A Deoxyfluoroalkylation-Aromatization Strategy to Access Fluoroalkyl Arenes

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General Considerations

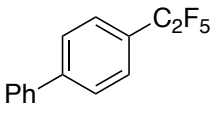
Air- and moisture-sensitive reactions were carried out in oven-dried one-dram vials or 20 mL scintillation vials sealed with poly(tetrafluoroethylene) (PTFE)-lined septa or round bottom flasks fitted with rubber septum under an atmosphere of dry nitrogen (N_2). Plastic syringes equipped with stainless-steel 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 and ^{19}F at 470 MHz) or Bruker Avance III 800 with a QCI cryoprobe (^{1}H at 800 MHz and 13C{^{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). ^{31}P NMR spectra were calibrated against the peak of PPh_3 (4.3 ppm). NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet), coupling constant in hertz (Hz), integration. High-resolution mass determinations were obtained by 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), argon (Ar), water (H_2O), ethyl acetate (EtOAc), diethyl ether (Et_2O), tetrahydrofuran (THF), acetonitrile (MeCN), dichloromethane (DCM), *o*-dichlorobenzene (*o*-DCB), ammonium chloride (NH_4Cl), sodium sulfate (Na_2SO_4), tetra-*n*-butylammonium fluoride (TBAF), cesium fluoride (CsF), magnesium

(Mg^0), Zinc (Zn^0), hexamethylphosphoramide (HMPA), trimethylpentafluoroethylsilane ($TMSC_2F_5$), trimethylheptafluoropropylsilane ($TMSC_3F_7$), perfluorobutyliodide (*n*-C_4F_9I), perfluoropentyliodide (*n*-$C_5F_{11}I$), perfluorohexyliodide (*n*-$C_6F_{13}I$), heptafluoroisopropyliodide (I–$C(CF_3)_2$–F), *n*-butyl lithium (*n*-BuLi) lithiumbis(trimethylsilyl)amide (LiHMDS), thionyl chloride ($SOCl_2$), 4-dimethylamino-pyridine (DMAP), *p*-toluenesulfonic acid monohydrate (PTSA•H_2O), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), room temperature (rt), and melting point (M.P.), aqueous (aq.), saturated (sat.).

Preparation of Ar–C_nF_m Products

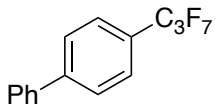


4-(Pentafluoroethyl)-1,1'-biphenyl (3a)

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv. 0.50 mmol). The vial was then brought into a N_2 filled glovebox. CsF (8 mg, 0.1 equiv., 50 µmol) was added followed by the addition of dry *o*-DCB (1.0 mL). The vial was then sealed with a PTFE septa and taken out of the glovebox. $TMSC_2F_5$ (105 µL, 1.20 equiv., 0.600 mmol) was injected via syringe, and the reaction was stirred for 15 h at rt. Reaction progress was monitored by ^{19}F NMR and GC-FID. Upon complete conversion, the vial was opened and PTSA•H_2O (192 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added sequentially. *o*-DCB (1.5 mL) was then added, and the vial was purged with a constant flow of N_2 for 2 mins, and the reaction was stirred for 24 h at 140 °C. The reaction was cooled to rt, whereupon complete conversion and yield were verified by ^{19}F NMR (92% yield). Solvents were removed *in vacuo* using a smart evaporator, and the residue was filtered through a plug of silica using Et_2O as an eluent to remove the baseline impurities. The filtrate was concentrated *in vacuo* using a rotary evaporator. The residue was then purified by normal phase silica gel flash column chromatography with 100% pentane to afford desired product **3a** as a colorless powder (106 mg, 78% yield). ^1H NMR of the isolated compound matched a previous report.[1]

^1H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 4H), 7.63 – 7.62 (m, 2H), 7.51 – 7.48 (m, 2H), 7.44 – 7.41 (m, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –85.2 (s, 3F), –115.2 (s, 2F).

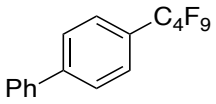


4-(Heptafluoropropyl)-1,1'-biphenyl (3b)

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv. 0.50 mmol). The vial was then brought into a N_2 filled glovebox. CsF (8 mg, 0.1 equiv., 50 µmol) was added followed by the addition of dry *o*-DCB (1.0 mL). The vial was then sealed with a PTFE septa and taken out of the glovebox. $TMSC_3F_7$ (73 mg, 1.2 equiv., 1.5 mmol) was injected via syringe, and the reaction was stirred for 15 h at rt. Reaction progress was monitored by ^{19}F NMR and GC-FID. Upon complete conversion, the vial was opened and PTSA•H_2O (192 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol) were added sequentially. Dry *o*-DCB (1.5 mL) was then added, the vial was purged with a constant flow of N_2 for 2 mins, and the reaction was stirred for 24 h at 140 °C. The reaction was cooled to rt, whereupon complete conversion and yield were verified by ^{19}F NMR (61% yield). Solvents were removed *in vacuo* using a smart evaporator, and the residue was filtered through a plug of silica using Et_2O as an eluent to remove the baseline impurities. The filtrate was concentrated *in vacuo* using a rotary evaporator. The residue was then purified by normal phase silica gel flash column chromatography with 100% pentane to afford desired product **3b** as a colorless powder (85 mg, 53% yield). ^1H NMR of the isolated compound matched a previous report. [2]

^1H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 5H), 7.51 – 7.41 (m, 3H), 7.22 – 7.20 (m, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –80.4 (t, *J* = 8.6 Hz, 3F), –112.0 (q, *J* = 9.0 Hz, 2F), –126.8 (s, 2F).



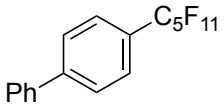
4-(Nonafluorobuty)l-1,1'-biphenyl (3c)

The 1,2-addition reaction was performed with a slight modification to a known procedure.[3] A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol) and lithium bromide (86 mg, 2.0 equiv., 1.0 mmol). The flask was evacuated and backfilled with N_2 (3x). Dry Et_2O (5.0 mL) was then added, followed by a slow addition of *n*-C_4F_9-I (190 µL, 2.2 equiv., 1.1 mmol). The reaction mixture was then cooled to –78 °C, whereupon MeLi (1.6 M in Et_2O, 625 µL, 2.00 equiv., 1.00 mmol) was added slowly, and the reaction was stirred for 2 h at –78 °C under an atmosphere of N_2. The reaction was then quenched

with aq. sat. NH_4Cl (5 mL) at –78 °C and extracted with Et_2O (10 mL x 3). The combined Et_2O layers were dried over anhydrous Na_2SO_4. Reaction progress was monitored by ^{19}F NMR and GC-FID. Et_2O was then removed *in vacuo* using a rotary evaporator, and the resulting solution was transferred to a 20 mL scintillation vial equipped with a stir bar using Et_2O (2 mL). This Et_2O was removed *in vacuo* using a rotary evaporator, and the reaction was charged with PTSA•H_2O (192 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol). The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was added, and the reaction was stirred for 14 h at 140 °C under an atmosphere of N_2. The reaction was then cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (52% yield). The solvents were removed *in vacuo* using a smart evaporator, and the residue was filtered through a plug of silica using Et_2O to remove the baseline impurities. The residue was then purified by normal phase silica gel flash column chromatography with 100% pentane to afford the desired product **3c** as a colorless solid (87 mg, 47% yield). ^1H NMR of the isolated compound matched a previous report.[2]

^1H NMR (800 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.63 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –81.5 (t, *J* = 12.2 Hz, 3F), –111.3 (t, *J* = 16.0 Hz, 2F), –123.1 – –123.3 (m, 2F), –126.1 (t, *J* = 14.5 Hz, 2F).



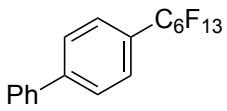
4-(Undecafluoropentyl)-1,1'-biphenyl (3d)

The 1,2-addition reaction was performed with a slight modification to a known procedure.[3] A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol) and lithium bromide (86 mg, 2.0 equiv., 1.0 mmol). The flask was evacuated and backfilled with N_2 (3x). Dry Et_2O (5.0 mL) was then added, followed by a slow addition of I–C_5F_{11} (210 µL, 2.2 equiv., 1.1 mmol). The reaction mixture was then cooled to –78 °C, whereupon MeLi (1.6 M in Et_2O, 625 µL, 2.00 equiv., 1.00 mmol) was added slowly, and the reaction was stirred for 2 h at –78 °C under an atmosphere of N_2. The reaction was then quenched with aq. sat. NH_4Cl (5 mL) and extracted with Et_2O (10 mL x 3). The combined Et_2O layers were dried over anhydrous Na_2SO_4. Conversion was checked by ^{19}F NMR. Et_2O was then removed *in vacuo* using a rotary evaporator, and the resulting solution was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar using Et_2O (2 mL). This Et_2O was removed *in vacuo* using a rotary evaporator, and the reaction was charged with PTSA•H_2O (192 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol). The vial was evacuated and backfilled with N_2

(3x). Dry *o*-DCB (2.5 mL) was added, and the reaction was stirred for 14 h at 140 °C under an atmosphere of N_2. The reaction was then cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (94% yield). The solvents were removed *in vacuo* using a smart evaporator, and the residue was filtered through a plug of silica using Et_2O to remove the baseline impurities. The residue was then purified by normal phase silica gel flash column chromatography with 100% pentane to afford the desired product **3d** as a colorless solid (154 mg, 73% yield). ^1H NMR of the isolated compound matched a previous report.[2]

^1H NMR (800 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –81.3 (t, *J* = 10.7 Hz, 3F), –111.1 (t, *J* = 14.5 Hz, 2F), –122.6 (d, *J* = 102.2 Hz, 4F), –126.7 (s, 2F)



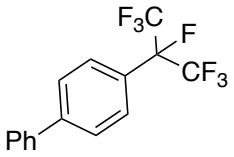
4-(Tridecafluorohexyl)-1,1'-biphenyl (3e)

The 1,2-addition reaction was performed with a slight modification to a known procedure.[3] A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol) and lithium bromide (86 mg, 2.0 equiv., 1.0 mmol). The flask was evacuated and backfilled with N_2 (3x). Dry Et_2O (5.0 mL) was then added, followed by a slow addition of $I–C_6F_{13}$ (238 µL, 2.20 equiv., 1.10 mmol). The reaction mixture was then cooled to –78 °C, whereupon MeLi (1.6 M in Et_2O, 625 µL, 2.00 equiv., 1.00 mmol) was added slowly, and the reaction was stirred for 2 h at –78 °C under an atmosphere of N_2. The reaction was then quenched with aq. sat. NH_4Cl (5 mL) and extracted with Et_2O (10 mL x 3). The combined Et_2O layers were dried over anhydrous Na_2SO_4. Conversion was checked by ^{19}F NMR. Et_2O was then removed *in vacuo* using a rotary evaporator, and the resulting solution was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar using Et_2O (2 mL). This Et_2O was removed *in vacuo* using a rotary evaporator, and the reaction was charged with PTSA•H_2O (192 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol). The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was added, and the reaction was stirred for 14 h at 140 °C under an atmosphere of N_2. The reaction was then cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (99% yield). The solvents were removed *in vacuo* using a smart evaporator, and the residue was filtered through a plug of silica using Et_2O to remove the baseline impurities. The residue was then purified by normal phase silica gel flash column

chromatography with 100% pentane to afford the desired product **3e** as a colorless solid (195 mg, 83% yield). ^{1}H NMR of the isolated compound matched a previous report.[4]

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 10.0 Hz, 2H), 7.48 (t, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 5.9 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –81.2 (t, *J* = 11.4 Hz, 3H), –111.1 (t, *J* = 15.3 Hz, 2H), –122.0 (s, 2F), –122.3 (s, 2F), –123.3 (s, 2F), –126.7 (s, 2F).

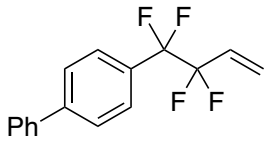


4-(Perfluoropropan-2-yl)-1,1'-biphenyl (3f)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.5 mmol). The flask was evacuated and backfilled with N_2 (3x). Dry Et_2O (2.5 mL) was then added followed by the addition of I–$C(CF_3)_2$–F (178 µL, 2.50 equiv., 1.00 mmol). The reaction mixture was cooled to –78 °C, whereupon MeLi (1.6 M in Et_2O, 937 µL, 3.00 equiv., 1.50 mmol) was added slowly, and the reaction was stirred for 2 h at –78 °C under an atmosphere of N_2. The reaction was then quenched with aq. sat. NH_4Cl (5 mL) and extracted with Et_2O (10 mL x 3). The combined Et_2O layers were dried over anhydrous Na_2SO_4. Conversion was checked by GC-FID, and yield was calculated by ^{19}F NMR. Et_2O was then removed *in vacuo* using a rotary evaporator, and the resulting solution was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar using Et_2O (2 mL). This Et_2O was removed *in vacuo* using a rotary evaporator, and the reaction was charged with PTSA•H_2O (192 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol). The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was added, and the reaction was stirred for 36 h at 140 °C under an atmosphere of N_2. The reaction was then cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (51% yield). The solvents were evaporated *in vacuo* using smart evaporator, and the residue was again filtered through a small plug of silica using Et_2O as eluent to remove the baseline impurities. The residue was purified by normal phase silica gel flash chromatography with 100% pentane to deliver the desired product **3f** as a colorless solid (72 mg, 45% yield). ^{1}H NMR of the isolated compound matched a previous report.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 4H), 7.64 – 7.60 (m, 2H), 7.48 (ddd, *J* = 7.8, 6.3, 1.3 Hz, 2H), 7.44 – 7.39 (m, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –76.2 (d, *J* = 7.8 Hz, 6F), –182.9 (hept, *J* = 7.8 Hz, 1F).



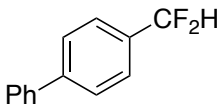
4-(1,1,2,2-Tetrafluorobut-3-en-1-yl)-1,1'-biphenyl (3g)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.5 mmol). The flask was evacuated and backfilled with N_2 (3x). Dry Et_2O (2.5 mL) was then added followed by the addition of 4-bromo-3,3,4,4-tetrafluorobut-1-ene (150 µL, 2.2 equiv., 1.1 mmol). The reaction mixture was then cooled to –78 °C, whereupon MeLi (1.6 M in Et_2O, 625 µL, 2.00 equiv., 1.00 mmol) was added slowly, and the reaction was stirred for 2 h at –78 °C under an atmosphere of N_2. The reaction was then quenched with aq. sat. NH_4Cl (5 mL) and extracted with Et_2O (10 mL x 3). Conversion was checked by ^{19}F NMR. The combined Et_2O layers were dried over anhydrous Na_2SO_4. Et_2O was then removed *in vacuo* using a rotary evaporator, and the resulting solution was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar using Et_2O (2 mL). This Et_2O was removed *in vacuo* using a rotary evaporator, and the reaction was charged with PTSA•H_2O (192 mg, 2.00 equiv., 1.00 mmol) and DDQ (341 mg, 3.00 equiv., 1.50 mmol). The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was added, and the reaction was stirred for 14 h at 140 °C under an atmosphere of N_2. The reaction was then cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (47% yield). The solvents were removed *in vacuo* using a smart evaporator, and the residue was filtered through a plug of silica using Et_2O to remove the baseline impurities. The residue was then purified by normal phase silica gel flash column chromatography with 100% pentane to afford the desired product **3g** as a colorless solid (64 mg, 46% yield). ^1H NMR of the isolated compound matched a previous report.[6]

^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.66 – 7.59 (m, 4H), 7.48 (ddd, *J* = 7.9, 6.3, 1.3 Hz, 2H), 7.45 – 7.37 (m, 1H), 6.06 (dq, *J* = 17.4, 11.8 Hz, 1H), 5.87 (dt, *J* = 17.3, 2.3 Hz, 1H), 5.72 (d, *J* = 11.1 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –112.3 (s, 2F), –114.8 (d, *J* = 12.2 Hz, 2F).

