

Supporting Information for

Photochemical Cyclopropenation of Alkynes with Diazirines as Carbene Precursors in Continuous Flow

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Table of Contents

1. General information.....	S2
2. Preparation and characterization of 2,2,2-trifluoromethyl diazirines¹	S3
2.1 General procedure for the synthesis of 2,2,2-trifluoromethyl O-tosyl oximes	S3
2.2 General procedure for the synthesis of 2,2,2-trifluoromethyl diaziridines.....	S8
2.3. Procedure for synthesis of 2,2,2-trifluoromethyl diazirines 1a–n	S11
3. UV-Vis spectra.....	S16
3.1. UV-Vis spectra of diazirines 1a–1n.....	S16
3.2. UV-Vis spectra of cyclopropene 2a.....	S17
4. Optimization studies.....	S17
4.1 Screening of photochemical cyclopropanation with medium-pressure mercury lamp:	S17
4.1.1 Wavelength filters.....	S18
4.2 Screening of flow conditions for the cyclopropanation of diazirine 1a.....	S18
4.2.1 Screening of photochemical cyclopropanation with light-emitting diodes (LEDs)	S18
4.2.2 Optimization of reaction conditions:	S19
5. Experimental procedures for the cyclopropanation reaction of diazirines in continuous flow	S20
5.1 Continuous flow setup for cyclopropene synthesis	S20
5.2 General procedure for the photochemical flow reactions of diazirines in continuous flow	S21
5.3 General procedure for the photochemical reactions of diazirines in batch	S28
5.4 Competition experiments	S29
5.4.1 General procedure for the competition reaction between internal and terminal alkynes	S29
5.4.2 General procedure for the competition reaction between internal alkynes and alkenes.....	S30
5.4.3 General procedure for the competition reaction between internal alkynes and alkenes.....	S31
5.5 General procedure for the TMS deprotection of 2ak.....	S32
5.6 Reaction monitoring using ReactIR.....	S32
6. Control experiments	S34
7. References.....	S38
8. NMR Spectra.....	S39

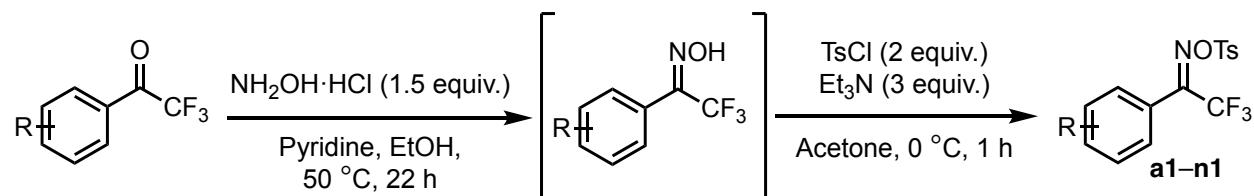
1. General information

All reactions were carried out in flame-dried glassware under an atmosphere of argon with magnetic stirring. All flow reactions were performed using a Vapourtec E-series easy-MedChem flow system using V-3 peristaltic pumps and PFA (polyfluoroalkoxy polymer) tubing (1.3 x 0.15 mm bore and wall) equipped with a UV-150 photochemical reactor kit using standard high efficiency LED (light-emitting diodes) and medium-pressure mercury reactor kit. Light sources used with the flow reactor are the commercial Gen-1 Vaportec units (see full details at: <https://www.vapourtec.com/products/flow-reactors/photocatalysis-led/>). The photochemical unit is temperature-controlled with a Vapourtec Cooled Module accessory. Batch photochemical reactions were done in borosilicate glass vials using LED strips (Govee 16.4 Feet RGB LED Light Strip, H61271A2 ,12 V, 24 watts) wrapped around a cardboard box (distance from vial: 5 cm edges x 2 cm top x 0 cm bottom) and cooled with a flow of compressed air. All starting material purchased from commercial suppliers were used without further purification. Oil baths (mineral oil) were used for reactions that required heating. Thin-layer chromatography (TLC) was carried out on 250 μ m commercial silica gel plates and compounds were visualized using UV absorbance (254 nm) and/or aqueous KMnO₄. Solvents were dried according to standard procedures. Automated flash column chromatography was performed on Biotage® Isolera One™ (SNAP Ultra cartridge). ¹H, ¹³C{¹H}, and ¹⁹F NMR spectra were recorded on Varian Inova 400 MHz and Agilent DD2 500 MHz spectrometers in CDCl₃. For ¹H NMR, chemical shifts are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (in Hz), and integration. For ¹³C{¹H} NMR, CDCl₃ was used as internal standard (δ = 77.16 ppm) and spectra were obtained with complete proton decoupling. For ¹⁹F NMR, no external standard was used. High-resolution mass spectra (HRMS) were recorded on LC/ESI-TOF (time-of-flight) mass spectrometer Agilent 6210 mass spectrometer using electrospray ionization (ESI). IR spectra were recorded on a NICOLET 380 FT-IR spectrometer with a ZnSe ATR accessory and are reported in reciprocal centimeter (cm⁻¹). Reaction monitoring with IR was performed using Mettler Toledo FlowIR™ cell with a silicon probe and recorded on a ReactIR™ 15 apparatus and data is processed on iC IR software. Melting points (mp) are uncorrected and were recorded on a MEL-TEMP® melting point apparatus. UV-Vis were recorded on an Agilent Cary 7000 Series UV-Vis-NIR spectrophotometer using CH₂Cl₂ as a blank and processed on Cary WinUV software.

2. Preparation and characterization of 2,2,2-trifluoromethyl diazirines¹

Diazirine substrates (**1a–1n**) are prepared following reported procedures.

2.1 General procedure for the synthesis of 2,2,2-trifluoromethyl O-tosyl oximes



Hydroxylamine hydrochloride (1.2 g, 15 mmol) was added to a solution of the 2,2,2-trifluoromethyl ketone (15 mmol) in pyridine (7.5 mL) and EtOH (4 mL). The reaction mixture was heated to 50 °C overnight. The reaction was cooled to room temperature and diluted with EtOAc, washed with 2 M aq. HCl, dried over MgSO₄, and concentrated under reduced pressure. The crude product was used as is for the next step.

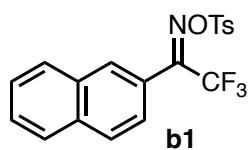
The crude 2,2,2-trifluoromethyl oxime was dissolved in acetone (80 mL) and cooled to 0 °C, to which Et₃N (6 mL) was added followed by tosyl chloride (3.2 g, 16.8 mmol). The reaction mixture was brought to room temperature and stirred for 1 h. The reaction was concentrated under reduced pressure. The crude residue was purified by flash chromatography (Biotage, SNAP ULTRA, 9:1 hexanes/EtOAc) to give the O-tosyl oxime of a mixture of both *E*- and *Z*-isomers.

2.1.1 Characterization of O-tosyl oximes (a1–n1)

1-([1,1'-Biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one O-tosyl oxime a1

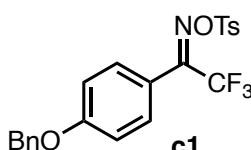
a1 Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (8 g, 89%). Exhibited spectral data identical to a previous report.²
¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 8.01–7.94 (m, 2H), 7.69–7.66 (m, 2H), 7.59–7.54 (m, 4H), 7.47–7.39 (m, 5H), 2.48 (s, 3H); (Minor-isomer): 7.98 (m, 2H), 7.74–7.68 (m, 2H), 7.66–7.60 (m, 4H), 7.50 (m, 5H), 2.50 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm): (Major-isomer): 153.8 (q, J = 31.5 Hz), 146.3, 144.8, 139.5, 131.4, 130.0 (q, J = 2.4 Hz), 129.3, 129.1, 128.0, 127.4, 127.2, 123.2, 117.5 (q, J = 285.6 Hz), 21.8; (Minor-isomer): 153.8 (q, J = 31.5 Hz), 146.4, 144.6, 139.5, 131.2, 129.4, 129.2, 128.9, 128.4 (q, J = 2.0 Hz), 127.7, 127.5, 127.3, 126.5, 119.8 (q, J = 277.3 Hz), 21.8. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -61.4 (Minor-isomer), -66.5 (Major-isomer).

2,2,2-Trifluoro-1-(naphthalen-2-yl)ethan-1-one O-tosyl oxime b1



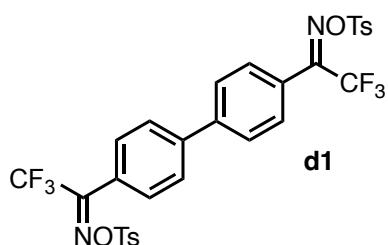
Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (6 g, 80%). mp: 64–66 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): (Major-isomer): 8.04–7.90 (m, 6H), 7.63–7.60 (m, 2H), 7.51 (d, J = 9.3 Hz, 1H), 7.41 (d, J = 9.3 Hz, 2H), 2.48 (s, 3H); (Minor-isomer): 7.90–7.81 (m, 6H), 7.59–7.54 (m, 2H), 7.46 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 2.46 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): (Major-isomer): 154.5 (q, J = 33.8 Hz), 146.3, 134.4, 133.9, 132.7, 132.4, 131.4, 130.0 (q, J = 1.6 Hz), 130.0, 129.2, 125.0, 124.5, 119.8 (q, J = 278.0 Hz), 21.8; (Minor-isomer): 154.1 (q, J = 32.2 Hz), 146.2, 134.3, 133.8, 132.6, 132.4, 131.2, 129.3, 129.2 (q, J = 1.6 Hz), 128.9, 124.9, 124.4, 116.4 (q, J = 283.3 Hz), 21.8. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –61.2 (Minor-isomer), –66.4 (Major-isomer). IR (cm^{-1}): 3256, 3064, 1596, 1377, 1194, 1148, 1095, 872, 750. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{NO}_3\text{S}$ 394.0719, found 394.0749.

1-(4-(Benzoyloxy)phenyl)-2,2,2-trifluoroethan-1-one O-tosyl oxime c1



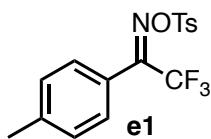
Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (932 mg, 42%). mp: 78–80 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): (Major-isomer): 7.95–7.87 (m, 2H), 7.42–7.33 (m, 9H), 7.03–6.99 (m, 2H), 5.12 (s, 2H), 2.48 (s, 3H); (Minor-isomer): 7.50–7.41 (m, 11H), 7.08–7.04 (m, 2H), 5.13 (s, 2H), 2.49 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): (Major-isomer): 161.7, 153.6 (q, J = 31.9 Hz), 146.0, 136.1, 131.6, 130.7 (q, J = 1.5 Hz), 129.9, 129.1, 128.8, 128.3, 127.5, 117.5 (q, J = 284.4 Hz), 116.7, 115.1, 70.2, 21.8; (Minor-isomer): 161.3, 153.2 (q, J = 32.8 Hz), 146.1, 136.1, 131.2, 130.8 (d, J = 1.1 Hz), 129.9, 129.3, 128.8, 128.4, 127.5, 120.1, 119.9 (q, J = 278.0 Hz), 115.1, 70.2, 21.8. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –61.4 (Minor-isomer), –65.9 (Major-isomer). IR (cm^{-1}): 3070, 2926, 1599, 1496, 1390, 1177, 1140, 812, 735. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_{22}\text{H}_{19}\text{F}_3\text{NO}_4\text{S}$ 450.0981 found 450.0966.

1,1'-([1,1'-Biphenyl]-4,4'-diyl)bis(2,2,2-trifluoroethan-1-one) O,O-ditosyl dioxime d1



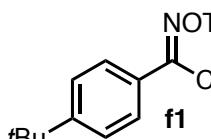
Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (1.6 g, 94%) by doubling the quantities of the above procedure. m.p. 50–52 °C. mp: 64–66 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): (Major-isomer): 7.97–7.90 (m, 3H), 7.75–7.63 (m, 5H), 7.55 (m, 4H), 7.45–7.39 (m, 4H), 2.48 (s, 6H); (Minor-isomer): 7.97–7.90 (m, 3H), 7.69 (d, J = 8.1 Hz, 5H), 7.58–7.51 (m, 4H), 7.44–7.34 (m, 4H), 2.49 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): (Major-isomer): 153.5 (q, J = 31.8 Hz), 146.3, 142.9, 132.2, 131.3, 130.0, 129.6 (d, J = 1.3 Hz), 127.5, 124.3, 118.5 (q, J = 285.2 Hz), 21.8; (Major-isomer): 153.5 (q, J = 33.5 Hz), 146.4, 142.9, 132.0, 131.0, 129.2 (d, J = 1.1 Hz), 129.2, 127.5, 127.0, 119.6 (q, J = 278.1 Hz), 21.8. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –61.4 (Minor-isomer), –66.5 (Major-isomer). IR (cm^{-1}): 3097, 2874, 1597, 1391, 1192, 1153, 1092, 885, 814. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for $\text{C}_{30}\text{H}_{26}\text{F}_6\text{N}_3\text{O}_6\text{S}_2$ 702.1162 found 702.1144.

2,2,2-Trifluoro-1-(*p*-tolyl)ethan-1-one O-tosyl oxime e1



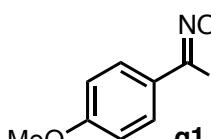
Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (2.6 g, 82%). Exhibited spectral data identical to a previous report.³ ¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.98–7.91 (m, 2H), 7.40–7.33 (m, 4H), 7.31–7.25 (m, 2H), 2.39 (s, 1H), 2.38 (s, 1H); (Minor-isomer): 7.98–7.91 (m, 1H), 7.51–7.44 (m, 1H), 7.32–7.25 (m, 4H), 2.45 (s, 1H), 2.44 (s, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 154.2 (q, J = 32.3 Hz), 146.4, 142.5, 131.2, 130.0, 129.5, 129.2, 128.8 (q, J = 1.4 Hz), 121.6, 119.8 (q, J = 277.5 Hz), 21.4, 21.3; (Minor-isomer): 147.3 (q, J = 32.5 Hz), 146.3, 142.7, 131.4, 129.5, 129.2, 129.1, 128.6 (q, J = 1.3 Hz), 124.8, 117.5 (q, J = 284.9 Hz), 21.6, 21.6. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): –61.5 (Minor-isomer), –66.5 (Major-isomer).

1-(4-(*Tert*-butyl)phenyl)-2,2-trifluoroethan-1-one O-tosyl oxime f1



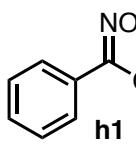
Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (1.6 g, 80%). mp: 68–70 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.93–7.90 (m, 2H), 7.44 (d, J = 2.2 Hz, 2H), 7.41–7.35 (m, 4H), 2.47 (s, 3H), 1.33 (s, 9H); (Minor-isomer): 7.94–7.89 (m, 2H), 7.51–7.48 (m, 2H), 7.42–7.37 (m, 4H), 2.49 (s, 3H), 1.35 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 155.5, 154.0 (q, J = 32.1 Hz), 145.9, 131.5, 129.9, 129.1, 128.7 (q, J = 1.2 Hz), 125.8, 121.6, 117.4 (q, J = 283.9 Hz), 35.0, 31.0, 21.8; (Minor-isomer): 155.3, 153.9 (q, J = 33.0 Hz), 146.1, 131.2, 129.9, 129.3, 128.4 (q, J = 1.2 Hz), 125.8, 124.8, 119.7 (q, J = 277.7 Hz), 35.0, 31.0, 21.8. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): –61.5 (Minor-isomer), –66.4 (Major-isomer). IR (cm^{−1}): 2968, 2872, 1595, 1396, 1196, 1389, 1150, 729. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for C₁₉H₂₄F₃N₂O₃S 417.1454 found 417.1413.

2,2,2-Trifluoro-1-(4-methoxyphenyl)ethan-1-one O-tosyl oxime g1

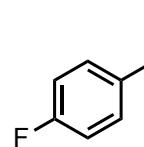


Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (3 g, 84%). Exhibited spectral data identical to a previous report.³ ¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.91 (d, J = 8.4 Hz, 2H), 7.49–7.43 (m, 2H), 7.40–7.33 (m, 2H), 6.95–6.89 (m, 2H), 3.84 (s, 3H), 2.46 (s, 3H); (Minor-isomer): 7.90 (d, J = 8.4 Hz, 2H), 7.41 (dt, J¹ = 7.9 Hz, J² = 1.1 Hz, 2H), 7.00–6.94 (m, 2H), 3.85 (s, 3H), 2.48 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 162.5, 153.6 (q, J = 31.8 Hz), 145.9, 131.5, 130.7 (q, J = 1.6 Hz), 129.9, 129.1, 118.7 (q, J = 284.5 Hz), 116.4, 114.2, 55.5, 21.8; (Minor-isomer): 162.1, 153.2 (q, J = 32.8 Hz), 146.1, 131.2, 130.7 (q, J = 1.3 Hz), 129.9, 129.3, 119.8 (q, J = 277.9 Hz), 119.8, 114.2, 55.4, 21.8. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): –61.4 (Minor-isomer), –66.0 (Major-isomer).

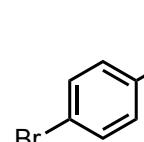
2,2,2-Trifluoro-1-phenylethan-1-one O-tosyl oxime h1


h1 Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (0.8 g, 73%). Exhibited spectral data identical to a previous report.³
¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.88 (d, *J* = 8.5 Hz, 3H), 7.42–7.29 (m, 2H), 2.45 (s, 3H); (Minor-isomer): 7.90 (d, *J* = 8.8 Hz, 3H), 7.48–7.41 (m, 2H), 2.43 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 154.1 (q, *J* = 33.4 Hz), 147.1, 146.5, 131.8, 131.1, 130.4, 129.2, 128.9, 128.3 (q, *J* = 1.2 Hz), 119.7 (q, *J* = 277.6 Hz), 21.7; (Minor-isomer): 154.0 (q, *J* = 32.2 Hz), 146.4, 141.5, 131.9, 131.3, 129.1, 128.8, 128.0 (q, *J* = 1.4 Hz), 127.6, 117.4 (q, *J* = 285.2 Hz), 21.7. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -61.4 (Minor-isomer), -66.7 (Major-isomer).

2,2,2-Trifluoro-1-(4-fluorophenyl)ethan-1-one O-tosyl oxime i1


i1 Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a semi solid (3.9 g, 77%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.90–7.89 (m, 2H), 7.46–7.44 (m, 2H), 7.42–7.37 (m, 2H), 7.37 (s br, 2H), 7.13–7.10 (m, 2H), 2.41 (s, 3H); (Minor-isomer): 7.89–7.88 (m, 2H), 7.43–7.42 (m, 2H), 7.35 (s br, 2H), 7.10–7.05 (m, 2H), 2.40 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 164.8 (d, *J* = 254.1 Hz), 153.0 (q, *J* = 32.2 Hz), 146.5, 131.2 (d, *J* = 7.9 Hz), 130.0, 129.0, 123.8, 119.5 (q, *J* = 256.2 Hz), 116.2, 116.0, 21.5; (Minor-isomer): 164.1 (d, *J* = 253.3 Hz), 153.0 (q, *J* = 33.8 Hz), 146.4, 131.0 (d, *J* = 8.4 Hz), 130.0, 129.1, 123.7, 119.5 (q, *J* = 260.2 Hz), 116.3, 116.1, 21.5. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -61.7 (Major-isomer), -66.8 (Minor-isomer) –106.2 (m, Minor-isomer), -106.7 (m, Major-isomer). IR (cm⁻¹): 3074, 2874, 1599, 1512, 1389, 1150, 729. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for C₁₅H₁₅F₃N₂O₃S 379.0434 found 379.0715.

1-(4-Bromophenyl)-2,2,2-trifluoroethan-1-one O-tosyl oxime j1


j1 Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (2 g, 95%). Exhibited spectral data identical to a previous report.⁴
¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.91–7.89 (m, 2H), 7.63–7.54 (m, 2H), 7.42–7.37 (m, 2H), 7.33–7.28 (m, 2H), 2.46 (s, 3H); (Minor-isomer): 7.89–7.87 (m, 2H), 7.57–7.49 (m, 2H), 7.40–7.35 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 153.0 (q, *J* = 33.5 Hz), 146.4, 141.5, 132.2, 131.2, 130.1 (q, *J* = 1.1 Hz), 129.2, 126.6, 123.3, 117.2 (q, *J* = 284.1 Hz), 21.7; (Minor-isomer): 153.0 (q, *J* = 34.4 Hz), 146.5, 146.4, 132.1, 130.9, 130.3 (q, *J* = 1.1 Hz), 129.2, 127.0, 126.9, 119.5 (q, *J* = 277.6 Hz), 21.7. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -61.5 (Minor-isomer), -66.8 (Major-isomer).

1-(3-Bromophenyl)-2,2,2-trifluoroethan-1-one O-tosyl oxime k1

NOTs Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (6.1 g, 96%). Exhibited spectral data identical to a previous report.⁵

¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.92–7.87 (m, 2H), 7.61 (q, J = 1.3 Hz, 1H), 7.49 (s, 1H), 7.40–7.34 (m, 3H), 7.29 (t, J = 7.9 Hz, 1H), 2.45 (s, 3H); (Minor-isomer): 7.93–7.85 (m, 2H), 7.63 (t, J = 2.0 Hz, 1H), 7.54 (s, 1H), 7.41–7.37 (m, 3H), 7.36–7.30 (m, 1H), 2.44 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 152.6 (q, J = 33.9 Hz), 146.6, 134.8, 131.6 (q, J = 1.4 Hz), 130.5, 130.4, 130.1, 127.1, 122.8, 119.4 (q, J = 277.5 Hz), 21.7; (Minor-isomer): 152.6 (q, J = 32.8 Hz), 146.5, 134.9, 130.9, 130.3, 129.1, 127.5 (q, J = 1.4 Hz), 127.0, 122.8, 117.1 (q, J = 283.8 Hz), 21.7. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -61.6 (Minor-isomer), -66.9 (Major-isomer).

2,2,2-Trifluoro-1-(4-(trifluoromethyl)phenyl)ethan-1-one O-tosyl oxime l1

NOTs Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (1.9 g, 75%). mp: 38–40 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.94–7.91 (m, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.42–7.40 (m, 2H), 2.49 (s, 3H); (Minor-isomer): 7.91–7.88 (m, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.39–7.38 (m, 2H), 2.47 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm): (Major-isomer only): 153.0 (q, J = 34.2 Hz), 146.7, 133.5 (q, J = 33.1 Hz), 131.0, 130.1, 129.4, 129.1, 128.2, 126.0 (q, J = 3.8 Hz), 123.4 (q, J = 272.7 Hz), 119.5 (q, J = 277.4 Hz), 21.78. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): (Minor-isomer): -61.5, -63.3; (Major-isomer): -63.3, -66.9. IR (cm⁻¹): 2992, 2928, 1597, 1456, 1389, 1181, 893, 818. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for C₁₆H₁₅F₆N₂O₃S 429.0702 found 429.0694.

2,2,2-Trifluoro-1-(2-methoxyphenyl)ethan-1-one O-tosyl oxime m1

NOTs Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (2.3 g, 45%). Exhibited spectral data identical to a previous report.⁶

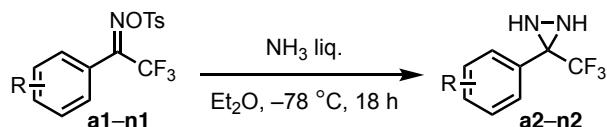
¹H NMR (500 MHz, CDCl₃) δ (ppm): (Major-isomer): 7.90–7.85 (m, 2H), 7.47 (m, 1H), 7.41–7.36 (m, 2H), 7.14–7.07 (m, 1H), 7.00–6.94 (m, 2H), 3.75 (s, 3H), 2.48 (s, 3H); (Minor-isomer): 7.95–7.80 (m, 2H), 7.47 (ddt, J^1 = 8.6 Hz, J^2 = 7.5 Hz, J^3 = 1.9 Hz, 1H), 7.12–7.09 (m, 2H), 7.02 (dd, J^1 = 7.5 Hz, J^2 = 0.9 Hz, 1H), 6.92 (dd, J^1 = 8.4, J^2 = 0.9 Hz, 2H), 3.78 (s, 3H), 2.46 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): (Major-isomer): 156.8, 153.0 (q, J = 34.7 Hz), 145.9, 132.9, 131.6, 130.9, 129.8, 129.1, 128.5, 120.6, 116.8 (q, J = 282.8 Hz), 111.5, 55.7, 21.8; (Minor-isomer): 158.5, 155.3 (q, J = 34.5 Hz), 145.9, 133.3, 131.6, 129.8, 129.6, 129.1, 128.8, 120.7, 119.4 (q, J = 276.9 Hz), 111.1, 55.7, 21.7. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -64.8 (Minor-isomer), -67.9 (Major-isomer).

2,2,2-Trifluoro-1-(2-fluorophenyl)ethan-1-one O-tosyl oxime n1

n1

Purified by flash column chromatography (9:1 hexanes/EtOAc). Isolated as a white solid (4 g, 78%).
mp: 48–50 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.92–7.86 (m, 2H), 7.58–7.49 (m, 1H), 7.42–7.36 (m, 2H), 7.25–7.15 (m, 2H), 7.14 (ddd, $J^1 = 9.7$ Hz, $J^2 = 8.4$ Hz, $J^3 = 1.0$ Hz, 1H), 2.47 (s, 3H); (Minor-isomer): 7.89 (dq, $J^1 = 8.6$ Hz, $J^2 = 2.1$ Hz, 2H), 7.58–7.49 (m, 1H), 7.42–7.36 (m, 2H), 7.30–7.22 (m, 3H), 2.48 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): (Major-isomer): 160.6 (d, $J = 253.1$ Hz), 152.0 (q, $J = 35.0$ Hz), 146.3, 133.9 (d, $J = 8.2$ Hz), 132.5 (d, $J = 8.5$ Hz), 131.2 (d, $J = 1.1$ Hz), 131.0 (q, $J = 1.2$ Hz), 130.0, 129.1, 124.6, 116.6 (q, $J = 283.1$ Hz), 116.4 (d, $J = 25.7$ Hz), 21.7; (Minor-isomer): 159.2 (d, $J = 253.8$ Hz), 150.0 (q, $J = 35.3$ Hz), 146.3, 133.7 (d, $J = 8.2$ Hz), 132.4 (d, $J = 8.1$ Hz), 129.9, 129.2, 128.8 (d, $J = 2.1$ Hz), 124.6 (d, $J = 3.5$ Hz), 120.4 (q, $J = 276.7$ Hz), 116.5, 116.3, 21.8. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): (Major-isomer): -64.3 (d, $J = 10.0$ Hz), -109.9 (m); (Minor-isomer): -65.0 (d, $J = 8.5$ Hz), -111.2 (m). IR (cm^{-1}): 2984, 1562, 1492, 1389, 1155, 1092, 893, 720. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for C₁₅H₁₅F₄N₂O₃S 379.0734 found 379.0722.

2.2 General procedure for the synthesis of 2,2,2-trifluoromethyl diaziridines



In a sealed microwave vial, the O-tosyl oxime (2 mmol) was dissolved in Et_2O (0.5 mL) and cooled to -78 °C. Anhydrous ammonia was condensed (ca. 10 mL). The mixture was stirred overnight and brought up slowly to room temperature. The solution was cooled again to -78 °C and a bleed needle was added to remove excess pressure. The vial was then de-capped, and the residual ammonia was left to slowly evaporate at room temperature. The residue was diluted with Et_2O and washed with H_2O , dried over MgSO_4 , and concentrated under reduced pressure to afford the corresponding diaziridine that was obtained clean and used as is for the oxidation into the diazirine.

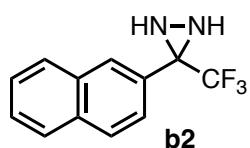
2.2.1 Characterizations of diaziridines a2–n2

3-(4,4'-Biphenyl)-3-(trifluoromethyl)diaziridine a2

a2

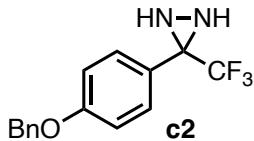
Isolated as a white solid (530 mg, quant.). Exhibited spectral data identical to a previous report.² ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.74–7.72 (m, 1H), 7.69–7.64 (m, 1H), 7.64–7.61 (m, 1H), 7.59–7.57 (m, 2H), 7.50–7.49 (m, 3H), 7.45–7.40 (m, 1H), 2.89 (d, $J = 8.6$ Hz, 1H), 2.32 (d, $J = 8.8$ Hz, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm): 131.9, 129.0, 129.0, 128.8, 127.5, 127.2, 127.0, 123.6 (q, $J = 278.4$ Hz), 121.6, 57.9 (q, $J = 36.0$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -75.3.

3-(Naphthalin-2-yl)-3-(trifluoromethyl)diaziridine b2



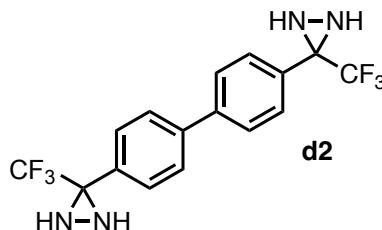
Isolated as a white solid (480 mg, quant.). Exhibited spectral data identical to a previous report.⁷ ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.15 (br s, 1H), 7.92–7.91 (m, 1H), 7.90–7.88 (m, 2H), 7.70–7.68 (m, 1H), 7.58–7.56 (m, 2H), 2.92 (d, J = 8.5 Hz, 1H), 2.37 (d, J = 8.5 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 134.0, 132.9, 129.1, 128.9, 128.5, 128.5, 127.9, 127.5, 127.0, 124.7, 123.7 (q, J = 278.8 Hz), 58.4 (q, J = 36.1 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -75.3.

3-(4-Benzoyloxyphenyl)-3-(trifluoromethyl)diaziridine c2



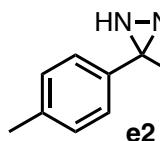
Isolated as a white solid (590 mg, quant.). mp: 80–82 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.56–7.55 (m, 2H), 7.47–7.37 (m, 5H), 7.04–7.02 (m, 2H), 5.10 (s, 2H), 2.79 (br s, 1H), 2.21 (br s, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm): 160.0, 136.5, 129.6, 128.7, 128.2, 127.5, 124.0, 123.7 (q, J = 278.2 Hz), 115.0, 70.1, 57.7 (q, J = 35.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -75.7. IR (cm⁻¹): 3200, 2926, 1614, 1520, 1014, 743. HR-MS (EI) m/z [M + H]⁺ calcd. for C₁₅H₁₄F₃N₂O 295.1053 found 295.1013.

Bis-(4,4'-Biphenyl)-3-(trifluoromethyl)diaziridine d2



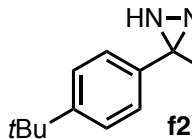
Isolated as a white solid (750 mg, quant.). mp: 150–152 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.74–7.72 (m, 4H), 7.66–7.64 (m, 4H), 2.85 (br s, 2H), 2.26 (br s, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 142.0, 131.3, 128.7, 127.6, 123.5 (q, J = 278.1 Hz), 57.8 (q, J = 36.2 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -75.4. IR (cm⁻¹): 3211, 2922, 1381, 1143, 953, 881, 819, 699. HR-MS (EI) m/z [M + H]⁺ calcd. for C₁₆H₁₃F₆N₄ 375.1039 found 375.1041.

3-(p-Tolyl)-3-(trifluoromethyl)diaziridine e2



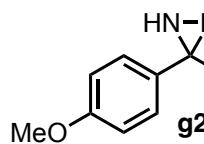
Isolated as a white solid (400 mg, quant.). Exhibited spectral data identical to a previous report.² ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.52–7.50 (m, 2H), 7.25–7.23 (m, 2H), 2.8 (br s, 1H), 2.39 (s, 3H), 2.2 (br s, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 140.4, 129.6, 129.4, 128.1, 123.7 (q, J = 278.4 Hz), 58.1 (q, J = 36.0 Hz), 21.4. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -75.7.

3-(4-Tert-butylphenyl)-3-(trifluoromethyl)diaziridine f2

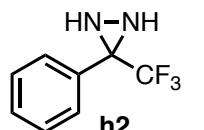


Isolated as a white solid (490 mg, quant.). mp: 68–70 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.54 (d, J = 8.8 Hz, 2H), 7.47–7.41 (m, 2H), 2.76 (br s, 1H), 2.20 (br s, 1H), 1.33 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 153.5, 128.9, 127.9, 125.9, 123.8 (q, J = 278.3 Hz), 58.0 (q, J = 36.0 Hz), 34.9, 31.3. ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -75.6. IR (cm⁻¹): 3248, 3150, 2966, 1402, 1142, 829, 689. HR-MS (EI) m/z [M + H]⁺ calcd. for C₁₂H₁₆F₃N₂ 245.1260 found 245.1268.

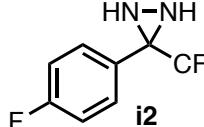
3-(4-Methoxyphenyl)-3-(trifluoromethyl)diaziridine g2


g2 Isolated as a white solid (440 mg, quant.). Exhibited spectral data identical to a previous report.⁸ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.70–7.46 (m, 2H), 6.97–6.90 (m, 2H), 3.84 (s, 3H), 2.76 (d, J = 8.9 Hz, 1H), 2.17 (d, J = 9.0 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 160.7, 129.5, 123.7, 123.7 (q, J = 278.2 Hz), 114.0, 57.6 (q, J = 35.9 Hz), 55.2. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -75.8.

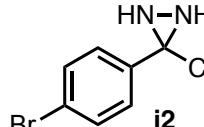
3-Phenyl-3-(trifluoromethyl)diaziridine h2


h2 Isolated as a white solid (380 mg, quant.). Exhibited spectral data identical to a previous report.⁹ ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.83–7.81 (m, 2H), 7.45–7.41 (m, 1H), 7.33–7.31 (m, 2H), 2.79 (br s, 1H), 2.23 (br s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm): 129.9, 129.0, 127.8, 126.5, 123.7 (q, J = 278.2 Hz), 58.3 (q, J = 35.9 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -75.6.

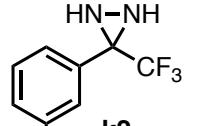
3-(4-Fluorophenyl)-3-(trifluoromethyl)diaziridine i2


i2 Isolated as a white semi solid (490 mg, quant.). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.64–7.61 (m, 2H), 7.14–7.10 (m, 2H), 2.82 (br s, 1H), 2.23 (br s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 163.6 (d, J = 250.3 Hz), 130.3 (d, J = 8.6 Hz), 127.6 (d, J = 3.3 Hz), 123.4 (q, J = 278.2 Hz), 115.9 (d, J = 21.9 Hz), 57.6 (q, J = 36.2 Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -75.7, -110.1. IR (cm^{-1}): 3256, 3234, 1610, 1516, 1394, 1219, 1134, 1097, 951, 841. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_8\text{H}_7\text{F}_4\text{N}_2$ 207.0545 found 207.0547.

3-(4-Bromophenyl)-3-(trifluoromethyl)diaziridine j2


j2 Isolated as a white semi solid (540 mg, quant.). Exhibited spectral data identical to a previous report.⁴ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.59–7.57 (m, 2H), 7.52–7.50 (m, 2H), 2.82 (br s, 1H), 2.21 (br s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 132.2, 130.8, 129.9, 124.8, 123.4 (q, J = 278.2 Hz), 57.8 (q, J = 36.3 Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -75.5.

3-(3-Bromophenyl)-3-(trifluoromethyl)diaziridine k2


k2 Isolated as a white semi solid (520 mg, quant.). Exhibited spectral data identical to a previous report.⁵ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.79 (s, 1H), 7.61–7.57 (m, 2H), 7.33–7.30 (m, 1H), 2.83 (br s, 1H), 2.24 (br s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 133.6, 131.7, 131.1, 130.5, 126.9, 123.5 (q, J = 278.2 Hz), 122.9, 57.7 (q, J = 36.4 Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -75.3.

3-(4-Trifluoromethylphenyl)-3-(trifluoromethyl)diaziridine I2

Isolated as a white semi solid (512 mg, quant.). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.80–7.78 (m, 2H), 7.72–7.70 (m, 2H), 2.88 (br s, 1H), 2.26 (br s, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 129.9, 128.9, 126.6, 126.0 (q, $J = 3.8$ Hz), 123.6 (q, $J = 273.2$ Hz), 123.4 (q, $J = 278.4$ Hz), 57.8 (q, $J = 35.6$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -63.0, -75.2. IR (cm^{-1}): 3356, 3259, 2962, 1599, 1526, 1325, 1128, 1067, 1018, 951, 844, 712. HR-MS (EI) m/z [M + Na]⁺ calcd. for $\text{C}_9\text{H}_6\text{F}_6\text{N}_2\text{Na}$ 279.0327 found 279.0921.

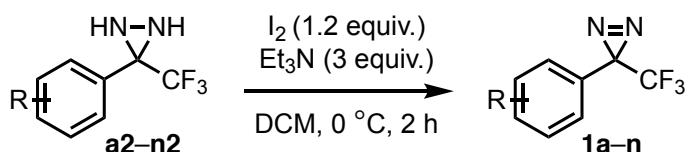
3-(2-Methoxyphenyl)-3-(trifluoromethyl)diaziridine m2

Isolated as a white solid (435 mg, quant.). Exhibited spectral data identical to a previous report.⁶ ^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.98–6.90 (m, 4H), 3.81 (s, 3H), 2.76 (br s, 1H), 2.56 (br s, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm): 131.5, 129.0, 123.6 (q, $J = 278.8$ Hz), 120.5, 120.4, 111.5, 111.1, 56.0 (q, $J = 37.2$ Hz), 55.4. ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -77.1.

3-(2-Fluorophenyl)-3-(trifluoromethyl)diaziridine n2

Isolated as a semi solid (480 mg, quant.). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.57–7.53 (m, 1H), 7.49–7.45 (m, 1H), 7.25–7.21 (m, 1H), 7.17–7.14 (m, 1H), 2.83 (br s, 1H), 2.49 (br s, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 161.5 (d, $J = 252.0$ Hz), 132.4 (d, $J = 8.3$ Hz), 131.1 (d, $J = 2.8$ Hz), 124.5 (d, $J = 3.6$ Hz), 123.2 (q, $J = 278.4$ Hz), 119.4 (d, $J = 13.9$ Hz), 116.2 (d, $J = 20.7$ Hz), 55.5 (q, $J = 38.0$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -77.4, -114.1. IR (cm^{-1}): 3259, 1620, 1499, 1230, 1142, 949, 758. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_8\text{H}_7\text{F}_4\text{N}_2$ 207.0545 found 207.0547.

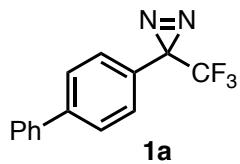
2.3. Procedure for synthesis of 2,2,2-trifluoromethyl diazirines 1a–n



To a solution of the diaziridine (30 mmol) in CH_2Cl_2 (50 mL) at 0 °C, I_2 (1.4 g, 36 mmol) and Et_3N (8.4 mL, 60 mmol) were added. The solution was stirred for 1h and the excess of I_2 was quenched with 1 M NaOH_{aq} . The mixture was extracted with CH_2Cl_2 , dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage, SNAP ULTRA, 100% hexanes) to give the desired diazirine **17**.

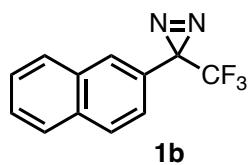
2.3.1. Characterizations of 2,2,2-trifluoromethyl diazirines 1a–n

3-([1,1'-Biphenyl]-4-yl)-3-(trifluoromethyl)-3*H*-diazirine 1a



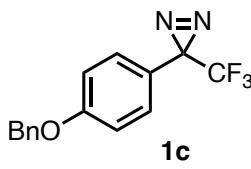
Purified by flash column chromatography (100% hexanes). Isolated as a white solid (6.5 g, 81%). Exhibited spectral data identical to a previous report.² ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.69–7.65 (m, 4H), 7.57–7.49 (m, 3H), 7.39–7.36 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 142.7, 139.9, 129.1, 128.1, 128.1, 127.6, 127.2, 127.0, 122.4 (q, *J* = 274.7 Hz), 28.1 (q, *J* = 39.8 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -65.0.

3-(Naphthalen-2-yl)-3-(trifluoromethyl)-3*H*-diazirine 1b



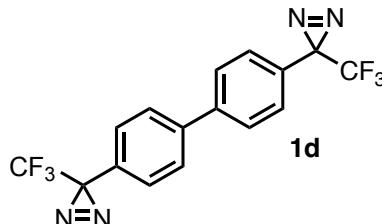
Purified by flash column chromatography (100% hexanes). Isolated as a white solid (364 mg, 77%). mp: 30–32 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.88–7.81 (m, 3H), 7.75–7.72 (m, 1H), 7.65–7.60 (m, 2H), 7.48–7.43 (m, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm): 133.5, 132.8, 128.9, 128.2, 127.8, 127.5, 127.1, 126.9, 126.6, 122.8, 122.7 (q, *J* = 274.6 Hz), 28.9 (q, *J* = 40.3 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -64.9. IR (cm⁻¹): 3065, 1622, 1599, 1323, 1149, 991, 816, 750. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for C₁₂H₁₃F₃N 228.0995 found 228.1045.

3-(4-(Benzylxy)phenyl)-3-(trifluoromethyl)-3*H*-diazirine 1c



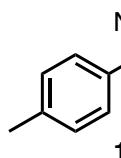
Purified by flash column chromatography (100% hexanes). Isolated as an off-white solid (371 mg, 63%). mp: 38–40 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.49–7.44 (m, 4H), 7.42–7.39 (m, 1H), 7.23–7.21 (m, 2H), 7.05–7.03 (m, 2H), 5.11 (s, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm): 159.9, 136.5, 128.8, 128.3, 128.3, 127.6, 122.4 (q, *J* = 274.6 Hz), 121.3, 115.4, 70.2, 28.4 (q, *J* = 40.6 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -65.5. IR (cm⁻¹): 3039, 1614, 1518, 1148, 1011, 696. HR-MS (EI) m/z [M + H]⁺ calcd. for C₁₅H₁₂F₃O 265.0840 found 265.0411.

4,4'-Bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)-1,1'-biphenyl 1d

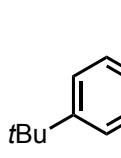


Double the equivalents to those reported in the general procedures were used to make the bis-diazirine. Purified by flash column chromatography (100% hexanes). Isolated as a yellow solid (461 mg, 62%). mp: 44–46 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.61–7.59 (m, 2H), 7.33–7.30 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm): 140.2, 128.1, 126.6, 126.2, 121.4 (q, *J* = 274.6 Hz), 27.6 (q, *J* = 40.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -65.3. IR (cm⁻¹): 3047, 1917, 1609, 1342, 1159, 935, 808. HR-MS (EI) m/z [M + H]⁺ calcd. for C₁₆H₉F₆ 314.0608 found 2314.0648.

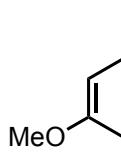
3-(*p*-Tolyl)-3-(trifluoromethyl)-3*H*-diazirine **1e**

 Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (381 mg, 81%). Exhibited spectral data identical to a previous report.¹⁰ ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.22 (d, $J = 6.7$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 2.39 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm): 139.0, 128.7, 125.6 (d, $J = 1.4$ Hz), 125.3, 121.5 (q, $J = 274.5$ Hz), 27.6 (q, $J = 40.3$ Hz), 20.3. ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -65.5.

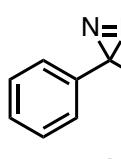
3-(4-(*Tert*-butyl)phenyl)-3-(trifluoromethyl)-3*H*-diazirine **1f**

 Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (869 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.52–7.49 (m, 2H), 7.24–7.22 (m, 2H), 1.39 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm): 152.2, 125.5, 125.4, 125.0, 121.5 (q, $J = 274.5$ Hz), 33.9, 30.2, 27.6 (q, $J = 40.3$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -65.4. IR (cm^{-1}): 2966, 1618, 1344, 1182, 1151, 939, 702. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_{12}\text{H}_{14}\text{F}_3$ 215.1048 found 215.1028.

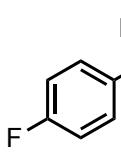
3-(4-Methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirine **1g**

 Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (322 mg, 75%). Exhibited spectral data identical to a previous report.¹⁰ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.16 (d, $J = 8.3$ Hz, 2H), 6.92 (dt, $J^1 = 8.9$ Hz, $J^2 = 3.0$ Hz, $J^3 = 2.2$ Hz, 2H), 3.82 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 160.7, 128.3, 123.4 (q, $J = 273.9$ Hz), 121.1, 114.5, 55.5, 28.3 (q, $J = 40.4$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -65.6.

3-Phenyl-3-(trifluoromethyl)-3*H*-diazirine **1h**

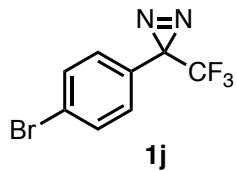
 Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (123 mg, 50%). Exhibited spectral data identical to a previous report.¹⁰ ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.43–7.41 (m, 3H), 7.24–7.22 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm): 130.9, 129.6, 128.8, 126.4, 122.2 (q, $J = 274.6$ Hz), 28.4 (q, $J = 40.4$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -65.4.

3-(4-Fluorophenyl)-3-(trifluoromethyl)-3*H*-diazirine **1i**

 Purified by flash column chromatography (100% hexanes). Isolated as a volatile colorless oil (74 mg, 20%). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.24–7.21 (m, 2H), 7.11–7.07 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm): 162.6 (d, $J = 250.8$ Hz), 127.9 (d, $J = 8.7$ Hz), 124.1 (d, $J = 3.1$ Hz), 121.3 (q, $J = 274.5$ Hz), 115.3 (q, $J = 22.2$ Hz), 27.3 (q, $J = 40.7$ Hz). ^{19}F NMR

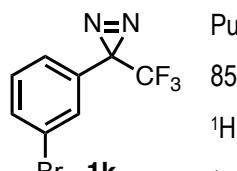
(376 MHz, CDCl₃) δ (ppm): -65.8, -110.2. IR (cm⁻¹): 3087, 1614, 1516, 1199, 937, 825. HR-MS (EI) m/z [M + H]⁺ calcd. for C₈H₅F₄ 177.0327 found 177.0319.

3-(4-Bromophenyl)-3-(trifluoromethyl)-3*H*-diazirine 1j



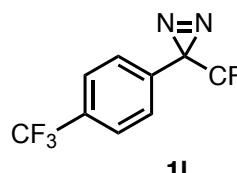
Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (452 mg, 85%). Exhibited spectral data identical to a previous report.⁴ ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.55 (dt, $J^1 = 8.9$ Hz, $J^2 = 2.5$ Hz, $J^3 = 2.0$ Hz, 2H), 7.08 (d, $J = 8.1$ Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 132.1, 128.1, 128.1, 124.3, 123.0 (q, $J = 274.4$ Hz), 28.1 (q, $J = 41.0$ Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -65.3.

3-(3-Bromophenyl)-3-(trifluoromethyl)-3*H*-diazirine 1k



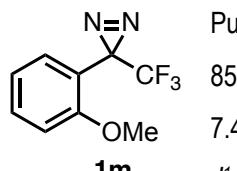
Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (452 mg, 85%). Exhibited spectral data identical to a previous report.⁵ ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.56–7.54 (m, 1H), 7.32 (s, 1H), 7.29–7.25 (m, 1H), 7.17–7.15 (m, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 132.1, 130.4, 129.5, 128.7, 124.3, 122.2, 121.0 (q, $J = 276.4$ Hz), 27.1 (q, $J = 41.0$ Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -65.2.

3-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-3*H*-diazirine 1l



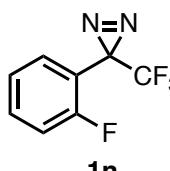
Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (401 mg, 79%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.68–7.66 (m, 2H), 7.33–7.31 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 132.1 (q, $J = 1.7$ Hz), 131.0 (q, $J = 33.2$ Hz), 126.0 (q, $J = 1.8$ Hz), 125.0 (q, $J = 3.7$ Hz), 120.9 (q, $J = 273.0$ Hz), 120.5 (q, $J = 275.4$ Hz), 27.4 (q, $J = 40.9$ Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -63.1, -65.0. IR (cm⁻¹): 2958, 1622, 1325, 1124, 939, 829. HR-MS (EI) m/z [M + K]⁺ calcd. for C₉H₄F₆K 264.9854 found 264.9484.

3-(2-Methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirine 1m



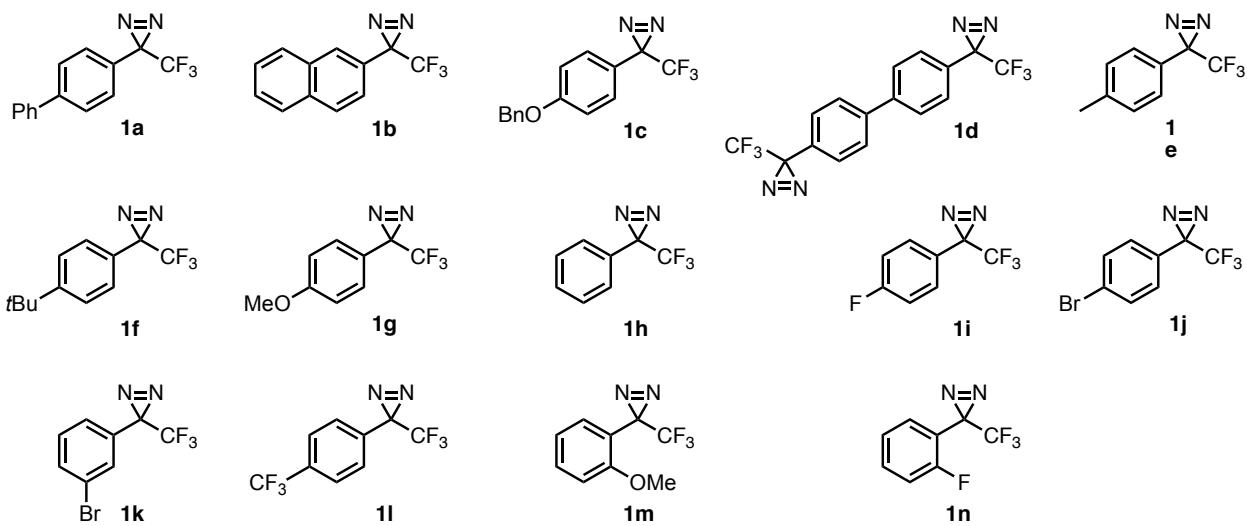
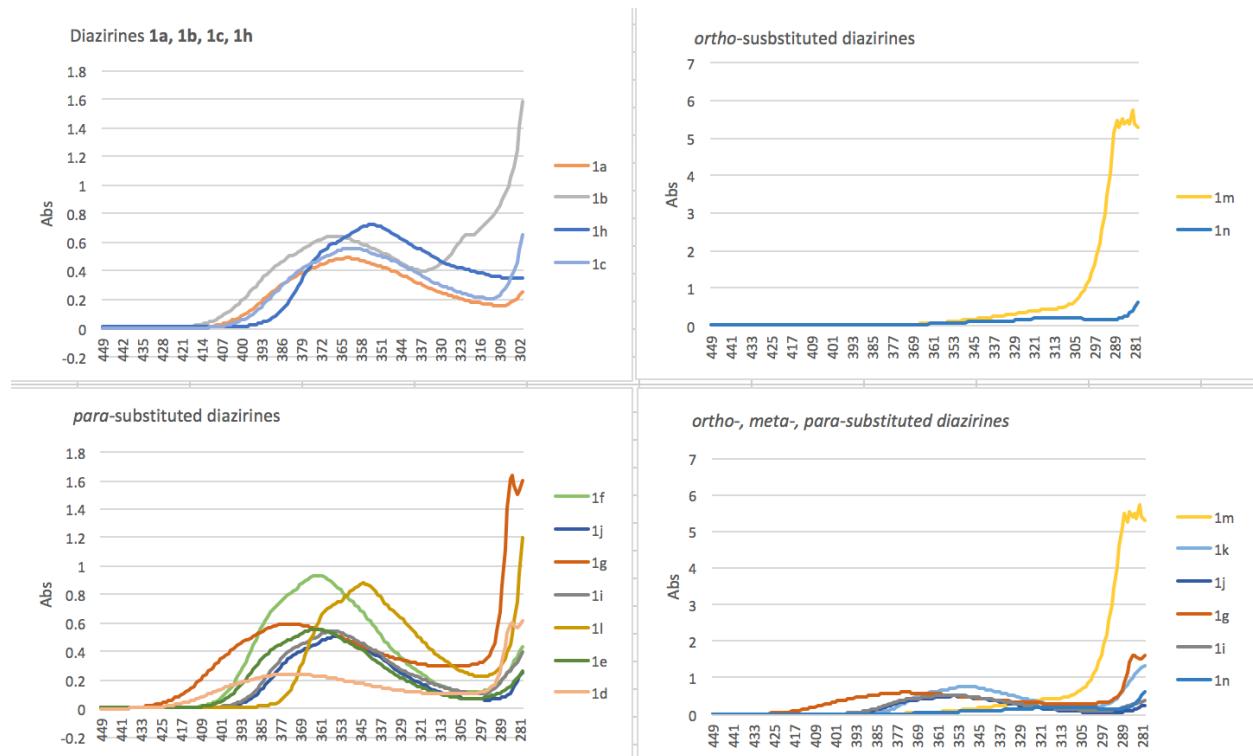
Purified by flash column chromatography (100% hexanes). Isolated as a colorless oil (452 mg, 85%). Exhibited spectral data identical to a previous report.⁶ ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.47 (dd, $J^1 = 7.6$ Hz, $J^2 = 1.7$ Hz, 1H), 7.41 (ddd, $J^1 = 8.4$ Hz, $J^2 = 7.4$ Hz, $J^3 = 1.7$ Hz, 1H), 6.98 (td, $J^1 = 7.5$ Hz, $J^2 = 1.0$ Hz, 1H), 6.93 (dd, $J^1 = 8.4$ Hz, $J^2 = 1.0$ Hz, 1H), 3.93 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm): 159.1, 131.3, 130.1, 127.0 (q, $J = 288.1$ Hz), 120.1, 115.8, 110.7, 54.8, 25.6 (q, $J = 42.6$ Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -69.3.

3-(2-Fluorophenyl)-3-(trifluoromethyl)-3*H*-diazirine 1n

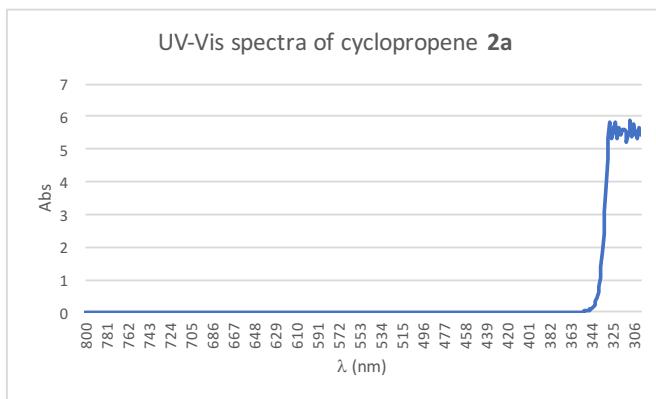
1n  Purified by flash column chromatography (100% hexanes). Isolated as a volatile colorless oil (189 mg, 46%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.52–7.41 (m, 2H), 7.20 (td, $J^1 = 7.6$ Hz, $J^2 = 1.1$ Hz, 1H), 7.15–7.10 (m, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 161.8 (d, $J = 253.2$ Hz), 131.9 (d, $J = 8.3$ Hz), 130.0 (d, $J = 2.3$ Hz), 124.0 (d, $J = 3.8$ Hz), 121.1 (q, $J = 274.4$ Hz), 115.8 (d, $J = 20.7$ Hz), 115.1 (d, $J = 14.5$ Hz), 24.6 (q, $J = 43.1$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -68.9, -113.0. IR (cm^{-1}): 3074, 1624, 1499, 1186, 1153, 941, 758. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_8\text{H}_5\text{F}_4$ 177.0327 found 177.0318.

3. UV-Vis spectra

3.1. UV-Vis spectra of diazirines 1a–1n

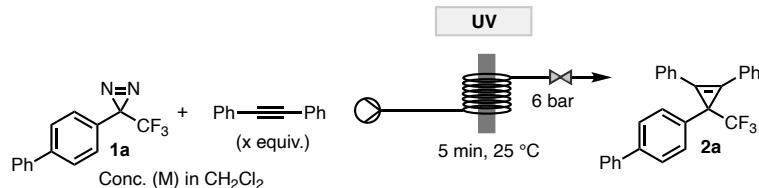


3.2. UV-Vis spectra of cyclopropene 2a



4. Optimization studies

4.1 Screening of photochemical cyclopropanation with medium-pressure mercury lamp:



Entry	Conc (M)	x (equiv)	Light type	Yield (%)
1	0.1	10	UV-band pass (350 nm)	77
2	0.1	1	UV-band pass (350 nm)	35
3	0.05	10	UV-band pass (350 nm)	77
4	0.025	10	UV-band pass (350 nm)	65
5	0.1	10	UV-band pass (320 nm)	76
6	0.1	10	UV-band pass (360 nm)	80
7	0.1	10	UV-band pass (420 nm)	88
8	0.1	10	UV-long pass (280 nm)	75
9	0.1	10	UV-long pass (300 nm)	70

4.1.1 Wavelength filters

- Band-pass wavelength filter:

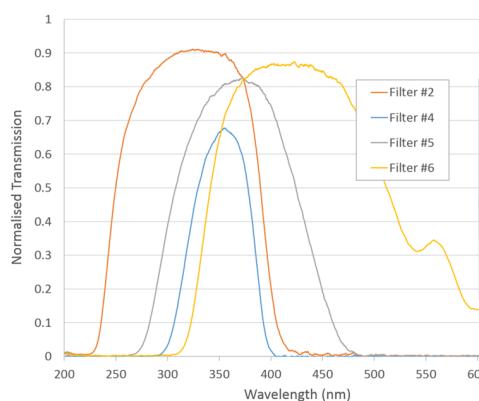


Figure S1a. Image source:
<https://www.vapourtec.com/products/flow-reactors/photochemistry-uv-150-photochemical-wavelength-filters/>

- Long-pass wavelength filter:

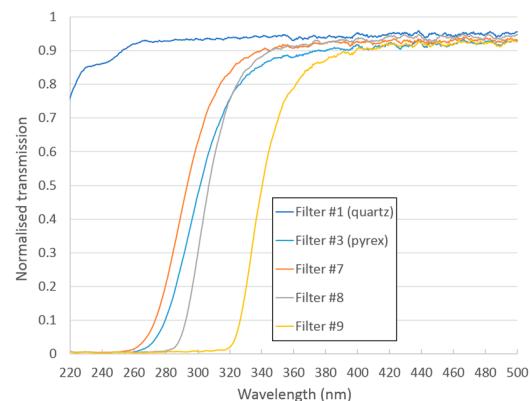
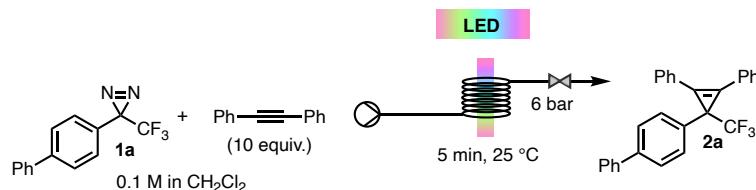


Figure S1b. Image source:
<https://www.vapourtec.com/products/flow-reactors/photochemistry-uv-150-photochemical-wavelength-filters/>

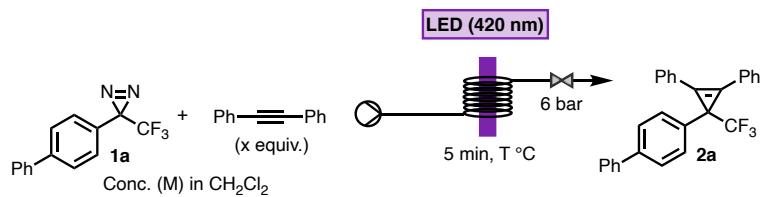
4.2 Screening of flow conditions for the cyclopropanation of diazirine 1a

4.2.1 Screening of photochemical cyclopropanation with light-emitting diodes (LEDs)



Entry	Light type	Yield (%)
1	LED (365 nm gen-2)	87
2	LED (365 nm)	81
3	LED (380 nm)	81
4	LED (405 nm)	88
5	LED (420 nm)	91
6	LED (450 nm)	10
7	LED (470 nm)	0
8	LED (495 nm)	0
9	LED (525 nm)	0

4.2.2 Optimization of reaction conditions



Entry	R	x (equiv)	Conc (M)	T (°C)	Yield (%)
1	Ph	10	0.1	25	91
2	Ph	5	0.1	25	80
3	Ph	1.1	0.4	25	43
4	Ph	10	0.2	25	95
5	Ph	10	0.05	25	85
6	Ph	10	0.2	10	84
7	Ph	10	0.4	25	93

5. Experimental procedures for the cyclopropenation reaction of diazirines in continuous flow

5.1 Continuous flow setup for cyclopropene synthesis

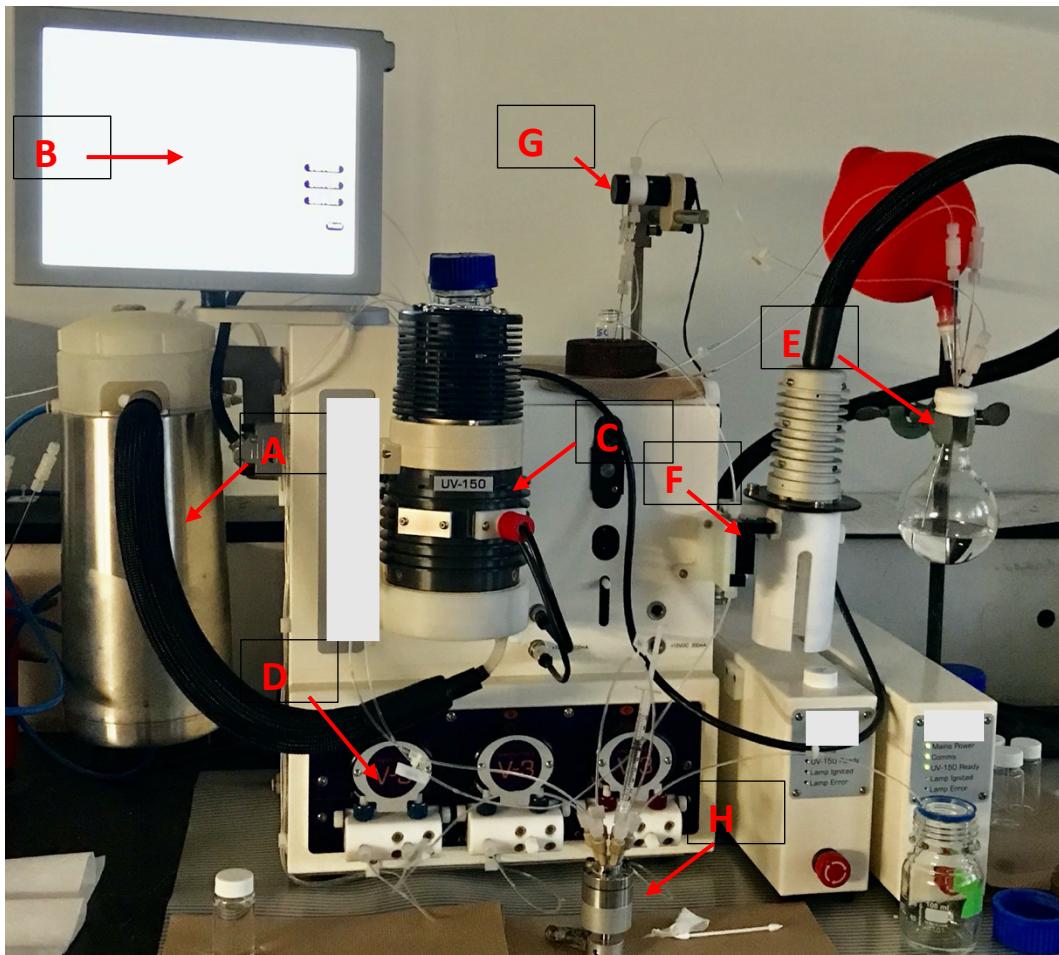
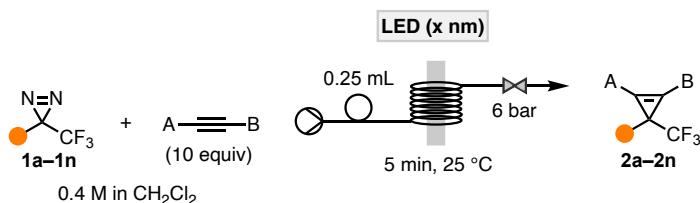


Figure S2. A: Cooling module: filled with dry ice; B: Control monitor; C: UV-150 photochemical reactor equipped with an LED lamp and PFA reactor; D: Peristaltic pump; E: CH₂Cl₂ feeding under argon atmosphere; F: Back-pressure regulator; G: Collection unit and post-reaction stream collection vial; H: Injection loop (0.25 mL).

5.2 General procedure for the photochemical flow reactions of diazirines in continuous flow



Flow reactions were set up on a Vapourtec® E-series Easy MedChem™ flow system. All necessary reactors and accessories were assembled as shown above. Before starting reactions, all reactor tubing were primed with anhydrous CH_2Cl_2 . Back pressure was set to 6 bar at 2 mL/min. A solution of the diazirine **1** and alkyne (10 equiv) in CH_2Cl_2 (0.4 M) was prepared and loaded into the injection loop (0.25 mL, reaction scale= 0.1 mmol). The flow rate was set to 2 mL/min for a 10 mL reactor volume (residence time = 5 min). The flow reactions were run under LED irradiation at 25 °C. The post-reaction stream containing the desired cyclopropene product (pre- and post-slug volume = 1 mL) was collected in a 30 mL vial. The solvent was removed under reduced pressure and the crude mixture was purified by flash column chromatography (Biotage, SNAP ULTRA, 100:0–99:1 hexanes/EtOAc) to give the desired cyclopropene **2**.

5.2.1. Characterization of 2,2,2-trifluoromethyl cyclopropenes **2a–am**

4-(2,3-Diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl **2a**

2a (Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as an off-white solid (38 mg, 93%).* mp: 118–120 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.83–7.77 (m, 4H), 7.61–7.52 (m, 2H), 7.55–7.49 (m, 8H), 7.49–7.39 (m, 4H), 7.39–7.29 (m, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.8, 140.1, 136.5, 131.7, 130.2, 130.0, 129.3, 128.9, 128.1, 127.4, 127.3, 127.1, 126.3, 126.1 (q, J = 279.3 Hz), 109.9, 33.7 (q, J = 34.9 Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –62.0. IR (cm^{-1}): 3026, 1495, 1447, 1162, 1126, 920, 750, 681. HR-MS (EI) m/z [M + NH_4]⁺ calcd. for $\text{C}_{28}\text{H}_{23}\text{F}_3\text{N}$ 430.1777 found 430.1769.

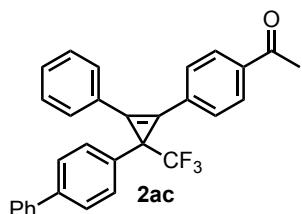
* This reaction was also run at 10 mmol scale (3 g, 73%) for a residence time of 50 min.

4-(2-(4-Nitrophenyl)-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl **2ab**

2ab (Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as an off-white solid (39 mg, 85%). mp: 110–112 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 8.40–8.33 (m, 2H), 7.97–7.88 (m, 2H), 7.83 (dd, J = 8.1, 1.5 Hz, 2H), 7.56–7.52 (m, 8H), 7.45–7.40 (m, 3H), 7.36–7.31 (m, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 148.0, 140.6, 140.5, 135.4, 132.6, 131.3, 130.8, 130.5, 129.6, 129.0, 127.9, 127.6, 127.5, 127.1, 125.3, 124.7, 115.1, 107.9 (CF_3 signal was not observed). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –

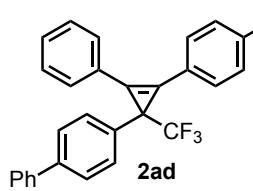
62.2. IR (cm^{-1}): 3103, 2214, 1591, 1508, 1344, 1103, 854, 748, 686. HR-MS (EI) m/z [M + H]⁺ calcd. for C₂₈H₁₉NO₂F₃ 458.1368 found 458.1330.

1-(4-(3-([1,1'-Biphenyl]-4-yl)-2-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)phenyl)ethan-1-one 2ac



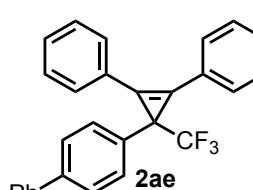
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as an off-white solid (26 mg, 57%). mp: 78–80 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.98–7.93 (m, 4H), 7.66–7.59 (m, 4H), 7.58–7.51 (m, 5H), 7.45–7.30 (m, 5H), 2.63 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 197.3, 136.2, 131.8, 131.7, 130.6, 130.4, 130.0, 129.4, 129.1, 128.9, 128.8, 128.5, 128.3, 128.2, 127.3, 127.0, 125.6, 122.7, 92.8, 88.7, 26.6 (CF₃ signal was not observed). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -62.1. IR (cm^{-1}): 2999, 2220, 1678, 1605, 1485, 1404, 1261, 959, 833, 756, 690. HR-MS (EI) m/z [M + H]⁺ calcd. for C₃₀H₂₂OF₃ 455.1617 found 455.1628.

4-(2-Phenyl-1-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ad



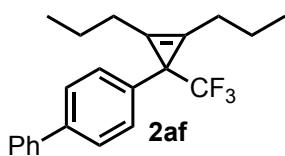
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as an off-white solid (40 mg, 83%). mp: 118–120 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.90 (d, *J* = 8.8 Hz, 2H), 7.84–7.80 (m, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.59–7.46 (m, 10H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.36–7.31 (m, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 140.5, 140.2, 135.7, 131.3 (q, *J* = 32.8 Hz), 130.6, 130.4, 130.0, 129.6, 129.3, 128.8, 127.8 (q, *J* = 1.4 Hz), 127.4, 127.3, 127.1, 127.0, 126.2 (q, *J* = 3.8 Hz), 125.5, 124.9, 122.7, 112.7, 108.4, 68.2. (CF₃ signal was not observed). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -62.1, -62.8. IR (cm^{-1}): 2926, 1616, 1325, 1159, 1121, 1108, 1065, 837, 739, 687. HR-MS (EI) m/z [M + H]⁺ calcd. for C₂₉H₁₈F₆ 481.1391 found 481.1361.

4-(2-(4-Fluorophenyl)-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ae



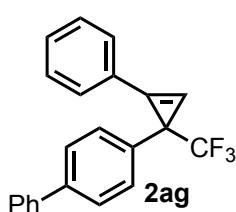
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a semi-solid (26 mg, 62%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.62–7.56 (m, 2H), 7.56–7.52 (m, 2H), 7.49–7.40 (m, 2H), 7.44–7.31 (m, 3H), 2.50 (d, *J* = 8.5 Hz, 4H), 1.76–1.61 (m, 4H), 1.02 (t, *J* = 7.5 Hz, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 163.6 (d, *J* = 252.1 Hz), 140.5 (d, *J* = 59.3 Hz), 136.3, 132.3, 132.1 (d, *J* = 8.6 Hz), 130.1, 130.1, 129.4, 128.8, 128.0, 127.9, 127.5, 127.5 (q, *J* = 266.7 Hz), 127.4, 127.1, 122.61 (d, *J* = 3.5 Hz), 116.7 (d, *J* = 22.3 Hz), 109.4, 108.9, 33.7 (q, *J* = 35.1 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -62.0, -109.0 (p, *J* = 7.4 Hz). IR (cm^{-1}): 2922, 1601, 1506, 1484, 1447, 1294, 1234, 1163, 1125, 924, 835, 760, 687. HR-MS (EI) m/z [M + H]⁺ calcd. for C₂₈H₁₉F₄ 431.1423 found 431.1447.

4-(2,3-Dipropyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2af



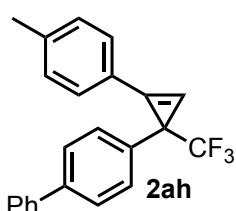
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a semi-solid (33 mg, 97%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.82–7.73 (m, 4H), 7.60–7.49 (m, 8H), 7.46–7.39 (m, 4H), 7.36–7.32 (m, 1H), 7.24–7.19 (m, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.8, 139.2, 138.8, 128.7, 127.8, 127.4 (q, $J = 277.6$ Hz), 127.2, 127.0, 127.0, 109.6, 32.8 (q, $J = 34.4$ Hz), 25.8, 20.6, 14.0. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –62.1. IR (cm^{-1}): 2962, 1489, 1300, 1151, 1115, 920, 696. HR-MS (EI) m/z [M + H] $^+$ calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_3$ 345.1830 found 345.1836.

4-(2-Phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ag



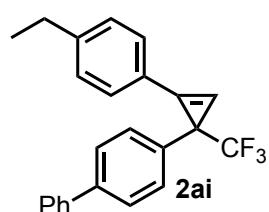
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (20 mg, 60%). mp: 120–122 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.77–7.64 (m, 2H), 7.60–7.54 (m, 4H), 7.54–7.42 (m, 8H), 7.40–7.32 (m, 1H), 7.23–7.19 (m, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.8, 140.2, 137.3, 130.6, 130.2, 129.2, 128.9, 128.2, 127.4, 127.3, 127.2, 125.7 (q, $J = 277.8$ Hz), 125.1, 117.4, 98.9 (q, $J = 3.1$ Hz), 32.0 (q, $J = 36.4$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –63.9. IR (cm^{-1}): 2962, 1489, 1300, 1151, 1115, 920, 696. HR-MS (EI) m/z [M + H] $^+$ calcd. for $\text{C}_{22}\text{H}_{16}\text{F}_3$ 337.1198 found 337.1190.

4-(2-(*p*-Tolyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ah



(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (21 mg, 61%). mp: 112–114 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.62–7.47 (m, 8H), 7.49–7.40 (m, 2H), 7.37–7.32 (m, 1H), 7.30–7.27 (m, 1H), 7.12 (q, $J = 1.5$ Hz, 1H), 2.42 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.9, 140.7, 140.0, 137.4, 130.0, 129.8, 128.8, 128.0 (q, $J = 1.5$ Hz), 127.3, 127.1, 127.1, 125.7 (q, $J = 277.4$ Hz), 122.2, 117.0 (q, $J = 2.2$ Hz), 97.6 (q, $J = 2.8$ Hz), 31.7 (q, $J = 34.9$ Hz), 21.6. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –63.9. IR (cm^{-1}): 3130, 1487, 1296, 1153, 1111, 922, 820, 696. HR-MS (EI) m/z [M + H] $^+$ calcd. for $\text{C}_{23}\text{H}_{18}\text{F}_3$ 351.1355 found 351.1326.

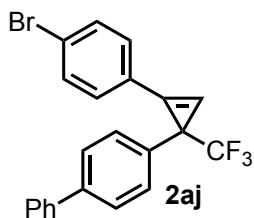
4-(2-(4-Ethylphenyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ai



(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (22 mg, 61%). mp: 88–90 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.64–7.46 (m, 8H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.38–7.24 (m, 3H), 7.11 (m, 1H), 2.70 (q, $J = 7.5$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 147.3, 140.8, 140.2, 137.5, 130.3, 128.9, 128.7, 128.2, 127.4, 127.3,

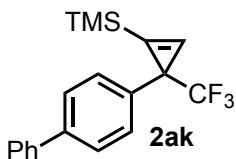
127.2, 125.8 (q, J = 279.1 Hz), 122.5, 117.2 (q, J = 2.3 Hz), 97.7 (q, J = 3.0 Hz), 32.0 (q, J = 35.4 Hz), 29.1, 15.5. ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -63.9. IR (cm^{-1}): 3130, 1489, 1298, 1154, 1110, 922, 837, 768, 694. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_{24}\text{H}_{20}\text{F}_3$ 365.1512 found 365.1568.

4-(2-(4-Bromophenyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2aj



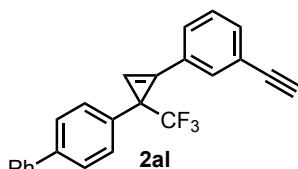
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (26 mg, 62%). mp: 98–100 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.64–7.60 (m, 2H), 7.59–7.52 (m, 6H), 7.51–7.42 (m, 4H), 7.42–7.31 (m, 1H), 7.25 (q, J = 1.5 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.7, 140.4, 136.9, 132.5, 131.5, 128.9, 128.1, 127.5, 127.4, 127.2, 126.6 (q, J = 277.7 Hz), 125.1, 124.1, 116.6, 99.9 (q, J = 3.2 Hz), 32.2 (q, J = 35.4 Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -64.0. IR (cm^{-1}): 3128, 1479, 1294, 1154, 1112, 922, 829, 694. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{Br}$ 415.0309 found 415.0347.

(3-([1,1'-Biphenyl]-4-yl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)trimethylsilane 2ak



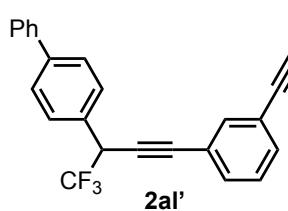
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (26 mg, 78%). mp: 48–50 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.60 (d, J = 6.0 Hz, 2H), 7.57–7.51 (m, 3H), 7.45 (t, J = 8.0 Hz, 2H), 7.38–7.34 (m, 3H), 0.26–0.24 (m, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.8, 139.6, 139.3, 128.9, 127.9, 127.7, 127.4, 127.2, 126.2 (q, J = 276.8 Hz), 127.0, 116.5 (q, J = 2.2 Hz), 29.9 (q, J = 35.5 Hz), -1.40. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -63.5. IR (cm^{-1}): 2965, 1703, 1489, 1304, 1153, 1113, 924, 839, 727, 692. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for $\text{C}_{19}\text{H}_{23}\text{F}_3\text{NSi}$ 350.1546 found 350.1575.

