

General informations.....	S4
Synthesis of aryl propargyl alcohols with a mono or a <i>gem</i> -difluoro alkyl side chain.....	S4
4,4-difluoro-1-phenyltridec-2-yn-1-ol (3a)	S4
4,4-difluoro-1-(4-methoxyphenyl)tridec-2-yn-1-ol (3b)	S4
4-(4,4-difluoro-1-hydroxytridec-2-yn-1-yl)benzotrile (3c)	S4
4,4-difluoro-1-(4-(trifluoromethyl)phenyl)tridec-2-yn-1-ol (3d)	S5
1-(4-chlorophenyl)-4,4-difluorotridec-2-yn-1-ol (3e)	S5
1-(3-chlorophenyl)-4,4-difluorotridec-2-yn-1-ol (3f)	S5
1-(2-chlorophenyl)-4,4-difluorotridec-2-yn-1-ol (3g)	S5
5,5-difluoro-2-phenyltetradec-3-yn-2-ol (5h)	S5
4,4-difluoro-1,1-diphenyltridec-2-yn-1-ol (5i).....	S5
4-fluoro-1-phenyltridec-2-yn-1-ol (4a)	S6
4-fluoro-1-(4-methoxyphenyl)tridec-2-yn-1-ol (4b)	S6
4-(4-fluoro-1-hydroxytridec-2-yn-1-yl)benzotrile (4c).....	S6
4-fluoro-1-(4-(trifluoromethyl)phenyl)tridec-2-yn-1-ol (4d)	S6
1-(4-chlorophenyl)-4-fluorotridec-2-yn-1-ol (4e)	S6
1-(3-chlorophenyl)-4-fluorotridec-2-yn-1-ol (4f)	S6
1-(2-chlorophenyl)-4-fluorotridec-2-yn-1-ol (4g).....	S7
5-fluoro-2-phenyltetradec-3-yn-2-ol (6h).....	S7
4-fluoro-1,1-diphenyltridec-2-yn-1-ol (6i)	S7
Synthesis of aryl-propargylic alcohols with a trifluoro methyl group	S7
4,4,4-trifluoro-1-phenylbut-2-yn-1-ol (8a)	S7
4,4,4-trifluoro-1-(4-methoxyphenyl)but-2-yn-1-ol (8b)	S7
trimethyl((5,5,5-trifluoro-2-phenylpent-3-yn-2-yl)oxy)silane (TMS ether of 9a)	S8
5,5,5-trifluoro-2-phenylpent-3-yn-2-ol (9a)	S8
Trimethyl((4,4,4-trifluoro-1,1-diphenylbut-2-yn-1-yl)oxy)silane (TMS ether of 10a)	S8
4,4,4-trifluoro-1,1-diphenylbut-2-yn-1-ol (10a)	S8
General procedure for the synthesis of Meyer-Schuster adducts [11a-18a].....	S8
Characterization of the 1:1 ratio of two diastereoisomers 12a oxybis(4,4-difluorotridec-2-yn-1,1-diyl)dibenzene.....	S8
12a (Mixture of diastereoisomers)	S9
(E)-4,4-difluoro-1-phenyltridec-1-en-3-one (11a)	S9
(E)-4,4-difluoro-1-(4-methoxyphenyl)tridec-1-en-3-one (11b)	S9
(E)-4,4-difluoro-1-(4-(trifluoromethyl)phenyl)tridec-1-en-3-one (11d)	S9
(E)-1-(4-chlorophenyl)-4,4-difluorotridec-1-en-3-one (11e)	S9
(E)-1-(3-chlorophenyl)-4,4-difluorotridec-1-en-3-one (11f)	S9
(E)-5,5-difluoro-2-phenyltetradec-2-en-4-one (14h)	S10
4,4-difluoro-1,1-diphenyltridec-1-en-3-one (14i)	S10
(E)-4-fluoro-1-phenyltridec-1-en-3-one (13a)	S10
(E)-4-fluoro-1-(4-methoxyphenyl)tridec-1-en-3-one (13b)	S10
(E)-4-fluoro-1-(4-(trifluoromethyl)phenyl)tridec-1-en-3-one (13d).....	S10
(E)-1-(4-chlorophenyl)-4-fluorotridec-1-en-3-one (13e).....	S10
(E)-1-(3-chlorophenyl)-4-fluorotridec-1-en-3-one (13f).....	S11
(E)-5-fluoro-2-phenyltetradec-2-en-4-one (15h).....	S11
4-fluoro-1,1-diphenyltridec-1-en-3-one (15i)	S11
(E)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-one (16b).....	S11
(E)-1,1,1-trifluoro-4-phenylpent-3-en-2-one (17a)	S11
1,1,1-trifluoro-4,4-diphenylbut-3-en-2-one (18a)	S11
Synthesis of heterocycles (21a) and (23a) from MSR adduct 11a	S12
<i>Synthesis of piperidine-1-carboximidamide, hydroiodide</i> (19) ^[21]	S12
4-(1,1-difluorodecyl)-6-phenyl-2-(piperidin-1-yl)pyrimidine (21a).....	S12
3-(1,1-difluorodecyl)-1,5-diphenyl-1H-pyrazole (23a).....	S12

Method 1: O ₂ aromatisation	S12
Method 2: DDQ aromatisation	S12
Additional references	S12
NMR spectra of 3a	S13
NMR spectra of 3b	S15
NMR spectra of 3c	S16
NMR spectra of 3d	S17
NMR spectra of 3e	S19
NMR spectra of 3f	S20
NMR spectra of 3g	S22
NMR spectra of 5i	S23
NMR spectra of 5j	S25
NMR spectra of 4a	S26
NMR spectra of 4b	S28
NMR spectra of 4c	S30
NMR spectra of 4d	S32
NMR spectra of 4e	S34
NMR spectra of 4f	S36
NMR spectra of 4g	S38
NMR spectra of 6h	S40
NMR spectra of 6i	S42
NMR spectra of 8a	S44
NMR spectra of 8b	S46
NMR spectra of 9aSi(Me)₃	S47
NMR spectra of 9a	S49
NMR spectra of 10aSi(Me)₃	S50
NMR spectra of 10a	S51
NMR spectra of 11b	S56
NMR spectra of 11f	S59
NMR spectra of 11d	S61
NMR spectra of 14h	S63
NMR spectra of 14i	S66
NMR spectra of 13a	S68
NMR spectra of 13b	S71
NMR spectra of 13d	S72
NMR spectra of 13e	S74
NMR spectra of 13f	S75
NMR spectra of 15h	S77
NMR spectra of 15i	S79
NMR spectra of 17a	S82
NMR spectra of 18a	S83
NMR spectra of 19a	S85
NMR spectra of 21a	S85
NMR spectra of 23a	S88

General informations

NMR spectra were performed on Bruker AVANCE 300, AVANCE 400 or AVANCE 500 spectrometers (^1H at 300, 400 or 500 MHz; ^{13}C at 75 MHz, 100 or 126 MHz). Solvent peaks were used as reference values with CDCl_3 at 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR, Chemical shifts δ are given in ppm, and the following abbreviations are used: singlet (s), broad singlet (bs), doublet (d), doublet of doublet (dd), doublet of doublet of doublet (ddd), triplet (t), triplet of doublet (td), quadruplet (q), doublet of quadruplet (dq), and multiplet (m). Non-Uniform Sampling (NUS) acquisition methods for multidimensional NMR within topspin were run to complete conventional measurements, which is uniformly sampled (US). The goal of NUS is to improve spectral resolution obtained in a given amount of measurement time to get a full set of ^{13}C peaks when conventional 2D experiments fail. (HSQC, HMBC were respectively ran with 25 and 50% of NUS). All corresponding products showed ^1H , and ^{13}C NMR spectra in agreement with the assigned structures. IR spectra were recorded on a Perkin Elmer (Spectrum 2) apparatus using a Universal ATR Sampling Accessory and spectra were analysed with spectragryph 1,2,4 version. High resolution mass spectra were recorded in the Centre Régional de Mesures Physiques de l'Ouest, Rennes (CRMPO), on a Maxis 4G. Reaction courses and product mixtures were routinely monitored by TLC on silica gel (precoated F254 Merck plates), and compounds were visualized under a UVP Mineralight UVGL-58 lamp (254 nm) and with KMnO_4/Δ . Column chromatography was performed using silica gel 60M (40–63 mm, 230–400 mesh). Anhydrous solvents were, for tetrahydrofuran distilled under sodium/benzophenone, and for acetonitrile refluxed first under sodium hydride and kept over activated 3.0 Angströms (Å) molecular sieves prior use. Reagents and grade solvents were purchased from Sigma-Aldrich, Fisher, Alfa Aesar, Manchester Organics and Acros without further purification. Reactions were performed under argon. Phosphomolybdic acid reagent ACS was purchased from Acros Organics, batch # A20025401, 100 G, as a green powder stored in an oven at 70 °C.

Synthesis of aryl propargyl alcohols with a mono or a gem-difluoro alkyl side chain

The preparation of [3a-5j] has been performed on 3.0 mmol scale and/or 10.0 mmol for 10a. All compounds are yellow to brown oils. N.B.: The use of pentane for the purification by chromatographic column was an imperative due to no compatibility of the Meyer-Schuster Rearrangement catalyst (phosphomolybdic acid) with trace amounts of others alkanes (hexane, heptane, cyclohexane) if used at this stage.

4,4-difluoro-1-phenyltridec-2-yn-1-ol (3a)

In a Schlenk tube cooled to -20°C , a solution of 3,3-difluorododec-1-yne (2.0 g, 10.0 mmol, 1.0 equiv.) in anhydrous tetrahydrofuran (2.0 mL per mmol), TMEDA (1.40 g, 1.80 mL, 12 mmol, 1.2 equiv.) was added. Then, a solution of *n*-BuLi in hexanes (5.6 mL, 10.5 mmol, 1.05 equiv.) was added dropwise at -20°C and the mixture was stirred for 5-30 mins. Benzaldehyde (1.0 mL, 10.0 mmol, 1.0 equiv.) diluted in anhydrous tetrahydrofuran (1.0 mL per mmol) was added and stirred for a further 5 min. Then, acetic acid (excess, 1 mL) was added. The volatiles were removed under vacuo and the residue purified by column chromatography on SiO_2 with an elution gradient from 1:99 to 10:90 acetone/pentane. After evaporation of the solvents, a yellow oil was obtained (2.83 g, 9.2 mmol, 92 %). Rf: 0.38 (eluent: cyclohexane/diethyl ether 90:10). ^1H NMR: (300 MHz, CDCl_3 , ppm) δ 7.58 – 7.51 (m, 2H, Ar), 7.47 – 7.36 (m, 3H, Ar), 5.56 (t, $J = 3.9$ Hz, 1H), 2.17 – 1.94 (m, 2H), 1.67 – 1.47 (m, 2H), 1.40 – 1.22 (m, 12H), 0.90 (t, $J = 6.7$ Hz, 3H). ^{19}F NMR: (282 MHz, CDCl_3 , ppm) δ -83.1 (td, $J_{\text{FH}} = 14.9$, 3.9 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 139.1, 128.9, 128.8, 126.6, 114.9 (t, $J_{\text{CF}} = 235$ Hz, CF_2), 86.4 (t, $J_{\text{CF}} = 6.8$ Hz, $\text{C}_{\beta=}$), 79.7 (t, $J_{\text{CF}} = 41$ Hz, $\text{C}_{\alpha=}$), 64.2 (t, $J_{\text{CF}} = 1.8$ Hz, CHOH), 39.2 (t, $J_{\text{CF}} = 26$ Hz, $\text{C}_{\alpha\text{-alk}}$), 31.9, 29.4, 29.3, 29.2, 28.9, 22.7 (t, $J_{\text{CF}} = 3.5$ Hz, $\text{C}_{\beta\text{-alk}}$), 22.6, 14.1. ^{19}F NMR: (282 MHz, CDCl_3 , ppm) δ -83.1 (td, $J_{\text{FH}} = 14.9$, 3.9 Hz). IR (film, ν cm^{-1}) 2922, 2855, 1690, 1603, 1450, 1332, 1077, 989, 760. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ Calculated for $[\text{C}_{19}\text{H}_{26}\text{O}\text{F}_2\text{Na}]$: 331.1844; found 331.1848 (1 ppm).

4,4-difluoro-1-(4-methoxyphenyl)tridec-2-yn-1-ol (3b)

Yield = 86%. Rf: 0.35 (eluent: pentane/ethyl acetate 95:5). ^1H NMR (300 MHz, CDCl_3) δ 7.53 – 7.40 (m, 2H), 6.99 – 6.88 (m, 2H), 5.49 (d, $J = 3.8$ Hz, 1H), 3.83 (s, 3H), 2.47 (s, 1H), 2.07 (m, 2H), 1.64 – 1.42 (m, 2H), 1.39 – 1.30 (m, 12H), 0.91 (t, 1H), ^{13}C NMR (75 MHz, CDCl_3) δ 160.0 ($\text{C}_{\text{Ar-IV}}$), 131.4 ($\text{C}_{\text{Ar-IV}}$), 128.1, 114.9 (t, $J_{\text{CF}} = 235$ Hz, CF_2), 114.2, 86.6 (t, $J_{\text{CF}} = 6.8$ Hz, $\text{C}_{\beta=}$), 79.5 (t, $J_{\text{CF}} = 41.2$ Hz, $\text{C}_{\alpha=}$), 63.8 (t, $J_{\text{CF}} = 1.8$ Hz, CHOH), 55.3, 39.2 (t, $J_{\text{CF}} = 23.5$ Hz, $\text{C}_{\alpha\text{-alk}}$), 31.9, 29.4, 29.3, 29.3, 28.9, 22.7 (t, $J_{\text{CF}} = 3.4$ Hz, $\text{C}_{\beta\text{-alk}}$), 22.7, 14.1. ^{19}F NMR: (282 MHz, CDCl_3 , ppm) δ -83.1 (td, $J_{\text{FH}} = 14.9$, 3.9 Hz). IR (film, ν cm^{-1}) 2926, 2855, 2252, 1611, 1511, 1464, 1442, 1304, 1248(s), 1173(s), 1095, 1031, 832, 766. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ Calculated for $[\text{C}_{20}\text{H}_{28}\text{O}_2\text{F}_2\text{Na}]$: 361.1949; found 361.1952 (1 ppm).

4-(4,4-difluoro-1-hydroxytridec-2-yn-1-yl)benzotrile (3c)

Yield = 55%. Rf: 0.30 (eluent: cyclohexane/diethyl ether 90:10). ^1H NMR (300 MHz, CDCl_3) δ 7.70 (q, $J = 8.4$ Hz, 4H), 5.63 (t, $J = 3.8$ Hz, 1H), 2.43 (s, 1H), 2.06 (m, 2H), 1.63 – 1.47 (m, 2H), 1.43-1.25 (m, 12H), 0.90 (t, $J = 6.7$ Hz, 3H). ^{19}F

NMR (282 MHz, CDCl₃) δ -83.40 (td, J = 14.7, 3.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 144.4, 132.5, 127.2, 118.4, 114.9 (C=N), 111.9 (t, J_{CF} = 235 Hz, CF₂), 85.3 (t, J_{CF} = 6.8 Hz, C_{β=}), 80.1 (t, J_{CF} = 41.1 Hz, C_{α=}), 63.0 (t, J_{CF} = 1.8 Hz, CHOH), 39.0 (t, J_{CF} = 23.5 Hz, C_{α-alk}), 31.8, 29.3, 29.3, 29.2, 28.9, 22.8 (t, J_{CF} = 3.4 Hz, C_{β-alk}), 22.7, 14.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -83.40 (td, J = 14.7, 3.5 Hz). IR (film, ν cm⁻¹) 2956, 2855, 2232, 1683, 857. HRMS (ESI): m/z [M+Na]⁺ Calculated for [C₂₀ H₂₅ O₂ N F₂ Na]: 356.1795; found 356.1795 (0 ppm).

4,4-difluoro-1-(4-(trifluoromethyl)phenyl)tridec-2-yn-1-ol (3d)

Yield = 84%. Rf: 0.35 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.72 – 7.54 (m, 4H), 5.59 (t, J = 3.7 Hz, 1H), 3.52 (s, 1H), 2.17 – 1.97 (m, 2H), 1.65 – 1.46 (m, 2H), 1.33 (m, 12H), 0.92 (t, J = 6.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 142.8, 130.9 (q, J_{CF} = 31.7 Hz, CF₃), 126.8 (2 x C_{H-Ar}), 125.7 (q, J_{CF} = 3.8 Hz, CHCF₃), 124.2 (q, J_{CF} = 303 Hz, CF₃), 114.8 (t, J_{CF} = 235 Hz, CF₂), 85.6 (t, J_{CF} = 6.7 Hz, C_{β=}), 80.1 (t, J_{CF} = 41.5 Hz, C_{α=}), 63.3 (t, J_{CF} = 1.8 Hz, CHOH), 39.1 (t, J_{CF} = 23.5 Hz, C_{α-alk}), 31.8, 29.4, 29.3, 29.2, 28.9, 22.6 (t, J_{CF} = 3.4 Hz, C_{β-alk}), 22.6, 14.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -62.75, -83.19 (td, J = 15.6, 4.3 Hz). IR (film, ν cm⁻¹) 2927, 2857, 1694, 829. HRMS (ASAP): m/z [M+H]⁺ Calculated for [C₂₀ H₂₆ O F₅]: 377.1898; found 377.1897 (0 ppm).

1-(4-chlorophenyl)-4,4-difluorotridec-2-yn-1-ol (3e)

Yield = 84%. Rf= 0.30 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.50 – 7.33 (m, 4H), 5.52 (s, 1H), 2.29 (s, 1H), 2.14 – 1.94 (m, 2H), 1.62 – 1.49 (m, 2H), 1.41 – 1.19 (m, 12H), 0.88 (t, J = 6.7 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.5, 134.8, 129.0, 128.0, 114.8 (t, J_{CF} = 233.1 Hz, CF₂), 85.9 (t, J_{CF} = 6.7 Hz, C_{β=}), 80.0 (t, J_{CF} = 6.7 Hz, C_{α=}), 63.5 (CHOH), 39.1, 31.8, 29.4, 29.3, 29.2, 28.9, 22.7, 22.6 (t, J_{CF} = 3.4 Hz, C_{β-alk}), 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -83.21 (td, J = 14.7, 3.9 Hz). IR (film, ν cm⁻¹) 2924, 2855, 2251, 1660, 1589, 844. HRMS (ESI): m/z [M+H]⁺ Calculated for [C₁₉ H₂₅ O Cl F₂] : 343.16347; found 343.1627 (2 ppm), : m/z [M-H₂O+H]⁺ Calculated for [C₁₉ H₂₄ Cl F₂] : 325.1529; found 325.1532 (1 ppm).

1-(3-chlorophenyl)-4,4-difluorotridec-2-yn-1-ol (3f)

Yield = 68%. Rf= 0.20 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.50 (m, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 5.52 (t, J = 3.7 Hz, 1H), 2.91 (s, 1H), 2.15 – 2.00 (m, 2H), 1.63 – 1.52 (m, 2H), 1.42 – 1.26 (m, 12H), 0.92 (t, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.9, 134.7, 134.7, 130.1, 130.1, 129.0, 129.0, 126.8, 126.7, 124.7, 114.8 (t, J_{CF} = 235 Hz, CF₂), 85.7 (t, J_{CF} = 6.7 Hz, C_{β=}), 80.0 (t, J_{CF} = 41 Hz, C_{α=}), 63.4 (t, J_{CF} = 1.8 Hz, CHOH), 39.1 (t, J_{CF} = 23.5 Hz, C_{α-alk}), 31.9, 29.4, 29.3, 29.3, 28.9, 22.7 (t, J_{CF} = 3.4 Hz, C_{β-alk}), 14.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -83.26 (td, J = 14.9, 3.4 Hz). IR (film, ν cm⁻¹) 2924, 2855, 1443, 947, 818, 756. HRMS (ESI): m/z [M+Na]⁺ Calculated for [C₁₉ H₂₅ O F₂ ³⁵Cl Na] : 365.1452; found 365.1453 (0 ppm).

1-(2-chlorophenyl)-4,4-difluorotridec-2-yn-1-ol (3g)

Yield = 76%. Rf: 0.45 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.67 (m, 1H), 7.46 – 7.26 (m, 3H), 5.89 (s, 1H), 3.06 (s, 1H), 2.25 – 2.05 (m, 2H), 2.09 – 1.99 (m, 2H), 1.62 – 1.45 (m, 3H), 1.45 – 1.32 (m, 12H), 0.93 (t, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 136.5, 132.7, 130.1, 129.9, 128.2, 127.4, 114.9 (t, J_{CF} = 235 Hz, CF₂), 85.4 (t, J_{CF} = 6.7 Hz, C_{β=}), 79.5 (t, J_{CF} = 41 Hz, C_{α=}), 61.5 (t, J_{CF} = 1.8 Hz, CHOH), 39.2 (t, J_{CF} = 23.5 Hz, C_{α-alk}), 31.9, 29.4, 29.3, 29.3, 28.9, 22.7 (t, J_{CF} = 3.4 Hz, C_{β-alk}), 14.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -83.25 (td, J = 16.0, 15.4, 4.0 Hz). IR (film, ν cm⁻¹) 2925, 2855, 2255, 1468, 1443, 754. HRMS (ESI): m/z [M+Na]⁺ Calculated for [C₁₉ H₂₅ O F₂ ³⁵Cl Na] : 365.1452; found 365.1457 (1 ppm).

5,5-difluoro-2-phenyltetradec-3-yn-2-ol (5h)

Yield = 24%. Rf: 0.50 (eluent: cyclohexane/diethyl ether 50:50). ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.62 (m, 2H), 7.49 – 7.32 (m, 3H), 2.21 – 2.01 (m, 2H), 1.84 (s, 3H), 1.61 (m, 2H), 1.49 – 1.24 (m, 12H), 0.95 (t, J = 7.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.2, 128.5, 128.1, 124.8, 115.0 (t, J_{CF} = 235 Hz, CF₂), 90.0 (t, J_{CF} = 6.7 Hz, C_{β=}), 78.1 (t, J_{CF} = 41 Hz, C_{α=}), 69.8, 62.6 (t, J_{CF} = 1.8 Hz, CCH₃OH), 39.3 (t, J_{CF} = 23.5 Hz, C_{α-alk}), 31.9, 29.4, 29.3, 29.3, 29.0, 22.8, 22.7 (t, J_{CF} = 3.4 Hz, C_{β-alk}), 14.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -82.87 (t, J = 14.9 Hz). IR (film, ν cm⁻¹) 2956, 2927, 2254, 763, 698. HRMS (ESI): m/z [M+Na]⁺ Calculated for [C₂₀ H₂₈ O F₂ Na] : 345.2000; found 345.1999 (0 ppm).

4,4-difluoro-1,1-diphenyltridec-2-yn-1-ol (5i)

Yield = 47%. Rf: 0.54 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.52 (m, 4H), 7.47 – 7.30 (m, 6H), 2.24 – 2.00 (m, 2H), 1.67 – 1.52 (m, 2H), 1.44 – 1.24 (m, 12H), 0.93 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.6, 128.5, 128.2, 125.9, 115.19 (t, J_{CF} = 235 Hz, CF₂), 89.2 (t, J_{CF} = 6.7 Hz, C_{β=}), 80.3 (t, J_{CF} = 41 Hz, C_{α=}), 74.3 (t, J_{CF} = 1.8 Hz, CPh₂OH), 39.2 (t, J_{CF} = 23.5 Hz, C_{α-alk}), 31.9, 29.4, 29.3, 29.3, 28.9, 22.8, 22.7 (t, J_{CF} = 3.4 Hz, C_{β-}

alk), 14.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -82.99 (t, *J* = 14.9 Hz). IR (film, v cm) 2924, 2854, 1585, 1567, 1146, 1189, 996, 941, 766, 694. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₂₅ H₃₀ O F₂ Na] : 407.2156; found 407.2162 (1 ppm).

[4a-6j] have been obtained as an unseparable 1:1 mixture of two diastereoisomers discernable with ¹⁹F and ¹³C NMR spectra, but not in ¹H NMR ones, except for 5j obtained as a single compound.

4-fluoro-1-phenyltridec-2-yn-1-ol (4a)

Yield = 69%. Rf: 0.30 (eluent: pentane/ethyl acetate 95:5). ¹H NMR (300 MHz, CDCl₃) δ 7.60 – 7.51 (m, 2H), 7.48 – 7.31 (m, 3H), 5.55 (d, *J* = 5.6 Hz, 1H), 5.34 – 5.03 (m, 1H), 2.01 – 1.75 (m, 2H), 1.57 – 1.46 (m, 2H), 1.30 (s, 12H), 0.91 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ, 140 (C_{IV-Ar}), 128.7 (C_{H-Ar}), 128.6 (C_{H-Ar}), 126.7 (C_{H-Ar}), 87.7 (d, *J*_{CF} = 10.4 Hz, C_{β=}), 83.5 (d, *J*_{CF} = 26.3 Hz, C_{α=}), 82.7 (d, *J*_{CF} = 168.6 Hz, C_{FH}), 64.5 (C_{HOH}), 35.8 (d, *J* = 22.3 Hz, C_{α-alk}), 31.9, 29.5, 29.4, 29.3, 29.1, 24.5 (d, *J* = 3.8 Hz, C_{β-alk}), 22.7, 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -173.42 (dtd, *J* = 47.7, 20.8, 6.1 Hz). IR (film, v cm) 2923, 2854, 1455, 917, 696. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₁₉ H₂₇ O F Na] : 313.1938; found 313.1938 (1 ppm).

4-fluoro-1-(4-methoxyphenyl)tridec-2-yn-1-ol (4b)

Yield = 69%. Rf: 0.45 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃, set of two diastereoisomers) δ 7.47 (d, *J* = 8.6 Hz, 2 x 2H), 6.90 (d, *J* = 8.6 Hz, 2 x 2H), 5.51 (d, *J* = 4.2 Hz, 2 x 1H), 5.35 – 5.04 (2 x dt, *J*_{HF} = 48.4 Hz, *J*_{HH} = 5.7, 1.4 Hz, 2 x 1H, 2 x CHF), 3.84 (s, 2 x 3H), 2.32 – 2.14 (br s, 2H, 2 x OH), 2.09 – 1.76 (m, 2 x 2H), 1.59 – 1.39 (m, 2 x H), 1.29 (s, 2 x 12H), 0.90 (t, *J* = 6.6 Hz, 2 x 3H). ¹³C NMR (75 MHz, CDCl₃) δ 159.8 (C_{IV-Ar}), 132.3 (C_{IV-Ar}), 128.1 (2 x C_{H-Ar}), 114.0 (2 x C_{H-Ar}), 87.8 (d, *J* = 10.4 Hz, C_{β=}), 83.3 (d, *J* = 26.3 Hz, C_{α=}), 82.7 (d, *J*_{CF} = 167.3 Hz, C_{FH}), 64.2 (C_{HOH}), 55.3, 35.8 (d, *J* = 22.5 Hz, C_{α-alk}), 31.9, 29.5, 29.4, 29.3, 29.1, 24.5 (C, d, *J* = 4.0 Hz, C_{β-alk}), 22.7, 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -173.24 and 173.25 (dtd, *J* = 48.3, 21.6, 6.5 Hz). IR (film, v cm⁻¹) 2923, 2854, 2046, 1611, 1511, 831, 805, 766. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₂₀ H₂₉ O₂ F Na] : 343.2043; found 343.2041 (1 ppm).

4-(4-fluoro-1-hydroxytridec-2-yn-1-yl)benzotrile (4c)

Yield = 68%. Rf: 0.30 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.73 – 7.61 (m, 4H), 5.60 (d, *J* = 5.6 Hz, 1H), 5.17 (dt, *J* = 48.5, 6.3 Hz, 1H), 1.84 (m, 2H), 1.53 – 1.42 (m, 2H), 1.28 (m, 12H), 0.89 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 145.0 (C_{IV-Ar}), 132.5 (C_{H-Ar}), 127.2 (C_{H-Ar}), 118.5 (C≡N), 112.2 (C_{IV-Ar}), 86.7 (d, *J*_{CF} = 10.4 Hz, C_{β=}), 84.5 (d, *J*_{CF} = 26.3 Hz, C_{α=}), 83.6 (d, *J*_{CF} = 168.2 Hz, C_{FH}), 81.4, 63.6 (C_{HOH}), 35.9 (d, *J*_{CF} = 22.3 Hz, C_{α-alk}), 35.6, 31.9, 29.4, 29.4, 29.3, 29.0, 24.5 (d, *J*_{CF} = 4.0 Hz, C_{β-alk}), 22.7, 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -173.85 and 173.91 (dtd, *J* = 48.3, 21.3, 6.3 Hz). IR (film, v cm) 2925, 2855, 2232, 1655, 852. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₂₀ H₂₆ O N F Na] : 338.1890 found 338.1888 (1 ppm).

4-fluoro-1-(4-(trifluoromethyl)phenyl)tridec-2-yn-1-ol (4d)

Yield = 69%. Rf: 0.18 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.67 (s, 4H), 5.61 (d, *J* = 5.6 Hz, 1H), 5.19 (dt, *J* = 48.4, 6.3 Hz, 1H), 1.88 (m, 2H), 1.65 – 1.42 (m, 2H), 1.29 (m, 12H), 0.90 (t, *J* = 6.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 143.6 (C_{IV-Ar}), 130.2 (q, *J*_{CF} = 32.7 Hz, C_{IV-Ar}CF₃), 126.8 (C_{H-Ar}), 125.6 (q, *J*_{CF} = 3.8 Hz, C_{H-Ar}), 123.8 (q, *J*_{CF} = 272.2 Hz, CF₃), 87.0 (d, *J*_{CF} = 10.4 Hz, C_{β=}), 84.2 (d, *J*_{CF} = 26.3 Hz, C_{α=}), 82.7 (d, *J*_{CF} = 167.9 Hz, C_{FH}), 63.8 (C_{HOH}), 35.7 (d, *J*_{CF} = 22.3 Hz, C_{α-alk}), 31.9, 29.4, 29.4, 29.2, 29.0, 24.5 (d, *J*_{CF} = 4.0 Hz, C_{β-alk}), 22.6, 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -173.85 and 173.91 (dtd, *J* = 48.3, 21.3, 6.3 Hz). IR (film, v cm) 2926, 2856, 1620, 857. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₂₀ H₂₆ O F₄ Na] : 338.1890 found 338.1888 (1 ppm).

1-(4-chlorophenyl)-4-fluorotridec-2-yn-1-ol (4e)

Yield = 65%. Rf: 0.68 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.50 (d, *J* = 5.6 Hz, 1H), 5.18 (dt, *J* = 48.5, 6.2 Hz, 1H), 2.05 – 1.73 (m, 2H), 1.64 – 1.42 (m, 2H), 1.29-1.22 (m, 12H), 0.91 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 138.5 (d, *J*_{CF} = 2.2 Hz, C_{IV-Ar}), 134.4 (C_{IV-Ar}), 128.8 (C_{H-Ar}), 128.0 (C_{H-Ar}), 87.4 (d, *J*_{CF} = 10.3 Hz, C_{β=}), 83.8 (d, *J*_{CF} = 26.3 Hz, C_{α=}), 82.6 (d, *J*_{CF} = 166.7 Hz, C_{FH}), 63.7 (C_{HOH}), 36.0 (d, *J*_{CF} = 22.3 Hz, 2 x C_{α-alk}), 35.7, 31.9, 29.5, 29.4, 29.3, 29.1, 24.5 (d, *J*_{CF} = 4.0 Hz, C_{β-alk}), 22.7, 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -173.26 (dtd, *J* = 46.8, 19.9, 4.8 Hz), -62.63 (s, CF₃). IR (film, v cm⁻¹) 2922, 2854, 1905 (w), 1596, 1006. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₁₉ H₂₆ ³⁵Cl O F Na] : 347.1548 found 347.1550 (0 ppm).

1-(3-chlorophenyl)-4-fluorotridec-2-yn-1-ol (4f)

Yield = 50%. Rf: 0.62 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.54 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.35 – 7.30 (m, 2H), 5.51 (d, *J* = 5.5 Hz, 1H), 5.19 (dtd, *J* = 48.4, 6.5, 1.4 Hz, 1H), 2.62 (br s, OH), 2.00 – 1.77 (m, 2H), 1.56 – 1.45 (m, 2H), 1.31 (d, *J* = 6.4 Hz, 14H), 0.97 – 0.86 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (75 MHz,

CDCl₃) δ 141.9 (C_{IV-Ar}), 134.6 (C_{IV-Ar}), 129.9, 128.6, 126.8 and 124.7 (C_{H-Ar}), 87.1 (d, *J*_{CF} = 2.2 Hz, C_{β=}), 83.9 (d, *J* = 26.3 Hz, C_{α=}), 82.6 (d, *J*_{CF} = 167.7 Hz, C_{FH}), 63.7 (C_{HOH}), 35.7 (d, *J* = 22.6 Hz, C_{α-alk}), 31.9, 29.5, 29.4, 29.3, 29.1, 24.5 (d, *J* = 4.0 Hz, C_{β-alk}), 22.7, 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -173.77 and 173.79 (dtd, *J* = 48.8, 19.2, 6.5 Hz). IR (film, v cm) 2924, 2854, 2219, 1654, 1573, 785, 727. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₁₉ H₂₆ ³⁵Cl O F Na]: 347.1548 found 347.1550 (0 ppm).

1-(2-chlorophenyl)-4-fluorotridec-2-yn-1-ol (4g)

Yield = 52%. Rf: 0.54 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.88 – 7.57 (m, 1H), 7.46 – 7.22 (m, 3H), 5.89 (dd, *J* = 5.8, 1.4 Hz, 1H), 5.34 – 5.03 (m, 1H), 2.02 – 1.76 (m, 2H), 1.61 – 1.44 (m, 2H), 1.32 (d, *J* = 11.8 Hz, 12H), 1.02 – 0.78 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.4 (C_{IV-Ar}), 132.7 (C_{IV-Ar}), 129.8 (C_{H-Ar}), 128.3 (C_{H-Ar}), 128.2 (C_{H-Ar}), 127.3 (C_{H-Ar}), 86.7 (d, *J*_{CF} = 2.2 Hz, C_{β=}), 83.3 (d, *J*_{CF} = 26.3 Hz, C_{α=}), 82.5 (d, *J*_{CF} = 168.0 Hz, 2 x C_{FH}), 61.8 (d, *J*_{CF} = 1.6 Hz, C_{HOH}), 37.3 (d, *J*_{CF} = 22.6 Hz, 2 x C_{α-alk}), 31.9, 29.5, 29.4, 29.3, 29.1, 24.5, 24.4 (d, *J* = 4.0 Hz, 2 x C_{β-alk}), 22.7, 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -173.72 and 173.73 (dtd, *J* = 48.8, 19.2, 6.5 Hz). IR (film, v cm) 2926, 2856, 2254, 1468, 1443, 907, 756, 732. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₁₉ H₂₆ ³⁵Cl O F Na]: 347.1548 found 347.1553 (1 ppm).

5-fluoro-2-phenyltetradec-3-yn-2-ol (6h)

Yield = 58%. Rf: 0.64 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.50 (d, *J* = 5.6 Hz, 1H), 5.18 (dt, *J* = 48.5, 6.2 Hz, 1H), 2.05 – 1.73 (m, 2H), 1.64 – 1.42 (m, 2H), 1.29-1.22 (m, 12H), 0.91 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 145.0 (C_{IV-Ar}), 128.4 (C_{H-Ar}), 127.9 (C_{H-Ar}), 124.9 (C_{H-Ar}), 91.4 (d, *J*_{CF} = 26.3 Hz, C_{β=}), 82.1 (d, *J*_{CF} = 166.7 Hz, C_{FH}), 81.7 (d, *J*_{CF} = 26.3 Hz, C_{α=}), 69.9 (C_{HOH}), 35.9 (d, *J* = 22.3 Hz, C_{α-alk}), 33.1, 31.9, 29.5, 29.5, 29.3, 29.1, 24.6 (d, *J*_{CF} = 4.0 Hz, C_{β-alk}), 22.7, 14.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -173.18 and -173.20 (dtd, *J* = 48.2, 19.2, 7.7 Hz). IR (film, v cm) 2924, 2854, 2061, 1493, 1449, 924, 762, 697. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₂₀ H₂₉ O F Na] : 327.2094 found 327.2098 (0 ppm).

4-fluoro-1,1-diphenyltridec-2-yn-1-ol (6i)

Yield = 34%. Rf: 0.28 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.54 (m, 4H), 7.41 – 7.27 (m, 6H), 5.26 (dt, *J* = 48.5, 6.3 Hz, 1H), 2.82 (s, 1H, OH), 2.05 – 1.80 (m, 2H), 1.65 – 1.44 (m, 2H), 1.44 – 1.18 (m, 12H), 0.91 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 144.5 (C_{IV-Ar}), 128.3 (C_{H-Ar}), 127.9 (C_{IV-Ar}), 126.0 (C_{H-Ar}), 90.7 (d, *J*_{CF} = 26.3 Hz, C_{β=}), 84.2 (d, *J*_{CF} = 26.3 Hz, C_{α=}), 82.2 (d, *J*_{CF} = 166.7 Hz, C_{FH}), 74.4 (C_{HOH}), 36.1 (d, *J*_{CF} = 22.3 Hz, C_{α-alk}), 31.9, 29.5 (2 x C), 29.3, 29.1, 24.6 (d, *J*_{CF} = 4.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -173.58 (dt, *J* = 47.6, 20.3 Hz). IR (film, v cm⁻¹) 2923, 2854, 1944, 1599, 1490, 1449, 766, 749, 696. HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₂₅ H₃₁ O F Na] : 389.2251 found 389.2255 (1 ppm).

Synthesis of aryl-propargylic alcohols with a trifluoro methyl group

LDA (5.0 mL of 1.0 M solution in cyclohexane) was added to a stirred solution of 2-bromo-3,3-trifluoropropene (0.86 g, 5.0 mmol) in THF (20 mL) at -20 °C. The resulting red/black solution was kept stirred for a further 10 min. Then, the electrophile (5.0 mmol, 1.0 equiv., dissolved in 5 mL of anhydrous THF) was added dropwise for a further 1 h stirring before warming to rt. Addition of acetic acid (2 mL) or trimethyl silyl chloride (3.0 equiv.) depending the example was finally done. The reaction mixture was poured into a saturated aqueous ammonium chloride solution and extracted with diethyl ether. The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. The resulting oil was purified by column chromatography on silica gel. Its NMR data are in agreement with literature.^[15]

4,4,4-trifluoro-1-phenylbut-2-yn-1-ol (8a)

Yield = 64%. Rf: 0.18 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.55 – 7.49 (m, 2H), 7.48 – 7.38 (m, 3H), 5.57 (dq, *J* = 5.9, 2.9 Hz, 1H), 2.33 (d, *J* = 6.4 Hz, 1H). ¹⁹F NMR (282 MHz, CDCl₃) δ -50.62 (d, *J* = 2.6 z). IR (film, v cm⁻¹) 2276, 1740, 1655, 1495, 1455, 1270 (s), 1134 (s), 1040, 981, 758 (m), 734 (m), 696.

4,4,4-trifluoro-1-(4-methoxyphenyl)but-2-yn-1-ol (8b)

Yield = 55%. Rf: 0.20 (eluent: pentane/ethyl acetate 95:5). ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.41 (m, 2H), 7.00 – 6.92 (m, 2H), 5.52 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.85 (s, 3H, Me), 2.36 (d, *J* = 6.1 Hz, OH). ¹³C NMR (101 MHz, CDCl₃) δ 160.3, 130.3, 128.1, 114.4, 113.7 (q, CF₃, *J*_{CF} = 256.5 Hz), 86.7 (q, C_{β=}, *J*_{CF} = 6.5 Hz), 73.2 (q, C_{α=}, *J*_{CF} = 52.5 Hz), 63.7 (q, C_{OH}, *J*_{CF} = 1.2 Hz), 55.4 (Me). ¹⁹F NMR (387 MHz, CDCl₃) δ -50.53 (d, *J* = 2.6 z). HRMS (ESI): *m/z* [M+Na]⁺ Calculated for [C₁₁ H₉ O₂ F₃ Na] : 253.0446 found 253.0450 (1 ppm). Its NMR data are in agreement with literature.¹⁵

In order to facilitate the purification of **9a** and **10a**, the products were first isolated as trimethylsilyl derivatives and then deprotected before to be used in MSR.

trimethyl((5,5,5-trifluoro-2-phenylpent-3-yn-2-yl)oxy)silane (TMS ether of **9a**)

Yield = 41 %. Rf: 0.88 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.65 – 7.53 (m, 3H), 7.48 – 7.28 (m, 4H), 1.83 (s, 3H), 0.20 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 178.5 (q, J_{CF} = 34.5 Hz, CO), 164.8, 140.2, 137.7, 131.2, 129.5, 129.4, 129.2, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 114.5 (q, J_{CF} = 291.9 Hz, CF₃), 114.5 (CH_{eth}). ¹⁹F NMR (282 MHz, CDCl₃) δ -50.61. IR (film, ν cm⁻¹) 2919, 2853, 1732, 1459, 1259, 800. HRMS (ESI): m/z [M+H]⁺ Calculated for [C₁₄ H₁₈ O F₃ Si]: 287.1073 found 287.1070 (1 ppm).

5,5,5-trifluoro-2-phenylpent-3-yn-2-ol (**9a**)

Yield = 90%. Rf: 0.30 (eluent: cyclohexane/diethyl ether 90:10). To a stirred solution of protected silyl ether **9a** (286 mg, 1.0 mmol) in MeOH (10 mL) was added K₂CO₃ (135 mg, 1.2 mmol, 1.2 equiv.) in THF. Progression of the reaction was monitored by ¹⁹F NMR spectroscopy. The reaction mixture was then poured into saturated aqueous ammonium chloride and extracted with diethyl ether. The organic phase dried over magnesium sulfate and the solvents were removed under reduced pressure. The resulting oil was used without further purification due to partial decomposition on column chromatography with silica gel. ¹H NMR (300 MHz, CDCl₃) δ 7.59 (dd, J = 8.2, 1.4 Hz, 2H), 7.52 – 7.30 (m, 3H), 1.84 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃) δ -50.60 (s).

Trimethyl((4,4,4-trifluoro-1,1-diphenylbut-2-yn-1-yl)oxy)silane (TMS ether of **10a**)

Yield = 34%. Rf: 0.70 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.55 (m, 4H), 7.47 – 7.39 (m, 4H), 7.38 – 7.31 (m, 2H), 0.22 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 144.3, 128.4, 128.0, 126.0, 114.4 (q, CF₃, J_{CF} = 256.5 Hz), 89.9 (q, C_β, J_{CF} = 6.5 Hz), 75.4 (q, C_{OH}, J_{CF} = 1.2 Hz), 75.3 (q, C_α, J_{CF} = 52.5 Hz), 1.3 (Me x 3). ¹⁹F NMR (376 MHz, CDCl₃) δ -50.52 (s). IR (film, ν cm⁻¹) 2255, 1599, 1491, 1450, 1263, 872, 841. HRMS (ESI): m/z [M+H]⁺ Calculated for [C₁₆ H₁₂ O F₃]: 277.0838 found 277.0838 (1 ppm).

4,4,4-trifluoro-1,1-diphenylbut-2-yn-1-ol (**10a**)

To a stirred solution of protected silyl derivative **10a** (1.09 g, 3.12 mmol) in MeOH (20 mL) was added a solution of tetra-*n*-butylammonium fluoride (5.0 ml, 5.0 mmol, 1.0 M, 1.5 equiv.) in THF. Progression of the reaction was monitored by ¹⁹F NMR spectroscopy. After 12 h, the reaction mixture was poured into a saturated aqueous ammonium chloride solution and extracted with diethyl ether. The organic phase was dried over magnesium sulfate and the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography on silica gel with chloroform as eluant to yield **10a** (0.56 g, 65%) as a colorless oil which solidified at rt. Rf: 0.35 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.88 – 7.74 (m, 2H), 7.68 – 7.48 (m, 4H), 7.45 – 7.32 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 142.6, 142.6, 137.6, 132.4, 130.1, 128.6, 128.5, 128.3, 125.9, 114.3 (q, CF₃, J_{CF} = 259.2 Hz), 89.3 (q, C_β, J_{CF} = 6.5 Hz), 74.2 (q, C_{OH}, J_{CF} = 1.2 Hz), 73.9 (q, C_α, J_{CF} = 52.5 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -50.33 (s). IR (film, ν cm⁻¹) 2925, 2855, 2252, 1490, 1450, 747, 695. HRMS (ESI): m/z [M+H]⁺ Calculated for [C₁₆ H₁₂ O F₃]: 277.0834 found 277.0838 (1 ppm).

General procedure for the synthesis of Meyer-Schuster adducts [**11a-18a**]

In a 5.0 mL vial capped tube (Ø 10 mm) with a magnet stirrer remaining vertically to ensure efficient stirring are added the selected aryl propargylic alcohol with a mono, or a *gem*-difluoro alkyl chain or a trifluoromethyl group (1.0 mmol), distilled AcOEt (50 µL, [1.0-2.0 M]) and then H₃PMo₁₂O₄₀·H₂O (3 mol%). The reaction mixture was stirred at 50°C for 2 hours with a rapid change of color of the heterogenous mixture from green to deep blue. In order to optimize the reaction conditions, for each compound, aliquots of the crude reaction were analyzed by ¹⁹F NMR to check the conversion. Then, the crude mixture was evaporated in vacuo and the residue plugged on the top of a silica 60M column chromatography followed by elution with cyclohexane/diethyl ether 95:5 to afford the targeted product.

N.B.: We have noticed that 1,2-dichlorobenzene was also effective, at 90°C, as a solvent for this phosphomolybdic acid-mediated MSR.

Characterization of the 1:1 ratio of two diastereoisomers **12a** oxybis(4,4-difluorotridec-2-yne-1,1-diyl)dibenzene

As indicated in the Table 1 of the manuscript, the MSR-reaction gave on several occasions a 1:1 mixture of **12a** which could be isolated. Below are listed the spectroscopic data of this mixture.

12a (Mixture of diastereoisomers)

For the selective synthesis of **12a**, we used a method described in the literature^[16] In a 5.0 mL vial cap tube (\varnothing 10 mm) with a magnet stirrer, was added **3a** (308 mg, 1.0 mmol) and $n\text{Bu}_4\text{NPF}_6$ (387 mg, 1.0 mmol) and the reaction vessel is left under stirring at 120°C for 6 hs. The crude mixture was analyzed by ^{19}F NMR to ensure full conversion. Then, it was purified from column chromatography eluting with 95:5 cyclohexane/diethyl ether gave a 1:1 mixture of **12a** in 95% yield. Rf: 0.28 (eluent: cyclohexane/diethyl ether 99:1). ^1H NMR (300 MHz, CDCl_3) δ 7.62 – 7.35 (m, 20H), 5.65 (t, J = 3.7 Hz, 2H), 5.33 (t, J = 3.8 Hz, 2H), 2.31 – 1.84 (m, 8H), 1.70 – 1.54 (m, 8H), 1.32 (d, J = 20.1 Hz, 48H), 1.07 – 0.85 (m, 12H). ^{19}F NMR (282 MHz, CDCl_3) δ -82.96 (td, J = 15.2, 14.7, 3.9 Hz), -83.24 (td, J = 15.6, 4.3 Hz) HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ Calculated for $[\text{C}_{38}\text{H}_{50}\text{O}_4\text{Na}]$: 621.3692; found 621.3692 (0 ppm). ^1H NMR (500 MHz, C_6D_6) δ 7.48 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 6.9 Hz, 2H), 7.11 – 6.92 (m, 9H), 5.67 (t, J = 3.6 Hz, 1H), 5.35 (t, J = 3.7 Hz, 1H), 1.99 – 1.75 (m, 5H), 1.64 – 1.41 (m, 7H), 1.37 – 1.26 (m, 8H), 1.25 – 1.18 (m, 12H), 1.14 (s, 7H), 1.11 – 1.02 (m, 16H), 0.98 – 0.82 (m, 9H). ^{19}F NMR (471 MHz, C_6D_6) δ -82.63 (t, J = 14.9 Hz), -82.86 (td, J = 14.9, 3.7 Hz). IR (film, ν cm^{-1}) 2926, 2855, 2290, 2253, 1455, 766, 720, 695. The structures of **12a** have been confirmed by extensive 2D NMR experiments.

(E)-4,4-difluoro-1-phenyltridec-1-en-3-one (11a)

Yield = 91%. Rf: 0.60 (eluent: cyclohexane/diethyl ether 90:10). ^1H NMR (300 MHz, CDCl_3) δ 7.90 (d, J = 15.9 Hz, 1H), 7.65 (dd, J = 7.4, 2.3 Hz, 2H), 7.45 (d, J = 6.3 Hz, 3H), 7.17 (d, J = 15.9 Hz, 1H), 2.27 – 1.97 (m, 2H), 1.64 – 1.44 (m, 2H), 1.44 – 1.14 (m, 12H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 189.5 (t, J_{CF} = 31 Hz, C=O), 147.4 (C_{eth}), 134.0 ($\text{C}_{\text{IV-Ar}}$), 131.5 ($\text{C}_{\text{H-Ph}}$), 129.0 ($\text{C}_{\text{H-Ph}}$), 128.9 ($\text{C}_{\text{H-Ph}}$), 119.0 (t, J_{CF} = 248.6 Hz, CF_2), 118 (C_{eth}), 33.3 (t, J_{CF} = 23.8 Hz, $\text{C}_{\alpha\text{-alk}}$), 31.8, 29.4, 29.3, 29.3, 29.2, 22.7, 21.4 (t, J_{CF} = 4.3 Hz, $\text{C}_{\beta\text{-alk}}$), 14.1. ^{19}F NMR (282 MHz, CDCl_3) δ -107.32 (t, J = 17.3 Hz). IR (film, ν cm^{-1}) 2924, 2855, 1754, 1706, 1683, 1609, 1577, 994, 766, 684. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ Calculated for $[\text{C}_{19}\text{H}_{26}\text{O}_2\text{Na}]$: 331.1843 found 331.1848 (1 ppm).

(E)-4,4-difluoro-1-(4-methoxyphenyl)tridec-1-en-3-one (11b)

Yield = 86%. Rf: 0.45 (eluent: cyclohexane/diethyl ether 90:10). ^1H NMR (300 MHz, CDCl_3) δ 7.87 (d, J = 15.8 Hz, 1H), 7.62 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 15.8 Hz, 1H), 6.96 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H), 2.35 – 1.89 (m, 2H), 1.50 (dd, J = 15.8, 7.9 Hz, 2H), 1.35–1.28 (m, 12H), 0.90 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 189.5 (t, J_{CF} = 31 Hz, C=O), 162.5 (C_{IV}), 147.4 (C_{IV}), 130.9 ($\text{C}_{\text{H-Ar}}$), 126.9 ($\text{C}_{\text{H-eth}}$), 119.0 (t, J_{CF} = 248.6 Hz, CF_2), 115.6 (C_{eth}), 114.6 ($\text{C}_{\text{H-Ar}}$), 55.4, (OCH_3), 33.3 (t, J_{CF} = 23.8 Hz, $\text{C}_{\alpha\text{-alk}}$), 31.8, 29.4, 29.3, 29.3, 29.2, 22.7, 21.4 (t, J_{CF} = 4.3 Hz, $\text{C}_{\beta\text{-alk}}$), 14.1. ^{19}F NMR (282 MHz, CDCl_3) δ -106.75 (t, J = 17.4 Hz, *Z*-isomer) and -107.28 (t, J = 17.4 Hz, *E*-isomer), *E:Z* ratio 12/1. IR (film, ν cm^{-1}) 2955, 2855, 1704, 1657, 1594, 1572, 1512, 827. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ Calculated for $[\text{C}_{20}\text{H}_{28}\text{O}_2\text{F}_2\text{Na}]$: 331.1949 found 331.1953 (1 ppm).

(E)-4,4-difluoro-1-(4-(trifluoromethyl)phenyl)tridec-1-en-3-one (11d)

Yield = 47%. Rf: 0.42 (eluent: cyclohexane/diethyl ether 90:10). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 16.0 Hz, 1H), 7.78 – 7.63 (m, 4H), 7.20 (d, J = 15.9 Hz, 1H), 2.35 – 1.84 (m, 2H), 1.54 – 1.41 (m, 2H), 1.26 (d, J = 4.4 Hz, 14H), 0.91 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 189.4 (CO), 145.2 (C_{eth}), 137.3 ($\text{C}_{\text{IV-Ar}}$), 132.9 (q, J_{CF} = 32.8 Hz, CF_3), 128.9 ($\text{C}_{\text{IV-Ar}}$), 128.9 ($\text{C}_{\text{H-Ar}}$), 126.0 ($\text{C}_{\text{H-Ar}}$), 120.3 (C_{eth}), 118.8 (t, J_{CF} = 250 Hz, CF_2), 33.1 ($\text{C}_{\alpha\text{-Alk}}$), 31.8, 29.3, 29.3, 29.2, 29.2, 22.6, 21.3 ($\text{C}_{\beta\text{-Alk}}$), 14.0 (CH_3). ^{19}F NMR (376 MHz, CDCl_3) δ -63.00, -107.24 (t, J = 17.5 Hz). IR (film, ν cm^{-1}) 2957, 2930, 2857, 1712, 1614, 1466, 1324(s), 1170, 1131, 1068, 831. HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ Calculated for $[\text{C}_{20}\text{H}_{26}\text{F}_5\text{O}]$: 377,1903 found : 377.1898 (1 ppm). N.B.: A rapid degradation of the sample occurred within 2 days in CDCl_3 .

(E)-1-(4-chlorophenyl)-4,4-difluorotridec-1-en-3-one (11e)

Yield = 84%. Rf: 0.33 (eluent: cyclohexane/diethyl ether 90:10). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 15.9 Hz, 1H), 7.65 – 7.53 (d, J = 8.4 Hz, 2H), 7.47 – 7.37 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 15.9 Hz, 1H), 2.15 – 1.95 (m, 2H), 1.54–1.47 (m, 2H), 1.30 (m, 12H), 0.91 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 189.3 (t, J_{CF} = 31.5 Hz, CO), 145.9, 137.5, 132.5, 130.0, 129.4, 118.9 (t, J_{CF} = 248.8 Hz, CF_2), 118.5, 33.2 (t, J_{CF} = 23.8 Hz, $\text{C}_{\alpha\text{-alk}}$), 31.8, 29.4, 29.3, 29.3, 29.2, 22.7, 21.3 (t, J_{CF} = 4.3 Hz, $\text{C}_{\beta\text{-alk}}$), 14.1. ^{19}F NMR (282 MHz, CDCl_3) δ -106.85 (t, J = 17.5 Hz, *Z*-isomer) and -107.21 (t, J = 17.5 Hz, *E*-isomer), *E:Z* ratio 50/1. IR (film, ν cm^{-1}) 2925, 2855, 1709, 1682, 1490, 1466, 986, 820. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ Calculated for $[\text{C}_{19}\text{H}_{25}\text{O}_2\text{F}_2\text{ClNa}]$: 365.1454 found 331.1454 (0 ppm).

(E)-1-(3-chlorophenyl)-4,4-difluorotridec-1-en-3-one (11f)

Yield = 39%. Rf: 0.45 (eluent: cyclohexane/diethyl ether 90:10). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 16.0 Hz, 1H), 7.63 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.28 (s, 1H), 7.15 (d, J = 16.0 Hz, 1H), 2.27 – 1.86 (m, 2H), 1.51 (m, 2H), 1.41 – 1.20 (m, 12H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 189.3

(t, $J_{CF} = 31.5$ Hz, CO), 145.6, 135.8, 135.2, 131.2, 130.3, 128.4, 127.1, 118.9 (t, $J_{CF} = 248.8$ Hz, CF_2), 33.1 (t, $J_{CF} = 23.8$ Hz, $C_{\alpha-alk}$), 31.8, 29.4, 29.3, 29.3, 29.2, 22.6, 21.3 (t, $J_{CF} = 4.3$ Hz, $C_{\beta-alk}$), 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.24 (t, $J = 17.5$ Hz). IR (film, ν cm^{-1}) 2924, 2854, 1708, 1611, 1566, 984, 856, 784, 673. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{19}H_{25}O_2F_2ClNa]$: 365.1454 found 365.1457 (1 ppm).

(E)-5,5-difluoro-2-phenyltetradec-2-en-4-one (14h)

Yield = 24%. Rf: 0.60 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.45 (m, 3H), 6.88 (s, 1H), 2.67 (d, $J = 1.2$ Hz, 3H), 2.17 – 1.93 (m, 2H), 1.56 – 1.44 (m, 2H), 1.44 – 1.21 (m, 12H), 0.90 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2 (t, $J_{CO} = 29$ Hz, CO), 161.4 (C_{IV-eth}), 142.0 (C_{IV-Ar}), 130.0 (CH-Ar), 128.7 (CH-Ar), 126.7 (CH-Ar), 118.9 (t, $J_{CF} = 24.8$ Hz, CF_2), 117.1 (CH-eth), 33.0 (t, $J_{CF} = 24.8$ Hz, $C_{\alpha-Alk}$), 31.8, 29.4, 29.3, 29.3, 29.2, 22.6, 21.4 (t, $J_{CF} = 4.8$ Hz, $C_{\beta-Alk}$), 19.2, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.30 (t, $J_{CF} = 17.2$ Hz). IR (film, ν cm^{-1}) 2924, 2855, 1697, 1595, 1574, 942, 800, 763, 694. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{20}H_{25}O_2F_2Na]$: 345.2000 found 345.1999 (0 ppm).

4,4-difluoro-1,1-diphenyltridec-1-en-3-one (14i)

Yield = 87%. Rf: 0.68 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 4H), 7.24 (d, $J = 1.7$ Hz, 1H), 7.23 – 7.21 (m, 1H), 7.07 (s, 1H), 2.13 – 1.95 (m, 2H), 1.56 – 1.46 (m, 2H), 1.41 – 1.24 (m, 12H), 0.90 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6 (t, $J_{CF} = 31.5$ Hz, CO), 161.1, 140.8, 138.4, 130.4, 129.1, 128.9, 128.9, 128.8, 128.6, 128.5, 128.1, 118.9 (t, $J_{CF} = 248.8$ Hz, CF_2), 116.8, 32.9 (t, $J_{CF} = 23.8$ Hz, $C_{\alpha-alk}$), 31.9, 29.4, 29.4, 29.3, 29.3, 22.7, 21.4, 21.4 (t, $J_{CF} = 4.3$ Hz, $C_{\beta-alk}$), 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.93 (t, $J = 17.5$ Hz). IR (film, ν cm^{-1}) 2924, 2854, 1704, 1585, 1567, 996, 941, 766, 694. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{25}H_{30}O_2F_2Na]$: 407.2162 found 407.2161 (0 ppm).

(E)-4-fluoro-1-phenyltridec-1-en-3-one (13a)

Yield = 78%. Rf: 0.65 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, $J = 16.0$ Hz, 1H), 7.64 (dd, $J = 6.5, 3.3$ Hz, 2H), 7.44 (m, 3H), 7.18 (dd, $J = 16.0, 3.3$ Hz, 1H), 5.10 – 4.85 (dt, $J = 6.1, 50.3$ Hz, 1H), 1.99 – 1.79 (m, 2H), 1.61 – 1.48 (m, 2H), 1.41 – 1.13 (m, 12H), 0.89 (t, $J = 6.1$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8 (d, $J_{CF} = 22.9$ Hz, CO), 145.1 (d, $J_{CF} = 3.2$ Hz, C_{eth}), 134.4, 131.0, 128.8, 128.7, 119.6 (d, $J_{CF} = 2.3$ Hz, C_{eth}), 96.7 (d, $J_{CF} = 184.1$ Hz, C_{HF}), 94.8, 32.5, 32.3 (d, $J_{CF} = 21.0$ Hz, $C_{\alpha-alk}$), 29.5, 29.4, 29.3, 29.2, 26.9, 24.6, 24.5 (d, $J_{CF} = 3.3$ Hz, $C_{\beta-alk}$), 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -191.99 (dtd, $J = 3.3, 17.5, 51.0$ Hz). IR (film, ν cm^{-1}) 2925, 2854, 1728, 1689, 1607, 990, 799, 758, 686. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{19}H_{27}OFNa]$: 313.1938 found 313.1939 (0 ppm).

(E)-4-fluoro-1-(4-methoxyphenyl)tridec-1-en-3-one (13b)

Yield = 72%. Rf: 0.70 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, $J = 16.0$ Hz, 1H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.05 (dd, $J = 15.9, 3.3$ Hz, 1H), 6.94 (d, $J = 8.8$ Hz, 2H), 5.08 – 4.83 (m, 1H), 2.00 – 1.78 (m, 2H), 1.56 – 1.44 (m, 2H), 1.28 (m, 12H), 0.90 (t, $J = 6.5$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9 (d, $J_{CF} = 22.5$ Hz, CO), 162.1, 144.9 (d, $J_{CF} = 3.2$ Hz, C_{eth}), 130.6, 127.3, 117.2 (C_{eth}), 114.5, 96.1 (d, $J_{CF} = 183.7$ Hz, C_{HF}), 55.4, 32.5 (d, $J_{CF} = 21.5$ Hz, $C_{\alpha-alk}$), 32.4, 31.9, 29.5, 29.4, 29.3, 24.6 (d, $J_{CF} = 3.3$ Hz, $C_{\beta-alk}$), 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -191.75 (dtd, $J = 3.7, 24.6, 50.7$ Hz). IR (film, ν cm^{-1}) 2922, 2855, 1690, 1450, 760. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{20}H_{29}O_2FNa]$: 343.2043 found 343.2048 (1 ppm).

(E)-4-fluoro-1-(4-(trifluoromethyl)phenyl)tridec-1-en-3-one (13d)

Yield = 50%. Rf: 0.55 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.55 (m, 5H), 7.43 – 7.06 (m, 1H), 5.22 – 4.74 (m, 1H), 2.00 – 1.79 (m, 2H), 1.58 – 1.45 (m, 2H), 1.29 (s, 12H), 1.01 – 0.52 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8 (d, $J_{CF} = 22.9$ Hz, CO), 143.0 (d, $J_{CF} = 3.1$ Hz, C_{eth}), 137.7 (CF_3-C_{IV}), 132.5 (q, $J_{CF} = 33.2$ Hz, CF_3), 132.1, 128.8 (C_{H-Ar}), 125.9 (q, $J_{CF} = 3.8$ Hz), 121.7 (d, $J_{CF} = 2.2$ Hz, C_{eth}), 95.8 (d, $J_{CF} = 179$ Hz), 32.3 (d, $J_{CF} = 21.5$ Hz), 31.9, 29.5, 29.3, 29.3, 29.2, 24.5 (d, $J_{CF} = 3.2$ Hz), 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.94, -192.28 (dtd, $J = 51.1, 23.8$ and 3.0 Hz). IR (film, ν cm^{-1}) 2925, 2855, 1694, 1612, 1466, 1415, 1321(s), 117(s), 1127(s), 1109, 1066(s), 1016, 824, 803. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{20}H_{26}O_2F_4Na]$: 381.1812 found 381.1812 (0 ppm).

(E)-1-(4-chlorophenyl)-4-fluorotridec-1-en-3-one (13e)

Yellow oil; Yield = 62%. Rf: 0.50 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, $J = 16.0$ Hz, 1H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.15 (dd, $J = 3.4, 16.0$ Hz, 1H), 5.16 – 4.82 (dt, $J = 6.5, 50.8$ Hz, 1H), 1.90 (m, 2H), 1.52 (m, 2H), 1.28 (s, 12H), 0.89 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9 (d, $J_{CF} = 22.5$ Hz, CO), 143.6 (d, $J_{CF} = 3.2$ Hz, C_{H-eth}), 136.9 (C_{IV-Ar}), 132.9 (C_{IV-Ar}), 129.9 (C_{H-Ar}), 129.3 (C_{H-Ar}), 119.9 (d, $J_{CF} = 2.4$ Hz,

C_{H-eth} , 95.8 (d, $J_{CF} = 184.2$ Hz, C_{HF}), 32.5 (d, $J_{CF} = 20.8$ Hz, $C_{\alpha-alk}$), 32.2, 29.5, 29.4, 29.3, 29.2, 24.5 (d, $J_{CF} = 3.1$ Hz, $C_{\beta-alk}$), 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -191.89 (Z-form), -192.0 (dtd, $J = 3.7, 23.8, 49.8$ Hz, E-form), E:Z ratio 30/1. IR (film, ν cm^{-1}) 2925, 2854, 1692, 1606, 1490, 1465, 1407, 1097, 986, 815. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{19}H_{26}O F^{35}Cl Na]$: 347.1548 found 347.1549 (1 ppm).

(E)-1-(3-chlorophenyl)-4-fluorotridec-1-en-3-one (13f)

Yield = 42%. Rf: 0.55 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, $J = 16.0$ Hz, 1H), 7.451 (m, 2H), 7.42 – 7.31 (m, 2H), 7.17 (dd, $J = 16.0, 3.2$ Hz, 1H), 5.16 – 4.77 (m, 1H), 2.01 – 1.75 (m, 4H), 1.49 (m, 12H), 1.28 (s, 19H), 0.98 – 0.82 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8 (d, $J_{CF} = 24.6$ Hz, CO), 143.3 (d, $J_{CF} = 3.4$ Hz, C_{eth}), 136.2, 135.0, 130.8, 130.2, 128.2, 120.7 (d, $J_{CF} = 2.3$ Hz, C_{eth}), 95.8 (d, $J_{CF} = 187.7$ Hz, C_{FH}), 32.3 (d, $J_{CF} = 20.7$ Hz, $C_{\alpha-alk}$), 29.5, 29.4, 29.4, 29.4, 29.3, 29.2, 24.4 (d, $J_{CF} = 3.3$ Hz, $C_{\beta-alk}$), 22.4, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -192.17 (dtd, $J = 50.3, 23.2$ and 3.39 Hz). IR (film, ν cm^{-1}) 2923, 2854, 1741, 1694, 1604, 1467, 1142, 985, 751. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{19}H_{26}O F^{35}Cl Na]$: 347.1548 found 347.1552 (1 ppm).

(E)-5-fluoro-2-phenyltetradec-2-en-4-one (15h)

Yield = 60%. Rf: 0.58 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.50 (m, 2H), 7.47 – 7.37 (m, 3H), 5.03 – 4.72 (ddd, $J = 4.8, 7.5, 50.5$ Hz, 1H), 2.63 (s, 3H), 1.99 – 1.81 (m, 2H), 1.54 – 1.48 (m, 2H), 1.30 (m, 12H), 0.90 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9 (d, $J_{CF} = 20.7$ Hz, CO), 158.1 (d, $J_{CF} = 1.9$ Hz, C_{H-eth}), 142.3 (C_{IV-Ar}), 129.6 (C_{H-Ar}), 128.6 (C_{H-Ar}), 126.6 (C_{H-Ar}), 118.6 (d, $J_{CF} = 2.4$ Hz, C_{H-eth}), 97.1 (d, $J_{CF} = 184.2$ Hz, C_{HF}), 32.6 (d, $J_{CF} = 20.8$ Hz, $C_{\alpha-alk}$), 31.9, 29.5, 29.4, 29.3 (2C), 24.6 (d, $J_{CF} = 3.1$ Hz, $C_{\beta-alk}$), 22.7, 18.9, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) -189.77 (dddd, $J = 3.4, 24.0, 27.5, 51.5$ Hz). IR (film, ν cm^{-1}) 2953, 2854, 1733, 1682, 1594, 1574, 1447, 1378, 869, 758, 693. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{20}H_{29}O F Na]$: 327.2094 found 327.2098 (1 ppm). The *E*-stereochemistry has been demonstrated with a NOESY correlation.

4-fluoro-1,1-diphenyltridec-1-en-3-one (15i)

Yield = 67%. Rf: 0.55 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 4H), 7.38 (d, $J = 4.4$ Hz, 4H), 7.28 – 7.20 (m, 2H), 6.99 (d, $J = 3.5$ Hz, 1H), 4.92 – 4.57 (dt, $J = 5.1, 6.1, 50.5$ Hz, 1H), 1.94 – 1.78 (m, 2H), 1.48 (m, 2H), 1.33 (m, 12H), 0.98 – 0.91 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0 (d, $J_{CF} = 20.7$ Hz, CO), 157.6 (d, $J_{CF} = 1.9$ Hz, C_{IV-eth}), 141.0, 138.8, 130.0, 129.3, 128.7, 128.6, 128.5, 128.2, 119.6 (d, $J_{CF} = 2.1$ Hz, C_{H-eth}), 95.8 (d, $J_{CF} = 185.5$ Hz, C_{HF}), 32.3 (d, $J_{CF} = 20.8$ Hz, $C_{\alpha-alk}$), 31.9, 29.5, 29.4, 29.3, 29.2, 24.6 (d, $J_{CF} = 3.1$ Hz, $C_{\beta-alk}$), 22.7, 14.1. ^{19}F NMR (376 Hz, $CDCl_3$) -190.22 (dddd, $J = 3.4, 24.1, 25.3, 50.7$ Hz). IR (film, ν cm^{-1}) 2924, 2854, 1690, 1588, 1509, 767, 694. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{25}H_{31}O F Na]$: 389.2251 found 389.2255 (1 ppm).

(E)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-one (16b)

Yield = 73%. Rf: 0.37 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, $J = 15.9$ Hz, 1H), 7.82 – 7.53 (m, 2H), 7.02 – 6.95 (m, 2H), 6.95 – 6.86 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9 (q, $J_{CF} = 35.5$ Hz, CO), 163.2 (C_{eth}), 149.9 (C_{IV-Ar}), 131.4 (C_{H-Ar}), 126.2 (C_{IV-Ar}), 122.3, 118.5, 114.7 (C_{H-Ar}), 116.5 (q, $J_{CF} = 283$ Hz), 114.1 (C_{H-eth}), 113.8, 110.8, 55.5 (OMe). ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.51. IR (film, ν cm^{-1}) 1699, 1586, 1565, 1510, 988, 831, 804, 760. HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{11}H_9O_2F_3Na]$: 253.04523 found 253.0450 (1 ppm). Its NMR data are in agreement with literature.^[17]

(E)-1,1,1-trifluoro-4-phenylpent-3-en-2-one (17a)

Yield = 25%. Rf: 0.60 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, $J = 7.8, 1.8$ Hz, 2H), 7.53 – 7.32 (m, 3H), 6.77 (s, 1H), 2.71 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.74. IR (film, ν cm^{-1}) 1578, 1564, 1376, 1286, 1189, 1133 (s), 1107 (s), 761, 746, 695. HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{11}H_{10}O F_3]$: 215.0678 found 215.0678 (0 ppm). Its NMR data are in agreement with literature.^[18]

1,1,1-trifluoro-4,4-diphenylbut-3-en-2-one (18a)

Yield = 84%. Rf: 0.60 (eluent: cyclohexane/diethyl ether 90:10). 1H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.38 (m, 9H), 7.32 – 7.24 (m, 2H), 6.95 (d, $J = 0.8$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5 (q, $J_{CF} = 35.8$ Hz, CO), 164.8 (C_{eth}), 140.2 (C_{IV-Ar}), 137.7 (C_{IV-Ar}), 131.2 (C_{IV-Ar}), 129.4 (C_{IV-Ar}), 129.2 (C_{H-Ar}), 128.9 (C_{H-Ar}), 128.7 (C_{H-Ar}), 128.3 (C_{H-Ar}), 122.2, 116.3 (q, $J_{CF} = 295$ Hz, CF_3), 114.5 (C_{H-eth}). ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.51. IR (film, ν cm^{-1}) 3061, 1713, 1563, 1491, 1447, 960, 864, 764, 696. HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{11}H_{12}O F_3]$: 277.0842 found 277.0836 (1 ppm). Its NMR data are in agreement with literature.^[7]

Synthesis of heterocycles (21a) and (23a) from MSR adduct 11a

Note: For both reactions, standard reactions conditions {ethanol with or without base,^[19] or high boiling non polar solvent (xylene)^[20]} failed to proceed. Only piperidine as a reagent with the use of 1,2-dichlorobenzene as solvent permit the reaction of the Meyer-Schuster enone derivative **11a** to afford the heterocycle targets **21a** and **22a**.

Synthesis of piperidine-1-carboximidamide, hydroiodide (**19**)^[21]

The synthesis of this reagent has been performed following literature procedure. ¹H NMR (300 MHz, DMSO) δ 7.14 (s, 3H), 3.43 – 3.34 (m, 4H), 1.58 (m, 2H), 1.57 – 1.42 (m, 4H). NMR data are in agreement with literature.

