Supplementary Information

Deoxytrifluoromethylation/Aromatization of Cyclohexan(en)ones to Access Highly Substituted Trifluoromethyl Arenes

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1. General Considerations

Air- and moisture-sensitive reactions were carried out in oven-dried one-dram vials or 20 mL scintillation vials sealed with poly(tetrafluoroethylene) (PTFE)-lined septa or round bottom flasks fitted with rubber septum under an atmosphere of dry nitrogen (N_2). Plastic syringes equipped with stainless-steel needles were used to transfer air- and moisture-sensitive liquid reagents. Reactions were stirred using a teflon-coated magnetic stir bar, and elevated temperatures were maintained using thermostat-controlled heating mantles. Organic solvents were removed *in vacuo* using a rotary evaporator with a diaphragm vacuum pump or a BioChromato's smart evaporator with a diaphragm vacuum pump and a spiral plug (vacuum vortex concentration). Thin-layer analytical chromatography was performed on silica gel UNIPLATE Silica Gel HLF UV254 plates, and spots were visualized by quenching of ultraviolet light (λ = 254 nm). Purification of products was accomplished by automated flash column chromatography on silica gel (VWR Common Silica Gel 60 Å, 40–60 μm; normal phase chromatography) or C18 silica gel (Teledyne RediSep Gold C18 High Performance Columns, 100 Å, 20–40 μm, reverse phase chromatography). The reverse phase flash chromatography was performed with gradient elution from 5% acetonitrile (MeCN) in water (H_2O) (with 0.1% AcOH) to 95% MeCN in H_2O (with 0.1% AcOH).

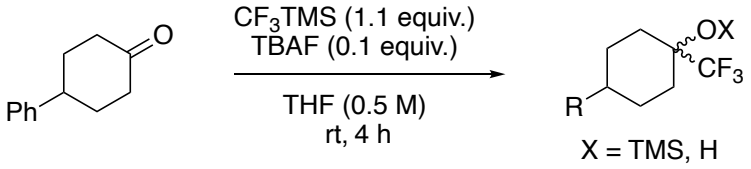
Unless otherwise noted, reagents were purchased from various commercial sources and used as received. NMR spectra were recorded on Bruker DRX 500 MHz (^{1}H at 500 MHz, ^{13}C {^{1}H} at 126 MHz, and ^{19}F at 470 MHz) or Bruker Avance III 800 with a QCI cryoprobe (^{1}H at 800 MHz and ^{13}C{^{1}H} at 201 MHz) nuclear magnetic resonance spectrometers. ^{1}H NMR spectra were calibrated against the peak of the residual $CHCl_3$ (7.26 ppm). ^{13}C{^{1}H} NMR spectra were calibrated against the peak of $CDCl_3$ (77.2 ppm). ^{19}F NMR spectra were calibrated against the peak of $CFCl_3$ (0.0 ppm). NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz), integration. High-resolution mass determinations were obtained by electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI) on a Waters LCT Premier mass spectrometer. Infrared spectra were measured on a PerkinElmer Spectrum Two Fourier Transform Infrared Spectrometer by drying samples on a diamond ATR sample base plate. Uncorrected melting points were measured on a Chemglass Digital Melting Point apparatus.

The chemical abbreviations utilized in this document include nitrogen (N_2), water (H_2O), ethyl acetate (EtOAc), diethyl ether (Et_2O), tetrahydrofuran (THF), acetonitrile (MeCN), chloroform ($CHCl_3$), dichloromethane (DCM), ethanol (EtOH), toluene (PhMe), *o*-dichlorobenzene (*o*-DCB), 1,2-dichloroethane (1,2-DCE), ammonium chloride (NH_4Cl), sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid (AcOH), triethyl amine (TEA), sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$), potassium carbonate (K_2CO_3), cesium carbonate (Cs_2CO_3), sodium thiosulfate ($Na_2S_2O_3$), chloro(1,5-cyclooctadiene)rhodium(I) dimer $[Rh(COD)Cl]_2$, lithium (Li^0), phosphorus tribromide (PBr_3), phosphorus trichloride (PCl_3), tetrakis(triphenylphosphine)palladium(0) {$Pd(PPh_3)_4$},

trimethylsilyl chloride (TMSCl), trifluoromethyltrimethylsilane ($TMSCF_3$), cesium fluoride (CsF), tetra-*n*-butylammonium fluoride (TBAF), *p*-toluenesulfonic acid monohydrate ($PTSA•H_2O$), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), thionyl chloride ($SOCl_2$), 4-dimethylaminopyridine (DMAP), *N*-bromosuccinimde (NBS), *N*-chlorosuccinimde (NCS), azobisisobutyronitrile (AIBN), copper(I) iodide (CuI), methyl iodide (MeI), hexafluoroisopropyl alcohol (HFIP), room temperature (rt), retention factor (R_f), and melting point (M.P.).

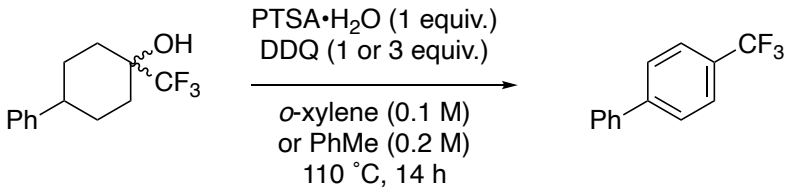
2. Procedures for Method Development

1,2-Addition Reaction on 4-Phenylcyclohexanone (Entry 1.1)



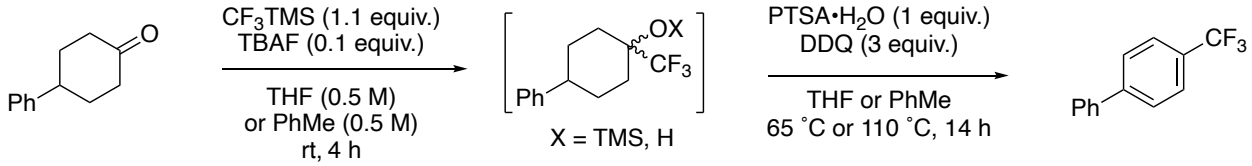
A one dram vial equipped with a stir bar was charged with 4-phenylcyclohexanone (17.4 mg, 0.100 equiv., 0.100 mmol), and the vial was evacuated and backfilled with N_2 (3x). THF (200 µL) was added followed by an addition of $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol). TBAF (1 M in THF) (10.0 µL, 0.10 equiv., 0.010 mmol) was slowly added (dropwise), and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard.

Dehydration/Aromatization Reaction on 4-Phenyl-1-(trifluoromethyl)cyclohexan-1-ol (Entry 1.2–1.3)



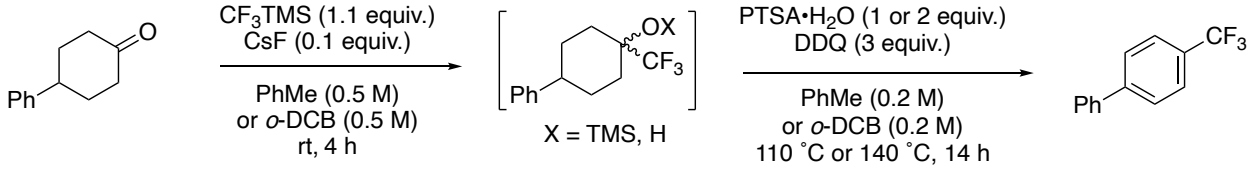
A one dram vial equipped with a stir bar was charged with 4-phenyl-1-(trifluoromethyl)cyclohexan-1-ol (24.3 mg, 1.00 equiv., 0.100 mmol), $PTSA•H_2O$ (19 mg, 1.0 equiv., 0.10 mmol) and DDQ (22.7 mg, 1.00 equiv., 0.100 mmol for Entry 1.2 or 68.1 mg, 3.00 equiv., 1.50 mmol for Entry 1.3). The flask was then evacuated and backfilled with N_2 (3x). *o*-Xylene (1.0 mL for Entry 1.2) or PhMe (0.50 mL for Entry 1.3) was then added, and the reaction was run for 14 h at 110 °C**.** The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

One Pot Method on 4-Phenylcyclohexanone to Access Ar–CF_3 with TBAF (Entry 1.4–1.5)



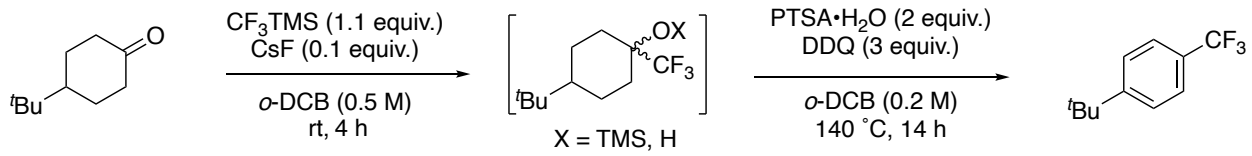
A one dram vial equipped with a magnetic stir bar was charged with 4-phenylcyclohexanone (17.4 mg, 0.10 equiv., 0.10 mmol). The flask was then evacuated and backfilled with N_2 (3x). THF (entry 1.4) or PhMe (entry 1.5) (200 µL) was added followed by an addition of $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol). TBAF (1 M in THF) (10 µL, 0.10 equiv., 0.010 mmol) was slowly added (dropwise) and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, PTSA•H_2O (19 mg, 1.0 equiv., 0.10 mmol) and DDQ (68.1 mg, 3.00 equiv., 0.30 mmol) were then added. THF (300 µL) for entry 1.4 or PhMe (300 µL) for entry 1.5 was then added, and the reaction was run for 14 h at 65 °C for entry 1.4 and 110 °C for entry 1.5. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

One Pot Method on 4-Phenylcyclohexanone to Access Ar–CF_3 with CsF (Entry 1.6–1.8)



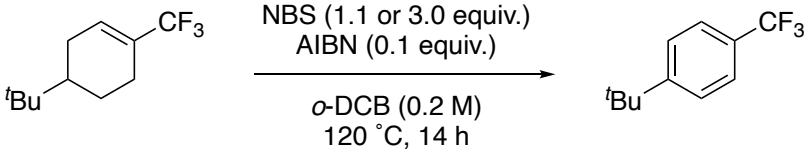
A one dram vial equipped with a magnetic stir bar was charged with 4-phenylcyclohexanone (17.4 mg, 0.100 equiv., 0.100 mmol). In a N_2 filled glovebox, CsF (1.5 mg, 0.10 equiv., 10 µmol) and PhMe (0.20 mL for entry 1.6) or *o*-DCB (0.20 mL for 1.7–1.8) were added. The vial was then taken out of glovebox and $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol) was added, and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, PTSA•H_2O (19 mg, 1.0 equiv., 0.10 mmol for entry 1.6–1.7 or 38 mg, 2.0 equiv., 0.20 mmol for entry 1.8) and DDQ (68.1 mg, 3.00 equiv., 0.30 mmol) were then added. PhMe (300 µL) for entry 1.6 or *o*-DCB (300 µL) for entry 1.7–1.8 was then added and the reaction was run for 14 h at 110 °C (entry 1.6–1.7) or 140 °C (entry 1.8). The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

One Pot Method on 4-*t*-Butylcyclohexanone to Access Ar–CF_3 with CsF (Entry 1.9)



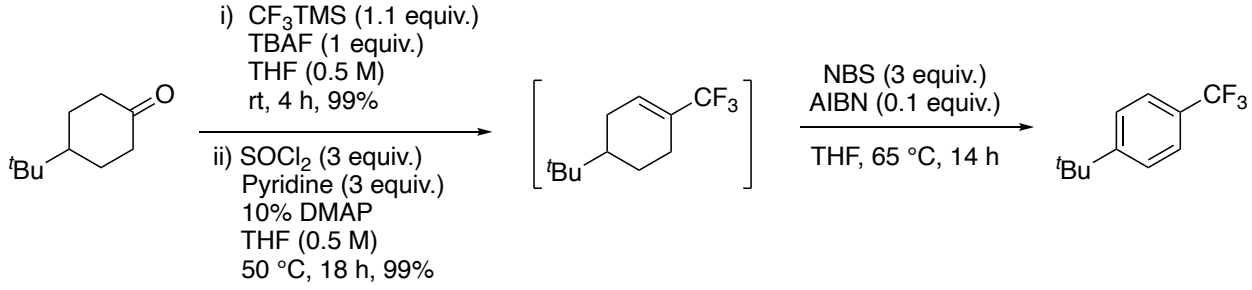
A one dram vial equipped with a magnetic stir bar was charged with 4-*t*-butylcyclohexanone (15.4 mg, 0.100 equiv., 0.100 mmol). In a N_2 filled glovebox, CsF (1.5 mg, 0.10 equiv., 10 µmol) and *o*-DCB (0.2 mL) were added. The vial was then taken out of glovebox and $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol) was added and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, PTSA•H_2O (38 mg, 2.0 equiv., 0.20 mmol) and DDQ (68.1 mg, 3.00 equiv., 0.300 mmol) were then added. *o*-DCB (300 µL) was then added, and the reaction was run for 14 h at 140 °C. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

Aromatization of 4-*t*-Butyl-1-(trifluoromethyl)cyclohex-1-ene (Entry 2.1–2.2)



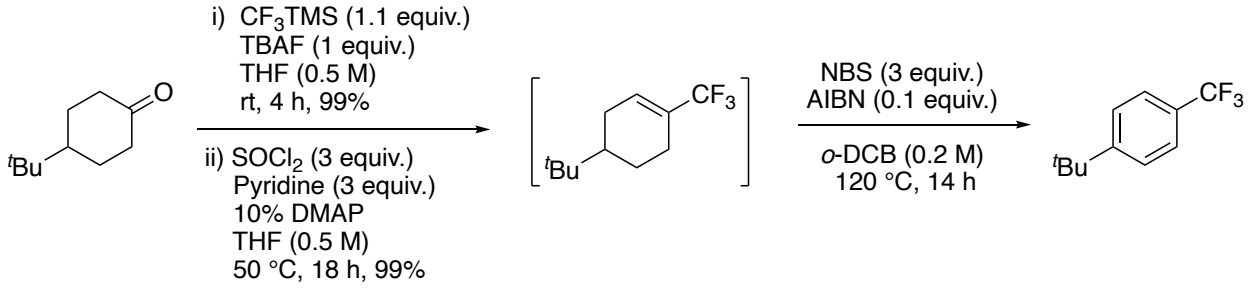
A one dram vial equipped with a stir bar was charged with 4-*t*-butyl-1-(trifluoromethyl)cyclohex-1-ene, AIBN (1.6 mg, 0.10 equiv., 0.010 mmol) and NBS (19.6 mg, 1.10 equiv., 0.110 mmol for entry 2.1 or 53.4 mg, 3.00 equiv., 0.300 mmol for entry 2.2), and the vial was evacuated and backfilled with N_2 (3x). *o*-DCB (0.50 mL) was added, and the reaction was run for 14 h at 120 °C. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

One-Pot Sequence on 4-*t*-Butylcyclohexanone to Access Ar–CF_3 (Entry 2.3)



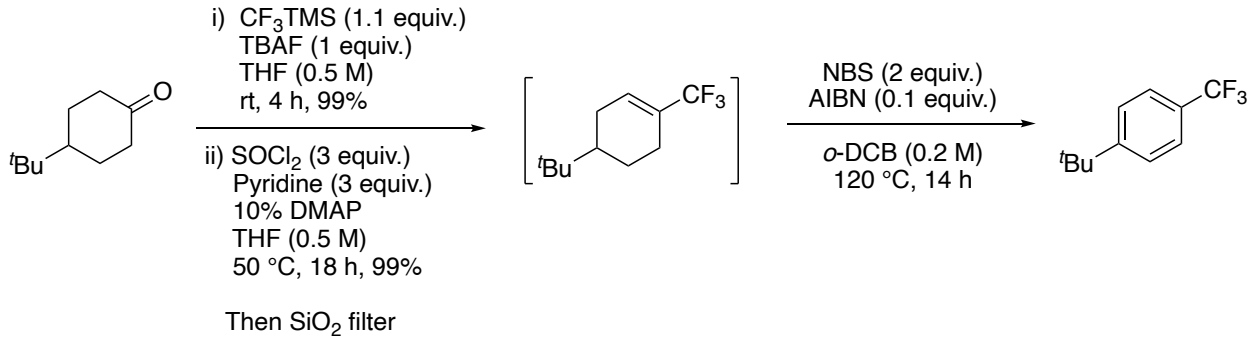
A one dram vial equipped with a stir bar was charged with 4-*t*-butylcyclohexanone (15.4 mg, 0.100 equiv., 0.100 mmol), and the vial was evacuated and backfilled with N_2 (3x). THF (200 µL) was added followed by an addition of $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol). TBAF (1 M in THF) (10 µL, 0.10 equiv., 0.010 mmol) was slowly added (dropwise), and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, DMAP (1.2 mg, 0.10 equiv., 0.010 mmol), pyridine (24 µL, 3.0 equiv., 0.30 mmol) and $SOCl_2$ (22 µL, 3.0 equiv., 0.30 mmol) were sequentially added. The reaction was run at 50 °C for 18 h. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. No addition of internal standard was required. AIBN (1.6 mg, 0.10 equiv., 0.010 mmol) and NBS (53.4 mg, 3.00 equiv., 0.300 mmol) were added. THF (300 µL) was added, and the reaction was run for 14 h at 65 °C. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

<u>One-Pot Sequence on 4-*t*-Butylcyclohexanone to Access Ar–CF_3 with a solvent swap (Entry 2.4)</u>



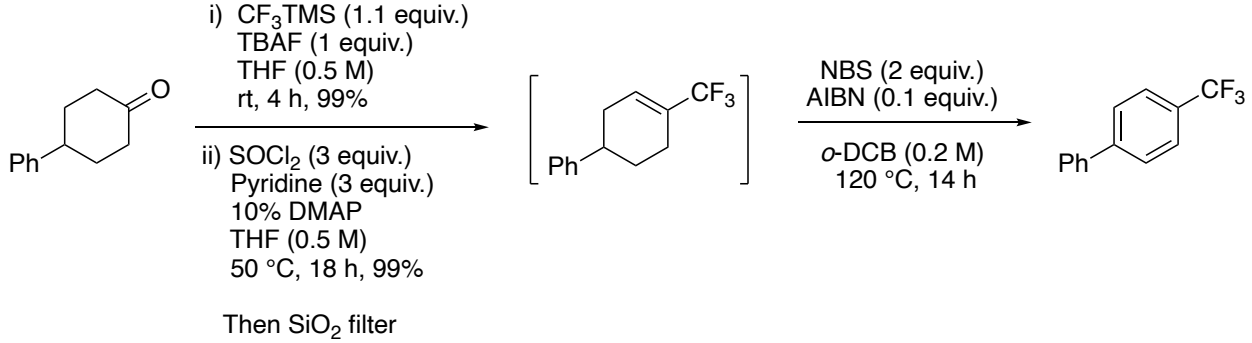
A one dram vial equipped with a stir bar was charged with 4-*t*-butylcyclohexanone (15.4 mg, 0.100 equiv., 0.100 mmol), and the vial was evacuated and backfilled with N_2 (3x). THF (200 µL) was added followed by an addition of $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol). TBAF (1 M in THF) (10 µL, 0.10 equiv., 0.010 mmol) was slowly added (dropwise), and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, DMAP (1.2 mg, 0.10 equiv., 0.010 mmol), pyridine (24 µL, 3.0 equiv., 0.30 mmol) and $SOCl_2$ (22 µL, 3.0 equiv., 0.30 mmol) were sequentially added. The reaction was run at 50 °C for 18 h. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. No addition of internal standard was required. The volatiles were then removed *in vacuo* using a rotary evaporator. AIBN (1.6 mg, 0.10 equiv., 0.010 mmol) and NBS (53.4 mg, 3.00 equiv., 0.300 mmol) were then added, and the vial was evacuated and backfilled with N_2 (3x). *o*-DCB (0.50 mL) was then added, and the reaction was run for 14 h at 120 °C. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

Two-Pot Sequence on 4-*t*-Butylcyclohexanone to Access Ar–CF_3 with a Silica Plug Filter and a Solvent Swap (Entry 2.5)



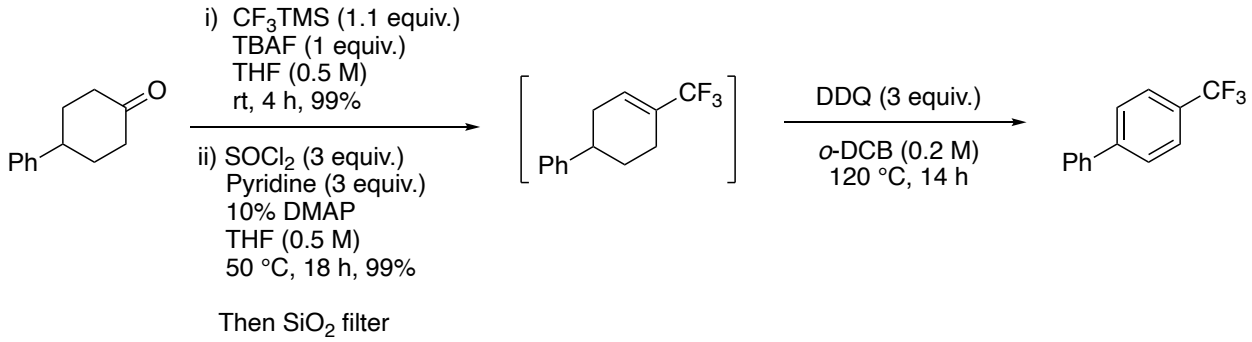
A one dram vial equipped with a stir bar was charged with 4-*t*-butylcyclohexanone (15.4 mg, 0.100 equiv., 0.100 mmol), and the vial was evacuated and backfilled with N_2 (3x). THF (200 µL) was added followed by an addition of $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol). TBAF (1 M in THF) (10 µL, 0.10 equiv., 0.010 mmol) was slowly added (dropwise), and the reaction was run for 4 h at rt. The reaction was then monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, DMAP (1.2 mg, 0.10 equiv., 0.010 mmol), pyridine (24 µL, 3.0 equiv., 0.30 mmol) and $SOCl_2$ (22 µL, 3.0 equiv., 0.30 mmol) were sequentially added. The reaction was run at 50 °C for 18 h. The reaction was then monitored by ^{19}F NMR with fluorobenzene as an internal standard. No addition of internal standard was required. The reaction mixture was filtered through a plug of silica and washed with Et_2O on a 1 dram vial. The volatiles were then removed *in vacuo* using a rotary evaporator. AIBN (1.6 mg, 0.10 equiv., 0.010 mmol) and NBS (35.6 mg, 2.00 equiv., 0.300 mmol) were then added, and the vial was evacuated and backfilled with N_2 (3x). *o*-DCB (0.50 mL) was then added, and the reaction was run for 14 h at 120 °C. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

Two-Pot Sequence on 4-Phenylcyclohexanone to Access Ar–CF_3 with a Silica Plug Filter and a Solvent Swap with NBS/AIBN (Entry 2.6)



A one dram vial equipped with a stir bar was charged with 4-phenylcyclohexanone (17.4 mg, 0.100 equiv., 0.100 mmol), and the vial was evacuated and backfilled with N_2 (3x). THF (200 µL) was added followed by an addition of $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol). TBAF (1 M in THF) (10.0 µL, 0.10 equiv., 0.010 mmol) was slowly added (dropwise), and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, DMAP (1.2 mg, 0.10 equiv., 0.010 mmol), pyridine (24 µL, 3.0 equiv., 0.30 mmol) and $SOCl_2$ (22 µL, 3.0 equiv., 0.30 mmol) were sequentially added. The reaction was run at 50 °C for 18 h. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. No addition of internal standard was required. The reaction mixture was filtered through a plug of silica and washed with Et_2O in a one dram vial. The volatiles were then removed *in vacuo* using a rotary evaporator. AIBN (1.6 mg, 0.10 equiv., 0.010 mmol) and NBS (35.6 mg, 2.00 equiv., 0.300 mmol) were then added, and the vial was evacuated and backfilled with N_2 (3x). *o*-DCB (0.50 mL) was then added, and the reaction was run for 14 h at 120 °C. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

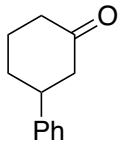
Two-Pot Sequence on 4-Phenylcyclohexanone to Access Ar–CF_3 with a Silica Plug Filter and a Solvent Swap with DDQ (Entry 2.7)



A one dram vial equipped with a stir bar was charged with 4-phenylcyclohexanone (17.4 mg, 0.100 equiv., 0.100 mmol), and the vial was evacuated and backfilled with N_2 (3x). THF (200 µL) was added followed by an addition of $TMSCF_3$ (16 µL, 1.1 equiv., 0.11 mmol). TBAF (1 M in THF) (10.0 µL, 0.10 equiv., 0.010 mmol) was slowly added (dropwise), and the reaction was run for 4 h at rt. The reaction was monitored by ^{19}F NMR with fluorobenzene as an internal standard. At completion, DMAP (1.2 mg, 0.10 equiv., 0.010 mmol), pyridine (24 µL, 3.0 equiv., 0.30 mmol) and $SOCl_2$ (22 µL, 3.0 equiv., 0.30 mmol) were sequentially added. The reaction was run at 50 °C for 18 h. The reaction was then monitored by ^{19}F NMR with fluorobenzene as an internal standard. No addition of internal standard was required. The reaction mixture was filtered through a plug of silica and washed with Et_2O in a one dram vial. The volatiles were then removed *in vacuo* using a rotary evaporator. DDQ (68 mg, 3.0 equiv., 0.30 mmol) was then added, and the vial was evacuated and backfilled with N_2

(3x). *o*-DCB (0.50 mL) was then added, and the reaction was run for 14 h at 120 °C. The reaction was monitored by ^{19}F NMR with HFIP as an internal standard.

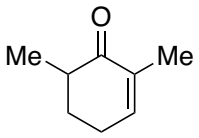
3. Preparation of Substrates



3-Phenylcyclohexan-1-one (2S)

The compound was prepared with a slight modification to a known procedure[1]. An oven dried 20 mL scintillation vial equipped with a magnetic stir bar was charged with phenylboronic acid (1.829 g, 1.500 equiv., 15.00 mmol) and $[Rh(COD)Cl]_2$ (49.0 mg, 0.10 equiv., 100 µmol). 1,4-Dioxane (9.0 mL) and distilled H_2O (1.5 mL) were added to the flask. A solution of cyclohex-2-en-1-one (490 mg, 1.00 equiv., 5.00 mmol) in 1,4-dioxane (2.0 mL) along with TEA (0.70 mL, 1.0 equiv., 5.0 mmol) were then added simultaneously. The reaction mixture was heated at 50 °C for 12 h under an atmosphere of N_2. At completion, the reaction mixture was cooled to rt and filtered through celite, then extracted with EtOAc (30 mL x 3) and H_2O (30 mL). The collected organic layer was washed with brine and dried with anhydrous Na_2SO_4. The organic layer was then concentrated *in vacuo* using a rotary evaporator, and subsequently purified by normal-phase flash chromatography with 0 → 20% EtOAc in hexanes to afford the desired product **2S** as a yellow oil (785 mg, 45%). The ^{1}H NMR spectra matched a previous report[2].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.23 (m, 3H), 3.04 (tt, *J* = 11.9, 4.0 Hz, 1H), 2.65 – 2.37 (m, 4H), 2.19 (ddq, *J* = 13.2, 6.8, 3.1 Hz, 1H), 2.12 (dtt, *J* = 13.2, 3.3, 1.8 Hz, 1H), 1.94–1.75 (m, 2H).

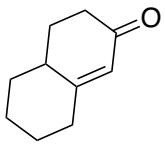


2,6-Dimethylcyclohex-2-en-1-one (6S)

The compound was prepared by following a known procedure[3]. A 3-neck 100 mL flask equipped with one reflux condenser, a bubbler and a stir bar was charged with 2,6-dimethylcyclohexanone (2.52 g, 20.0 mmol, 1.00 equiv.), NBS (3.91 g, 22.0 mmol, 1.10 equiv.), and AIBN (164 mg, 1.00 mmol, 0.0500 equiv.). The flask was evacuated and backfilled with N_2. 1,2-DCE (20 mL) was then added, and the flask was heated with a heat gun until the reaction initiated (vigorous exotherm and generation of gas), at which time the heat was removed. The reaction mixture cooled down below to 80 °C. The solution was then refluxed for 14 h under an atmosphere of N_2. At completion, the mixture was cooled to rt and was then transferred to a separatory funnel and washed successively

with saturated $Na_2S_2O_3$ (aq.) (2 mL), 2 M NaOH (aq.) (5 mL) and then brine (10 mL). Each aqueous phase was extracted one additional time with EtOAc (10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* using rotary evaporator. The resulting oil was then purified by hand column chromatography with 10% EtOAc in Hexane to deliver desired product **6S** as a colorless oil (648 mg, 26% yield). The ^{1}H NMR spectra matched a previous report[3].

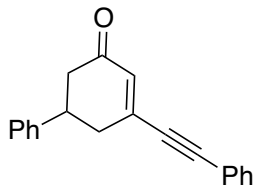
^{1}H NMR (800 MHz, $CDCl_3$) δ 6.69 (s, 1H), 2.45 – 2.36 (m, 3H), 2.07 – 2.03 (m, 1H), 1.79 – 1.77 (m, 3H), 1.63 (s, 1H), 1.09 – 0.96 (m, 3H).



4,4a,5,6,7,8-Hexahydronaphthalen-2(3*H*)-one (7S)

The compound was prepared with slight modification to a known procedure[4]. An oven dried 2-neck 500 mL round bottom flask equipped with a magnetic stir bar was charged with 6-methoxy-1,2,3,4-tetrahydronaphthalene (1.62 g, 1.00 equiv., 10.0 mmol). The flask was then evacuated and backfilled with N_2 (3x). THF (10.0 mL), *t*-butyl alcohol (2.4 mL, 2.5 equiv., 25 mmol), and ethylenediamine (4.0 mL, 6.0 equiv., 0.060 mol) were then added in sequence. The flask was then connected to a bubbler for a gas outlet and cooled to 0 °C. Li^0 (208 mg, 3.00 equiv., 30.0 mmol) was added to the solution. The reaction mixture was stirred at 0 °C for 1 h. Saturated aqueous NH_4Cl (10.0 mL) was added to the reaction mixture and the resulting mixture was stirred until the remaining Li^0 was quenched (observed visually). The resulting mixture was held at 0 °C, and acidified with concentrated HCl until the solution reached pH = 2. The resulting mixture was poured into a separatory funnel, and the product was then extracted with Et_2O (100 mL × 3). The organic extracts were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* under reduced pressure. The resulting residue was purified by normal-phase flash chromatography using 0 → 20% EtOAc in hexanes to afford the desired product **7S** as an amber oil (623 mg, 42%). The ^{1}H NMR spectra matched a previous report[5].

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (s, 1H), 2.46 – 2.35 (m, 2H), 2.33 – 2.24 (m, 2H), 2.18 (td, *J* = 13.4, 4.7 Hz, 1H), 2.12 – 2.03 (m, 1H), 1.98 – 1.85 (m, 2H), 1.85 – 1.78 (m, 1H), 1.61 (dtt, *J* = 13.6, 9.3, 4.7 Hz, 1H), 1.53–1.31 (m, 2H), 1.19 (qd, *J* = 12.7, 3.5 Hz, 1H).



5-(Phenylethynyl)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (**9S**)

A 20 mL scintillation vial equipped with a stir bar was charged with 5-bromo-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (1.0 g, 1.0 equiv., 4.0 mmol). The vial was taken to the glove box and bis-(triphenylphosphino)-palladium(II) dichloride (42 mg, 0.020 equiv., 0.060 mmol), and CuI (38 mg, 0.050 equiv., 0.20 mmol) were added. The vial was removed from the glovebox, and TEA (10.0 mL, 18.0 equiv., 72.0 mmol) and ethynylbenzene (0.88 mL, 2.0 equiv., 8.0 mmol) were added. The reaction was stirred at 90 °C overnight. At completion, the solvents were removed *in vacuo* using a rotary evaporator, and the residue was diluted with Et_2O (10 mL), and the solution was filtered through a plug of silica using Et_2O (10 mL) as an eluent. After removal of the solvent *in vacuo* using a rotary evaporator, the crude reaction mixture was purified with normal phase flash chromatography with 0 → 30% EtOAc in hexanes to afford the desired compound (**9S**) as a brown powder (498 mg, 46% yield).

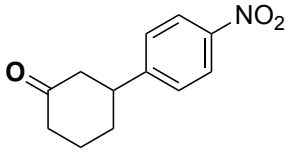
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.39 – 7.35 (m, 5H), 7.29 – 7.26 (m, 3H), 6.40 – 6.37 (m, 1H), 3.42 (ddt, *J* = 13.3, 11.1, 4.4 Hz, 1H), 2.83 (dddd, *J* = 17.6, 4.4, 1.5, 0.7 Hz, 1H), 2.80 – 2.72 (m, 2H), 2.67 (dd, *J* = 16.4, 13.3 Hz, 1H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 198.2, 142.6, 142.4, 132.0, 131.9, 129.5, 128.8, 128.5, 127.1, 126.7, 121.8, 100.2, 88.2, 44.1, 40.4, 38.2.

IR (film) 3029, 2199, 1665, 1600, 1585, 1490, 1442 cm^{-1}

HRMS (APCI)$^+$ *m/z* calc'd for $C_{20}H_{17}O$ $[M+H]^+$ 273.1279, found 273.1280.

M.P. 102–104 °C

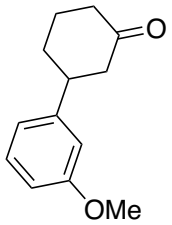


3-(4-Nitrophenyl)cyclohexan-1-one (10S)

The compound was prepared following a known procedure[1]. An oven dried 20 mL scintillation vial equipped with a magnetic stir bar was charged with 4-nitrophenylboronic acid (1.25 g, 1.50 equiv., 7.50 mmol) and $[Rh(COD)Cl]_2$ (24.7 mg, 0.10 equiv., 50.0 µmol). 1,4-Dioxane (4.2 mL) and distilled H_2O (0.70 mL) were added to the flask. Then, a solution of cyclohex-2-en-1-one (480 mg, 1.0 equiv., 5.0 mmol) in aqueous dioxane (2.0 mL) along with TEA (0.70 mL, 1.0 equiv., 5.0 mmol) were added

simultaneously. The reaction mixture was heated at 50 °C for 12 h under an atmosphere of N_2. At completion, the reaction mixture was cooled to rt and filtered through the celite, then extracted with EtOAc (30 mL x 3) and H_2O (30 mL). The collected organic layer was washed with brine and dried with anhydrous Na_2SO_4. The organic layer was then concentrated *in vacuo* using a rotary evaporator, and subsequently purified by normal-phase flash chromatography with 0 → 50% EtOAc in hexanes to afford the desired product **10S** as a colorless powder (715 mg, 57.0%). The ^{1}H NMR spectra matched a previous report[6].

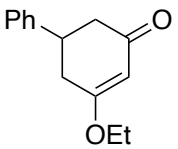
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 7.86 (m, 2H), 7.37 – 7.16 (m, 2H), 3.01 (tt, *J* = 11.8, 3.9 Hz, 1H), 2.52 – 2.20 (m, 4H), 2.11 – 1.91 (m, 2H), 1.82 – 1.55 (m, 2H).



3-(3-Methoxyphenyl)cyclohexanone (11S)

The compound was prepared following a known procedure[1]. An oven dried 20 mL scintillation vial equipped with a magnetic stir bar was charged with (3-methoxyphenyl)boronic acid (228 mg, 1.50 equiv., 7.50 mmol) and $[Rh(COD)Cl]_2$ (24.7 mg, 0.100 equiv., 50.0 µmol). 1,4-Dioxane (2.6 mL) and distilled H_2O (0.40 mL) were added to the flask. Then, a solution of cyclohex-2-en-1-one (0.49 mg, 1.0 equiv., 5.0 mmol) in aqueous dioxane (2.0 mL) along with TEA (0.70 mL, 1.0 equiv., 5.0 mmol) were added simultaneously. The reaction mixture was heated at 50 °C for 12 h under an atmosphere of N_2. At completion, the reaction mixture was cooled to rt and filtered through the celite, then extracted with EtOAc (30 mL x 3) and H_2O (30 mL). The collected organic layer was washed with brine and dried over anhydrous Na_2SO_4. The organic layer was then concentrated *in vacuo* using a rotary evaporator, and subsequently purified by reverse phase flash chromatography with gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) to 95% MeCN in H_2O (with 0.1% AcOH) to afford the desired compound **11S** as a yellow liquid (160 mg, 80% yield). The ^{1}H NMR spectra matched a previous report[6].

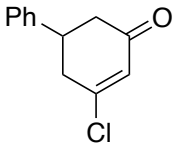
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 6.82 – 6.76 (m, 3H), 3.80 (s, 3H), 2.98 (tt, *J* = 11.9, 3.9 Hz, 1H), 2.61 – 2.34 (m, 4H), 2.17 – 2.05 (m, 2H), 1.88 – 1.74 (m, 2H).



5-Ethoxy-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (14S)

The compound was prepared with slight modification to a known procedure[7]. An oven dried 20 mL scintillation vial equipped with a magnetic stir bar was charged with 5-phenylcyclohexanes-1,3-dione (1.9 g, 1.0 equiv., 10 mmol) and iodine (128 mg, 0.100 equiv., 1.00 mmol). The vial was taken into the glovebox, and EtOH (10.0 mL) and PhMe (1.0 mL) were added. The reaction mixture was then stirred for 18 h at rt. At completion, the solvent was evaporated using rotary evaporator and the reaction mixture was resuspended with EtOAc (20 mL). An aqueous saturated $Na_2S_2O_3$ solution (20 mL) was then added. The aqueous layer was then extracted with EtOAc (20 mL x 3) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and purified by normal-phase chromatography with 0 → 40% EtOAc in hexanes to afford the desired product **14S** as a yellow oil (1.13 g, 52%). The ^{1}H NMR spectra matched a previous report[7].

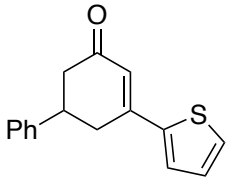
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.23 (m, 3H), 5.44 (s, 1H), 4.02 – 3.84 (m, 2H), 3.42 – 3.30 (m, 1H), 2.72 – 2.62 (m, 3H), 2.61 – 2.52 (m, 1H), 1.38 (t, *J* = 7.0 Hz, 3H).



5-Chloro-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (15S)

An oven-dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with 5-phenylcyclohexane-1,3-dione (1.13 g, 1.00 equiv., 6.00 mmol). The flask was evacuated and backfilled with N_2 (3x). $CHCl_3$ (7.0 mL) and PCl_3 (315 µL, 0.600 equiv., 3.60 mmol) were then added, and the reaction was refluxed for 3 h. At completion, the reaction was quenched with ice. The $CHCl_3$ was then removed using a rotary evaporator to afford an aqueous suspension that was subsequently extracted with Et_2O (30 mL x 3). The combined organic phases were dried with Na_2SO_4, filtered, and concentrated *in vacuo* using a rotary evaporator. The compound was then purified by a normal phase chromatography with 0 → 15% EtOAc in hexanes to afford the desired compound **15S** as a colorless solid (623 mg, 50% yield). The ^{1}H NMR spectra matched a previous report[7].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.20 (m, 3H), 6.33 (d, *J* = 1.9 Hz, 1H), 3.62 – 3.35 (m, 1H), 3.07 – 2.85 (m, 2H), 2.77 – 2.58 (m, 2H).



5-(Thiophen-2-yl)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (**16P**)

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 5-bromo-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one (0.40 g, 1.0 equiv., 1.6 mmol), thiophen-3-ylboronic acid (245 mg, 1.20 equiv., 1.91 mmol), $Pd(Ph_3)_4$ (184 mg, 0.100 equiv., 0.160 mmol), and K_2CO_3 (0.640 g, 3.00 equiv.,

4.80 mmol). The flask was evacuated and backfilled with N_2 (3x). 1,4-Dioxane (8.0 mL) and H_2O (2.0 mL) were then added to the flask, and the reaction mixture was stirred at 80 °C for 14 h. At completion, the solvents were removed *in vacuo* using a smart evaporator. The compound was dissolved in Et_2O (3 mL) and filtered through a plug of celite. Purification was performed using normal phase flash chromatography with 0 → 30% EtOAc in hexanes to afford the desired compound **16S** as a colorless powder (318 mg, 79% yield).

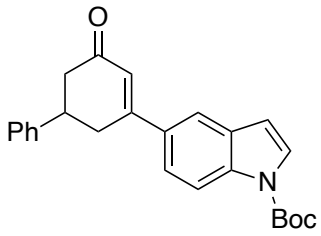
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.41 – 7.36 (m, 4H), 7.33 – 7.28 (m, 3H), 6.51 (s, 1H), 3.49 – 3.42 (m, 1H), 3.09 (dd, *J* = 17.4, 4.5 Hz, 1H), 2.89 (ddt, *J* = 17.5, 11.3, 1.8 Hz, 1H), 2.78 – 2.69 (m, 2H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 199.4, 152.4, 143.2, 140.3, 128.8, 127.1, 126.83, 126.76, 125.3, 125.1, 123.6, 44.0, 40.7, 36.0.

IR (film) 2247, 2161, 1600, 1453, 1416, 1111, 1135 cm^{-1}

HRMS (APCI)$^+$ *m/z* calc'd $C_{16}H_{15}OS$ $[M+H]^+$ 255.0843, found 255.0841.

M.P. 118–120 °C



***Tert*-butyl 5-(5-oxo-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)-1*H*-indole-1-carboxylate (17S):**

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 5-bromo-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (1.26 g, 1.00 equiv., 5.00 mmol), *t*-butyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (2.06 g, 1.20 equiv., 6.00 mmol), $Pd(Ph_3)_4$ (578 mg, 0.100 equiv., 0.500 mmol), and K_2CO_3 (2.07 g, 3.00 equiv., 15.0 mmol). The vial was evacuated and backfilled with N_2 (3x). 1,4-Dioxane (8.0 mL) and H_2O (2.0 mL) were then added to the flask and the reaction mixture was run at 80 °C for 14 h. At completion, the solvents were removed *in vacuo* using a smart evaporator. The residue was dissolved in MeCN (3.0 mL) and filtered through a plug of celite. Purification was performed by reverse phase flash chromatography with a gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) to 95% MeCN in H_2O (with 0.1% AcOH) to afford the desired compound **17S** as a brown powder (990 mg, 51% yield).

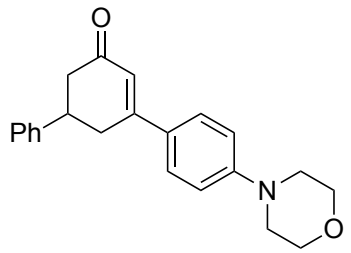
^{1}H NMR (800 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.78 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.54 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.39 (tt, *J* = 7.5, 1.7 Hz, 2H), 7.36 – 7.33 (m, 2H), 7.31 – 7.28 (m, 1H), 6.60 – 6.57 (m, 2H), 3.49 (ddt, *J* = 13.1, 11.2, 4.4 Hz, 1H), 3.17 (ddd, *J* = 17.4, 4.4, 1.4 Hz, 1H), 3.00 (ddd, *J* = 17.5, 11.2, 2.4 Hz, 1H), 2.84 – 2.71 (m, 2H), 1.68 (s, 9H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 199.2, 159.2, 149.4, 143.3, 132.8, 130.8, 128.8, 128.7, 127.01, 126.99, 126.8, 124.5, 122.4, 119.0, 115.3, 107.4, 84.2, 43.9, 41.1, 36.6, 28.1, 24.9.

IR (film) 2978, 1733, 1659, 1600, 1470, 1369, 1335 cm^{-1}

HRMS (APCI)$^+$ *m/z* calc'd $C_{25}H_{26}NO_3$ $[M+H]^+$ 388.1912, found 388.1913

M.P. 125–126 °C



4''-Morpholino-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one (18S)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 5-bromo-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (627 mg, 1.00 equiv., 2.50 mmol), (4-morpholinophenyl)boronic acid (621 mg, 1.20 equiv., 3.00 mmol), $Pd(PPh_3)_4$ (289 mg, 0.100 equiv., 0.250 mmol), and K_2CO_3 (1.04 g, 3.00 equiv., 7.50 mmol). The flask was evacuated and backfilled with N_2 (3x). 1,4-Dioxane (8.0 mL) and H_2O (2.0 mL) were then added, and the reaction mixture was heated at 80 °C for 14 h. At completion, the solvents were removed *in vacuo* using a smart evaporator. The residue was redissolved in MeCN, filtered through a plug of celite and purified by reverse phase flash chromatography with gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) in MeCN to 95% MeCN in H_2O (with 0.1% AcOH) to afford the title compound **18S** as a brown powder (460 mg, 55%).

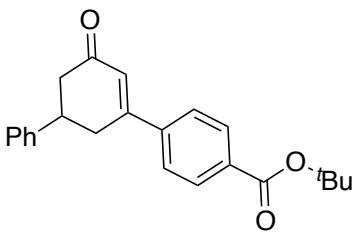
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.9 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.25 (s, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.20 (s, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.44 (d, *J* = 2.5 Hz, 1H), 3.83 – 3.79 (m, 4H), 3.37 (ddt, *J* = 13.0, 11.3, 4.4 Hz, 1H), 3.21 – 3.18 (m, 4H), 3.02 (dd, *J* = 17.4, 4.4 Hz, 1H), 2.80 (ddd, *J* = 17.5, 11.3, 2.4 Hz, 1H), 2.72 – 2.62 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 158.0, 152.4, 143.4, 128.7, 128.2, 127.5, 127.0, 126.8, 122.3, 114.5, 66.5, 48.0, 43.8, 40.9, 35.8.

IR (film) 3651, 3043, 2958, 2887, 2834, 1646, 1589, 1552 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{22}H_{24}NO_2$ $[M+H]^+$ 334.1807, found 334.1809.

M.P. 146–148 °C



***Tert*-butyl 5'-oxo-2',3',4',5'-tetrahydro-[1,1':3',1''-terphenyl]-4-carboxylate (19S)**

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 5-bromo-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one (1.26 g, 1.00 equiv., 5.00 mmol), 4-(*t*-butoxycarbonyl)phenyl)boronic acid (1.33 g, 1.20 equiv., 6.00 mmol), $Pd(Ph_3)_4$ (578 mg, 0.100 equiv., 0.500 mmol), and K_2CO_3 (2.07 g, 3.00 equiv., 15.0 mmol). The vial was evacuated and backfilled with N_2 (3x). 1,4-Dioxane (8.0 mL) and H_2O (2.0 mL) were then added to the flask, and the reaction mixture was stirred at 80 °C for 14 h. At completion, the solvents were removed *in vacuo* using a smart evaporator. The residue was dissolved in DCM (10 mL), and the solution was filtered through a plug of celite. Purification was performed by normal phase flash chromatography with a gradient of 0 → 30% EtOAc in hexane to afford the desired compound **19S** as a colorless powder (1.25 g, 71% yield).

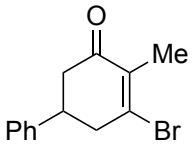
^{1}H NMR (800 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 6.54 (d, *J* = 2.5 Hz, 1H), 3.48 (ddt, *J* = 13.5, 11.1, 4.4 Hz, 1H), 3.05 (dd, *J* = 17.7, 4.5 Hz, 1H), 2.96 (ddd, *J* = 17.7, 11.1, 2.5 Hz, 1H), 2.80 (dd, *J* = 16.4, 4.1 Hz, 1H), 2.78 – 2.72 (m, 1H), 1.60 (s, 9H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 199.0, 165.0, 157.6, 142.9, 142.2, 133.3, 129.8, 128.9, 127.2, 126.7, 126.3, 125.9, 81.4, 77.1, 43.9, 40.9, 36.3, 28.2, 28.1.

IR (film) 2976, 1709, 1664, 1607, 1454, 1408, 1368 cm^{-1}

HRMS (APCI)$^+$ *m/z* calc'd for $C_{23}H_{25}O_3$ $[M+H]^+$ 349.1803, found 349.1804

M.P. 110–112 °C



5-Bromo-4-methyl-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (23S)

An oven-dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with 5-hydroxy-4-methyl-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (0.890 g, 1.00 equiv., 4.40 mmol). The flask was then evacuated and backfilled with N_2 (3x). DCM (10.0 mL) and PBr_3 (1 M in DCM) (2.6 mL, 0.60 equiv., 2.6 mmol) were then added to the flask. The reaction was refluxed for 14 h. At completion, the reaction was quenched with ice. The DCM was then removed *in vacuo* using a rotary evaporator to afford an aqueous suspension that was extracted with Et_2O (30 mL x 3). The collected Et_2O was then washed with a saturated brine solution (50 mL) and dried with anhydrous Na_2SO_4. The compound was purified by normal phase flash chromatography with 0 → 20% EtOAc in hexanes to afford the desired compound **23S** as a colorless powder (412 mg, 35% yield).

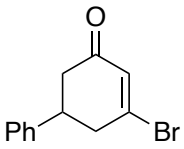
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (ddd, *J* = 7.7, 6.3, 1.3 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 3.43 (ddd, *J* = 17.9, 10.1, 4.6 Hz, 1H), 3.20 – 3.04 (m, 2H), 2.79 (ddd, *J* = 16.1, 4.2, 1.4 Hz, 1H), 2.70 (dd, *J* = 16.2, 13.3 Hz, 1H), 2.00 (dd, *J* = 2.4, 1.5 Hz, 3H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 194.7, 145.8, 141.8, 136.3, 128.8, 127.2, 126.5, 45.2, 43.9, 40.7, 15.5.

IR (film) 2959, 2999, 2036, 2017, 1677, 1623, 1495 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{13}H_{14}BrO$ $[M+H]^+$ 265.0228, found 265.0229.

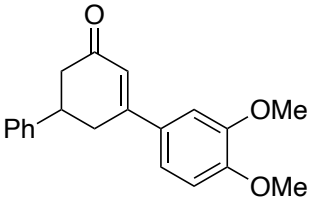
M.P. 54–55 °C



5-Bromo-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (24S)

An oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was charged with 5-phenylcyclohexane-1,3-dione (941 mg, 1.00 equiv., 5.00 mmol). The flask was evacuated and backfilled withN_2 (3x). DCM (10.0 mL) and PBr_3 (1.0 M in DCM) (3.0 mL, 0.60 equiv., 3.0 mmol) were then added. The reaction was refluxed for 14 h. At completion, the reaction was quenched with ice. The DCM was evaporated to afford an aqueous suspension, which was subsequently extracted with Et_2O (30 mL x 3). The collected Et_2O was washed with saturated brine solution (50 mL) and dried with anhydrous Na_2SO_4. The compound was purified using flash chromatography with 0 → 20% EtOAc in hexanes to afford the title compound **24S** as a colorless powder (635 mg, 51% yield). The ^{1}H NMR spectra matched a previous report[7].

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 2H), 6.58 (s, 1H), 3.51 – 3.44 (m, 1H), 3.12 – 3.01 (m, 2H), 2.73 (dd, *J* = 16.4, 4.2 Hz, 1H), 2.66 (ddd, *J* = 16.1, 13.2, 1.7 Hz, 1H).



3'',4''-Dimethoxy-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one (25S)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 5-bromo-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (627 mg, 1.00 equiv., 2.50 mmol), (3,4-dimethoxyphenyl)boronic acid (545 mg, 1.20 equiv., 3.00 mmol), $Pd(Ph_3)_4$ (289 mg, 0.100 equiv., 0.250 mmol), and K_2CO_3 (1.04 g, 3.00 equiv., 7.50 mmol). The flask was evacuated and backfilled with N_2 (3x). 1,4-Dioxane (8.0 mL) and H_2O (2.0 mL) were then added to the flask and the reaction mixture was run at 80 °C for 14 h. At completion, the solvents were removed *in vacuo* using a smart evaporator. The compound was dissolved in MeCN (3.0 mL) and filtered through a plug of celite and purification was performed by reverse phase flash chromatography with a gradient elution from 5% MeCN in H_2O

(with 0.1% AcOH) to 95% MeCN in H_2O (with 0.1% AcOH) to afford the desired compound **25S** as a colorless powder (380 mg, 49% yield).

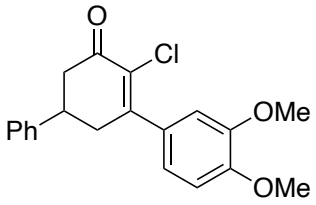
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.09 (d, *J* = 2.2 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.45 (ddt, *J* = 12.8, 11.2, 4.4 Hz, 1H), 3.07 (ddd, *J* = 17.4, 4.4, 1.3 Hz, 1H), 2.90 (ddd, *J* = 17.5, 11.2, 2.4 Hz, 1H), 2.77 (dd, *J* = 16.4, 4.5 Hz, 1H), 2.73 (dd, *J* = 16.3, 13.1 Hz, 1H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 199.2, 158.2, 151.0, 149.0, 143.3, 130.6, 128.8, 127.1, 126.8, 123.6, 119.5, 110.9, 108.9, 55.92, 55.94, 43.8, 41.0, 36.1.

IR (film) 2937, 2156, 2011, 1659, 1595, 1577, 1516 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{20}H_{21}O_3$ $[M+H]^+$ 309.1490, found 309.1487.

M.P. 140–141 °C



4'-Chloro-3'',4''-dimethoxy-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one (26S)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 3'',4''-dimethoxy-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one (925 mg, 1.00 equiv., 3.00 mmol) and NCS (441 mg, 1.10 equiv., 3.30 mmol). The flask was evacuated and backfilled with N_2 (3x). MeCN (12.0 mL) was then added, and the reaction was run at 70 °C for 14 h. At completion, the reaction was quenched with H_2O (5.0 mL), and MeCN was then removed using a rotary evaporator to afford the aqueous suspension, which was then extracted with DCM (20 mL x 3). The collected DCM layer was then washed with brine, dried with anhydrous Na_2SO_4, and purified using normal-flash chromatography with 0 → 40% EtOAc in hexanes to afford the desired compound **26S** as a colorless solid (412 mg, 40% yield).

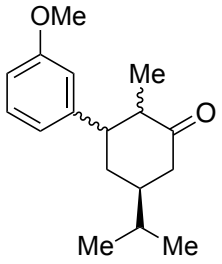
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 3H), 7.07 – 7.03 (m, 1H), 7.01 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.91 (d, *J* = 10.6 Hz, 6H), 3.55 (s, 1H), 3.05 (d, *J* = 7.9 Hz, 2H), 3.00 (s, 1H), 2.94 – 2.85 (m, 1H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 191.3, 155.0, 149.8, 148.5, 142.0, 130.7, 128.9, 128.7, 127.3, 126.6, 120.7, 111.1, 110.7, 56.0, 55.9, 44.5, 41.6, 40.0.

