Electrochemical Trifluoromethylation of Alkynes: The Unique Role of DMSO as a Masking Auxiliary

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Supporting Information

General Considerations

General Reagent Information

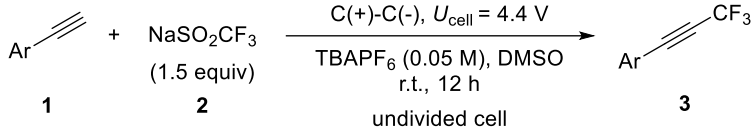
All reagents required for the synthesis of CF_3-alkynes **3** were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organic, or TCI chemical companies. Sodium trifluoromethanesulfinate ($NaSO_2CF_3$) was purchased from Ambeed. Flash column chromatography was performed using ZEOCHEM ZEOprep silica gel 60 (60-200 mesh). Electrochemical reactions were performed using mkc3405 power supply from MK power company or ElectraSyn 2.0 with accessories including vials and electrodes from IKA. Graphite electrode (10 x 20 mm, thickness 2 mm) was purchased from Qingdao-Baofeng graphite company. After each reaction, the graphite electrode surface was washed with acetone/ethanol three times and sonicated using acetone/distilled water for 10 minutes.

General Analytical Information

The synthesized CF_3-alkynes **3** were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, FT-IR spectroscopy, and mass spectrometry. NMR spectra were recorded on a Bruker 400 MHz Avance-Core instrument (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR) and Varian 600 MHz instrument (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR and 564 MHz for ^{19}F NMR). ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to chloroform-D (77.23 ppm), and all were obtained with ^{1}H decoupling. The coupling constants were reported in hertz (Hz) and the multiplicities were denoted using abbreviations, such as: s for singlet, d for doublet, t for triplet, q for quartet, dd for doublet of doublets, dt for doublet of triplets, dq for doublet of quartet, qq for quartet of quartet, and m for multiplet. FT-IR spectra were recorded on a Nicolet 6700 Thermo Scientific FT-IR spectrometer. Reactions were monitored by thin layer chromatography (TLC) or GC-MS of the crude reaction mixture using *n*-dodecane as the internal standard and products were detected by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector. Mass spectral data of all unknown compounds were acquired at the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high-resolution mass spectrometer. A quadrupole mass analyzer was used for HRMS measurements. For cyclic voltammetry measurement, CHI620E potentiostat (CH Instruments) was used.

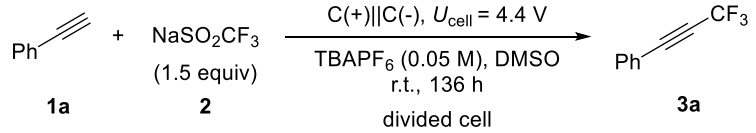
Experimental Details

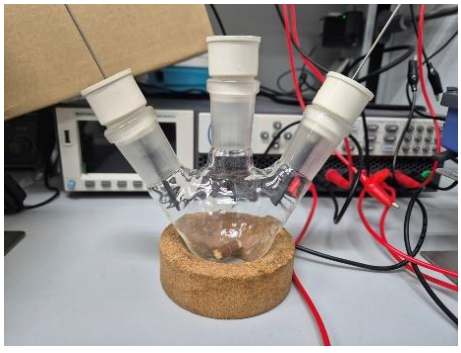
General Procedure for Electrochemical Synthesis of CF_3-alkynes.



A reaction tube equipped with stirring bar was charged with phenyl acetylene derivative **1** (0.3 mmol, 1.0 equiv.), sodium trifluoromethanesulfinate **2** (70 mg, 0.45 mmol, 1.5 equiv.), $TBAPF_6$ (117 mg, 3mmol, 1.0 equiv.), in DMSO (6 mL). The reaction tube was sealed with a silicon septum screw cap and then purged with argon gas using a balloon for 10 minutes. A two-electrode setup with graphite plates both for anode and cathode (surface area = 1 × 1 × 0.2 cm^3) was used. The constant potential electrolysis was performed at 4.4 V. The reaction progress was monitored using TLC and/or fluorine NMR (^{19}F NMR). After completion, the mixture was diluted with dichloromethane (20 mL) and washed with brine. The combined organic layer was dried over $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The resultant residue was purified by flash column chromatography to yield the corresponding CF_3-alkynes **3**.

Gram Scale Reaction of Electrochemical Synthesis of CF_3-alkynes

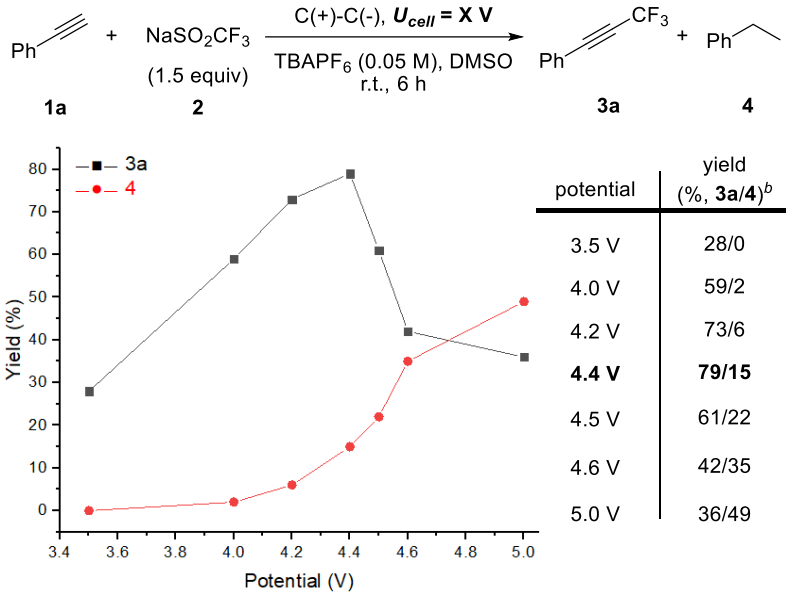




A reaction tube equipped with stirring bar was charged with phenyl acetylene **1a** (20 mmol, 1.0 equiv.), sodium trifluoromethanesulfinate **2** (4.68 g, 30 mmol, 1.5 equiv.), and $TBAPF_6$ (1.45 g, 3.75 mmol) in DMSO (75 mL). The reaction tube was sealed with a silicon septum screw cap and then purged with argon gas using a balloon for 10 minutes. A two-electrode

setup with graphite plates both for anode and cathode (surface area = 1 × 4 × 0.2 cm^3) was used. The electrolysis was performed constant potential at 4.4 V. The reaction progress was monitored using TLC and/or ^{19}F NMR. After completion, the mixture was diluted with dichloromethane (200 mL) and washed with brine (150 × 2 mL). The combined organic layer was dried over $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The resultant residue was purified by flash column chromatography to yield the corresponding CF_3-alkyne **3a** (56%, 2.85 g).

Optimization of Cell Potential[a,b]

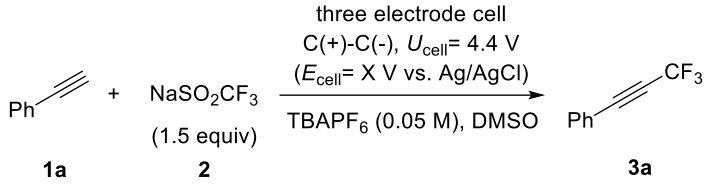


potential	yield (%, **3a**/**4**)[b]
3.5 V	28/0
4.0 V	59/2
4.2 V	73/6
4.4 V	**79/15**
4.5 V	61/22
4.6 V	42/35
5.0 V	36/49

Figure S1. [a]0.1 mmol scale. [b]Yields were determined by GC-MS dodecane as an internal standard.

Mechanistic Experiments

Measurement of response cell potential over time



1a **2** **3a**

reaction time	E_{cell} (V vs. Ag/AgCl)
0 h	0.9 V (5.2 mA)
1 h	1.0 V (4.9 mA)
2 h	1.1 V (4.0 mA)
3.5 h	1.2 V (3.1 mA)
5 h	1.2 V (2.9 mA)
6.5 h	1.2 V (2.6 mA)

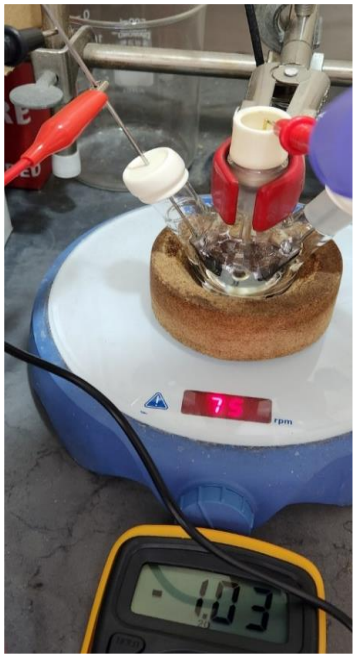
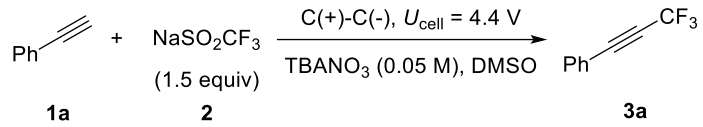


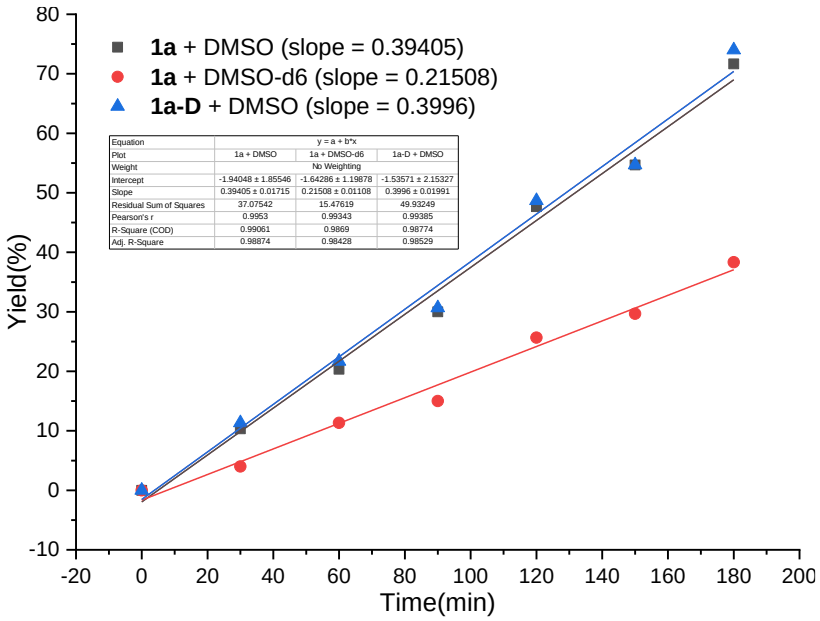
Figure S2. Photographs of using power supply reaction setup; E_{cell} measurement using multimeter.

Kinetic Isotope Effect Experiments[a,b]



1a **2** **3a**

time	phenylacetylene + DMSO	phenylacetylene-**D** + DMSO	phenylacetylene + DMSO-**d6**
30 min	10%	11%	4%
60 min	20%	22%	11%
90 min	30%	31%	15%
120 min	48%	49%	26%
150 min	55%	55%	30%
180 min	72%	74%	38%



Equation	y = a + b*x		
Plot	1a + DMSO	1a + DMSO-d6	1a-D + DMSO
Weight	No Weighting		
Intercept	-1.94048 ± 1.85546	-1.64286 ± 1.19878	-1.53571 ± 2.15327
Slope	0.39405 ± 0.01715	0.21508 ± 0.01108	0.3996 ± 0.01991
Residual Sum of Squares	37.07542	15.47619	49.93249
Pearson's r	0.9953	0.99343	0.99385
R-Square (COD)	0.99061	0.9869	0.98774
Adj. R-Square	0.98874	0.98428	0.98529

Figure S3. [a]0.1 mmol scale. [b]Yields were determined by GC-MS dodecane as an internal standard.

KIE = k_H/k_D = slope of (**1a** + DMSO)/slope of (**1a** + DMSO-d6) = 1.83

An oven-dried standard 20 mL ElectraSyn vial equipped with a magnetic stir bar was brought into a glove box. A vial charged with phenyl acetylene **1a/1a-D** (0.3 mmol, 1.0 equiv.), sodium trifluoromethanesulfinate (0.45 mmol, 1.5 equiv.), and $TBAPF_6$ (0.3 mmol, 1.0 equiv.) and anhydrous DMSO/DMSO-d6 (6 mL) in the glove box and installed the cap. The vial positioned in the ElectraSyn and the mixture was electrolyzed under constant potential condition (4.4 V). The reaction progress was monitored by TLC and ^{19}F NMR.

Cyclic Voltammetry Experiments

The ground-state oxidation potential (E_{ox}) of phenylacetylene **1a**, sodium trifluoromathanesulfinate **2** ($NaSO_2CF_3$), DMSO, and mixtures were determined by cyclic voltammetry. Samples were dissolved at a concentration of 5 mM in 5 mL of degassed acetonitrile (MeCN) containing 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). A three-elecrode cell assembly consisting of a glassy carbon (GC) working electrode, a Pt coiled counter electrode, and Ag/AgCl pseudo reference electrode was employed for the voltammetric measurements. Voltammograms were measured at a scan rate of 30 mV s^{-1}. Oxidations were measured by scanning potentials in positive direction. Data was analyzed by using Origin pro software. All resulted redox potentials were calibrated using ferrocene redox couple (0.42 V vs. Ag/AgCl).

Electrochemical Synthesis of CF_3-alkynes Using Divided Cell.

The electrolysis was carried out using IKA Electrasyn 2.0 in H-type divided cell (IKA Pro-Divide; purchased from IKA) equipped magnetic stirrer bars on anodic chamber and cathodic chamber. Graphite electrode (purchased from IKA) was used as anode and cathode. The anodic chamber was charged acetylene **1** (0.3 mmol, 1.0 equiv.), sodium trifluoromethanesulfinate **2** (0.45 mmol, 1.5 equiv.), and $TBAPF_6$ (0.3 mmol, 1.0 equiv.) in DMSO (6 mL). The cathodic chamber was charged sulfuric acid (0.1 M) and $TBAPF_6$ (0.3 mmol) in DMSO (6 mL). The electrolysis was performed constant potential at 9 V. The reaction progress was monitored using TLC and ^{19}F NMR. After completion, the working electrode cell reaction mixture was diluted with dichloromethane (20 mL) and washed with brine. The combined organic layer was dried with $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The resultant residue was purified by flash column chromatography to yield the corresponding CF_3-alkynes **3**.

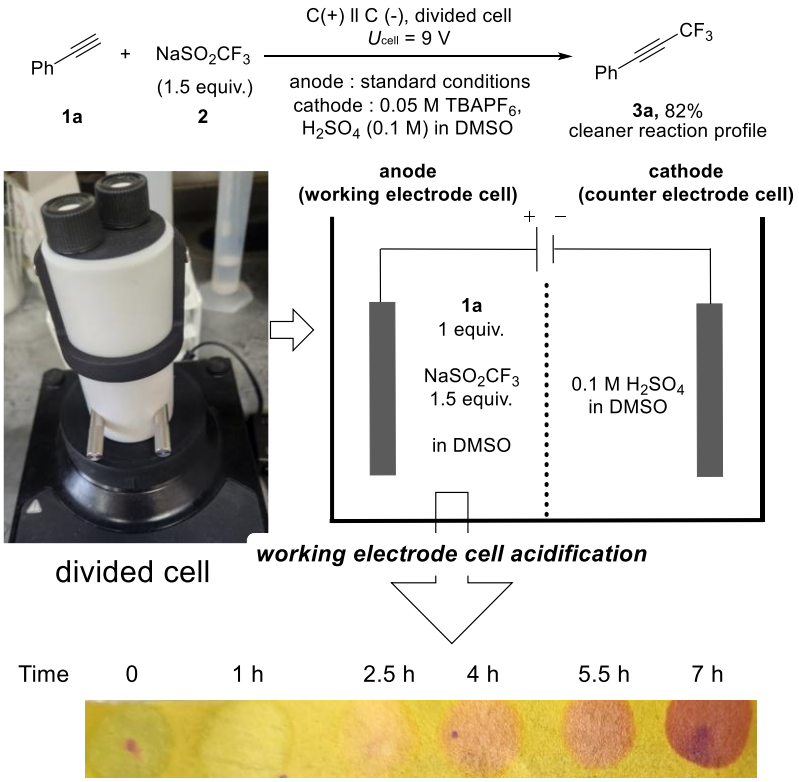


Figure S4.

Details of DFT Studies

All calculations were performed by using the density functional theory (DFT) with the GAUSSIAN 16 program package[S-1]. For the initial calculation of geometry optimizations, (U)M06-2X[S-2] functional with TZVP[S-3] basis set were used. For the calculation of DMSO-SO_2CF_3 stabilization, def2TZVP[S-4] basis set were used for the geometry optimization. Frequency calculation and transition state structures were performed for all stationary points to confirm the local minima, thermodynamic parameters including Gibbs free energies at 298 K. Solvent effects were considered at the polarizable continuum model (PCM) method[S-5] in dimethylsulfoxide solvent (ε = 46.8). All transition state structures were visualized by GaussView 6[S-6] and CYLview[S-7].

All calculated free energy differences (ΔG) are given by following equation (Eq 1.)

$$\Delta G = \Sigma G_{298}(\text{product}) - \Sigma G_{298}(\text{reactant}) \qquad (1)$$

The redox potential relative to the Ag/AgCl pseudo-reference electrode is given by following equation (Eq 2.)

$$\Delta E = -\frac{1}{F}(\Delta G - \Delta G_{SHE} - 0.197) \qquad (2)$$

ΔG_{SHE} = 4.44 eV (The absolute potential of standard hydrogen electrode)

Cartesian coordinates and energies of all optimized intermediate geometries

DMSO

E(RM062X/def2TZVP): -553.201905 a. u.

G_{298}(RM062X/def2TZVP): -553.150214 a. u.

Charge = 0 / Multiplicity = 1

C	-1.34525300	-0.78674400	0.18711400
H	-1.32486100	-1.76206600	-0.29652800
H	-2.26933300	-0.26839600	-0.05929600
H	-1.23551300	-0.87987300	1.26679500
S	-0.00006000	0.21663400	-0.44313200
O	-0.00078500	1.47305100	0.37783800
C	1.34599500	-0.78551800	0.18716600
H	1.23627300	-0.87942200	1.26679900
H	1.32630400	-1.76049000	-0.29726600
H	2.26991800	-0.26673300	-0.05878000

SO_2CF_3 radical

E(UM062X/def2TZVP): -886.247387 a. u.

G_{298}(UM062X/def2TZVP): -553.150214 a. u.

Charge = 0 / Multiplicity = 2

C	0.87080200	0.00003700	0.00400600
S	-1.01212100	0.00000200	-0.33433900
O	-1.47485700	-1.25949200	0.19501700
O	-1.47521700	1.25934100	0.19502600
F	1.05917500	-0.00032800	1.30600100
F	1.39098500	-1.07932500	-0.53081000
F	1.39092100	1.07975800	-0.53018500

DMSO-SO_2CF_3 radical

E(UM062X/def2TZVP): -1439.443003 a. u.

G_{298}(UM062X/def2TZVP): -1439.382483 a. u.

Charge = 0 / Multiplicity = 2

S	-2.31285200	-0.11467200	-0.24307900
O	-3.31359300	-0.10214700	-1.32087900
C	-2.64246900	1.21598300	0.88666000
H	-2.48045500	2.13994800	0.33593800
H	-3.67882400	1.12210100	1.20573100
H	-1.94167000	1.12511400	1.71103200
C	-2.48529300	-1.60251800	0.70703600
H	-1.80438700	-1.53684200	1.55004300
H	-3.52683200	-1.66737700	1.01659900
H	-2.21612100	-2.42548400	0.04928700
O	-0.11853300	-0.12361600	0.42251300
S	0.85117900	0.67525100	-0.45265400
C	2.34284700	-0.37214900	-0.03510800
O	1.21006100	1.95564000	0.18032100
F	2.56625100	-0.39801400	1.27429100
F	2.17851100	-1.62289400	-0.45991600
F	3.42424500	0.13050300	-0.63038200

B

E(UM062X/def2TZVP): -1199.166968 a. u.

G_{298}(UM062X/def2TZVP): -1199.004969 a. u.

Charge = 0 / Multiplicity = 2

C	-3.34193900	-1.37971000	-0.09845600
C	-1.96310500	-1.42089200	0.06149700
C	-1.22994100	-0.24166900	0.20611000
C	-1.90378000	0.98126900	0.17571500
C	-3.28385700	1.02346200	0.02057700
C	-4.00423700	-0.15731500	-0.11470100
H	-3.89954400	-2.30117500	-0.20799500
H	-1.44077400	-2.36994700	0.07548900
H	-1.33840900	1.90128900	0.26725700
H	-3.79525100	1.97751400	0.00367600
H	-5.07967900	-0.12505800	-0.23533700
C	0.24493300	-0.30572100	0.39587900
C	1.21005800	-0.06125600	-0.59850100
H	2.26755100	-0.16113400	-0.40223800
C	0.84000000	0.27599800	-1.97104600
F	1.92247000	0.34991700	-2.77020200
F	0.19556300	1.47221600	-2.11248500
F	-0.00420200	-0.61351200	-2.56624300
S	0.82025900	-0.16807000	1.99636900
C	-0.44360700	-0.81696300	3.08048100
H	-1.35247700	-0.22918400	2.97542400
H	-0.60526400	-1.85273000	2.79224600
H	-0.03488700	-0.74662100	4.08615100
C	1.05355100	1.53627200	2.57670300
H	1.45052800	1.50125400	3.58912900
H	1.76863600	1.97854700	1.88577800
H	0.09587600	2.05042000	2.53327000
O	2.13617700	-0.84135200	2.20699400

B^{+}

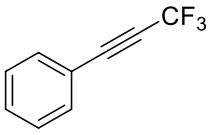
E(RM062X/TZVP): -1199.042957 a. u.

G_{298}(RM062X/TZVP): -1198.875467 a. u.

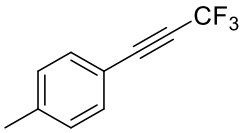
Charge = 1 / Multiplicity = 1

C	-3.36339500	-1.03735400	0.11973100
C	-1.98634300	-1.12469000	0.25507500
C	-1.21576900	0.03777300	0.20856200
C	-1.82030200	1.28046600	0.01763800
C	-3.19920400	1.35673800	-0.11571000
C	-3.96881400	0.20127800	-0.05990800
H	-3.96277900	-1.93738900	0.14957700
H	-1.50859100	-2.08947500	0.37490400
H	-1.21285600	2.17543600	-0.03946000
H	-3.67010200	2.31887900	-0.26666300
H	-5.04408100	0.26472700	-0.16458300
C	0.25344200	-0.04353400	0.34367800
C	1.19094200	-0.11840800	-0.58357800
H	2.24694800	-0.15551100	-0.33973200
C	0.83905000	-0.14042300	-2.05246000
F	1.92662100	-0.37074300	-2.78732100
F	0.32272900	1.02758600	-2.44676400
F	-0.05321700	-1.09040600	-2.34026100
S	0.92315700	-0.00600400	2.02834300
C	0.12726500	-1.33653200	2.90896200
H	-0.95054000	-1.19911700	2.85306400
H	0.44703000	-2.25806800	2.42658800
H	0.48719200	-1.27697200	3.93440400
C	0.34083300	1.51684400	2.74949100
H	0.65009800	1.49541700	3.79287400
H	0.83501100	2.31721600	2.20191100
H	-0.74206600	1.56278300	2.64962000
O	2.39239200	-0.11467000	2.03356100

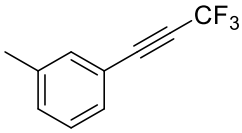
Analytic Data for Synthesized Compounds



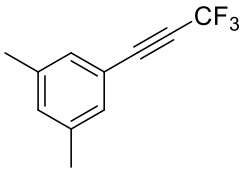
(3,3,3-trifluoroprop-1-yn-1-yl)benzene, [S-8] **3a** was prepared according to general procedure: yellow oil; yield = 74%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 8.0, 7.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 132.66 (q, *J* = 1.5 Hz), 131.10, 128.87, 118.76 (q, *J* = 1.8 Hz), 115.14 (q, *J* = 257.5 Hz), 86.77 (q, *J* = 6.6 Hz), 75.91 (q, *J* = 52.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.83; **IR (neat):** ν_{max} = 2883, 2835, 2249, 1313, 1137 cm^{-1}; **LRMS** m/z (EI) calc. for $C_9H_5F_3$ [M+] = 170.1, found 170.1; R_f = 0.6 (hex).



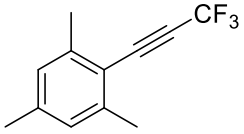
1-methyl-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-9] **3ab** was prepared according to general procedure: yellow oil; yield = 61%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.68, 132.58 (q, *J* = 1.5 Hz), 129.62, 115.67 (q, *J* = 1.8 Hz), 115.18 (q, *J* = 257.5 Hz), 87.15 (q, *J* = 6.2 Hz), 75.46 (q, *J* = 52.5 Hz), 21.89; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.59; **IR (neat):** ν_{max} = 2921, 2853, 2252, 1461, 1144 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_7F_3$ [M+] = 184.1, found 184.1; R_f = 0.7 (hex).



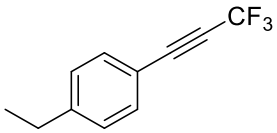
1-methyl-3-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-10] **3ac** was prepared according to general procedure: yellow oil; yield = 62%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 2.37 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.75, 133.13 (q, J = 1.5 Hz), 131.98, 129.76 (q, J = 1.5 Hz) 128.75, 118.55 (q, J = 1.8 Hz), 115.11 (q, J = 257.5 Hz), 87.03 (q, J= 6.6 Hz), 75.59 (q, J = 52.5 Hz) 21.35; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.71; **IR (neat):** ν_{max} = 2980, 2925, 2889, 2233, 1319, 1143 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_7F_3$ [M+] = 184.1, found 184.1; R_f = 0.7 (hex).



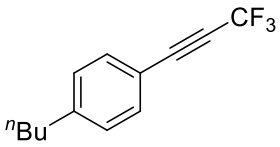
1,3-dimethyl-5-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-11] **3ad** was prepared according to general procedure: colorless oil; yield = 71%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.19 (s, 2H), 7.10 (s, 1H), 2.32 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.60, 133.00, 130.27 (q, *J* = 1.5 Hz), 118.33 (q, *J* = 1.8 Hz), 115.14 (q, *J* = 257.5 Hz), 87.31 (q, *J* = 6.2 Hz), 75.25 (q, *J* = 52.5 Hz), 21.24; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.62; **IR (neat):** ν_{max} = 2988, 2872, 2251, 1392, 1142 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{11}H_9F_3$ [M+] = 198.1, found 198.1; R_f = 0.6 (hex).



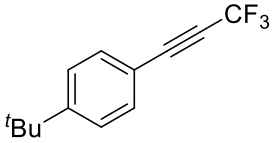
1,3,5-trimethyl-2-(3,3,3-trifluoroprop-1-yn-1-yl)benzene, **3ae** was prepared according to general procedure: white solid; yield = 78%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.90 (s, 2H), 2.41 (s, 6H), 2.31 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.08 (q, *J* = 1.5 Hz), 140.98, 128.19, 115.59 (q, *J* = 1.8 Hz), 115.51 (q, *J* = 257.1 Hz), 85.47 (q, *J* = 6.6 Hz), 83.13 (q, *J* = 52.1 Hz), 21.67, 20.77; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.03; **IR (neat):** ν_{max} = 2988, 2872, 2251, 1142, 1066 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{12}H_{11}F_3$ [M+] = 212.0813, Found 212.0816; $\boldsymbol{R_f}$ = 0.6 (hex).



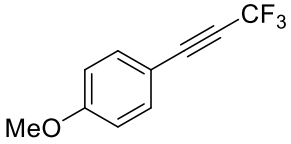
1-ethyl-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-10] **3af** was prepared according to general procedure: yellow oil; yield = 71%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.90, 132.69 (q, *J* = 1.5 Hz), 128.45, 115.85 (q, *J* = 1.8 Hz), 115.18 (q, *J* = 257.5 Hz), 87.19 (q, *J* = 6.6 Hz), 75.42 (q, *J* = 52.5 Hz), 29.18, 15.35; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.58; **IR (neat):** ν_{max} = 2989, 2902, 2251, 1260, 1057 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{11}H_9F_3$ [M+] = 198.1, found 1.1; $\boldsymbol{R_f}$ = 0.7 (hex).



1-butyl-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-10] **3ag** was prepared according to general procedure: yellow oil; yield = 84%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.60 (tt, *J* = 7.8, 7.6 Hz, 2H), 1.35 (qt, *J* = 7.8, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.64, 132.60 (q, *J* = 1.5 Hz), 128.98, 115.81 (q, *J* = 1.8 Hz), 115.18 (q, *J* = 257.5 Hz), 87.21 (q, *J* = 6.6 Hz), 75.43 (q, *J* = 52.5 Hz), 35.93, 33.43, 22.49, 14.09; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.57; **IR (neat):** ν_{max} = 2988, 2892, 2252, 1317, 1163 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{13}H_{13}F_3$ [M+] = 226.2, found 226.2; $\boldsymbol{R_f}$ = 0.6 (hex).

