Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

**Contents**

## General

$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded by the analytical departments of the Organisch-Chemisches Institut at the Westfälische Wilhelms-Universität and of the Department Chemie at Johannes Gutenberg-Universität Mainz. Following spectrometers were used: An Avance II 400 (Bruker), a DD2 500 (Agilent), a DD2 600 (Agilent), an Avance III HD 300 (Bruker), an Avance III HD 400 (Bruker). Spectra were recorded at 26 °C (unless otherwise noted). Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($^{1}$H NMR $CHCl_3$: $\delta$ = 7.26 ppm, $CHDCl_2$: $\delta$ = 5.32 ppm, $C_6HD_5$: $\delta$ = 7.16 ppm, $(CHD_2)(CD_3)CO$ = 2.05 ppm, $(CHD_2)(CD_3)SO$ = 2.50 ppm; $^{13}$C NMR $CDCl_3$: $\delta$ = 77.16 ppm, $CD_2Cl_2$: $\delta$ = 53.84 ppm, $C_6D_6$ $\delta$ = 128.06 ppm, $(CD_3)_2CO$ = 29.84 ppm $(CD_3)_2SO$ = 39.5 ppm). Chemical shifts of $^{19}$F NMR are referenced to internal or external standards according to *Togni* and coworkers.[1] The data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet or combinations of these), coupling constants (Hz) and integration. Apparent multiplicity, which occurs as a result of accidental equality of coupling constants to magnetically non-equivalent protons, is marked as *app.*

Infrared (IR) spectra were obtained either on a Perkin-Elmer 100 FT-IR spectrometer or on a Jasco FT/IR-4100 and are reported in wavenumbers ($cm^{-1}$). Bands are characterized as broad (br), strong (s), medium (m), and weak (w).

Melting points were measured on a Büchi B-540 melting-point apparatus and are reported uncorrected.

High Resolution Mass Spectrometry (HRMS) was performed by the analytical departments of the Organisch-Chemisches Institut at the Westfälische Wilhelms-Universität and of the Department Chemie at Johannes Gutenberg-Universität Mainz. Spectra were recorded on a Bruker Daltonics MicroTof, on a Thermo-Fisher Scientific Orbitrap LTQ XL or an Agilent G6545AQ-ToF. Signals are reported as mass to charge ratio *m/z*.

Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 589 nm wavelength (sodium D-line) using a standard 10 cm cell (1 mL). Specific rotations, $[\alpha]_D^{20}$, are reported in degree mL/(g·dm) at the specific temperature. Concentrations (*c*) are given in grams per 100 mL of the specific solvent.

UV/vis absorption spectra were recorded on a V-670 UV-Vis-NIR spectrometer from Jasco at ambient temperature in a 10 mm cell.

Elementary Analysis (EA) was performed by the analytical department of the Organisch-Chemisches Institut at the Westfälische Wilhelms-Universität using a Elementar Analysensysteme Gmbh - Vario EL III.

Analytical HPLC measurements were performed on the following system: Knauer HPLC Pump Smartline 1000 with degassing unit, Knauer Autosampler Smartline 3950, Knauer UV-detector Smartline 2550, Knauer RI-detector Smartline 2300. Separation was performed using Lux® i-Cellulose-5 (4.6 x 250 nm x 5 µm, Phenomenex Ltd.), Lux® Cellulose-1 (4.6 x 250 nm x 5 µm, Phenomenex Ltd.), Lux® Amylose-1 (4.6 x 250 nm x 5 µm, Phenomenex Ltd.), Lux® i-Amylose-3 (4.6 x 250 nm x 5 µm, Phenomenex Ltd.), or Reprosil Chiral-AMS (4.6 x 250 nm x 5 µm, Dr Maisch GmBH.).

Purification was performed either with standard column chromatography techniques using 60 M silica gel (0.04-0.063 mm, MACHEREY-NAGEL), on an automated flash chromatography system *Biotage Isolera One* utilizing *Biotage Sfär Silica D-Duo* 60 µm columns (5 g, 25 g, 100 g) or on an automated flash chromatography system Teledyne Isco with *Biotage Sfär Silica C18-Duo* 100 Å 30 µm columns (12 g). Glass silica gel plates 60 F254 (Merck) were used for thin layer chromatography (TLC) using UV light (254/366 nm), $KMnO_4$ (1.5 g KMnO4, 5 g $NaHCO_3$ and 5 mL NaOH 10% in 200 mL $H_2O$), CAM (0.5g $Ce(NH_4)_2(NO_3)_6$ and 24.0 g of $(NH_4)_6Mo_7O_{24}\cdot_4H_2O$, 28 mL $H_2SO_4$ in 200 mL $H_2O$), DNPH (12 g 2,4-dinitrophenylhydrazine, 60 mL $H_2SO_4$, and 80 mL of $H_2O$ in 200 mL EtOH), $FeCl_3$ (1 g in 2 mL HCl (conc.) and 50 mL of $H_2O$ in 200 mL EtOH) for detection.

Chemicals were purchased from *Alfa Aesar*, *Acros Organics*, *Sigma Aldrich*, *BLDpharm*, *FluoroChem*, *Carbolution* or *ABCR* and used as received. All work-up and purification procedures were carried out with pre-distilled technical grade solvents. EtOH was purified prior to use applying standard techniques (distilled over activated Mg turnings). Dry solvents were either dried with standard techniques ($CH_2Cl_2$ distilled over $P_2O_5$ and stored over activated 4 Å molecular sieves), or collected from a *MBraun MB SPS-800* ($Et_2O$, THF). A positive argon pressure was used to pass the solvents through the following columns:

$CH_2Cl_2$: 2 x MB-KOL-A
$Et_2O$: 1 x MB-KOL-A and 1 x MB-KOL MT2-250
THF: 2 x MB-KOL MT2-150°C

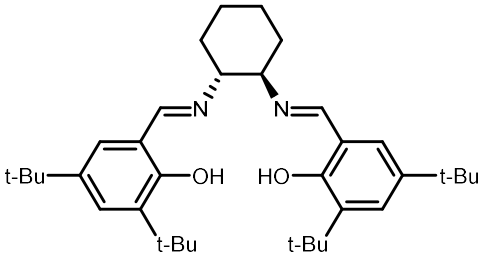
All reactions involving air or moisture sensitive reagents were carried out in oven- (125 °C) and flame-dried glassware under nitrogen atmosphere using standard *Schlenk* techniques. Reactions requiring heating were conducted using aluminium blocks as heating source.

***X-Ray diffraction:*** Data sets for compounds **[10e]** and **[13]** were collected with a Bruker D8 Venture PHOTON III diffractometer. Programs used: data collection: APEX3 V2016.1-0[2] (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A[2] (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A[2] (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7[2] (Bruker AXS Inc., **2014**); structure solution *SHELXT-2015*[3] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2015*[4] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics, *XP*[5] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *w*$R^2$ values are given for all reflections.

Data sets for compounds **[5j]** were collected with a STOE IPDS-2T Diffractometer system. Programs used: data collection: X-Area WinXpose 2.0.22.0[6] (*X-RED* and *X-AREA*, Stoe & Cie, **2019**), cell refinement: X-Area Recipe 1.36.0[6] (*X-RED* and *X-AREA*, Stoe & Cie, **2019**), data reduction: X-Area Integrate 1.78.3[6] (*X-RED* and *X-AREA*, Stoe & Cie, **2019**), structure solution *SHELXT-2014*[3] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2018/3* [4] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics Platon[7] (Spek, A. L. *Acta Cryst.,* **2009**, *D65*, 148-155). *R*-values are given for observed reflections, and *w*$R^2$ values are given for all reflections.

## 1. Synthesis of starting materials

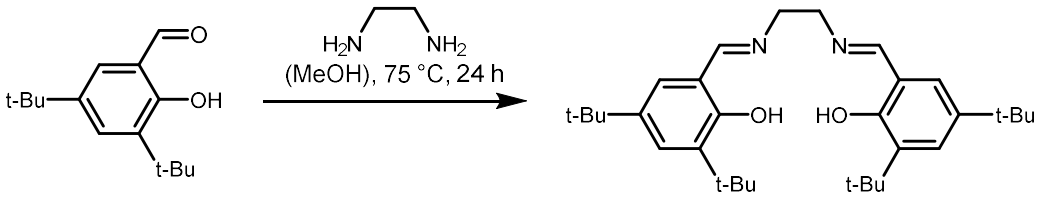
### 1.1. Ligand synthesis




**6,6'-((1E,1'E)-(((1R,2R)-Cyclohexane-1,2-diyl)bis(azaneylylidene))bis-(methaneylylidene))-bis(2,4-di-tert-butylphenol) [S1]**

According to a literature known procedure[8] (1*R*,2*R*)-(–)-1,2-cyclohexanediamine (2.00 g, 17.5 mmol, 1.00 eq.) was dissolved in EtOH (30 mL), and added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (8.21 g, 35.0 mmol, 2.00 eq.) in EtOH (30 mL). The mixture was heated to 80 °C for 4 h and cooled to –18 °C afterwards. The resulting precipitate was filtered off and washed with small portions of cold EtOH to gain the salen ligand as a yellow solid (8.80 g, 16.1 mmol, 92%).

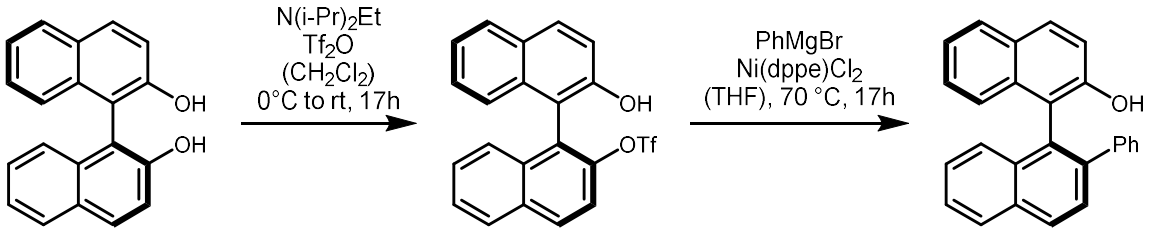
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 13.72 (s, 2H, O*H*), 8.31 (s, 2H, C*H*N), 7.31 (d, *J* = 2.5 Hz, 2H, C$H_{arom.}$), 6.99 (d, *J* = 2.5 Hz, 2H, C$H_{arom.}$), 3.38 – 3.27 (m, 2H, C*H*), 1.99 – 1.91 (m, 2H, C$H_2$), 1.88 (dq, *J* = 8.0, 2.8 Hz, 2H, C$H_2$), 1.80 – 1.67 (m, 2H, C$H_2$), 1.48 (dt, *J* = 9.7, 2.7 Hz, 2H C$H_2$), 1.42 (s, 18H, C$H_3$), 1.24 (s, 18H, C$H_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 166.0 (*C*HN), 158.1 ($C_q$), 140.0 ($C_q$), 136.5 ($C_q$), 126.9, 126.2, 118.0 ($C_q$), 72.6 (*C*H), 35.1 (*C*$H_2$), 34.2 ($C_q$), 33.4 ($C_q$), 31.6 (*C*$H_3$), 29.6 (*C*$H_3$), 24.5 (*C*$H_2$). Obtained spectroscopic data are in agreement to those previously reported.[8]




**6,6'-((1*E*,1'*E*)-(Ethane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(2,4-di-*tert*-butylphenol) [S2]**

The achiral salen ligand 6,6'-((1E,1'E)-(ethane-1,2-diylbis(azaneylylidene))bis-(methaneylylidene))bis(2,4-di-tert-butylphenol) was prepared following a literature known protocol with minor alterations[9] Therefore 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10.0 mmol, 2.00 eq.) was dissolved in MeOH (75 mL) before ethylenediamine (330 µL, 5.00 mmol, 1.00 eq.) was added and the mixture was heated to 75 °C for 24 h. The solvent was partially removed after cooling to rt. The concentrated mixture was cooled to 0 °C and the precipitate was filtered off and washed with cold MeOH to yield the salen ligand as pure yellow crystals (2.10 g, 4.26 mmol, 43%).

**$^1$H NMR (500 MHz, $CDCl_3$)**: $\delta$ = 8.39 (s, 2H, C*H*N), 7.37 (d, *J* = 2.5 Hz, 2H, C$H_{arom.}$), 7.07 (d, *J* = 2.4 Hz, 2H, C$H_{arom.}$), 3.93 (s, 4H, C$H_2$), 1.44 (s, 18H, C$H_3$), 1.29 (s, 18H, C$H_2$). **$^{13}$C NMR (126 MHz, $CDCl_3$)**: $\delta$ = 167.7 (*C*HN), 158.2 ($C_q$), 140.2 ($C_q$), 136.8 ($C_q$), 127.2 (*C*H), 126.2 (*C*H), 118.0 ($C_q$), 59.8 (*C*$H_2$), 35.2 ($C_q$), 34.3 ($C_q$), 31.6 (*C*$H_3$), 29.6 (*C*$H_3$). Obtained spectroscopic data are in agreement to those previously reported.[10]




**(S)-2'-Phenyl-[1,1'-binaphthalen]-2-ol [S3]**

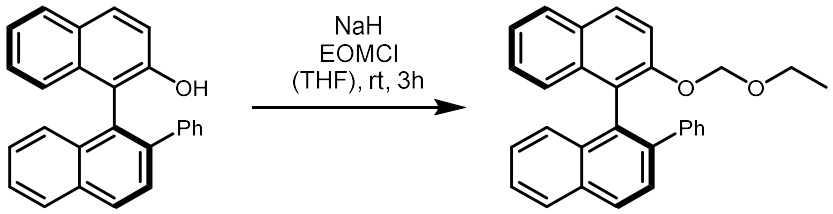
According to a literature known procedure[11] (*S*)-BINOL (2.00 g, 6.89 mmol, 1.00 eq.) was dissolved in $CH_2Cl_2$ (40 mL) and *N*,*N*-diisopropylethylamine (1.32 mL, 7.68 mmol, 1.10 eq.) was added slowly. The solution was cooled to 0 °C and trifluoromethanesulfonic anhydride (1.25 mL, 7.68 mmol, 1.10 eq.) was added dropwise and the reaction mixture was allowed to warm up to rt and was stirred for 17 h. $NH_4Cl$ aq. (40 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3 x 40 mL). The combined organic phases were washed with Brine (3 x 50 mL) and were dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was used without further purification.

Mg-turnings (1.68 g, 69.80 mmol, 10.00 eq.) were activated with $I_2$ in a flame-flame-dried Schlenk-flask under nitrogen atmosphere and dry THF (35 ml) was added. Bromobenzene (3.72 mL, 34.90 mmol, 5.00 eq.) was added dropwise at a rate to sustain constant reflux and the mixture was stirred 2 h at rt.

The crude product was dissolved in THF (30 mL) under nitrogen atmosphere and the Grignard-solution was added at 0 °C *via* a transfer cannula and the mixture was stirred at 70 °C for 17 h. After cooling to rt, $NH_4Cl$ aq. (50 mL) was added and the aqueous phase was extracted with $Et_2O$ (3 x 50 mL). The combined organic fractions were washed with $NaHCO_3$ aq. (3 x 50 mL), Brine (3 x 50 mL), were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude mixture was purified *via* automated FC (CyH:$Et_2O$, 95:5 to 80:20) and the product was obtained as a colorless solid (1.89 g, 5.46 mmol, 76%).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 8.09 (d, *J* = 8.5 Hz, 1H, C$H_{arom.}$), 7.99 (dt, *J* = 8.3, 1.1 Hz, 1H, C$H_{arom.}$), 7.78 (d, *J* = 8.5 Hz, 1H, C$H_{arom.}$), 7.72 (d, *J* = 8.5 Hz, 1H, C$H_{arom.}$), 7.52 (ddd, *J* = 8.1, 6.0, 2.0 Hz, 1H, C$H_{arom.}$), 7.36 – 7.27 (m, 3H, C$H_{arom.}$), 7.23 (ddd, *J* = 15.0, 6.6, 1.5 Hz, 2H, C$H_{arom.}$), 7.18 – 7.11 (m, 3H, C$H_{arom.}$), 7.12 – 7.02 (m, 4H, C$H_{arom.}$), 4.84 (s, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 151.1 ($C_q$), 141.7 ($C_q$), 140.9 ($C_q$), 134.3 ($C_q$), 133.4 ($C_q$), 133.3 ($C_q$), 130.0 (*C*H), 129.6 (*C*H), 128.8 ($C_q$), 128.7 (*C*H), 128.7 (*C*H), 128.6 ($C_q$), 128.3 (*C*H), 128.2 (*C*H), 127.8 (*C*H), 127.3 (*C*H), 127.1 (*C*H), 126.7 (*C*H), 126.6 (*C*H), 126.5 (*C*H), 125.2 (*C*H), 123.3 (*C*H), 117.8 ($C_q$),

117.3 (*C*H).[a] **HRMS (APCI)**: Calculated for $C_{26}H_{17}O$ $[M-H]^-$: 345.1279, Found: 345.1281. Obtained spectroscopic data are in agreement to those previously reported.[12]

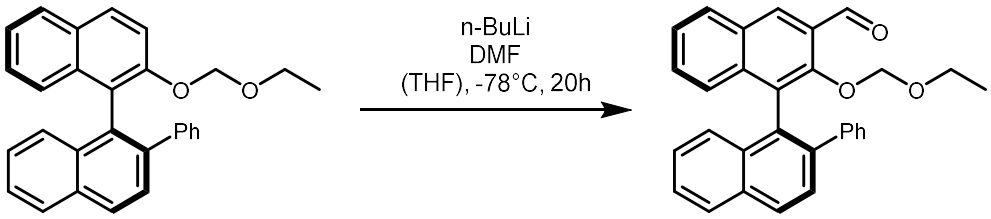



**(S)-2-(Ethoxymethoxy)-2'-phenyl-1,1'-binaphthalene [S4]**

According to a literature known procedure[13] (S)-2'-phenyl-[1,1'-binaphthalen]-2-ol (1.89 g, 5.40 mmol, 1.00 eq.) was dissolved in dry THF (20 mL) in a flame-dried Schlenk-flask under nitrogen atmosphere and a dispersion of sodium hydride in mineral oil (60% NaH, 198 mg, 5.90 mmol, 1.10 eq.) was added portion wise at 0 °C and the mixture was stirred for 50 min at 0 °C. 2-Methoxy-ethoxymethylchlorid (0.60 mL, 6.50 mmol, 1.20 eq.) was added dropwise at 0 °C and the mixture was stirred for 20 min at 0°C and 1 h at rt. $H_2O$ (50 mL) and $Et_2O$ (50 mL) were added and the organic phase was extracted with $Et_2O$ (3 x 50 mL). The combined organic fractions were washed with brine (3 x 50 mL) and were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified *via* automated FC (CyH:$Et_2O$, 100:0 to 95:5). The product was obtained as a colorless solid (1.73 g, 4.27 mmol, 79%).

**M.P.:** 103.2 – 105.4 °C. **IR (neat)**: 3058 (w), 2974 (w), 1938 (w), 1593 (w), 1507 (m), 1233 (s), 1147 (m), 1109(m), 1056 (m), 1031 (s), 1011 (s), 904 (m), 822 (m), 763 (s), 700 (s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 7.81 (d, $J$ = 8.6 Hz, 1H, C$H_{arom.}$), 7.76 (d, $J$ = 8.3 Hz, 1H, C$H_{arom.}$), 7.68 (d, $J$ = 8.5 Hz, 1H, C$H_{arom.}$), 7.62 (d, $J$ = 9.1 Hz, 1H, C$H_{arom.}$), 7.58 (d, $J$ = 8.8 Hz, 1H, C$H_{arom.}$), 7.53 (d, $J$ = 9.1 Hz, 1H, C$H_{arom.}$), 7.49 (dq, $J$ = 8.5, 0.9 Hz, 1H, C$H_{arom.}$), 7.41 – 7.31 (m, 3H, C$H_{arom.}$), 7.24 (ddd, $J$ = 8.2, 6.8, 1.2 Hz, 1H, C$H_{arom.}$), 7.11 – 6.94 (m, 3H, C$H_{arom.}$), 6.92 – 6.84 (m, 2H, C$H_{arom.}$), 6.84 – 6.77 (m, 1H, C$H_{arom.}$), 4.74 (d, $J$ = 7.2 Hz, 1H, C$H_2$), 4.61 (d, $J$ = 7.2 Hz, 1H, C$H_2$), 3.24 – 2.96 (m, 2H, C$H_2$), 0.83 (t, $J$ = 7.1 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 153.7 ($C_q$), 142.7 ($C_q$), 140.6 ($C_q$), 135.1 ($C_q$), 133.9 ($C_q$), 133.5 ($C_q$), 132.7 ($C_q$), 129.9 (*C*H), 129.8 (*C*H), 129.3 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 127.7 (*C*H), 127.4 (*C*H), 127.0 (*C*H), 126.8 (*C*H), 126.6 (*C*H), 126.2 (*C*H), 126.0 (*C*H), 124.1 (*C*H), 123.3 (*C*H), 116.6 (*C*H), 93.6 (*C*$H_2$), 63.9 (*C*$H_2$), 15.1 (*C*$H_3$). **HRMS (APCI)**: Calculated for $C_{29}H_{24}O_2K$ $[M+K]^+$: 443.1413, Found: 443.1408.

[a] Missing signals under solvent peak.

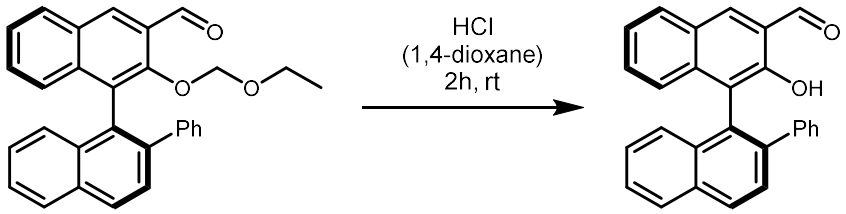



**(S)-2-(Ethoxymethoxy)-2'-phenyl-[1,1'-binaphthalene]-3-carbaldehyde [S5]**

According to a literature known procedure[11] (S)-2-(ethoxymethoxy)-2'-phenyl-1,1'-binaphthalene (1.54 g, 3.80 mmol, 1.00 eq.) was dissolved in dry THF (15 mL) under nitrogen atmosphere. The reaction flask was cooled to –78 °C, *n*-BuLi (2.5 M, 1.90 mL, 4.60 mmol, 1.20 eq.) was added dropwise and the mixture was stirred at –78 °C for 30 min and for 90 min at rt. The flask was cooled to –78 °C and *N*,*N*-Dimethylformamide (1.50 mL, 19.00 mmol, 5.00 eq.) was added dropwise. The reaction mixture was stirred at –78 °C for 15 min and at rt for 14 h. $NH_4Cl$ aq. (25 mL) was added and the organic phase was extracted with $Et_2O$ (3 x 25 mL). The combined organic fractions were washed with brine (3 x 25 mL) and were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified *via* automated FC (CyH:$Et_2O$, 95:5 to 90:10). The product was obtained as an off-white foam (0.78 g, 1.80 mmol, 47%).

**IR (neat)**: 2975 (w), 2877 (w), 2365 (w), 2341 (w), 1689 (s), 1619 (m), 1587 (m), 1496 (m), 1353 (m), 1101 (s), 1072 (m), 1038 (m), 960 (s), 926 (m), 824 (m), 764 (s), 701 (s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 10.44 (s, 1H, C*H*O), 8.44 (d, *J* = 0.8 Hz, 1H, C$H_{arom.}$), 7.80 (d, *J* = 8.5 Hz, 1H, C$H_{arom.}$), 7.75 (d, *J* = 8.2 Hz, 1H, C$H_{arom.}$), 7.61 (d, *J* = 8.5 Hz, 1H, C$H_{arom.}$), 7.55 – 7.48 (m, 1H, C$H_{arom.}$), 7.30 (dd, *J* = 8.5, 1.0 Hz, 1H, C$H_{arom.}$), 7.29 – 7.24 (m, 3H, C$H_{arom.}$), 7.24 – 7.19 (m, 1H, C$H_{arom.}$), 7.01 (dddd, *J* = 12.0, 8.2, 6.8, 1.4 Hz, 2H, C$H_{arom.}$), 6.94 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 1H, C$H_{arom.}$), 6.89 – 6.83 (m, 2H, C$H_{arom.}$), 6.83 – 6.77 (m, 1H, C$H_{arom.}$), 4.59 (d, *J* = 6.1 Hz, 1H, C$H_2$), 4.38 (d, *J* = 6.1 Hz, 1H, C$H_2$), 3.03 (dq, *J* = 9.4, 7.0 Hz, 1H, C$H_2$), 2.74 (dq, *J* = 9.4, 7.0 Hz, 1H, C$H_2$), 0.63 (t, *J* = 7.1 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 189.9 (*C*HO), 154.0 ($C_q$), 142.2 ($C_q$), 141.5 ($C_q$), 137.8 ($C_q$), 133.8 ($C_q$), 133.2 ($C_q$), 131.7 (*C*H), 131.3 ($C_q$), 130.5 (*C*H), 130.1 ($C_q$), 129.8 ($C_q$), 129.7 ($C_q$), 129.3 (*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.9 (*C*H), 128.4 (*C*H), 127.9 (*C*H), 127.3 (*C*H), 127.2 (*C*H), 127.1 (*C*H), 126.6 (*C*H), 126.2 (*C*H), 125.8 (*C*H), 98.7 ($CH_2$), 65.2 ($CH_2$), 14.7 ($CH_3$).[b] **HRMS (APCI)**: Calculated for $C_{30}H_{24}O_3Na$ $[M+Na]^+$: 455.1623, Found: 455.1618.

[b] Missing signals under solvent peak.

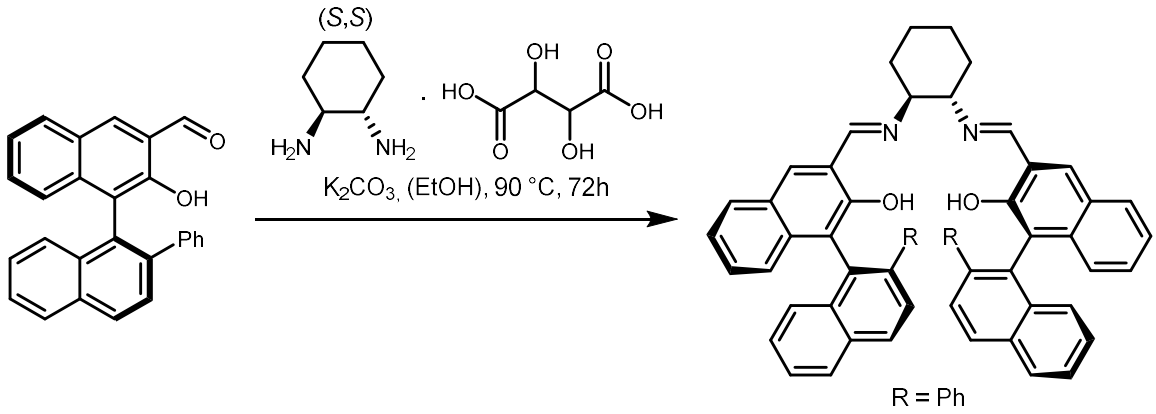



**(S)-2-Hydroxy-2'-phenyl-[1,1'-binaphthalene]-3-carbaldehyde [S6]**

According to a literature known procedure[11] (S)-2-(ethoxymethoxy)-2'-phenyl-[1,1'-binaphthalene]-3-carbaldehyde (850 mg, 1.97 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (12 mL) and conc. HCl (4 mL) was added dropwise at rt. The mixture was stirred for 2 h and water was added (20 mL). A yellow precipitate was formed, that was filtered off, was washed with water (3 x 20 mL) and was dried over $P_4O_{10}$ for 17 h. The product was obtained as a bright yellow solid (686 mg, 1.83 mmol, 93%).

**$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 10.88 (s, 1H, C*H*O), 9.27 (s, 1H, C*H*$_{arom.}$), 7.80 (d, *J* = 8.4 Hz, 1H, C*H*$_{arom.}$), 7.77 (dt, *J* = 8.1, 0.9 Hz, 1H, C*H*$_{arom.}$), 7.61 (d, *J* = 8.5 Hz, 1H, C*H*$_{arom.}$), 7.48 (dq, *J* = 8.4, 0.9 Hz, 1H, C*H*$_{arom.}$), 7.43 – 7.35 (m, 3H, C*H*$_{arom.}$), 7.29 – 7.21 (m, 2H, C*H*$_{arom.}$), 7.21 (s, 1H, O*H*), 7.10 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H, C*H*$_{arom.}$), 6.95 (tt, *J* = 6.8, 5.1 Hz, 2H, C*H*$_{arom.}$), 6.90 – 6.83 (m, 2H, C*H*$_{arom.}$), 6.82 – 6.75 (m, 1H, C*H*$_{arom.}$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 196.7 (C*H*O), 154.4 (*C*$_q$), 142.7 (*C*$_q$), 141.4 (*C*$_q$), 138.3 (*C*$_q$), 137.9 (*C*H), 133.6 (*C*$_q$), 133.5 (*C*$_q$), 130.7 (*C*$_q$), 130.4 (*C*H), 129.8 (*C*H), 129.1 (*C*H), 128.8 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 127.8 (*C*H), 127.3 (*C*$_q$), 127.0 (*C*H), 126.9 (*C*H), 126.7 (*C*H), 126.1 (*C*H), 125.8 (*C*H), 124.1 (*C*H), 121.9 (*C*$_q$), 121.7 (*C*$_q$).[c] **HRMS (APCI)**: Calculated for $C_{27}H_{17}O_2$ [M-H]$^-$: 373.1229, Found: 373.1250. Obtained spectroscopic data are in agreement to those previously reported.[12]

[c] Missing signals under solvent peak.

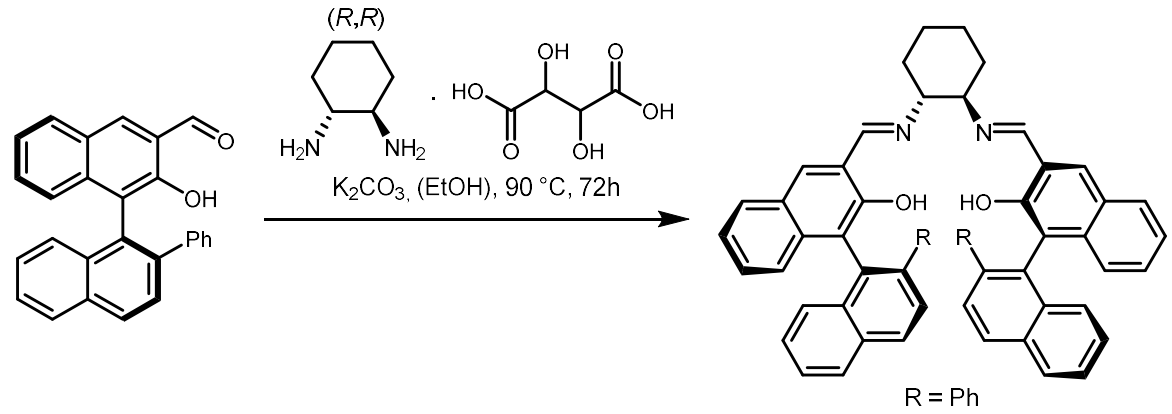



**3-((E)-(((1S,2S)-2-(((E)-((S)-2-Hydroxy-2'-phenyl-[1,1'-binaphthalen]-3-yl)methylene)amino)cyclohexyl)imino)methyl)-2'-phenyl-[1,1'-binaphthalen]-2-ol [S7]**

According to a literature known procedure,[14] (1*S*,2*S*)-(–)-1,2-cyclohexanediamine D-tartrate (60 mg, 0.23 mmol, 1.00 eq.) was stirred with $K_2CO_3$ (63 mg, 0.45 mmol, 2.00 eq.) in EtOH (5 mL) and $H_2O$ (1 mL) for 15 min, before (S)-2-hydroxy-2'-phenyl-[1,1'-binaphthalene]-3-carbaldehyde (170 mg, 0.45 mmol, 2.00 eq.) was added. The mixture was heated to reflux for 4 h. Water (10 mL) was added and the flask was cooled to –18 °C. A yellow precipitate was formed, that was filtered off, was washed with water (3 x 20 mL) and ice-cold EtOH (3 x 5 mL). The product was dried in-vacuo and was obtained as a pale yellow solid (164 mg, 0.20 mmol, 87%).

**M.P.:** decomp. >250 °C. **IR (neat)**: 3052 (w), 2925 (w), 2860 (w), 1631 (s), 1444 (w), 1346 (w), 1261 (w), 1029 (w), 946 (w), 823 (m), 748 (s), 700 (s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 13.06 (s, 2H, C*H*N), 7.79 (t, *J* = 4.2 Hz, 4H, C$H_{arom.}$), 7.75 (d, *J* = 8.2 Hz, 2H, C$H_{arom.}$), 7.64 (d, *J* = 8.4 Hz, 2H, C$H_{arom.}$), 7.55 – 7.48 (m, 6H, C$H_{arom.}$), 7.33 (dd, *J* = 8.6, 1.1 Hz, 2H, C$H_{arom.}$), 7.24 (s, 2H, O*H*), 7.20 (td, *J* = 8.2, 1.3 Hz, 4H, C$H_{arom.}$), 6.98 (dddd, *J* = 20.2, 8.3, 6.8, 1.4 Hz, 4H, C$H_{arom.}$), 6.90 – 6.82 (m, 4H, C$H_{arom.}$), 6.80 – 6.72 (m, 2H, C$H_{arom.}$), 6.68 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 2H, C$H_{arom.}$), 2.86 – 2.70 (m, 2H, C$H_2$), 1.55 – 1.35 (m, 4H, C$H_2$), 1.33 – 1.20 (m, 2H, C$H_2$), 1.10 – 0.92 (m, 2H, C$H_2$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 165.5 (*C*HN), 155.6 ($C_q$-OH), 143.0 ($C_q$), 141.0 ($C_q$), 136.1 ($C_q$), 133.8 ($C_q$), 133.7 (*C*H), 133.6 ($C_q$), 132.2 ($C_q$), 129.2 (*C*H), 129.1, 128.8 (*C*H), 128.6 ($C_q$), 128.5 (*C*H), 128.4 (*C*H), 127.7 (*C*H), 127.4 ($C_q$), 126.9 (*C*H), 126.7 (*C*H), 126.6 (*C*H), 125.9 (*C*H), 125.5 (*C*H), 123.3 (*C*H), 120.5 ($C_q$), 72.9 (*C*H), 32.6 (*C*$H_2$), 24.1 (*C*$H_2$).[d] **HRMS (ESI)**: Calculated for $C_{60}H_{47}N_2O_2$ $[M+H]^+$: 827.3638, Found: 827.3622.

[d] Missing signals under solvent peak.

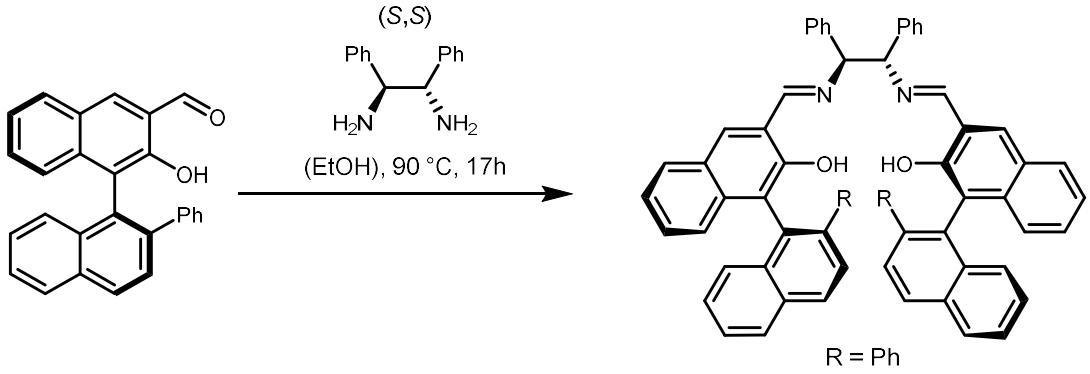



**(S)-3-((E)-(((1R,2R)-2-(((E)-((R)-2-hydroxy-2'-phenyl-[1,1'-binaphthalen]-3-yl)methylene)amino)cyclohexyl)imino)methyl)-2'-phenyl-[1,1'-binaphthalen]-2-ol [epi-S7]**

According to a literature known procedure with minor alterations,[15] (1R,2R)-cyclohexane-1,2-diamine L-tartrate (62 mg, 0.24 mmol, 1.00 eq.) was stirred with $K_2CO_3$ (65 mg, 0.47 mmol, 2.00 eq.) in EtOH (8 mL) and $H_2O$ (1 mL) for 15 min, before (S)-2-hydroxy-2'-phenyl-[1,1'-binaphthalene]-3-carbaldehyde (176 mg, 0.47 mmol, 2.00 eq.) was added. The mixture was heated to reflux for 60 h. Water (10 mL) was added and the flask was cooled to –18 °C. A yellow precipitate was formed, that was filtered off, was washed with water (3 x 20 mL) and ice-cold EtOH (3 x 5 mL). The product was dried in-vacuo and was obtained as a pale yellow solid (183 mg, 0.22 mmol, 92%).

**M.P.:** decomp. >250 °C. **IR (neat)**: 2930 (w), 2357 (w), 2315 (w), 2252 (w), 1631 (m), 1497 (w), 1453 (w), 1347 (w), 1260 (w), 1032 (w), 749 (s), 701 (m). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 13.25 (s, 2H, C*H*N), 7.95 (s, 2H, C$H_{arom}$), 7.85 (d, $J$ = 8.5 Hz, 2H, C$H_{arom}$), 7.78 (d, $J$ = 8.5 Hz, 2H, C$H_{arom}$), 7.74 – 7.67 (m, 4H, C$H_{arom}$), 7.43 – 7.37 (m, 4H, C$H_{arom}$), 7.36 – 7.31 (m, 4H, O*H*, C$H_{arom}$), 7.24 (ddd, $J$ = 8.1, 6.7, 1.2 Hz, 2H, C$H_{arom}$), 7.15 – 7.13 (m, 2H, C$H_{arom}$), 7.07 (ddd, $J$ = 8.3, 6.8, 1.3 Hz, 2H, C$H_{arom}$), 6.90 (dqd, $J$ = 8.0, 6.7, 1.5 Hz, 4H, C$H_{arom}$), 6.33 (t, $J$ = 7.7 Hz, 4H, C$H_{arom}$), 6.23 – 6.16 (m, 2H, C$H_{arom}$), 2.92 – 2.79 (m, 2H, C*H*), 1.56 – 1.46 (m, 2H, C$H_2$), 1.47 – 1.39 (m, 2H, C$H_2$), 1.34 (d, $J$ = 12.3 Hz, 2H, C$H_2$), 1.11 – 0.95 (m, 2H, C$H_2$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = δ 165.5 (*C*HN), 156.1 ($C_q$-OH), 142.5 ($C_q$), 140.8 ($C_q$), 135.4 ($C_q$), 133.9 ($C_q$), 133.8 (*C*H), 133.6 ($C_q$), 132.3 ($C_q$), 129.0 ($C_q$), 128.7 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.0 (*C*H), 127.7 ($C_q$), 127.2 ($C_q$), 126.8 (*C*H), 126.0 (*C*H), 125.2 (*C*H), 123.4 (*C*H), 120.9 (*C*H), 120.4 (*C*H), 73.2 (*C*H), 32.6 ($CH_2$), 24.2 ($CH_2$).[e] **HRMS (ESI)**: Calculated for $C_{60}H_{47}N_2O_2$ $[M+H]^+$: 827.3638, Found: 827.3633.

[e] Missing signals under solvent peak.

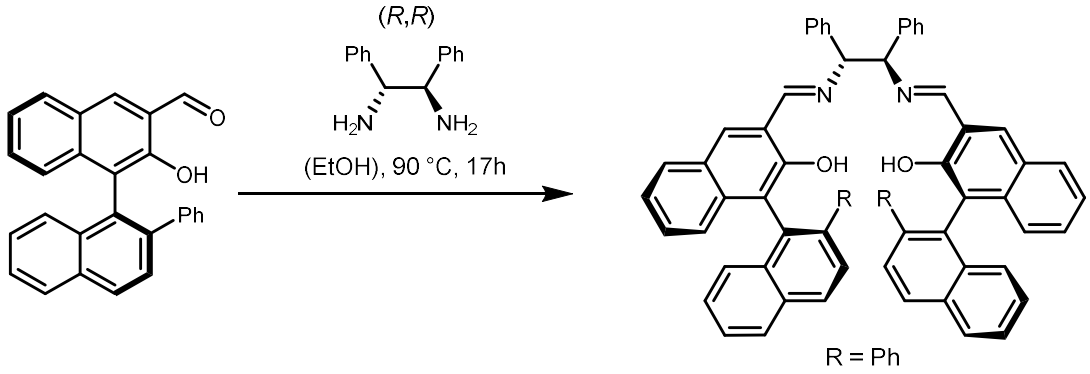



**(S)-3-((E)-(((1S,2S)-2-(((E)-((R)-2-hydroxy-2'-phenyl-[1,1'-binaphthalen]-3-yl)methylene)amino)-1,2-diphenylethyl)imino)methyl)-2'-phenyl-[1,1'-binaphthalen]-2-ol [S8]**

According to a literature known procedure with minor alterations,[9] (S)-2-hydroxy-2'-phenyl-[1,1'-binaphthalene]-3-carbaldehyde (200 mg, 0.53 mmol, 2.00 eq.) was dissolved in EtOH (4 mL) and (1*S*,2*S*)-1,2-diphenylethylenediamine (57 mg, 0.27 mmol, 1.00 eq.) was added. The mixture was heated to 80 °C for 23 h before it was cooled to –18 °C. A yellow precipitate was formed, that was filtered off to yield a yellow solid (163 mg, 0.18 mmol, 67%).

**M.P.:** decomp. >250 °C. **IR (neat)**: 2959 (w), 2919 (m), 2856 (w), 1631(s), 1453 (m), 1348 (w), 1182 (w), 1055 (m), 942 (m), 865 (m), 820 (s), 738 (m). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 13.02 (s, 2H, C*H*N), 8.58 (s, 2H, C$H_{arom}$), 8.10 (d, $J$ = 8.5 Hz, 2H, C$H_{arom}$), 7.99 (d, $J$ = 8.2 Hz, 2H, C$H_{arom}$), 7.73 (d, $J$ = 8.5 Hz, 2H, C$H_{arom}$), 7.68 (s, 2H, O*H*), 7.69 – 7.61 (m, 2H, C$H_{arom}$), 7.38 – 7.32 (m, 4H, C$H_{arom}$), 7.31 – 7.28 (m, 4H, C$H_{arom}$), 7.27 (s, 4H, C$H_{arom}$), 7.24 (d, $J$ = 1.8 Hz, 4H, C$H_{arom}$), 7.18 – 7.13 (m, 4H, C$H_{arom}$), 7.07 (dd, $J$ = 14.2, 7.3 Hz, 5H, C$H_{arom}$), 6.99 (p, $J$ = 4.5 Hz, 5H, C$H_{arom}$), 6.58 (t, $J$ = 7.7 Hz, 2H, C$H_{arom}$), 4.71 (s, 2H, C*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 166.2 (*C*HN), 154.6 ($C_q$-OH), 142.1 ($C_q$), 140.5 ($C_q$), 139.0 ($C_q$), 135.4 ($C_q$), 133.9 (*C*H), 133.1 ($C_q$), 132.9 ($C_q$), 131.2 ($C_q$), 129.0 (*C*H), 128.8 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.4 (*C*H), 128.4 (*C*H), 128.1 (*C*H), 128.0 (*C*H), 127.9 (*C*H), 127.4 (*C*H), 127.2 ($C_q$), 126.5 (*C*H), 126.5 (*C*H), 125.9 (*C*H), 125.8 (*C*H), 125.0 (*C*H), 123.3 (*C*H), 120.0 ($C_q$), 119.9 (*C*H), 81.3 (*C*H).[f] **HRMS (ESI)**: Calculated for $C_{68}H_{49}N_2O_2$ $[M+H]^+$: 925.3794, Found: 925.3778.

[f] Missing signals under solvent peak.

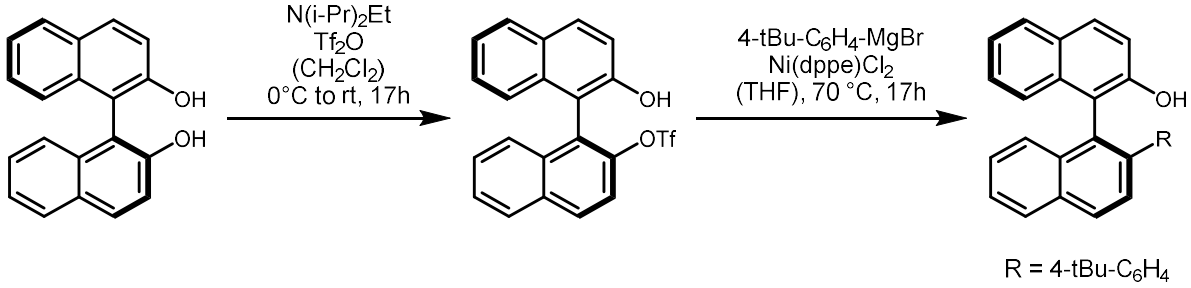



**(S)-3-((E)-(((1R,2R)-2-(((E)-((R)-2-hydroxy-2'-phenyl-[1,1'-binaphthalen]-3-yl)methylene)amino)-1,2-diphenylethyl)imino)methyl)-2'-phenyl-[1,1'-binaphthalen]-2-ol [epi-S8]**

According to a literature known procedure,[9] (S)-2-hydroxy-2'-phenyl-[1,1'-binaphthalene]-3-carbaldehyde (136 mg, 0.36 mmol, 2.00 eq.) was dissolved in EtOH (4 mL) and (1*R*,2*R*)-1,2-diphenylethylenediamine (39 mg, 0.18 mmol, 1.00 eq.) was added. The mixture was heated to 80 °C for 17 h before it was cooled to –18 °C. A yellow precipitate was formed, that was filtered off to yield a yellow solid (84 mg, 0.09 mmol, 50%).

**M.P.:** decomp. >250 °C. **IR (neat)**: 3060 (w), 2870 (w), 1953 (w), 1629 (s), 1495 (m), 1442 (w), 1346 (w), 1120 (w), 1029 (w), 942 (w), 822 (m), 762 (w), 735 (m), 698 (s). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 12.82 (s, 2H, C*H*N), 8.26 (s, 2H, C$H_{arom}$), 8.07 (d, *J* = 8.5 Hz, 2H, C$H_{arom}$), 7.97 (d, *J* = 8.3 Hz, 2H, C$H_{arom}$), 7.69 (d, *J* = 8.5 Hz, 2H, C$H_{arom}$), 7.45 (ddd, *J* = 8.1, 6.1, 1.8 Hz, 2H, C$H_{arom}$), 7.32 (s, 2H, O*H*), 7.28 (d, *J* = 6.8 Hz, 2H, C$H_{arom}$), 7.23 (ddd, *J* = 8.2, 3.3, 1.2 Hz, 4H, C$H_{arom}$), 7.19 – 7.15 (m, 6H, C$H_{arom}$), 7.15 – 7.10 (m, 10H, C$H_{arom}$), 7.08 – 6.96 (m, 4H, C$H_{arom}$), 6.46 (t, *J* = 7.7 Hz, 4H, C$H_{arom}$), 6.38 – 6.29 (m, 2H, C$H_{arom}$), 4.60 (s, 2H, C*H*).**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 166.5 (*C*HN), 154.8 ($C_q$-OH), 142.1 ($C_q$), 140.7 ($C_q$), 138.6 ($C_q$), 135.4 ($C_q$), 134.1 ($C_q$), 133.1 ($C_q$), 133.0 ($C_q$), 131.2 ($C_q$), 128.8 (*C*H), 128.6 (*C*H), 128.6 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 128.3 (*C*H), 128.1 (*C*H), 127.9 (*C*H), 127.4 (*C*H), 127.2 ($C_q$), 126.6 (*C*H), 126.5 (*C*H), 126.4 (*C*H), 125.8 (*C*H), 124.9 (*C*H), 123.3 (*C*H), 120.3 ($C_q$), 120.0 (*C*H), 81.5 (*C*H).[g] **HRMS (ESI)**: Calculated for $C_{68}H_{48}N_2O_2Na$ $[M+Na]^+$: 947.3619, Found: 947.3611.

[g] Missing signals under solvent peak.




**(S)-2'-(4-(tert-Butyl)phenyl)-[1,1'-binaphthalen]-2-ol [S9]**

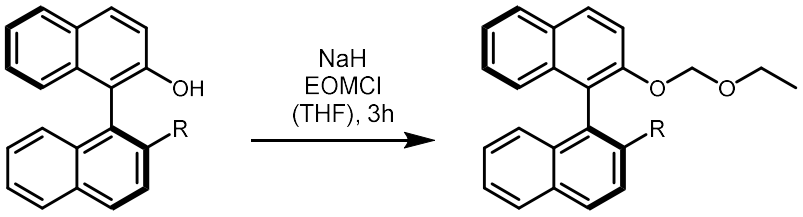
According to a literature known procedure,[16] (*S*)-BINOL (5.12 g, 17.88 mmol, 1.00 eq.) was dissolved in $CH_2Cl_2$ (80 mL) and *N*,*N*-diisopropylethylamine (3.30 mL, 19.30 mmol, 1.08 eq.) was added slowly. The solution was cooled to 0 °C and trifluoromethanesulfonic anhydride (3.20 mL, 19.30 mmol, 1.08 eq.) was added dropwise and the reaction mixture was allowed to warm up to rt and was stirred for 17 h. $NH_4Cl$ aq. (80 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3 x 80 mL). The combined organic phases were washed with Brine (3 x 80 mL) and were dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was used without further purification.

Mg-turnings (4.32 g, 179.00 mmol, 10.00 eq.) were activated with $I_2$ in a flame-flame-dried Schlenk-flask under nitrogen atmosphere and dry THF (70 ml) was added. 1-Bromo-4-(tert-butyl)benzene (11.43 mL, 65.94 mmol, 3.68 eq.) was added dropwise and the mixture was stirred at 70 °C for 3 h.

The crude product was dissolved in THF (50 mL) under nitrogen atmosphere and the Grignard-solution was added at 0 °C *via* a transfer cannula and the mixture was stirred at 70 °C for 17 h. After cooling to rt, $NH_4Cl$ aq. (50 mL) was added and the aqueous phase was extracted with $Et_2O$ (3 x 100 mL). The combined organic fractions were washed with $NaHCO_3$ (50 mL), Brine (3 x 100 mL), were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude mixture was purified *via* automated FC (CyH:$Et_2O$, 95:5 to 80:20) and the product was obtained as a colorless solid (4.12 g, 10.24 mmol, 57%).

**M.P.:** 178.2 – 182.8 °C. **IR (neat)**: 3495 (m), 2963 (m), 2340 (w), 1620 (w), 1469 (w), 1381 (w), 1204 (m), 1024 (w), 817 (s), 733 (m). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 7.78 (d, $J$ = 8.5 Hz, 1H, C$H_{arom.}$), 7.73 (d, $J$ = 8.2 Hz, 1H, C$H_{arom.}$), 7.62 (d, $J$ = 8.5 Hz, 1H, C$H_{arom.}$), 7.56 – 7.49 (m, 1H, C$H_{arom.}$), 7.45 (d, $J$ = 8.9 Hz, 1H, C$H_{arom.}$), 7.43 (dd, $J$ = 8.5, 1.0 Hz, 1H, C$H_{arom.}$), 7.27 – 7.19 (m, 4H, C$H_{arom.}$), 7.09 (d, $J$ = 8.9 Hz, 1H, C$H_{arom.}$), 7.08 – 7.01 (m, 2H, C$H_{arom.}$), 7.01 – 6.98 (m, 1H, C$H_{arom.}$), 6.98 – 6.93 (m, 2H, C$H_{arom.}$), 4.72 (s, 1H, O$H$), 0.99 (s, 10H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 151.8 ($C_q$), 149.9 ($C_q$), 142.0 ($C_q$), 138.6 ($C_q$), 135.1 ($C_q$), 134.0 ($C_q$), 133.7 ($C_q$), 130.3 (*C*H), 129.6 (*C*H), 129.3 (*C*H), 128.8 (*C*H), 128.6, (*C*H) 127.5 (*C*H), 127.1 (*C*H), 126.9 (*C*H), 126.5 (*C*H), 125.5 (*C*H), 125.1 (*C*H), 123.5 (*C*H), 118.3 ($C_q$), 117.9 (*C*H), 34.3

($C_q$), 31.2 ($CH_3$).[h] **HRMS (APCI)**: Calculated for $C_{30}H_{25}O$ [M-H]$^-$: 401.1905, Found: 401.1909.




R = 4-tBu-$C_6H_4$ R = 4-tBu-$C_6H_4$

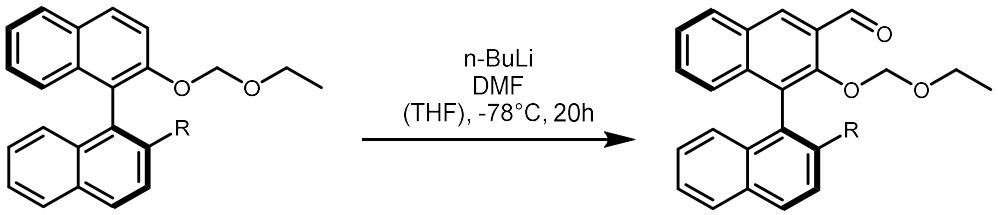
**(S)-2-(4-(tert-Butyl)phenyl)-2'-(ethoxymethoxy)-1,1'-binaphthalene [S10]**

(S)-2'-(4-(tert-Butyl)phenyl)-[1,1'-binaphthalen]-2-ol (4.00 g, 9.95 mmol, 1.00 eq.) was dissolved in dry THF (35 mL) in a flame-flame-dried Schlenk-flask under nitrogen atmosphere and a dispersion of sodium hydride in mineral oil (60% NaH, 368 mg, 10.95 mmol, 1.10 eq.) was added portion wise at 0 °C and the mixture was stirred for 50 min at 0 °C. 2-Methoxy-ethoxymethylchlorid (1.11 mL, 11.94 mmol, 1.20 eq.) was added dropwise at 0 °C and the mixture was stirred for 20 min at 0°C and 3 h at rt. $H_2O$ (50 mL) and $Et_2O$ (50 mL) were added and the organic phase was extracted with $Et_2O$ (3 x 50 mL). The combined organic fractions were washed with brine (3 x 50 mL) and were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified *via* automated FC (CyH:$Et_2O$, 100:0 to 95:5). The product was obtained as an off-white solid (3.36 g, 7.29 mmol, 73%).

**M.P.:** 87 – 88 °C. **IR (neat)**: 3578 (w), 2952 (s), 2916 (s), 2899 (m), 2366 (w), 2359 (w), 2347 (w), 1505 (m), 1269 (m), 1234 (m), 1055 (m), 1034 (s), 1015 (s), 816 (s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 7.83 (d, $J$ = 8.5 Hz, 1H, C$H_{arom.}$), 7.77 (d, $J$ = 8.5 Hz, 1H, C$H_{arom.}$), 7.76 (d, $J$ = 8.1 Hz, 1H, C$H_{arom.}$), 7.63 – 7.59 (m, 1H, C$H_{arom.}$), 7.61 – 7.57 (m, 1H, C$H_{arom.}$), 7.53 (d, $J$ = 9.1 Hz, 1H, C$H_{arom.}$), 7.47 (dq, $J$ = 8.5, 0.9 Hz, 1H, C$H_{arom.}$), 7.45 – 7.41 (m, 1H, C$H_{arom.}$), 7.38 – 7.32 (m, 2H, C$H_{arom.}$), 7.23 (ddd, $J$ = 8.1, 6.8, 1.2 Hz, 1H, C$H_{arom.}$), 7.10 (ddd, $J$ = 8.2, 6.8, 1.3 Hz, 1H, C$H_{arom.}$), 7.03 (dt, $J$ = 8.6, 1.7 Hz, 2H, C$H_{arom.}$), 7.02 – 6.97 (m, 2H, C$H_{arom.}$), 4.77 (d, $J$ = 7.2 Hz, 1H, C$H_2$), 4.60 (d, $J$ = 7.2 Hz, 1H, C$H_2$), 3.26 – 2.98 (m, 2H, C$H_2$), 1.02 (s, 9H, *t*Bu-C$H_3$), 0.84 (t, $J$ = 7.1 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 153.5 ($C_q$), 149.3 ($C_q$), 140.5 ($C_q$), 139.9 ($C_q$), 135.4 ($C_q$), 134.0 ($C_q$), 133.5 ($C_q$), 132.5 ($C_q$), 129.9 (*C*H), 129.8 ($C_q$), 129.1 (*C*H), 129.0 (*C*H), 128.6 (*C*H), 128.5 (*C*H), 128.5 (*C*H), 127.4 (*C*H), 127.0 (*C*H), 126.6 (*C*H), 126.3 (*C*H), 125.8 (*C*H), 124.8 (*C*H), 124.1 (*C*H), 123.5 ($C_q$), 116.7 (*C*H), 93.5 ($CH_2$), 63.8 ($CH_2$), 34.3 ($C_q$), 31.2 (*t*Bu-*C*$H_3$), 15.2 ($CH_3$).[i] **HRMS (ESI)**: Calculated for $C_{33}H_{36}O_2N$ [M+$NH_4$]$^+$: 478.2746, Found: 478.2736.

[h] Missing signals under solvent peak.

[i] Missing signals under solvent peak.



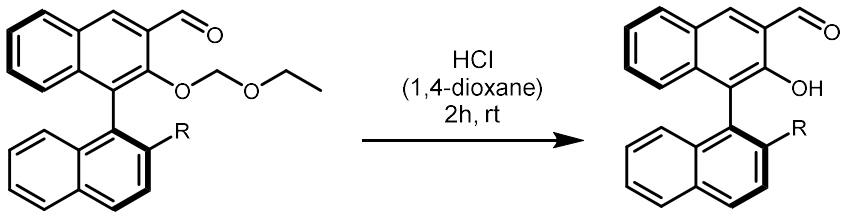

R = 4-tBu-$C_6H_4$ R = 4-tBu-$C_6H_4$

**(S)-2'-(4-(tert-Butyl)phenyl)-2-(ethoxymethoxy)-[1,1'-binaphthalene]-3-carbaldehyde [S11]**

(S)-2-(4-(tert-Butyl)phenyl)-2'-(ethoxymethoxy)-1,1'-binaphthalene (3.04 g, 6.60 mmol, 1.00 eq.) was dissolved in dry THF (50 mL) under nitrogen atmosphere. The reaction flask was cooled to –78 °C, *n*-BuLi (2.5 M, 3.17 mL, 7.92 mmol, 1.20 eq.) was added dropwise and the mixture was stirred at –78 °C for 30 min and for 90 min at rt. The flask was cooled to –78 °C and *N*,*N*-Dimethylformamide (2.55 mL, 33.00 mmol, 5.00 eq.) was added dropwise. The reaction mixture was stirred at –78 °C for 15 min and at rt for 21 h. $NH_4Cl$ aq. (30 mL) was added and the organic phase was extracted with $Et_2O$ (3 x 30 mL). The combined organic fractions were washed with brine (3 x 30 mL) and were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified *via* automated FC (CyH:$Et_2O$, 100:0 to 95:5). The product was obtained as an off-white foam (1.69 g, 3.45 mmol, 52%).

**IR (neat)**: 2928 (m), 1691 (s), 1620 (w), 1589 (w), 1500 (w), 1364 (w), 1205 (w), 1186 (w), 1137 (s), 1102 (m), 965 (s), 821 (m), 736 (w), 715 (w). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 10.43 (s, 1H, C*H*O), 8.43 (s, 1H, C$H_{arom.}$), 7.82 (d, $J$ = 8.5 Hz, 1H, C$H_{arom.}$), 7.75 (d, $J$ = 8.1 Hz, 1H, C$H_{arom.}$), 7.70 (d, $J$ = 8.5 Hz, 1H, C$H_{arom.}$), 7.55 – 7.50 (m, 1H, C$H_{arom.}$), 7.33 (ddt, $J$ = 8.2, 1.5, 0.8 Hz, 1H, C$H_{arom.}$), 7.31 – 7.27 (m, 3H, C$H_{arom.}$), 7.23 (ddd, $J$ = 8.1, 6.8, 1.2 Hz, 1H, C$H_{arom.}$), 7.05 – 6.93 (m, 5H, C$H_{arom.}$), 4.60 (d, $J$ = 6.1 Hz, 1H, C$H_2$), 4.39 (d, $J$ = 6.1 Hz, 1H, C$H_2$), 3.04 (dq, $J$ = 9.4, 7.1 Hz, 1H, C$H_2$), 2.76 (dq, $J$ = 9.4, 7.0 Hz, 1H, C$H_2$), 0.99 (s, 9H, *t*Bu-C$H_3$), 0.65 (t, $J$ = 7.0 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 189.9 (*C*HO), 154.0 ($C_q$), 149.8 ($C_q$), 141.3 ($C_q$), 139.4 ($C_q$), 138.0 ($C_q$), 133.9 ($C_q$), 133.2 ($C_q$), 131.6 (*C*H), 131.2 ($C_q$), 130.6 (*C*H), 130.2 ($C_q$), 130.0 ($C_q$), 129.9 ($C_q$), 129.3 (*C*H), 129.2 (*C*H), 129.0 (*C*H), 128.9 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 127.3 (*C*H), 127.1 (*C*H), 126.8 (*C*H), 126.1 (*C*H), 125.8 (*C*H), 125.0 (*C*H), 98.6 (*C*$H_2$), 65.3 (*C*$H_2$), 34.3 ($C_q$), 31.2 (*t*Bu-*C*$H_3$), 14.7 (*C*$H_3$).[j] **HRMS (ESI)**: Calculated for $C_{34}H_{32}O_3Na$ $[M+Na]^+$: 511.2249, Found: 511.2237.

[j] Missing signals under solvent peak.



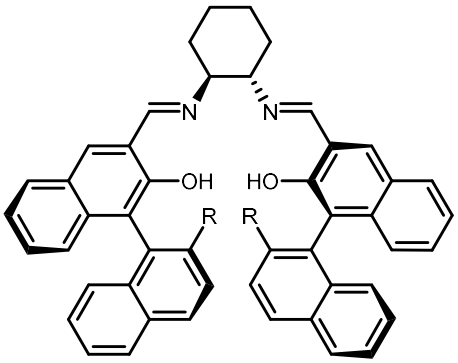

R = 4-tBu-$C_6H_4$ R = 4-tBu-$C_6H_4$

**(S)-2'-(4-(tert-Butyl)phenyl)-2-hydroxy-[1,1'-binaphthalene]-3-carbaldehyde [S12]**

(S)-2'-(4-(tert-Butyl)phenyl)-2-(ethoxymethoxy)-[1,1'-binaphthalene]-3-carbaldehyde (1.68 g, 3.44 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (24 mL) and conc. HCl (8 mL) was added dropwise at rt. The mixture was stirred for 3 h and water was added (20 mL). A yellow precipitate was formed, that was filtered off, was washed with water (3 x 50 mL) and was dried at 60 °C for 48 h. The product was obtained as a bright yellow solid (1.38 g, 3.21 mmol, 93%).

**M.P.:** decomp. >250 °C. **IR (neat)**: 2960 (w), 2952 (w), 2927 (w), 2916 (m), 1656 (s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) =10.89 (s, 1H, C*H*O), 9.25 (s, 1H, C*H*$_{arom.}$), 7.81 (d, *J* = 8.4 Hz, 1H, C*H*$_{arom.}$), 7.77 (d, *J* = 8.1 Hz, 1H, C*H*$_{arom.}$), 7.68 (d, *J* = 8.4 Hz, 1H, C*H*$_{arom.}$), 7.47 – 7.41 (m, 3H, C*H*$_{arom.}$), 7.40 – 7.37 (m, 1H, C*H*$_{arom.}$), 7.30 – 7.26 (m, 1H, C*H*$_{arom.}$), 7.26 – 7.22 (m, 1H, C*H*$_{arom.}$), 7.18 (s, 1H, O*H*), 7.09 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H, C*H*$_{arom.}$), 7.03 – 6.99 (m, 2H, C*H*$_{arom.}$), 6.99 – 6.91 (m, 2H, C*H*$_{arom.}$), 0.98 (s, 9H, *t*Bu-C*H*$_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 196.7 (*C*HO), 154.4 (*C*$_q$), 149.4 (*C*$_q$), 141.4 (*C*$_q$), 140.0 (*C*$_q$), 138.5 (*C*$_q$), 137.9 (*C*H), 133.6 (*C*H), 130.6 (*C*$_q$), 130.4 (*C*H), 129.9 (*C*H), 129.2 (*C*H), 128.9 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 127.3 (*C*$_q$), 126.8 (*C*H), 126.7 (*C*H), 126.0 (*C*H), 125.9 (*C*H), 124.9 (*C*H), 124.0 (*C*H), 122.0 (*C*$_q$), 121.8 (*C*$_q$), 34.3 (*C*$_q$), 31.2 (*C*H$_3$).[k] **HRMS (ESI)**: Calculated for $C_{31}H_{27}O_2$ $[M+H]^+$: 431.2011, Found: 431.2004.

[k] Missing signals under solvent peak.



R = 4-tBu-$C_6H_4$

**2'-(4-(tert-Butyl)phenyl)-3-((E)-(((1R,2R)-2-(((E)-((S)-2'-(4-(tert-butyl)phenyl)-2-hydroxy-[1,1'-binaphthalen]-3-yl)methylene)amino)cyclohexyl)imino)methyl)-[1,1'-binaphthalen]-2-ol [S13]**

According to a literature known procedure with minor alterations,[15] (1*S*,2*S*)-(–)-1,2-cyclohexanediamine D-tartrate (186 mg, 0.71 mmol, 1.00 eq.) was stirred with $K_2CO_3$ (195 mg, 1.41 mmol, 2.0 eq.) in EtOH (25 mL) and $H_2O$ (4 mL) for 15 min, before (S)-2'-(4-(tert-butyl)phenyl)-2-hydroxy-[1,1'-binaphthalene]-3-carbaldehyde (606 mg, 1.41 mmol, 2.00 eq.) was added. The mixture was heated to reflux for 72 h. Water (70 mL) was added and the flask was cooled to –18 °C. A yellow precipitate was formed, that was filtered off, was washed with water (3 x 20 mL) and ice-cold EtOH (3 x 10 mL). The product was dried *in vacuo* at 60 °C for 4 d and was obtained as a yellow solid (0.60 g, 0.64 mmol, 91%).)

**M.P.:** decomp. >250 °C. **IR (neat)**: 3031 (w), 2959 (w), 2928 (w), 2868 (w), 1631 (s), 1507 (w), 1339 (w), 817 (m), 753 (m). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 13.04 (s, 2H, C*H*N), 7.81 (d, *J* = 8.5 Hz, 2H, C*H*$_{arom.}$), 7.78 – 7.74 (m, 4H, C*H*$_{arom.}$), 7.72 (d, *J* = 8.4 Hz, 2H, C*H*$_{arom.}$), 7.56 – 7.52 (m, 4H, C*H*$_{arom.}$), 7.52 – 7.48 (m, 2H, C*H*$_{arom.}$), 7.33 – 7.24 (m, 4H, C*H*$_{arom.}$), 7.20 (s, 2H, O*H*), 7.23 – 7.17 (m, 2H, C*H*$_{arom.}$), 7.04 – 6.91 (m, 8H, C*H*$_{arom.}$), 6.64 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 2H, C*H*$_{arom.}$), 2.85 – 2.72 (m, 2H, C*H*), 1.51 – 1.35 (m, 4H, C*H*$_2$), 1.34 – 1.16 (m, 2H, C*H*$_2$), 1.08 – 0.96 (m, 2H, C*H*$_2$), 0.96 (s, 18H, C*H*$_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 165.5 (*C*HN), 155.6 (*C*$_q$), 149.1 (*C*$_q$), 140.9 (*C*$_q$), 140.2 (*C*$_q$), 136.3 (*C*$_q$), 133.9 (*C*$_q$), 133.8 (*C*H), 133.5 (*C*$_q$), 132.1 (*C*$_q$), 129.2 (*C*H), 129.1 (*C*H), 129.0 (*C*H), 128.6, 128.6 (*C*H), 128.4 (*C*H), 127.5 (*C*$_q$), 126.8 (*C*H), 126.5 (*C*H), 125.8 (*C*H), 125.5 (*C*H), 124.9 (*C*H), 123.2 (*C*H), 120.7 (*C*$_q$), 120.6 (*C*$_q$), 72.9 (*C*H), 34.2 (*C*H$_2$), 32.5 (*C*$_q$), 31.2 (*C*H$_3$), 24.1 (*C*H$_2$).[l] **HRMS (ESI)**: Calculated for $C_{68}H_{63}N_2O_2$ $[M+H]^+$: 939.4890, Found: 939.4871.

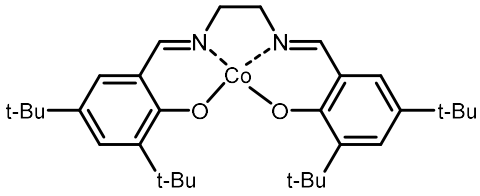
[l] Missing signals under solvent peak.

## 1.2. Synthesis of cobalt complexes

### General procedure A for the preparation of $Co^{II}$·salen type complexes

Following a literature known protocol with minor alterations,[17] EtOH was deaerated by purging with a flow of nitrogen for 10 min. $Co(OAc)_2 \cdot 4H_2O$ (1.00 eq.) was dissolved under inert atmosphere in the deaerated EtOH and stirred until complete solvation of the salt took place. Then salen-type ligand (1.00 eq.) was added and the mixture was heated to reflux for 17 h. The solution was cooled to –18 °C, the resulting precipitate was filtered off and washed with small portions of cold EtOH. The filtrate could be concentrated, and the residue could be recrystallized to gain a second crop of the complex.

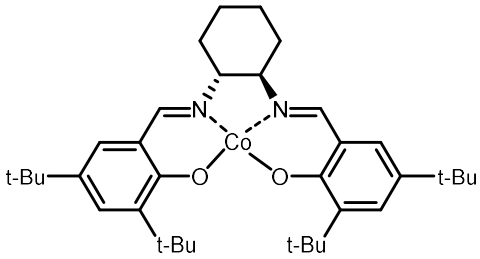
The solid complexes are stable towards air and moisture, while the ethanolic $Co^{II}$-solution is labile for oxidation through acidic impurities.




### $Co^{II}$·salen [3a]

Following general procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (127 mg, 0.51 mmol) was reacted with achiral salen ligand [**S2**] (250 mg, 0.51 mmol) to yield the dark red complex [**3a**] (219 mg, 0.398 mmol, 78%).

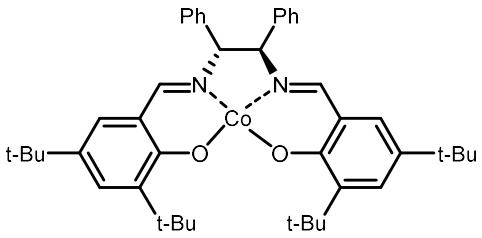
**Elemental analysis** calcd (%) for $C_{32}H_{46}CoN_2O_2$: C 69.92, H 8.44, N 5.10; found: C 69.55, H 8.23, N 5.00.




### $Co^{II}$·salen [epi-3b]

Following general procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (623 mg, 2.50 mmol, 1.00 eq.) was reacted with achiral salen ligand [**S2**] (1.37 g, 2.50 mmol, 1.00 eq.) to yield the dark red complex [**epi-3b**] (771 mg, 1.28 mmol, 51%).

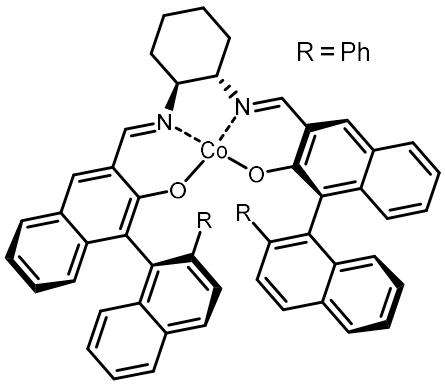
**Elemental analysis** calcd (%) for $C_{36}H_{52}CoN_2O_2$: C 71.62, H 8.68, N 4.64; found: C 71.62, H 8.57, N 4.57.




**$Co^{II}$·salen [3d]**

Following general procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (38.6 mg, 0.155 mmol, 1.00 eq.) was reacted with achiral salen ligand (100 mg, 0.155 mmol, 1.00 eq.) to yield the dark red complex [**3d**] (80 mg, 0.113 mmol, 73%).

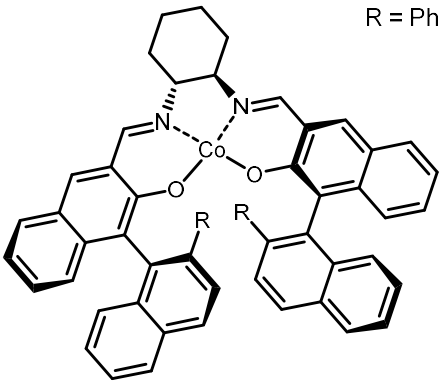
**Elemental analysis** calcd (%) for $C_{44}H_{54}CoN_2O_2$: C 75.30, H 7.76, N 3.99; found: C 75.16, H 7.63, N 3.78.




**$Co^{II}$·salen [4a]**

Following general procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (37 mg, 0.15 mmol, 1.00 eq.) was reacted with the chiral salen ligand [**S7**] (122 mg, 0.15 mmol, 1.00 eq.) to yield the orange-brown complex [**4a**] (94 mg, 0.10 mmol, 66%).

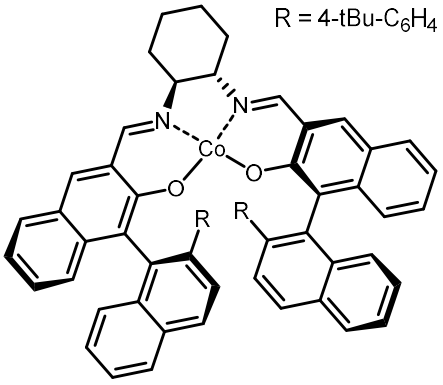
**M.P.:** decomp. >250 °C. **IR (neat)**: 3058 (w), 2931 (w), 2331 (w), 1586 (s), 1548 (m), 1446 (m), 1413 (m), 1333 (s), 1148 (m), 820 (m), 759 (w), 735 (s). **HRMS (ESI):** Calculated for $C_{60}H_{44}CoN_2O_2$ $[M]^+$: 883.2735, Found: 883.2720.




**$Co^{II}$·salen [epi-4a]**

Following general procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (37 mg, 0.15 mmol, 1.00 eq.) was reacted with the chiral salen ligand [**epi-S7**] (126 mg, 0.15 mmol, 1.00 eq.) to yield the orange-brown complex [**epi-4a**] (103 mg, 0.12 mmol, 80%).

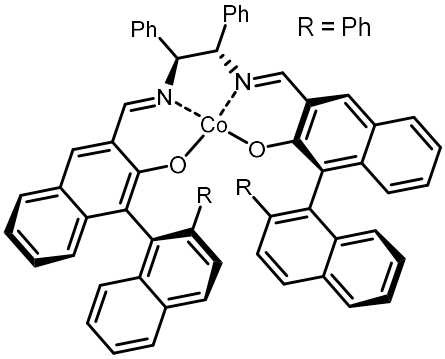
**M.P.:** decomp. >250 °C. **IR (neat)**: 3058 (w), 2929 (w), 2855 (w), 2357 (w), 1631 (m), 1595 (m), 1495 (w), 1446 (w), 1331 (m), 1147 (m), 866 (w), 819 (m), 743 (s), 700 (s). **HRMS (ESI):** Calculated for $C_{60}H_{45}CoN_2O_2$ $[M+H]^+$: 884.2813, Found: 884.2801.




**$Co^{II}$·salen [4b]**

Following general procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (130 mg, 0.52 mmol, 1.00 eq.) was reacted with the chiral salen ligand [**S13**] (487 mg, 0.52 mmol, 1.00 eq.) to yield the orange-brown complex [**4b**] (454 mg, 0.46 mmol, 88%).

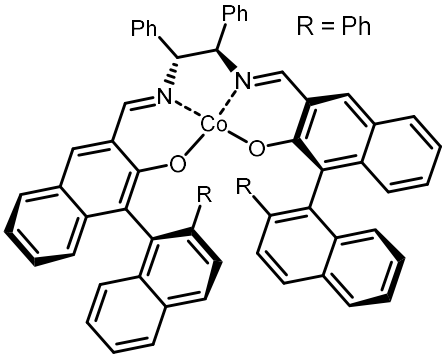
**M.P.:** decomp. >250 °C. **IR (neat)**: 2961 (w), 2947 (w), 2861 (w), 1589 (m), 1445 (w), 1422 (w), 1333 (w), 1146 (w), 816 (w), 749 (s). **HRMS (ESI):** Calculated for $C_{68}H_{61}CoN_2O_2$ $[M+H]^+$: 996.4065, Found: 995.4060.




**Co$^{II}$·salen [4c]**

Following General procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (40 mg, 0.16 mmol, 1.00 eq.) was reacted with the chiral BINOL-type ligand [**S8**] (148 mg, 0.16 mmol, 1.00 eq.) to yield the orange-brown complex [zz] (124 mg, 0.13 mmol, 81%).

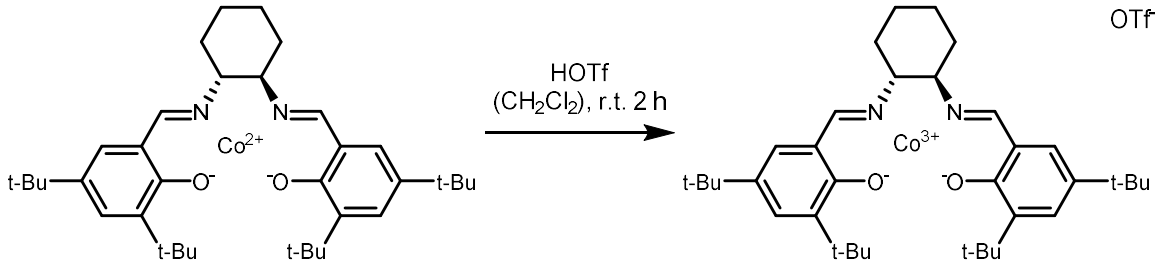
**M.P.:** decomp. >250 °C. **IR (neat)**: 3050 (w), 2931 (m), 2353 (w), 2249 (w), 1717 (w), 1587 (s), 1497 (s), 1454 (s), 1320 (s), 1026 (m), 822 (m). **HRMS (ESI):** Calculated for $C_{68}H_{47}CoN_2O_2$ $[M+H]^+$: 982.2969, Found: 982.2960.




**Co$^{II}$·salen [epi-4c]**

Following General procedure **A**, $Co(OAc)_2 \cdot 4H_2O$ (17 mg, 0.07 mmol, 1.00 eq.) was reacted with the chiral BINOL-type ligand [**epi-S8**] (62 mg, 0.07 mmol, 1.00 eq.) to yield the orange-brown complex [zz] (32 mg, 0.03 mmol, 43%).

**M.P.:** decomp. >250 °C. **IR (neat)**: 3058 (w), 2931 (w), 2346 (w), 630(s), 1591 (m), 1495 (m), 1453 (m), 1347 (m), 1147 (m), 1028 (m), 822 (m), 738 (m), 700 (s). **HRMS (ESI):** Calculated for $C_{68}H_{47}CoN_2O_2$ $[M+H]^+$: 982.2969, Found: 982.2948.




**Co$^{II}$·salen [3c]**

According to a literature known procedure[18] (*R*,*R*)-(–)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) (250 mg, 0.414 mmol, 1.00 eq.) was dissolved in dry $CH_2Cl_2$ (4 mL) after complete solvation triflic acid (38 µL, 0.435 mmol, 1.05 eq.) was added. The solution was stirred open to air for 2 h at rt. The solvent was removed *in vacuo* and the residue was taken up in pentane the remaining solids were filtered off and washed with pentane. The solids were dissolved in $CH_2Cl_2$ and again filtered. The filtrate was concentrated and the solvent was removed *in vacuo* to obtain the desired Co$^{II}$·salen [**3c**] complex as a dark green solid (198 mg, 0.263 mmol, 65%).

**$^1$H NMR** (400 MHz, $(CD_3)_2SO$): $\delta$ = 7.82 (*s*, 2H, C*H*), 7.63 – 7.35 (*m*, 4H, C$H_{arom.}$), 3.60 (*d*, *J* = 7.7 Hz, 2H), 3.07 (*d*, *J* = 11.8 Hz, 2H), 2.04 – 1.98 (*m*, 2H), 1.96 – 1.85 (*m*, 2H), 1.74 (*s*, 18H, (C$H_3$)$_3$), 1.64 – 1.53 (*m*, 2H), 1.30 (*s*, 18H, (C$H_3$)$_3$). **$^{19}$F NMR** (376 MHz, $(CD_3)_2SO$): –77.8 (*s*, C$F_3$).

The obtained spetroscopic data are in agreement to those previously reported.[18]

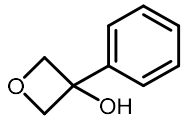
### 1.3. Synthesis of oxetanols

General procedure **B** for the preparation of aryl-substituted oxetanols from oxetan-3-one

3-substituted oxetanols were prepared following a lab-own protocol. A halogenated arene (1.20 eq.) was dissolved in dry THF (0.1 M) under inert atmosphere and cooled to –78°C at which temperature *n*-BuLi (2.5 M, 1.20 eq.) was added dropwise. After 1 h, oxetan-3-one (1.00 eq.) was added slowly and the mixture was stirred at –78°C for 3 h, before it was slowly warmed up to rt for 17 h. The solution was diluted with $Et_2O$ and $NH_4Cl$ sat. was added. The organic phase was separated, and the aqueous phase was extracted with $Et_2O$ (3x). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The products were isolated after FC or automated FC.

General procedure **C** for the preparation of alkynyl-substituted oxetanols from oxetan-3-one

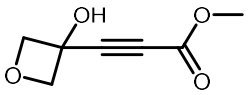
3-substituted oxetanols were prepared following a lab-own protocol. Monosubstituted alkyne (1.20 eq.) was dissolved in dry THF (0.1 M) under inert atmosphere and cooled to –78°C at which temperature *n*-BuLi (2.5 M, 1.20 eq.) was added dropwise. After 1 h, 3-oxetanone (1.00 eq.) was added slowly and the mixture was stirred at –78°C for 3 h, before it was slowly warmed up to rt for 17 h. The solution was diluted with $Et_2O$ and $NH_4Cl$ sat. was added. The organic phase was separated, and the aqueous phase was extracted with $Et_2O$ (3x). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The products were isolated after FC or automated FC.




**3-Phenyloxetan-3-ol [1a]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and bromobenzene (630 µL, 6.00 mmol, 1.20 eq.). The desired product was obtained after FC ($Et_2O$ : pentane, 4:1) as a colorless solid (679 mg, 4.52 mmol, 90%).

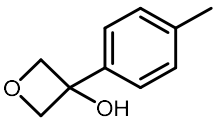
**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.62 – 7.56 (m, 2H, C$H_{arom.}$), 7.46 – 7.39 (m, 2H, C$H_{arom.}$), 7.37 – 7.32 (m, 1H, C$H_{arom.}$), 4.96 – 4.87 (m, 4H, C$H_2$), 2.89 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 142.4 ($C_q$), 128.9 (*C*H), 128.1 (*C*H), 124.6 (*C*H), 85.8 (*C*$H_2$), 75.9 ($C_q$). Spectroscopic data was in agreement to those previously reported.[19]



**Methyl 3-(3-hydroxyoxetan-3-yl)propiolate [1c]**

Following general procedure **C** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and methyl propiolate (540 µL, 6.00 mmol, 1.20 eq.), the desired product was obtained after automated FC (CyH:EtOAc, 90:10 to 70:30) as a yellow oil (167 mg, 1.07 mmol, 21%).

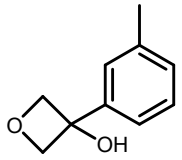
**IR (neat)**: 3395 (w), 2953 (w), 2880 (w), 2240 (w), 1718 (s), 1437 (m), 1275 (s), 1153 (m), 984 (m), 918 (w), 866 (m), 750 (s). **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 4.87 (dd, $J$ = 6.8, 1.0 Hz, 2H, C$H_2$), 4.72 (dd, $J$ = 6.8, 1.0 Hz, 2H, C$H_2$), 3.81 (s, 3H, C$H_3$), 3.72 (s, 1H, O$H$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 153.8 ($C_q$), 85.5 ($C_q$), 83.5, ($CH_2$), 77.4, ($C_q$), 66.6 ($C_q$), 53.3 ($CH_3$). **HRMS (APCI):** Calculated for $C_7H_9O_4$ $[M+H]^+$: 157.0501, Found: 157.0492.



**3-(p-Tolyl)oxetan-3-ol [1d]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 4-methyl-bromobenzene (730 µL, 6.00 mmol, 1.20 eq.). The desired product was obtained after automated FC (CyH:EtOAc, 80:20 to 65:35 ) as a colorless solid (486 mg, 2.96 mmol, 59%).

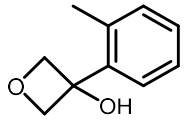
**M.P.**: 66 – 68 °C. **IR (neat)**: $\tilde{\nu}$ = 3397 (m), 2955 (w), 2874 (w), 2360 (w), 2341 (w), 2329 (w), 1738 (w), 1516 (w), 1450 (w), 1417 (w), 1379 (w), 1328 (w), 1280 (w), 1231 (w), 1213 (w), 1173 (m), 1141 (w), 1114 (w), 1064 (w), 1022 (w), 971 (s), 879 (m), 816 (s), 720 (w). **$^{1}$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.48 – 7.43 (m, 2H, C$H_{arom.}$), 7.25 – 7.21 (m, 2H, C$H_{arom.}$), 4.92 – 4.86 (m, 4H, C$H_2$), 2.90 (br, 1H, O$H$), 2.37 (s, 3H, C$H_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 139.4 ($C_q$), 137.7 ($C_q$), 129.4 ($CH$), 124.5 ($CH$), 85.6 ($CH_2$), 75.7 ($C_q$), 21.1 ($CH_3$).



**3-(m-Tolyl)oxetan-3-ol [1e]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 3-methyl-iodobenzene (770 µL, 6.00 mmol, 1.20 eq.). The desired product was obtained after automated FC (CyH:EtOAc, 80:20 to 60:40 ) as a colorless solid (458 mg, 2.79 mmol, 56%).

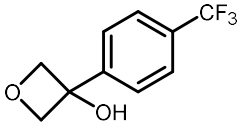
**M.P.**: 41 – 43 °C. **IR (neat)**: $\tilde{\nu}$ = 3401 (m), 2959 (w), 2948 (w), 2820 (w), 2883 (w), 2874 (w), 2356 (w), 1610 (w), 1492 (w), 1455 (w), 1325 (w), 1284 (w), 1200 (m), 1178 (w), 1165 (m), 1143 (w), 1072 (w), 970 (s), 905 (m), 848 (m), 786 (m), 703 (s), 683 (w). **$^1$H NMR (400 MHz, CDCl$_3$)**: $\delta$ = 7.44 – 7.37 (m, 2H, C$H_{arom.}$), 7.33 (t, $J$ = 7.5 Hz, 1H, C$H_{arom.}$), 7.20 – 7.16 (m, 1H, C$H_{arom.}$), 4.92 (app. q, $J$ = 6.8 Hz, 4H, C$H_2$), 3.05 (br, 1H, O$H$), 2.42 (s, 3H, C$H_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)**: $\delta$ = 142.4 ($C_q$), 138.6 ($C_q$), 128.8 (*C*H), 128.7 (*C*H), 125.3 (*C*H), 121.6 (*C*H), 85.7 (*C*H$_2$), 75.9 ($C_q$), 21.7 (*C*H$_3$).




**3-(o-Tolyl)oxetan-3-ol [1f]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 2-mehtyl-iodobenzene (765 µL, 6.00 mmol, 1.20 eq.). The desired product was obtained after automated FC (CyH:EtOAc 80:20 to 60:40) as a yellow oil (683 mg, 4.15 mmol, 83%).

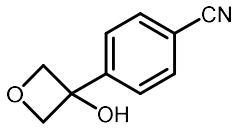
**IR (neat)**: $\tilde{\nu}$ = 3396 (m), 2951 (m), 2876 (w), 2352 (w), 1491 (w), 1456 (m), 1397 (w), 1176 (w), 1131 (m), 1064 (w), 1033 (m), 975 (s), 950 (w), 881 (m), 831 (m), 760 (s), 729 (s). **$^1$H NMR (400 MHz, CDCl$_3$)**: $\delta$ = 7.28 – 7.15 (m, 3H, C$H_{arom.}$), 7.18 – 7.09 (m, 1H, C$H_{arom.}$), 5.25 – 5.16 (m, 2H, C$H_2$), 4.91 – 4.82 (m, 2H, C$H_2$), 2.57 (br, 1H, O$H$), 2.25 (s, 3H, C$H_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)**: $\delta$ = 139.4 ($C_q$), 136.5 ($C_q$), 131.8 (*C*H), 128.9 (*C*H), 126.1 (*C*H), 125.8 (*C*H), 83.6 (*C*H$_2$), 78.0 ($C_q$), 19.3 (*C*H$_3$).




**3-(4-(Trifluoromethyl)phenyl)oxetan-3-ol [1g]**

Following general procedure **B** with minor alterations using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.20 mL, 5.50 mmol, 1.10 eq.) and 4-trifluoromethyl-bromobenzene (770 µL, 6.00 mmol, 1.10 eq.). The desired product was obtained after automated FC (CyH:EtOAc, 80:20 to 70:30 ) as a colorless solid (838 mg, 3.84 mmol, 77%).

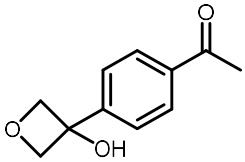
**M.P.**: 122 – 123 °C. **IR (neat)**: $\tilde{\nu}$ = 3380 (m), 2973 (m), 2891 (w), 2364 (w), 2331 (w), 1740 (w), 1380 (w), 1328 (s), 1166 (m), 1128 (s), 1107 (s), 1076 (m), 1016 (w), 951 (s), 913 (w), 844 (w), 817 (m), 734 (s). **$^1$H NMR (400 MHz, CDCl$_3$)**: $\delta$ = 7.80 – 7.73 (m, 2H, C$H_{arom.}$), 7.66 – 7.70 (m, 2H, C$H_{arom.}$), 4.97 – 4.90 (m, 2H, C$H_2$), 4.91 – 4.85 (m, 2H, C$H_2$), 3.11 (s, 1H, O$H$). **$^{13}$C NMR (101 MHz, CDCl$_3$)**: $\delta$ = 146.3 ($C_q$), 146.3 (*C*H), 130.3 (q, $^2J$ = 32.6 Hz, $C_q$), 125.8 (q, $^3J$ = 3.7 Hz, *C*H), 125.0 (*C*H), 124.1 (q, $^1J$ = 272.0 Hz, *C*F$_3$), 86.1 (*C*H$_2$), 75.5 ($C_q$). **$^{19}$F NMR (377 MHz, CDCl$_3$)** $\delta$ = – 62.5 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{10}H_8F_3O_2$ $[M+H]^-$: 217.0476, Found: 217.0476.




**4-(3-Hydroxyoxetan-3-yl)benzonitrile [1h]**

4-iodobenzonitrile (1.20 g, 5.00 mmol, 1.00 eq.) was dissolved in dry THF (20 mL) under inert atmosphere and cooled to –78 °C before iPrMgCl (2.0 M, 2.5 mL, 5.00 mmol, 1.00 eq.) was added slowly. The mixture was slowly warmed up to –20 °C and kept at this temperature for 1 h before it was cooled again to –78 °C. At which temperature oxetan-3-one (480 µL, 7.50 mmol, 1.50 eq.) was added. The temperature was raised to –20 °C and stirred for 1 h, then 1 h at 0 °C followed by 6 h at rt. The solvent was removed and the product was obtained *via* recrystallization (EtOAc:CyH, 95:5) as a colorless solid (489 mg, 2.79 mmol, 56%).

**M.P.**: 171 – 172 °C. **IR (neat)**: $\tilde{\nu}$ = 3338 (m), 3009 (w), 2964 (w), 2877 (w), 2225 (w), 1737 (w), 1721 (w), 1596 (w), 1547 (m), 1436 (m), 1405 (w), 1346 (m), 1325 (w), 1293 (w), 1237 (w), 1205 (m), 1178 (s), 1132 (w), 1108 (w), 1016 (w), 978 (s), 954 (m), 877 (s), 842 (m), 778 (w), 751 (w), 729 (m), 661 (w). **$^1$H NMR (400 MHz, CDCl$_3$)**: $\delta$ = 7.84 – 7.78 (m, 2H, C*H*$_{arom.}$), 7.75 – 7.70 (m, 2H, C*H*$_{arom.}$), 4.97 – 4.92 (m, 2H, C*H*$_2$), 4.88 – 4.82 (m, 2H, C*H*$_2$), 2.74 (s, 1H, O*H*). **$^{13}$C NMR (101 MHz, CDCl$_3$)**: $\delta$ = 147.6 ($C_q$), 132.6 (*C*H), 125.3 (*C*H), 118.7 ($C_q$), 111.9 ($C_q$), 86.1 (*C*H$_2$), 75.4 ($C_q$). **HRMS (APCI)**: Calculated for $C_{10}H_9NO_2$ $[M+H]^+$: 176.0712, Found: 176.0702.

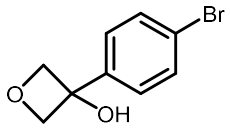



**1-(4-(3-Hydroxyoxetan-3-yl)phenyl)ethan-1-one [1i]**

1-(4-(3-hydroxyoxetan-3-yl)phenyl)ethan-1-one [**1i**] was prepared according to a literature known protocol.[20] 3-(4-(2-Methyl-1,3-dioxolan-2-yl)phenyl)oxetan-3-ol [**1u**] (150 mg, 0.635 mmol, 1.00 eq.) was dissolved in acetone (5 mL) and water (10 µL) before Montmorrilonite K10 (190 mg) was added. The mixture was stirred for 6 h at 55 °C. The mixture was filtered through celite and the solvent was removed. The product was obtained *via* automated FC (CyH:EtOAc, 70:30 to 60:40) as a colorless solid (102 mmg, 0.531 mmol, 84%).

**M.P.**: 131 – 132 °C. **IR (neat)**: $\tilde{\nu}$ = 3344 (m), 2954 (m), 2927 (m), 2853 (w), 2238 (w), 1678 (s), 1608 (m), 1428 (w), 1360 (m), 1307 (w), 1270 (s), 1183 (m), 1108 (m), 1014 (m), 976 (m), 960 (s), 910 (m), 874 (m), 833 (s), 809 (m), 734 (s), 704 (w), 661 (m), 646 (s). **$^1$H NMR (400 MHz, CDCl$_3$)**: $\delta$ = 8.02 – 7.97 (m, 2H, C*H*$_{arom.}$), 7.76 – 7.72 (m, 2H, C*H*$_{arom.}$), 4.96 – 4.93 (m, 2H, C*H*$_2$), 4.89 – 4.86 (m, 2H, C*H*$_2$), 3.22 (br, 1H, O*H*), 2.62 (s, 3H, C*H*$_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)**: $\delta$ = 198.0 ($C_q$), 147.6 ($C_q$), 136.6 ($C_q$),

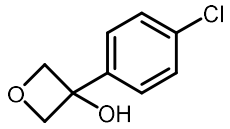
128.9 (*C*H), 124.8 (*C*H), 86.0 (*C*$H_2$), 75.6 (*C*$_q$), 26.8 (*C*$H_3$). **HRMS (APCI)**: Calculated for $C_{11}H_{13}O_3$ $[M+H]^+$: 193.0865, Found: 193.0854.




**3-(4-Bromophenyl)oxetan-3-ol [1j]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.20 mL, 5.50 mmol, 1.10 eq.) and 1-bromo-4-iodobenzene (1.70 g, 6.00 mmol, 1.20 eq.). The desired product was obtained after automated FC (CyH:EtOAc 70:30 to 65:35) as a colorless solid (714 mg, 3.12 mmol, 62%).

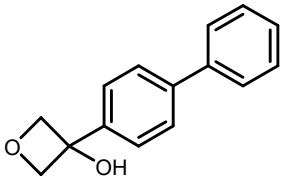
**M.P.**: 82 – 83 °C. **IR (neat)**: $\tilde{\nu}$ = 3369 (m), 2957 (w), 2879 (w), 2332 (w), 2251 (w), 1593 (w), 1488 (w), 1411 (w), 1398 (w), 1265 (w), 1176 (w), 1138 (w), 1102 (w), 1071 (w), 1009 (m), 978 (m), 952 (w), 909 (m), 873 (w), 821 (m), 734 (s). **$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.58 – 7.53 (m, 2H, C*H*$_{arom.}$), 7.52 – 7.47 (m, 2H, C*H*$_{arom.}$), 4.92 – 4.89 (m, 2H, C*H*$_2$), 4.87 – 4.83 (m, 2H, C*H*$_2$), 2.70 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 141.5 (*C*$_q$), 131.9 (*C*$_q$), 126.4 (*C*H), 122.1 (*C*H), 85.9 (*C*$H_2$), 75.6 (*C*$_q$). **HRMS (APCI)**: Calculated for $C_9H_8BrO$ $[M-OH]^+$: 210.9759, Found: 210.9749.




**3-(4-Chlorophenyl)oxetan-3-ol [1k]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 1-chloro-4-iodobenzene (1.43 g, 6.00 mmol, 1.20 eq.). The desired product was obtained after automated FC (CyH:EtOAc 70:30 to 65:35) as a colorless solid (869 mg, 4.71 mmol, 94%).

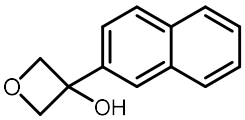
**M.P.**: 71 – 72 °C. **IR (neat)**: $\tilde{\nu}$ = 3353 (m), 2969 (w), 2881 (w), 2368 (w), 1922 (w), 1663 (w), 1577 (w), 1544 (w), 1490 (w), 1437 (w), 1233 (w), 1181 (m), 1141 (w), 1100 (m), 1050 (w), 1012 (m), 971 (s), 953 (m), 908 (w), 876 (m), 824 (s), 731 (m). **$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.56 – 7.52 (m, 2H, C*H*$_{arom.}$), 7.41 – 7.36 (m, 2H, C*H*$_{arom.}$), 4.87 (app. q, *J* = 7.0 Hz, 4H, C*H*$_2$), 3.05 (br, 1H). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 140.9 (*C*$_q$), 133.9 (*C*$_q$), 128.9 (*C*H), 126.1 (*C*H), 85.9 (*C*$H_2$), 75.5 (*C*$_q$). **HRMS (APCI)**: Calculated for $C_9H_8ClO$ $[M-OH]^+$: 167.0264, Found: 167.0255.




**3-([1,1'-Biphenyl]-4-yl)oxetan-3-ol [1l]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 4-iodo-1,1'-biphenyl (1.68 g, 6.00 mmol, 1.20 eq.). The desired product was obtained after recrystallization ($CH_2Cl_2$:petroleum ether) as a colorless solid (660 mg, 2.92 mmol, 58%).

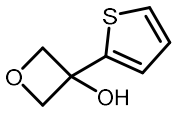
**M.P.**: 140 – 141 °C. **IR (neat)**: $\tilde{\nu}$ = 3375 (m), 2366 (w), 2326 (w), 1543 (w), 1486 (w), 1423 (w), 1187 (w), 1093 (w), 966 (m), 909 (m), 877 (w), 831 (m), 764 (m), 731 (m), 699 (m), 668 (m), 660(m). **$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.72 – 7.62 (m, 4H, C*H*$_{arom.}$), 7.64 – 7.57 (m, 2H, C*H*$_{arom.}$), 7.50 – 7.42 (m, 2H, C*H*$_{arom.}$), 7.41 – 7.33 (m, 1H, C*H*$_{arom.}$), 5.01 – 4.92 (m, 4H, C*H*$_2$), 2.56 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 141.4 ($C_q$), 141.0 ($C_q$), 140.6 ($C_q$), 129.0 (*C*H), 127.7 (*C*H), 127.5 (*C*H), 127.2 (*C*H), 125.1 (*C*H), 85.8 (*C*H$_2$), 75.9 ($C_q$). **HRMS (APCI)**: Calculated for $C_{15}H_{13}O$ [M-OH]$^+$: 209.0966, Found: 209.0996.




**3-(Naphthalen-2-yl)oxetan-3-ol [1m]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 2-bromonaphthalene (1.24 g, 6.00 mmol, 1.20 eq.). The desired product was obtained after automated FC (CyH:EtOAc 70:30 to 65:35) as a colorless solid (836 mg, 4.18 mmol, 84%).

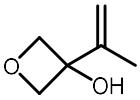
**M.P.**: 110 – 110 °C. **IR (neat)**: $\tilde{\nu}$ = 3341 (m), 3054 (w), 2965 (m), 2892 (w), 2358 (w), 2339 (w), 2332 (w), 2172 (w), 1721 (m), 1602 (w), 1421 (w), 1358 (w), 1314 (w), 1271 (s), 1250 (m), 1231 (m), 1192 (w), 1147 (w), 1127 (w), 1027 (w), 964 (s), 951 (m), 903 (w), 857 (s), 841 (s), 822 (s), 742 (m), 714 (m), 687 (w). **$^1$H NMR (300 MHz, $CDCl_3$)**: $\delta$ = 8.01 (d, *J* = 1.9 Hz, 1H, C*H*$_{arom.}$), 7.93 (d, *J* = 8.6 Hz, 1H, C*H*$_{arom.}$), 7.90 – 7.84 (m, 2H, C*H*$_{arom.}$), 7.74 (dd, *J* = 8.6, 1.9 Hz, 1H, C*H*$_{arom.}$), 7.57 – 7.47 (m, 2H, C*H*$_{arom.}$), 5.07 – 4.96 (m, 4H, C*H*$_2$), 2.60 (br, 1H, C*H*$_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 139.6 ($C_q$), 133.1 ($C_q$), 133.0 ($C_q$), 129.0 (*C*H), 128.4 (*C*H), 127.8 (*C*H), 126.7 (*C*H), 126.5 (*C*H), 123.3 (*C*H), 122.8 (*C*H), 85.7 (*C*H$_2$), 76.1 ($C_q$). **HRMS (APCI)**: Calculated for $C_{13}H_{11}O$ [M-OH]$^+$: 183.0810, Found: 183.0802.




**3-(Thiophen-2-yl)oxetan-3-ol [1n]**

Following general procedure **B** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 2-bromothiophene (978 mg, 6.00 mmol, 1.20 eq.). The desired product was obtained after automated FC (CyH:EtOAc 70:30 to 60:40) as a colorless solid (575 mg, 3.68 mmol, 74%).

**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.29 (dd, $J$ = 5.1, 1.2 Hz, 1H, C$H_{arom.}$), 7.16 (dd, $J$ = 3.6, 1.2 Hz, 1H, C$H_{arom.}$), 7.03 (dd, $J$ = 5.0, 3.6 Hz, 1H, C$H_{arom.}$), 4.91 – 4.84 (m, 4H, C$H_2$), 3.50 (s, 1H, O$H$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 146.9 ($C_q$), 127.4 (*C*H), 125.4 (*C*H), 123.7 (*C*H), 85.9 ($CH_2$), 74.5 ($C_q$). Spectroscopic data was in agreement to those reported previously.[21]

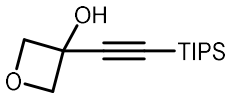



**3-(Prop-1-en-2-yl)oxetan-3-ol [1o]**

Oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.) was dissolved in dry THF (20 mL), isopropenylmagnesium bromide (0.5 M, 12.0 mL, 6.00 mmol, 1.20 eq.) was added at –78 °C and stirred for 30 min before it was slowly warmed to rt over 1.5 h. $Et_2O$ (25 mL) and $NH_4Cl$ sat. (20 mL) were added and the organic phase was separated. The aqueous phase was extracted with $Et_2O$ (3 x 25 mL). The combined organic phases were dried over $Na_2SO_4$. The solvent was removed and the product was obtained as a colorless oil (446 mg, 3.91 mmol, 78%) after automated FC (CyH:EtOAc, 70:30).

**IR (neat)**: $\tilde{\nu}$ = 3399 (m), 2954 (w), 2878 (w), 2360 (w), 2331 (w), 1732 (w), 1715 (w), 1650 (w), 1459 (w), 1447 (w), 1439 (w), 1375 (w), 1332 (w), 1267 (w), 1187 (s), 1141 (w), 1122 (m), 1060 (w), 1038 (w), 971 (s), 904 (s), 874 (m), 826 (w), 813 (w), 726 (w), 655 (w), 622 (m), 615 (m), 593 (m), 584 (m). **$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 5.10 (app. *t*, $J$ = 0.9 Hz, 1H, C$H_2$), 5.02 (app. p, $J$ = 1.4 Hz, 1H, C$H_2$), 4.82 – 4.76 (m, 2H, C$H_2$), 4.68 – 4.61 (m, 2H, C$H_2$), 2.26 (br, 1H, O$H$), 1.91 (dd, J = 1.4, 0.8 Hz, 3H, C$H_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 144.5 ($C_q$), 111.9 ($CH_2$), 82.5 ($CH_2$), 18.0 ($CH_3$).[m] **HRMS (APCI)**: Calculated for $C_8H_{14}NO_2$ [M+MeCN+H]$^+$: 156.1025, Found: 156.1016.

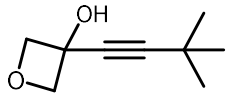
[m] One signal missing due to signal overlapping.




**3-((Triisopropylsilyl)ethynyl)oxetan-3-ol [1p]**

Following general procedure **C** using oxetan-3-one (193 µL, 3.00 mmol, 1.00 eq.), *n*-BuLi (1.60 M, 2.25 mL, 3.60 mmol, 1.20 eq.) and 1-(triisopropylsilyl)-1-propyne (811 µL, 3.60 mmol, 1.20 eq.), the desired product was obtained *via* automated FC (pentane:$Et_2O$, 60:40) as a colorless oil (635 mg, 2.50 mmol, 83%).

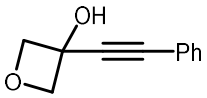
**IR (neat)**: 3394 (m), 2948 (s), 2866 (s), 2172 (w), 1464 (m), 1235 (m), 1135 (m), 988 (s), 920 (s), 883 (s), 838 (s), 772 (m). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 4.84 (dd, $J$ = 6.4, 1.0 Hz, 2H, C$H_2$), 4.72 (dd, $J$ = 6.5, 0.9 Hz, 2H, C$H_2$), 2.65 (s, 1H, O$H$), 1.08 (s, 21H, C$H$, C$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 106.5 ($C_q$), 88.1 ($C_q$), 84.9 ($CH_2$), 67.5 ($C_q$), 18.7 ($CH_3$), 11.2 ($CH$). **HRMS (APCI):** Calculated for $C_{14}H_{27}O_2Si$ $[M+H]^+$: 255.1780, Found: 255.1771.




**3-(3,3-Dimethylbut-1-yn-1-yl)oxetan-3-ol [1q]**

Following general procedure **C** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and 3,3-dimethyl-1-butyne (750 µL, 6.00 mmol, 1.20 eq.), the desired product was obtained *via* automated FC (CyH:EtOAc, 90:10 to 80:20) as a colorless solid (699 mg, 4.53 mmol, 91%).

**M.P.:** 58 – 59 °C. **IR (neat)**: 3345 (m), 2972 (s), 2876 (w), 1278 (m), 1136 (s), 973 (s), 849 (m), 747 (s). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 4.78 (dd, $J$ = 6.4, 0.9 Hz, 2H, C$H_2$), 4.68 (dd, $J$ = 6.4, 0.9 Hz, 2H, C$H_2$), 2.83 (s, 1H, O$H$), 1.22 (s, 9H, C$H_3$).**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 95.5 ($C_q$), 85.2 ($CH_2$), 78.2 ($C_q$), 67.3 ($C_q$), 30.9 ($CH_3$), 27.5 ($C_q$). **HRMS (APCI):** Calculated for $C_9H_{15}O_2$ $[M+H]^+$: 155.1072, Found: 155.1065.

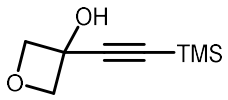



**3-(Phenylethynyl)oxetan-3-ol [1r]**

Following general procedure **C** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (2.50 M, 2.40 mL, 6.00 mmol, 1.20 eq.) and phenylacetylene (659 µL, 6.00 mmol, 1.20 eq.), the desired product was obtained *via* FC (pentane:$Et_2O$, 70:30) as a colorless solid (791 mg, 4.54 mmol, 91%).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 7.48 – 7.42 (m, 2H, C$H_{arom.}$), 7.39 – 7.29 (m, 3H, C$H_{arom.}$), 4.94 (d, $J$ = 6.5 Hz, 2H, C$H_2$), 4.80 (dd, $J$ = 6.5, 1.0 Hz, 2H, C$H_2$), 2.86 (s, 1H,

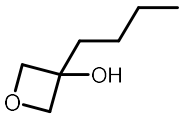
O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 131.8 (*C*H), 129.1 (*C*H), 128.6 (*C*H), 121.9 ($C_q$), 88.0 ($C_q$), 86.5 ($C_q$), 84.8 (*C*$H_2$), 67.7 ($C_q$). Spectroscopic data was in agreement to those previously reported.[22]




**3-((Trimethylsilyl)ethynyl)oxetan-3-ol [1s]**

Following general procedure **C** using oxetan-3-one (320 µL, 5.00 mmol, 1.00 eq.), *n*-BuLi (1.60 M, 3.75 mL, 6.00 mmol, 1.20 eq.) and trimethylsilylacetylene (854 µL, 6.00 mmol, 1.20 eq.), the desired product was obtained *via* FC (pentane:$Et_2O$, 85:15) as a colorless oil (800 mg, 4.70 mmol, 94%).

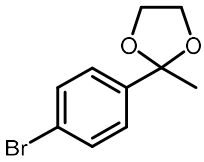
**IR (neat)**: 3396 (w), 2953 (w), 2880 (w), 2180 (w), 1251 (m), 1134 (m), 978 (m), 921 (m), 839 (s). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 4.83 (dd, *J* = 6.5, 1.0 Hz, 2H, C*H*$_2$), 4.69 (dd, *J* = 6.6, 0.9 Hz, 2H, C*H*$_2$), 2.61 (s, 1H, O*H*), 0.19 (s, 9H, C*H*$_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 104.2 ($C_q$), 91.7 ($C_q$), 84.6 (*C*$H_2$), 67.5 ($C_q$), -0.1 (*C*$H_3$). **HRMS (APCI):** Calculated for $C_8H_{15}O_2Si$ $[M+H]^+$: 171.0841, Found: 171.0836.




**3-Butyloxetan-3-ol [1t]**

Oxetan-3-one (500 µL, 7.77 mmol, 1.00 eq.) was dissolved in dry THF (8 mL), *n*-BuLi (2.50 M, 3.42 mL, 8.55 mmol, 1.10 eq.) was added at –78 °C. The mixture was stirred for 2 h before it was slowly warmed to rt over 2 h and stirred at rt for 1h. $Et_2O$ (8 mL) and $NH_4Cl$ sat. (10 mL) were added. The organic phase was separated and the aqueous phase was extracted with $Et_2O$ (3 x 8 mL). The combined organic fractions were dried over $Na_2SO_4$ and the solvent was removed. The desired product was obtained *via* automated FC (CyH:EtOAc, 80:20 to 50:50) as a colourless oil (706 mg, 5.42 mmol, 70%)).

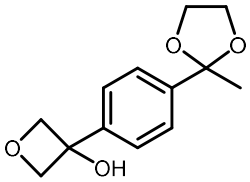
**IR (neat)**: 3403 (m), 2954 (m), 2871 (m), 2358 (w), 1465 (w), 1240 (m), 1073 (m), 965 (s), 831 (m). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) = 4.56 (d, *J* = 6.7 Hz, 2H, C*H*$_2$), 4.53 – 4.48 (m, 2H, C*H*$_2$), 2.53 (s, 1H, O*H*), 1.87 – 1.76 (m, 2H, C*H*$_2$), 1.36 (dtd, *J* = 9.1, 4.6, 3.1 Hz, 4H, C*H*$_2$), 0.99 – 0.87 (m, 3H, C*H*$_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) = 84.1 (*C*$H_2$), 74.8 ($C_q$), 37.6 (*C*$H_2$), 25.5 (*C*$H_2$), 23.0 (*C*$H_2$), 14.1 (*C*$H_3$). **HRMS (APCI):** Calculated for $C_9H_{18}O_2N$ $[M+MeCN+H]^+$: 172.1338, Found: 172.1334.




**2-(4-Bromophenyl)-2-methyl-1,3-dioxolane [S14]**

Following a literature known protocol,[23] 4'-bromoacetophenone (3.00 g, 15.1 mmol, 1.00 eq.) and *para*-toluenesulfonic acid monohydrate (143 mg, 0.75 mmol, 5 mol%) were dissolved in toluene (30 mL) and ethylene glycol (22.6 mmol, 1.26 mL, 1.50 eq.) was added. The mixture was heated to reflux in a *Dean-Stark*-apparatus for 17 h. After cooling to rt, $NaHCO_3$ sat. (15 mL) was added. The organic phase was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 x 30 mL). The combined organic fractions were dried over $MgSO_4$, and the solvent was removed. The product was obtained as a colorless solid (3.40 g, 93%).

**$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.49 – 7.44 (m, 2H, C$H_{arom.}$), 7.38 – 7.33 (m, 2H, C$H_{arom.}$), 4.06 – 4.01 (m, 2H, C$H_2$), 3.78 – 3.73 (m, 2H, C$H_2$), 1.63 (s, 3H, C$H_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 142.5 ($C_q$), 131.3 (*C*H), 127.2 (*C*H), 121.9 ($C_q$), 108.5 ($C_q$), 64.5 ($CH_2$), 27.5 ($CH_3$). Spectroscopic data was in agreement to those previously reported.[23]

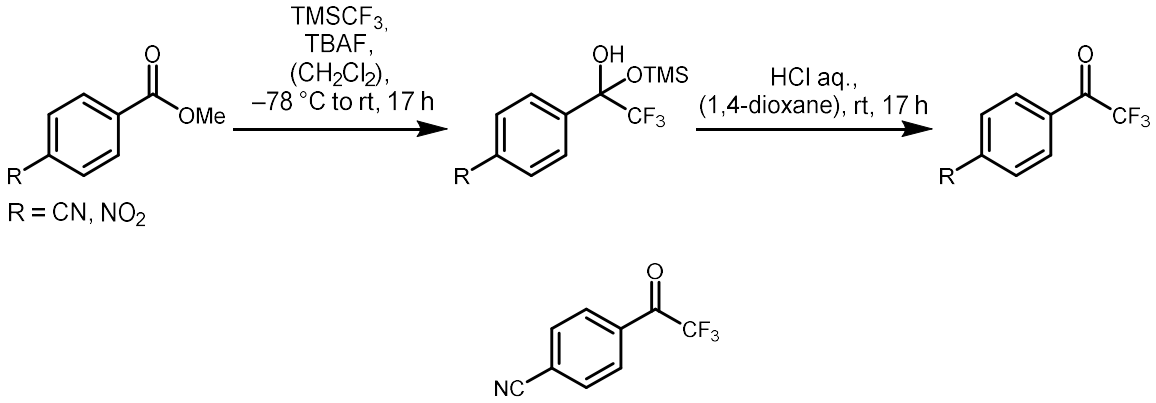



**3-(4-(2-Methyl-1,3-dioxolan-2-yl)phenyl)oxetan-3-ol [1u]**

Following general procedure **B** with minor alterations using oxetan-3-one (340 µL, 5.33 mmol, 1.20 eq.), *n*-BuLi (2.50 M, 1.78 mL, 4.44 mmol, 1.00 eq.) and 2-(4-bromophenyl)-2-methyl-1,3-dioxolane (1.08 g, 4.44 mmol, 1.00 eq.). The desired product was obtained after recrystallization (petroleum ether:EtOAc) as a colorless solid (863 mg, 3.65 mmol, 82%).

**M.P.**: 128 – 129 °C. **IR (neat)**: $\tilde{\nu}$ = 3362 (m), 2891 (w), 1423 (w), 1373 (w), 1455 (w), 1226 (w), 1194 (m), 1097 (m), 1036 (s), 1013 (m), 963 (s), 952 (m), 873 (m), 830 (m), 656 (m). **$^1$H NMR (600 MHz, DMSO-$d_6$)**: $\delta$ = 7.60 – 7.56 (m, 2H, C$H_{arom.}$), 7.45 – 7.42 (m, 2H, C$H_{arom.}$), 6.35 (s, 1H, O*H*), 4.77 – 4.74 (m, 2H, C$H_2$), 4.69 – 4.65 (m, 2H, C$H_2$), 4.01 – 3.95 (m, 2H, C$H_2$), 3.71 – 3.64 (m, 2H, C$H_2$), 1.55 (s, 3H, C$H_3$). **$^{13}$C NMR (151 MHz, DMSO-$d_6$)**: $\delta$ = 143.8 ($C_q$), 142.2 ($C_q$), 125.0 (*C*H), 124.5 (*C*H), 108.1 ($C_q$), 85.3 ($CH_2$), 73.9 ($C_q$), 64.1 ($CH_2$), 27.4 ($CH_3$). **HRMS (APCI)**: Calculated for $C_{13}H_{17}O_4$ $[M+H]^+$: 237.1127, Found: 273.1123.

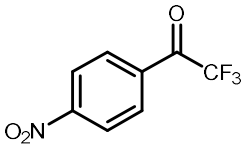
## 1.4. Synthesis of trifluoroacetophenone derivatives




### 4'-Cyano-2,2,2-trifluoroacetophenone [6d]

According to a literature known protocol with minor alterations,[24] methyl 4-cyanobenzoate (1.00 g, 6.21 mmol, 1.00 eq.) and trifluoromethyl-trimethylsilane (1.53 mL, 10.3 mmol, 1.66 eq.) were dissolved in dry $CH_2Cl_2$ (60 mL) under Argon atmosphere and cooled to –78 °C. tetrabutylammoniumfluoride (1M in THF, 370 µL, 0.37 mmol, 6 mol%) was added slowly. After 1 h at –78 °C the solution was allowed to warm up to rt over 17 h. $NH_4Cl$ aq. was added to the reaction mixture and the aqueous phase was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The resulting oil was redissolved in a mixture of 1,4-dioxane:HCl:$H_2O$ (3:1:1, 6 mL) and stirred for 17 h at rt After removal of the solvent *in vacuo* the product was obtained after FC (pentane:EtOAc, 10:1 to 4:1) as a pale yellow solid (263 mg, 1.32 mmol, 21%).

**$^1$H NMR** (400 MHz, $C_6D_6$): $\delta$ = 7.39 – 7.31 (m, 2H, C$H_{arom.}$), 6.81 – 6.75 (m, 2H, C$H_{arom.}$). **$^{13}$C NMR** (101MHz, $C_6D_6$): $\delta$ = 179.3 (q, $^2J_{C\text{-}F}$ = 35.8 Hz, $C_q$), 132.4 (CH), 132.2 ($C_q$), 129.9 (q, $^4J_{C\text{-}F}$ = 2.2 Hz), 118.6 ($C_q$), 117.4 ($C_q$), 116.74 (q, $^1J_{C\text{-}F}$ = 291.1 Hz). **$^{19}$F NMR** (377 MHz, $C_6D_6$): $\delta$ = – 71.6 (*s*, $CF_3$). Obtained spectroscopic data are in agreement to those previously reported.[25]

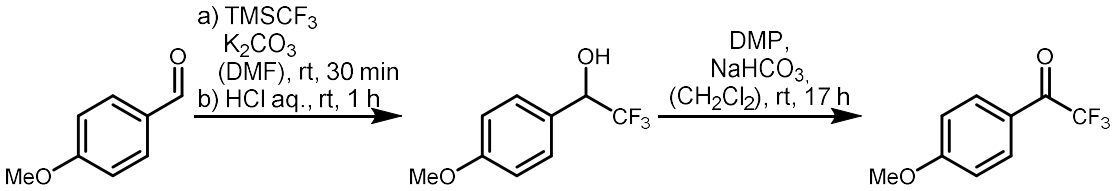



### 4'-Nitro-2,2,2-trifluoroacetophenone [6e]

According to a literature known protocol with minor alterations,[24] methyl 4-nitrobenzoate (3.00 g, 16.6 mmol, 1.00 eq.) and trifluoromethyltrimethylsilane (4.07 mL, 27.5 mmol, 1.66 eq.) were dissolved in dry $CH_2Cl_2$ (150 mL) under Argon atmosphere and cooled to –78 °C. tetrabutylammoniumfluoride (1M in THF, 550 µL, 0.55 mmol, 6 mol%) was added slowly. After 1 h at –78 °C the solution was allowed to warm up to rt over 17 h. $NH_4Cl$ aq. was added to the reaction mixture and the aqueous phase was extracted with $CH_2Cl_2$ (3x 50 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The resulting oil was

redissolved in a mixture of 1,4-dioxane:HCl:$H_2O$ (3:1:1, 20 mL) and stirred for 17 h at rt. After removal of the solvent *in vacuo* the product was obtained after FC (pentane:EtOAc, 3:1 to 1:1) as a pale yellow solid (1.91 g, 8.81 mmol, 53%).