IR (film) 3001, 2835, 2834, 1682, 1600, 1583, 1514 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{20}H_{20}ClO_3$ $[M+H]^+$ 343.1022, found 343.1089

M.P. 174–176 °C

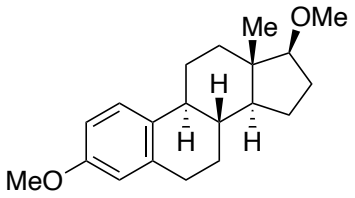


(5*S*)-5-Isopropyl-3-(3-methoxyphenyl)-2-methylcyclohexan-1-one (27S)

The compound was prepared following a known procedure[8]. An oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was charged with iodine (17 mg, 1.0 mol%, 0.070 mmol) and magnesium (1.23 g, 7.60 equiv., 50.7 mmol). The flask was evacuated and backfilled with N_2 (3x) and cooled to 0 °C in an ice bath. THF (20.0 mL) was then added followed by an addition of 1,2-dibromoethane (50 µL, 0.1 equiv., 0.6 mmol). Then, 1-bromo-3-methoxybenzene (3.2 mL, 3.8 equiv., 25 mmol) dissolved in THF (5.0 mL) was slowly added. The Grignard reagent was allowed to form for 1 h at 0 °C. CuI (2.41 g, 1.90 equiv., 12.7 mmol) was added to the freshly prepared Grignard reagent at 0 °C. A solution of (*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one (1.00 g, 1.00 equiv., 6.70 mmol) and TMSCl (4.3 mL, 5.1 equiv., 34 mmol) in THF (5.0 mL) was added slowly, and the reaction was allowed to run for 2 h at 0 °C. At completion, the reaction mixture was quenched with saturated NH_4Cl solution (30 mL) and extracted with EtOAc (30 mL x 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* with rotary evaporator to afford silyl enol ether, which was filtered through a silica plug with Et_2O (5 mL x 2). The Et_2O was removed under reduced pressure and an oily compound was formed. Without further purification, the oily compound was taken in an oven dried 25 mL round bottom flask equipped with a magnetic stir bar and Et_2O (0.010 L) was then added. The solution was then stirred at 0 °C for 10 mins. A solution of TBAF in THF (1.0 M, 1.1 mL, 0.16 equiv., 1.1 mmol) was then added, and the reaction was allowed to continue for 2 h at 0 °C. At completion, the volatiles were removed *in vacuo* with a rotary evaporator, and the crude mixture was purified by a normal-phase flash column chromatography with 0 → 30% EtOAc in hexanes to afford (5*S*)-3-(3-methoxyphenyl)-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one as an oily compound (995 mg, 58% yield).

Then, a 25 mL oven dried round bottom flask equipped with a magnetic stir bar was charged with (5*S*)-3-(3-methoxyphenyl)-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one (0.700 g, 2.70 equiv., 1.30 mmol) and EtOH (7.0 mL). 5% Pd/C (40.0 mg, 0.0100 equiv., 0.0100 mmol) was then added to the flask, and the side of the flask was rinsed with EtOH (1.0 mL). The solution was then charged with H_2 (1 balloon) and stirred placed at rt for 14 h. At completion, the hydrogen balloon was removed, and the reaction was purged with N_2 (3x). The reaction mixture was then filtered through celite, washed with EtOH, and concentrated *in vacuo* with a rotary evaporator to afford the desired compound **27S** as a clear oil in a diastereomeric mixture (1.7:1) (642 mg, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 1H), 6.89 – 6.68 (m, 3H), 3.81 (d, *J* = 1.8 Hz, 3H), 2.81 – 2.41 (m, 3H), 2.34–2.18 (m, 1H), 2.16 – 1.92 (m, 1H), 1.87 – 1.47 (m, 3H), 1.06 – 0.70 (m, 10H).
^{13}C NMR (201 MHz, $CDCl_3$) δ 213.1, 212.7, 159.8, 159.7, 145.9, 145.6, 129.59, 129.55, 119.6, 119.51, 113.33, 113.28, 111.4, 111.30, 55.1, 51.9, 49.9, 47.7, 45.2, 44.8, 44.2, 42.3, 38.1, 36.1, 32.7, 28.9, 20.8, 20.4, 19.4, 19.3, 18.3, 12.9, 12.1.
IR (film) 2960, 2933, 2872, 2836, 1708, 1599, 1584 cm^{-1}.
HRMS (APCI)$^+$ *m/z* calc'd $C_{17}H_{25}O_2$ $[M+H]^+$ 261.1854, found 261.1848.

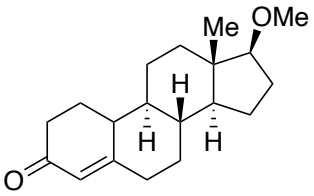


(8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (Precursor to 28S)

The compound was prepared following a known procedure[9]. A 250 mL round bottom flask equipped with a stir bar was charged with β-estradiol (11.8 g, 43.2 mmol, 1.00 equiv.). NaH (60% dispersion in mineral oil) (8.27 g, 207 mmol, 4.78 equiv.) was added and the flask was evacuated and backfilled with N_2 (3x). THF (25 mL) was then added, and the reaction was cooled to 0 °C. The reaction mixture was stirred for 15 mins. MeI (24.8 mL, 398 mmol, 9.20 equiv.) was then added slowly by syringe, and the reaction mixture was stirred overnight and warmed slowly to rt. The reaction mixture was quenched with 100 mL ice water, and an effervescence was observed. As the effervescence ceased, the reaction mixture was concentrated *in vacuo* to afford an aqueous suspension, which was extracted with EtOAc (100 mL x 3), washed with aqueous $NaHCO_3$, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to afford dimethoxy-β-estra-1,3,5(10)-triene as a yellow powder (8.05 g, 62% yield). The ^{1}H NMR spectrum matched a previous report[9].

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.63 (d, *J* = 2.8 Hz, 1H), 3.78 (d, *J* = 1.6 Hz, 3H), 3.38 (d, *J* = 1.6 Hz, 3H), 3.31 (t, *J* = 8.3 Hz, 1H), 2.85 (dq, *J* = 17.7, 8.3 Hz, 2H), 2.28 (ddt, *J* = 13.0, 6.6, 3.2 Hz, 1H), 2.19 (td, *J* = 11.2, 4.2 Hz, 1H), 2.06 (ddt, *J* = 15.2, 12.6, 3.0 Hz, 2H), 1.87 (ddt, *J* = 11.2, 5.3, 2.4 Hz, 1H), 1.69 (dddd, *J* = 12.3, 9.7, 7.0, 3.0 Hz,

1H), 1.50 (tt, *J* = 13.1, 6.3 Hz, 2H), 1.45 (dd, *J* = 11.0, 2.6 Hz, 1H), 1.43 – 1.39 (m, 1H), 1.39 – 1.29 (m, 2H), 1.26 – 1.18 (m, 1H), 0.79 (s, 3H).



(8R,9S,13S,14S,17S)-17-Methoxy-13-methyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (28S)

The compound was prepared with a slight modification from a known procedure[4]. A 500 mL round bottom flask equipped with a magnetic stir bar was charged with (8*R*,9*S*,13*S*,14*S*,17*S*)-17-methoxy-13-methyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[a]phenanthren-3-one (7.06 g, 1.00 equiv., 23.5 mmol). The flask was evacuated and backfilled with N_2 (3x). THF (50.0 mL), ethylene diamine (9.4 mL, 6.0 equiv., 140 mmol), and *t*-butanol (5.7 mL, 2.5 equiv., 59 mmol) were sequentially added. The flask was then connected to a bubbler for a gas outlet and cooled down to 0 °C. Li^0 (815 mg, 5.00 equiv., 117 mmol) was then added to the solution. The reaction was run for 2 h at 0 °C. Saturated aq. NH_4Cl (10 mL) was added to the reaction mixture until the remaining Li^0 was quenched (observed visually). The resulting mixture was cooled with an ice bath and conc. HCl was then added until pH = 2 and the resulting mixture was extracted with Et_2O (30 mL × 3). The organic extracts were combined, dried over anhydrous Na_2SO_4, and purified by reverse-phase chromatography with gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) to 95% MeCN in H_2O (with 0.1% AcOH) to afford the desired compound **28S** as a colorless powder (2.98 g, 44% yield).

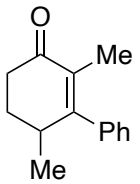
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (s, 1H), 3.35 (s, 3H), 3.24 (t, *J* = 8.4 Hz, 1H), 2.51 – 2.37 (m, 2H), 2.32 – 2.17 (m, 3H), 2.14 – 1.98 (m, 2H), 1.94 (dd, *J* = 12.2, 3.2 Hz, 1H), 1.89 – 1.77 (m, 2H), 1.69 –1.43 (m, 3H), 1.42 – 1.16 (m, 4H), 1.10 – 0.97 (m, 2H), 0.85 (td, *J* = 10.9, 3.8 Hz, 1H), 0.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 166.6, 124.5, 90.5, 57.8, 49.9, 49.5, 42.9, 42.5, 40.1, 37.6, 36.4, 35.4, 30.6, 27.5, 26.5, 26.1, 23.0, 11.4.

IR (film) 2926, 2866, 1725, 1671, 1618, 1450, 1381 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{19}H_{29}O_2$ $[M+H]^+$ 289.2167, found 289.2166.

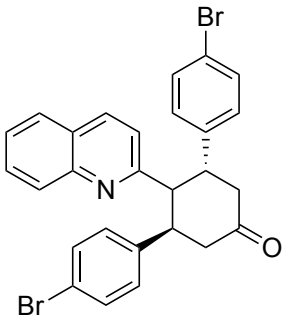
M.P. 115–117 °C



2,6-Dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (29S)

The compound was prepared following a known procedure[10]. A 50 mL round bottom flask equipped with a stir bar was charged with $Pd(OAc)_2$ (220 mg, 1.0 mmol, 0.10 equiv), BINOL Phosphoric acid (350 mg, 1.0 mmol, 0.1 0equiv.), and NaOH (400 mg, 10 mmol, 1 equiv.). Propiophenone (1.30 g, 10.0 mmol, 1.00 equiv.), pent-1-en-3-ol (5.20 g, 60.0 mmol, 6.00 equiv.) and 1,2-DCE (8.0 mL) were then added. 4 Å molecular sieves were then added to the reaction mixture and stirred at rt for 24 h. After 24 h, the volatiles were removed *in vacuo* using rotary evaporator. The crude reaction mixture was then purified using flash column chromatography with 25% EtOAc in Hexane as an eluent to afford the desired compound as a colorless oil (155 mg, 8% yield). The ^{1}H NMR spectra matched a previous report[10].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.21 – 7.04 (m, 2H), 2.82 – 2.78 (m, 1H), 2.66 (ddd, *J* = 16.6, 11.6, 4.9 Hz, 1H), 2.49 – 2.44 (m, 1H), 2.35 – 2.28 (m, 1H), 1.91 – 1.85 (m, 1H), 1.62 (d, *J* = 1.4 Hz, 3H), 1.02 (d, *J* = 7.1 Hz, 3H).



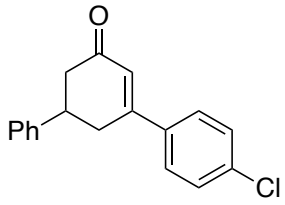
(3*R*,5*R*)-3,5-Bis(4-bromophenyl)-4-(quinolin-2-yl)cyclohexan-1-one (30S)

The compound was prepared by following a previously established procedure[11].

A 20 mL scintillation vial equipped with a stir bar was charged with (1*E*,4*E*)-1,5-bis(4-bromophenyl)penta-1,4-dien-3-one (118 mg, 0.300 mmol, 1.00 equiv.) and 2-methylquinoline (56 mg, 0.39 mmol, 1.3 equiv.). $CoCl_2$ (3.8 mg, 0.030 mmol, 0.10 equiv.), and 1,4-dioxane (1.0 mL) were added to the vial in the glove box. The reaction mixture was stirred at 120 °C for 24 h. At completion, the crude reaction mixture was quenched with a saturated solution of aqueous $NaHCO_3$ (10 mL) and extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine solution

and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* with a rotary evaporator and purification was performed by reverse phase flash chromatography with a gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) to 95% MeCN in H_2O (with 0.1% AcOH) to afford the desired compound **30S** as a brown powder (90 mg, 56%). The ^{1}H NMR spectra matched a previous report[11].

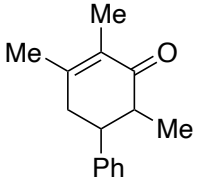
^{1}H NMR (800 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.71 (q, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.49 (d, *J* = 8.2 Hz, 2H), 6.36 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 1H), 3.82 (td, *J* = 8.6, 5.3 Hz, 2H), 3.40 (d, *J* = 15.7 Hz, 0H), 3.29 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.98 – 2.83 (m, 1H), 2.81 (dd, *J* = 15.8, 8.8 Hz, 1H).



4''-Chloro-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one (31S)

The compound was prepared with a slight modification to a known procedure[12]. An oven-dried 25 mL round bottom flask equipped with a stir bar was charged with (*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (1.0 g, 1.0 equiv., 4.1 mmol) was dissolved in MeOH (5.0 mL). Cs_2CO_3 (2.0 g, 1.5 equiv., 6.2 mmol) was added at rt, and the reaction mixture was evacuated and backfilled with N_2 three times. Acetone (0.60 mL, 2.0 equiv., 8.2 mmol) was then added, and the reaction was refluxed for 14 h. At the completion as shown by TLC, the reaction was quenched with saturated aqueous NH_4Cl and the reaction mixture was extracted with Et_2O (30 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated by a rotary evaporator. The compound was purified by a normal phase flash chromatography using 0 →10% EtOAc in hexanes to afford the desired compound **31S** as a colorless oil (440 mg, 38% yield). The ^{1}H NMR spectra matched a previous report [12].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.6, 2.9 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.42 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 6.50 (dd, *J* = 14.4, 2.4 Hz, 1H), 3.49 – 3.39 (m, 1H), 3.04 – 2.97 (m, 1H), 2.94 – 2.87 (m, 1H), 2.78 – 2.67 (m, 2H).



2,4,5-Trimethyl-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (32S)

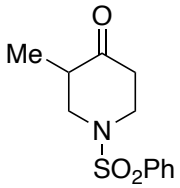
An oven-dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with *(E)*-4-phenylbut-3-en-2-one (1.00 g, 1.00 equiv., 6.80 mmol). The flask was evacuated and backfilled with N_2 (3x). MeOH (5.0 mL) was then added followed by an addition of NaOMe (443 mg, 1.20 equiv., 8.20 mmol). Pentan-3-one (0.90 mL, 1.2 equiv., 8.2 mmol,) was then added, and the reaction was refluxed for 14 h. At completion (as shown by TLC), the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture was extracted with Et_2O (30 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* by a rotary evaporator. The compound was purified by normal phase flash chromatography with 0 → 10% EtOAc in hexanes to afford the desired compound **32S** as a clear oil (380 mg, 26% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.25 – 7.21 (m, 2H), 2.93 – 2.85 (m, 1H), 2.71 – 2.62 (m, 1H), 2.61 – 2.55 (m, 1H), 2.52 – 2.43 (m, 1H), 1.95 (s, 3H), 1.84 (s, 3H), 0.95 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 152.6, 143.5, 130.5, 128.8, 127.6, 126.9, 48.1, 46.0, 41.5, 21.4, 13.4, 11.4.

IR (Film) 3028, 2925, 1661, 1641, 1453, 1375, 1308, 1059, 760, 701 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{15}H_{19}O$ $[M + H]^+$ 215.1435, found 215.1434.



3-Methyl-1-(phenylsulfonyl)piperidin-4-one (35S)

The compound was prepared with a slight modification to a known procedure[13].

A 500 ml round bottom flask equipped with a magnetic stir bar was charged with 3-methyl-1-piperidin-4-one hydrochloride (2.24 g, 1.00 equiv., 15.0 mmol), benzene sulfonyl chloride (2.3 mL, 1.2 equiv., 18 mmol), and K_2CO_3 (5.18 g, 2.5 equiv., 37.5 mmol). The vial was evacuated and backfilled with N_2 (3x). $CHCl_3$ (0.010 L) and H_2O (0.010 L) were then added, and the reaction was run for 14 h at rt. At completion, the reaction was quenched by aqueous saturated $NaHCO_3$ solution (30 mL). The $CHCl_3$ was then removed *in vacuo* using a rotary evaporator to afford the aqueous suspension, which was then filtered through a sintered funnel *in vacuo* using a vacuum pump. The residue was washed with H_2O (5 mL x 3) and then with pentane (5 mL). The residue was transferred to a vial and was subjected to rotary evaporator to deliver the desired product **35S** as a colorless powder (2.94 g, 78% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.65 – 7.60 (m, 1H), 7.58 – 7.54 (m, 2H), 3.89 – 4.06 (m, 2H), 2.83 (t, *J* = 11.7 Hz, 1H), 2.73 (dd, *J* = 8.3, 5.2 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.49 – 2.42 (m, 2H), 1.06 – 1.02 (m, 3H).

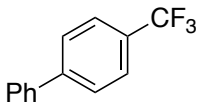
^{13}C NMR (201 MHz, $CDCl_3$) δ 207.5, 136.4, 133.1, 129.3, 127.4, 52.4, 46.5, 44.2, 40.1, 11.6.

IR (film) 2980, 2885, 1716, 1584, 1471, 1446, 1364 cm^{-1}.

HRMS (APCI)$^{+}$ *m/z* calc'd $C_{12}H_{16}NO_3S$ $[M+H]^+$ 254.0850, found 254.0838.

M.P. 114–116 °C

4. Preparation of Ar–CF_3 Compounds

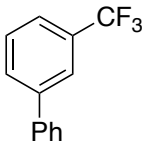


4-(Trifluoromethyl)-1,1'-biphenyl (1P)

The general method **A** was followed. In step 1, 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 14 h at 140 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified using normal phase flash chromatography with 100% pentane to deliver the desired compound **1P** as a colorless powder (93 mg, 84% yield). The ^{1}H NMR data matched a previous report[14].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.60 (d, *J* = 6.9 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –62.8 (s, 3F).

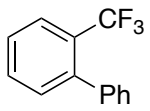


3-(Trifluoromethyl)-1,1'-biphenyl (2P)

The general method **A** was followed. In step 1, 3-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and PhMe (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added. The reaction was run for 24 h at 110 °C in PhMe (2.5 mL). At completion, MeOH (1.0 mL) was added remove the PhMe by azeotropic distillation, and the PhMe-MeOH mixture was removed *in vacuo* using a rotary evaporator. The crude reaction mixture was purified using normal phase flash chromatography with 100% pentane to deliver the desired compound **2P** as a clear oil (55 mg, 49% yield). The ^{1}H NMR data matched a previous report[15].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 5.1, 3.3 Hz, 3H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.50 (td, *J* = 6.9, 1.6 Hz, 2H), 7.46 – 7.39 (m, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.1 (s, 3F).

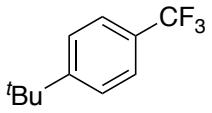


2-(Trifluoromethyl)-1,1'-biphenyl (3P)

The general method **B** was followed. In step 1, 2-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 18 h at 50 °C, and the silica plug filter was pushed with Et_2O. In step 3, AIBN (8.2 mg, 0.10 equiv., 0.050 mmol) and NBS (178 mg, 2.00 equiv., 1.00 mmol) were added and the reaction was run for 24 h at 90 °C in 1,2-DCE (2.5 mL). The residue was purified by normal phase flash chromatography with 100% pentane to deliver the desired product **3P** as a clear oil (49 mg, 44% yield). The ^{1}H NMR data matched a previous report[16].

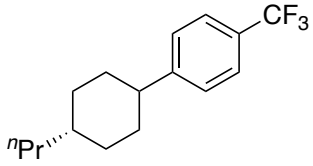
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.41 (q, *J* = 5.2 Hz, 3H), 7.34 (t, *J* = 6.6 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –57.3 (s, 3F).



1-(*t*-Butyl)-4-(trifluoromethyl)benzene (**4P**)

The general method **B** was followed. In step 1, 4-*t*-butylcyclohexan-1-one (77 mg, 1.0 equiv., 0.5 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 18 h at 50 °C, and the silica plug filter was pushed with Et_2O. In step 3, AIBN (8.2 mg, 0.10 equiv., 0.050 mmol) and NBS (178 mg, 2.00 equiv., 1.00 mmol) were added and the reaction was run for 14 h at 120 °C in *o*-DCB (2.5 mL). At completion, the crude ^{19}F NMR yield was 79%. However, the compound was not isolated due to volatile nature of compound, ii) lower boiling point than *o*-DCB, and iii) similar R_f with *o*-DCB.



1-(4-Propylcyclohexyl)-4-(trifluoromethyl)benzene (5P)

The general method **B** was followed. In step 1, 4'-propyl-[1,1'-bi(cyclohexan)]-4-one (111 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (1.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 18 h at 50 °C, and the silica plug filter was pushed with Et_2O. In step 3, AIBN (8.2 mg, 0.10 equiv., 0.05 mmol) and NBS (178 mg, 2.00 equiv., 1.00 mmol) were added, and the reaction was run for 14 h at 120 °C in *o*-DCB (2.5 mL). The residue was purified by normal phase flash chromatography with 100% pentane to afford the desired product **5P** as a clear oil (57 mg, 42% yield).

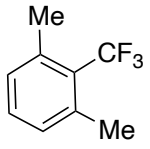
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 2.52 (tt, *J* = 12.2, 3.3 Hz, 1H), 1.88 (ddd, *J* = 8.8, 4.7, 3.0 Hz, 3H), 1.46 (dd, *J* = 12.3, 3.3 Hz, 1H), 1.40 – 1.33 (m, 2H), 1.32 – 1.28 (m, 2H), 1.24 – 1.20 (m, 2H), 1.09 – 1.03 (m, 2H), 0.90 (dt, *J* = 17.9, 7.4 Hz, 4H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 151.8, 133.3, 128.0 (q, *J* = 16 Hz), 127.2, 127.1, 125.1 (q, *J* = 4.6 Hz), 124.3 (q, *J* = 271 Hz), 44.5, 39.6, 36.9, 34.0, 33.3, 19.9, 14.3.

^{19}F NMR (470 MHz, $CDCl_3$) δ –62.8 (s, 3F).

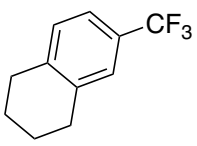
IR (film) 2957, 2923, 2851, 1618, 1584, 1449, 1418 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{16}H_{21}F_2$ $[M - F]^+$ 251.1611, found 251.1604.



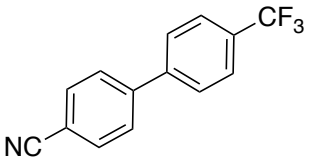
1,3-Dimethyl-2-(trifluoromethyl)benzene (6P)

The general method **A** was followed. In step 1, 2,6-dimethylcyclohex-2-en-1-one (87.0 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 14 h at 140 °C in *o*-DCB (2.5 mL). At completion, the crude ^{19}F NMR yield was 56%. However, the compound was not isolated due to i) volatile nature of compound, ii) lower boiling point than *o*-DCB and iii) similar R_f with *o*-DCB.



6-(Trifluoromethyl)-1,2,3,4-tetrahydronaphthalene (7P)

The general method **A** was followed. In step 1, 4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (75 mg, 1.0 equiv., 0.5 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (113 mg, 1.00 equiv., 50.0 µmol) were added, and the reaction was run for 14 h at 140 °C in *o*-DCB (2.5 mL). At completion, the crude ^{19}F NMR yield was 62%. However, the compound was not isolated due to i) volatile nature of compound, ii) lower boiling point than *o*-DCB, and iii) similar R_f with *o*-DCB.

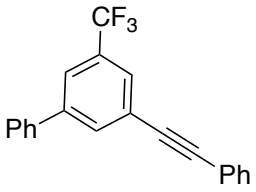


4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (8P)

The general method **A** was followed. In step 1, 4-(4-oxocyclohexyl)benzonitrile (0.100 g, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 36 h at 50 °C. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 1.00 equiv., 1.50 mmol) were added. The reaction was run for 36 h at 140 °C in *o*-DCB (5.0 mL). The crude reaction mixture was purified using normal phase flash chromatography with 4% EtOAc in hexanes to deliver the desired compound **8P** as a colorless solid (79 mg, 64% yield). The ^1H NMR data matched a previous report[17].

^1H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 8H).

^{19}F NMR (470 MHz, $CDCl_3$) **δ** –63.0 (s, 3F).



3-(Phenylethynyl)-5-(trifluoromethyl)-1,1'-biphenyl (9P)

The general method **A** was followed. In step 1, 5-(phenylethynyl)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (136 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (89 µL, 1.2 equiv., 0.55 mmol), CsF (22 mg, 0.30 equiv., 0.15 mmol), and *o*-DCB (2.5 mL) were added, and the reaction was run for 14 h at rt. In step 2, DDQ (227 mg, 2.00 equiv., 1.00 mmol) was added, and the reaction was run for 24 h at 100 °C in *o*-DCB (2.5 mL). No PTSA•H_2O was added. The crude reaction mixture was purified by normal phase flash chromatography with 100% pentane to deliver the desired compound **9P** as a clear oil (71 mg, 44% yield).

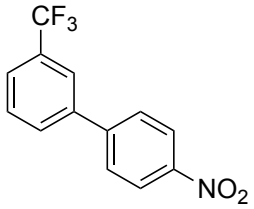
^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.78 (d, *J* = 6.0 Hz, 2H), 7.64 – 7.61 (m, 2H), 7.59 – 7.56 (m, 2H), 7.51 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H), 7.40 – 7.37 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 139.0, 133.3, 131.8, 131.5 (q, *J* = 32.6 Hz), 129.1, 128.8, 128.5, 128.4, 127.0 (q, *J* = 4.1 Hz), 124.8, 123.6 (q, *J* = 4.1 Hz), 122.7, 122.6, 91.0, 87.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.3 (s, 3F).

IR (film) 3658, 2980, 2223, 1599, 1572, 1443, 1370 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{21}H_{13}F_3$ $[M]^+$ 322.0969, found 322.0962.

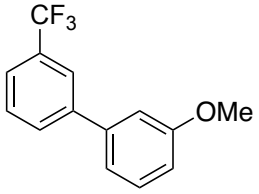


4'-Nitro-3-(trifluoromethyl)-1,1'-biphenyl (10P)

The general method **B** was followed. In step 1, 3-(4-nitrophenyl)cyclohexan-1-one (109 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (1.0 mL) were added, and the reaction was run for 12 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 24 h at 50 °C, and the silica plug filter was pushed with DCM. In step 3, In step 3, AIBN (8.2 mg, 0.10 equiv., 0.05 mmol) and NBS (356 mg, 4.00 equiv., 2.00 mmol) were added, and the reaction was run for 14 h at 120 °C in *o*-DCB. The crude reaction mixture was purified by normal phase flash chromatography with 0 → 10% EtOAc in hexanes to deliver the desired compound **10P** as a colorless powder (66 mg, 49% yield). The ^{1}H NMR data matched a previous report[18].

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.6 Hz, 2H), 7.86 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.2 (s, 3F).



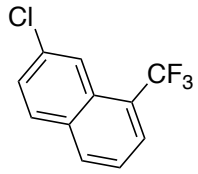
3-Methoxy-3'-(trifluoromethyl)-1,1'-biphenyl (11P)

The general method **A** was followed. In step 1, 3-(3-methoxyphenyl)cyclohexan-1-one (102 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 24 h at 140 °C in *o*-DCB (5.0 mL). The crude reaction mixture was purified by

normal phase flash chromatography with 7% EtOAc in hexanes to deliver the desired compound **11P** as a colorless solid (103 mg, 82% yield). The ^{1}H NMR data matched the previous report[17].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.16 – 7.08 (m, 1H), 6.96 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.89 (s, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.0 (s, 3F).



7-Chloro-1-(trifluoromethyl)naphthalene (12P)

The general method **A** was followed. In step 1, 7-chloro-3,4-dihydronaphthalen-1(2*H*)-one (90 mg, 1.0 equiv., 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 12 h at 50 °C. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (454 mg, 4.00 equiv., 2.00 mmol) were added, and the reaction was run for 48 h at 140 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified using normal phase flash chromatography with 100% pentane to afford the desired compound **12P** as a colorless powder (52 mg, 45% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.64–7.42 (m, 2H).

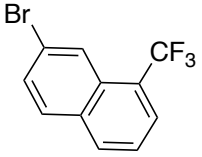
^{13}C NMR (201 MHz, $CDCl_3$) δ 133.8, 132.5, 132.0, 130.2, 129.5, 127.6, 124.3 (q, *J* = 273.4 Hz), 125.5 (q; J = 30 Hz), 125.6 (q, *J* = 5.9 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –60.4 (s, 3F).

IR (film) 2922, 2849, 2047, 1627, 1584, 1501, 1429 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd for $C_{11}H_6ClF_3$ $[M]^+$ 230.0110, found 230.0104.

M.P. 65–67 °C



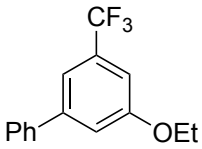
7-Bromo-1-(trifluoromethyl)naphthalene (13P)

The general method **A** was followed. In step 1, 7-bromo-3,4-dihydronaphthalen-1(2*H*)-one (112 mg, 0.500 mmol, 1.00 equiv.), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 24 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 24 h at 140 °C in *o*-DCB (5.0 mL). The crude reaction mixture was purified by

normal phase flash chromatography with 100% hexanes to afford the desired compound **13P** as a colorless powder (97 mg, 71% yield). The ^{1}H NMR data matched the previous report[19].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –60.3 (s, 3F).



3-Ethoxy-5-(trifluoromethyl)-1,1'-biphenyl (14P)

The general method **A** was followed. In step 1, 5-ethoxy-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (108 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, DDQ (227 mg, 2.00 equiv., 1.00 mmol) was added, and the reaction was run for 14 h at 120 °C in *o*-DCB (2.5 mL). No PTSA•H_2O was added. The crude reaction mixture was purified using a normal flash chromatography with 0 → 10% EtOAc in hexanes to deliver the desired compound **14P** as a colorless powder (96 mg, 72% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 (dd, *J* = 14.1, 6.6 Hz, 2H), 7.25 (s, 1H), 7.09 (s, 1H), 4.12 (q, *J* = 6.9 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H).

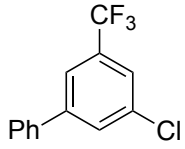
^{13}C NMR (201 MHz, $CDCl_3$) δ 159.4, 143.4, 139.8, 132.1 (q, *J* = 32.0 Hz), 128.9, 128.0, 127.1, 124.0 (q, *J* = 272.4 Hz), 116.8, 116.2 (q, *J* = 4.4 Hz), 109.8 (q, *J* = 4.6 Hz), 63.9, 14.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.7 (s, 3F).

IR (film) 2981, 2883, 2025, 1600, 1457, 1528 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{13}H_9F_3O$ $[M - Et + H]^+$ 238.0605, found 238.0601.

M.P. 65 – 67 °C



3-Chloro-5-(trifluoromethyl)-1,1'-biphenyl (15P)

The general method **A** was followed. In step 1, 5-chloro-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (103 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, PTSA•H_2O (95 mg, 1.0 equiv., 0.50 mmol) and DDQ (227 mg, 2.00 equiv., 1.00 mmol), and the reaction was run for 24 h at 120 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified using normal phase flash chromatography with 100% pentane to afford the desired compound **15P** as a clear oil (97 mg, 76%).

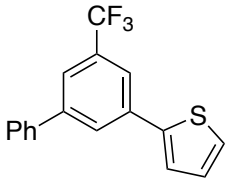
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.71 (s, 1H), 7.60 – 7.55 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 6.8 Hz, 1H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 143.9, 138.4, 135.2, 132.6 (q, *J* = 32.8), 130.5, 129.1, 128.6, 127.1, 123.3 (q, *J* = 273.1), 122.2 (q, *J* = 4.6) 124.1, 124.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.3 (s, 3F).

IR (film) 3066, 2856, 2926, 1589, 1577, 1498, 1441 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{13}H_8ClF_3$ $[M]^+$ 256.0261, found 256.0265.



2-(5-(Trifluoromethyl)-[1,1'-biphenyl]-3-yl)thiophene (16P)

The general method **A** was followed. In step 1, 5-(thiophen-2-yl)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (127 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (8.0 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (2.5 mL) were added. The reaction was run for 12 h at 50 °C. In step 2, PTSA•H_2O (95 mg, 1.0 equiv., 0.50 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol), and the reaction was run for 14 h at 140 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified using normal phase flash chromatography with 0 → 20% EtOAc in hexanes to afford the desired compound **16P** as a colorless powder (94 mg, 62% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.84 (s, 1H), 7.79 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.60 (s, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.50 – 7.44 (m, 3H).

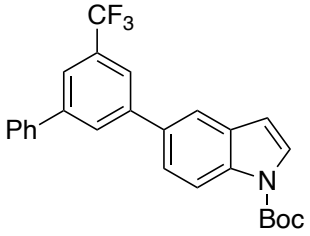
^{13}C NMR (201 MHz, $CDCl_3$) δ 142.67, 140.83, 139.71, 137.10, 131.68 (q, *J* = 32.0 Hz), 128.99, 128.40, 128.13, 127.22, 126.83, 126.15, 122.51, 121.91, 121.60.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.1 (s, 3F).

IR (film) 2922, 1601, 1447, 1411, 1342, 1264, 1167 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{17}H_{11}F_3S$ $[M]^+$ 304.0533 , found 304.0515.

M.P. 66–67 °C



***Tert*-butyl 5-(5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)-1*H*-indole-1-carboxylate (17P)**

The general method **A** was followed. In step 1, *tert*-butyl 5-(5-oxo-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)-1*H*-indole-1-carboxylate (194 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (89 µL, 1.2 equiv., 0.60 mmol), CsF (38 mg, 0.50 equiv., 0.25 mmol), and *o*-DCB (4.0 mL) were added. The reaction was stirred for 24 h at rt. In step 2, DDQ (227 mg, 2.00 equiv., 1.00 mmol) was added and the reaction was stirred for 14 h at 100 °C in *o*-DCB (4 mL). No PTSA•H_2O was added. The crude reaction mixture was purified by reverse phase flash chromatography with gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) in MeCN to 95% MeCN in H_2O (with 0.1% AcOH) to afford the title compound **17P** as a brown oil (87 mg, 40% yield).

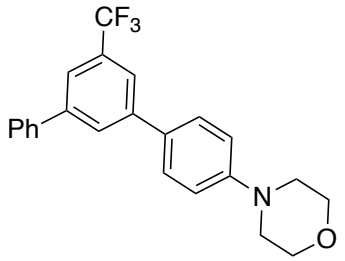
^{1}H NMR (800 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.02 (t, *J* = 1.9 Hz, 1H), 7.88 – 7.77 (m, 3H), 7.69 – 7.64 (m, 3H), 7.63 – 7.59 (m, 1H), 7.52 – 7.48 (m, 2H), 7.42 (ddt, *J* = 7.8, 6.9, 1.3 Hz, 1H), 6.65 (dd, *J* = 3.7, 0.8 Hz, 1H), 1.70 (s, 9H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 149.6, 143.0, 142.5, 139.9, 134.4, 131.4 (q, *J* = 32.2 Hz), 129.4, 129.0, 128.0, 127.3, 126.8, 123.6, 122.8 (q, *J* = 3.8 Hz), 122.2 (q, *J* = 3.8 Hz), 119.5, 115.6, 107.4, 83.9, 28.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ –62.9 (s, 3F).

IR (film) 2919, 1593, 1499, 1337, 1289, 1111, 850, 752 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{21}H_{15}F_3N$ $[M\text{-}Boc+H_2]^+$ 338.1156 , found 338.1154.



4-(5'-(Trifluoromethyl)-[1,1':3',1''-terphenyl]-4-yl)morpholine (18P)

The general method **C** was followed. In step 1, 4''-morpholino-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'H)-one (166 mg, 1.00 equiv., 0.500 mmol),), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (2.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was

run for 18 h at 50 °C, and the basic alumina plug filter was pushed with DCM (3 mL x 3). In step 3, DDQ (125 mg, 1.10 equiv., 0.600 mmol) was added and the reaction was run for 14 h at 110 °C in *o*-DCB. At completion, the reaction was cooled down to rt and quenched with 6 M NaOH solution until pH = 9. The compound was then extracted with DCM (10 mL x 3), and the combined organic layer was dried with anhydrous Na_2SO_4 and purified using normal phase flash chromatography with pre-neutralized silica (column was pre-washed with 50 mL 1% TEA in hexanes 3 times) with 0 → 80% DCM in hexanes to afford the desired compound **18P** as a clear oil (109 mg, 57% yield).

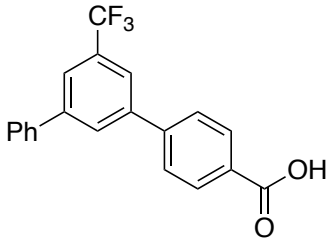
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 15.2 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.55 – 7.36 (m, 4H), 7.26 (d, *J* = 2.6 Hz, 3H), 7.08 – 6.91 (m, 2H), 3.94 – 3.85 (m, 4H), 3.36 – 3.15 (m, 4H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 151.1, 142.5, 142.1, 139.9, 130.1 (q, *J* = 107.57 Hz), 128.8, 128.5, 128.2, 127.9 (q, *J* = 14.5 Hz), 127.2, 127.1, 122.0, 115.7, 115.6, 114.7, 66.8, 48.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.0 (s, 3F).

IR (film) 3037, 2960, 2920, 2851, 1731, 1609, 1519 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{23}H_{21}F_3NO$ $[M+H]^+$ 384.1575, found 384.1569.



5'-(Trifluoromethyl)-[1,1':3',1''-terphenyl]-4-carboxylic acid (19P1)

The general method **A** was followed. In step 1, *tert*-butyl-5'-oxo-2',3',4',5'-tetrahydro-[1,1':3',1''-terphenyl]-4-carboxylate (174 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (23 mg, 0.30 equiv., 0.15 mmol), and *o*-DCB (2.5 mL) were added. The reaction was stirred for 24 h at rt. In step 2, PTSA•H_2O (95 mg, 1.0 equiv., 0.50 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) was added and the reaction was stirred for 14 h at 120 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified by reverse phase flash chromatography with gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) in MeCN to 95% MeCN in H_2O (with 0.1% AcOH) to afford the title compound **19P1** as a brown powder (147 mg, 86% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 2H), 8.00 (s, 1H), 7.88 – 7.85 (m, 1H), 7.80 – 7.74 (m, 2H), 7.66 (dt, *J* = 8.2, 1.6 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.46 – 7.42 (m, 1H).

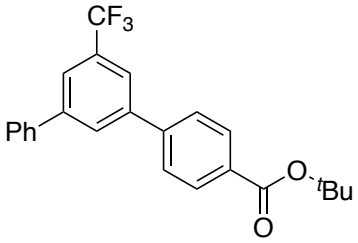
^{13}C NMR (201 MHz, $CDCl_3$) δ 170.8, 144.9, 142.9, 141.3, 139.4, 131.9 (q, *J* = 32.0 Hz), 130.9, 129.4, 128.7, 128.3, 127.4, 127.2, 123.9 (q, *J* = 273.7 Hz), 123.7, 122.8 (q, *J* = 4.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.0 (s, 3F).

IR (film) 3657, 2972, 1610, 1462, 1382, 1251, 1072 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{20}H_{14}F_3O_2$ $[M+H]^+$ 343.0945, found 343.0935.

M.P. 158–160 °C



***Tert*-butyl 5'-(trifluoromethyl)-[1,1':3',1''-terphenyl]-4-carboxylate (19P2)**

The general method **A** was followed. In step 1, *tert*-butyl 5'-oxo-2',3',4',5'-tetrahydro-[1,1':3',1''-terphenyl]-4-carboxylate (174 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (23 mg, 0.30 equiv., 0.15 mmol), and *o*-DCB (2.5 mL) were added. The reaction was run for 24 h at rt. In step 2, DDQ (227 mg, 2.00 equiv., 1.00 mmol) was added and the reaction was run for 24 h at 100 °C in *o*-DCB (2.5 mL). No PTSA•H_2O was added. The crude reaction mixture was purified by reverse phase flash chromatography with gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) in MeCN to 95% MeCN in H_2O (with 0.1% AcOH) to afford the title compound **19P2** as a brown oil (88 mg, 44% yield).

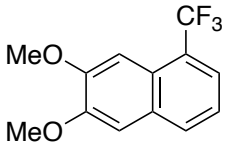
^{1}H NMR (800 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 2H), 7.98 (s, 1H), 7.84 (d, *J* = 17.7 Hz, 2H), 7.71 – 7.69 (m, 2H), 7.52 – 7.49 (m, 2H), 7.45 – 7.42 (m, 1H), 1.64 (s, 9H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 165.4, 143.5, 142.8, 141.6, 139.5, 131.8 (q, *J* = 32.0 Hz), 131.6, 130.1, 129.3, 129.0, 128.2, 127.2, 127.0, 123.4 (q, *J* = 4.2 Hz), 122.7 (q, *J* = 4.2 Hz), 81.2, 28.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.0 (s, 3F).

IR (film) 3657, 2980, 2971, 2888, 1472, 1462, 1381 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{20}H_{13}F_3O_2$ $[M-{}^t\text{Bu}+H]^+$ 342.0867, found 342.0872.



6,7-Dimethoxy-1-(trifluoromethyl)naphthalene (20P)

The general method **A** was followed. In step 1, 6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (103 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 12 h at 140 °C in *o*-DCB (5.0 mL). The crude reaction mixture was purified using normal phase flash chromatography with 0 → 20% EtOAc in hexanes to afford the desired compound **20P** as a colorless powder (109 mg, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.44 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.16 (s, 1H), 4.03 (s, 3H), 4.01 (s, 3H).

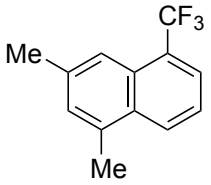
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 149.6, 130.8, 130.0, 124.9 (q, *J* = 273.3 Hz), 124.6 (q, *J* = 29.58), 122.7 (q, *J* = 6 Hz), 122.5, 106.8, 102.9, 55.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ –60.9 (s, 3F).

IR (film) 3006, 2886, 2834, 1681, 1628, 1589, 1511 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{13}H_{11}F_3O_2$ $[M]^+$ 256.0711, found 256.0705.

M.P. 94–96 °C



1,3-Dimethyl-5-(trifluoromethyl)naphthalene (21P)

The general method **A** was followed. In step 1, 6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (87 mg, 1.0 equiv., 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 12 h at 140 °C in *o*-DCB (5.0 mL). The crude reaction mixture was purified by normal phase flash chromatography with 100% pentane to afford the desired compound **21P** as a clear oil (64 mg, 59% yield).

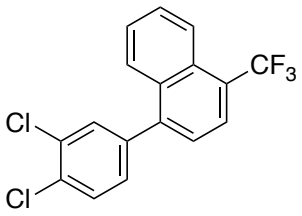
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 1.4 Hz, 1H), 2.69 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 137.1, 134.7, 131.3, 129.7, 129.5, 128.5, 124.4, 125.9, 124.3, 123.0, 121.4, 22.1, 19.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ –59.9 (s, 3F).

IR (film) 2924, 2854, 2212, 1647, 1558, 1502, 1415 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{13}H_{11}F_3$ $[M]^+$ 224.0812, found 224.0806.



1-(3,4-Dichlorophenyl)-4-(trifluoromethyl)naphthalene (22P)

The general method **A** was followed. In step 1, 4-(3,4-dichlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (145 mg, 1.0 equiv., 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10

equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 24 h at 140 °C in *o*-DCB (5.0 mL). The crude reaction mixture was purified by normal phase flash chromatography with 100% hexanes to deliver the desired compound **22P** as a colorless solid (129 mg, 76% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.32 (dd, *J* = 8.1, 2.0 Hz, 1H).

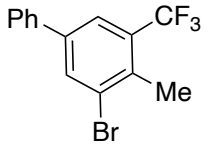
^{13}C NMR (201 MHz, $CDCl_3$) δ 142.2, 139.6, 132.6, 132.3, 131.8, 131.5, 130.4, 129.3, 129.1, 127.6, 127.0, 126.3, 126.2 (q, *J* = 30.0 Hz), 125.2, 124.6, 124.5 (q, *J* = 273.4 Hz), 124.0 (q, *J* = 5.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –60.1 (s, 3F).

IR (film) 2929, 1518, 1474, 1330, 1276, 1185, 1148, 1122, 1033, 992, 850, 825, 765, 659, 475 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{17}H_9Cl_2F_3$ $[M]^+$ 340.0033, found 340.0030.

M.P. 89–90 °C



3-Bromo-4-methyl-5-(trifluoromethyl)-1,1'-biphenyl (23P)

The general method **B** was followed. In step 1, 5-bromo-4-methyl-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (132 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (1.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 24 h at 50 °C, and the silica plug filter was pushed with Et_2O. In step 3, In step 3, AIBN (8.2 mg, 0.10 equiv., 0.050 mmol) and NBS (356 mg, 4.00 equiv., 2.00 mmol) were added and the reaction was run for 18 h at 120 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified by normal phase flash chromatography with 100% pentane to deliver the desired product **23P** as a colorless powder (82 mg, 52% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.99 – 7.79 (m, 1H), 7.77 (d, *J* = 11.8 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 2.59 – 2.53 (m, 3H).

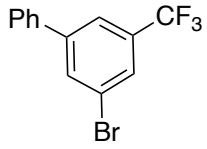
^{13}C NMR (201 MHz, $CDCl_3$) δ 141.6–137.7 (m), 136.9, 135.1, 133.8 (d, *J* = 157.5 Hz), 132.1–129.9 (m), 129.0, 128.2, 127.8, 126.9 (d, *J* = 5.8 Hz), 124.9–122.2 (m), 17.5 (d, *J* = 636.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –61.5 (s, 3F).

IR (film) 3065, 3034, 2877, 1601, 1559, 1463, 1405 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{14}H_{10}BrF_3$ $[M]^+$ 313.9900, found 313.9903.

M.P. 77–79 °C



3-Bromo-5-(trifluoromethyl)-1,1'-biphenyl (24P)

The general method **A** was followed. In step 1, 5-bromo-4-methyl-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one (125 mg, 1.00 equiv. 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 24 h at 50 °C. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 24 h at 140 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified by normal phase flash chromatography with 100% pentane to deliver the desired compound **24P** as a clear oil (97 mg, 64% yield).

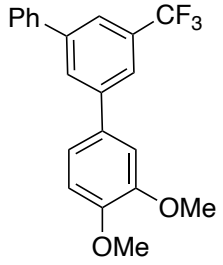
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.78 – 7.72 (m, 2H), 7.58 – 7.55 (m, 2H), 7.50 – 7.45 (m, 2H), 7.45 – 7.41 (m, 1H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 144.0, 138.3, 133.4, 132.7 (q, *J* = 32.8 Hz), 129.1, 128.6, 127.1, 126.9 (q, *J* = 4.3 Hz), 123.0, 123.2 (q, *J* = 273.0) 122.7, 122.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.3 (s, 3F).

IR (film) 3065, 3041, 1951, 1585, 1576, 1458, 1445 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{13}H_8BrF_3$ $[M]^+$ 299.9761, found 299.9759.



3,4-Dimethoxy-5'-(trifluoromethyl)-1,1':3',1''-terphenyl (25P)

The general method **A** was followed. In step 1, 3'',4''-dimethoxy-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one (154 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 12 h at 50 °C. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 14 h at 140 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified using normal phase flash chromatography with 0 → 40% EtOAc in hexanes to deliver the desired compound **25P** as a colorless powder (126 mg, 70% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.14 (s, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H).

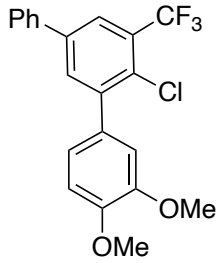
^{13}C NMR (201 MHz, $CDCl_3$) δ 149.4, 149.3, 142.6, 142.4, 139.8, 132.7, 131.6 (q, *J* = 32.1 Hz), 125.0 (q, *J* = 275.4 Hz), 122.4, 122.3, 122.3, 122.3, 119.7, 110.4, 56.0, 56.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.0 (s, 3F).

IR (film) 3059, 2836, 2164, 1605, 1518, 1465, 1441 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{21}H_{18}F_3O_2$ $[M+H]^+$ 359.1258, found 359.1257.

M.P. 68–70 °C



6'-Chloro-3,4-dimethoxy-5'-(trifluoromethyl)-1,1':3',1''-terphenyl (26P)

The general method **C** was followed. In step 1, 5-bromo-4-methyl-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (171 mg, 1.00 equiv. 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (1.0 mL) were added, and the reaction was run for 12 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 18 h at 50 °C. The crude reaction mixture was then pushed through a silica plug filter and washed with DCM. In step 3, DDQ (227 mg, 2.00 equiv., 1.00 mmol) was added and the reaction was run for 12 h at 120 °C in *o*-DCB. At completion, the solvents were evaporated using smart evaporator, and the residue was again filtered through a small plug of silica using Et_2O as an eluent to remove the baseline impurities. The crude reaction mixture was purified by normal-phase flash chromatography with 0 → 20% EtOAc in hexanes to deliver the desired compound **26P** as a colorless powder (114 mg, 58% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.73 (s, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.99 – 6.96 (m, 2H), 3.95 (s, 3H), 3.92 (s, 3H).

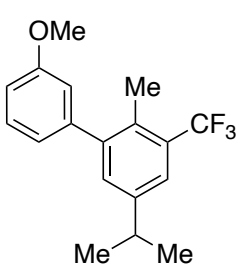
^{13}C NMR (201 MHz, $CDCl_3$) δ 149.0, 148.5, 143.3, 139.7, 133.0, 129.1, 128.3, 127.0, 124.9, 121.9, 112.8, 110.8, 56.0, 55.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.0 (s, 3F).

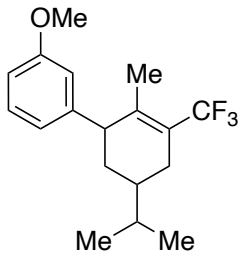
IR (film) 2930, 2842, 2196, 1604, 1515, 1464, 1435 cm^{-1}

HRMS (APCI)$^+$ *m/z* calc'd $C_{21}H_{17}ClF_3O_2$ $[M+H]^+$ 393.0869, found 393.0867

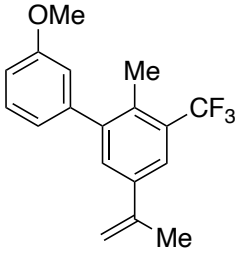
M.P. 126–127 °C



Desired Product



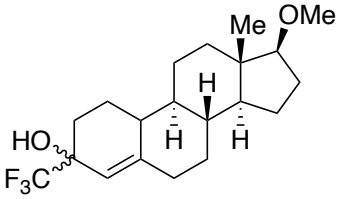
Unreacted Vinyl–CF_3 Intermediate



Undesired Overoxidized Side Product

5-Isopropyl-3'-methoxy-2-methyl-3-(trifluoromethyl)-1,1'-biphenyl (**27P**)

The general method **C** was followed. In step 1, (5*R*)-5-isopropyl-3-(3-methoxyphenyl)-2-methylcyclohexan-1-one (130 mg, 1.00 equiv. 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (1.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 18 h at 50 °C. The crude reaction mixture was then pushed through a silica plug filter and washed with Et_2O. In step 3, DDQ (227 mg, 2.00 equiv., 1.00 mmol) was added and the reaction was run for 48 h at 110 °C in *o*-DCB. At completion, the crude ^{19}F NMR yield was 38%. The product was not isolated because of co-elution of unreacted vinyl–CF_3 intermediate and undesired overoxidized side products in different chromatographic systems.



17-Methoxy-13-methyl-3-(trifluoromethyl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-*1H*-cyclopenta[a]phenanthren-3-ol (28–S1)

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 17-methoxy-13-methyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-*3H*-cyclopenta[a]phenanthren-3-one (144 mg, 1.00 equiv., 0.500 mmol). The vial was evacuated and backfilled with N_2 (3x). THF (1.0 mL) was then added followed by the addition of $TMSCF_3$ (0.2 mL, 1.0 equiv., 1.2 mmol). TBAF (1.0 M in THF) (0.50 mL, 2.5 equiv., 1.0 mmol) was then added slowly. The reaction was allowed to run for 24 h at rt under N_2. The reaction was quenched with saturated aqueous NH_4Cl, and the reaction mixture was extracted with Et_2O (30 X 3 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* using a rotary evaporator. Purification by normal-phase flash chromatography using 20% EtOAc in hexanes delivered the title compound (**28–S1**) as a mixture of two diastereomers (3:1) as a colorless oil (160 mg, 89% yield).

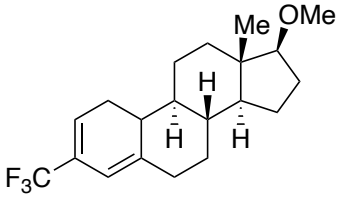
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 – 5.32 (m, 1H), 3.34 (d, *J* = 2.0 Hz, 3H), 3.23 (dt, *J* = 8.4, 3.1 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.16 – 1.98 (m, 4H), 1.91 (td, *J* = 8.4, 3.4 Hz, 2H), 1.85 – 1.72 (m, 3H), 1.69 – 1.53 (m, 3H), 1.51 – 1.41 (m, 1H), 1.32 – 1.18 (m, 4H), 1.05 – 0.89 (m, 2H), 0.78 (d, *J* = 3.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5 (q, *J* = 6.2 Hz), 127.3, 125.1, 115.8, 90.8, 90.8, 71.2, 58.0, 50.2, 50.2, 50.1, 48.8, 48.7, 43.2, 43.1, 42.0, 41.5, 41.2, 41.0, 40.4, 38.0, 37.9, 36.0, 35.8, 35.2, 32.2, 32.0, 30.9, 28.3, 28.2, 27.7, 26.3, 23.2, 22.8, 22.1, 21.6, 11.7, 11.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ –83.6, –81.5 (s, 3:1, 3F).

IR (film) 3400, 2930, 2865, 1451, 1364, 1131, 1096, 991, 969, 732 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{20}H_{28}F_3O$ $[M - H_2O + H]^+$ 341.2089, found 341.2092.



17-Methoxy-13-methyl-3-(trifluoromethyl)-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[a]phenanthrene (28–S2)

A 20 mL scintillation vial was equipped with a magnetic stir bar and charged with 17-methoxy-13-methyl-3-(trifluoromethyl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a] phenanthren-3-ol **28–S1** (160 mg, 1.00 equiv., 0.450 mmol). The vial was sealed with a rubber septum and evacuated and backfilled with N_2 (3x). THF (4.0 mL) was then added followed by the addition of Burgess reagent (213 mg, 2.00 equiv., 0.900 mmol). The reaction was allowed to run for 1 h at rt and 23 h at 40 °C. The reaction was quenched with saturated aqueous brine, and the reaction mixture was extracted with Et_2O (30 mL x 3). The combined organic phases were dried with Na_2SO_4, filtered, and concentrated *in vacuo* using a rotary evaporator. Purification by a normal-phase flash chromatography with 20% EtOAc in hexanes delivered the desired compound (**28–S2**) as a clear oil (136 mg, 90% yield).

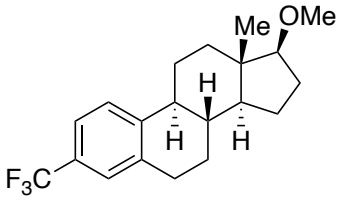
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47 (s, 1H), 5.78 (s, 1H), 3.36 (s, 3H), 3.26 (t, *J* = 8.3 Hz, 1H), 2.32 (d, *J* = 16.9 Hz, 1H), 2.26 – 2.16 (m, 3H), 2.08 – 2.00 (m, 1H), 1.96–1.87 (m, 2H), 1.72 (d, *J* = 30.3 Hz, 1H), 1.62 – 1.56 (m, 2H), 1.52 – 1.42 (m, 2H), 1.30 – 1.25 (m, 3H), 1.16–1.09 (m, 1H), 1.07 – 1.00 (m, 1H), 0.96 – 0.89 (m, 1H), 0.79 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.7, 131.1 (q, *J* = 6.1 Hz), 130.4, 125.4 (q, *J* = 33.5 Hz), 123.8, 90.9, 58.0, 50.9, 43.8, 43.1, 40.8, 37.8, 36.6, 31.3, 27.8, 26.6, 26.4, 23.22, 23.17, 11.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ –69.1 (s, 3F).

IR (film) 3341, 2971, 2886, 1467, 1379, 1162, 1128, 950, 816, 668 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{20}H_{28}F_3O$ $[M + H]^+$ 341.2086, found 341.2071.