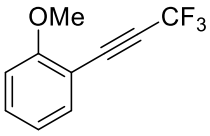


1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-8] **3ah** was prepared according to general procedure: yellow oil; yield = 79%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.75, 132.46 (q, *J* = 1.6 Hz), 125.91, 115.66 (q, *J* = 3.7 Hz), 115.18 (q, *J* = 257.5 Hz), 87.15 (q, *J* = 6.6 Hz), 75.43 (q, *J* = 52.5 Hz), 35.28, 31.26; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.55; **IR (neat):** ν_{max} = 2967, 2872, 2252, 1317, 1135 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{13}H_{13}F_3$ [M+] = 226.2, found 226.2; $\boldsymbol{R_f}$ = 0.7 (hex).

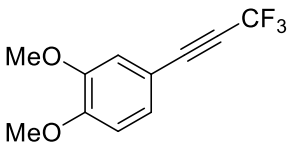


1-methoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-8] **3ai** was prepared according to general procedure: yellow oil; yield = 52%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.84 (s,

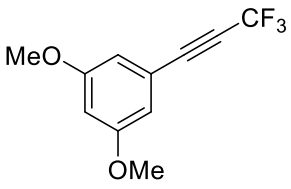
3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.75, 134.38 (q, *J* = 1.5 Hz), 115.16 (q, *J* = 277.9 Hz), 114.54, 110.54 (q, *J* = 1.8 Hz), 87.26 (q, *J* = 6.5 Hz), 75.02 (q, *J* = 52.3 Hz), 55.62; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.39; **IR (neat):** ν_{max} = 2988, 2927, 2841, 2249, 1607, 1511, 1130 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_7F_3O$ [M+] = 200.0, found 200.0; R_f = 0.4 (hex/ethyl acetate = 20/1).



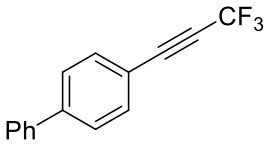
1-methoxy-2-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-9] **3aj** was prepared according to general procedure: yellow oil; yield = 77%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.43 (ddd, *J* = 8.5, 8.5, 1.4 Hz, 1H), 6.95 (dd, *J* = 8.5, 7.6 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.49, 134.58 (q, *J* = 1.5 Hz), 132.69, 120.74, 115.23 (q, *J* = 257.5 Hz), 111.10, 108.02 (q, *J* = 1.8 Hz), 83.93 (q, *J* = 6.6 Hz), 79.56 (q, *J* = 52.5 Hz), 56.04; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.44; **IR (neat):** ν_{max} = 2928, 2832, 22505, 1494, 1318, 1127 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_7F_3O$ [M+] = 200.0, found 200.0; R_f = 0.5 (hex/ethyl acetate = 20/1).



1,2-dimethoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene, **3ak** was prepared according to general procedure: yellow oil; yield = 42%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.18 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.73, 149.06, 126.65 (q, *J* = 1.5 Hz), 115.23 (q, *J* = 257.5 Hz), 114.76 (q, *J* = 1.8 Hz), 111.25, 110.56, 87.31 (q, *J* = 6.2 Hz), 74.80 (q, *J* = 52.5 Hz), 56.24, 56.20; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.40; **IR (neat):** ν_{max} = 2935, 2850, 2239, 1515, 1253, 1128 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{11}H_9F_3O_2$ [M+] = 230.0555, Found 230.0556; R_f = 0.3 (hex/ethyl acetate = 20/1).

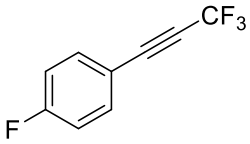


1,3-dimethoxy-5-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-12] **3al** was prepared according to general procedure: yellow oil; yield = 49%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.69 (d, *J* = 2.3 Hz, 2H), 6.56 (t, *J* = 2.3 Hz, 1H), 3.80 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.90, 119.86 (q, *J* = 1.8 Hz), 114.99 (q, *J* = 257.8 Hz), 110.32 (q, *J* = 1.5 Hz),104.43, 86.70 (q, *J* = 6.6 Hz), 75.24 (q, *J* = 52.9 Hz), 55.75; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.79; **IR (neat):** ν_{max} = 3010, 2940, 2837, 2250, 1593, 1262, 1137 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{11}H_9F_3O_2$ [M+] = 230.2, found 230.2; R_f = 0.4 (hex/ethyl acetate = 20/1).

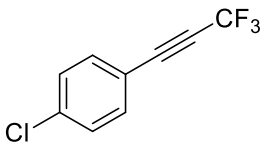


4-(3,3,3-trifluoroprop-1-yn-1-yl)-1,1'-biphenyl,[S-8] **3am** was prepared according to general procedure: white solid; yield = 75%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.62 (m, 4H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.48 (dd, *J* = 8.0, 7.0 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.92, 139.89, 133.11 (q, *J* = 1.5

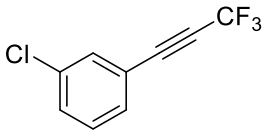
Hz), 129.22, 128.45, 127.51, 127.35; 117.41 (q, *J* = 1.8 zxe44Hz), 115.13 (q, *J* = 257.5 Hz), 86.76 (q, *J* = 6.6 Hz), 76.42 (q, *J* = 52.5 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.66; **IR (neat):** ν_{max} = 3037, 2927, 2855, 2253, 1485, 1318, 1123 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{15}H_9F_3$ [M+] = 246.1, found 246.1; R_f = 0.4 (hex).



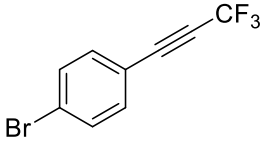
1-fluoro-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-9] **3an** was prepared according to general procedure: yellow oil; yield = 92%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.10 (dd, *J* = 8.6 Hz, 8.6 Hz, 2H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ164.23 (d, *J* = 254.6 Hz), 134.93 (dq, *J* = 9.0, 1.5 Hz), 116.45 (d, *J* = 22.3 Hz), 114.82 (q, *J* = 1.8 Hz), 114.98 (q, *J* = 257.8 Hz), 85.72 (q, *J* = 6.6 Hz), 76.36 (q, *J* = 52.8 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.89 (s, 3F), -106.07 (s, 1F); **IR (neat):** ν_{max} = 2987, 2925, 2250, 1392, 1143, 1066 cm^{-1}; **LRMS** m/z (EI) calc. for $C_9H_4F_4$ [M+] = 188.0, found 188.0; R_f = 0.7 (hex).



1-chloro-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-13] **3ao** was prepared according to general procedure: yellow oil; yield = 90%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.59, 133.87 (q, *J* = 1.5 Hz), 129.37, 117.10 (q, *J* = 1.8 Hz), 114.93 (q, *J* = 258.2 Hz), 85.52 (q, *J* = 6.2 Hz), 76.76 (q, *J* = 52.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.02; **IR (neat):** ν_{max} = 2987, 2902, 2251, 1289, 1066 cm^{-1}; **LRMS** m/z (EI) calc. for $C_9H_4ClF_3$ [M+] = 204.0, found 204.0; R_f = 0.7 (hex).

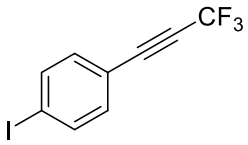


1-chloro-3-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-8] **3ap** was prepared according to general procedure: yellow oil; yield = 85%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 2.4, 1.6 Hz, 1H), 7.46 (ddd, *J* = 7.9, 2.4, 1.2 Hz, 1H), 7.45 (ddd, *J* = 7.9, 1.6, 1.2 Hz, 1H), 7.34, (dd, *J* = 7.9, 7.9 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.90, 132.47 (q, *J* = 1.5 Hz), 131.49, 130.77 (q, *J* = 1.5 Hz), 130.18, 120.39 (q, *J* = 1.8 Hz), 114.83 (q, *J* = 258.6 Hz), 85.00 (q, *J* = 6.6 Hz), 77.30 (q, *J* = 53.2 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.15; **IR (neat):** ν_{max} = 2955, 2924, 2854, 2247, 1462, 1261 cm^{-1}; **LRMS** m/z (EI) calc. for $C_9H_4ClF_3$ [M+] = 204.0, found 204.0; R_f = 0.7 (hex).

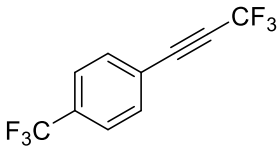


1-bromo-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-8] **3aq** was prepared according to general procedure: yellow oil; yield = 91%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.97 (q, *J* = 1.8 Hz), 132.30, 125.95, 117.62 (q, *J* = 1.9 Hz), 114.94 (q, *J* = 258.2 Hz), 85.58 (q, *J* = 6.6 Hz), 76.88 (q, *J* = 52.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.05; **IR (neat):**

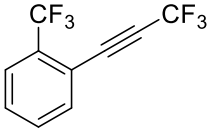
ν_{max} = 2930, 2883, 2255, 1487, 1310, 1128 cm^{-1}; **LRMS** m/z (EI) calc. for $C_9H_4BrF_3$ [M+] = 248.1, found 248.1; $\boldsymbol{R_f}$ = 0.7 (hex).



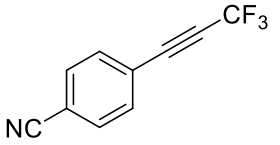
1-iodo-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-9] **3ar** was prepared according to general procedure: white solid; yield = 53%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.19, 133.86 (q, *J* = 1.5 Hz), 118.13 (q, *J* = 1.8 Hz), 114.93 (q, *J* = 258.2 Hz), 97.97, 85.73 (q, *J* = 6.6 Hz), 77.07 (q, *J* = 52.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.05; **IR (neat):** ν_{max} = 2925, 2854, 2255, 1486, 1312, 1142 cm^{-1}; **LRMS** m/z (EI) calc. for $C_9H_4F_3I$ [M+] = 296.0, found 296.0; $\boldsymbol{R_f}$ = 0.5 (hex).



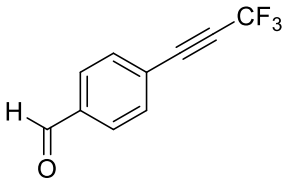
1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene,[S-9] **3as** was prepared according to general procedure: colorless oil; yield = 90%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.04 (q, *J* = 1.5 Hz), 132.88 (q, *J* = 33.5 Hz), 125.88 (q, *J* = 3.8 Hz), 123.65 (q, *J* = 273.5 Hz), 122.97 (q, *J* = 1.8 Hz), 114.75 (q, *J* = 258.2 Hz), 84.81 (q, *J* = 6.2 Hz), 77.72 (q, *J* = 53.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.32 (s, 3F), -63.27 (s, 3F); **IR (neat):** ν_{max} = 2977, 2930, 2887, 2251, 1316, 1135 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_4F_6$ [M+] = 238.0, found 238.0; $\boldsymbol{R_f}$ = 0.8 (hex).



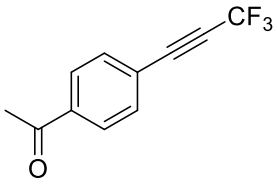
1-(trifluoromethyl)-2-(3,3,3-trifluoroprop-1-yn-1-yl)benzene, **3at** was prepared according to general procedure: colorless oil; yield = 91%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 – 7.69 (m, 2H), 7.63 – 7.56 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.07 (q, *J* = 1.8 Hz), 133.17 (qq, *J* = 31.8, 1.1 Hz), 131.94 (q, *J* = 1.1 Hz), 131.04, 126.50 (q, *J* = 4.9 Hz), 123.11 (q, *J* = 274.2 Hz), 116.83 (qq, *J* = 2.5, 1.8 Hz), 114.80 (q, *J* = 258.6 Hz), 83.86 (q, *J* = 6.4 Hz), 80.51 (qq, *J* = 53.6, 1.1 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.78 (s, 3F), -62.18 (s, 3F); **IR (neat):** ν_{max} = 2929, 2890, 2251, 1317, 1164 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_4F_6$ [M+] = 238.0, found 238.0; $\boldsymbol{R_f}$ = 0.8 (hex).



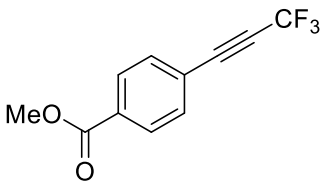
4-(3,3,3-trifluoroprop-1-yn-1-yl)benzonitrile,[S-12] **3au** was prepared according to general procedure: yellow oil; yield = 79%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.20 (q, *J* = 1.5 Hz), 132.53, 123.34 (q, *J* = 1.8 Hz), 117.84, 114.79, 114.62 (q, *J* = 258.9 Hz), 84.21 (q, *J* = 6.6 Hz), 79.08 (q, *J* = 53.6 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.51; **IR (neat):** ν_{max} = 2998, 2918, 2259, 2233, 1503, 1310, 1140 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_4F_3N$ [M+] = 195.1, found 195.1; $\boldsymbol{R_f}$ = 0.4 (hex/ethyl acetate = 20/1).



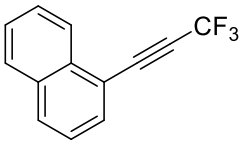
4-(3,3,3-trifluoroprop-1-yn-1-yl)benzaldehyde,[S-13] **3av** was prepared according to general procedure: yellow oil; yield = 81%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.06 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.21, 137.60, 133.29 (q, *J* = 1.5 Hz), 129.80, 124.45 (q, *J* = 1.8 Hz), 114.76 (q, *J* = 258.6 Hz), 85.11 (q, *J* = 6.6 Hz), 78.60 (q, *J* = 53.2 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.33; **IR (neat):** ν_{max} = 2920, 2851, 2256, 1705, 1308, 1135 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{10}H_5F_3O$ [M+] = 198.3, found 198.3; R_f = 0.3 (hex/ethyl acetate = 10/1).



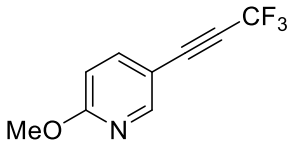
1-(4-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl)ethan-1-one,[S-14] **3aw** was prepared according to general procedure: yellow oil; yield = 79%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.14, 138.59, 132.90 (q, *J* = 1.5 Hz), 128.56, 123.14 (q, *J* = 1.8 Hz), 114.81 (q, *J* = 258.2 Hz), 85.38 (q, *J* = 6.6 Hz), 78.15 (q, *J* = 53.2 Hz), 26.90; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.22; **IR (neat):** ν_{max} = 2979, 2927, 2878, 2259, 1682, 1313, 1130 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{11}H_7F_3O$ [M+] = 212.1, found 212.1; R_f = 0.4 (hex/ethyl acetate = 10/1).



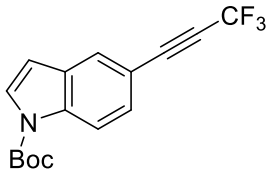
Methyl 4-(3,3,3-trifluoroprop-1-yn-1-yl)benzoate,[S-15] **3ax** was prepared according to general procedure: yellow oil; yield = 83%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.16, 132.65 (q, *J* = 1.5 Hz), 132.31, 129.91, 123.06 (q, *J* = 1.8 Hz), 114.83 (q, *J* = 258.6 Hz), 85.47 (q, *J* = 6.2 Hz), 77.96 (q, *J* = 52.9 Hz), 52.72; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -50.20; **IR (neat):** ν_{max} = 2988, 2987, 2251, 1649, 1277, 1056 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{11}H_7F_3O_2$ [M+] = 228.0, found 228.0; R_f = 0.4 (hex/ethyl acetate = 15/1).



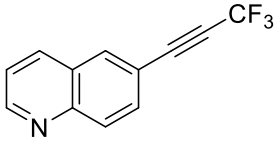
1-(3,3,3-trifluoroprop-1-yn-1-yl)naphthalene,[S-8] **3b** was prepared according to general procedure: yellow oil; yield = 85%; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.1 Hz, 1H), 7.65 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.58 (ddd, *J* = 1.2, 6.8, 8.1 Hz, 1H), 7.48 (dd, *J* = 7.1, 8.3 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ , 133.37 (q, *J* = 1.5 Hz), 132.74 (q, *J* = 1.8 Hz), 133.20, 131.75, 128.81, 128.05, 127.26, 125.53, 125.21, 116.21 (q, *J* = 1.8 Hz), 115.28 (q, *J* = 257.2 Hz), 85.38 (q, *J* = 6.4 Hz), 80.37 (q, *J* = 52.7 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -49.47; **IR (neat):** ν_{max} = 3086, 2927, 2878, 2244, 1311, 1133 cm^{-1}; **LRMS** m/z (EI) calc. for $C_{13}H_7F_3$ [M+] = 220.1, found 220.1; R_f = 0.5 (hex/ethyl acetate = 50/1).



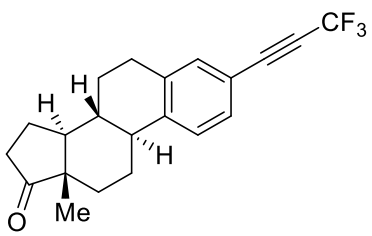
2-methoxy-5-(3,3,3-trifluoroprop-1-yn-1-yl)pyridine, **3c** was prepared according to general procedure: yellow oil; yield = 75%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.38 (d, *J* = 2.4 Hz, 1H), 7.69 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.17, 151.96 (q, *J* = 1.5 Hz), 141.76 (q, *J* = 1.5 Hz), 115.01 (q, *J* = 257.8 Hz), 111.46, 108.56 (q, *J* = 1.8 Hz), 84.38 (q, *J* = 6.4 Hz), 77.13 (q, *J* = 52.6 Hz), 54.22; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.82; **IR (neat):** ν_{max} = 2988, 2871, 2251, 1392, 1261, 1142 cm^{-1}; **HRMS** m/z (EI) calc. for $C_9H_6F_3NO$ [M+] = 201.0401, Found 201.0400; $\boldsymbol{R_f}$ = 0.4 (hex/ethyl acetate = 30/1).



tert-butyl 5-(3,3,3-trifluoroprop-1-yn-1-yl)-1*H*-indole-1-carboxylate, **3d** was prepared according to general procedure: yellow oil; yield = 60%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.65 (d, *J* = 3.7 Hz, 1H), 7.48 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.58 (d, *J* = 3.7 Hz, 1H), 1.68 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.47, 136.41, 130.68, 128.27 (q, *J* = 1.5 Hz), 127.72, 126.04 (q, *J* = 1.8 Hz), 115.77, 115.26 (q, *J* = 259.3 Hz), 112.60 (q, *J* = 1.8 Hz), 107.19, 87.92 (q, *J* = 6.4 Hz), 84.76, 74.85 (q, *J* = 52.5 Hz), 28.36; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.41; **IR (neat):** ν_{max} = 3012, 2989, 2866, 2253, 1691, 1481, 1361, 1153 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{16}H_{14}F_3NO_2$ [M+] = 309.0929, Found 309.0974; $\boldsymbol{R_f}$ = 0.45 (hex/ethyl acetate = 10/1).

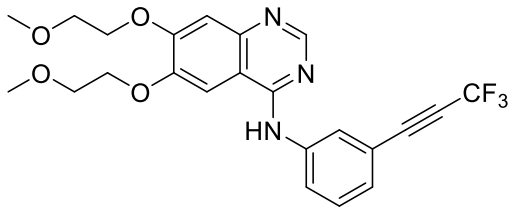


6-(3,3,3-trifluoroprop-1-yn-1-yl)quinoline, **3e** was prepared according to general procedure: white solid; yield = 75%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.98 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.10 (d, *J* = 1.8 Hz, 1H), 7.77 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.47 (dd, *J* = 8.4, 4.3 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.31, 133.71 (q, *J* = 1.5 Hz), 131.60 (q, *J* = 1.2 Hz), 130.48, 127.87, 122.49, 116.87 (q, *J* = 2.3 Hz), 114.95 (q, *J* = 258.2 Hz), 86.11 (q, *J* = 6.6 Hz), 76.70 (q, *J* = 52.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.92; **IR (neat):** ν_{max} = 2993, 2879, 2250, 1481, 1370, 1161 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{12}H_6F_3N$ [M+] = 221.0452, Found 221.0452; $\boldsymbol{R_f}$ = 0.45 (hex/ethyl acetate = 3/1).



(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(3,3,3-trifluoroprop-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one, **3f** was prepared according to the procedure, using a divided cell: pale yellow oil; yield = 70%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 2H), 7.27 – 7.21 (m, 1H), 2.96 – 2.85 (m, 2H), 2.52 (dd, *J* = 18.7, 9.0 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.37 – 2.26 (m, 1H),

2.24 – 1.93 (m, 4H), 1.65 – 1.44 (m, 6H), 0.92 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 220.69, 143.45, 137.40, 133.12 (q, *J* = 1.8 Hz), 129.89 (q, *J* = 1.5 Hz), 125.95, 115.95 (q, *J* = 2.2 Hz), 115.13 (q, *J* = 257.3 Hz), 87.12 (q, *J* = 6.5 Hz), 75.37 (q, *J* = 52.1 Hz), 50.69, 48.09, 44.74, 37.97, 36.01, 31.71, 29.21, 26.35, 25.71, 21.78, 14.02; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.54; **IR (neat):** ν_{max} = 3011, 2933, 2870, 2251, 1739, 1322, 1198, 1136 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{21}H_{21}F_3O$ [M+] = 346.1544, Found 346.1547; $\boldsymbol{R_f}$ = 0.3 (hex/ethyl acetate = 5/1).



6,7-bis(2-methoxyethoxy)-*N*-(3-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl)quinazolin-4-amine, **3g** was prepared according to the procedure, using a divided cell: pale yellow oil; yield = 50%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.62 (d, *J* = 12.0 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.23 (m, 3H), 7.15 (d, *J* = 2.8 Hz, 1H), 4.25 – 4.21 (m, 2H), 4.20 – 4.16 (m, 2H), 3.80 – 3.78 (m, 2H), 3.78 – 3.76 (m, 2H), 3.42 (s, 3H), 3.41 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.57, 154.84, 153.38, 149.04, 147.02, 138.97, 129.17, 127.96 (q, *J* = 1.1 Hz), 125.29 (q, *J* = 1.1 Hz), 124.31, 122.65, 119.24 (q, *J* = 1.8 Hz), 114.99 (q, *J* = 257.2 Hz), 109.27 (q, *J* = 2.4 Hz), 102.82, 86.53 (q, *J* = 6.5 Hz), 75.87 (q, *J* = 52.5 Hz), 71.11, 70.57, 69.29, 68.49, 59.47, 59.40; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -49.77; **IR (neat):** ν_{max} = 3292, 2998, 2926, 2850, 2246, 1163, 1532, 1432, 1242, 1130 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{22}F_3N_3O_4$ [M+] = 461.1562, Found 461.1560; $\boldsymbol{R_f}$ = 0.3 (hex/ethyl acetate = 1/4).

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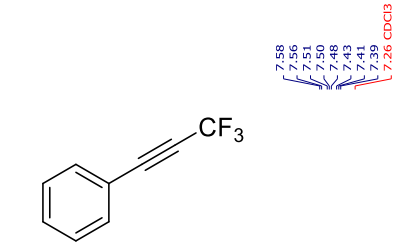
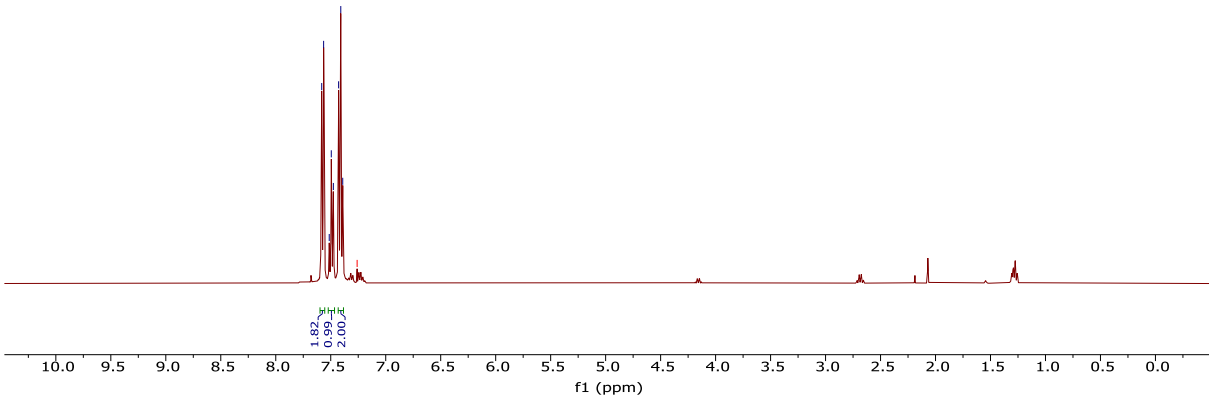
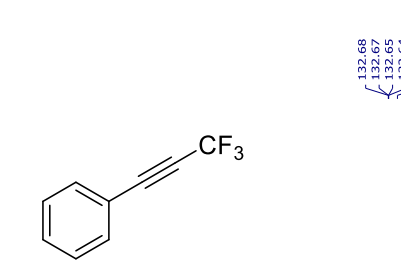
NMR Spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR)

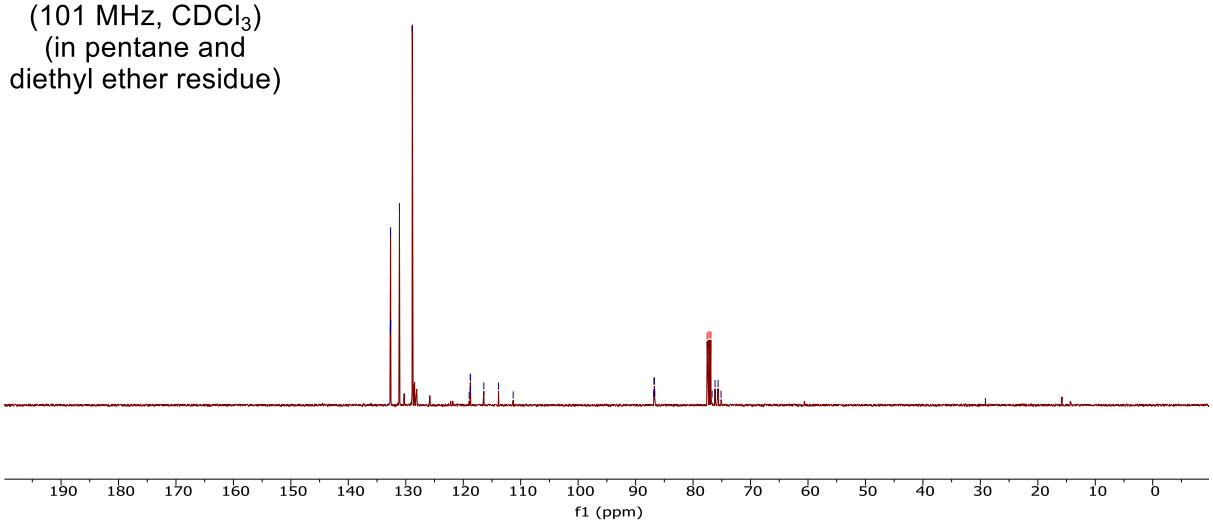


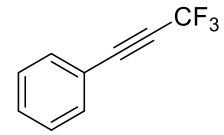
3a, ^{1}H NMR
(400 MHz, $CDCl_3$)
(in pentane and
diethyl ether residue)



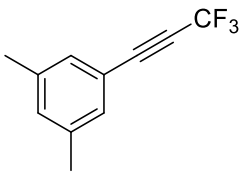


3a, ^{13}C NMR
(101 MHz, $CDCl_3$)
(in pentane and
diethyl ether residue)

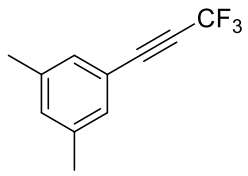




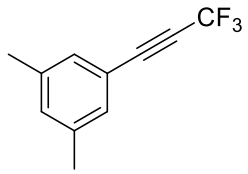
3a, ^{19}F NMR
(376 MHz, $CDCl_3$)



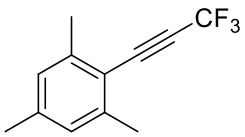
3ad, ^{1}H NMR
(400 MHz, $CDCl_3$)



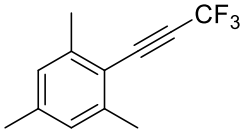
3ad, ^{13}C NMR
(101 MHz, $CDCl_3$)



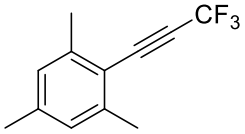
3ad, ^{19}F NMR
(376 MHz, $CDCl_3$)



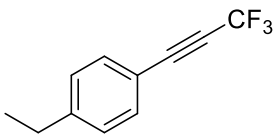
3ae, ^{1}H NMR
(400 MHz, $CDCl_3$)