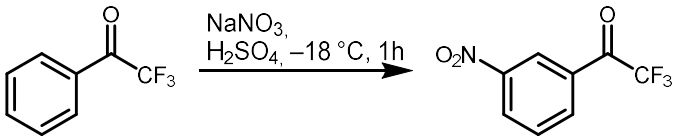
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ = 8.45 – 8.37 (*m*, 2H, C*H*$_{arom.}$), 8.30 – 8.23 (*m*, 2H, C*H*$_{arom.}$). **$^{13}$C NMR** (151MHz, $CDCl_3$): $\delta$ = 179.5 (*q*, $^2J_{C\text{-}F}$ = 36.6 Hz, *C*=O), 151.7 ($C_q$), 134.4 ($C_q$), 131.4 (*q*, $^4J_{C\text{-}F}$ = 2.2 Hz, *C*H), 124.4 (*C*H), 116.4 (*q*, $^1J_{C\text{-}F}$ = 290.8 Hz, *C*$F_3$). **$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ = – 71.8 (*s*, C*F*$_3$). Obtained spectroscopic data are in agreement to those previously reported.[26]




**4'-Methoxy-2,2,2-trifluoroacetophenone [S15]**

4-Methoxy benzaldehyde (1.00 g, 7.34 mmol, 1.00 eq.), $K_2CO_3$ (10 mg, 73 µmol, 0.01 eq.) and trifluoromethyltrimethylsilane (1.30 mL µL, 8.81 mmol, 1.20 eq.) were dissolved in dry DMF (70 mL) according to a literature known procedure.(citation) After 30 min at rt HCl aq. (1N, 30 mL) was added and the mixture was stirred for 1 h at rt before $Et_2O$ (30 mL) was added. The organic phase was separated and the aqueous phase was extracted with $Et_2O$ (3x30 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was dissolved in dry $CH_2Cl_2$ (70 mL) and *Dess-Martin* periodinane (7.47 g, 17.6 mmol, 2.40 eq.) and $NaHCO_3$ (2.47 g, 29.4 mmol, 4.00 eq.) were added. The mixture was stirred at rt for 17 h before $Na_2S_2O_3$ sat. and $NaHCO_3$ sat. were added. The mixture was filtered over celite. The organic phase was separated, and the aqueous phase was extracted with $CH_2Cl_2$ (3x30 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product was obtained after FC (pentane:$Et_2O$, 10:1) as a colourless oil (263 mg, 1.32 mmol, 21%)

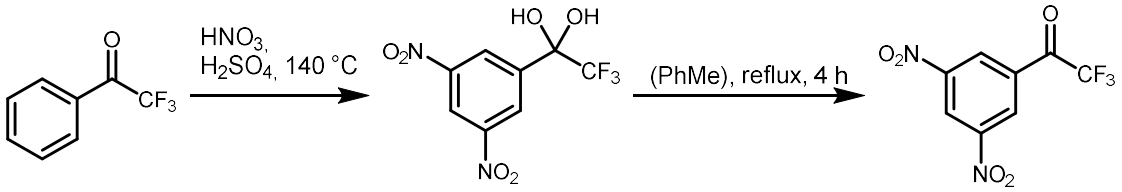
**$^1$H NMR** (300 MHz, $CDCl_3$): $\delta$ = 8.12 – 8.01 (*m*, 2H, C*H*$_{arom.}$), 7.07 – 6.95 (*m*, 2H, C*H*$_{arom.}$). **$^{13}$C NMR** (101MHz, $CDCl_3$): $\delta$ = 179.09 (*q*, $^2J_{C\text{-}F}$ = 34.5 Hz, *C*=O), 165.56 ($C_q$), 132.90 (*q*, $^4J_{C\text{-}F}$ = 2.2 Hz, *C*H), 122.96 ($C_q$), 117.07 (*q*, $^1J_{C\text{-}F}$ = 291.5 Hz, *C*$F_3$), 114.59 (*C*H), 55.85 (O*C*$H_3$). **$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ = – 70.9 (*s*, C*F*$_3$). Obtained spectroscopic data are in agreement to those previously reported.[27]




**3'-Nitro-2,2,2-trifluoroacetophenone [S16]**

According to a literature known procedure[28] 2,2,2,-trifluoroacetophenone (500 µL, 3.56 mmol, 1.00 eq.) was dissolved in $H_2SO_4$ conc. (35 mL) and $NaNO_3$ (317 mg, 3.74 mmol, 1.05 eq.) was added portionwise at –18 °C and stirred for 1 h before the reaction mixture was warmed up to rt The mixture was poured on ice and treated with KOH aq. (1 N) until the pH reached 10. The aqueous phase was extracted with $CH_2Cl_2$:iPrOH (4:1, 3x 15 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product was obtained after FC (pentane:EtOAc, 5:1) as a pale brown solid (347 mg, 1.58 mmol, 44%)

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ = 8.92 (*s*, 1H, C*H*$_{arom.}$), 8.58 (*ddd*, *J* = 8.2, 2.2, 1.1 Hz, 1H, C*H*$_{arom.}$), 8.45 – 8.35 (*m*, 1H, C*H*$_{arom.}$), 7.82 (app *t*, *J* = 8.1 Hz, 1H, C*H*$_{arom.}$). **$^{13}$C NMR** (101MHz, $CDCl_3$): $\delta$ = 135.4 (*q*, *J* = 2.1 Hz, *C*H), 131.3 (*C*$_q$), 130.8 (*C*H), 129.8 (*C*H), 125.1 (*q*, *J* = 2.4 Hz, *C*H), 116.4 (*q*, $^1J_{C\text{-}F}$ = 290.5 Hz, *C*$F_3$). One signal missing. Obtained spectroscopic data are in agreement to those previously reported.[28]




**3'5'-Dinitro-2,2,2-trifluoroacetophenone monohydrate [13]**

2,2,2, Trifluoroacetophenone (2.00 g, 11.5 mmol, 1.00 eq.) was dissolved in $H_2SO_4$ conc. (50 mL) and $HNO_3$ aq. (65%, 15 mL) was added slowly at 0 °C and stirred for 30 min before the reaction mixture was heated to 130 °C. After 4 h the reaction mixture was cooled down to rt before another portion of $HNO_3$ aq. (65%, 15 mL) was added. The solution was refluxed at 130 °C for 3 d before it was poured on ice. The aqueous phase was extracted with $Et_2O$ (3 x 25 mL) and the organic phase was carefully washed with $NaHCO_3$ sat. until no gas evolution was observed. The organic phase was dried over $K_2CO_3$ and the solvent was removed *in vacuo*. The crude product was recrystallised from $H_2O$ to yield the hydrate as colourless crystals (1.12 g, 3.95 mmol, 34%).

**M.P.**: 84 – 85 °C. **IR (neat)**: $\tilde{\nu}$ = 3479 (w), 3107 (w), 2357 (w), 1632 (w), 1542 (s), 1345 (s), 1260 (w),1180 (s), 1153 (m), 1116 (m), 1075 (s), 972 (w), 916 (m), 773 (w), 732 (s), 712 (s), 678 (m). **$^1$H NMR** (400 MHz, $(CD_3)_2SO$): $\delta$ = 8.91 (t, $^4J_{H\text{-}H}$ = 2.1 Hz, 1H, C*H*$_{arom.}$), 8.67 (d, $^4J_{H\text{-}H}$ = 2.1 Hz, 2H, C*H*$_{arom.}$), 8.45 (s, 2H, O*H*). **$^{13}$C NMR** (101 MHz, $(CD_3)_2SO$): $\delta$ = 148.0 (*C*$_q$), 142.7 (*C*$_q$), 127.4 (*C*H), 122.8 (q, $^1J_{C\text{-}F}$ = 289.0 Hz), 119.7 (*C*H), 91.8 (q, $^2J_{C\text{-}F}$ = 32.0 Hz). **$^{19}$F NMR** (376 MHz, $(CD_3)_2SO$): $\delta$ = – 82.6 (*s*, C*F*$_3$). **HRMS (APCI)**: Calculated for $C_8H_4F_3N_2O_6$ [M-H]$^-$: 281.0021, Found: 281.0027.

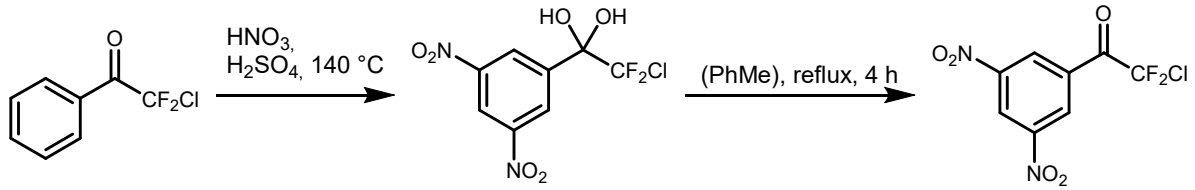
The protons of the OH-groups could be identified through $^{1}H,^{1}H$-EXSY correlation to the signals of residual water.

A sample of Hydrate [**13**] suitable for X-ray analysis was obtained after dissolving 3'5'-dinitro-2,2,2-trifluoroacetophenone [**2**] in $CDCl_3$ and slowly evaporating the solvent open to air.

### 3'5'-Dinitro-2,2,2-trifluoroacetophenone [2]

3'5'-Dinitro-2,2,2-trifluoroacetophenone monohydrate [**13**] was refluxed with toluene in a *Dean-Stark* apparatus for 4 h. The water-free product was obtained as a light yellow solid (quantitative conversion of the hydrate)

**M.P.**: 70 – 71 °C. **IR (neat)**: $\tilde{\nu}$ = 3103 (w), 1741 (m), 1631 (m), 1545 (s), 1461 (w), 1345 (s), 1204 (s), 1149 (s), 1121 (s), 1079 (w), 1010 (s), 921 (m), 773 (w), 730 (s), 720 (s), 703(s). **$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ = 9.37 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 9.19 (dd, $J$ = 2.0, 0.9 Hz, 2H, C$H_{arom.}$).**$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ = 177.4 (q, $^{2}J_{C\text{-}F}$ = 38.0 Hz, $C_q$), 149.3 ($C_q$), 132.6 ($C_q$), 129.6 (q, $^{4}J_{C\text{-}F}$ = 2.2 Hz, *C*H), 124.5 (*C*H), 116.0 (q, $^{1}J_{C\text{-}F}$ = 290.2 Hz, *C*$F_3$). **$^{19}$F NMR** (377 MHz, $CDCl_3$): $\delta$ = – 71.8 (*s*, C$F_3$). **HRMS (APCI)**: Calculated for $C_8H_3F_3N_2O_5$ $[M]^{-}$: 263.9994, Found: 263.9968.



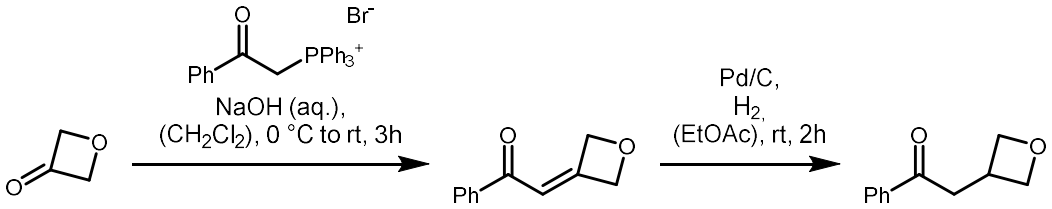

### 3'5'-Dinitro-2,2-difluoro-2-chloroacetophenone [17]

2,2-Difluoro-2-chloroacetophenone (2.00 g, 10.5 mmol, 1.00 eq.) was dissolved in $H_2SO_4$ conc. (50 mL) and $HNO_3$ aq. (65%, 10 mL) was added slowly at 0 °C and stirred for 30 min before the reaction mixture was heated to 100 °C. After 3 h the reaction mixture was cooled down to rt before another portion of $HNO_3$ aq. (65%, 10 mL) was added. The solution was refluxed at 140 °C for 3 d before it was poured on ice. The aqueous phase was extracted with $Et_2O$ (3 x 100 mL) and the organic phase was carefully washed with $NaHCO_3$ sat. until no gas evolution was observed. The organic phase was dried over $K_2CO_3$ and the solvent was removed *in vacuo*. The crude product was recrystallised from $H_2O$ and the 3'5'-Dinitro-2,2-difluoro-2-chloroacetophenone monohydrate was separated *via* automated FC ($CH_2Cl_2$ to CyH:EtOAc, 40:60) and afterwards refluxed with toluene in a *Dean-Stark* apparatus for 4 h. The water-free product was obtained as a light yellow solid (685 mg, 2.44 mmol, 23%).

**M.P.**: 32 – 33 °C. **IR (neat)**: $\tilde{\nu}$ = 3101 (w), 1735 (m), 1629 (m), 1546 (s), 1345 (s), 1281 (w), 1190 (m), 1147 (m), 1121 (m), 1026 (m), 942 (m), 838 (w), 730 (s), 706 (s). **$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ = 9.36 – 9.34 (m, 1H, C$H_{arom.}$), 9.25 – 9.23 (m, 2H, C$H_{arom.}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ = 177.8 (t, $^{3}J_{C\text{-}F}$ = 31.5 Hz, $C_q$), 149.1 ($C_q$), 132.2 ($C_q$), 130.0 (t, $^{5}J_{C\text{-}F}$ = 2.8 Hz, *C*H), 124.2 (*C*H), 119.4 (t, $^{2}J_{C\text{-}F}$ = 303.9 Hz, *C*$F_2$Cl).

**$^{19}$F NMR** (282 MHz, $CDCl_3$): $\delta$ = – 62.1 (*s*, C*F*$_2$Cl). **HRMS (APCI)**: Calculated for $C_9H_4ClF_2N_2O_7$ $[M+HCOO]^-$: 324.9675, Found: 324.9676.

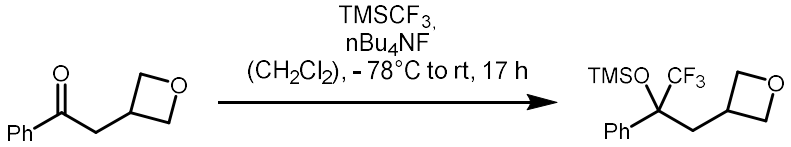
## 1.5. Carbinol synthesis




### 2-(Oxetan-3-ylidene)-1-phenylethan-1-one [S17]

2-(oxetan-3-ylidene)-1-phenylethan-1-one was prepared following a lab own procedure. Phenacyltriphenylphosphoniumbromide (5.07 g, 11.0 mmol, 1.10 eq.) was dissolved in $CH_2Cl_2$ (14 mL), NaOH (2N, 14 mL) was added and the mixture was stirred vigorously for 15 min. The organic phase was separated and cooled to 0 °C before a solution of 3-oxetanone (640 µL, 10.0 mmol, 1.00 eq.) in $CH_2Cl_2$ (5 mL) was added slowly. The mixture was stirred at rt after complete addition for 3 h, after which time the solvent was removed. The residue was taken up in $Et_2O$:petroleum ether (1:1, 15 mL) and the precipitate was filtered off and washed with $Et_2O$:petroleum ether (1:1). The filtrate was reduced and redissolved in EtOAc (10 mL) under inert atmosphere, then Pd/C (5% w/w, 213 mg, 0.10 mmol, 1.00 mol%) was added. The atmosphere was changed to $H_2$ and $H_2$ was bubbled through the solution for 10 min. The mixture was stirred for 2 h at rt before the solids were filtered off. The solvent was removed and the product was obtained as a colorless wax-like solid (482 mg, 2.74 mmol, 27%) after FC (EtOAc:CyH, 20:80)

**M.P.**: < 35 °C. **IR (neat)**: $\tilde{\nu}$ = 2968 (w), 2871 (w), 1474 (s), 1595 (w), 1449 (w), 1408 (w), 1350 (w), 1230 (w), 1212 (w), 965 (s), 949 (w), 859 (w), 762 (s), 690 (s), 671(w). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 7.73 – 7.66 (m, 2H, C$H_{arom.}$), 7.15 – 7.11 (m, 1H, C$H_{arom.}$), 7.07 – 7.02 (m, 2H, C$H_{arom.}$), 4.77 (dd, J = 7.8, 6.0 Hz, 2H, C$H_2$), 4.19 (t, J = 6.2 Hz, 2H, C$H_2$), 3.17 (pt, J = 7.7, 6.3 Hz, 1H, C$H$), 2.64 (d, J = 7.5 Hz, 2H, C$H_2$).**$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 197.3 ($C_q$), 137.2 ($C_q$), 132.9 (CH), 128.6 (CH), 128.2 (CH), 76.9 ($CH_2$), 42.3 ($CH_2$), 31.3 (CH). **HRMS (ESI)**: Calculated for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0916, Found: 177.0911.

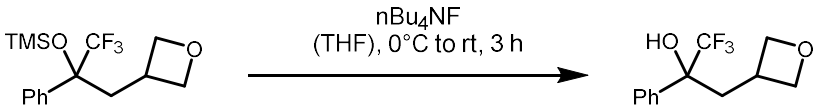



### Trimethyl((1,1,1-trifluoro-3-(oxetan-3-yl)-2-phenylpropan-2-yl)oxy)silane [S18]

The trifluoromethylation was conducted according to a literature known protocol with minor changes.[24] 2-(oxetan-3-ylidene)-1-phenylethan-1-one (250 mg, 1.42 mmol, 1.00 eq.) and trifluoromethyltrimethylsilane (350 µL, 2.36 mmol, 1.66 eq.) were dissolved in dry $CH_2Cl_2$ (15 mL) and cooled to –78 °C before TBAF (1M in THF, 43 µL, 0.43 mmol, 3.00 mol%) was added slowly. The mixture was stirred at –78 °C for 2 h and was warmed up to rt over 17 h. $NH_4Cl$ sat. (10 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3x15 mL). The combined organic

fractions were dried over $Na_2SO_4$. The product was obtained after filtration through silica with $CH_2Cl_2$ as a colorless solid (374 mg, 1.17 mmol, 83%).

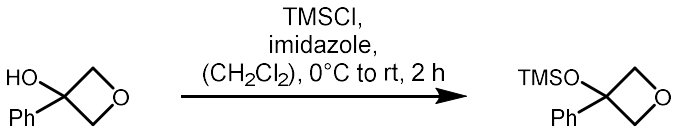
**M.P.**: 54–55 °C. **IR (neat)**: $\tilde{\nu}$ = 2968 (w), 1268 (w), 1256 (w), 1167 (s), 978 (w), 915 (w), 844 (s), 759 (w), 697 (w), 670 (m), 656 (m). **$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.48 – 7.43 (m, 2H, C$H_{arom.}$), 7.39 – 7.30 (m, 3H, C$H_{arom.}$), 4.62 (dd, $J$ = 8.3, 5.9 Hz, 1H, C$H_2$), 4.47 (dd, $J$ = 7.6, 5.9 Hz, 1H, C$H_2$), 4.13 (dd, $J$ = 8.1, 6.1 Hz, 1H, C$H_2$), 4.02 (dd, $J$ = 7.4, 6.1 Hz, 1H, C$H_2$), 3.16 – 3.00 (m, 1H, C$H_2$), 2.52 – 2.27 (m, 2H, C$H_{2f}$), 0.21 (s, 9H, C$H_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 137.9 ($C_q$), 128.5 (*C*H), 128.3 (*C*H), 126.3 (*C*H), 125.6 (q, $^1J_{C\text{-}F}$ = 287.4 Hz, *C*$F_3$), 79.9 (d, $^2J_{C\text{-}F}$ = 28.2 Hz, $C_q$), 77.7 (*C*$H_2$), 40.2 (*C*$H_2$), 30.6 (*C*H), 1.9 (*C*$H_3$).**$^{19}$F NMR (377 MHz, $CDCl_3$)** $\delta$ = – 76.4 (s, 3F, C$F_3$). **HRMS (ESI)**: Calculated for $C_{15}H_{22}F_3O_2Si$ $[M+H]^+$: 319.1341, Found: 319.1328.




**1,1,1-Trifluoro-3-(oxetan-3-yl)-2-phenylpropan-2-ol [11]**

1,1,1-trifluoro-3-(oxetan-3-yl)-2-phenylpropan-2-ol was prepared following a literature known protocol[29] by dissolving trimethyl((1,1,1-trifluoro-3-(oxetan-3-yl)-2-phenylpropan-2-yl)oxy)silane (250 mg, 0.785 mmol, 1.00 eq.) in THF (10 mL) and cooling to 0 °C before TBAF (1N in THF, 785 µL, 1.00 eq.) was added. The mixture was stirred for 1 h at 0 °C and for 2 h at rt before $NH_4Cl$ sat. (10 mL) was added. The organic phase was separated, and the aqueous phase was extracted with $CH_2Cl_2$ (3x10 mL). The combined organic fractions were dried over $Na_2SO_4$ and the solvent was removed. The product was obtained after FC (EtOAc:CyH, 20:80) as a slightly yellow solid (154 mg, 0.625 mmol, 80%).

**M.P.**: 87–88 °C. **IR (neat)**: $\tilde{\nu}$ = 3269 (w), 2968 (w), 1273 (w), 1164 (s), 1020 (w), 965 (w), 957 (w), 914 (m), 767 (w), 704 (s), 661 (s), 634 (s), 618 (s). **$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.50 – 7.45 (m, 2H, C$H_{arom.}$), 7.42 – 7.33 (m, 3H, C$H_{arom.}$), 4.64 (dd, $J$ = 8.2, 6.1 Hz, 1H, C$H_2$), 4.49 (dd, $J$ = 7.2, 6.1 Hz, 1H, C$H_2$), 4.29 (dd, $J$ = 8.2, 6.1 Hz, 1H, C$H_2$), 4.10 (dd, $J$ = 7.2, 6.1 Hz, 1H, C$H_2$), 3.12 – 3.03 (m, 1H, C*H*), 3.03 (s, 1H, O*H*), 2.48 – 2.34 (m, 1H, C$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 136.4 ($C_q$), 128.8 (*C*H), 128.6 (*C*H), 125.8 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 125.7 (q, $^1J_{C\text{-}F}$ = 286.0 Hz), 77.9 (*C*$H_2$), 77.4 (*C*$H_2$), 77.2 (q, $^2J_{C\text{-}F}$ = 28.1 Hz), 39.3 (*C*$H_2$), 30.3 (*C*H). **$^{19}$F NMR (377 MHz, $CDCl_3$)** $\delta$ = – 79.5 (s, 3F, C$F_3$).




**Trimethyl((3-phenyloxetan-3-yl)oxy)silane [S19]**

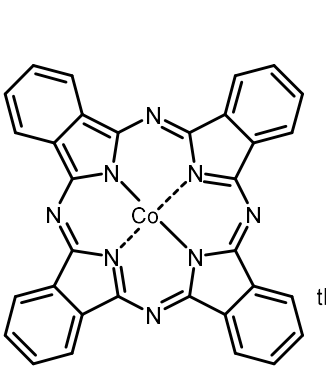
3-phenyloxetan-3-ol (50.0 mg, 0.33 mmol, 1.00eq.) and imidazole (68.0 mg, 1.00 mmol, 3.00 eq.) were dissolved in $CH_2Cl_2$ (6 mL) and cooled to 0 °C according to a literature known protocol[30] before TMSCl (105 µL, 0.832 mmol, 2.50 eq.) was added slowly. The mixture was allowed to warm up to rt over 2 h before $NH_4Cl$ sat. (5 mL) and $CH_2Cl_2$ (5 mL) were added. The organic phase was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3x5 mL). The combined organic fractions were dried over $Na_2SO_4$ and the solvent was removed. The crude material was filtered through silica with $CH_2Cl_2$ to yield the product as a colorless oil (65 mg, 0.292 mmol, 88%).

**IR (neat)**: $\tilde{\nu}$ = 3057 (w), 2955 (w), 1448 (w), 1277 (w), 1254 (m), 1190 (m), 1079 (w), 985 (m), 916 (w), 845 (s), 758 (s), 700 (s), 657 (w), 641 (w), 624 (s). **$^1$H NMR (400 MHz, $CDCl_3$)**: $\delta$ = 7.61 – 7.56 (m, 2H, C*H*$_{arom.}$), 7.43 – 7.38 (m, 2H, C*H*$_{arom.}$), 7.34 – 7.29 (m, 1H, C*H*$_{arom.}$), 5.05 – 4.99 (m, 2H, C*H*$_2$), 4.83 – 4.80 (m, 2H, C*H*$_2$), 0.09 (s, 9H, C*H*$_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)**: $\delta$ = 144.0 (*C*$_q$), 128.6 (*C*H), 127.7 (*C*H), 124.9 (*C*H), 86.0 (*C*$H_2$), 1.6 (*C*$H_3$). **HRMS (ESI)**: Calculated for $C_{12}H_{19}O_2Si$ $[M+H]^+$: 223.1154, Found: 223.1141.

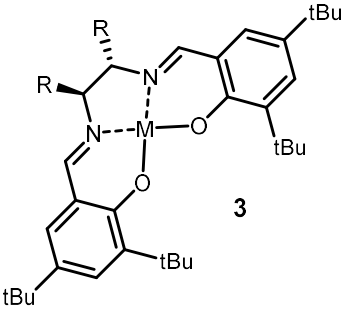
## 2. Optimization of the asymmetric oxetane ring-opening

### Optimization tables

Used catalysts during the optimization:

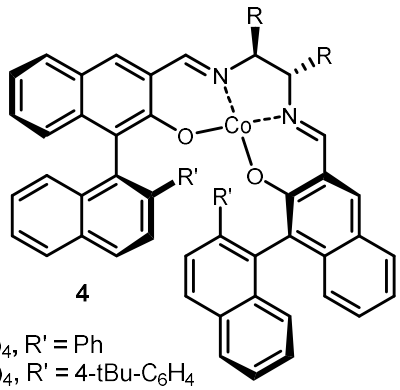


Co(phthalocyanine)



3

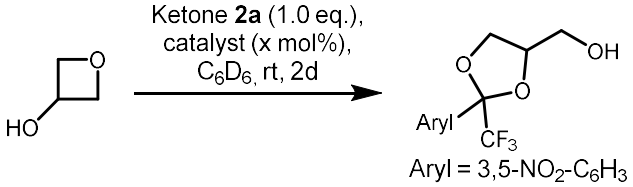
**3a** R = H, M = Co
**3b** R = $(CH_2)_4$, M = Co
**3c** R = $(CH_2)_4$, M = Co-OTf
**3d** R = Ph, M = Co
**3f** R = $(CH_2)_4$, M = Mn-Cl
**3g** R = $(CH_2)_4$, M = Al-Cl



4

**4a** R = $(CH_2)_4$, R' = Ph
**4b** R = $(CH_2)_4$, R' = 4-tBu-$C_6H_4$
**4c** R = Ph, R' = Ph

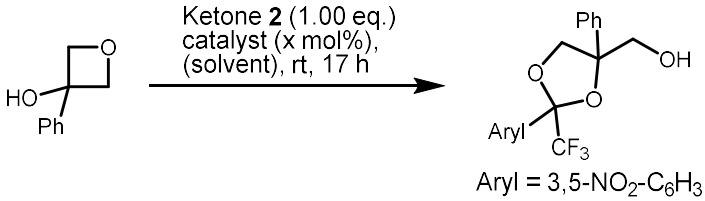
Table 1: Initial findings for ring-opening reactions of oxetanes, conversion based on $^{19}F$ NMR experiments.




Aryl = 3,5-$NO_2$-$C_6H_3$

| entry | catalyst | equivalents | conversion |
|---|---|---|---|
| 1 | $Co^{II}$·salen **3a** | 1 mol% | 95% |
| 2 | $Co^{II}$·salen **3b** | 1 mol% | 92% |
| 3 | (TfO)$Co^{III}$ salen **3c** | 1 mol% | <5% |
| 4 | $Co^{II}$ (phthalocyanine) | 1 mol% | 0% |
| 5 | $Co(acac)_2$ | 1 mol% | 0% |
| 6 | $Co(acac)_3$ | 1 mol% | 0% |
| 7 | $Sc(OTf)_3$ premixed with 15 mol% Bn-Box ligand | 10 mol% | 0% |
| 8 | (Cl)$Mn^{III}$·salen **3f** | 1 mol% | <5% |
| 9 | (Cl)Al·salen **3g** | 1 mol% | <5% |
| 10 | (R)-3,3′-Bis-(9-anthracenyl)-1,1′-binaphthyl-2,2′-diyl-hydrogenphosphat | 10 mol% | 0% |
| 11 | (R)-3,3′-Bis-(2,4,6-triisopropyl-phenyl)-1,1′-binaphthyl-2,2′-diyl-hydrogenphosphat | 5 mol% | 0% |
| 12 | (R)-3,3′-Bis-(2,4,6-triethyl-phenyl)-1,1′-binaphthyl-2,2′-diyl-hydrogenphosphat | 5 mol% | 0% |

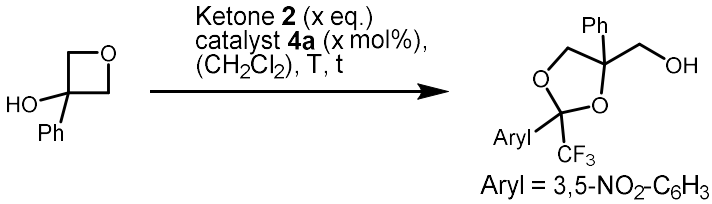
Table 2: Solvent and catalyst optimization, reactions were carried out on a 0.1 mmol scale in 0.5 mL solvent, yield and *dr* based on $^{19}F$ NMR experiments using trifluorotoluene as an internal standard, *er* determined *via* chiral HPLC analysis.




Aryl = 3,5-$NO_2$-$C_6H_3$

| entry | solvent | catalyst | catalyst loading | yield | *dr* | *er* |
|---|---|---|---|---|---|---|
| 1 | $C_6D_6$ | **3b** | 2 mol% | 92% | 79:21 | 60:40 |
| 2 | $CH_2Cl_2$ | **3b** | 2 mol% | > 98% | 79:21 | 60:40 |
| 3 | $CH_3CN$ | **3b** | 2 mol% | > 98% | 79:21 | 60:40 |
| 4 | MTBE | **3b** | 2 mol% | 50% | 80:20 | 60:40 |
| 5 | $CH_2Cl_2$ | **3a** | 1 mol% | 95% | 76:24 | - |
| 6 | $CH_2Cl_2$ | **3c** | 1 mol% | < 5% | n.d. | n.d. |
| 7 | $CH_2Cl_2$ | **3d** | 1 mol% | 48% | 78:22 | 60:40 |
| 8 | $CH_2Cl_2$ | **4a** | 1 mol% | 90% | 90:10 | 75:25 |
| 9 | $CH_2Cl_2$ | *epi*-**4a** | 1 mol% | 52% | 90:10 | 58:42 |
| 10 | $CH_2Cl_2$ | **4b** | 1 mol% | 88% | 96:4 | 86:14 |
| 11 | $CH_2Cl_2$ | **4c** | 1 mol% | < 5% | n.d. | n.d. |
| 12 | $CH_2Cl_2$ | *epi*-**4c** | 1 mol% | < 5% | n.d. | n.d. |

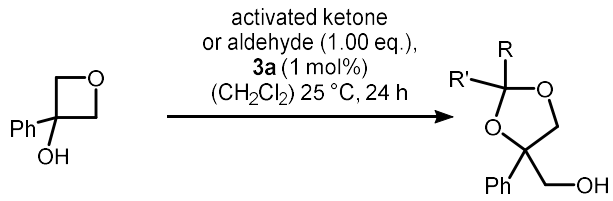
Table 3 Catalyst loading and temperature optimization, reactions were carried out on a 0.1 mmol scale in varying concentrations with catalyst **4a,** yield and *dr* based on $^{19}F$ NMR experiments using trifluoro-toluene as an internal standard.



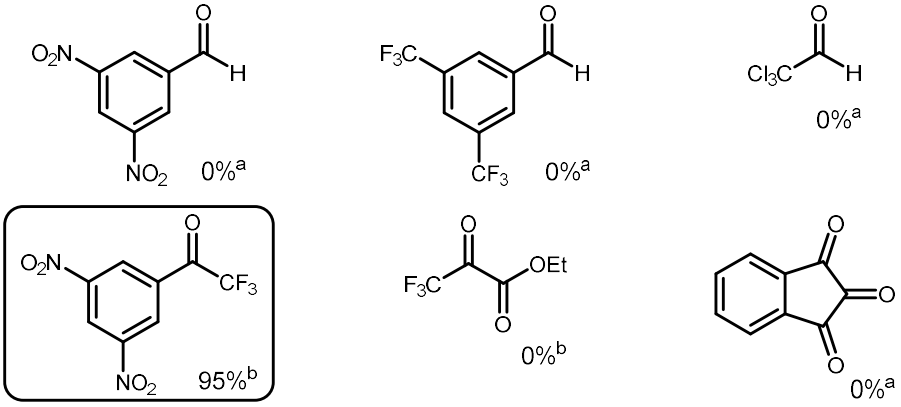

Aryl = 3,5-$NO_2$-$C_6H_3$

| Entry | equivalents of **2** | catalyst loading | T | t | concentration | yield | *dr* |
|---|---|---|---|---|---|---|---|
| 1 | 1.00 | 1 mol% | rt | 2.5 h | 0.2 M | 26% | n.d. |
| 2 | 1.20 | 1 mol% | rt | 2.5 h | 0.2 M | 29% | n.d. |
| 3 | 1.40 | 1 mol% | rt | 2.5 h | 0.2 M | 34% | n.d. |
| 4 | 1.00 | 2 mol% | rt | 2.5 h | 0.2 M | 49% | n.d. |
| 5 | 1.00 | 4 mol% | rt | 2.5 h | 0.2 M | 87% | n.d. |
| 6 | 1.00 | 1 mol% | 5 °C | 17 h | 0.2 M | 50% | 96:4 |
| 7 | 1.00 | 1 mol% | –20 °C | 17 h | 0.2 M | 23% | 96:4 |
| 8 | 1.00 | 1 mol% | rt | 4 h | 0.8 M | 49% | n.d. |
| 9 | 1.00 | 1 mol% | rt | 4 h | 0.05 M | 40% | n.d. |

Table 4 Optimisation of reactive carbonyl compound, reactions were carried out on a 0.1 mmol scale, yield based on NMR experiments with internal standard.




**1a**

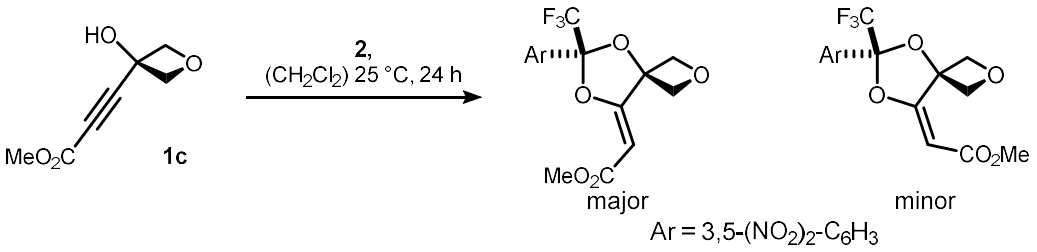



[a] yield based on $^{1}H$ NMR experiments using mesitylene as internal standard

[b] yield based on $^{19}F$ NMR experiments using trifluorotoluene as internal standard

## 3. Mechanistic experiments

### Uncatalyzed oxy-Michael addition to oxetanes bearing activated alkyne substituents




### Methyl 2-(6-(3,5-dinitrophenyl)-6-(trifluoromethyl)-2,5,7-trioxaspiro[3.4]octan-8-ylidene)acetate [*rac*-10c]

Ketone [**2**] (26.4 mg, 0.10 mmol, 1.00 eq.) and methyl 3-(3-hydroxyoxetan-3-yl)propiolate (15.6 mg, 0.10 mmol, 1.00 eq.) were dissolved in dry $CH_2Cl_2$ (0.50 mL) at room temperature. The temperature was maintained for 24 h before silica gel was added and filtered off. The resulting silica gel plug was flushed with $Et_2O$, and the filtrate was concentrated. NMR yield and *rr* of the crude reaction mixture was determined by $^{19}F$ NMR using $PhCF_3$ (12.2 µL, 0.10 mmol) as the internal standard. A mixture of both configurational isomers was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 70:30) as an off-white solid (32.0 mg, 0.080 mmol, 80%, E/Z (40/60)).

**Mixture:**

**M.P.:** 117 – 120 °C. **IR (neat)**: 2961 (w), 2947 (w), 2861 (w), 1589 (m), 1445 (w), 1422 (w), 1333 (w), 1146 (w), 816 (w), 749 (s). **HRMS (APCI):** Calculated for $C_{15}H_{10}F_3N_2O_9$ $[M-H]^-$: 419.0338, Found: 419.0354 **Optical Rotation**: $[\alpha]_D^{25}$ = – 1.5 (*c* = 1.00, $CHCl_3$) for a racemic mixture of both configurational isomers (*E*/*Z* 60/40). The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Amylose-3, 22 °C, 0.5 mL/min, 80:20 hexane:isopropanol, 210 nm, $t_{major}$ = 17.330 min, 18.217 min, $t_{minor}$ = 21.939 min, 31.255 min). See section 15 for HPLC chromatograms. Relative configuration determined *via* NOE-experiments.

**Major *Z*-isomer:**

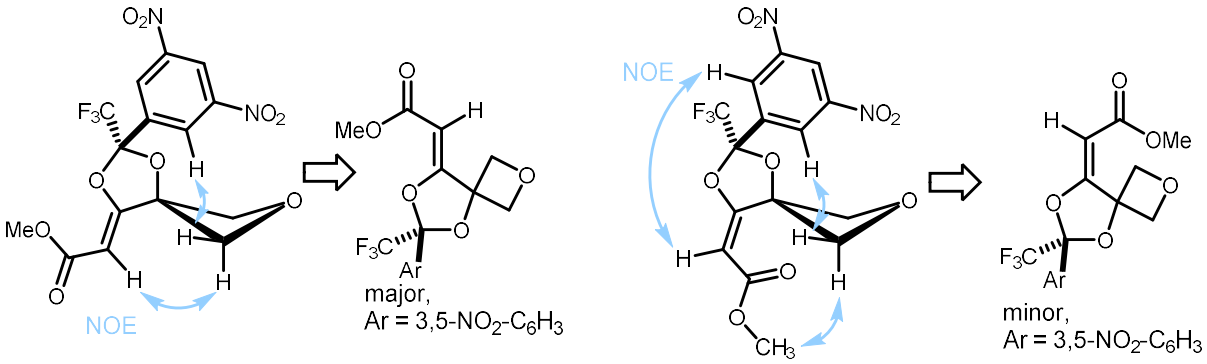
**$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.55 (d, *J* = 2.1 Hz, 2H, C$H_{arom.}$), 8.32 (t, *J* = 2.1 Hz, 1H, C$H_{arom.}$), 5.48 (s, 1H, C*H*), 4.66 (d, *J* = 7.7 Hz, 1H, C$H_2$), 4.41 (dd, *J* = 7.9, 1.1 Hz, 1H, C$H_2$), 4.23 (d, *J* = 7.9 Hz, 1H, C$H_2$), 4.01 (dt, *J* = 7.8, 1.0 Hz, 1H, C$H_2$), 3.45 (s, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 163.6 ($C_q$), 162.4 ($C_q$), 148.4 ($C_q$), 134.5 ($C_q$), 126.4 (*C*H), 121.2 (q, $^1J_{C-F}$ = 289.2 Hz, $CF_3$), 121.1 (*C*H), 106.2 (t, $^2J_{C-F}$ = 34.3 Hz, $C_q$), 92.1 (*C*H), 86.2 ($C_q$), 82.5 (*C*$H_2$), 80.4 (*C*$H_2$), 51.4 (*C*$H_3$). [n] **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 83.36 (s, 3F, C$F_3$).

[n] One signal missing due to signal overlap

**Minor *E*-isomer:**

**$^{1}$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.41 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.36 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 5.61 (s, 1H, C$H$), 5.26 (dd, $J$ = 7.6, 1.1 Hz, 1H, C$H_2$), 5.22 (dd, $J$ = 7.5, 1.0 Hz, 1H, C$H_2$), 4.73 (dt, $J$ = 7.6, 1.1 Hz, 1H, C$H_2$), 4.47 (dd, $J$ = 7.4, 1.2 Hz, 1H, C$H_2$), 3.38 (s, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 165.2 ($C_q$), 162.9 ($C_q$), 148.4 ($C_q$), 134.7 ($C_q$), 126.2 (*C*H), 121.5 (q, $^{1}J_{C\text{-}F}$ = 290.3 Hz, *C*F$_3$), 121.0 (*C*H), 103.7 (t, $^{2}J_{C\text{-}F}$ = 34.2 Hz, $C_q$), 96.7 (*C*H), 89.1 ($C_q$), 80.4 (*C*H$_2$), 79.4 (*C*H$_2$), 51.4 (*C*H$_3$).[o] **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 83.10 (s, 3F, C*F*$_3$).

Relative configuration determined *via* NOE-experiments:




[o] Missing signals under solvent peak

**Hammett-plot of the hemi-ketal formation**

For varying trifluoroacetophenone derivatives the equilibrium position of the formation of hemiketals was examined, therefore the corresponding trifluoroacetophenone (0.1 mmol, 1.00 eq.) was dissolved in dry $CDCl_3$ (700 µL) and 1-pentanol (0.1 mmol, 1.00 eq.) was added. The reaction was monitored by $^{1}H$ NMR and $^{19}F$ NMR spectroscopy until no further conversion was observed. The spectra of 4'-Nitro-2,2,2-trifluoroacetophenone and its hemiketal with 1-pentanol are shown below to demonstrate the chemical shifts of the ketone and hemiketal. In case of very electron-poor trifluoroacetophenone derivates a small amount, typically less than 2%, is converted to the hydrate due to a trace amount of water in the used solvent.

Hemiketal **[10e]** could be prepared by following the same protocol using 4'-Nitro-2,2,2-trifluoroacetophenone **[6e]** (0.1 mmol, 1.00 eq.) and benzyl alcohol (0.1 mmol, 1.00 eq.). The solvent of the reaction mixture was slowly evaporated to yield a sample suitable for X-ray analysis

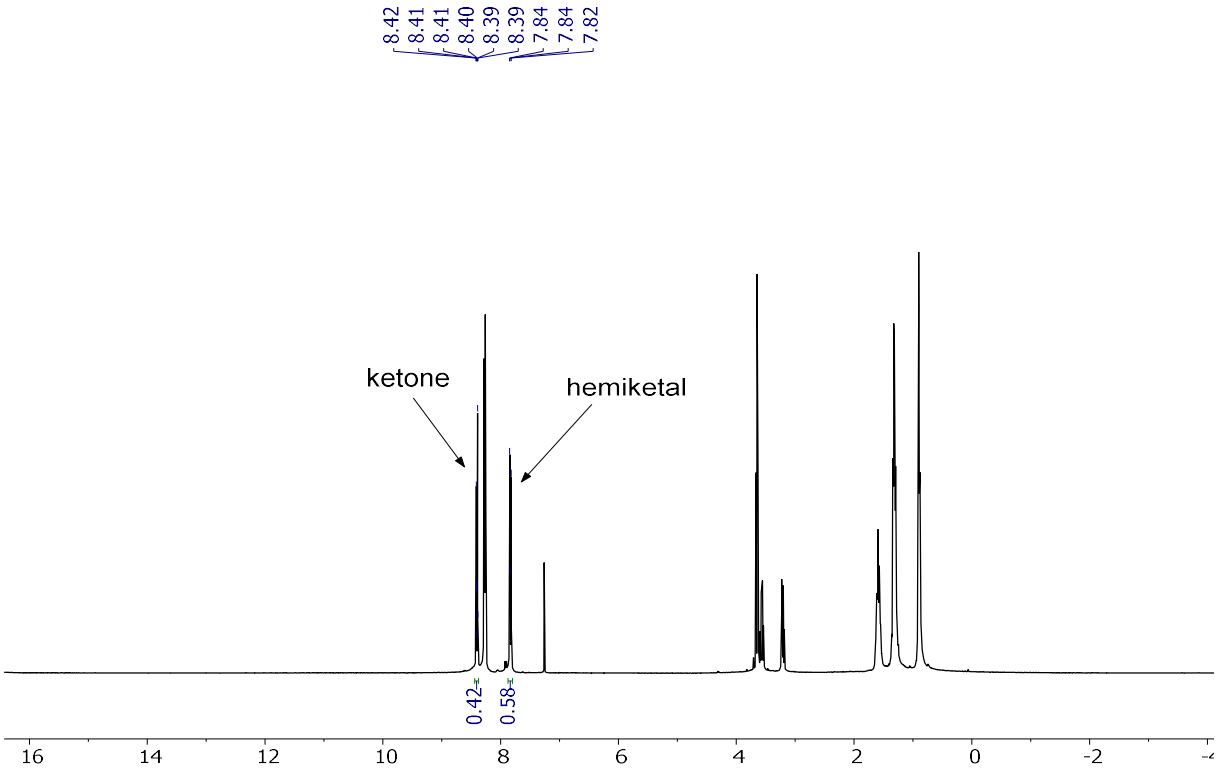



Figure 1: $^{1}H$ NMR spectrum of 4'-nitro-2,2,2-trifluoroacetophenone with 1-pentanol in $CDCl_3$ after 7 days.

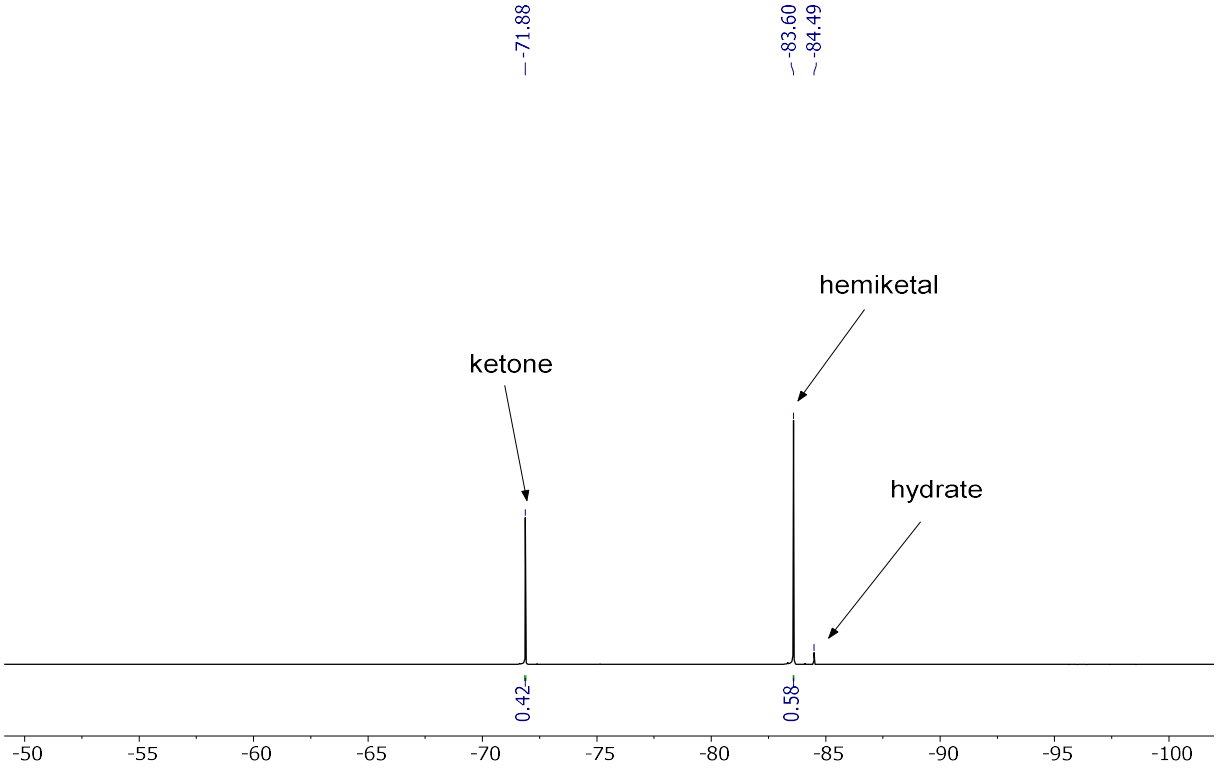



Figure 2: $^{19}F$ NMR spectrum of 4'-nitro-2,2,2-trifluoroacetophenone with 1-pentanol in $CDCl_3$ after 7 days.

The equilibrium constants of the reactions were determined by simple integration of the corresponding signals in the $^{1}H$ NMR and $^{19}F$ NMR spectra.

$$k = \frac{I(ketone)}{I(hemiacetal)}$$

The σ values used for the calculations in the *Hammett*-equation can be found in the literature.[31]

$$\log k = \sigma \cdot \rho$$

Table 5: equilibrium constants and $\sigma_p$ values for the *Hammett*-plot of hemiketal formation of trifluoroacetophenone derivatives.

| Entry | substituent | σ | I(ketone) | I(hemiketal) | k | log k |
|---|---|---|---|---|---|---|
| 1 | 4-OMe | -0.27 | 100 | 0 | 0.0000 | n.d. |
| 2 | 4-H | 0.00 | 94 | 6 | 0.0638 | -1.1950 |
| 3 | 4-F | 0.06 | 93 | 7 | 0.0753 | -1.1234 |
| 4 | 4-Br | 0.23 | 87 | 13 | 0.1494 | -0.8256 |
| 5 | 4-CN | 0.66 | 53 | 47 | 0.8868 | -0.0522 |
| 6 | 3-$NO_2$ | 0.71 | 53 | 47 | 0.8868 | -0.0522 |
| 7 | 4-$NO_2$ | 0.78 | 41 | 59 | 1.4390 | 0.1581 |

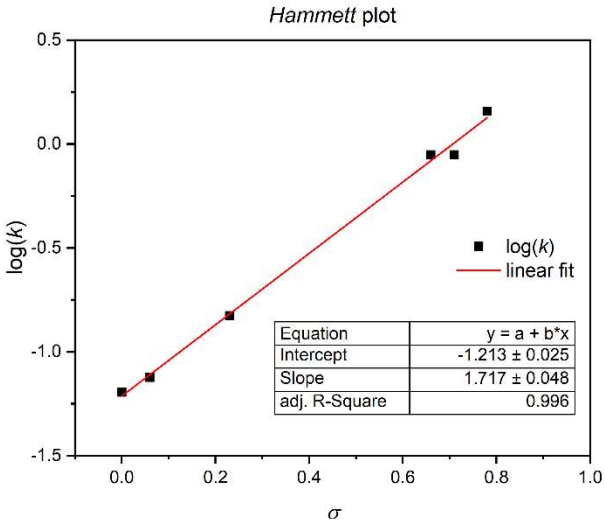
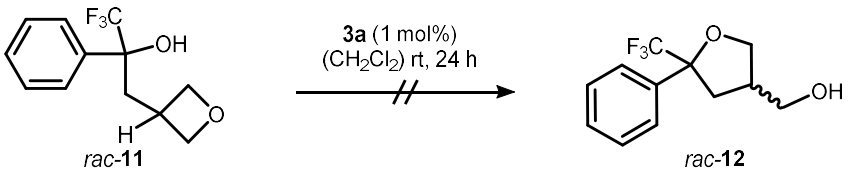



Figure 3: *Hammett*-plot of the hemiketal formation of trifluoroacetophenone derivatives with 1-pentanol.

**Attempts of ring-closing reaction with model substrate *rac*-11**

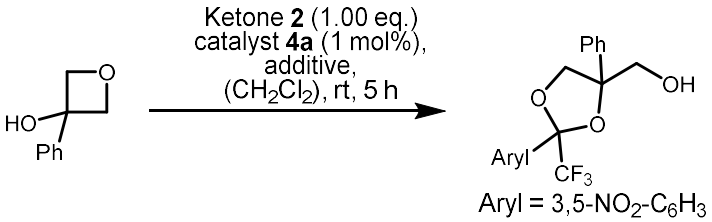



The trifluoromethyl substituted alcohol *rac*-**10** (24.6 mg, 0.10 mmol, 1.00 eq.) was dissolved in $CH_2Cl_2$ (0.5 mL) and $Co^{II}$ catalyst **3a** or **4a** (1 mol%) were added. The reaction was monitored through $^{19}F$ NMR with 0.1 mmol of trifluorotoluene as internal standard. No product was observed within 24 h of reaction time.

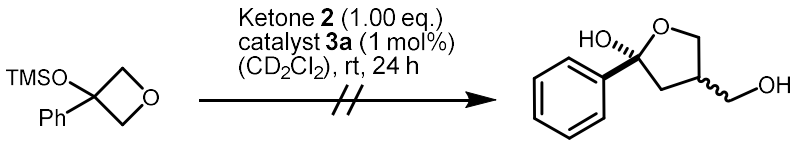
**Investigating the role of Hydrate [13]**

Exchanging Ketone **2** through its hydrate and subjecting it to otherwise unchanged reaction conditions with alcohol **1a** (1.00 eq.) and catalyst **4a** (1 mol%) in $CH_2Cl_2$ is inhibiting the reaction:

Table 6: Reactions were carried out on a 0.1 mmol scale in 0.5 mL solvent with catalyst **4a,** yield and *dr* based on $^{19}F$ NMR experiments using trifluorotoluene as an internal standard.



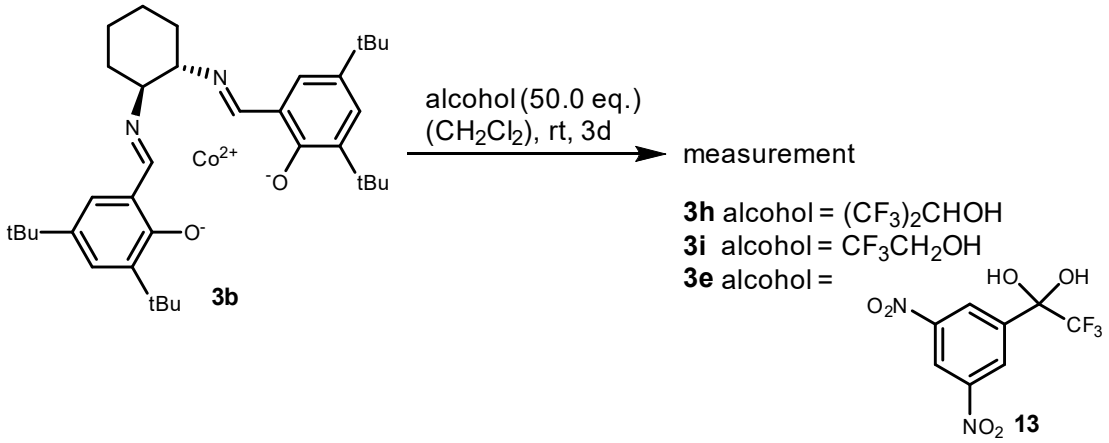

| Entry | Equivalents of **2** | Catalyst loading | Additive | yield |
|---|---|---|---|---|
| 1 | 1.00 | 1 mol% | - | 47% |
| 2 | 0.50 | 1 mol% | 0.50 eq. **[13]** | 9% |
| 3 | 0.00 | 1 mol% | 1.00 eq. **[13]** | 2% |
| 4 | 1.00 | 1 mol% | 1.00 eq. $H_2O$ | 7% |




The protected alcohol **S18** was subjected to the standard reaction conditions with catalyst **3a** (1 mol%) on a 0.1 mmol scale in 1 mL $CH_2Cl_2$ with Ketone **2** (1.00 eq.). No reaction took place after 24 h of reaction time. It can be therefore concluded, that the hydrate **[13]** which is partially formed, is not the active nucleophile in the reaction.

## UV/vis spectra of catalysts

The oxidation of Co(II)-complexes by weakly acidic alcohols was achieved by dissolving commercial $Co^{II}$·salen [**3b**] (1.00 eq.) in $CH_2Cl_2$ and adding the corresponding alcohol (50.0 eq.). The solvent was removed to dryness after stirring for 3 d at rt. The residue was directly used for UV/vis-absorption measurements. Each spectrum was recorded as solutions of the corresponding Co-complexes in $CH_2Cl_2$ at rt with a concentration of $c = 5 \cdot 10^{-5}$ mol/L.




Scheme 1: Oxidation of $Co^{II}$·salen [**3b**] with weakly acidic alcohols.

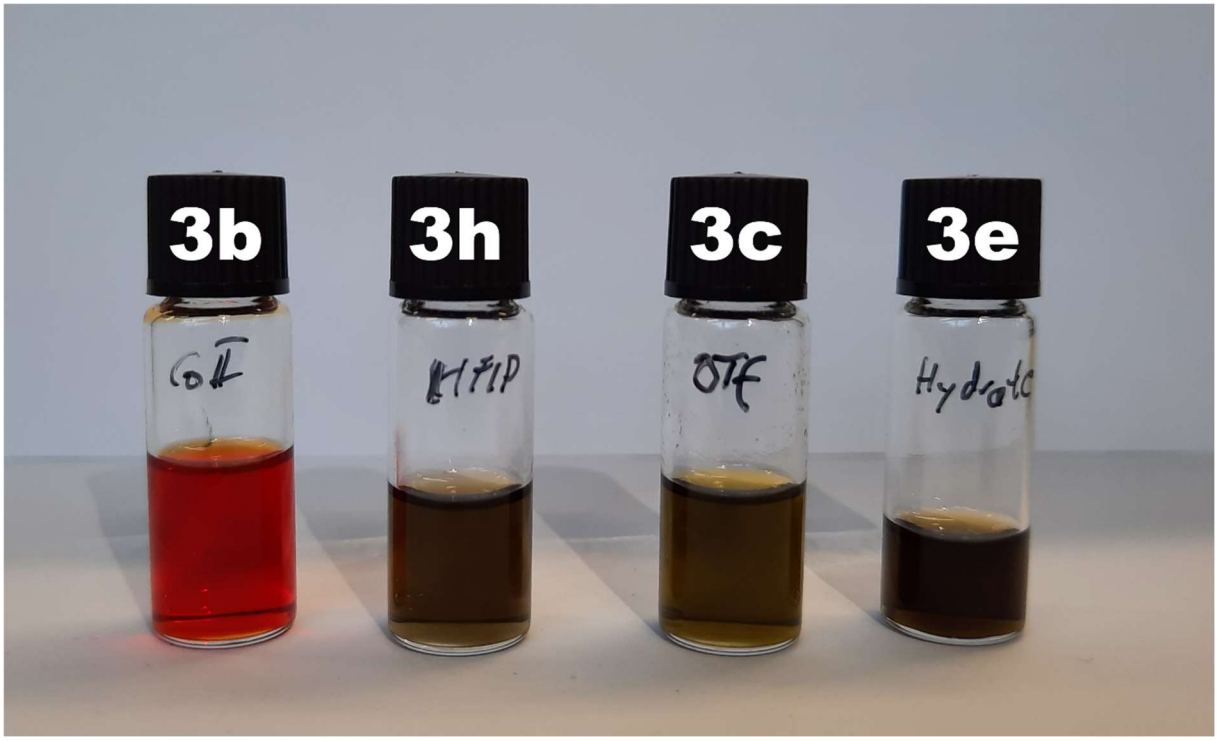



Figure 4: Solutions of different Co·salen species, from the left: 1st $Co^{II}$·salen [**3b**], 2nd (X)$Co^{III}$·salen [**3h**], 3rd (TfO)$Co^{III}$·salen [**3c**] and 4th (X)$Co^{III}$·salen [**3e**].

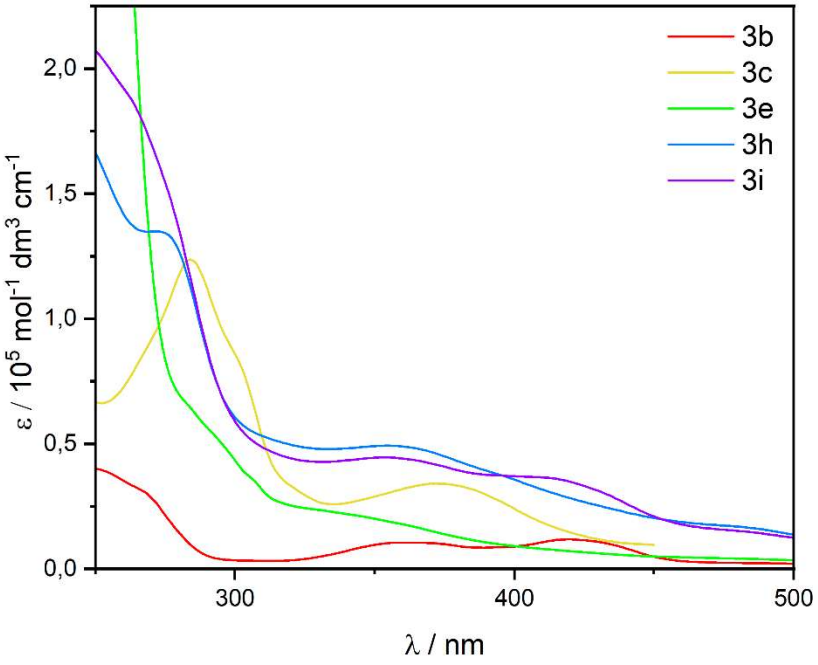



Figure 5: UV spectra of Co-complexes after attempted oxidation with weakly acidic alcohols, UV spectrum of $Co^{II}$·salen [**3b**] and (TfO)$Co^{III}$·salen [**3c**] as reference.

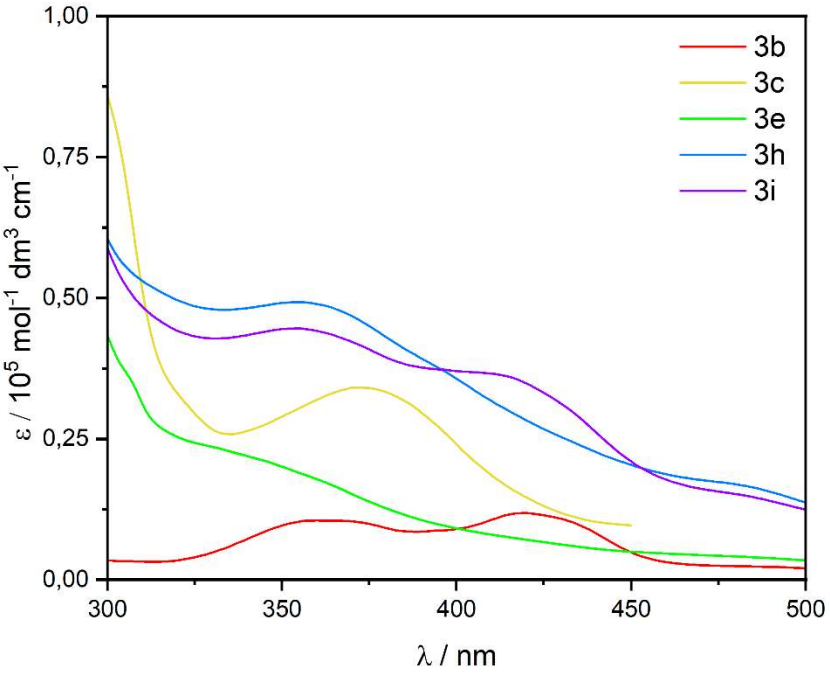
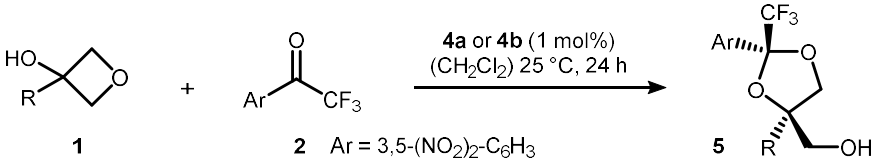



Figure 6: Extracted UV spectra of Co-complexes after attempted oxidation with weakly acidic alcohols, UV spectrum of $Co^{II}$·salen [**3b**] and (TfO)$Co^{III}$·salen [**3c**] as reference.

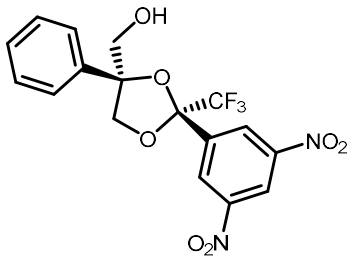
## 4. Substrate scope

General procedure **D** for the desymmetrisation of 3-substituted oxetanols




**1** **2** Ar = 3,5-$(NO_2)_2$-$C_6H_3$ **5**

Ketone [**2**] (52.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen complex (1 mol%) were dissolved in dry $CH_2Cl_2$ (0.4 M) at room temperature. To this solution the corresponding 3-substituted oxetanol (0.20 mmol, 1.00 eq.) was added. The temperature was maintained for 24 h before silica gel was added and filtered off. The resulting silica gel plug was flushed with $Et_2O$, and the filtrate was concentrated. NMR yield and dr of the crude reaction mixture were determined by $^{19}F$ NMR using $PhCF_3$ (12.2 µL, 0.10 mmol) as the internal standard. The product diastereomers were separated by silica gel column chromatography or RP-MPLC.

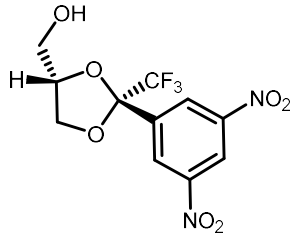



**((2*R*,4*S*)-4-(Phenyl)-2-(3,5-dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5a]**

Following the general procedure **D** using 3-phenyl-oxetan-3-ol [**1a**] (30.0 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (68.0 mg, 0.164 mmol, 82%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3522 (w), 3112 (w), 2917 (w), 2280 (w), 1543 (s), 1346 (s), 1328 (w), 1200 (m), 1182 (m), 1135 (s), 1104 (m), 1070 (m), 1007 (m), 997 (m), 914 (m), 860 (w), 813 (w), 765 (w), 730 (s), 705 (s), 665 (w), 656 (w), 639 (w), 617 (m), 608 (m). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.56 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.10 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 6.93 – 6.88 (m, 2H, C$H_{arom.}$), 6.87 – 6.80 (m, 3H, C$H_{arom.}$), 4.42 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.86 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.57 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 3.28 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 1.64 – 1.37 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.1 ($C_q$), 139.0 ($C_q$), 138.5 ($C_q$), 128.7 (*C*H), 127.0 (*C*H), 126.0 (*C*H), 125.8 (*C*H), 122.3 (q, $^1J_{C\text{-}F}$ = 287.8 Hz, *C*$F_3$), 120.2 (*C*H), 104.5 (q, $^2J_{C\text{-}F}$ = 33.2 Hz, $C_q$), 89.7 ($C_q$), 72.4 (*C*$H_2$), 67.0 (*C*$H_2$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 81.4 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{18}H_{14}F_3N_2O_9$ [M+HCOO]$^-$: 456.0651, Found: 456.0654. **Optical Rotation**: $[\alpha]_D^{25}$ = +20.6 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched

sample of 86:14 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Amylose-3 column, 22 °C, 1 mL/min, 95:05 hexane:isopropanol, 254 nm, $t_{minor}$ = 20.203 min, $t_{major}$ = 17.186 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**((2R,4S)-2-(3,5-Dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5b]**

Following the general procedure **D** using oxetan-3-ol [**1b**] (13 µL, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), a mixture of both diastereomers (56.0 mg, 0.166 mmol, 83%) was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 70:30) as a colorless oil.

**Mixture:**

**IR (neat)**: 3100 (m), 2929 (m), 1547 (s), 1347 (s), 1181 (s), 1145 (s), 1108 (s), 1068 (s), 1060 (s), 1004 (s), 912 (m), 759 (w), 730 (s), 709 (s). **HRMS (APCI):** Calculated for $C_{11}H_8F_3N_2O_7$ [M-H]$^-$: 337.0284, Found: 337.0265. **Optical Rotation**: $[\alpha]_D^{25}$ = – 8.4 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 72:28 *dr* and 79:21 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 95:05 hexane:isopropanol, 254 nm, $t_{minor}$ = 30.971 min and 37.661 min, $t_{major}$ = 33.244 min and 42.113). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

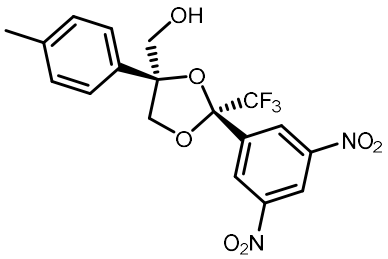
**Major diastereomer:**

**$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.56 (d, *J* = 2.1 Hz, 2H, C$H_{arom.}$), 8.40 (t, *J* = 2.1 Hz, 1H, C$H_{arom.}$), 3.67 – 3.58 (m, 2H, C$H_2$), 3.46 – 3.39 (m, 1H, C*H*), 3.27 – 3.17 (m, 2H, C$H_2$), 1.35 (s, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 148.4 ($C_q$-$NO_2$), 138.8 ($C_q$), 126.9 (*C*H), 122.3 (q, $^1J_{C\text{-}F}$ = 287.9 Hz, *C*$F_3$), 120.3 (*C*H), 103.9 (q, $^2J_{C\text{-}F}$ = 33.3 Hz, $C_q$), 79.5 (*C*H), 68.8 (*C*$H_2$), 61.0 (*C*$H_2$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.73 (s, 3F, C$F_3$).

**Minor diastereomer:**

**$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.63 (d, *J* = 2.1 Hz, 2H, C$H_{arom.}$), 8.34 (t, *J* = 2.1 Hz, 1H, C$H_{arom.}$), 3.99 (tt, *J* = 7.0, 3.9 Hz, 1H, C*H*), 3.74 – 3.67 (m, 2H, C$H_2$), 3.48 (ddd, *J* = 7.9, 6.8, 1.0 Hz, 1H, C$H_2$), 3.10 (dd, *J* = 12.1, 3.8 Hz, 1H, C$H_2$), 2.84 (dd, *J* = 12.1, 3.8 Hz, 1H, C$H_2$), 1.03 (s, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 148.3 ($C_q$-$NO_2$), 138.7 ($C_q$), 126.9 (*C*H), 122.9 (q, $^1J_{C\text{-}F}$ = 289.9 Hz, *C*$F_3$), 120.2 (*C*H), 104.1 (q,

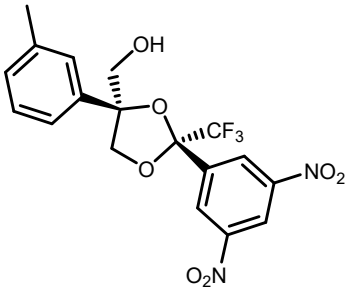
$^{2}J_{C\text{-}F}$ = 33.0 Hz, $C_q$), 80.4 (*C*H), 68.2 (*C*$H_2$), 60.8 (*C*$H_2$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.78 (s, 3F, C$F_3$).




**((2*R*,*4*S)-2-(3,5-Dinitrophenyl)-4-(*p*-tolyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5d]**

Following the general procedure **D** using 3-(p-tolyl)oxetan-3-ol [**1d**] (32.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (67.0 mg, 0.156 mmol, 78%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

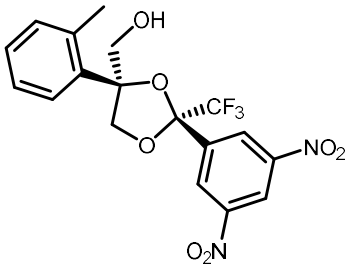
**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3512 (w), 2916 (w), 2281 (w), 1770 (w), 1544 (s), 1346 (s), 1246 (w), 1199 (m), 1185 (m), 1135 (s), 1104 (m), 1064 (m), 1013 (m), 998 (m), 914 (m), 815 (m), 759 (w), 729 (s), 709 (s), 657 (w), 638 (w). **$^{1}$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.59 (d, *J* = 2.1 Hz, 2H, C$H_{arom.}$), 8.09 (t, *J* = 2.1 Hz, 1H, C$H_{arom.}$), 6.78 (*app.* q, *J* = 8.4 Hz, 4H, C$H_{arom.}$), 4.45 (d, *J* = 8.5 Hz, 1H, C$H_2$), 3.92 (d, *J* = 8.6 Hz, 1H, C$H_2$), 3.60 (d, *J* = 12.1 Hz, 1H, C$H_2$), 3.31 (d, *J* = 12.1 Hz, 1H, C$H_2$), 1.89 (s, 3H, C$H_3$), 1.34 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.1 ($C_q$), 138.6 (2x$C_q$), 136.1 ($C_q$), 129.3 (*C*H), 127.1 (*C*H), 125.8 (*C*H), 122.4 (q, $^{1}J_{C\text{-}F}$ = 287.9 Hz, *C*$F_3$), 120.1 (*C*H), 104.5 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz, $C_q$), 89.8 ($C_q$), 72.4 (*C*$H_2$), 67.1 (*C*$H_2$), 20.7 (*C*$H_3$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 81.4 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{18}H_{15}F_3N_2O_7$ $[M]^-$: 428.0831, Found: 428.0836. **Optical Rotation**: $[\alpha]_D^{25}$ = +9.8 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 85:15 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Cellulose-5 column, 22 °C, 0.5 mL/min, 90:10 hexane:isopropanol, 254 nm, $t_{minor}$ = 22.182 min, $t_{major}$ = 18.659 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**((2*R*,*4*S)-2-(3,5-Dinitrophenyl)-4-(*m*-tolyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5e]**

Following the general procedure **D** using 3-(m-tolyl)oxetan-3-ol [**1e**] (32.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (68.0 mg, 0.159 mmol, 80%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3523 (w), 3096 (w), 2962 (w), 2917 (w), 2280 (w), 1544 (s), 1345 (s), 1328 (w), 1200 (m), 1183 (m), 1134 (s), 1104 (m), 1063 (w), 1009 (w), 998 (w), 914 (m), 786 (w), 730 (s), 708 (s), 656 (w), 637 (m), 623 (w), 615 (m). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.57 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.10 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 6.87 – 6.80 (m, 3H, C$H_{arom.}$), 6.69 (d, $J$ = 7.6 Hz, 1H, C$H_{arom.}$), 6.64 (d, $J$ = 7.8 Hz, 1H, C$H_{arom.}$), 4.43 (d, $J$ = 8.5 Hz, 1H, C$H_2$), 3.88 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.59 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 3.30 (d, $J$ = 12.1 Hz, 1H, C$H_2$), 2.02 (s, 3H), 1.55 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.0 ($C_q$), 139.0 ($C_q$), 138.6 ($C_q$), 138.5 ($C_q$), 129.4 (*C*H), 128.7 (*C*H), 127.1(*C*H), 126.6 (*C*H), 122.8 (*C*H), 122.3 (q, $^1J_{C\text{-}F}$ = 287.8 Hz, *C*$F_3$), 120.1 (*C*H), 104.5 (q, $^2J_{C\text{-}F}$ = 33.3 Hz, $C_q$), 89.8 ($C_q$), 72.3 (*C*$H_2$), 67.2 (*C*$H_2$), 21.2 (*C*$H_3$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 81.4 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{18}H_{15}F_3N_2O_7$ $[M]^-$: 428.0831, Found: 428.0834. **Optical Rotation**: $[\alpha]_D^{25}$ = +12.6 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 85:15 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Cellulose-5 column, 22 °C, 2 mL/min, 98:02 hexane:isopropanol, 254 nm, $t_{minor}$ = 20.151 min, $t_{major}$ = 17.331 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

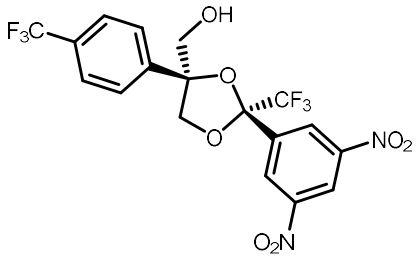



**((2*R*,*4*S)-2-(3,5-Dinitrophenyl)-4-(*o*-tolyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5f]**

Following the general procedure **D** using 3-(o-tolyl)oxetan-3-ol [**1f**] (32.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major

diastereomer (73.0 mg, 0.170 mmol, 85%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3581 (w), 3113 (w), 2917 (w), 2280 (w), 1544 (s), 1345 (s), 1330 (m), 1203 (m), 1183 (m), 1136 (s), 1105 (m), 1070 (m), 1012 (w), 998 (w), 914 (w), 812 (w), 765 (m), 729 (s), 707 (m), 669 (w), 659 (w), 638 (w). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.56 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.04 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.15 – 7.09 (m, 1H, C$H_{arom.}$), 6.94 – 6.89 (m, 1H, C$H_{arom.}$), 6.85 (td, $J$ = 7.4, 1.5 Hz, 1H, C$H_{arom.}$), 6.78 – 6.73 (m, 1H, C$H_{arom.}$), 4.51 (d, $J$ = 8.7 Hz, 1H, C$H_{arom.}$), 3.67 (d, $J$ = 8.7 Hz, 1H, C$H_2$), 3.64 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 3.45 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 1.97 (s, 3H, C$H_3$), 1.53 – 1.28 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.2 ($C_q$), 138.3 ($C_q$), 137.1 ($C_q$), 134.4 ($C_q$), 132.4 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 127.3 (*C*H), 127.0 (*C*H), 126.2 (*C*H), 122.1 (q, $^1J_{C\text{-}F}$ = 286.2 Hz), 120.4 (*C*H), 104.2 (q, $^2J_{C\text{-}F}$ = 33.5 Hz), 90.8 ($C_q$), 72.3 ($CH_2$), 66.8 ($CH_2$), 20.6 ($CH_3$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 81.5 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{18}H_{15}F_3N_2O_7$ [M]$^-$: 428.0831, Found: 428.0833. **Optical Rotation**: $[\alpha]_D^{25}$ = −11.7 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 82:18 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Cellulose-5 column, 22 °C, 2 mL/min, 98:02 hexane:isopropanol, 254 nm, $t_{minor}$ = 20.637 min, $t_{major}$ = 18.968 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

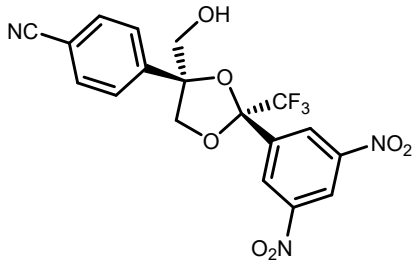



**((2*R*,4*S*)-2-(3,5-Dinitrophenyl)-2-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-4-yl)methanol [5g]**

Following the general procedure **D** using 3-(4-(trifluoromethyl)phenyl)oxetan-3-ol [**1g**] (43.6 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (70.0 mg, 0.145 mmol, 73%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3457 (w), 3110 (w), 2978 (w), 2280 1546 (s), 1346 (s), 1327 (s), 1241 (w), 1200 (m), 1168 (m), 1132 (s), 1067 (m), 1013 (m), 999 (m), 915 (w), 841 (w), 813 (w), 759 (w), 730 (s), 709 (m), 684 (w), 658 (w), 638 (w), 624 (w), 612 (m). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.51 (d, $J$ = 2.0 Hz, 2H, C$H_{arom.}$), 8.11 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.20 (d, $J$ = 8.2 Hz, 2H, C$H_{arom.}$), 6.76 (d, $J$ = 8.2 Hz, 2H, C$H_{arom.}$), 4.30 (d, $J$ = 8.7 Hz, 1H, C$H_2$), 3.65 (d, $J$ = 8.8 Hz, 1H, C$H_2$), 3.44 (d, $J$ = 11.8 Hz, 1H, C$H_2$), 3.19 (d, $J$ = 11.8 Hz, 1H, C$H_2$), 1.23 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.2 ($C_q$), 143.1 ($C_q$), 138.0 ($C_q$), 130.9 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, $C_q$), 126.8 (*C*H), 126.2 (*C*H), 125.6 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, *C*H), 124.3 (*app.* d, $^1J_{C\text{-}F}$ = 272.0 Hz, *C*$F_3$), 122.2

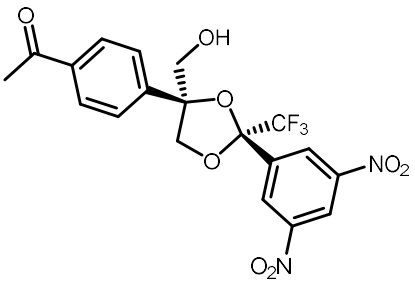
(q, $^{1}J_{C\text{-}F}$ = 288.0 Hz, *C*$F_3$), 120.4 (*C*H), 104.7 (q, $^{2}J_{C\text{-}F}$ = 33.5 Hz, $C_q$), 89.1 ($C_q$), 72.5 (*C*$H_2$), 66.7 (*C*$H_2$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 62.9 (s, 3F, C*F*$_3$), – 81.4 (s, 3F, C*F*$_3$). **HRMS (APCI)**: Calculated for $C_{19}H_{13}F_6N_2O_9$ [M+HCOO]$^-$: 527.0525, Found: 527.0531. **Optical Rotation**: $[\alpha]_D^{25}$ = +19.0 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 96:4 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 95:05 hexane:isopropanol, 254 nm, $t_{minor}$ = 20.287 min, $t_{major}$ = 13.878 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**4-((2*R*,4*S*)-2-(3,5-Dinitrophenyl)-4-(hydroxymethyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)benzonitrile [5h]**

Following the general procedure **D** using 4-(3-hydroxyoxetan-3-yl)benzonitrile [**1h**] (35.0 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (66.0 mg, 0.150 mmol, 75%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless solid.

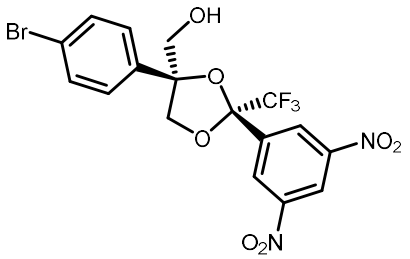
**Major diastereomer [3a]: M.P.**: 196 – 198 °C. **IR (neat)**: $\tilde{\nu}$ = 3456 (w), 2917 (w), 2280 (w), 1544 (s), 1346 (s), 1326 (w), 1198 (m), 1188 (m), 1134 (m), 1103 (w), 1063 (w), 1013 (w), 994 (w), 915 (w), 836 (w), 813 (w), 730 (s), 709 (s), 693 (w), 668 (w), 650 (w). **$^{1}$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.51 (d, *J* = 2.1 Hz, 2H, C*H*$_{arom.}$), 8.22 (t, *J* = 2.1 Hz, 1H, C*H*$_{arom.}$), 6.91 (d, *J* = 8.5 Hz, 2H, C*H*$_{arom.}$), 6.65 (d, *J* = 8.5 Hz, 2H, C*H*$_{arom.}$), 4.29 (d, *J* = 8.8 Hz, 1H, C*H*$_2$), 3.61 (d, *J* = 8.8 Hz, 1H, C*H*$_2$), 3.45 (d, *J* = 11.7 Hz, 1H, C*H*$_2$), 3.22 (d, *J* = 11.7 Hz, 1H, C*H*$_2$), 1.57 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.3 ($C_q$), 143.8 ($C_q$), 138.0 ($C_q$), 132.1 (*C*H), 126.4 (*C*H), 122.1 (d, $^{1}J_{C\text{-}F}$ = 287.8 Hz, *C*$F_3$), 120.4 (*C*H), 117.9 ($C_q$), 112.8 ($C_q$), 104.7 (q, $^{2}J_{C\text{-}F}$ = 33.6 Hz, $C_q$), 89.0 ($C_q$), 72.4 (*C*$H_2$), 66.6 (*C*$H_2$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 82.2 (s, 3F, C*F*$_3$). **HRMS (APCI)**: Calculated for $C_{19}H_{12}F_3N_3O_9$ [M+HCOO]$^-$: 486.0604, Found: 486.0600. **Optical Rotation**: $[\alpha]_D^{25}$ = +1.8 (*c* = 0.50, acetone) for an enantiomerically enriched sample of 94:6 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Cellulose-5 column, 22 °C, 1 mL/min, 80:20 hexane:isopropanol, 254 nm, $t_{minor}$ = 21.652 min, $t_{major}$ = 13.880 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].



**1-(4-((2*R*,4*S*)-2-(3,5-Dinitrophenyl)-4-(hydroxymethyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)phenyl)ethan-1-one [5i]**

Following the general procedure **D** using 1-(4-(3-hydroxyoxetan-3-yl)phenyl)ethan-1-one [**1i**] (38.4 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (60.0 mg, 0.131 mmol, 66%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless solid.

**Major diastereomer [3a]: M.P.**: 135 – 137 °C. **IR (neat)**: $\tilde{\nu}$ = 3475 (w), 3113 (w), 2962 (w), 2924 (m), 2852 (w), 2343 (w), 1701 (s), 1609 (w), 1546 (s), 1462 (w), 1407 (w), 1347 (s), 1267 (m), 1248 (m), 1200 (m), 1183 (m), 1135 (s), 1103 (m), 1064 (m), 1005 (m), 958 (w), 913 (w), 834 (w), 801 (w), 729 (s), 708 (s), 683 (w). **$^1$H NMR (400 MHz, acetone-d6)**: $\delta$ = 8.96 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 8.75 (d, $J$ = 2.0 Hz, 2H, C$H_{arom.}$), 7.84 – 7.81 (m, 2H, C$H_{arom.}$), 7.56 – 7.52 (m, 2H, C$H_{arom.}$), 4.89 (d, $J$ = 8.9 Hz, 1H, C$H_2$), 4.65 (d, $J$ = 8.8 Hz, 1H, C$H_2$), 4.62 (t, $J$ = 6.2 Hz, 1H, O$H$), 4.05 (dd, $J$ = 11.8, 6.3 Hz, 1H, C$H_2$), 3.90 (dd, $J$ = 11.7, 6.3 Hz, 1H, C$H_2$), 2.48 (s, 3H, C$H_3$). **$^{13}$C NMR (101 MHz, acetone-d6)**: $\delta$ = 197.5 ($C_q$), 149.6 ($C_q$), 145.4 ($C_q$), 139.7 ($C_q$), 137.6 ($C_q$), 128.8 (*C*H), 128.0 (*C*H), 127.2 (*C*H), 122.9 (*app*. d, $^1J_{C\text{-}F}$ = 287.7 Hz, *C*$F_3$), 121.1 (*C*H), 104.9 (q, $^2J_{C\text{-}F}$ = 33.3 Hz, $C_q$), 90.9 ($C_q$), 74.2 (*C*$H_2$), 67.1 (*C*$H_2$), 26.6 (*C*$H_3$). **$^{19}$F NMR (377 MHz, acetone-d6)** $\delta$ = – 82.9 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{20}H_{16}F_3N_2O_{10}$ [M+HCOO]$^-$: 501.0757, Found: 501.0761. **Optical Rotation**: $[\alpha]_D^{25}$ = +2.1 (*c* = 1.00, acetone) for an enantiomerically enriched sample of 83:17 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® Amylose-1 column, 22 °C, 0.5 mL/min, 80:20 hexane:isopropanol, 254 nm, $t_{minor}$ = 41.267 min, $t_{major}$ = 24.111 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**((2*R*,*4*S)-4-(4-Bromophenyl)-2-(3,5-dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5j]**

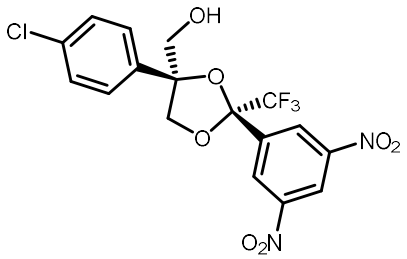
Following the general procedure **D** using 3-(4-bromophenyl)oxetan-3-ol [**1j**] (45.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (78.0 mg, 0.158 mmol, 79%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3556 (br), 3099 (w), 2920 (w), 2371 (w), 2279 (w), 1631 (w), 1596 (w), 1544 (s), 1490 (w), 1346 (s), 1330 (w), 1202 (m), 1185 (m), 1135 (s), 1104 (m), 1070 (w), 1007 (m), 914 (m), 828 (w), 729 (s), 710 (m), 680 (w), 663 (w), 655 (w). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.50 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.10 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.09 – 7.02 (m, 2H, C$H_{arom.}$), 6.53 – 6.46 (m, 2H, C$H_{arom.}$), 4.29 (d, $J$ = 8.7 Hz, 1H, C$H_{arom.}$), 3.65 (d, $J$ = 8.7 Hz, 1H, C$H_2$), 3.42 (d, $J$ = 11.9 Hz, 1H, C$H_2$), 3.14 (d, $J$ = 11.9 Hz, 1H, C$H_2$), 1.40 – 1.11 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.1 ($C_q$), 138.1 ($C_q$), 138.0 ($C_q$), 131.8 (*C*H), 128.6 (*C*H), 127.5 (*C*H), 126.8 (*C*H), 123.0 ($C_q$), 122.2 (q, $^1J_{C\text{-}F}$ = 287.9 Hz, *C*$F_3$), 120.3 (*C*H), 104.5 (q, $^2J_{C\text{-}F}$ = 33.2 Hz, $C_q$), 89.1 ($C_q$), 72.3 (*C*$H_2$), 66.7 (*C*$H_2$). **$^{19}$F NMR (282 MHz, $C_6D_6$)** $\delta$ = – 81.4 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{17}H_{12}BrF_3N_2O_7$ $[M]^-$: 491.9780, Found: 491.9776. **Optical Rotation**: $[\alpha]_D^{25}$ = −5.7 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 91:9 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 90:10 hexane:isopropanol, 254 nm, $t_{minor}$ = 24.101 min, $t_{major}$ = 25.526 min). See section 15 for HPLC chromatograms.

A sample suitable for X-ray analysis was obtained after dissolving ((2R,4S)-4-(4-bromophenyl)-2-(3,5-dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [**5j**] in $C_6F_6$ and slowly evaporating the solvent. Absolute stereochemistry determined through X-ray diffraction (see section 13).

***Gram scale:***

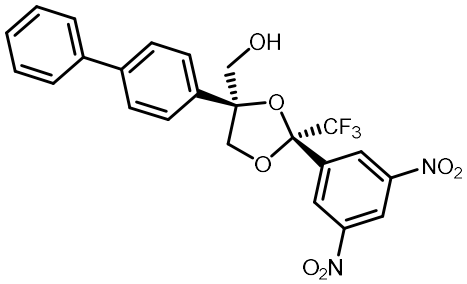
Following the general procedure **D** using 3'5'-dinitro-2,2,2-trifluoroacetophenone [**2**] (792 mg, 3.00 mmol, 1.00 eq.), 3-(4-bromophenyl)oxetan-3-ol [**1j**] (687 mg, 3.00 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (30.0 mg, 30.0 µmol, 1.0 mol%), the major diastereomer (782 mg, 1.59 mmol, 53%) was obtained *via* automated FC (CyH:$Et_2O$, 75:25) as a colorless foam.




**((2*R*,*4*S)-4-(4-Chlorophenyl)-2-(3,5-dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5k]**

Following the general procedure **D** using 3-(4-chlorophenyl)oxetan-3-ol [**1k**] (36.9 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (75.0 mg, 0.167 mmol, 83%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3568 (w), 3093 (w), 2917 (w), 2280 (w), 1770 (w), 1544 (s), 1494 (w), 1346 (s), 1239 (w), 1199 (m), 1185 (m), 1135 (s), 1103 (m), 1063 (w), 1011 (m), 993 (w), 915 (w), 831 (w), 729 (s), 708 (m). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.52 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.14 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 6.96 – 6.89 (m, 2H, C$H_{arom.}$), 6.63 – 6.59 (m, 2H, C$H_{arom.}$), 4.34 (d, $J$ = 8.7 Hz, 1H, C$H_2$), 3.71 (d, $J$ = 8.7 Hz, 1H, C$H_2$), 3.48 (d, $J$ = 11.9 Hz, 1H, C$H_2$), 3.20 (d, $J$ = 11.9 Hz, 1H, C$H_2$), 1.34 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.2 ($C_q$), 138.3 ($C_q$), 137.5 ($C_q$), 134.8 ($C_q$), 128.8 (*C*H), 127.2 (*C*H), 126.9 (*C*H), 122.2 (q, $^1J_{C\text{-}F}$ = 287.9 Hz, *C*$F_3$), 120.3 (*C*H), 104.6 (q, $^2J_{C\text{-}F}$ = 33.4 Hz, $C_q$), 89.2 ($C_q$), 72.4 (*C*$H_2$), 66.8 (*C*$H_2$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 81.4 (s, 3F, C*F*$_3$). **HRMS (APCI)**: Calculated for $C_{17}H_{12}ClF_3N_2O_7$ $[M]^-$: 448,0285, Found: 448,0274. **Optical Rotation**: $[\alpha]_D^{25}$ = +1.7 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 93:7 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 2 mL/min, 95:05 hexane:isopropanol, 254 nm, $t_{minor}$ = 14.683 min, $t_{major}$ = 9.490 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [5j] .

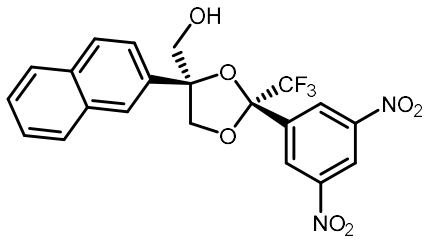



**((2*R*,*4*S)-4-([1,1'-Biphenyl]-4-yl)-2-(3,5-dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5l]**

Following the general procedure **D** using 3-([1,1'-biphenyl]-4-yl)oxetan-3-ol [**1l**] (45.3 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the

major diastereomer (70.0 mg, 0.142 mmol, 71%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless solid.

**Major diastereomer [3a]: M.P.**: 66 – 68 °C. **IR (neat)**: $\tilde{\nu}$ = 3401 (w), 3097 (w), 2939 (w), 2280 (w), 1543 (s), 1488 (w), 1345 (s), 1325 (w), 1203 (m), 1187 (m), 1135 (s), 1103 (w), 1068 (w), 1006 (w), 996 (w), 915 (w), 841 (w), 812 (w), 767 (m), 729 (s), 707 (m), 657 (w). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.59 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.06 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.30 – 7.23 (m, 4H, C$H_{arom.}$), 7.14 – 7.03 (m, 3H, C$H_{arom.}$), 6.94 – 6.89 (m, 1H, C$H_{arom.}$), 4.44 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.88 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.60 (d, $J$ = 11.9 Hz, 1H, C$H_2$), 3.31 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 1.36 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.1 ($C_q$), 142.1 ($C_q$), 140.3 ($C_q$), 137.9 ($C_q$), 129.2 ($C$H), 127.5 ($C$H), 127.3 ($C$H), 127.0 ($C$H), 126.3 ($C$H), 122.3 (q, $^1J_{C\text{-}F}$ = 287.9 Hz, $C$F$_3$), 120.2 ($C$H), 104.6 (q, $^2J_{C\text{-}F}$ = 33.4 Hz, $C_q$). 89.6 ($C_q$), 72.5 ($C$H$_2$), 67.1 ($C$H$_2$).[p] **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 82.3 (s, 3F, C$F_3$). **HRMS (ESI)**: Calculated for $C_{23}H_{17}F_3N_2O_7Na$ [M+Na]$^+$: 513.0886, Found: 513.0883. **Optical Rotation**: $[\alpha]_D^{25}$ = −20.9 ($c$ = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 85:15 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 95:5 hexane:isopropanol, 254 nm, $t_{minor}$ = 31.619 min, $t_{major}$ = 20.706 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [5j] .



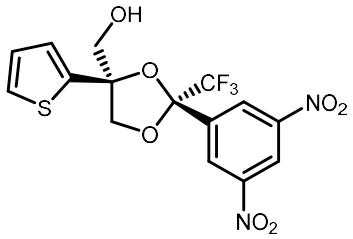

**((2*R*,4*S*)-2-(3,5-Dinitrophenyl)-4-(naphthalen-2-yl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5m]**

Following the general procedure **D** using 3-(naphthalen-2-yl)oxetan-3-ol [**1m**] (40.1 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (81.0 mg, 0.174 mmol, 87%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3434 (w), 2917 (w), 1543 (s), 1346 (s), 1328 (w), 1200 (m), 1185 (m), 1135 (s), 1103 (w), 1065 (w), 1008 (w), 996 (w), 914 (w), 815 (w), 730 (s), 707 (m), 683 (w), 655 (w). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.62 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 7.98 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.65 – 7.58 (m, 1H, C$H_{arom.}$), 7.51 (d, $J$ = 1.9 Hz, 1H, C$H_{arom.}$), 7.40 (*app.* t, $J$ = 8.1 Hz, 2H, C$H_{arom.}$), 7.20 – 7.17 (m, 1H, C$H_{arom.}$), 7.09 (ddd, $J$ = 8.2, 6.9, 1.3 Hz, 1H, C$H_{arom.}$), 6.92 (dd, $J$ = 8.6, 1.9 Hz, 1H, C$H_{arom.}$), 4.52 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 4.02 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.67 (d, $J$ = 12.1 Hz, 1H, C$H_2$), 3.40 (d, $J$ = 12.1 Hz, 1H, C$H_2$), 1.65 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz,**

[p] Missing signals under solvent peak.

**$C_6D_6$)**: $\delta$ = 148.0 ($C_q$), 136.2 ($C_q$), 133.2 ($C_q$), 133.1 ($C_q$), 128.7 (*C*H), 128.1 (*C*H), 127.2 (*C*H), 127.1 (*C*H), 127.1 (*C*H), 125.3 (*C*H), 123.2 (*C*H), 122.4 (q, $^1J_{C\text{-}F}$ = 287.8 Hz, *C*$F_3$), 120.1 (*C*H), 104.6 (q, $^2J_{C\text{-}F}$ = 33.3 Hz, $C_q$), 90.0 ($C_q$), 72.5 (*C*$H_2$), 67.1 (*C*$H_2$).[q] **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 82.3 (s, 3F, C*F*$_3$). **HRMS (APCI)**: Calculated for $C_{21}H_{15}F_3N_2O_7$ [M]$^-$: 464.0831, Found: 464.0828. **Optical Rotation**: $[\alpha]_D^{25}$ = −25.4 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 88:12 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 95:5 hexane:isopropanol, 254 nm, $t_{minor}$ = 37.407 min, $t_{major}$ = 22.872 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

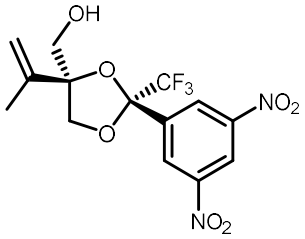



**((2*R*,4*S*)-2-(3,5-Dinitrophenyl)-4-(thiophen-2-yl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5n]**

Following the general procedure **D** using 3-(thiophen-2-yl)oxetan-3-ol [**1n**] (31.2 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (67.0 mg, 0.159 mmol, 80%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3438 (w), 3098 (w), 2918 (w), 2357 (w), 2273 (w), 1631 (w), 1543 (s), 1345 (s), 1327 (w), 1184 (m), 1152 (w), 1133 (s), 1105 (m), 1064 (m), 1005 (m), 997 (m), 914 (m), 849 (w), 813 (w), 729 (s), 707 (s), 679 (w). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.60 (d, *J* = 2.1 Hz, 2H, C*H*$_{arom.}$), 8.21 (t, *J* = 2.1 Hz, 1H, C*H*$_{arom.}$), 6.52 (dd, *J* = 5.0, 1.3 Hz, 1H, C*H*$_{arom.}$), 6.37 – 6.13 (m, 2H, C*H*$_{arom.}$), 4.35 (dd, *J* = 8.6, 1H, C*H*$_2$), 3.96 (dd, *J* = 8.7 Hz, 1H, C*H*$_2$), 3.65 (d, *J* = 12.1 Hz, 1H, C*H*$_2$), 3.34 (d, *J* = 12.2 Hz, 1H, C*H*$_2$), 1.56 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 147.7 ($C_q$), 141.9 ($C_q$), 138.0 ($C_q$), 126.8 (*C*H), 126.7 (*C*H), 125.9 (*C*H), 124.9 (*C*H), 122.0 (q, $^1J_{C\text{-}F}$ = 288.5 Hz, *C*$F_3$), 119.7 (*C*H), 104.3 (q, $^2J_{C\text{-}F}$ = 33.3 Hz, $C_q$), 87.2 ($C_q$), 73.4 (*C*$H_2$), 65.9 (*C*$H_2$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 82.3 (s, 3F, C*F*$_3$). **HRMS (APCI)**: Calculated for $C_{15}H_{11}F_3N_2O_7S$ [M]$^-$: 420.0239, Found: 420,0240. **Optical Rotation**: $[\alpha]_D^{25}$ = +32.9 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 89:11 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 0.5 mL/min, 95:5 hexane:isopropanol, 254 nm, $t_{minor}$ = 68.893 min, $t_{major}$ = 47.824 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

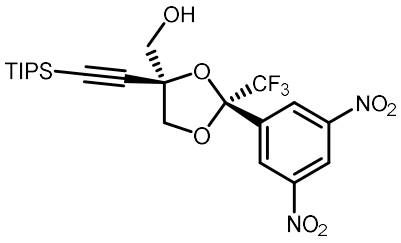
[q] Missing signals under solvent peak.




**((2*R*,4*S*)-2-(3,5-Dinitrophenyl)-4-(prop-1-en-2-yl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5o]**

Following the general procedure **D** with minor alterations, using 3-(prop-1-en-2-yl)oxetan-3-ol [**1o**] (22.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%) the reaction was run at 40 °C for 24 h. The major diastereomer (81.0 mg, 0.174 mmol, 87%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3593 (w), 3100 (w), 1623 (w), 1543 (s), 1346 (s), 1197 (m), 1179 (m), 1135 (m), 1103 (m), 1063 (w), 996 (m), 914 (m), 811 (w), 729 (s), 708 (s). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.58 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.23 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 4.55 – 4.49 (m, 2H, C$H_2$), 3.96 (d, $J$ = 8.7 Hz, 1H, C$H_2$), 3.56 (d, $J$ = 8.7 Hz, 1H, C$H_2$), 3.38 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 3.27 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 1.30 (br, 1H, *O*H), 1.26 – 1.21 (m, 3H, C$H_3$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.2 ($C_q$), 142.0 ($C_q$), 138.8 ($C_q$), 126.8 (*C*H), 122.3 (q, $^1J_{C\text{-}F}$ = 288.4 Hz, *C*$F_3$), 120.2 (*C*H), 114.3 (*C*$H_2$), 104.3 (q, $^2J_{C\text{-}F}$ = 33.3 Hz, $C_q$), 90.7 ($C_q$), 71.3 (*C*$H_2$), 64.2 (*C*$H_2$), 19.2 (*C*$H_3$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 82.3 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{14}H_{13}F_3N_2O_7$ [M]$^-$: 378.0675, Found: 378.0677. **Optical Rotation**: $[\alpha]_D^{25}$ = +26.1 ($c$ = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 83:17 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 95:5 hexane:isopropanol, 254 nm, $t_{minor}$ = 18.835 min, $t_{major}$ = 13.812 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

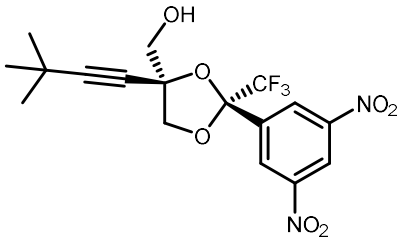



**((2R,4S)-2-(3,5-Dinitrophenyl)-2-(trifluoromethyl)-4-((triisopropylsilyl)ethynyl)-1,3-dioxolan-4-yl)methanol [5p]**

Following the general procedure **D** using 3-((triisopropylsilyl)ethynyl)oxetan-3-ol [**1p**] (50.9 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4a**] (1.9 mg, 2.0 µmol, 1.0 mol%), the

major diastereomer (90.0 mg, 0.174 mmol, 87%) was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 80:20) as a yellow oil.

**IR (neat)**: 3968 (w), 3891 (w), 3842 (w), 3780 (w), 3492 (w), 3108 2949 (m), 2868 (w), 1631 (w), 1547 (s), 1463 (w), 1345 (s), 1315 (w), 1202 (m), 1134 (m), 1105 (m), 1067 (m), 1006 (m), 915 (w), 882 (w), 831 (w), 730 (s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.78 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.64 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 4.12 (d, $J$ = 7.9 Hz, 1H, C$H_2$), 3.75 (dd, $J$ = 7.9, 1.0 Hz, 1H, C$H_2$), 3.57 (dd, $J$ = 12.4, 4.6 Hz, 1H, C$H_2$), 3.32 (dd, $J$ = 12.4, 8.6 Hz, 1H, C$H_2$), 1.66 (dd, $J$ = 8.9, 5.2 Hz, 1H, O$H$), 0.74 (dd, $J$ = 7.2, 1.9 Hz, 18H, C$H_3$), 0.68 – 0.58 (m, 3H, C$H$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 148.7 ($C_q$), 139.3 ($C_q$), 127.3 (*C*H), 122.4 (q, $^1J_{C\text{-}F}$ = 287.9 Hz, *C*$F_3$), 120.2 (*C*H), 104.6 (q, $^2J_{C\text{-}F}$ = 33.5 Hz, $C_q$) 103.6 ($C_q$), 90.5 ($C_q$), 81.3 (*C*q), 74.1 (*C*$H_2$), 64.0 (*C*$H_2$), 18.3 (*C*$H_3$), 10.9 (*C*H). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.76 (s, 3F, C$F_3$). **HRMS (APCI):** Calculated for $C_{23}H_{30}F_3N_2O_9Si$ [M+HCOO]$^-$: 563.1673, Found: 563.1671. **Optical Rotation**: $[\alpha]_D^{25}$ = + 37.1 ($c$ = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 91:09 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Cellulose-5 column, 22 °C, 1 mL/min, 98:02 hexane:isopropanol, 254 nm, $t_{minor}$ = 6.350 min, $t_{major}$ = 6.891 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

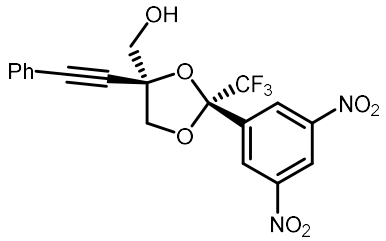



**((2R,4S)-4-(3,3-Dimethylbut-1-yn-1-yl)-2-(3,5-dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5q]**

Following the general procedure **D** using 3-(3,3-dimethylbut-1-yn-1-yl)oxetan-3-ol [**1q**] (30.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4a**] (1.9 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (73.0 mg, 0.175 mmol, 87%) was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 80:20) as an off-white solid.

**M.P.:** 72 – 75 °C. **IR (neat)**: 3101 (w), 2972 (w),1547 (s), 1346 (s), 1319 (w), 1202 (m), 1185 (m), 1134 (m), 1105 (w), 1065 (w), 1008 (w), 915 (w), 774 (m), 756 (m), 731 (s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.77 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.52 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 4.11 (d, $J$ = 7.9 Hz, 1H, C$H_2$), 3.65 (dd, $J$ = 7.9, 0.9 Hz, 1H, C$H_2$), 3.59 (dd, $J$ = 12.3, 5.1 Hz, 1H, C$H_2$), 3.34 (dd, $J$ = 12.3, 8.5 Hz, 1H, C$H_2$), 1.69 (dd, $J$ = 8.7, 5.4 Hz, 1H, O$H$), 0.73 (s, 9H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 148.4 ($C_q$), 139.3 ($C_q$), 127.5 (CH), 122.3 (q, $^1J_{C\text{-}F}$ = 287.4 Hz, *C*$F_3$), 120.1 (CH), 104.5 (q, $^2J_{C\text{-}F}$ = 33.4 Hz, $C_q$),.98.0 ($C_q$), 81.5 (CH), 75.5 ($C_q$), 73.9 (CH), 64.5 (CH), 30.2 (*C*$H_3$), 27.2 ($C_q$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.66 (s, 3F, C$F_3$). **HRMS (APCI):** Calculated for $C_{18}H_{18}F_3N_2O_9$ [M+CHOO]$^-$: 463.0964, Found: 463.0967. **Optical Rotation**: $[\alpha]_D^{25}$ = + 35.4 ($c$ = 1.00, $CHCl_3$) for an enantiomerically enriched sample of

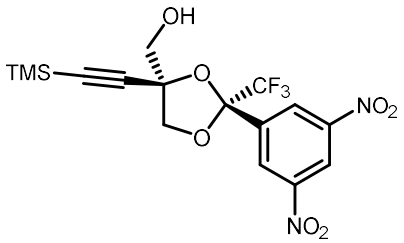
88:12 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 95:05 hexane:isopropanol, 210 nm, $t_{major}$ = 13.311 min, $t_{minor}$ = 15.586 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**((2R,4S)-2-(3,5-Dinitrophenyl)-4-(phenylethynyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5r]**

Following the general procedure **D** using 3-(phenylethynyl)oxetan-3-ol [**1r**] (34.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4a**] (1.9 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (81.0 mg, 0.184 mmol, 92%) was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 80:20) as a yellow oil.

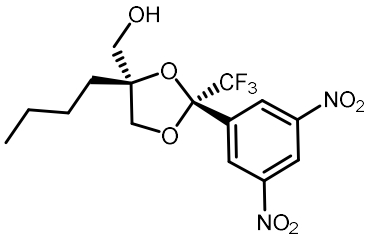
**IR (neat)**: 3631 (w), 3495 (w), 3440 (w), 3101 (w), 2926 (w), 2237 (w), 1631 (w), 1600 (w), 1544 (s), 1491 (w), 1346 (s), 1321 (w), 1201 (s), 1186 (s), 1137 (s), 1105 (s), 1069 (m), 1062 (m), 1008 (m), 915 (m). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.78 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.27 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.10 – 7.02 (m, 2H, C$H_{arom.}$), 6.89 – 6.74 (m, 3H, C$H_{arom.}$), 4.20 (d, $J$ = 8.1 Hz, 1H, C$H_2$), 3.83 (dd, $J$ = 8.0, 1.0 Hz, 1H, C$H_2$), 3.69 (d, $J$ = 12.2 Hz, 1H, C$H_2$), 3.48 (d, $J$ = 12.3 Hz, 1H, C$H_2$), 1.80 (s, 1H, O$H$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 148.3 ($C_q$), 138.6 ($C_q$), 131.6 (*C*H), 129.7 (*C*H), 128.7 (*C*H), 127.2 (*C*H), 122.2 (q, $^1J_{C\text{-}F}$ = 287.8 Hz, *C*$F_3$), 120.9 ($C_q$), 120.3 (*C*H), 104.9 (q, $^2J_{C\text{-}F}$ = 33.5 Hz, $C_q$), 89.0 ($C_q$), 85.5 ($C_q$), 81.8 (*C*H), 73.9 (*C*$H_2$), 64.5 (*C*$H_2$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.48 (s, 3F, C$F_3$). **HRMS (APCI):** Calculated for $C_{20}H_{14}F_3N_2O_9$ $[M+CHOO]^-$: 483.0651, Found: 483.0629. **Optical Rotation**: $[\alpha]_D^{25}$ = – 1.9 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 86:14 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Cellulose-5 column, 22 °C, 1 mL/min, 98:02 hexane:isopropanol, 254 nm, $t_{major}$ = 23.972 min, $t_{minor}$ = 26.535 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**((2R,4S)-2-(3,5-Dinitrophenyl)-2-(trifluoromethyl)-4-((trimethylsilyl)ethynyl)-1,3-dioxolan-4-yl)methanol [5s]**

Following the general procedure **D** using 3-((trimethylsilyl)ethynyl)oxetan-3-ol [**1s**] (34.1 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4a**] (1.9 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (72.0 mg, 0.17 mmol, 85%) was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 80:20) as a colorless oil.

**IR (neat)**: 3681 (w), 3672 (w), 3616 (w), 3474 (w), 3110 (w), 2960 (w), 2897 (w), 1631 (w), 1547 (s), 1346 (m), 1320(w), 1275 (m), 1260 (m), 1203 (m), 1188 (m), 1134 (m), 1106 (m), 1065 (w), 1008 (w), 915 (w), 860 (m), 846 (m), 764 (s), 730 (s), 707 (m). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.76 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.52 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 4.08 (d, $J$ = 8.1 Hz, 1H, C$H_2$), 3.71 (d, $J$ = 9.0 Hz, 1H, C$H_2$), 3.58 (d, $J$ = 12.3 Hz, 1H, C$H_2$), 3.35 (d, $J$ = 12.3 Hz, 1H, C$H_2$), 1.66 (s, 1H, O$H$), -0.17 (s, 9H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 148.4 ($C_q$), 138.9 ($C_q$), 127.4 ($C$H), 122.2 (q, $^1J_{C\text{-}F}$ = 287.5 Hz, $C$F$_3$); 120.2 ($C$H), 104.7 (q, $^2J_{C\text{-}F}$ = 33.5 Hz, $C_q$); 101.4 ($C_q$), 94.4 ($C_q$), 81.3 ($C_q$), 73.7 ($C$H$_2$), 64.3 ($C$H$_2$), -0.8 ($C$H$_3$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.59 (s, 3F, C$F_3$). **HRMS (APCI):** Calculated for $C_{17}H_{18}F_3N_2O_9Si$ [M+CHOO]$^-$: 479.0734, Found: 479.0730. **Optical Rotation**: $[\alpha]_D^{25}$ = + 45.8 ($c$ = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 92:08 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS column, 22 °C, 1 mL/min, 99:01 hexane:isopropanol, 254 nm, $t_{major}$ = 21.051 min, $t_{minor}$ = 27.267 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

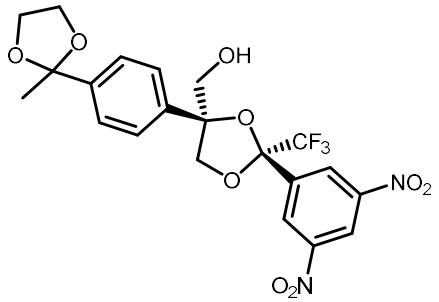



**((2R,4S)-4-Butyl-2-(3,5-dinitrophenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5t]**

Following the general procedure **D** using 3-butyloxetan-3-ol [**1t**] (26.0 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4a**] (1.9 mg, 2.0 µmol, 1.0 mol%), the major diastereomer

(61.0 mg, 0.155 mmol, 78%) was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 80:20) as a colorless oil.

**IR (neat)**: 3484 (w),3110 (w), 2960 (w), 2360 (w), 2335 (w), 1547 (s), 1347 (s), 1184 (s), 1140 (s), 1106 (m), 1070 (m), 1000 (m), 918 (m), 729 (s), 710(s). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.64 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.36 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 3.95 (d, $J$ = 8.3 Hz, 1H; C$H_2$), 3.45 – 3.26 (m, 3H, C$H_2$), 1.43 (s, 1H, O$H$), 1.20 – 1.10 (m, 2H, $CH_2$), 1.07 – 0.76 (m, 4H, $CH_2$), 0.68 (t, $J$ = 7.1 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 148.4 ($C_q$), 139.9 ($C_q$), 126.9 ($C$H), 122.5 (q, $^1J_{C\text{-}F}$ = 288.6 Hz, $CF_3$), 120.2 ($C$H), 104.0 (q, $^2J_{C\text{-}F}$ = 33.0 Hz, $C_q$), 88.9 ($C_q$), 73.0 ($CH_2$), 63.4 ($CH_2$), 34.4 ($CH_2$), 26.1 ($CH_2$), 23.1 ($CH_2$), 13.9 ($CH_3$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.66 (s, 3F, $CF_3$). **HRMS (APCI):** Calculated for $C_9H_{18}O_2N$ [M+MeCN+H]$^+$: 172.1338, Found: 172.1334. **Optical Rotation**: $[\alpha]_D^{25}$ = – 3.4 ($c$ = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 72:28 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Cellulose-5 column, 22 °C, 0.25 mL/min, 90:10 hexane:isopropanol, 210 nm, $t_{major}$ = 23.741 min, $t_{minor}$ = 25.151 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].

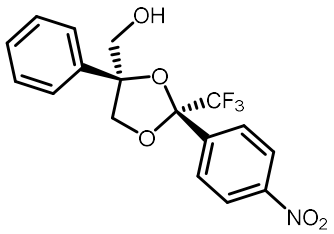



**((2*R*,*4*S)-2-(3,5-Dinitrophenyl)-4-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [5u]**

Following the general procedure **D** using 3-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)oxetan-3-ol [**1u**] (38.4 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (70.0 mg, 0.140 mmol, 70%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless solid.

**M.P.**: 133 – 135 °C. **IR (neat)**: $\tilde{\nu}$ = 3457 (w), 3112 (w), 2987 (w), 2917 (w), 2362 (w), 2279 (w), 1546 (s), 1346 (s), 1200 (m), 1186 (m), 1135 (m), 1103 (w), 1040 (w), 1012 (w), 998 (w), 915 (w), 834 (w), 730 (s), 709 (m), 667 (w), 657 (w), 648 (w), 633 (m), 617 (s), 607 (s). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.56 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.08 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.43 (d, $J$ = 8.4 Hz, 2H, C$H_{arom.}$), 6.92 (d, $J$ = 8.4 Hz, 2H, C$H_{arom.}$), 4.43 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.87 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.58 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 3.49 – 3.39 (m, 2H, C$H_2$), 3.31 (d, $J$ = 11.9 Hz, 1H, C$H_2$), 3.25 – 3.14 (m, 2H, C$H_2$), 1.49 (s, 3H, C$H_3$), 1.34 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 148.1 ($C_q$), 145.1 ($C_q$), 138.7 ($C_q$), 138.4 ($C_q$), 127.0 ($C$H), 125.9 ($C$H), 125.7 ($C$H), 122.3 (q, $^1J_{C\text{-}F}$ = 287.8 Hz, $CF_3$), 120.1 ($C$H), 108.6 ($C_q$), 104.5 (q, $^2J_{C\text{-}F}$ = 33.2 Hz, $C_q$), 89.6 ($C_q$), 72.6 ($CH_2$), 67.1 ($CH_2$), 64.6 (2x$CH_2$), 28.0 ($CH_3$). **$^{19}$F NMR (377 MHz, $C_6D_6$)**

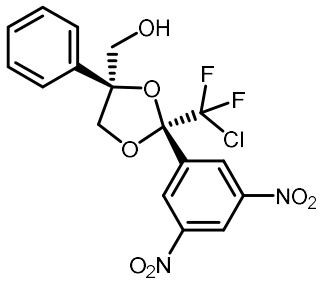
$\delta$ = – 82.1 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{21}H_{19}F_3N_2O_9$ $[M]^-$: 500.1043, Found: 500.1047. **Optical Rotation**: $[\alpha]_D^{25}$ = +5.0 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 71:29 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® Cellulose-1 column, 22 °C, 1 mL/min, 90:10 hexane:isopropanol, 254 nm, $t_{minor}$ = 46.432 min, $t_{major}$ = 23.644 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**((2*R*,4*S*)-2-(4-nitrophenyl)-4-phenyl-2-(trifluoromethyl)-1,3-dioxolan-4-yl)methanol [16a]**

Following the general procedure **D** with minor alterations using 3-phenyl-oxetan-3-ol [**1a**] (30.0 mg, 0.20 mmol, 1.00 eq.), 4'-nitro-2,2,2-trifluoroacetophenone [**6e**] (43.8 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (11.0 mg, 0.030 mmol, 15%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless oil.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3424 (m), 2986 (w), 2941 (m), 1527 (s), 1351 (s), 1189 (s), 1099 (s), 1068 (m), 851 (s), 759 (s), 727 (s), 703 (s). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 7.61 – 7.55 (m, 2H, C$H_{arom.}$), 7.38 – 7.34 (m, 2H, C$H_{arom.}$), 6.94 – 6.83 (m, 5H, C$H_{arom.}$), 4.40 (d, *J* = 8.4 Hz, 1H, C$H_2$), 3.82 (d, *J* = 8.4 Hz, 1H, C$H_2$), 3.61 (d, *J* = 11.9 Hz, 1H, C$H_2$), 3.38 (d, *J* = 11.9 Hz, 1H, C$H_2$), 1.32 (br, 1H, O*H*). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 149.0 ($C_q$), 140.7 ($C_q$), 139.6 ($C_q$), 128.4 (*C*H), 128.2 (*C*H), 127.9 (*C*H), 125.8 (*C*H), 123.3 (*C*H), 122.8 (q, $^1J_{C\text{-}F}$ = 288.0 Hz), 105.4 (d, $^2J_{C\text{-}F}$ = 32.6 Hz), 89.1 ($C_q$), 72.7 ($CH_2$), 67.1 ($CH_2$). **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 81.3 (s, 3F, C$F_3$). **HRMS (APCI)**: Calculated for $C_{18}H_{15}F_3NO_7$ $[M+HCOO]^-$: 414.0801, Found: 414.0806. **Optical Rotation**: $[\alpha]_D^{25}$ = +14.0 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 77:23 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Reprosil Chiral-AMS, 22 °C, 1 mL/min, 95:05 hexane:isopropanol, 254 nm, $t_{minor}$ = 20.203 min, $t_{major}$ = 17.186 min). See section 15 for HPLC chromatograms. Absolute stereochemistry determined through analogy with [**5j**].




**((2*R*,4*S*)-2-(chlorodifluoromethyl)-2-(3,5-dinitrophenyl)-4-phenyl-1,3-dioxolan-4-yl)methanol [18a]**

Following the general procedure **D** with minor alterations using 3-phenyl-oxetan-3-ol [**1a**] (30.0 mg, 0.20 mmol, 1.00 eq.), 3'5'-dinitro-2,2-difluoro-2-chloroacetophenone [**17**] (56.1 mg, 0.20 mmol, 1.00 eq.) and $Co^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the major diastereomer (63.0 mg, 0.146 mmol, 73%) was obtained *via* RP-MPLC (MeCN:$H_2O$, 50:50) as a colorless foam.

**Major diastereomer [3a]: IR (neat)**: $\tilde{\nu}$ = 3341 (m), 3114 (m), 2927 (m), 1628 (w), 1545 (s), 1345 (s), 1232 (w), 1127 (m), 1061 (m), 1033 (m), 911 (m), 760 (m). **$^1$H NMR (400 MHz, $C_6D_6$)**: $\delta$ = 8.59 (d, $J$ = 2.0 Hz, 2H, C$H_{arom.}$), 8.09 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 6.91 – 6.85 (m, 2H, C$H_{arom.}$), 6.84 – 6.78 (m, 3H, C$H_{arom.}$), 4.43 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.88 (d, $J$ = 8.6 Hz, 1H, C$H_2$), 3.60 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 3.29 (d, $J$ = 12.0 Hz, 1H, C$H_2$), 1.63 – 1.38 (br, 1H, O$H$). **$^{13}$C NMR (101 MHz, $C_6D_6$)**: $\delta$ = 147.8 ($C_q$), 139.0 ($C_q$), 138.9 ($C_q$), 128.6 (*C*H), 128.6 (*C*H), 127.7 (*C*H), 127.1 (t, $^1J_{C\text{-}F}$ = 301.9 Hz, *C*$F_2$Cl), 125.8 (*C*H), 120.0 (*C*H), 107.1 (t, $^2J_{C\text{-}F}$ = 28.1 Hz, $C_q$), 89.7 ($C_q$), 72.4 *C*$H_2$, 67.2 *C*$H_2$. **$^{19}$F NMR (377 MHz, $C_6D_6$)** $\delta$ = – 67.5 (s, 2F, C$F_2$Cl). **HRMS (APCI)**: Calculated for $C_{18}H_{14}ClF_2N_2O_9$ $[M+HCOO]^-$: 475.0356, Found: 475.0363. **Optical Rotation**: $[\alpha]_D^{25}$ = +12.2 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 74:26 *er*. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Amylose-3 column, 22 °C, 1 mL/min, 95:05 hexane:isopropanol, 254 nm, $t_{minor}$ = 20.097 min, $t_{major}$ = 23.786 min). See section 15 for HPLC chromatograms. Relative configuration was determined *via* 2D-$^1$H,$^1$H NOESY experiments. Absolute stereochemistry determined through analogy with [**5j**].

## 5. Determination of the relative configuration of 1,3-dioxolanes

The both diastereotopic $CH_2$-groups of the susbtrates **[5a]** and **[5d]** to **[5u]** are unambiguously identified *via* gHMBC or COSY experiments. The relative configuration of the formed major diastereoisomer could be determined *via* 2D-$^1$H,$^1$H NOESY experiments. For electron donating (R = *t*Bu) and withdrawing (R = Br) groups NOE interactions could be observed for the protons in *ortho*-position. It can therefore be concluded, that the two aromatic substituents are positioned *syn* to each other. Another NOE effect was observed for the *ortho*-protons of one aromatic ring and one of the $CH_2$-group protons inside the ring.

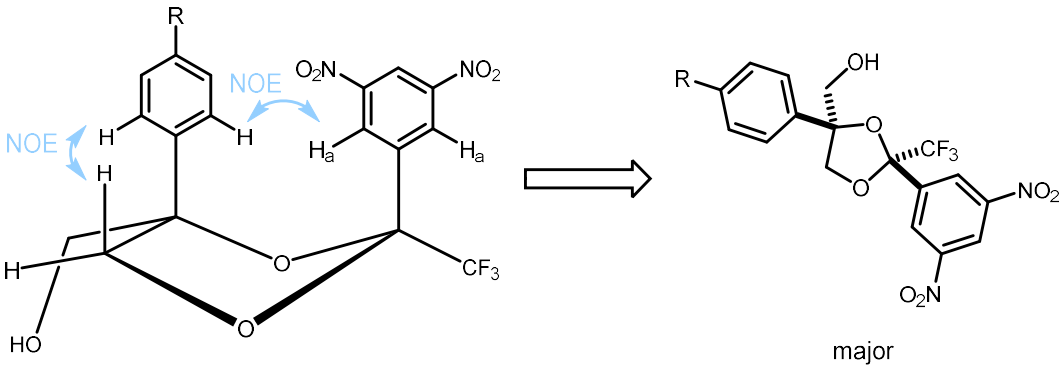



Figure 7: Summary of relevant NOE interactions and model of the relative configuration.

## 6. Conditions for deprotection of 1,2-diols

Several attempts for the deprotection of the formed 1,3-dioxolanes were made. Neither basic nor acidic media promoted the hydrolysis of **[5j]**. Nucleophilic ring opening was not observed. Reducing conditions, other than entry **S19m** were applied to the TIPS-protected alcohol. These reactions led to reduction of the nitro groups to amino groups. The fully reduced species is not susceptible for hydrolysis in either acidic or basic media. Attempts for the oxidation of the 1,3-dioxolane core to a more labile species were performed on the TIPS protected derivative of 1,3-dioxolane **[5j]** without any sign of oxidation. Partial Cleavage of the TIPS-group could be observed in some entries.

