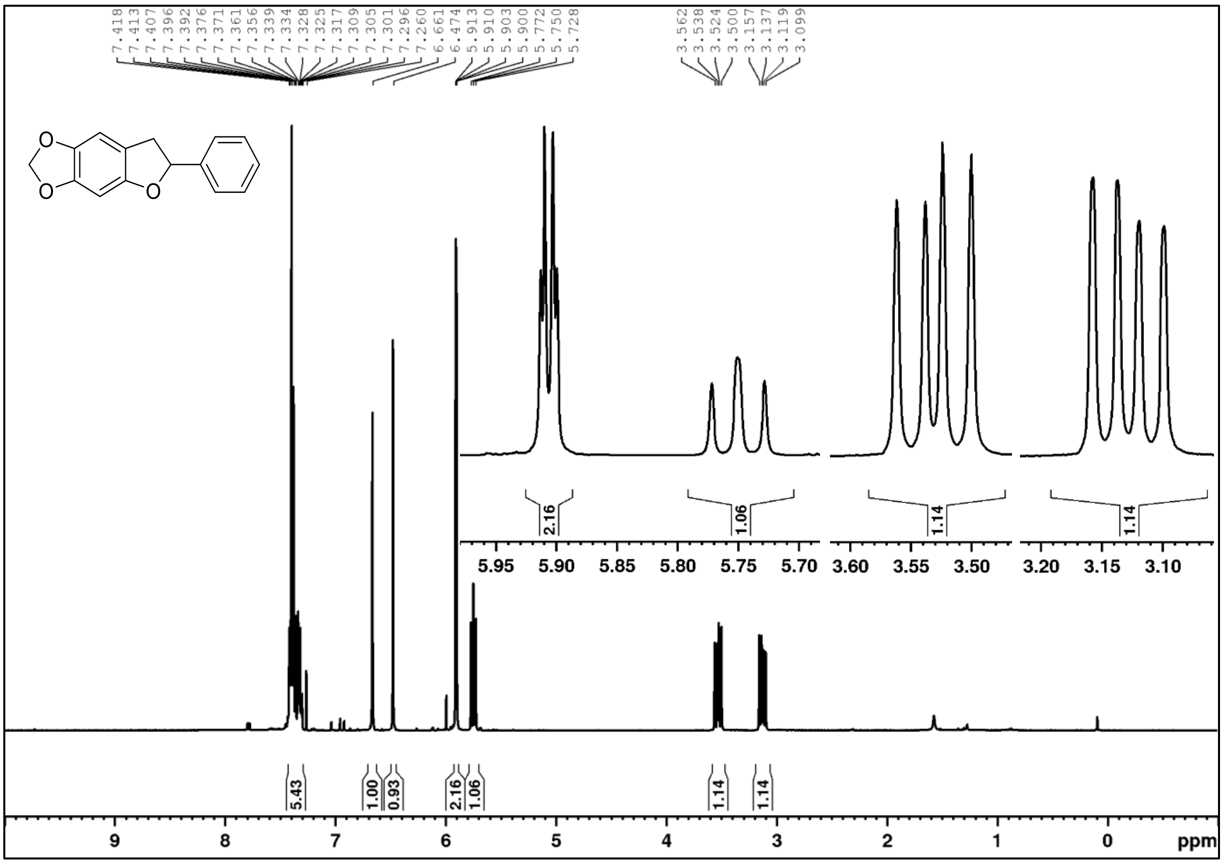


$^{13}$C NMR (101 MHz, CDCl$_3$)

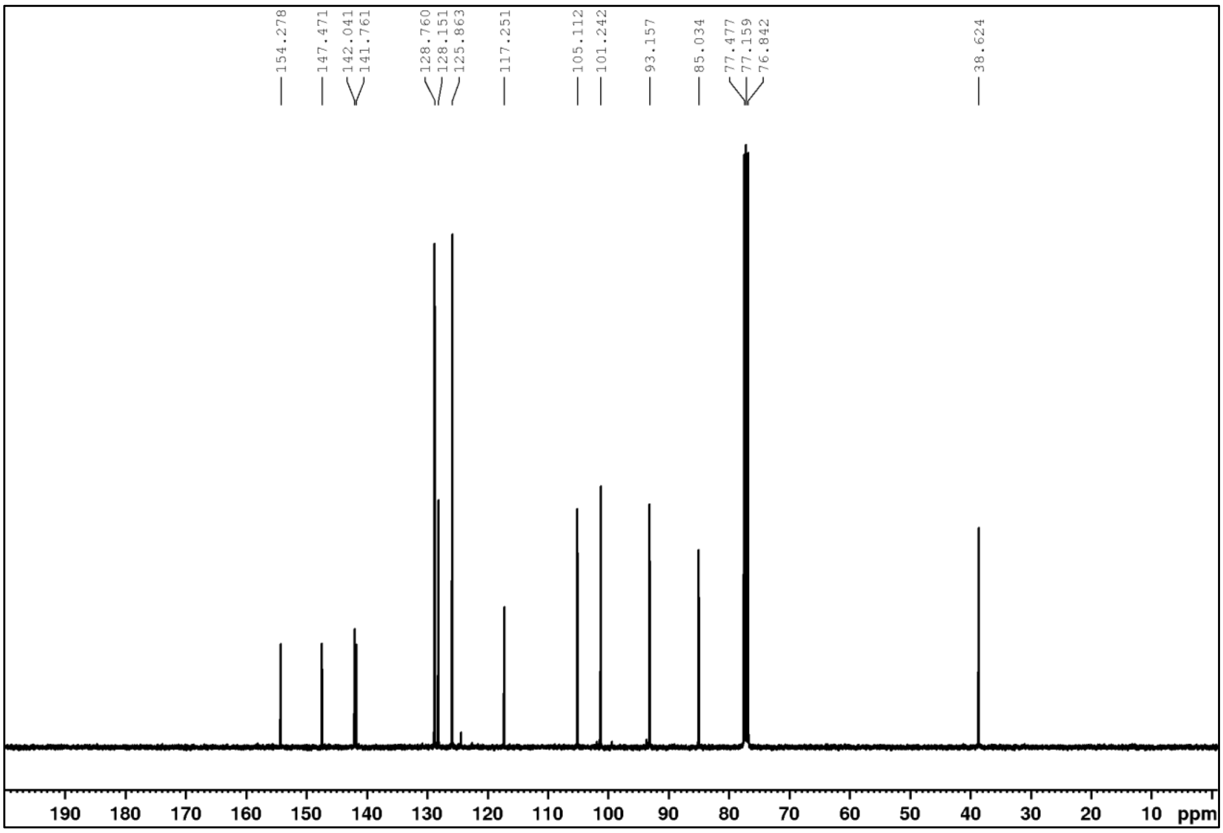


**6-Phenyl-6,7-dihydro-[1,3]dioxolo[4,5-f]benzofuran (4e)**

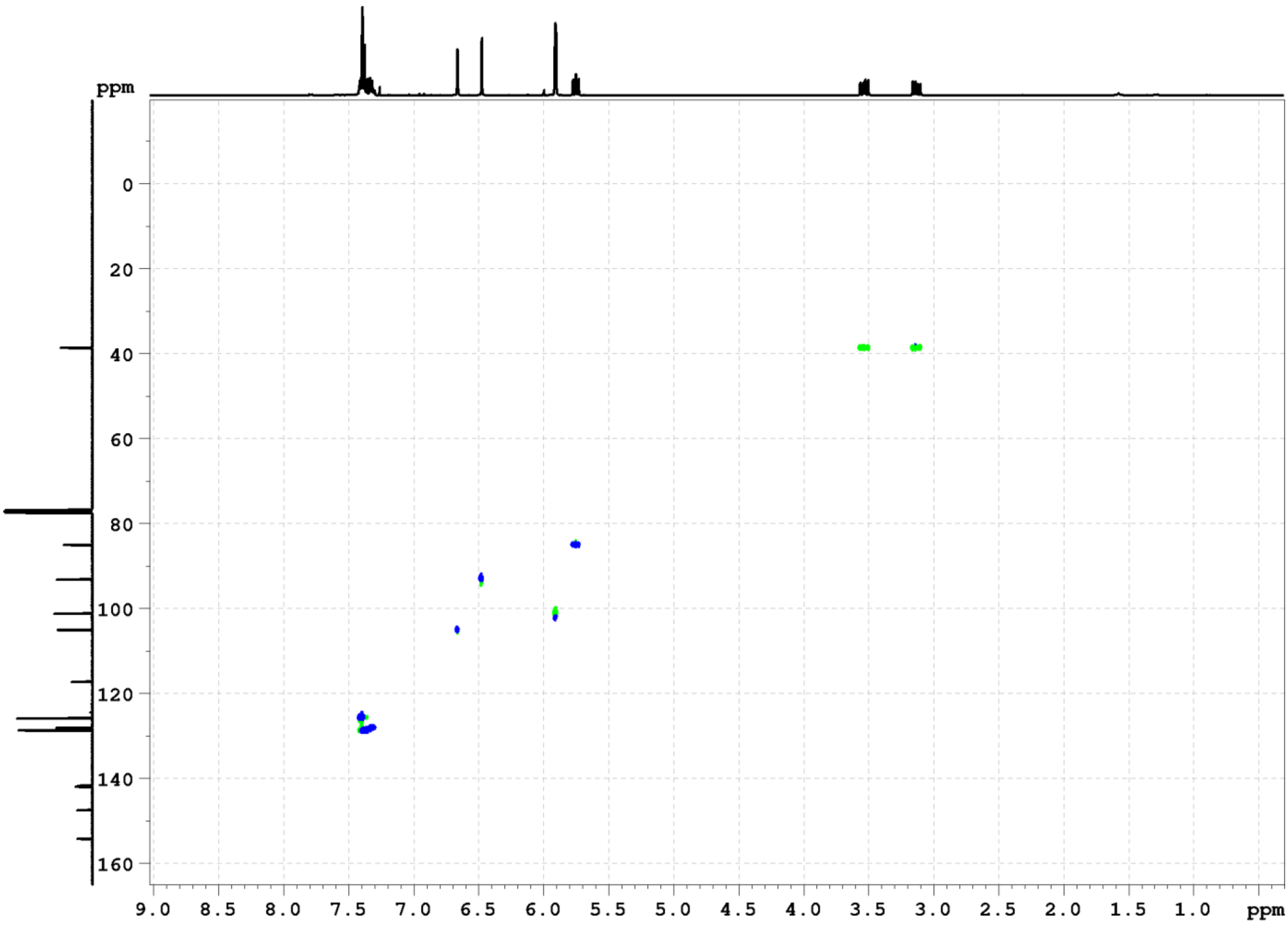
$^1$H NMR (400 MHz, $CDCl_3$)



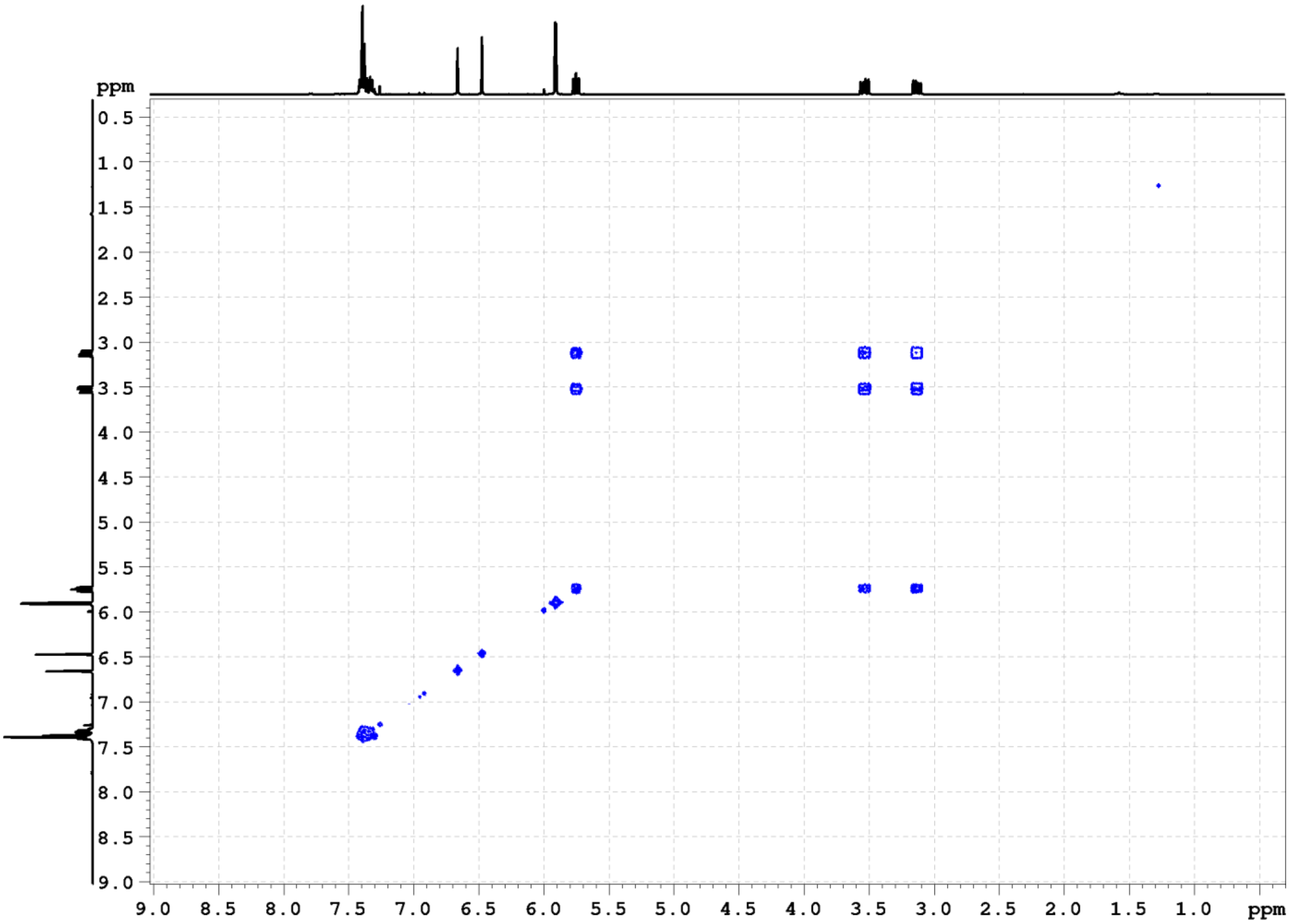
$^{13}$C NMR (101 MHz, $CDCl_3$)



HSQC ($CDCl_3$)

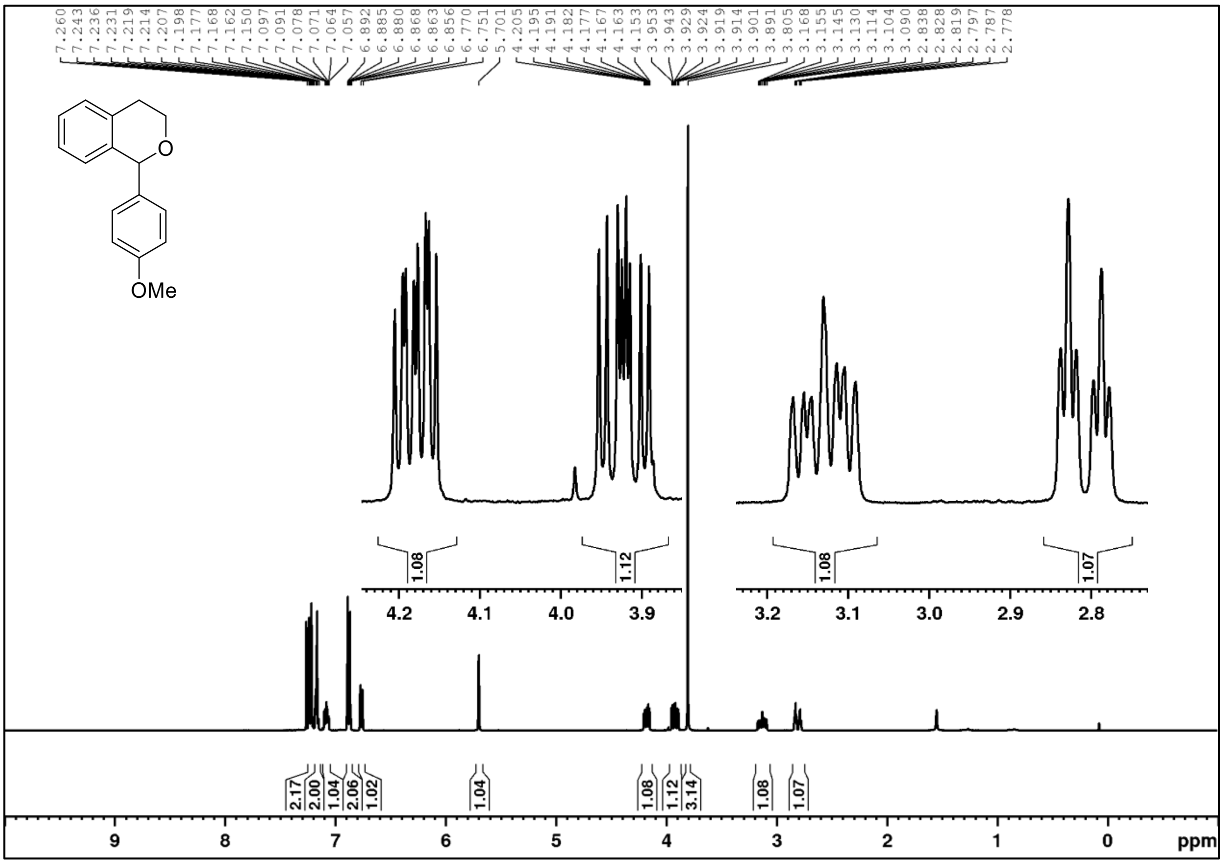

ppm
0
20
40
60
80
100
120
140
160
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

$^1H$-$^1H$ COSY ($CDCl_3$)



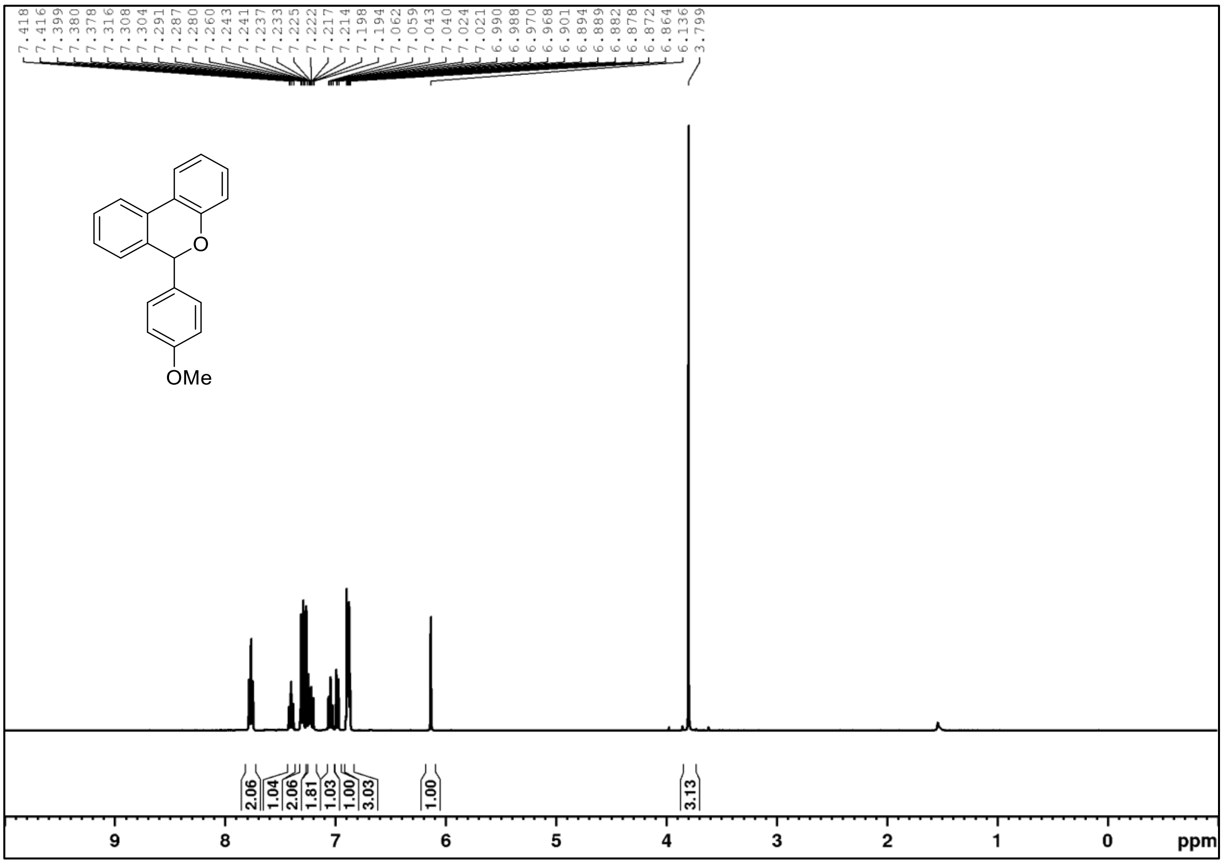
**1-(4-Methoxyphenyl)isochromane (5b)**

$^1$H NMR (400 MHz, CDCl$_3$)

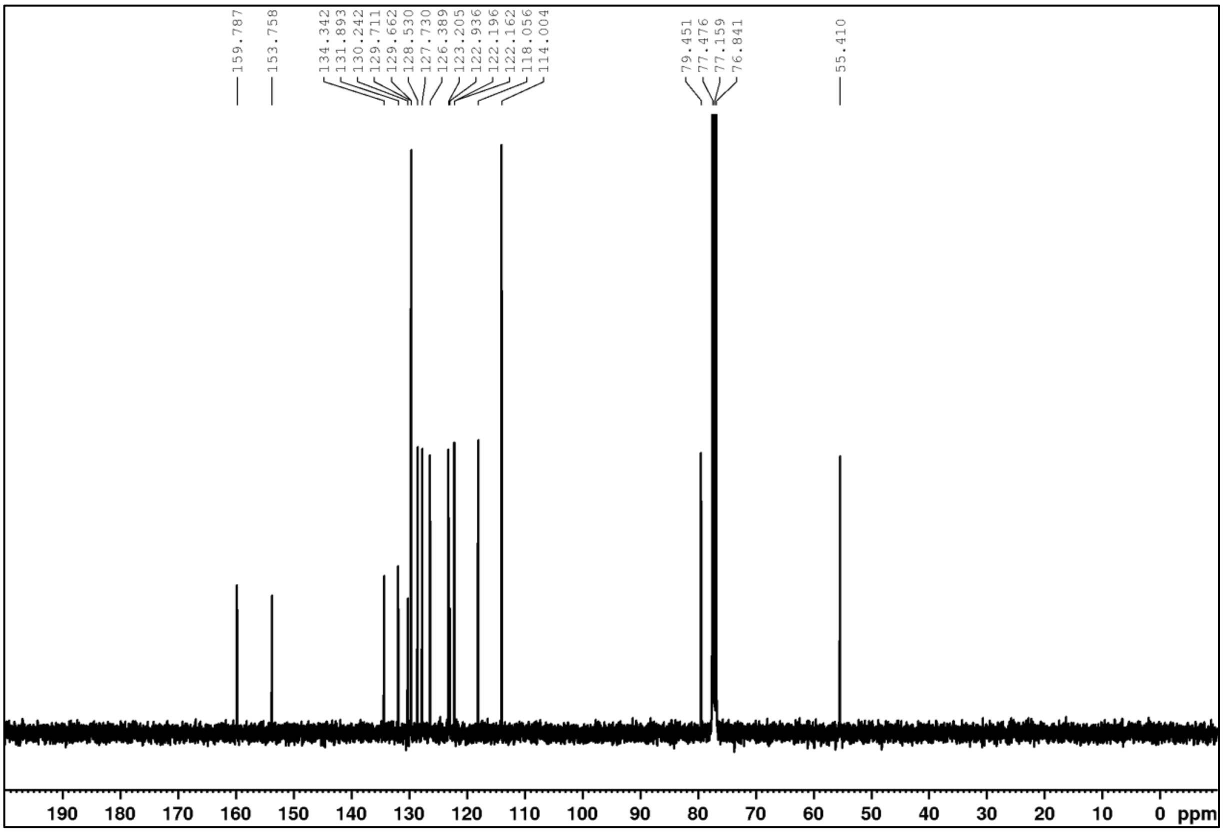


**6-(4-Methoxyphenyl)-6*H*-benzo[*c*]chromene (5c)**

$^1$H NMR (400 MHz, CDCl$_3$)

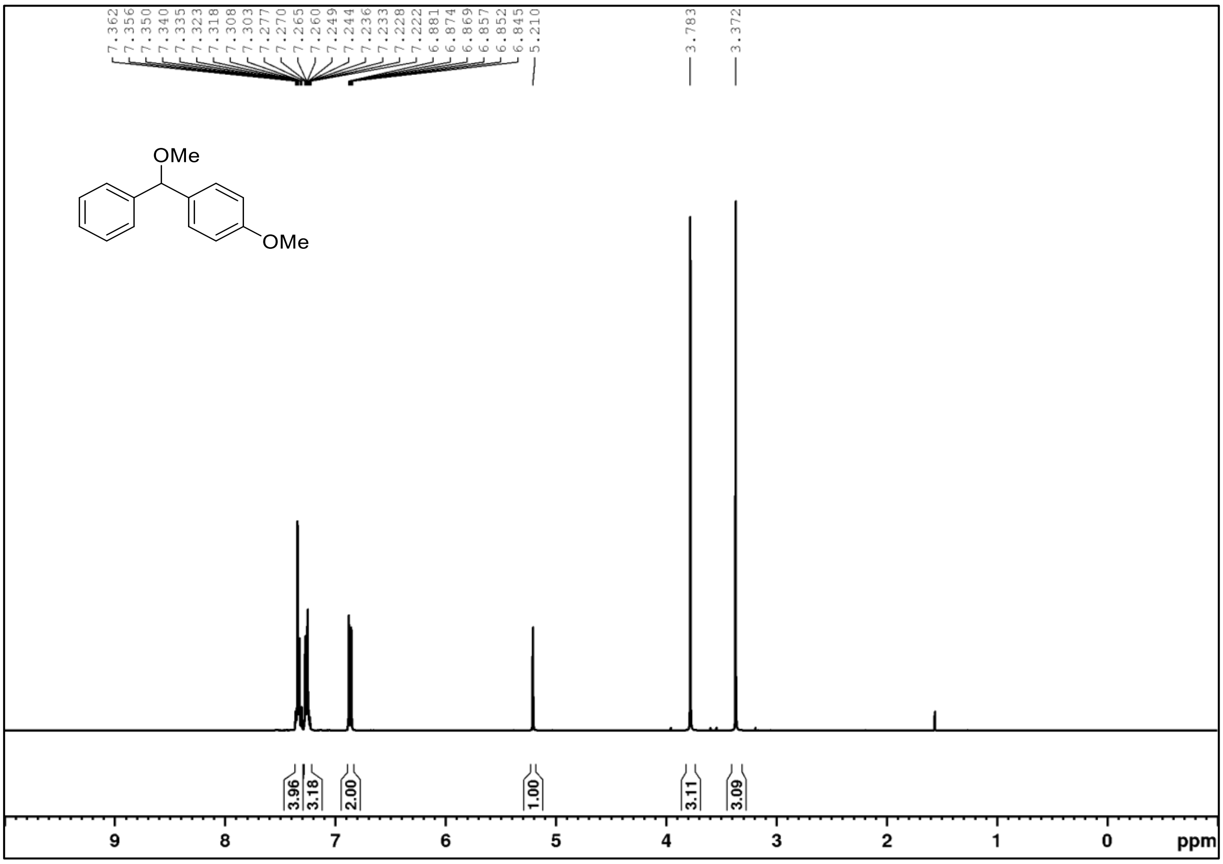


$^{13}$C NMR (101 MHz, CDCl$_3$)

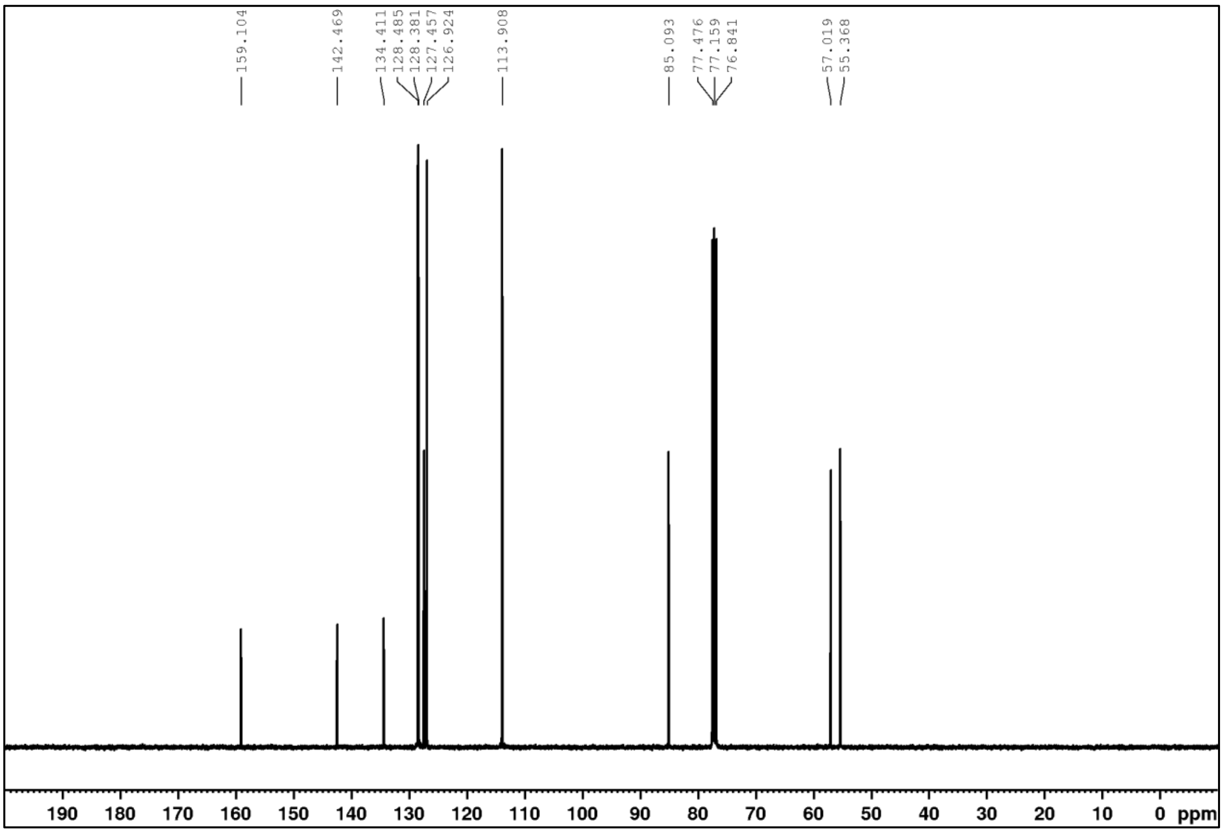


**1-Methoxy-4-(methoxy(phenyl)methyl)benzene (7a)**

$^{1}H$ NMR (400 MHz, $CDCl_3$)

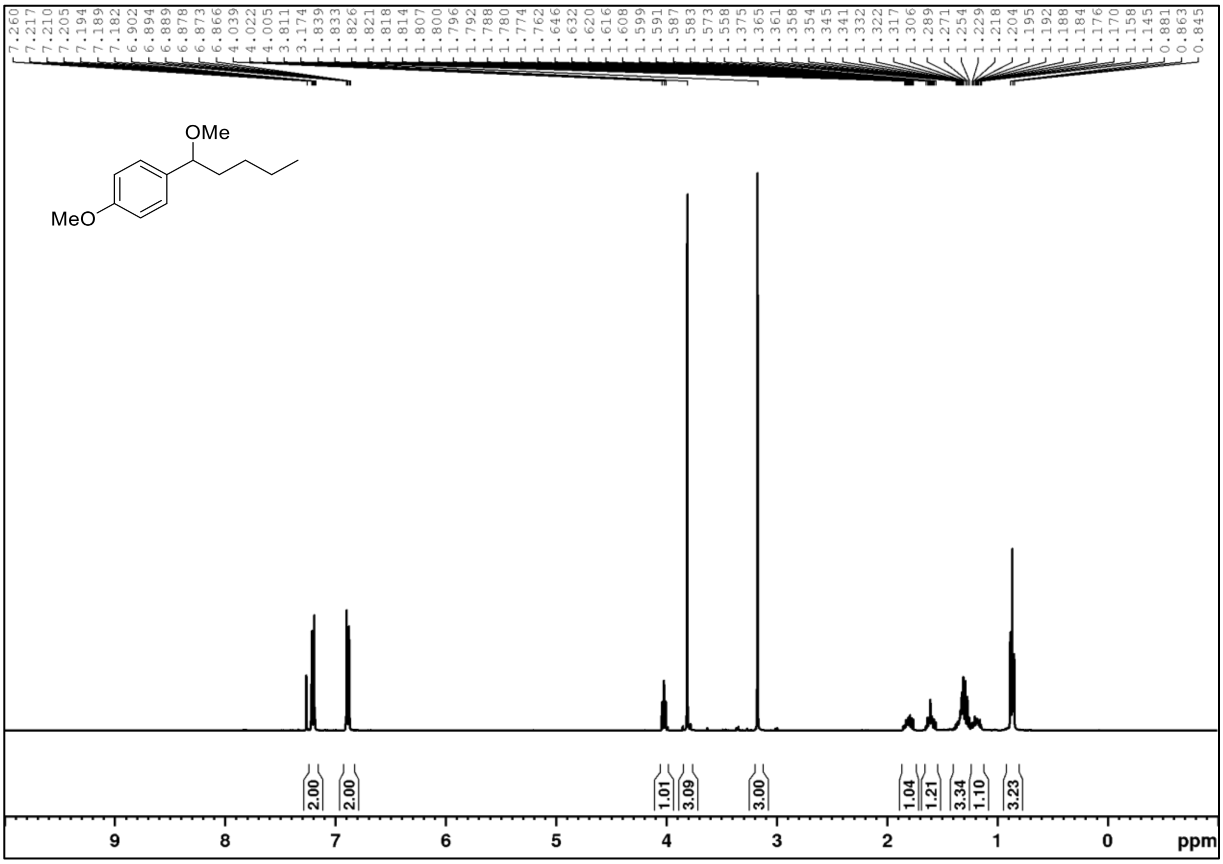


$^{13}C$ NMR (101 MHz, $CDCl_3$)

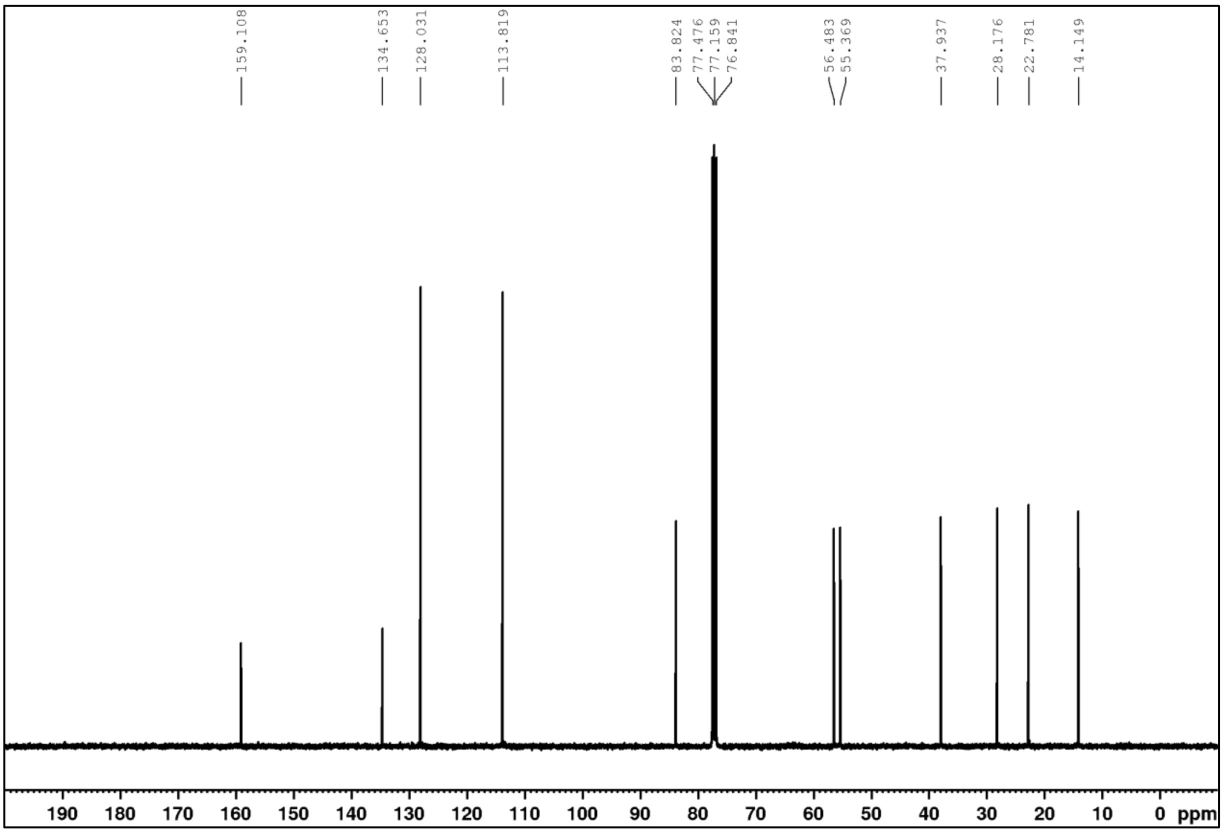


**1-Methoxy-4-(1-methoxypentyl)benzene (7c)**

$^{1}$H NMR (400 MHz, $CDCl_3$)

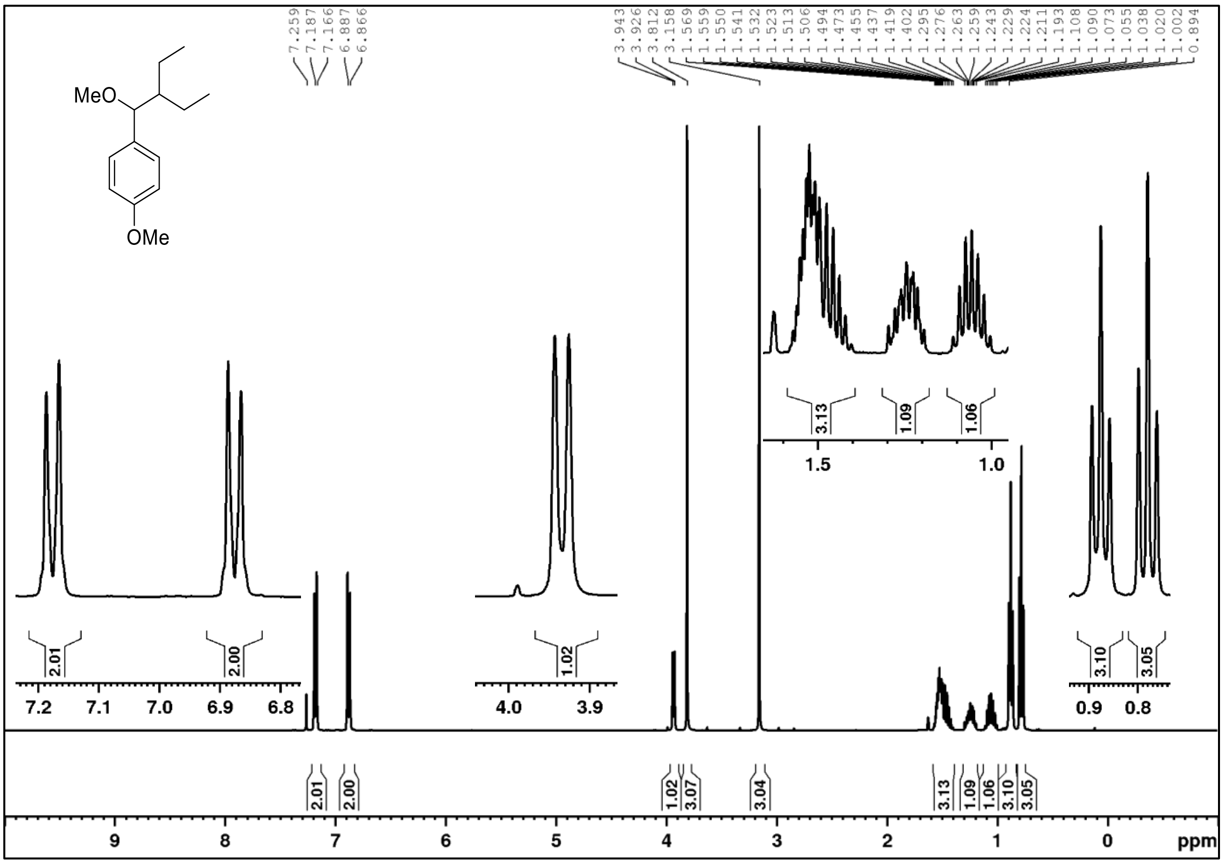


$^{13}$C NMR (101 MHz, $CDCl_3$)

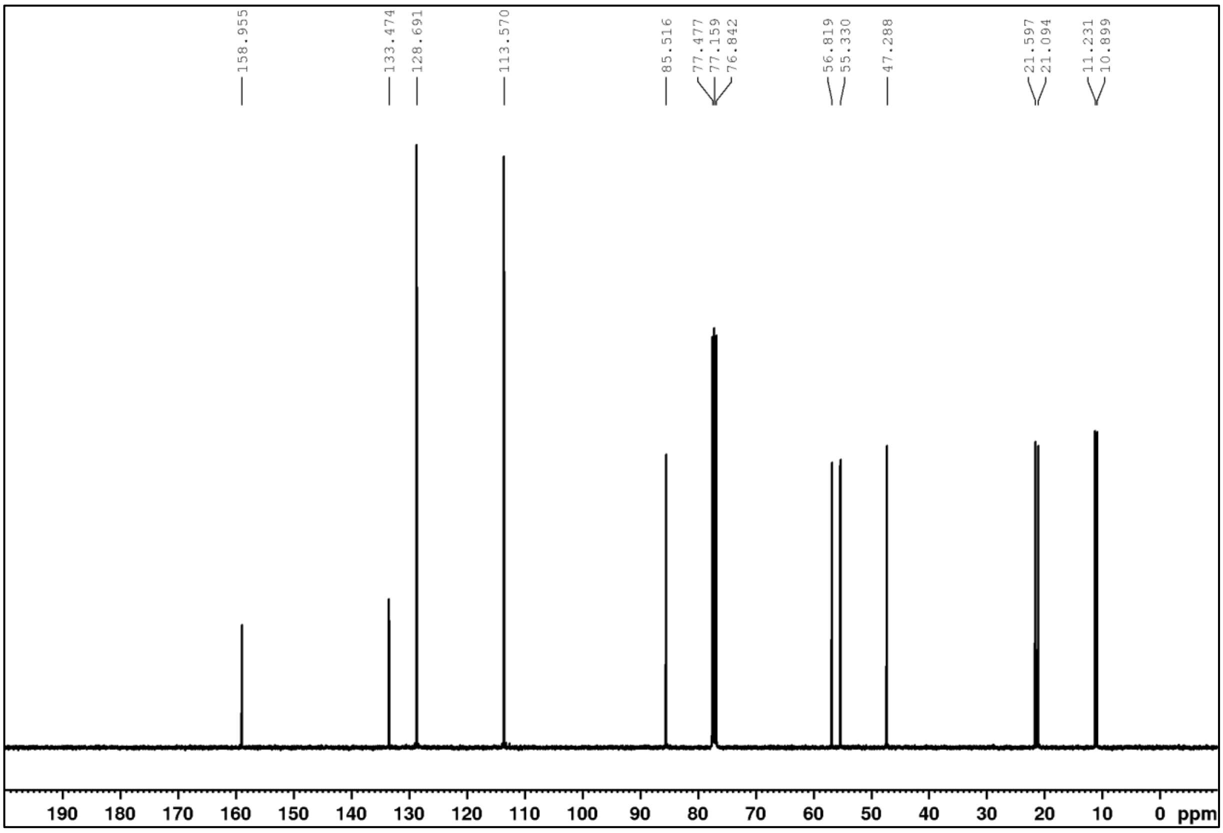


**1-(2-Ethyl-1-methoxybutyl)-4-methoxybenzene (7d)**

$^1$H NMR (400 MHz, CDCl$_3$)

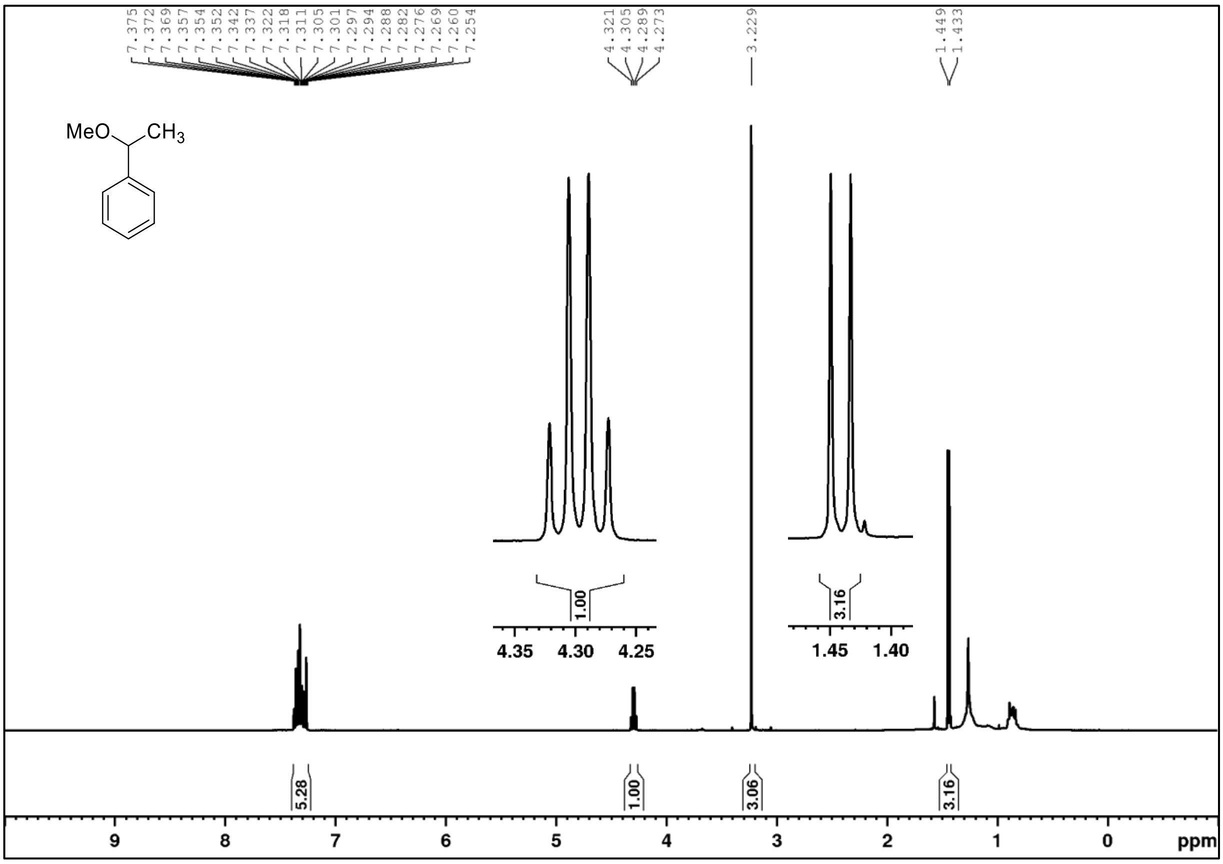


$^{13}$C NMR (101 MHz, CDCl$_3$)