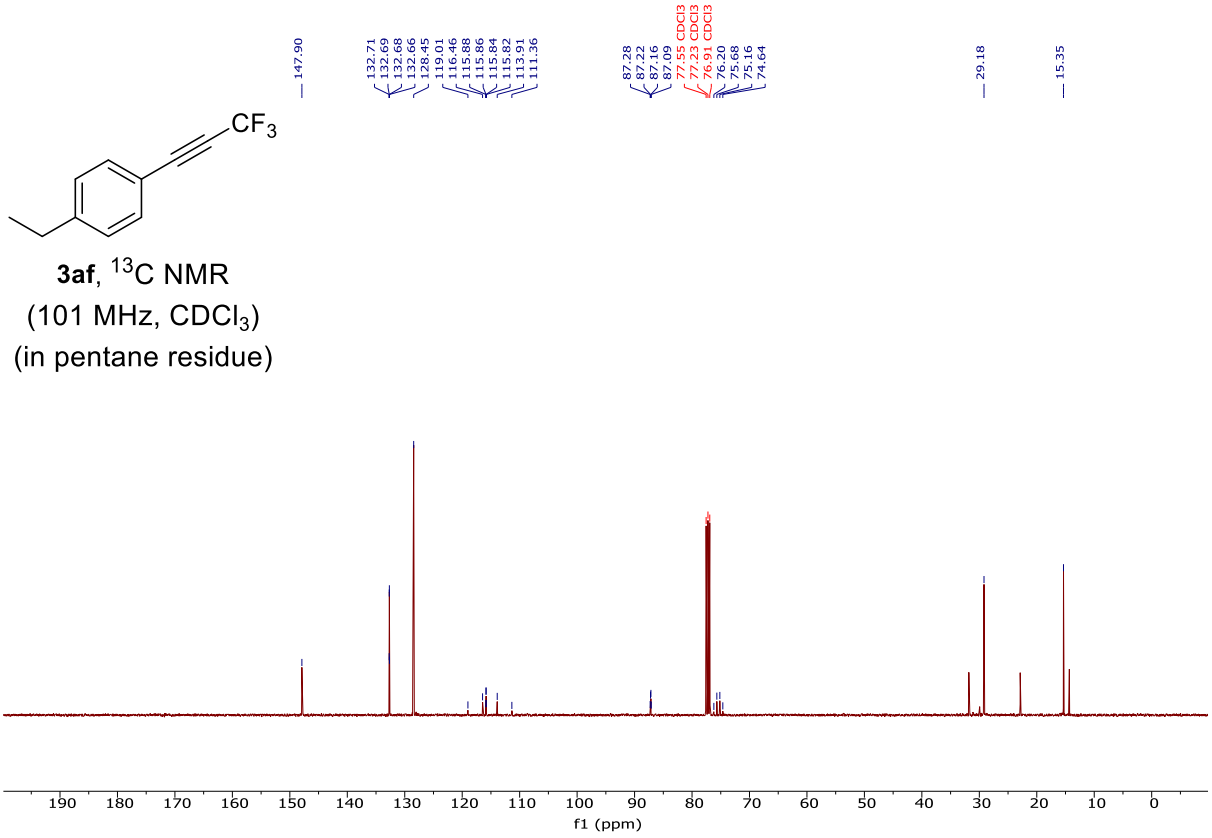
3ae, ^{13}C NMR
(101 MHz, $CDCl_3$)



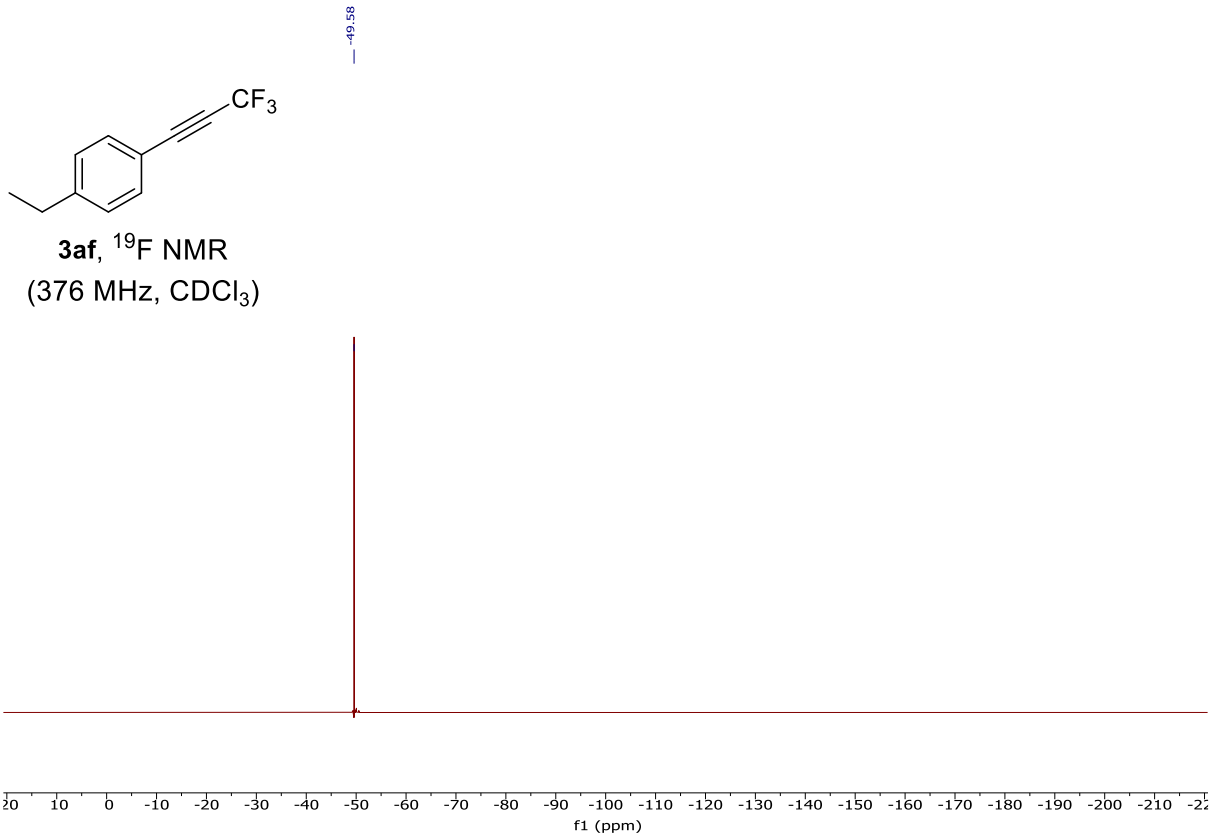
3ae, ^{19}F NMR
(376 MHz, $CDCl_3$)



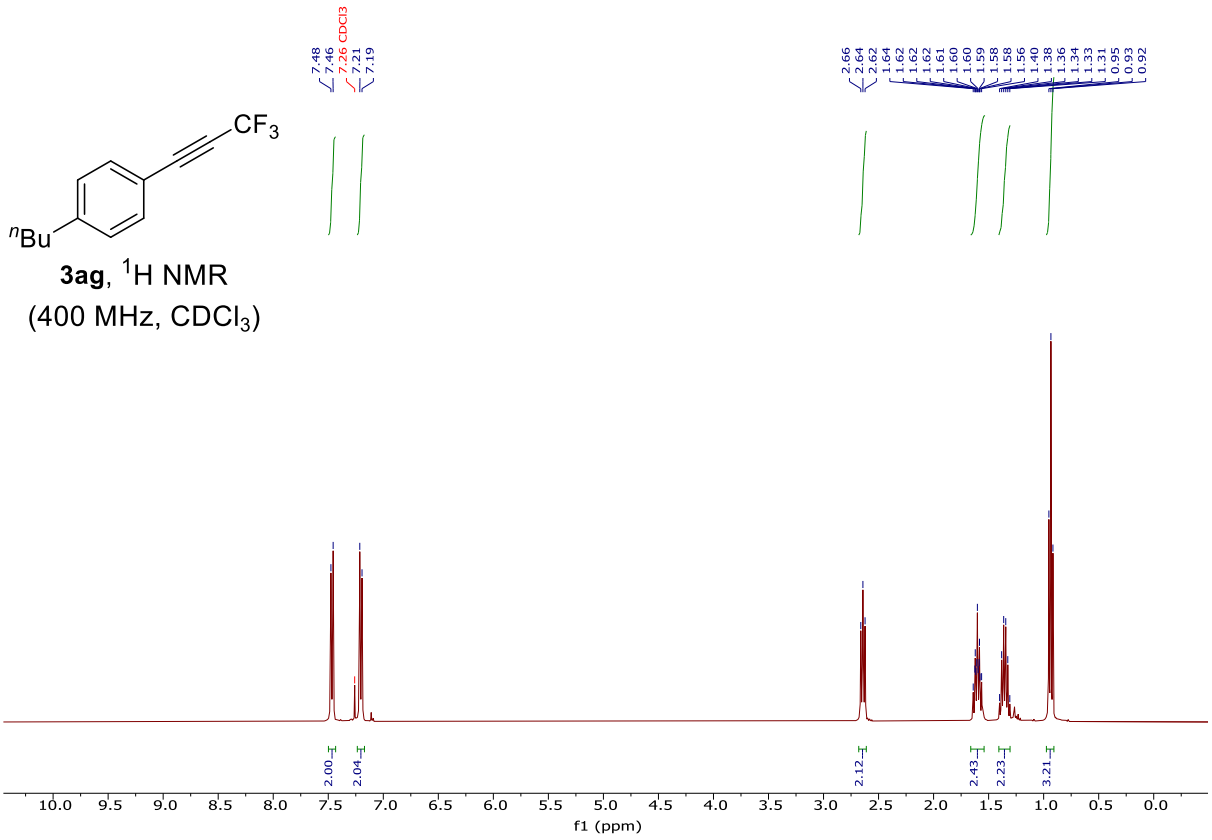
3af, ^{1}H NMR
(400 MHz, $CDCl_3$)
(in pentane residue)



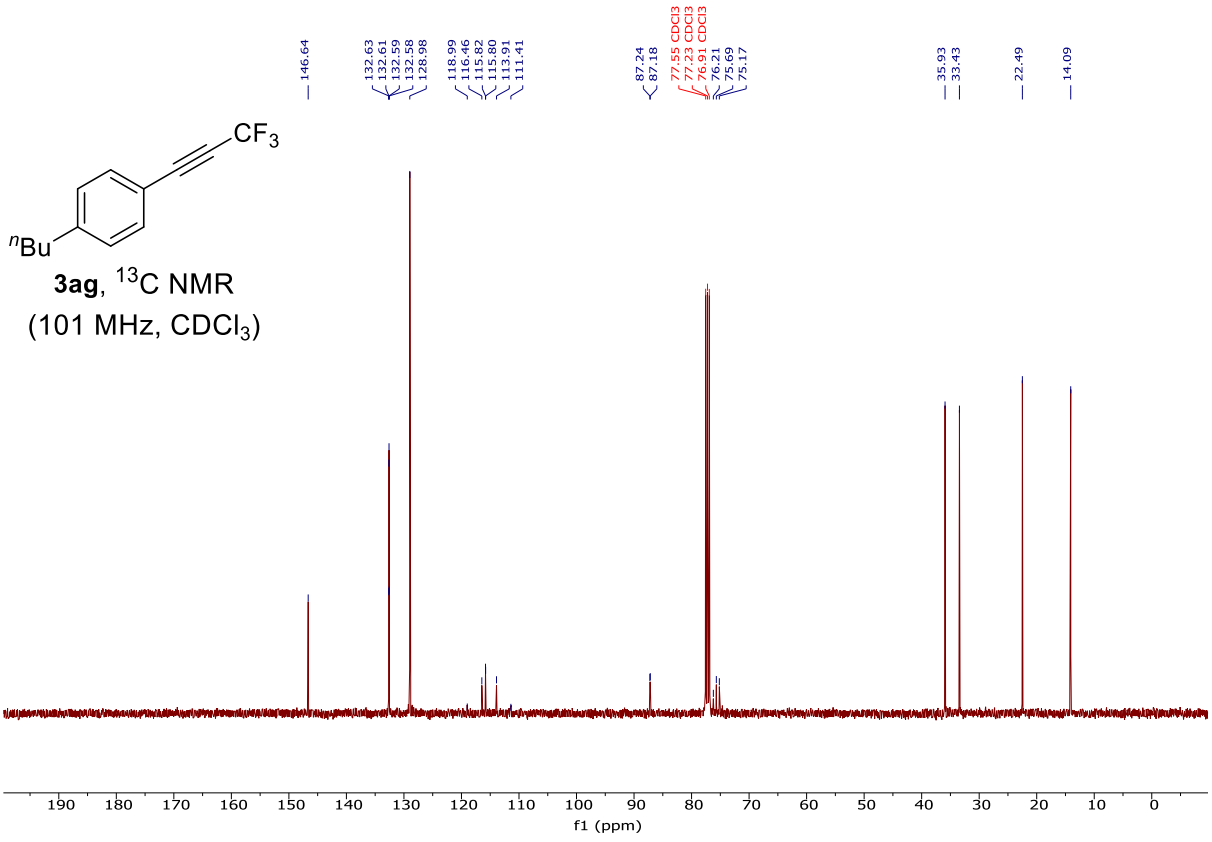
3af, ^{13}C NMR
(101 MHz, $CDCl_3$)
(in pentane residue)



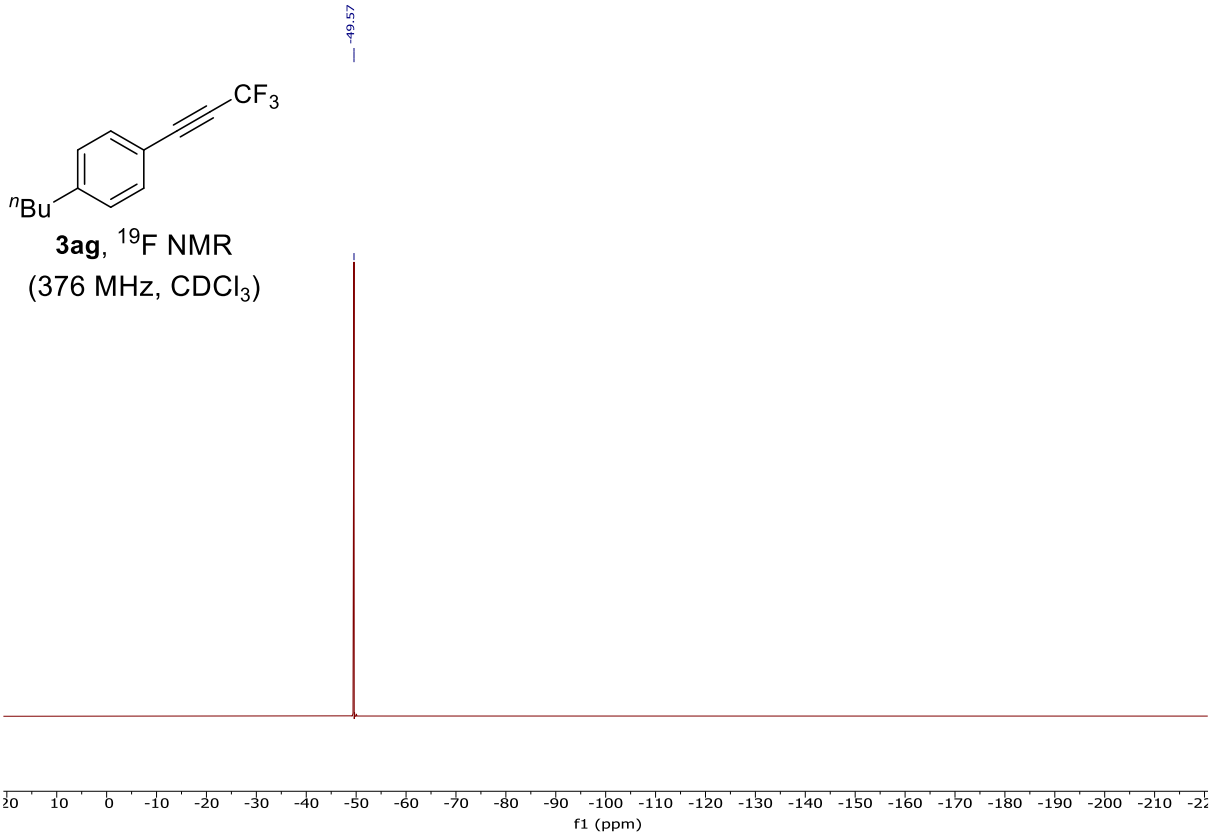
3af, ^{19}F NMR
(376 MHz, $CDCl_3$)



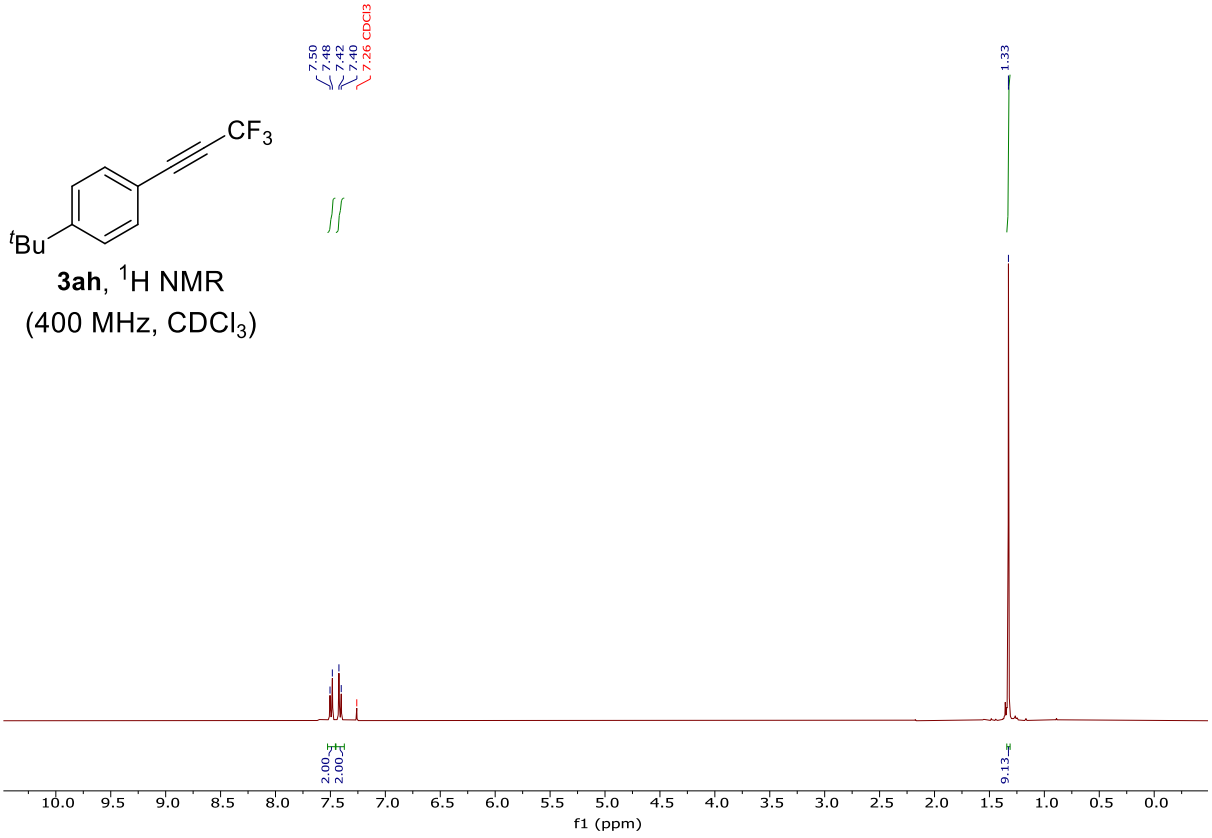
3ag, ^{1}H NMR
(400 MHz, $CDCl_3$)



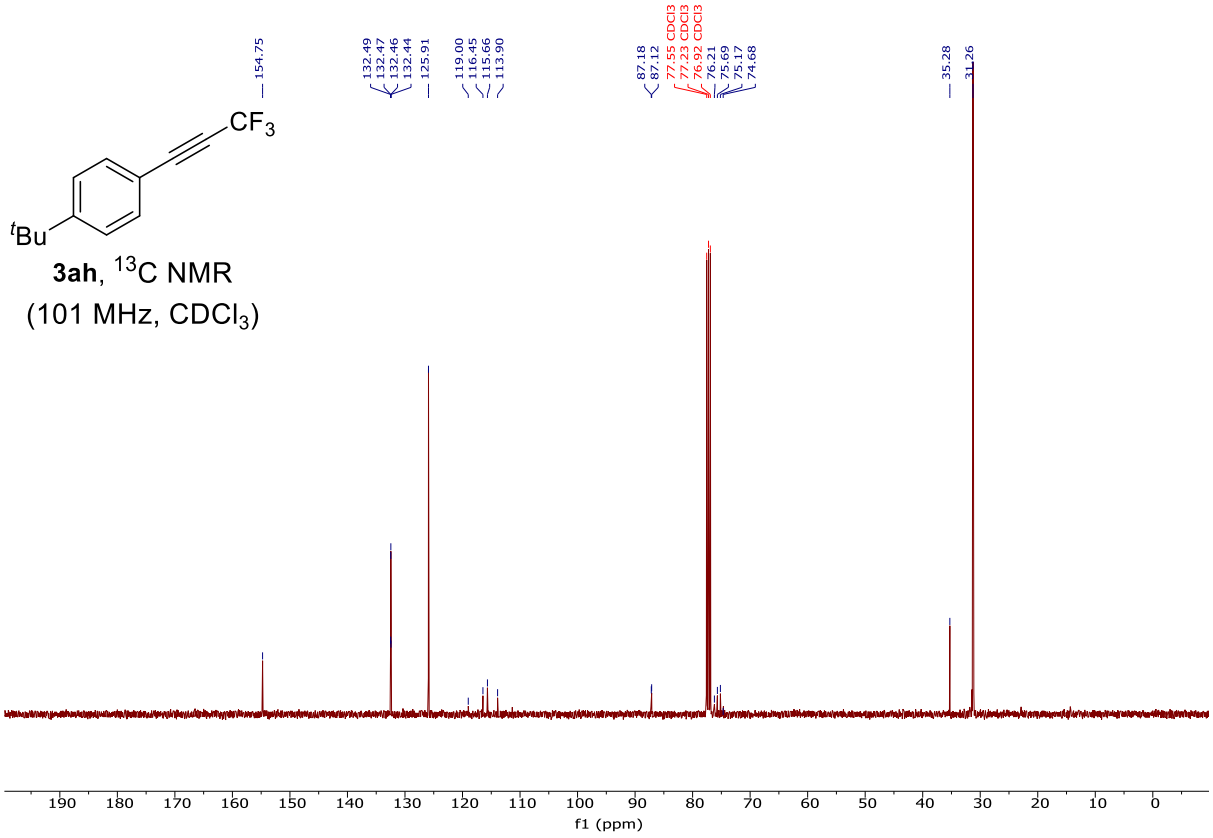
3ag, ^{13}C NMR
(101 MHz, $CDCl_3$)



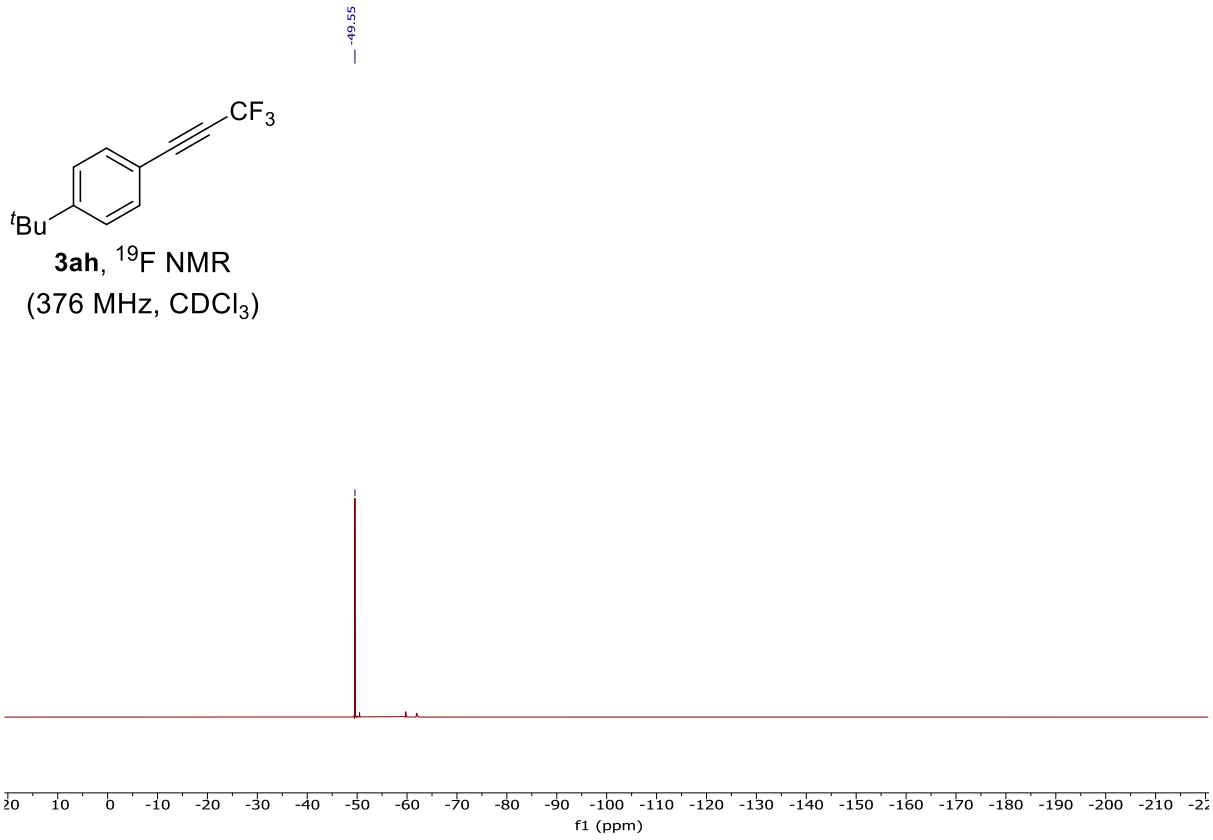
3ag, ^{19}F NMR
(376 MHz, $CDCl_3$)



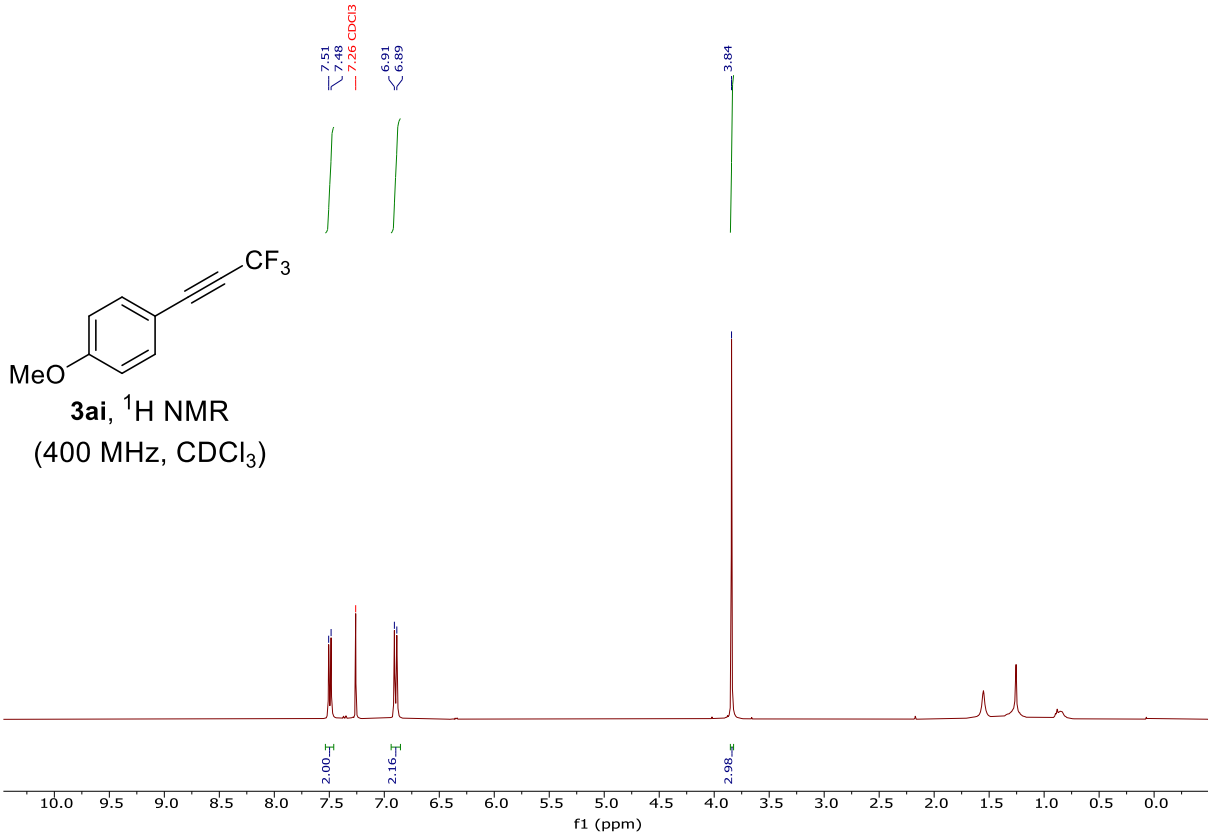
3ah, ^{1}H NMR
(400 MHz, $CDCl_3$)