4-(1,1-difluorodecyl)-6-phenyl-2-(piperidin-1-yl)pyrimidine (**21a**)

To a stirred solution of **11a** (412 mg, 1.33 mmol, 1.0 equiv.) in 1,2-dichlorobenzene (3.0 ml) at 90°C was added piperidine-1-carboximidamide, hydroiodide (**19a**) (405 mg, 1.59 mmol, 1.2 equiv.), piperidine (226 mg, 2.66 mmol, 2.0 equiv.) and fresh crushed NaOH pellets (64 mg, 1.59 mmol, 1.2 equiv.), within 12 hours with complete conversion of the intermediate **20a** (aliquot of the crude mixture subjected to ¹⁹F NMR). After evaporation of the solvent, the residue was purified by chromatography column with 2:98 diethyl ether/cyclohexane as eluent affording **19a** as a brown oil (349 mg, 64% yield). Rf: 0.60 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (500 MHz, CDCl₃) δ 8.11 (dd, J = 6.6, 2.9 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.18 (s, 1H), 3.96 – 3.90 (m, 4H), 2.35 – 2.21 (m, 2H), 1.75 – 1.69 (m, 2H), 1.69 – 1.65 (m, 4H), 1.52 – 1.44 (m, 2H), 1.39 – 1.33 (m, 12H), 0.90 (t, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 166.0, 163.9 (t, J_{CF} = 29.9 Hz), 161.9, 137.7, 130.6, 128.7, 127.2, 121.4 (t, J_{CF} = 243.7 Hz, CF₂), 100.1, (t, J_{CF} = 4.6 Hz), 44.9, 35.6 (t, J_{CF} = 24.8 Hz, C $_{\alpha}$ -alk), 31.9, 29.4, 29.3, 29.3, 26.9, 25.8, 24.9, 22.7, 22.0 (t, J_{CF} = 4.6 Hz, C $_{\beta}$ -alk), 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -101.37 (t, J = 16.9 Hz). IR (film, ν cm⁻¹) 2924, 2853, 2317, 1589, 1558, 1510, 1495, 1463, 1447, 979, 954, 841, 770, 691. HRMS (ESI): m/z [M+H]⁺ Calculated for [C₂₅ H₃₆ N₃ F₂]: 416.2871 found 416.2872 (0 ppm).

3-(1,1-difluorodecyl)-1,5-diphenyl-1H-pyrazole (**23a**)

Method 1: O₂ aromatisation

To a stirred solution of **11a** (210 mg, 0.68 mmol, 1.0 equiv.) in 1,2-dichlorobenzene (2.0 ml) at 60°C, was added piperidine (57 mg, 0.68 mmol, 1.0 equiv.) and phenylhydrazine (73 mg, 0.68 mmol, 1.0 equiv.) and the reaction mixture was stirred for a further 12 h. Analysis of the crude mixture subjected by ¹⁹F NMR demonstrated a complete conversion of the intermediate **22a**, affording the new heterocycle **23a**. After evaporation of the volatiles, the residue was column chromatographed on silica gel with 2:98 diethylether/cyclohexane to afford **23a** as a reddish oil (141 mg, 0.35 mmol, 52%).

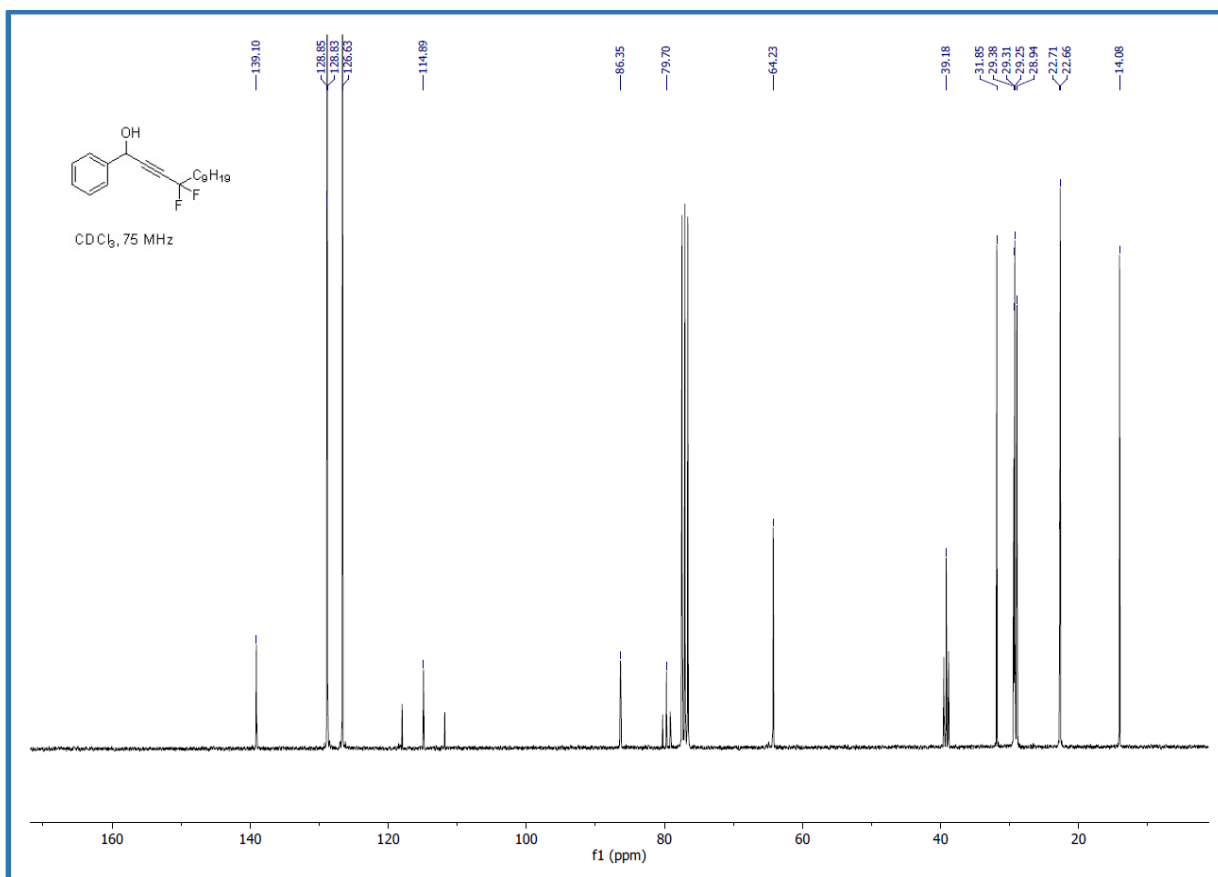
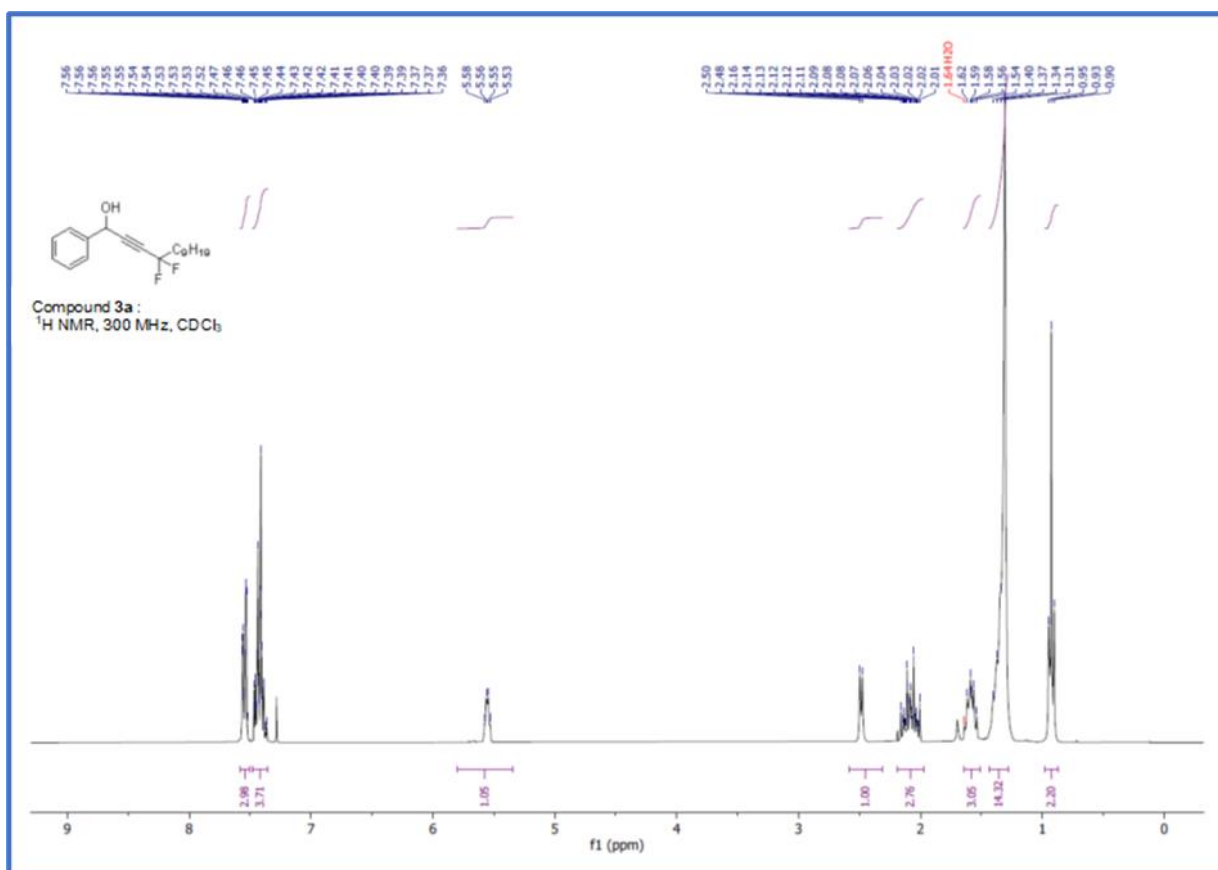
Method 2: DDQ aromatisation

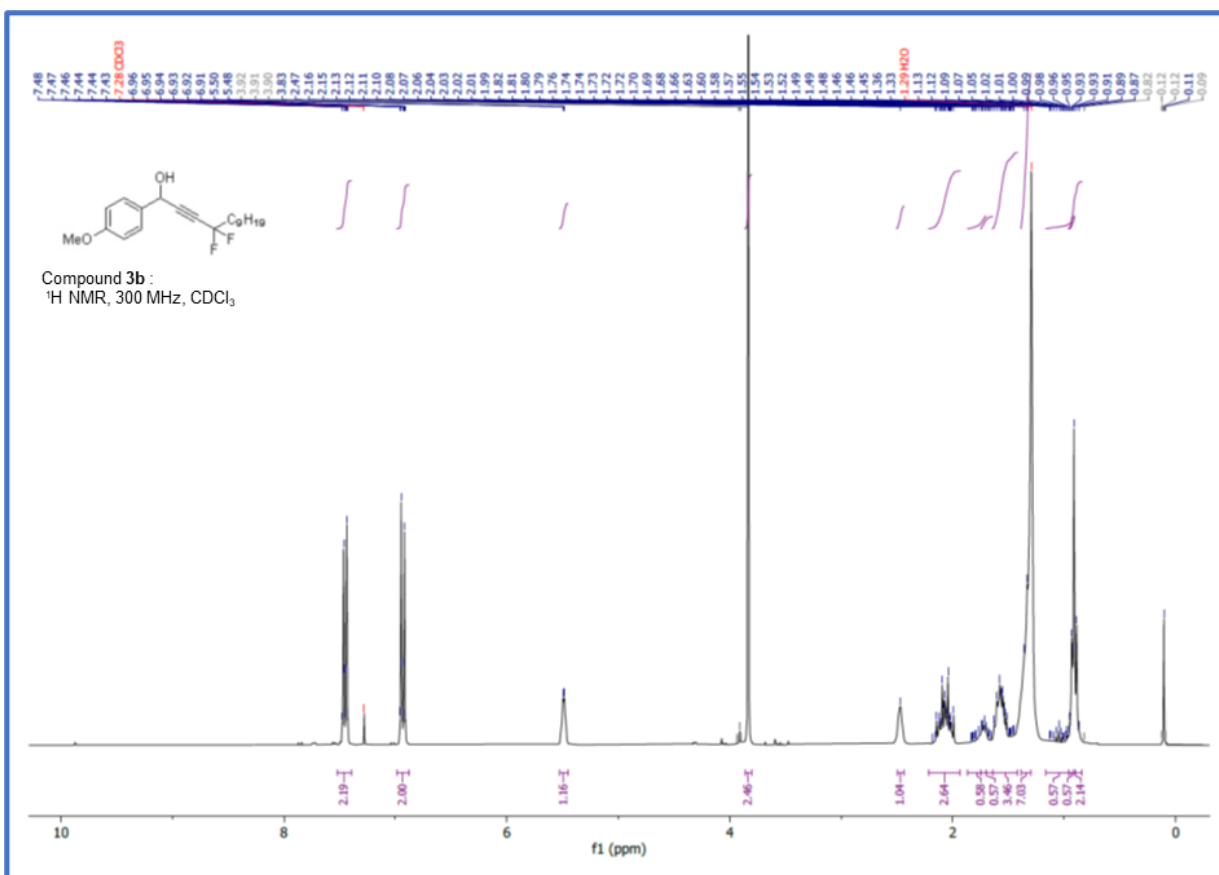
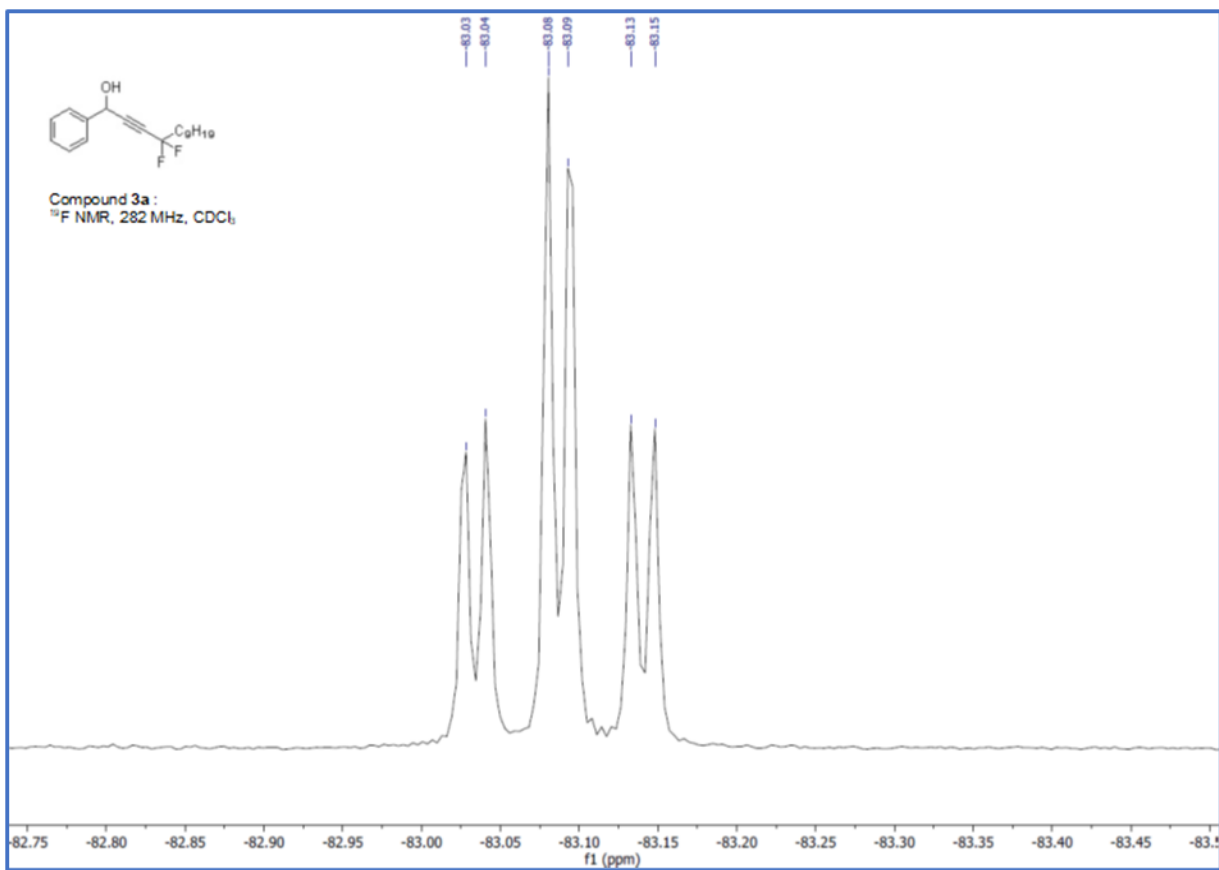
To a stirred solution of **11a** (148 mg, 0.48 mmol, 1.0 equiv.) in 1,2-dichlorobenzene (2.0 ml) at 60°C, was added piperidine (82 mg, .96 mmol, 2.0 equiv.) and phenylhydrazine (62 mg, .96 mmol, 1.2 equiv.) and the reaction mixture was stirred during 1 h to obtain a complete conversion to the intermediate **22a**. Addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (108 mg, 0.48 mmol, 1.0 equiv.) and stirring for a further 1 h afforded the heterocycle **23a** (64 mg, 33%) after purification by column chromatography. Rf: 0.55 (eluent: cyclohexane/diethyl ether 90:10). ¹H NMR (300 MHz, CDCl₃) δ 7.55 – 7.09 (m, 10H), 6.70 (s, 1H), 2.52 – 2.24 (m, 2H), 1.78 – 1.55 (m, 2H), 1.47 – 1.11 (m, 12H), 0.91 (t, J = 6.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 149.7 (t, J_{CF} = 33.8 Hz, CO), 144.1, 139.7, 130.0, 129.0, 128.8, 128.6, 128.5, 127.9, 125.5, 120.4 (t, J_{CF} = 238.0 Hz, CF₂), 105.3, 37.0 (t, J_{CF} = 25.6 Hz, C $_{\alpha}$ -alk), 31.9, 29.5, 29.4, 29.3, 29.3, 22.7, 22.1 (t, J_{CF} = 4.6 Hz, C $_{\beta}$ -alk), 14.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -92.55 (t, J_{CH} = 16.5 Hz, CF₂). IR (film, ν cm⁻¹) 2926, 2854, 2330, 2260, 1598, 1493, 1466, 1445, 907, 811, 762, 730, 694. HRMS (ESI): m/z [M+Na]⁺ Calculated for [C₂₅ H₃₀ F₂ N₂ Na]: 419.2269 found 419.2268 (0 ppm).

Additional References

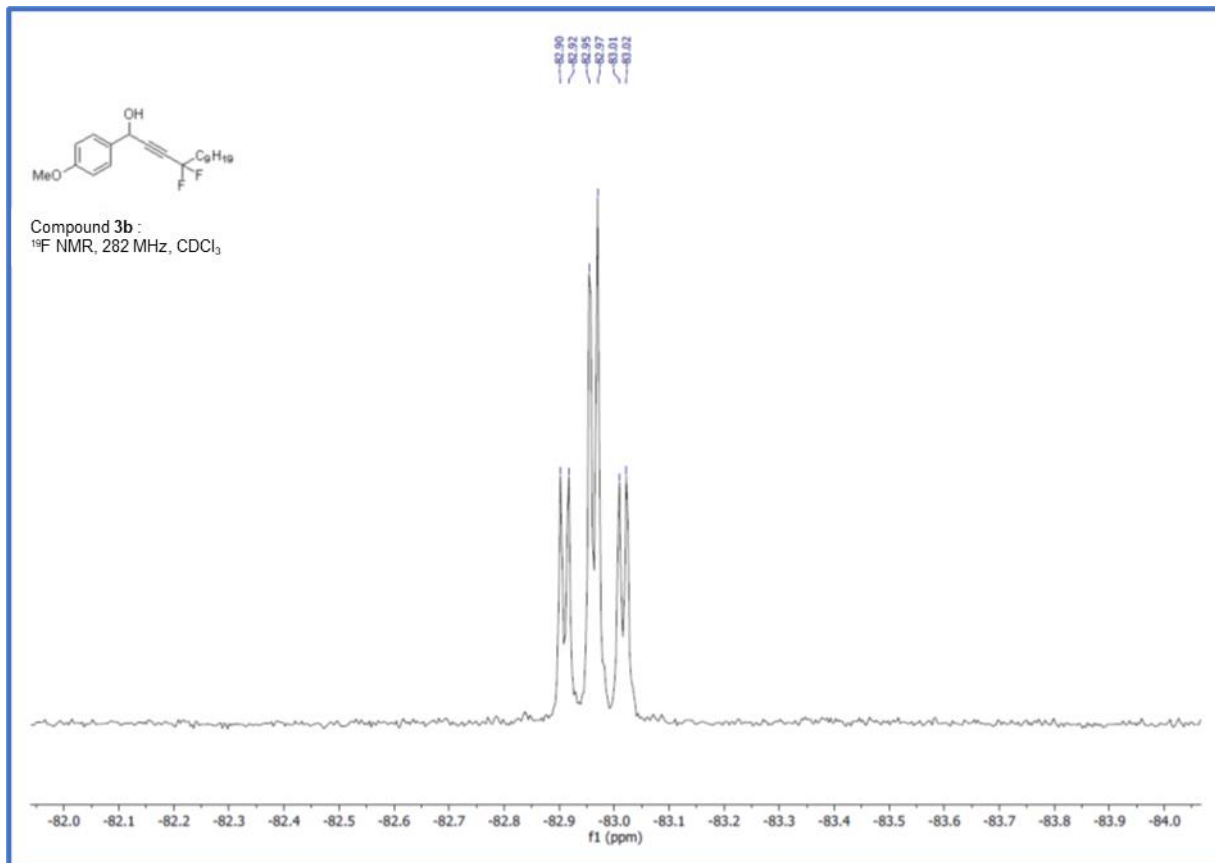
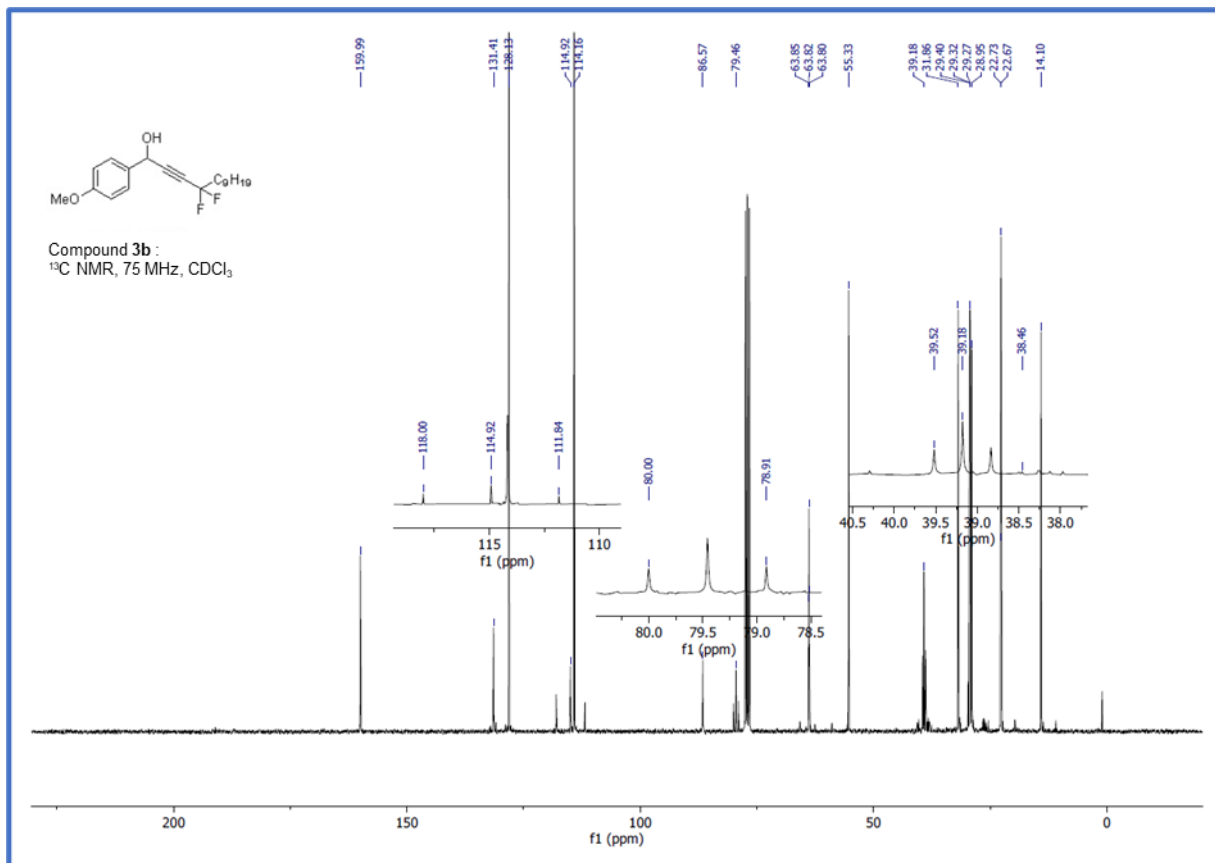
- [15] A. T. Davies, J. E. Taylor, J. Douglas, C. J. Collett, L. C. Morrill, C. Fallan, A. M. Z. Slawin, G. Churchill, A. D. Smith, *J. Org. Chem.* **2013**, *78*, 9243–9257.
[16] A. Pareek, R. Dada, M. Rana, A. K. Sharma, S. Yaragorla, *RSC Adv.* **2016**, *6*, 89732–89743.
[17] C. Yamagami, N. Motohashi, M. Akamatsu, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2281–2285.
[18] V. G. Nenajdenko, I. D. Gridnev, E. S. Balenkova, *Tetrahedron* **1994**, *50*, 11023–11038.
[19] A. N. E. Dine, A. Khalaf, D. Grée, O. Tasseau, F. Fares, N. Jaber, P. Lesot, A. Hachem, R. Grée, *Beilstein J. Org. Chem.* **2013**, *9*, 1943–1948.
[20] A. Agarwal, K. Srivastava, S. K. Puri, P. M. S. Chauhan, *Bioorg. Med. Chem.* **2005**, *13*, 4645–4650.
[21] Z. Zubovics, K. Szilágyi, F. Vida, F. András, K. Sutka, E. Hodula, T. Szekeres, G. Fehér, I. Moravcsik, P. Mátyus, L. Sebestyén, H. Szabó, E. Zára, E. Horváth, L. Toldy, *Pyrimidine Derivatives*, 1997. WO9714685 A1.

NMR spectra of 3a

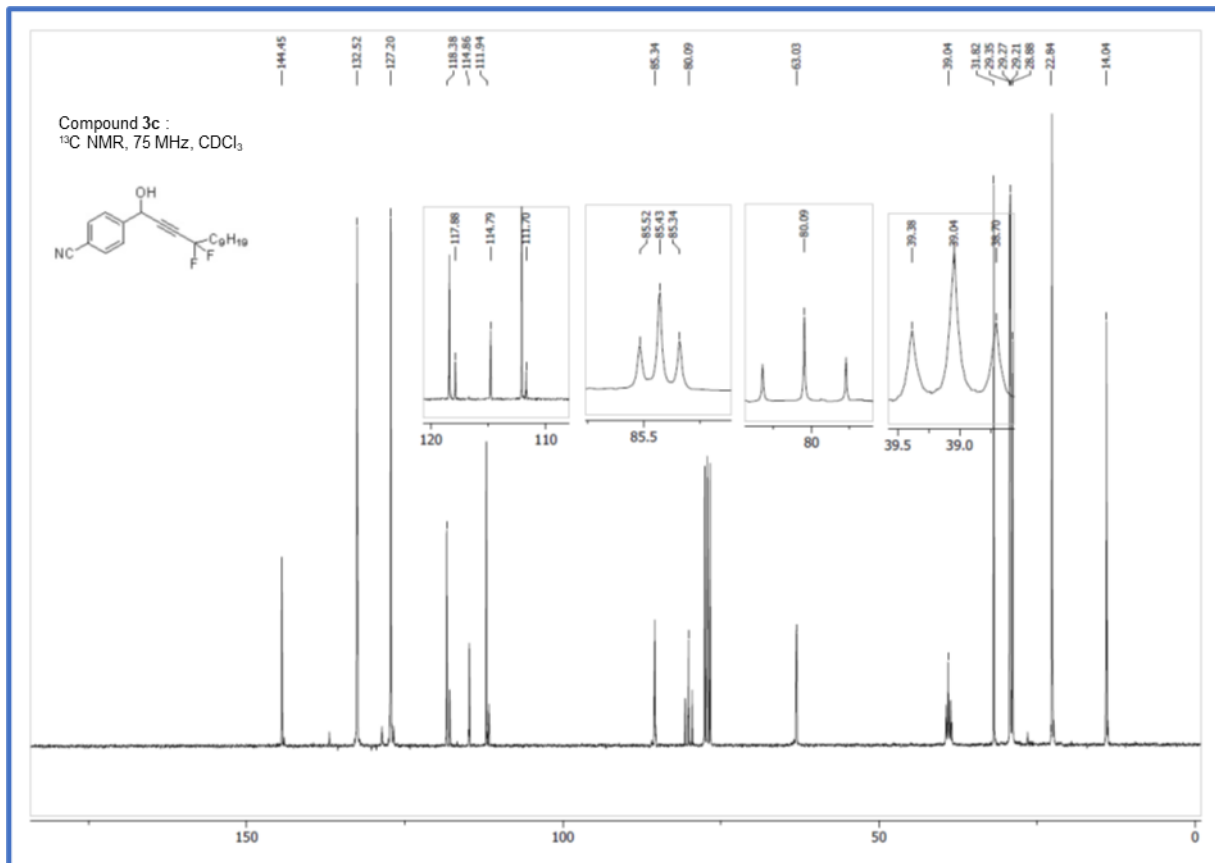
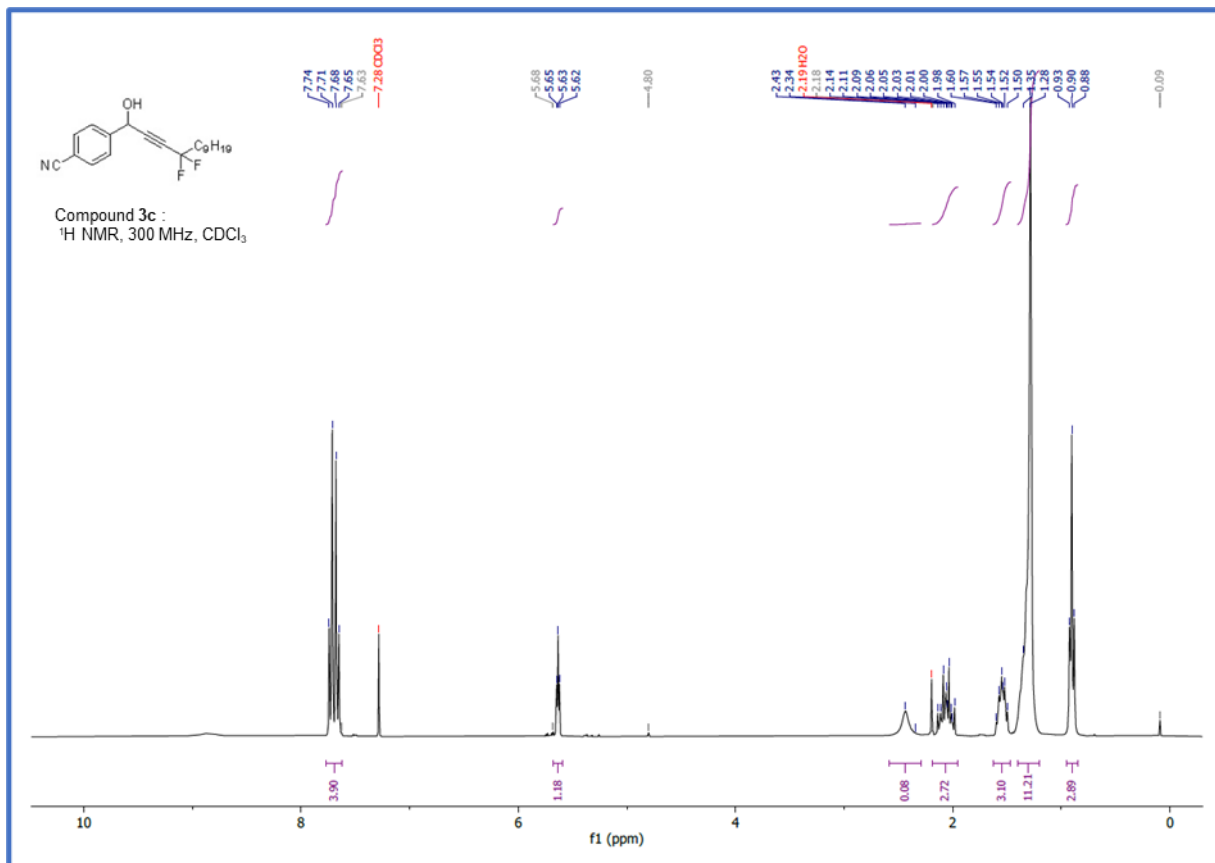


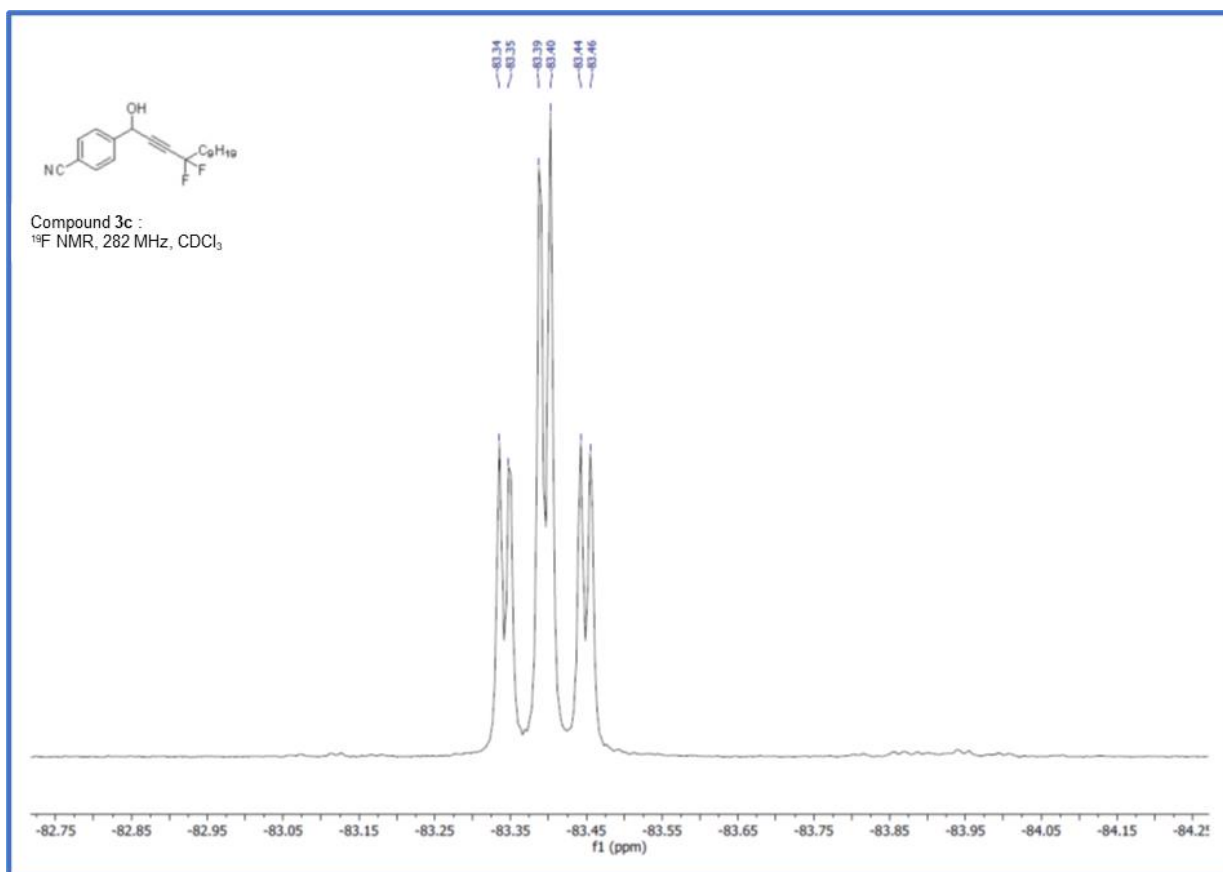


NMR spectra of 3b

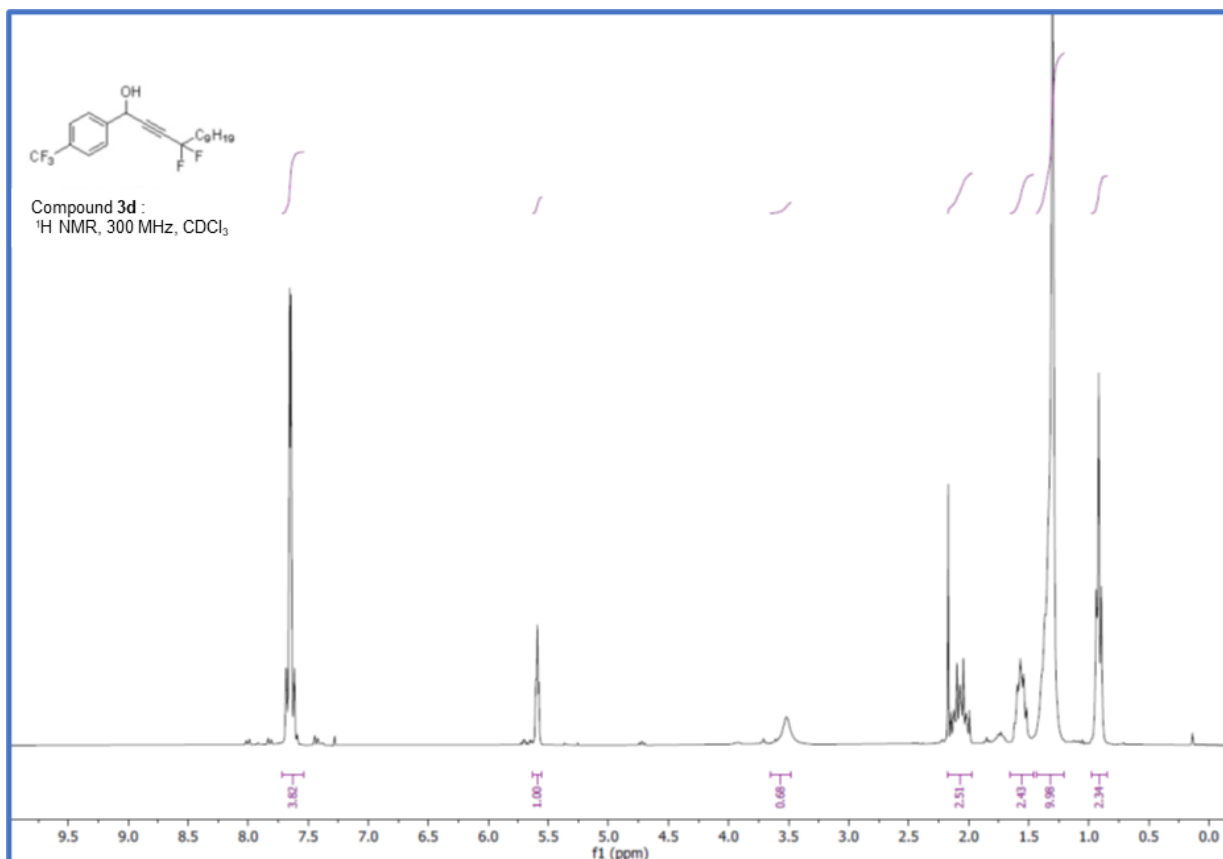


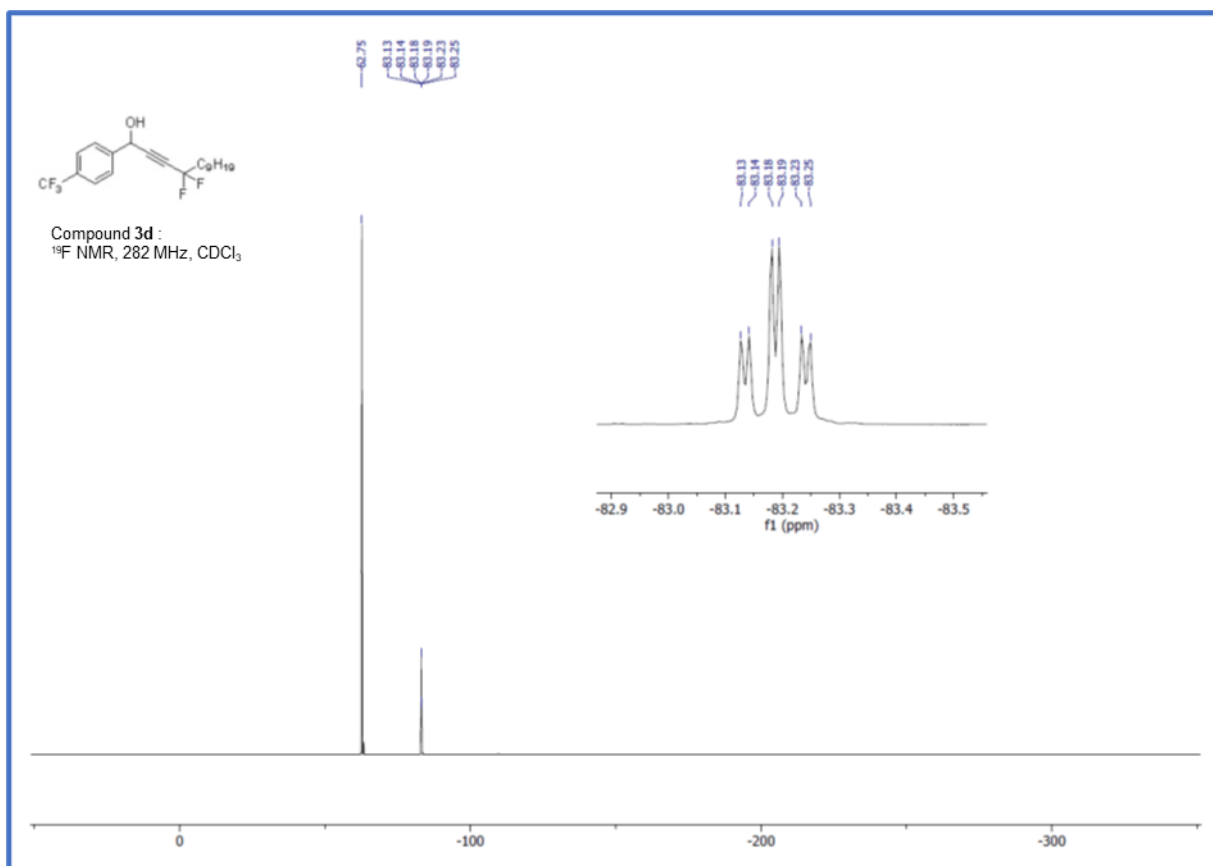
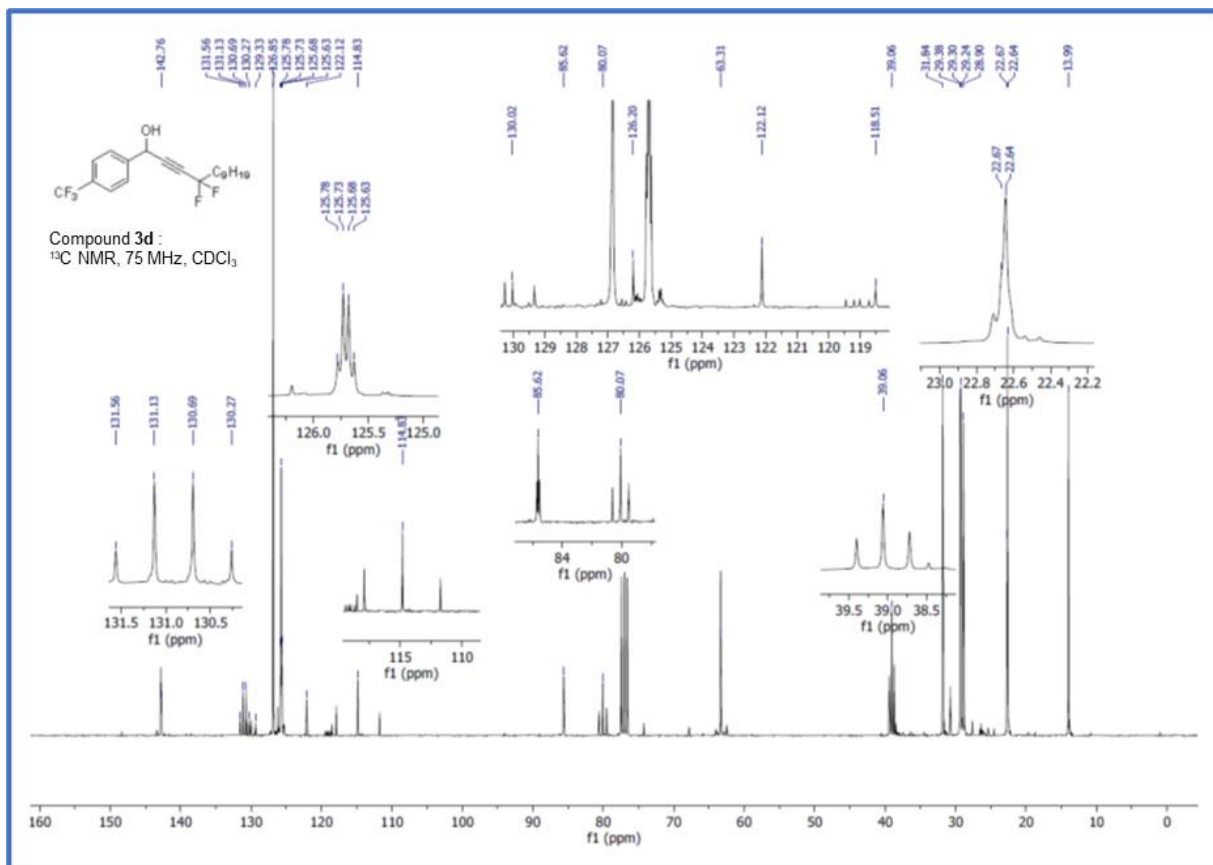
NMR spectra of 3c



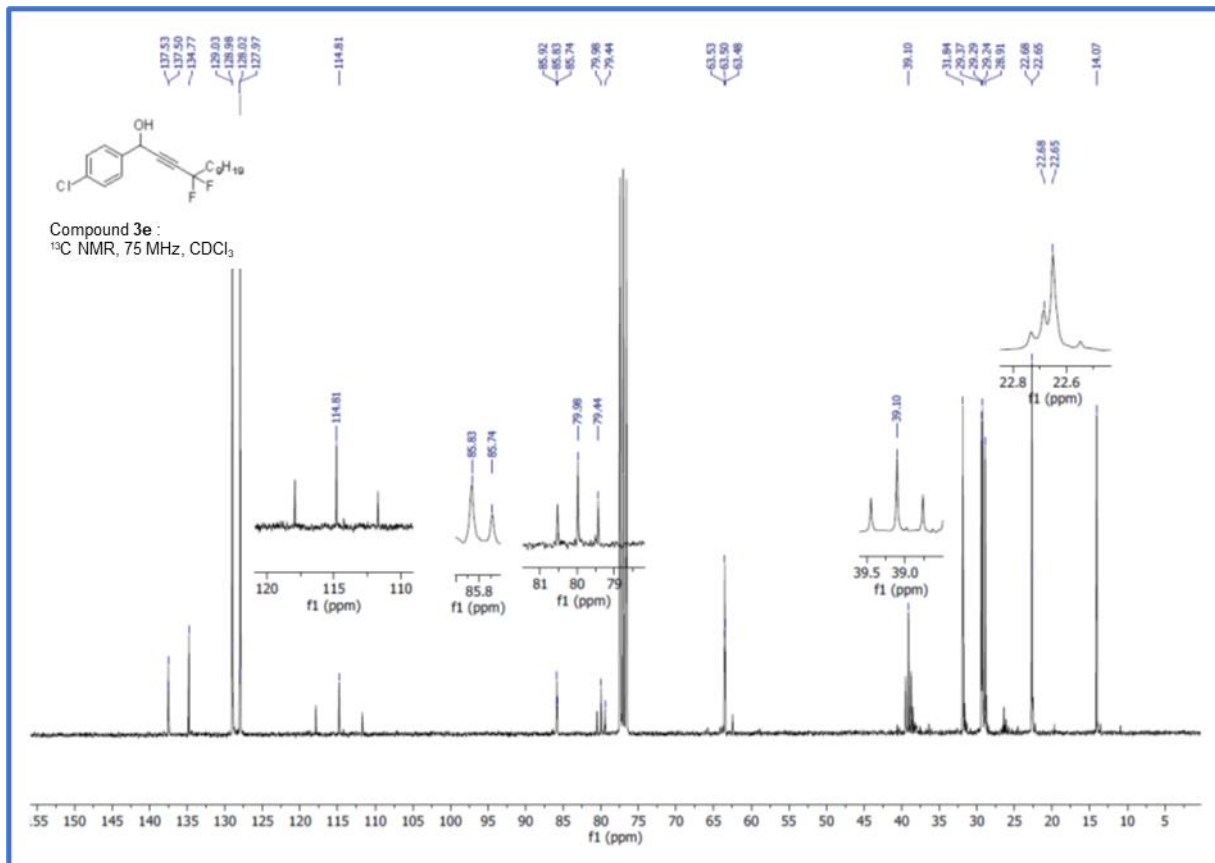
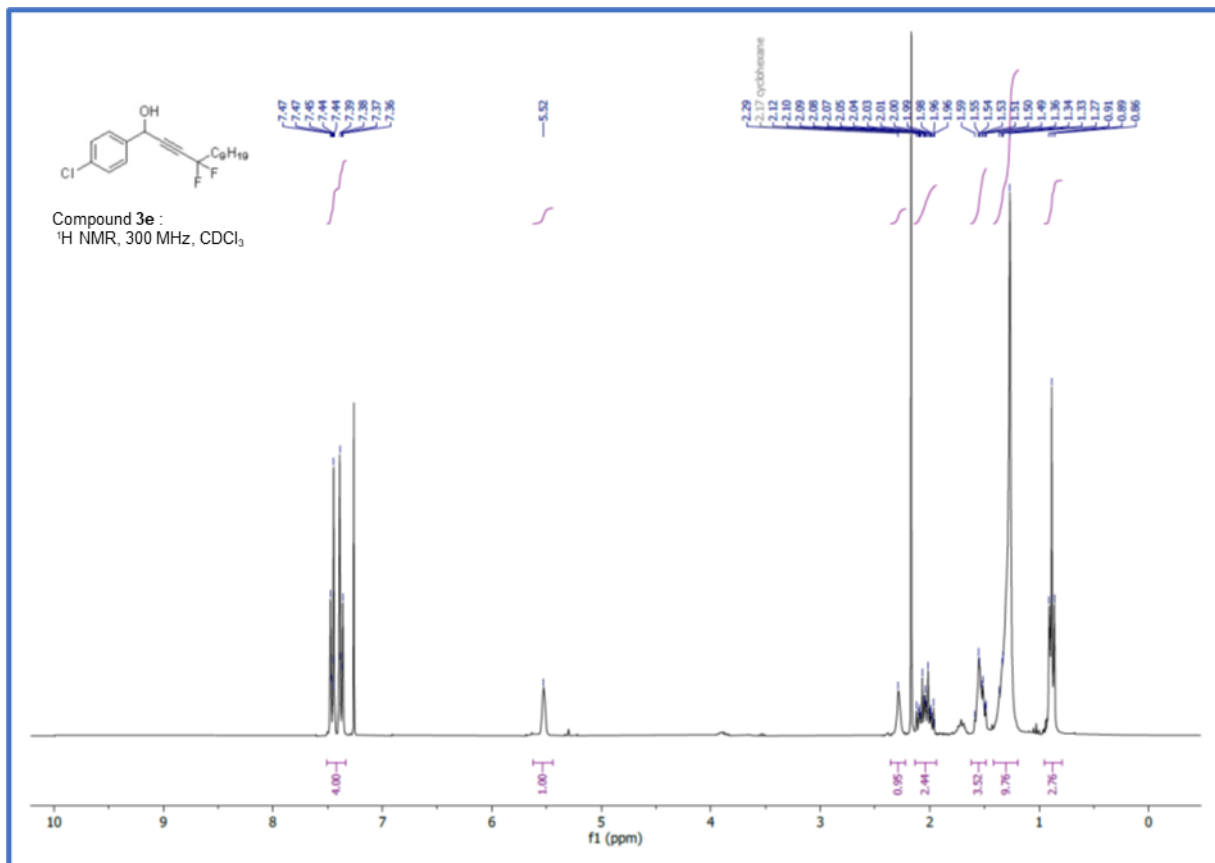


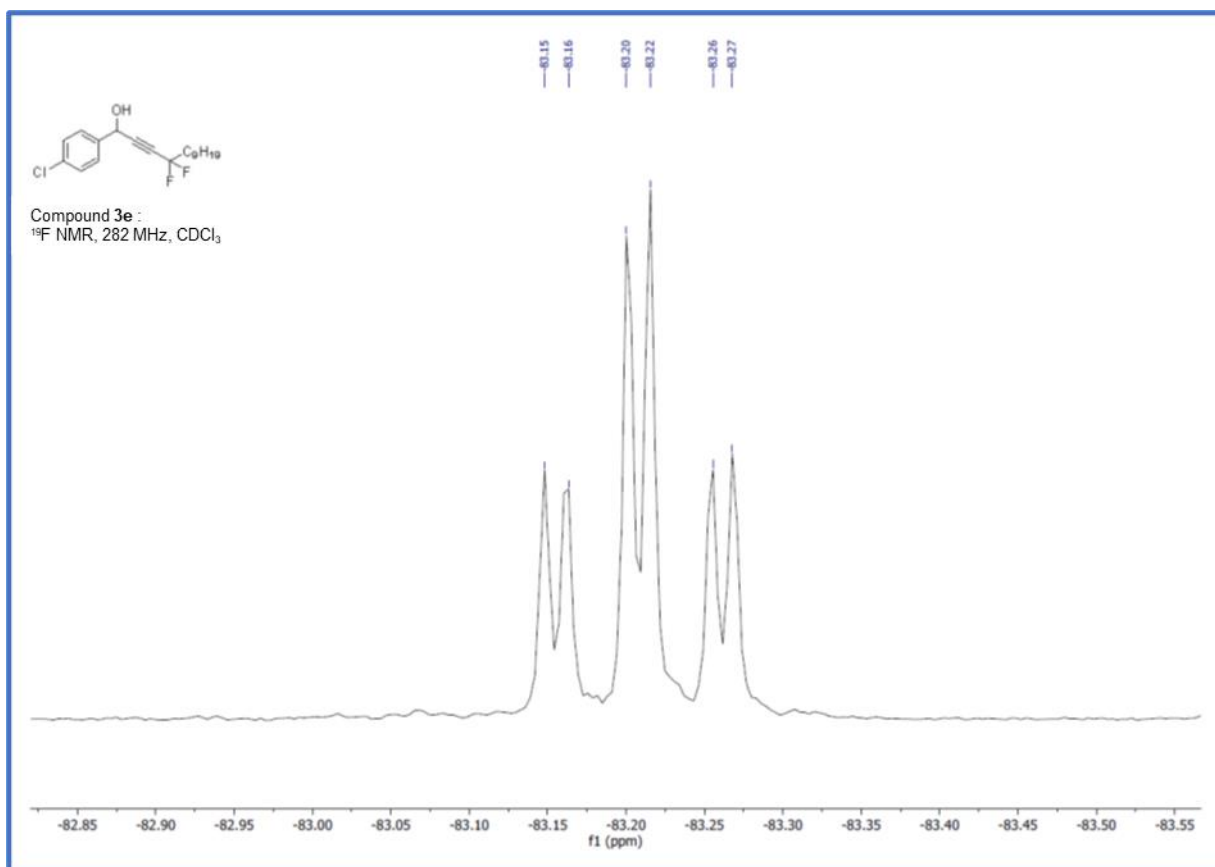
NMR spectra of 3d



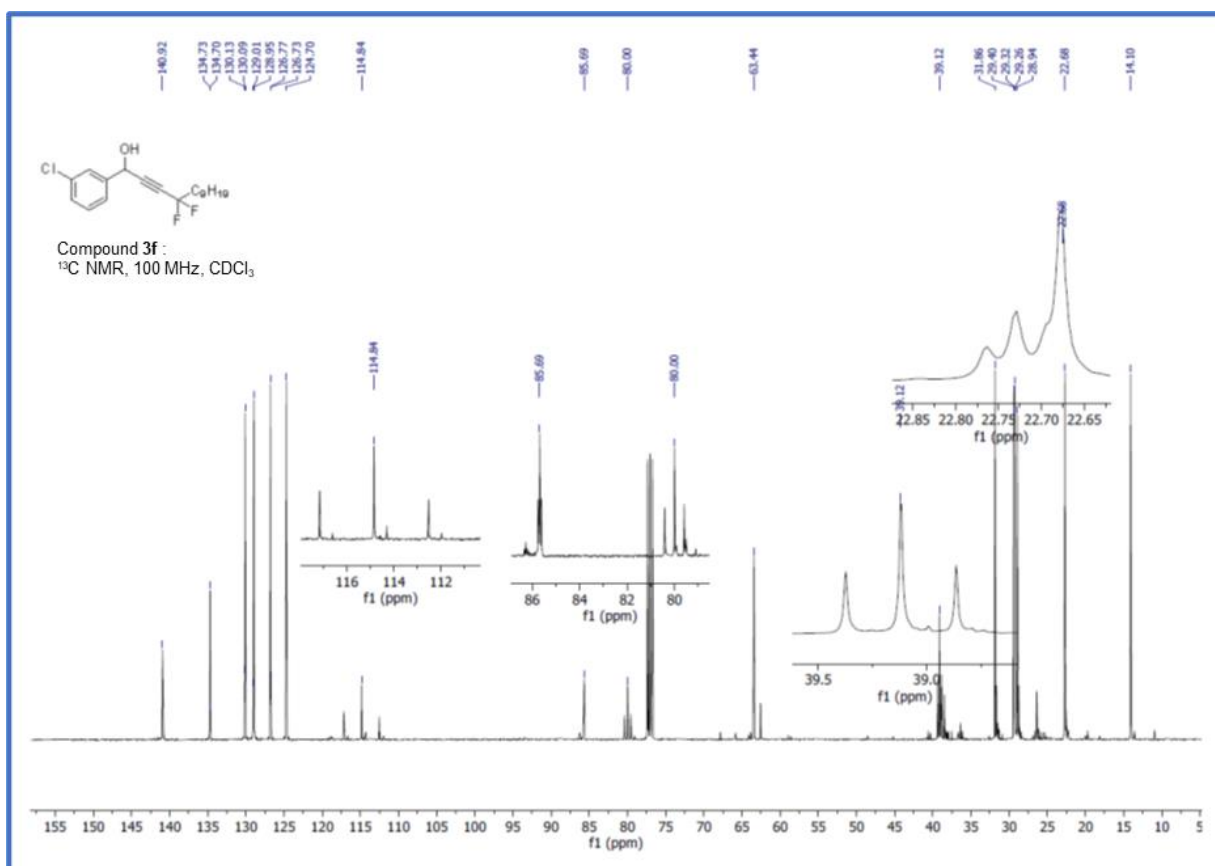


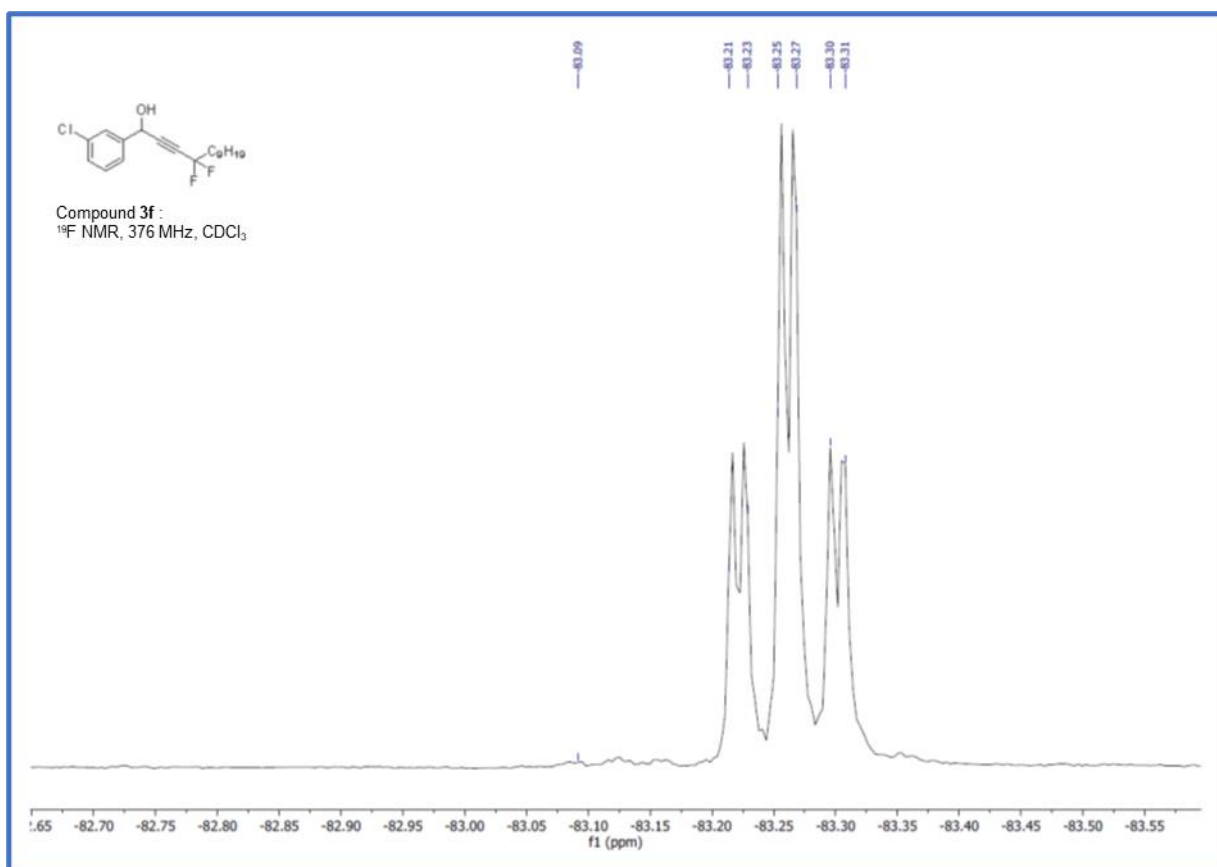
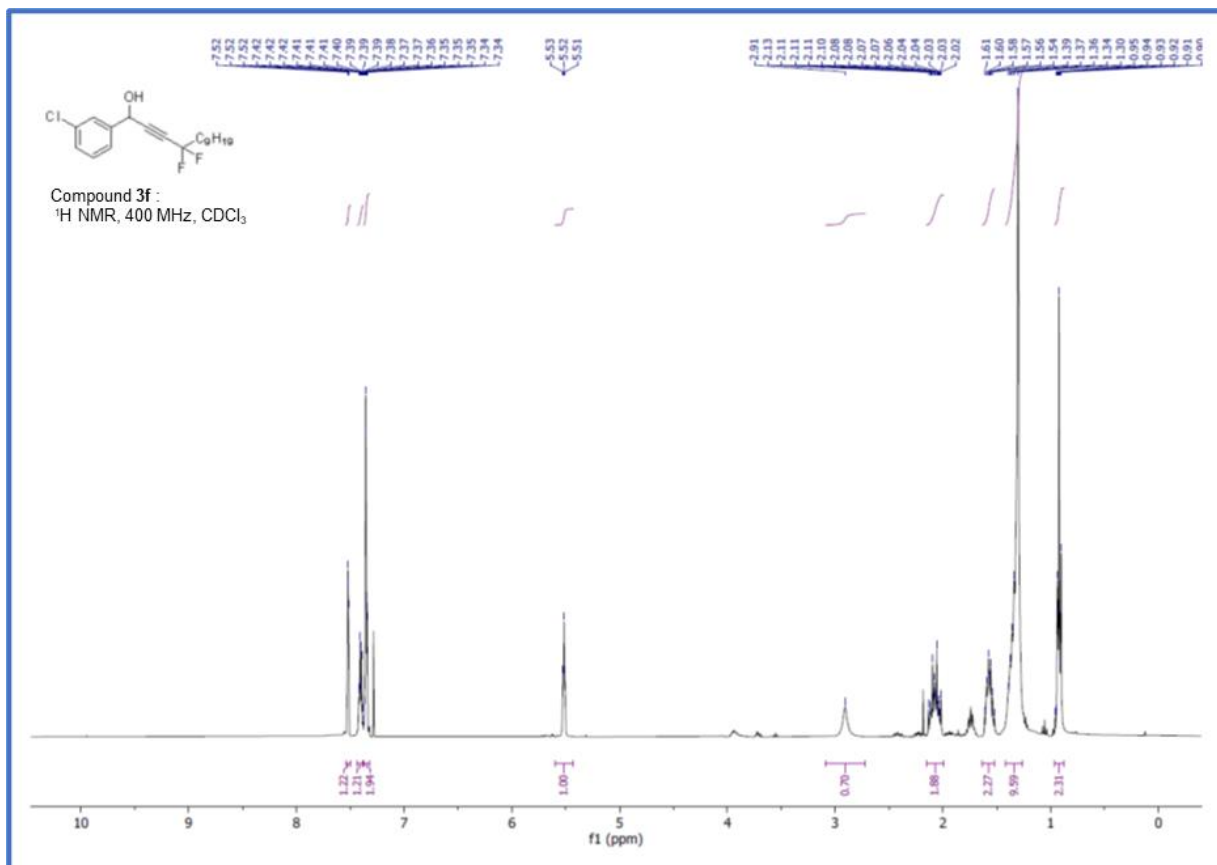
NMR spectra of 3e



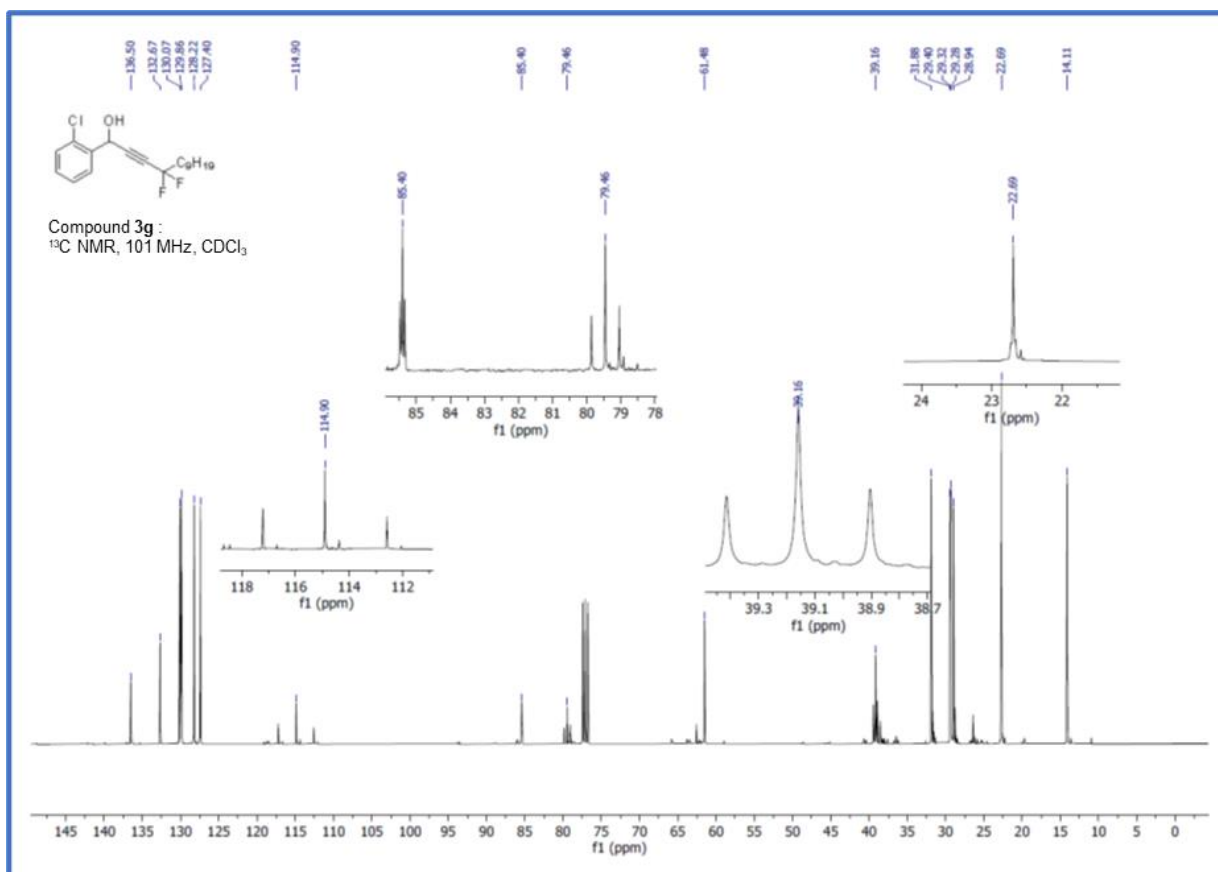
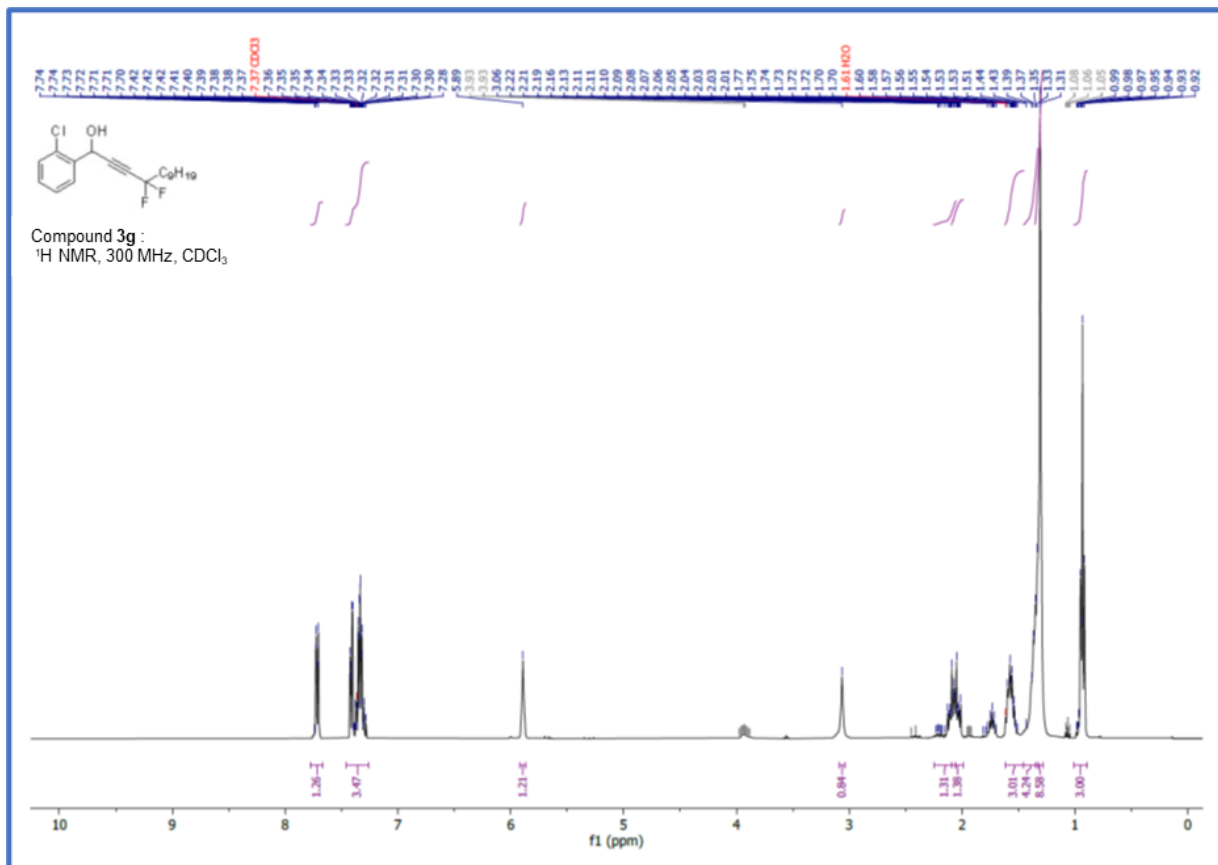