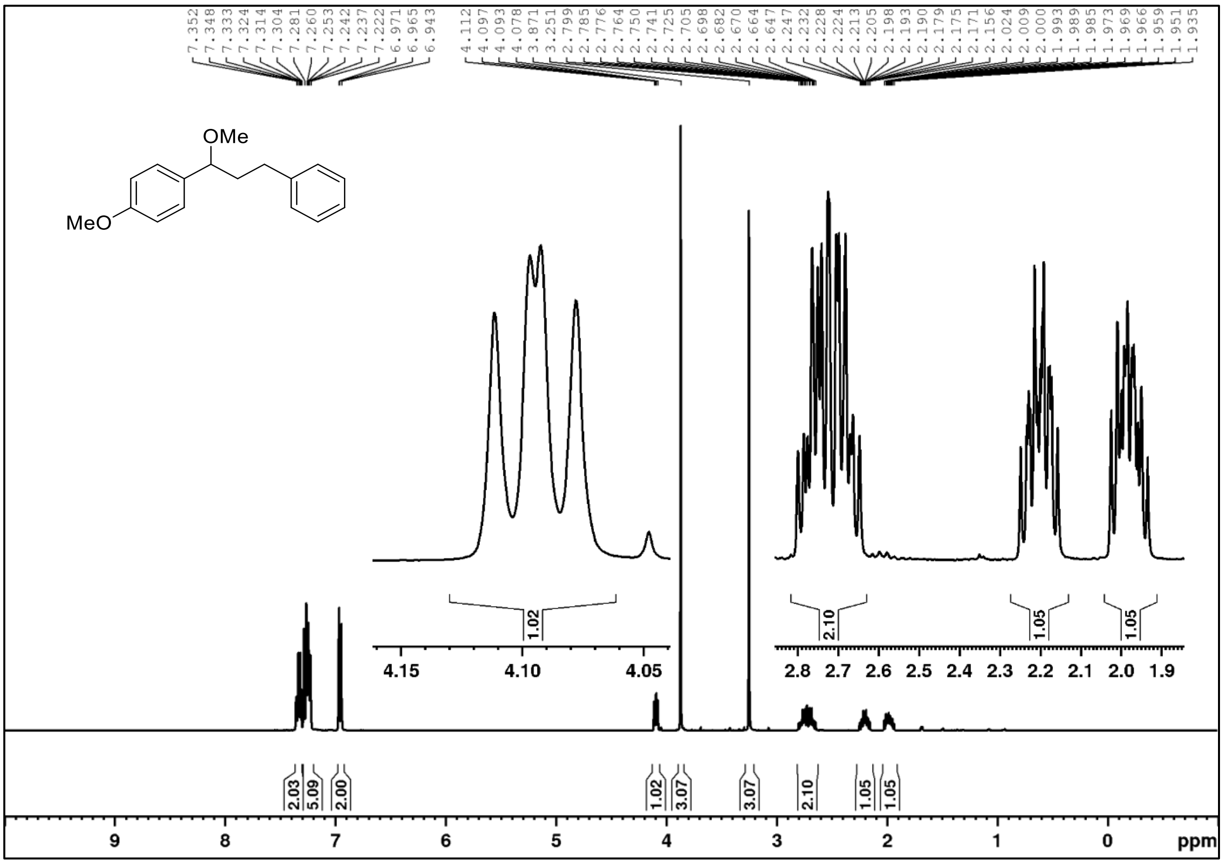
**(1-Methoxyethyl)benzene (7e)**

$^1$H NMR (400 MHz, CDCl$_3$)

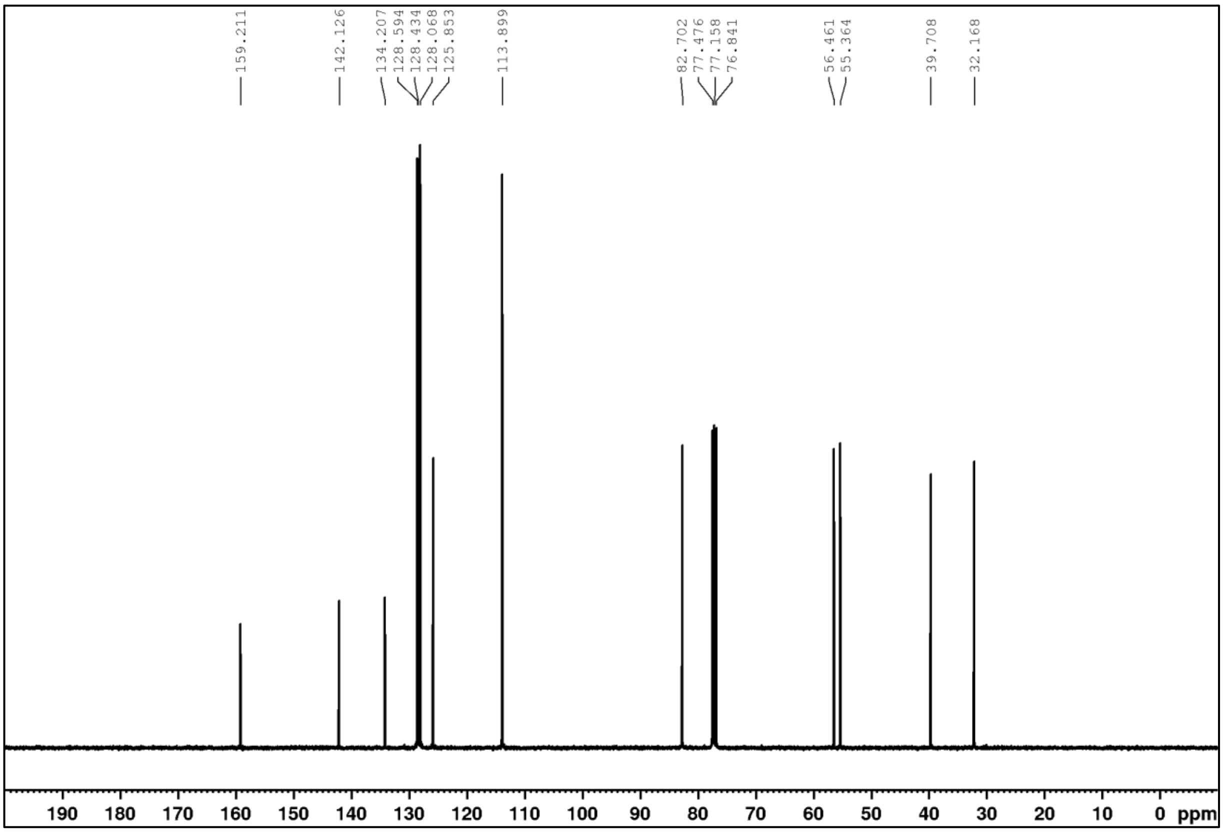


**1-Methoxy-4-(1-methoxy-3-phenylpropyl)benzene (7f)**

$^1$H NMR (400 MHz, CDCl$_3$)

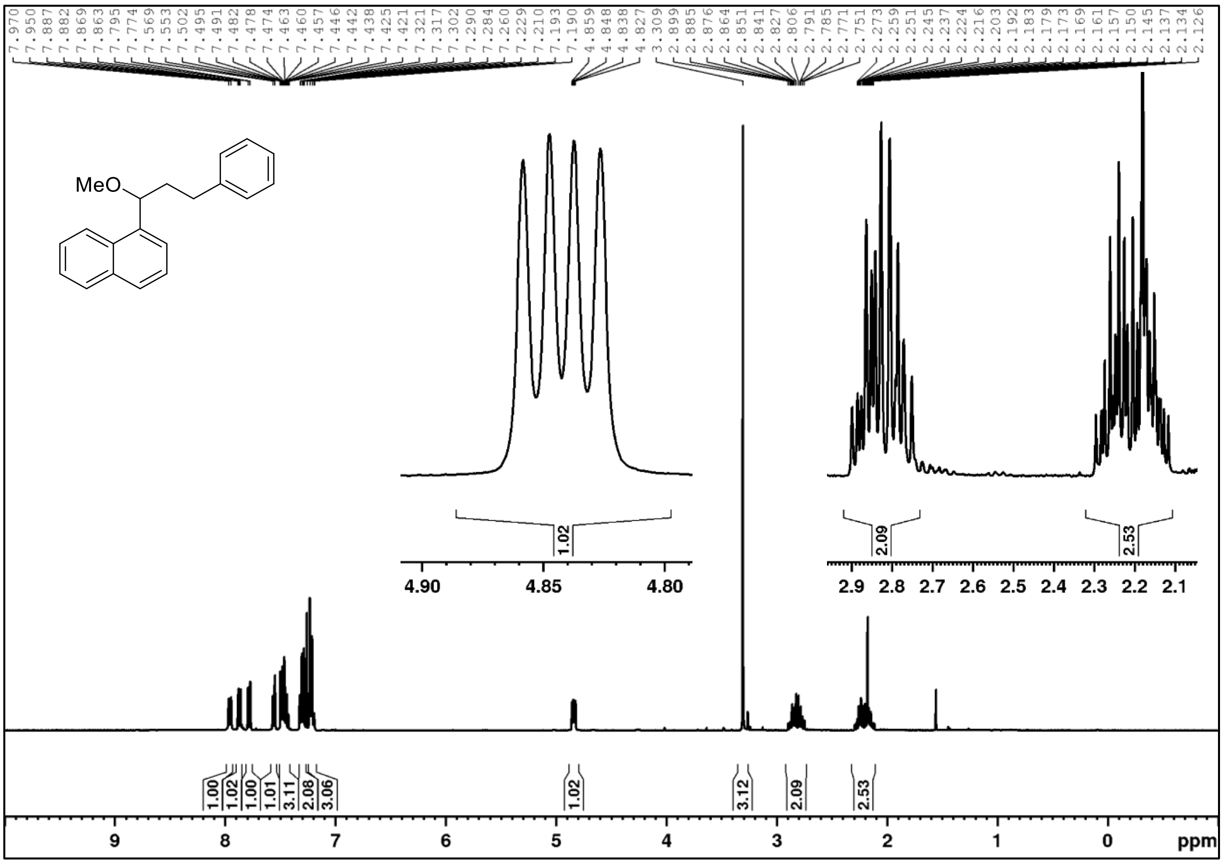


$^{13}$C NMR (101 MHz, CDCl$_3$)

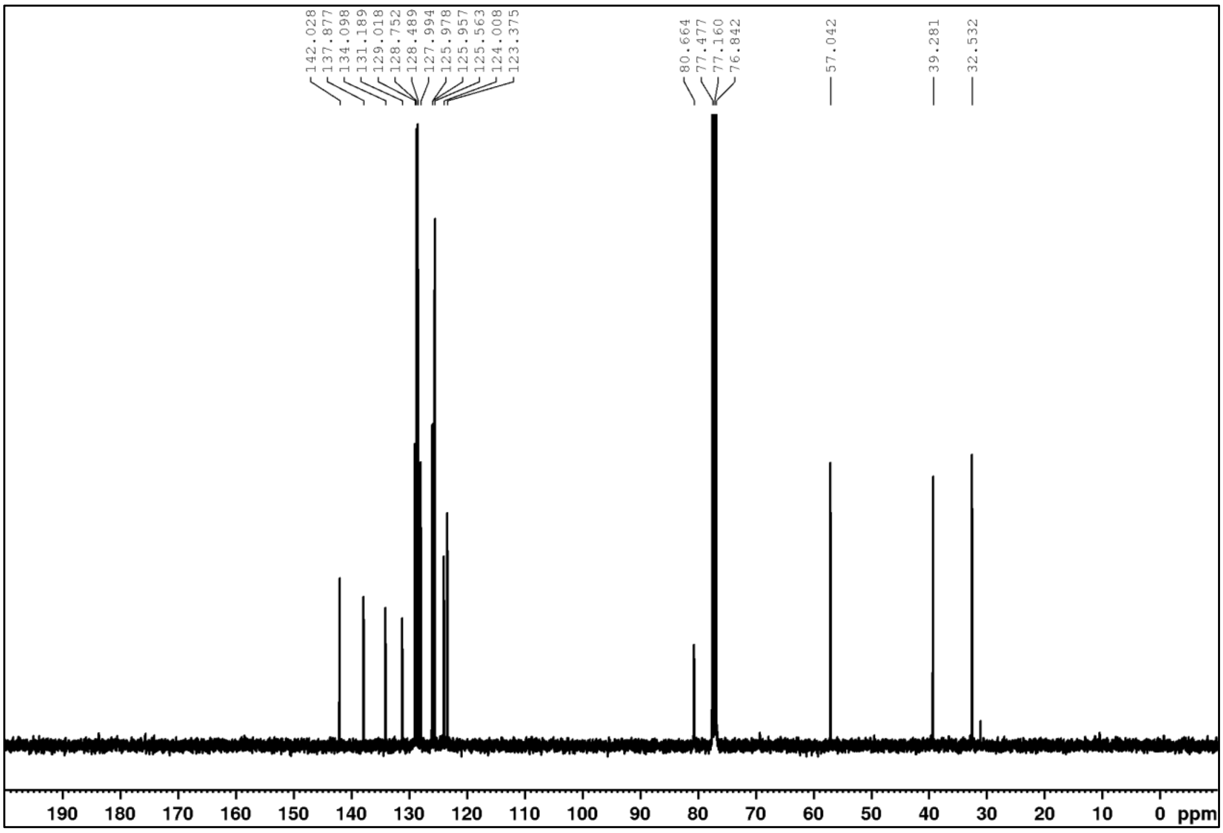


**1-(1-Methoxy-3-phenylpropyl)naphthalene (7h)**

$^{1}H$ NMR (400 MHz, $CDCl_3$)

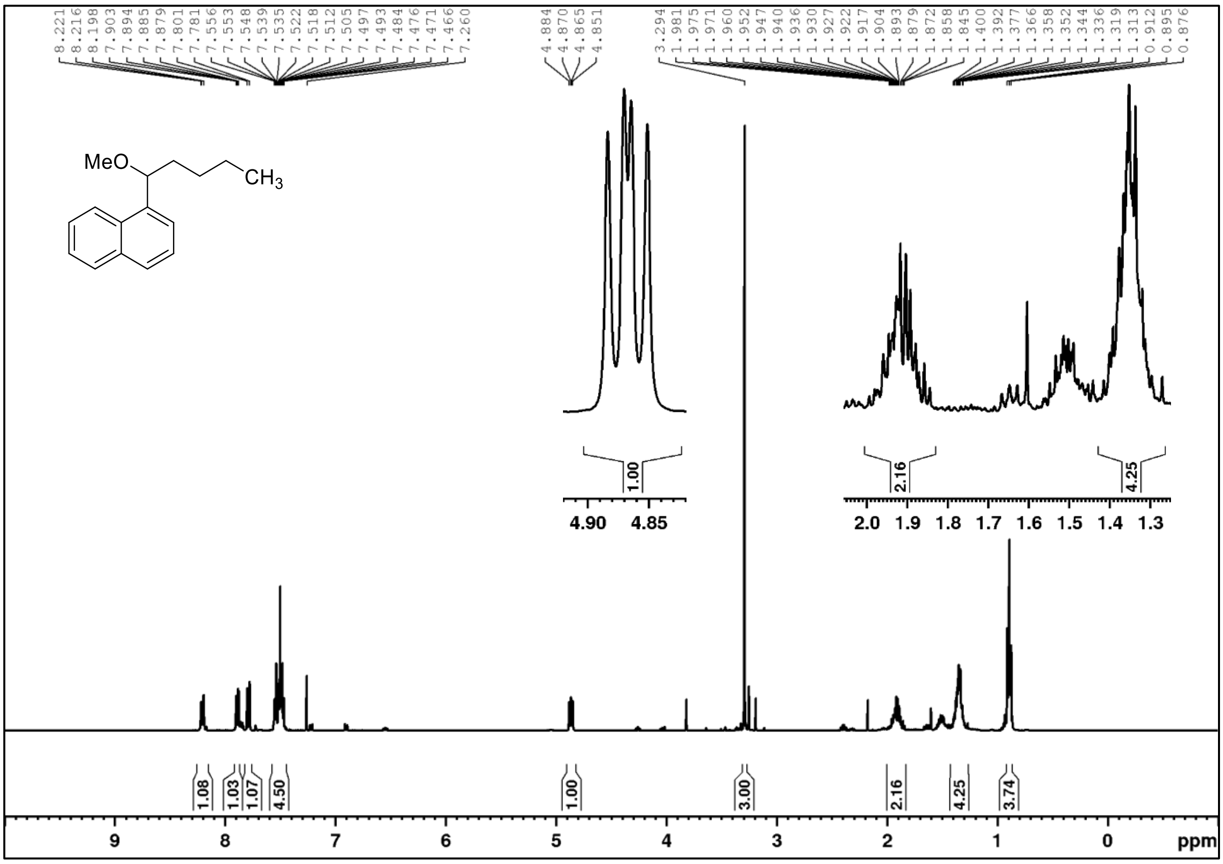


$^{13}C$ NMR (101 MHz, $CDCl_3$)

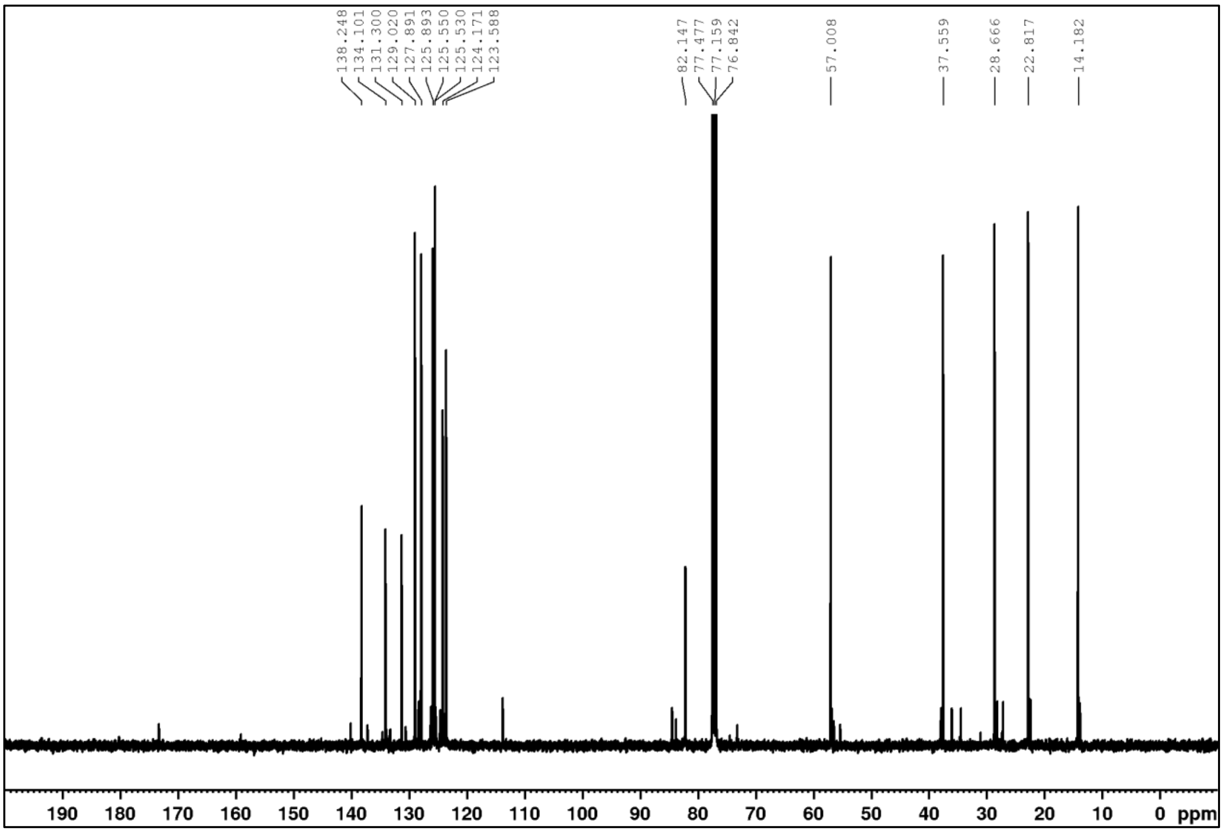


**1-(1-Methoxypentyl)naphthalene (7i)**

$^{1}$H NMR (400 MHz, CDCl$_3$)

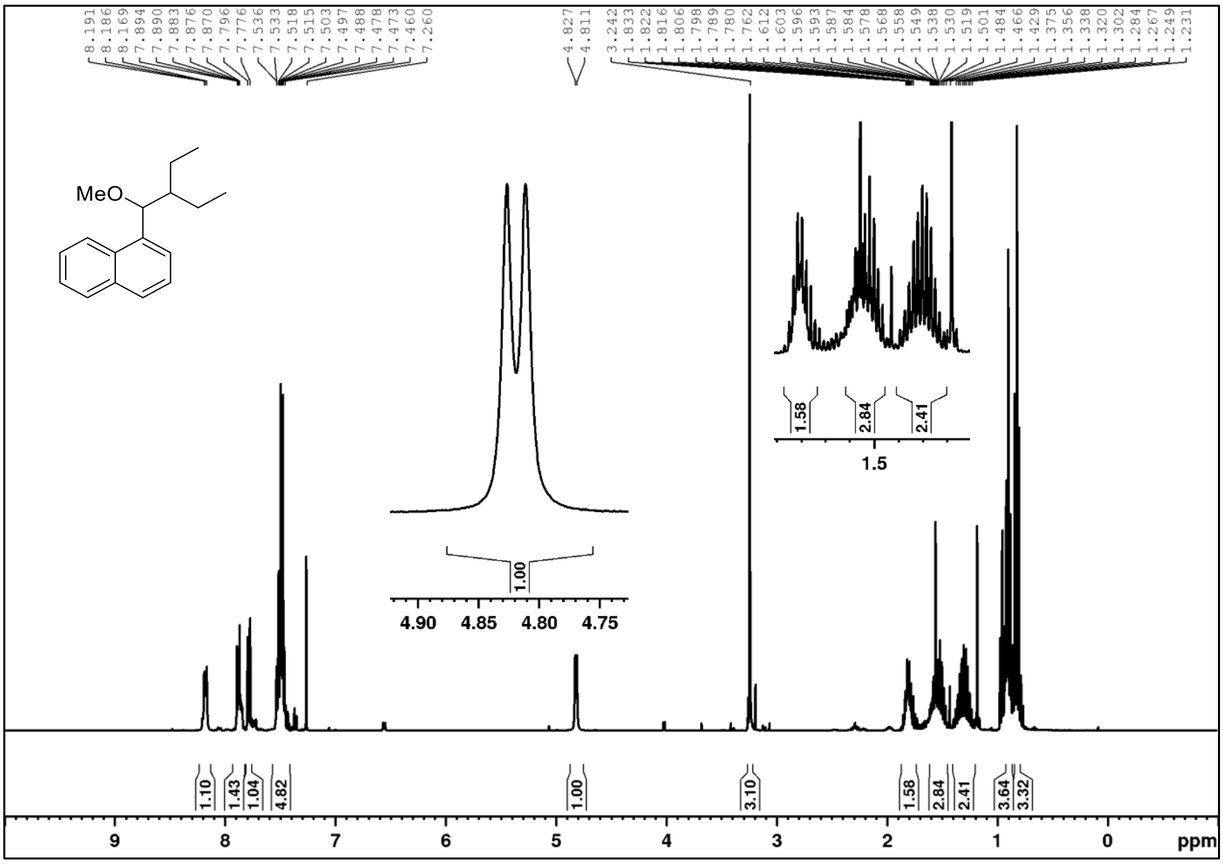


$^{13}$C NMR (101 MHz, CDCl$_3$)

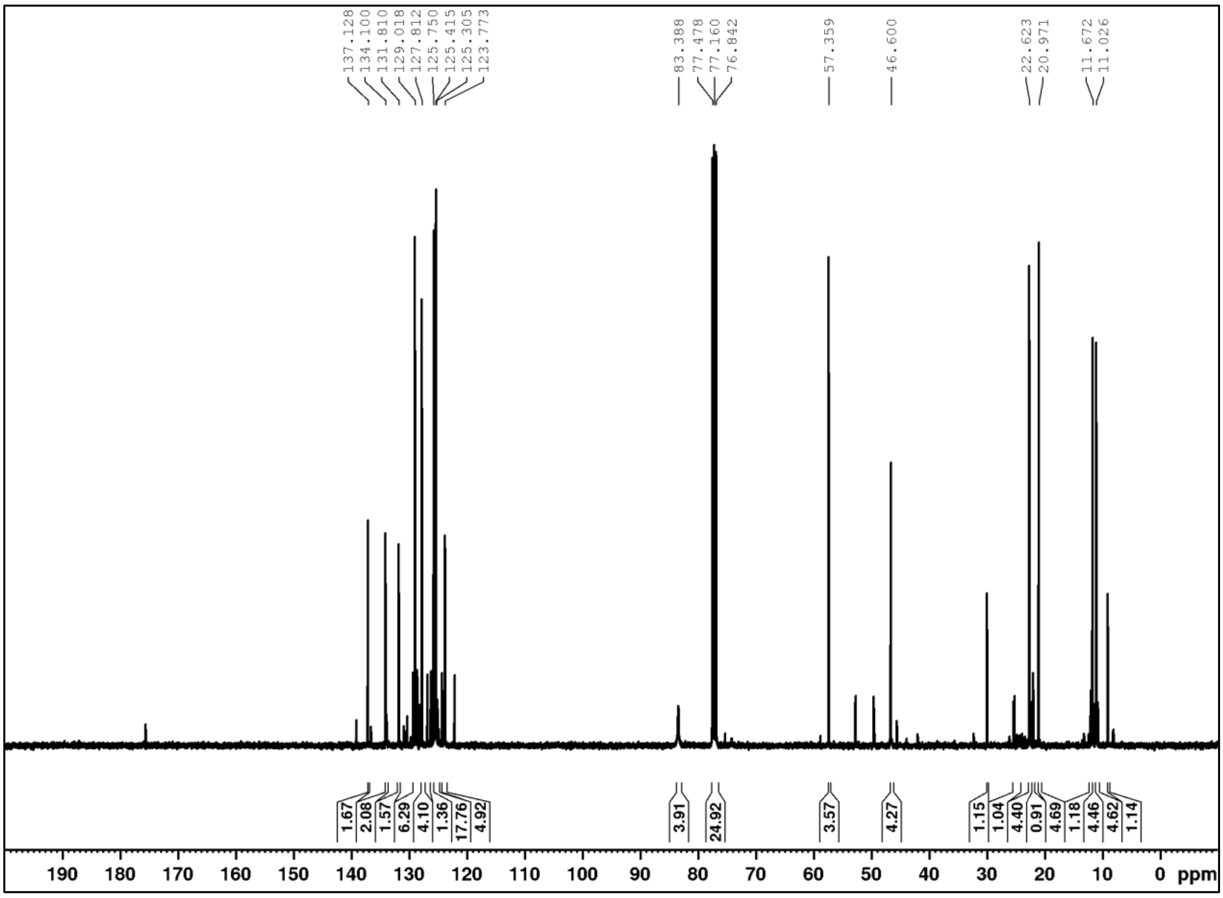


## 1-(2-Ethyl-1-methoxybutyl)naphthalene (7j)

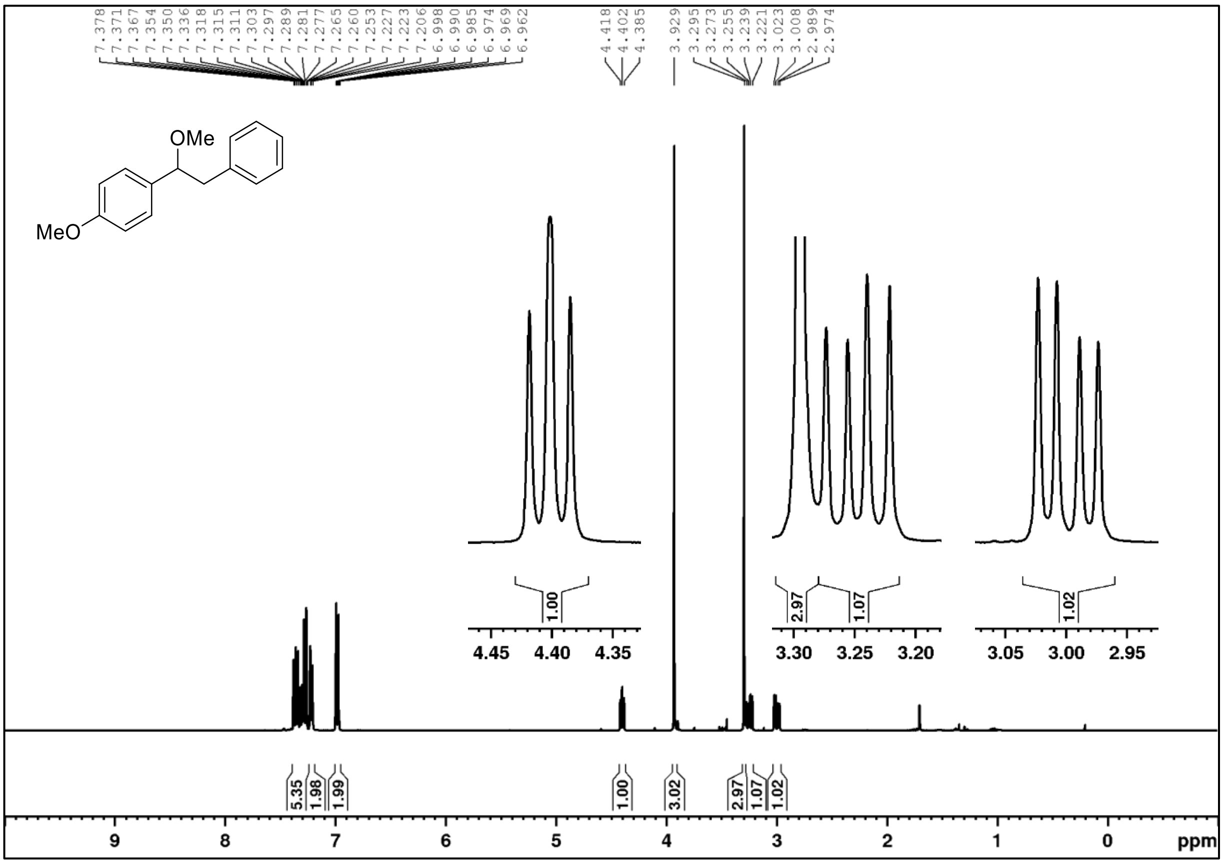
$^1$H NMR (400 MHz, $CDCl_3$)



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

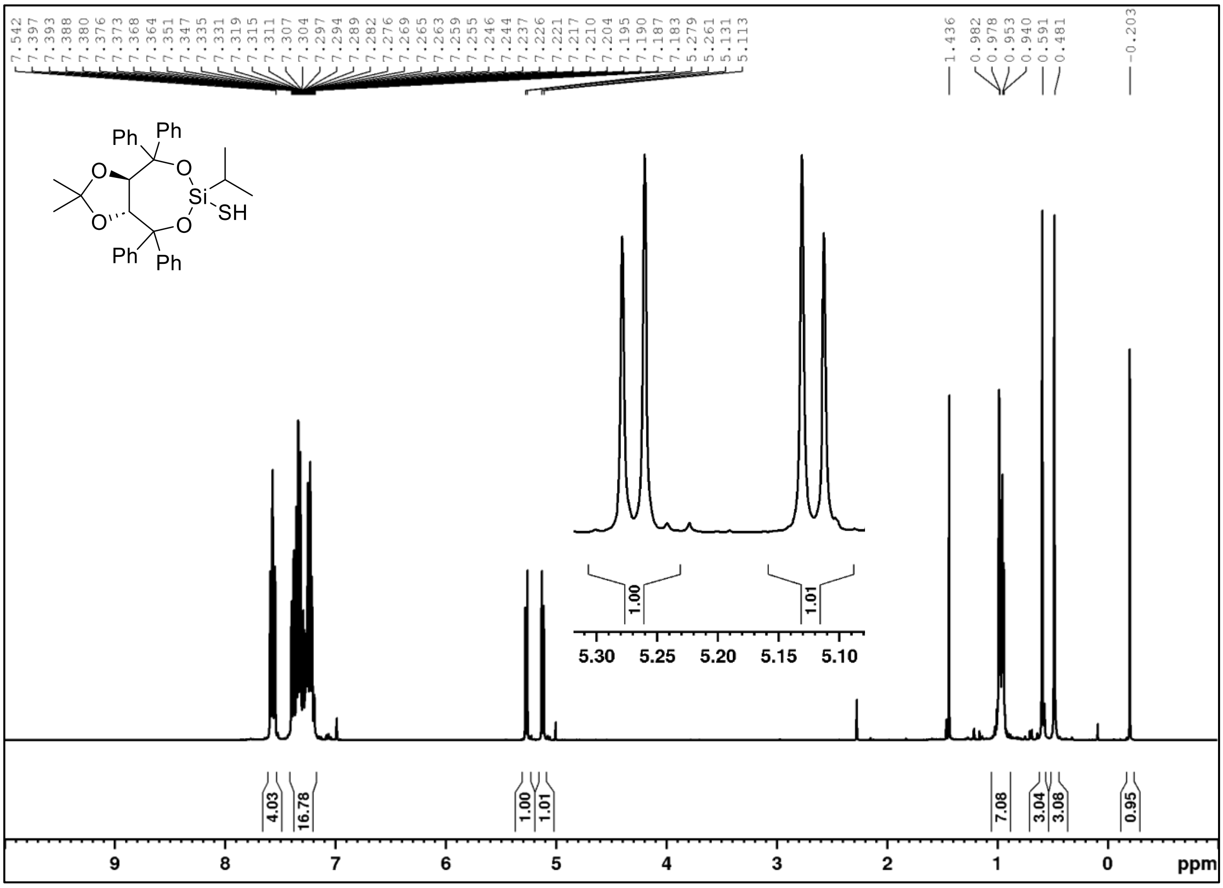


**Methoxy-4-(1-methoxy-2-phenylethyl)benzene (7k)** $^1$H NMR (400 MHz, CDCl$_3$)

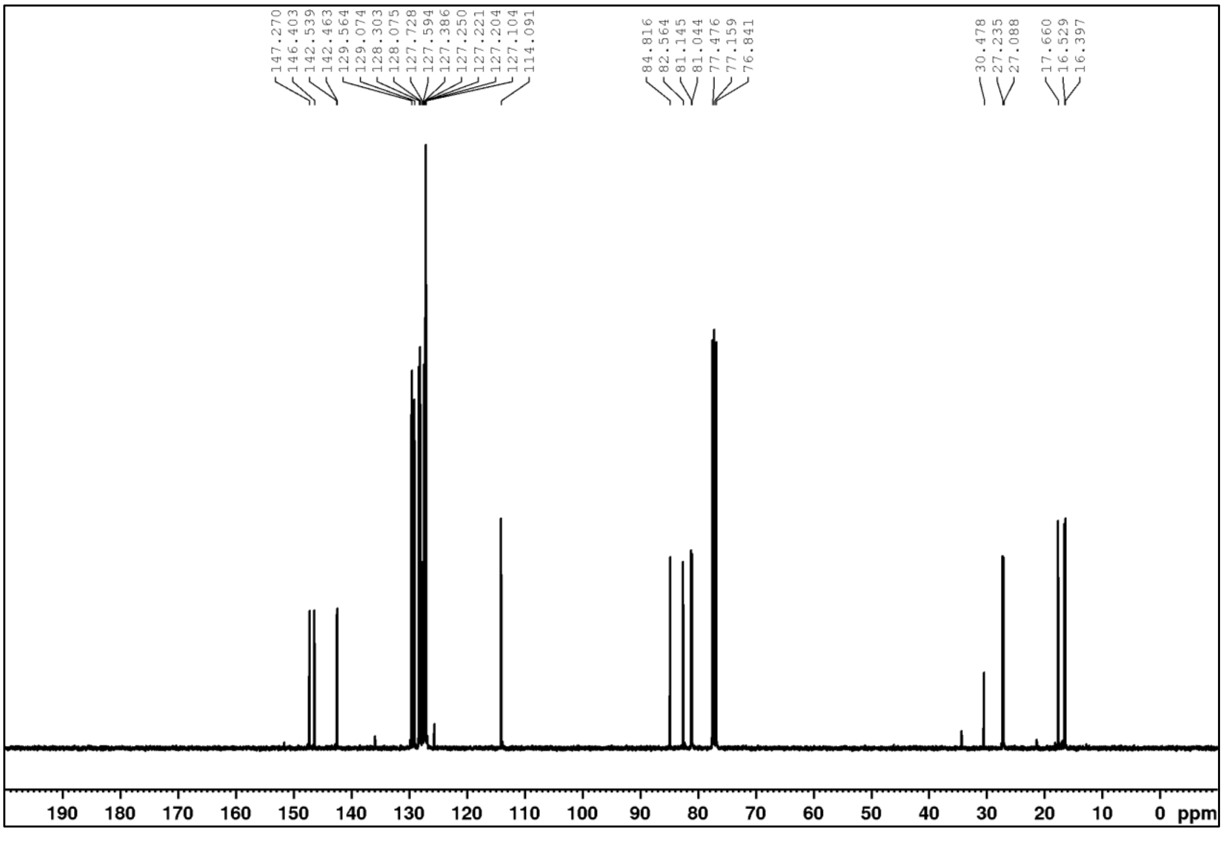


**(3a*R*,8a*R*)-6-isopropyl-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*R*,*R*)-10a)**

$^1$H NMR (400 MHz, CDCl$_3$)

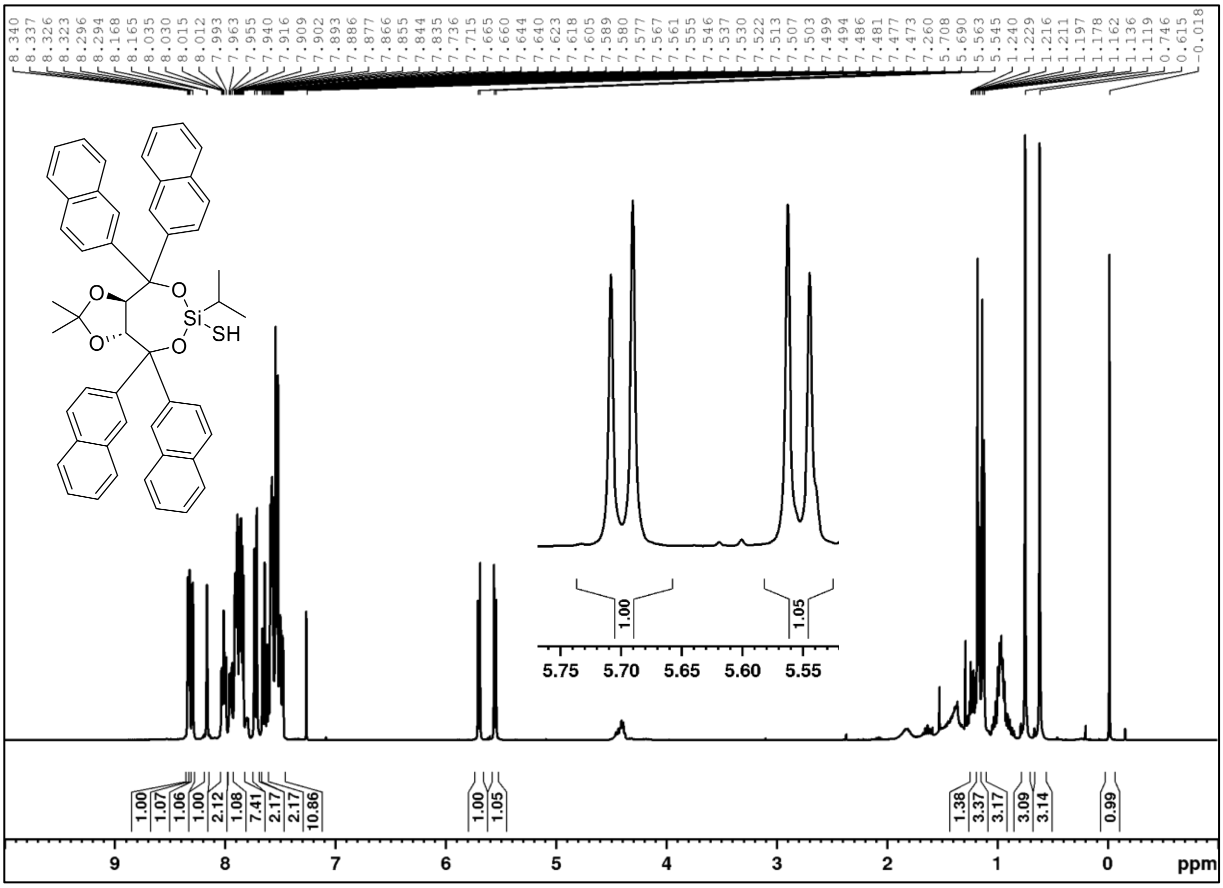


$^{13}$C NMR (101 MHz, CDCl$_3$)

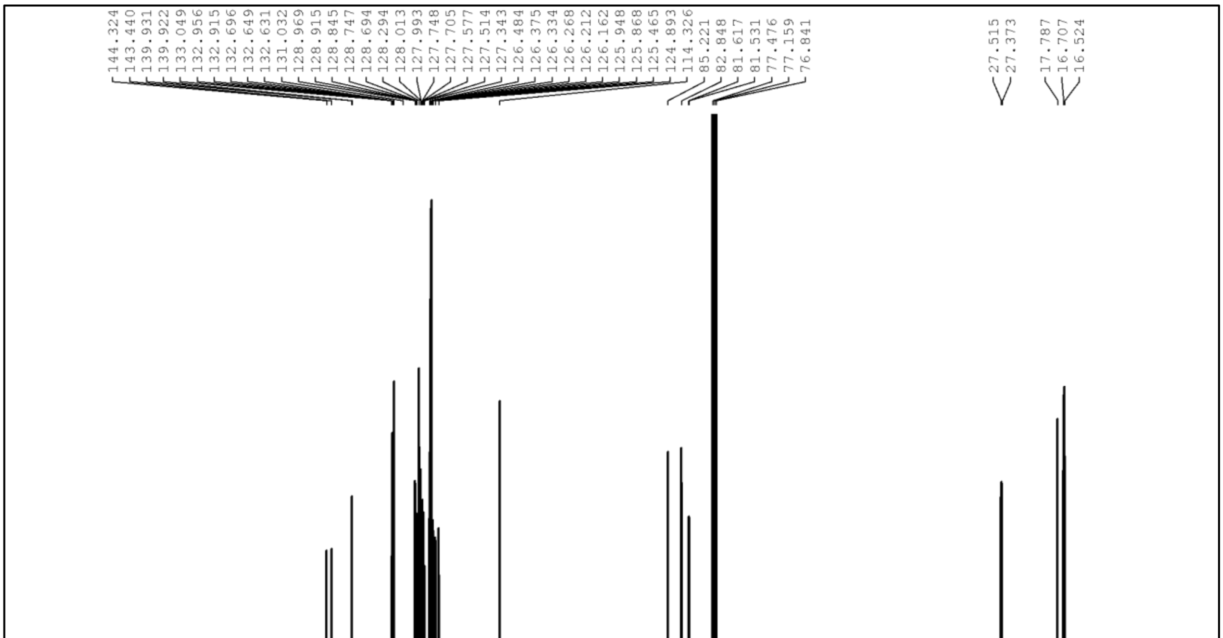


**(3a*R*,8a*R*)-6-Isopropyl-2,2-dimethyl-4,4,8,8-tetra(naphthalen-2-yl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*R*,*R*)-10b)**

$^1$H NMR (400 MHz, CDCl$_3$)

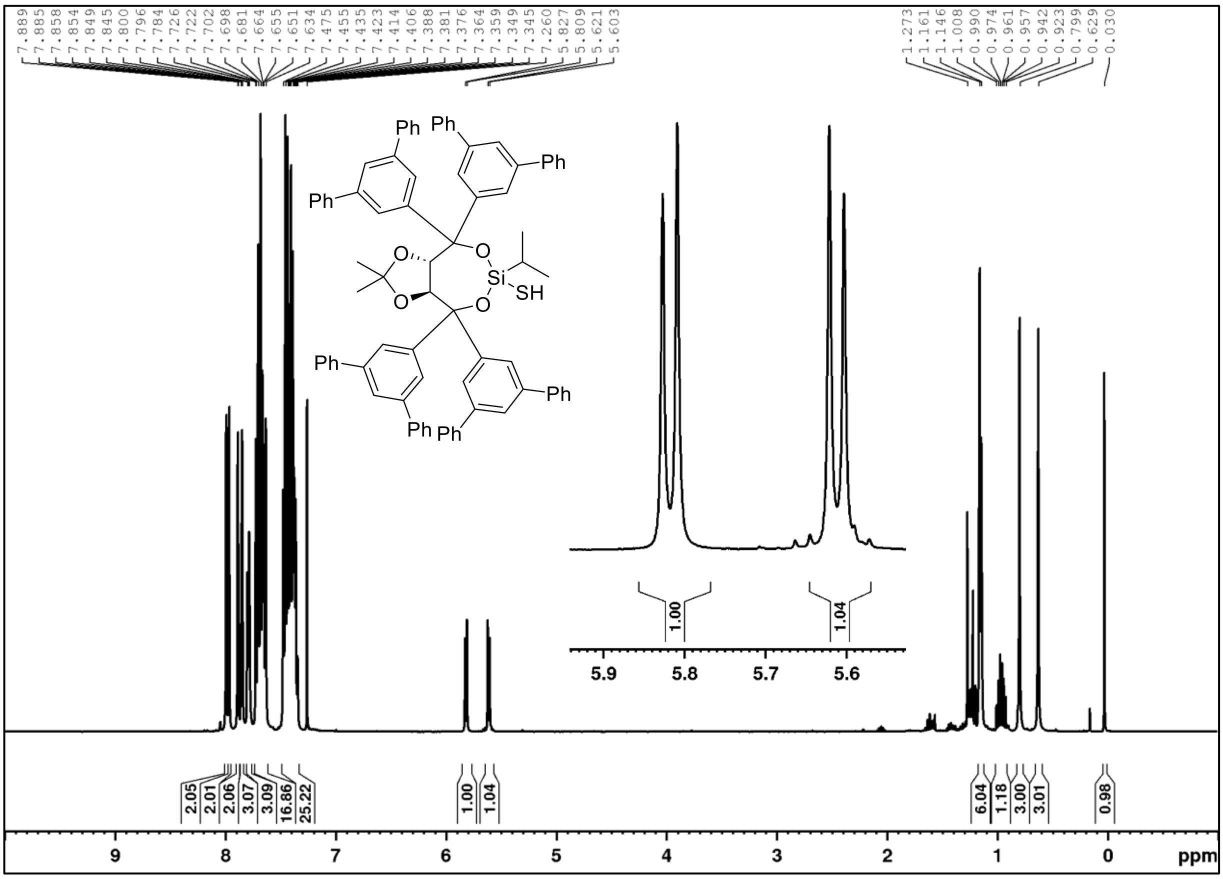


$^{13}$C NMR (101 MHz, CDCl$_3$)