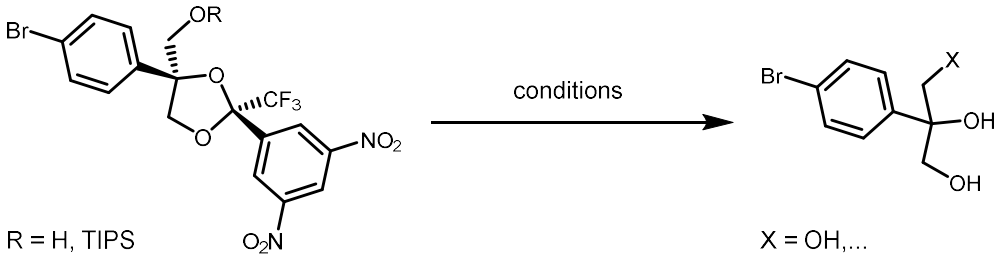
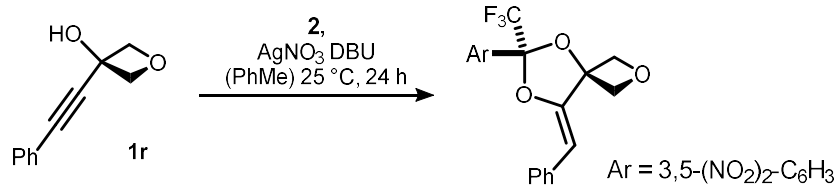



Table 7: Conditions for deprotection of 1,2-diols

| entry | | entry | conditions | yield |
|---|---|---|---|---|
| 1 | hydrolytic | **S19a** | PPTS (20 mol%), (MeOH), rt ,17 h | 0% |
| 2 | | **S19b** | pTsOH (20 mol%), (MeOH), rt, 17 h | 0% |
| 3 | | **S19c** | HCl (1N), (MeOH), rt, 17 h | 0% |
| 4 | | **S19d** | HCl (6N), (MeOH), 60 °C, 4 h | 0% |
| 5 | | **S19e** | TfOH (1.00 eq.), (TFA), rt, 17h 4 h | 0% |
| 6 | | **S19f** | KOH aq. (2N), (MeOH), 60°C, 17 h | 0% |
| 7 | | **S19g** | KOH aq. (2N), (THF), 60°C, 17 h | 0% |
| 8 | | **S19h** | $BBr_3$ (6.00 eq.), $CH_2Cl_2$, rt. 17 h | 0% |
| 9 | nucleophilic | **S19i** | benzo[d]thiazole-2-thiol (2.00 eq.), $BF_3OEt_2$ (1.00 eq.), (DCE), 60°C, 17 h | 0% |
| 10 | | **S19j** | EtSH (10.0 eq.), NaOMe (10.0 eq.), (PhMe), 80 °C, 16 h | 0% |
| 11 | | **S19k** | CH2=CHMgBr (2.00 eq.), 0°C to rt, 17 h | 0% |
| 12 | | **S19l** | TMSI (1.00 eq.), ($CH_2Cl_2$), rt, 17 h | 0% |
| 13 | reducing | **S19m** | Pd/C (5 mol%), $H_2$, (MeOH), rt, 1 h | 0% |
| 14 | | **S19n** | $LiBHEt_3$, (1.00 eq.), (THF), – 20 °C to rt, 20 h | 0% |
| 15 | | **S19o** | DIBAL-H (4.00 eq.), ($CH_2Cl_2$), rt, 16 h | 0% |
| 16 | oxidative | **S19p** | CAN (1.00 eq.), (MeCN:$H_2O$, 1:1), rt, 17 h | 0% |
| 17 | | **S19q** | $RuCl_3 \cdot H_2O$ (0.20 eq.), $NaIO_4$ (4.00 eq.), (MeCN:$H_2O$:$CCl_4$, 1:1.5:1), 40 °C, 3d | 0% |
| 18 | | **S19r** | Cumene hydroperoxide (1.00 eq.), KOtBu (9.00 eq.), ($CH_2Cl_2$), reflux, 24 h | 0% |
| 19 | | **S19s** | $K_3[Fe(CN)_6]$ (10.0 eq.), ($NaHCO_3$ aq. sat.) 100 °C, 24 h | 0% |
| 20 | | **S19t** | $K_3[Fe(CN)_6]$ (10.0 eq.), (NaOH, 2N). 100 °C, 24 h | 0% |
| 21 | | **S19u** | $Mn_2O_7$ (2.00 eq.), (EtOAc:$CCl_4$, 1:1), – 40 °C, 30 min | 0% |
| 22 | photo-chemical | **S19v** | *hv* (245 nm), (MeCN:$H_2O$, 95:5), rt, 16 h | 0% |

## 7. Further functionalizations

### 7.1. Nucleophilic addition to alkynes

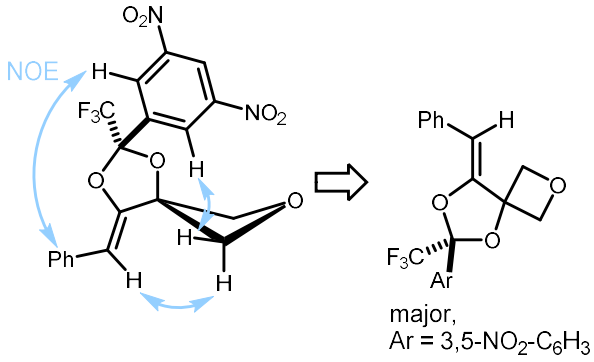



**(R,Z)-8-Benzylidene-6-(3,5-dinitrophenyl)-6-(trifluoromethyl)-2,5,7-trioxaspiro[3.4]octane [19r]**

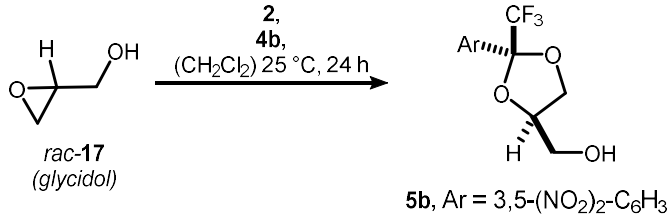
Following a literature known protocol with minor alterations,[32] ketone [**2**] (63.4 mg, 0.24 mmol, 1.20 eq.), 3-(phenylethynyl)oxetan-3-ol **[5r]** (32.0 mg, 0.20 mmol, 1.00 eq.), $AgNO_3$ (3.4 mg, 20.0 µmol, 10.0 mol%) and 1,8-diazabicyclo[5.4.0]-7-undecene (3.0 µL, 20.0 µmol, 10.0 mol%) were dissolved in dry toluene (1.3 mL) at room temperature. The temperature was maintained for 24 h before silica gel was added and filtered off. The resulting silica gel plug was flushed with $Et_2O$, and the filtrate was concentrated. NMR yield and *rr* of the crude reaction mixture was determined by $^{19}F$ NMR using $PhCF_3$ (12.2 µL, 0.10 mmol) as the internal standard. A racemic mixture of the desired product was obtained *via* automated FC (CyH:$Et_2O$, 100:0 to 70:30) as a pale yellow solid (85.0 mg, 0.19 mmol, 95%).

**M.P.:** 158.5 – 160.5 °C. **IR (neat)**: 1727 (w), 1701 (w), 1548 (s), 1347 (s), 1319 (w), 1299 (m), 1200 (s), 1147 (s), 1036 (w), 1004 (m), 913 (w), 846 (w), 777 (m), 759 (w), 731 (m), 711 (m). **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.56 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.36 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 7.60 – 7.54 (m, 2H, C$H_{arom.}$), 7.21 (t, $J$ = 7.8 Hz, 2H, C$H_{arom.}$), 7.08 – 7.02 (m, 1H, C$H_{arom.}$), 5.85 (s, 1H, C$H$), 4.89 (d, $J$ = 7.7 Hz, 1H, C$H_2$), 4.67 (d, $J$ = 8.9 Hz, 1H, C$H_2$), 4.53 (d, $J$ = 7.7 Hz, 1H, C$H_2$), 4.41 – 4.33 (m, 1H, C$H_2$). **$^{13}$C NMR** (101 MHz, $C_6D_6$) $\delta$ (ppm) = 150.3 ($C_q$), 148.4 ($C_q$), 135.6 ($C_q$), 133.4 ($C_q$), 129.2 (*C*H), 128.6 (*C*H), 126.4 (*C*H), 121.6 (q, $^1J_{C\text{-}F}$ = 289.6 Hz, *C*$F_3$), 120.9 (*C*H), 104.9 (q, $^2J_{C\text{-}F}$ = 34.0 Hz, $C_q$), 101.3 (*C*H), 85.9 (*C*H), 83.6 ($C_q$), 83.6 (*C*$H_2$), 81.6 (*C*$H_2$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 83.33 (s, 3F, C$F_3$). **HRMS (APCI):** Calculated for $C_{19}H_{12}F_3N_2O_7$ $[M\text{-}H]^-$: 437.0597, Found: 437.0604 **Optical Rotation**: $[\alpha]_D^{25}$ = +0.0 ($c$ = 1.00, $CHCl_3$) for a racemic sample. The enantiomeric purity was established by HPLC analysis using a chiral column (Lux® i-Amylose-3, 22 °C, 1 mL/min, 80:20 hexane:isopropanol, 254 nm, t = 6.298 min and 6.882 min). See section 15 for HPLC chromatograms.

The relative configuration was established through 2D-$^{1}$H,$^{1}$H NOESY experiments. The configuration of the double bond was determined in analogy to a literature precedent.[32]




## 7.2. Ring-opening reaction of 3-membered rings




Following the general procedure **D** using *rac*-glycidol [**20**] (45.8 mg, 0.20 mmol, 1.00 eq.) and Co$^{II}$·salen [**4b**] (2.0 mg, 2.0 µmol, 1.0 mol%), the product was obtained *via* RP-MPLC (MeCN:H2O, 50:50) as a colorless oil (65 mg, 96%) and a diastereomeric mixture with 63:37 *dr*.

The obtained spectroscopic data matched to those obtained from substrate **[5b]**.

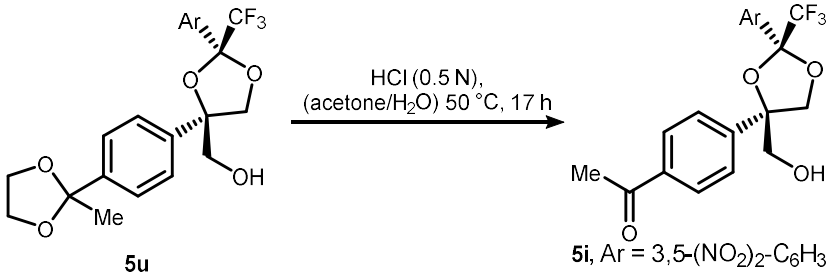
**Major diastereomer:**

**$^{1}$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.54 (d, $J$ = 2.1 Hz, 2H, C$H_{arom.}$), 8.37 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 3.65 – 3.54 (m, 2H, C$H_2$), 3.43 – 3.35 (m, 1H, C$H$), 3.26 – 3.11 (m, 2H, C$H_2$), 1.42 – 1.14 (br, 1H, O$H$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.74 (s, 3F, C$F_3$).

**Minor diastereomer:**

**$^{1}$H NMR** (400 MHz, $C_6D_6$) $\delta$ (ppm) = 8.61 (d, $J$ = 2.3 Hz, 2H, C$H_{arom.}$), 8.31 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 4.02 – 3.90 (m, 1H, C$H_2$), 3.73 – 3.65 (m, 2H, C$H_2$), 3.51 – 3.43 (m, 1H, C$H_2$), 3.05 (dd, $J$ = 12.1, 3.9 Hz, 1H, C$H_2$), 2.78 (dd, $J$ = 12.1, 3.6 Hz, 1H, C$H_2$), 0.88 (br, 1H, O$H$). **$^{19}$F NMR** (377 MHz, $C_6D_6$) $\delta$ (ppm) = – 81.79 (s, 3F, C$F_3$).

## 7.3. Chemoselective deprotection




**5u** **5i**, Ar = 3,5-$(NO_2)_2$-$C_6H_3$

3-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)oxetan-3-ol [**1u**] (50 mg, 0.10 mmol, 1.00 eq.) was dissolved in acetone (1mL) and HCl aq. (1N, 1 mL) was added. The mixture was heated to 50 °C for 17 h before EtOAc (4 mL) and $NaHCO_3$ sat. (4 mL) were added. The aqueous phase was extracted with EtOAc (3x4 mL). The combined organic fractions were dried over $Na_2SO_4$ and the solvent was removed. The crude mixture was analyzed by $^1$H NMR with 0.1 mmol mesitylene as an internal standard.

The product was isolated after RP-FC (MeCN:$H_2O$, 50:50) as a colorless solid (43 mg, 94%).

**$^1$H NMR (300 MHz, acetone-d6)**: $\delta$ = 8.96 (t, $J$ = 2.1 Hz, 1H, C$H_{arom.}$), 8.78 – 8.71 (m, 2H, C$H_{arom.}$), 7.86 – 7.80 (m, 2H, C$H_{arom.}$), 7.57 – 7.50 (m, 2H, C$H_{arom.}$), 4.89 (dd, $J$ = 8.9, 0.9 Hz, 1H, C$H_2$), 4.67 – 4.61 (m, 1H, C$H_2$), 4.04 (d, $J$ = 11.7 Hz, 1H, C$H_2$), 3.89 (d, $J$ = 11.7 Hz, 1H, C$H_2$), 2.48 (s, 3H, C$H_3$). **$^{19}$F NMR (282 MHz, acetone-d6)** $\delta$ = – 81.7 (s, 3F, C$F_3$).

The obtained spectroscopic data were identical to those of substrate **[5i]**.

## 8. Crystallographic data

### 8.1. X-ray crystal structure analysis of [10e] (wie 9750):

A colorless needle-like specimen of $C_{15}H_{12}F_3N_2O_4$, approximate dimensions 0.058 mm x 0.101 mm x 0.334 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1224 frames were collected. The total exposure time was 23.74 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 22240 reflections to a maximum θ angle of 68.36° (0.83 Å resolution), of which 2578 were independent (average redundancy 8.627, completeness = 99.4%, $R_{int}$ = 5.26%, $R_{sig}$ = 3.99%) and 2349 (91.12%) were greater than $2\sigma(F^2)$.The final cell constants of a = 13.5889(3) Å, b = 9.9317(2) Å, c = 20.9678(4) Å, volume = 2829.83(10) Å$^3$, are based upon the refinement of the XYZ-centroids of 9928 reflections above 20 σ(I) with 8.434° < 2θ < 136.6°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.747. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6900 and 0.9340. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P* b c a, with Z = 8 for the formula unit, $C_{15}H_{12}F_3N_2O_4$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 212 variables converged at R1 = 3.38%, for the observed data and wR2 = 8.27% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.275 e$^-$/Å$^3$ and the largest hole was -0.272 e$^-$/Å$^3$ with an RMS de*via*tion of 0.047 e$^-$/Å$^3$. On the basis of the final model, the calculated density was 1.536 g/cm$^3$ and F(000), 1344 e$^-$. The hydrogen at O2 atom was refined freely. CCDC Nr.: 2130260.

### 8.2. X-ray crystal structure analysis of [13] (wie 9886)

A colorless plate-like specimen of $C_8H_5F_3N_2O_6$, approximate dimensions 0.049 mm x 0.101 mm x 0.197 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Cu Ims ($CuK_\alpha$, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1609 frames were collected. The total exposure time was 14.90 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an monoclinic unit cell yielded a total of 16992 reflections to a maximum θ angle of 68.15° (0.83 Å resolution), of which 1797 were independent (average redundancy 9.456, completeness = 96.8%, $R_{int}$ = 4.75%, $R_{sig}$ = 2.59%) and 1736 (96.61%) were greater than $2\sigma(F^2)$.The final cell constants of of a = 6.15030(10) Å, b = 12.5829(3) Å, c = 13.1818(3) Å, β = 93.6830(10)°, volume = 1018.01(4) Å$^3$, are based upon the refinement of the XYZ-centroids of 9978 reflections above 20 σ(I) with 13.46° < 2θ < 136.3°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.851. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7280 and 0.9200. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$ 1, with Z = 4 for the formula unit, $C_8H_5F_3N_2O_6$. The final

anisotropic full-matrix least-squares refinement on $F^2$ with 180 variables converged at R1 = 3.02%, for the observed data and wR2 = 7.53% for all data. The goodness-of-fit was 1.089. The largest peak in the final difference electron density synthesis was 0.273 $e^-/Å^3$ and the largest hole was -0.210 $e^-/Å^3$ with an RMS de*via*tion of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.841 $g/cm^3$ and F(000), 568 $e^-$. The hydrogen atoms at O1 and O2 were refined freely. CCDC Nr.: 2130259.

### 8.3. X-ray crystal structure analysis of [5j] (ass6091)

A colorless block-like specimen of $C_{17}H_{12}F_3N_2O_7$, approximate dimensions 0.080 mm x 0.260 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a STOE IPDS-2T Diffractometer system. CCDC number: 2141905

Table 8: Crystal data and structure refinement for [5j] (ass6091)

| | |
|---|---|
| Identification code | ass6091 |
| Empirical formula | $C_{17}H_{12}BrF_3N_2O_7$ |
| moiety formula | $C_{17}H_{12}BrF_3N_2O_7$ |
| Formula weight | 493.20 |
| Temperature | 120(2) K |
| Wavelength, radiation type | 0.71073Å, MoKα |
| Diffractometer | STOE IPDS 2T |
| Crystal system | Orthorhombic |
| Space group name, number | P $2_12_12_1$, (19) |
| Unit cell dimensions | a = 10.9727(5) Å<br>b = 11.7950(4) Å<br>c = 14.1878(7) Å |
| Volume | 1836.23(14) $Å^3$ |
| Number of reflections and range used for lattice parameters | 9257<br>2.87° <=θ<= 28.47° |
| Z | 4 |
| Density (calculated) | 1.784 $Mg/m^3$ |
| Absorption coefficient | 2.314 $mm^{-1}$ |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8306 and 0.5223 |
| F(000) | 984 |
| Crystal size, color and form | 0.080 x 0.260 x 0.280 $mm_3$, colorless block |
| Theta range for data collection | 2.871 to 27.957°. |
| Index ranges | -14<=h<=12, -13<=k<=15, -18<=l<=16 |
| Number of reflections: | |
| collected | 7188 |
| independent | 4369 [R(int) = 0.0314] |
| observed [I>2sigma(I)] | 4002 |
| Completeness to theta = 25.2° | 99.8 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4369 / 0 / 317 |
| Goodness-of-fit on $F^2$ | 1.075 |
| Final R indices [I>2sigma(I)] | R1 = 0.0358, wR2 = 0.0778 |
| R indices (all data) | R1 = 0.0425, wR2 = 0.0816 |
| Absolute structure parameter | 0.013(8) |
| Largest diff. peak and hole | 0.605 and -0.319 $eÅ^{-3}$ |
| Remark | hydrogen atoms localized and refined with isotropic thermal displacement parameters |

## 9. References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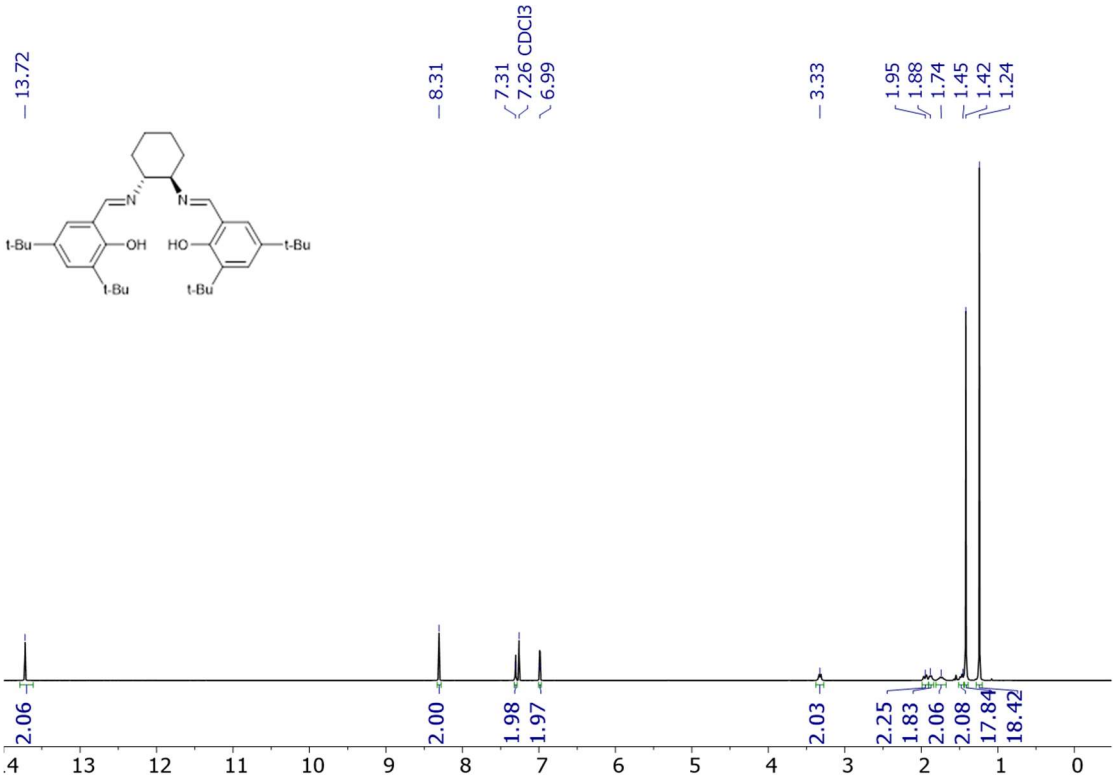
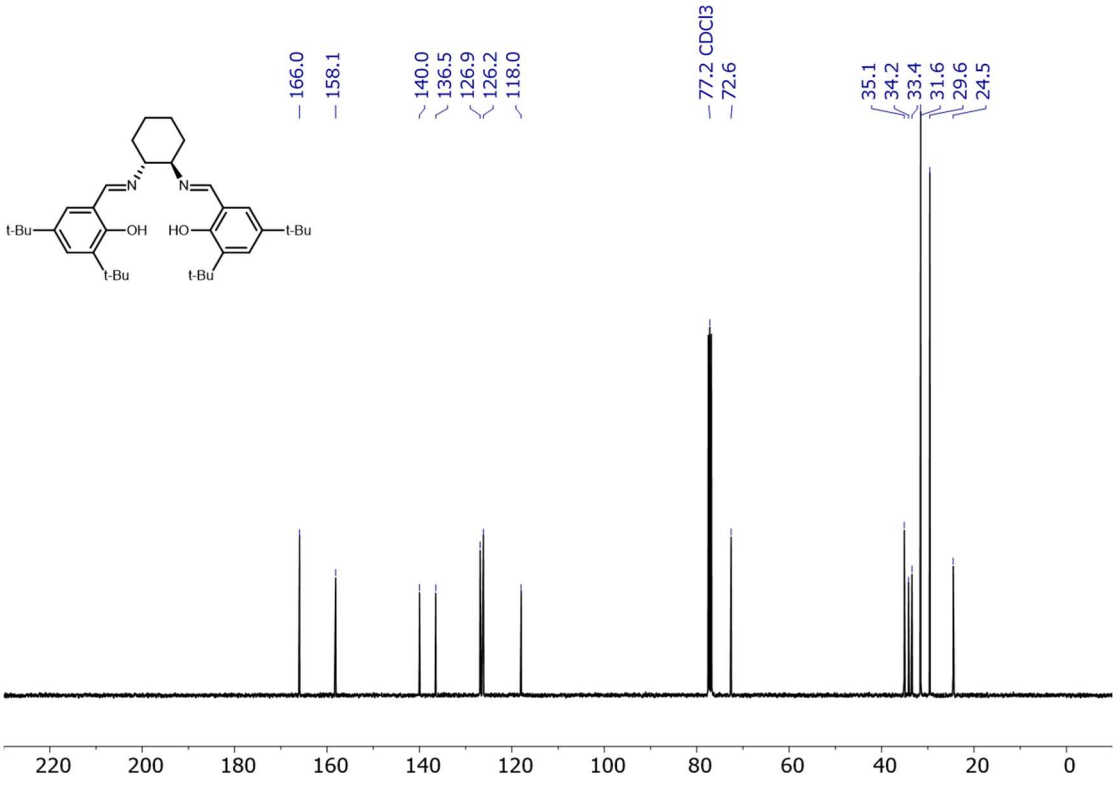
## 10. NMR spectra, HPLC traces, and cartesian coordinates

### 10.1. NMR data

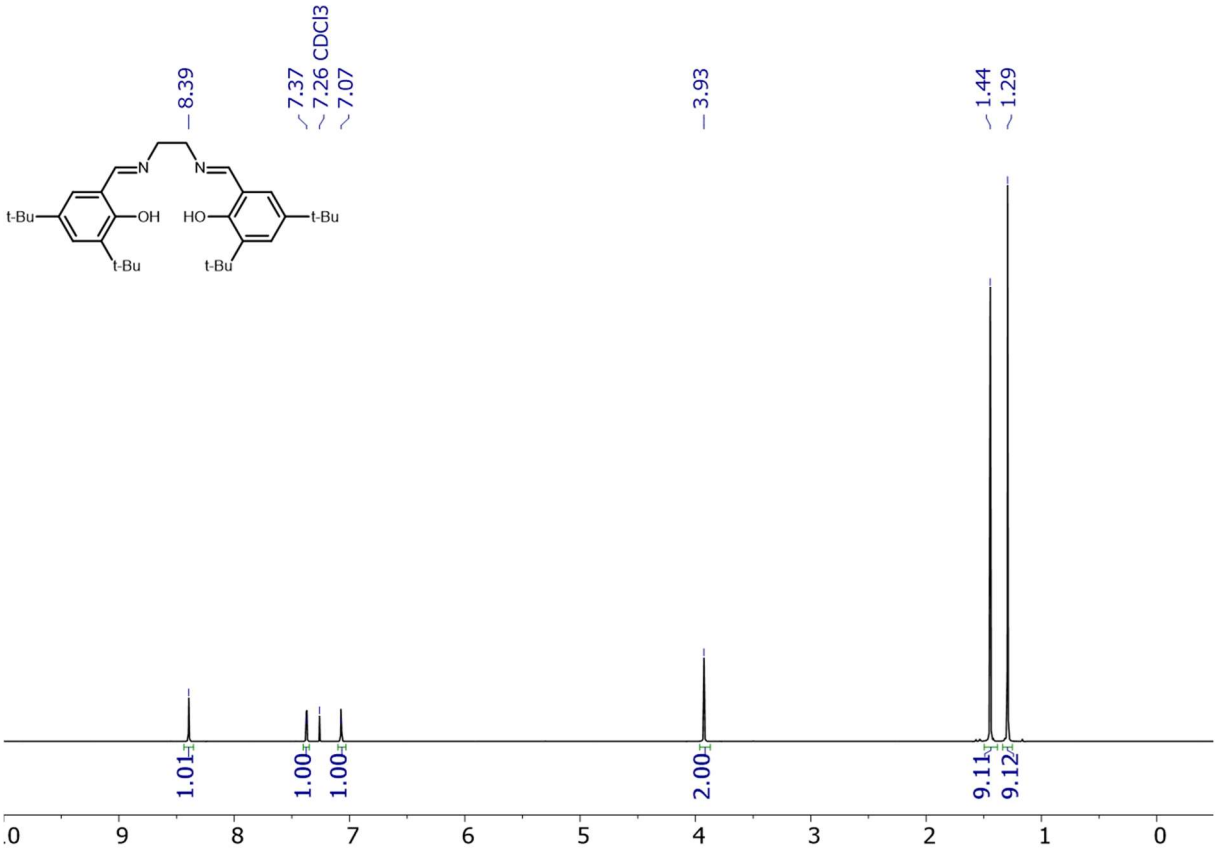
**[S1], $^{1}H$, $CDCl_3$, 400 MHz**



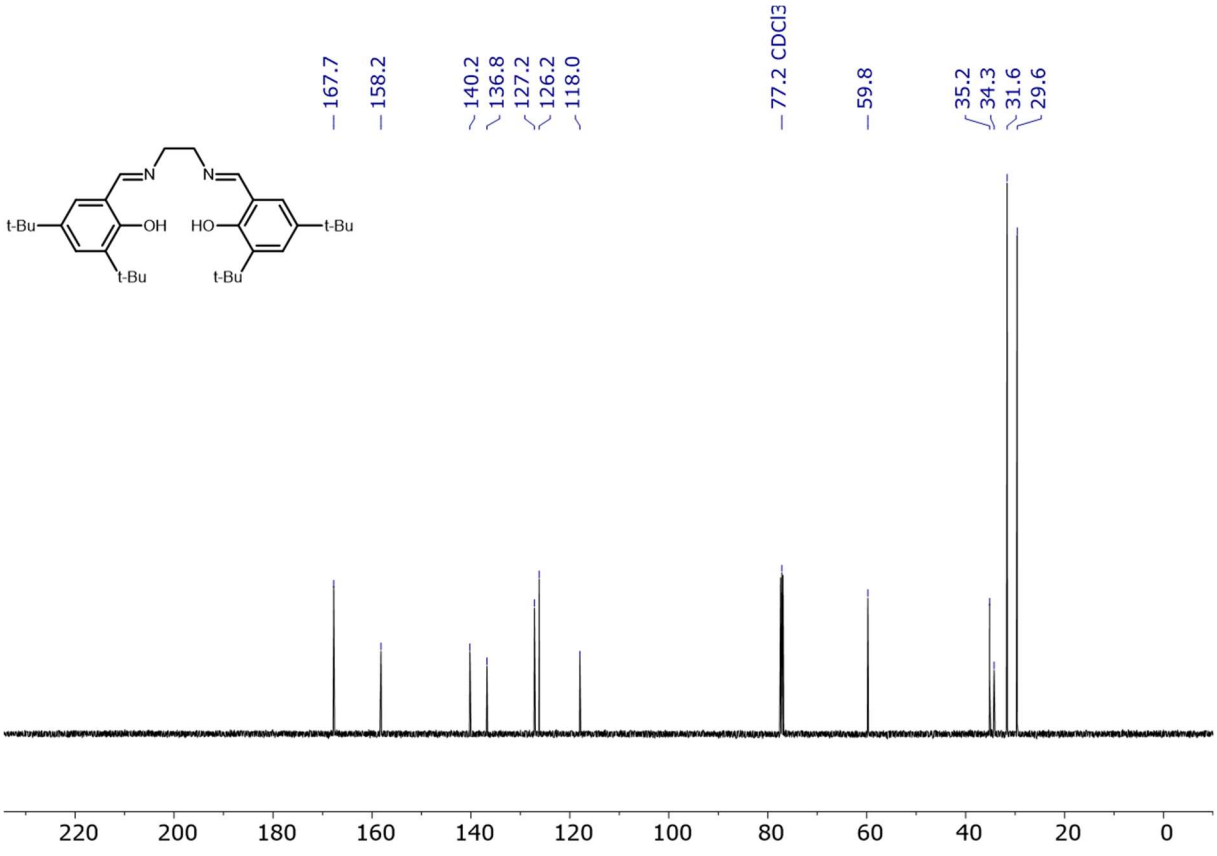

**[S1], $^{13}C$, $CDCl_3$, 101 MHz**



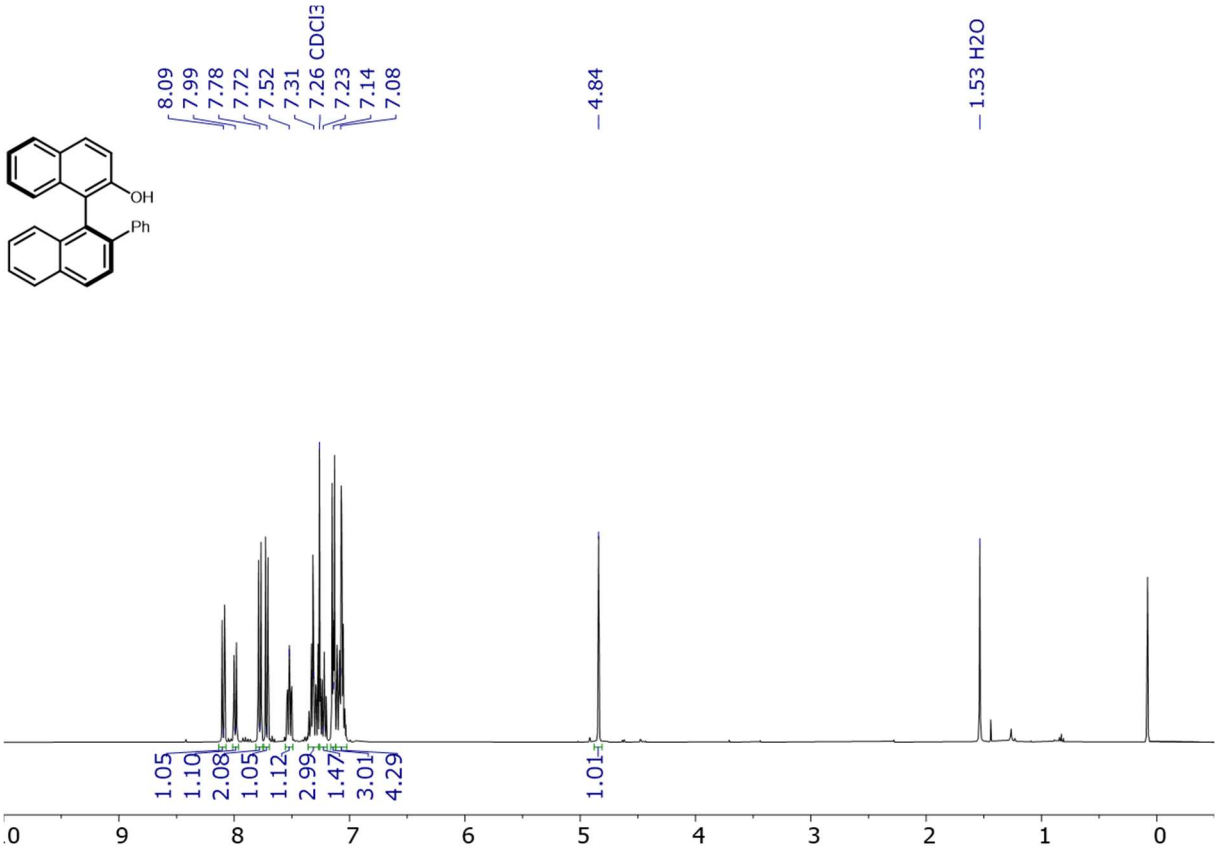
**[S2], $^{1}H$, $CDCl_3$, 500 MHz**



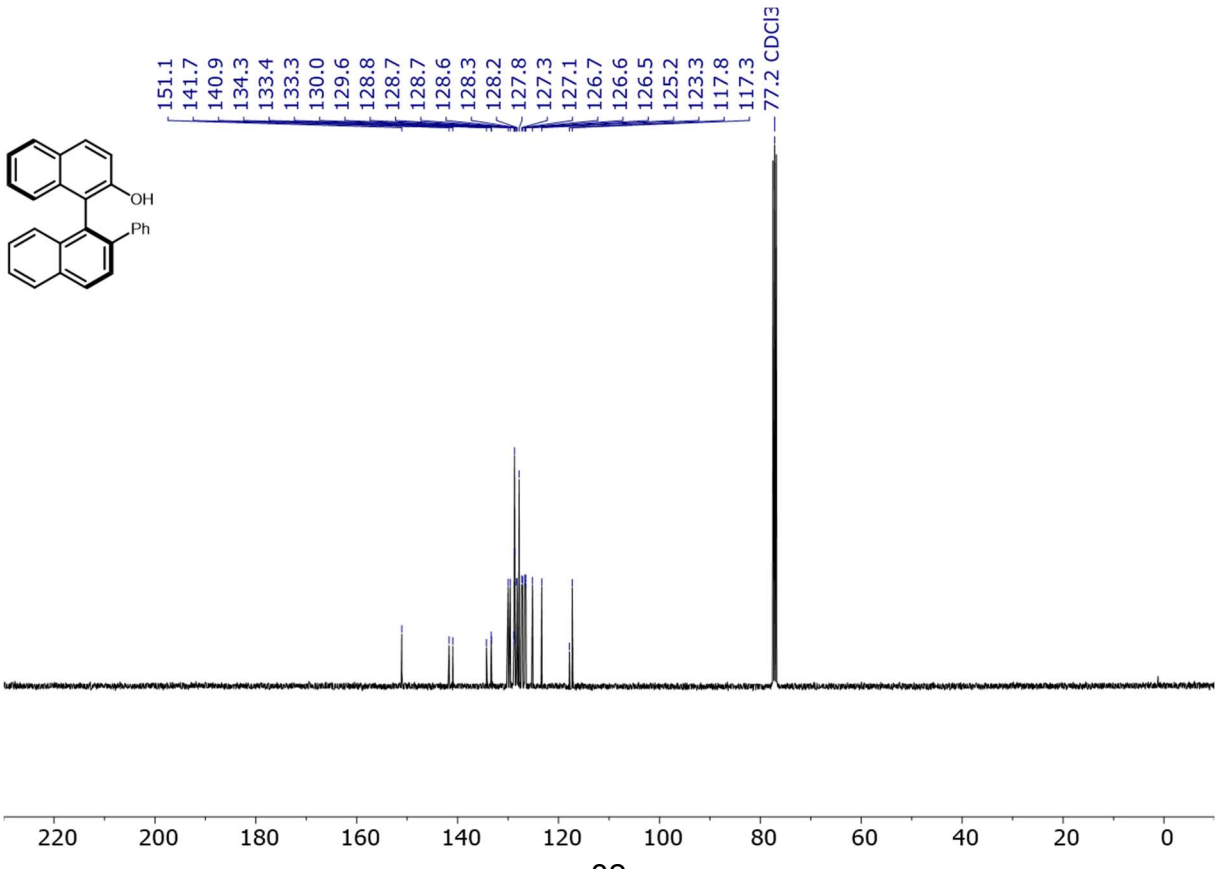

**[S2], $^{13}C$, $CDCl_3$, 126 MHz**



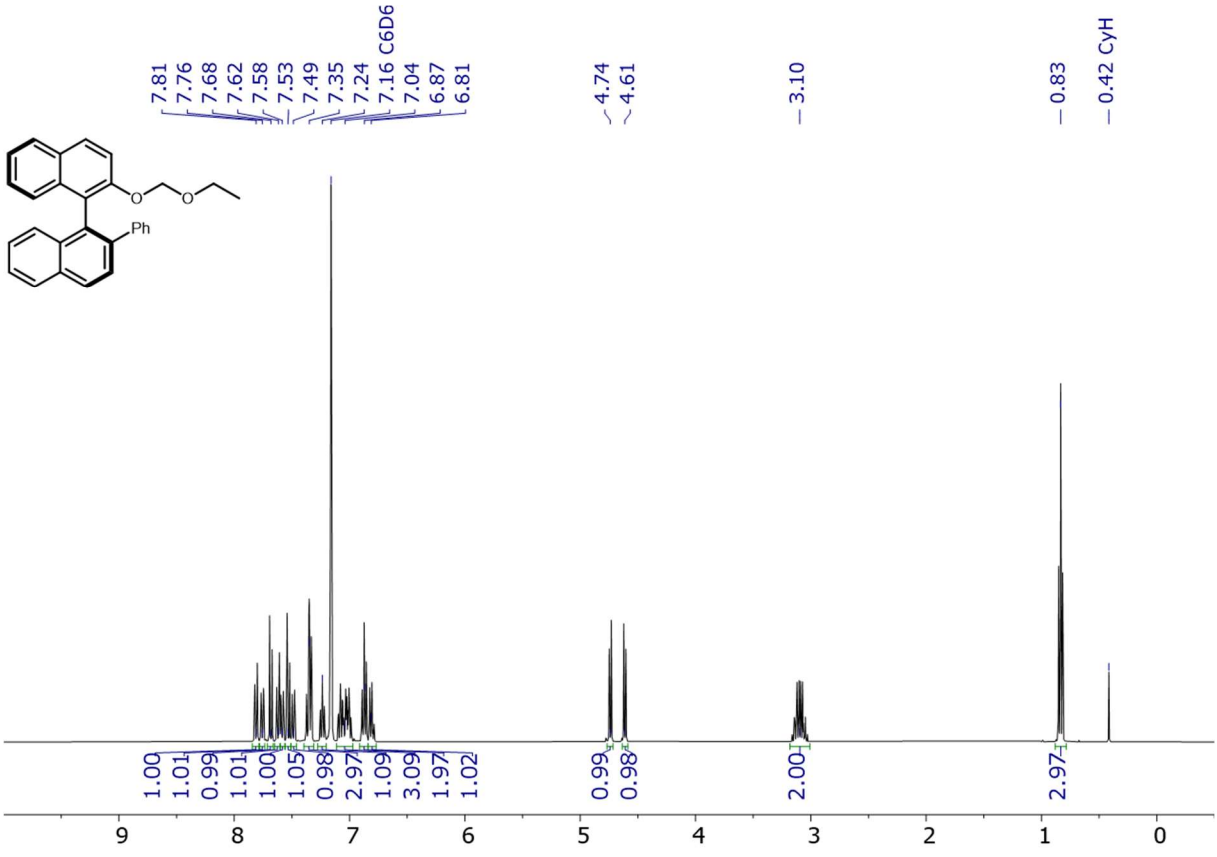
**[S3], $^{1}H$, $CDCl_3$, 400 MHz**



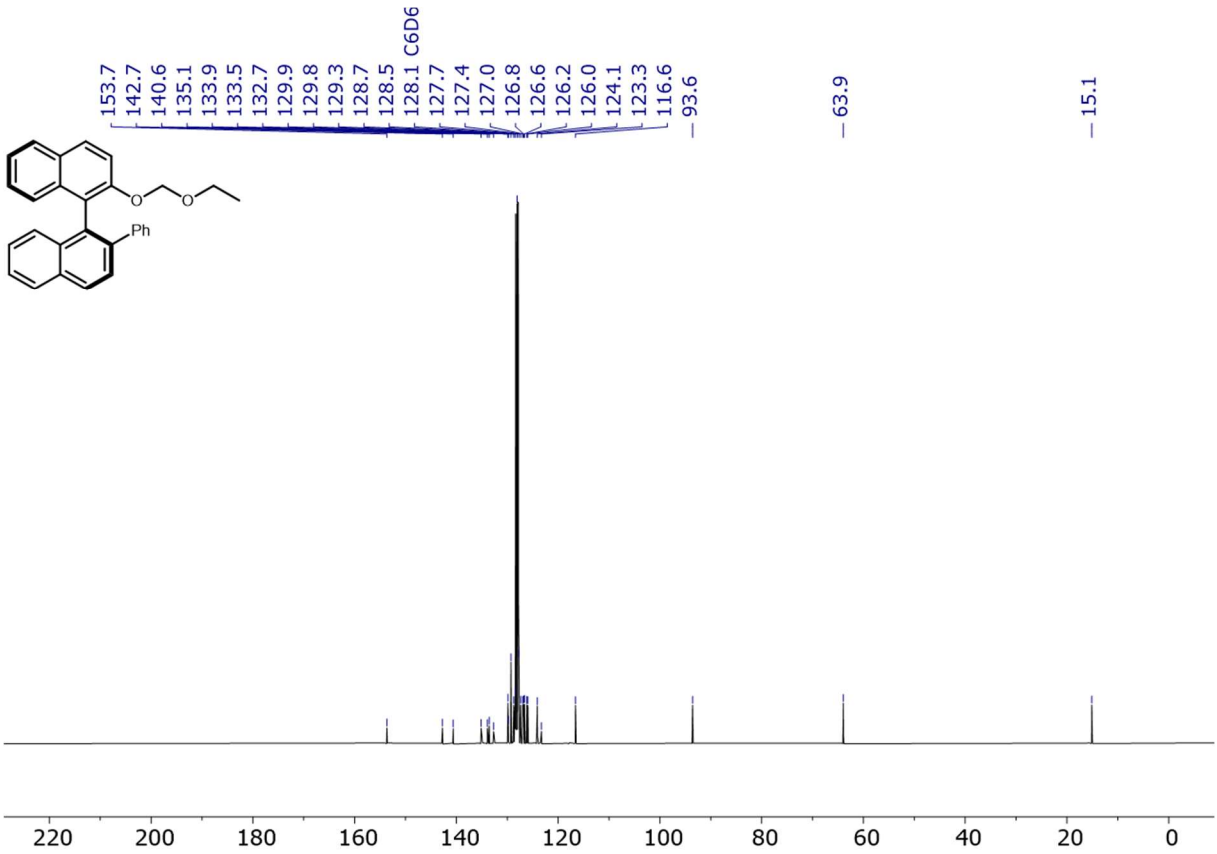

**[S3], $^{13}C$, $CDCl_3$, 101 MHz**



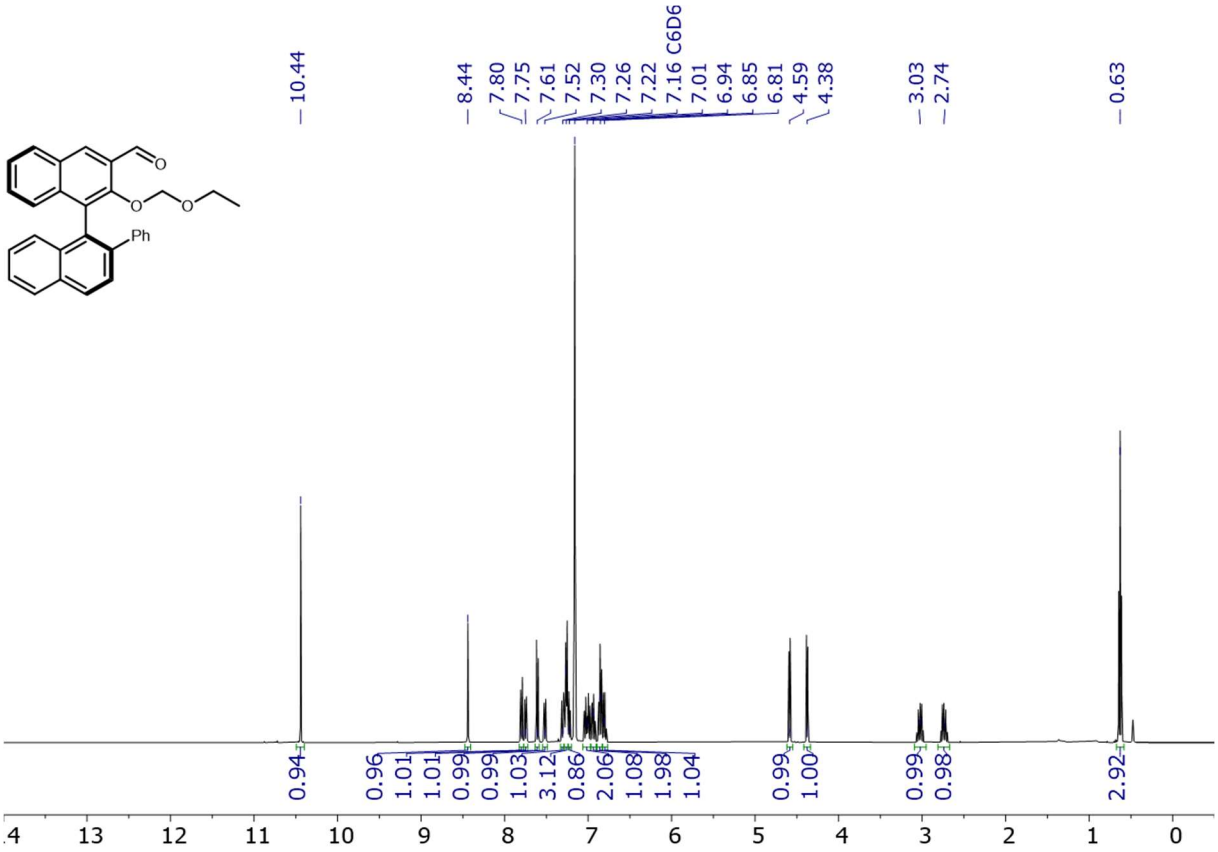
**[S4], $^{1}H$, $C_6D_6$, 400 MHz**



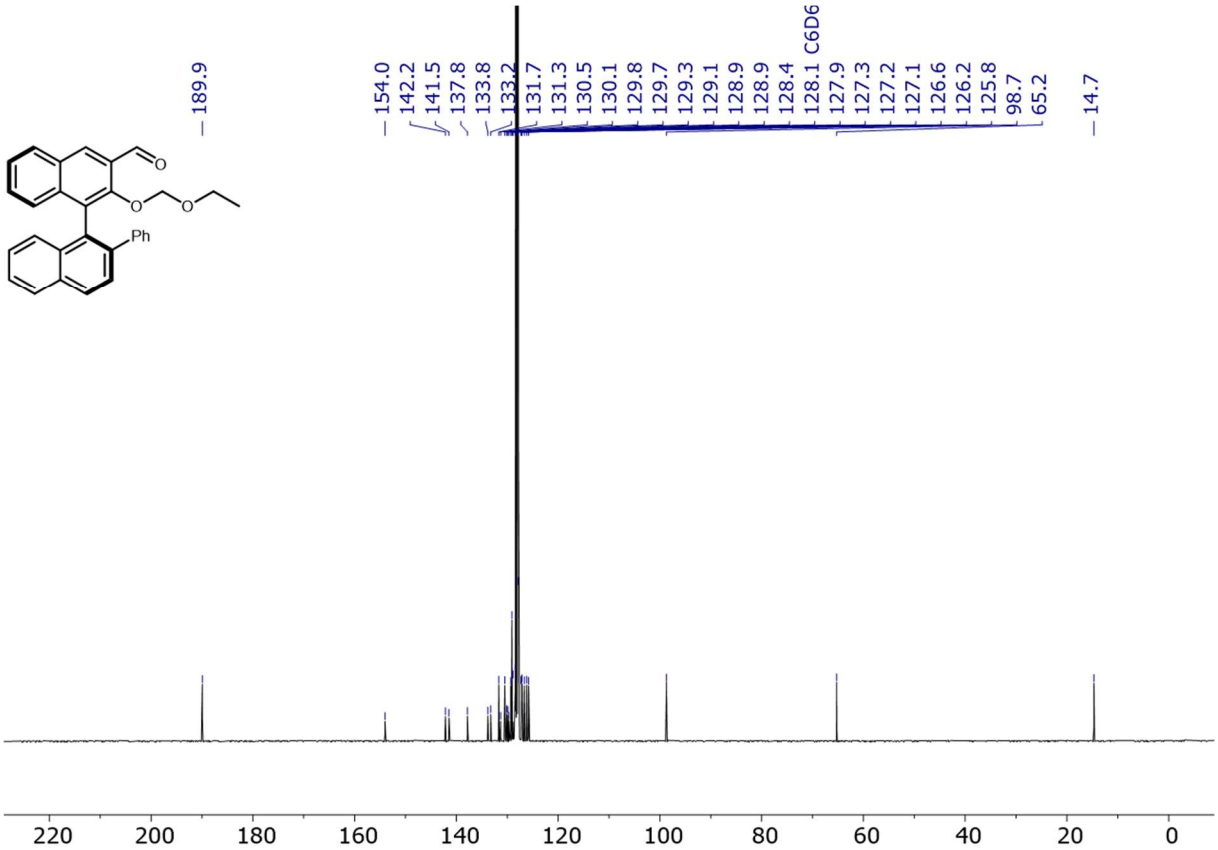

**[S4], $^{13}C$, $C_6D_6$, 101 MHz**



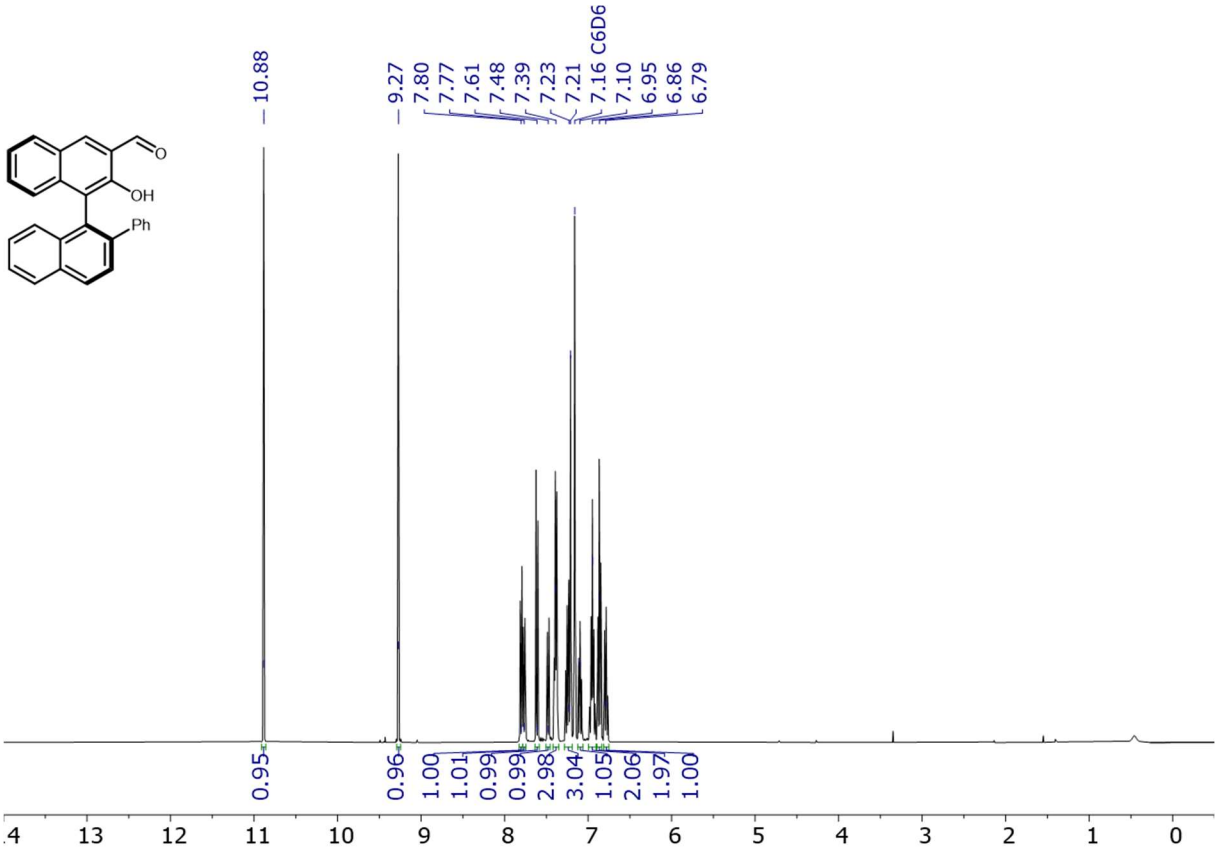
**[S5], $^{1}H$, $C_6D_6$, 400 MHz**



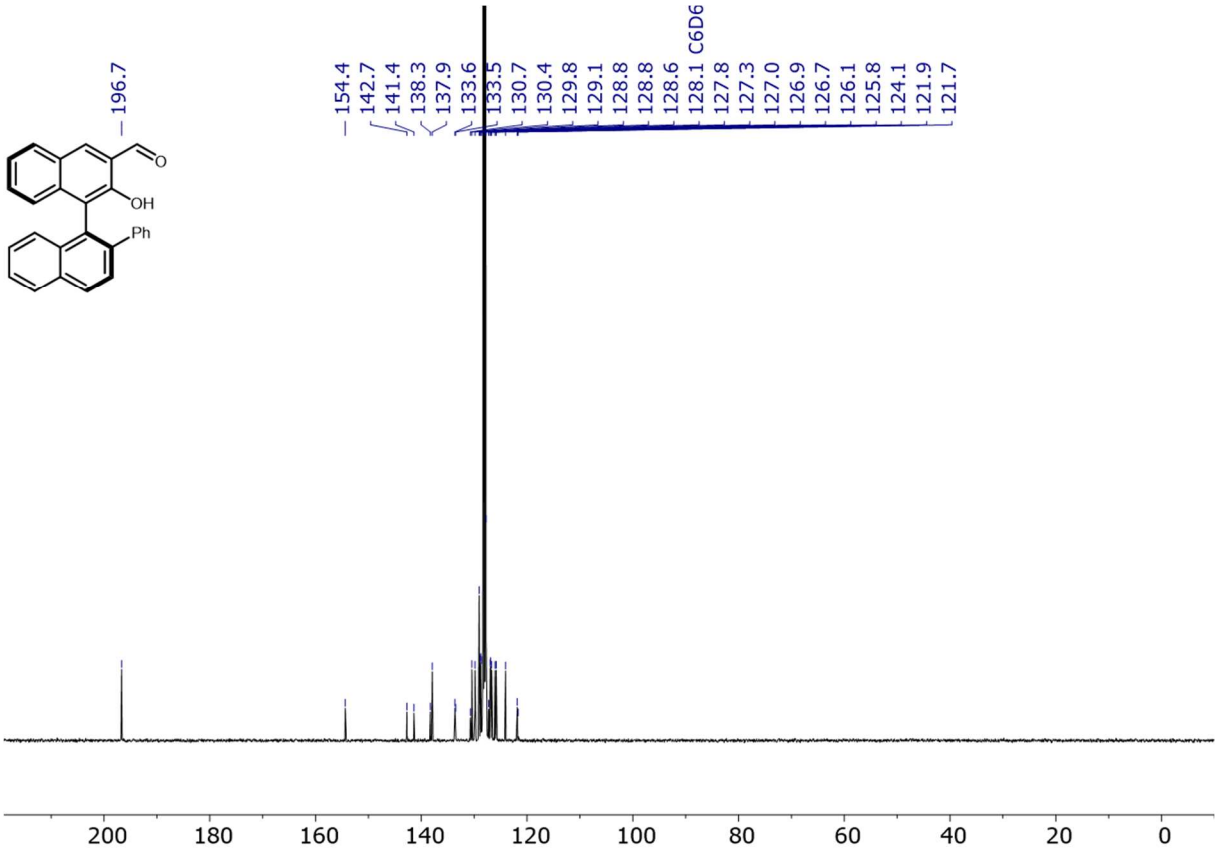

**[S5], $^{13}C$, $C_6D_6$, 101 MHz**



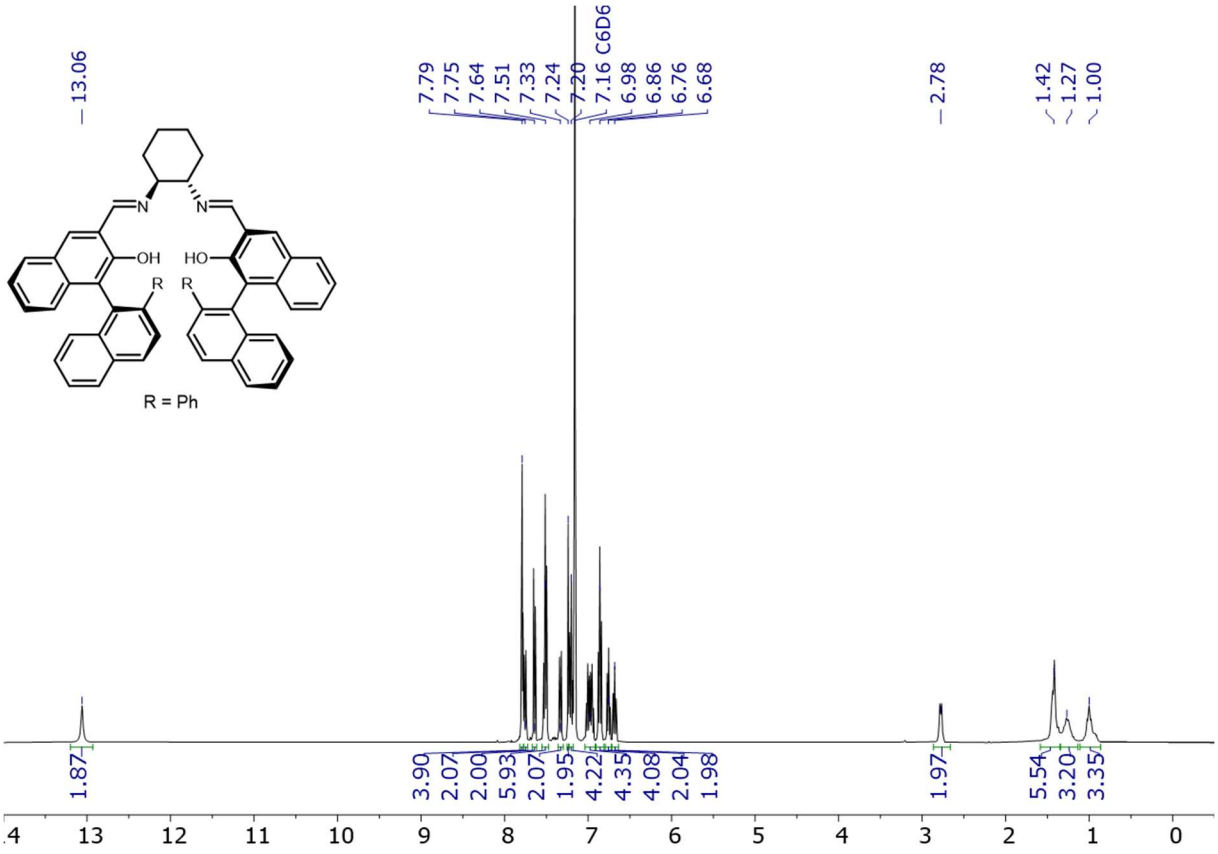
**[S6], $^{1}H$, $C_6D_6$, 400 MHz**



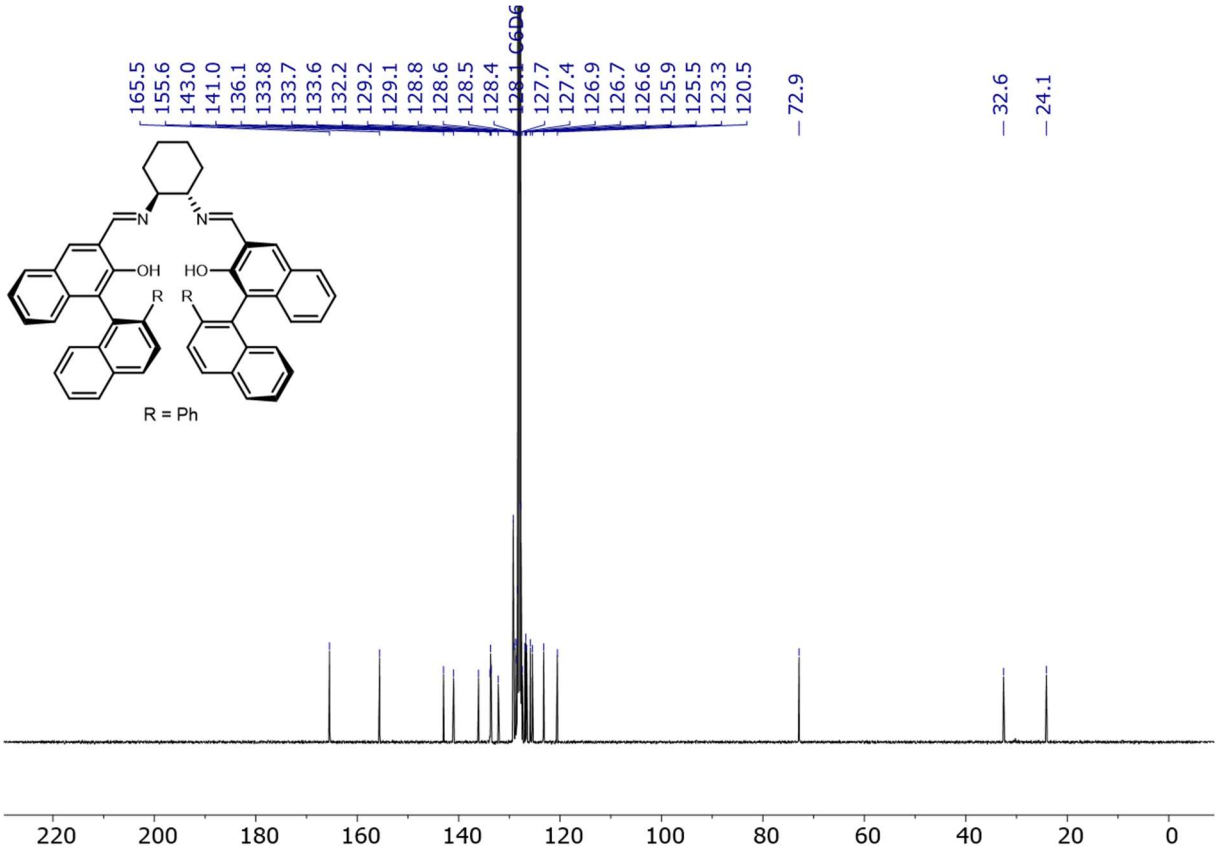

**[S6], $^{13}C$, $C_6D_6$, 101 MHz**



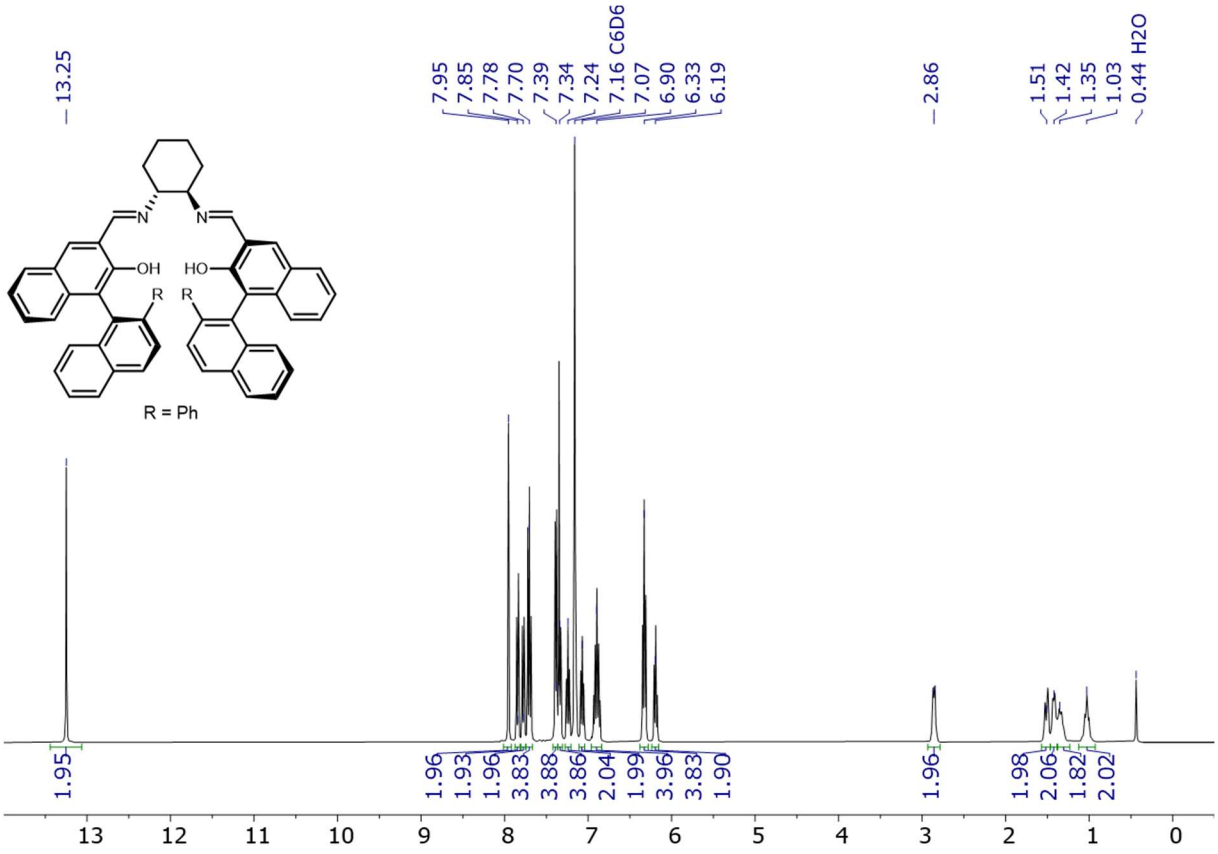
**[S7], $^{1}H$, $C_6D_6$, 400 MHz**



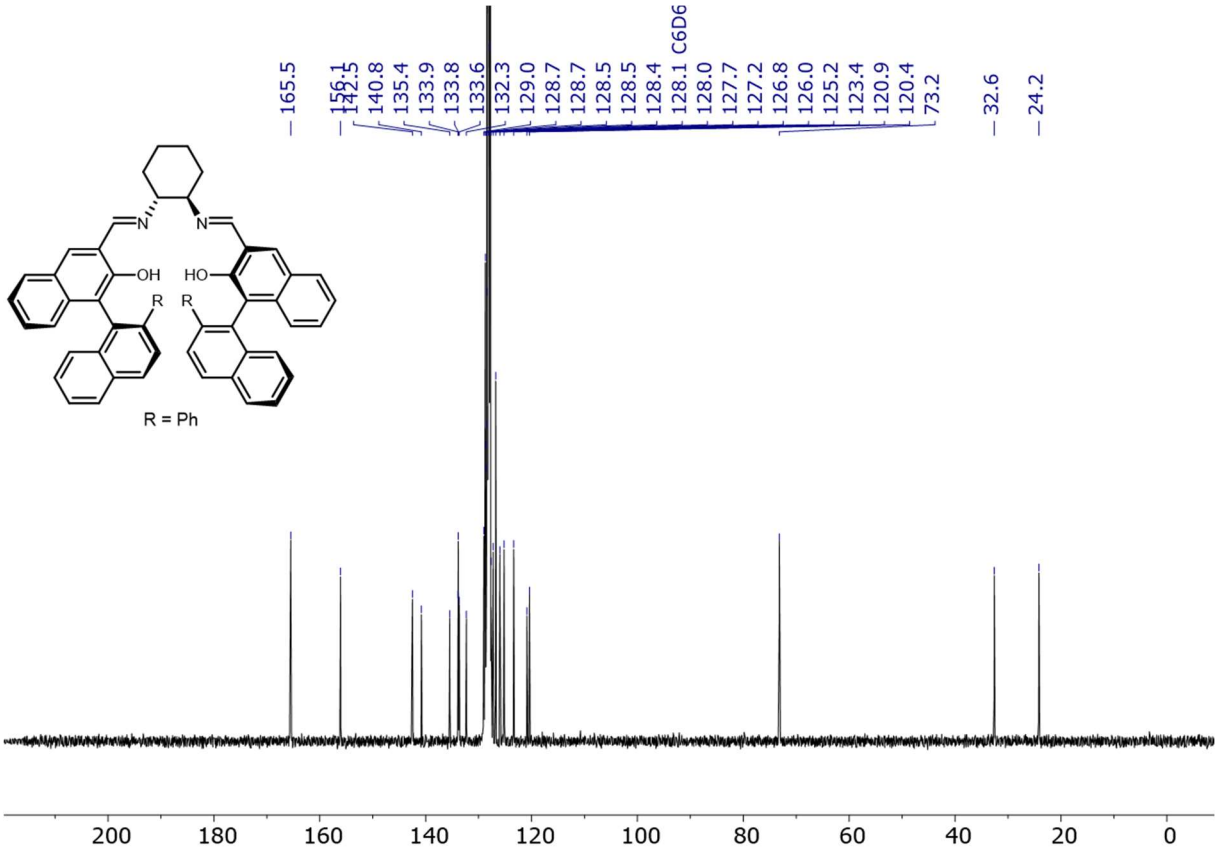

**[S7], $^{13}C$, $C_6D_6$, 101 MHz**



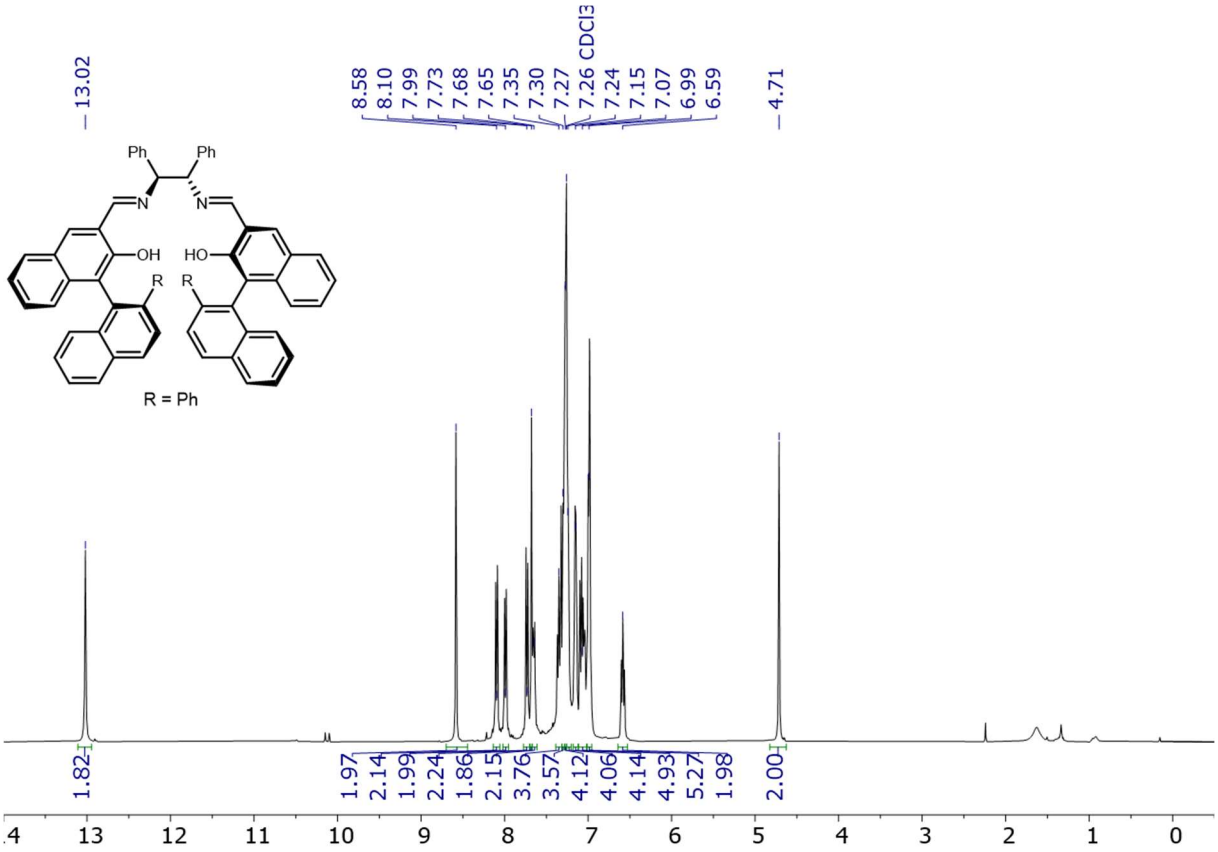
**[epi-S7], $^{1}H$, $CDCl_3$, 400 MHz**



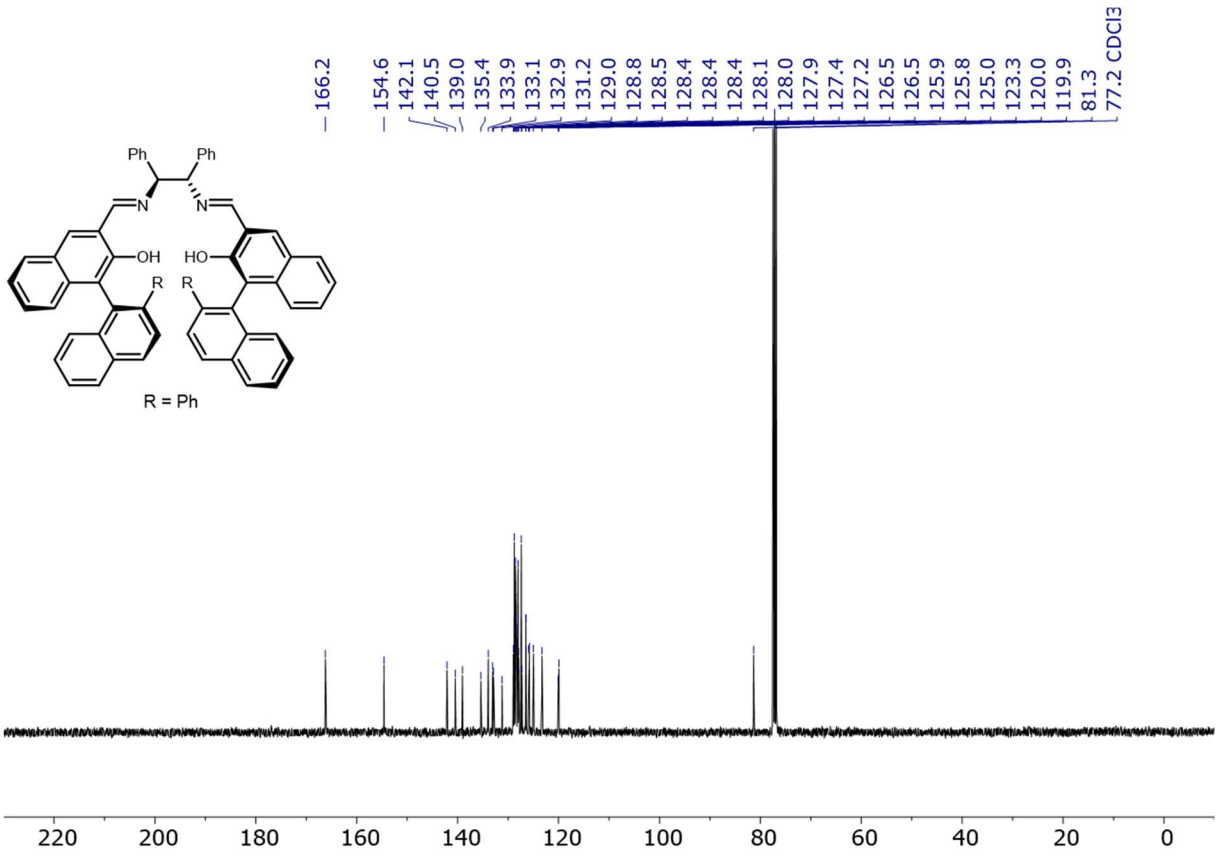

**[epi-S7], $^{13}C$, $CDCl_3$, 101 MHz**



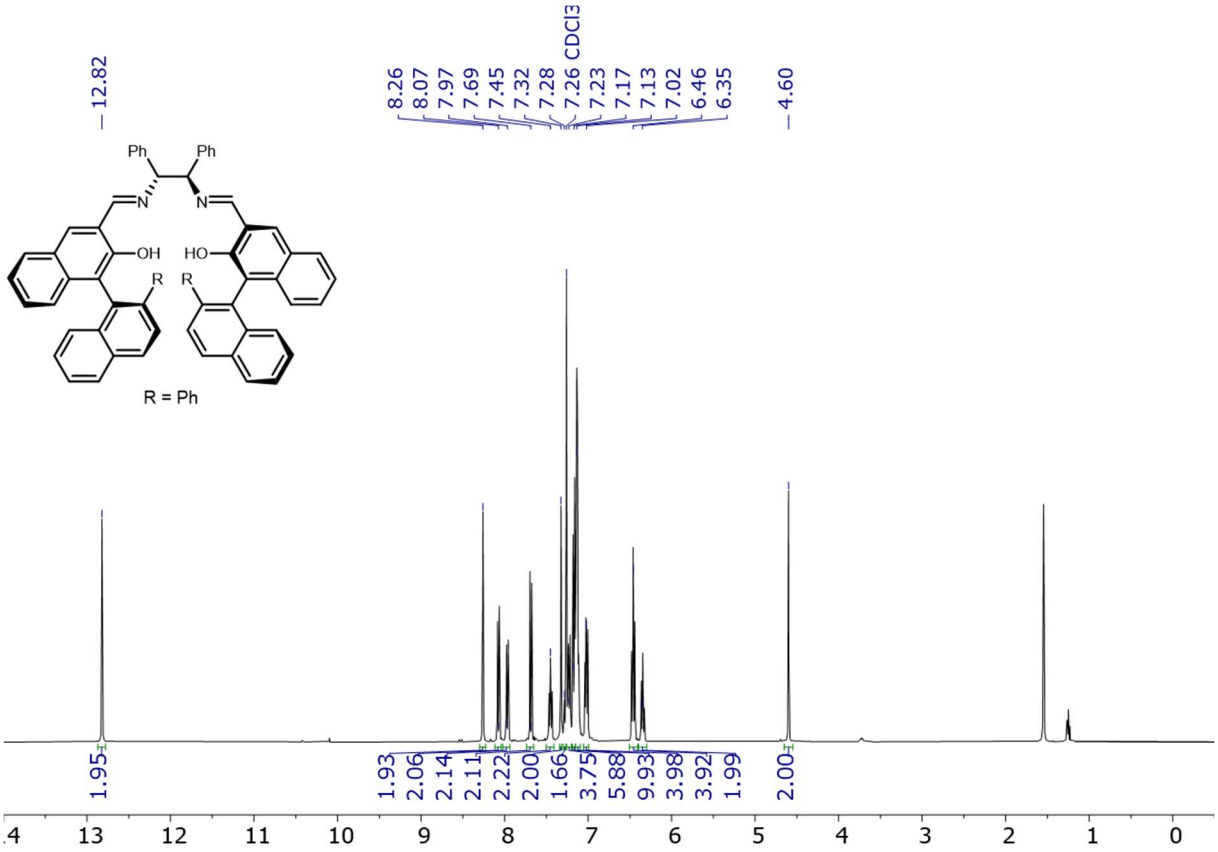
**[S8], $^{1}H$, $CDCl_3$, 400 MHz**



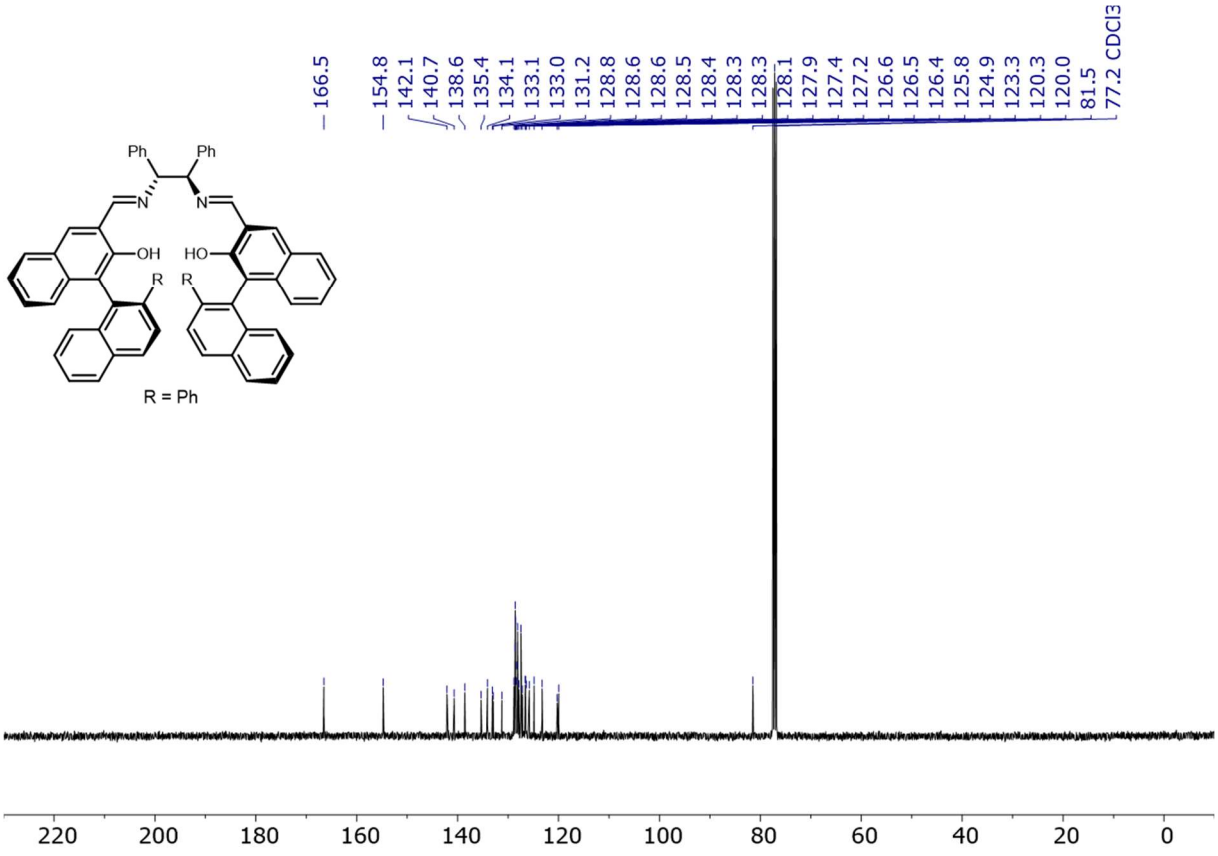

**[S8], $^{13}C$, $CDCl_3$, 101 MHz**



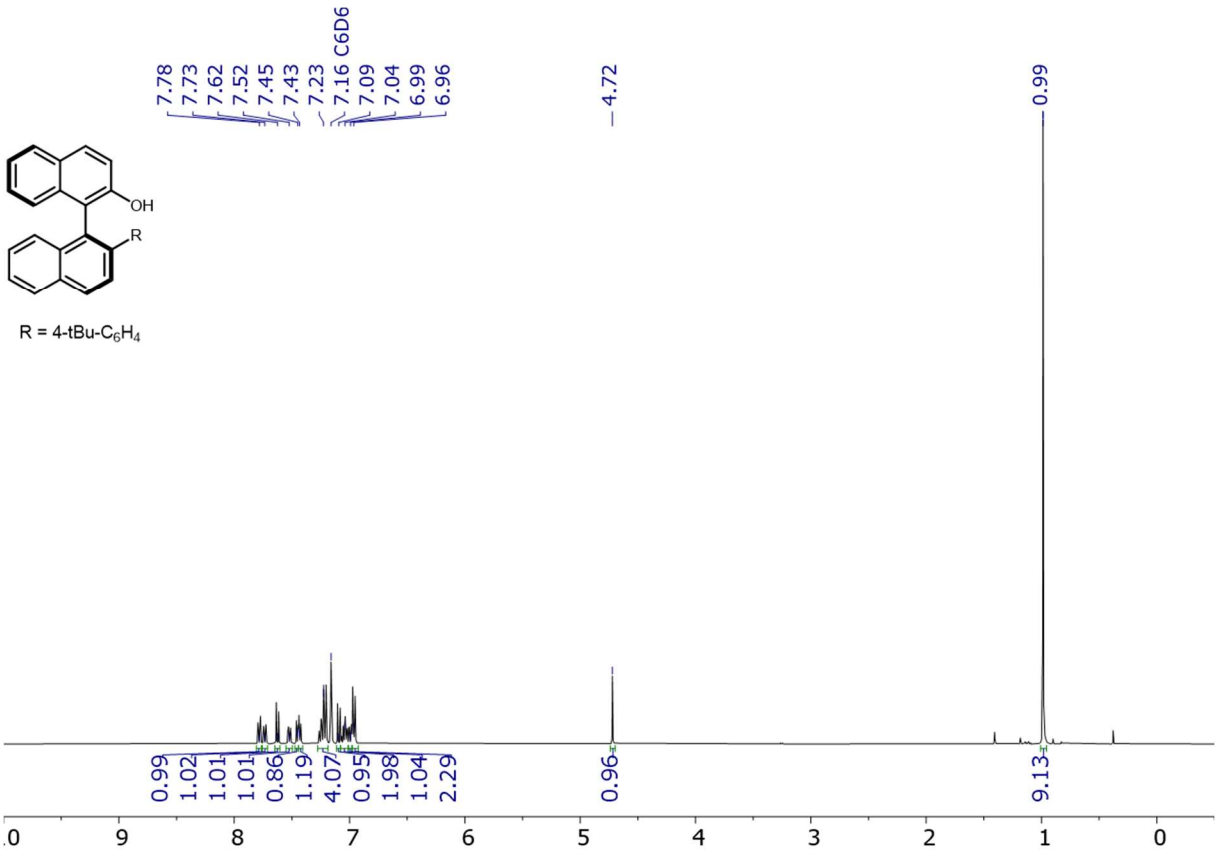
**[epi-S8], $^{1}H$, $C_6D_6$, 400 MHz**