17-Methoxy-13-methyl-3-(trifluoromethyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene (28P)

A 20 mL scintillation vial was equipped with a magnetic stir bar and charged with 17-methoxy-13-methyl-3-(trifluoromethyl)-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[a] phenanthrene **28–S2** (136 mg, 1.00 equiv., 0.400 mmol). DDQ (227 mg, 2.50 equiv., 1.00 mmol) was then added. The vial was sealed with a rubber septum and evacuated and backfilled with N_2 (3x). *o*-DCB (4.0 mL) was added, and the reaction was allowed to run for 24 h at 100 °C. The solvent was removed *in vacuo* using a smart evaporator followed by dissolving in Et_2O and adding saturated aq. $NaHCO_3$. The reaction mixture was extracted with Et_2O (30 mL x 3), and the combined organic phases were dried with Na_2SO_4, filtered, and concentrated *in vacuo* by a rotary evaporator. Purification by reverse phase column chromatography with a gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) to 95% MeCN in in H_2O (with 0.1% AcOH) recovered 42 mg (31%) of the starting material and afforded the title compound in a mixture of overoxidized products. The mixture was further purified by preparative TLC using 5% Et_2O in pentane to deliver the desired compound **28P** as a clear oil (38 mg, 28% yield, 40% BRSM).

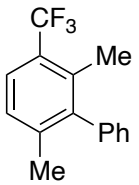
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 12.7, 8.0 Hz, 2H), 7.32 (s, 1H), 3.38 (s, 3H), 3.32 (t, *J* = 8.3 Hz, 1H), 2.90 (m, 2H), 2.42 – 2.22 (m, 2H), 2.20 – 2.03 (m, 2H), 2.00 – 1.88 (m, 1H), 1.74 – 1.67 (m, 1H), 1.55 – 1.49 (m, 2H), 1.46–1.39 (m, 2H), 1.39 – 1.32 (m, 2H), 1.23 – 1.18 (m, 1H), 0.79 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 137.6, 128.0 (q, *J* = 32.0 Hz), 125.9, 125.8 (q, *J* = 6.1 Hz), 123.9, 122.4 (q, *J* = 4.1 Hz), 90.8, 58.1, 50.5, 44.5, 43.3, 38.2, 38.1, 29.6, 27.8, 27.0, 26.3, 23.2, 11.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ –62.9 (s, 3F).

IR (film) 2924, 2851, 2324, 1454, 1327, 1275, 1159, 1122, 896, 749 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd for $C_{20}H_{26}F_3O$ $[M + H]^+$ 339.1929, found 339.1911.



2,6-Dimethyl-3-(trifluoromethyl)-1,1'-biphenyl (29P)

The general method **A** was followed. In step 1, 2,6-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (100.1 mg, 0.5000 mmol, 1.000 equiv.), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 48 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 24 h at 140 °C in *o*-DCB (5.0 mL). The crude reaction mixture was purified using normal phase flash chromatography with 100% hexanes to deliver the desired compound **29P** as a yellow oil (74 mg, 59% yield).

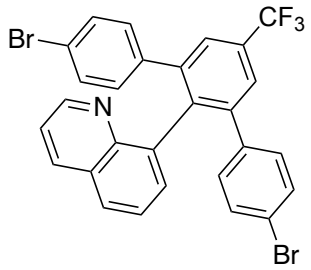
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.47–7.44 (m, 2H), 7.40–7.34 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.16–6.95 (m, 2H), 2.12 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 143.7, 140.3, 140.0, 134.7, 128.8, 128.6, 127.1, 127.0, 126.7 (q, *J* = 30.2 Hz), 124.8 (q, *J* = 273.4 Hz), 124.5 (q, *J* = 5.3 Hz), 21.2, 16.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ –61.2 (s, 3F).

IR (film) 2919, 1599, 1457, 1419, 1383, 1322, 1238, 1210, 1177, 1119, 1047, 825, 769, 616, 481 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{15}H_{13}F_3$ $[M]^+$ 250.0969, found 250.0965.



8-(4,4''-Dibromo-5'-(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl)quinoline (30P)

The general method **C** was followed. In step 1, 3,5-bis(4-bromophenyl)-4-(isoquinolin-1-yl)cyclohexan-1-one (268 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (2.0 mL) were added, and the reaction was run for 12 h at 35 °C. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 18 h at 50 °C. The crude reaction mixture was then pushed through a basic alumina plug filter and washed with DCM (3 mL x 3). In step 3, DDQ (341 mg, 3.00 equiv., 1.50 mmol) was added, and the reaction was run for 14 h at 120 °C in *o*-DCB. At completion, the reaction was cooled down to rt and quenched with 6 M NaOH solution until pH = 9. The compound was then extracted with DCM (10 mL x 3), and the combined organic layer was dried over anhydrous Na_2SO_4 and purified using normal phase flash chromatography with pre-neutralized silica (column was pre-washed with 50 mL 1% TEA in hexanes 3 times) with 0 → 60% DCM in hexanes to afford the desired compound **30P** as a colorless powder (134 mg, 46% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.3 Hz, 1H), 7.81 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 4.4 Hz, 3H), 7.64 (d, *J* = 5.7 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.25 – 7.22 (m, 4H), 6.99 (d, *J* = 6.6 Hz, 4H), 6.96 – 6.92 (m, 1H).

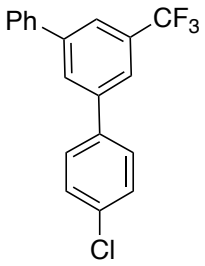
^{13}C NMR (201 MHz, $CDCl_3$) δ 157.2, 147.2, 141.8, 141.7, 138.7, 135.6, 131.1, 131.0, 129.8, 129.1, 127.4, 126.9, 126.3, 126.1, 123.6, 121.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.12 (s, 3F).

IR (film) 3056, 2921, 2851, 2206, 1618, 1592, 1558 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calcd $C_{28}H_{17}Br_2F_3N$ $[M+H]^+$ 581.9679, found 581.9671.

M.P. 137–138 °C



4-Chloro-5'-(trifluoromethyl)-1,1':3',1''-terphenyl (**31P**)

The general method **A** was followed. In step 1, 4''-chloro-1',6'-dihydro-[1,1':3',1''-terphenyl]-5'(2'*H*)-one (141 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added, and the reaction was run for 24 h at rt. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 24 h at 120 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified by normal phase flash chromatography with 5% EtOAc in hexanes to deliver the desired compound **31P** as a clear oil (143 mg, 86% yield).

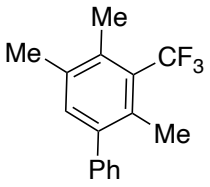
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.82 (s, 1H), 7.77 (s, 1H), 7.64 (dd, *J* = 7.2, 1.9 Hz, 2H), 7.59 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.52 – 7.41 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 141.6, 139.7, 138.4, 134.5, 132.0 (q, *J* = 32.2 Hz), 129.4, 129.2, 128.7, 128.4, 127.4, 124.9, 123.23, 123.21, 122.69, 122.66.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.0 (s, 3F).

IR (film) 2923, 2851, 1450, 1363, 1266, 1127, 1168, 824, 762, 699 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{19}H_{12}ClF_3$ $[M]^+$ 332.0573, found 332.0558.



2,4,5-Trimethyl-3-(trifluoromethyl)-1,1'-biphenyl (32P)

The general method **A** was followed. In step 1, 2,4,5-trimethyl-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (110 mg, 1.0 equiv., 0.50 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), CsF (7.5 mg, 0.10 equiv., 0.050 mmol), and *o*-DCB (1.0 mL) were added. The reaction was run for 24 h at 50 °C. In step 2, PTSA•H_2O (191 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added, and the reaction was run for 24 h at 140 °C in *o*-DCB (2.5 mL). The crude reaction mixture was purified using normal phase flash chromatography with 5% EtOAc in hexanes to deliver the desired compound **32P** as a clear oil (107 mg, 81% yield).

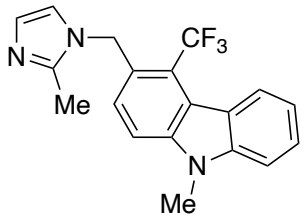
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.41–7.34 (m, 1H), 7.30 – 7.25 (m, 2H), 7.21 (s, 1H), 2.44 (q, *J* = 3.2 Hz, 3H), 2.35 (s, 3H), 2.32 (q, *J* = 4.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 141.7, 135.7, 135.5, 134.45, 132.5, 129.6, 129.06, 128.8 (q, *J* = 27 Hz), 128.3, 127.5 (q, *J* = 277.1Hz), 125.3, 20.8, 18.6 (q, *J* = 4.7 Hz), 16.9 (q, *J* = 4.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –52.4 (s, 3F).

IR (film) 3061, 2945, 1466, 1331, 1243, 1107, 1018, 766, 719, 701 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{16}H_{15}F_3$ $[M]^+$ 264.1125, found 264.1117.



9-Methyl-3-((2-methyl-1*H*-imidazol-1-yl)methyl)-4-(trifluoromethyl)-9*H*-carbazole (33P)

The general method **A** was followed with a minor modification. In step 1, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with ondansetron (110 mg, 1.0 equiv., 0.50 mmol). The vial was taken to glove box and CsF (8 mg, 0.1 equiv., 0.05 mmol) and THF (1.0 mL) were added. The vial was taken out of glove box and $TMSCF_3$ (110 µL, 1.5 equiv., 0.75 mmol) was added. The reaction mixture was stirred at rt for 4 h, after which a second bolus of $TMSCF_3$ (110 µL, 1.5 equiv., 0.75 mmol) was added. The reaction mixture was stirred at rt for 20 h and then filtered over basic alumina with Et_2O and evaporated. The residue was dissolved in *o*-DCB (4.0 mL), and DDQ (125 mg, 1.10 equiv., 0.550 mmol) and PTSA•H_2O (105 mg, 1.10 equiv. 0.550 mmol) were added. The reaction was stirred at 120 °C for 24 h. The solvent was evaporated *in vacuo* using a smart evaporator, and the residue was resuspended in saturated aqueous $NaHCO_3$ to afford an aqueous suspension. The aqueous suspension was then extracted with Et_2O (30 mL x 3), and the combined organic phases were dried with Na_2SO_4, filtered, and concentrated *in vacuo* using a rotary evaporator. Purification by a reverse-phase flash chromatography with a gradient elution from 5% MeCN in H_2O (with 0.1% AcOH) to 95% MeCN in H_2O (with 0.1% AcOH) delivered the desired compound **33P** as a clear oil (81 mg, 47% yield).

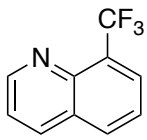
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.48 (dd, *J* = 17.1, 8.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 1.2 Hz, 1H), 6.80 (d, *J* = 1.4 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 5.46 (q, *J* = 2.6 Hz, 2H), 3.87 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 142.1, 141.3, 127.6, 127.3, 127.0, 125.3, 125.0, 124.9, 124.5 (q, *J* = 6.3 Hz), 120.8, 120.1, 112.6, 109.0, 48.0 (q, *J* = 7.1 Hz), 29.3, 13.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ –55.10 (s, 3F).

IR (film) 2928,1481, 1424, 1352, 1303, 1198, 1113, 1065, 747, 733 cm^{-1}.

HRMS (APCI)$^+$ *m/z* calc'd $C_{19}H_{17}F_3N_3$ $[M + H]^+$ 344.1374, found 344.1375.

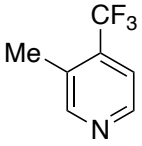


8-(Trifluoromethyl)quinoline (**34P**)

The general method **C** was followed. In step 1, 3,5-bis(4-bromophenyl)-4-(isoquinolin-1-yl)cyclohexan-1-one (268 mg, 1.00 equiv., 0.500 mmol), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL, 1.0 equiv., 0.50 mmol), and THF (2.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 8 h at rt. The crude reaction mixture was pushed through a basic alumina plug filter and washed with DCM. In step 3, DDQ (341 mg, 3.00 equiv., 1.50 mmol) was added and the reaction was run for 14 h at 120 °C in *o*-DCB. At completion, the reaction was cooled down to rt and quenched with 6 M NaOH solution until pH = 9. The compound was then extracted with DCM (10 mL x 3), and the combined organic layer was dried with anhydrous Na_2SO_4 and purified using normal phase flash chromatography with pre-neutralized silica (where the column was pre-washed with 50 mL 1% TEA in hexanes 3 times) with 0 → 80% DCM in hexanes to afford the desired compound **34P** as a colorless powder (56 mg, 57% yield). The ^{1}H NMR data matched the previous report[20].

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 – 9.06 (m, 1H), 8.24 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –60.8 (s, 3F).



3-Methyl-4-(trifluoromethyl)pyridine (35P)

The general method **C** was followed. In step 1, 3-methyl-1-(phenylsulfonyl)piperidin-4-one (127 mg, 1.00 equiv., 0.500 mmol),), $TMSCF_3$ (81 µL, 1.1 equiv., 0.55 mmol), TBAF (1 M in THF) (0.50 mL,

1.0 equiv., 0.50 mmol), and THF (2.0 mL) were added, and the reaction was run for 4 h at rt. In step 2, DMAP (6.1 mg, 0.10 equiv., 0.050 mmol), pyridine (121 µL, 3.00 equiv., 1.50 mmol.), $SOCl_2$ (109 µL, 3.00 equiv., 1.50 mmol) were sequentially added, and the reaction was run for 24 h at 60 °C, and the reaction was cooled to rt and quenched with aq. $CuSO_4$ solution. The compound was extracted with DCM (10 mL x 3), and the combined organic layer was dried with anhydrous Na_2SO_4 and purified using normal phase flash chromatography with 0–50% EtOAc in hexanes to afford the desired compound in quantitative yield as an amber oil. In step 3, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with isolated compound and DDQ (341 mg, 3.00 equiv., 1.50 mmol). The vial was evacuated and backfilled with N_2 (3x). Then 1,2-DCE (2.5 mL) was added, and the reaction was run for 14 h at 90 °C. At completion, the reaction was cooled down to rt and quenched with 6 M NaOH solution until pH = 9. The compound was then extracted with DCM (10 mL x 3), and the combined organic layer was dried with anhydrous Na_2SO_4 and purified using normal phase flash chromatography with pre-neutralized silica (where the column was pre-washed with 50 mL 1% TEA in hexanes 3 times) with 0 → 80% DCM in hexanes to deliver the desired compound **35P** as a clear oil (51 mg, 63% yield). The ^{1}H NMR data matched the previous report[21].

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.60 – 8.59 (m, 2H), 7.47 (d, *J* = 5.0 Hz, 1H), 2.48 (s, 3H).

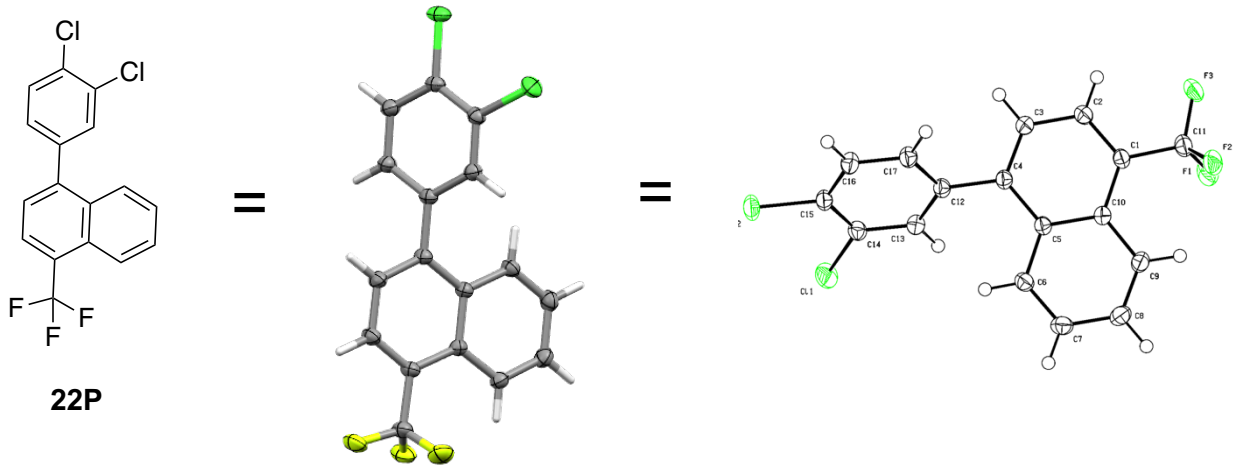
^{19}F NMR (470 MHz, $CDCl_3$) δ –64.6 (s, 3F).

5. Crystallography of 22P

5.1. Structure Tables

A super saturated solution of **22P** was prepared by adding *n*-pentane (3.0 mL) to 200.0 mg of **22P** in a 20 mL scintillation vial. The vial was then heated at 35 °C for 15 mins to prepare a translucent solution. The vial was first cooled to rt for 1 h and then placed at –20 °C for 24 h to afford the crystals of the compound. A colorless, rod-shaped crystal of **22P** was mounted on the goniometer. Data were collected from a shock-cooled single crystal at 150 K on a Bruker AXS D8 Quest three circle diffractometer with a fine focus sealed tube X-ray source using a Triumph curved graphite crystal as monochromator and a Photon II charge-integrating pixel array (CPAD) detector. The diffractometer was equipped with a low temperature device and used Mo K_α radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied[22,23]. The structure was solved by dual methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2019/2[24,25]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data for the structures reported here have been deposited with the Cambridge

Crystallographic Data Centre[26]. CCDC 2366007 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif[27]. The CIF file has no alert level A and Alert Level B.



Supplementary Table 1. Crystal data and structure refinement for 22P

CCDC number	2366007
Empirical formula	$C_{17}H_9Cl_2F_3$
Formula weight	341.14
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	7.0567(3)
b [Å]	11.9003(5)
c [Å]	17.1456(7)
α [°]	90
β [°]	95.0965(16)
γ [°]	90
Volume [Å^3]	1434.14(10)
Z	4
ρ_{calc} [gcm^{-3}]	1.580
μ [mm^{-1}]	0.477
F(000)	688
Crystal size [mm^3]	0.450×0.280×0.220
Crystal colour	colourless
Crystal shape	rod
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.17 to 66.42 (0.65 Å)

Index ranges	−10 ≤ h ≤ 10 −18 ≤ k ≤ 18 −26 ≤ l ≤ 26
Reflections collected	60846
Independent reflections	5488 R_{int} = 0.0468 R_{sigma} = 0.0229
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	5488/0/199
Absorption correction T_{min}/T_{max} (method)	0.6439/0.7465 (multi-scan)
Goodness-of-fit on F^2	1.026
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0363 wR_2 = 0.0873
Final *R* indexes [all data]	R_1 = 0.0524 wR_2 = 0.0956
Largest peak/hole [eÅ^{-3}]	0.45/−0.39

Supplementary Table 2. Atomic coordinates and U_{eq} [Å^2] 22P

Atom	*x*	*y*	*z*	U_{eq}
Cl1	-0.14781(5)	0.71905(3)	0.27262(2)	0.03507(9)
Cl2	0.10392(5)	0.92683(3)	0.33409(2)	0.03106(8)
F1	0.54322(13)	0.04839(7)	0.34412(6)	0.0398(2)
F2	0.69451(12)	0.08459(7)	0.45601(5)	0.03345(18)
F3	0.82168(11)	0.12284(7)	0.35006(5)	0.03314(18)
C1	0.56882(16)	0.23976(9)	0.38111(7)	0.0200(2)
C8	0.13468(18)	0.19580(11)	0.48882(8)	0.0268(2)
H8	0.072558	0.137535	0.514583	0.032
C9	0.29798(17)	0.17307(10)	0.45406(7)	0.0230(2)
H9	0.347617	0.098816	0.455778	0.028
C10	0.39417(15)	0.25876(9)	0.41550(6)	0.01857(19)
C11	0.65631(18)	0.12476(10)	0.38261(7)	0.0253(2)
C12	0.33040(16)	0.57254(9)	0.36471(6)	0.01953(19)
C13	0.14738(16)	0.59105(10)	0.32896(7)	0.0211(2)
H13	0.070291	0.528992	0.311436	0.025
C14	0.07761(16)	0.69955(10)	0.31892(7)	0.0215(2)
C15	0.18919(17)	0.79110(9)	0.34468(7)	0.0218(2)
C16	0.37164(18)	0.77362(10)	0.37936(7)	0.0241(2)
H16	0.448822	0.835925	0.396286	0.029
C17	0.44183(16)	0.66501(10)	0.38939(7)	0.0226(2)
H17	0.566992	0.653542	0.413294	0.027
C2	0.65915(17)	0.32568(10)	0.34636(7)	0.0236(2)
H2	0.776564	0.311919	0.324921	0.028
C3	0.57953(17)	0.43441(10)	0.34208(7)	0.0235(2)
H3	0.643743	0.492970	0.317507	0.028
C4	0.40990(16)	0.45697(9)	0.37304(6)	0.01926(19)
C5	0.31573(15)	0.36950(9)	0.41198(6)	0.01827(19)
C6	0.14658(16)	0.38955(10)	0.44910(7)	0.0222(2)
H6	0.093488	0.462958	0.447921	0.027
C7	0.05877(17)	0.30525(11)	0.48646(7)	0.0268(2)
H7	-0.054009	0.320655	0.510942	0.032

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Supplementary Table 3. Anisotropic displacement parameters [Å^2] for 22P.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	0.02426(14)	0.03421(17)	0.04480(19)	0.00645(14)	−0.00775(12)	0.00495(12)
Cl2	0.03774(16)	0.01873(13)	0.03676(17)	0.00428(11)	0.00362(13)	0.00875(11)
F1	0.0434(5)	0.0228(4)	0.0526(5)	−0.0128(4)	0.0000(4)	0.0012(3)
F2	0.0383(4)	0.0286(4)	0.0340(4)	0.0111(3)	0.0060(3)	0.0115(3)
F3	0.0336(4)	0.0281(4)	0.0395(4)	0.0020(3)	0.0134(3)	0.0129(3)
C1	0.0221(5)	0.0176(5)	0.0203(5)	0.0000(4)	0.0026(4)	0.0037(4)
C8	0.0260(5)	0.0253(6)	0.0296(6)	0.0048(5)	0.0047(5)	−0.0042(4)
C9	0.0246(5)	0.0182(5)	0.0260(5)	0.0024(4)	0.0012(4)	−0.0014(4)
C10	0.0198(4)	0.0173(4)	0.0185(4)	0.0003(4)	0.0010(4)	0.0009(4)

C11	0.0288(5)	0.0195(5)	0.0280(6)	0.0002(4)	0.0048(4)	0.0053(4)
C12	0.0223(5)	0.0177(5)	0.0187(4)	0.0016(4)	0.0024(4)	0.0027(4)
C13	0.0224(5)	0.0189(5)	0.0217(5)	0.0005(4)	0.0008(4)	0.0002(4)
C14	0.0207(5)	0.0223(5)	0.0212(5)	0.0032(4)	0.0010(4)	0.0030(4)
C15	0.0261(5)	0.0174(5)	0.0223(5)	0.0025(4)	0.0043(4)	0.0045(4)
C16	0.0266(5)	0.0183(5)	0.0271(5)	0.0004(4)	−0.0002(4)	−0.0001(4)
C17	0.0223(5)	0.0195(5)	0.0254(5)	0.0010(4)	−0.0009(4)	0.0016(4)
C2	0.0237(5)	0.0224(5)	0.0255(5)	0.0027(4)	0.0075(4)	0.0045(4)
C3	0.0240(5)	0.0198(5)	0.0277(5)	0.0042(4)	0.0080(4)	0.0020(4)
C4	0.0215(5)	0.0172(4)	0.0191(5)	0.0014(4)	0.0021(4)	0.0026(4)
C5	0.0194(4)	0.0176(4)	0.0178(4)	0.0005(3)	0.0015(4)	0.0020(4)
C6	0.0215(5)	0.0232(5)	0.0225(5)	0.0008(4)	0.0048(4)	0.0037(4)
C7	0.0226(5)	0.0308(6)	0.0278(6)	0.0031(5)	0.0072(4)	0.0004(4)

Supplementary Table 4. Bond lengths and angles for 22P.

Atom–Atom	**Length [Å]**
Cl1–C14	1.7292(12)
Cl2–C15	1.7277(11)
F1–C11	1.3434(15)
F2–C11	1.3508(15)
F3–C11	1.3377(14)
C1–C2	1.3691(16)
C1–C10	1.4307(15)
C1–C11	1.5006(16)
C8–C9	1.3706(17)
C8–C7	1.4075(18)
C8–H8	0.9500
C9–C10	1.4203(16)
C9–H9	0.9500
C10–C5	1.4287(15)
C12–C17	1.3960(16)
C12–C13	1.3970(15)
C12–C4	1.4874(15)
C13–C14	1.3872(16)
C13–H13	0.9500
C14–C15	1.3929(17)
C15–C16	1.3851(17)
C16–C17	1.3894(16)
C16–H16	0.9500
C17–H17	0.9500
C2–C3	1.4099(16)
C2–H2	0.9500
C3–C4	1.3782(15)
C3–H3	0.9500
C4–C5	1.4317(15)
C5–C6	1.4218(15)
C6–C7	1.3680(17)
C6–H6	0.9500
C7–H7	0.9500
Atom–Atom–Atom	**Angle [°]**
C2–C1–C10	120.85(10)

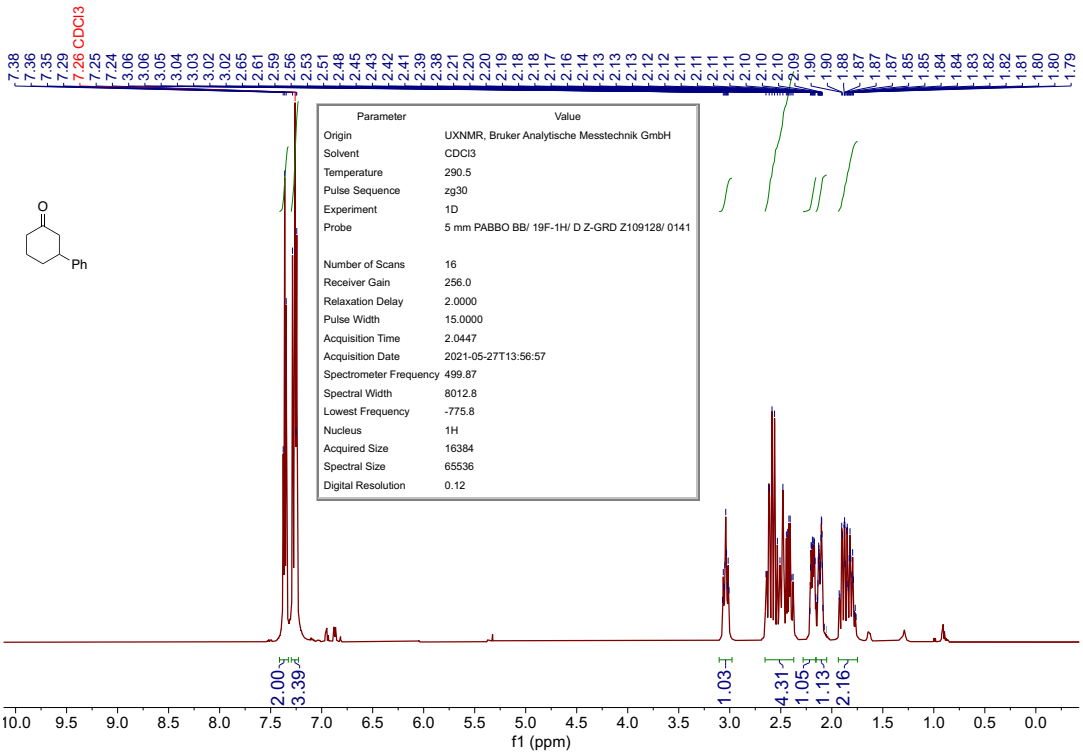
C2–C1–C11	118.81(10)
C10–C1–C11	120.34(10)
C9–C8–C7	120.18(11)
C9–C8–H8	119.9
C7–C8–H8	119.9
C8–C9–C10	121.05(11)
C8–C9–H9	119.5
C10–C9–H9	119.5
C9–C10–C5	118.85(10)
C9–C10–C1	122.90(10)
C5–C10–C1	118.24(10)
F3–C11–F1	106.60(10)
F3–C11–F2	105.86(10)
F1–C11–F2	106.20(10)
F3–C11–C1	112.41(10)
F1–C11–C1	112.52(10)
F2–C11–C1	112.73(10)
C17–C12–C13	118.85(10)
C17–C12–C4	120.15(10)
C13–C12–C4	120.93(10)
C14–C13–C12	120.35(11)
C14–C13–H13	119.8
C12–C13–H13	119.8
C13–C14–C15	120.28(10)
C13–C14–Cl1	118.93(9)
C15–C14–Cl1	120.78(9)
C16–C15–C14	119.77(10)
C16–C15–Cl2	119.16(9)
C14–C15–Cl2	121.07(9)
C15–C16–C17	120.02(11)
C15–C16–H16	120.0
C17–C16–H16	120.0
C16–C17–C12	120.72(11)
C16–C17–H17	119.6
C12–C17–H17	119.6
C1–C2–C3	120.61(10)
C1–C2–H2	119.7
C3–C2–H2	119.7
C4–C3–C2	120.97(10)
C4–C3–H3	119.5
C2–C3–H3	119.5
C3–C4–C5	119.53(10)
C3–C4–C12	118.44(10)
C5–C4–C12	122.03(10)
C6–C5–C10	118.26(10)
C6–C5–C4	121.98(10)
C10–C5–C4	119.75(9)
C7–C6–C5	121.31(11)
C7–C6–H6	119.3
C5–C6–H6	119.3
C6–C7–C8	120.33(11)
C6–C7–H7	119.8
C8–C7–H7	119.8

Supplementary Table 5. Torsion angles for 22P.

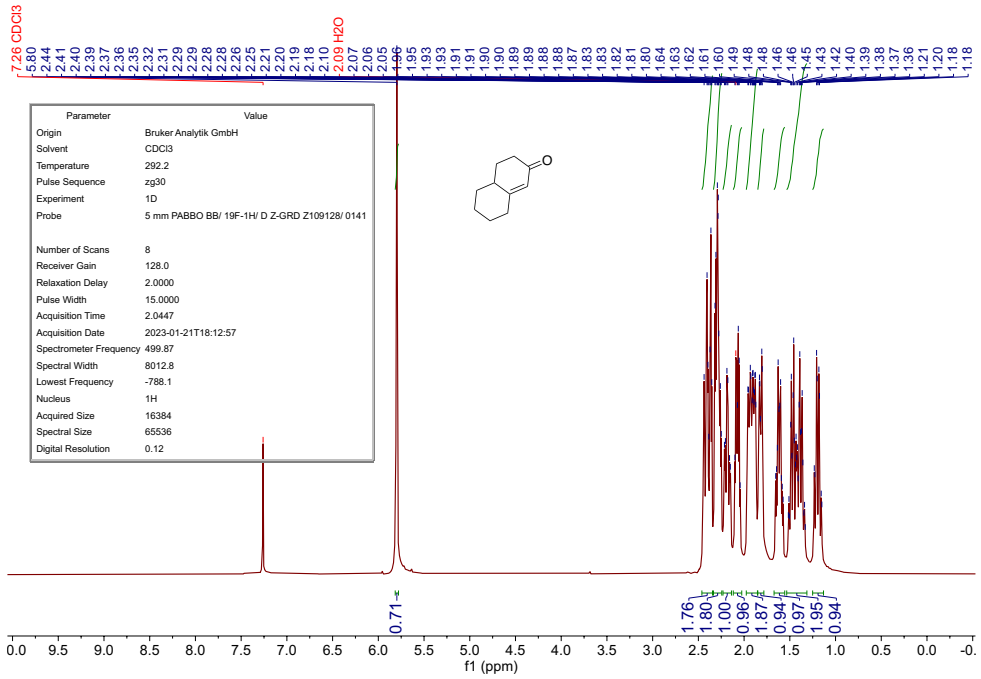
Atom–Atom–Atom–Atom	Torsion Angle [°]
C7–C8–C9–C10	0.31(19)
C8–C9–C10–C5	−1.28(17)
C8–C9–C10–C1	177.51(11)
C2–C1–C10–C9	−178.23(11)
C11–C1–C10–C9	1.74(17)
C2–C1–C10–C5	0.56(16)
C11–C1–C10–C5	−179.47(10)
C2–C1–C11–F3	1.87(16)
C10–C1–C11–F3	−178.10(10)
C2–C1–C11–F1	−118.49(13)
C10–C1–C11–F1	61.53(15)
C2–C1–C11–F2	121.43(12)
C10–C1–C11–F2	−58.54(15)
C17–C12–C13–C14	−0.56(17)
C4–C12–C13–C14	−177.57(10)
C12–C13–C14–C15	−0.26(17)
C12–C13–C14–Cl1	178.70(9)
C13–C14–C15–C16	1.01(17)
Cl1–C14–C15–C16	−177.93(9)
C13–C14–C15–Cl2	−179.03(9)
Cl1–C14–C15–Cl2	2.03(14)
C14–C15–C16–C17	−0.94(18)
Cl2–C15–C16–C17	179.11(9)
C15–C16–C17–C12	0.12(18)
C13–C12–C17–C16	0.63(17)
C4–C12–C17–C16	177.66(11)
C10–C1–C2–C3	−1.50(18)
C11–C1–C2–C3	178.53(11)
C1–C2–C3–C4	0.34(19)
C2–C3–C4–C5	1.72(18)
C2–C3–C4–C12	−178.30(11)
C17–C12–C4–C3	−53.34(15)
C13–C12–C4–C3	123.63(12)
C17–C12–C4–C5	126.65(12)
C13–C12–C4–C5	−56.39(15)
C9–C10–C5–C6	1.51(16)
C1–C10–C5–C6	−177.33(10)
C9–C10–C5–C4	−179.67(10)
C1–C10–C5–C4	1.49(15)
C3–C4–C5–C6	176.15(11)
C12–C4–C5–C6	−3.84(17)
C3–C4–C5–C10	−2.62(16)
C12–C4–C5–C10	177.39(10)
C10–C5–C6–C7	−0.85(17)
C4–C5–C6–C7	−179.63(11)
C5–C6–C7–C8	−0.12(19)
C9–C8–C7–C6	0.4(2)