4-(2-(3-Ethynylphenyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2al



(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (19 mg, 53%). mp: 82–84 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.79 (br s, 1H), 7.66–7.63 (m, 1H), 7.57–7.54 (m, 5H), 7.48–7.47 (m, 2H), 7.44–7.41 (m, 3H), 7.36–7.32 (m, 1H), 7.25 (br s, 1H), 3.14 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.7, 140.4, 137.0, 134.1, 133.5, 130.3, 129.3, 128.9, 128.1, 127.5, 127.4, 127.2, 126.2 (q, J = 277.8 Hz), 125.5, 123.4, 116.8, 100.3 (q, J = 2.9 Hz), 82.6, 78.6, 32.3 (q, J = 35.7 Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -64.0. IR (cm^{-1}): 3276, 3128, 2924, 1717, 1487, 1298, 1147, 1121, 921, 723, 692. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_{24}\text{H}_{16}\text{F}_3$ 361.1199 found 361.1061.

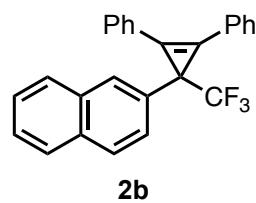
4-(4-(3-Ethynylphenyl)-1,1,1-trifluorobut-3-yn-2-yl)-1,1'-biphenyl 2al'



(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (7 mg, 19%). mp: 50–52 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.74–7.69 (m, 3H), 7.62–7.58 (m, 2H), 7.57–7.56 (m, 2H), 7.47–7.44 (m, 3H), 7.39–7.36 (m, 1H), 6.49 (d, J = 2.2 Hz, 1H), 4.31 (q, J = 9.9 Hz, 1H), 3.13 (s, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 148.6, 144.6, 142.2, 141.2, 134.9, 132.3, 131.5, 129.4, 129.0, 128.3, 127.6, 126.2 (q, J = 2.7 Hz), 126.1 (q, J = 279.9 Hz), 125.9, 125.2, 122.8, 120.1, 83.3, 78.0, 52.6 (q, J = 29.7 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -67.2 (d, J = 8.7 Hz). IR (cm⁻¹): 3294, 2924, 1601, 1490, 1323, 1256, 1149, 1103, 760, 692, 624. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for C₂₄H₁₉F₃N 378.1464 found 378.1433.

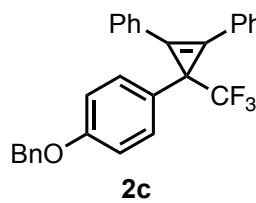
Despite multiple attempts, compound **2am** was not isolated and could only be identified in the crude reaction mixture.

2-(2,3-Diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)naphthalene 2b



(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (32 mg, 78%). mp: 82–84 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.06 (br s, 1H), 7.83–7.81 (m, 4H), 7.79–7.74 (m, 3H), 7.55–7.49 (m, 5H), 7.46–7.43 (m, 4H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 135.0, 133.4, 132.5, 131.8, 130.2, 130.0, 129.3, 128.2, 128.1, 127.6, 126.6, 126.3, 126.3, 126.0, 125.4, 127.2 (q, J = 278.8 Hz), 109.9, 34.0 (q, J = 34.9 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -61.7. IR (cm⁻¹): 3060, 1447, 1286, 1153, 1121, 752, 685. HR-MS (EI) m/z [M + H]⁺ calcd. for C₂₆H₁₉F₃ 387.1355 found 387.1358.

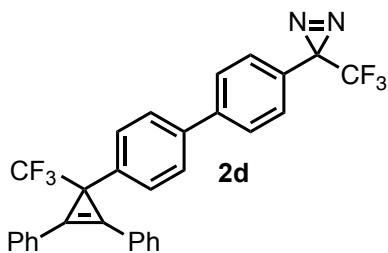
(3-(4-(benzyloxy)phenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene 2c



(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (26 mg, 79%). mp: 90–92 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.81–7.79 (m, 3H), 7.53–7.50 (m, 3H), 7.47–7.37 (m, 9H), 7.34–7.31 (m, 1H), 6.93–6.91 (m, 2H), 5.03 (s, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 158.1, 137.1, 130.1, 130.7, 130.1, 129.9, 129.3, 129.1, 128.7, 128.1, 127.6, 127.2 (q, J = 280.2 Hz), 126.5, 114.9, 110.5, 70.1, 33.2 (q, J = 34.9 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ (ppm): -62.4. IR (cm⁻¹): 3025, 1609, 1512, 1445, 1288, 1242, 1153, 1124, 1009, 835, 746, 683. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for C₂₉H₂₅ONF₃ 460.1883 found 460.1847.

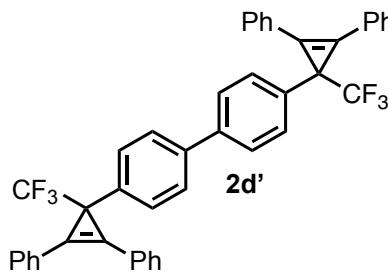
3-(4'-(2,3-Diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-[1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)-3*H*-diazirine

2d



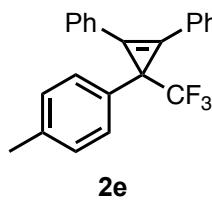
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (13 mg, 30%). mp: 58–60 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.82–7.76 (m, 5H), 7.57–7.47 (m, 8H), 7.47–7.41 (m, 5H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 139.4, 136.4, 130.0, 129.8, 129.2, 127.9, 127.0, 126.1, 109.8 (q, $J = 2.5$ Hz), 33.6 (q, $J = 33.8$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –62.0, –65.1. IR (cm^{-1}): 2924, 1716, 1265, 1168, 1126, 1029, 754, 683. HR-MS (EI) m/z [M + H] $^+$ calcd. for $\text{C}_{30}\text{H}_{19}\text{F}_6\text{N}_2$ 521.1452 found 521.1434.

4,4'-Bis(2,3-diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2d'



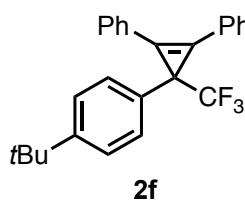
(Purple LED lamp, 420 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (36 mg, 54%). mp (decomp.): 219–221 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.82 – 7.75 (m, 8H), 7.57 – 7.48 (m, 12H), 7.48 – 7.41 (m, 8H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 139.5, 136.5, 130.2, 130.0, 129.3, 128.1, 127.2, 126.3, 110.0, 33.6 (q, $J = 34.6$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –62.01. IR (cm^{-1}): 3078, 1497, 1448, 1295, 1145, 1119, 921, 754, 685. HR-MS (EI) m/z [M + NH $_4$] $^+$ calcd. for $\text{C}_{44}\text{H}_{32}\text{NF}_6$ 688.2433 found 688.2444.

(3-(*p*-Tolyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene 2e



(Purple LED lamp, 405 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (20 mg, 57%). Exhibited spectral data identical to a previous report.¹¹ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.79–7.77 (m, 4H), 7.52–7.48 (m, 4H), 7.45–7.40 (m, 4H), 7.11–7.09 (m, 2H), 2.31 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 137.9, 134.5, 131.8, 130.5, 130.1, 129.9, 129.3, 129.2, 127.6, 127.3 (q, $J = 280.2$ Hz), 110.2 (q, $J = 2.4$ Hz), 33.6 (q, $J = 34.9$ Hz), 21.2. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –62.2.

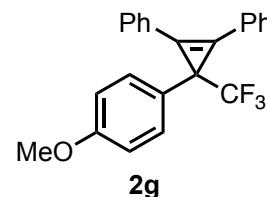
(3-(4-Tert-butylphenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene 2f



(Purple LED lamp, 405 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (20 mg, 50%). mp: 66–68 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.80–7.79 (m, 4H), 7.52–7.49 (m, 4H), 7.46–7.43 (m, 4H), 7.31–7.30 (m, 2H), 1.28 (s, 9H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 150.0, 134.4, 131.8, 130.2, 129.9, 129.2, 127.5, 127.2 (q, $J = 280.2$ Hz), 126.5, 125.5, 110.3 (q, $J = 2.4$ Hz), 34.5, 33.5 (q, $J = 34.9$ Hz).

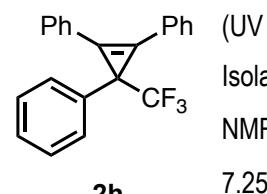
Hz), 31.4. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -62.1. IR (cm^{-1}): 2961, 1499, 1447, 1163, 1124, 926, 754, 687. HR-MS (EI) m/z [M + NH₄]⁺ calcd. for $\text{C}_{26}\text{H}_{27}\text{NF}_3$ 410.2090 found 410.2058.

(3-(4-Methoxyphenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene 2g



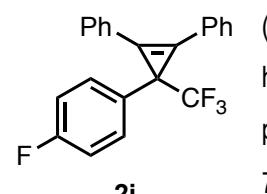
(Purple LED lamp, 405 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (19 mg, 51%). Exhibited spectral data identical to a previous report.¹¹ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.80–7.78 (m, 4H), 7.53–7.49 (m, 4H), 7.47–7.42 (m, 4H), 6.85–6.83 (m, 2H), 3.77 (s, 3H). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 158.8, 130.1, 129.9, 129.4, 129.3, 129.1, 129.0, 127.3 (q, $J = 278.6$ Hz), 126.5, 114.0, 110.6 (q, $J = 2.4$ Hz), 55.3, 33.2 (q, $J = 34.9$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -62.4.

(3-(Trifluoromethyl)cycloprop-1-ene-1,2,3-triyl)tribenzene 2h



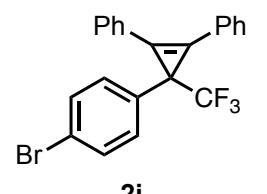
(UV LED lamp, 380 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (4 mg, 12%). Exhibited spectral data identical to a previous report.¹¹ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.78–7.76 (m, 4H), 7.51–7.48 (m, 6H), 7.45–7.41 (m, 2H), 7.32–7.25 (m, 2H), 7.25–7.21 (m, 1H). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 137.5, 131.8, 130.2, 129.9, 129.3, 128.6, 127.7, 127.2, 127.3 (q, $J = 278.6$ Hz), 126.4, 110.0 (q, $J = 2.4$ Hz), 33.8 (q, $J = 34.9$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -62.4.

(3-(4-Fluorophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene 2i



(UV LED lamp, 380 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (12 mg, 34%). Exhibited spectral data identical to a previous report.¹¹ ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.77–7.75 (m, 4H), 7.52–7.49 (m, 4H), 7.46–7.42 (m, 4H), 6.99–6.95 (m, 2H). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 161.9 (d, $J = 277.9$ Hz), 133.2, 131.6, 130.0, 129.9, 129.3, 129.2, 126.0, 126.9 (q, $J = 279.6$ Hz), 115.3 (d, $J = 21.4$ Hz), 110.1 (q, $J = 2.3$ Hz), 33.1 (q, $J = 35.2$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -62.3, -115.4.

(3-(4-Bromophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene 2j



(UV LED lamp, 380 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (15 mg, 37%). mp: 48–50 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.75–7.74 (m, 4H), 7.52–7.49 (m, 4H), 7.46–7.43 (m, 2H), 7.41–7.36 (m, 4H). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 136.6, 131.8, 130.2, 130.1, 129.4, 129.3, j127.2 (q, $J = 275.7$ Hz), 126.7, 125.9, 121.2, 109.5, 33.5 (q, $J = 34.9$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -62.1. IR (cm^{-1}): 2924, 1489, 1445, 1296, 1165, 1109, 920, 827, 754, 689. HR-MS (EI) m/z [M + H]⁺ calcd. for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{Br}$ 415.0304 found 415.0349.

(3-(4-Bromophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyldibenzene 2k

2k (UV LED lamp, 380 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white semi solid (10 mg, 24%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.76–7.74 (m, 4H), 7.64 (s, 1H), 7.53–7.50 (m, 4H), 7.46–7.43 (m, 2H) 7.42–7.34 (m, 2H), 7.16–7.13 (m, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.0, 131.8, 130.6, 130.4, 130.2, 130.2, 130.1, 129.4, 127.1 (q, $J = 278.9$ Hz), 125.8, 122.8, 109.4 (q, $J = 2.6$ Hz), 33.5 (q, $J = 35.1$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -61.9. IR (cm^{-1}): 2924, 1562, 1296, 1163, 1122, 935, 754, 685. HR-MS (EI) m/z [M + H] $^+$ calcd. for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{Br}$ 415.0304 found 415.0373.

(3-(4-Trifluoromethylphenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyldibenzene 2l

2l (UV LED lamp, 380 nm). Purified by flash column chromatography (100:0–99:1 hexanes/EtOAc). Isolated as a white solid (20 mg, 51%). mp: 40–42 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.76–7.74 (m, 1H), 7.56–7.54 (m, 4H), 7.53–7.50 (m, 2H) 7.39–7.34 (m, 7H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 131.8, 130.1, 129.4, 128.5, 128.4, 126.8 (q, $J = 278.8$ Hz), 126.6, 125.5 (q, $J = 3.8$ Hz), 124.2 (q, $J = 271.8$ Hz), 123.4, 109.1 (q, $J = 2.1$ Hz), 89.5, 33.7 (q, $J = 35.0$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -61.9, -62.6. IR (cm^{-1}): 3065, 1495, 1443, 1325, 1163, 1119, 1067, 918, 749, 685. HR-MS (EI) m/z [M + H] $^+$ calcd. for $\text{C}_{23}\text{H}_{15}\text{F}_6$ 405.1078 found 405.1072.

5.3 General procedure for the photochemical reactions of diazirines in batch

A solution of the diazirine **1** and alkyne (10 equiv) in CH_2Cl_2 (0.4 M) were stirred under purple LED irradiation (See below). Reactions were monitored by TLC. After 24 h reactions were still incomplete. The solvent was removed under reduced pressure and 3-fluoro-4-nitrotoluene was added as an internal standard for yield calculation by ^{19}F NMR.

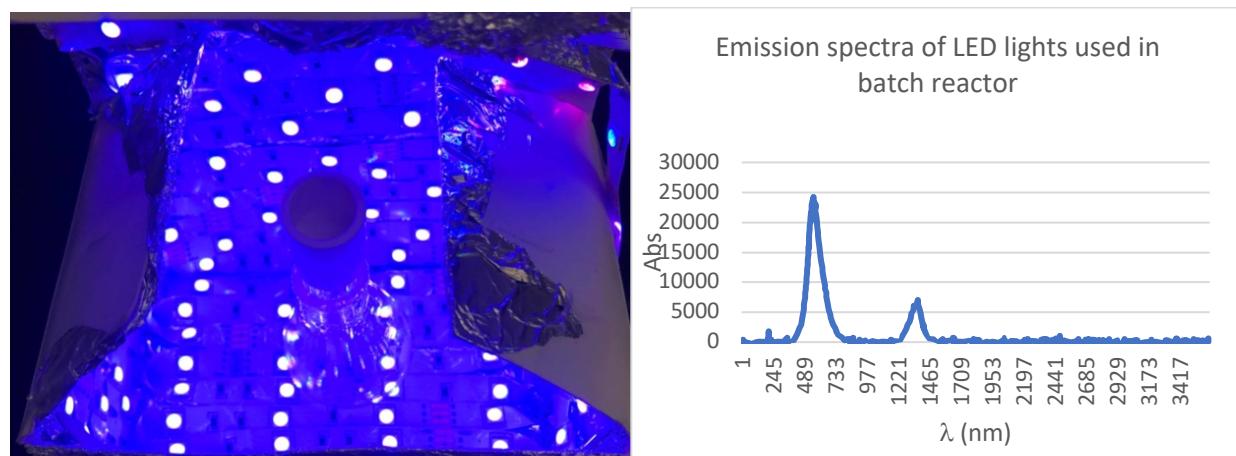
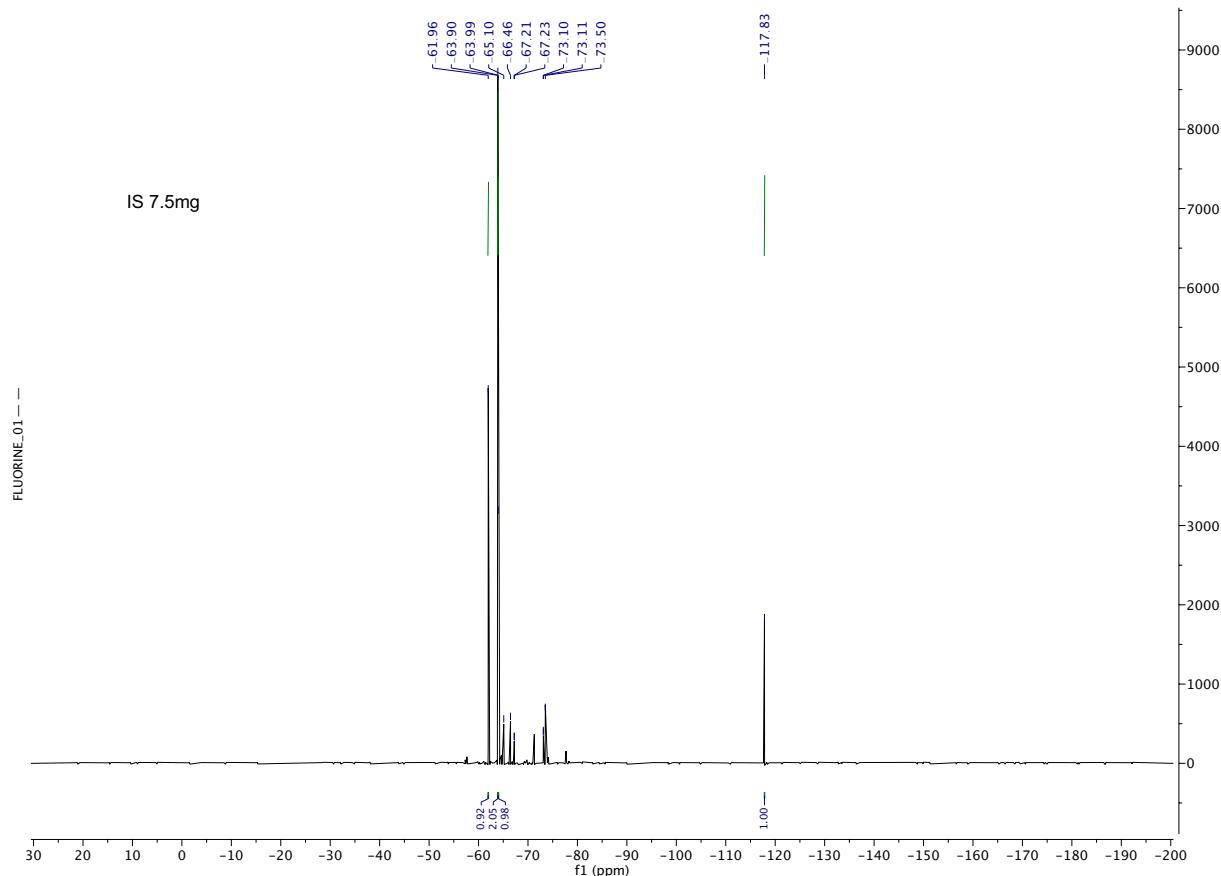
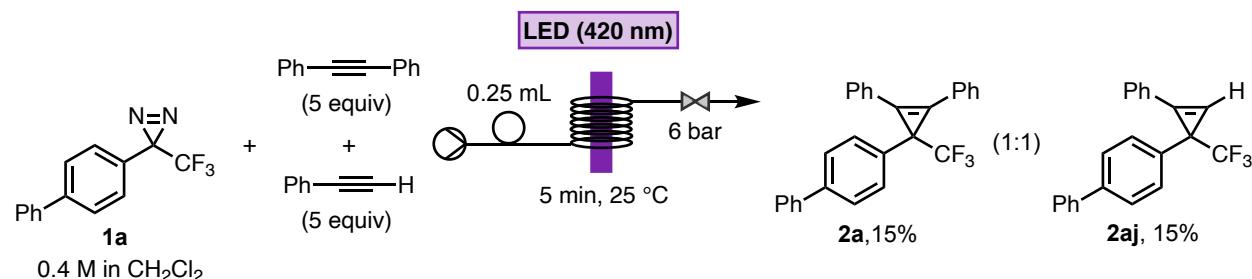


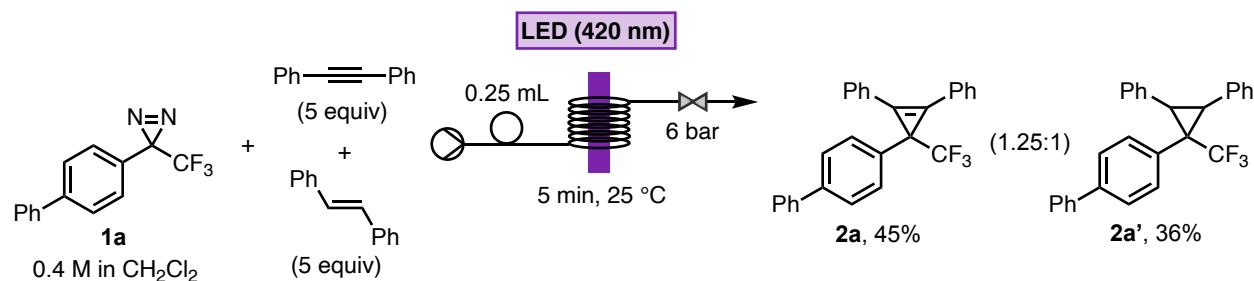
Figure S3. Batch setup with LED light strips

5.4 Competition experiments

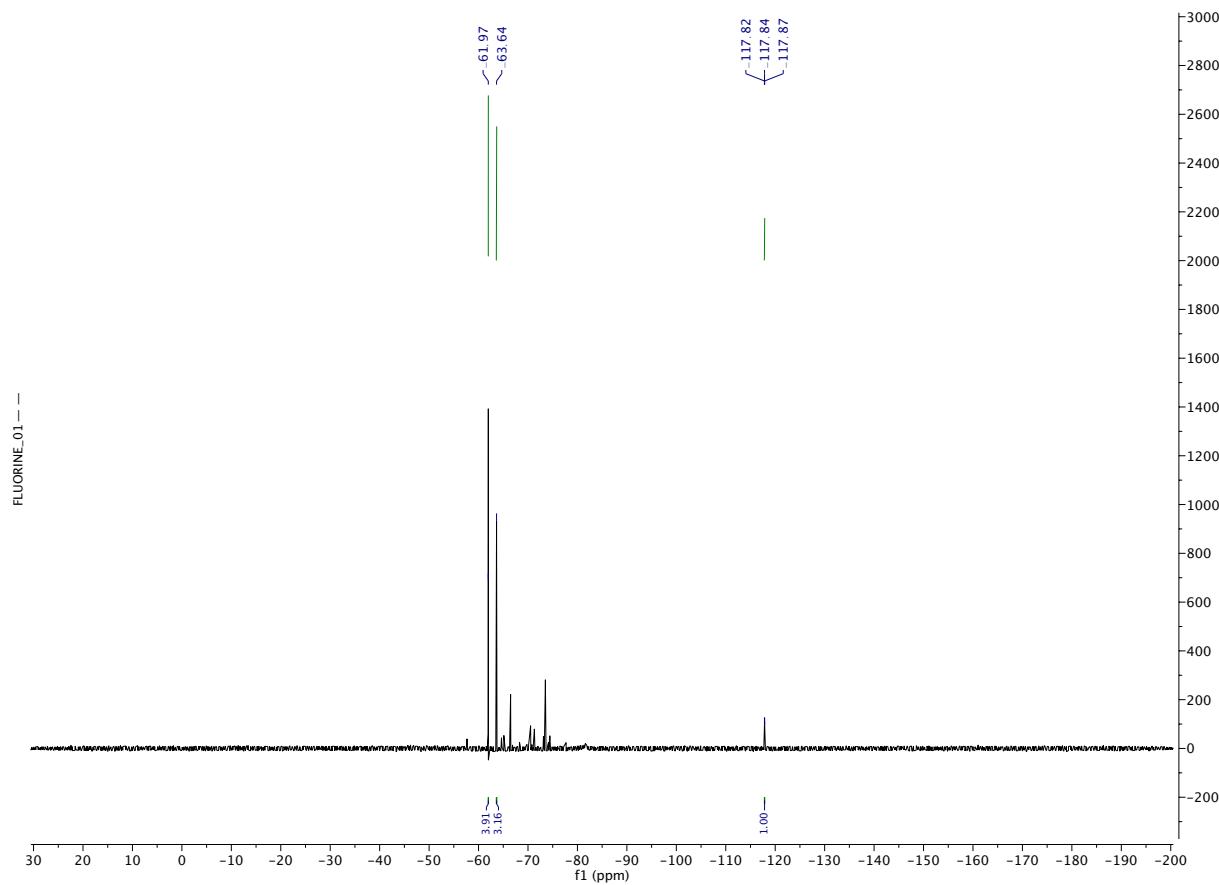
5.4.1 General procedure for the competition reaction between internal and terminal alkynes



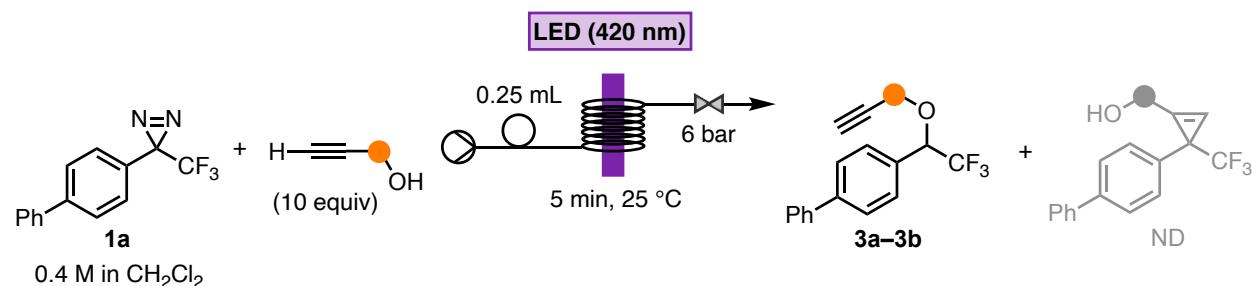
5.4.2 General procedure for the competition reaction between internal alkynes and alkenes



The general flow procedure described in 5.2 was used. A solution of the diazirine **1a**, diphenyl acetylene (5 equiv), and (*E*)-1,2-diphenylethene (5 equiv) in CH_2Cl_2 (0.4 M to **1a**) was prepared and loaded into the injection loop (0.25 mL, reaction scale = 0.1 mmol). The flow rate was set to 2 mL/min for a 10 mL reactor volume (residence time = 5 min). The flow reactions were run under LED irradiation (420 nm) at 25 °C. The post-reaction stream containing the desired cyclopropene product (pre- and post-slug volume = 1 mL) was collected in a 30 mL vial. The solvent was removed under reduced pressure. The crude mixture was analyzed by ^{19}F NMR using 3-fluoro-4-nitrotoluene as an internal standard (-117.83 ppm). The obtained spectra are displayed below:



5.4.3 General procedure for the competition reaction between internal alkynes and alkenes



The general flow procedure described in **5.2** was used. A solution of the diazirine **1a** and the propargyl alcohol (10 equiv.) in CH_2Cl_2 (0.4 M to **1a**) was prepared and loaded into the injection loop (0.25 mL, reaction scale= 0.1 mmol). The flow rate was set to 2 mL/min for a 10 mL reactor volume (residence time = 5 min). The flow reactions were run under LED irradiation (420 nm) at 25 °C. The post-reaction stream containing the desired cyclopropene product (pre- and post-slug volume = 1 mL) was collected in a 30 mL vial. The solvent was removed under reduced pressure and the crude mixture was purified by flash column chromatography (Biotage, SNAP ULTRA, 100–7/3 hexanes:EtOAc) to give the compounds **3a** and **3b**.

5.4.3.1 Characterization of 2,2,2-trifluoromethyl ether **3a** and **3b**

4-(2,2,2-Trifluoro-1-(pent-4-yn-1-yloxy)ethyl)-1,1'-biphenyl **3a**

3a

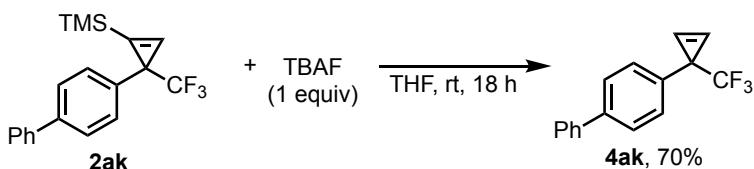
Purified by flash column chromatography (100:0–70:30 hex/EtOAc). Isolated as a colorless oil (18 mg, 58%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.63 (m, 4H), 7.52 (d, J = 8.5 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.42 – 7.35 (m, 1H), 4.67 (q, J = 6.6 Hz, 1H), 3.67 (td, J = 6.0, 3.2 Hz, 2H), 2.37 (tdd, J = 7.0, 5.8, 2.7 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 1.91 – 1.81 (m, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 142.4, 140.4, 131.8, 128.9, 128.6, 127.6, 127.3, 127.2, 122.7 (q, J = 259.4 Hz), 83.5, 79.9 (q, J = 31.1 Hz), 69.0, 68.8, 28.5, 15.1. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -6.59 (d, J = 6.8 Hz). IR (cm^{-1}): 3289, 2915, 1489, 1370, 1270, 1174, 1135, 1095, 1011, 763, 693. HR-MS (EI) m/z (compound did not ionize).

4-(2,2,2-Trifluoro-1-(prop-2-yn-1-yloxy)ethyl)-1,1'-biphenyl **3b**

3b

Purified by flash column chromatography (100:0–70:30 hex/EtOAc). Isolated as a white solid (20 mg, 70%). mp: 48–50 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.70 – 7.63 (m, 2H), 7.64 – 7.58 (m, 2H), 7.54 (d, J = 9.2 Hz, 2H), 7.53 – 7.43 (m, 2H), 7.43 – 7.36 (m, 1H), 5.02 (q, J = 6.7 Hz, 1H), 4.40 (dd, J = 15.9, 2.4 Hz, 1H), 4.13 (dd, J = 16.0, 2.4 Hz, 1H), 2.53 (t, J = 2.4 Hz, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 142.8, 140.3, 130.5, 128.9, 128.9, 127.7, 127.5, 127.2, 124.8 (q, J = 281.0 Hz), 77.8, 77.4 (q, J = 31.8 Hz), 76.1, 56.7. ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): -76.05 (d, J = 5.2 Hz). IR (cm^{-1}): 3288, 2913, 1489, 1369, 1259, 1175, 1134, 1097, 1018, 764, 692. HR-MS (EI) m/z (compound did not ionize).

5.5 General procedure for the TMS deprotection of **2ak**

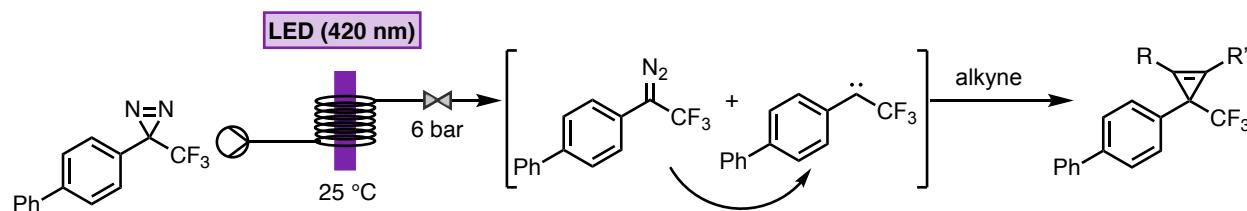


The cyclopropene **2ak** (0.06 mmol, 20 mg) was dissolved in 0.3 mL of anhydrous THF. TBAF (1 M in THF, 60 μ L, 1 equiv) was added and the reaction mixture was stirred for 18 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (Biotage, SNAP ULTRA, 100% hexanes) to give the compound **4ak**.

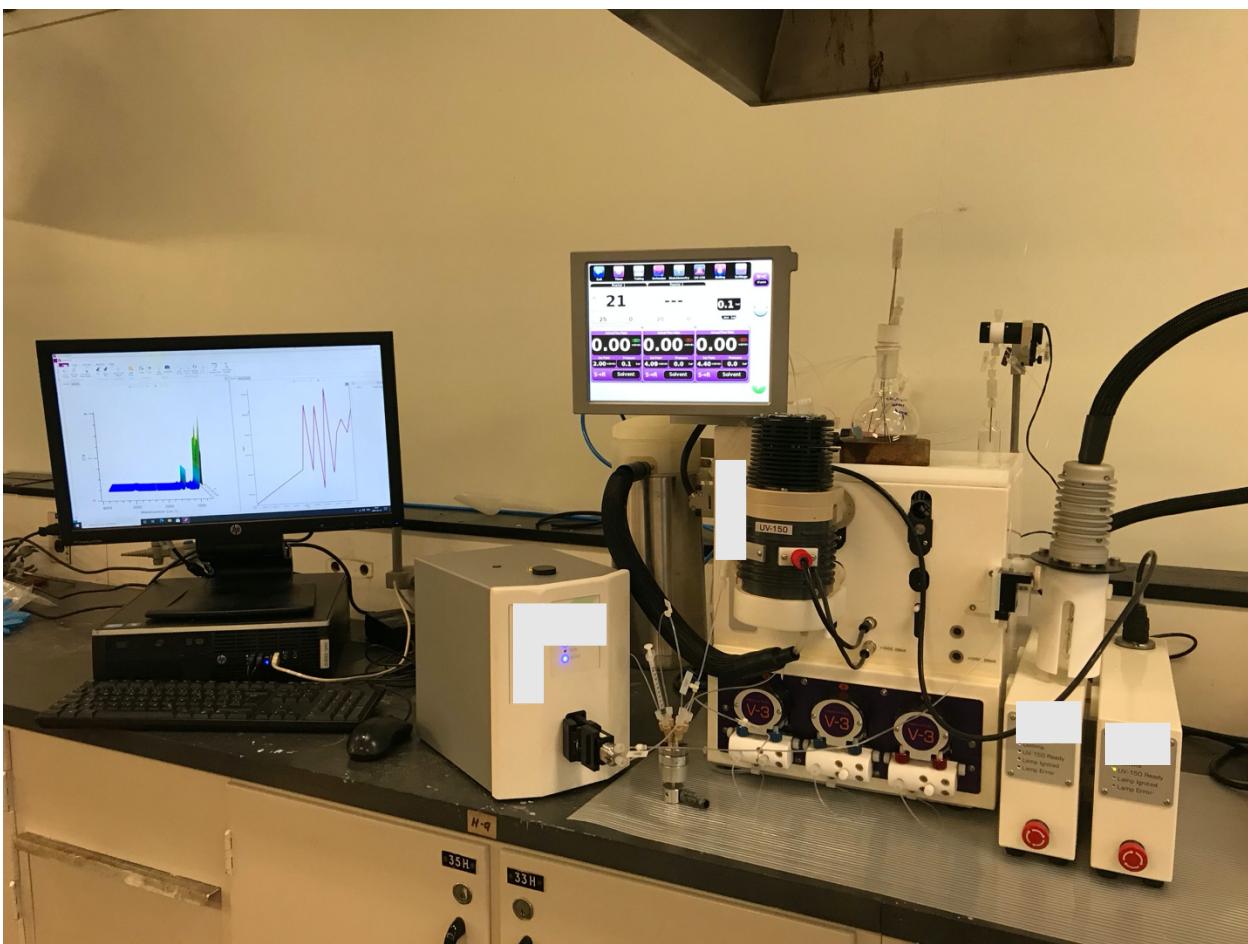
4-(1-(Trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl **4ak**

4ak Isolated as a white solid (11 mg, 70%). mp: 58–60 °C. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.59–7.55 (m, 4H), 7.46–7.43 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.37–7.34 (m, 1H), 7.29 (q, J = 1.5 Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm): 140.8, 140.4, 137.8, 128.9, 128.2, 128.1, 127.5, 127.3, 127.1 (q, J = 276.6 Hz), 127.2, 108.0 (q, J = 2.8 Hz), 29.4 (q, J = 36.0 Hz). ^{19}F NMR (470 MHz, CDCl_3) δ (ppm): –65.6. IR (cm^{-1}): 3142, 3032, 1653, 1487, 1259, 1119, 831, 764, 735. HR-MS (EI) m/z (compound did not ionize).

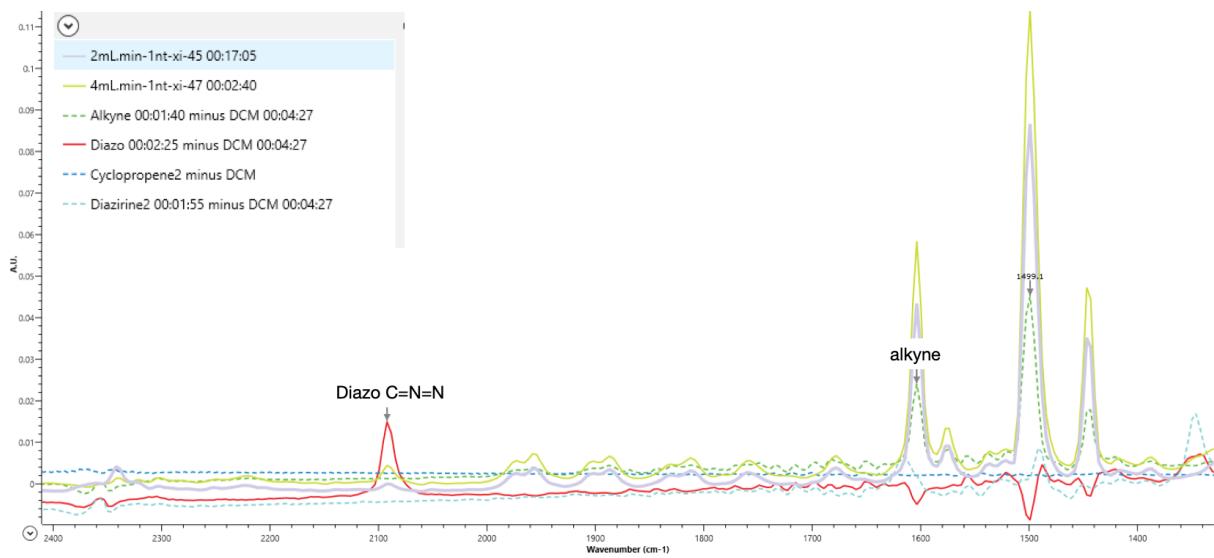
5.6 Reaction monitoring using ReactIR



The general flow procedure described in **5.2** was used. A solution of the diazirine **1a** and diphenyl acetylene (10 equiv) in CH_2Cl_2 (0.4 M to **1a**) was prepared and loaded into the injection loop (0.25 mL, reaction scale = 0.1 mmol). The flow reactions were run under LED irradiation (420 nm) at 25 °C in a 10 mL tube reactor. The outlet of the reactor was connected to the ReactIR using a silicon probe and reaction monitoring was done in real time. The flow rate was varied from 2 to 4 mL/min for a better detection of reaction intermediates. The figure below is the setup used for this experiment:



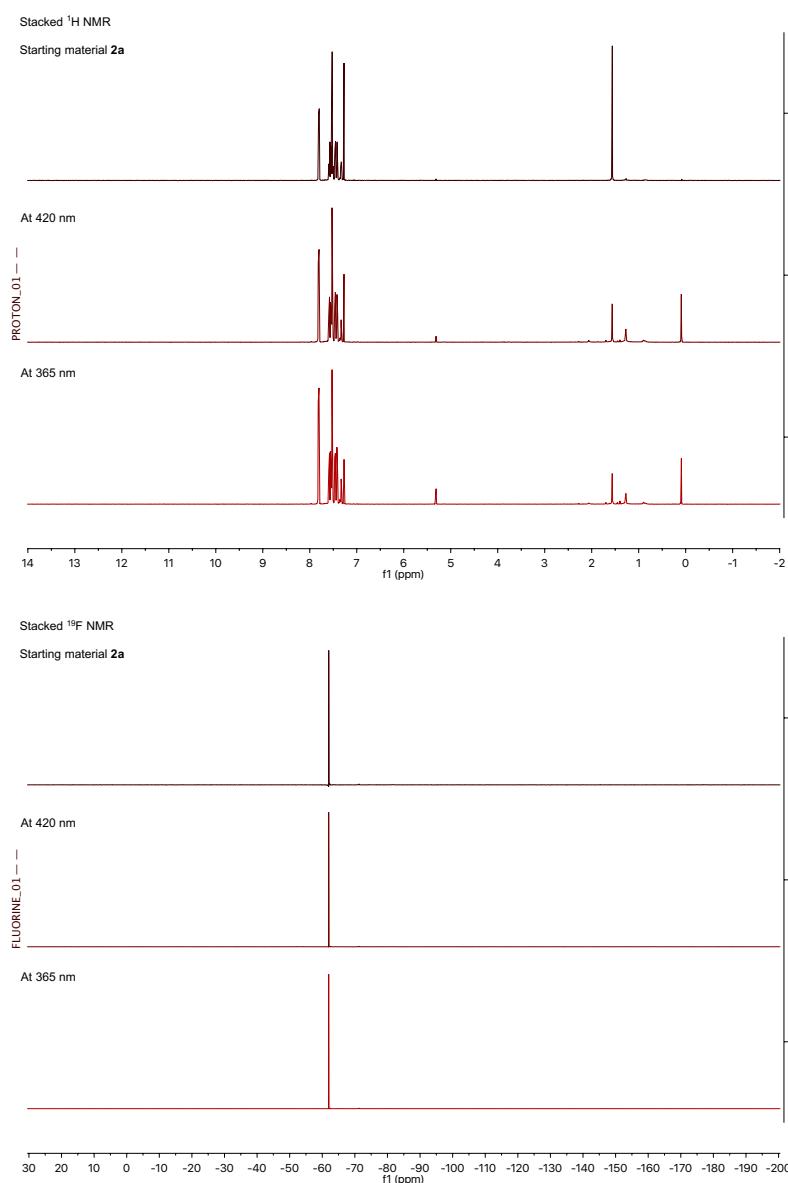
On the left: ReactIR equipment; On the right: flow setup



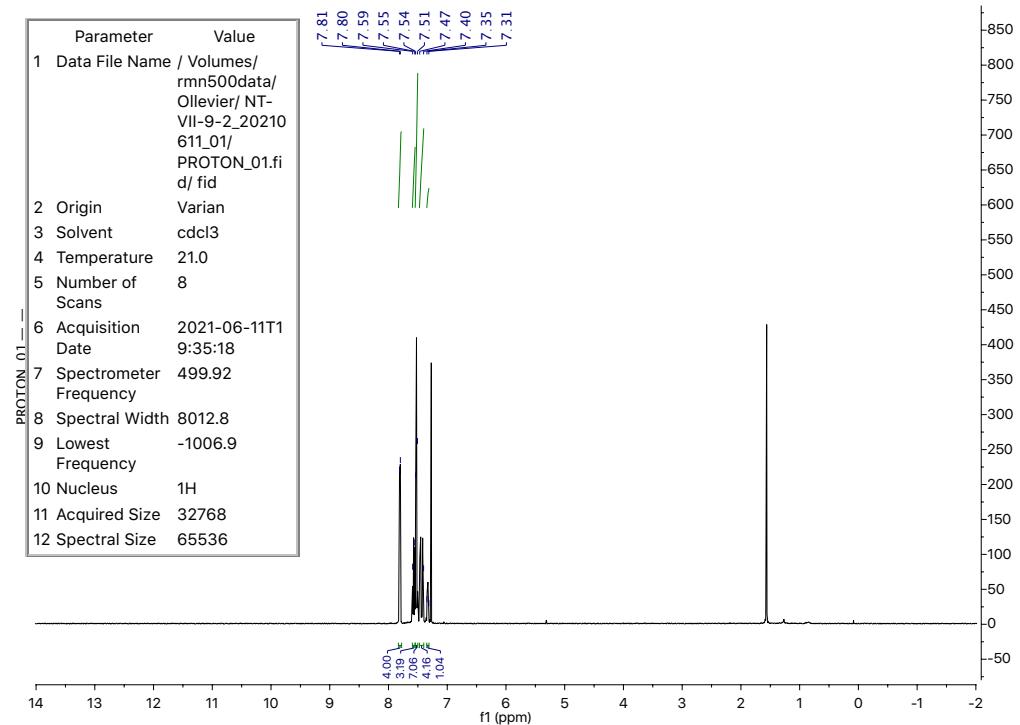
From the obtained IR spectrum, the characteristic peak of the diazo compound at 2100 cm^{-1} was observed with increased intensity when the flow rate was increased from 2 to 4 mL/min.

6. Control experiments

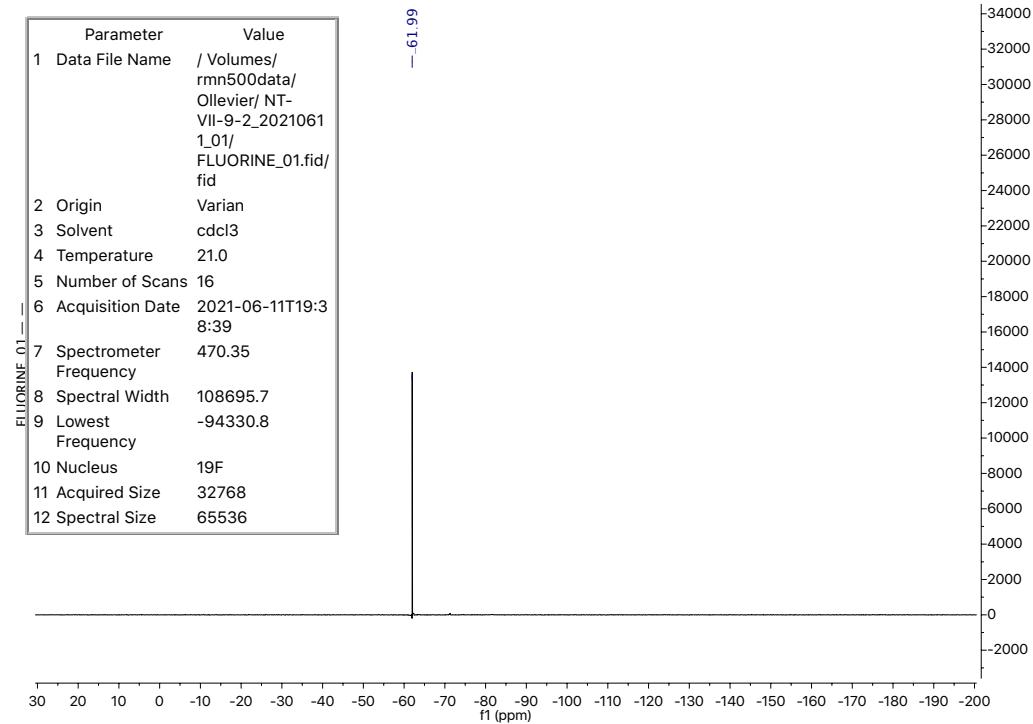
A solution of cyclopropene **2a** in CH_2Cl_2 (0.1 M) was prepared and loaded into the injection loop (0.25 mL). The flow rate was set to 2 mL/min for a 10 mL reactor volume (residence time = 5 min). The flow reactions were run under LED irradiation (A: 420 nm and B: 365 nm) at 25 °C. The post-reaction stream containing the cyclopropene product (pre- and post-slug volume = 1 mL) was collected in a 10 mL vial. The solvent was removed under reduced pressure. ^1H and ^{19}F NMR of the mixture were recorded and compared to the starting material **2a**. The obtained spectra are displayed below (Stacked + individual spectra):



¹H NMR spectra of **2a** (Starting material)

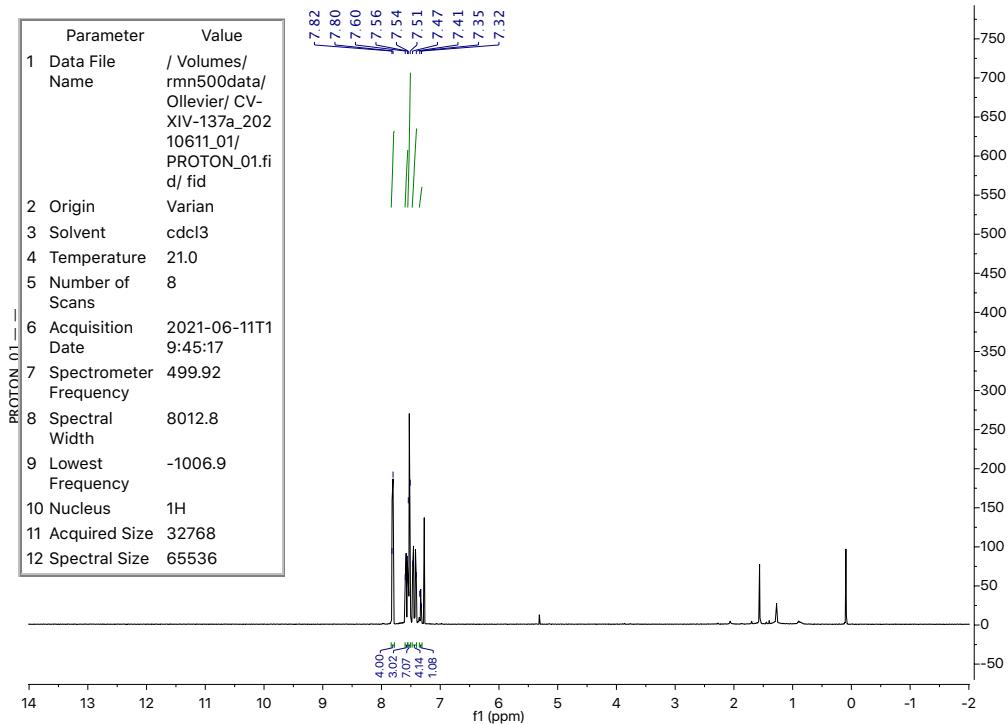


¹⁹F NMR spectra of **2a** (Starting material)

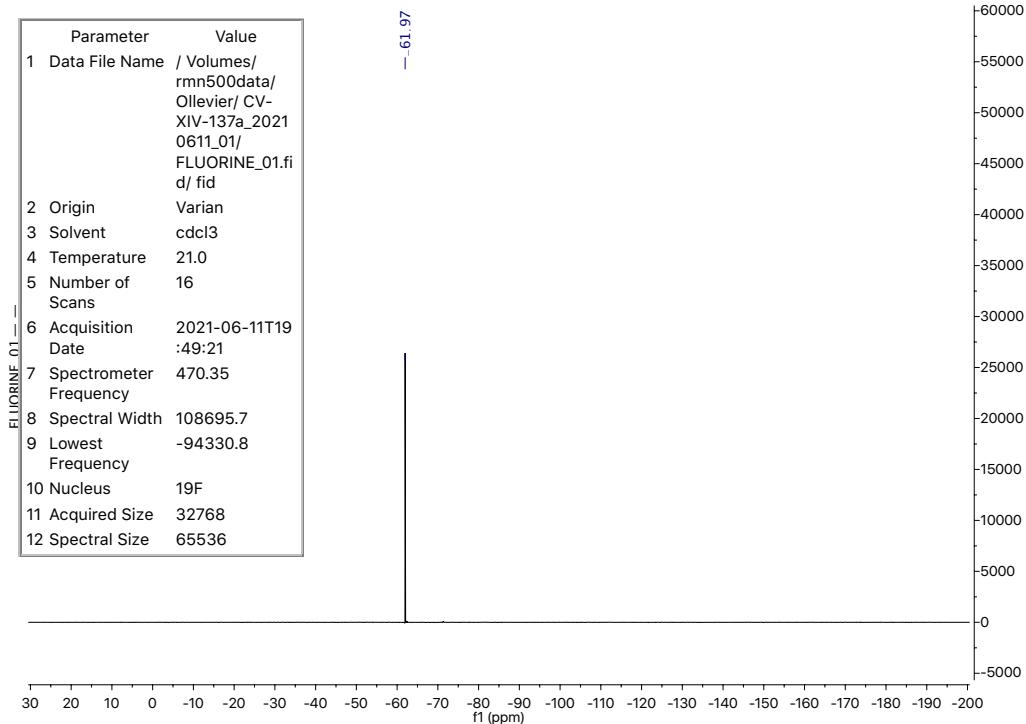


A: 420 nm

¹H NMR spectra of the mixture

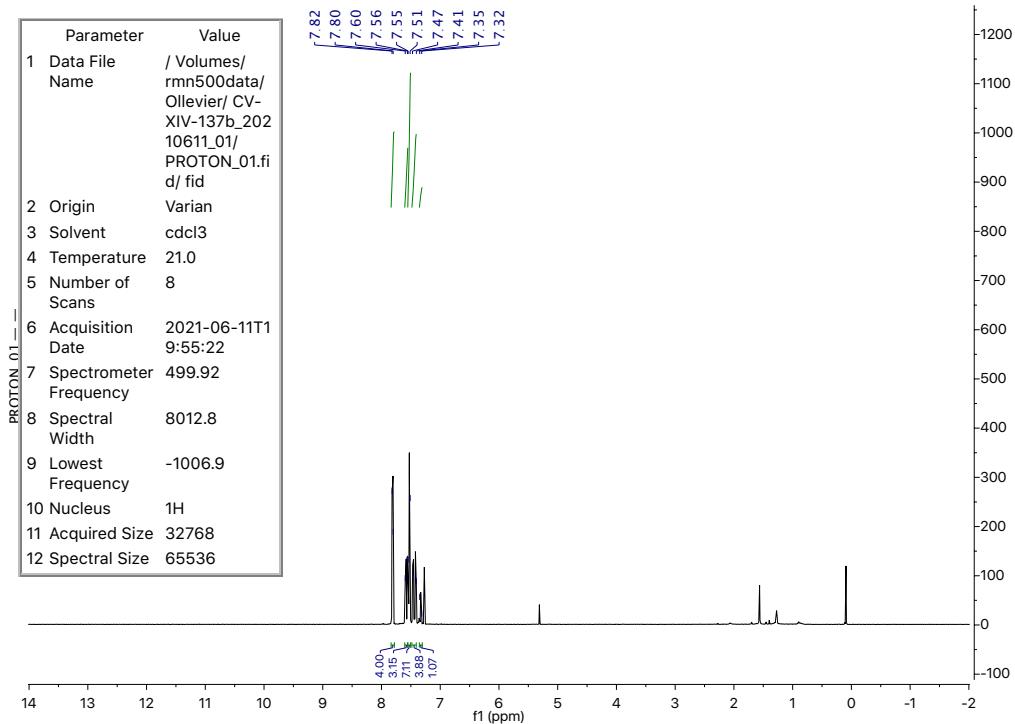


¹⁹F NMR spectra of the mixture

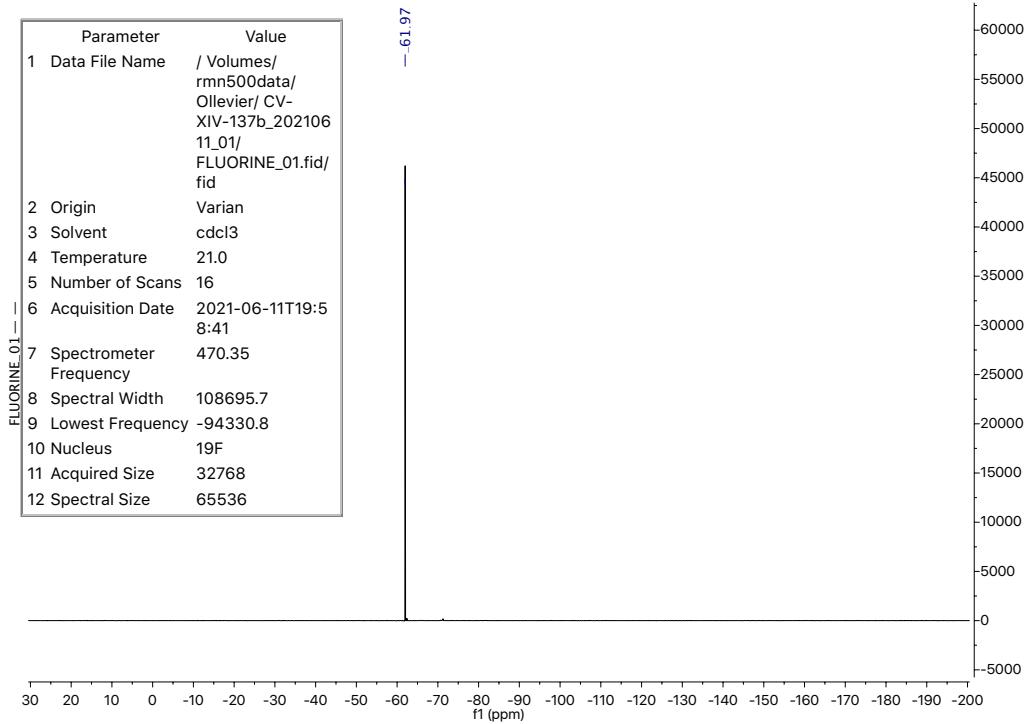


B: 365 nm

¹H NMR spectra of the mixture



¹⁹F NMR spectra of the mixture

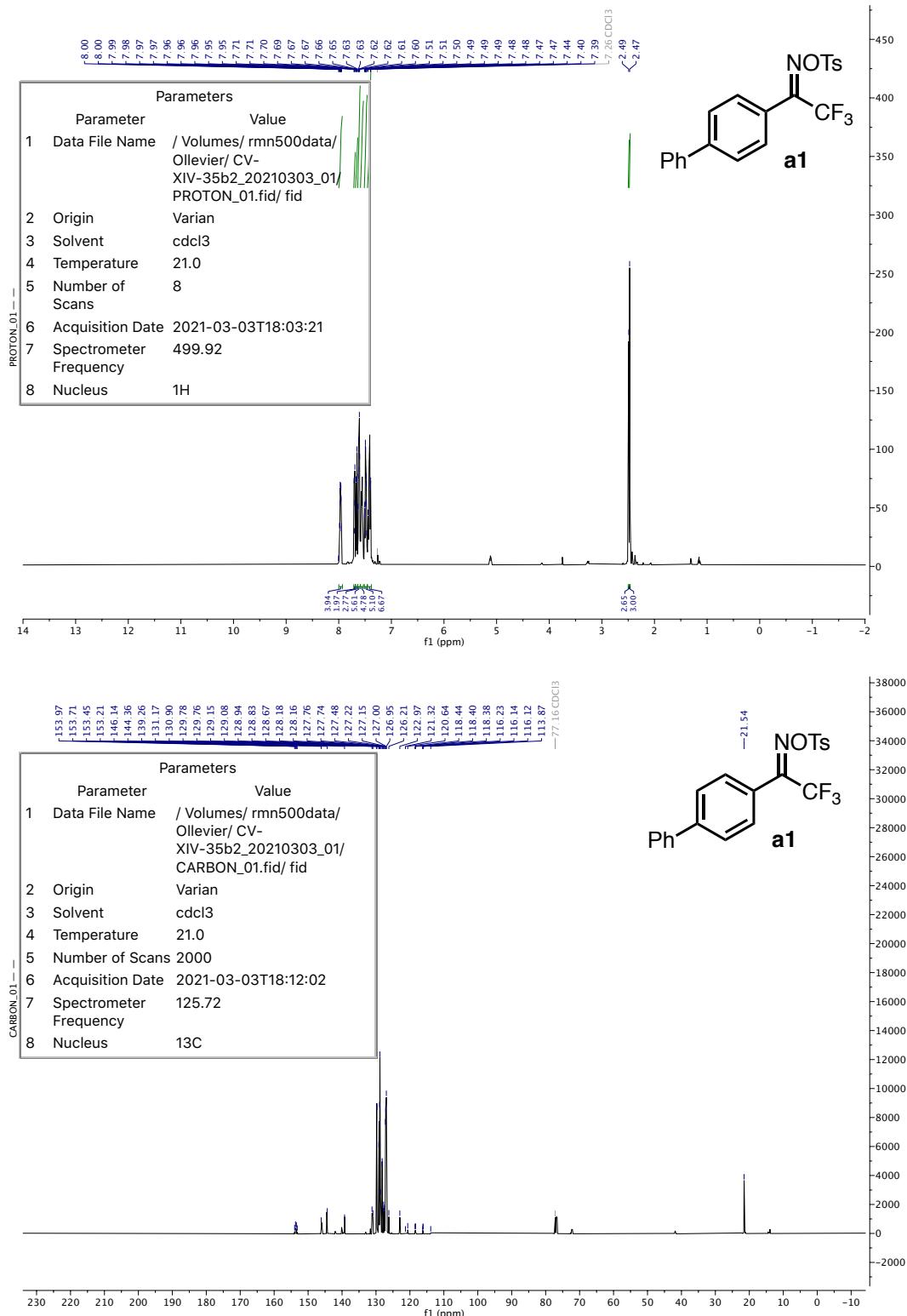


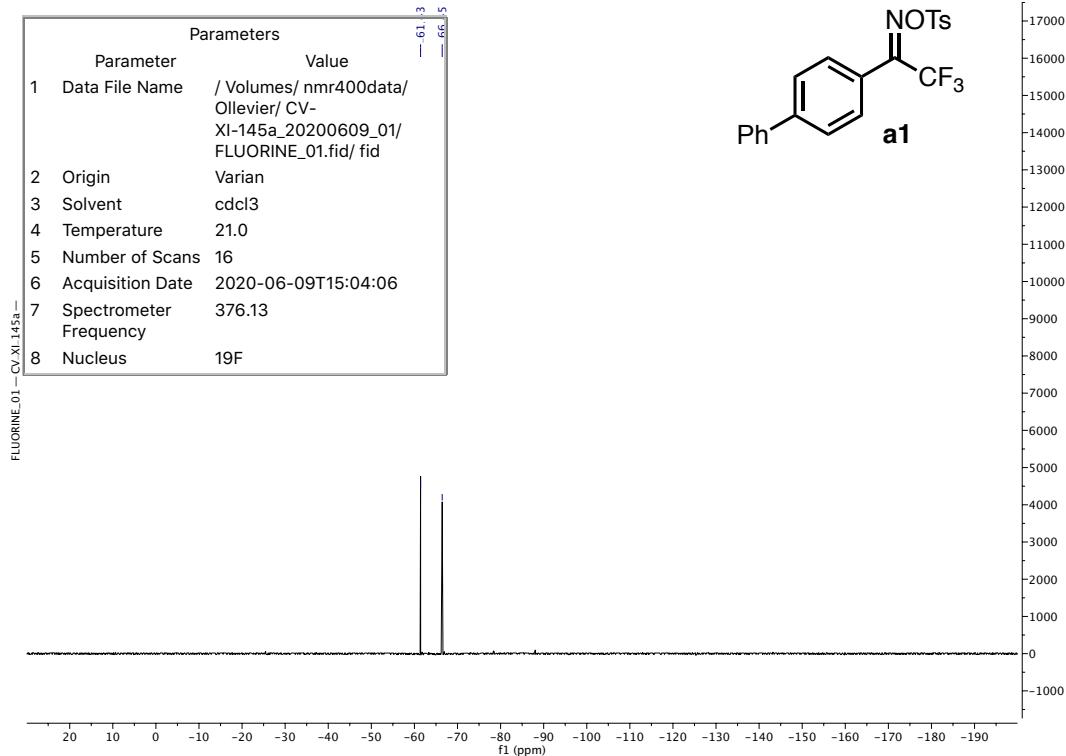
7. References

1. Manzi, L.; Barrow, A. S.; Scott, D.; Layfield, R.; Wright, T. G.; Moses, J. E.; Oldham, N. J., Carbene footprinting accurately maps binding sites in protein-ligand and protein-protein interactions. *Nat. Commun.* **2016**, 7, 13288.
2. Richardson, S. K.; Ife, R. J., Swern oxidation of diaziridines to diazirines. *J. Chem. Soc. Perkin Trans. 1989*, 1172-1174.
3. Wang, L.; Yoshida, T.; Muto, Y.; Murai, Y.; Tachrim, Z. P.; Ishida, A.; Nakagawa, S.; Sakihama, Y.; Hashidoko, Y.; Masuda, K.; Hatanaka, Y.; Hashimoto, M., Synthesis of Diazirine-Based Photoreactive Saccharin Derivatives for the Photoaffinity Labeling of Gustatory Receptors. *Eur. J. Org. Chem.* **2015**, 3129-3134.
4. Bender, T.; Huss, M.; Wieczorek, H.; Grond, S.; von Zezschwitz, P., Convenient Synthesis of a [1-14C]Diazirinylbenzoic Acid as a Photoaffinity Label for Binding Studies of V-ATPase Inhibitors. *Eur. J. Org. Chem.* **2007**, 3870-3878.
5. Kogon, A. A.; Bochkariov, D. E.; Baskunov, B. P.; Cheprakov, A. V., 2,3-Dihydroxy-3-{3-[3-(trifluoromethyl)diazirin-3-yl]phenyl}propionic Acid. A Cleavable Carbene-Generating Reagent Used for Photocrosslinking. *Liebigs Ann. Chem.* **1992**, 1992, 879-881.
6. Lee, K.; Ban, H. S.; Naik, R.; Hong, Y. S.; Son, S.; Kim, B.-K.; Xia, Y.; Song, K. B.; Lee, H.-S.; Won, M., Identification of Malate Dehydrogenase 2 as a Target Protein of the HIF-1 Inhibitor LW6 using Chemical Probes. *Angew. Chem., Int. Ed.* **2013**, 52, 10286-10289.
7. Protasova, I.; Bulat, B.; Jung, N.; Bräse, S., Synthesis of Diaziridines and Diazirines via Resin-Bound Sulfonyl Oximes. *Org. Lett.* **2017**, 19, 34-37.
8. Hatanaka, Y.; Hashimoto, M.; Kurihara, H.; Nakayama, H.; Kanaoka, Y., A Novel Family of Aromatic Diazirines for Photoaffinity Labeling. *J. Org. Chem.* **1994**, 59, 383-387.
9. Protasova, I.; Bulat, B.; Jung, N.; Bräse, S., Synthesis of Diaziridines and Diazirines via Resin-Bound Sulfonyl Oximes. *Org. Lett.* **2017**, 19, 34-37.
10. Wang, L.; Murai, Y.; Yoshida, T.; Ishida, A.; Masuda, K.; Sakihama, Y.; Hashidoko, Y.; Hatanaka, Y.; Hashimoto, M., Alternative one-pot synthesis of (trifluoromethyl)phenyldiazirines from tosyloxime derivatives: application for new synthesis of optically pure diazirinylphenylalanines for photoaffinity labeling. *Org. Lett.* **2015**, 17, 616-619.
11. Barroso, R.; Jimenez, A.; Perez-Aguilar, M. C.; Cabal, M. P.; Valdes, C., Synthesis of 1,3-diaryl-3-trifluoromethylcyclopropenes by transition-metal-free reaction of 2,2,2-trifluoroacetophenone tosylhydrazones with alkynes: the effect of the trifluoromethyl group. *Chem. Commun.* **2016**, 52, 3677-3680.