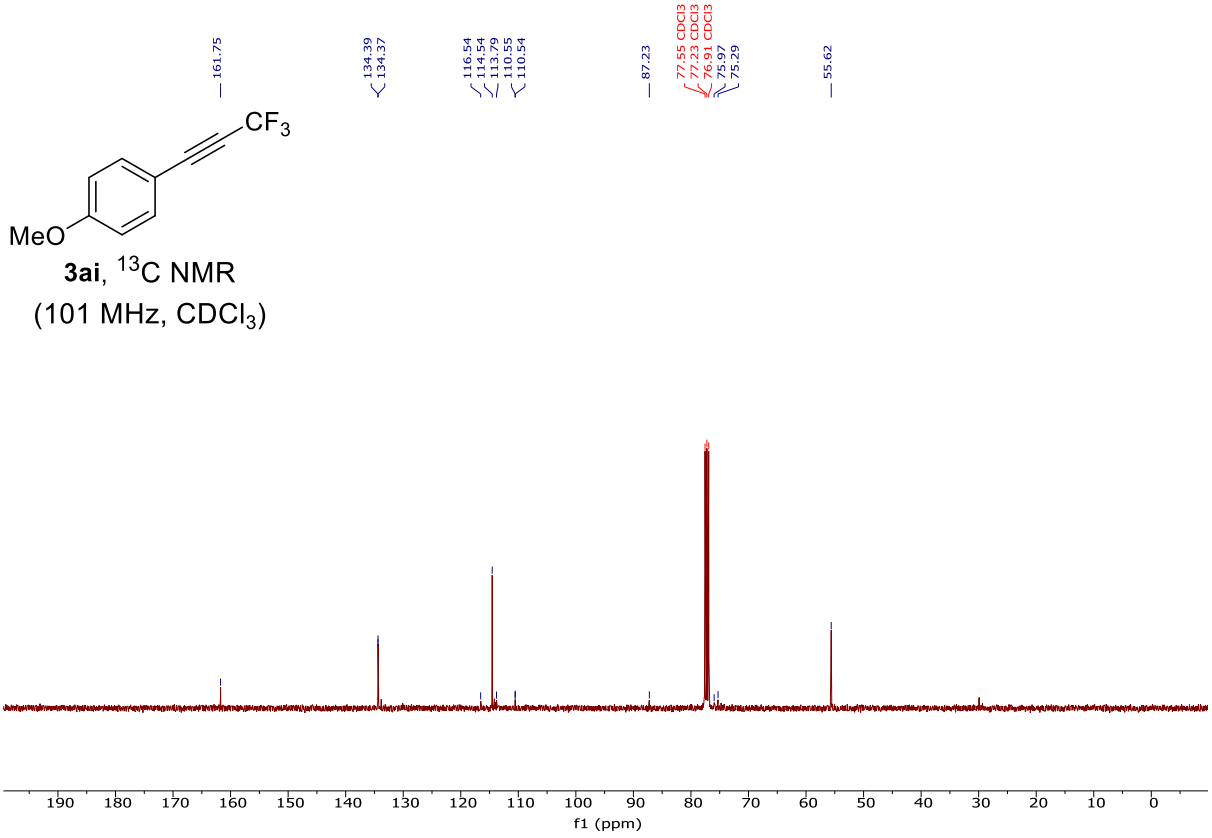
3ah, ^{13}C NMR
(101 MHz, $CDCl_3$)



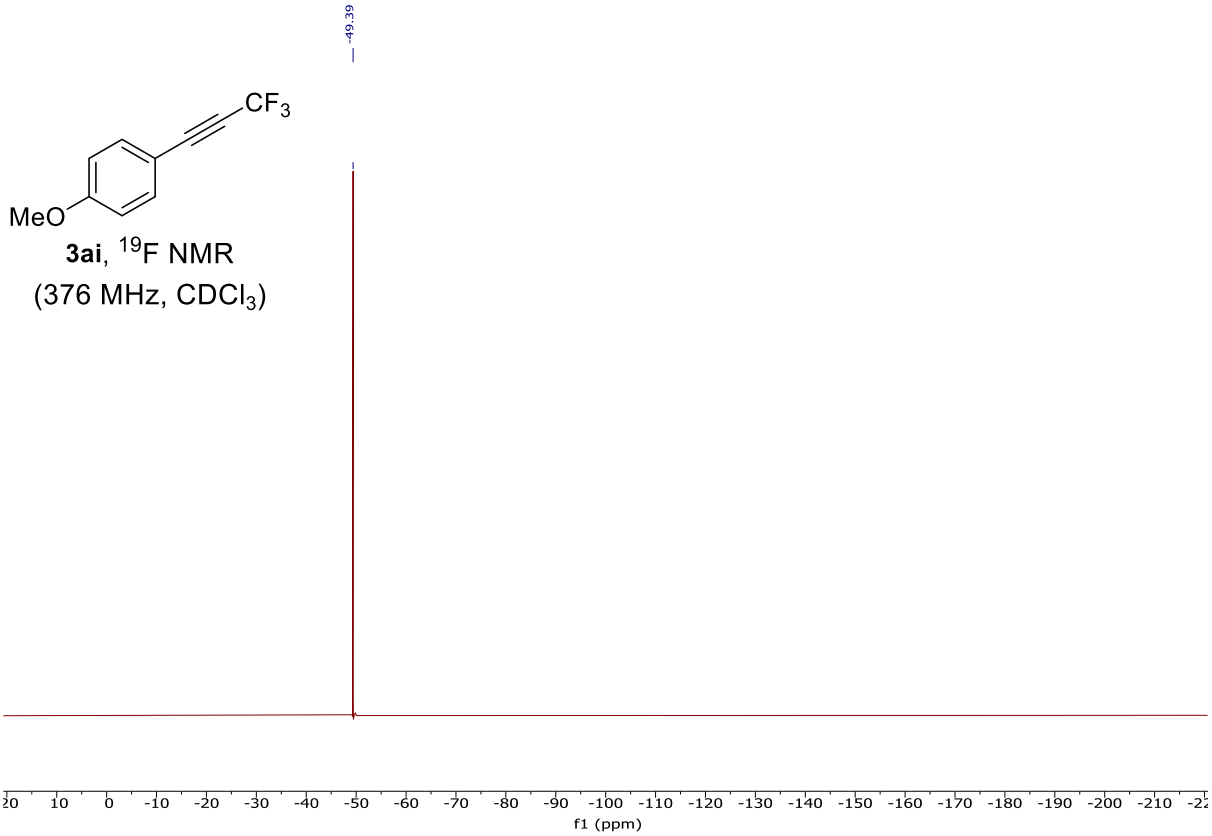
3ah, ^{19}F NMR
(376 MHz, $CDCl_3$)



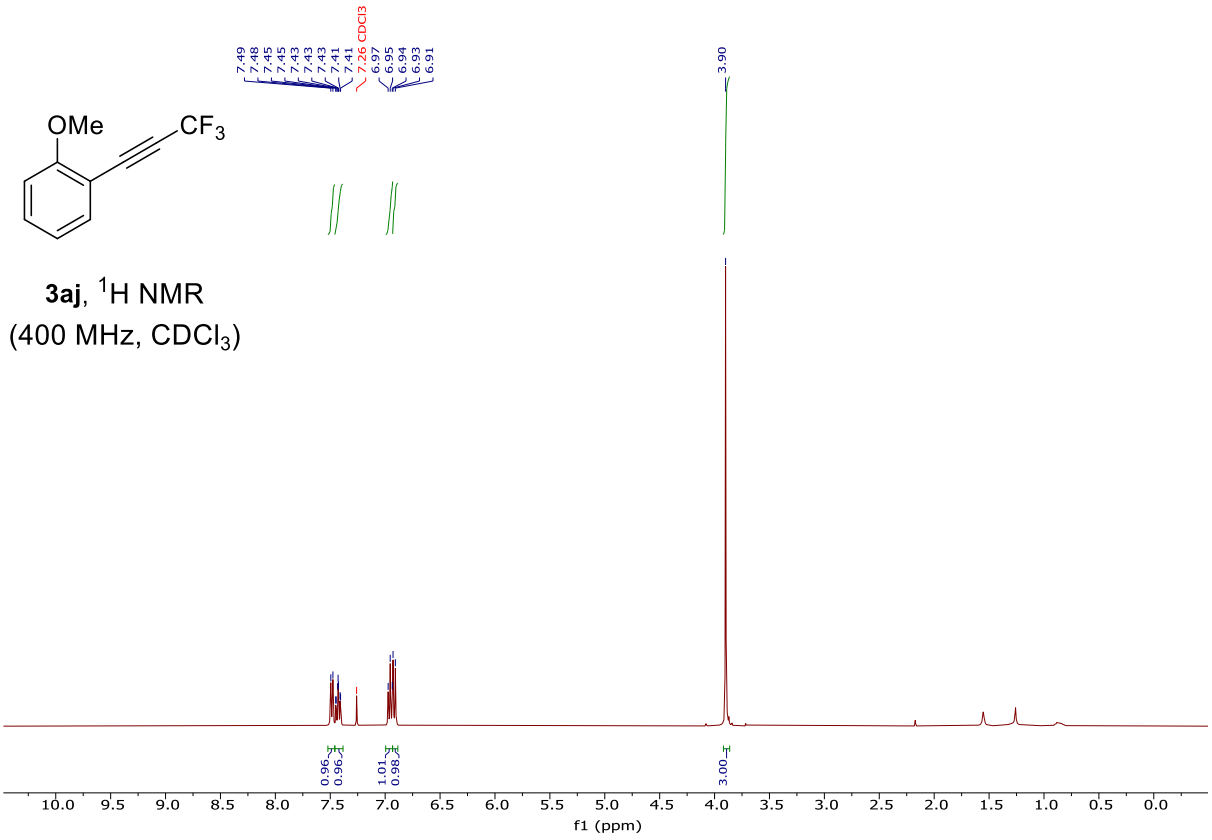
3ai, ^{1}H NMR
(400 MHz, $CDCl_3$)



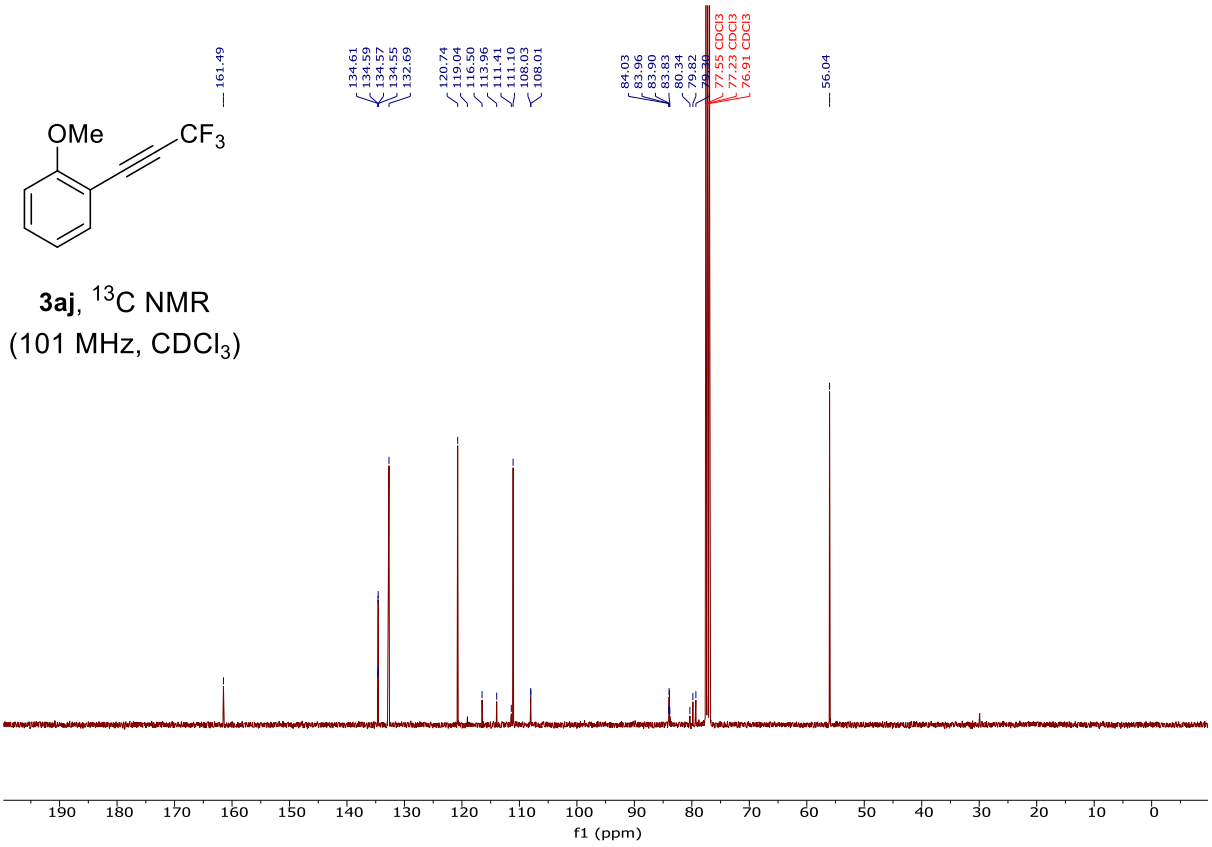
3ai, ^{13}C NMR
(101 MHz, $CDCl_3$)



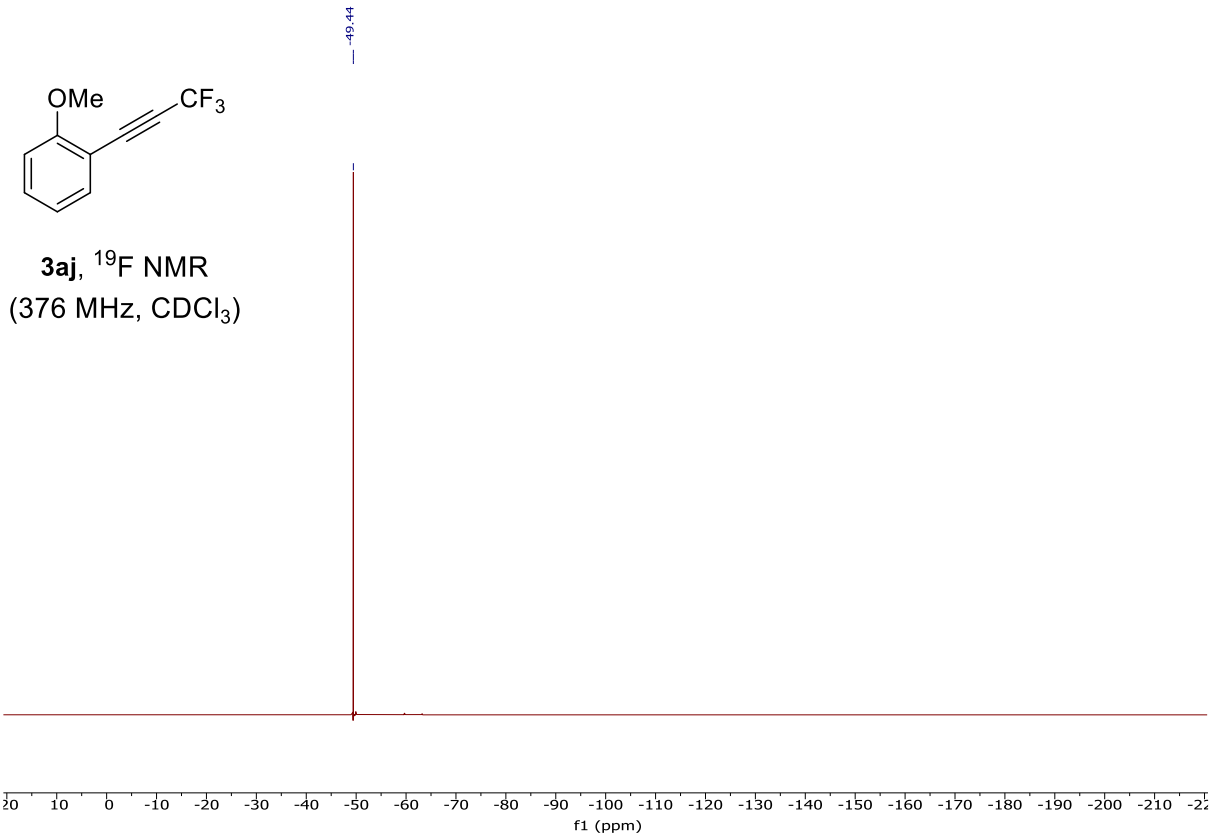
3ai, ^{19}F NMR
(376 MHz, $CDCl_3$)



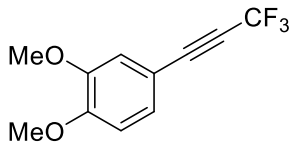
3aj, ^{1}H NMR
(400 MHz, $CDCl_3$)



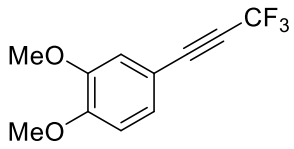
3aj, ^{13}C NMR
(101 MHz, $CDCl_3$)



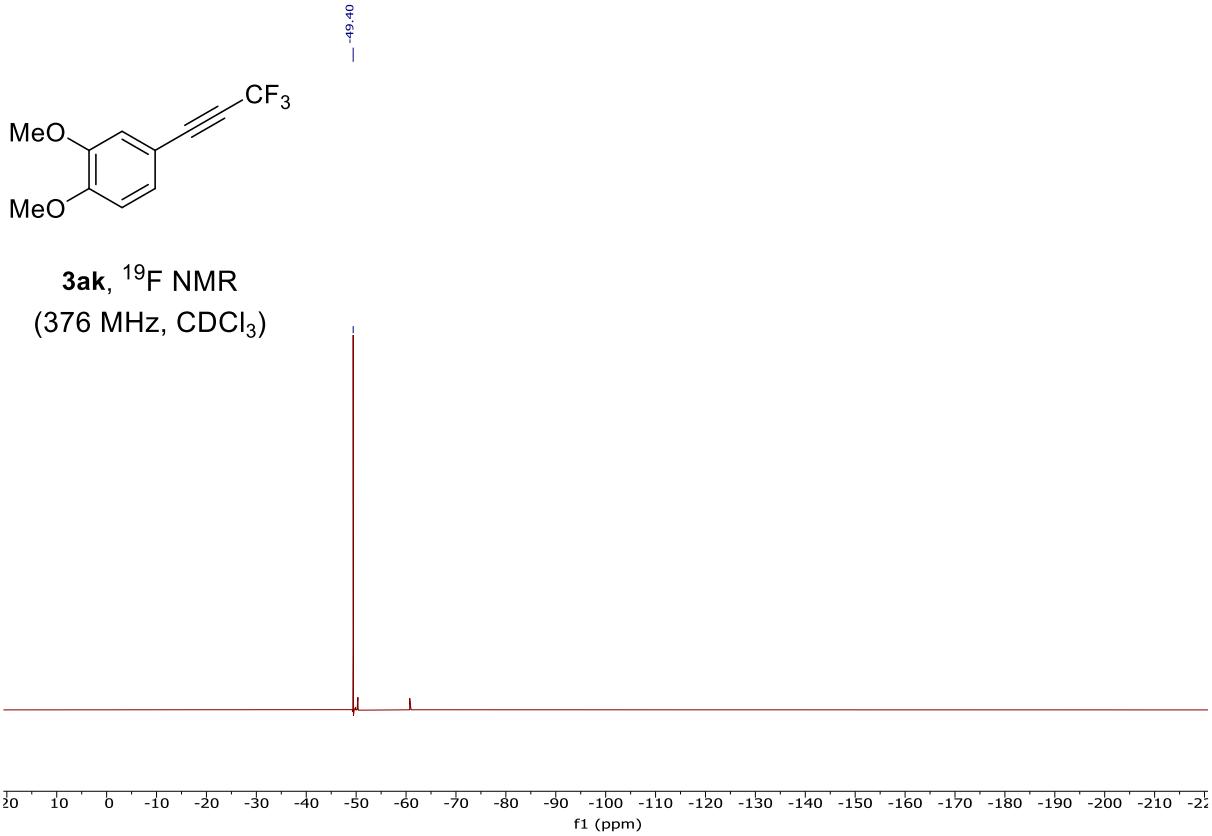
3aj, ^{19}F NMR
(376 MHz, $CDCl_3$)



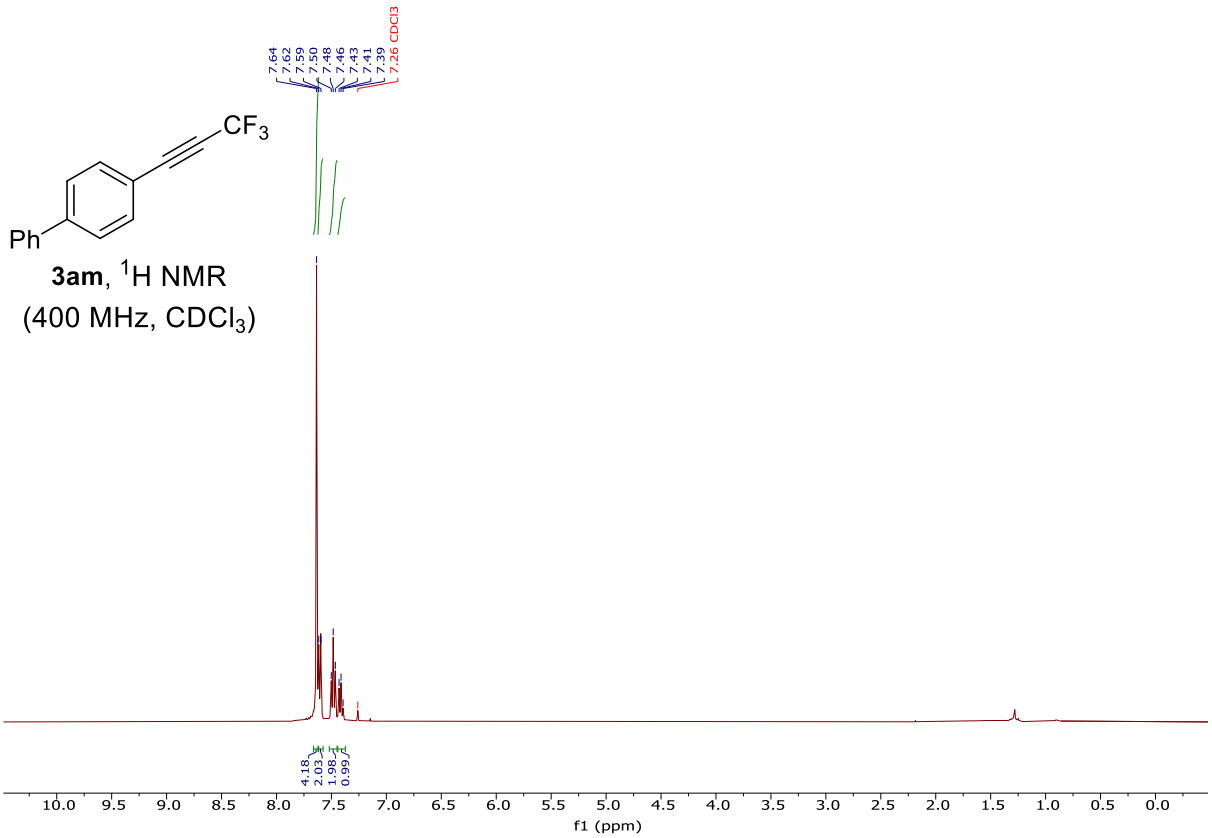
3ak, ^{1}H NMR
(400 MHz, $CDCl_3$)



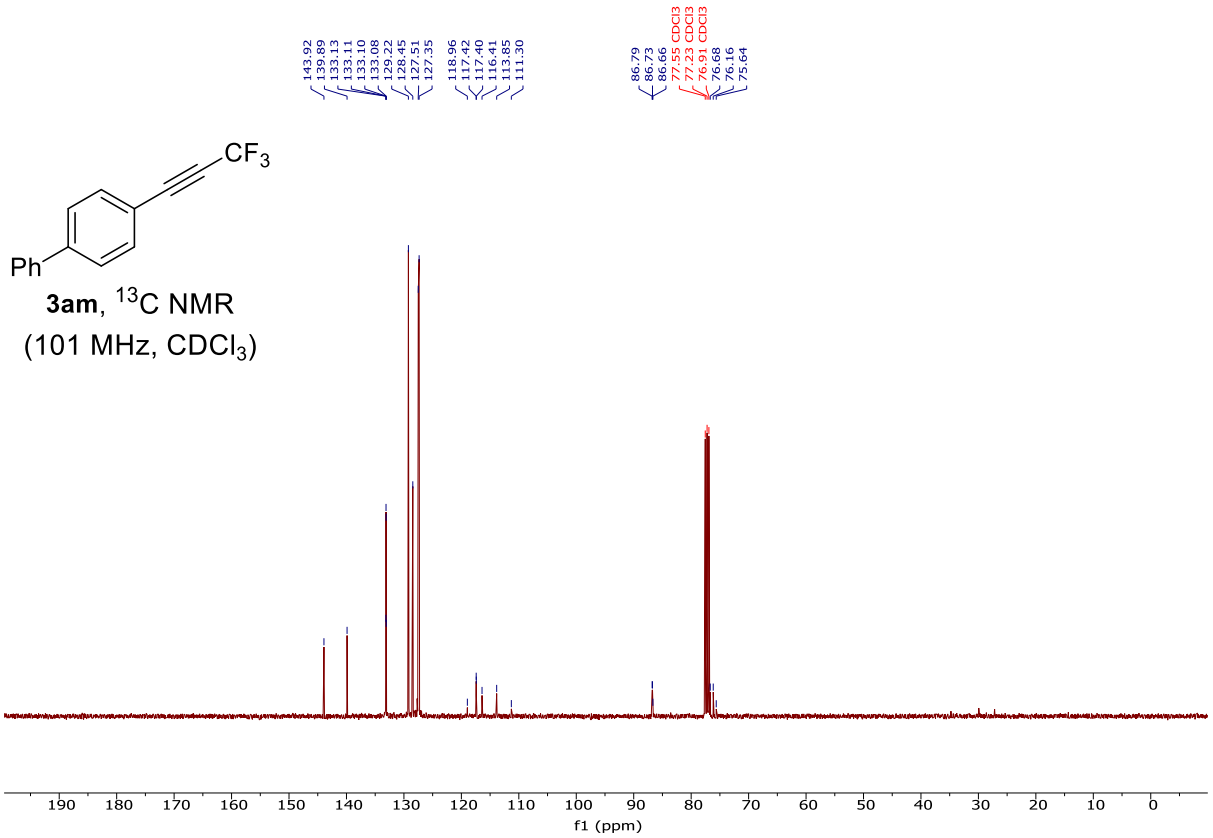
3ak, ^{13}C NMR
(101 MHz, $CDCl_3$)