6. NMR Spectra of Compounds

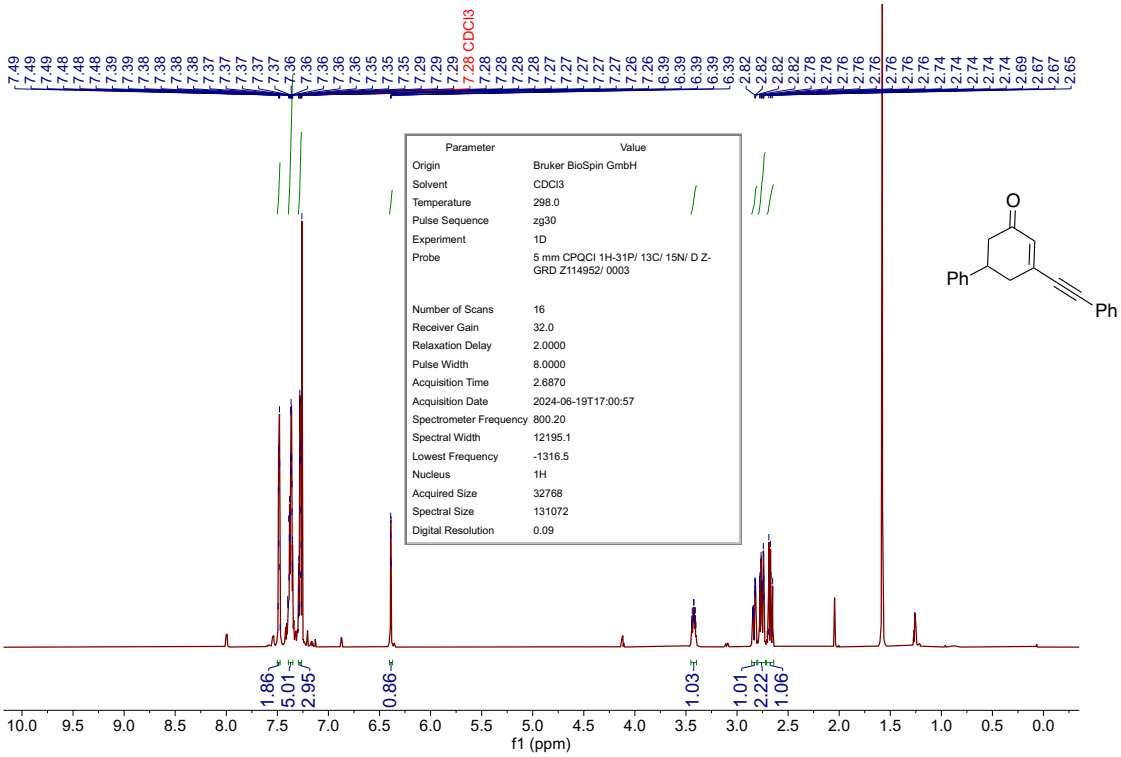
^{1}H NMR of **2S**



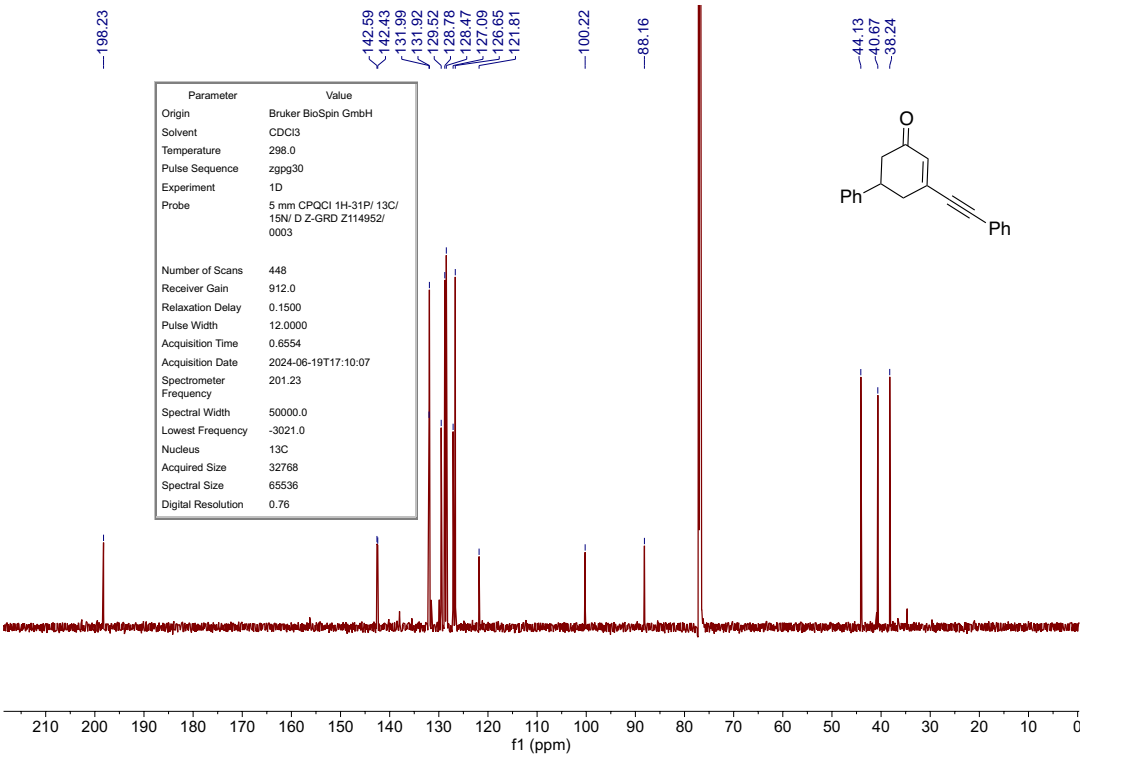
^{1}H NMR of **7S**



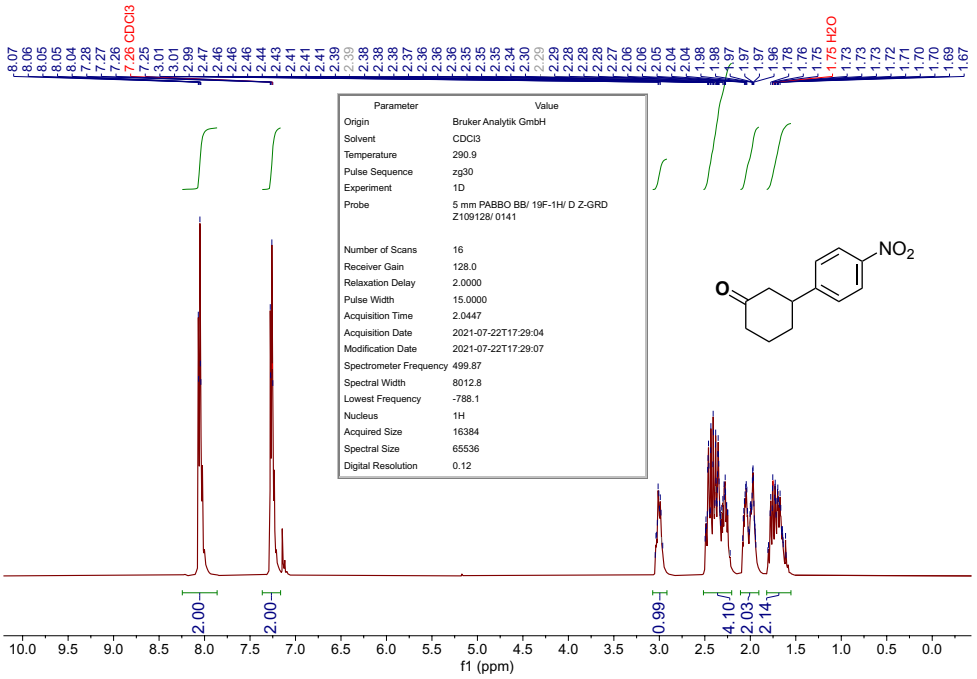
^{1}H NMR of **9S**



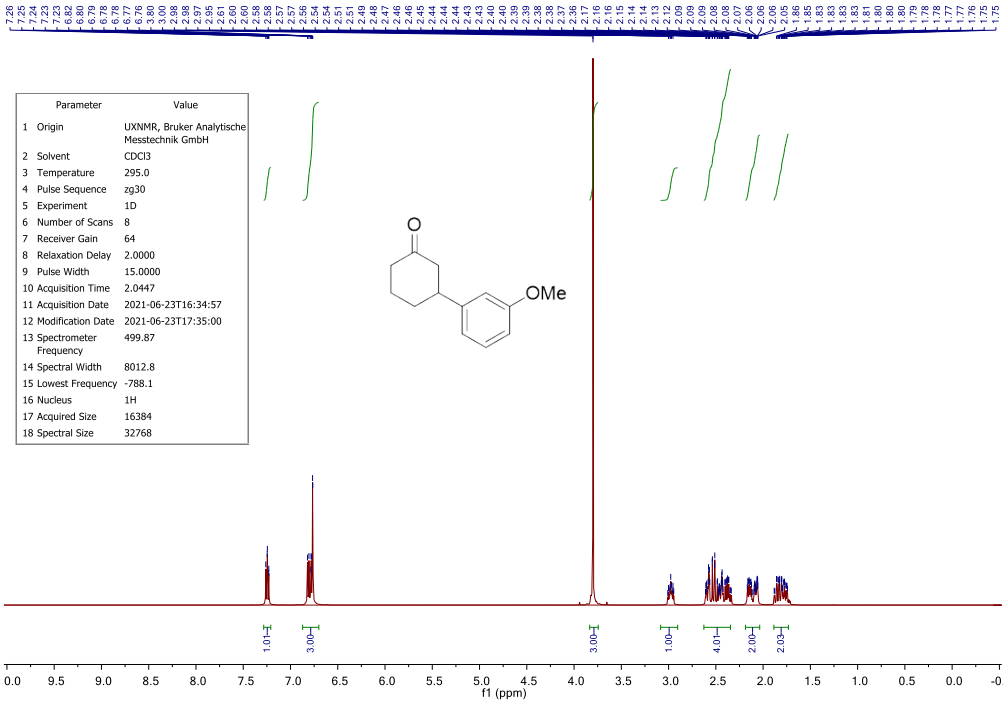
^{13}C NMR of **9S**



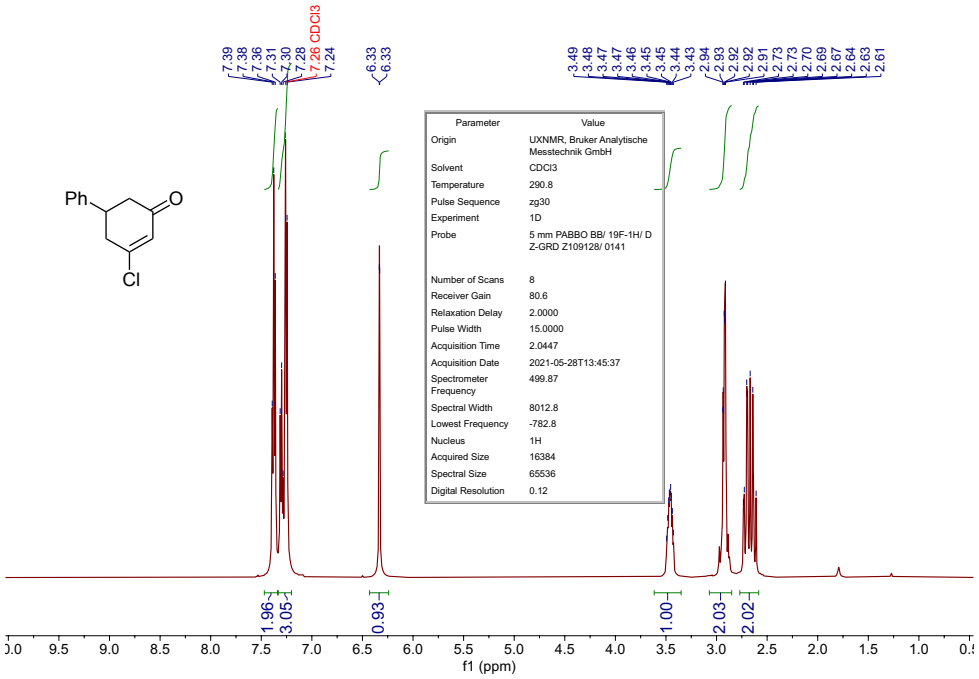
^{1}H NMR of **10S**



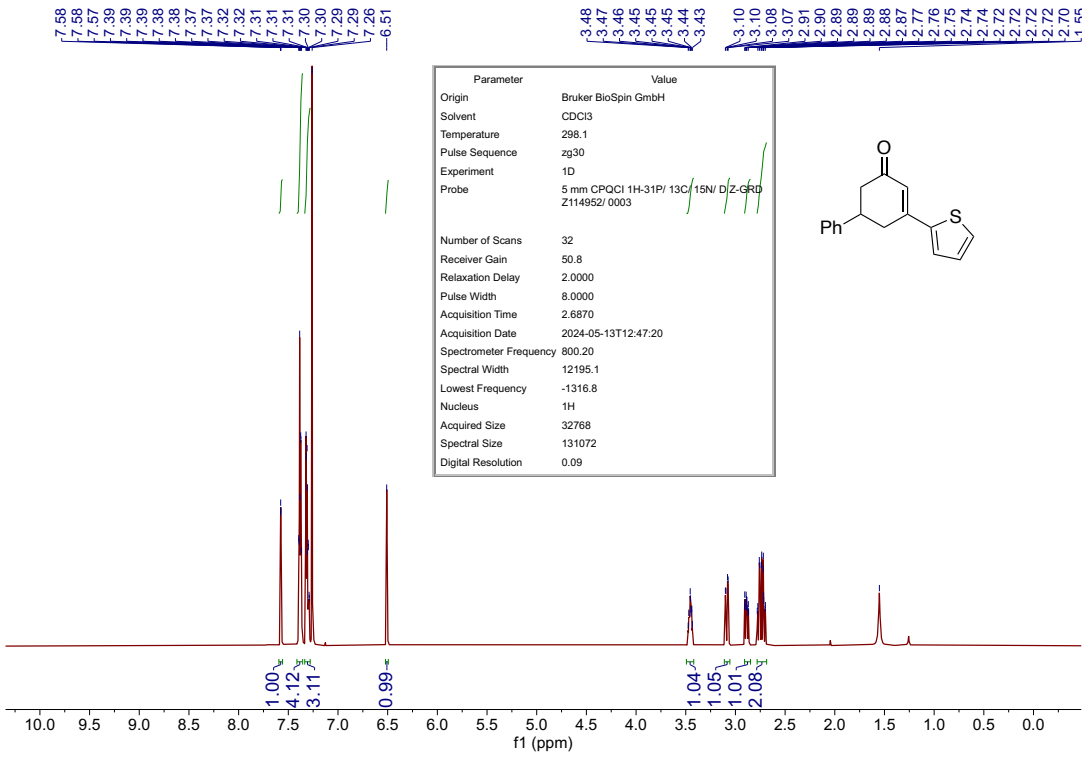
^{1}H NMR of **11S**



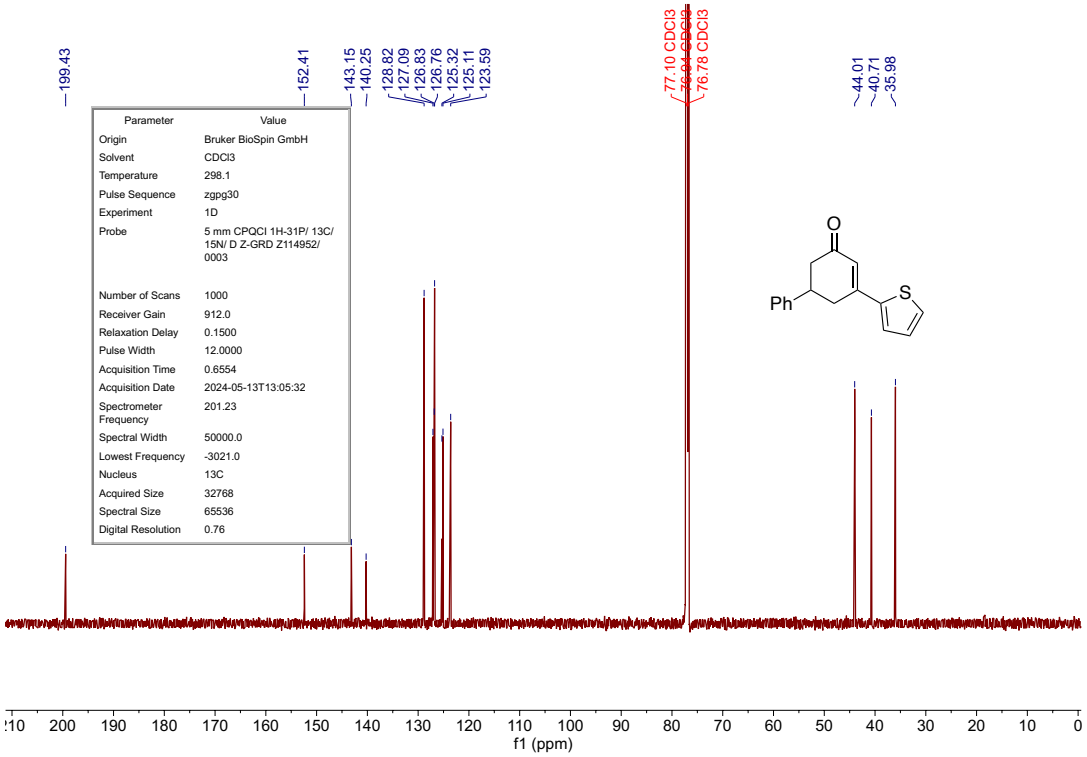
^{1}H NMR of **15S**



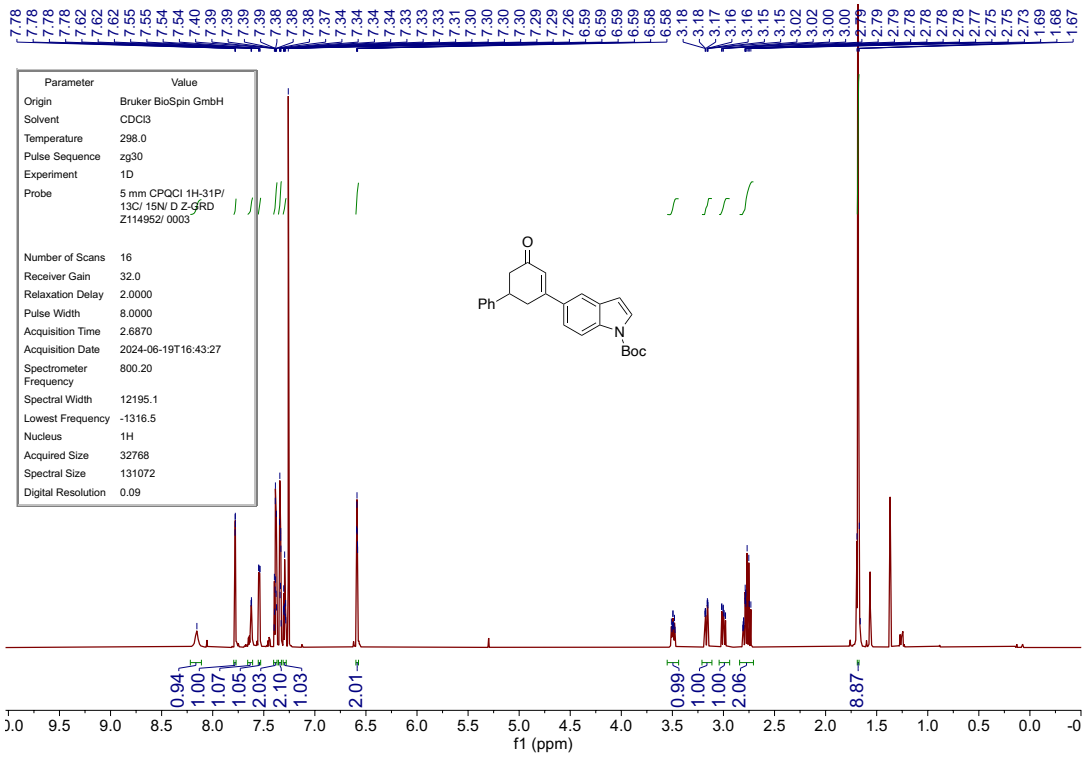
^{1}H NMR of **16S**



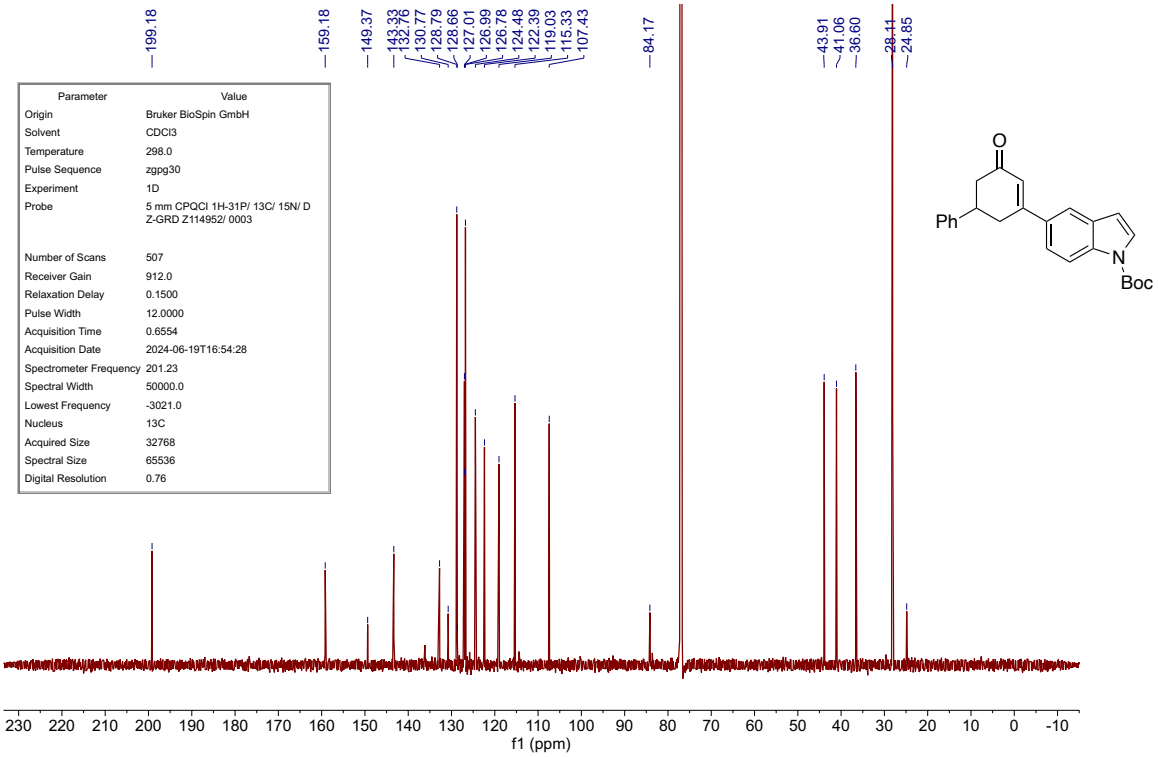
^{13}C NMR of **16S**



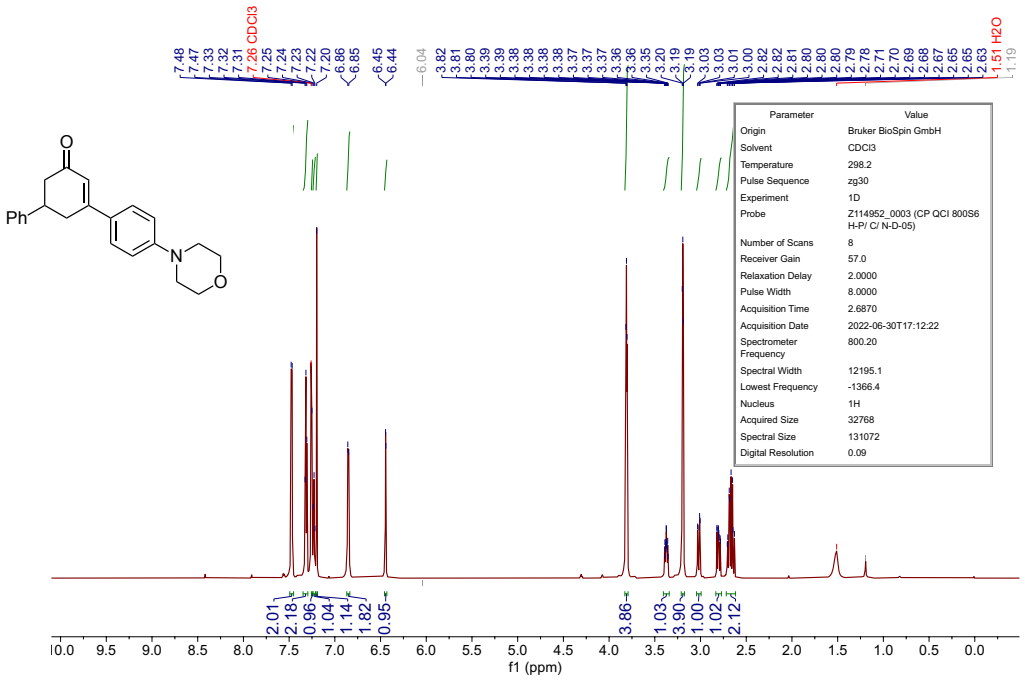
1H NMR of **17S**



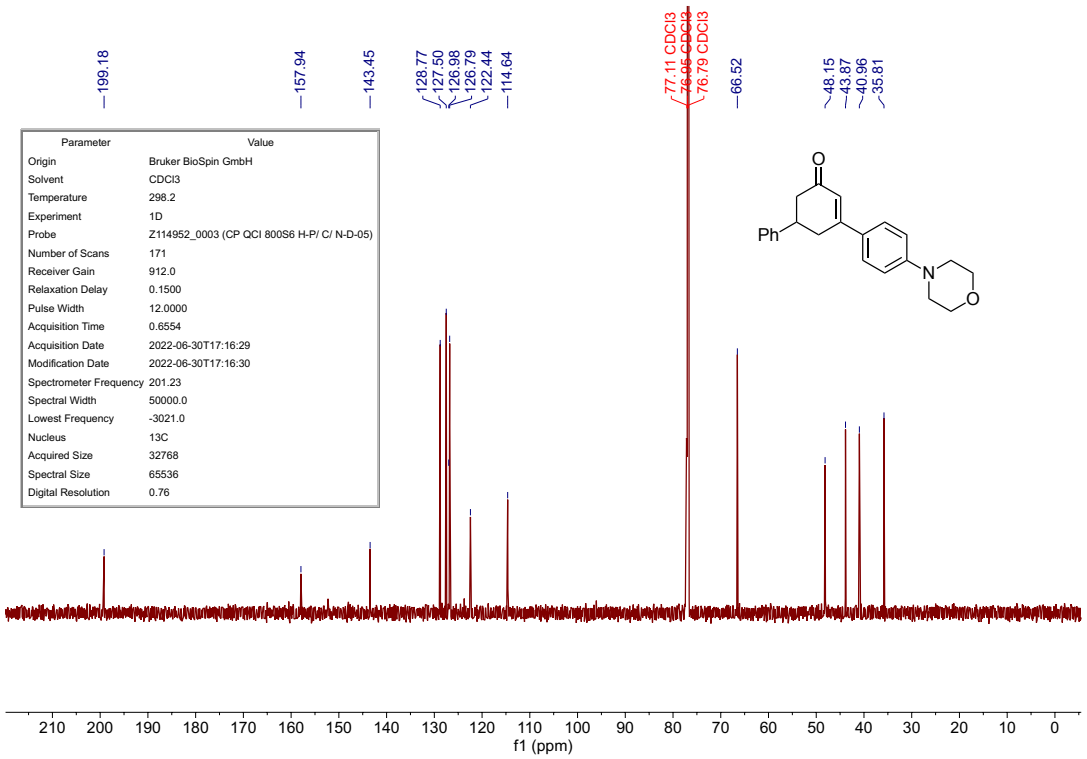
^{13}C NMR of **17S**



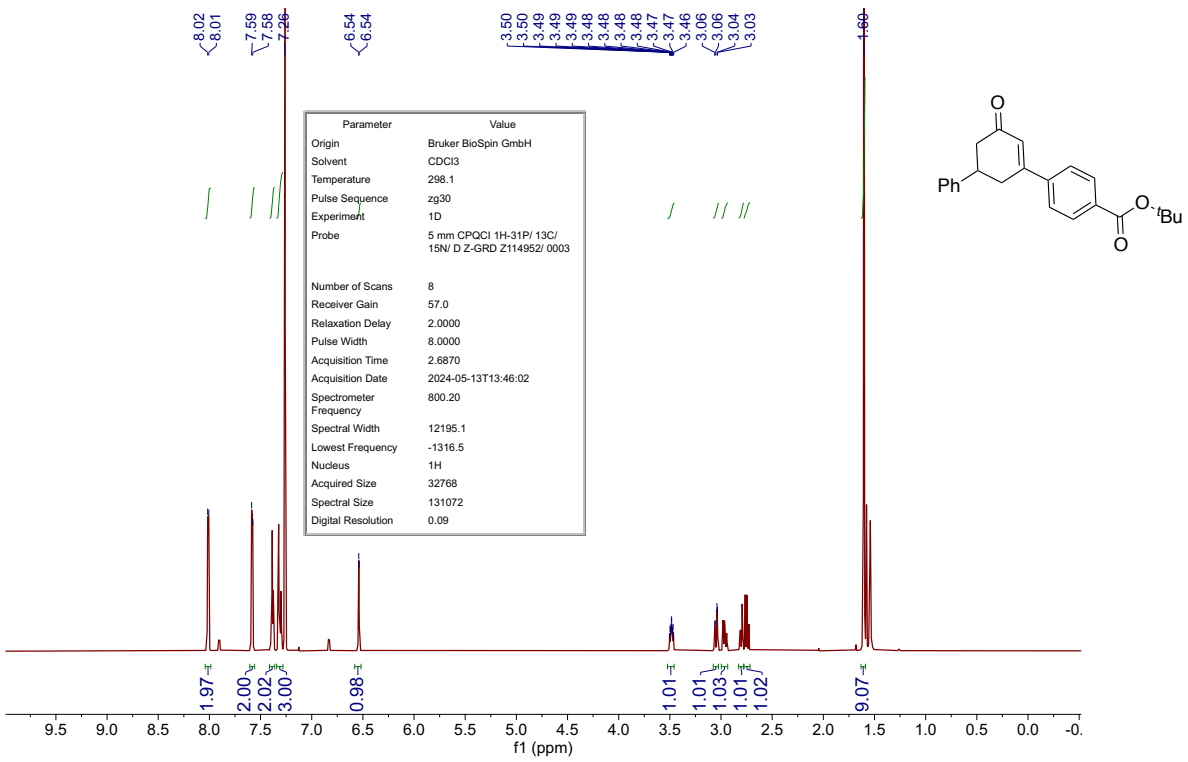
^{1}H NMR of **18S**



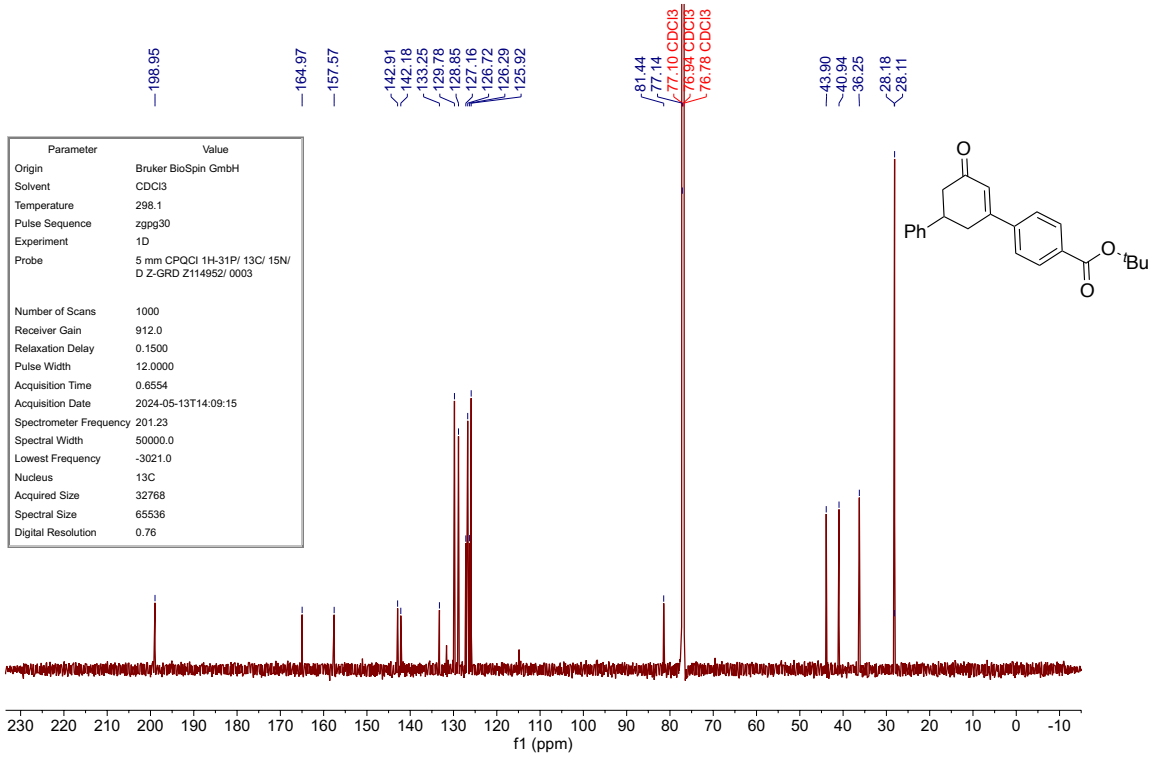
^{13}C NMR of **18S**



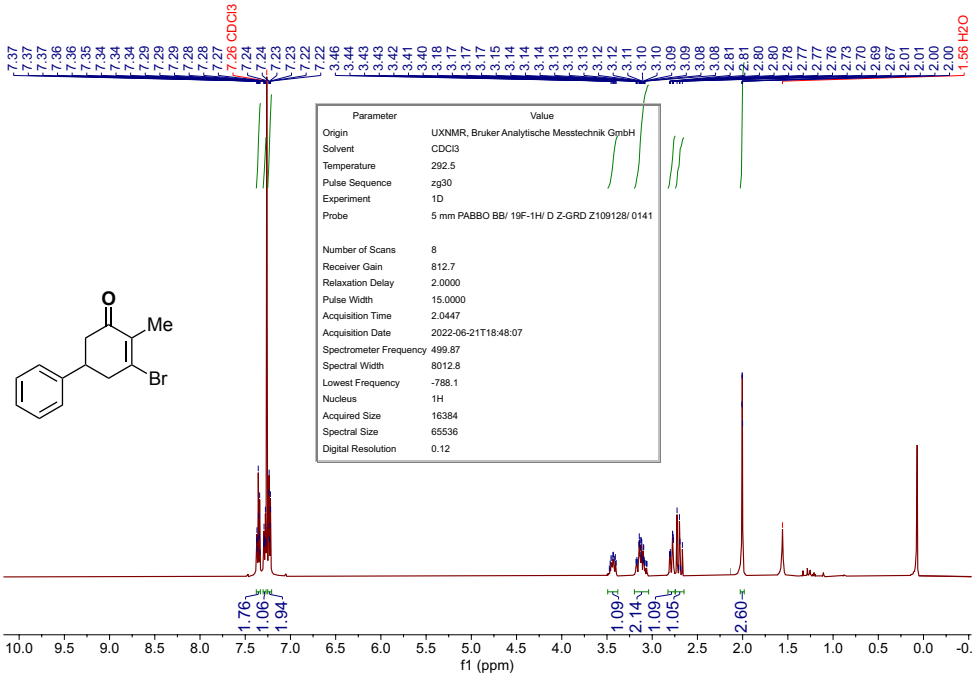
^{1}H NMR of **19S**



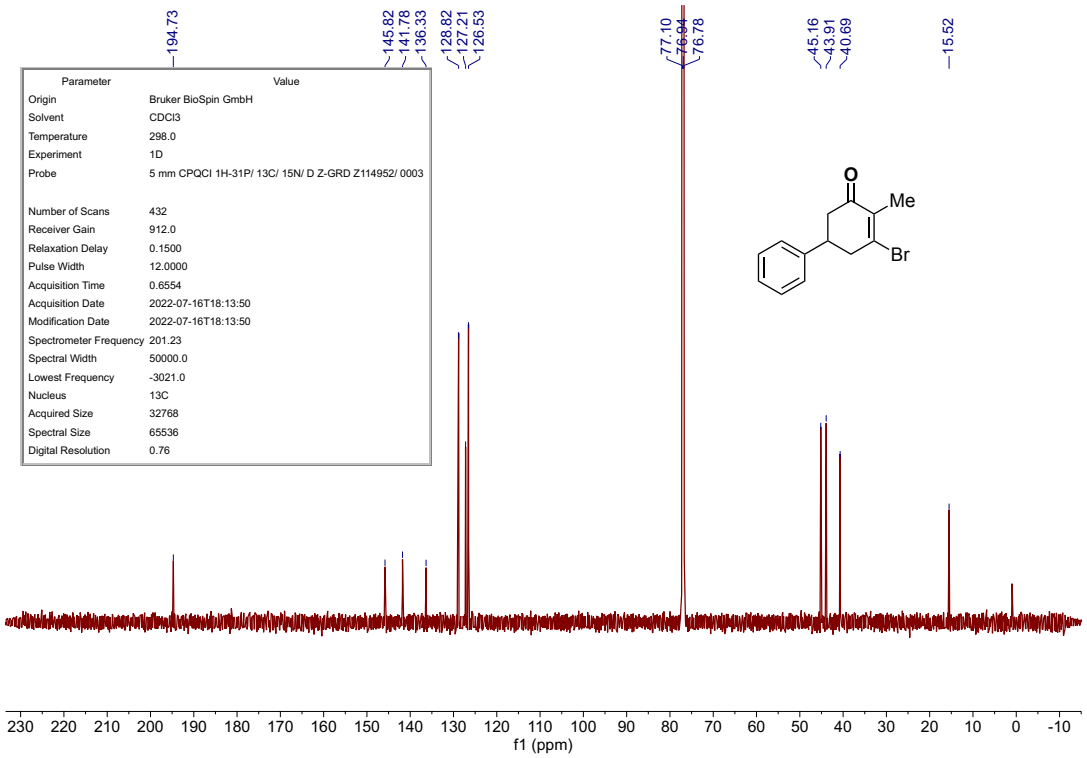
^{13}C NMR of **19S**



^{1}H NMR of **23S**

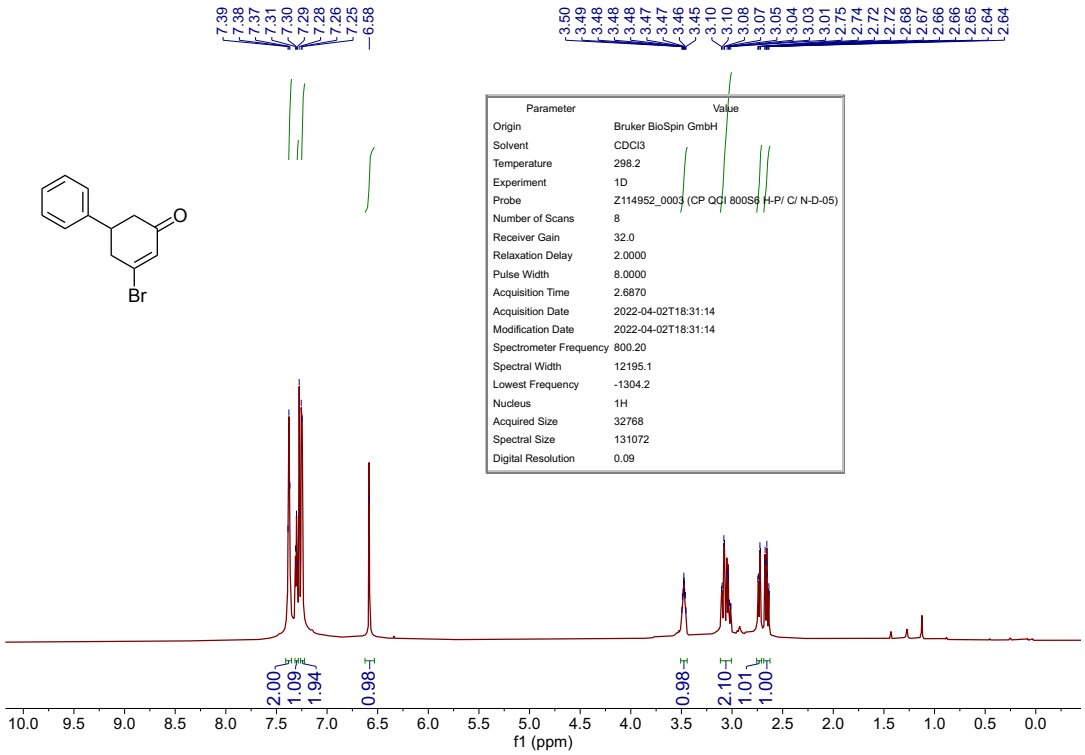


^{13}C NMR of **23S**



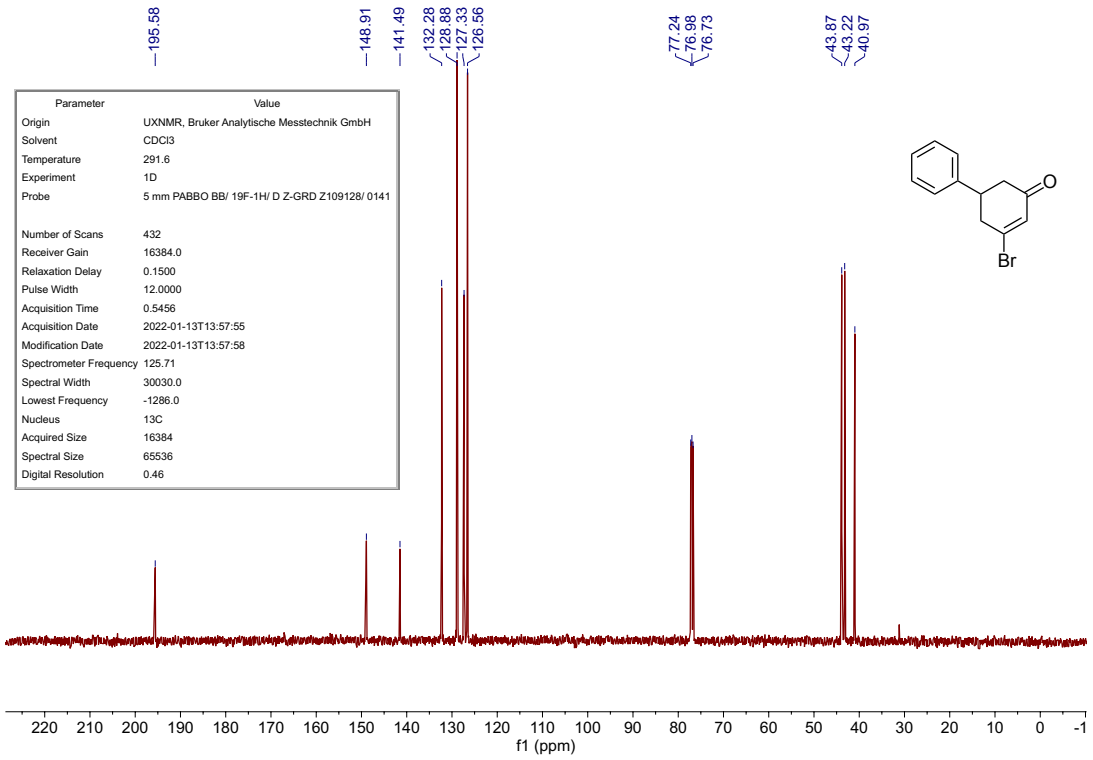
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	432
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2022-07-16T18:13:50
Modification Date	2022-07-16T18:13:50
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{1}H NMR of **24S**



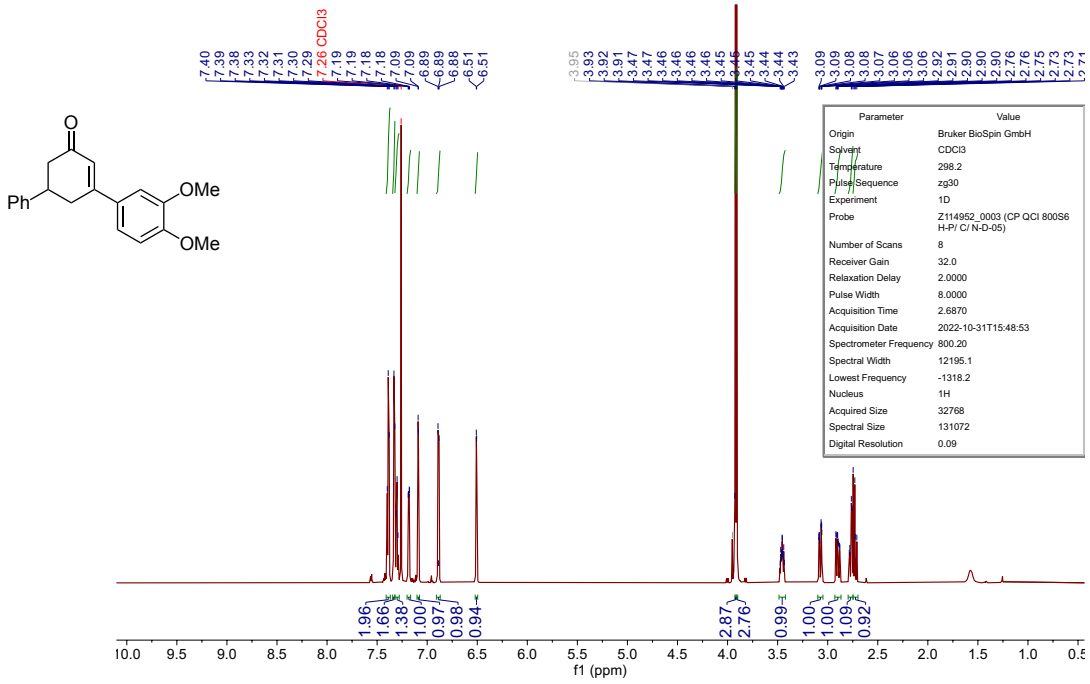
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 1H-P/ C/ N-D-05)
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2022-04-02T18:31:14
Modification Date	2022-04-02T18:31:14
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1304.2
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{13}C NMR of **24S**



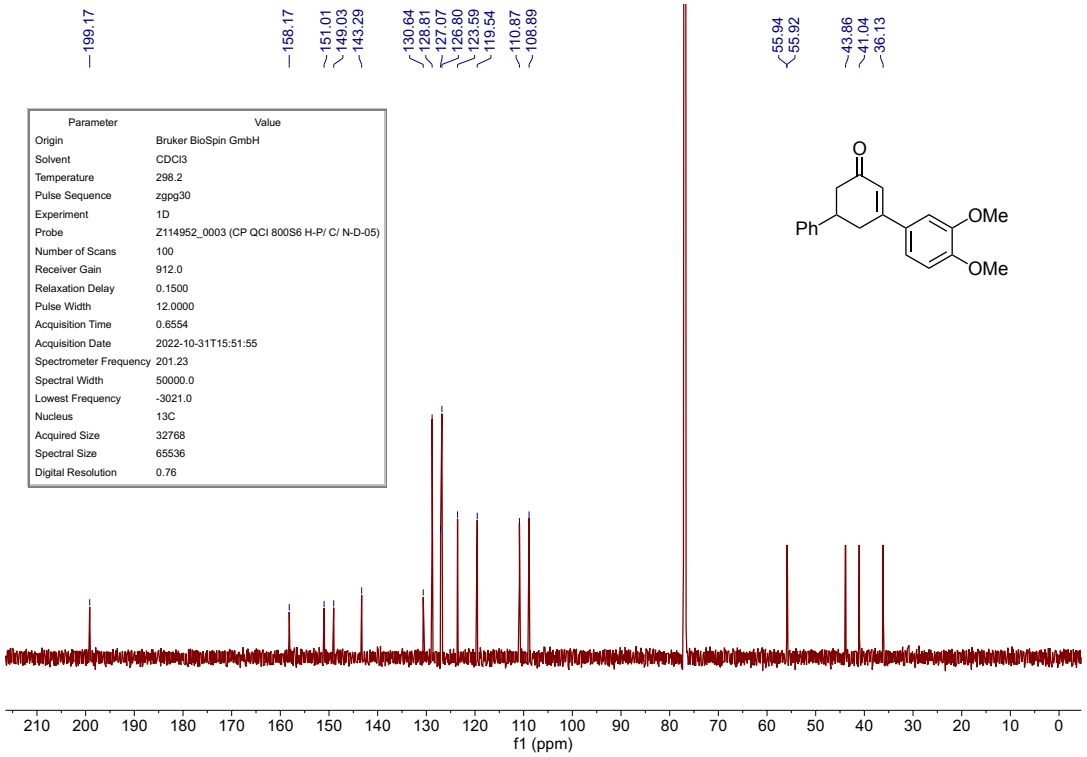
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	291.6
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	432
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.5456
Acquisition Date	2022-01-13T13:57:55
Modification Date	2022-01-13T13:57:58
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.46

^{1}H NMR of **25S**

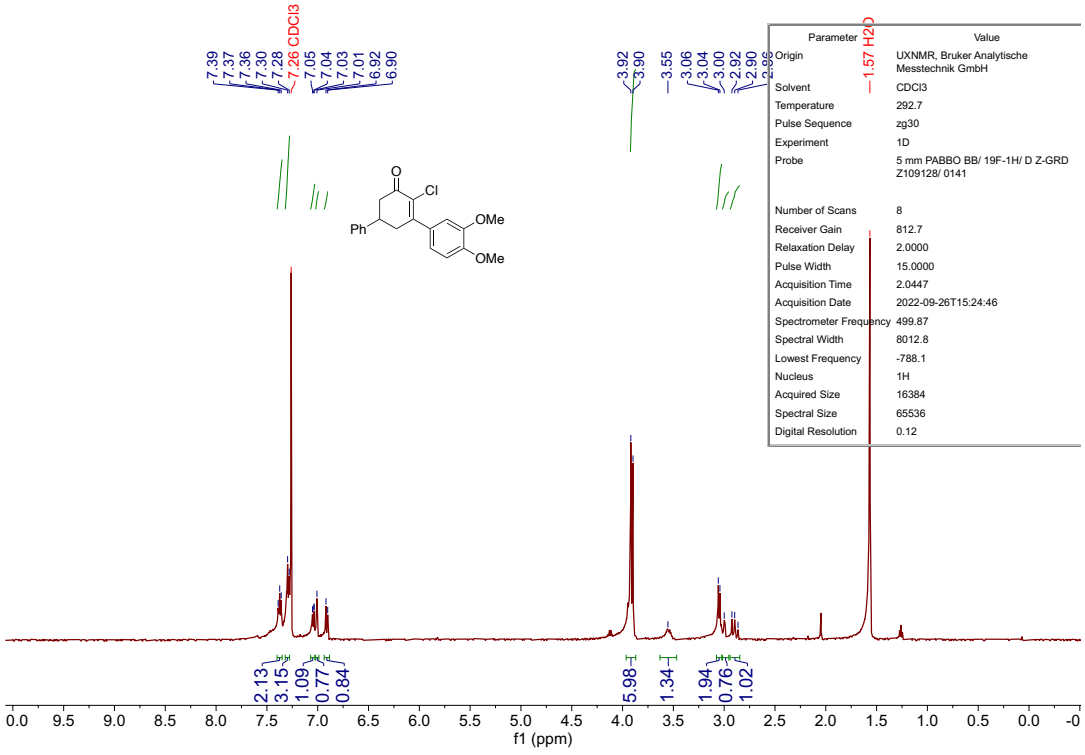


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2022-10-31T15:48:53
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1318.2
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

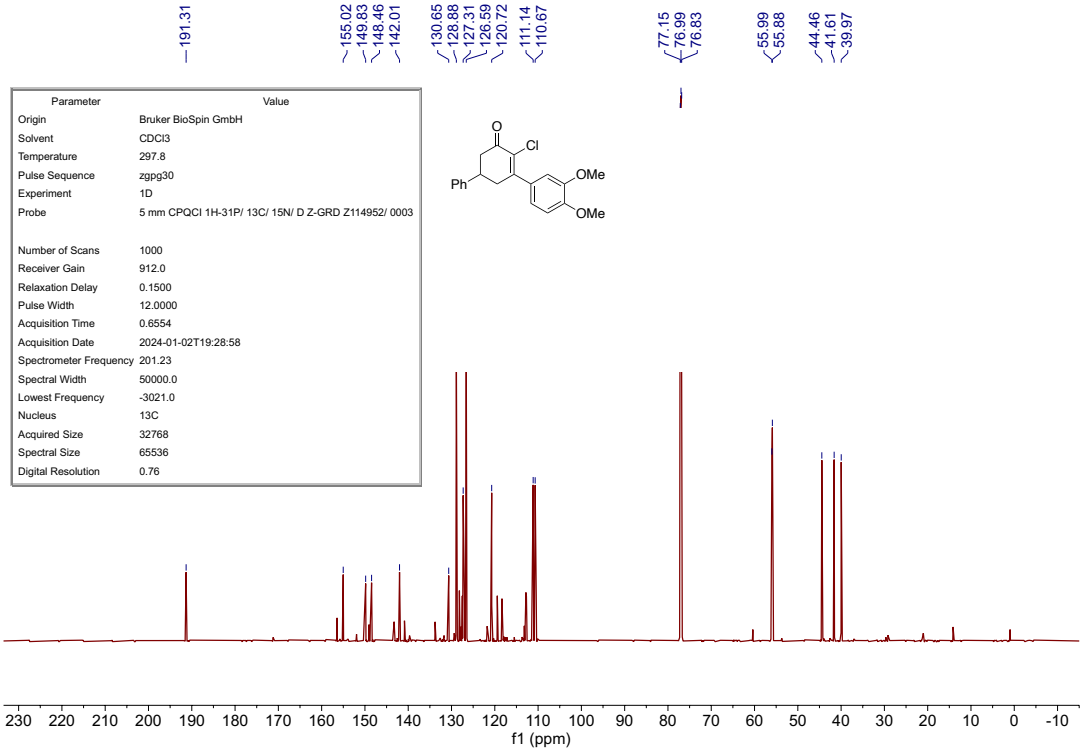
^{13}C NMR of **25S**



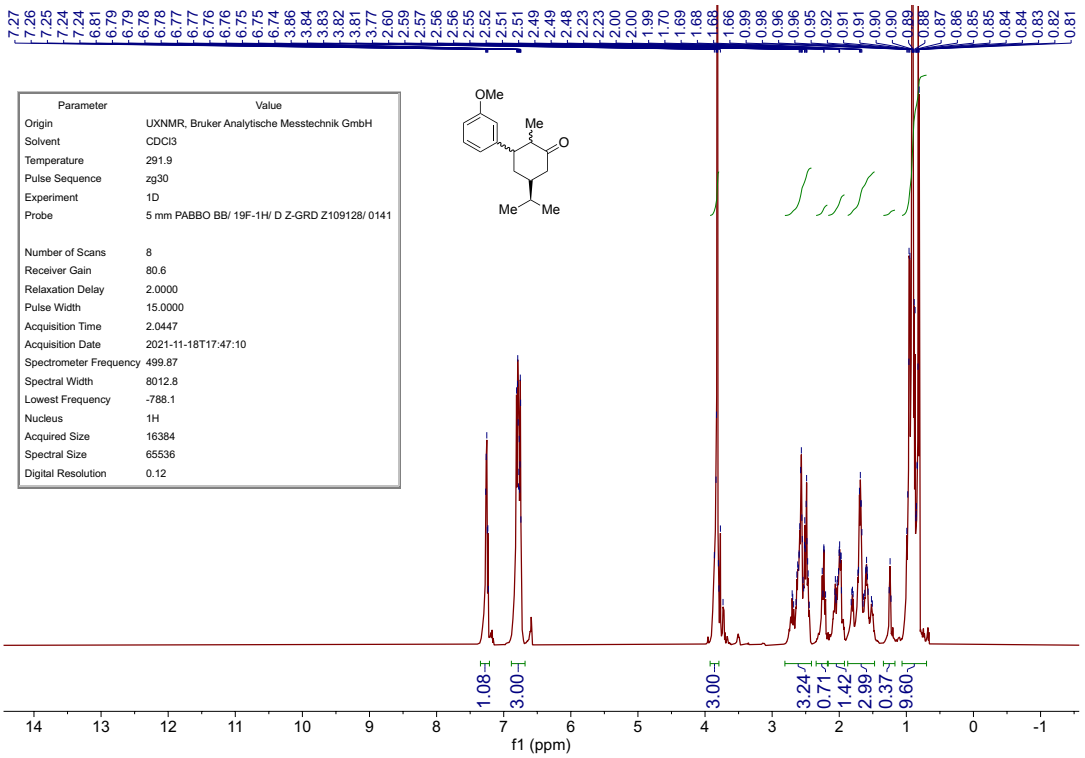
^{1}H NMR of **26S**



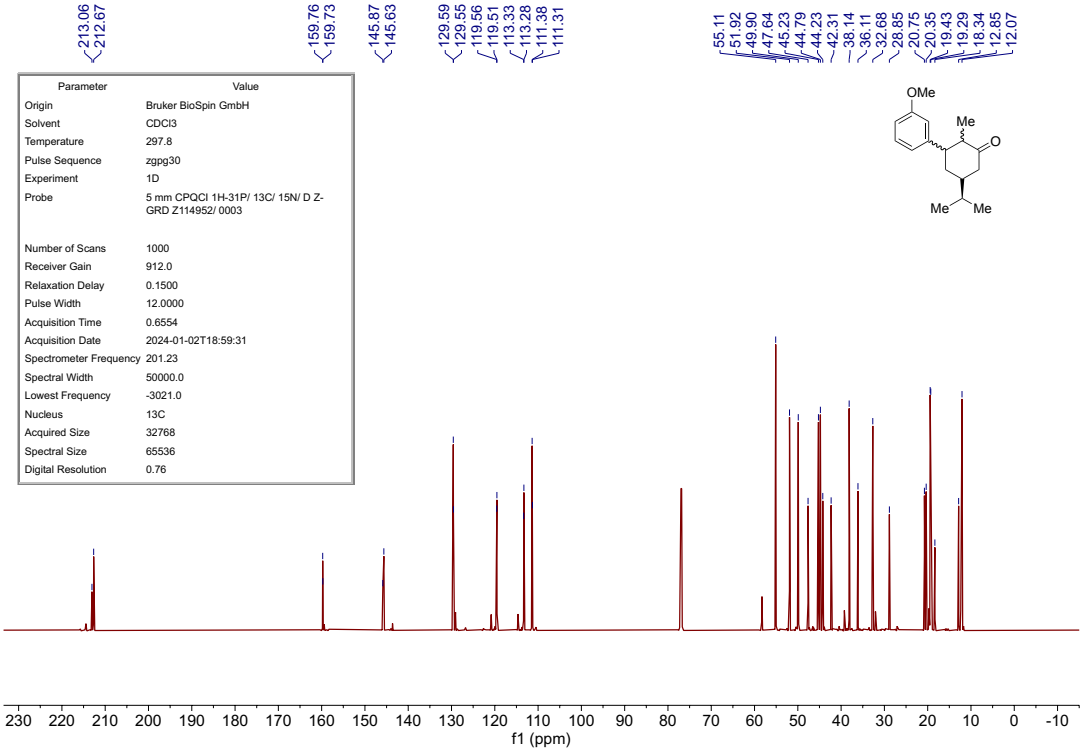
^{13}C NMR of **26S**



^{1}H NMR of **27S**

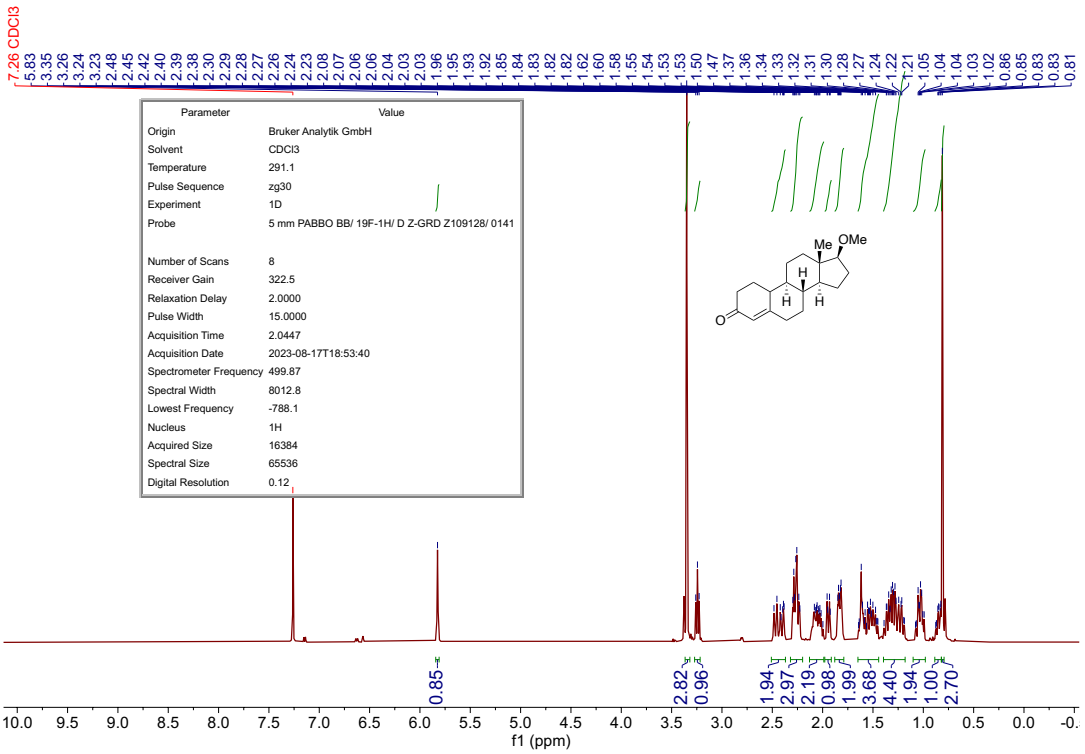


^{13}C NMR of **27S**



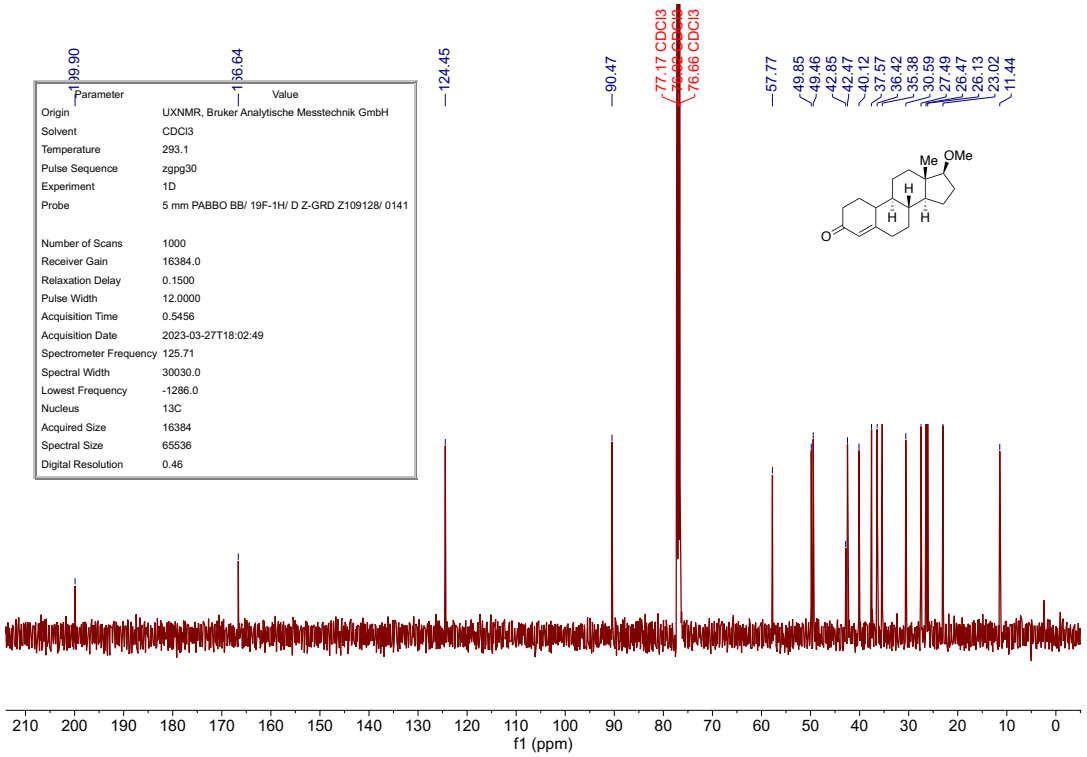
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	1000
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2024-01-02T18:59:31
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{1}H NMR of **28S**

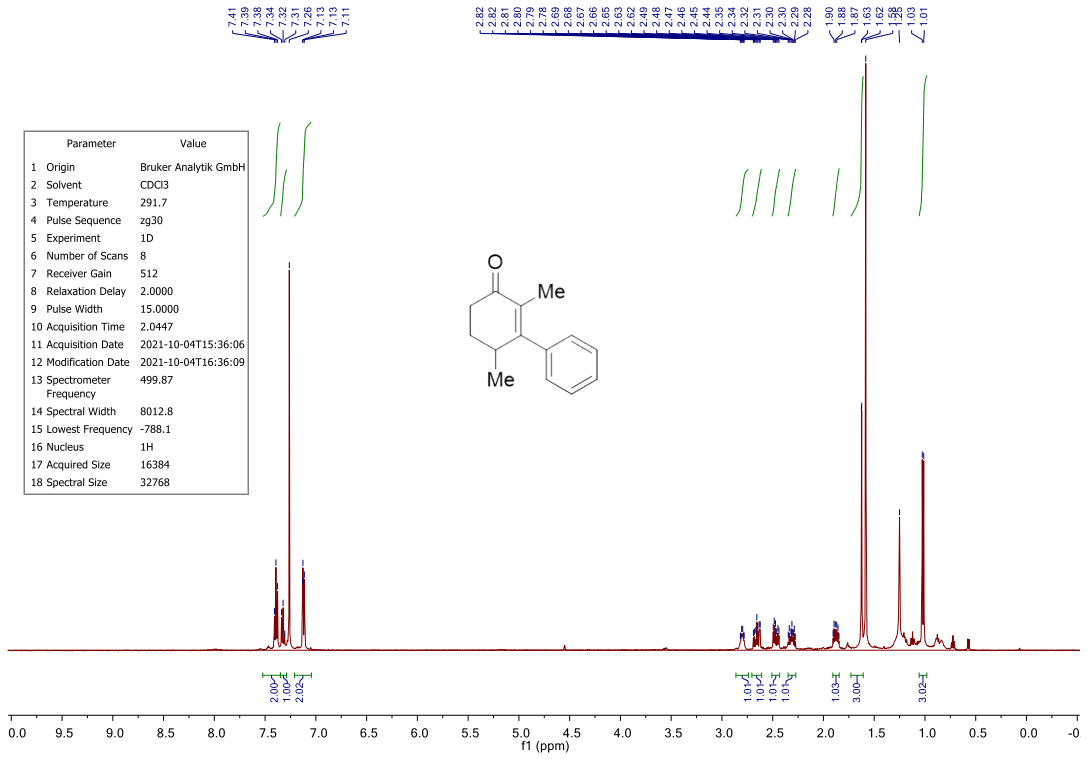


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	322.5
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	2.0447
Acquisition Date	2023-08-17T18:53:40
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

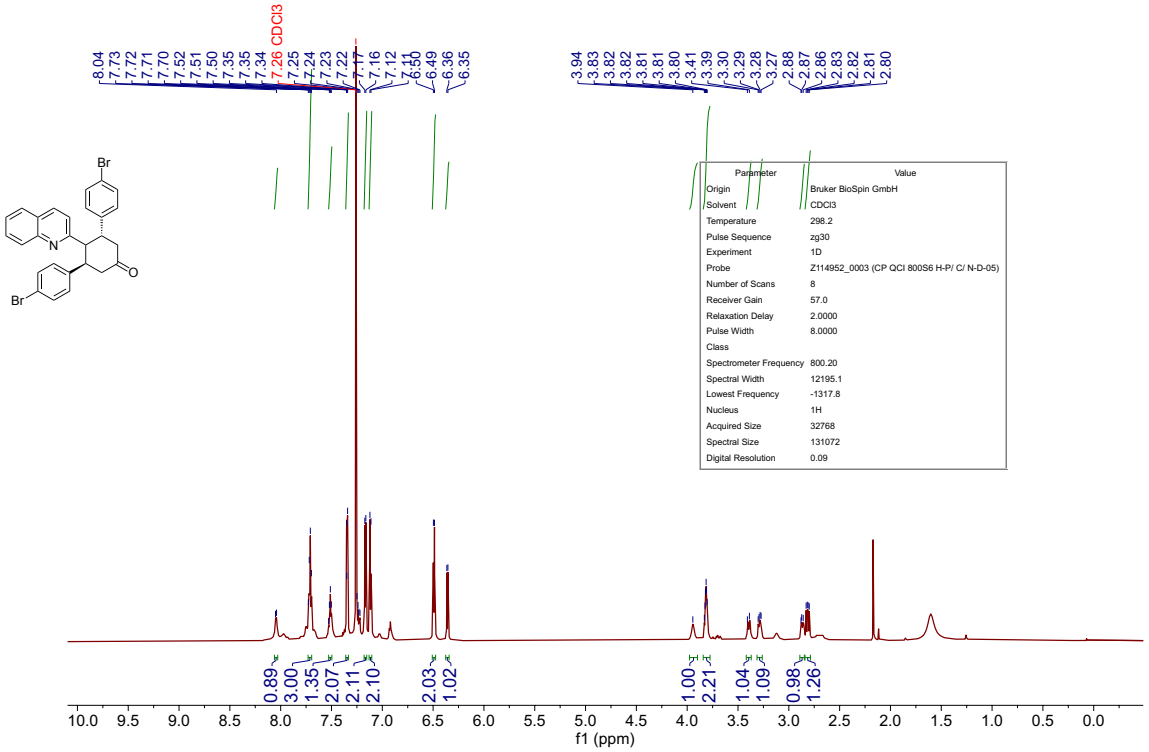
^{13}C NMR of **28S**



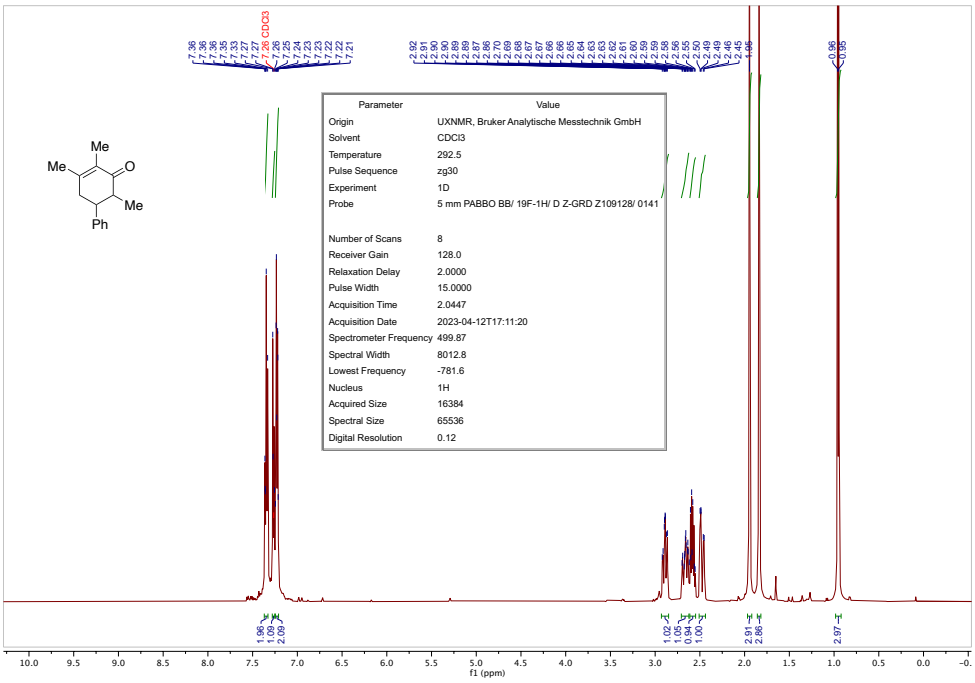
^{1}H NMR of **29S**



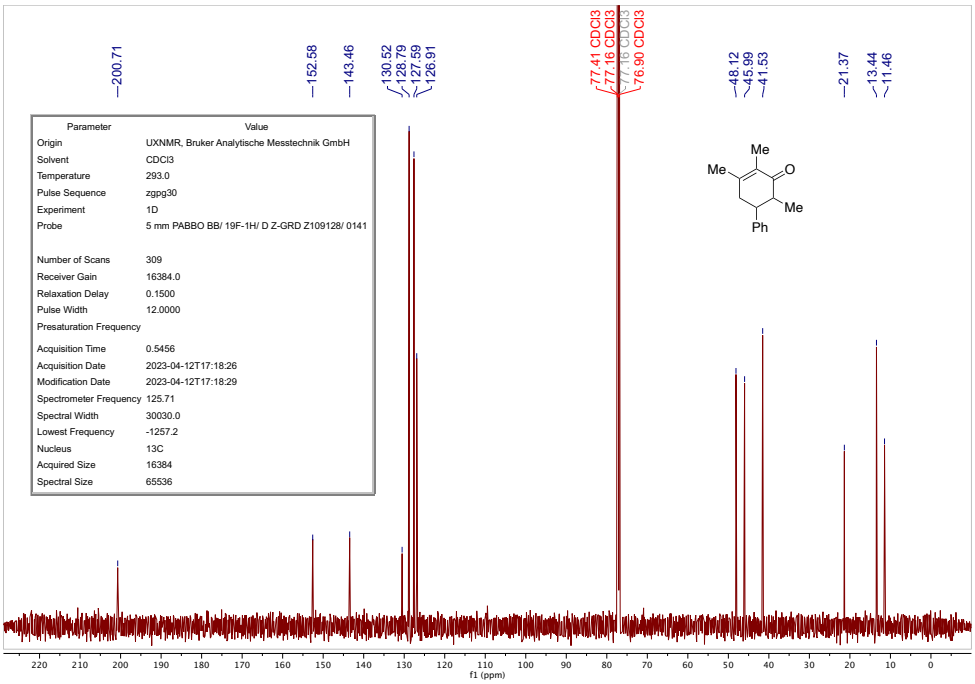
^{1}H NMR of **30S**



^{1}H NMR of **32S**

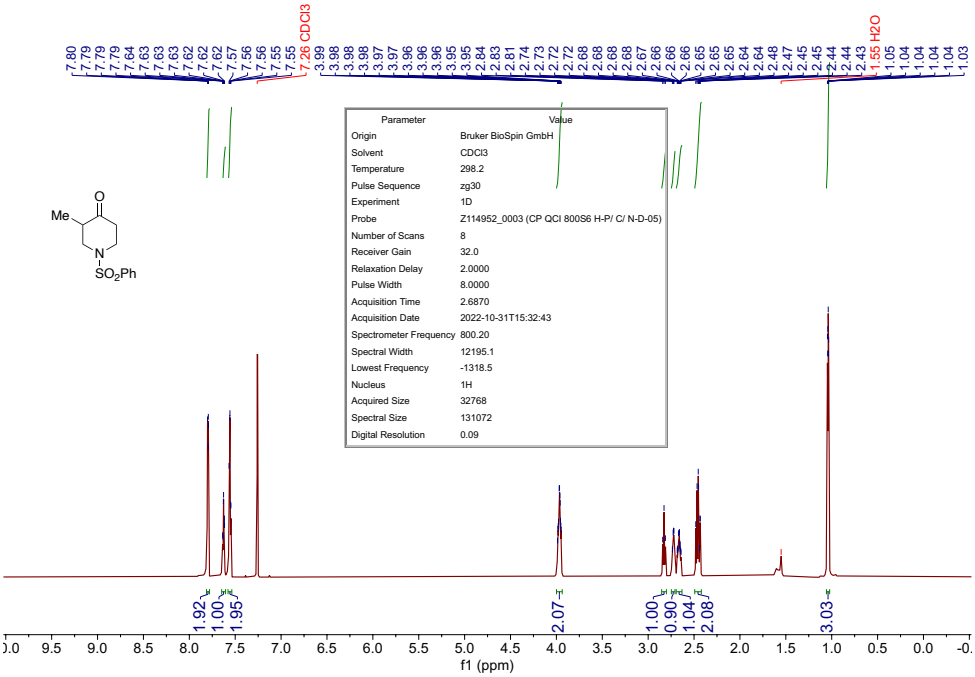


^{13}C NMR of **32S**



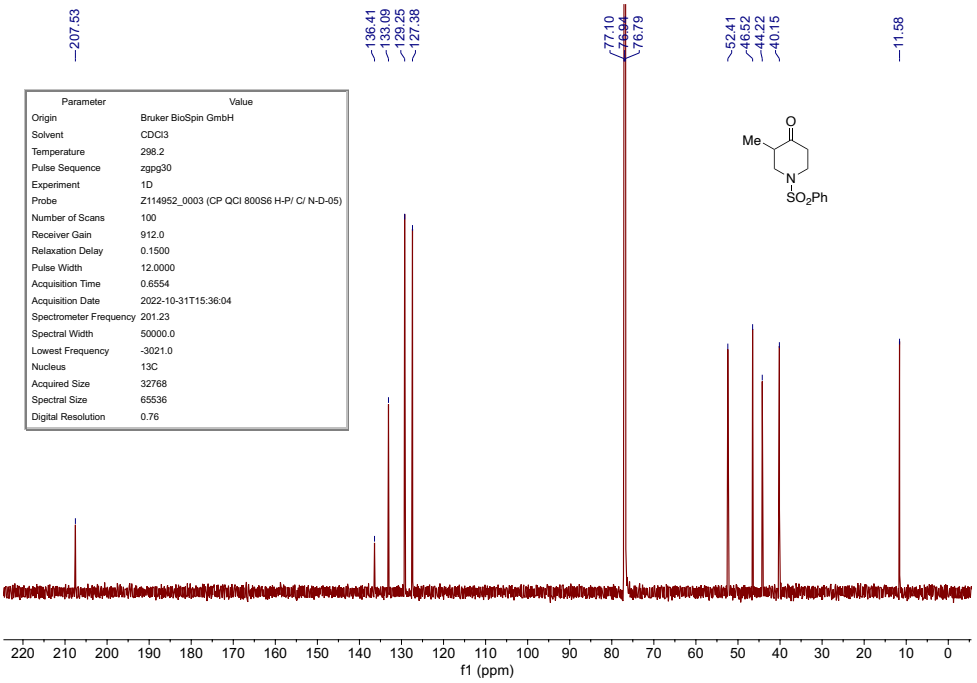
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	309
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-04-12T17:18:26
Modification Date	2023-04-12T17:18:29
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1257.2
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