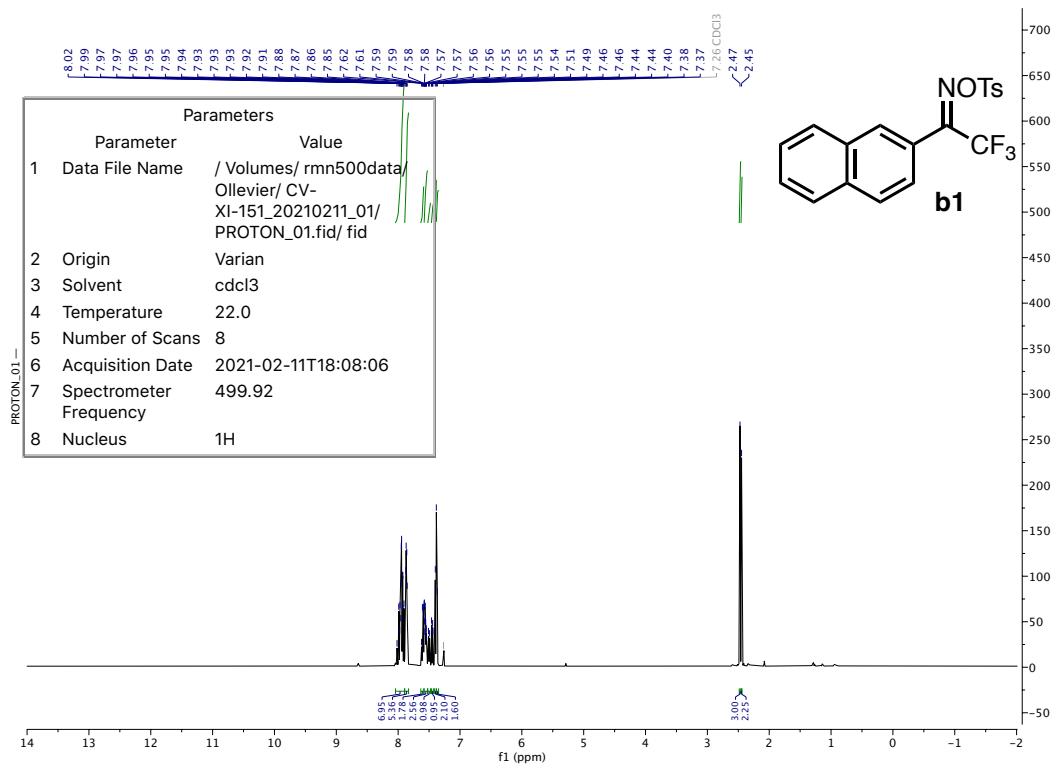
8. NMR Spectra

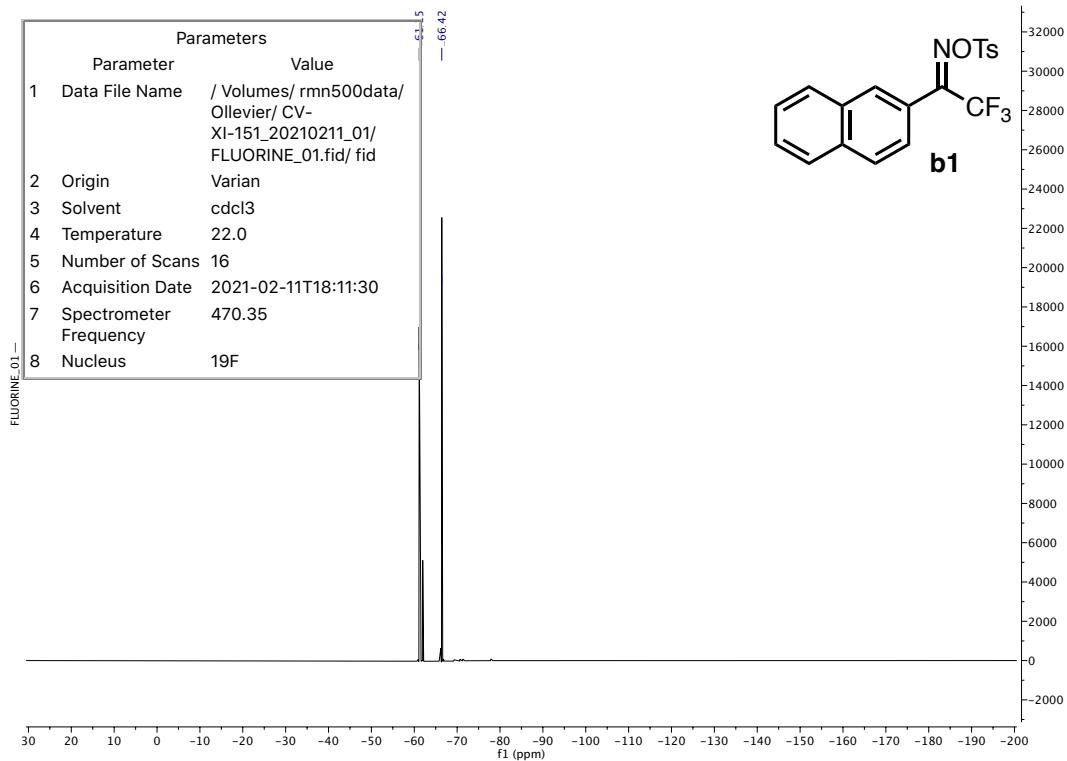
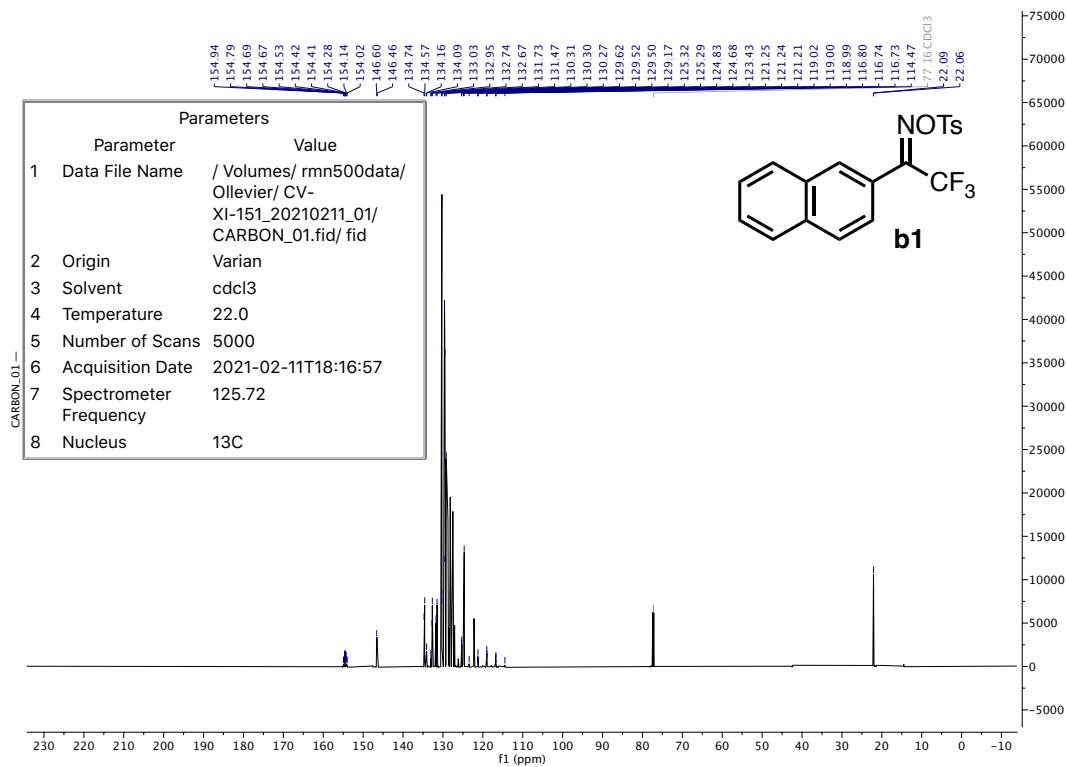
1-([1,1'-Biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one O-tosyl oxime a1



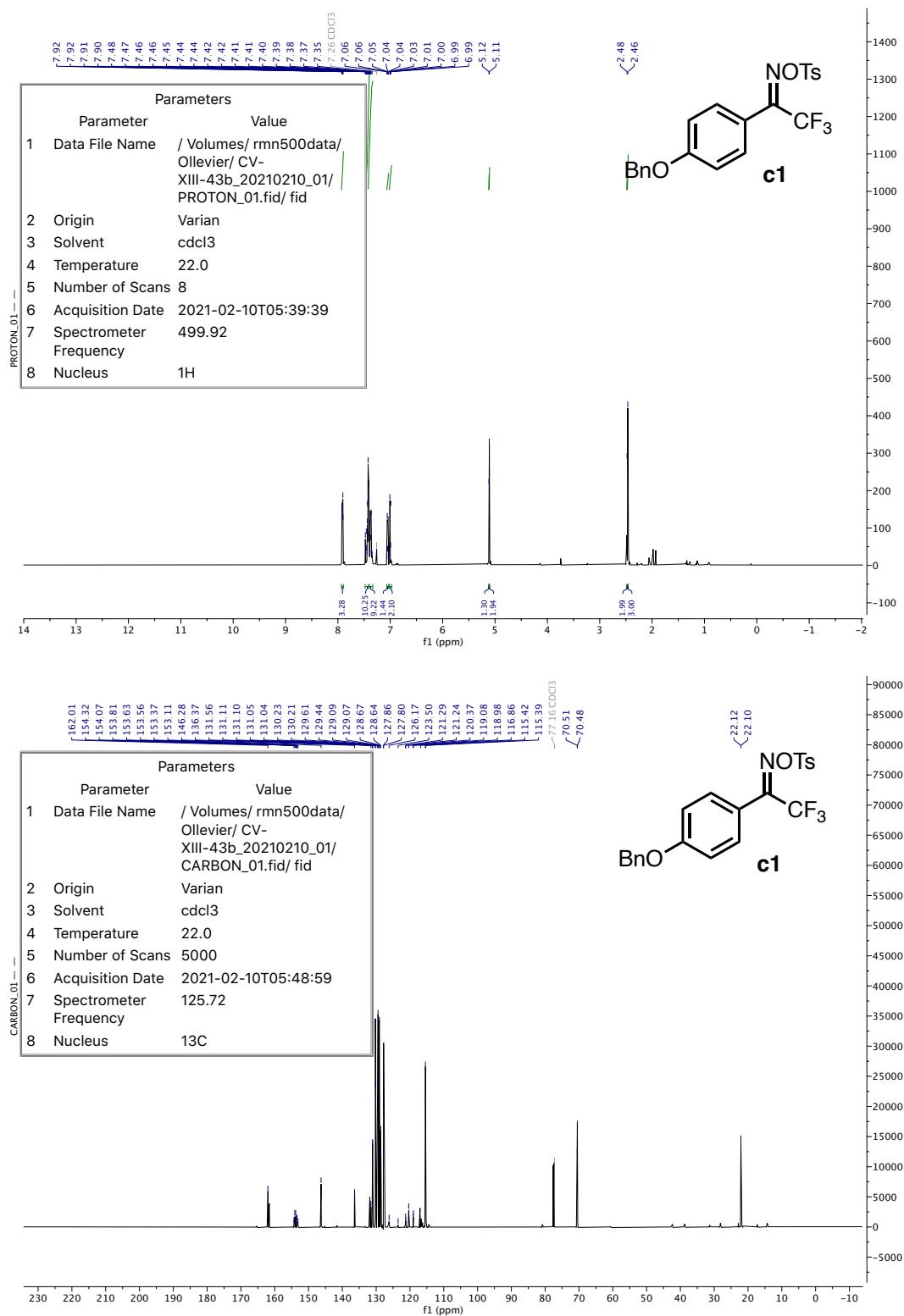


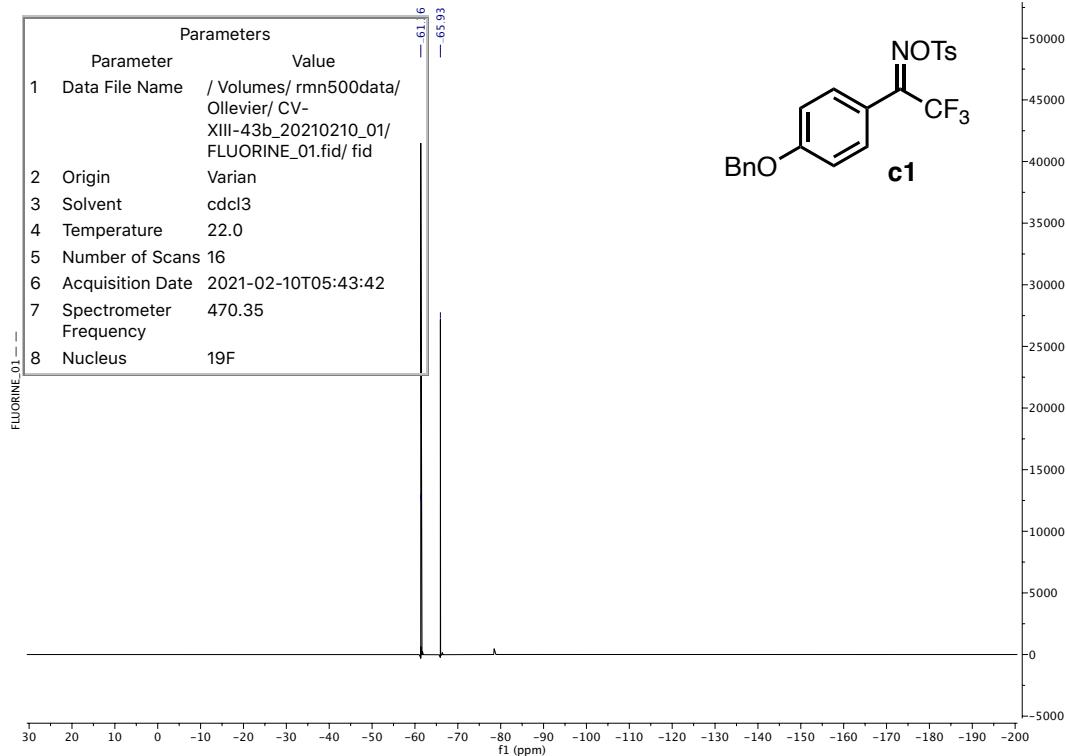
2,2,2-Trifluoro-1-(naphthalen-2-yl)ethan-1-one O-tosyl oxime b1



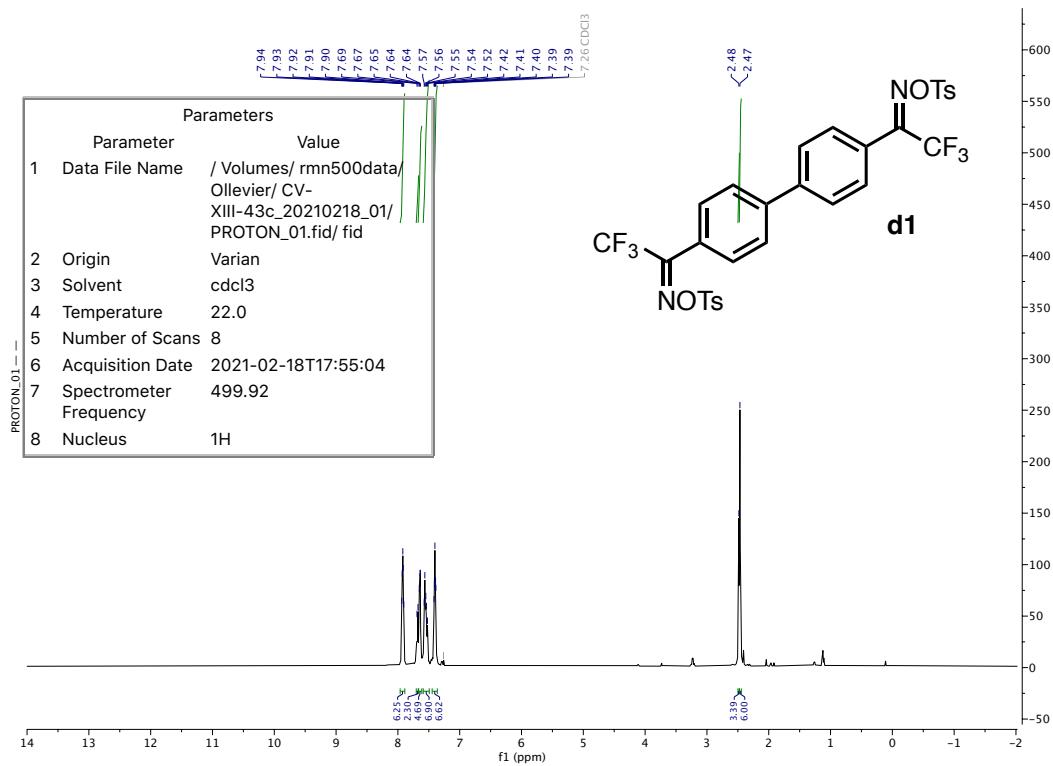


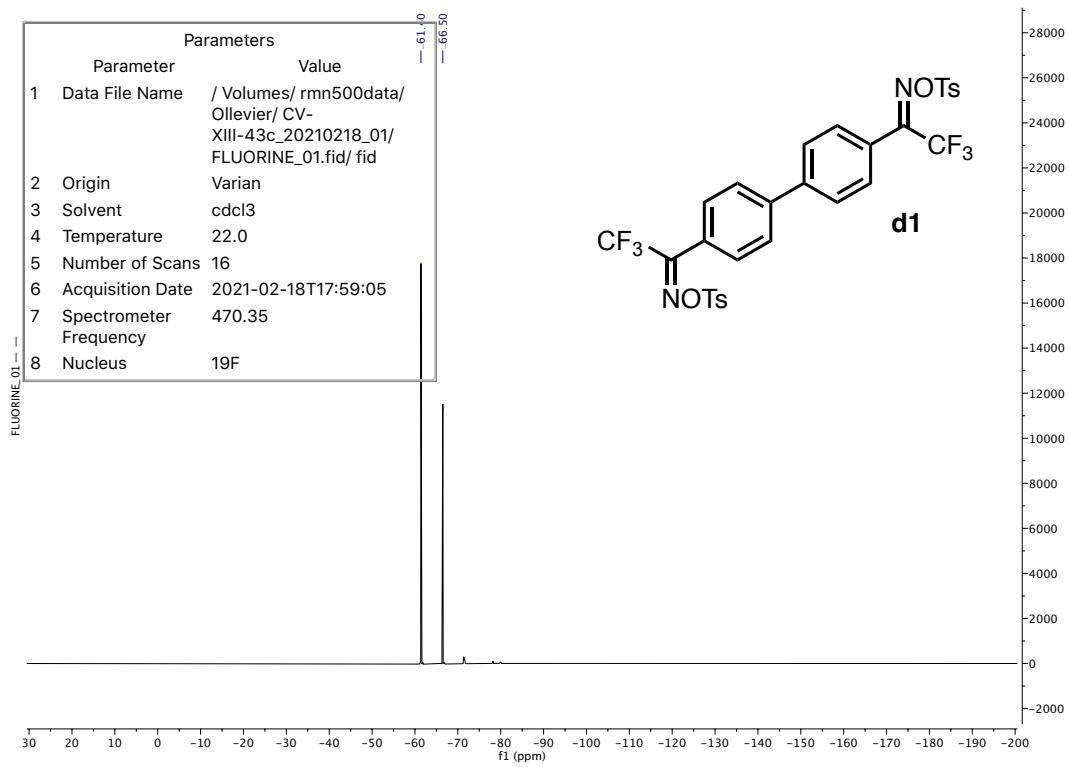
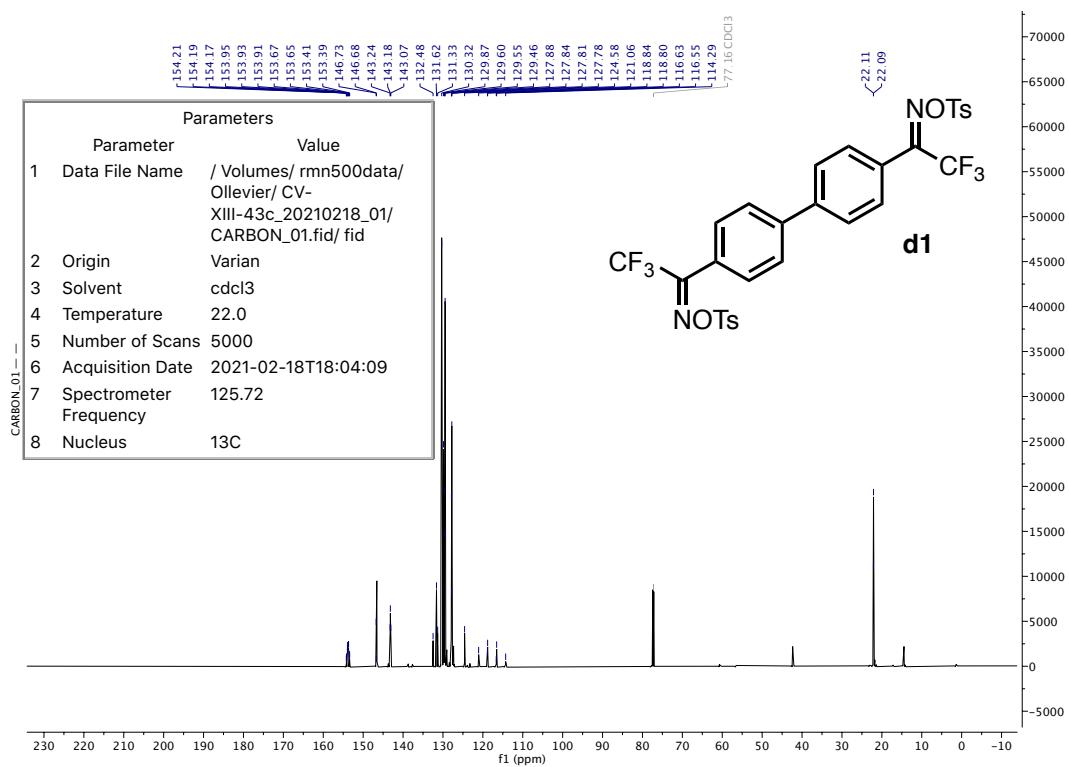
1-(4-(BenzylOxy)phenyl)-2,2,2-trifluoroethan-1-one O-tosyl oxime c1



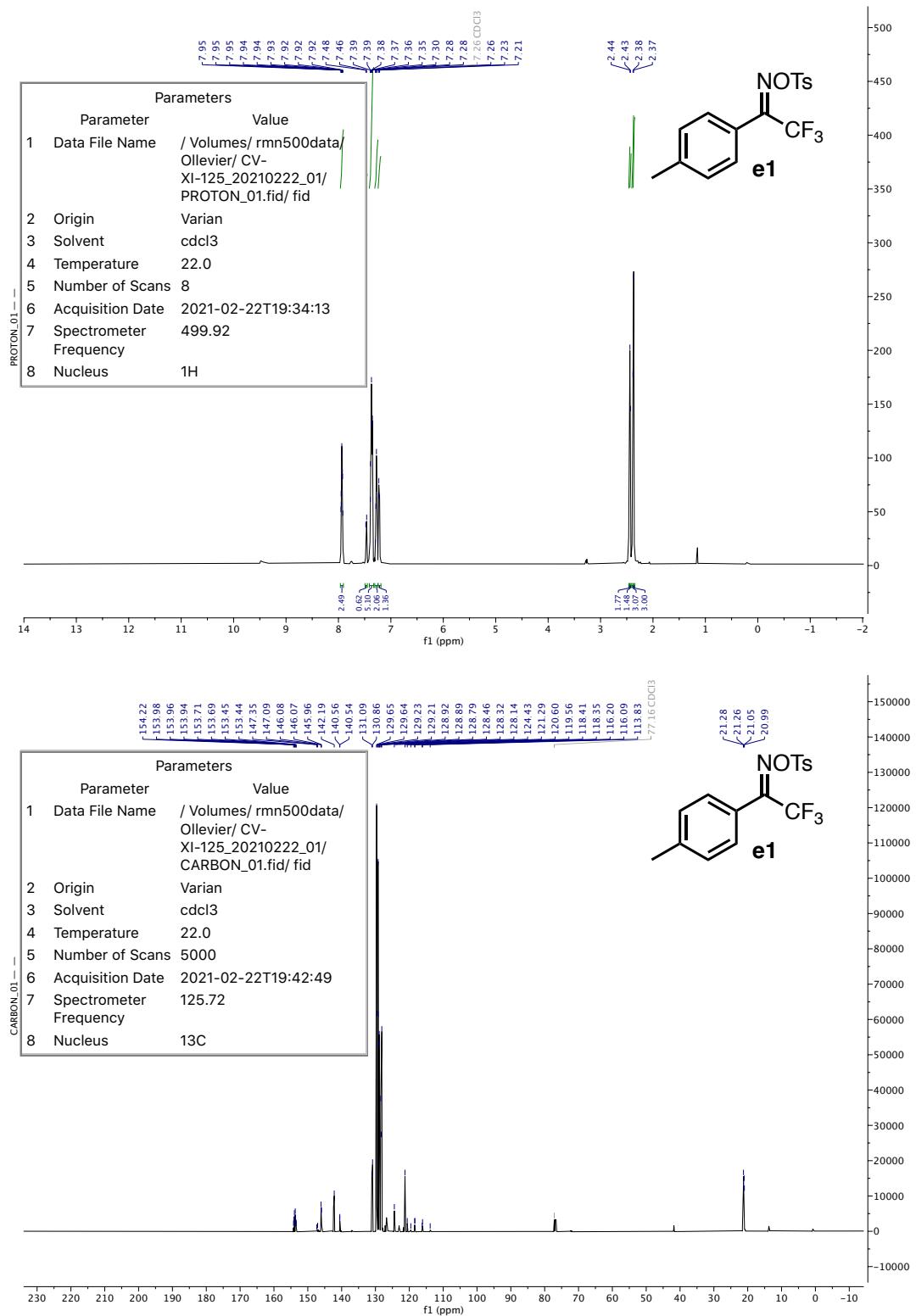


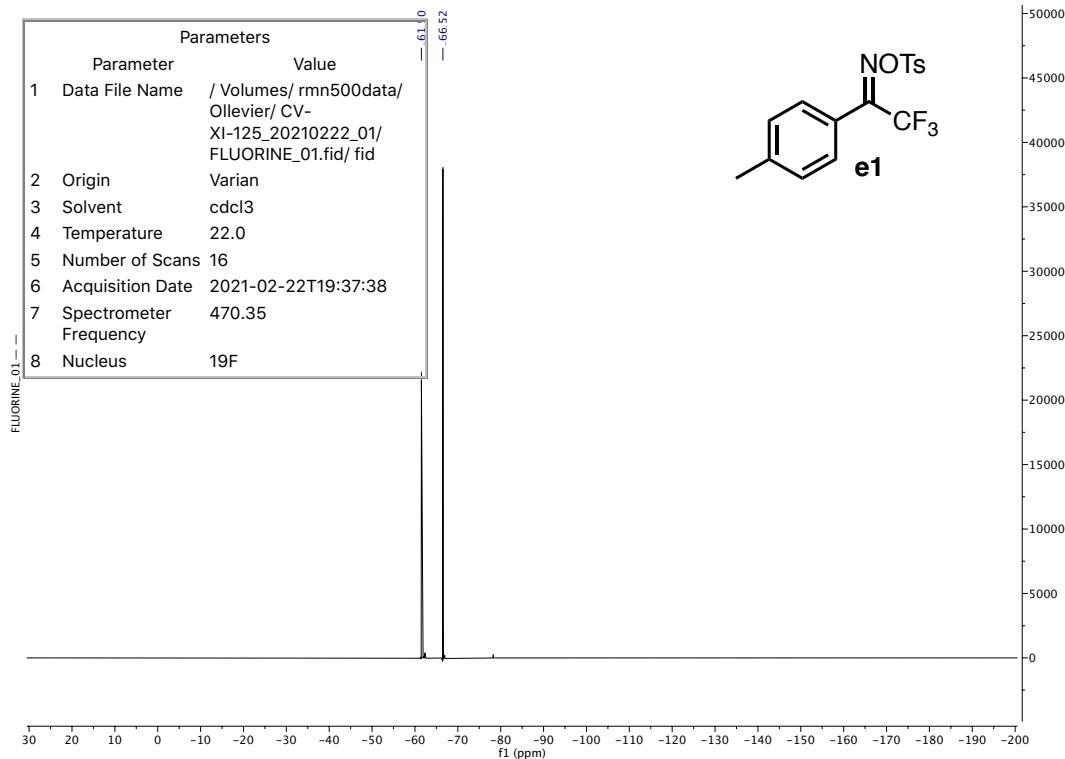
1,1'-([1,1'-Biphenyl]-4,4'-diyl)bis(2,2,2-trifluoroethan-1-one) O,O-ditosyl dioxime d1



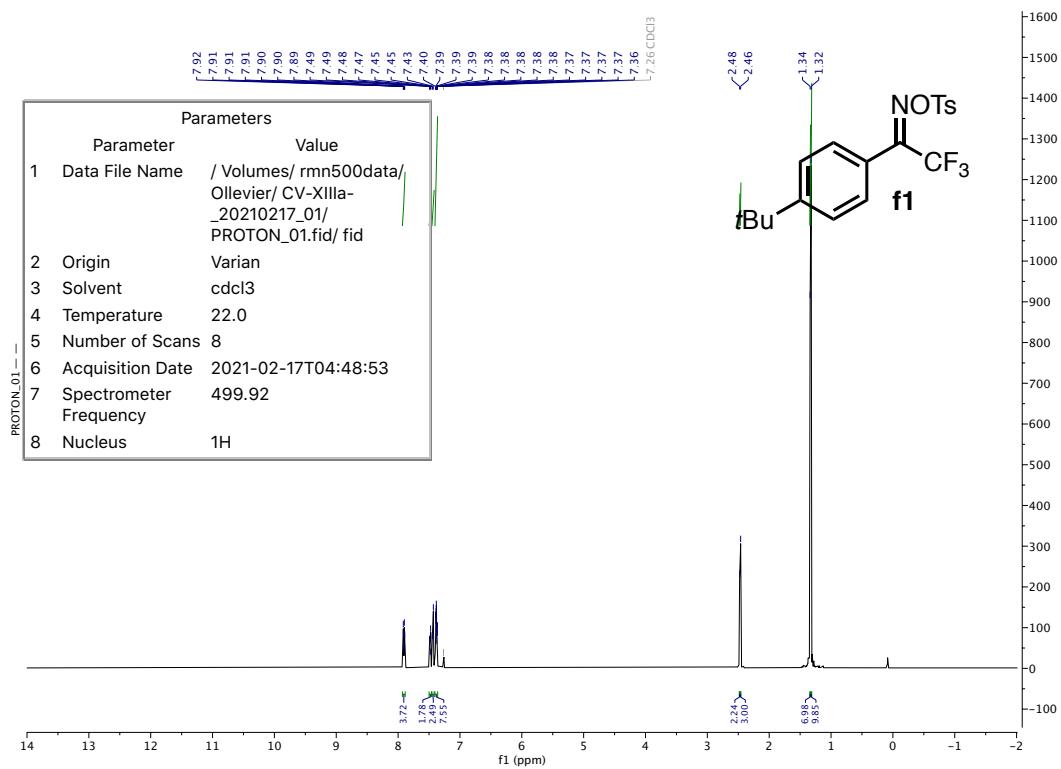


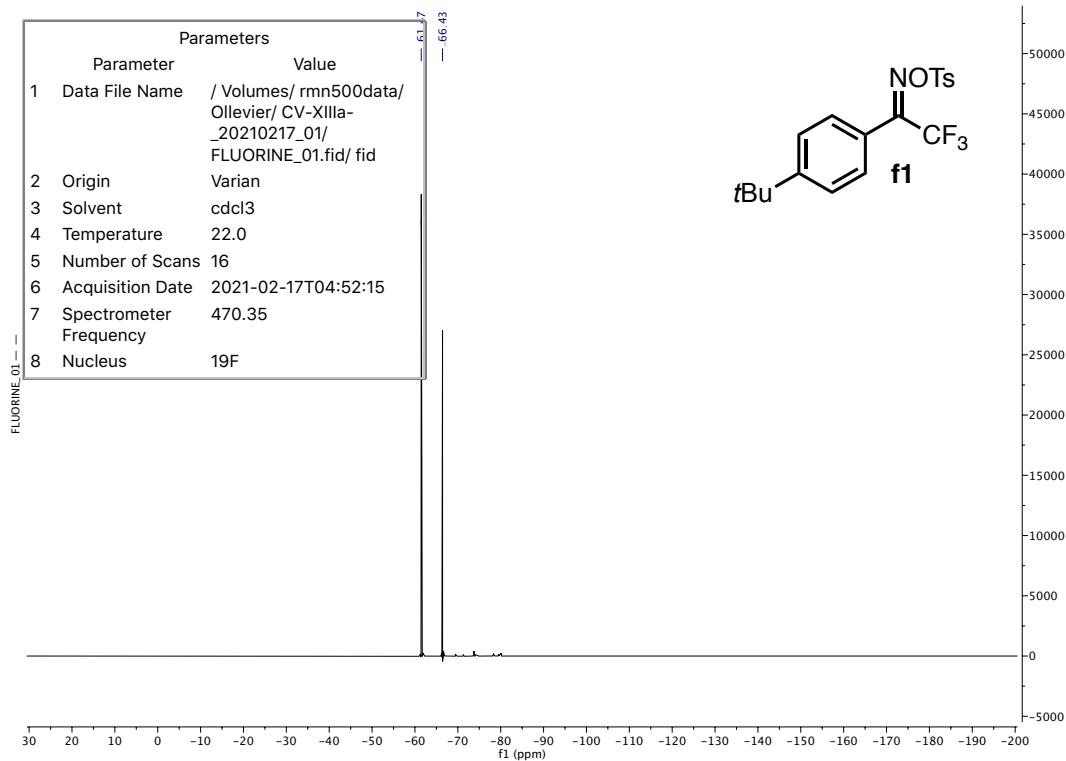
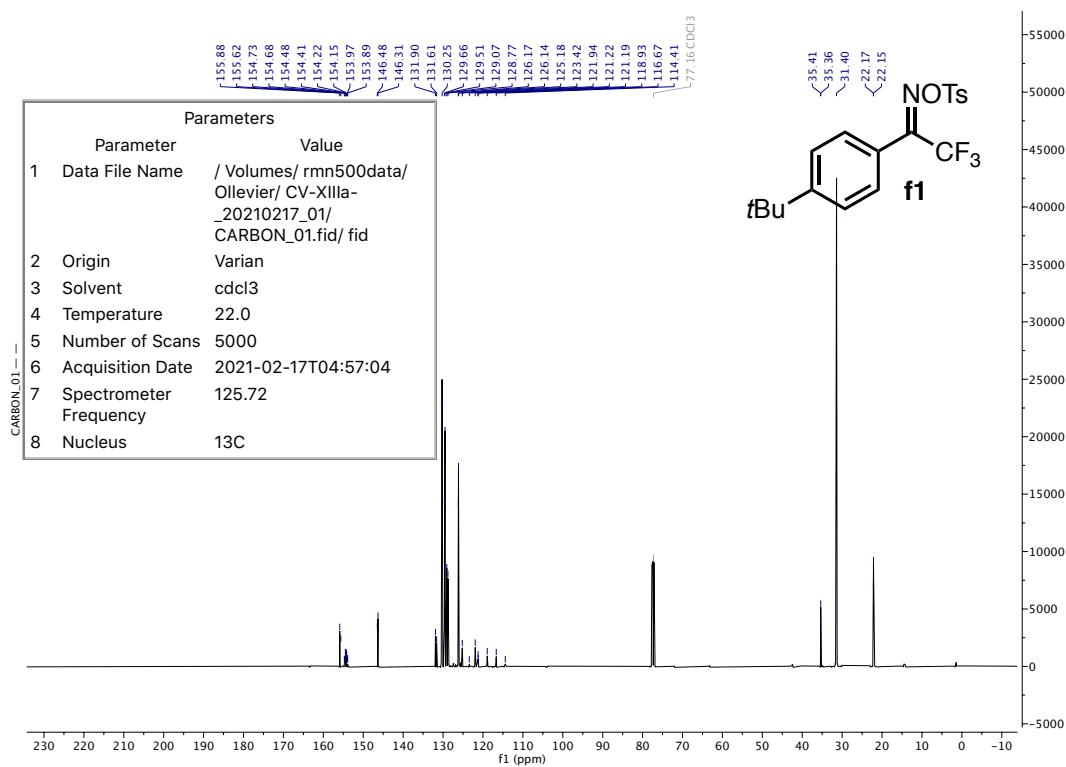
2,2,2-Trifluoro-1-(*p*-tolyl)ethan-1-one O-tosyl oxime e1



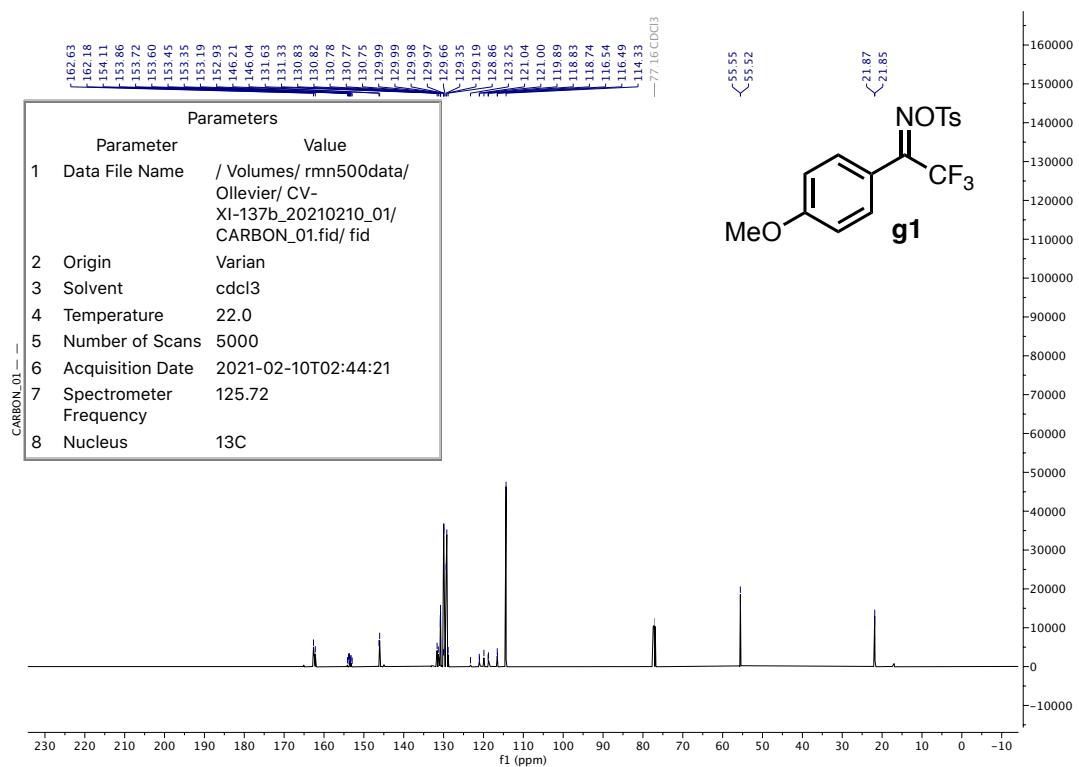
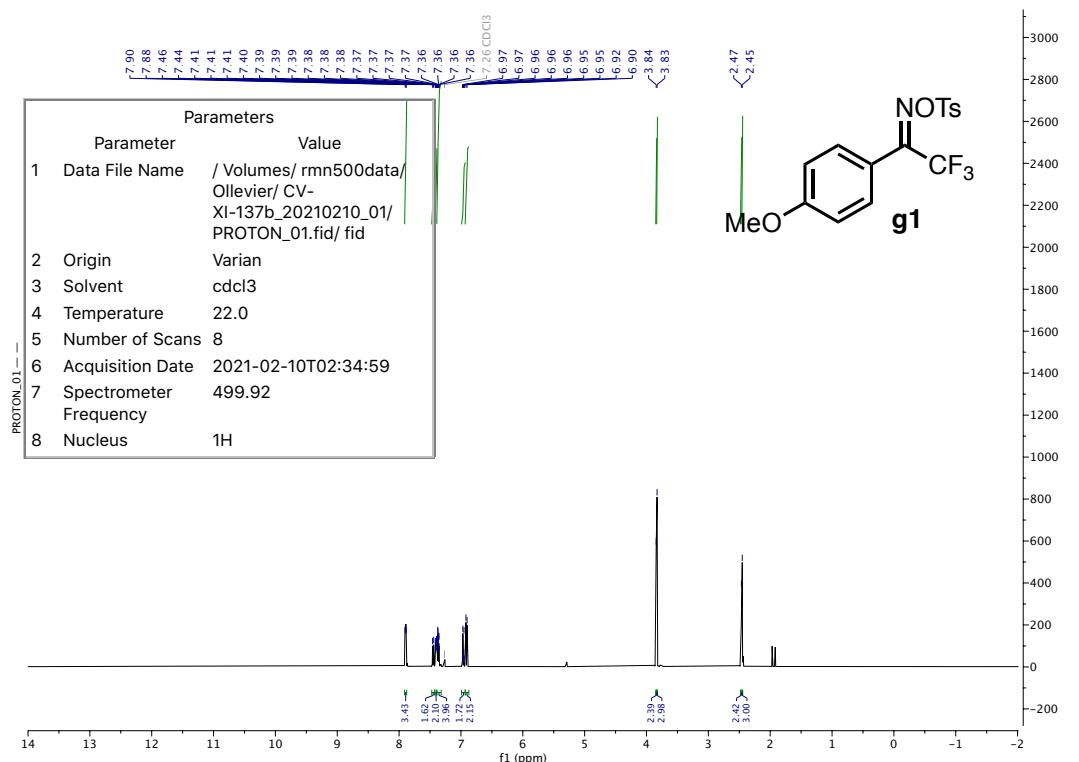


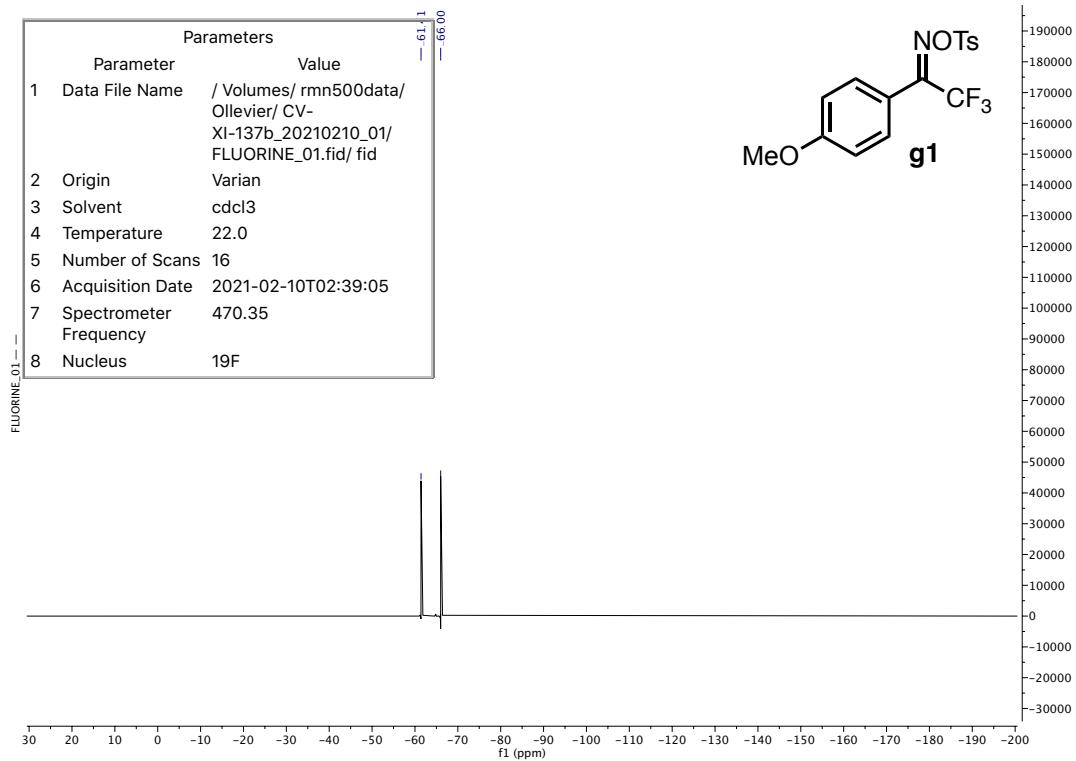
1-(4-(*Tert*-butyl)phenyl)-2,2,2-trifluoroethan-1-one O-tosyl oxime f1



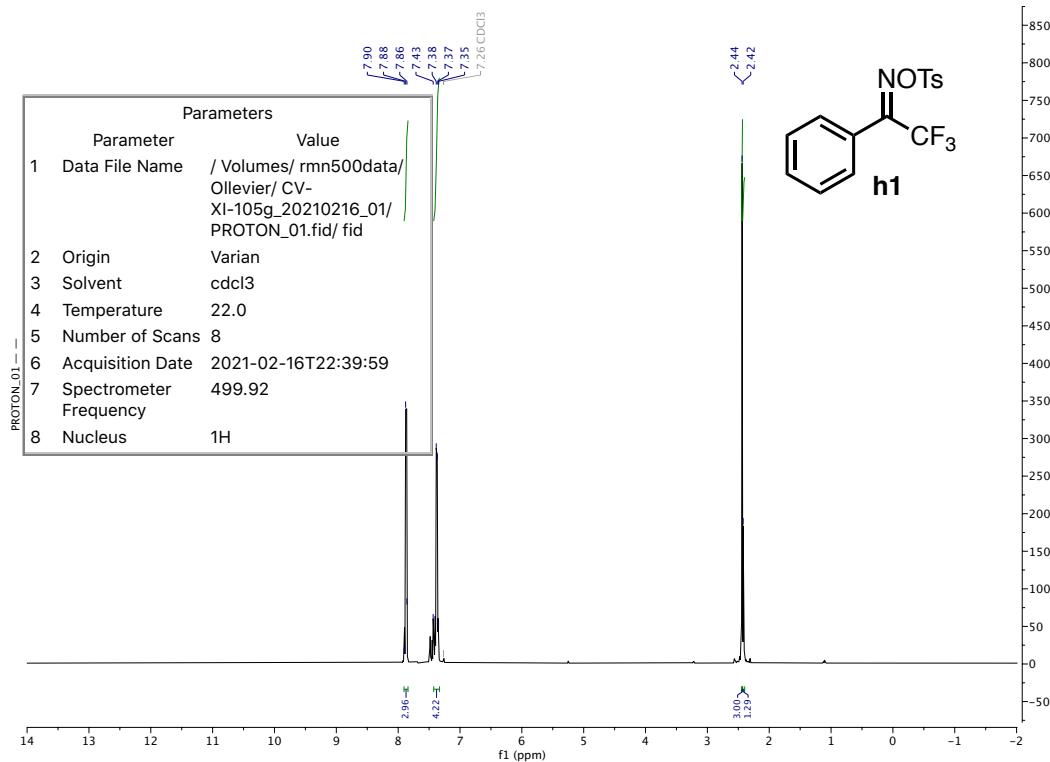


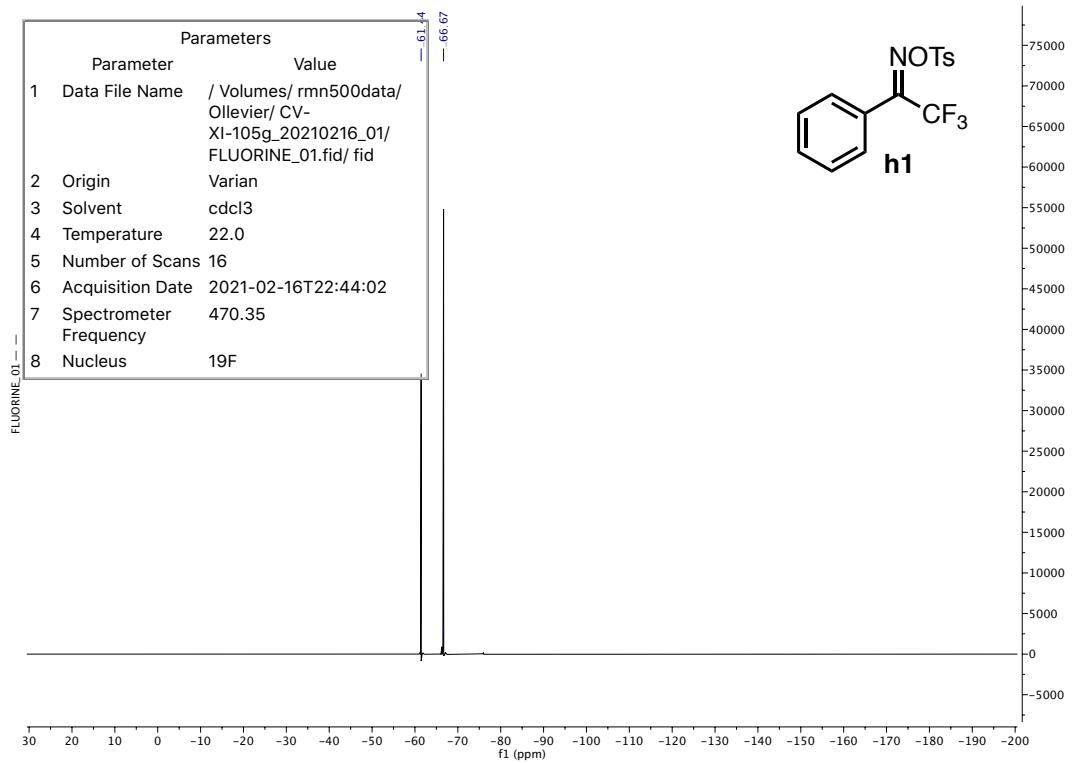
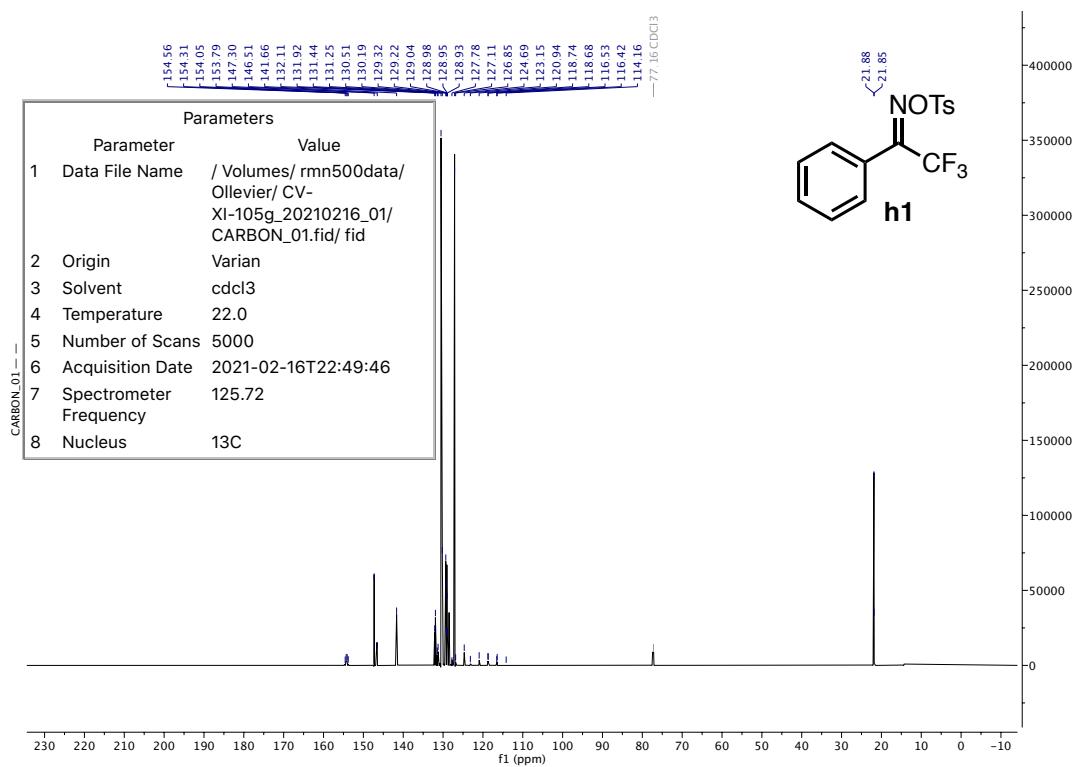
2,2,2-Trifluoro-1-(4-methoxyphenyl)ethan-1-one O-tosyl oxime g1



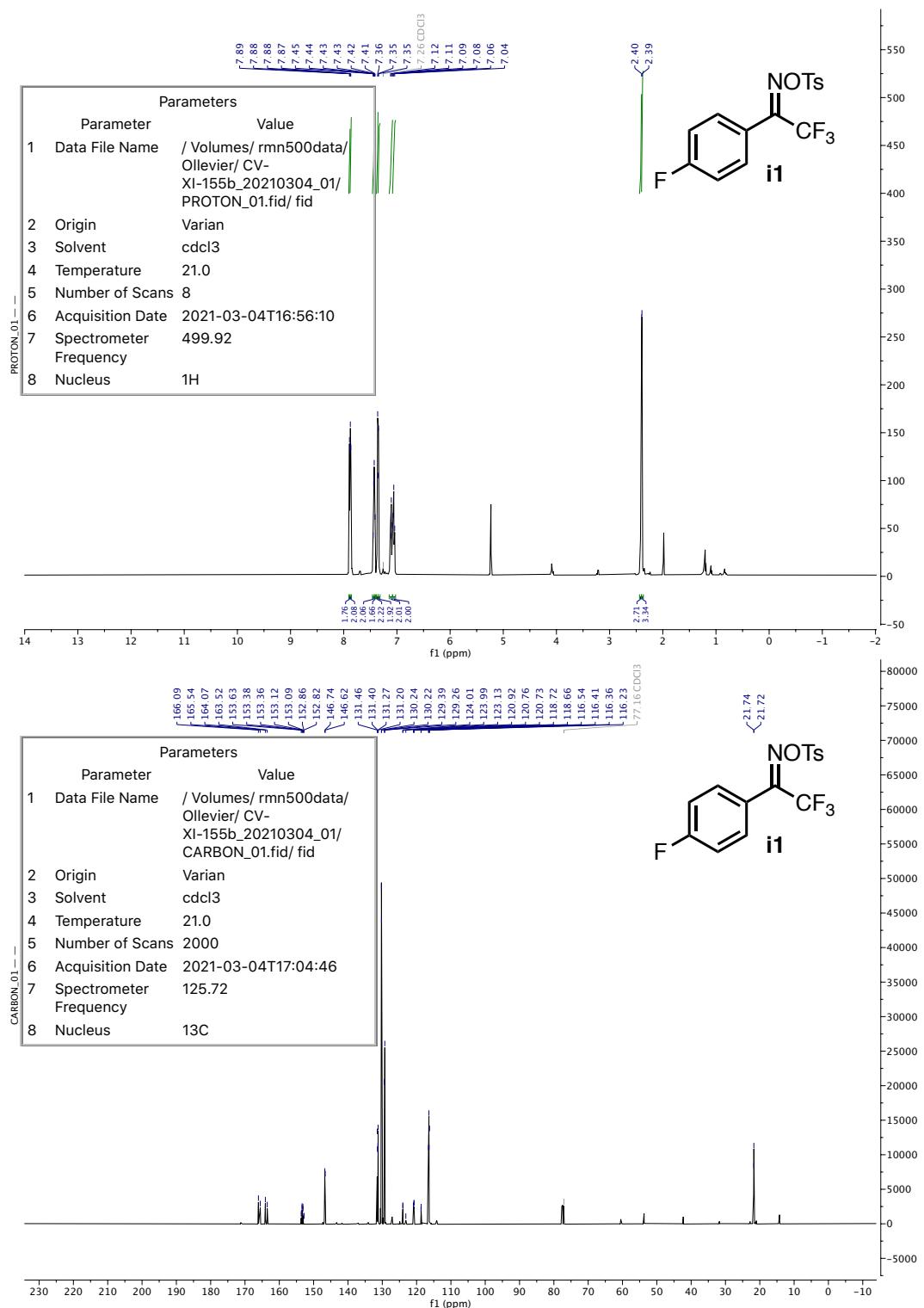


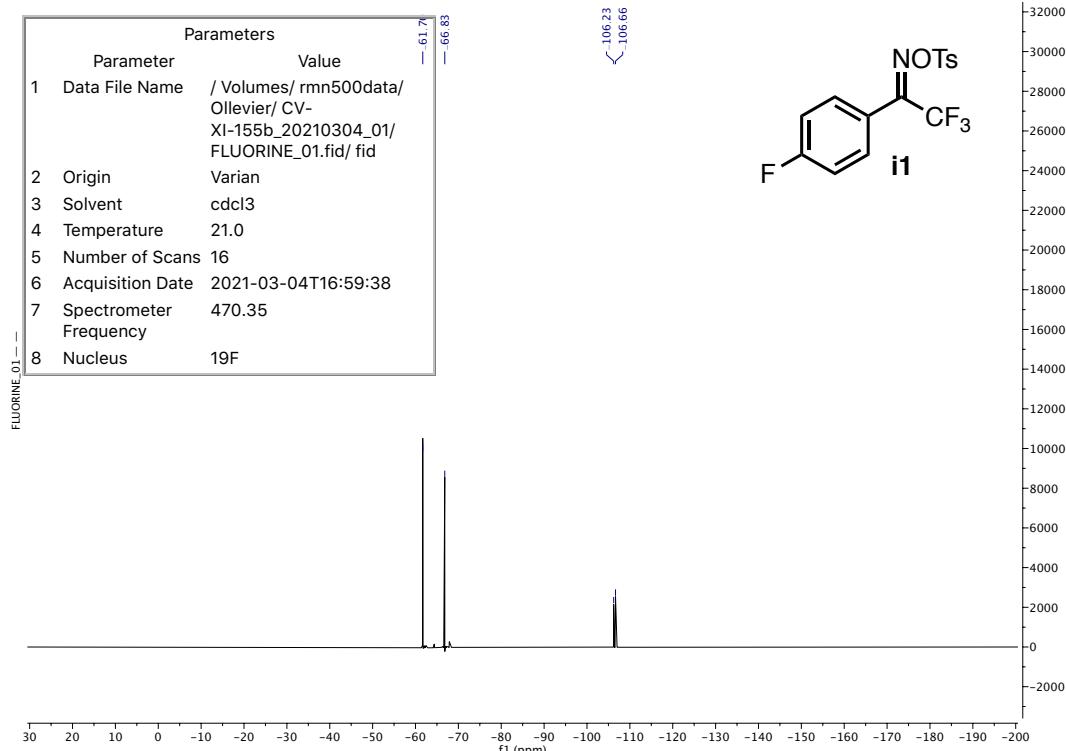
2,2,2-Trifluoro-1-phenylethan-1-one O-tosyl oxime h1



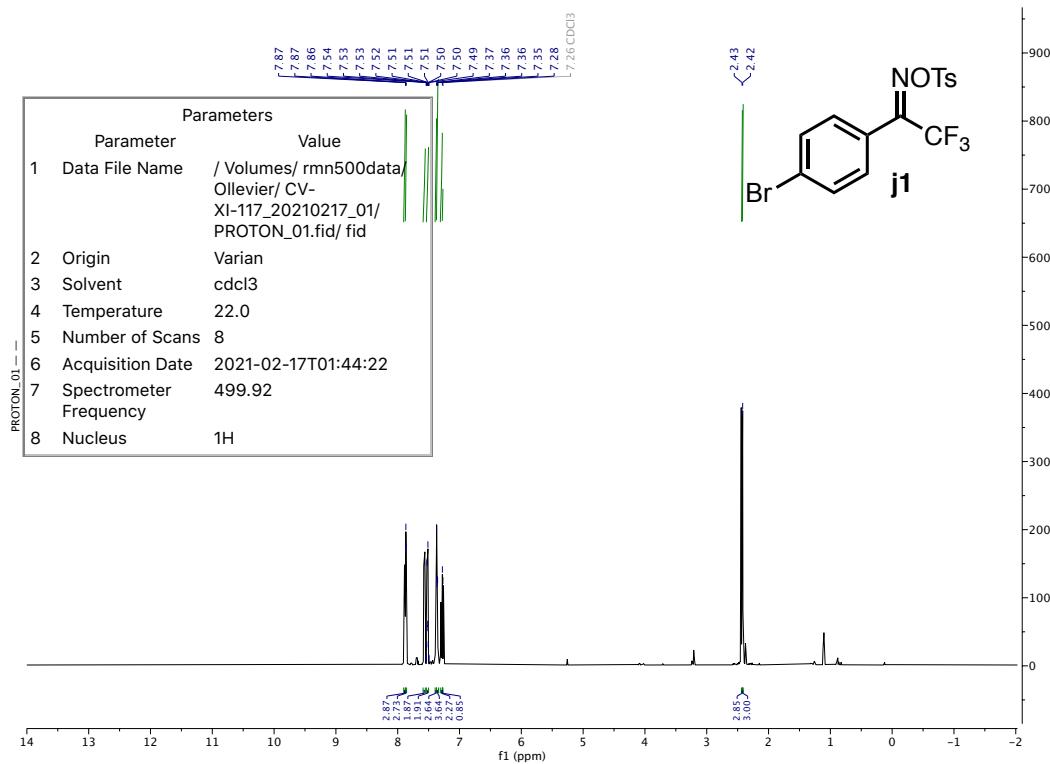


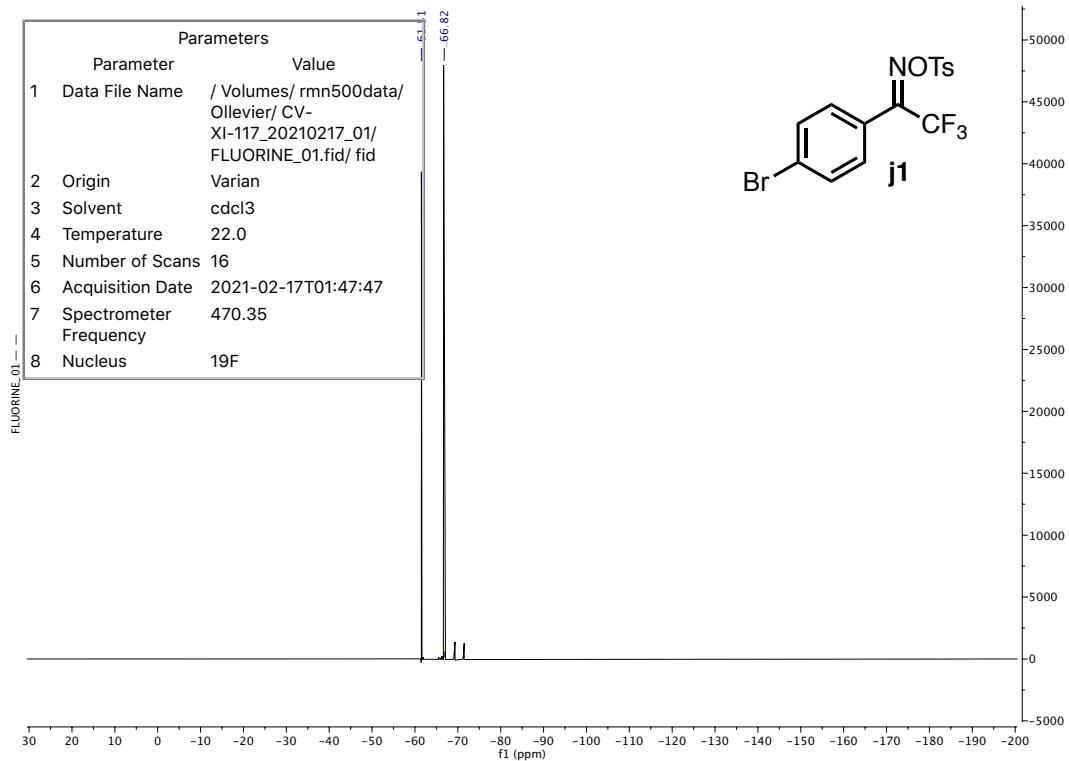
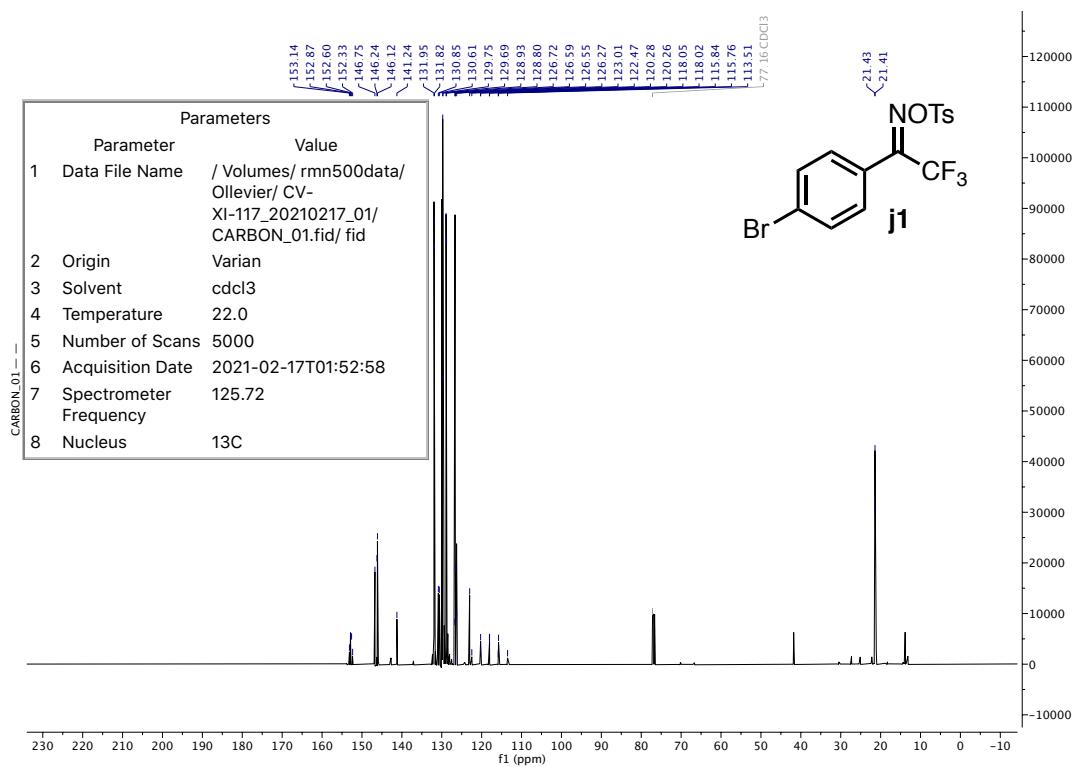
2,2,2-Trifluoro-1-(4-fluorophenyl)ethan-1-one O-tosyl oxime i1



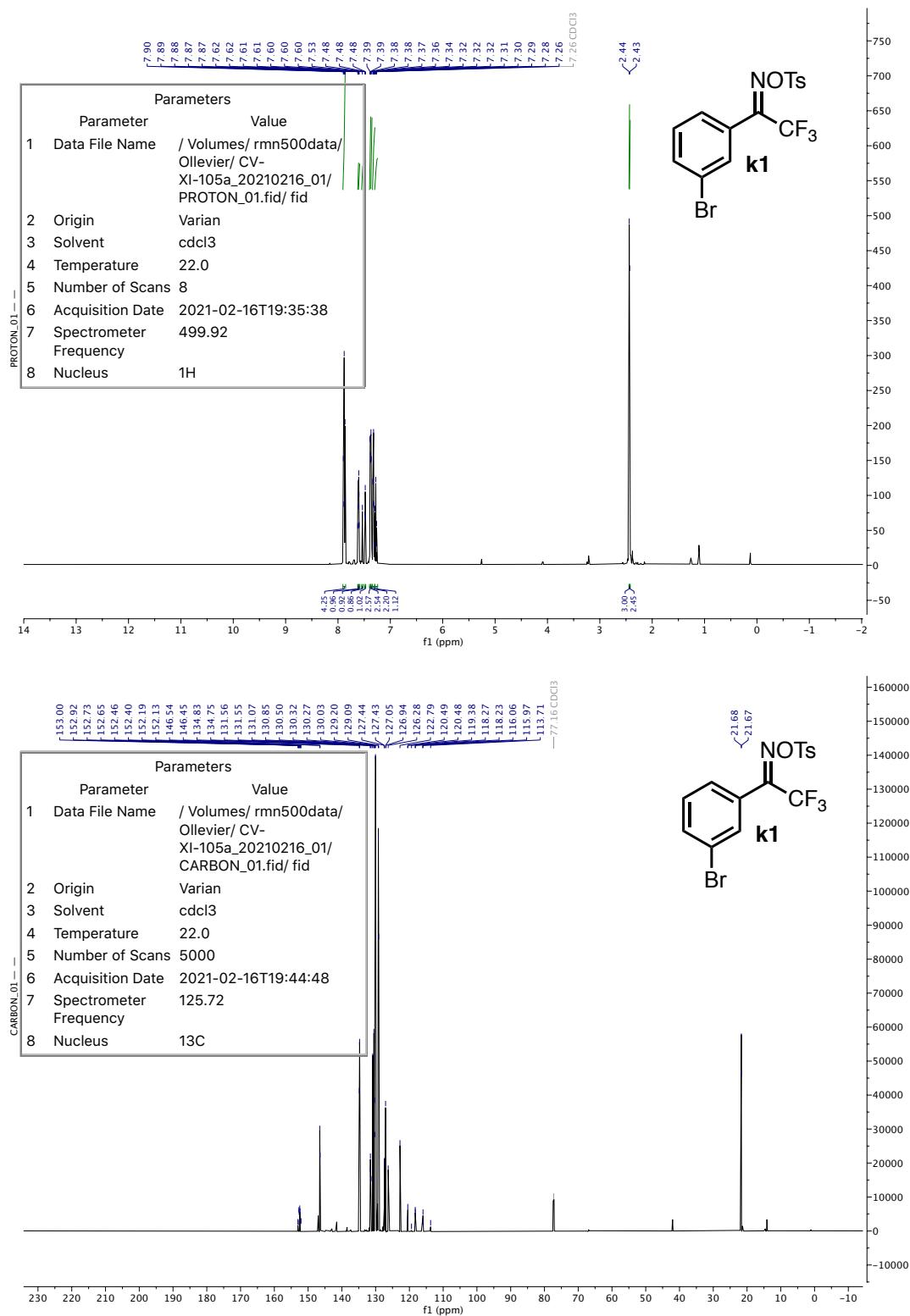


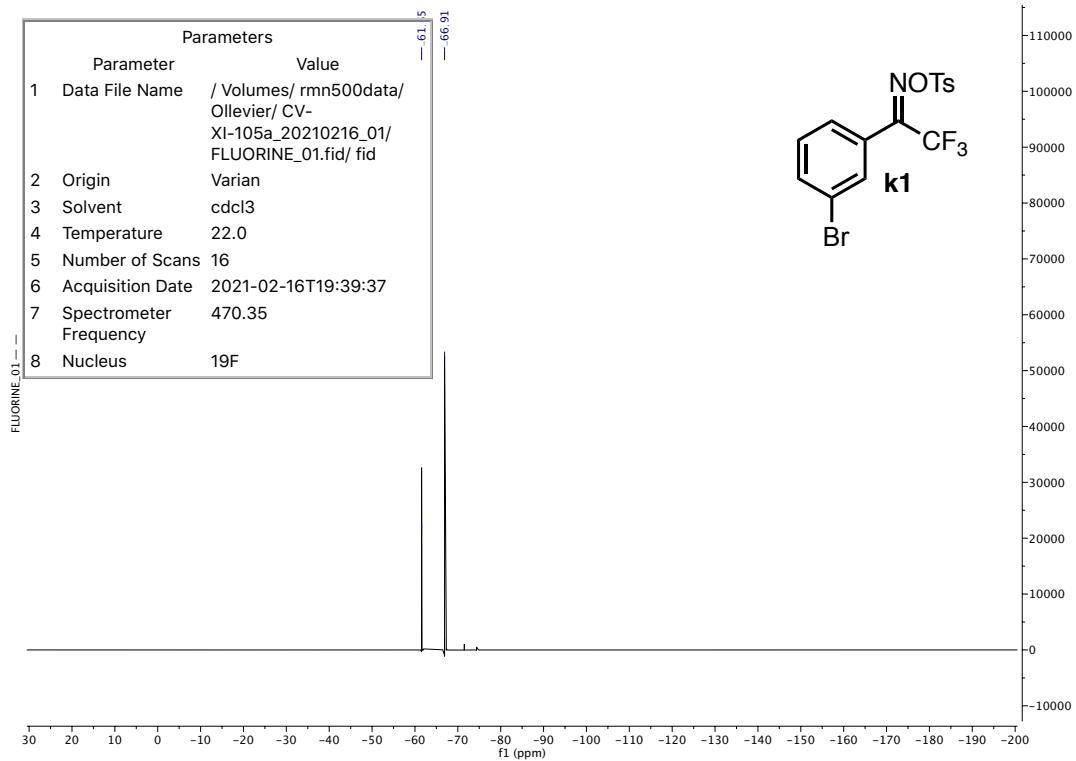
1-(4-Bromophenyl)-2,2,2-trifluoroethan-1-one O-tosyl oxime j1



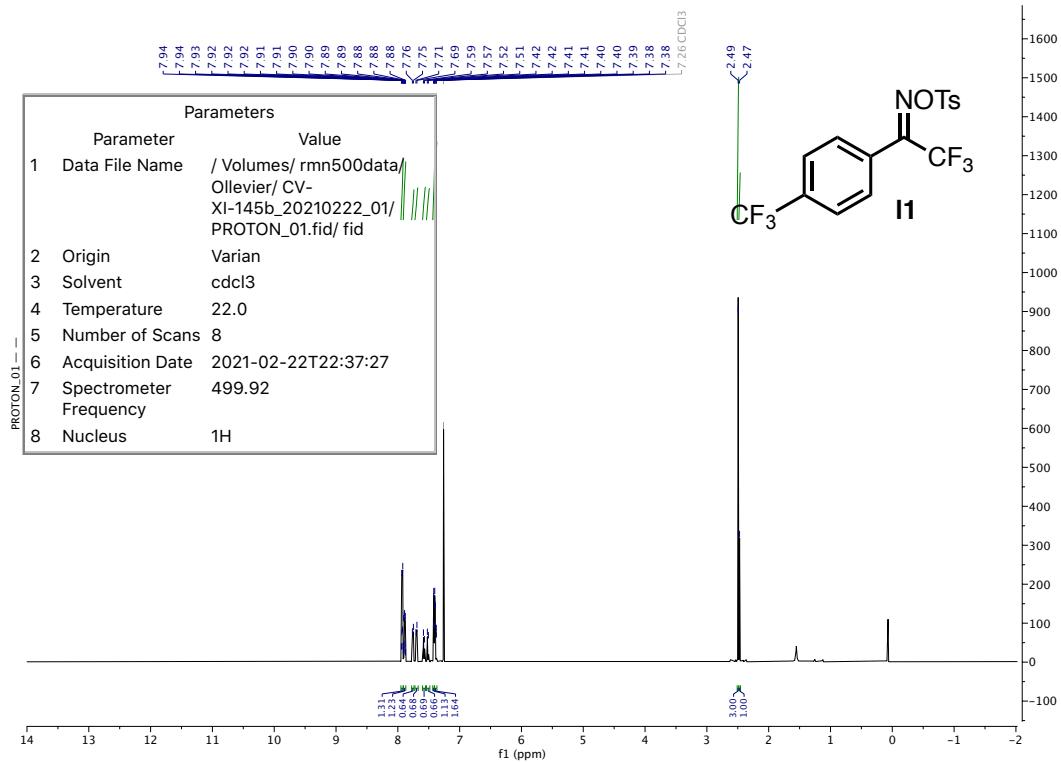


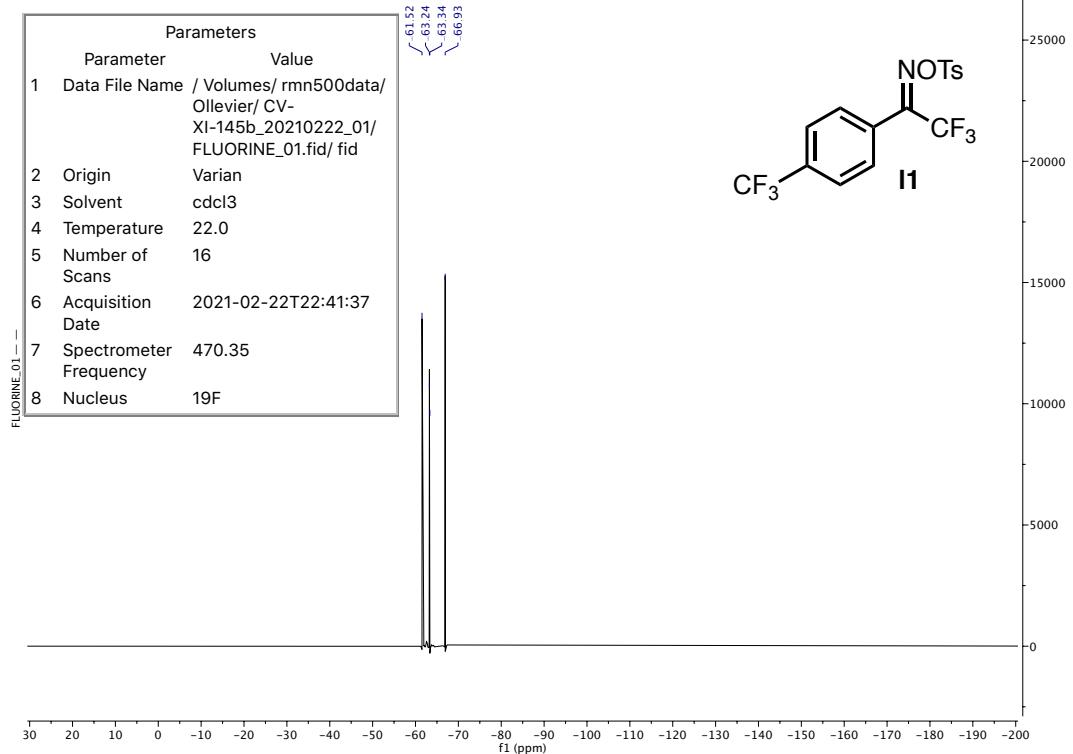
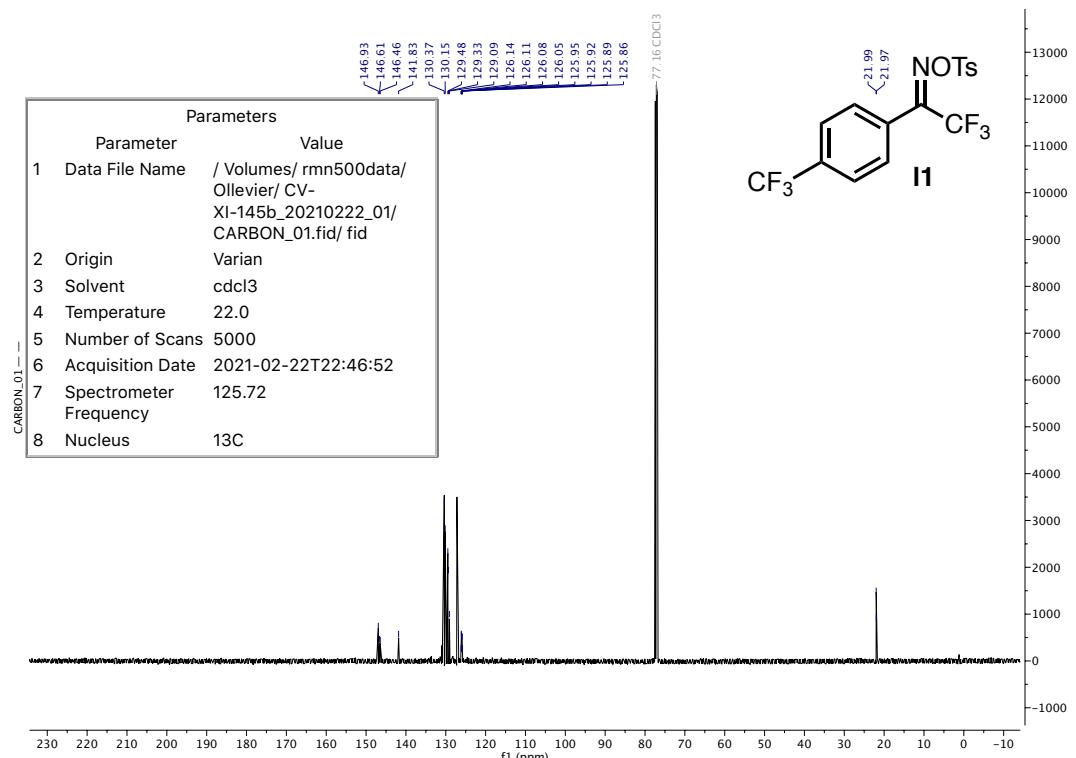
1-(3-Bromophenyl)-2,2,2-trifluoroethan-1-one O-tosyl oxime k1



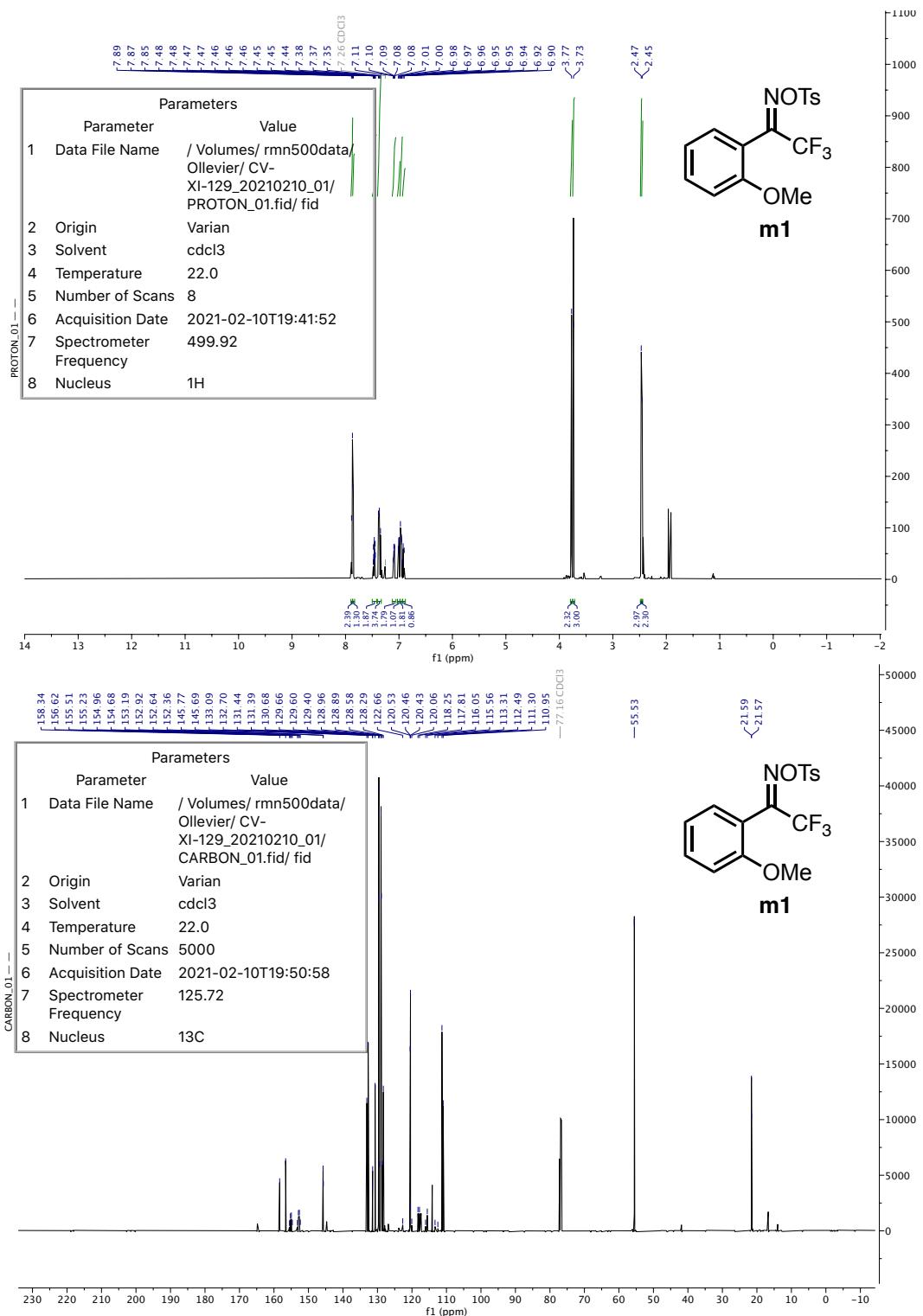


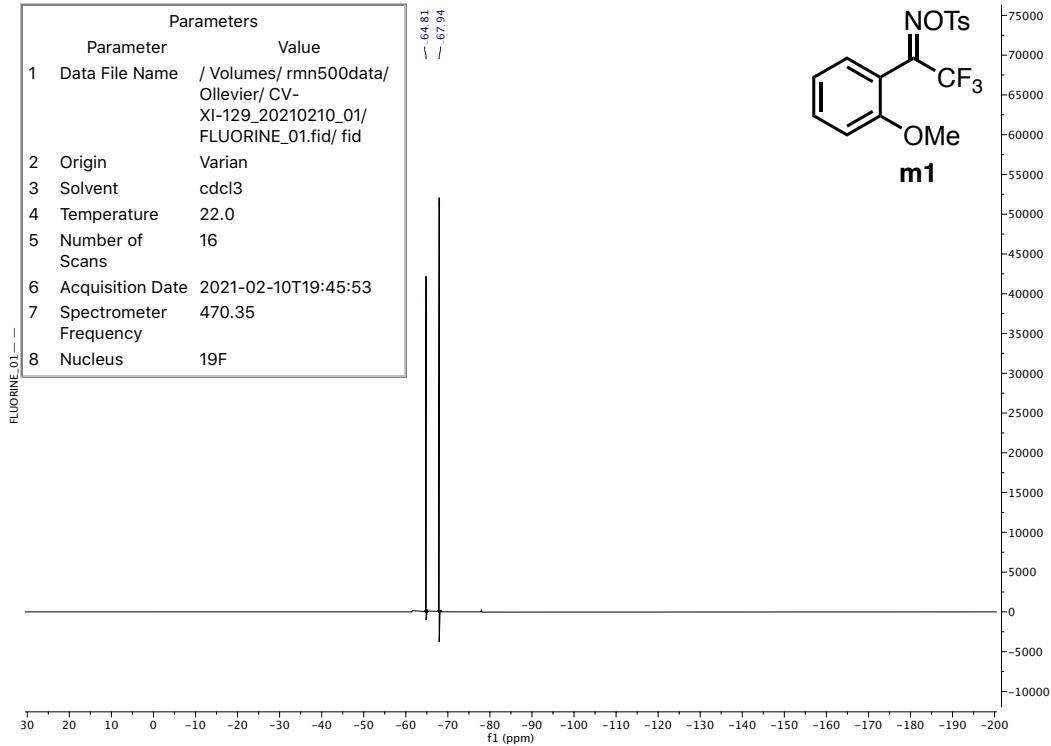
2,2,2-Trifluoro-1-(4-(trifluoromethyl)phenyl)ethan-1-one O-tosyl oxime I1