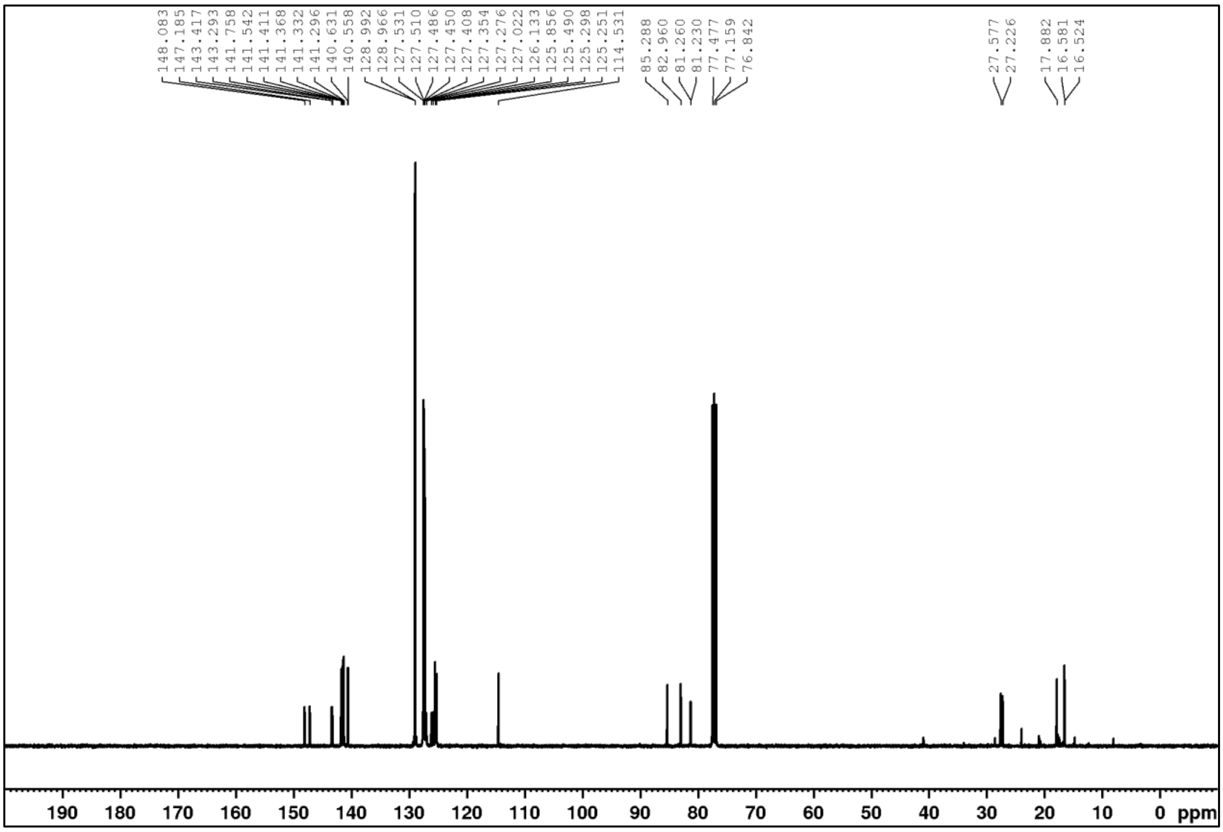


**(3a*S*,8a*S*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-isopropyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*S*,*S*)-10c)**

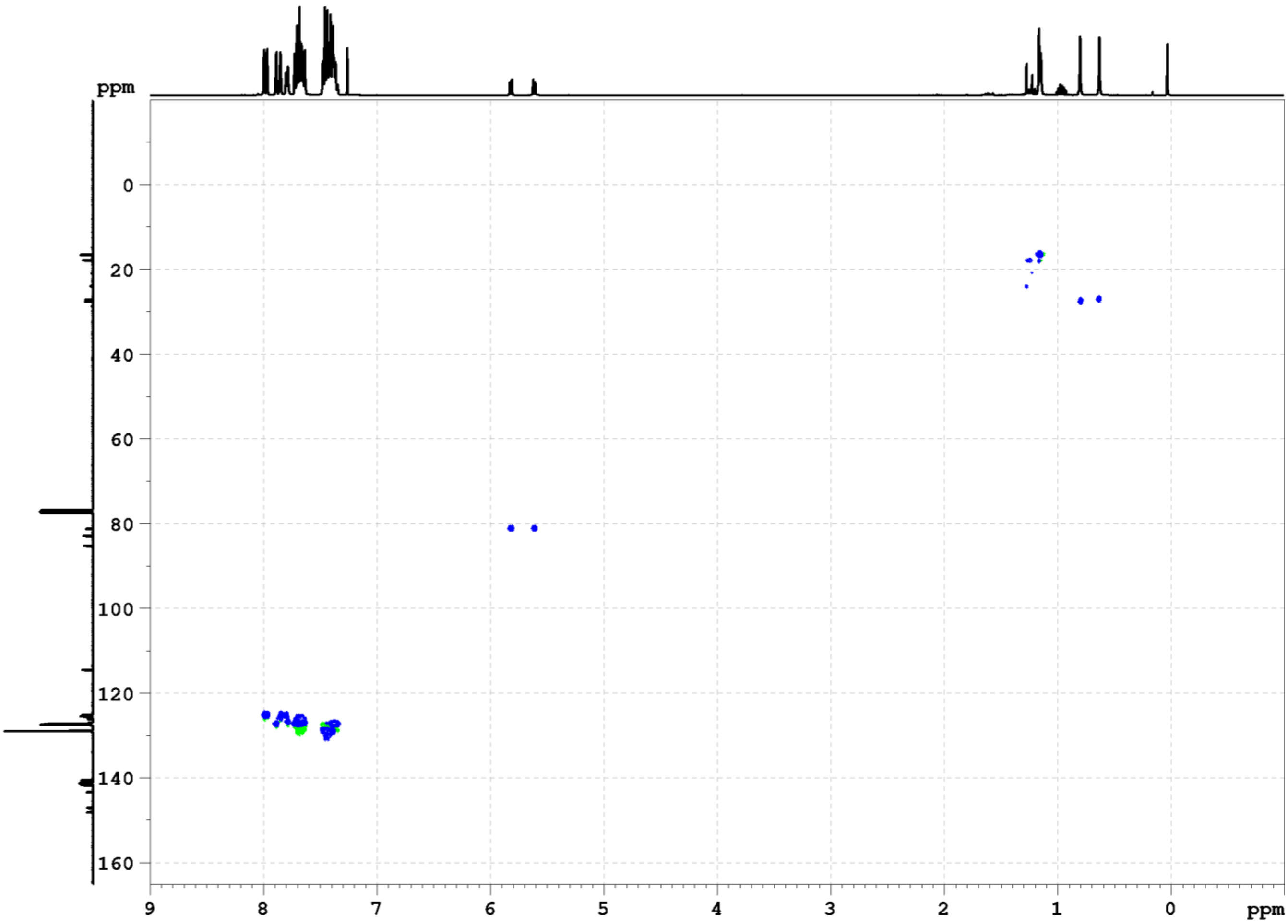
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (101 MHz, CDCl$_3$)

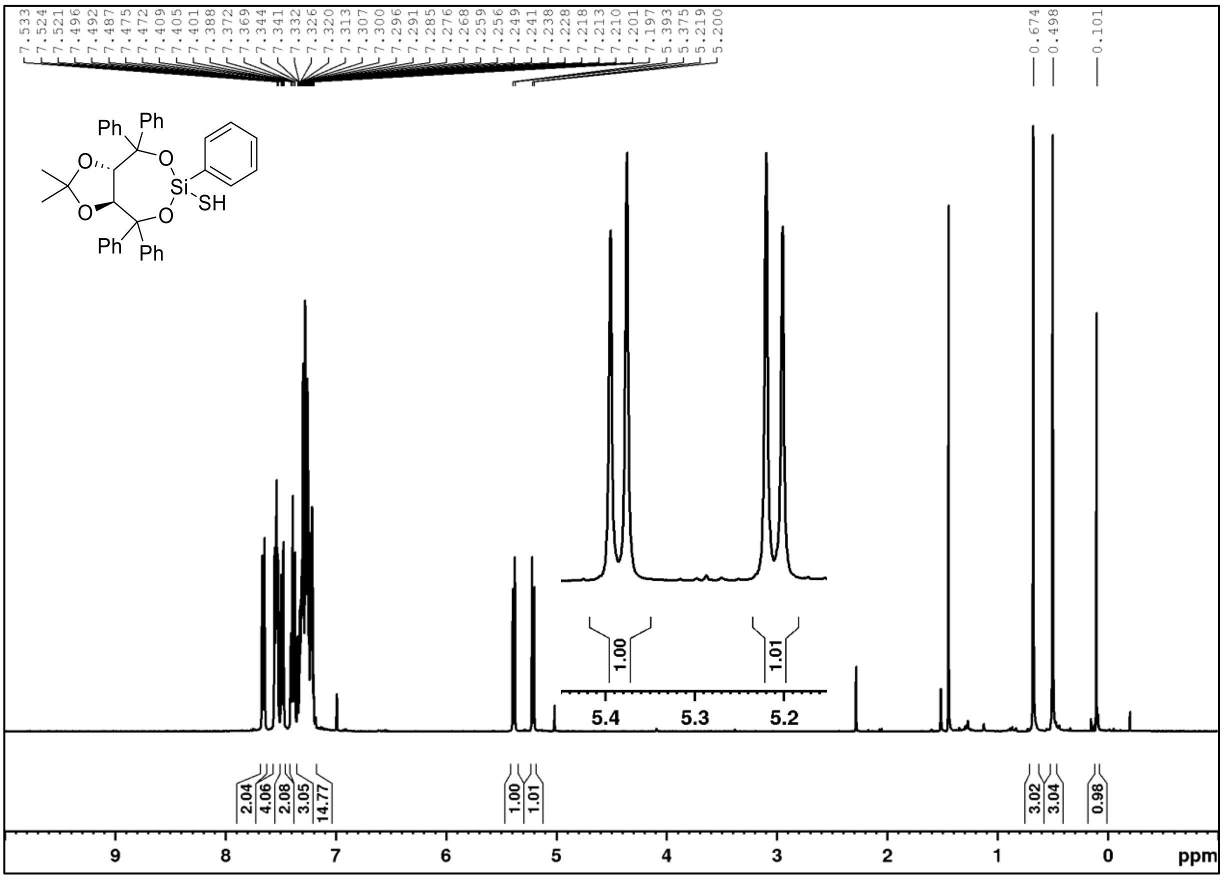


HSQC (CDCl$_3$)

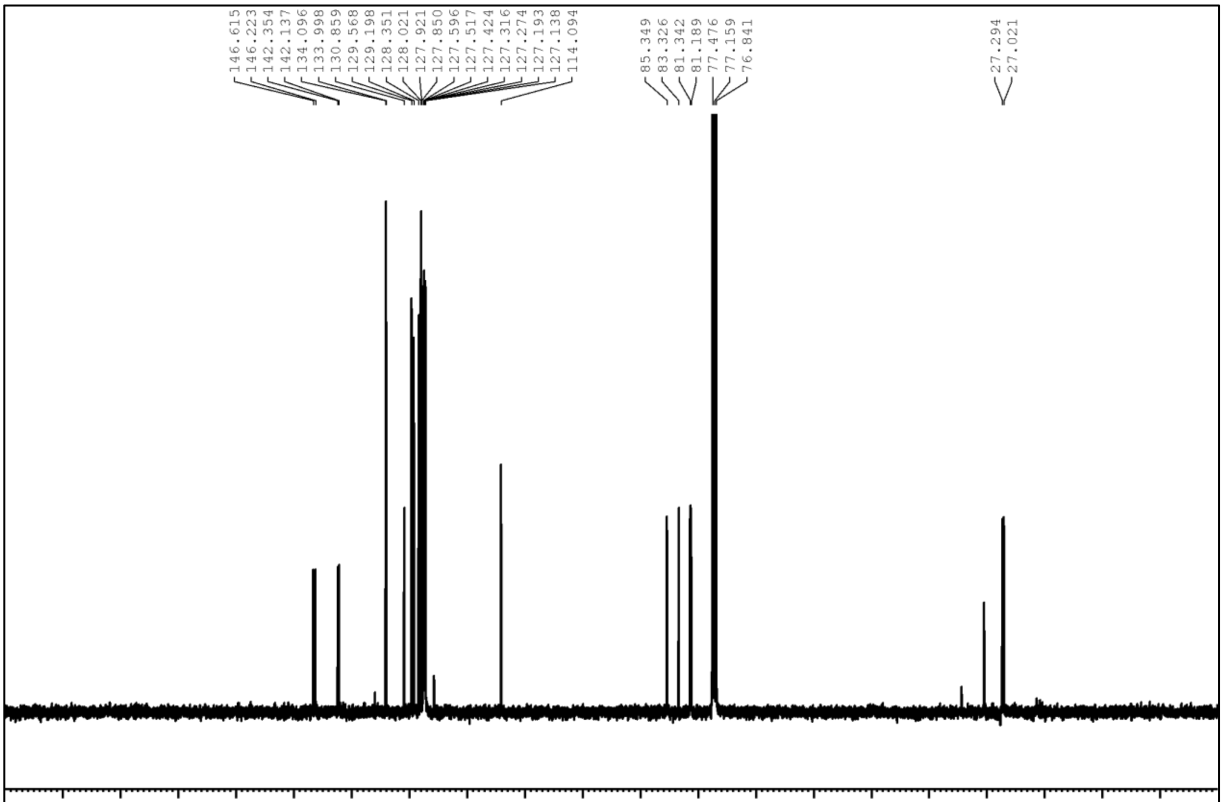


**(3a*S*,8a*S*)-2,2-Dimethyl-4,4,6,8,8-pentaphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine-6-thiol ((*S*,*S*)-10d)**

$^1$H NMR (400 MHz, CDCl$_3$)

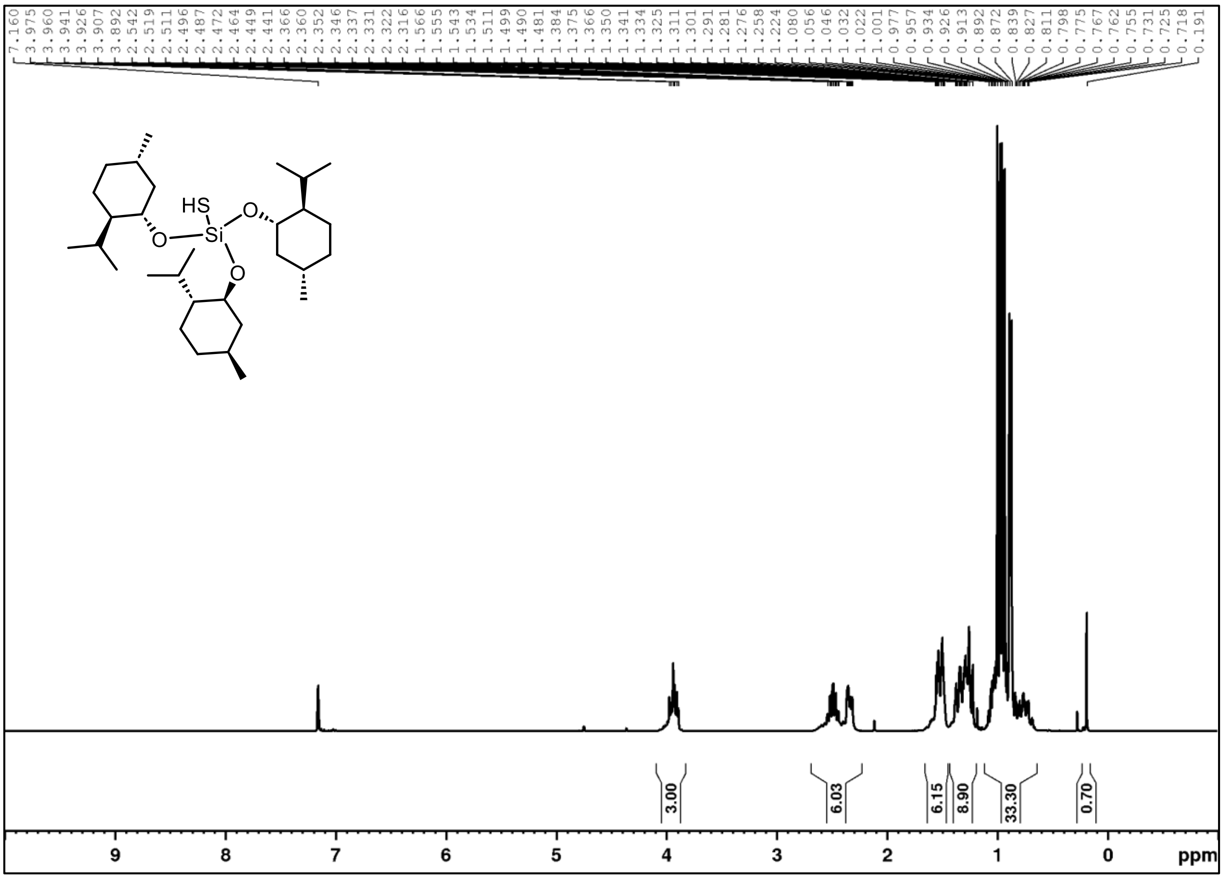


$^{13}$C NMR (101 MHz, CDCl$_3$)

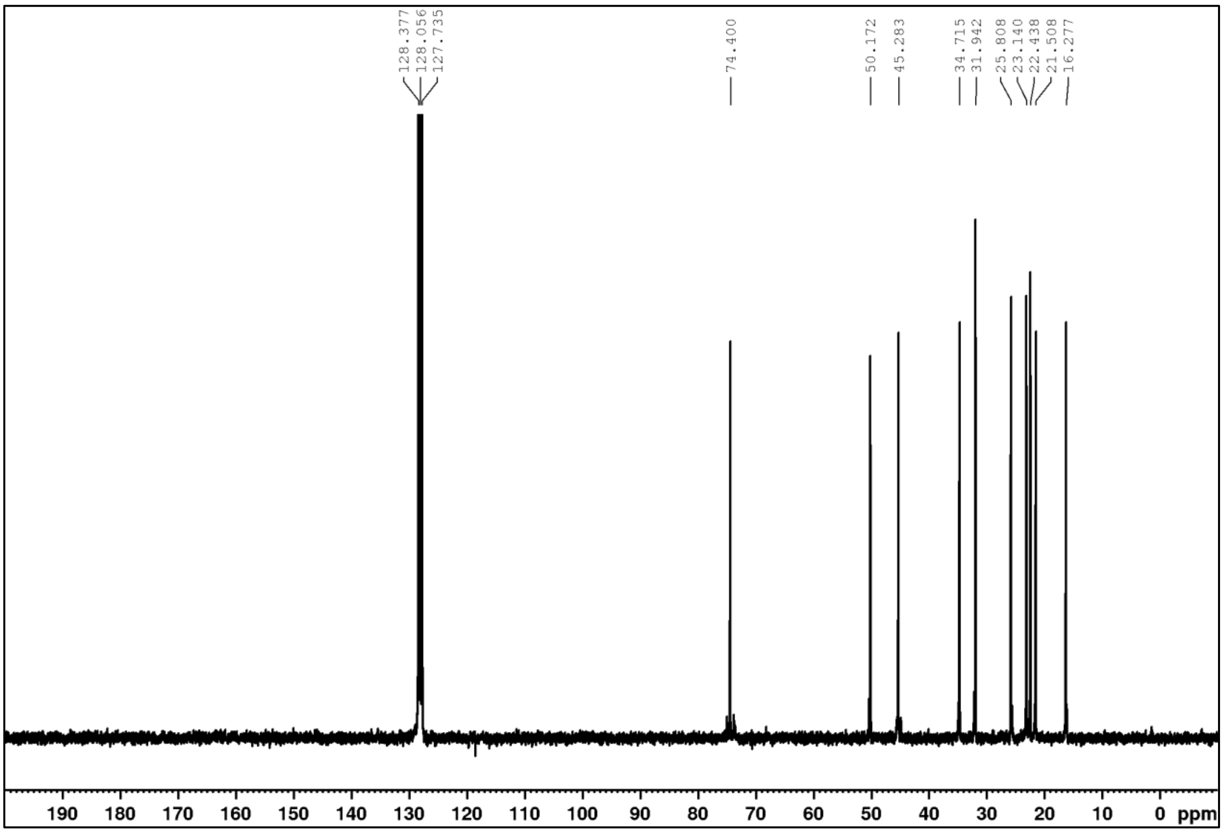


**Tris((1*S*,2*R*,5*S*)-menthoxy)silane thiol (11)**

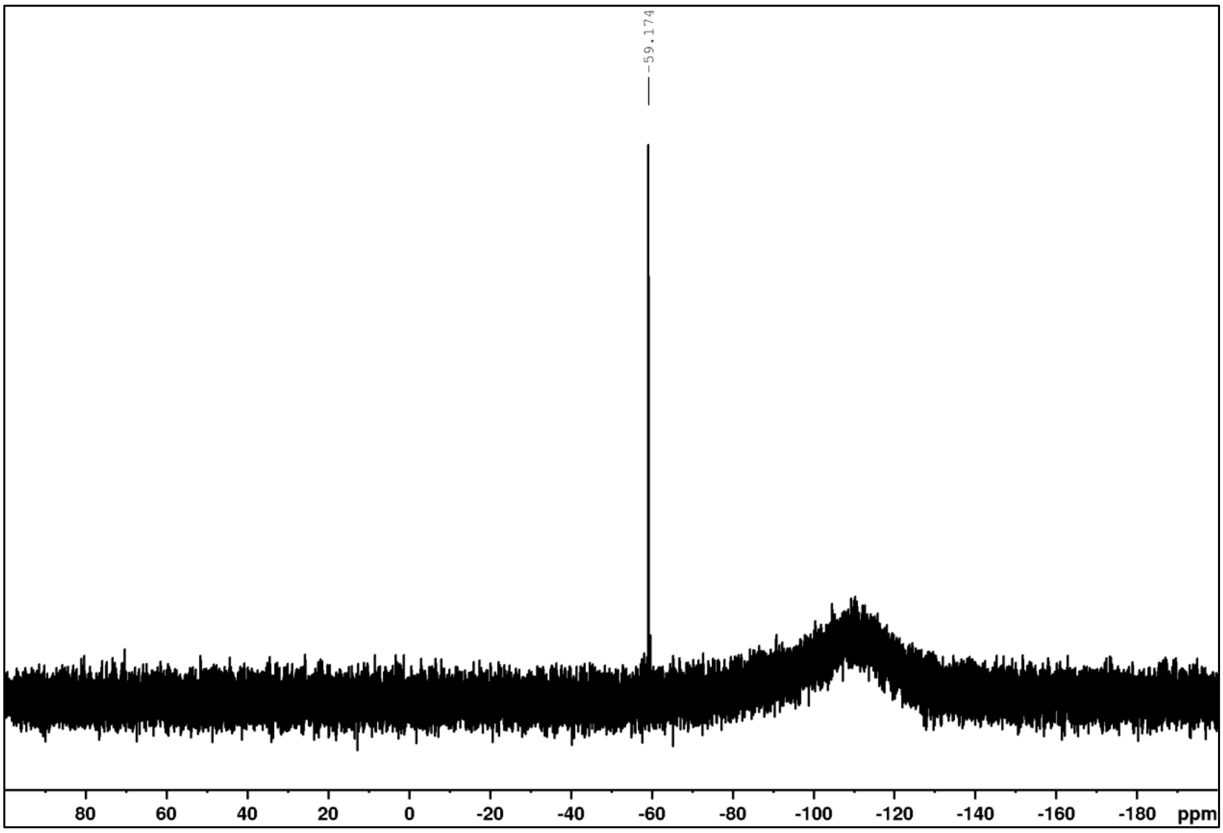
$^1$H NMR (400 MHz, $C_6D_6$)



$^{13}$C NMR (101 MHz, $C_6D_6$)

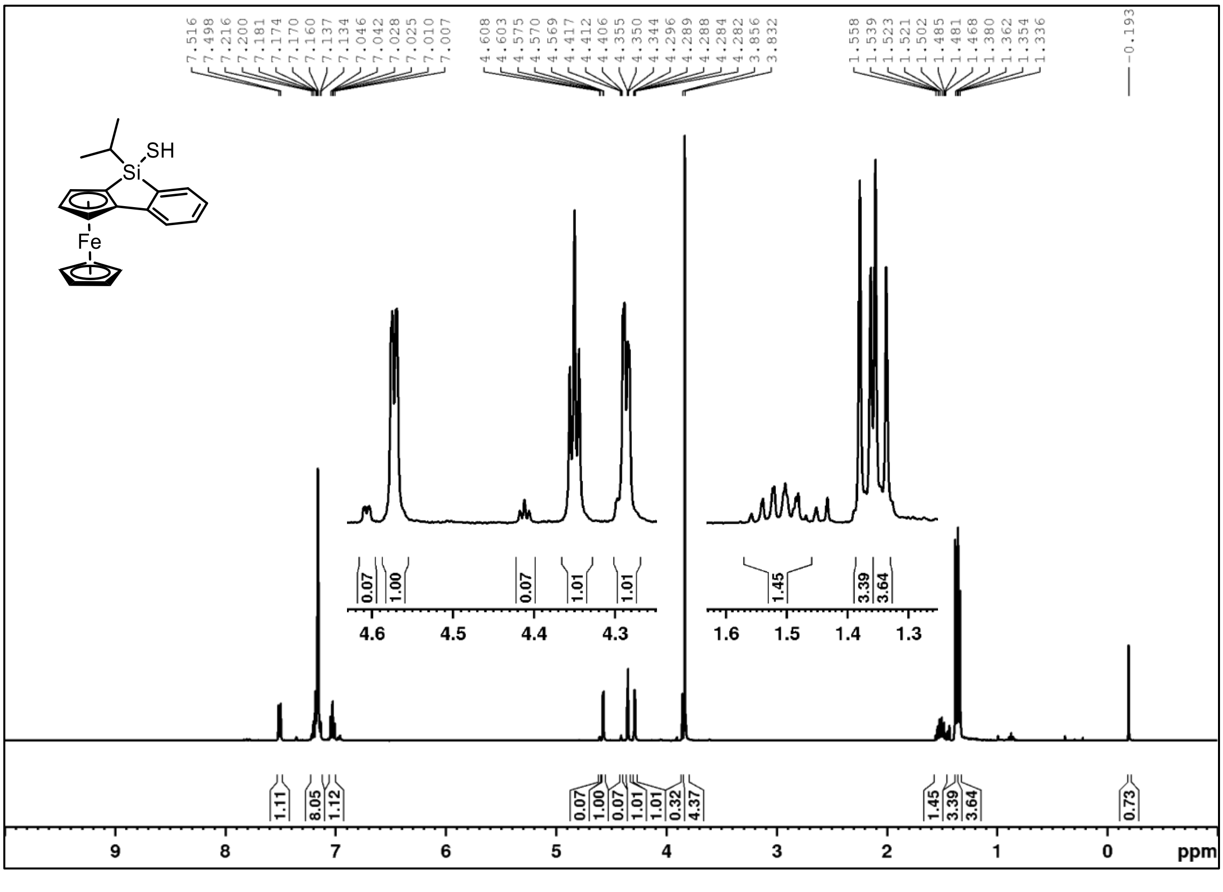


$^{29}Si\{^1H\}$ NMR (79.5 MHz, $C_6D_6$)

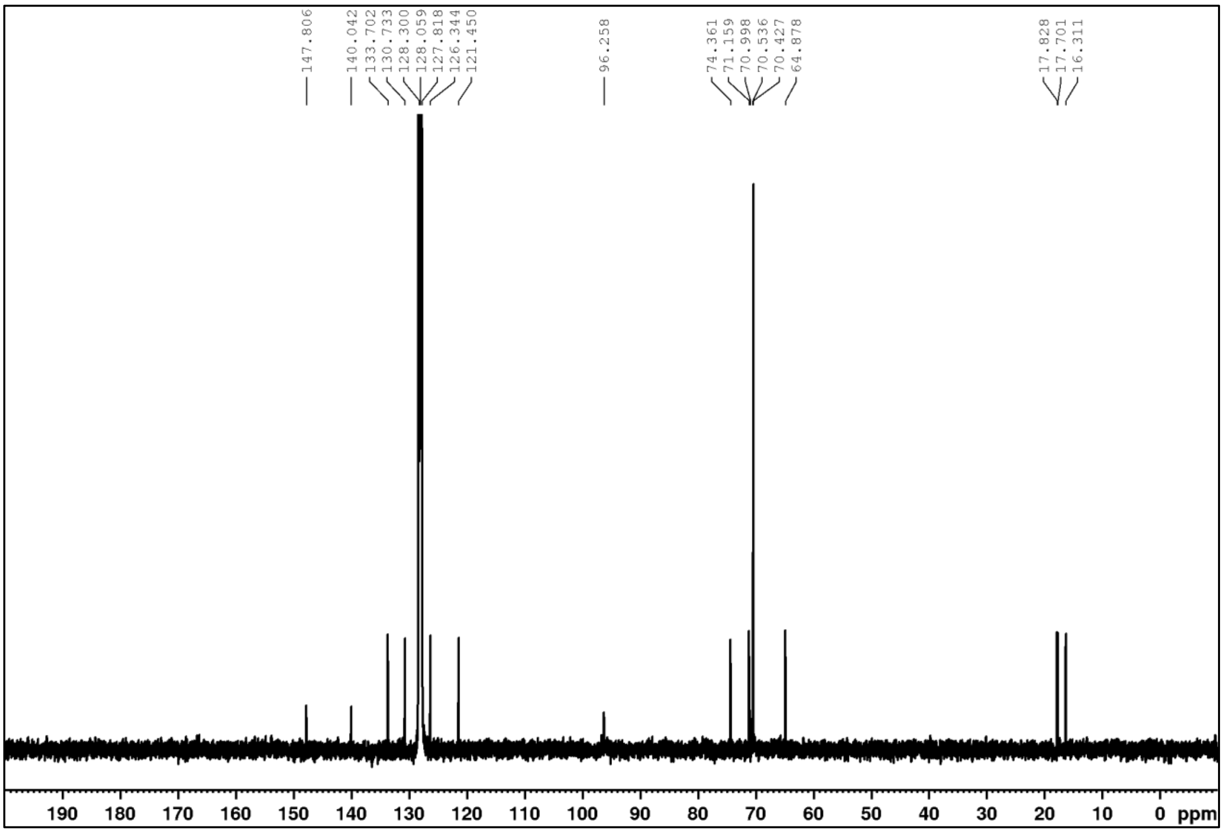


**12a**

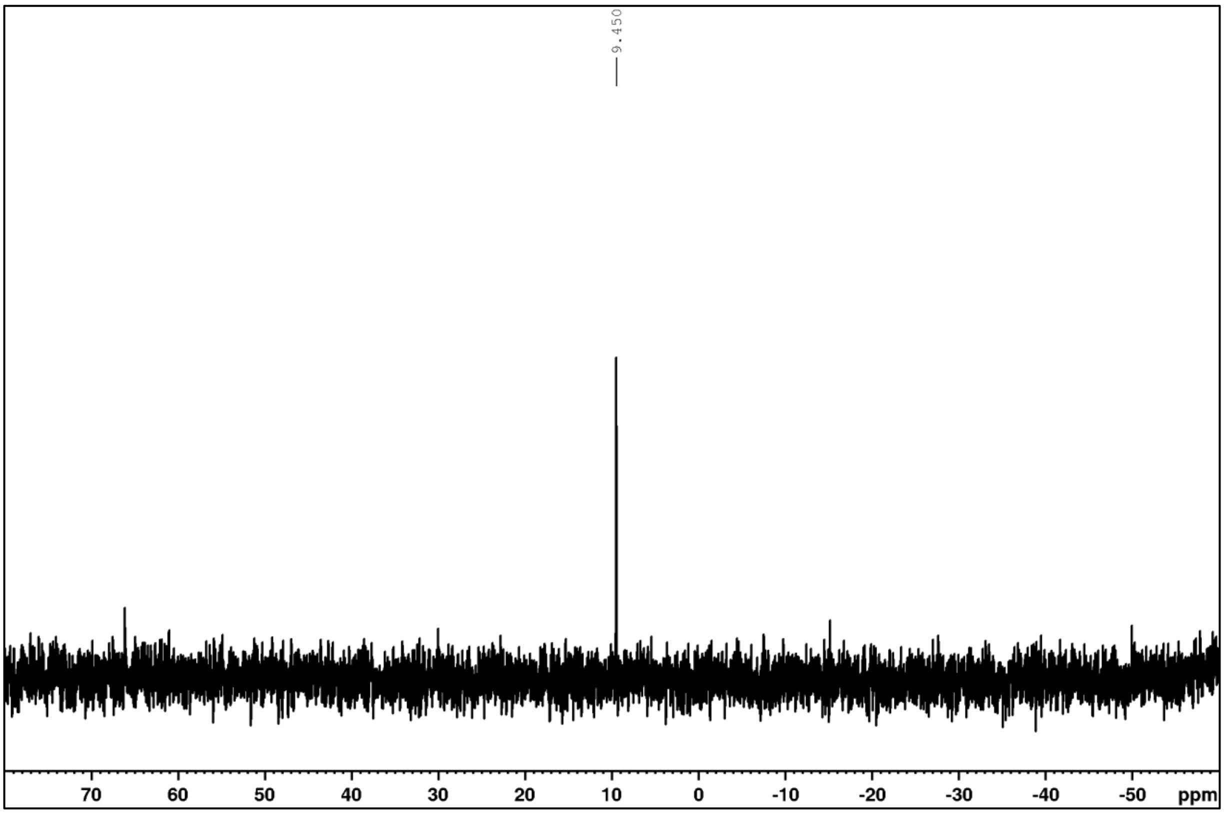
$^1H$ NMR (400 MHz, $C_6D_6$)



$^{13}C$ NMR (101 MHz, $C_6D_6$)

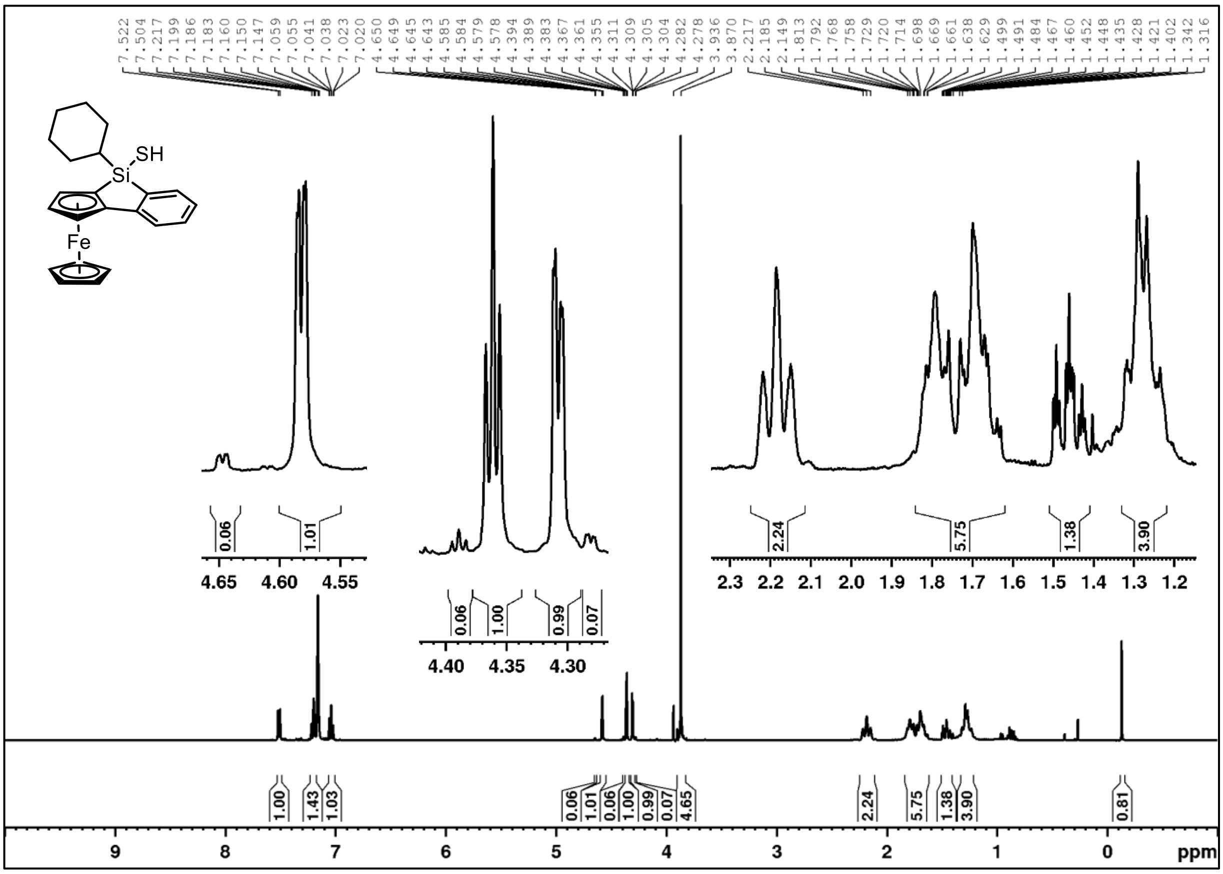


$^{29}Si\{^1H\}$ NMR (79.5 MHz, $C_6D_6$)

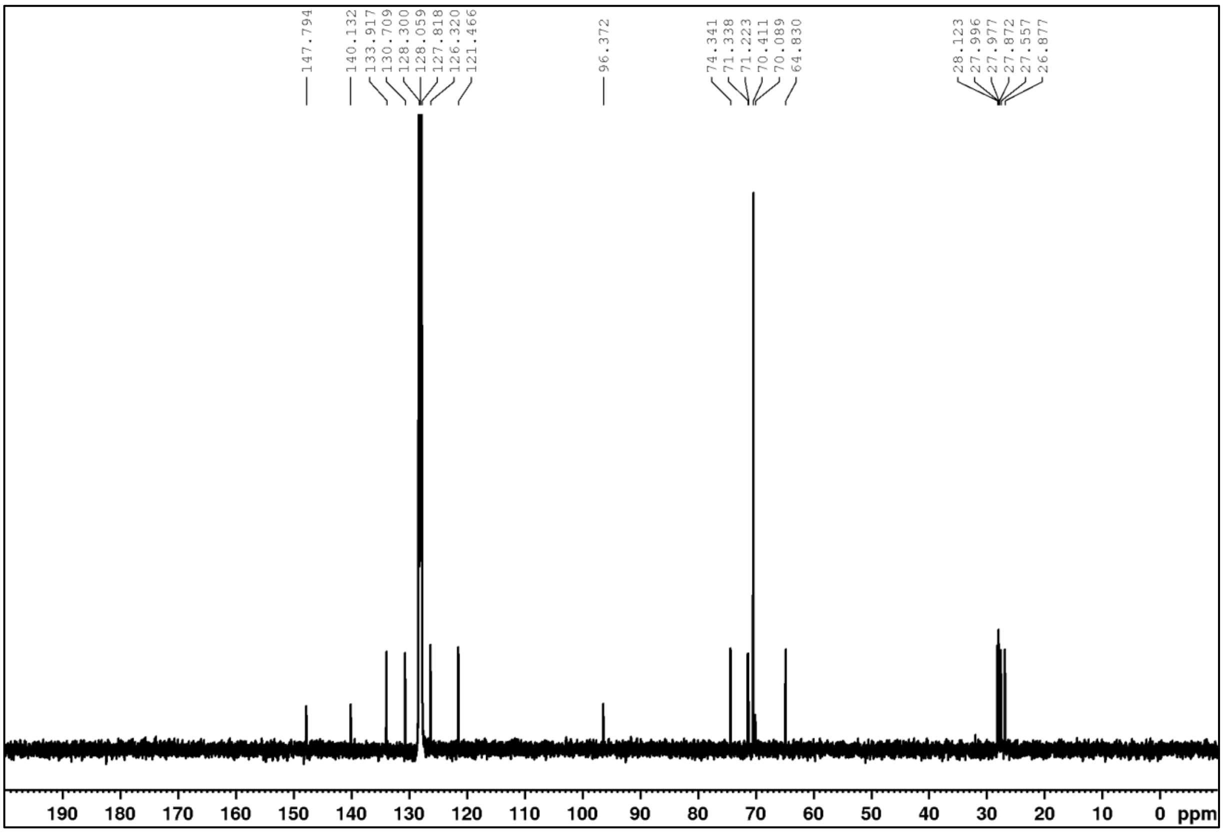


**12b**

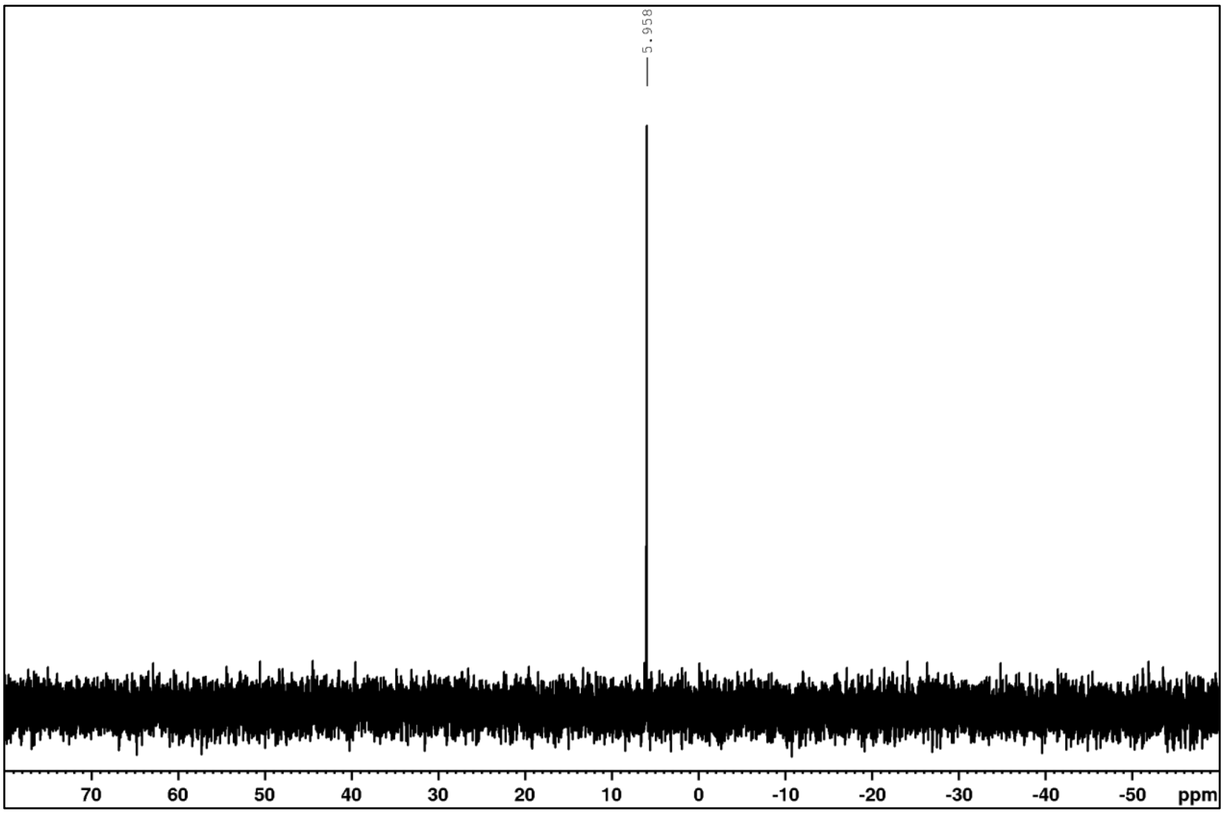
$^{1}H$ NMR (400 MHz, $C_6D_6$)



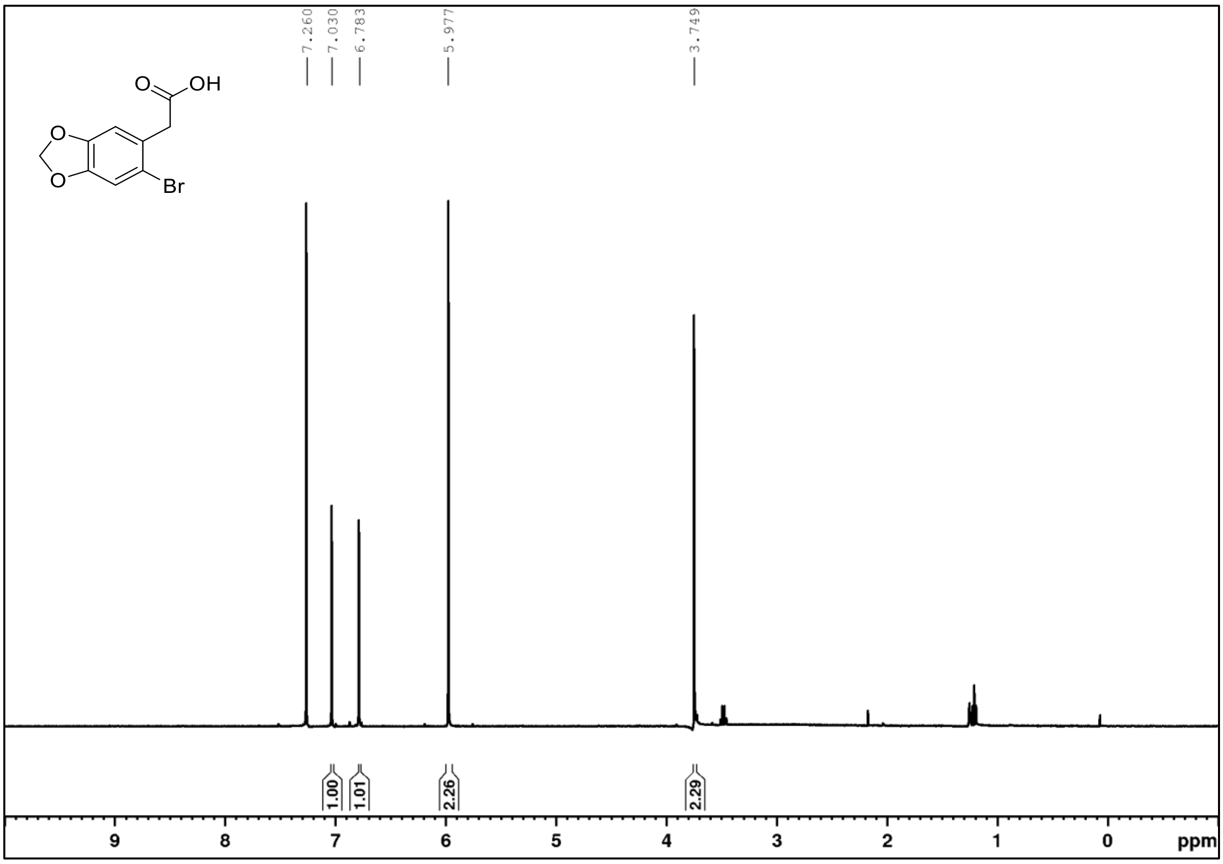
$^{13}C$ NMR (101 MHz, $C_6D_6$)