^{1}H NMR of **35S**



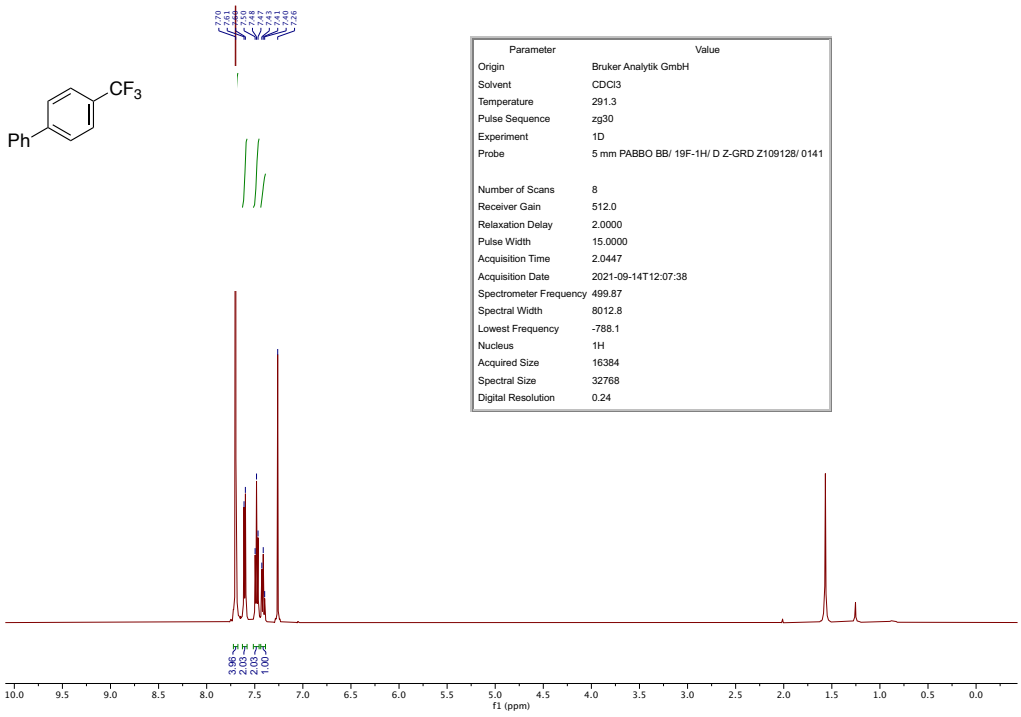
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2022-10-31T15:32:43
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1318.5
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{13}C NMR of **35S**



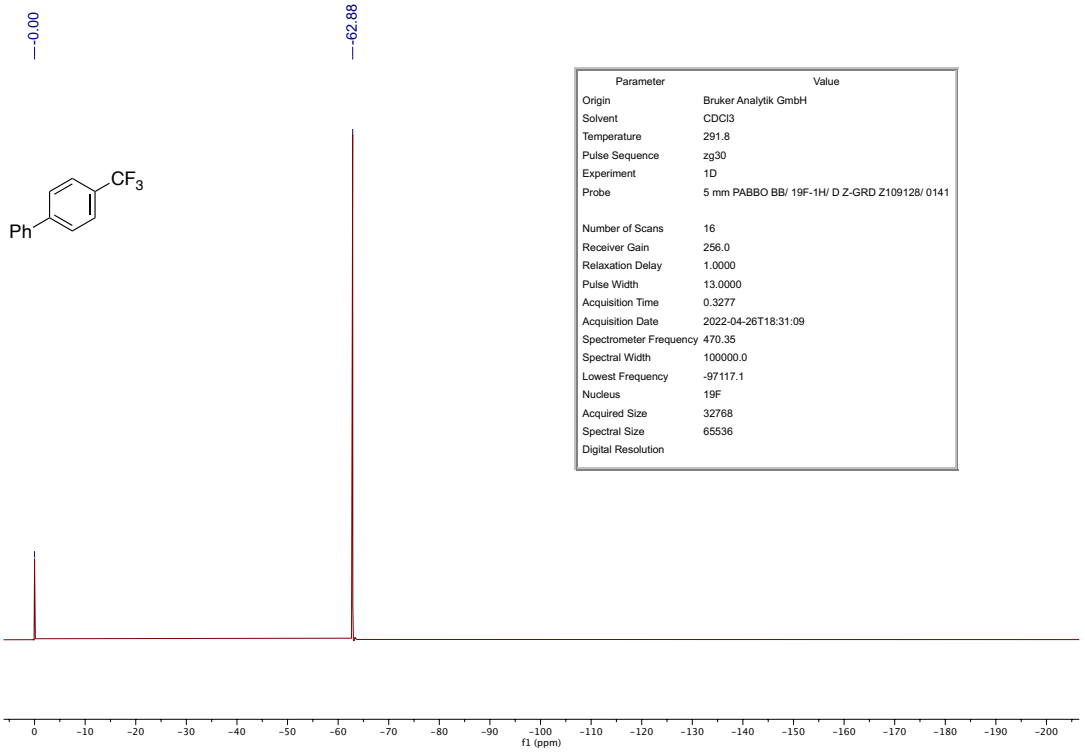
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	100
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2022-10-31T15:36:04
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{1}H NMR of **1P**



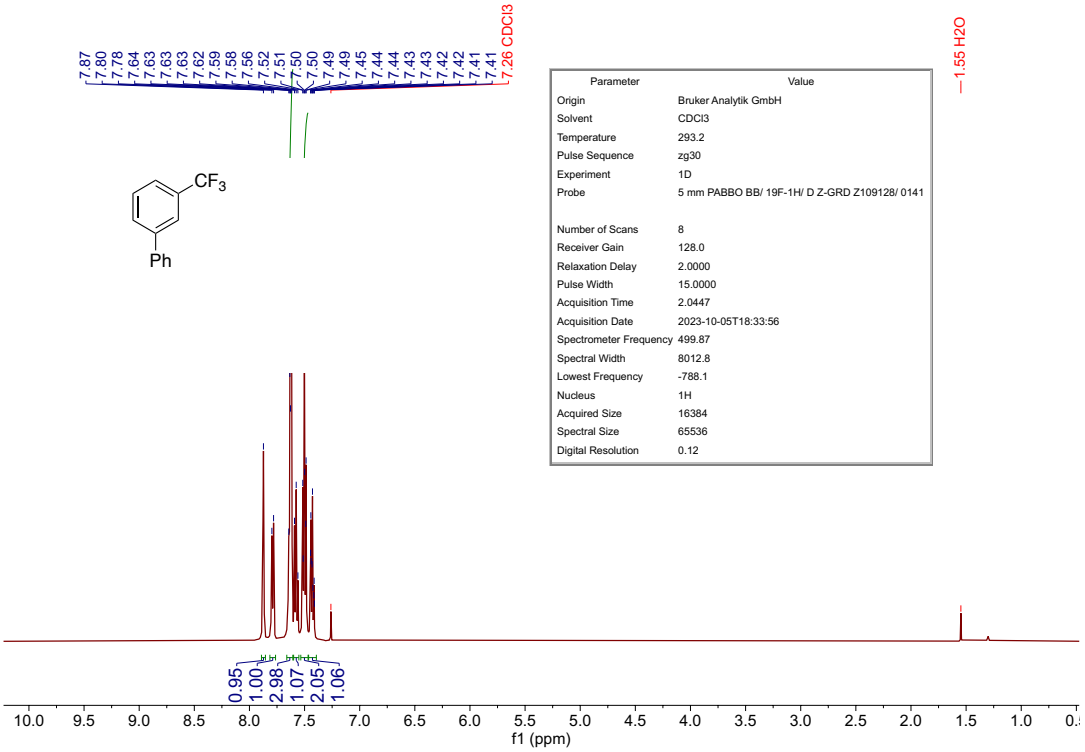
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	512.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	2.0447
Acquisition Date	2021-09-14T12:07:38
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	32768
Digital Resolution	0.24

^{19}F NMR of **1P**



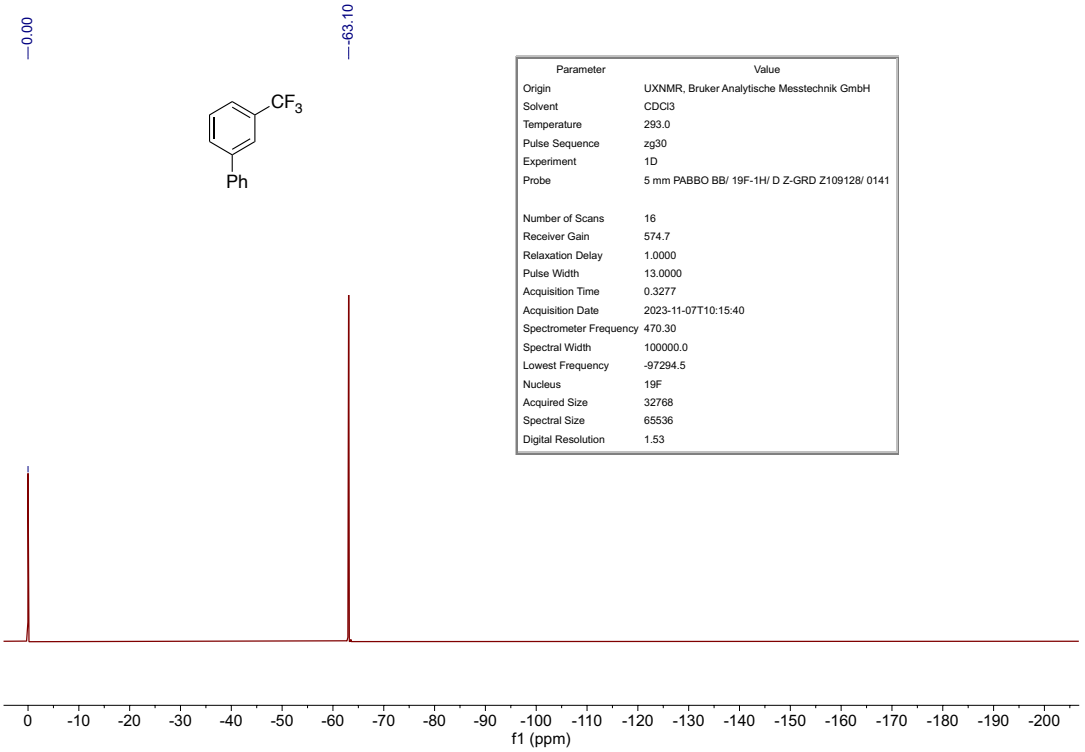
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2022-04-26T18:31:09
Spectrometer Frequency	470.35
Spectral Width	100000.0
Lowest Frequency	-97117.1
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	

^{1}H NMR of **2P**



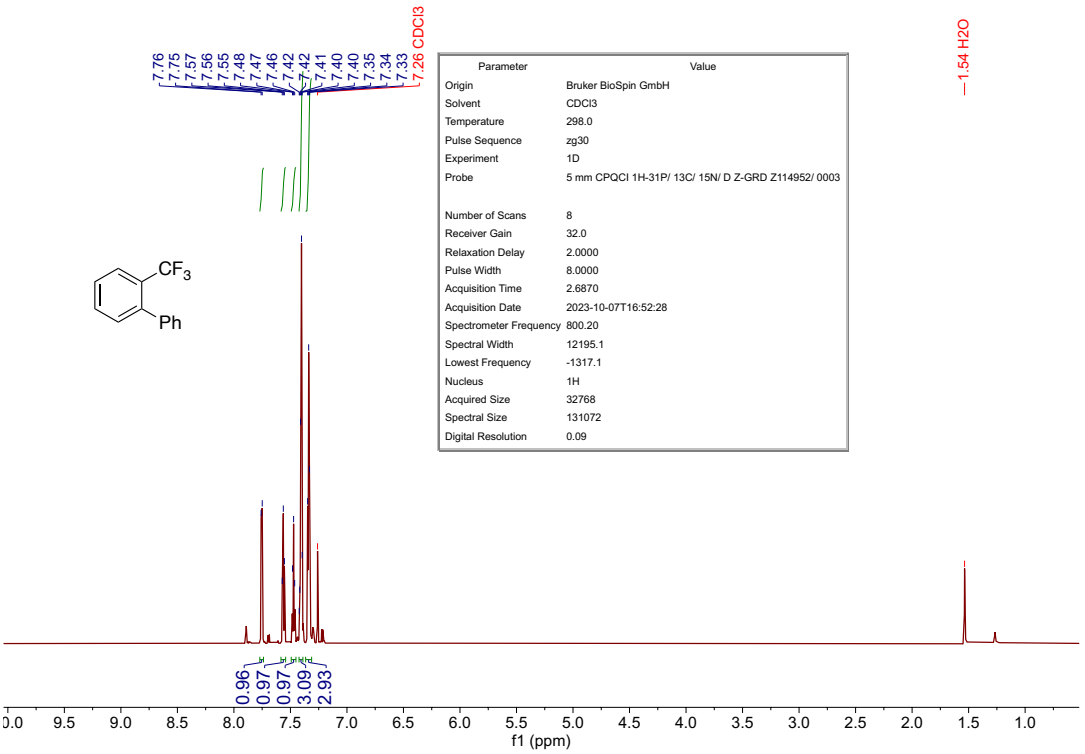
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	2.0447
Acquisition Date	2023-10-05T18:33:56
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

^{19}F NMR of **2P**



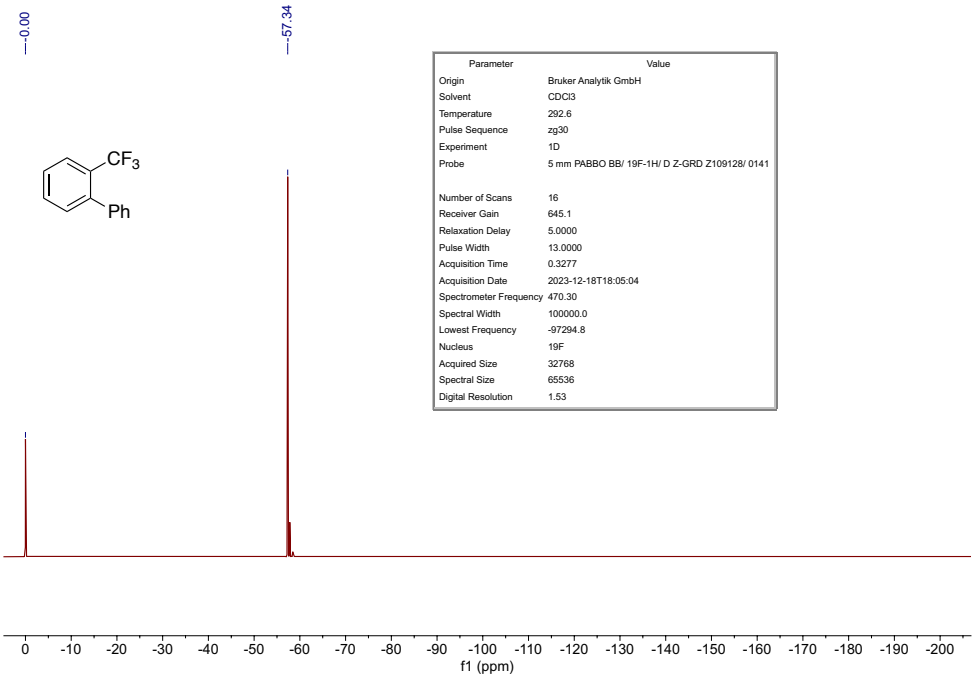
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-11-07T10:15:40
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97294.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **3P**



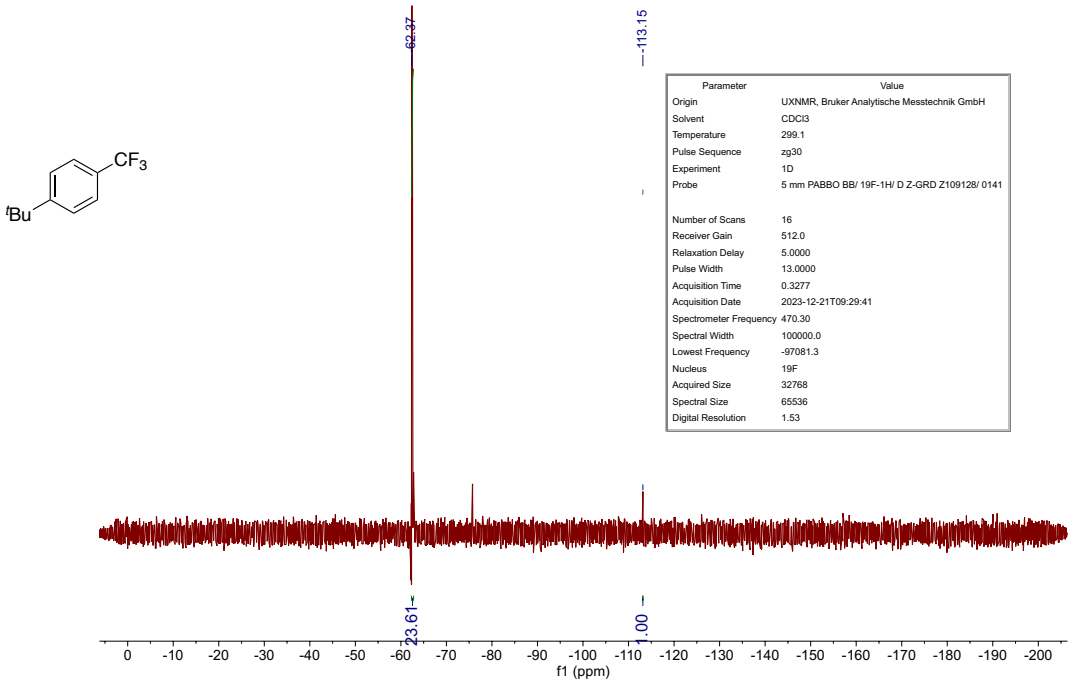
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2023-10-07T16:52:28
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1317.1
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{19}F NMR of **3P**



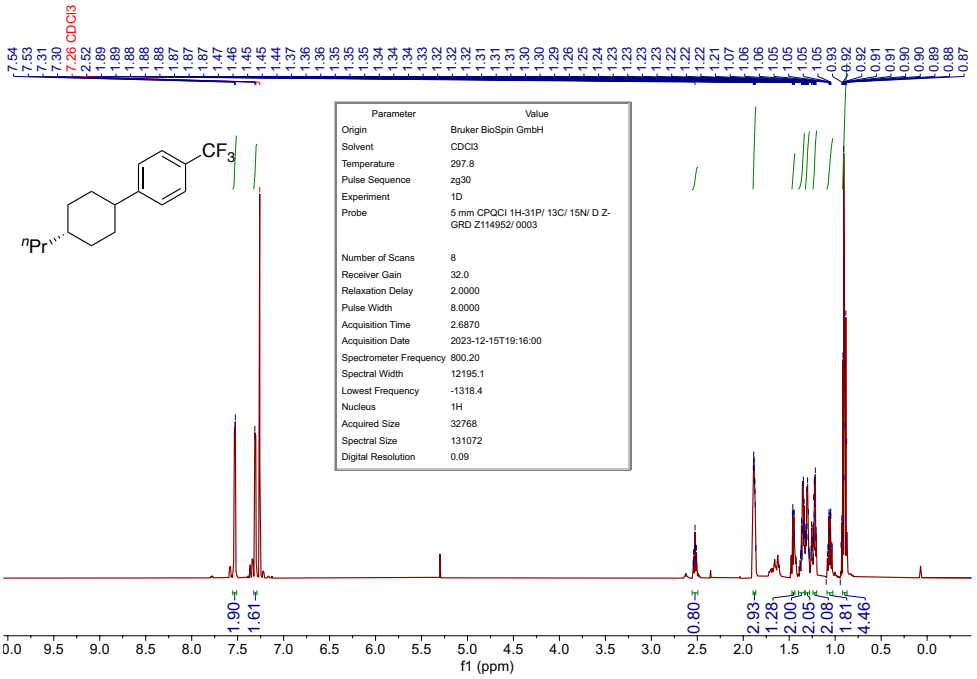
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-12-18T18:05:04
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97294.8
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{19}F NMR of **4P**

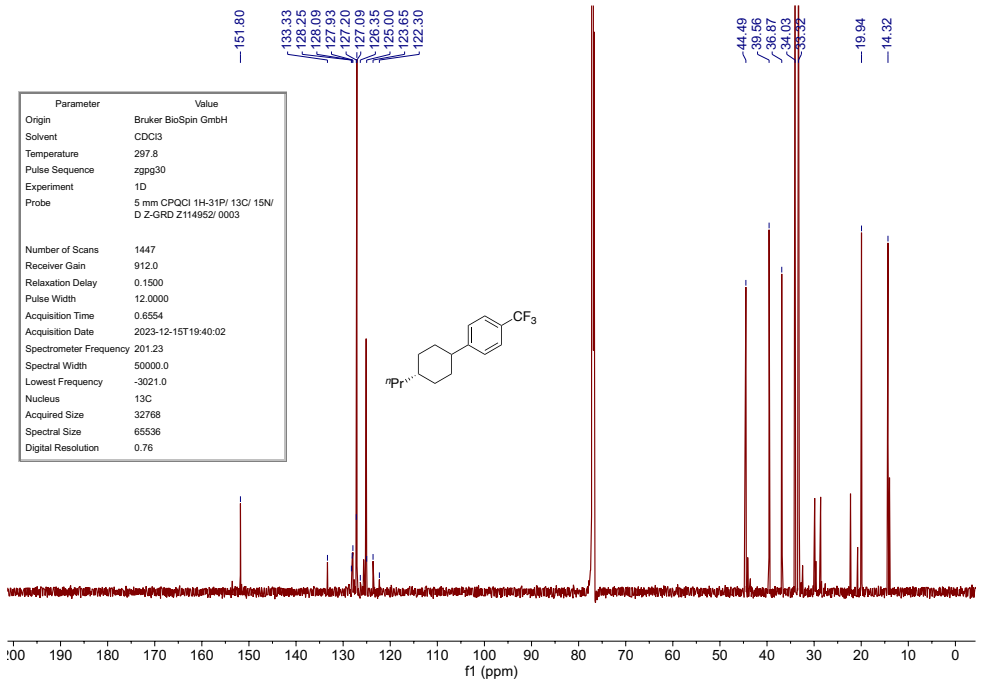


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	299.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-12-21T09:29:41
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97081.3
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

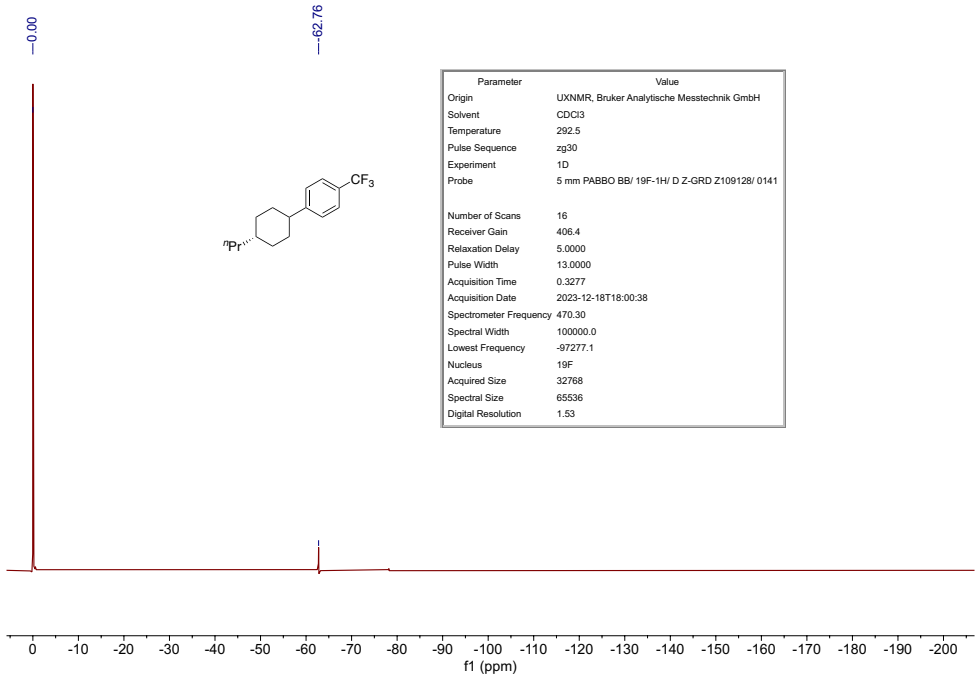
^{1}H NMR of **5P**



^{13}C NMR of **5P**

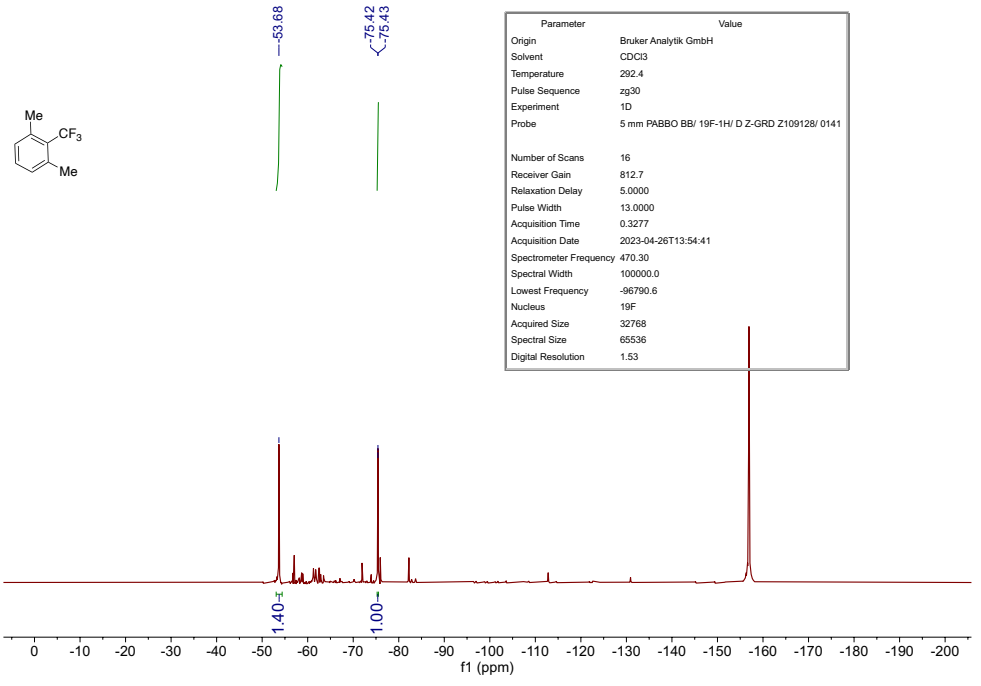


^{19}F NMR of **5P**



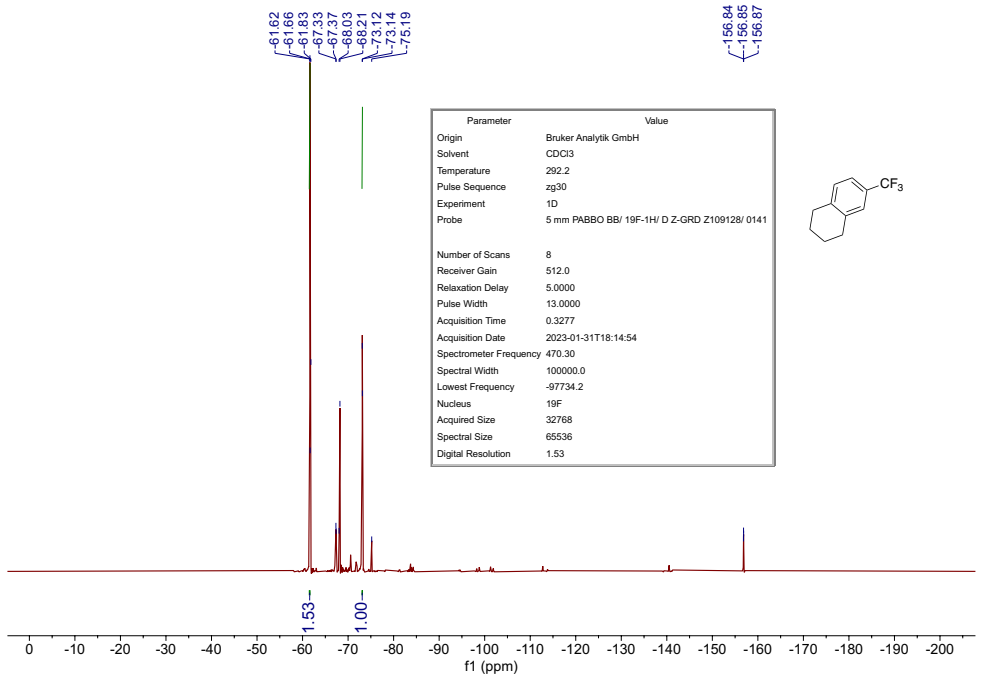
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	406.4
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-12-18T18:00:38
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97277.1
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{19}F NMR of **6P**

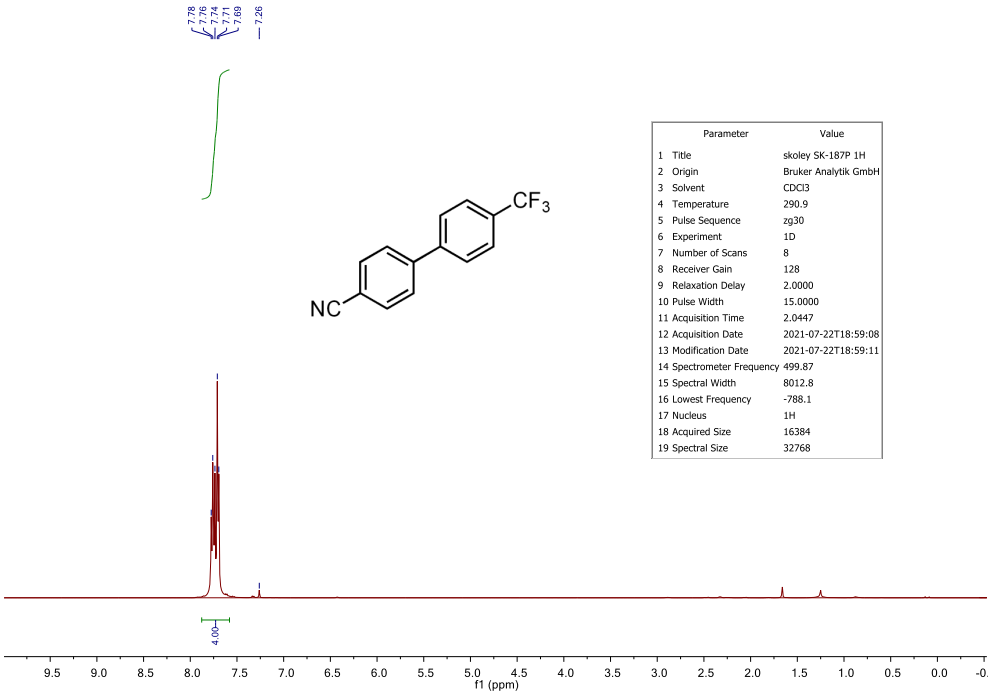


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	812.7
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-04-26T13:54:41
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-96790.6
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

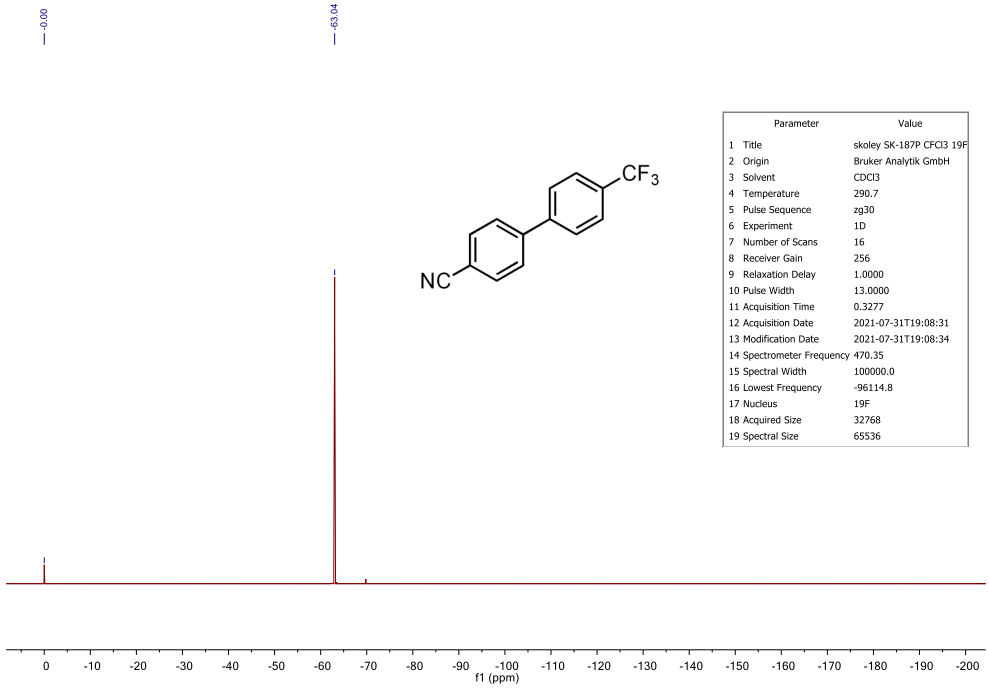
^{19}F NMR of **7P**



^{1}H NMR of **8P**

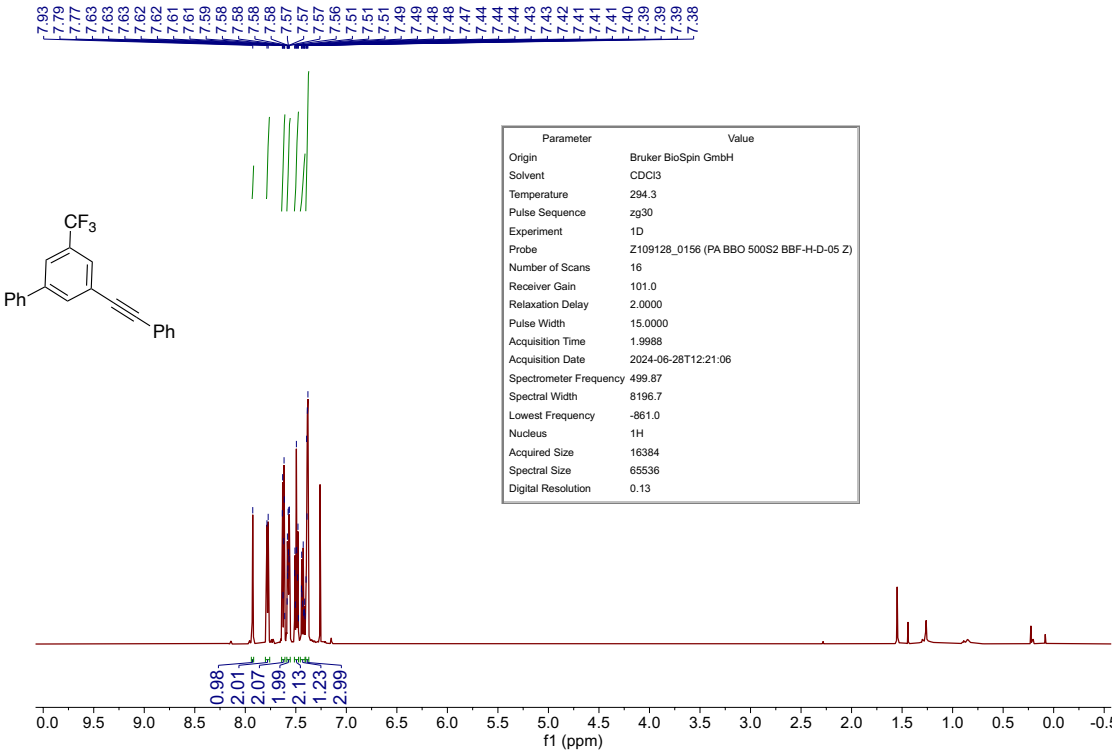


^{19}F NMR of **8P**



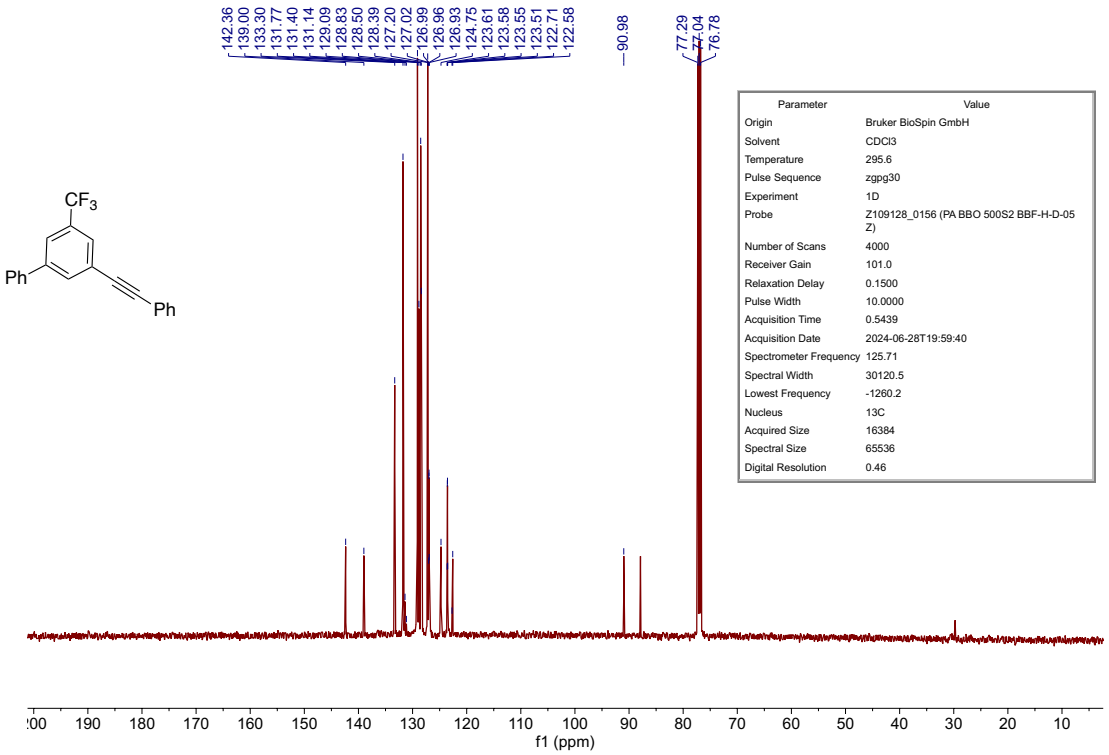
	Parameter	Value
1	Title	skoley SK-187P CFCl3 19F
2	Origin	Bruker Analytik GmbH
3	Solvent	CDCl3
4	Temperature	290.7
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	256
9	Relaxation Delay	1.0000
10	Pulse Width	13.0000
11	Acquisition Time	0.3277
12	Acquisition Date	2021-07-31T19:08:31
13	Modification Date	2021-07-31T19:08:34
14	Spectrometer Frequency	470.35
15	Spectral Width	100000.0
16	Lowest Frequency	-96114.8
17	Nucleus	19F
18	Acquired Size	32768
19	Spectral Size	65536

^{1}H NMR of **9P**

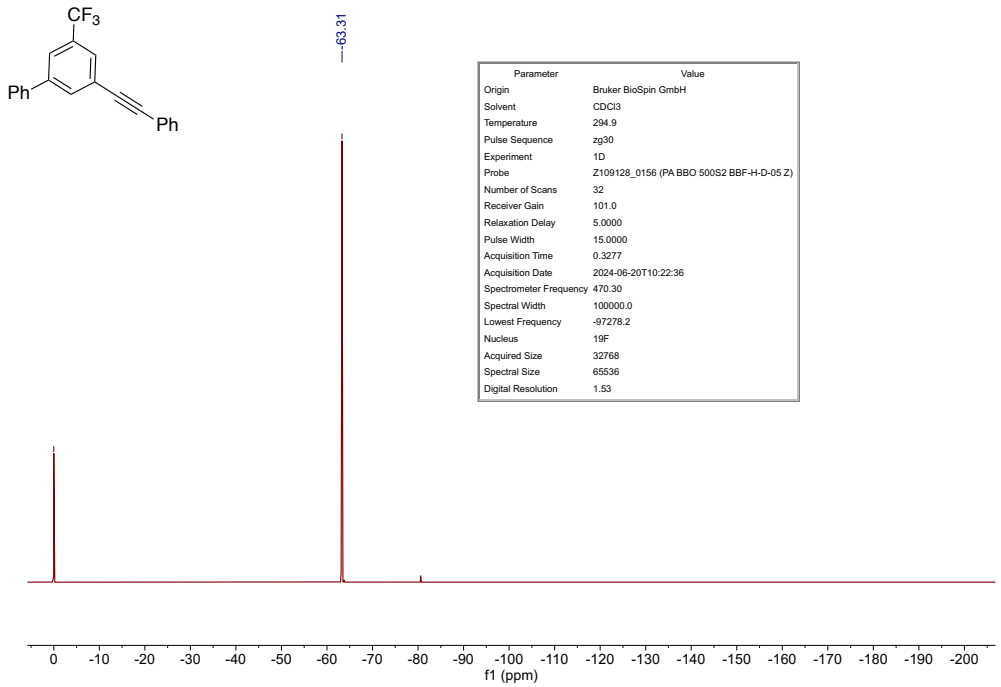


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.3
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	1.9988
Acquisition Date	2024-06-28T12:21:06
Spectrometer Frequency	499.87
Spectral Width	8196.7
Lowest Frequency	-861.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.13

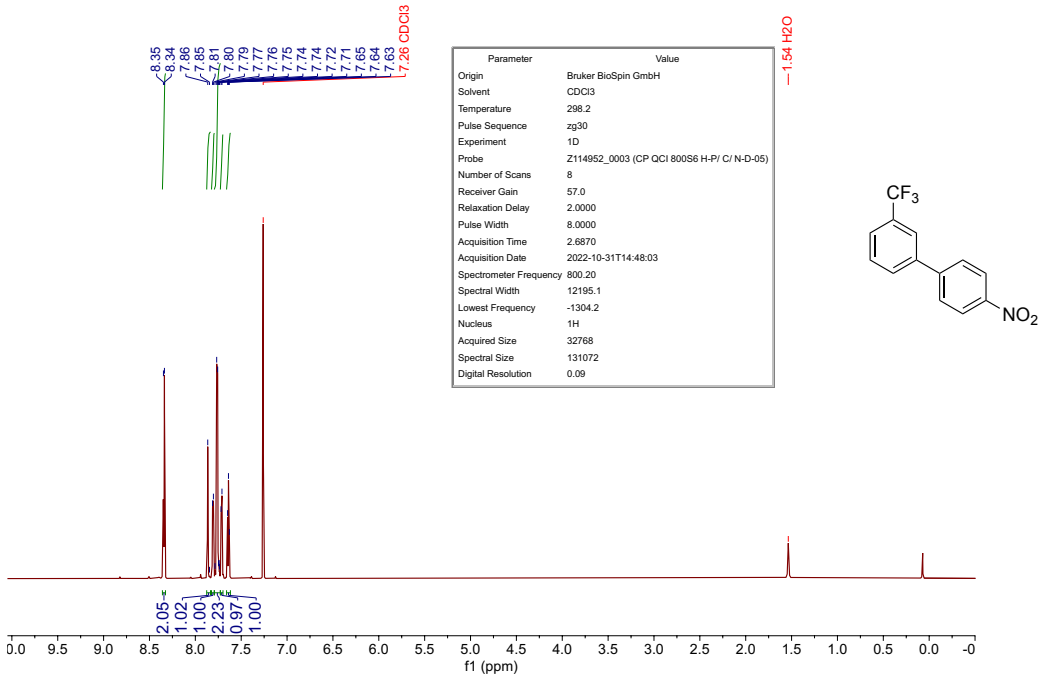
^{13}C NMR of **9P**



^{19}F NMR of **9P**

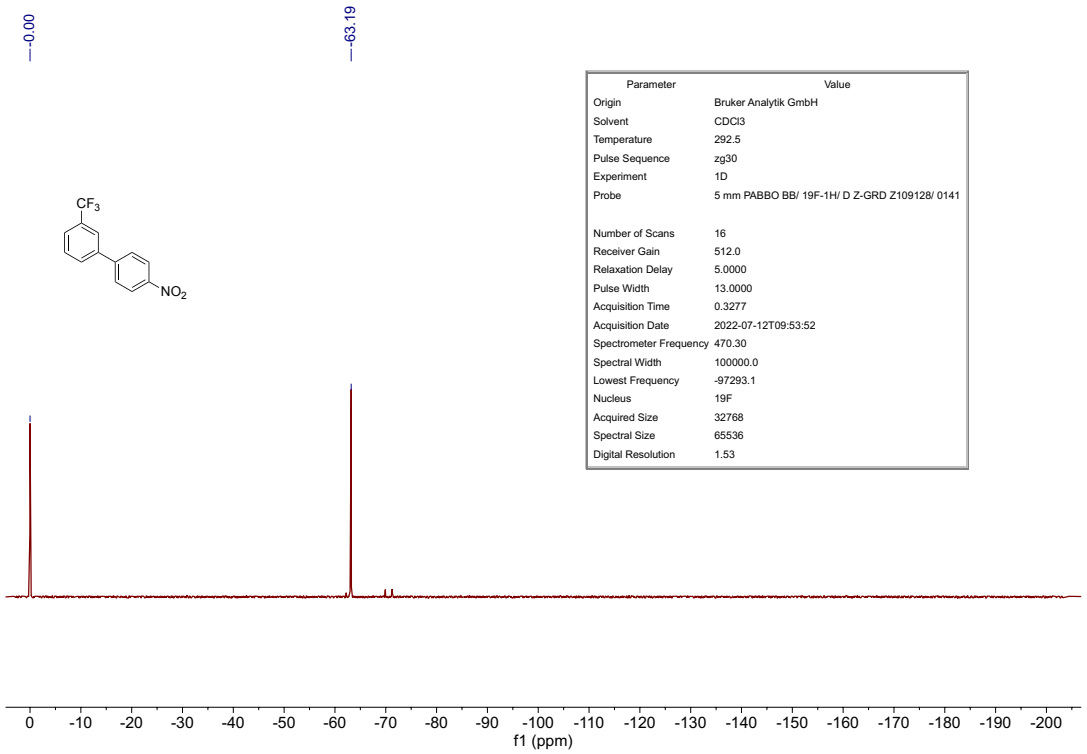


^{1}H NMR of **10P**



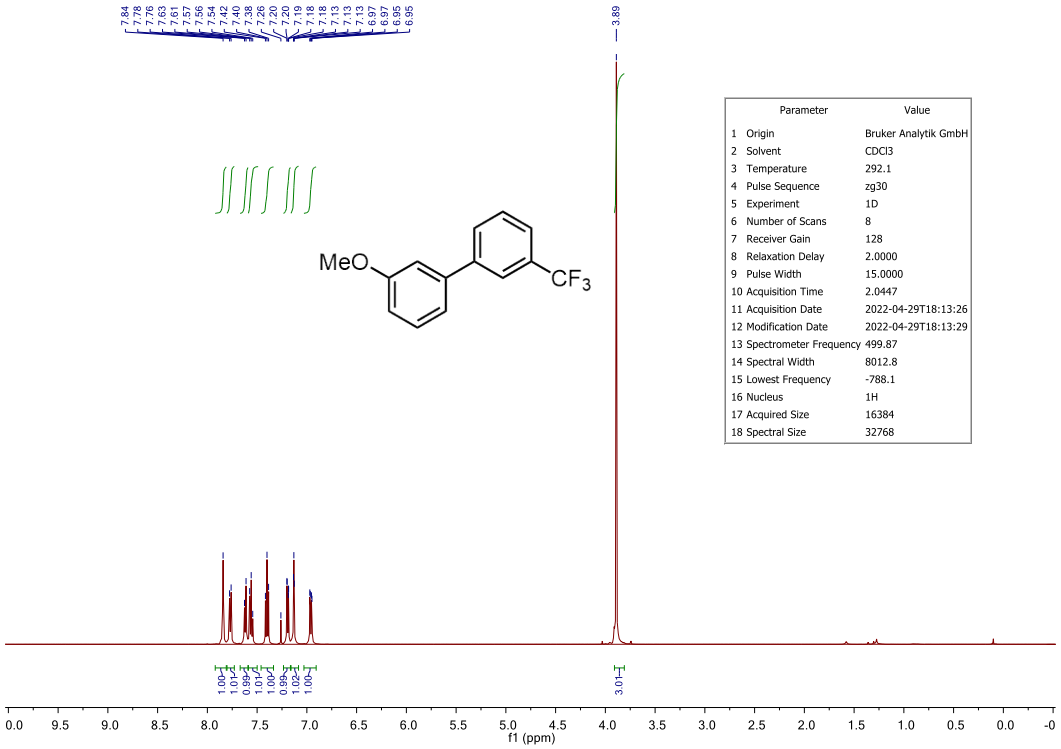
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	8
Receiver Gain	57.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2022-10-31T14:48:03
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1304.2
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{19}F NMR of **10P**



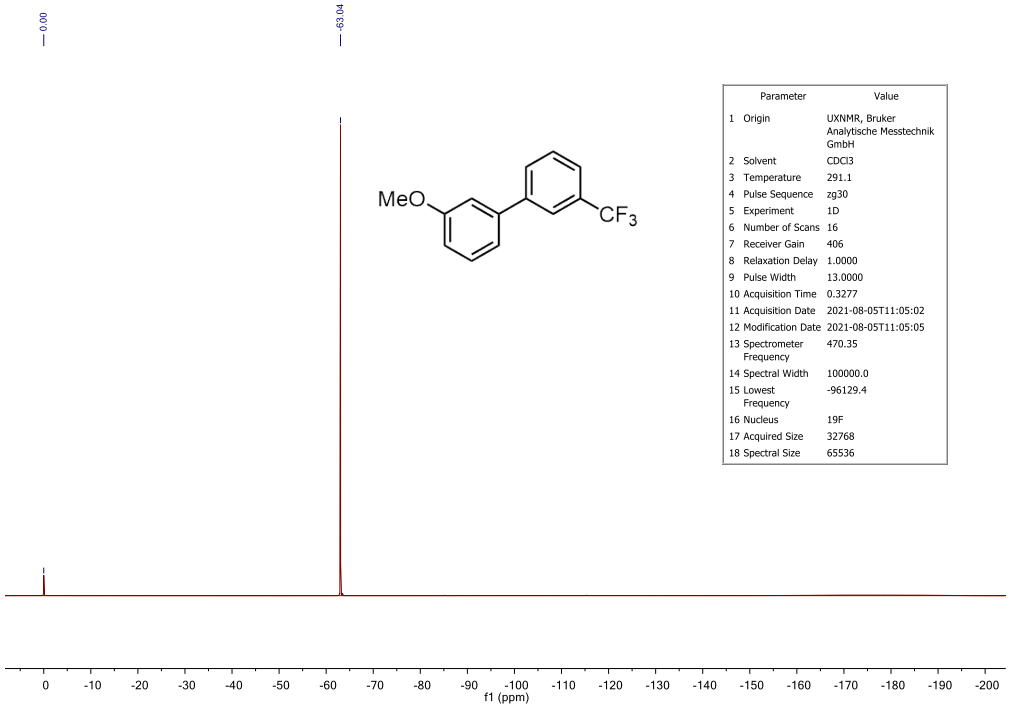
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2022-07-12T09:53:52
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97293.1
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **11P**



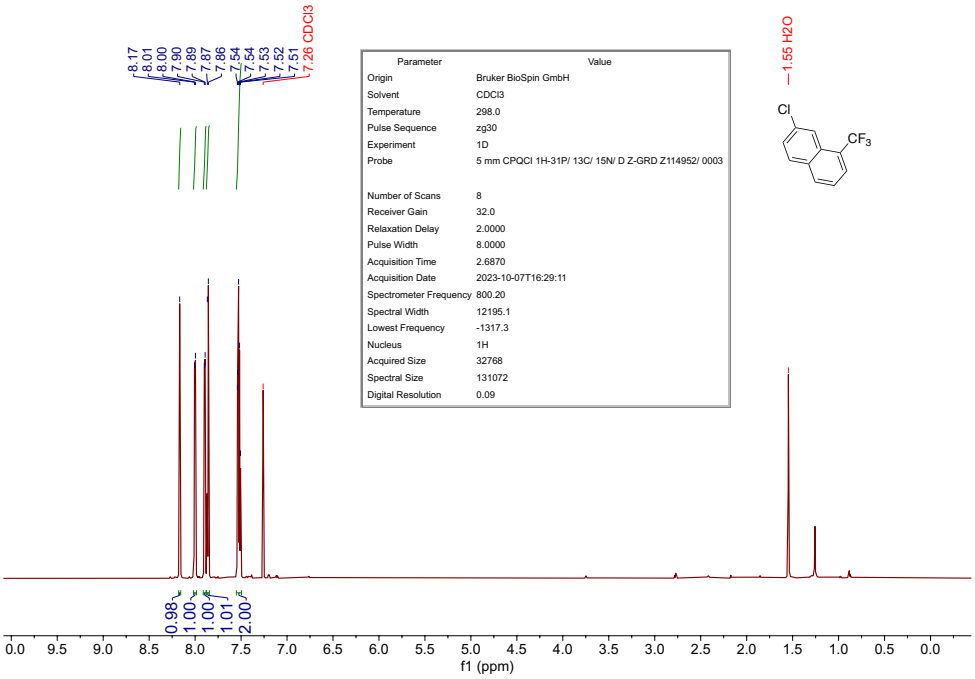
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Solvent	CDCl3
3	Temperature	292.1
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	8
7	Receiver Gain	128
8	Relaxation Delay	2.0000
9	Pulse Width	15.0000
10	Acquisition Time	2.0447
11	Acquisition Date	2022-04-29T18:13:26
12	Modification Date	2022-04-29T18:13:29
13	Spectrometer Frequency	499.87
14	Spectral Width	8012.8
15	Lowest Frequency	-788.1
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	32768