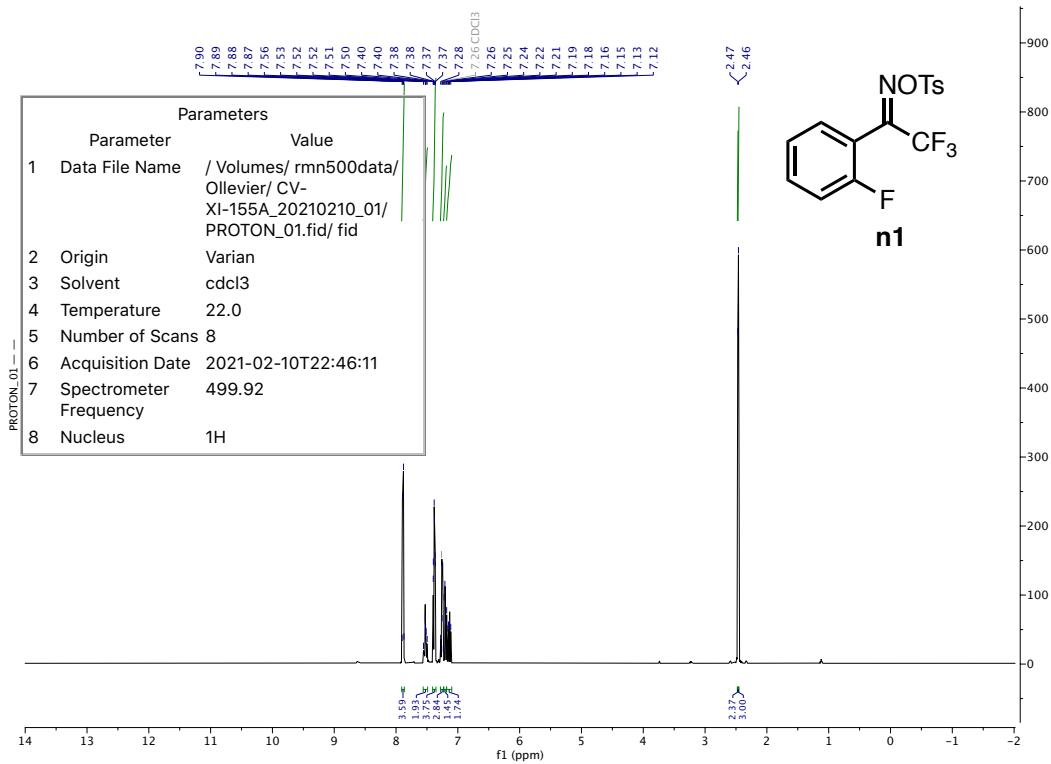


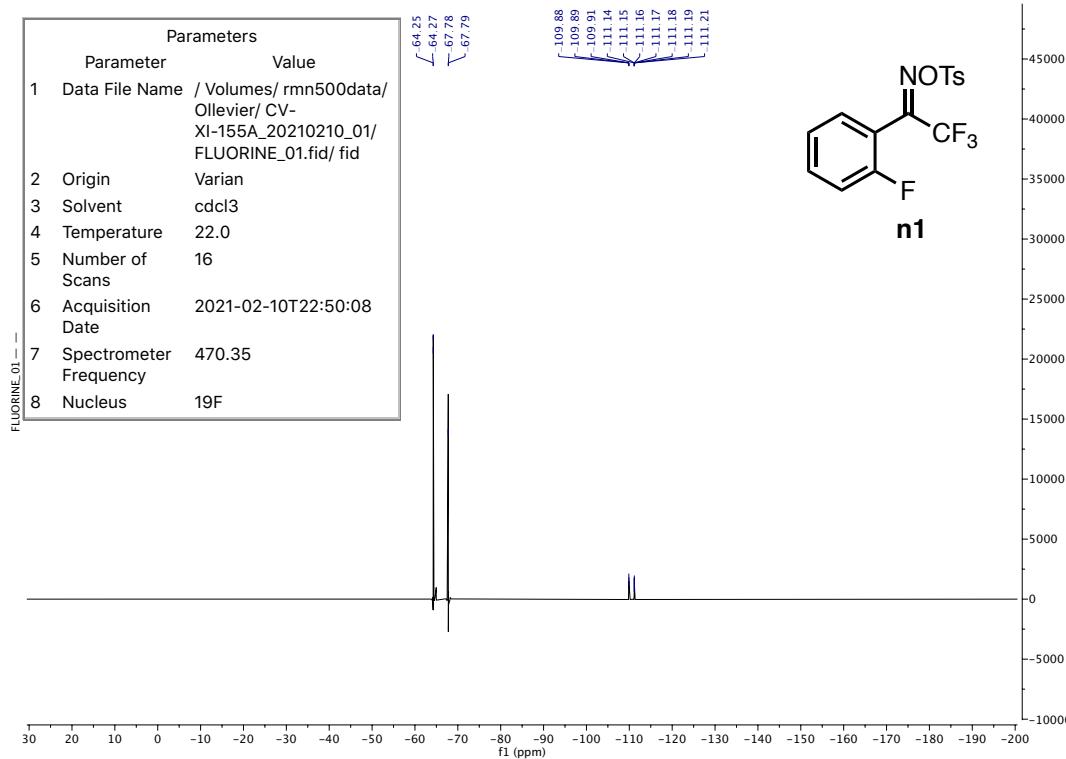
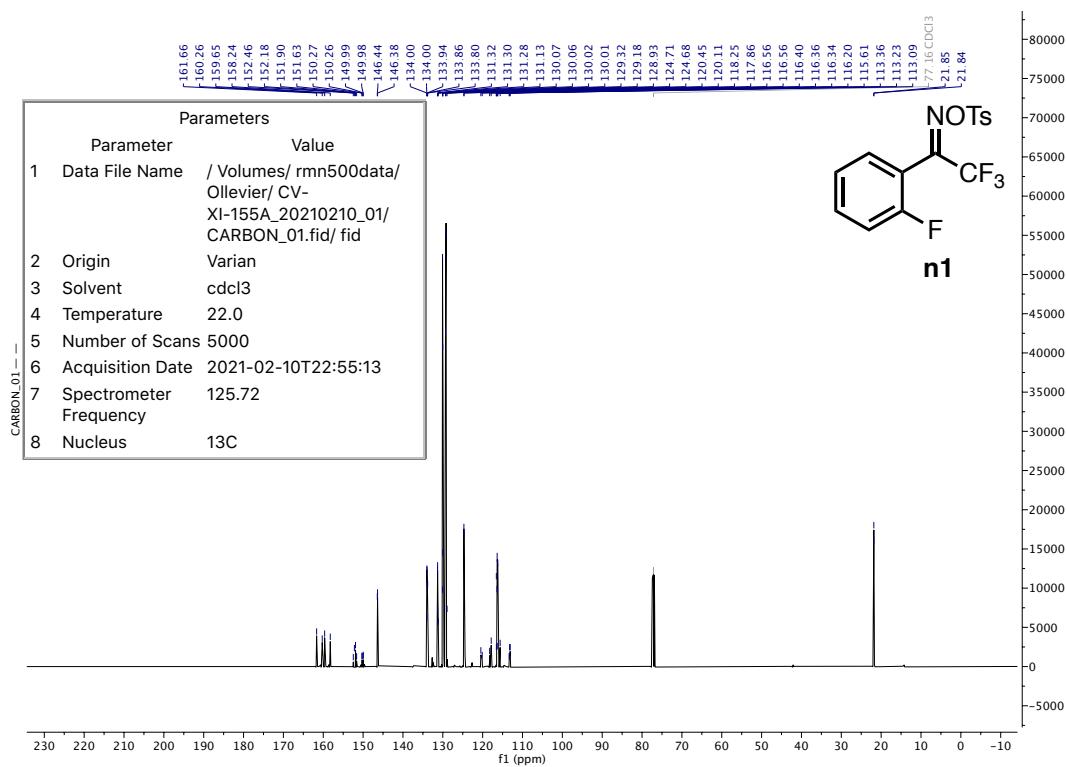
2,2,2-Trifluoro-1-(2-methoxyphenyl)ethan-1-one O-tosyl oxime m1



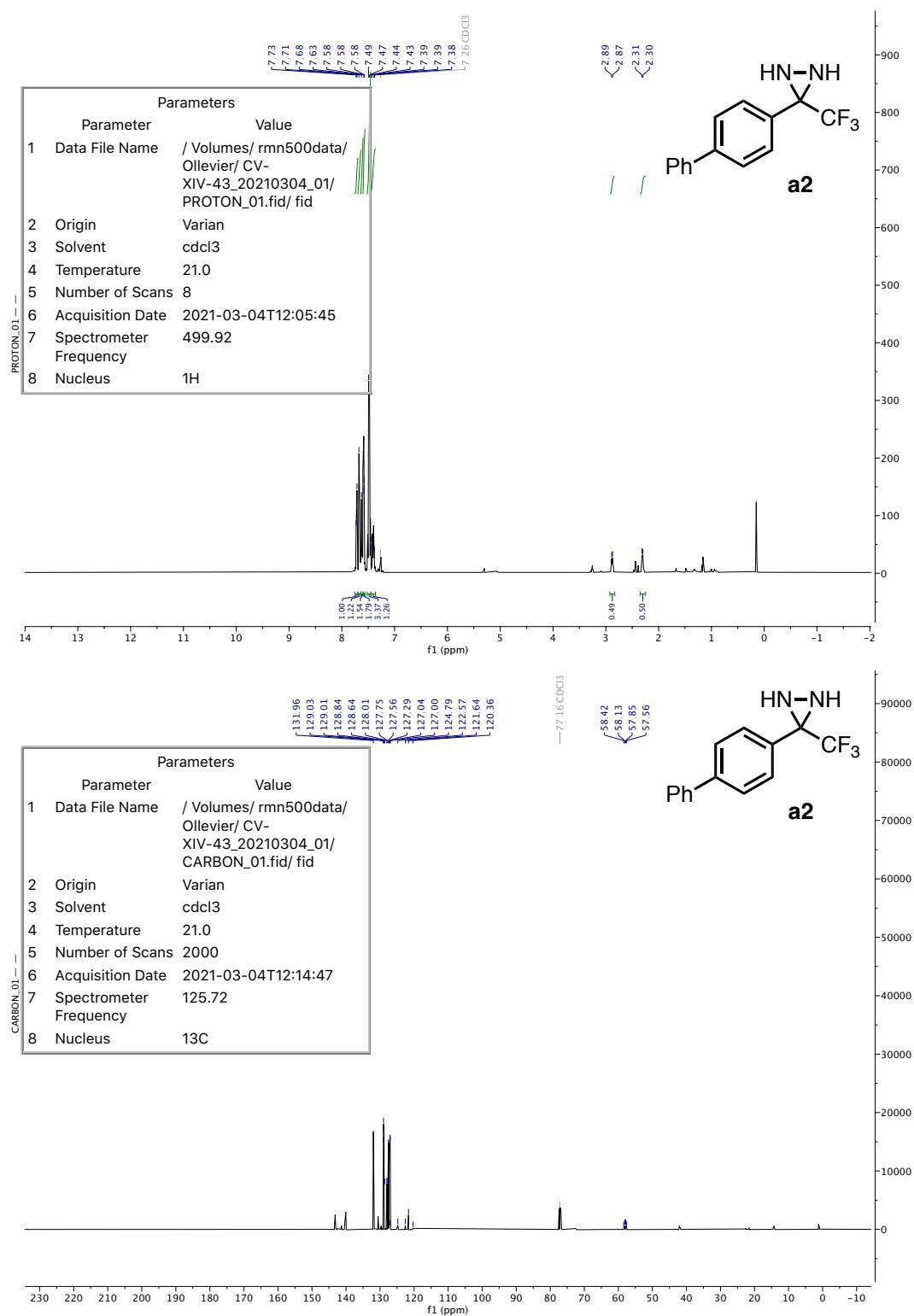


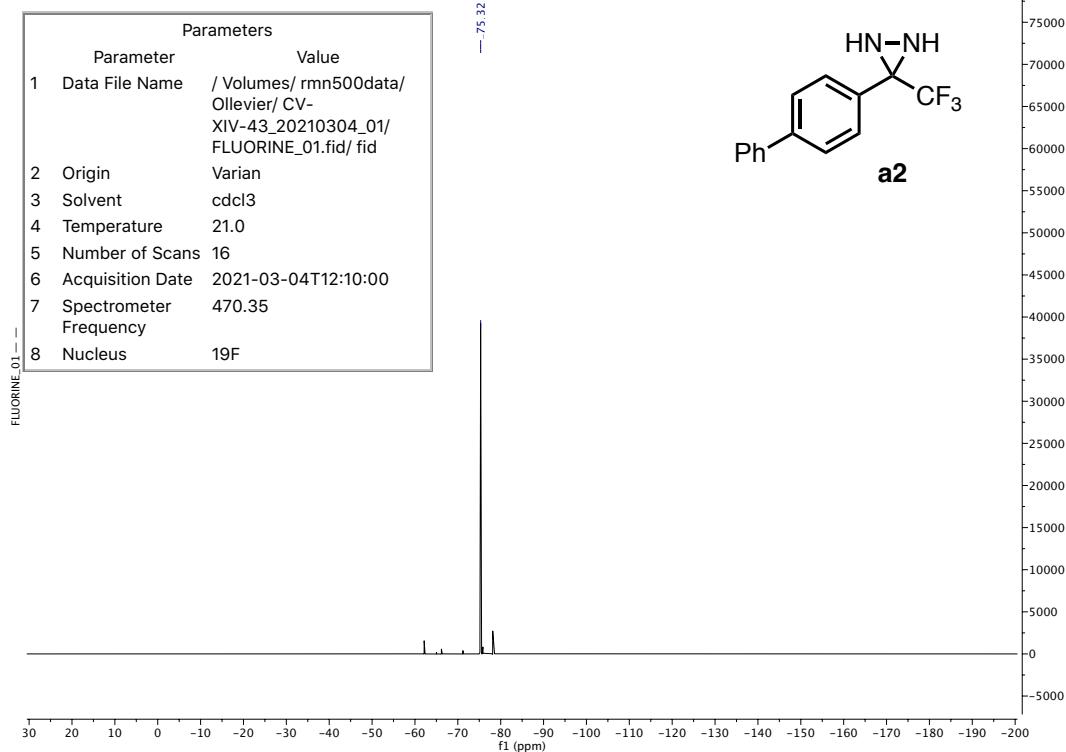
2,2,2-Trifluoro-1-(2-fluorophenyl)ethan-1-one O-tosyl oxime n1



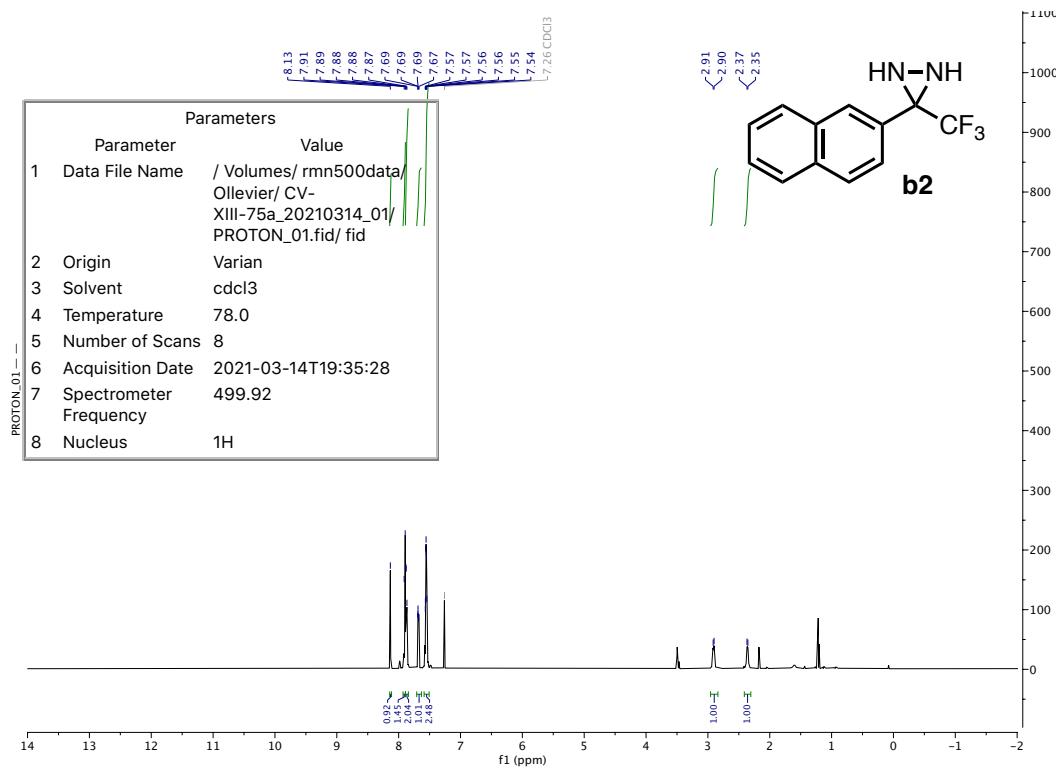


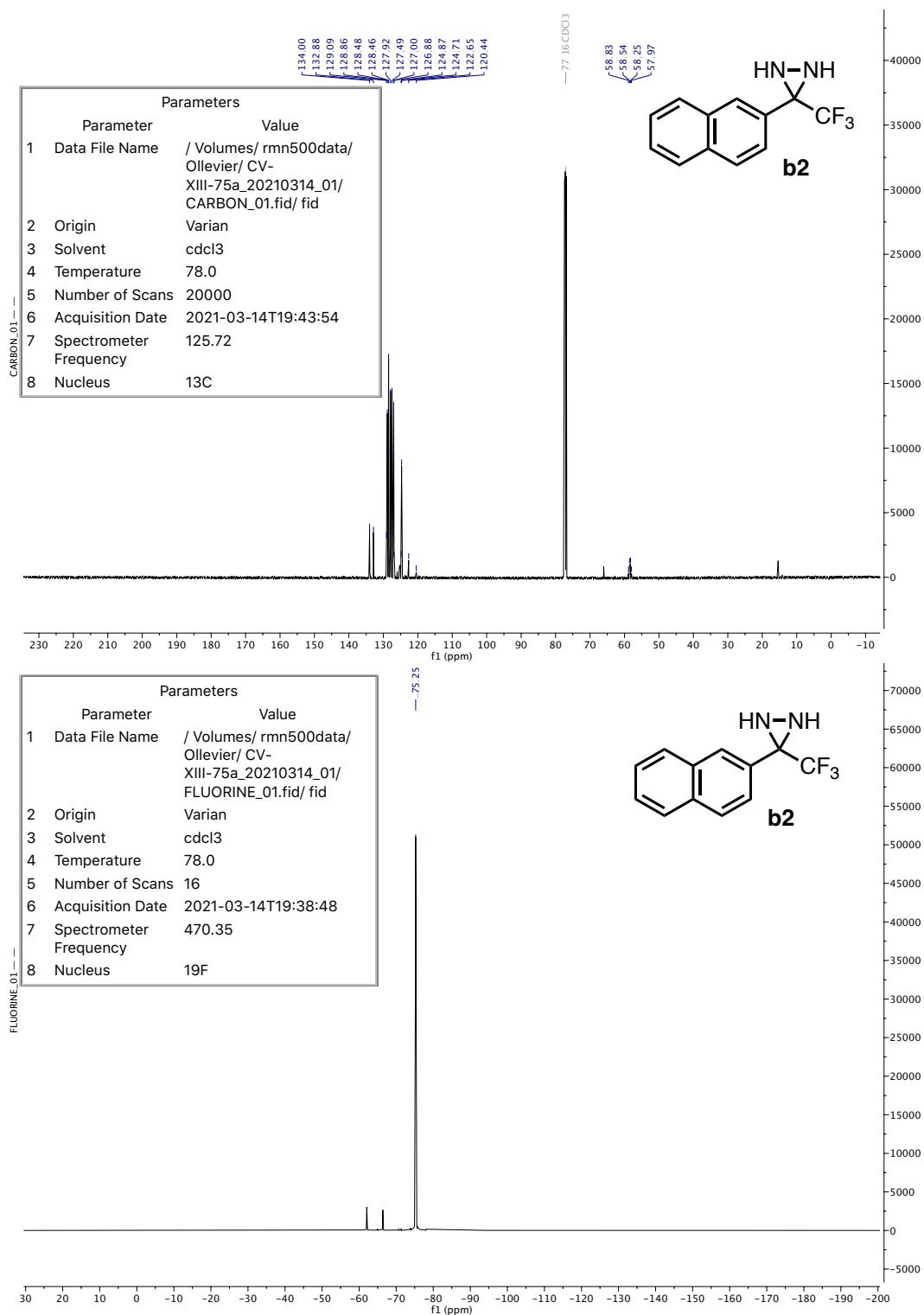
3-(4,4'-Biphenyl)-3-(trifluoromethyl)diaziridine a2



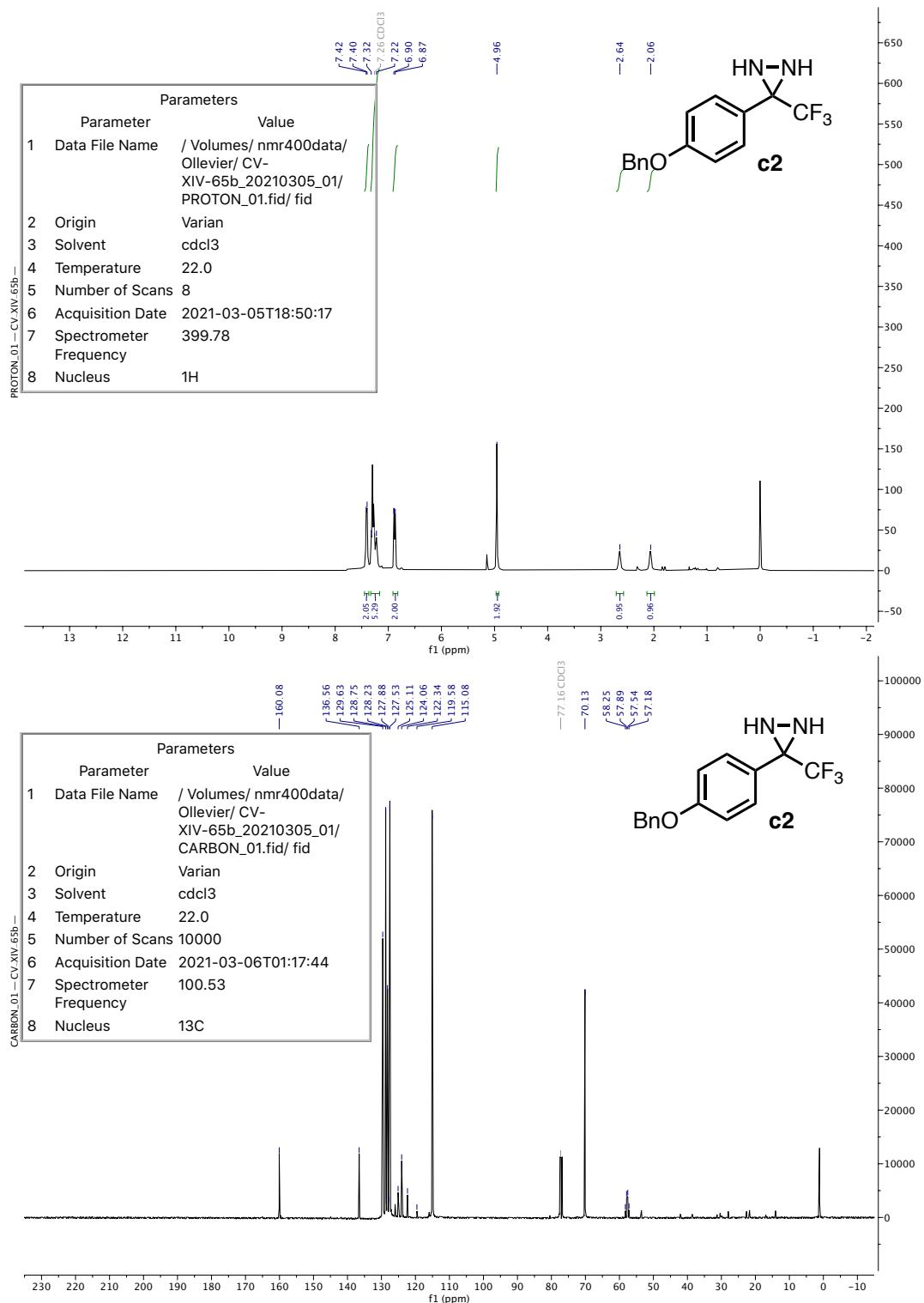


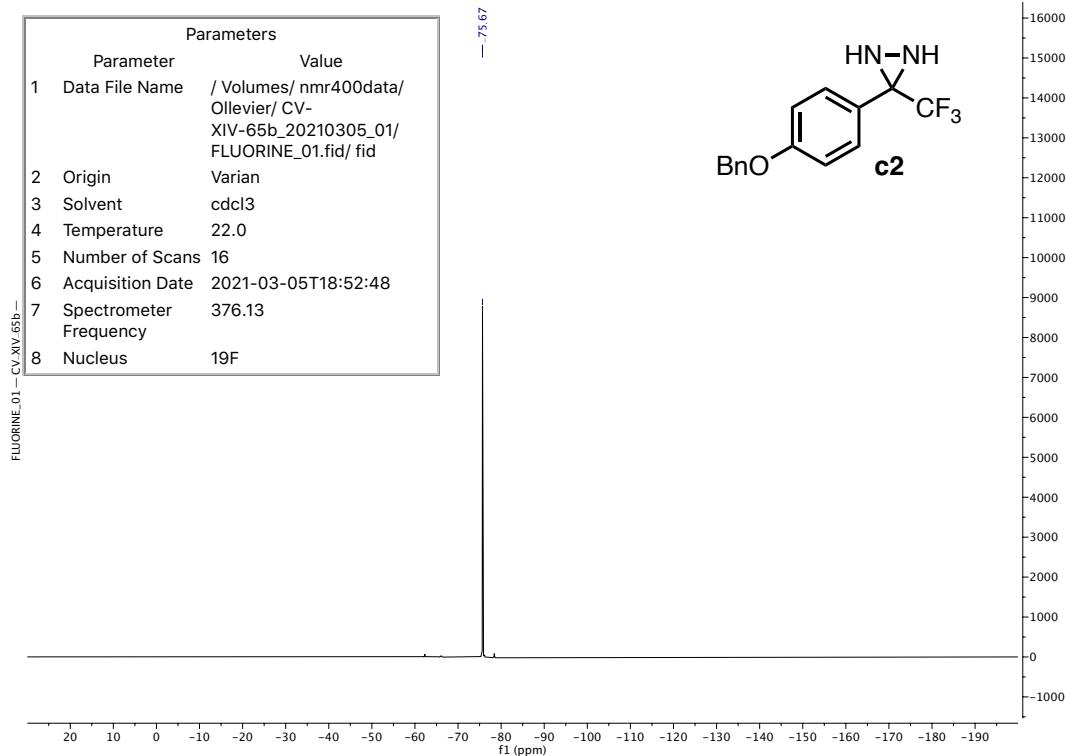
3-(Naphthalin-2-yl)-3-(trifluoromethyl)diaziridine **b2**



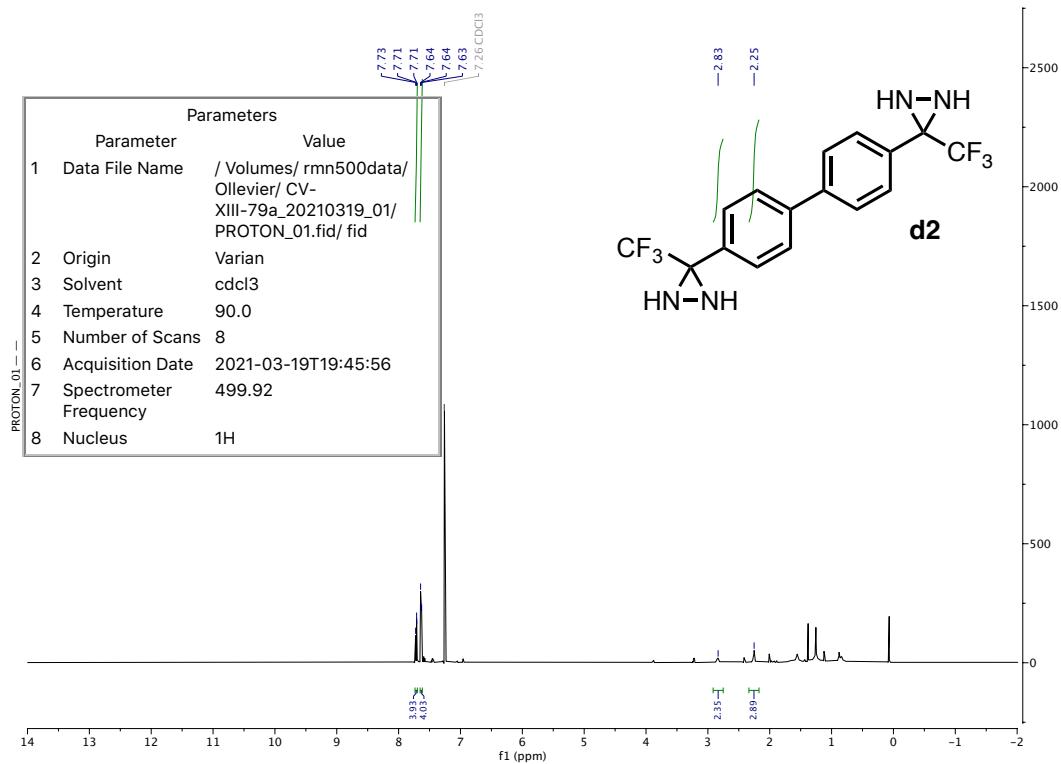


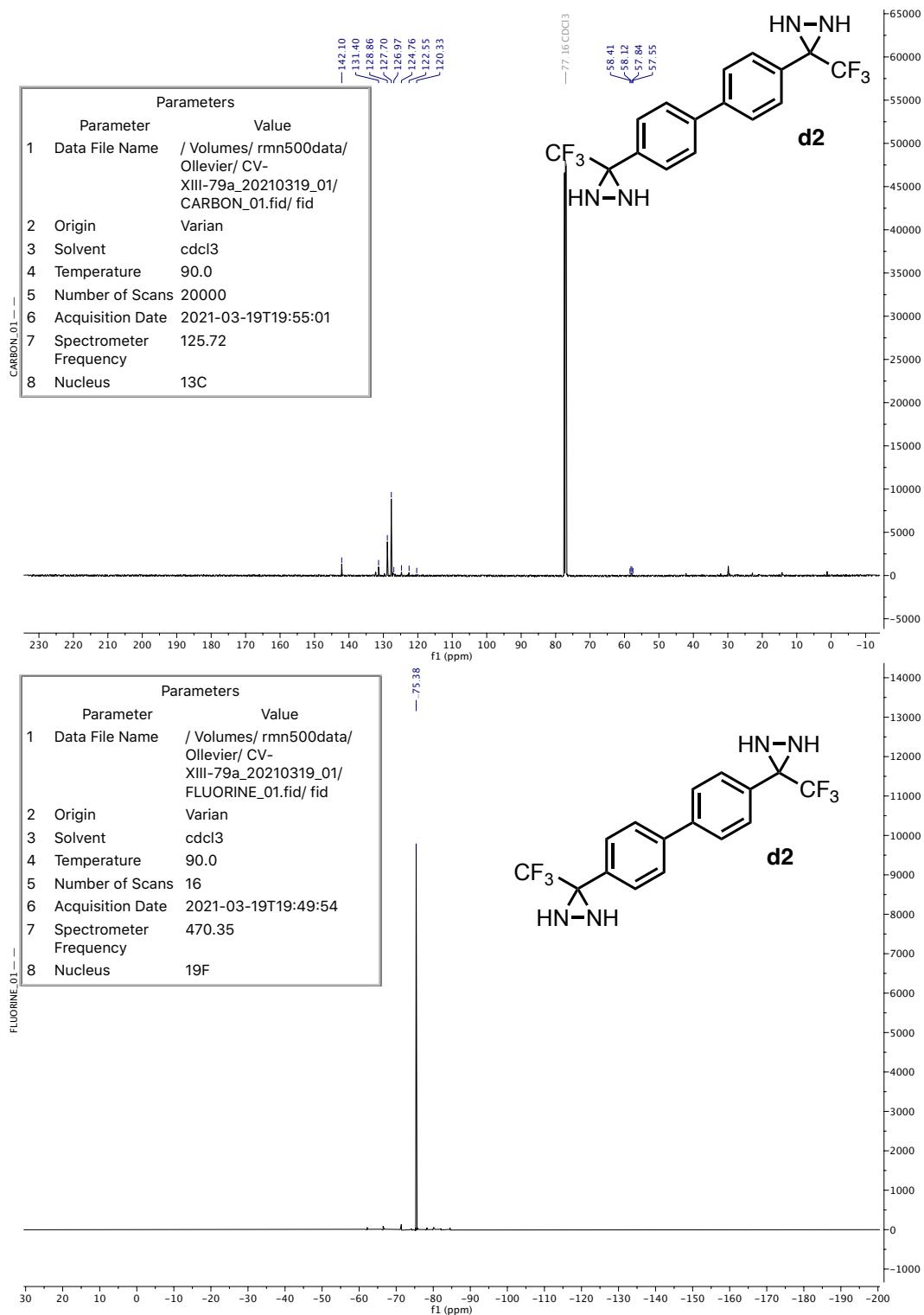
3-(4-Benzylxyphenyl)-3-(trifluoromethyl)diaziridine c2



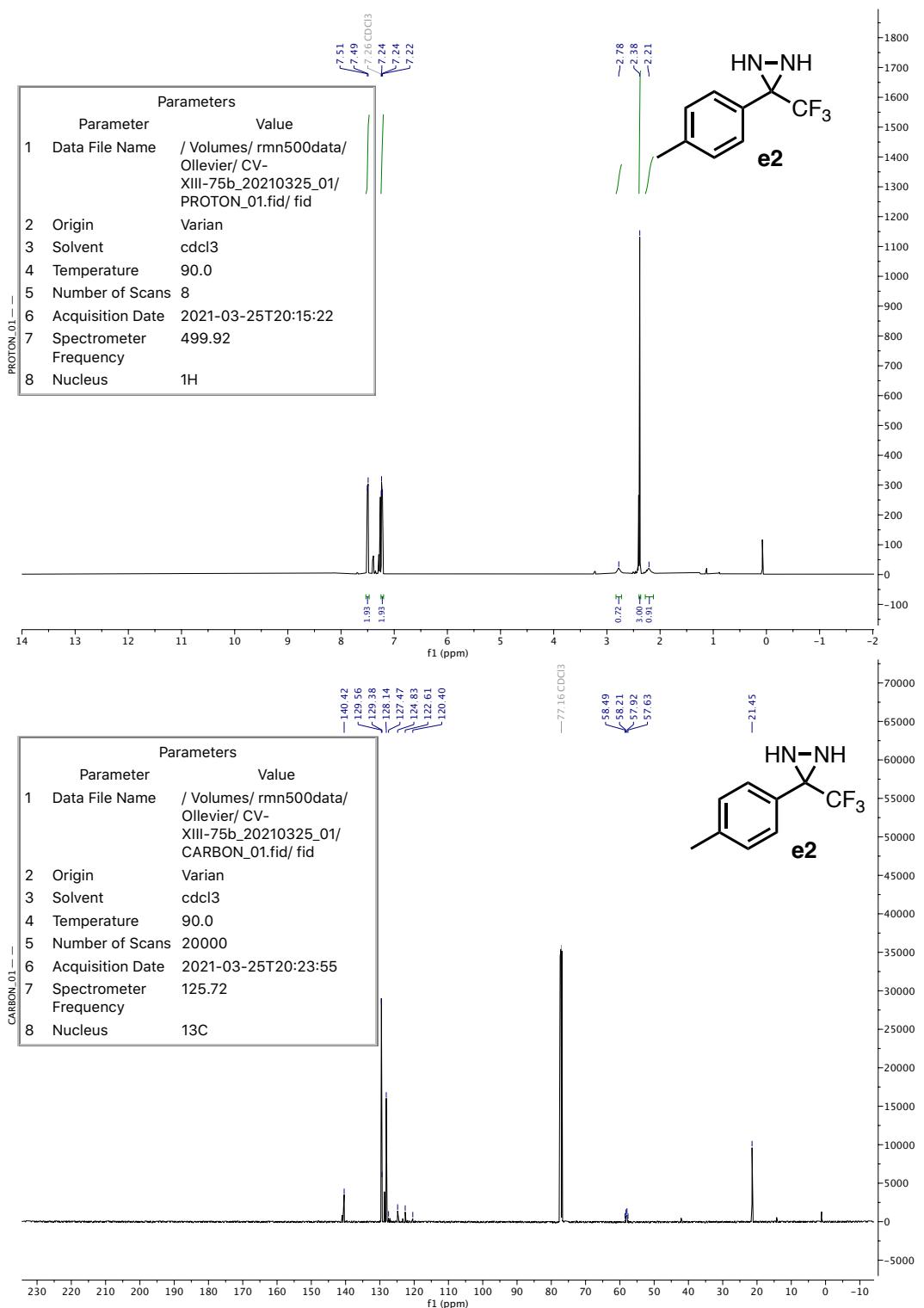


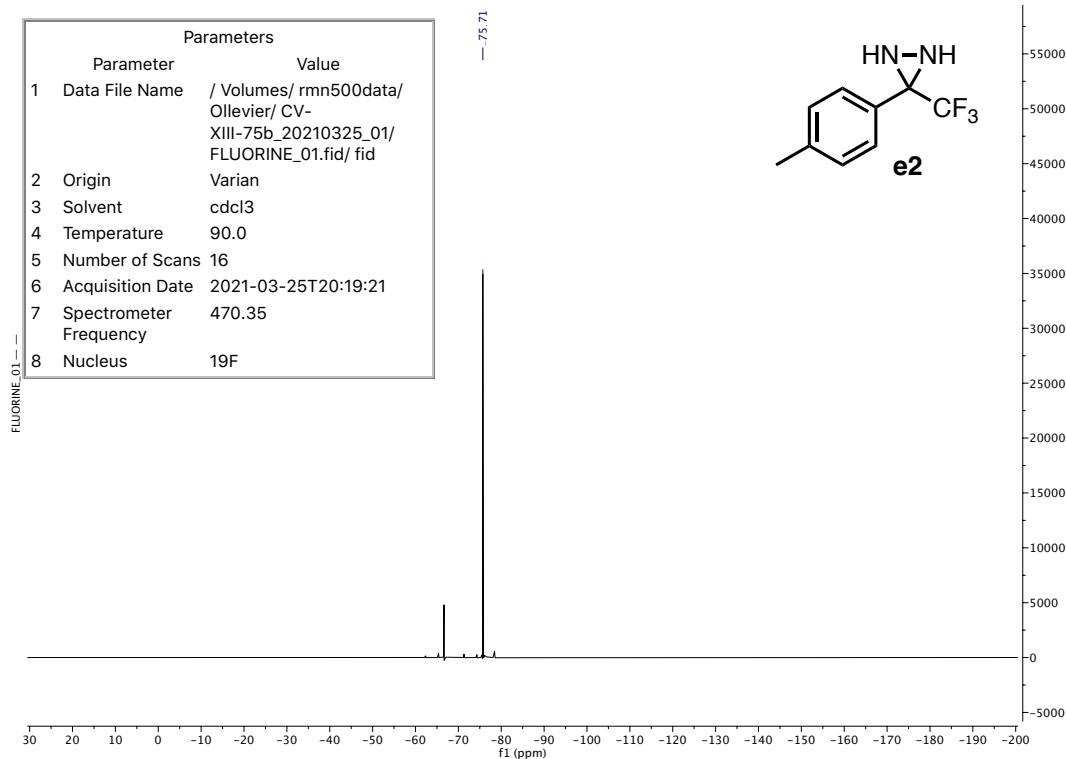
Bis-(4,4'-biphenyl)-3-(trifluoromethyl)diaziridine d2



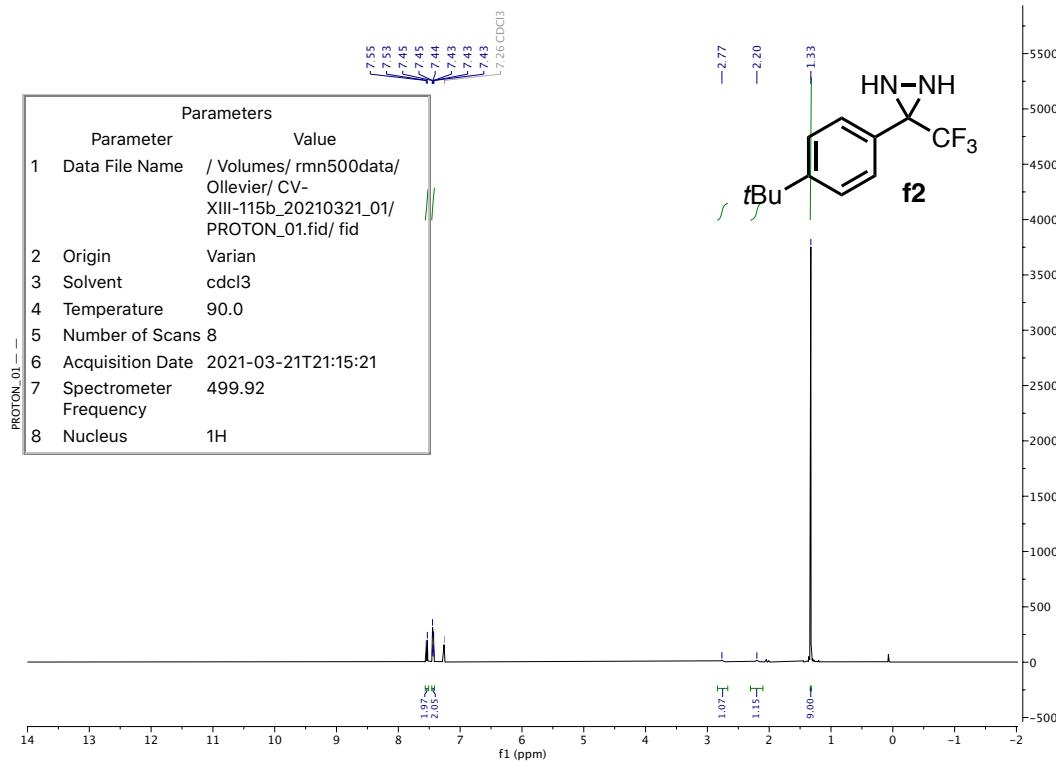


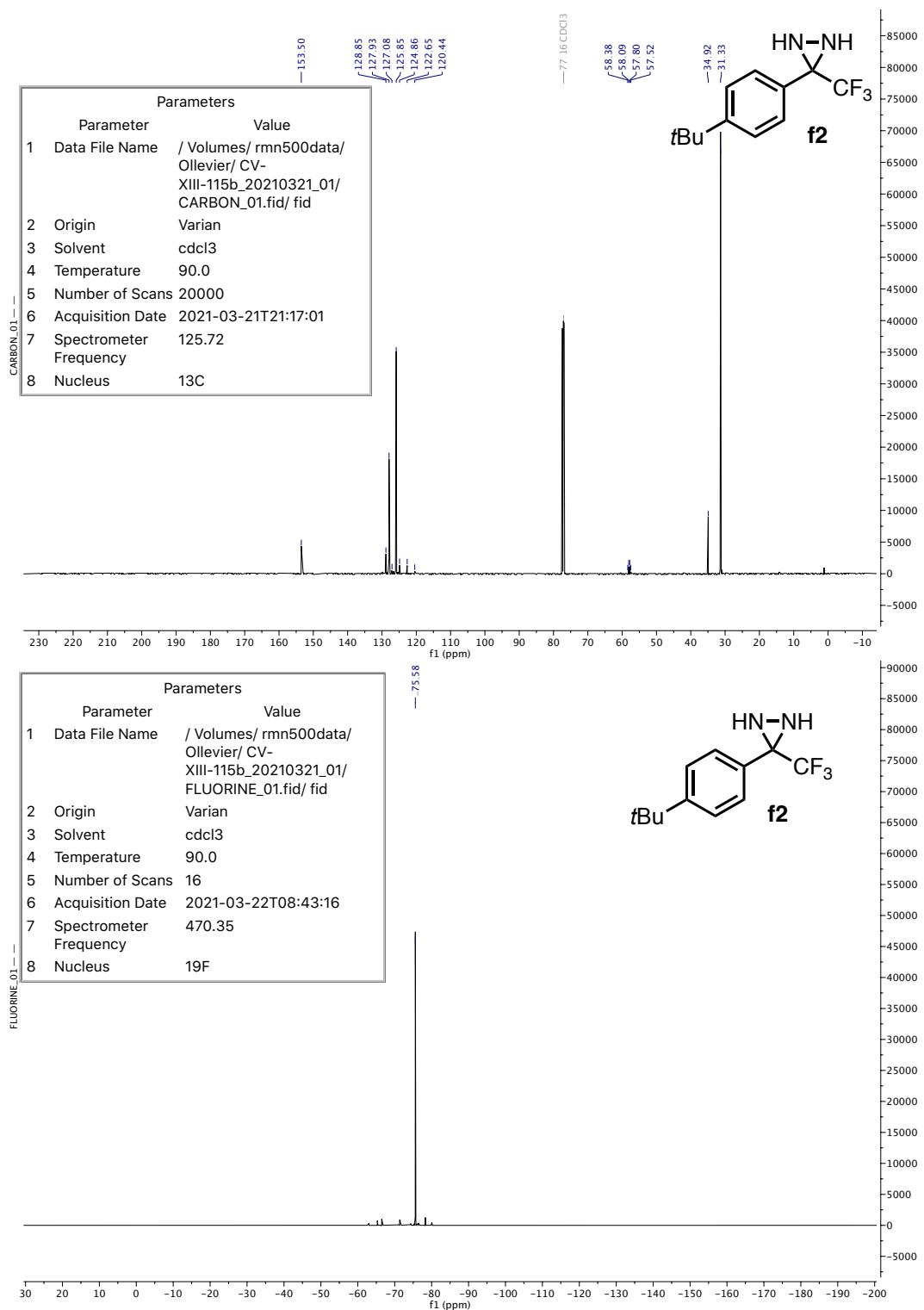
3-(*p*-Tolyl)-3-(trifluoromethyl)diaziridine e2



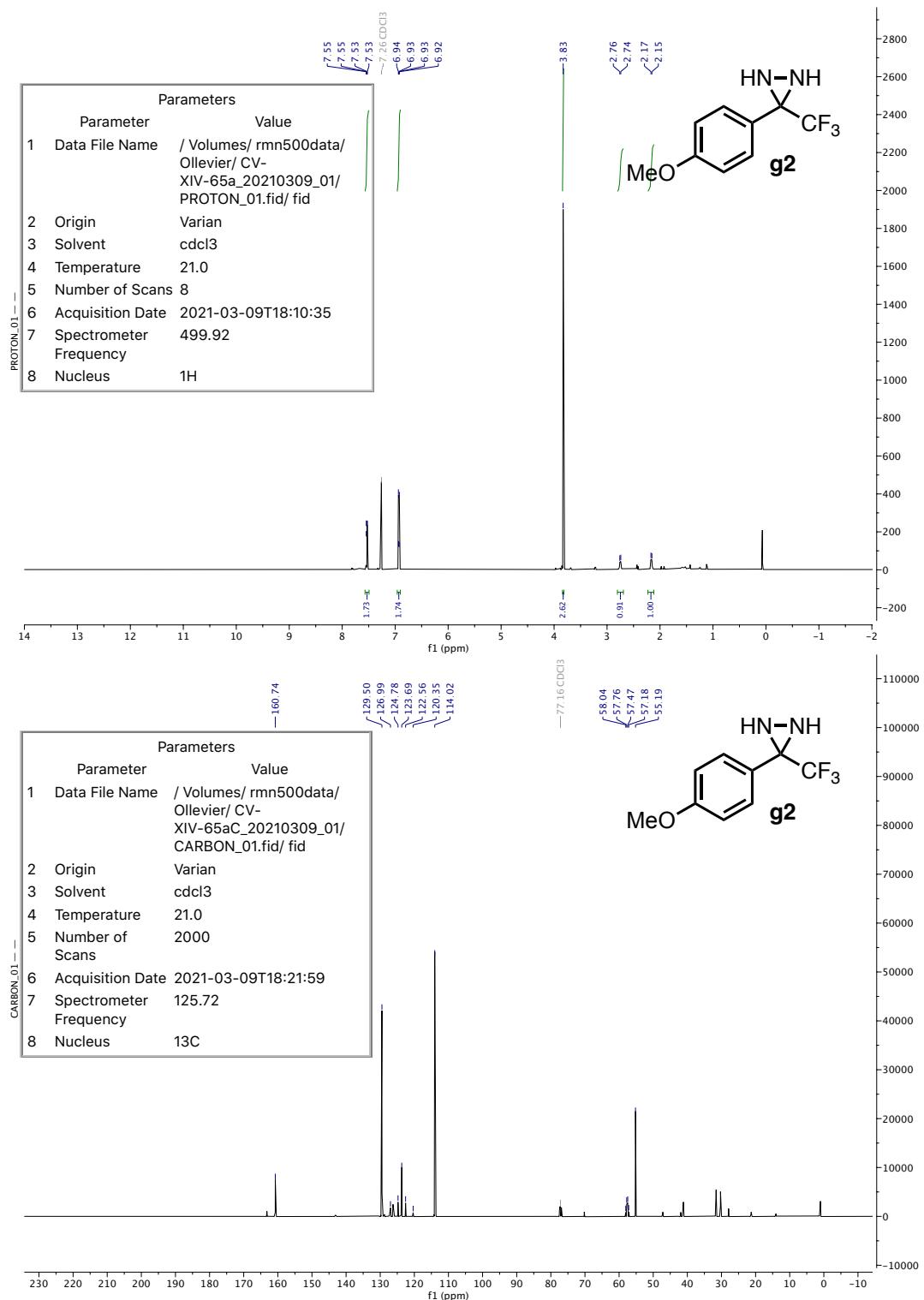


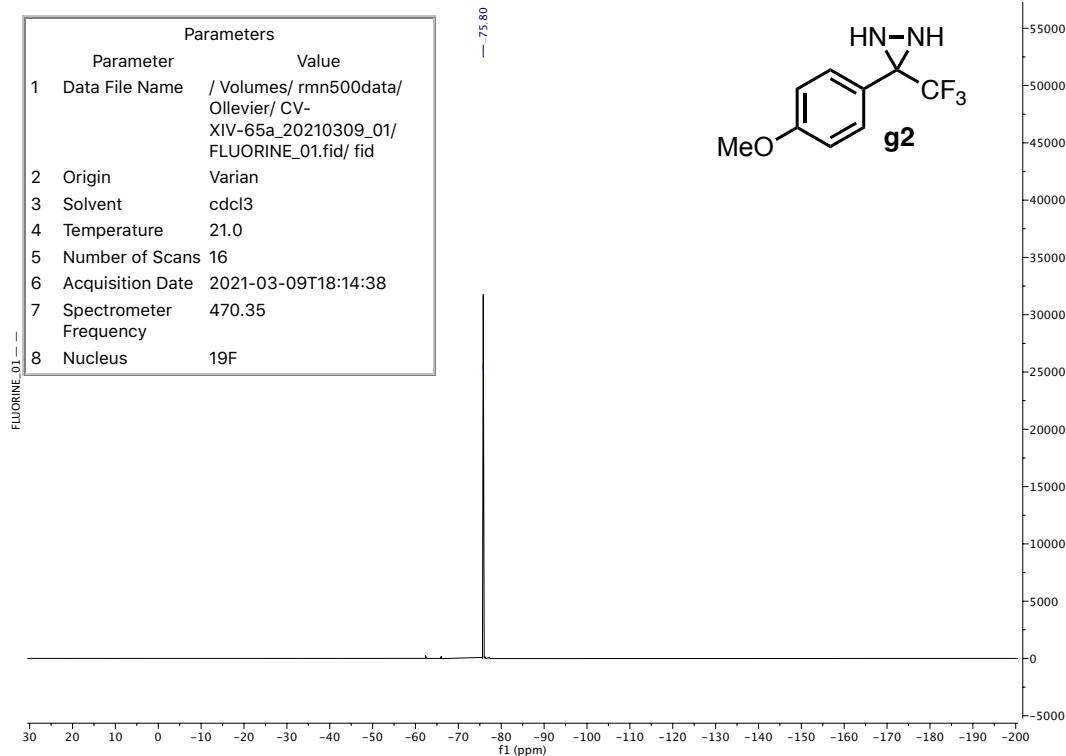
3-(4-Tert-butylphenyl)-3-(trifluoromethyl)diaziridine **f2**



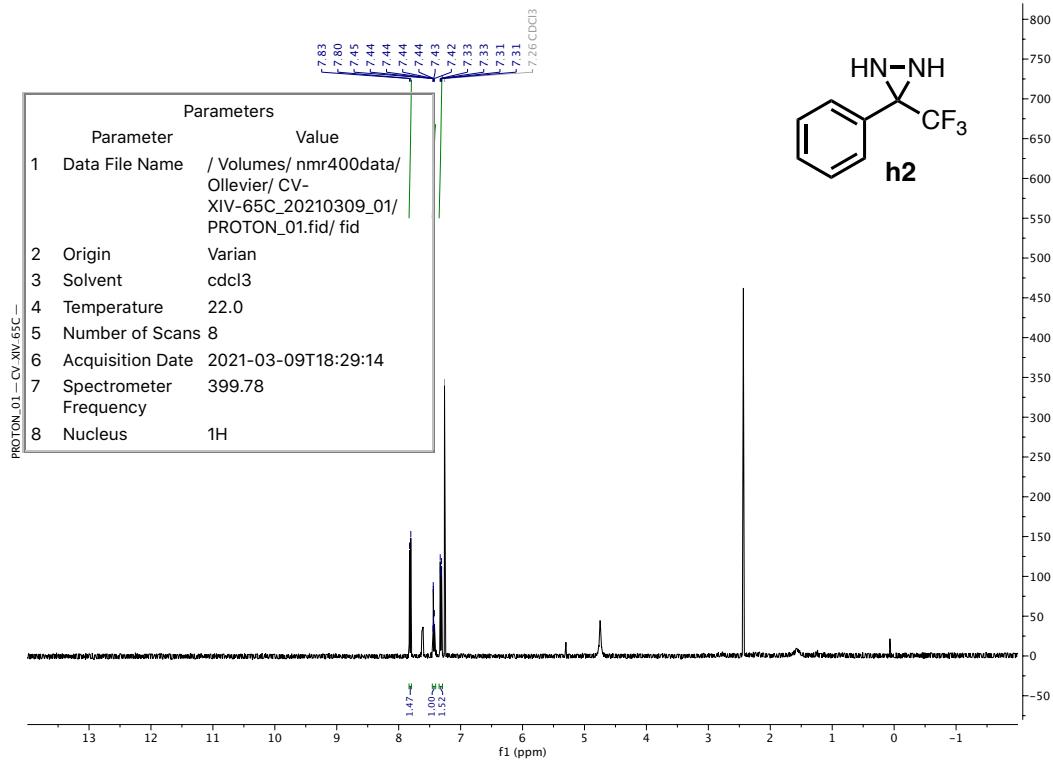


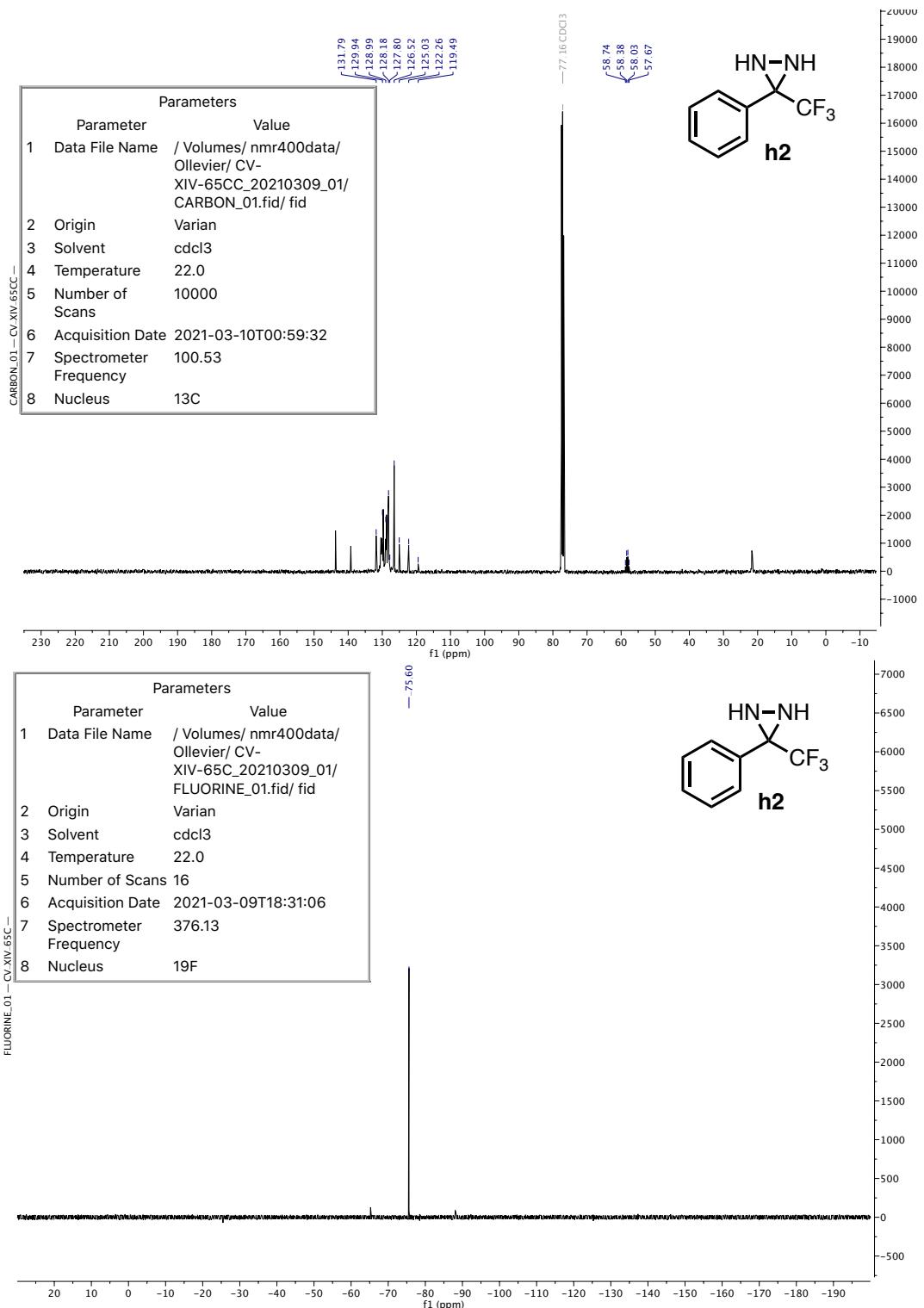
3-(4-Methoxyphenyl)-3-(trifluoromethyl)diaziridine g2



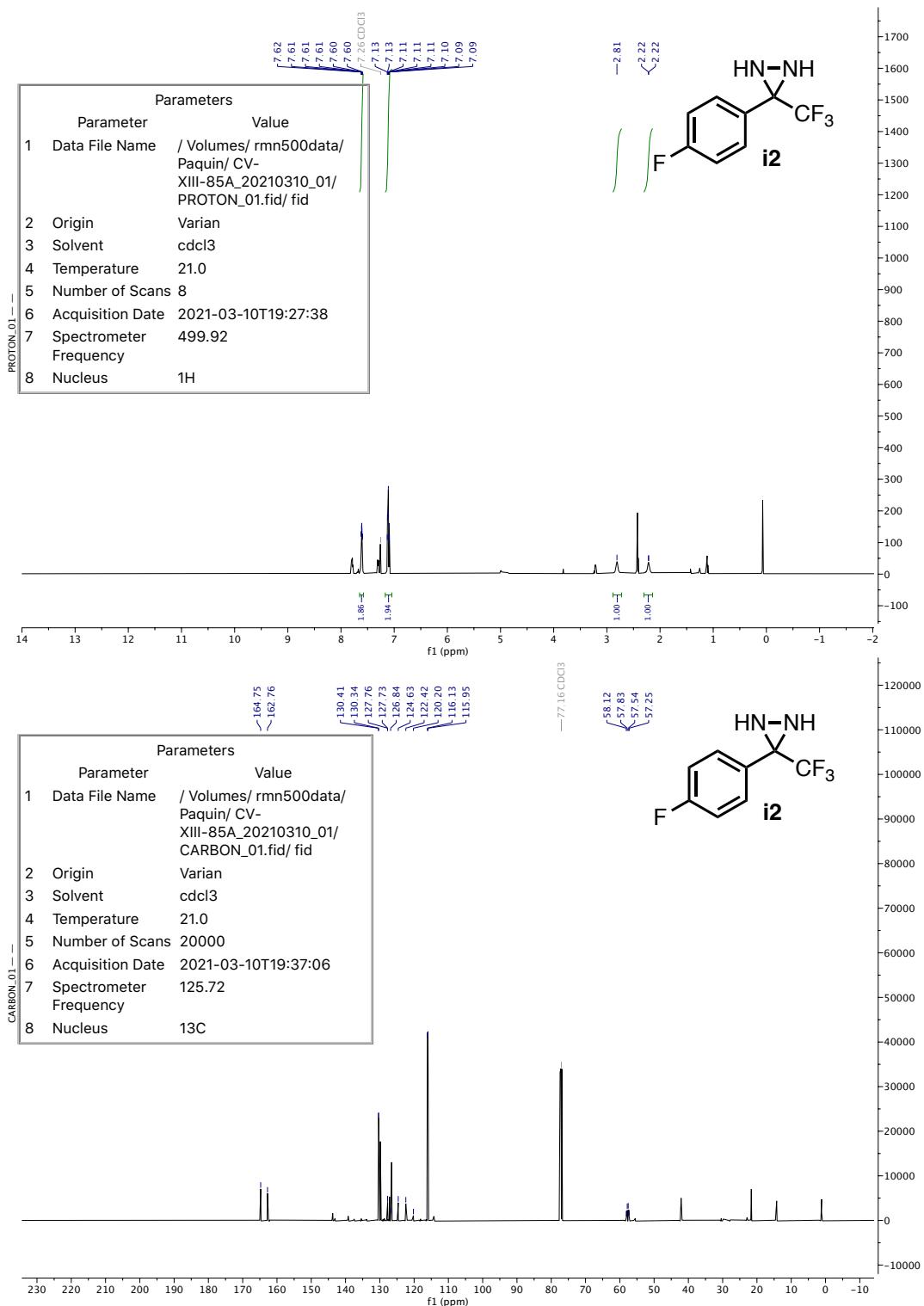


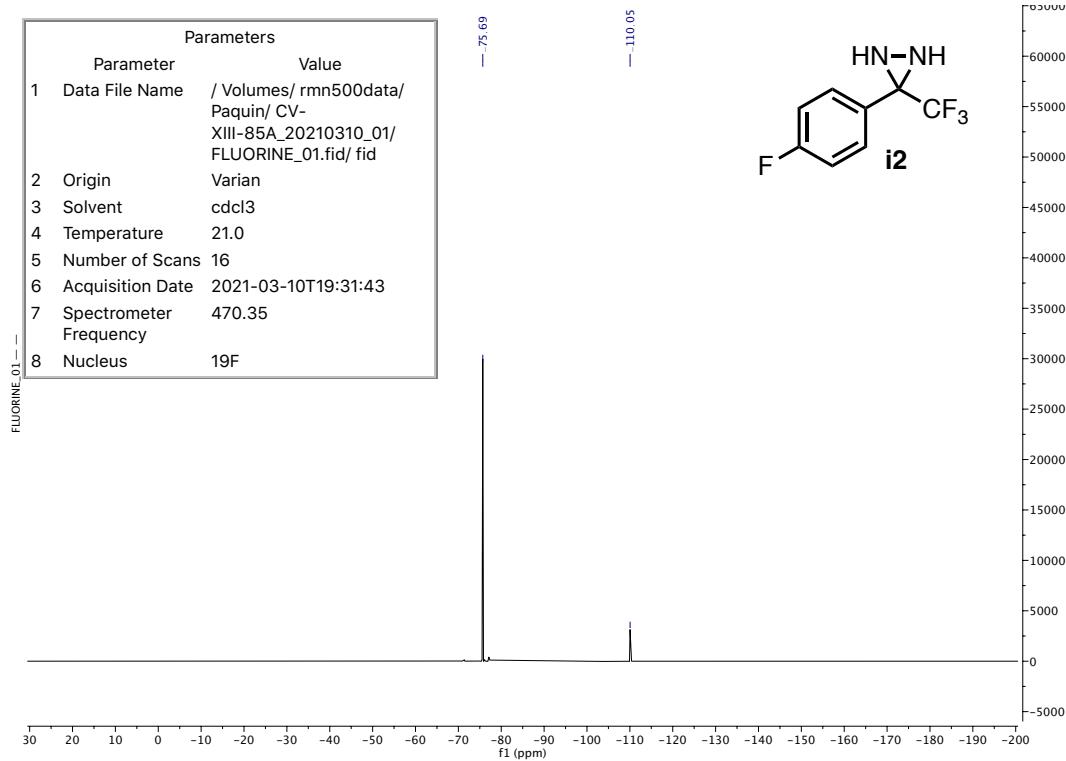
3-Phenyl-3-(trifluoromethyl)diaziridine h2



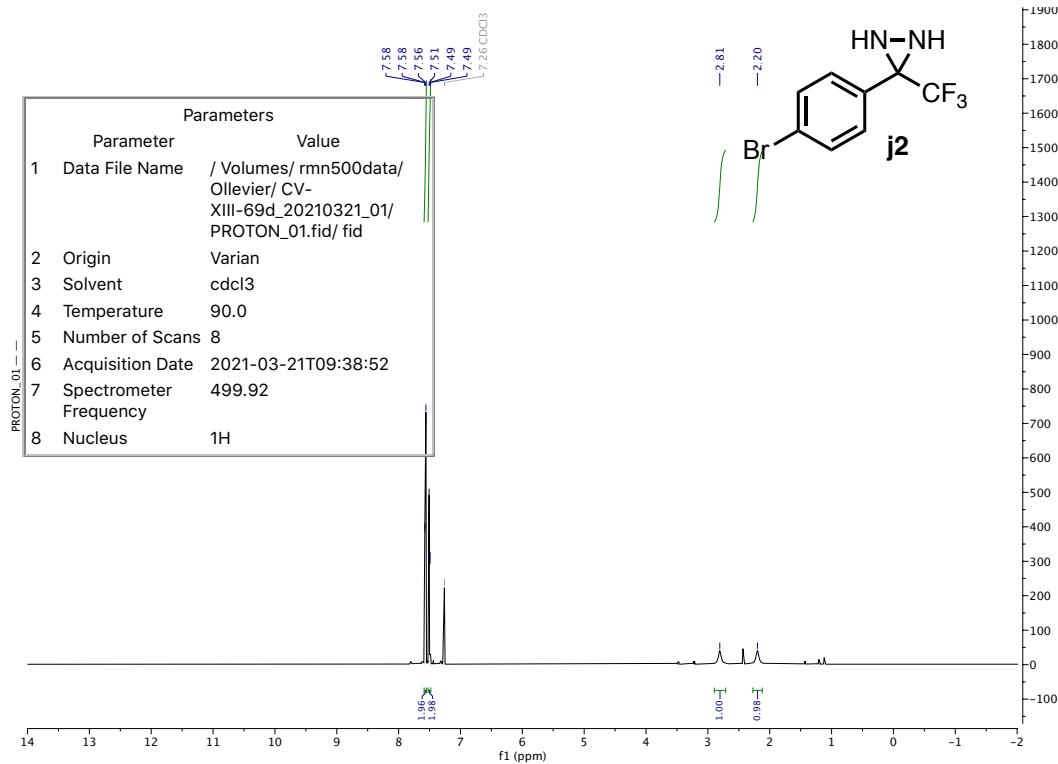


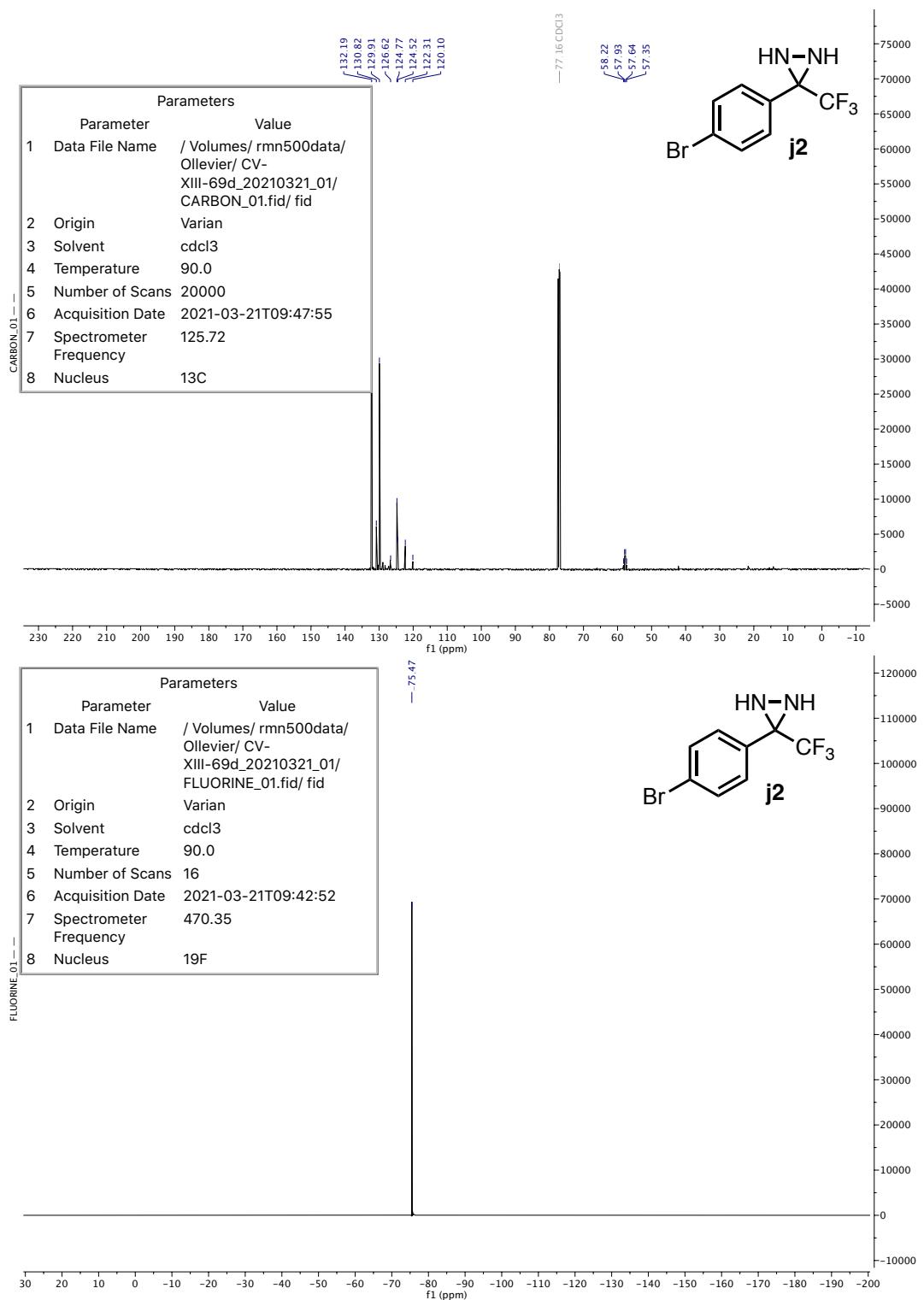
3-(4-Fluorophenyl)-3-(trifluoromethyl)diaziridine i2



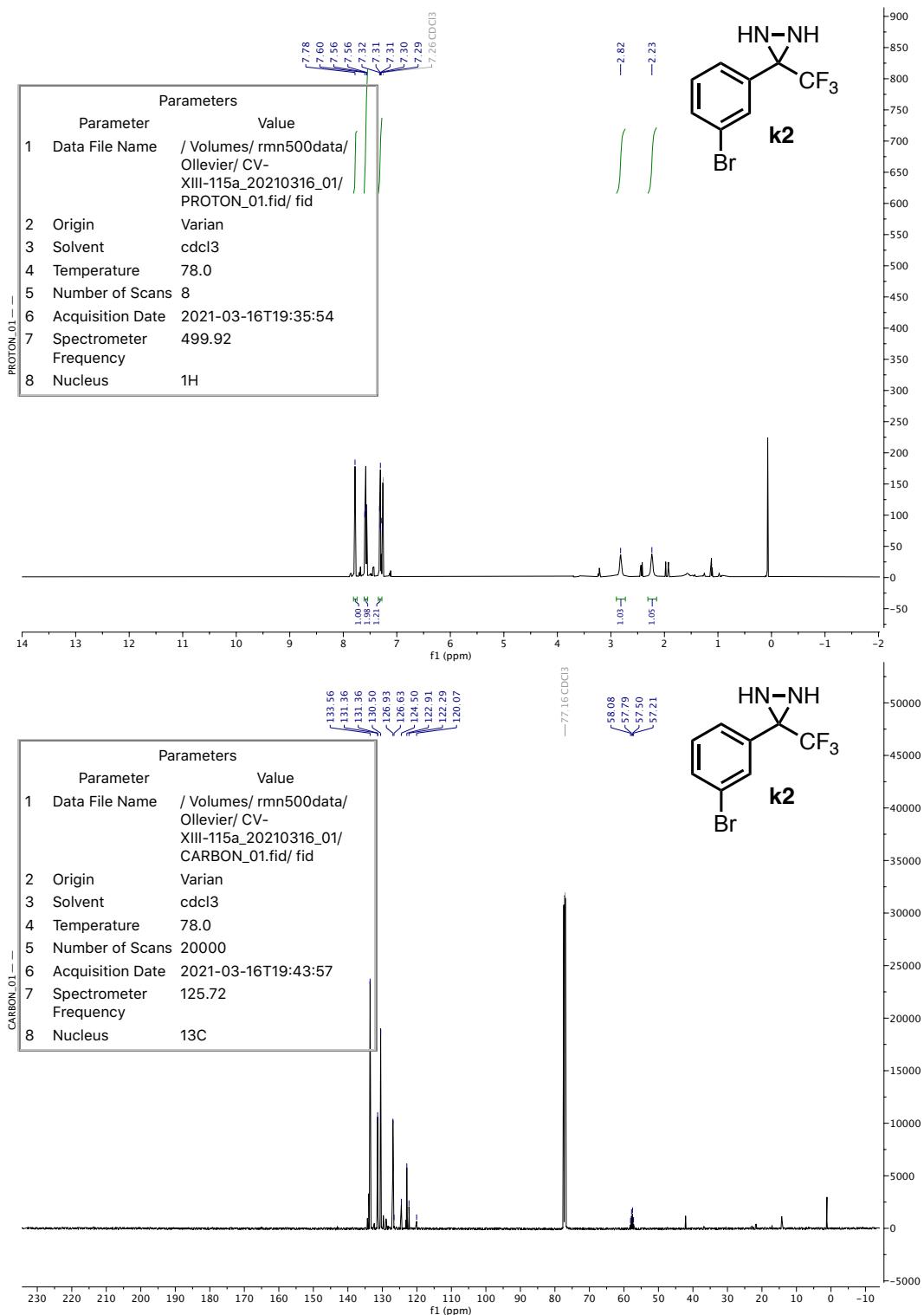


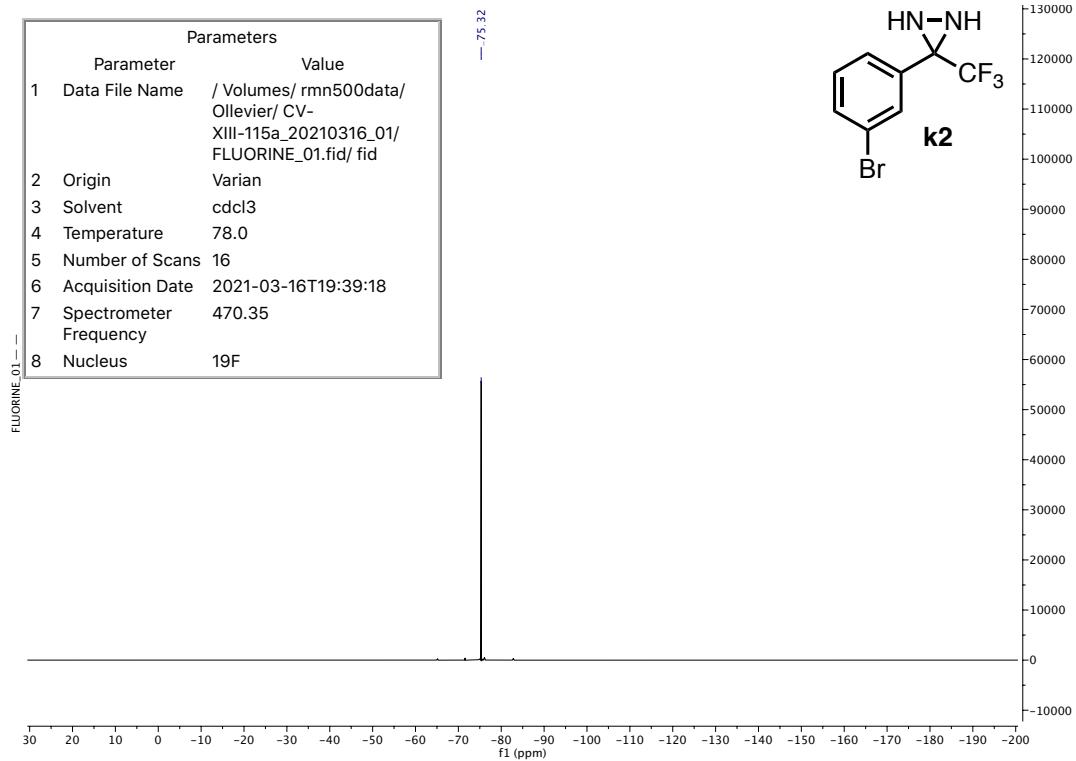
3-(4-Bromophenyl)-3-(trifluoromethyl)diaziridine **j2**