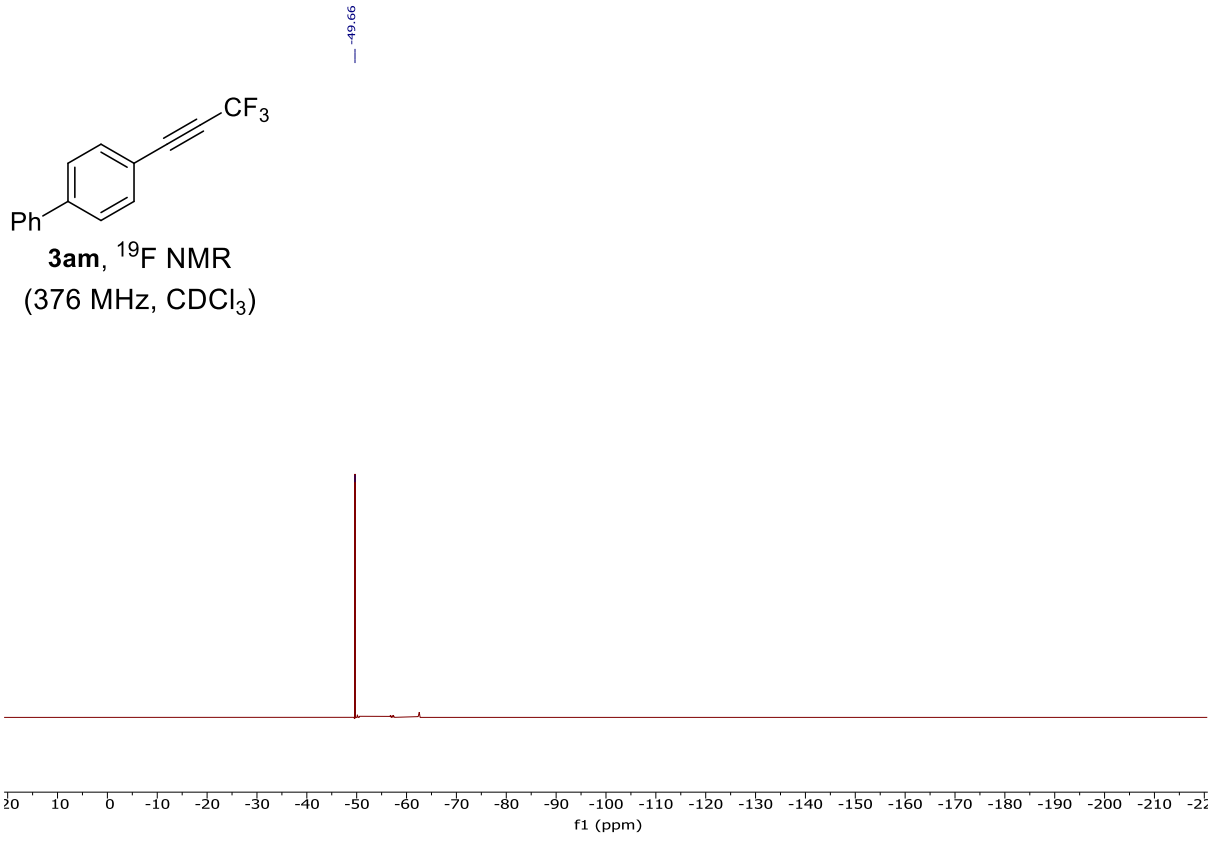
3ak, ^{19}F NMR
(376 MHz, $CDCl_3$)



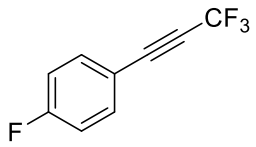
3am, ^{1}H NMR
(400 MHz, $CDCl_3$)



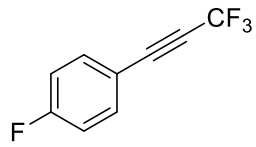
3am, ^{13}C NMR
(101 MHz, $CDCl_3$)



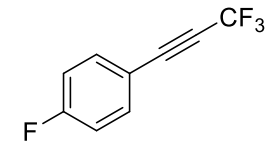
3am, ^{19}F NMR
(376 MHz, $CDCl_3$)



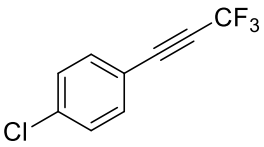
3an, ^{1}H NMR
(400 MHz, $CDCl_3$)
(in pentane and
diethyl ether residue)

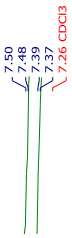


3an, ^{13}C NMR
(101 MHz, $CDCl_3$)
(in pentane and
diethyl ether residue)

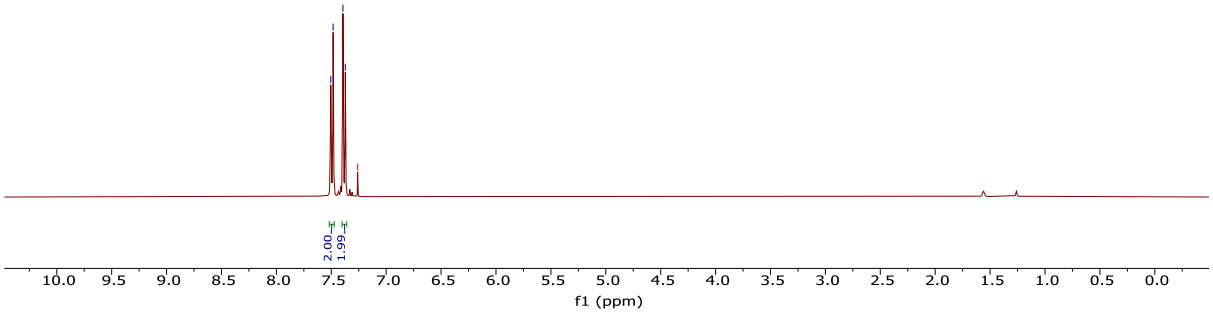


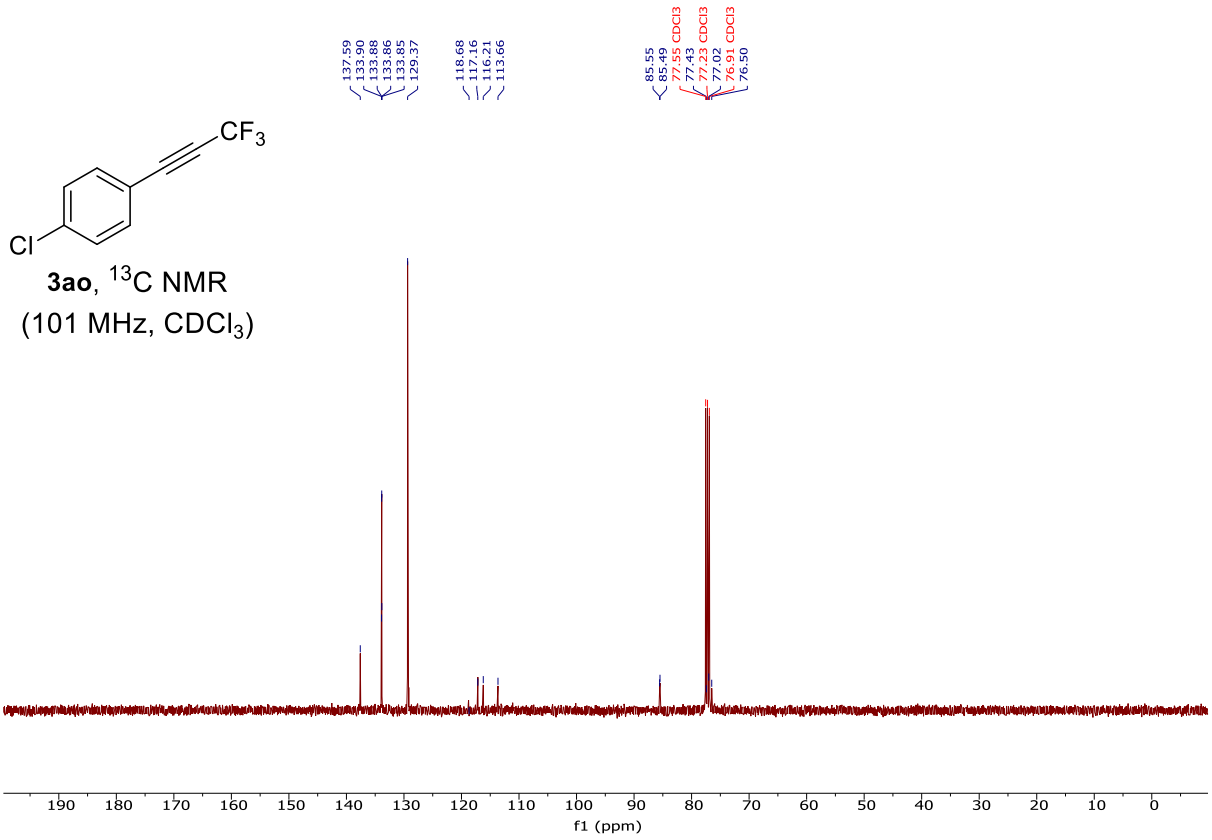
3an, ^{19}F NMR
(376 MHz, $CDCl_3$)



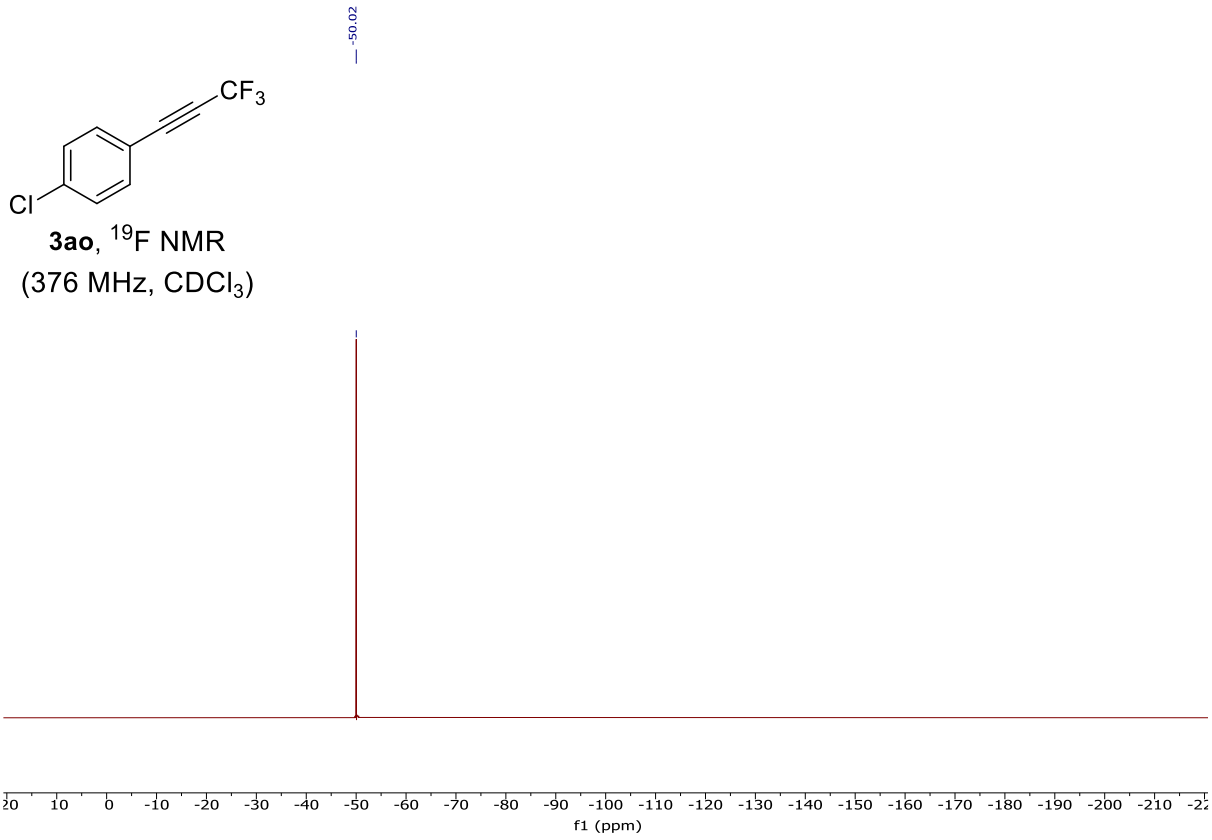


3ao, ^{1}H NMR
(400 MHz, $CDCl_3$)

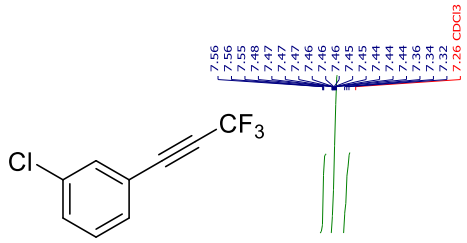




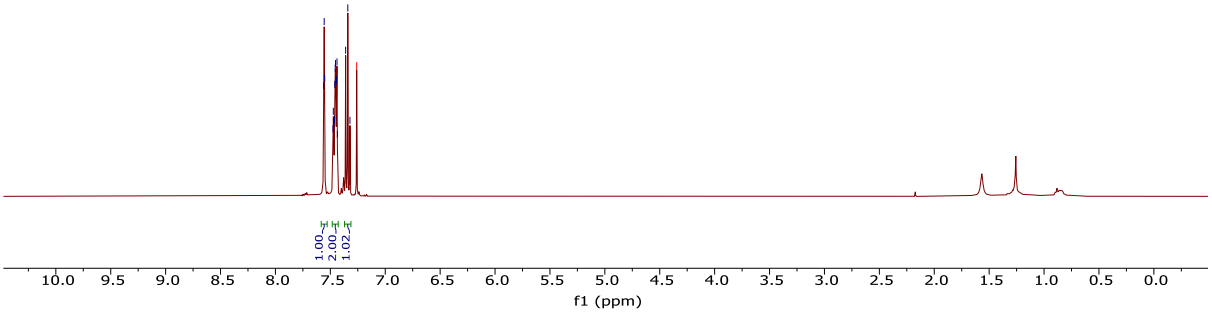
3ao, ^{13}C NMR
(101 MHz, $CDCl_3$)



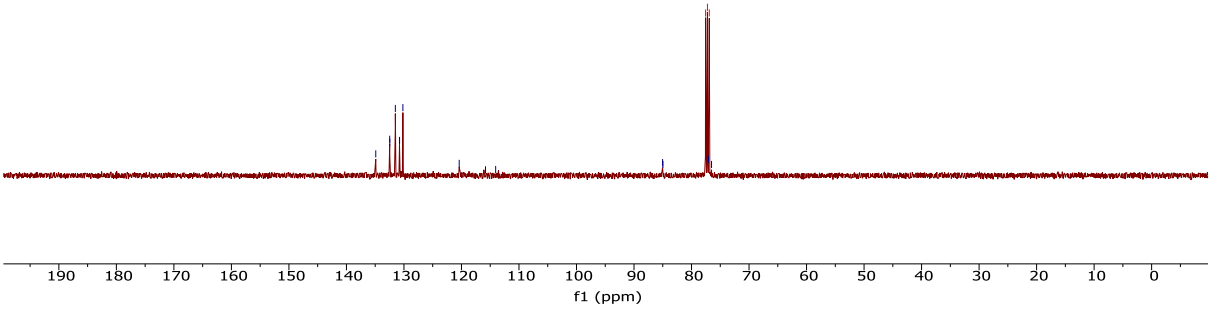
3ao, ^{19}F NMR
(376 MHz, $CDCl_3$)

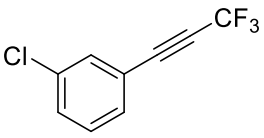


3ap, ^{1}H NMR
(400 MHz, $CDCl_3$)

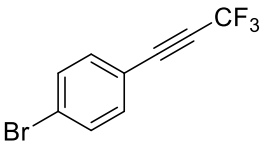


3ap, ^{13}C NMR
(101 MHz, $CDCl_3$)

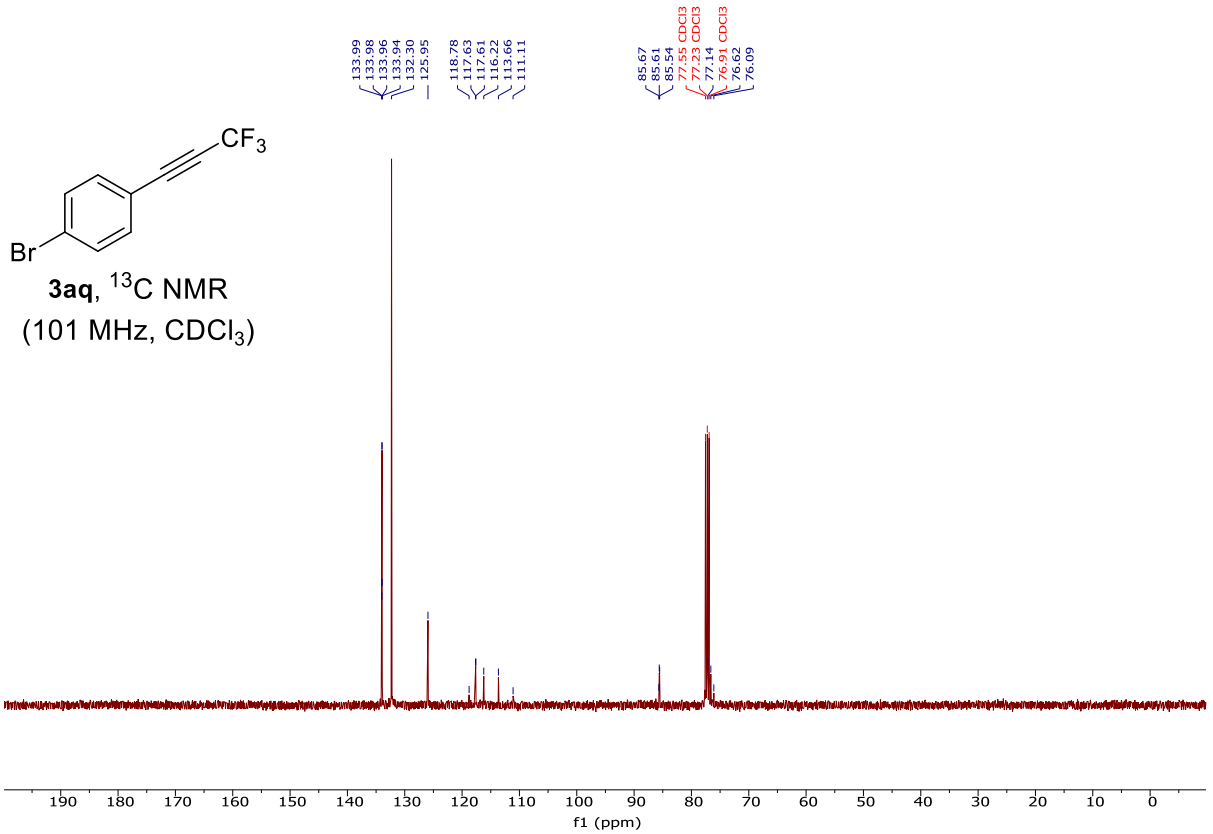




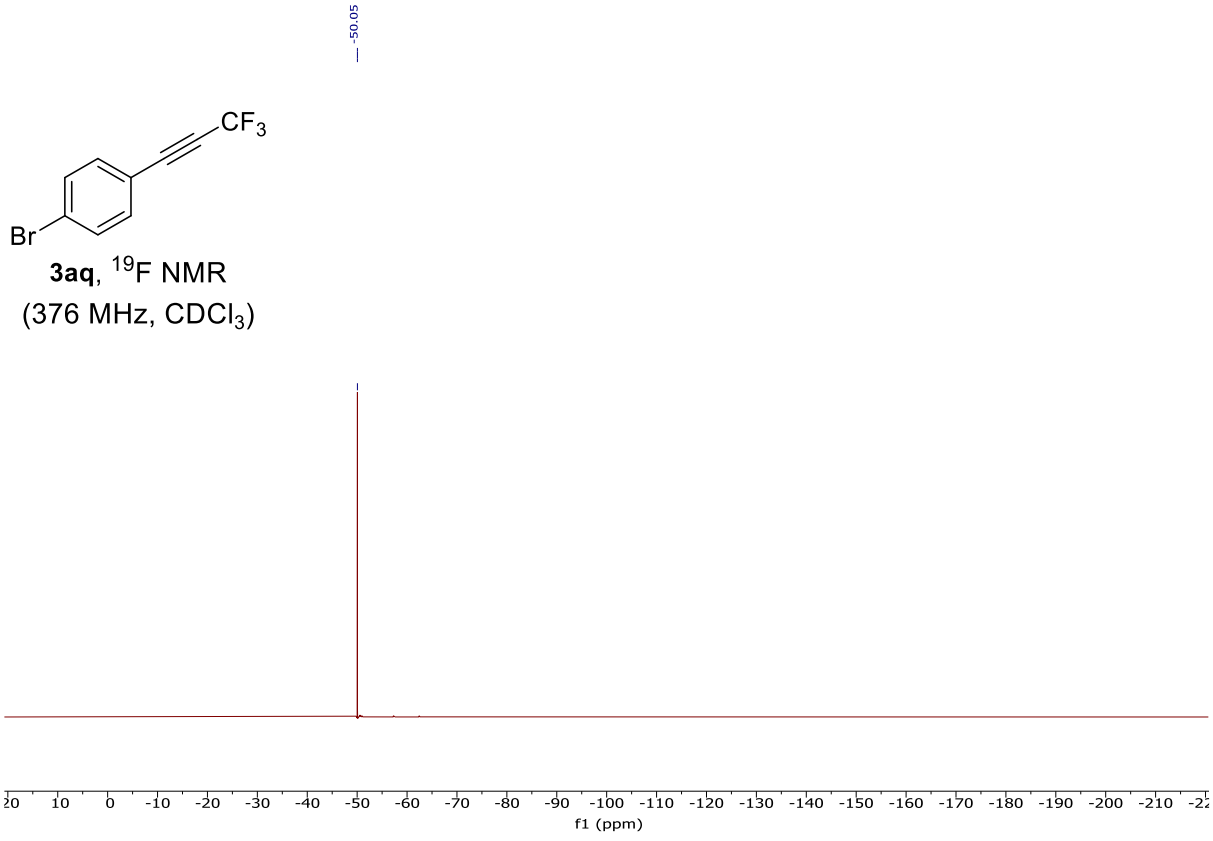
3ap, ^{19}F NMR
(376 MHz, $CDCl_3$)



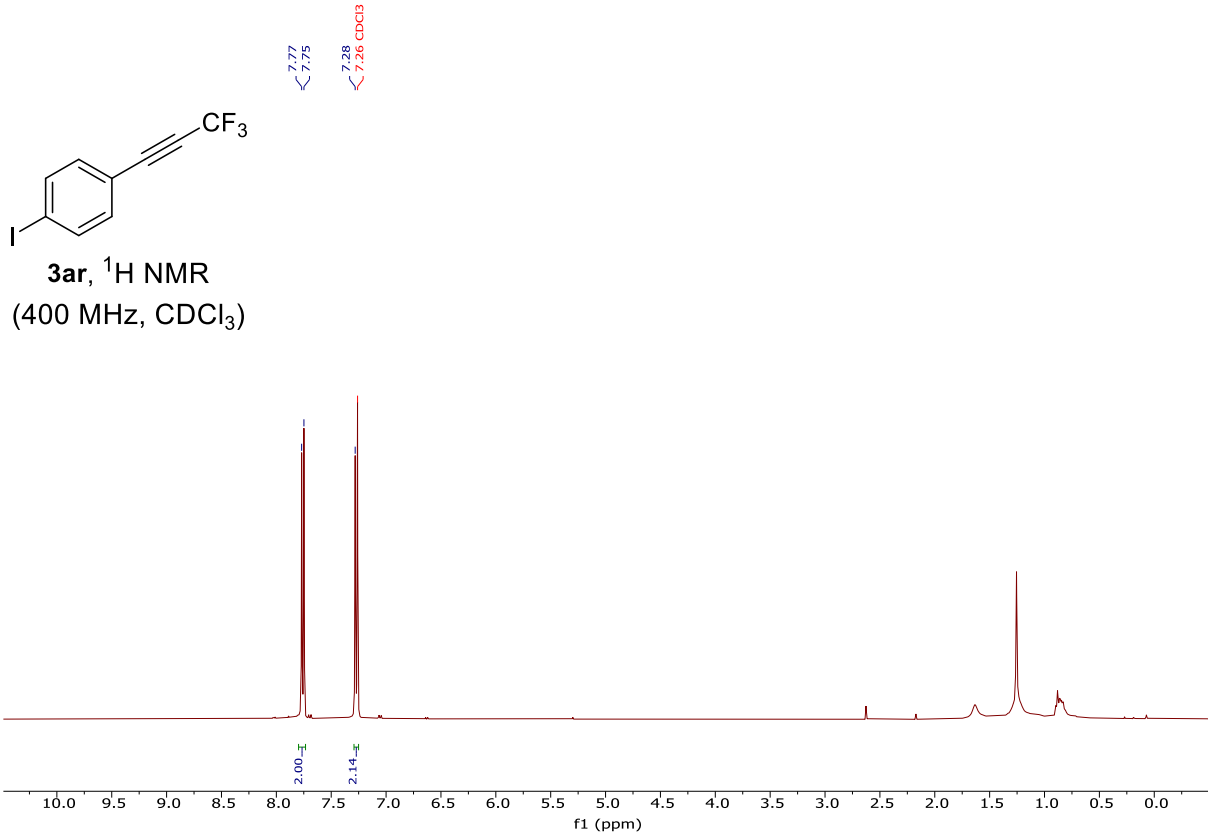
3aq, ^{1}H NMR
(400 MHz, $CDCl_3$)



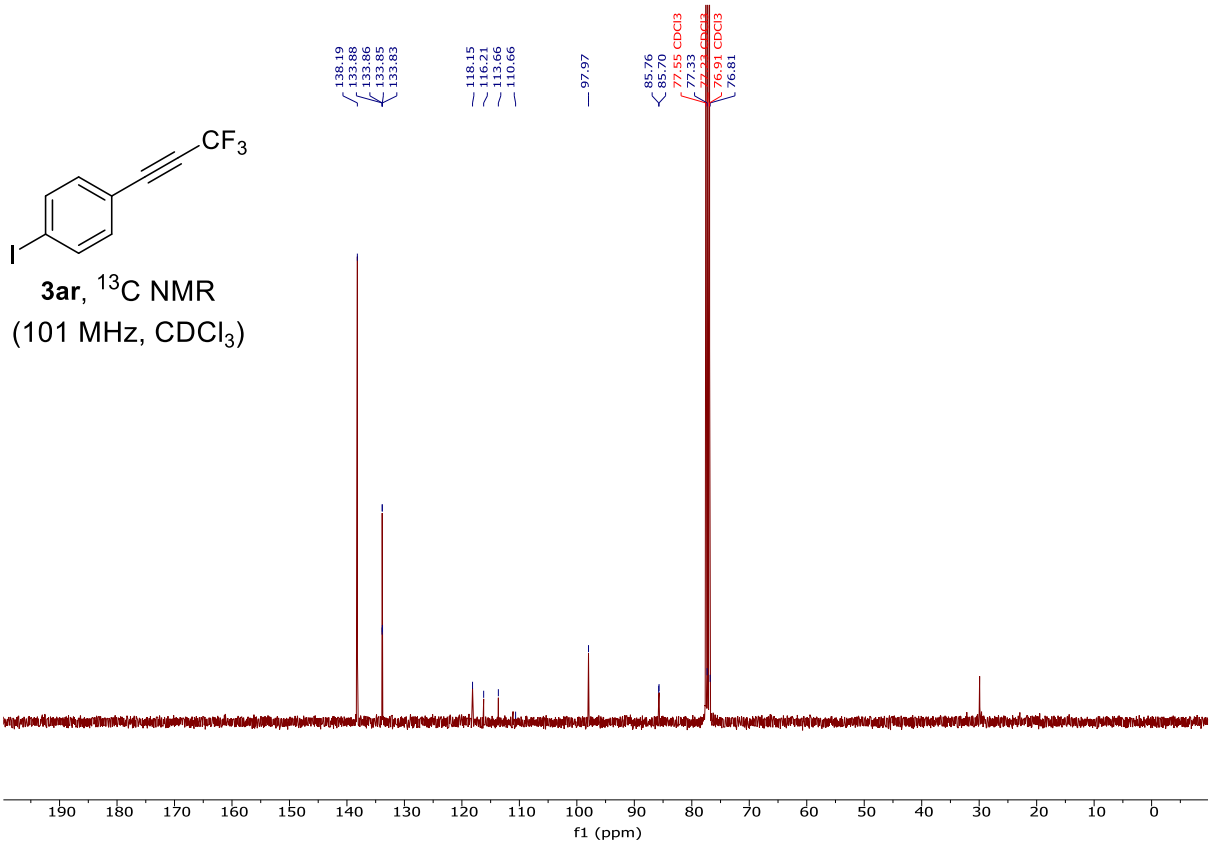
3aq, ^{13}C NMR
(101 MHz, $CDCl_3$)



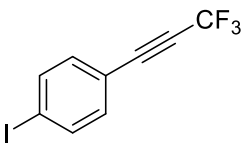
3aq, ^{19}F NMR
(376 MHz, $CDCl_3$)



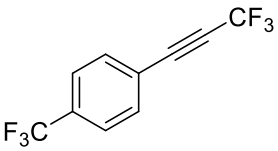
3ar, ^{1}H NMR
(400 MHz, $CDCl_3$)