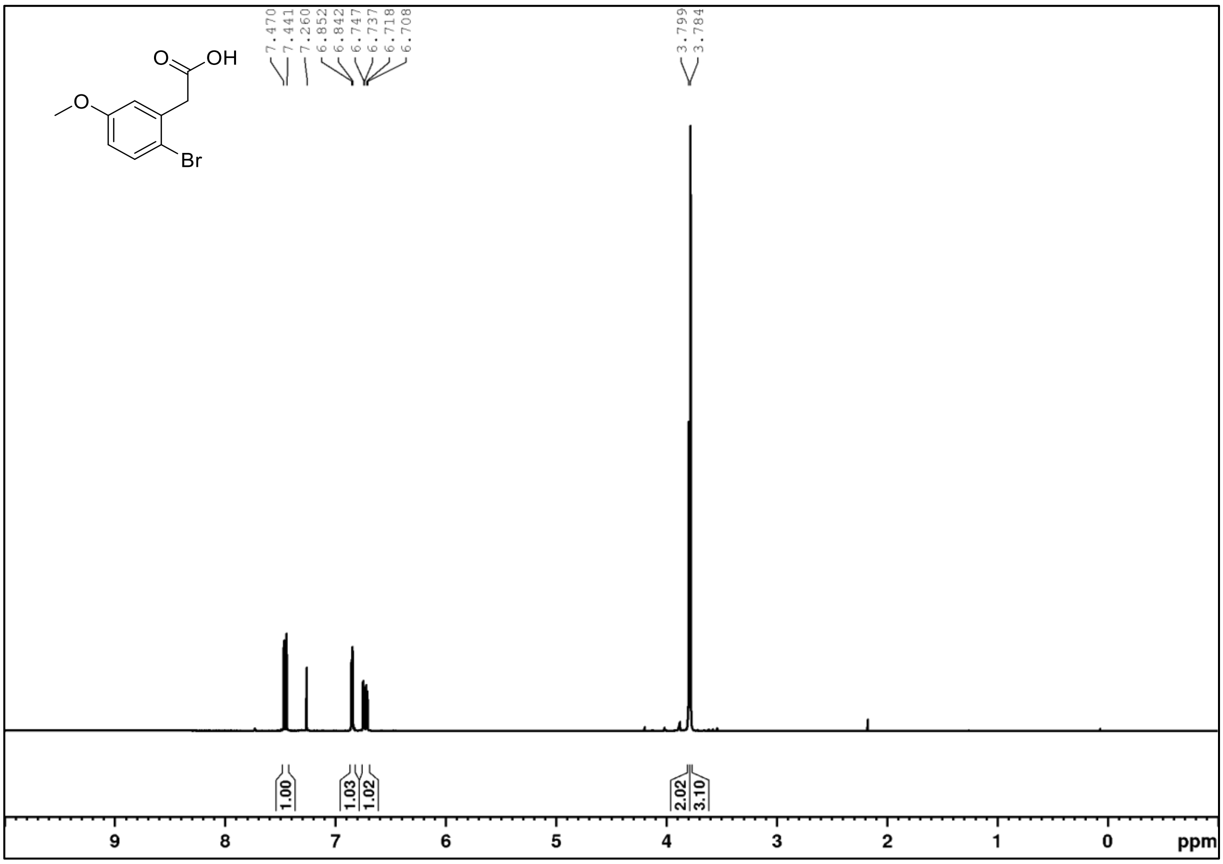
$^{29}Si\{^1H\}$ NMR (79.5 MHz, $C_6D_6$)



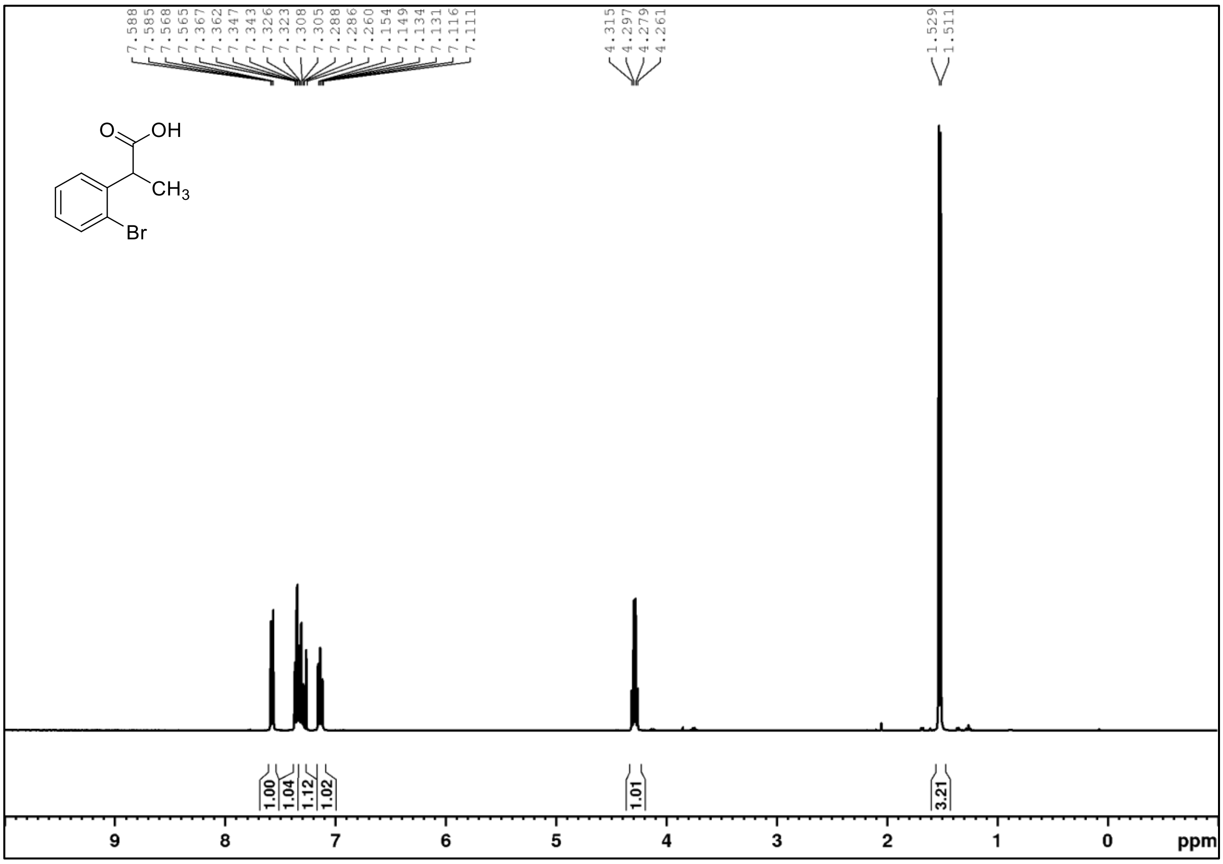
**2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)acetic acid (14c)** $^1$H NMR (400 MHz, $CDCl_3$)



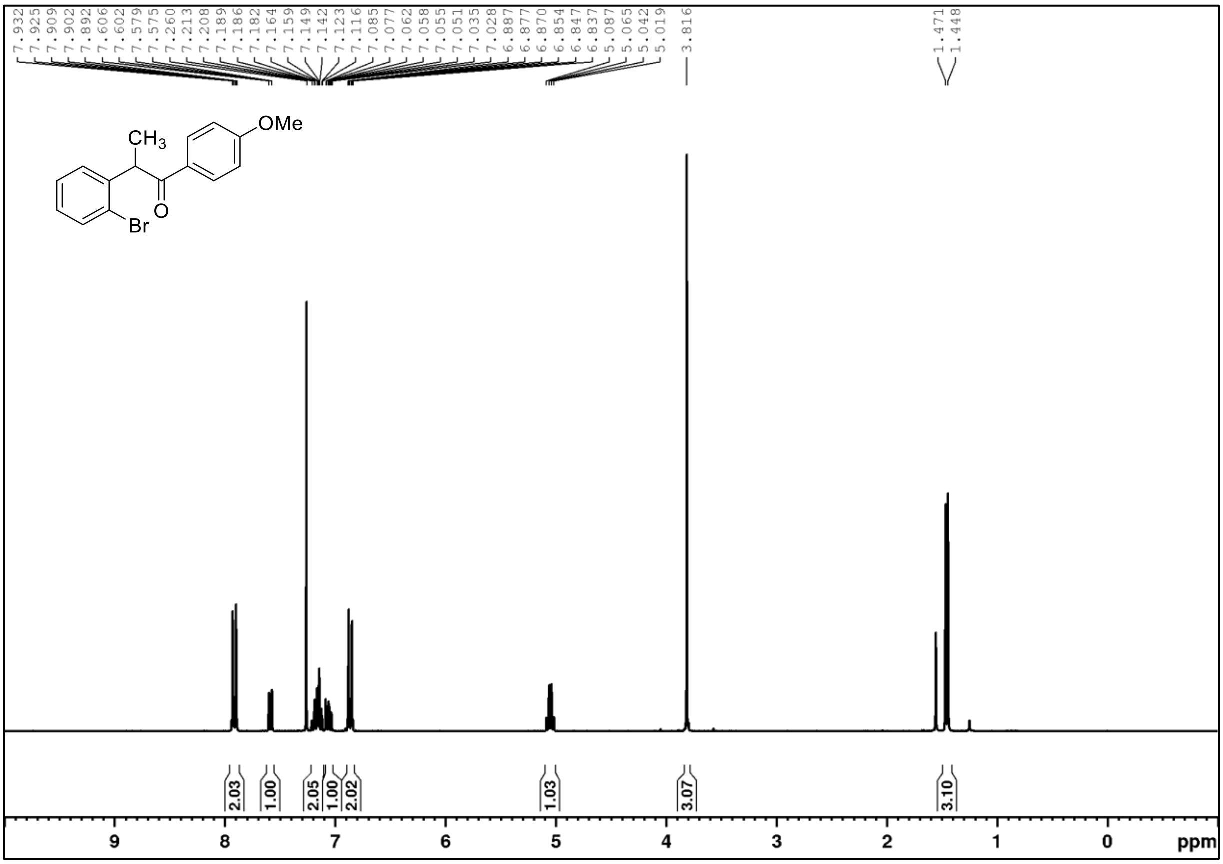
**2-(2-Bromo-5-methoxyphenyl)acetic acid (14d)** $^1$H NMR (400 MHz, $CDCl_3$)



**2-(2-Bromophenyl)propanoic acid (14e)** $^1$H NMR (400 MHz, CDCl$_3$)

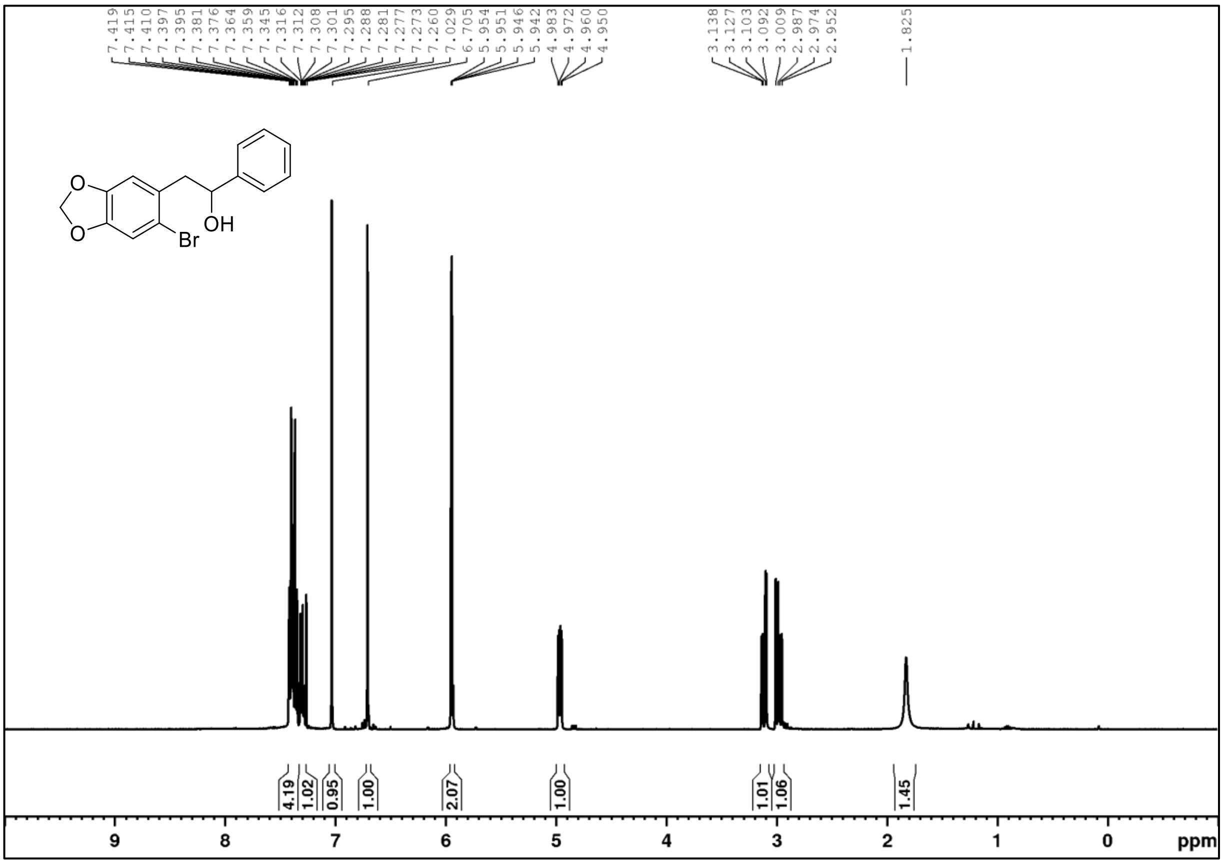


**2-(2-Bromophenyl)-1-(4-methoxyphenyl)propan-1-one (16a)** $^1$H NMR (400 MHz, CDCl$_3$)

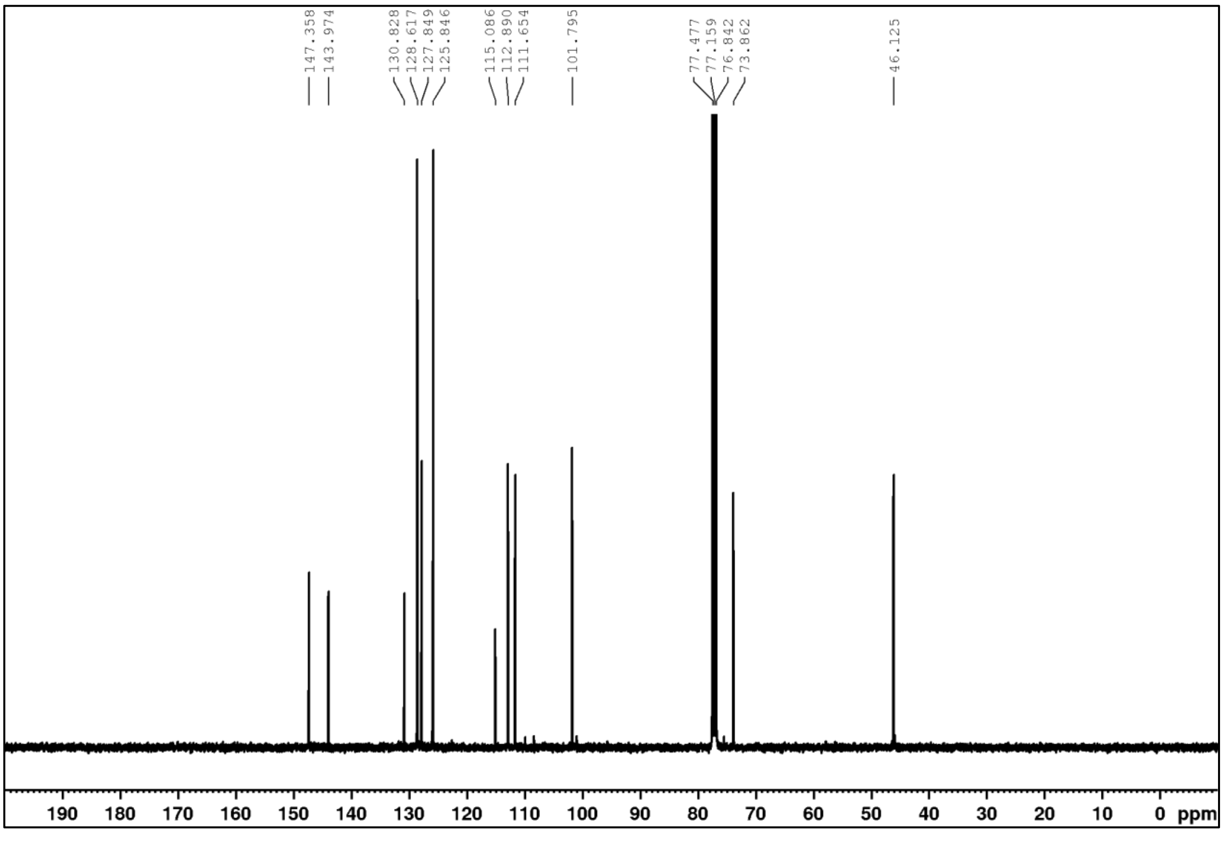


**2-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-1-phenylethan-1-ol (18c)**

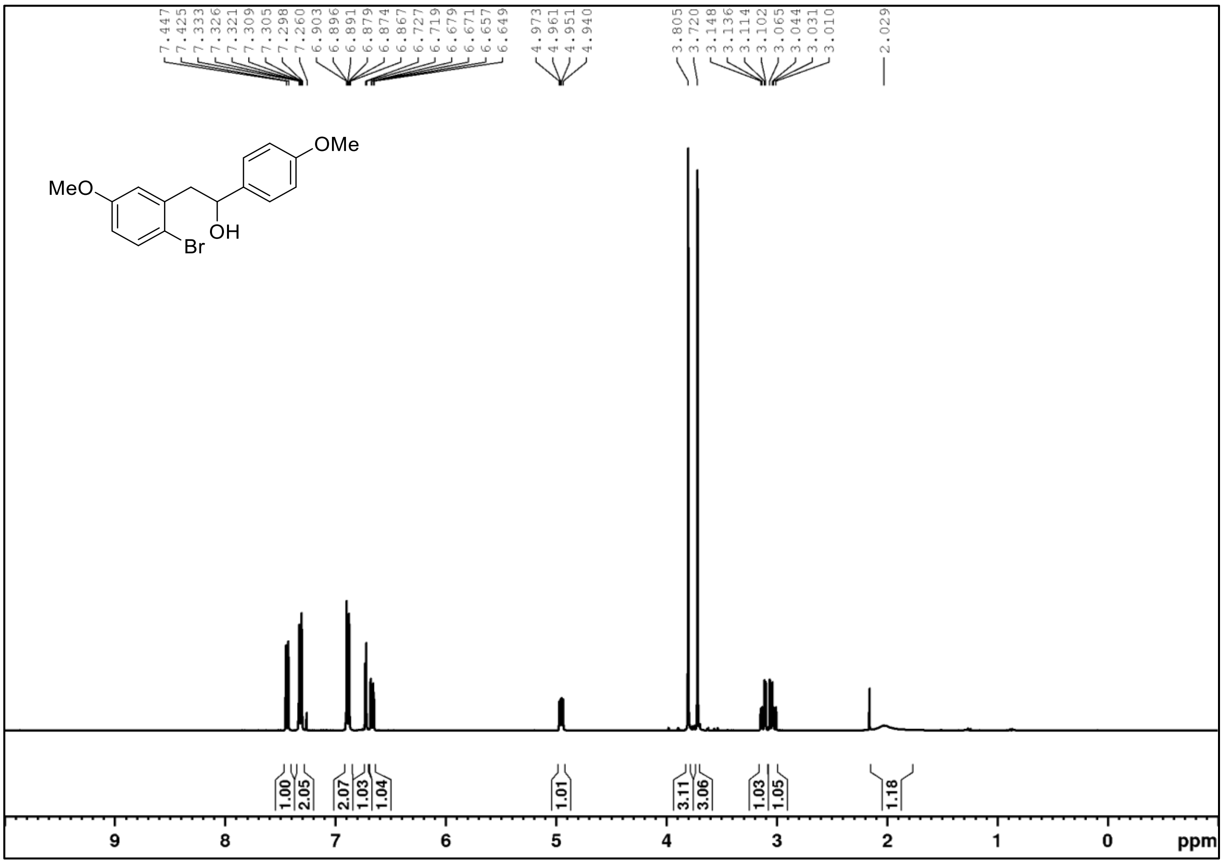
$^{1}H$ NMR (400 MHz, $CDCl_3$)



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

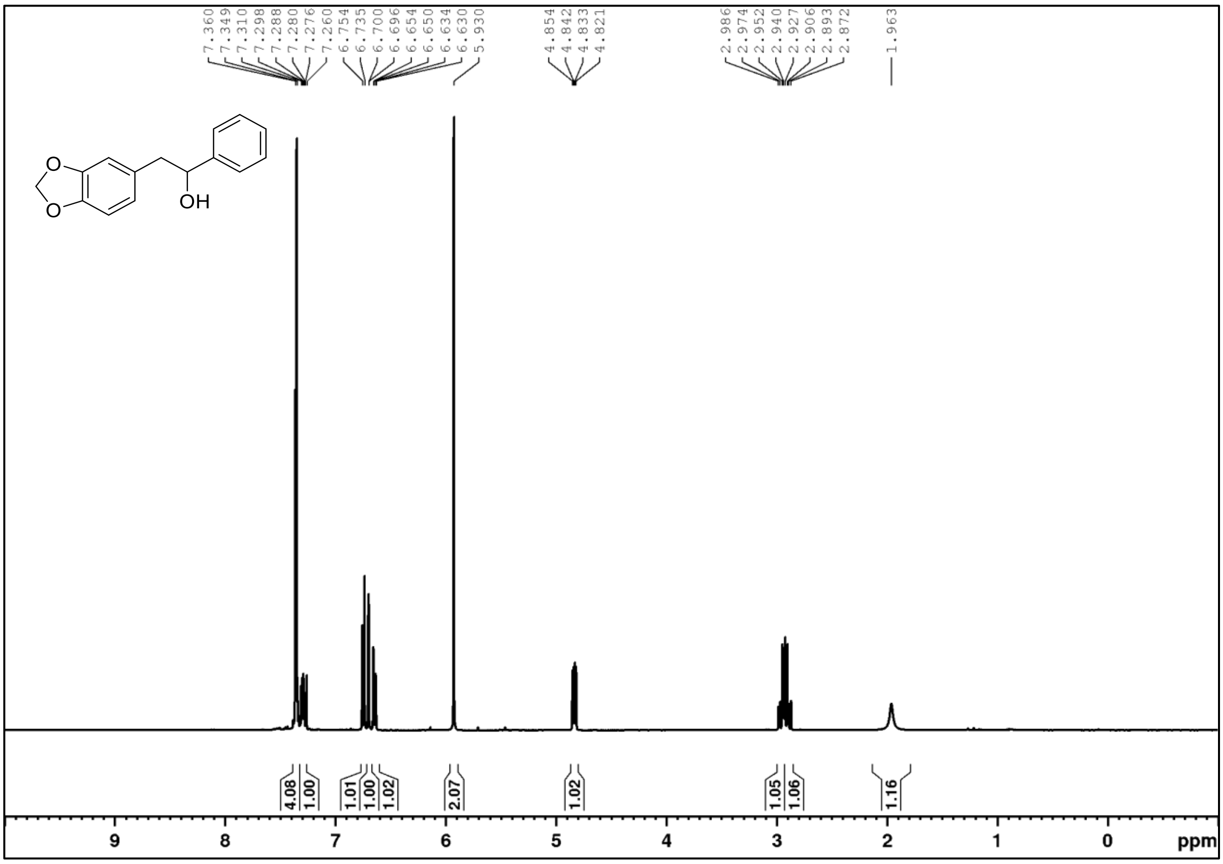


**2-(2-Bromo-5-methoxyphenyl)-1-(4-methoxyphenyl)ethan-1-ol (18d)** $^{1}$H NMR (400 MHz, $CDCl_3$)

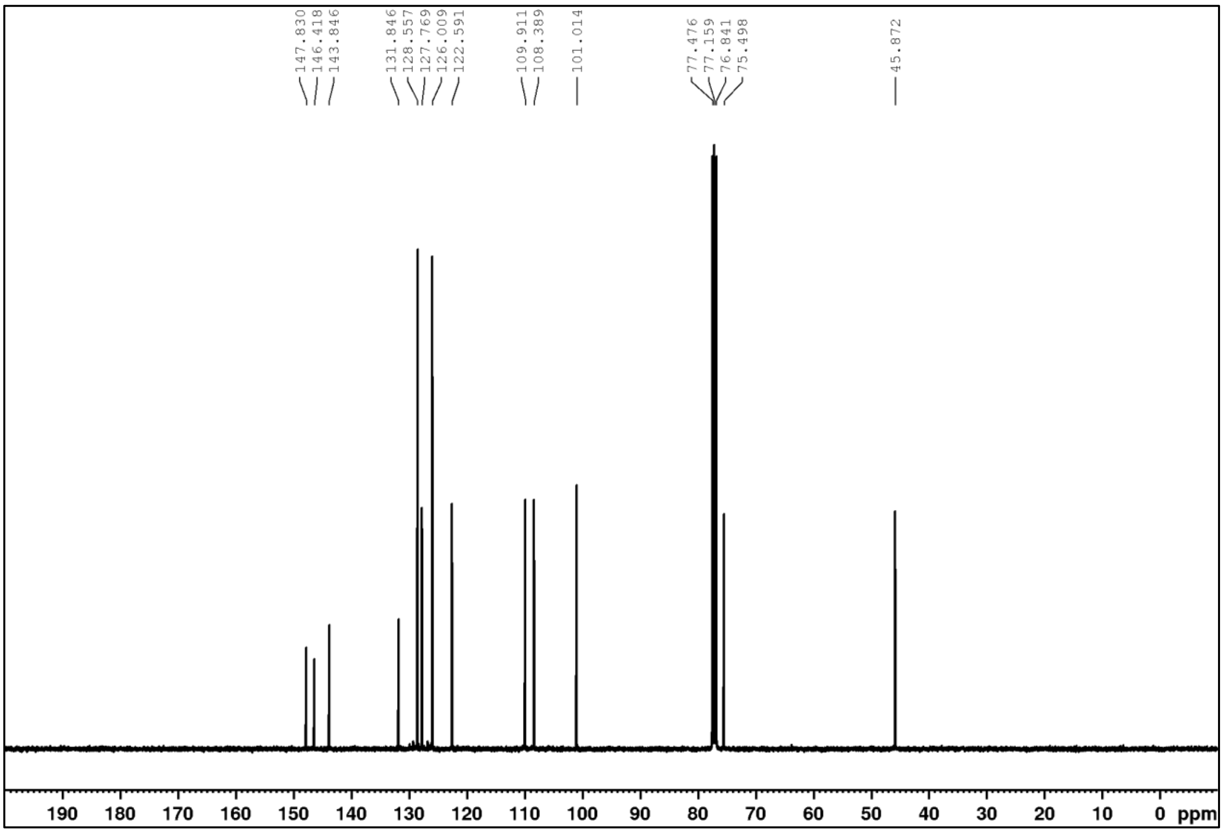


**2-(Benzo[*d*][1,3]dioxol-5-yl)-1-phenylethan-1-ol (18e)**

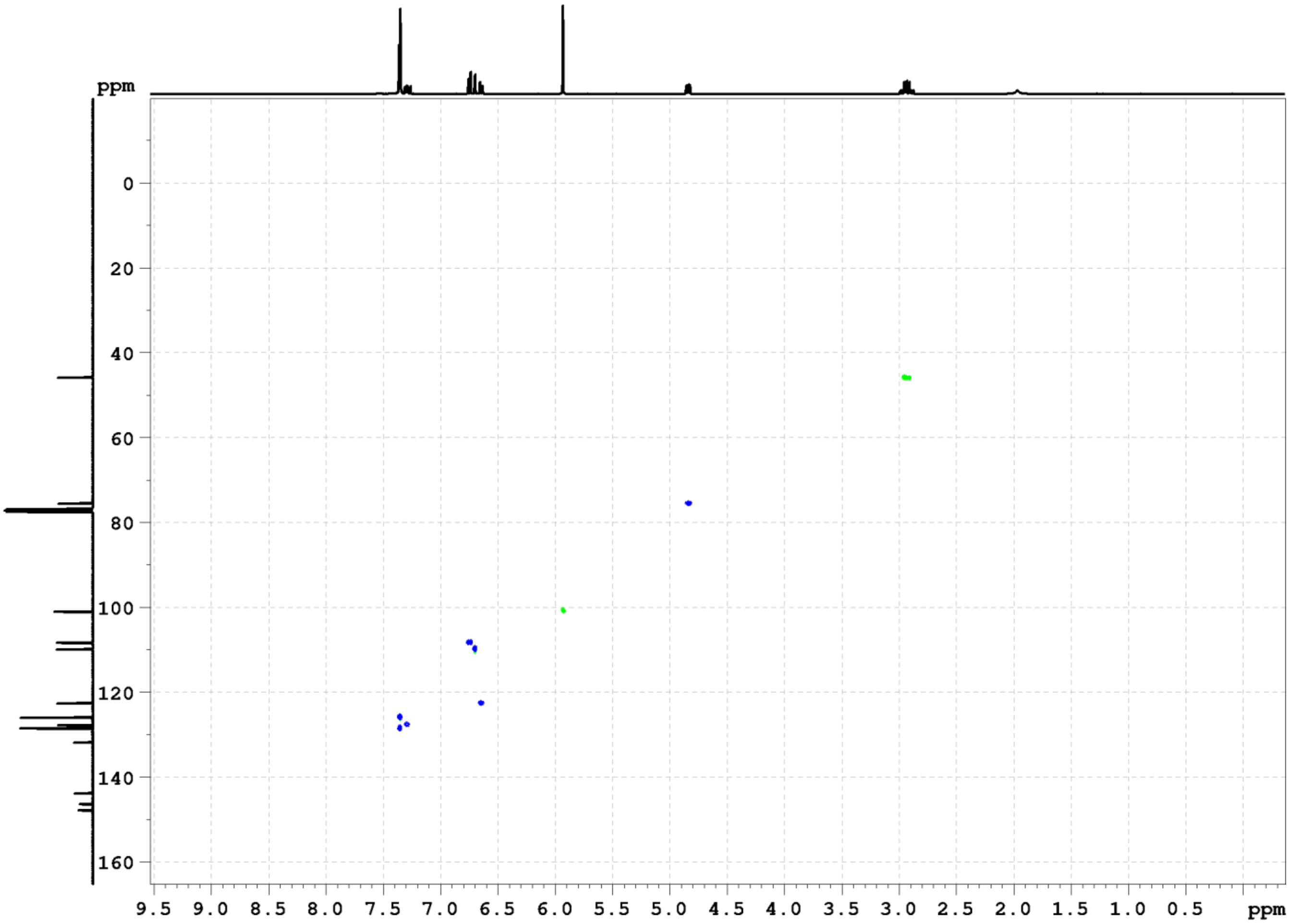
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (101 MHz, CDCl$_3$)

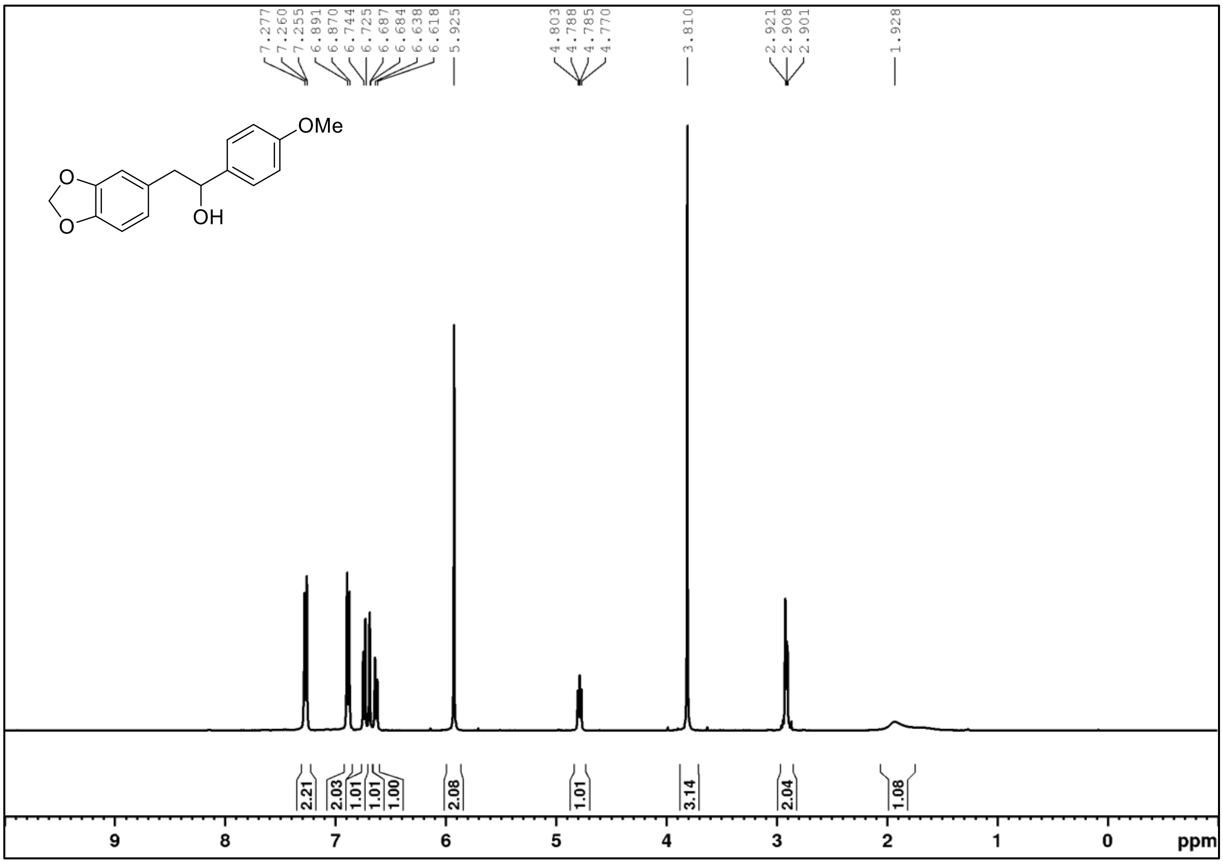


HSQC (CDCl$_3$)

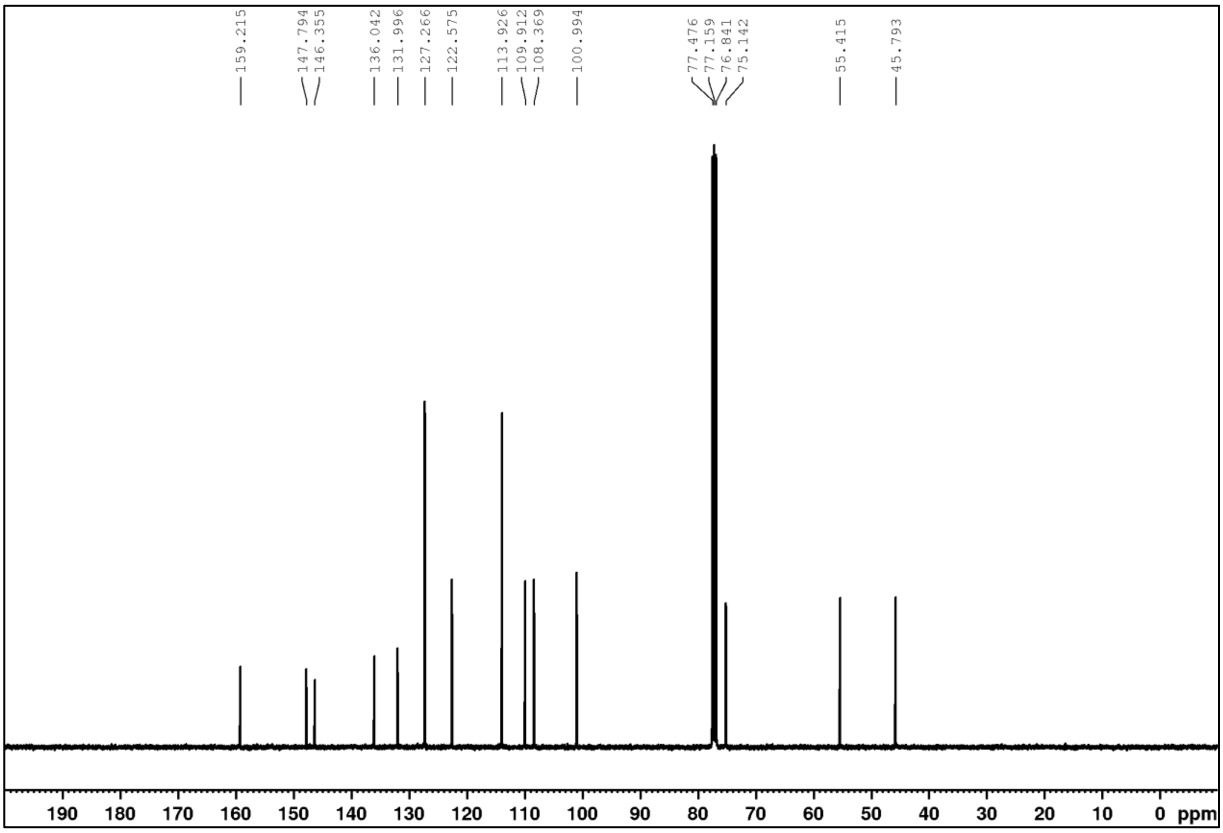

ppm
0
20
40
60
80
100
120
140
160
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

**2-(Benzo[*d*][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)ethan-1-ol (18f)**

$^{1}$H NMR (400 MHz, CDCl$_3$)

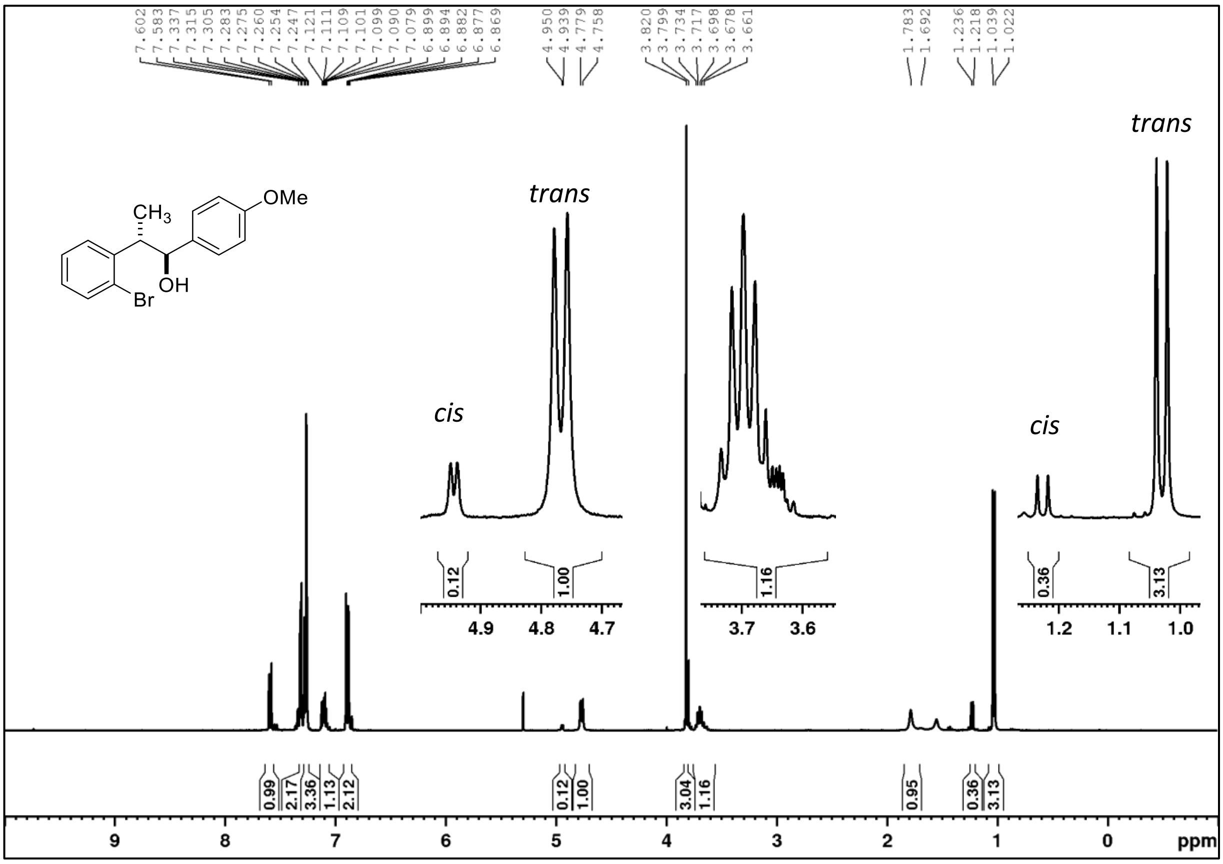


$^{13}$C NMR (101 MHz, CDCl$_3$)

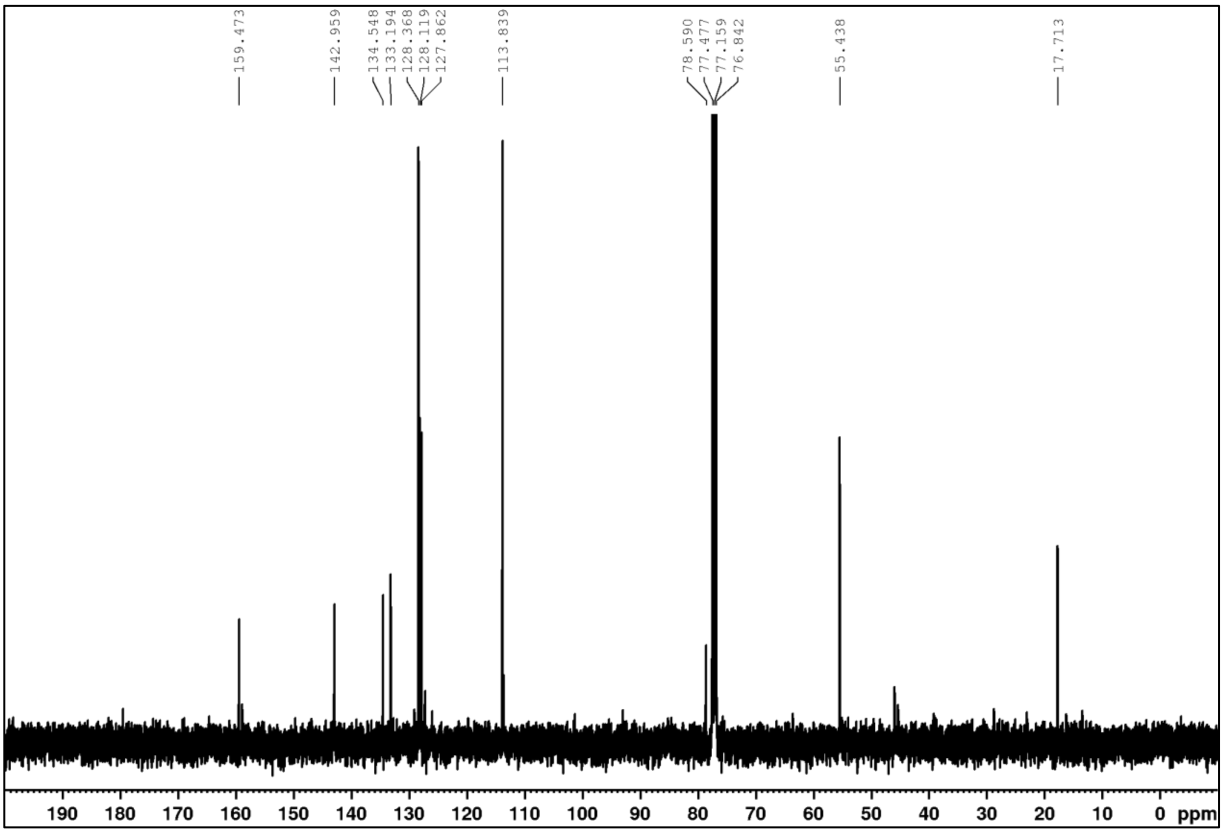


**2-(2-Bromophenyl)-1-(4-methoxyphenyl)propan-1-ol (18g)**

$^1$H NMR (400 MHz, CDCl$_3$)