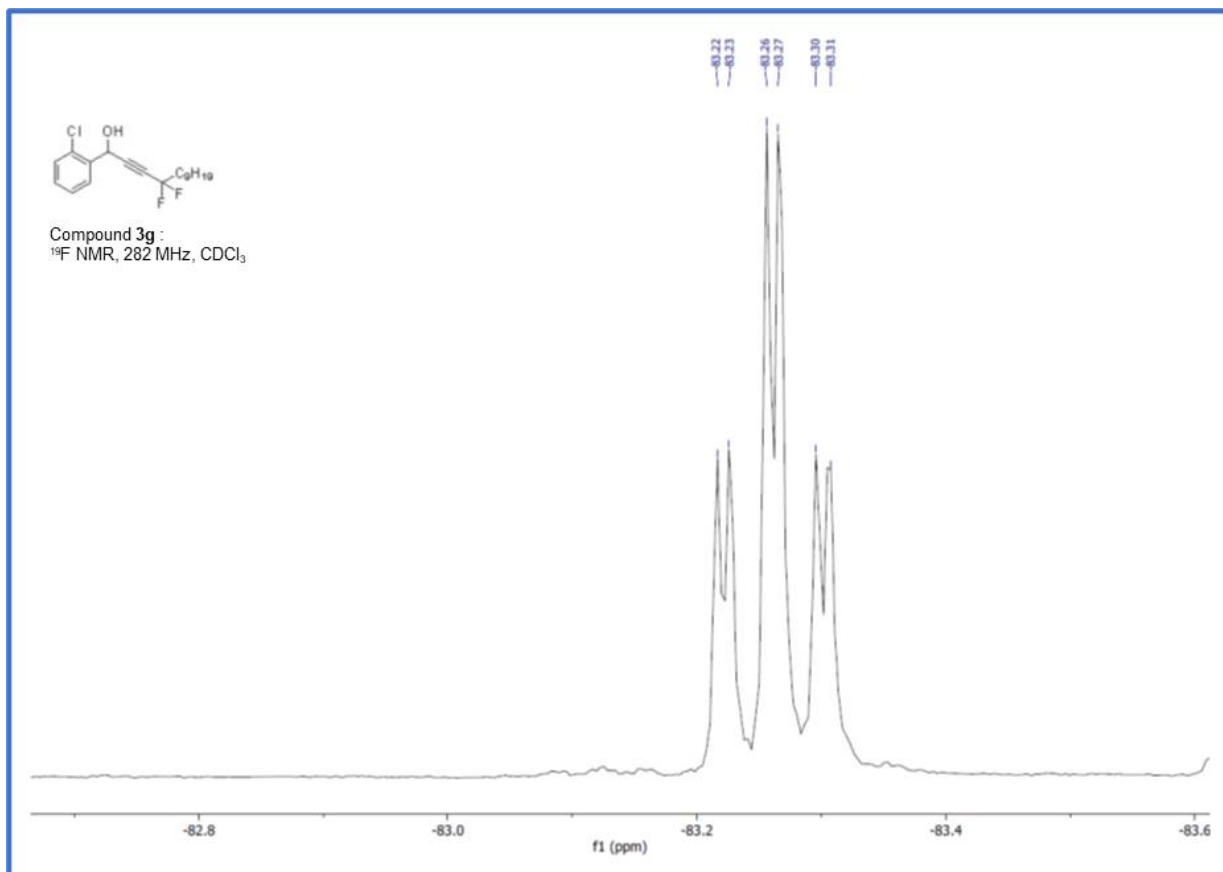
NMR spectra of 3f



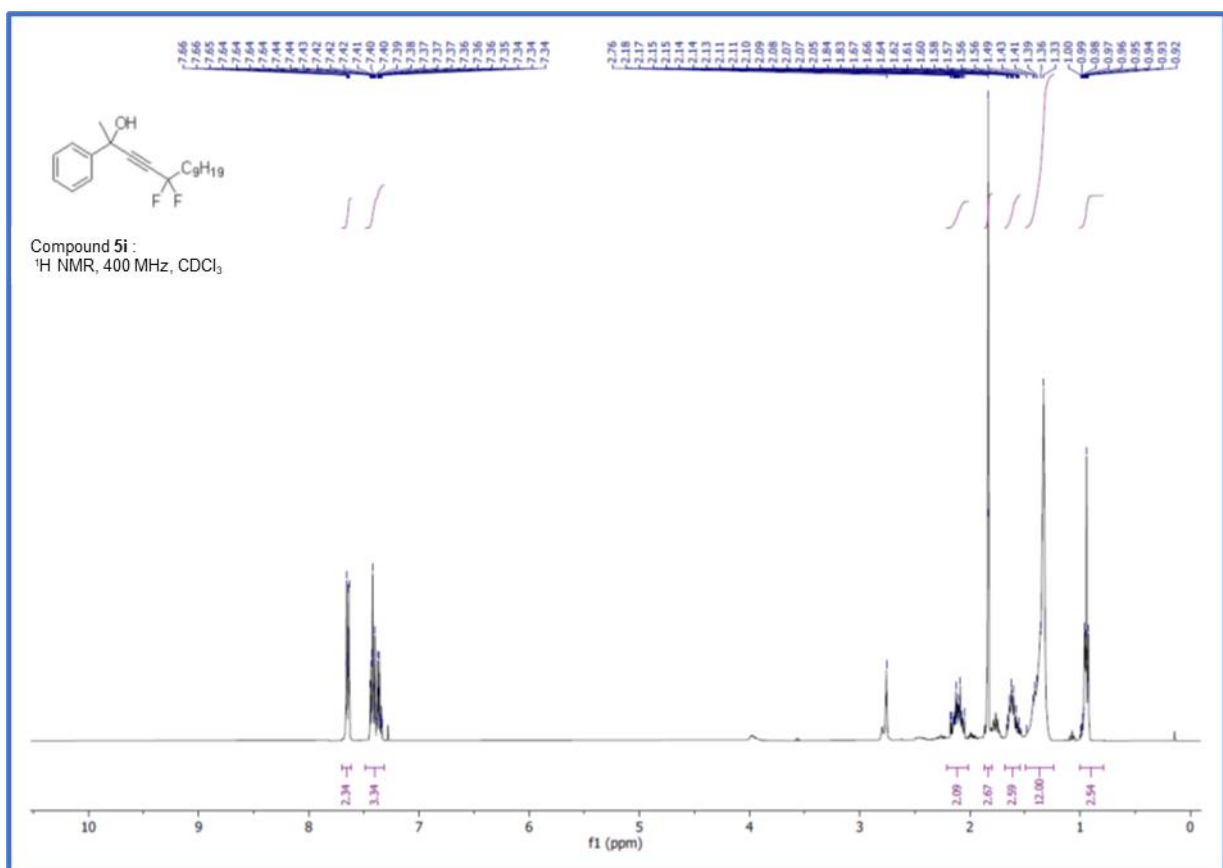


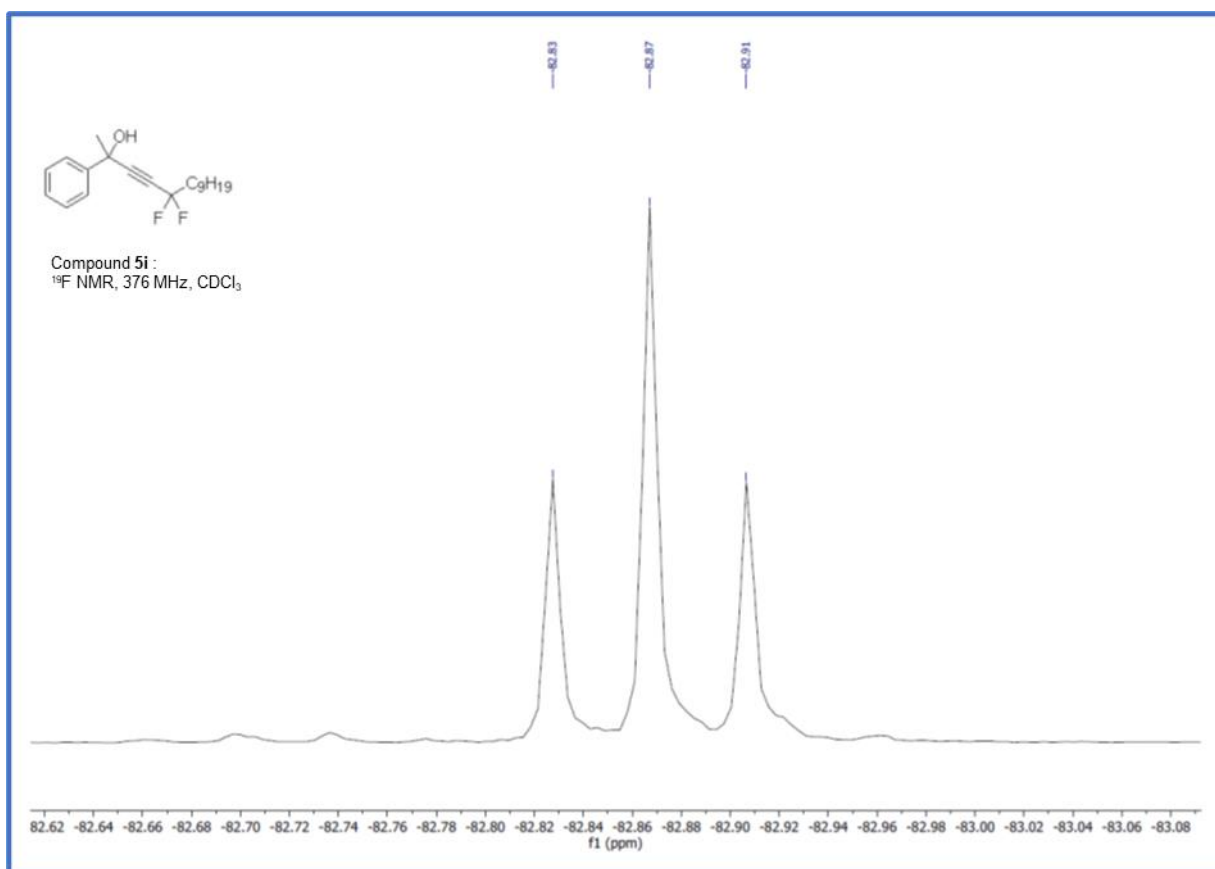
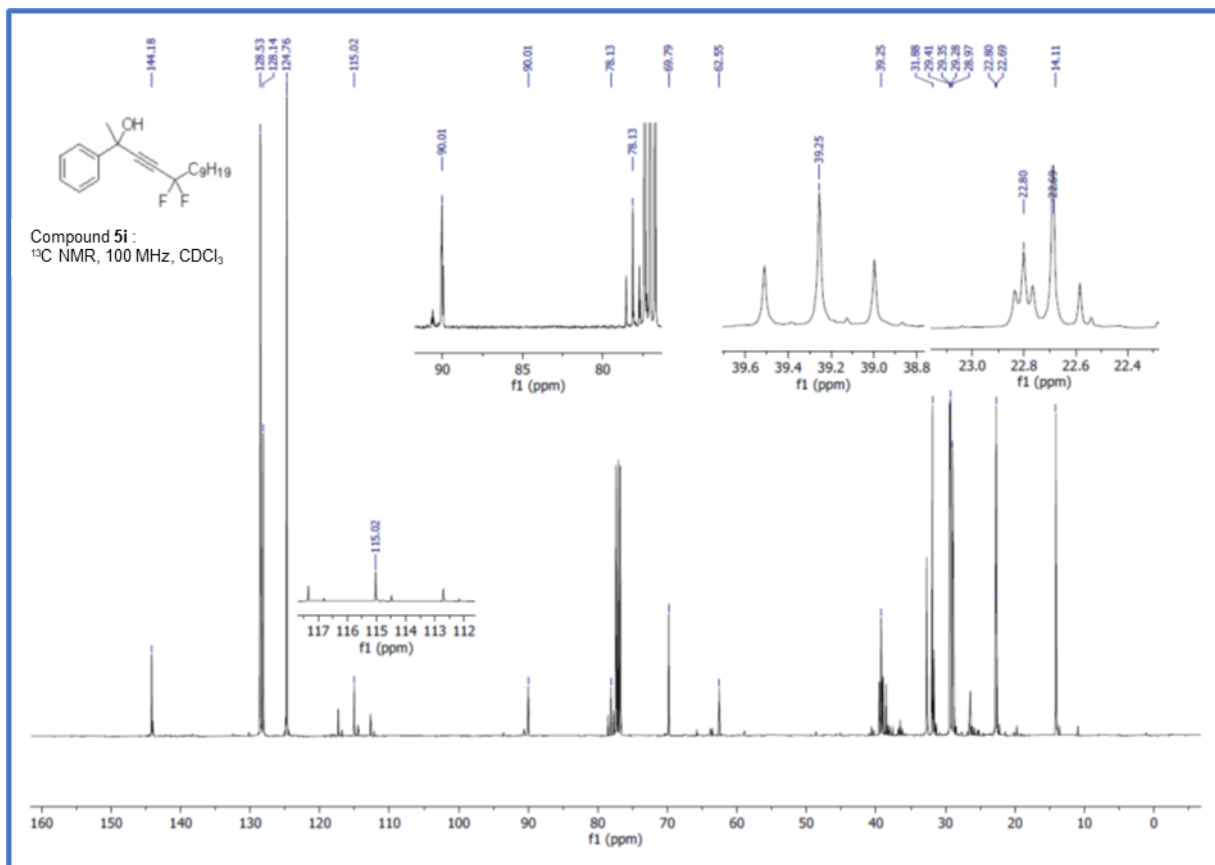
NMR spectra of 3g



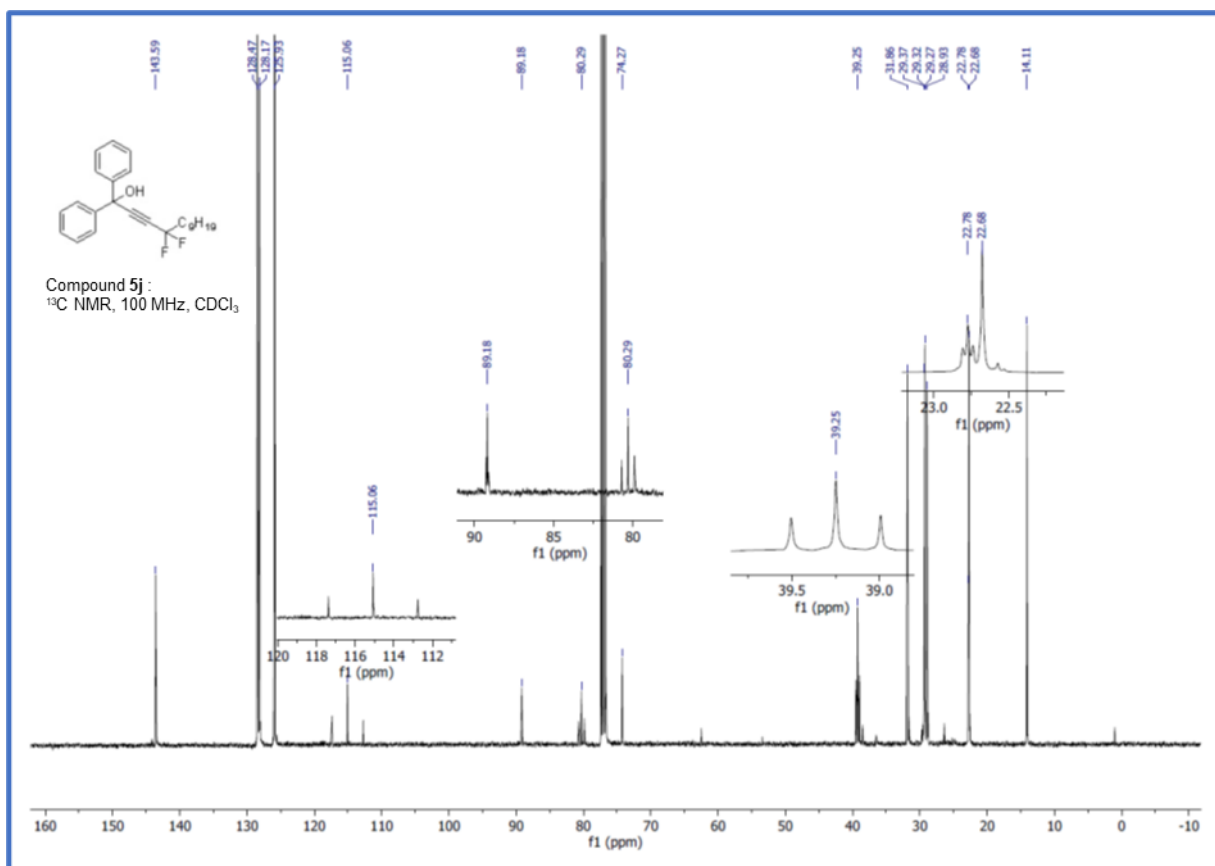
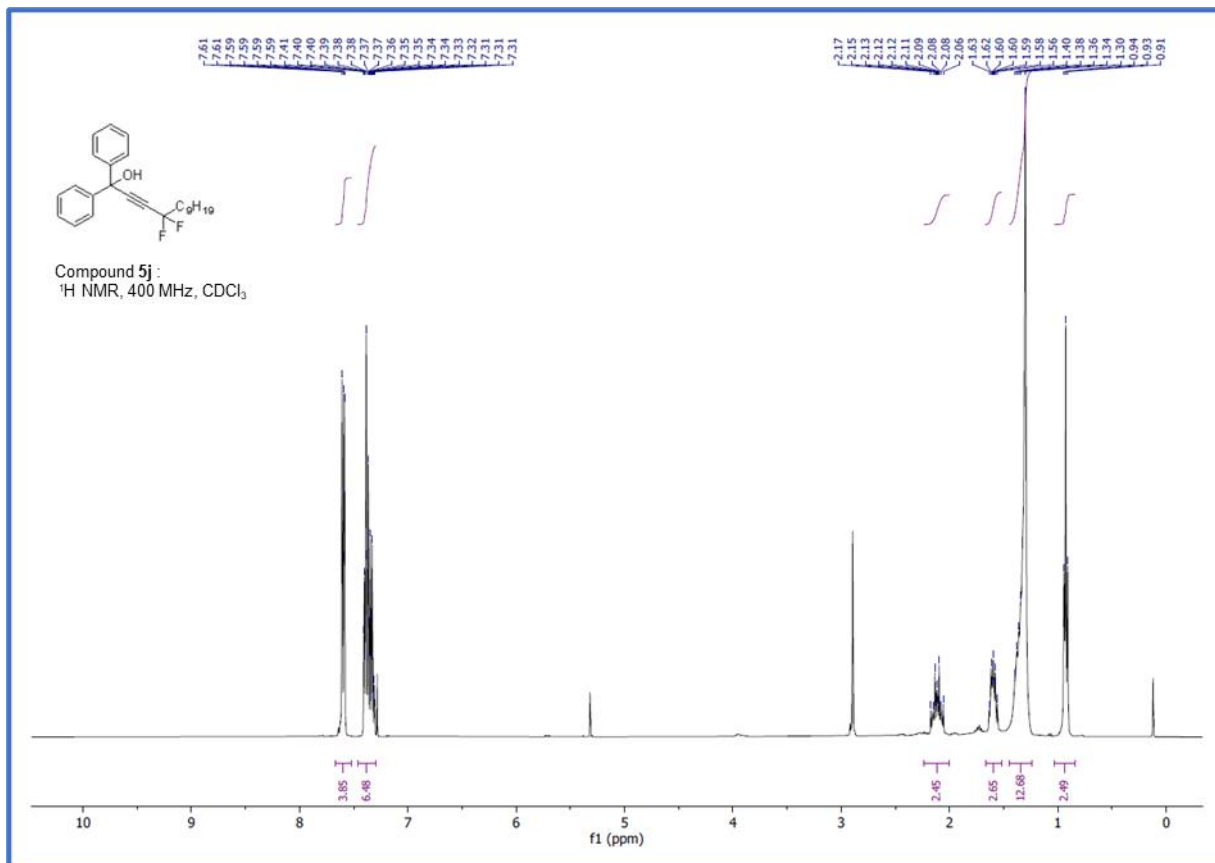


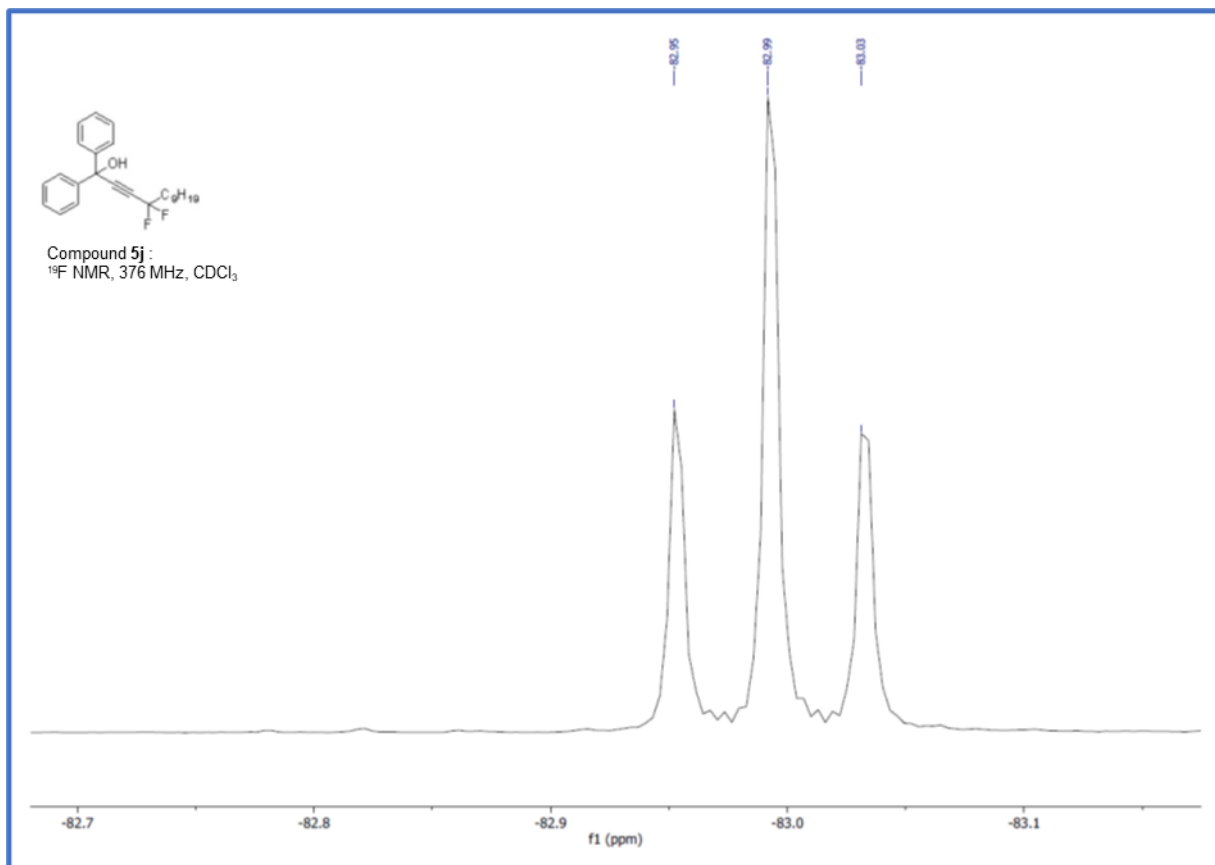
NMR spectra of 5i



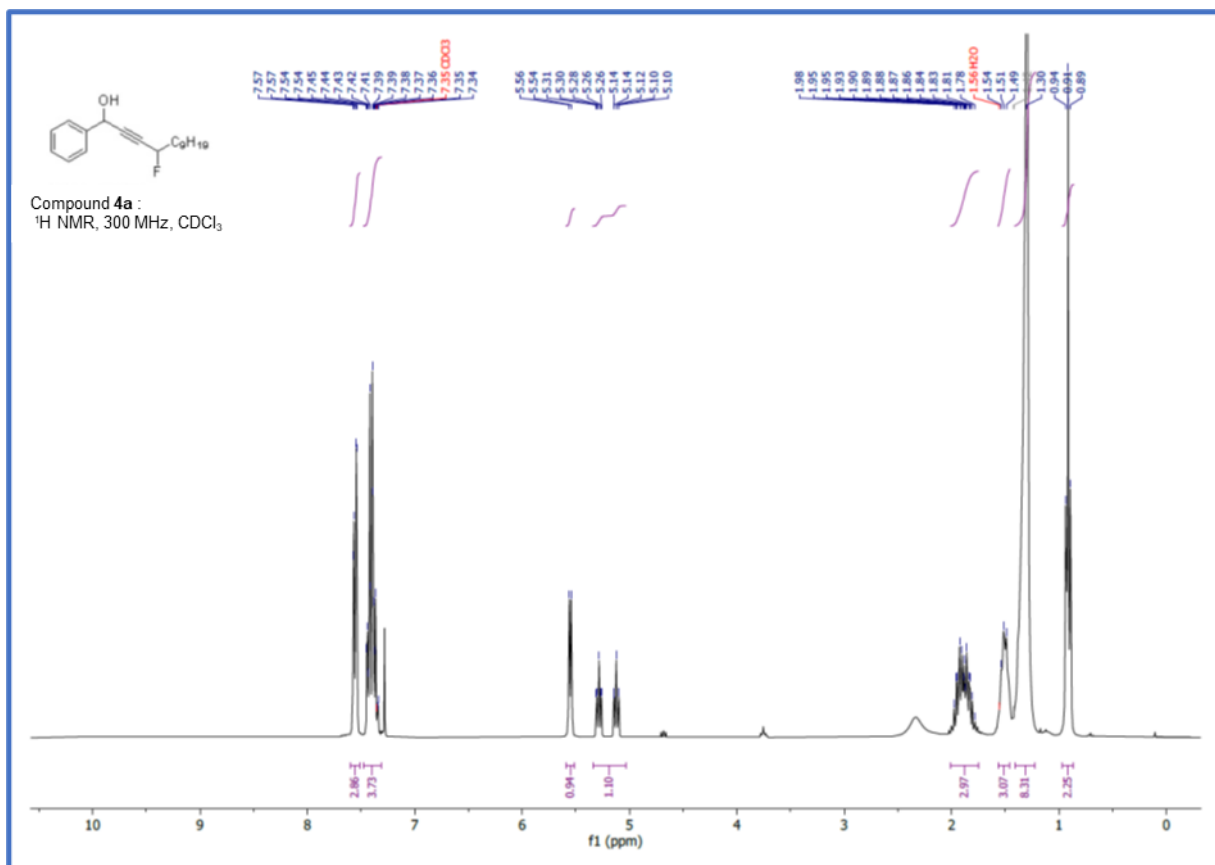


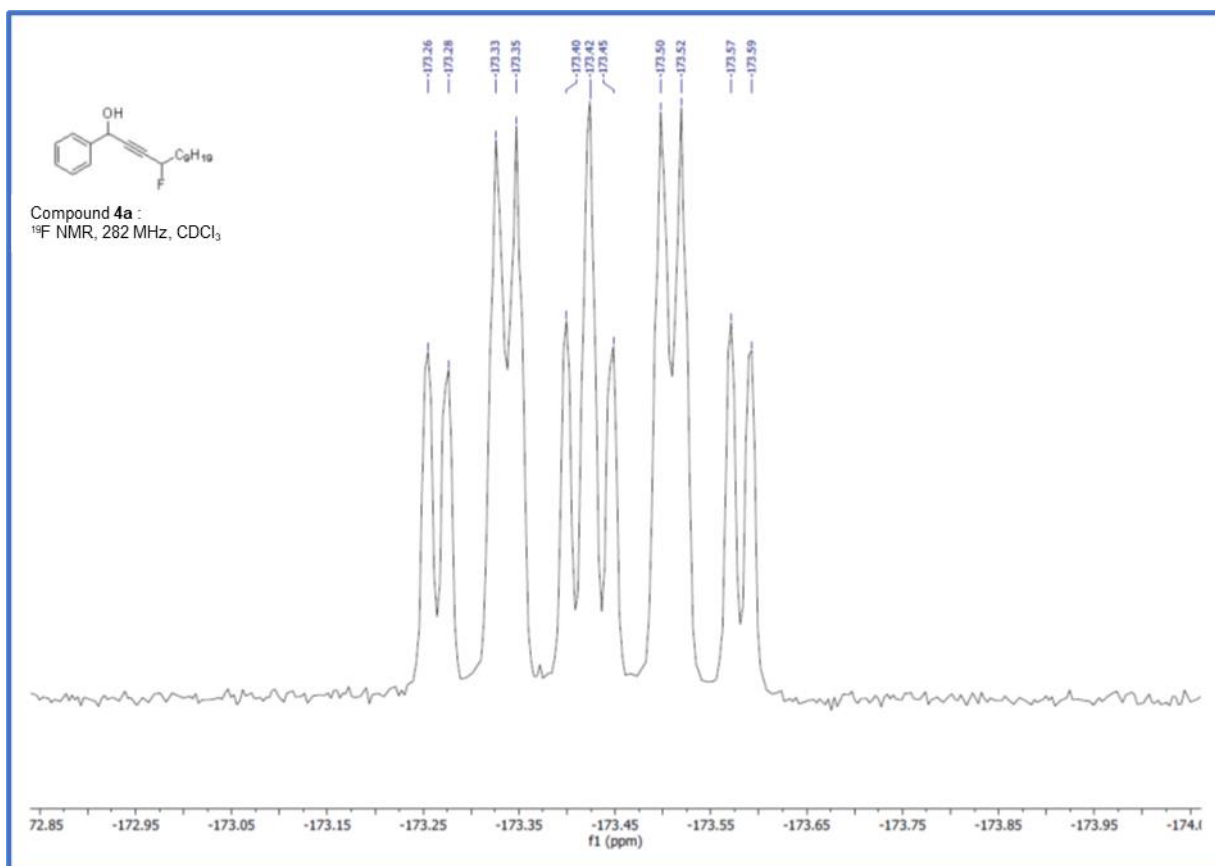
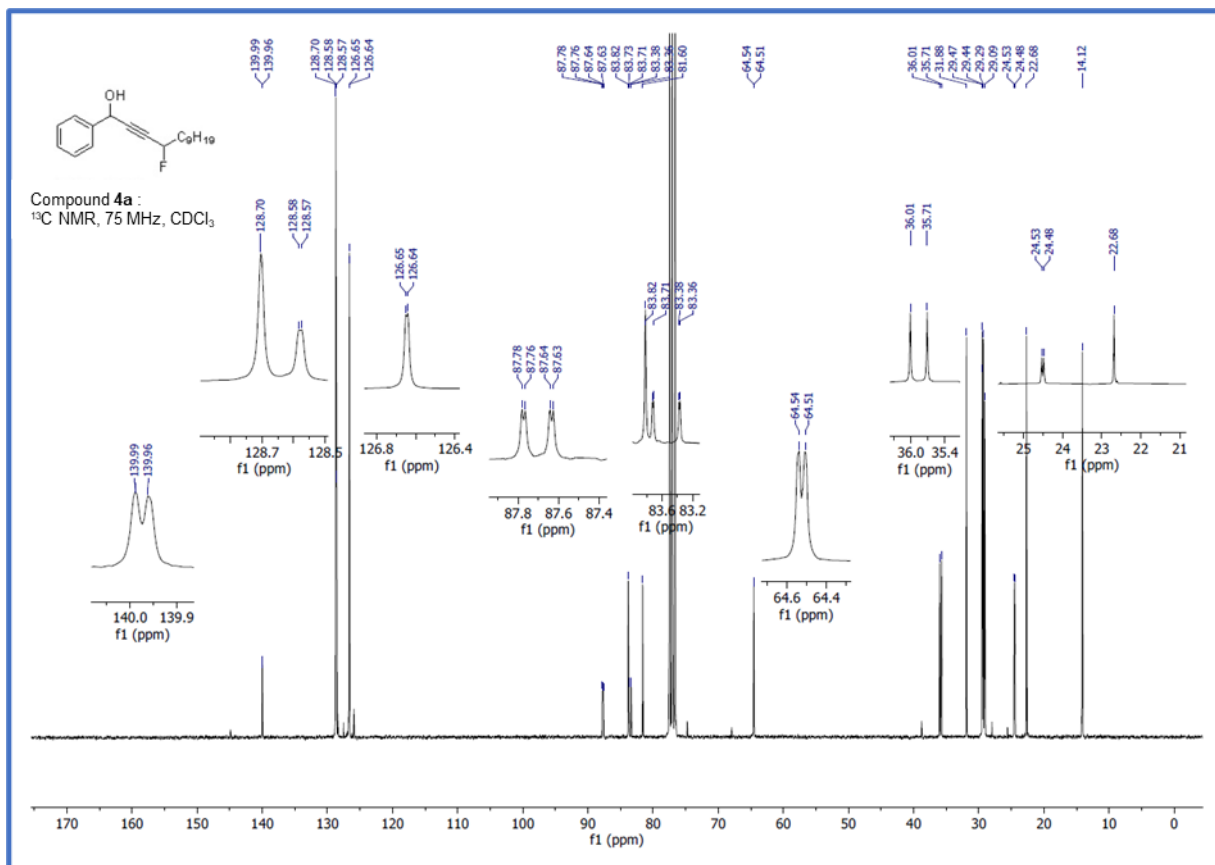
NMR spectra of 5j

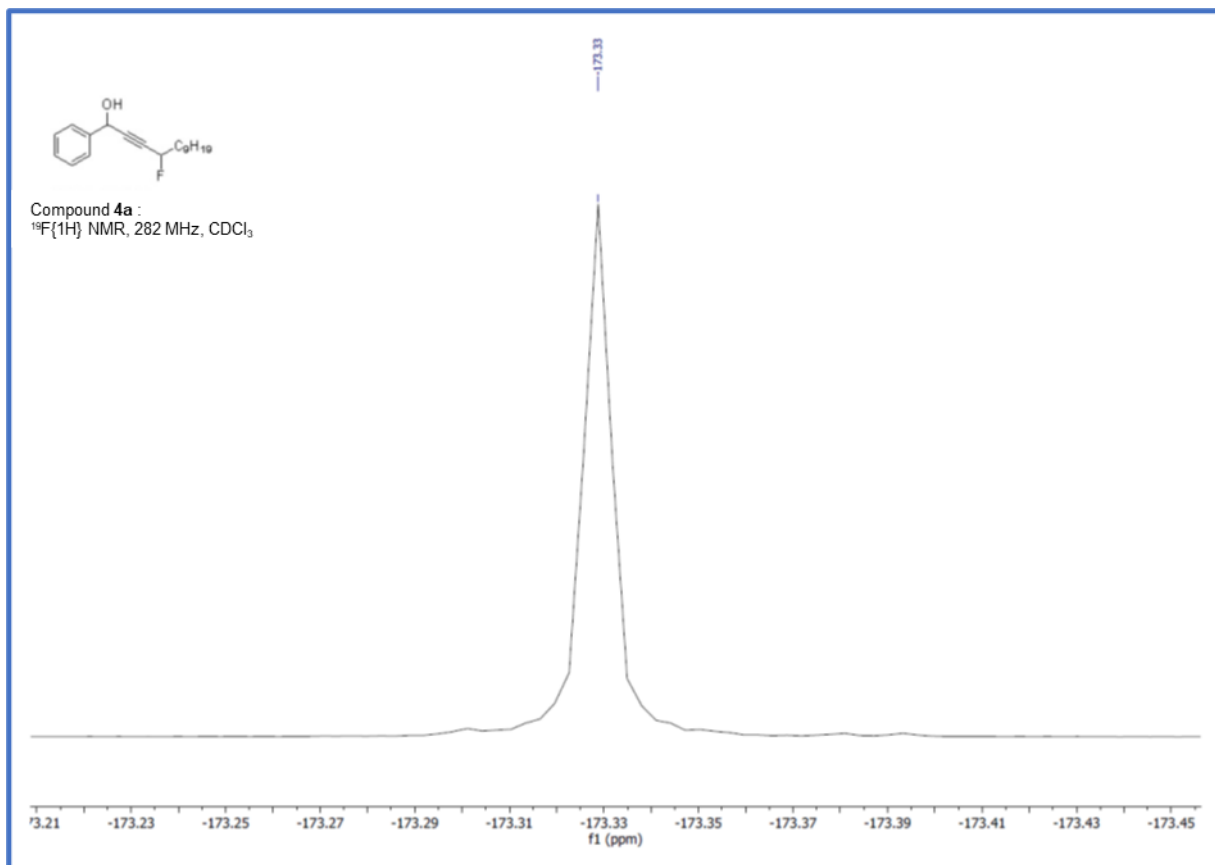




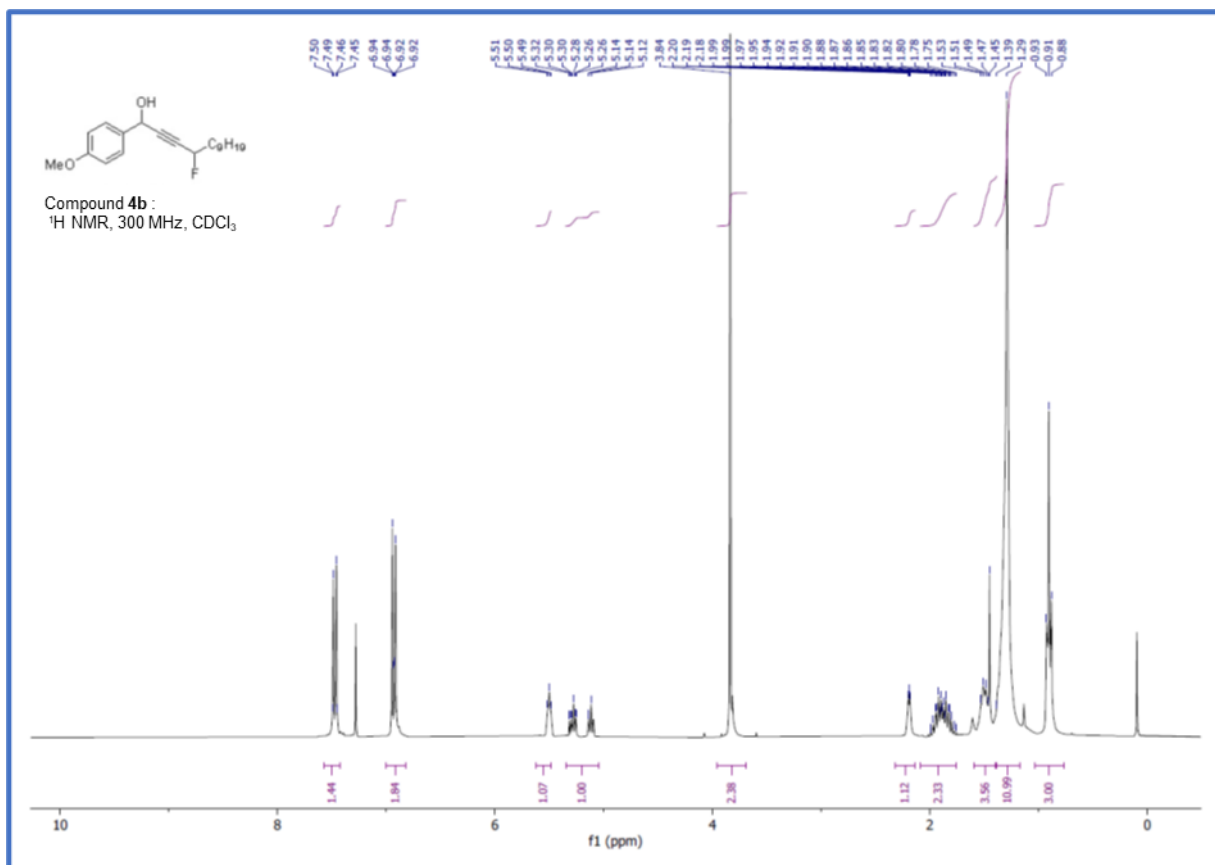
NMR spectra of 4a

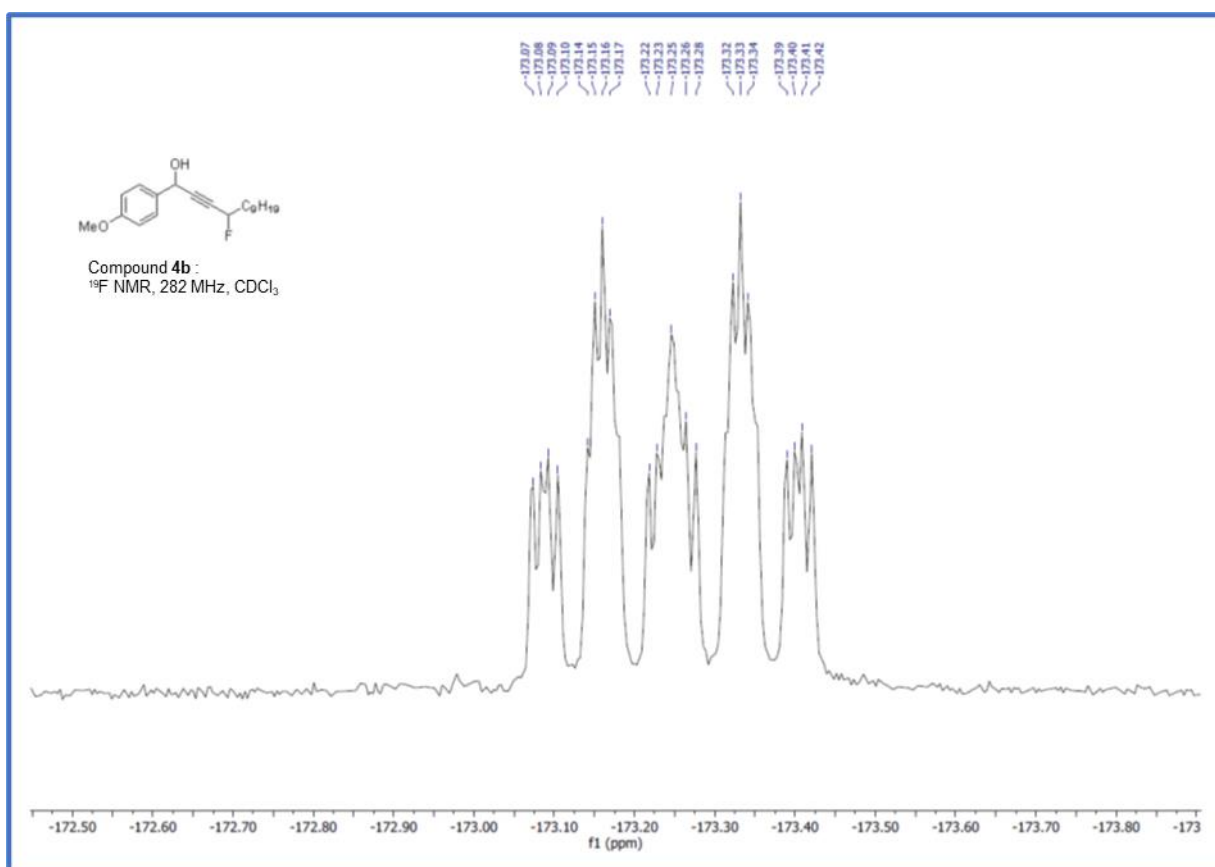
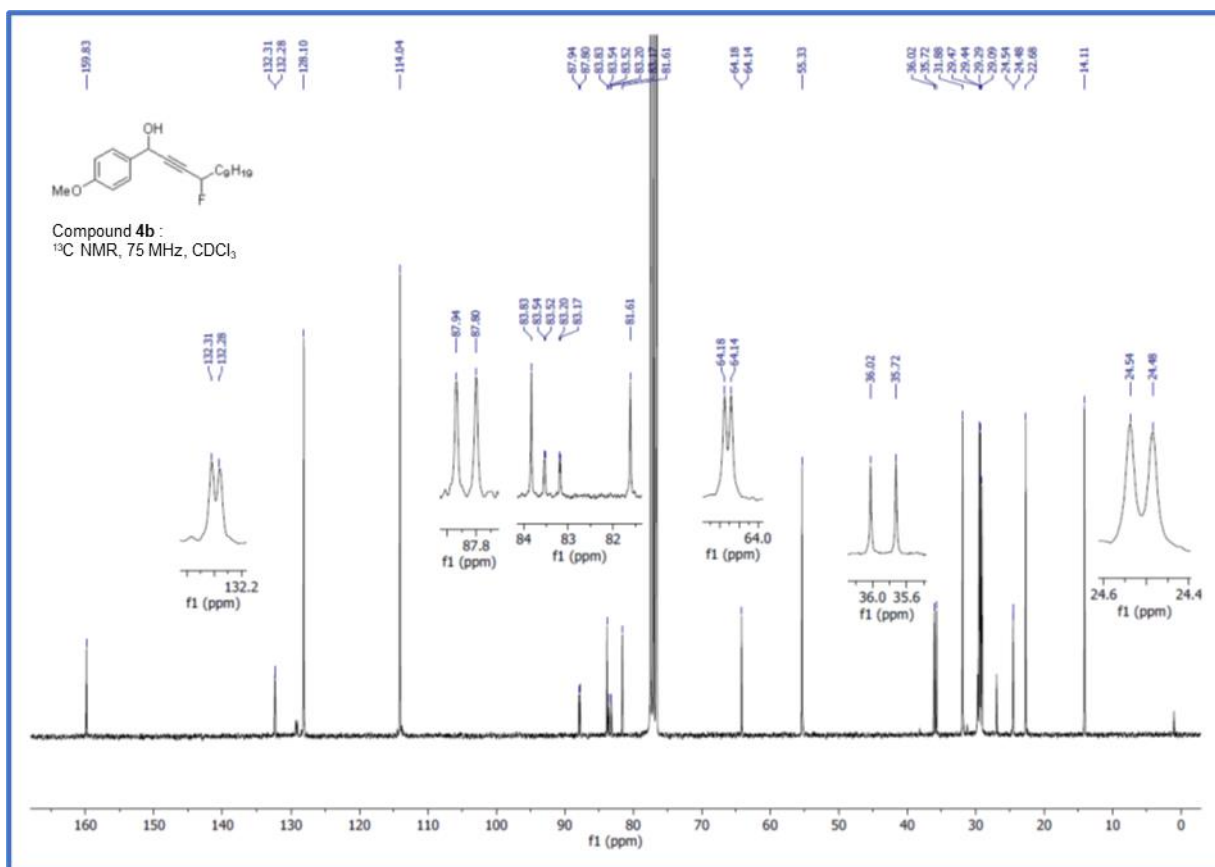


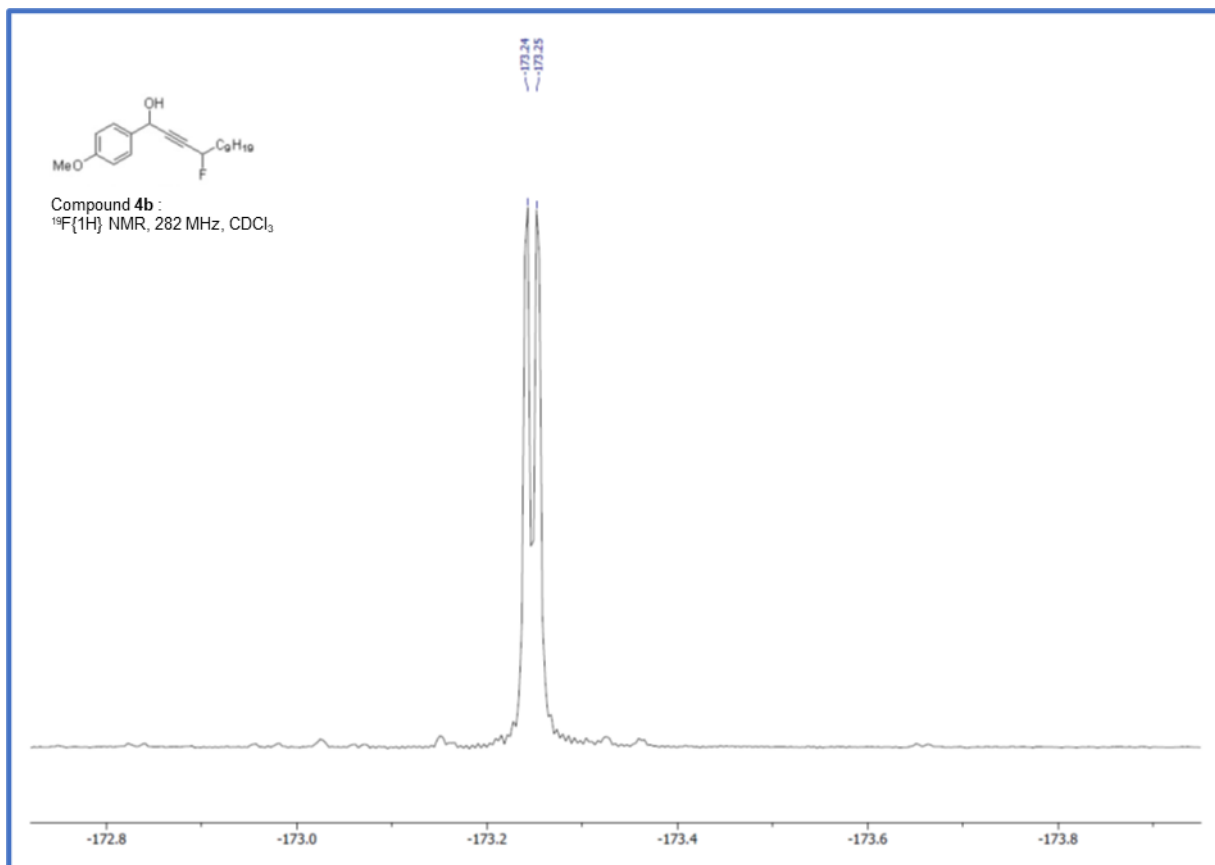




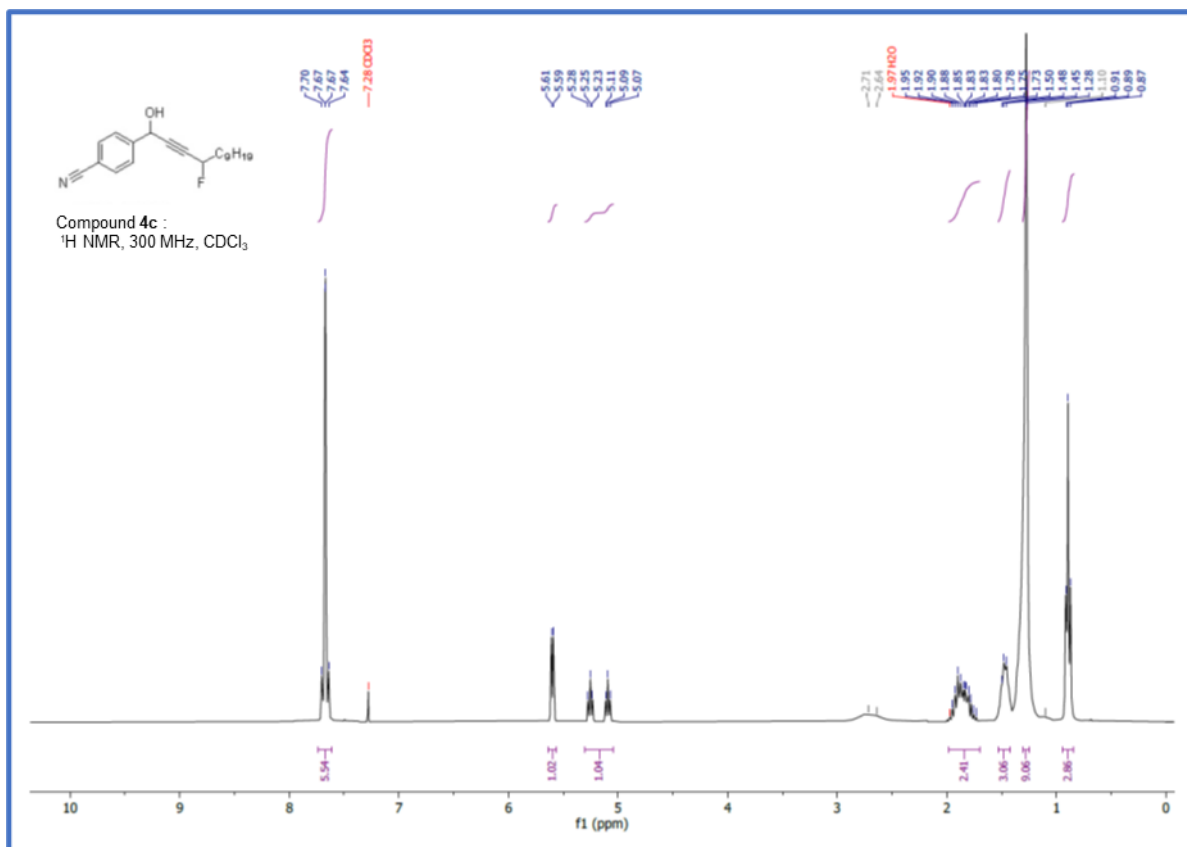
NMR spectra of 4b

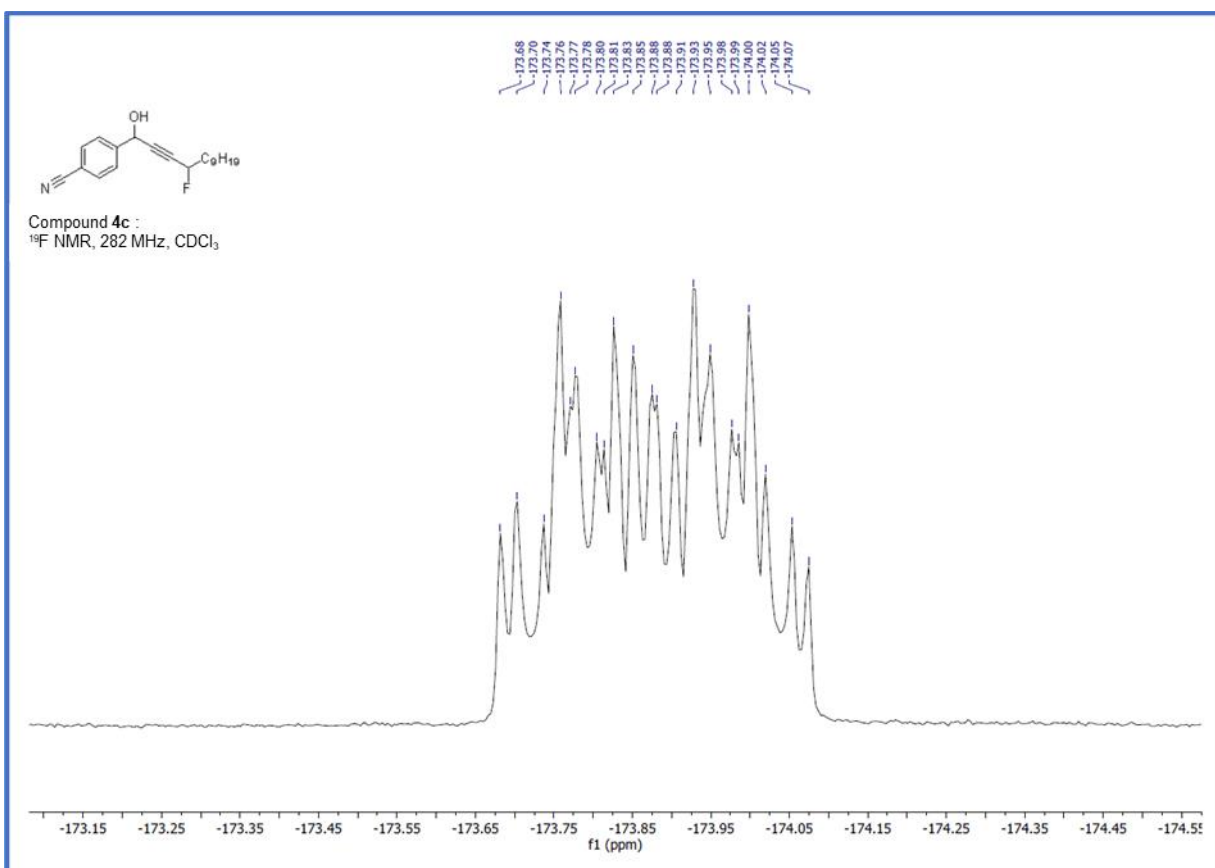
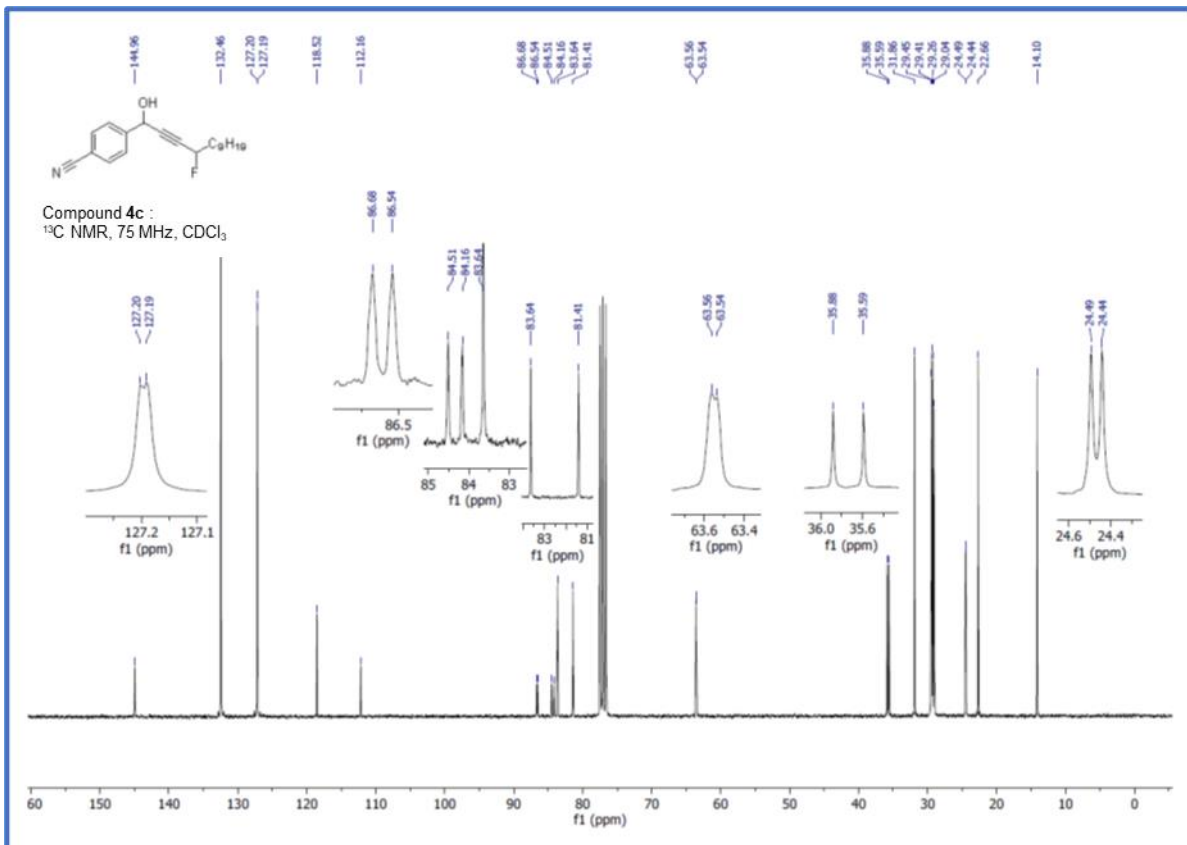


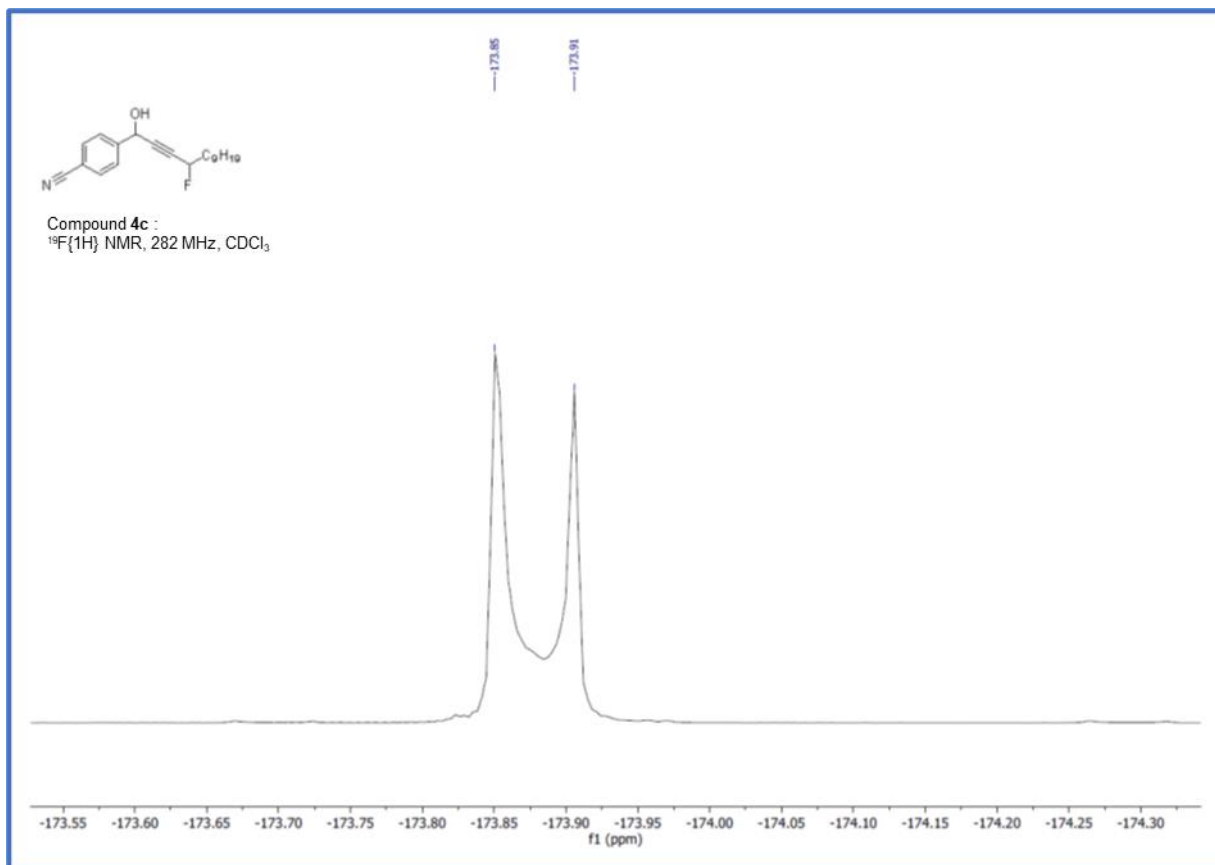




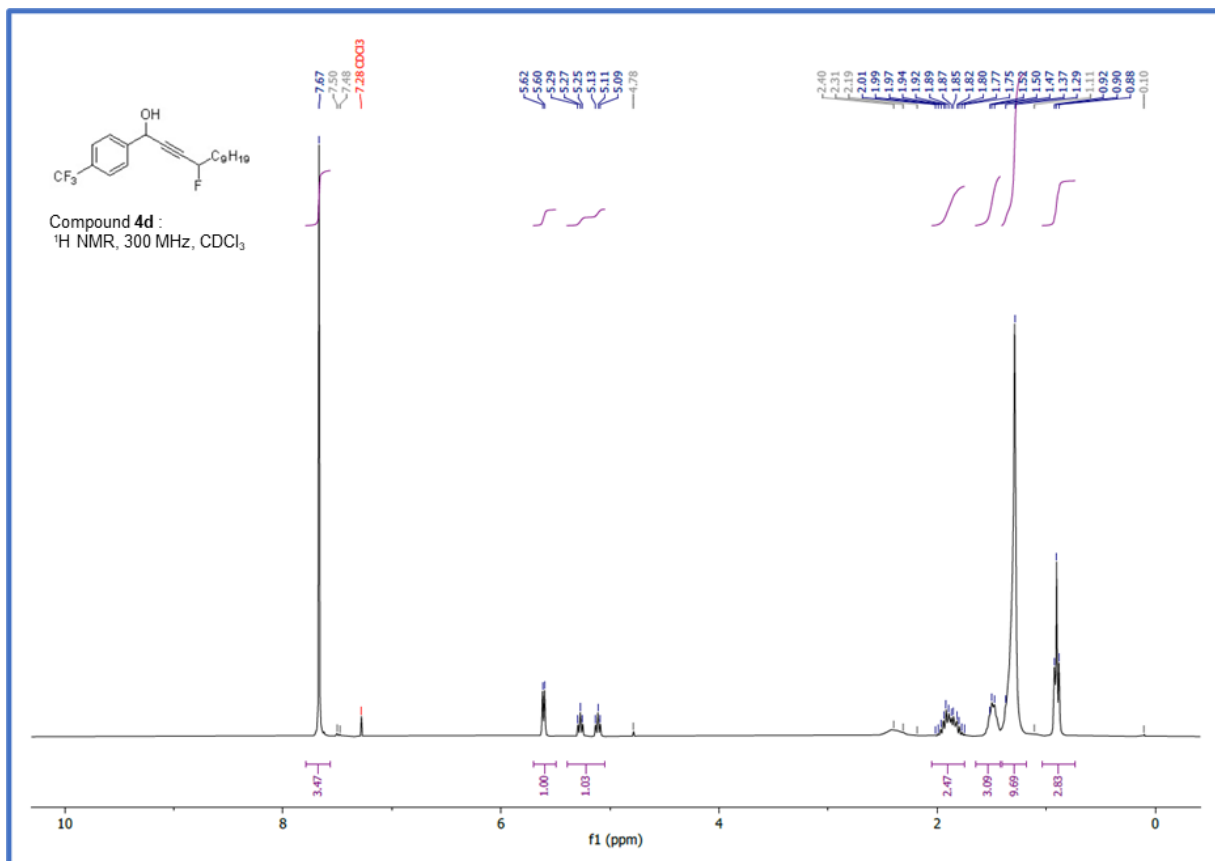
NMR spectra of 4c

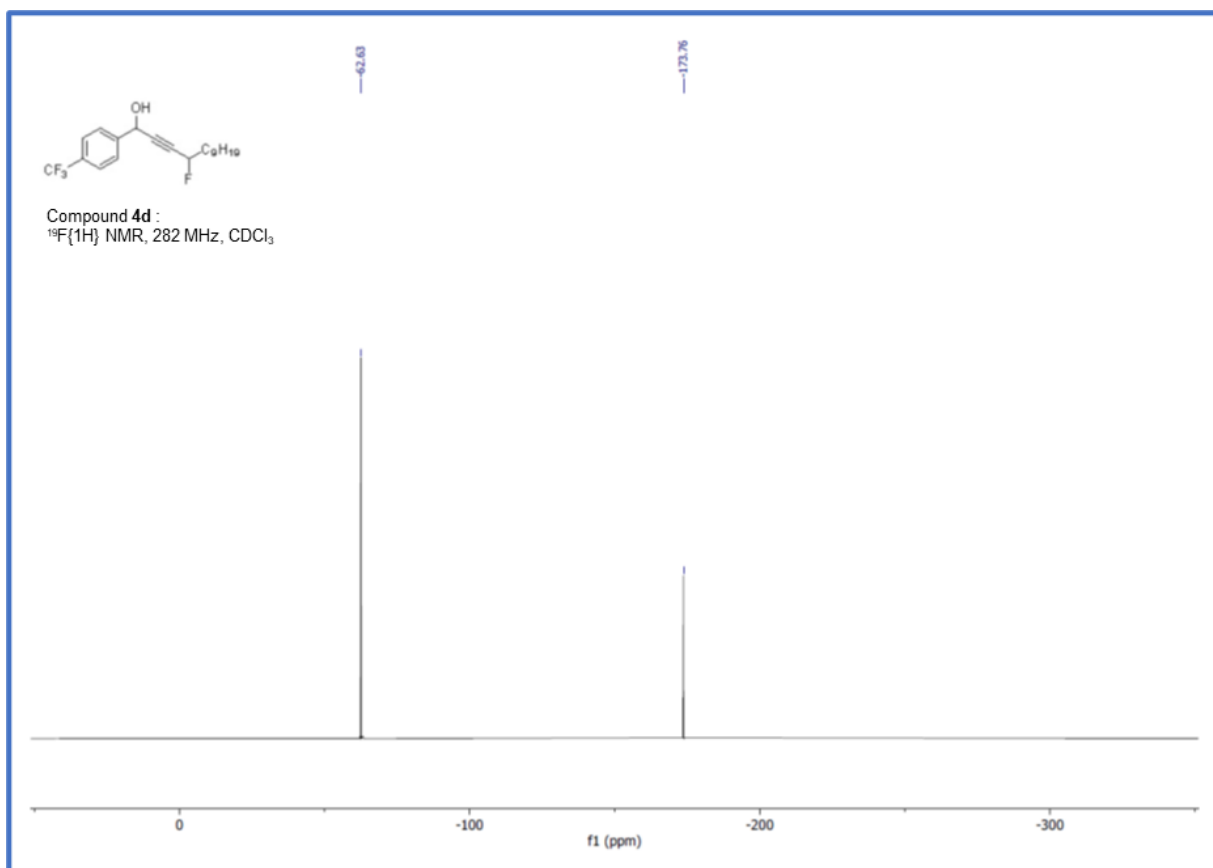
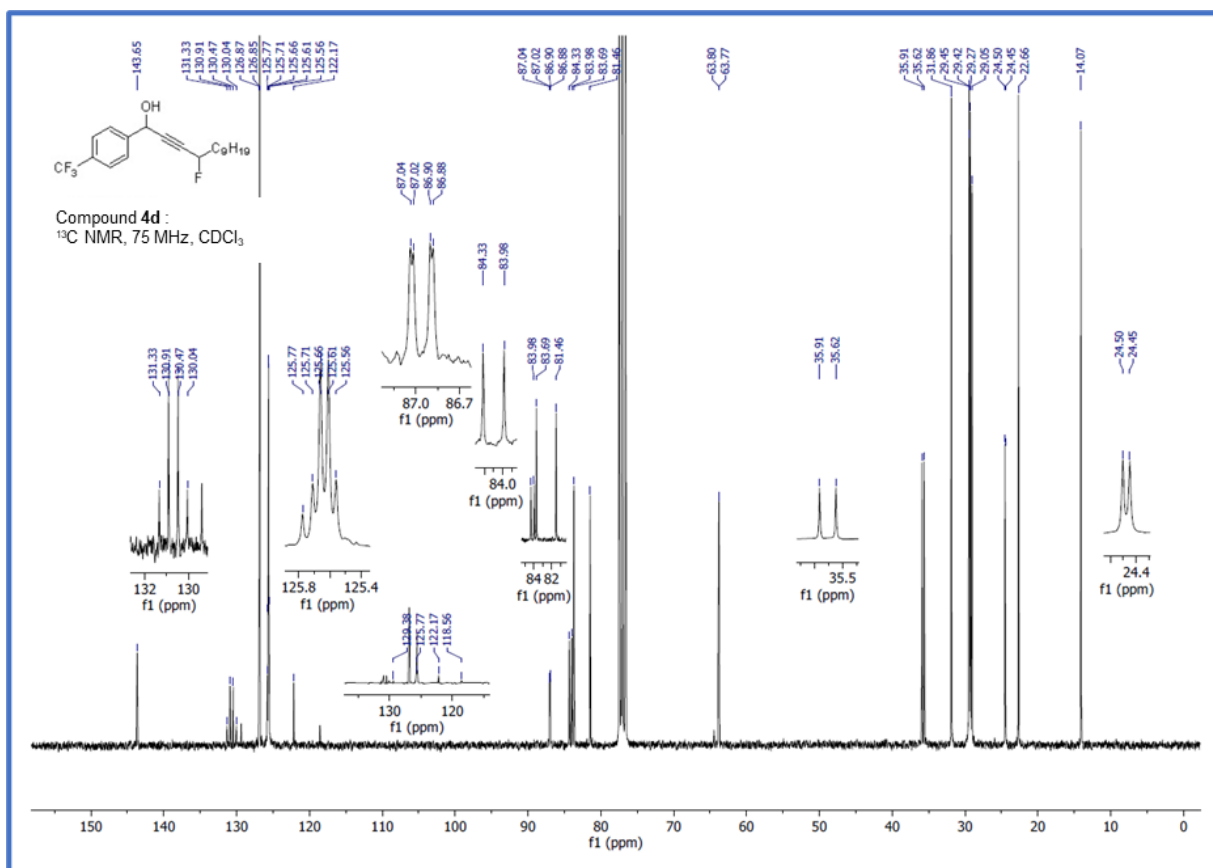