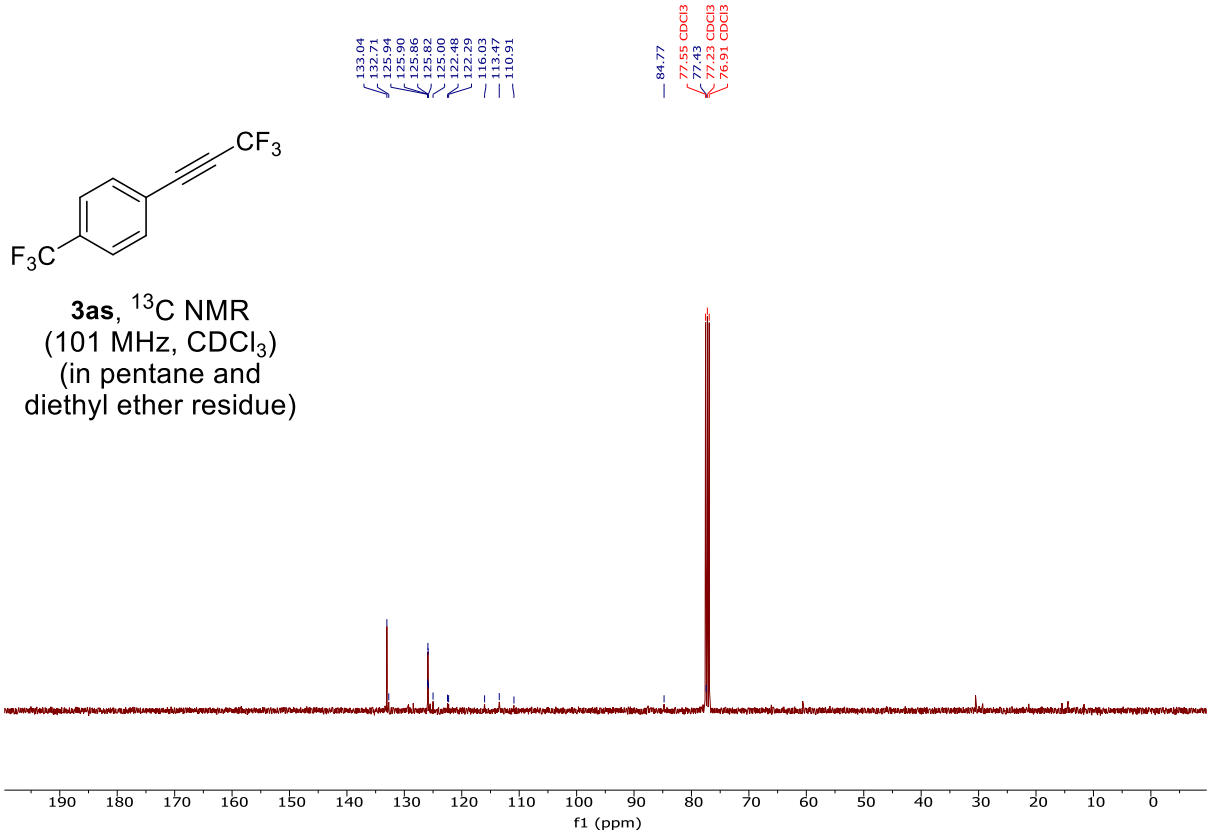
3ar, ^{13}C NMR
(101 MHz, $CDCl_3$)



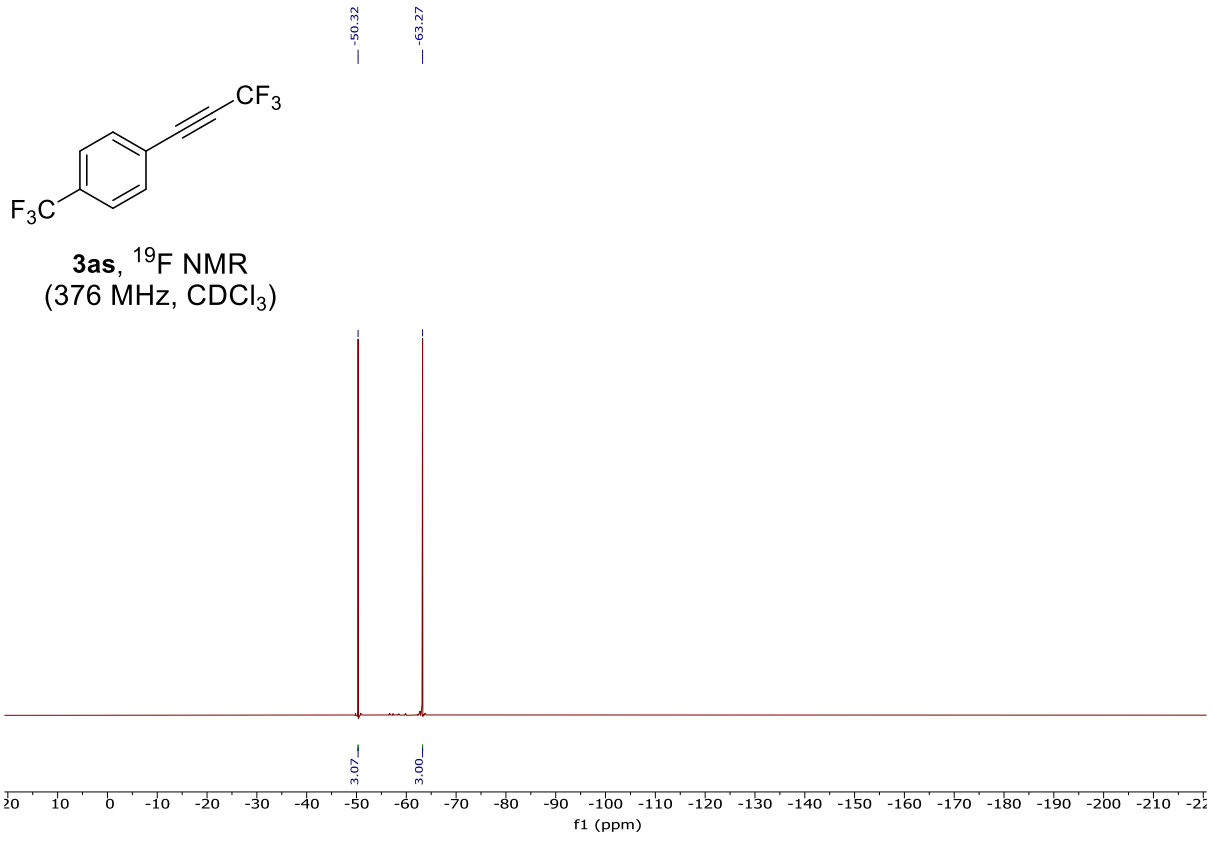
3ar, ^{19}F NMR
(376 MHz, $CDCl_3$)



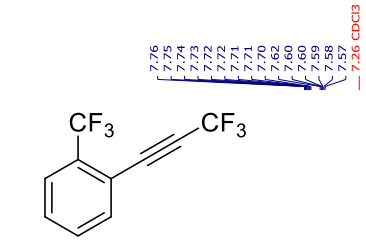
3as, ^{1}H NMR
(400 MHz, $CDCl_3$)
(in pentane and
diethyl ether residue)



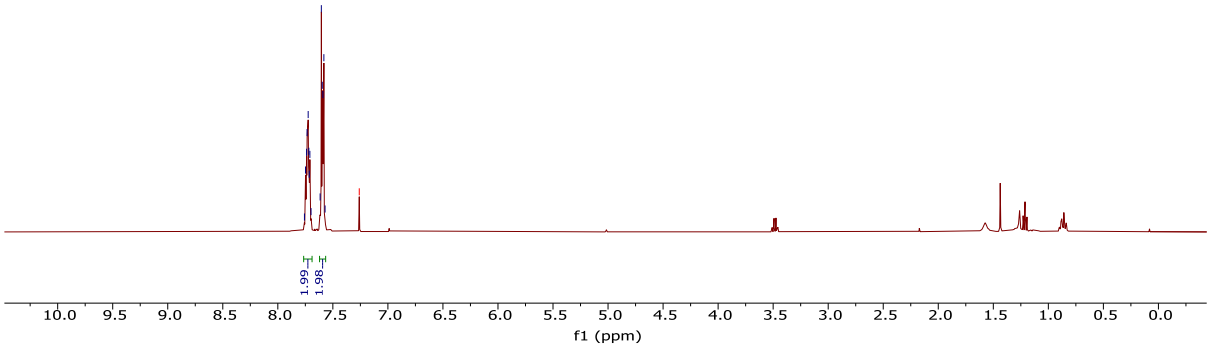
3as, ^{13}C NMR (101 MHz, $CDCl_3$) (in pentane and diethyl ether residue)



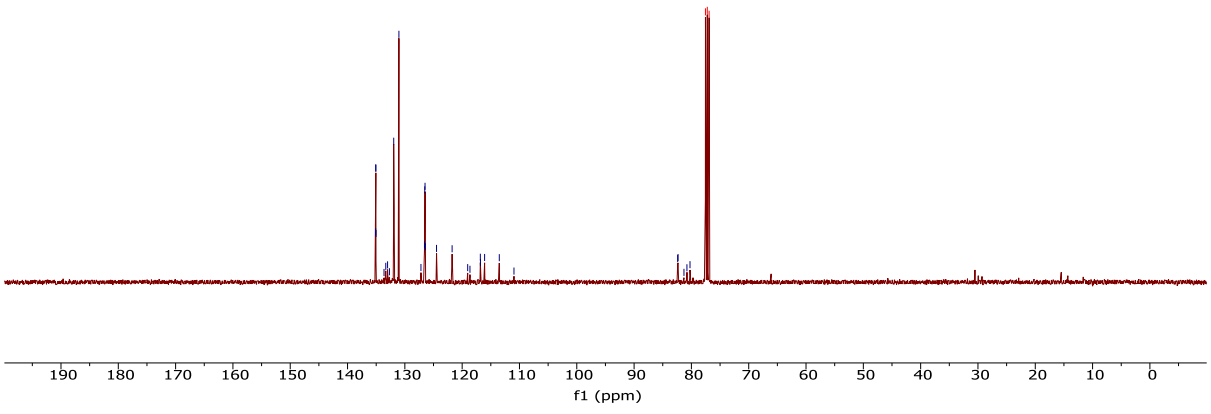
3as, ^{19}F NMR (376 MHz, $CDCl_3$)

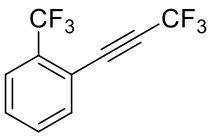


3at, ^{1}H NMR
(400 MHz, $CDCl_3$)
(in pentane and
diethyl ether residue)

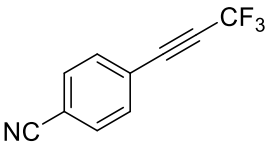


3at, ^{13}C NMR
(101 MHz, $CDCl_3$)
(in pentane and
diethyl ether residue)

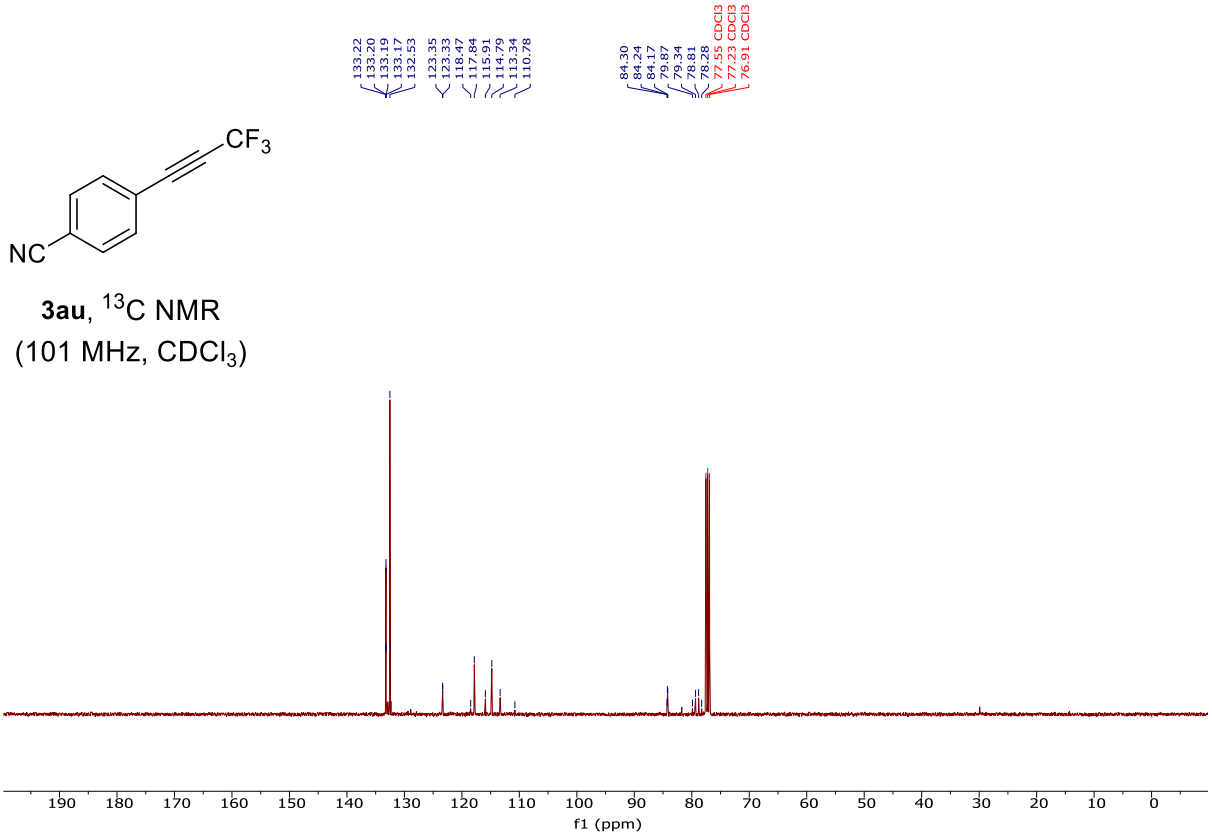




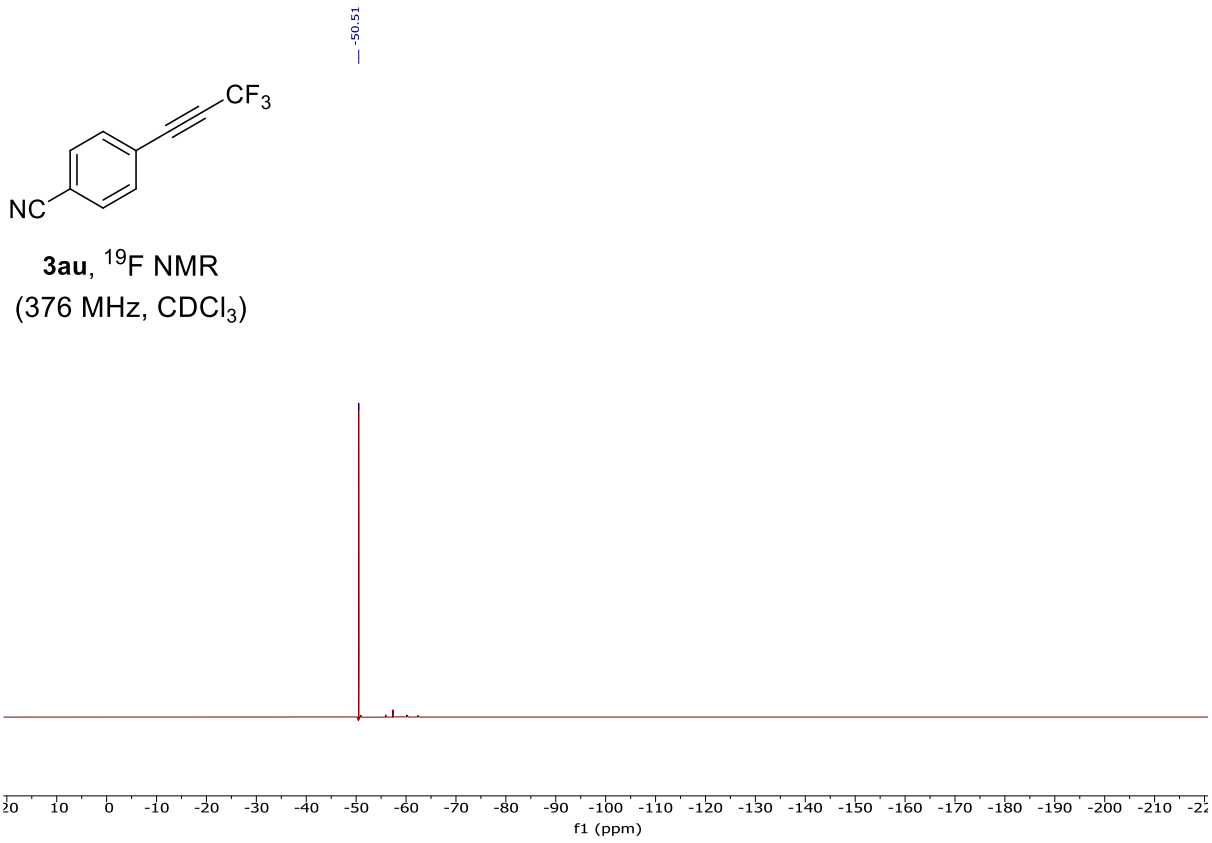
3at, ^{19}F NMR
(376 MHz, $CDCl_3$)



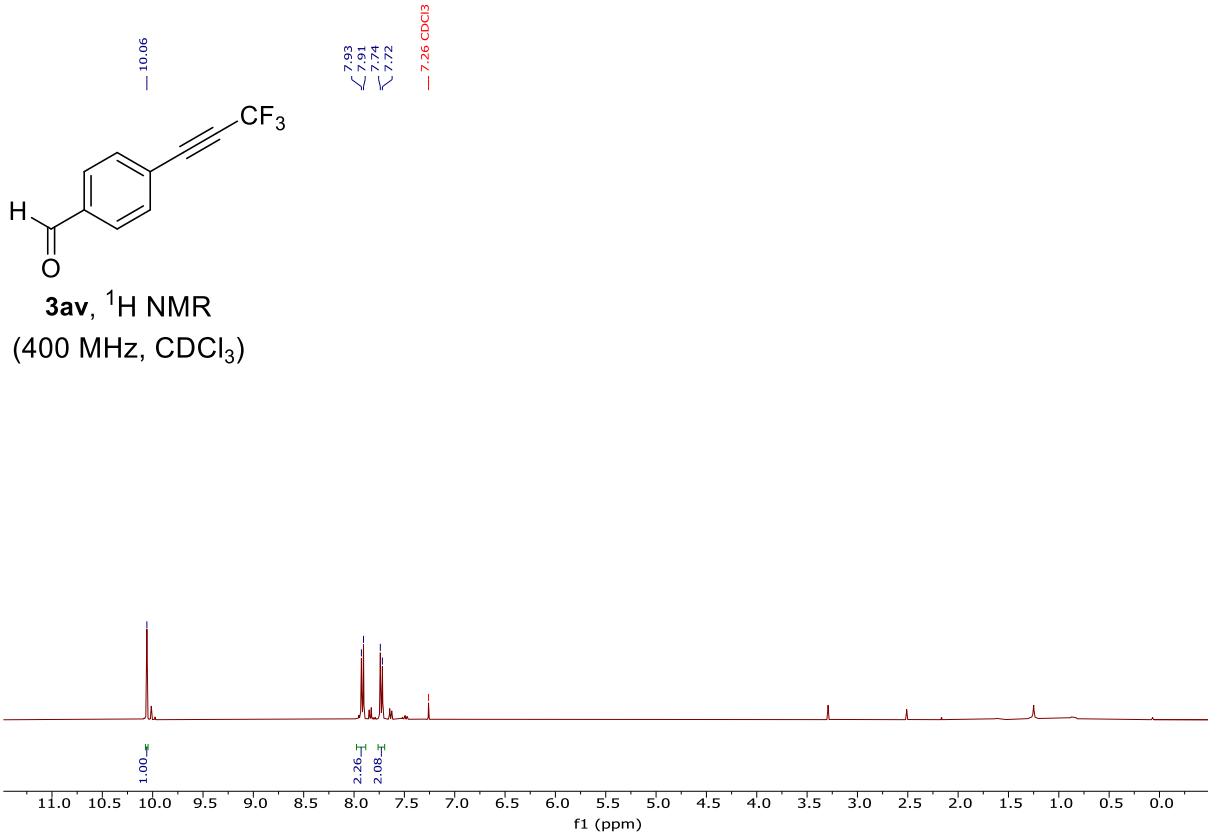
3au, ^{1}H NMR
(400 MHz, $CDCl_3$)



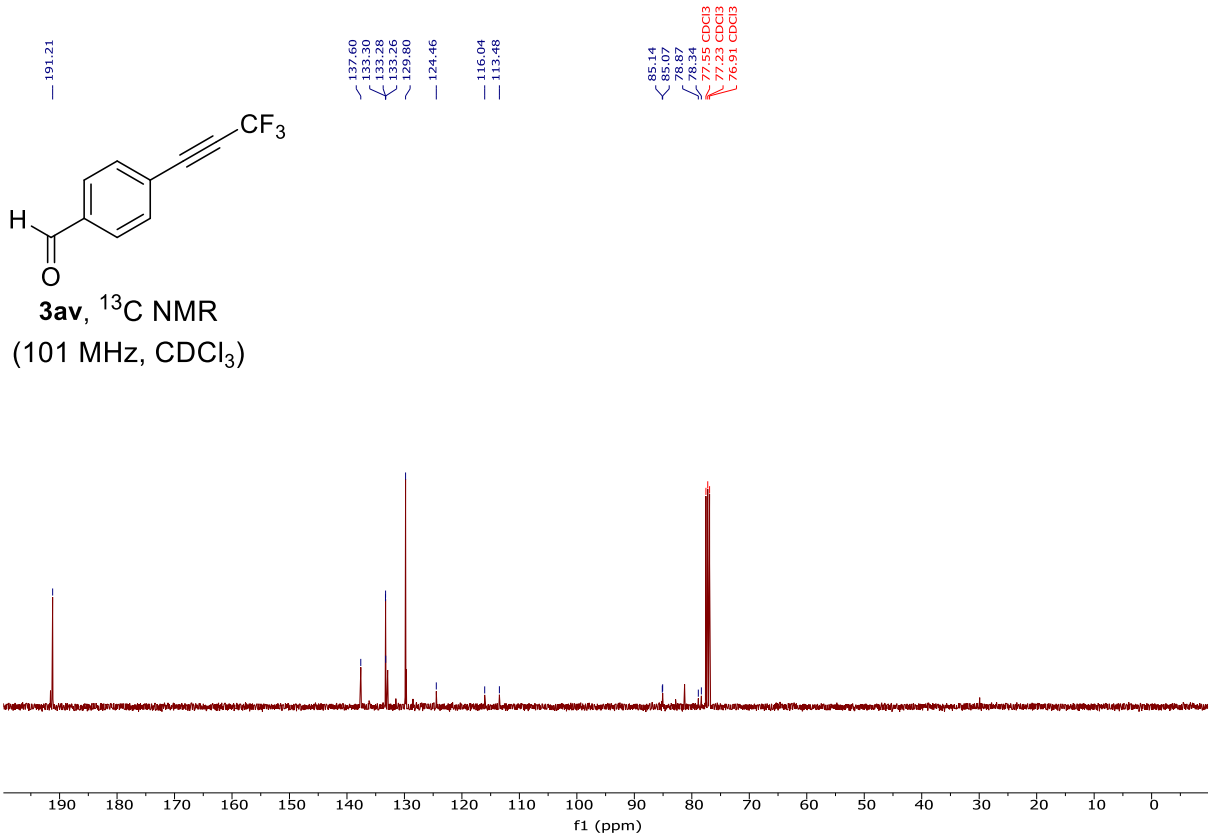
3au, ^{13}C NMR
(101 MHz, $CDCl_3$)



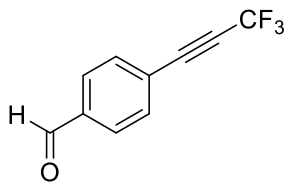
3au, ^{19}F NMR
(376 MHz, $CDCl_3$)



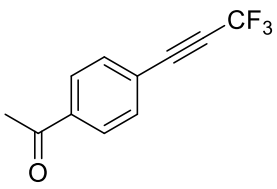
3av, ^{1}H NMR
(400 MHz, $CDCl_3$)



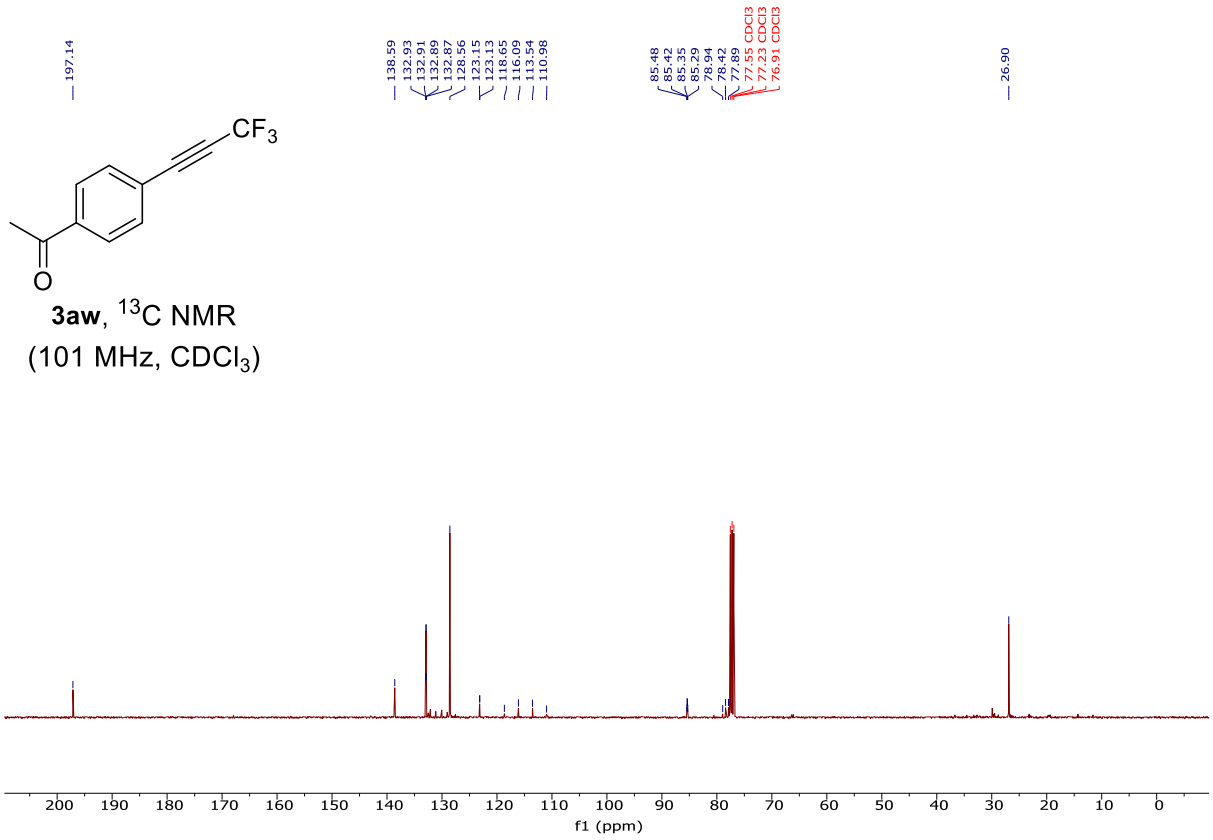
3av, ^{13}C NMR
(101 MHz, $CDCl_3$)



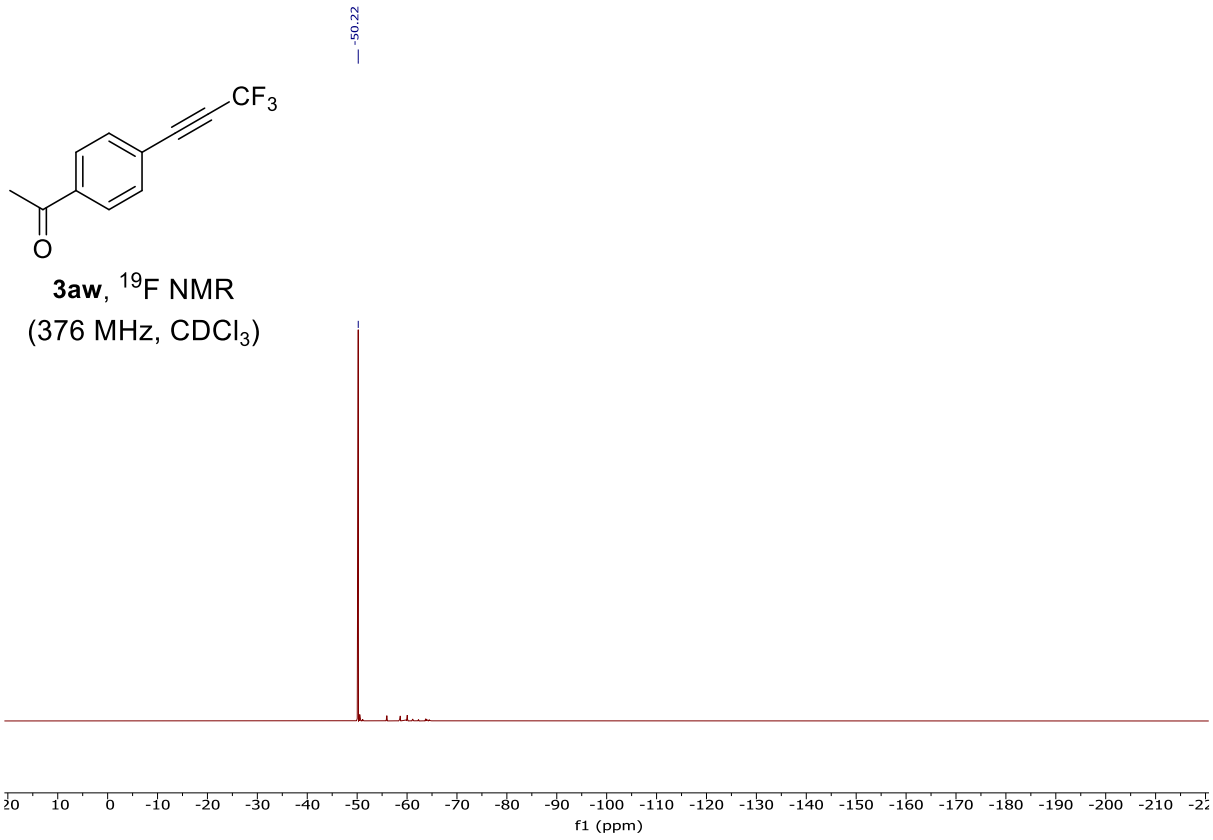
3av, ^{19}F NMR
(376 MHz, $CDCl_3$)