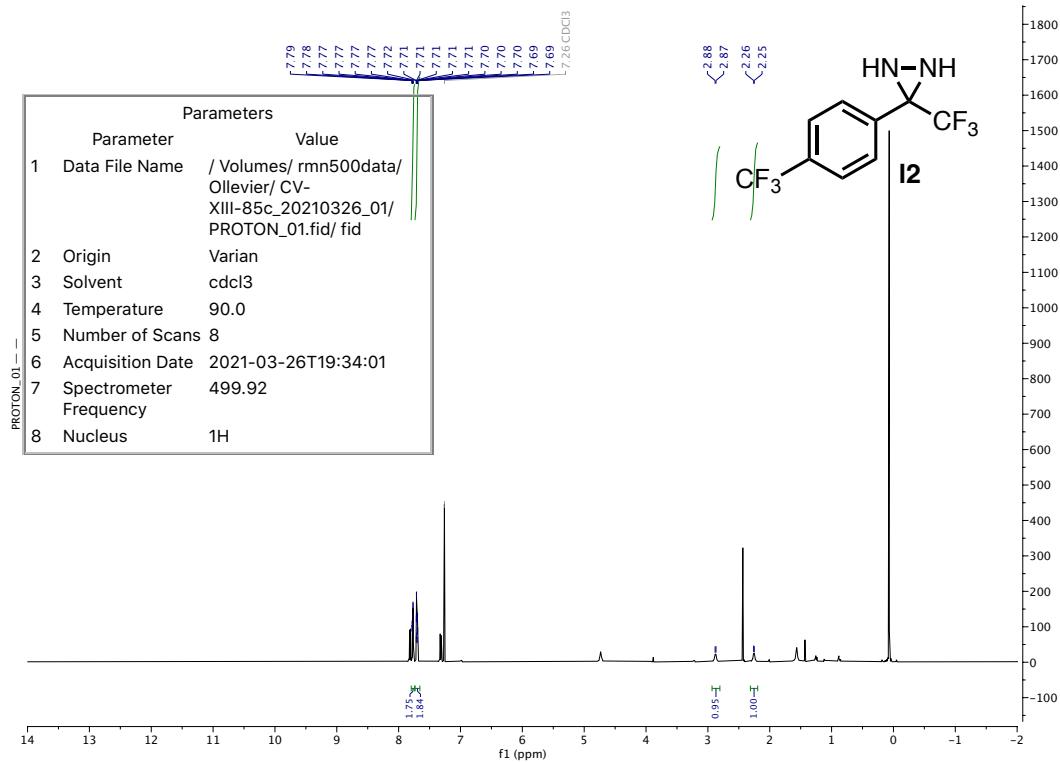


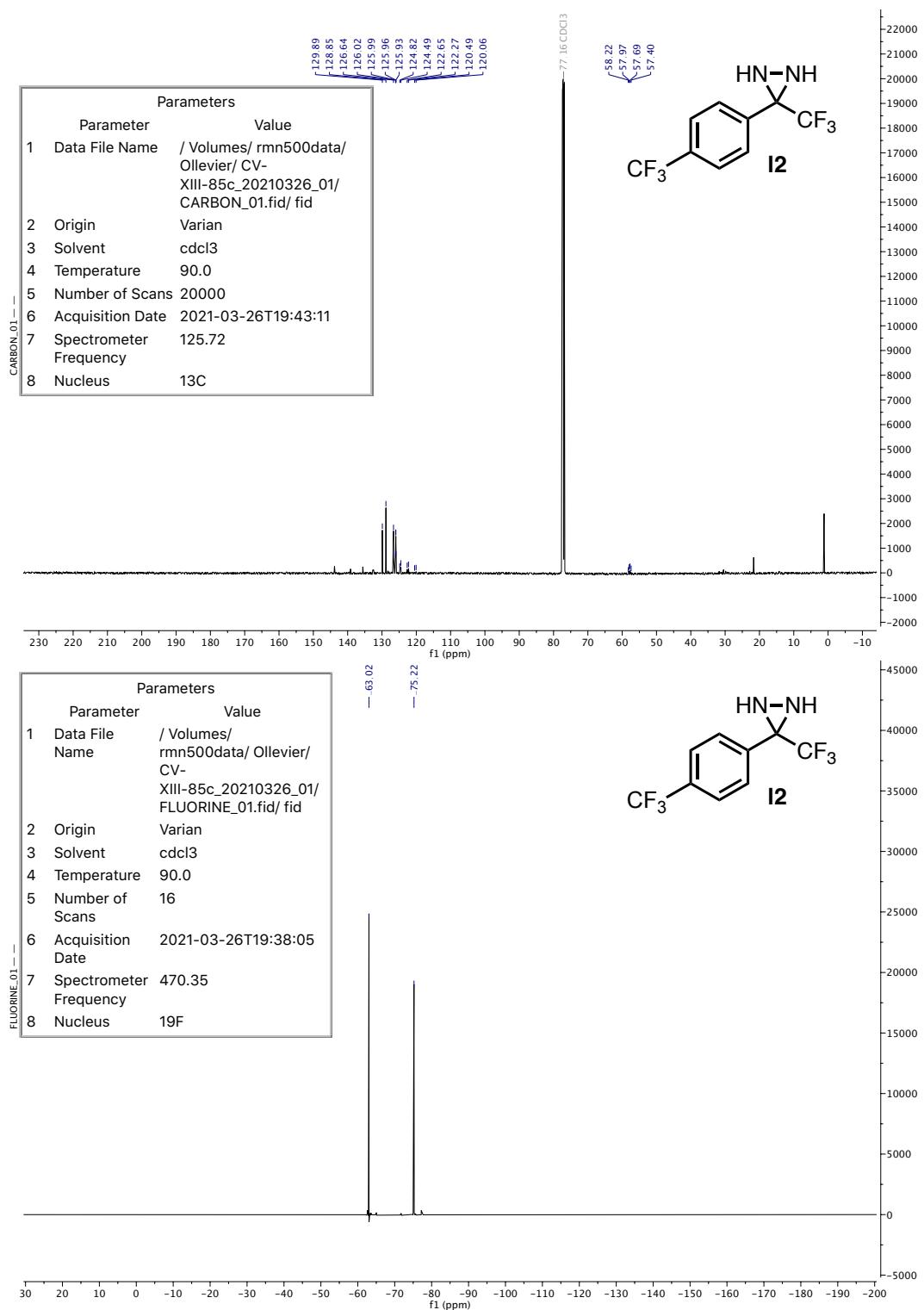
3-(3-Bromophenyl)-3-(trifluoromethyl)diaziridine k2



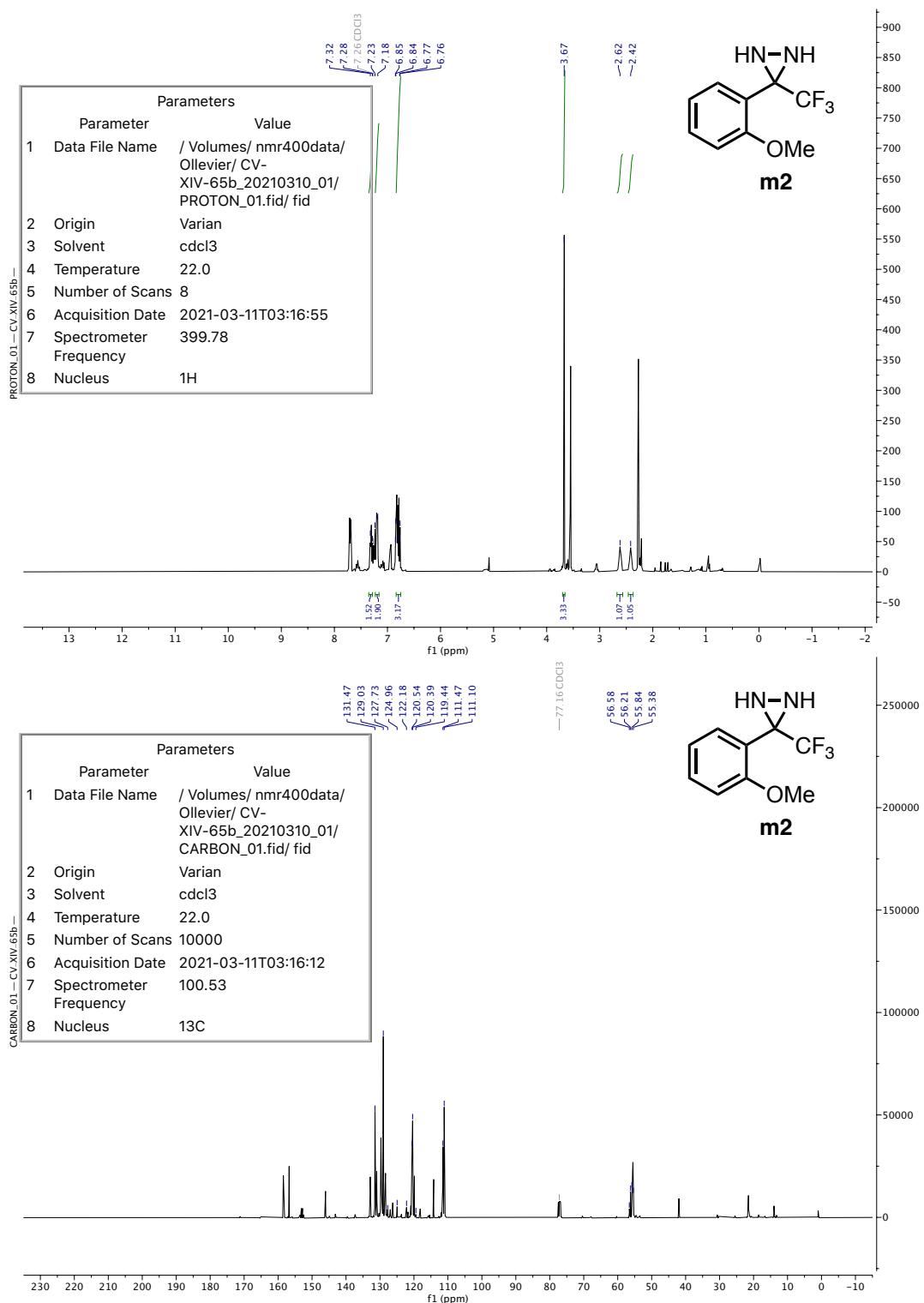


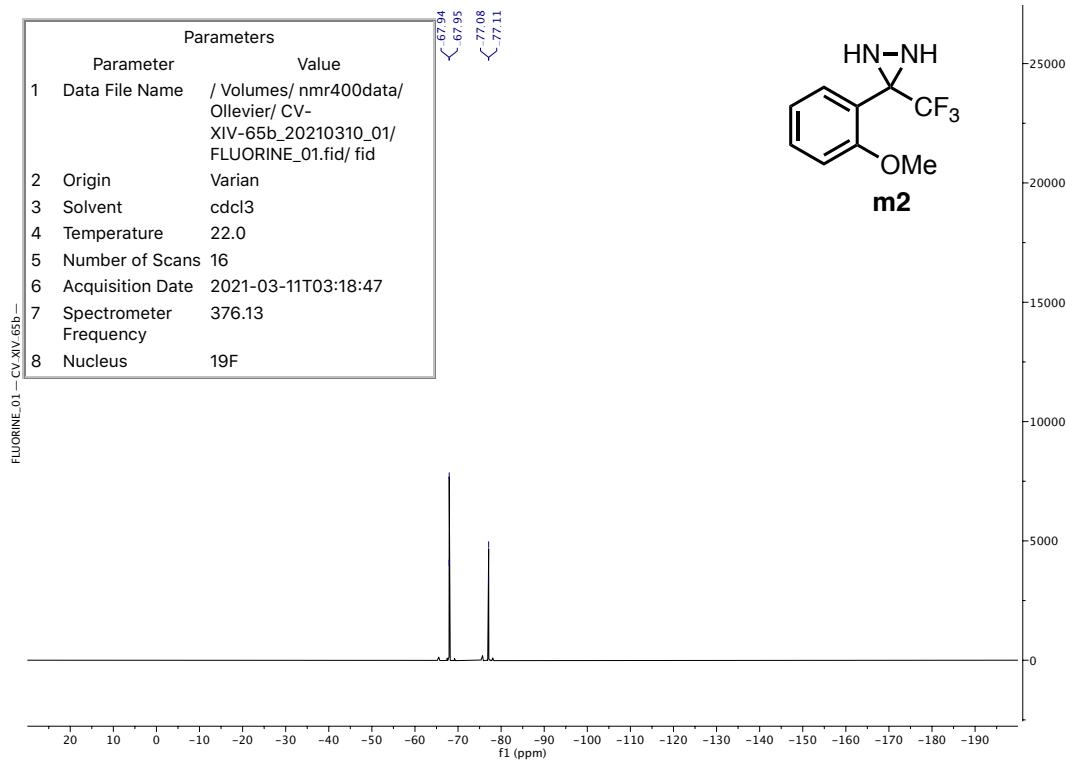
3-(4-Trifluoromethylphenyl)-3-(trifluoromethyl)diaziridine I2



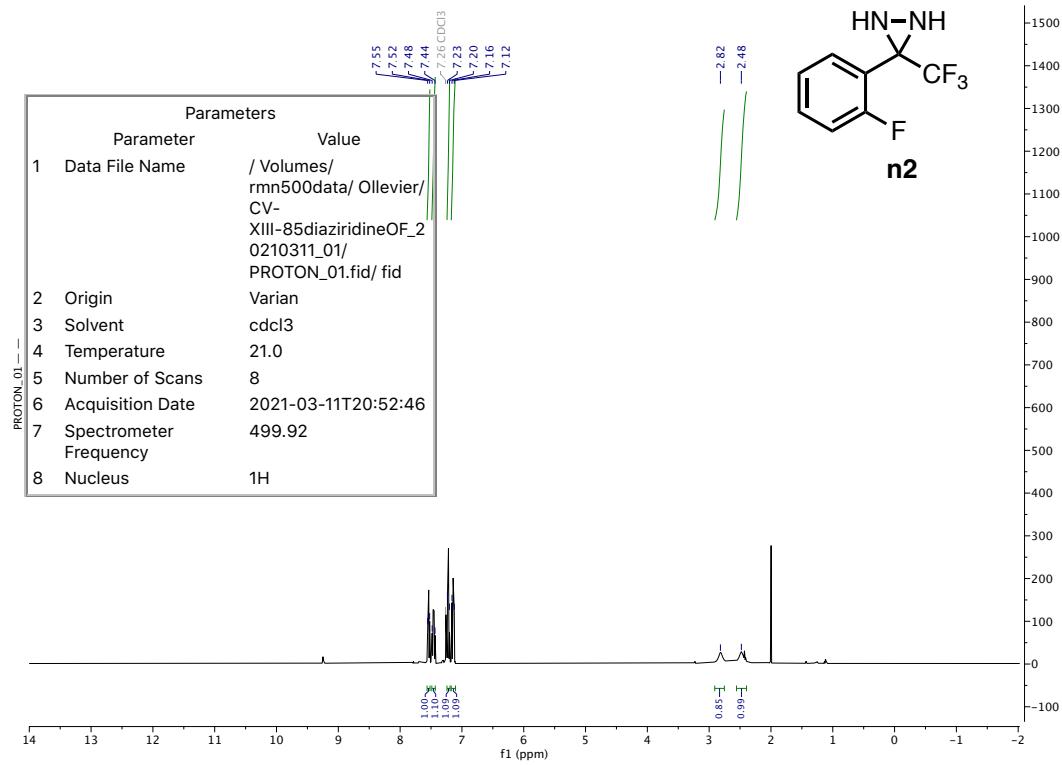


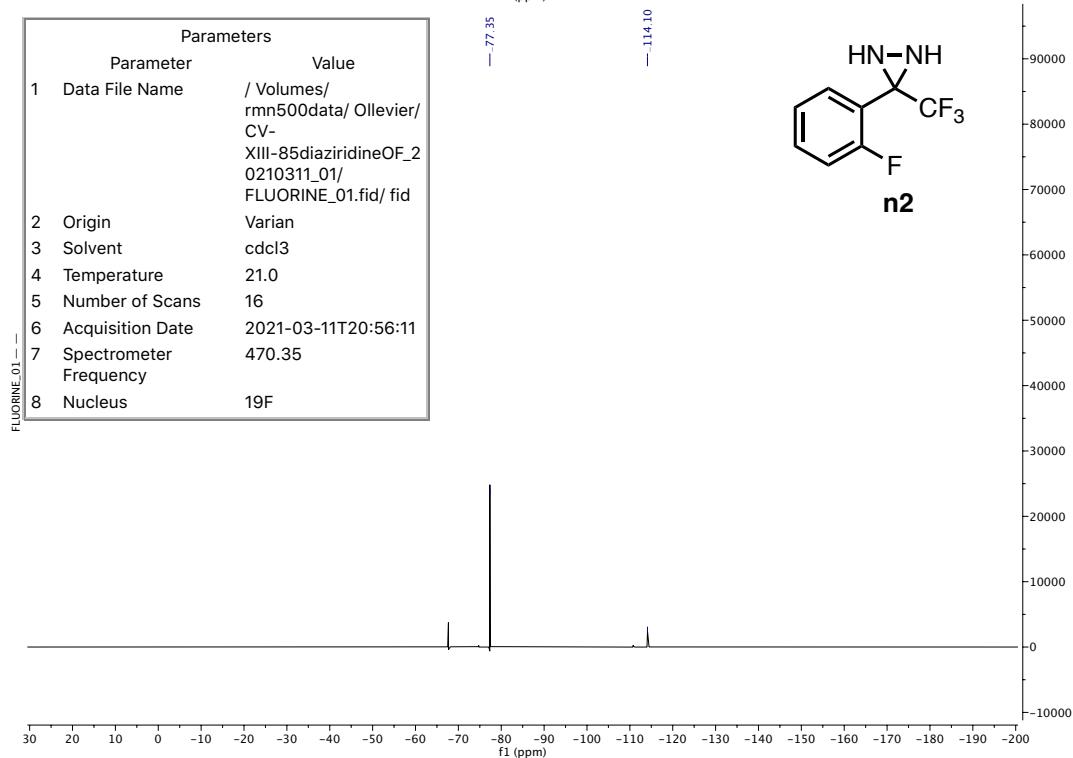
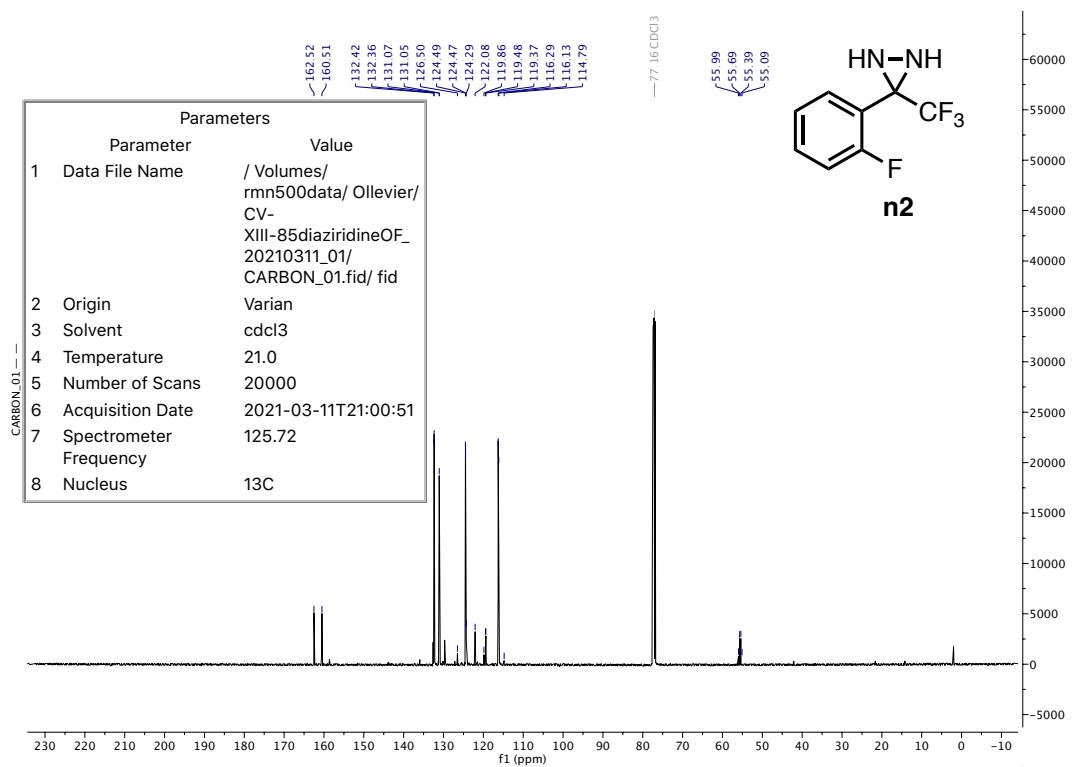
3-(2-Methoxyphenyl)-3-(trifluoromethyl)diaziridine m2



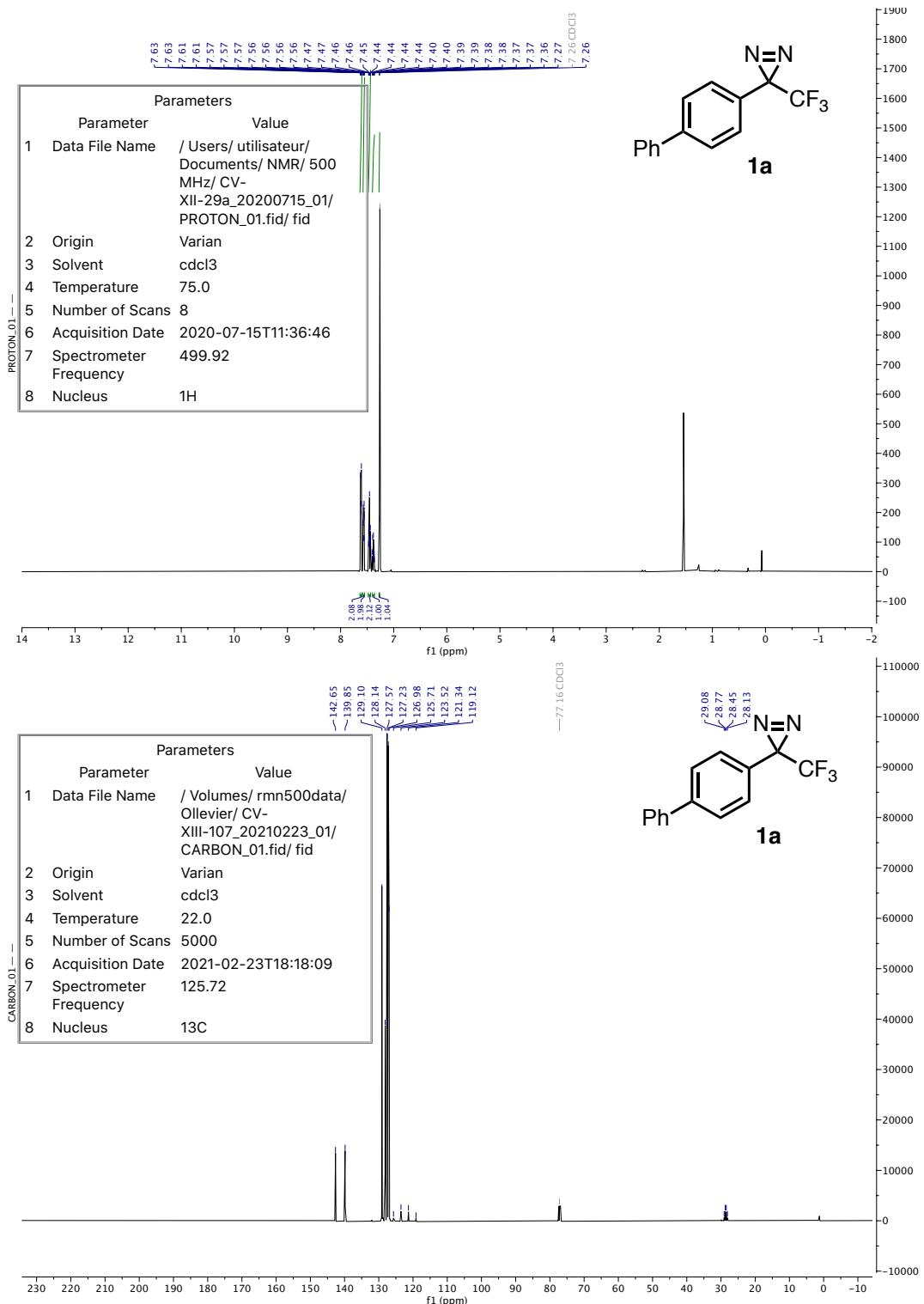


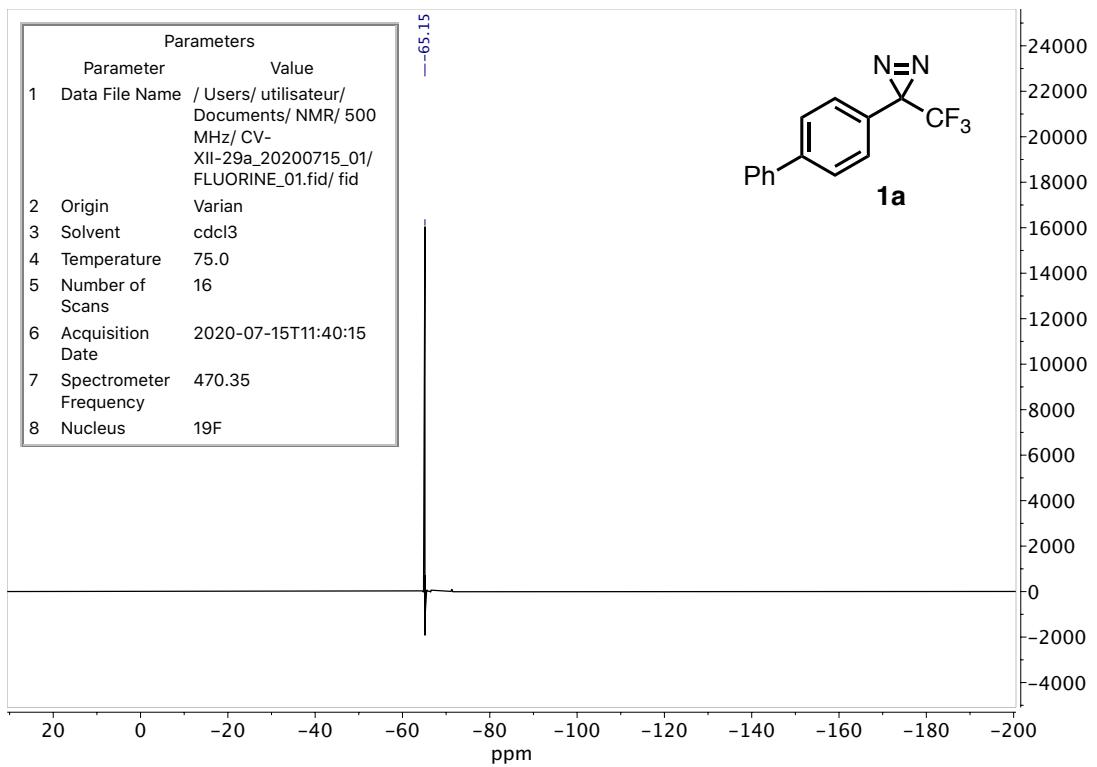
3-(2-Fluorophenyl)-3-(trifluoromethyl)diaziridine n2



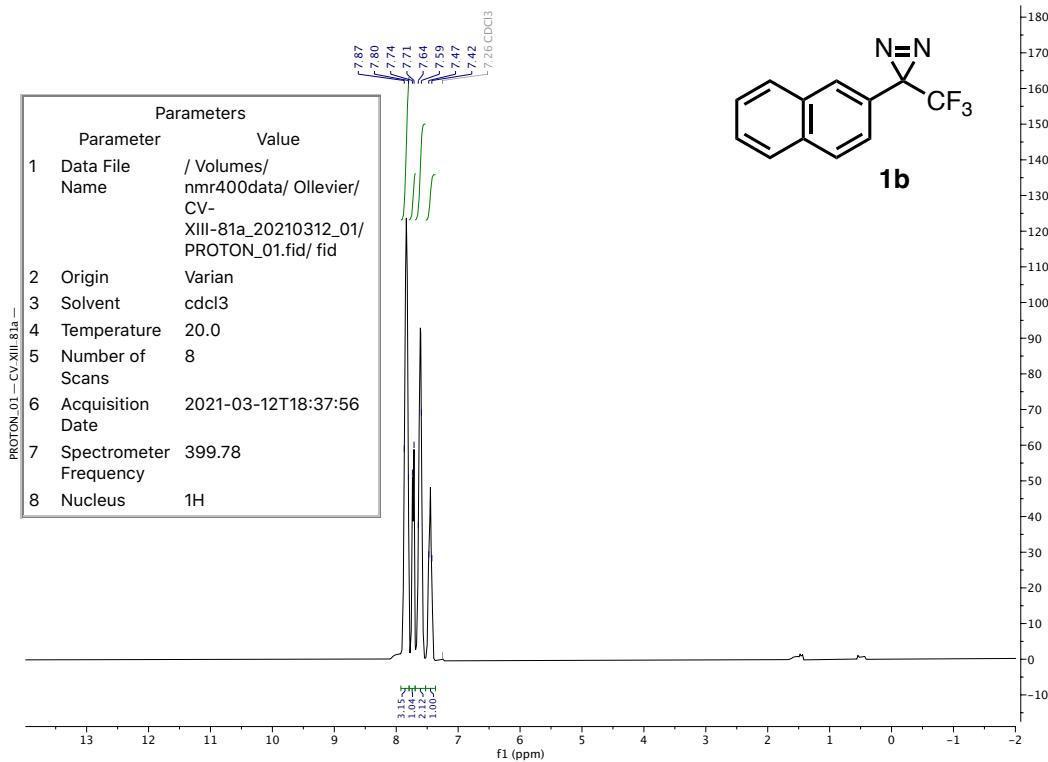


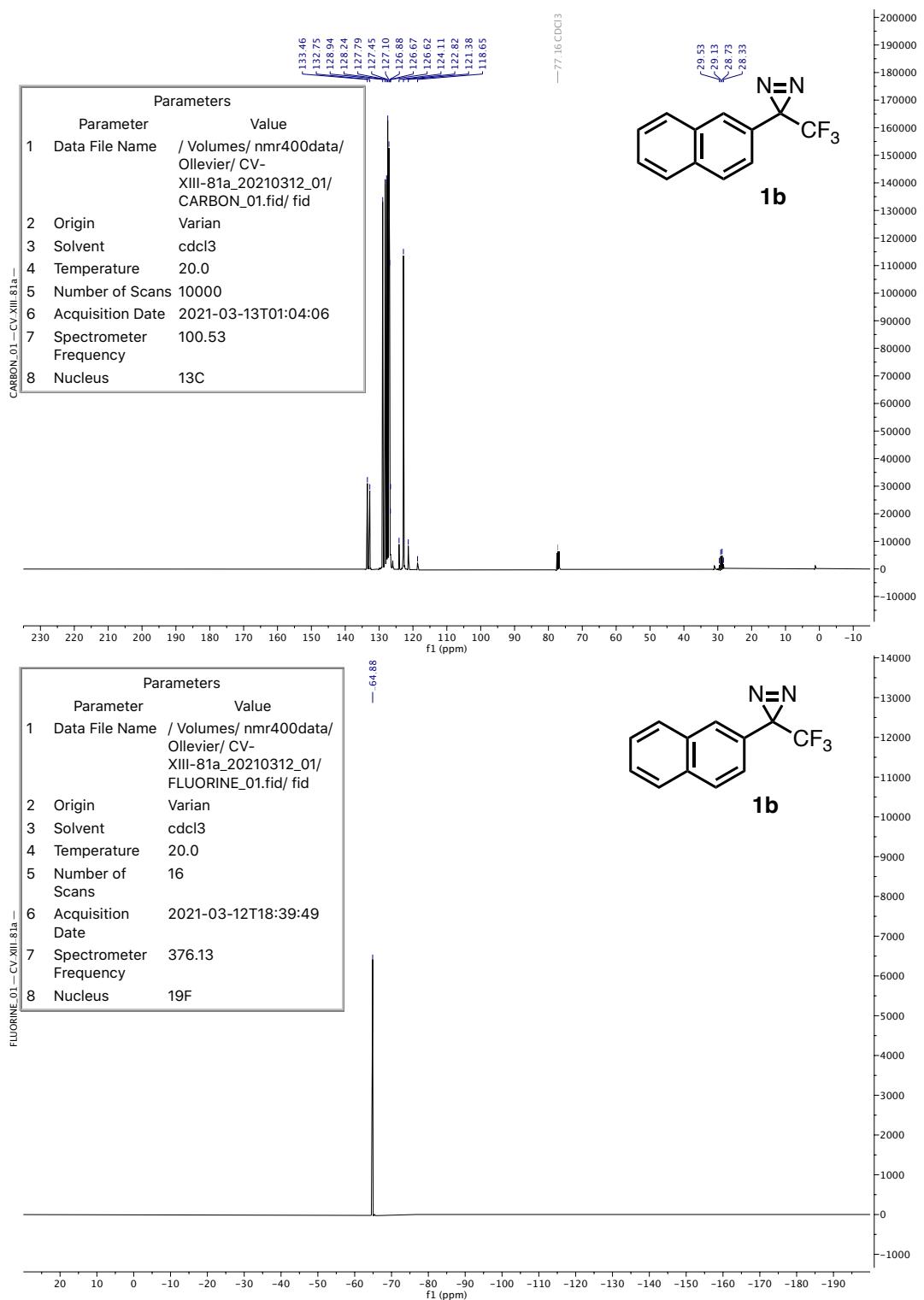
3-([1,1'-Biphenyl]-4-yl)-3-(trifluoromethyl)-3*H*-diazirine **1a**



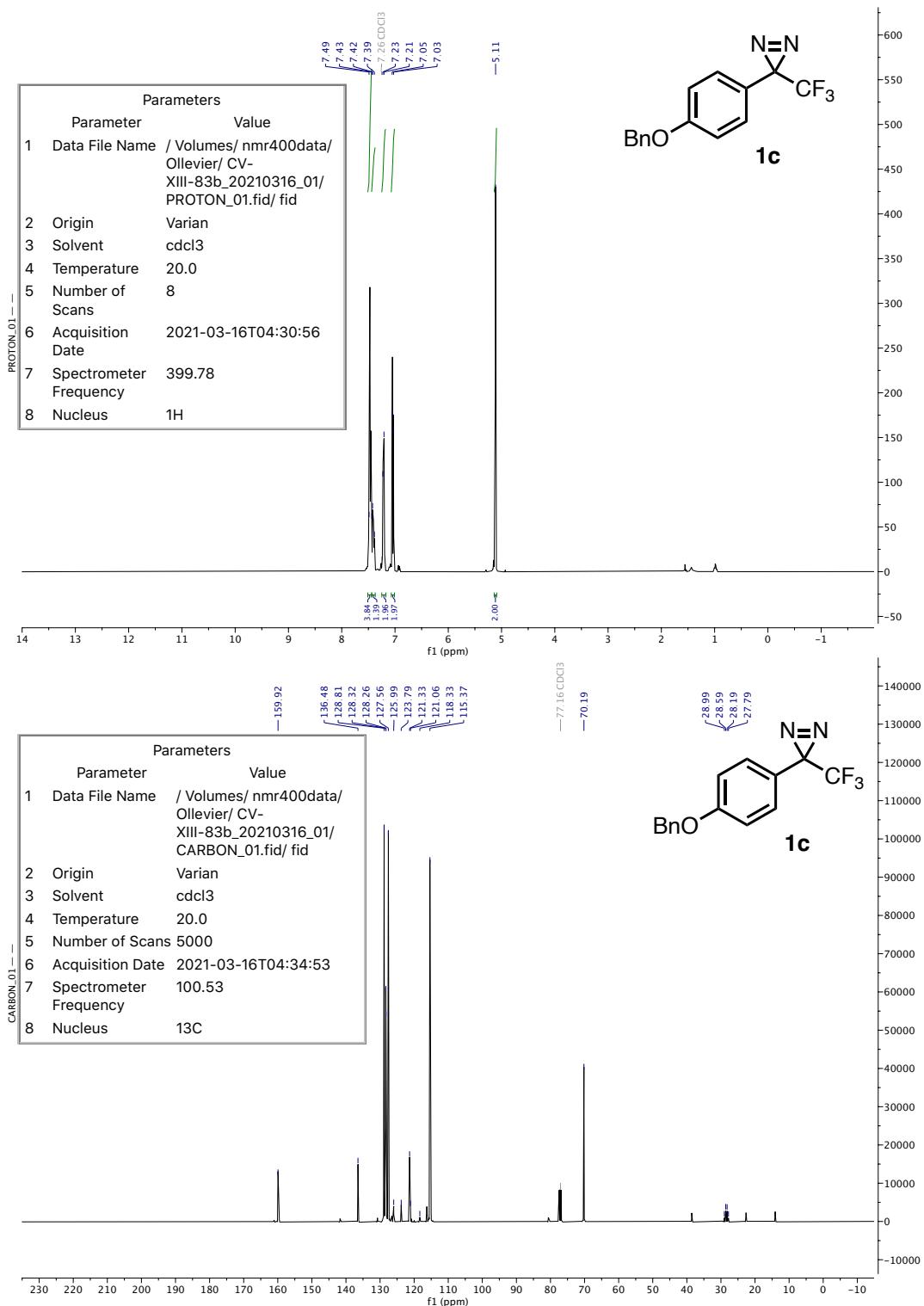


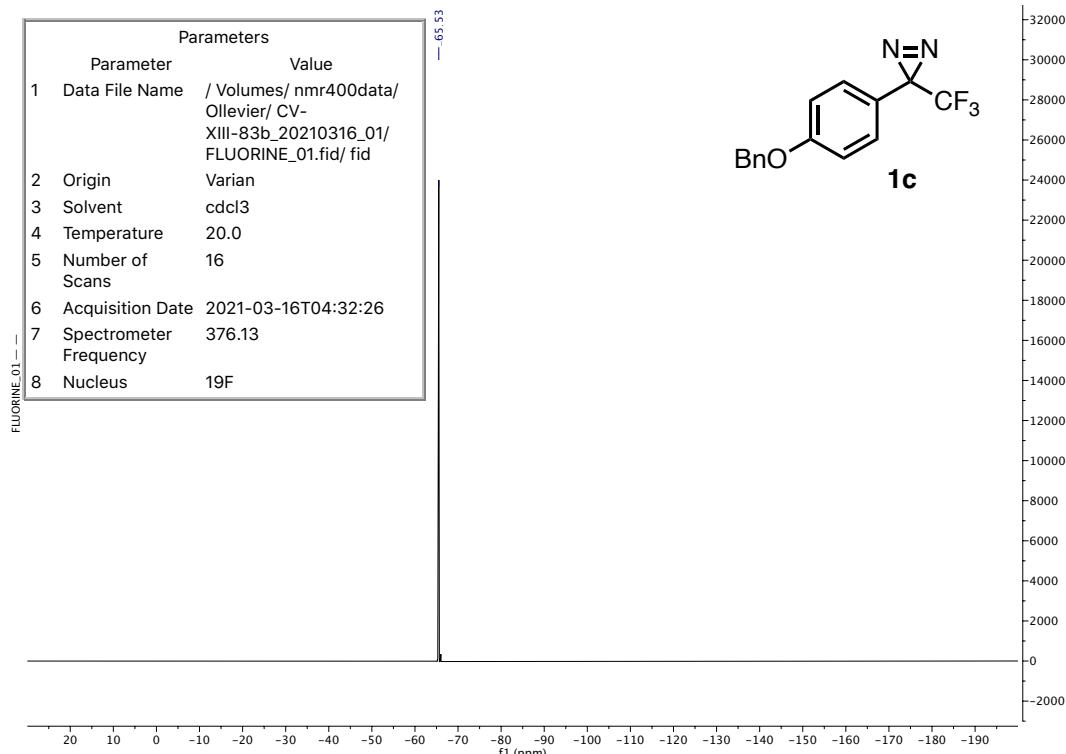
3-(Naphthalen-2-yl)-3-(trifluoromethyl)-3H-diazirine 1b



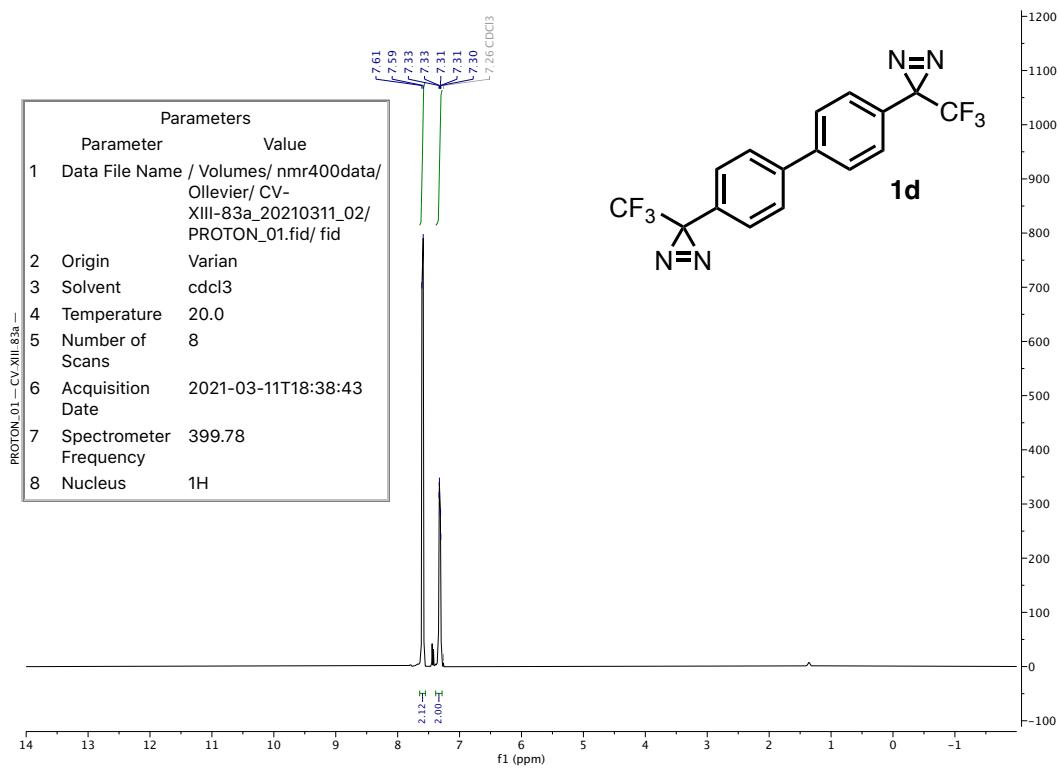


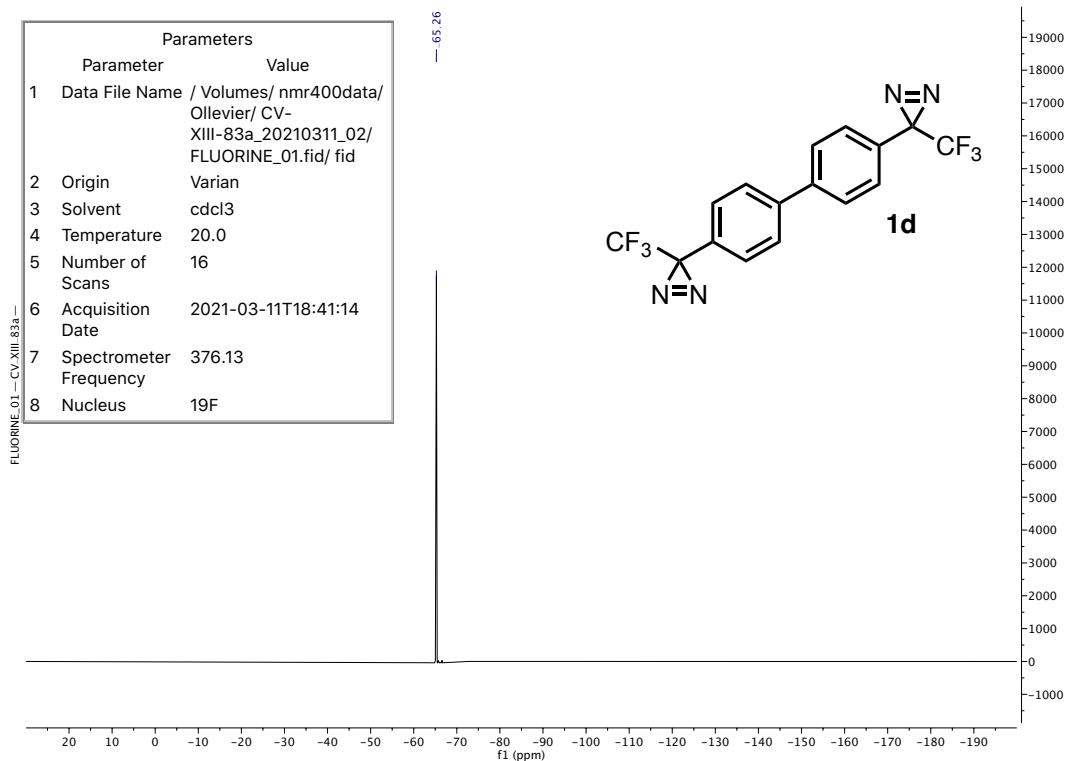
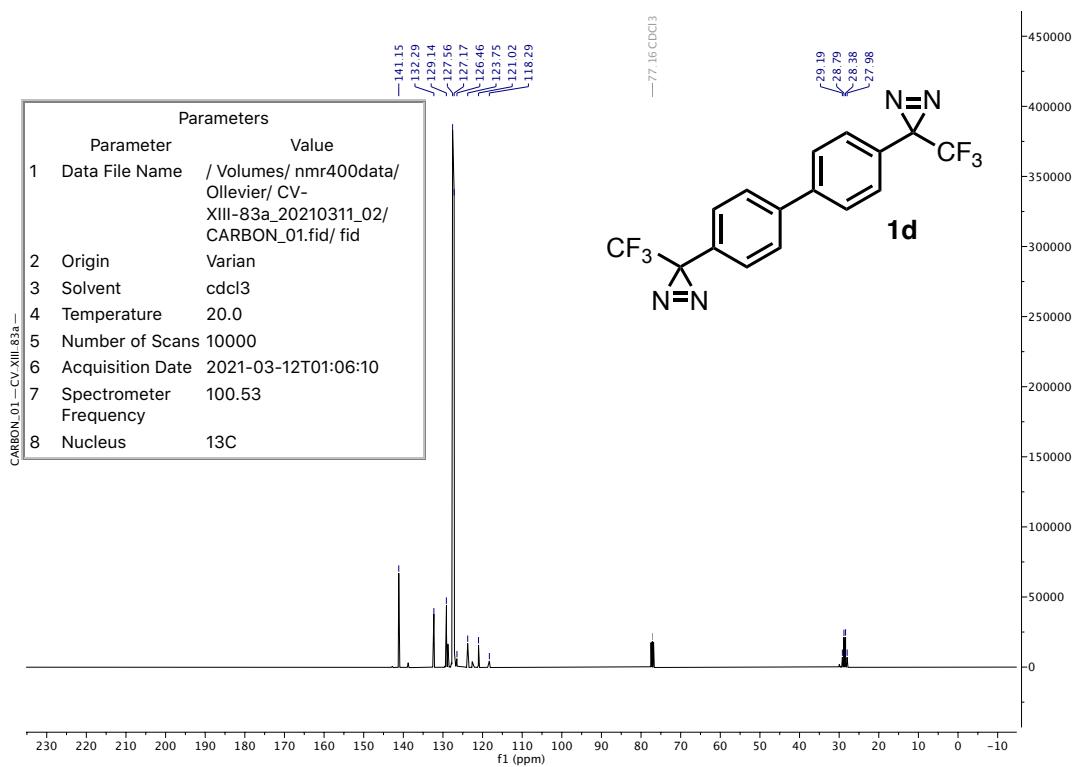
3-(4-(BenzylOxy)phenyl)-3-(trifluoromethyl)-3*H*-diazirine **1c**



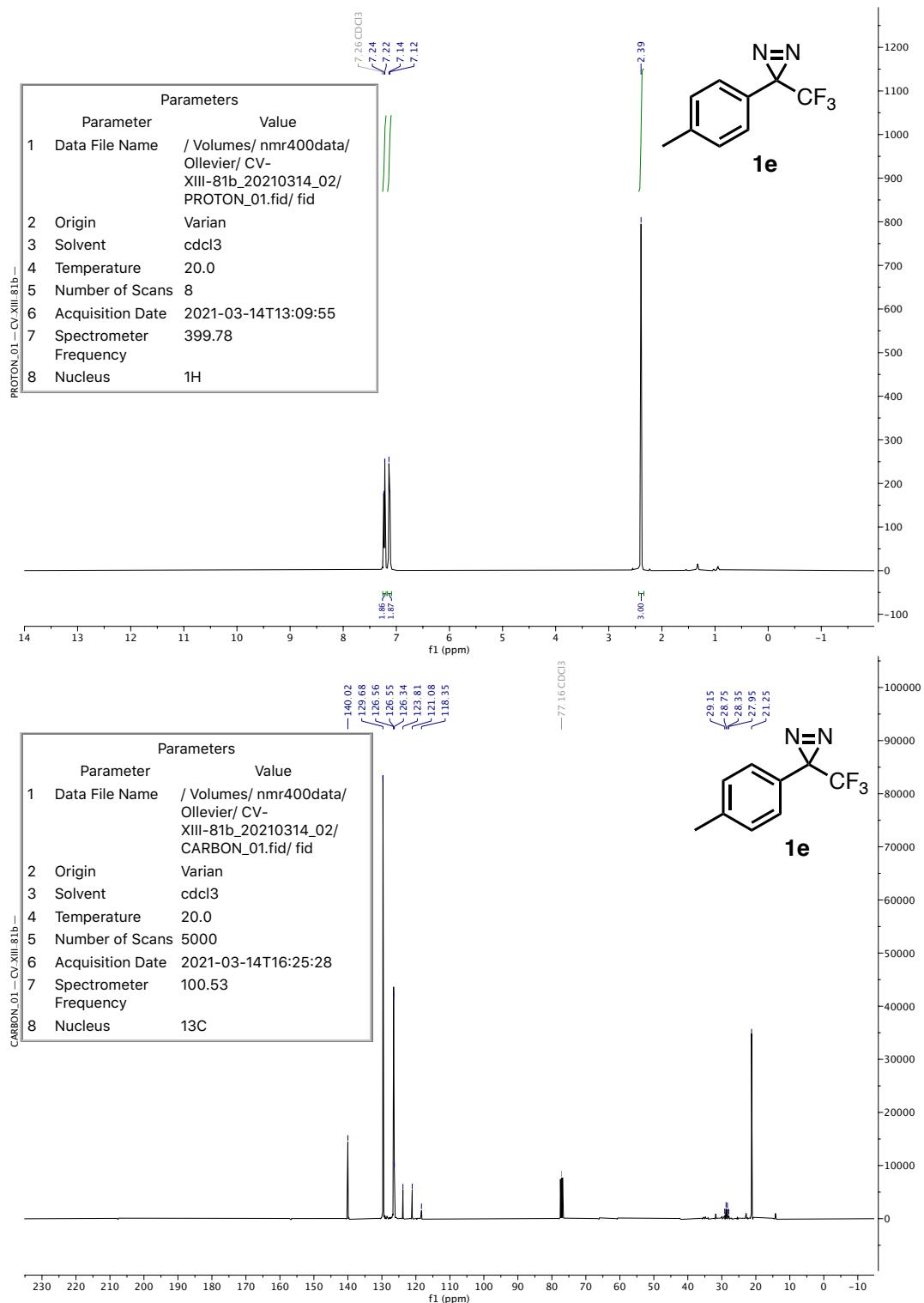


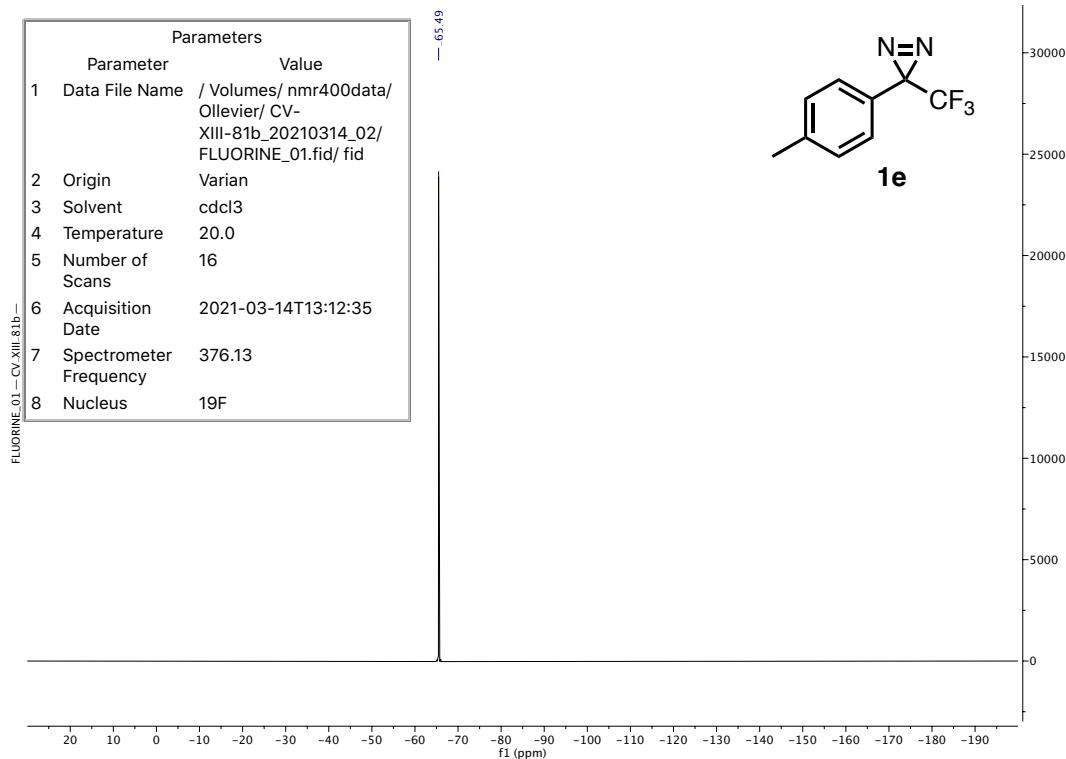
4,4'-Bis(3-(trifluoromethyl)-3H-diazirin-3-yl)-1,1'-biphenyl 1d



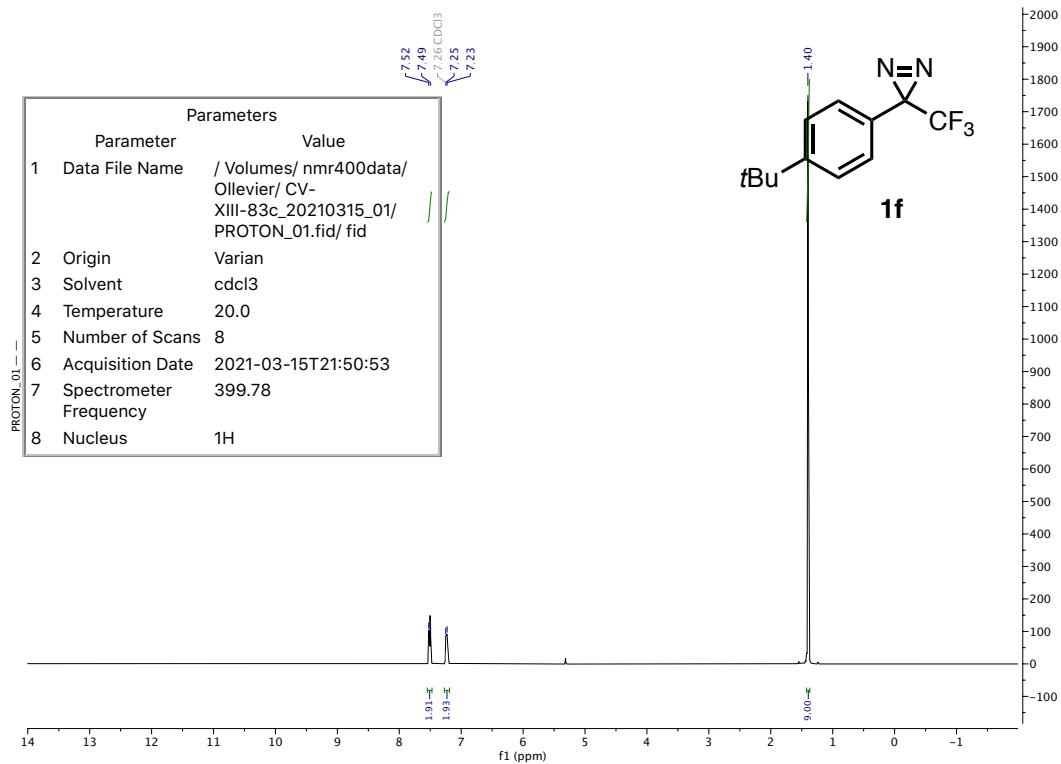


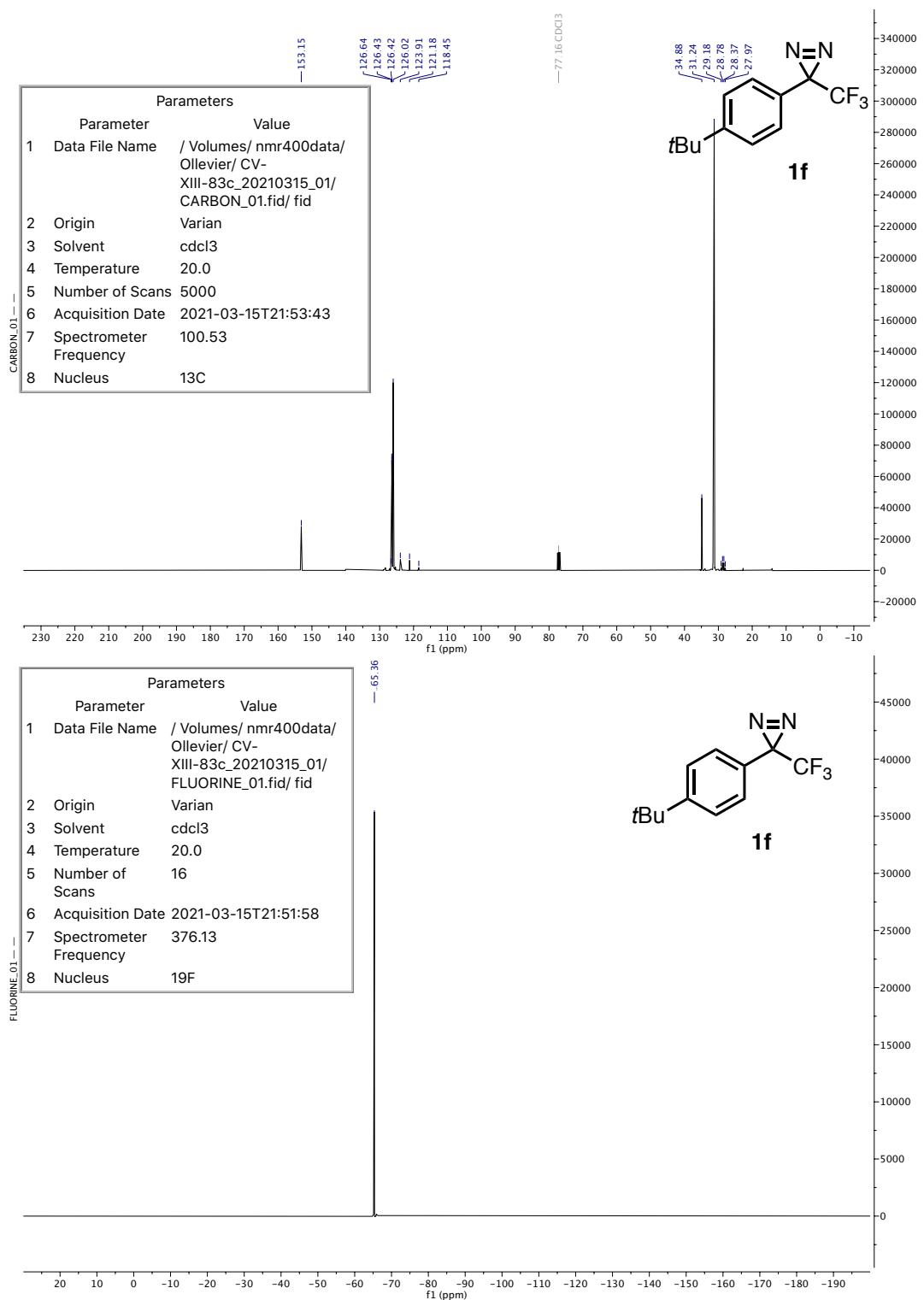
3-(*p*-Tolyl)-3-(trifluoromethyl)-3*H*-diazirine **1e**



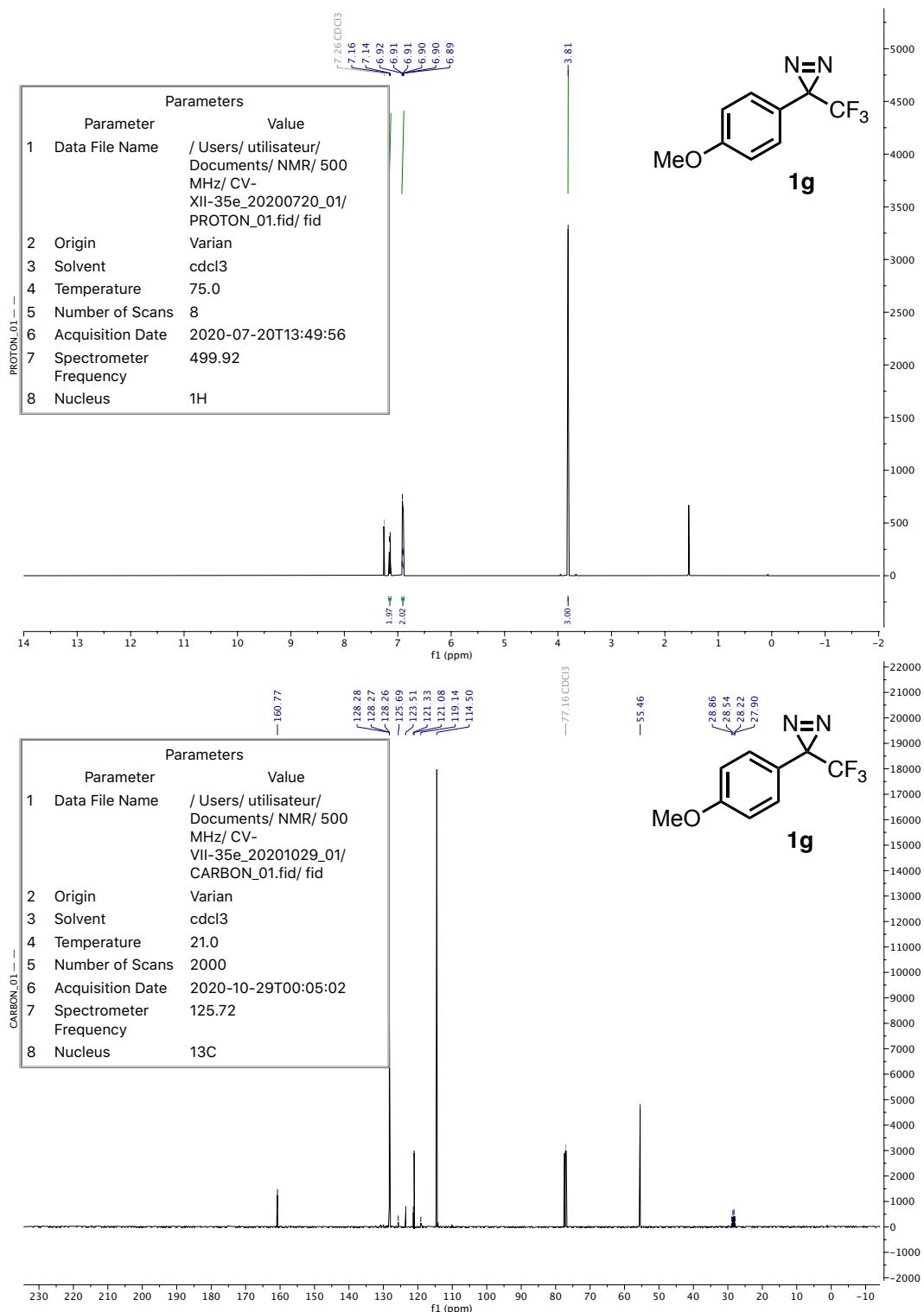


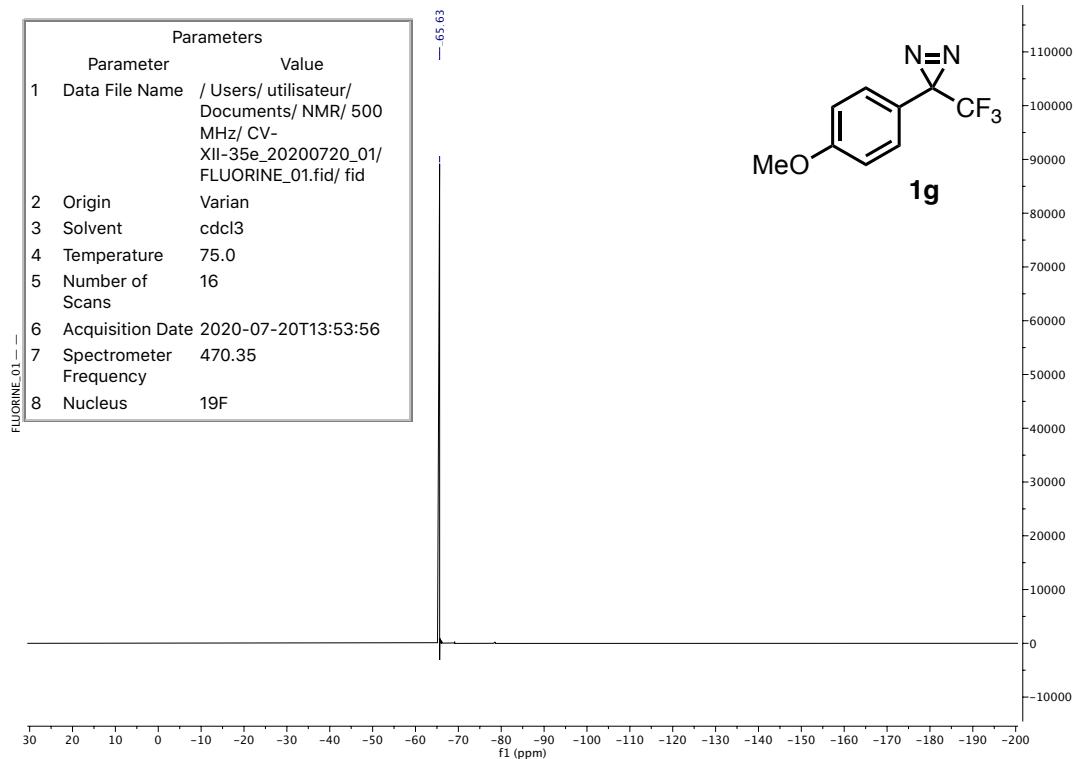
3-(4-(*Tert*-butyl)phenyl)-3-(trifluoromethyl)-3*H*-diazirine **1f**



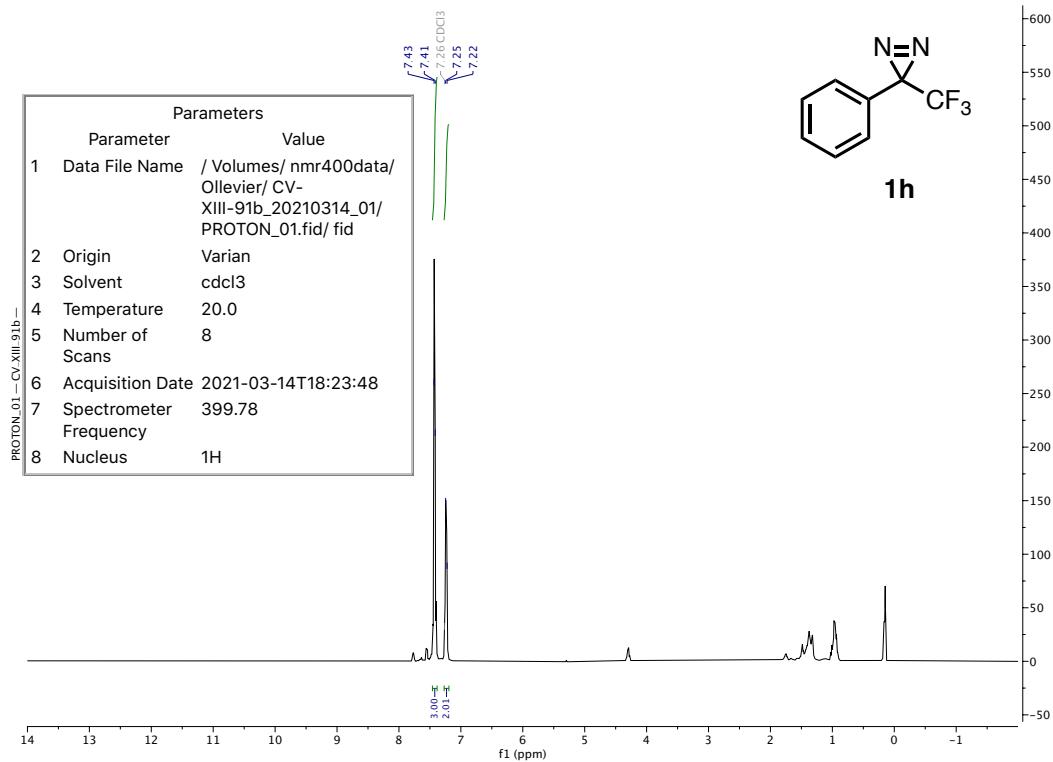


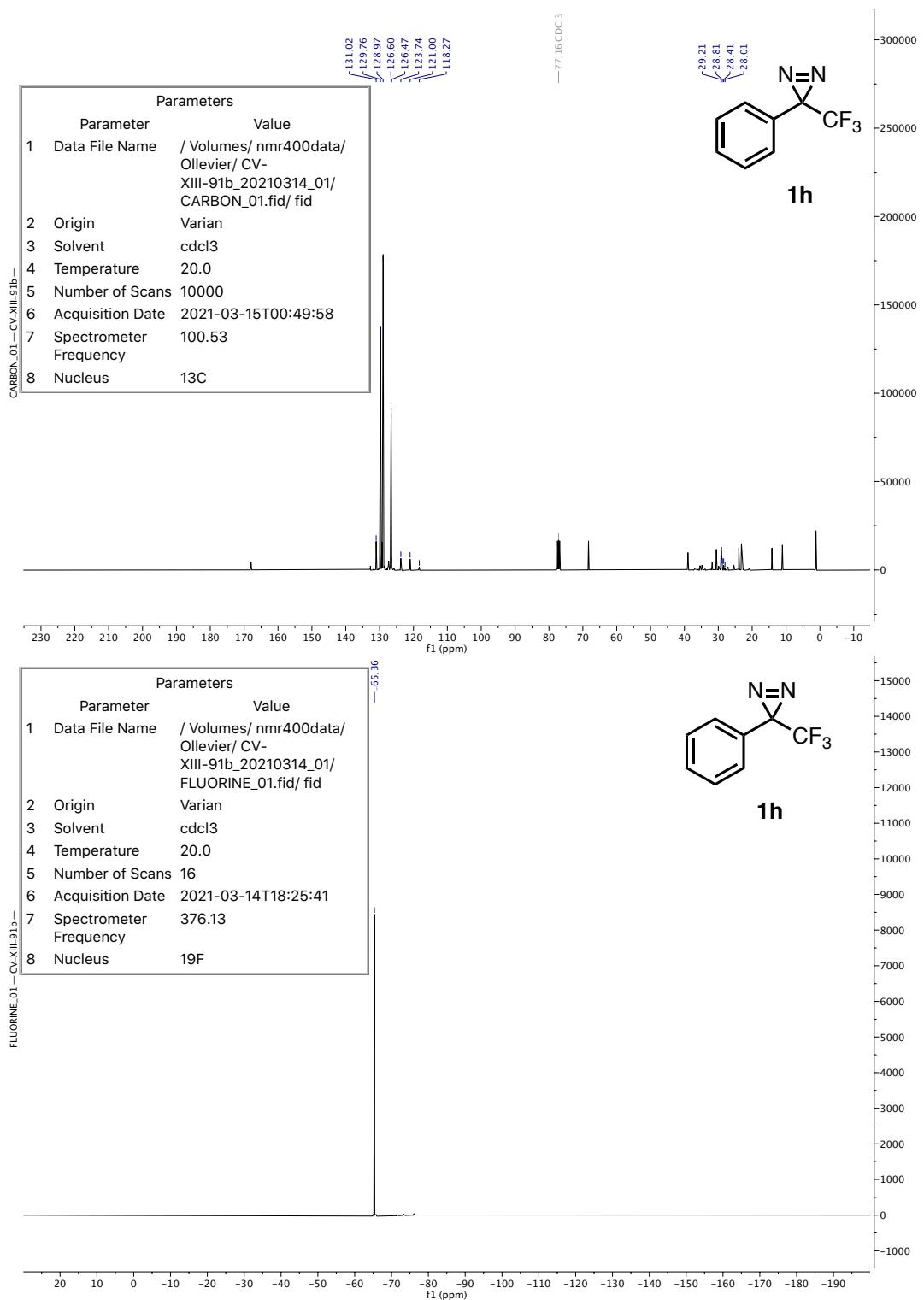
3-(4-Methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirine **1g**



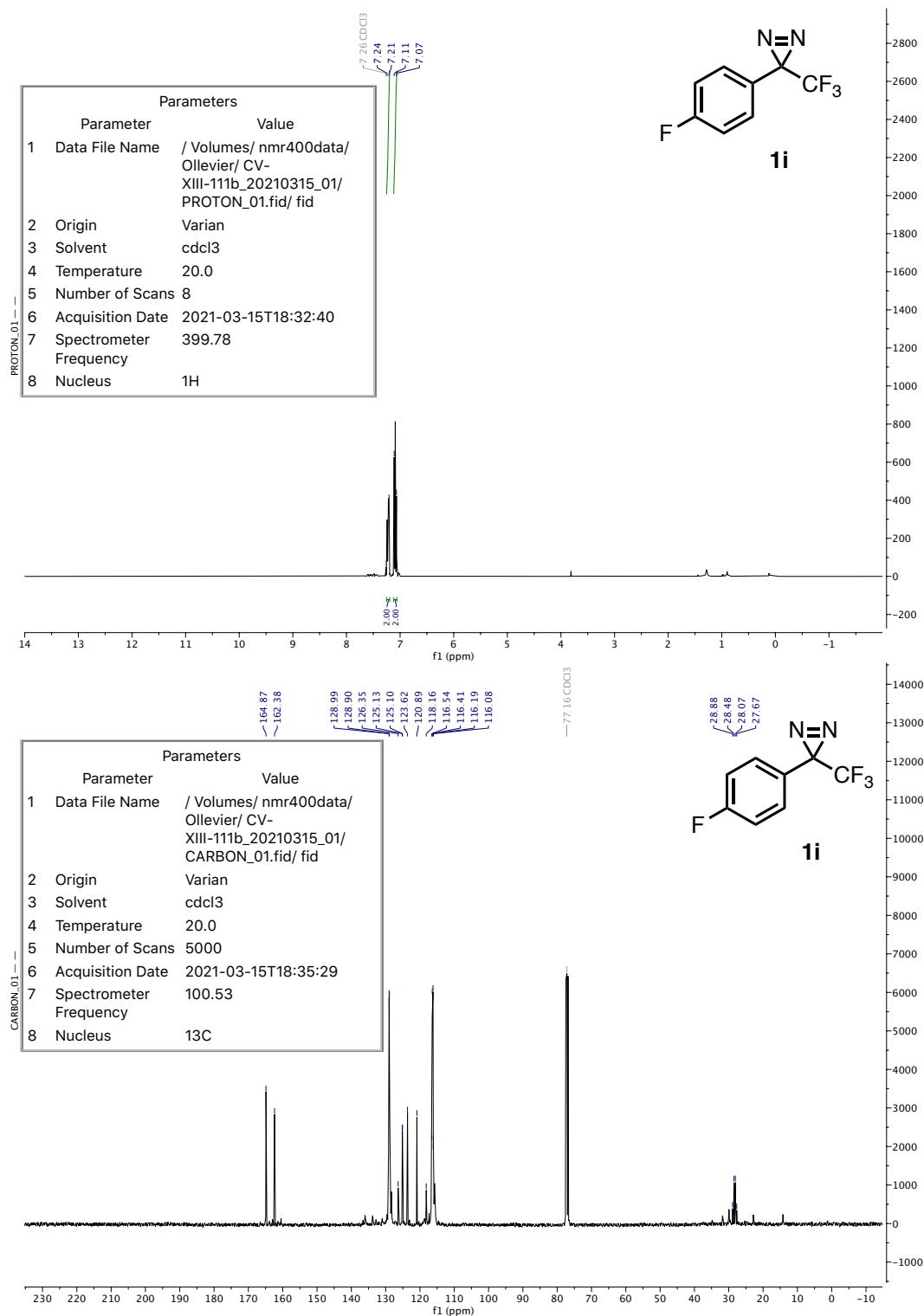


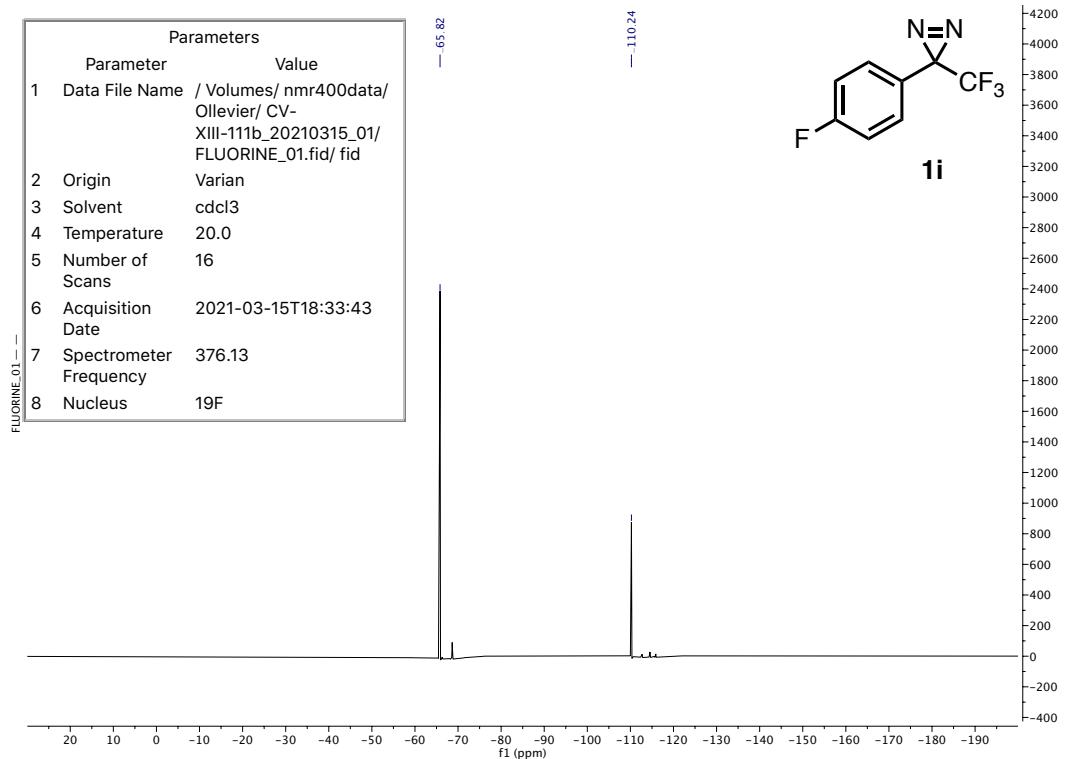
3-Phenyl-3-(trifluoromethyl)-3H-diazirine 1h