Preparation of Ar–CF_2R and Perfluorophenyl Arene Compounds

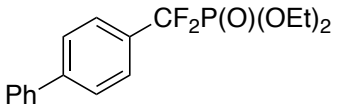


4-(Difluoromethyl)-1,1'-biphenyl (3h)

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol). The vial was brought into a N_2 filled glovebox, where CsF (15 mg, 0.20 equiv., 0.10 mmol) and dry THF (1 mL) were added in sequence. The vial was taken out of the glovebox, where HMPA (435 µL, 5.00 equiv., 2.50 mmol) and (difluoromethyl)(trimethyl)silane (140 µL, 2.0 equiv., 1.0 mmol) were injected in sequence. The resulting mixture was subsequently stirred at 60 °C for 48 h under an Ar-filled balloon. TBAF (1 M in THF, 1.5 mL, 3.0 equiv., 1.5 mmol) was added at the end of this period, and the mixture was stirred for another 1 h. THF was then removed *in vacuo* using a rotary evaporator, and the reaction was diluted with H_2O and extracted with EtOAc (10 mL x 3). The combined EtOAc layers were dried over anhydrous Na_2SO_4, then concentrated *in vacuo* using a rotary evaporator. The resulting residue was dissolved in Et_2O (1 mL) and transferred to a 25 mL round bottom flask equipped with a magnetic stir bar. The Et_2O was removed *in vacuo* using a rotary evaporator. DMAP (6.0 mg, 0.10 equiv., 0.050 mmol) was added and the flask was evacuated and backfilled with N_2 (3x). Dry THF (1 mL) was then added followed by a sequential addition of pyridine (120 µL, 3.0 equiv., 1.5 mmol), and $SOCl_2$ (110 µL, 3.0 equiv., 1.5 mmol). The reaction was then stirred at 50 °C for 18 h under an atmosphere of N_2. After 18 h, complete conversion was verified by ^{19}F NMR. The crude reaction mixture was then filtered through a plug of silica with Et_2O as an eluent. The solvents were removed *in vacuo* using a rotary evaporator, and the resulting residue was dissolved in Et_2O (2 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stir bar. This Et_2O was removed *in vacuo* using a rotary evaporator and DDQ (340 mg, 3.00 equiv., 1.50 mmol) was added. The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was then added, and the reaction was stirred for 14 h at 120 °C under an atmosphere of N_2. The reaction was cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (49% yield). The solvents were removed by a smart evaporator, and the residue was filtered through a plug of silica using Et_2O as eluent to remove the baseline impurities. The residue was then purified by normal phase silica gel flash column chromatography with 100% pentane to afford the desired compound (46 mg, 45% yield) as a colorless solid. ^1H NMR of the isolated compound matched a previous report.[7]

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (dd, *J* = 12.3, 7.8 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 6.83 – 6.60 (t, *J* = 56.5, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –110.8 (d, *J* = 56.5 Hz, 2F).



Diethyl ([1,1'-biphenyl]-4-yldifluoromethyl)phosphonate (3i)

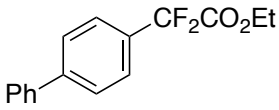
A 25 mL round bottom flask equipped with a magnetic stir bar was charged with diisopropylamine (77 µL, 1.1 equiv., 550 µmol). Dry THF (5 mL) was then added, and the flask was cooled to 0 °C. A solution of *n*-BuLi (2.1 M in hexanes, 260 µL, 1.1 equiv., 550 µmol) was added in a dropwise fashion. The mixture was stirred at 0 °C for 20 min and then cooled to –78 °C. A solution of diethyl(difluoromethyl)phosphonate (78 µL, 1.0 equiv., 0.5 mmol) was added in a dropwise fashion, followed by stirring at –78 °C for 30 min. An anhydrous solution of 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol) in dry THF (2 mL) was then added. The mixture was stirred for 4 h at −78 °C under an atmosphere of N_2 and then warmed to 0 °C. The reaction was then quenched with aq. sat. NH_4Cl (5 mL) and THF was removed *in vacuo* using a rotary evaporator. The resulting residue was then extracted with EtOAc (10 mL x 3). Conversion and yield were determined by GC-FID and ^{19}F NMR respectively. EtOAc was dried with anhydrous Na_2SO_4, then concentrated *in vacuo* using a rotary evaporator and transferred to a 25 mL round bottom flask equipped with a magnetic stir bar with DCM. The DCM was further removed *in vacuo* using a rotary evaporator. To this crude reaction mixture, DMAP (6 mg, 0.1 equiv., 50 µmol) was added and the vial was evacuated and backfilled with N_2 (3x). Dry THF (1 mL) was then added followed by a sequential addition of pyridine (120 µL, 3.0 equiv., 1.5 mmol) and $SOCl_2$ (110 µL, 3.0 equiv., 1.5 mmol). The reaction was stirred for 50 °C for 18 h under an atmosphere of N_2. After 18 h, complete conversion was verified by ^{19}F NMR. The crude reaction mixture was then filtered through a plug of silica with DCM as an eluent. The solvents were removed *in vacuo* using a rotary evaporator, and the resulting residue was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar with DCM. The DCM was further removed *in vacuo* using a rotary evaporator and DDQ (340 mg, 3.00 equiv., 1.50 mmol) was added. The vial was evacuated and backfilled with N_2 (3x). *o*-DCB (2.5 mL) was then added, and the reaction was stirred for 14 h at 120 °C under an atmosphere of N_2. The reaction was cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (40% yield). The solvents were evaporated by using smart evaporator, and the residue was again filtered through a plug of silica with DCM as an eluent to remove the baseline impurities. The filtrate was concentrated in *vacuo* using a rotary evaporator. The residue

was then purified by normal phase silica gel flash chromatography using 0→40% EtOAc in hexanes to afford the desired product (61 mg, 36% yield) as a colorless solid. ^{1}H NMR of the isolated compound matched a previous report.[8]

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.68 (t, *J* = 6.5 Hz, 4H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 4.28 – 4.16 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –108.8 (d, *J* = 115.0 Hz, 2F).

^{31}P NMR (202 MHz, $CDCl_3$) δ 7.4 (t, *J* = 116.7 Hz, 1P).



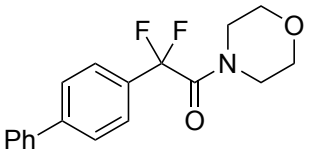
Ethyl 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (**3j**)

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with Zn^0 (65 mg, 2.0 equiv., 1.0 mmol) followed by an addition of 1,2-dibromoethane (2.0 µL, 0.050 equiv., 25 µmol) and dry THF (1.0 mL). The vial was heated with a heat gun till it suddenly boiled and then was cooled down. This heating and cooling cycle was repeated 4 more times. Ethyl bromodifluoroacetate (130 µL, 2.0 equiv., 1.0 mmol) and 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.5 mmol) were added in the N_2-filled glove box. The vial was taken outside of the glove box and the reaction was stirred for 24 h at rt under an atmosphere of N_2. After 24 h, aq. sat. NH_4Cl (5 mL) and aq. sat. NaCl (5 mL) were added. THF was removed *in vacuo* using a rotary evaporator and the aqueous layer was extracted with EtOAc (10 mL x 3). Conversion and yield were determined by GC-FID and ^{19}F NMR respectively. EtOAc was dried with anhydrous Na_2SO_4, then concentrated *in vacuo* using a rotary evaporator and transferred to a 25 mL round bottom flask equipped with a magnetic stir bar with DCM. The DCM was further removed *in vacuo* using a rotary evaporator. To this crude reaction mixture, DMAP (6 mg, 0.1 equiv., 50 µmol) was added and the vial was evacuated and backfilled with N_2 (3x). Dry THF (1 mL) was then added followed by sequential addition of pyridine (120 µL, 3.0 equiv., 1.5 mmol) and $SOCl_2$ (110 µL, 3.0 equiv., 1.5 mmol). The reaction was stirred for 50 °C for 18 h under an atmosphere of N_2. After 18 h, complete conversion was verified by ^{19}F NMR. The crude reaction mixture was then filtered through a plug of silica with DCM as an eluent. The solvents were removed *in vacuo* using a rotary evaporator, and the resulting residue was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar with DCM. The DCM was further removed *in vacuo* using a rotary evaporator, and DDQ (340 mg, 3.00 equiv., 1.50 mmol) was added. The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was then added, and the reaction was stirred for 14 h at 120 °C under an atmosphere of N_2. The reaction was cooled to rt, and complete conversion and yield

were verified by ^{19}F NMR (83% yield). The solvents were evaporated by using smart evaporator, and the residue was again filtered through a plug of silica with DCM as an eluent to remove the baseline impurities. The filtrate was concentrated in *vacuo* using a rotary evaporator. The residue was then purified by normal phase silica gel flash chromatography using 0→20% EtOAc in hexanes gradient to afford the desired compound **3j** (85 mg, 62%) yield as an amber oil. ^{1}H NMR of the isolated compound matched a previous report.[9]

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 4H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –104.2 (s, 2F).



2-([1,1'-biphenyl]-4-yl)-2,2-Difluoro-1-morpholinoethan-1-one (3k)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.5 mmol). The flask was evacuated and backfilled with N_2 (3x). Dry Et_2O (2.5 mL) was then added followed by the addition of 2-bromo-2,2-difluoro-1-morpholinoethan-1-one (305 mg, 2.50 equiv., 1.25 mmol). The reaction mixture was cooled to –78 °C, whereupon MeLi (1.6 M in Et_2O, 937 µL, 3.00 equiv., 1.50 mmol) was added slowly, and the reaction was stirred for 2 h at –78 °C under an atmosphere of N_2. The reaction was then quenched with aq. sat. NH_4Cl (5 mL) and extracted with Et_2O (10 mL x 3). Conversion and yield were determined by GC-FID and ^{19}F NMR respectively. Et_2O was dried with anhydrous Na_2SO_4, then concentrated *in vacuo* using a rotary evaporator and transferred to a 25 mL round bottom flask equipped with a magnetic stir bar with Et_2O. The Et_2O was further removed *in vacuo* using a rotary evaporator. To this crude reaction mixture, DMAP (6 mg, 0.1 equiv., 50 µmol) was added and the vial was evacuated and backfilled with N_2 (3x). Dry THF (1 mL) was then added followed by sequential addition of pyridine (120 µL, 3.0 equiv., 1.5 mmol) and $SOCl_2$ (110 µL, 3.0 equiv., 1.5 mmol). The reaction was stirred for 50 °C for 18 h under an atmosphere of N_2. After 18 h, complete conversion was verified by ^{19}F NMR. The crude reaction mixture was then filtered through a plug of basic alumina with DCM as an eluent. The solvents were removed *in vacuo* using a rotary evaporator, and the resulting residue was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar with DCM. The DCM was further removed *in vacuo* using a rotary evaporator, and DDQ (340 mg, 3.00 equiv., 1.50 mmol) was added. The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was then added, and the reaction was stirred for

14 h at 80 °C under an atmosphere of N_2. The reaction was cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (45% yield). The solvents were evaporated by using smart evaporator, and the residue was again filtered through a plug of silica with DCM as an eluent to remove the baseline impurities. The filtrate was concentrated in *vacuo* using a rotary evaporator. The residue was purified by reverse phase flash chromatography 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) to deliver the desired product **3k** as a colorless solid (68 mg, 43% yield).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.64 – 7.58 (m, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 3.73 (s, 4H), 3.54 (s, 4H).

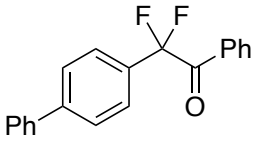
^{13}C NMR (201 MHz, $CDCl_3$) δ 162.2 (t, *J* = 30.4 Hz), 143.9, 139.8, 132.2 (t, *J* = 25.0 Hz), 129.0, 128.1, 127.5, 127.3, 125.7 (t, *J* = 6.0 Hz), 115.8 (t, *J* = 250.9 Hz), 66.7, 66.4, 46.7, 43.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ –94.9 (s, 2F).

IR (film) 2858, 2923, 1670, 1488, 1459, 1440, 1141, 1115, cm^{-1}

HRMS (APCI)$^+$ m/z calc'd $C_{18}H_{19}F_2NO_2$ $[M+H]^+$ 318.1305, found 318.1309

M.P. 103-105 °C



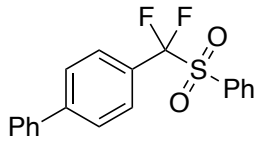
2-([1,1'-biphenyl]-4-yl)-2,2-difluoro-1-phenylethan-1-one (3l)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (87 mg, 1.0 equiv., 0.50 mmol). The flask was evacuated and backfilled with N_2 (3x). and (2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (342 mg, 3.00 equiv., 1.50 mmol) and Dry DCM (1.0 mL) were then added followed by a slow addition of $TiCl_4$ (110 µL, 2.0 equiv., 1.0 mmol), and the reaction was stirred at 0 °C for 2 h under an atmosphere of N_2. Conversion and yield were determined by GC-FID and ^{19}F NMR respectively. The reaction was quenched with ice water, and the aqueous layer was extracted with DCM (10 x 3 mL). DCM was dried with anhydrous Na_2SO_4, concentrated *in vacuo* using a rotary evaporator and transferred to a 25 mL round bottom flask equipped with a magnetic stir bar with DCM. The DCM was further removed *in vacuo* using a rotary evaporator. To this crude reaction mixture, DMAP (6 mg, 0.1 equiv., 50 µmol) was added and the vial was evacuated and backfilled with N_2 (3x). Dry THF (1 mL) was then added followed by sequential addition of pyridine (120 µL, 3.0 equiv., 1.5 mmol) and $SOCl_2$ (110 µL, 3.0 equiv., 1.5 mmol). The reaction was stirred for 50 °C for 18 h under an atmosphere of N_2. After 18 h, complete conversion was verified by ^{19}F NMR. The crude reaction mixture was

then filtered through a plug of silica with DCM as an eluent. The solvents were removed *in vacuo* using a rotary evaporator, and the resulting residue was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar with DCM. This DCM was removed *in vacuo* using a rotary evaporator and DDQ (340 mg, 3.00 equiv., 1.50 mmol) was added. The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was then added, and the reaction was stirred for 14 h at 120 °C under an atmosphere of N_2. The reaction was cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (99% yield). The solvents were evaporated by using smart evaporator, and the residue was again filtered through a plug of silica with DCM as an eluent to remove the baseline impurities. The filtrate was concentrated in *vacuo* using a rotary evaporator. The residue was then purified by normal phase silica gel flash chromatography using 0→20% EtOAc in hexanes to deliver the desired product **3l** as a colorless solid (130 mg, 84% yield). ^1H NMR of the isolated compound matched a previous report.[10]

^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (dt, J = 7.6, 1.1 Hz, 2H), 7.68 (s, 4H), 7.66 – 7.55 (m, 3H), 7.53 – 7.43 (m, 4H), 7.41 – 7.34 (m, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –97.8 (s, 2F).