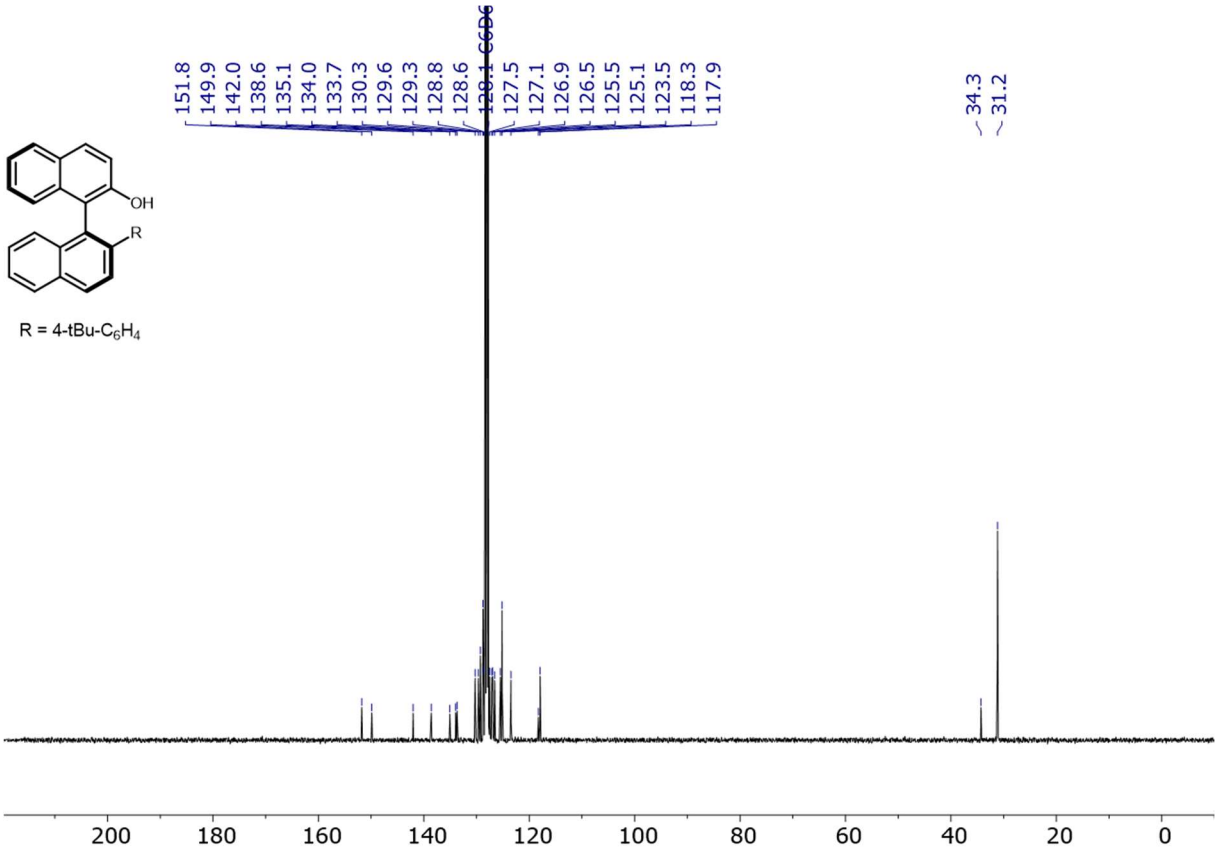

**[epi-S8], $^{13}C$, $C_6D_6$, 101 MHz**



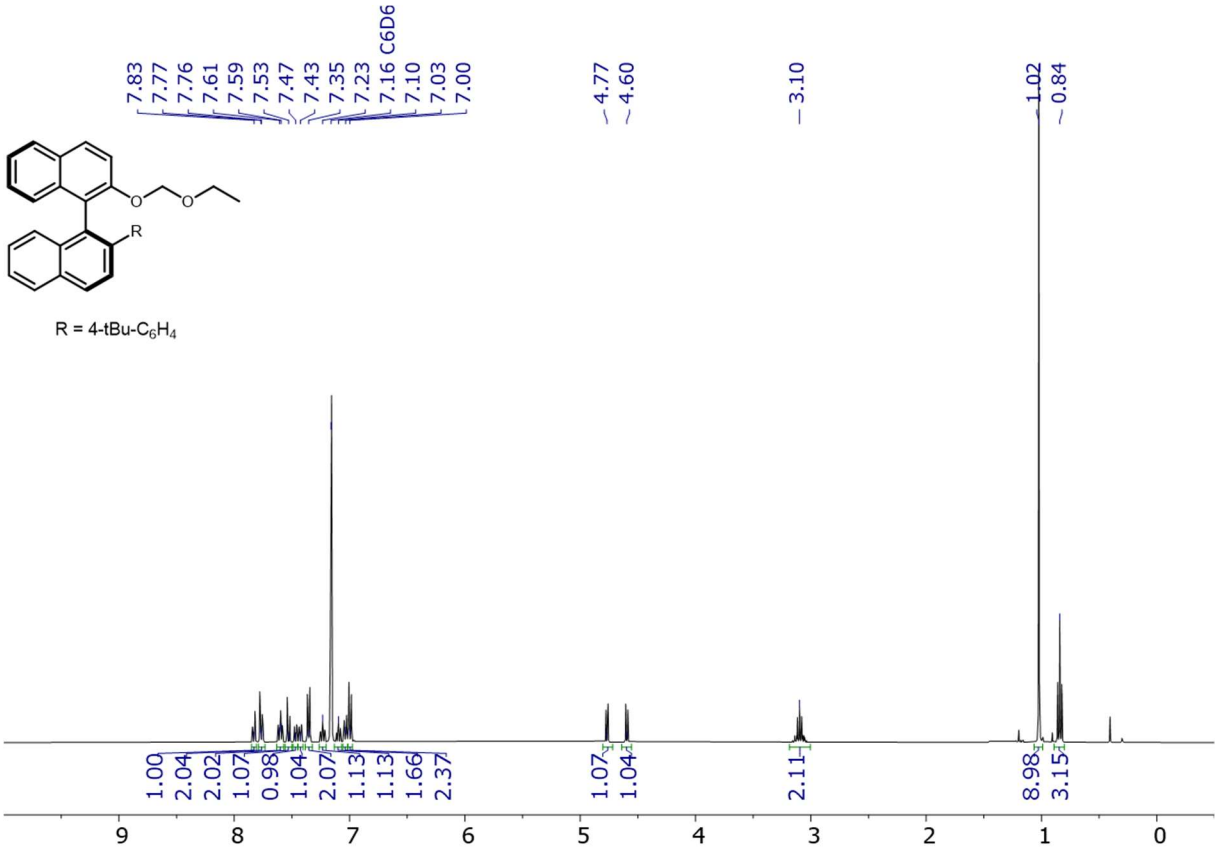
**[S9], $^{1}H$, $C_6D_6$, 400 MHz**



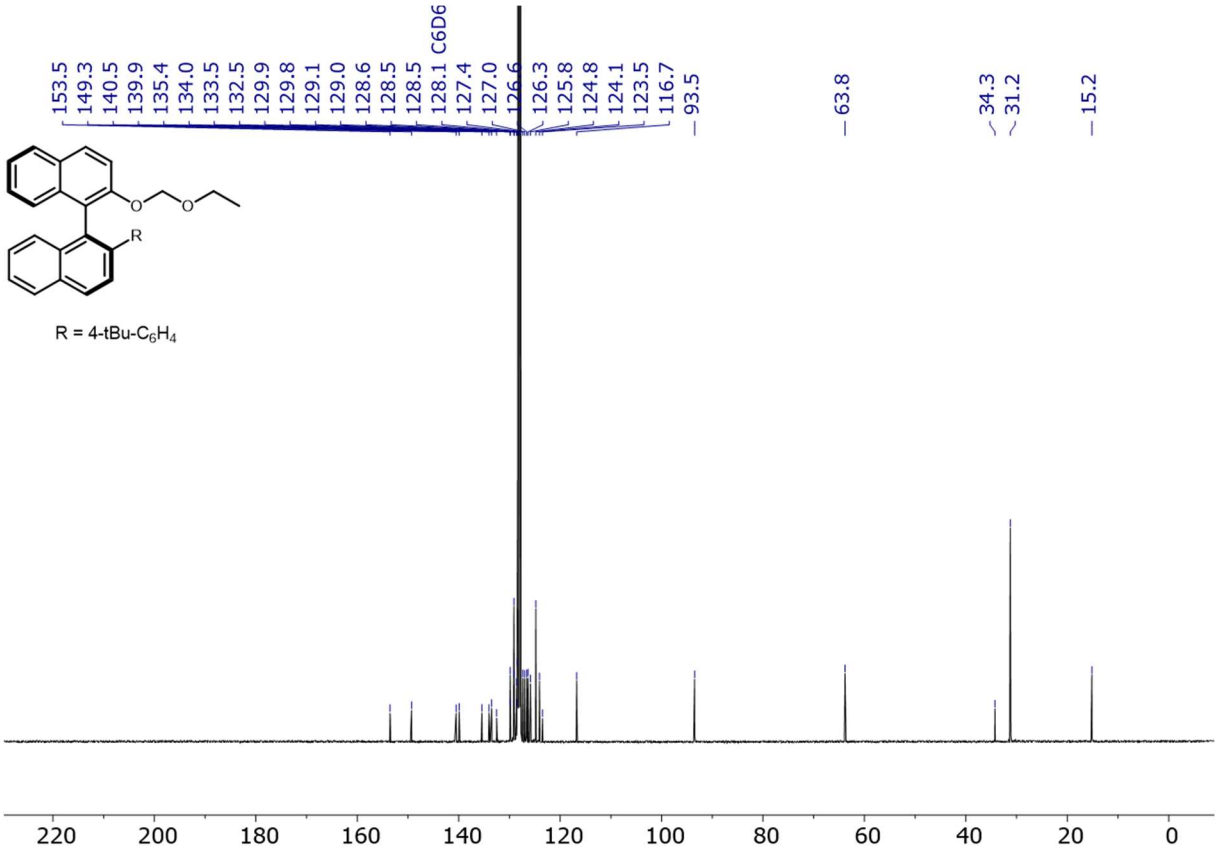

**[S9], $^{13}C$, $C_6D_6$, 101 MHz**



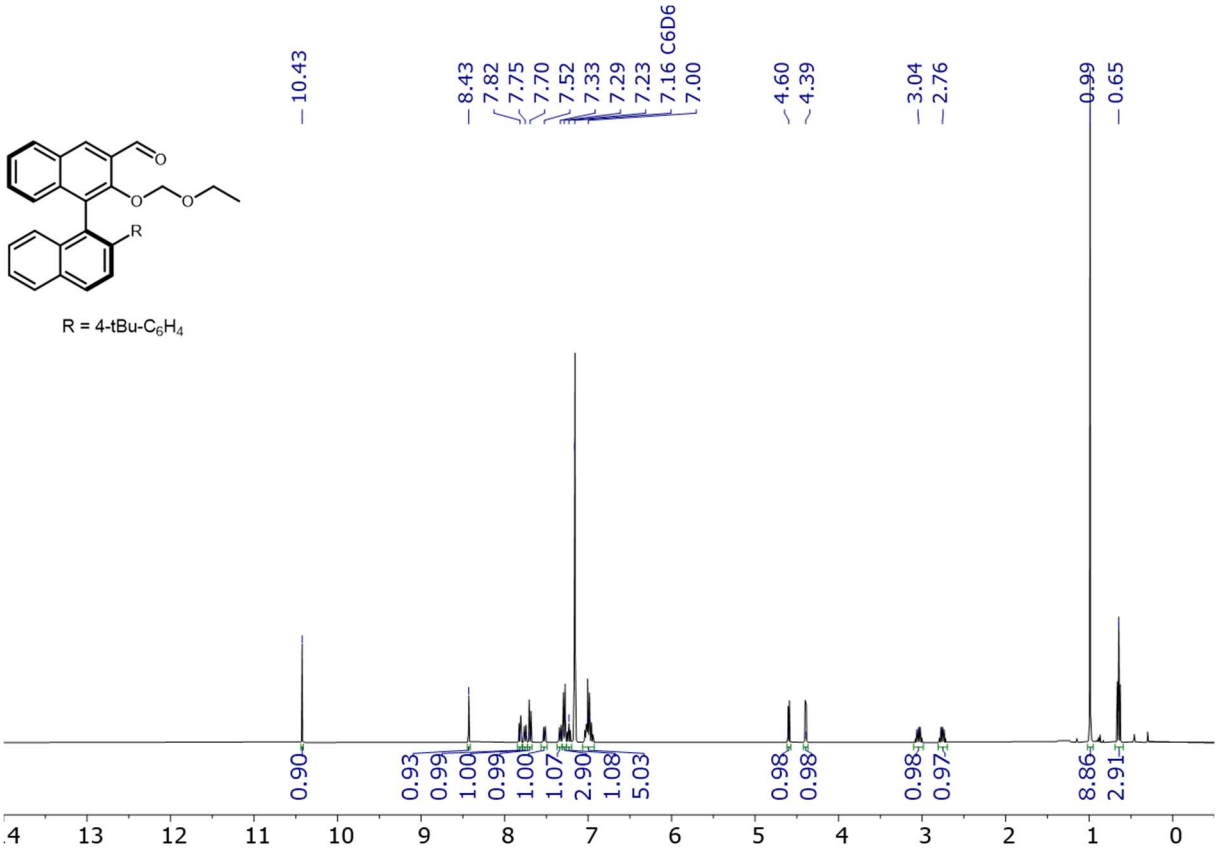
**[S10], $^{1}H$, $C_6D_6$, 400 MHz**



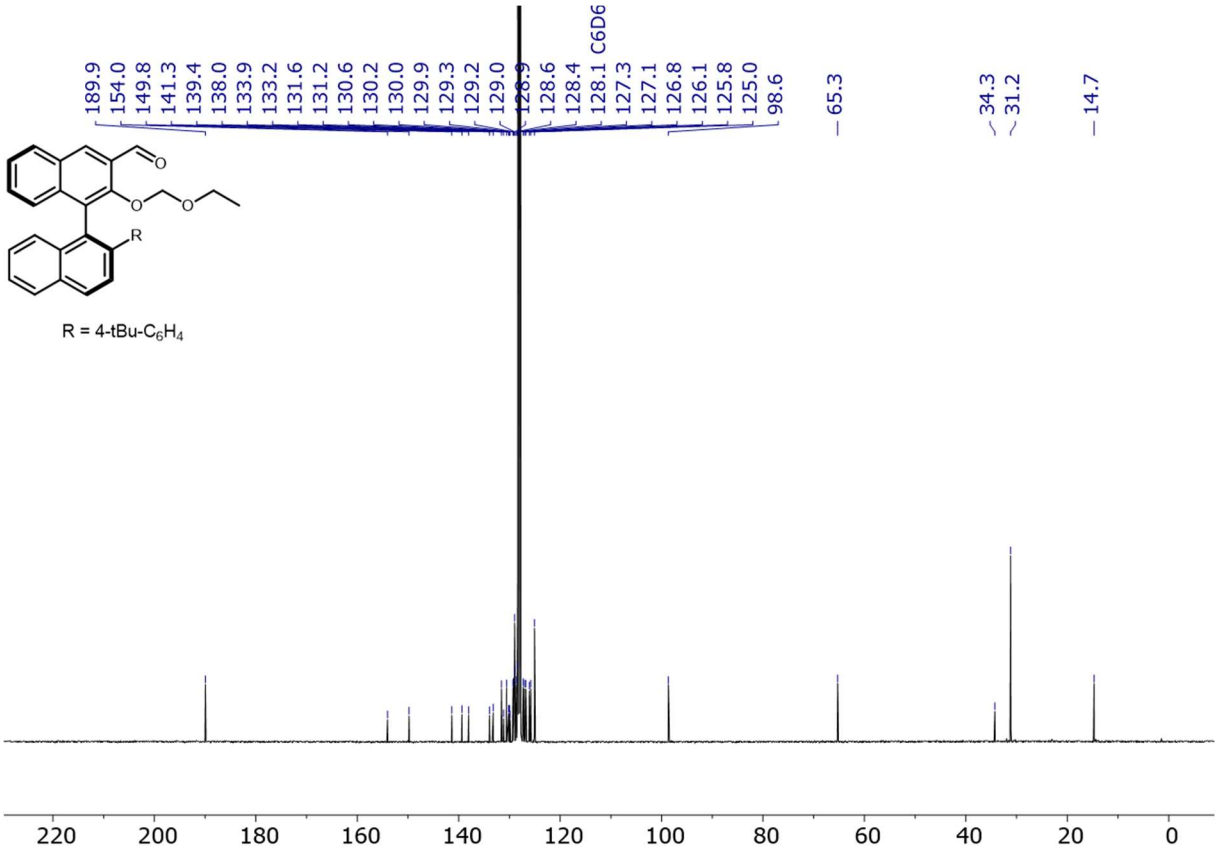

**[S10], $^{13}C$, $C_6D_6$, 101 MHz**



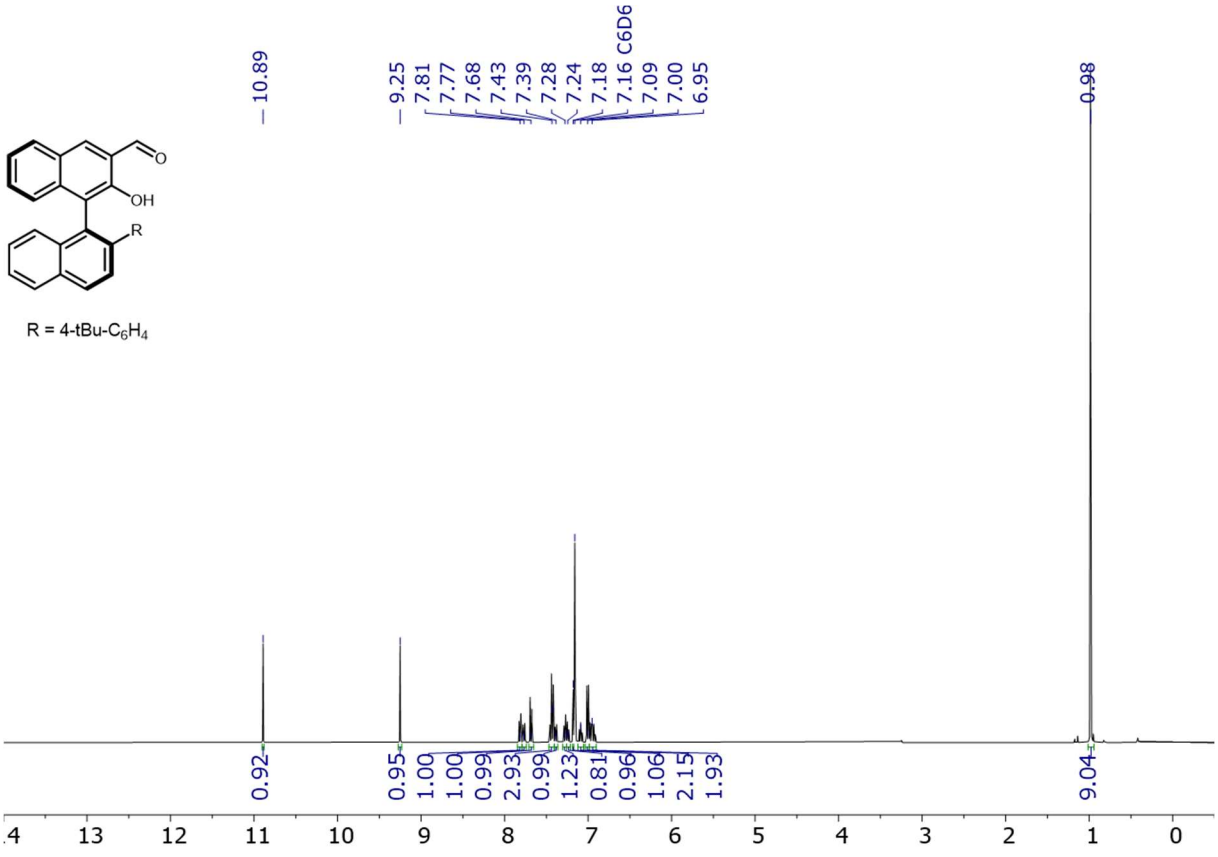
**[S11], $^{1}H$, $C_6D_6$, 400 MHz**



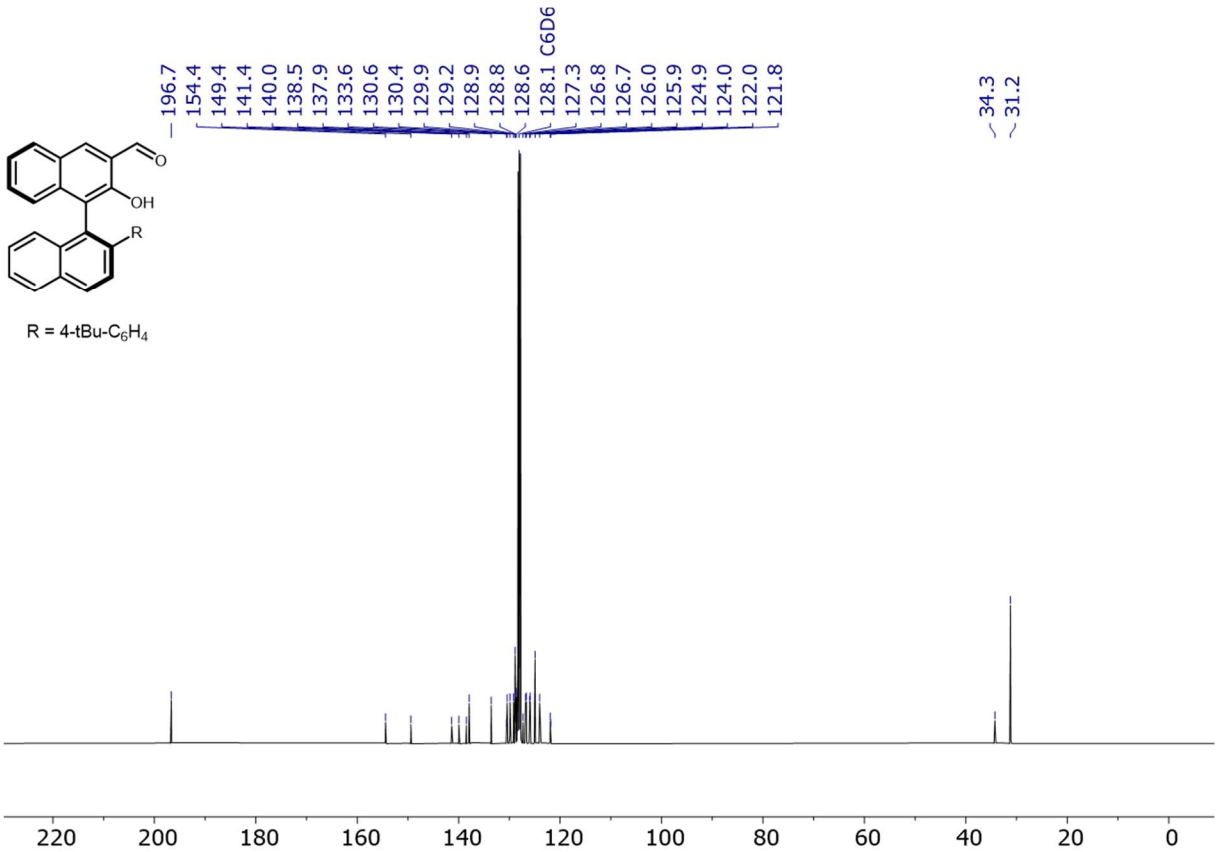

**[S11], $^{13}C$, $C_6D_6$, 101 MHz**



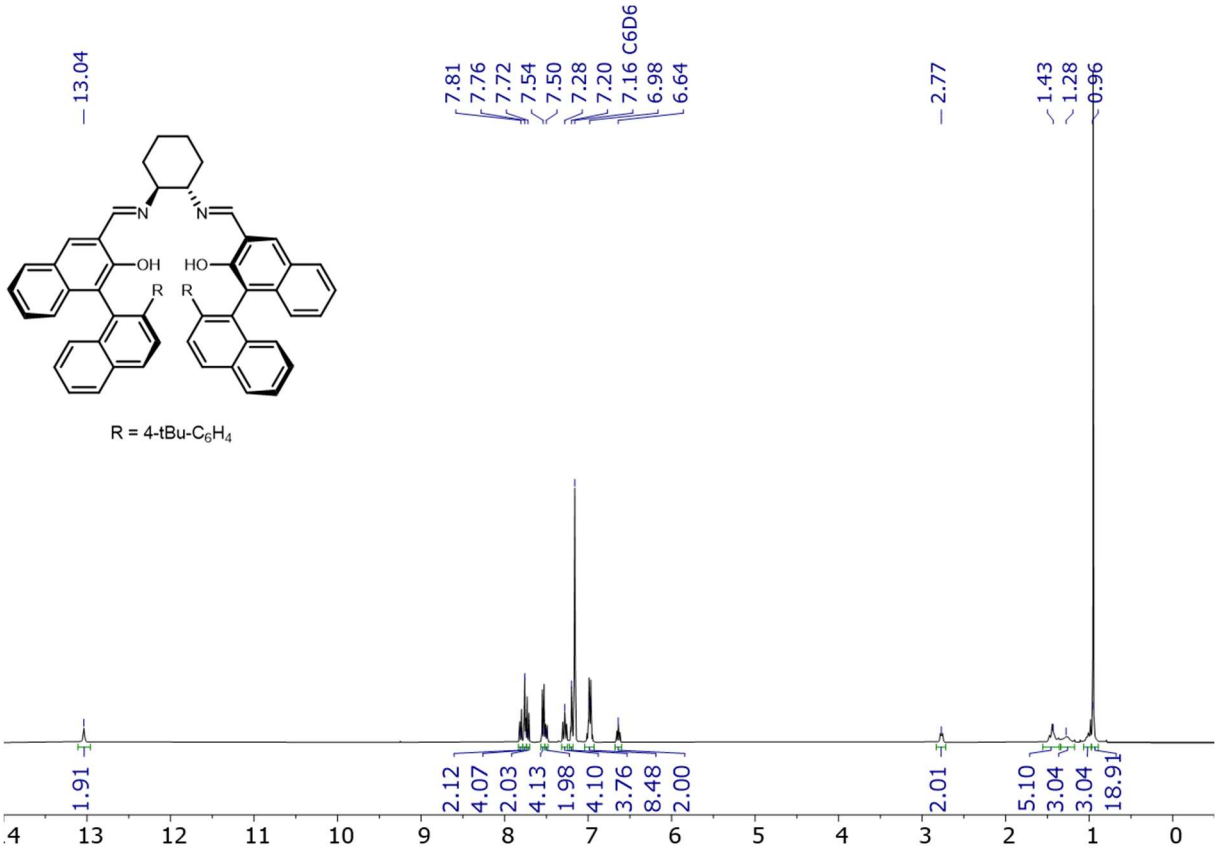
**[S12], $^{1}H$, $C_6D_6$, 400 MHz**



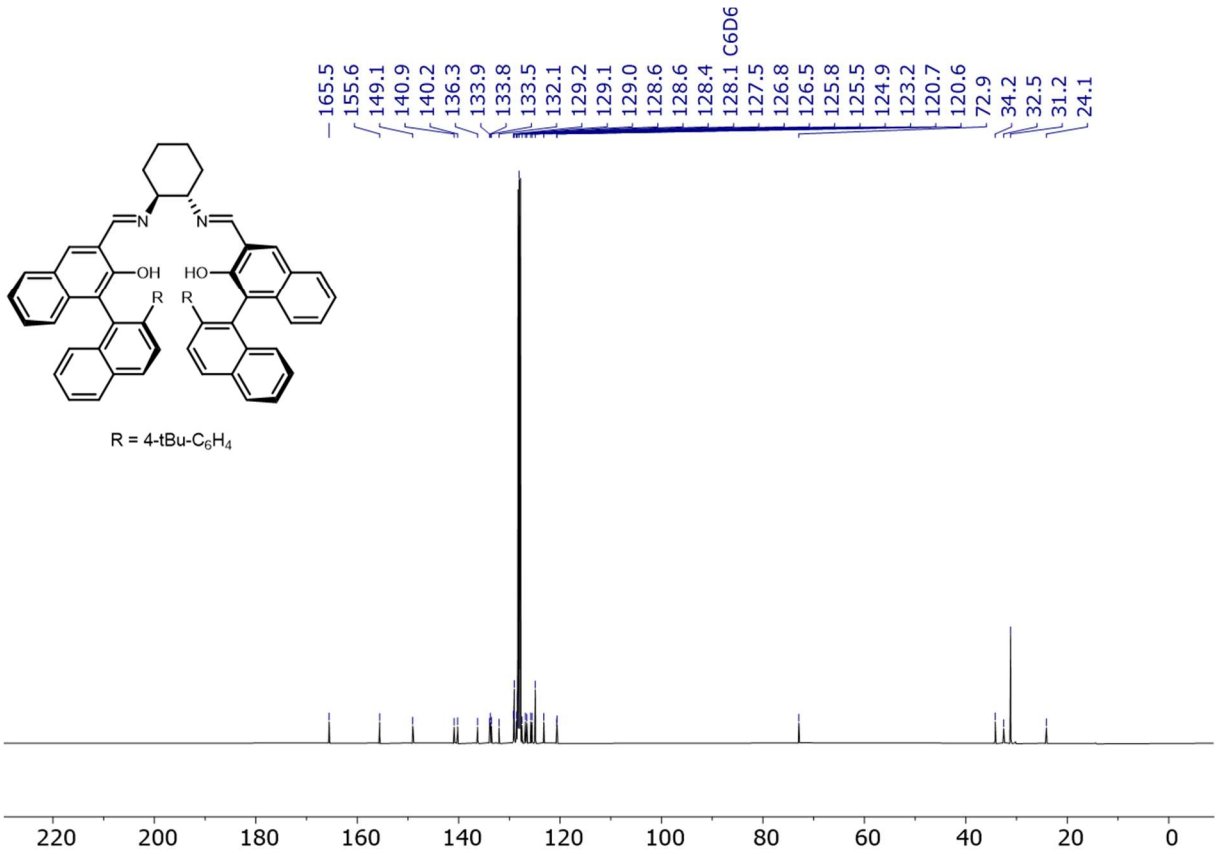

**[S12], $^{13}C$, $C_6D_6$, 101 MHz**



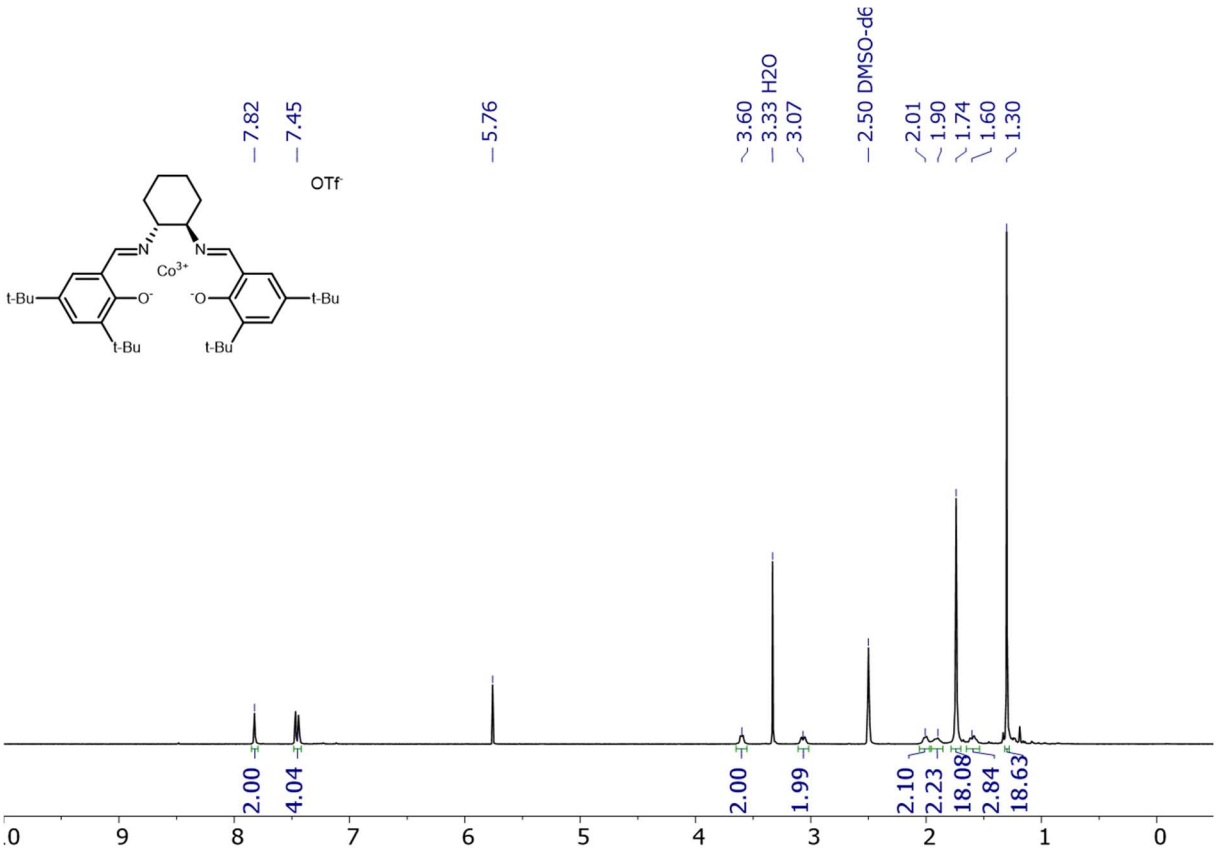
**[S13], $^{1}H$, $C_6D_6$, 400 MHz**



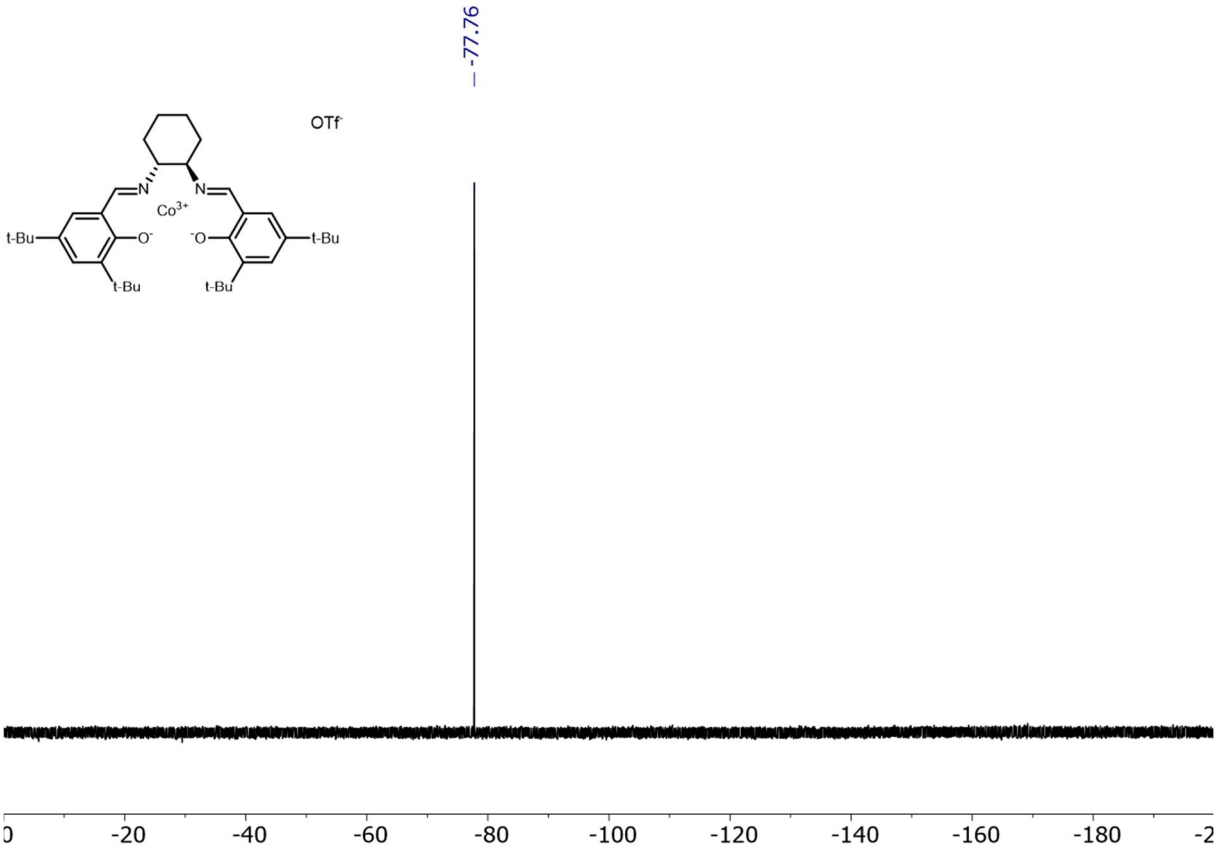

**[S13], $^{13}C$, $C_6D_6$, 101 MHz**



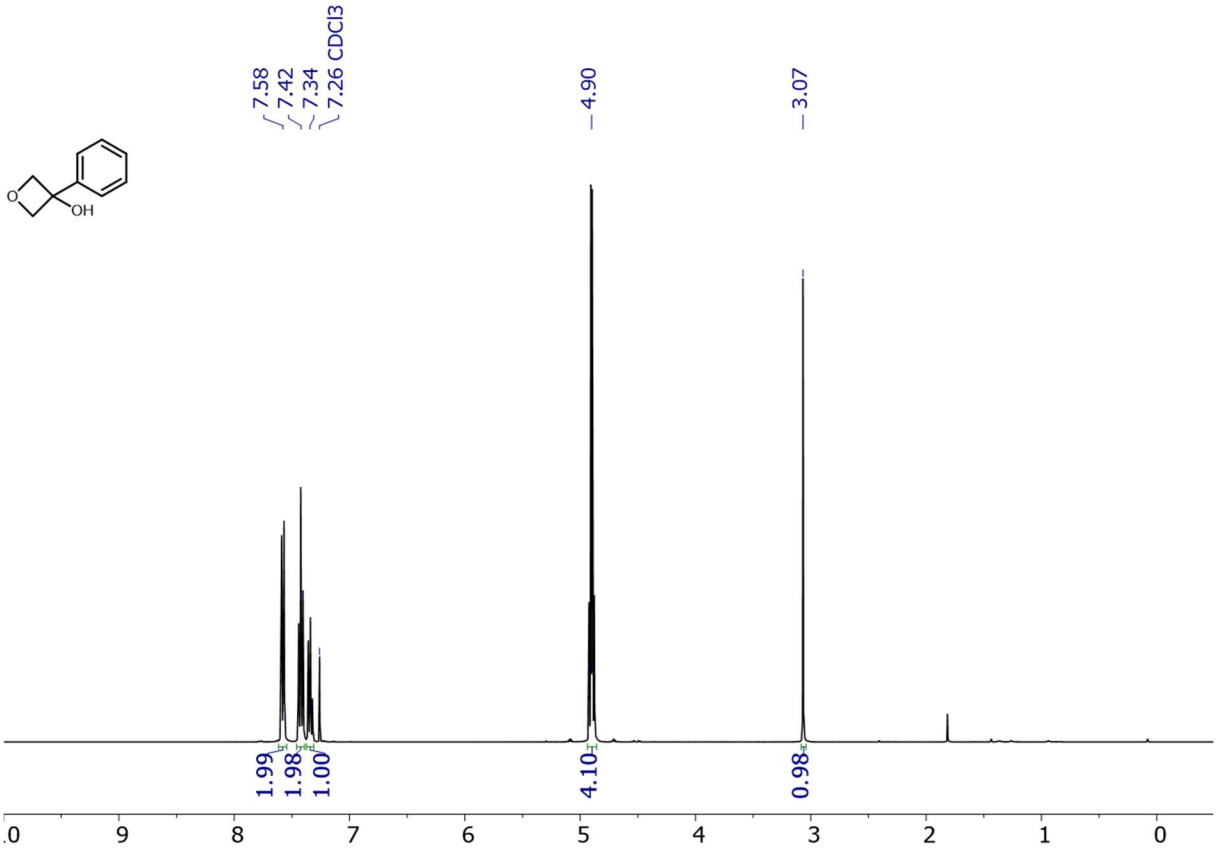
**[3c], $^{1}$H, DMSO-d6, 400 MHz**



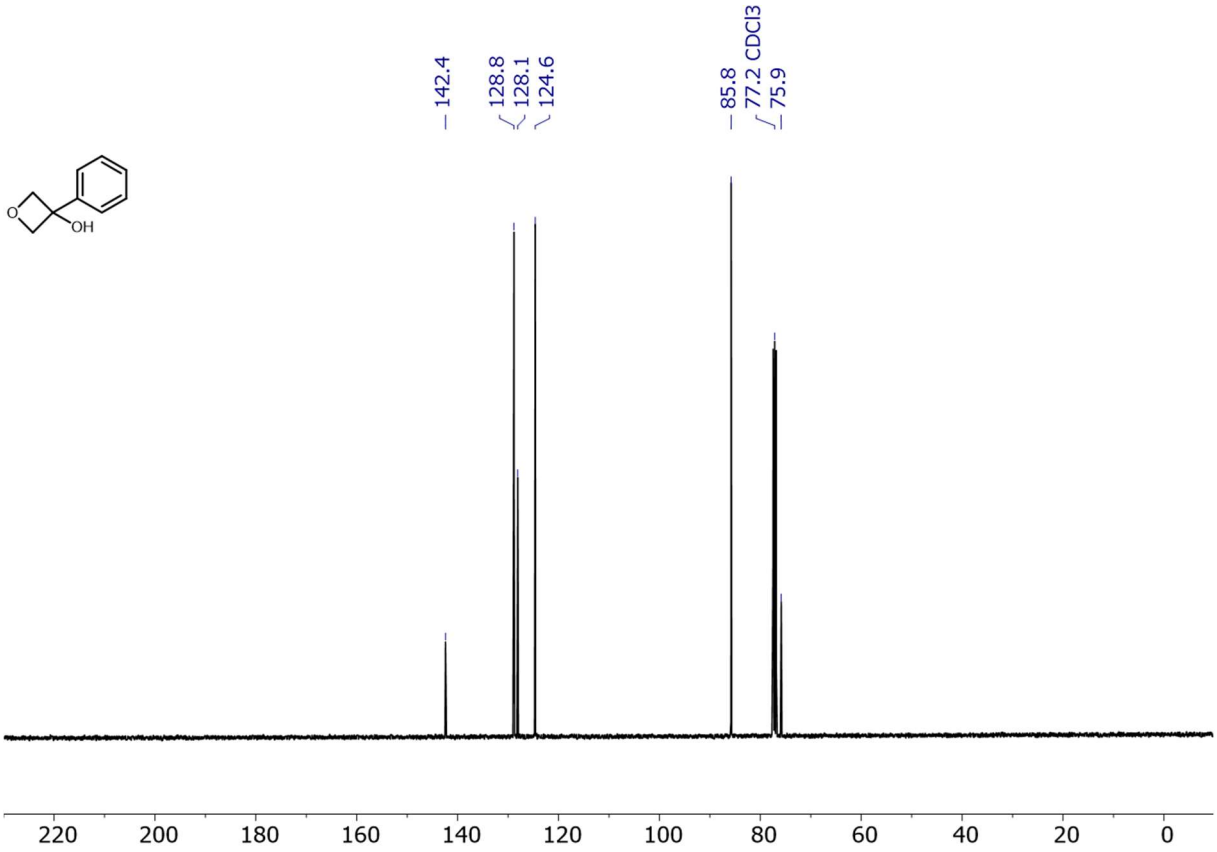

**[3c], $^{19}$F, DMSO-d6, 376 MHz**



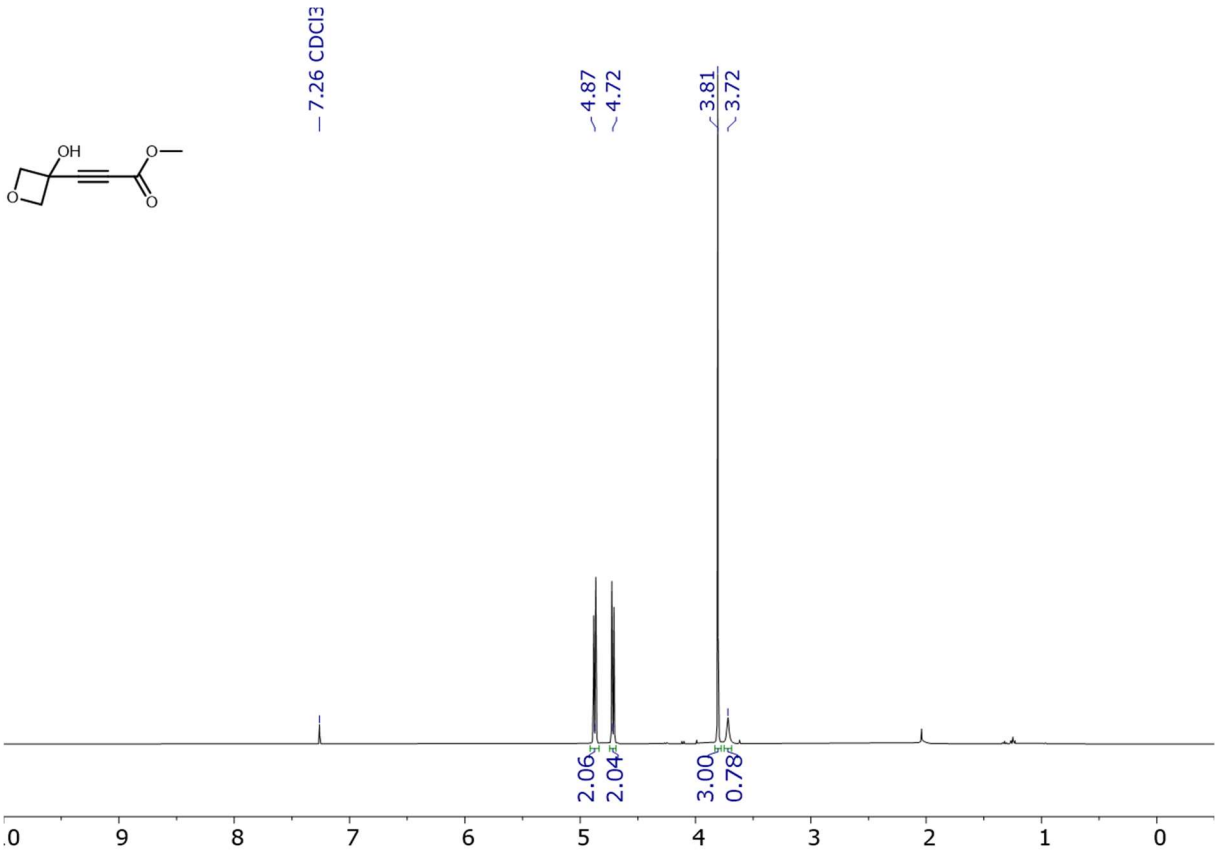
**[1a], $^{1}H$, $CDCl_3$, 400 MHz**



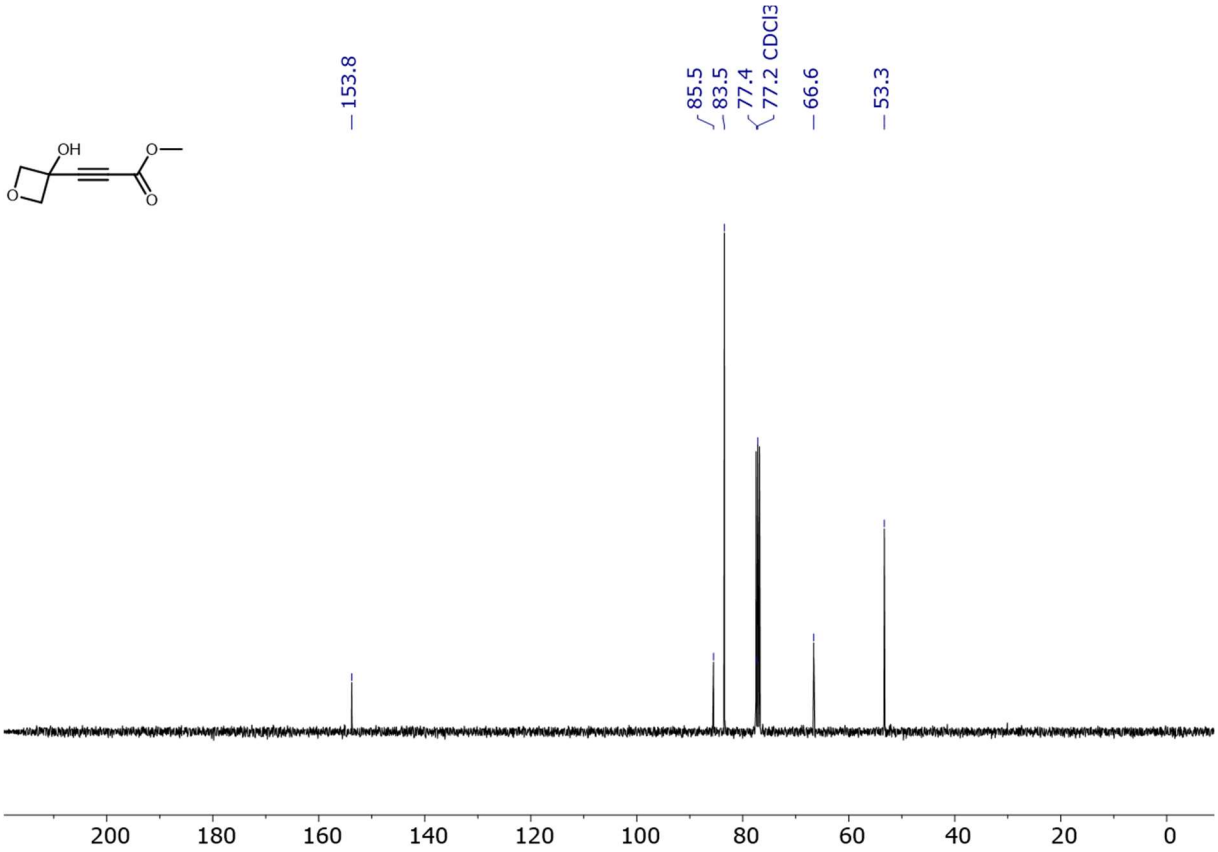

**[1a], $^{13}C$, $CDCl_3$, 101 MHz**



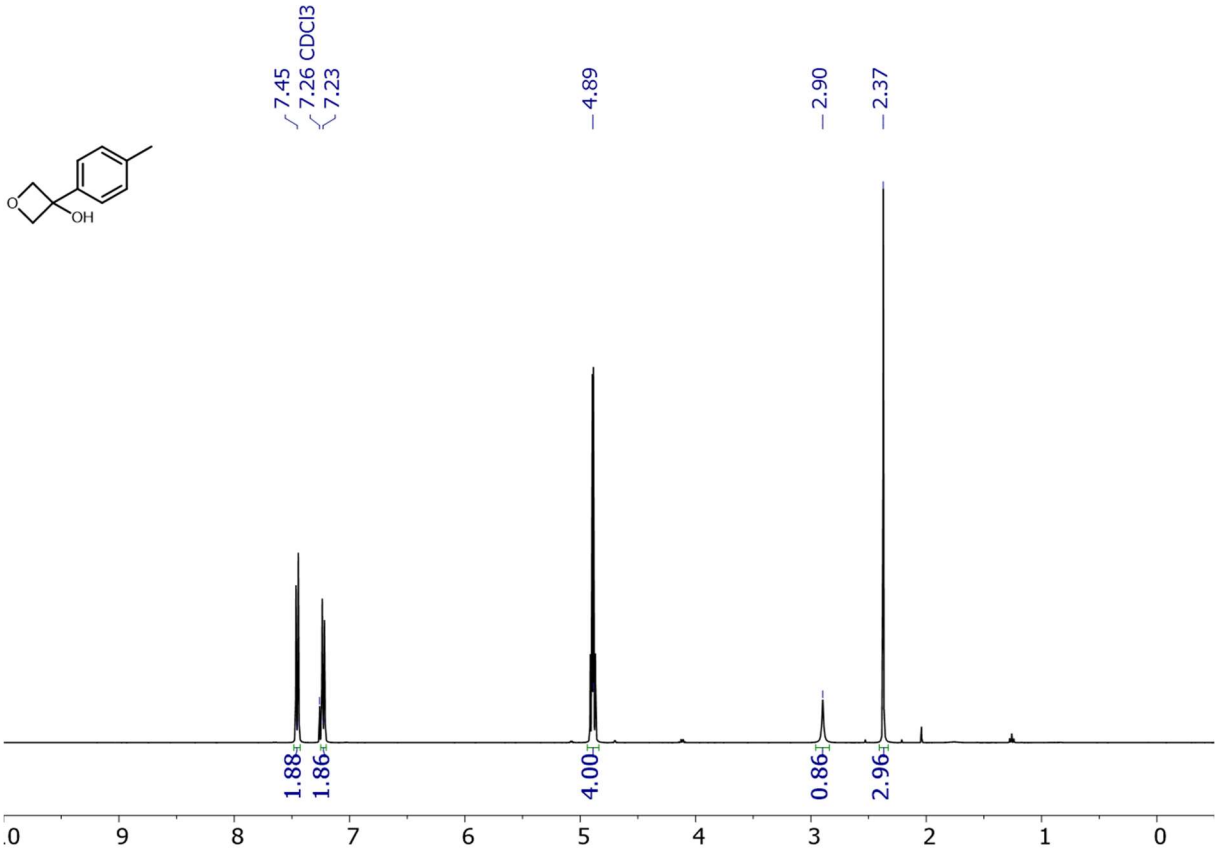
**[1c], $^{1}H$, $CDCl_3$, 400 MHz**



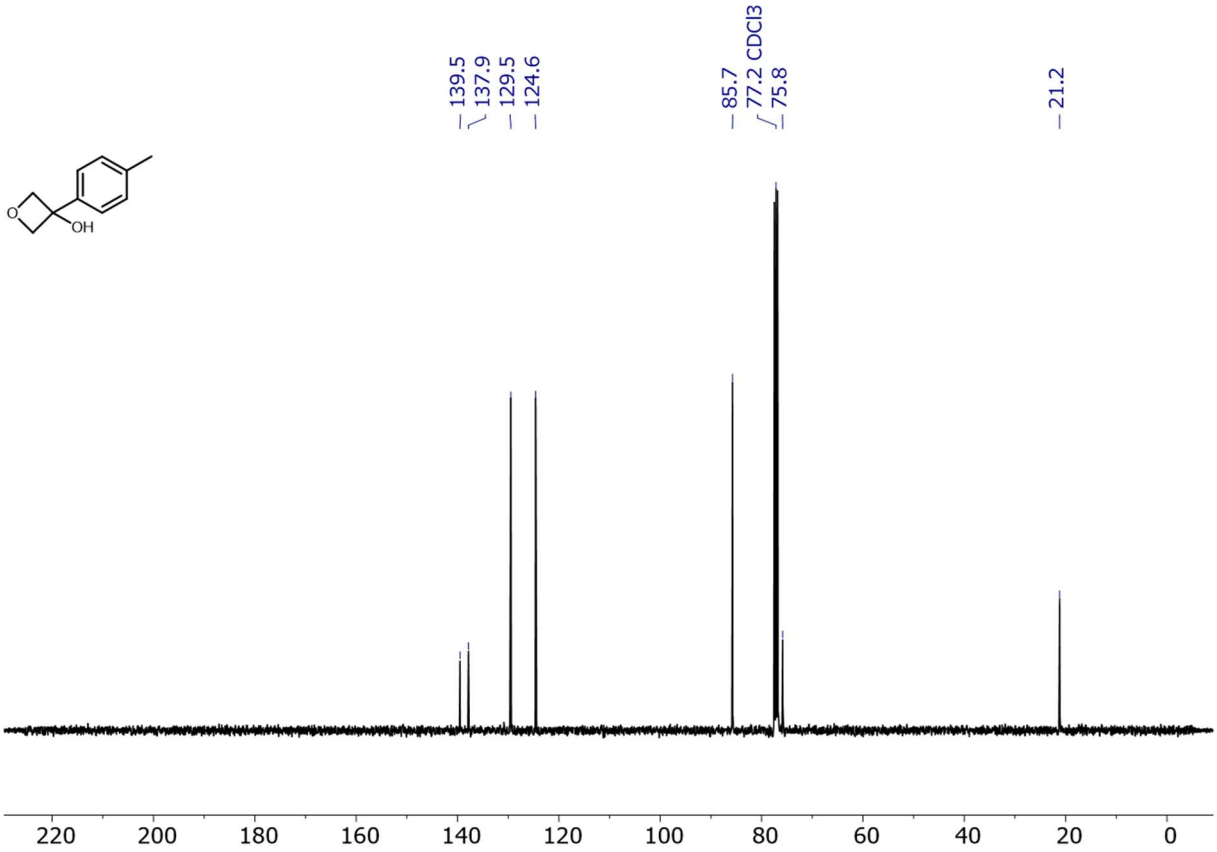

**[1c], $^{13}C$, $CDCl_3$, 101 MHz**



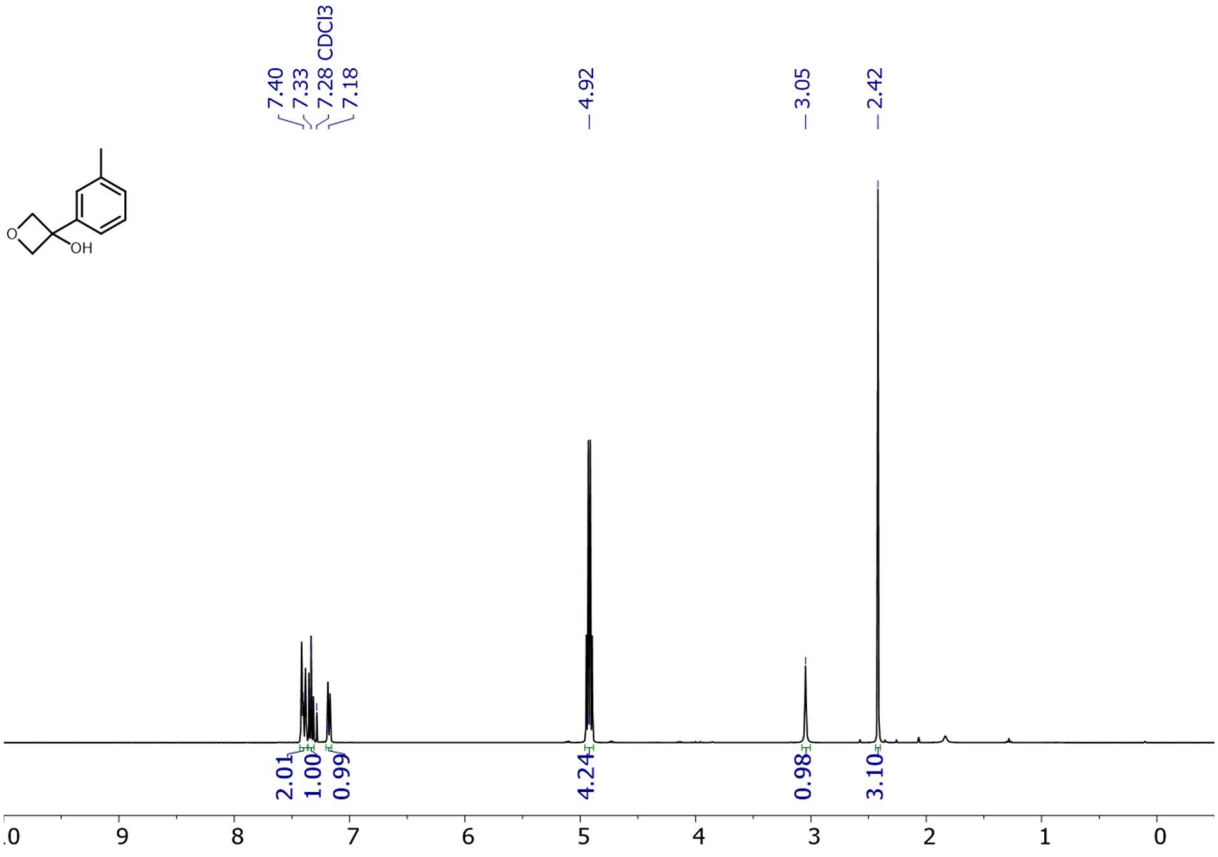
**[1d], $^{1}H$, $CDCl_3$, 400 MHz**



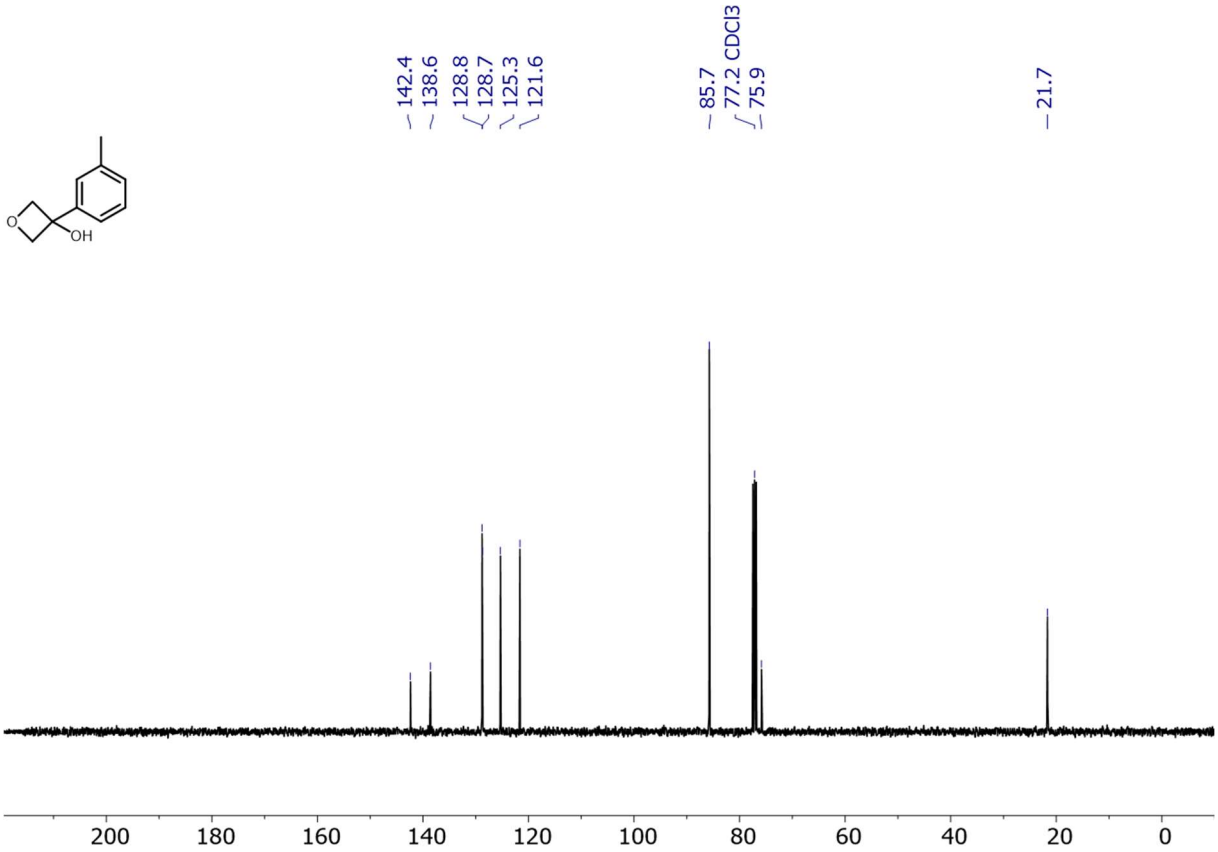

**[1d], $^{13}C$, $CDCl_3$, 101 MHz**



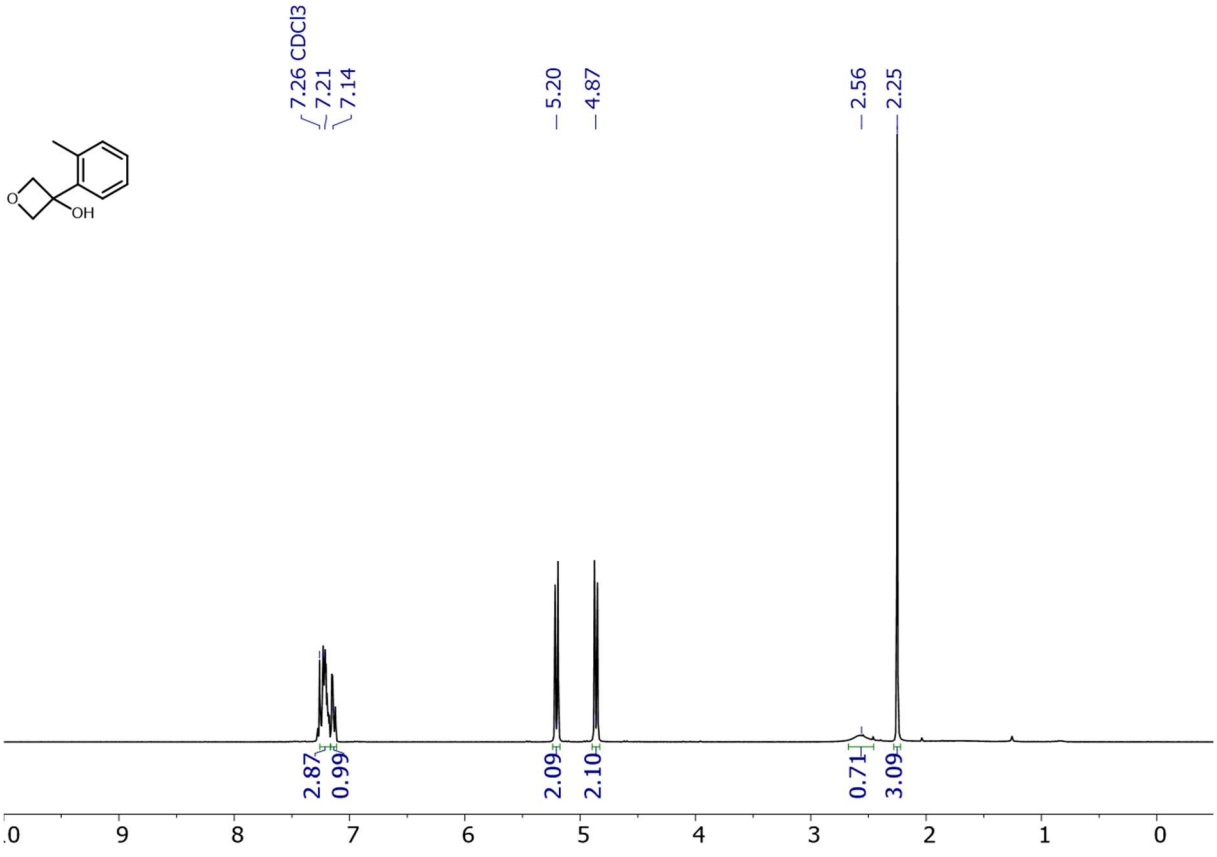
**[1e], $^{1}H$, $CDCl_3$, 400 MHz**



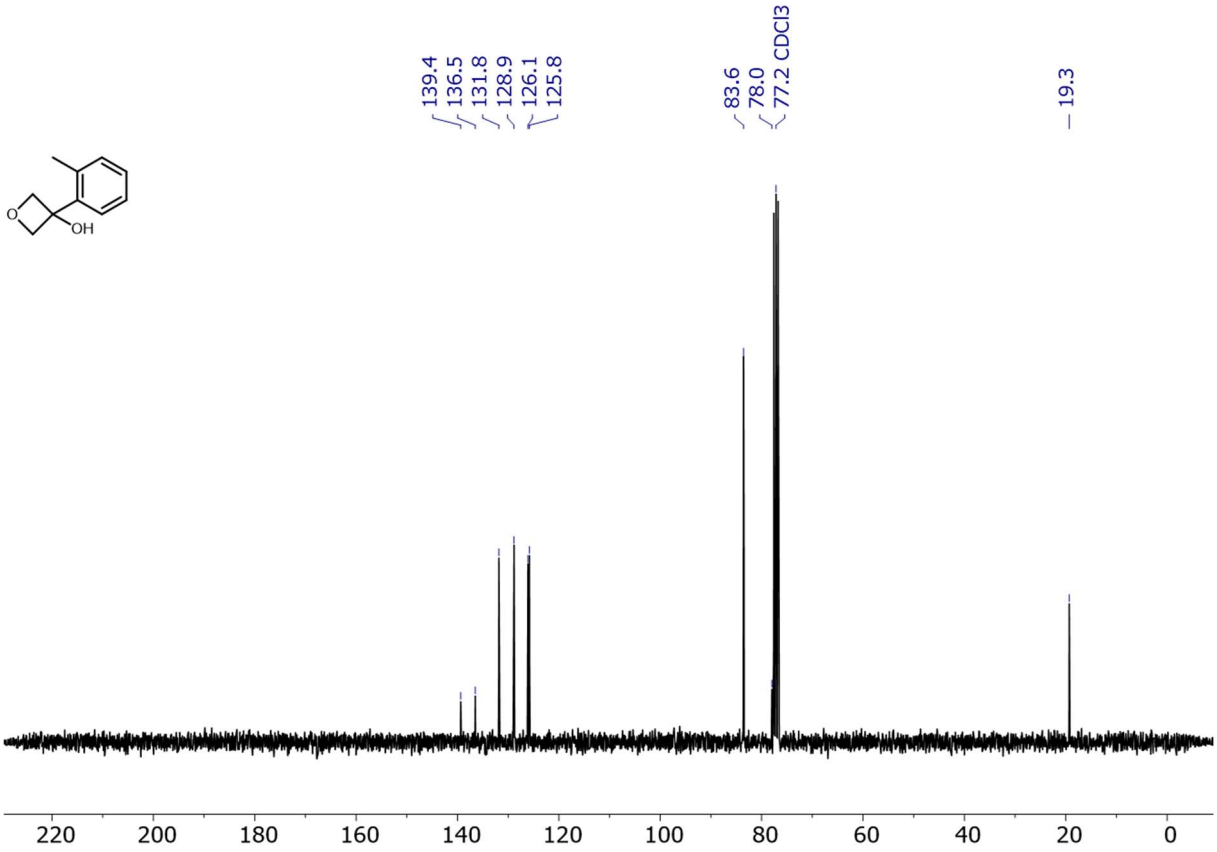

**[1e], $^{13}C$, $CDCl_3$, 101 MHz**



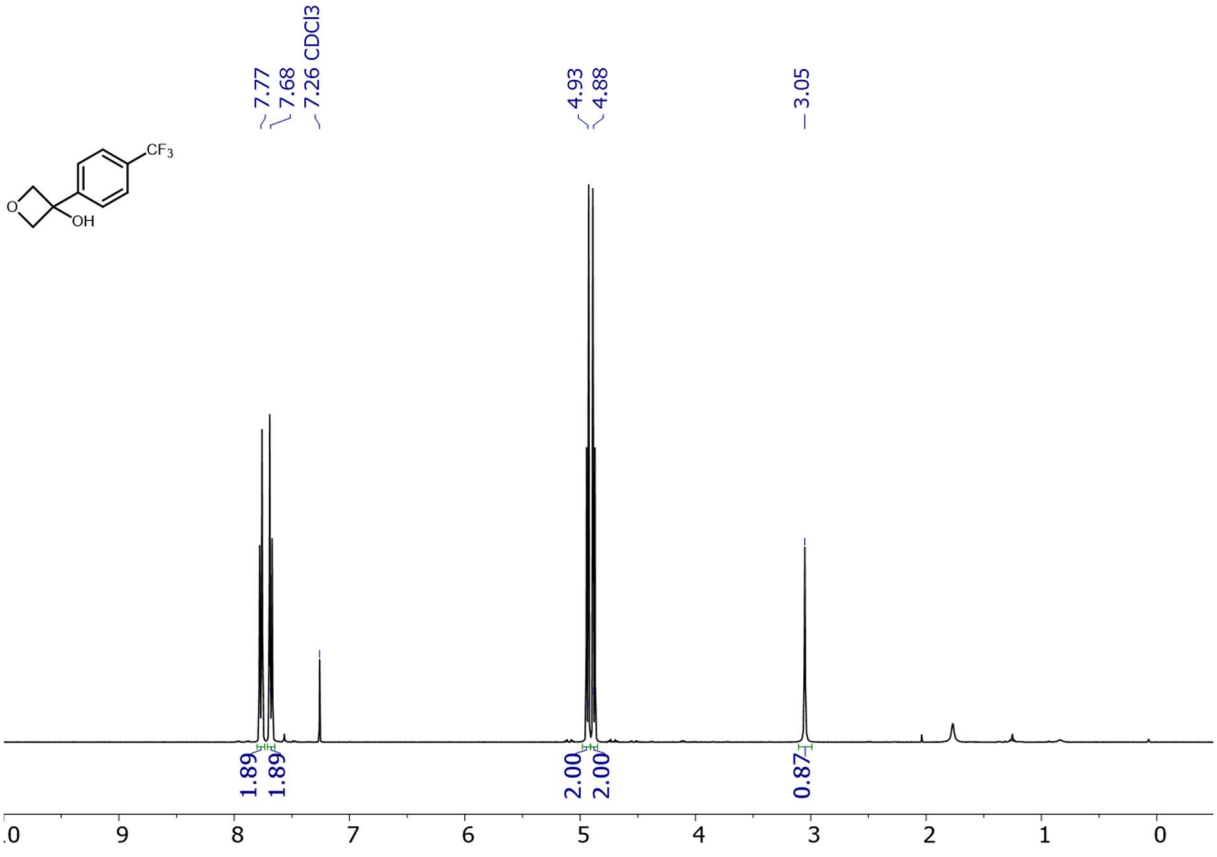
**[1f], $^{1}H$, $CDCl_3$, 400 MHz**



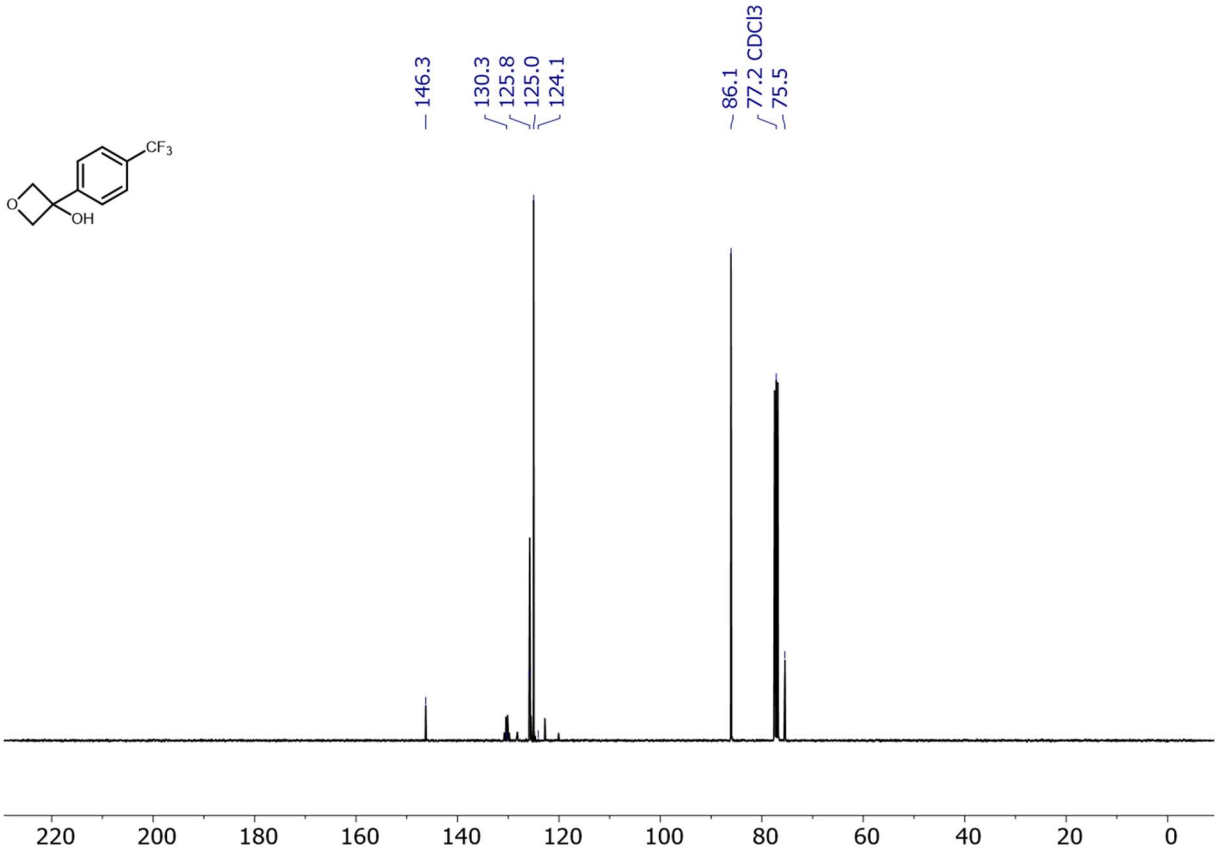

**[1f], $^{13}C$, $CDCl_3$, 101 MHz**



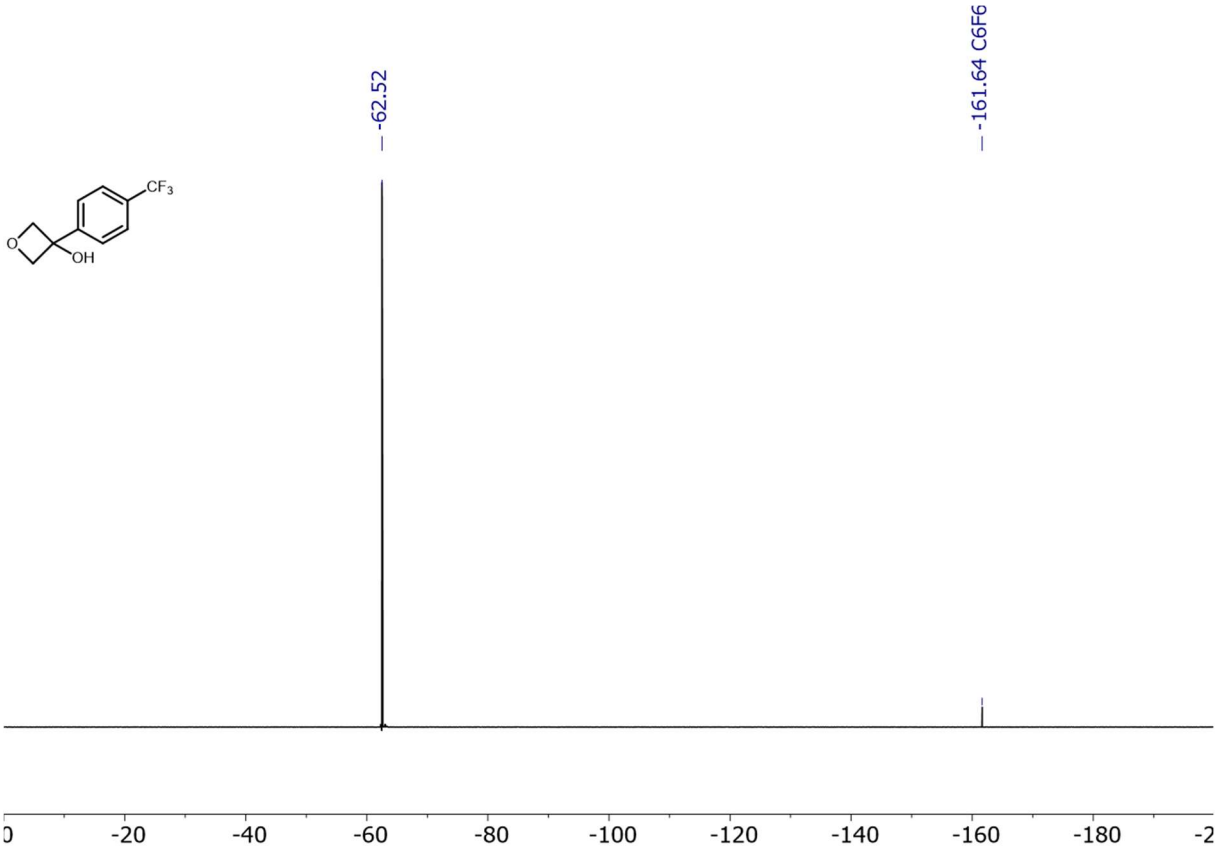
**[1g], $^{1}H$, $CDCl_3$, 400 MHz**



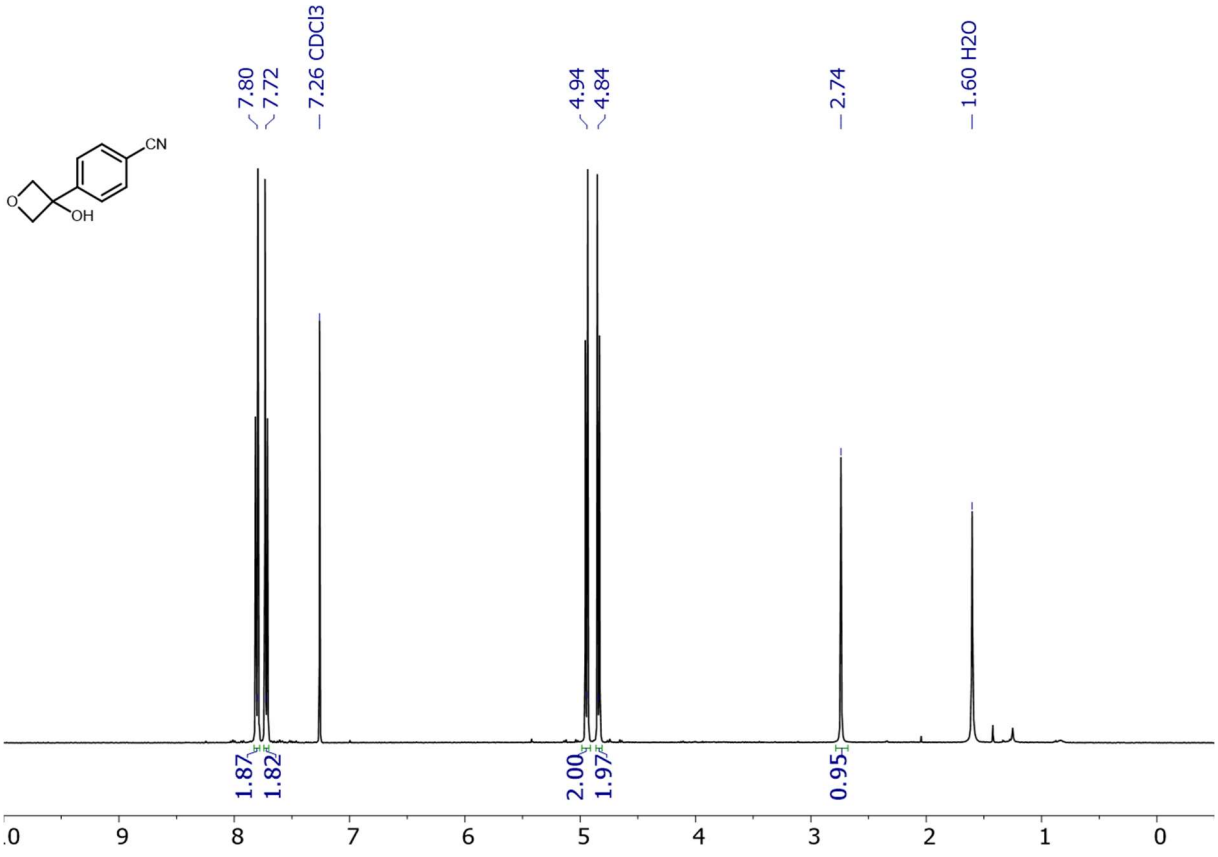

**[1g], $^{13}C$, $CDCl_3$, 101 MHz**



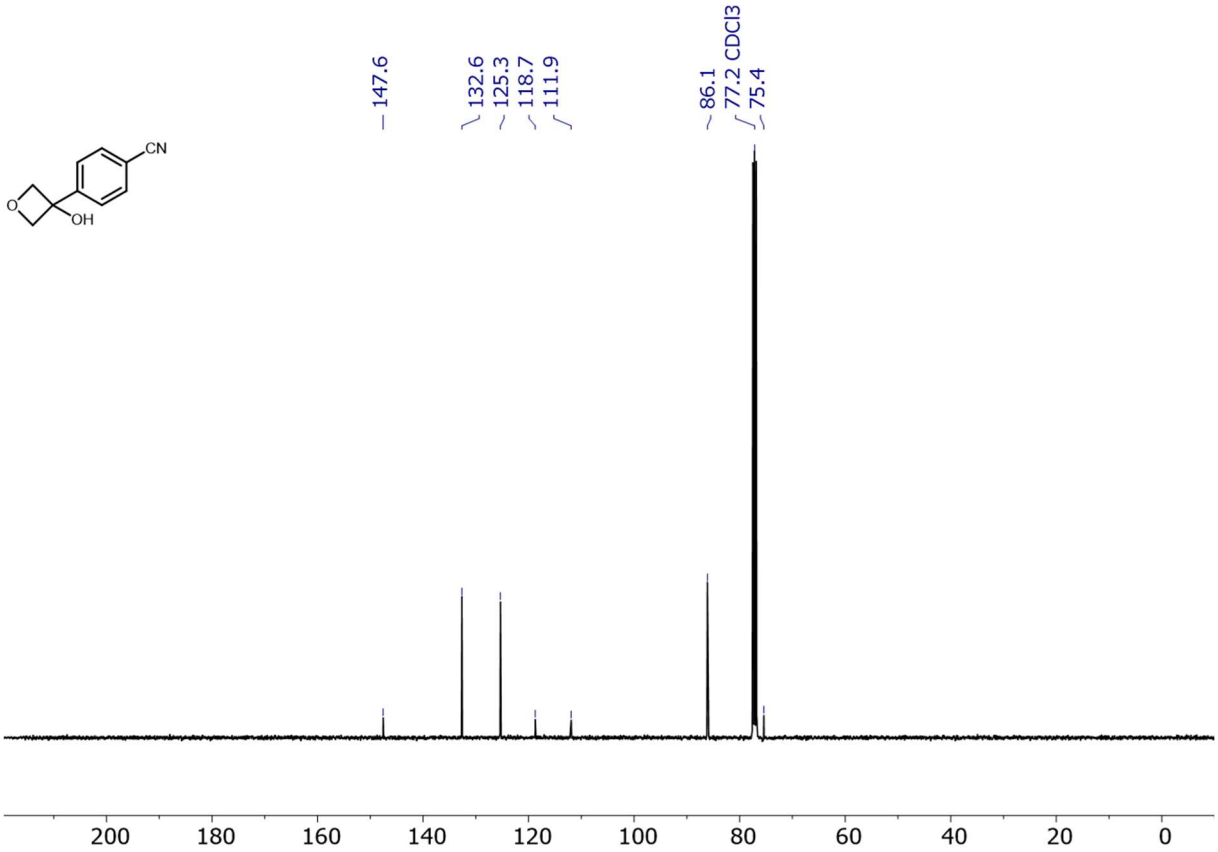
**[1g], $^{19}F$, $CDCl_3$, 377 MHz**



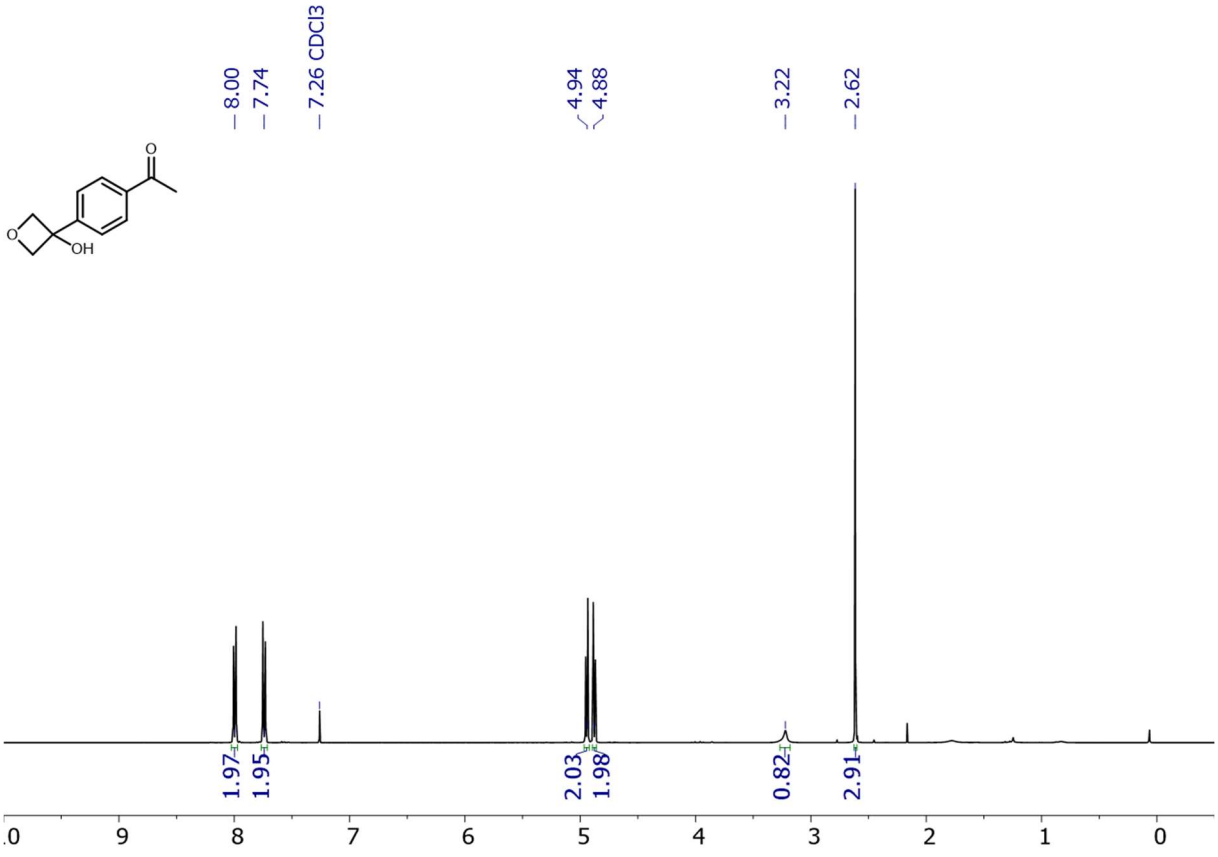
**[1h], $^{1}H$, $CDCl_3$, 400 MHz**



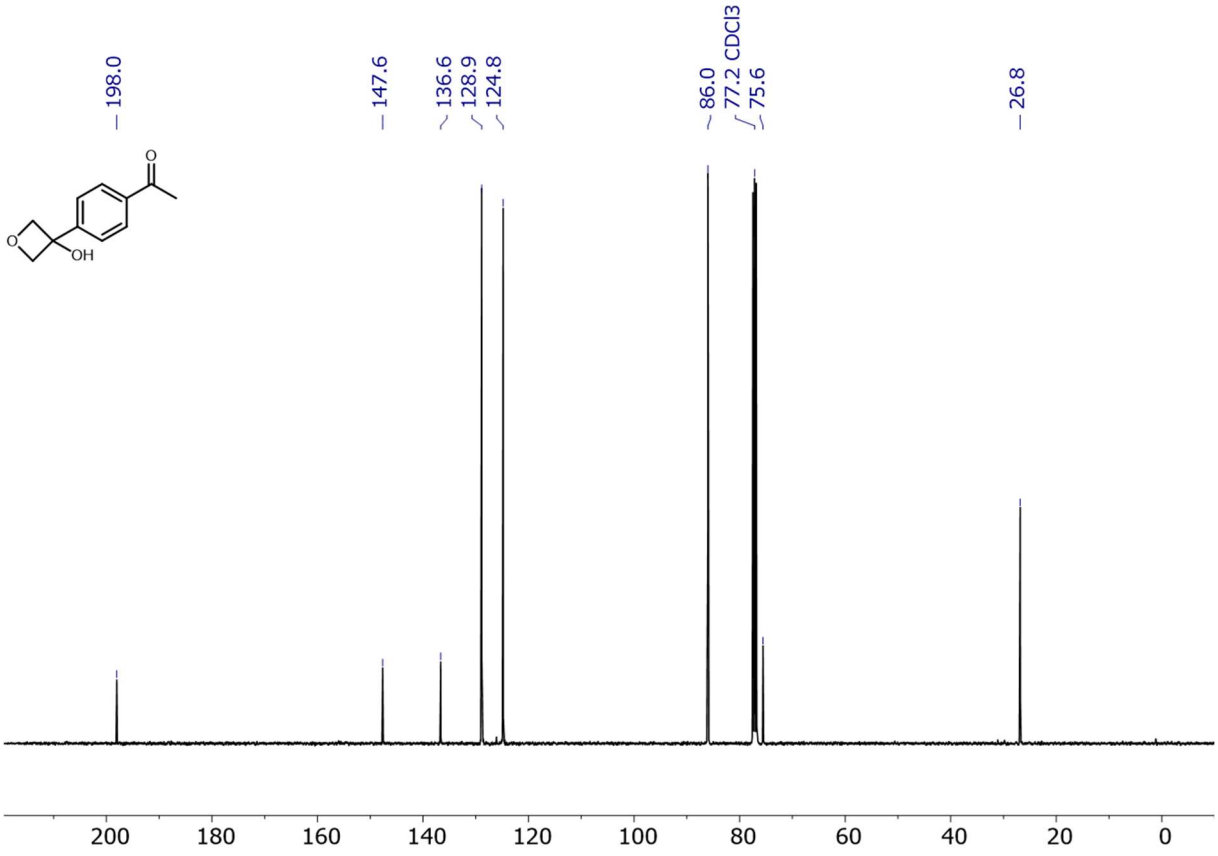

**[1h], $^{13}C$, $CDCl_3$, 101 MHz**



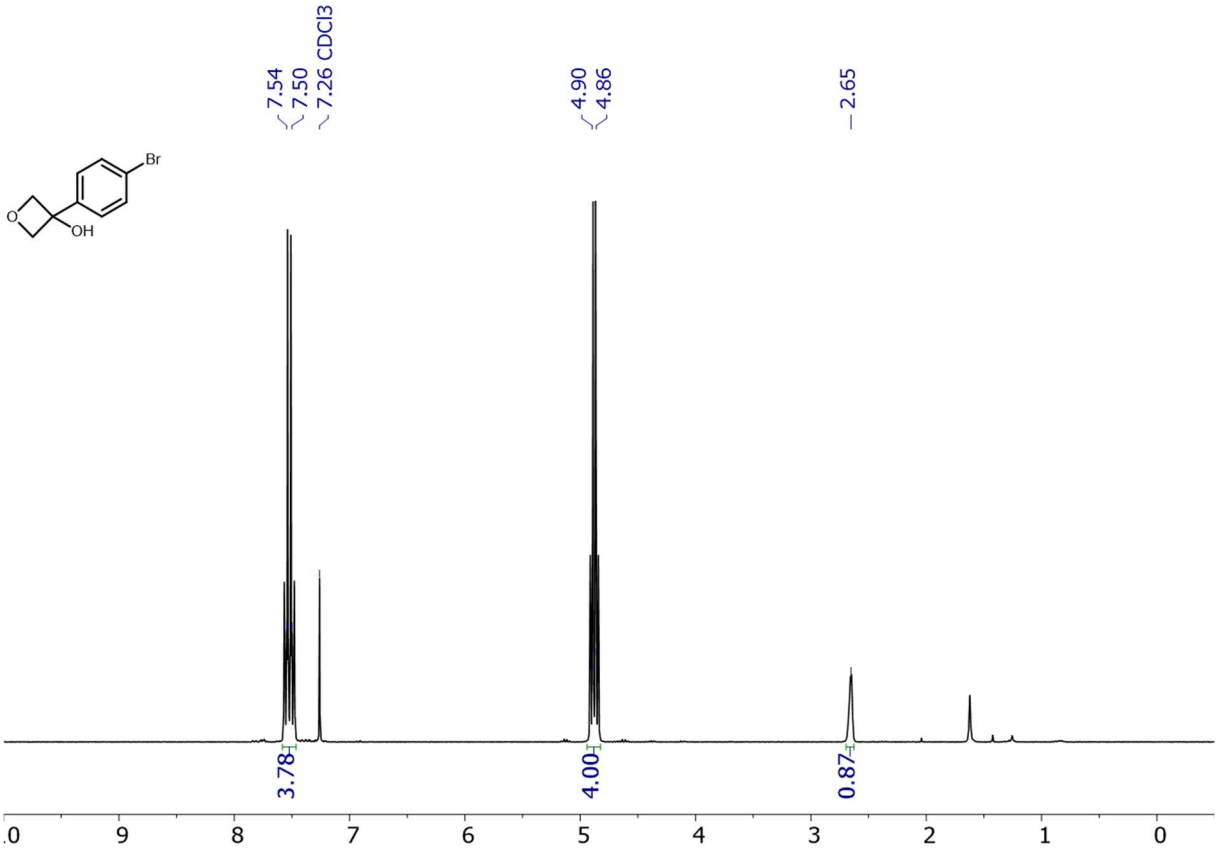
**[1i], $^{1}H$, $CDCl_3$, 400 MHz**



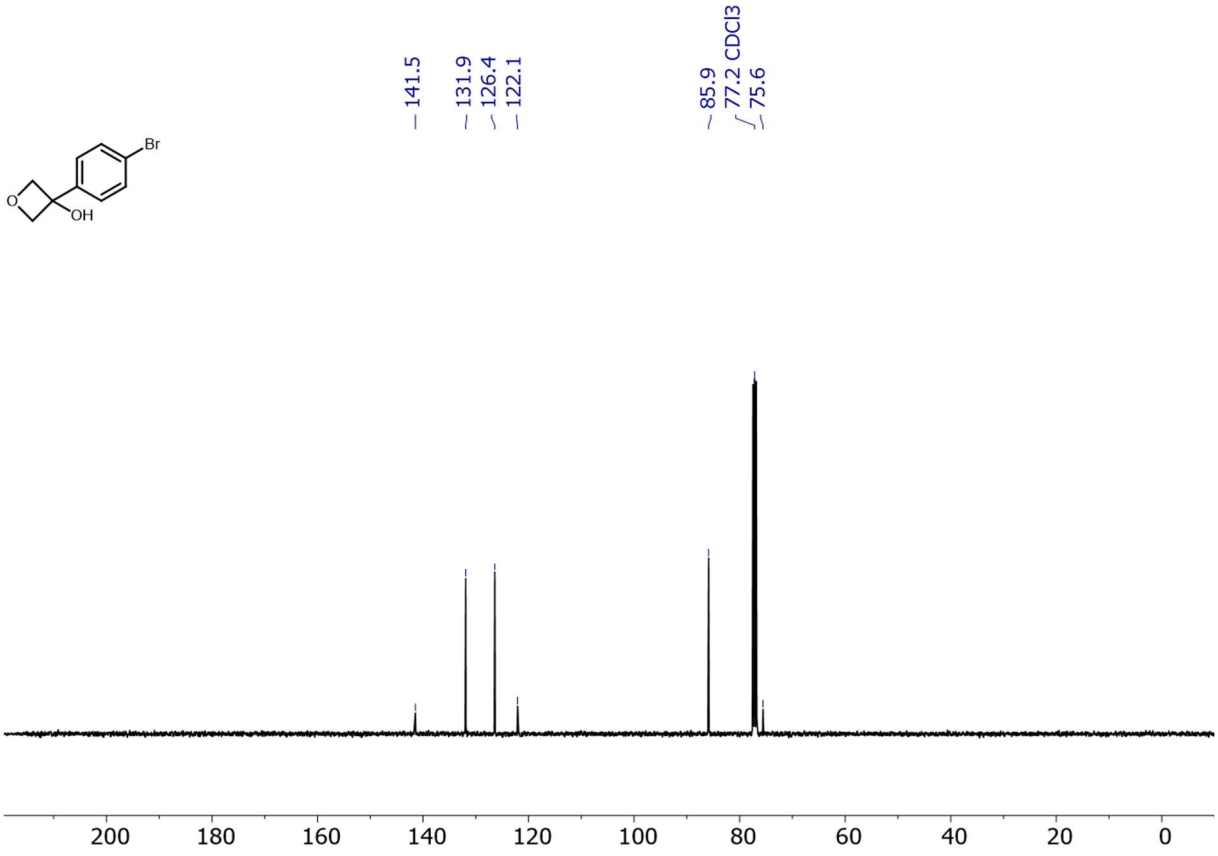

**[1i], $^{13}C$, $CDCl_3$, 101 MHz**



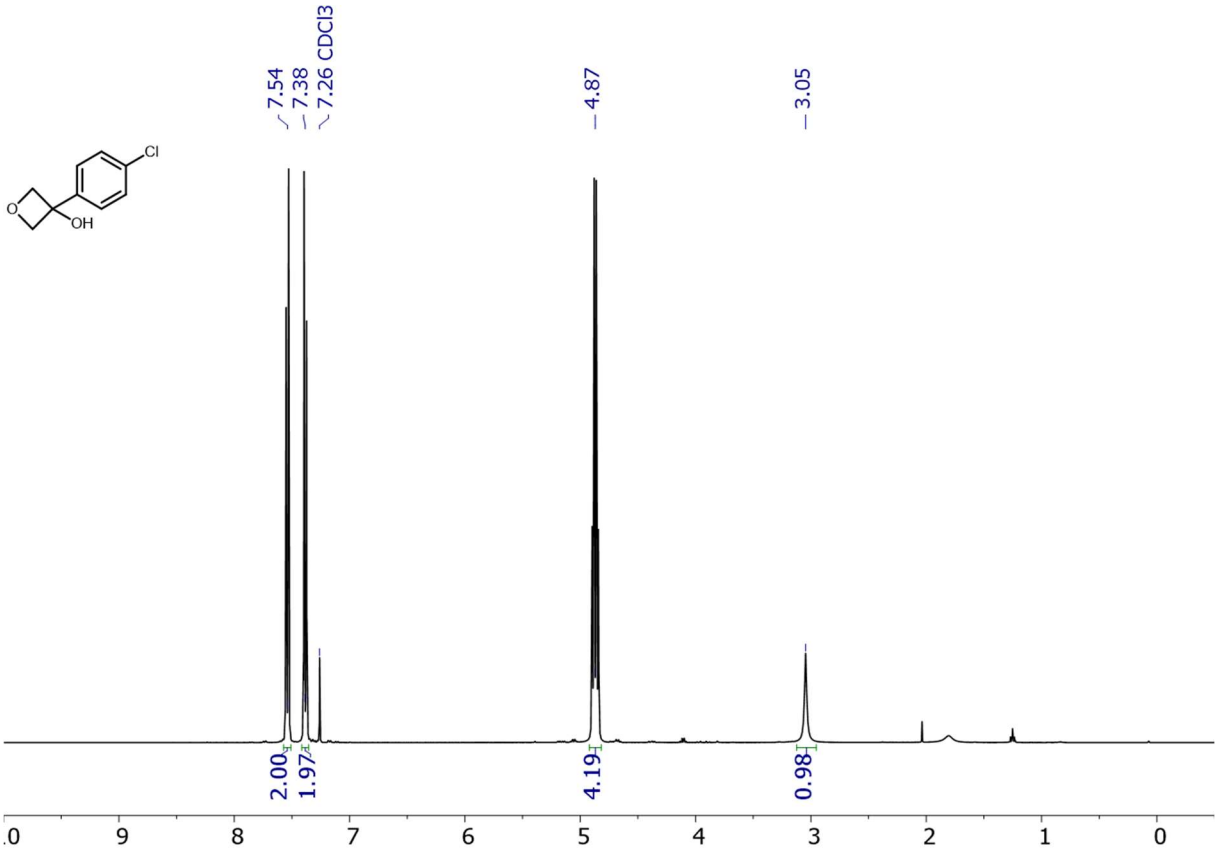
**[1j], $^{1}H$, $CDCl_3$, 400 MHz**



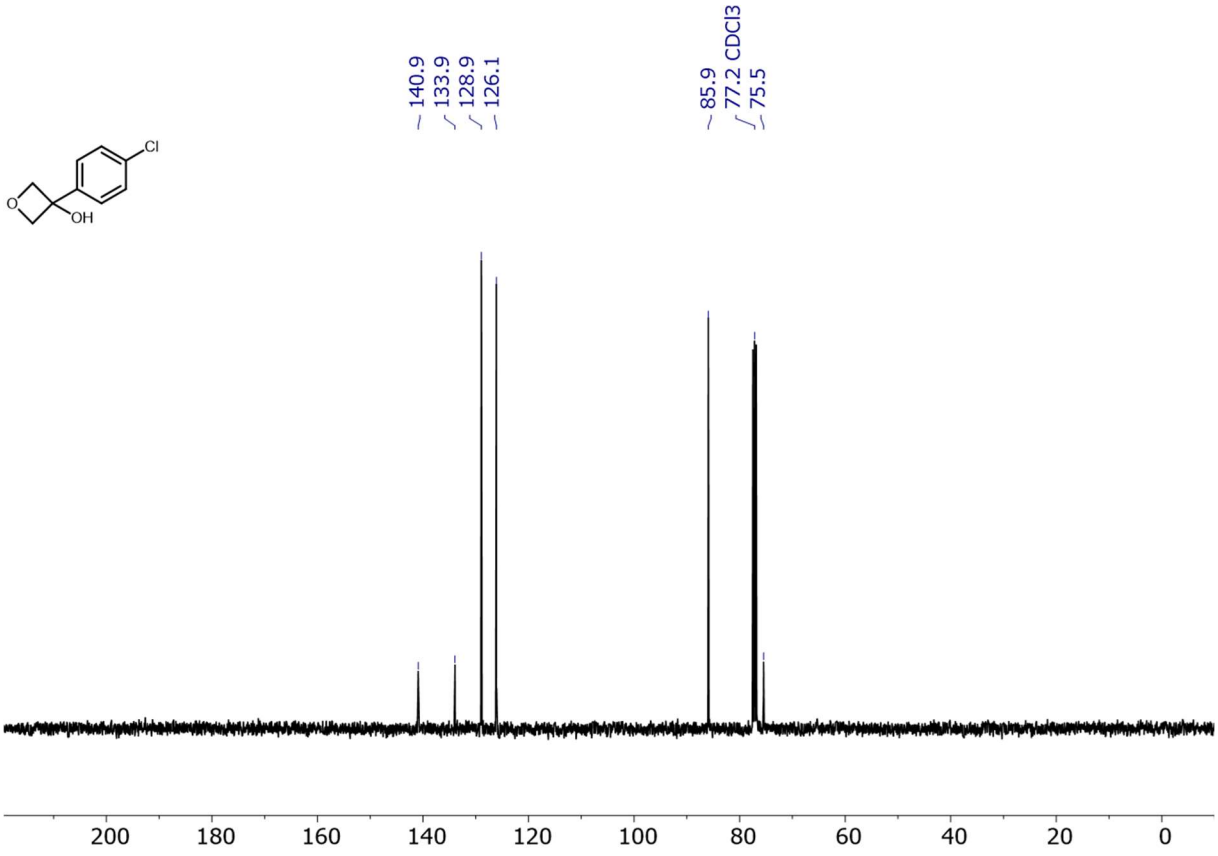

**[1j], $^{13}C$, $CDCl_3$, 101 MHz**



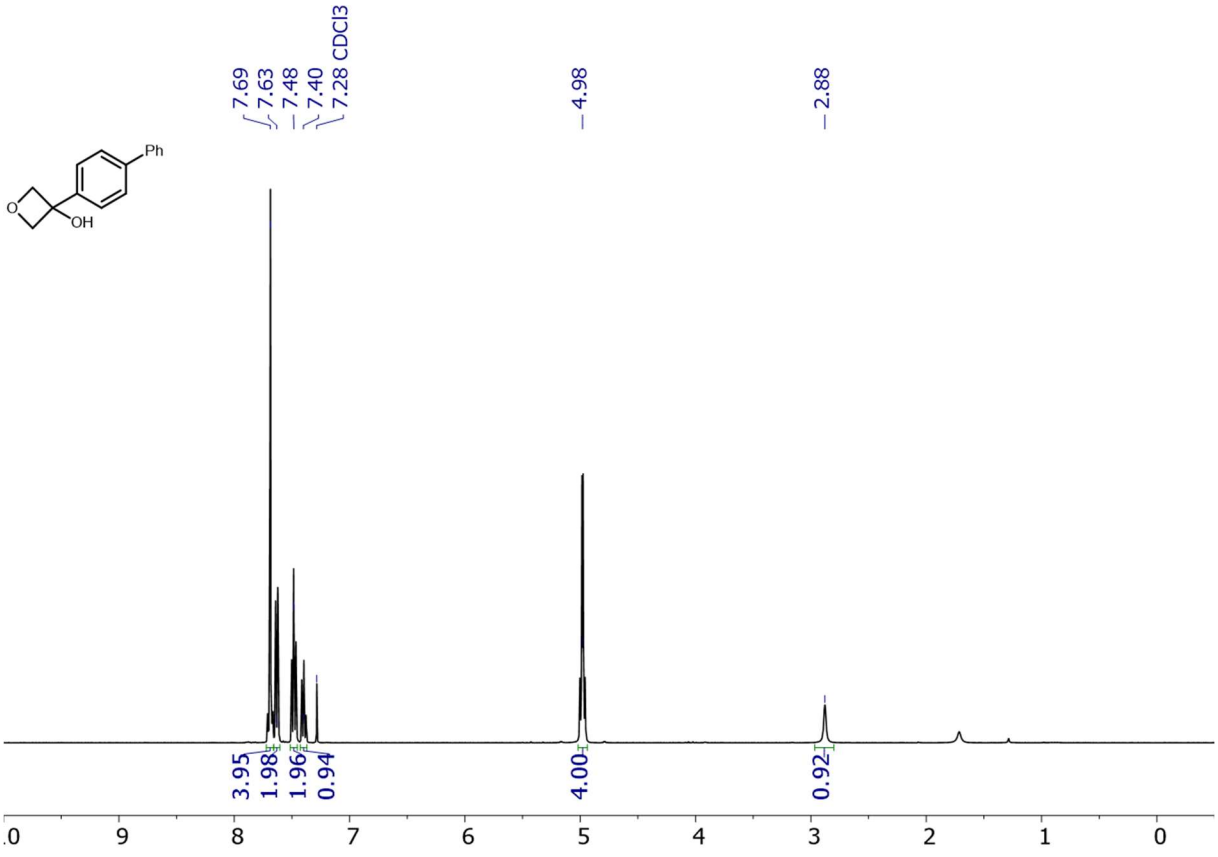
**[1k], $^{1}H$, $CDCl_3$, 400 MHz**



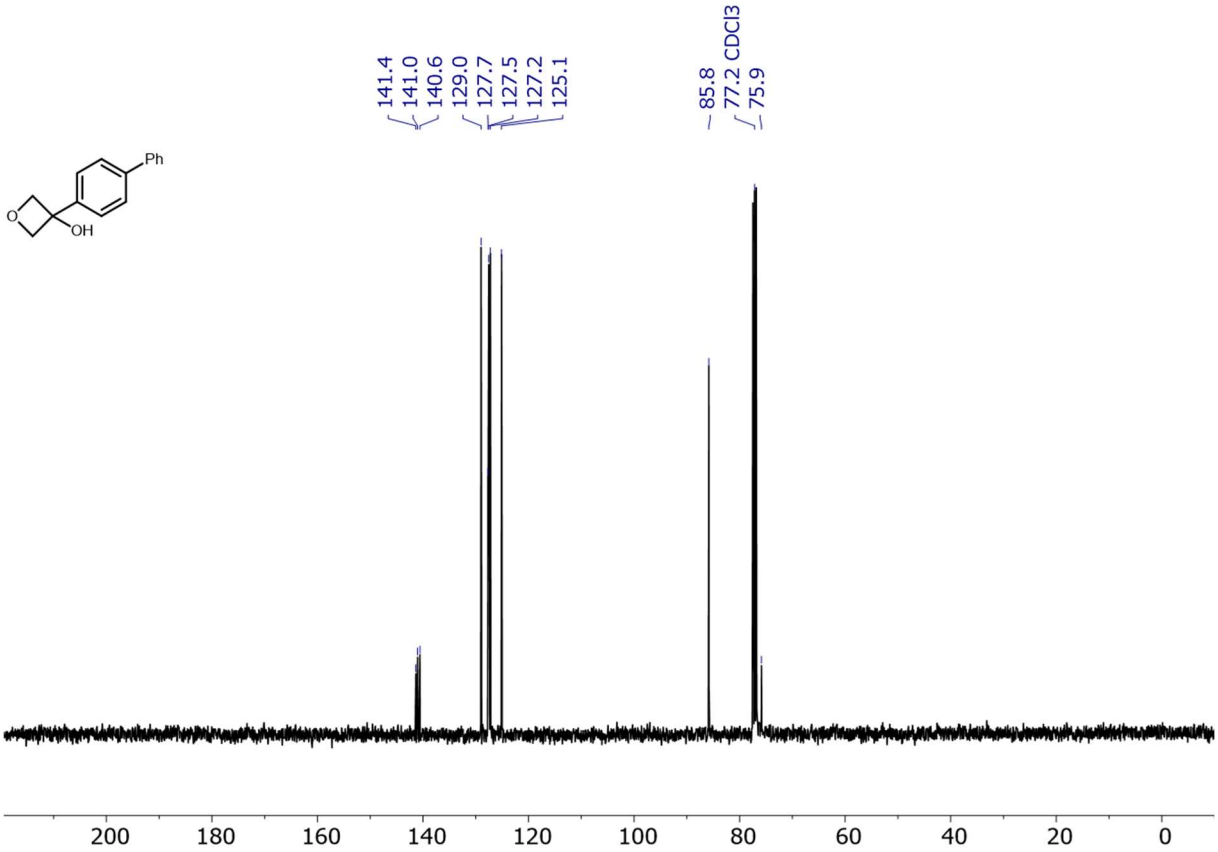

**[1k], $^{13}C$, $CDCl_3$, 101 MHz**



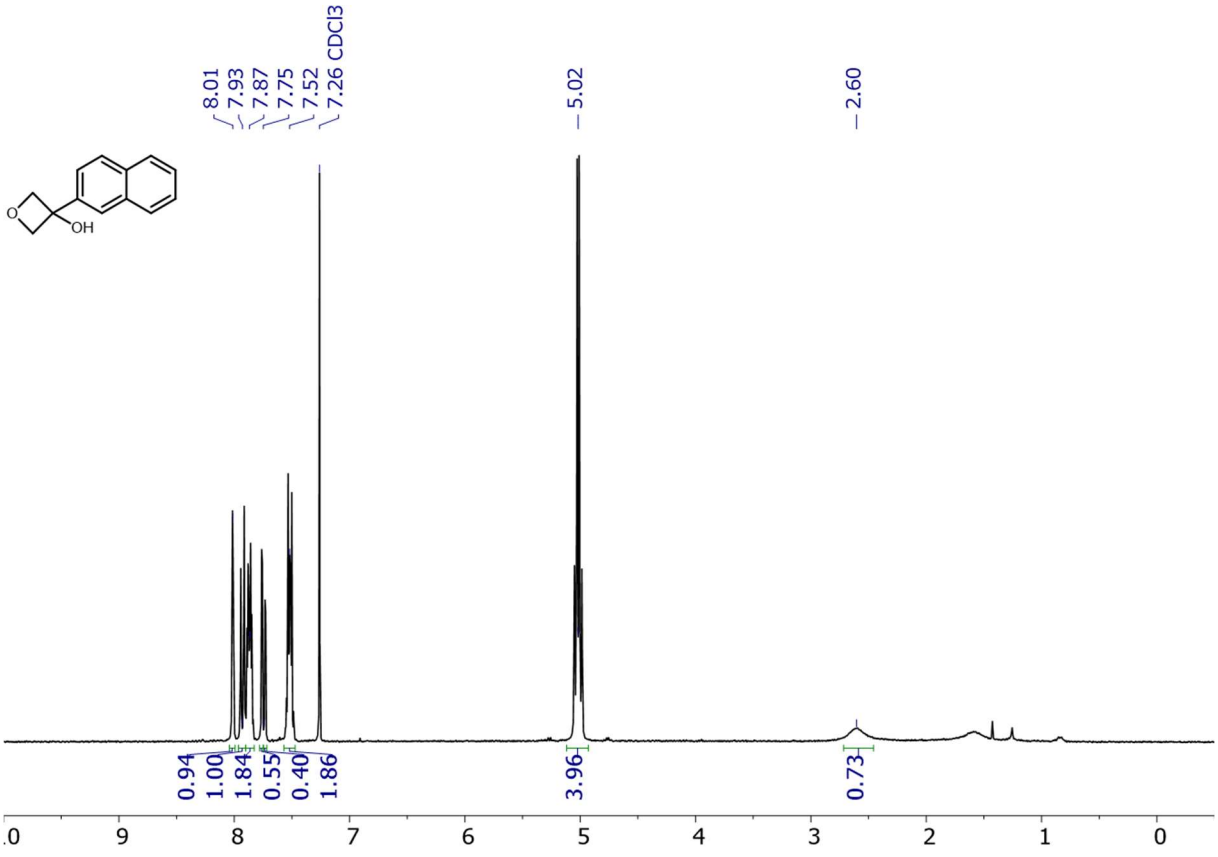
**[1l], $^{1}H$, $CDCl_3$, 400 MHz**



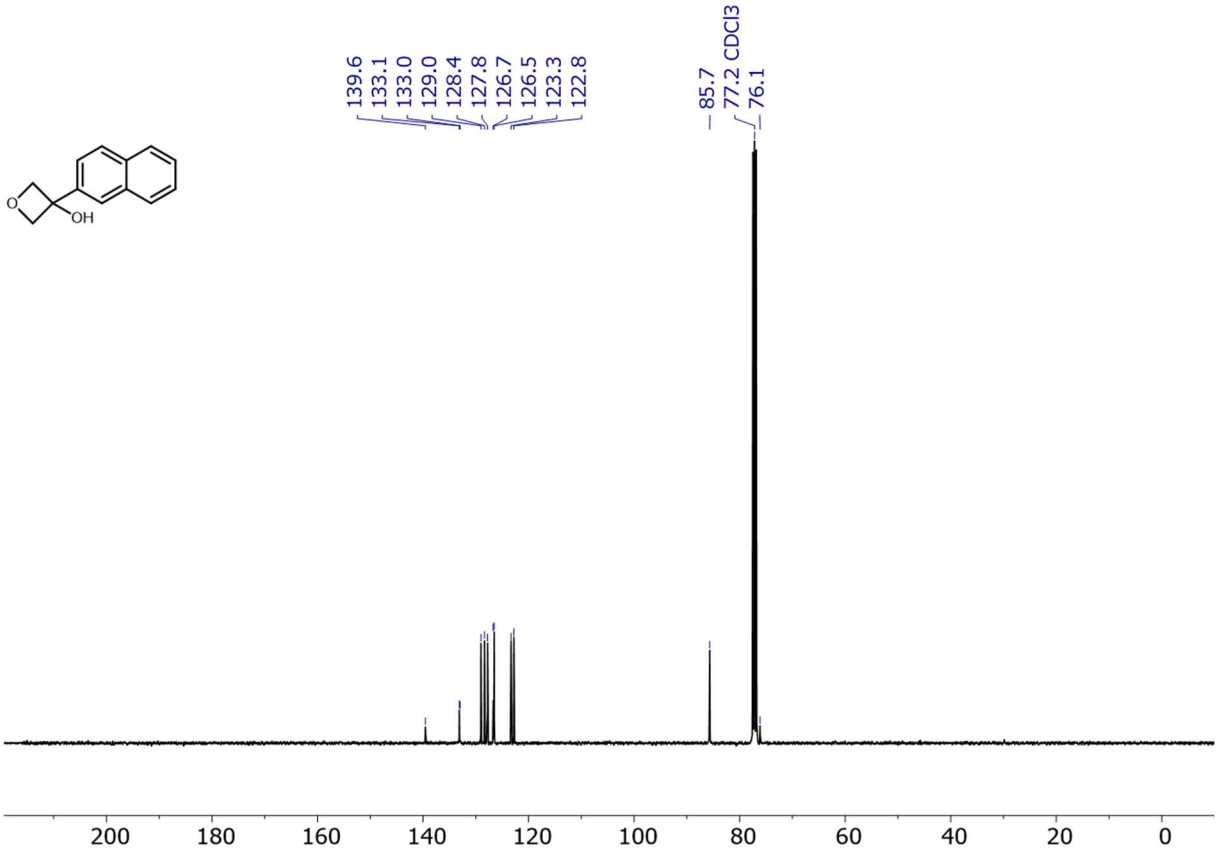

**[1l], $^{13}C$, $CDCl_3$, 101 MHz**



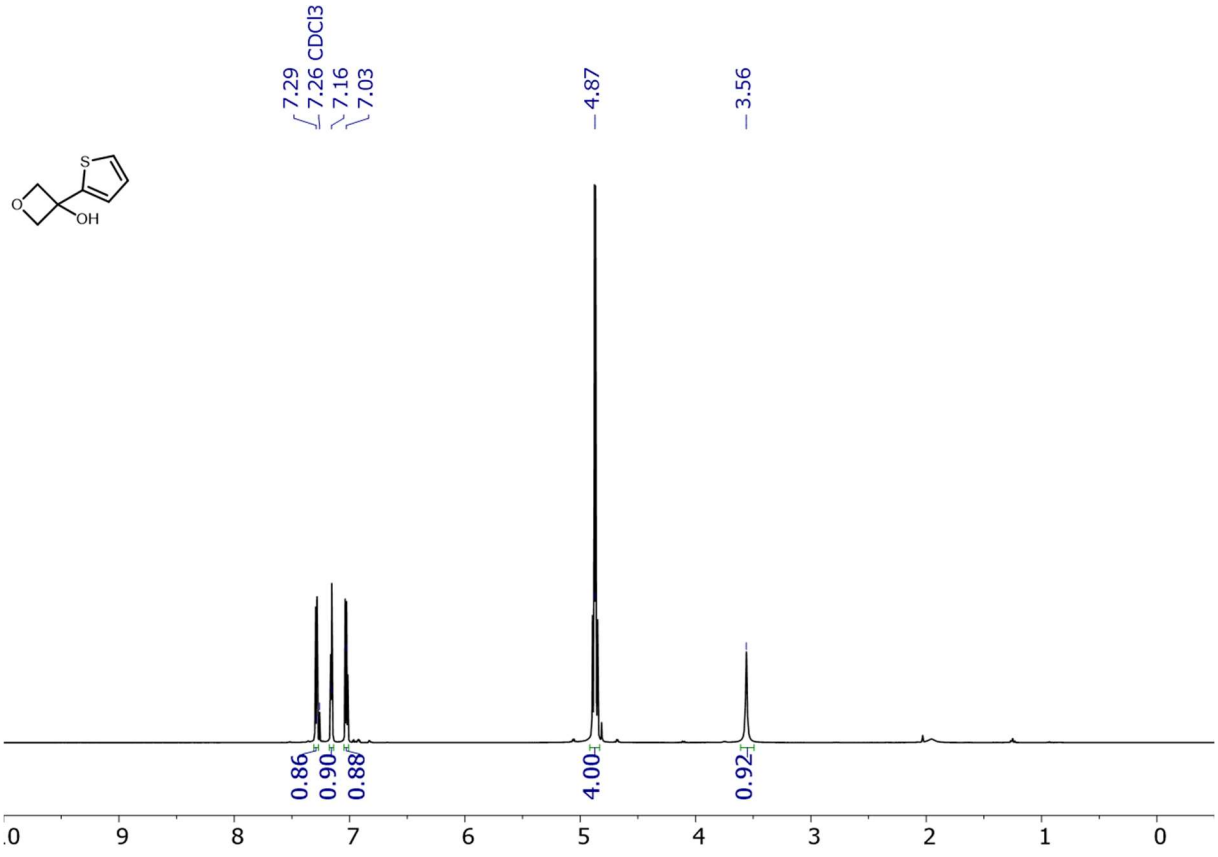
**[1m], $^{1}H$, $CDCl_3$, 400 MHz**



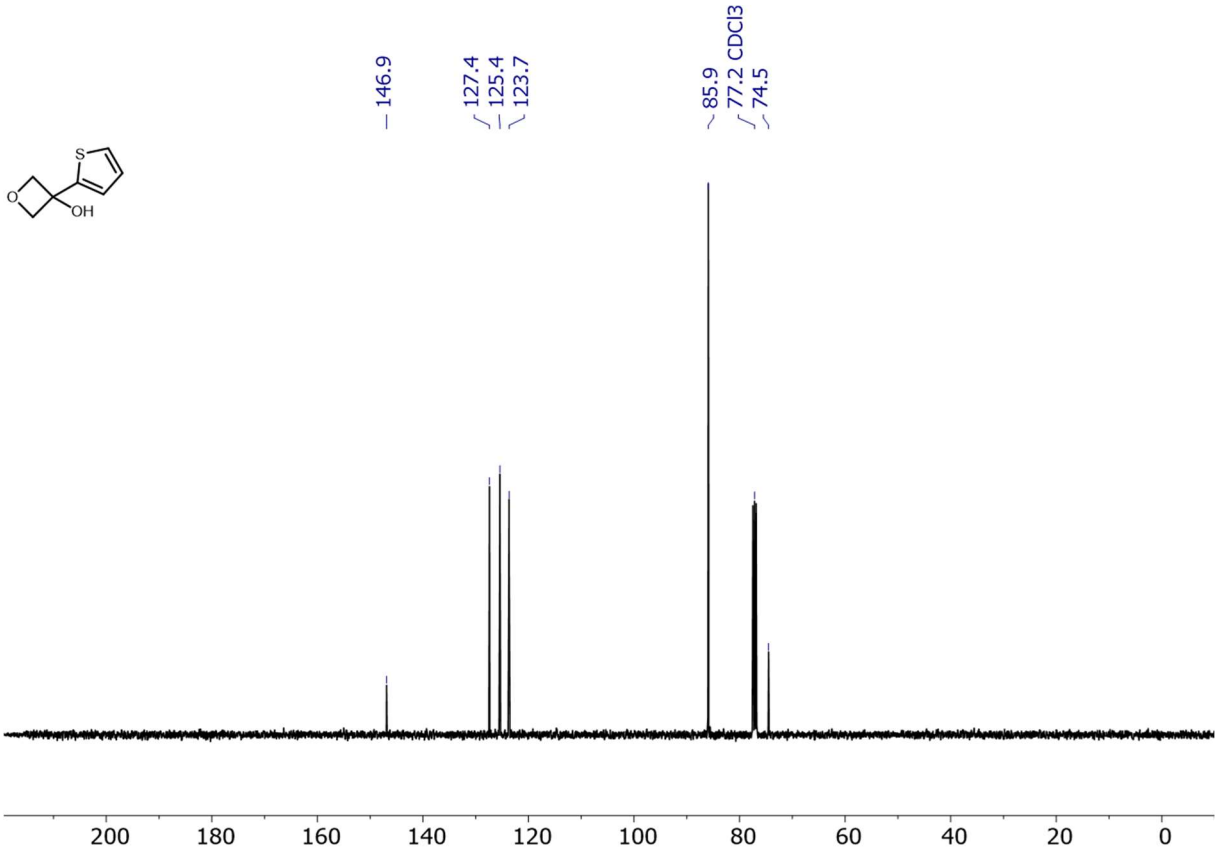

**[1m], $^{13}C$, $CDCl_3$, 101 MHz**



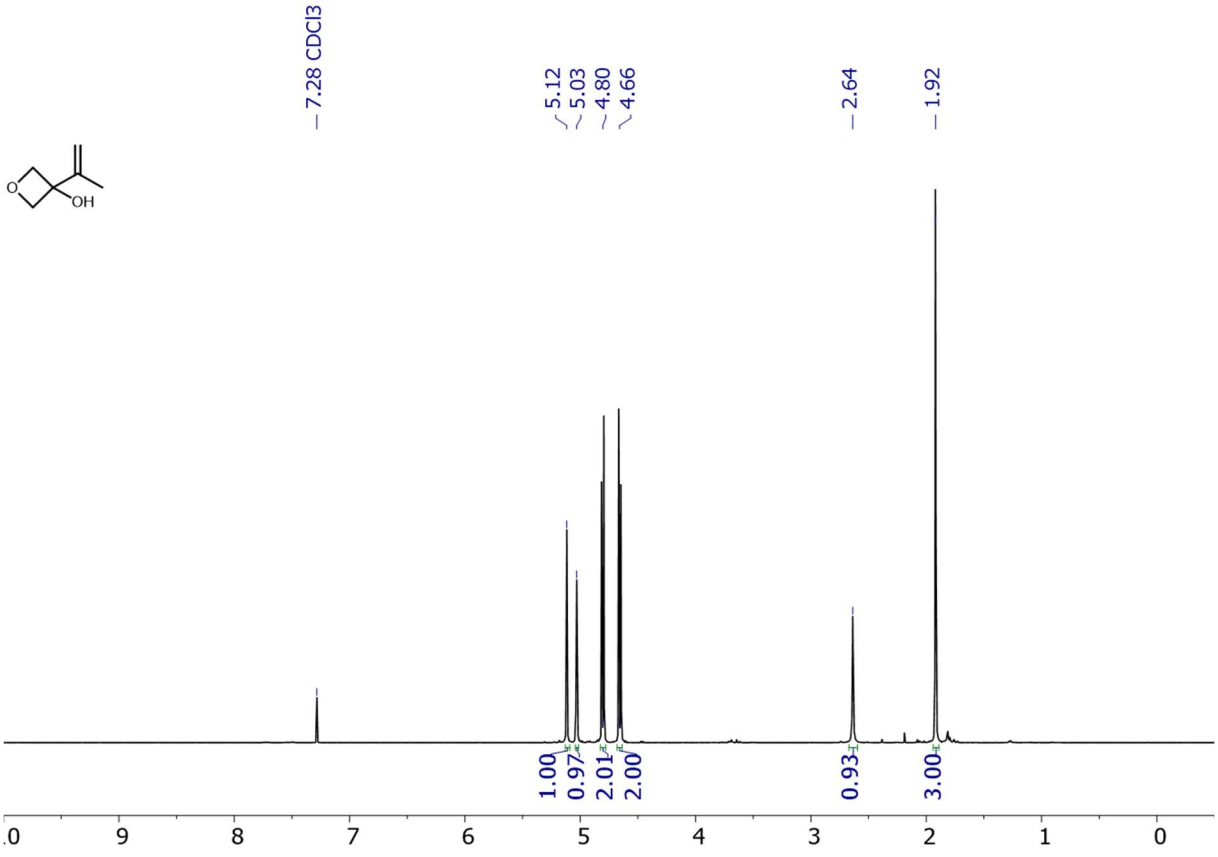
**[1n], $^{1}H$, $CDCl_3$, 400 MHz**



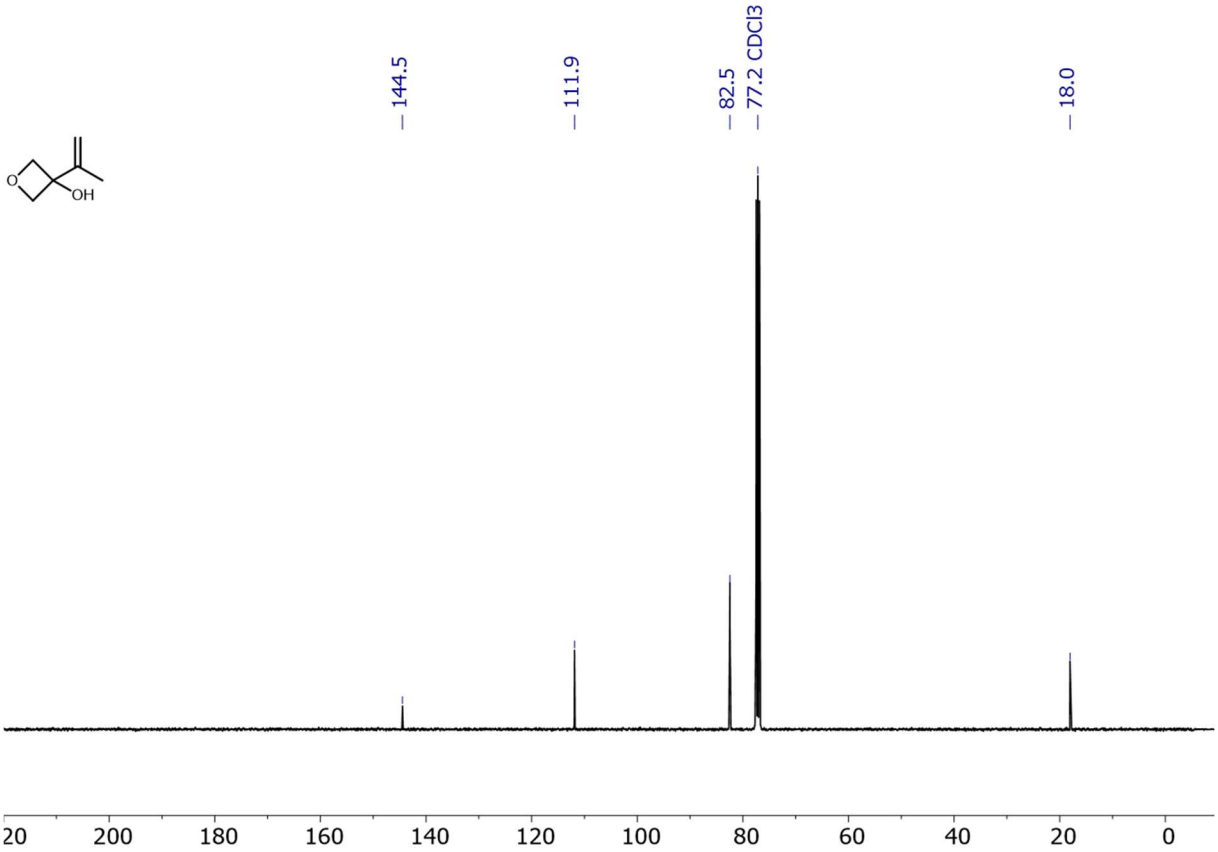

**[1n], $^{13}C$, $CDCl_3$, 101 MHz**



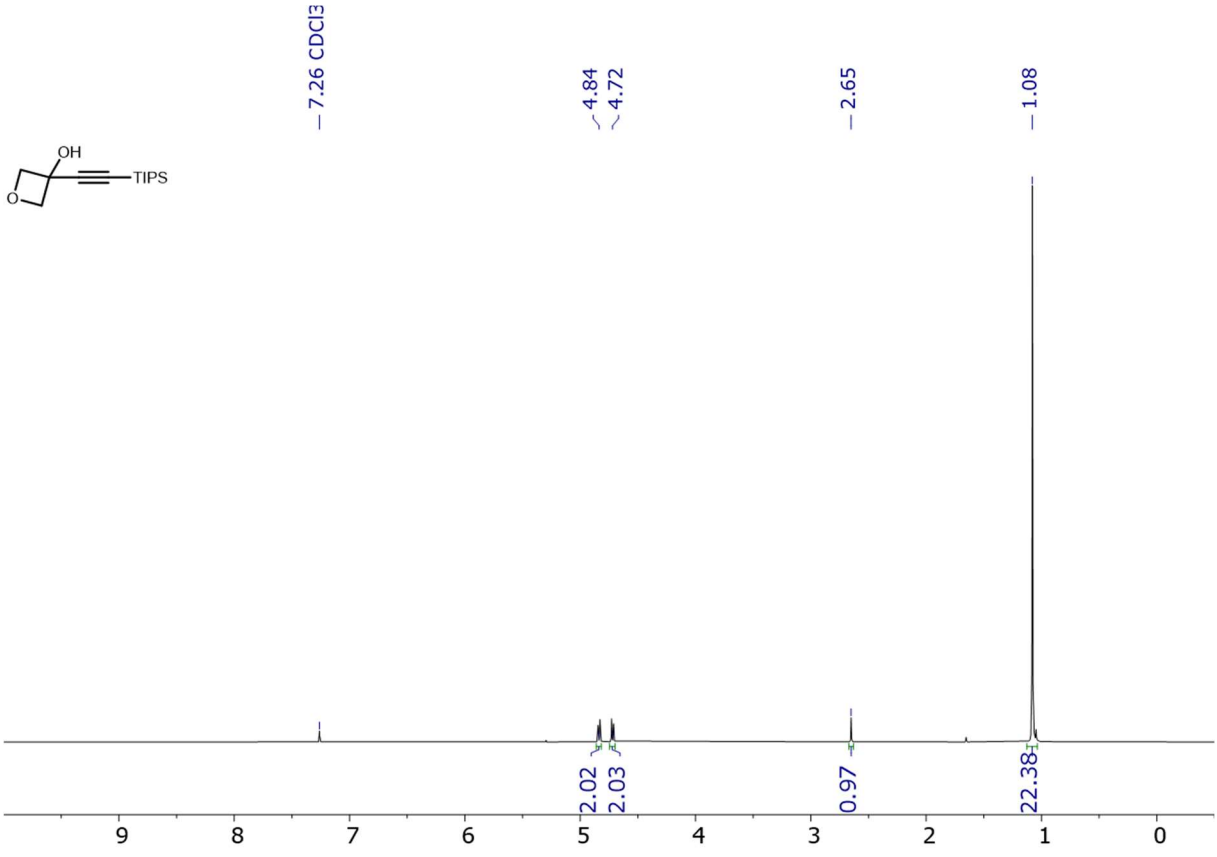
**[1o], $^{1}H$, $CDCl_3$, 400 MHz**



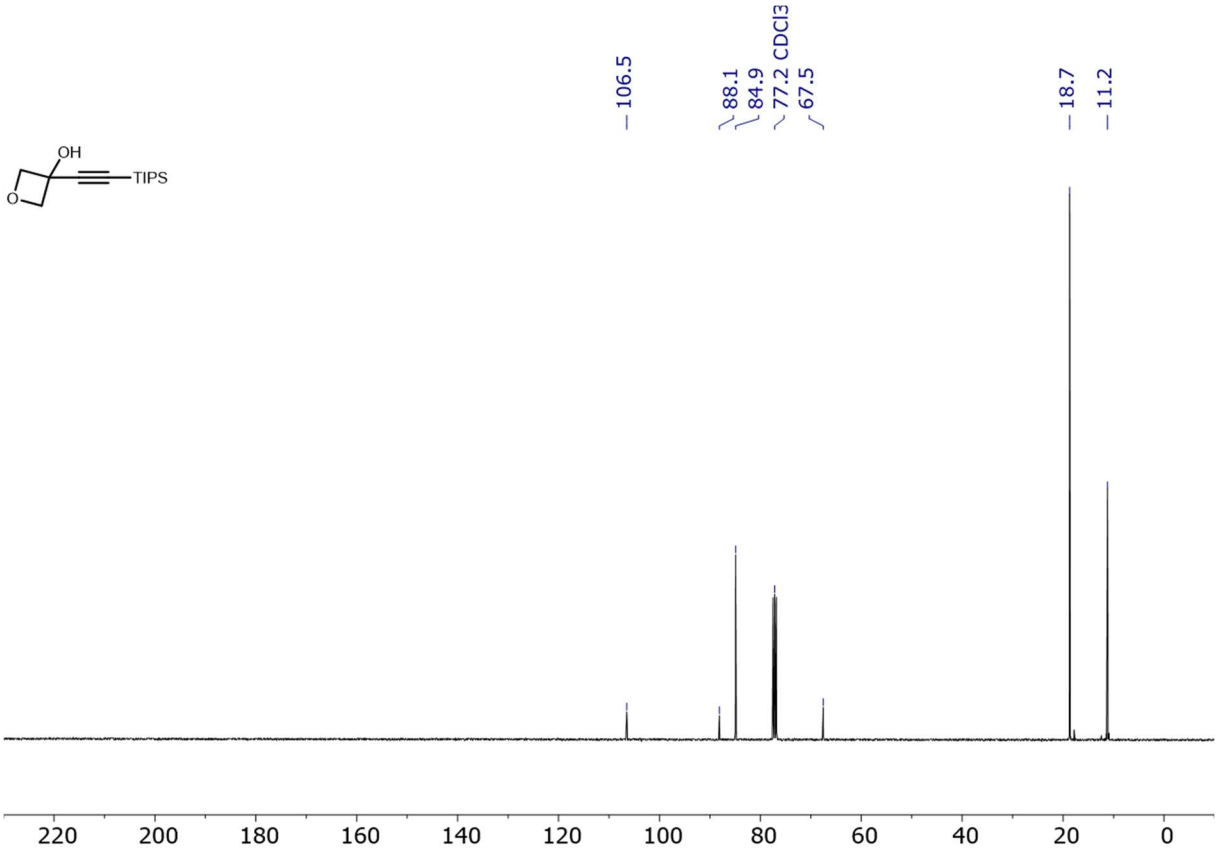