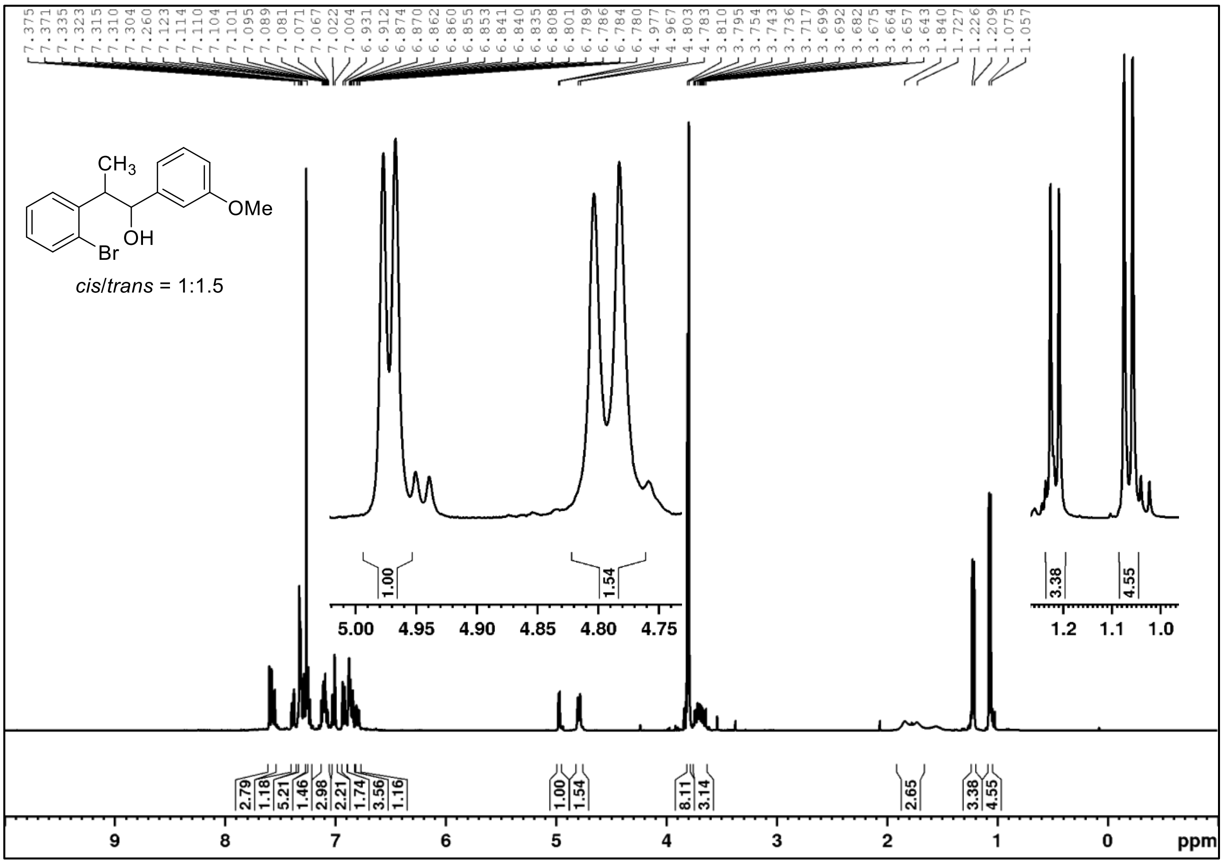


$^{13}$C NMR (101 MHz, CDCl$_3$)

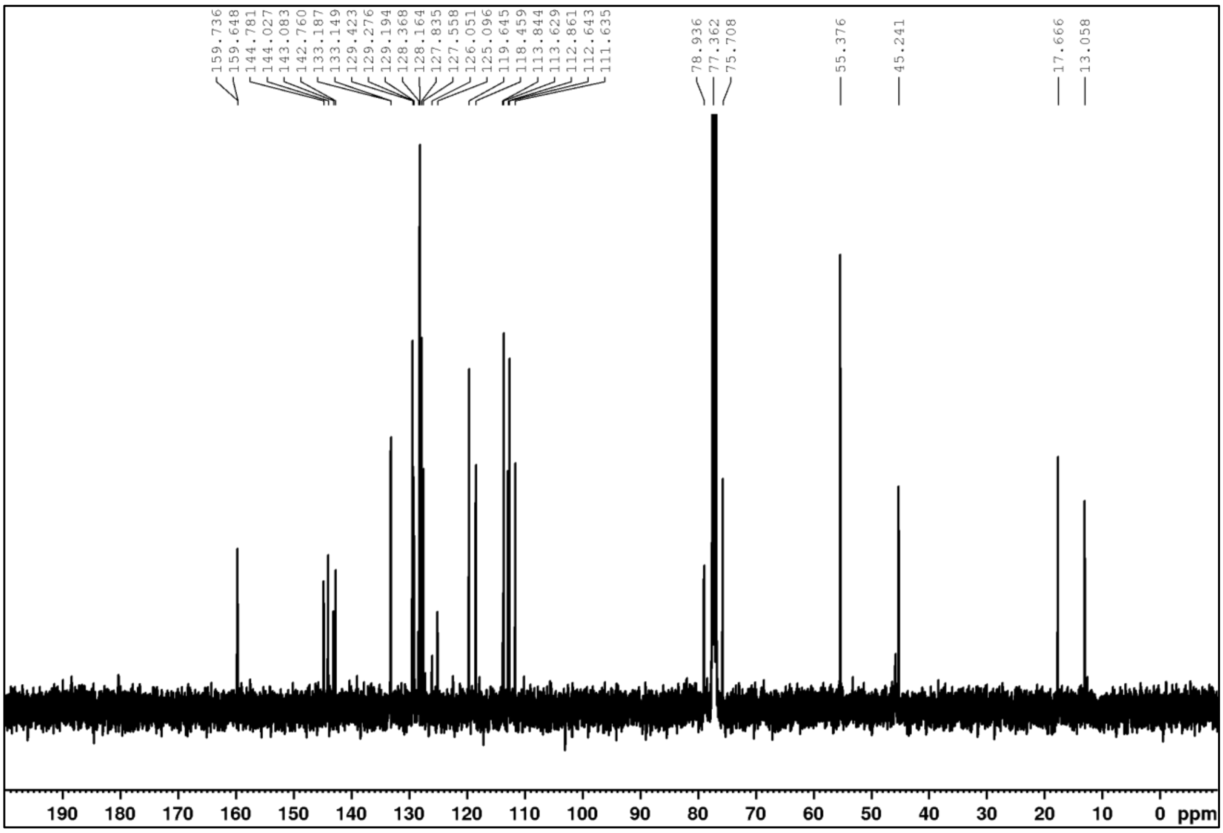


**2-(2-Bromophenyl)-1-(3-methoxyphenyl)propan-1-ol (18h)**

$^1$H NMR (400 MHz, CDCl$_3$)

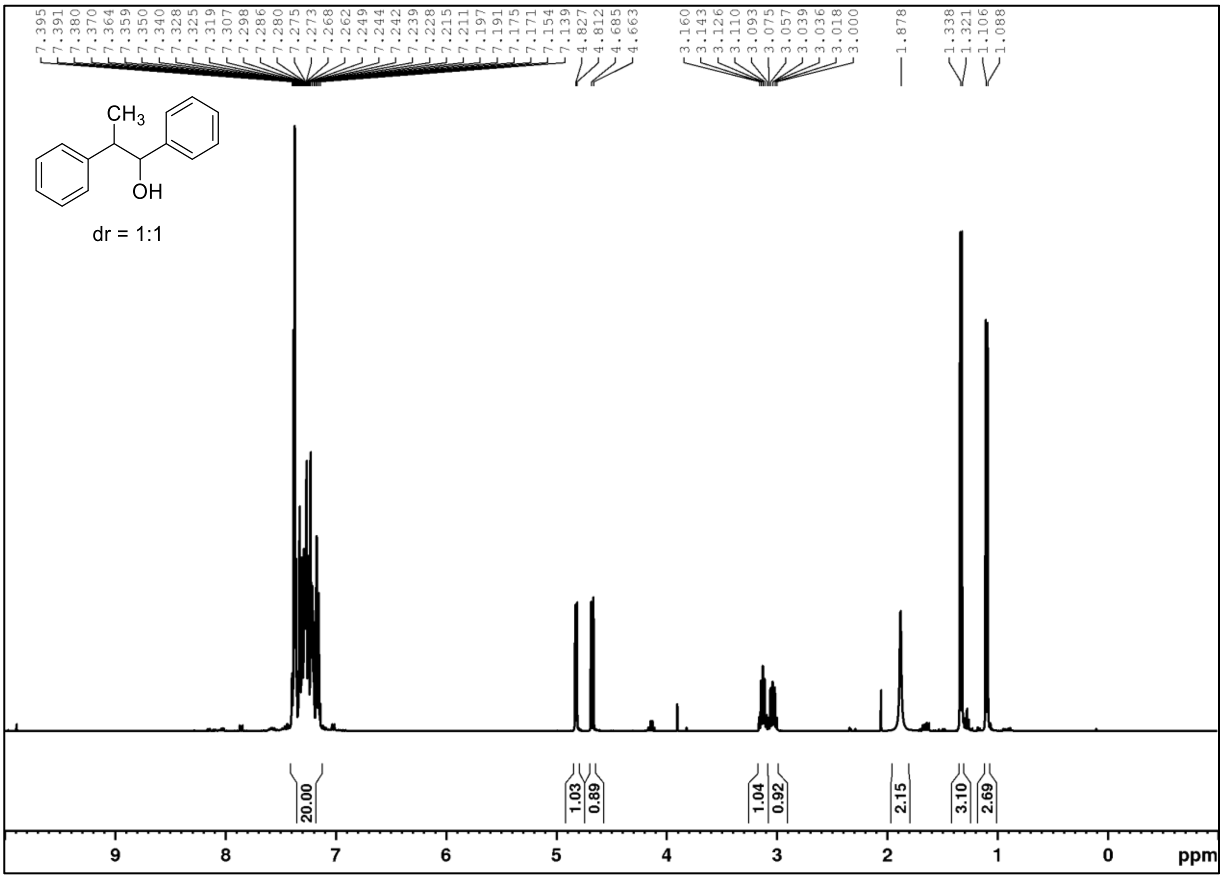


$^{13}$C NMR (101 MHz, CDCl$_3$)

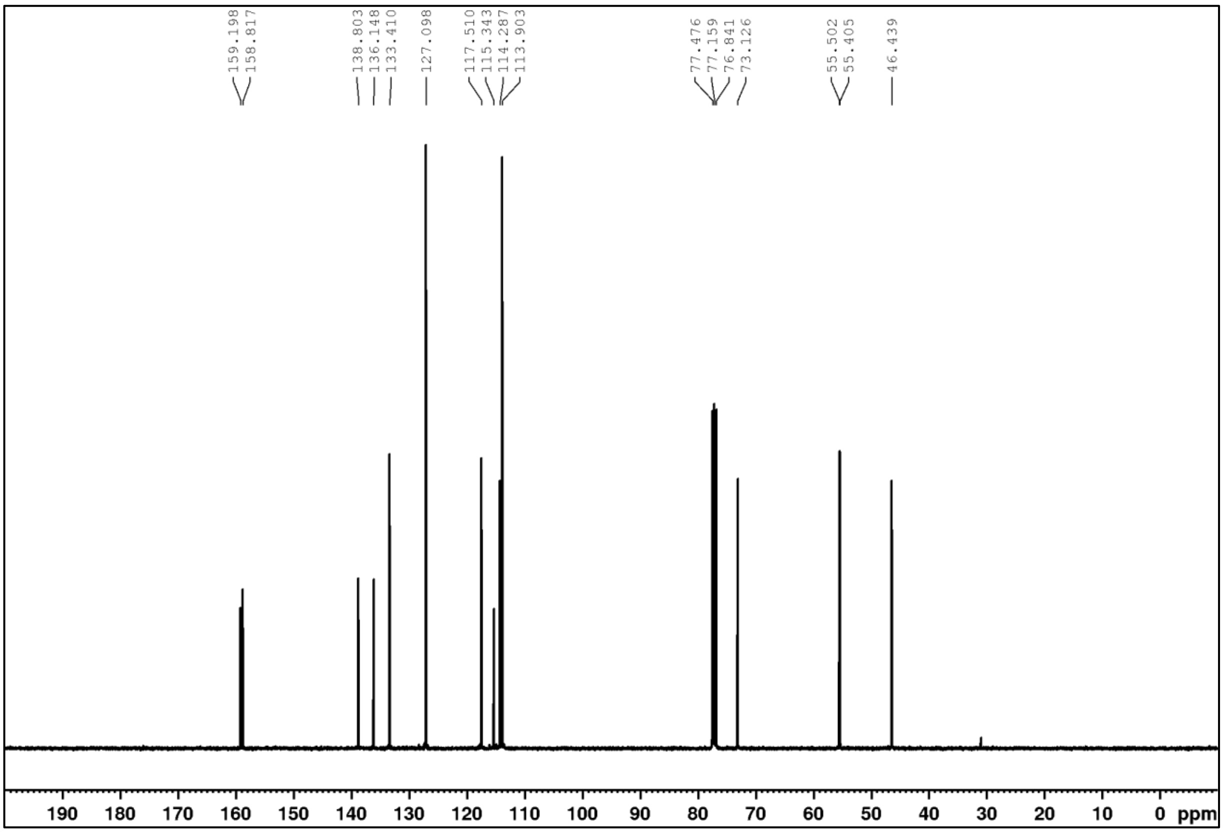


**1,2-Diphenylpropan-1-ol (18i)**

$^1$H NMR (400 MHz, CDCl$_3$)

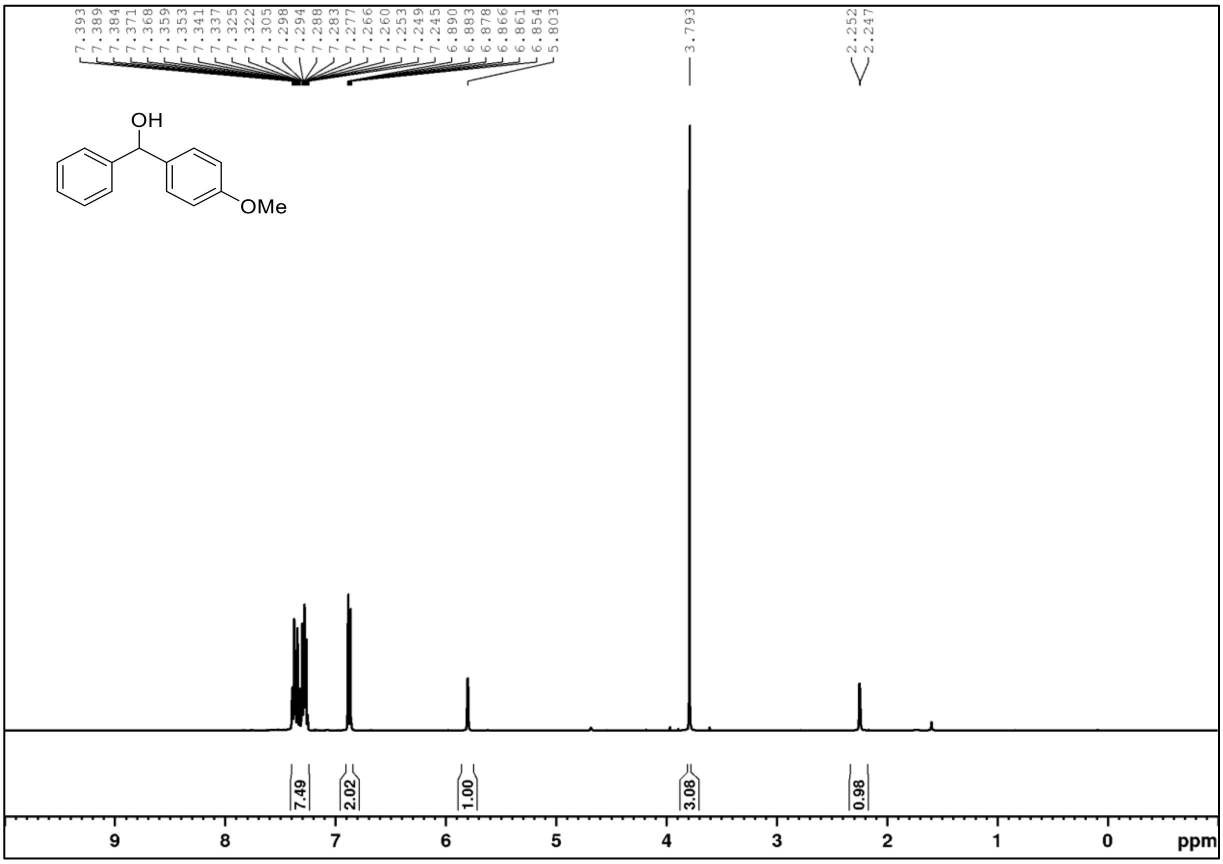


$^{13}$C NMR (101 MHz, CDCl$_3$)

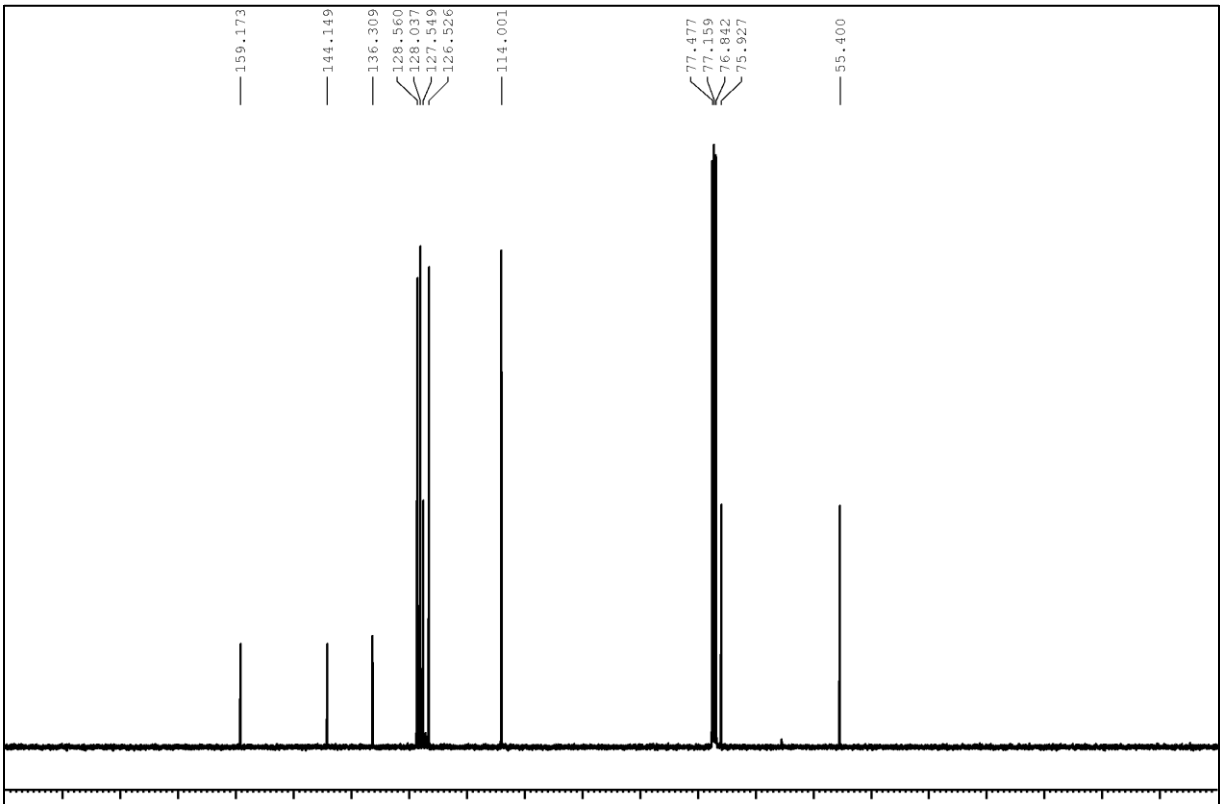


**(4-Methoxyphenyl)(phenyl)methanol (18m)**

$^1$H NMR (400 MHz, CDCl$_3$)

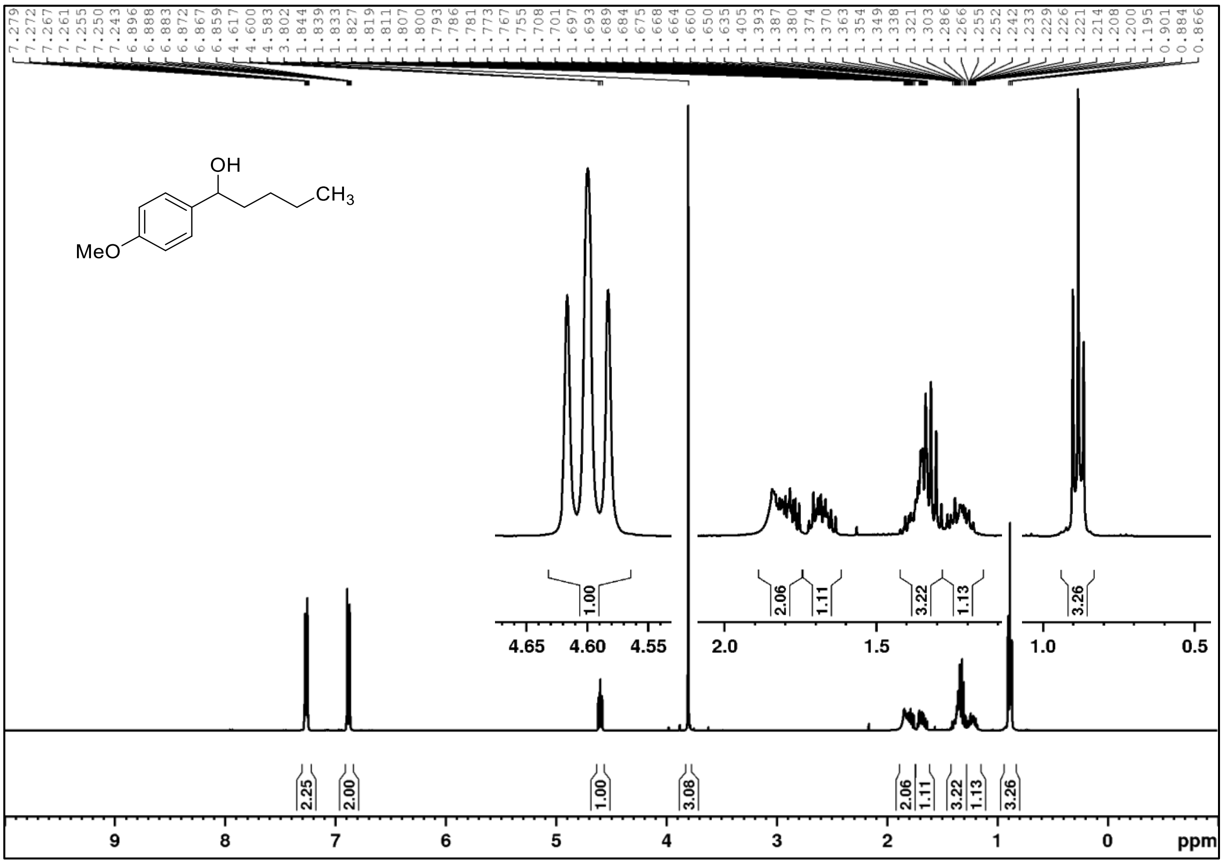


$^{13}$C NMR (101 MHz, CDCl$_3$)

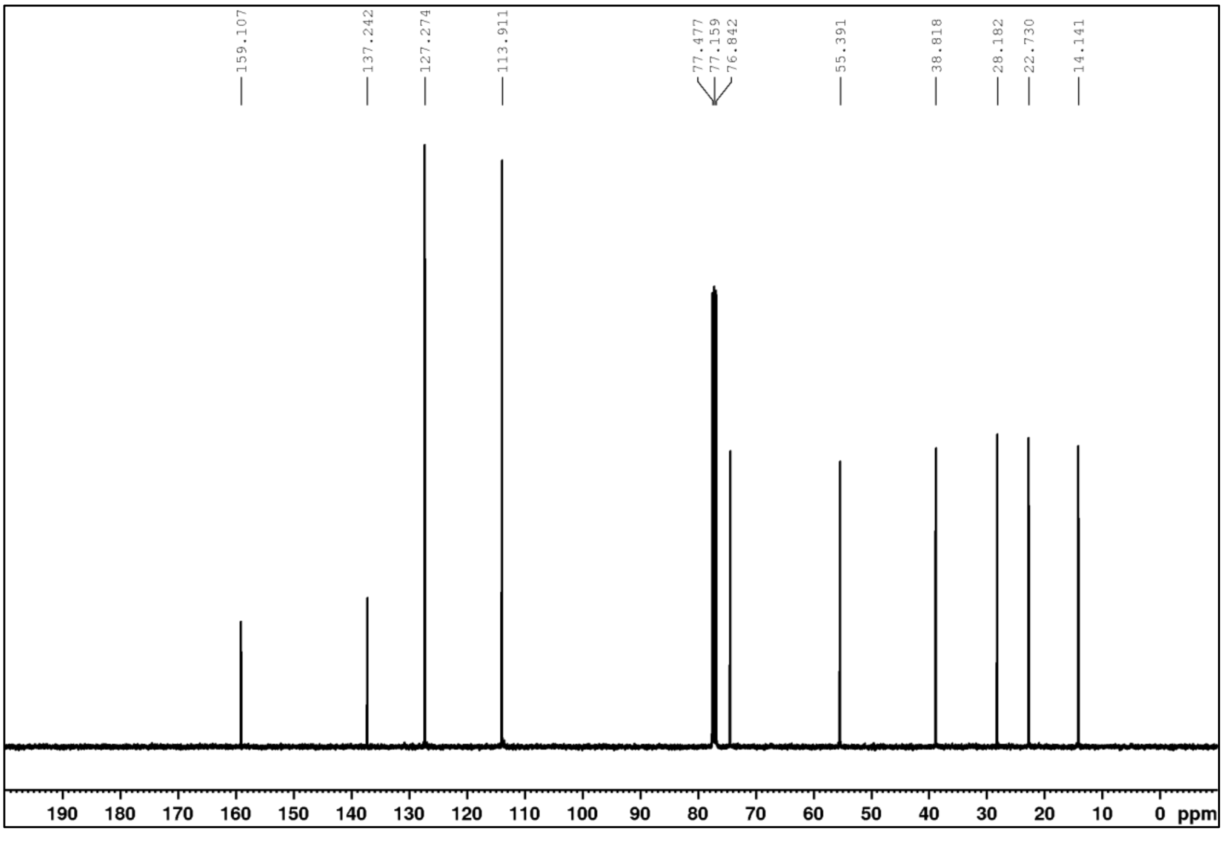


## 1-(4-Methoxyphenyl)pentan-1-ol (18n)

$^1$H NMR (400 MHz, CDCl$_3$)

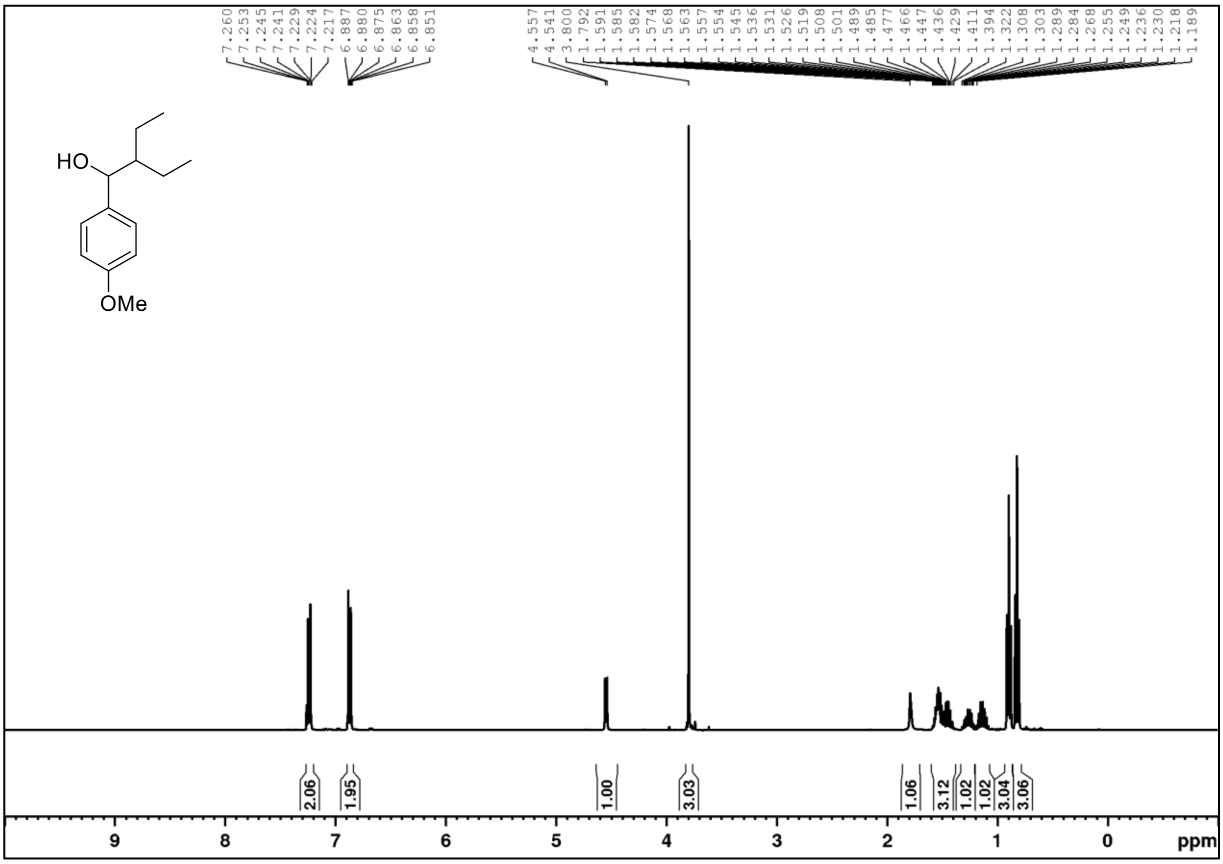


$^{13}$C NMR (101 MHz, CDCl$_3$)

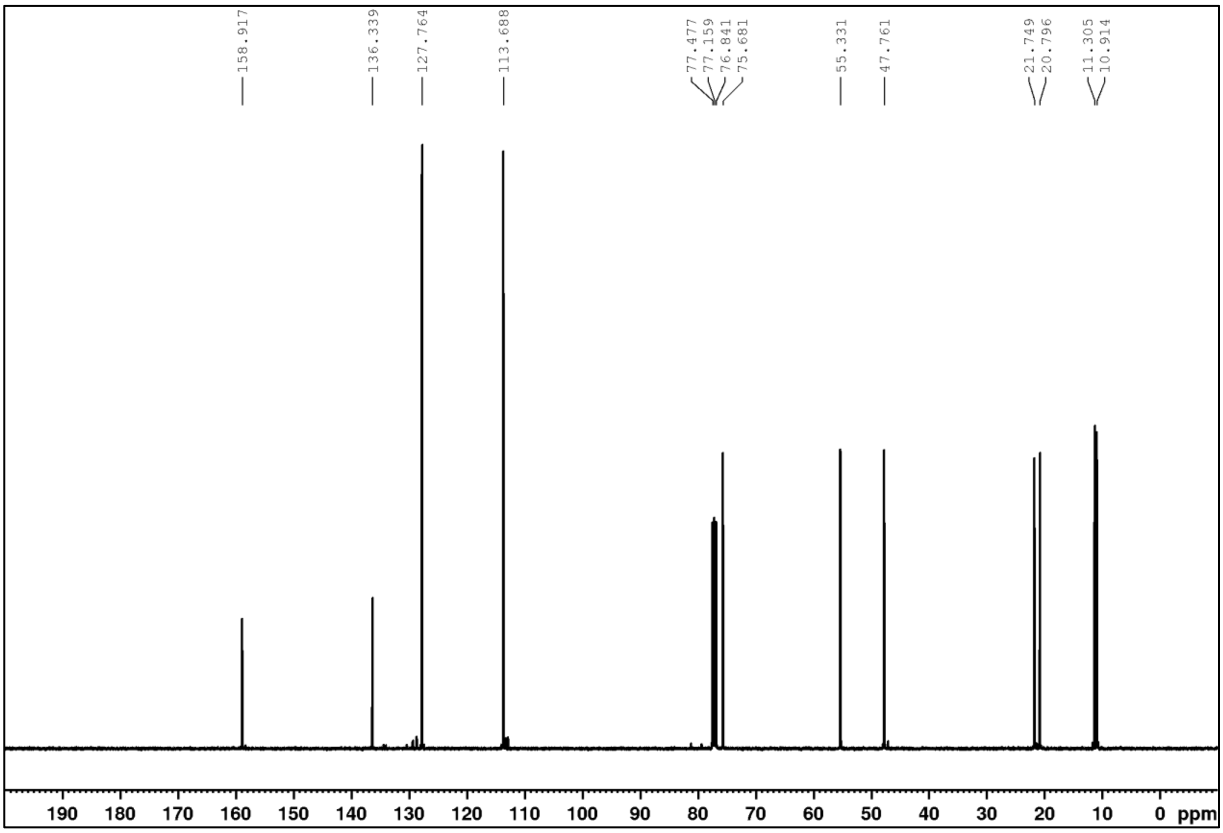


**2-Ethyl-1-(4-methoxyphenyl)butan-1-ol (18o)**

$^1$H NMR (400 MHz, CDCl$_3$)

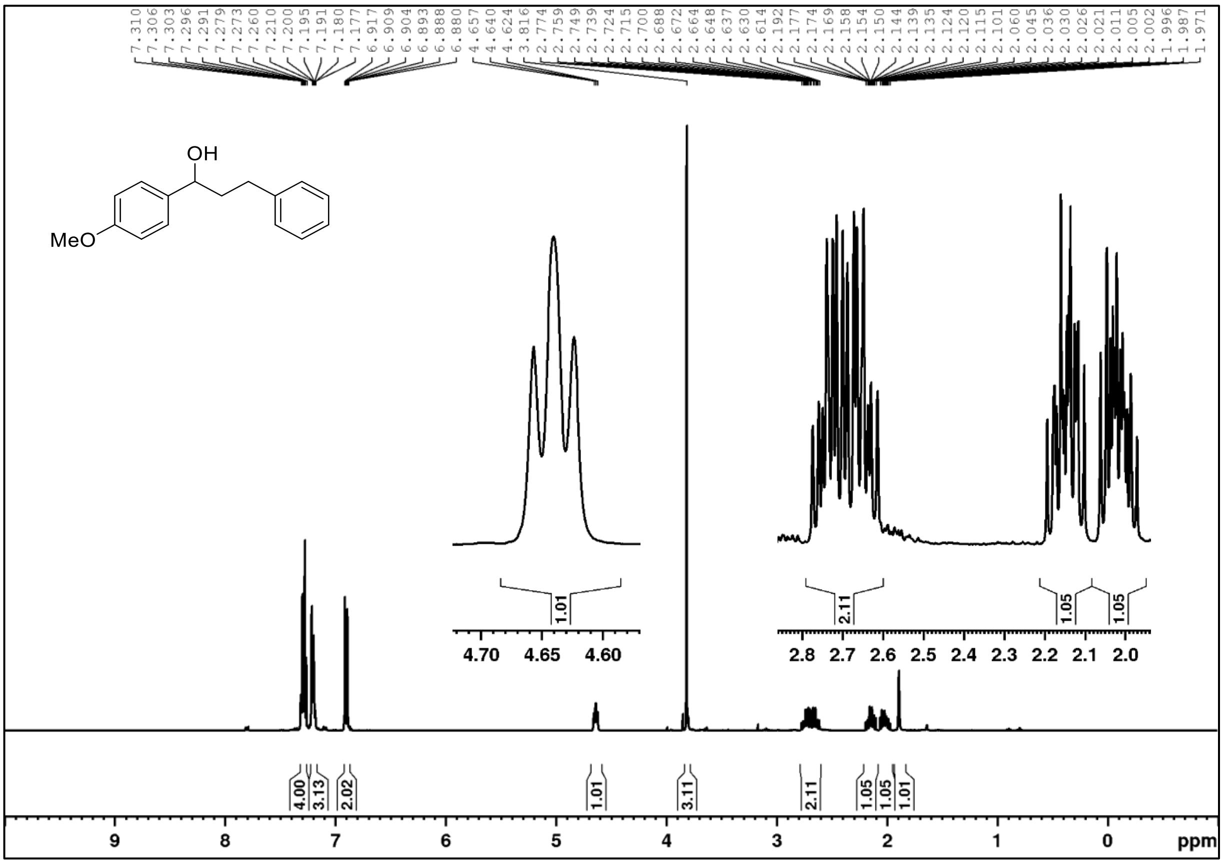


$^{13}$C NMR (101 MHz, CDCl$_3$)

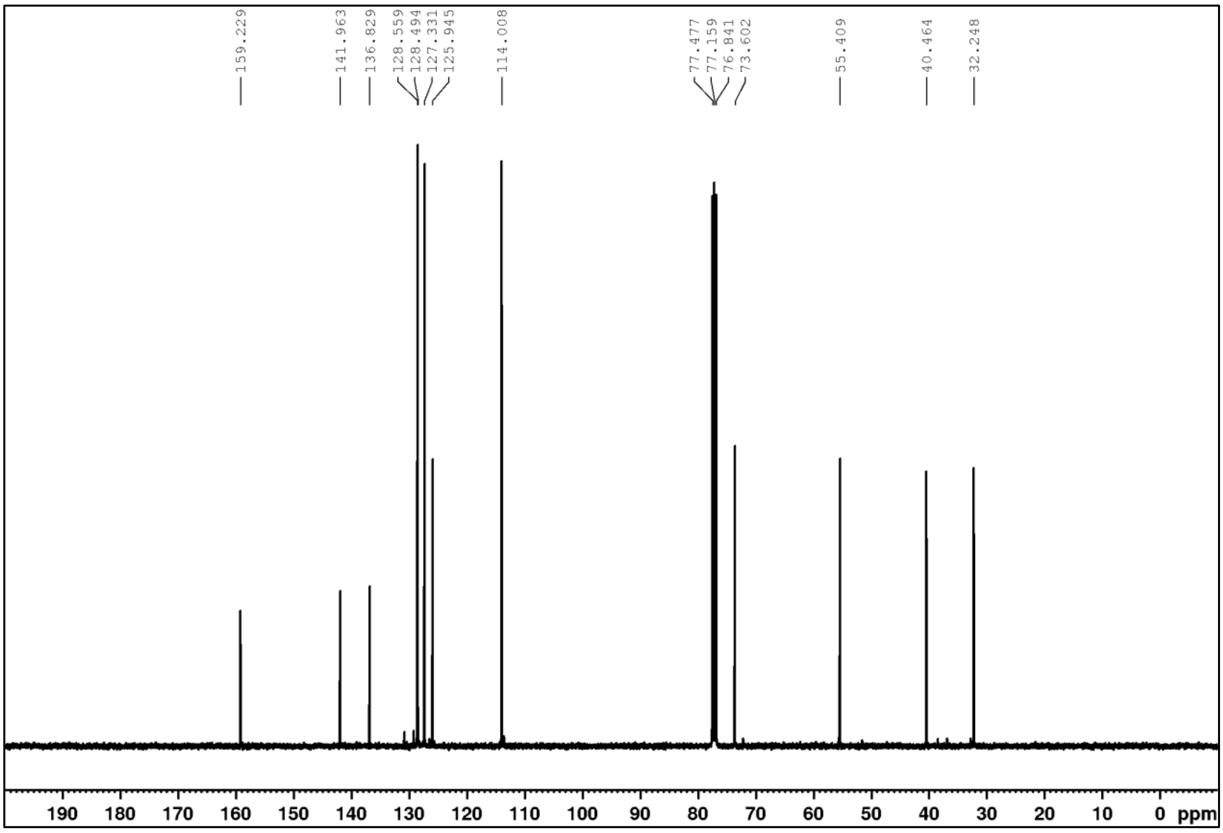


**1-(4-Methoxyphenyl)-2-phenylpropan-1-ol (18p)**

$^{1}$H NMR (400 MHz, $CDCl_3$)

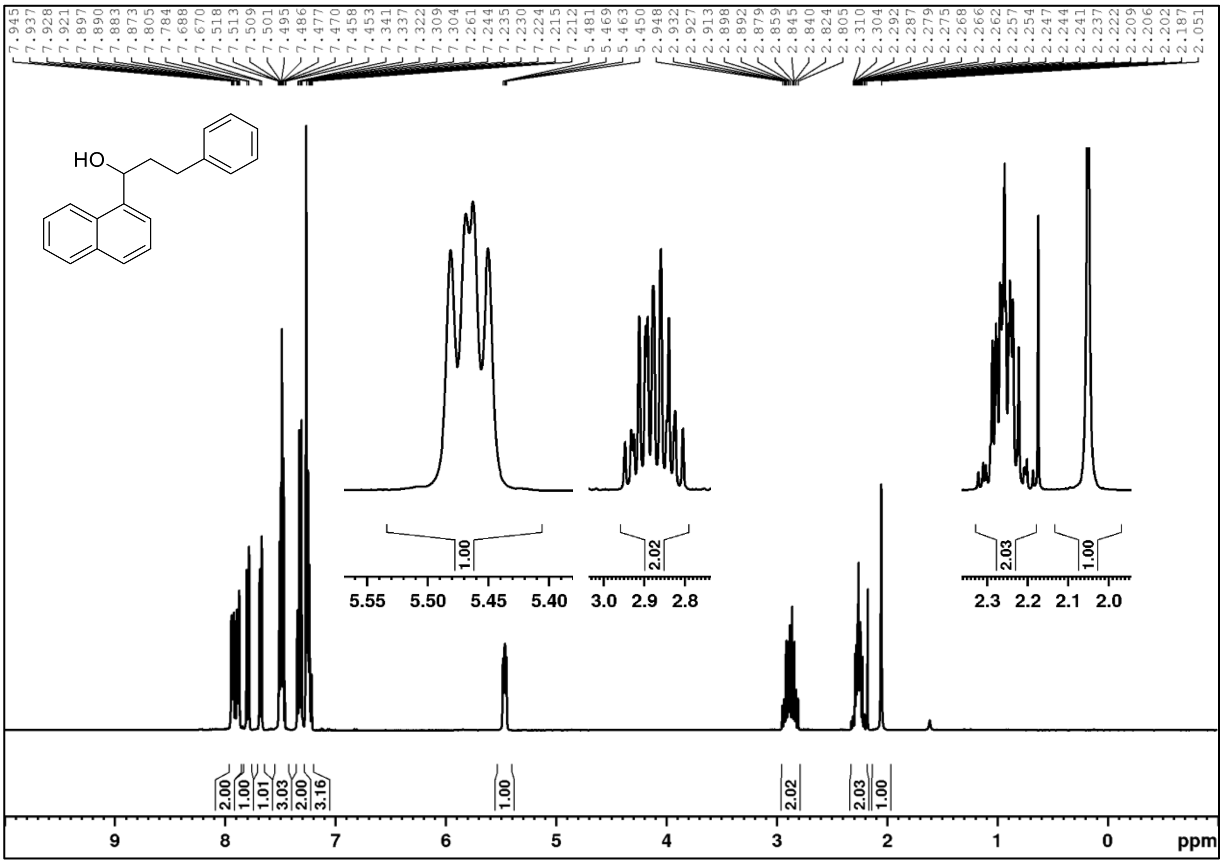


$^{13}$C NMR (101 MHz, $CDCl_3$)

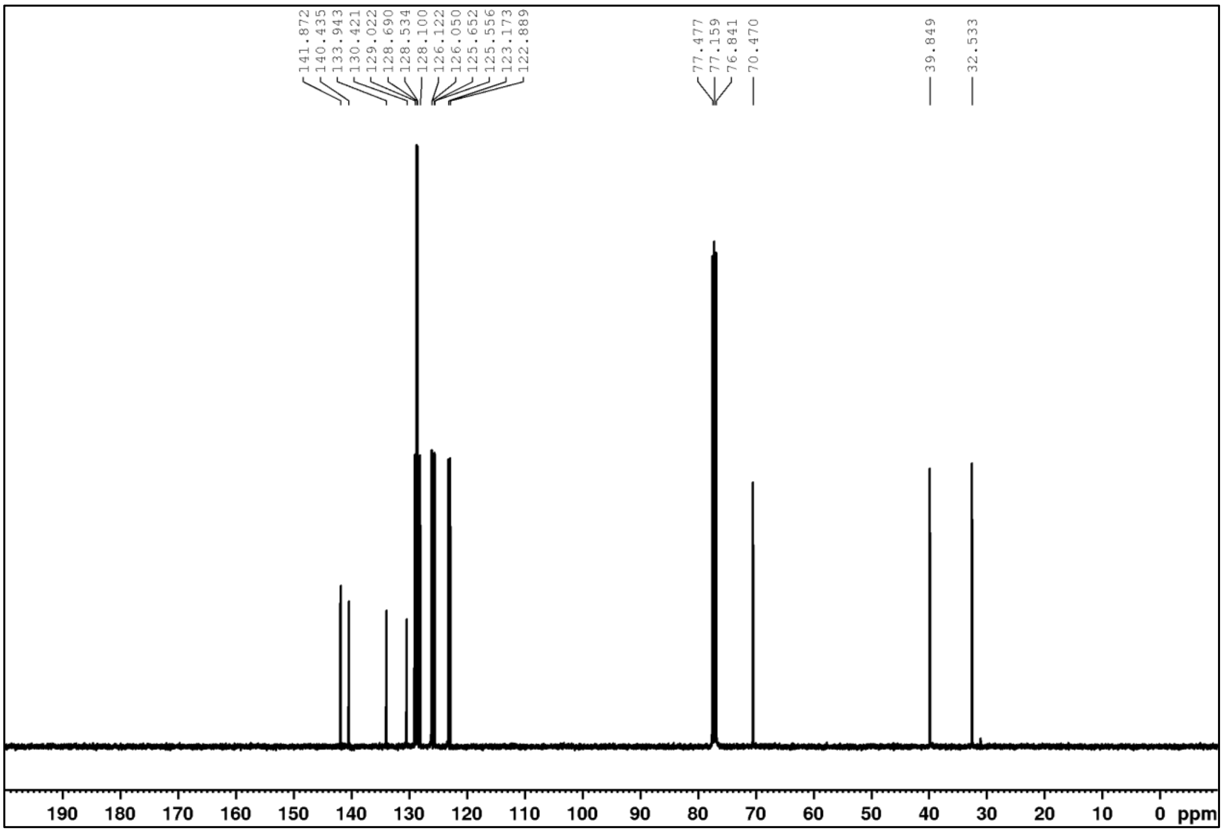


**1-(Naphthalen-1-yl)-3-phenylpropan-1-ol (18q)**

$^1$H NMR (400 MHz, CDCl$_3$)