4-(difluoro(phenylsulfonyl)methyl)-1,1'-biphenyl (3m)

The 1,2-addition was performed with a slight modification to a known procedure.[11] A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-phenylcyclohexan-1-one (174 mg, 2.00 equiv., 1.00 mmol). The flask was evacuated and backfilled with N_2 (3x). Dry THF (1.0 mL) and HMPA (1.3 mL, 15 equiv., 7.5 mmol) were added followed by an addition of ((difluoromethyl)sulfonyl)benzene (96 mg, 1.0 equiv., 0.50 mmol). The flask was then cooled to –78 °C. LiHMDS (1 M in THF, 1.0 mL, 2.0 equiv., 1.0 mmol) was added dropwise. The reaction mixture was then stirred at –78 °C for 2 h under an atmosphere of N_2 and quenched with. NH_4Cl (10 mL) was at –78 °C. The reaction was warmed to rt and was extracted with Et_2O (10 mL × 3). Conversion and yield were determined by GC-FID and ^{19}F NMR respectively. Et_2O was dried with anhydrous Na_2SO_4, then concentrated *in vacuo* using a rotary evaporator and transferred to a 25 mL round bottom flask equipped with a magnetic stir bar with Et_2O. The Et_2O was further removed *in vacuo* using a rotary evaporator. To this crude reaction mixture, DMAP (6 mg, 0.1 equiv., 50 μmol) was added and the vial was evacuated and backfilled with N_2 (3x). Dry THF (1 mL) was

then added followed by sequential addition of pyridine (120 µL, 3.0 equiv., 1.5 mmol) and $SOCl_2$ (110 µL, 3.0 equiv., 1.5 mmol). The reaction was stirred for 50 °C for 18 h under an atmosphere of N_2. After 18 h, the reaction was cooled to rt and complete conversion was verified by ^{19}F NMR. The crude reaction mixture was then filtered through a plug of silica with Et_2O as an eluent. The residue mixture was purified using normal phase silica gel flash chromatography with 0→20% EtOAc in hexanes to afford an amber colored viscous oil (79% yield). A 20 mL scintillation vial equipped with a magnetic stir bar was charged with the isolated product and DDQ. The vial was evacuated and backfilled with N_2 (3x). *o*-DCB (2.5 mL) was then added, and the reaction was stirred for 14 h at 120 °C under an atmosphere of N_2. The reaction was cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (63% yield). The solvents were evaporated by using smart evaporator, and the residue was again filtered through a plug of silica with Et_2O as an eluent to remove the baseline impurities. The filtrate was concentrated in *vacuo* using a rotary evaporator. The residue was then purified by normal phase silica gel flash chromatography using 0→20% EtOAc in hexanes to deliver the desired product **3m** as a colorless solid (106 mg, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.81 – 7.72 (m, 5H), 7.64 (dd, *J* = 15.7, 7.6 Hz, 4H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H).

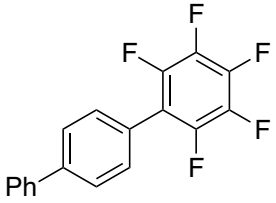
^{13}C NMR (201 MHz, $CDCl_3$) δ 145.3, 139.7, 135.2, 132.8, 130.9, 129.1 (d, *J* = 59.5 Hz), 128.5 – 128.0 (m), 127.3 (d, *J* = 9.2 Hz), 125.1 (t, *J* = 22.1 Hz), 121.9 (t, *J* = 286.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –102.4 (s, 2F)

IR (film) 2955, 2922, 1609, 1564, 1406, 1171, 1142 cm^{-1}

HRMS (APCI)$^+$ m/z calc'd $C_{19}H_{14}F_2O_2S$ $[M]^+$ 344.0682, found 344.1491

M.P. 202–204 °C



2,3,4,5,6-pentafluoro-1,1':4',1''-terphenyl (3n)

To a 25 mL round bottom flask equipped with a stir bar was added Mg^0 (24 mg, 2.0 equiv., 1.0 mmol), dry Et_2O (2 mL), and 1,2-dibromoethane (2.0 µL, 0.050 equiv., 25 µmol). The flask was cooled to 0 °C and bromoperfluorobenzene (68 µL, 1.0 equiv., 550 µmol) was added. The reaction was stirred at 0 °C for 30 mins and then stirred at rt for 14 h under an atmosphere of N_2. Then, 4-phenylcyclohexan-1-one (87.1 mg, 1.0 equiv., 0.5 mmol) dissolved in dry Et_2O (2 mL) was added,

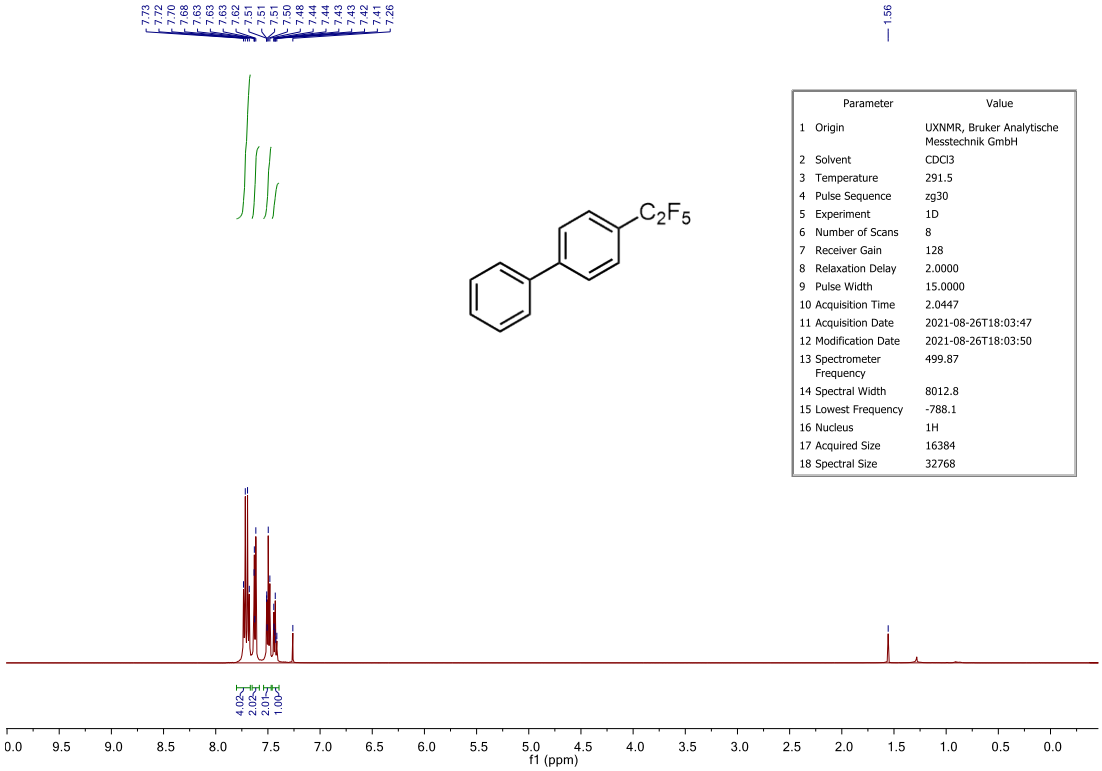
and the reaction was refluxed for 4 h. At completion, the reaction was quenched with aq. sat. NH_4Cl. The aqueous layer was extracted with Et_2O (10 mL x 3). Conversion and yield were checked by GC-FID and ^{19}F NMR respectively. The combined organic layer was dried with anhydrous Na_2SO_4, then concentrated *in vacuo* using a rotary evaporator and transferred to a 25 mL round bottom flask equipped with a magnetic stir bar with Et_2O. The Et_2O was further removed *in vacuo* using a rotary evaporator. To this crude reaction mixture, DMAP (6 mg, 0.1 equiv., 50 µmol) was added, and the vial was evacuated and backfilled with N_2 (3x). Dry THF (1 mL) was then added followed by sequential addition of pyridine (120 µL, 3.0 equiv., 1.5 mmol) and $SOCl_2$ (110 µL, 3.0 equiv., 1.5 mmol). The reaction was stirred for 50 °C for 18 h under an atmosphere of N_2. After 18 h, complete conversion was verified by ^{19}F NMR. The crude reaction mixture was then filtered through a plug of silica with Et_2O as an eluent. The solvents were removed *in vacuo* using a rotary evaporator, and the resulting residue was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar with Et_2O. The Et_2O was further removed *in vacuo* using a rotary evaporator, and DDQ (340 mg, 3.00 equiv., 1.50 mmol) was added. The vial was evacuated and backfilled with N_2 (3x). Dry *o*-DCB (2.5 mL) was then added, and the reaction was stirred for 14 h at 120 °C under an atmosphere of N_2. The reaction was cooled to rt, and complete conversion and yield were verified by ^{19}F NMR (51% yield). The solvents were evaporated by using smart evaporator, and the residue was again filtered through a plug of silica with Et_2O as an eluent to remove the baseline impurities. The filtrate was concentrated in *vacuo* using a rotary evaporator. The residue was then purified by normal phase silica gel flash column chromatography with 100% pentane as an eluent to afford the desired product **3n** (75 mg, 47% yield) as colorless powder. ^1H NMR of the isolated compound matched a previous report.[12]

^1H NMR (800 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.1 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ –143.6 – –143.8 (m, 2F), –156.0 (t, *J* = 22.1 Hz, 1F), –162.1 – –163.0 (m, 2F).

NMR Spectra of Compounds

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



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14	Spectral Width	8012.8
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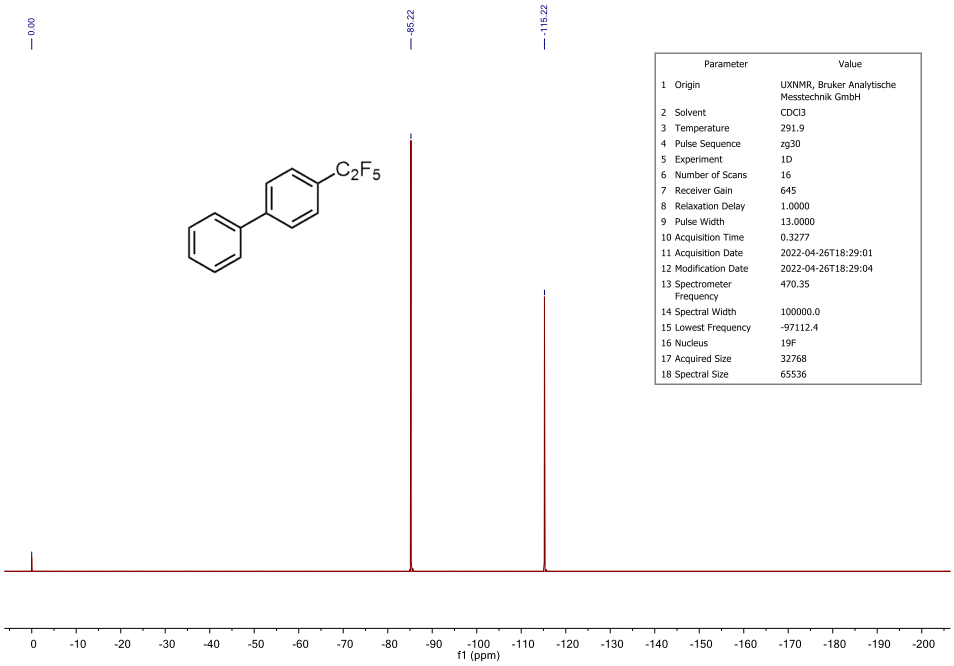
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	32768

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



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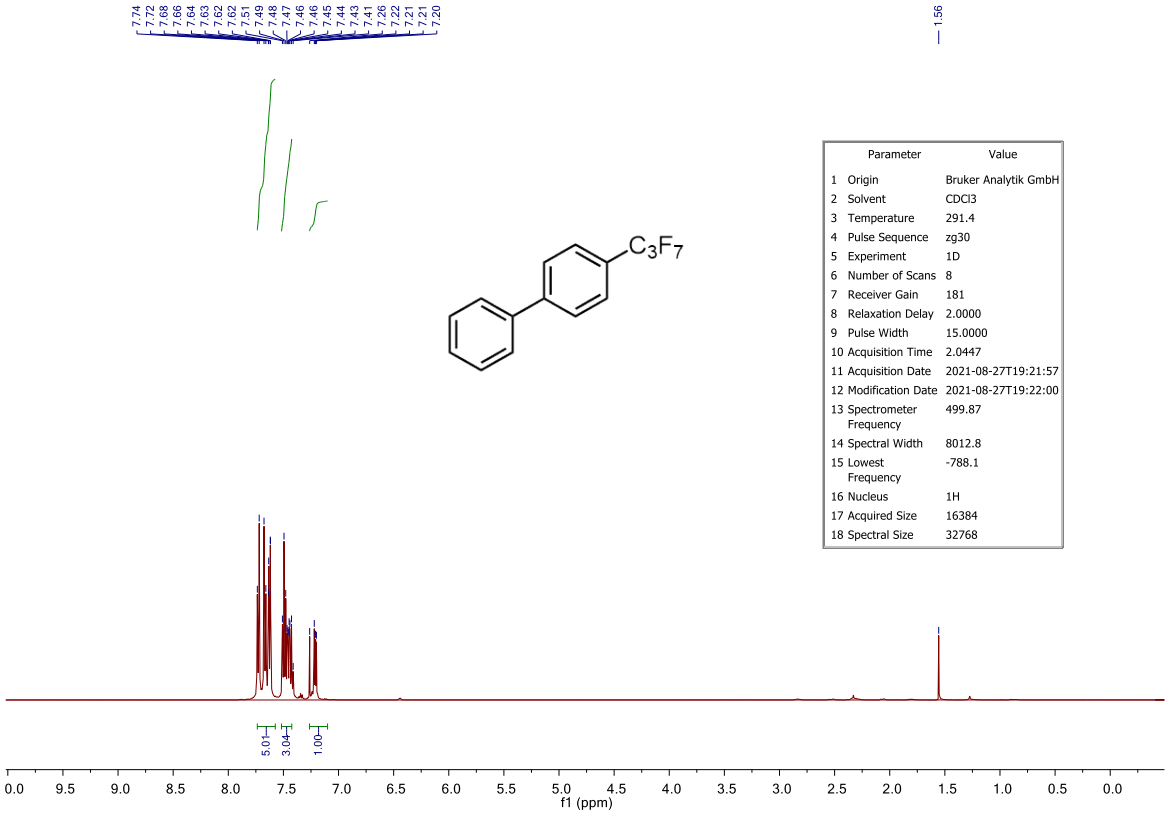
^{1}H NMR of **3b**:



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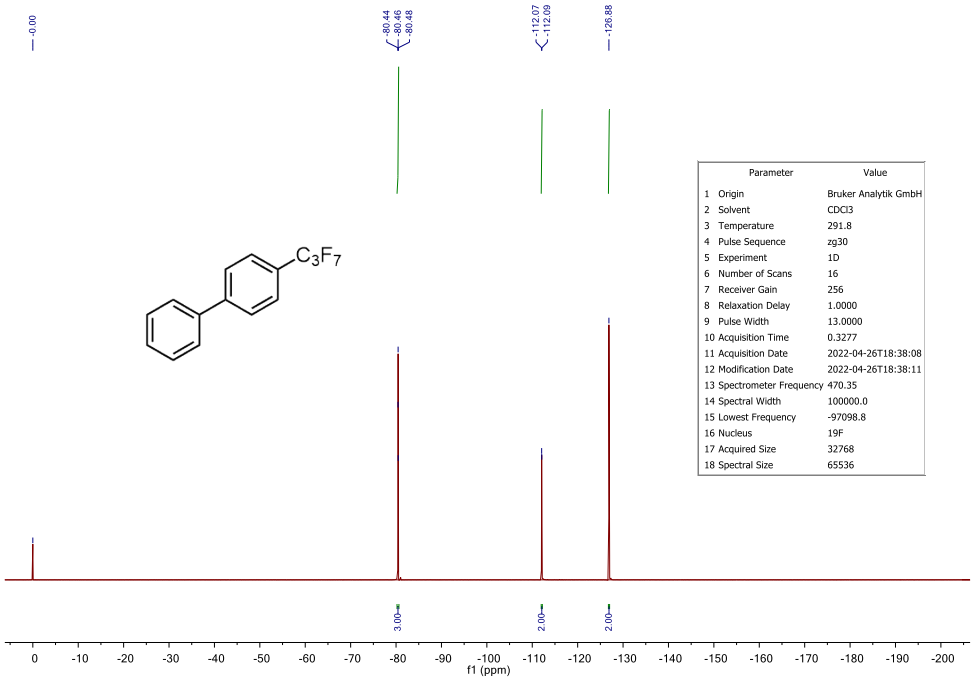
17	Acquired Size	16384
18	Spectral Size	32768

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



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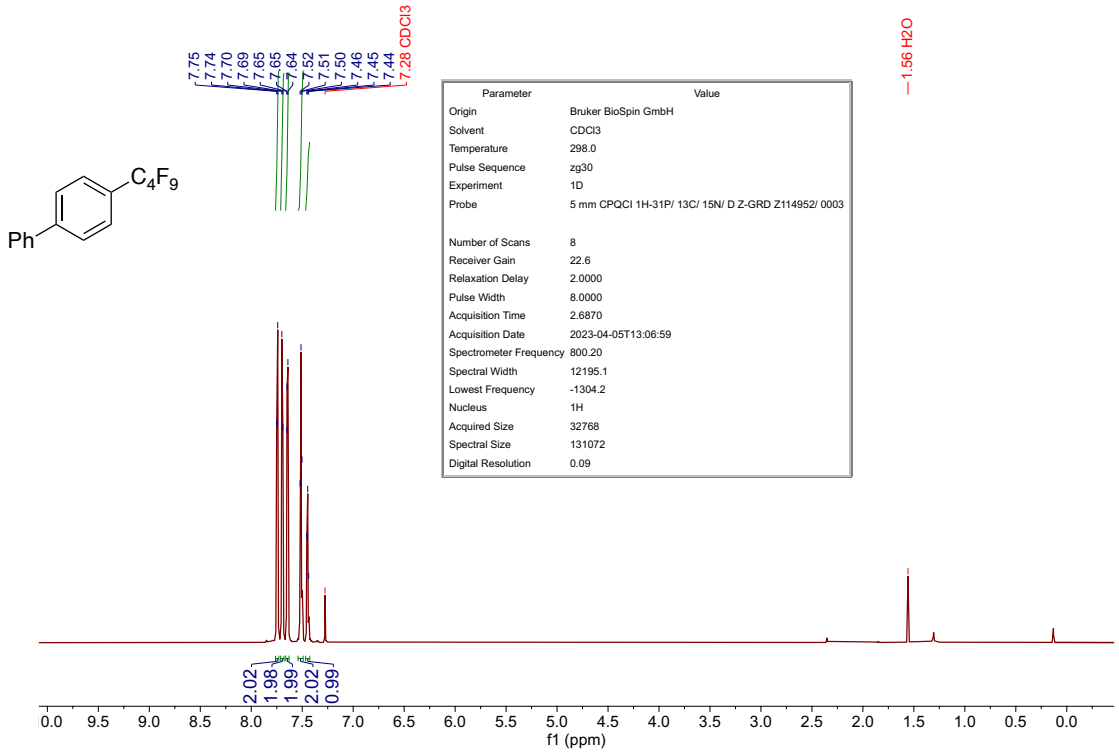
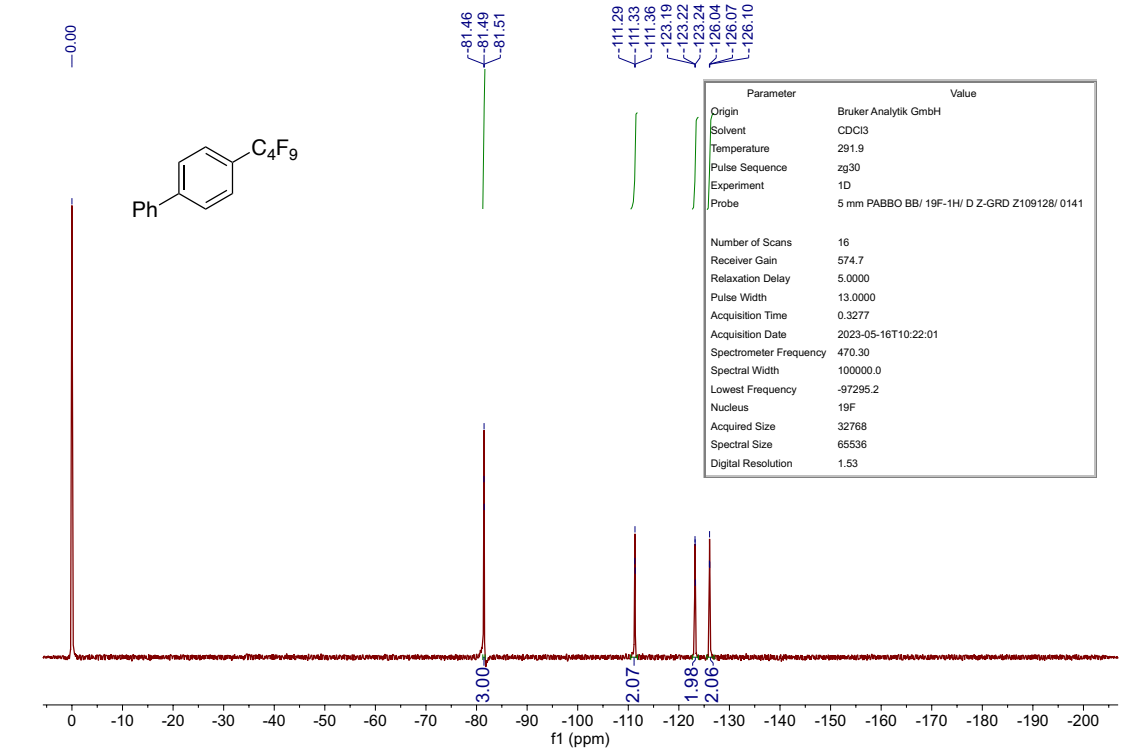
16	Nucleus	19F
17	Acquired Size	32768
18	Spectral Size	65536

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



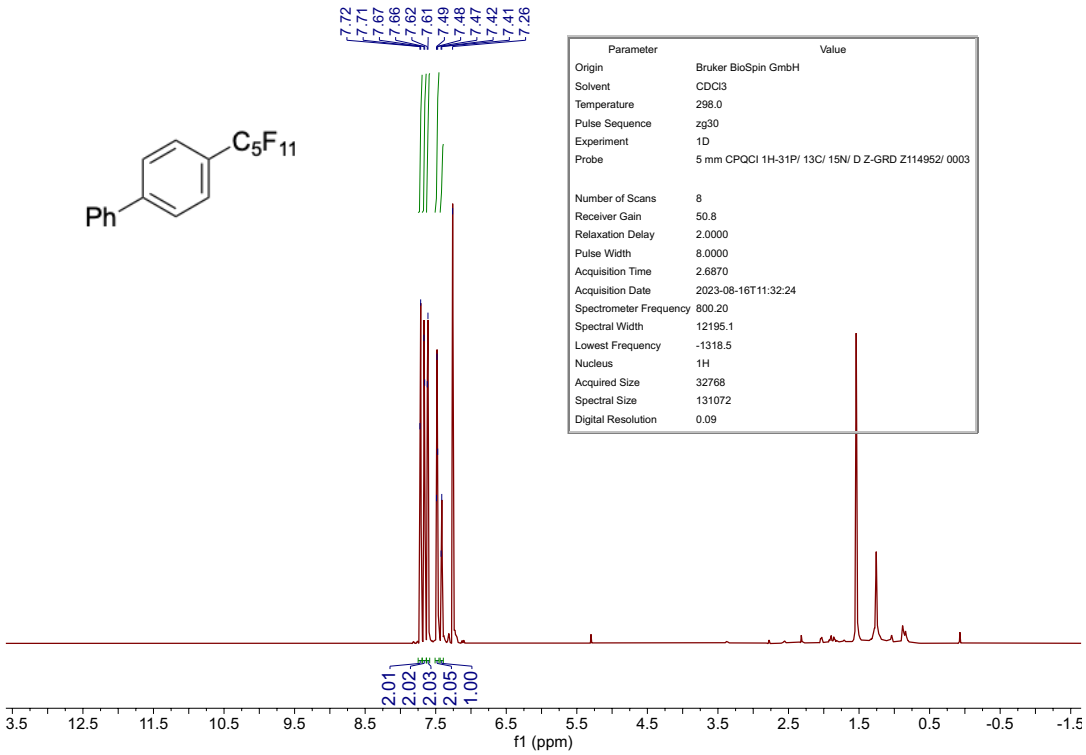
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	22.6
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2023-04-05T13:06:59
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 **3c**

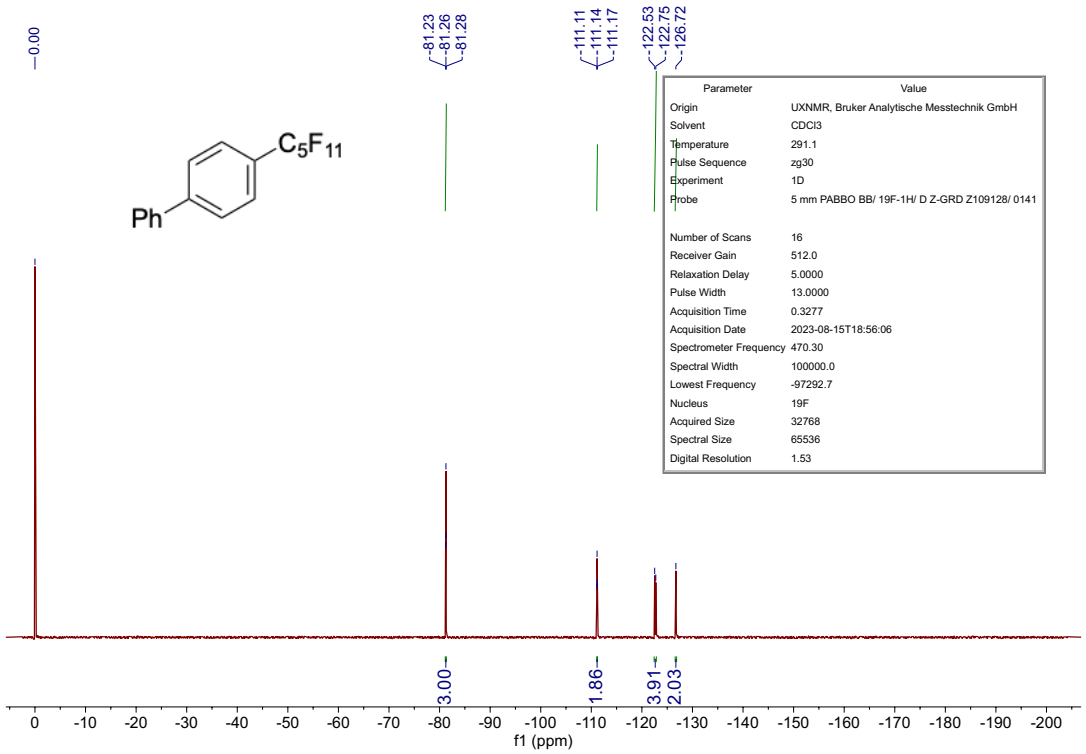


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-05-16T10:22:01
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97295.2
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