**[1o], $^{13}C$, $CDCl_3$, 101 MHz**



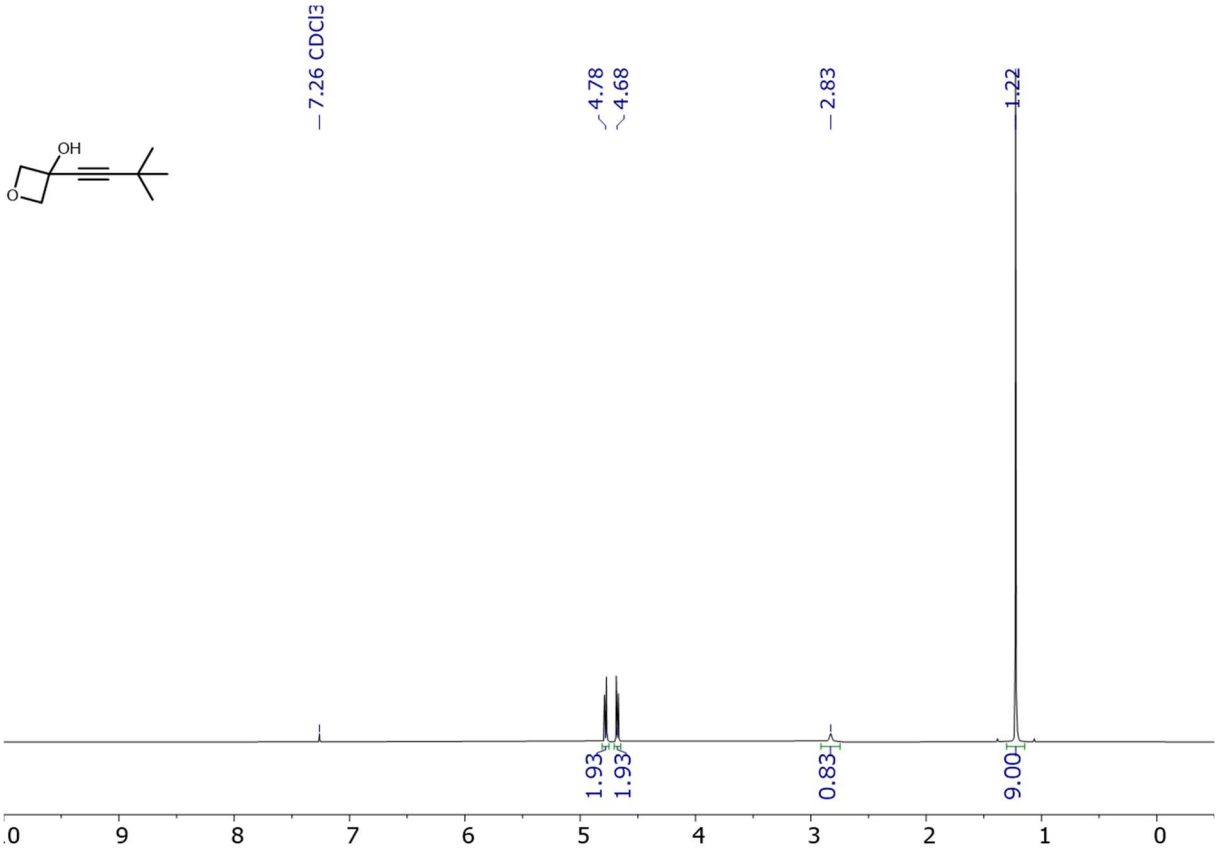
**[1p], $^{1}H$, $CDCl_3$, 400 MHz**



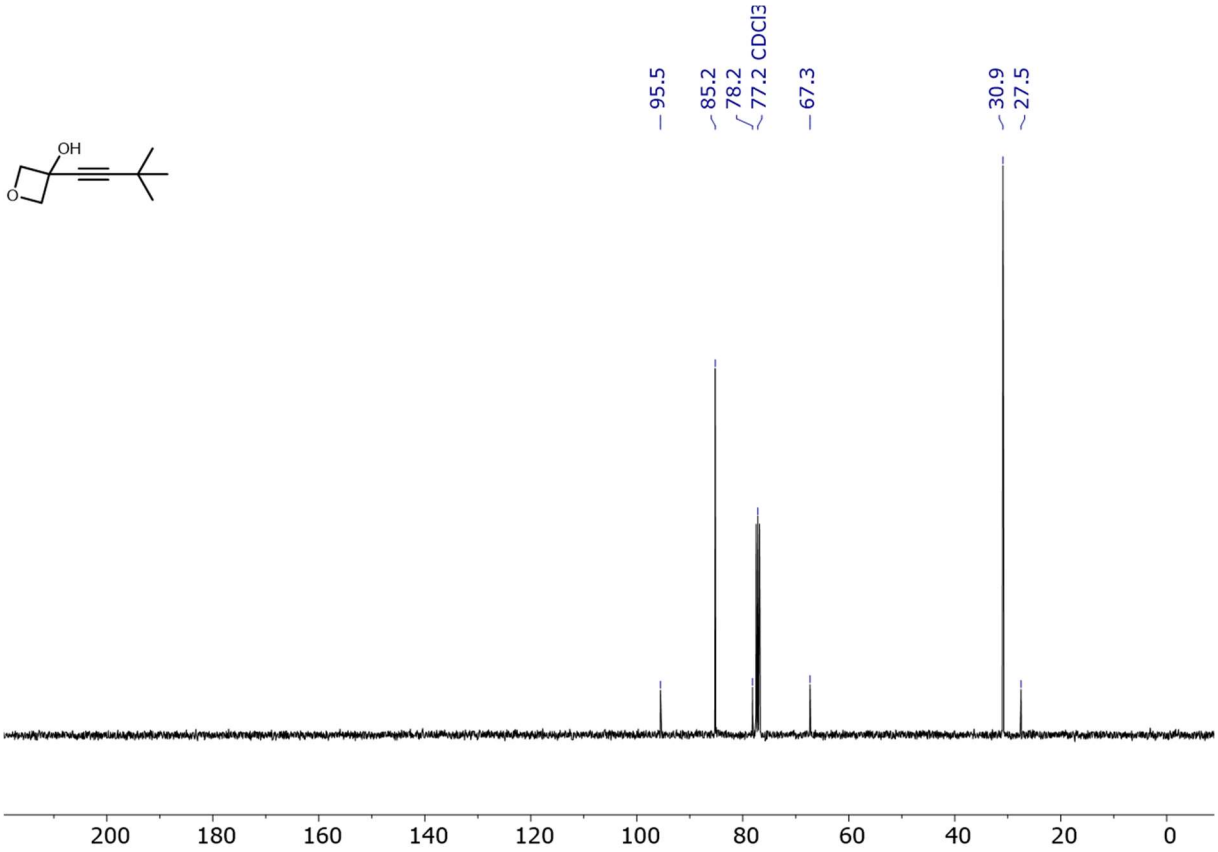

**[1p], $^{13}C$, $CDCl_3$, 101 MHz**



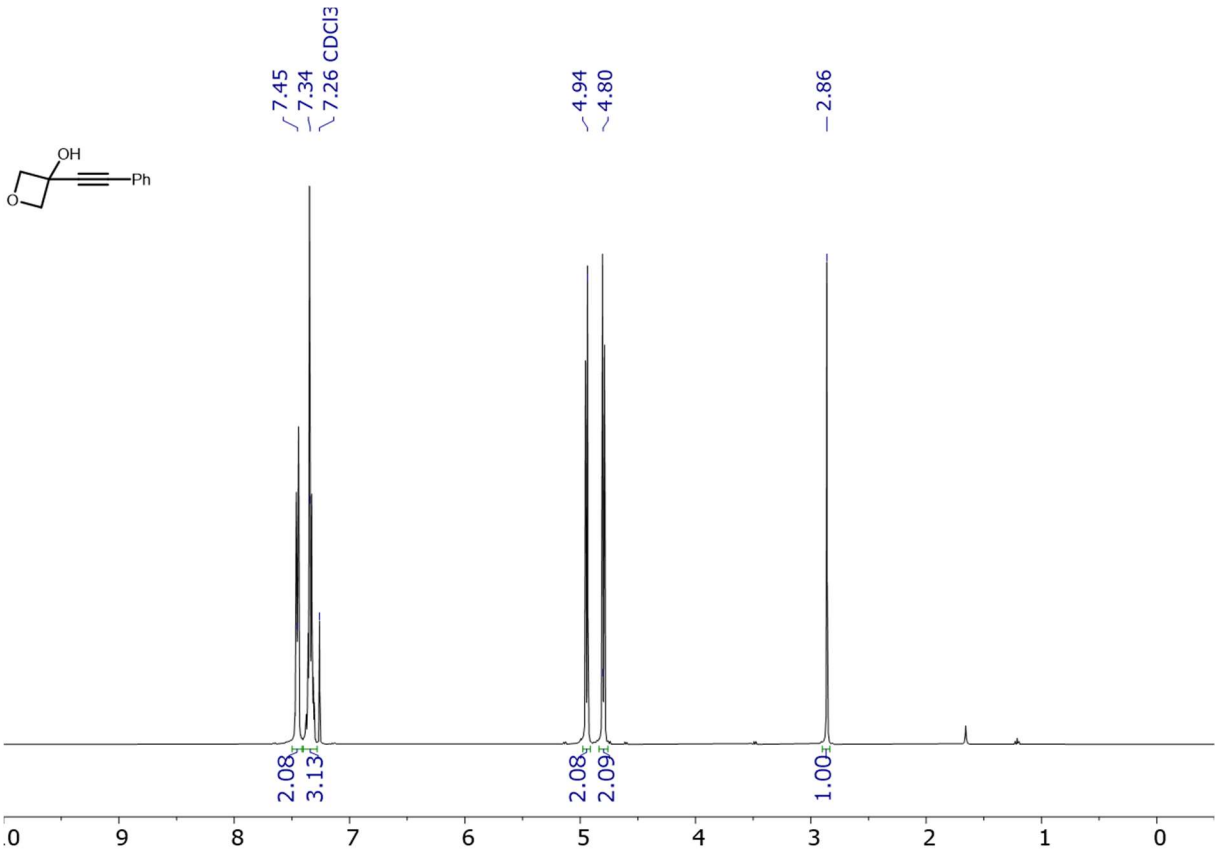
**[1q], $^{1}H$, $CDCl_3$, 400 MHz**



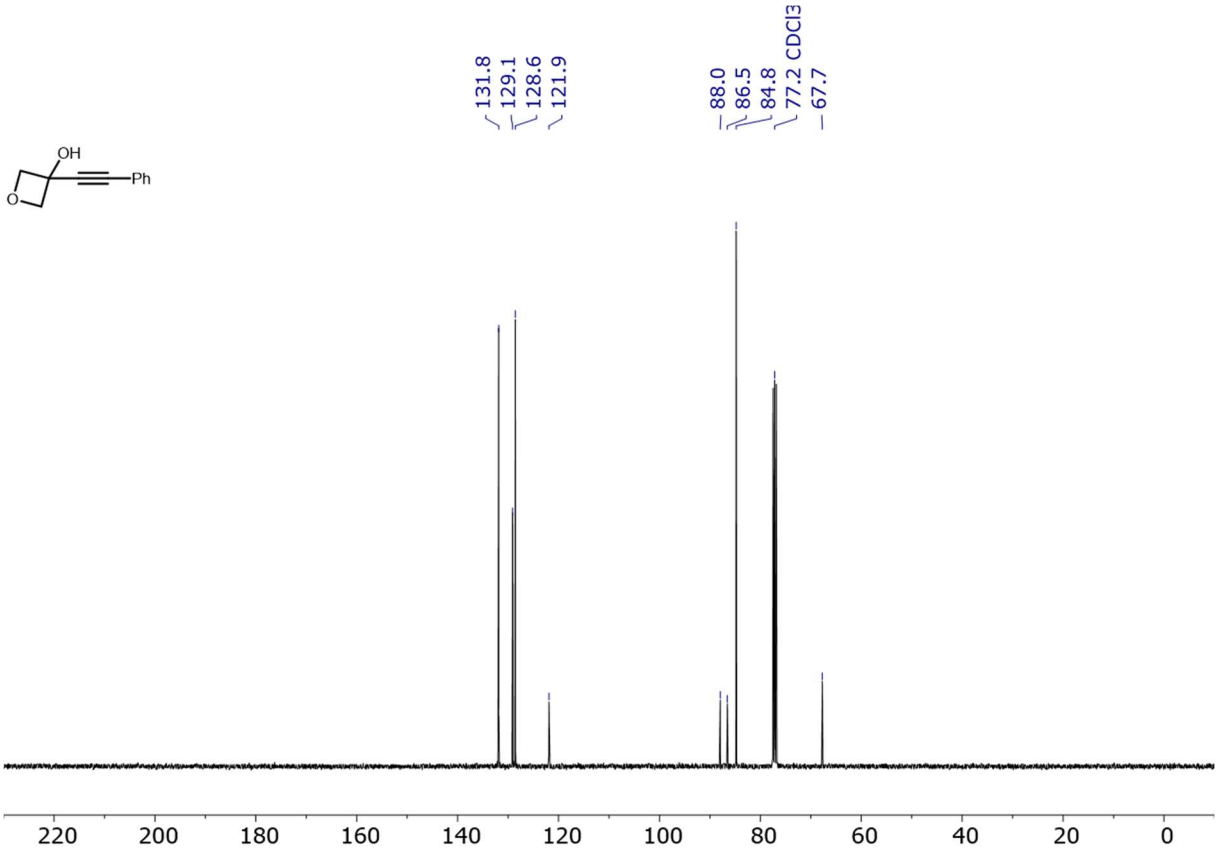

**[1q], $^{13}C$, $CDCl_3$, 101 MHz**



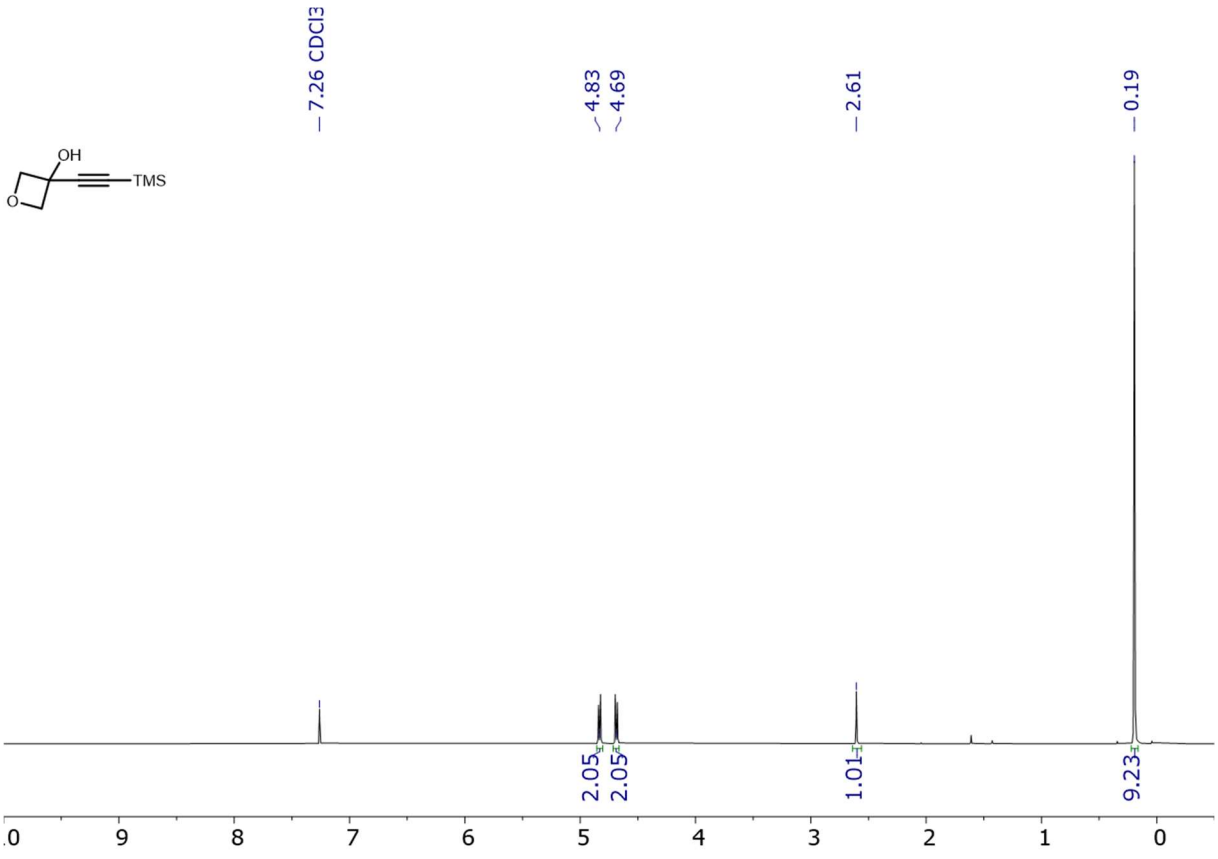
**[1r], $^{1}H$, $CDCl_3$, 400 MHz**



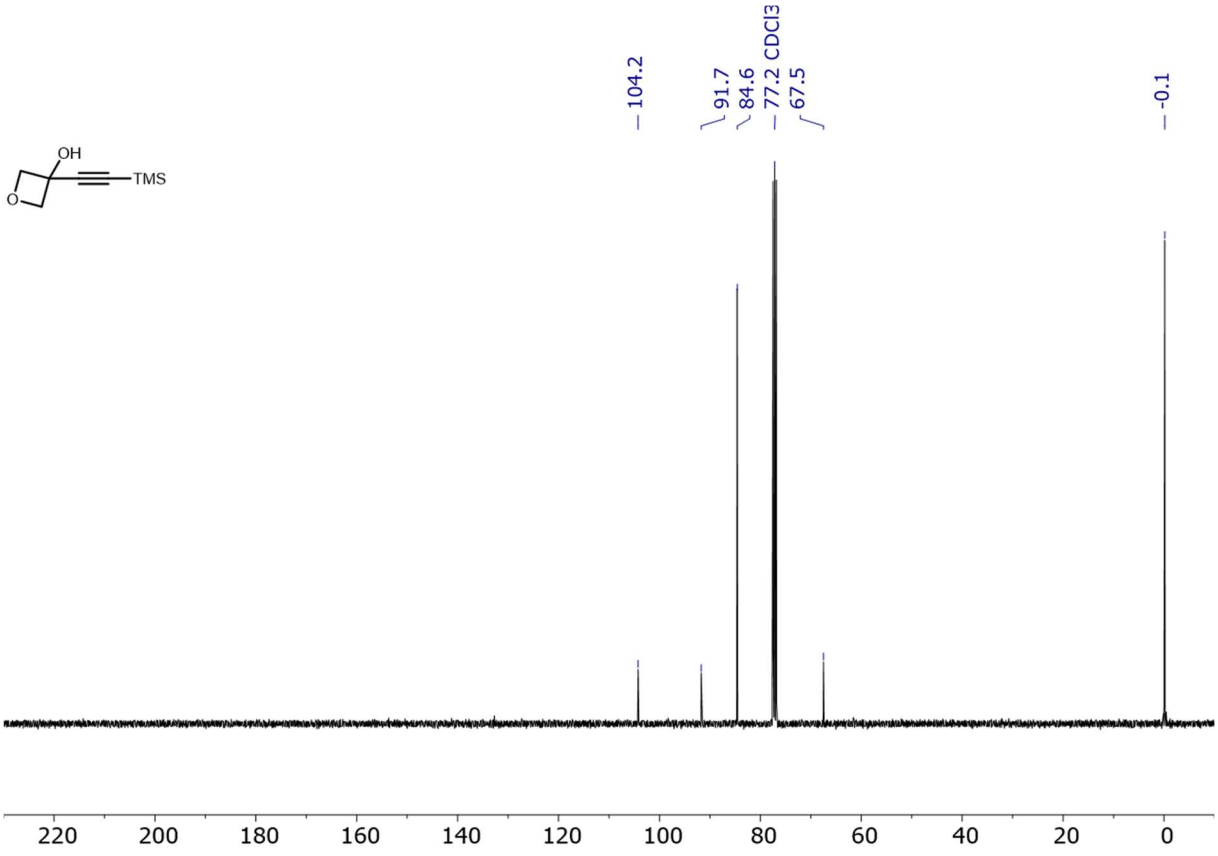

**[1r], $^{13}C$, $CDCl_3$, 101 MHz**



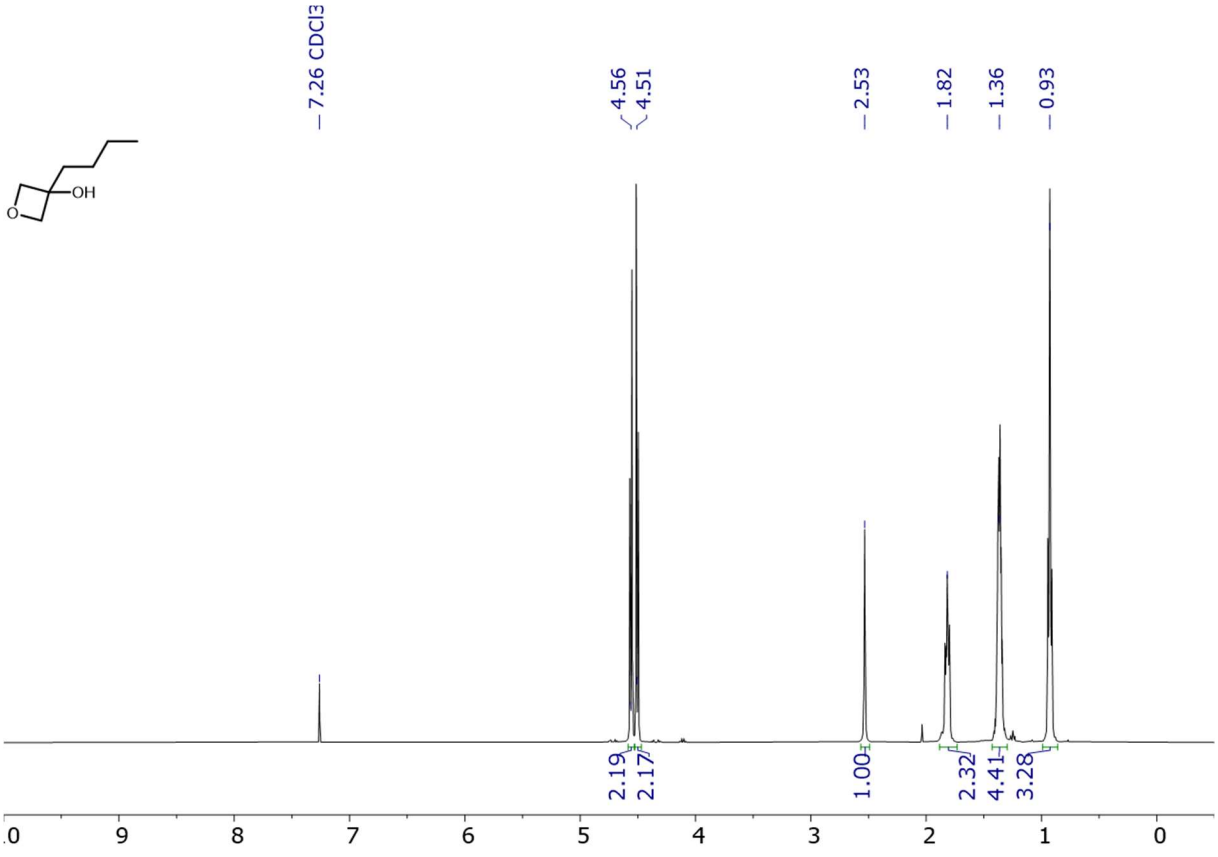
**[1s], $^{1}H$, $CDCl_3$, 400 MHz**



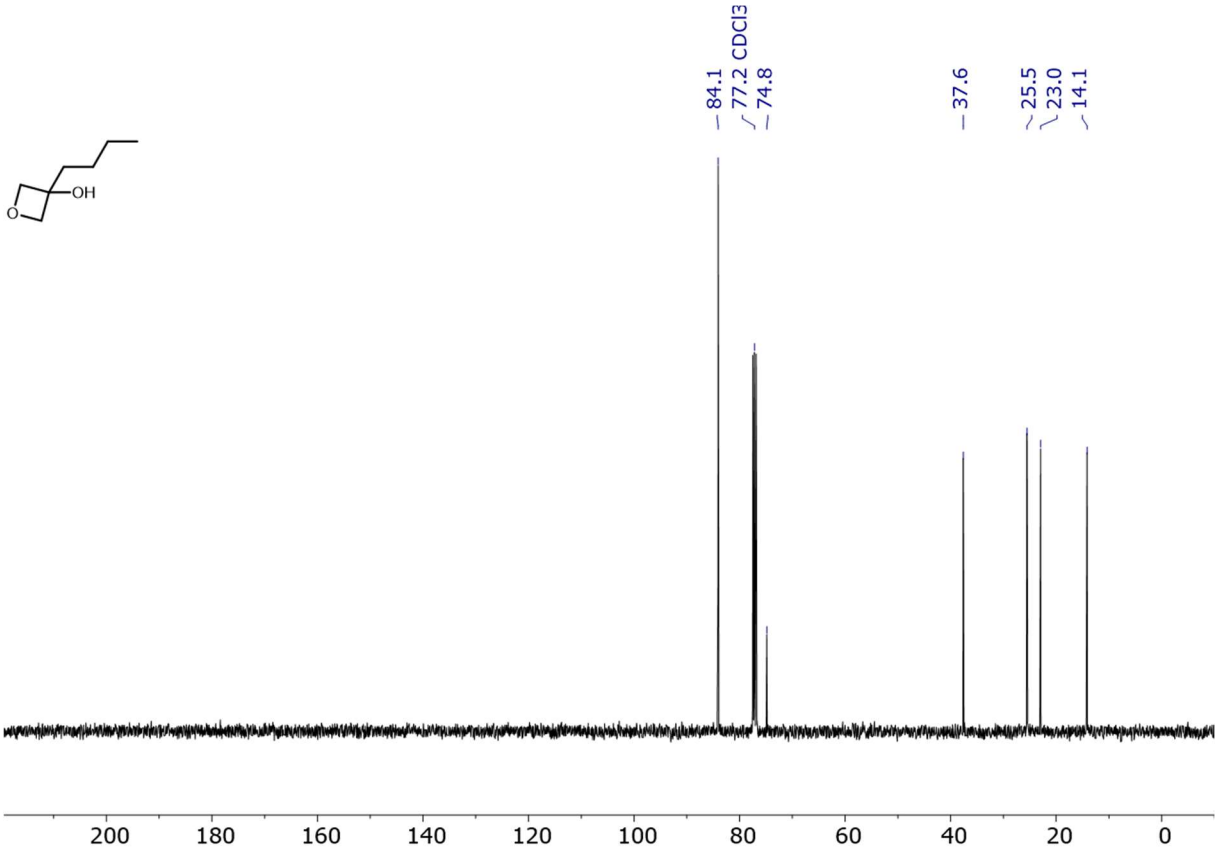

**[1s], $^{13}C$, $CDCl_3$, 101 MHz**



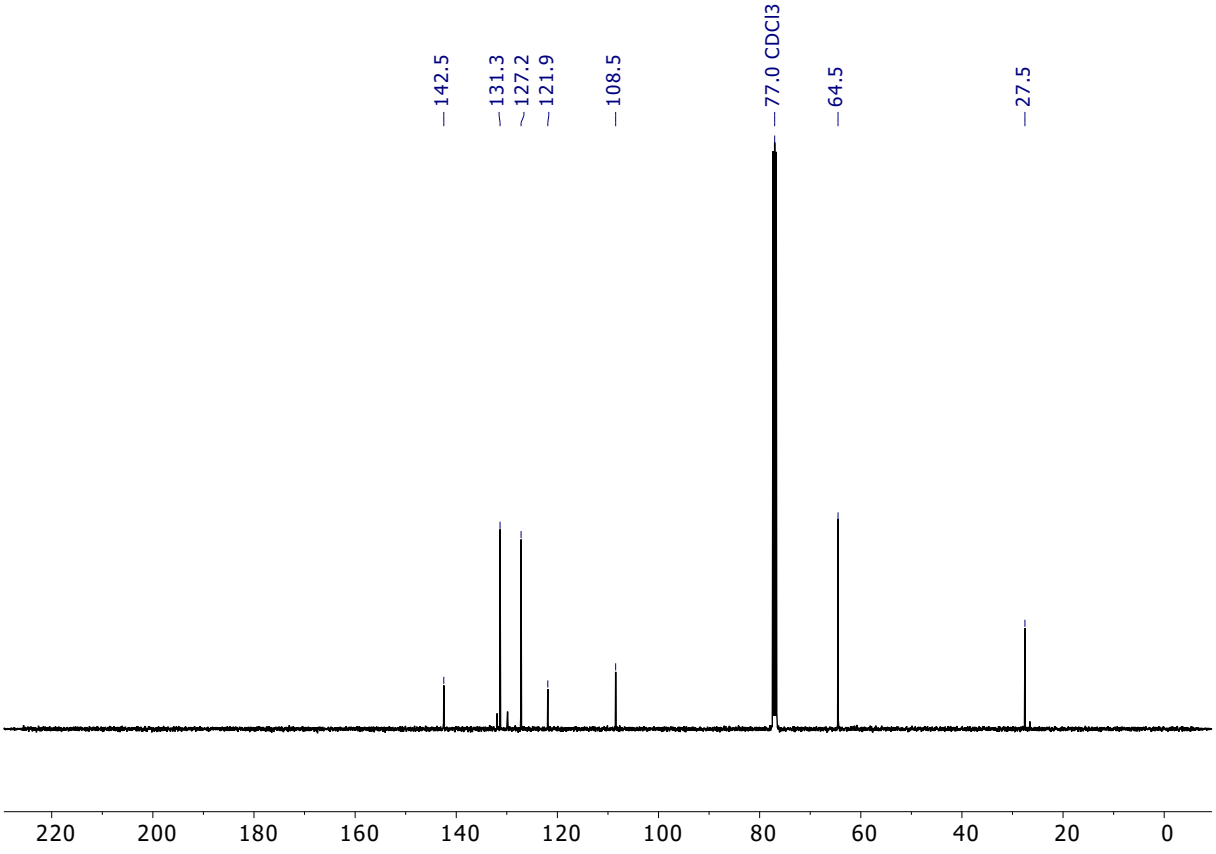
**[1t], $^{1}H$, $CDCl_3$, 400 MHz**



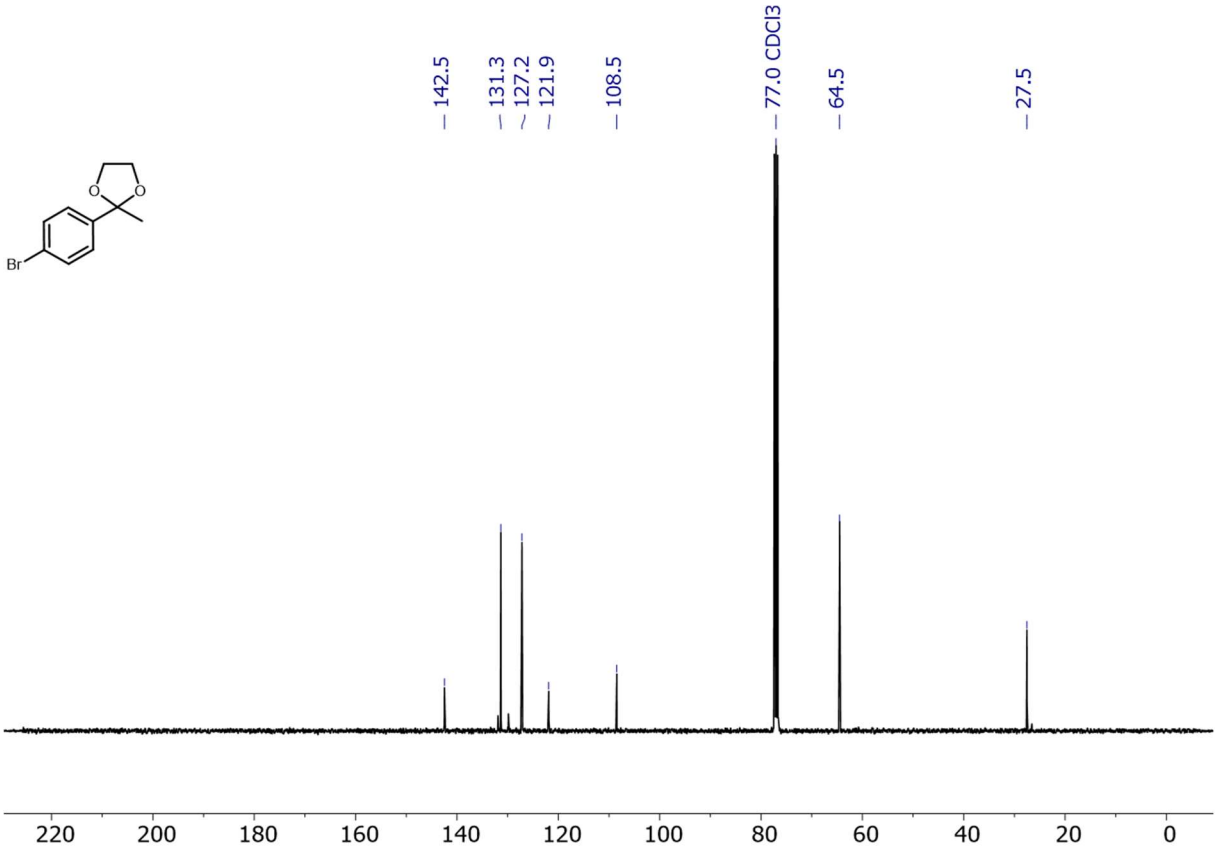

**[1t], $^{13}C$, $CDCl_3$, 101 MHz**



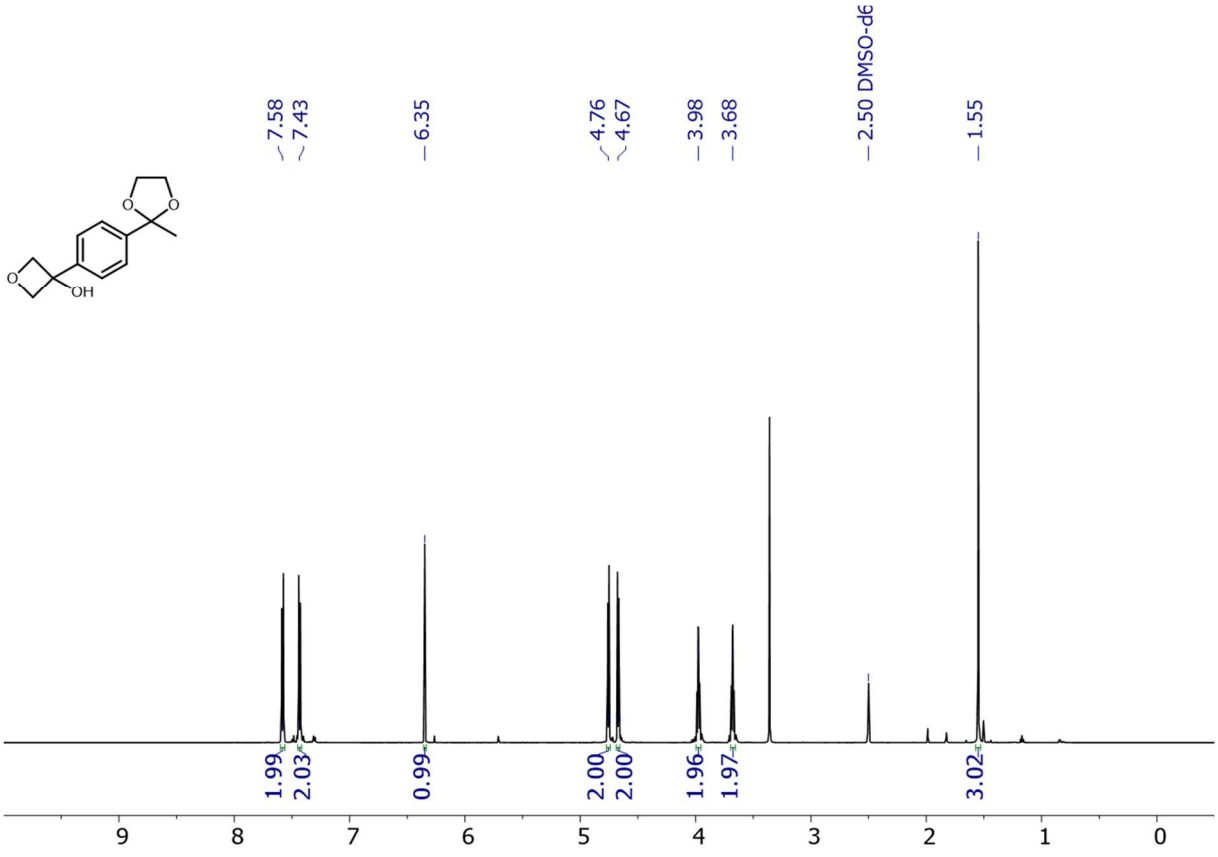
**[S14], $^{1}H$, $CDCl_3$, 400 MHz**



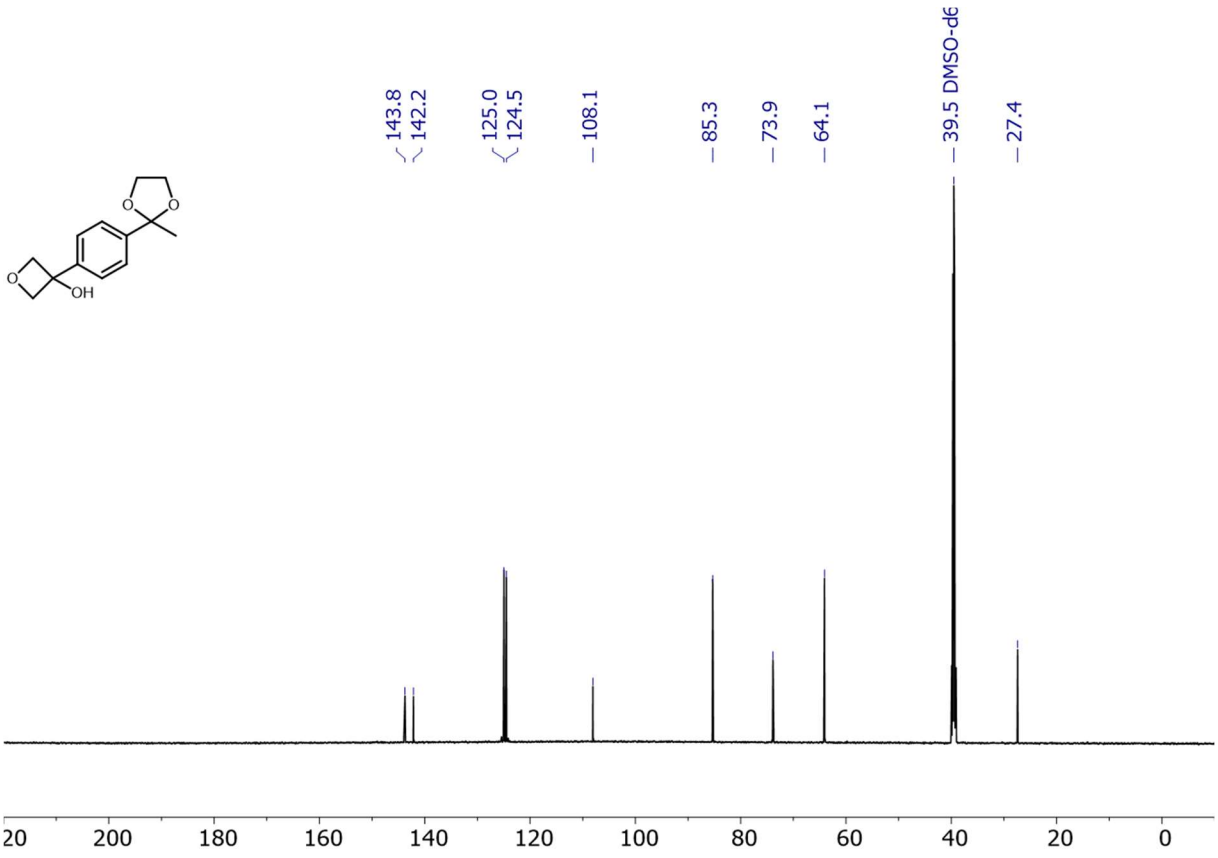

**[S14], $^{13}C$, $CDCl_3$, 101 MHz**



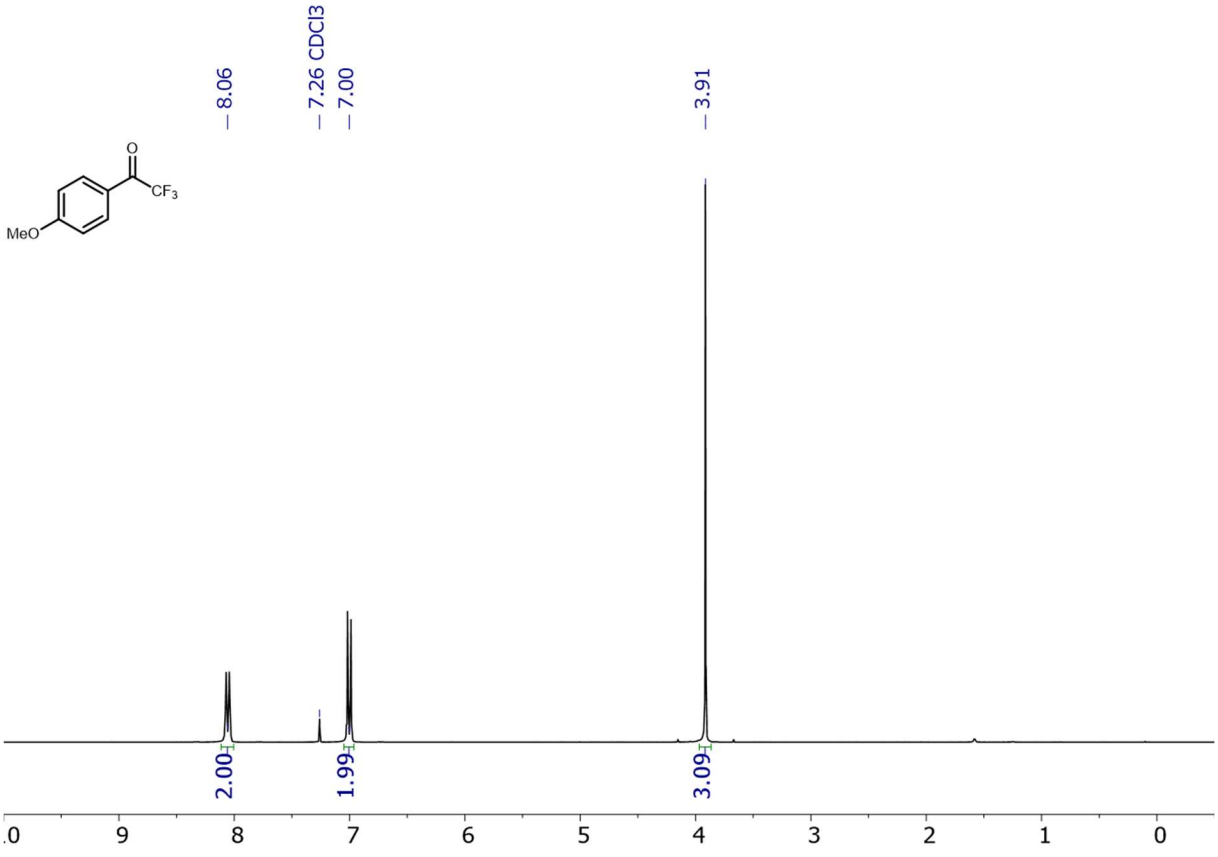
**[1u], $^{1}$H, DMSO-d6, 600 MHz**



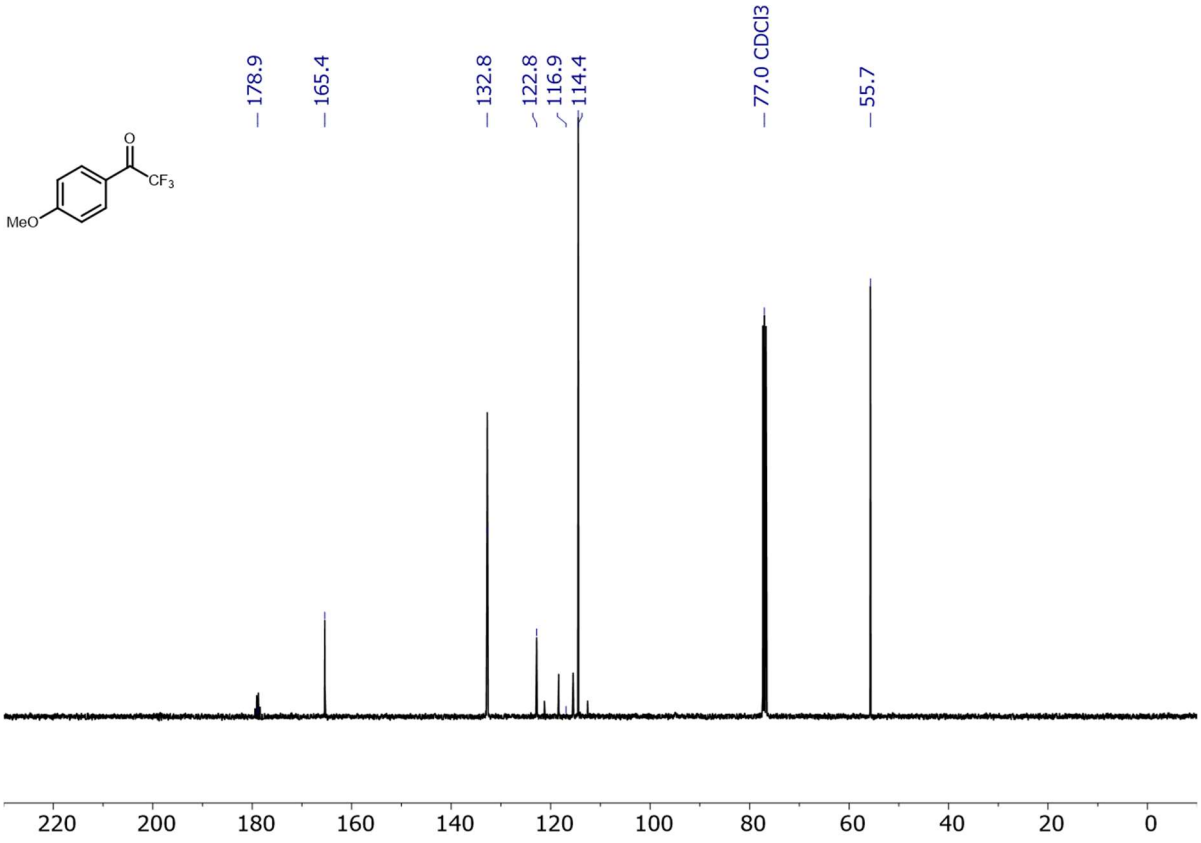

**[1u], $^{13}$C, DMSO-d6, 151 MHz**



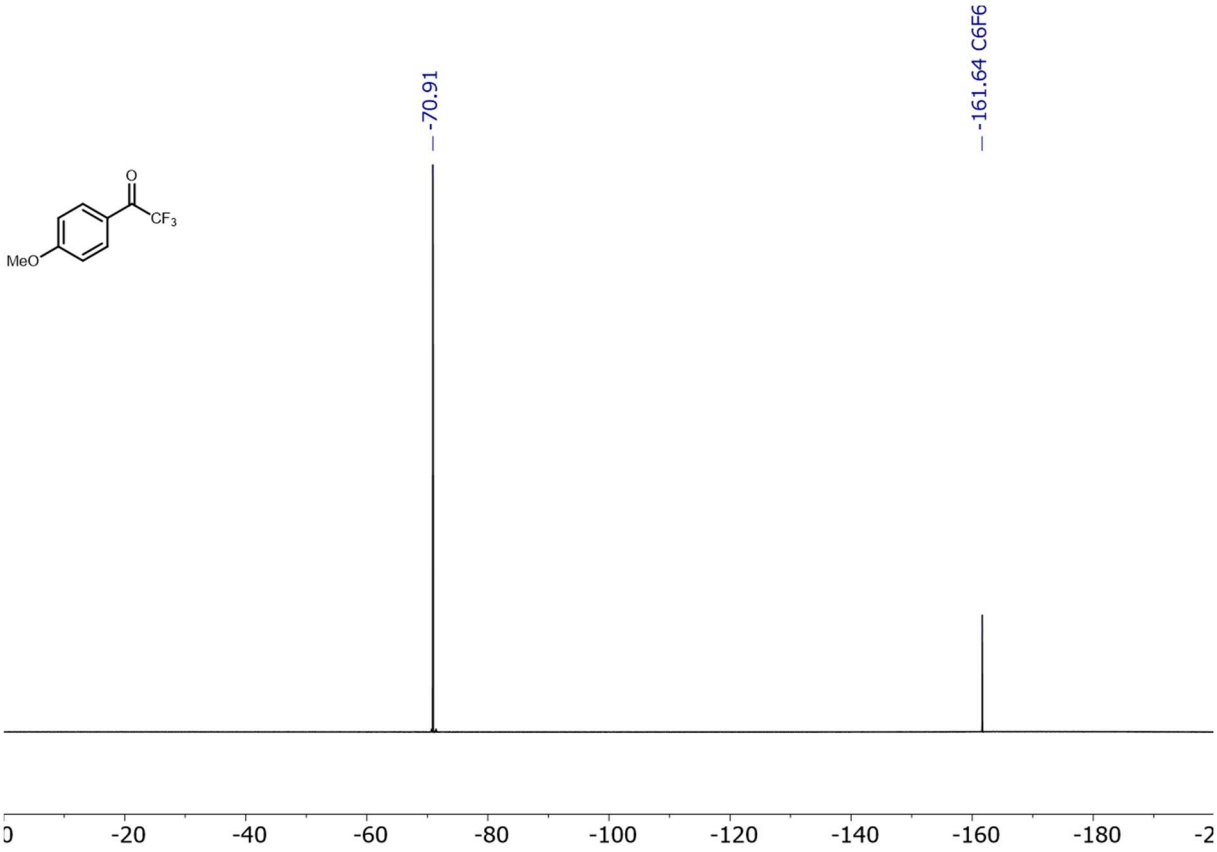
**[S15], 1H, CDCl3, 300 MHz**



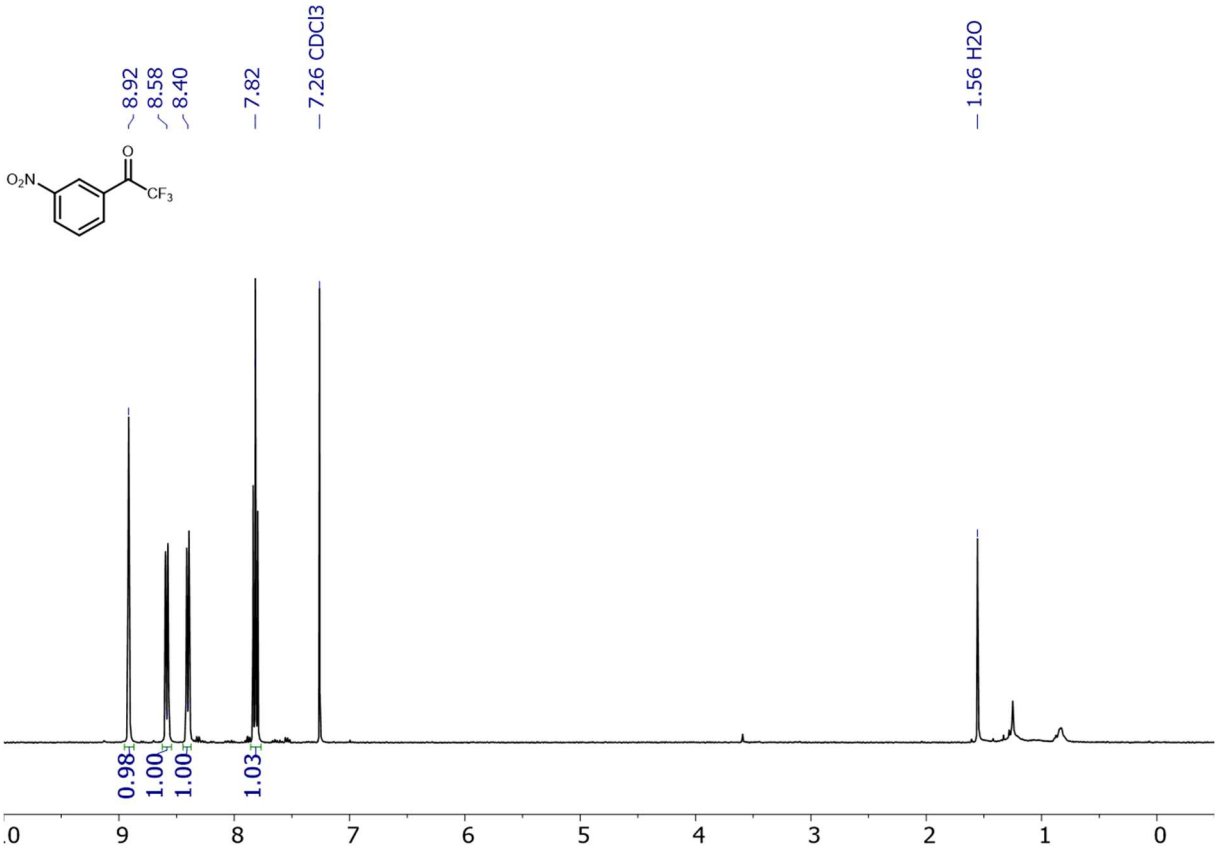

**[S15], $^{13}C$, $CDCl_3$, 101 MHz**



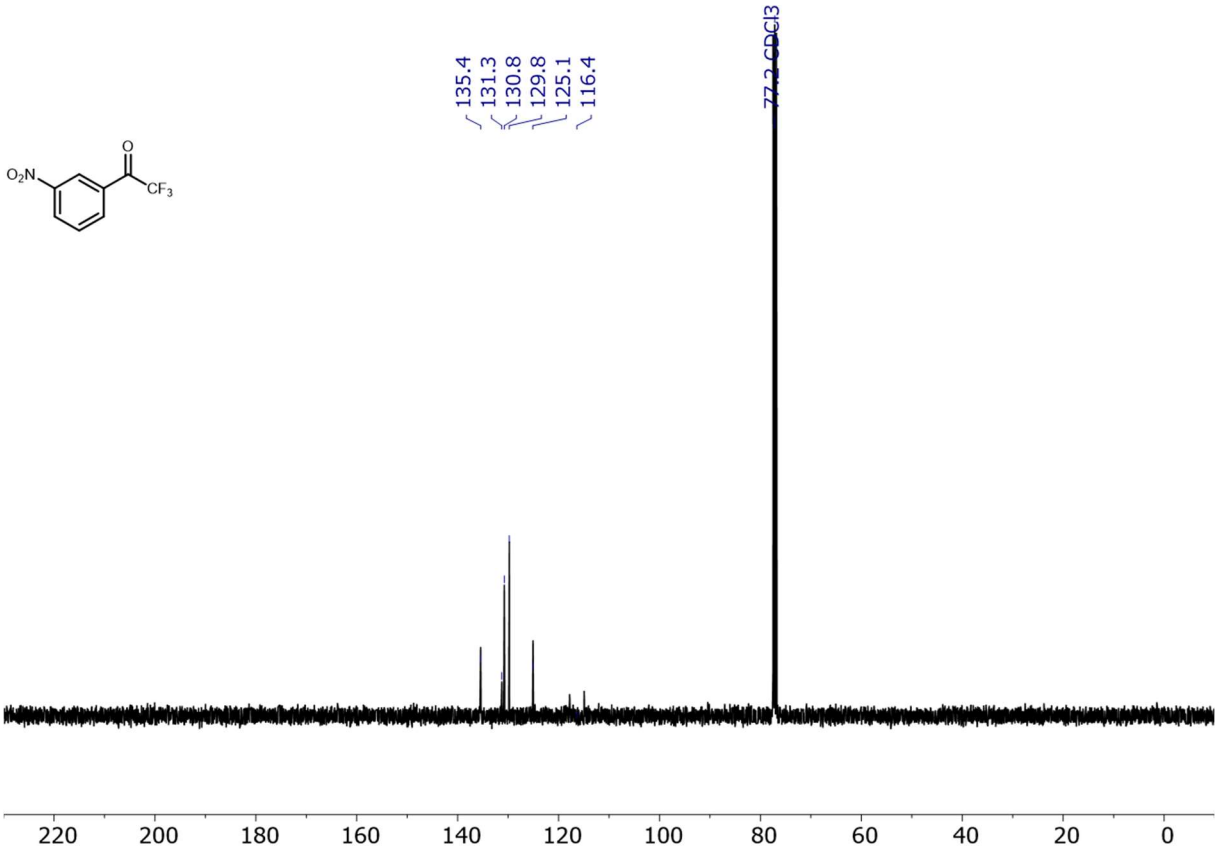
**[S15], $^{19}F$, $CDCl_3$, 376 MHz**



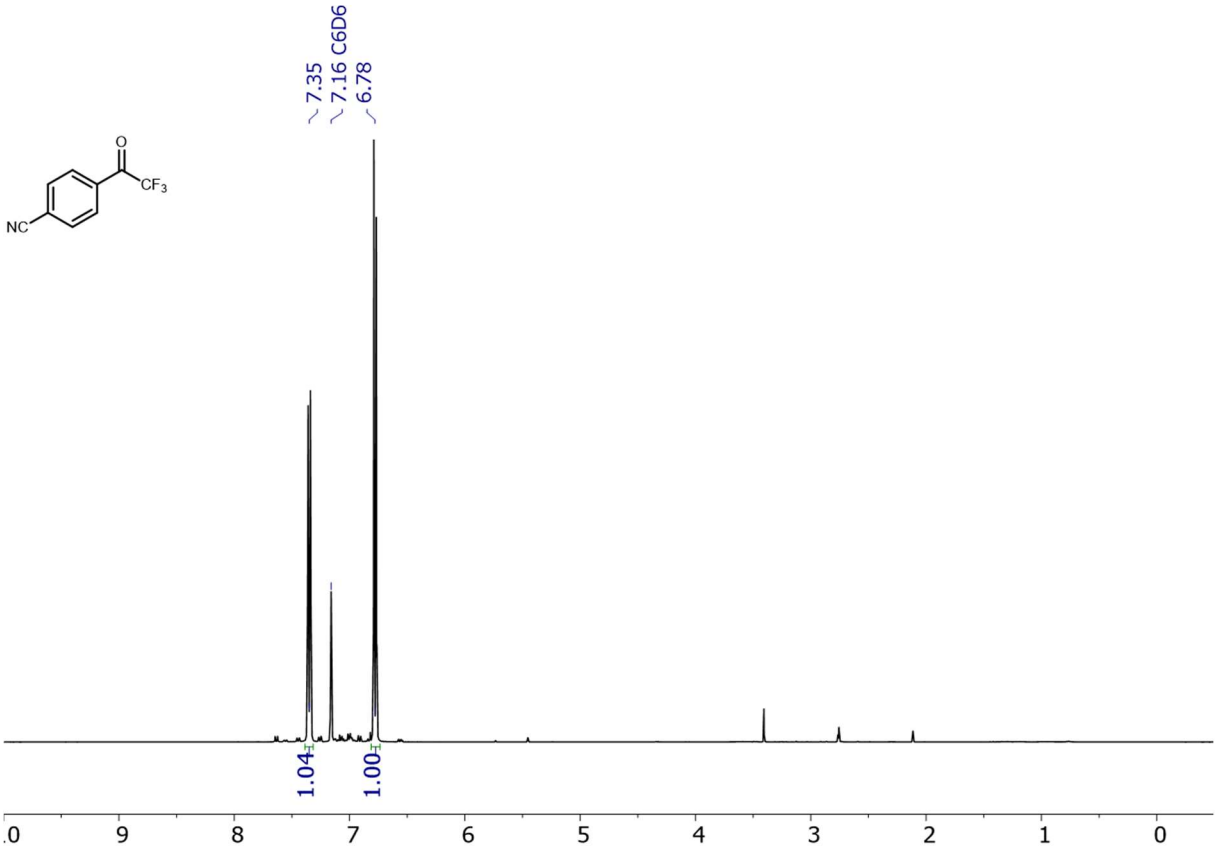
**[S16], $^{1}H$, $CDCl_3$, 400 MHz**



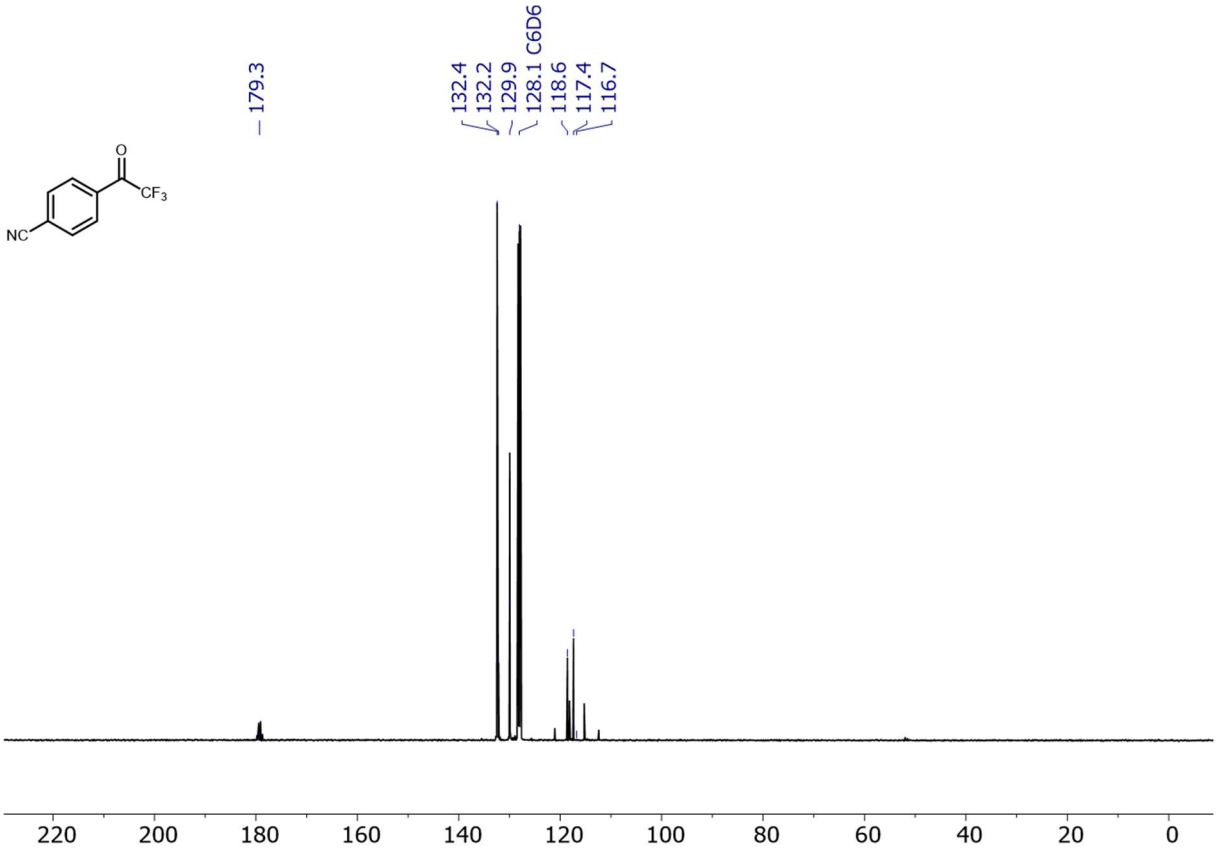

**[S16], $^{13}C$, $CDCl_3$, 101 MHz**



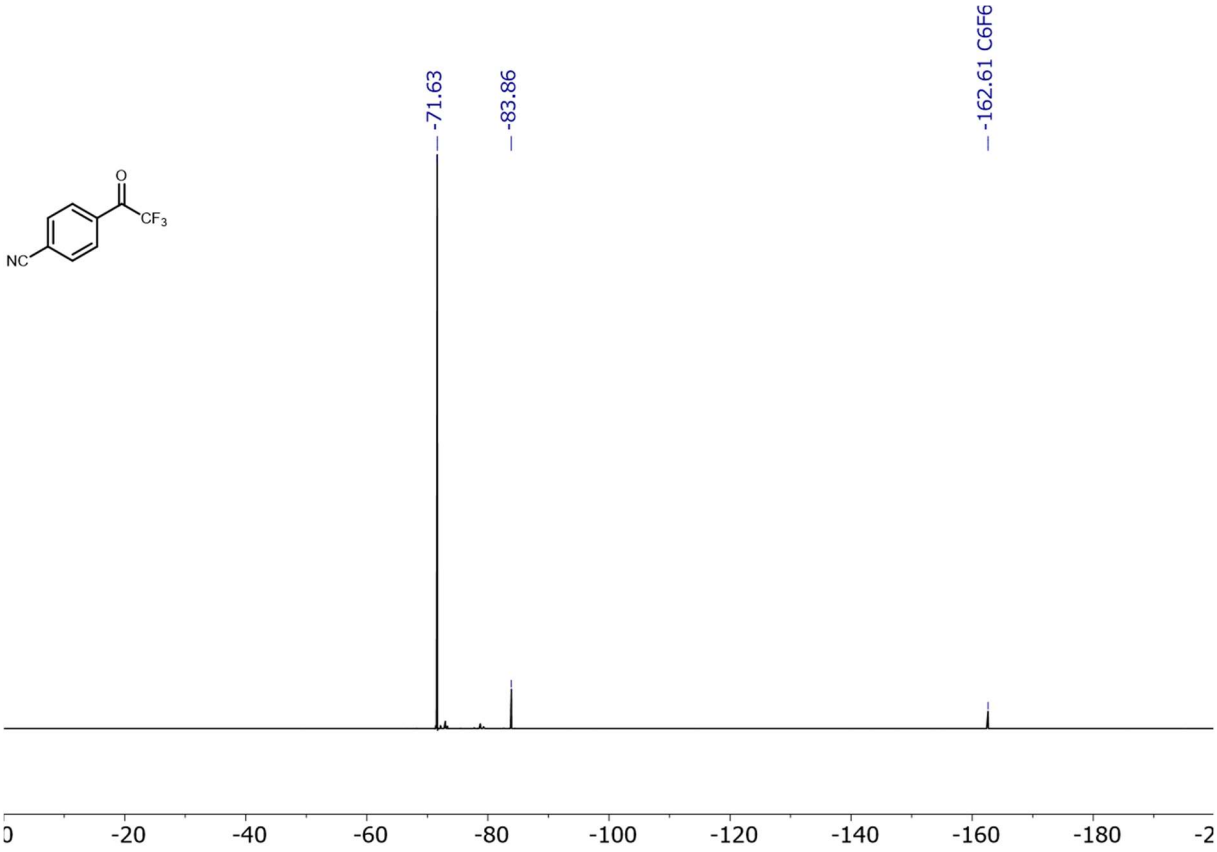
**[6d], $^{1}H$, $CDCl_3$, 400 MHz**



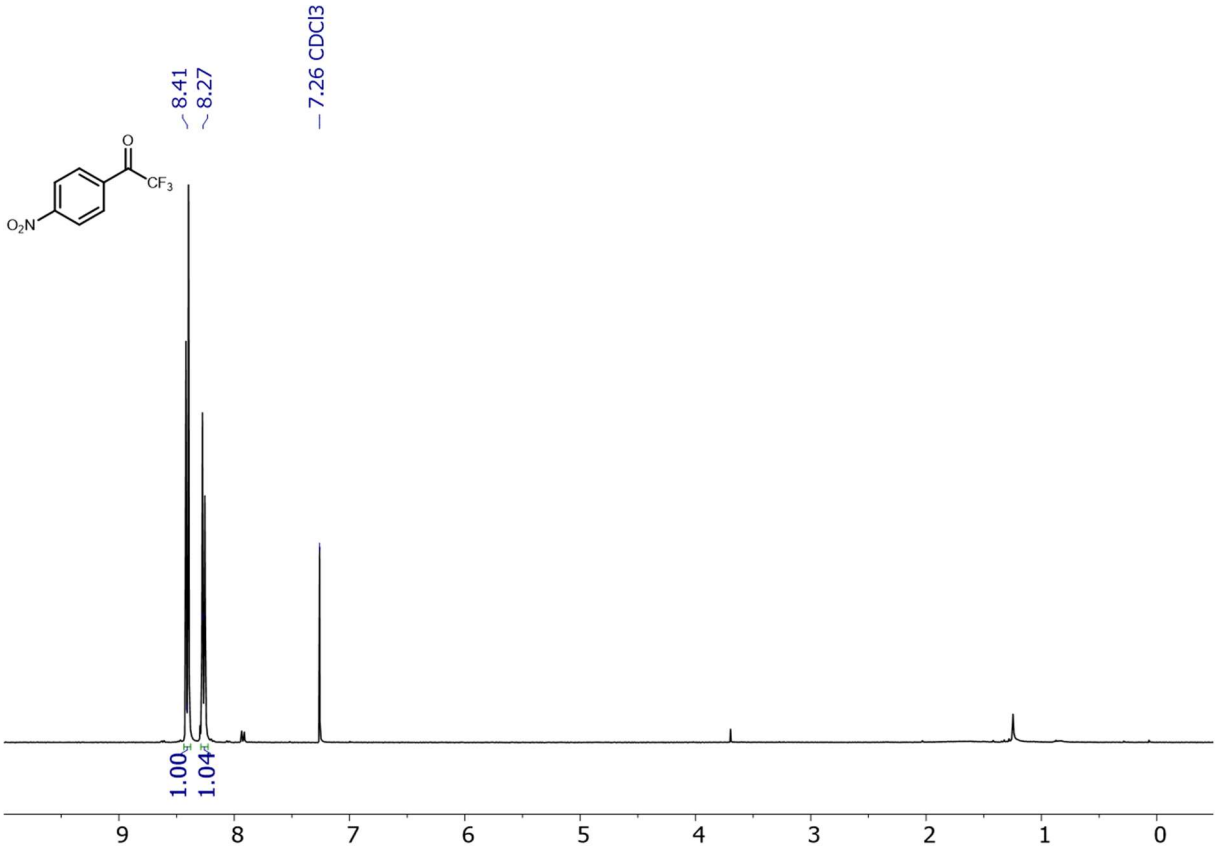

**[6d], $^{13}C$, $CDCl_3$, 101 MHz**



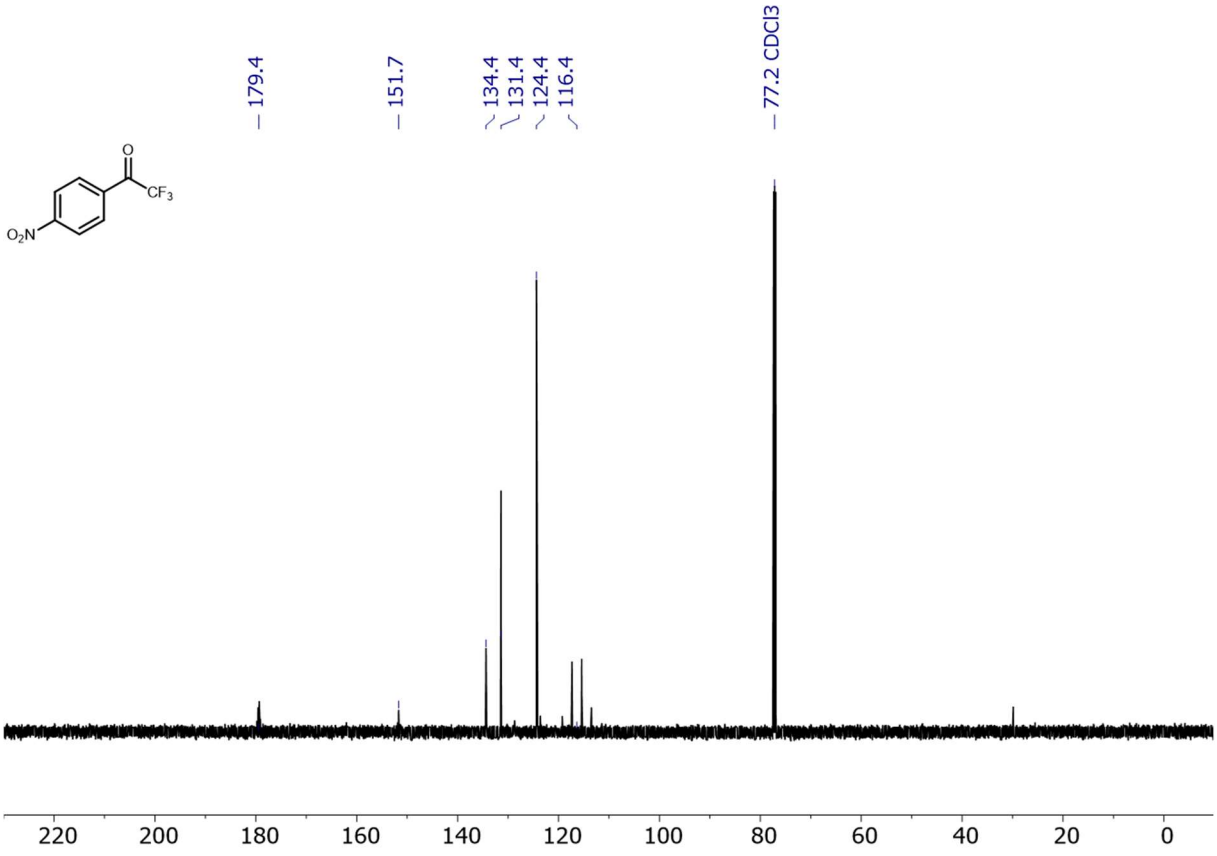
**[6d], $^{19}F$, $CDCl_3$, 377 MHz**



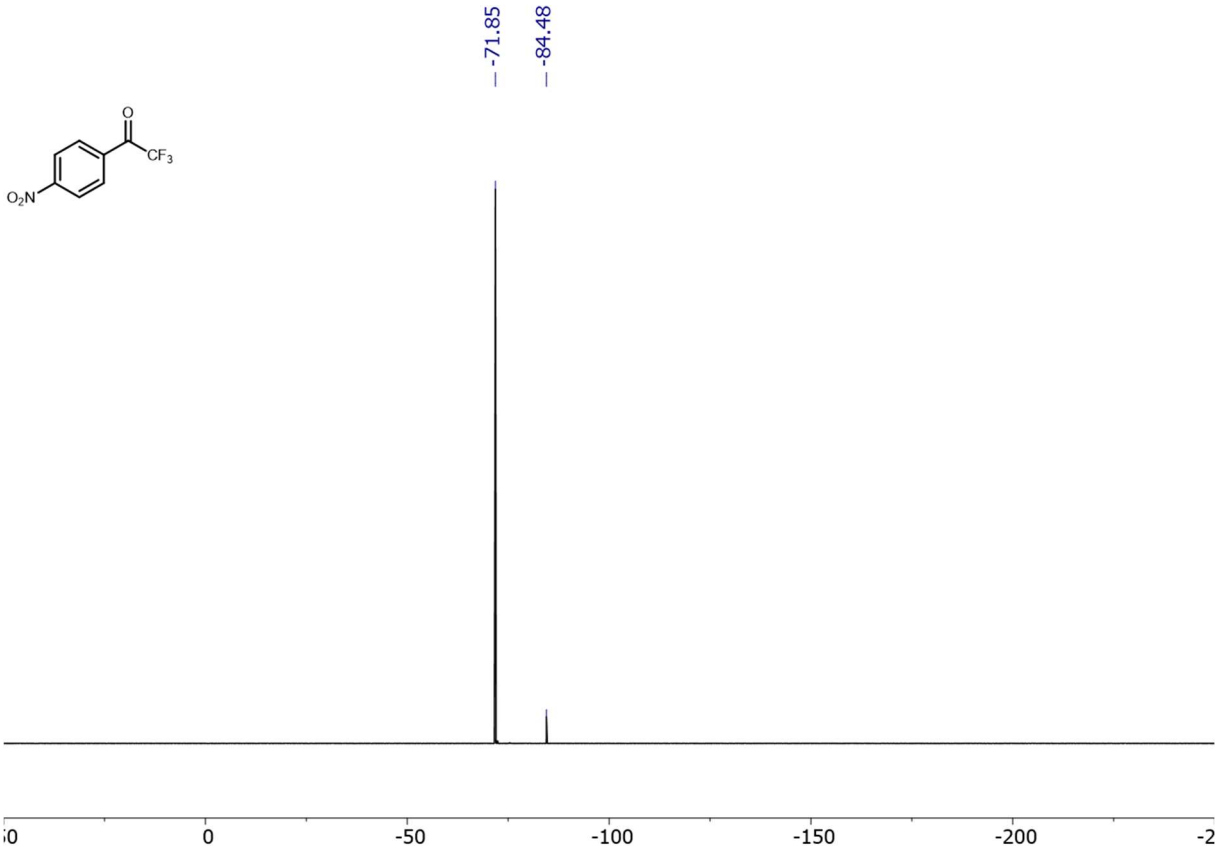
**[6e], $^{1}H$, $CDCl_3$, 400 MHz**



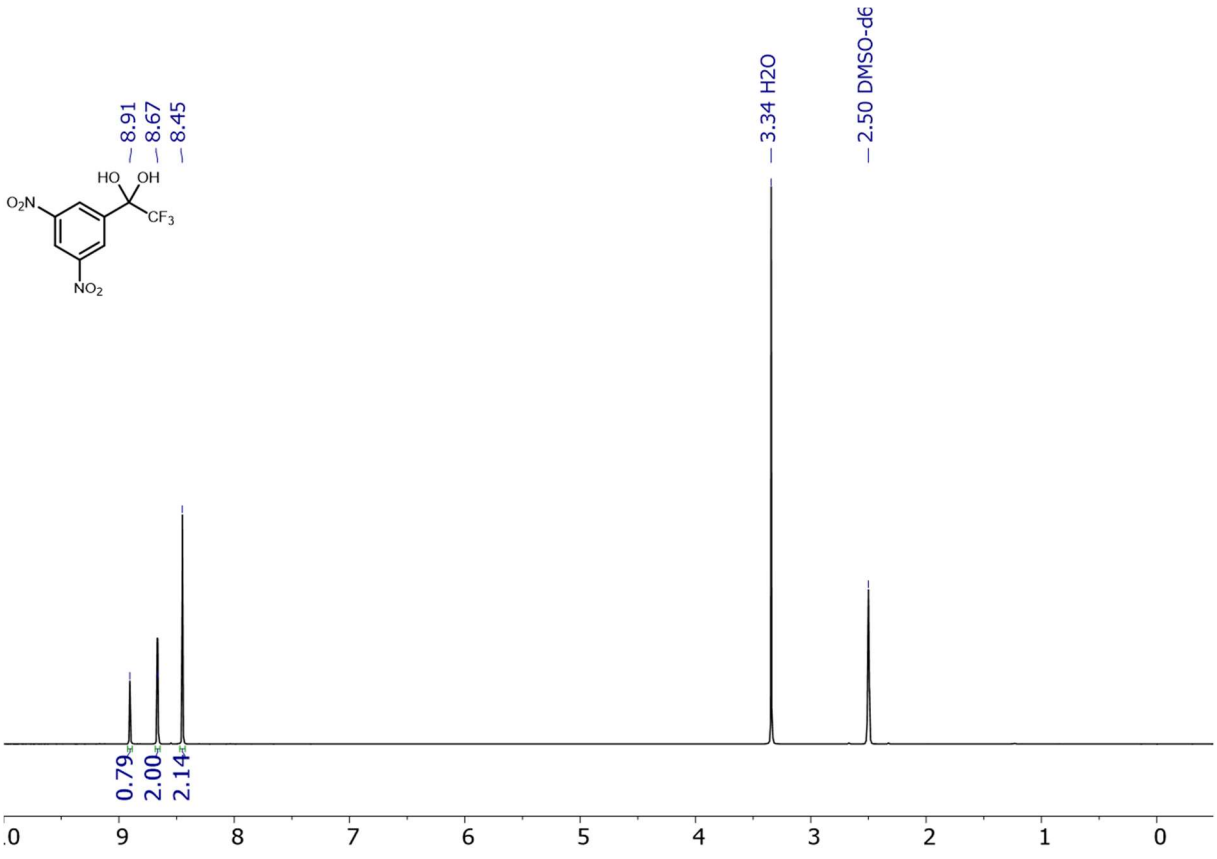

**[6e], $^{13}C$, $CDCl_3$, 151 MHz**



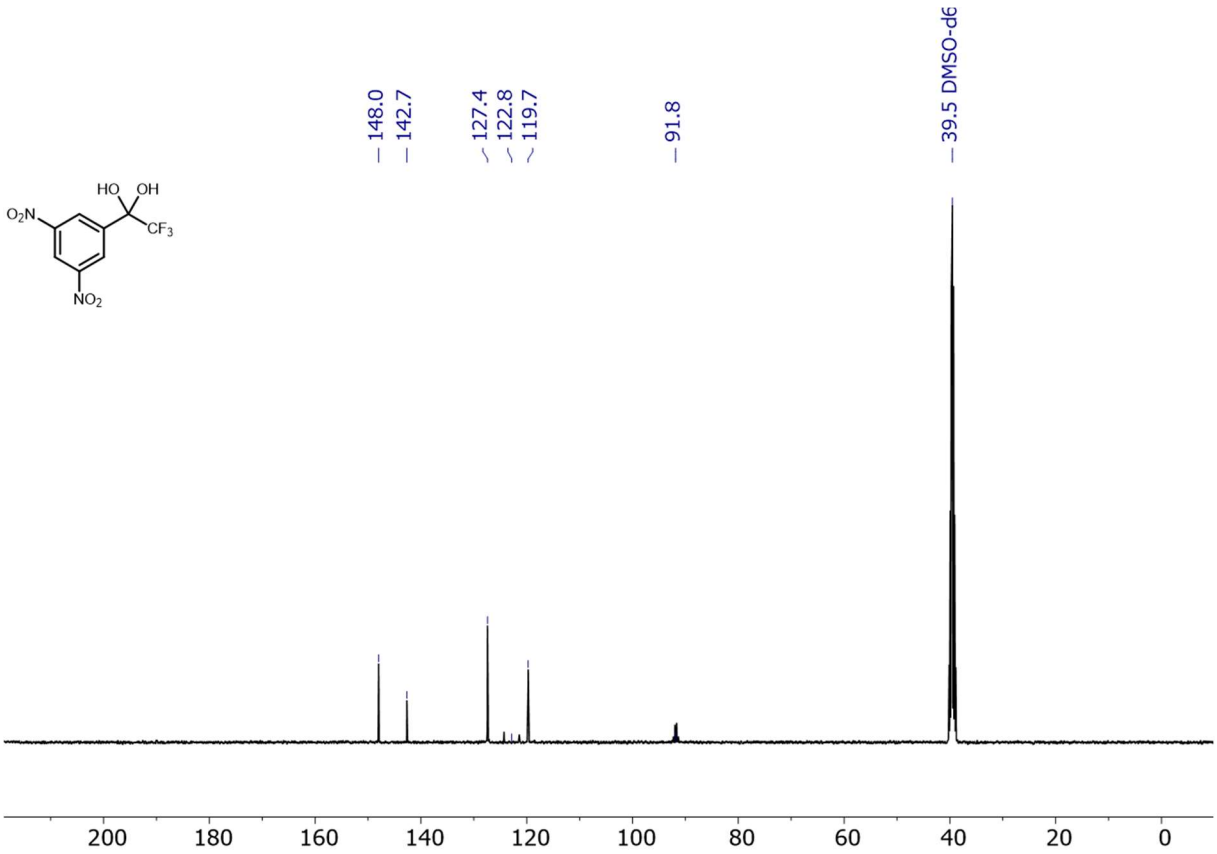
**[6e], $^{19}F$, $CDCl_3$, 376 MHz**



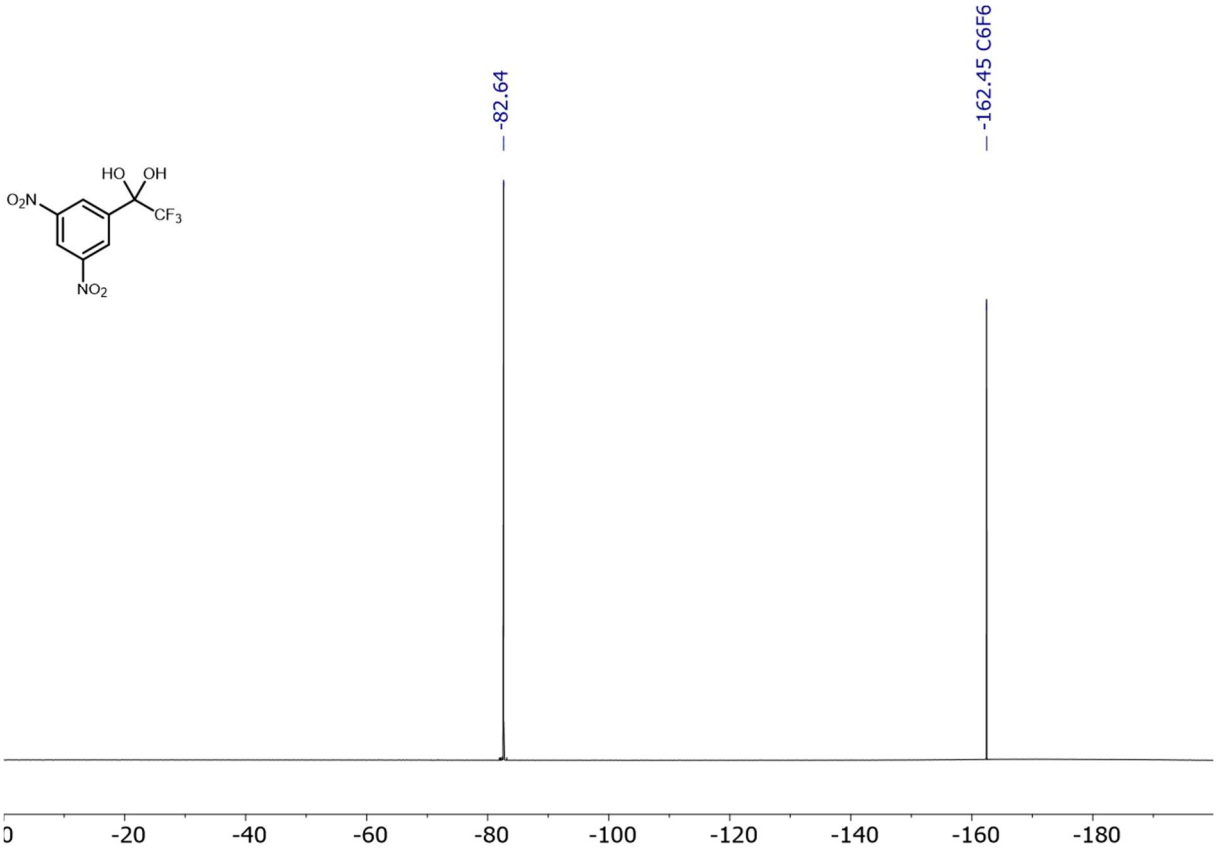
**[13], $^{1}$H, DMSO-d6, 400 MHz**



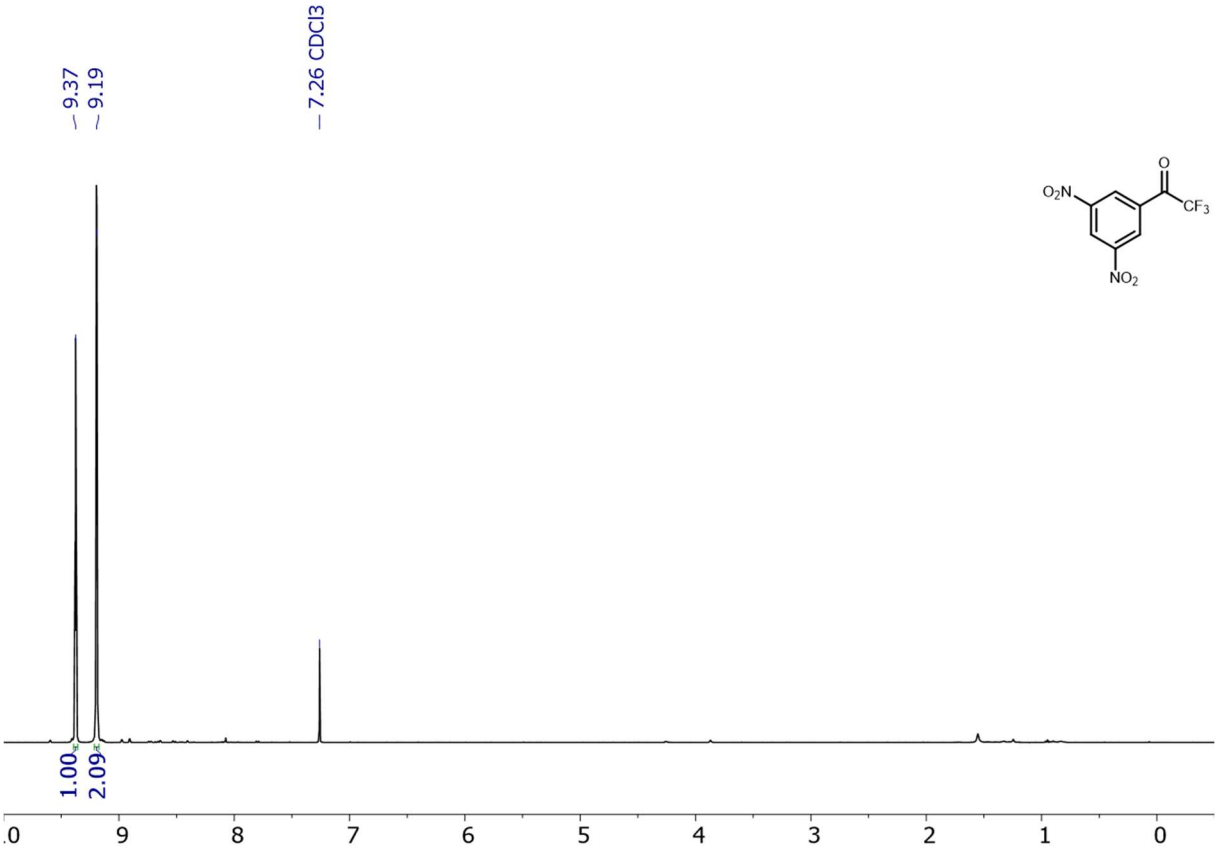

**[13], $^{13}$C, DMSO-d6, 101 MHz**



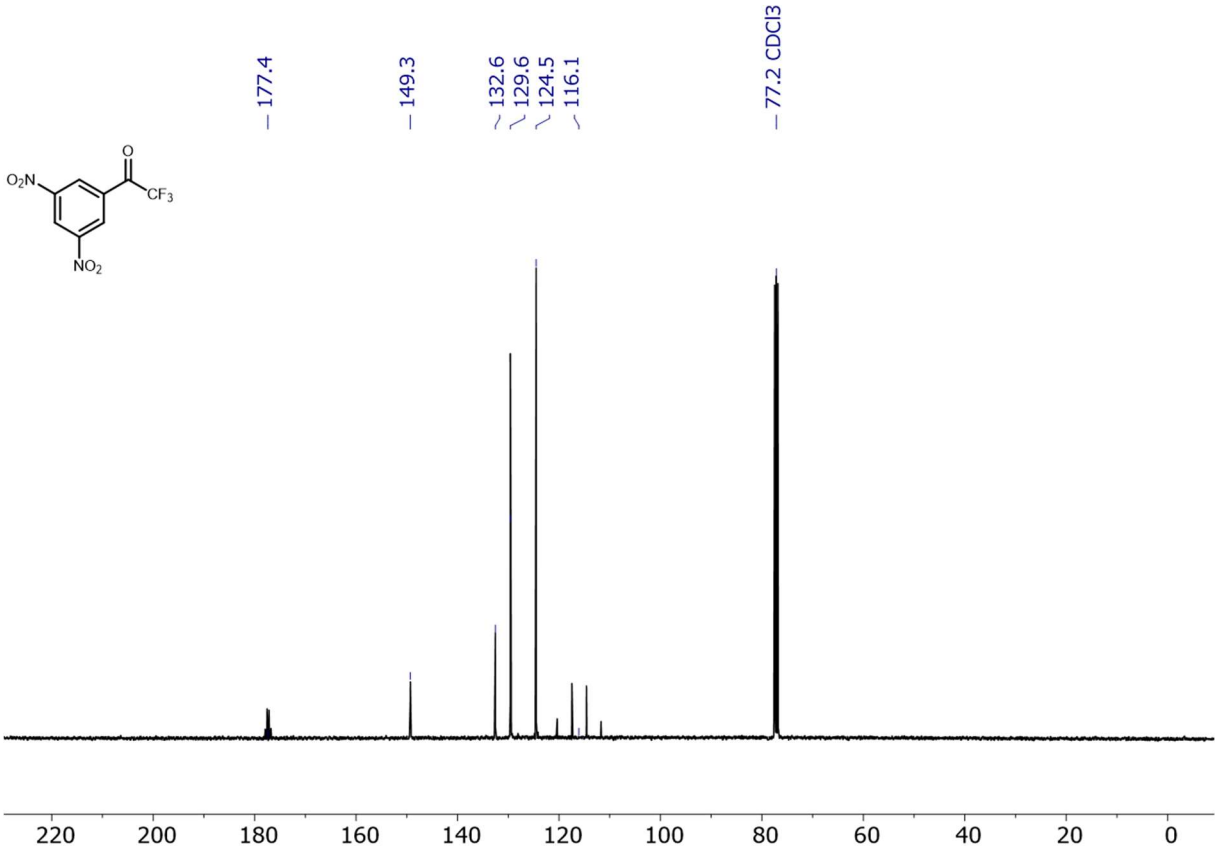
**[13], $^{19}F$, DMSO-d6, 376 MHz**



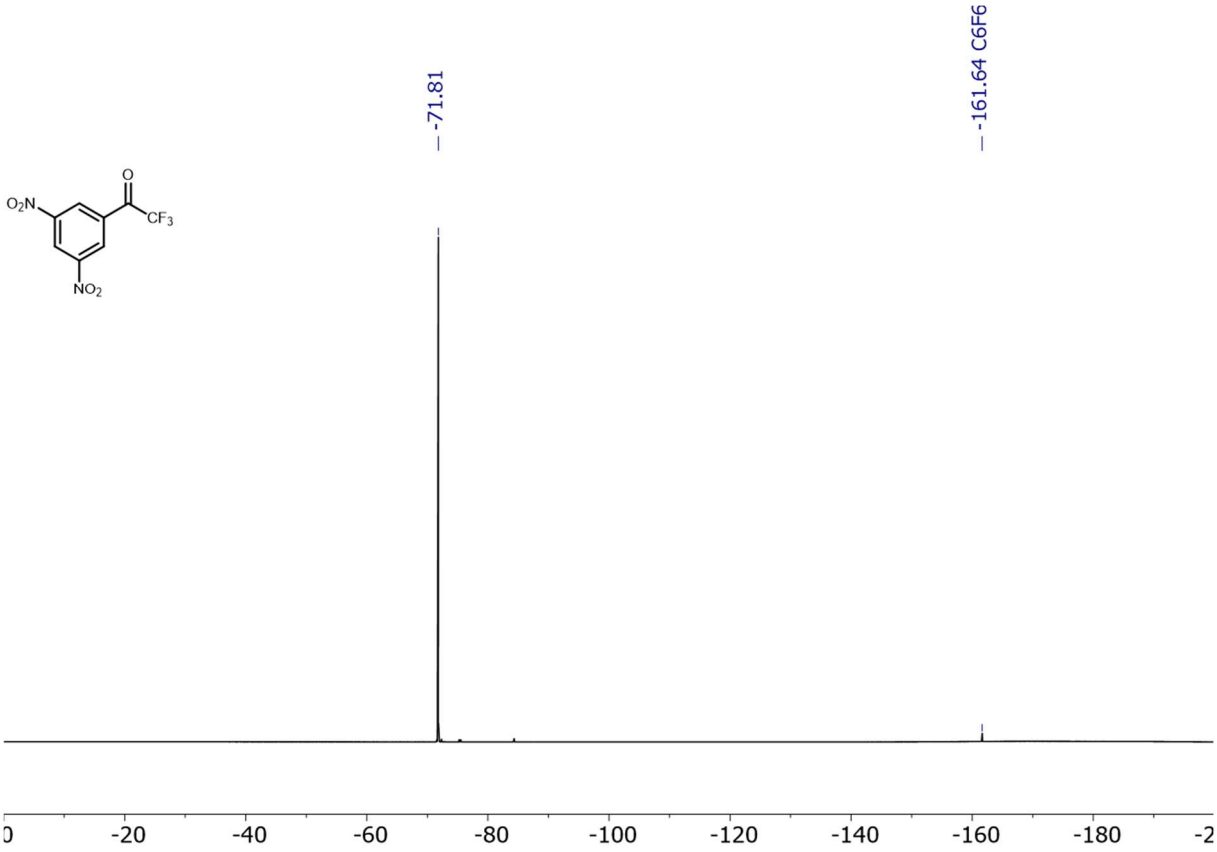
**[2], $^{1}H$, $CDCl_3$, 400 MHz**



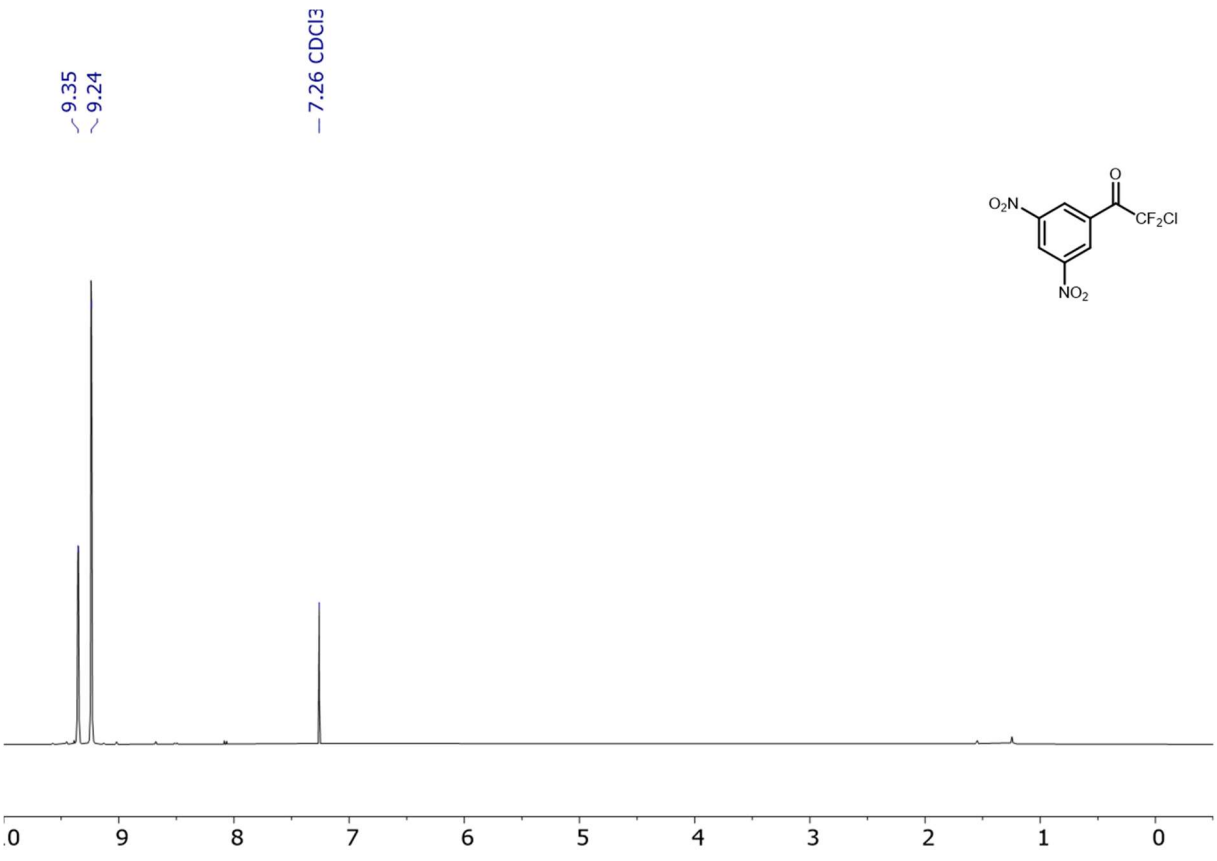

**[2], $^{13}C$, $CDCl_3$, 101 MHz**



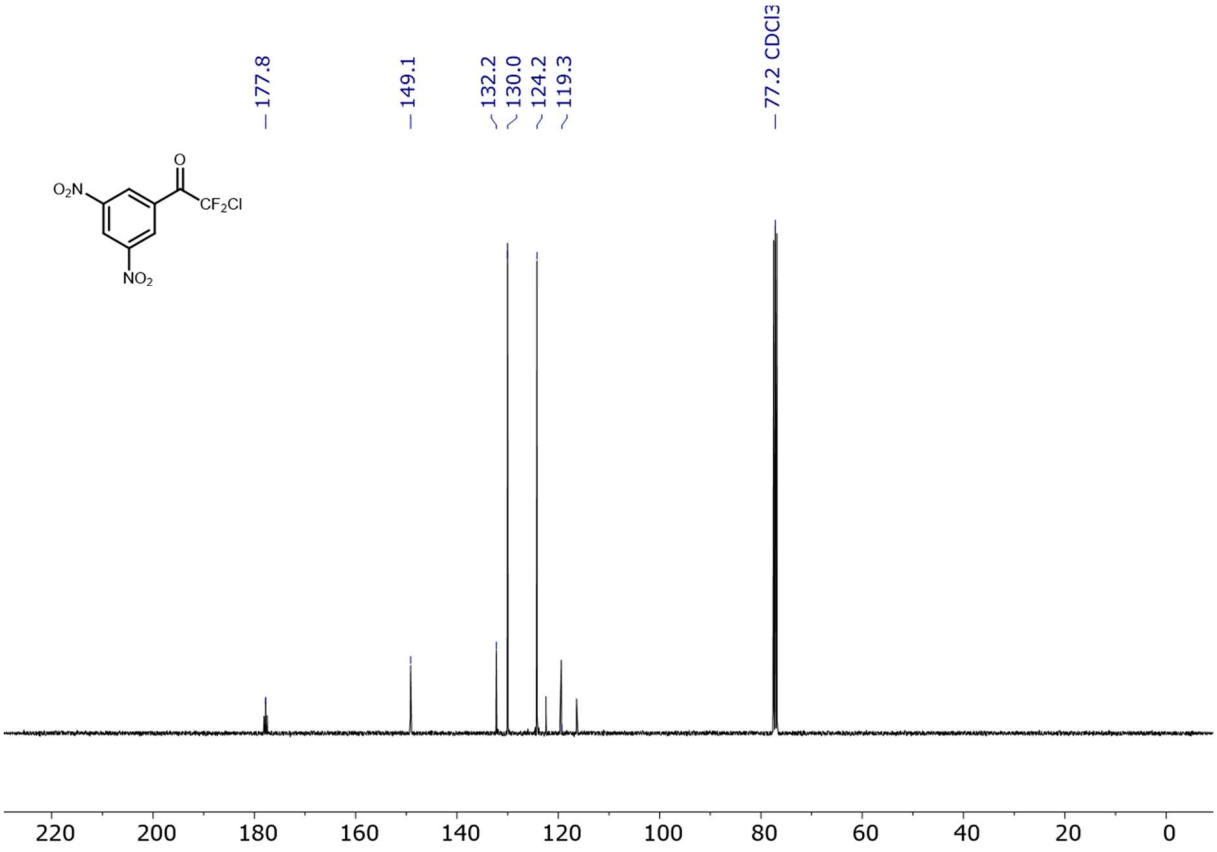
**[2], $^{19}F$, $CDCl_3$, 377 MHz**



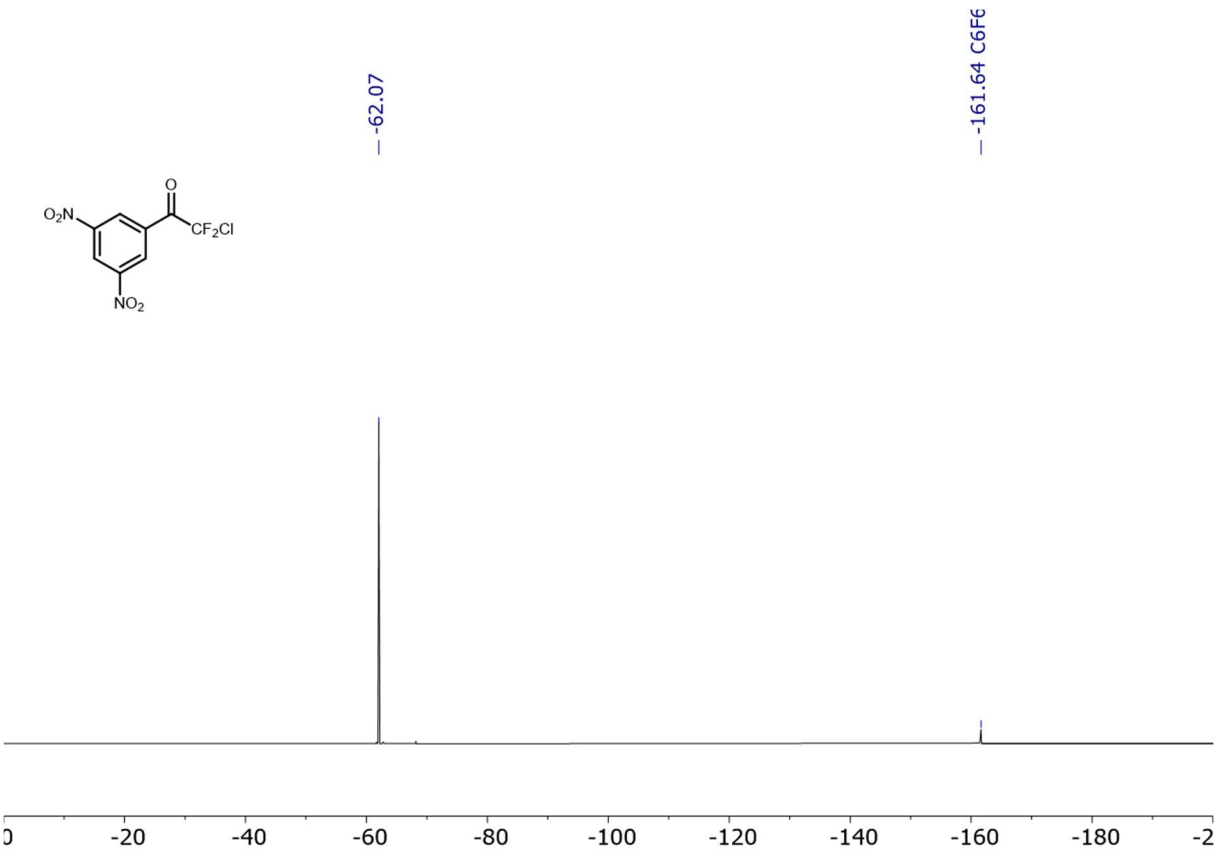
**[17], $^{1}H$, $CDCl_3$, 400 MHz**



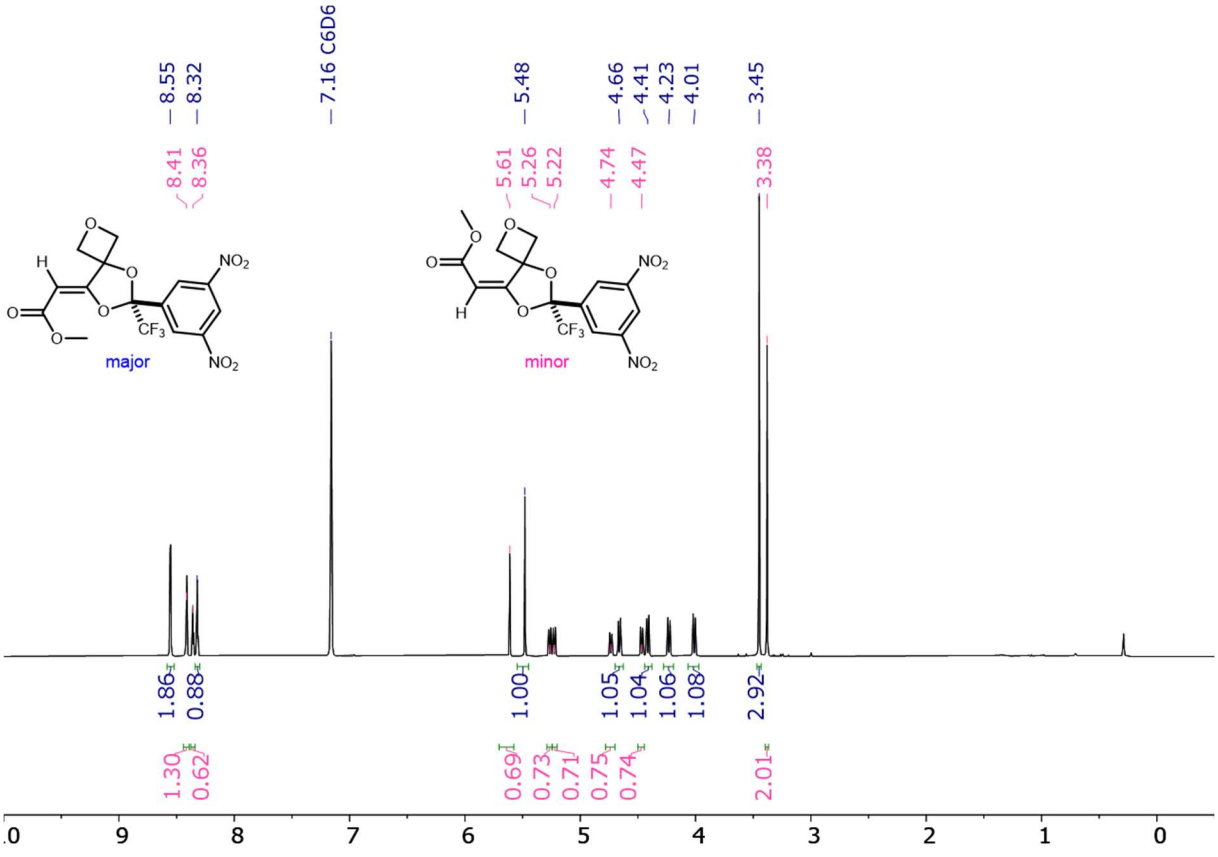

**[17], $^{13}C$, $CDCl_3$, 101 MHz**



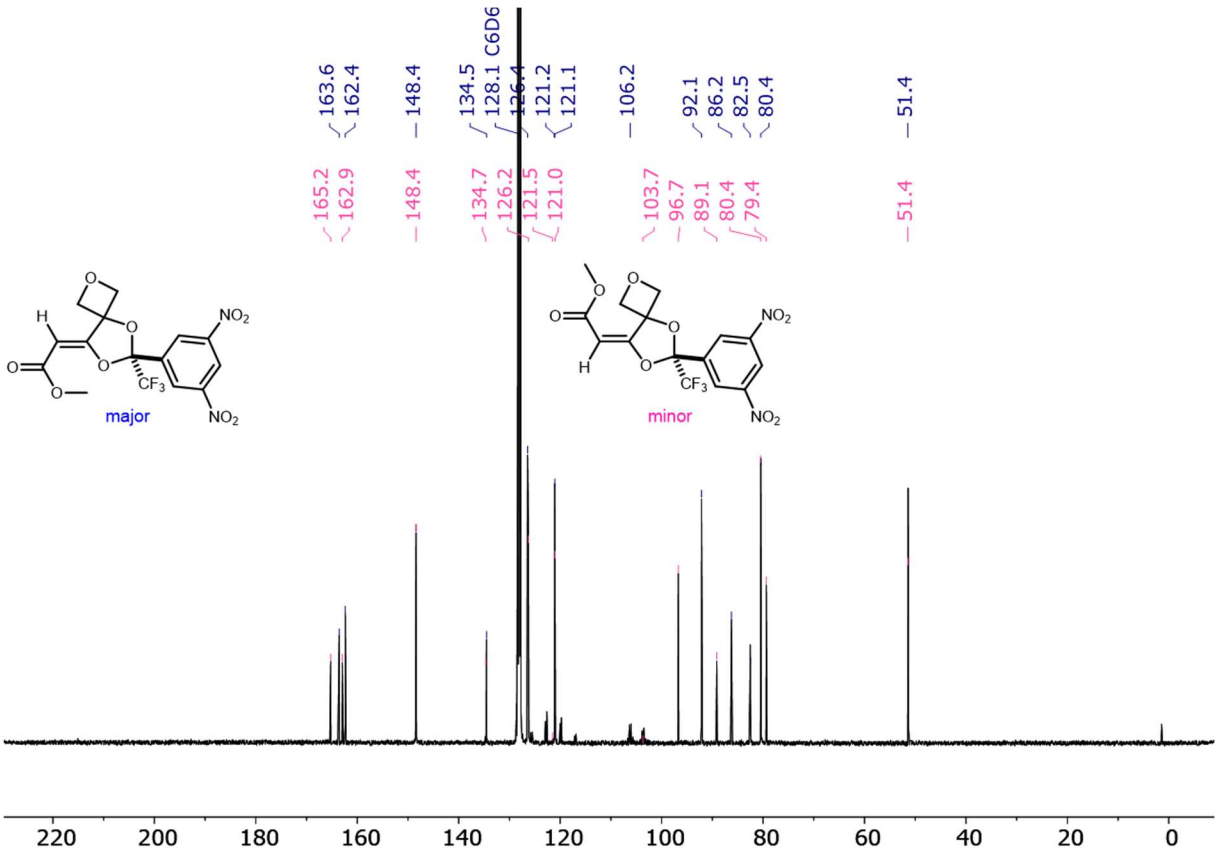
**[17], $^{19}F$, $CDCl_3$, 282 MHz**



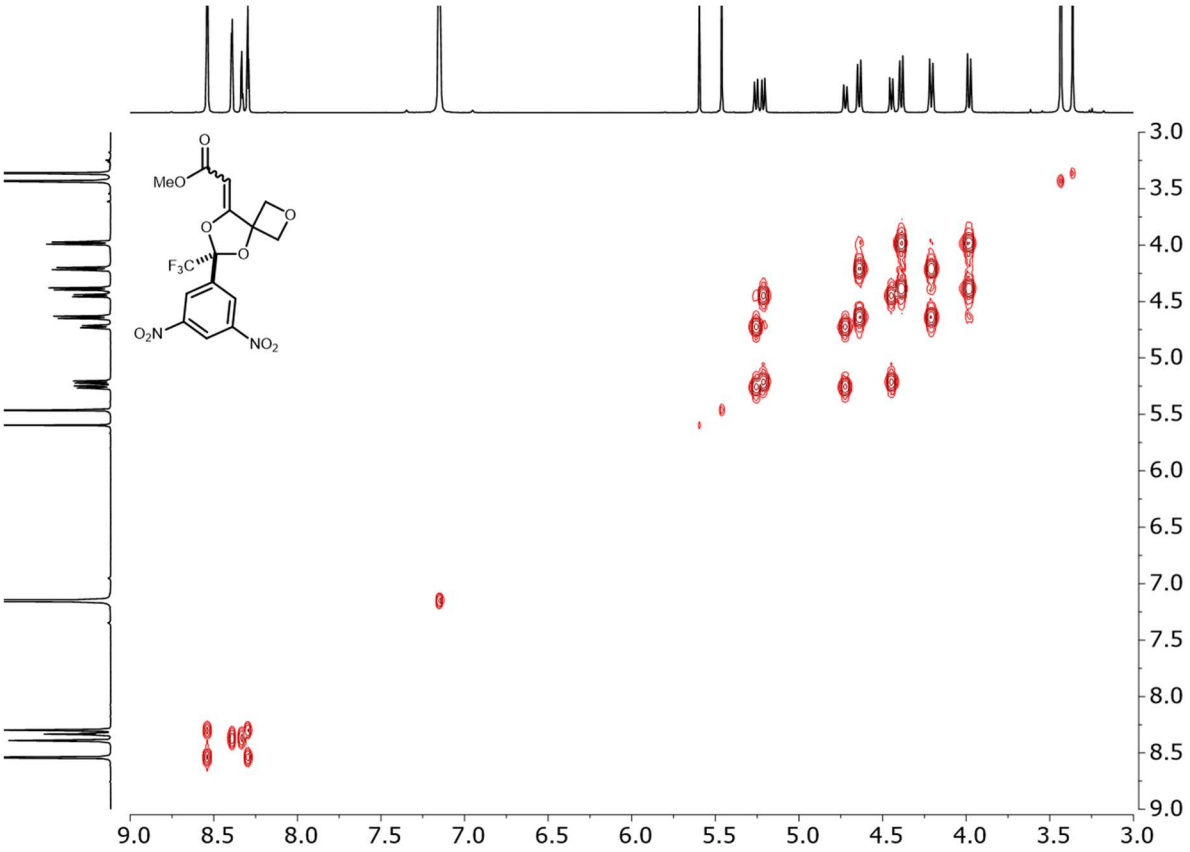
**[*rac*-10c], $^{1}H$, $C_6D_6$, 400 MHz**



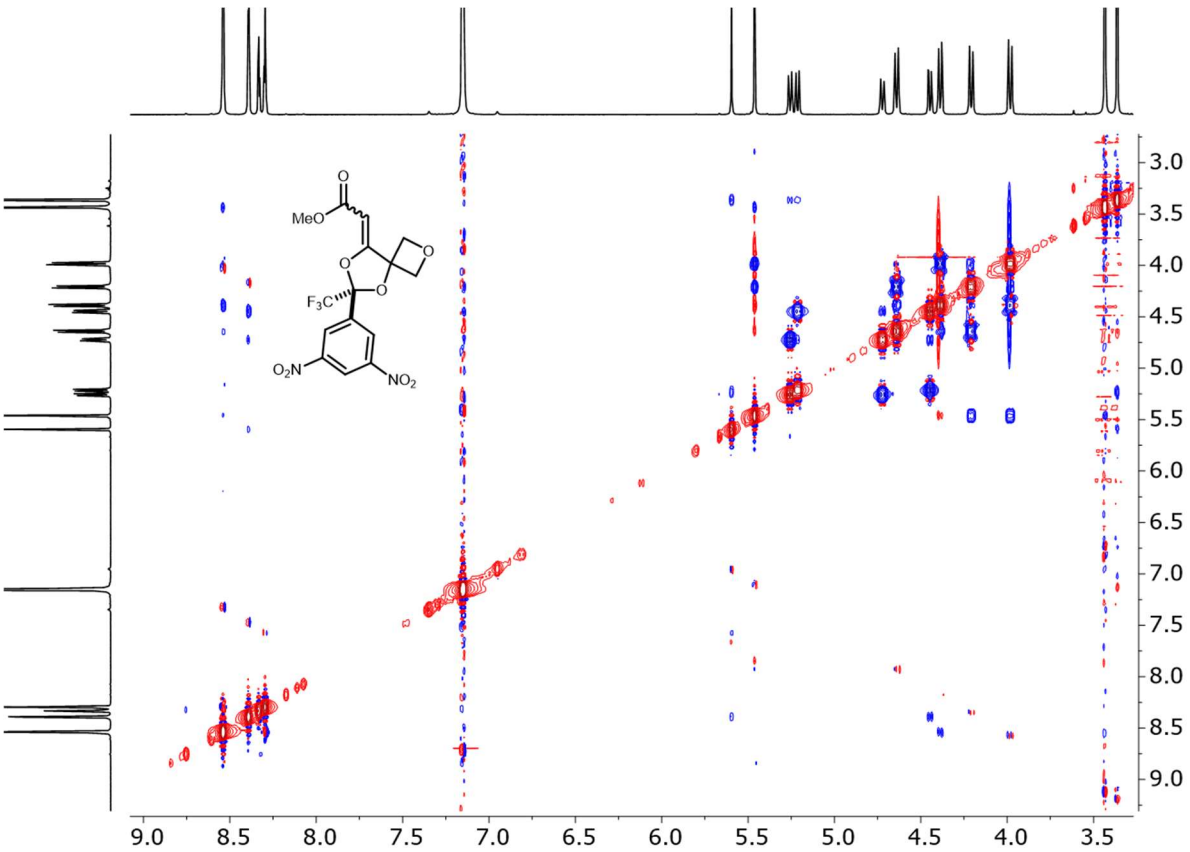

**[*rac*-10c], $^{13}C$, $C_6D_6$, 101 MHz**



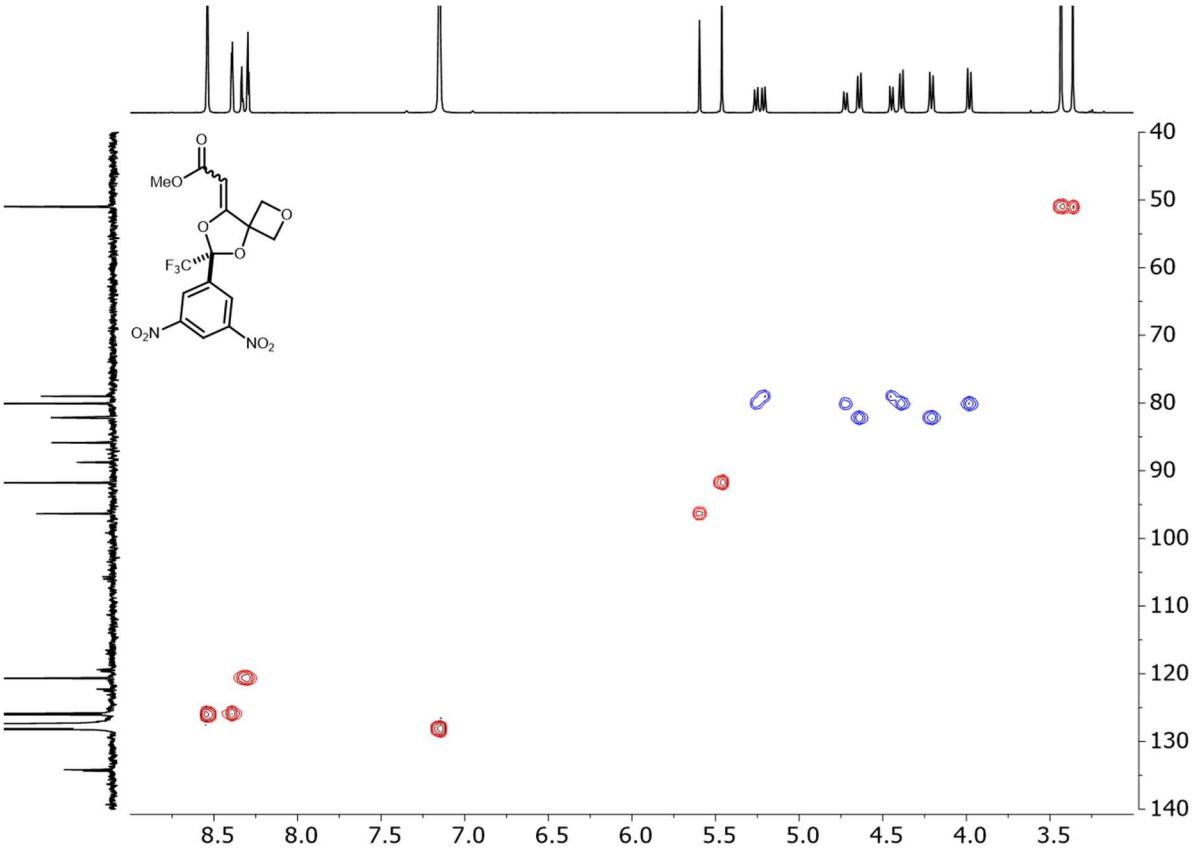
**[*rac*-10c], $^{1}$H-$^{1}$H-COSY, $C_6D_6$**



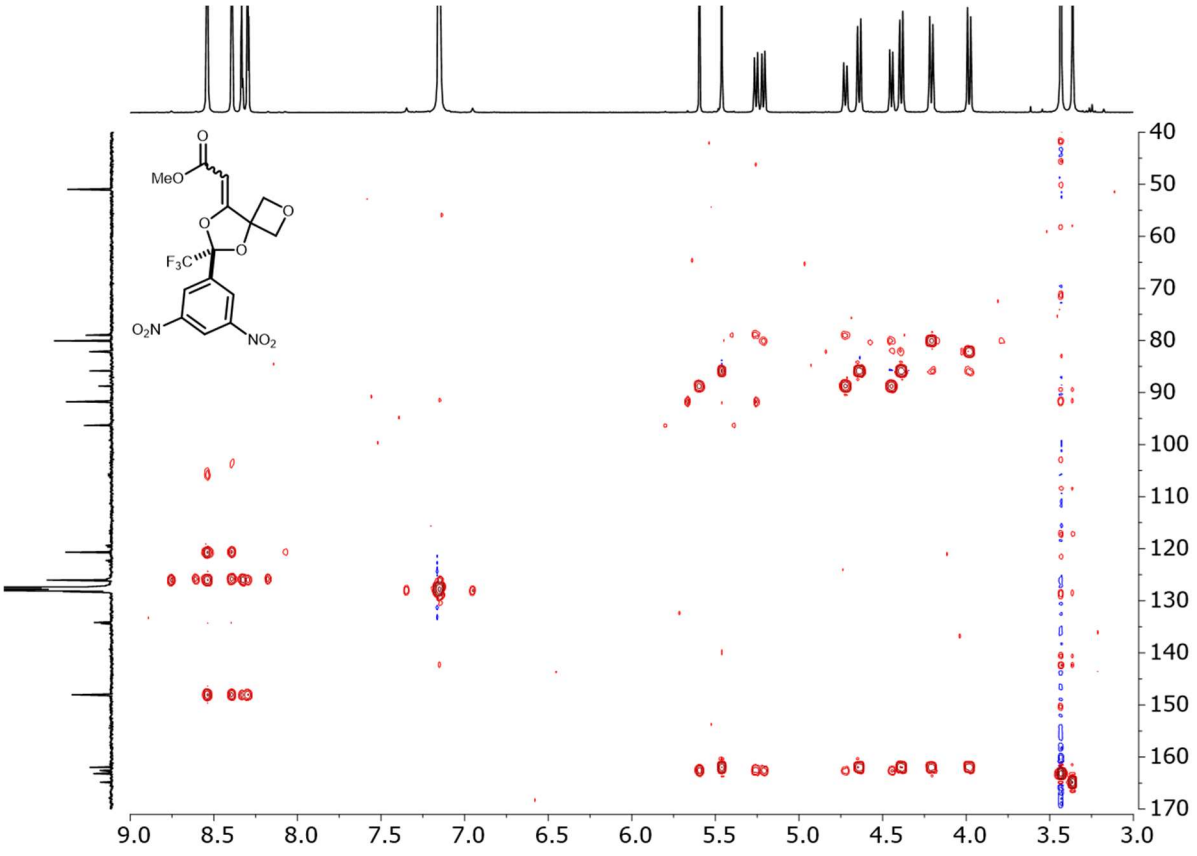

**[*rac*-10c], $^{1}$H-$^{1}$H NOESY, $C_6D_6$**



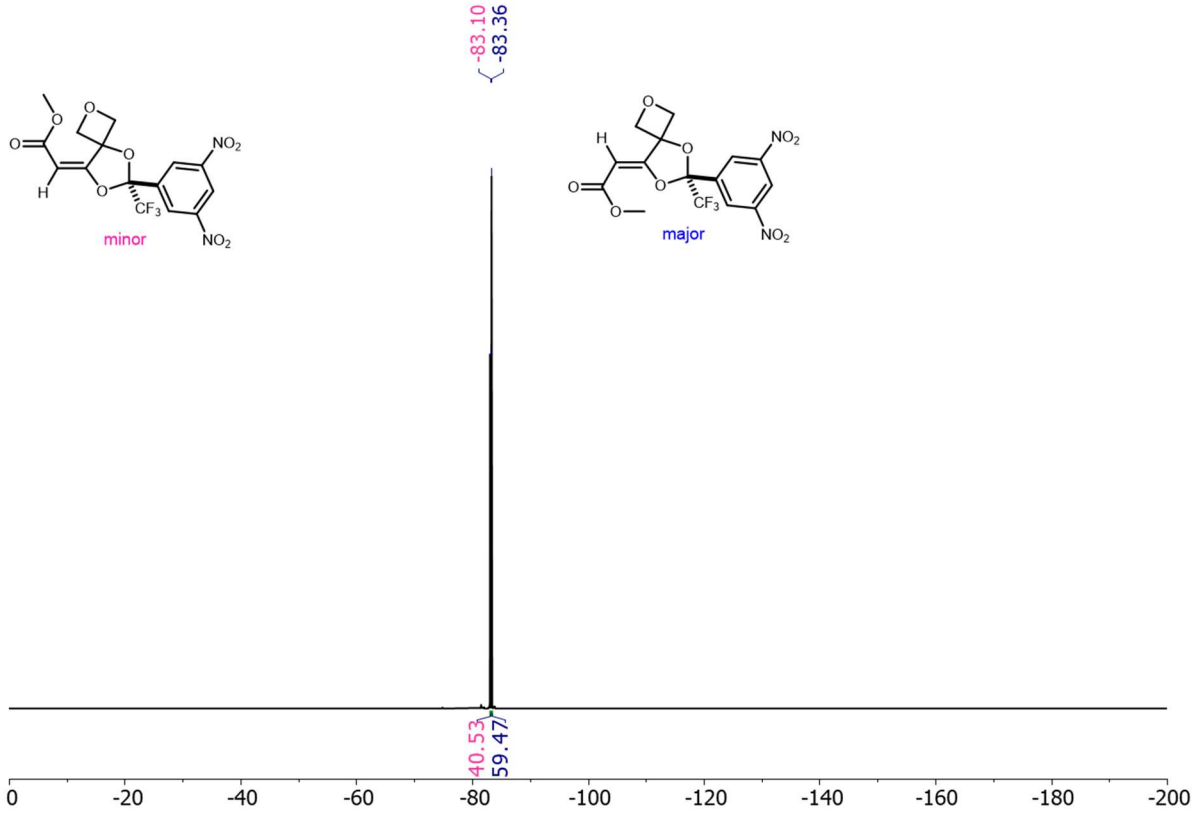
**[*rac*-10c], HSQC, $C_6D_6$**



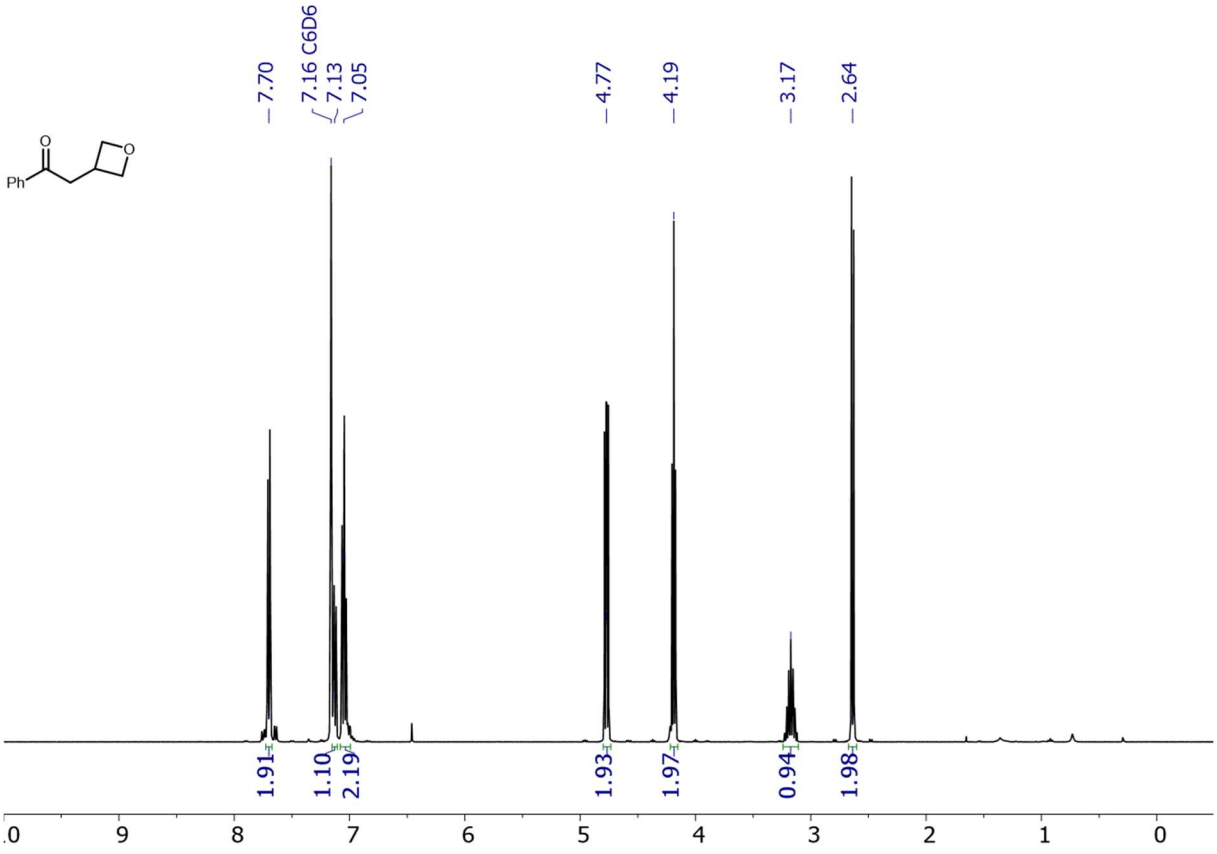

**[*rac*-10c], HMBC, $C_6D_6$**



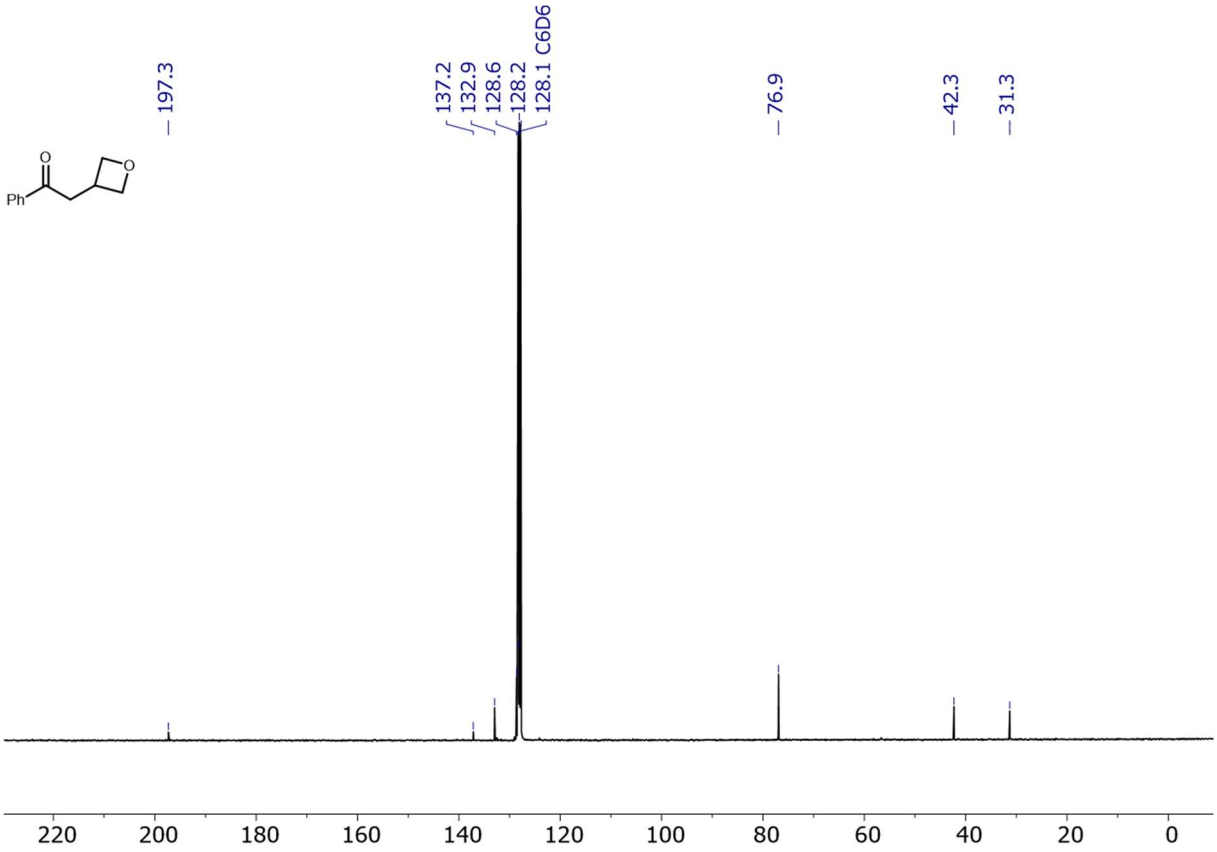
**[*rac*-10c], $^{19}F$, $C_6D_6$, 377 MHz**