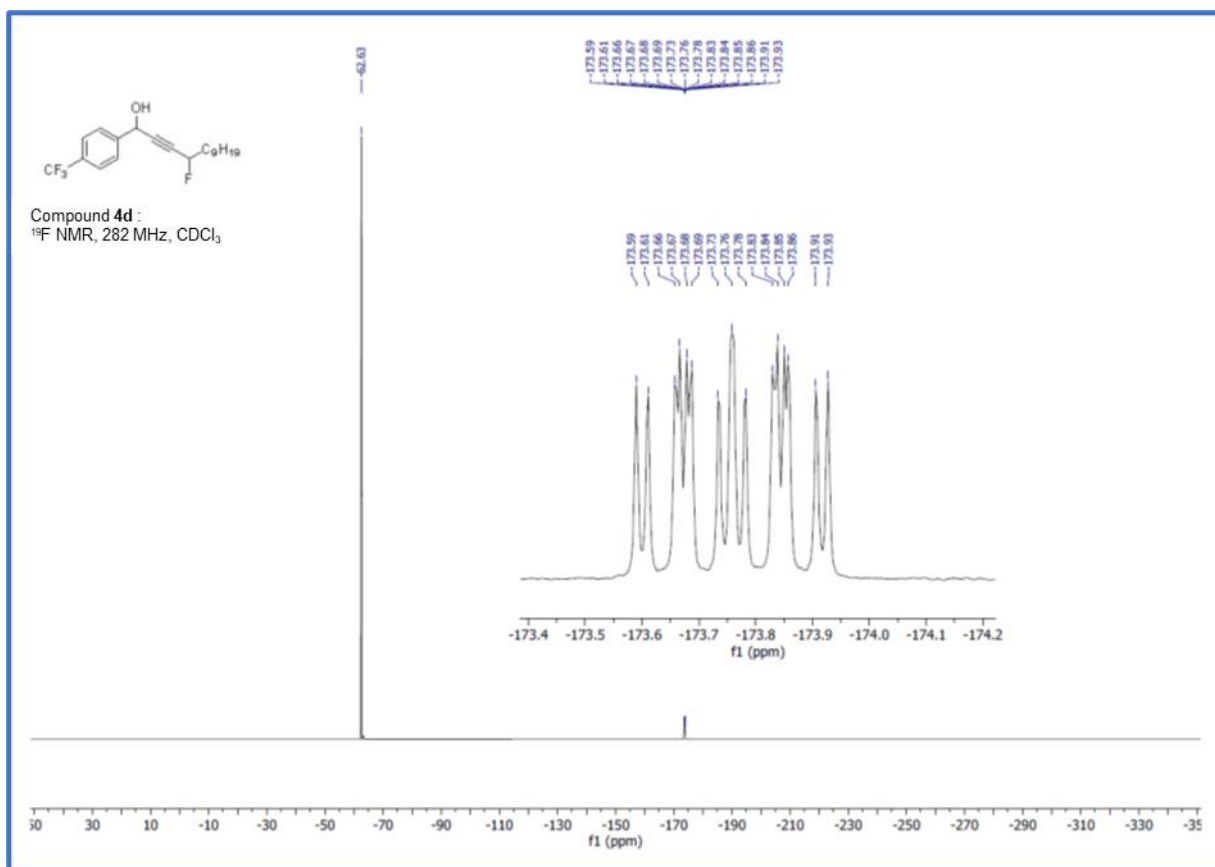




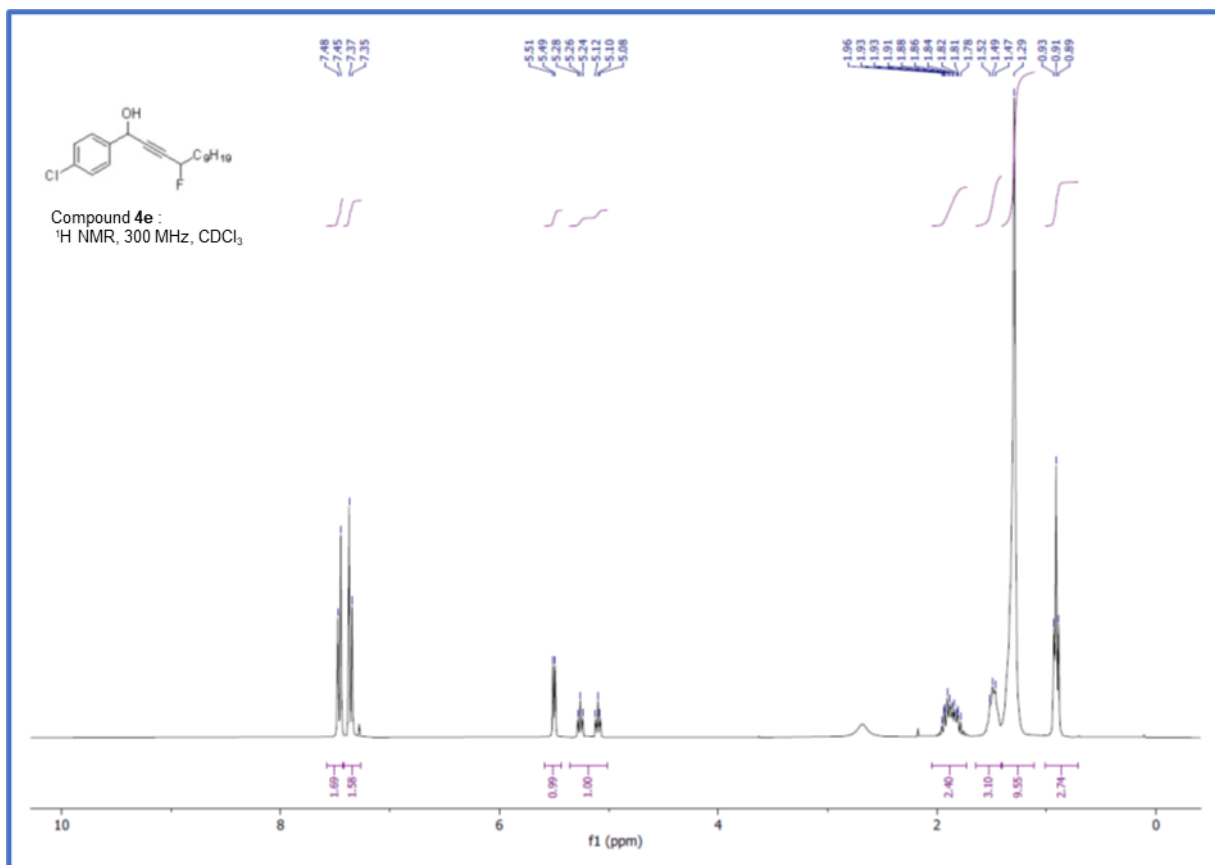
NMR spectra of 4d

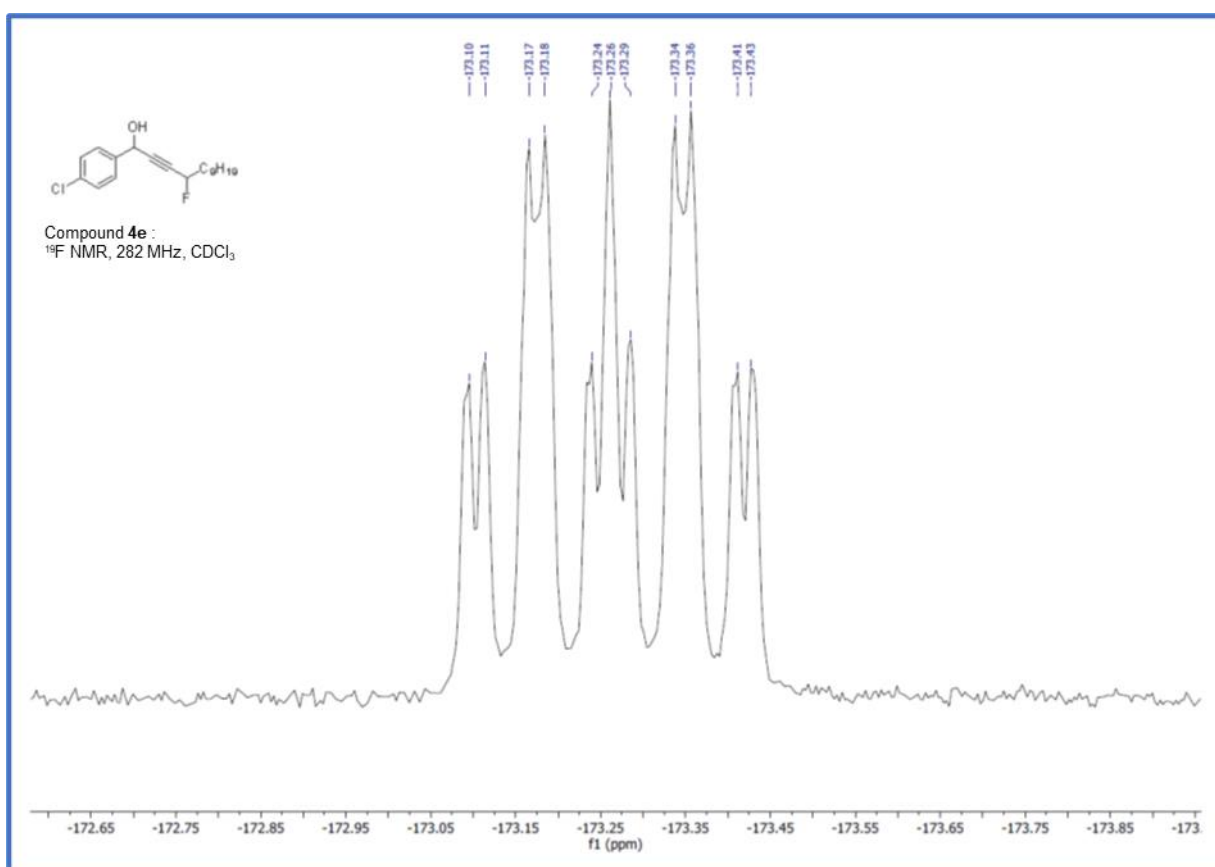
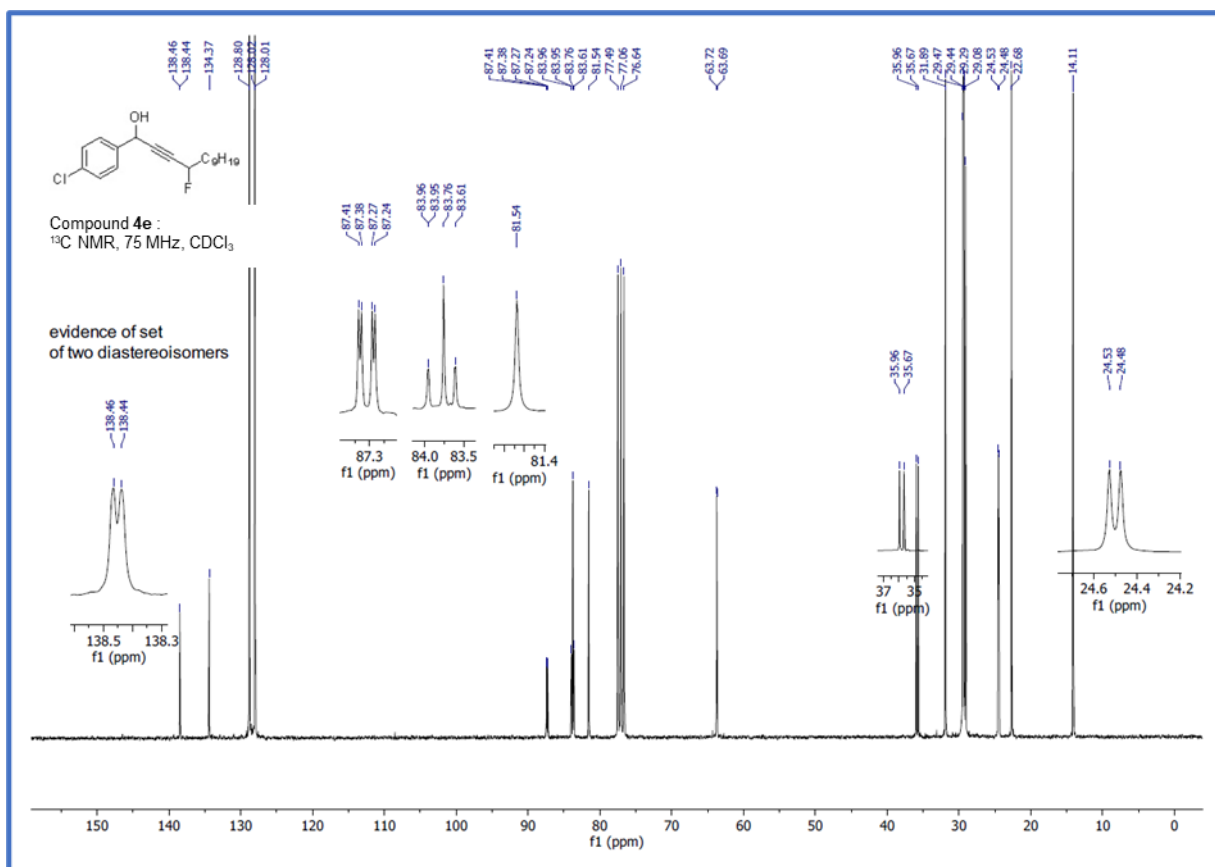


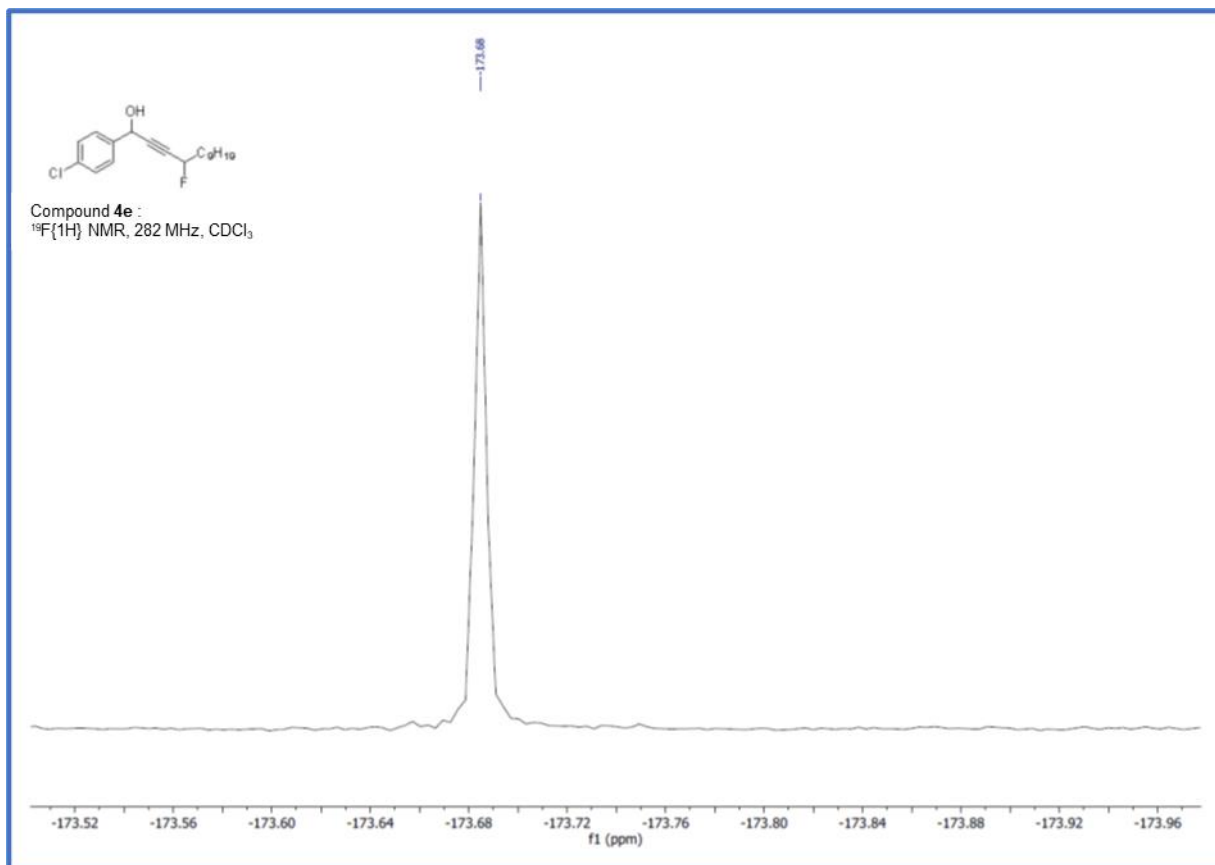




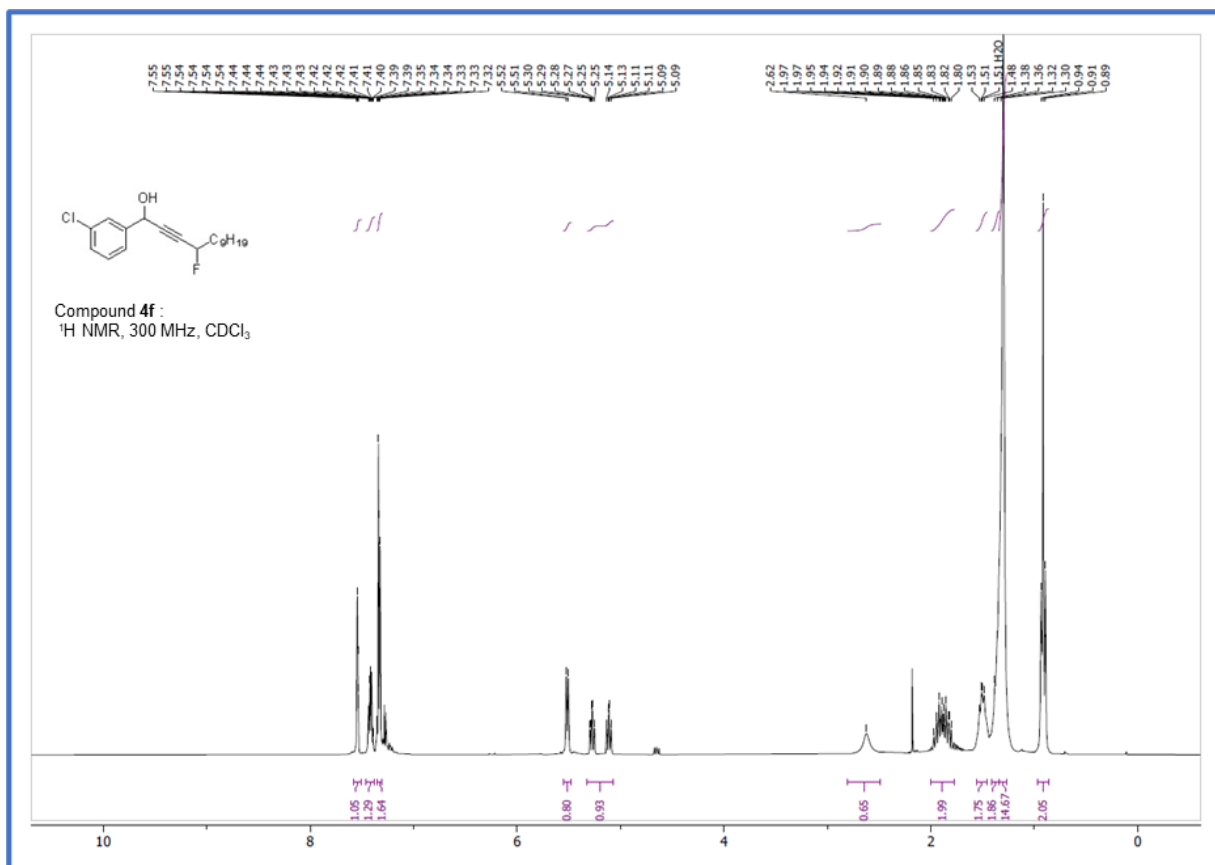
NMR spectra of **4e**

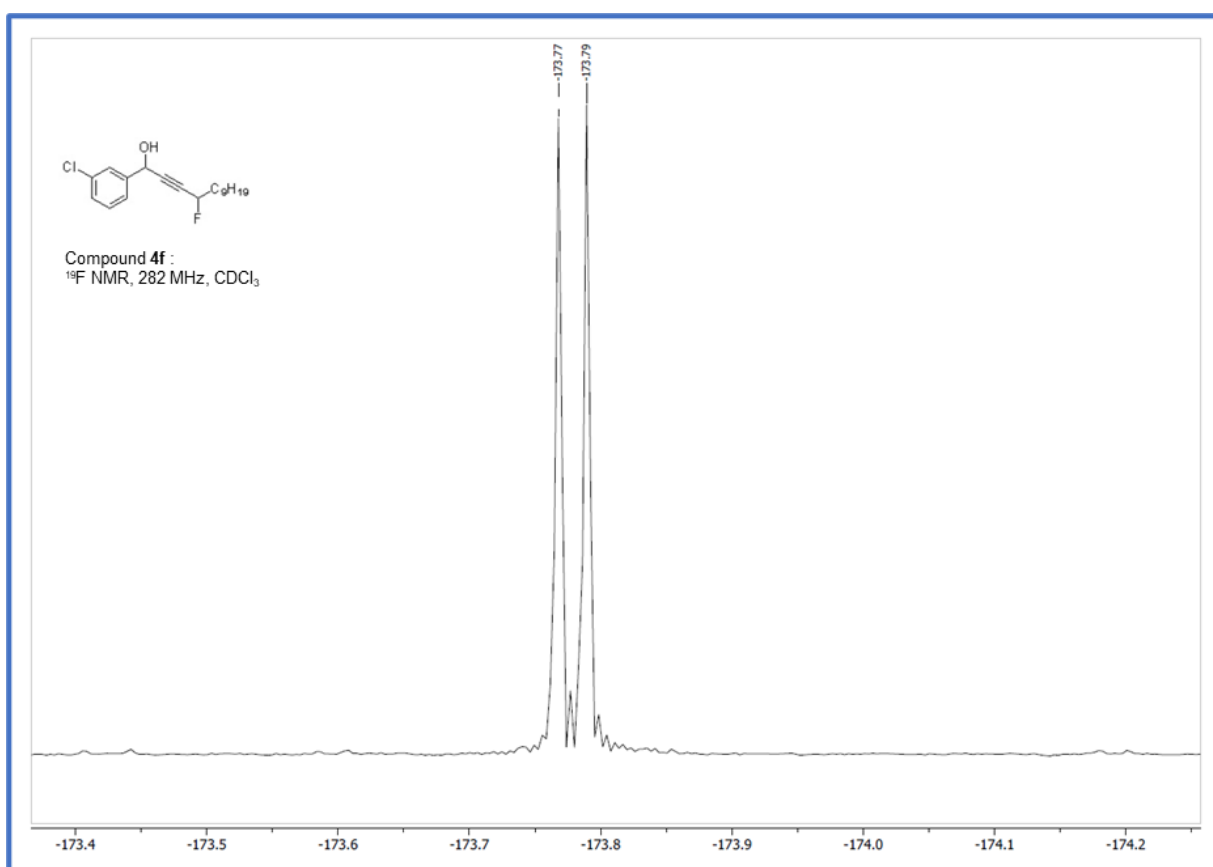
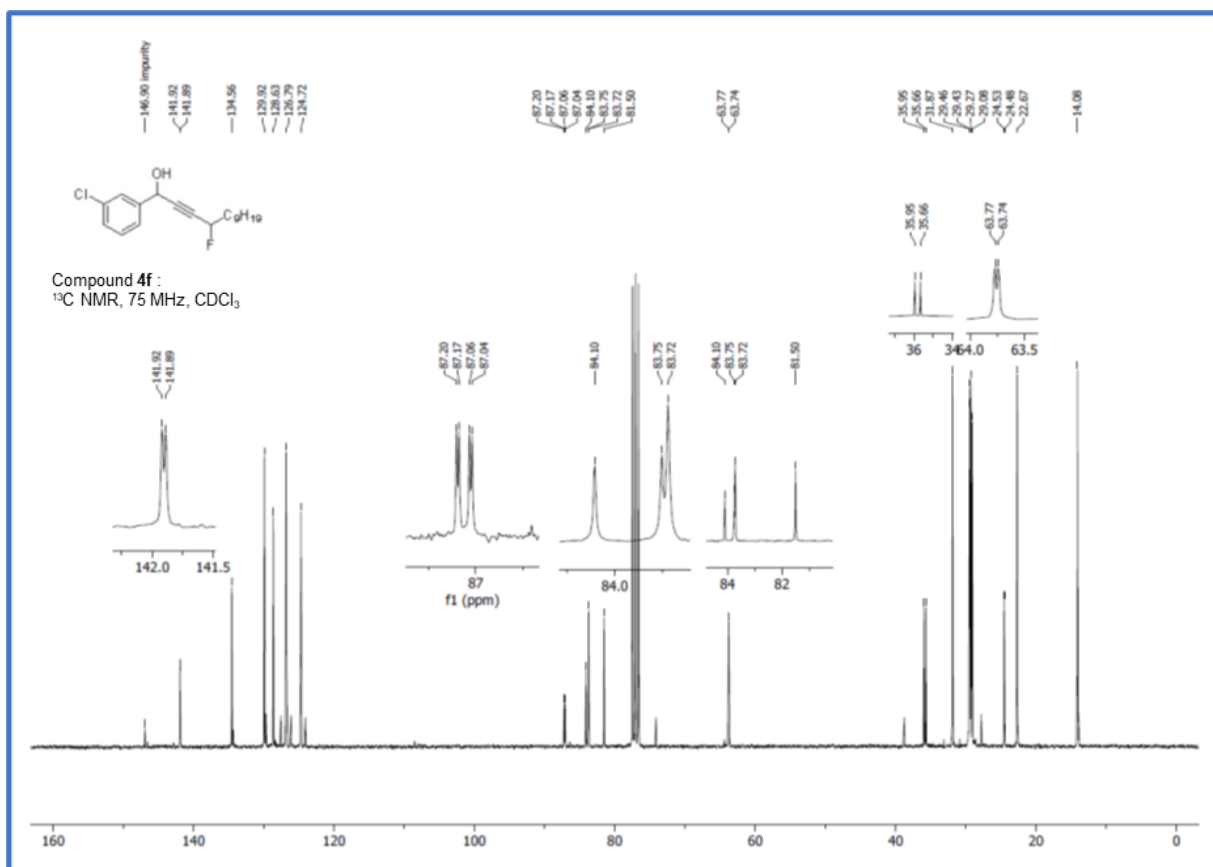


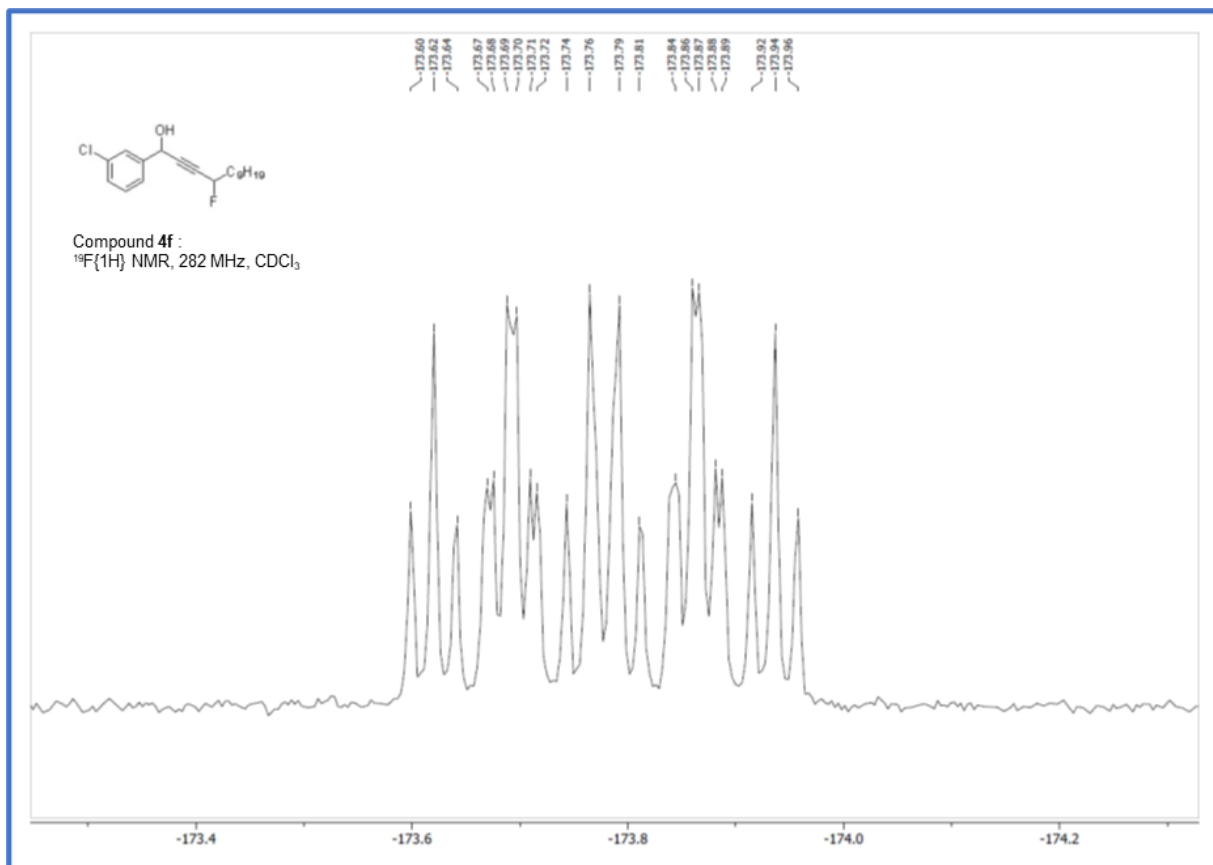




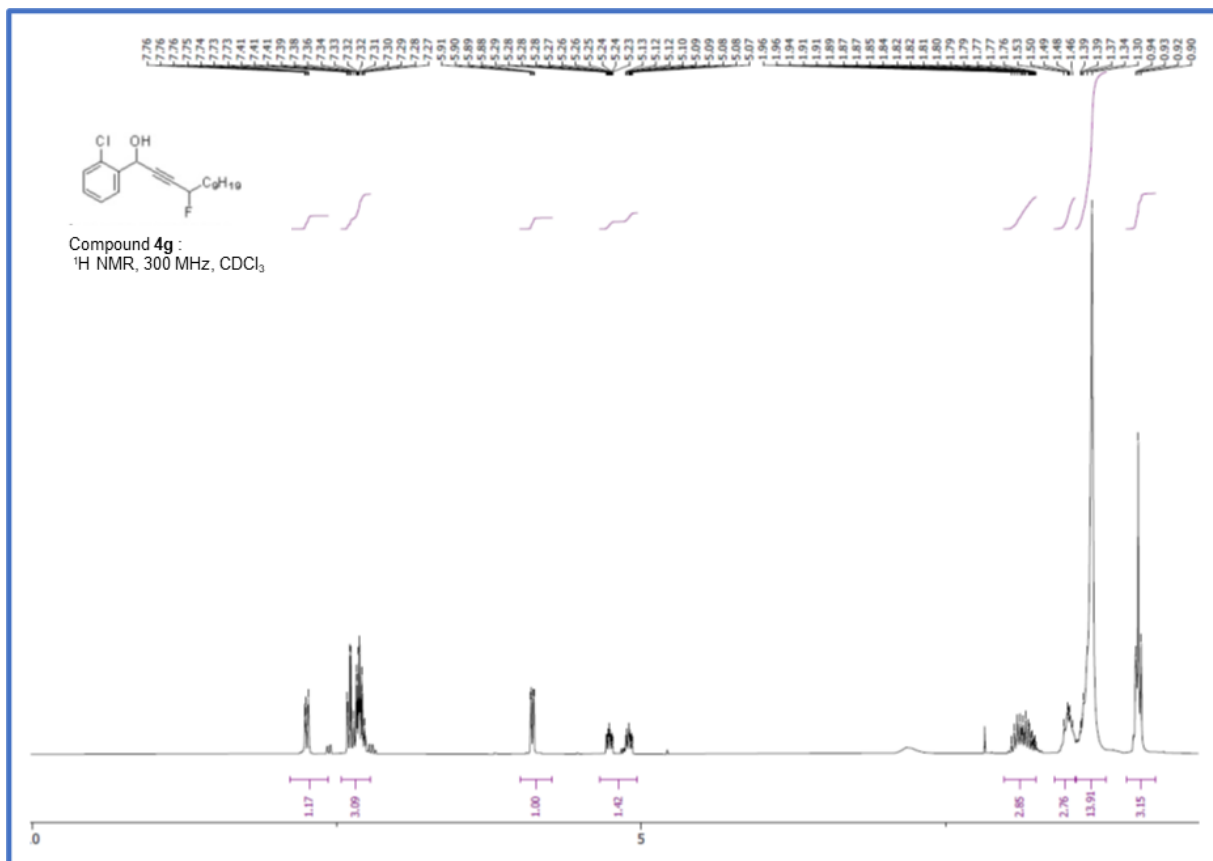
NMR spectra of 4f

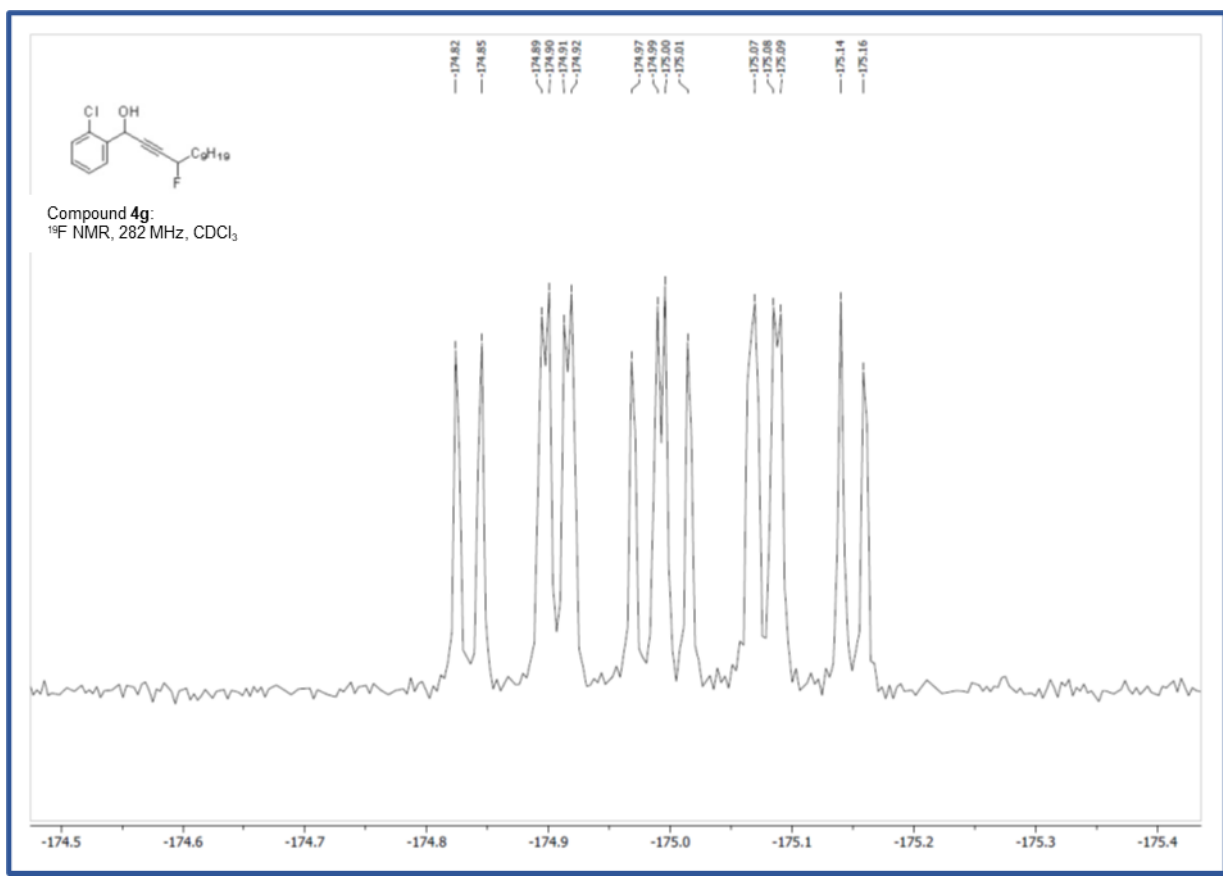
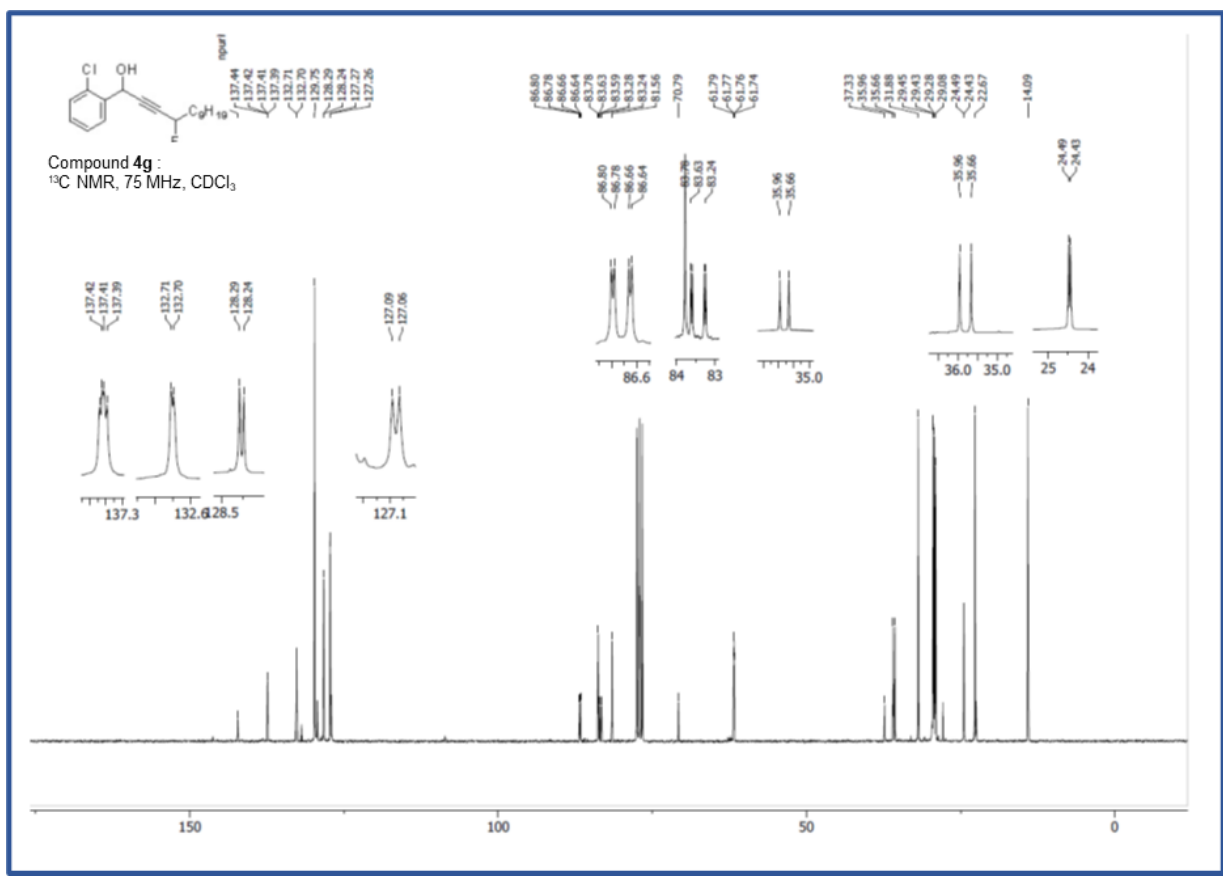




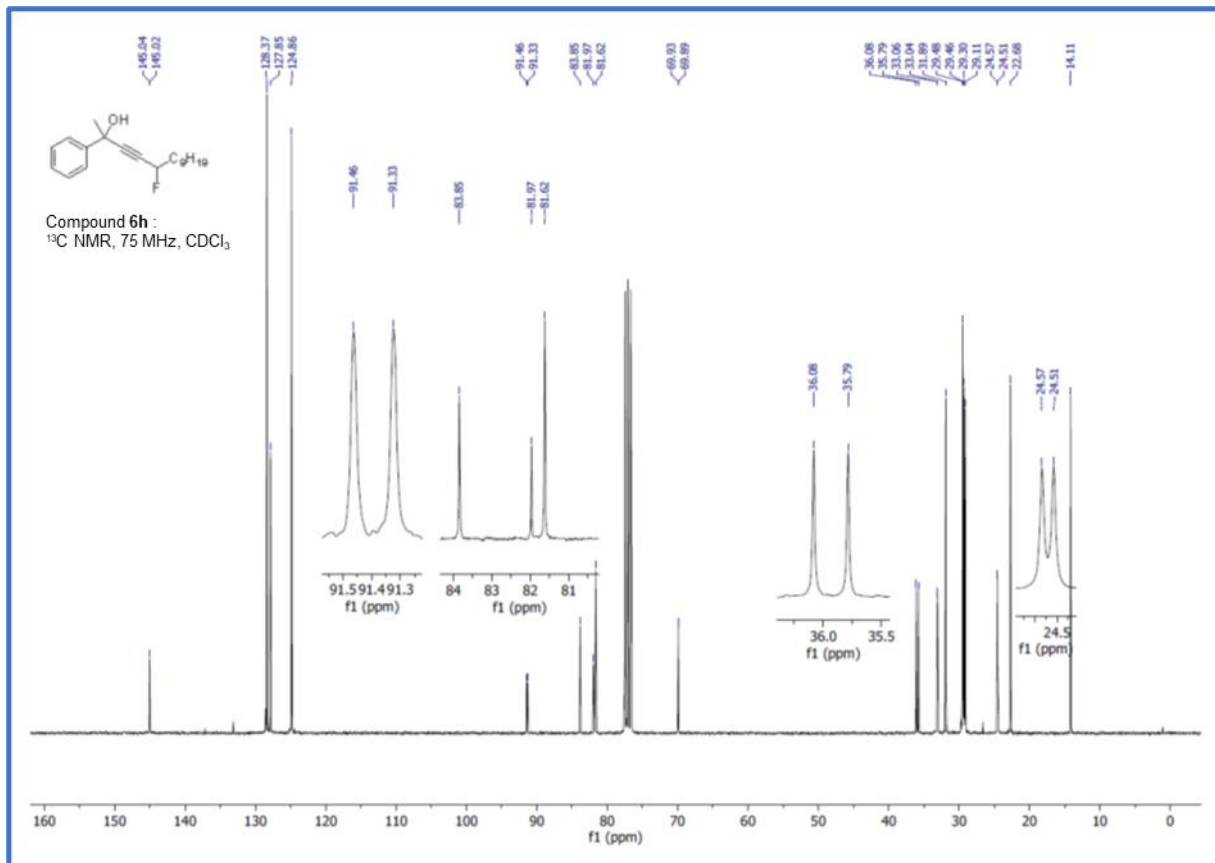
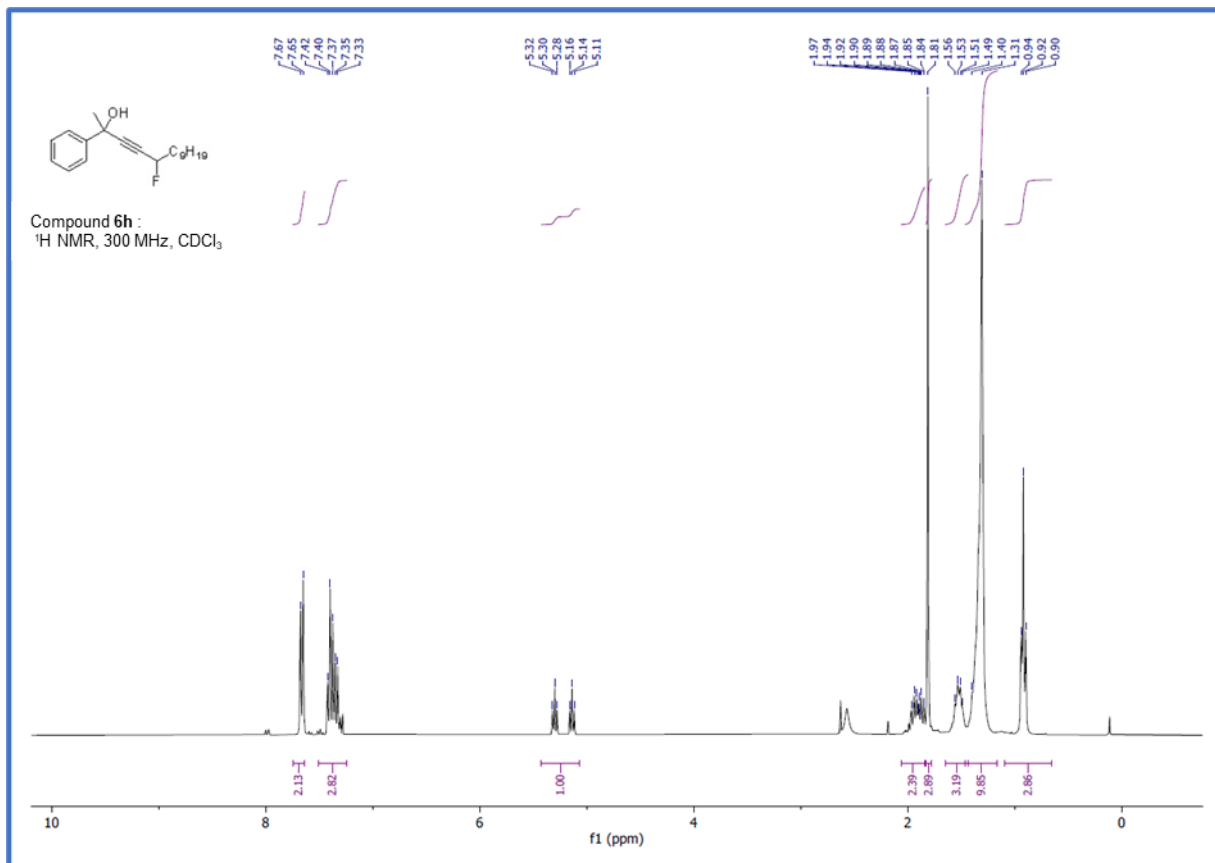


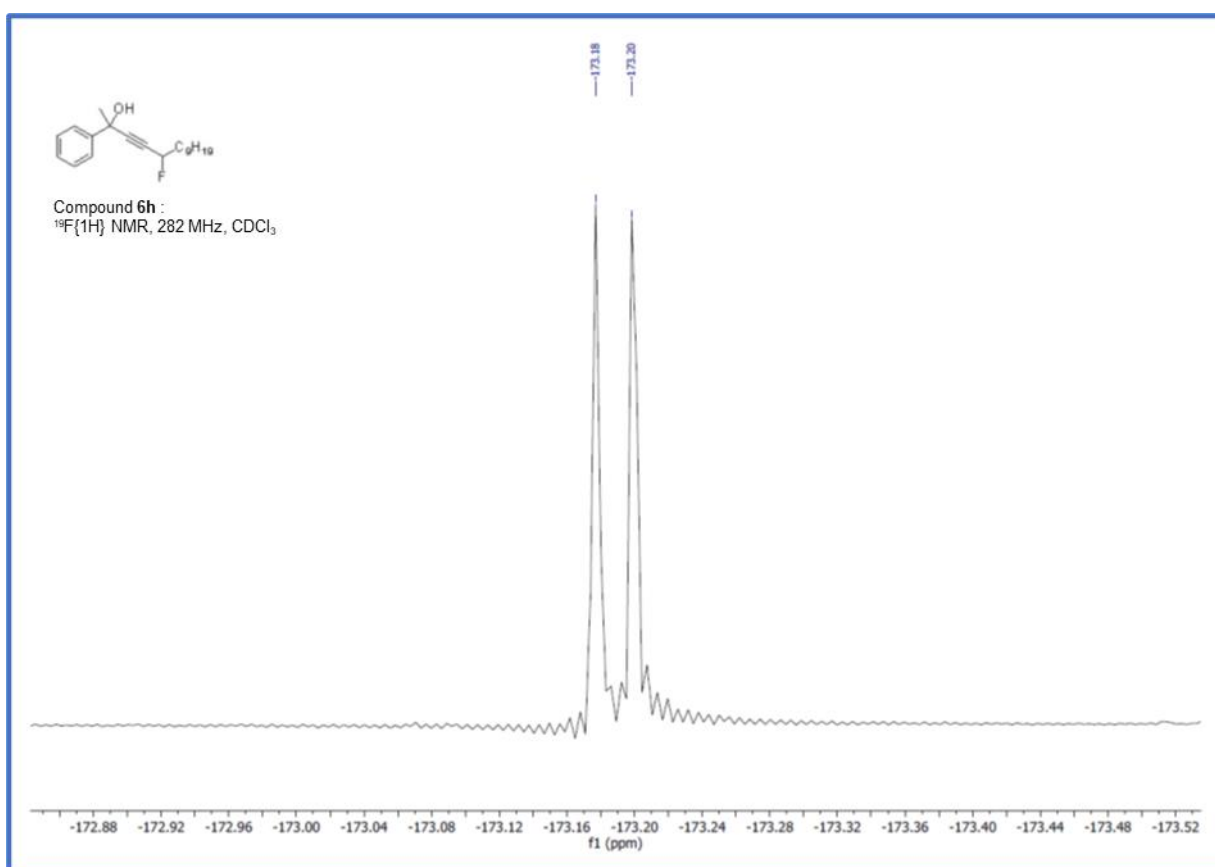
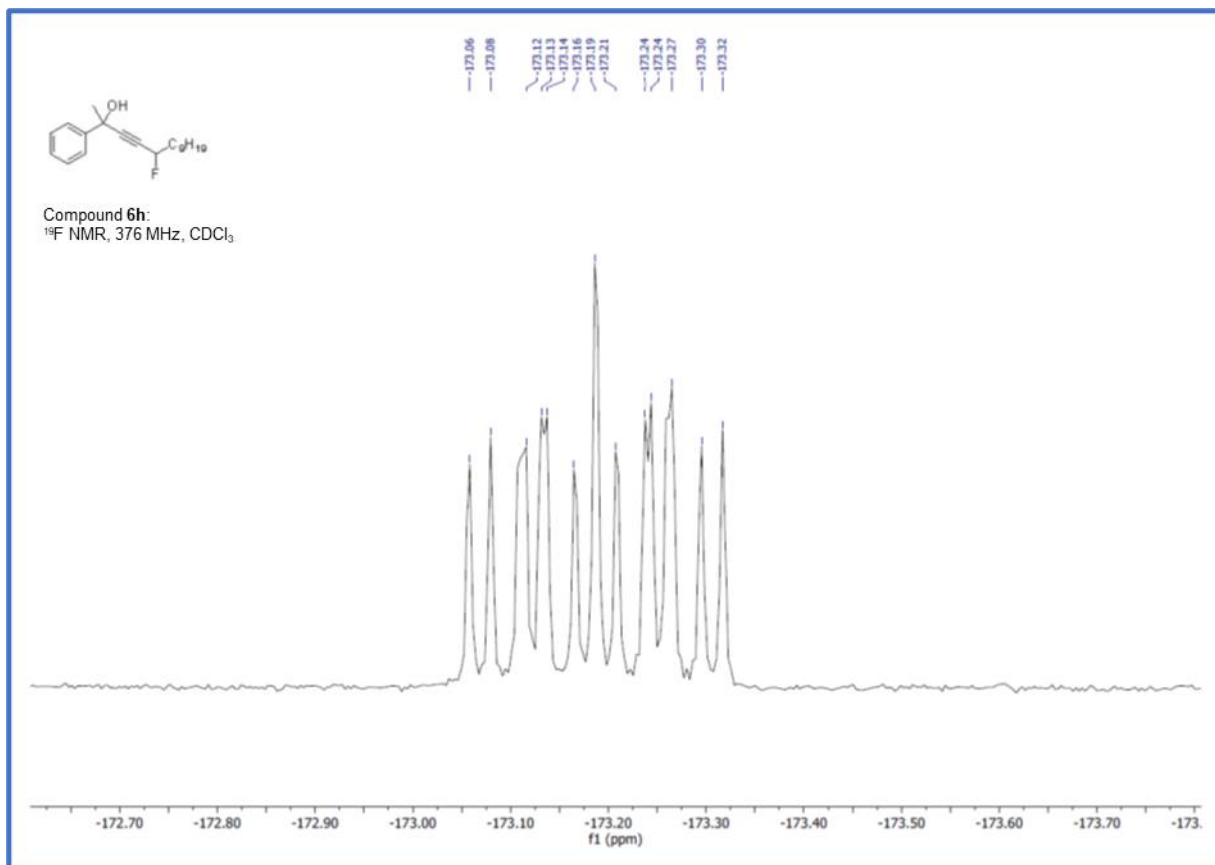
NMR spectra of 4g



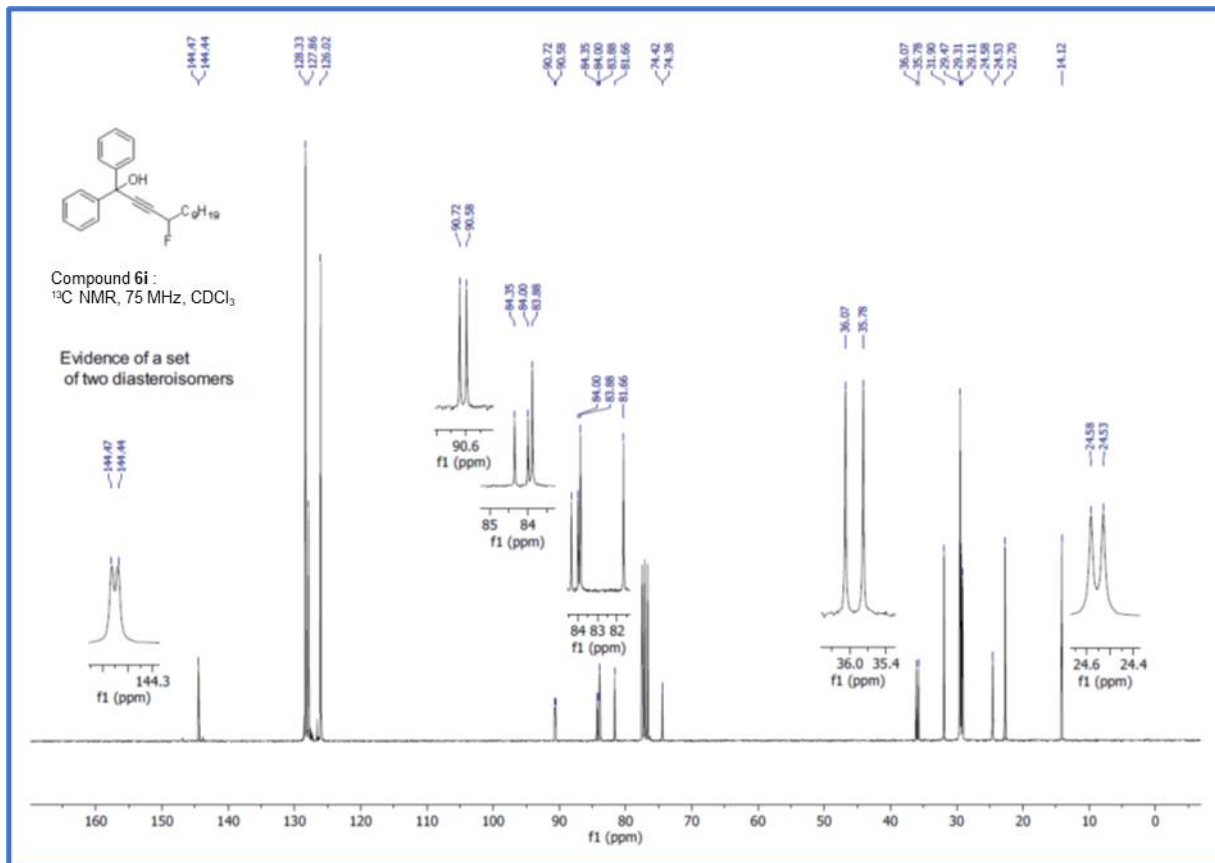
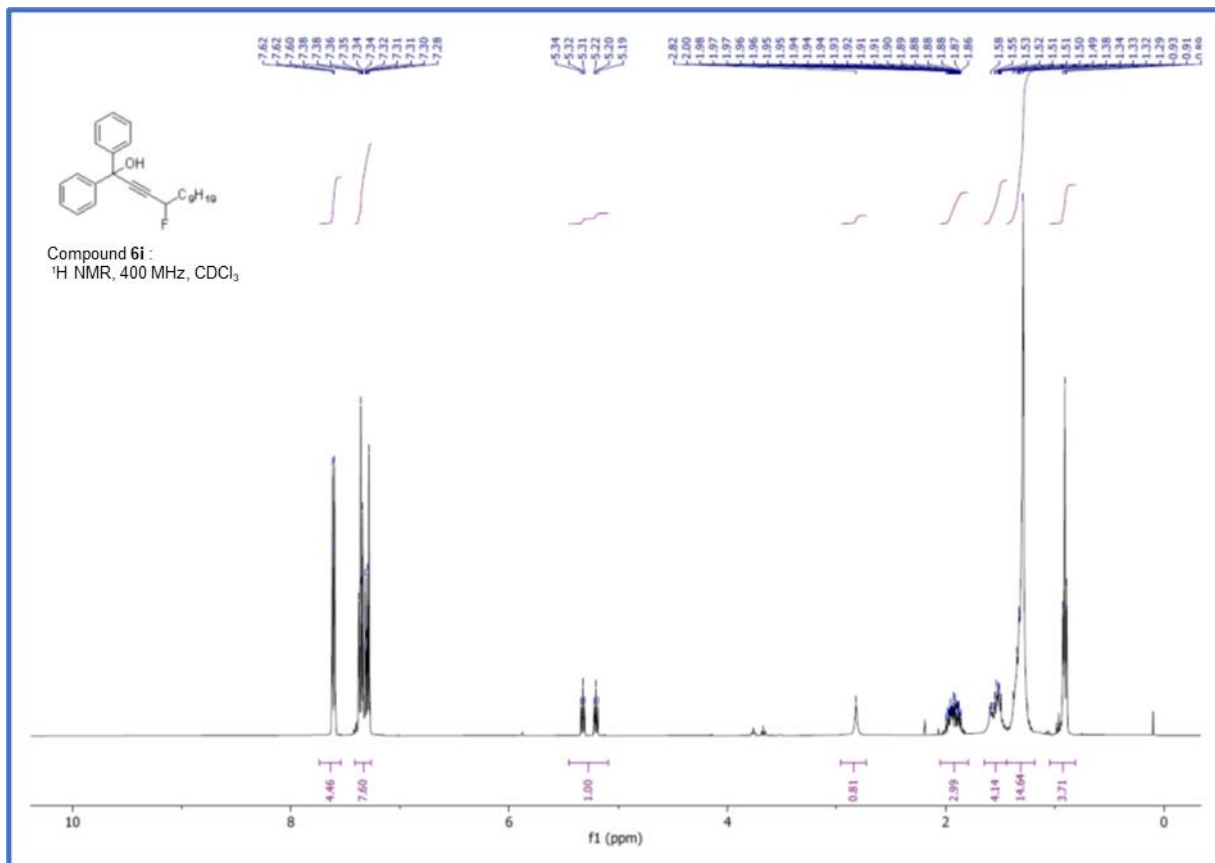


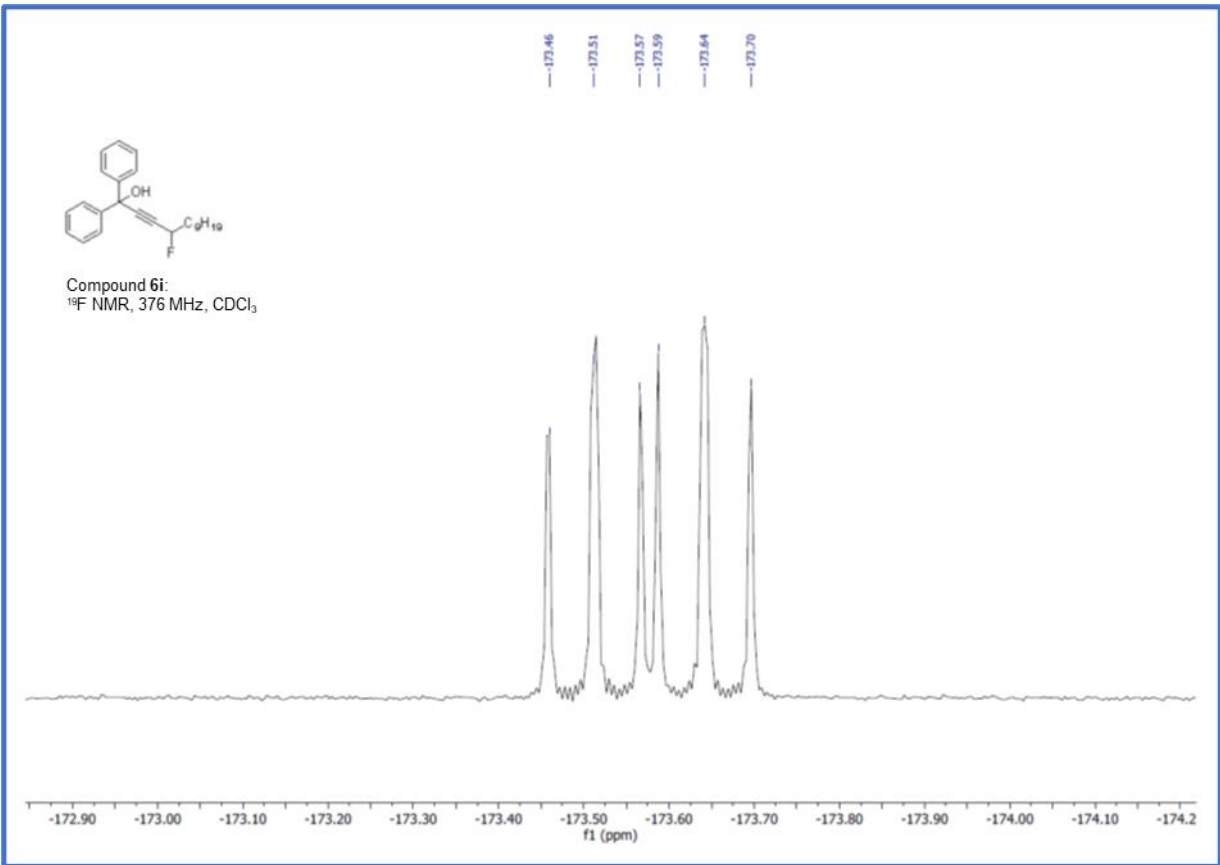
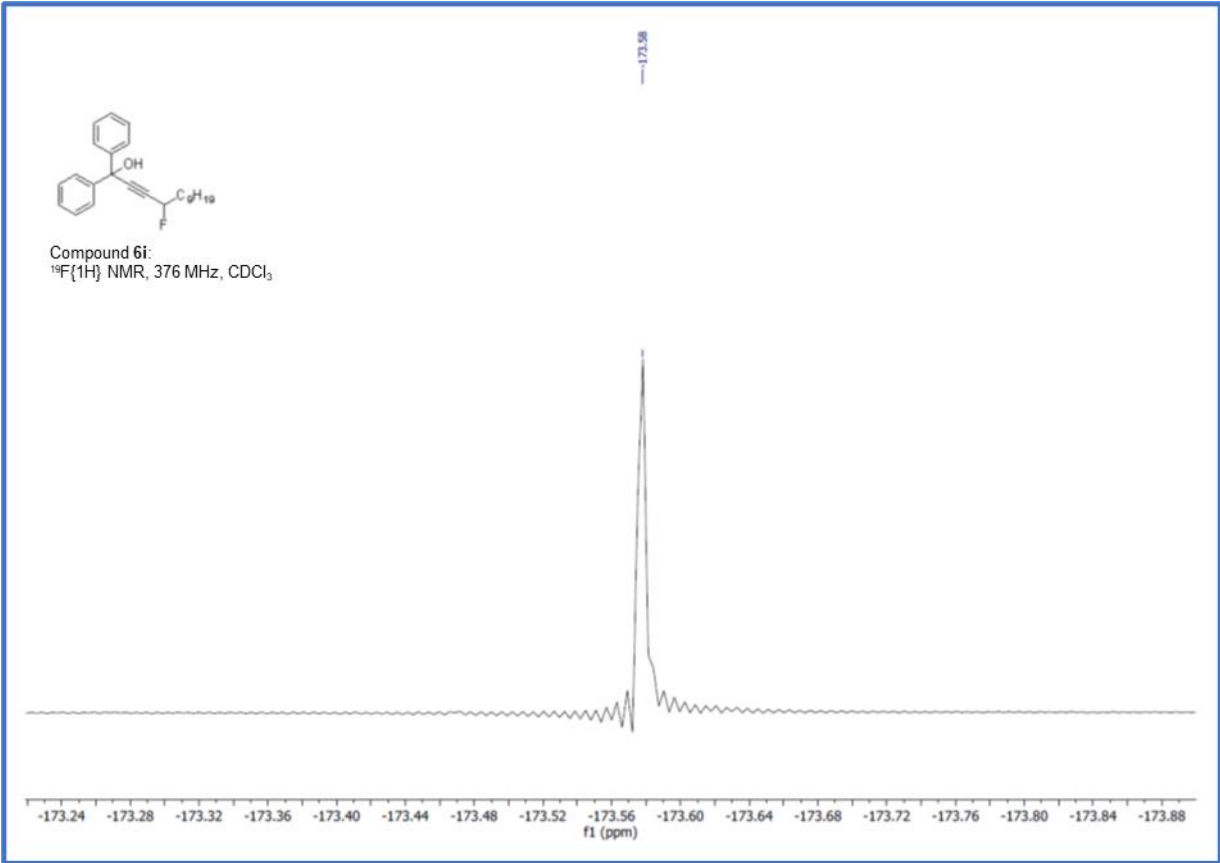
NMR spectra of 6h



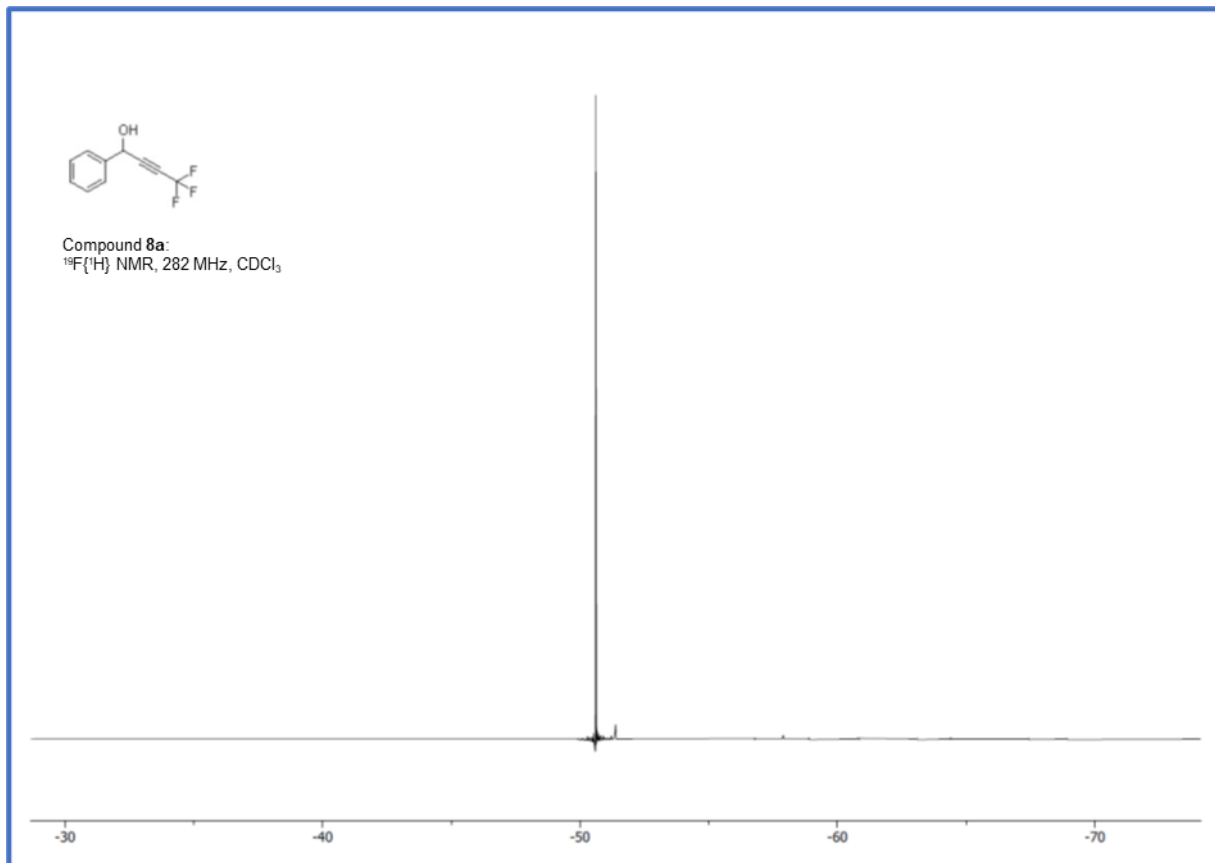
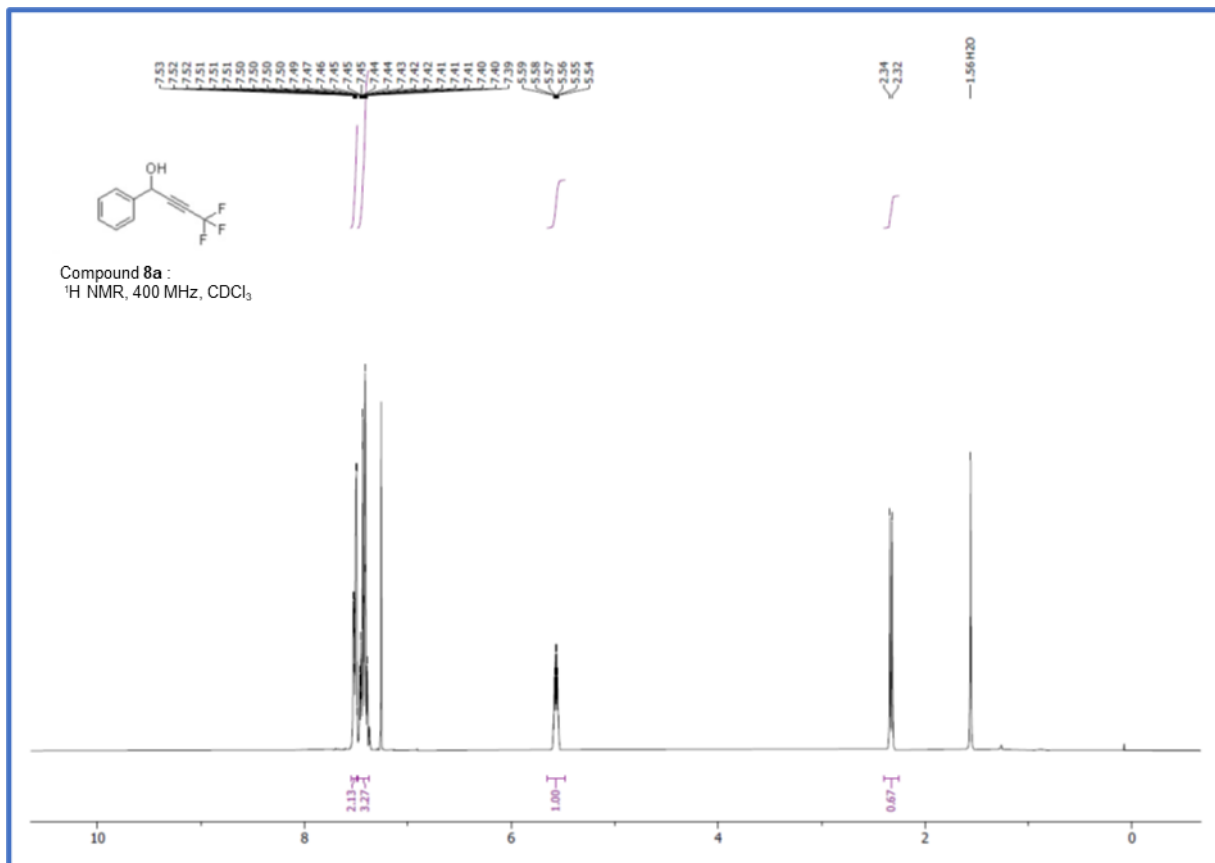