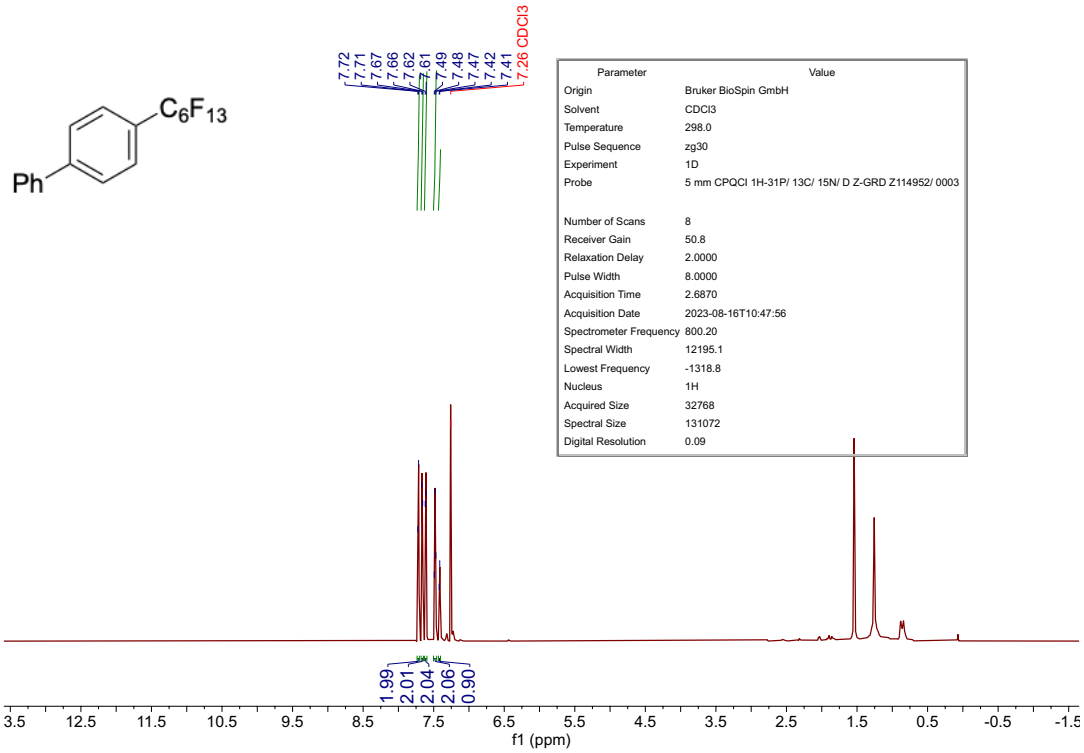
^{1}H NMR of **3d**



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

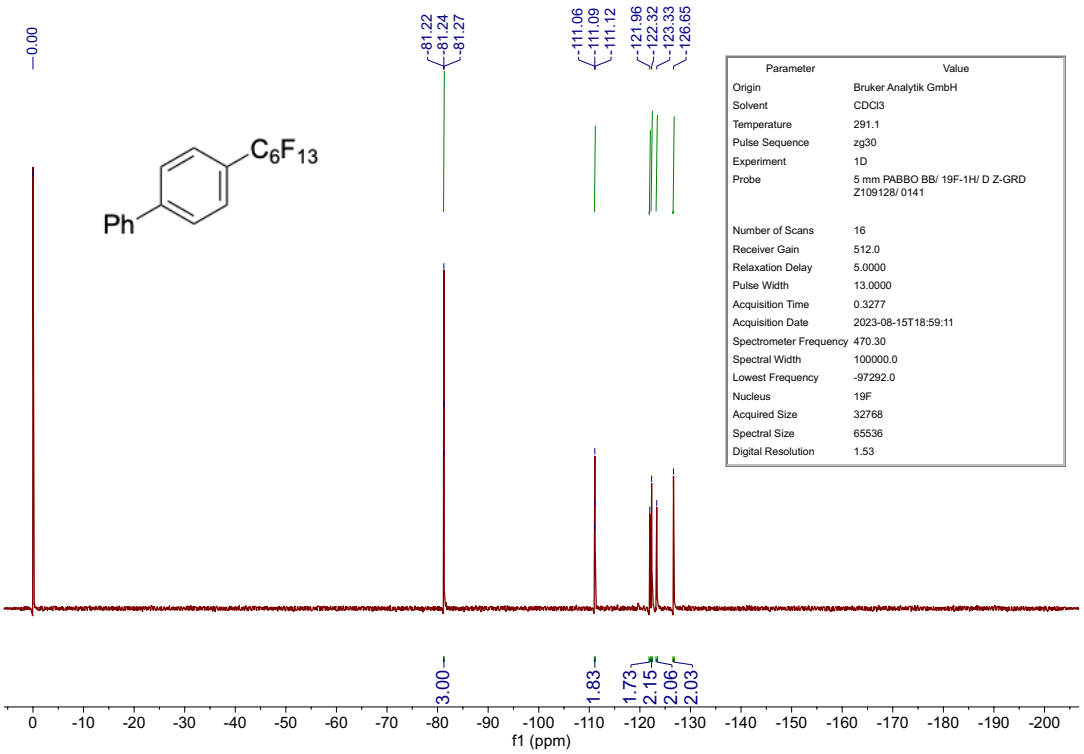


^{1}H NMR of **3e**



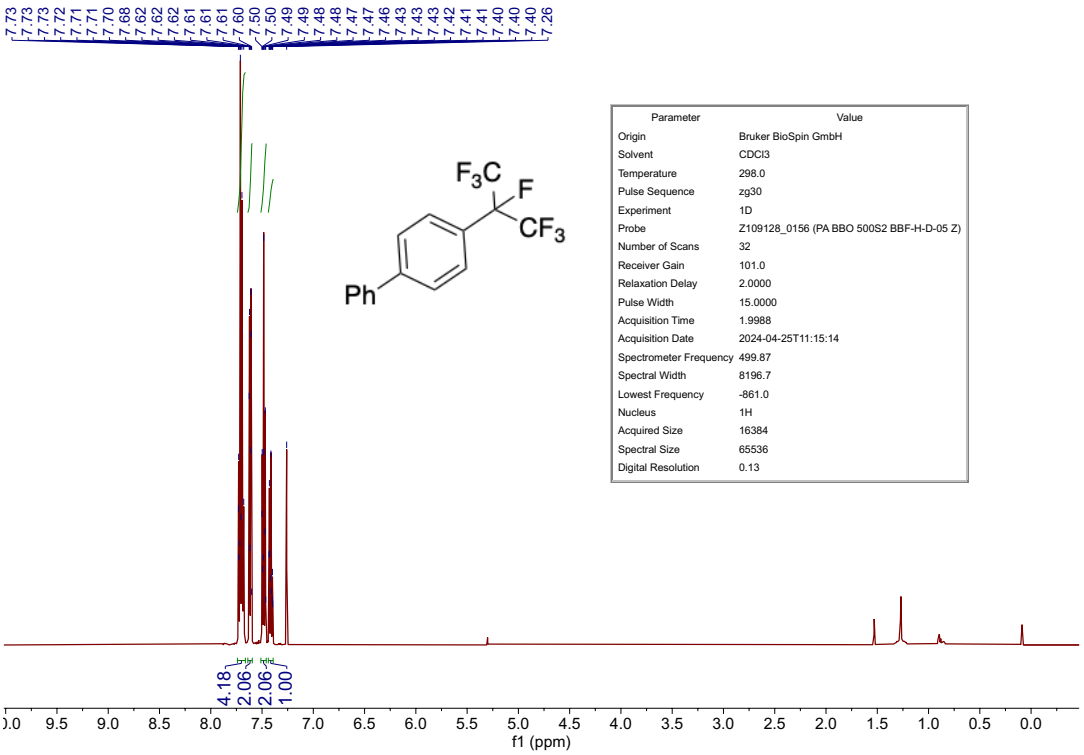
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	50.8
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2023-08-16T10:47:56
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1318.8
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

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

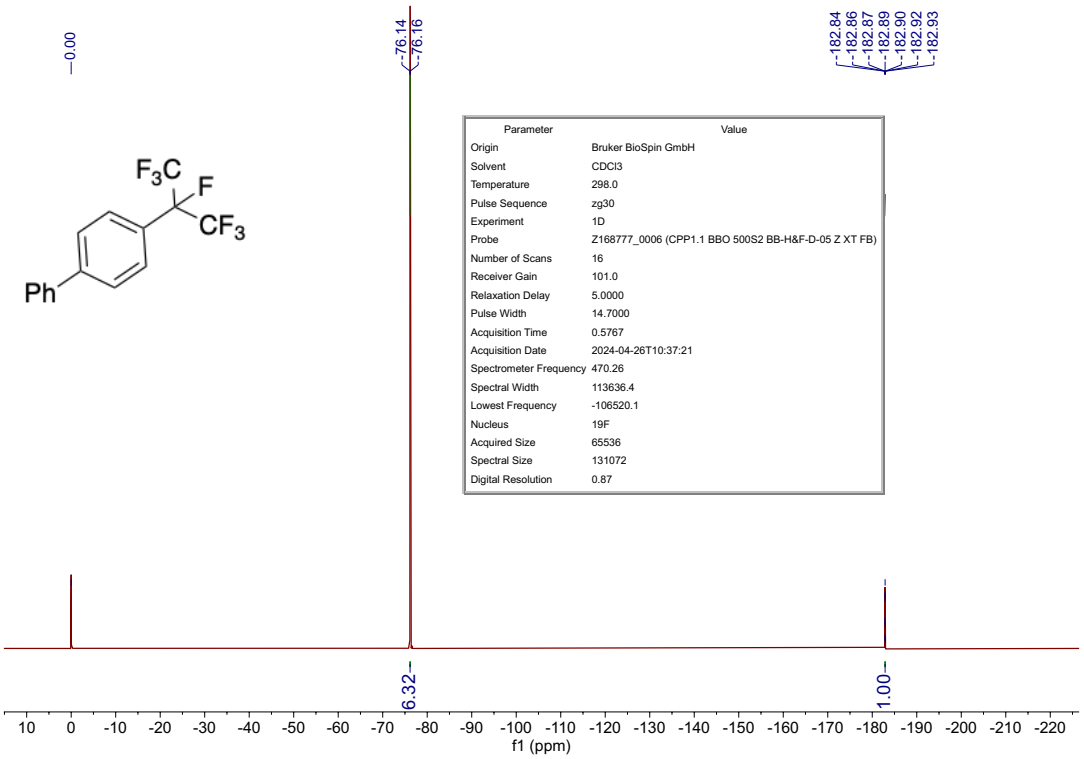


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-08-15T18:59:11
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97292.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