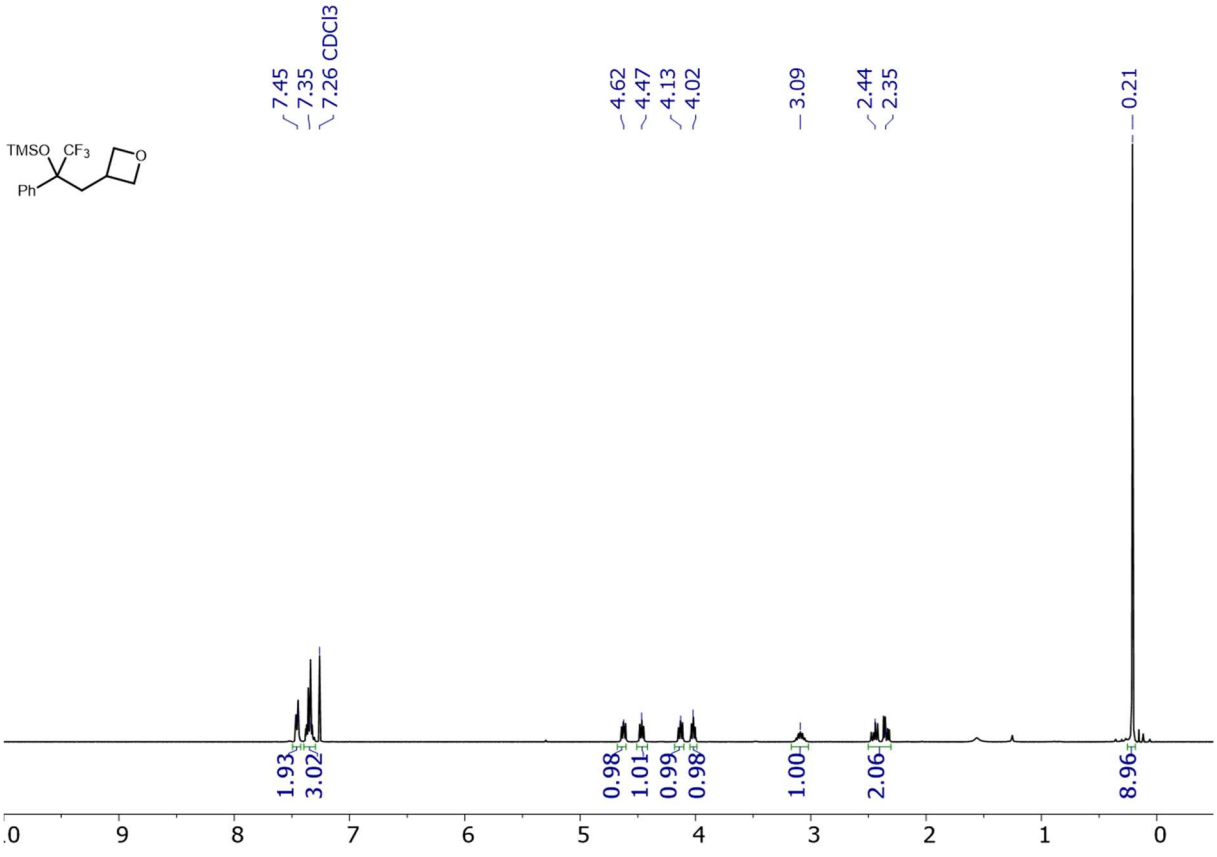
**[S17], $^{1}H$, $C_6D_6$, 400 MHz**



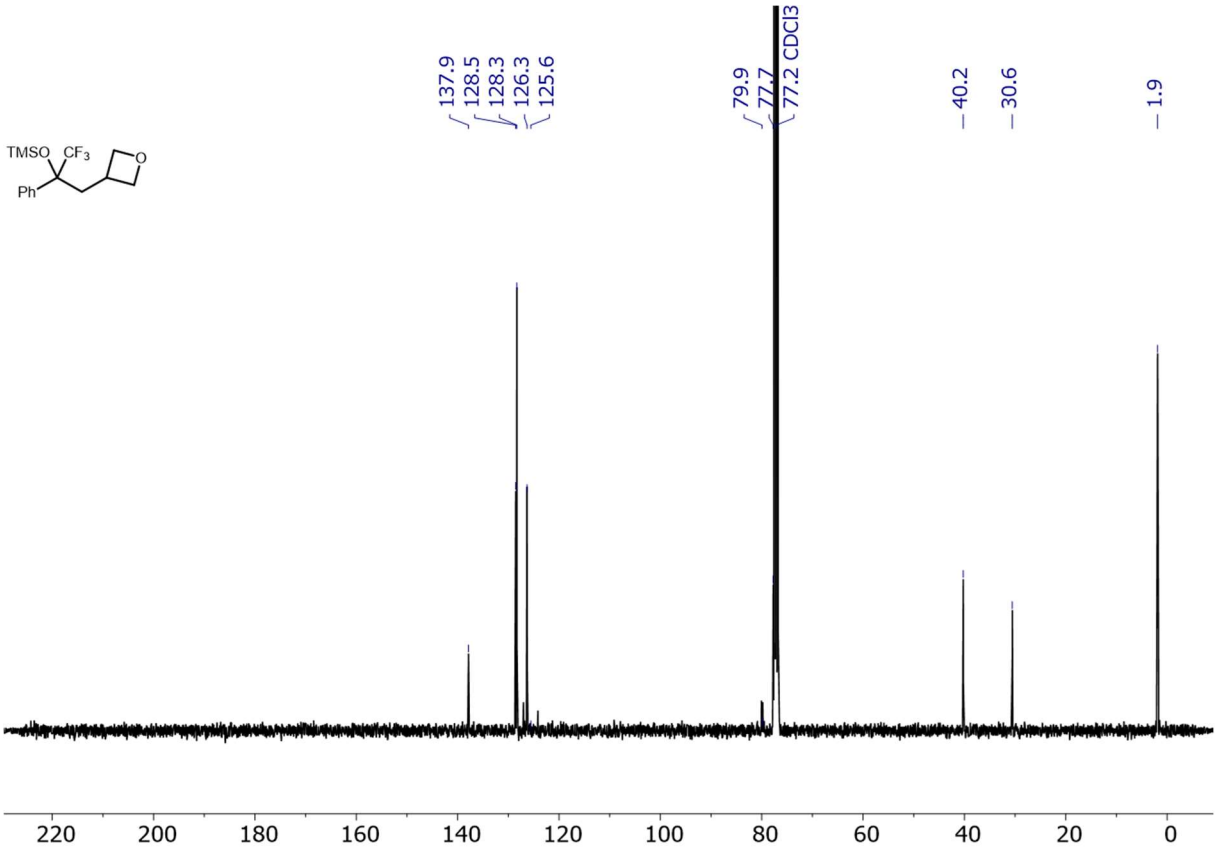

**[S17], $^{13}C$, $C_6D_6$, 101 MHz**



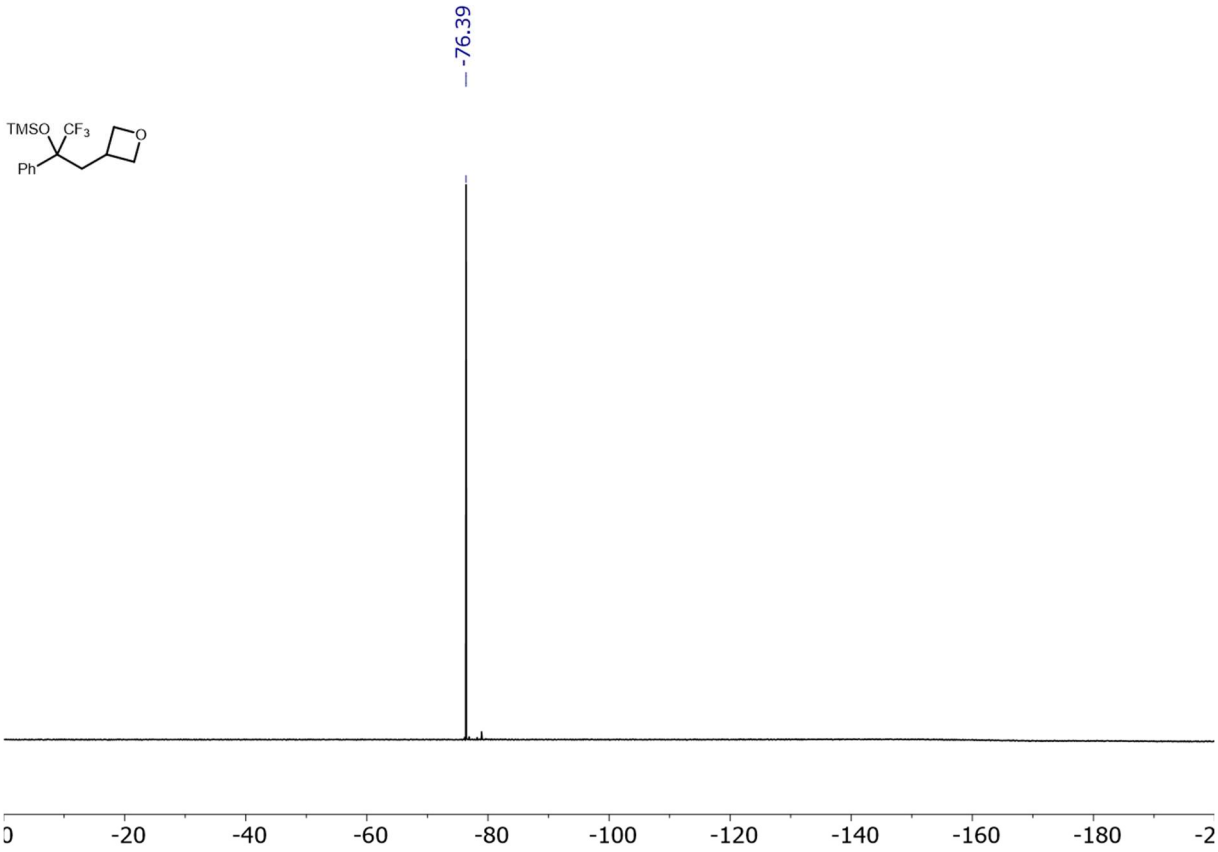
**[S18], $^{1}H$, $CDCl_3$, 400 MHz**



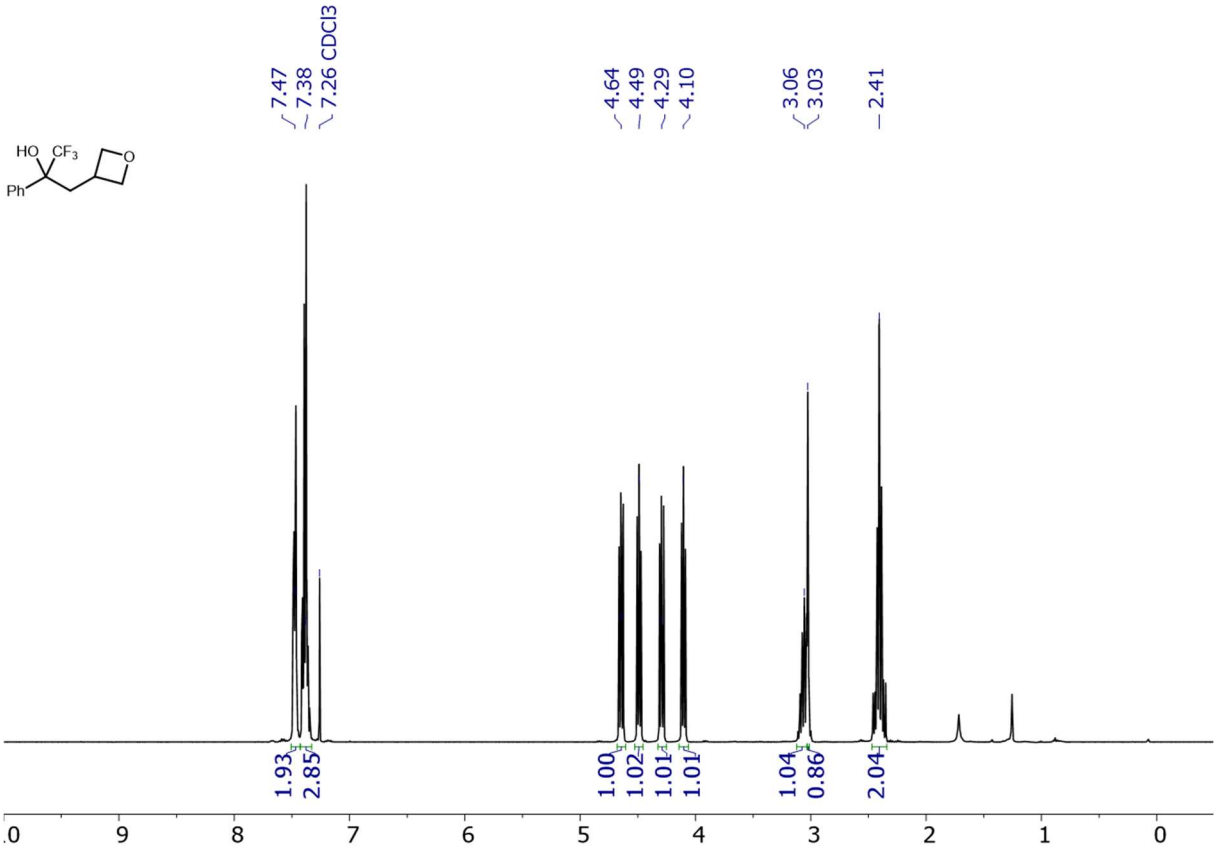

**[S18], $^{13}C$, $CDCl_3$, 101 MHz**



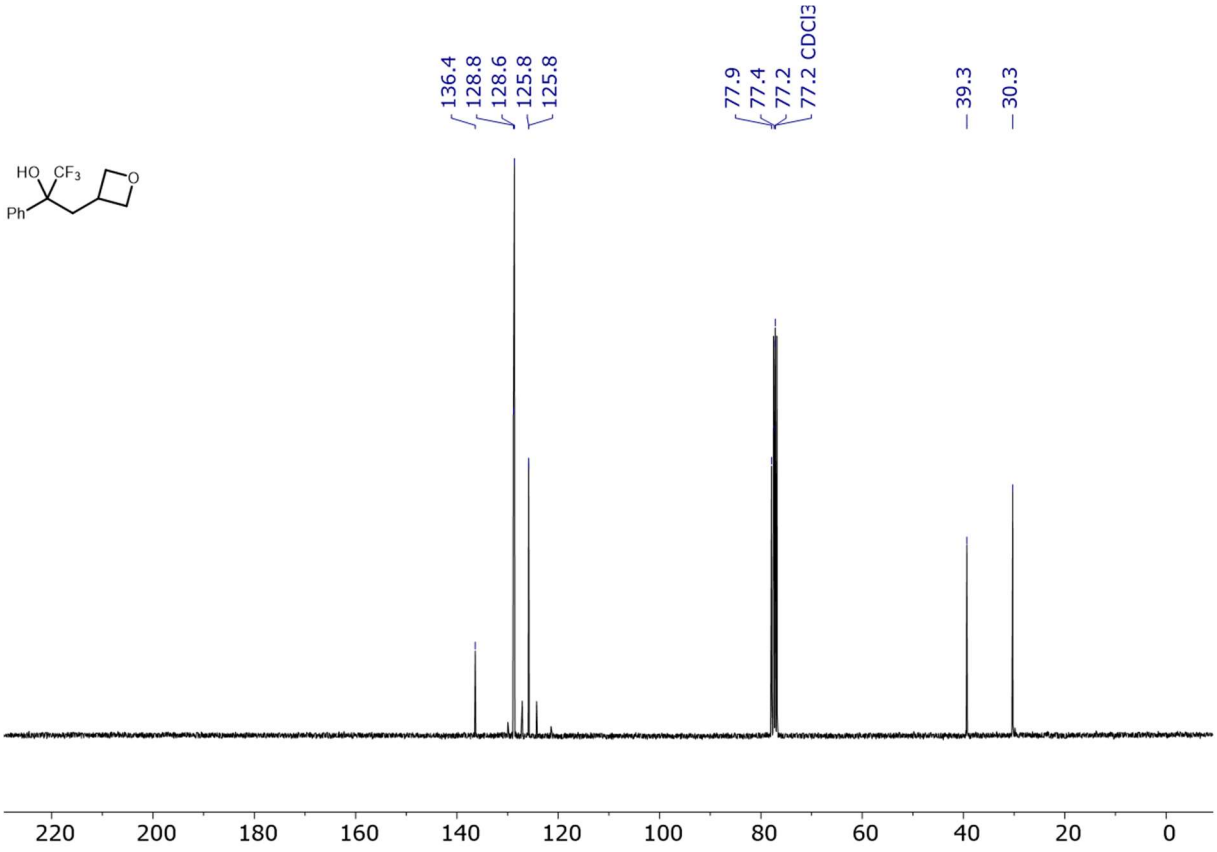
**[S18], $^{19}F$, $CDCl_3$, 377MHz**



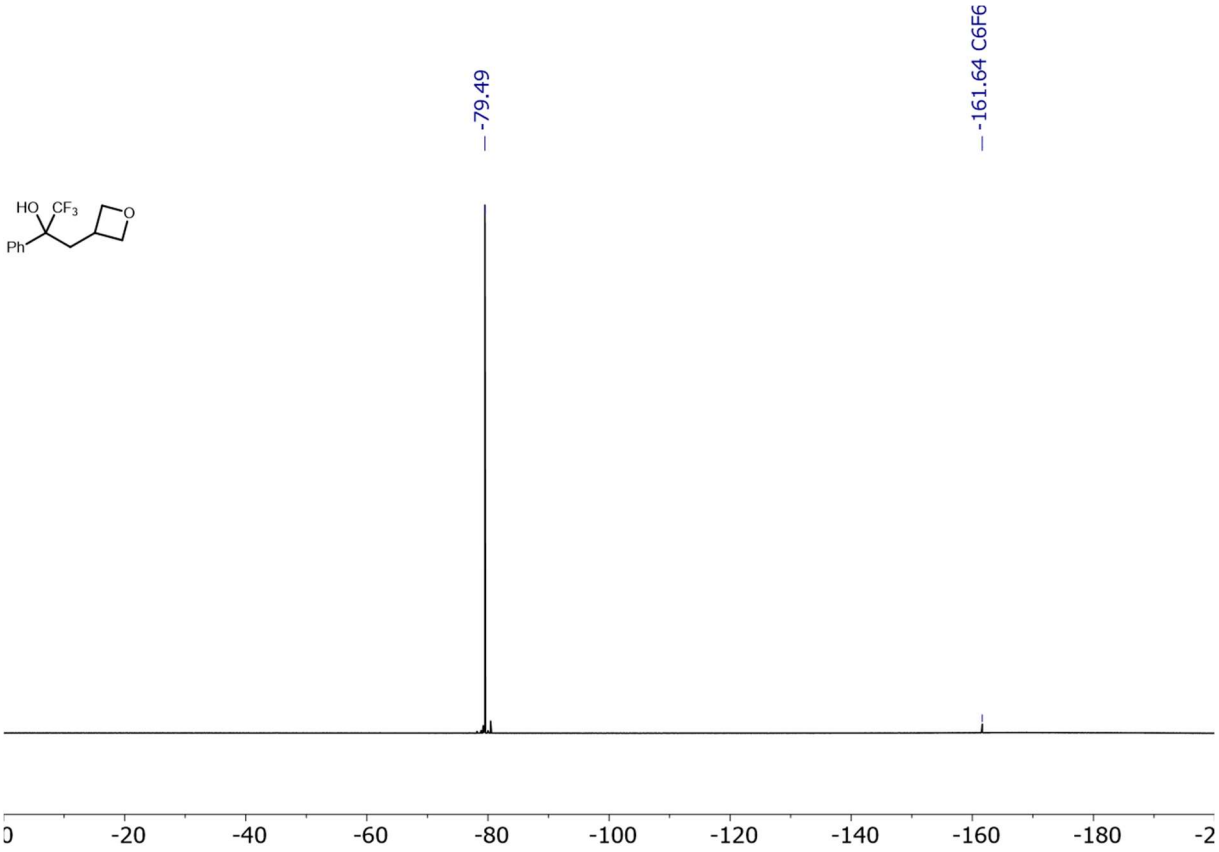
**[*rac*-11], $^{1}H$, $CDCl_3$, 400 MHz**



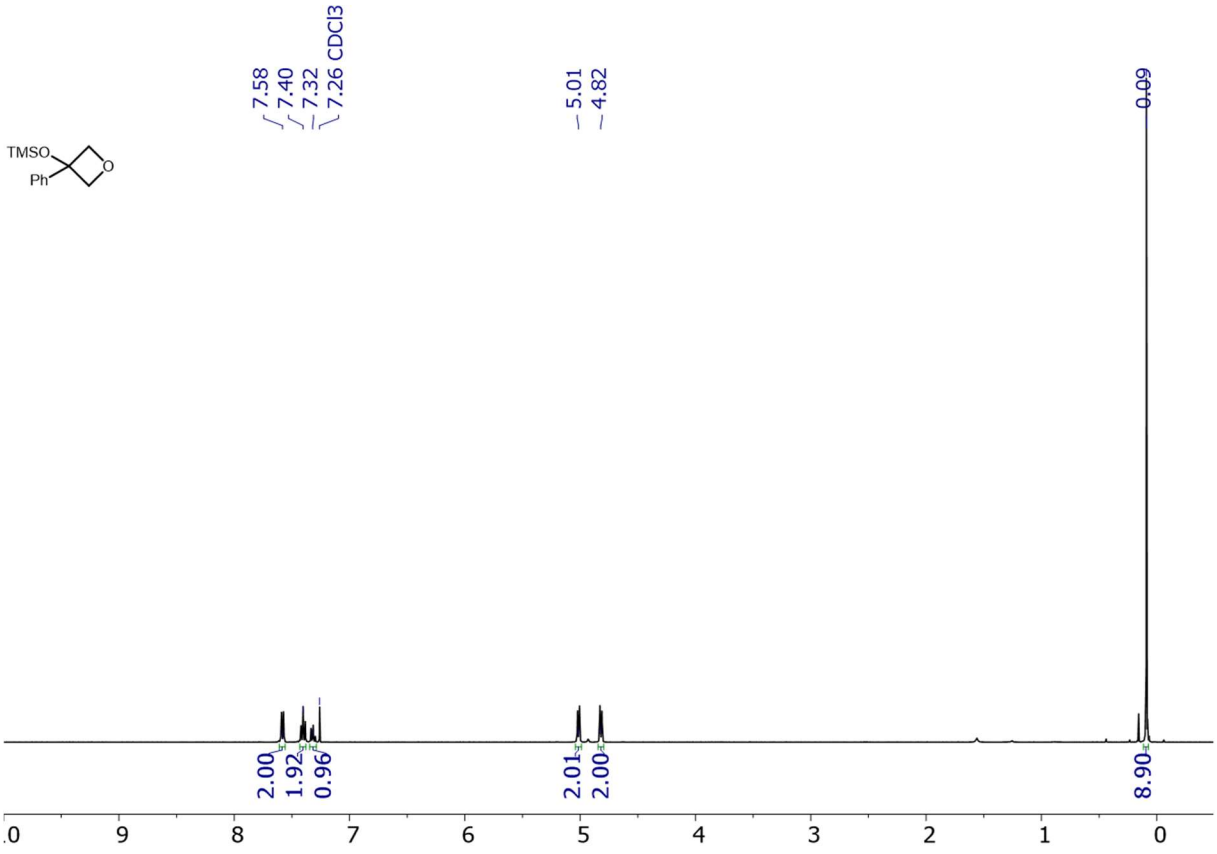

**[*rac*-11], $^{13}C$, $CDCl_3$, 101 MHz**



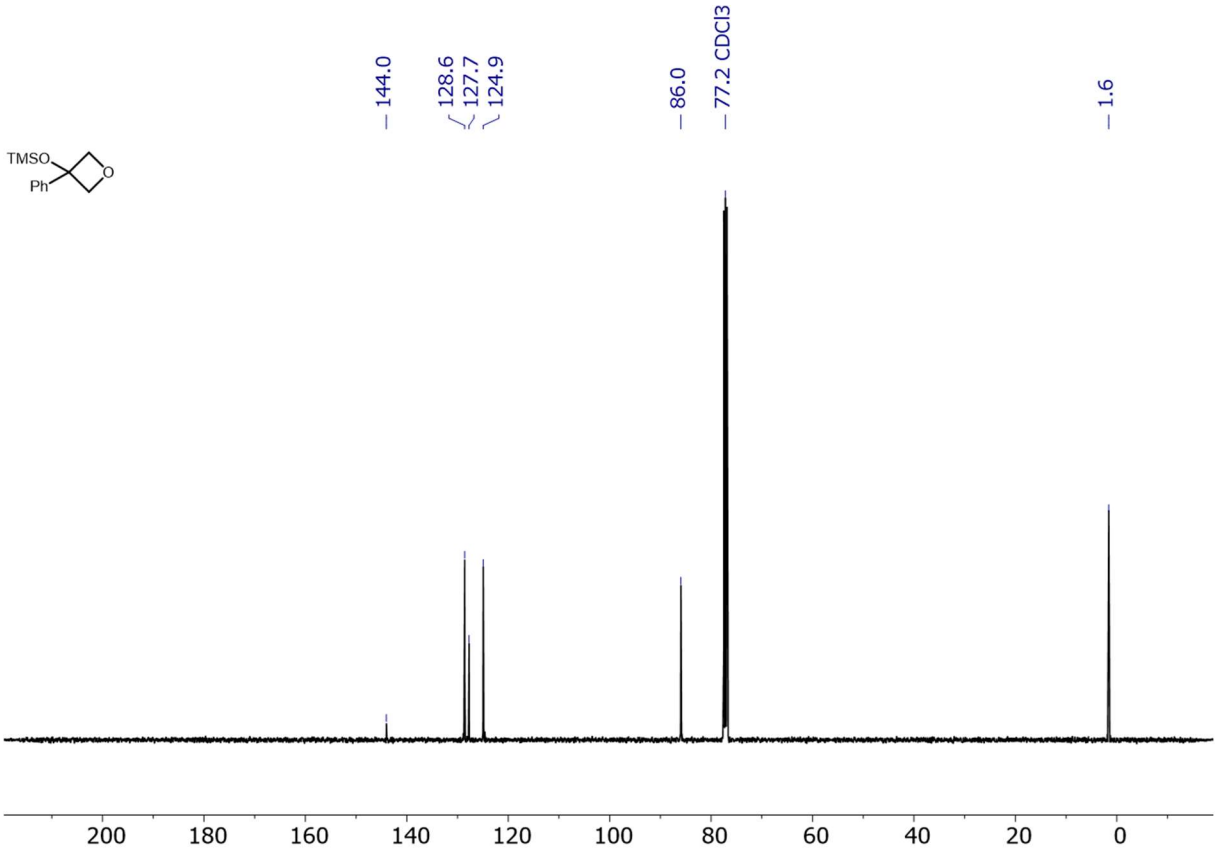
**[*rac*-11], $^{19}F$, $CDCl_3$, 377 MHz**



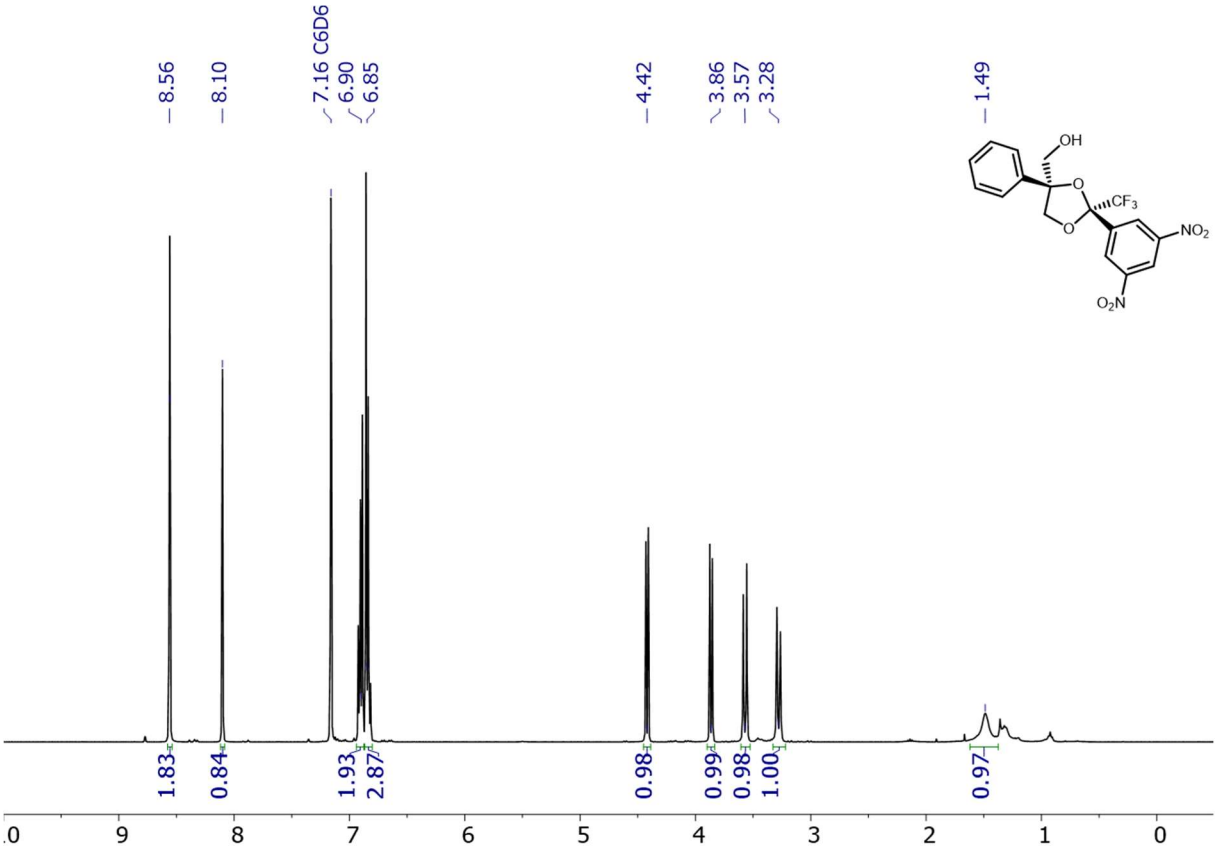
**[S19], $^{1}H$, $CDCl_3$, 400 MHz**



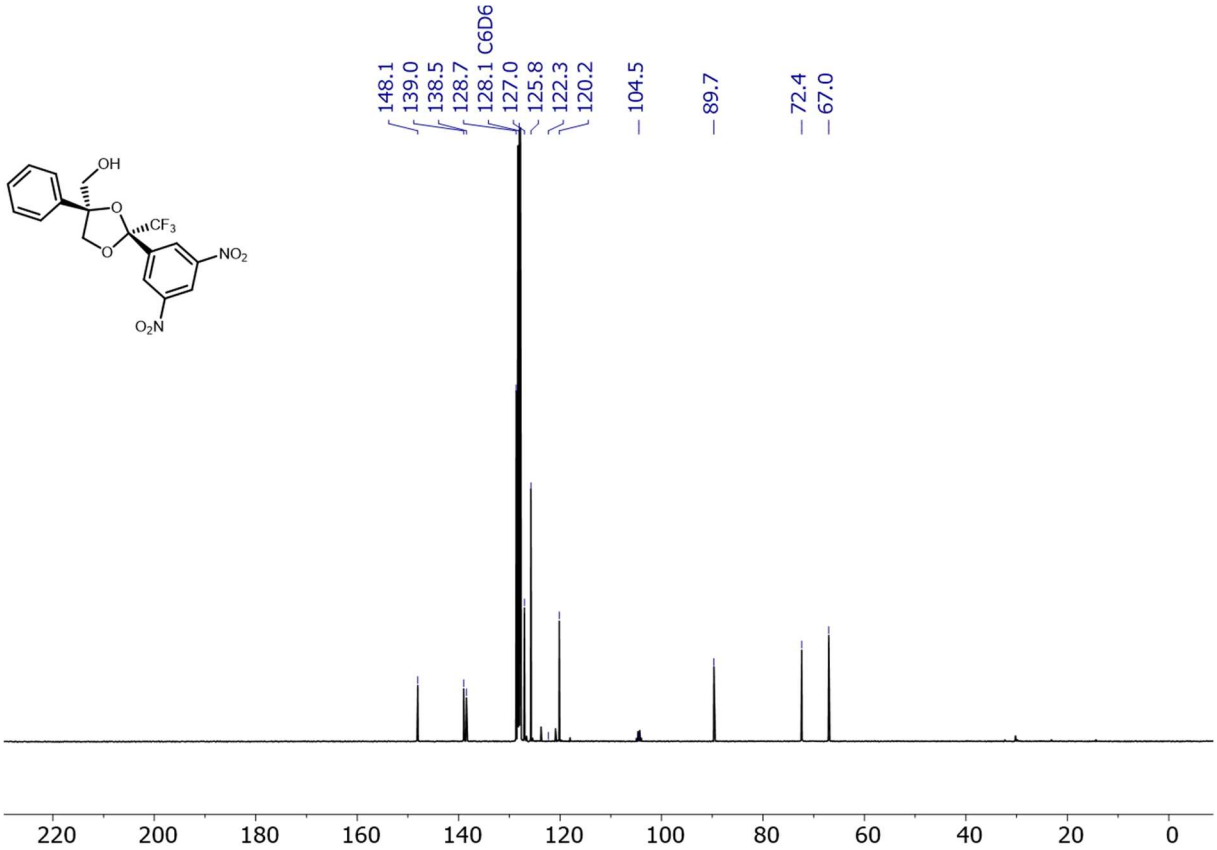

**[S19], $^{13}C$, $CDCl_3$, 101 MHz**



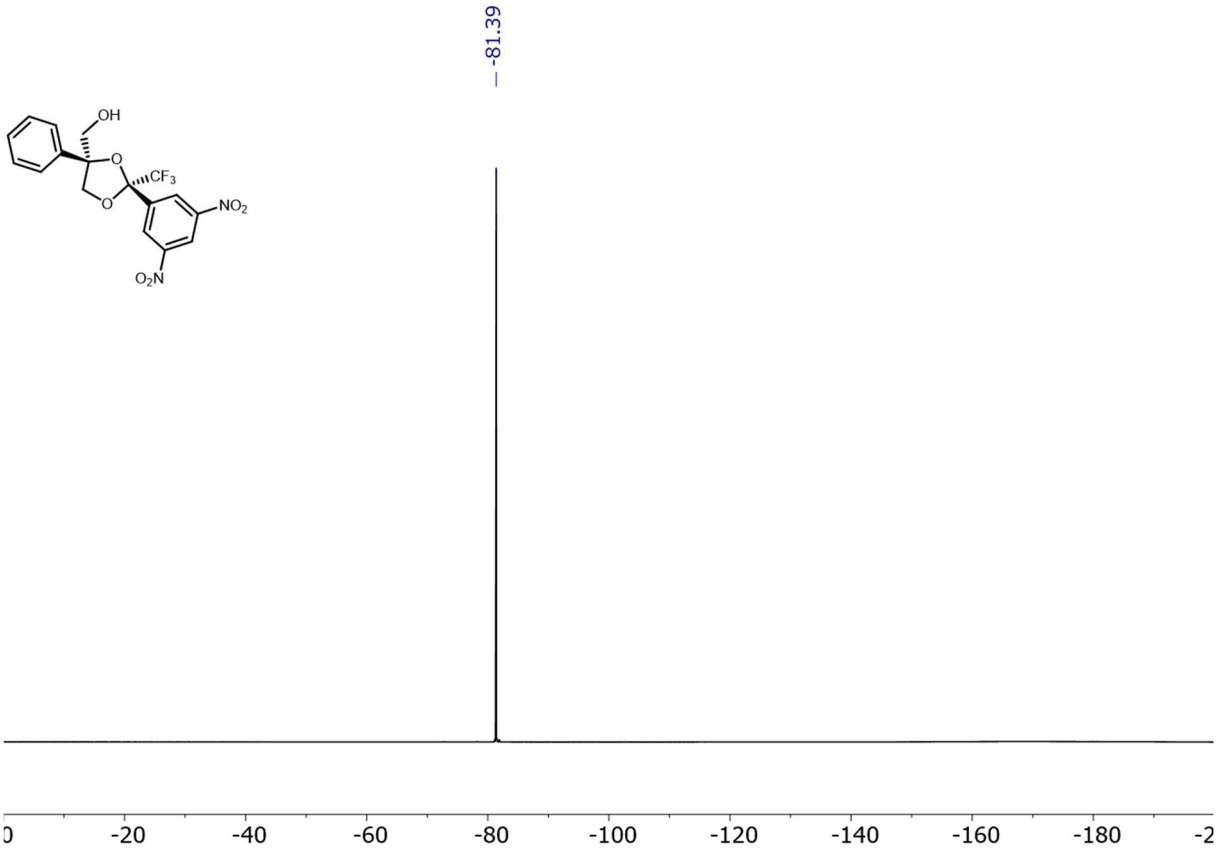
**[5a], $^{1}H$, $C_6D_6$, 400 MHz**



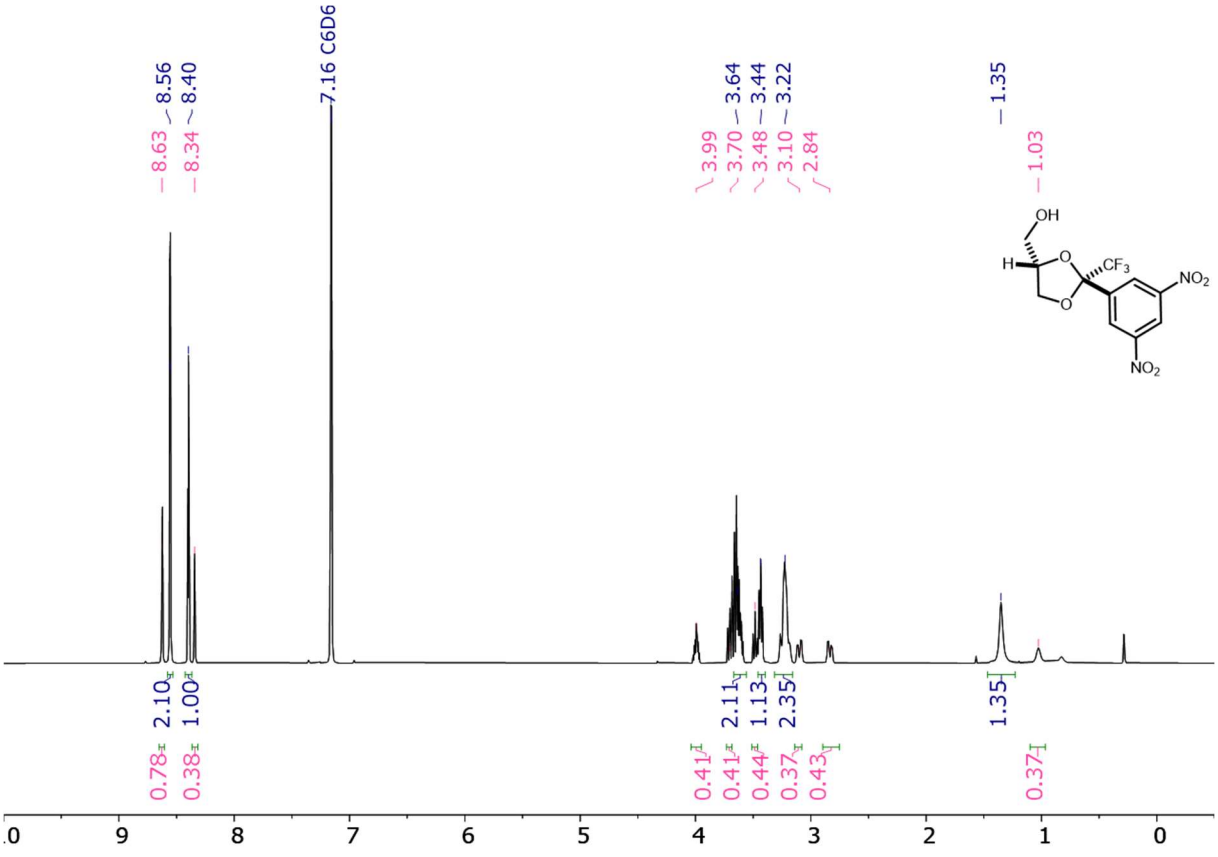

**[5a], $^{13}C$, $C_6D_6$, 101 MHz**



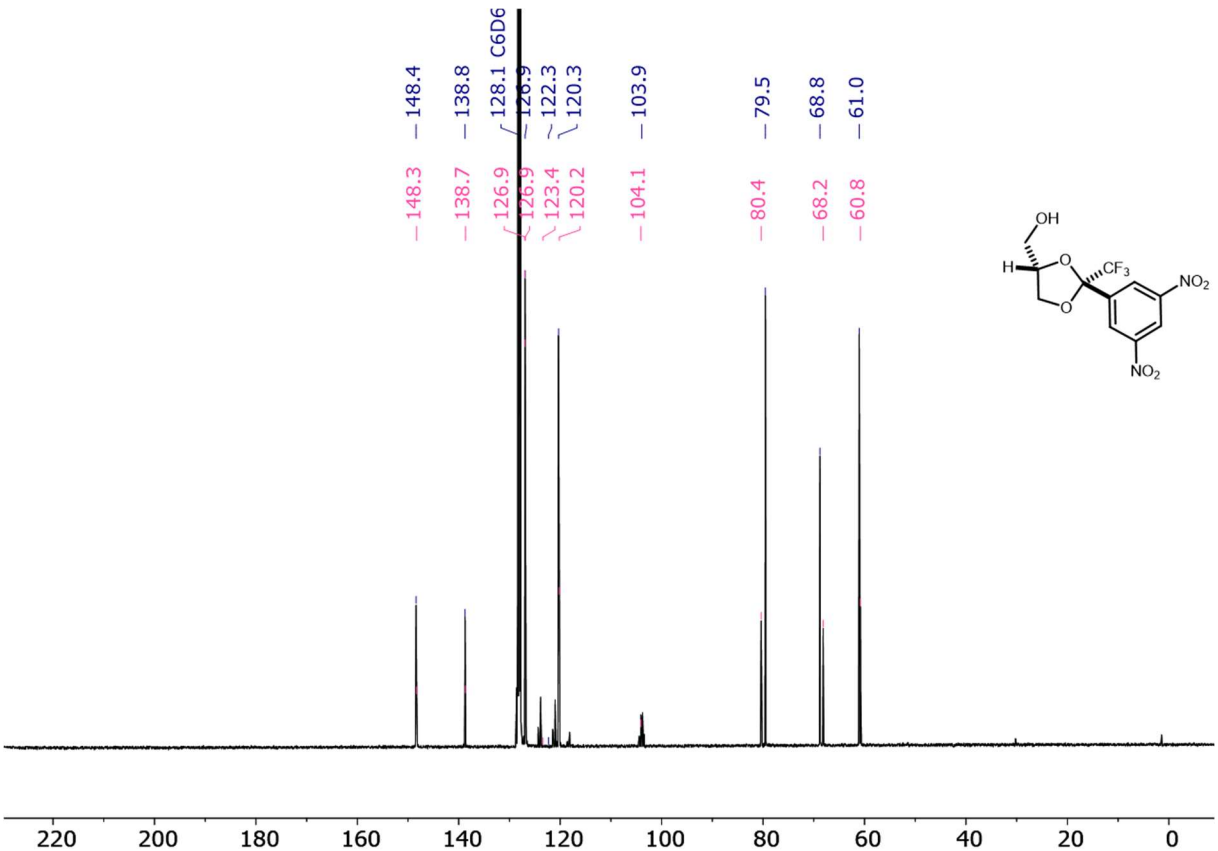
**[5a], $^{19}F$, $C_6D_6$, 377 MHz**



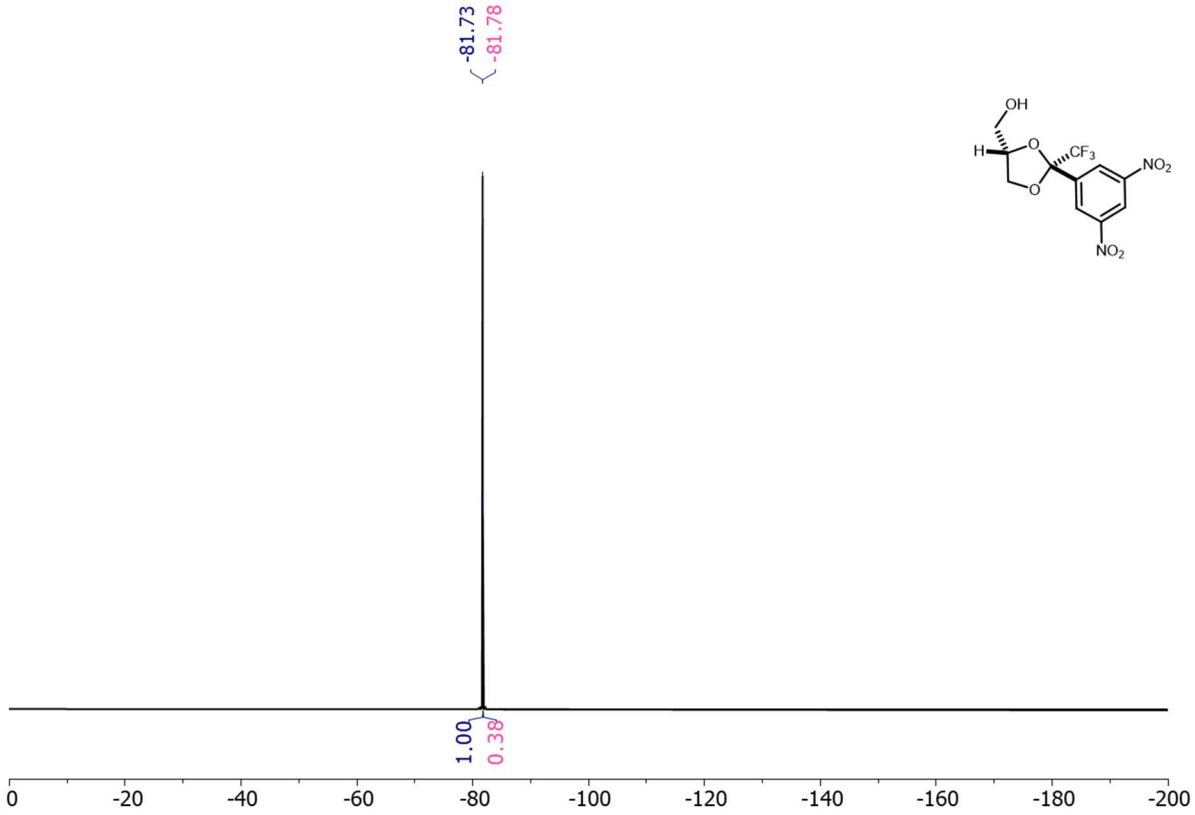
**[5b], $^{1}H$, $C_6D_6$, 400 MHz**



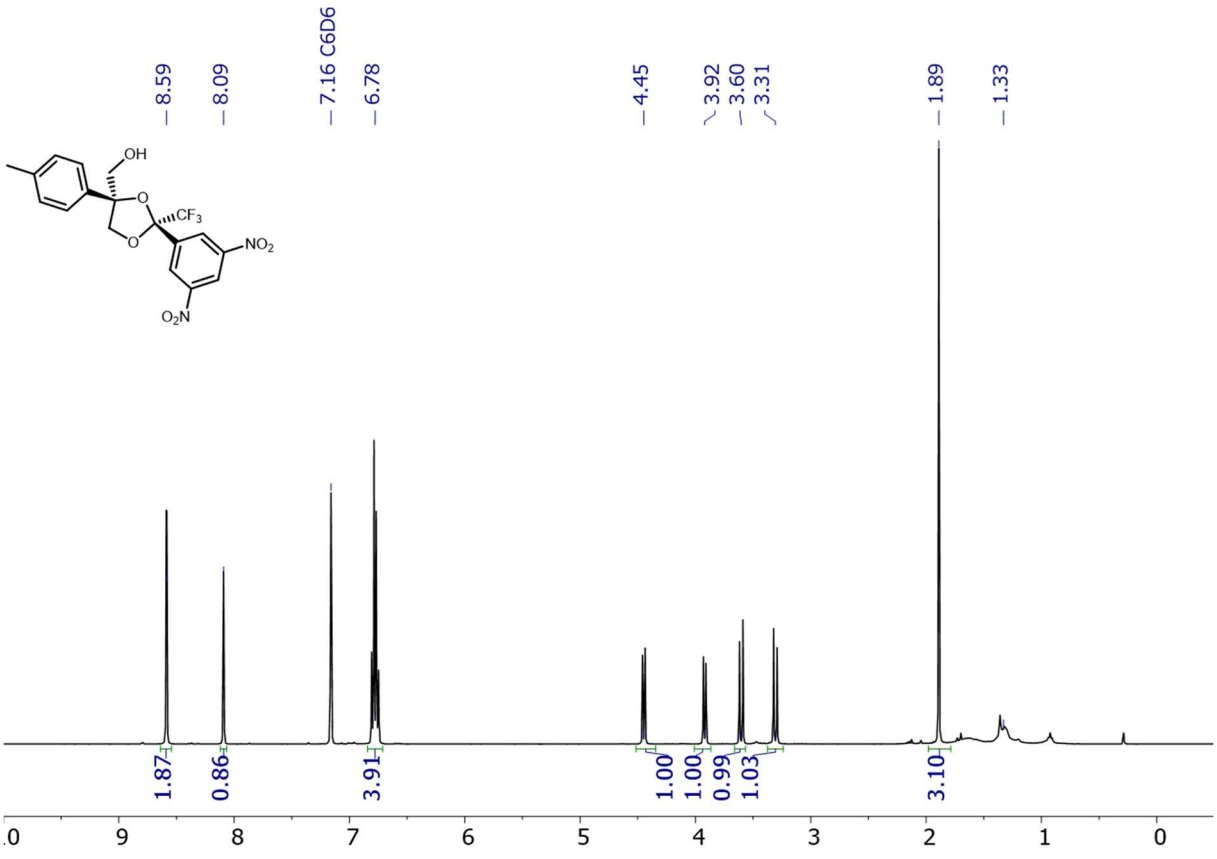

**[5b], $^{13}C$, $C_6D_6$, 101 MHz**



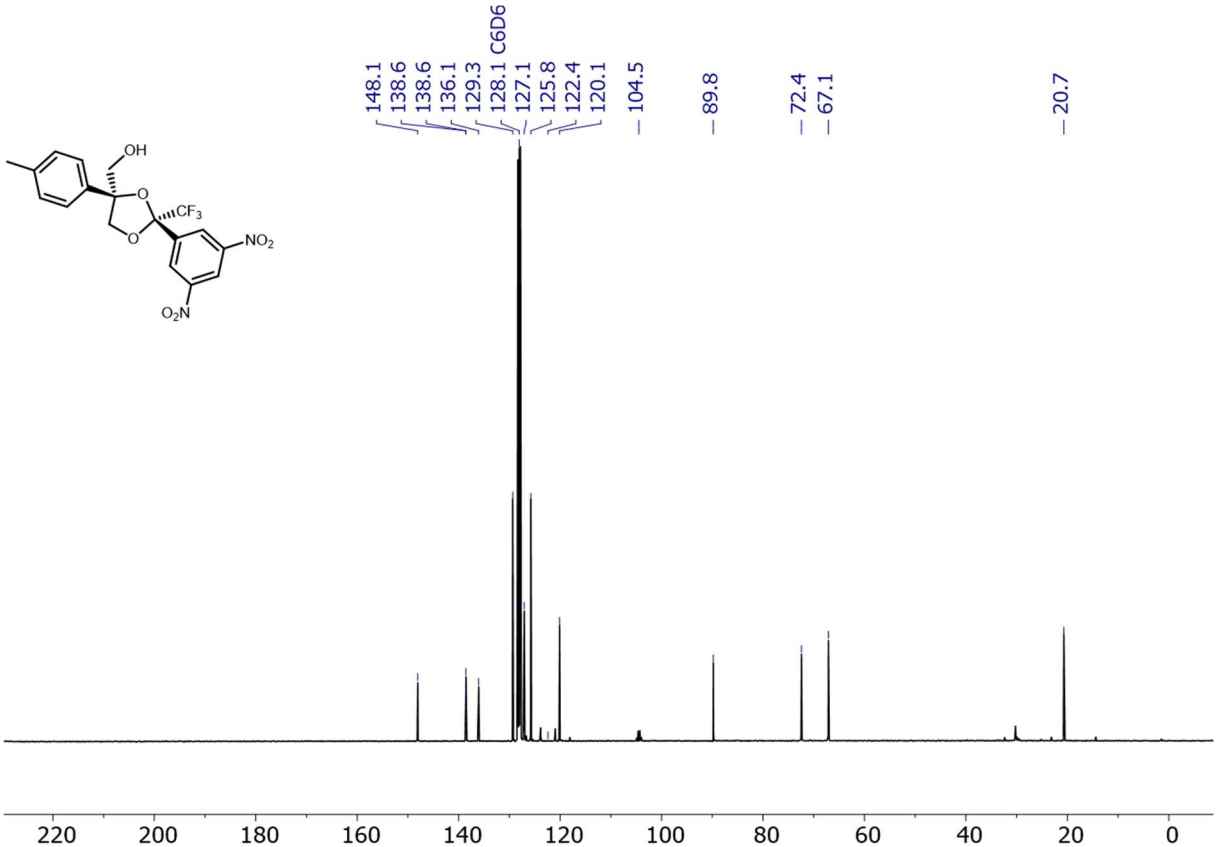
**[5b], $^{19}F$, $C_6D_6$, 377 MHz**



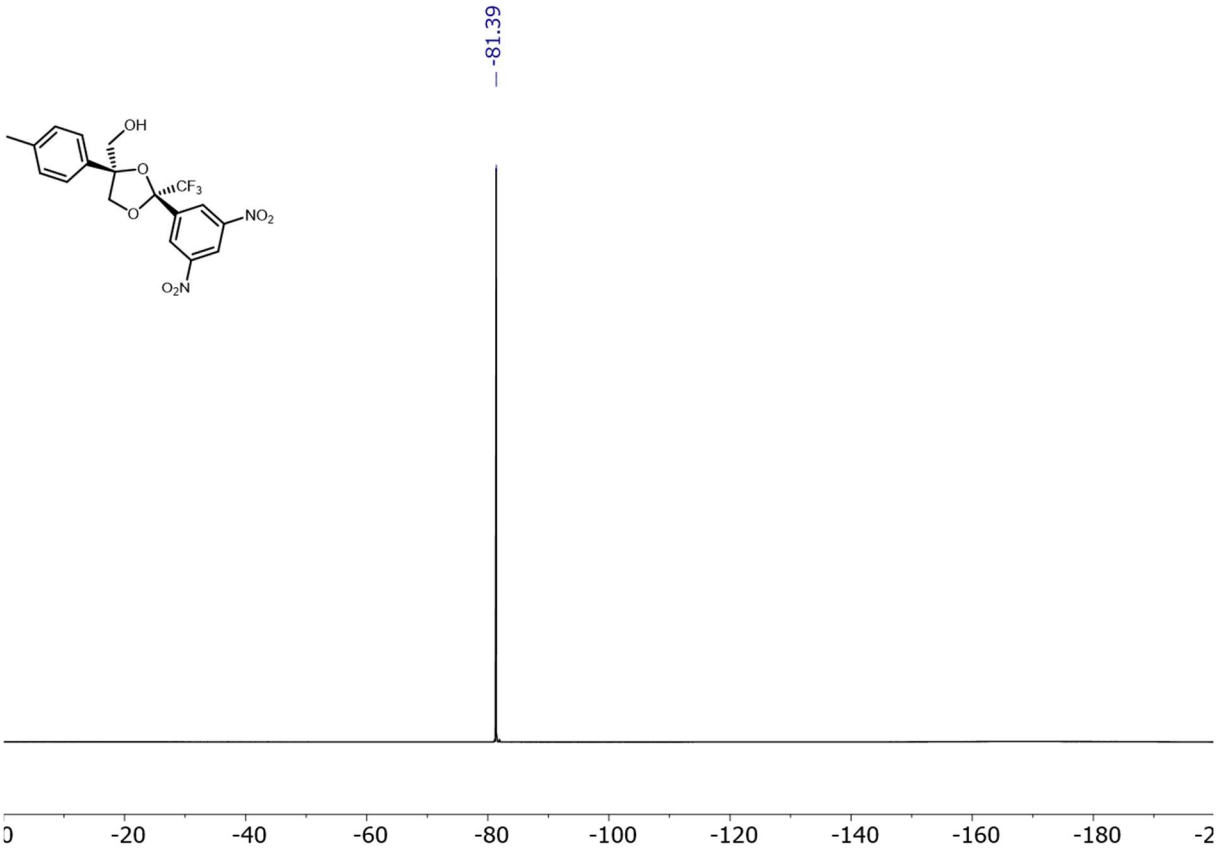
**[5d], $^{1}H$, $C_6D_6$, 400 MHz**



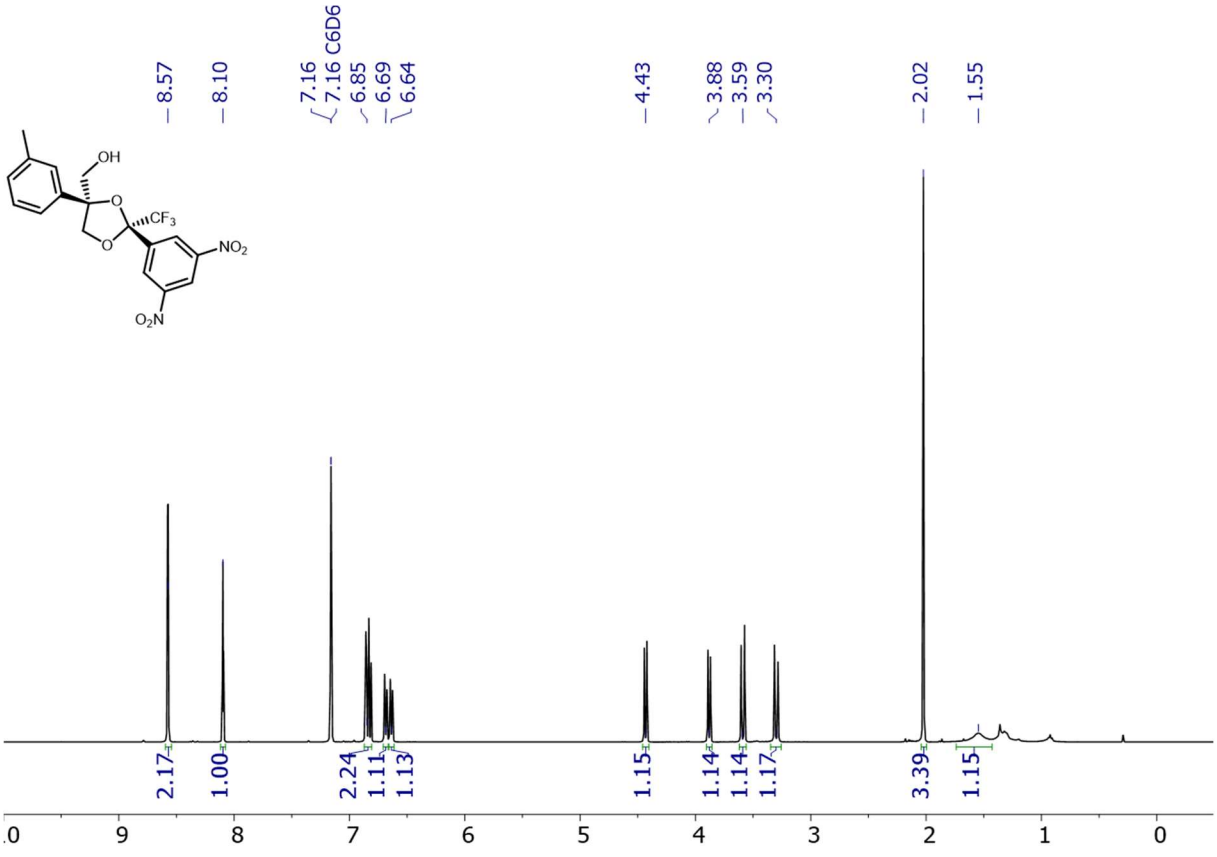

**[5d], $^{13}C$, $C_6D_6$, 101 MHz**



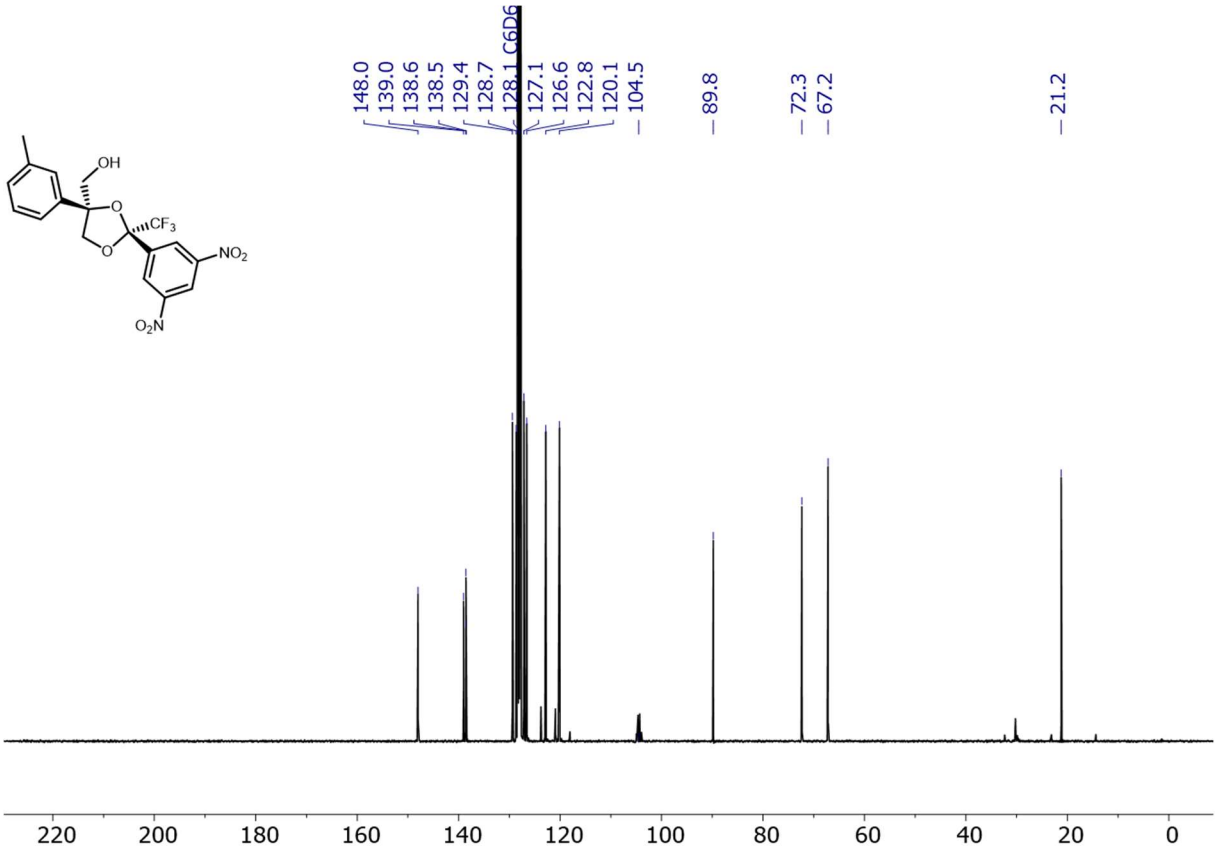
**[5d], $^{19}F$, $C_6D_6$, 377 MHz**



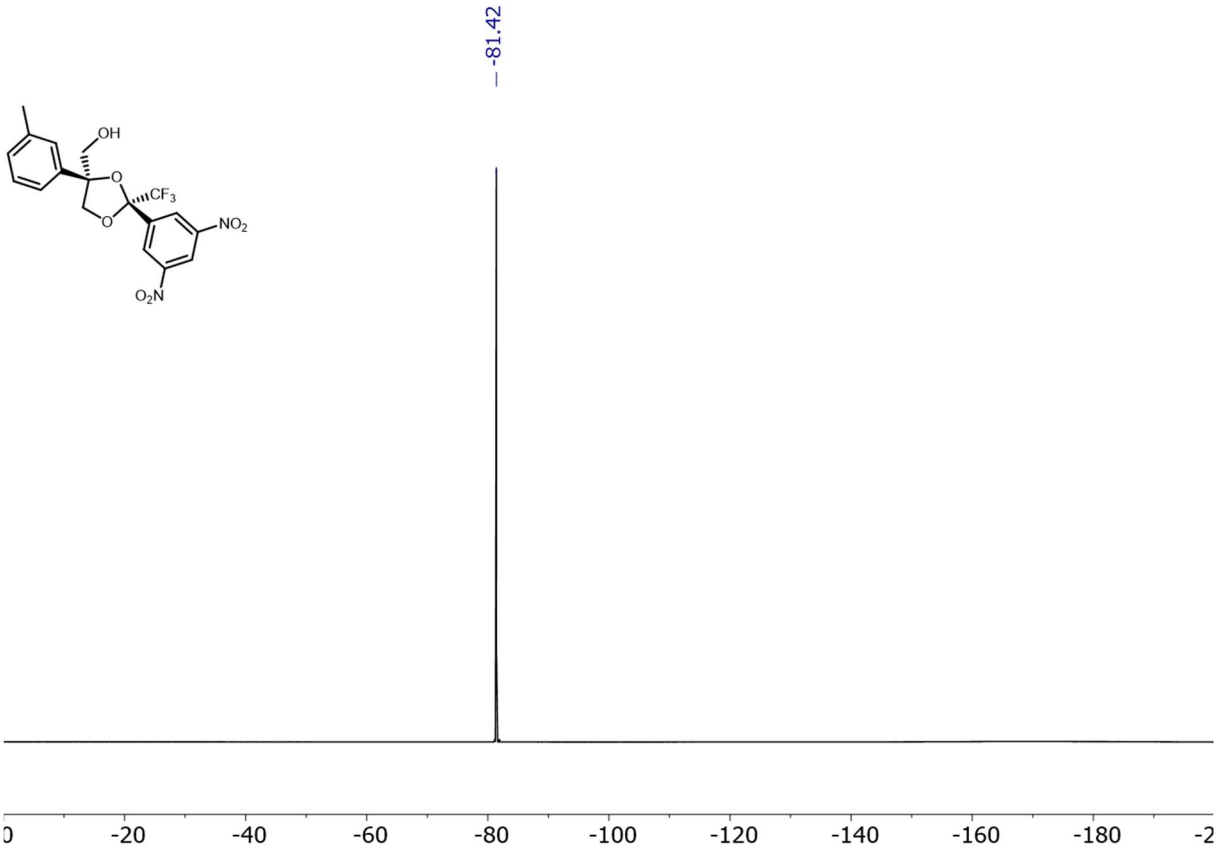
**[5e], $^{1}H$, $C_6D_6$, 400 MHz**



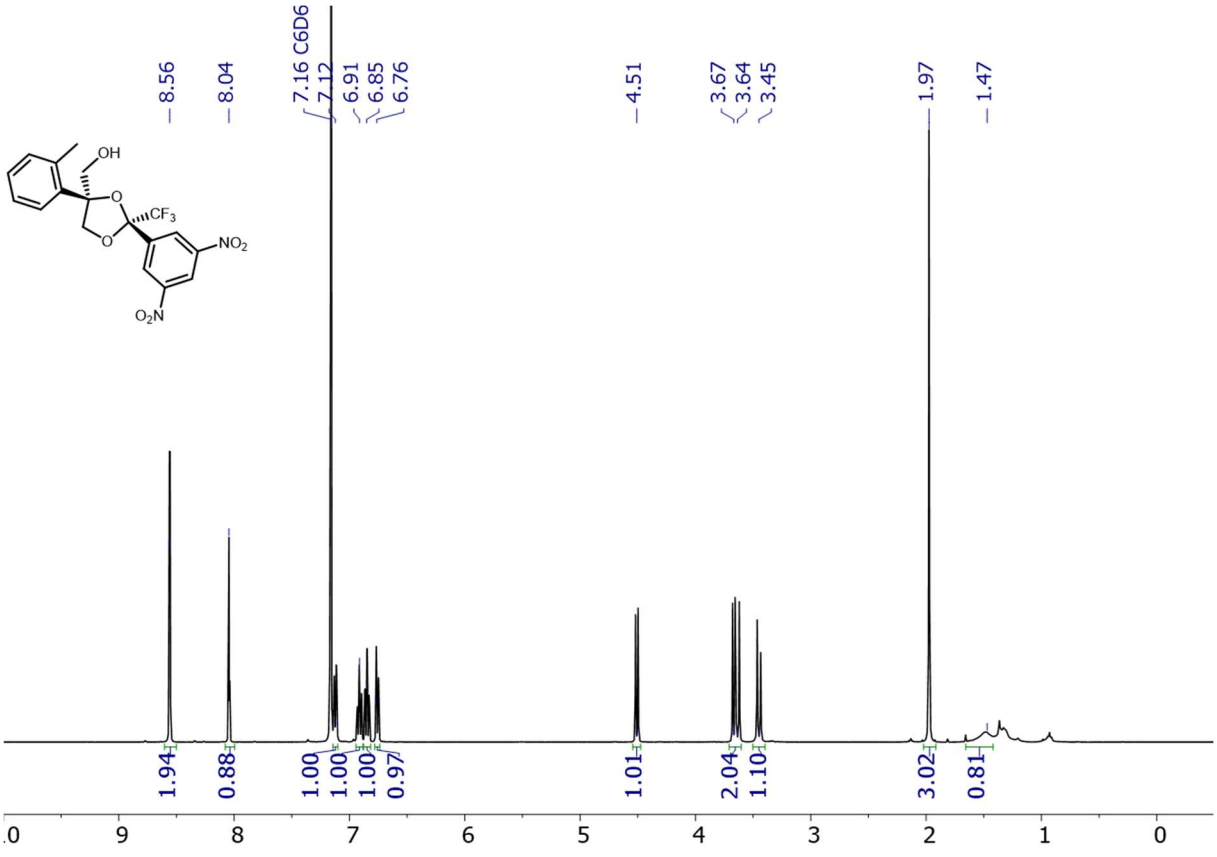

**[5e], $^{13}C$, $C_6D_6$, 101 MHz**



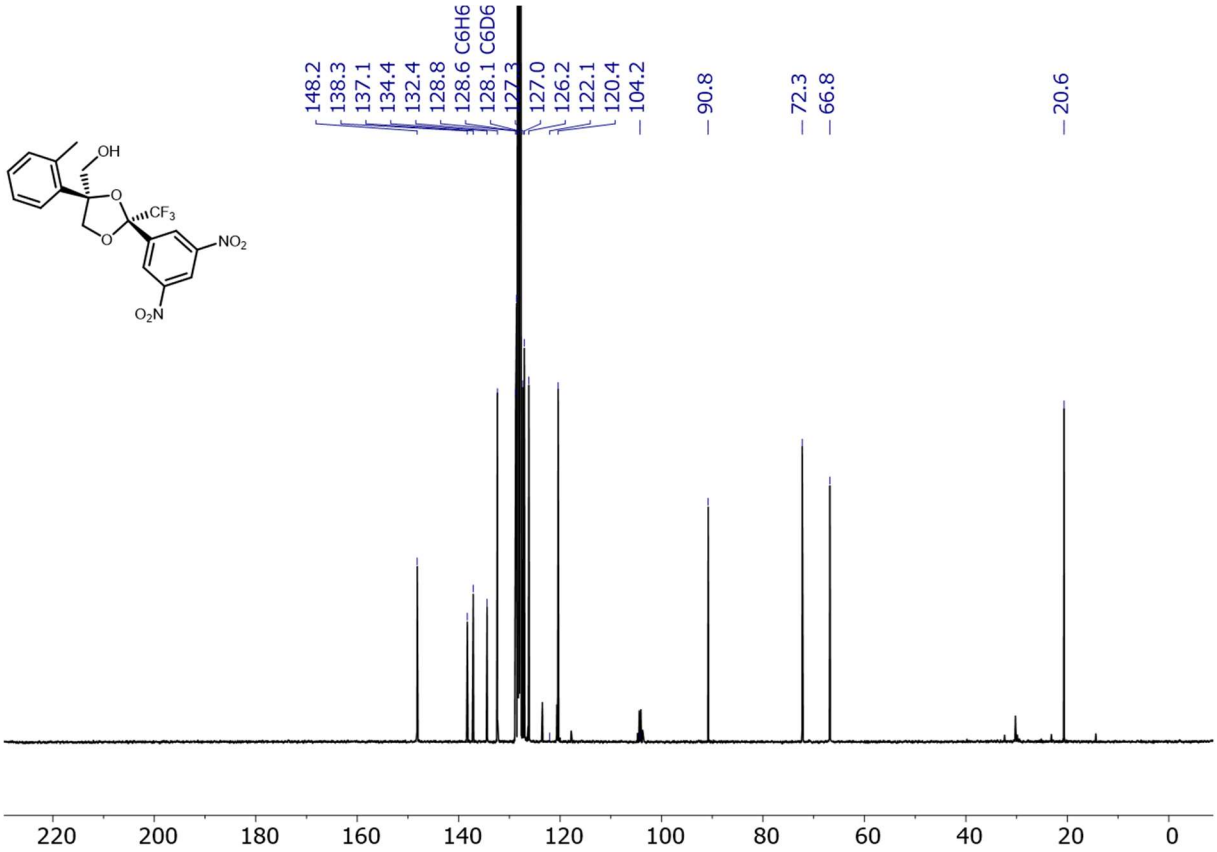
**[5e], $^{19}F$, $C_6D_6$, 377 MHz**



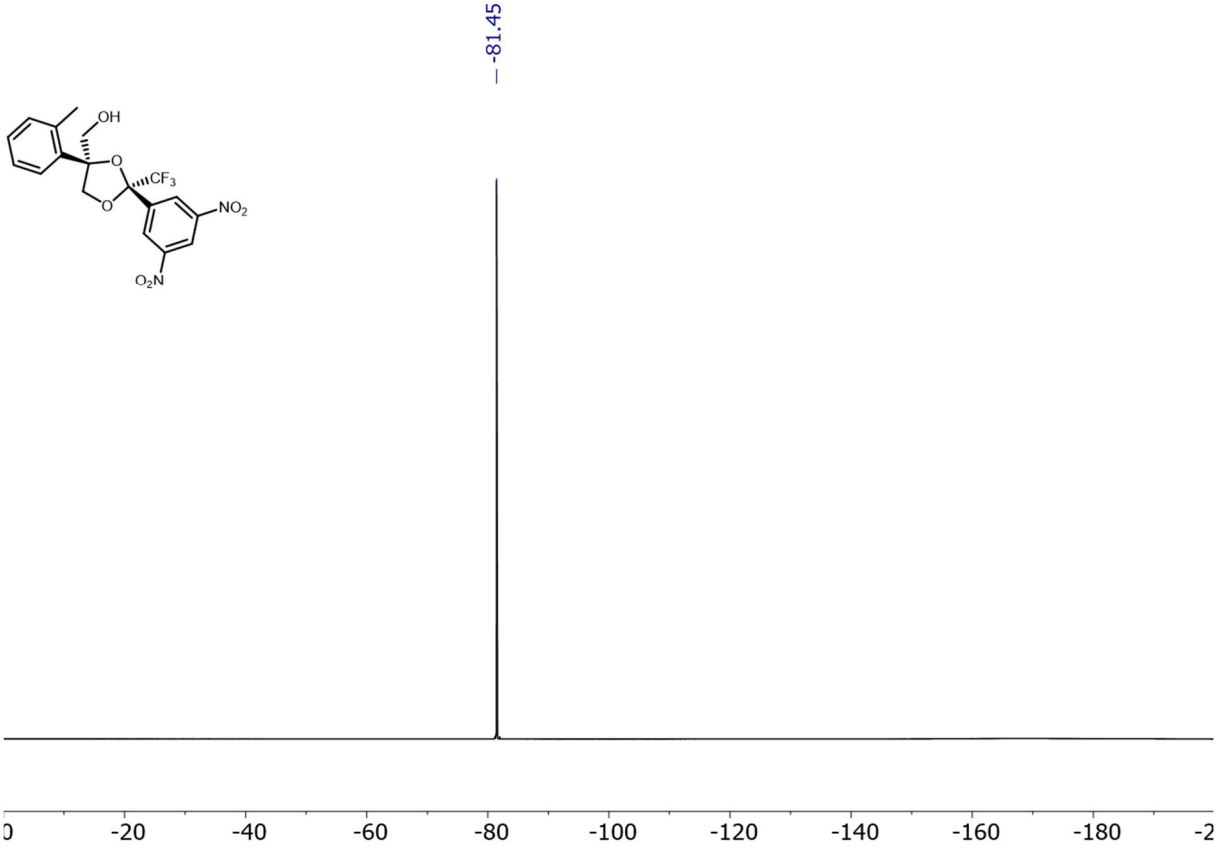
**[5f], $^{1}H$, $C_6D_6$, 400 MHz**



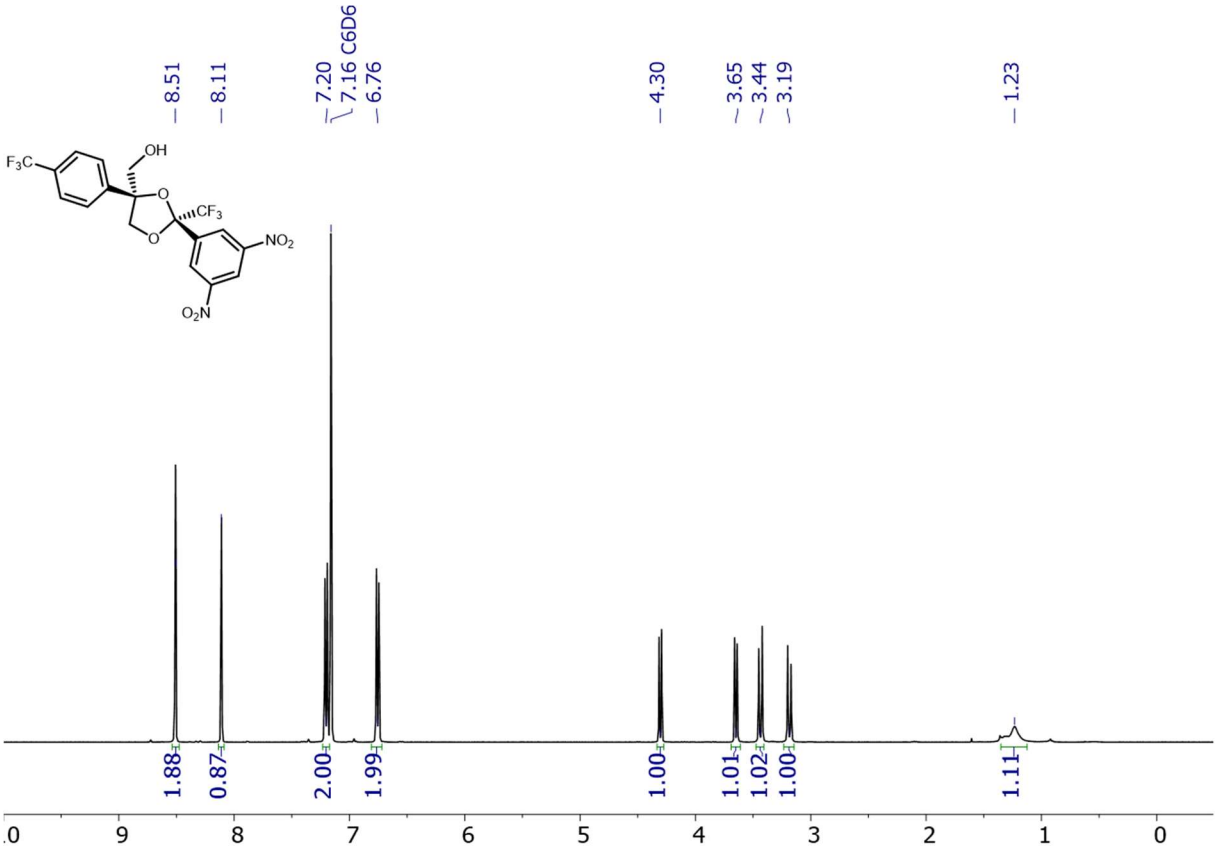

**[5f], $^{13}C$, $C_6D_6$, 101 MHz**



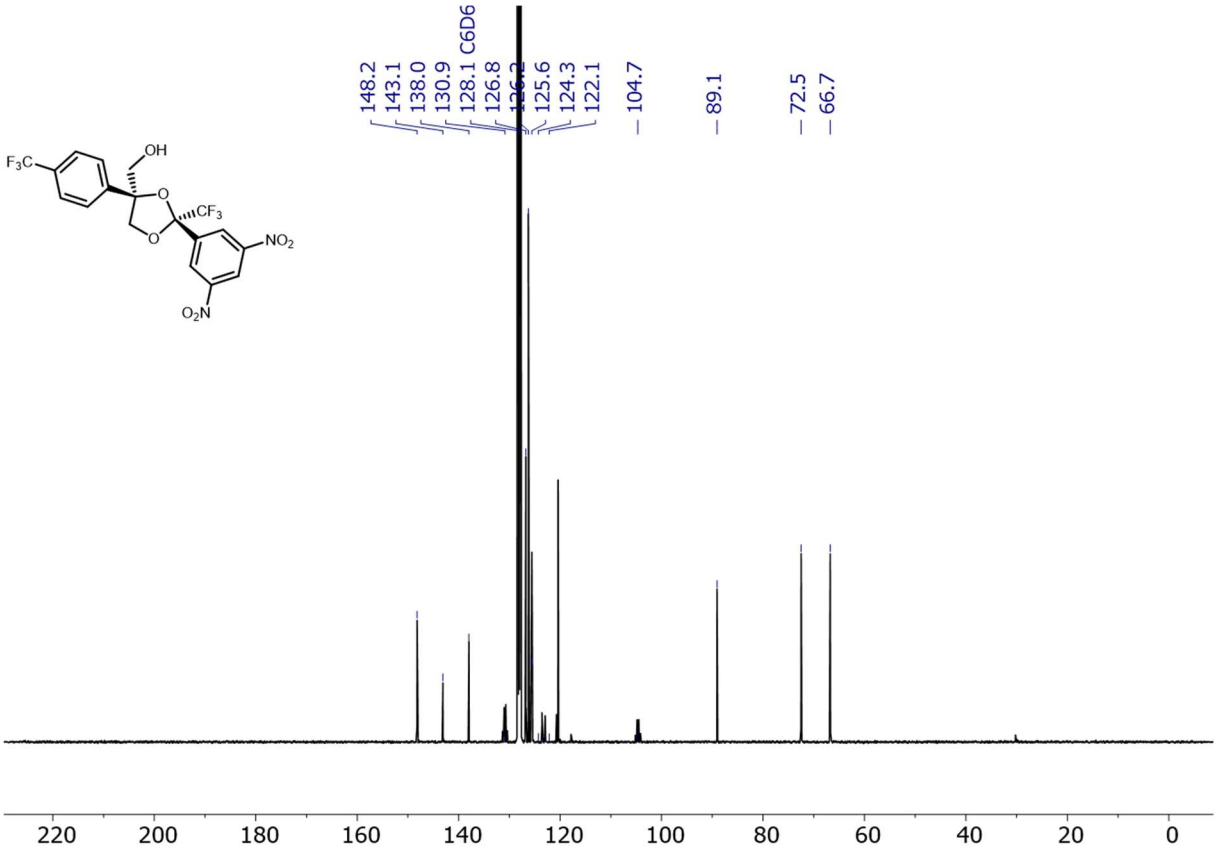
**[5f], $^{19}F$, $C_6D_6$, 377 MHz**



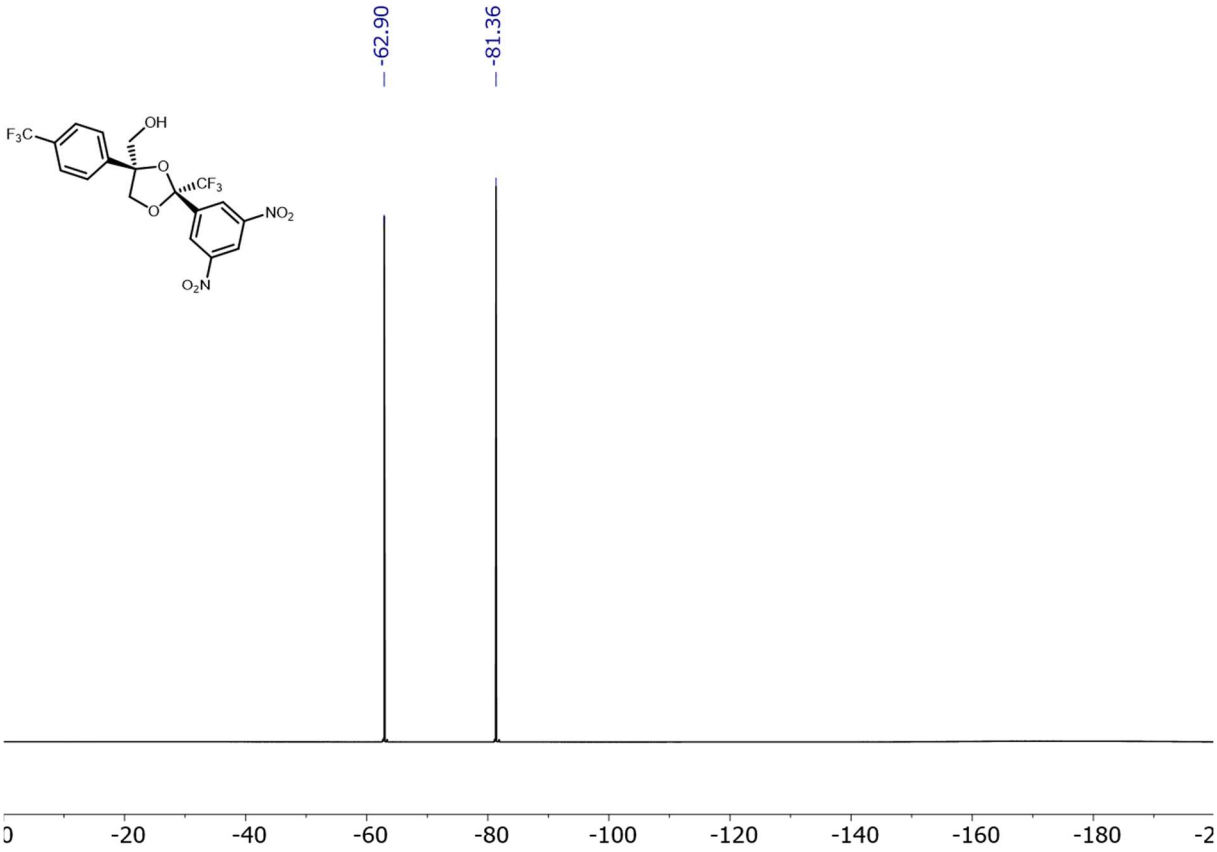
**[5g], $^{1}H$, $C_6D_6$, 400 MHz**



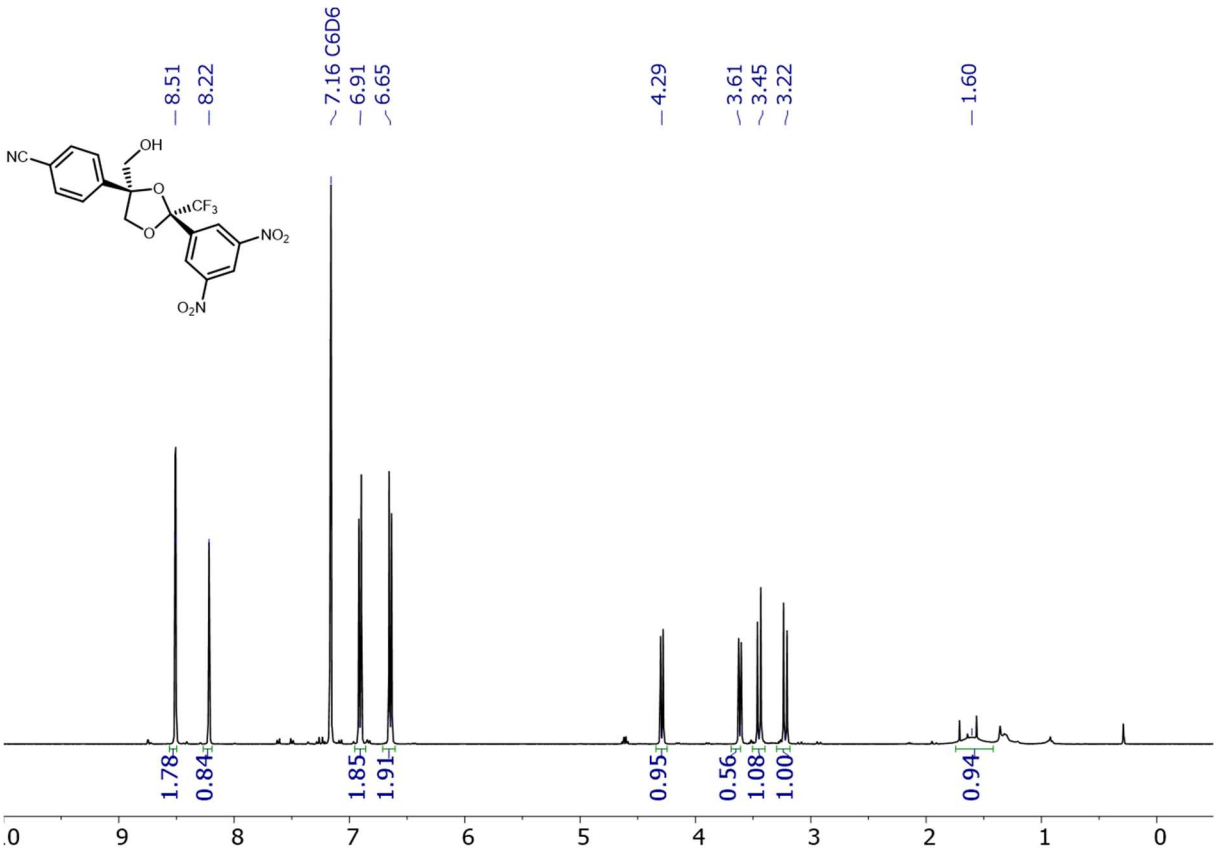

**[5g], $^{13}C$, $C_6D_6$, 101 MHz**



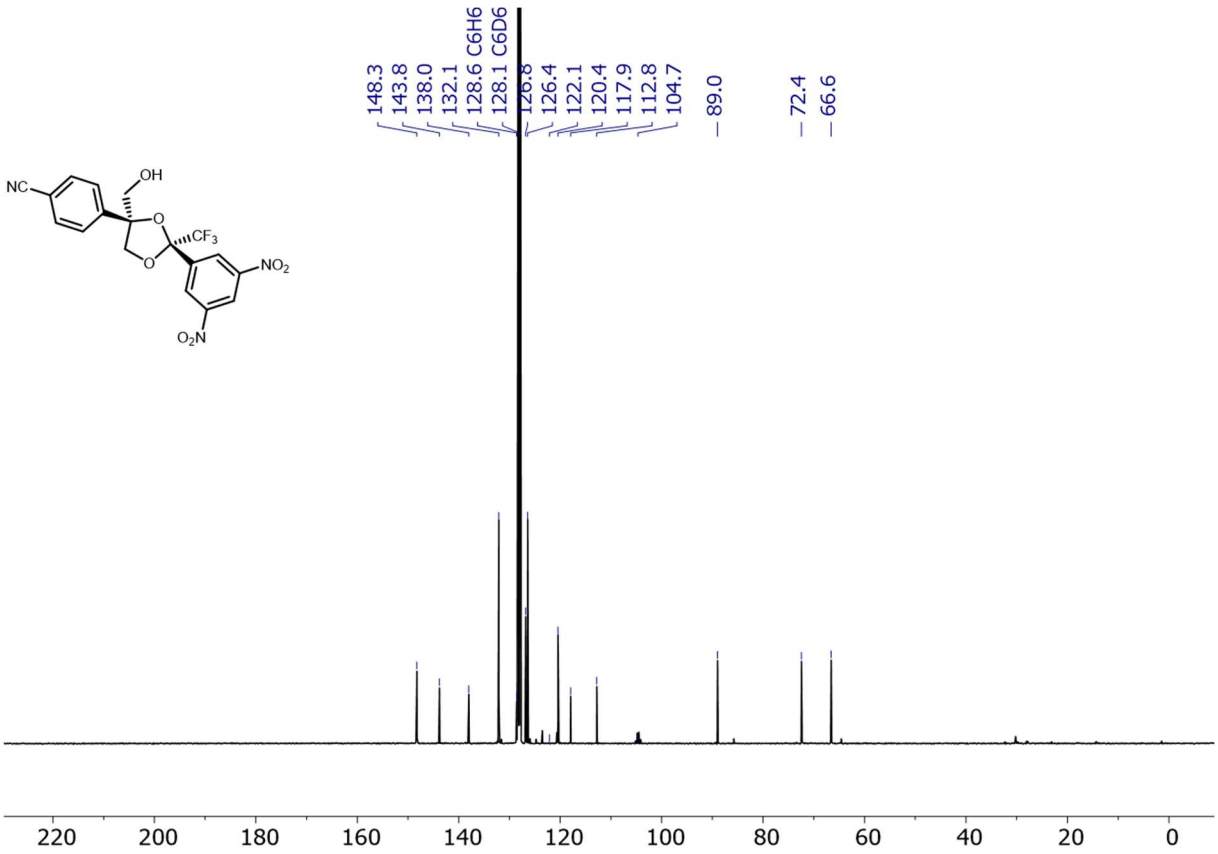
**[5g], $^{19}F$, $C_6D_6$, 377 MHz**



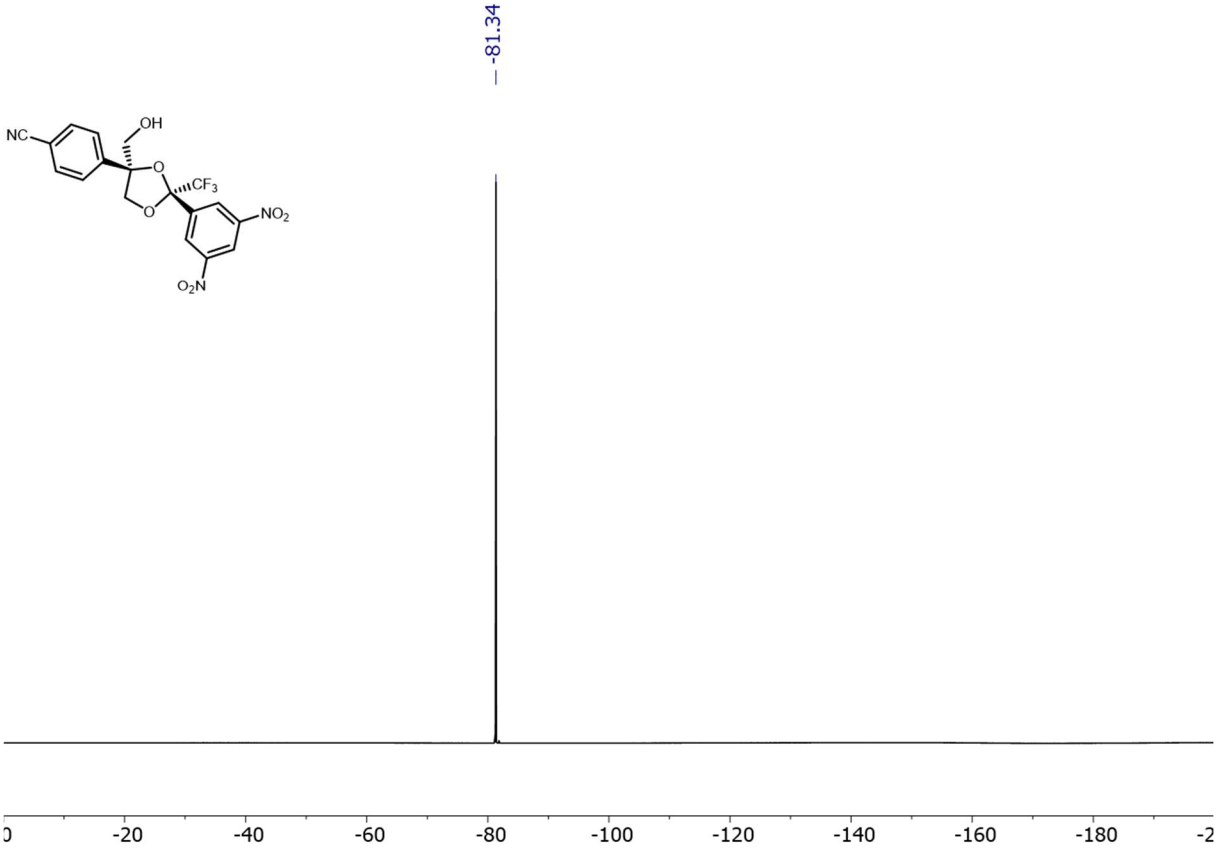
**[5h], $^{1}H$, $C_6D_6$, 400 MHz**



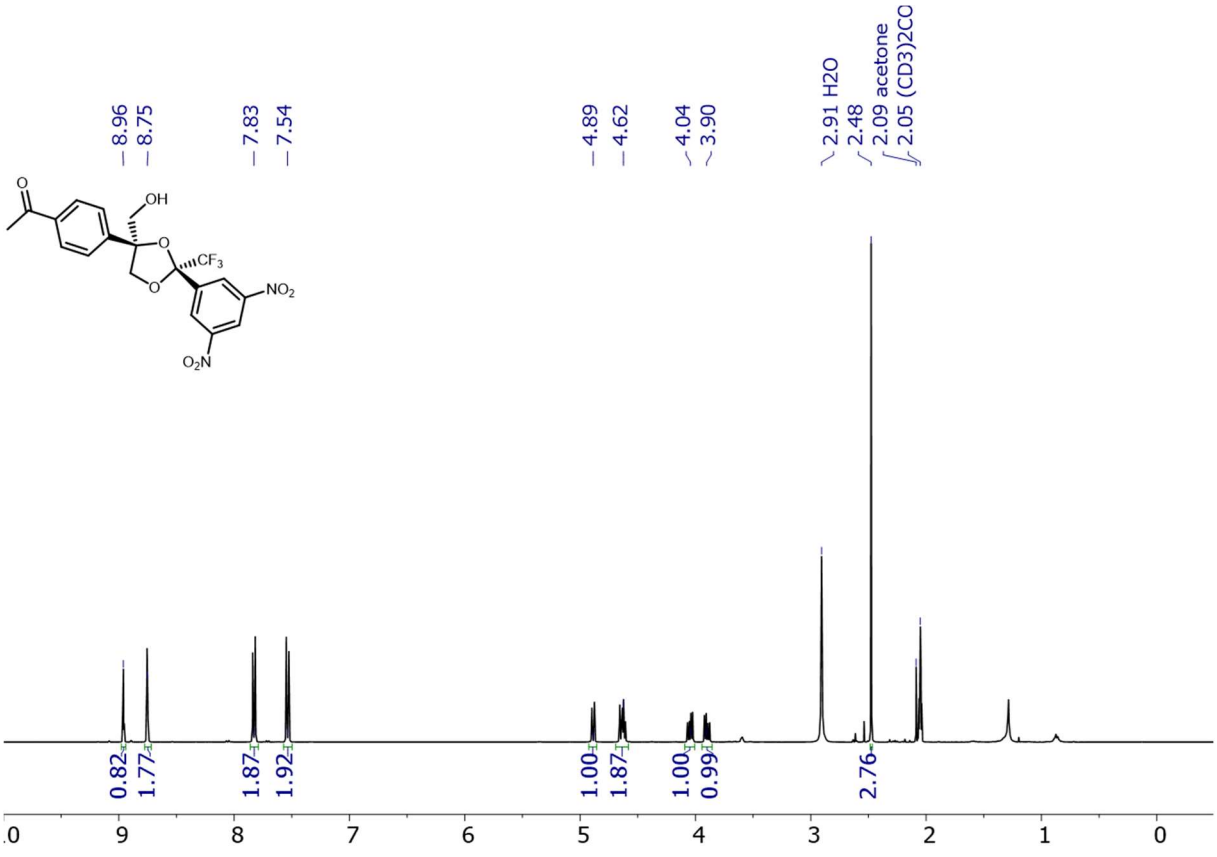

**[5h], $^{13}C$, $C_6D_6$, 101 MHz**



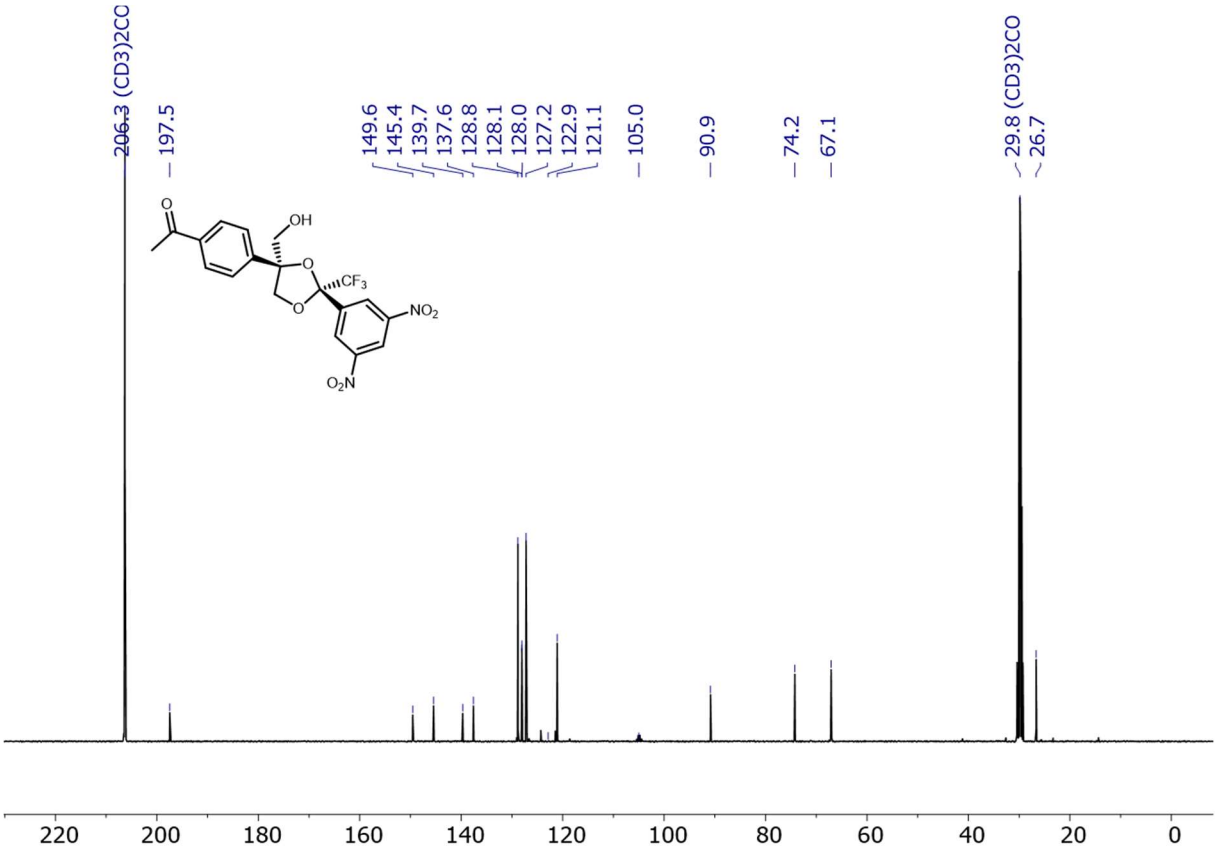
**[5h], $^{19}F$, $C_6D_6$, 377 MHz**



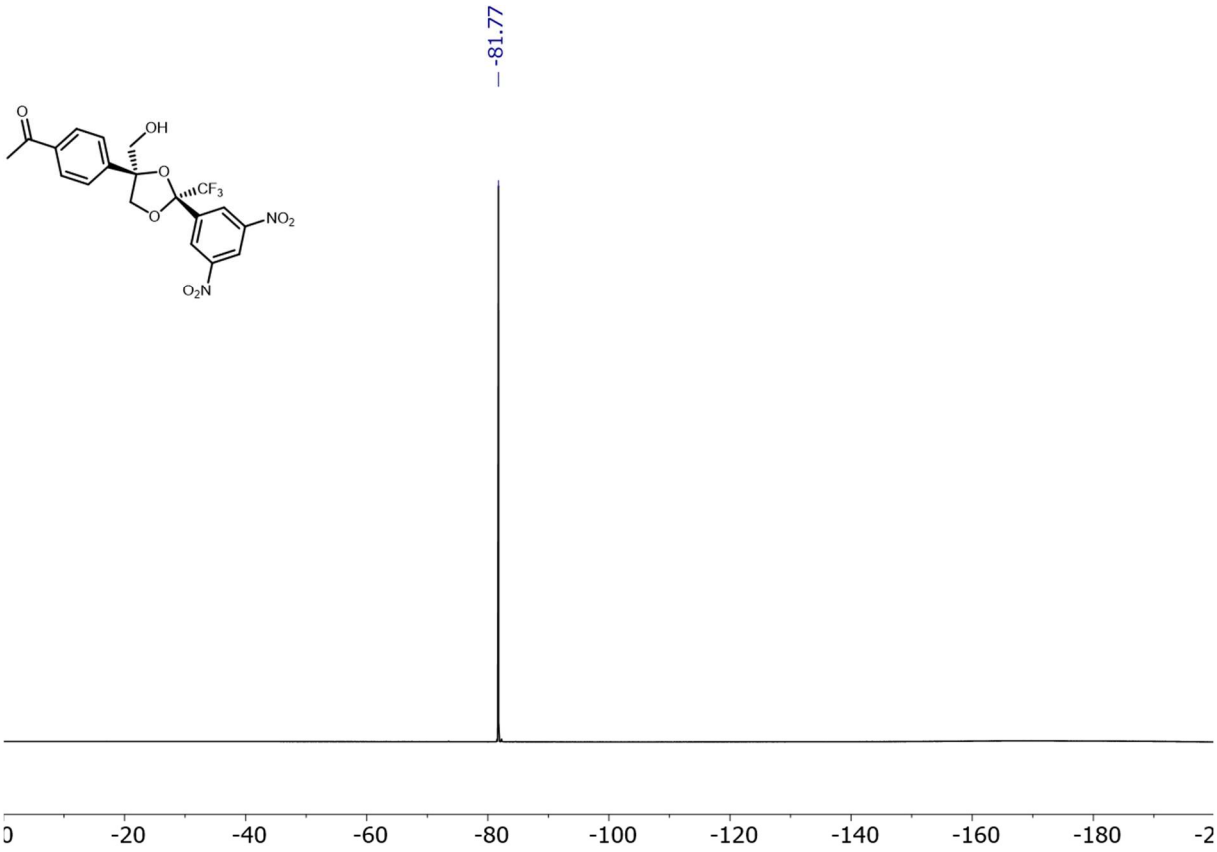
**[5i], $^{1}$H, acetone-d6, 400 MHz**



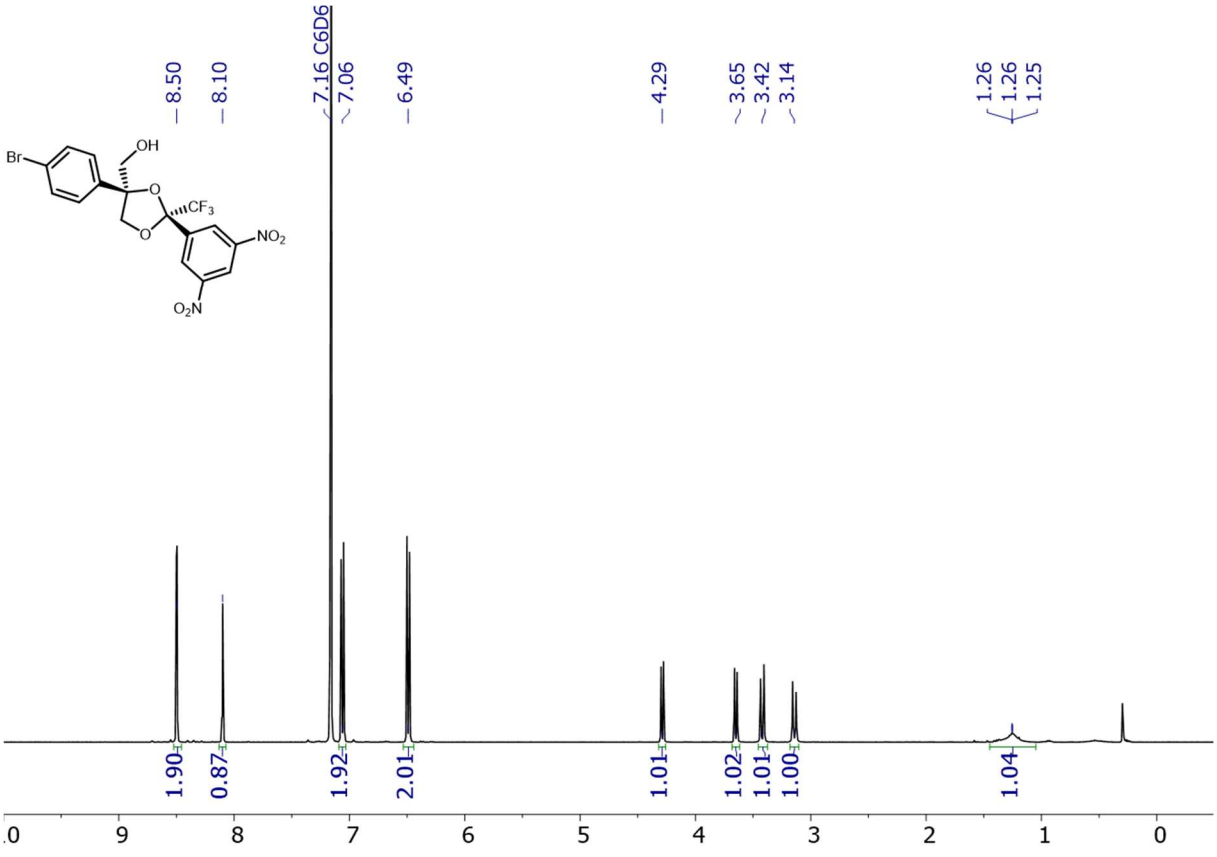

**[5i], $^{13}$C, acetone-d6, 101 MHz**



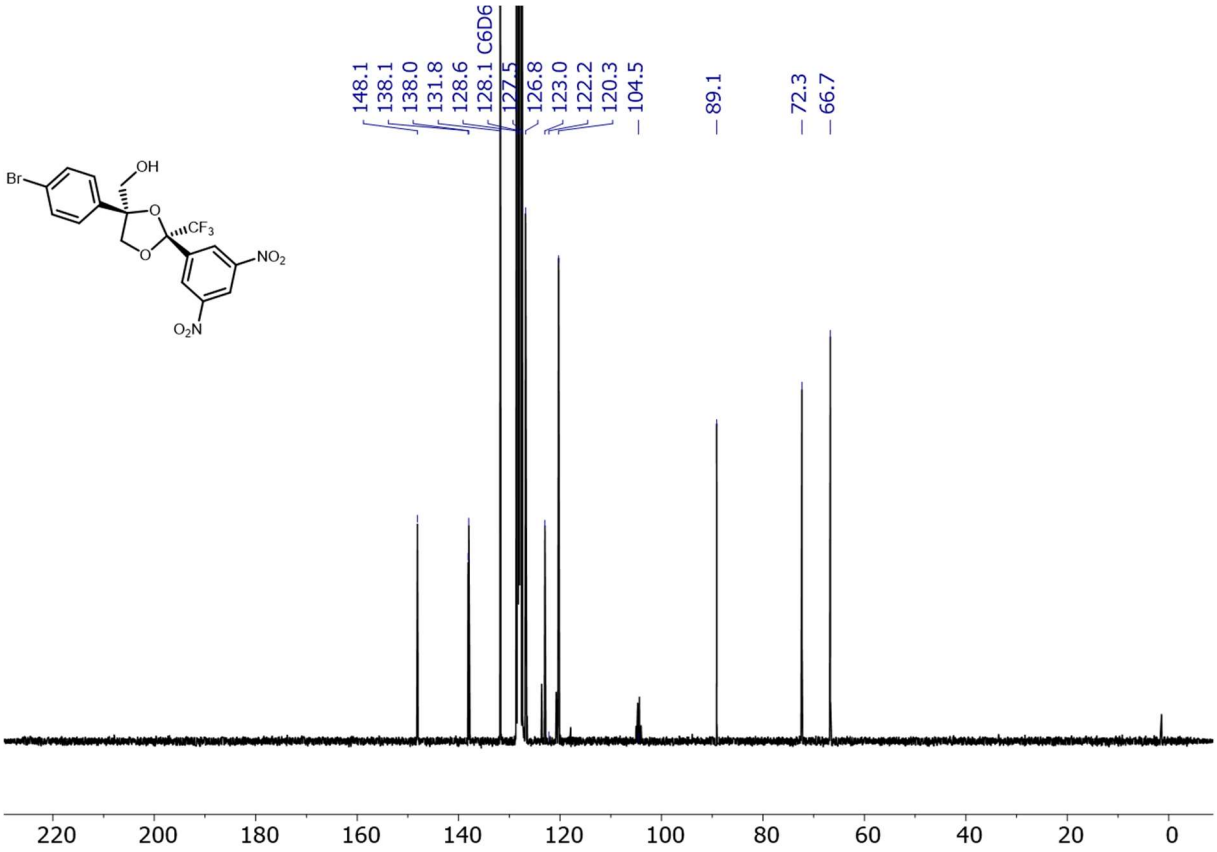
**[5i], $^{19}F$, acetone-d6, 377 MHz**



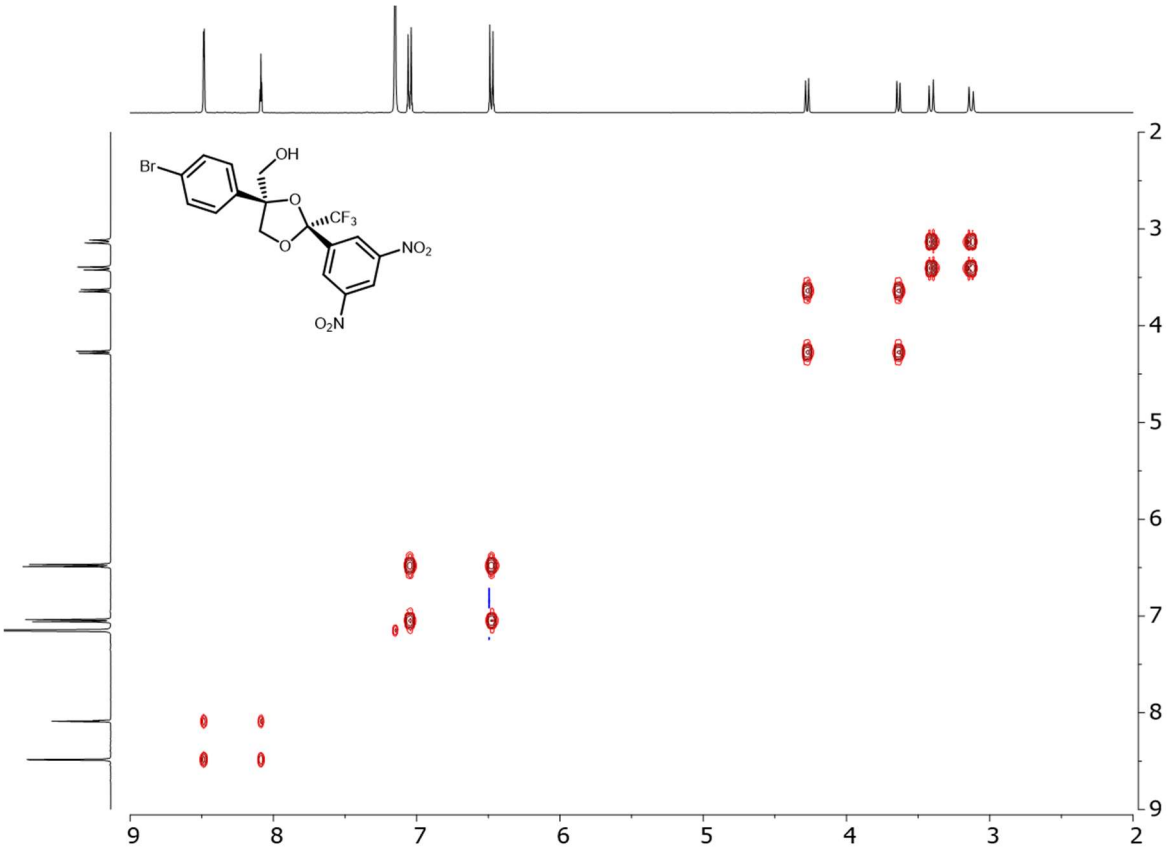
**[5j], $^{1}H$, $C_6D_6$, 400 MHz**



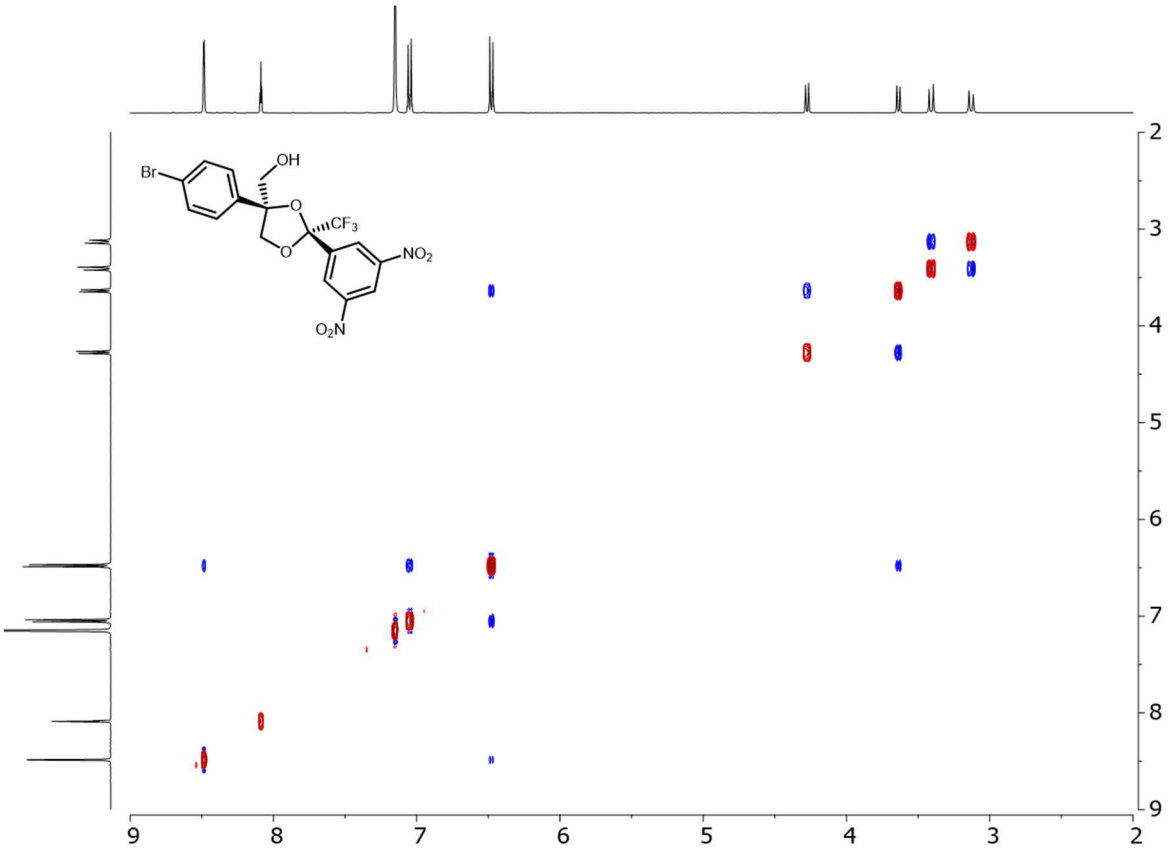

**[5j], $^{13}C$, $C_6D_6$, 101 MHz**



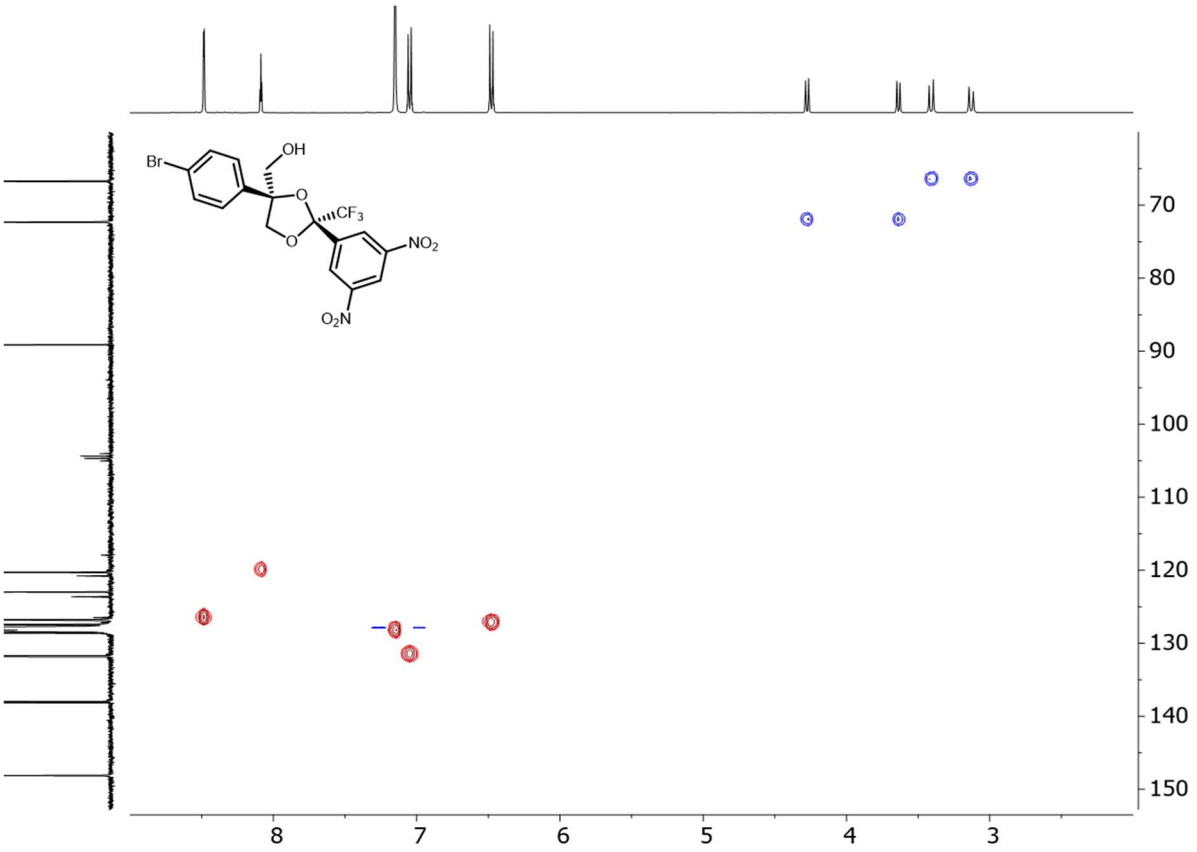
**[5j], $^{1}H$-$^{1}H$-COSY, $C_6D_6$**