^{19}F NMR of **11P**



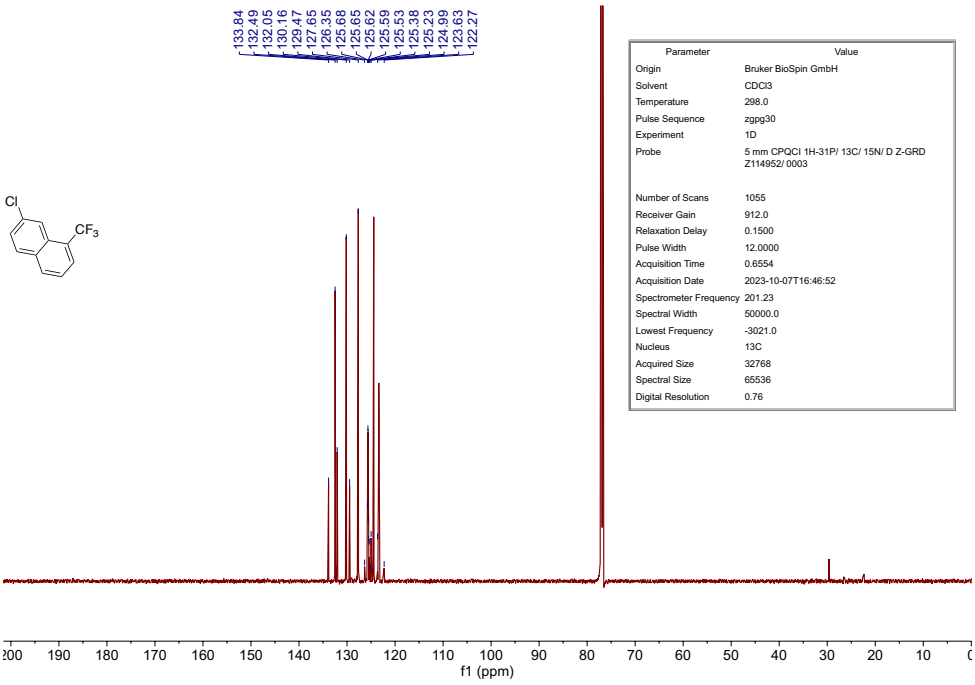
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Solvent	CDCl3
3	Temperature	291.1
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	16
7	Receiver Gain	406
8	Relaxation Delay	1.0000
9	Pulse Width	13.0000
10	Acquisition Time	0.3277
11	Acquisition Date	2021-08-05T11:05:02
12	Modification Date	2021-08-05T11:05:05
13	Spectrometer Frequency	470.35
14	Spectral Width	100000.0
15	Lowest Frequency	-96129.4
16	Nucleus	19F
17	Acquired Size	32768
18	Spectral Size	65536

^{1}H NMR of **12P**



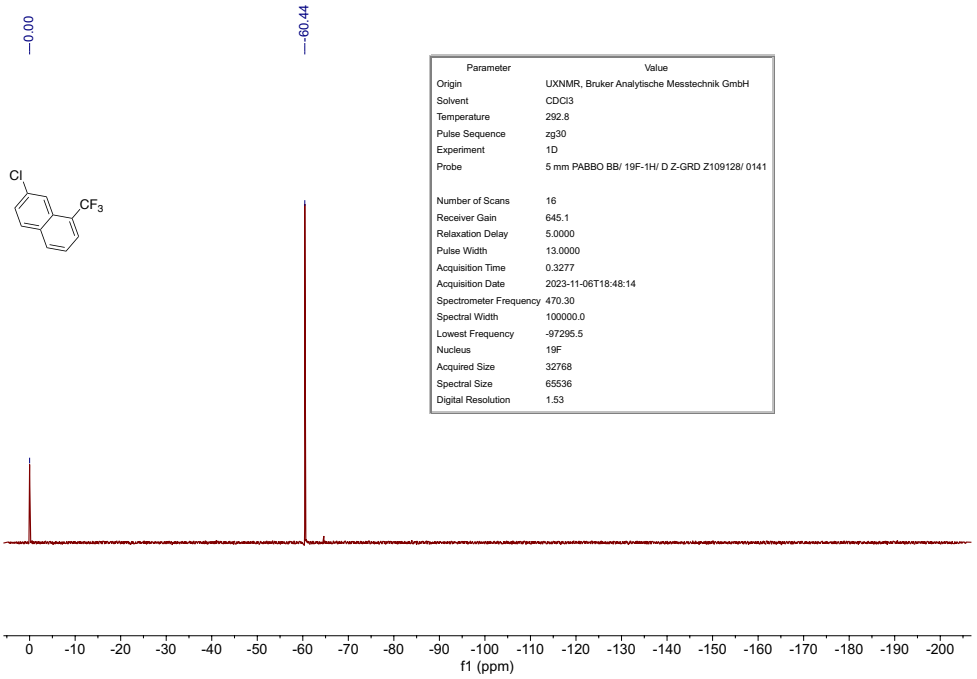
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2023-10-07T16:29:11
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1317.3
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{13}C NMR of **12P**



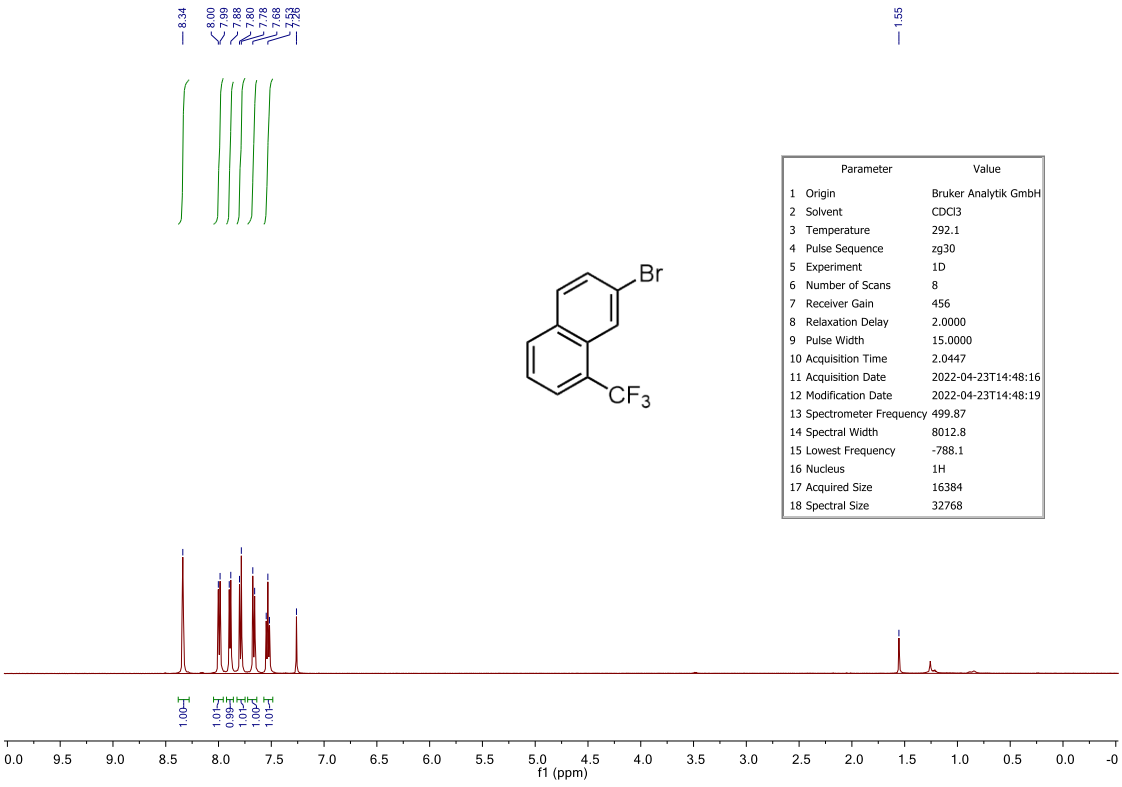
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	1055
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2023-10-07T16:46:52
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{19}F NMR of **12P**



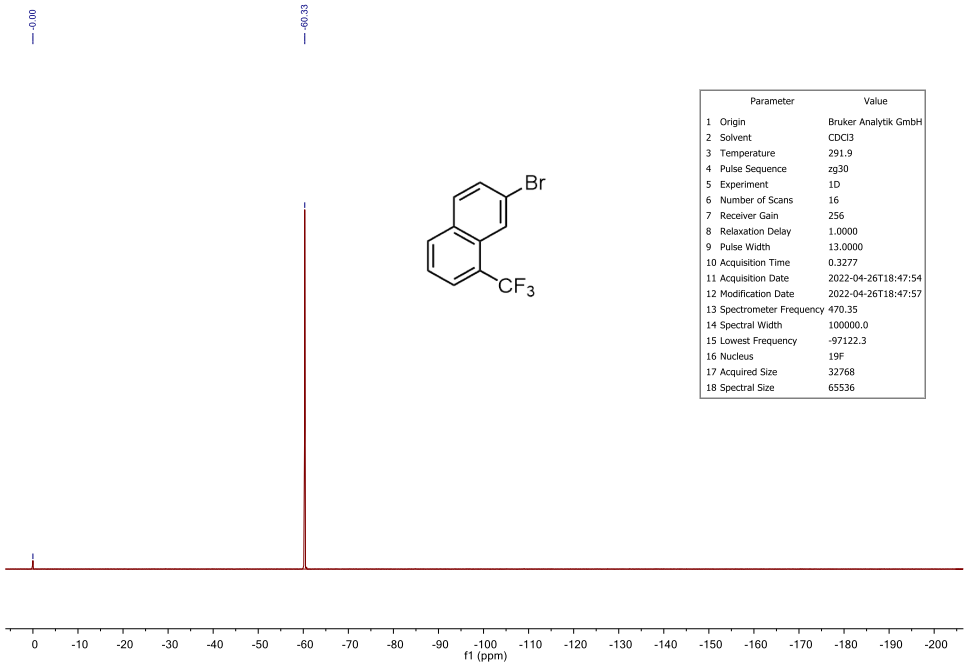
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-11-06T18:48:14
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97295.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **13P**

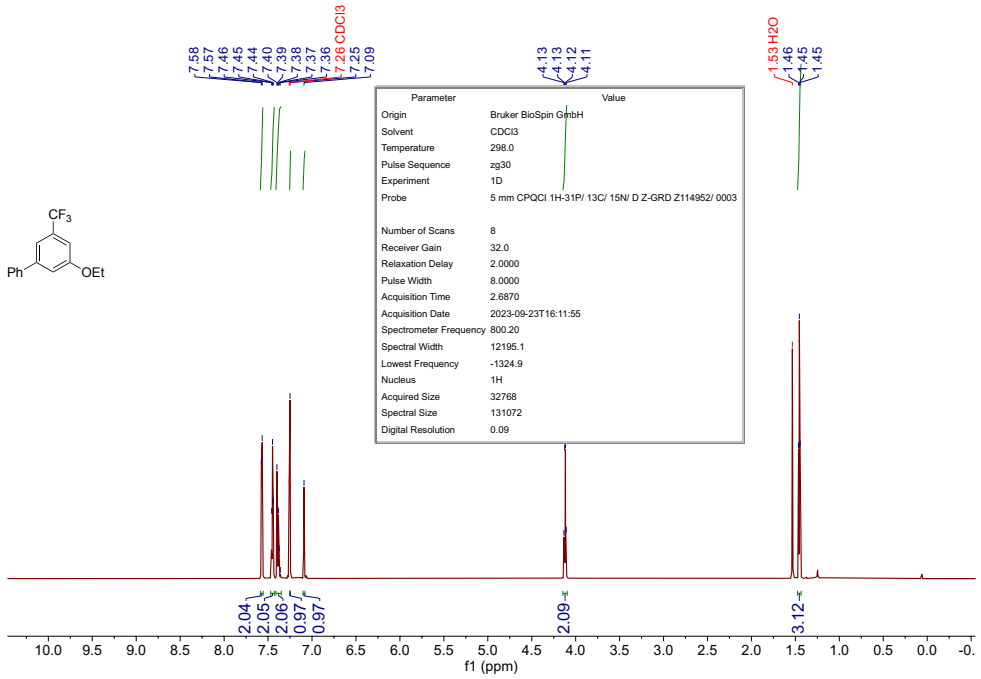


	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Solvent	CDCl3
3	Temperature	292.1
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	8
7	Receiver Gain	456
8	Relaxation Delay	2.0000
9	Pulse Width	15.0000
10	Acquisition Time	2.0447
11	Acquisition Date	2022-04-23T14:48:16
12	Modification Date	2022-04-23T14:48:19
13	Spectrometer Frequency	499.87
14	Spectral Width	8012.8
15	Lowest Frequency	-788.1
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	32768

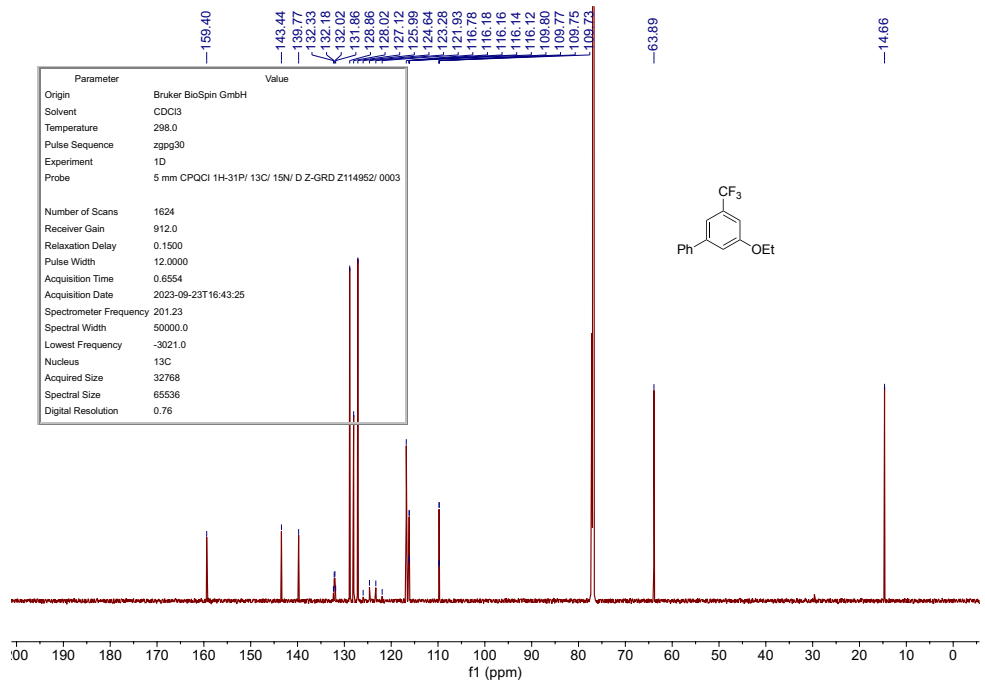
^{19}F NMR of **13P**



^{1}H NMR of **14P**

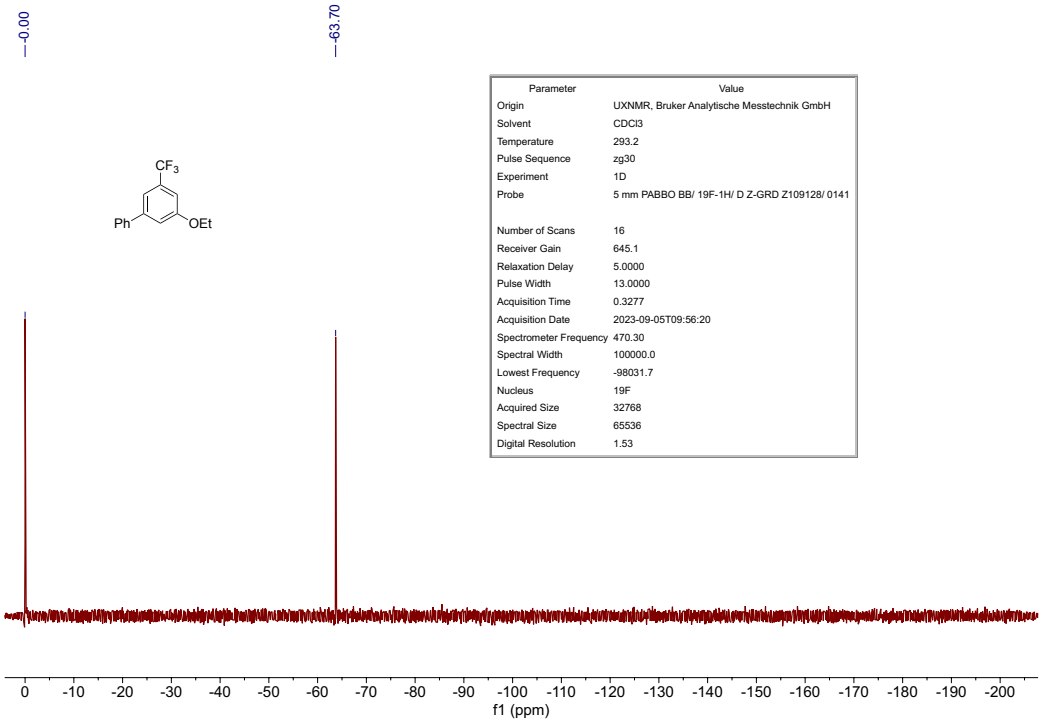


^{13}C NMR of **14P**



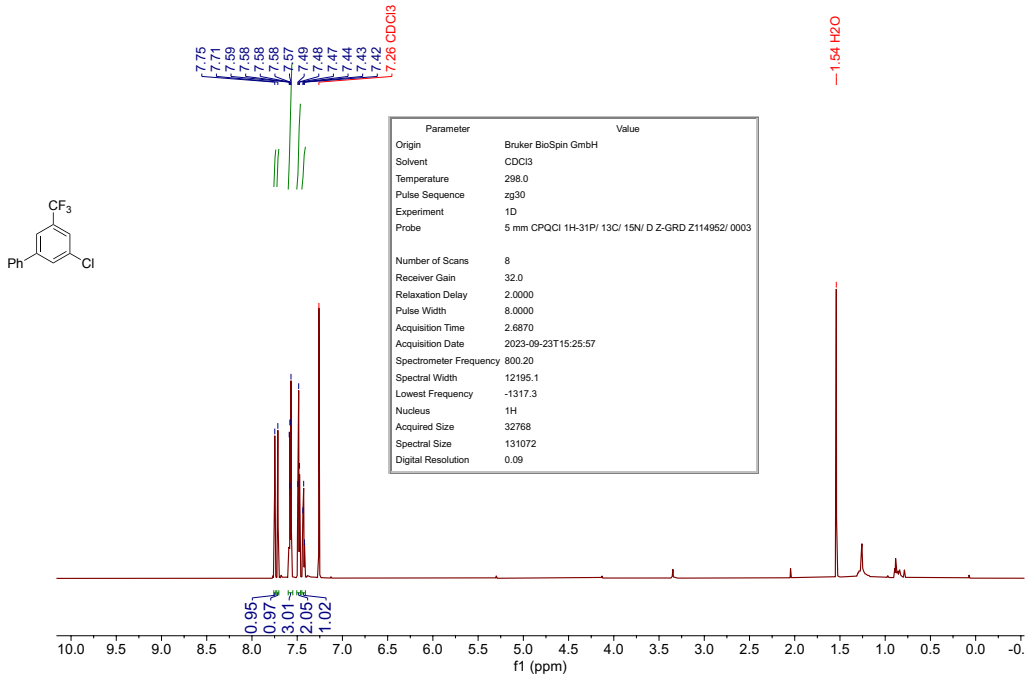
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	1624
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2023-09-23T16:43:25
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{19}F NMR of **14P**

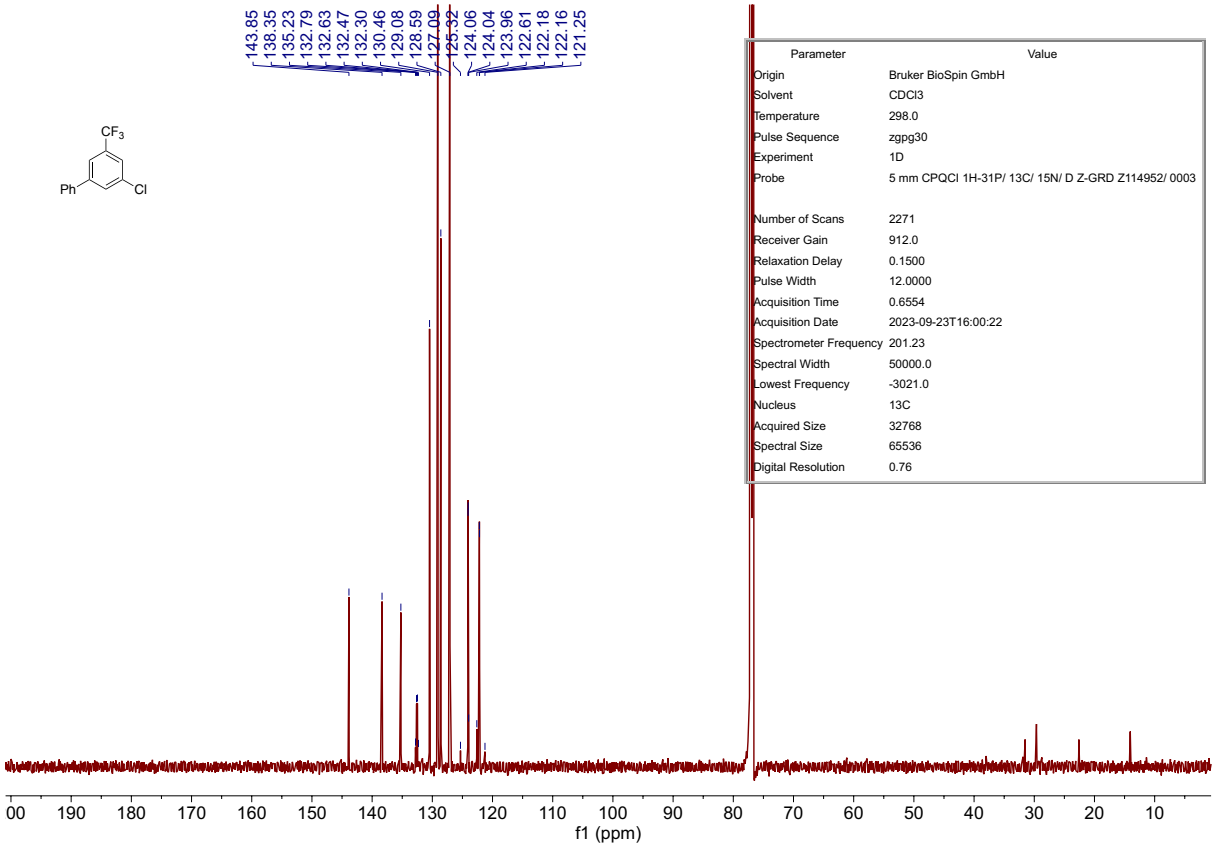


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-09-05T09:56:20
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-98031.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

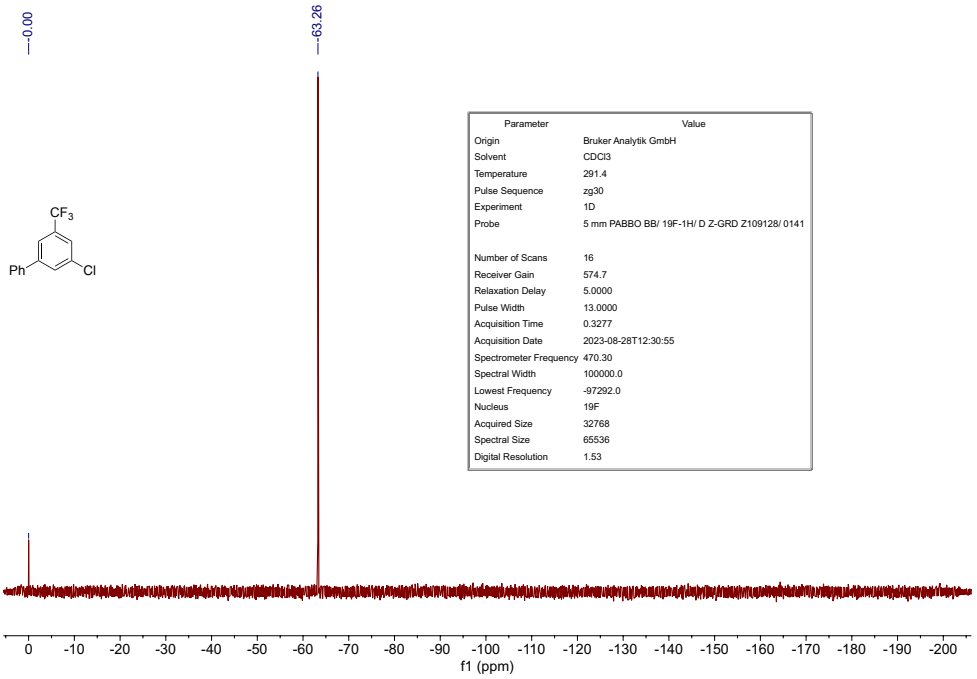
^{1}H NMR of **15P**



^{13}C NMR of **15P**

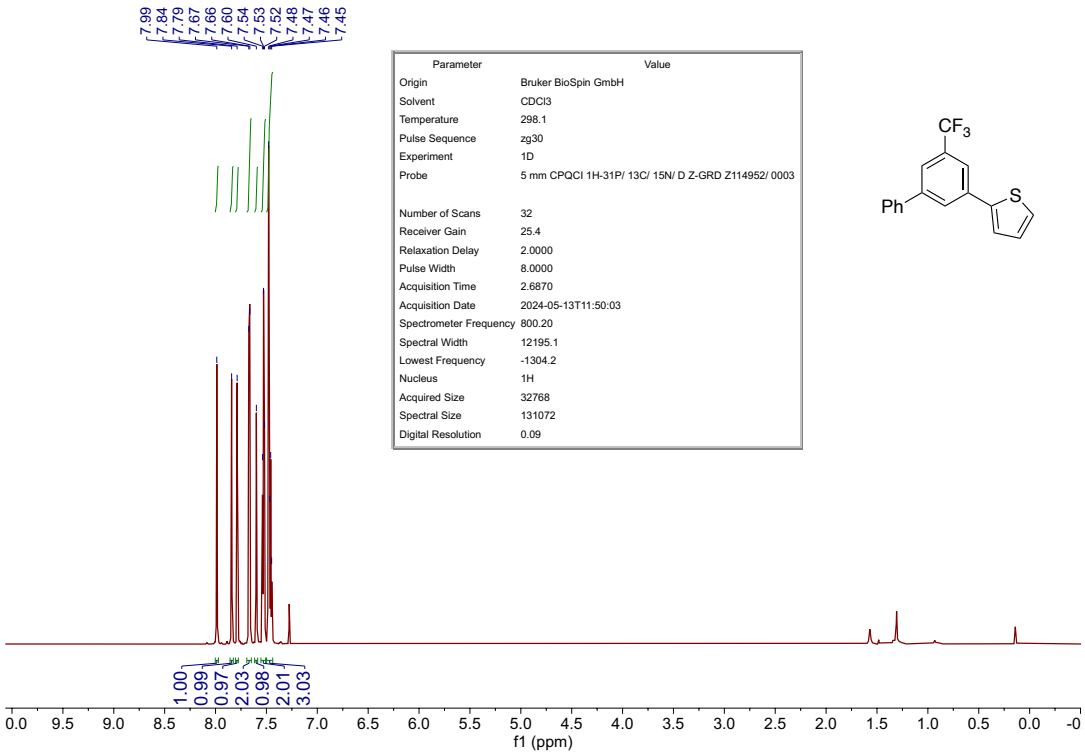


^{19}F NMR of **15P**



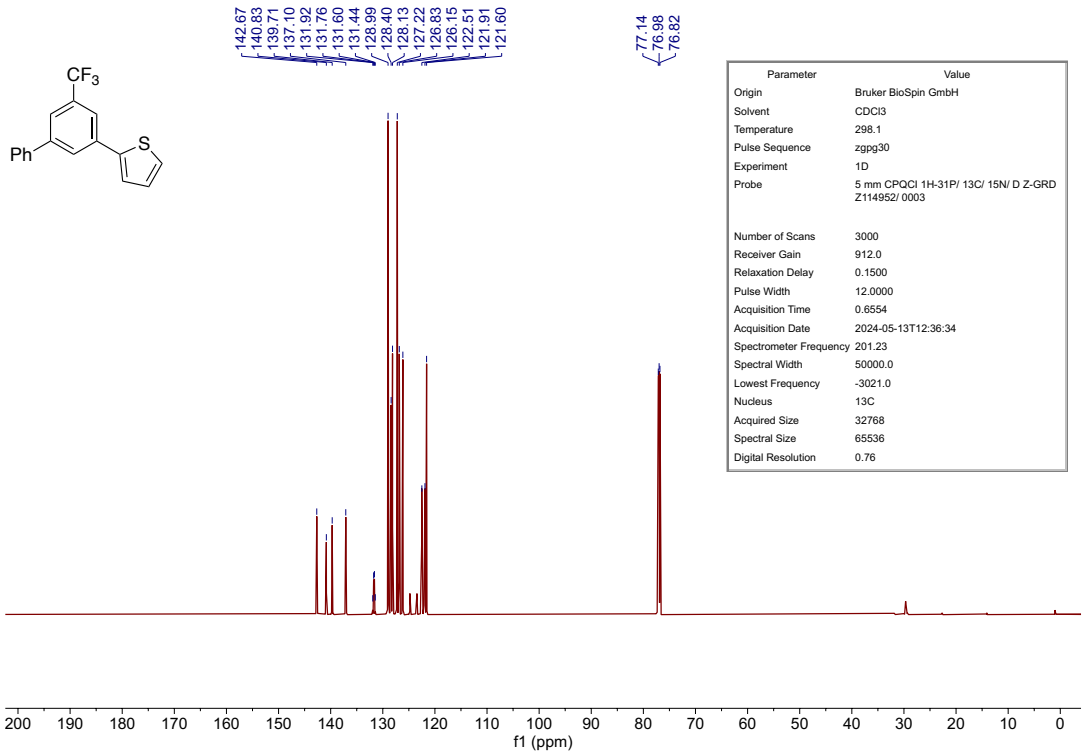
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-08-28T12:30:55
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97292.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **16P**

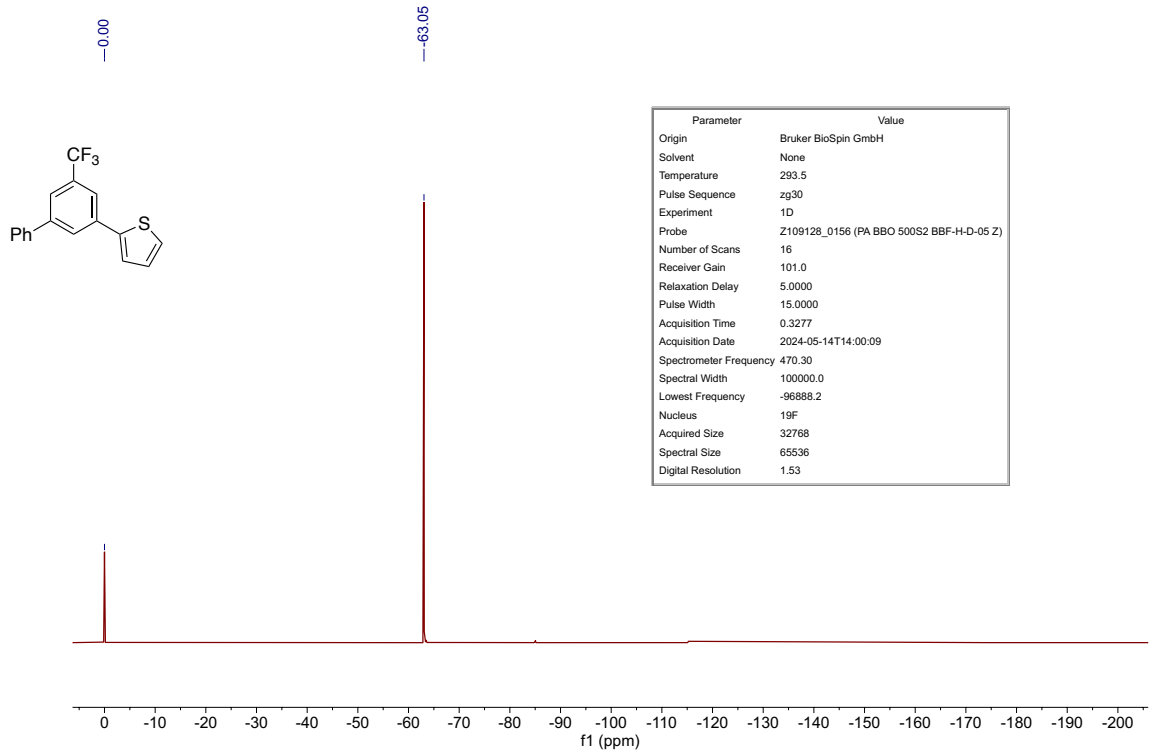


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	32
Receiver Gain	25.4
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2024-05-13T11:50:03
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1304.2
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

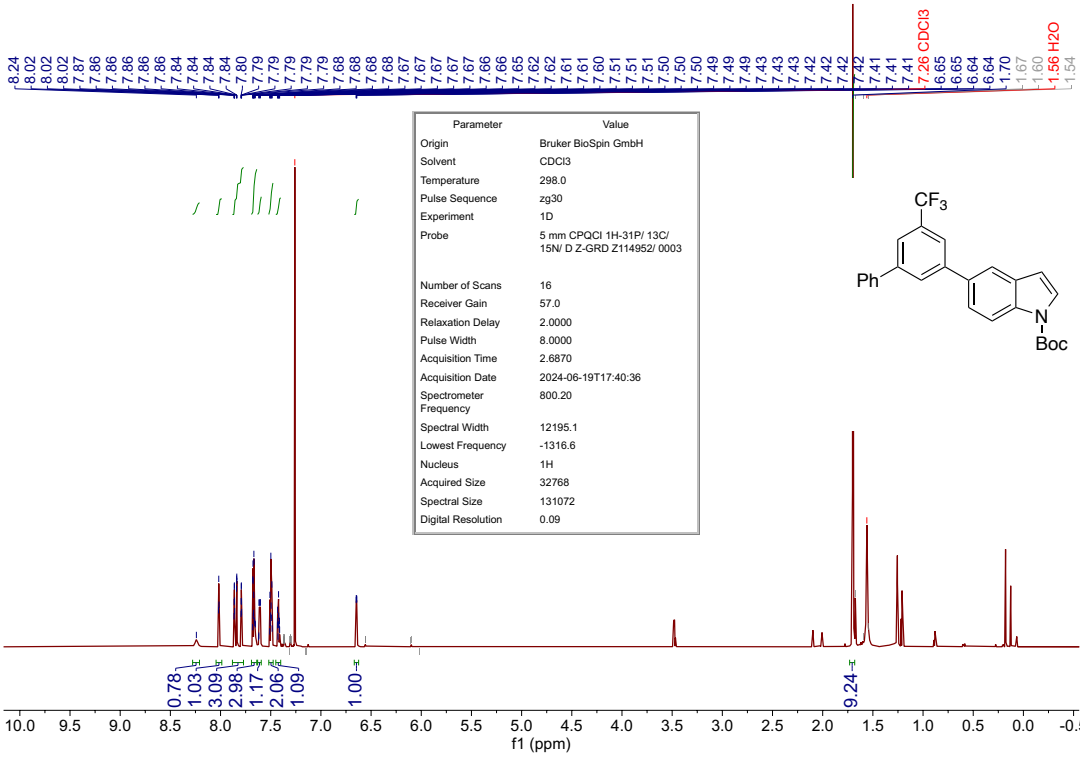
^{13}C NMR of **16P**



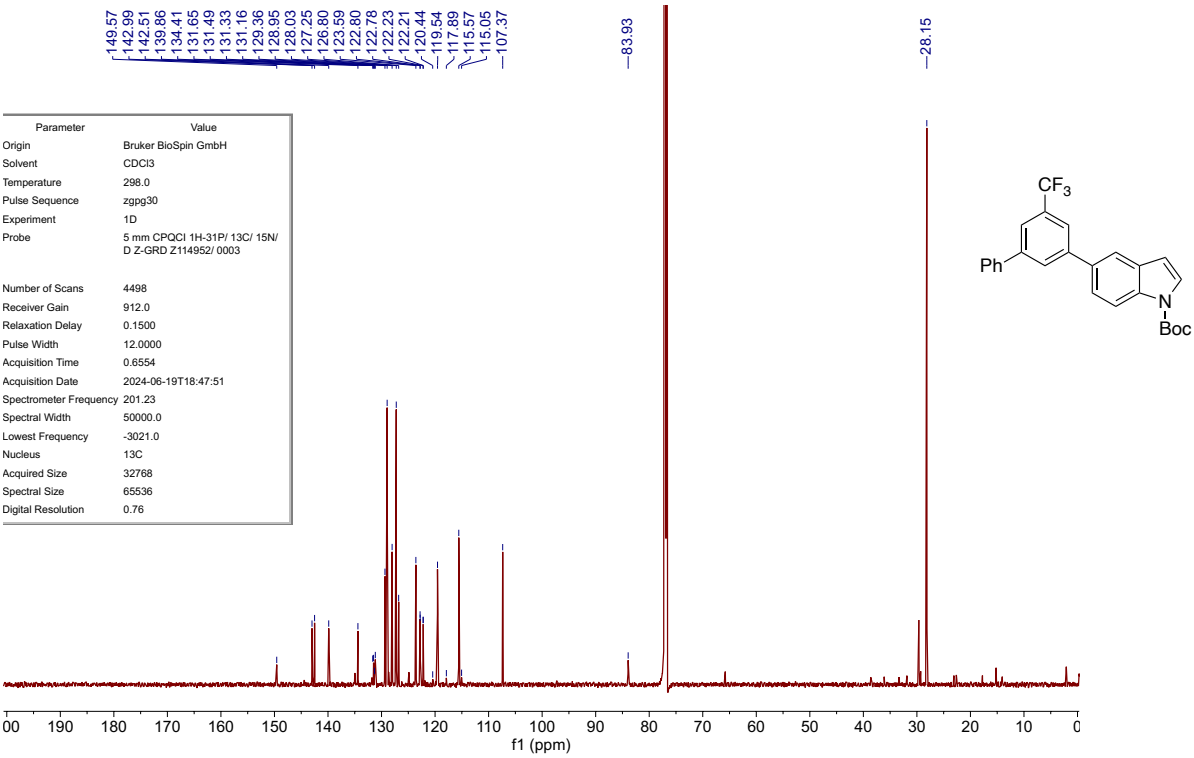
^{19}F NMR of **16P**



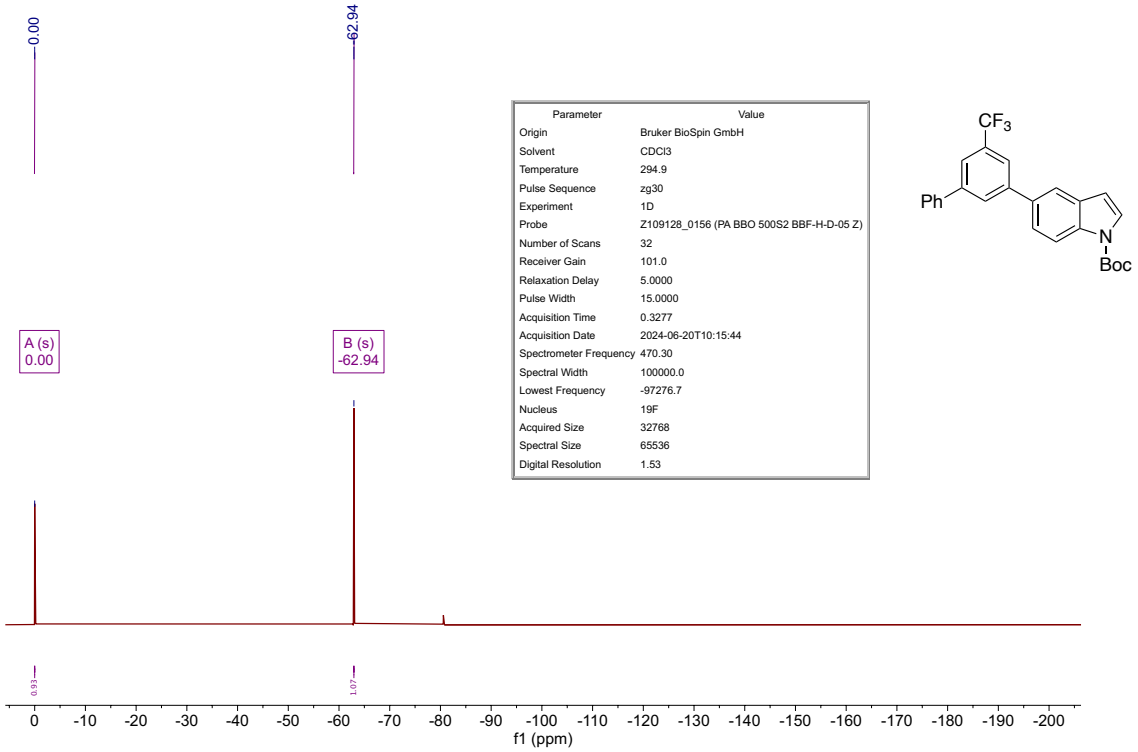
^{1}H NMR of **17P**



^{13}C NMR of **17P**

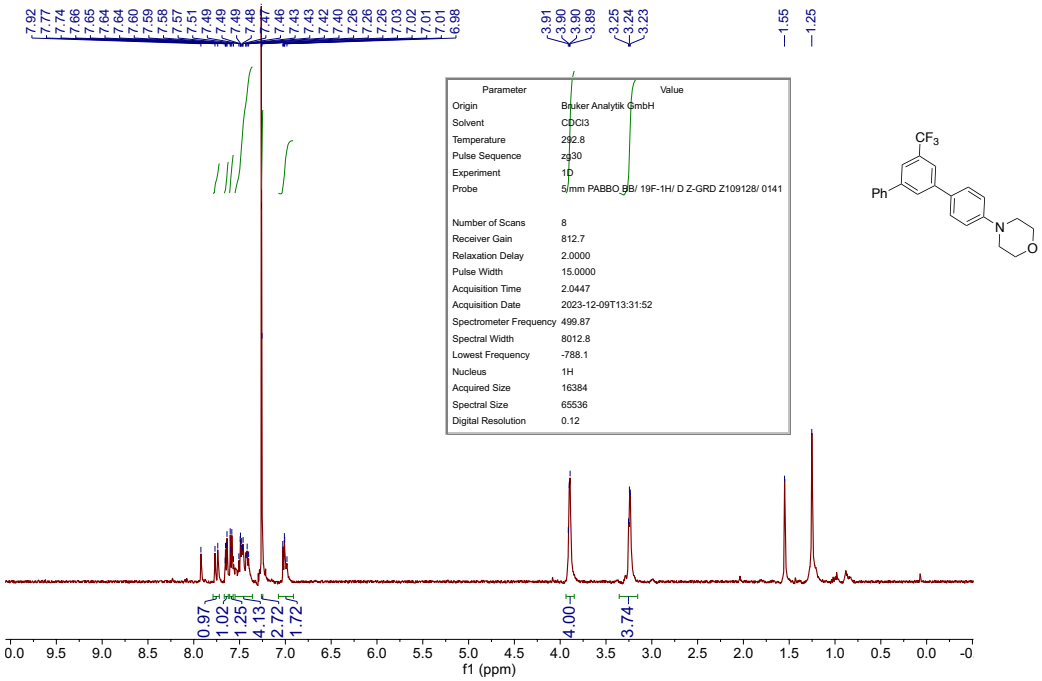


^{19}F NMR of **17P**



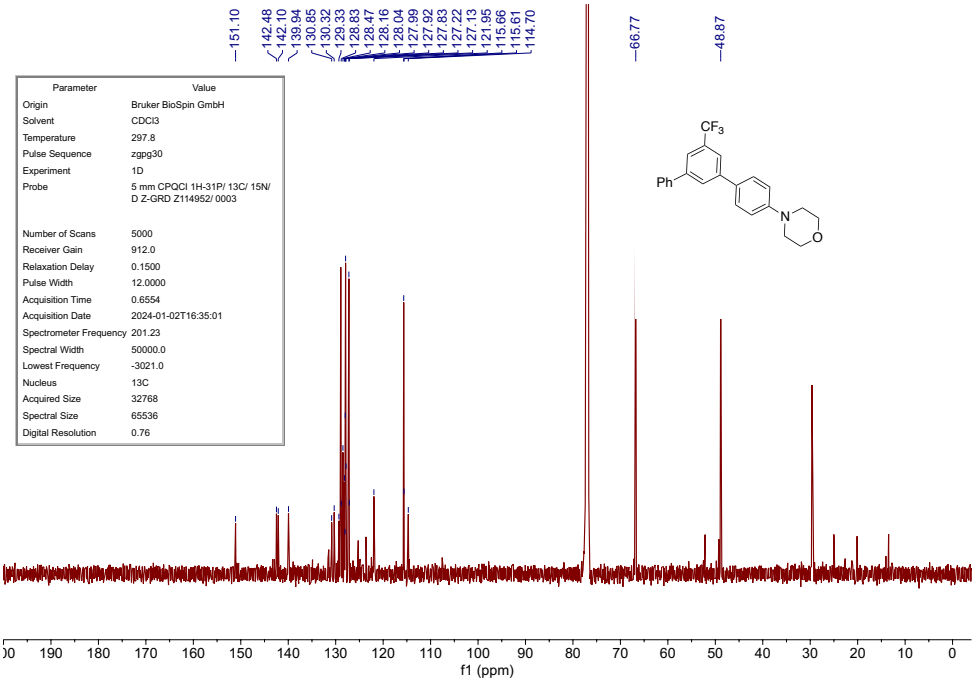
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	32
Receiver Gain	101.0
Relaxation Delay	5.0000
Pulse Width	15.0000
Acquisition Time	0.3277
Acquisition Date	2024-06-20T10:15:44
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97276.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **18P**



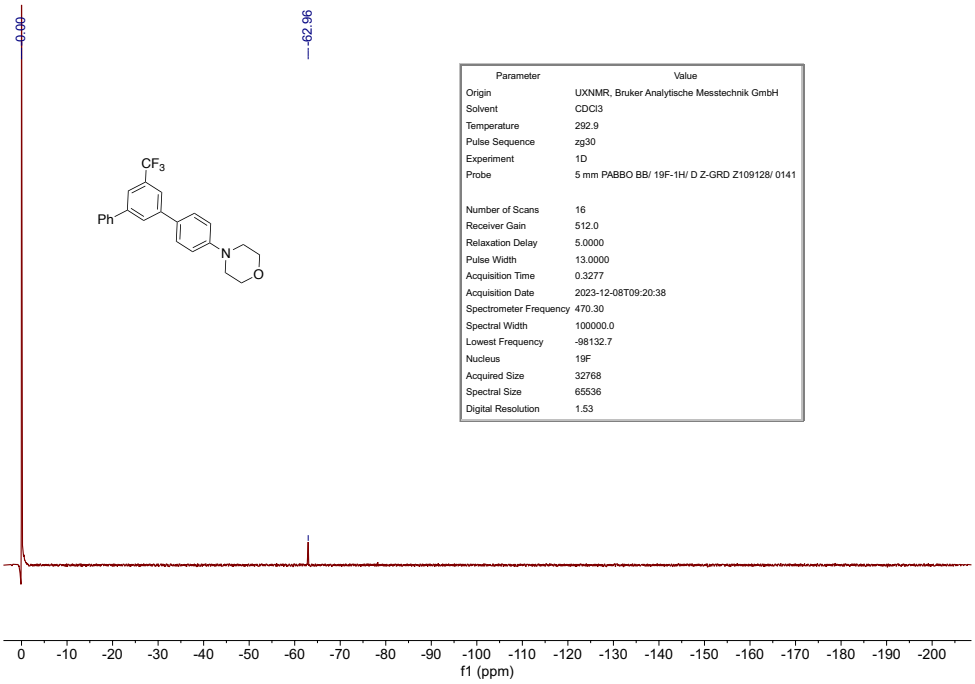
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	812.7
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	2.0447
Acquisition Date	2023-12-09T13:31:52
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

^{13}C NMR of **18P**



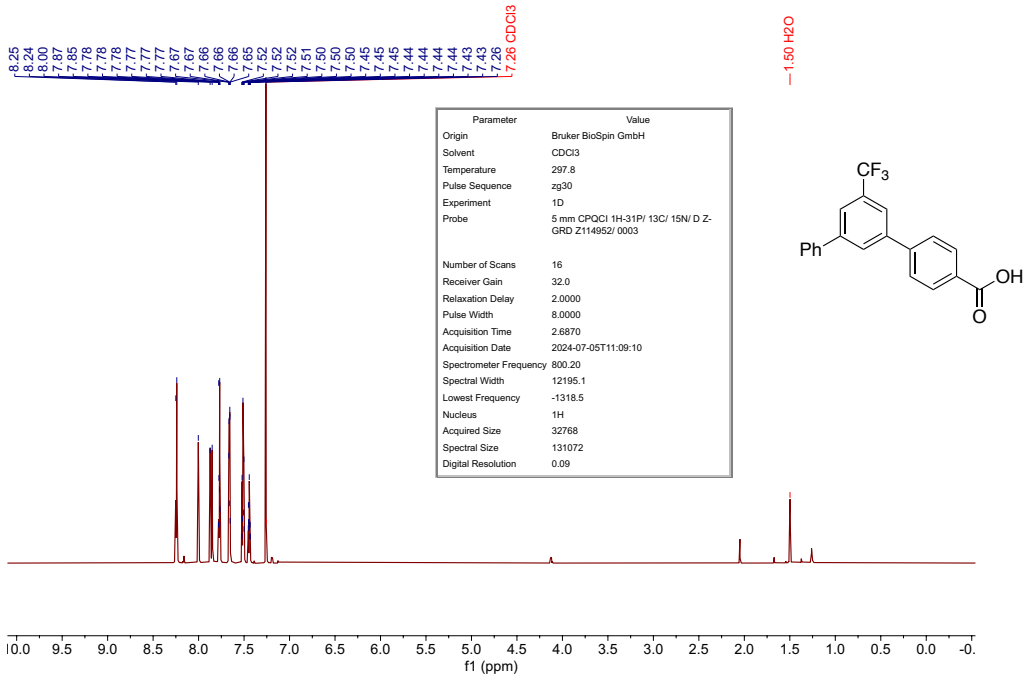
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	5000
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2024-01-02T16:35:01
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{19}F NMR of **18P**

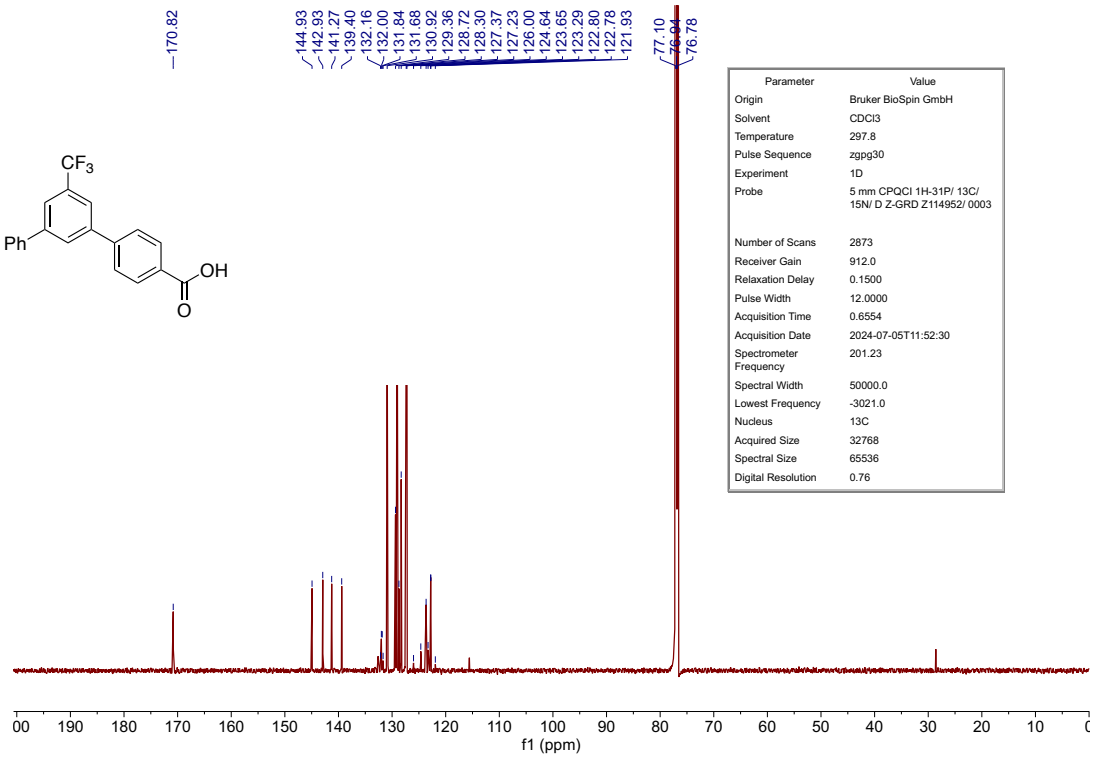


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-12-08T09:20:38
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-98132.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