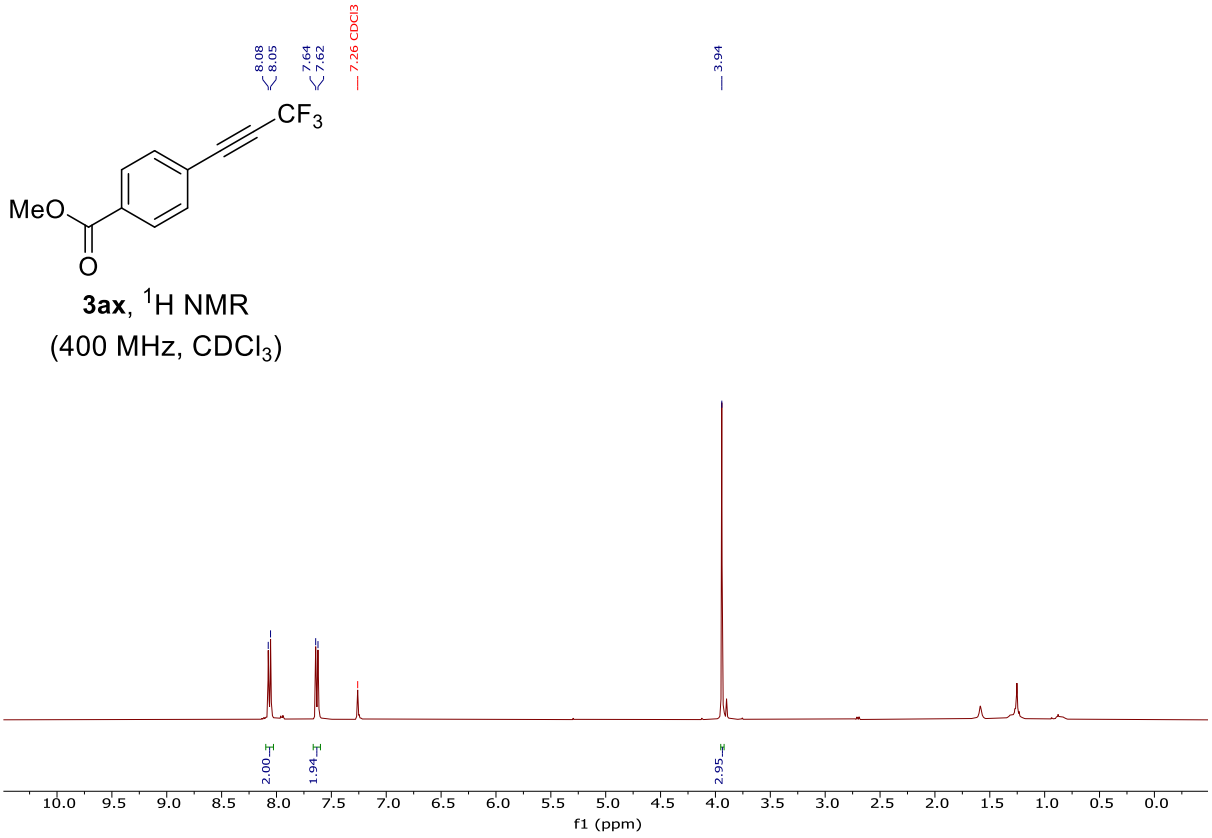
3aw, ^{1}H NMR
(400 MHz, $CDCl_3$)



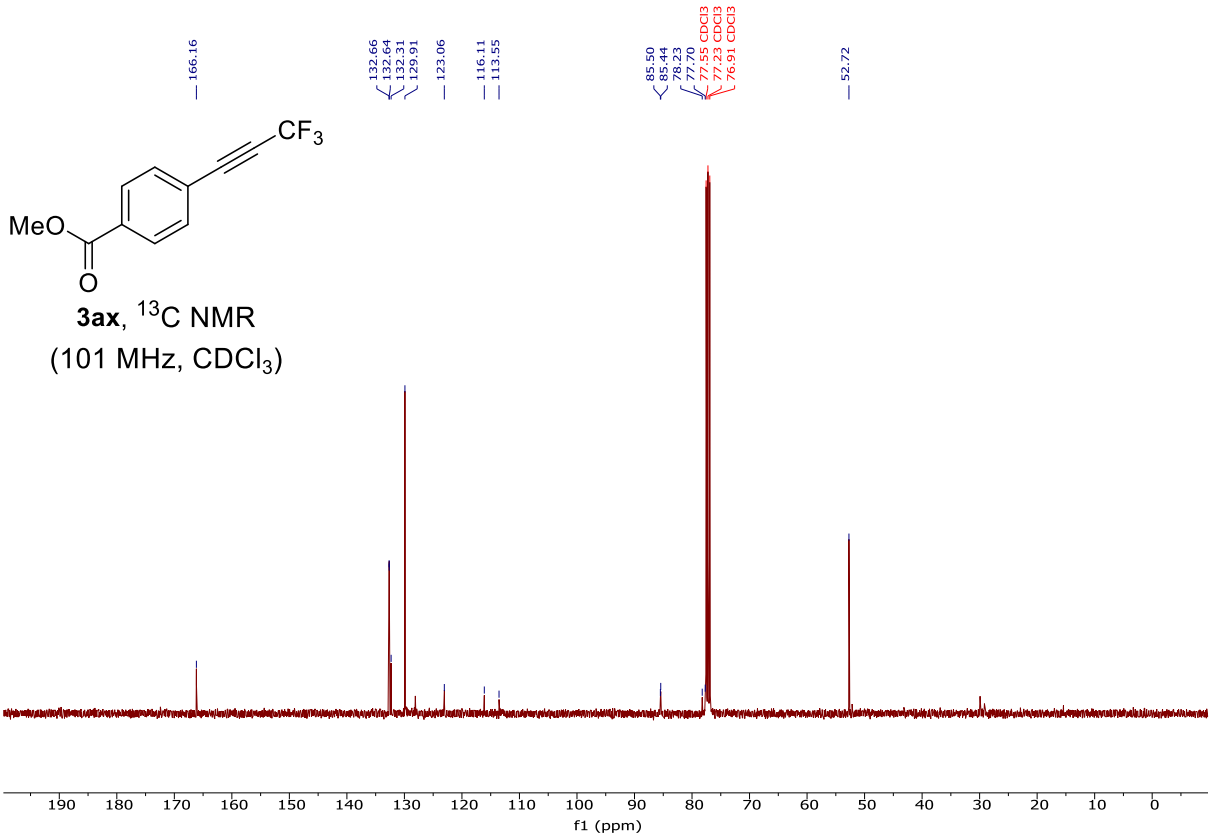
3aw, ^{13}C NMR
(101 MHz, $CDCl_3$)



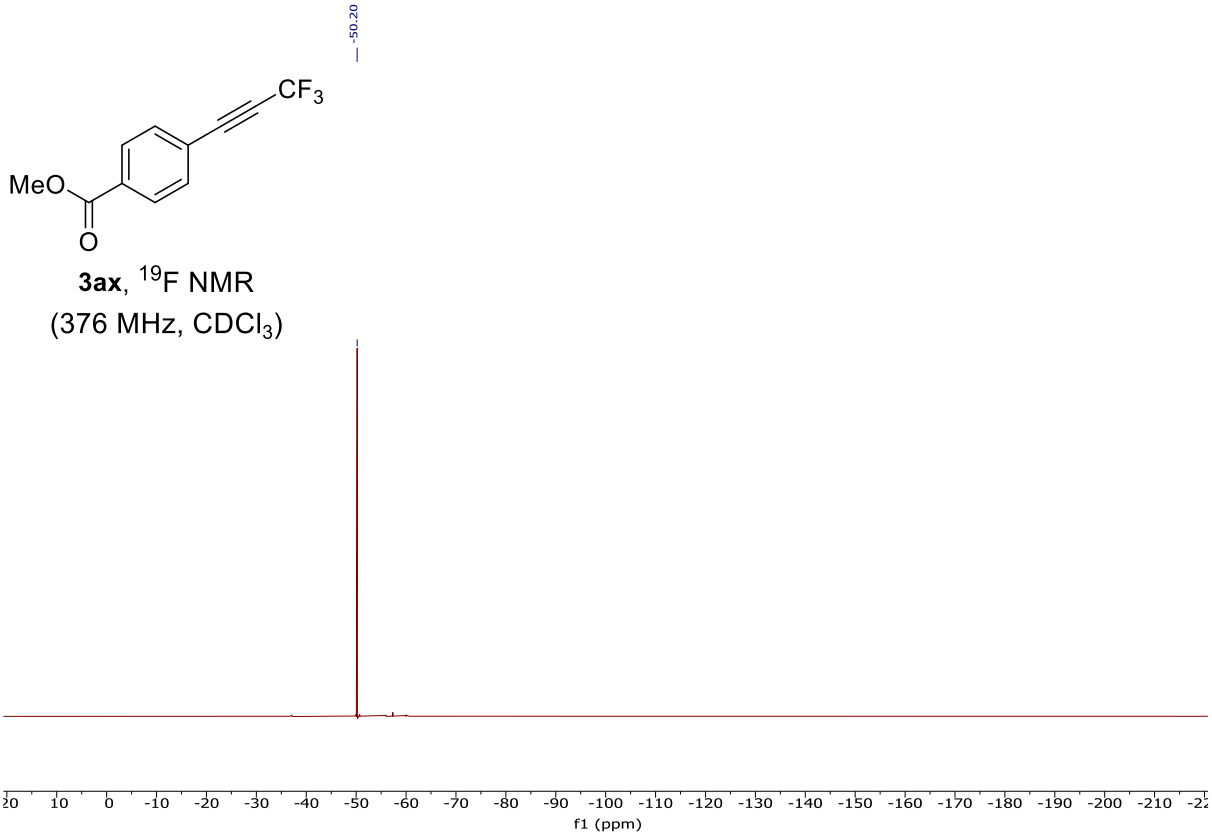
3aw, ^{19}F NMR
(376 MHz, $CDCl_3$)



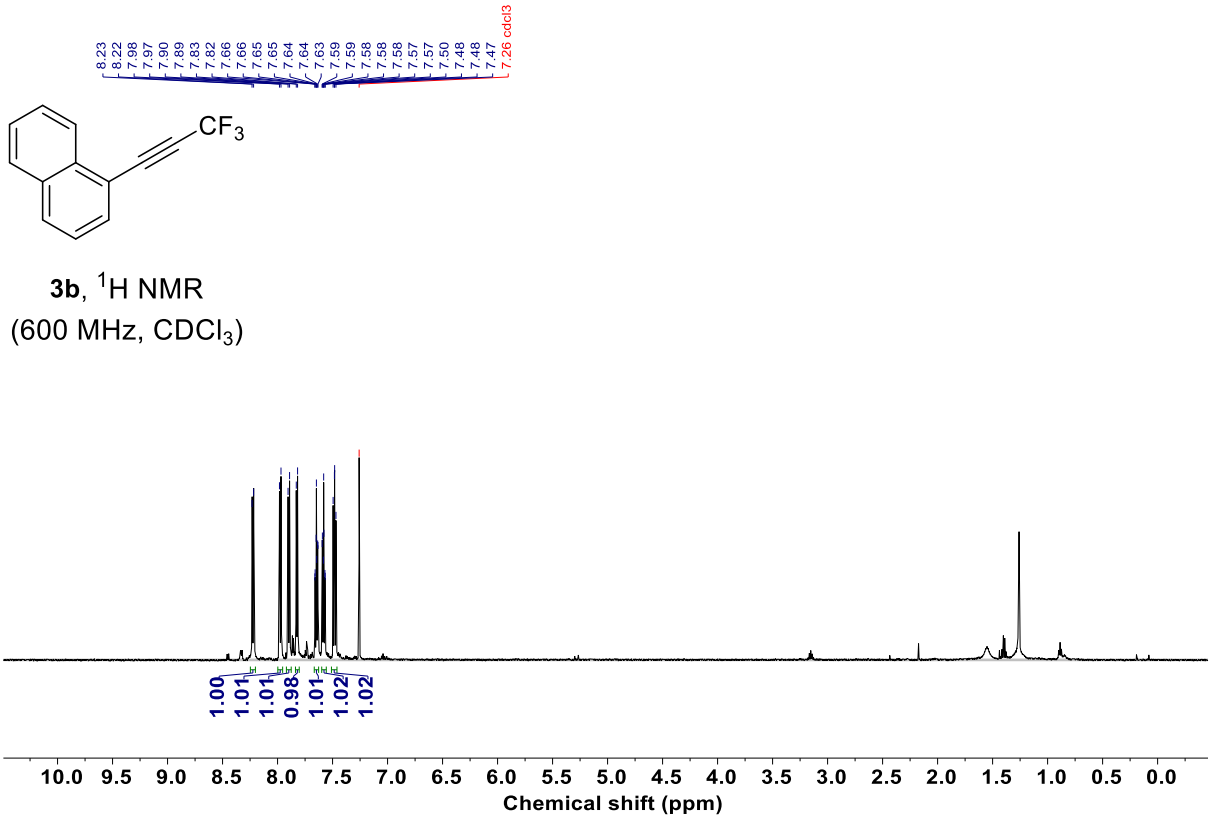
3ax, ^{1}H NMR
(400 MHz, $CDCl_3$)



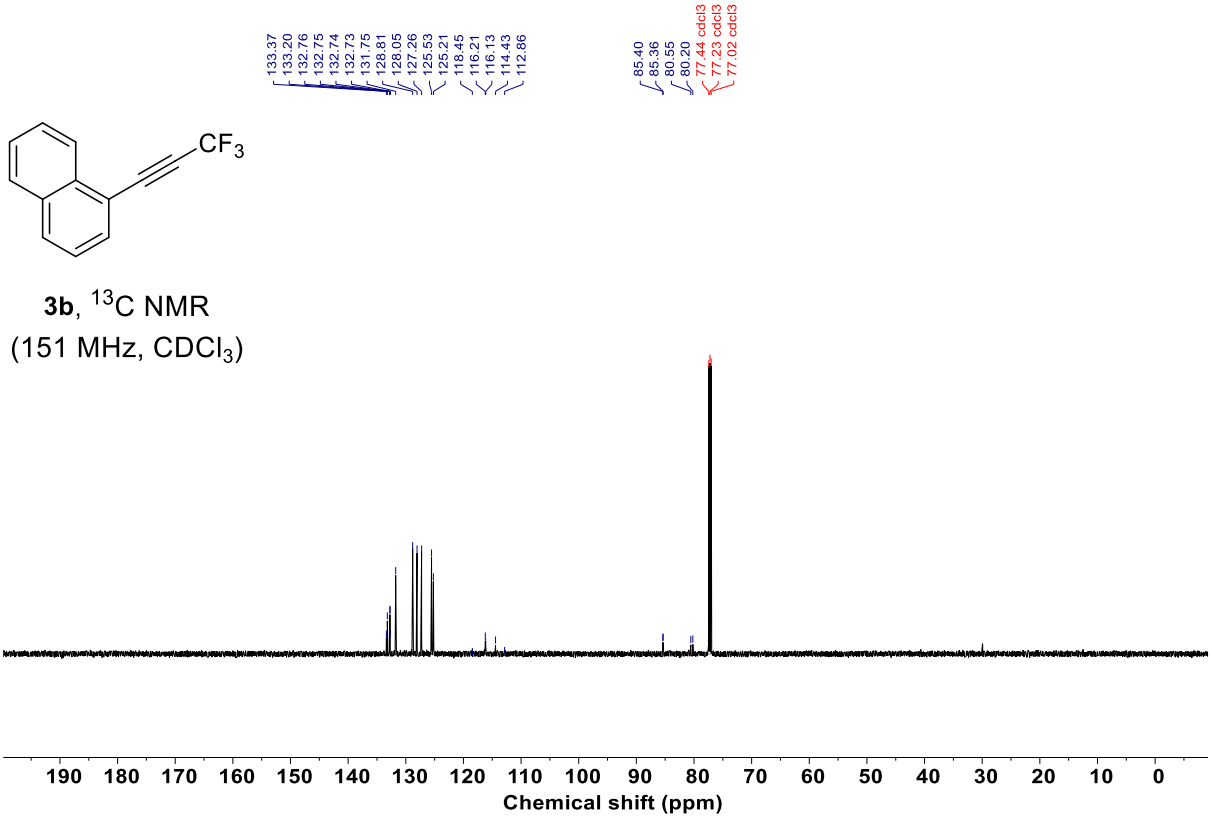
3ax, ^{13}C NMR
(101 MHz, $CDCl_3$)



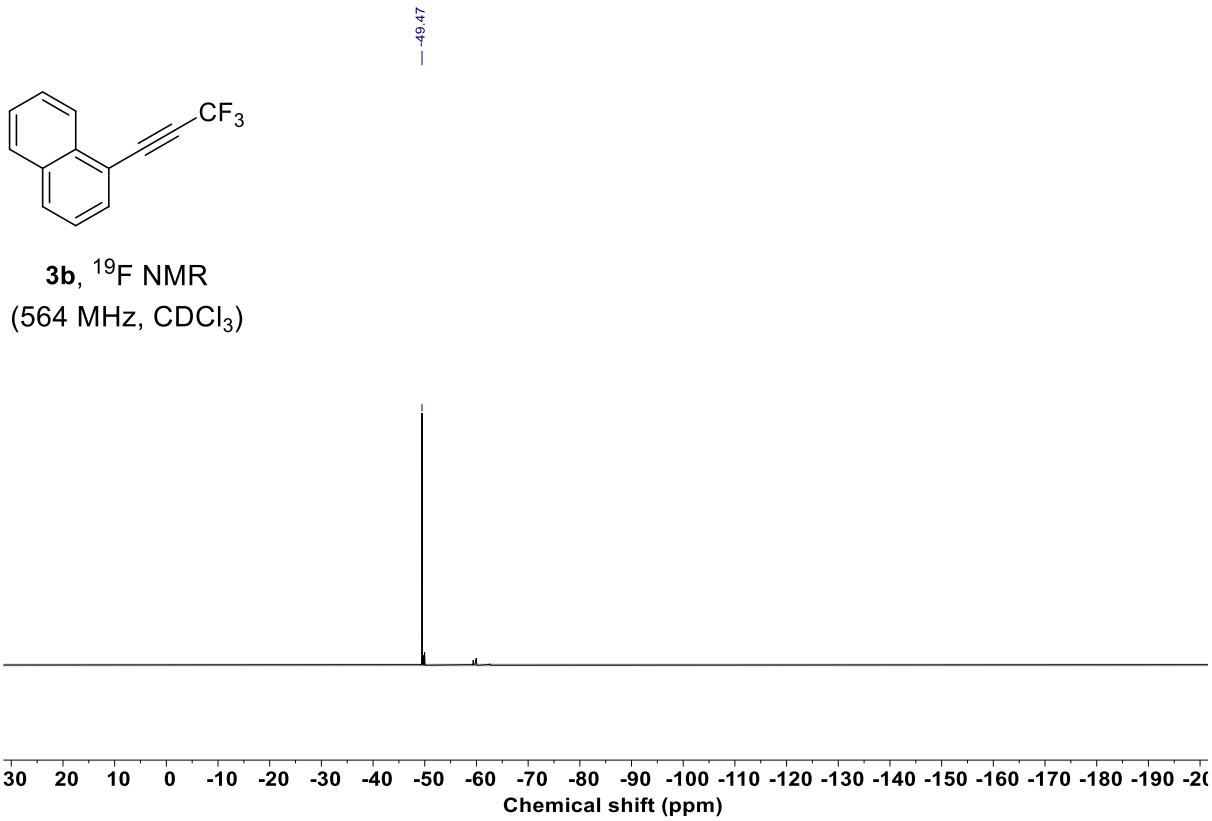
3ax, ^{19}F NMR
(376 MHz, $CDCl_3$)



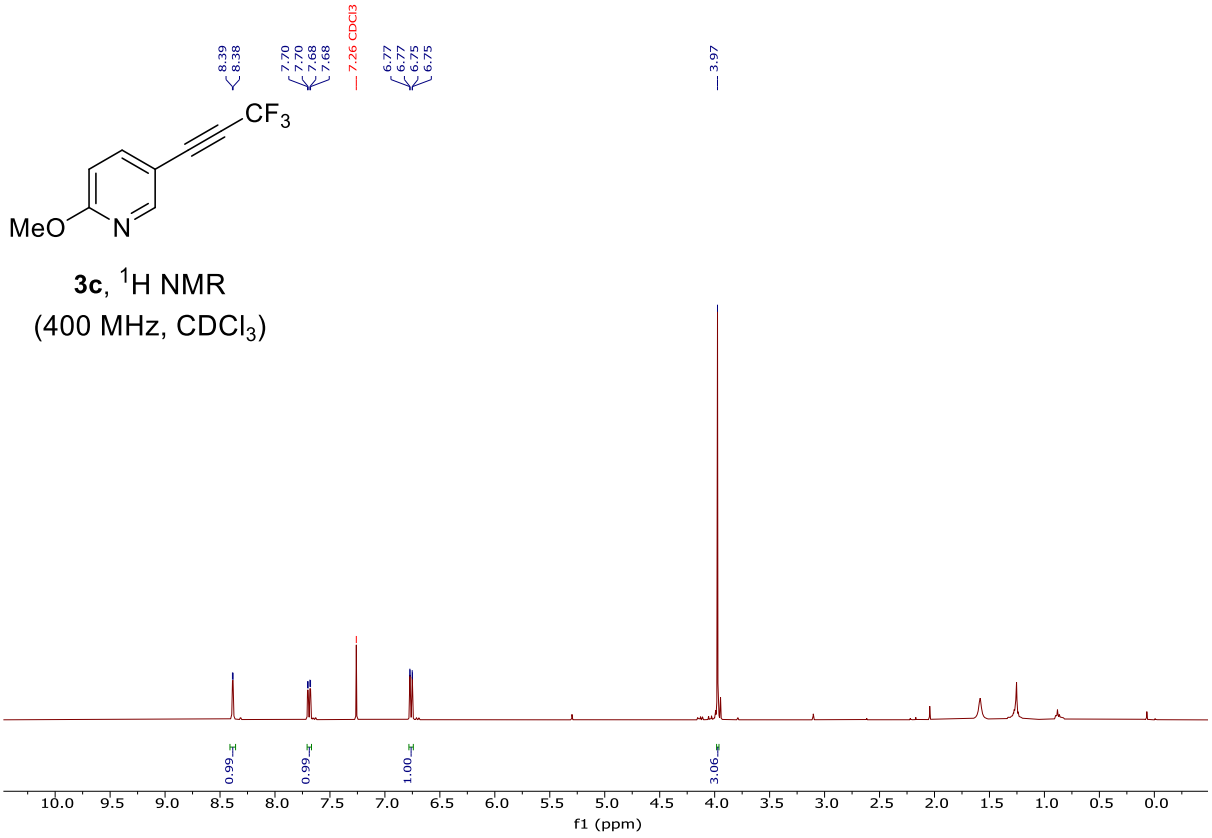
3b, ^{1}H NMR
(600 MHz, $CDCl_3$)



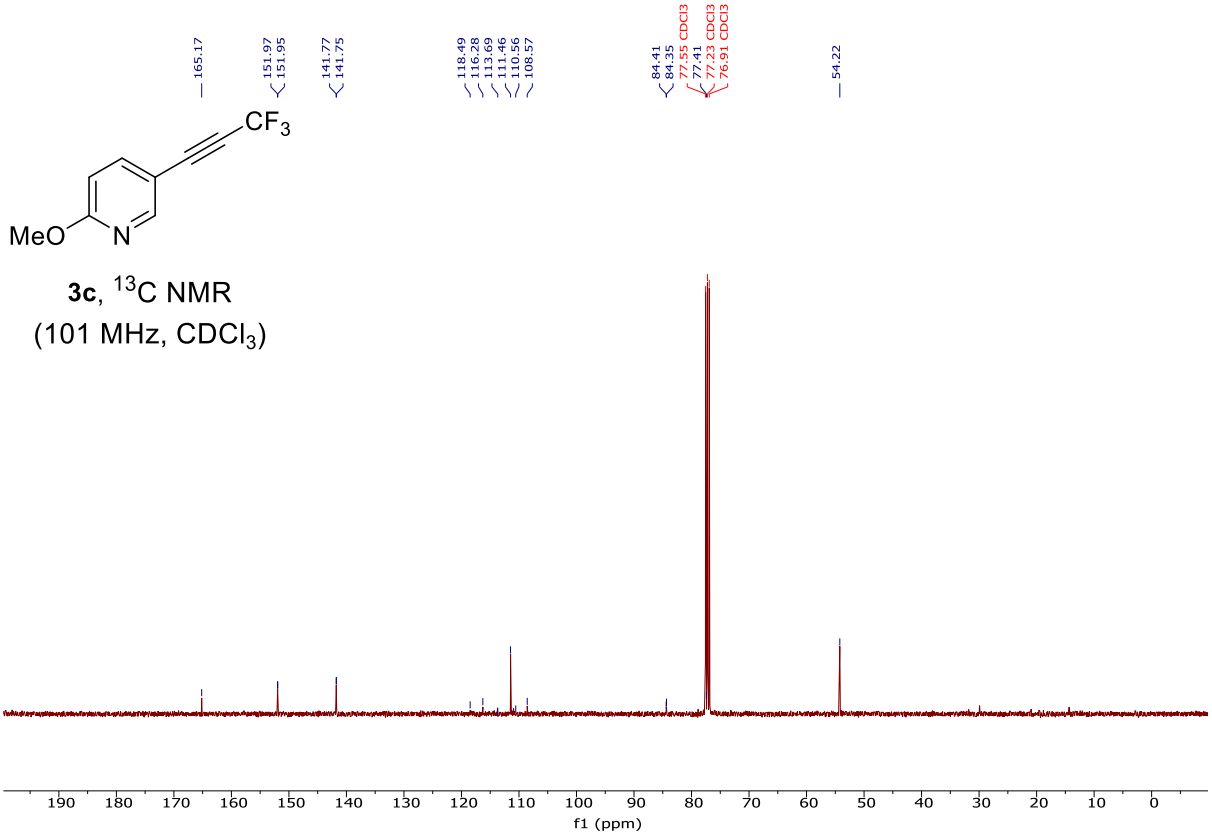
3b, ^{13}C NMR
(151 MHz, $CDCl_3$)



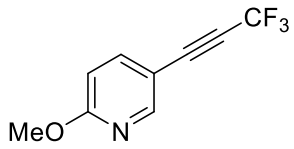
3b, ^{19}F NMR
(564 MHz, $CDCl_3$)



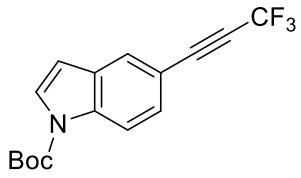
3c, ^{1}H NMR
(400 MHz, $CDCl_3$)