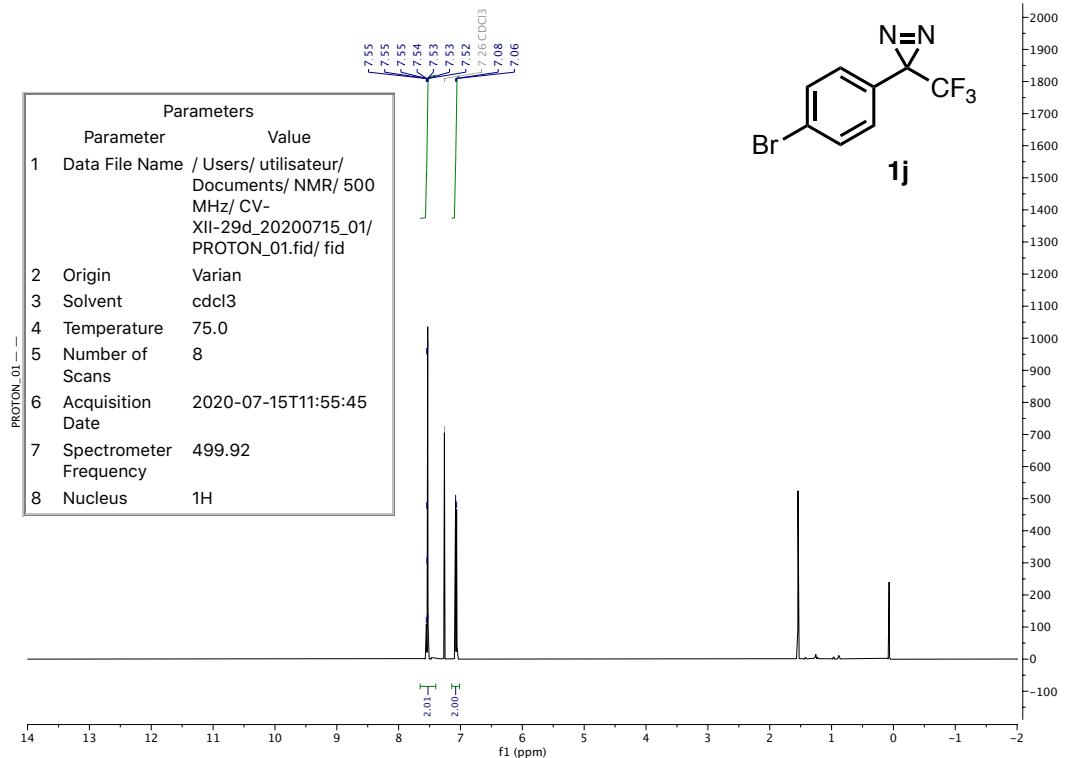


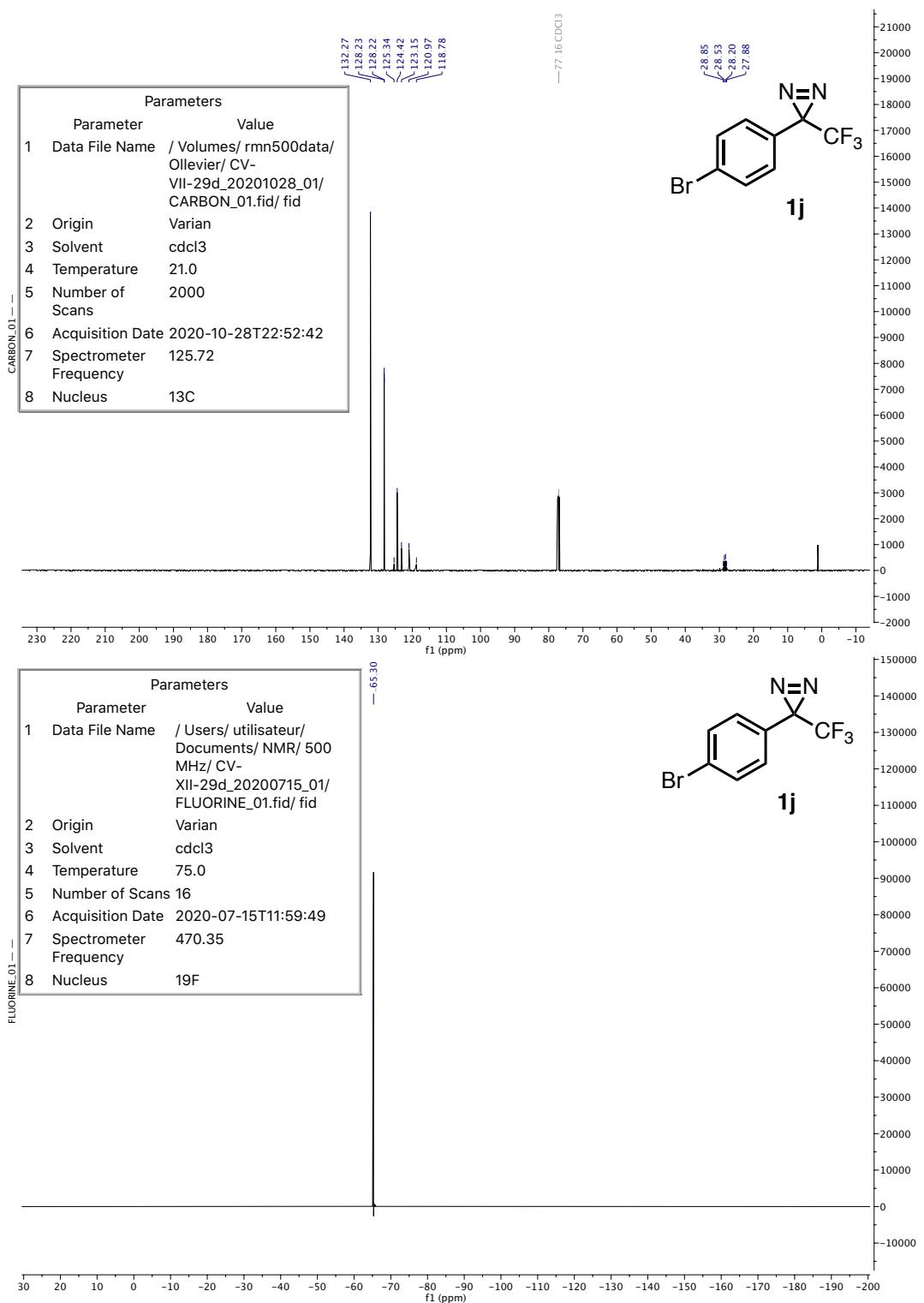
3-(4-Fluorophenyl)-3-(trifluoromethyl)-3*H*-diazirine **1i**



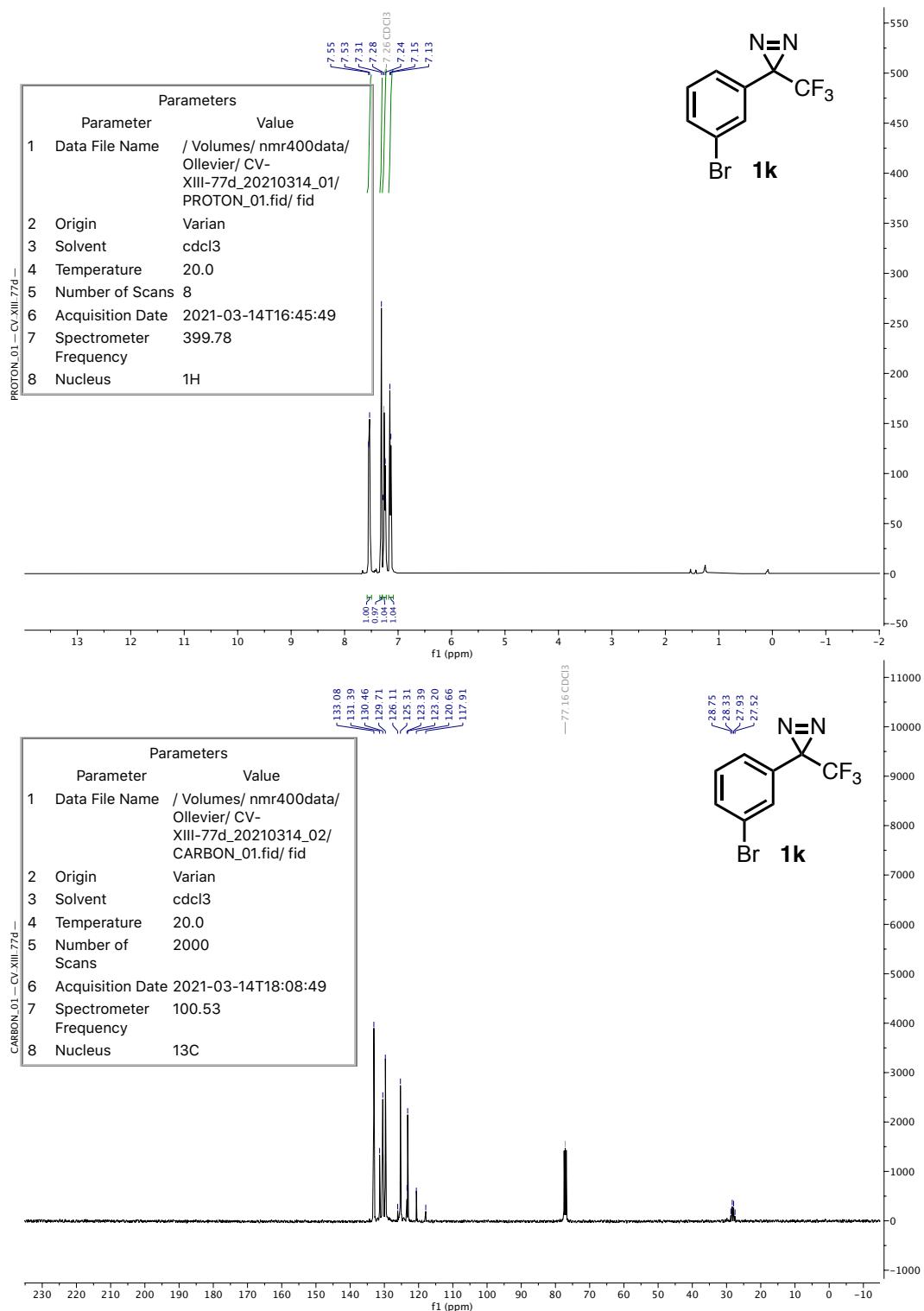


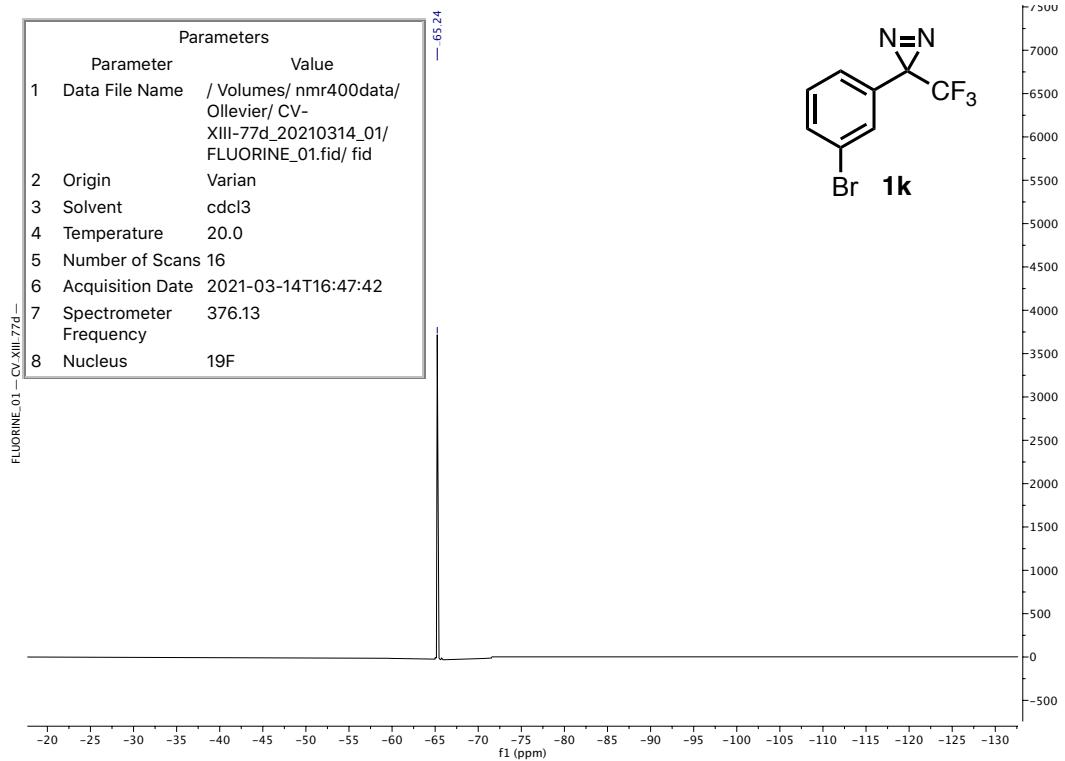
3-(4-Bromophenyl)-3-(trifluoromethyl)-3H-diazirine 1j



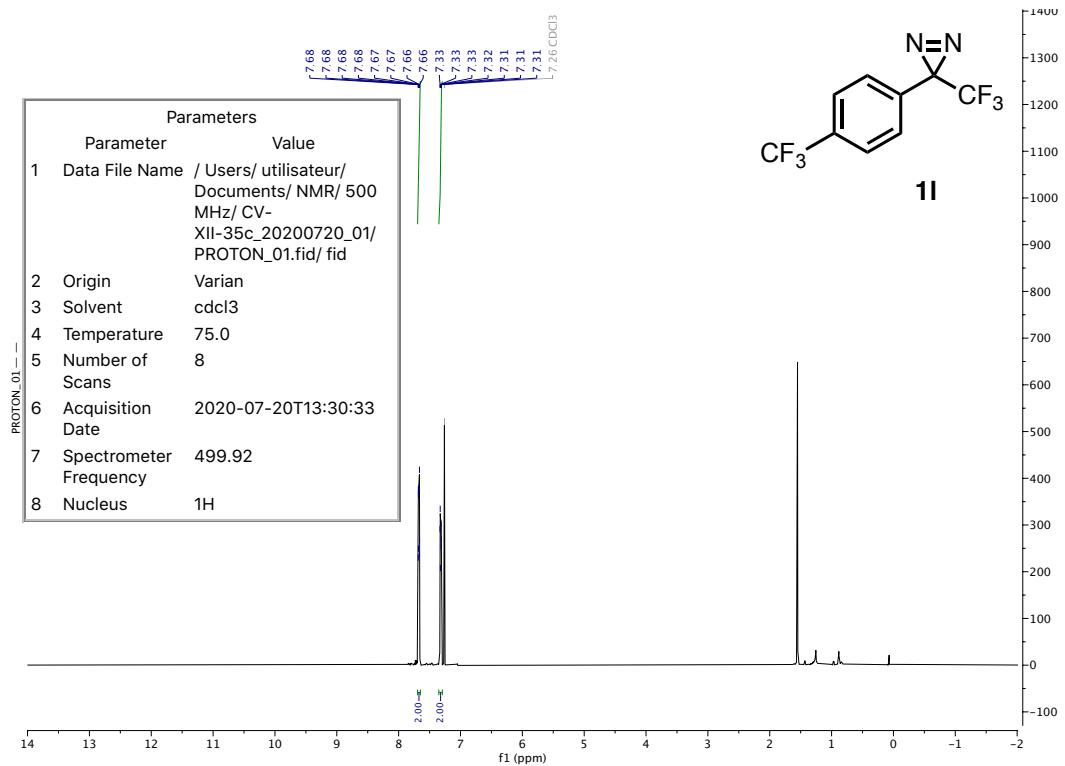


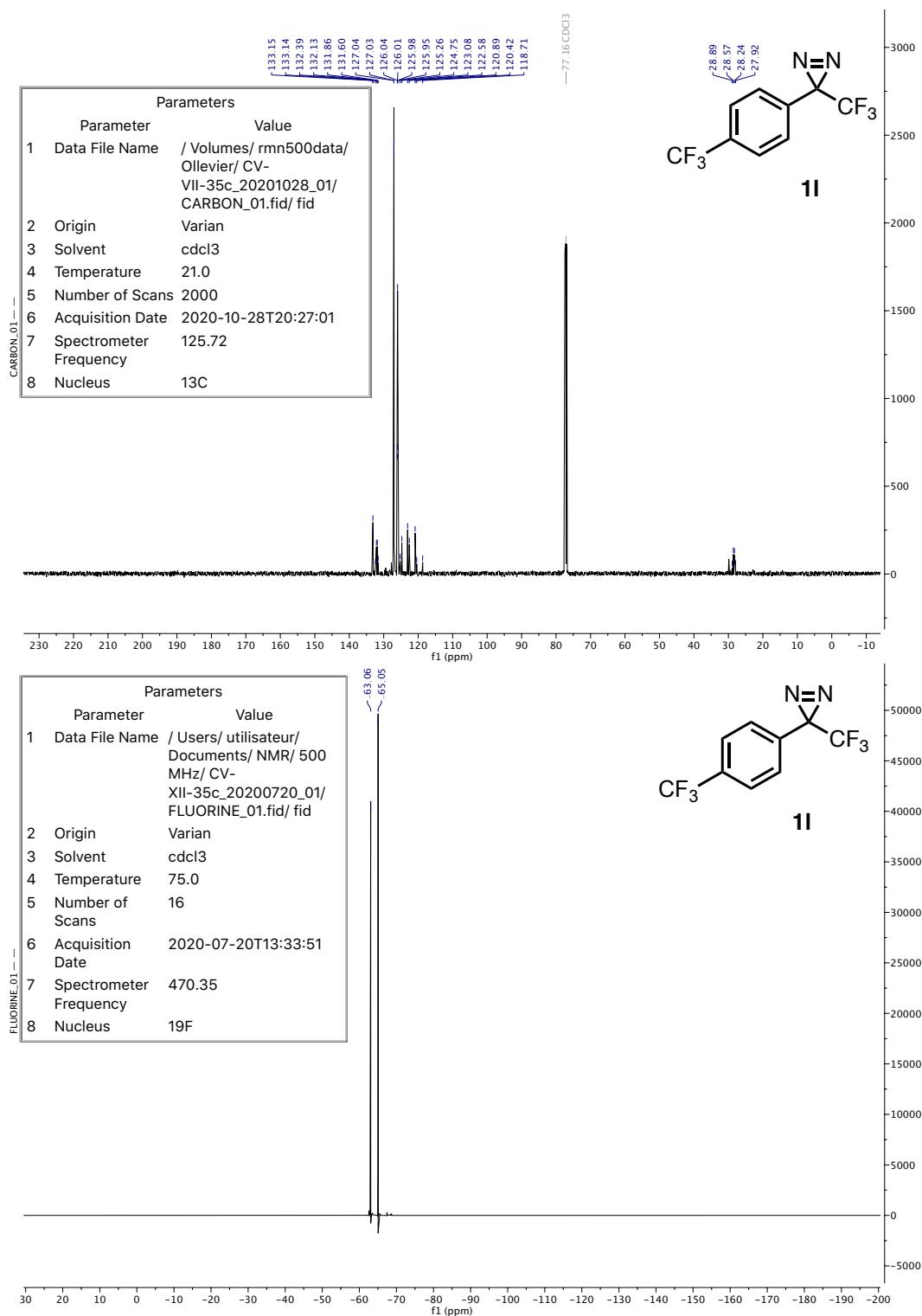
3-(3-Bromophenyl)-3-(trifluoromethyl)-3*H*-diazirine **1k**



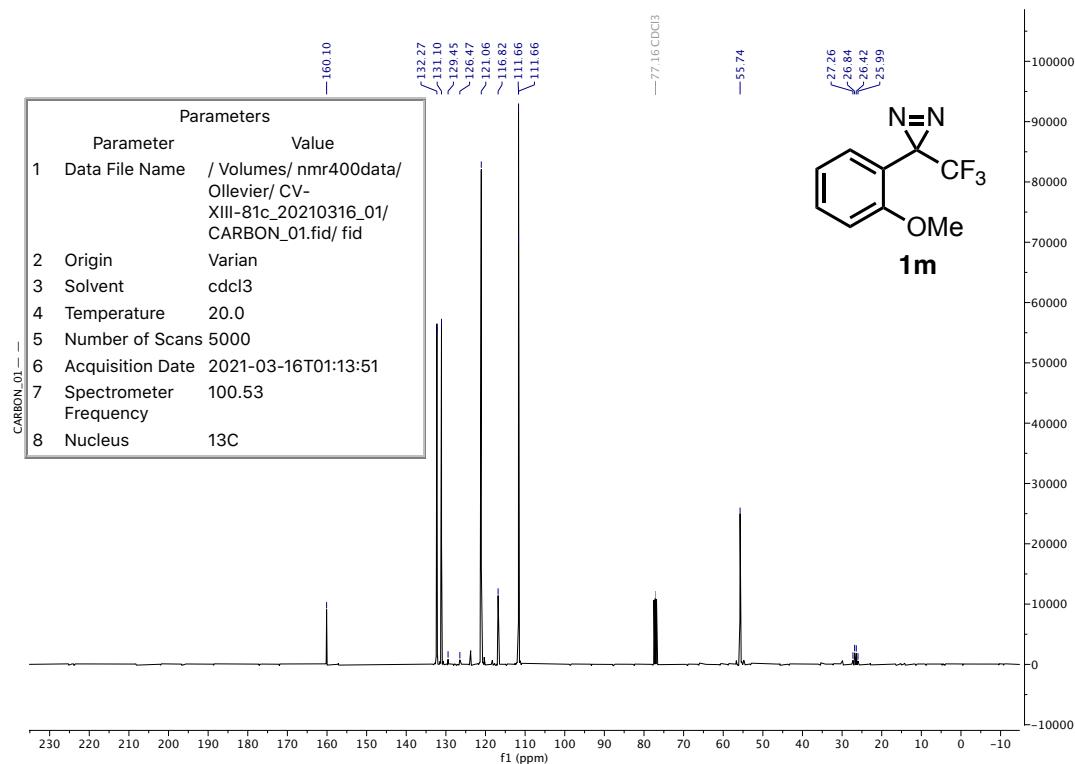
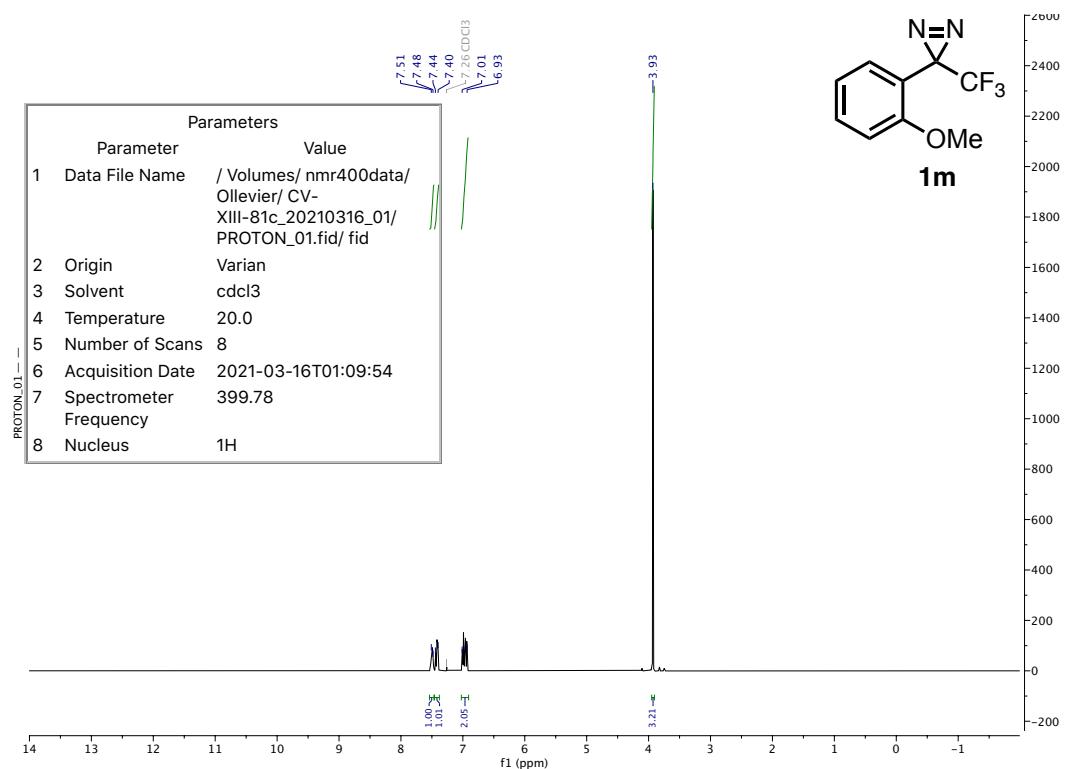


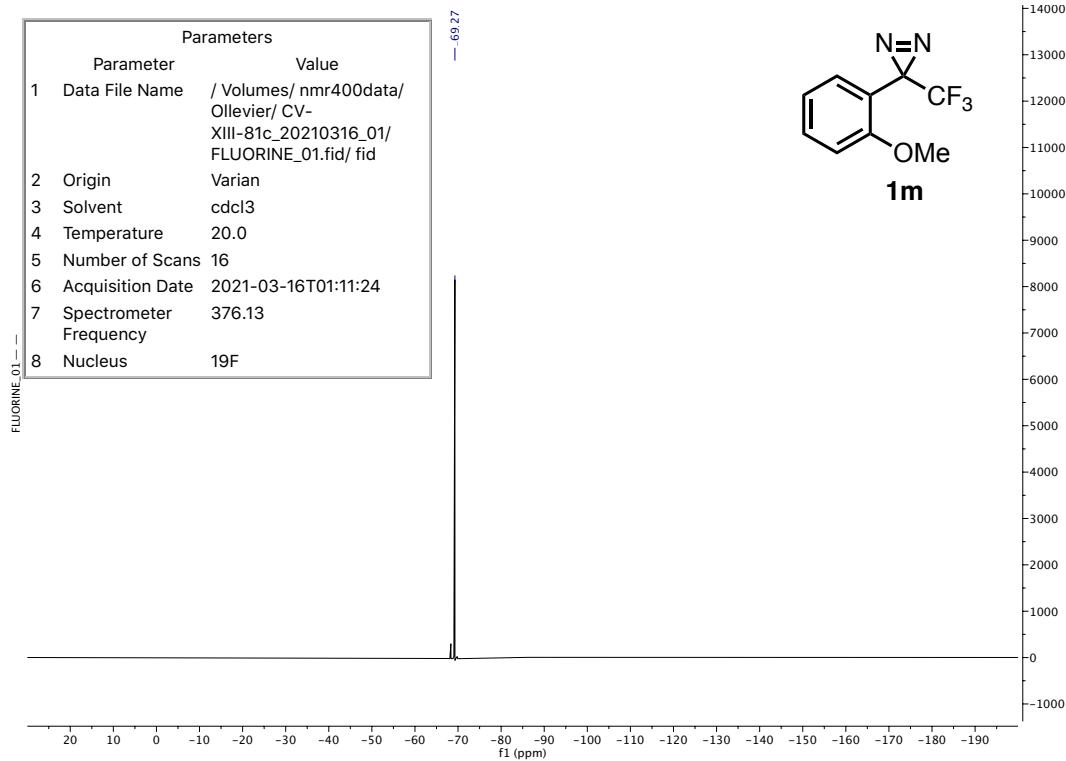
3-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-3*H*-diazirine 1l



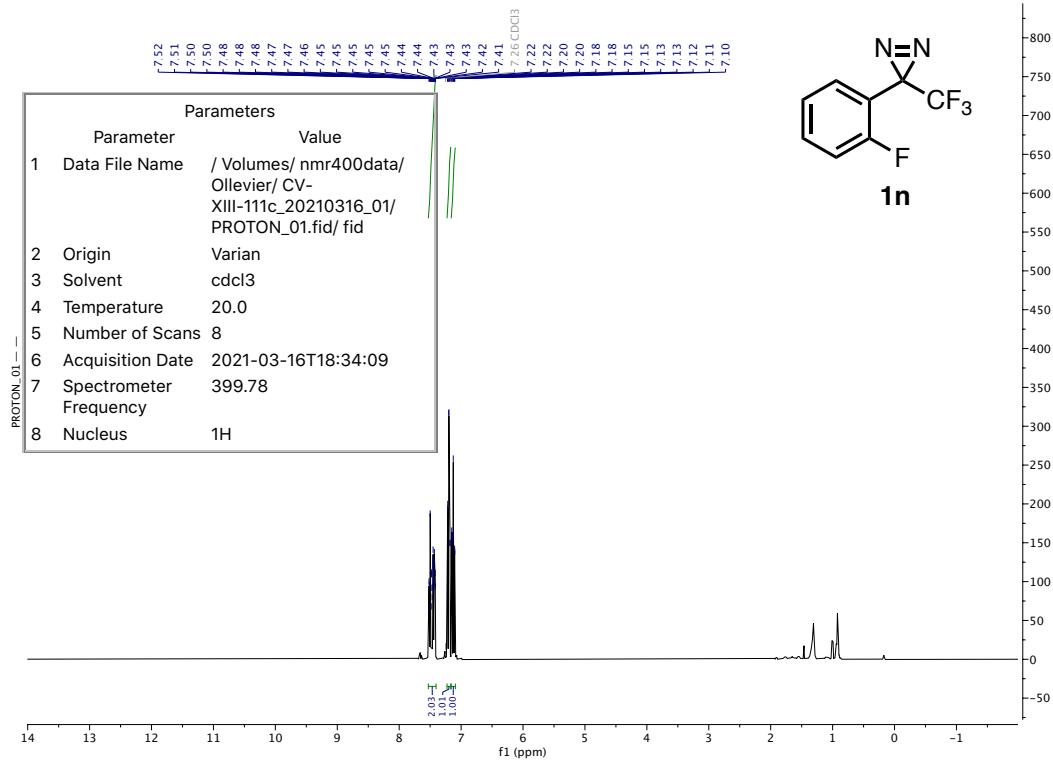


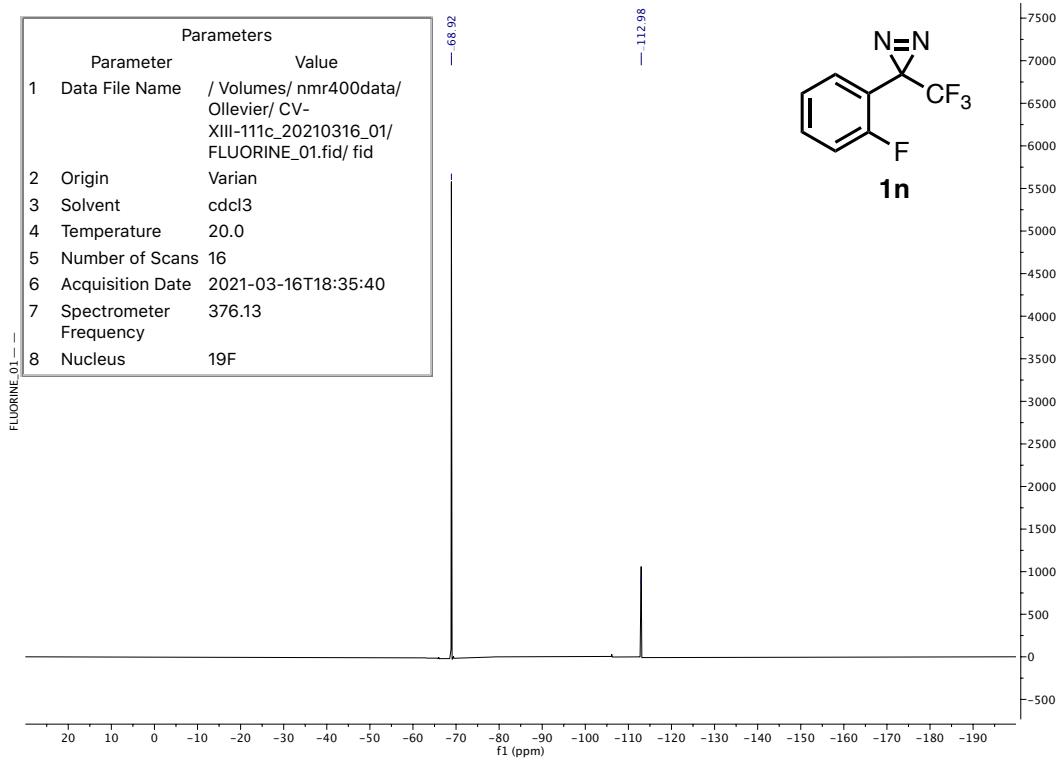
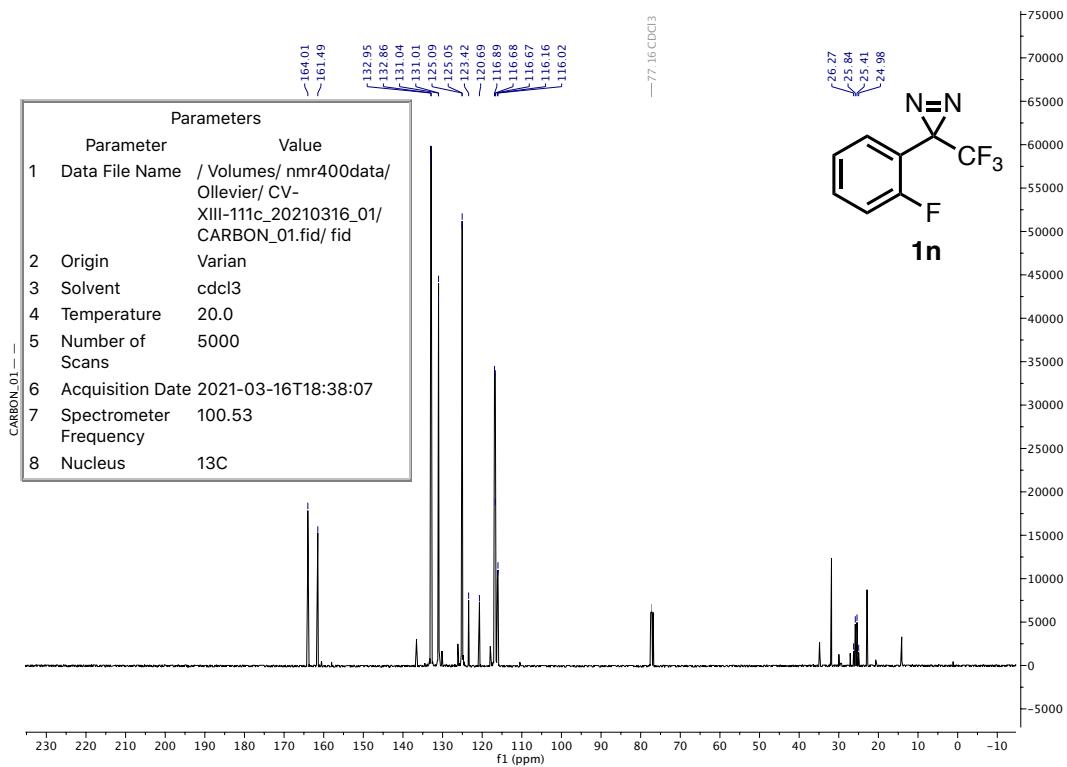
3-(2-Methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirine 1m



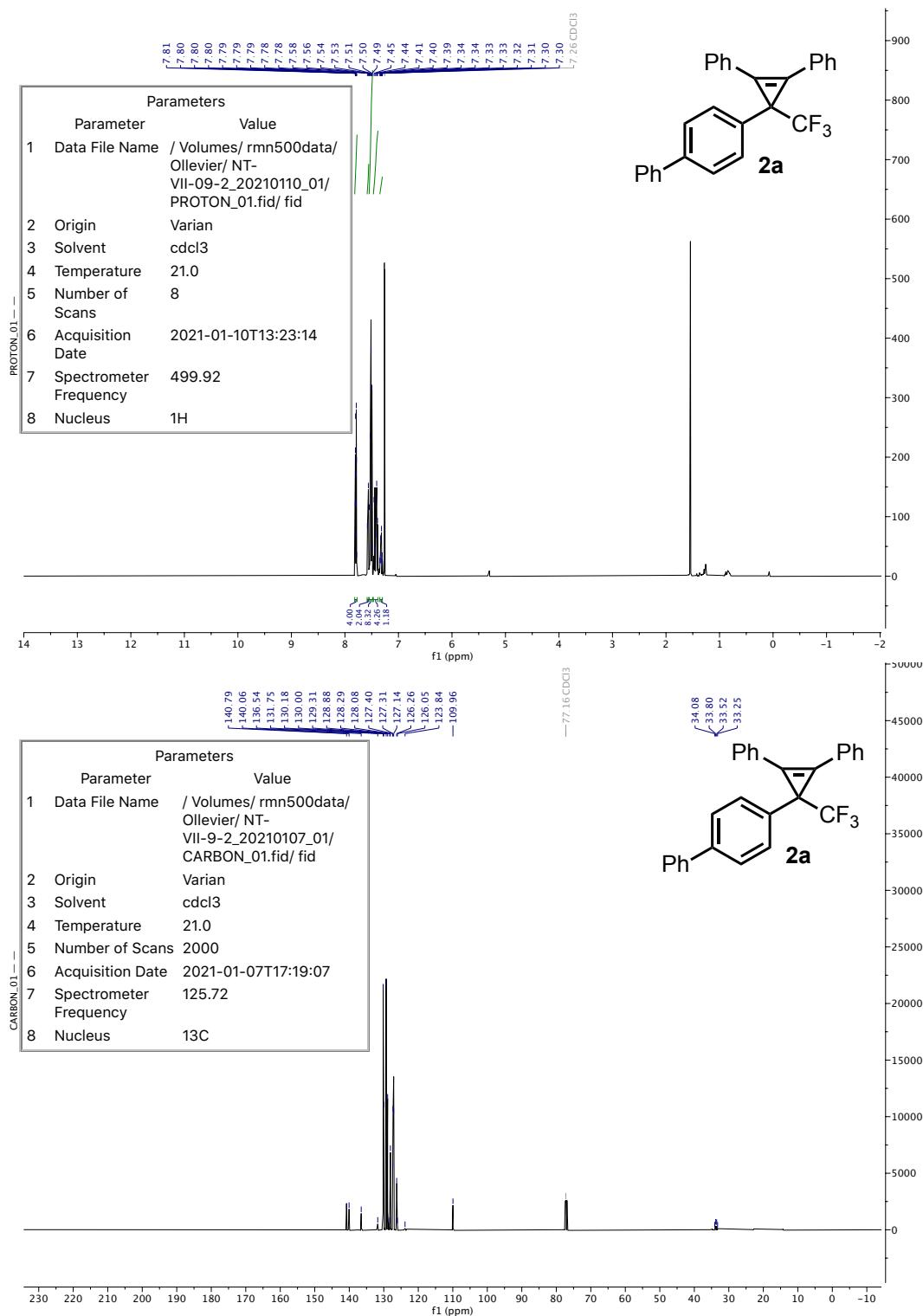


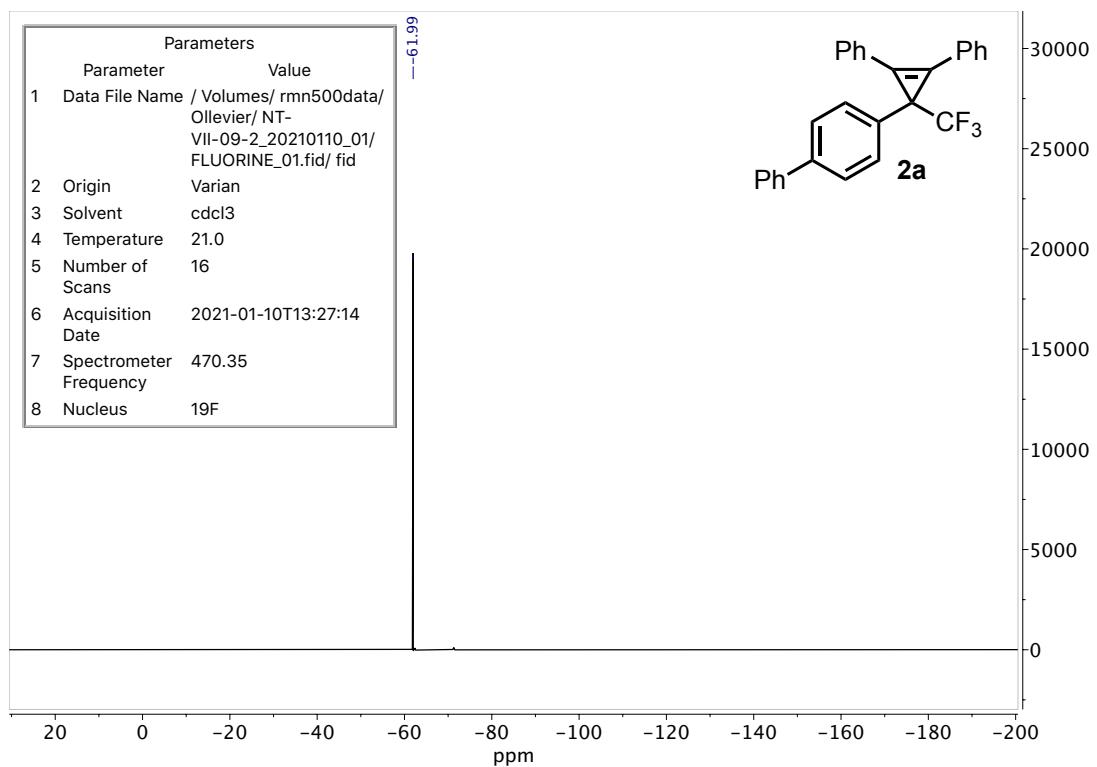
3-(2-Fluorophenyl)-3-(trifluoromethyl)-3H-diazirine 1n



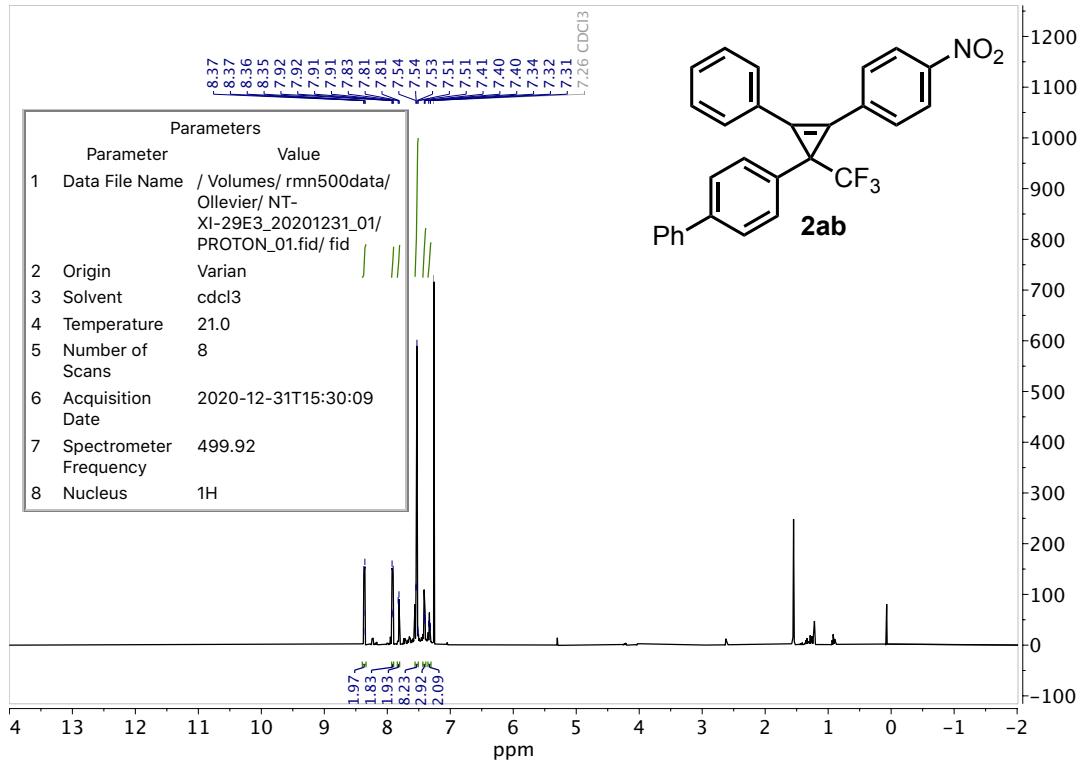


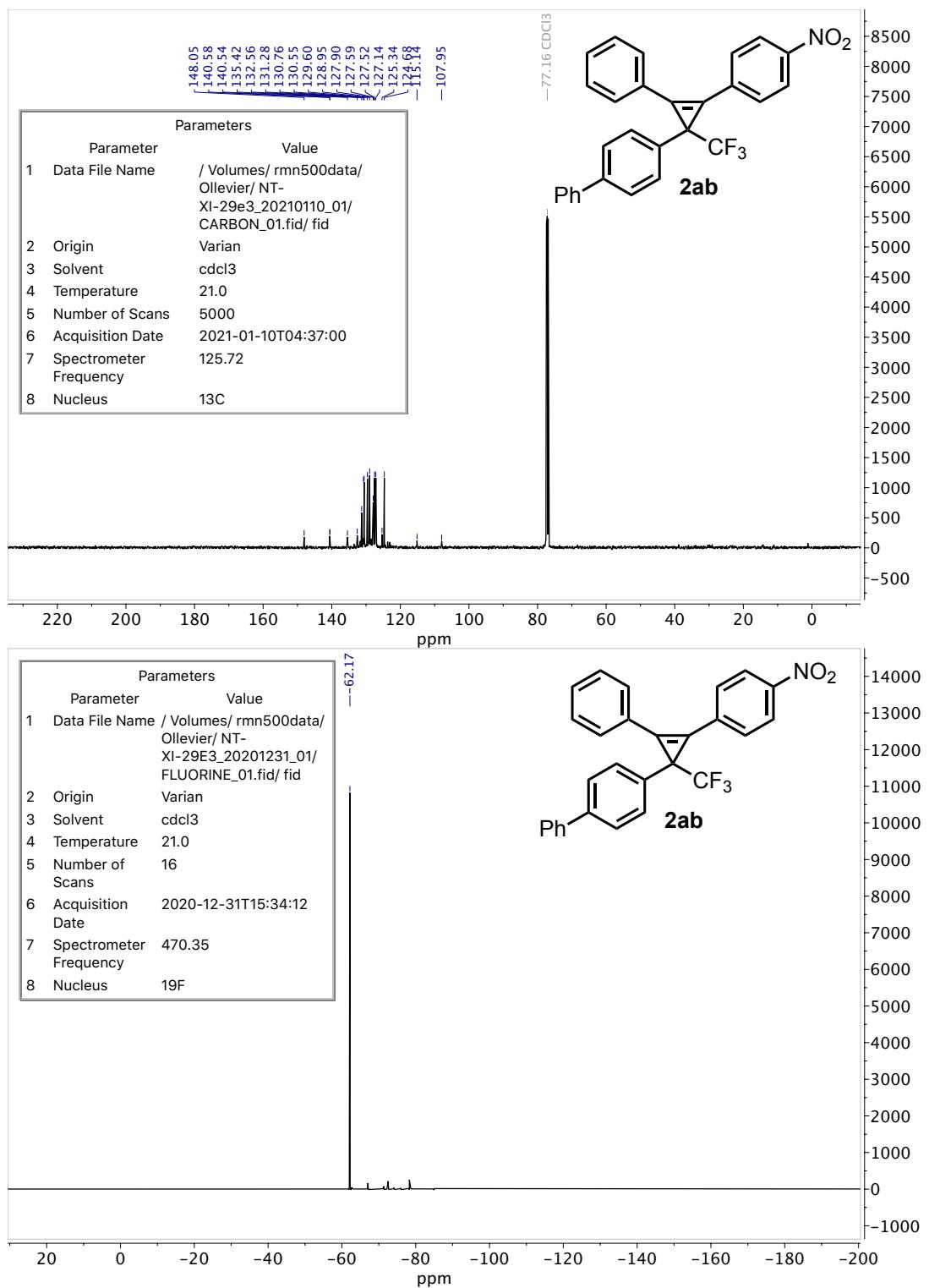
4-(2,3-Diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2a



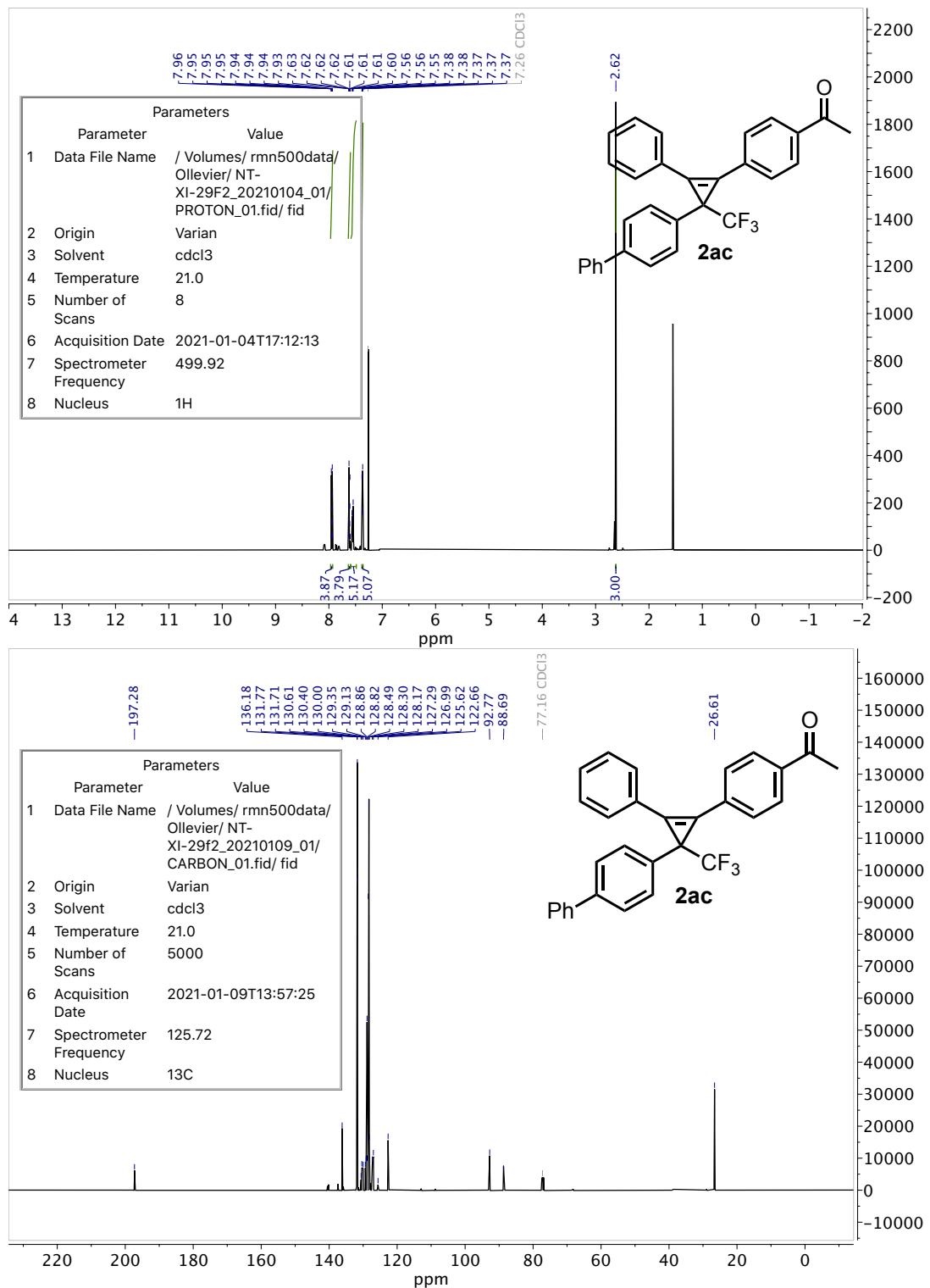


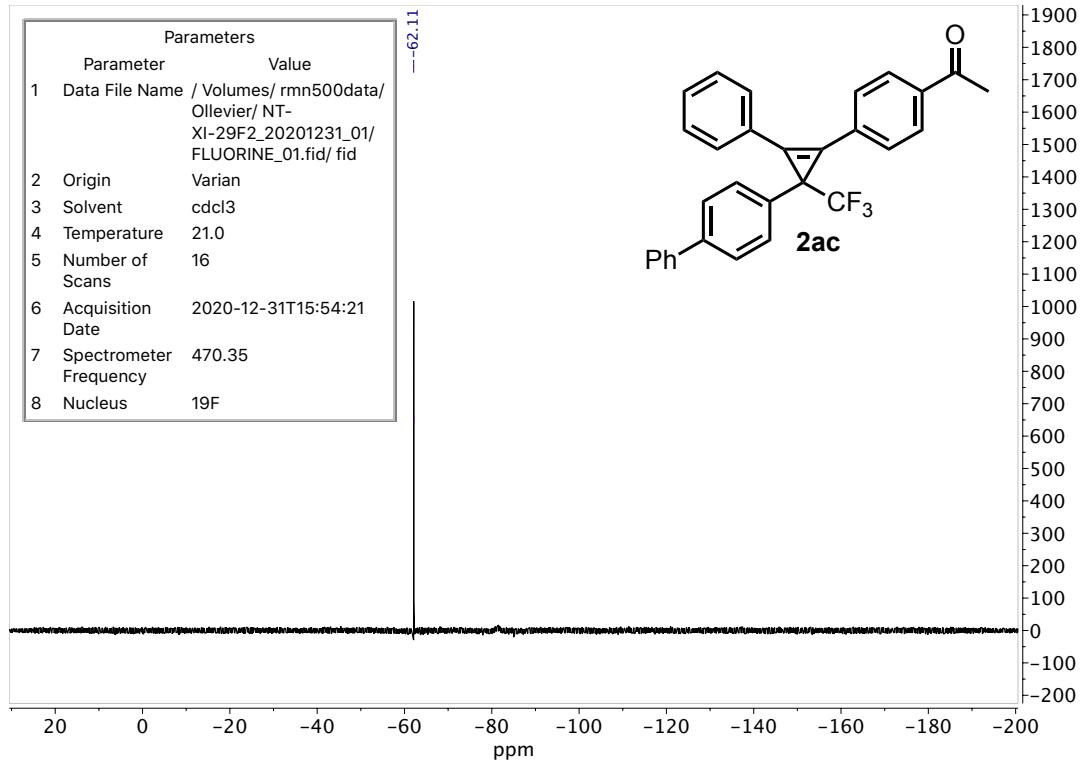
4-(2-(4-Nitrophenyl)-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ab



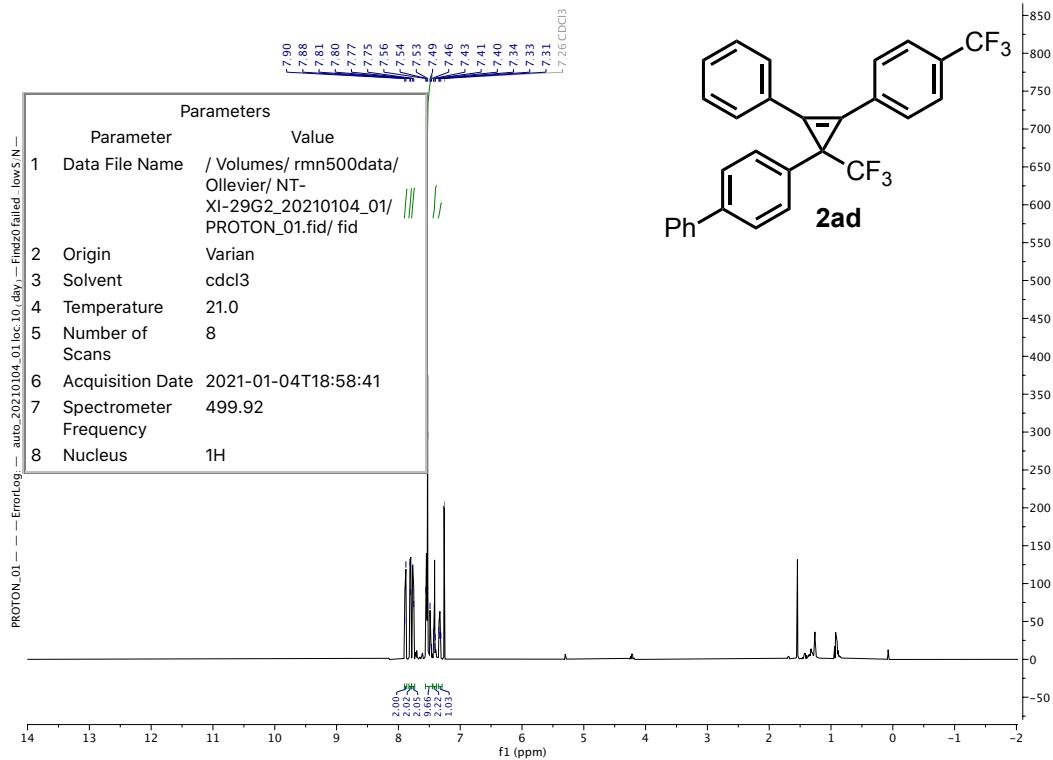


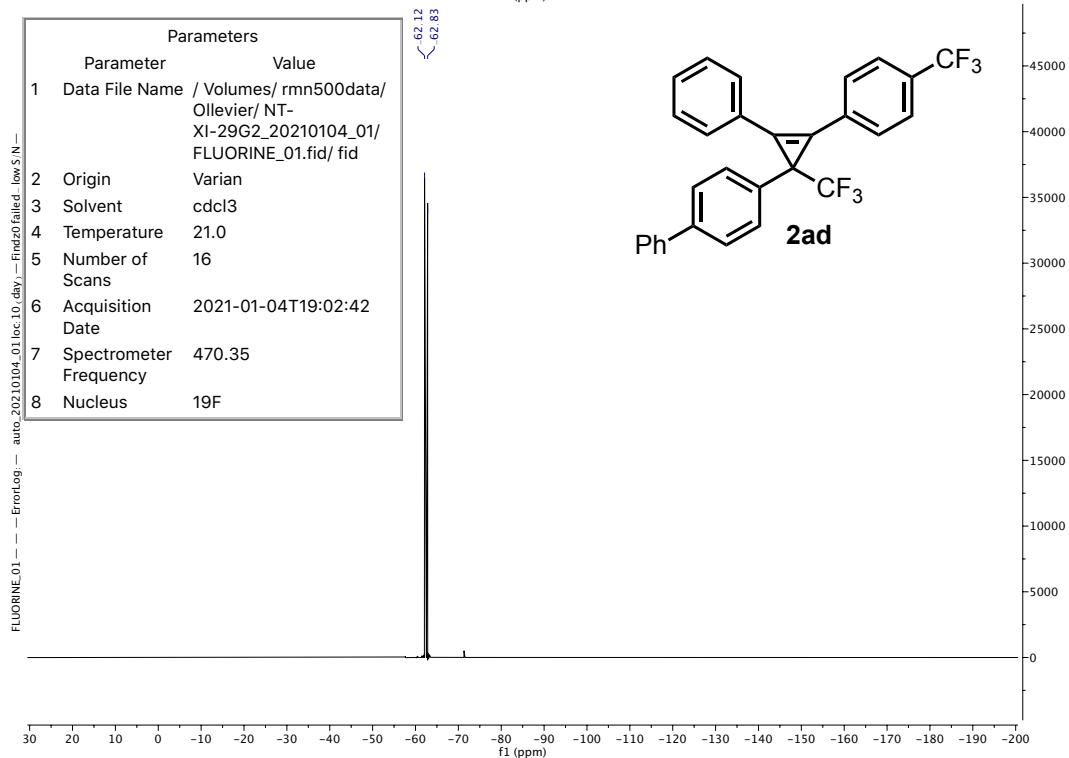
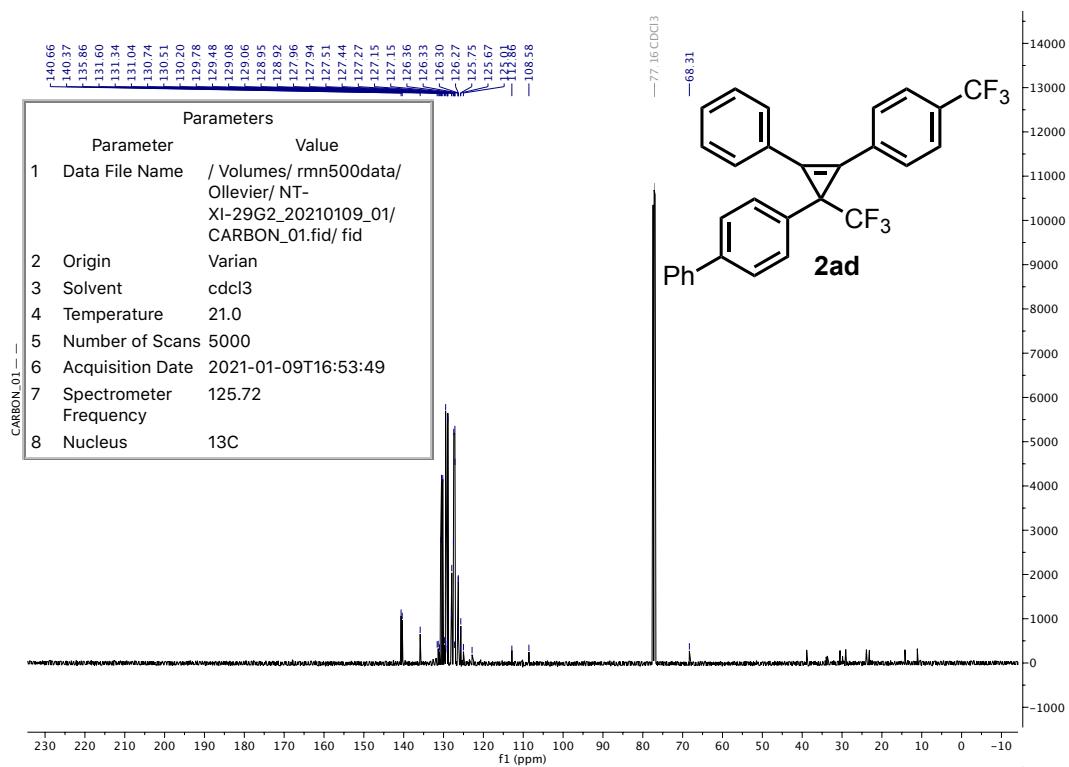
1-(4-(3-([1,1'-Biphenyl]-4-yl)-2-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)phenyl)ethan-1-one 2ac



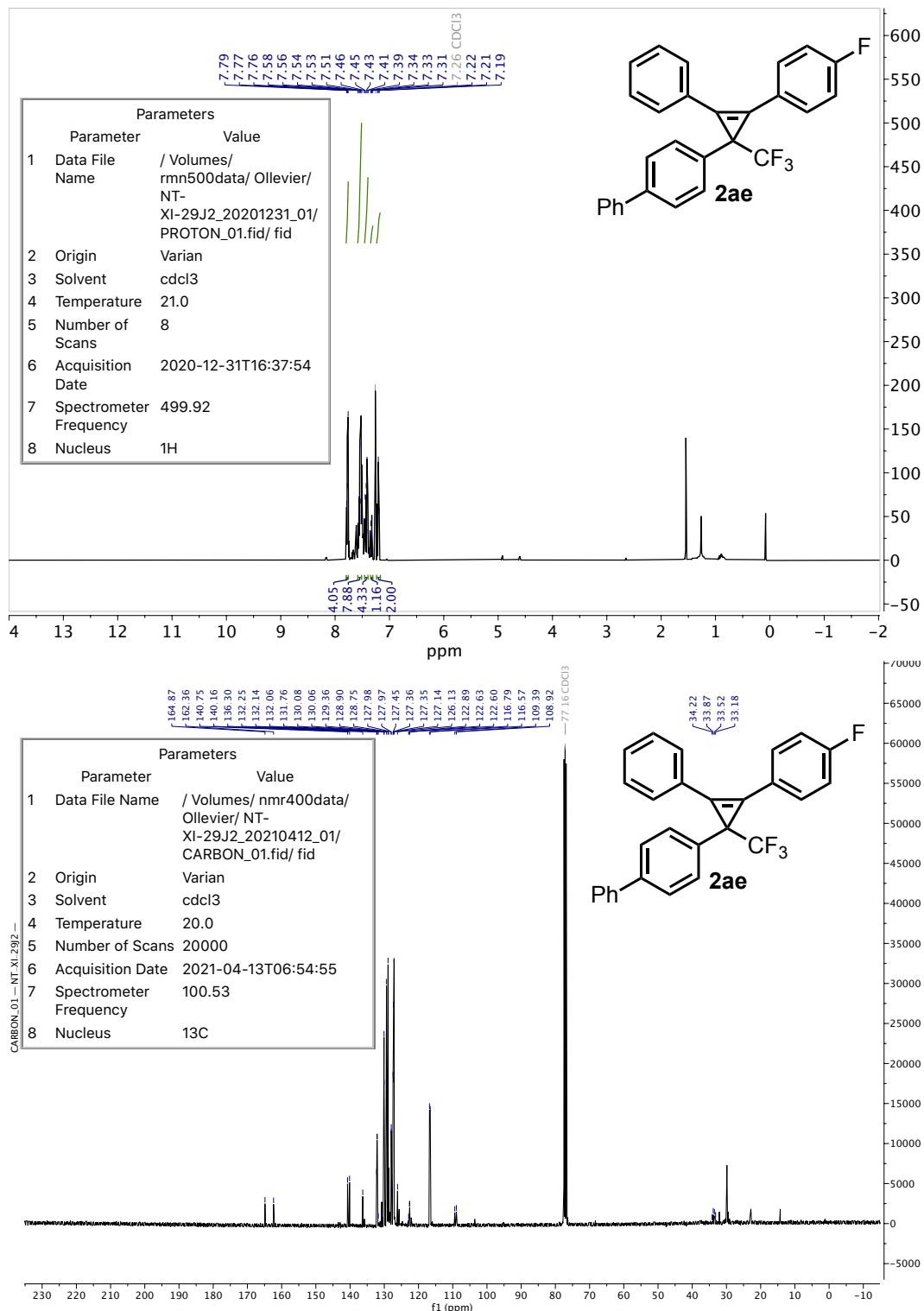


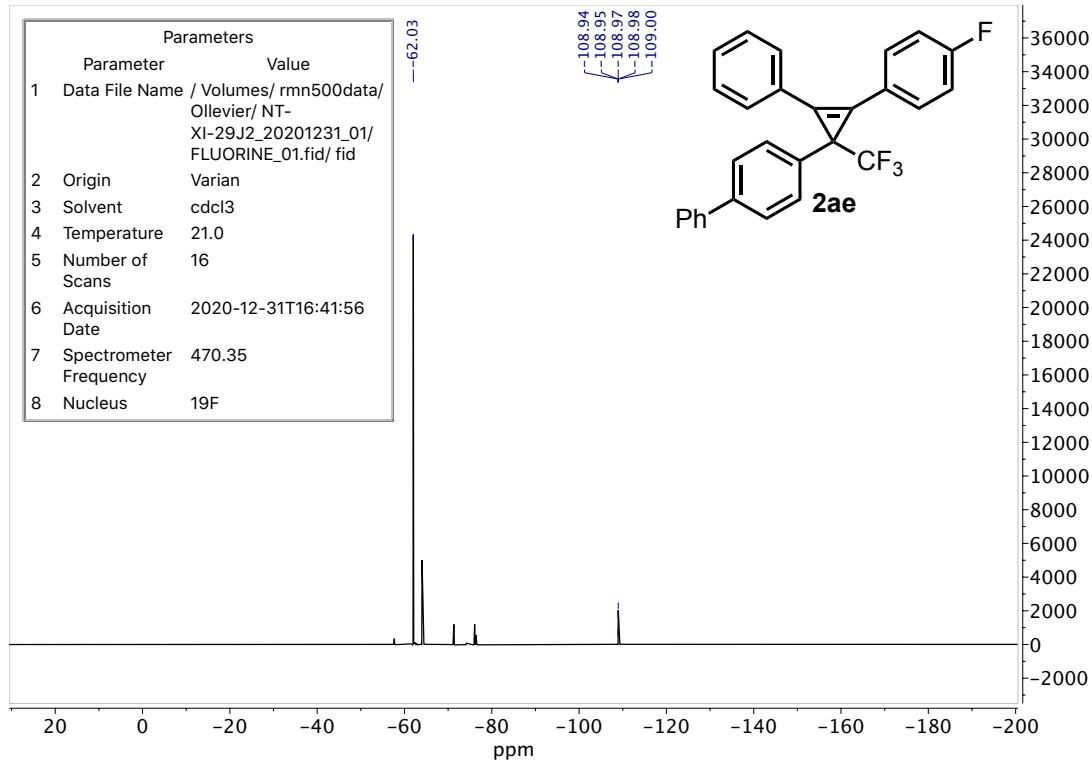
4-(2-Phenyl-1-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ad



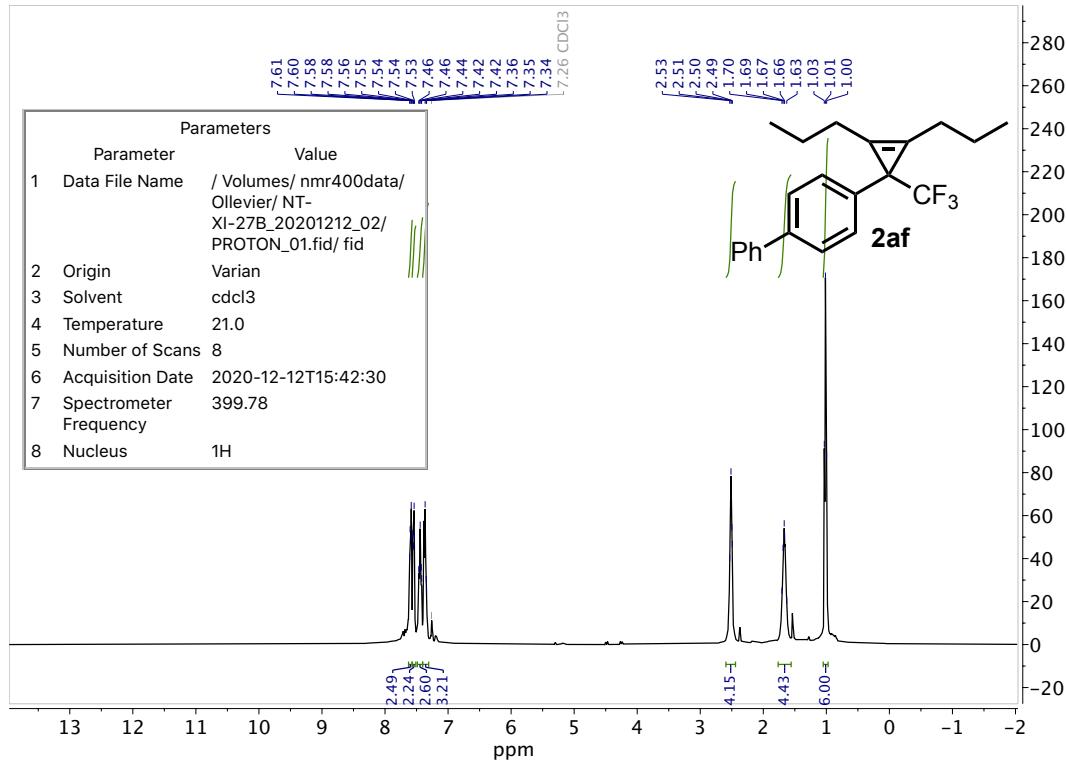


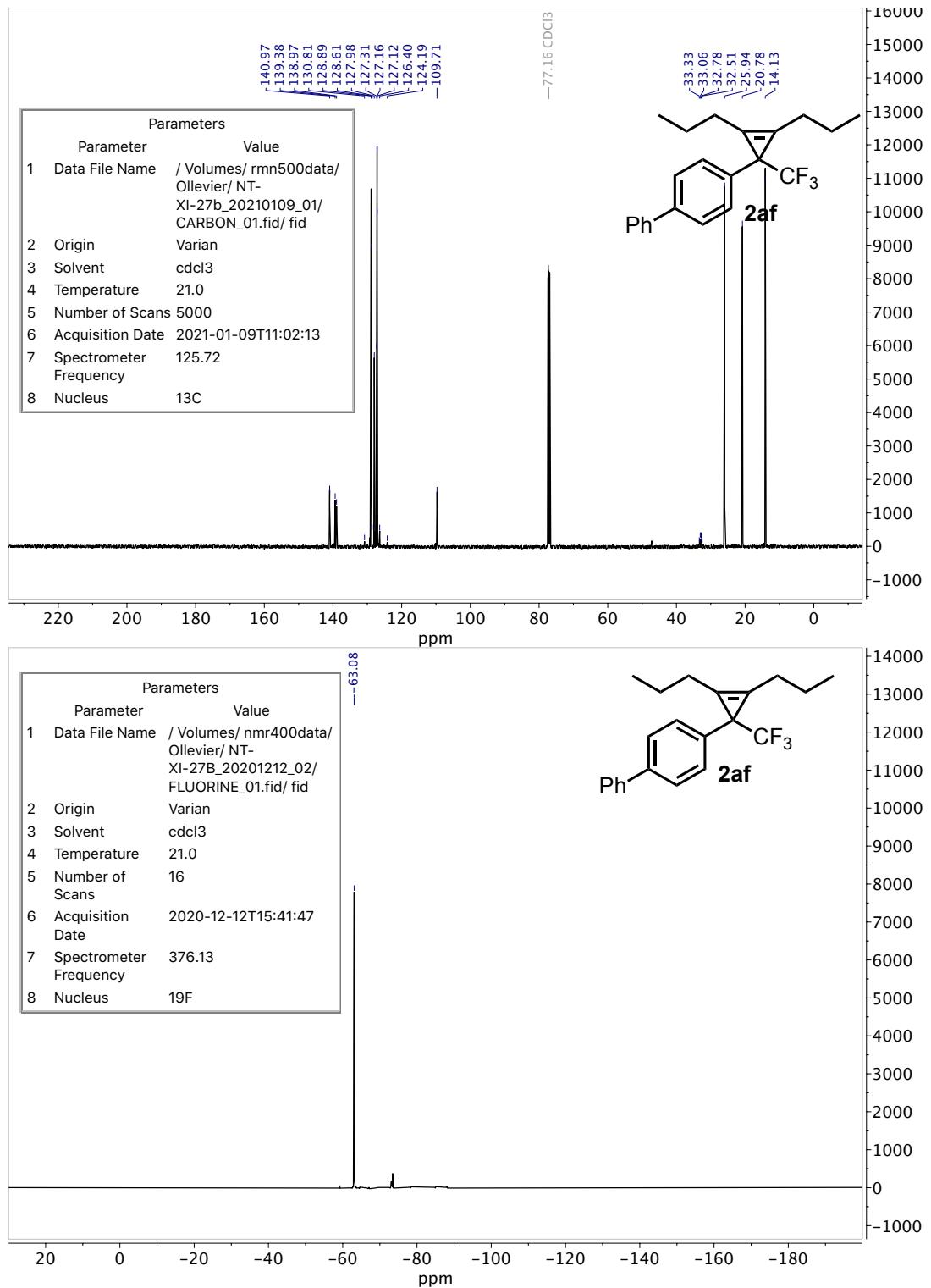
4-(2-(4-Fluorophenyl)-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ae