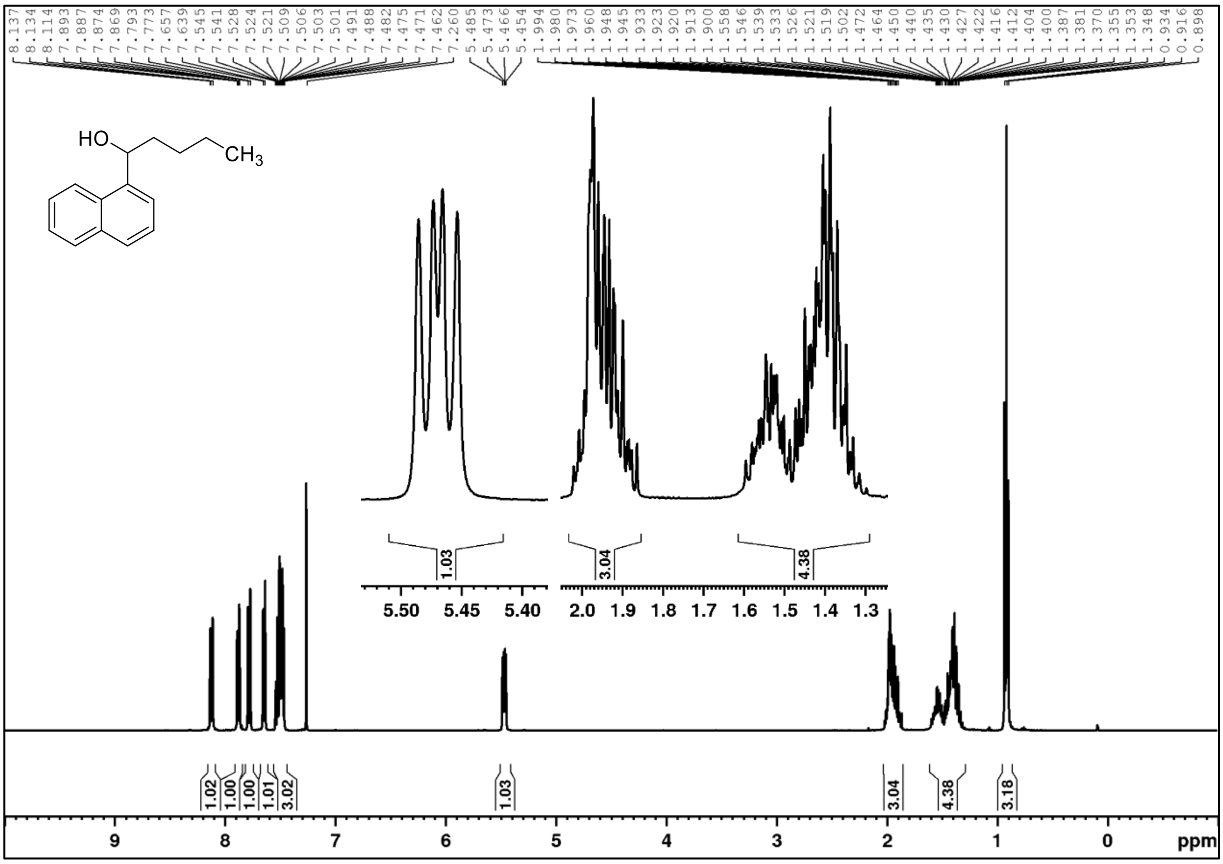


$^{13}$C NMR (101 MHz, CDCl$_3$)

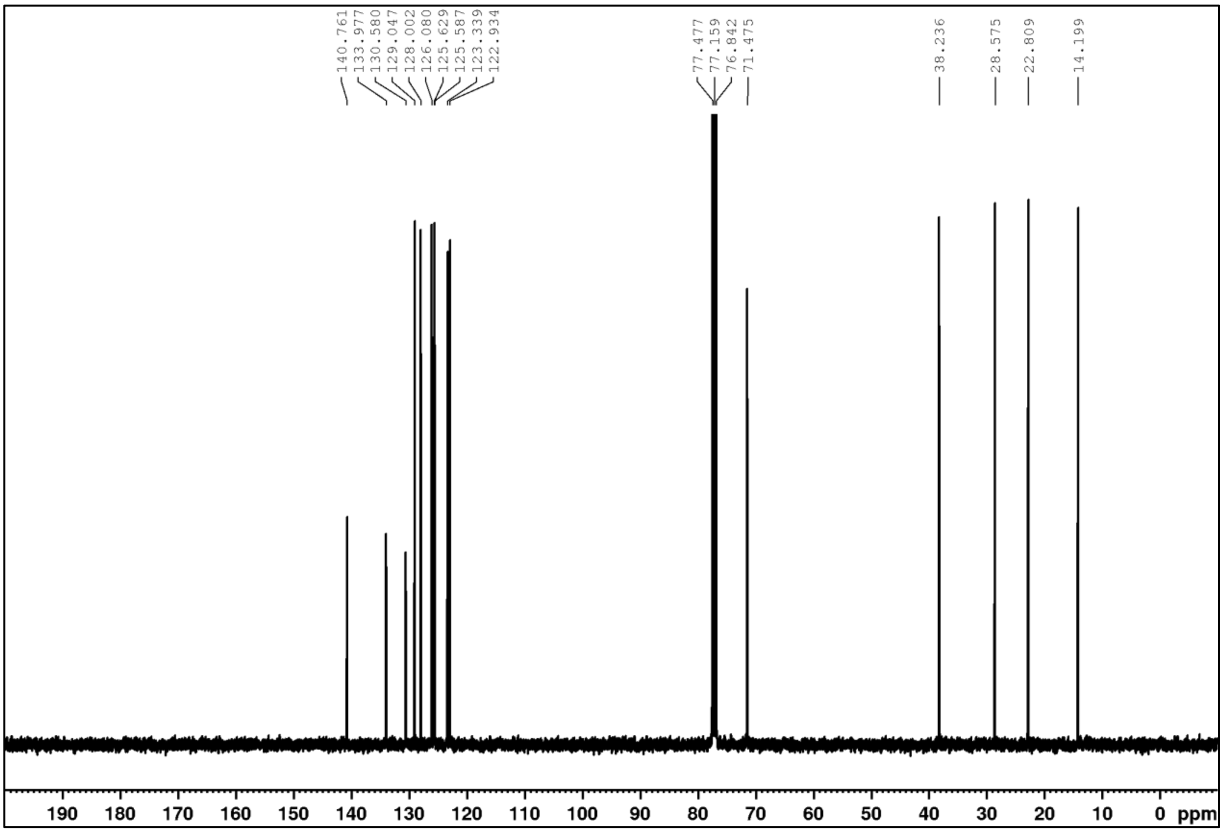


**1-(Naphthalen-1-yl)pentan-1-ol (18r)**

$^1$H NMR (400 MHz, CDCl$_3$)

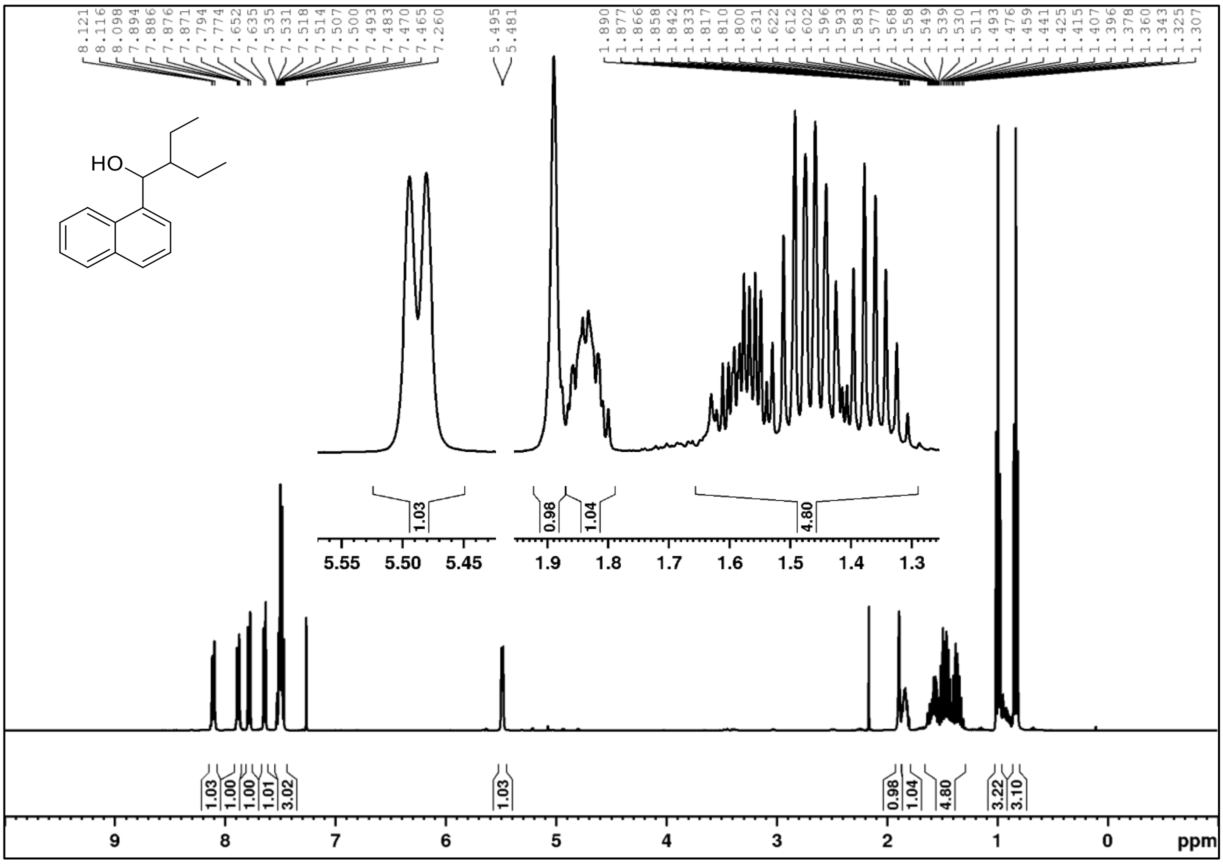


$^{13}$C NMR (101 MHz, CDCl$_3$)

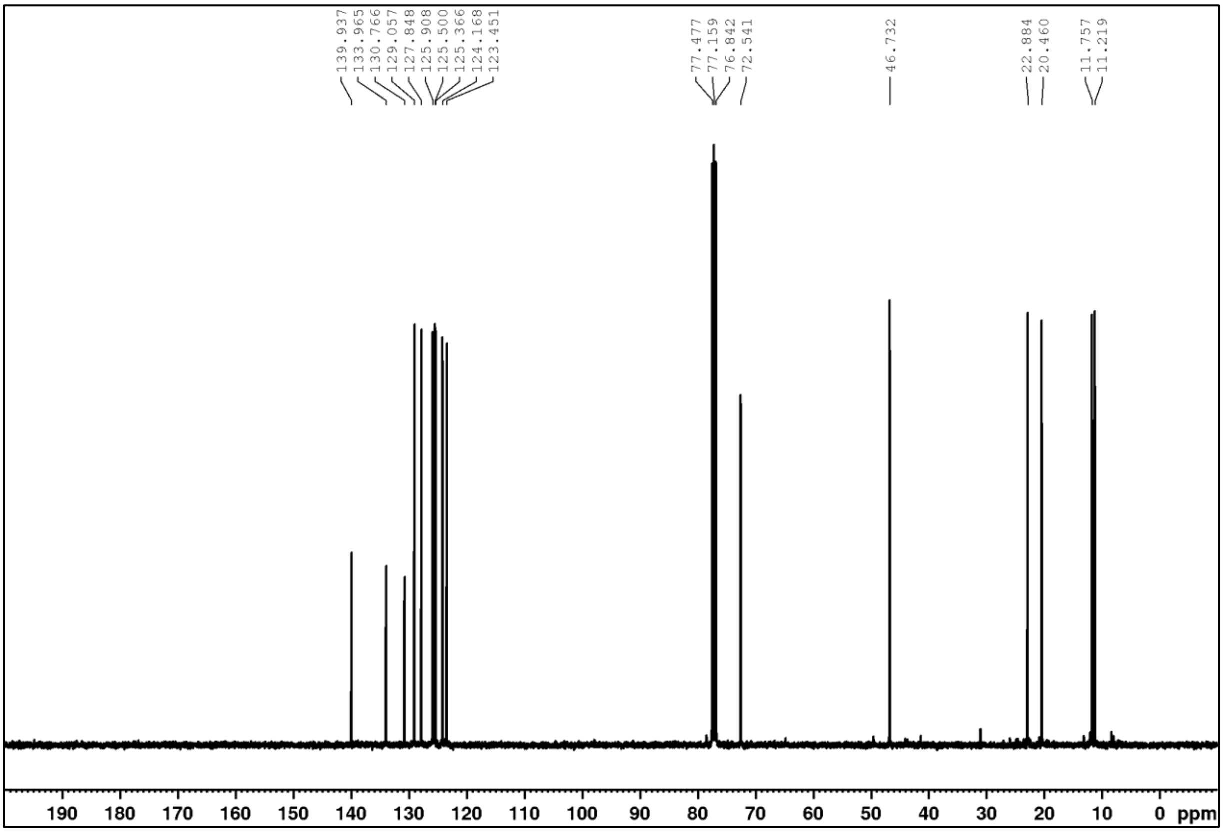


**2-Ethyl-1-(naphthalen-1-yl)butan-1-ol (18s)**

$^1$H NMR (400 MHz, CDCl$_3$)

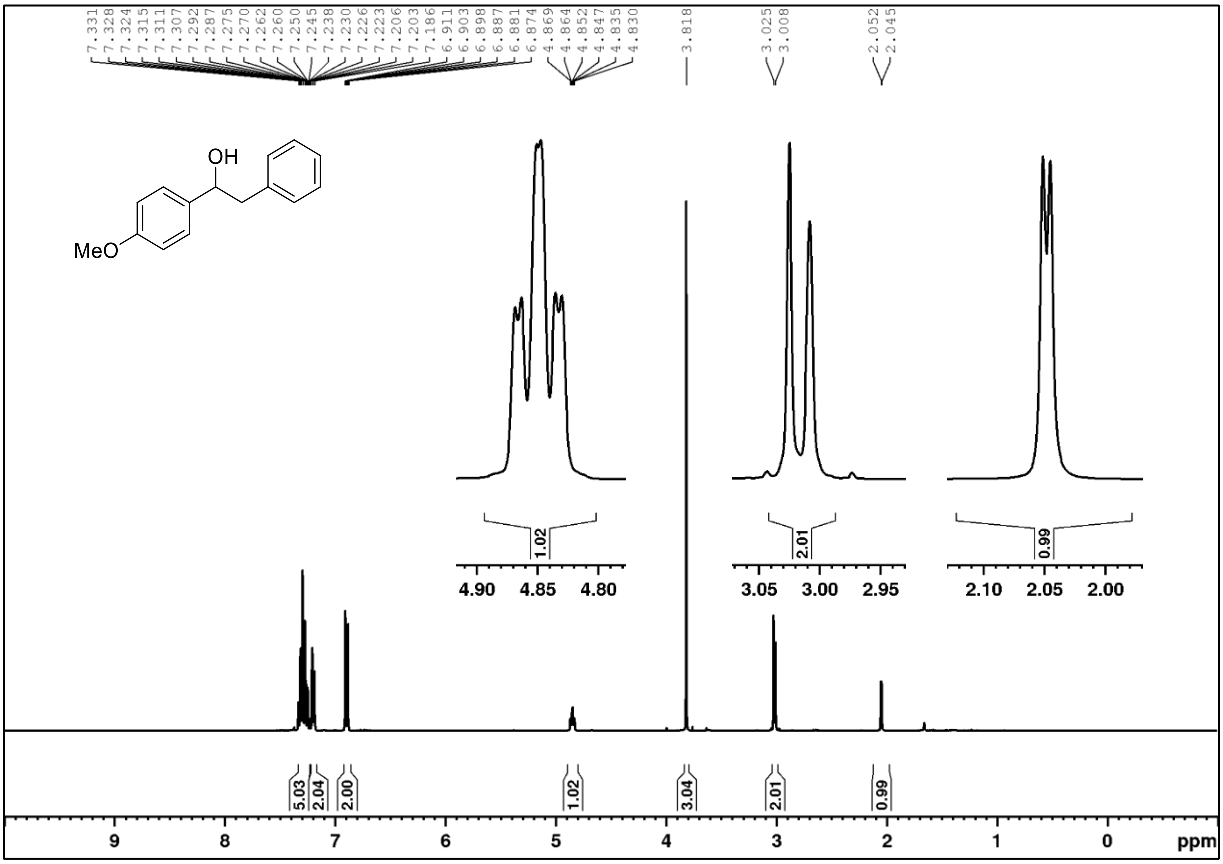


$^{13}$C NMR (101 MHz, CDCl$_3$)

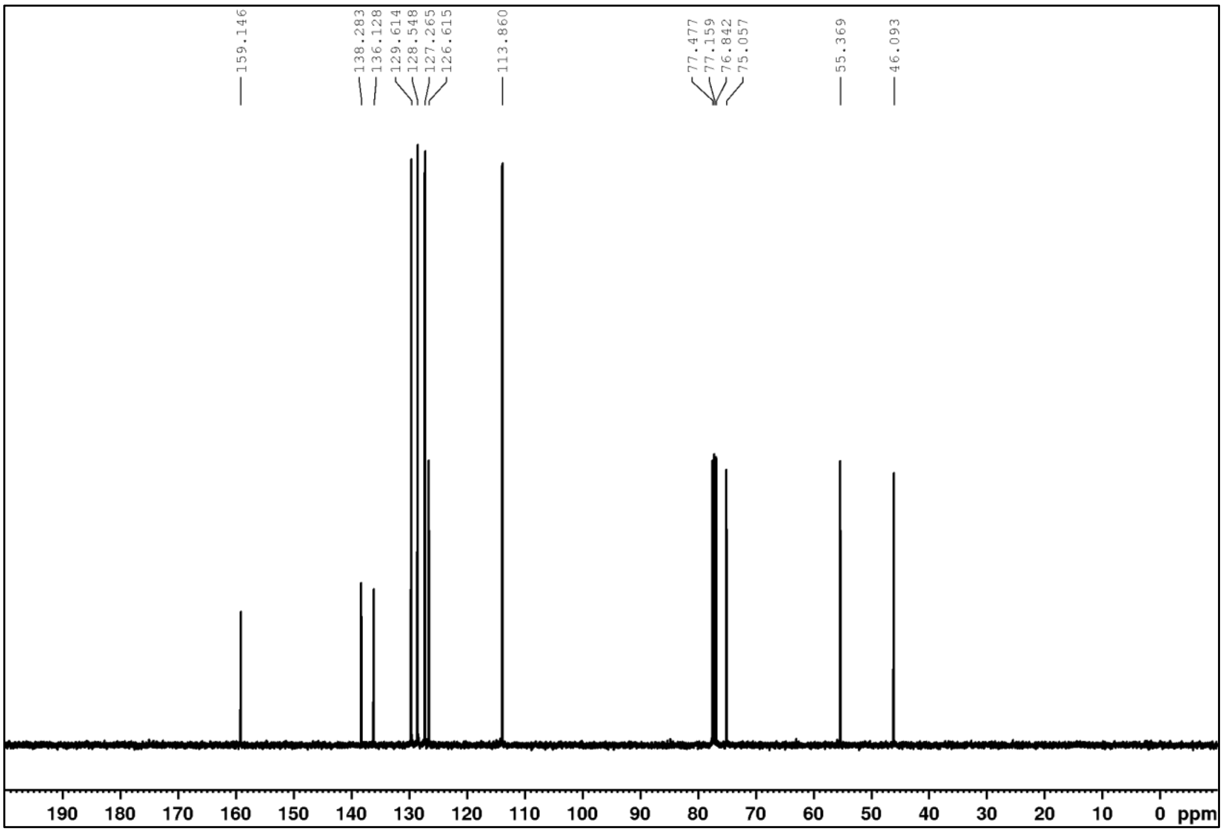


# 1-(4-Methoxyphenyl)-2-phenylethan-1-ol (18t)

$^1$H NMR (400 MHz, CDCl$_3$)

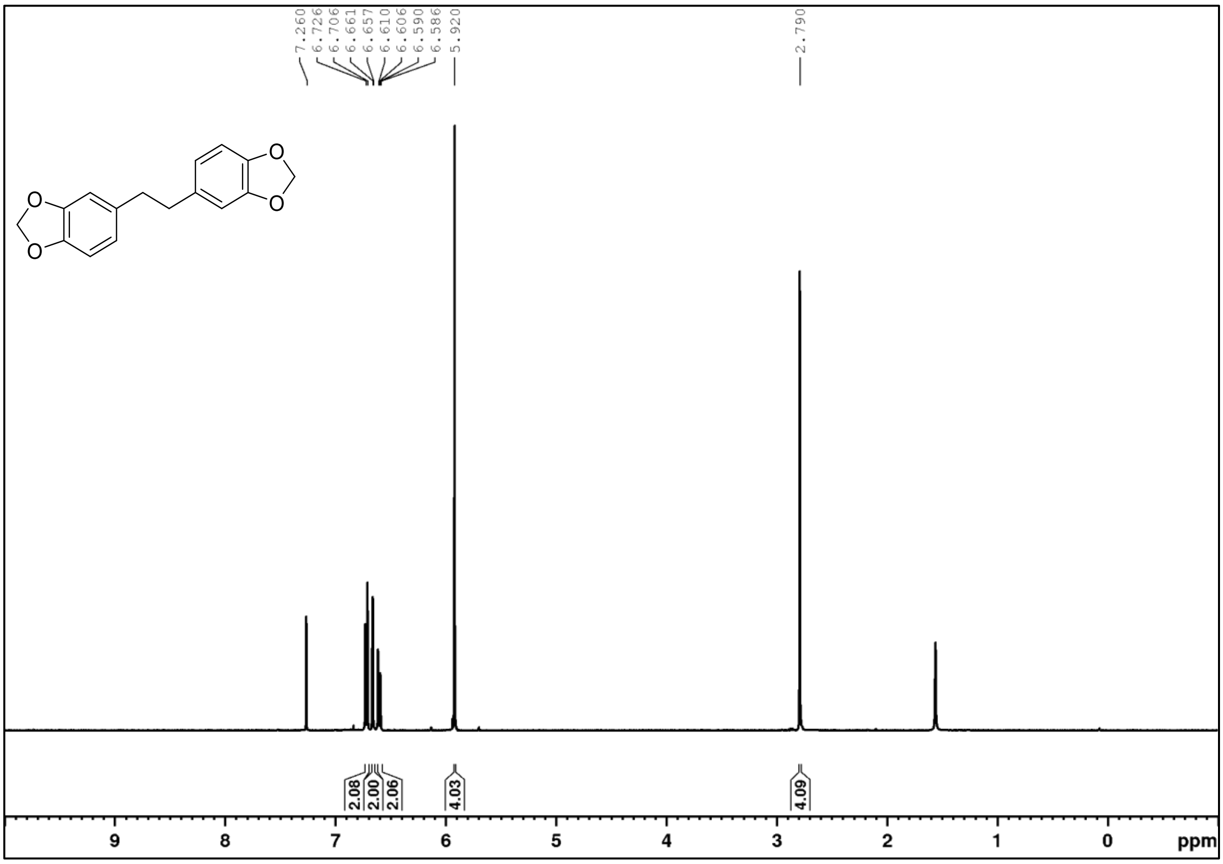


$^{13}$C NMR (101 MHz, CDCl$_3$)

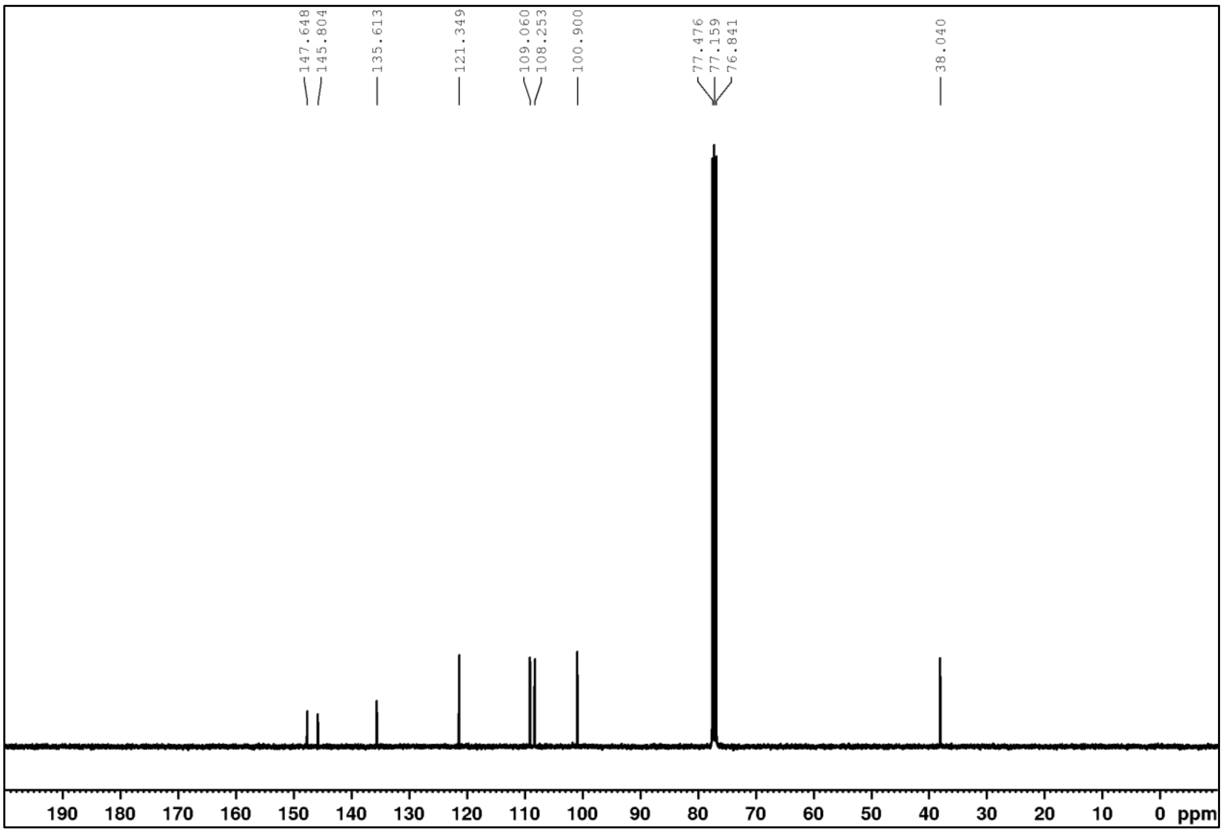


**1,2-Bis(benzo[d][1,3]dioxol-5-yl)ethane (19)**

$^1$H NMR (400 MHz, CDCl$_3$)

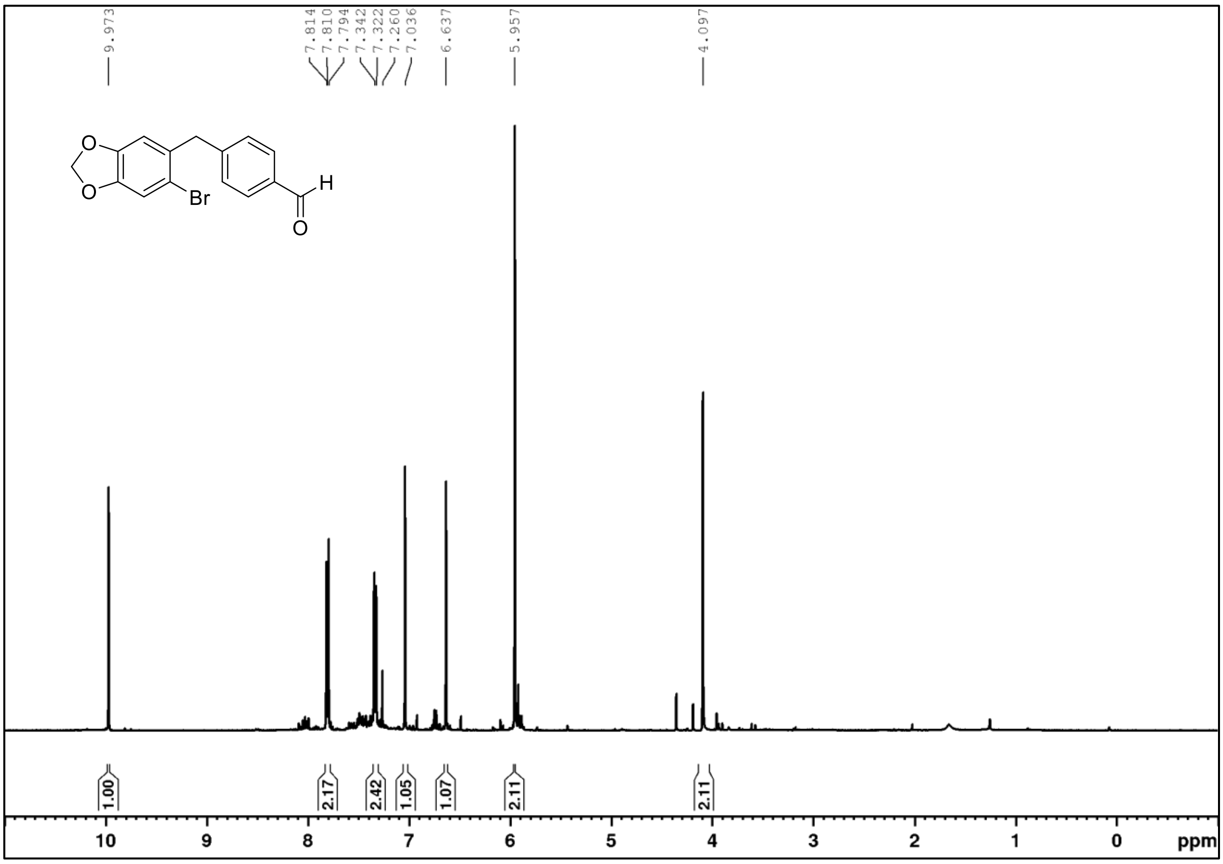


$^{13}$C NMR (101 MHz, CDCl$_3$)

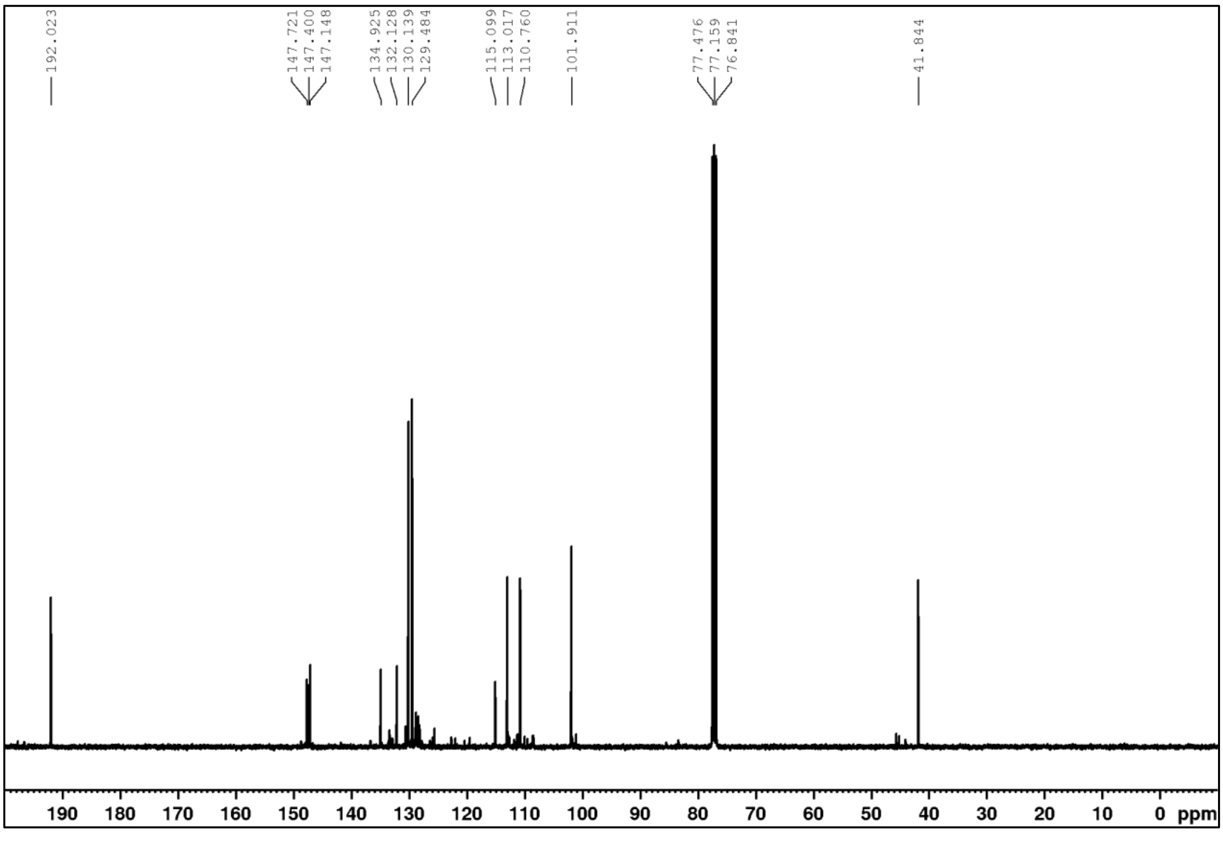


**4-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)benzaldehyde (20b)**

$^{1}$H NMR (400 MHz, CDCl$_3$)

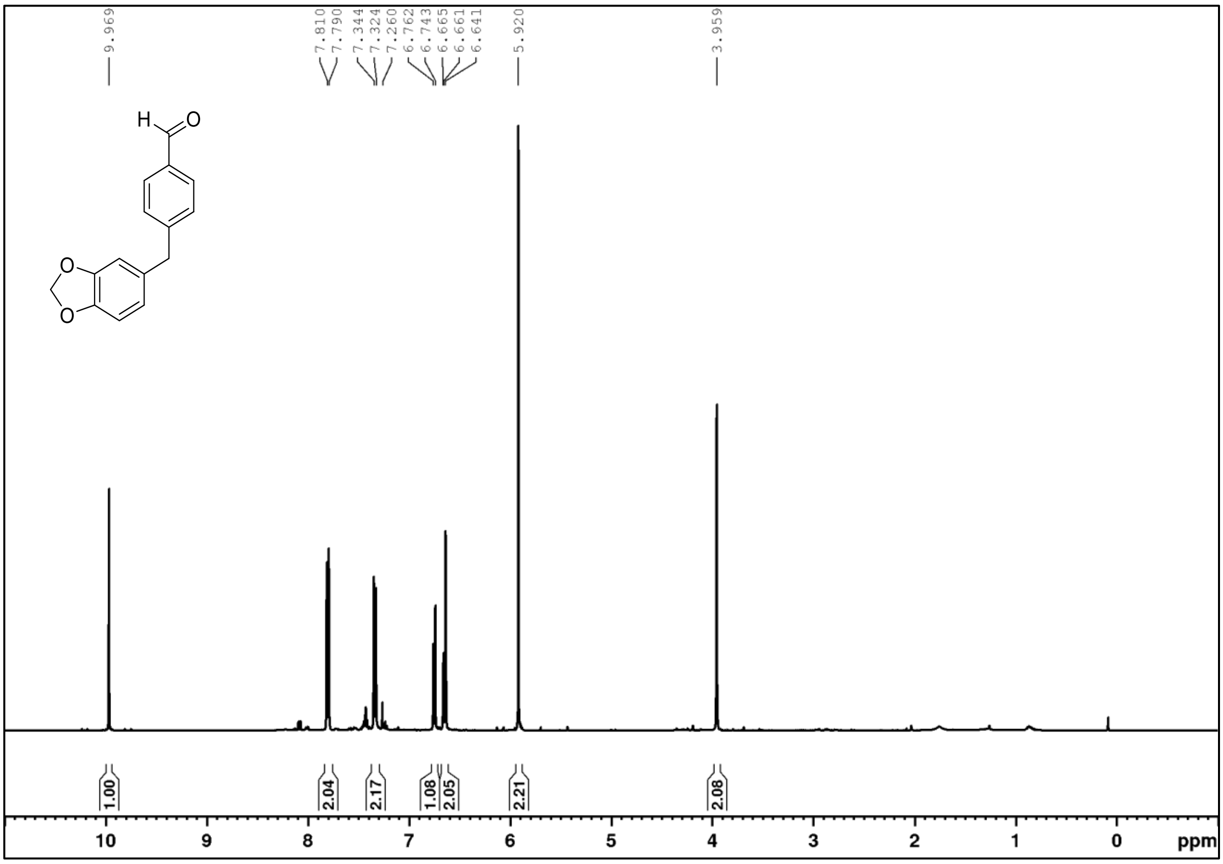


$^{13}$C NMR (101 MHz, CDCl$_3$)

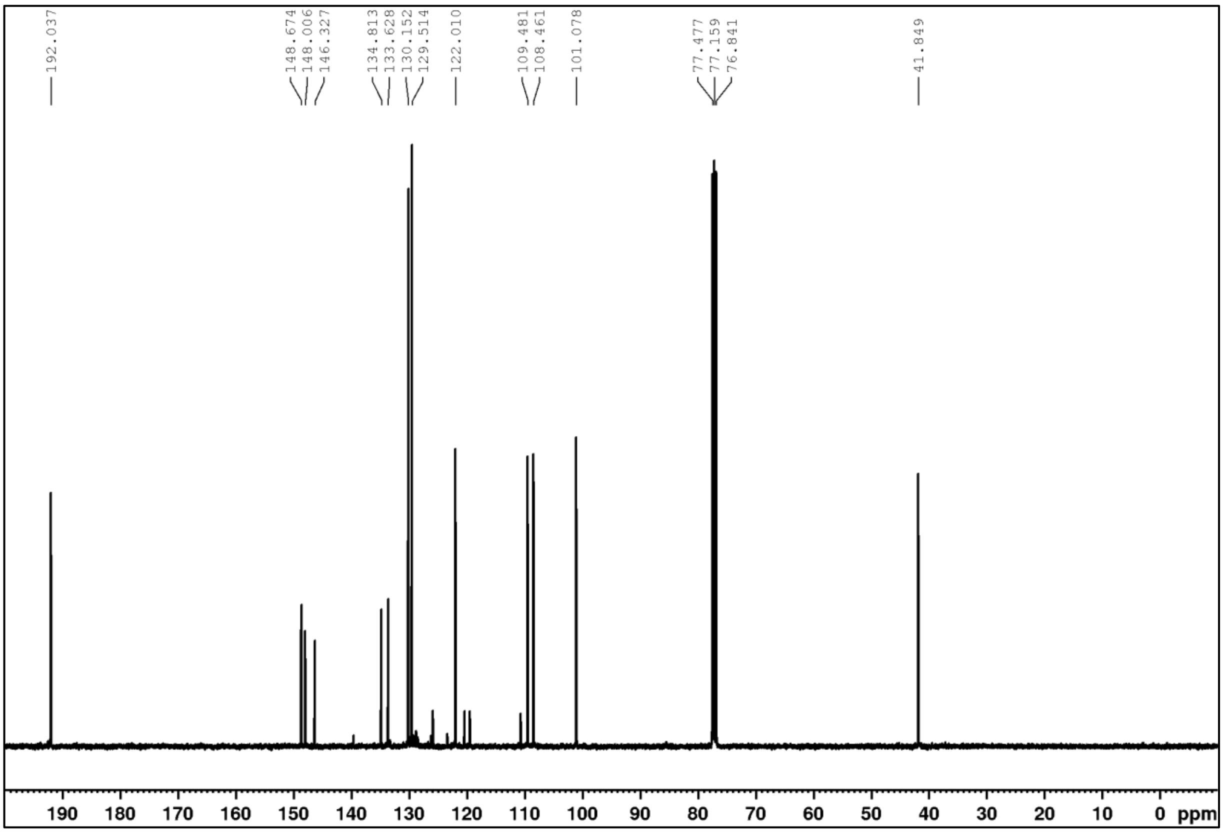


**4-(Benzo[*d*][1,3]dioxol-5-ylmethyl)benzaldehyde (20c)**

$^{1}$H NMR (400 MHz, CDCl$_3$

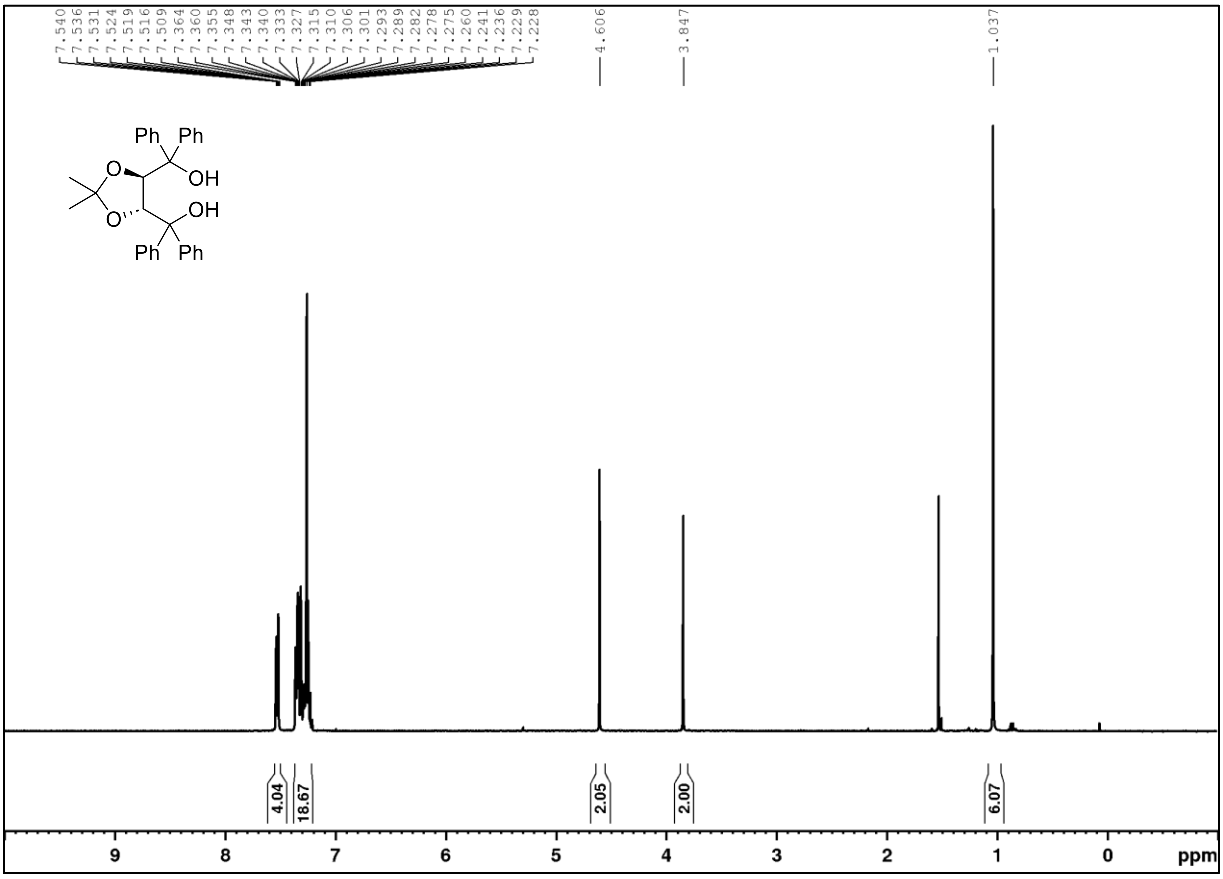


$^{13}$C NMR (101 MHz, CDCl$_3$)



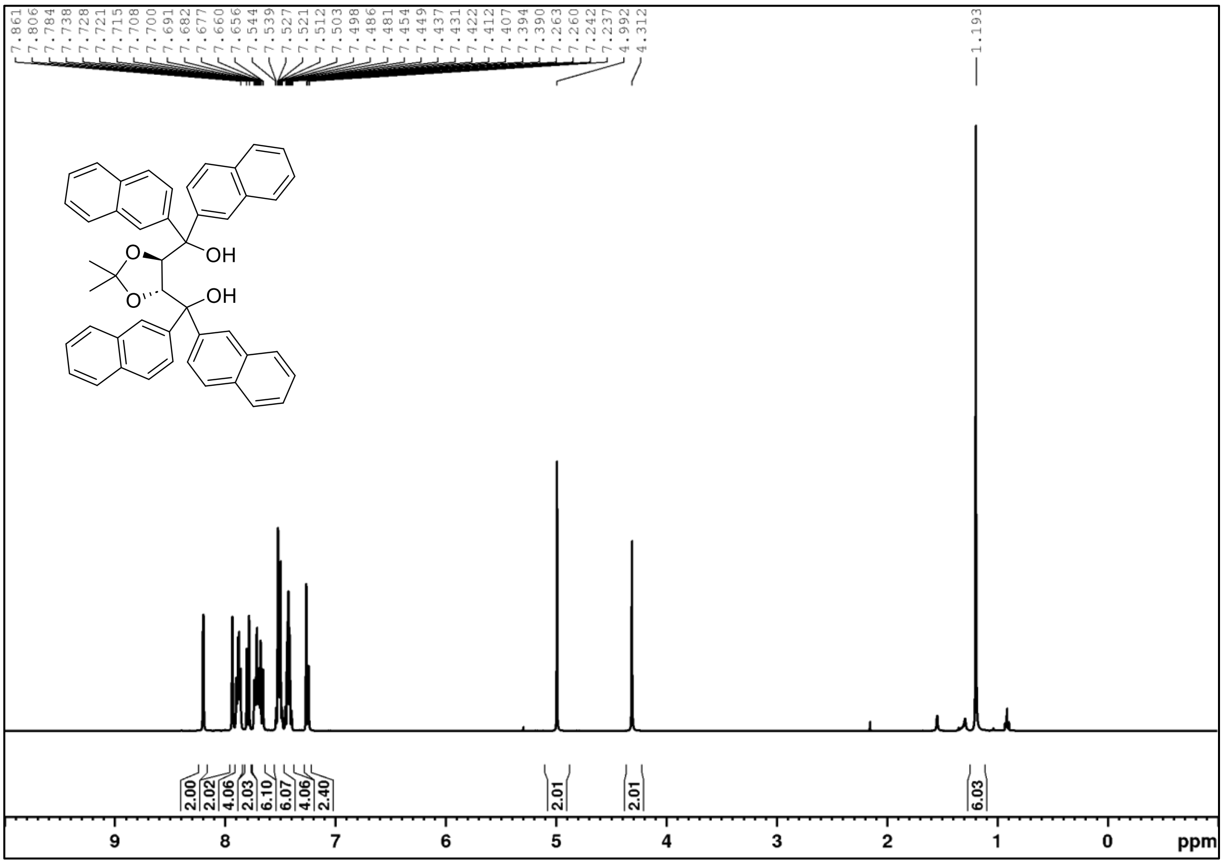
**((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) ((*R*,*R*)-28a)**

$^1$H NMR (400 MHz, $CDCl_3$)