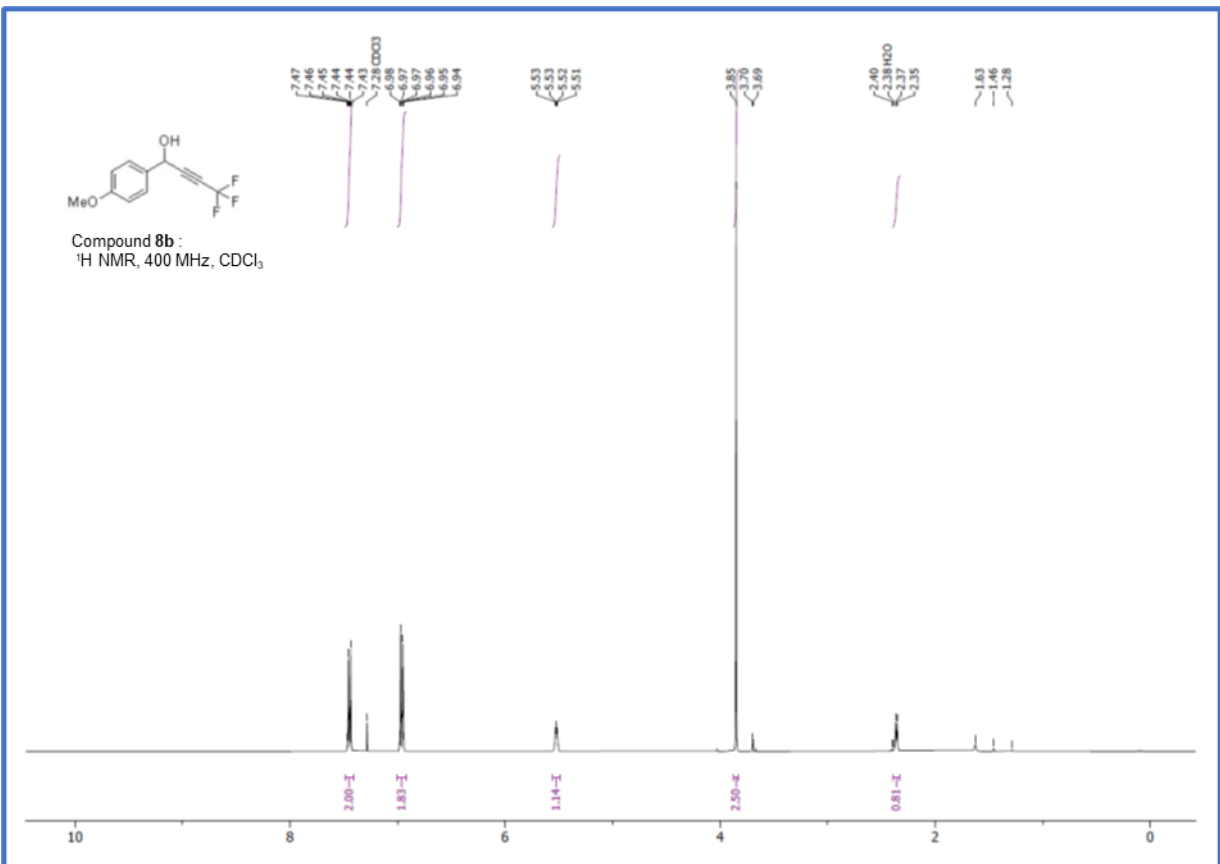
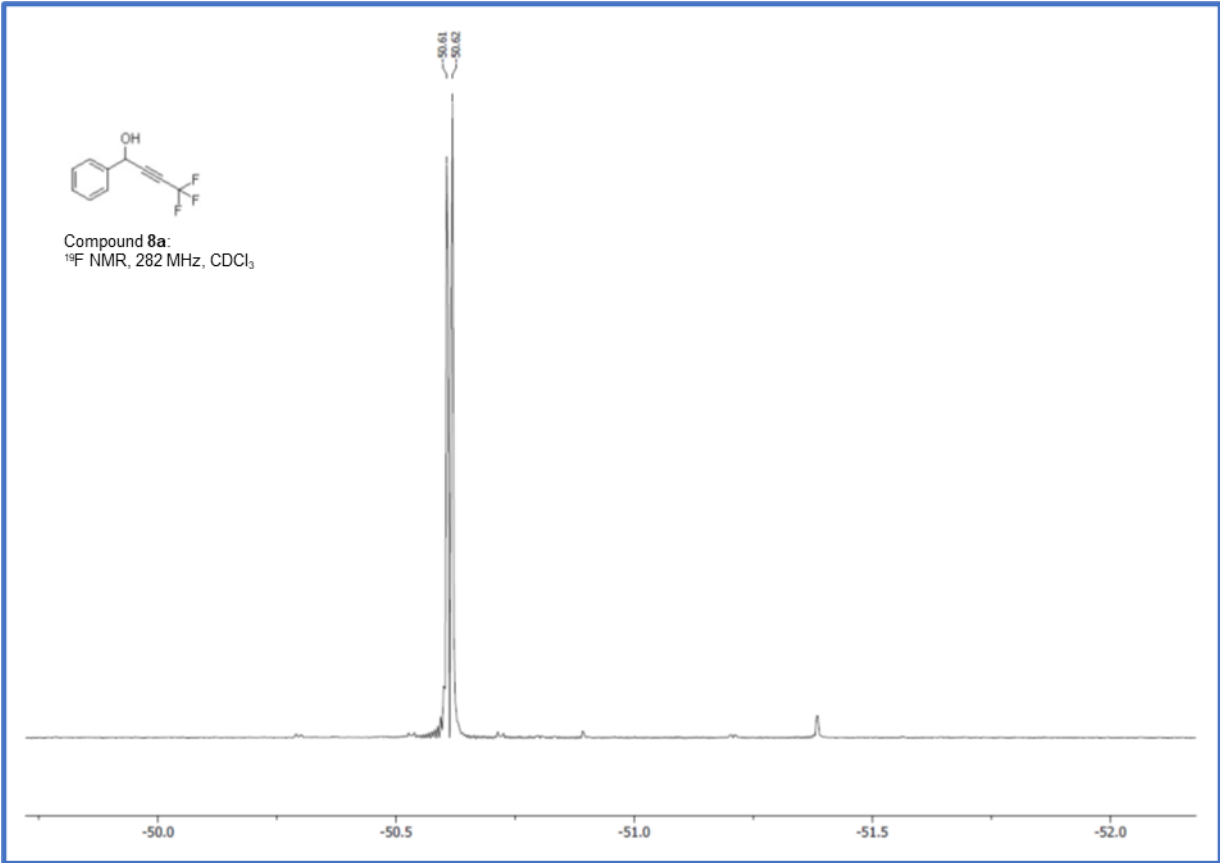
NMR spectra of 6i



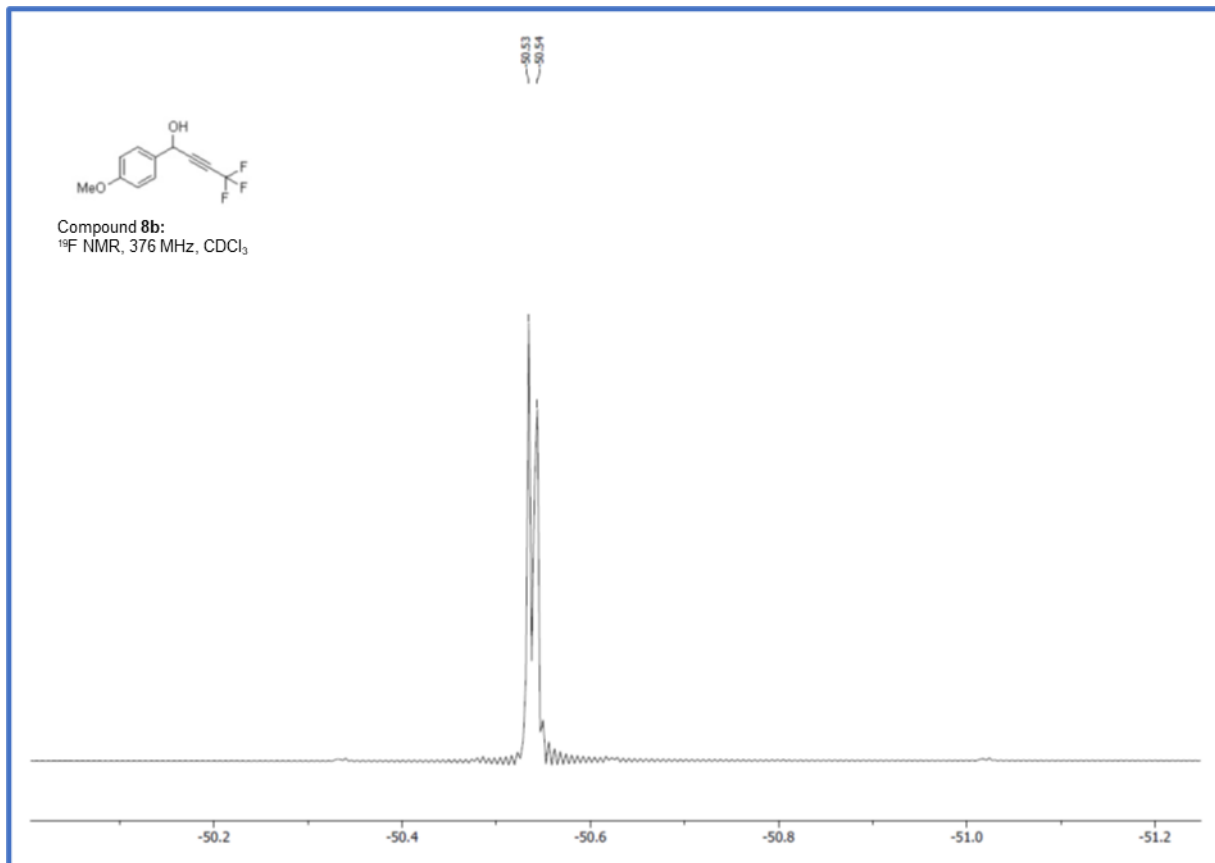
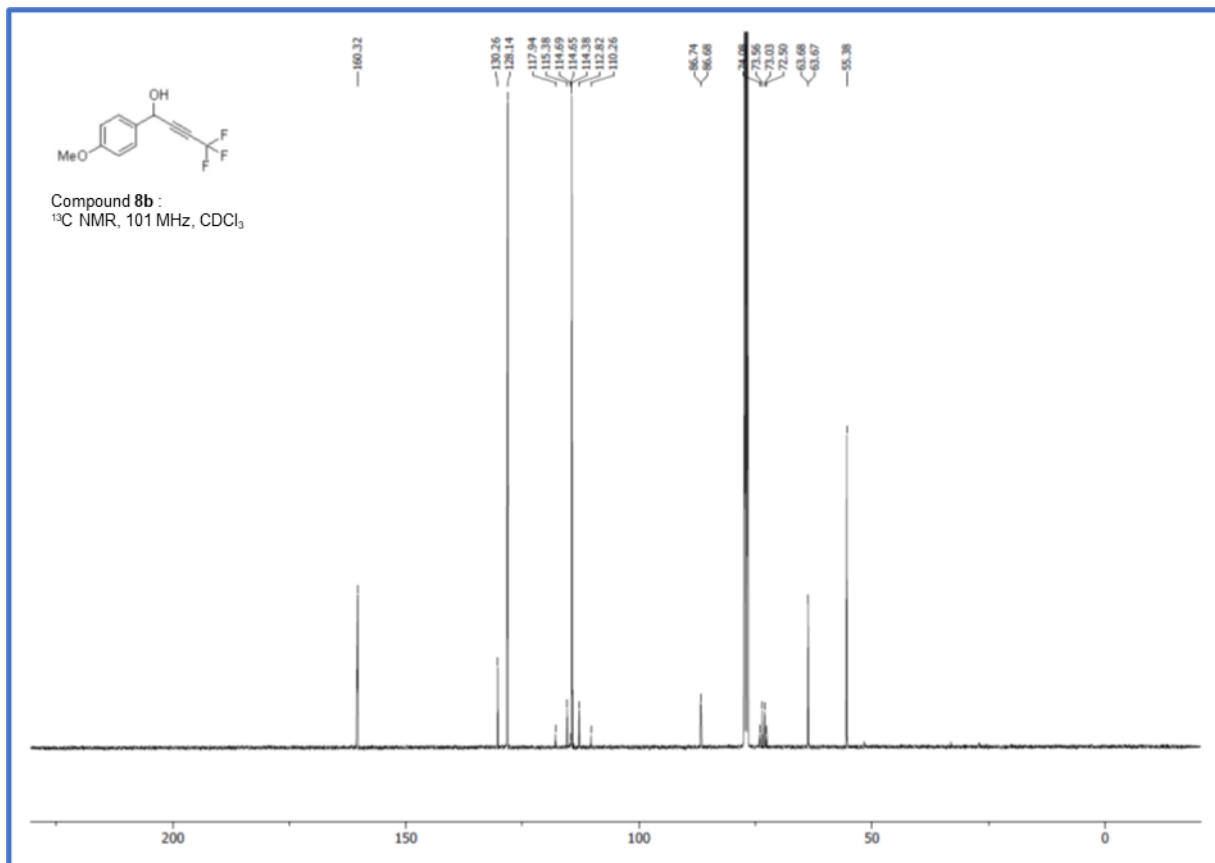


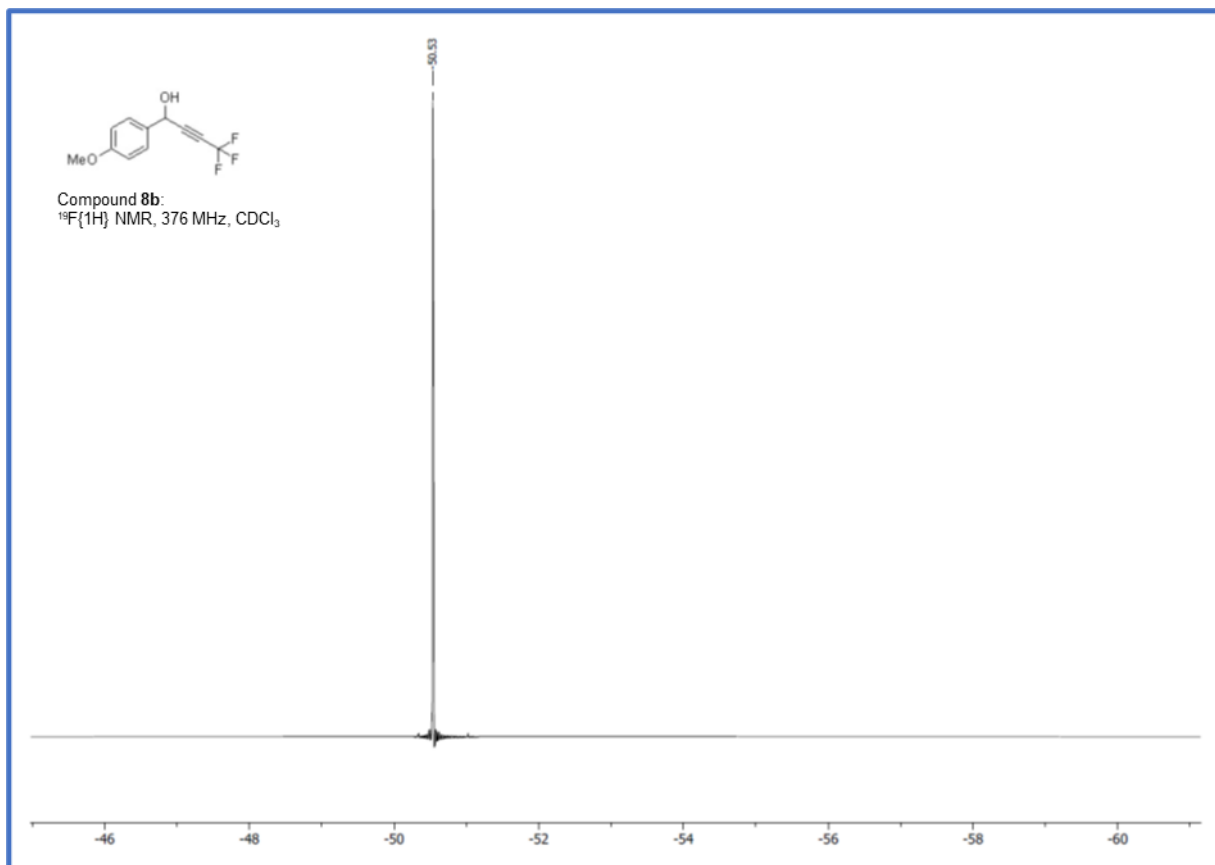
NMR spectra of 8a



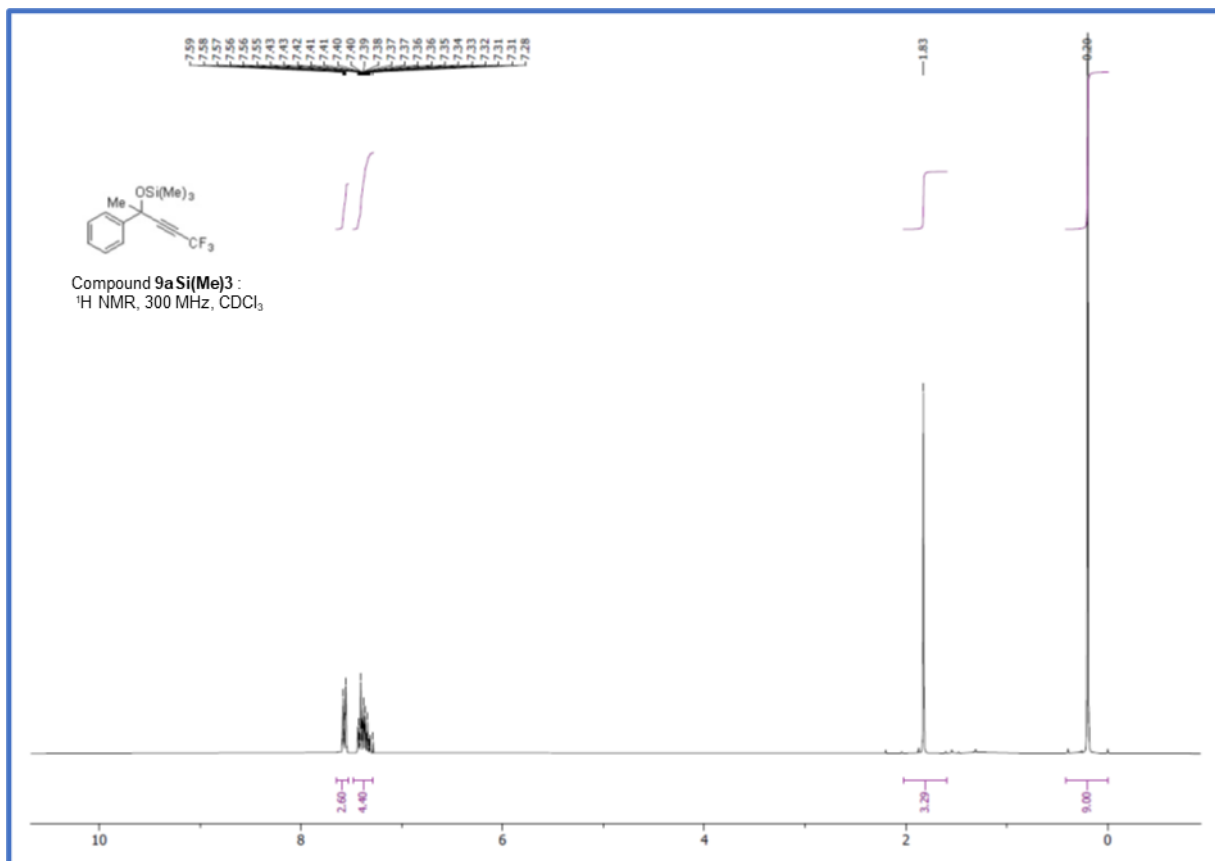


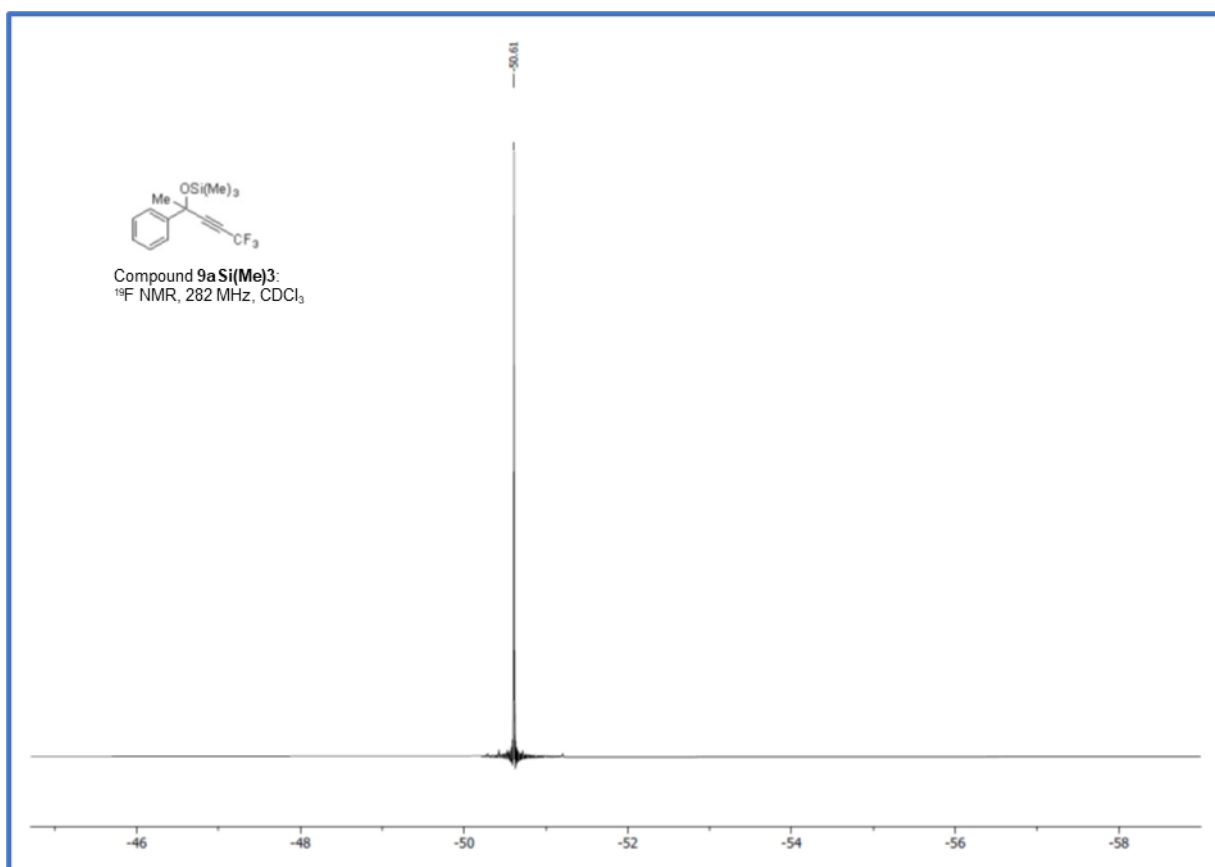
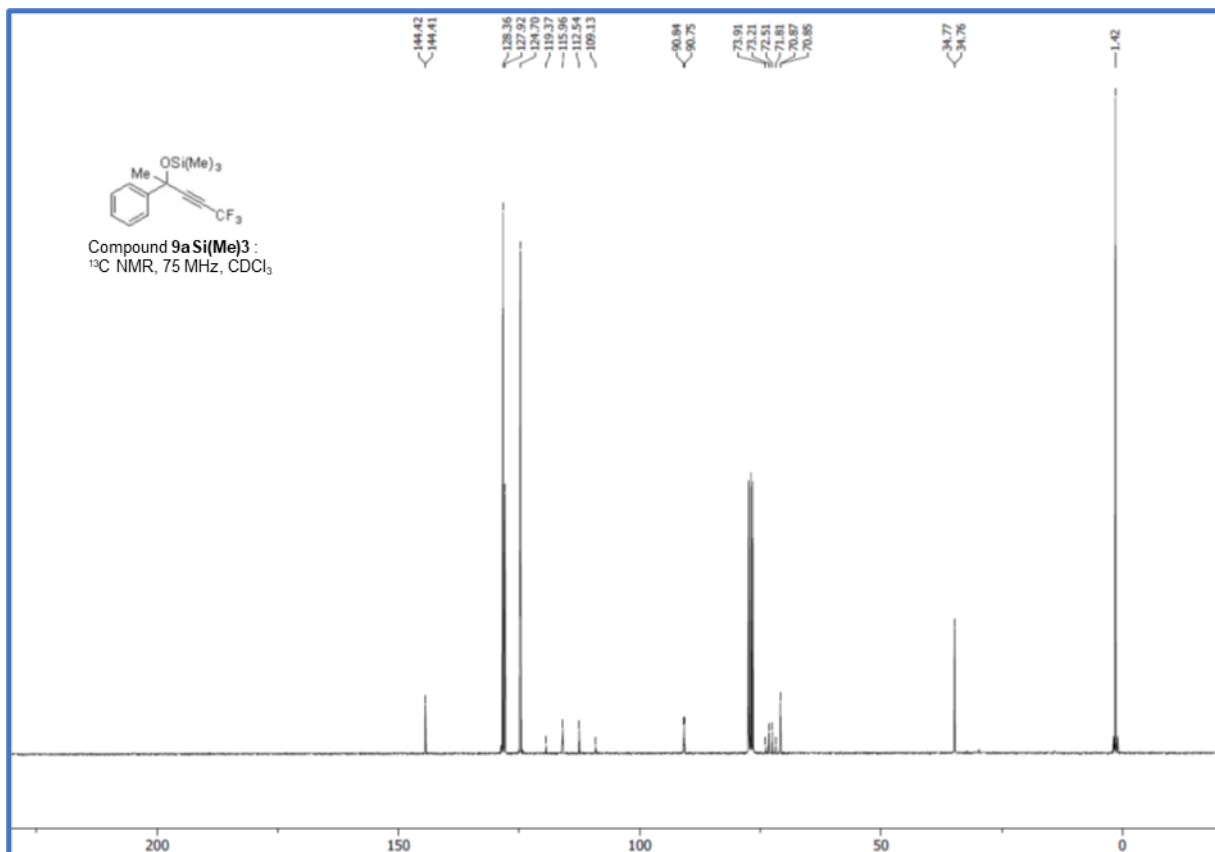
NMR spectra of 8b



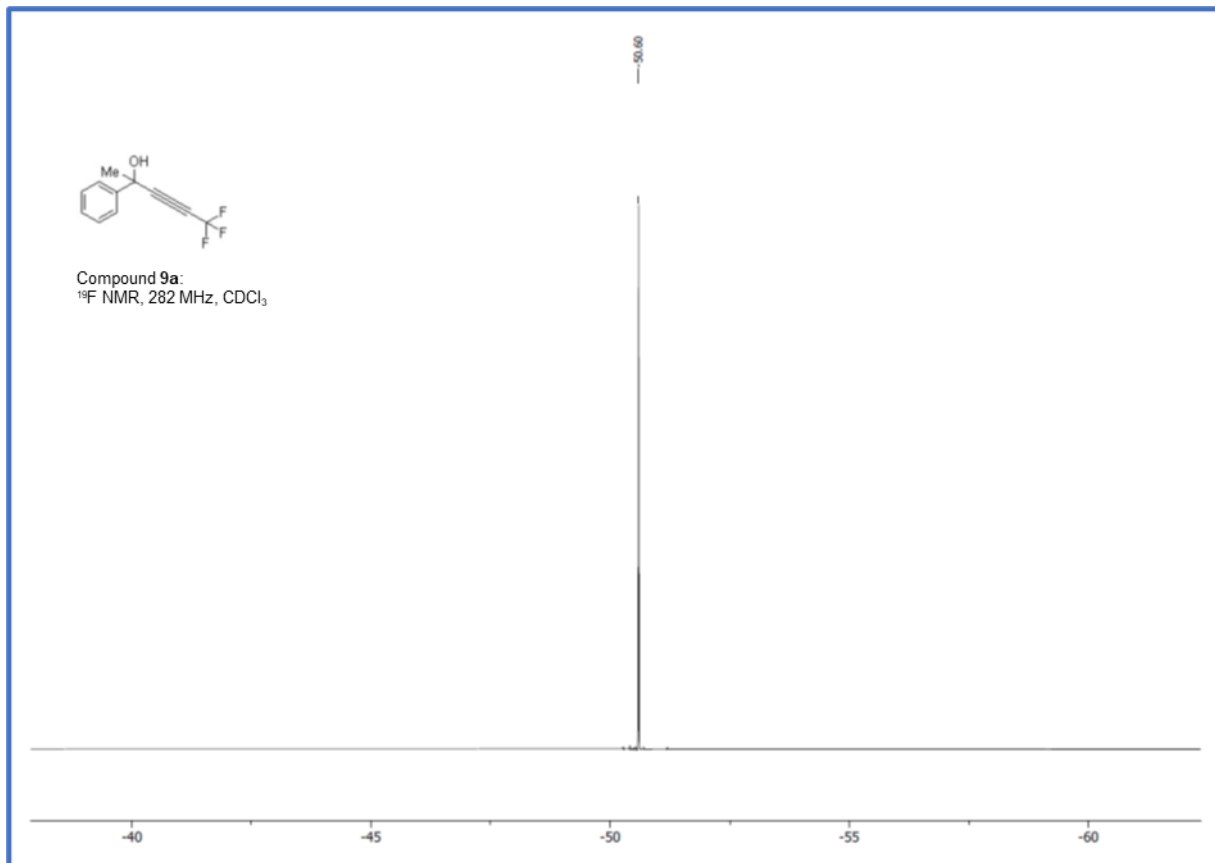
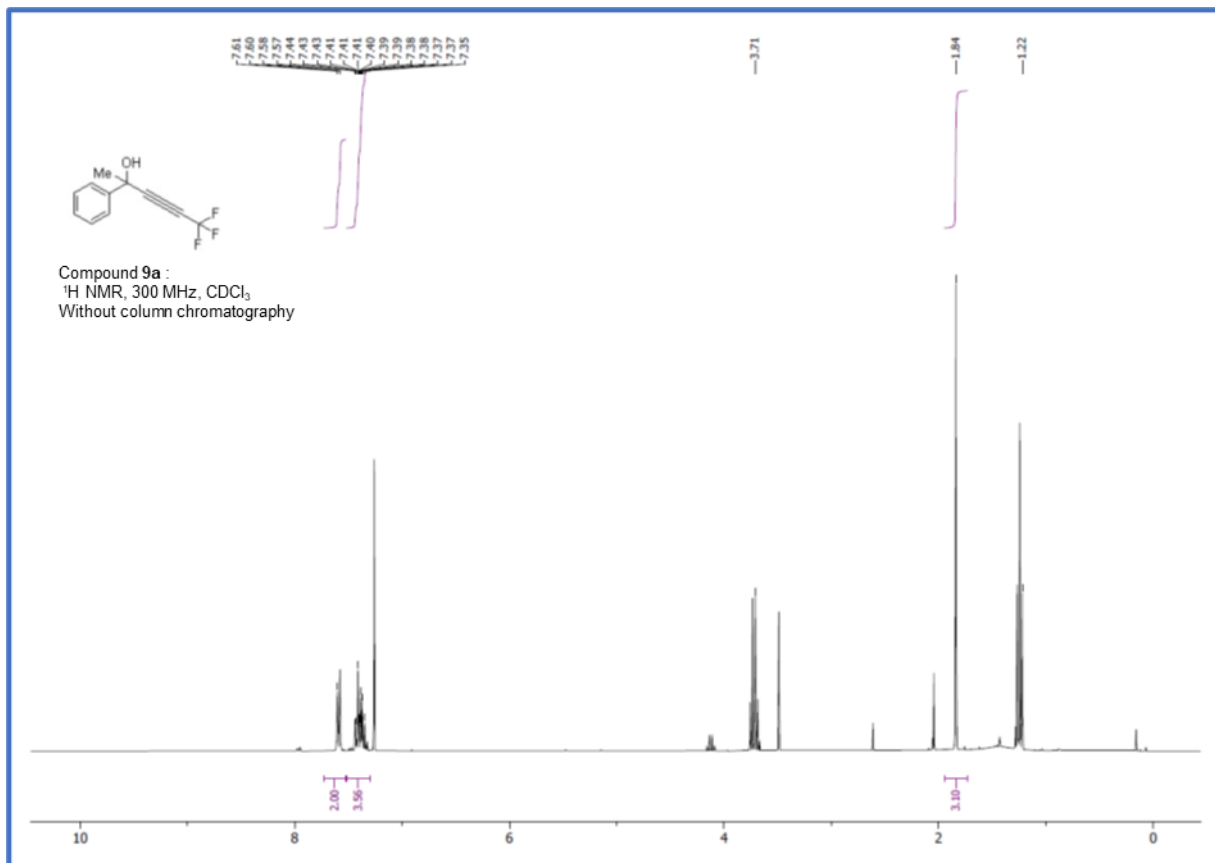


NMR spectra of 9aSi(Me)₃

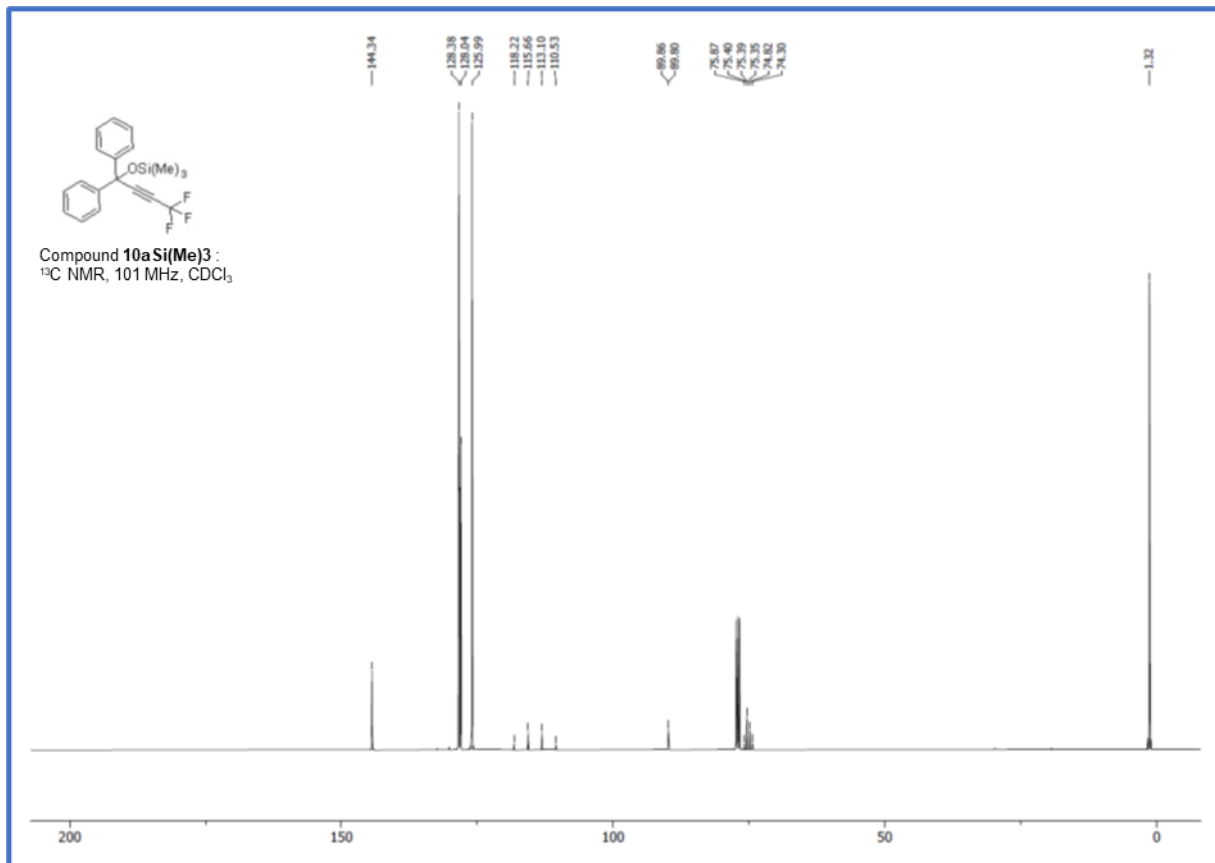
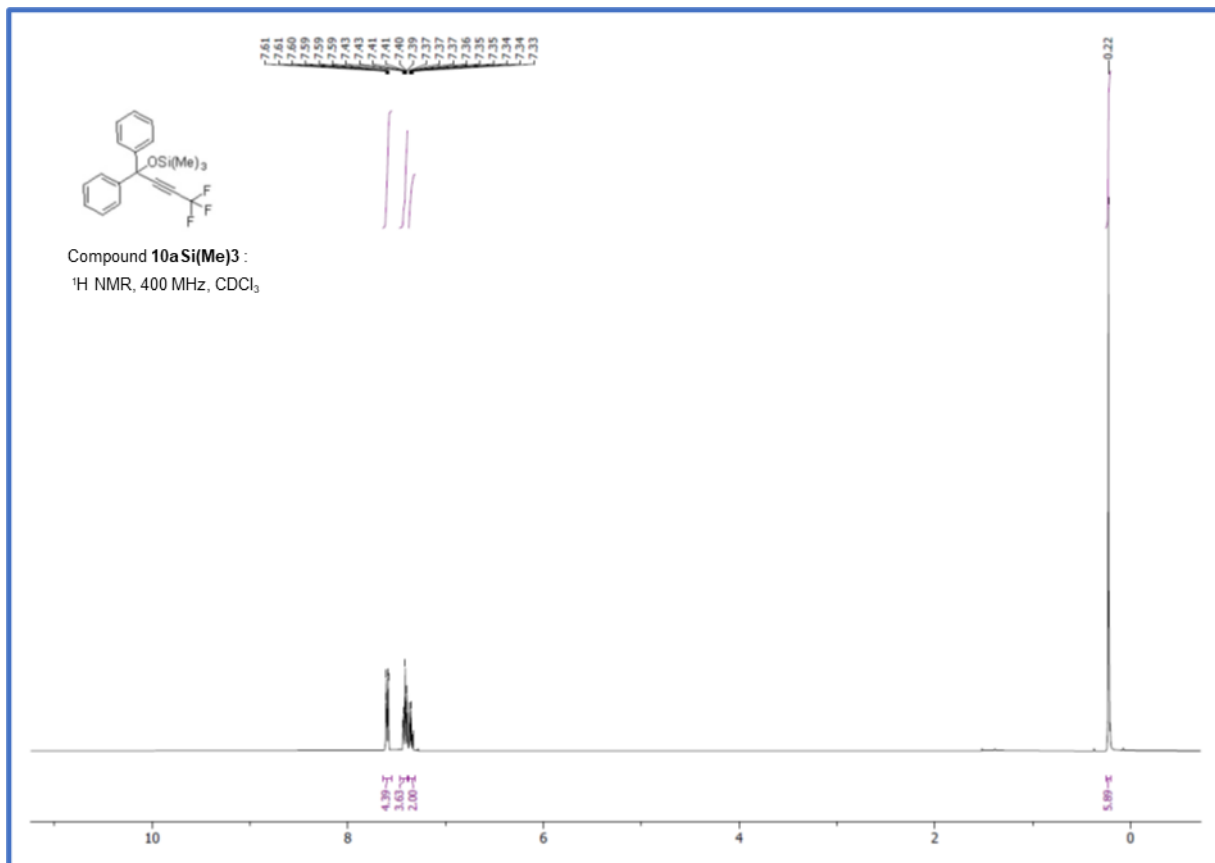


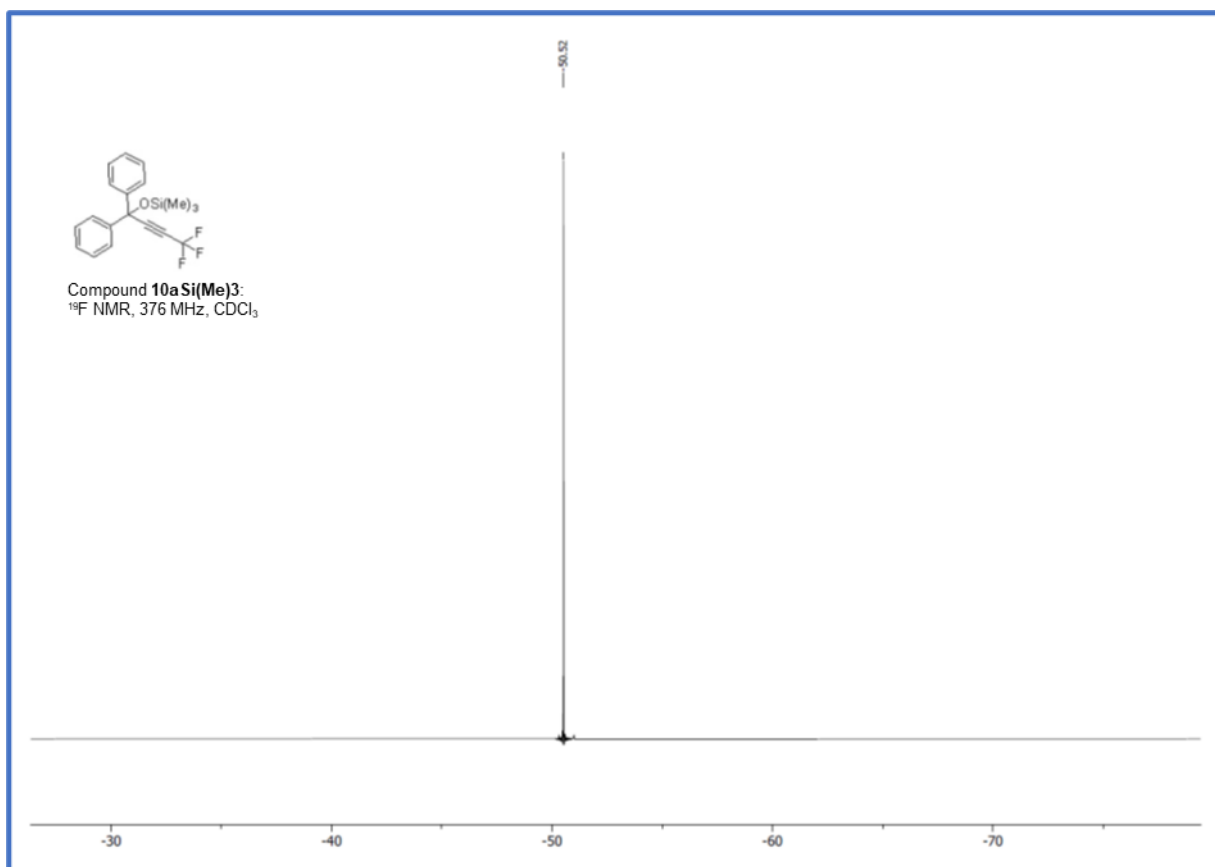


NMR spectra of 9a

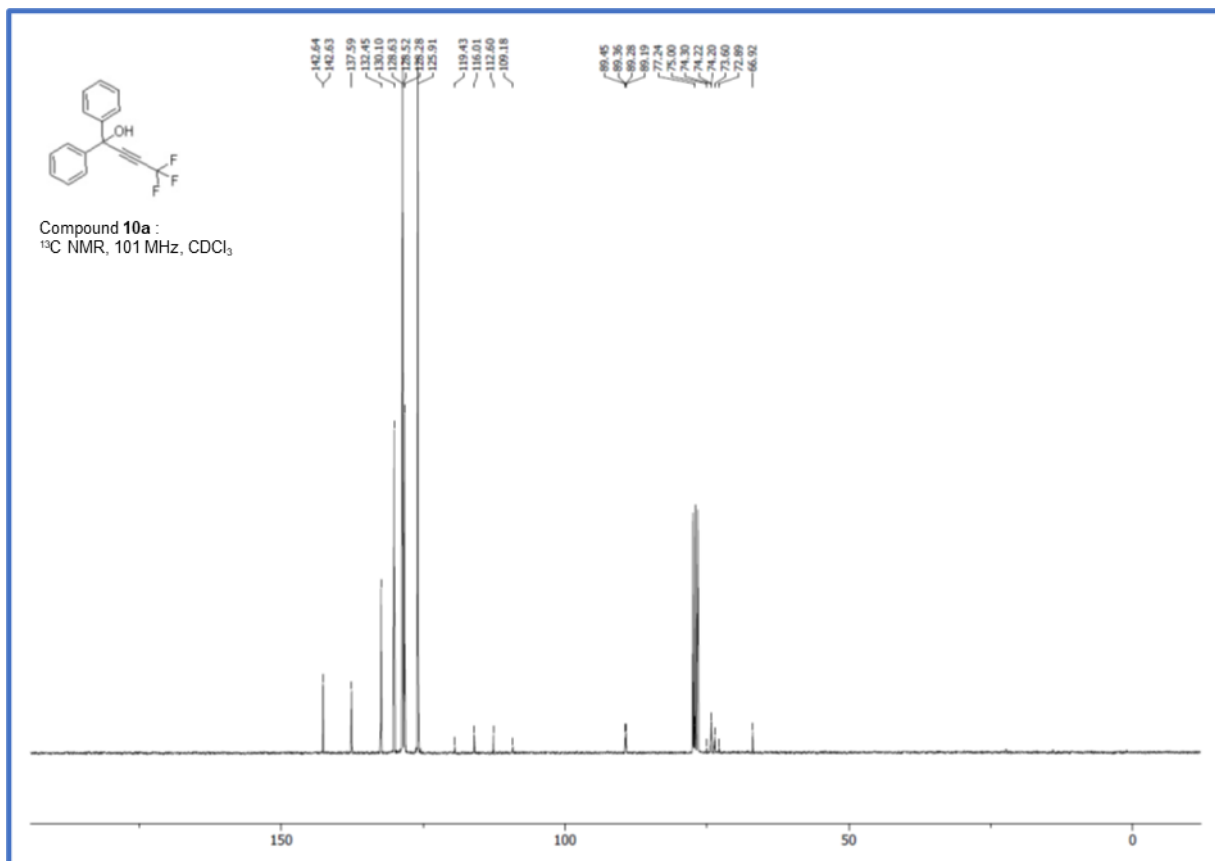


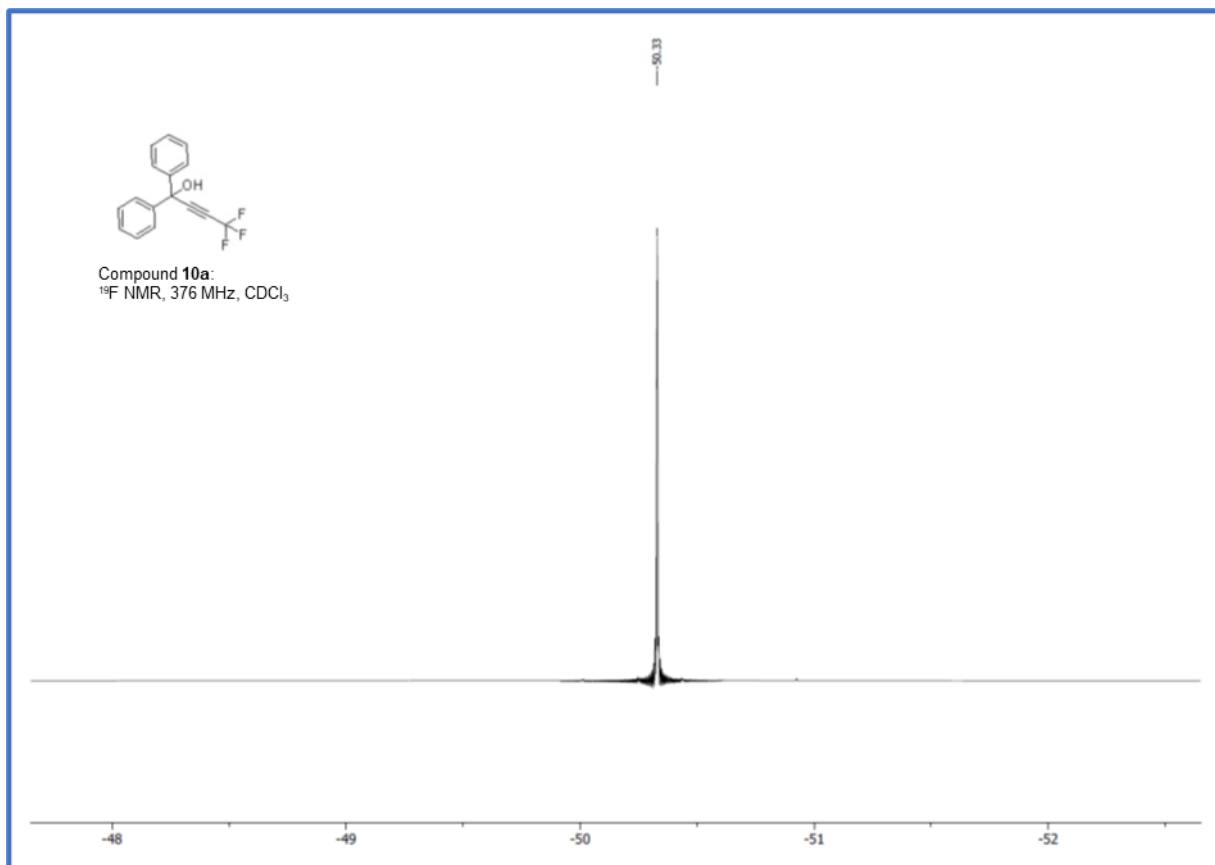
NMR spectra of 10aSi(Me)₃



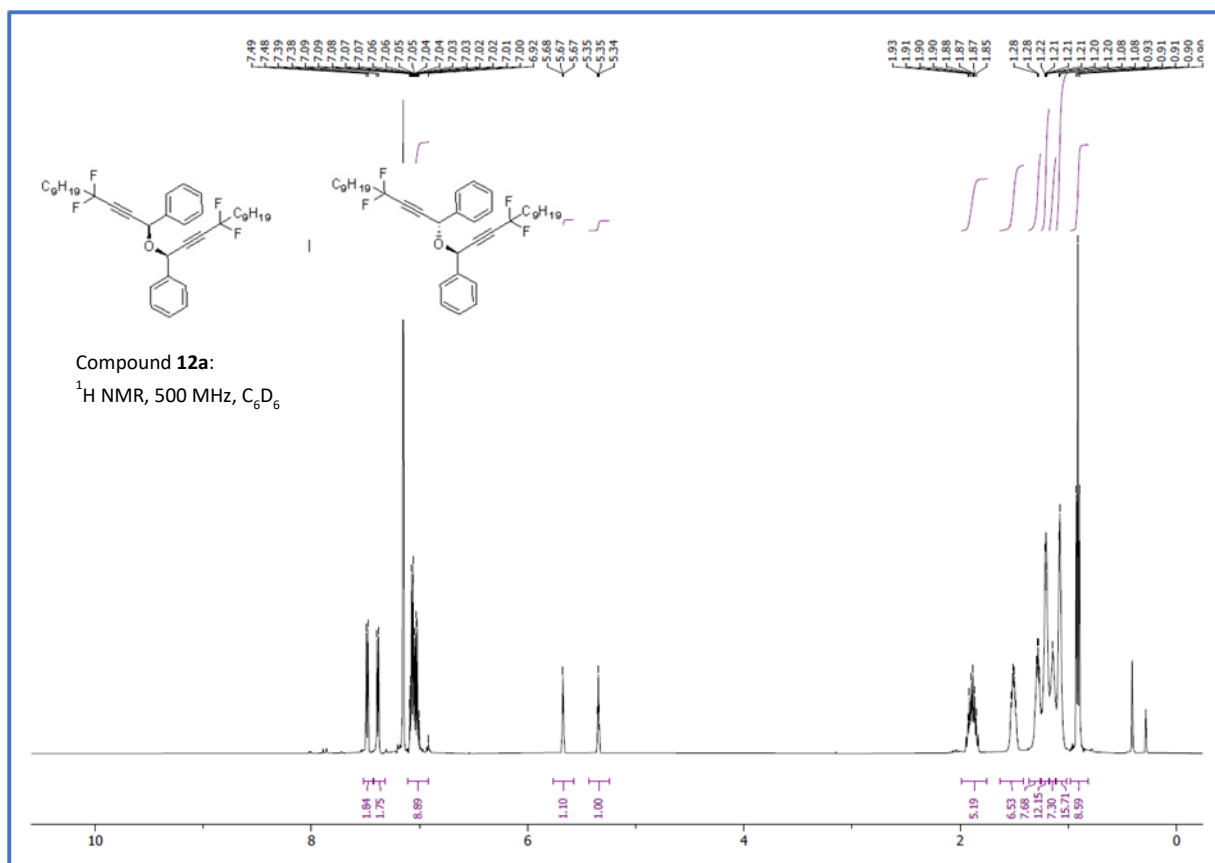


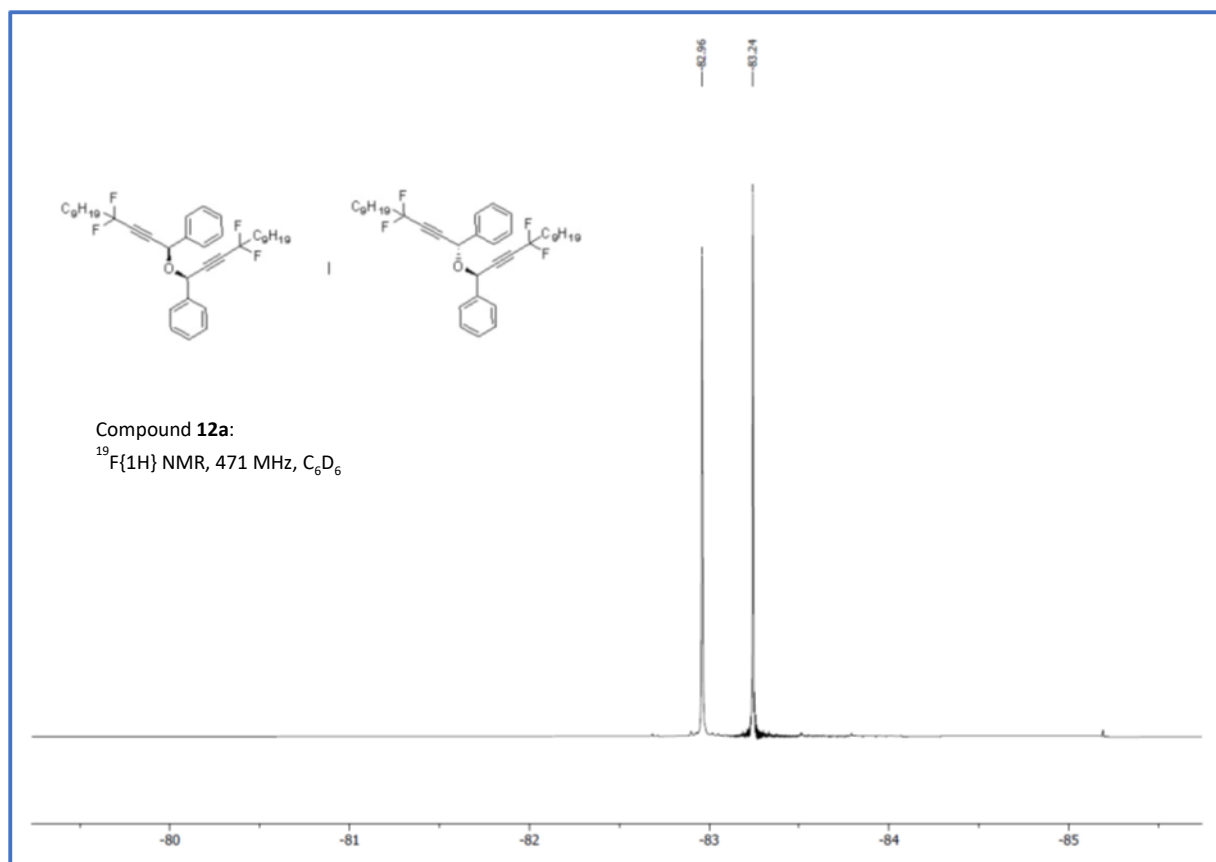
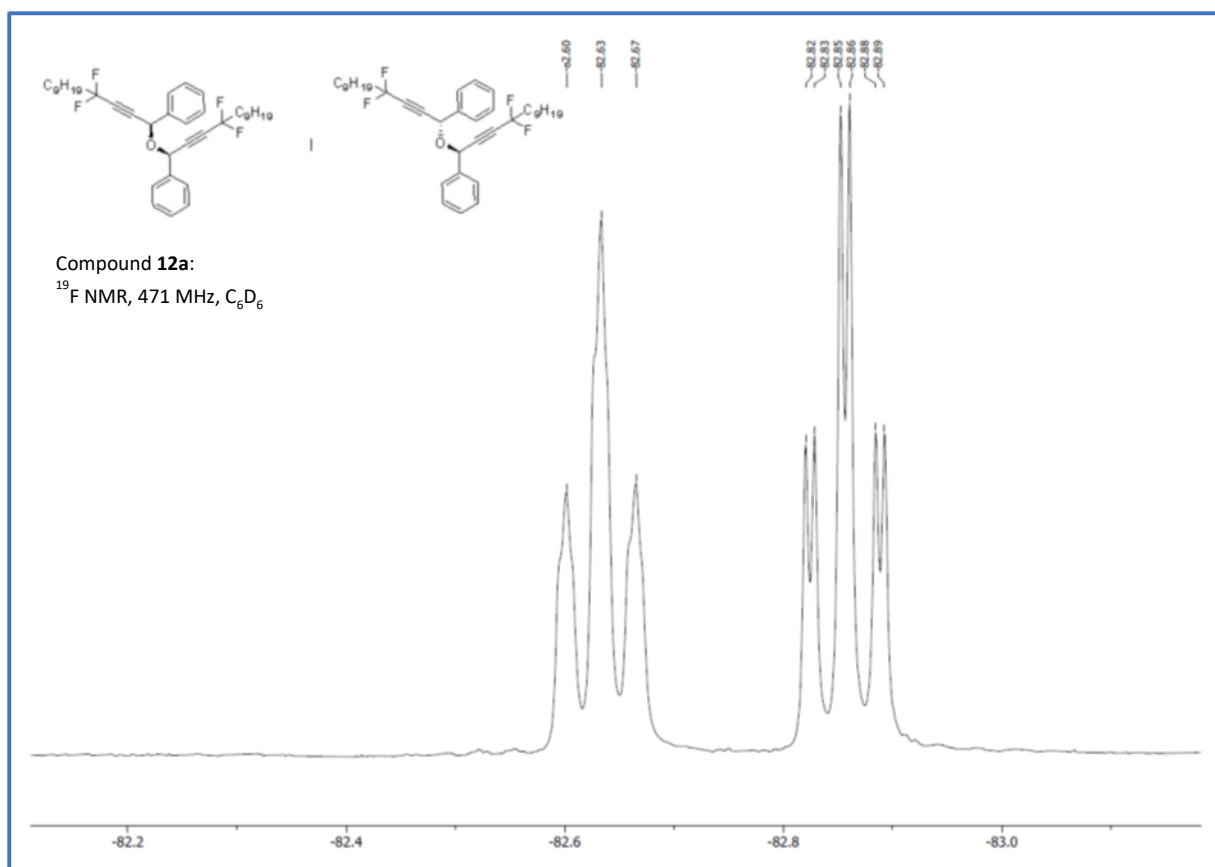
NMR spectra of 10a

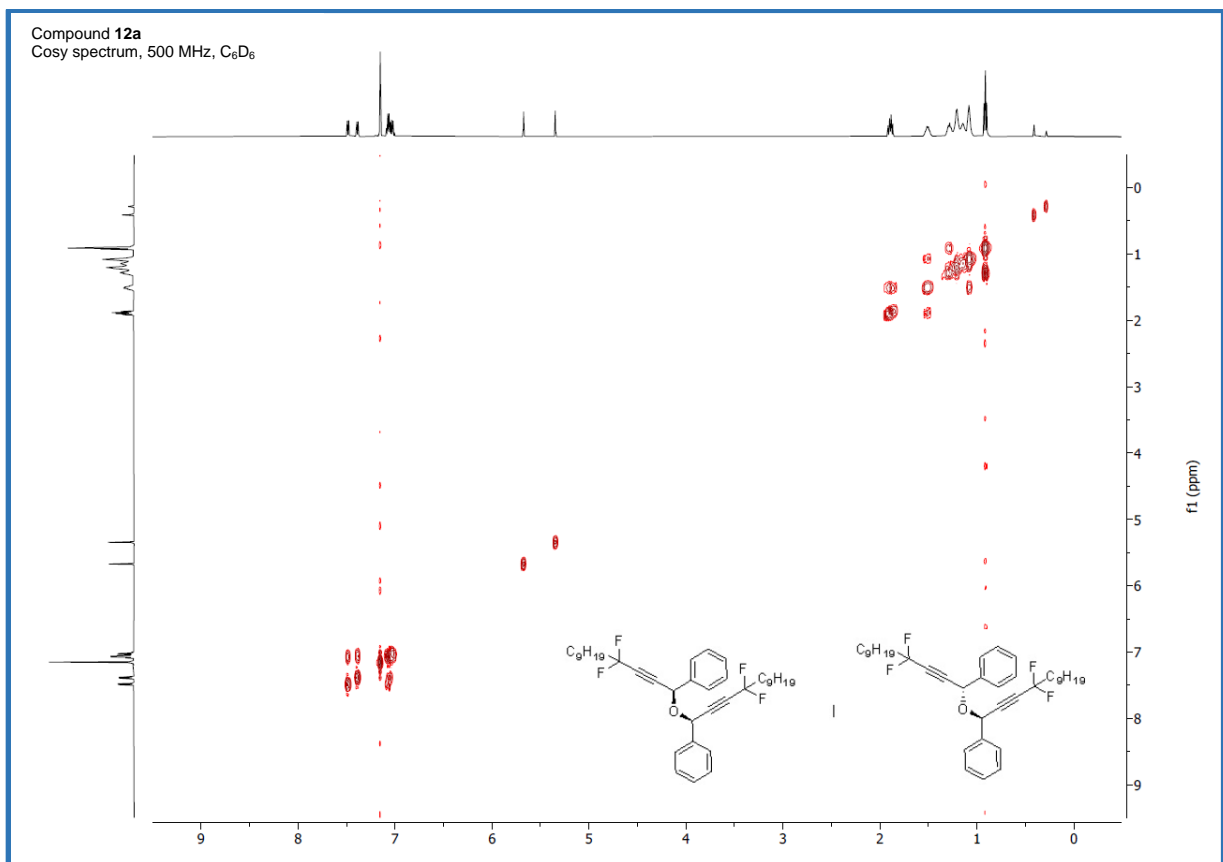
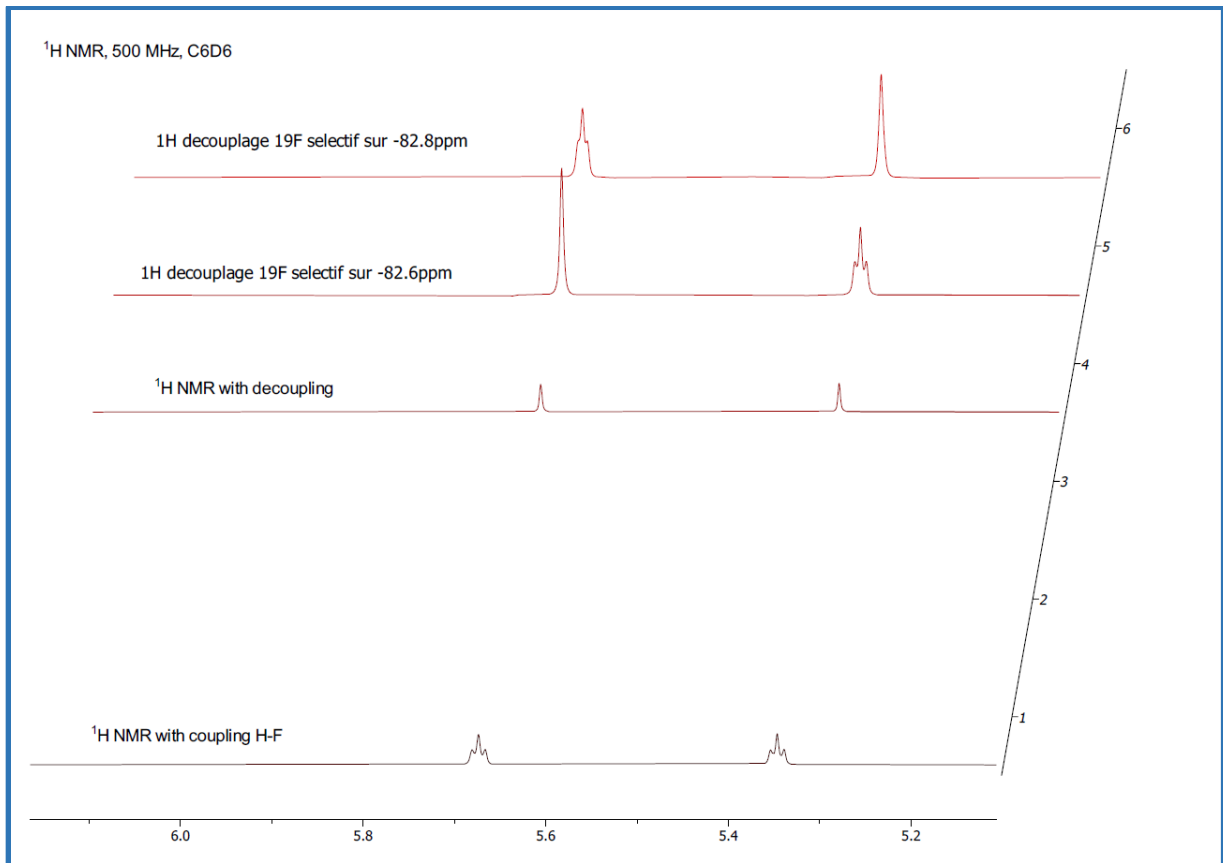




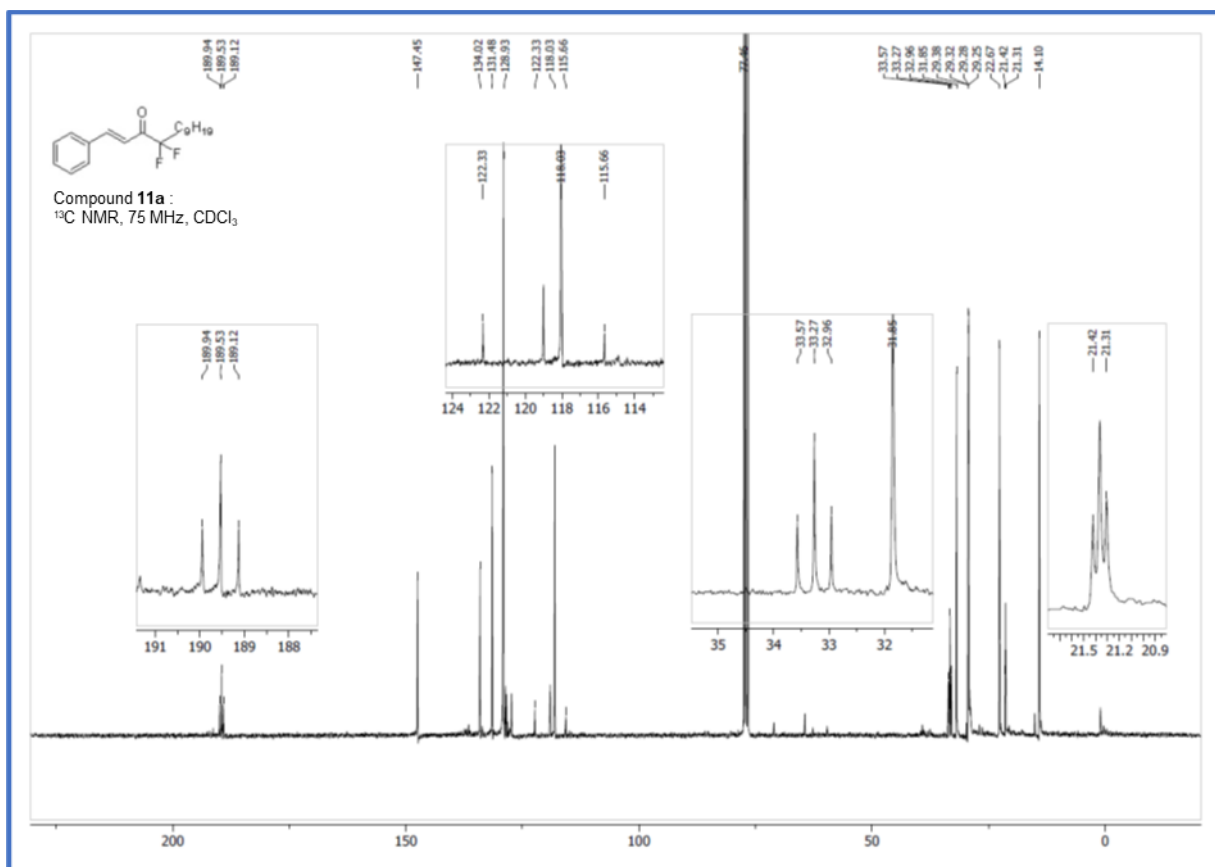
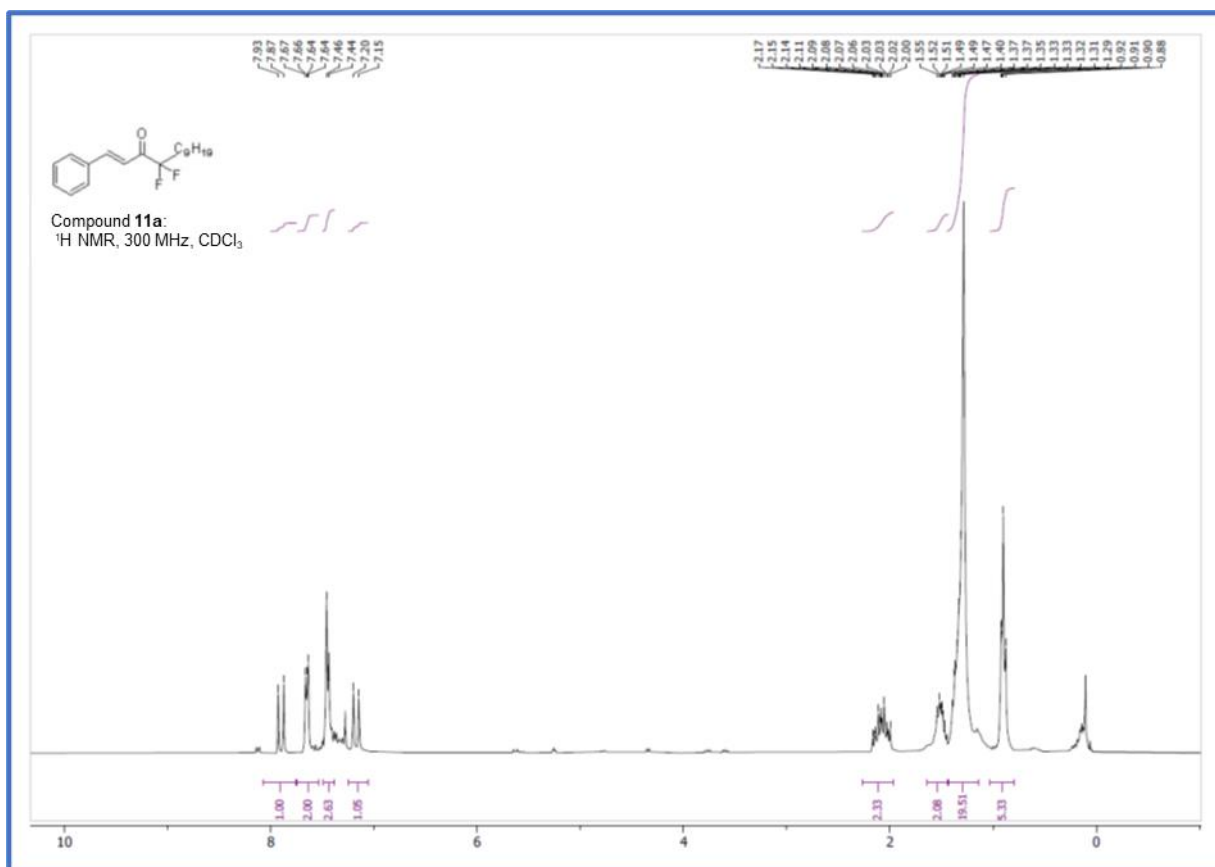
NMR Spectra of Mixture (12a)