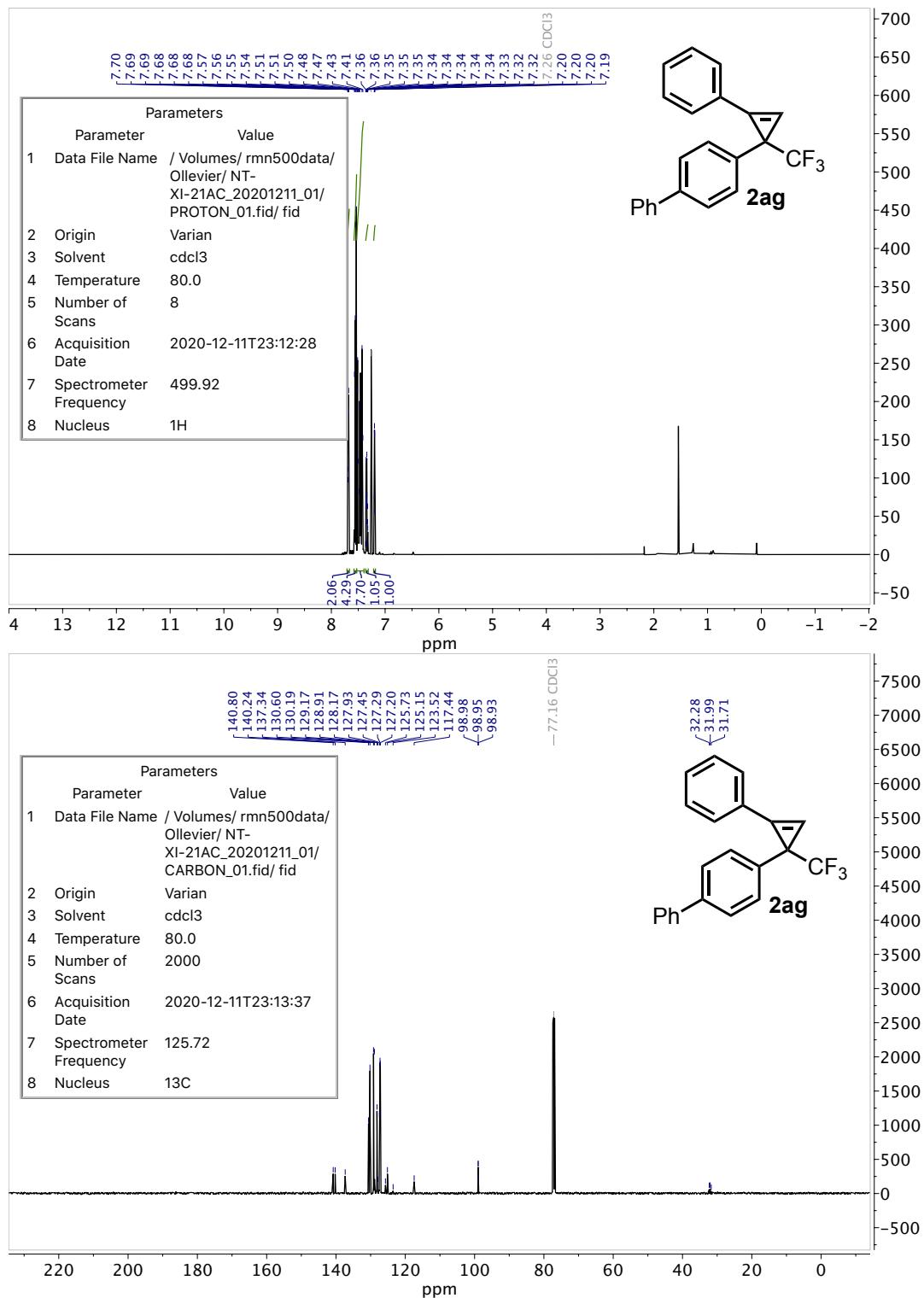


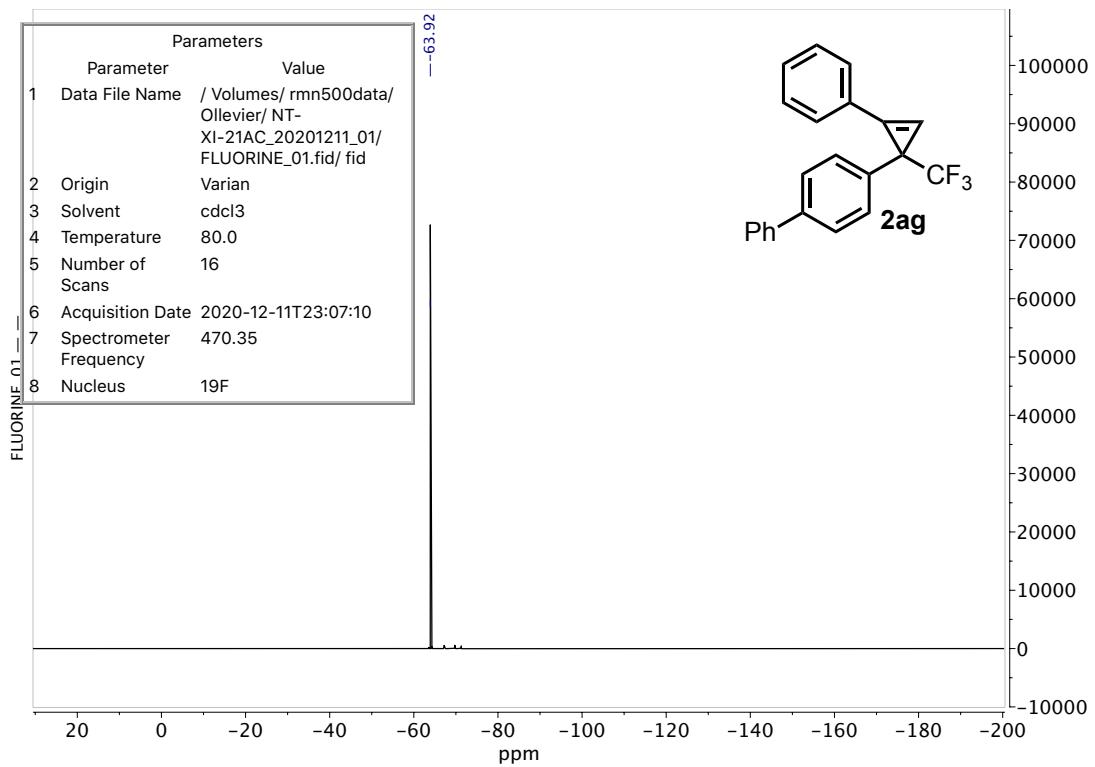
4-(2,3-Dipropyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2af



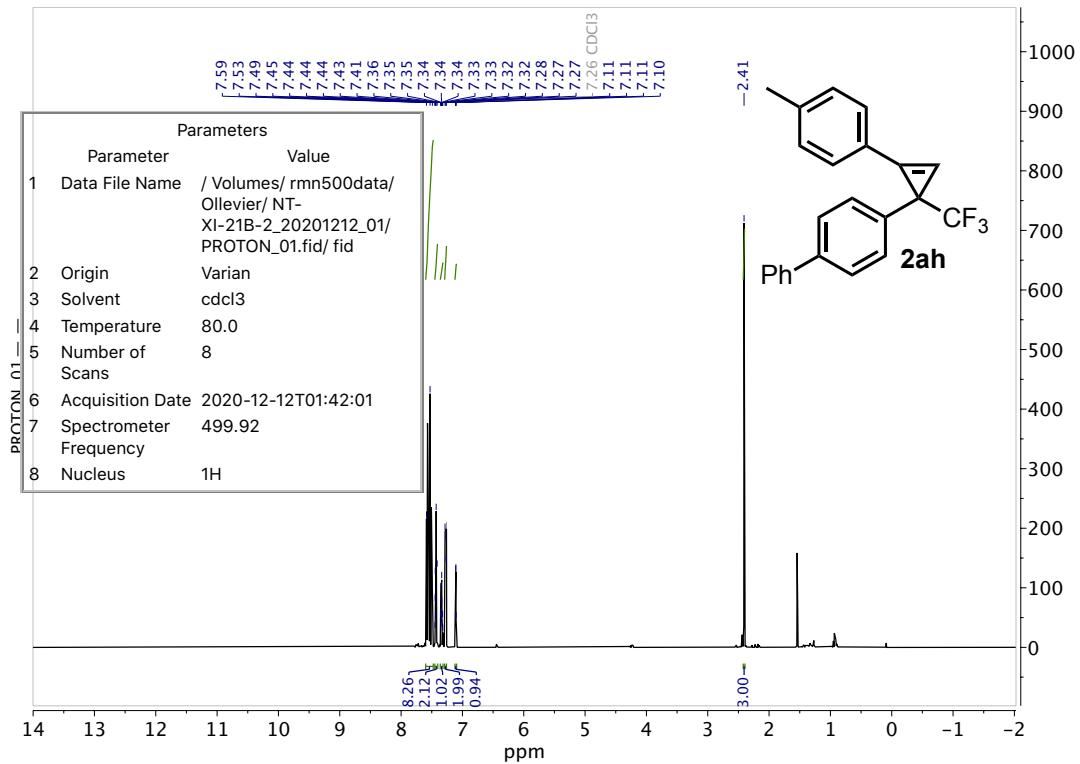


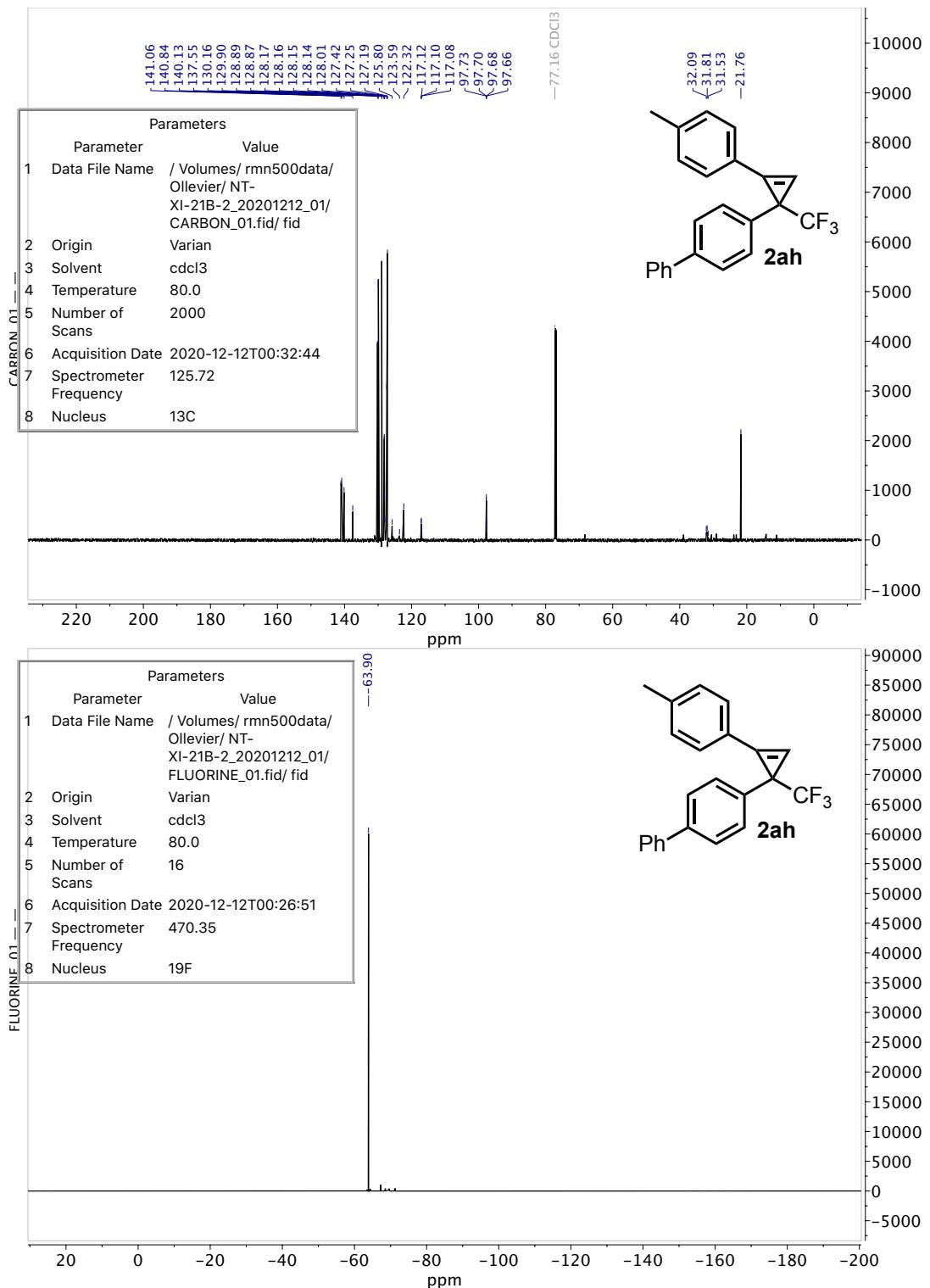
4-(2-Phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ag



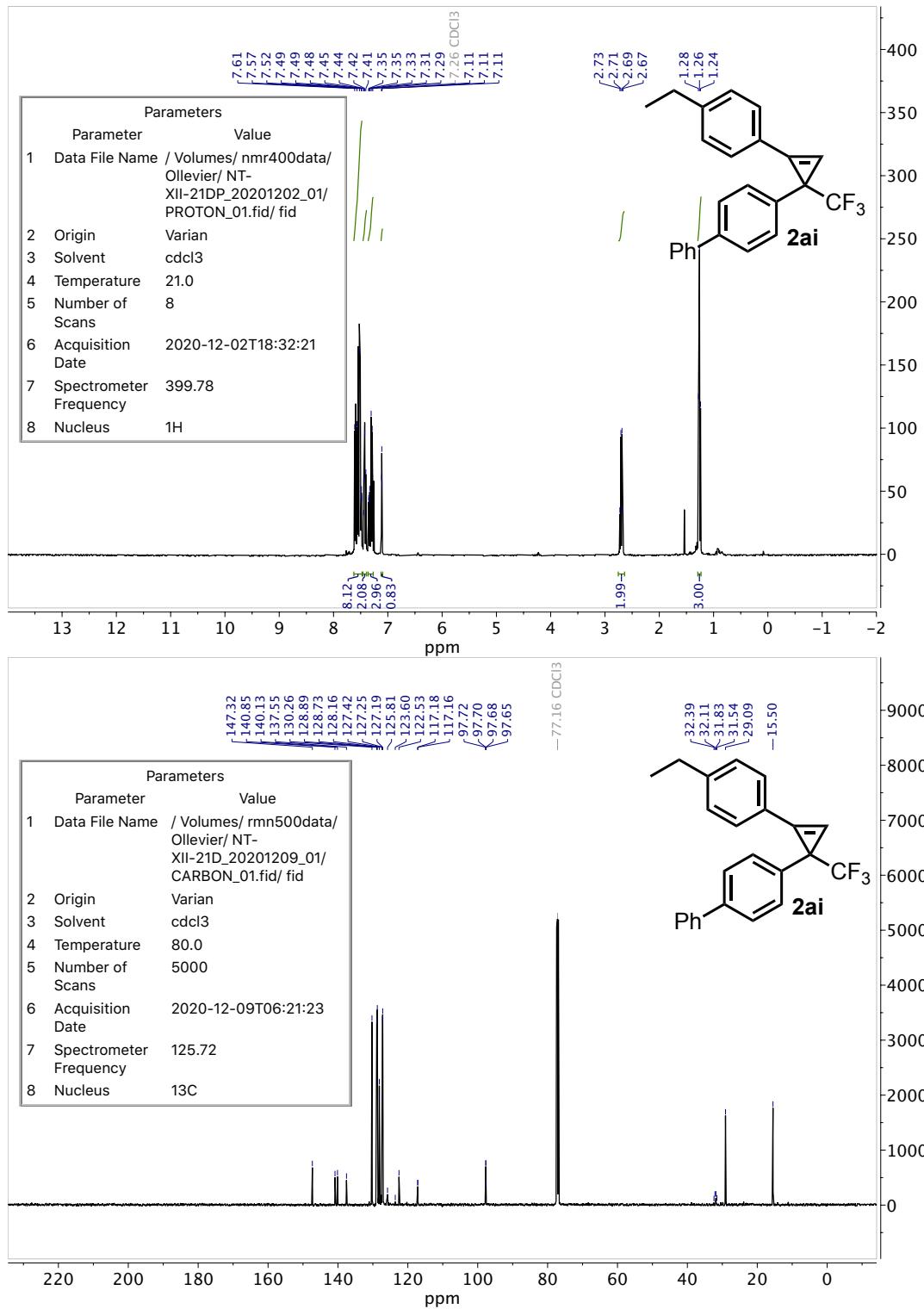


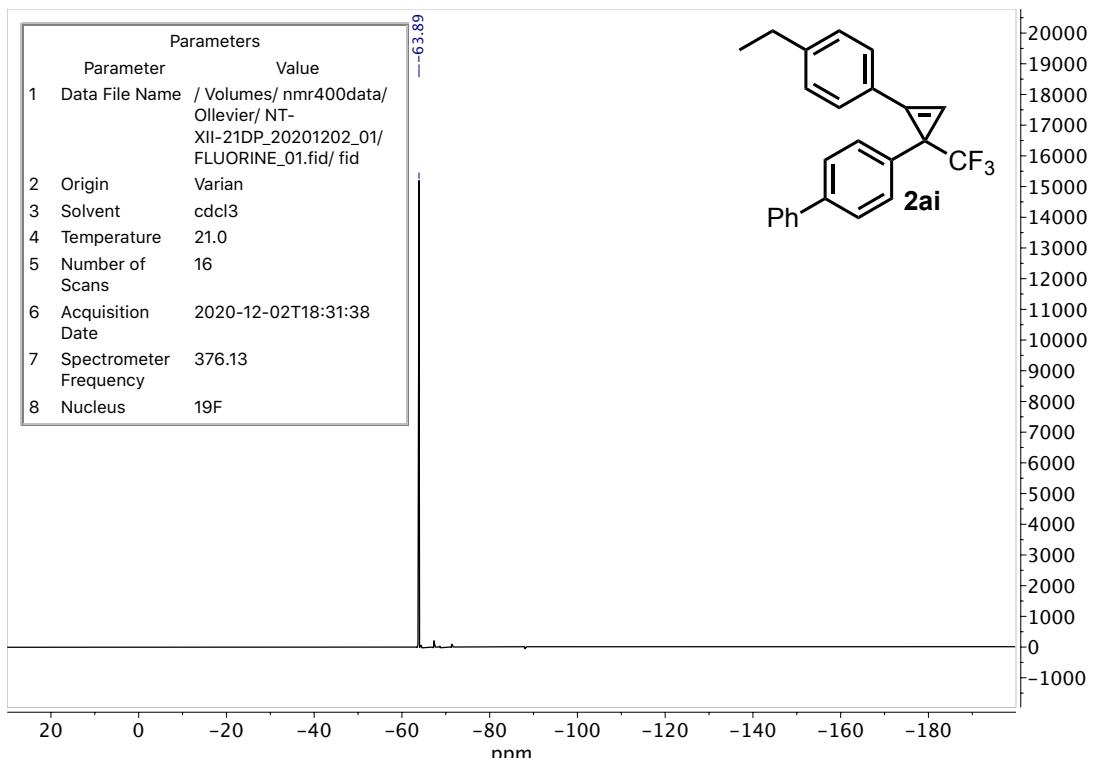
4-(2-(*p*-Tolyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ah



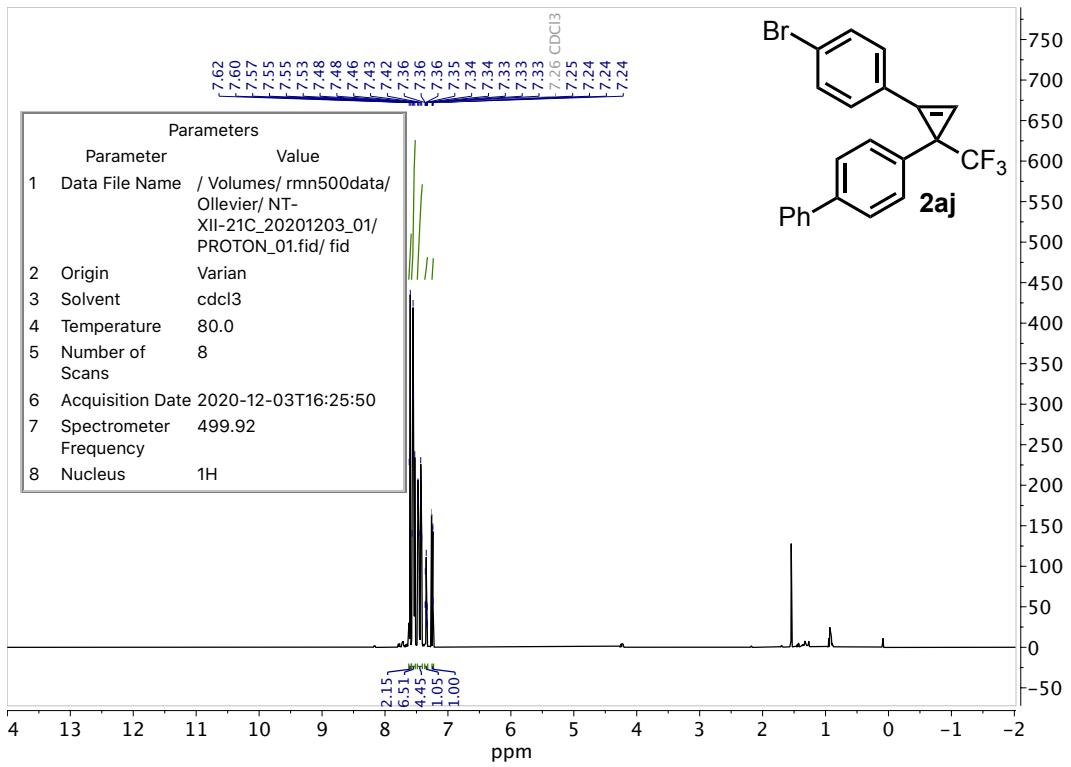


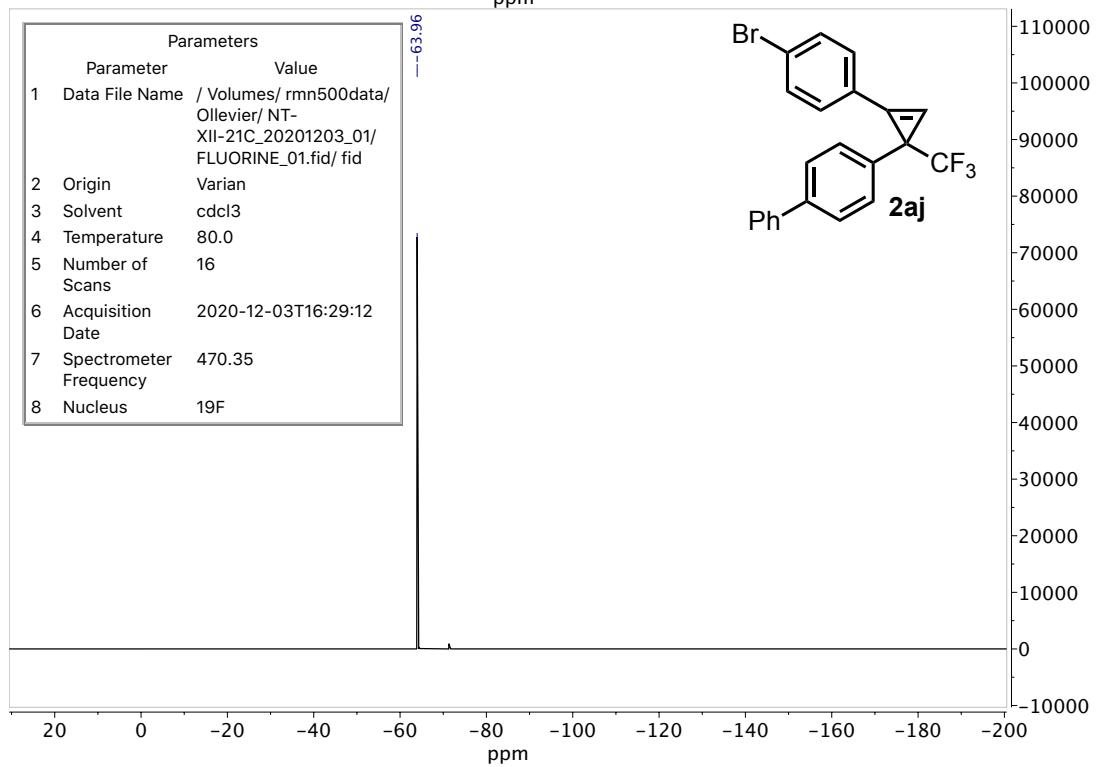
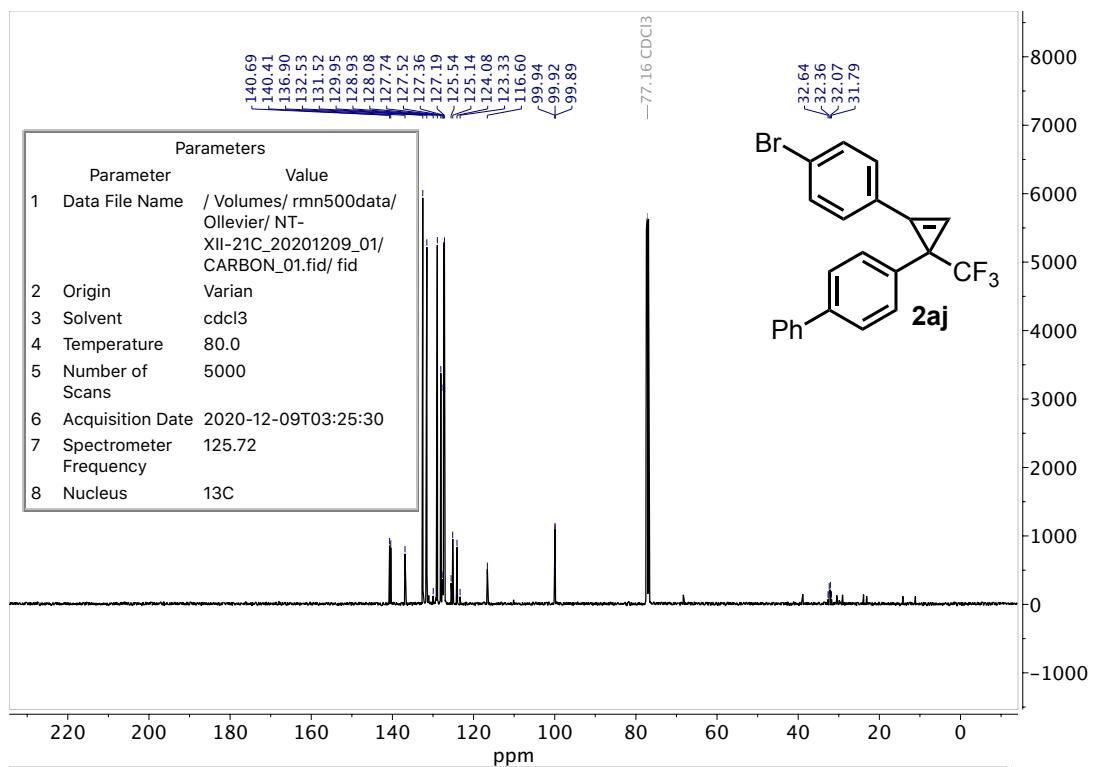
4-(2-(4-Ethylphenyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2ai



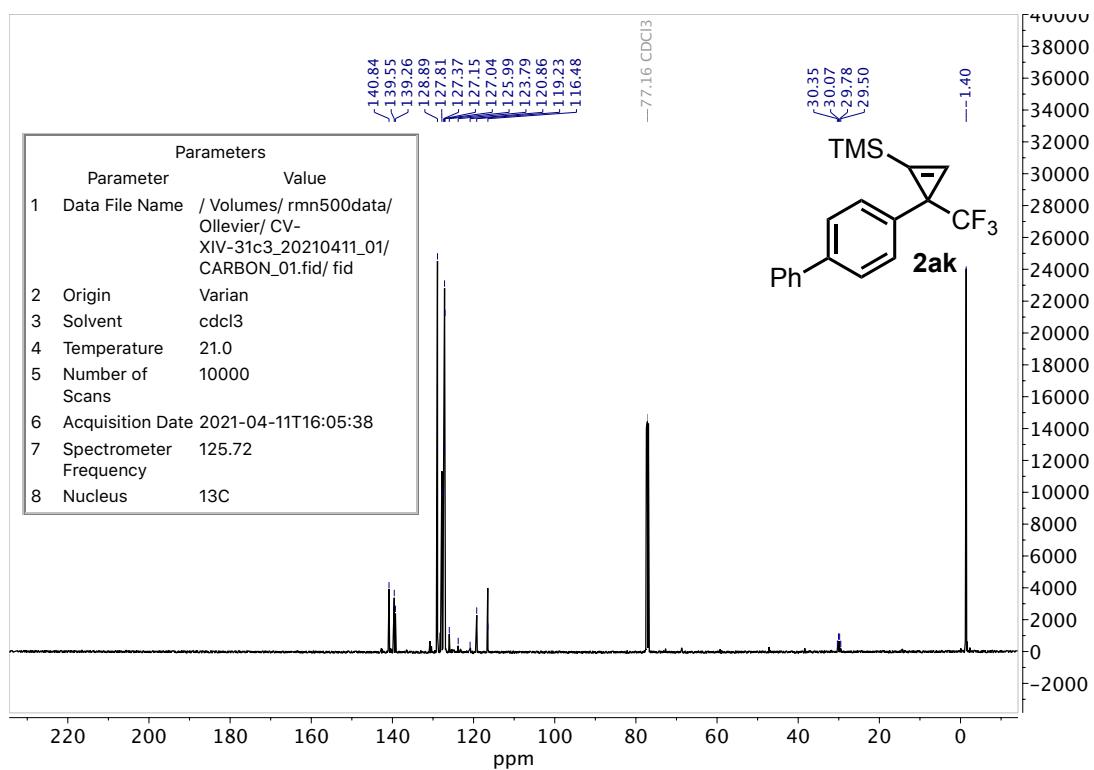
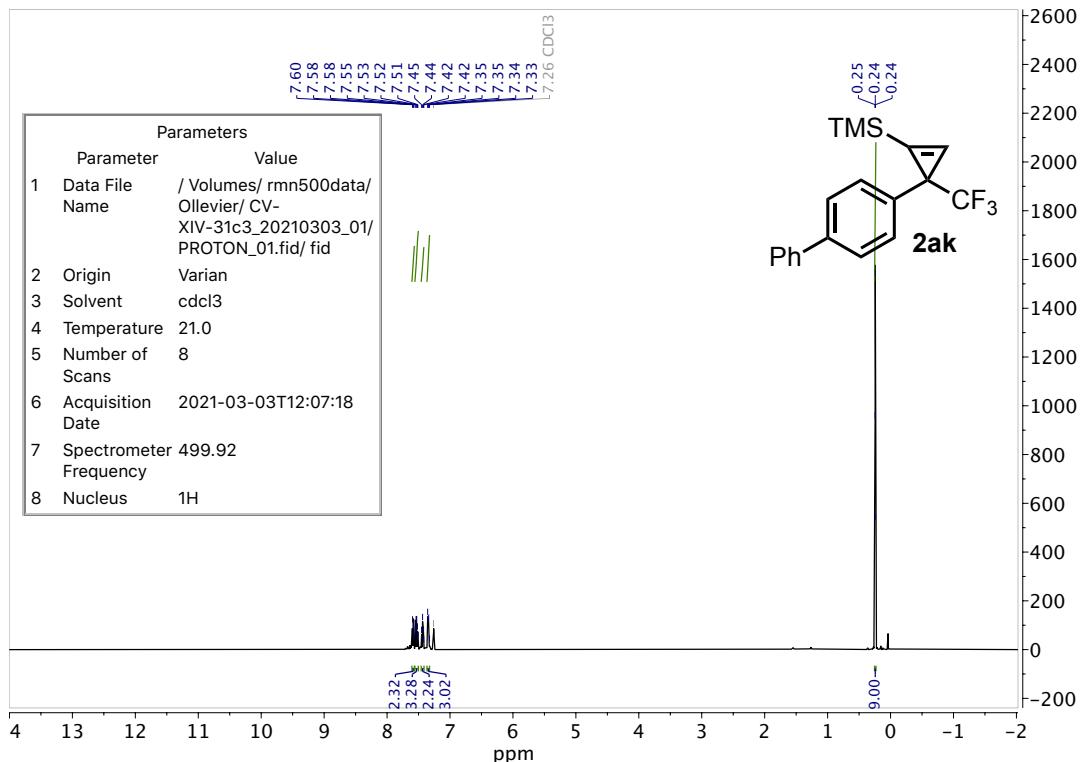


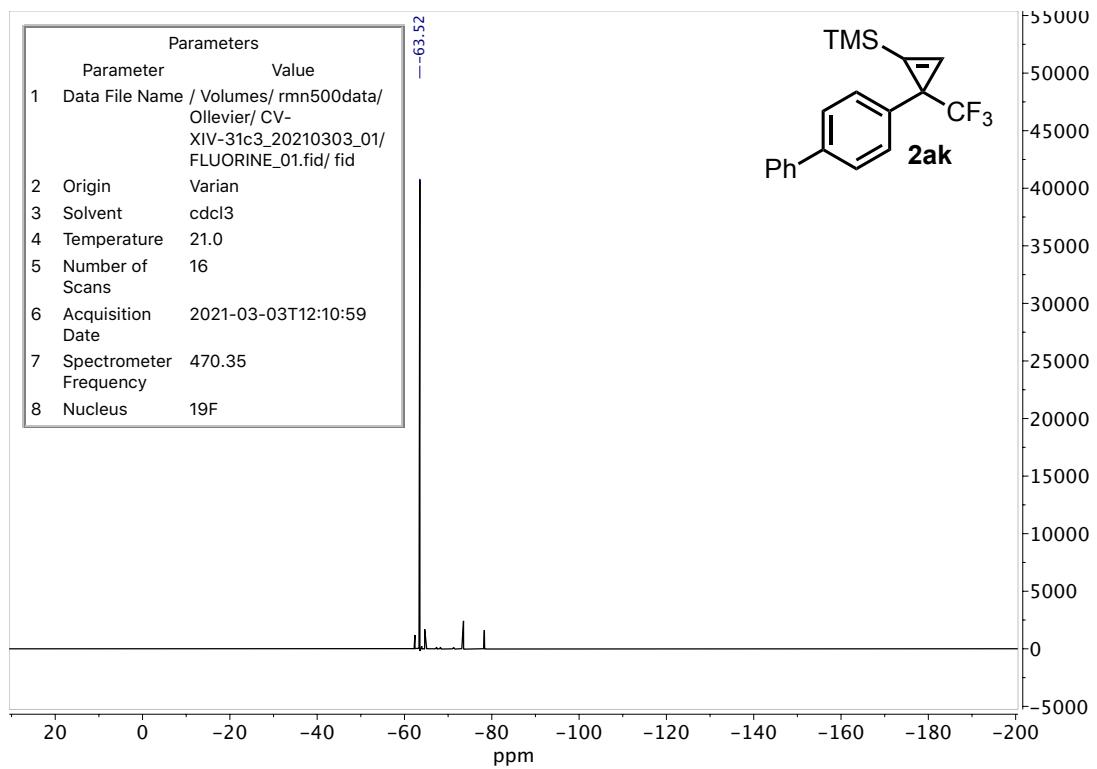
4-(2-(4-Bromophenyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl **2aj**



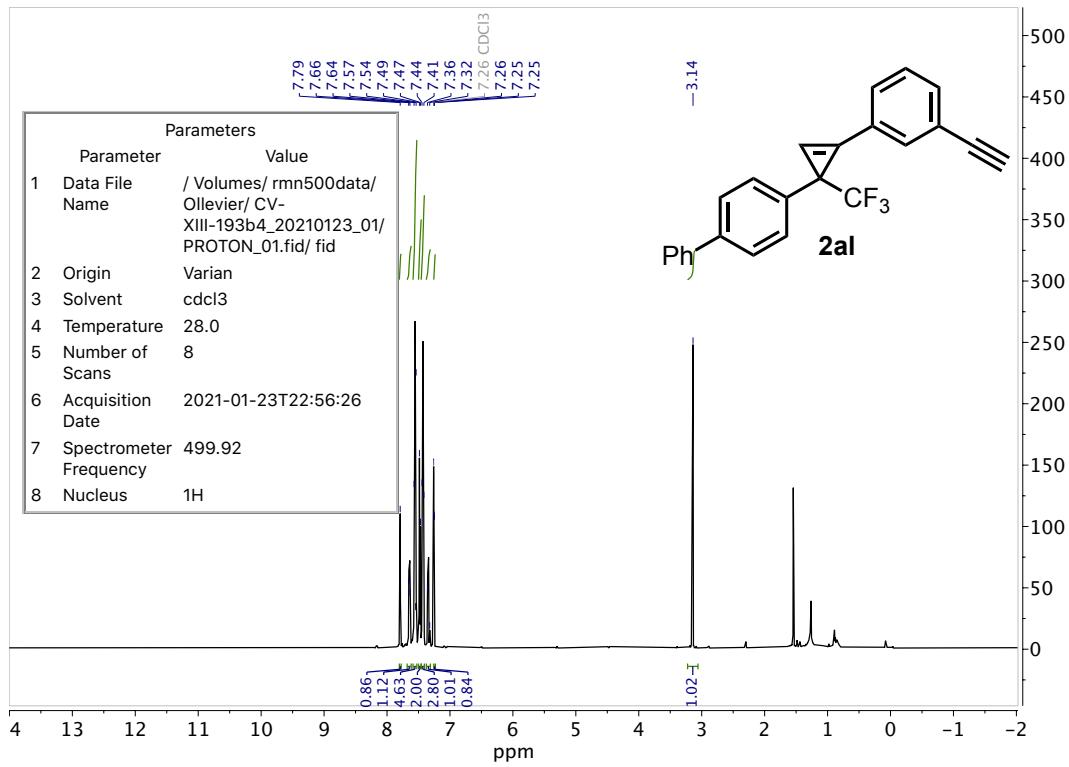


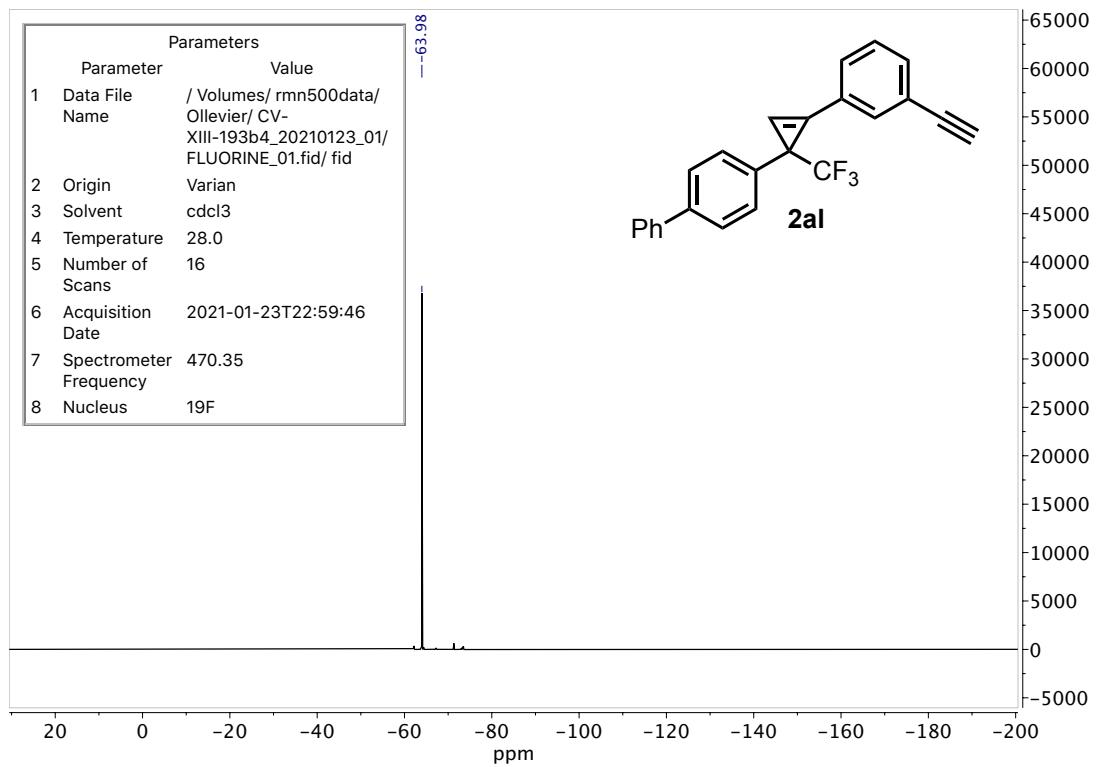
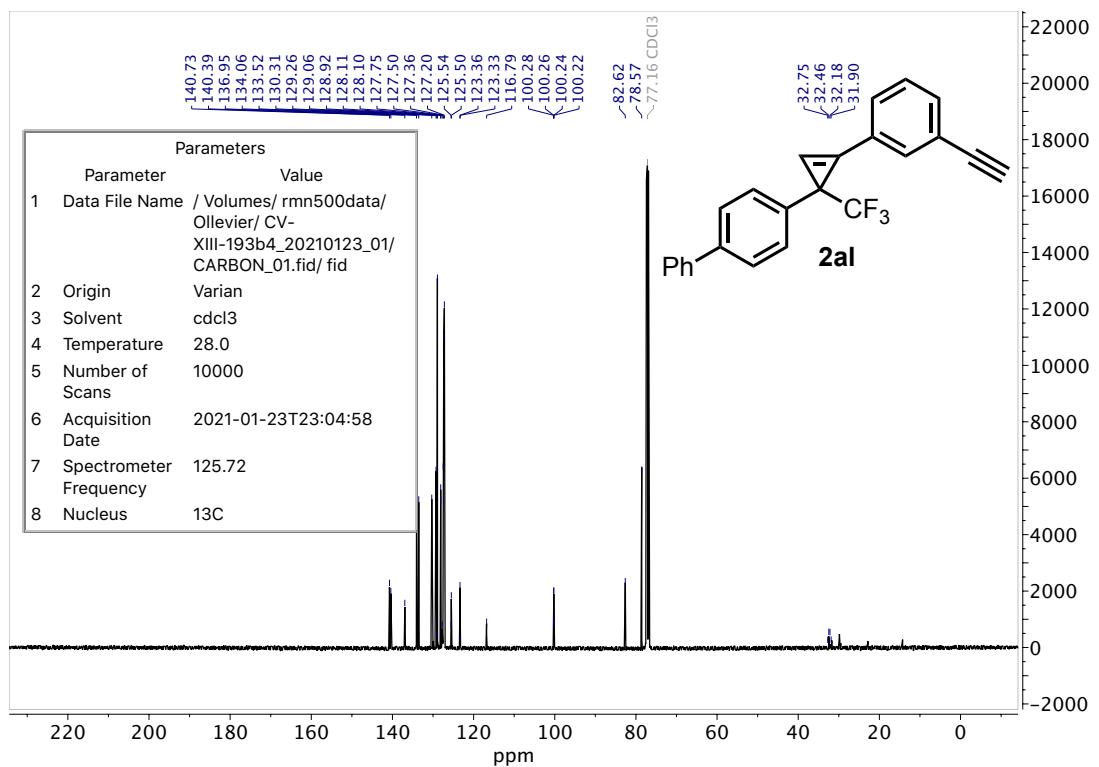
(3-([1,1'-Biphenyl]-4-yl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)trimethylsilane 2ak



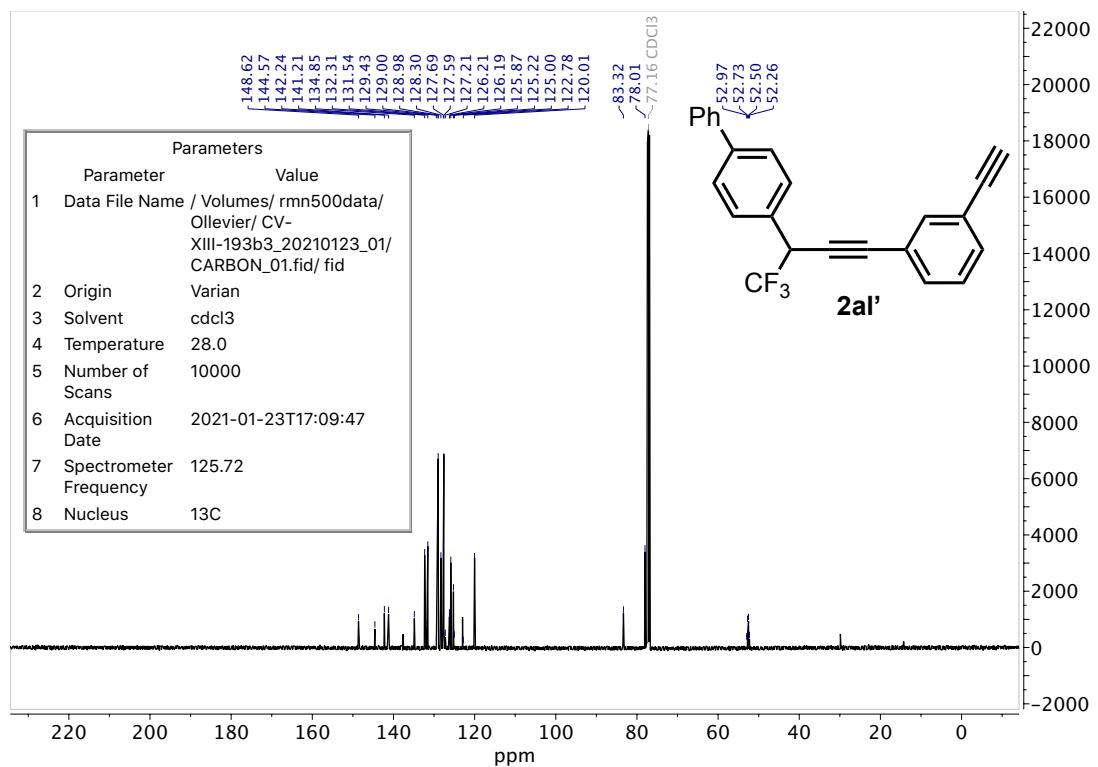
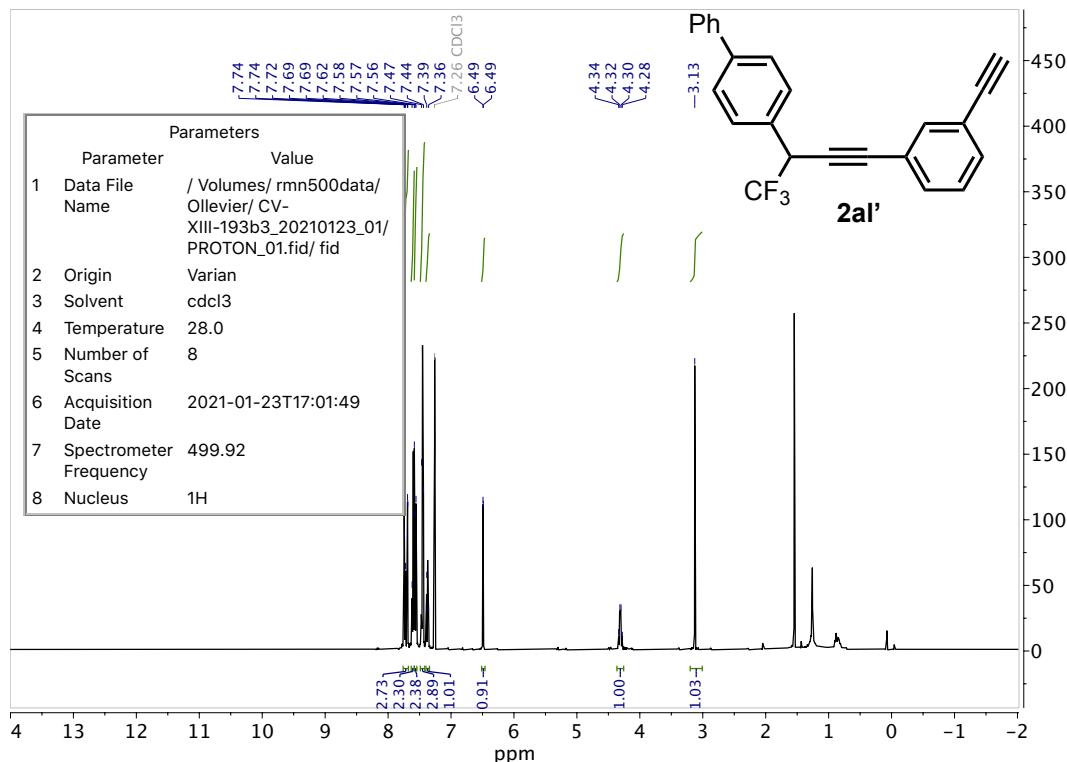


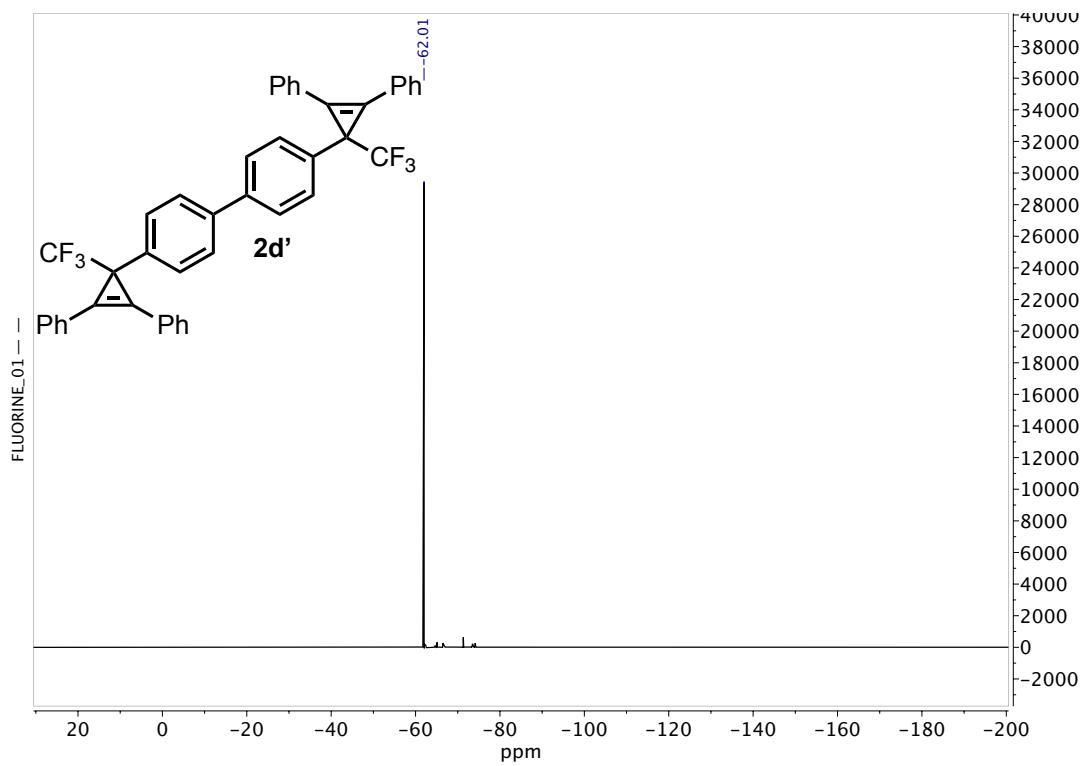
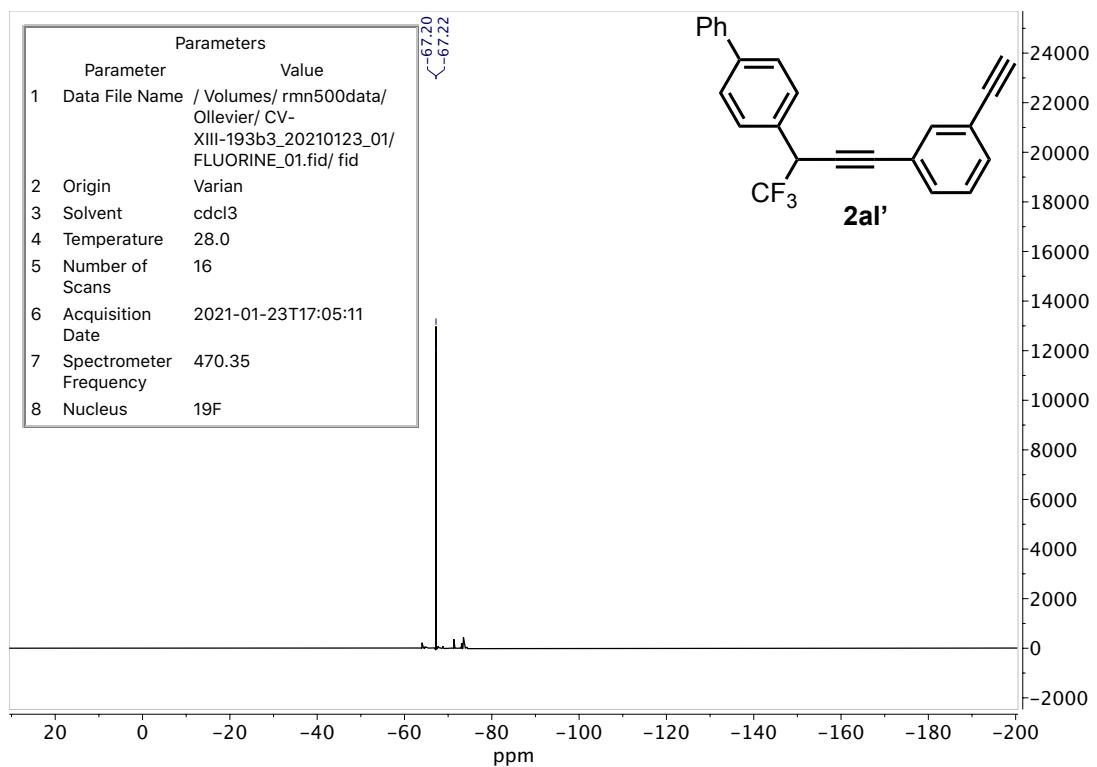
4-(2-(3-Ethynylphenyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2al



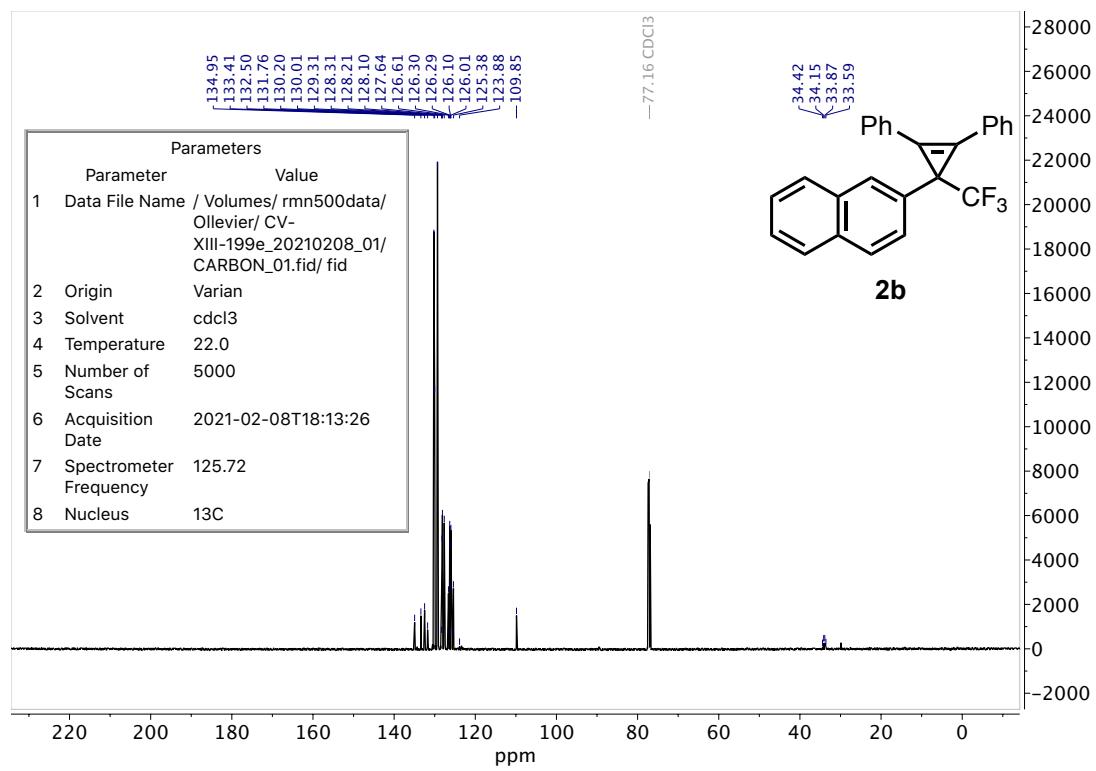
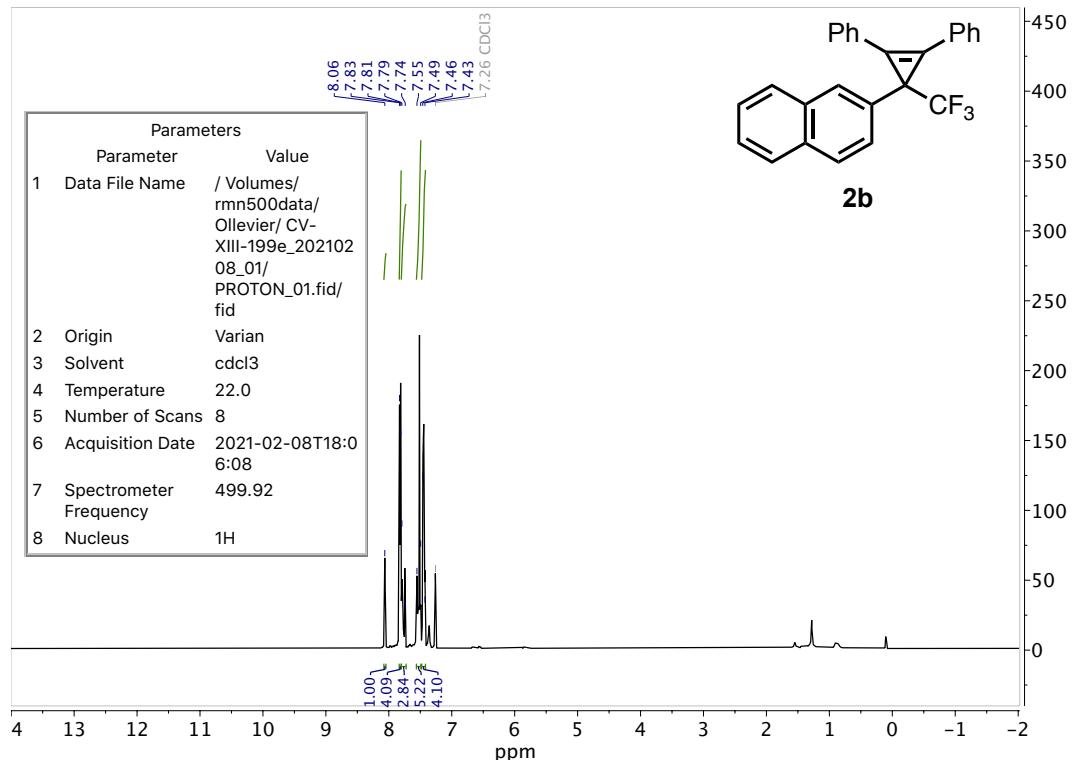


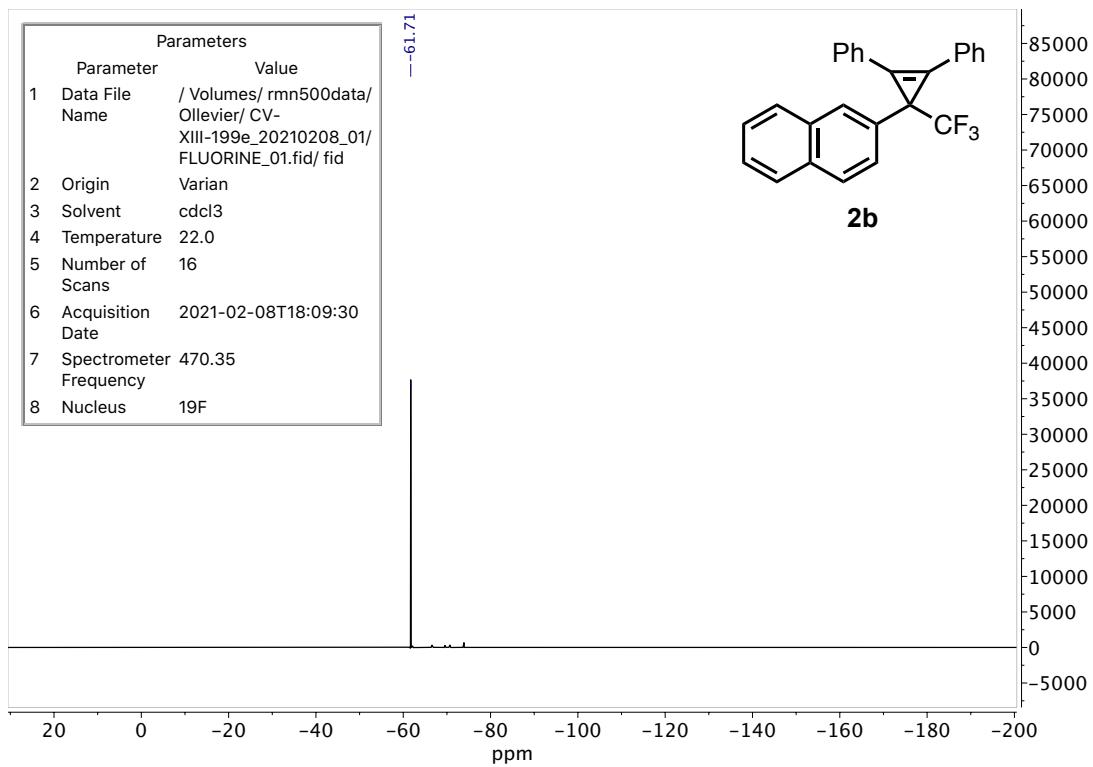
4-(4-(3-Ethynylphenyl)-1,1,1-trifluorobut-3-yn-2-yl)-1,1'-biphenyl 2al'



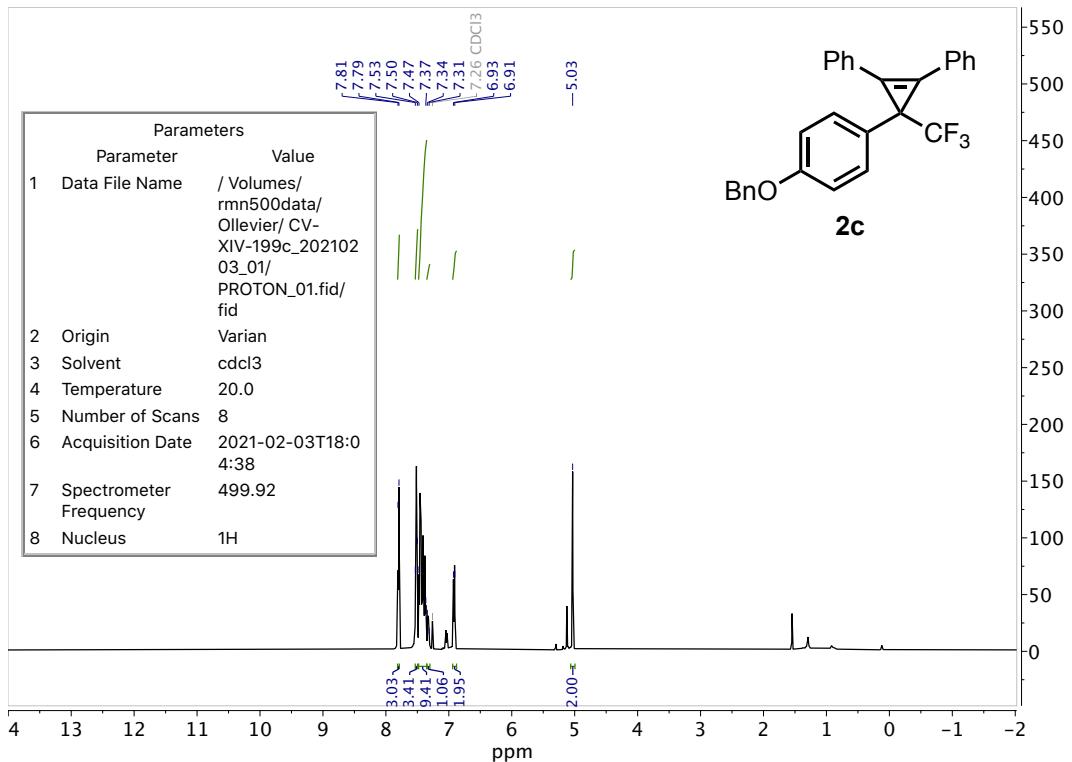


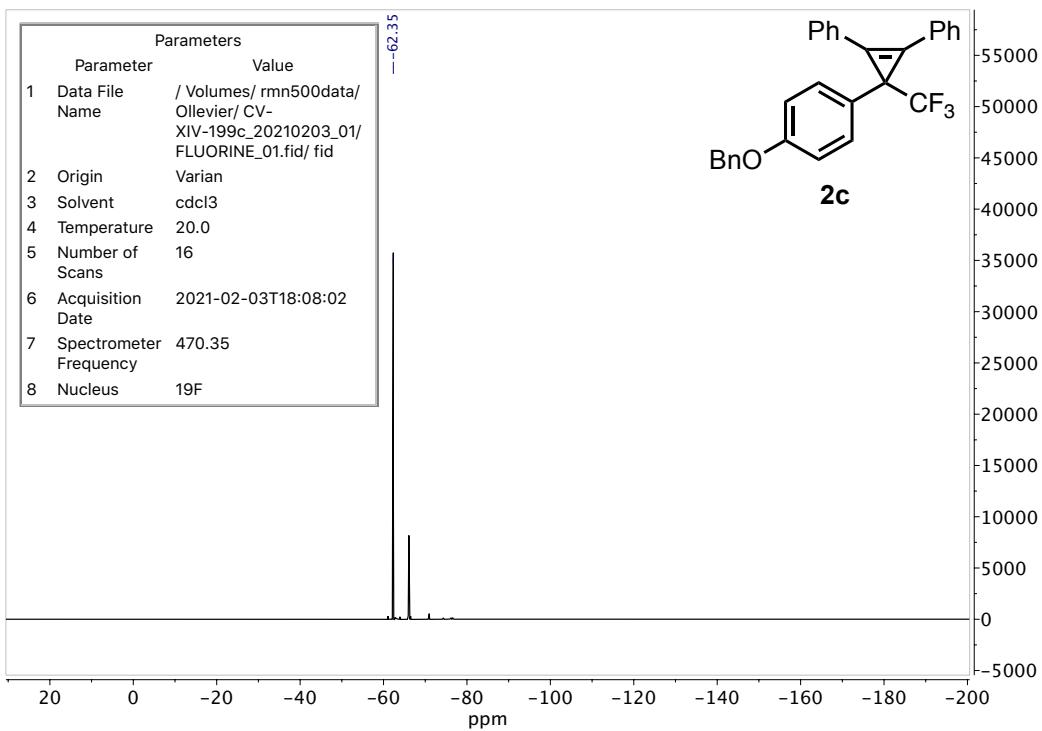
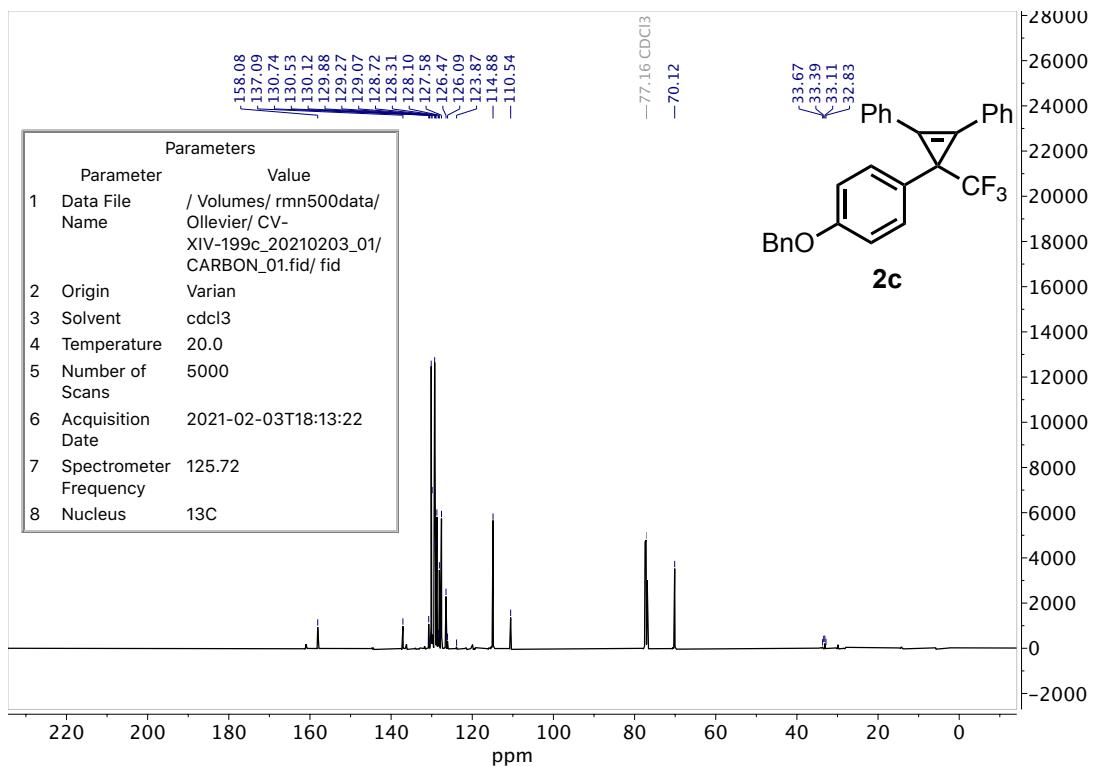
2-(2,3-Diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)naphthalene 2b





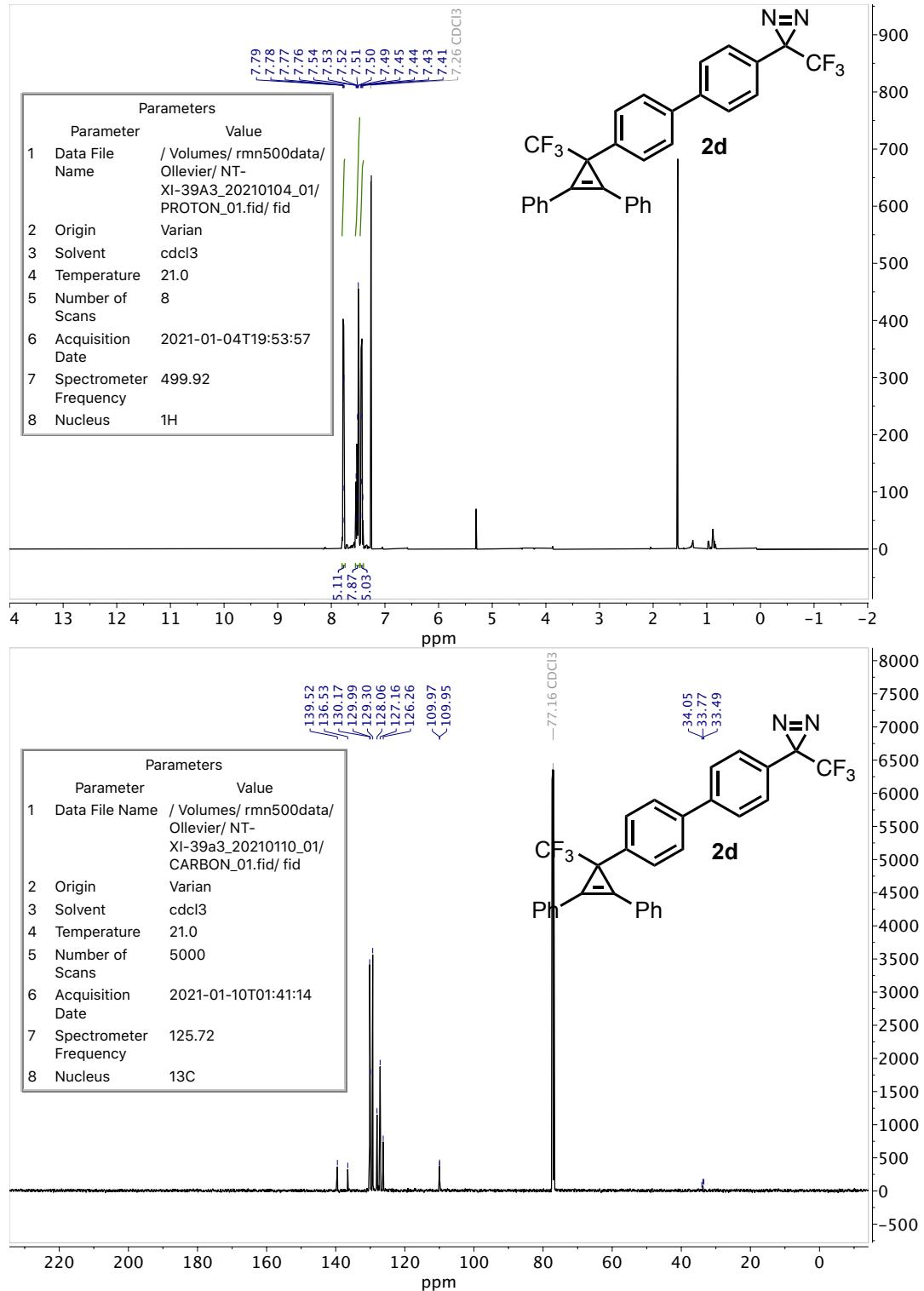
(3-(4-(Benzylxy)phenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyldibenzene **2c**

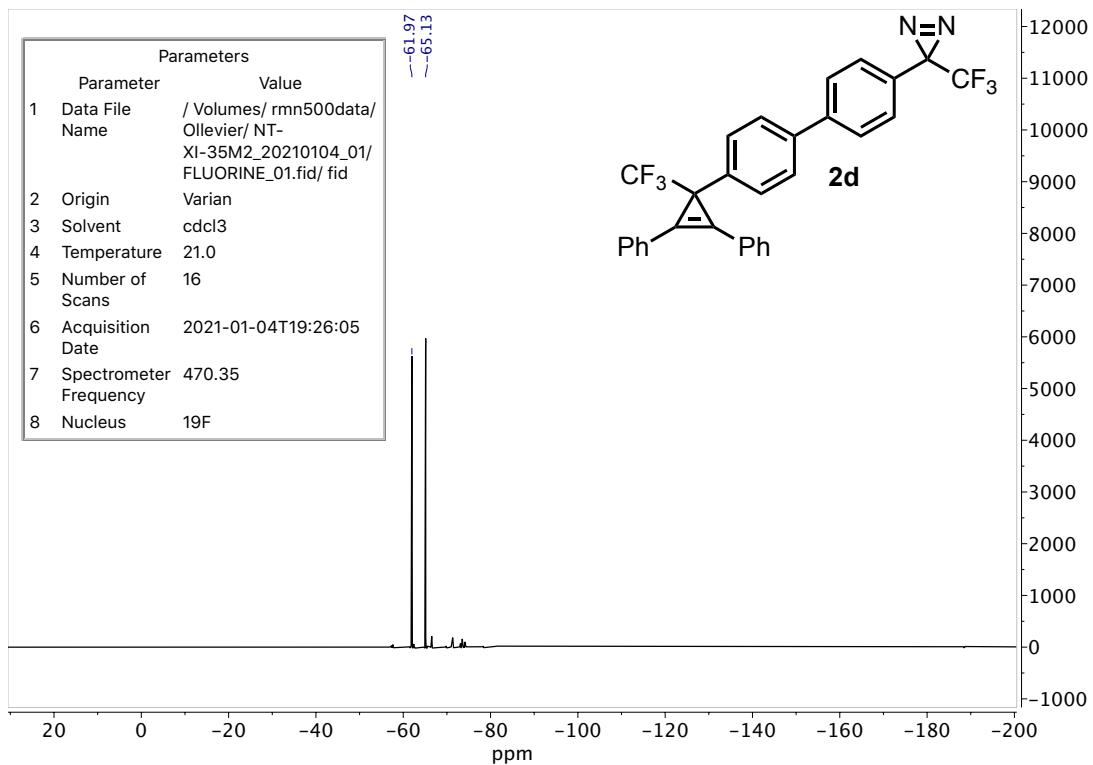




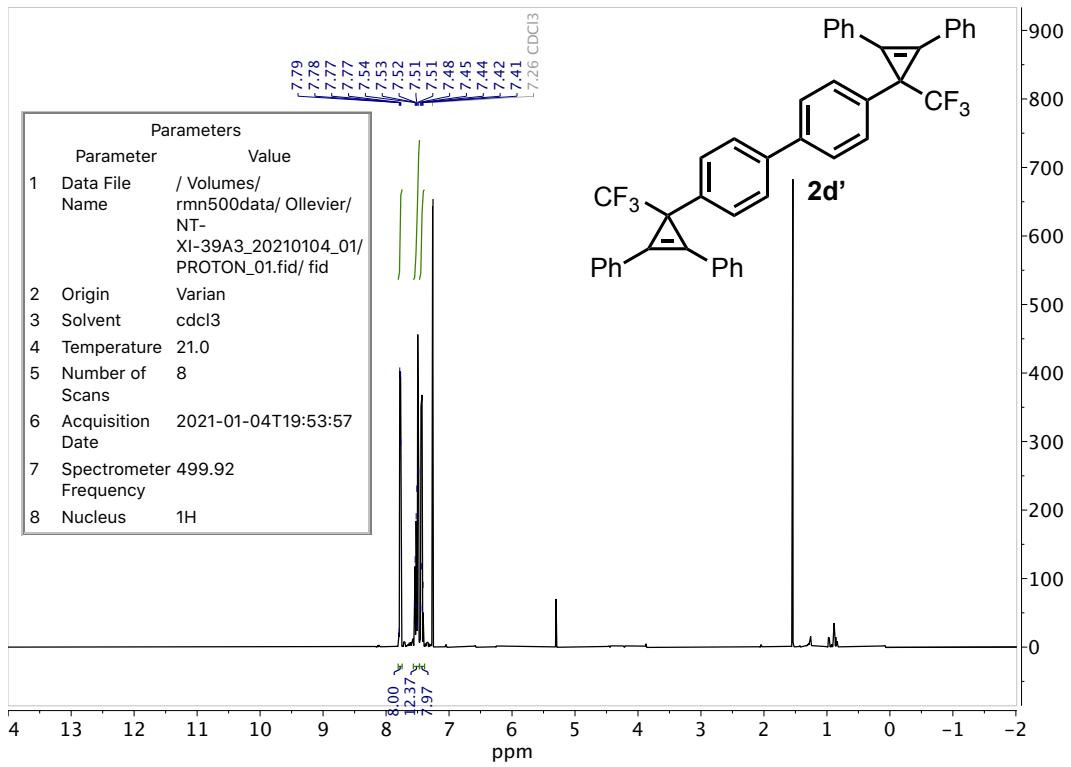
3-(4'-(2,3-Diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-[1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)-3*H*-diazirine