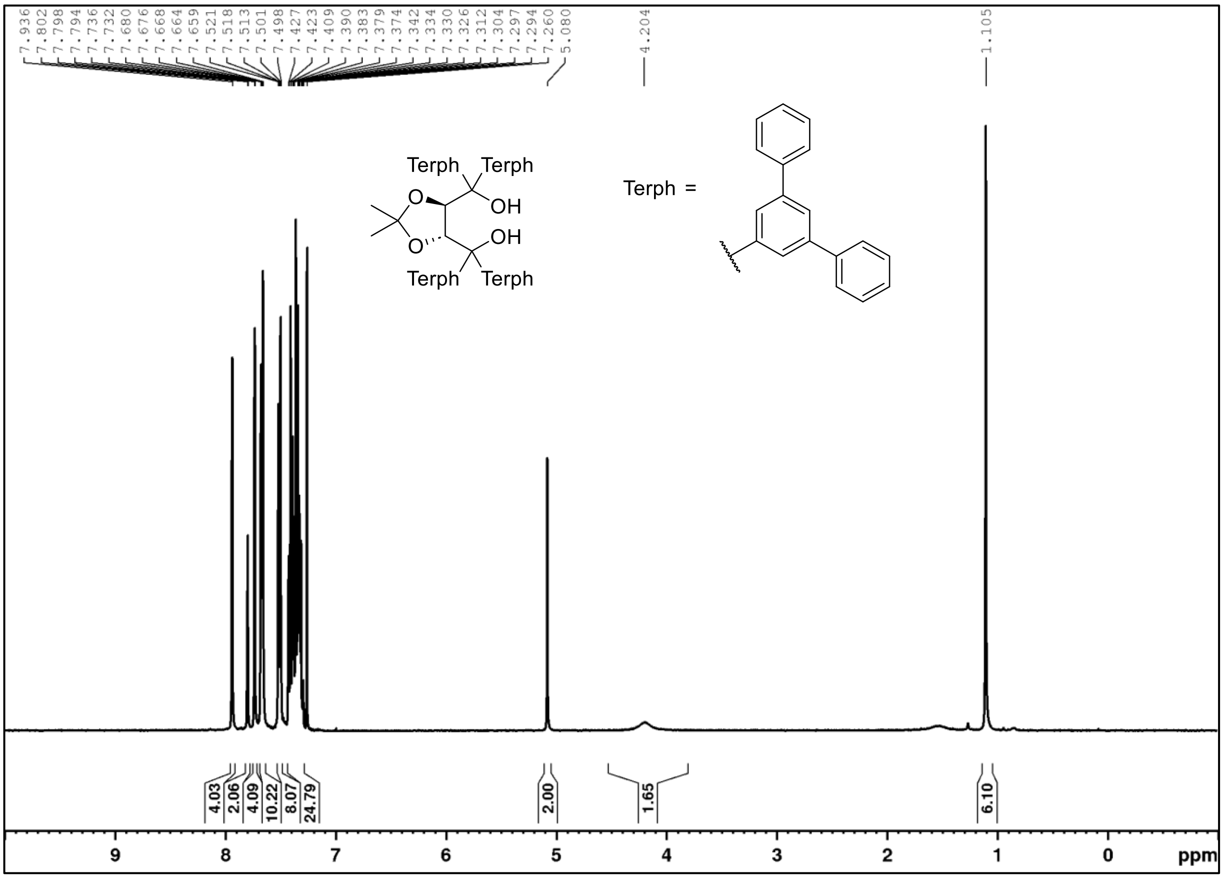
**((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(di(naphthalen-2-yl)methanol) ((*R*,*R*)-28b)**

$^1$H NMR (400 MHz, $CDCl_3$)

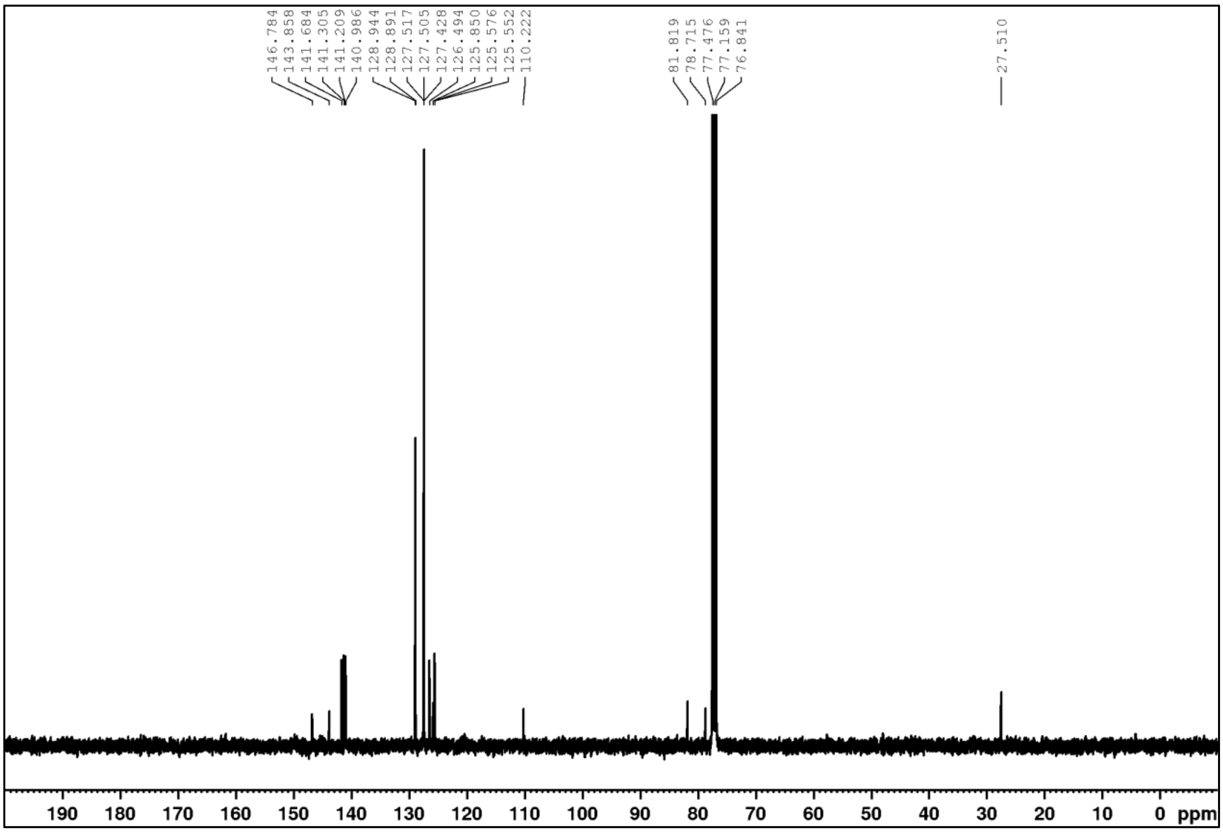


## ((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(di([1,1':3',1''-terphenyl]-5'-yl)methanol) ((*R*,*R*)-28c)

$^1$H NMR (400 MHz, CDCl$_3$)

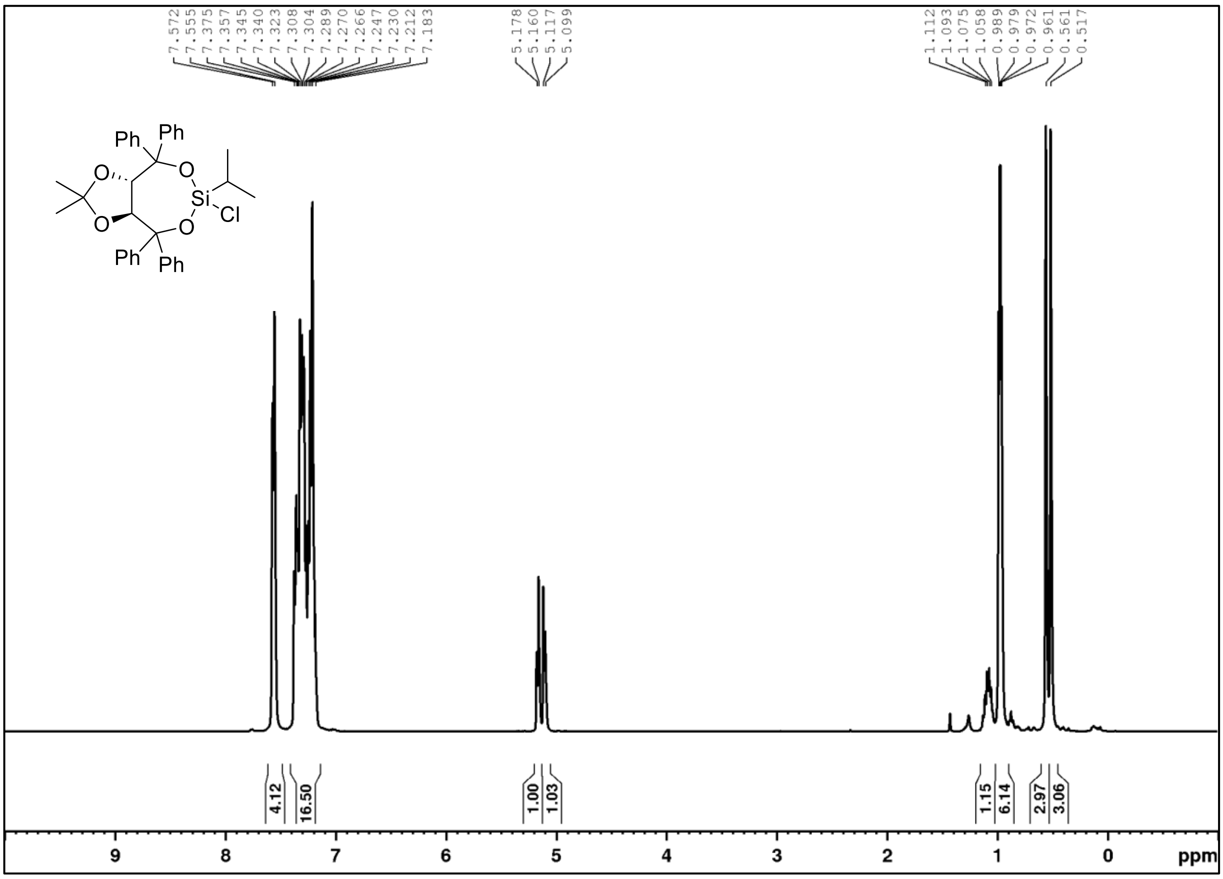


$^{13}$C NMR (101 MHz, CDCl$_3$)

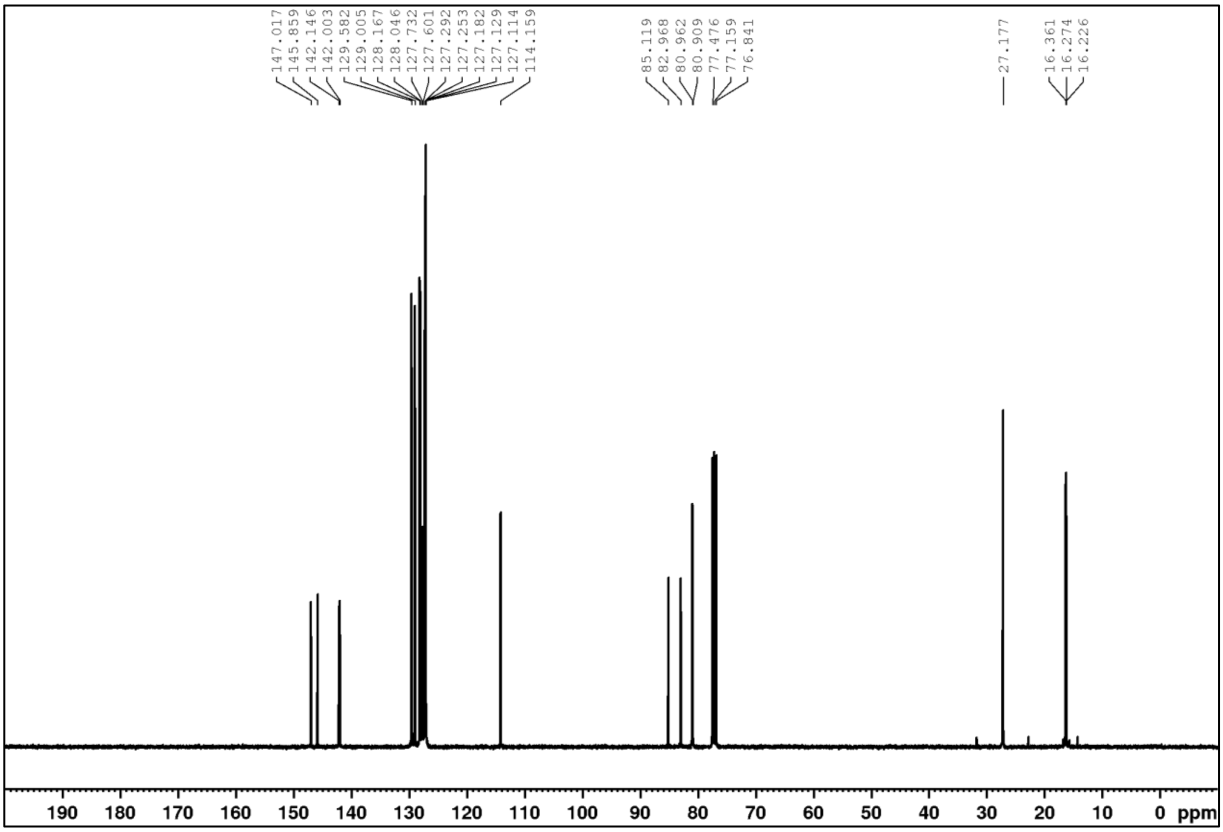


**(3a*S*,8a*S*)-6-Chloro-6-isopropyl-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*S*,*S*)-30a)**

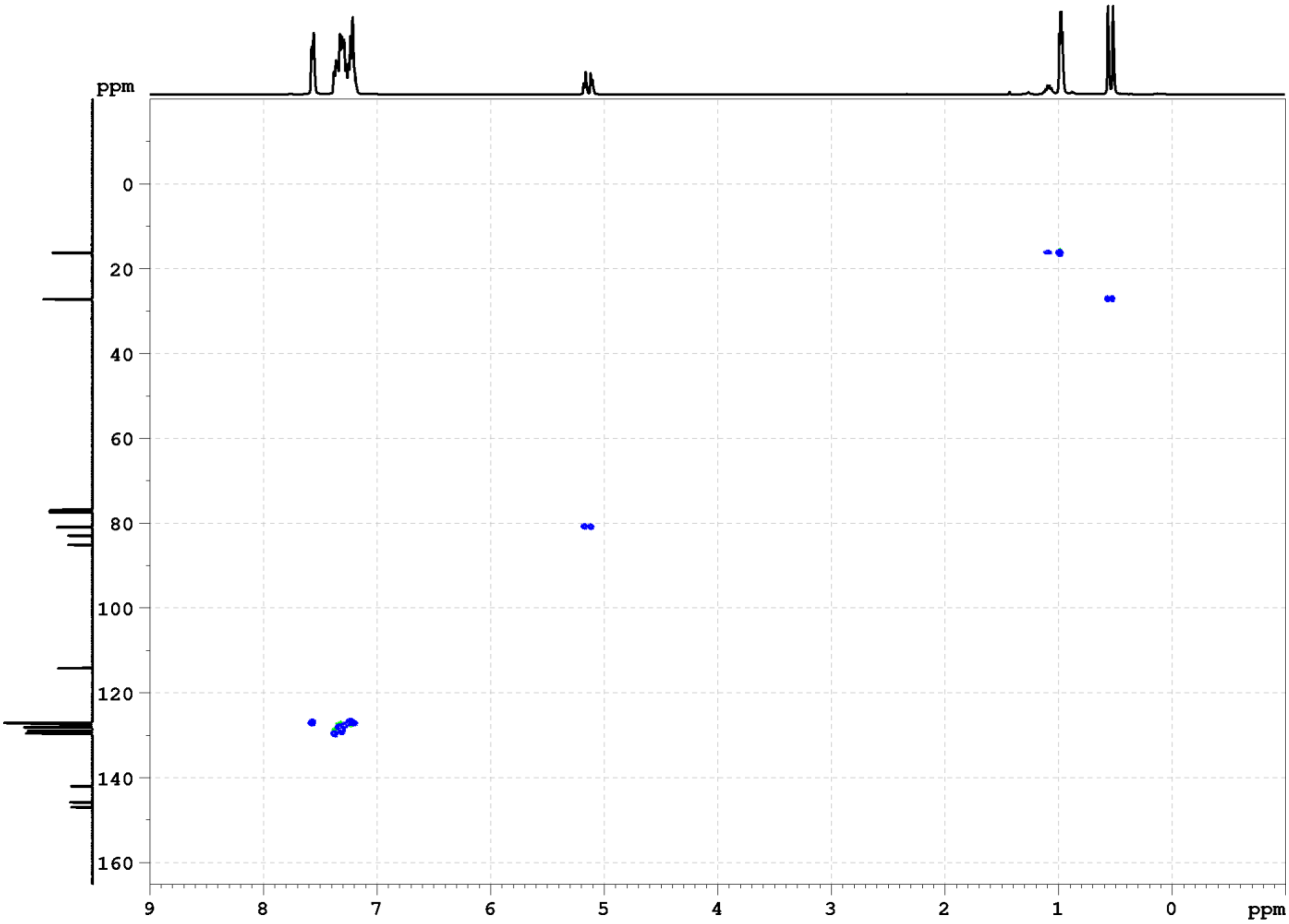
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (101 MHz, CDCl$_3$)

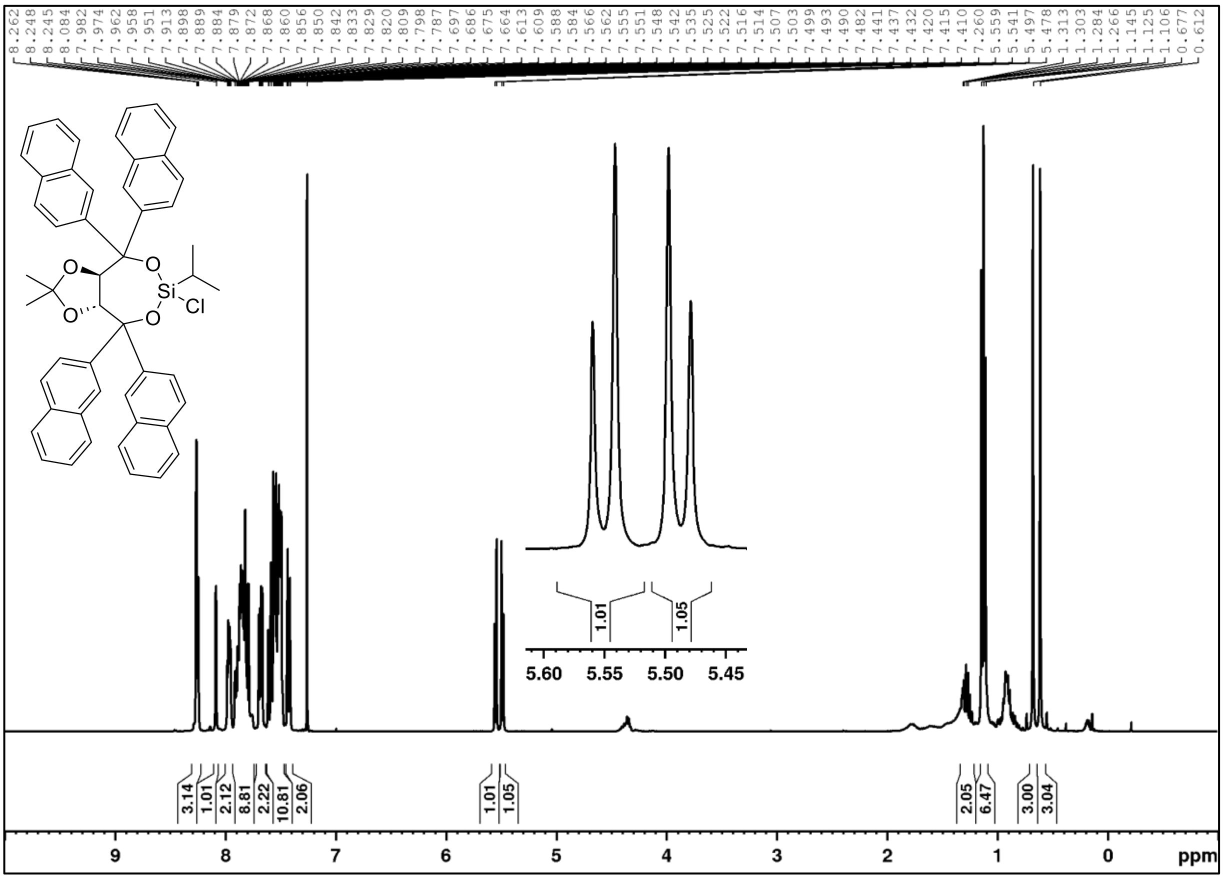


HSQC (CDCl₃)

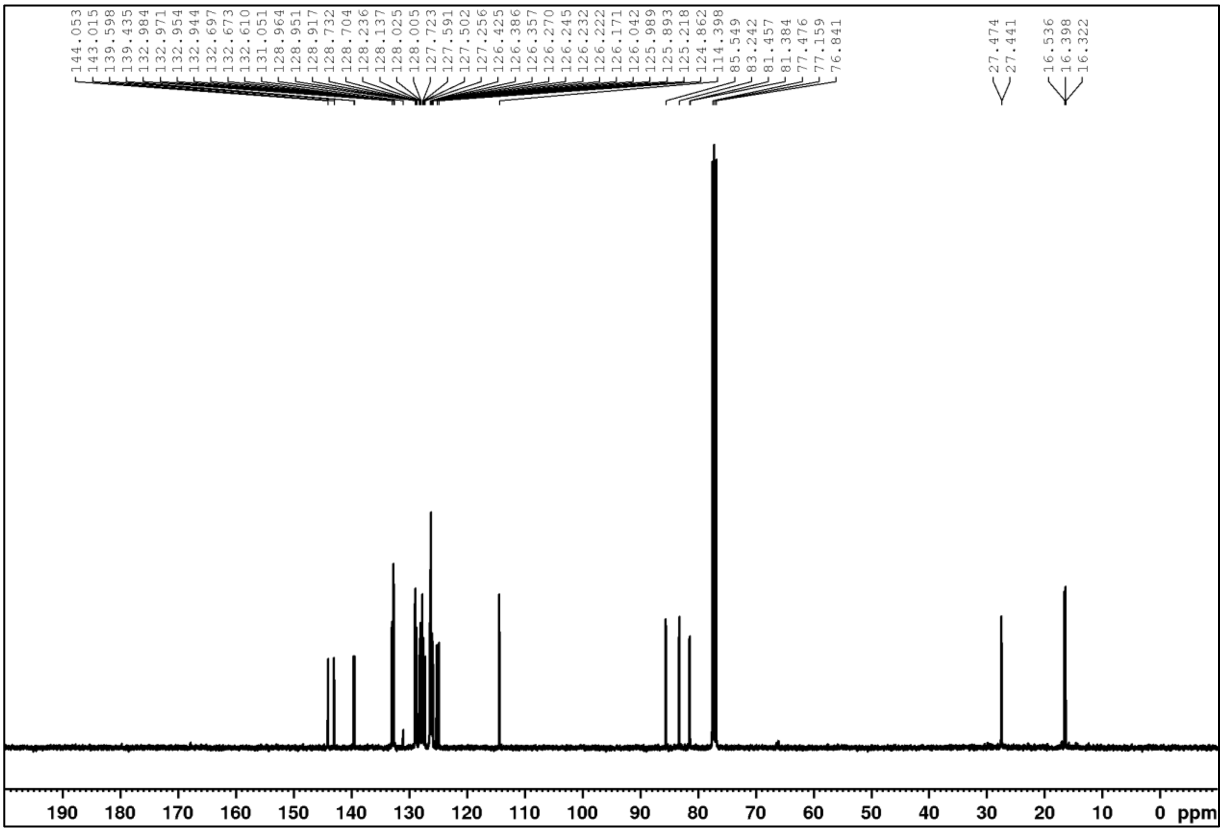


**(3a*R*,8a*R*)-6-chloro-6-isopropyl-2,2-dimethyl-4,4,8,8-tetra(naphthalen-2-yl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*R*,*R*)-30b)**

$^1$H NMR (400 MHz, CDCl$_3$)

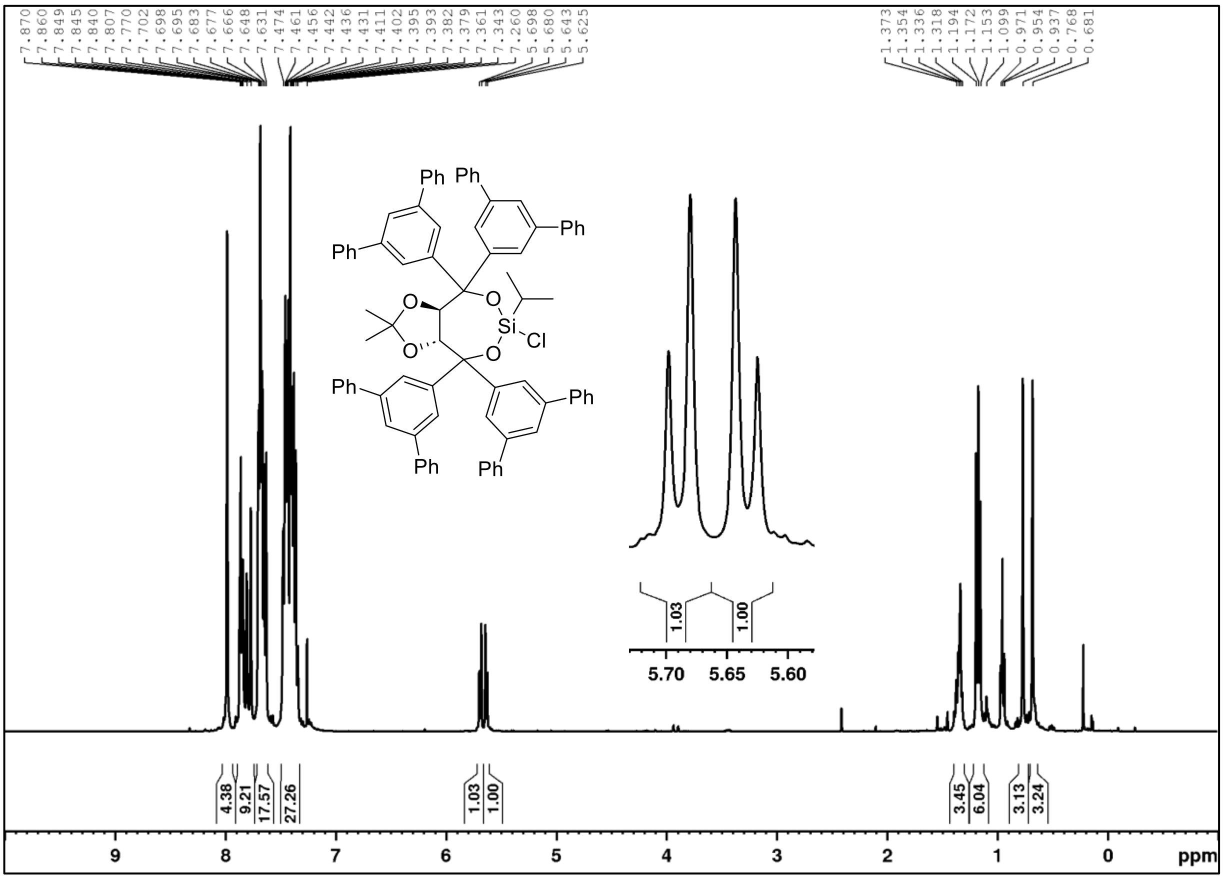


$^{13}$C NMR (101 MHz, CDCl$_3$)

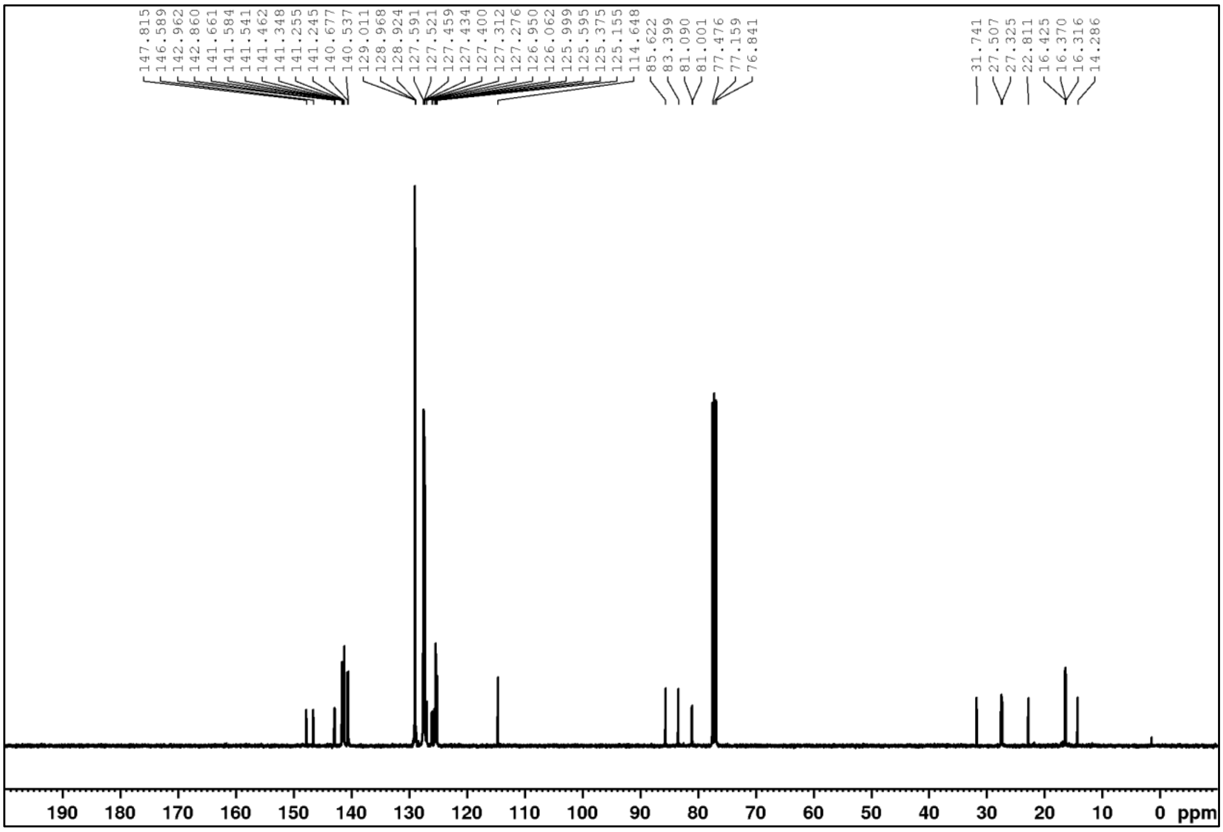


**(3a*R*,8a*R*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-chloro-6-isopropyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*R*,*R*)-30c)**

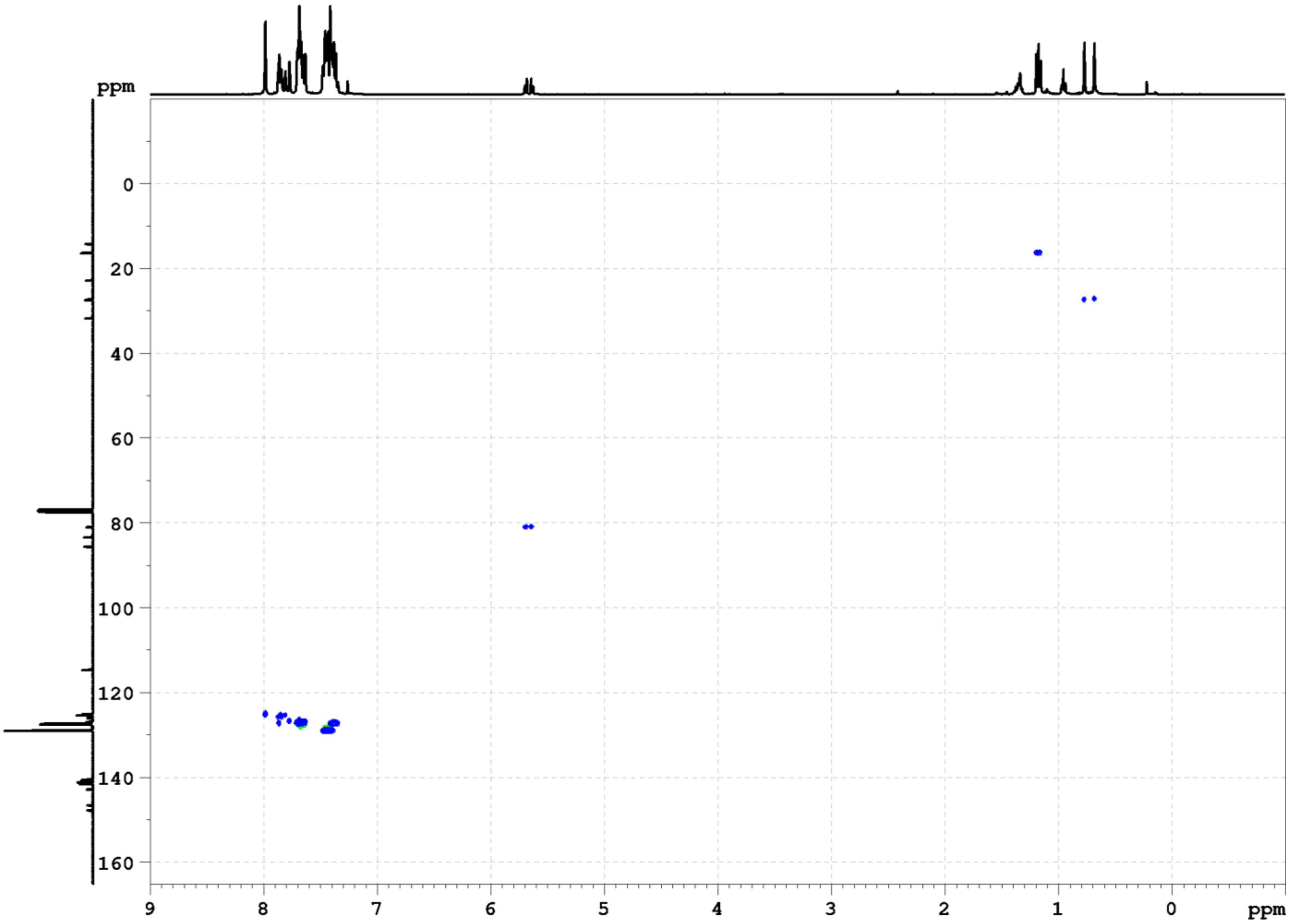
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (101 MHz, CDCl$_3$)

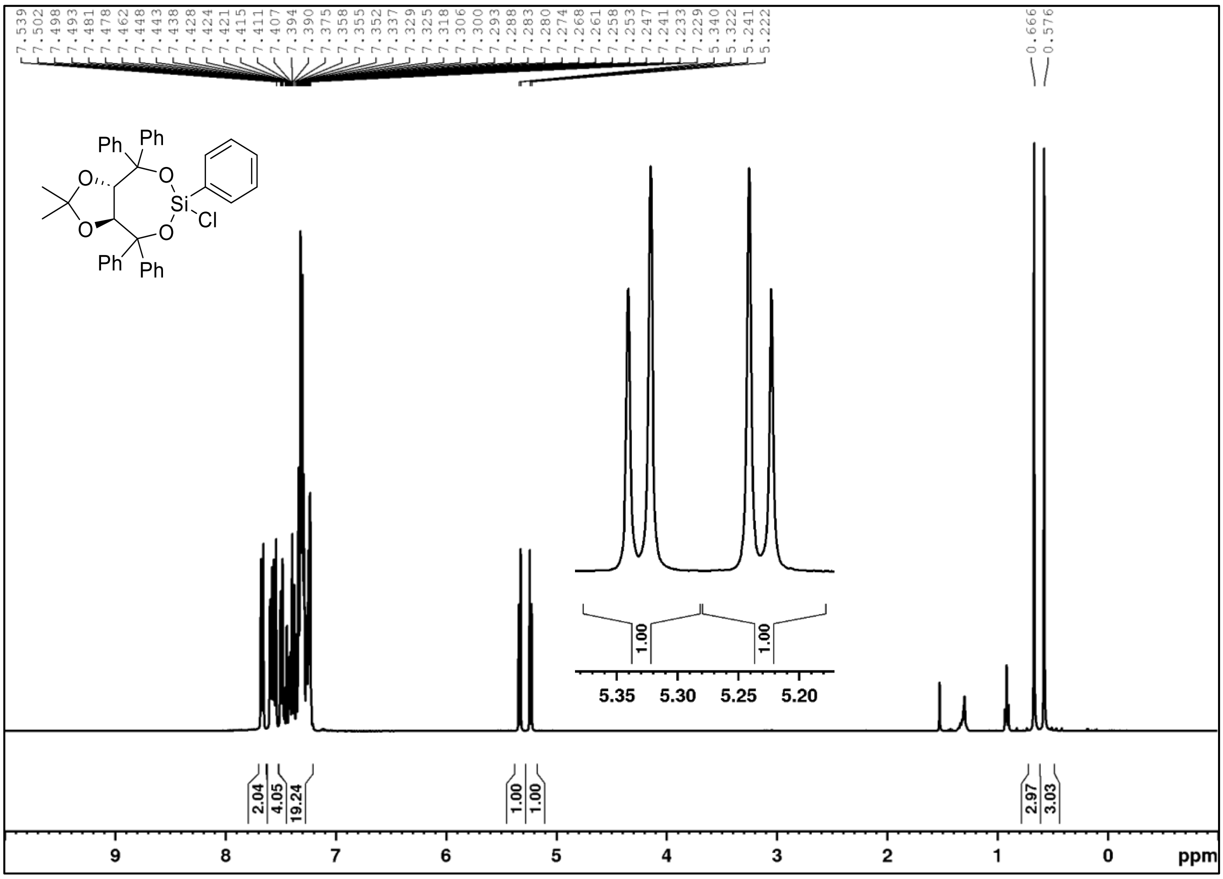


HSQC ($CDCl_3$)

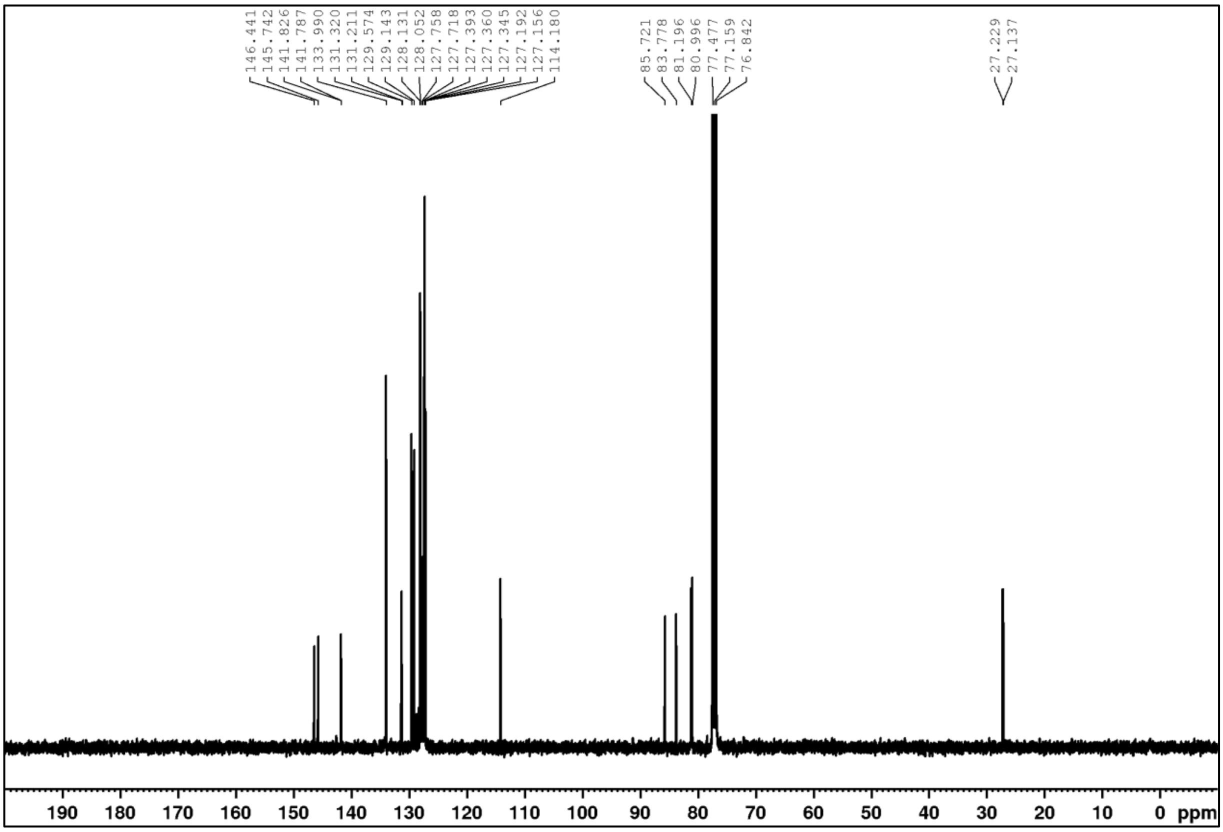


**(3a*R*,8a*R*)-6-Chloro-2,2-dimethyl-4,4,6,8,8-pentaphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*R*,*R*)-30d)**

$^1$H NMR (400 MHz, CDCl$_3$)

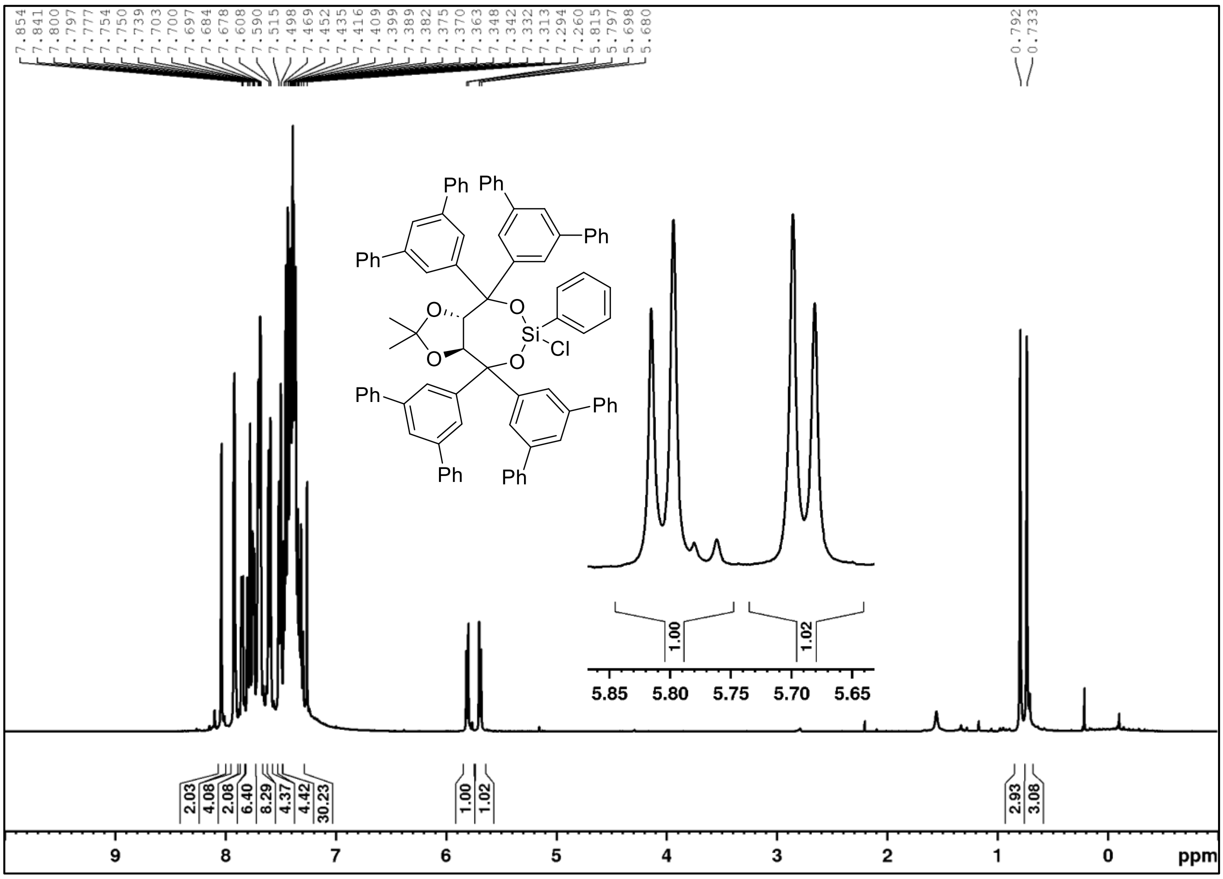


$^{13}$C NMR (101 MHz, CDCl$_3$)



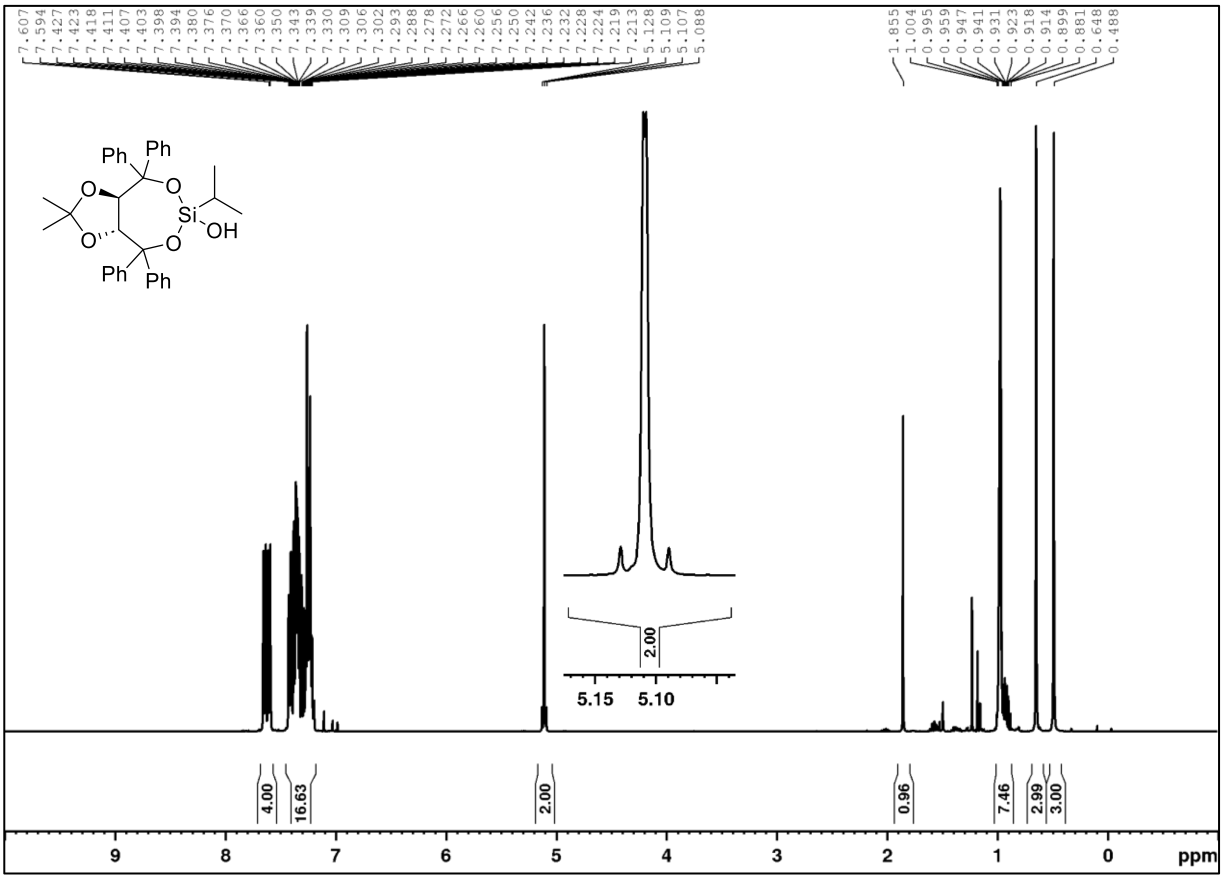
**(3a*S*,8a*S*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-chloro-2,2-dimethyl-6-phenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepine ((*S*,*S*)-30e)**