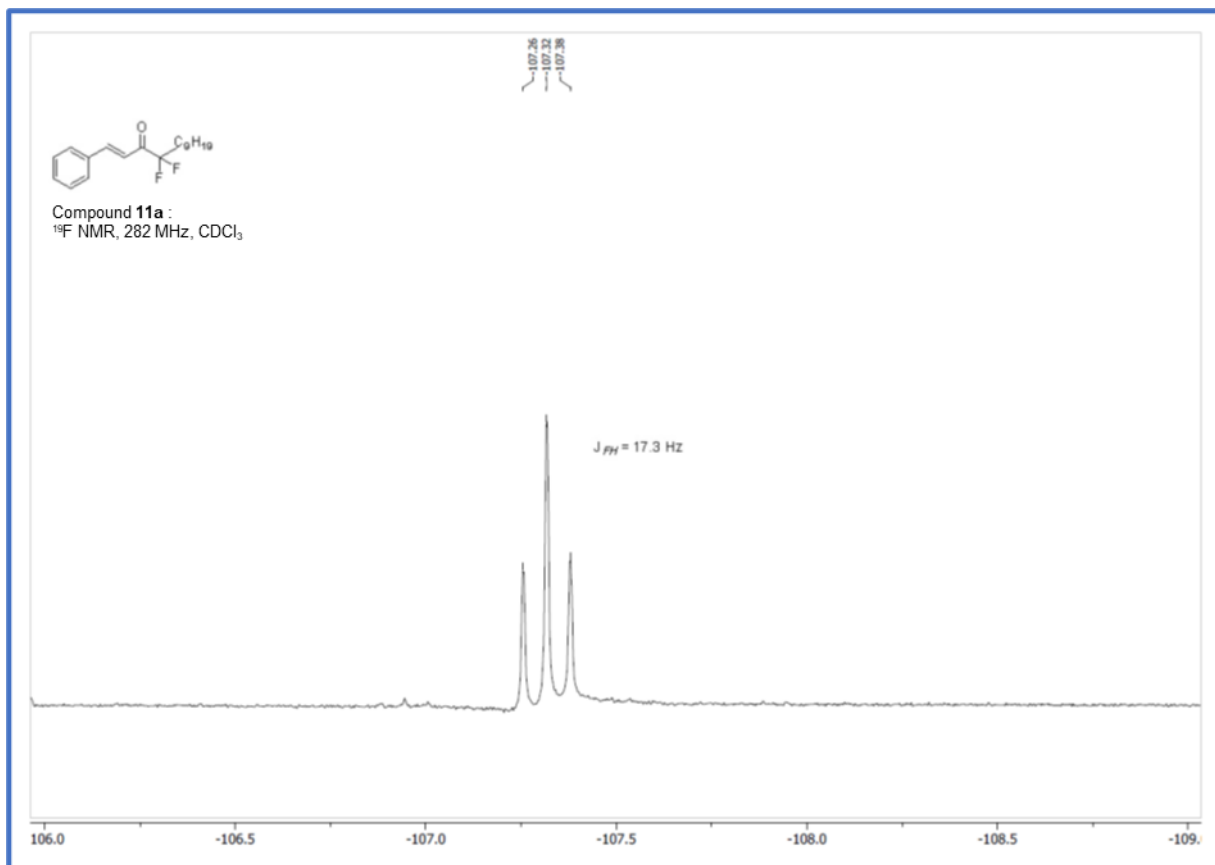




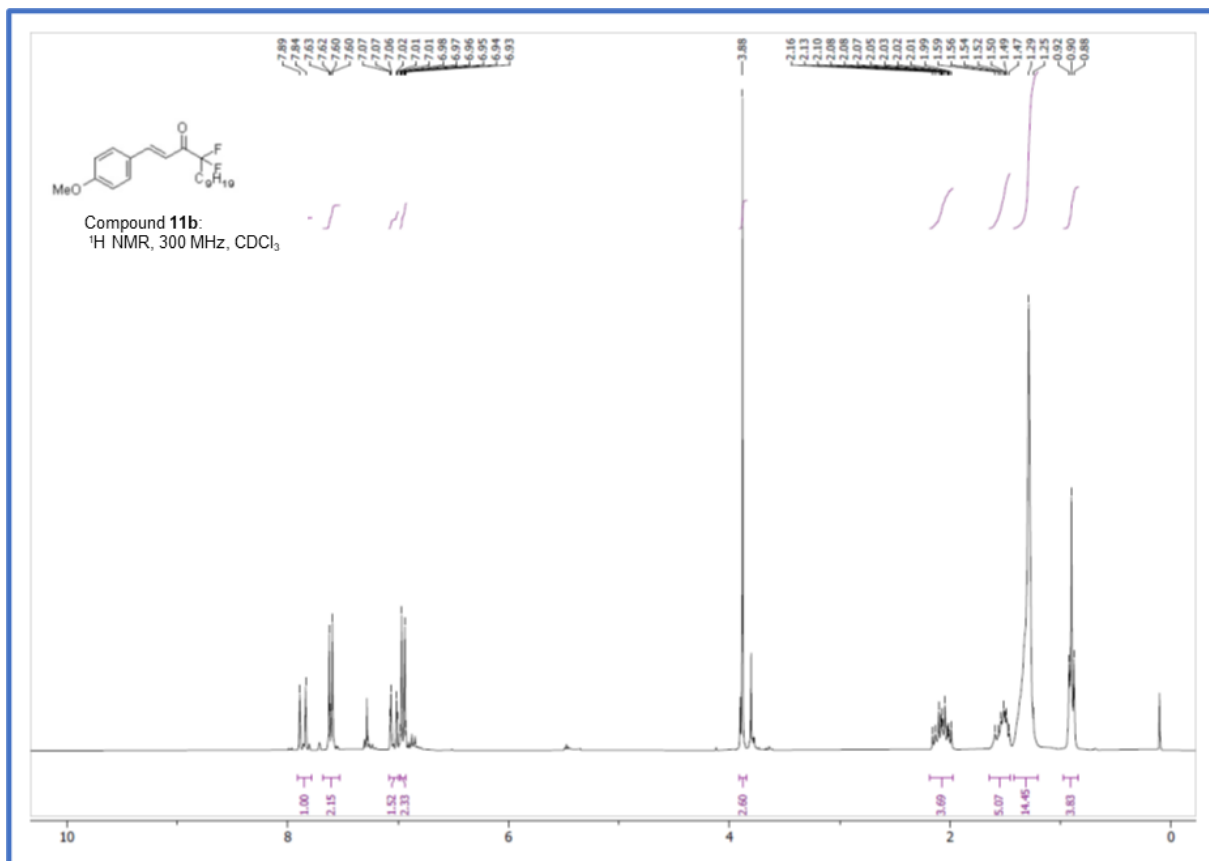


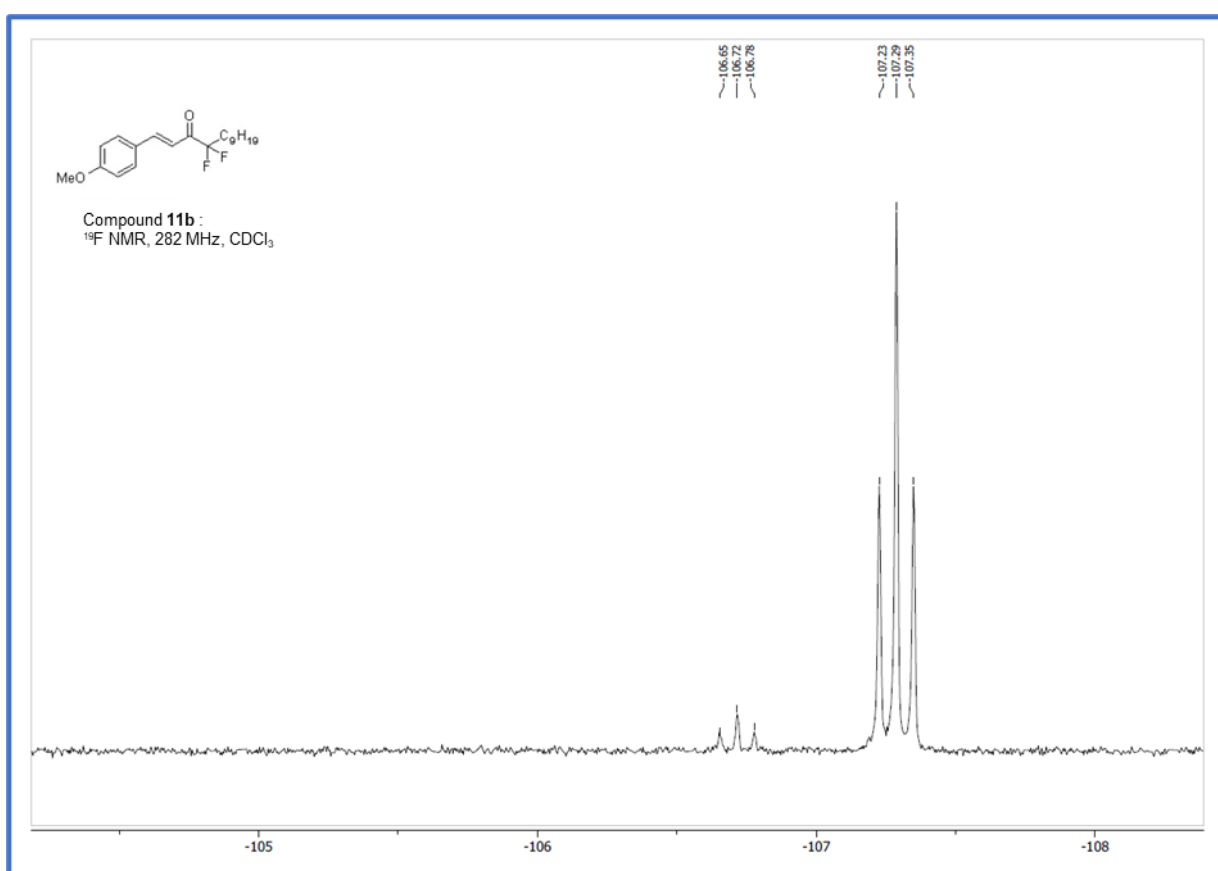
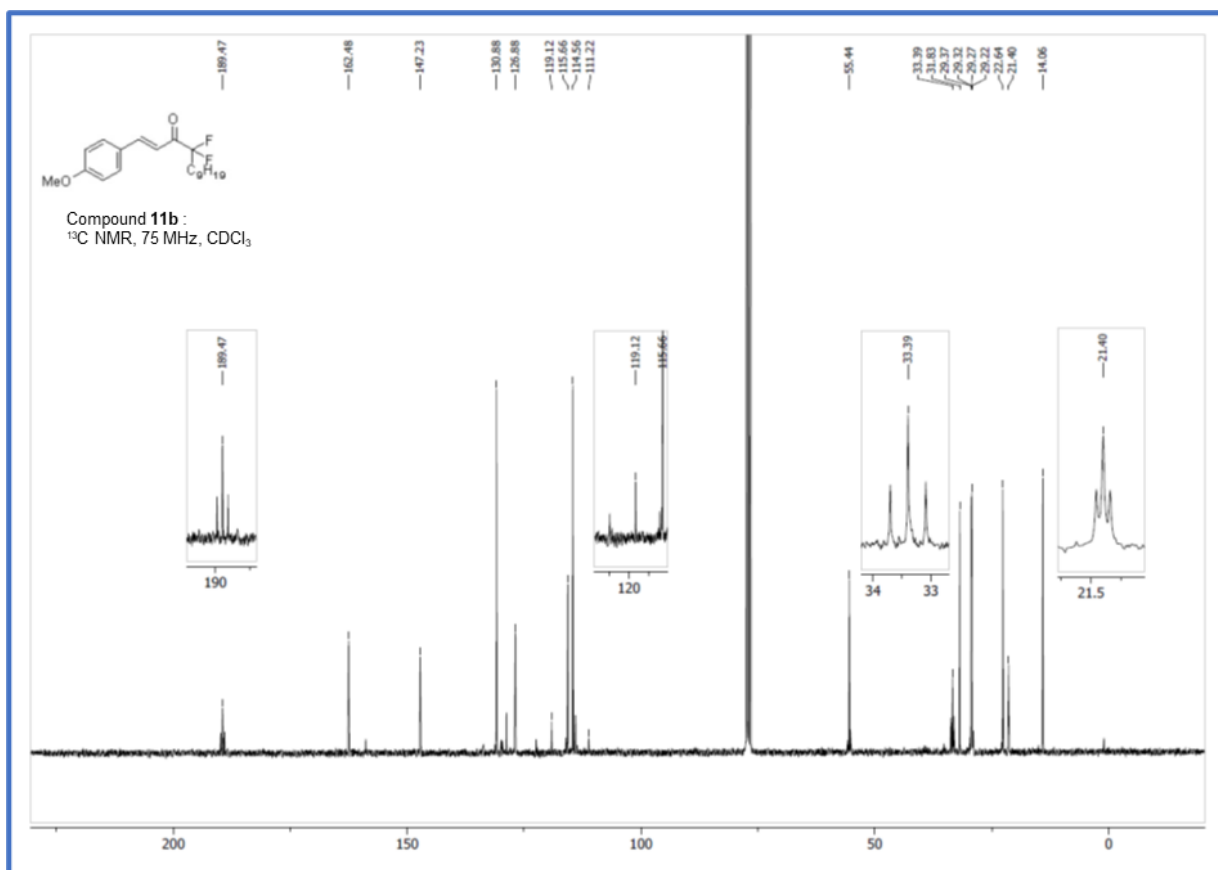
NMR spectra of 11a



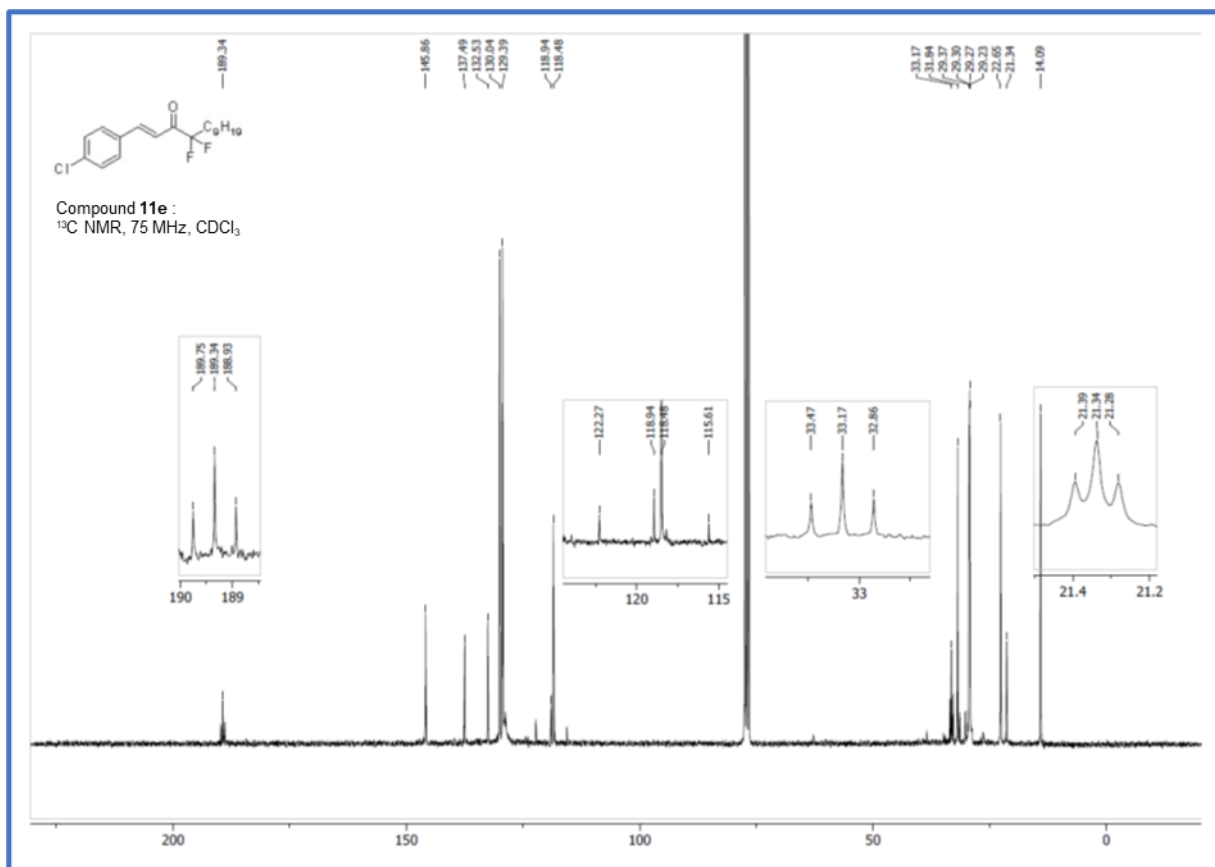
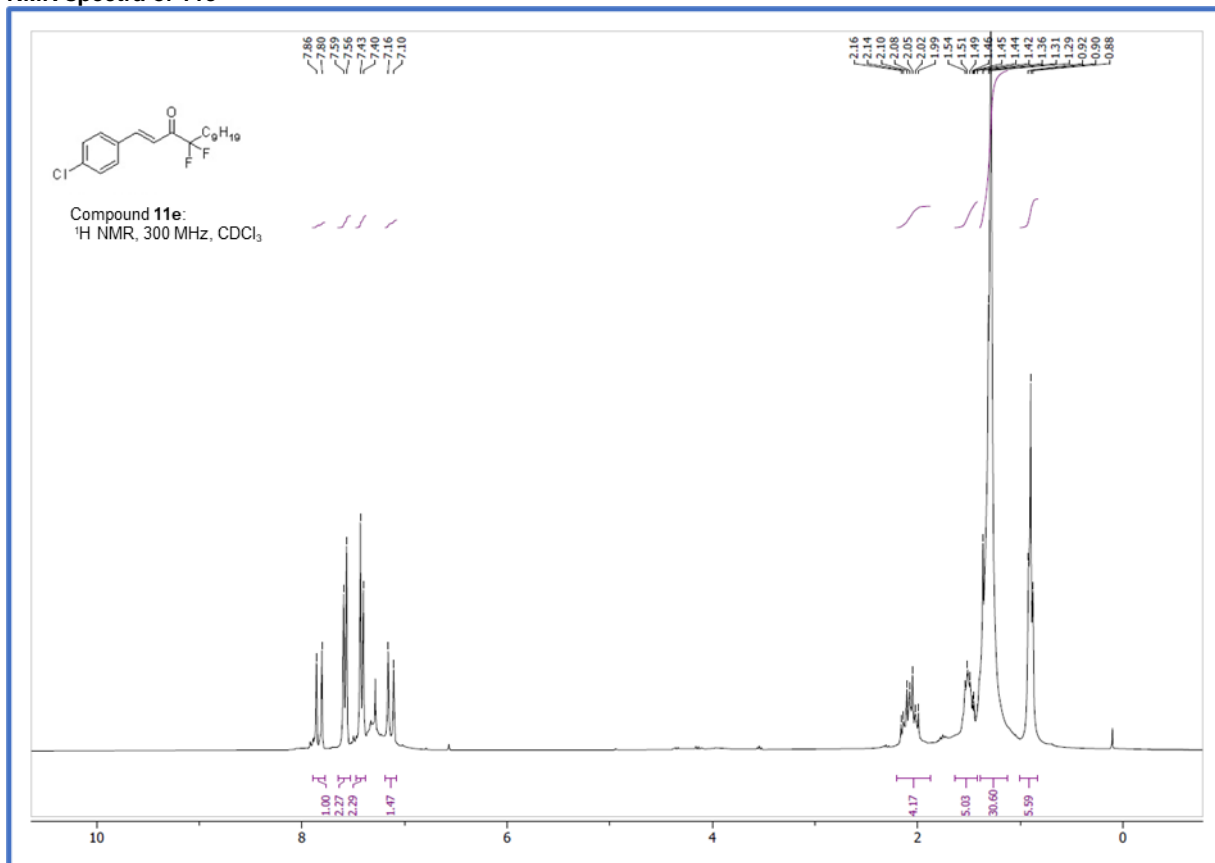


NMR spectra of 11b

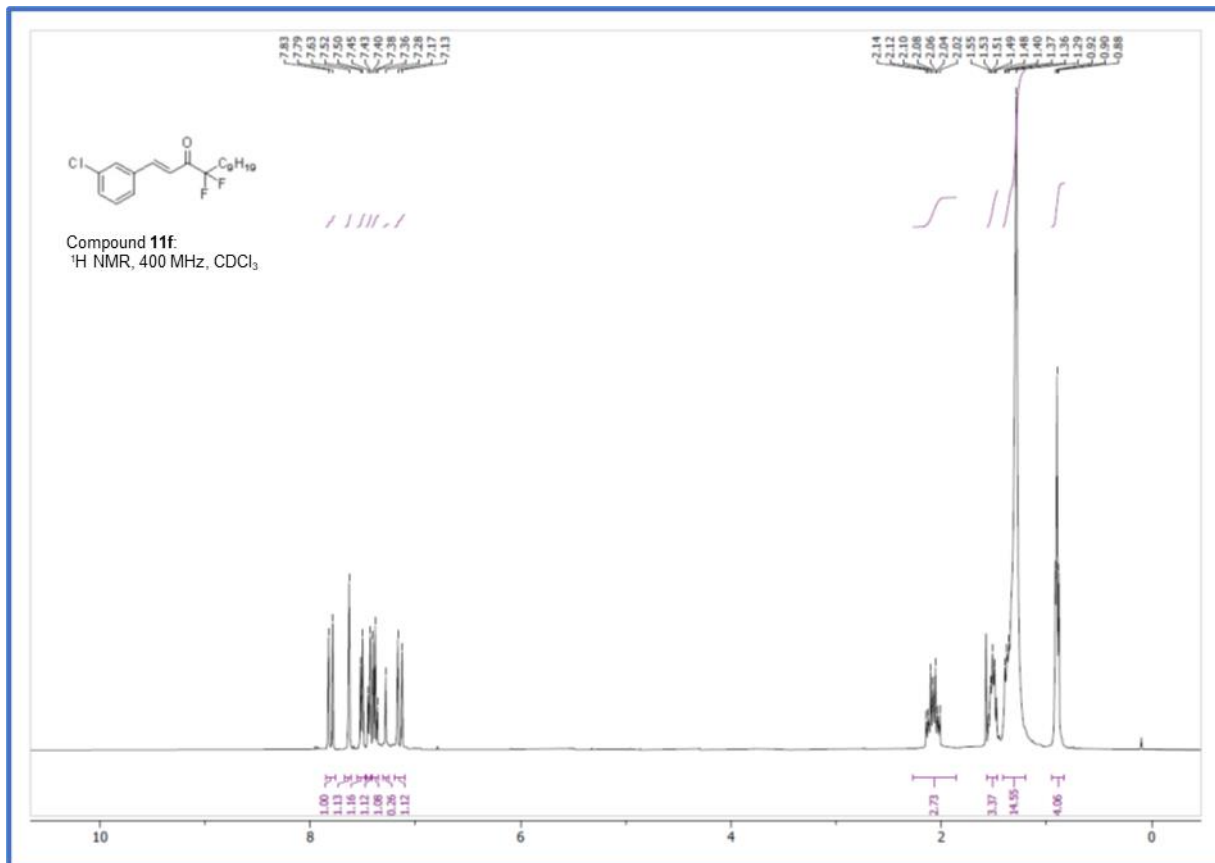
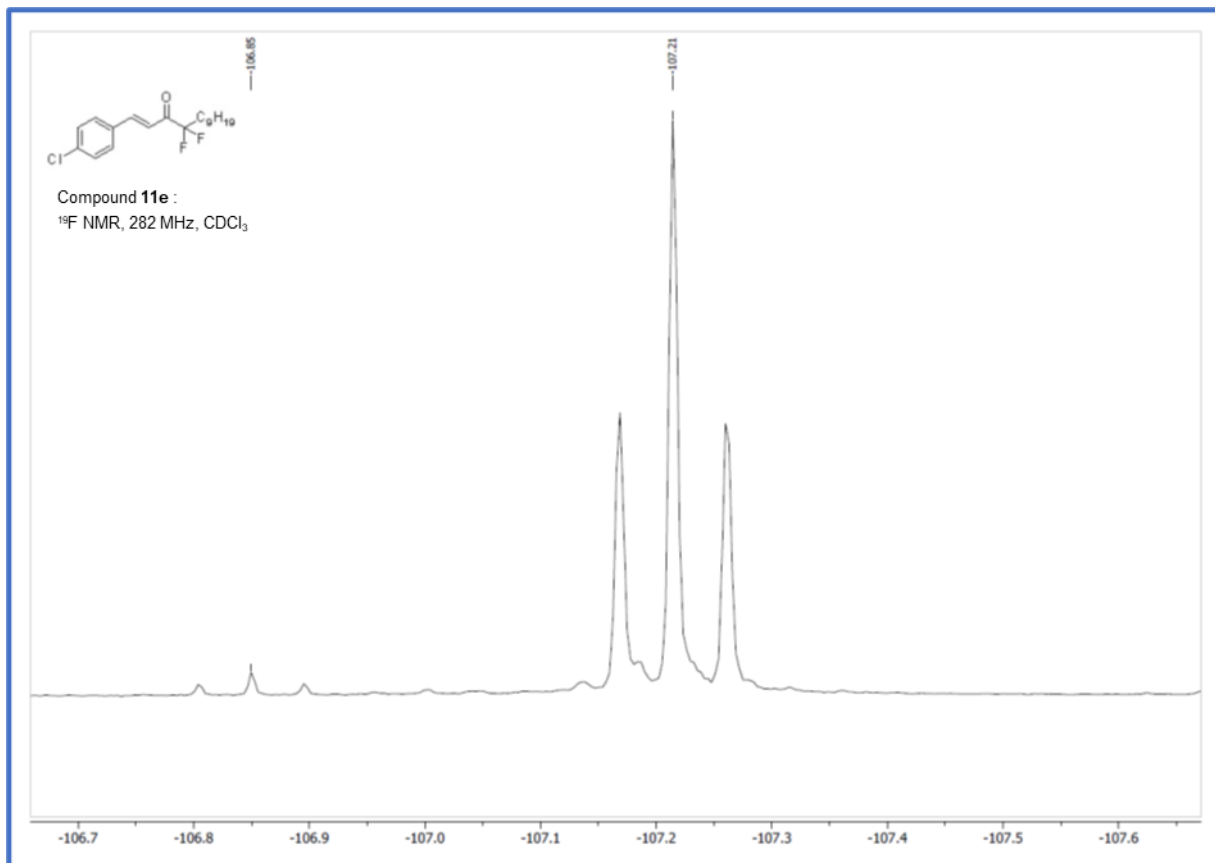


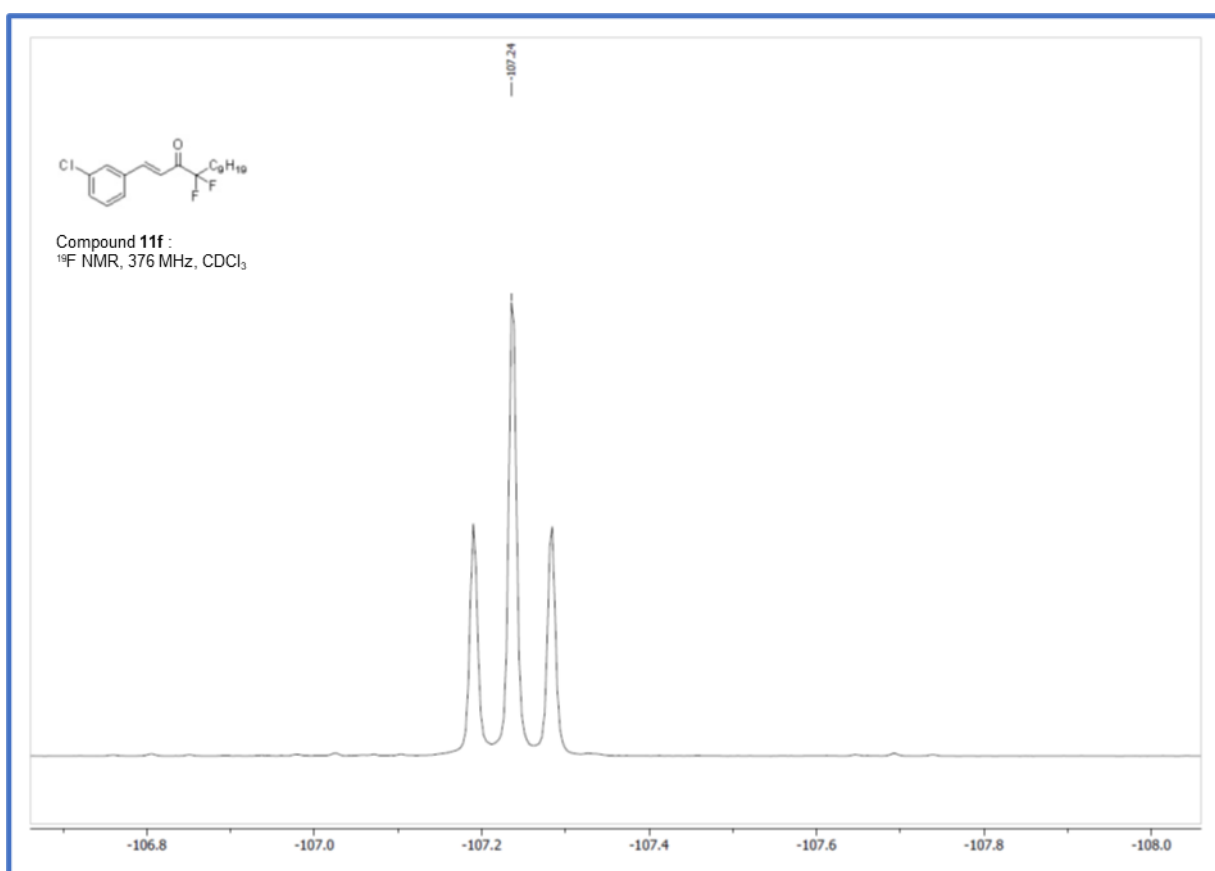
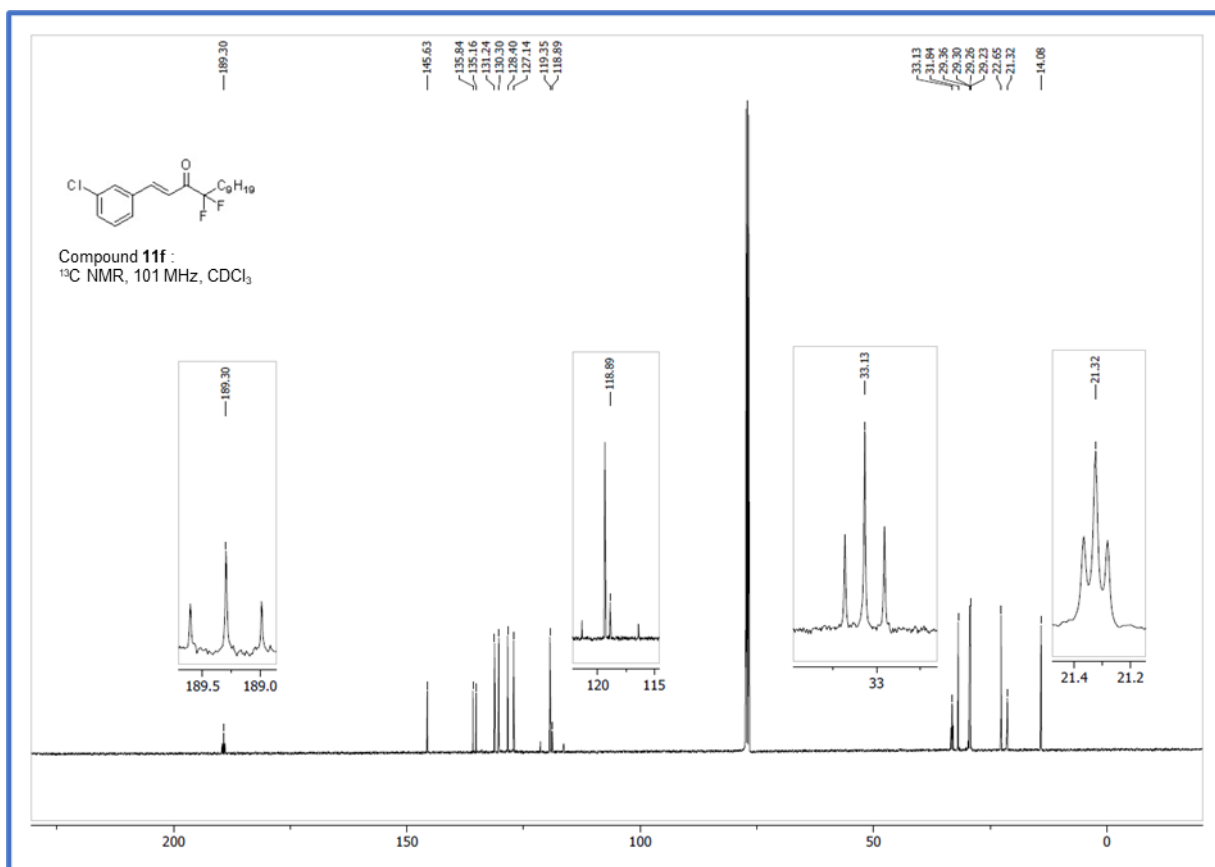


NMR spectra of 11e

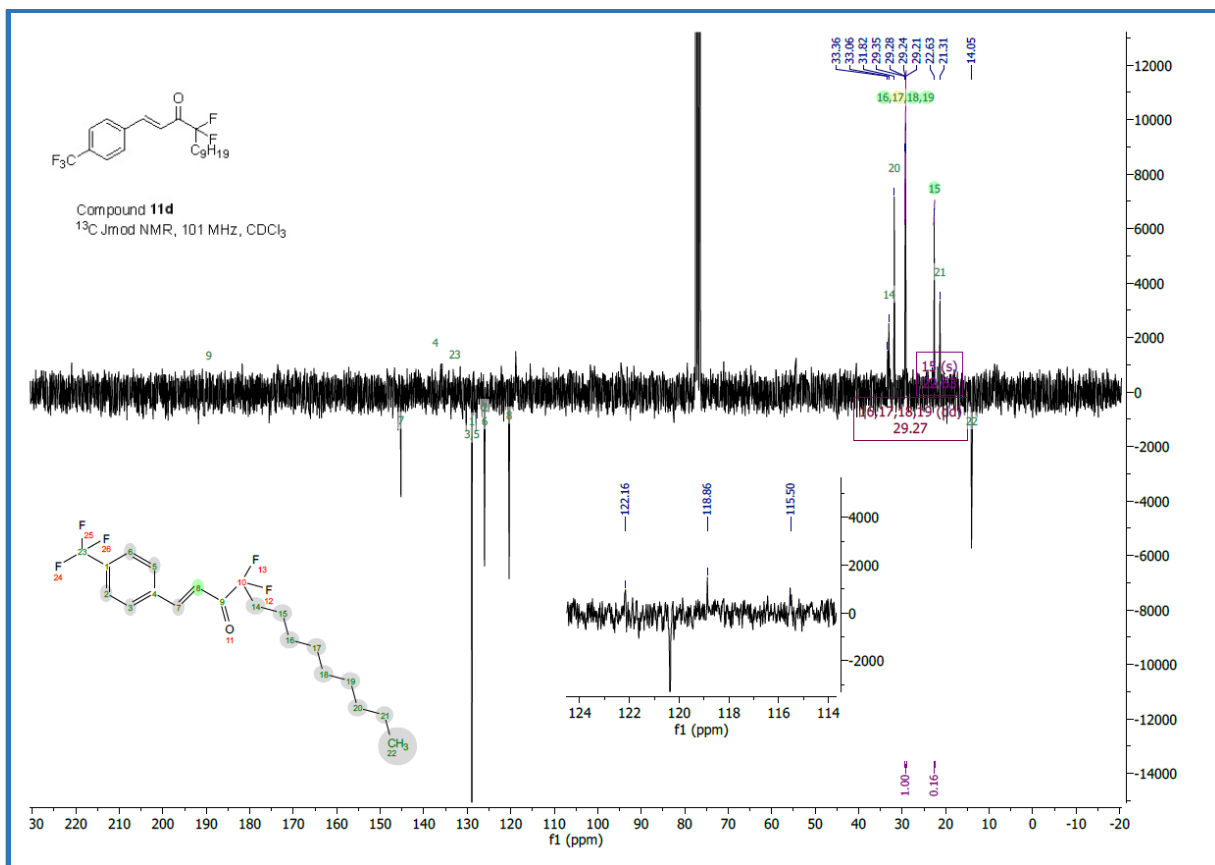
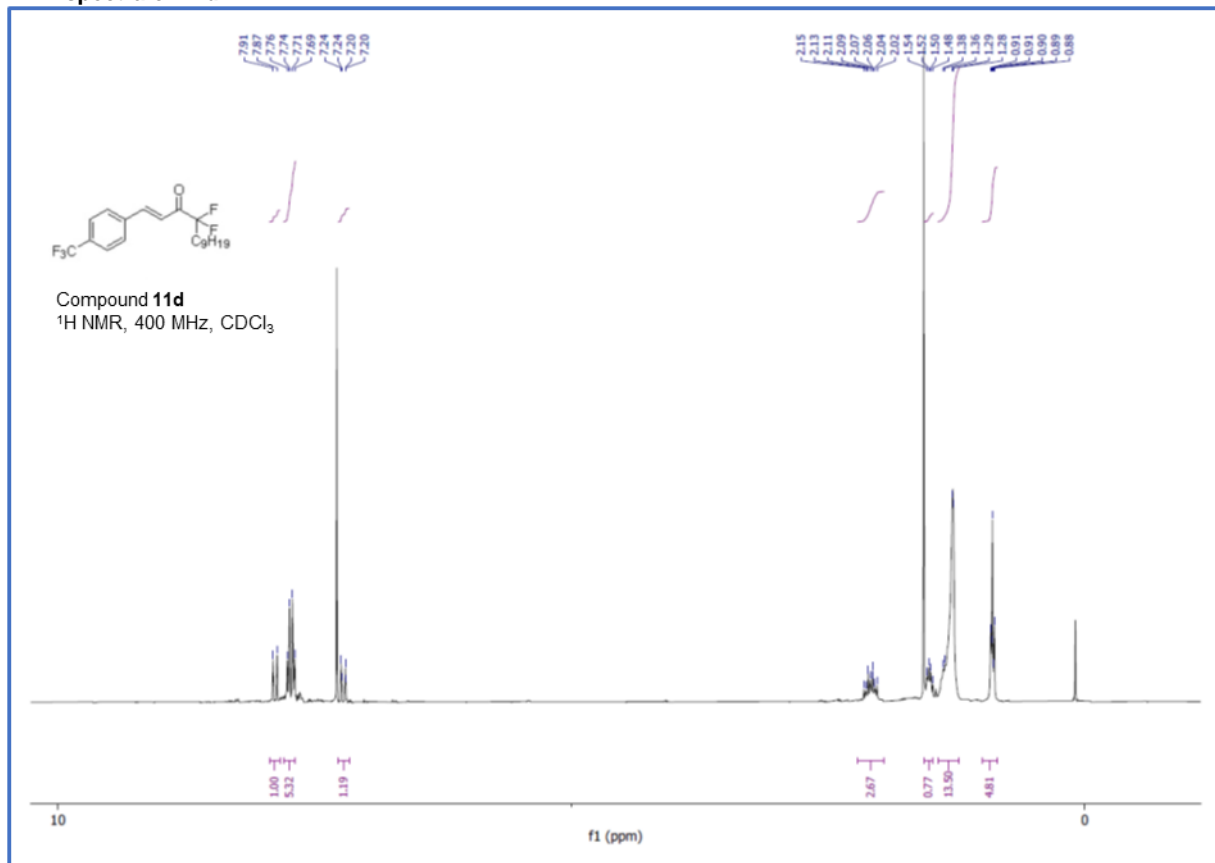


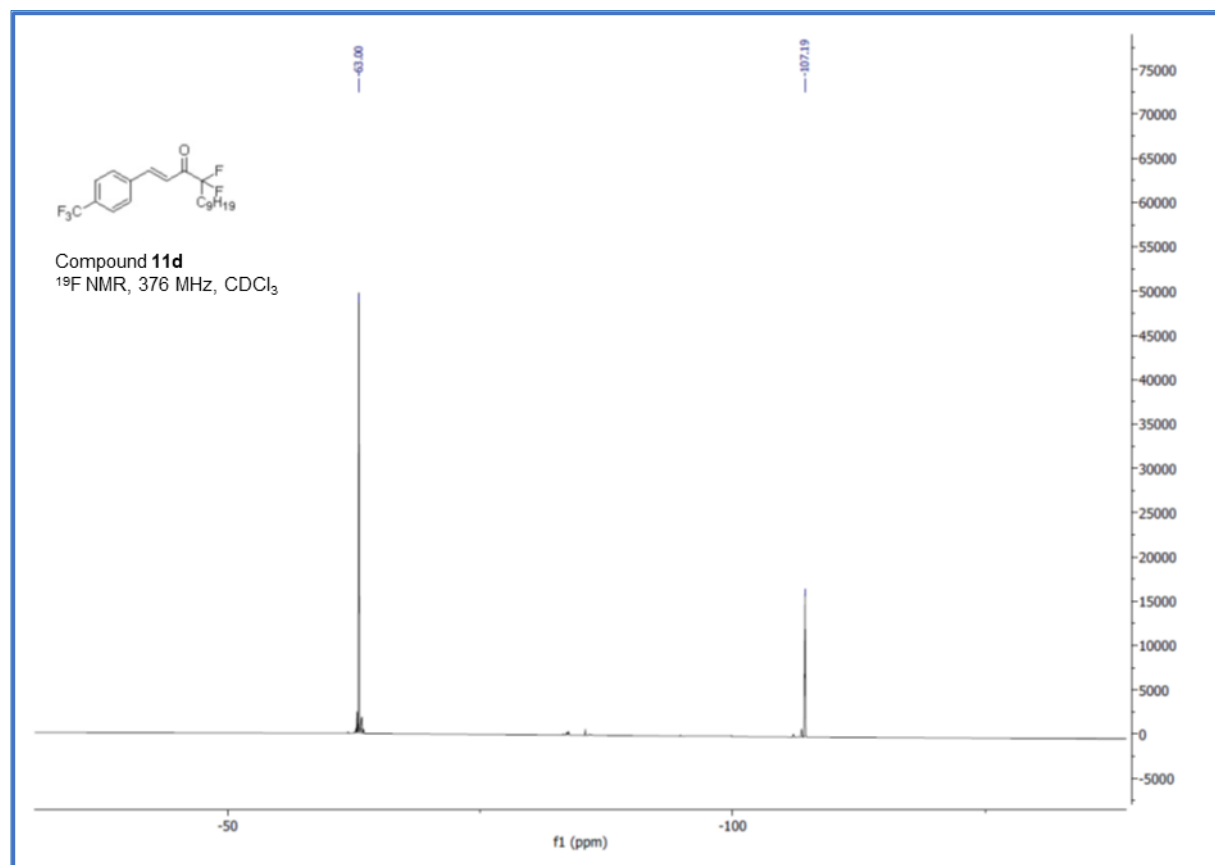
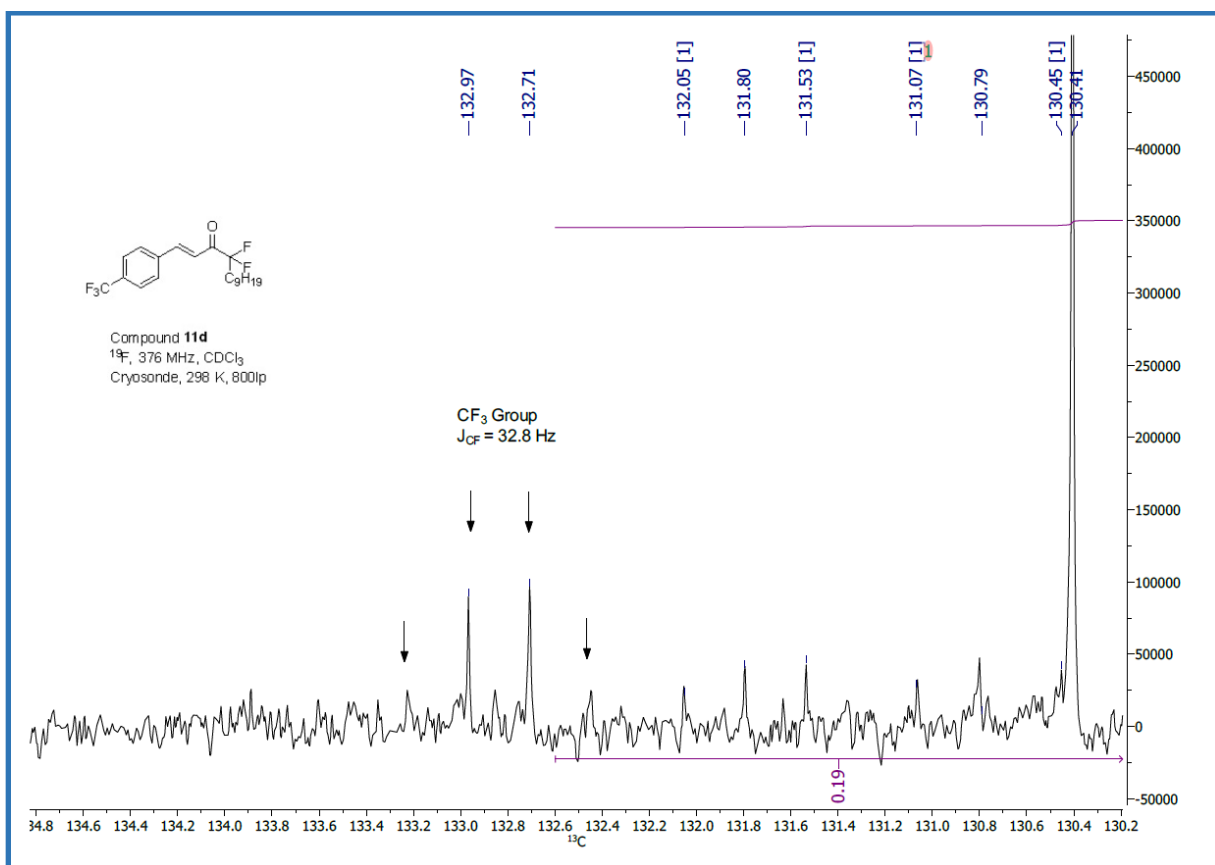
NMR spectra of 11f

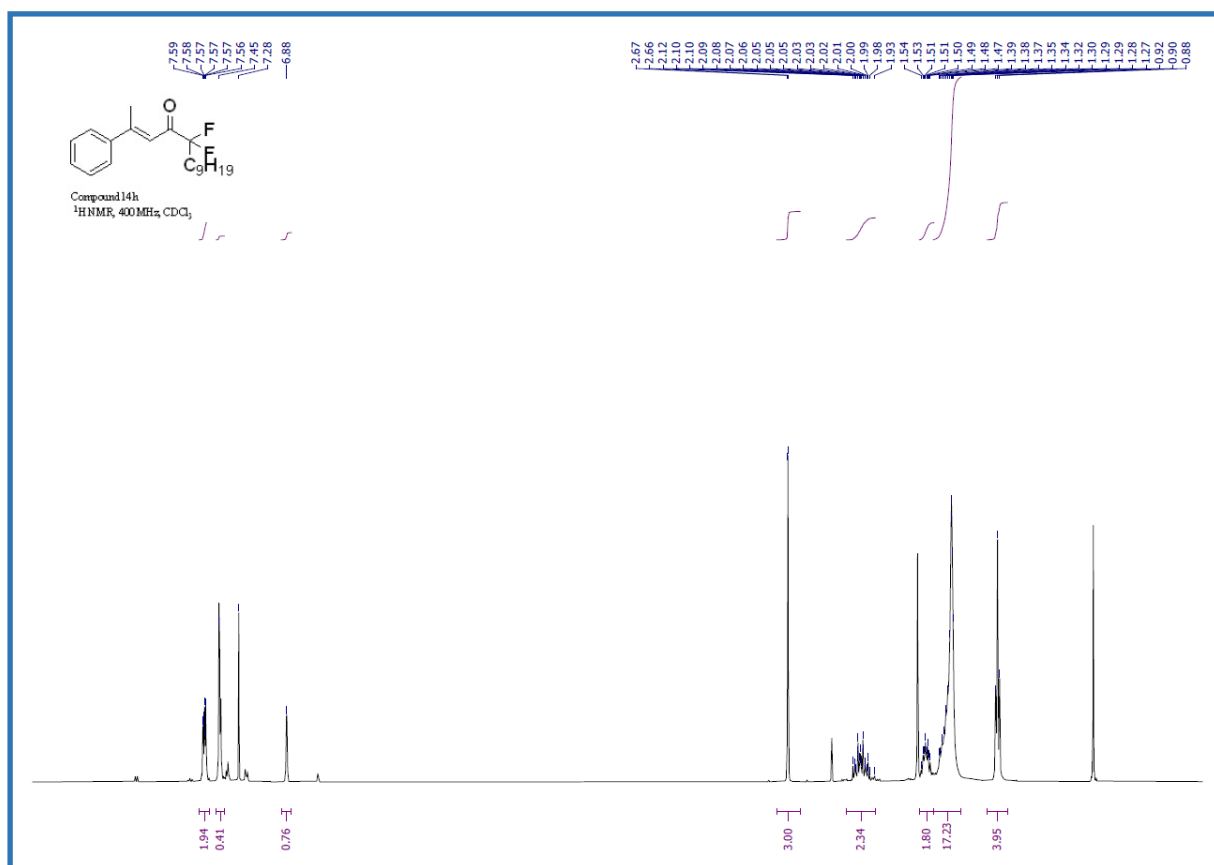
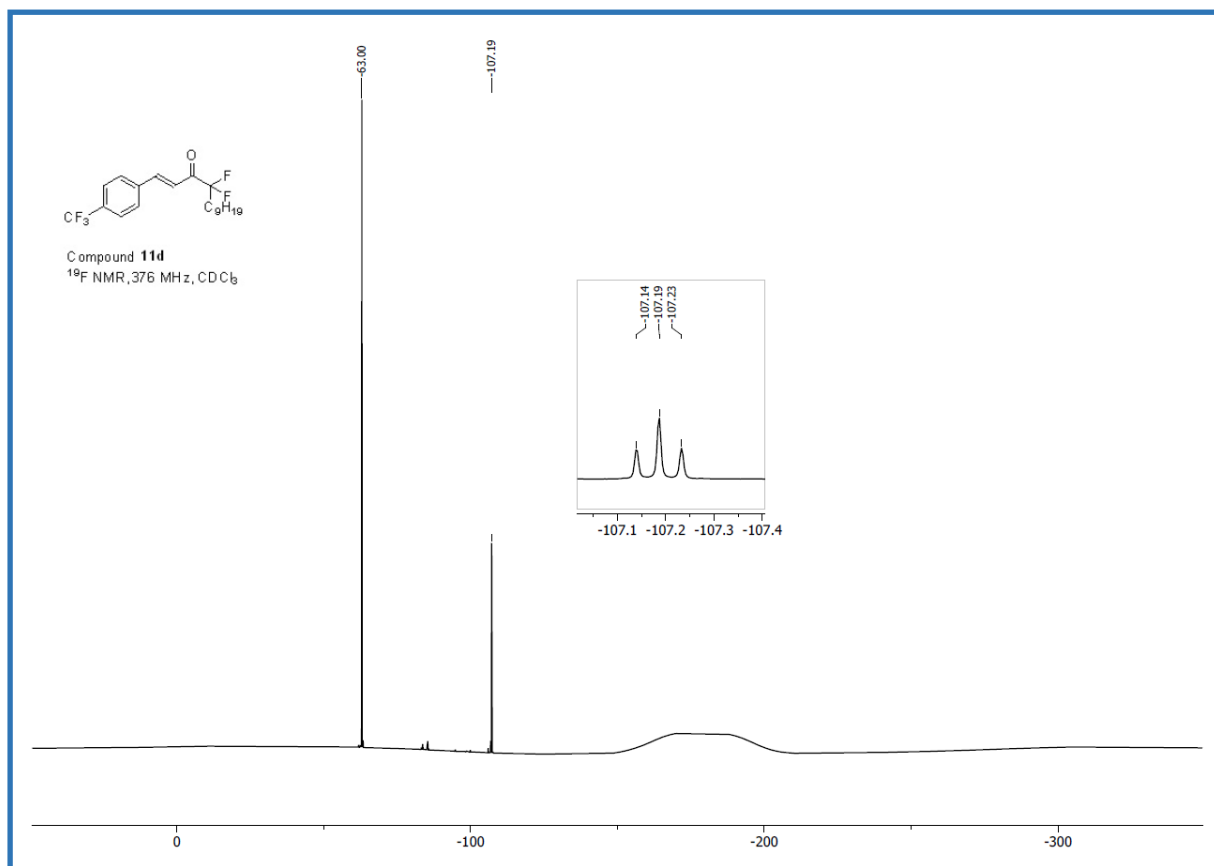


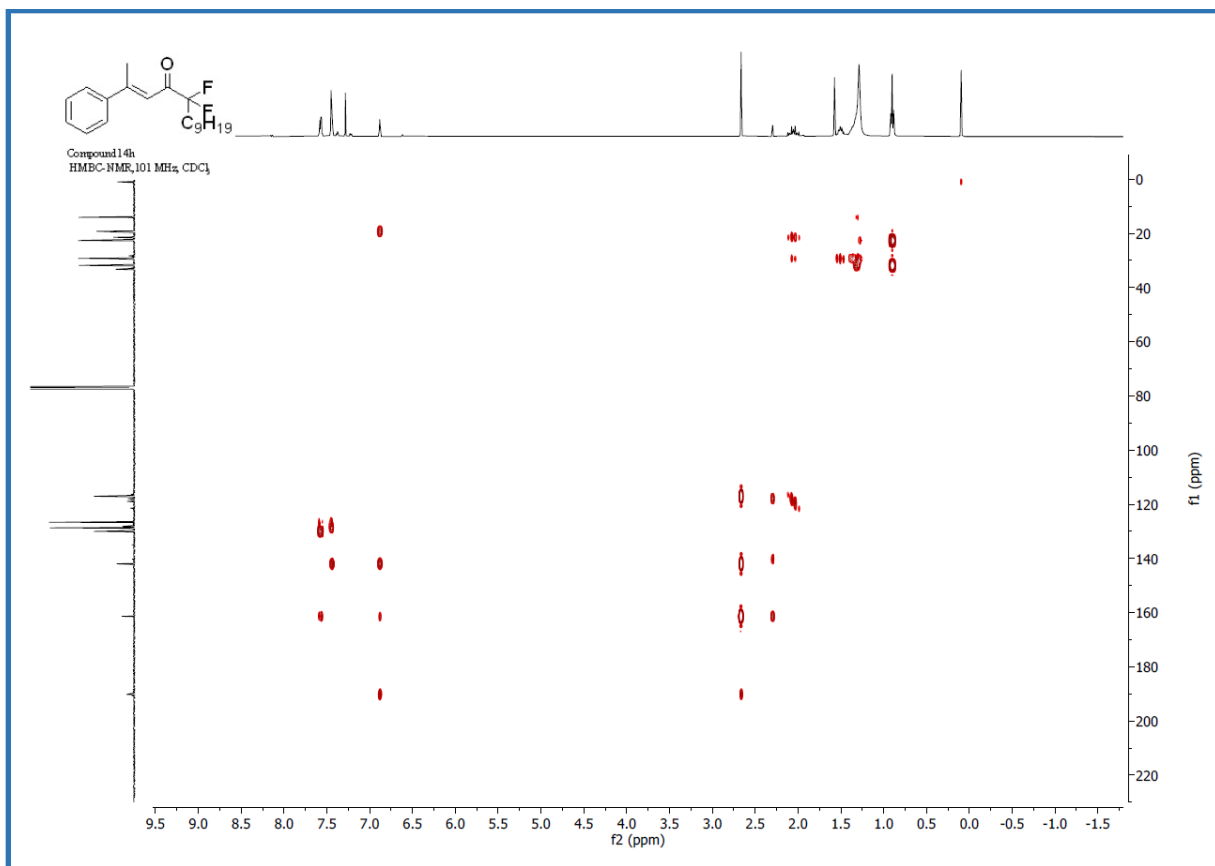
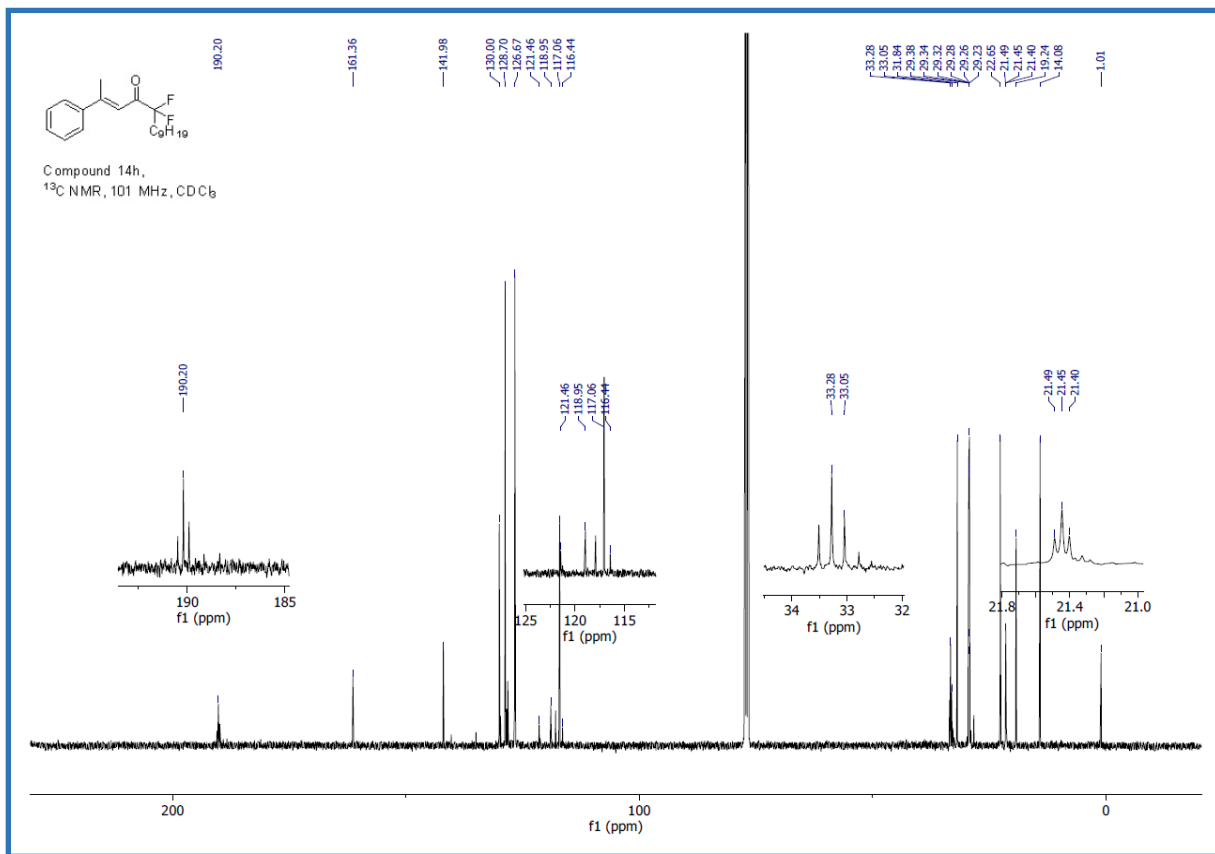


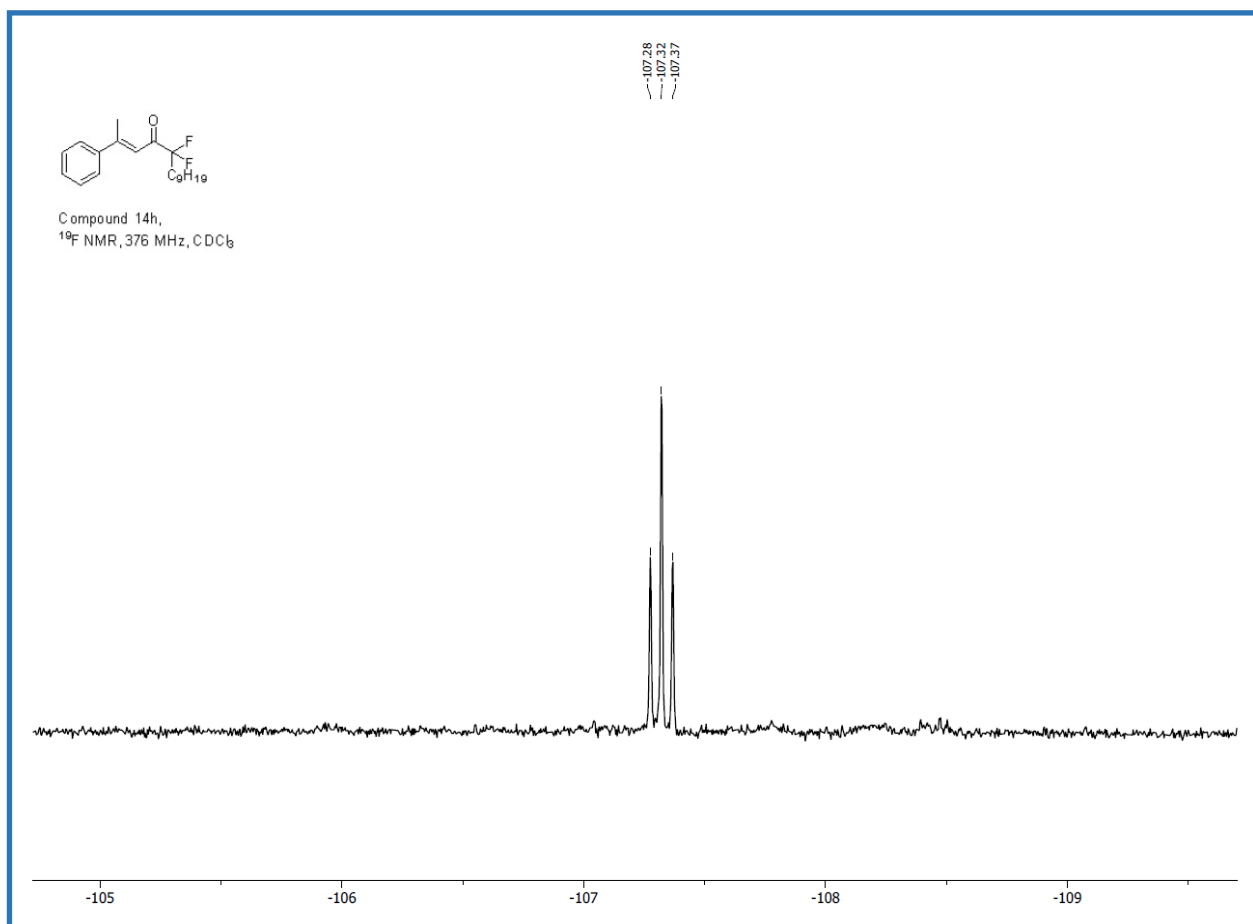
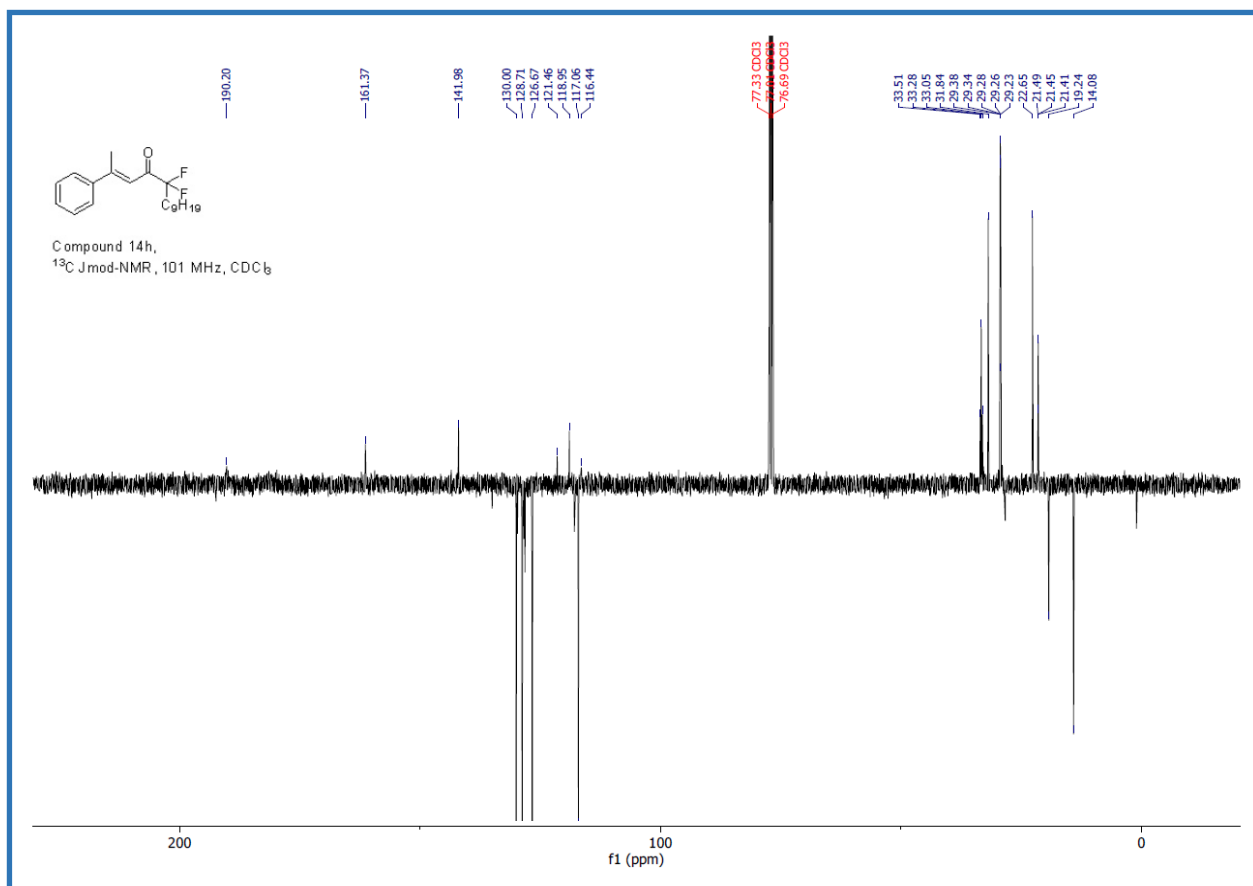
NMR spectra of 11d

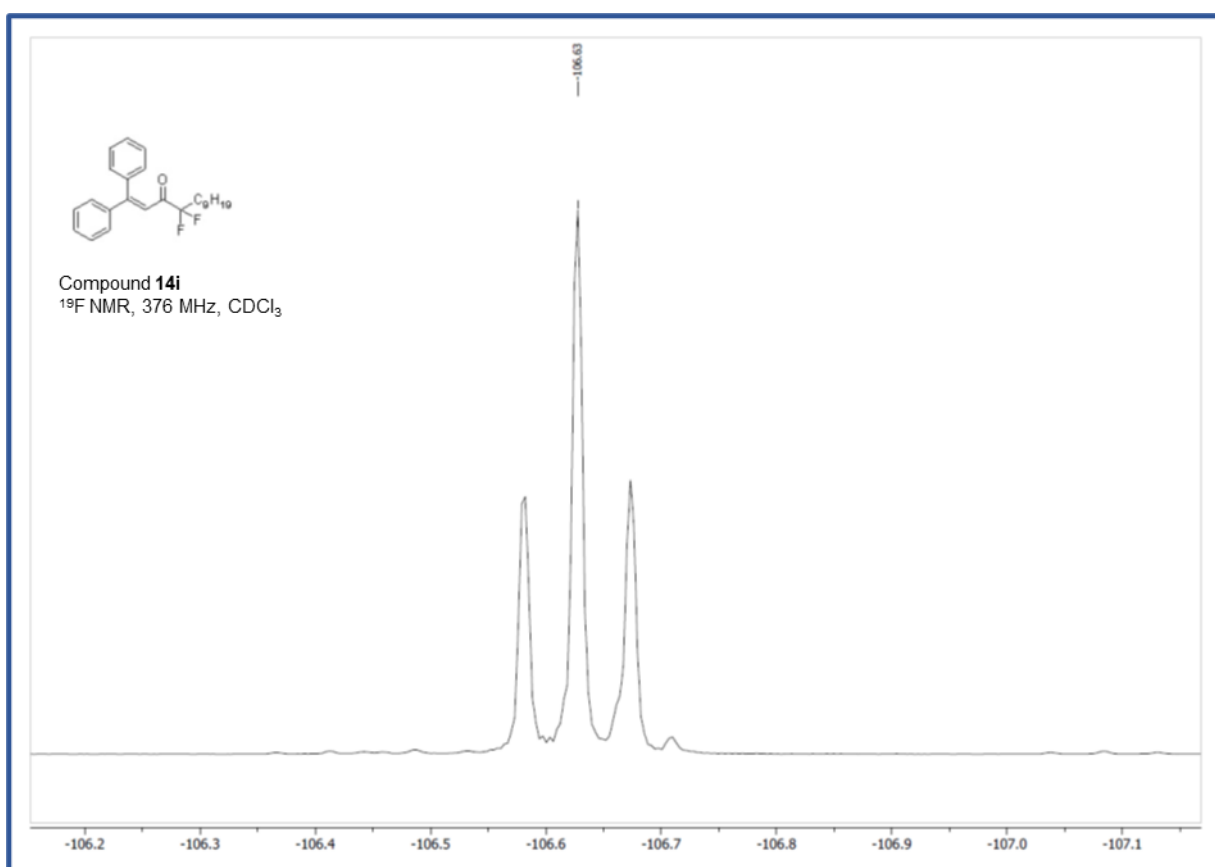
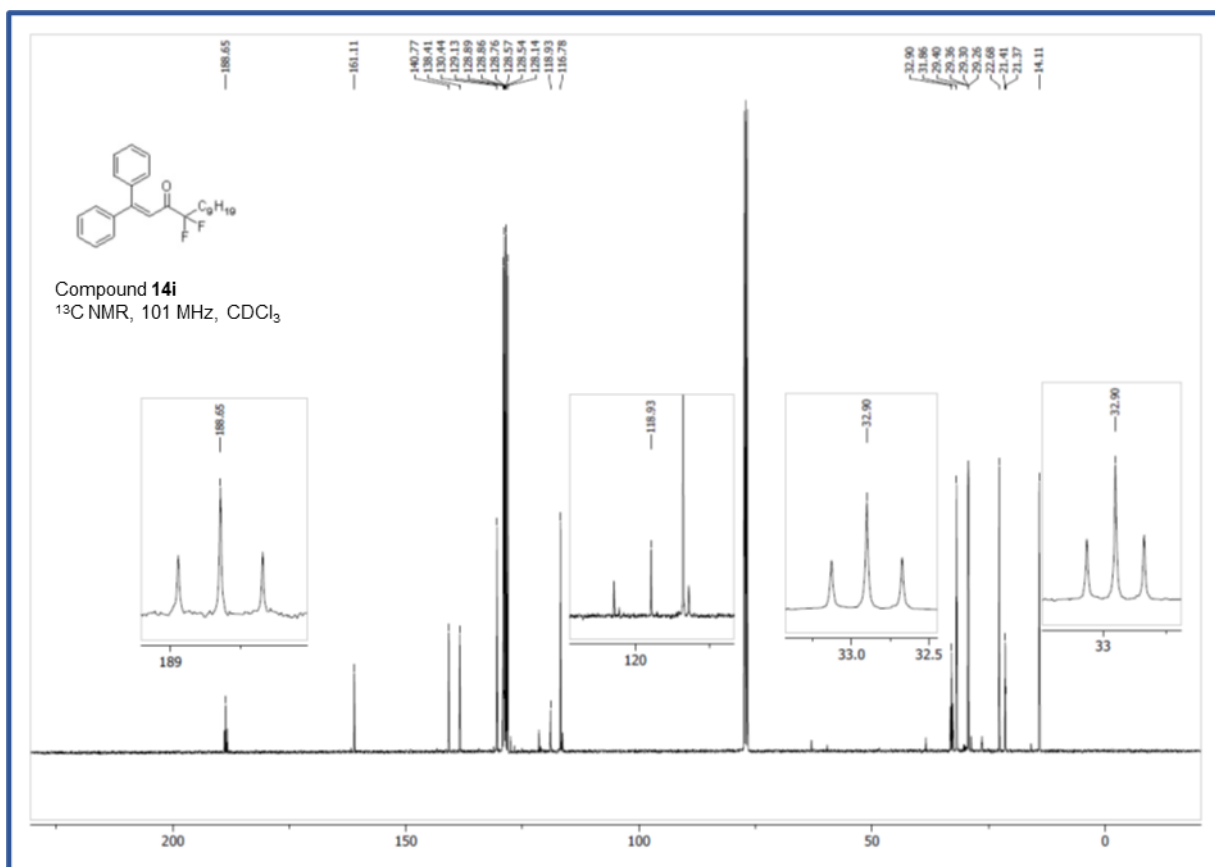