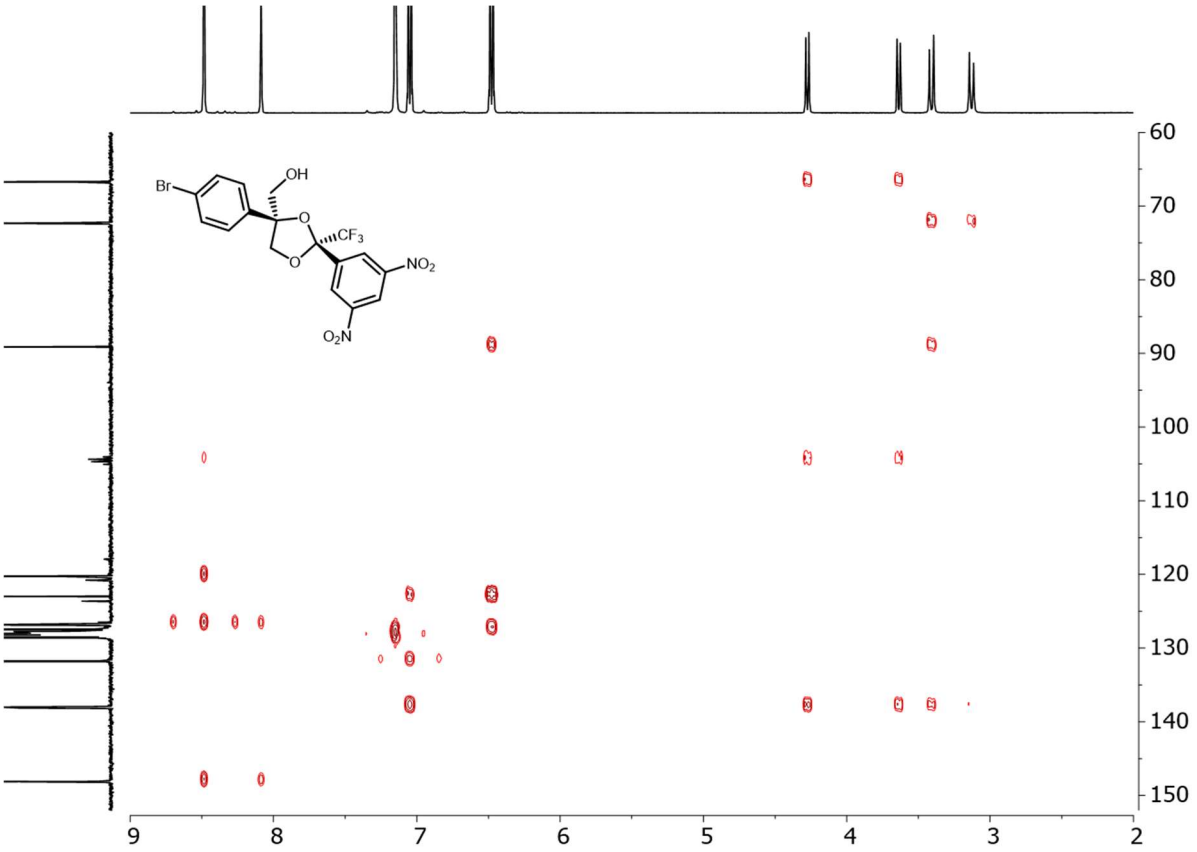

**[5j], $^{1}H$-$^{1}H$ NOESY, $C_6D_6$**



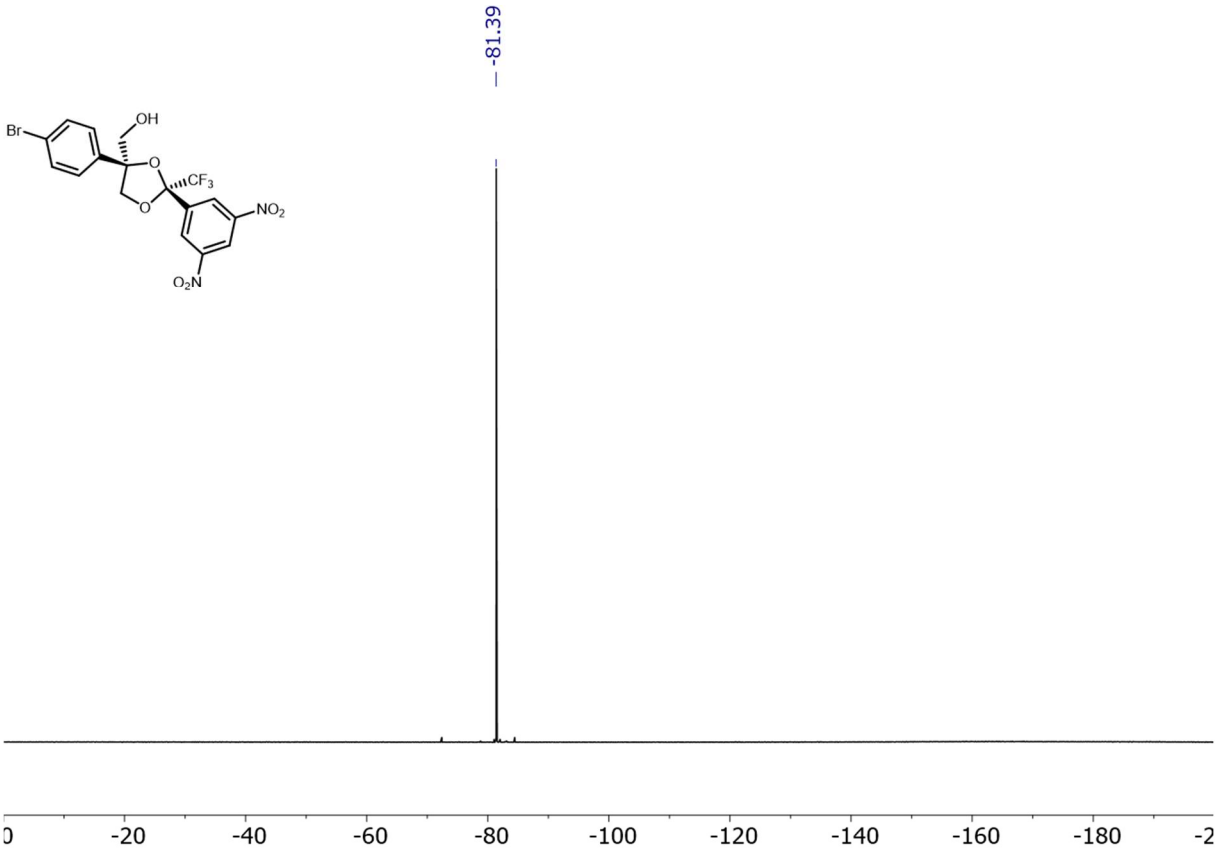
**[5j], HSQC, $C_6D_6$**



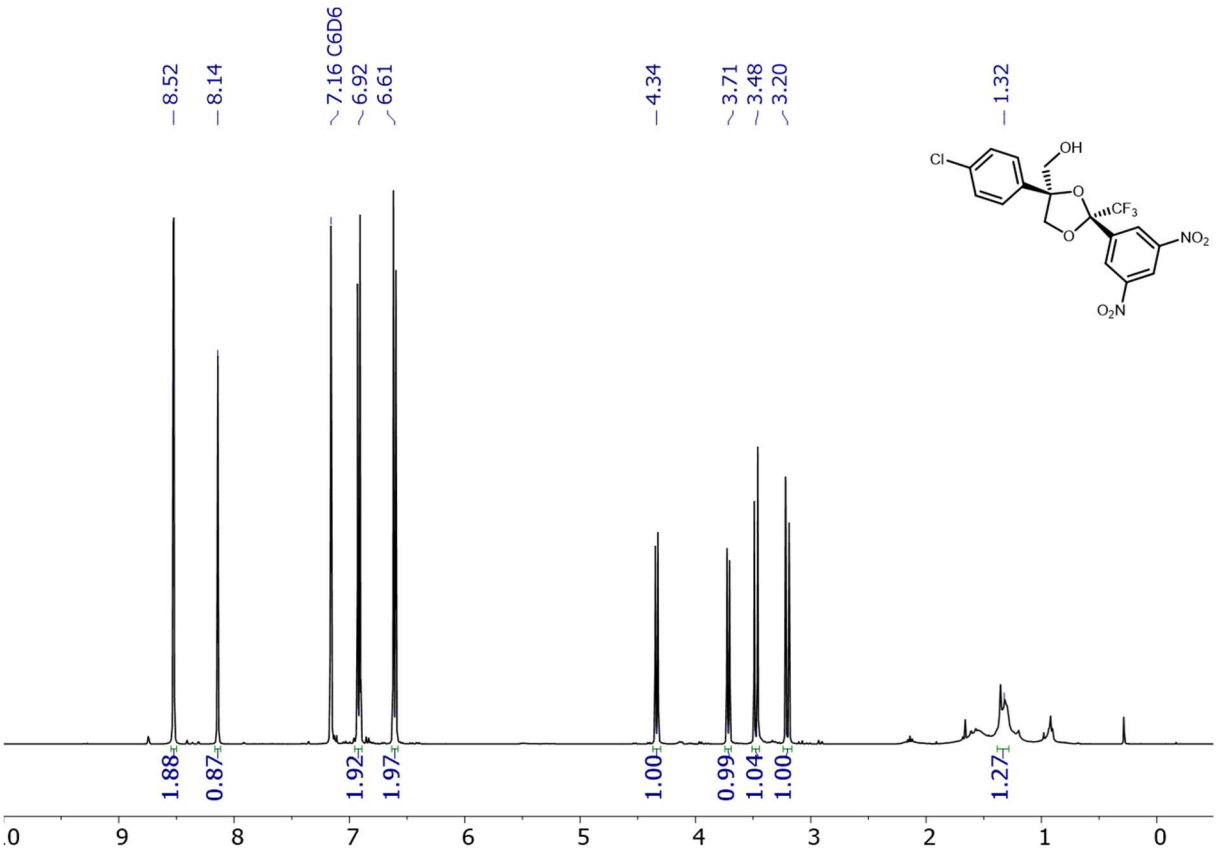

**[5j], HMBC, $C_6D_6$**



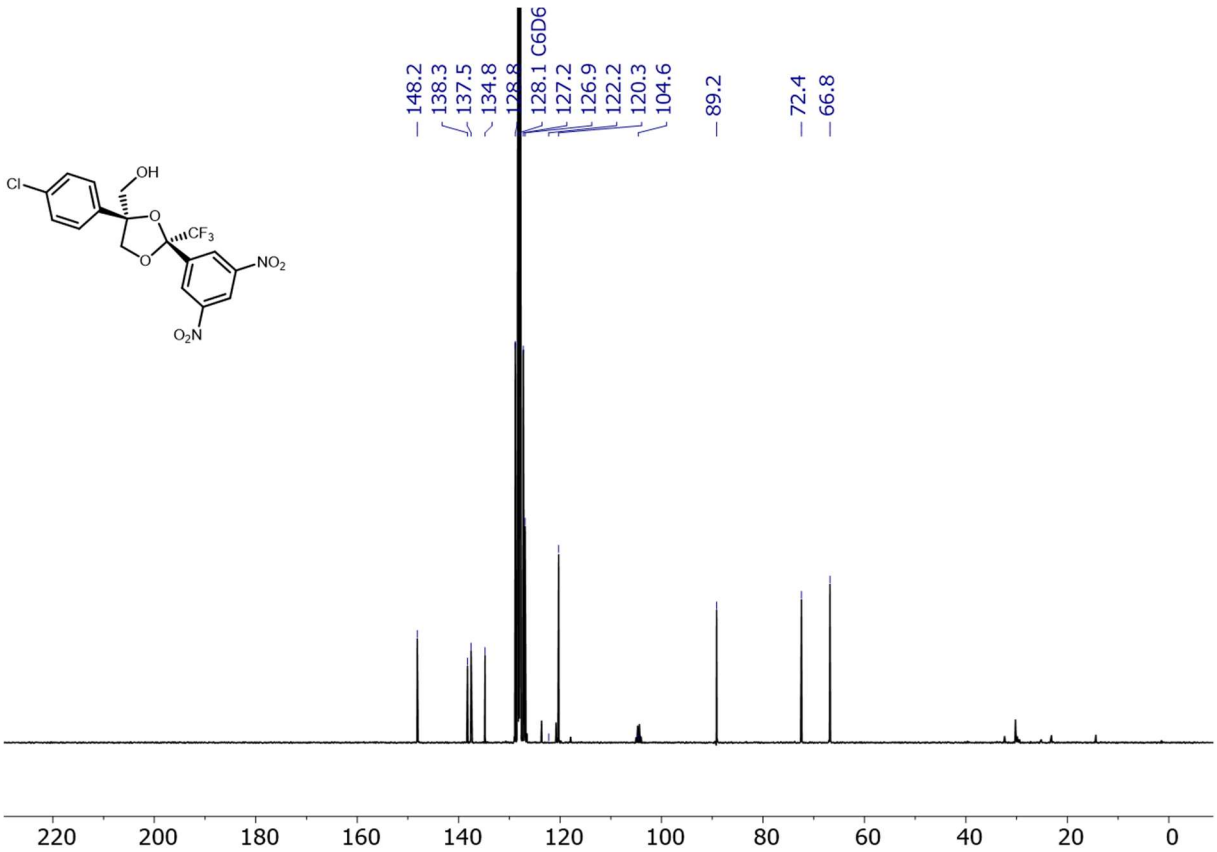
**[5j], $^{19}F$, $C_6D_6$, 282 MHz**



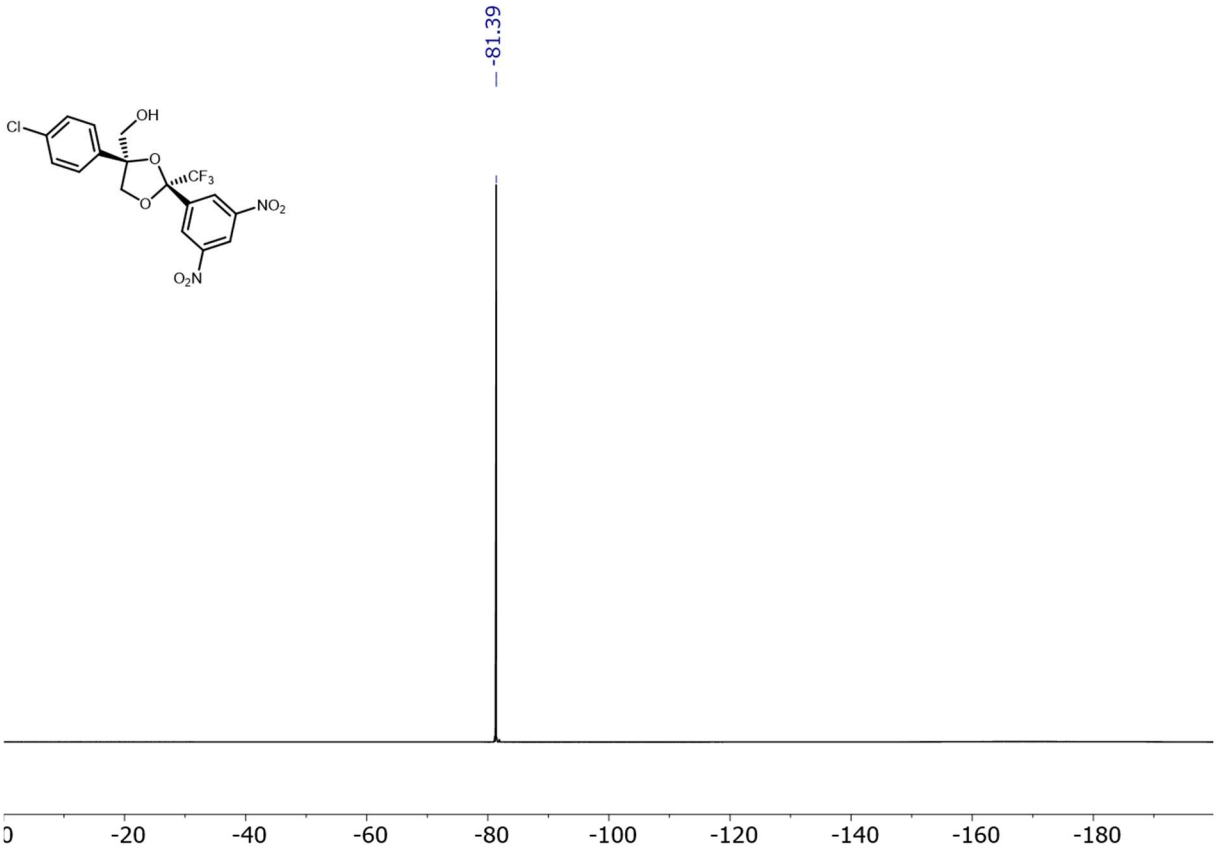
**[5k], $^{1}H$, $C_6D_6$, 400 MHz**



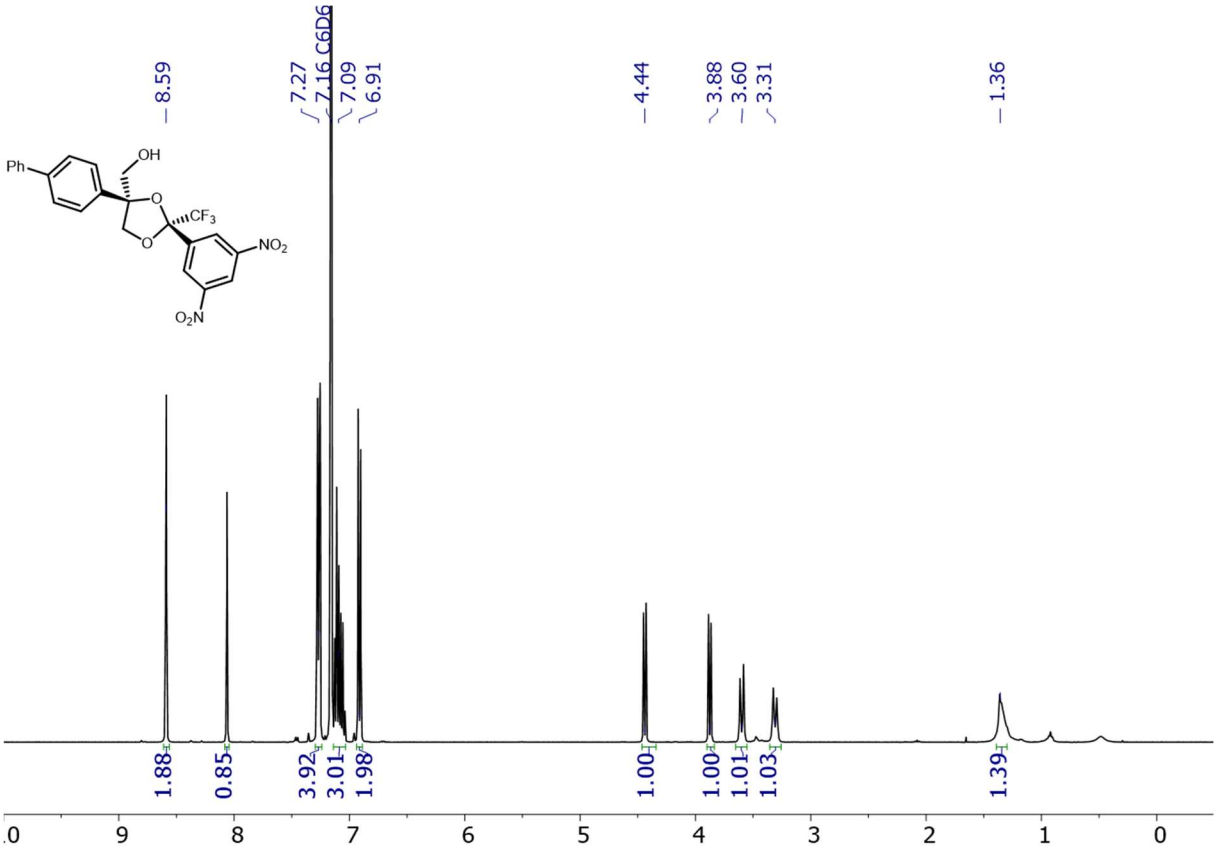

**[5k], $^{13}C$, $C_6D_6$, 101 MHz**



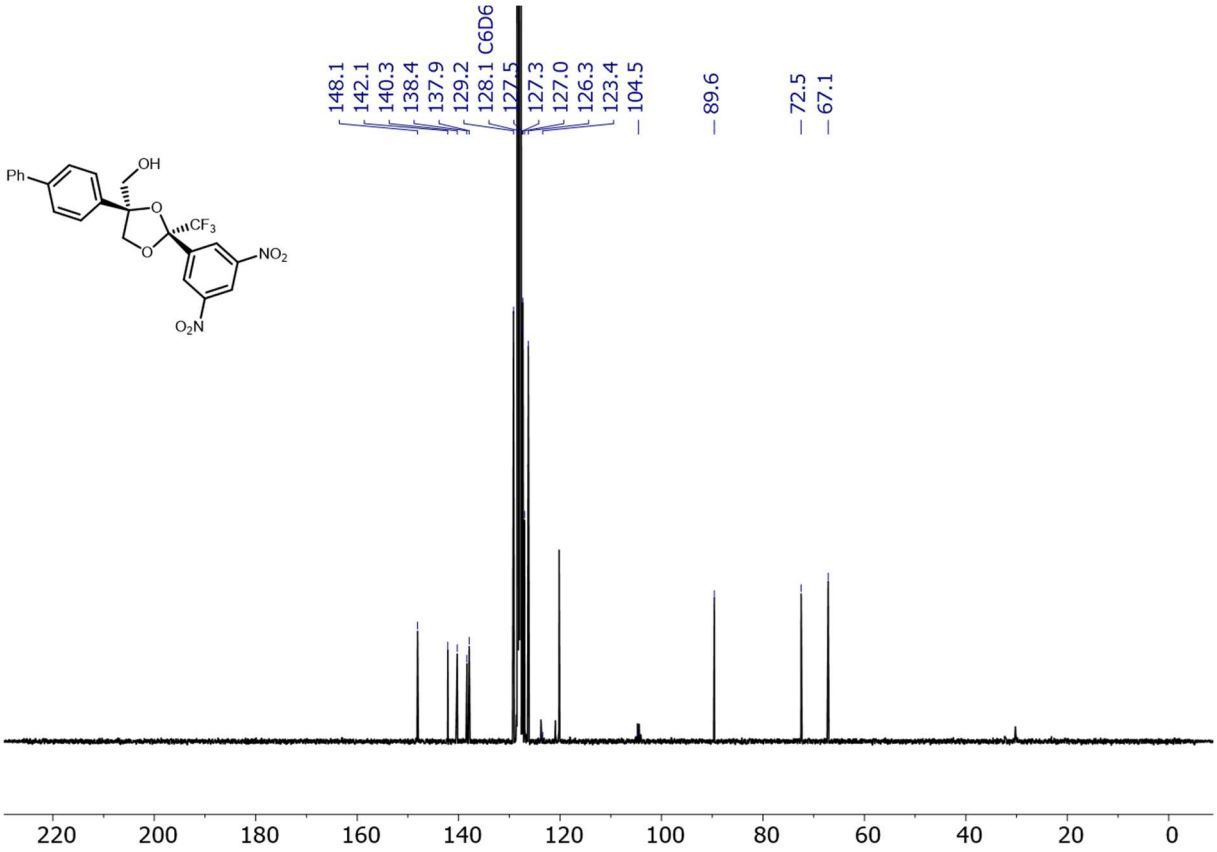
**[5k], $^{19}F$, $C_6D_6$, 377 MHz**



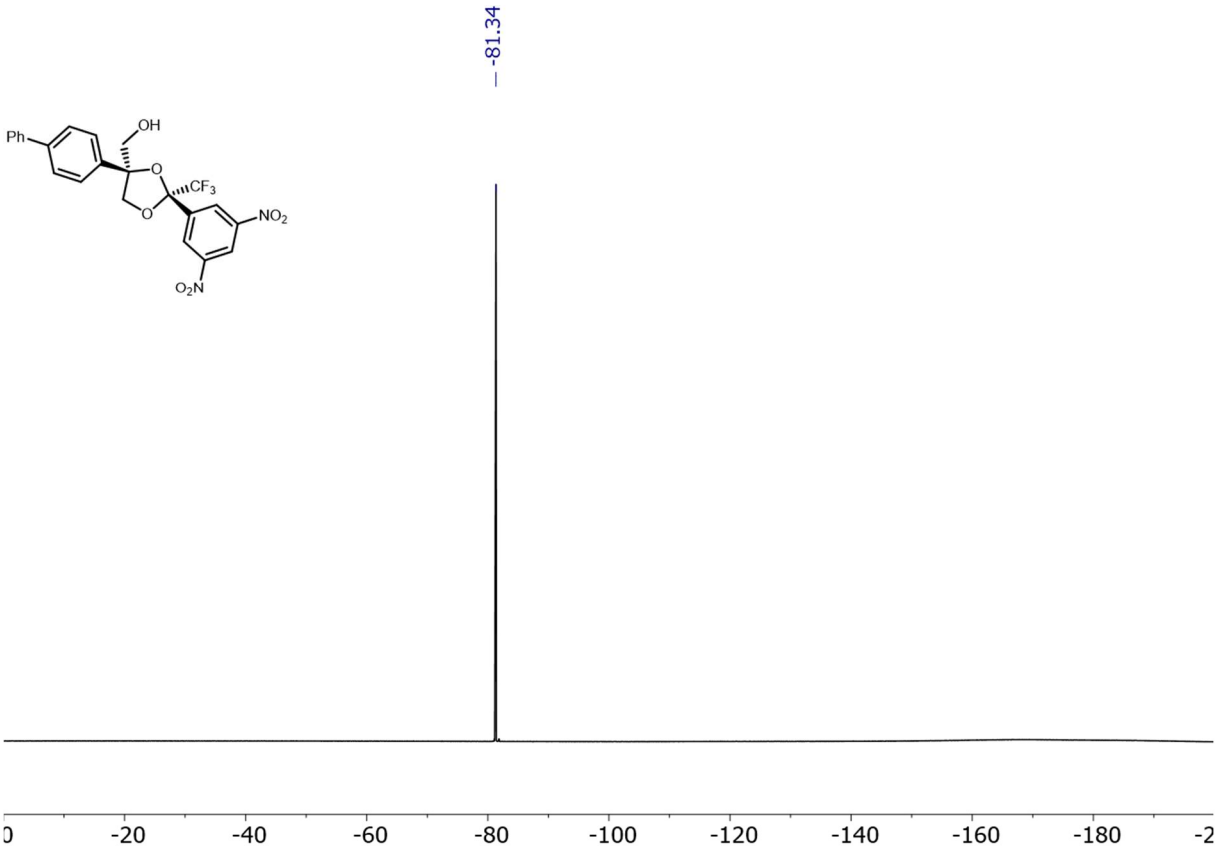
**[5l], $^{1}H$, $C_6D_6$, 400 MHz**



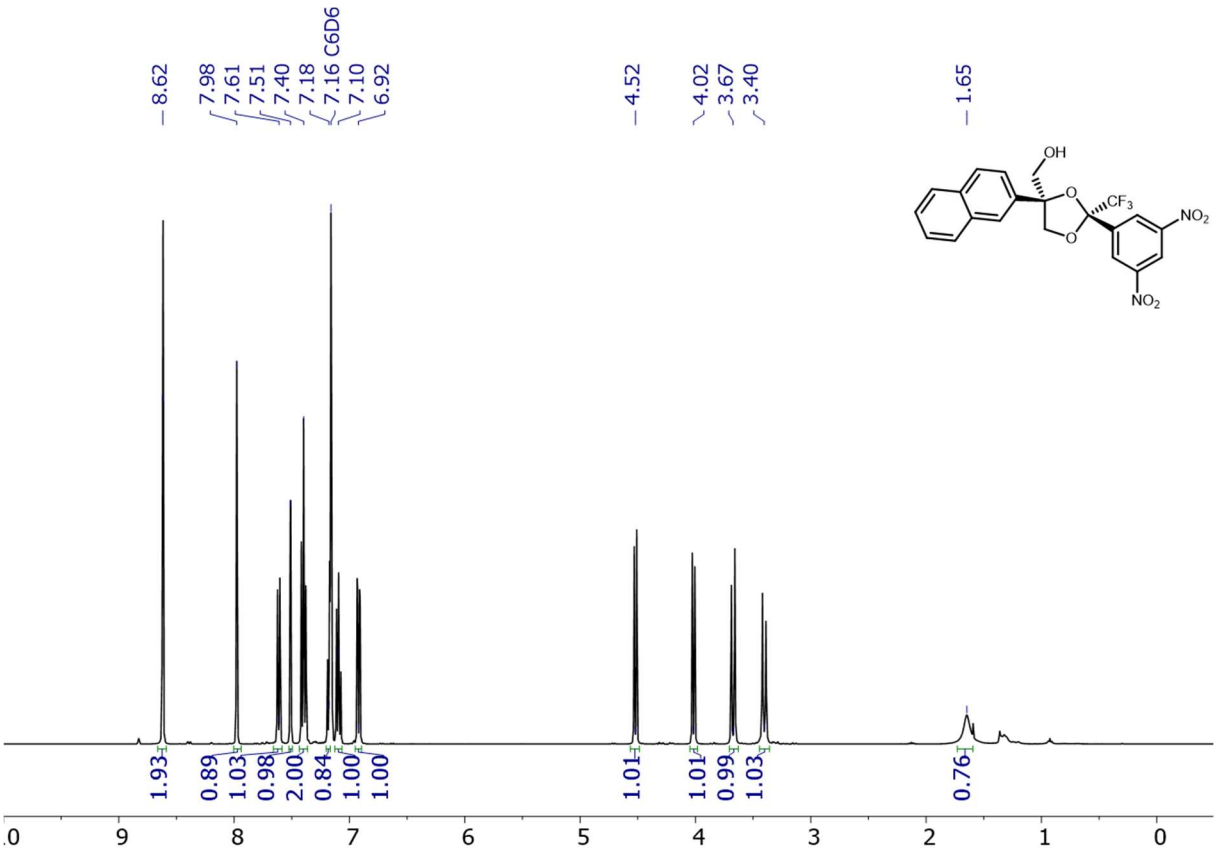

**[5l], $^{13}C$, $C_6D_6$, 101 MHz**



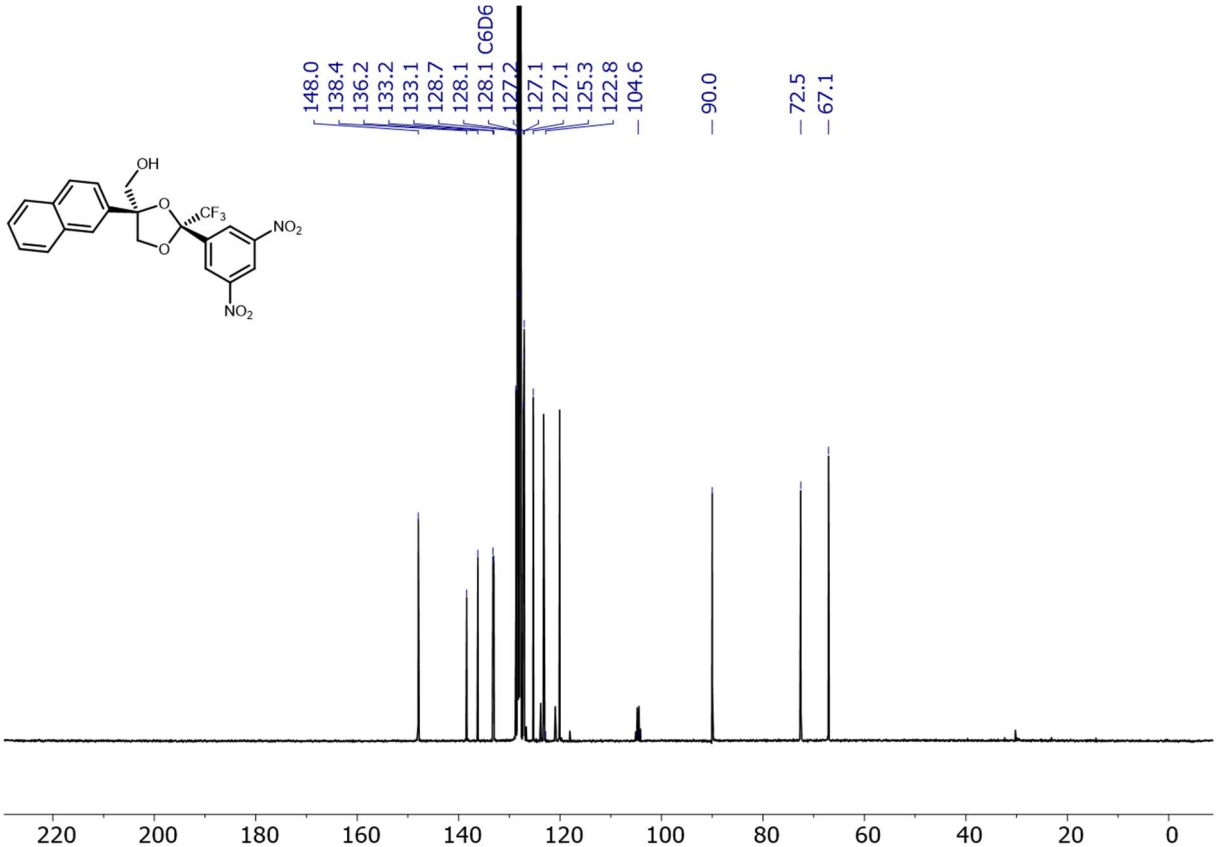
**[5l], $^{19}F$, $C_6D_6$, 377 MHz**



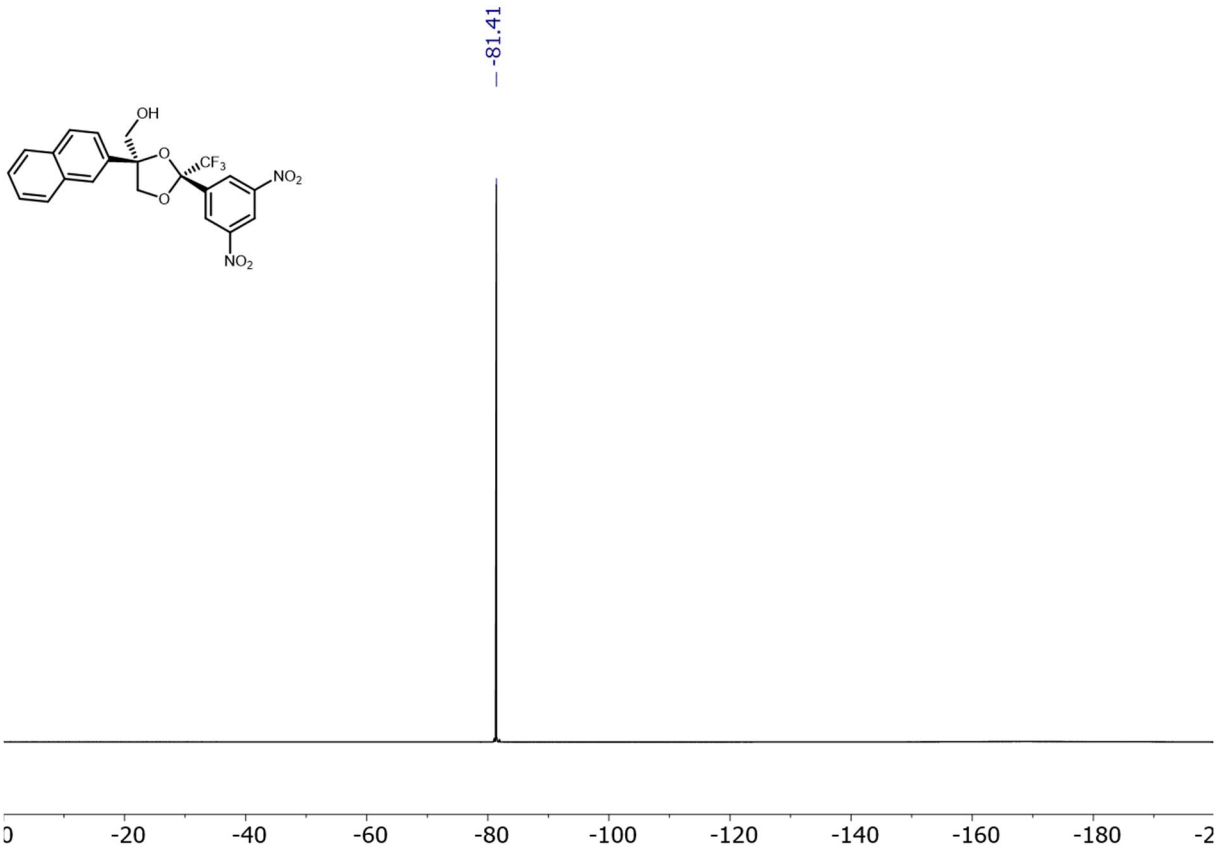
**[5m], $^{1}H$, $C_6D_6$, 400 MHz**



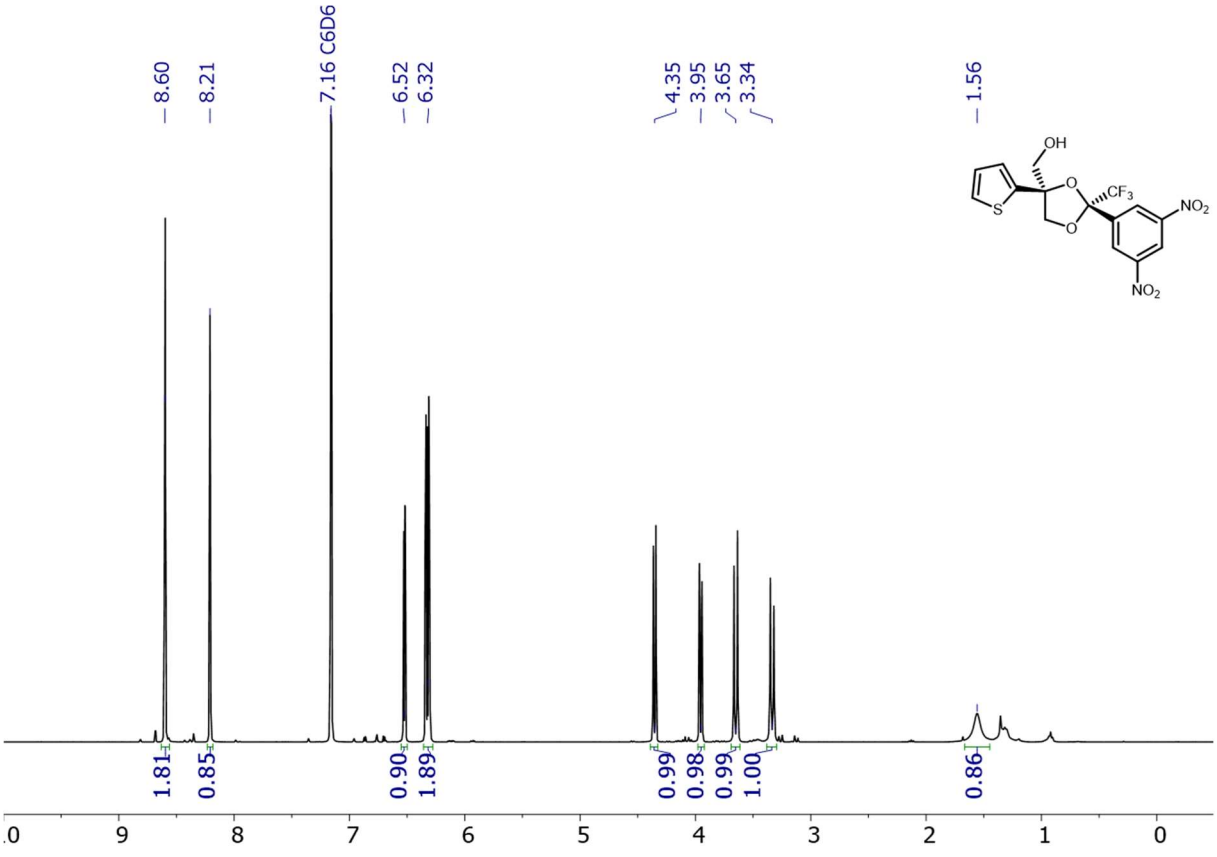

**[5m], $^{13}C$, $C_6D_6$, 101 MHz**



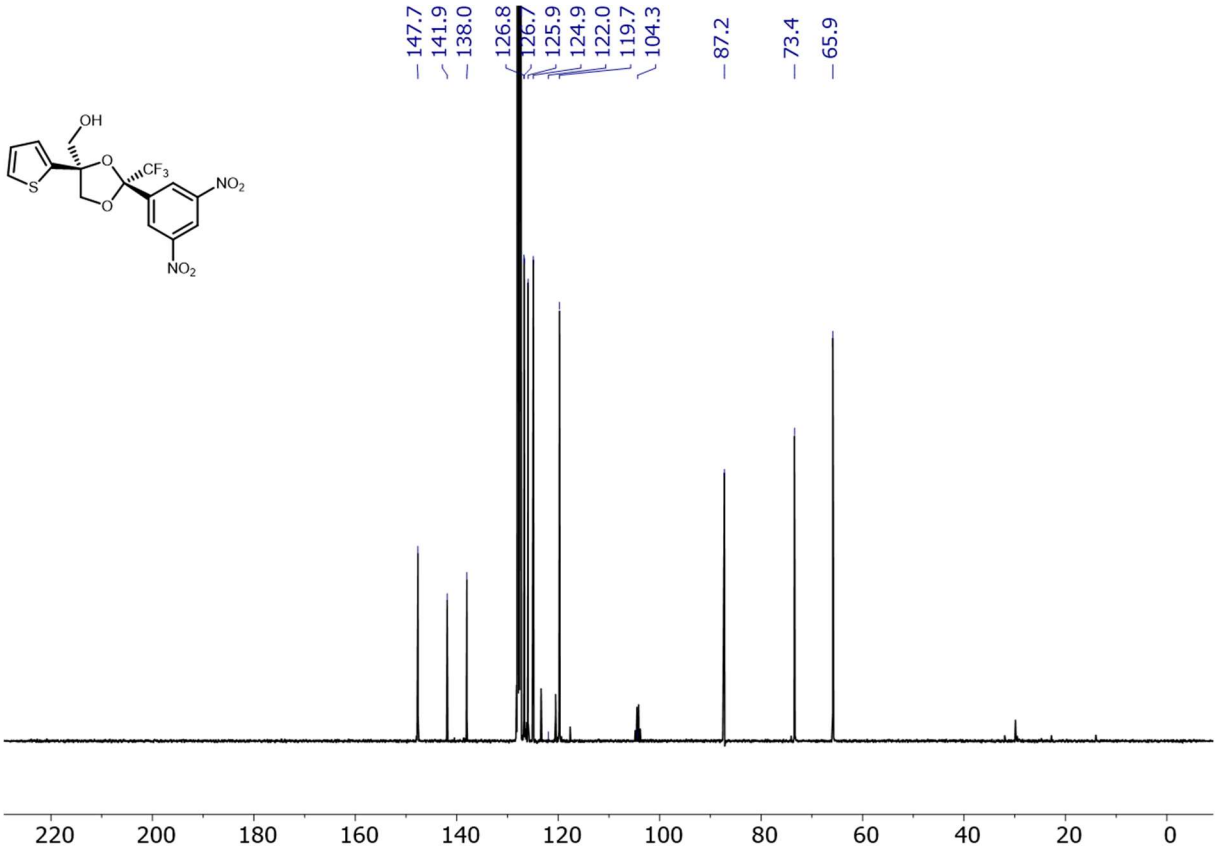
**[5m], $^{19}F$, $C_6D_6$, 377 MHz**



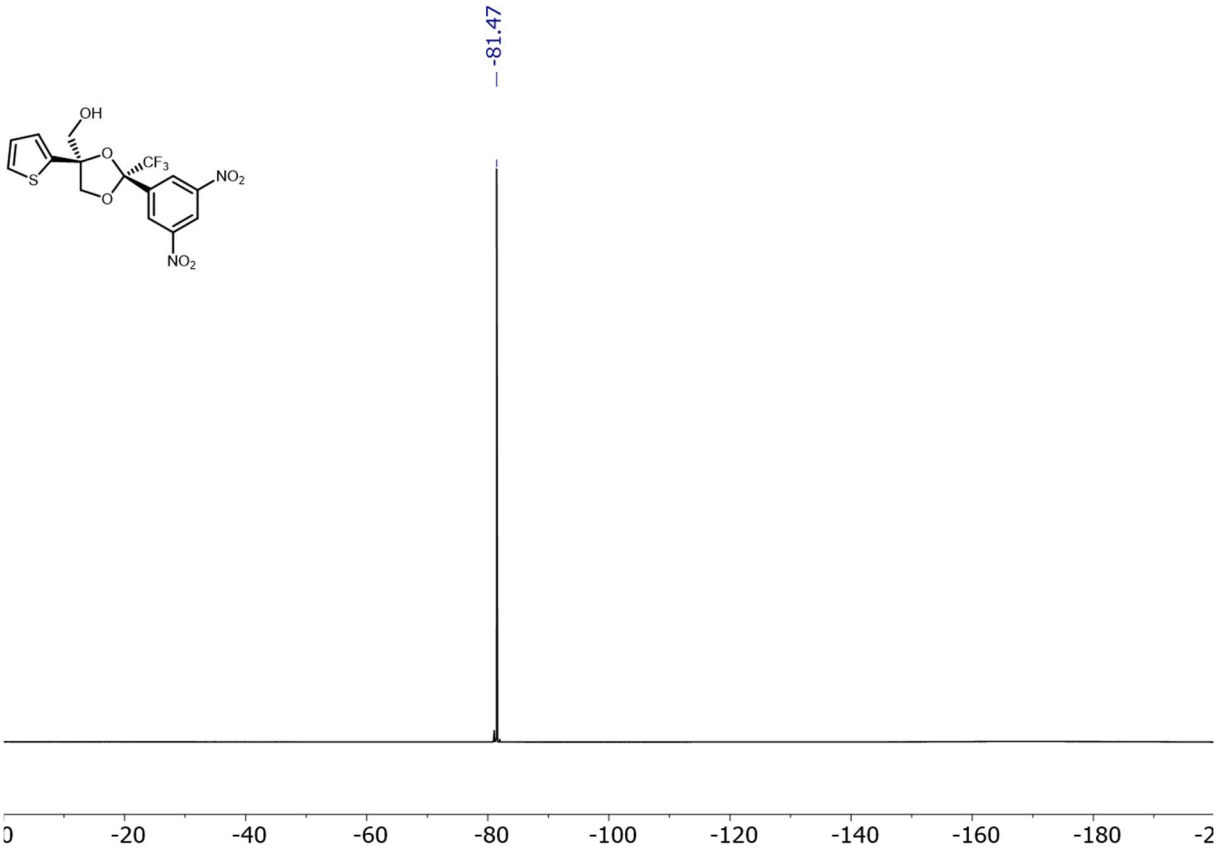
**[5n], $^{1}H$, $C_6D_6$, 400 MHz**



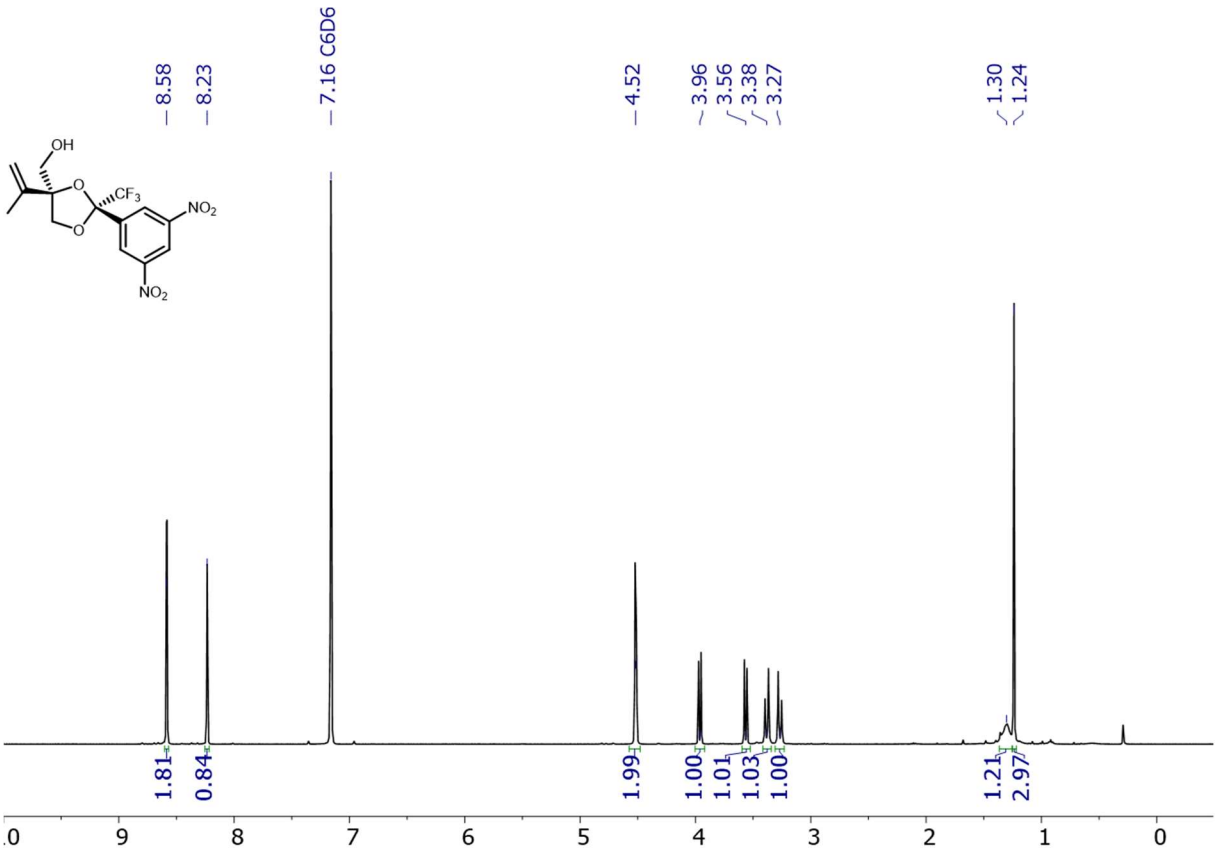

**[5n], $^{13}C$, $C_6D_6$, 101 MHz**



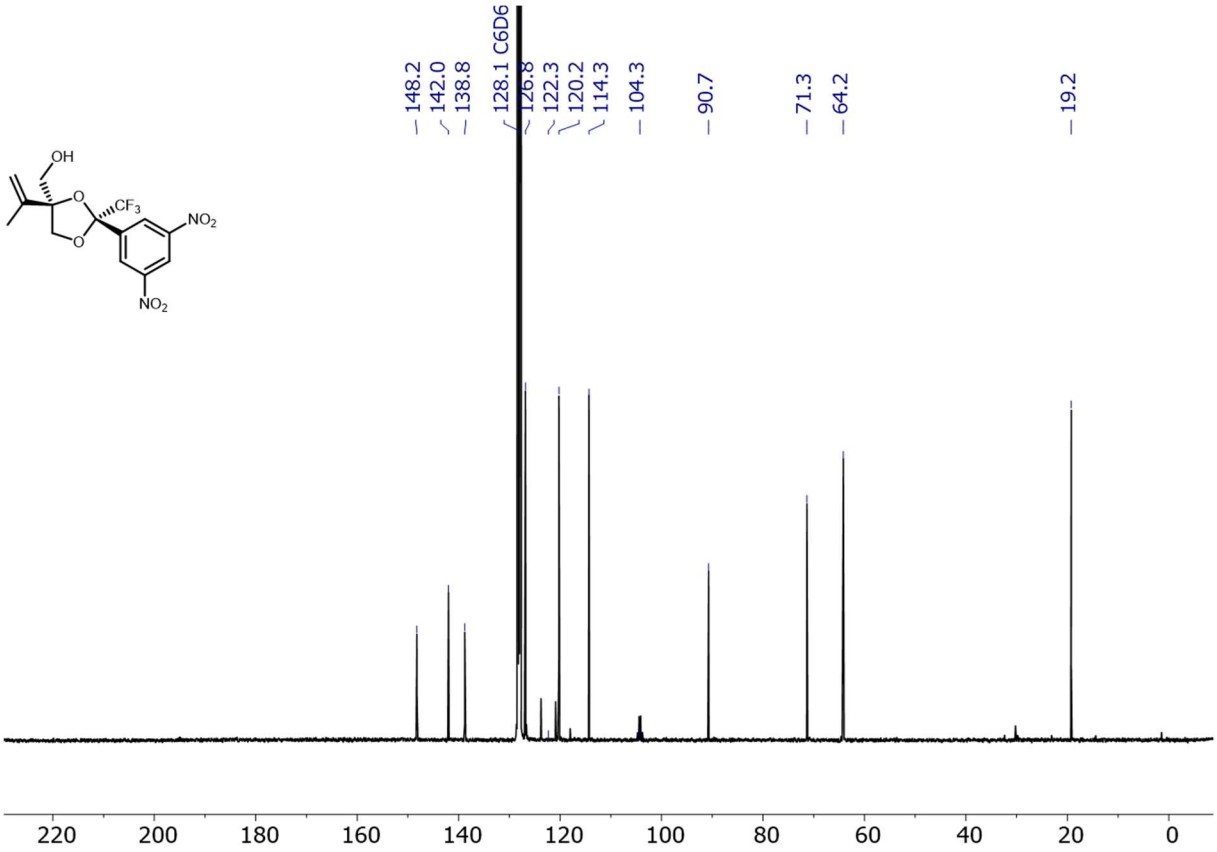
**[5n], $^{19}F$, $C_6D_6$, 377 MHz**



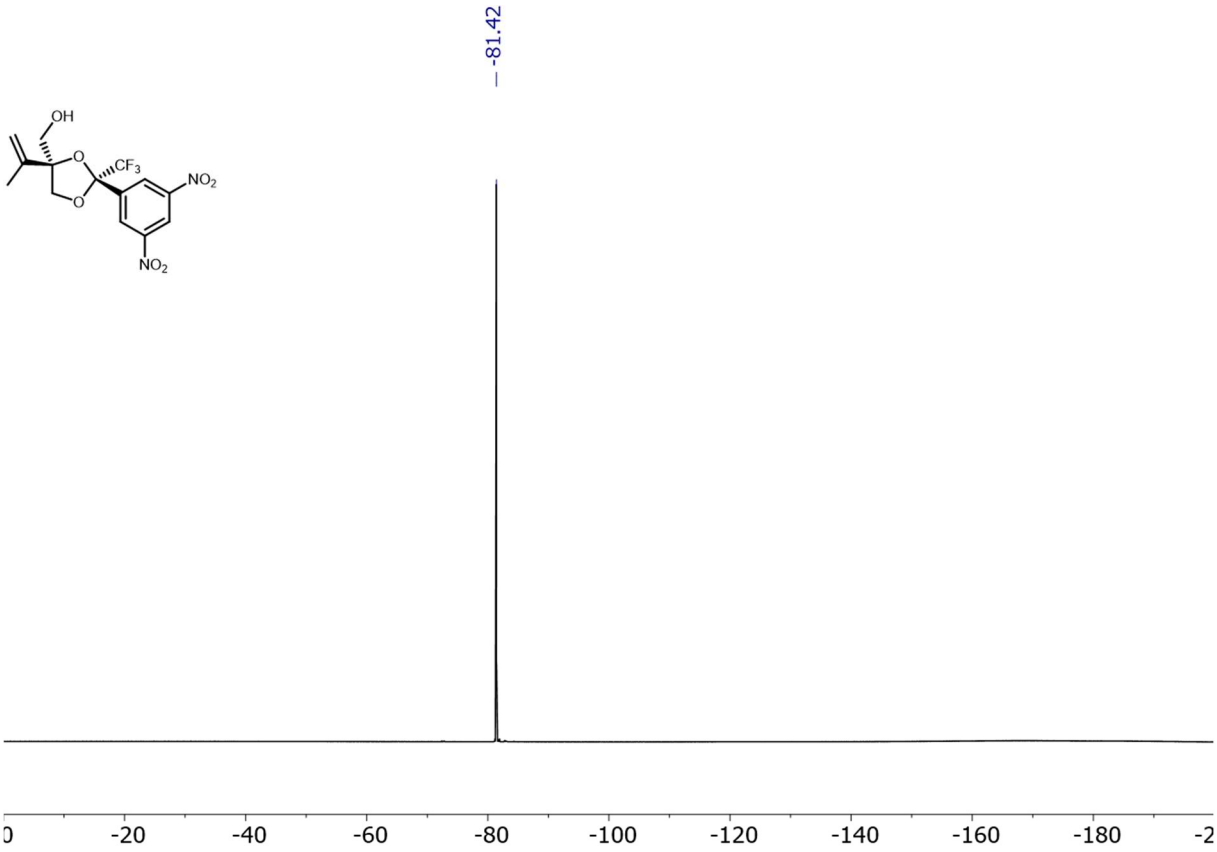
**[5o], $^{1}H$, $C_6D_6$, 400 MHz**




**[5o], $^{13}C$, $C_6D_6$, 101 MHz**

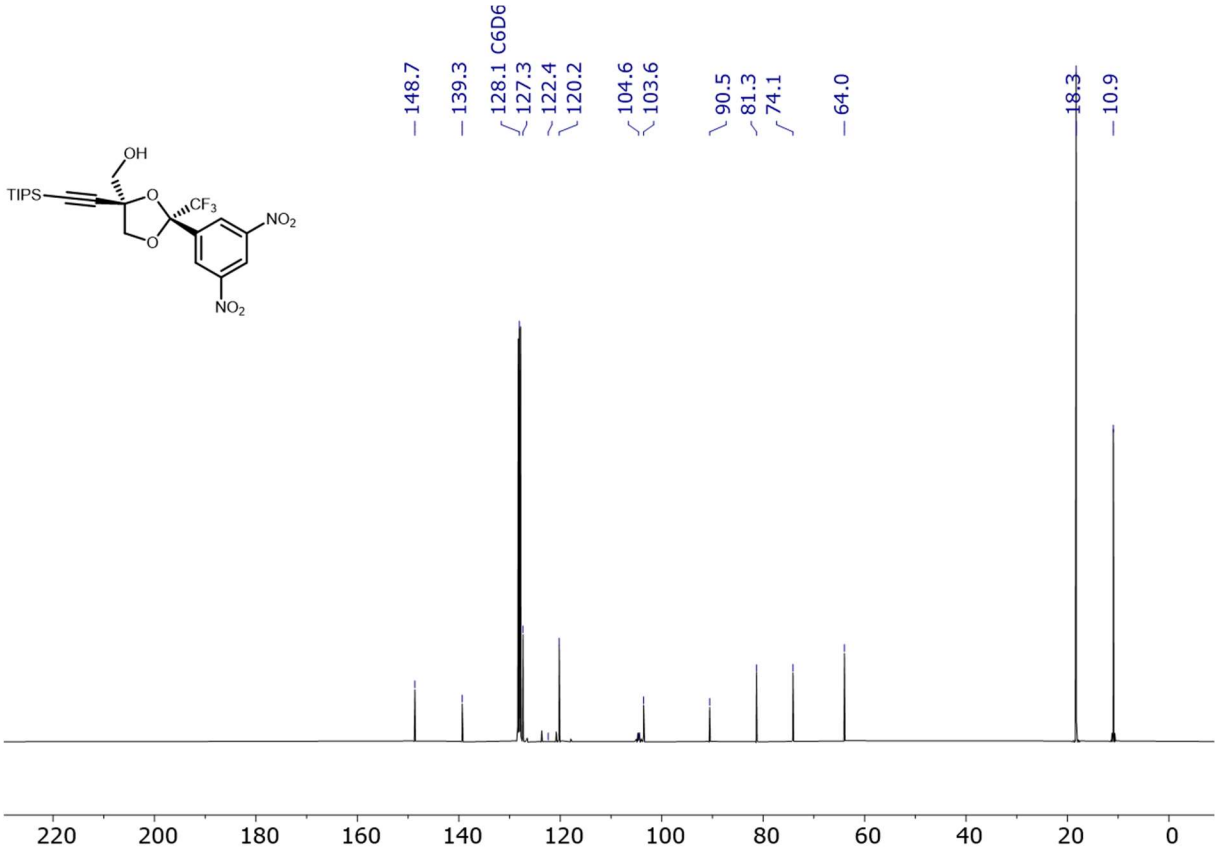


**[5o], $^{19}F$, $C_6D_6$, 377 MHz**

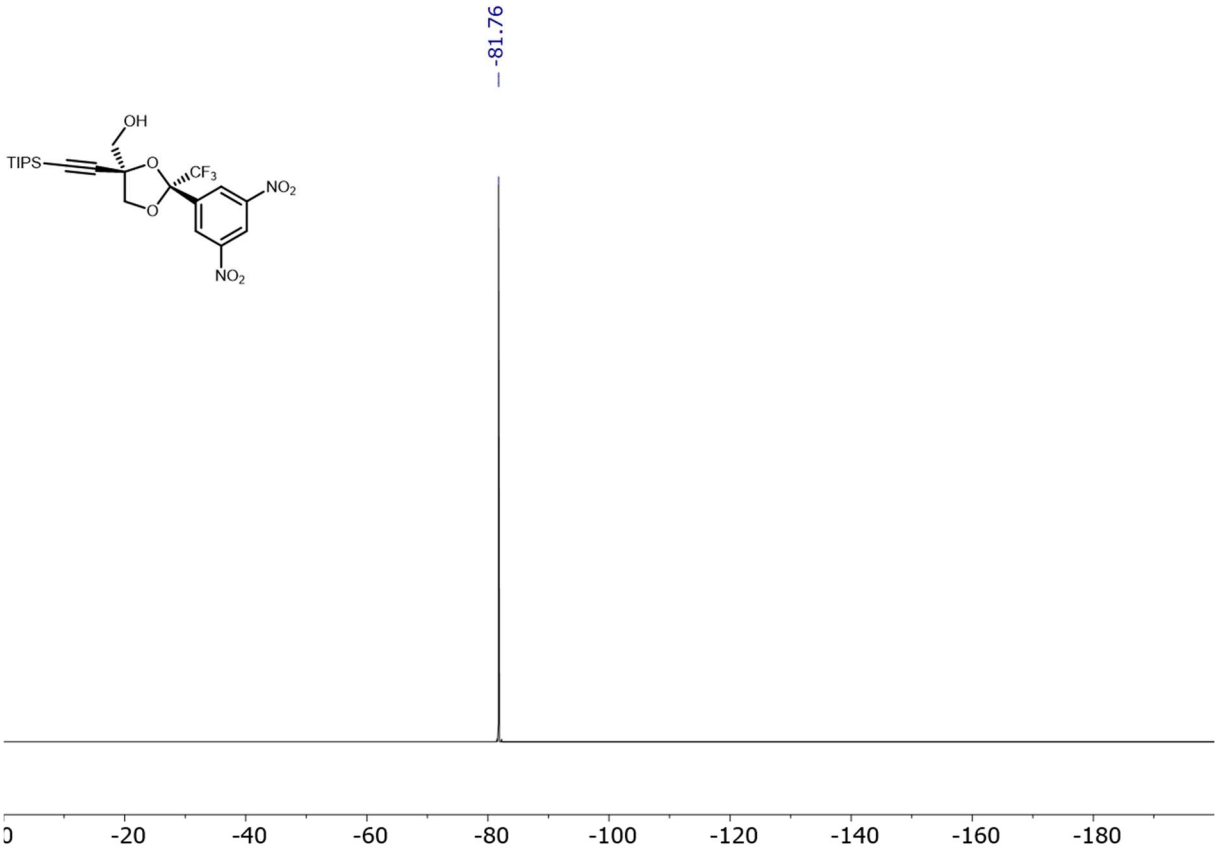


**[5p], $^{1}H$, $C_6D_6$, 400 MHz**

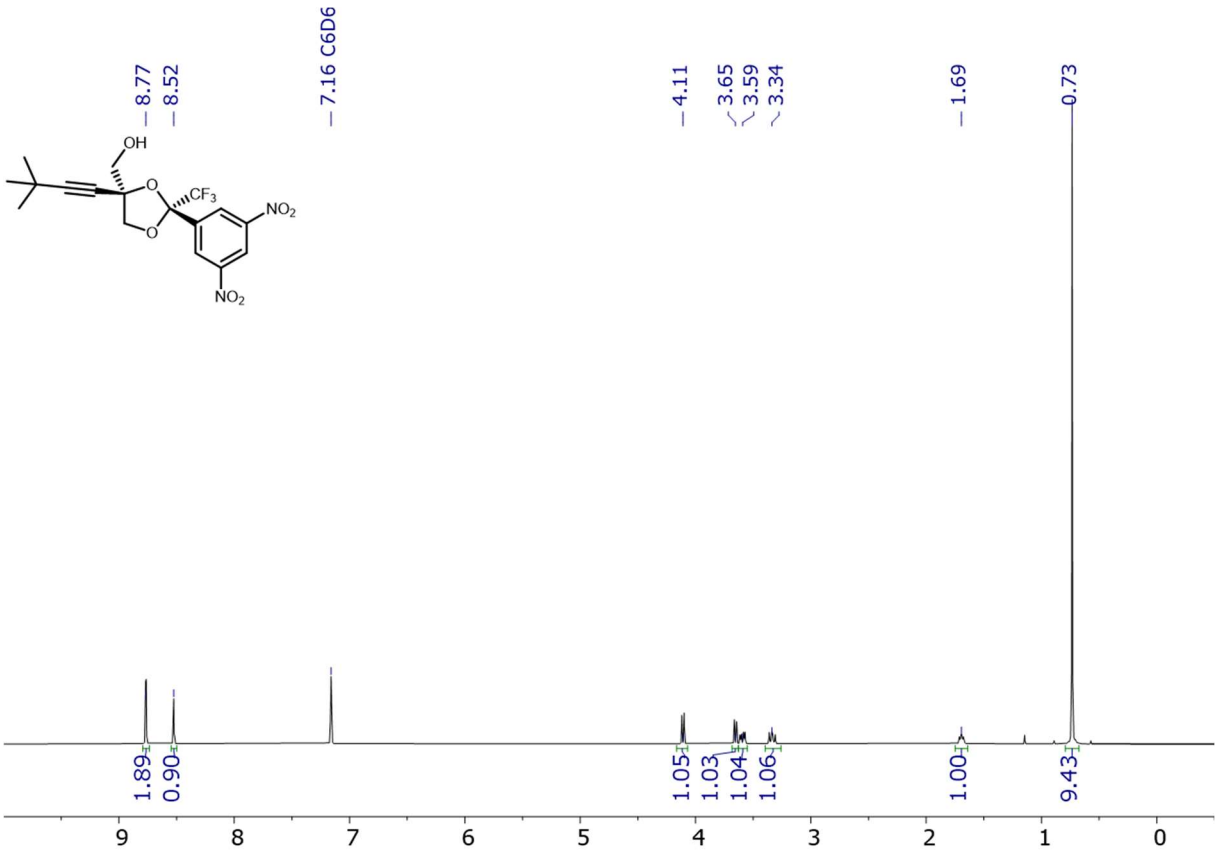

**[5p], $^{13}C$, $C_6D_6$, 101 MHz**



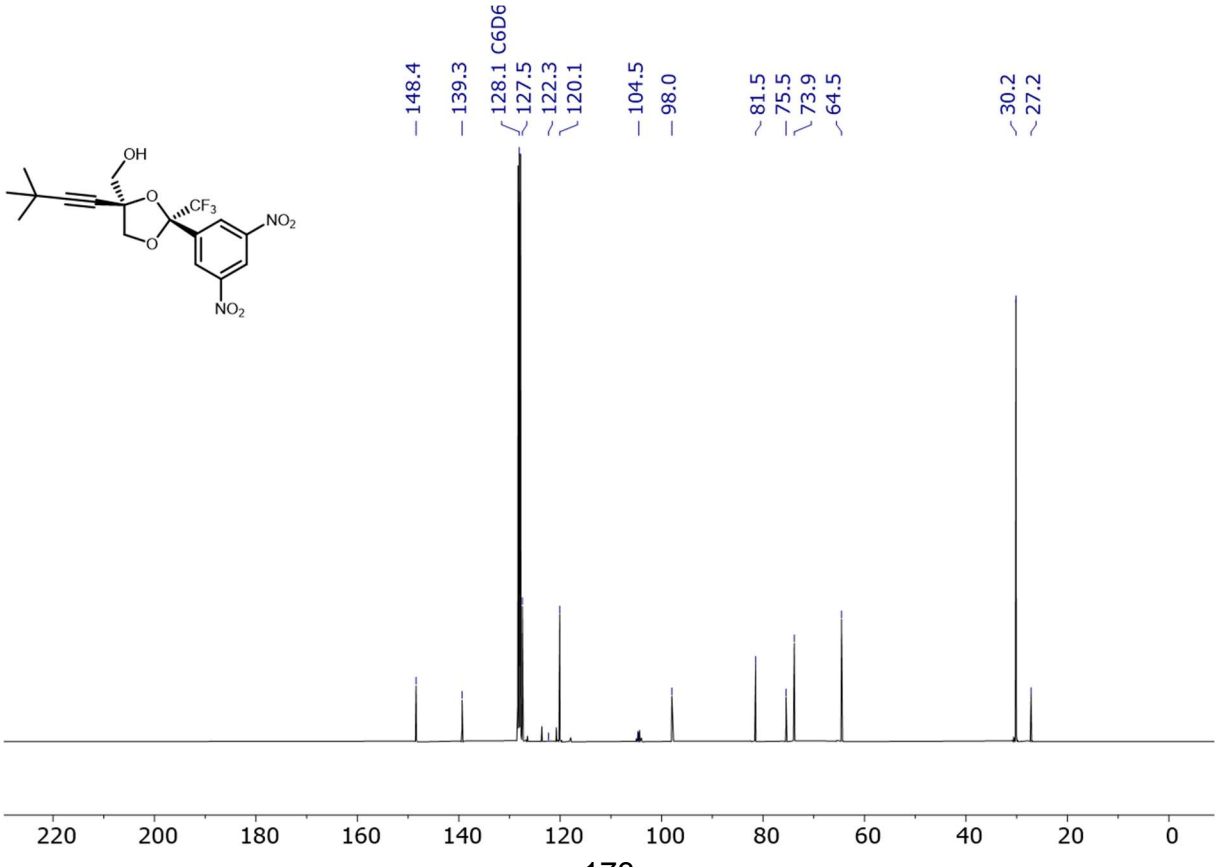
**[5p], $^{19}F$, $C_6D_6$, 377 MHz**



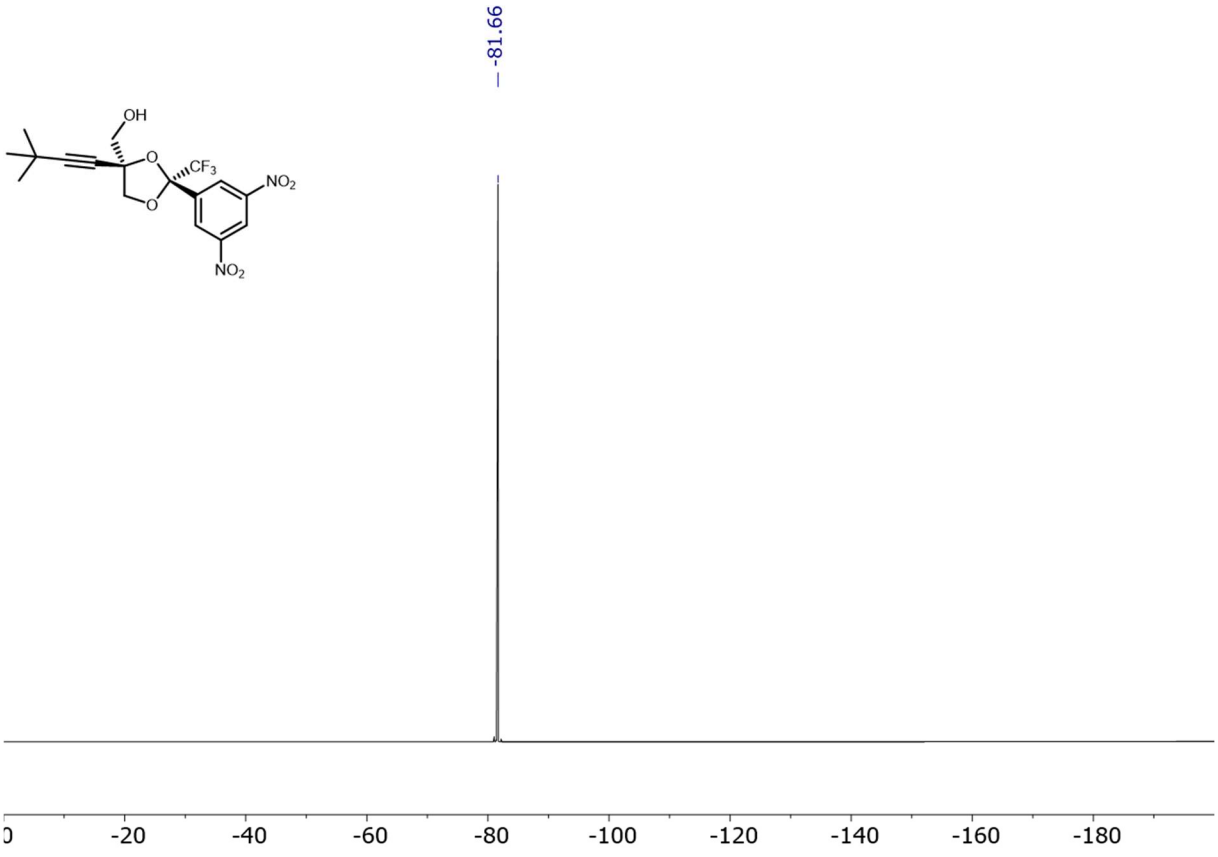
**[5q], $^{1}H$, $C_6D_6$, 400 MHz**



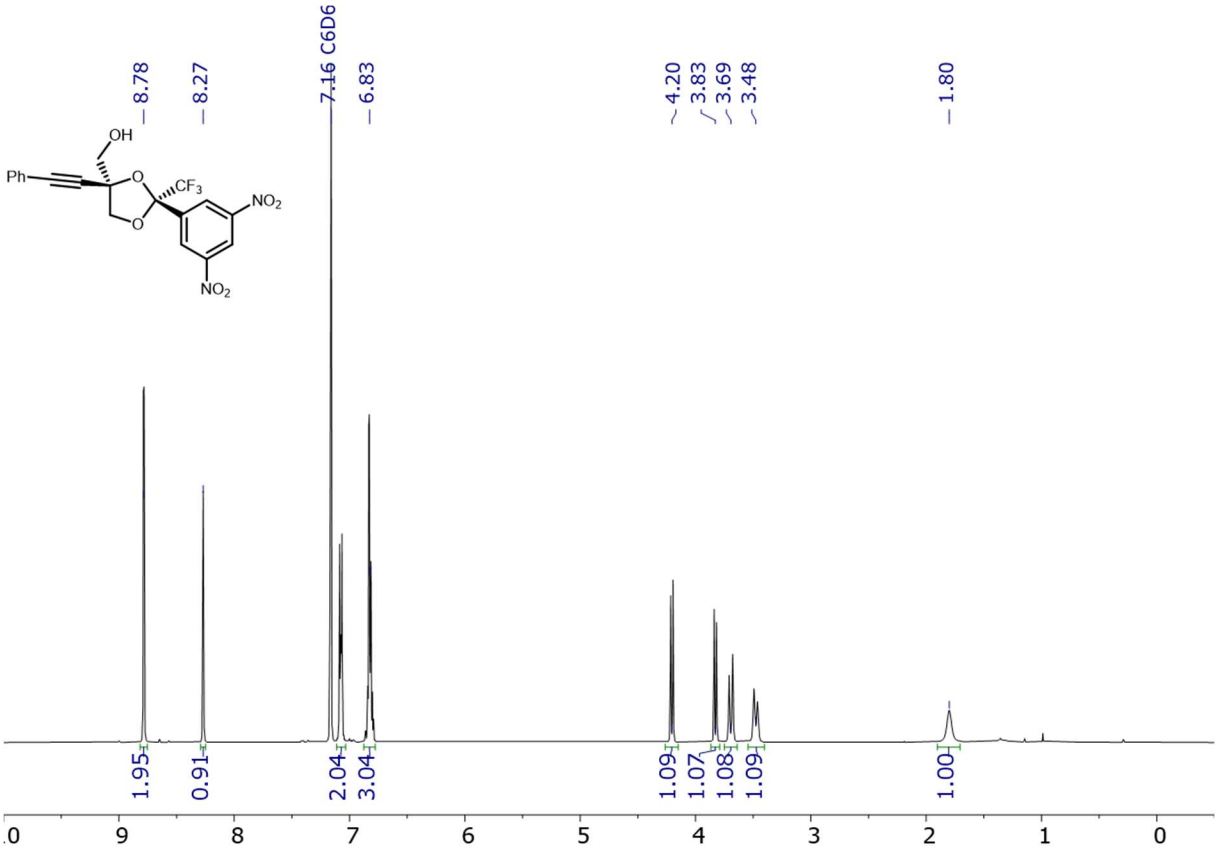

**[5q], $^{13}C$, $C_6D_6$, 101 MHz**



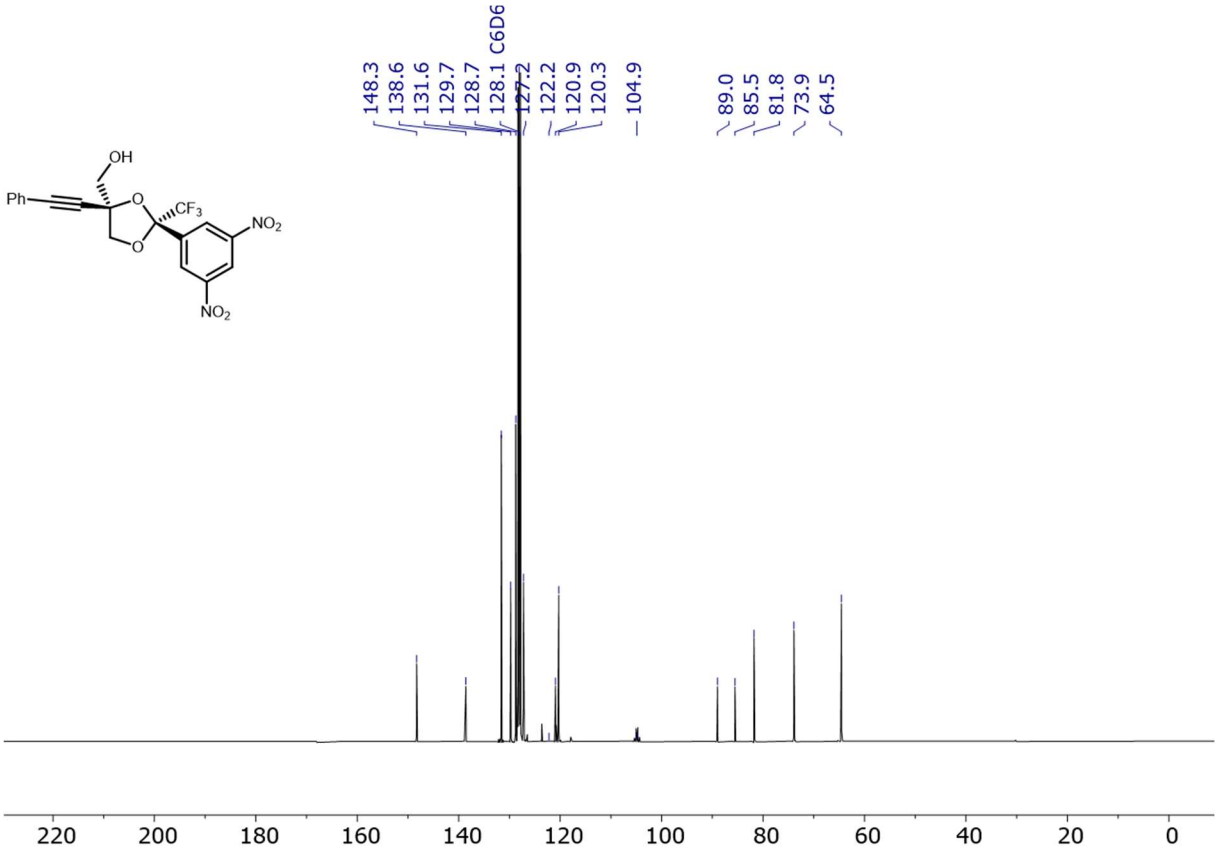
**[5q], $^{19}F$, $C_6D_6$, 377 MHz**



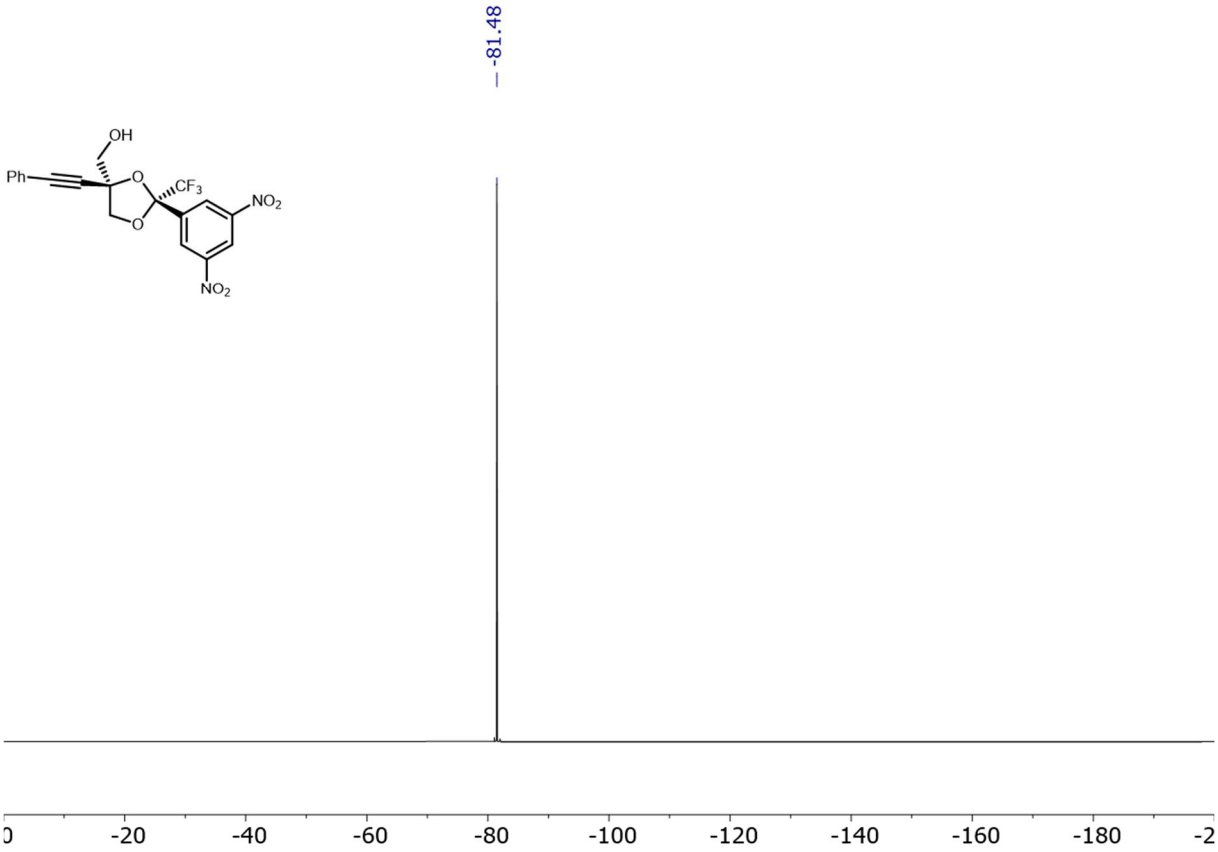
**[5r], $^{1}H$, $C_6D_6$, 400 MHz**



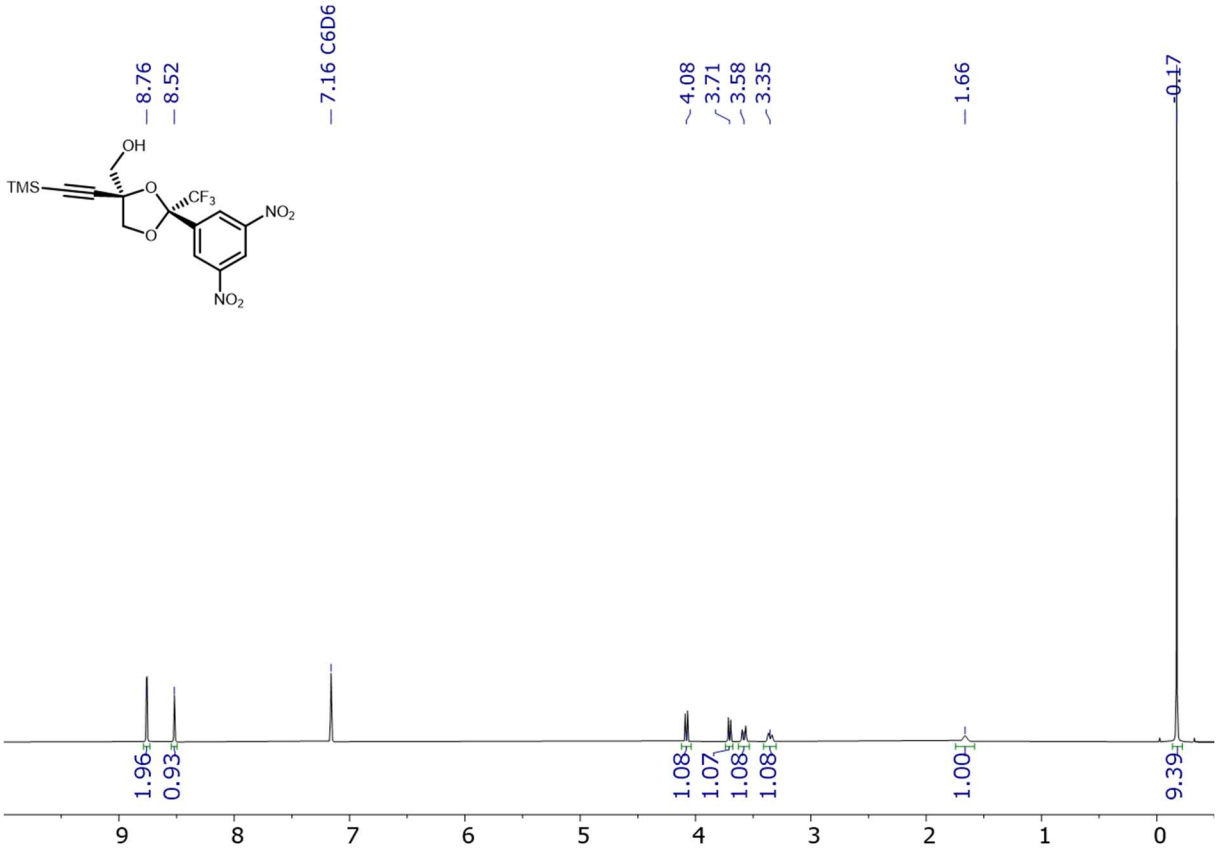

**[5r], $^{13}C$, $C_6D_6$, 101 MHz**



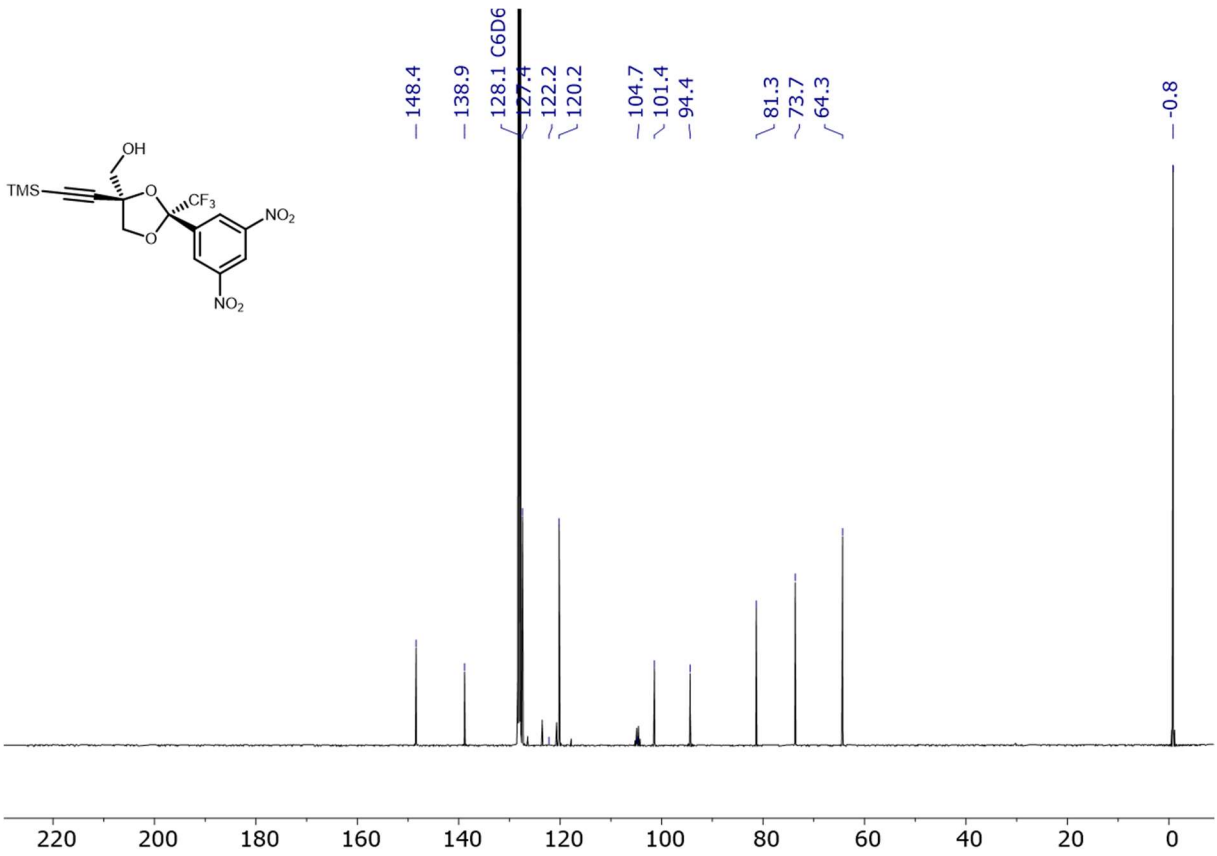
**[5r], $^{19}F$, $C_6D_6$, 377 MHz**



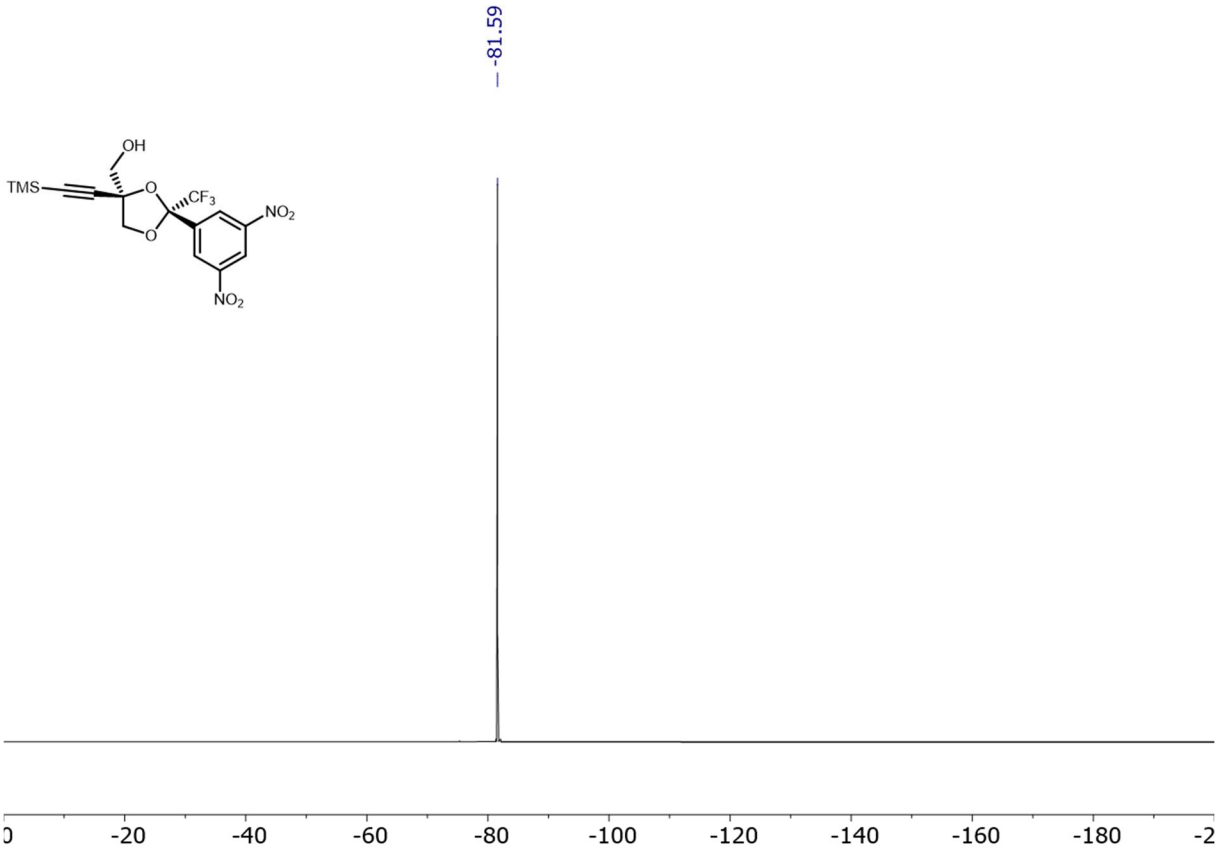
**[5s], $^{1}H$, $C_6D_6$, 400 MHz**



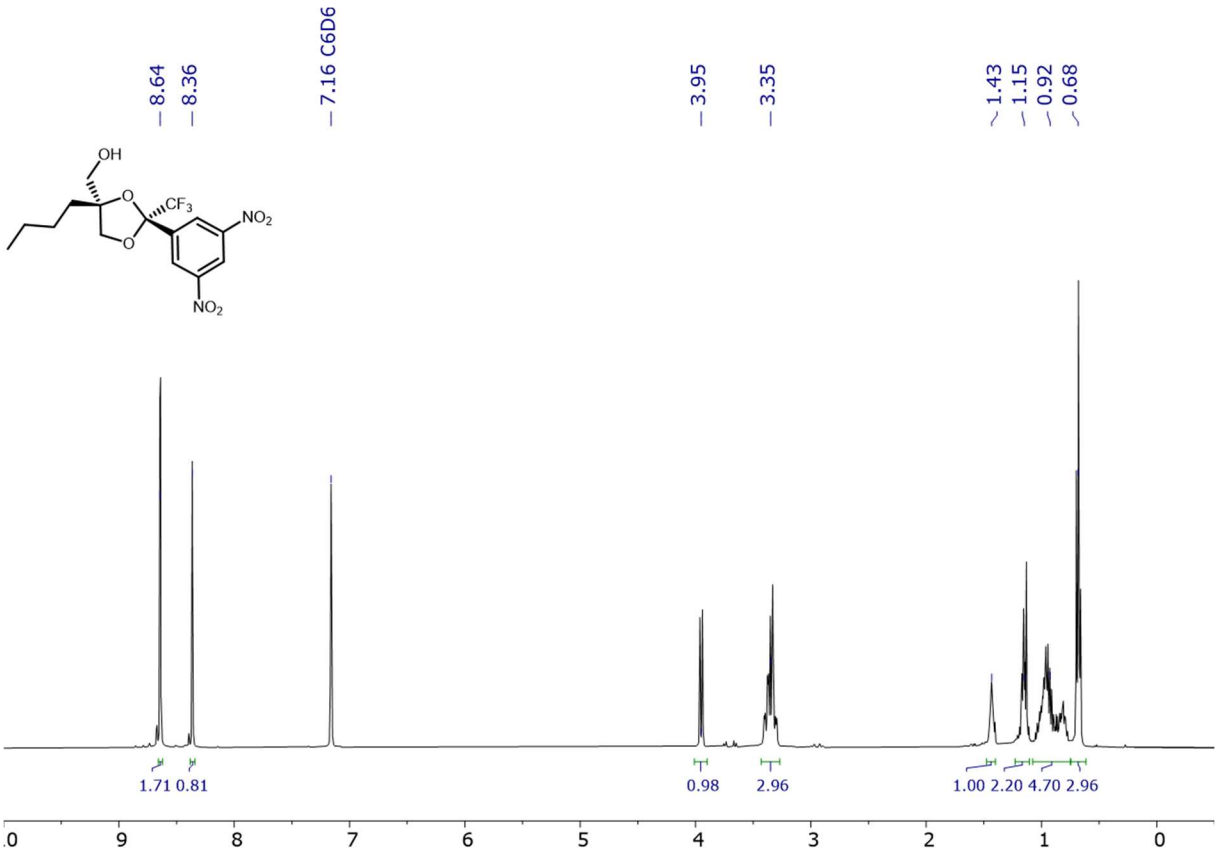

**[5s], $^{13}C$, $C_6D_6$, 101 MHz**



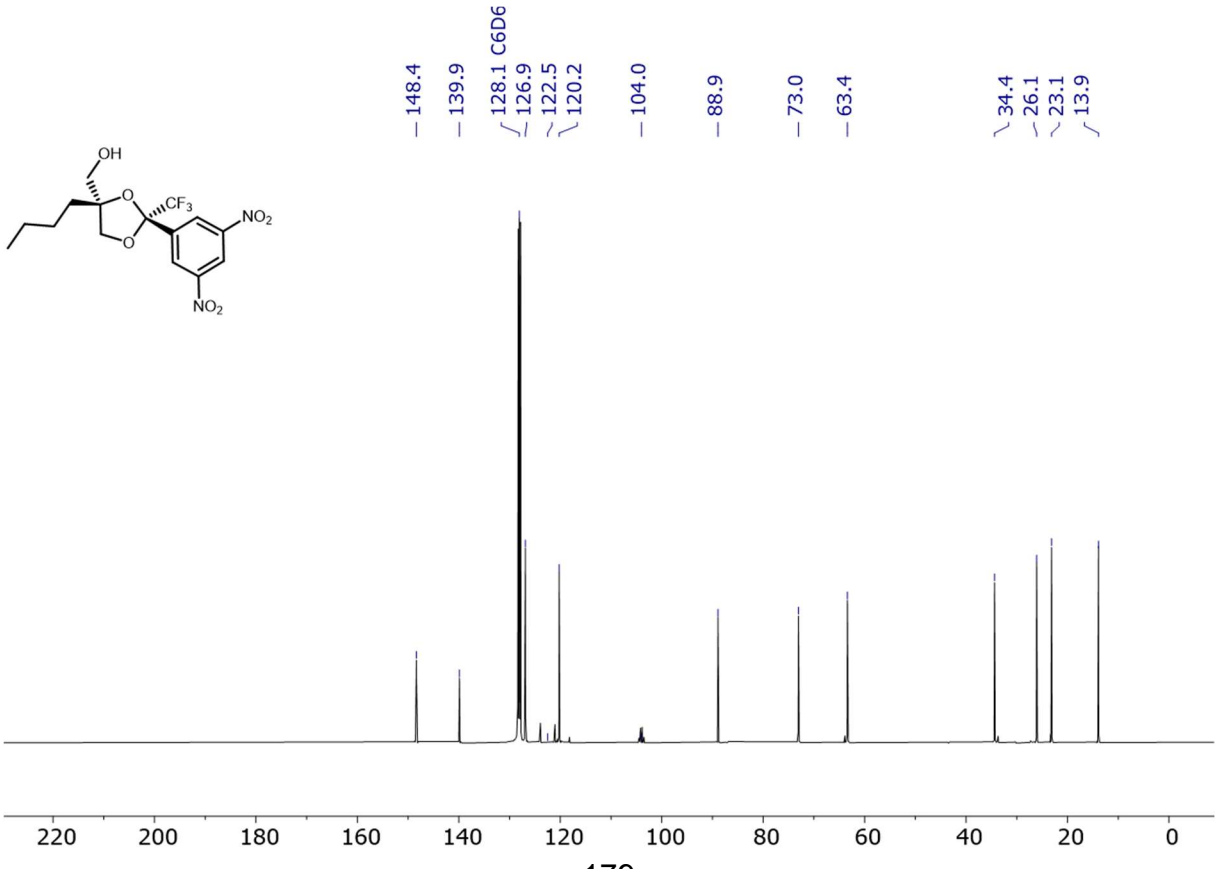
**[5s], $^{19}F$, $C_6D_6$, 377 MHz**



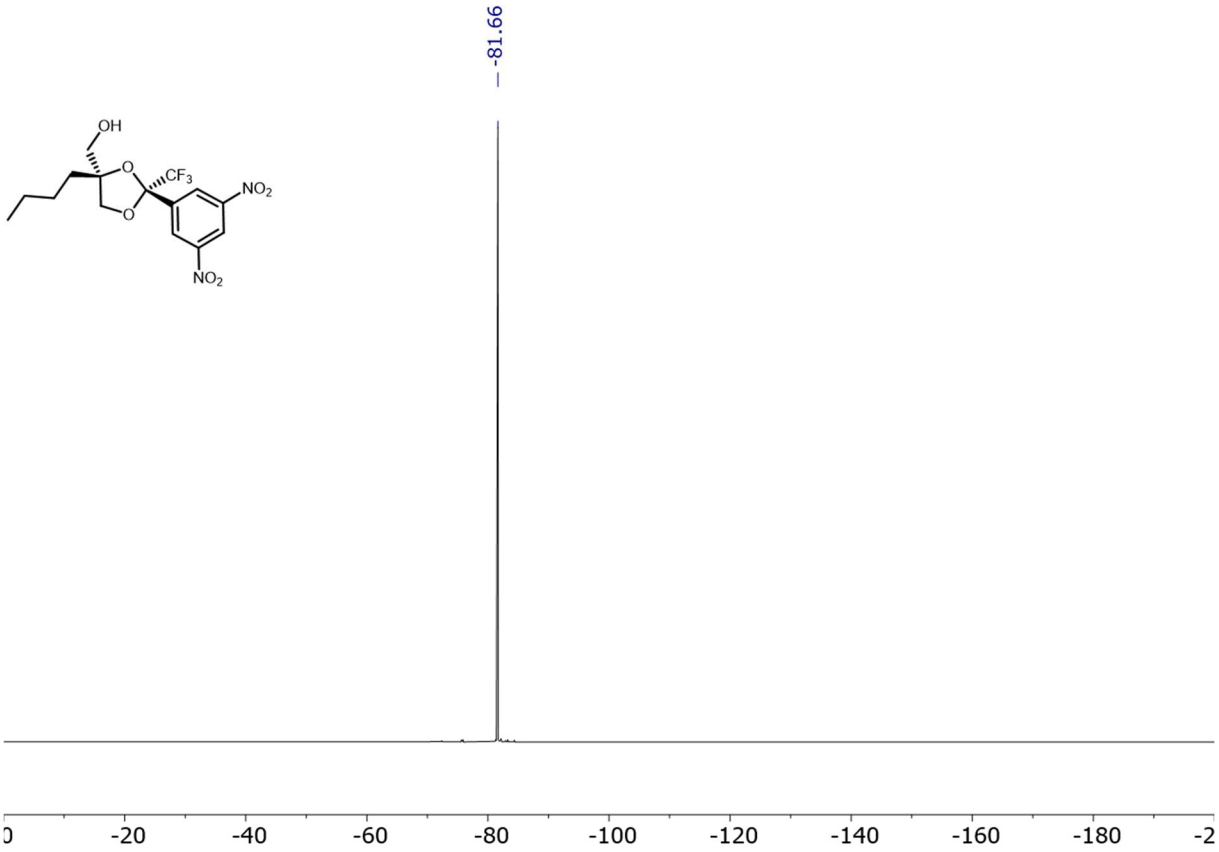
**[5t], $^{1}H$, $C_6D_6$, 400 MHz**



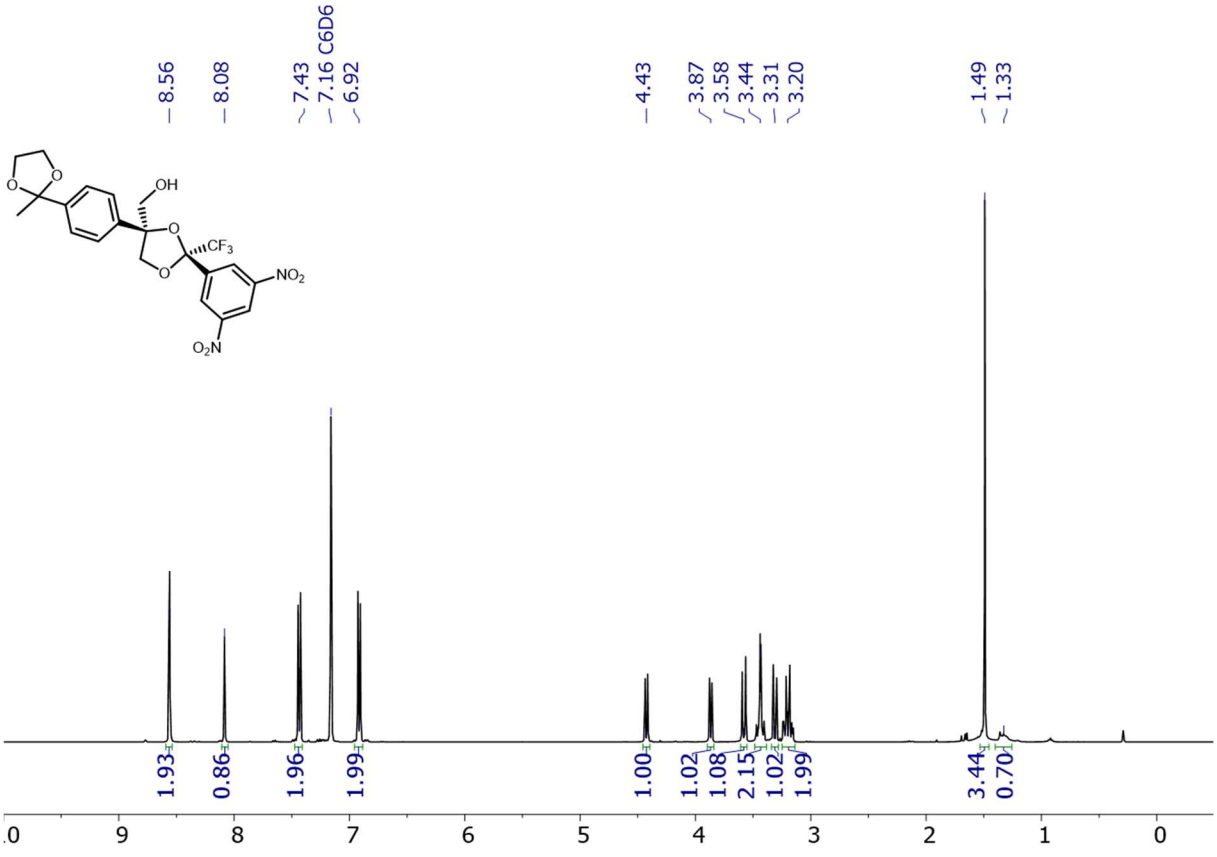

**[5t], $^{13}C$, $C_6D_6$, 101 MHz**



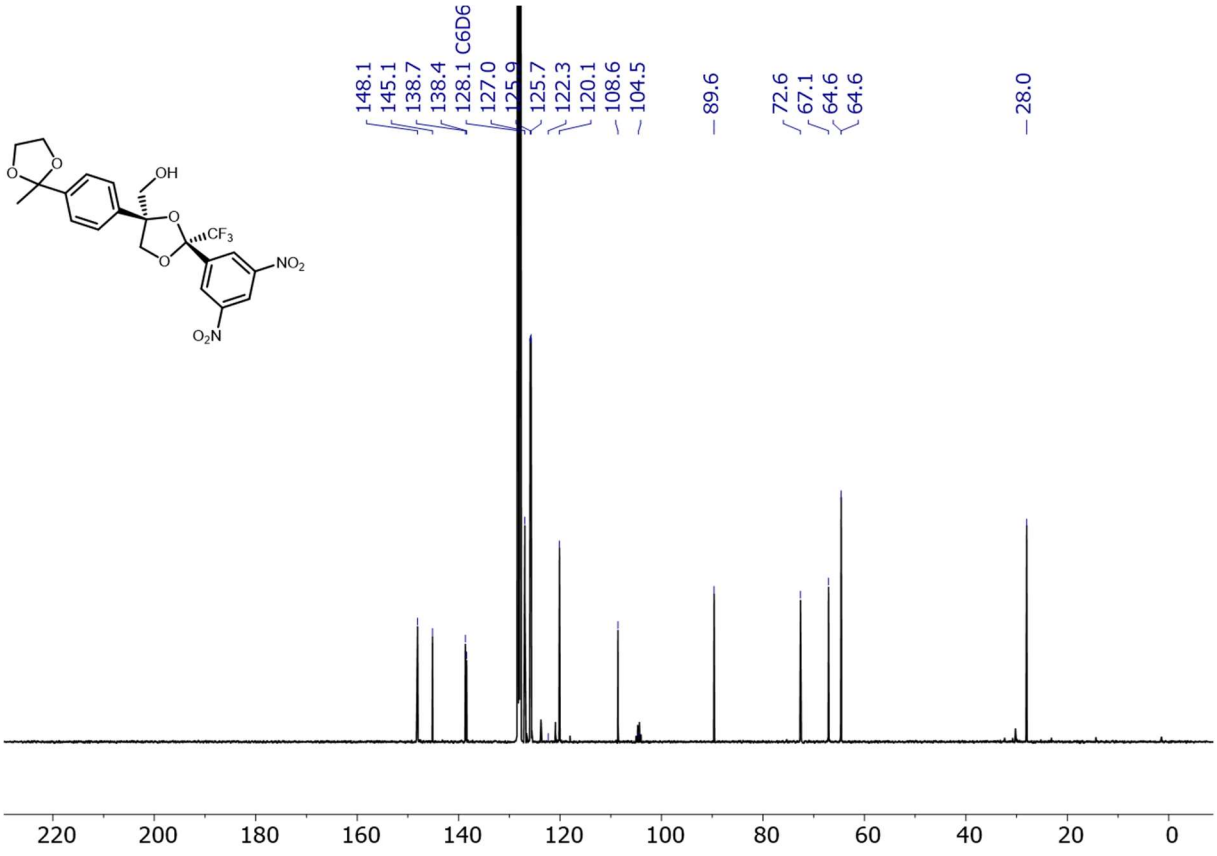
**[5t], $^{19}F$, $C_6D_6$, 377 MHz**



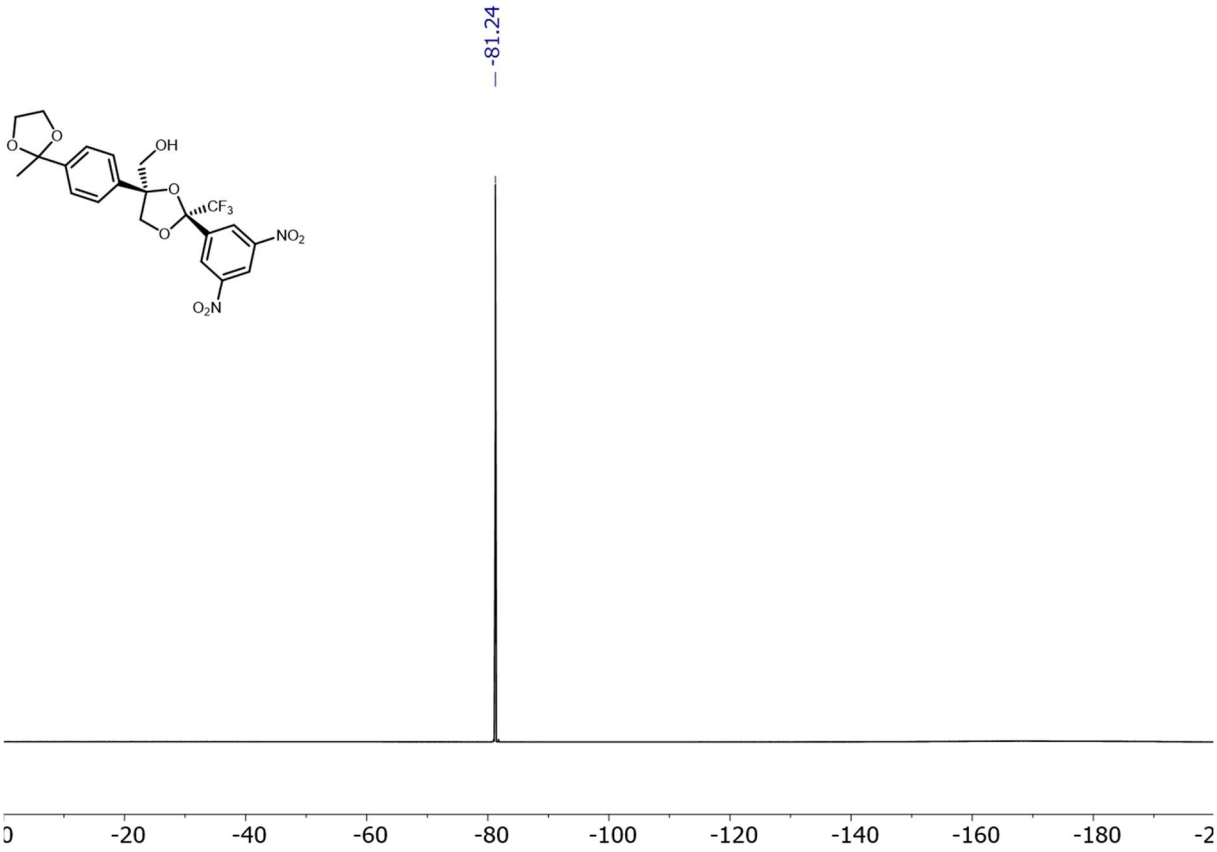
**[5u], $^{1}H$, $C_6D_6$, 400 MHz**



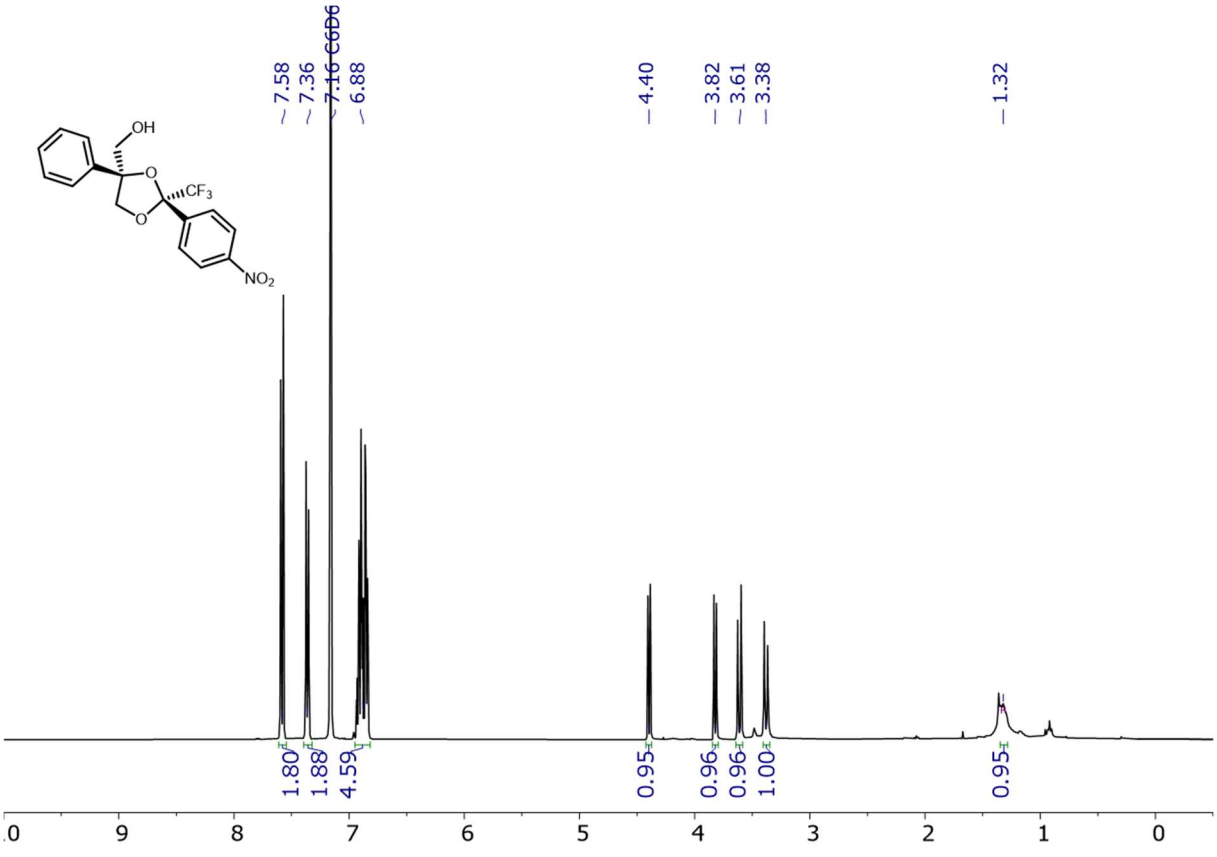

**[5u], $^{13}C$, $C_6D_6$, 101 MHz**



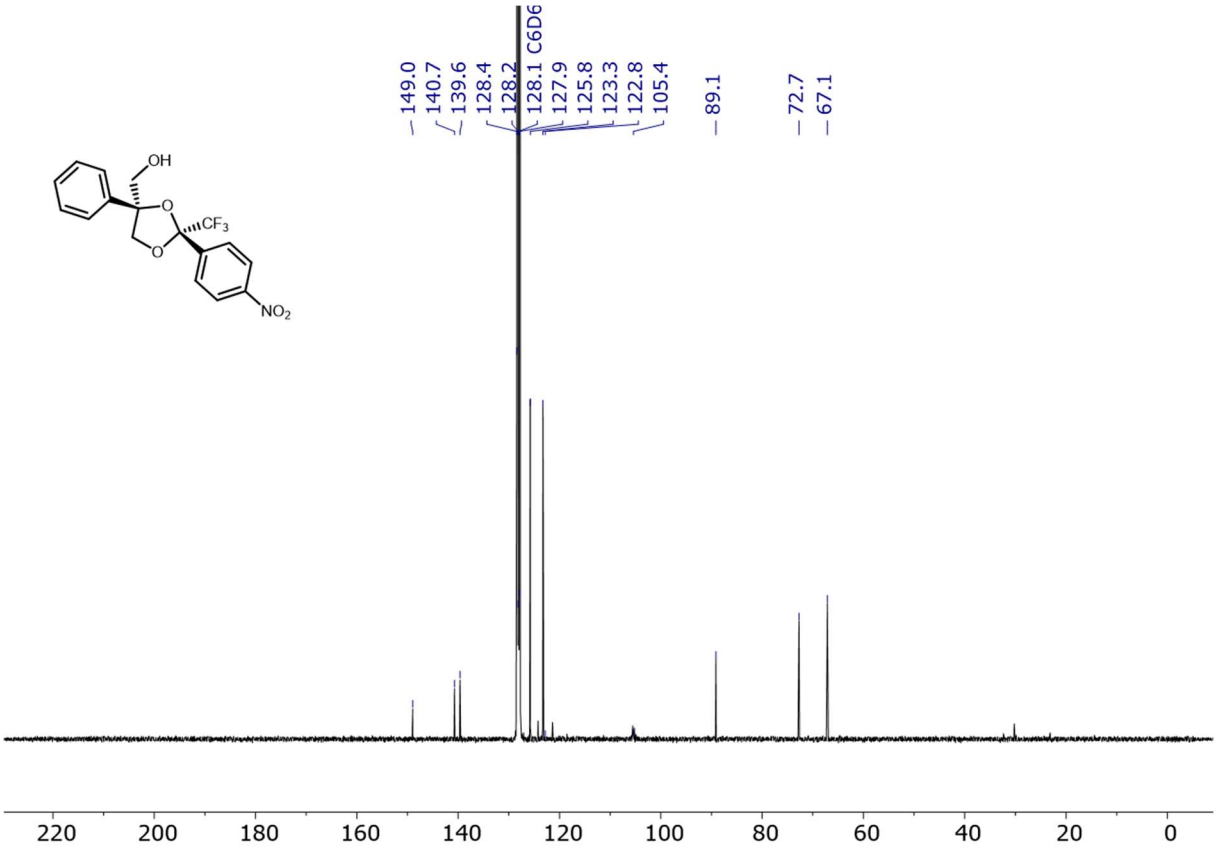
**[5u], $^{19}F$, $C_6D_6$, 377 MHz**



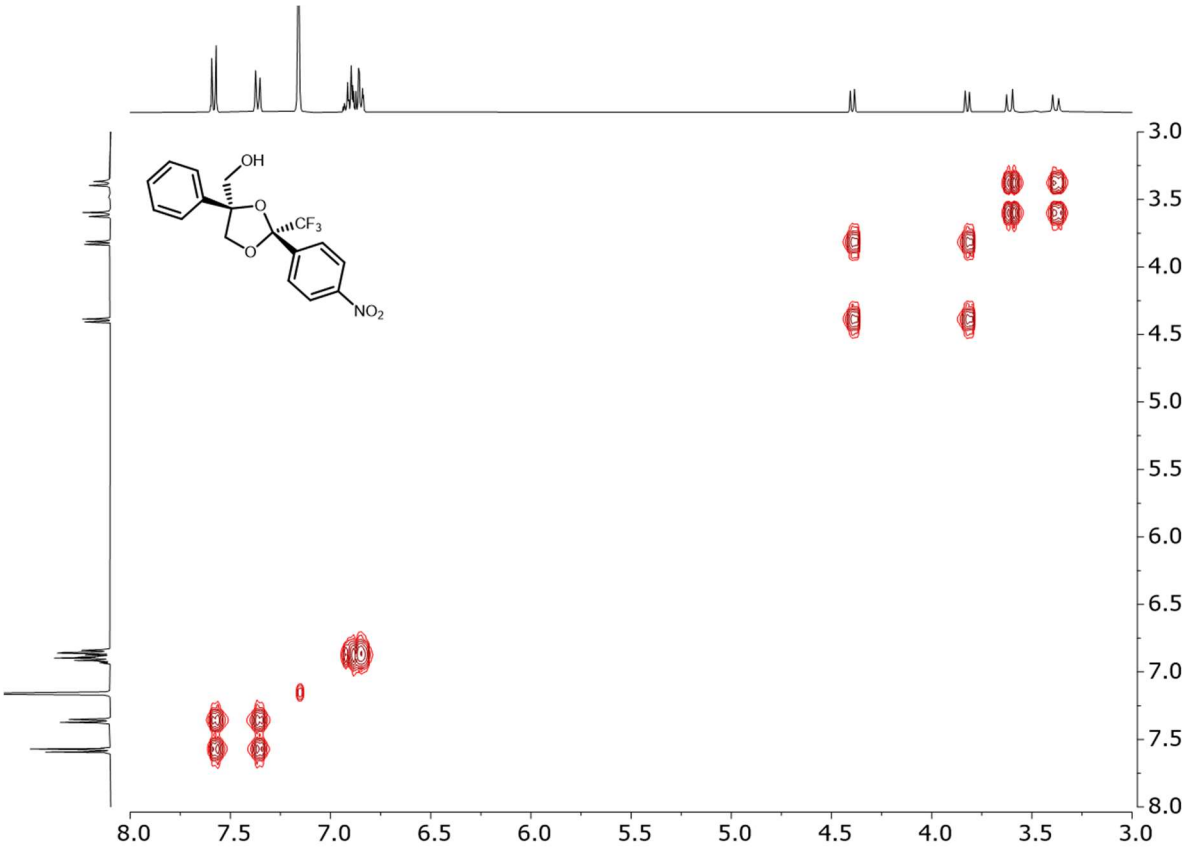
**[16a], $^{1}H$, $C_6D_6$, 400 MHz**



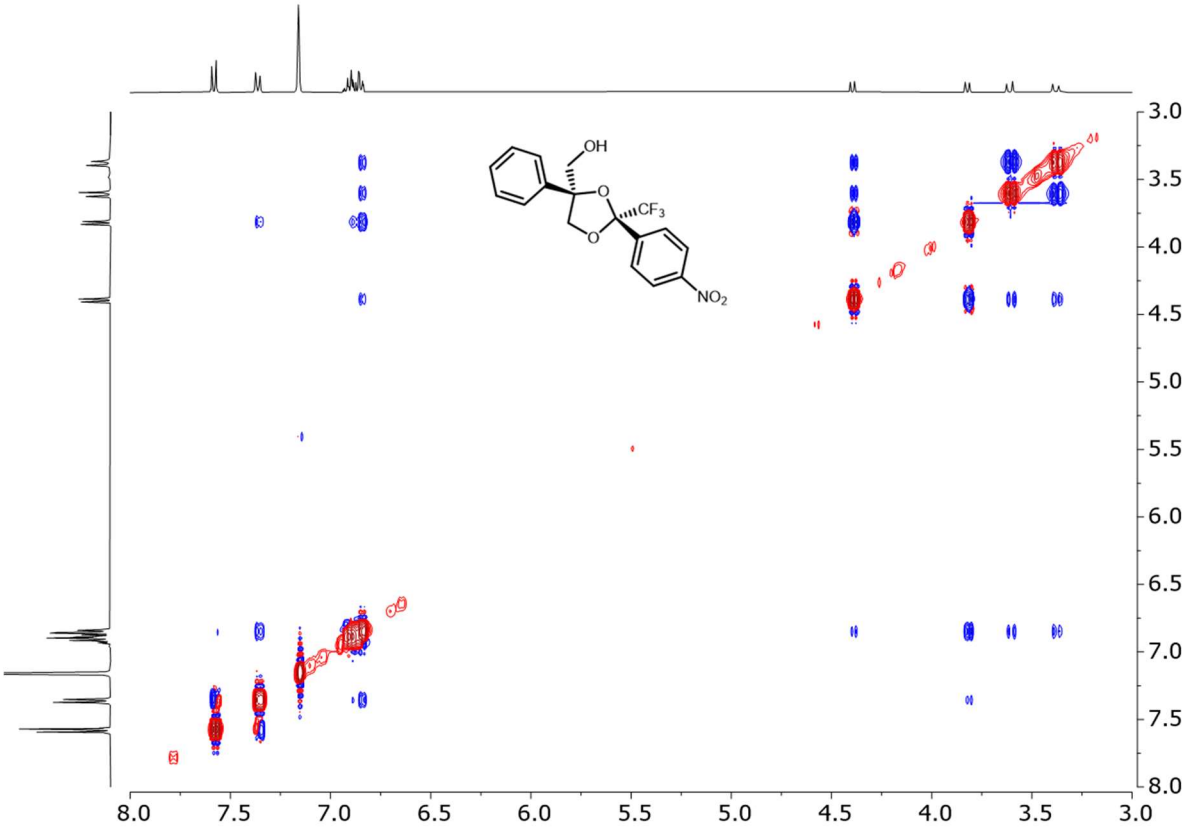

**[16a], $^{13}C$, $C_6D_6$, 101 MHz**



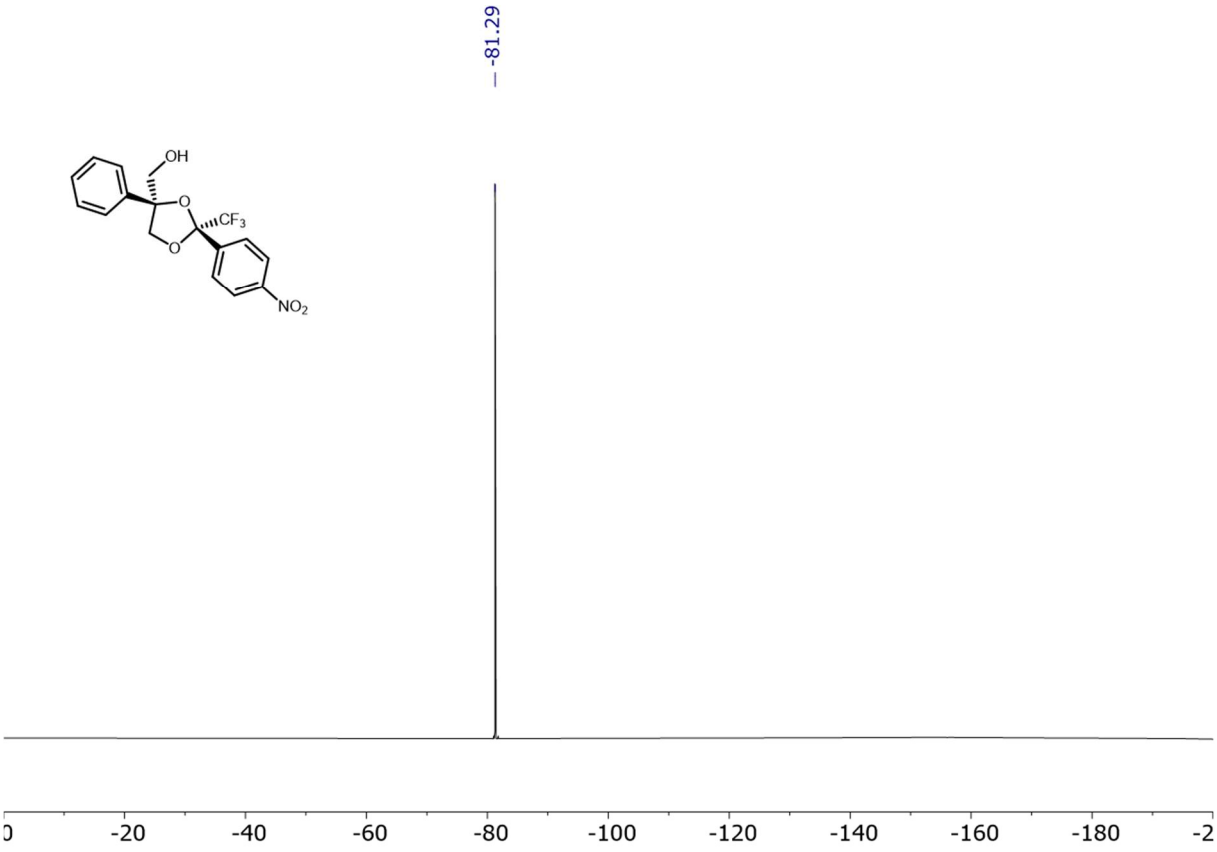
**[16a], $^{1}H$-$^{1}H$-COSY, $C_6D_6$**