$^1$H NMR (400 MHz, CDCl$_3$)

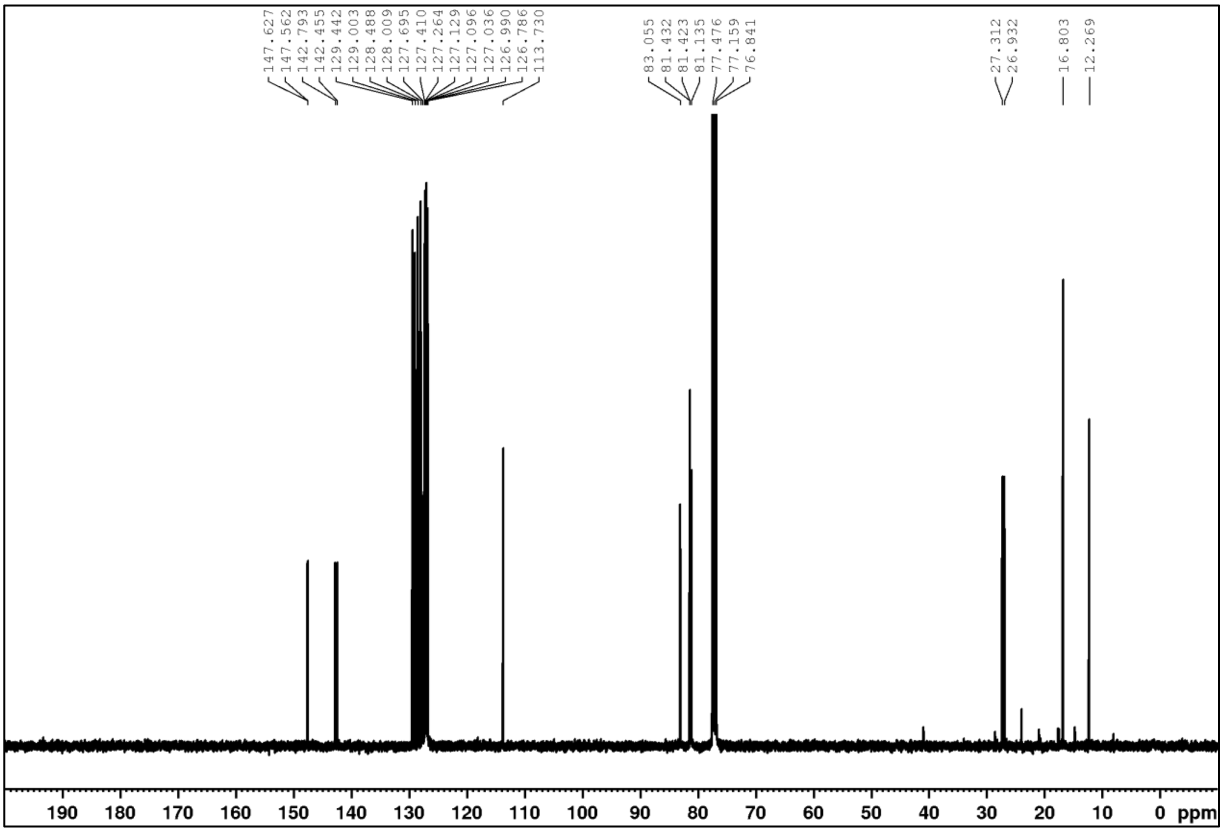


**(3a*R*,8a*R*)-6-Isopropyl-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*R*,*R*)-31a)**

$^1$H NMR (400 MHz, CDCl$_3$)

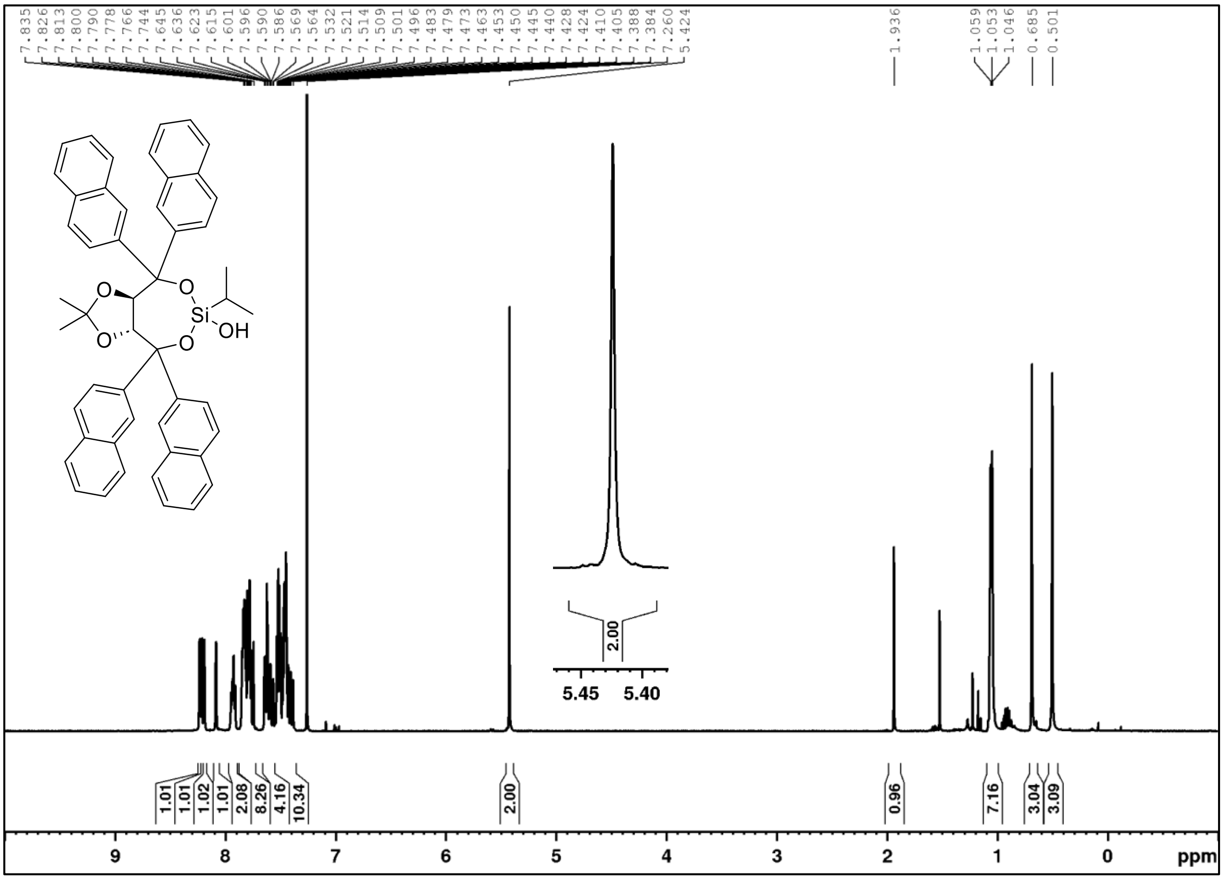


$^{13}$C NMR (101 MHz, CDCl$_3$)

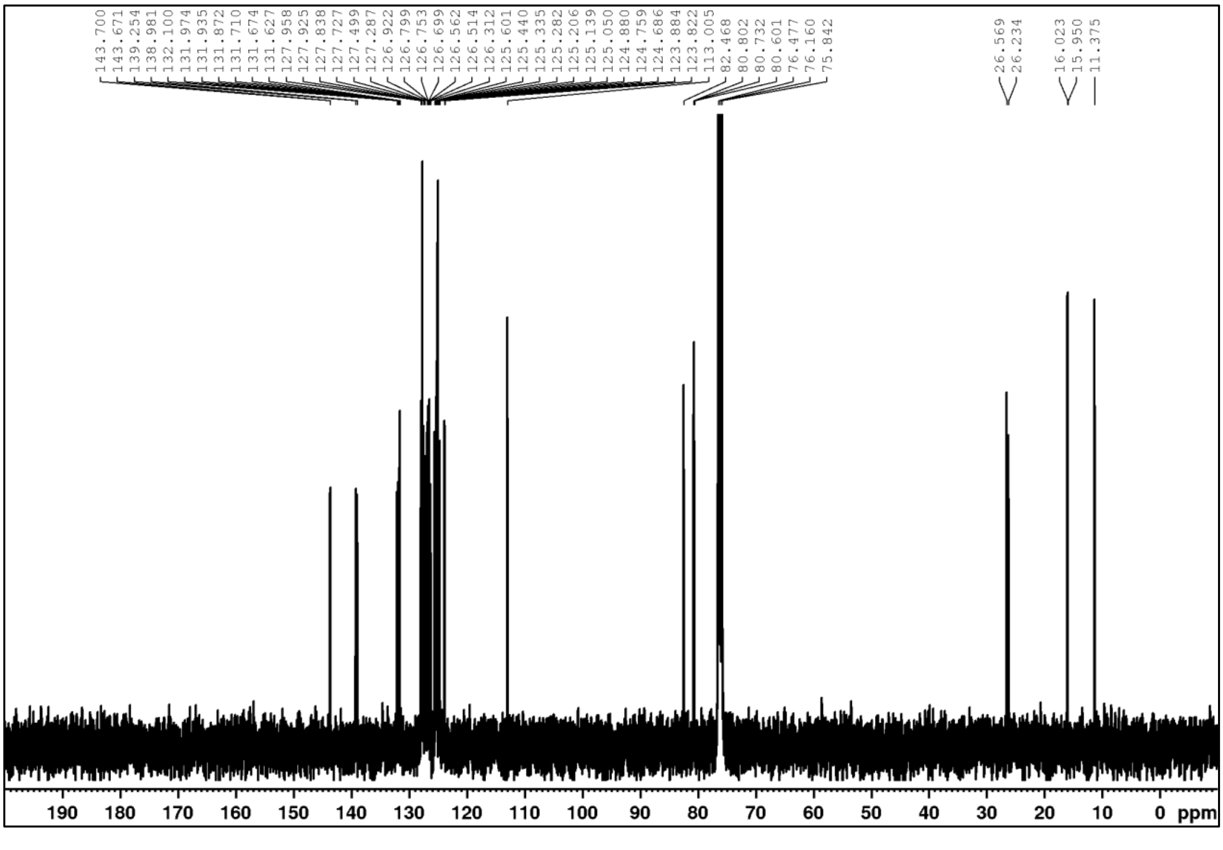


**(3a*R*,8a*R*)-6-Isopropyl-2,2-dimethyl-4,4,8,8-tetra(naphthalen-2-yl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*R*,*R*)-31b)**

$^{1}$H NMR (400 MHz, CDCl$_3$)

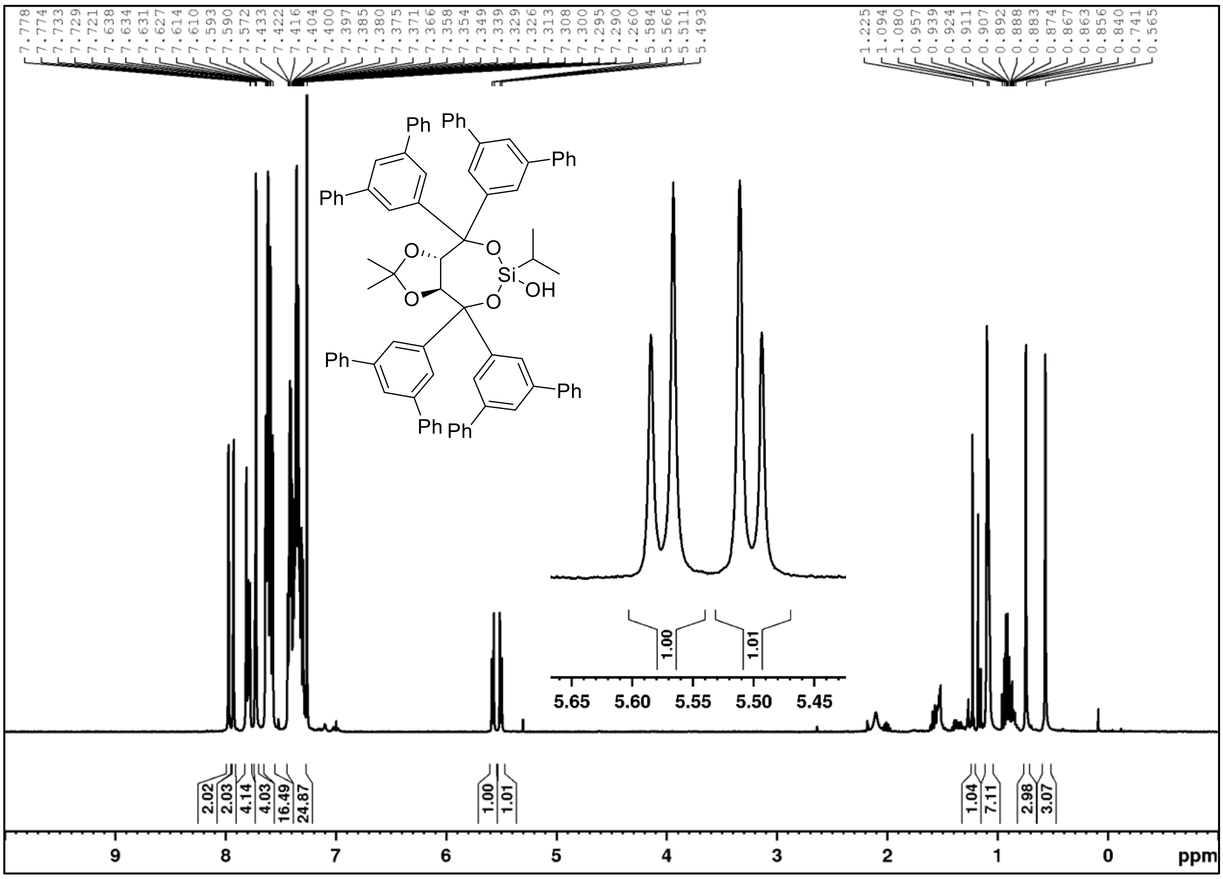


$^{13}$C NMR (101 MHz, CDCl$_3$)

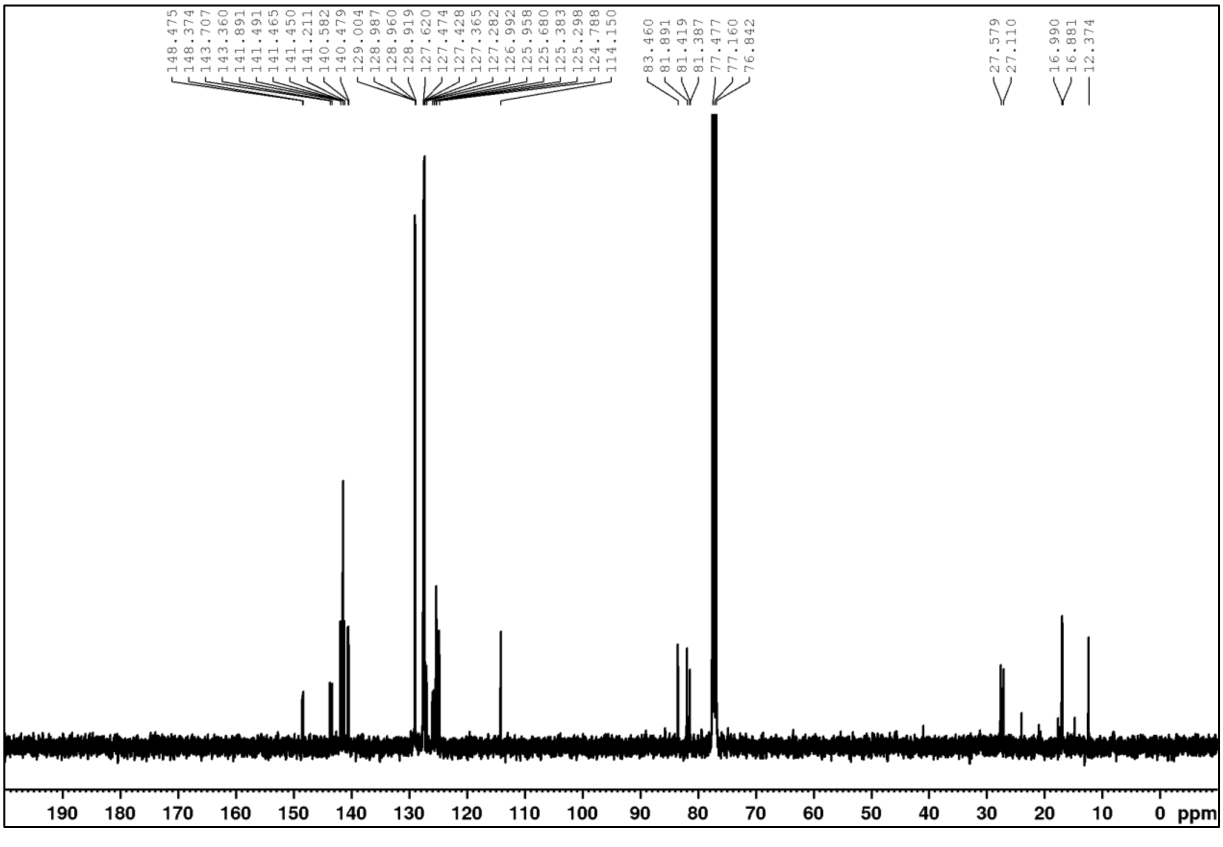


**(3a*S*,8a*S*)-4,4,8,8-Tetra([1,1':3',1''-terphenyl]-5'-yl)-6-isopropyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*S*,*S*)-31c)**

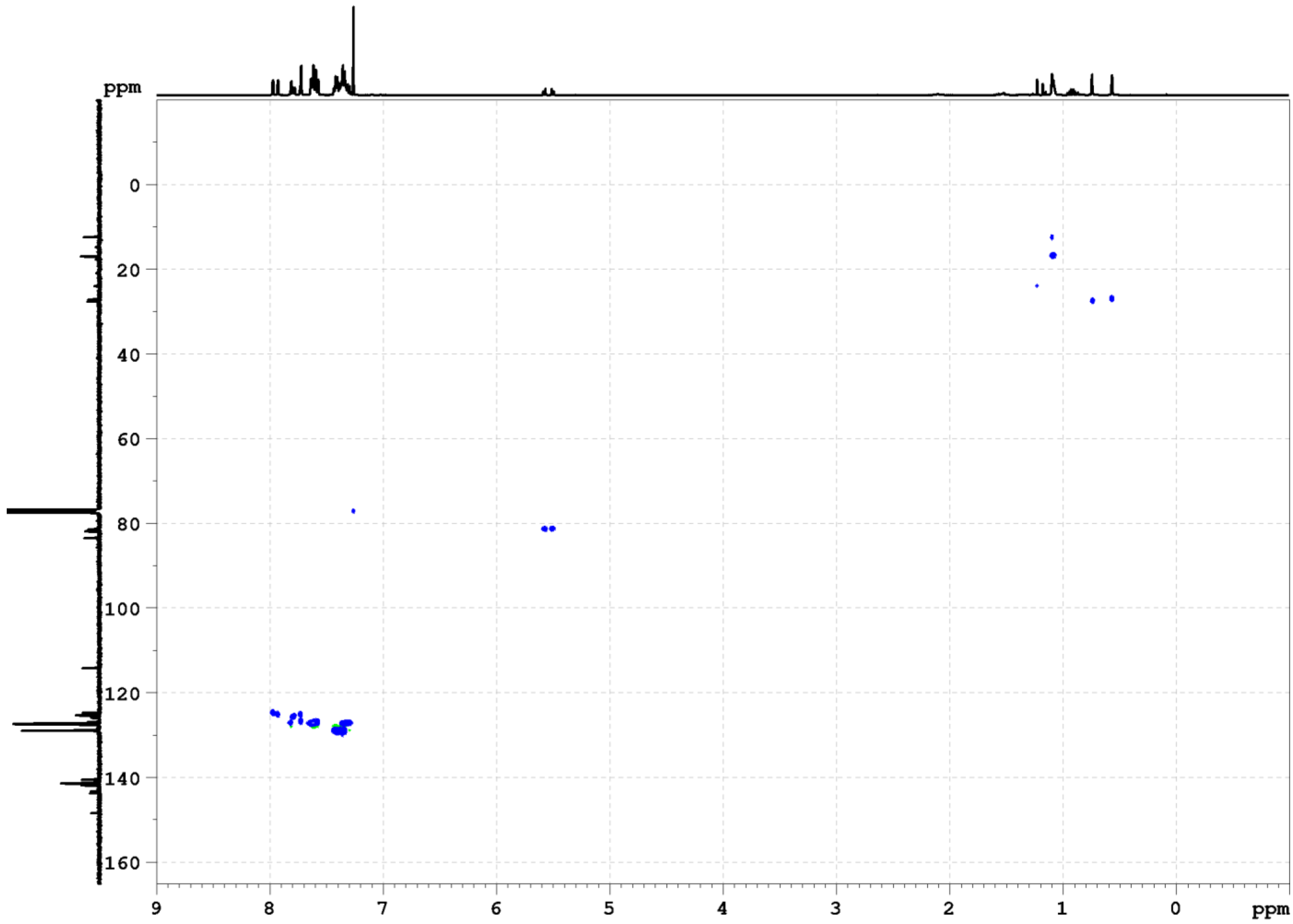
$^1$H NMR (400 MHz, $CDCl_3$)



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

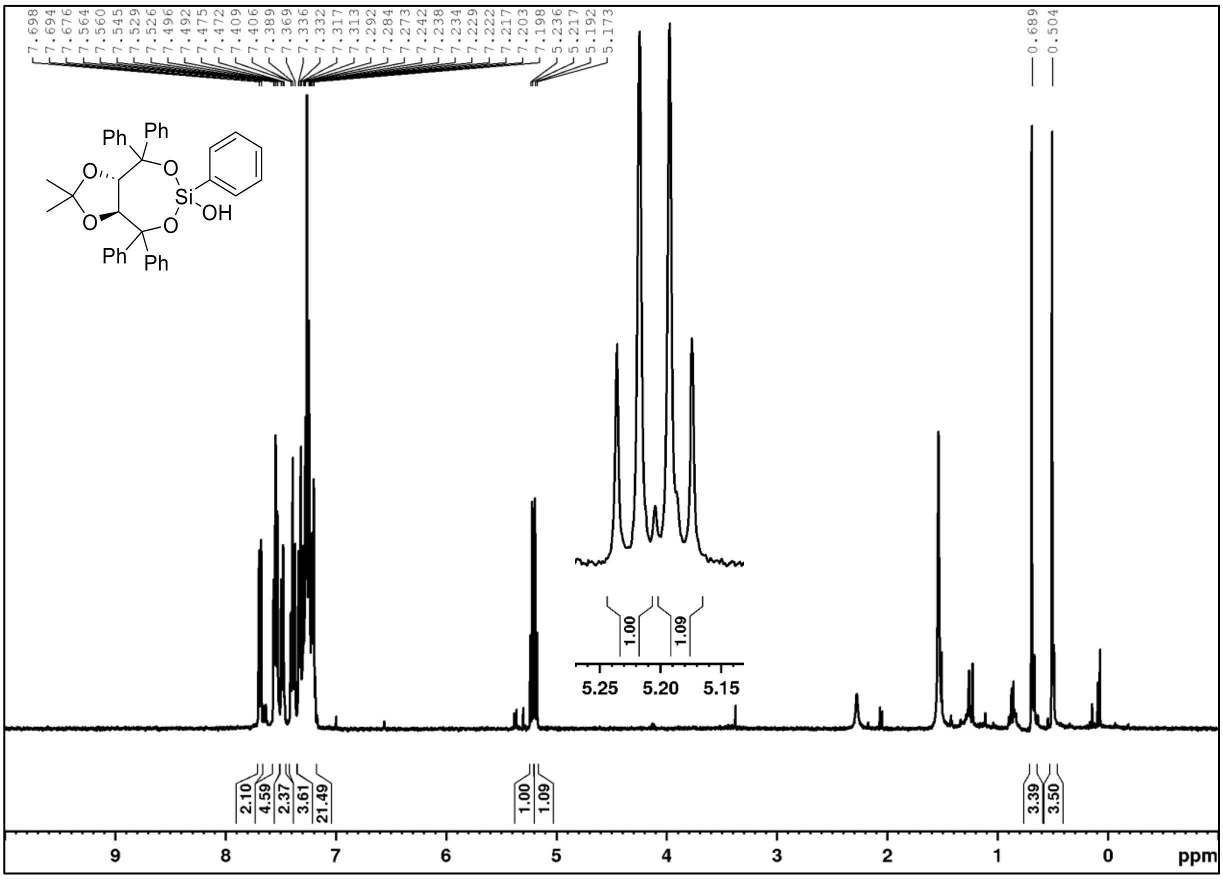


HSQC (CDCl$_3$)



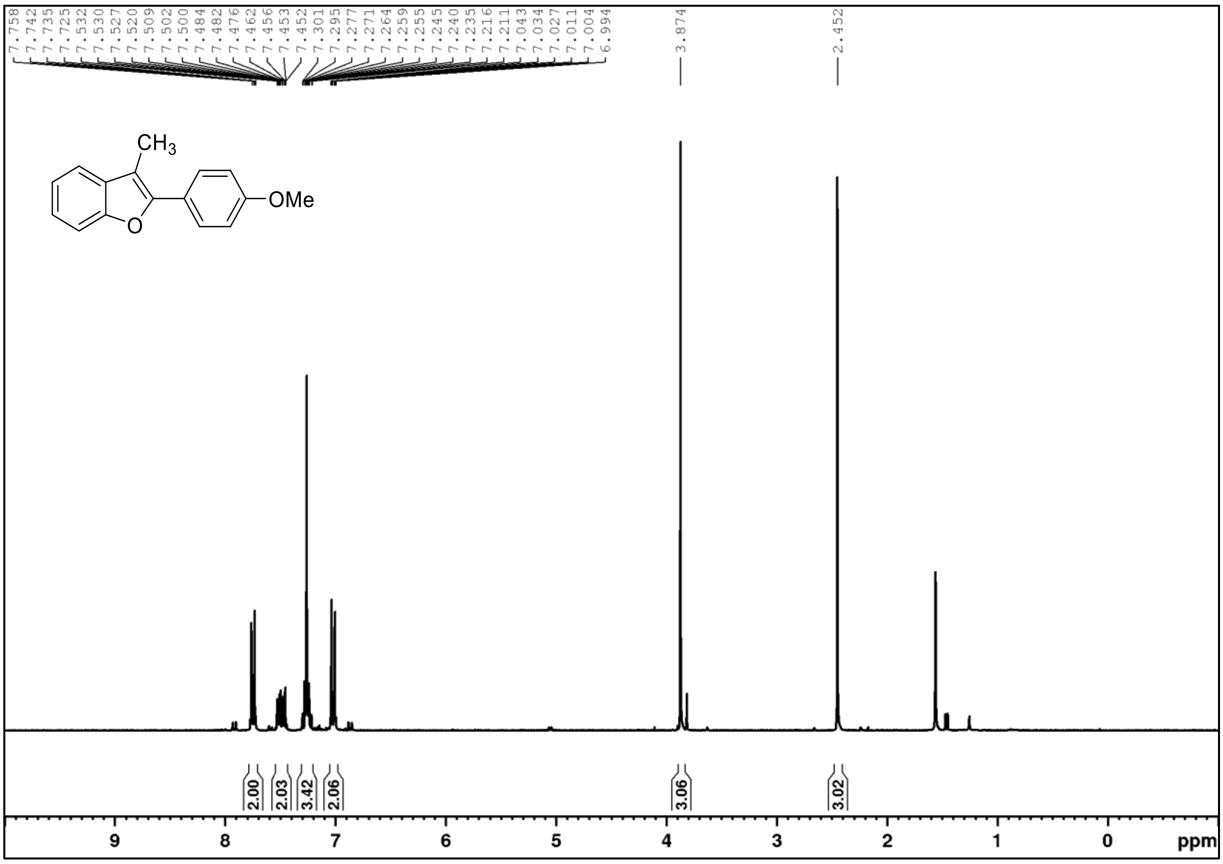
### (3a*S*,8a*S*)-2,2-dimethyl-4,4,6,8,8-pentaphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxasilepin-6-ol ((*S*,*S*)-31d)

$^1$H NMR (400 MHz, $CDCl_3$)

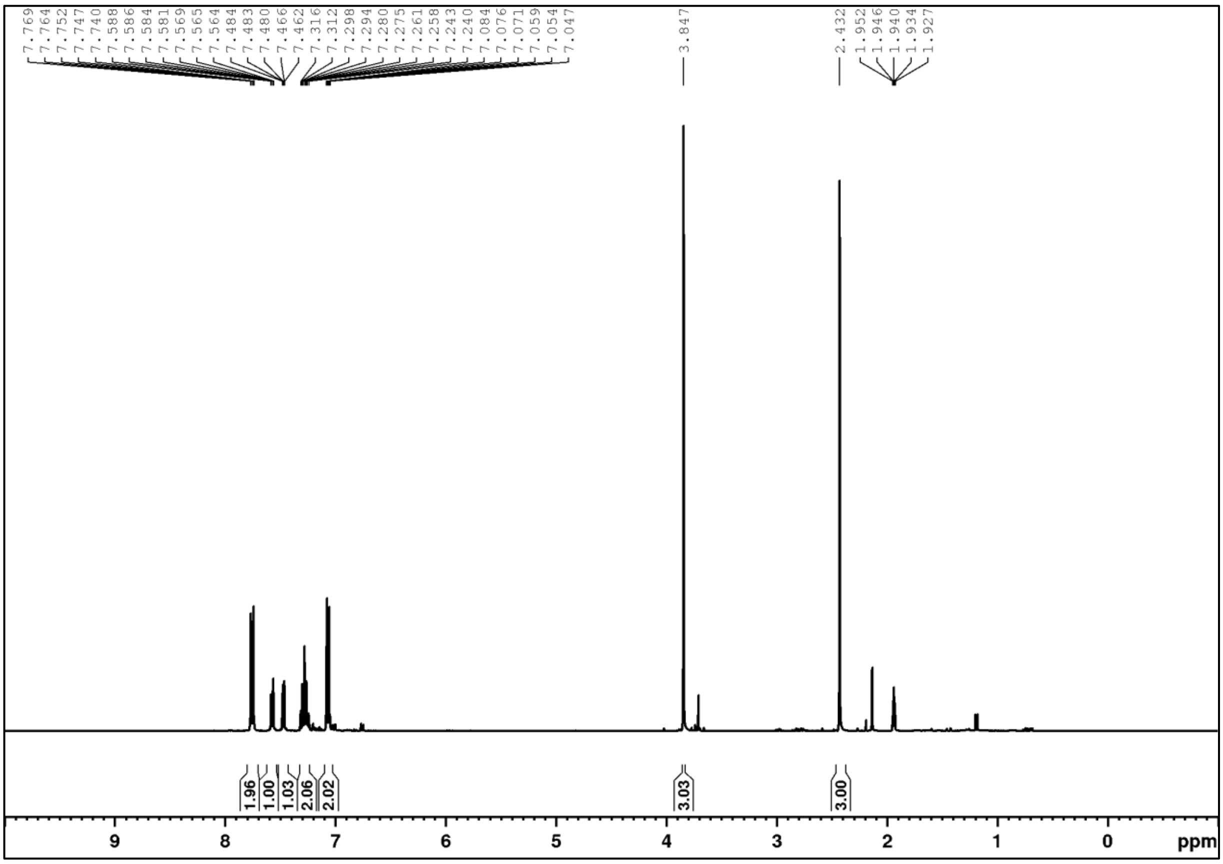


**2-(4-Methoxyphenyl)-3-methylbenzofuran (35)**

$^1$H NMR (400 MHz, CDCl$_3$)



$^1$H NMR (400 MHz, CD$_3$CN)



Benzofuran derivative **35** was measured in CD$_3$CN for comparison with the side product observed upon C-H activation of dihydrobenzofuran **4c**.

# 12 References

1 *ChrysAlisPro Software System*, Rigaku Oxford Diffraction, 2020.

2 R. C. Clark and J. S. Reid, The analytical calculation of absorption in multifaceted crystals, *Acta Crystallogr.*, 1995, **51**, A51, 887-897.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

4 G. M. Sheldrick, SHELXT - integrated space-group and crystal-structure determination, *Acta Crystallogr.*, 2015, **71**, A71, 3-8.

5 G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr.*, 2015, **71**, C71, 3-8.

6 J. Brecher, Graphical representation of stereochemical configuration (IUPAC Recommendations 2006), *Pure Appl. Chem.*, 2006, **78**, 1897–1970.

7 S. Engle, Preparation of 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile, *Org. Synth.*, 2019, **96**, 455–473.

8 E. Speckmeier, T. G. Fischer and K. Zeitler, A Toolbox Approach To Construct Broadly Applicable Metal-Free Catalysts for Photoredox Chemistry: Deliberate Tuning of Redox Potentials and Importance of Halogens in Donor-Acceptor Cyanoarenes, *J. Am. Chem. Soc.*, 2018, **140**, 15353–15365.

9 S. Grotjahn and B. König, Photosubstitution in Dicyanobenzene-based Photocatalysts, *Org. Lett.*, 2021, **23**, 3146–3150.

10 D. J. Frank, L. Guiet, A. Käslin, E. Murphy and S. P. Thomas, Iron-catalysed alkene hydrogenation and reductive cross-coupling using a bench-stable iron(ii) pre-catalyst, *RSC Adv.*, 2013, **3**, 25698.

11 S. Grotjahn, C. Graf, J. Zelenka, A. Pattanaik, L. Müller, R. J. Kutta, J. Rehbein, J. Roithová, R. M. Gschwind, P. Nuernberger and B. König, Reactivity of Superbasic Carbanions Generated via Reductive Radical-Polar Crossover in the Context of Photoredox Catalysis, *Angew. Chem., Int. Ed.*, 2024, e202400815.

12 Y. Wang, H. Di, F. Chen, Y. Xu, Q. Xiao, X. Wang, H. Wei, Y. Lu, L. Zhang, J. Zhu, L. Lan and J. Li, Discovery of Benzocycloalkane Derivatives Efficiently Blocking Bacterial Virulence for the Treatment of Methicillin-Resistant S. aureus (MRSA) Infections by Targeting Diapophytoene Desaturase (CrtN), *J. Med. Chem.*, 2016, **59**, 4831–4848.

13 S. J. Park, J. R. Price and M. H. Todd, Oxidative arylation of isochroman, *J. Org. Chem.*, 2012, **77**, 949–955.

14 Y. Li, M. Wan, S. Sun, Z. Fu, H. Huang and L. Liu, Efficient access to chiral benzo [c] chromenes via asymmetric transfer hydrogenation of ketals, *Org. Chem. Front.*, 2018, **5**, 1280–1283.

15 M. Presset, J. Paul, G. N. Cherif, N. Ratnam, N. Laloi, E. Léonel, C. Gosmini and E. Le Gall, CoI -Catalyzed Barbier Reactions of Aromatic Halides with Aromatic Aldehydes and Imines, *Chem. Eur. J.*, 2019, **25**, 4491–4495.

16 W. Muramatsu, K. Nakano and C.-J. Li, Simple and direct sp3 C-H bond arylation of tetrahydroisoquinolines and isochromans via 2,3-dichloro-5,6-dicyano-1,4-benzoquinone oxidation under mild conditions, *Org. Lett.*, 2013, **15**, 3650–3653.

17 W. Zhong, Y. Wu and X. Zhang, Efficient chemoselective addition of Grignard reagents to carbonyl compounds in 2-methyltetrahydrofuran, *J. Chem. Res.*, 2009, **2009**, 370–373.

18 P. Huang, G. Zhang, Z. Wang and J. Wu, Silver-Catalyzed Synthesis of Benzyl Ethers via Alkoxylation of Benzylic C(sp3 )-H Bonds, *Chem. Asian J.*, 2023, **18**, e202300425.

19 K. J. Garcia, M. M. Gilbert and D. J. Weix, Nickel-Catalyzed Addition of Aryl Bromides to Aldehydes To Form Hindered Secondary Alcohols, *J. Am. Chem. Soc.*, 2019, **141**, 1823–1827.

20 C. Schneider, R. Jackstell, B. U. W. Maes and M. Beller, Palladium-Catalyzed Alkoxycarbonylation of sec - Benzylic Ethers, *Eur. J. Org. Chem.*, 2020, **2020**, 932–936.

21 P. Satyanarayana, G. M. Reddy, H. Maheswaran and M. L. Kantam, Tris(acetylacetonato)rhodium(III)-Catalyzed α-Alkylation of Ketones, β-Alkylation of Secondary Alcohols and Alkylation of Amines with Primary Alcohols, *Adv. Synth. Catal.*, 2013, **355**, 1859–1867.

22 Q. Xu, J. Chen, H. Tian, X. Yuan, S. Li, C. Zhou and J. Liu, Catalyst-free dehydrative α-alkylation of ketones with alcohols: green and selective autocatalyzed synthesis of alcohols and ketones, *Angew. Chem., Int. Ed.*, 2014, **53**, 225–229.

23 J. Bouffard and K. Itami, A nickel catalyst for the addition of organoboronate esters to ketones and aldehydes, *Org. Lett.*, 2009, **11**, 4410–4413.

24 J. H. Harenberg, N. Weidmann, A. J. Wiegand, C. A. Hoefer, R. R. Annapureddy and P. Knochel, (2-Ethylhexyl)sodium: A Hexane-Soluble Reagent for Br/Na-Exchanges and Directed Metalations in Continuous Flow, *Angew. Chem., Int. Ed.*, 2021, **60**, 14296–14301.

25 C. Zhou and Z. Wang, Cadmium-Mediated Carbonyl Benzylation in Tap Water, *Synthesis*, 2005, 1649–1655.

26 G. Fumagalli, S. Boyd and M. F. Greaney, Oxyarylation and aminoarylation of styrenes using photoredox catalysis, *Org. Lett.*, 2013, **15**, 4398–4401.

27 L. Zou, B. Wang, H. Mu, H. Zhang, Y. Song and J. Qu, Development of tartaric acid derived chiral guanidines and their application to catalytic enantioselective α-hydroxylation of β-dicarbonyl compounds, *Org. Lett.*, 2013, **15**, 3106–3109.

28 A. K. Beck, P. Gysi, L. La Vecchia and D. Seebach, (4R,5R)-2,2-DIMETHYL-a,a,a',a'-TETRA(NAPHTH-2-YL)-1,3-DIOXOLANE-4,5-DIMETHANOL FROM DIMETHYL TARTRATE AND 2-NAPHTHYL-MAGNESIUM BROMIDE, *Org. Synth.*, 1999, **76**, 12.

29 Y.-X. Wang, S.-L. Qi, Y.-X. Luan, X.-W. Han, S. Wang, H. Chen and M. Ye, Enantioselective Ni-Al Bimetallic Catalyzed exo-Selective C-H Cyclization of Imidazoles with Alkenes, *J. Am. Chem. Soc.*, 2018, **140**, 5360–5364.

30 T. Zhang, Y.-X. Luan, S.-J. Zheng, Q. Peng and M. Ye, Chiral Aluminum Complex Controls Enantioselective Nickel-Catalyzed Synthesis of Indenes: C-CN Bond Activation, *Angew. Chem., Int. Ed.*, 2020, **59**, 7439–7443.

31 Q.-S. Liu, D.-Y. Wang, Z.-J. Yang, Y.-X. Luan, J.-F. Yang, J.-F. Li, Y.-G. Pu and M. Ye, Ni-Al Bimetallic Catalyzed Enantioselective Cycloaddition of Cyclopropyl Carboxamide with Alkyne, *J. Am. Chem. Soc.*, 2017, **139**, 18150–18153.

32 F. Schneider, K. Samarin, S. Zanella and T. Gaich, Total synthesis of the complex taxane diterpene canataxpropellane, *Science*, 2020, **367**, 676–681.

33 J. Beckmann, D. Dakternieks and E. R. Tiekink, Chiral trialkoxysilanols derived from terpene alcohols, *J. Organomet. Chem.*, 2002, **648**, 188–192.

34 W. Ma, L.-C. Liu, K. An, T. He and W. He, Rhodium-Catalyzed Synthesis of Chiral Monohydrosilanes by Intramolecular C-H Functionalization of Dihydrosilanes, *Angew. Chem., Int. Ed.*, 2021, **60**, 4245–4251.

35 A. Kunai and J. Ohshita, Selective synthesis of halosilanes from hydrosilanes and utilization for organic synthesis, *J. Organomet. Chem.*, 2003, **686**, 3–15.

36 A. L. Berger, K. Donabauer and B. König, Photocatalytic carbanion generation from C-H bonds - reductant free Barbier/Grignard-type reactions, *Chem. Sci.*, 2019, **10**, 10991–10996.

37 H. Kruse and S. Grimme, A geometrical correction for the inter- and intra-molecular basis set superposition error in Hartree-Fock and density functional theory calculations for large systems, *J. Chem. Phys.*, 2012, **136**, 154101.

38 S. Grimme, A. Hansen, S. Ehlert and J.-M. Mewes, r2SCAN-3c: A "Swiss army knife" composite electronic-structure method, *J. Chem. Phys.*, 2021, **154**, 64103.

39 J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew and J. Sun, Correction to "Accurate and Numerically Efficient r2SCAN Meta-Generalized Gradient Approximation", *J. Phys. Chem. Lett.*, 2020, **11**, 9248.

40 J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew and J. Sun, Accurate and Numerically Efficient r2SCAN Meta-Generalized Gradient Approximation // Accurate and Numerically Efficient r 2 SCAN Meta-Generalized Gradient Approximation, *J. Phys. Chem. Lett.*, 2020, **11**, 8208–8215.

41 E. Caldeweyher, C. Bannwarth and S. Grimme, Extension of the D3 dispersion coefficient model, *J. Chem. Phys.*, 2017, **147**, 34112.

42 F. Neese, F. Wennmohs, U. Becker and C. Riplinger, The ORCA quantum chemistry program package, *J. Chem. Phys.*, 2020, **152**, 224108.

43 F. Neese, Software update: The ORCA program system—Version 5.0, *WIREs Comput. Mol. Sci.*, 2022, **12**. DOI: 10.1002/wcms.1606.

44 F. Neese, Software update: the ORCA program system, version 4.0, *WIREs Comput. Mol. Sci.*, 2018, **8**. DOI: 10.1002/wcms.1327.

45 F. Neese, The ORCA program system, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73–78.

46 L. C. Finney, L. J. Mitchell and C. J. Moody, Visible light mediated oxidation of benzylic sp3 C–H bonds using catalytic 1,4-hydroquinone, or its biorenewable glucoside, arbutin, as a pre-oxidant, *Green Chem.*, 2018, **20**, 2242–2249.

47 W. Chen, Z. Xie, H. Zheng, H. Lou and L. Liu, Structurally diverse α-substituted benzopyran synthesis through a practical metal-free C(sp3)-H functionalization, *Org. Lett.*, 2014, **16**, 5988–5991.

48 X. Tong, S.-S. Luo, H. Shen, S. Zhang, T. Cao, Y.-P. Luo, L.-L. Huang, X.-T. Ma and X.-W. Liu, Nickel-catalyzed defluorinative alkylation of C(sp 2 )–F bonds, *Org. Chem. Front.*, 2021, **8**, 4533–4542.

49 Z. Chen, M. Pitchakuntla and Y. Jia, Synthetic approaches to natural products containing 2,3-dihydrobenzofuran skeleton, *Nat. Prod. Rep.*, 2019, **36**, 666–690.

50 K. Donabauer, M. Maity, A. L. Berger, G. S. Huff, S. Crespi and B. König, Photocatalytic carbanion generation - benzylation of aliphatic aldehydes to secondary alcohols, *Chem. Sci.*, 2019, **10**, 5162–5166.

51 L. S. Hutchings-Goetz, C. Yang, J. W. B. Fyfe and T. N. Snaddon, Enantioselective Syntheses of Strychnos and Chelidonium Alkaloids through Regio- and Stereocontrolled Cooperative Catalysis, *Angew. Chem., Int. Ed.*, 2020, **59**, 17556–17564.

52 H. Adams, N. J. Gilmore, S. Jones, M. P. Muldowney, S. H. von Reuss and R. Vemula, Asymmetric synthesis of corsifuran A by an enantioselective oxazaborolidine reduction, *Org. Lett.*, 2008, **10**, 1457–1460.

53 M. Dochnahl and G. C. Fu, Catalytic asymmetric cycloaddition of ketenes and nitroso compounds: enantioselective synthesis of alpha-hydroxycarboxylic acid derivatives, *Angew. Chem., Int. Ed.*, 2009, **48**, 2391–2393.

54 A. Potrząsaj, M. Musiejuk, W. Chaładaj, M. Giedyk and D. Gryko, Cobalt Catalyst Determines Regioselectivity in Ring Opening of Epoxides with Aryl Halides, *J. Am. Chem. Soc.*, 2021, **143**, 9368–9376.

55 K. Sato, Y. Inoue, T. Mori, A. Sakaue, A. Tarui, M. Omote, I. Kumadaki and A. Ando, Csp3-csp3 homocoupling reaction of benzyl halides catalyzed by rhodium, *Org. Lett.*, 2014, **16**, 3756–3759.

56 F. S. Melkonyan, D. E. Kuznetsov, M. A. Yurovskaya and A. V. Karchava, One-pot synthesis of substituted indoles via titanium(IV) alkoxide mediated imine formation – copper-catalyzed N-arylation, *RSC Adv.*, 2013, **3**, 8388.

57 B. B. Snider, L. Han and C. Xie, Synthesis of 2,3-Dihydrobenzofurans by Mn(OAc)3 -Based Oxidative Cycloaddition of 2-Cyclohexenones with Alkenes. Synthesis of (±)-Conocarpan, *J. Org. Chem.*, 1997, **62**, 6978–6984.

58 W.-H. Cheung, S.-L. Zheng, W.-Y. Yu, G.-C. Zhou and C.-M. Che, Ruthenium porphyrin catalyzed intramolecular carbenoid C-H insertion. Stereoselective synthesis of cis-disubstituted oxygen and nitrogen heterocycles, *Org. Lett.*, 2003, **5**, 2535–2538.

59 C. Chen and P. G. Dormer, Synthesis of benzobfurans via CuI-catalyzed ring closure, *J. Org. Chem.*, 2005, **70**, 6964–6967.

60 M. Wan, S. Sun, Y. Li and L. Liu, Organocatalytic Redox Deracemization of Cyclic Benzylic Ethers Enabled by An Acetal Pool Strategy, *Angew. Chem., Int. Ed.*, 2017, **56**, 5116–5120.

61 E. Pinosa, E. Bassan, S. Cetin, M. Villa, S. Potenti, F. Calogero, A. Gualandi, A. Fermi, P. Ceroni and P. G. Cozzi, Light-Induced Access to Carbazole-1,3-dicarbonitrile: A Thermally Activated Delayed Fluorescent (TADF) Photocatalyst for Cobalt-Mediated Allylations, *J. Org. Chem.*, 2023, **88**, 6390–6400.