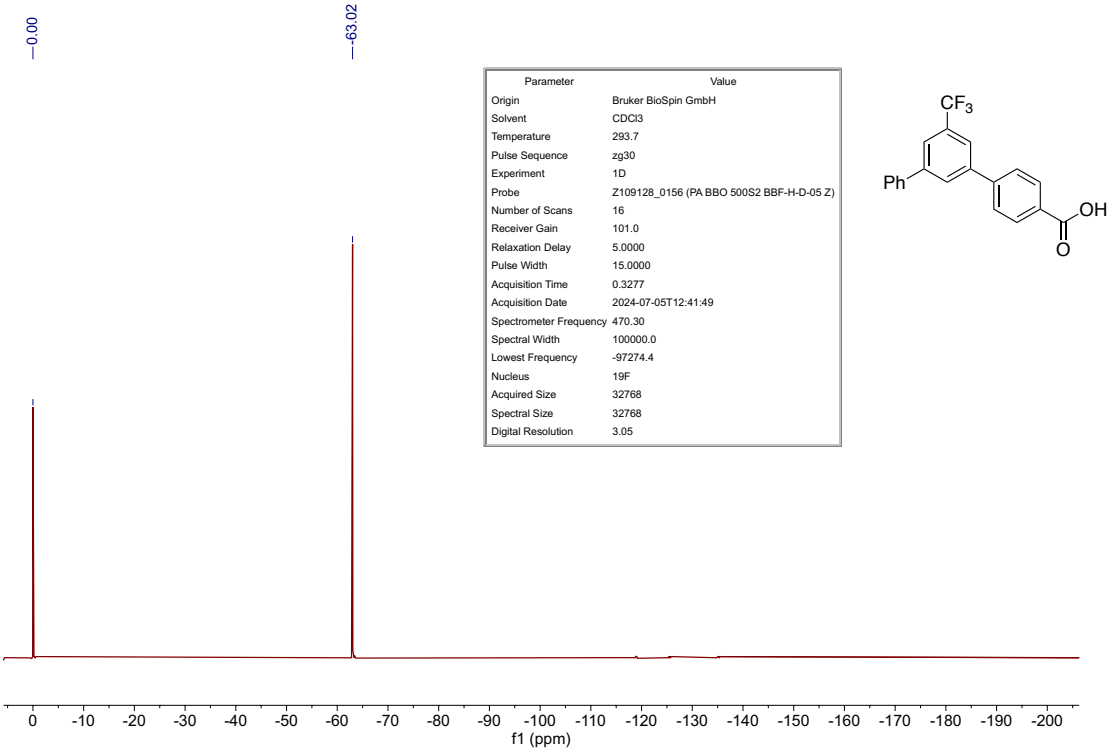
^{1}H NMR of **19P1**



^{13}C NMR of **19P1**

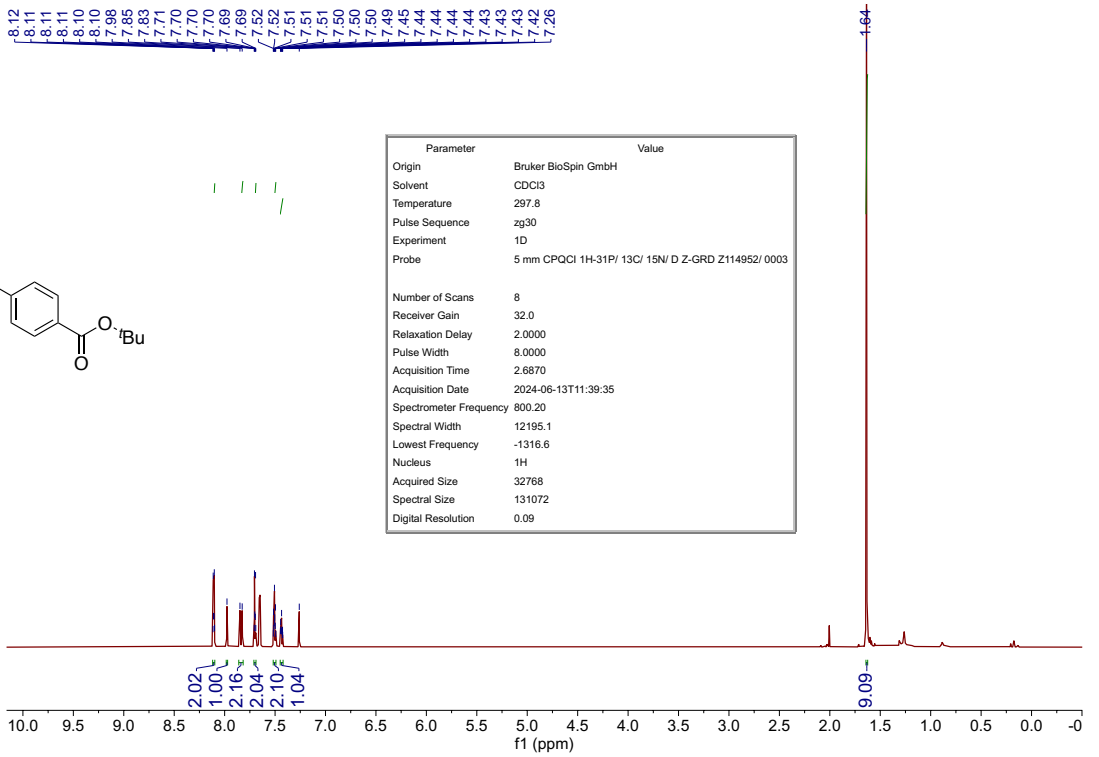


^{19}F NMR of **19P1**



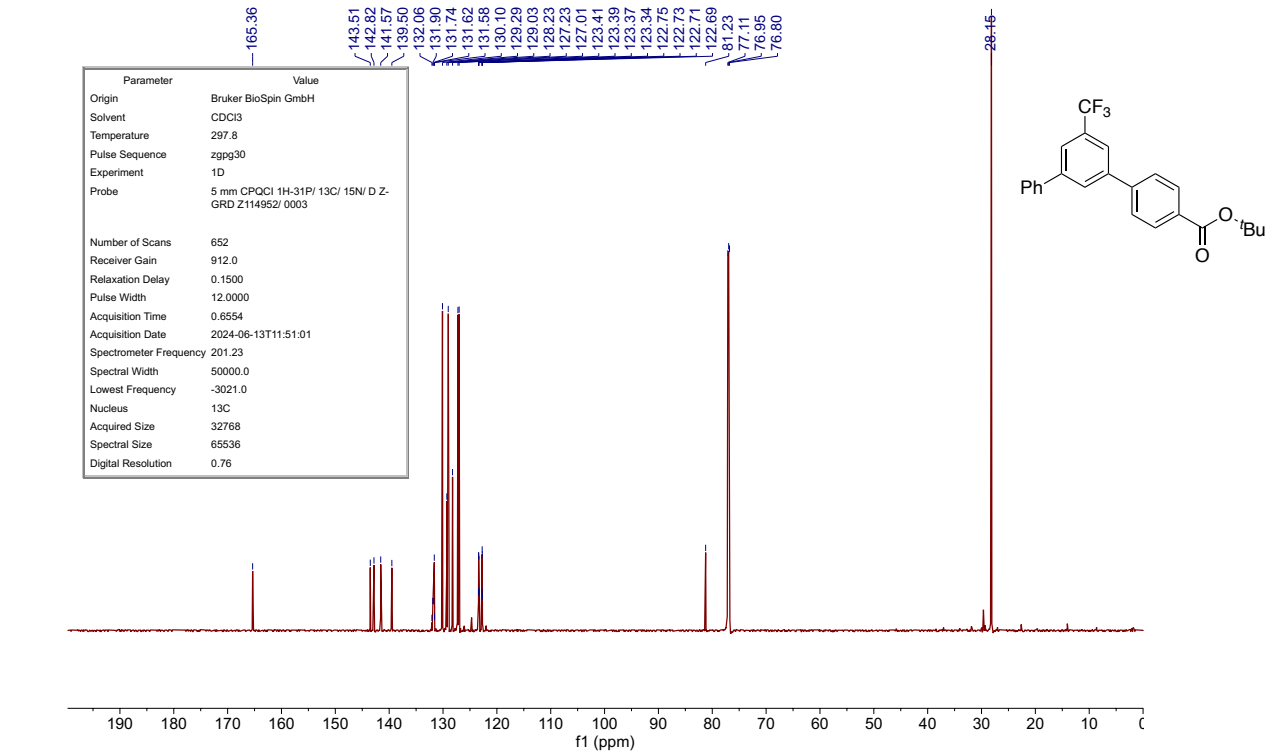
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	5.0000
Pulse Width	15.0000
Acquisition Time	0.3277
Acquisition Date	2024-07-05T12:41:49
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97274.4
Nucleus	19F
Acquired Size	32768
Spectral Size	32768
Digital Resolution	3.05

^{1}H NMR of **19P2**



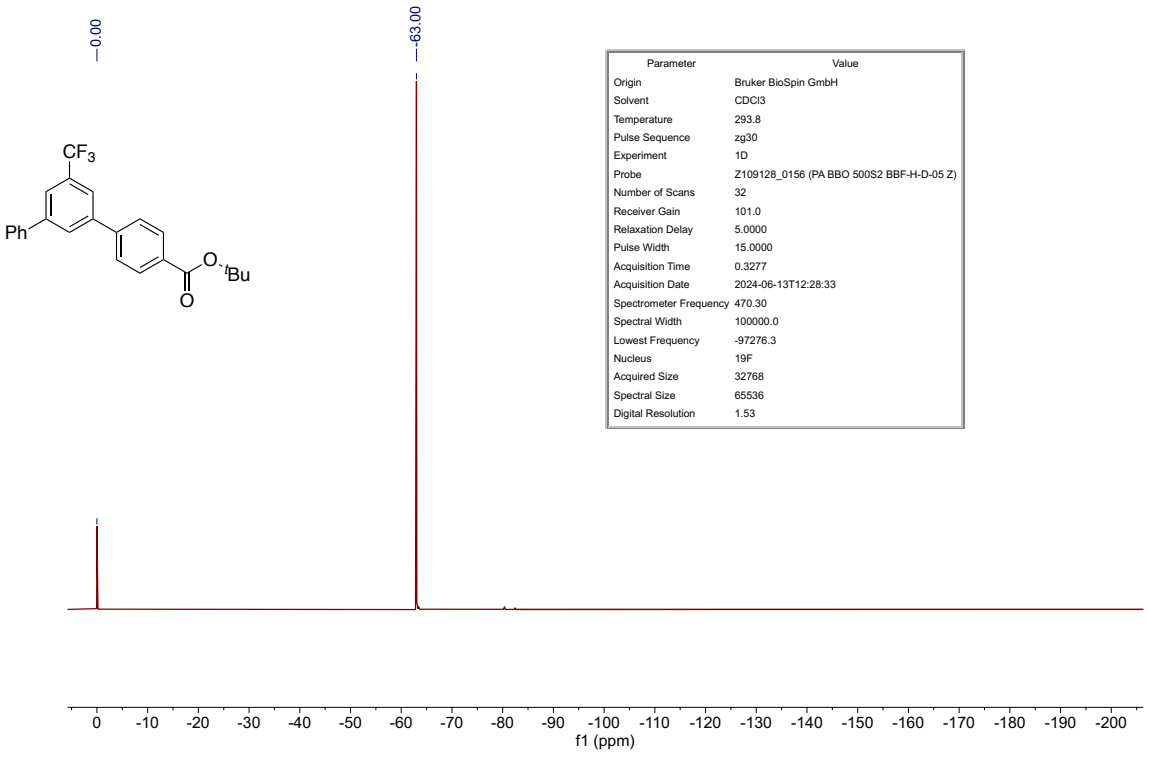
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2024-06-13T11:39:35
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1316.6
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{13}C NMR of **19P2**



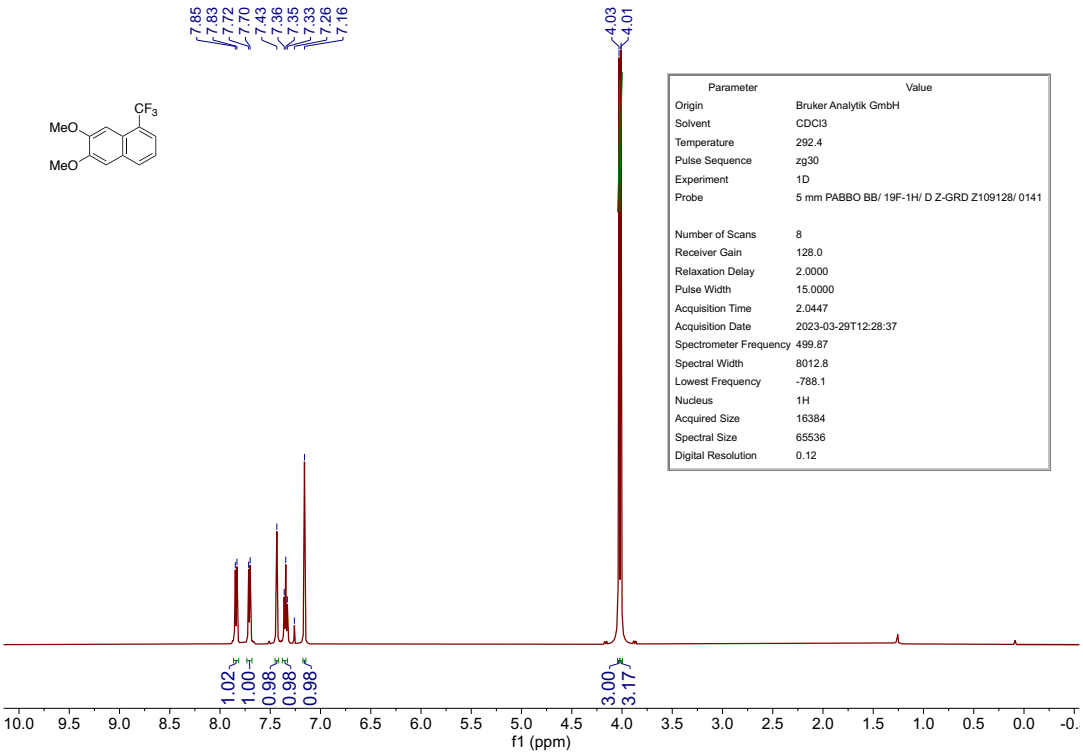
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	652
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2024-06-13T11:51:01
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{19}F NMR of **19P2**



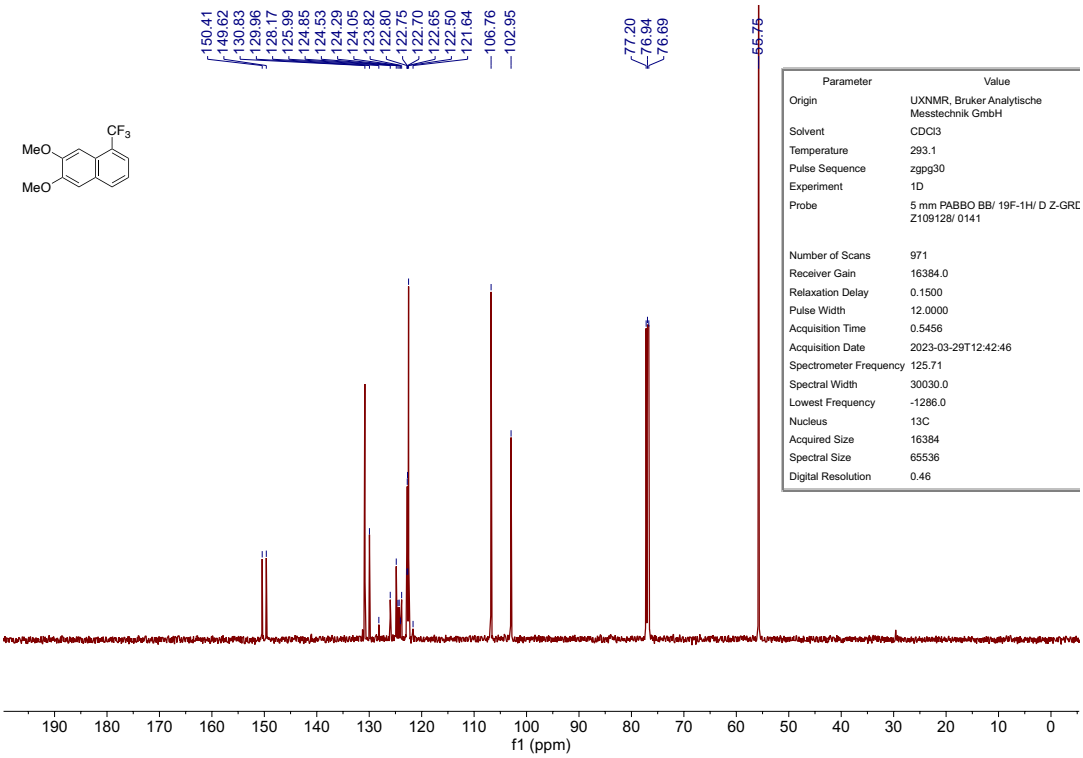
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	32
Receiver Gain	101.0
Relaxation Delay	5.0000
Pulse Width	15.0000
Acquisition Time	0.3277
Acquisition Date	2024-06-13T12:28:33
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97276.3
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **20P**



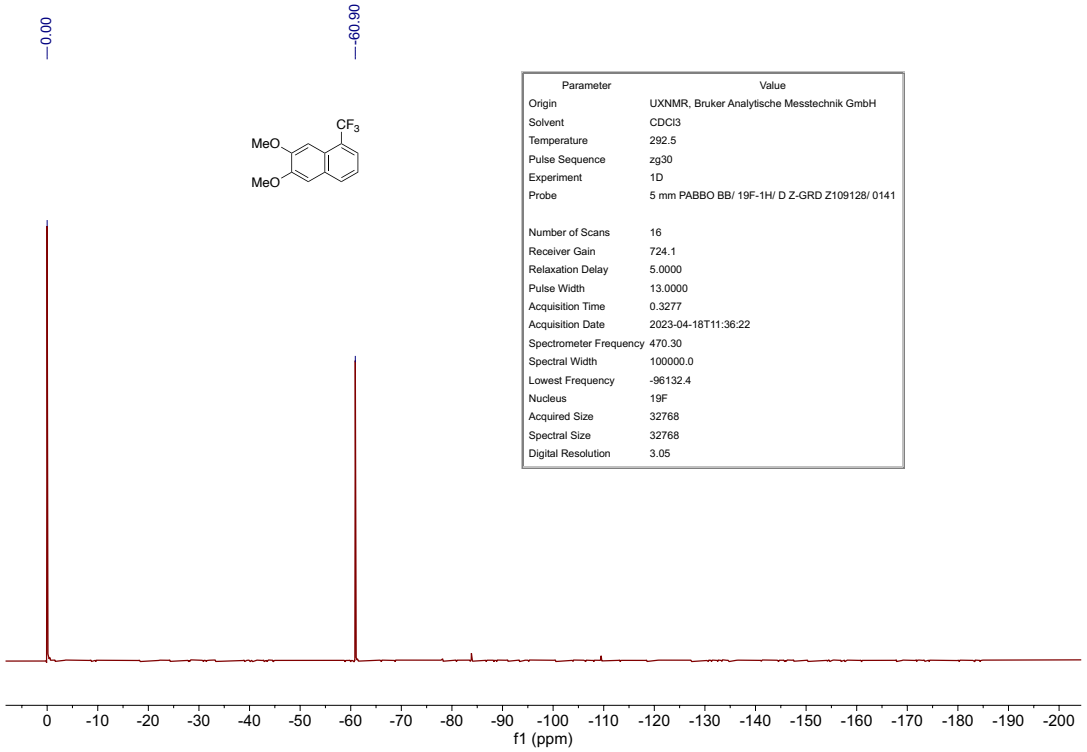
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	2.0447
Acquisition Date	2023-03-29T12:28:37
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

^{13}C NMR of **20P**

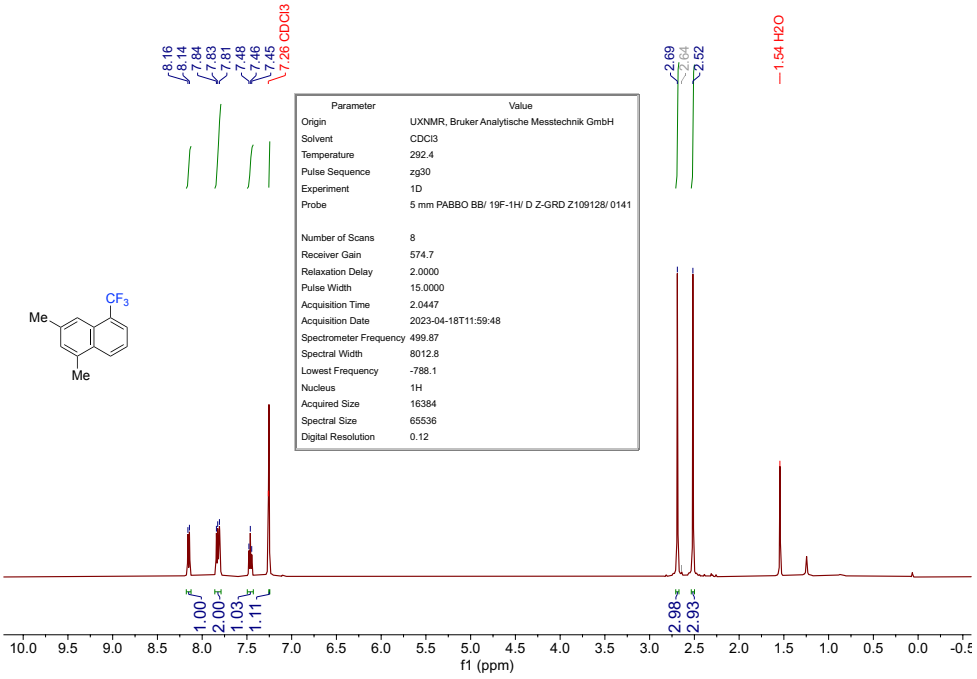


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	971
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.5456
Acquisition Date	2023-03-29T12:42:46
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.46

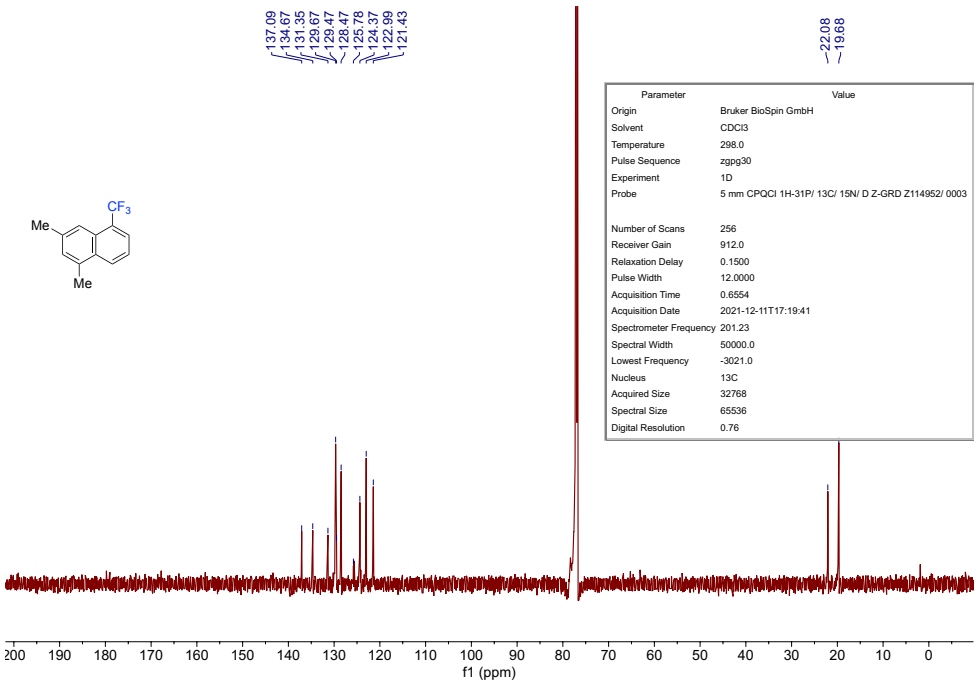
^{19}F NMR of **20P**



^{1}H NMR of **21P**

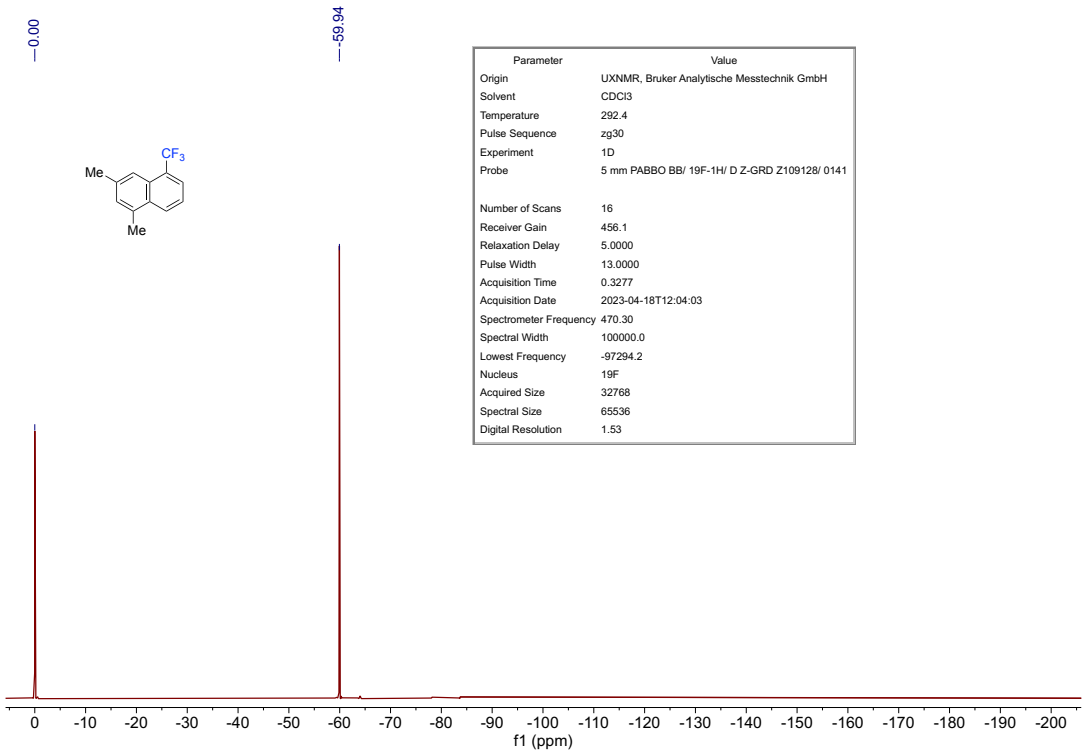


^{13}C NMR of **21P**



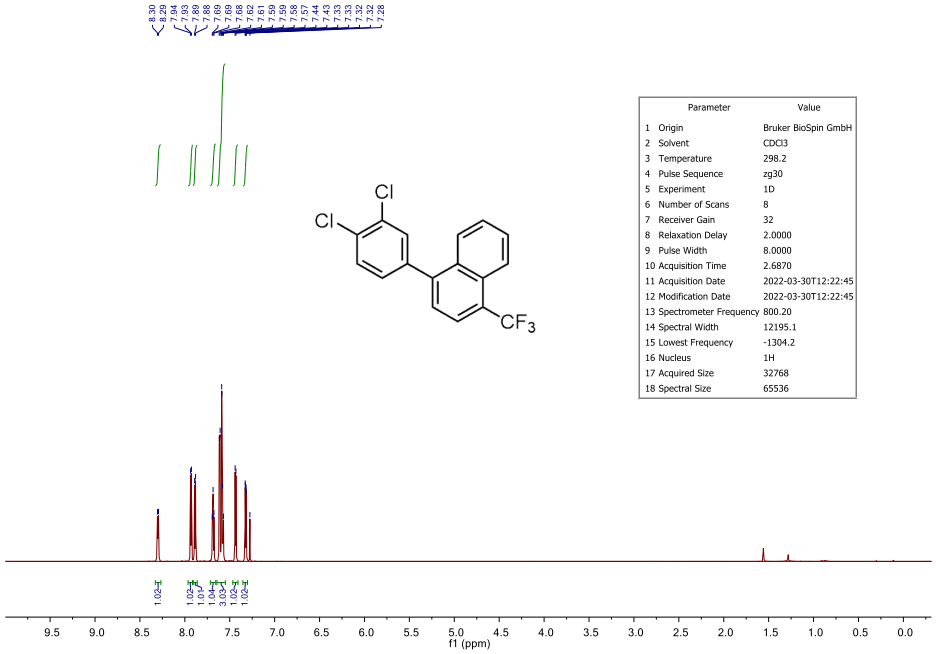
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	256
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2021-12-11T17:19:41
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{19}F NMR of **21P**



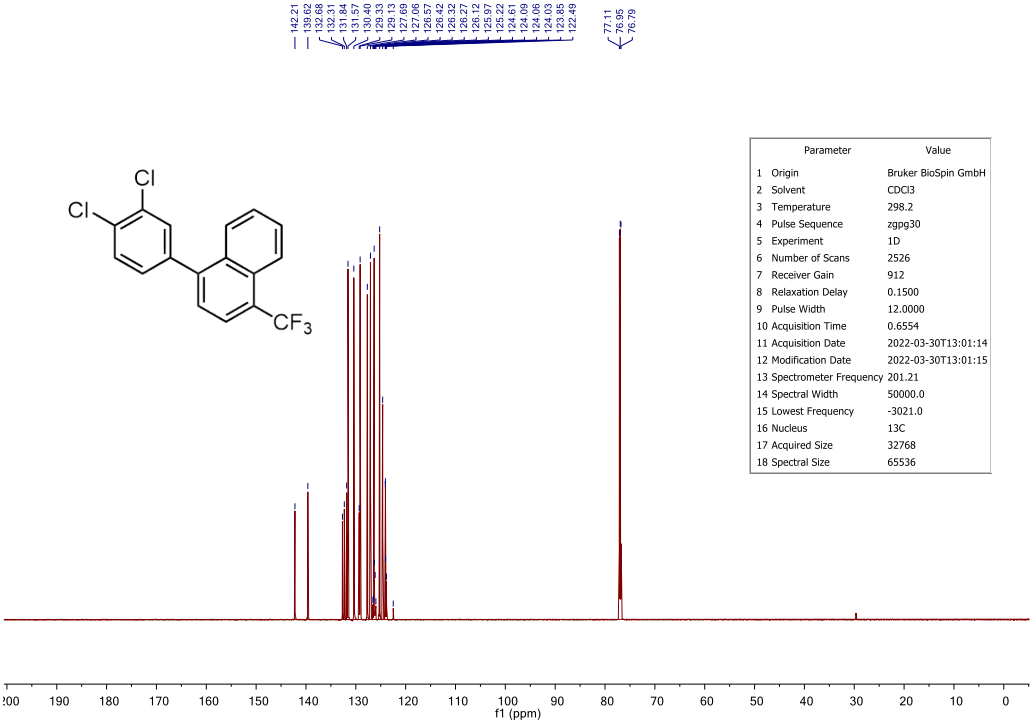
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	456.1
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-04-18T12:04:03
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97294.2
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **22P**



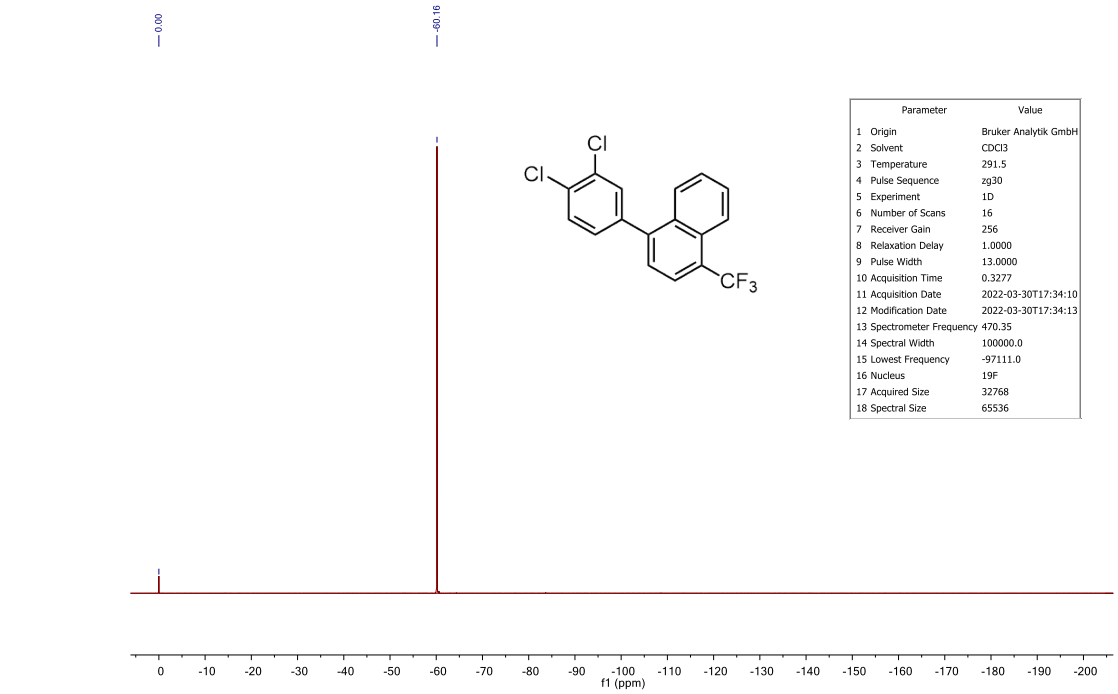
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.2
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	8
7	Receiver Gain	32
8	Relaxation Delay	2.0000
9	Pulse Width	8.0000
10	Acquisition Time	2.6870
11	Acquisition Date	2022-03-30T12:22:45
12	Modification Date	2022-03-30T12:22:45
13	Spectrometer Frequency	800.20
14	Spectral Width	12195.1
15	Lowest Frequency	-1304.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

^{13}C NMR of **22P**

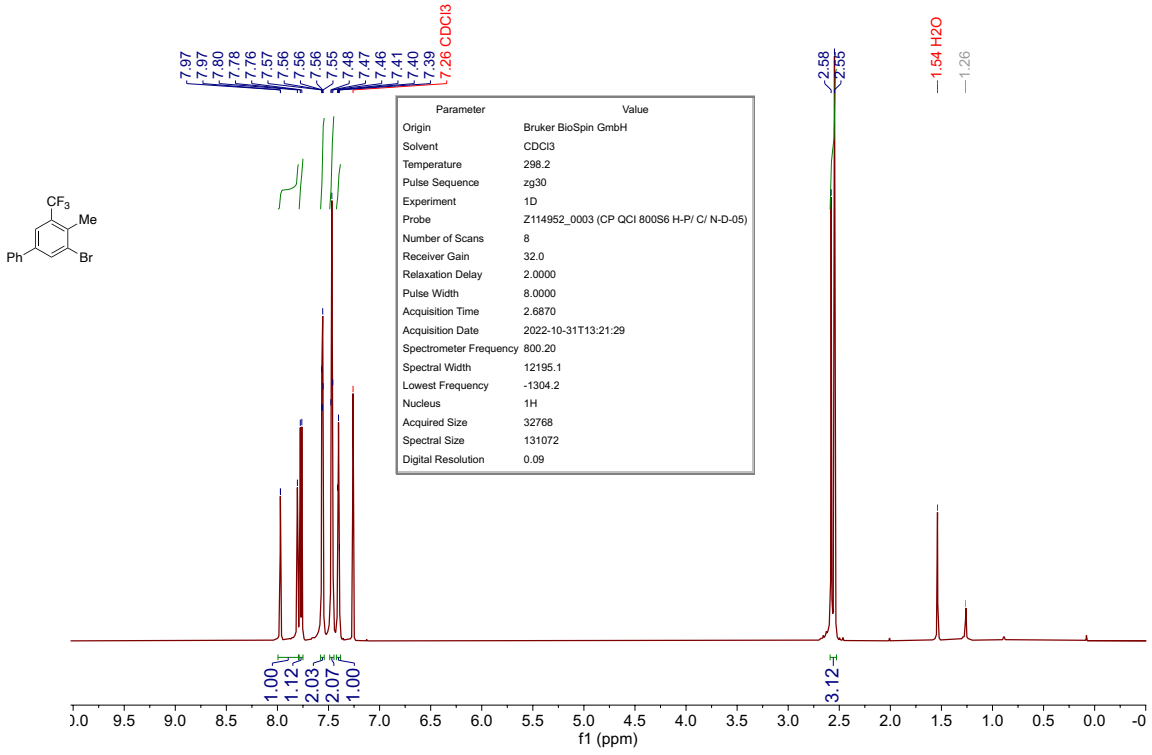


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.2
4	Pulse Sequence	zgpg30
5	Experiment	1D
6	Number of Scans	2526
7	Receiver Gain	912
8	Relaxation Delay	0.1500
9	Pulse Width	12.0000
10	Acquisition Time	0.6554
11	Acquisition Date	2022-03-30T13:01:14
12	Modification Date	2022-03-30T13:01:15
13	Spectrometer Frequency	201.21
14	Spectral Width	50000.0
15	Lowest Frequency	-3021.0
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

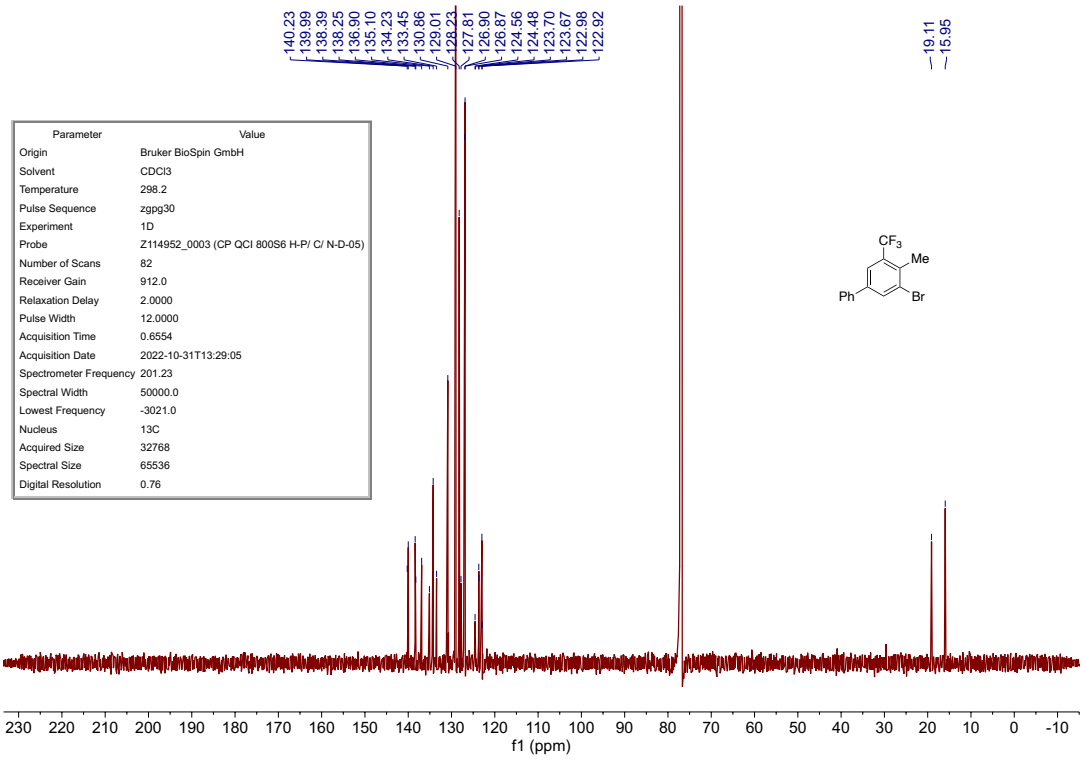
^{19}F NMR of **22P**



^{1}H NMR of **23P**

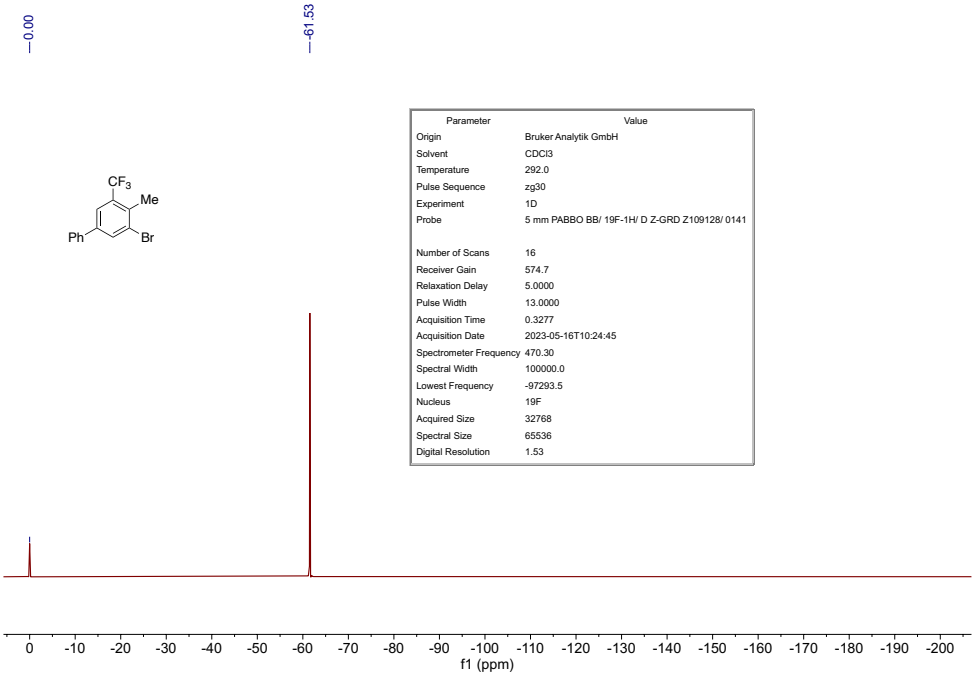


^{13}C NMR of **23P**



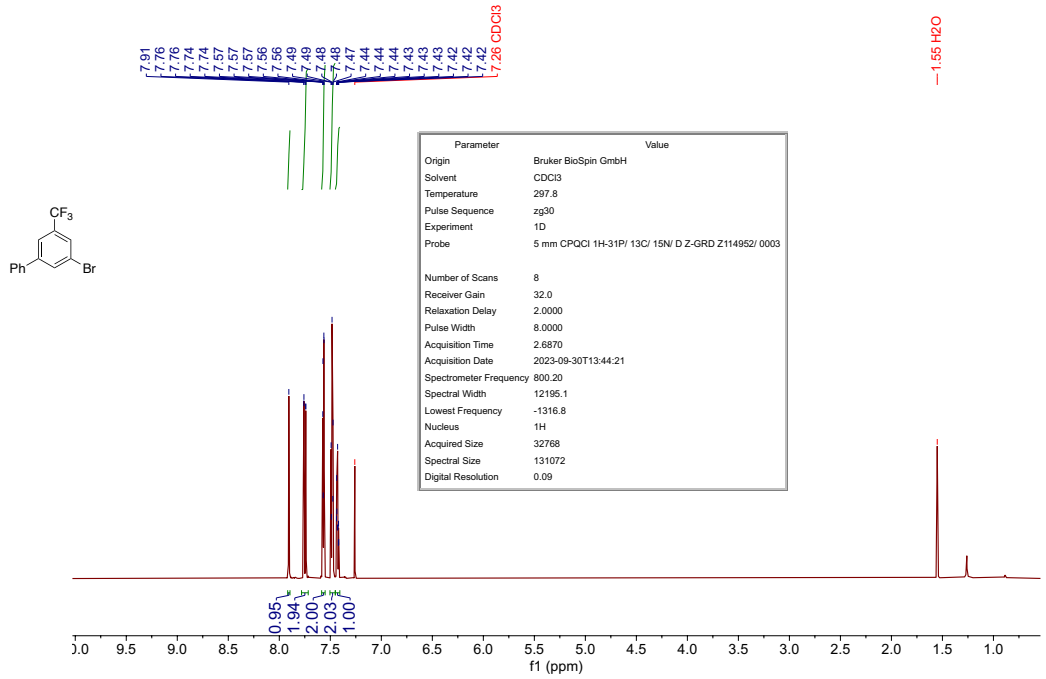
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	82
Receiver Gain	912.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2022-10-31T13:29:05
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{19}F NMR of **23P**

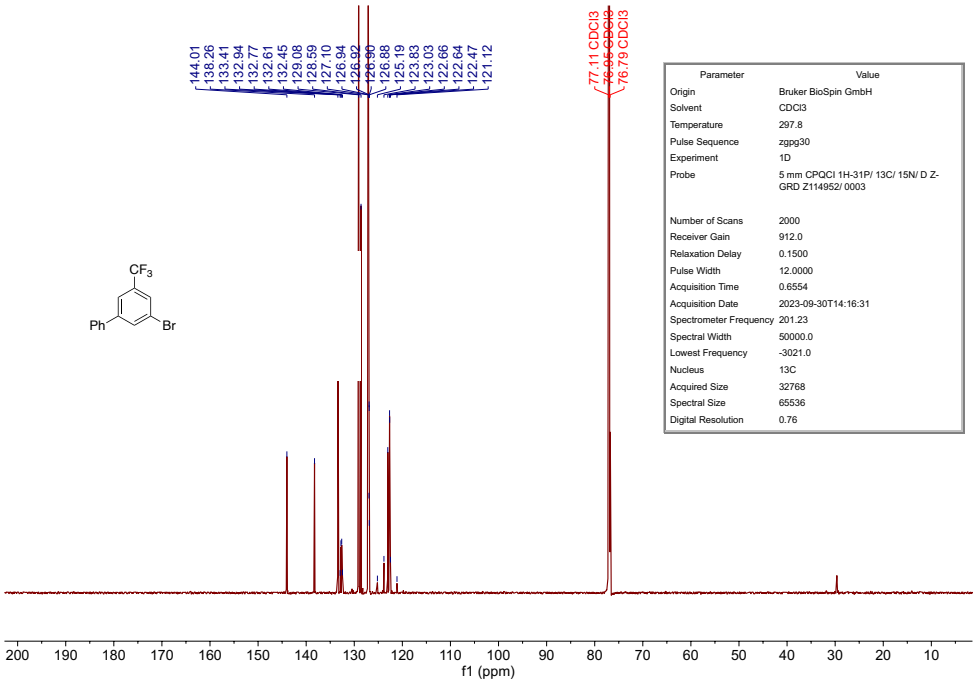


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-05-16T10:24:45
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97293.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

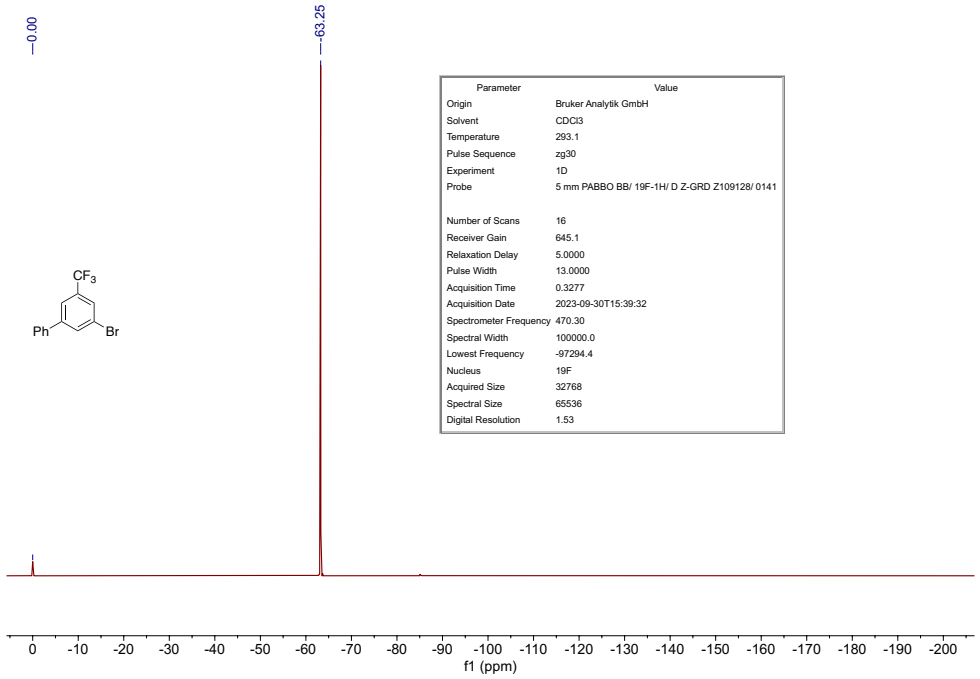
^{1}H NMR of **24P**



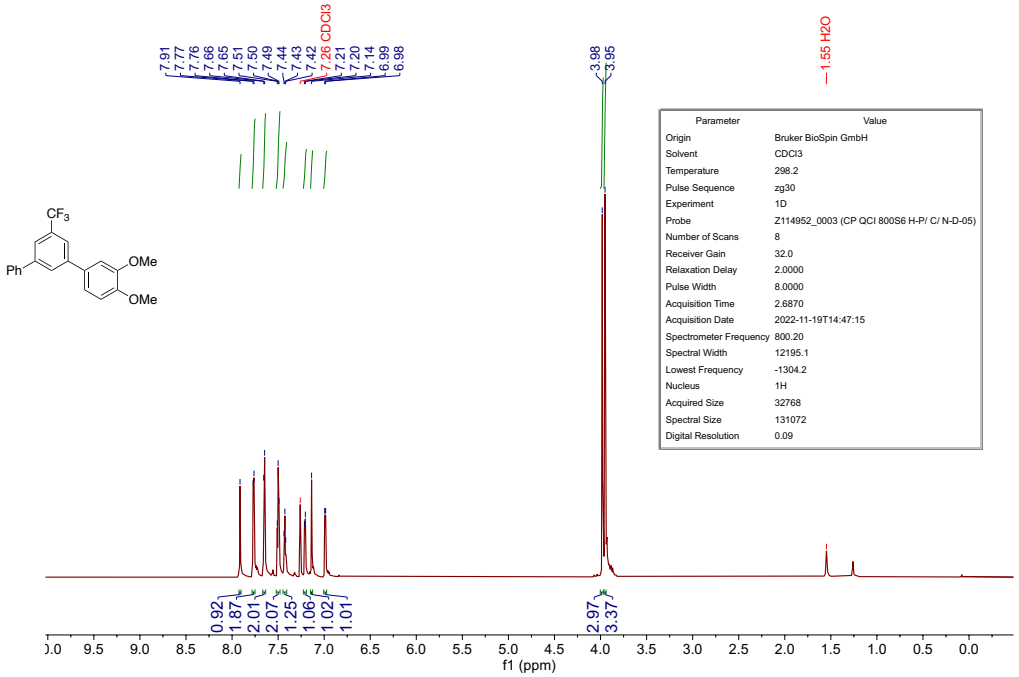
^{13}C NMR of **24P**



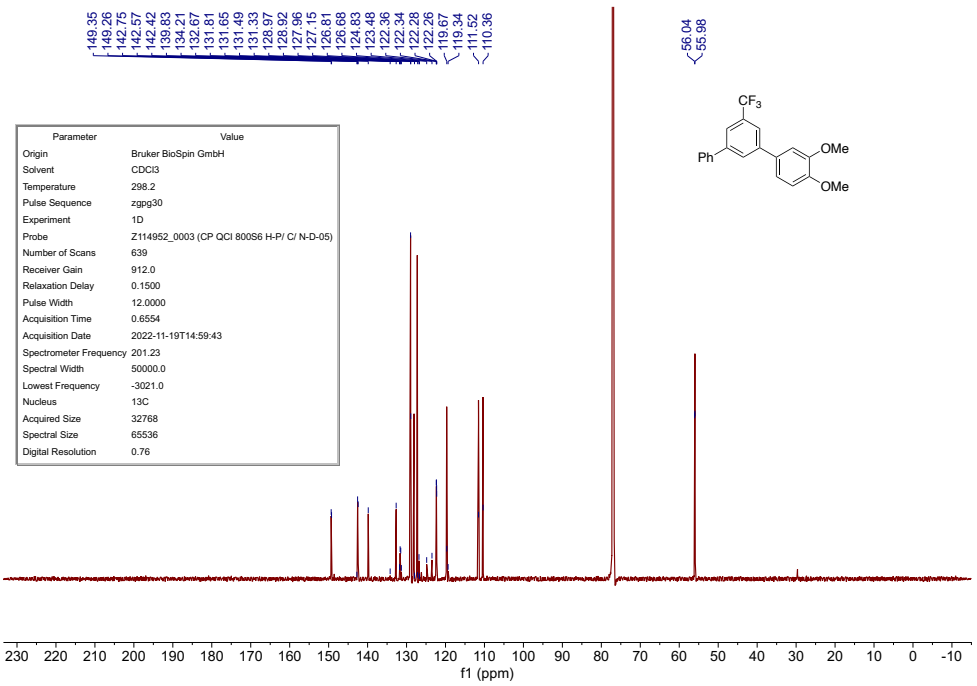
^{19}F NMR of **24P**



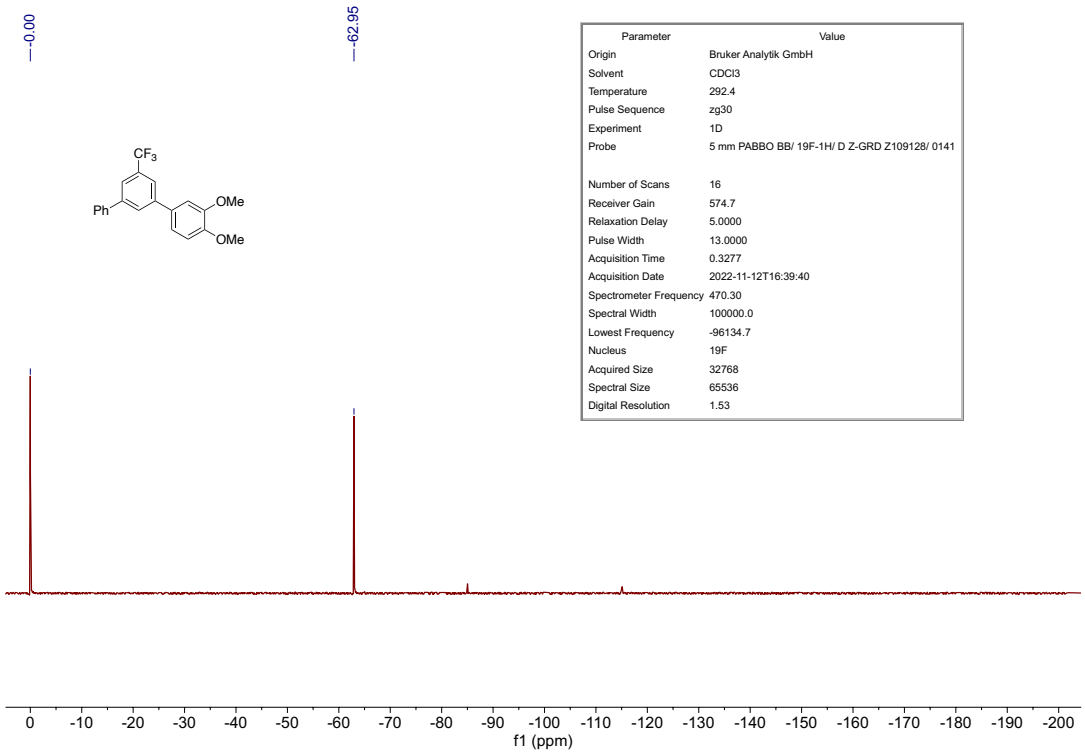
^{1}H NMR of **25P**



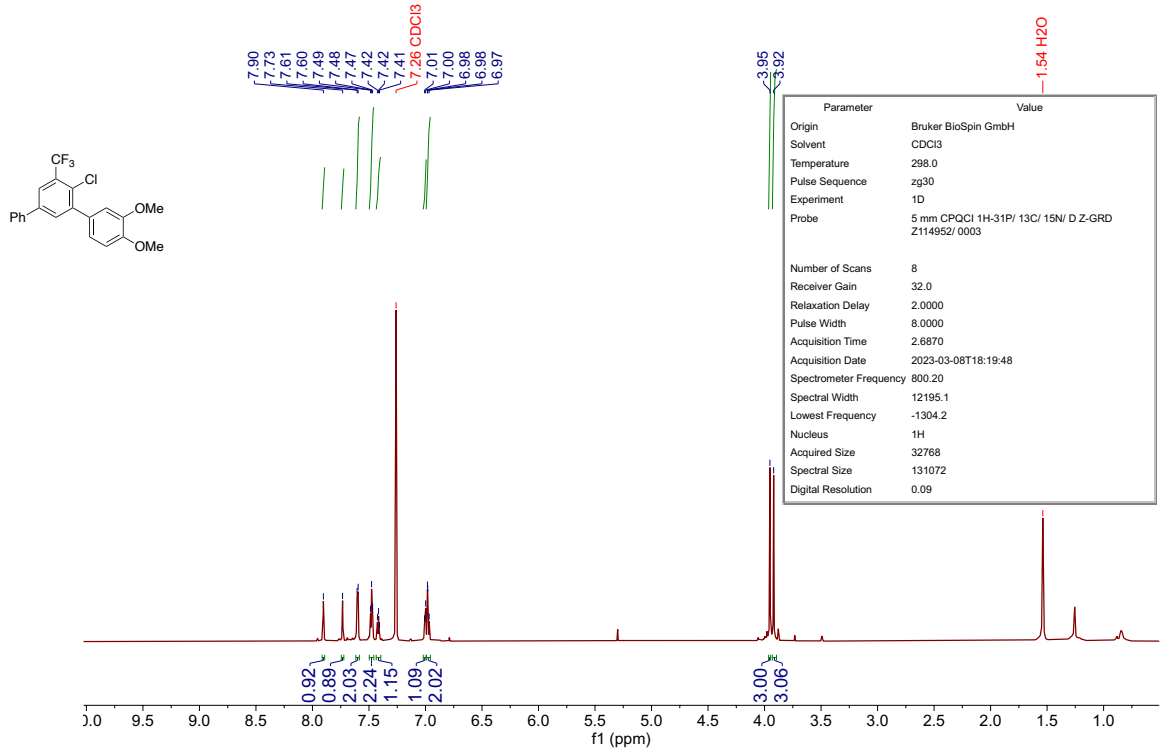
^{13}C NMR of **25P**



^{19}F NMR of **25P**

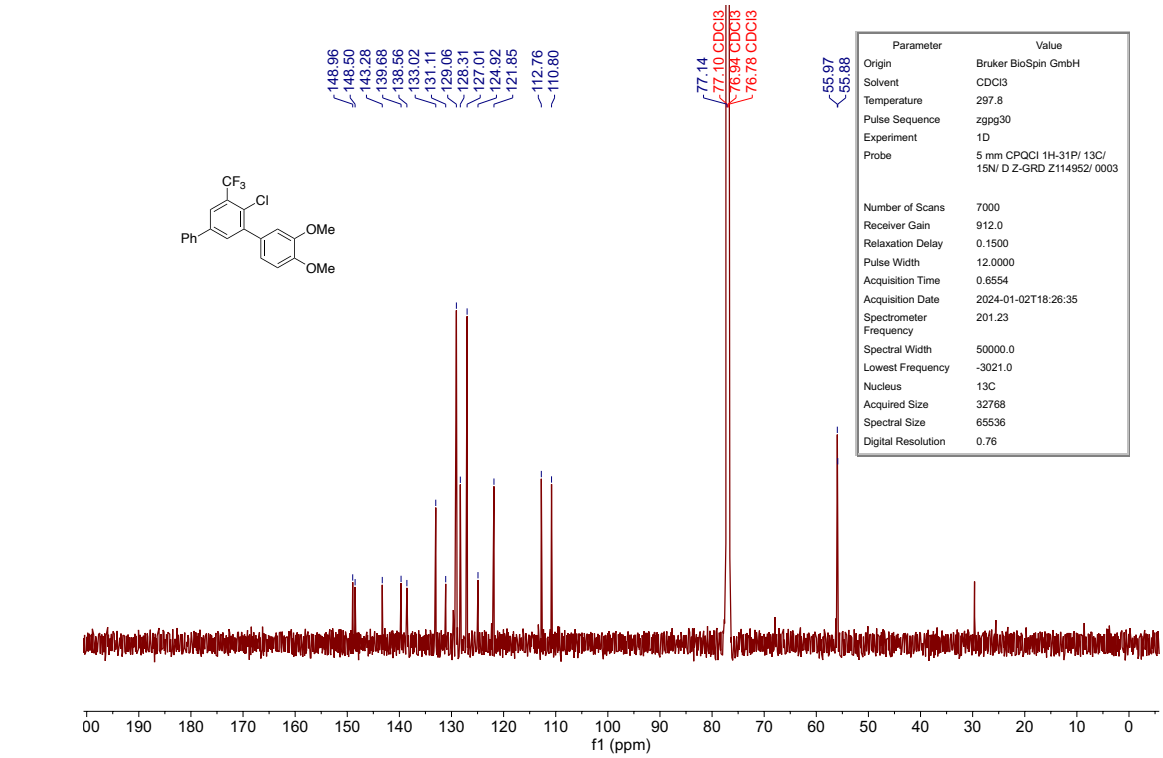


^{1}H NMR of **26P**



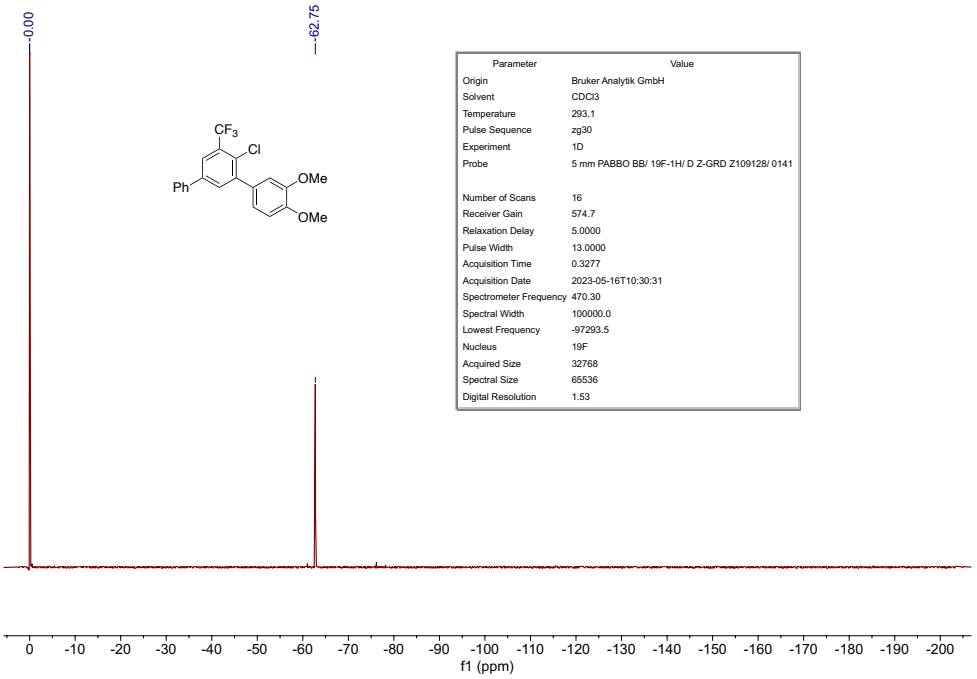
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2023-03-08T18:19:48
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1304.2
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{13}C NMR of **26P**