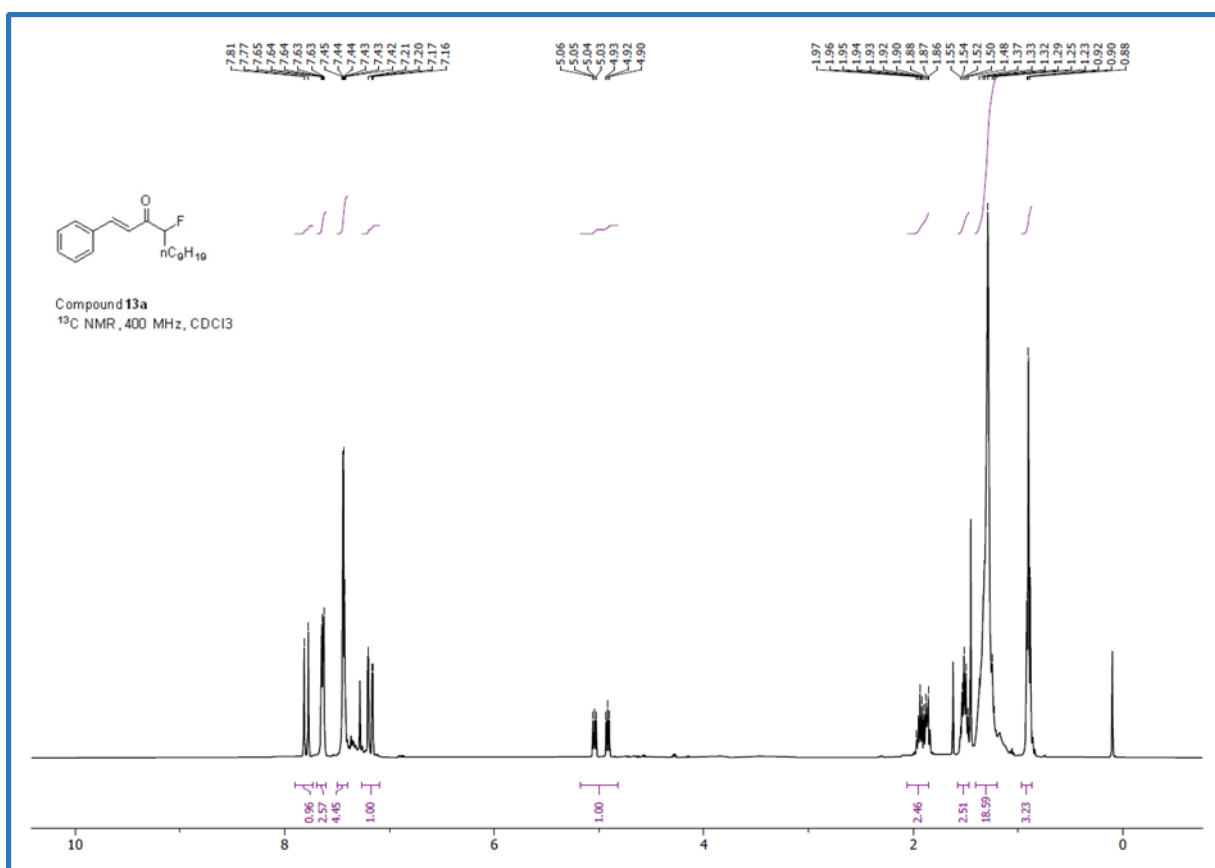
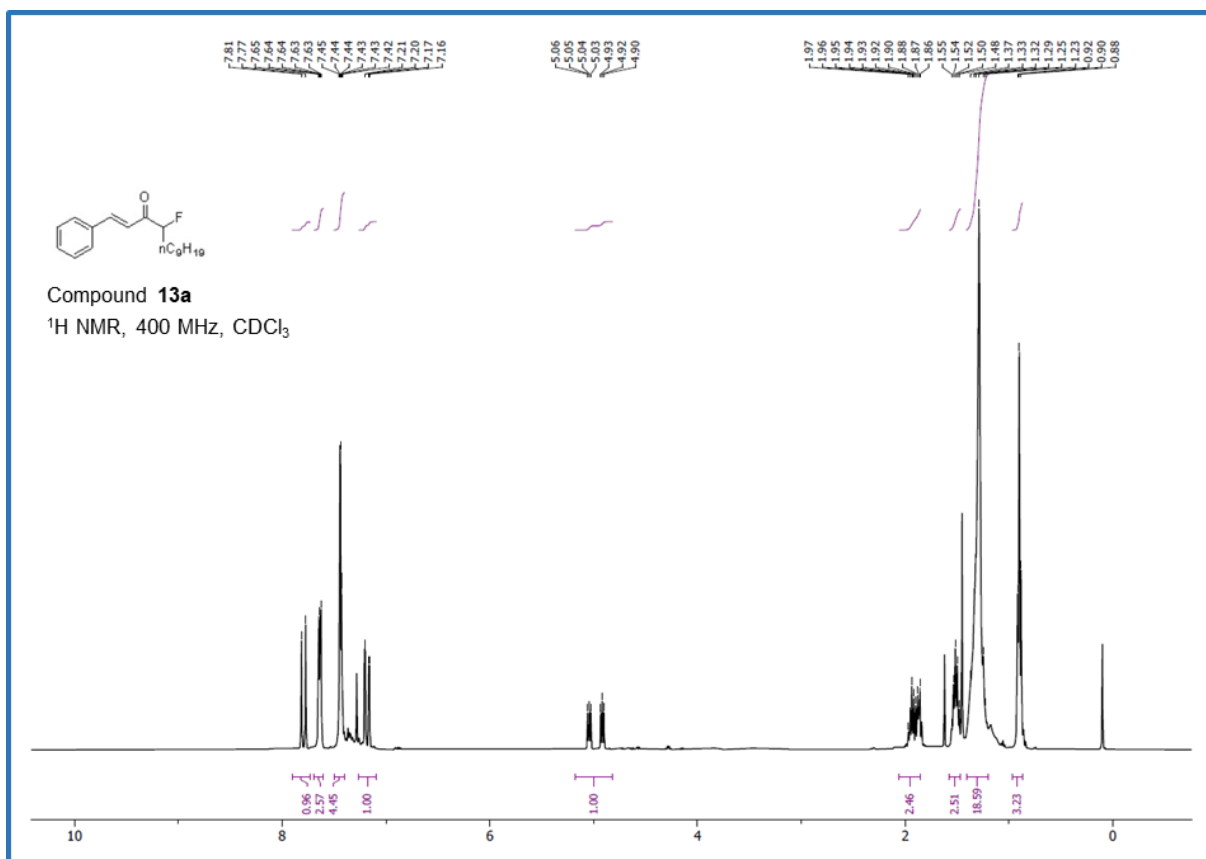


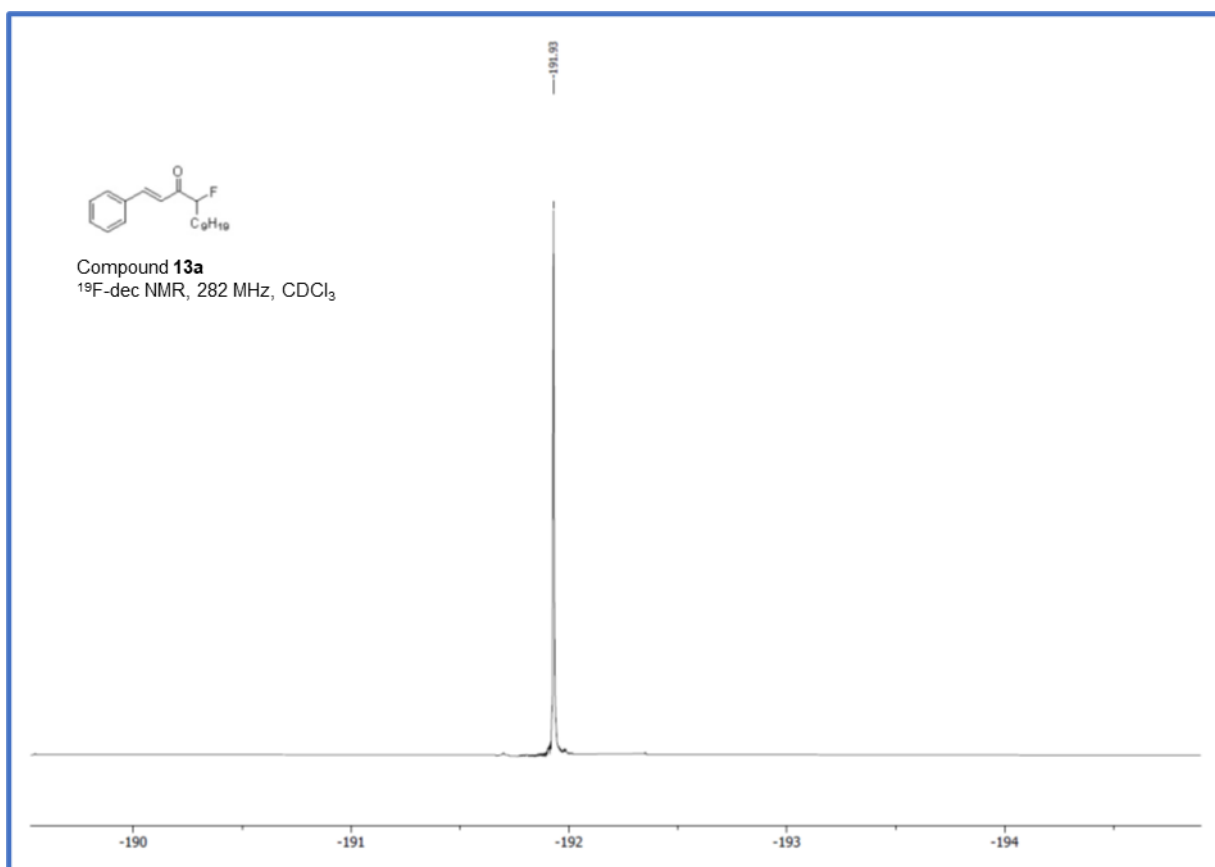
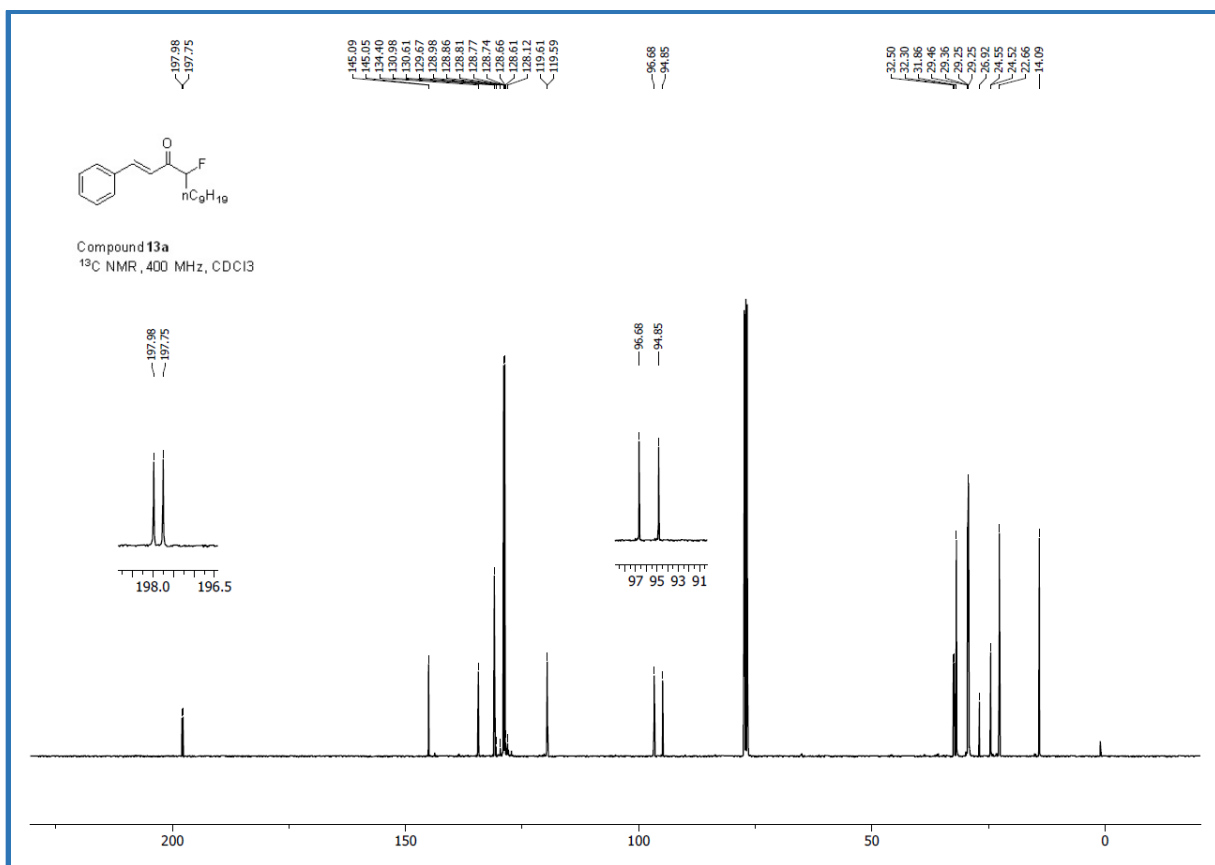


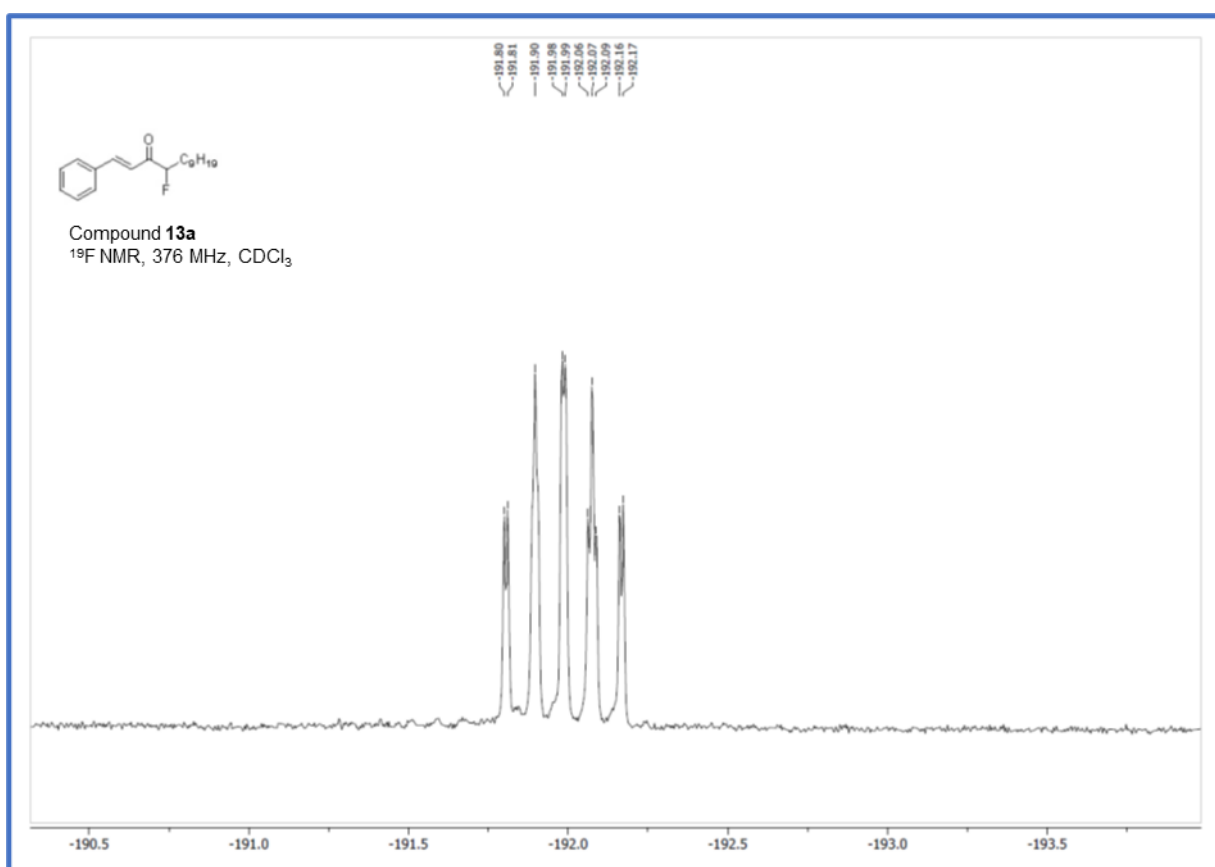
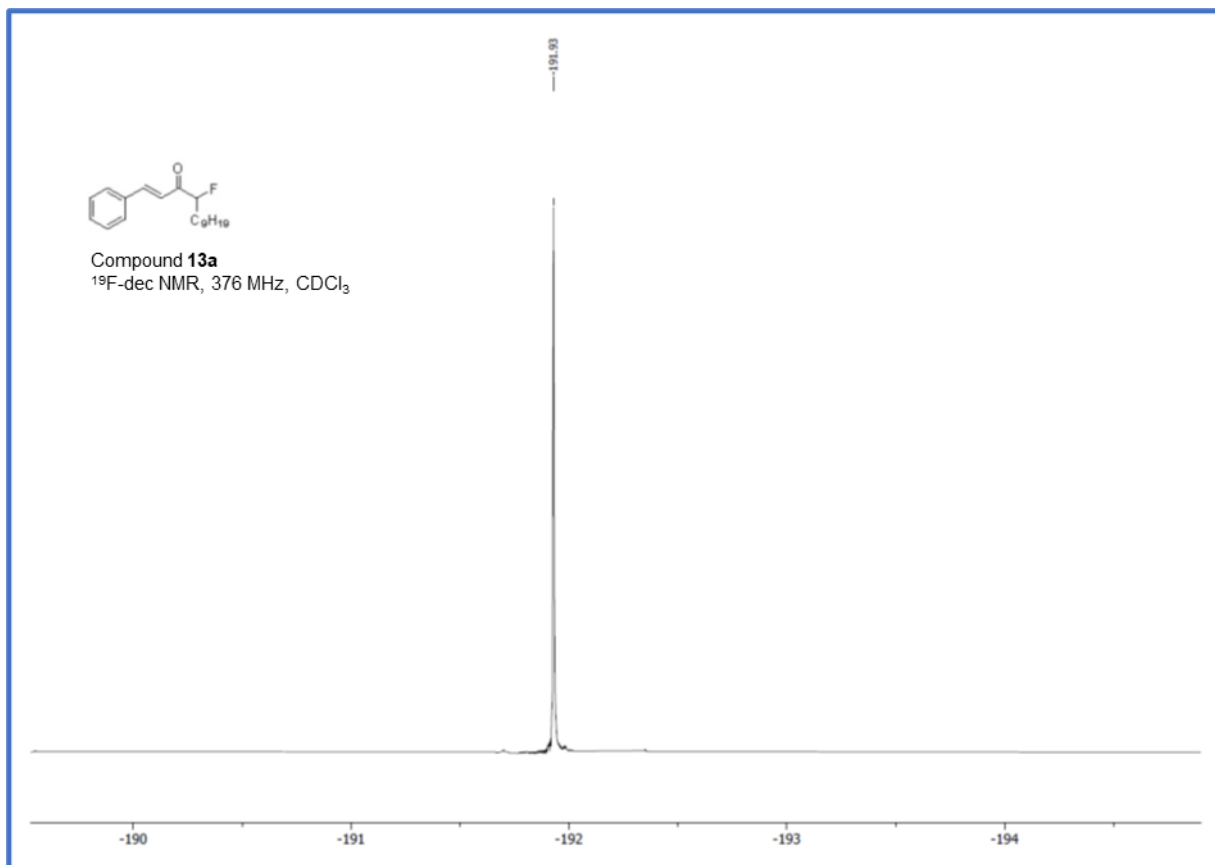




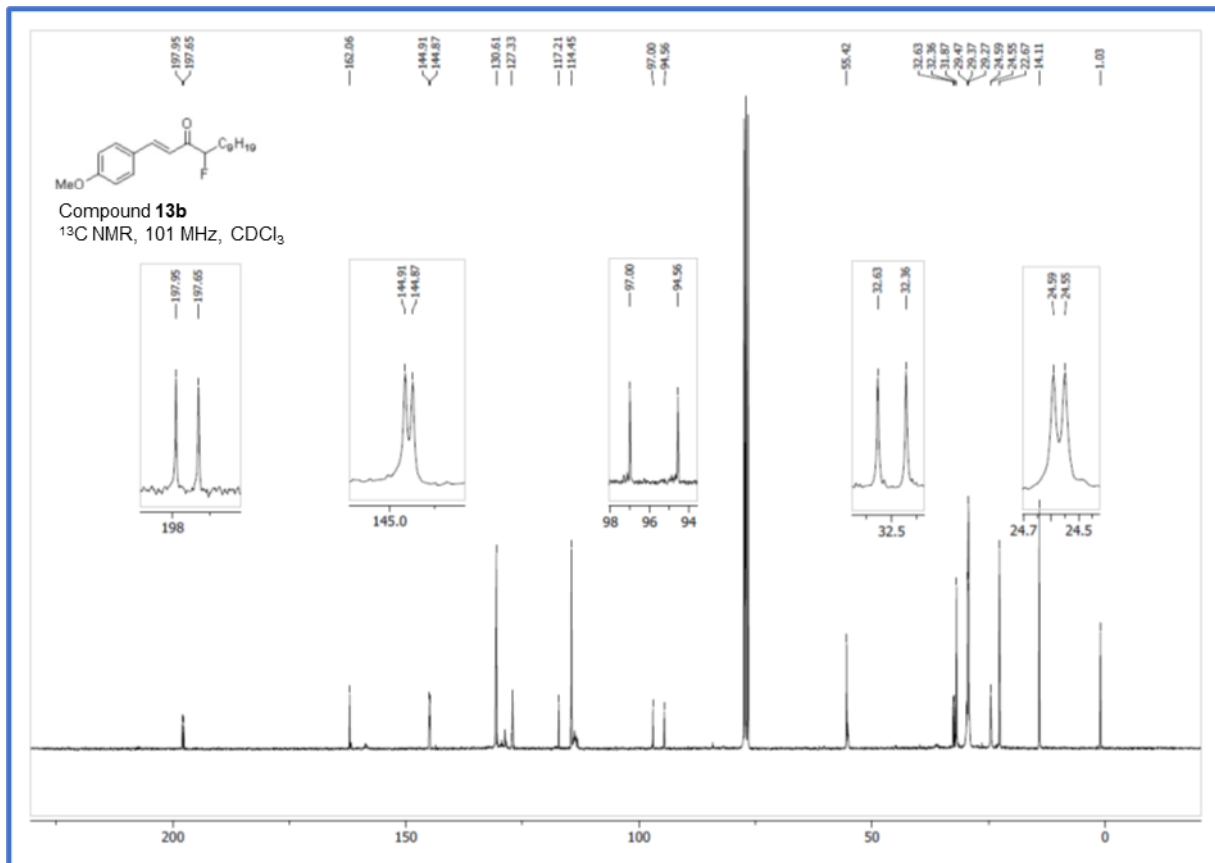
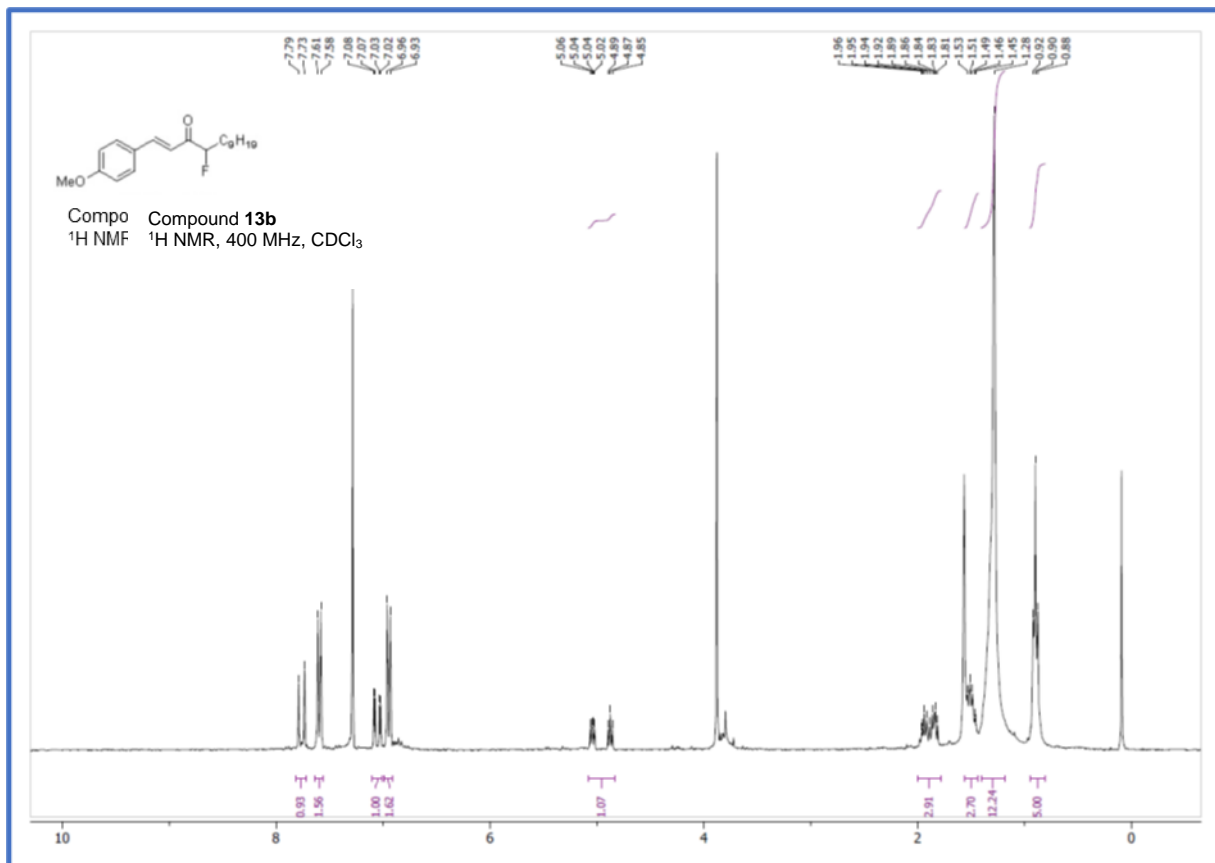
NMR spectra of 13a

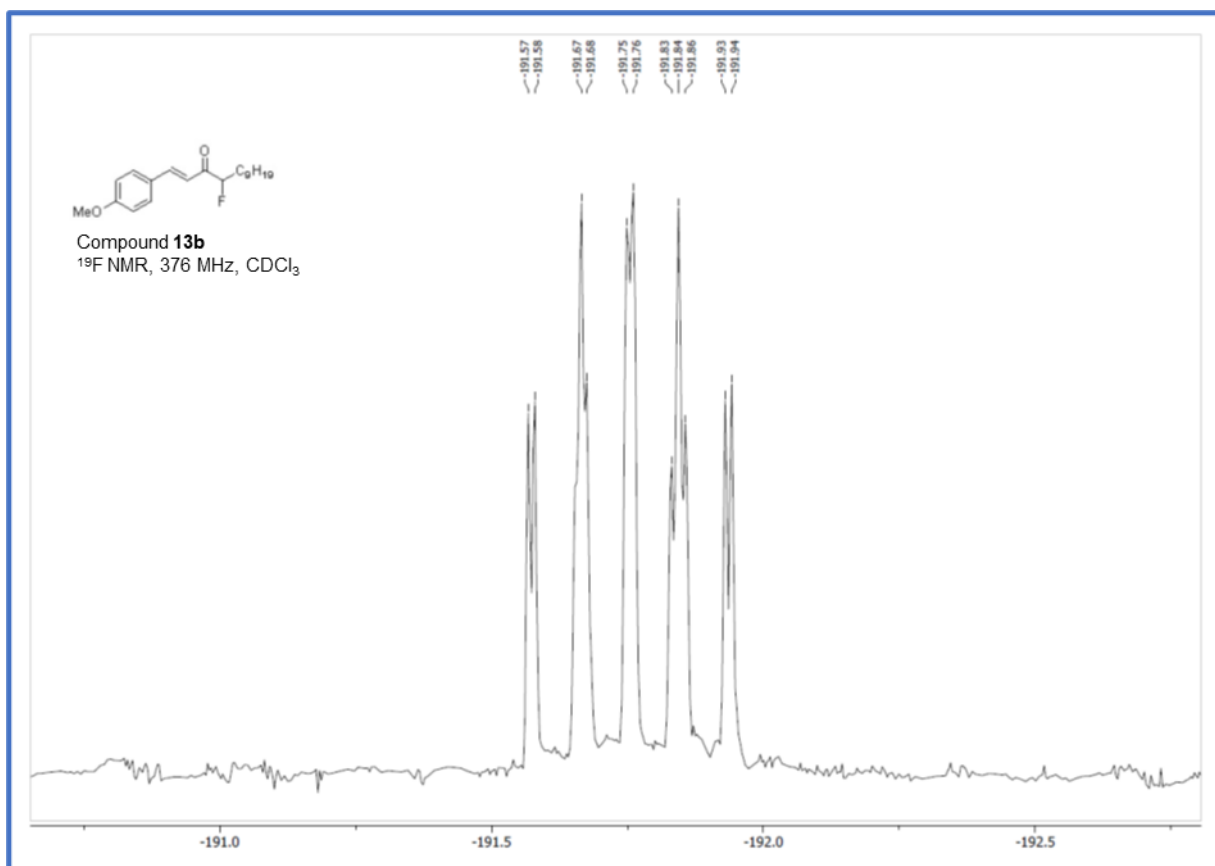




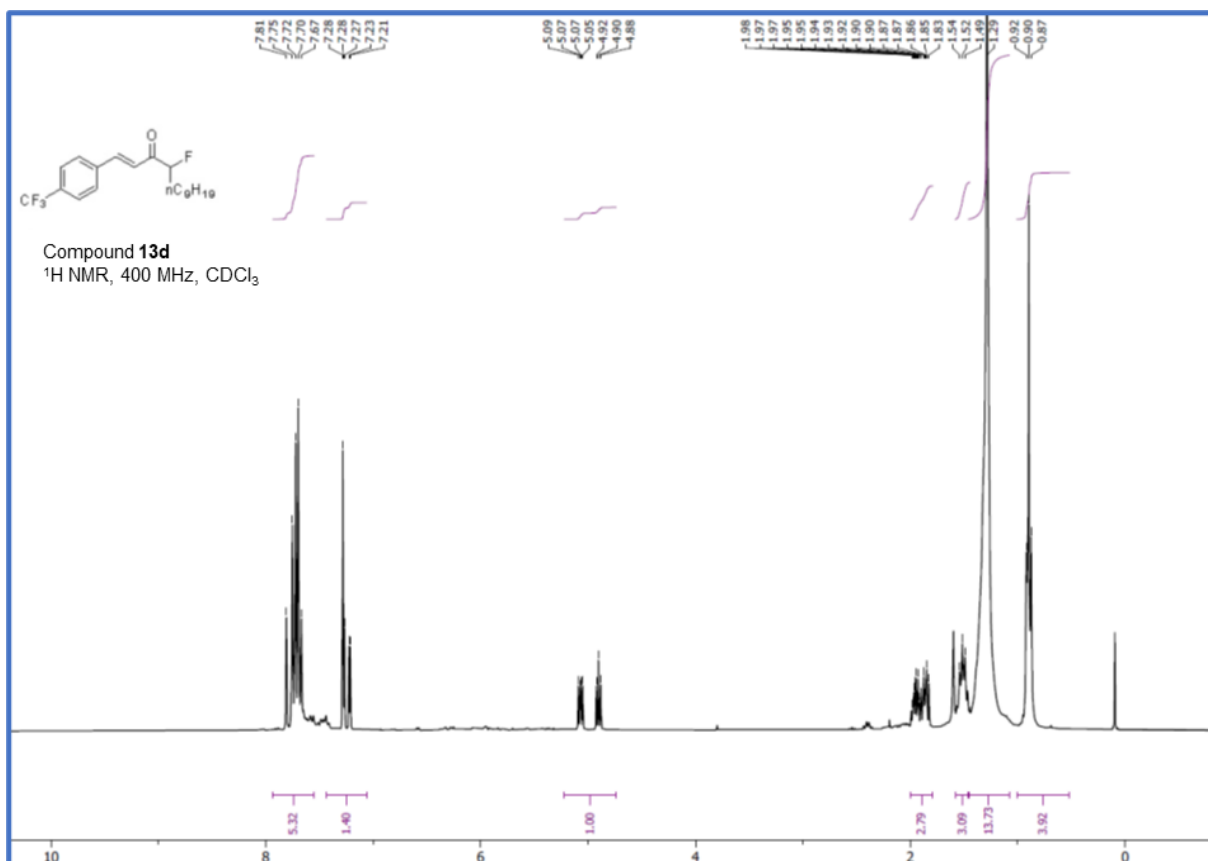


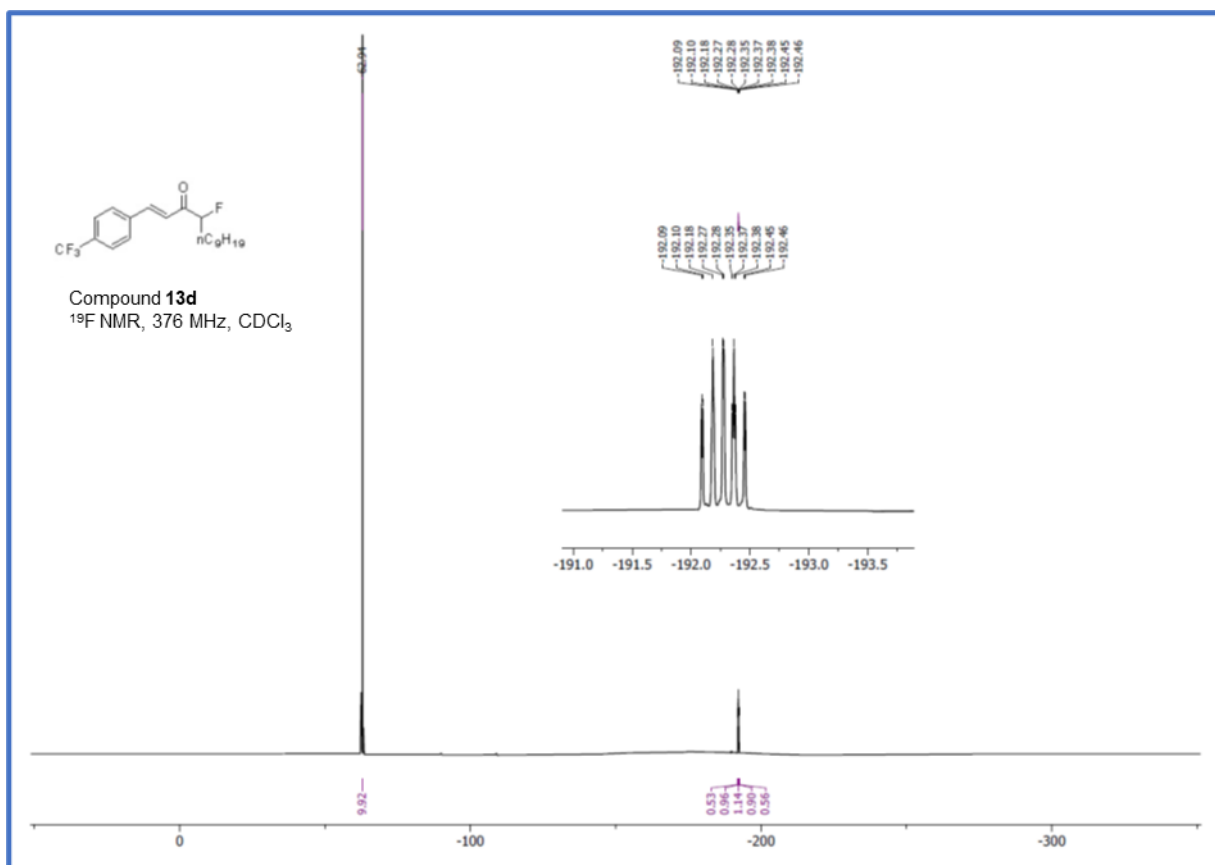
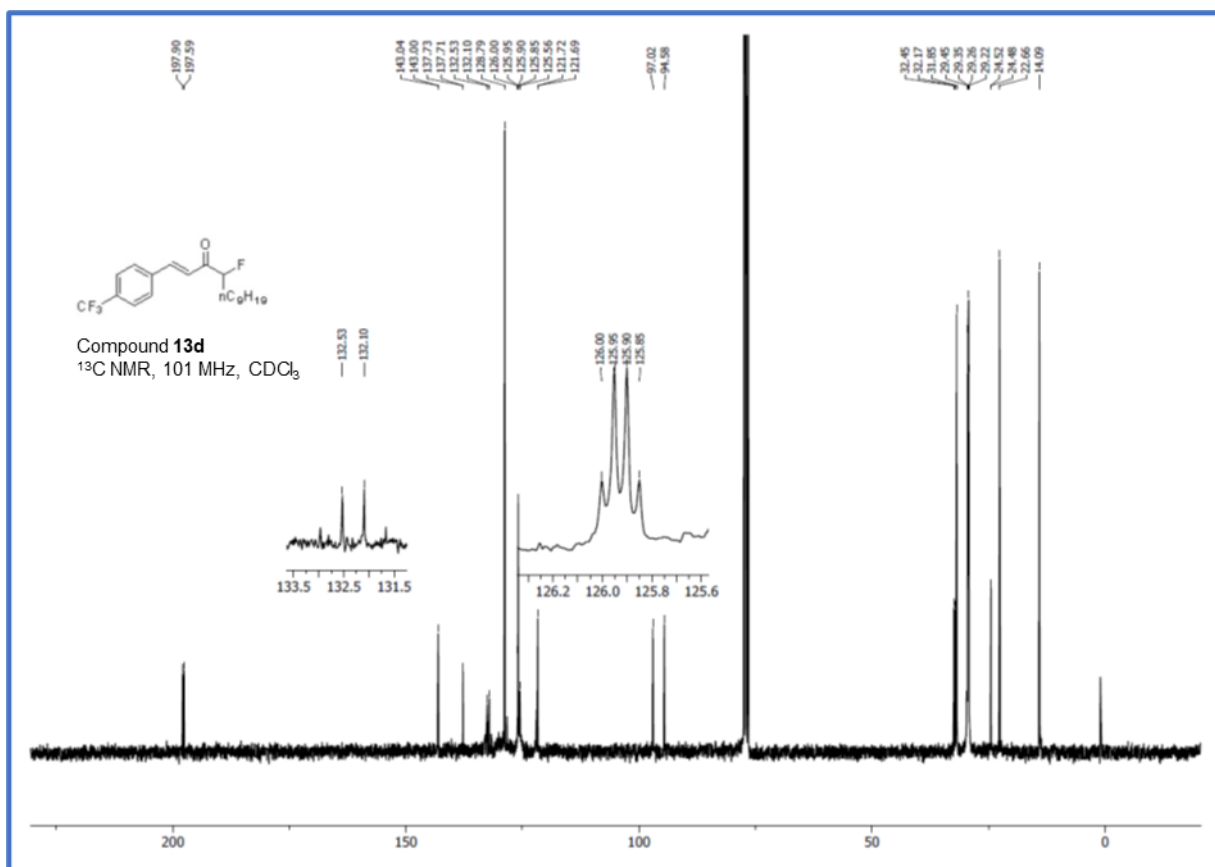
NMR spectra of 13b



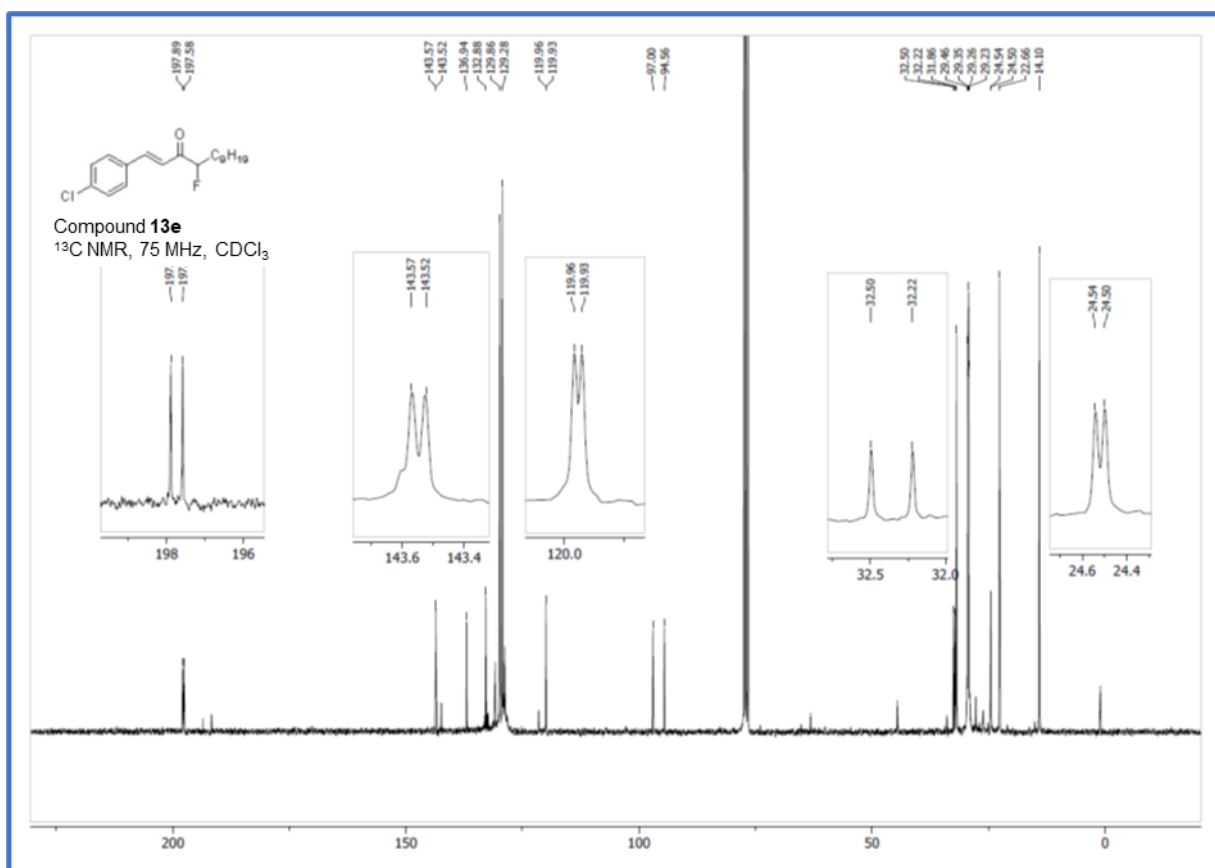
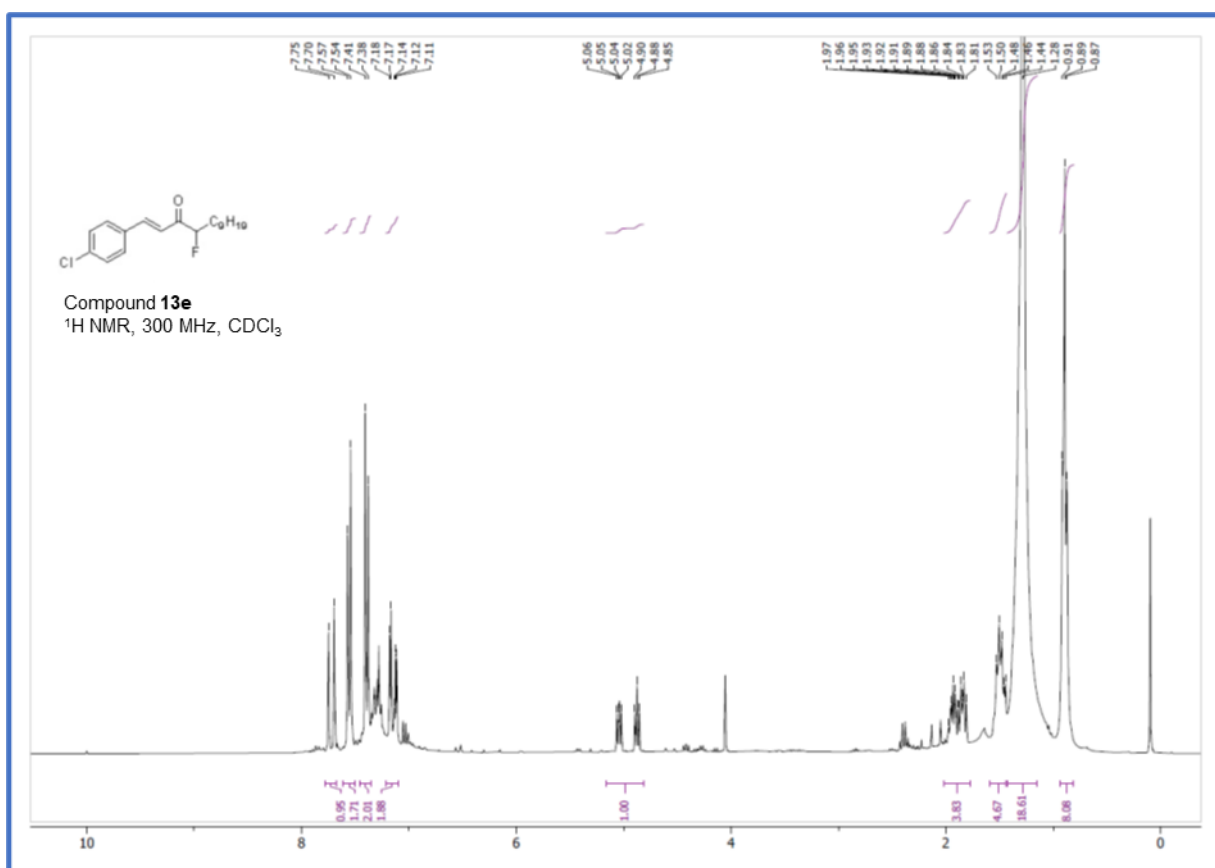


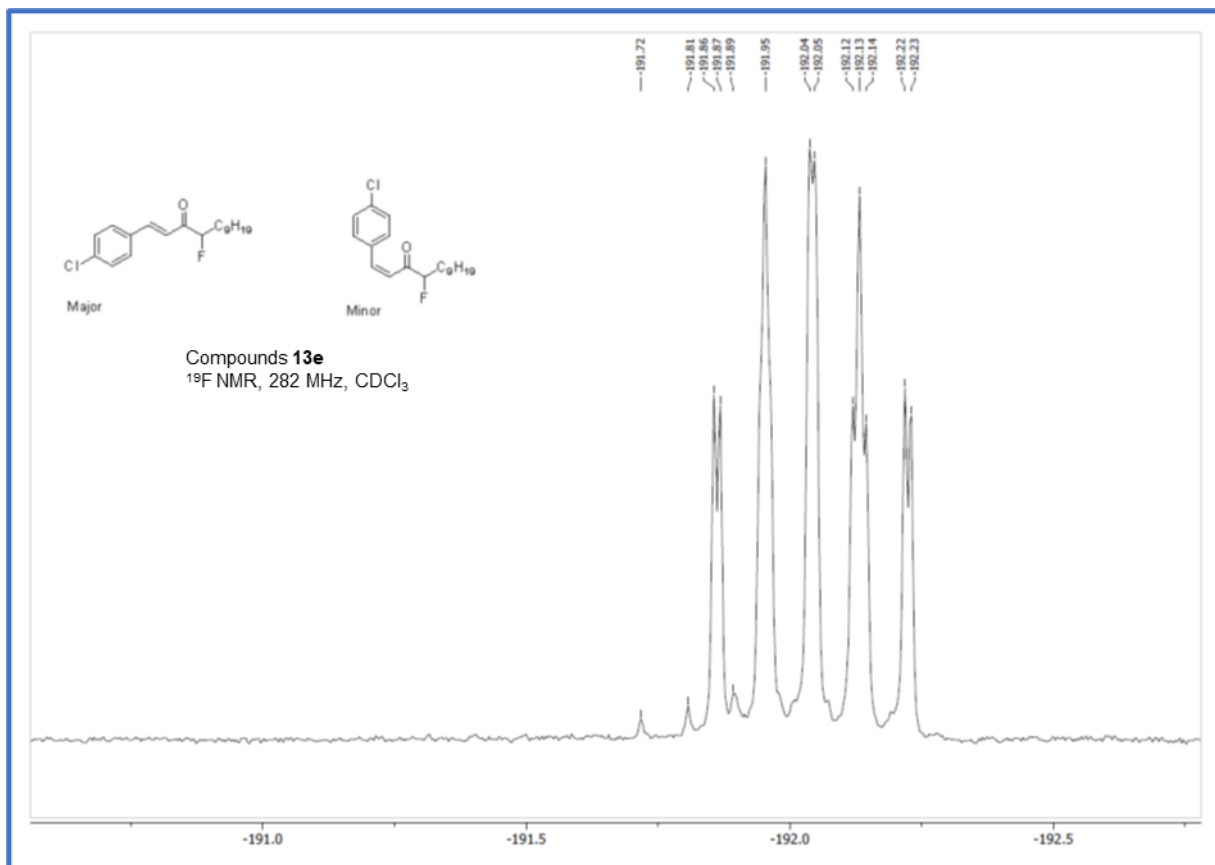
NMR spectra of 13d



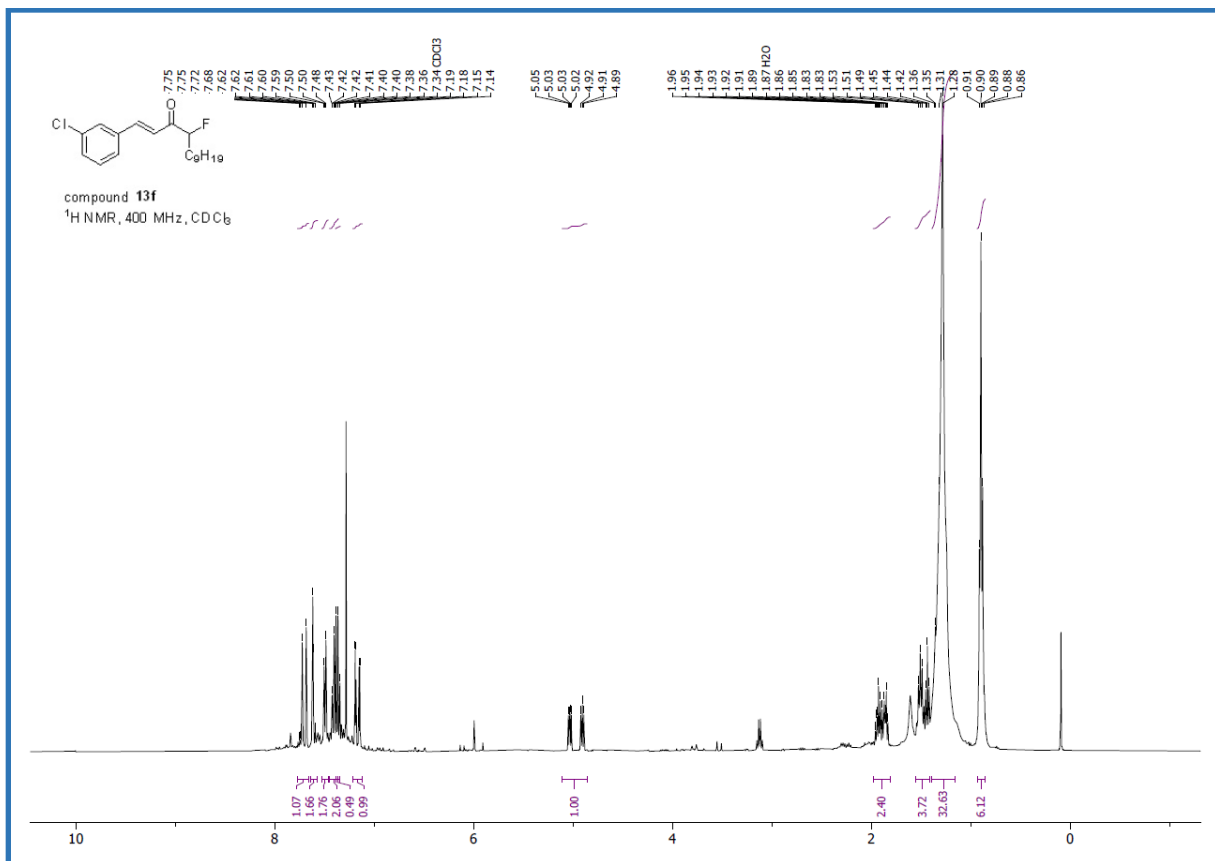


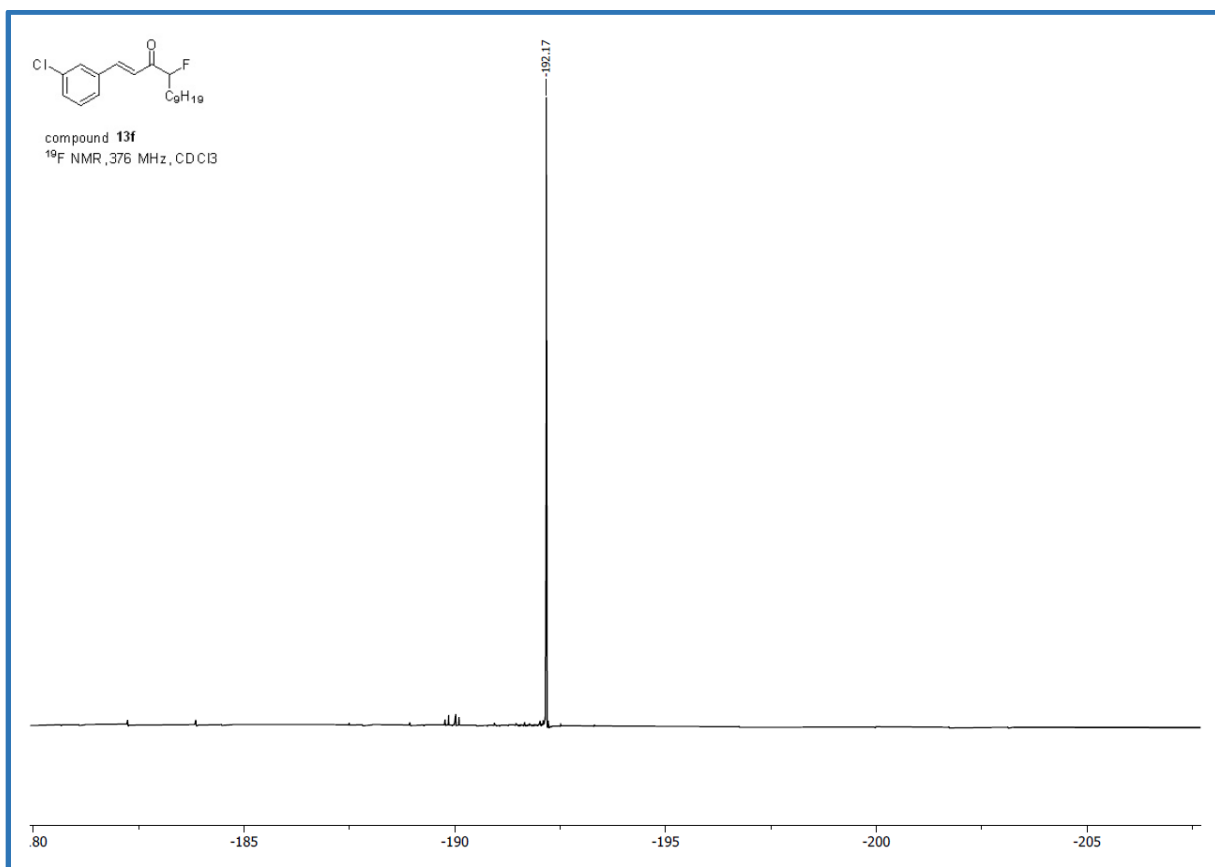
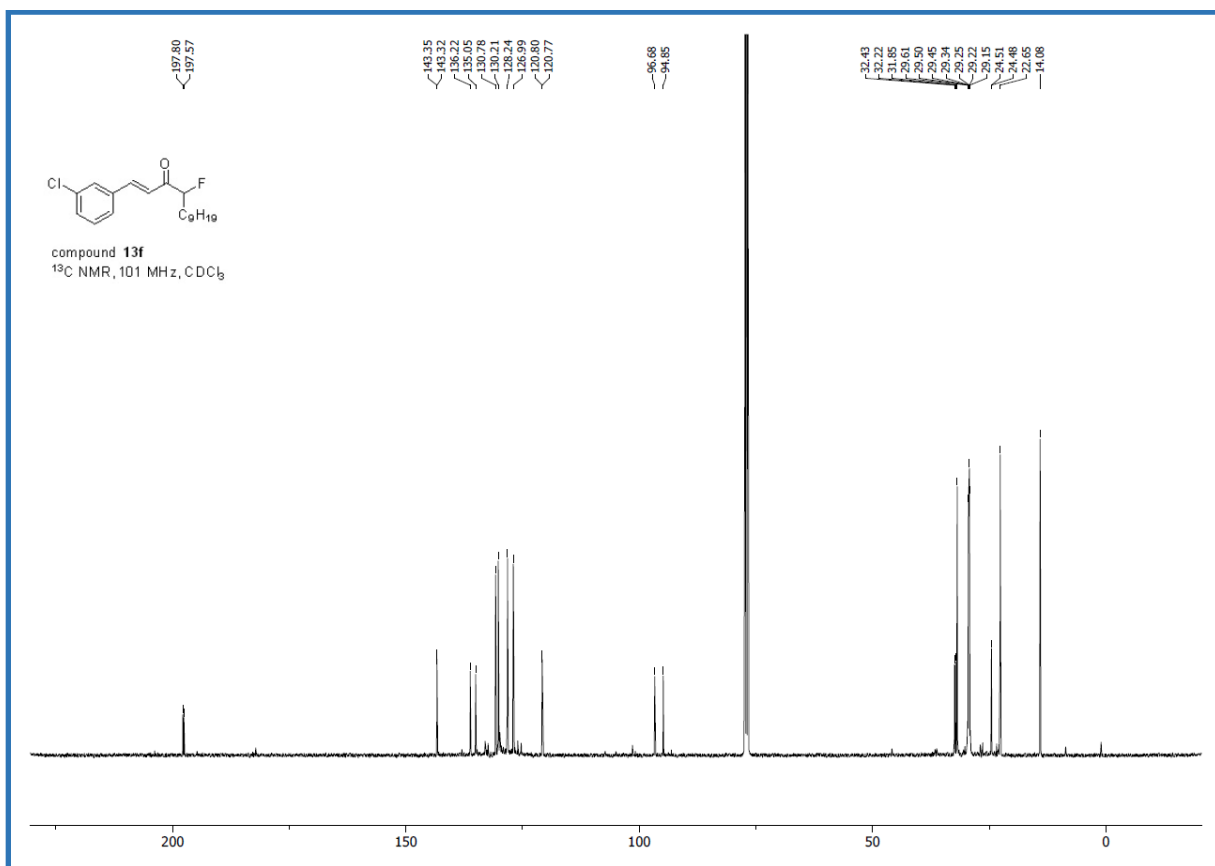
NMR spectra of 13e

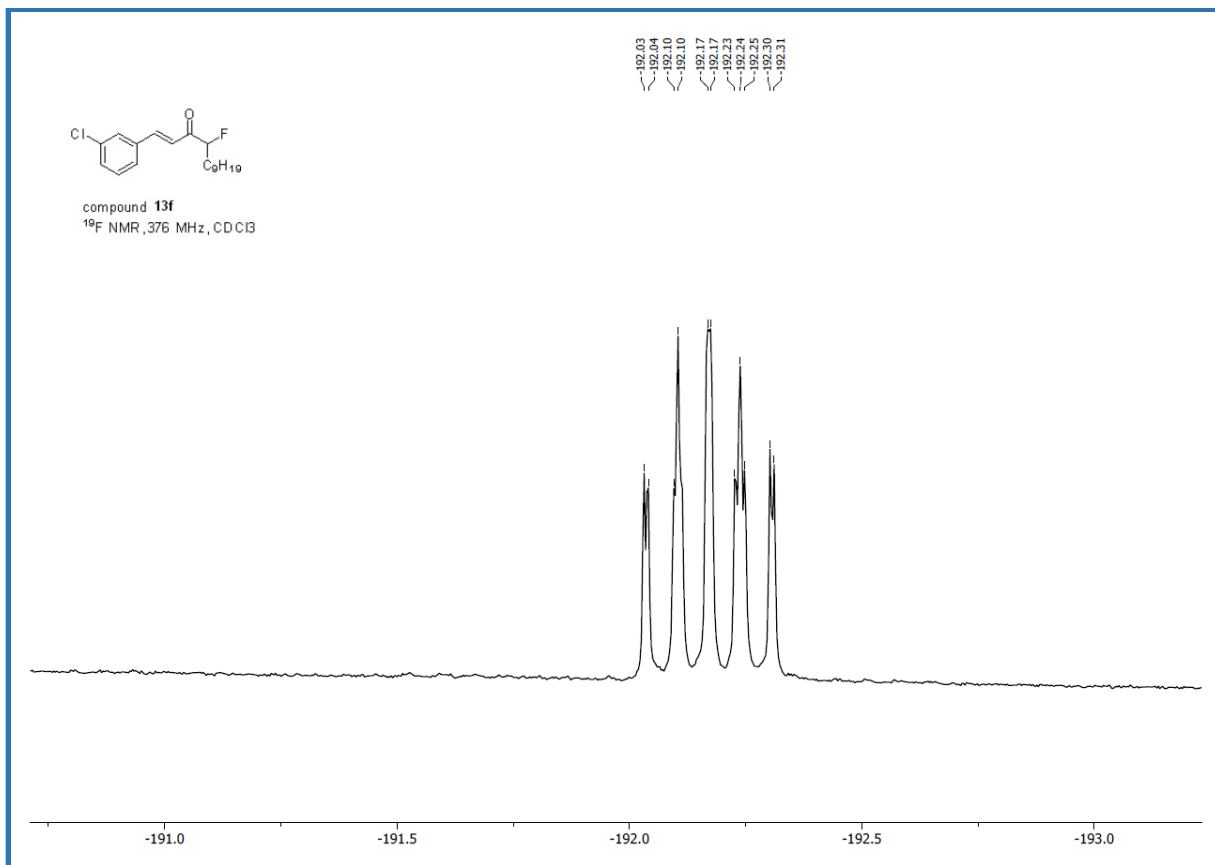




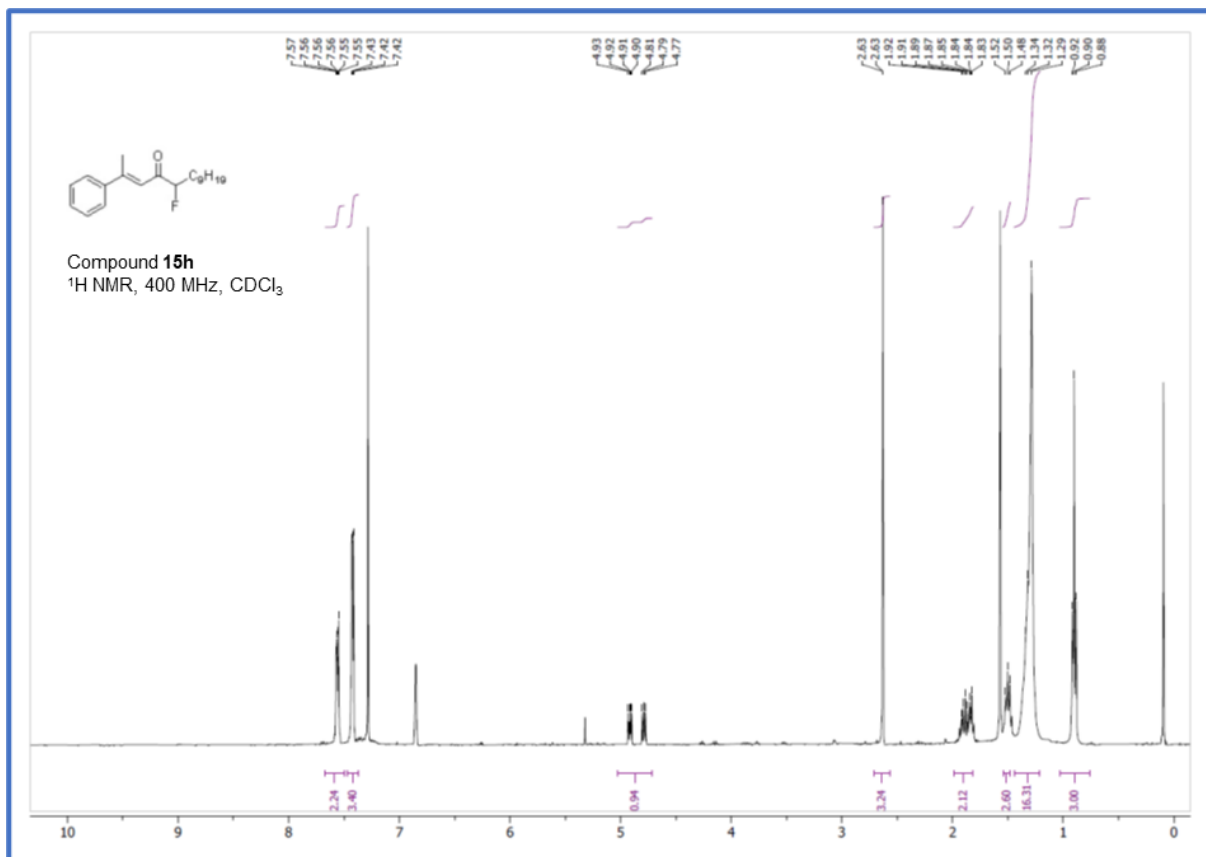
NMR spectra of **13f**

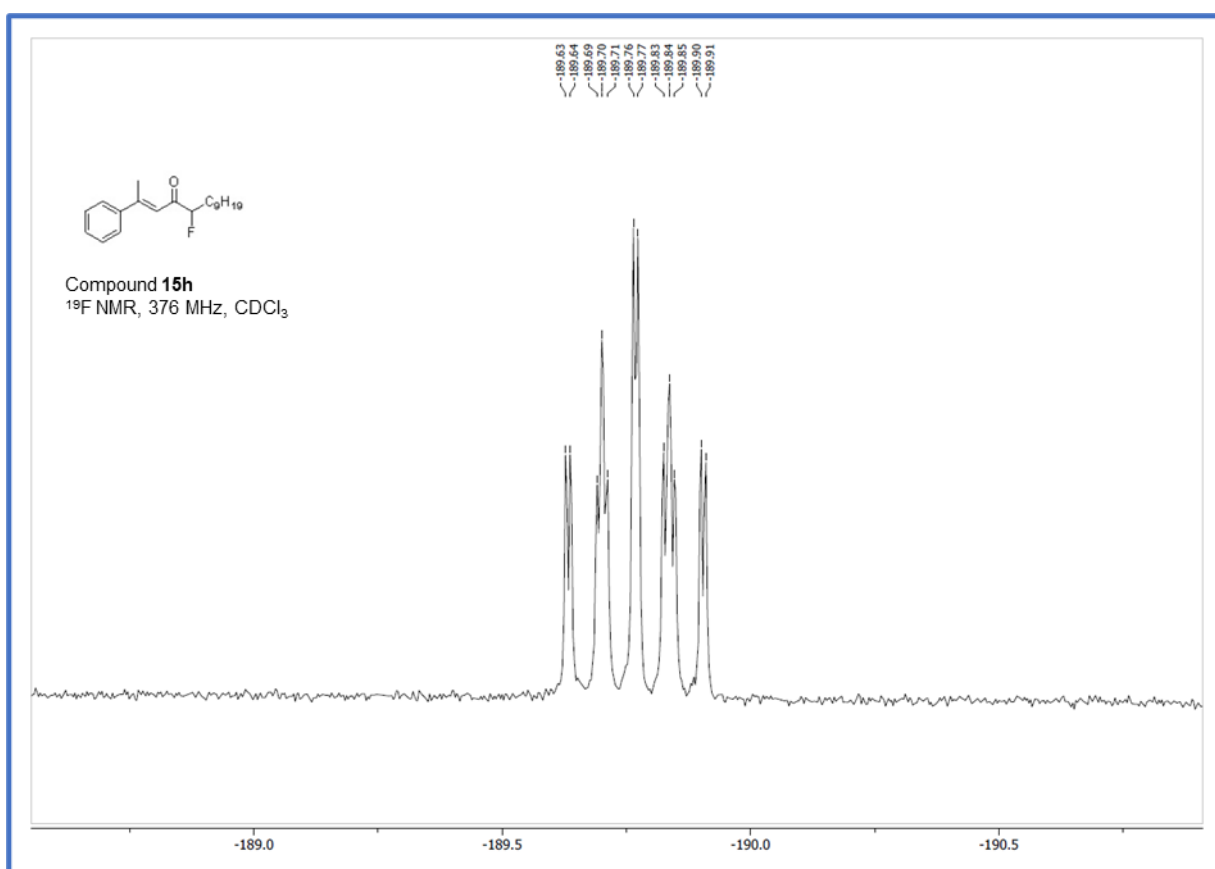
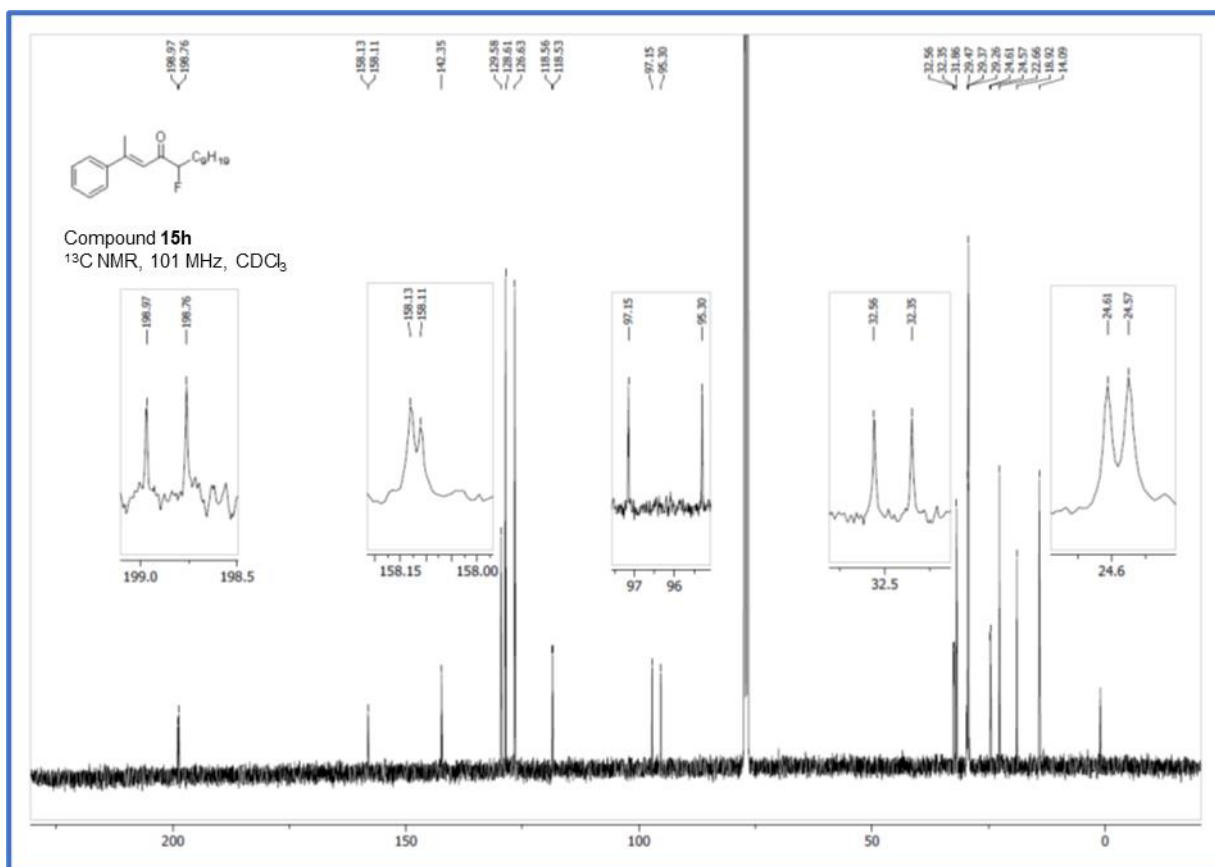