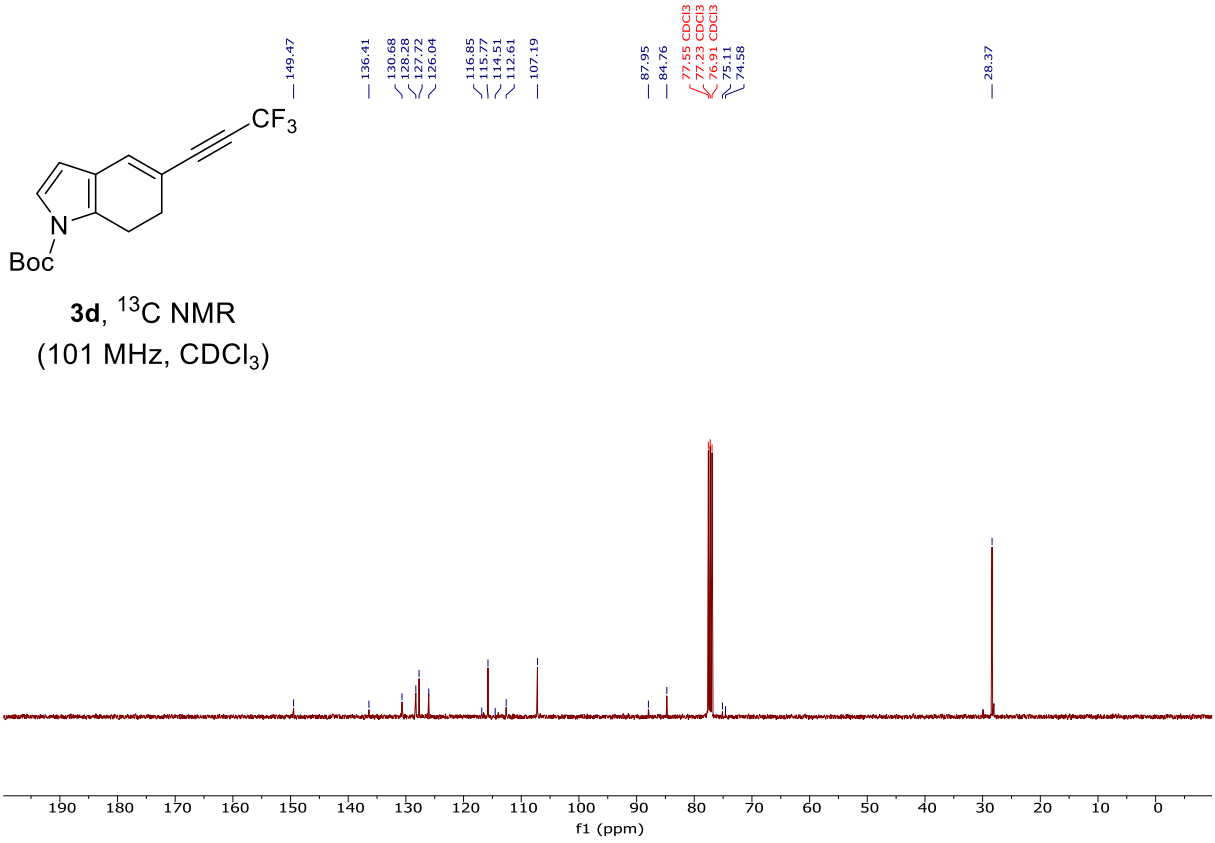
3c, ^{13}C NMR
(101 MHz, $CDCl_3$)



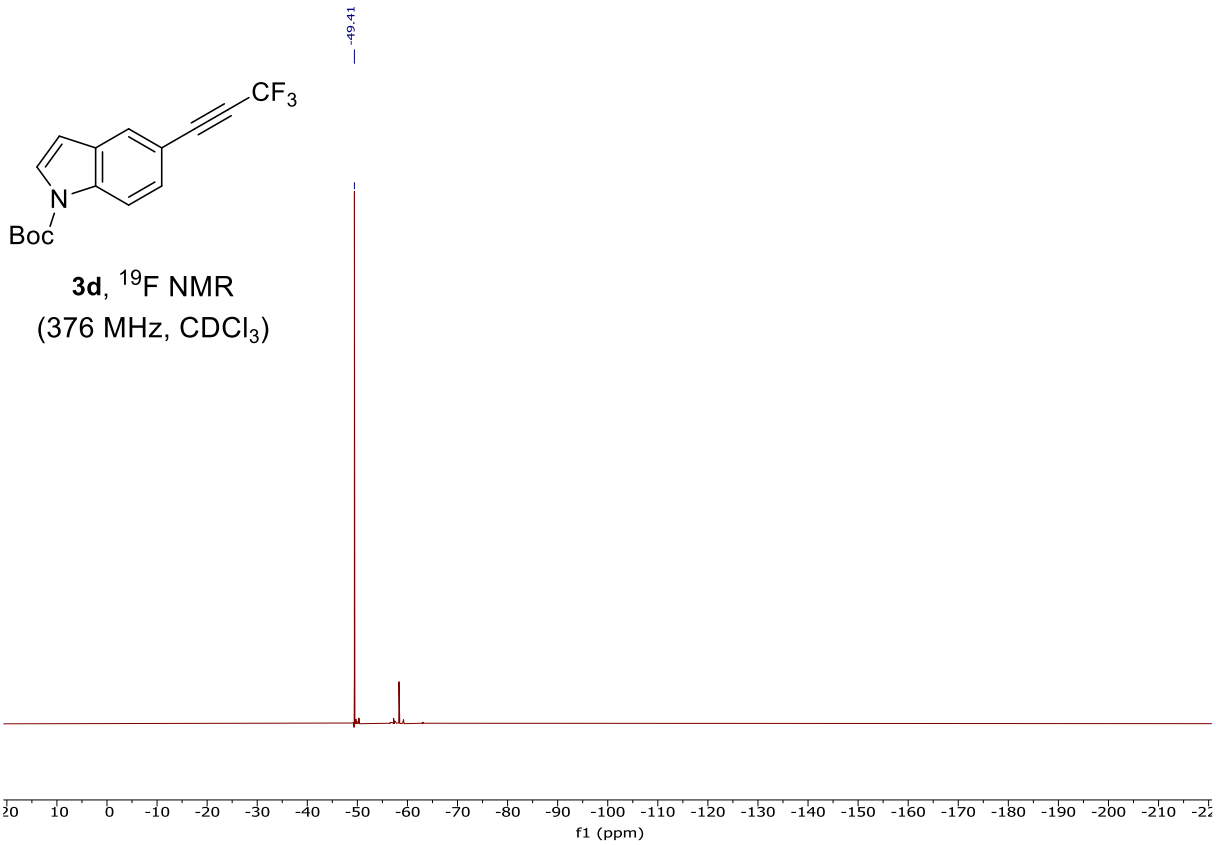
3c, ^{19}F NMR
(376 MHz, $CDCl_3$)



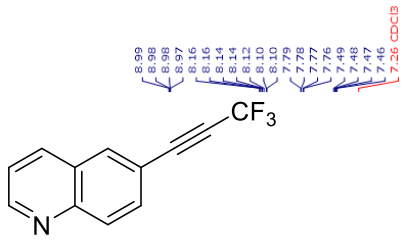
3d, ^{1}H NMR
(400 MHz, $CDCl_3$)



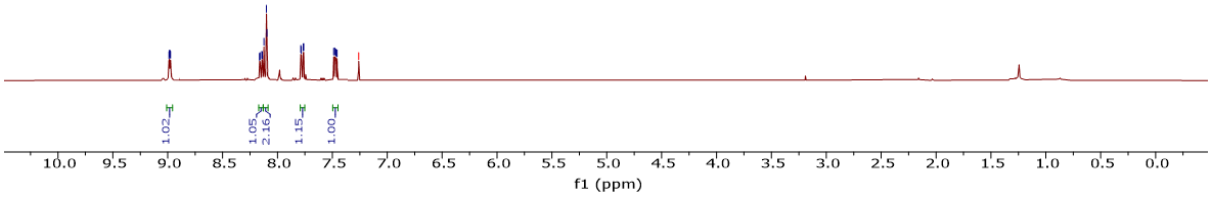
3d, ^{13}C NMR
(101 MHz, $CDCl_3$)

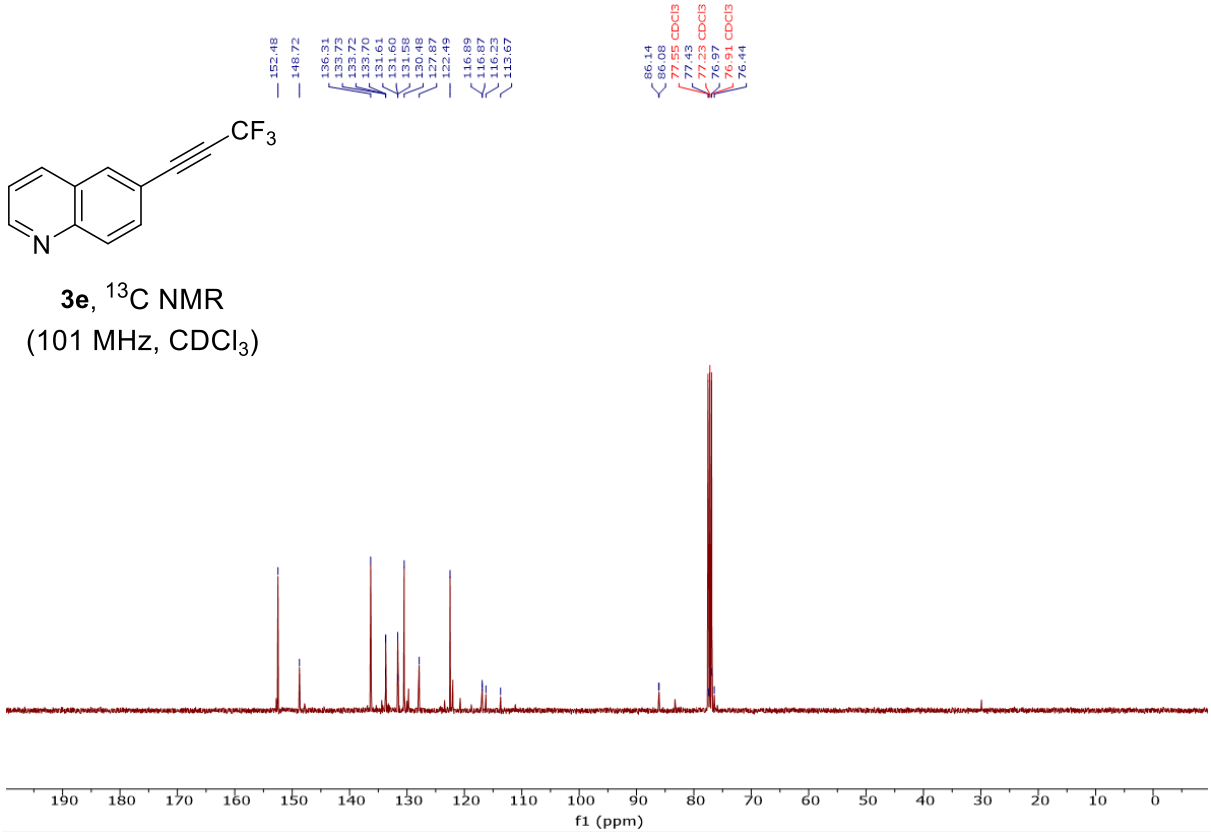


3d, ^{19}F NMR
(376 MHz, $CDCl_3$)

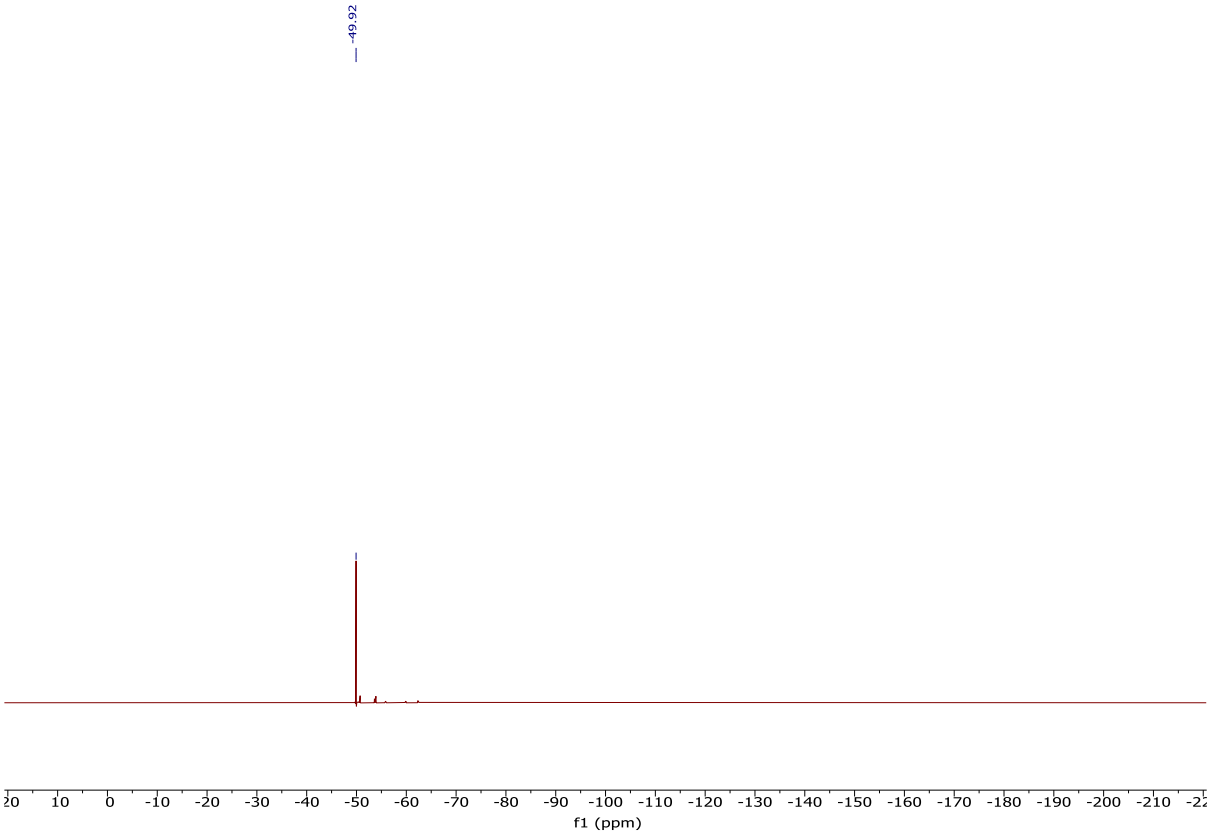


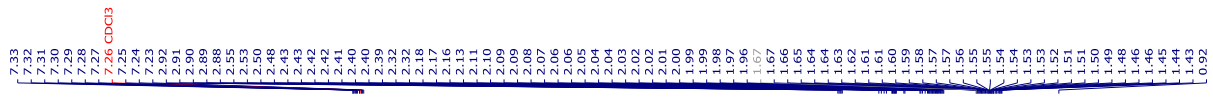
3e, ^{1}H NMR
(400 MHz, $CDCl_3$)

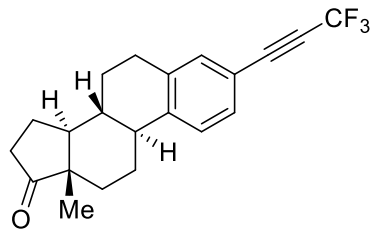




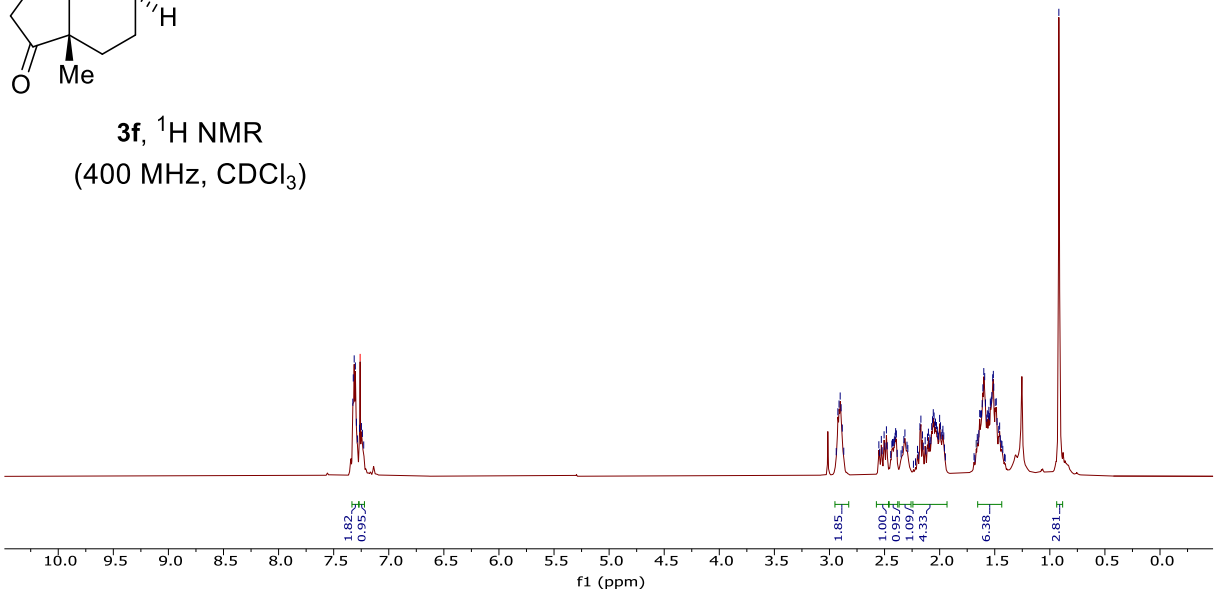
3e, ^{13}C NMR
(101 MHz, $CDCl_3$)

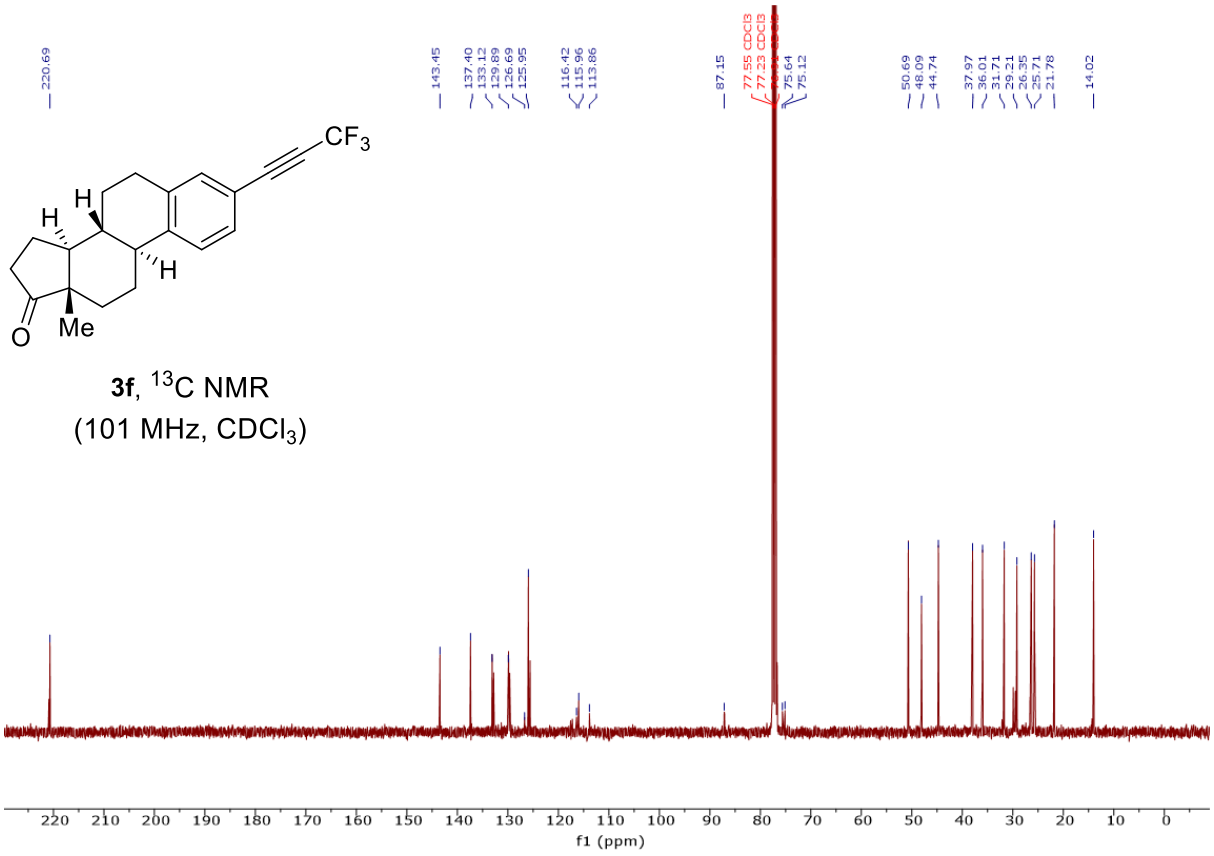




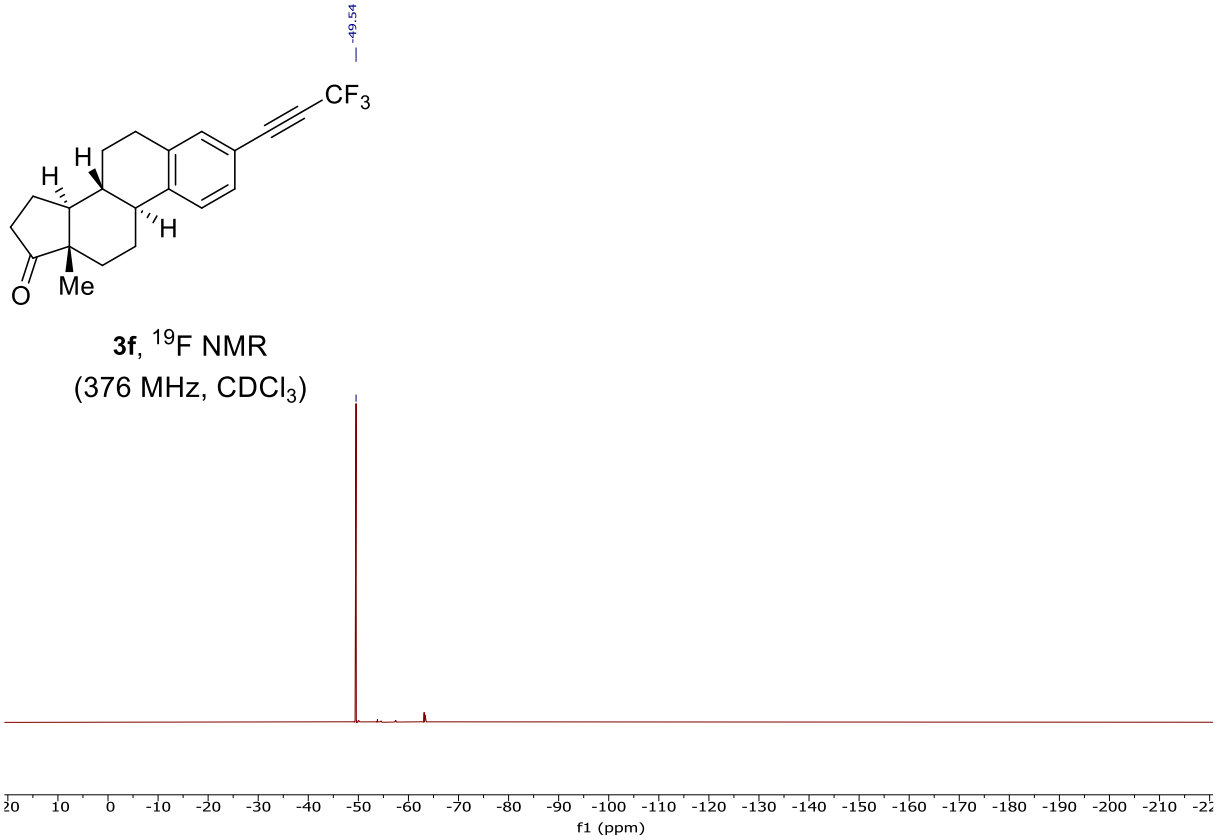


3f, ^{1}H NMR
(400 MHz, $CDCl_3$)

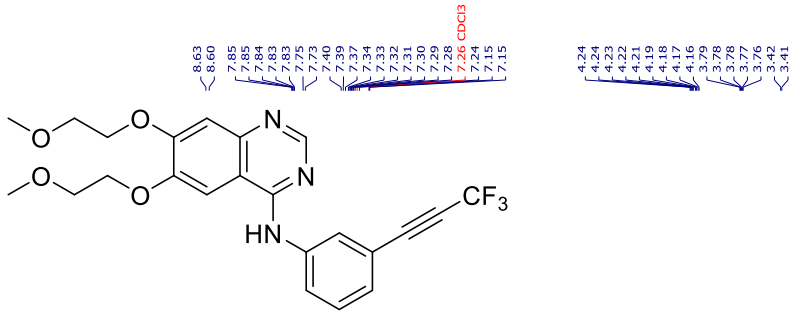




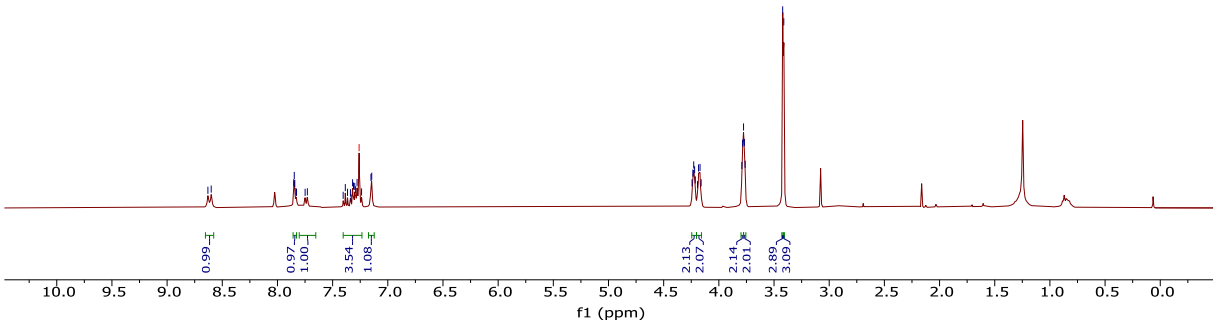
3f, ^{13}C NMR
(101 MHz, $CDCl_3$)

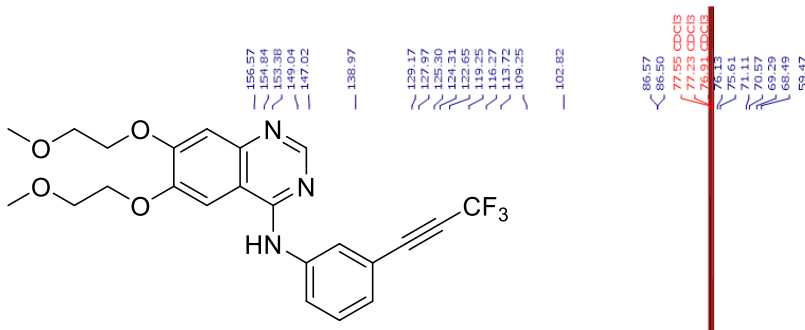


3f, ^{19}F NMR
(376 MHz, $CDCl_3$)

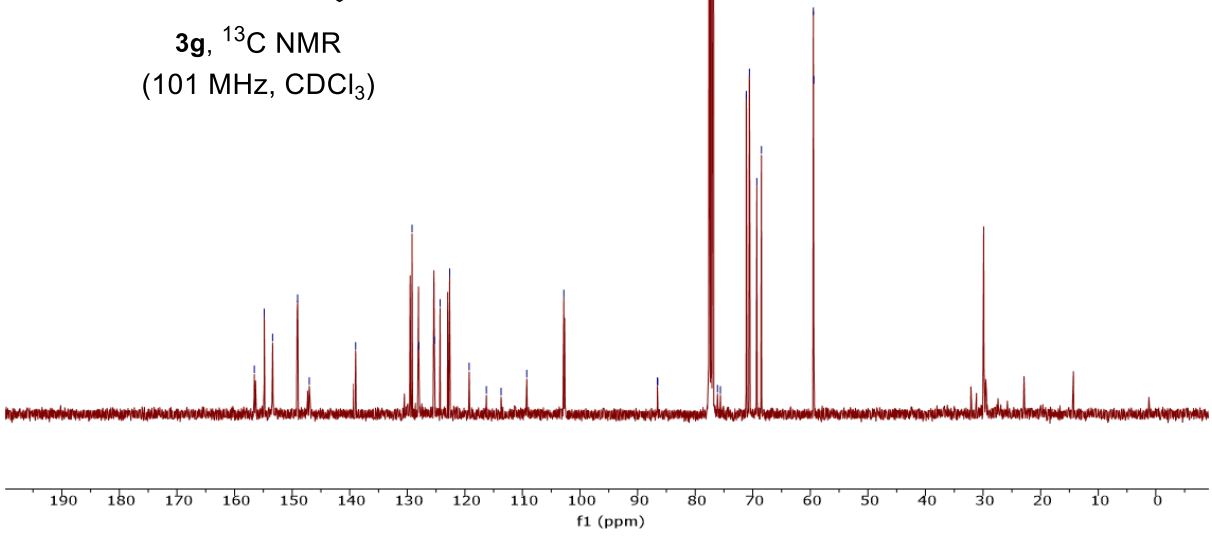


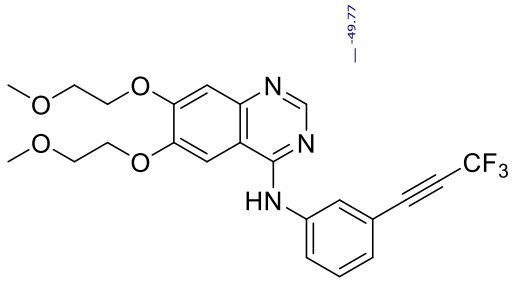
3g, ^{1}H NMR
(400 MHz, $CDCl_3$)





3g, ^{13}C NMR
(101 MHz, $CDCl_3$)





3g, ^{19}F NMR
(376 MHz, $CDCl_3$)