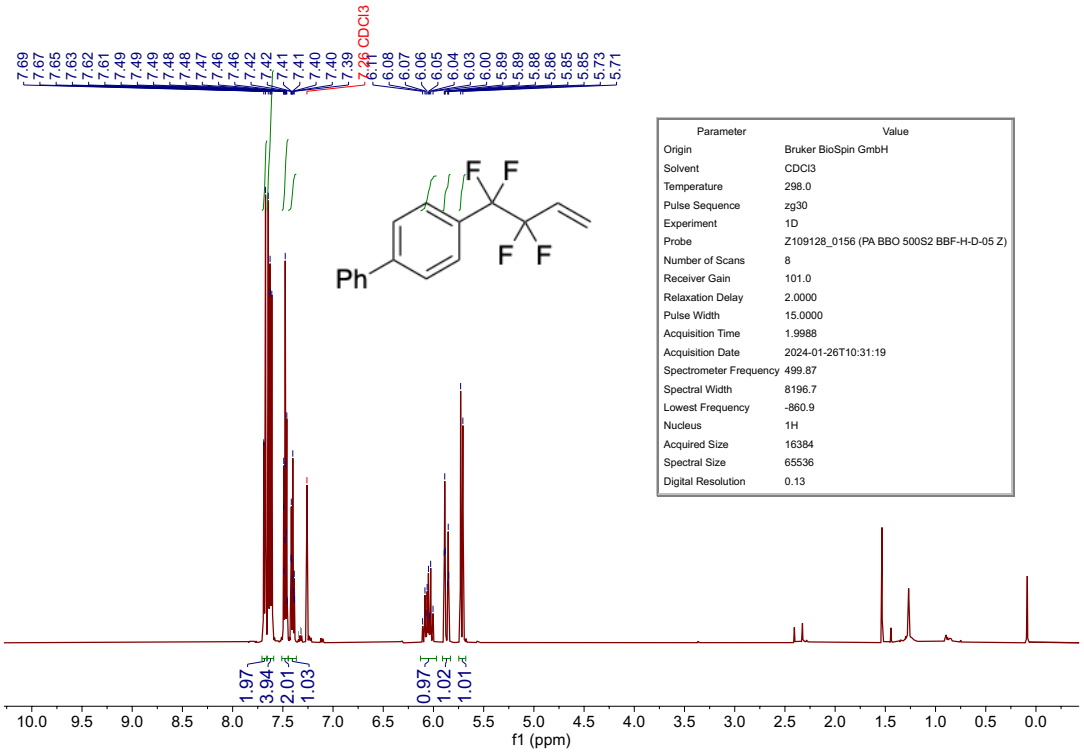
^{1}H NMR of 3f



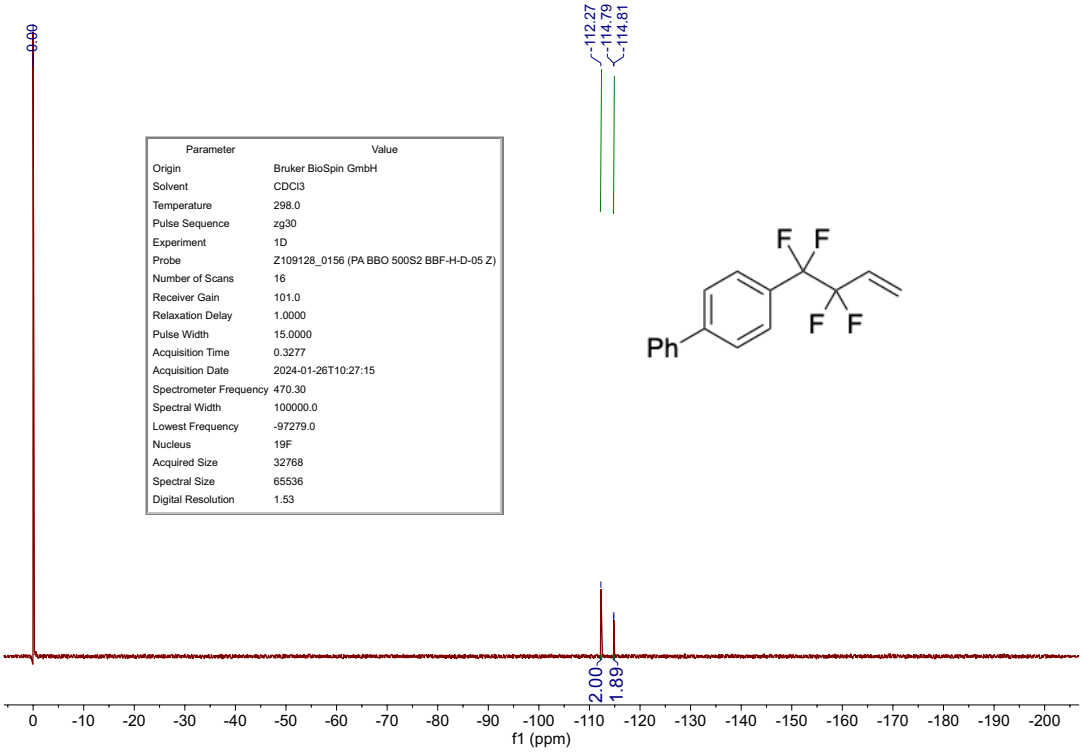
^{19}F NMR of **3f**



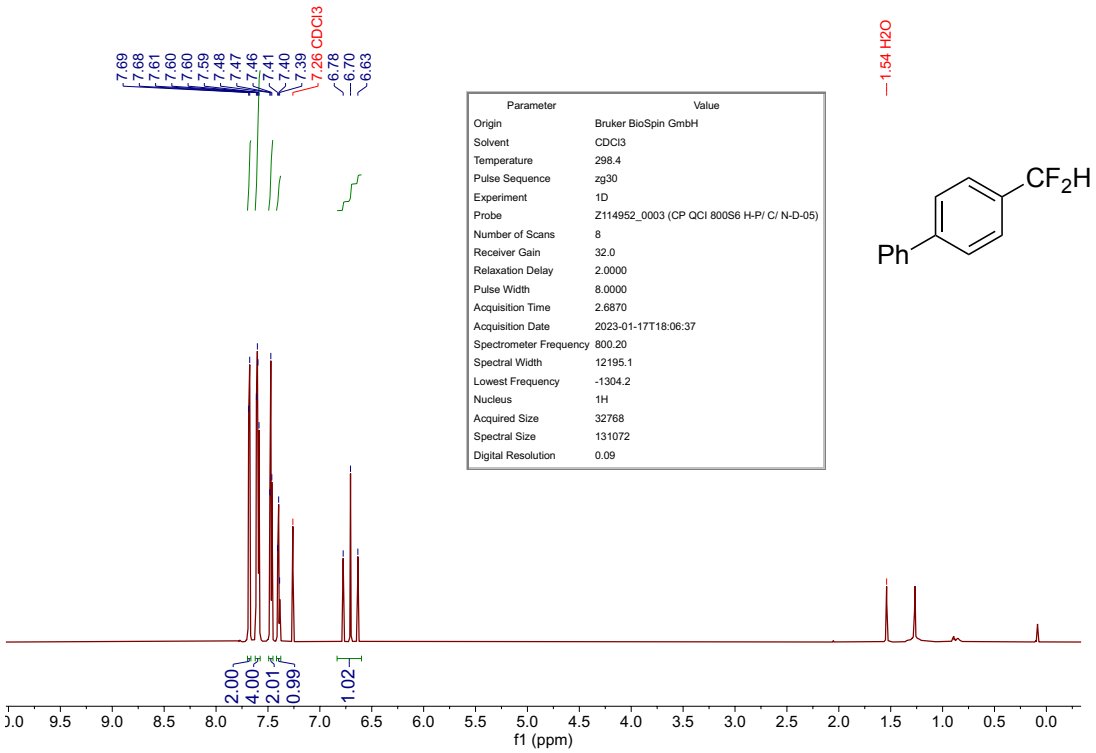
^{1}H NMR of **3g**



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

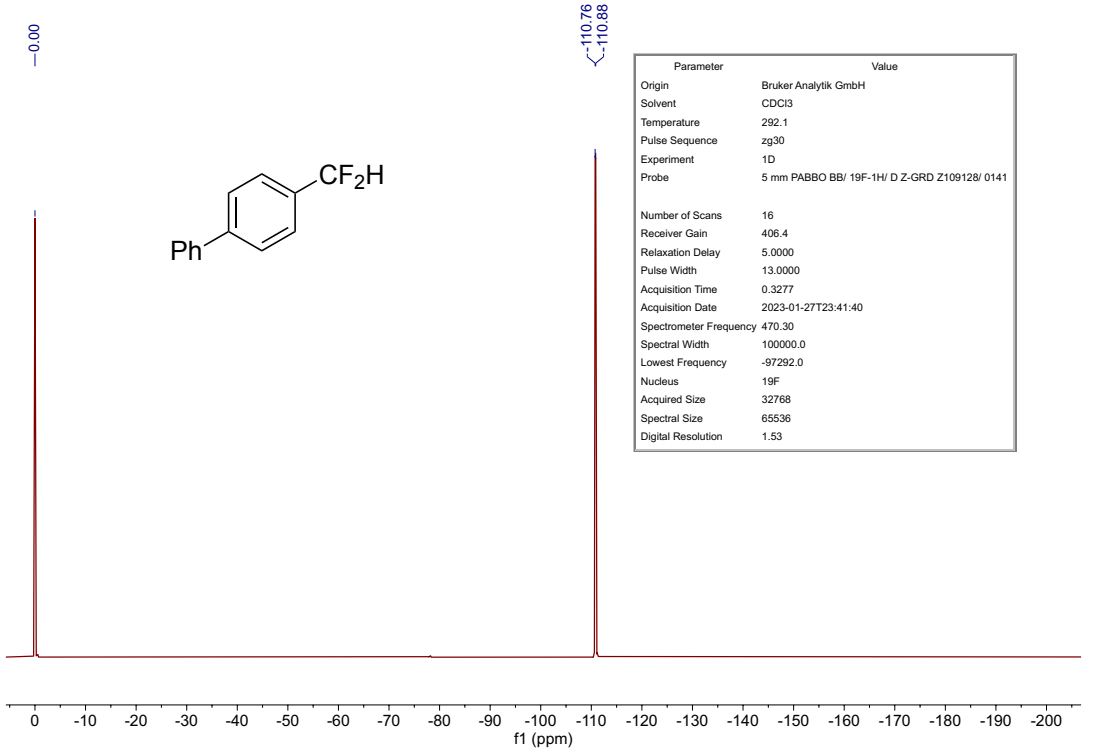


^{1}H NMR of **3h**



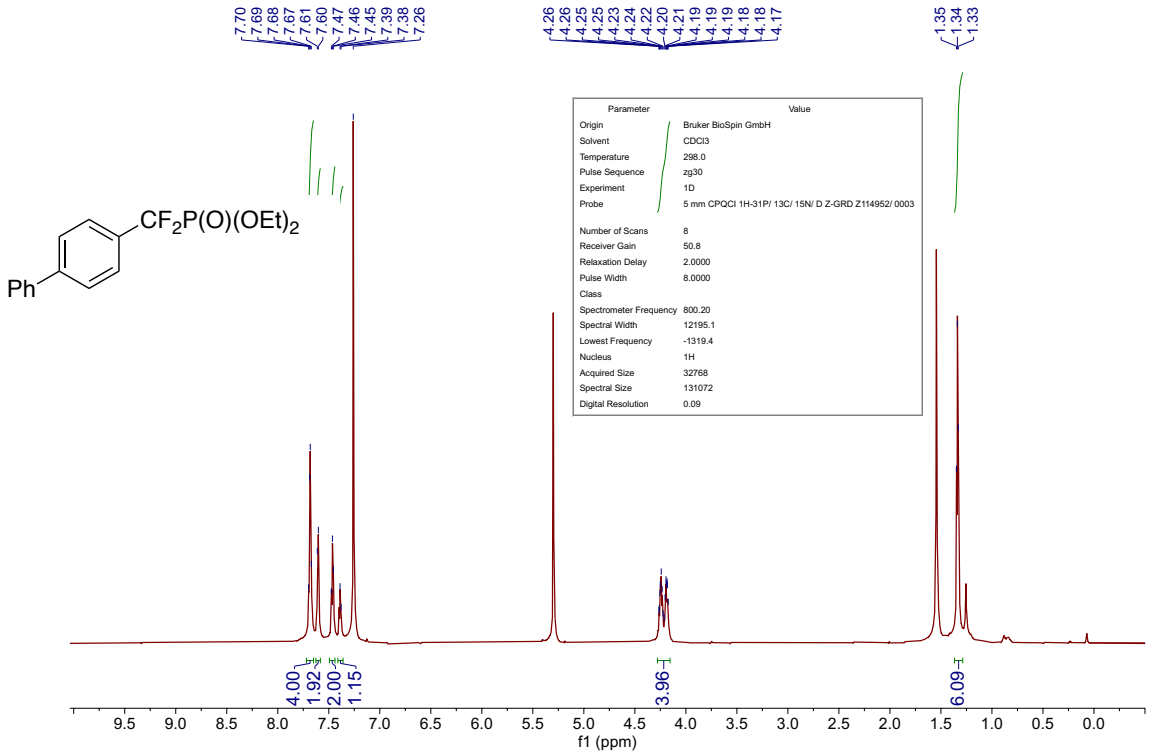
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.4
Pulse Sequence	zg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	2.6870
Acquisition Date	2023-01-17T18:06:37
Spectrometer 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 **3h**

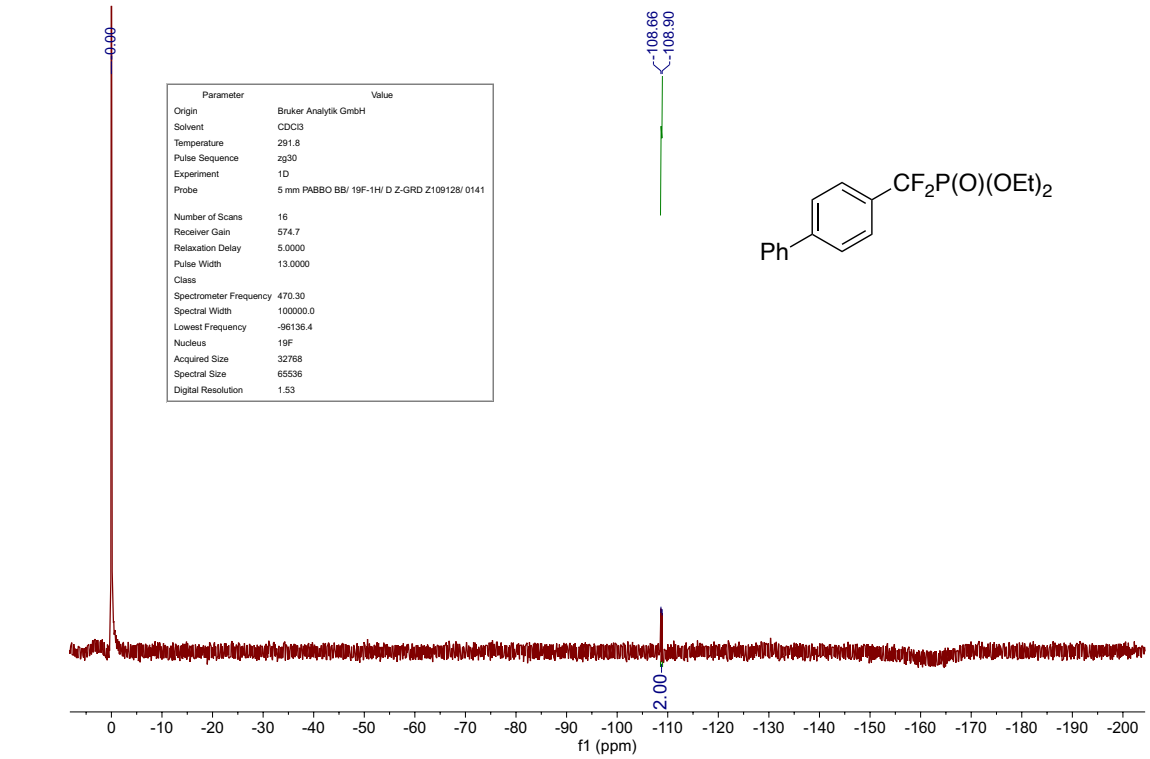


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	406.4
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-01-27T23:41:40
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97292.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