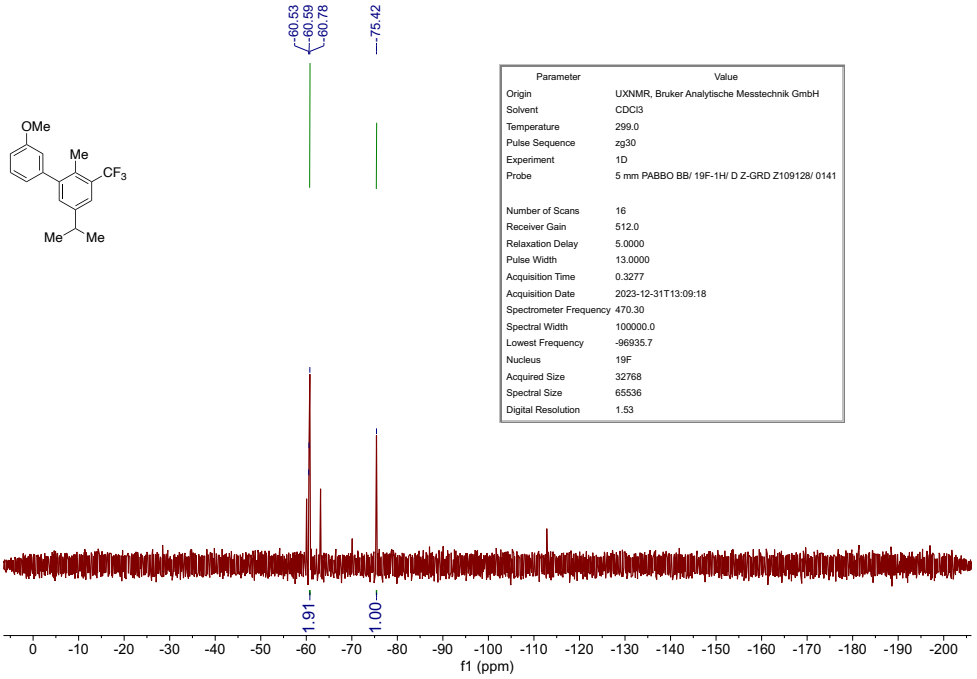
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	7000
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2024-01-02T18:26:35
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

^{19}F NMR of **26P**



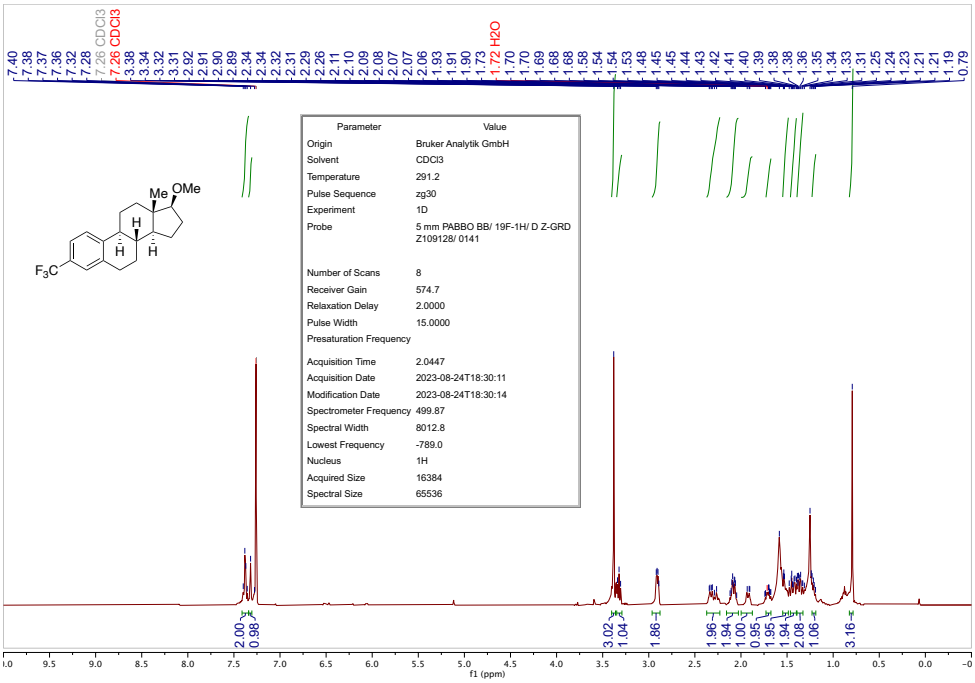
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-05-16T10:30:31
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97293.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{19}F NMR of **27P**

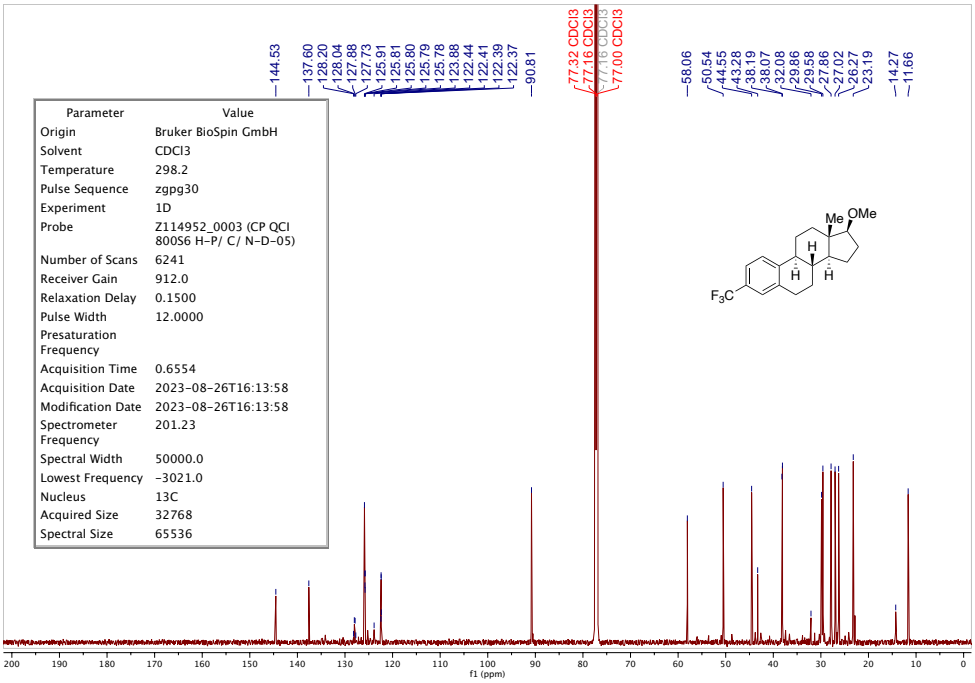


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	299.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-12-31T13:09:18
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-96935.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

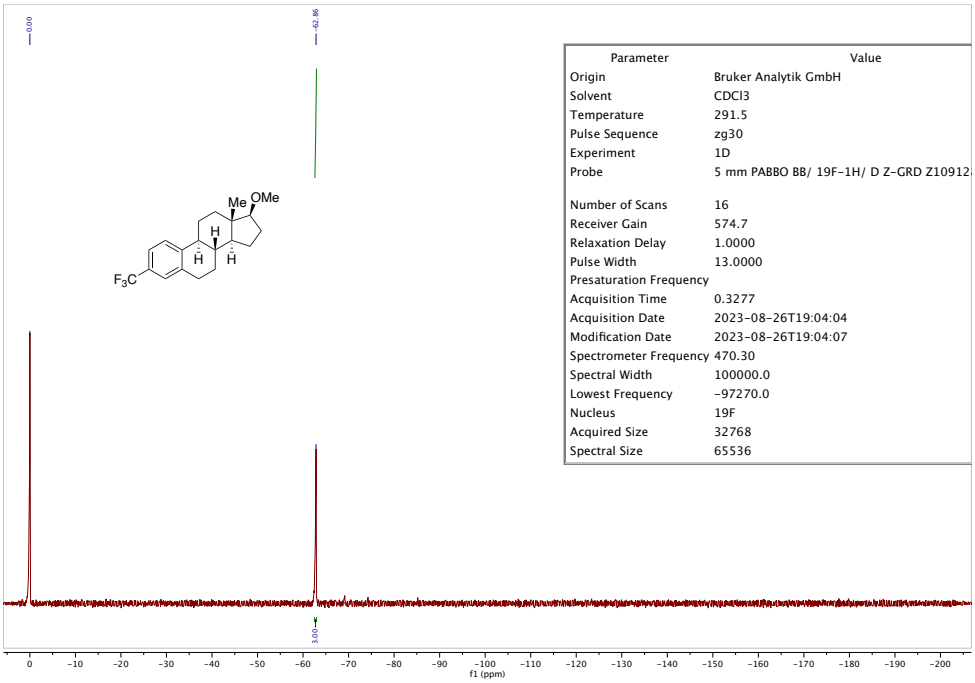
^{1}H NMR of **28P**



^{13}C NMR of **28P**

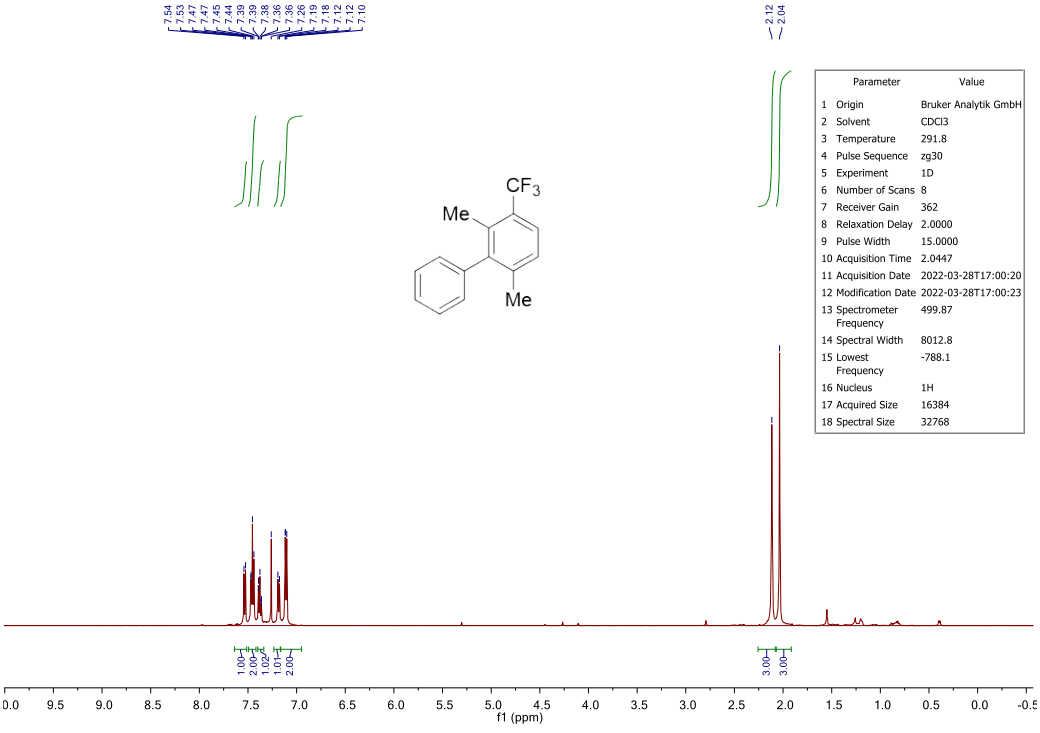


^{19}F NMR of **28P**



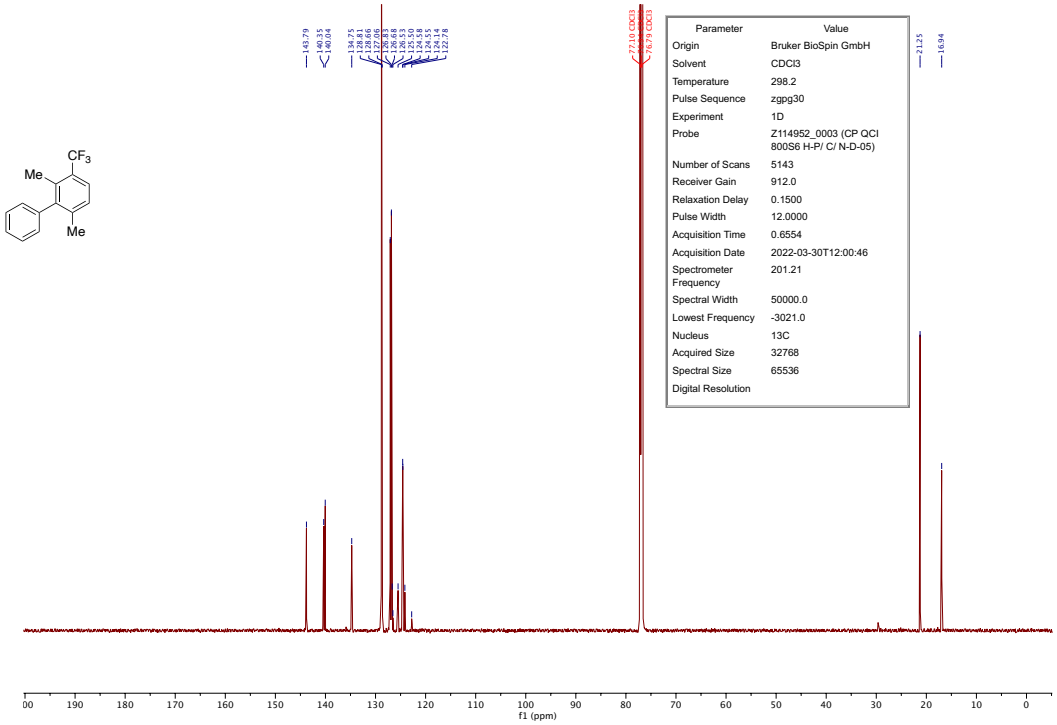
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z10912
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-08-26T19:04:04
Modification Date	2023-08-26T19:04:07
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97270.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

^{1}H NMR of **29P**



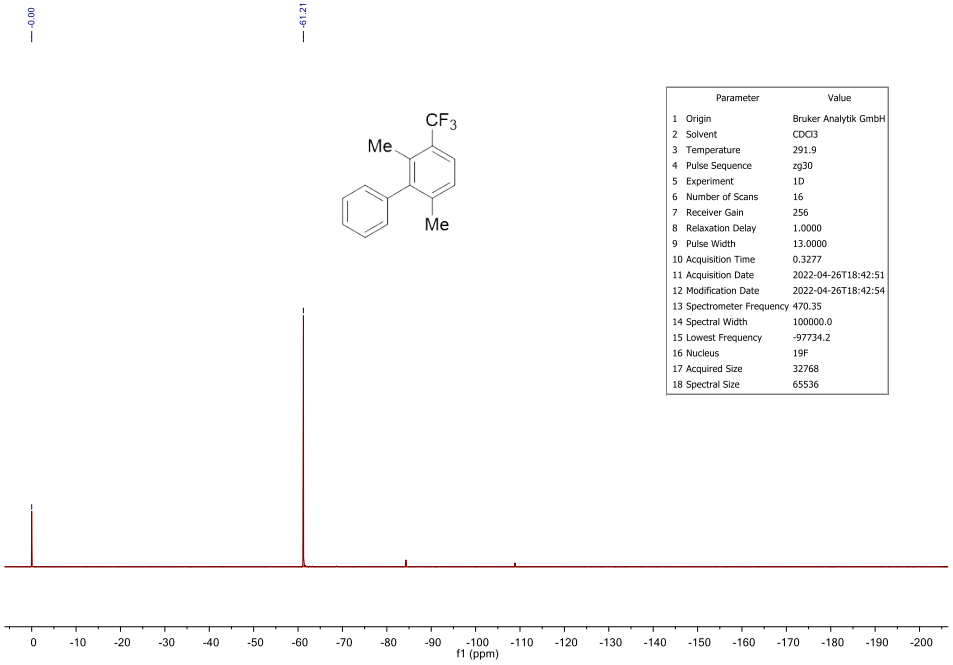
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Solvent	CDCl3
3	Temperature	291.8
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	8
7	Receiver Gain	362
8	Relaxation Delay	2.0000
9	Pulse Width	15.0000
10	Acquisition Time	2.0447
11	Acquisition Date	2022-03-28T17:00:20
12	Modification Date	2022-03-28T17:00:23
13	Spectrometer Frequency	499.87
14	Spectral Width	8012.8
15	Lowest Frequency	-788.1
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	32768

^{13}C NMR of **29P**



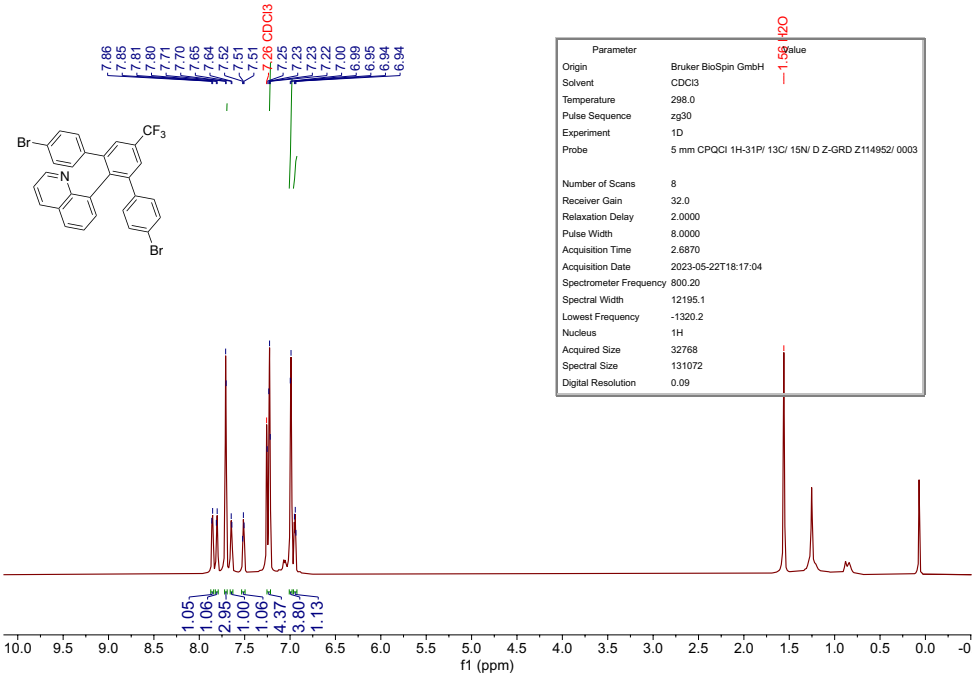
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	5143
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2022-03-30T12:00:46
Spectrometer Frequency	201.21
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	

^{19}F NMR of **29P**

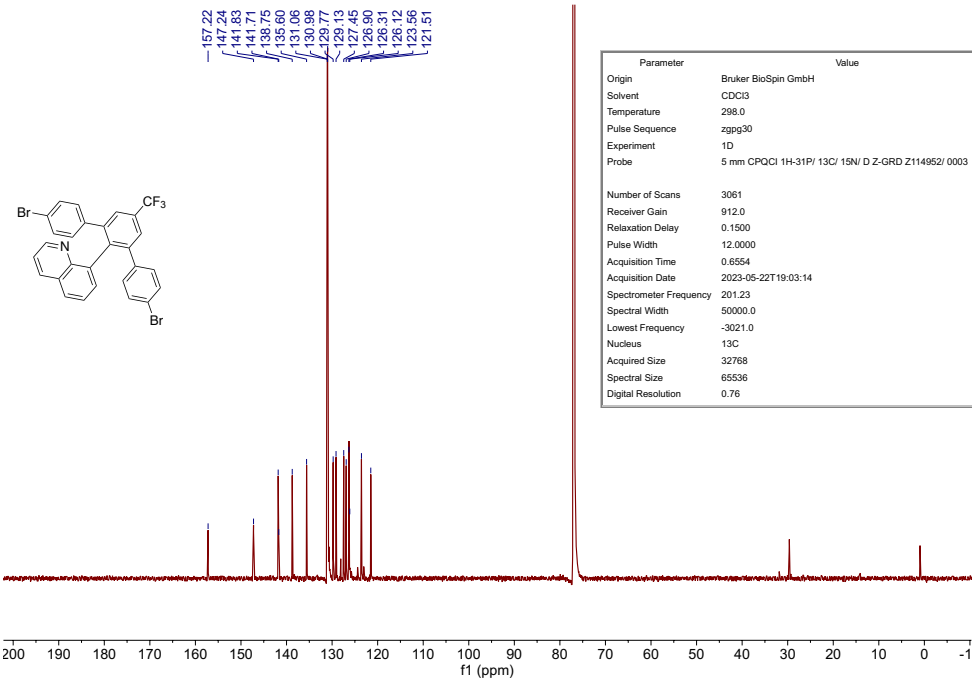


	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Solvent	CDCl3
3	Temperature	291.9
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	16
7	Receiver Gain	256
8	Relaxation Delay	1.0000
9	Pulse Width	13.0000
10	Acquisition Time	0.3277
11	Acquisition Date	2022-04-26T18:42:51
12	Modification Date	2022-04-26T18:42:54
13	Spectrometer Frequency	470.35
14	Spectral Width	100000.0
15	Lowest Frequency	-97734.2
16	Nucleus	19F
17	Acquired Size	32768
18	Spectral Size	65536

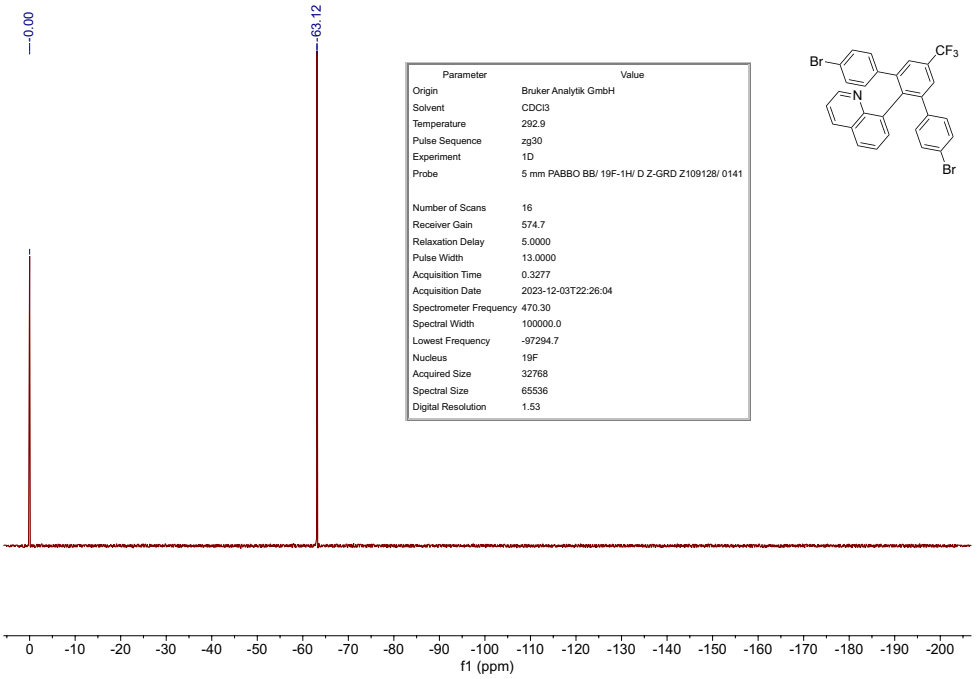
^{1}H NMR of **30P**



^{13}C NMR of **30P**

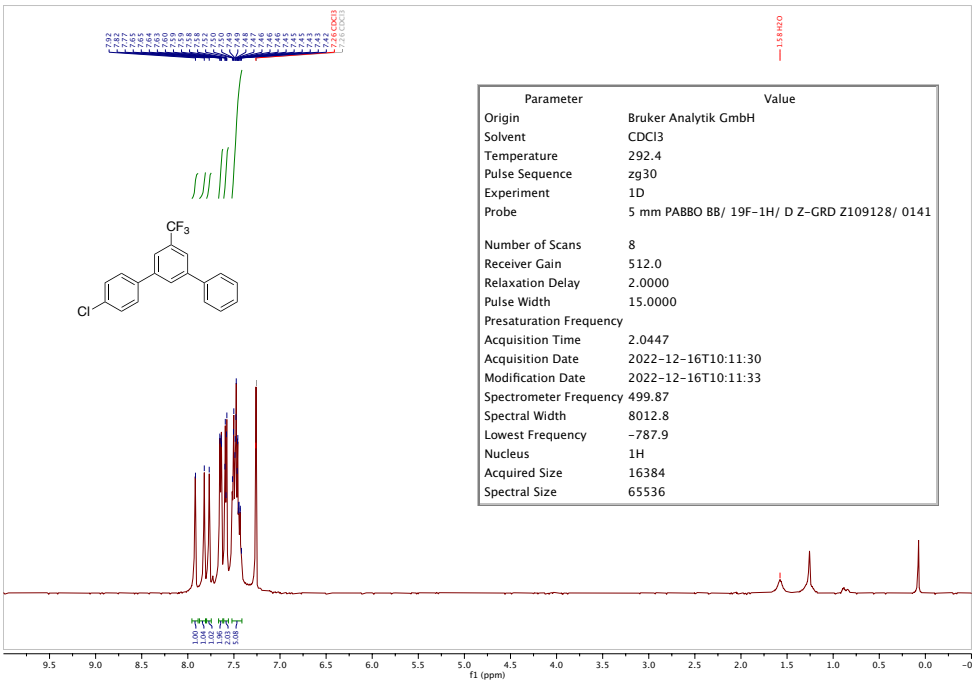


^{19}F NMR of **30P**



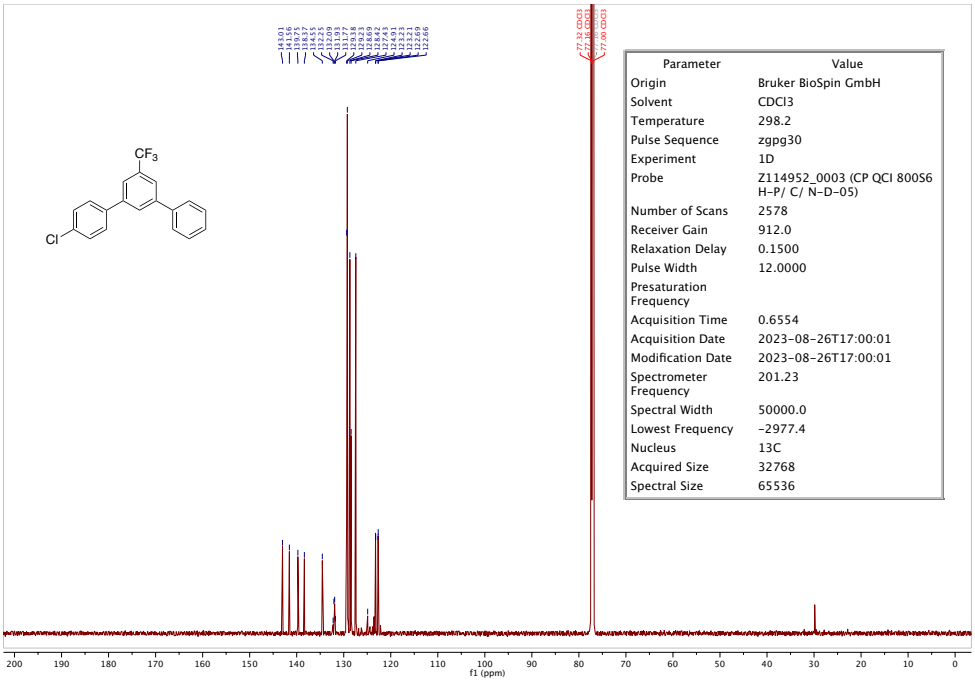
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-12-03T22:26:04
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97294.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

^{1}H NMR of **31P**



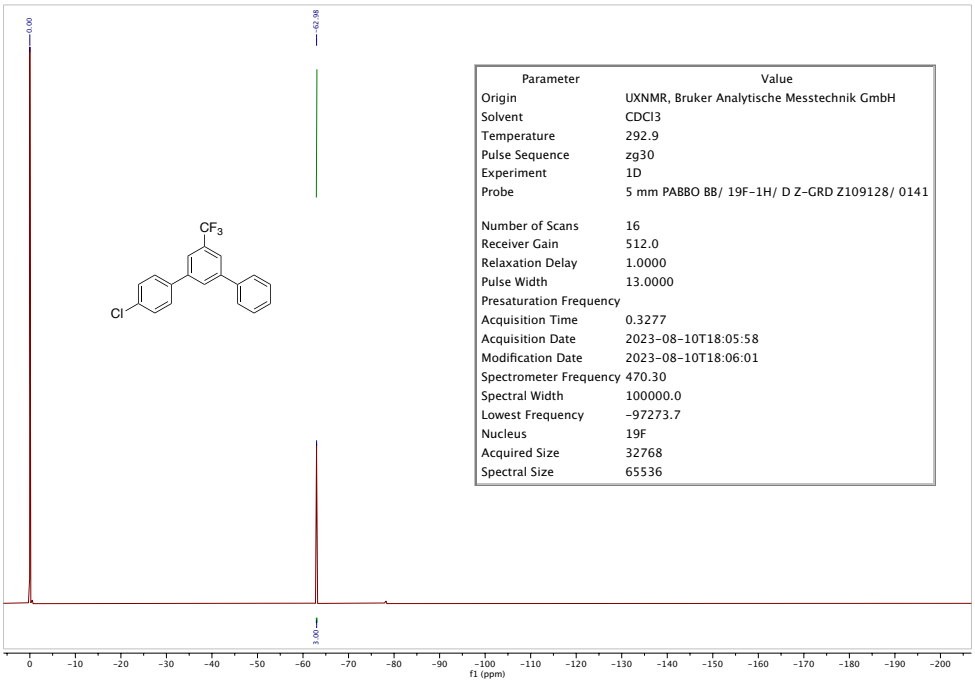
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	512.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2022-12-16T10:11:30
Modification Date	2022-12-16T10:11:33
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-787.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

^{13}C NMR of **31P**



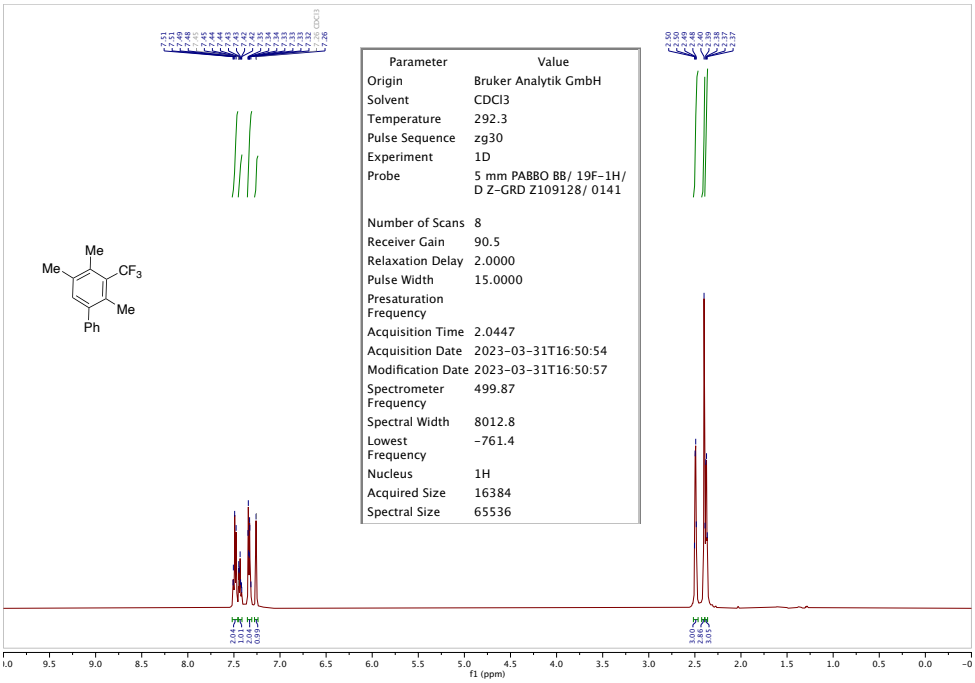
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	2578
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2023-08-26T17:00:01
Modification Date	2023-08-26T17:00:01
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-2977.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

^{19}F NMR of **31P**

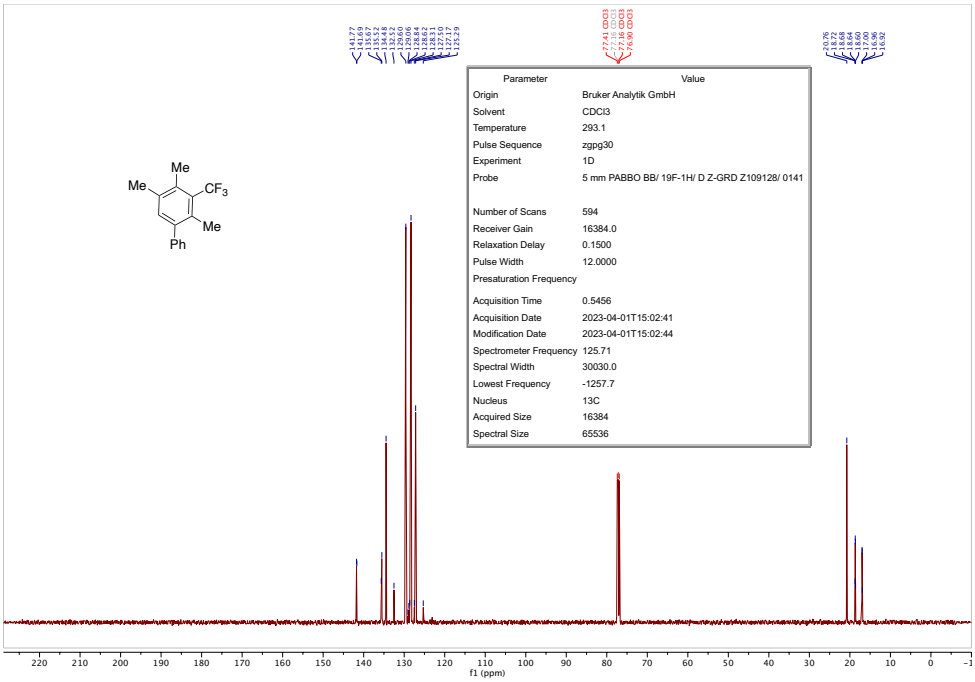


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-08-10T18:05:58
Modification Date	2023-08-10T18:06:01
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97273.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

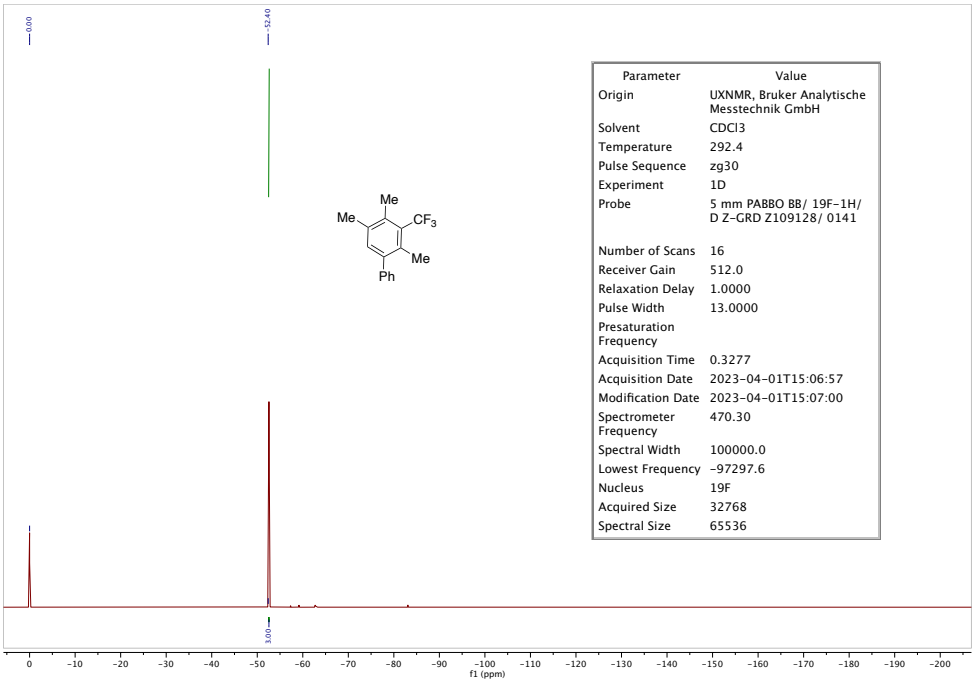
^{1}H NMR of **32P**



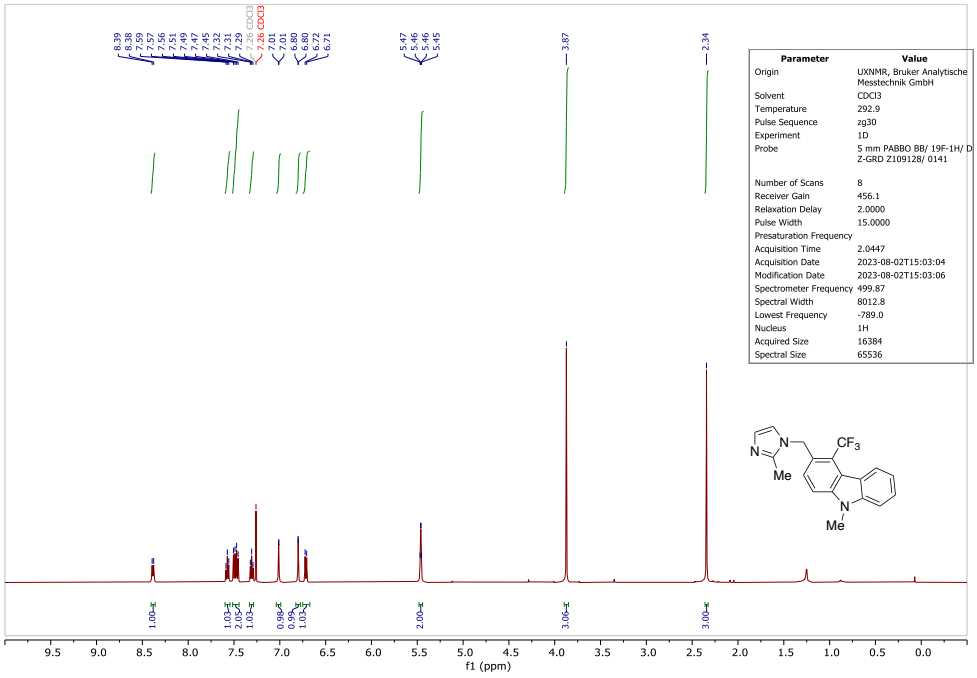
^{13}C NMR of **32P**



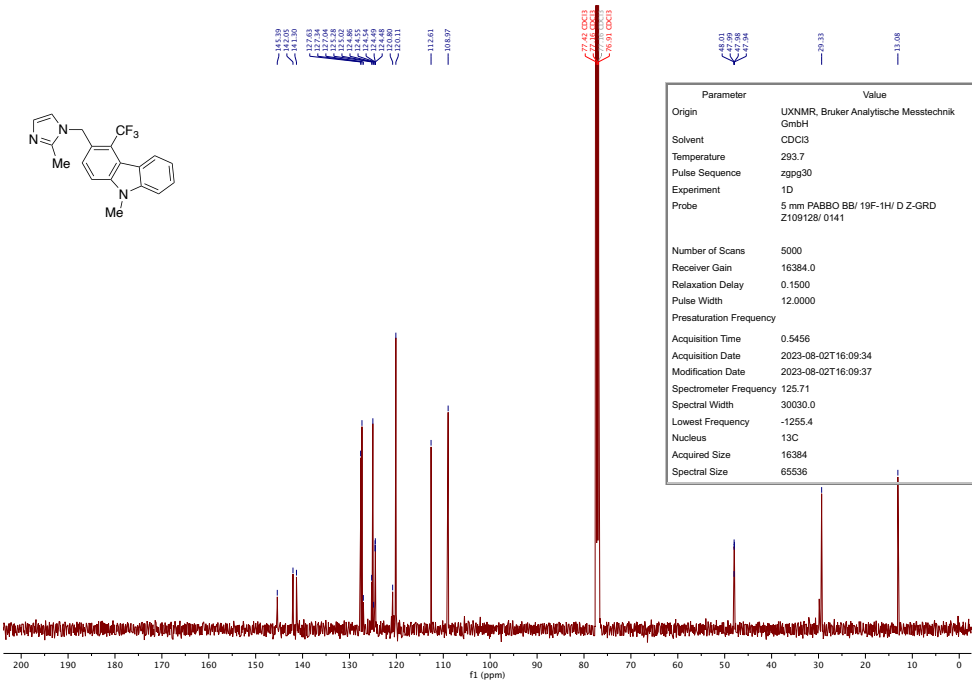
^{19}F NMR of **32P**



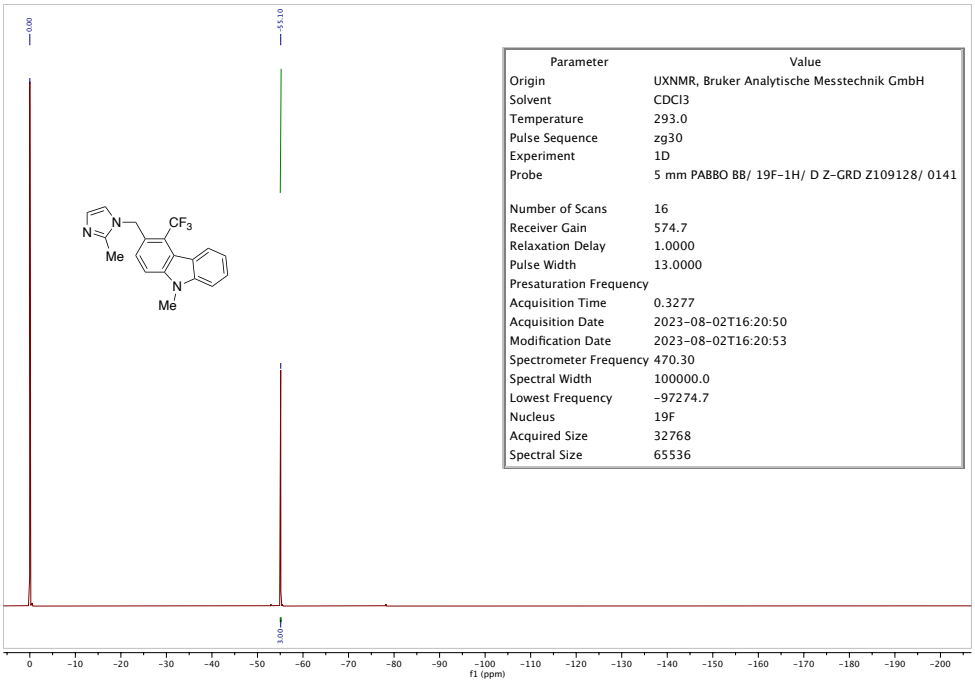
^{1}H NMR of **33P**



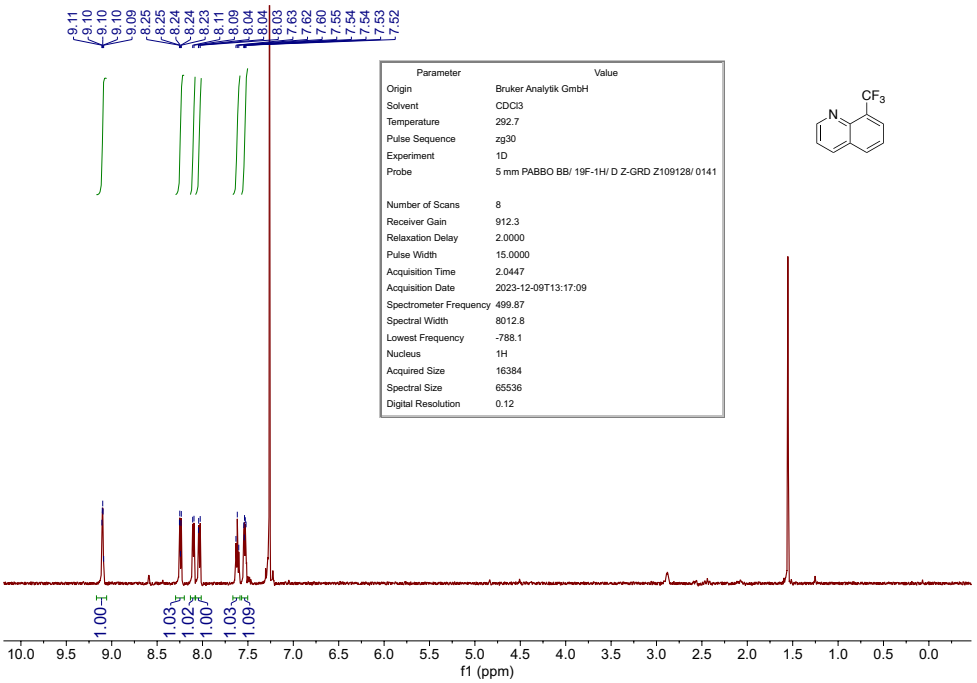
^{13}C NMR of **33P**



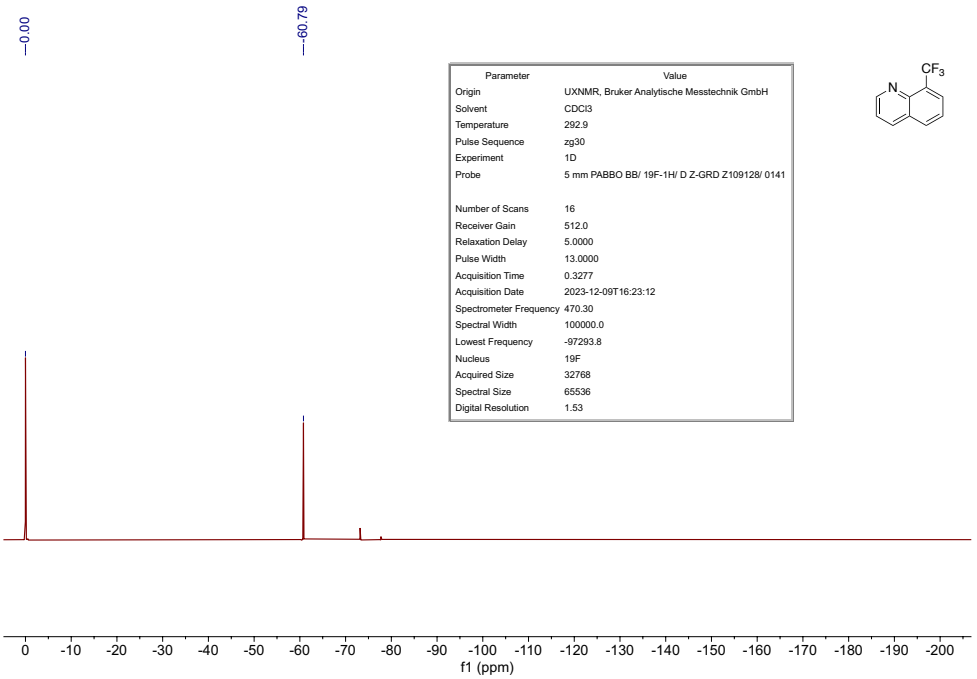
^{19}F NMR of **33P**



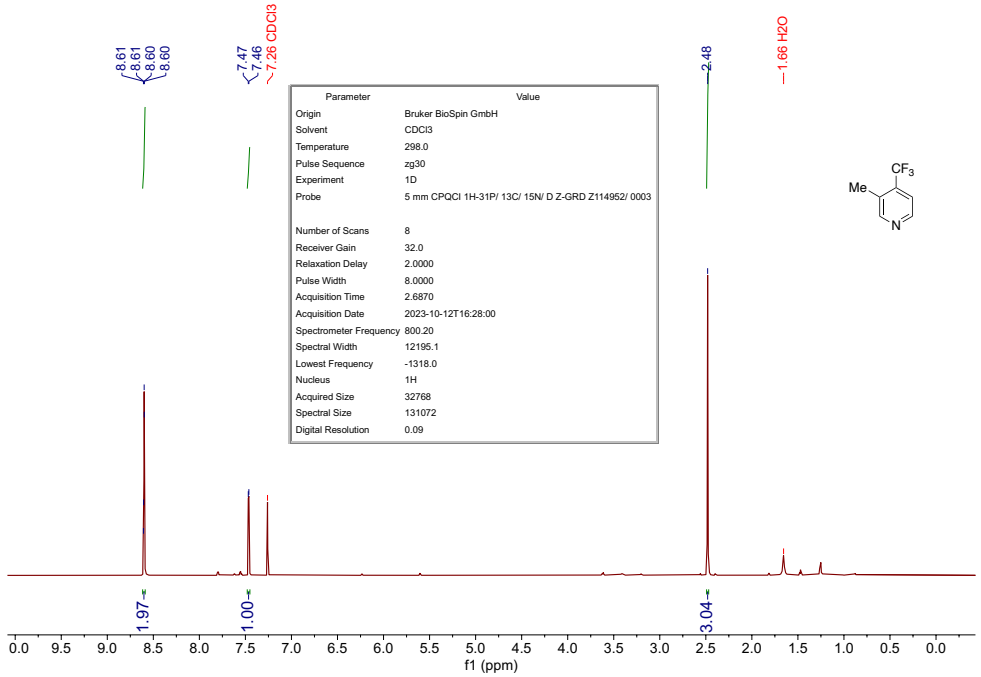
^{1}H NMR of **34P**



^{19}F NMR of **34P**

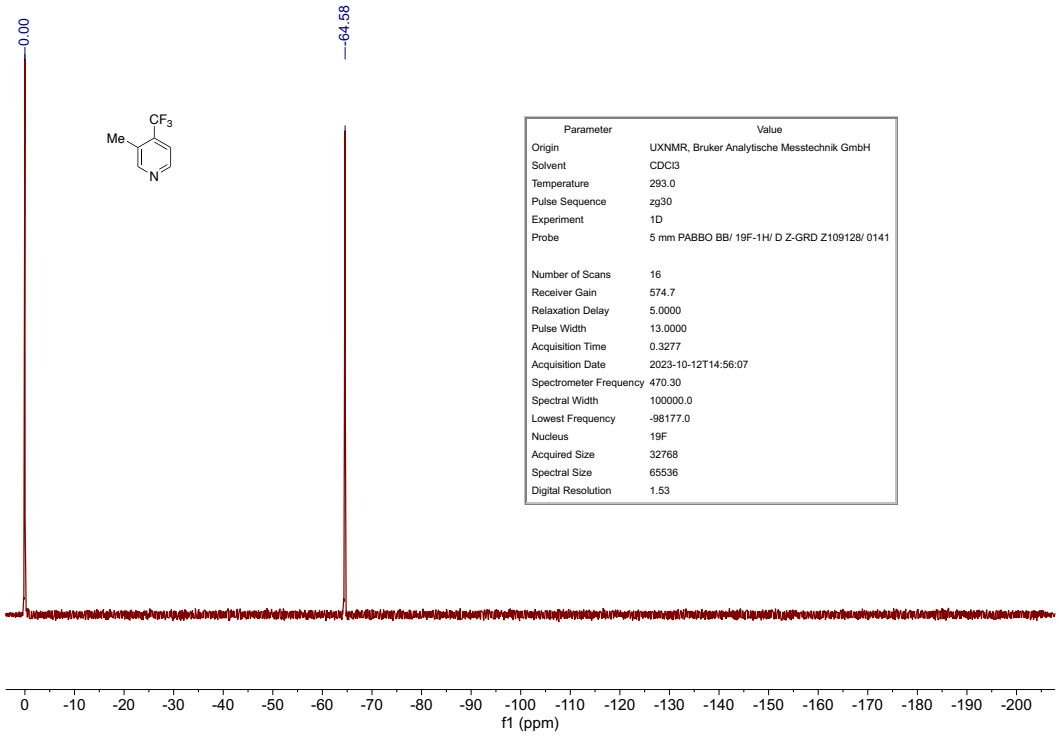


^{1}H NMR of **35P**



Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2023-10-12T16:28:00
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1318.0
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

^{19}F NMR of **35P**



Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-10-12T14:56:07
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-98177.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

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