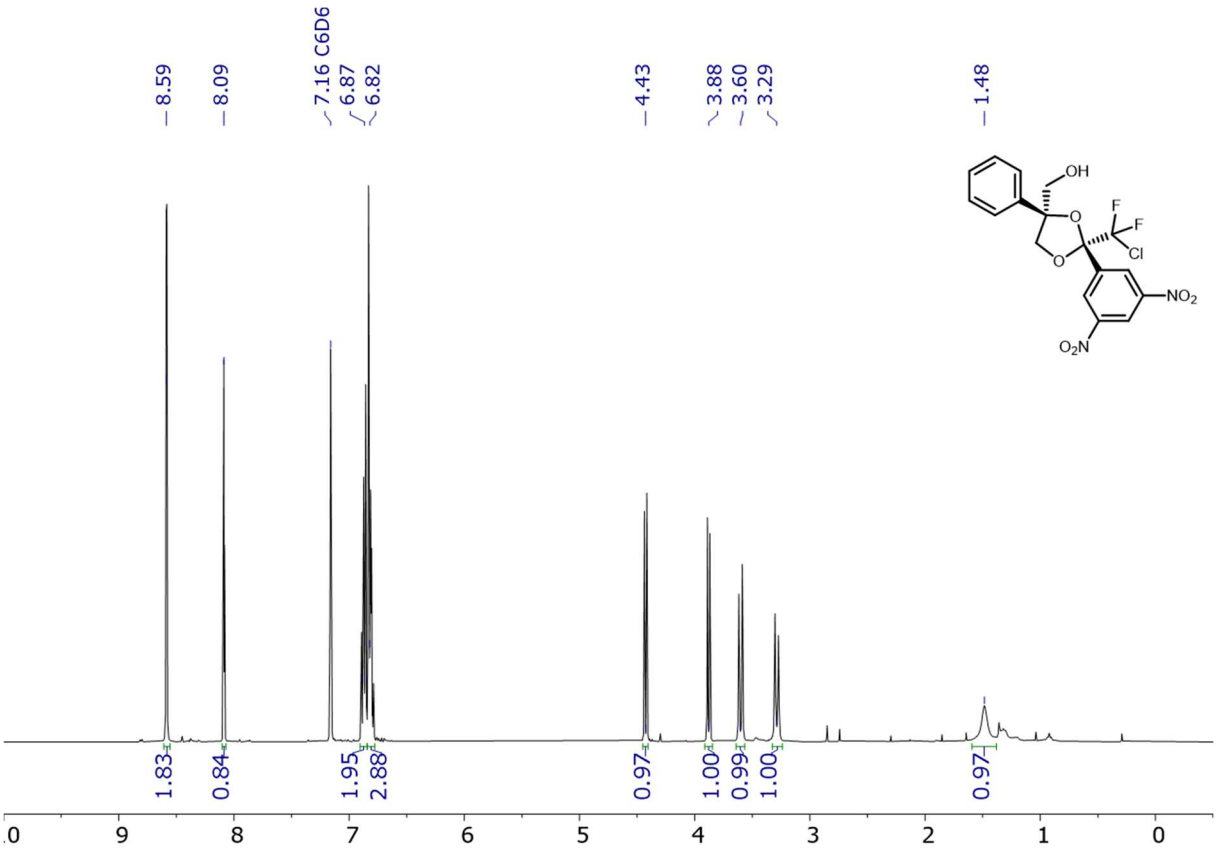

**[16a], $^{1}H$-$^{1}H$ NOESY, $C_6D_6$**



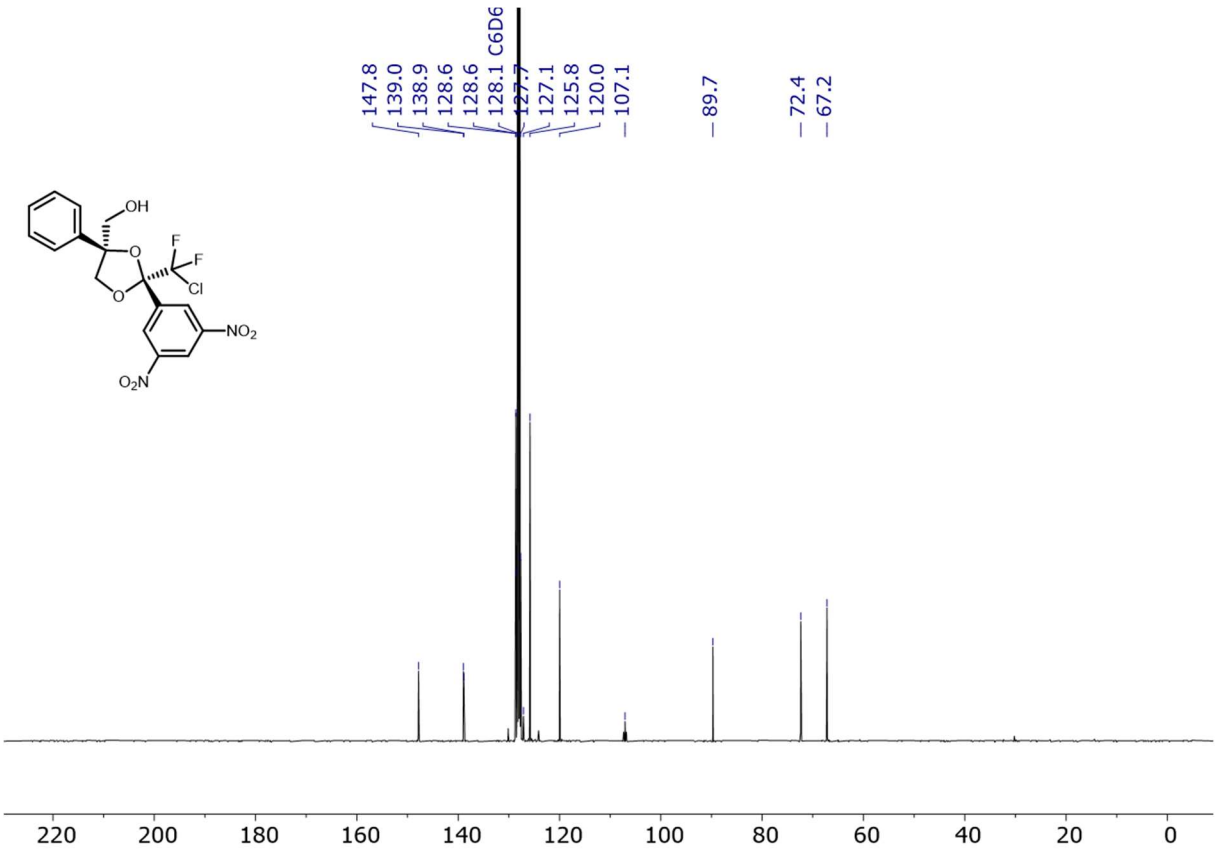
**[16a], $^{19}F$, $C_6D_6$, 377 MHz**



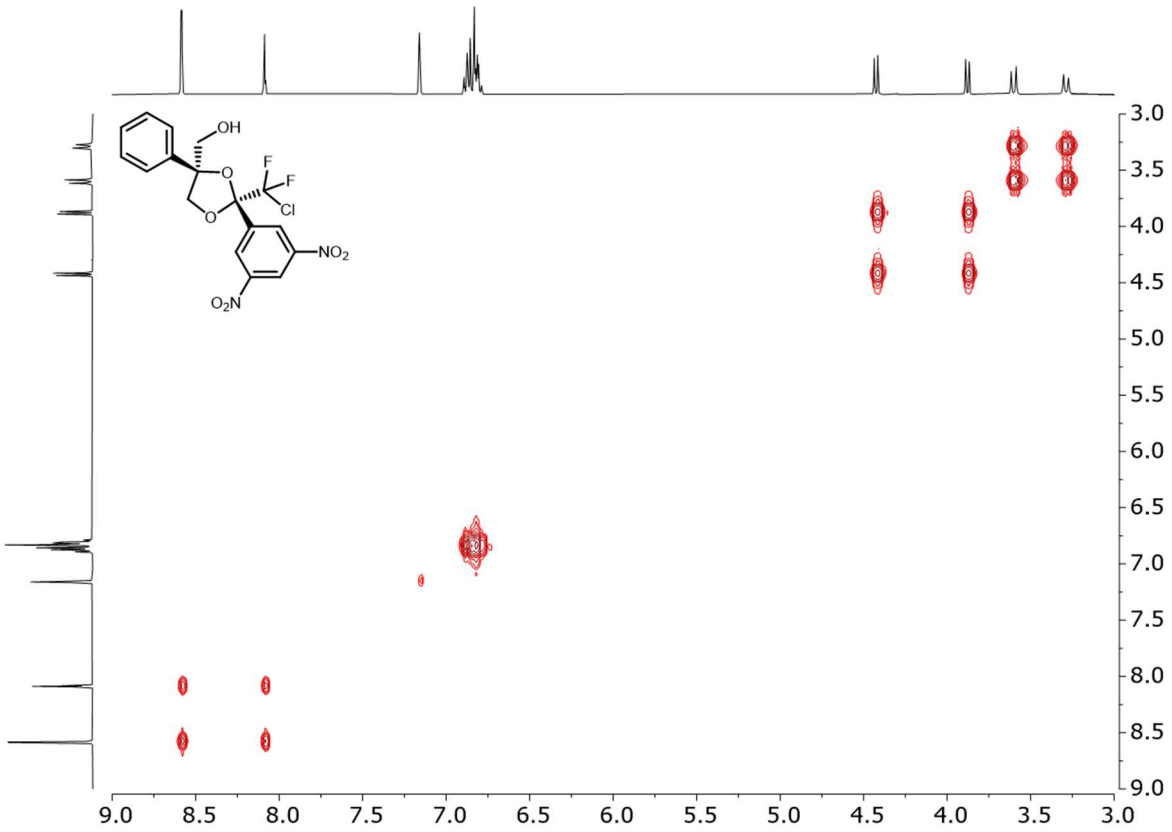
**[18a], $^{1}H$, $C_6D_6$, 400 MHz**



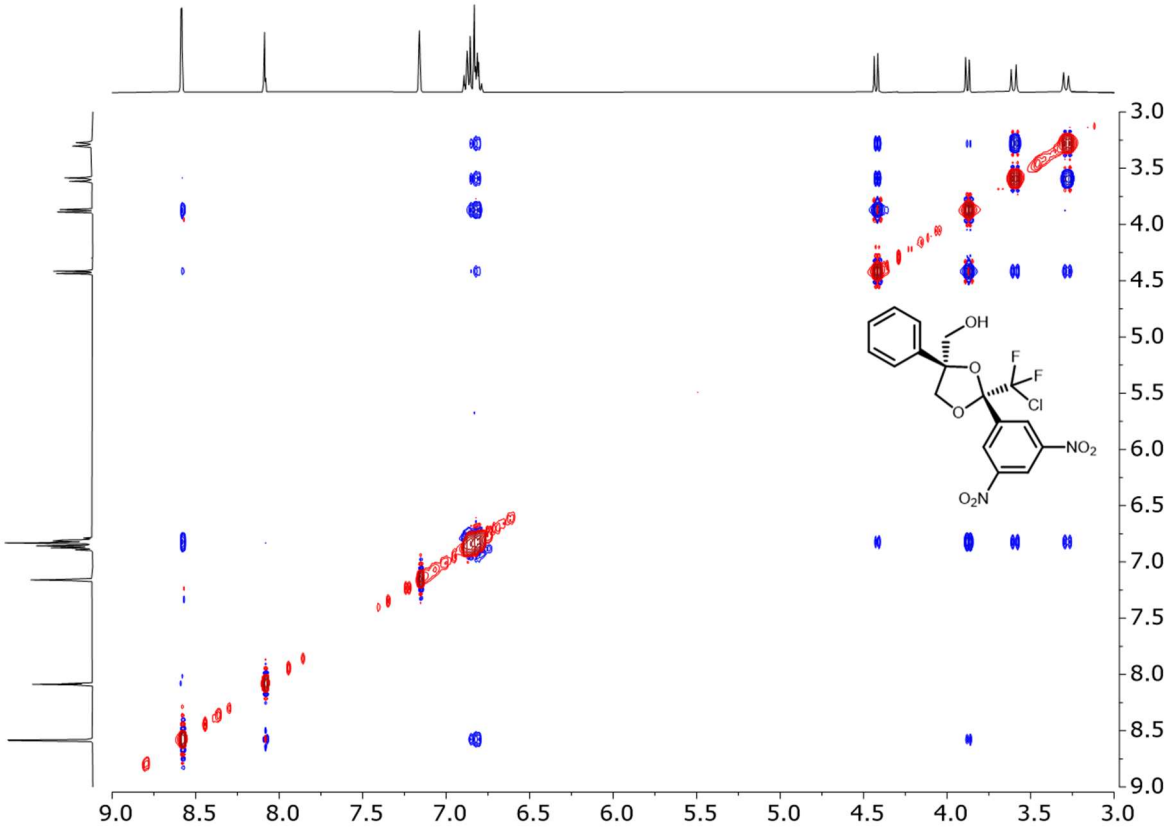

**[18a], $^{13}C$, $C_6D_6$, 101 MHz**



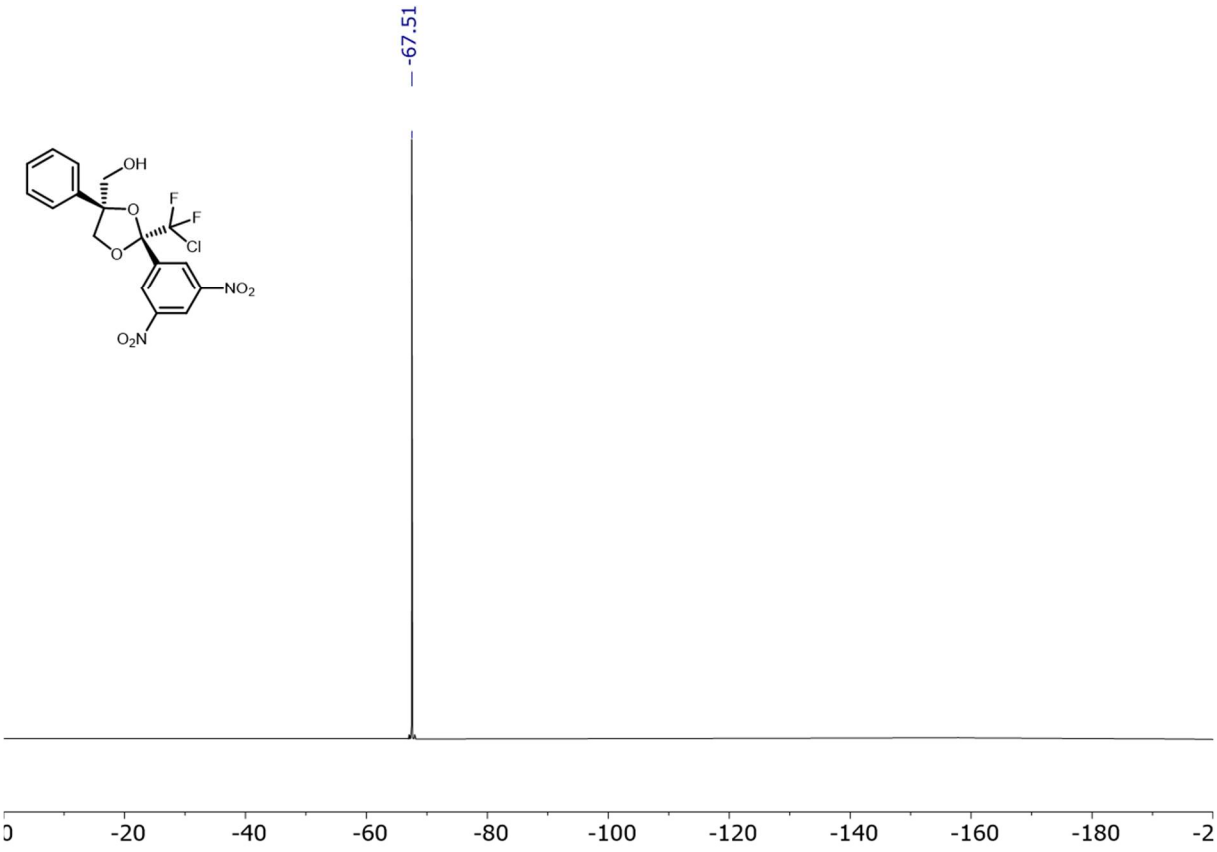
**[18a], $^{1}H$-$^{1}H$-COSY, $C_6D_6$**



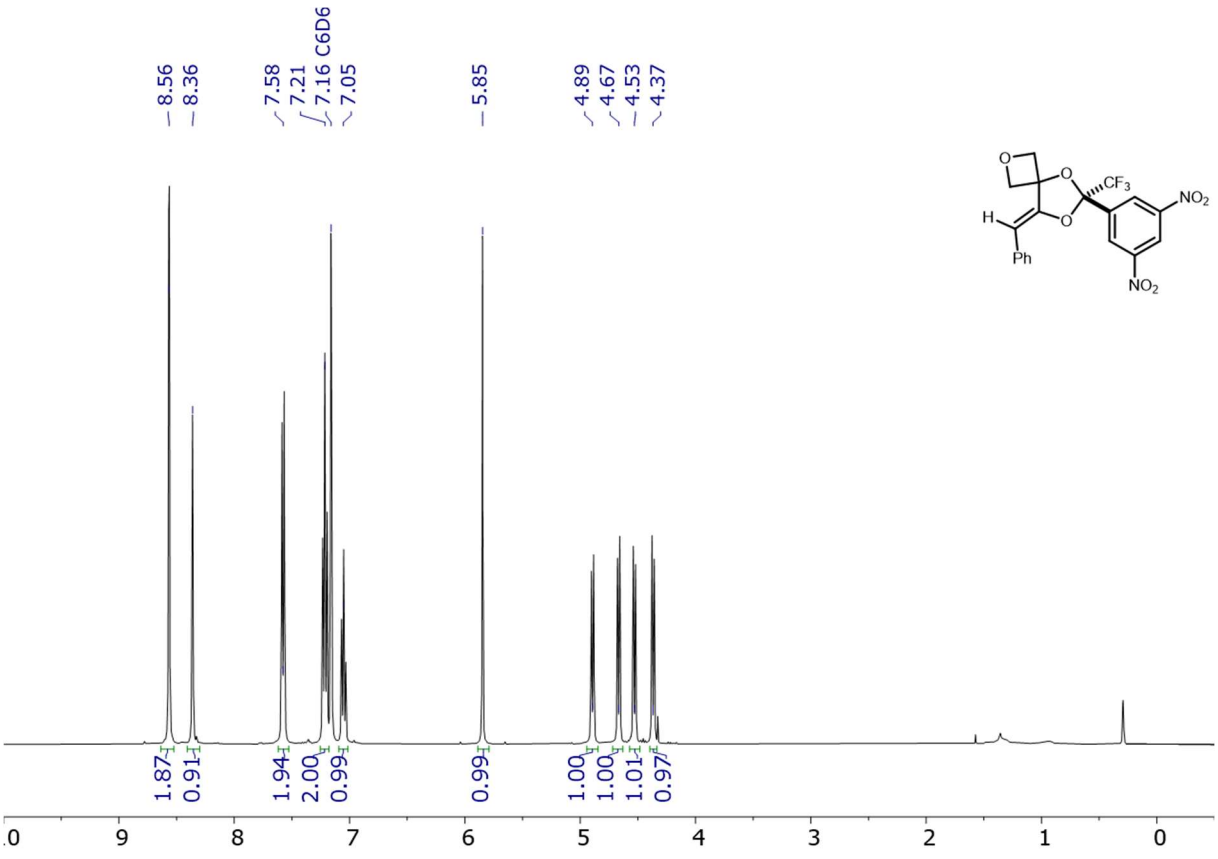

**[18a], $^{1}H$-$^{1}H$ NOESY, $C_6D_6$**



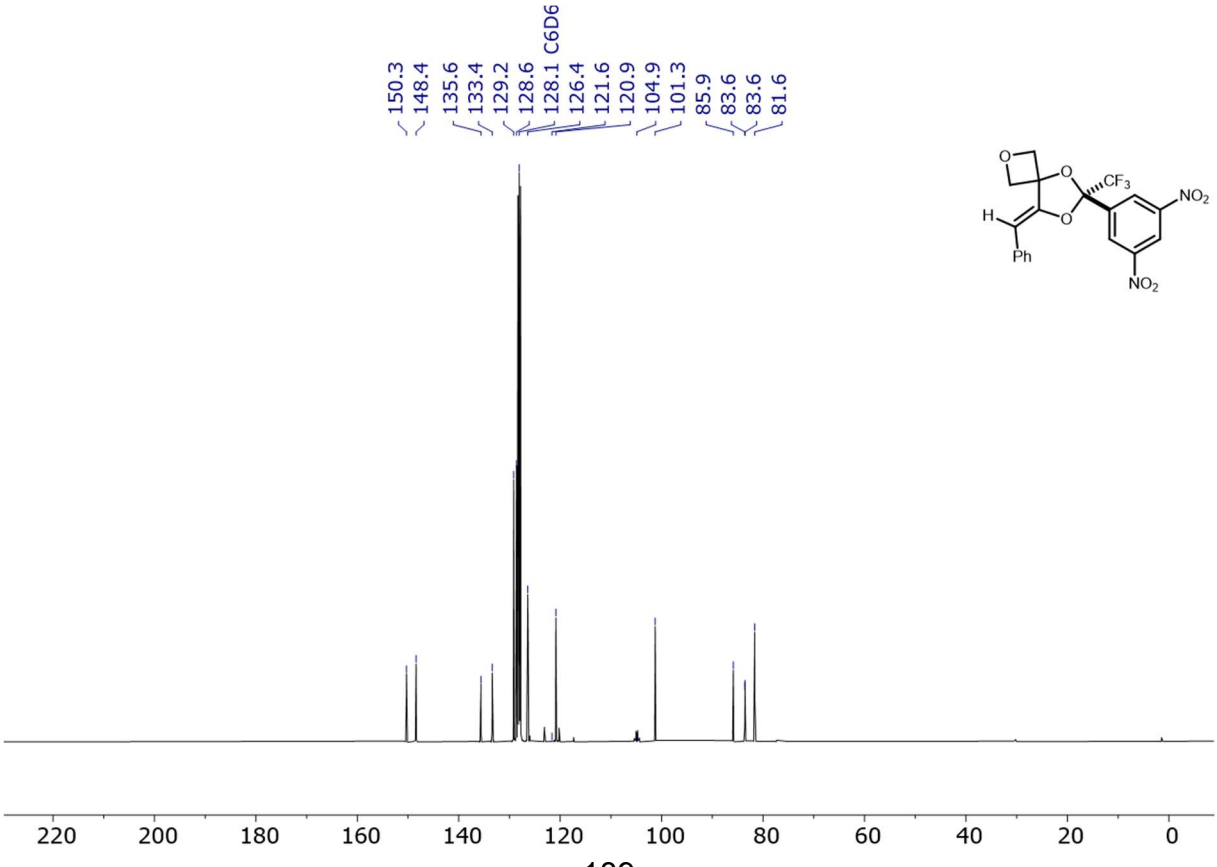
**[18a], $^{19}F$, $C_6D_6$, 377 MHz**



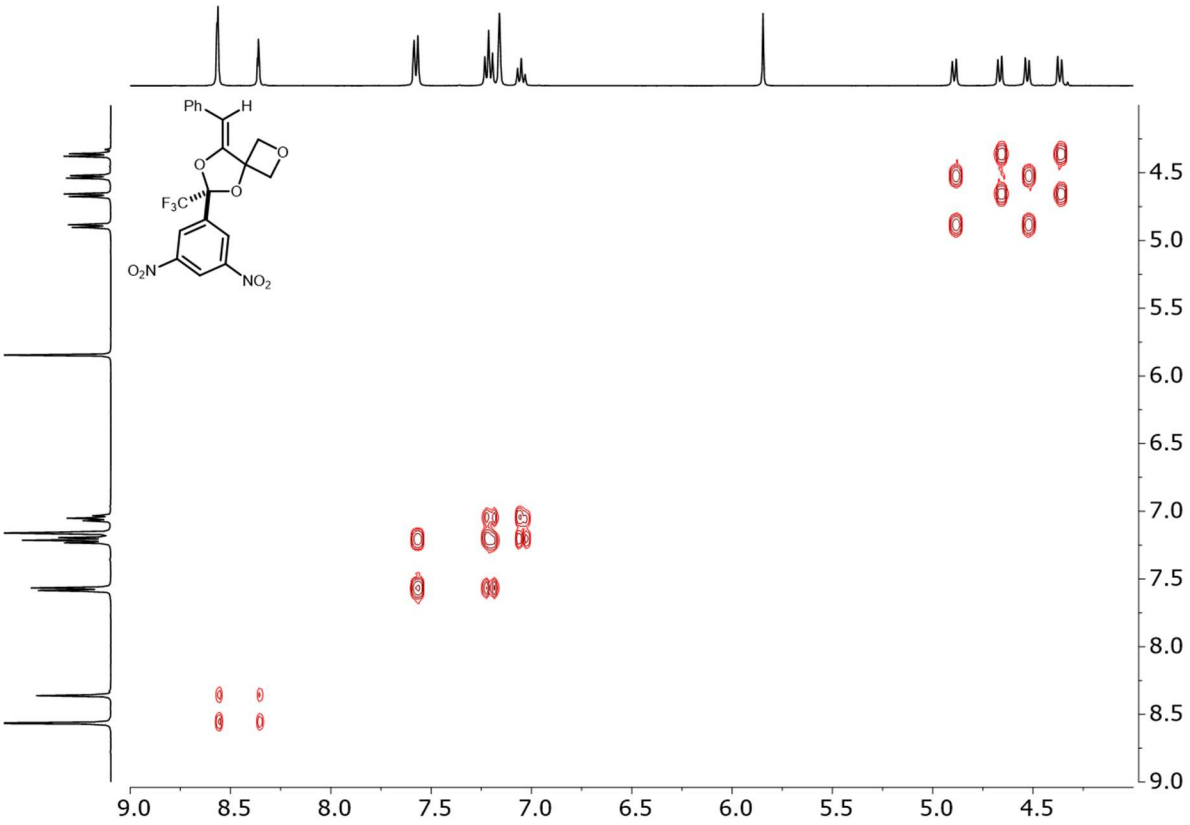
**[19r], $^{1}H$, $C_6D_6$, 400 MHz**



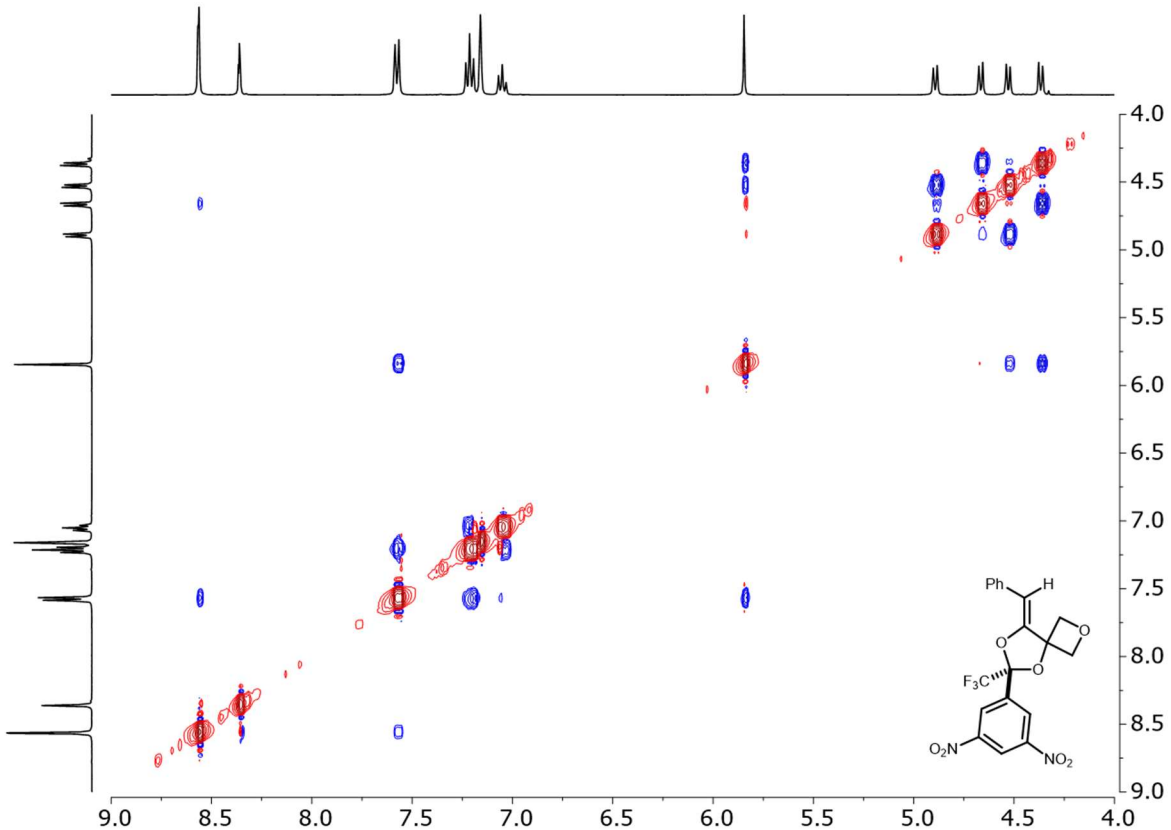

**[19r], $^{13}C$, $C_6D_6$, 101 MHz**



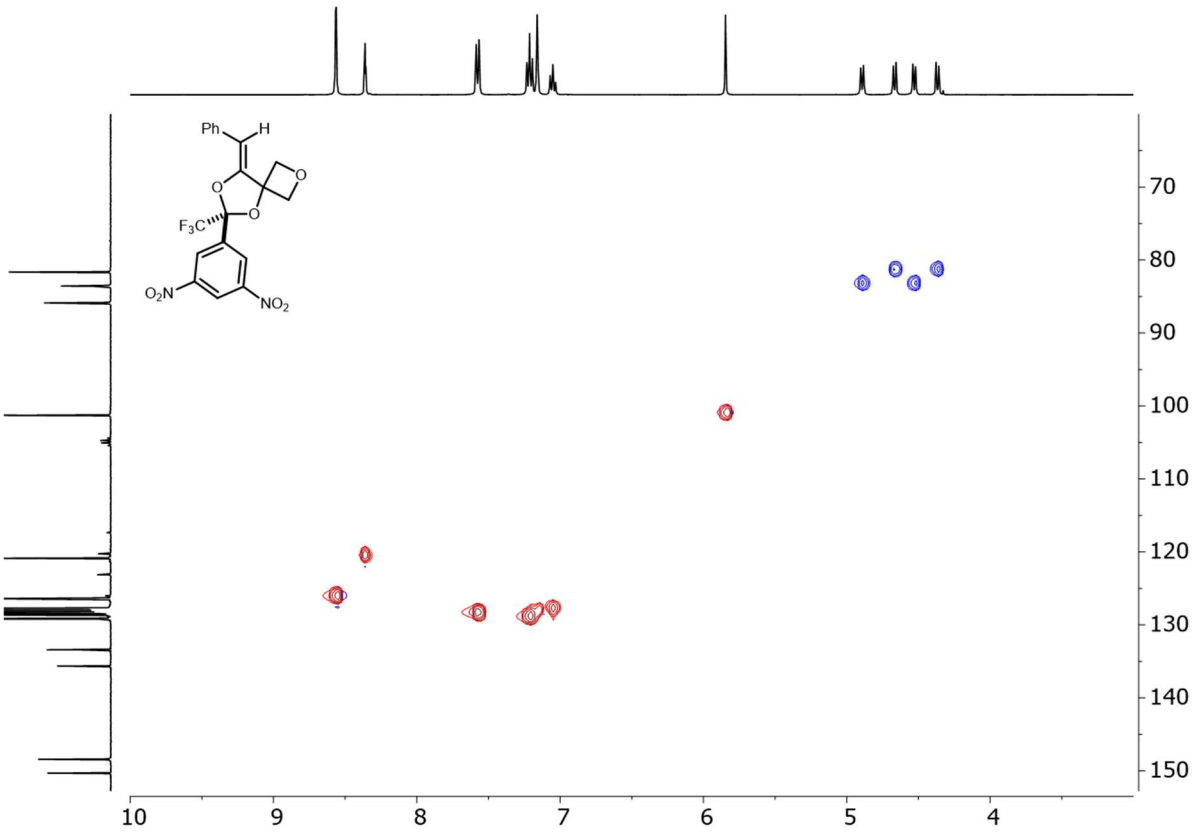
**[19r], $^{1}H$-$^{1}H$-COSY, $C_6D_6$**



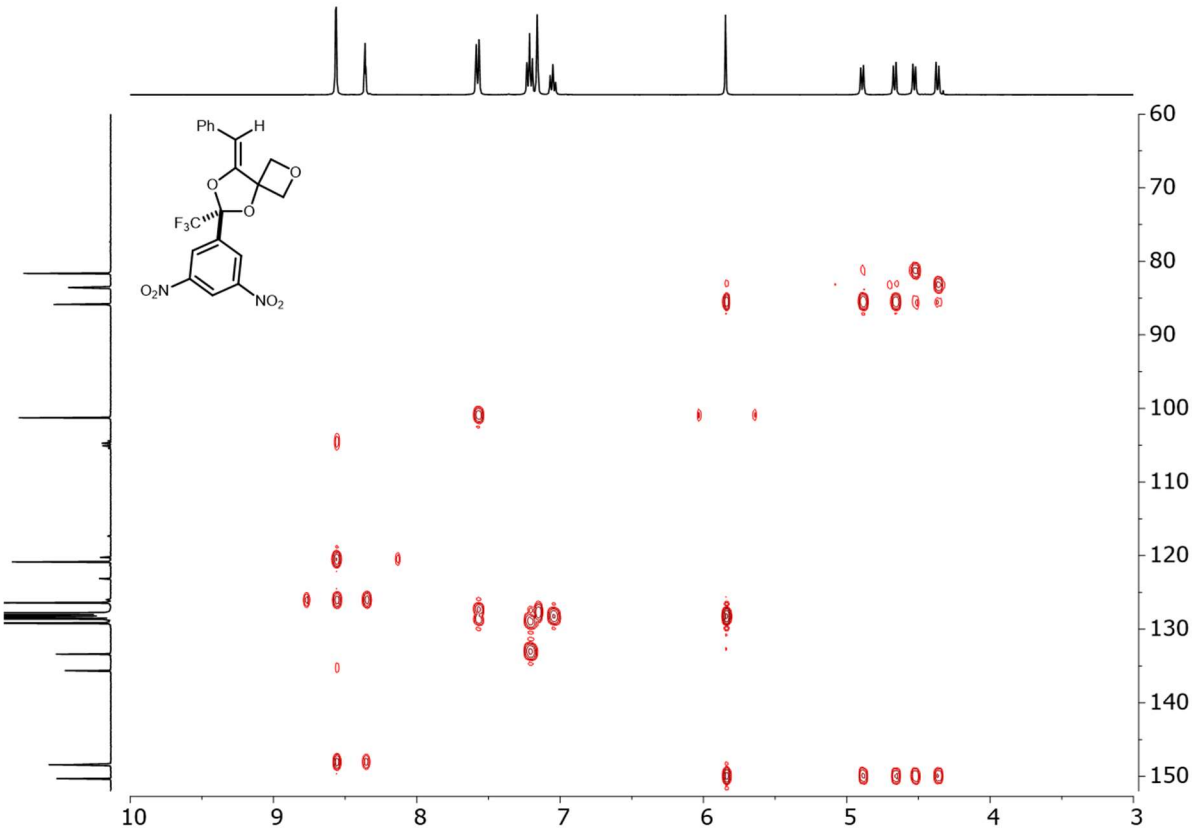

**[19r], $^{1}H$-$^{1}H$ NOESY, $C_6D_6$**



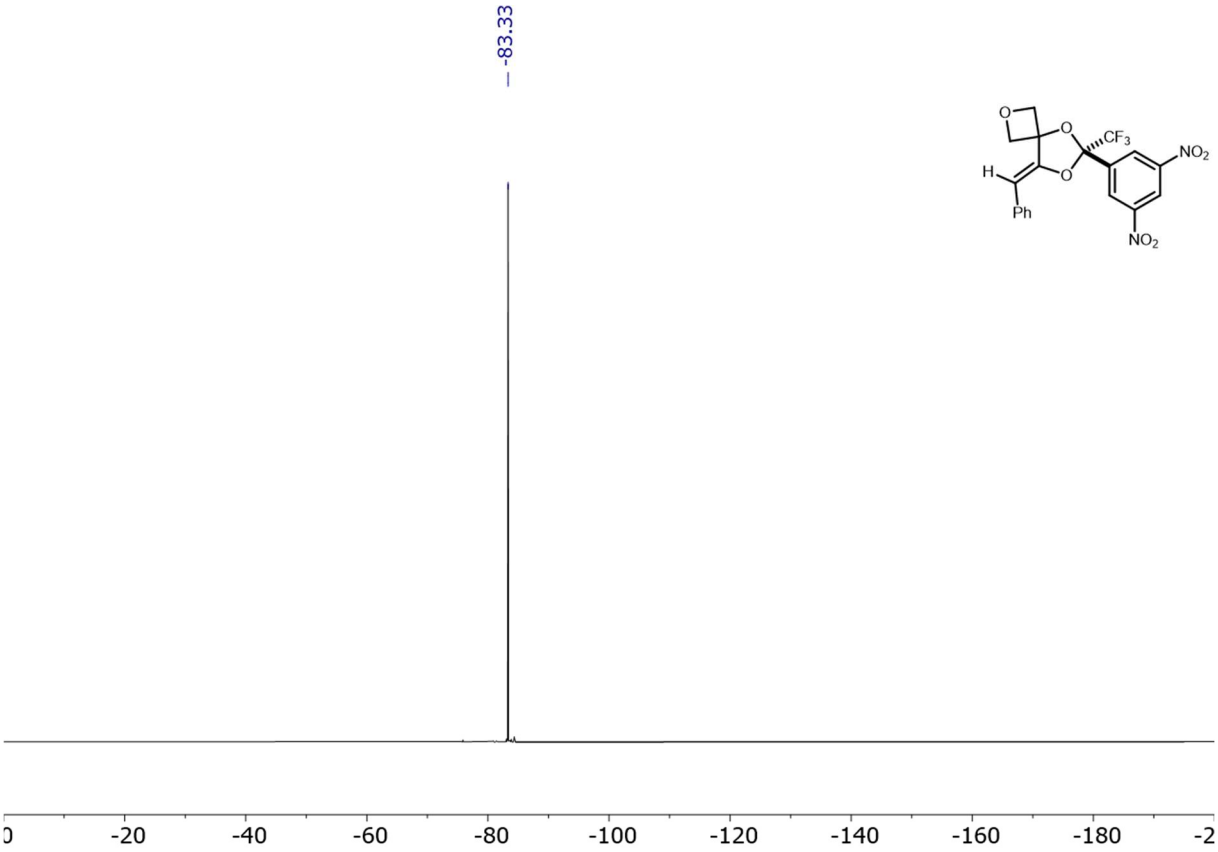
**[19r], HSQC, $C_6D_6$**



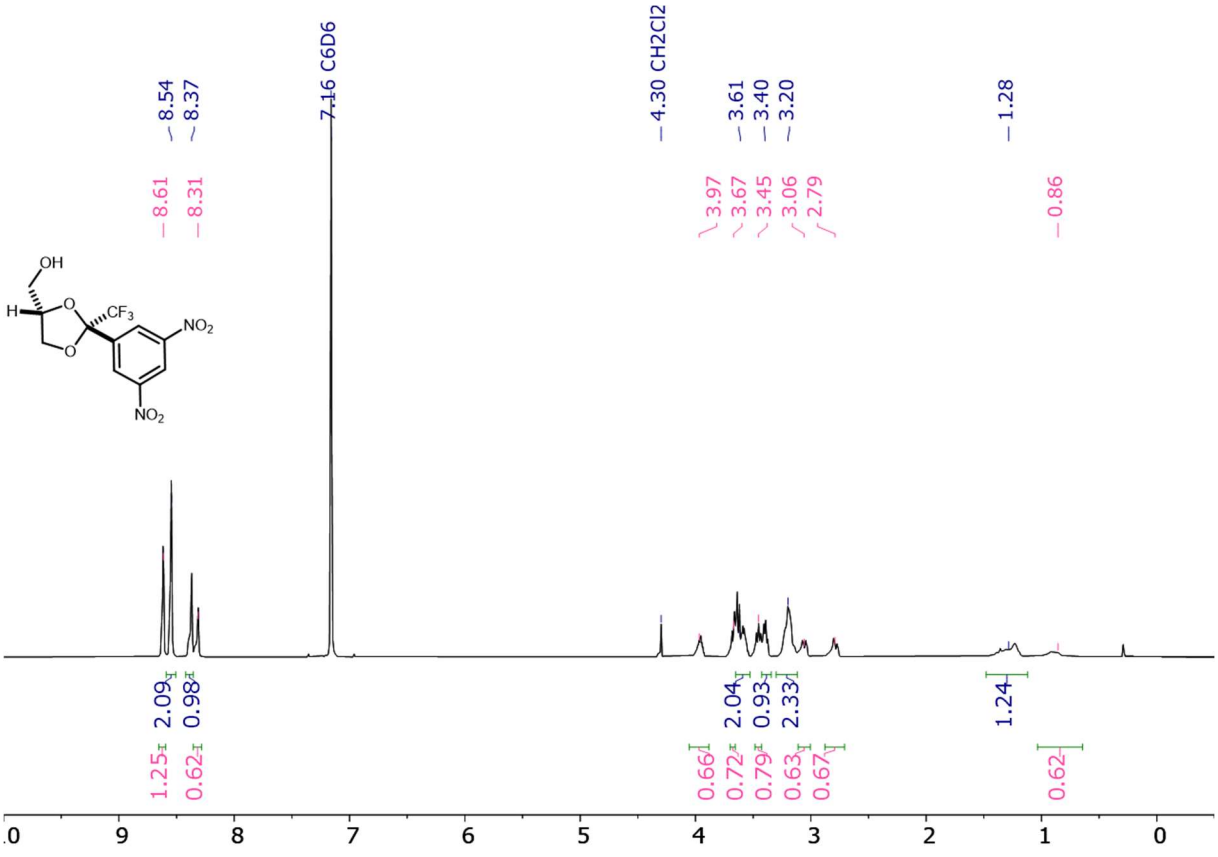

**[19r], HMBC, $C_6D_6$**



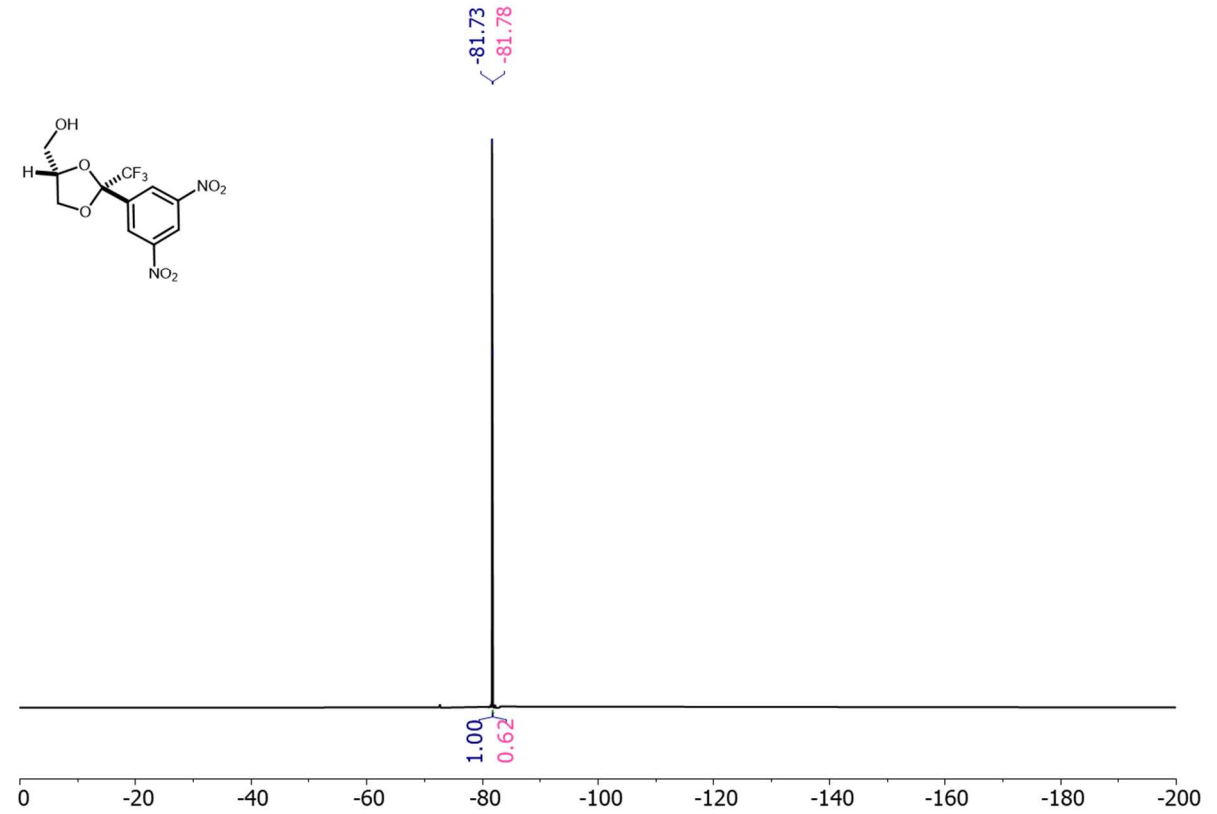
**[19r], $^{19}F$, $C_6D_6$, 377 MHz**



**[5b] from [*rac*-20], $^{1}H$, $C_6D_6$, 400 MHz**




**[5b] from [rac-20], $^{19}F$, $C_6D_6$, 377 MHz**

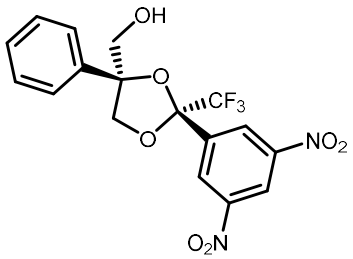


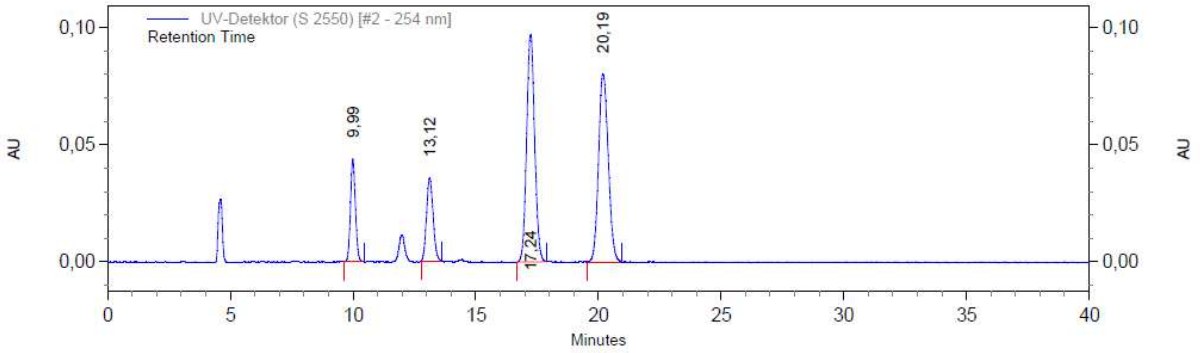
## 10.3. HPLC traces

**[5a]**

top: racemic sample

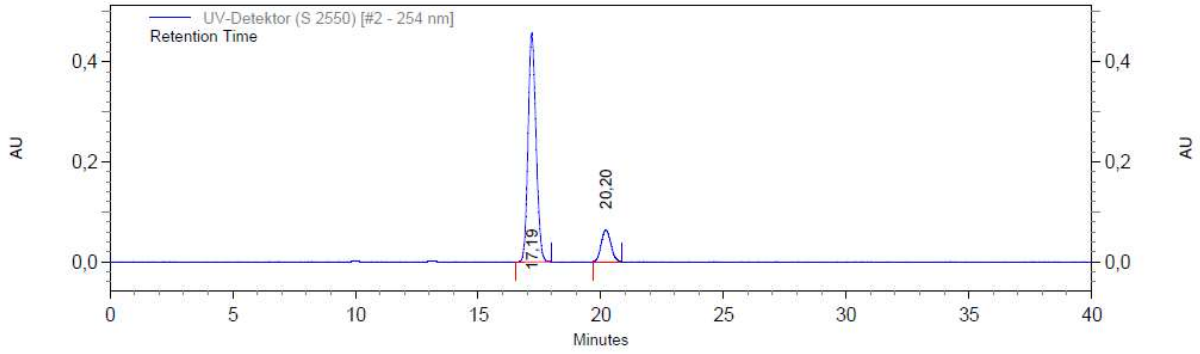
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| | Retention Time | Area | Area % |
|---|---|---|---|
| | 9,994 | 614407 | 10,80 |
| | 13,124 | 657166 | 11,56 |
| | 17,240 | 2205157 | 38,78 |
| | 20,186 | 2209892 | 38,86 |



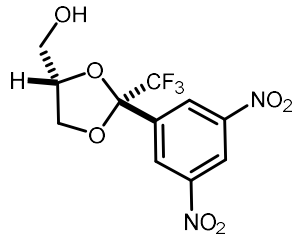

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

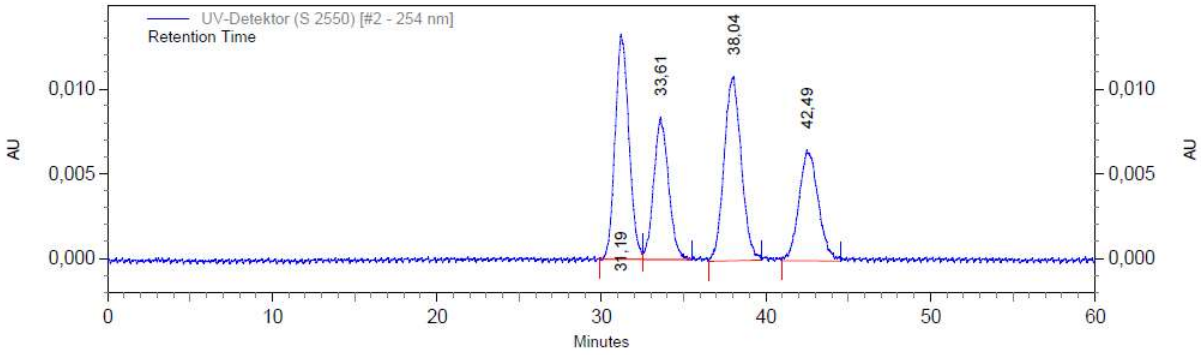
| | Retention Time | Area | Area % |
|---|---|---|---|
| | 17,186 | 10348746 | 85,58 |
| | 20,203 | 1743528 | 14,42 |

**[5b]**

top: racemic sample

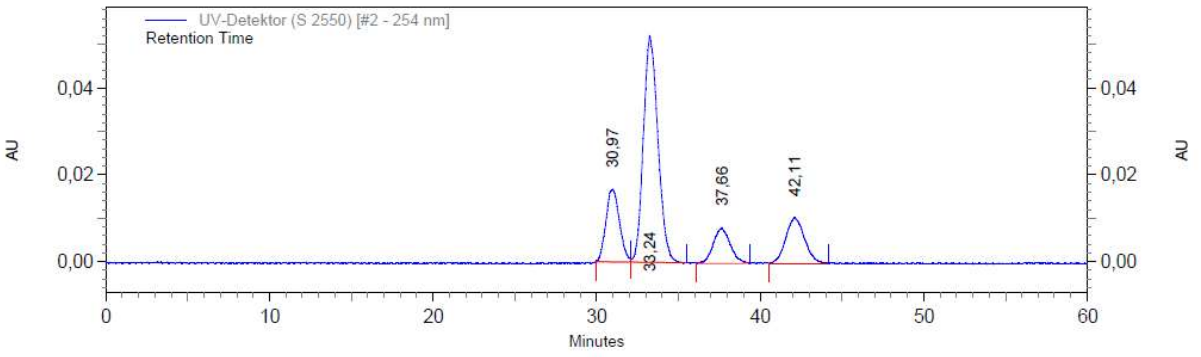
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 31,188 | 770860 | 29,49 |
| 33,606 | 523219 | 20,02 |
| 38,044 | 788082 | 30,15 |
| 42,488 | 531581 | 20,34 |

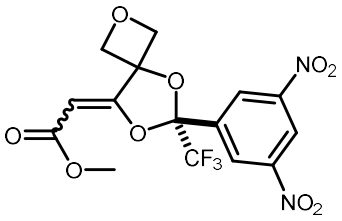


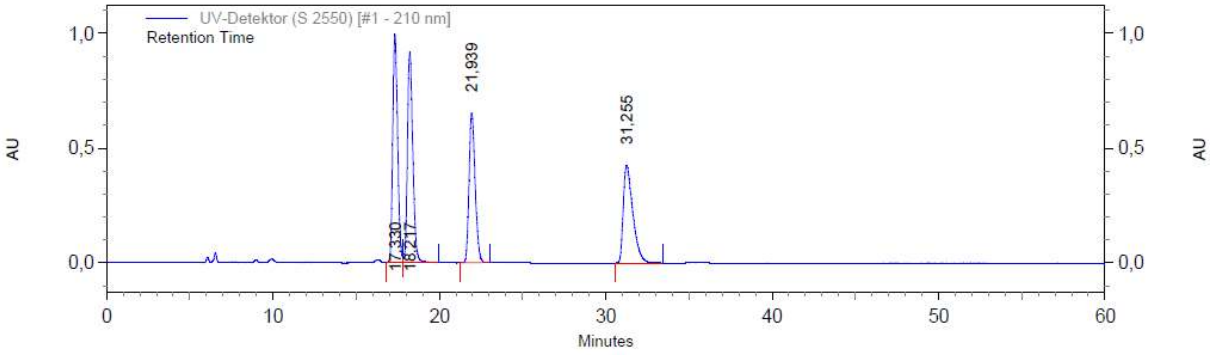

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 30,971 | 965888 | 17,16 |
| 33,244 | 3219806 | 57,20 |
| 37,661 | 590525 | 10,49 |
| 42,113 | 853259 | 15,16 |

**[5c]**

top: racemic sample



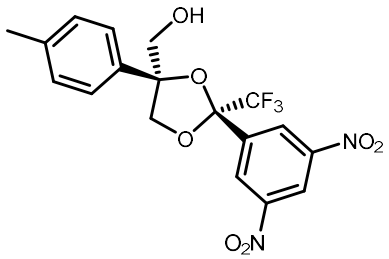

**UV-Detektor (S 2550) [#1 - 210 nm] Results**

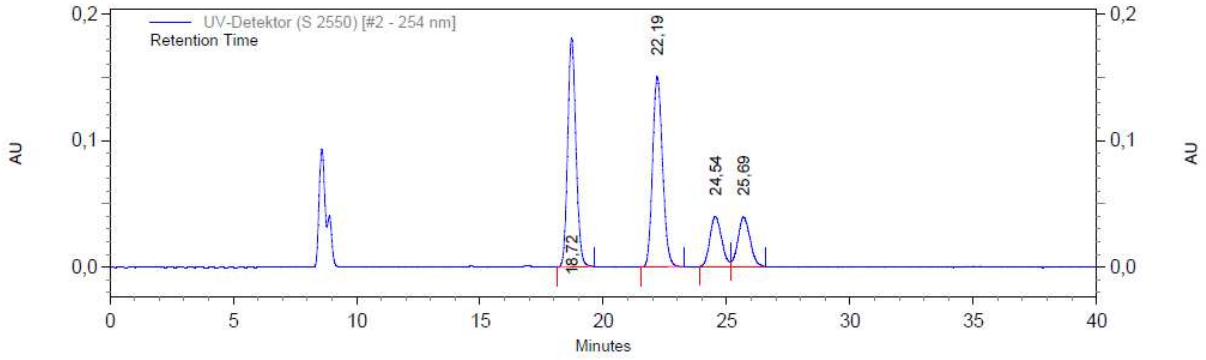
| Retention Time | Area | Area % |
|---|---|---|
| 17,330 | 20219869 | 27,12 |
| 18,217 | 20632360 | 27,68 |
| 21,939 | 16675848 | 22,37 |
| 31,255 | 17017538 | 22,83 |

**[5d]**

top: racemic sample

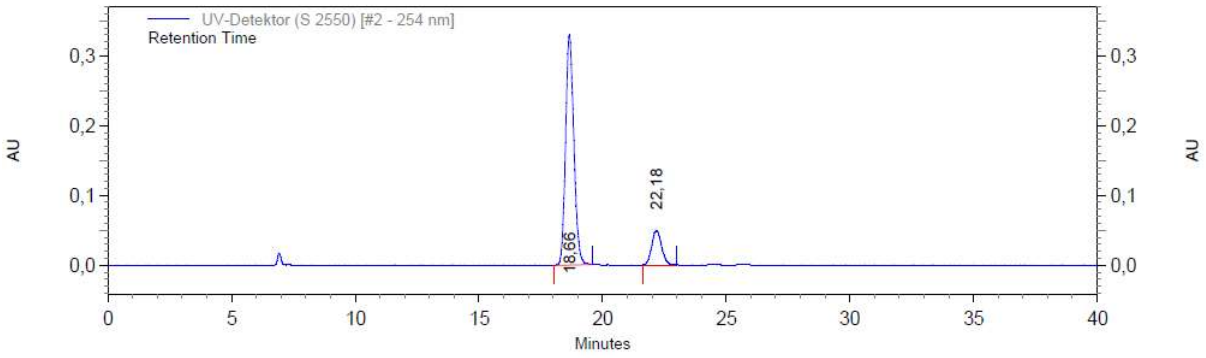
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 18,716 | 4233357 | 38,06 |
| 22,191 | 4235099 | 38,08 |
| 24,541 | 1308125 | 11,76 |
| 25,688 | 1345305 | 12,10 |



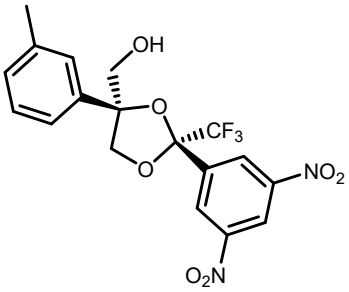

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

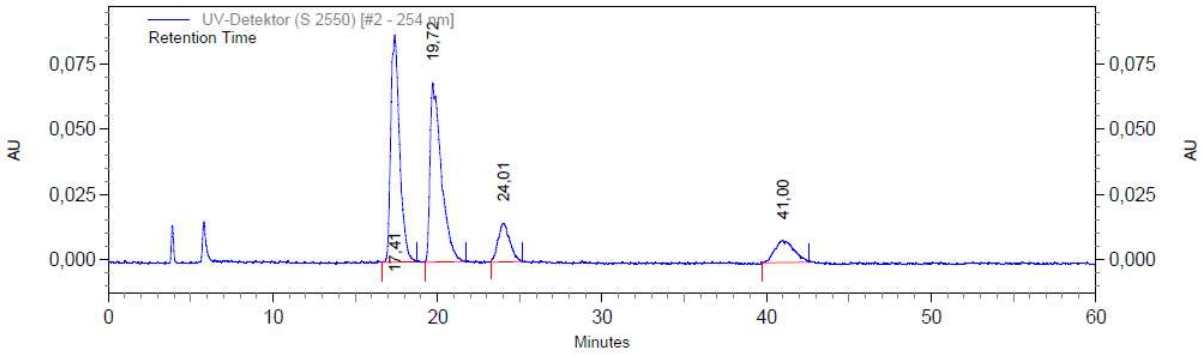
| Retention Time | Area | Area % |
|---|---|---|
| 18,659 | 7702288 | 84,87 |
| 22,182 | 1372770 | 15,13 |

**[5e]**

top: racemic sample

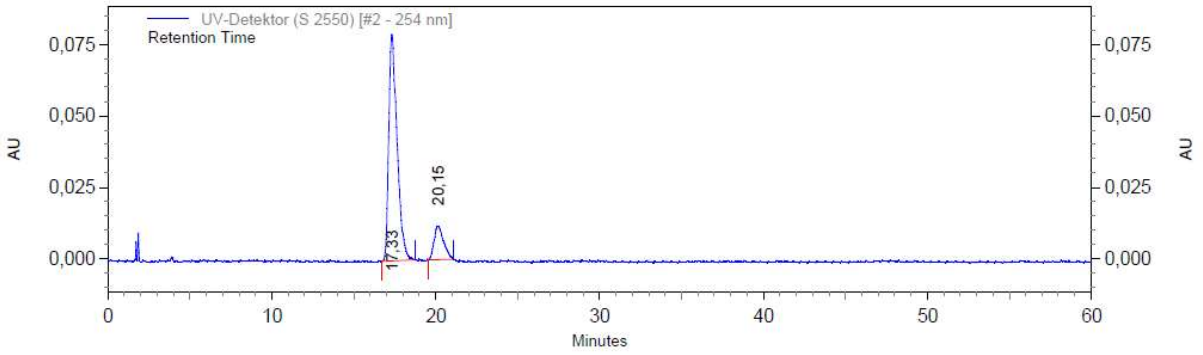
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| | Retention Time | Area | Area % |
|---|---|---|---|
| | 17,408 | 3246194 | 41,00 |
| | 19,720 | 3263611 | 41,22 |
| | 24,011 | 725967 | 9,17 |
| | 41,000 | 680922 | 8,60 |



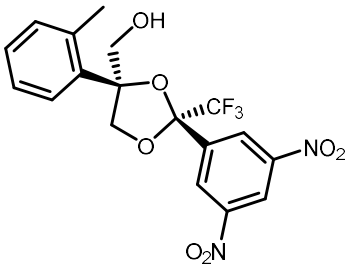

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

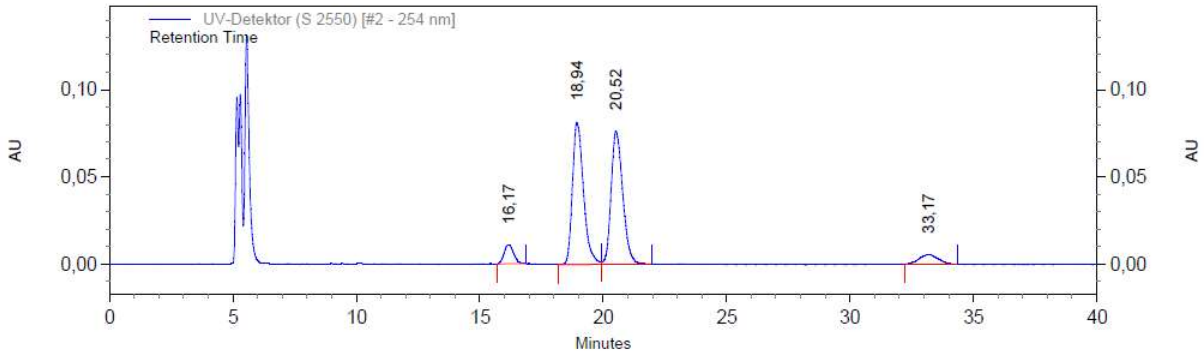
| | Retention Time | Area | Area % |
|---|---|---|---|
| | 17,331 | 2798840 | 85,44 |
| | 20,151 | 476975 | 14,56 |

**[5f]**

top: racemic sample

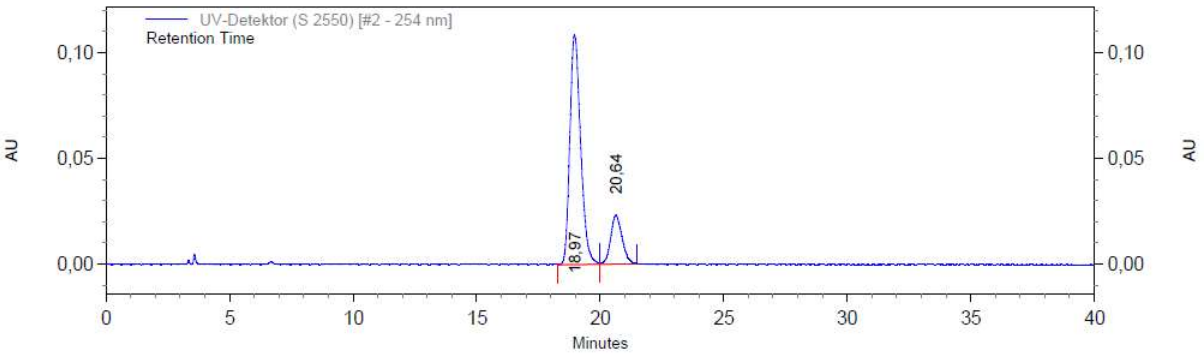
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 16,167 | 296666 | 5,25 |
| 18,936 | 2536925 | 44,94 |
| 20,516 | 2510502 | 44,47 |
| 33,169 | 301358 | 5,34 |



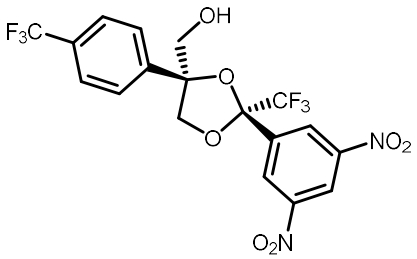

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

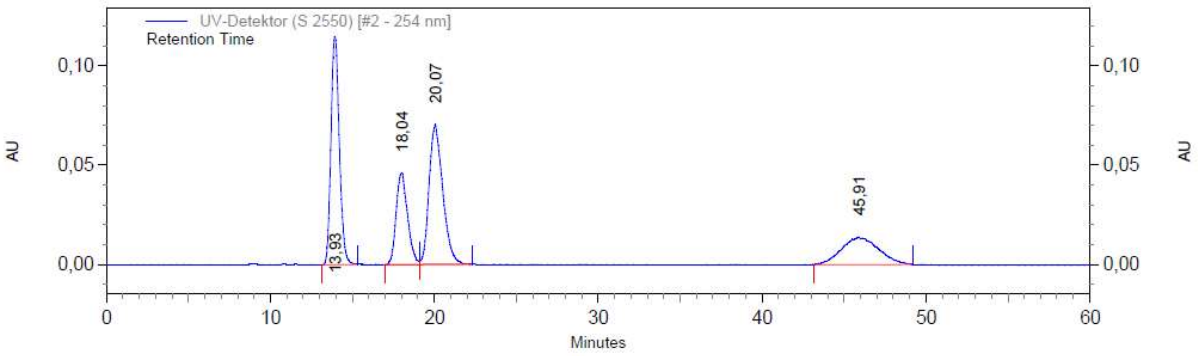
| Retention Time | Area | Area % |
|---|---|---|
| 18,968 | 3296768 | 81,62 |
| 20,637 | 742437 | 18,38 |

**[5g]**

top: racemic sample

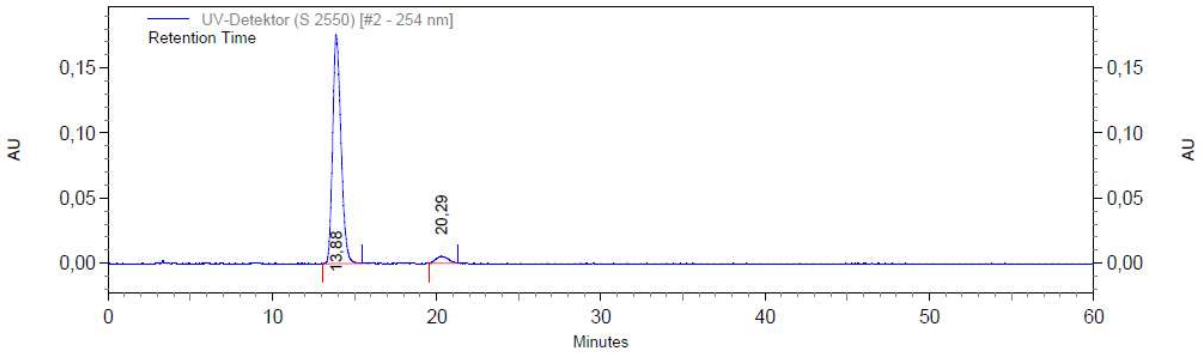
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 13,934 | 4068277 | 32,45 |
| 18,038 | 2231701 | 17,80 |
| 20,069 | 4078516 | 32,53 |
| 45,905 | 2157426 | 17,21 |



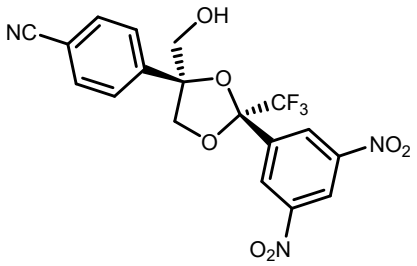

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

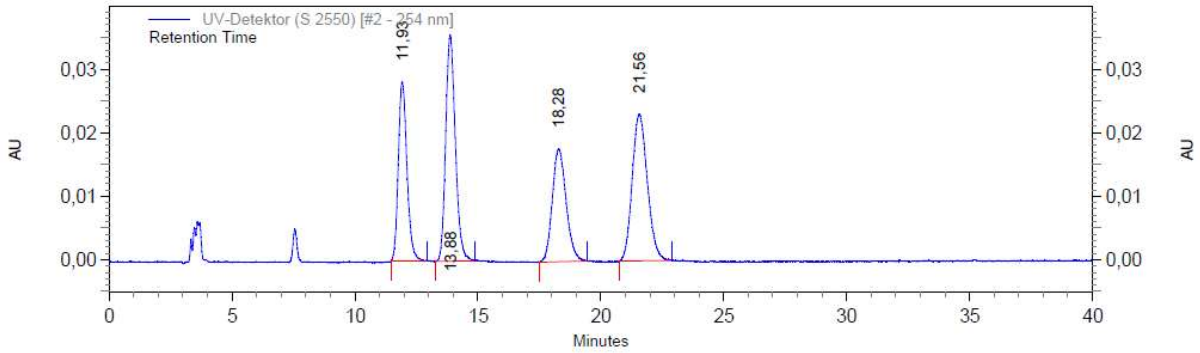
| Retention Time | Area | Area % |
|---|---|---|
| 13,878 | 6226805 | 95,79 |
| 20,287 | 273717 | 4,21 |

**[5h]**

top: racemic sample

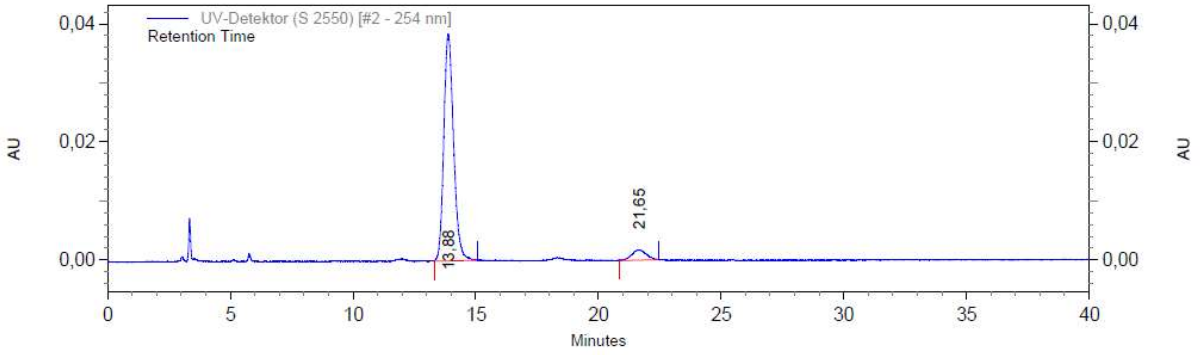
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 11,926 | 690003 | 20,60 |
| 13,879 | 973999 | 29,07 |
| 18,278 | 693107 | 20,69 |
| 21,559 | 993127 | 29,64 |



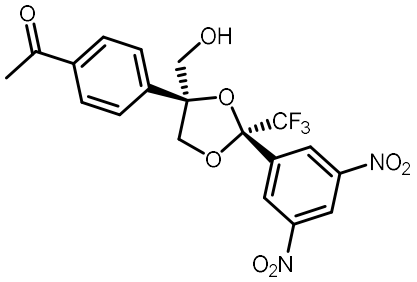

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

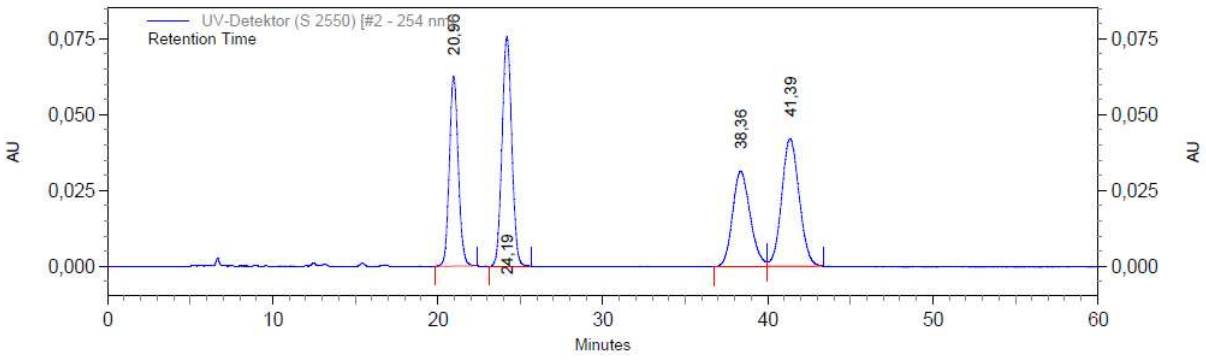
| Retention Time | Area | Area % |
|---|---|---|
| 13,880 | 1062847 | 93,64 |
| 21,652 | 72246 | 6,36 |

**[5i]**

top: racemic sample

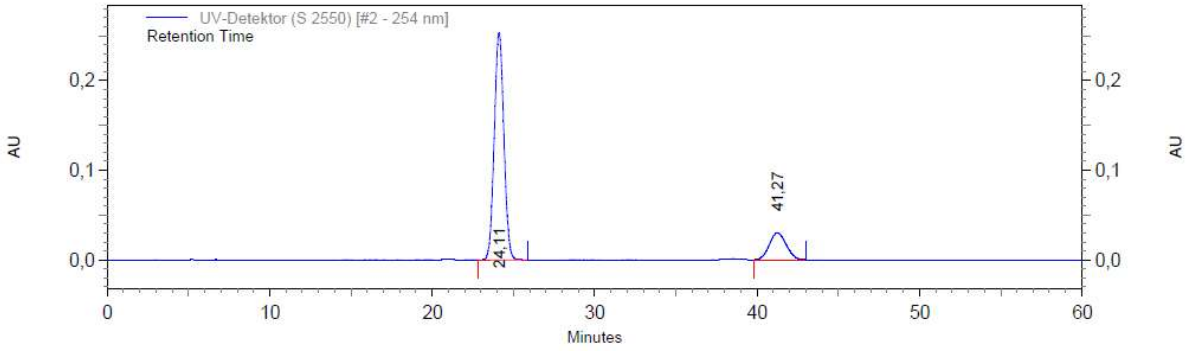
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 20,964 | 2360140 | 21,63 |
| 24,191 | 3109634 | 28,50 |
| 38,360 | 2333988 | 21,39 |
| 41,387 | 3107468 | 28,48 |



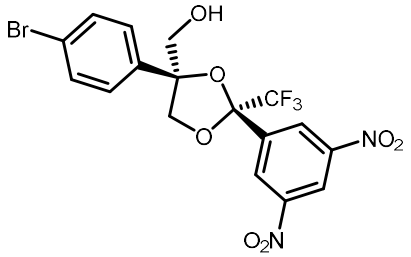

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

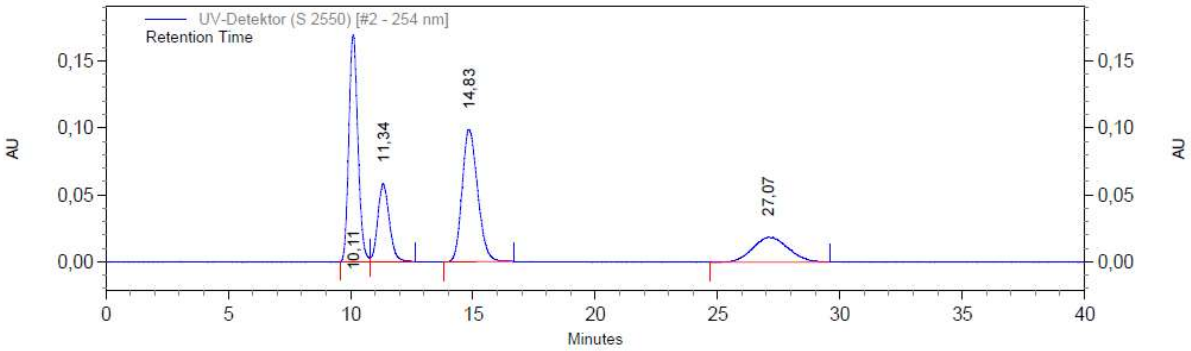
| Retention Time | Area | Area % |
|---|---|---|
| 24,111 | 10408891 | 82,64 |
| 41,267 | 2187048 | 17,36 |

**[5j]**

top: racemic sample

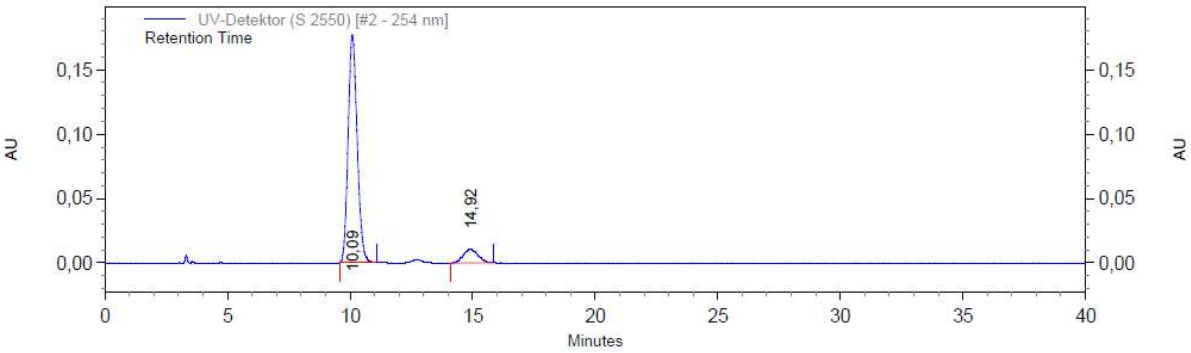
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 10,106 | 4375777 | 34,82 |
| 11,336 | 1916359 | 15,25 |
| 14,830 | 4384074 | 34,88 |
| 27,075 | 1892171 | 15,06 |



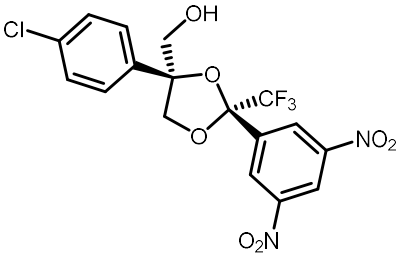

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

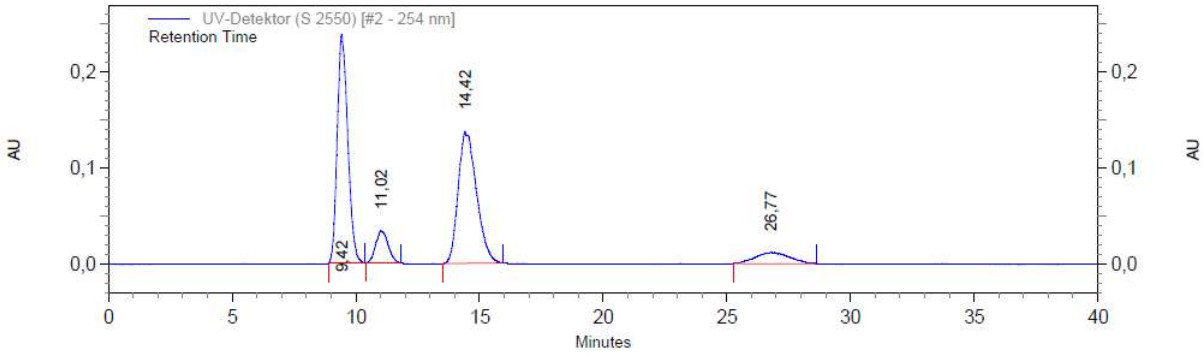
| Retention Time | Area | Area % |
|---|---|---|
| 10,092 | 4541153 | 91,03 |
| 14,917 | 447207 | 8,97 |

**[5k]**

top: racemic sample

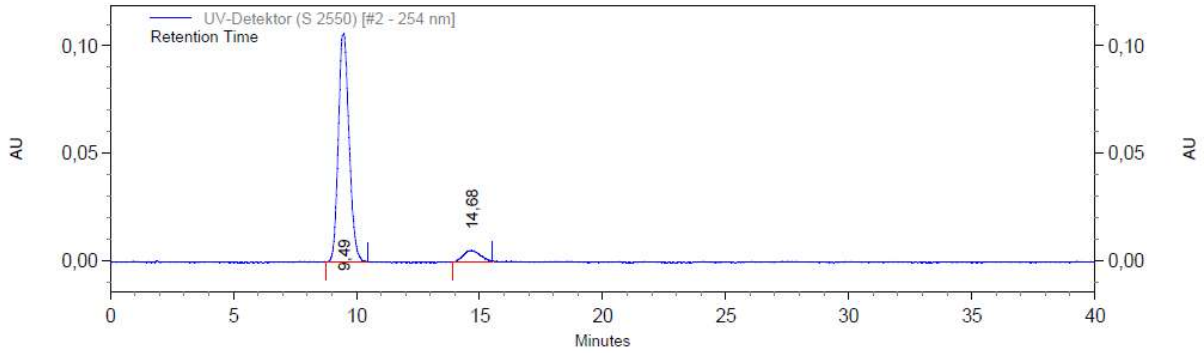
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 9,423 | 7056254 | 42,94 |
| 11,020 | 1184784 | 7,21 |
| 14,415 | 7059685 | 42,97 |
| 26,773 | 1130285 | 6,88 |



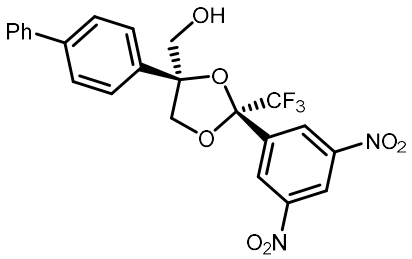

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

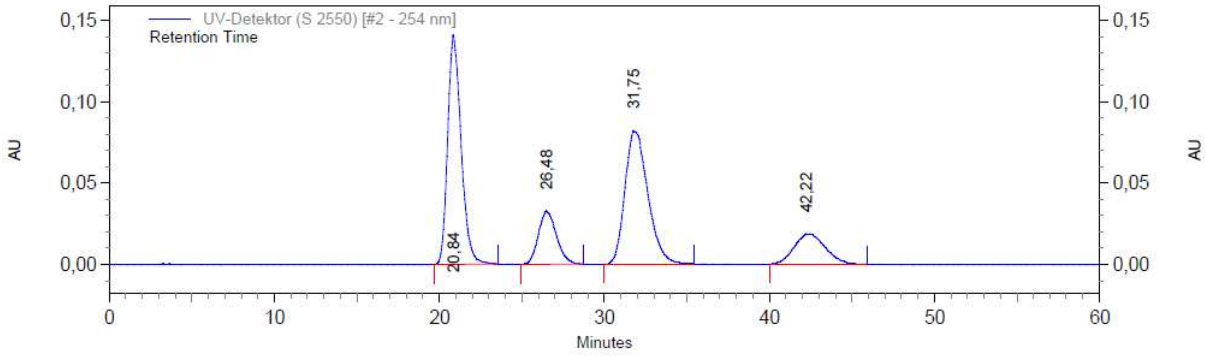
| Retention Time | Area | Area % |
|---|---|---|
| 9,490 | 3238669 | 92,78 |
| 14,683 | 251980 | 7,22 |

**[5l]**

top: racemic sample

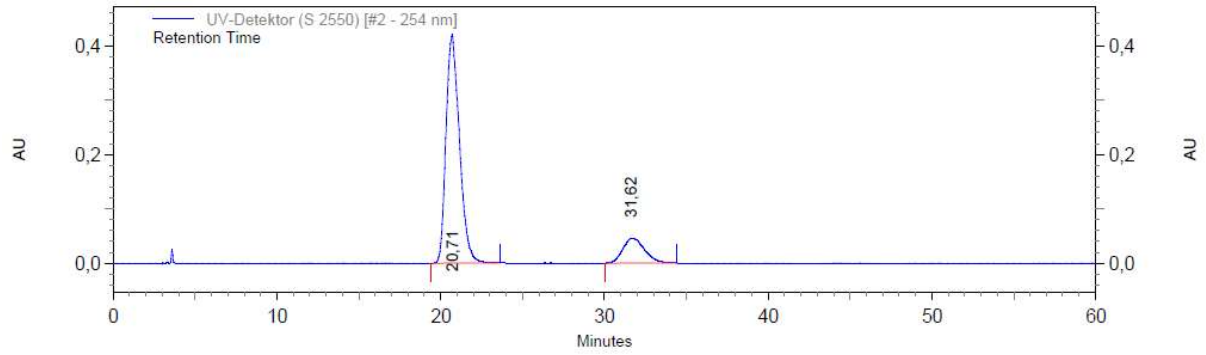
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| | Retention Time | Area | Area % |
|---|---|---|---|
| | 20,845 | 7964484 | 38,18 |
| | 26,479 | 2495380 | 11,96 |
| | 31,751 | 7927572 | 38,00 |
| | 42,224 | 2473161 | 11,86 |



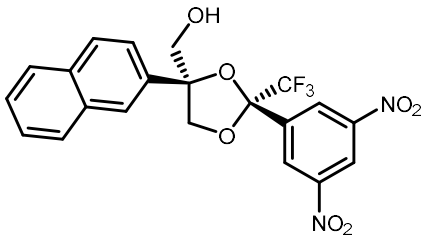

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

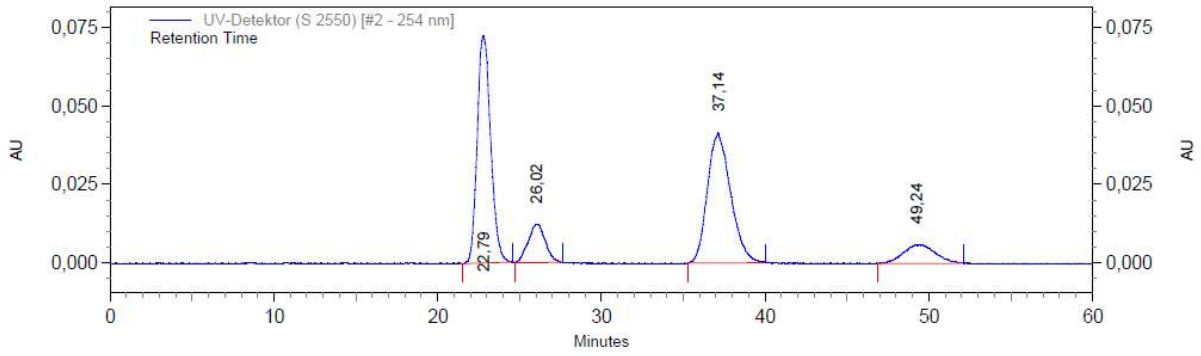
| | Retention Time | Area | Area % |
|---|---|---|---|
| | 20,706 | 23975597 | 84,86 |
| | 31,619 | 4277266 | 15,14 |

**[5m]**

top: racemic sample

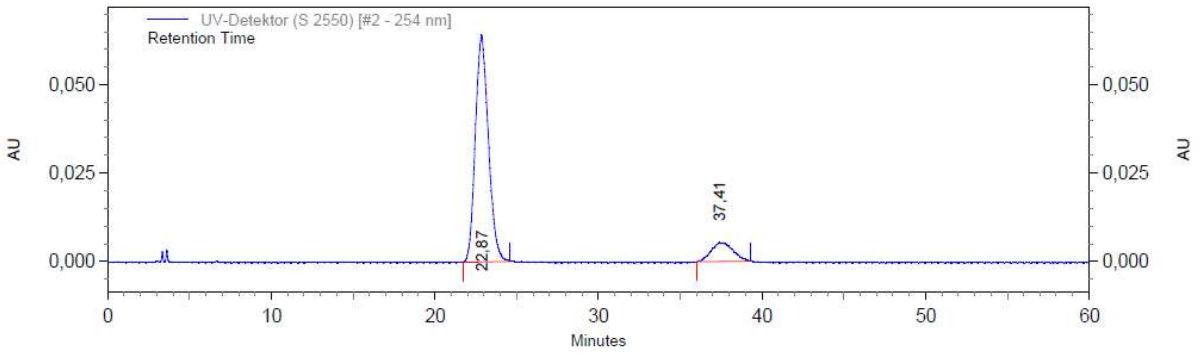
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 22,789 | 4126798 | 41,54 |
| 26,025 | 893318 | 8,99 |
| 37,139 | 4080621 | 41,08 |
| 49,243 | 832708 | 8,38 |



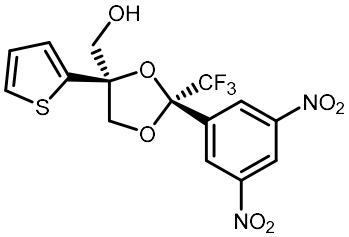

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

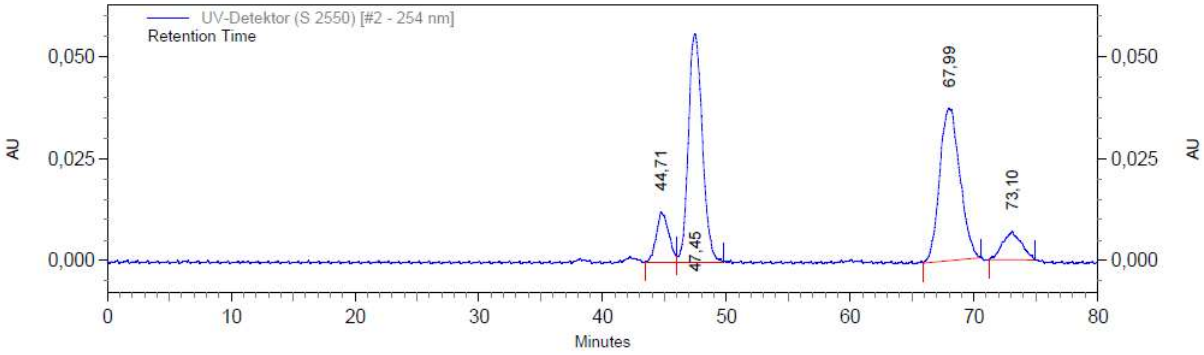
| Retention Time | Area | Area % |
|---|---|---|
| 22,872 | 3554017 | 87,91 |
| 37,407 | 488757 | 12,09 |

**[5n]**

top: racemic sample

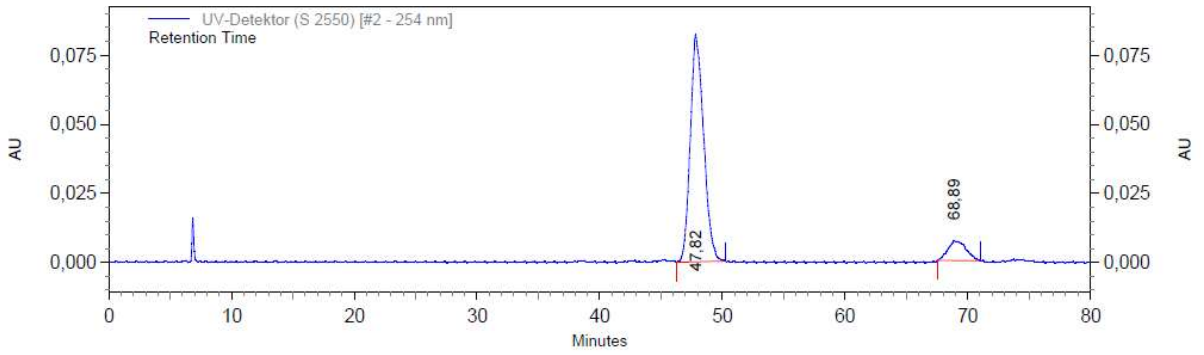
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 44,714 | 843326 | 8,26 |
| 47,454 | 4378905 | 42,88 |
| 67,994 | 4264530 | 41,76 |
| 73,105 | 724373 | 7,09 |



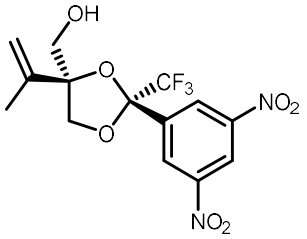

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

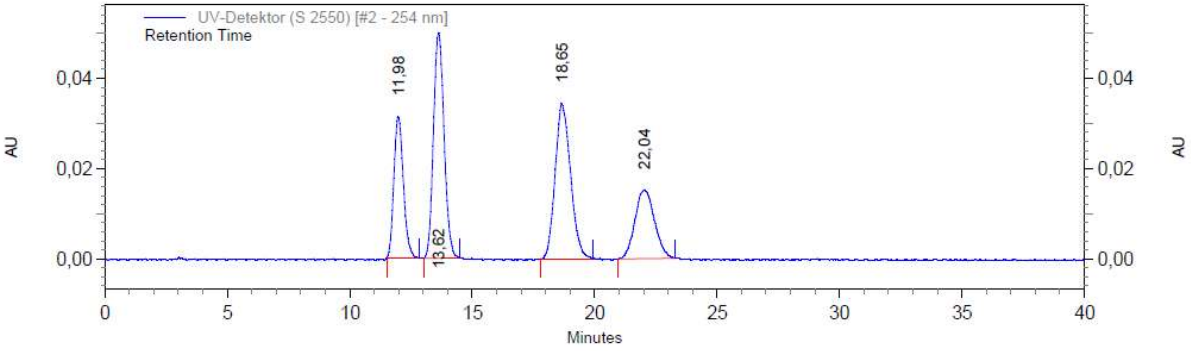
| Retention Time | Area | Area % |
|---|---|---|
| 47,824 | 6242746 | 89,48 |
| 68,893 | 733892 | 10,52 |

**[5o]**

top: racemic sample

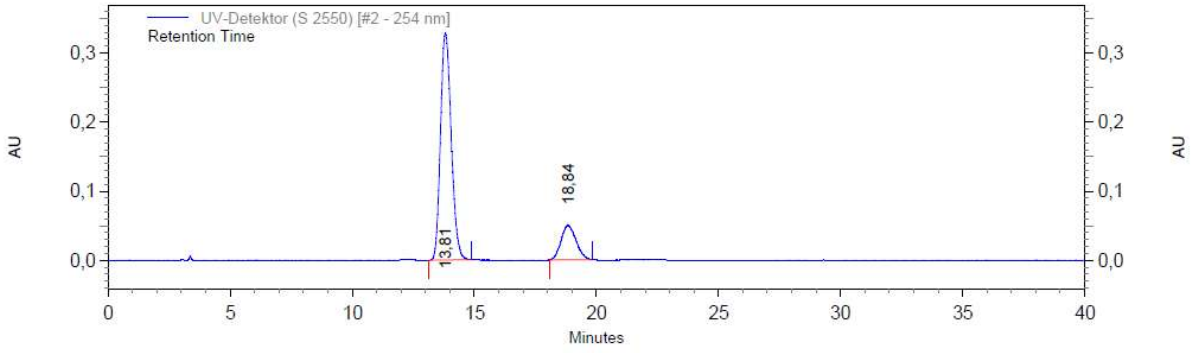
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 11,980 | 845338 | 17,95 |
| 13,624 | 1505700 | 31,97 |
| 18,654 | 1509140 | 32,04 |
| 22,040 | 849854 | 18,04 |



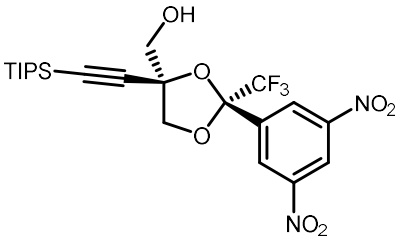

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

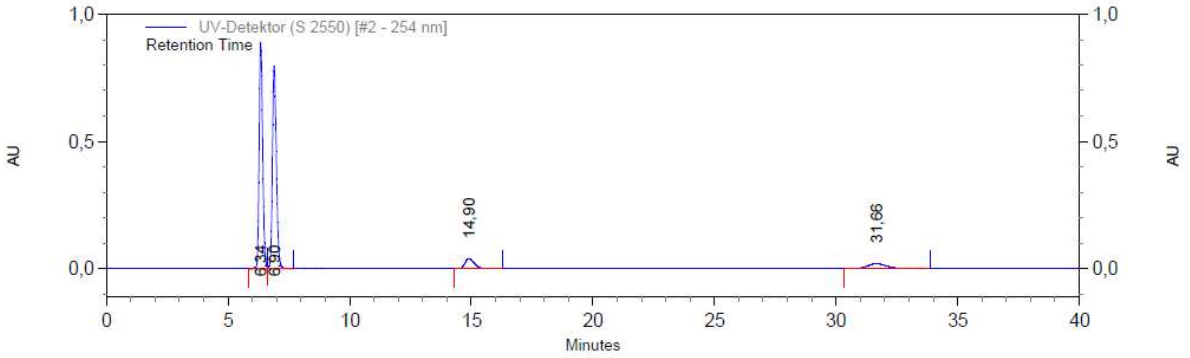
| Retention Time | Area | Area % |
|---|---|---|
| 13,812 | 10059458 | 82,55 |
| 18,835 | 2126861 | 17,45 |

**[5p]**

top: racemic sample

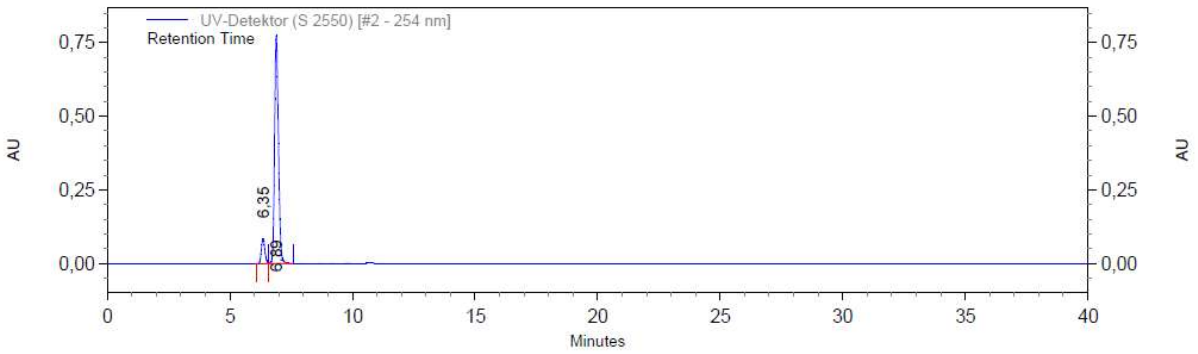
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 6,341 | 8874205 | 44,32 |
| 6,895 | 8953165 | 44,72 |
| 14,901 | 1080902 | 5,40 |
| 31,657 | 1114228 | 5,56 |



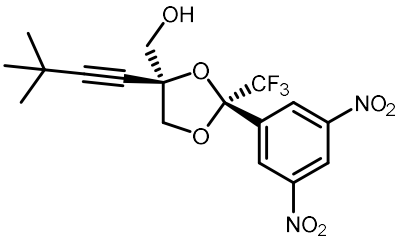

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

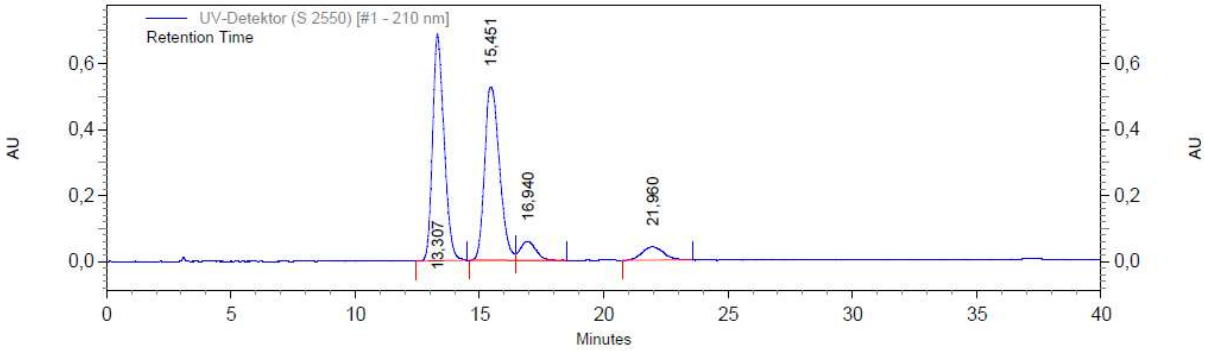
| Retention Time | Area | Area % |
|---|---|---|
| 6,350 | 840477 | 9,06 |
| 6,891 | 8434870 | 90,94 |

**[5q]**

top: racemic sample

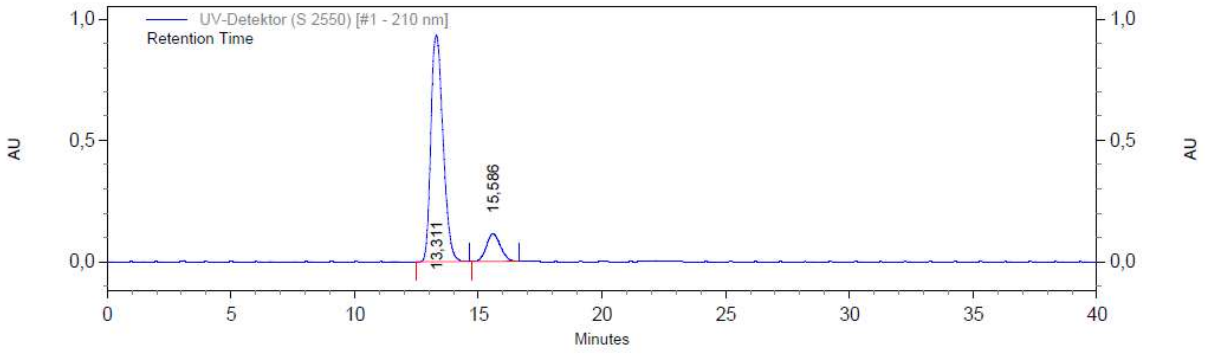
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#1 - 210 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 13,307 | 21941588 | 44,97 |
| 15,451 | 21859589 | 44,80 |
| 16,940 | 2533268 | 5,19 |
| 21,960 | 2461111 | 5,04 |



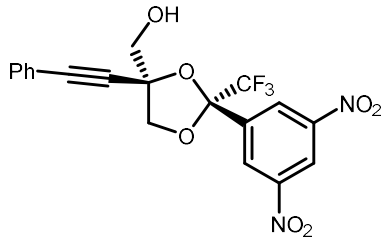

**UV-Detektor (S 2550) [#1 - 210 nm] Results**

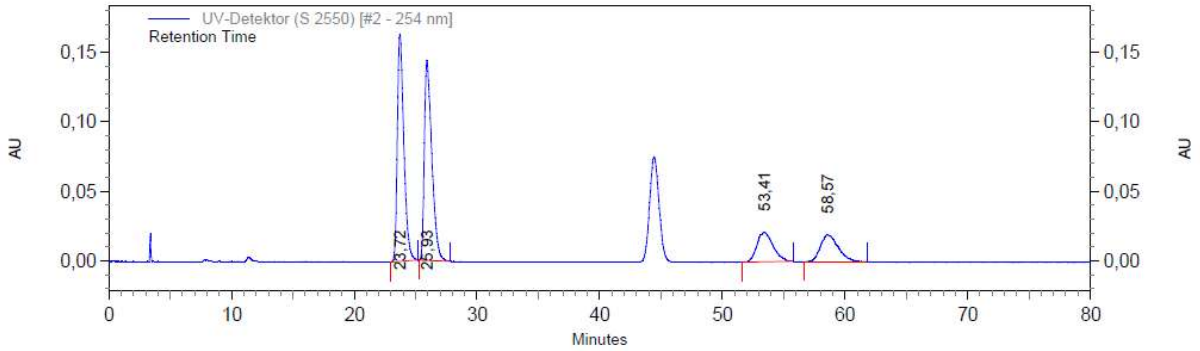
| Retention Time | Area | Area % |
|---|---|---|
| 13,311 | 31978914 | 87,72 |
| 15,586 | 4476856 | 12,28 |

**[5r]**

top: racemic sample

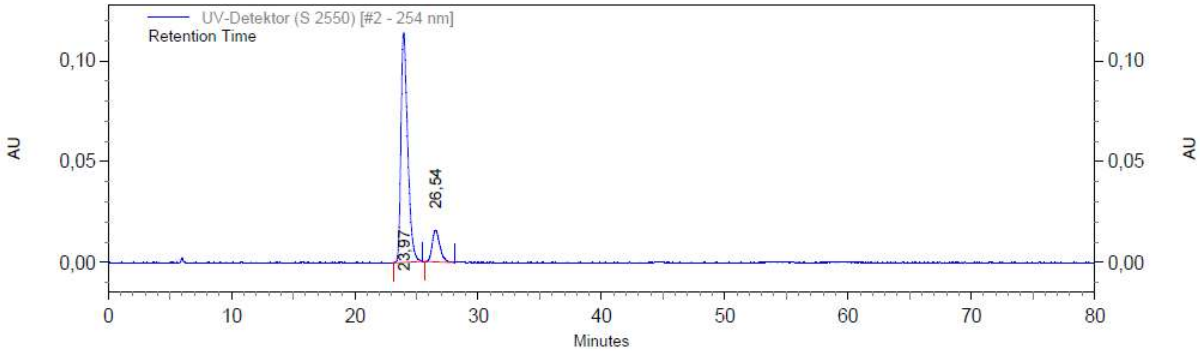
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| | Retention Time | Area | Area % |
|---|---|---|---|
| | 23,719 | 6049795 | 37,74 |
| | 25,926 | 6058532 | 37,80 |
| | 53,410 | 1942601 | 12,12 |
| | 58,570 | 1977768 | 12,34 |



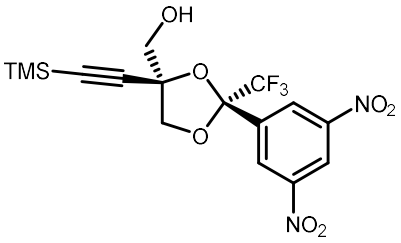

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

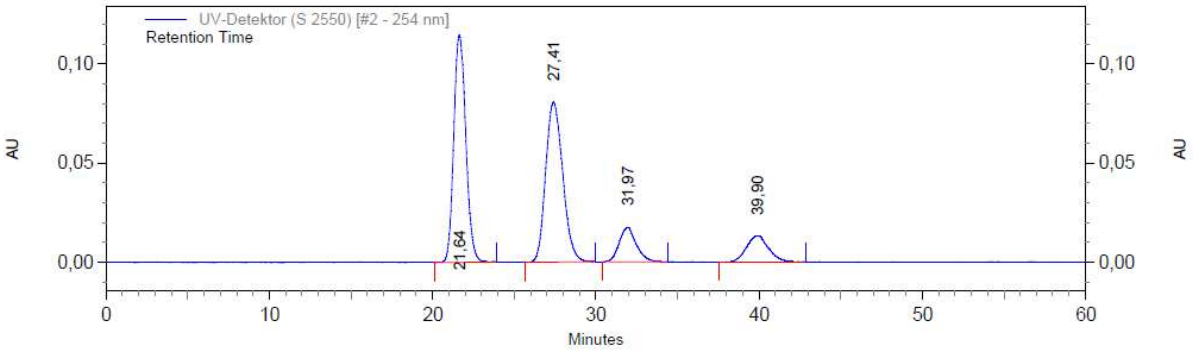
| | Retention Time | Area | Area % |
|---|---|---|---|
| | 23,972 | 4290756 | 86,29 |
| | 26,535 | 681944 | 13,71 |

**[5s]**

top: racemic sample

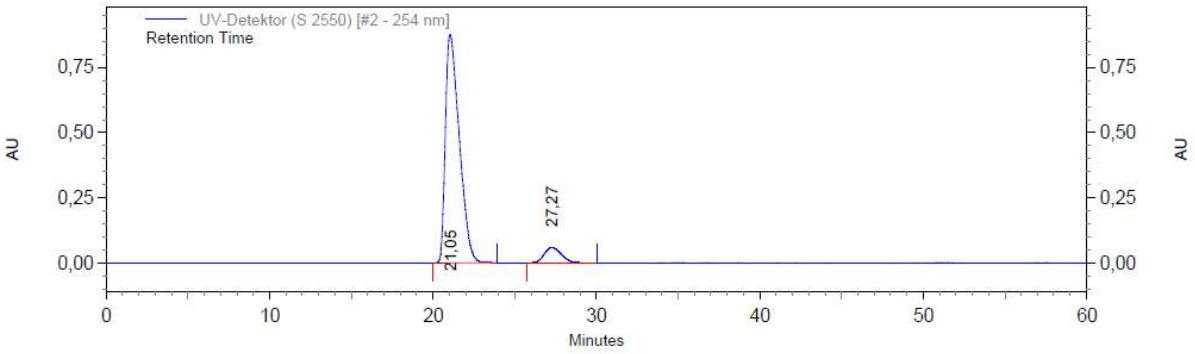
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 21,640 | 5888504 | 41,28 |
| 27,408 | 5870847 | 41,16 |
| 31,968 | 1262209 | 8,85 |
| 39,901 | 1242673 | 8,71 |



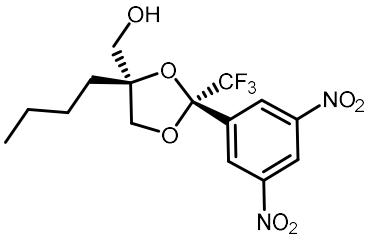

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

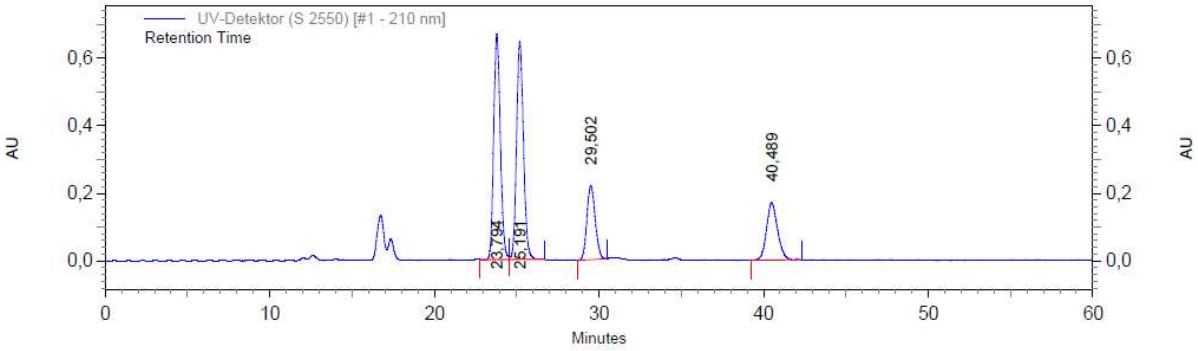
| Retention Time | Area | Area % |
|---|---|---|
| 21,051 | 51883031 | 92,42 |
| 27,267 | 4254934 | 7,58 |

**[5t]**

top: racemic sample

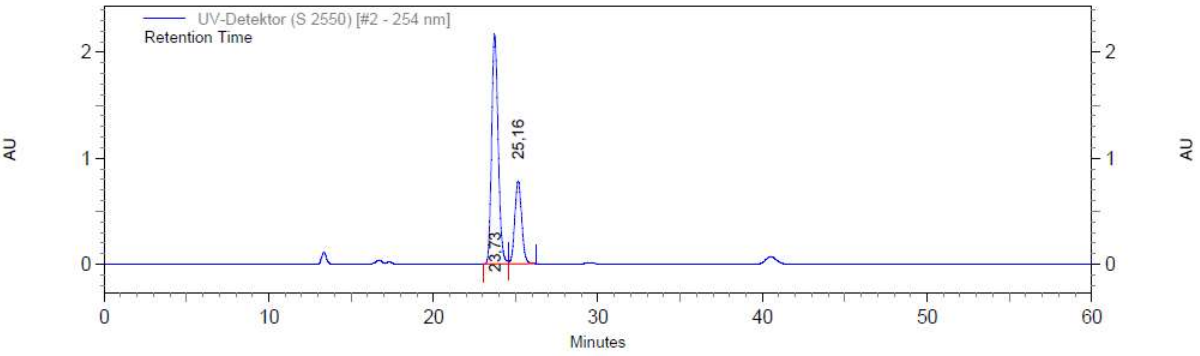
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#1 - 210 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 23,794 | 18618518 | 35,09 |
| 25,191 | 18815223 | 35,46 |
| 29,502 | 7656616 | 14,43 |
| 40,489 | 7974223 | 15,03 |



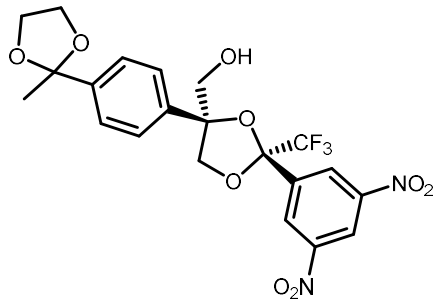

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

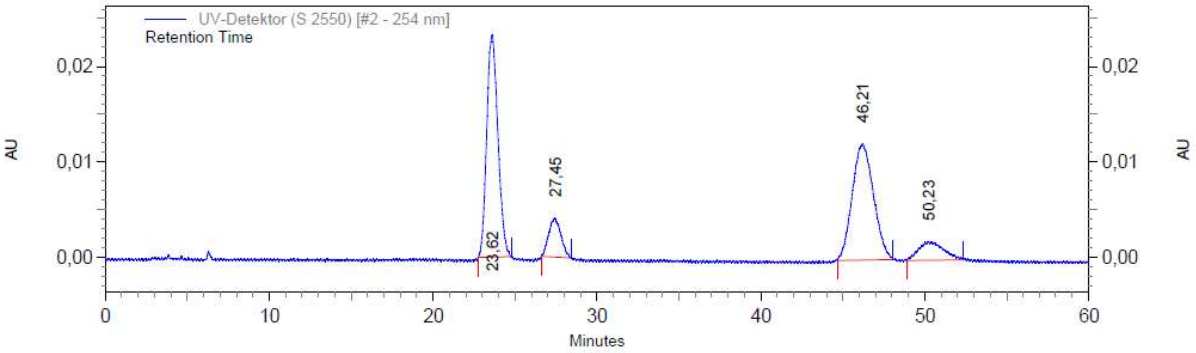
| Retention Time | Area | Area % |
|---|---|---|
| 23,725 | 59476009 | 72,42 |
| 25,155 | 22645386 | 27,58 |

**[5u]**

top: racemic sample

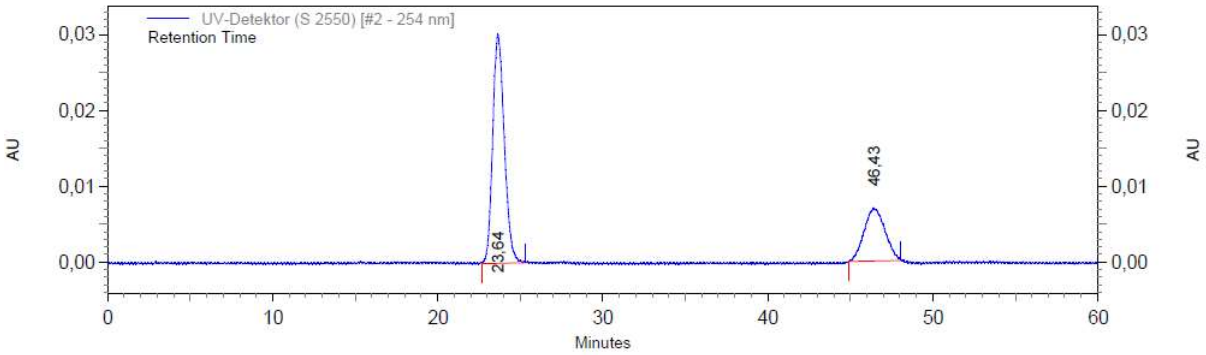
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 23,620 | 1102124 | 42,07 |
| 27,453 | 209364 | 7,99 |
| 46,210 | 1100045 | 41,99 |
| 50,234 | 208221 | 7,95 |



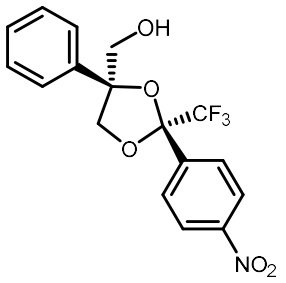

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

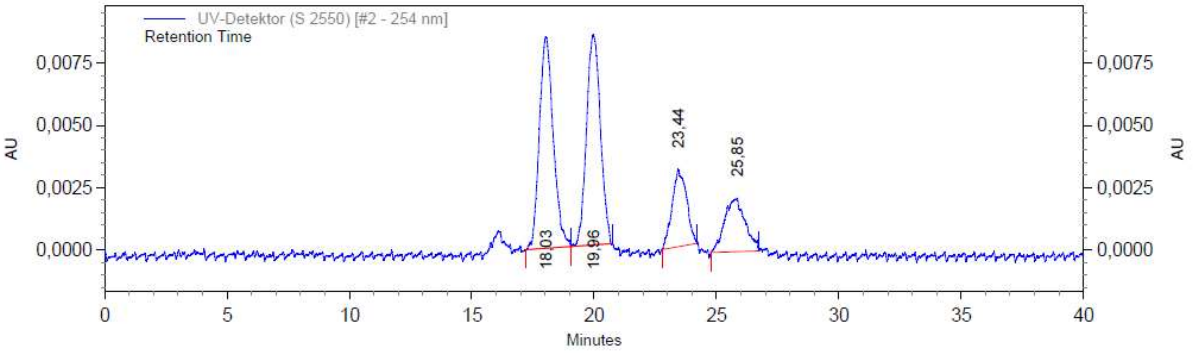
| Retention Time | Area | Area % |
|---|---|---|
| 23,644 | 1471549 | 70,64 |
| 46,432 | 611678 | 29,36 |

**[16a]**

top: racemic sample

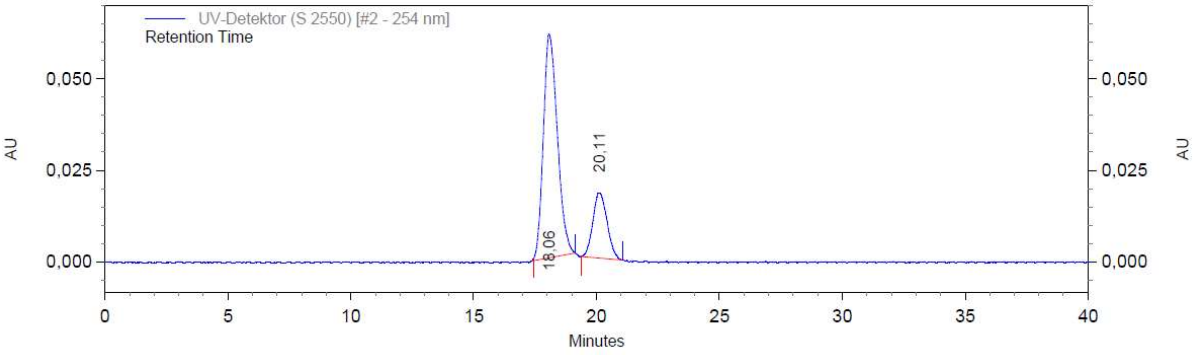
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 18,033 | 335775 | 36,44 |
| 19,962 | 333872 | 36,23 |
| 23,439 | 126532 | 13,73 |
| 25,851 | 125391 | 13,61 |



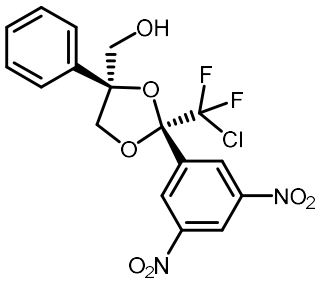

**UV-Detektor (S 2550) [#2 - 254 nm] Results**

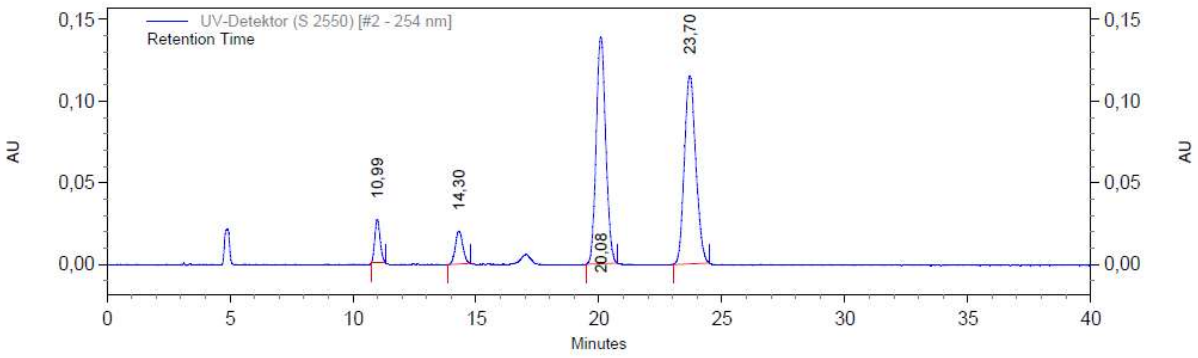
| Retention Time | Area | Area % |
|---|---|---|
| 18,061 | 2423370 | 77,06 |
| 20,106 | 721277 | 22,94 |

**[18a]**

top: racemic sample

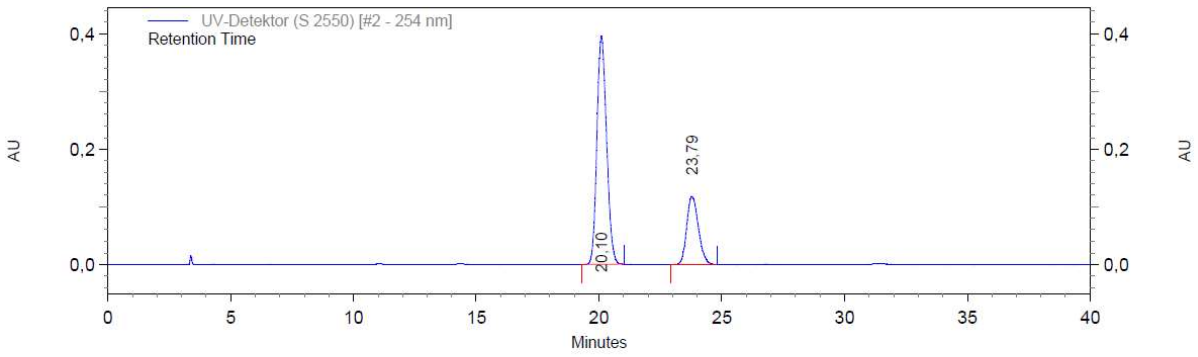
bottom: enantioenriched sample




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

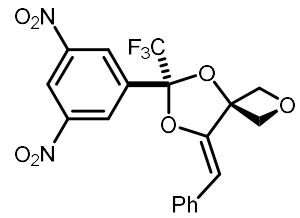
| Retention Time | Area | Area % |
|---|---|---|
| 10,988 | 411133 | 4,95 |
| 14,304 | 423824 | 5,10 |
| 20,080 | 3742769 | 45,05 |
| 23,701 | 3730837 | 44,90 |

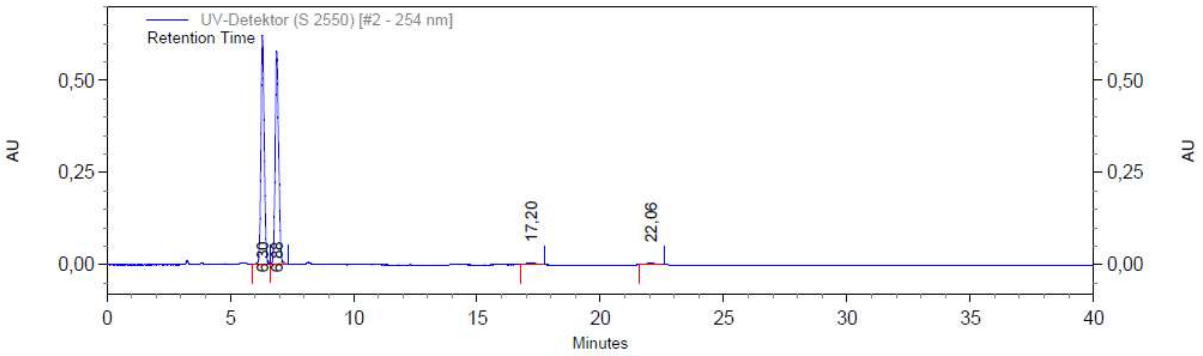



**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 20,097 | 10874210 | 73,52 |
| 23,786 | 3916634 | 26,48 |

**[19r]**




**UV-Detektor (S 2550) [#2 - 254 nm] Results**

| Retention Time | Area | Area % |
|---|---|---|
| 6,298 | 5684109 | 48,92 |
| 6,882 | 5667664 | 48,78 |
| 17,200 | 146596 | 1,26 |
| 22,056 | 120180 | 1,03 |