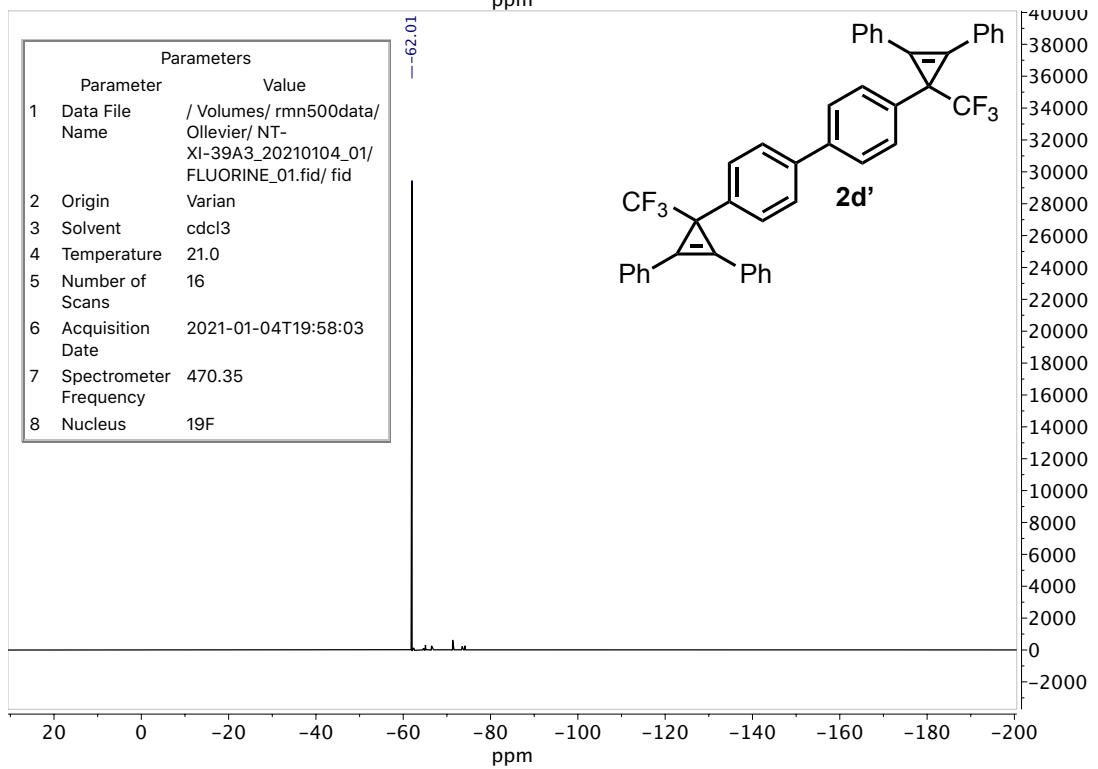
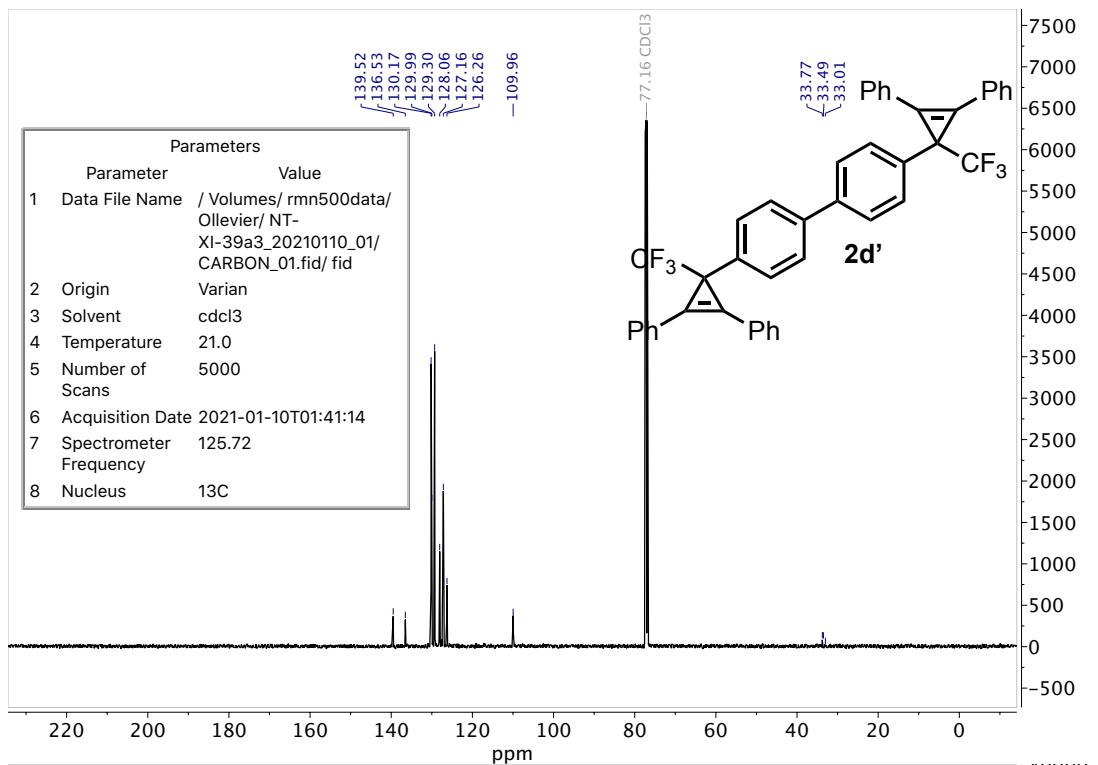
2d



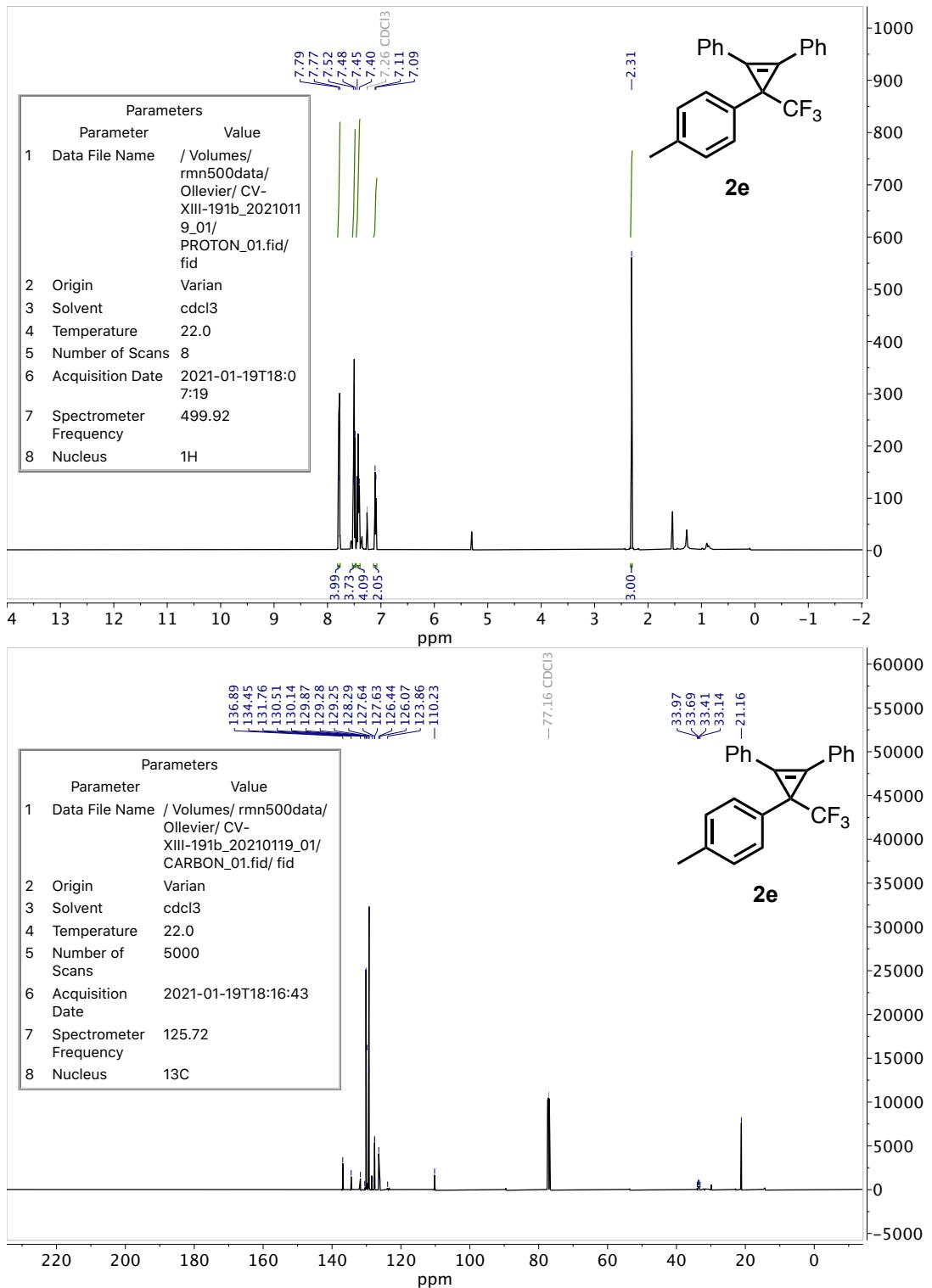


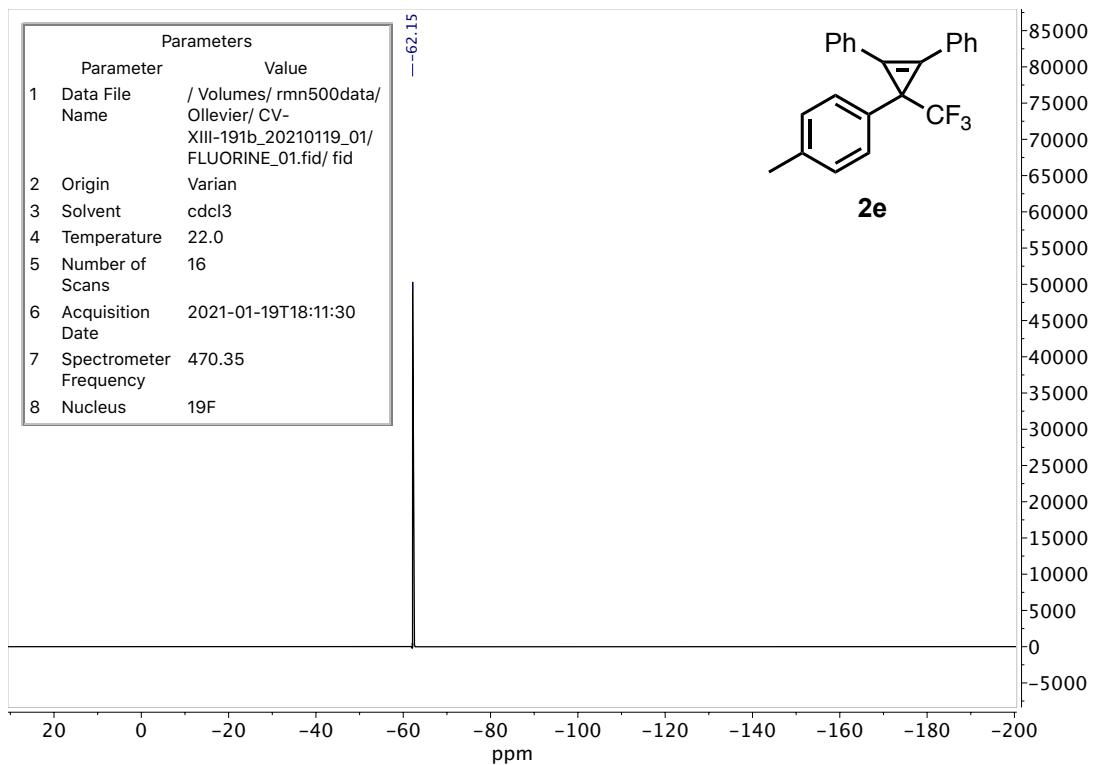
4,4'-Bis(2,3-diphenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 2d'



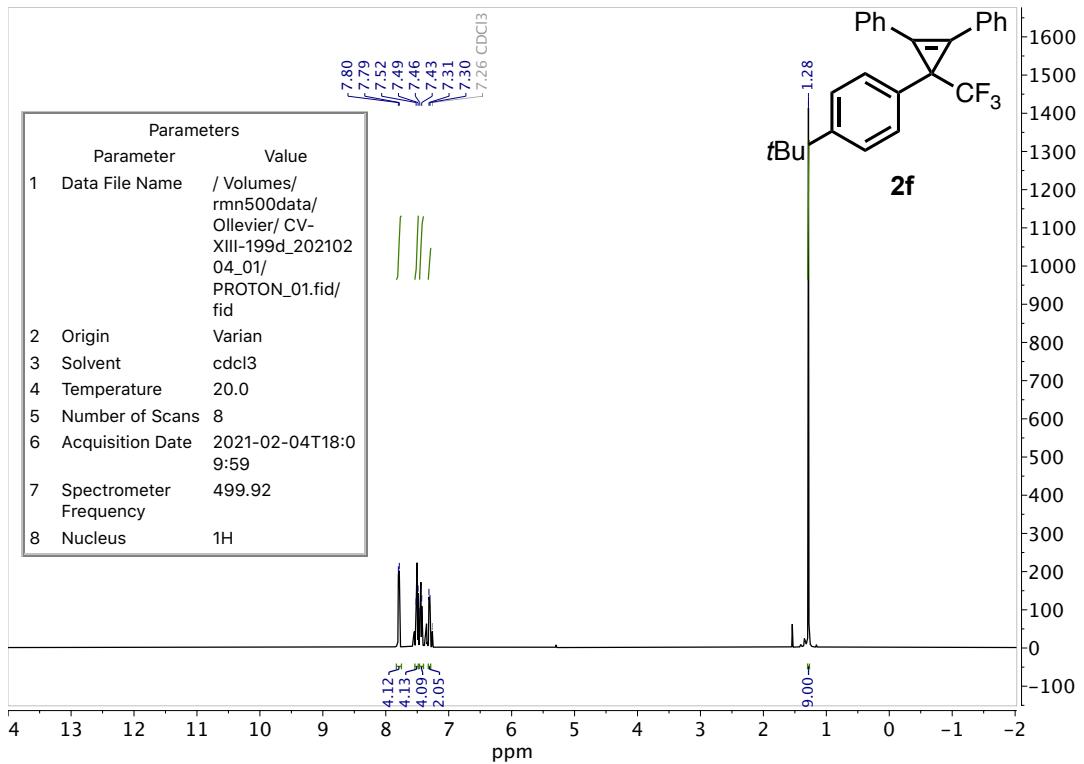


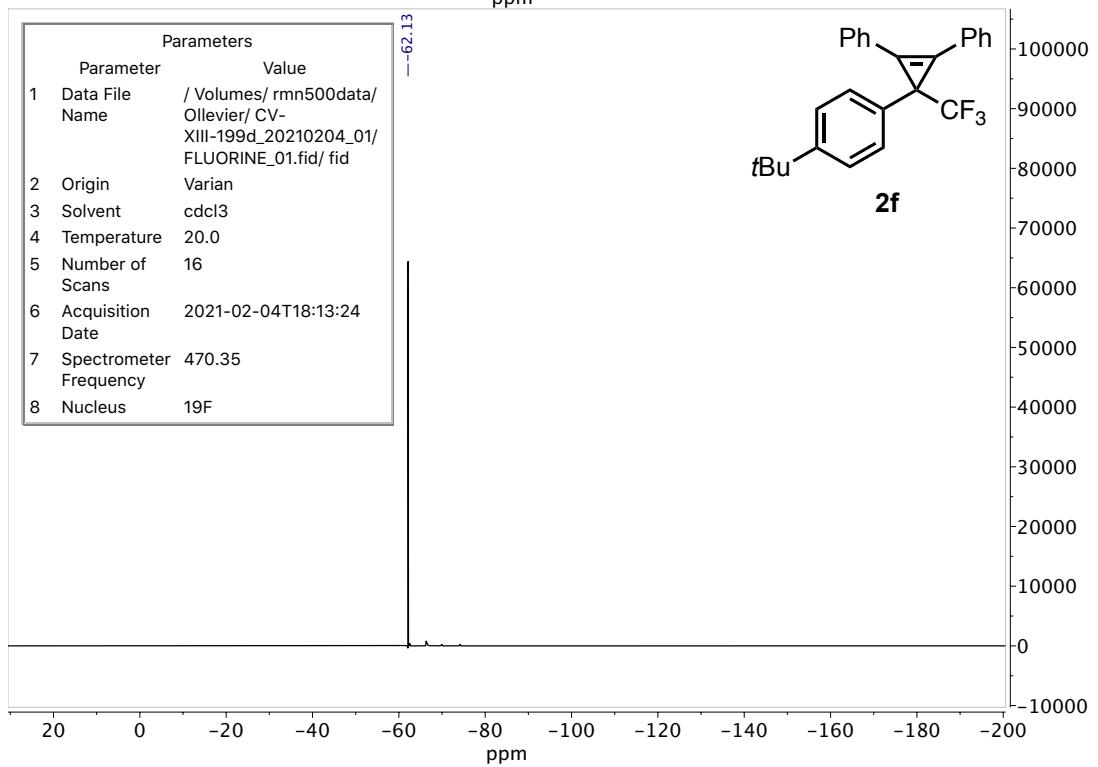
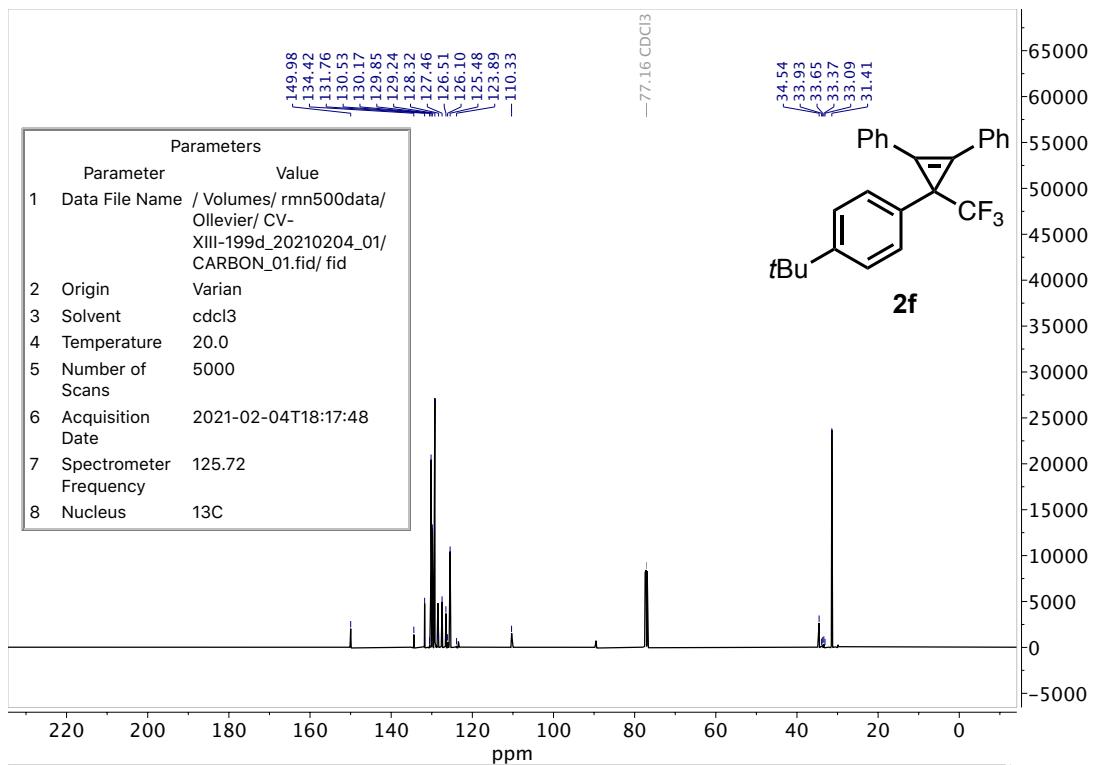
(3-(*p*-Tolyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diy) dibenzene 2e



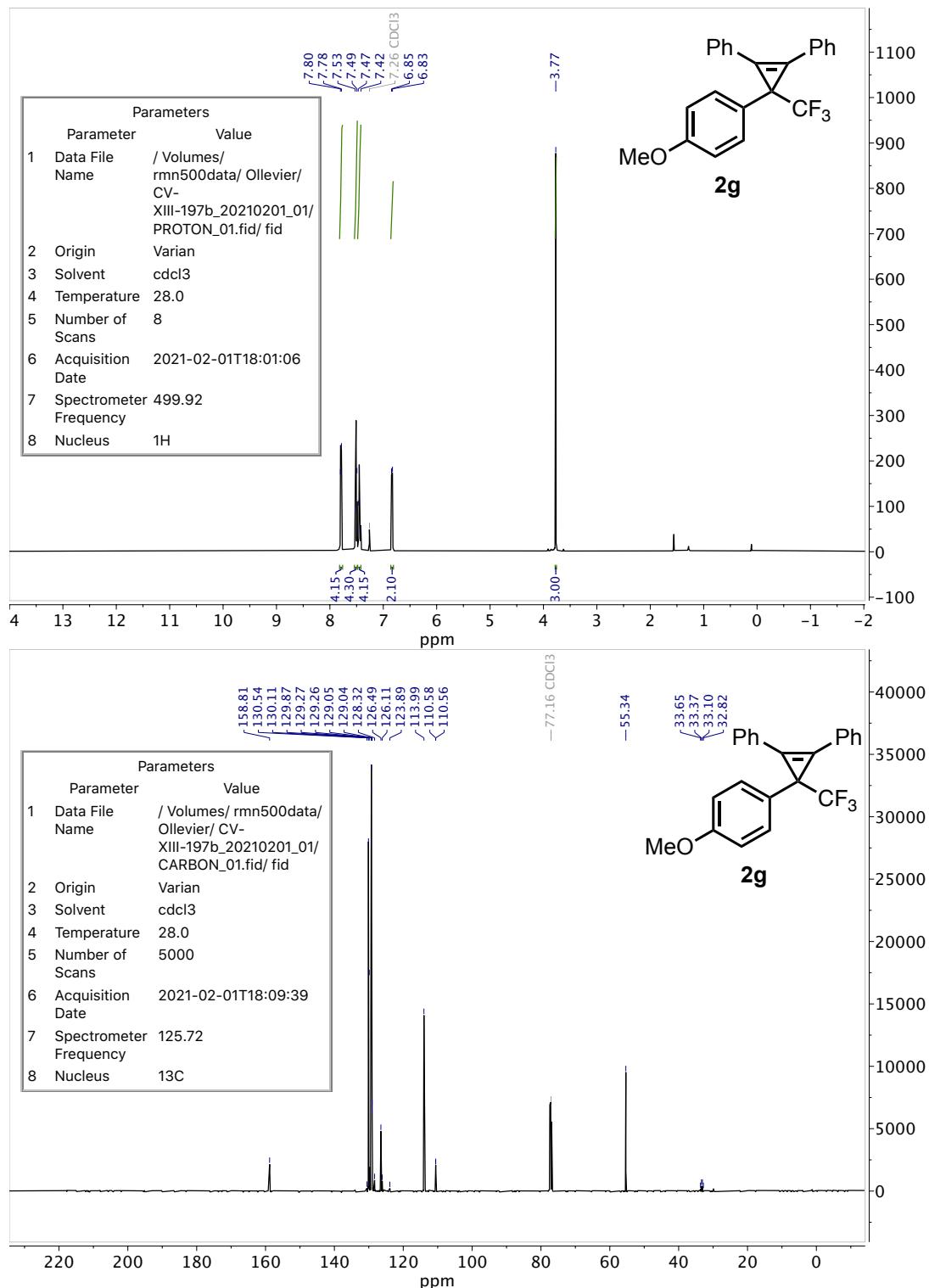


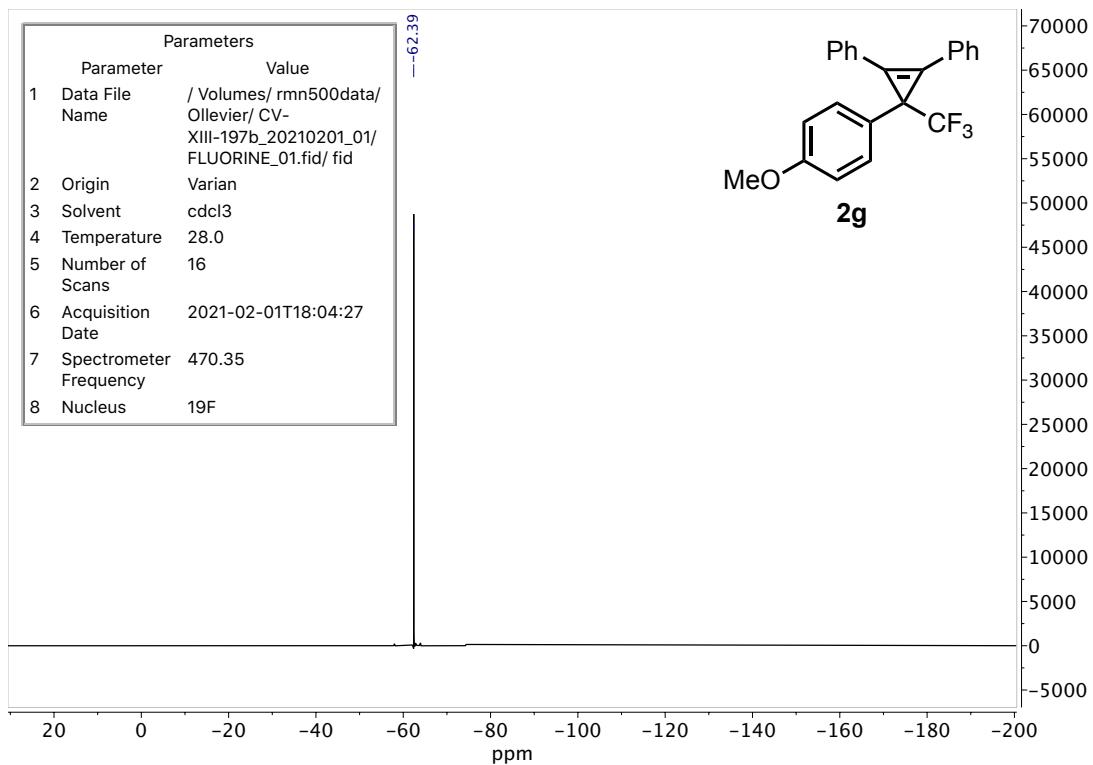
(3-(4-(tert-Butyl)phenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyldibenzene **2f**



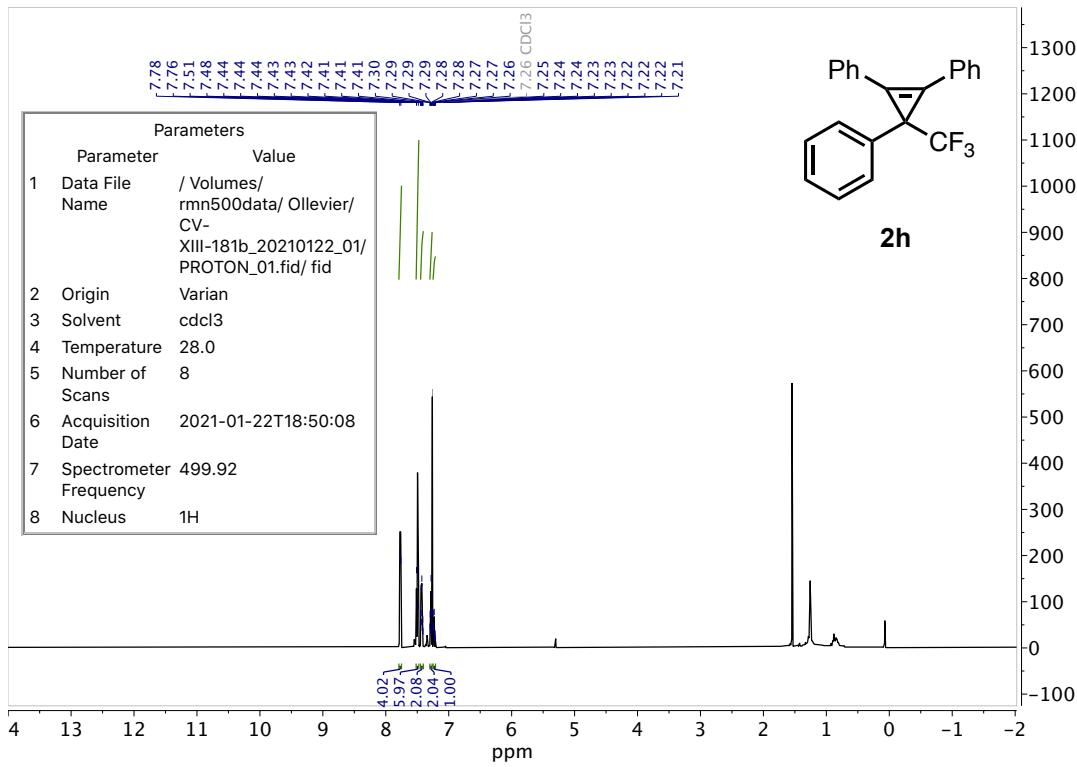


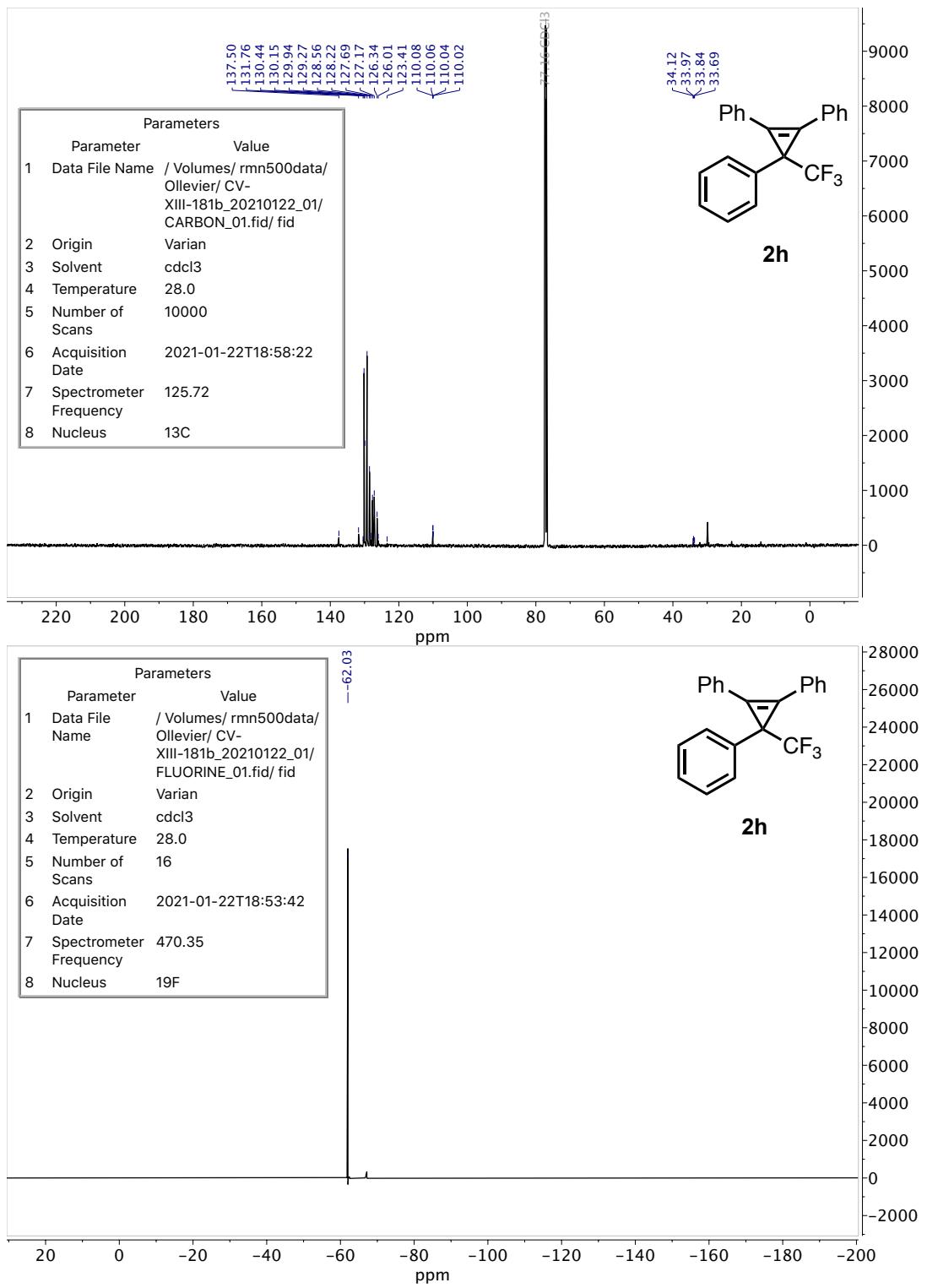
(3-(4-Methoxyphenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diy) dibenzene 2g



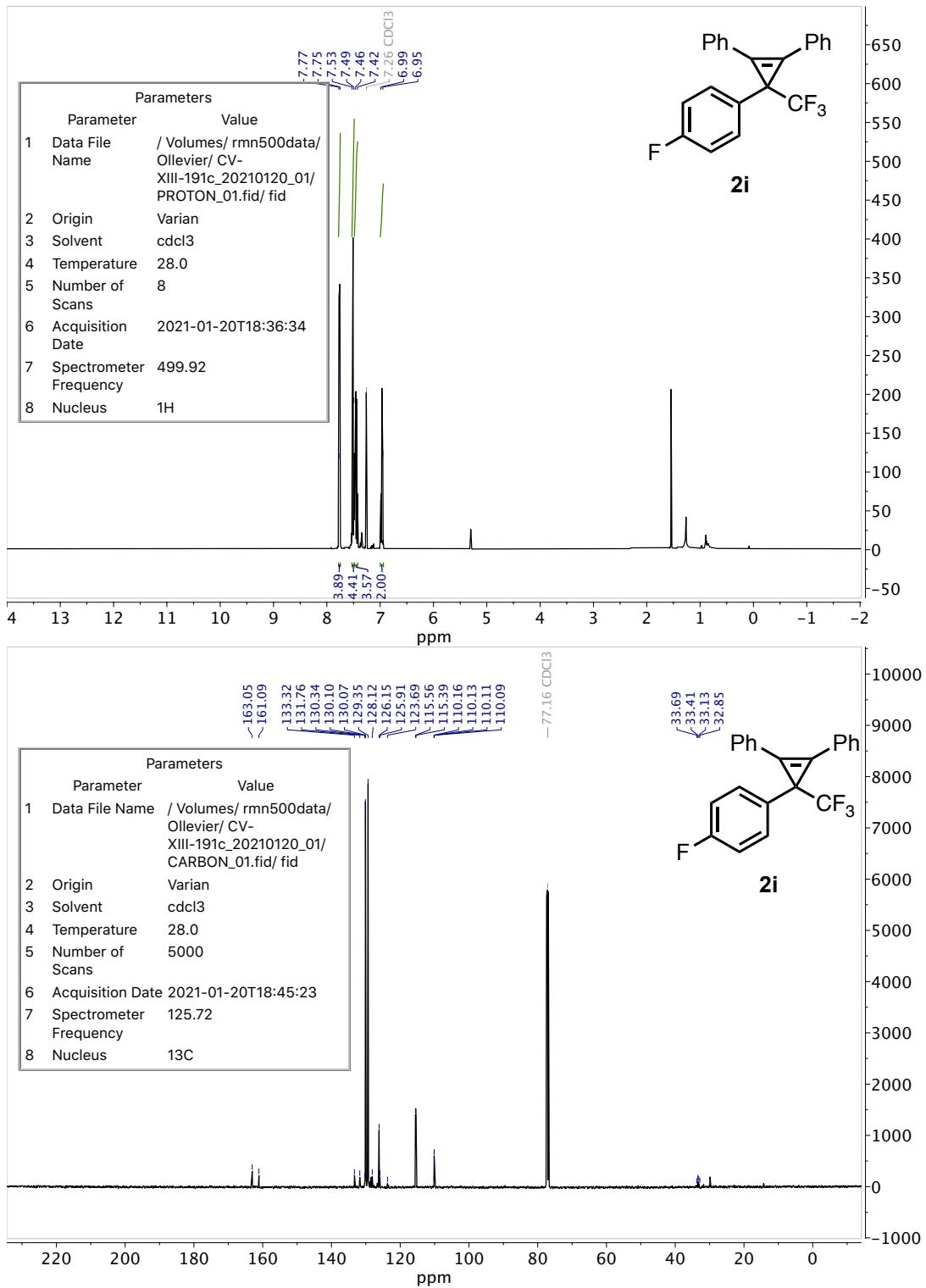


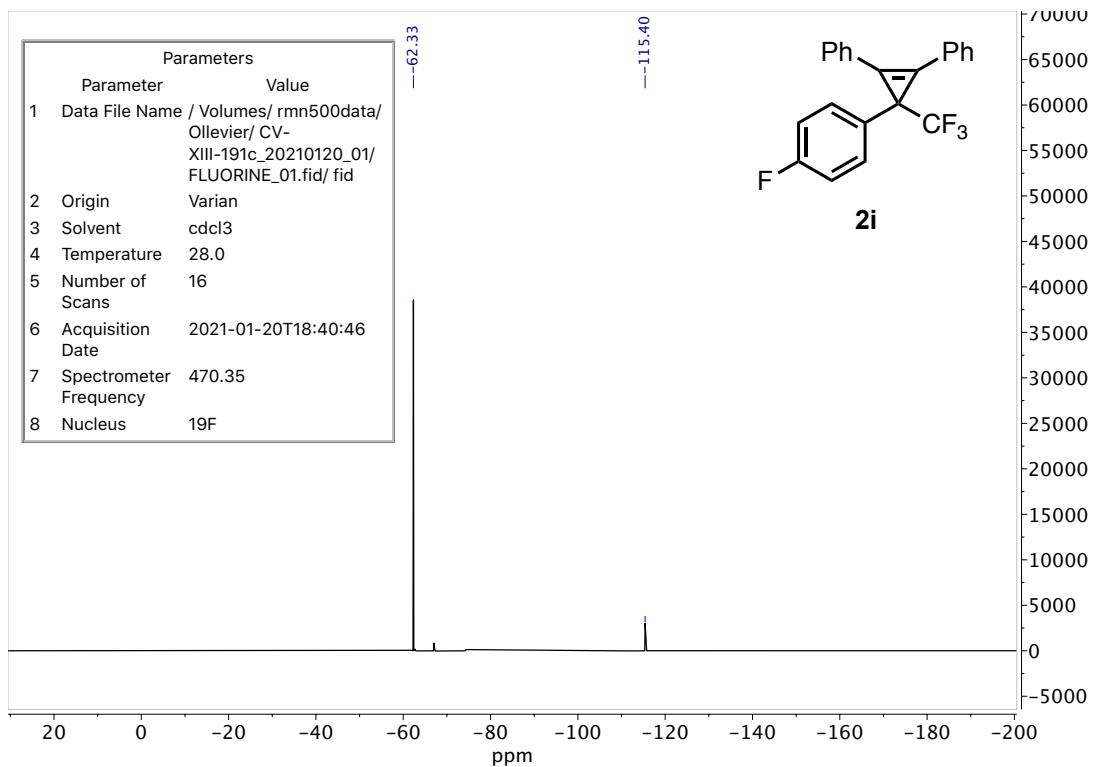
(3-(Trifluoromethyl)cycloprop-1-ene-1,2,3-triyl)tribenzene **2h**



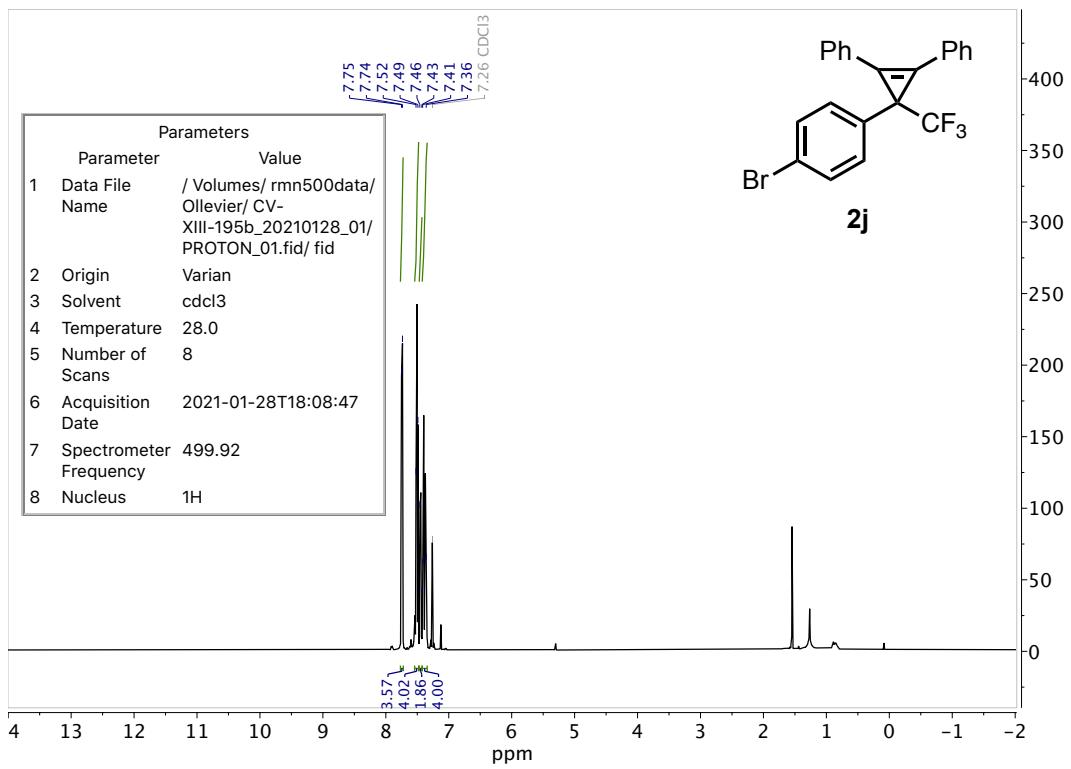


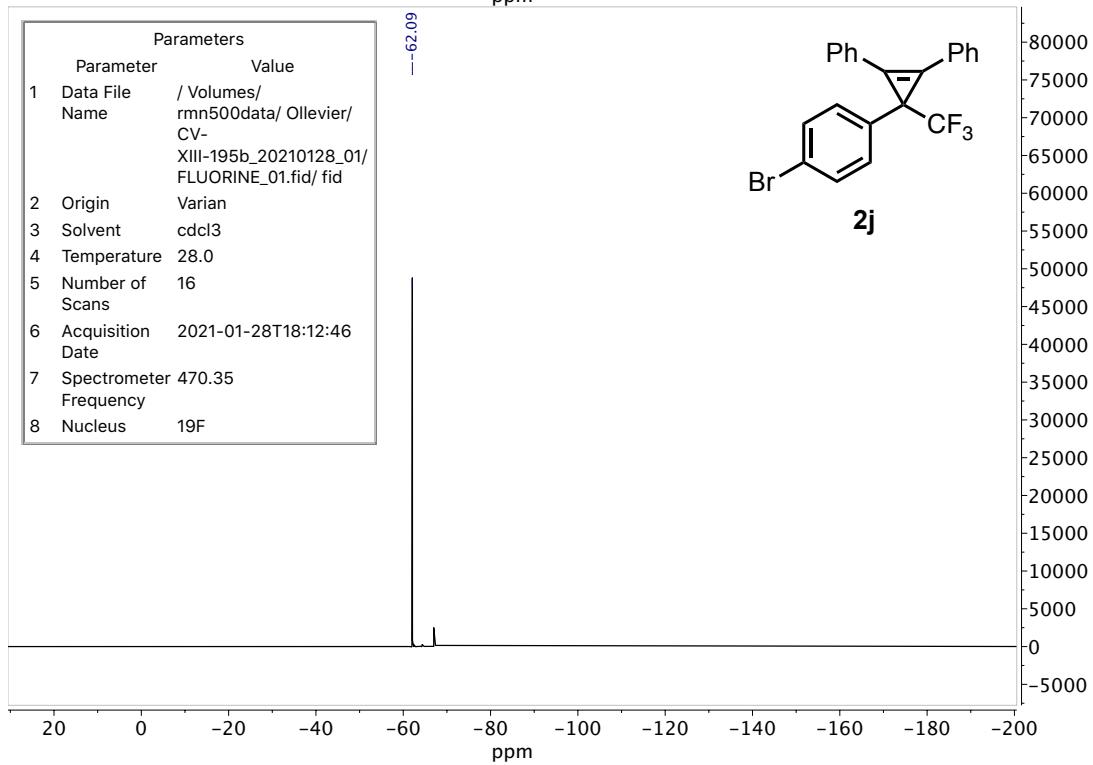
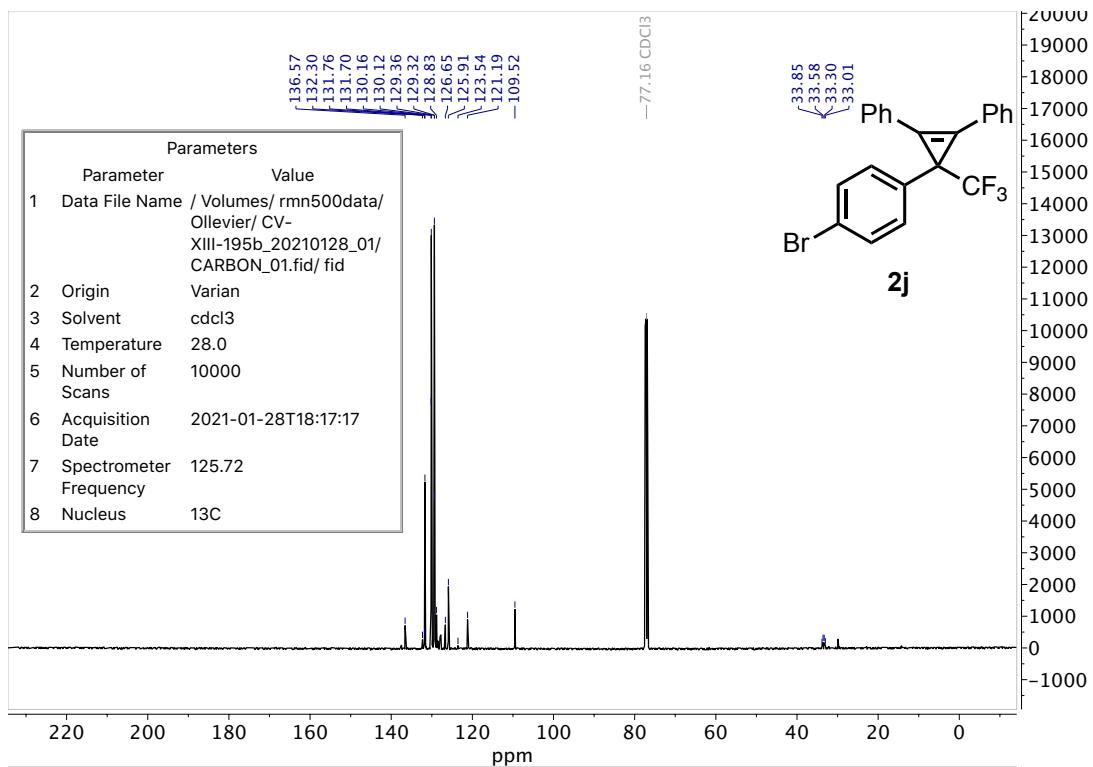
(3-(4-Fluorophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diy) dibenzene 2i



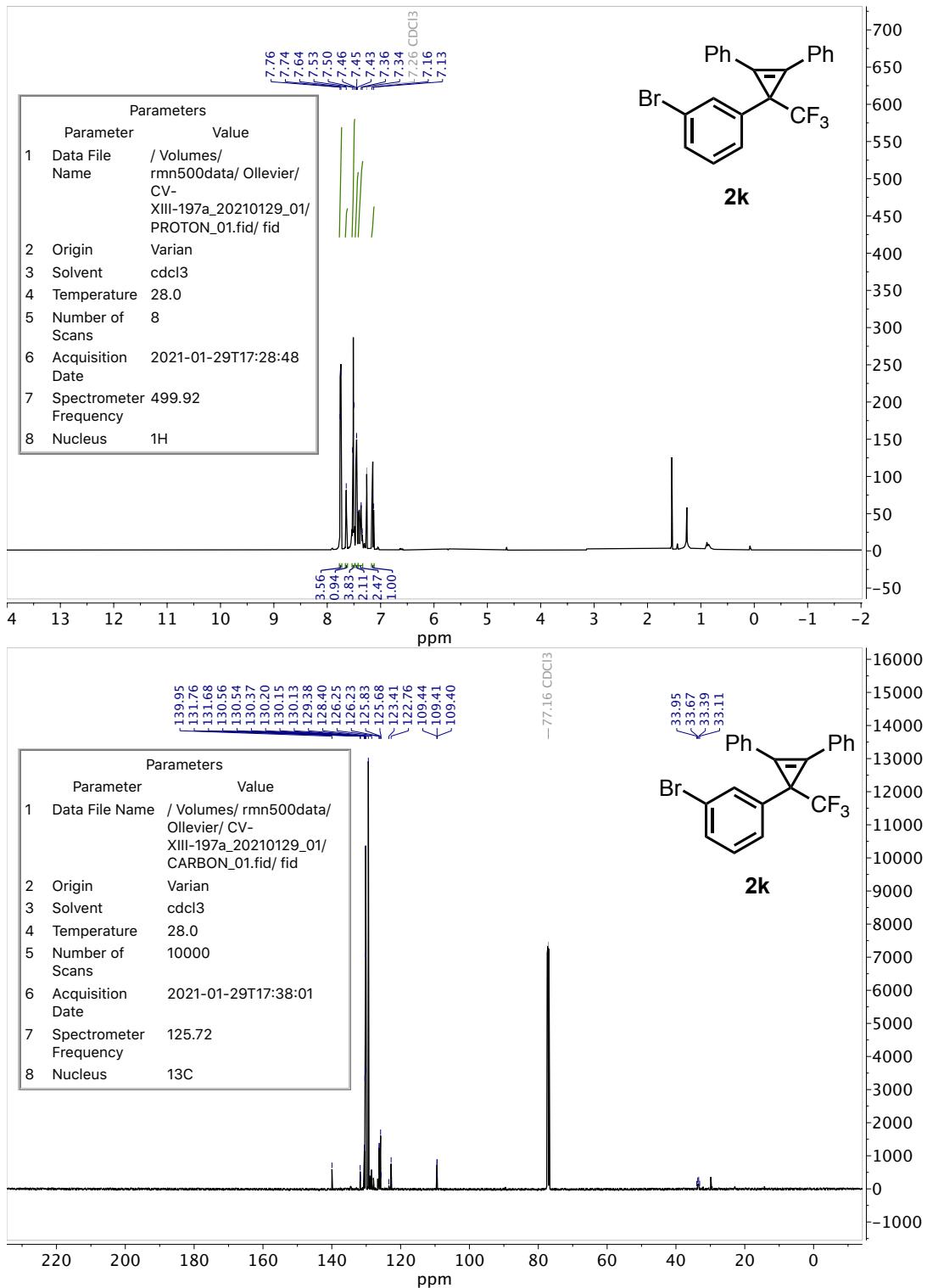


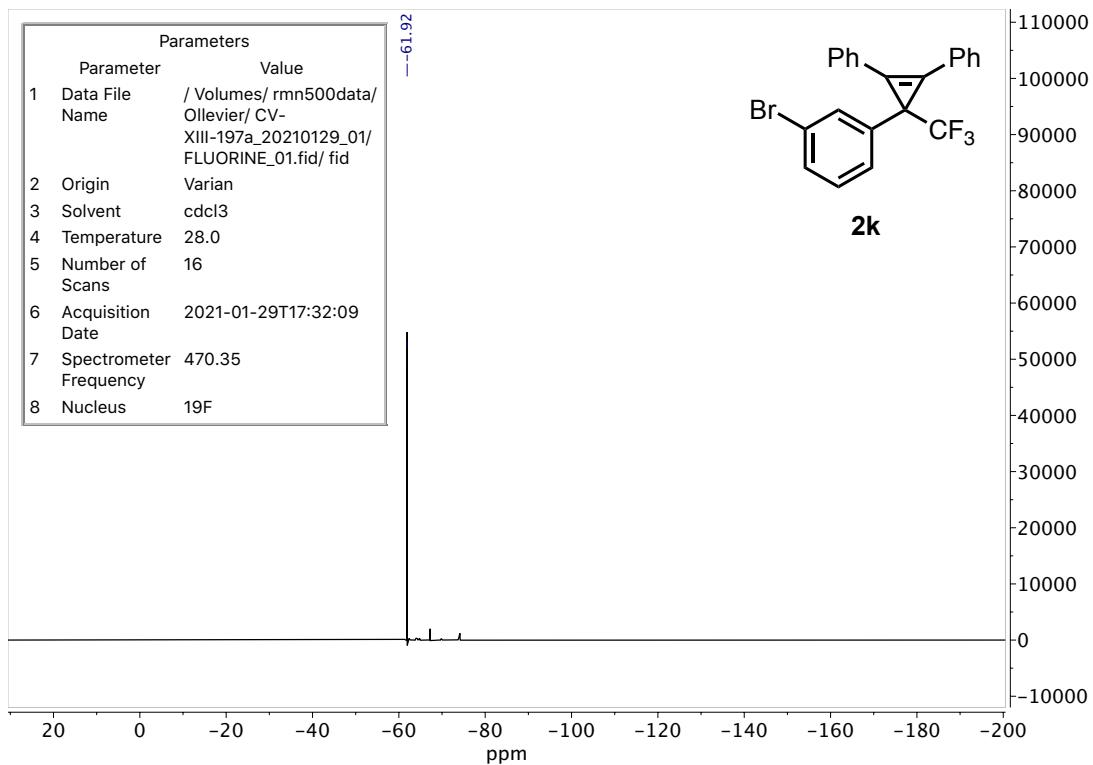
(3-(4-Bromophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyldibenzene **2j**



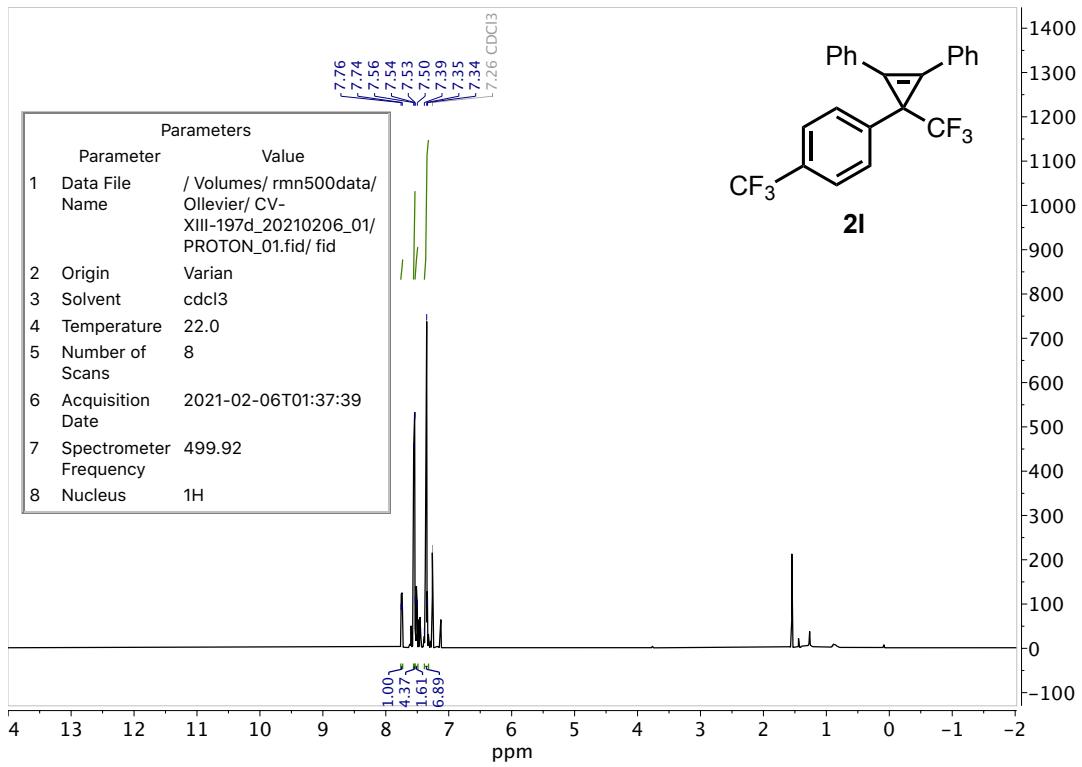


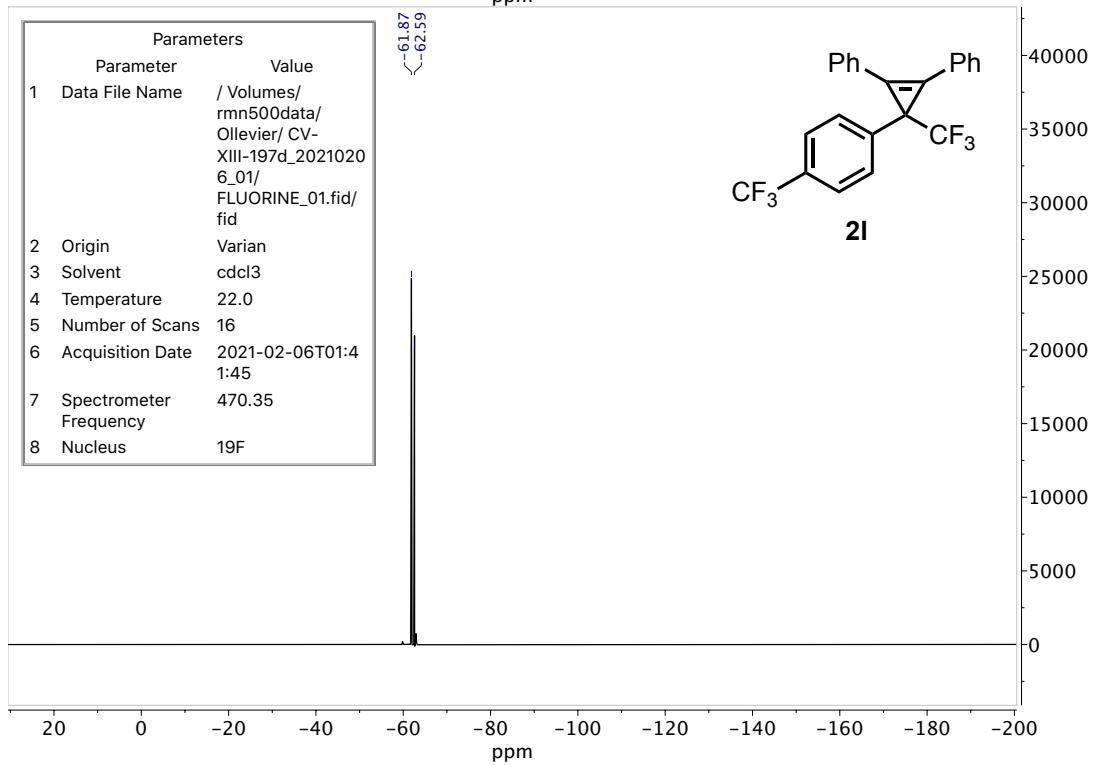
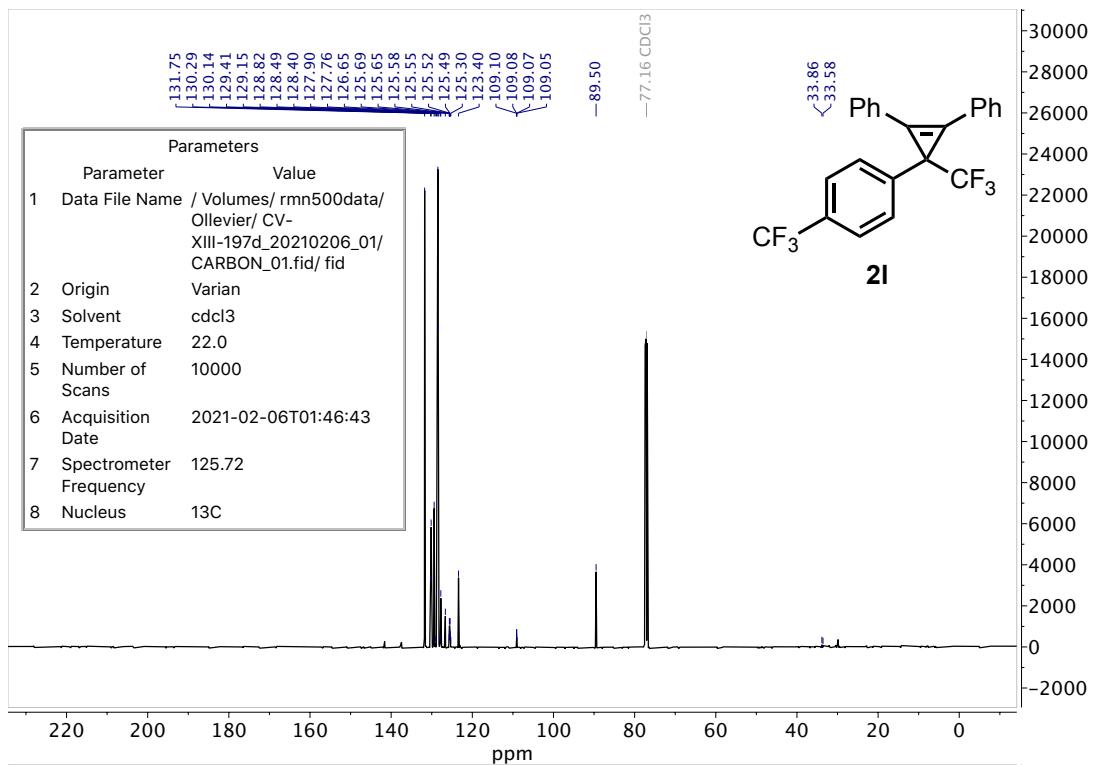
(3-(3-Bromophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyldibenzene 2k



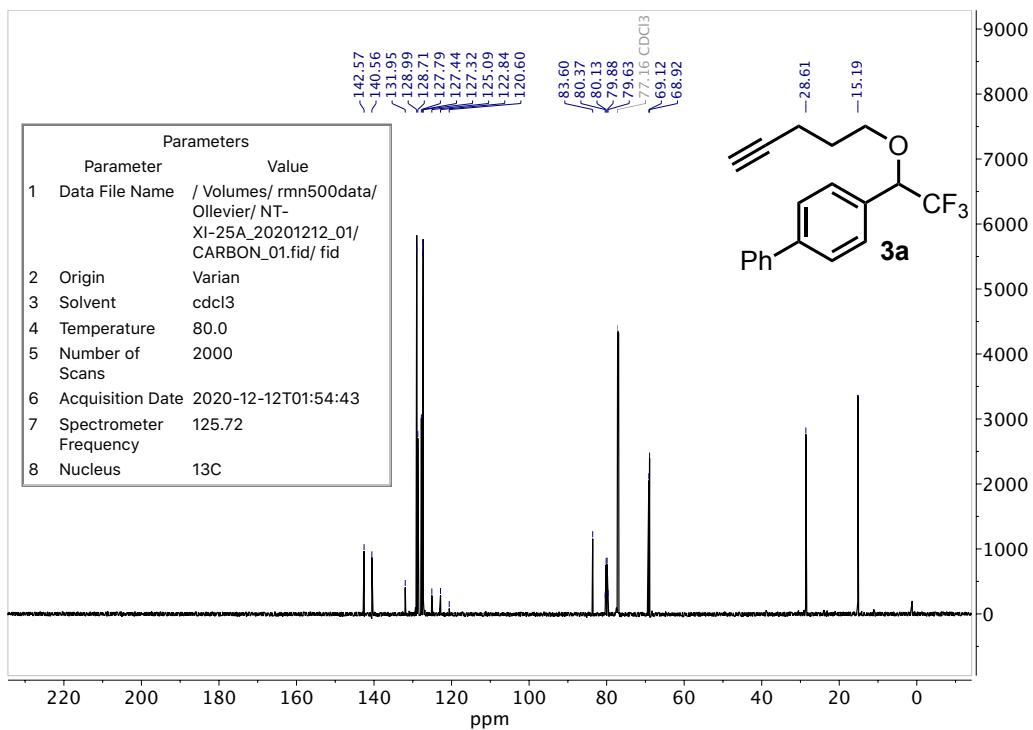
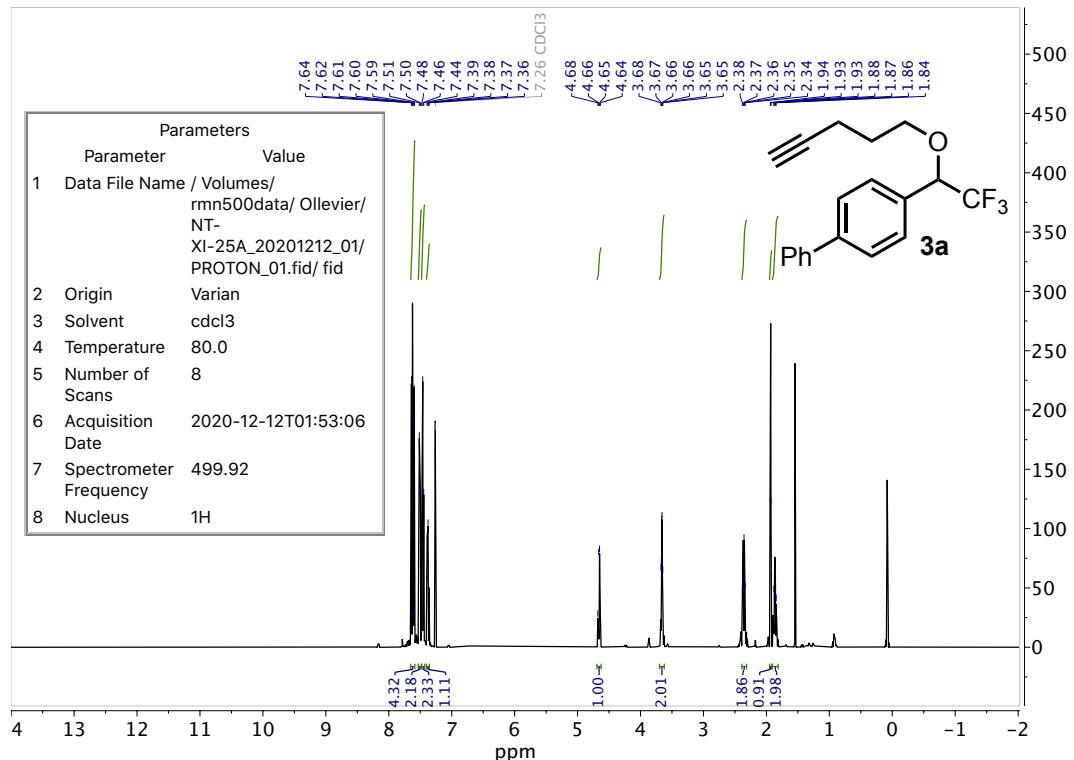


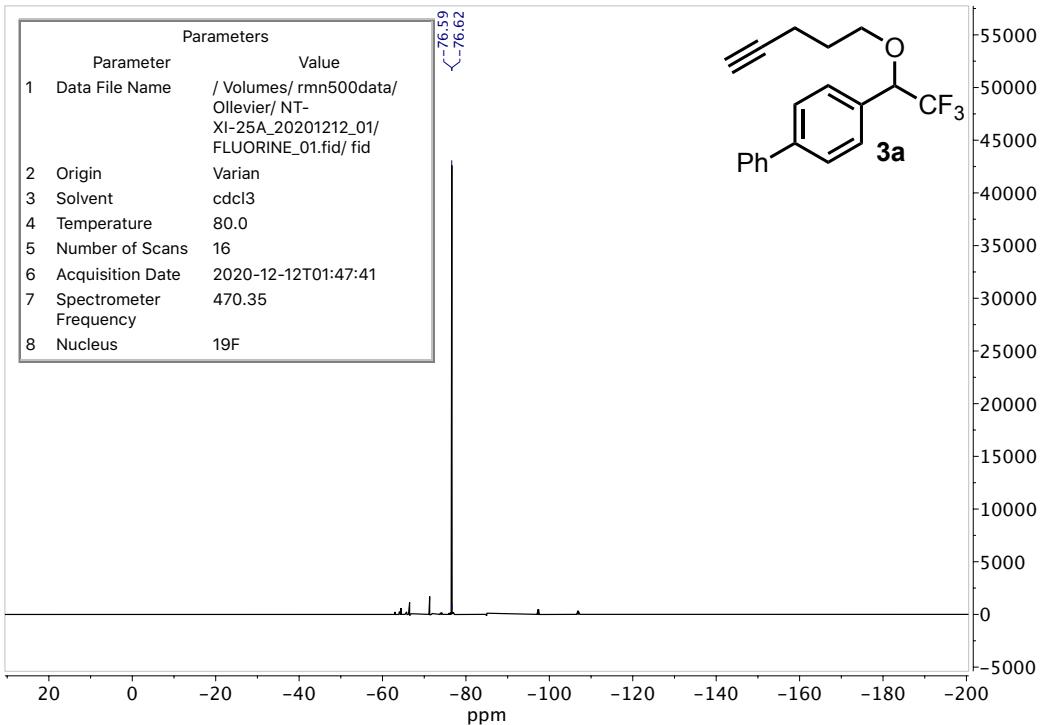
(3-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)cycloprop-1-ene-1,2-diy)dibenzene **2l**



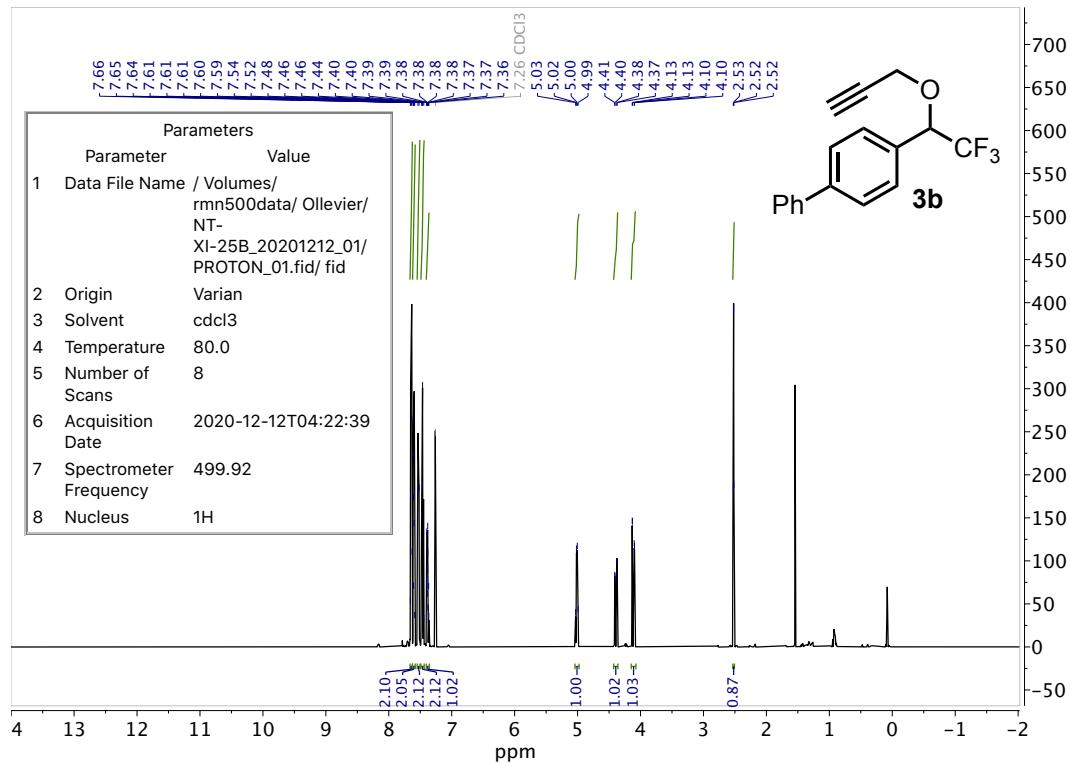


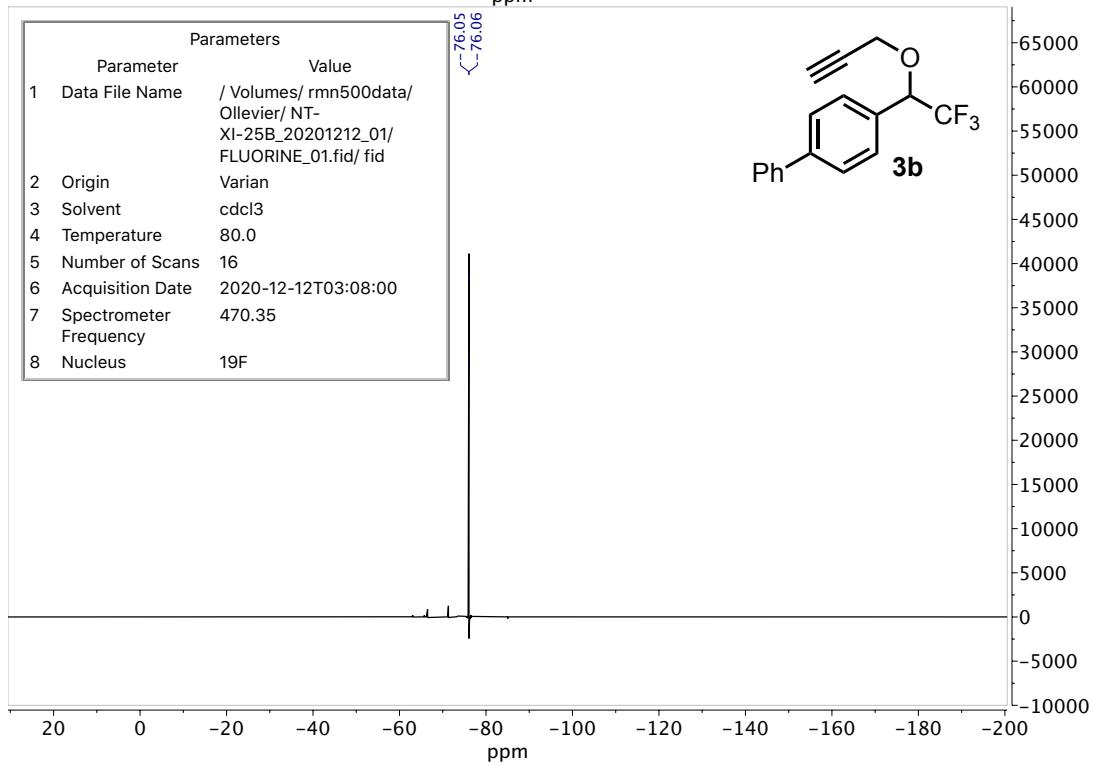
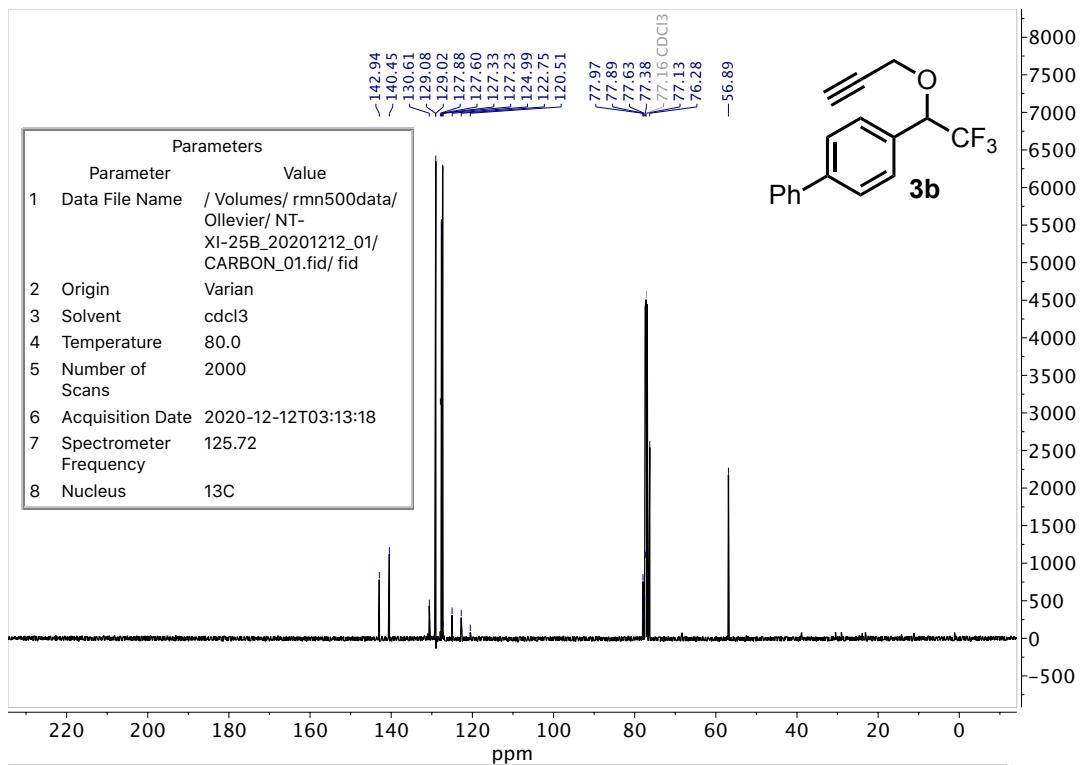
4-(2,2,2-trifluoro-1-(pent-4-yn-1-yloxy)ethyl)-1,1'-biphenyl 3a





4-(2,2,2-trifluoro-1-(prop-2-yn-1-yloxy)ethyl)-1,1'-biphenyl 3b





4-(1-(Trifluoromethyl)cycloprop-2-en-1-yl)-1,1'-biphenyl 4ak