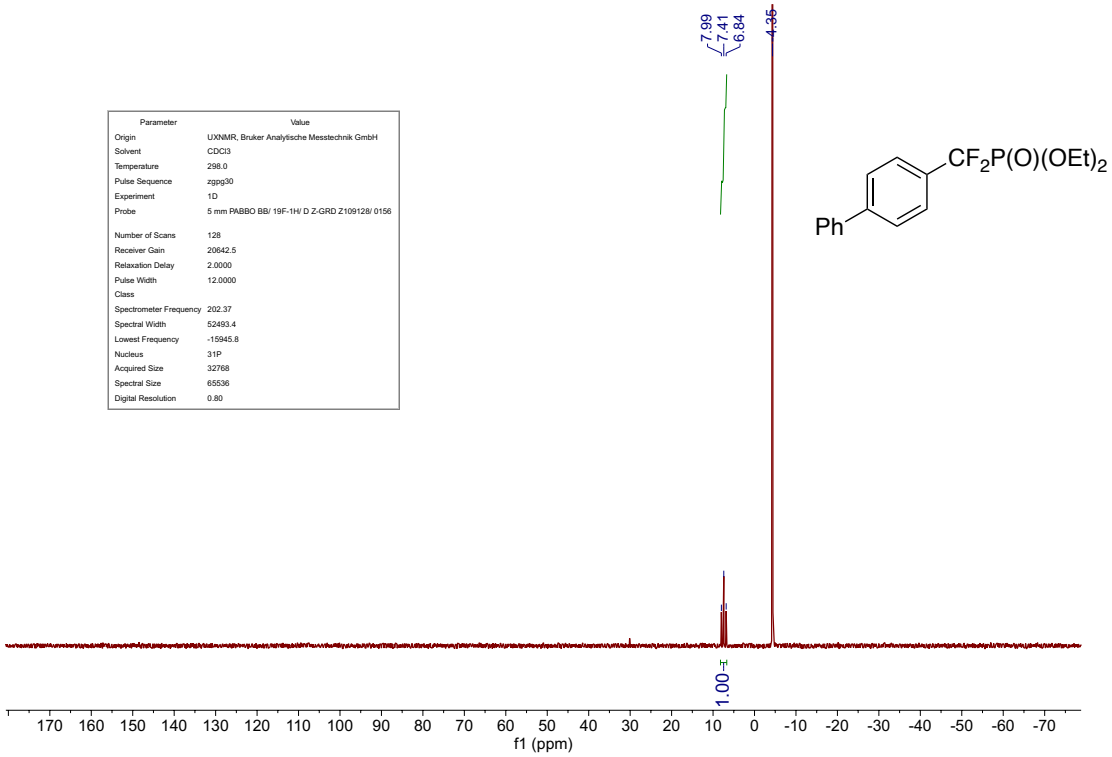
^{1}H NMR of **3i**



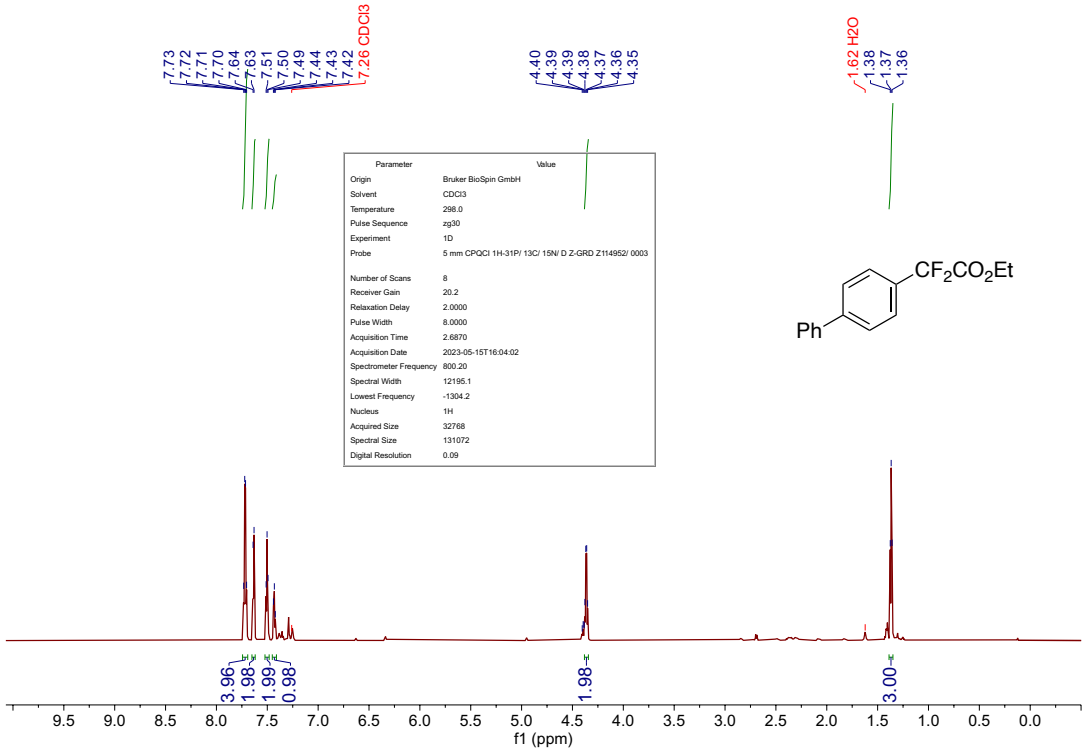
^{19}F NMR of **3i**



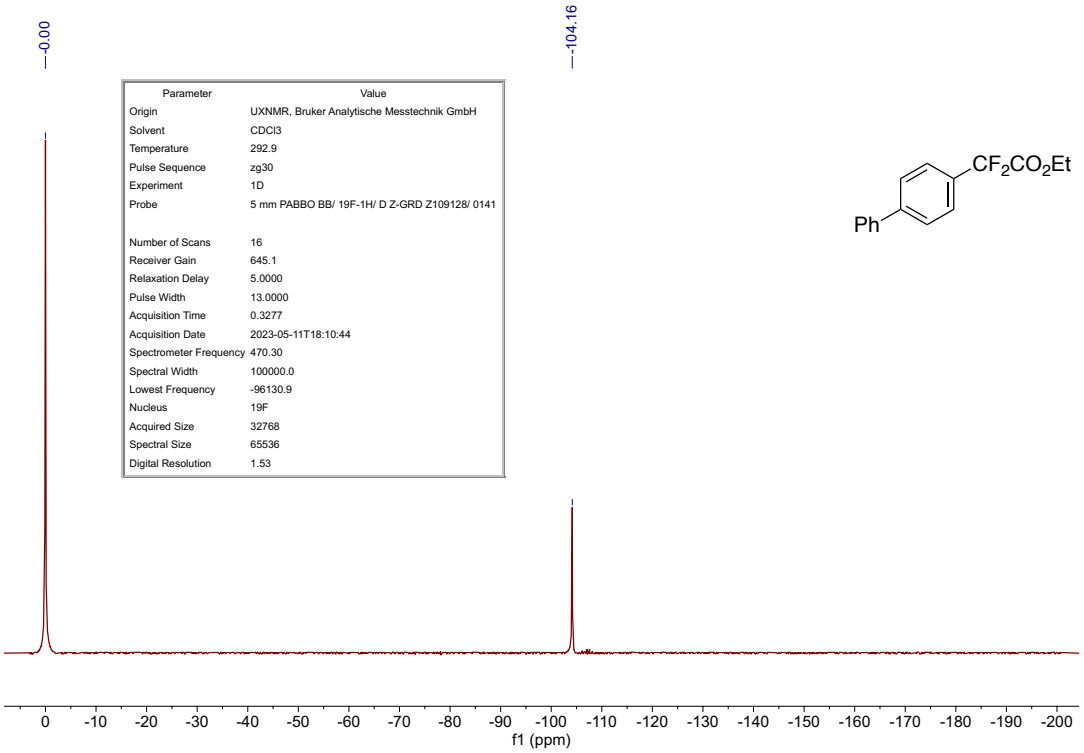
^{31}P NMR of **3i**



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

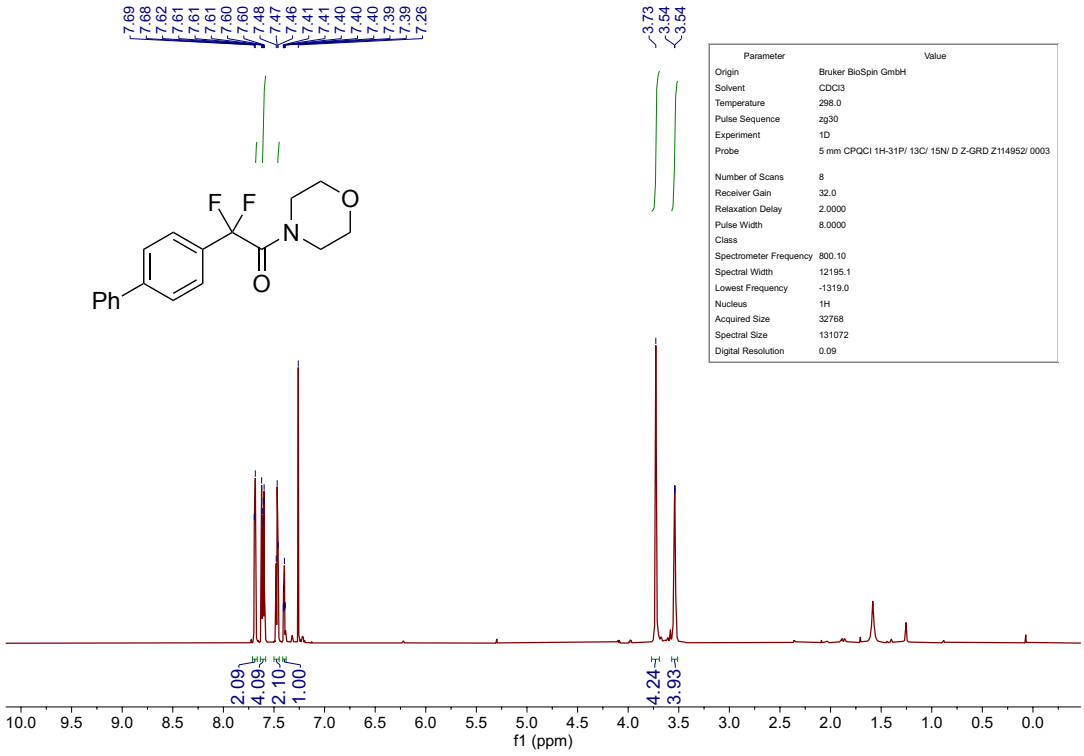


^{19}F NMR of **3j**



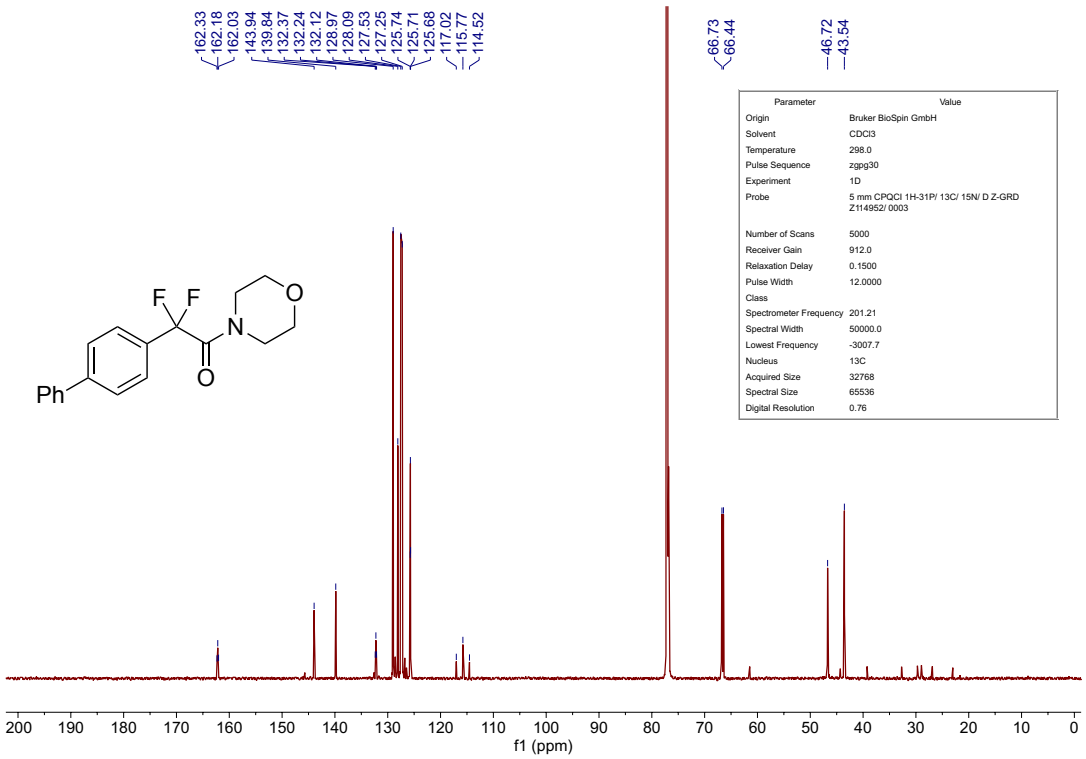
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	5.0000
Pulse Width	13.0000
Acquisition Time	0.3277
Acquisition Date	2023-05-11T18:10:44
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-96130.9
Nucleus	19F
Acquired Size	32768
Spectral Size	65536
Digital Resolution	1.53

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

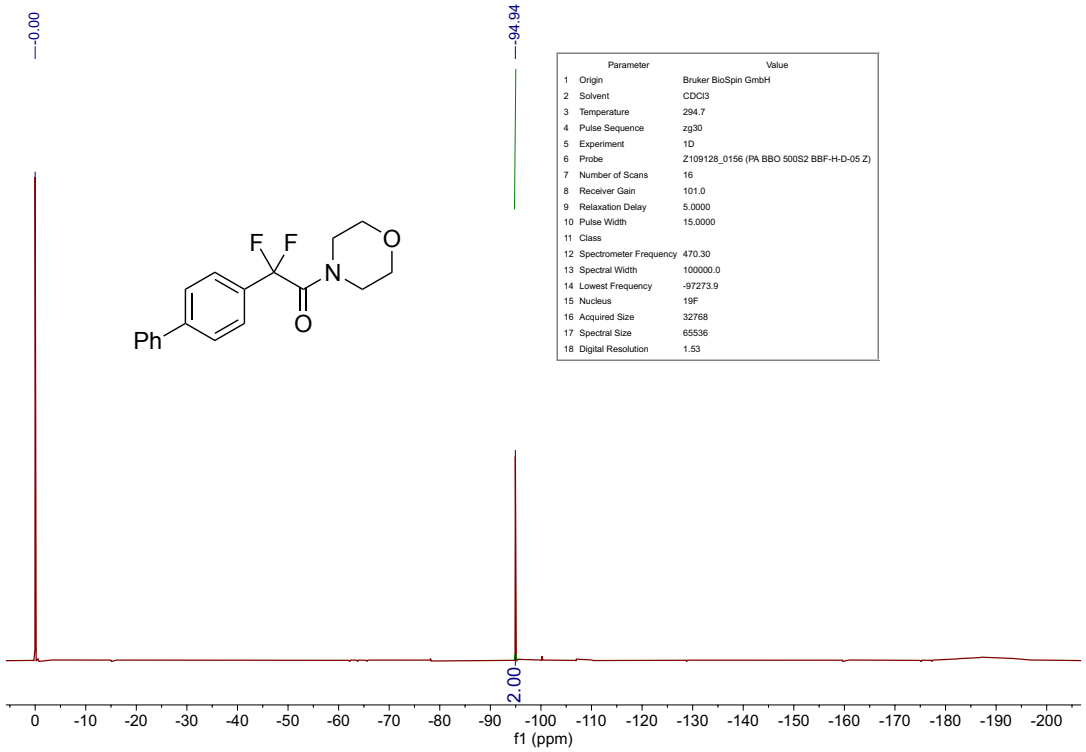


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Class	
Spectrometer Frequency	800.10
Spectral Width	12195.1
Lowest Frequency	-1319.0
Nucleus	1H
Acquired Size	32768
Spectral Size	131072
Digital Resolution	0.09

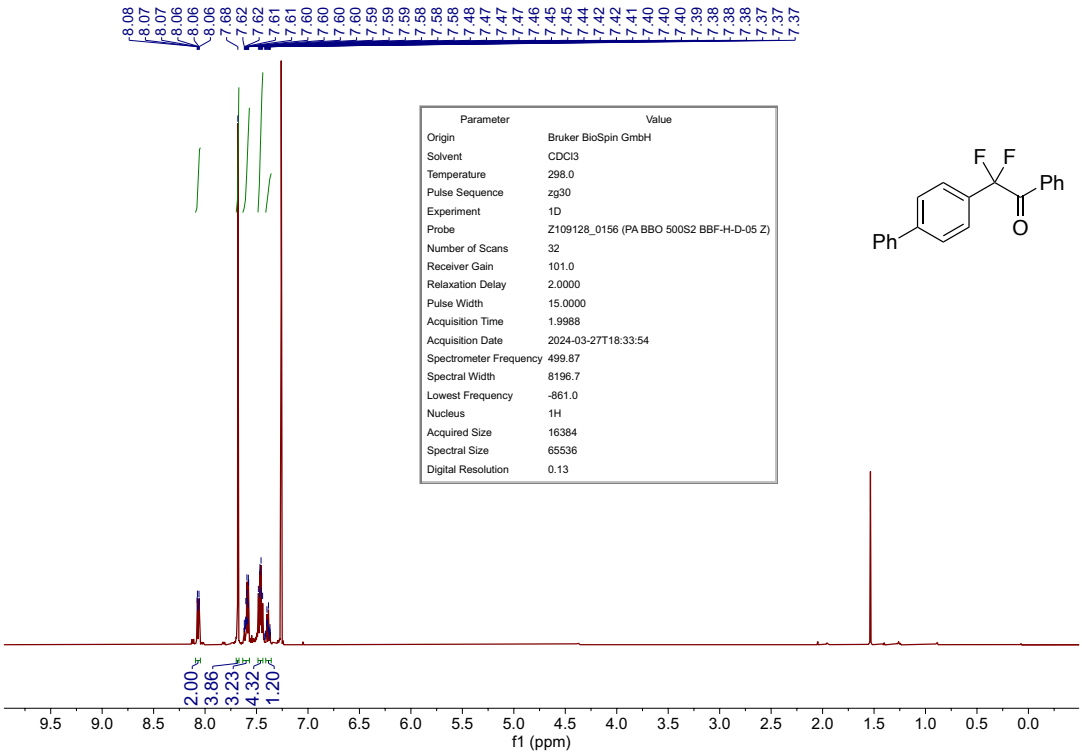
^{13}C NMR of **3k**



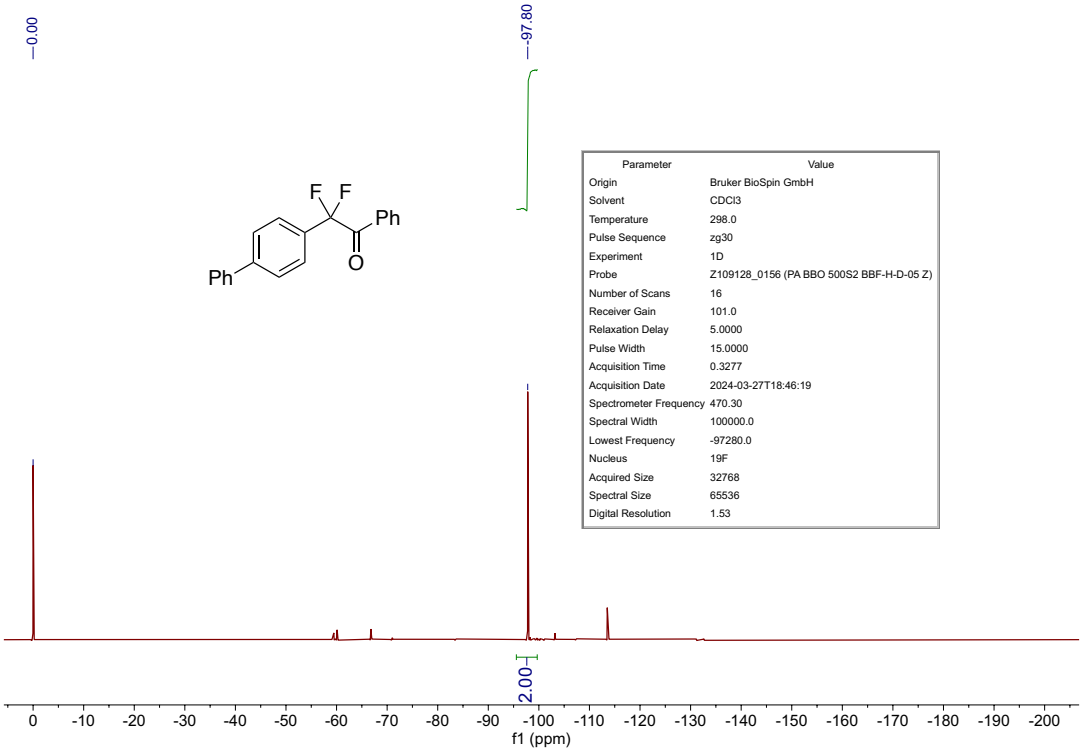
^{19}F NMR of **3k**



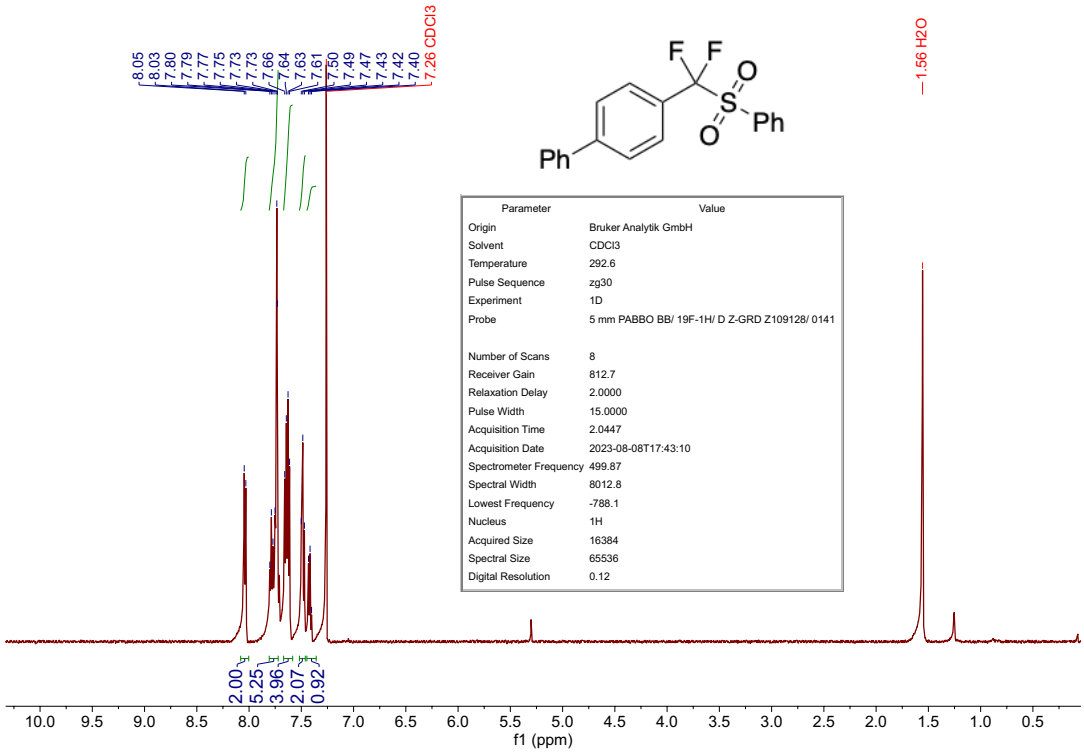
^{1}H NMR of **3l**



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

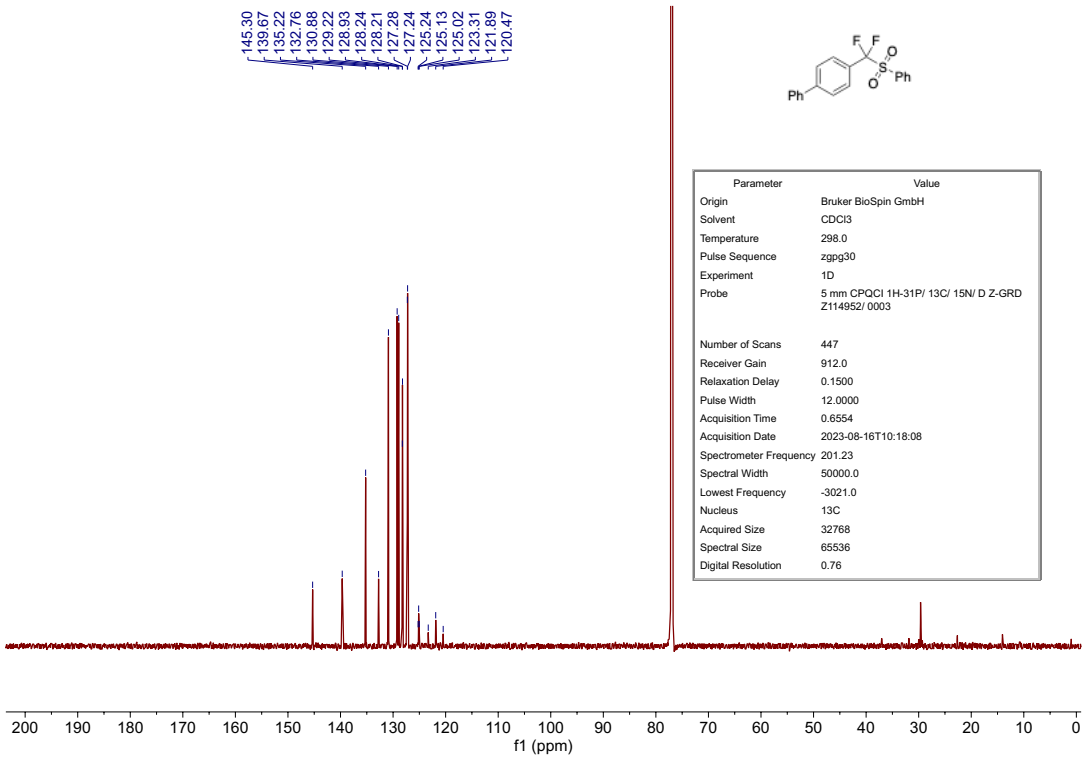


^{1}H NMR of **3m**



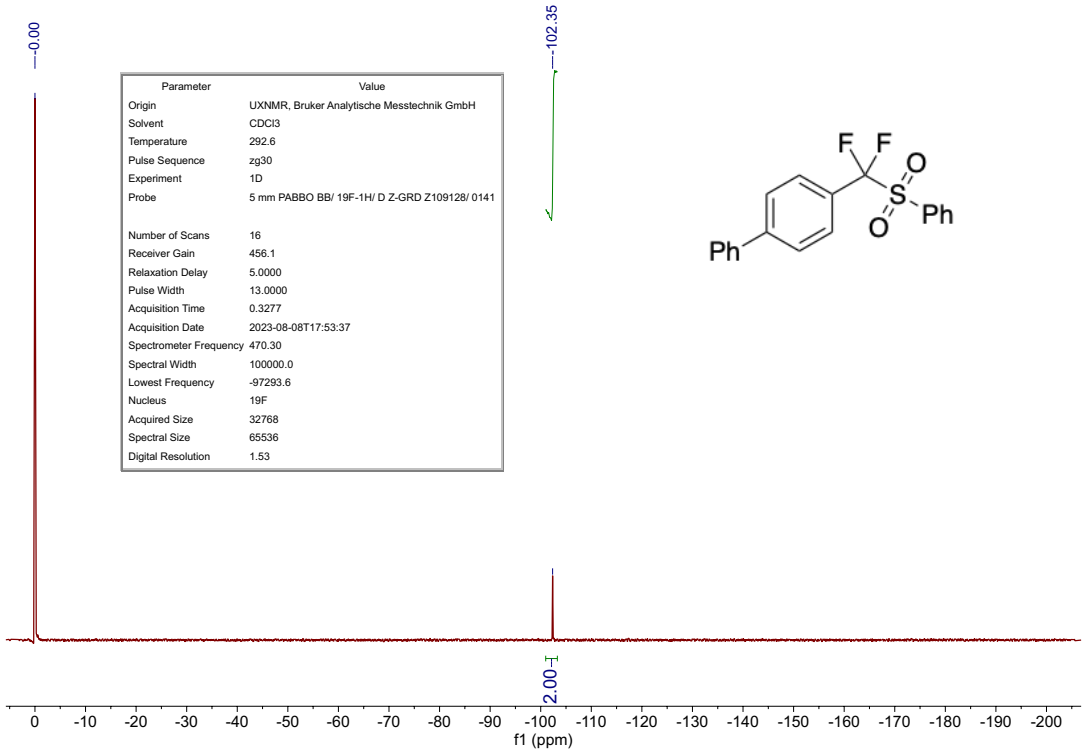
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	812.7
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	2.0447
Acquisition Date	2023-08-08T17:43:10
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 **3m**

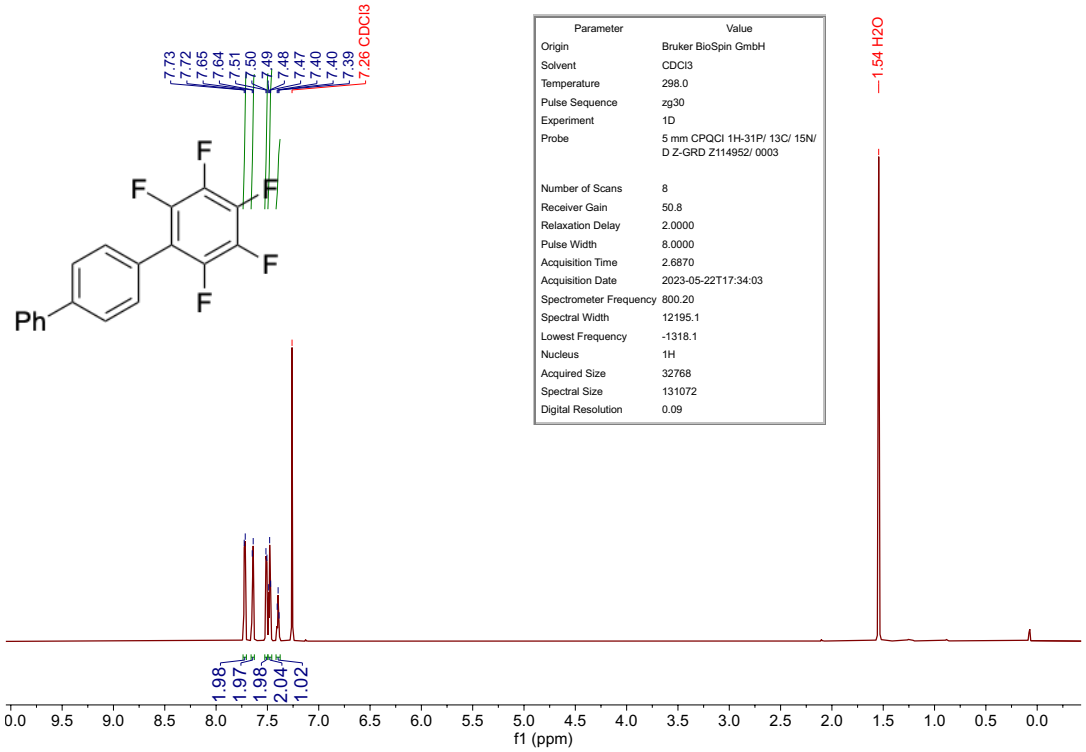


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	447
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Acquisition Time	0.6554
Acquisition Date	2023-08-16T10:18:08
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-3021.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.76

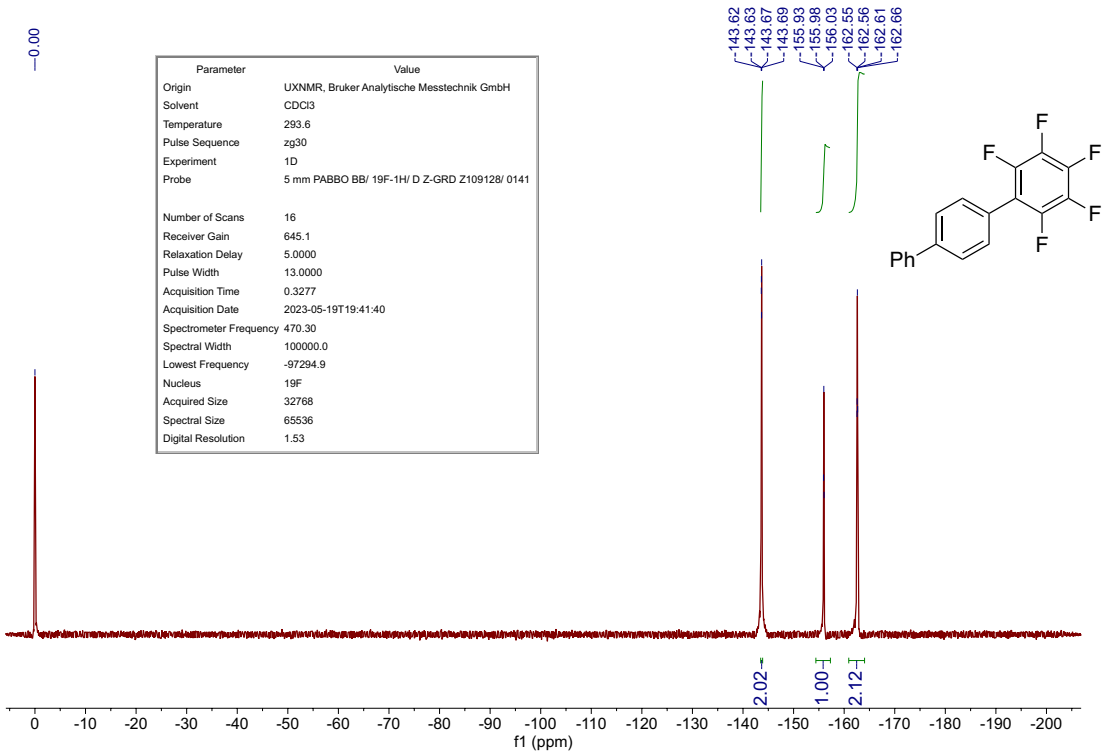
^{19}F NMR of **3m**



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



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


-0.00
-143.62
-143.63
-143.67
-143.69
-155.93
-155.98
-156.03
-162.55
-162.56
-162.61
-162.66
Parameter Value
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Solvent CDCl3
Temperature 293.6
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 2023-05-19T19:41:40
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97294.9
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
Digital Resolution 1.53
F
F
F
F
F
Ph
2.02
1.00
2.12
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

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