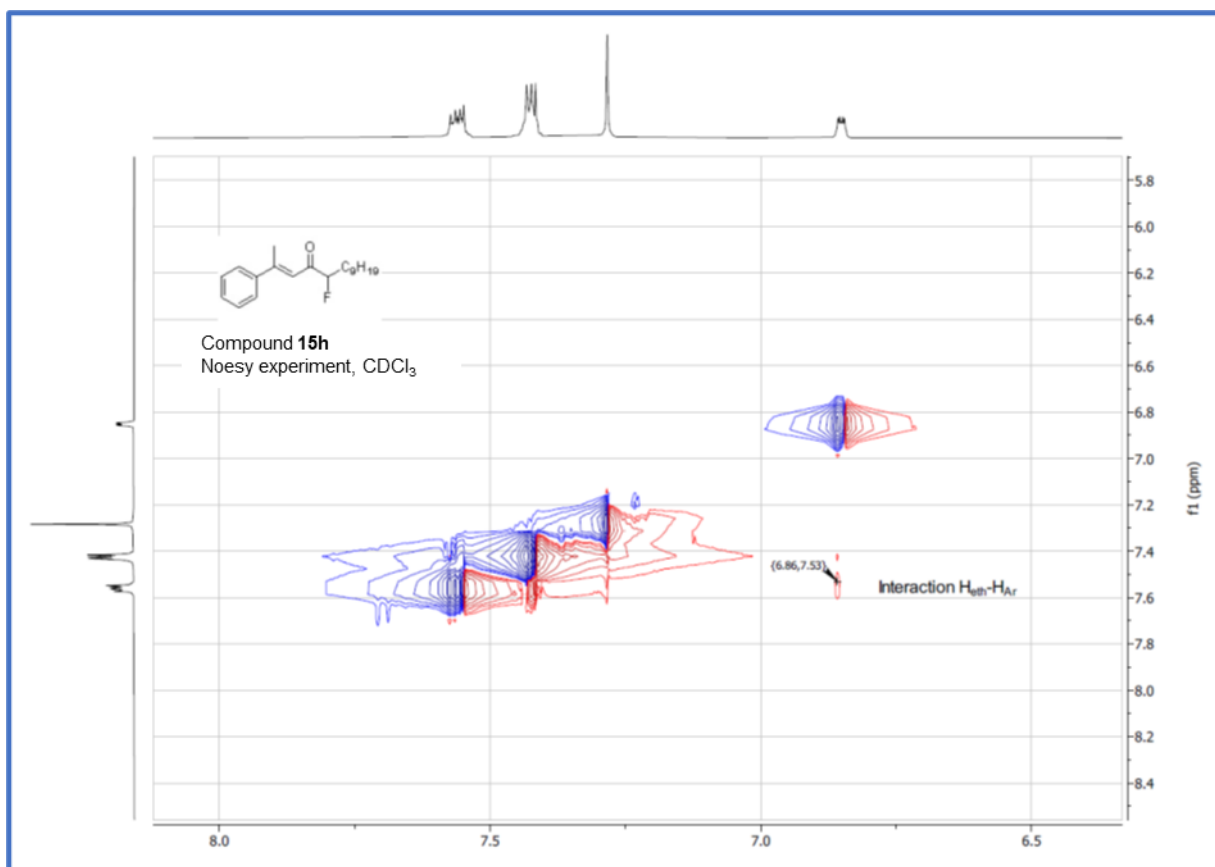




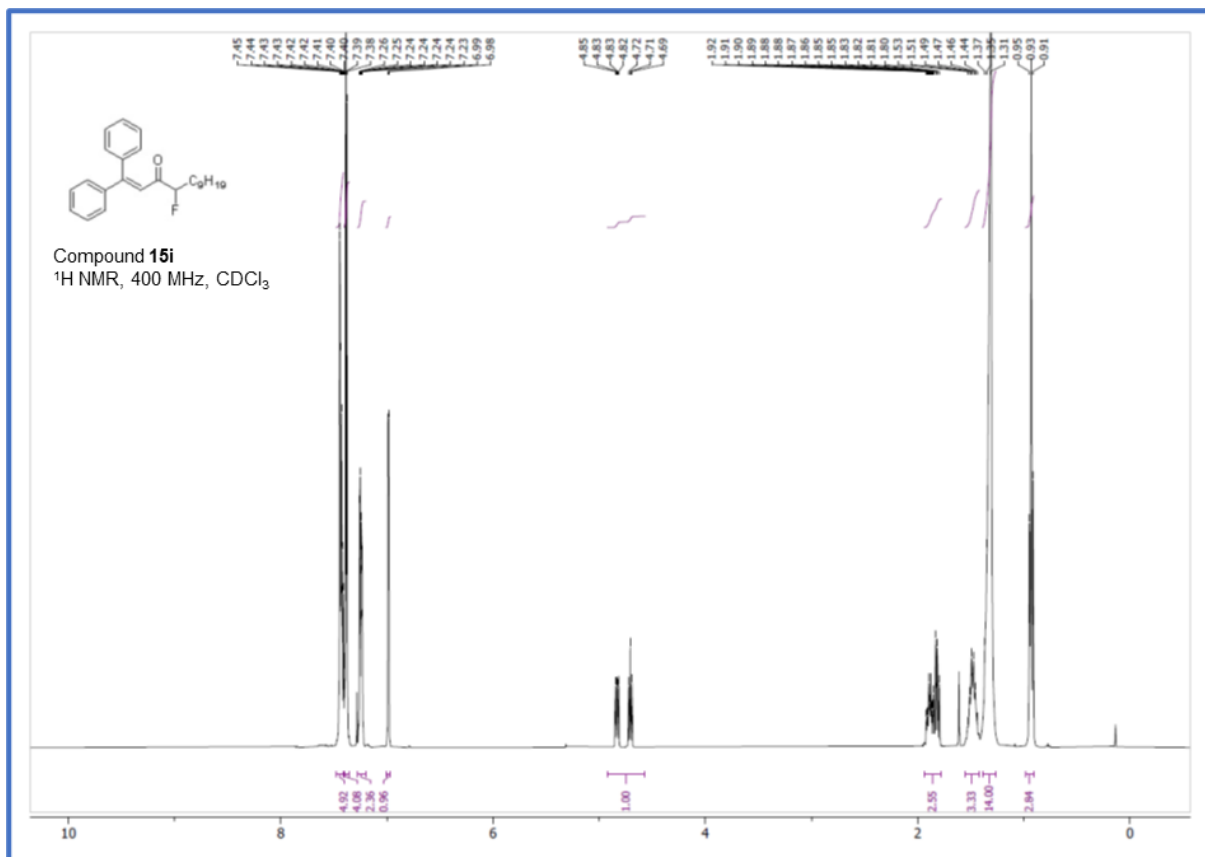
NMR spectra of 15h

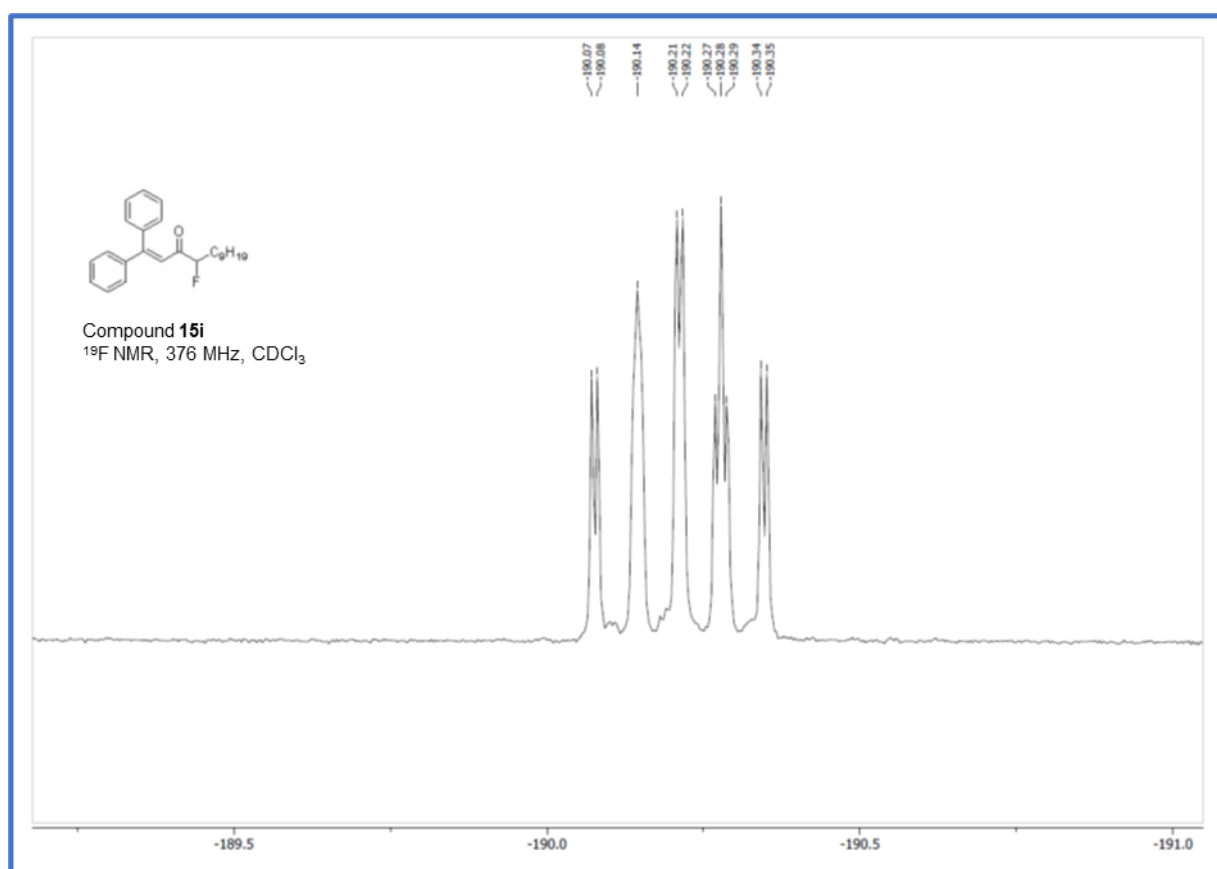
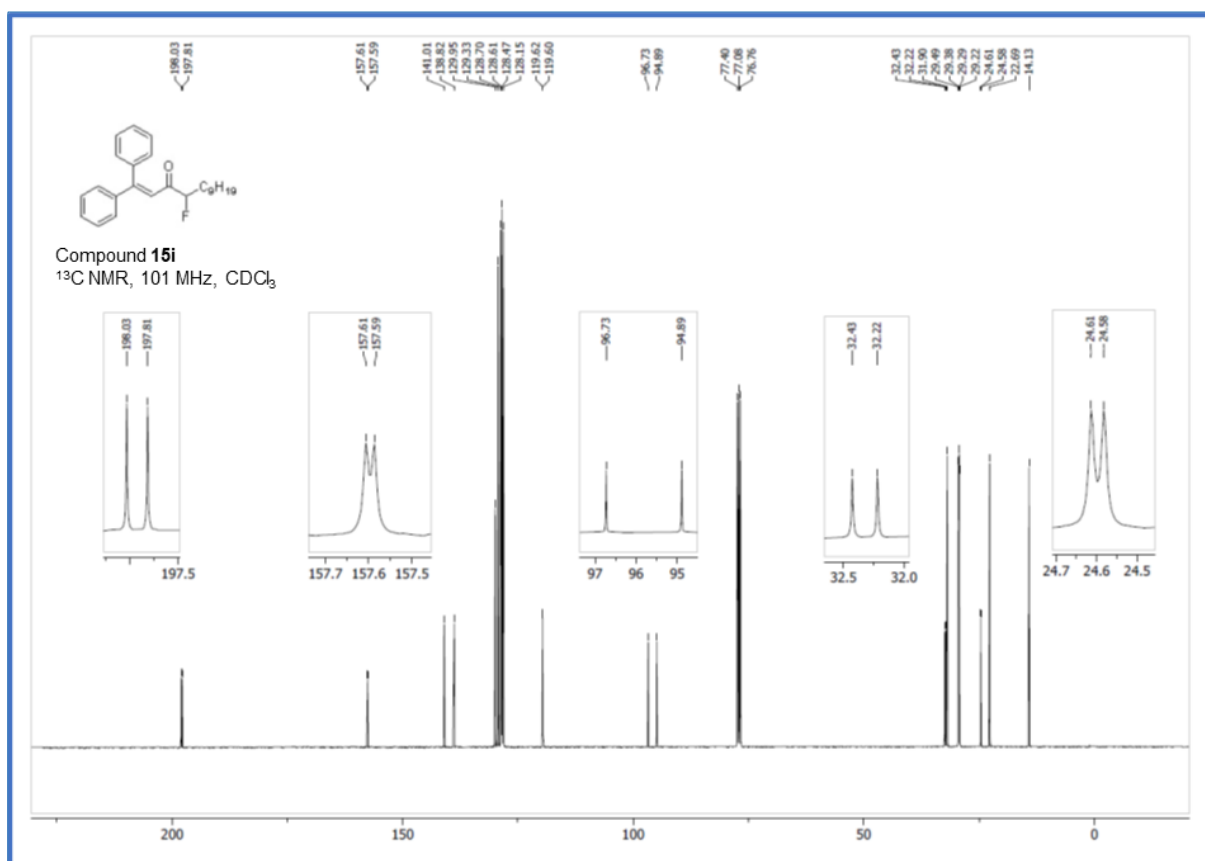




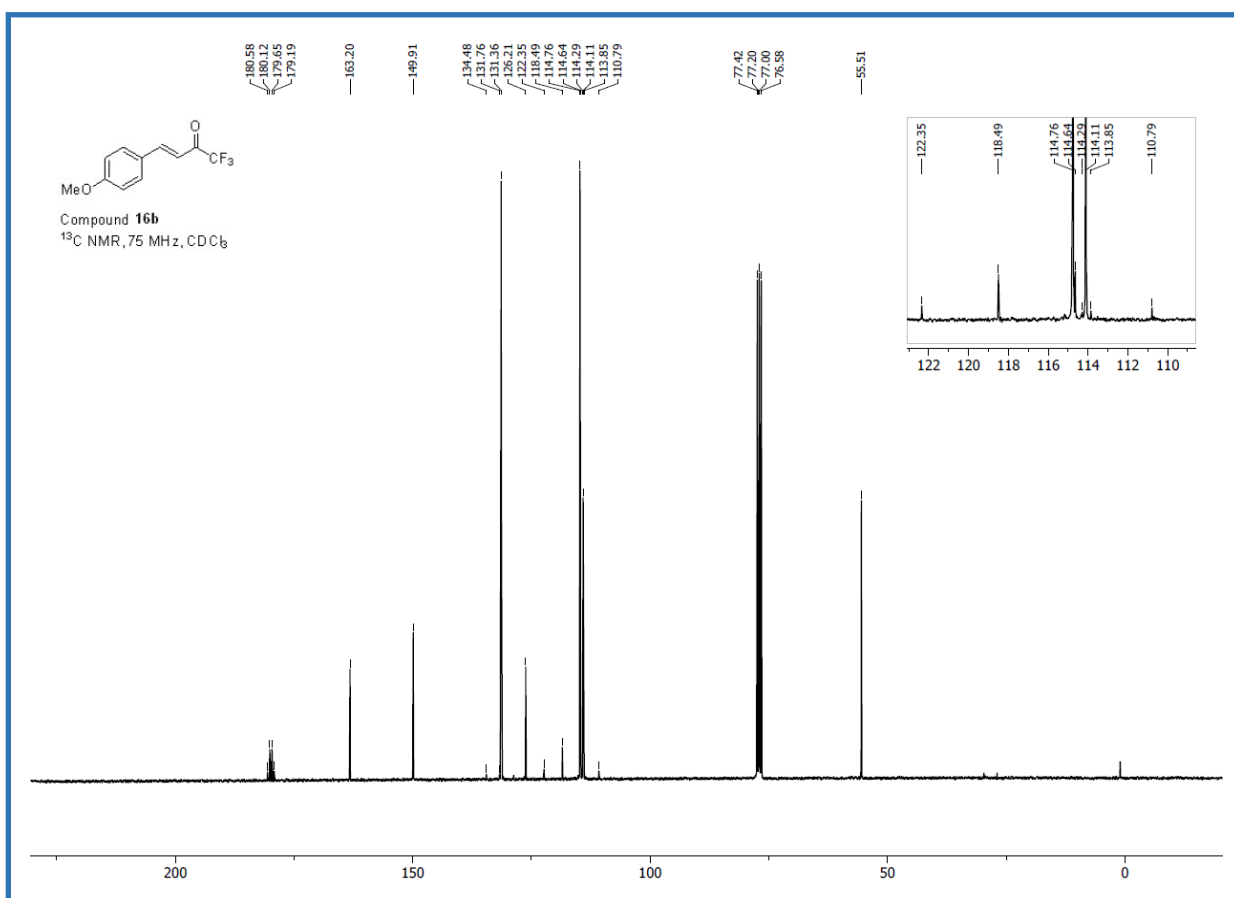
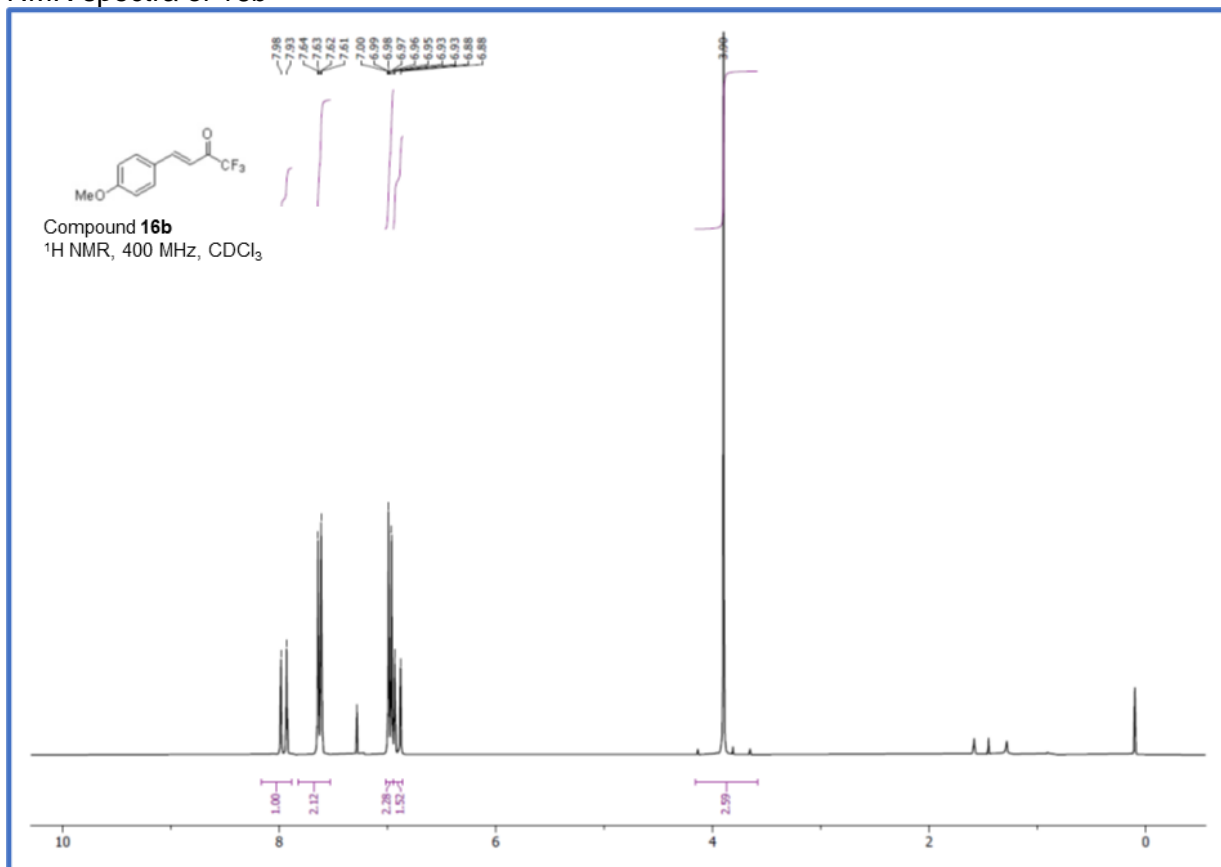


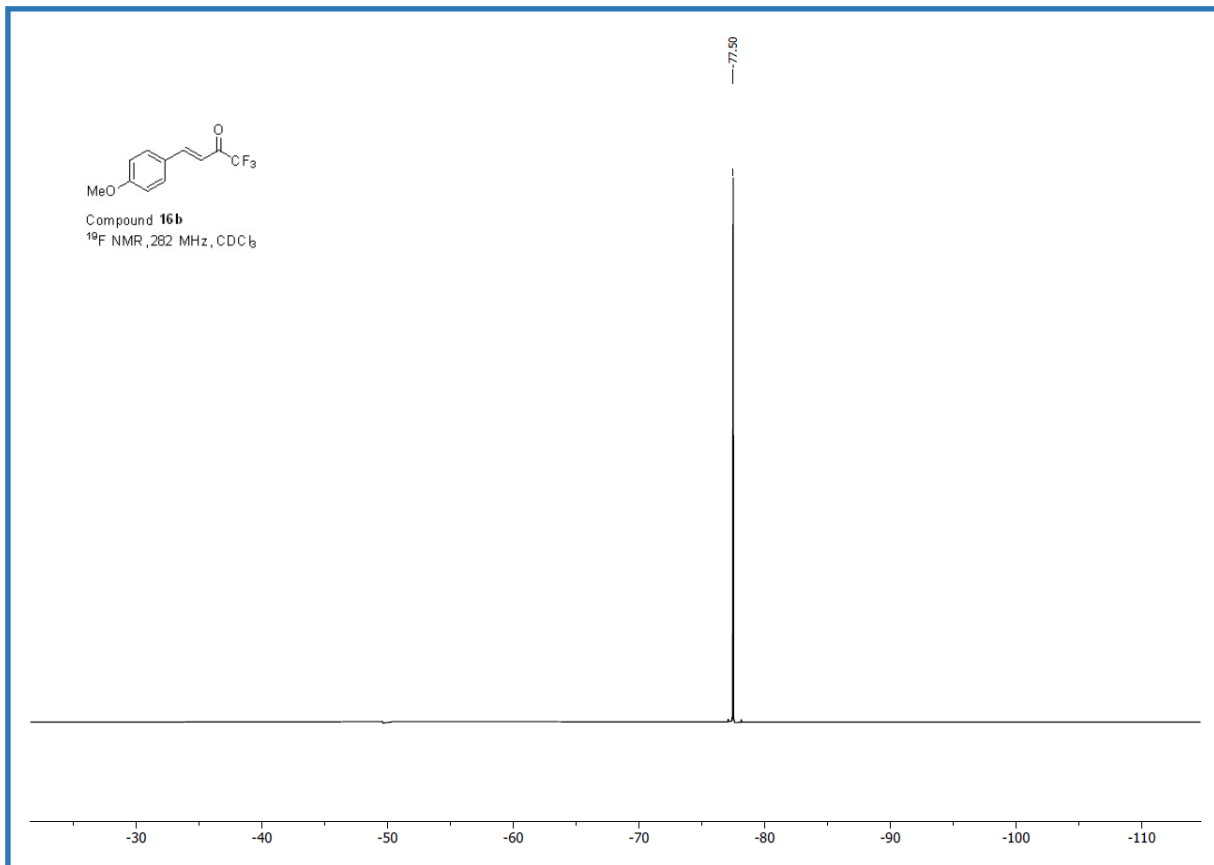
NMR spectra of 15i



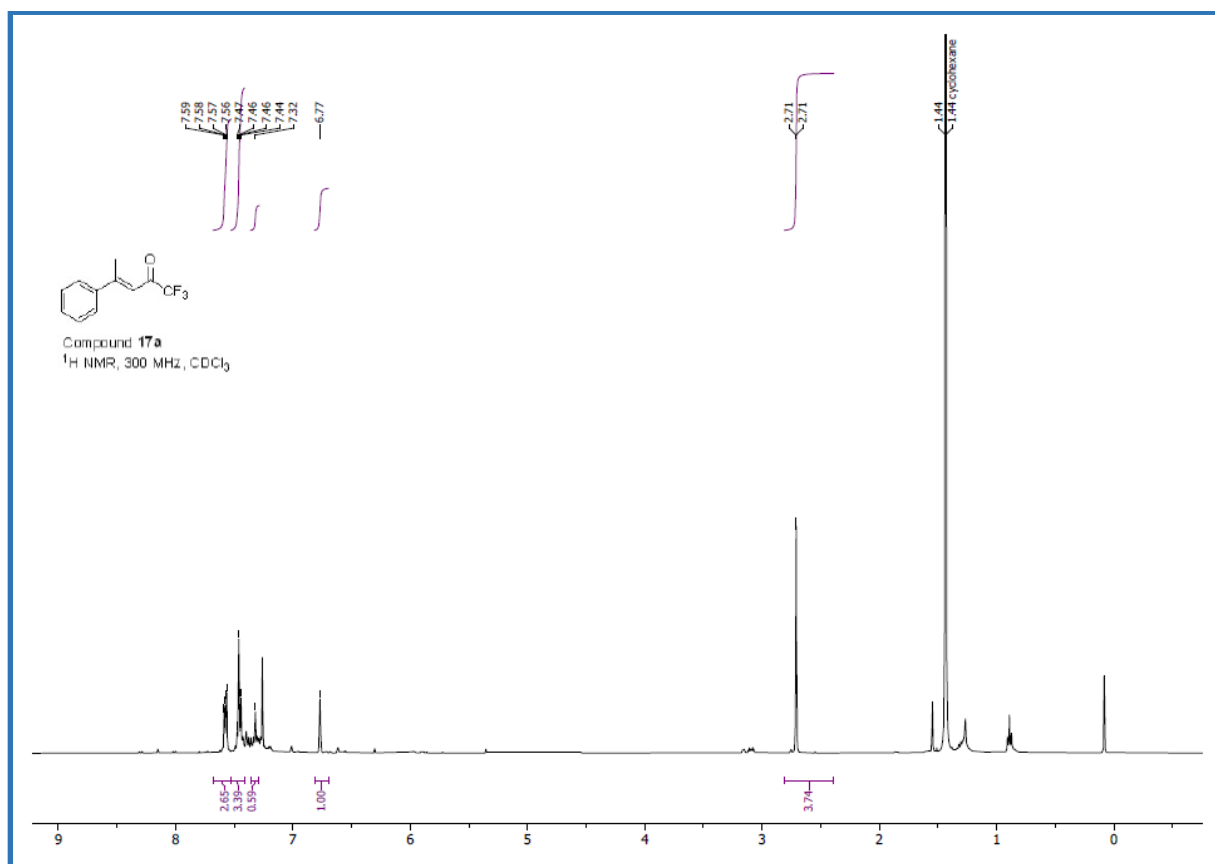


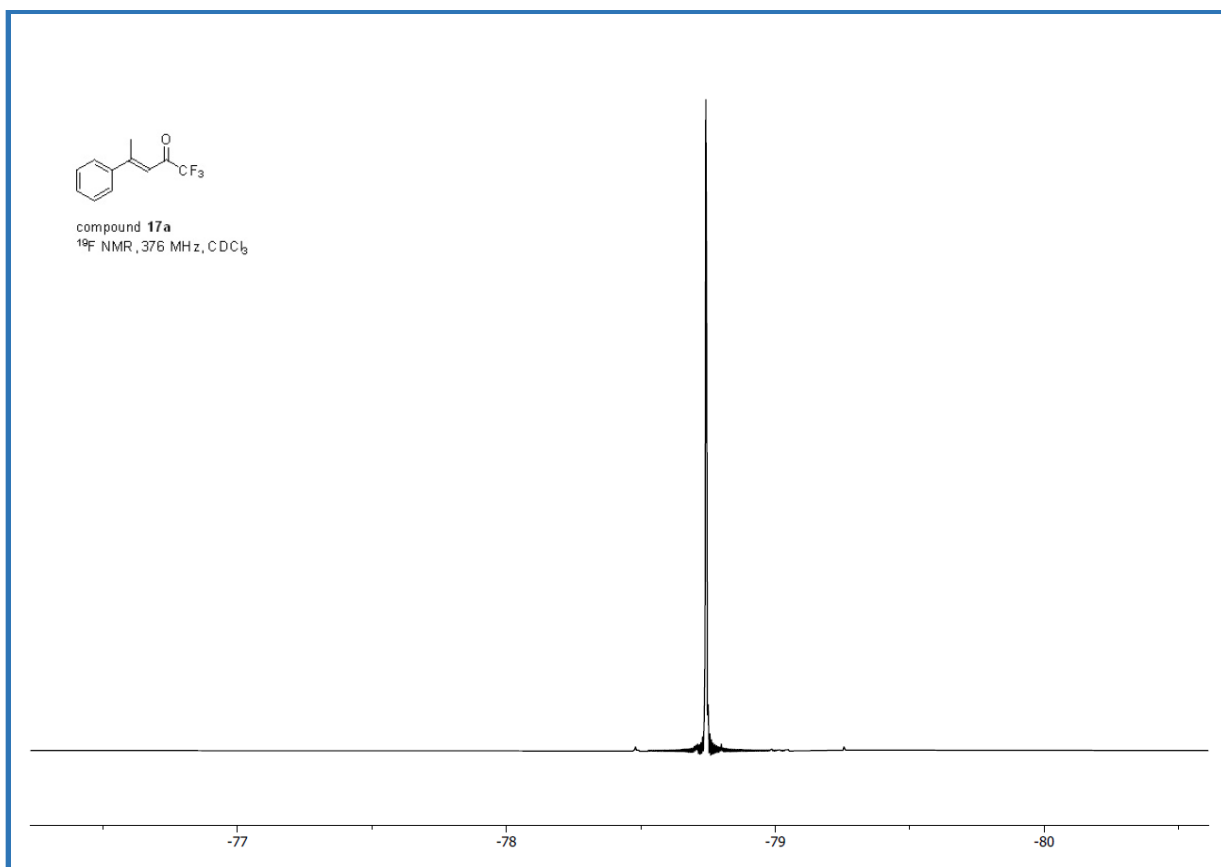
NMR spectra of 16b



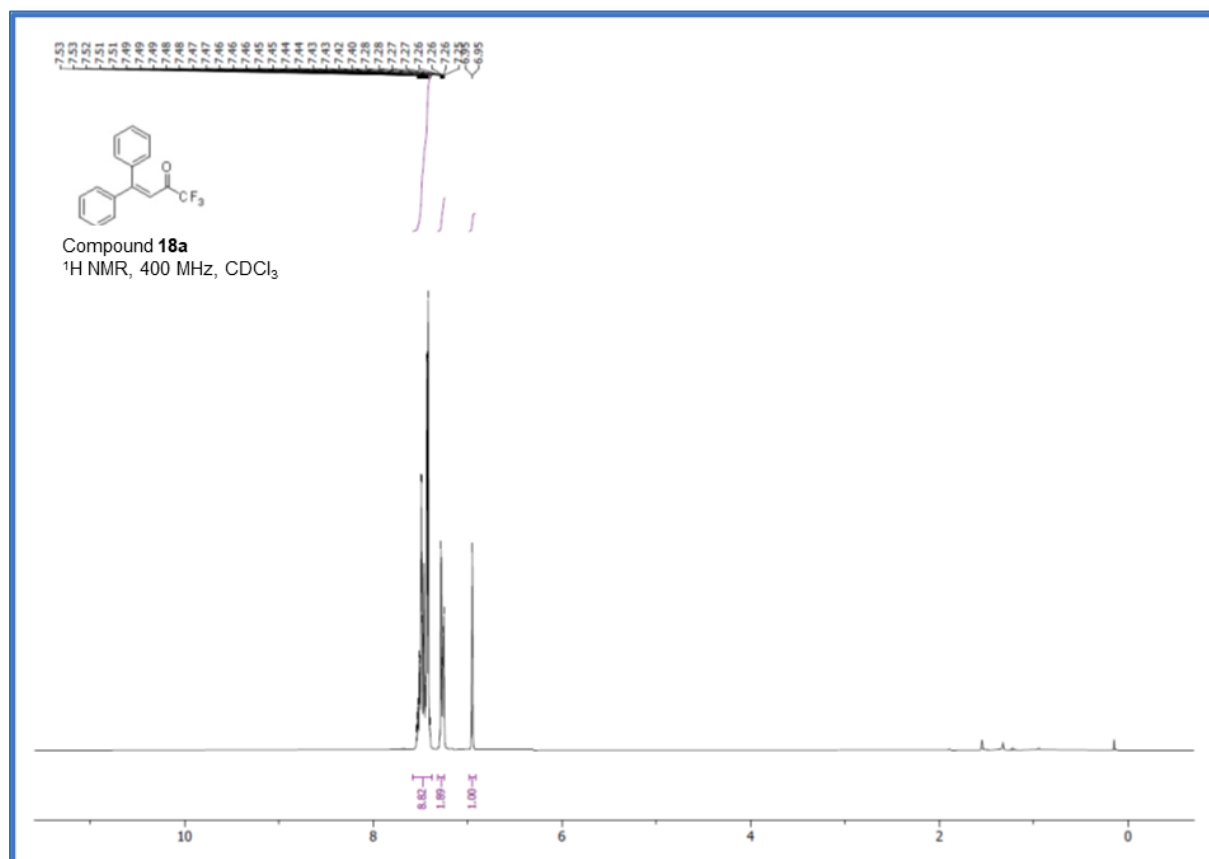


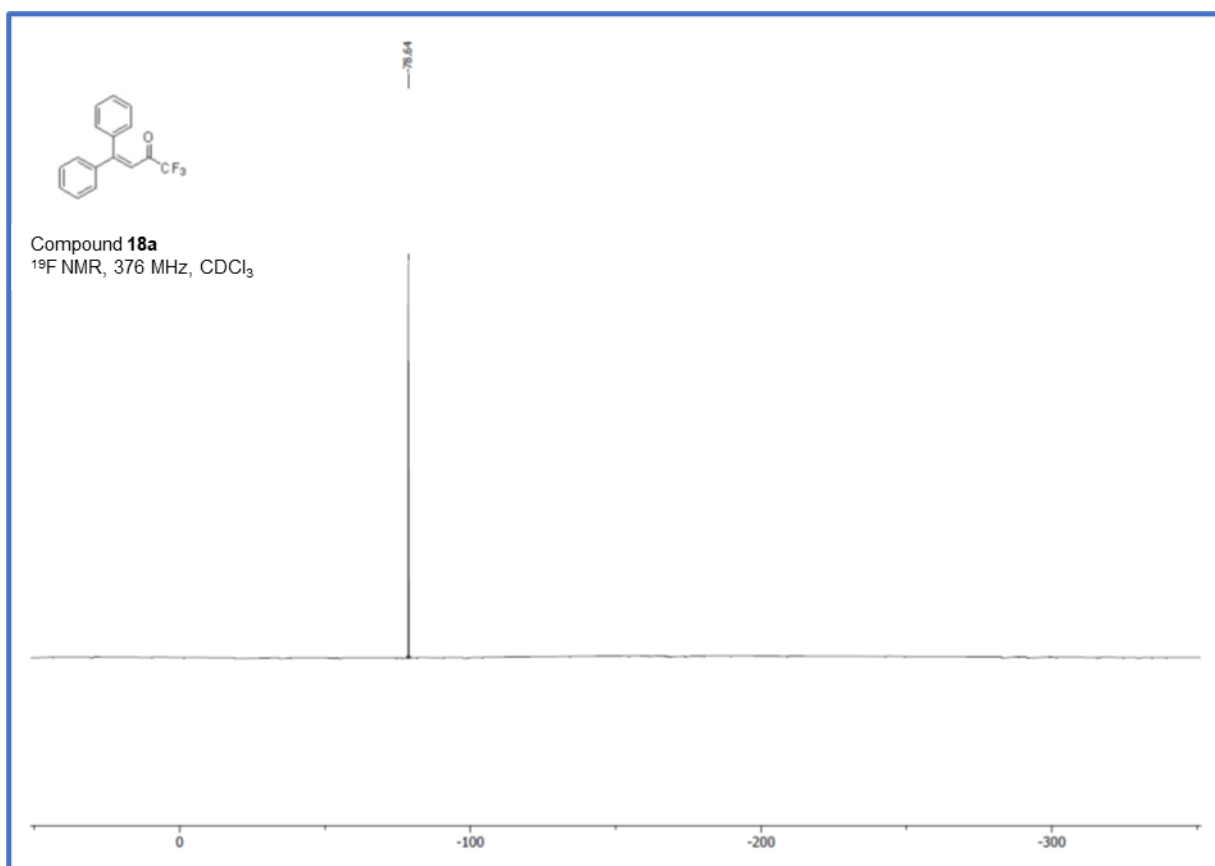
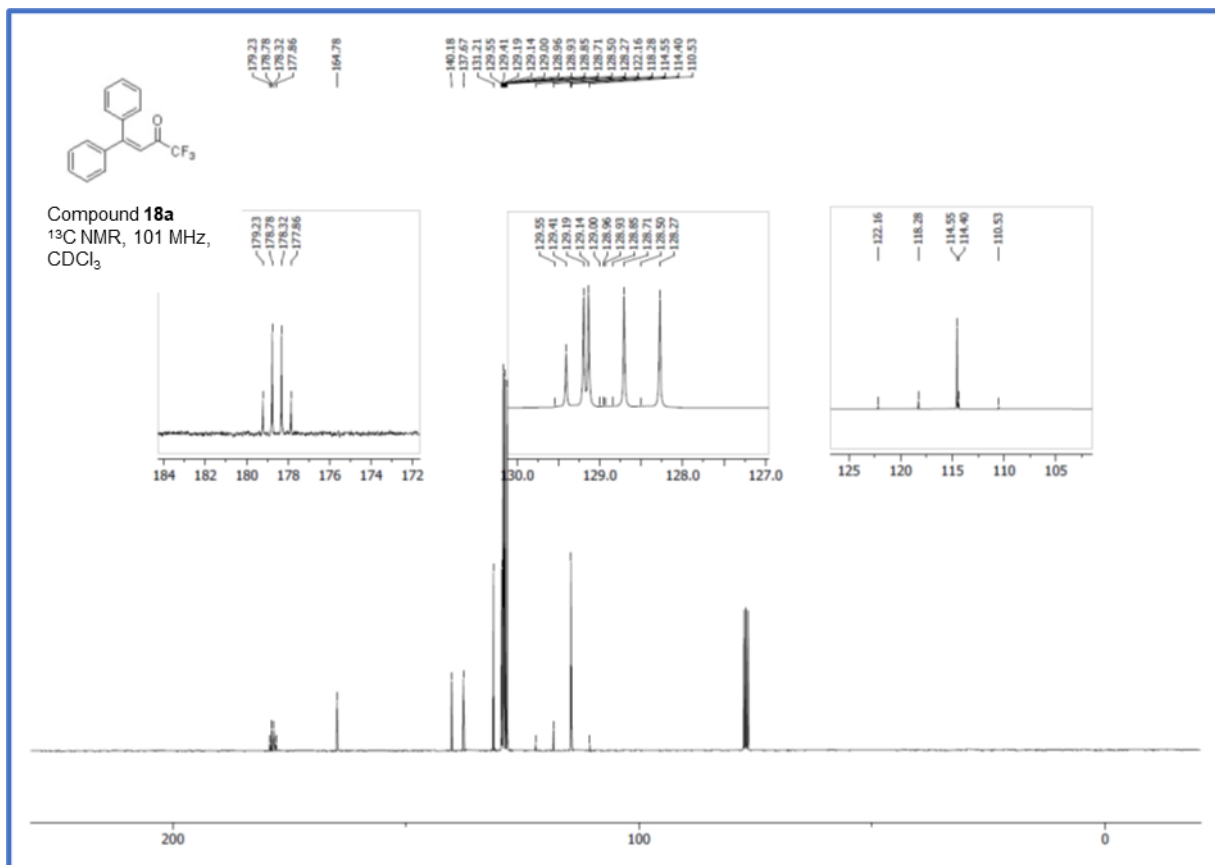
NMR spectra of 17a



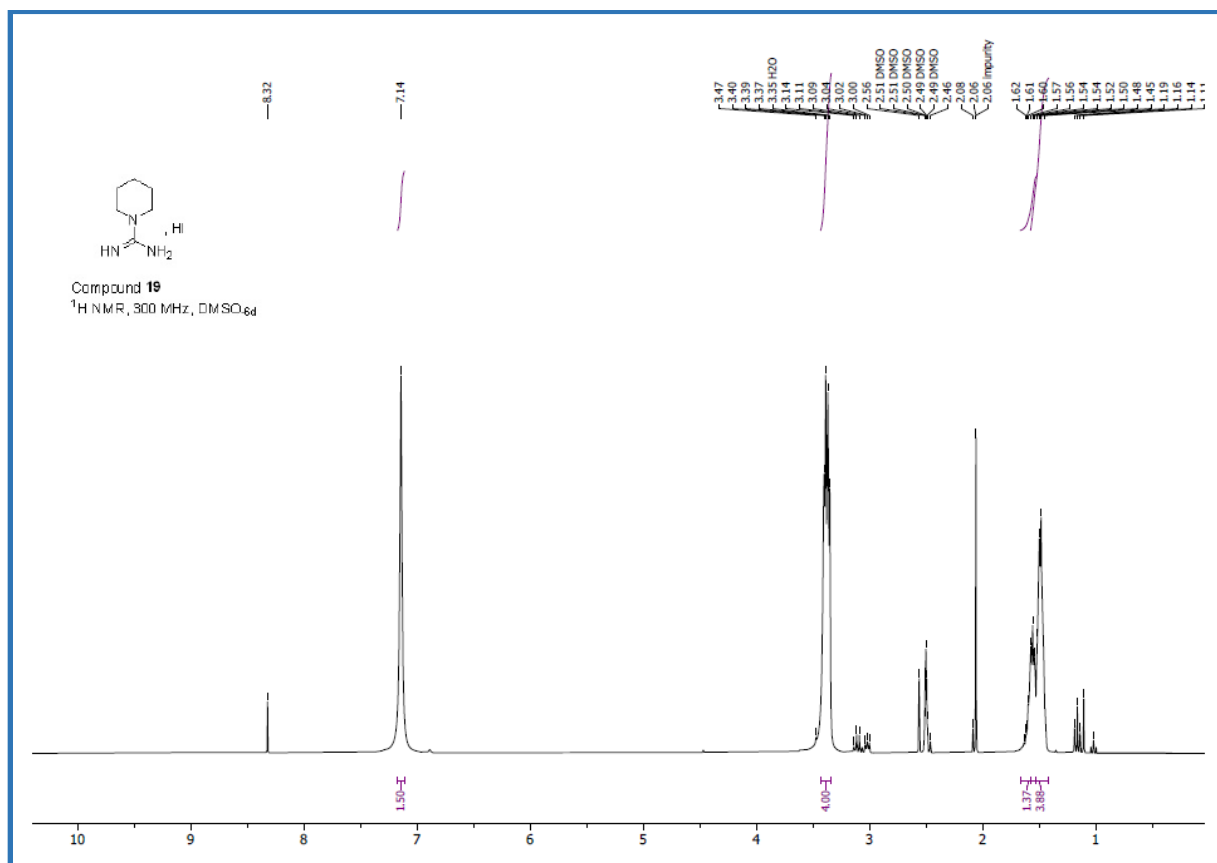


NMR spectra of 18a

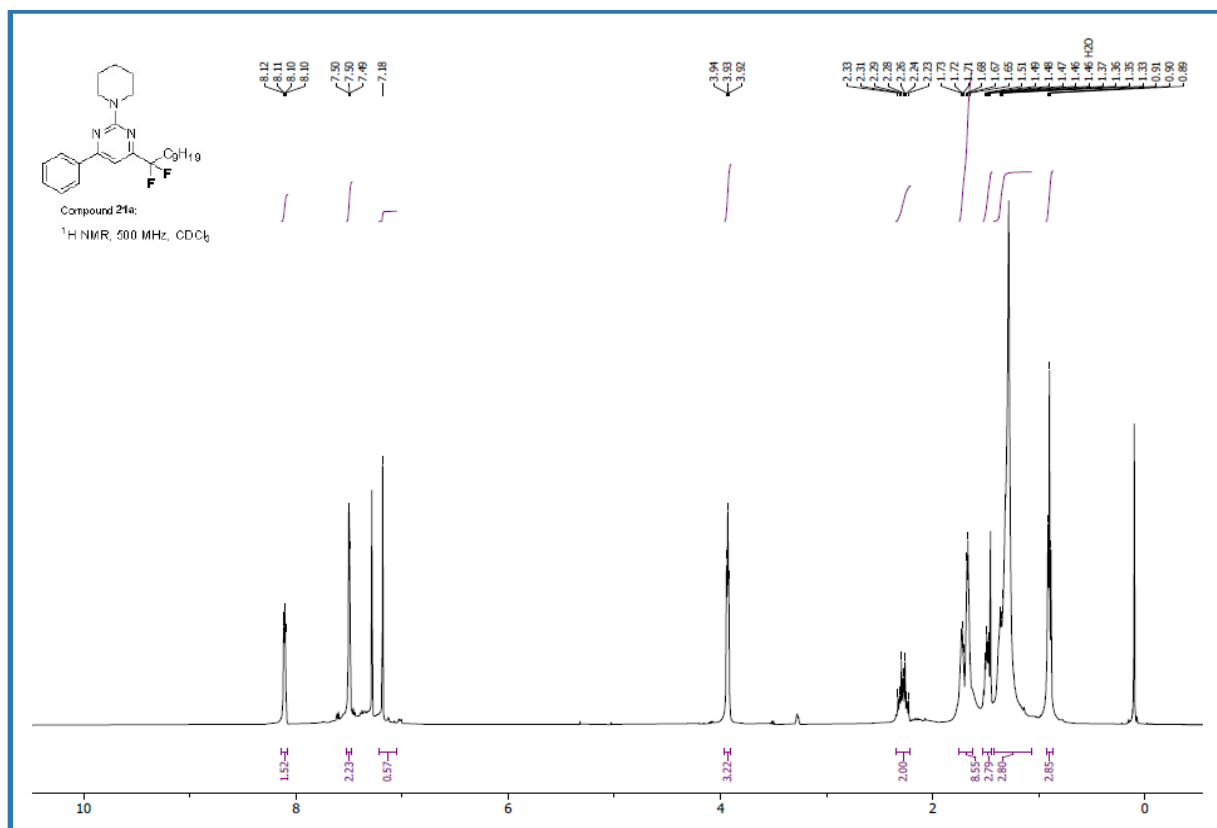


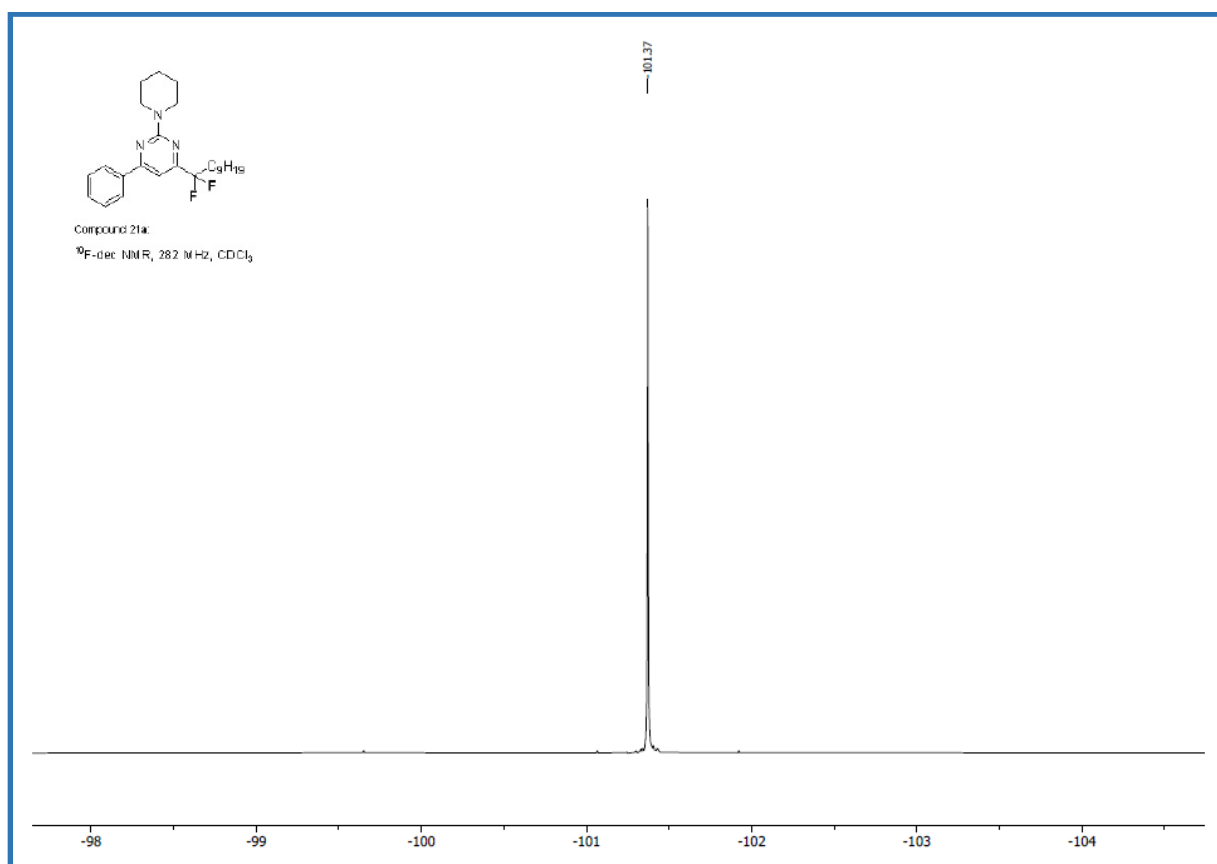
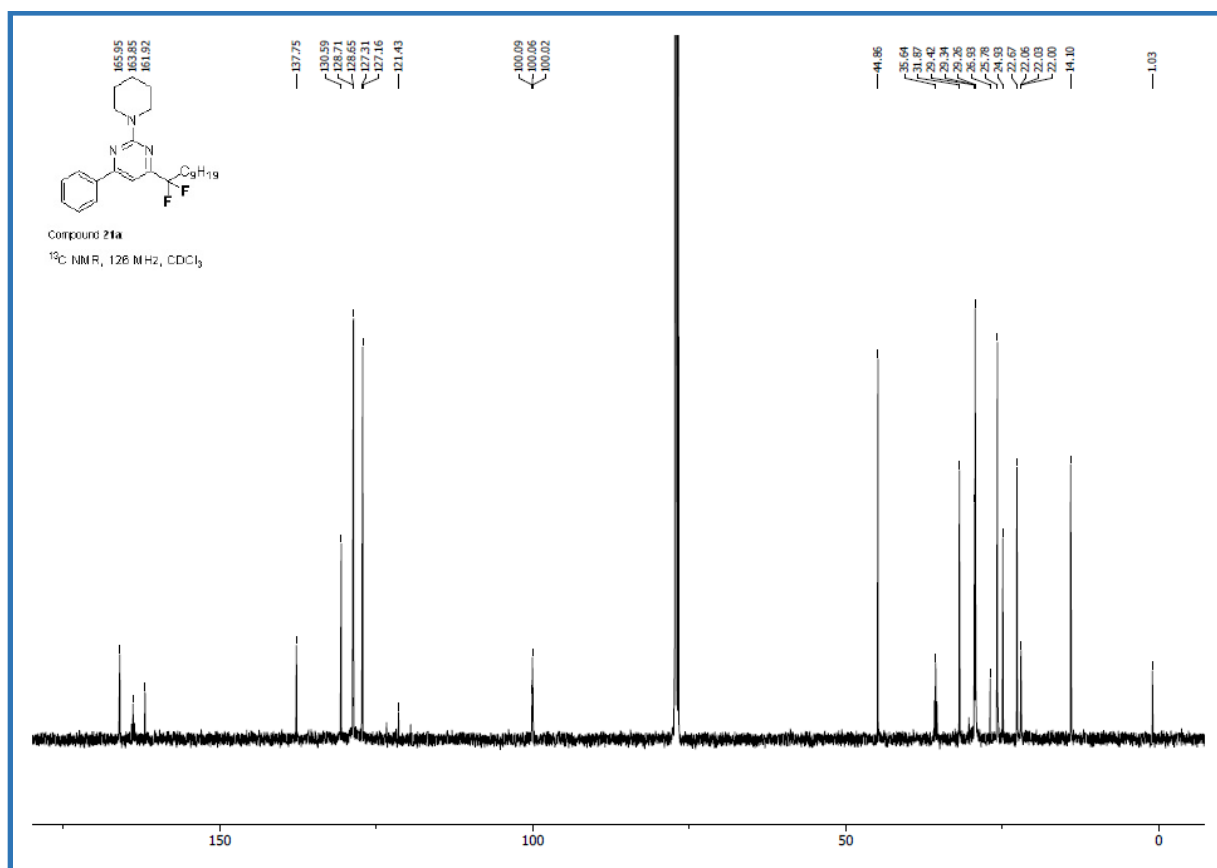


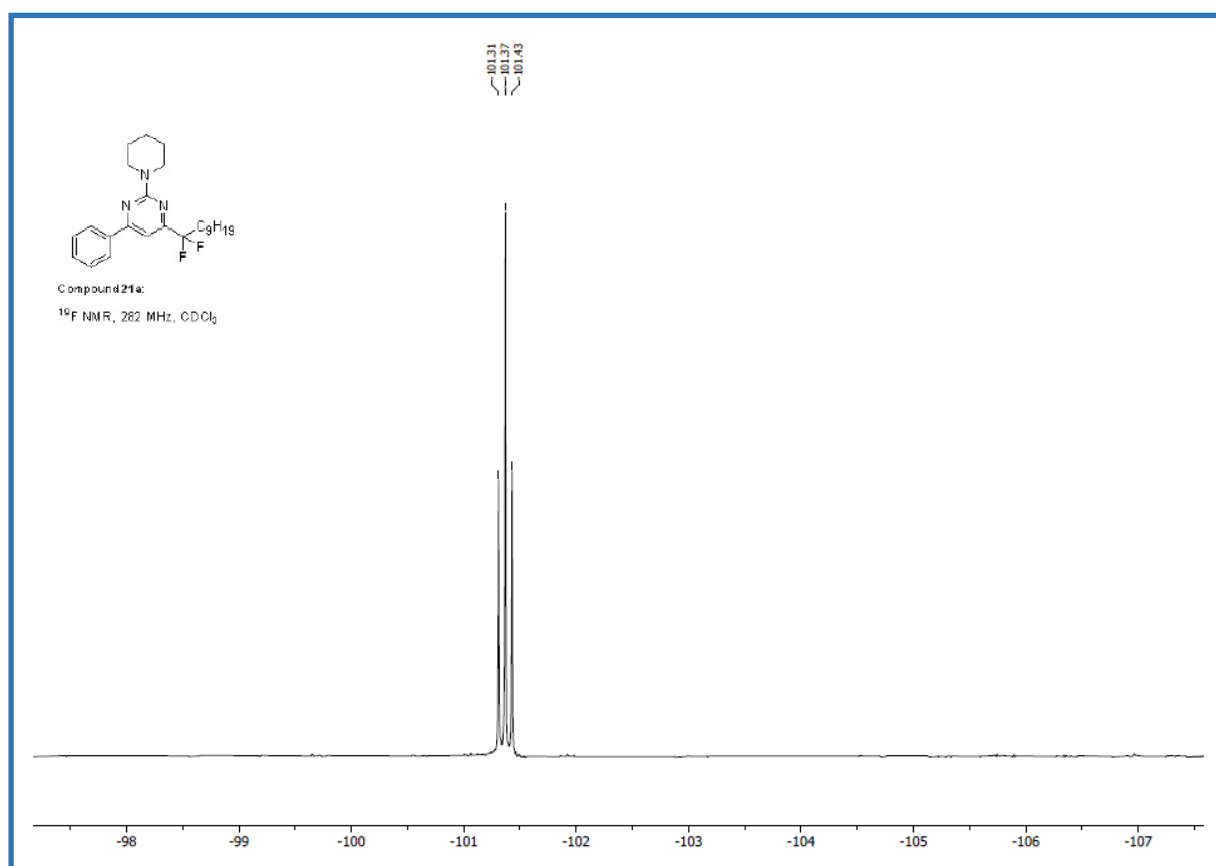
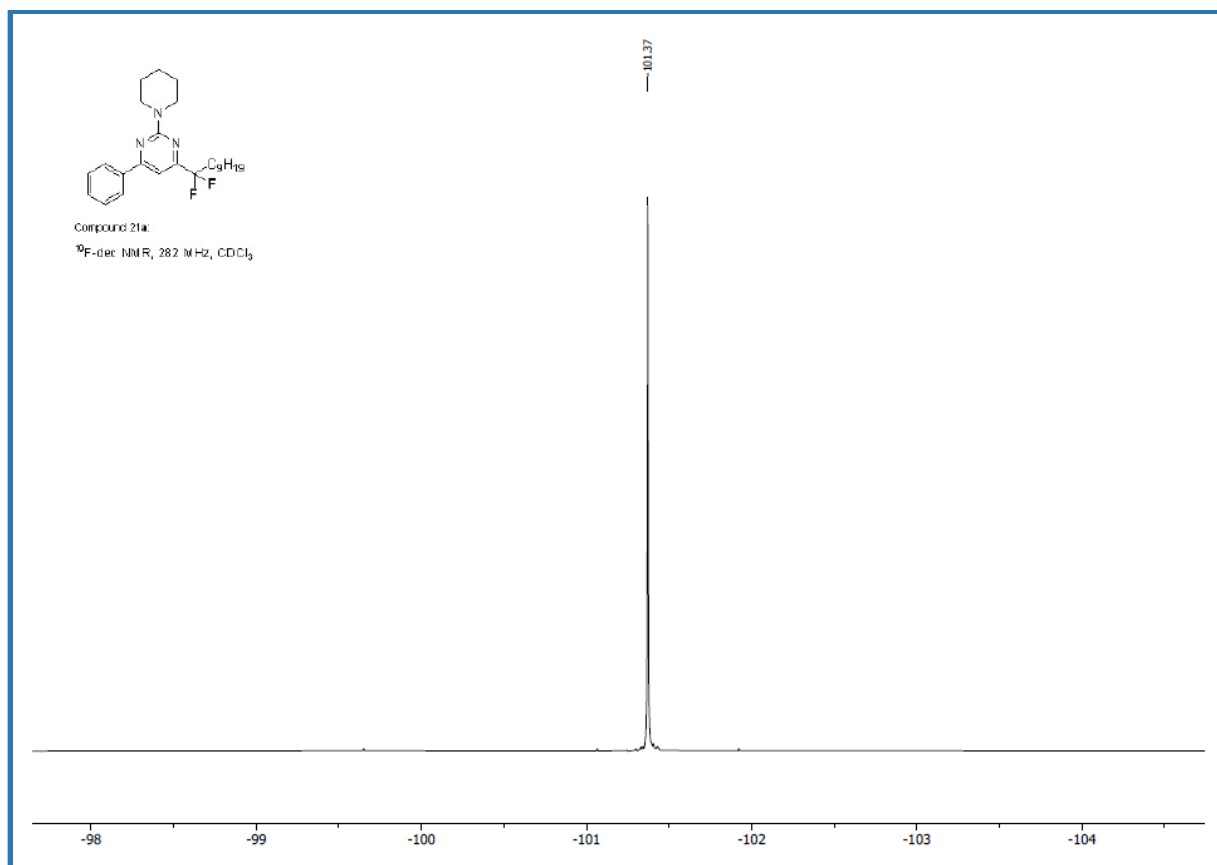
NMR spectra of 19

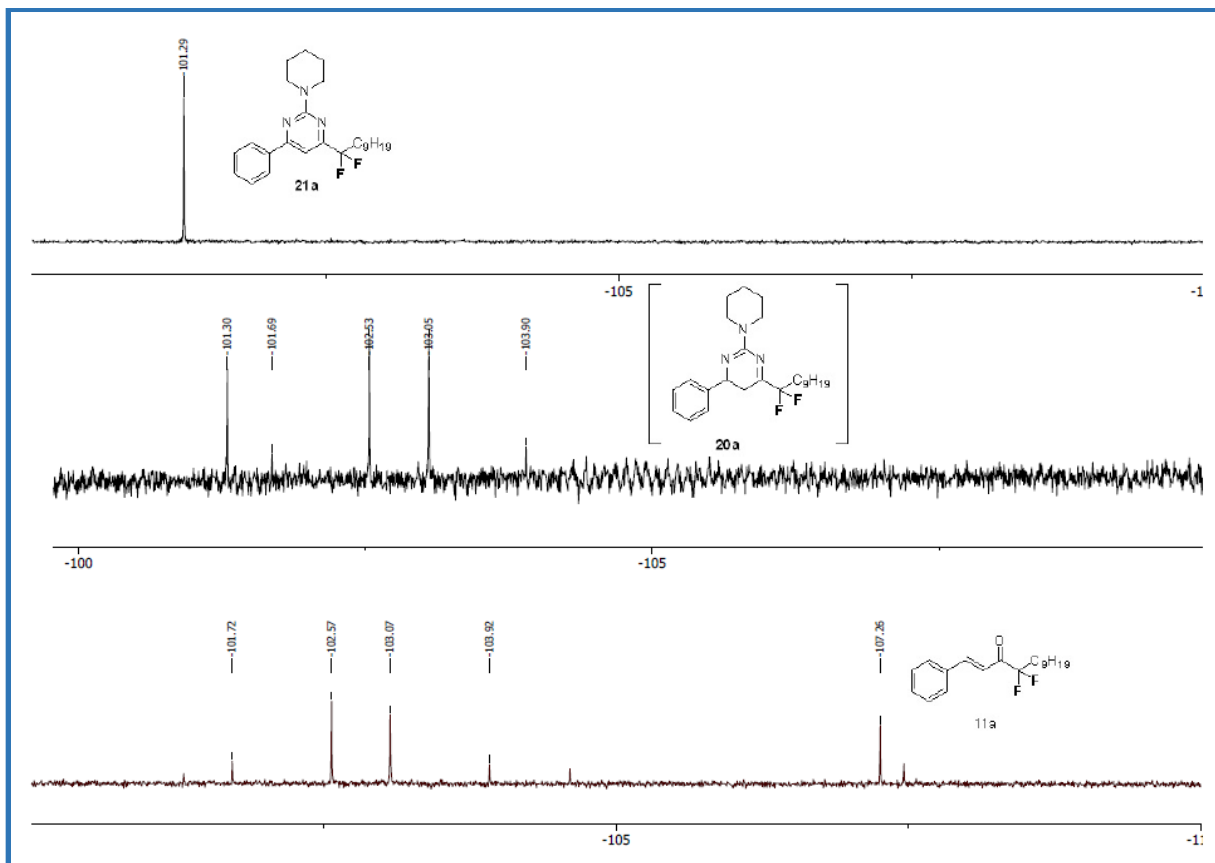


NMR spectra of 21a

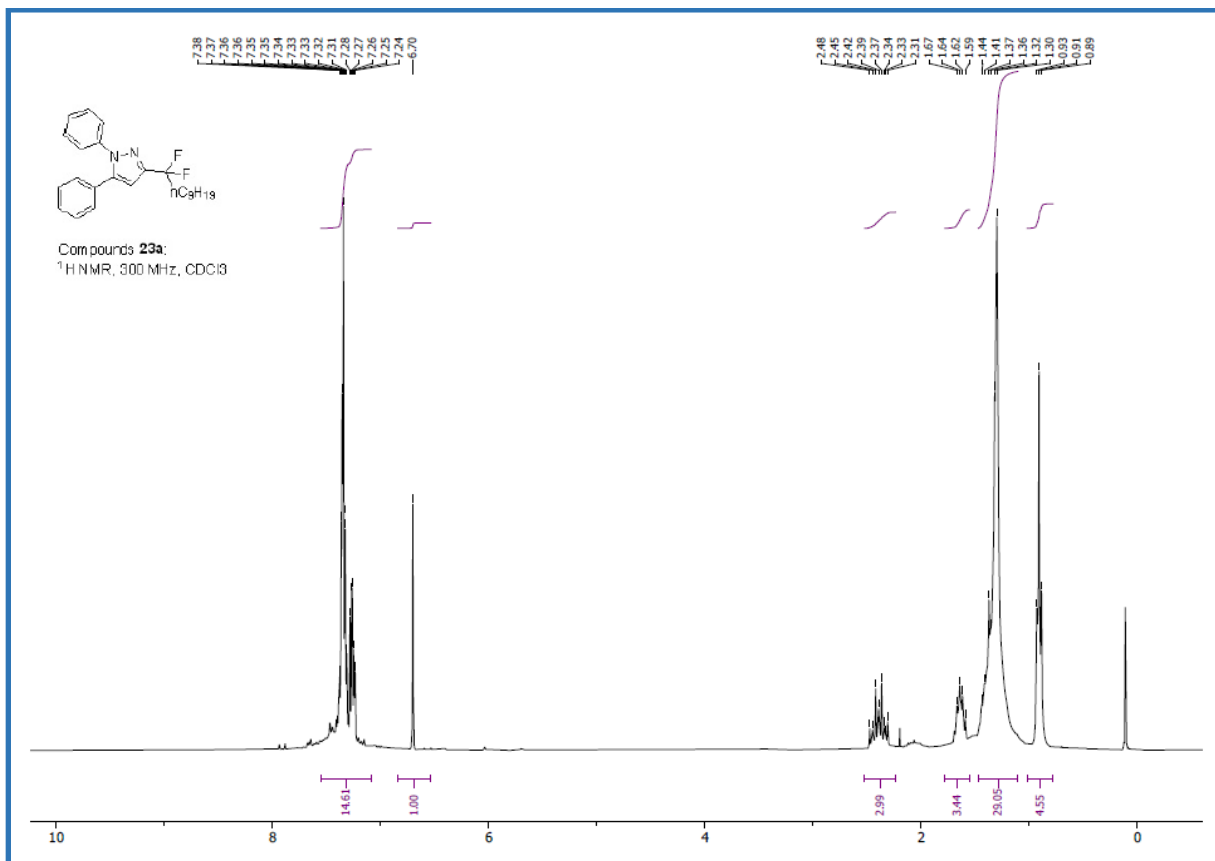


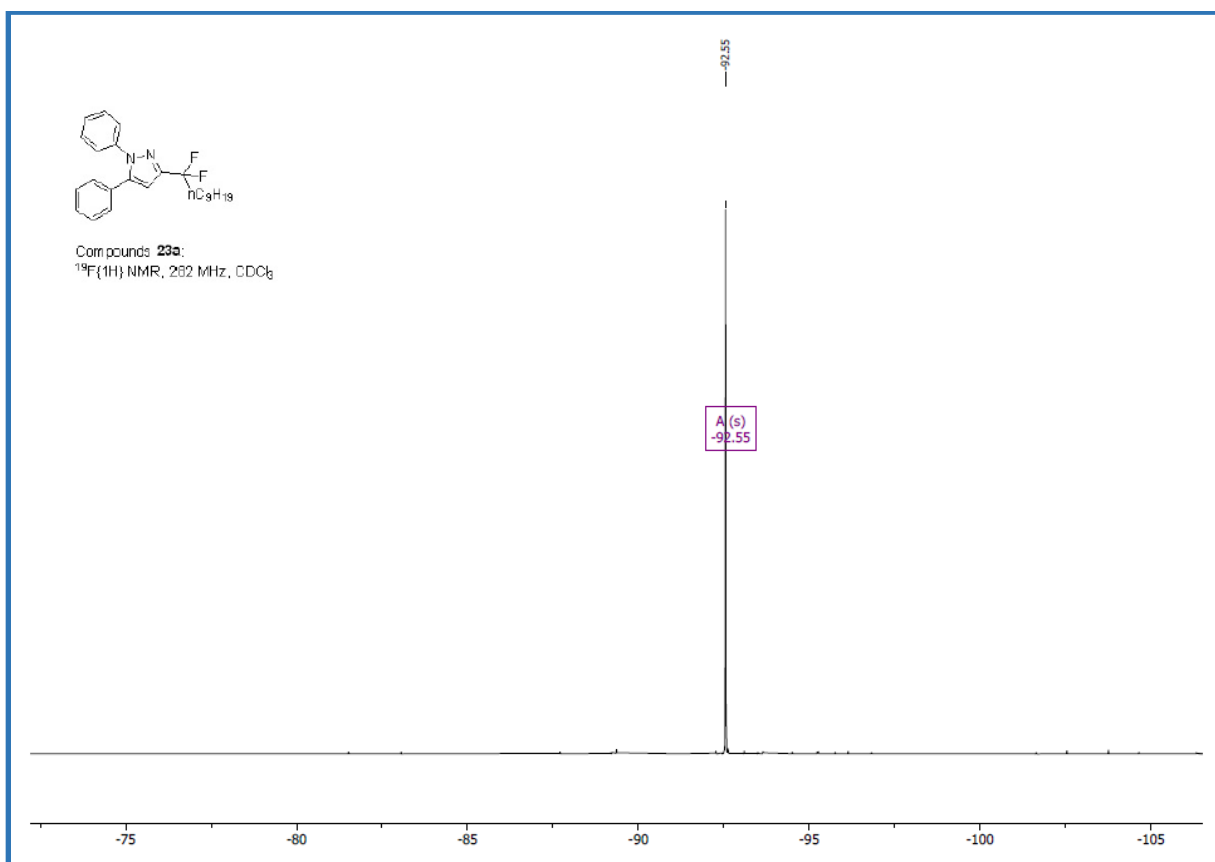
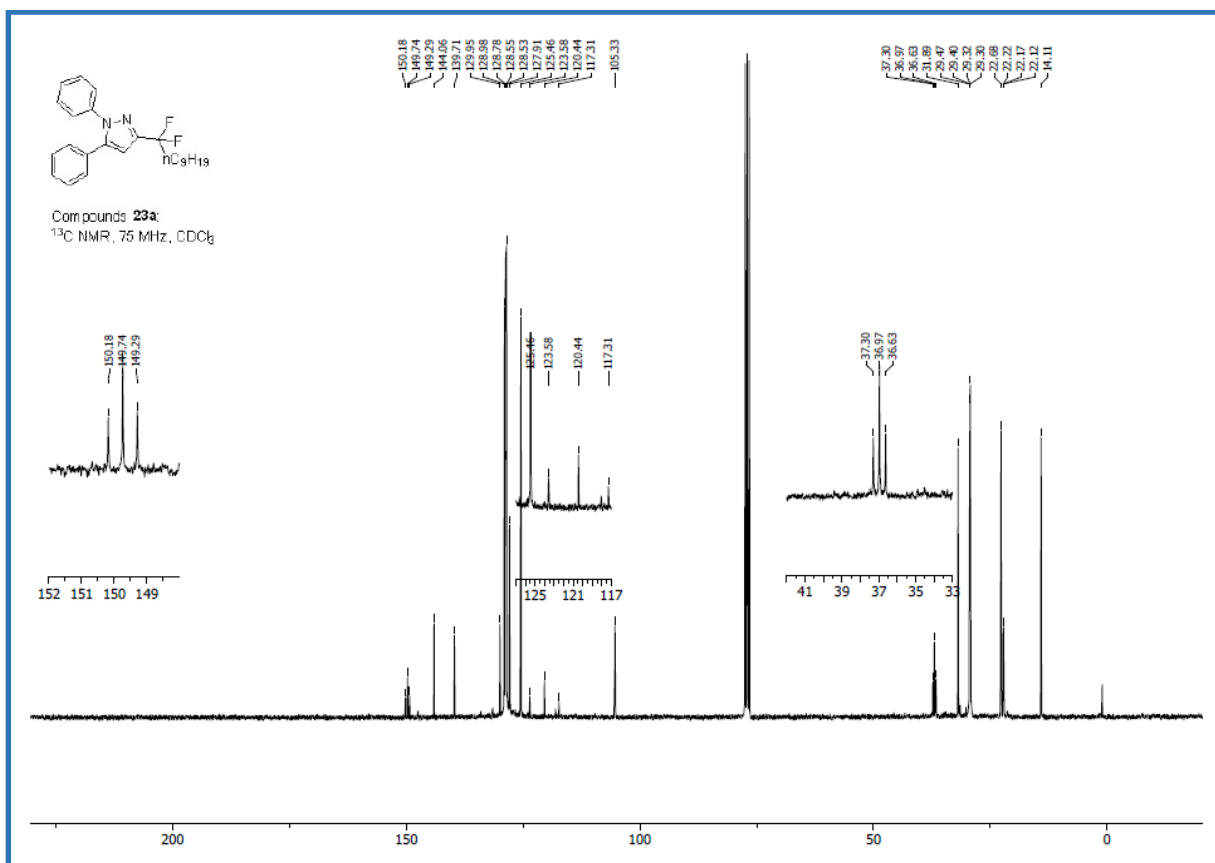






NMR spectra of 23a





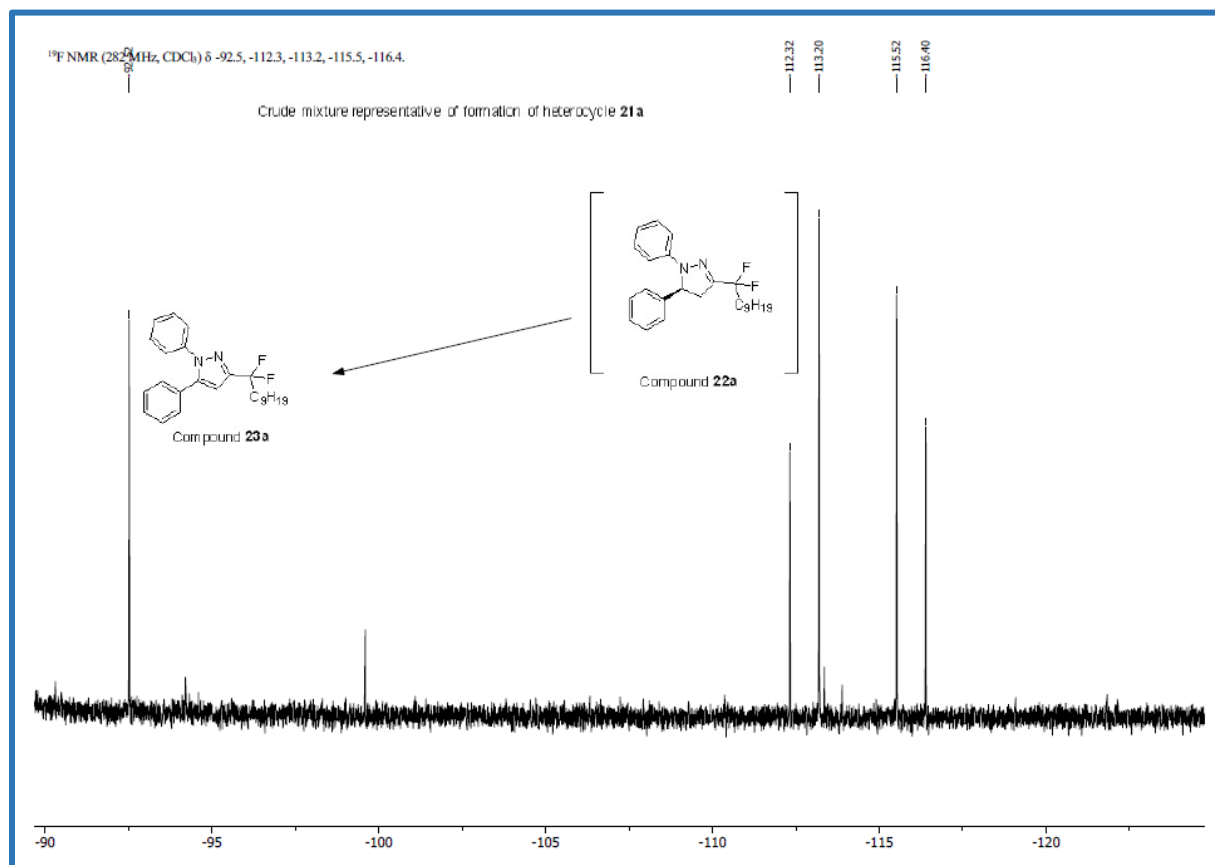
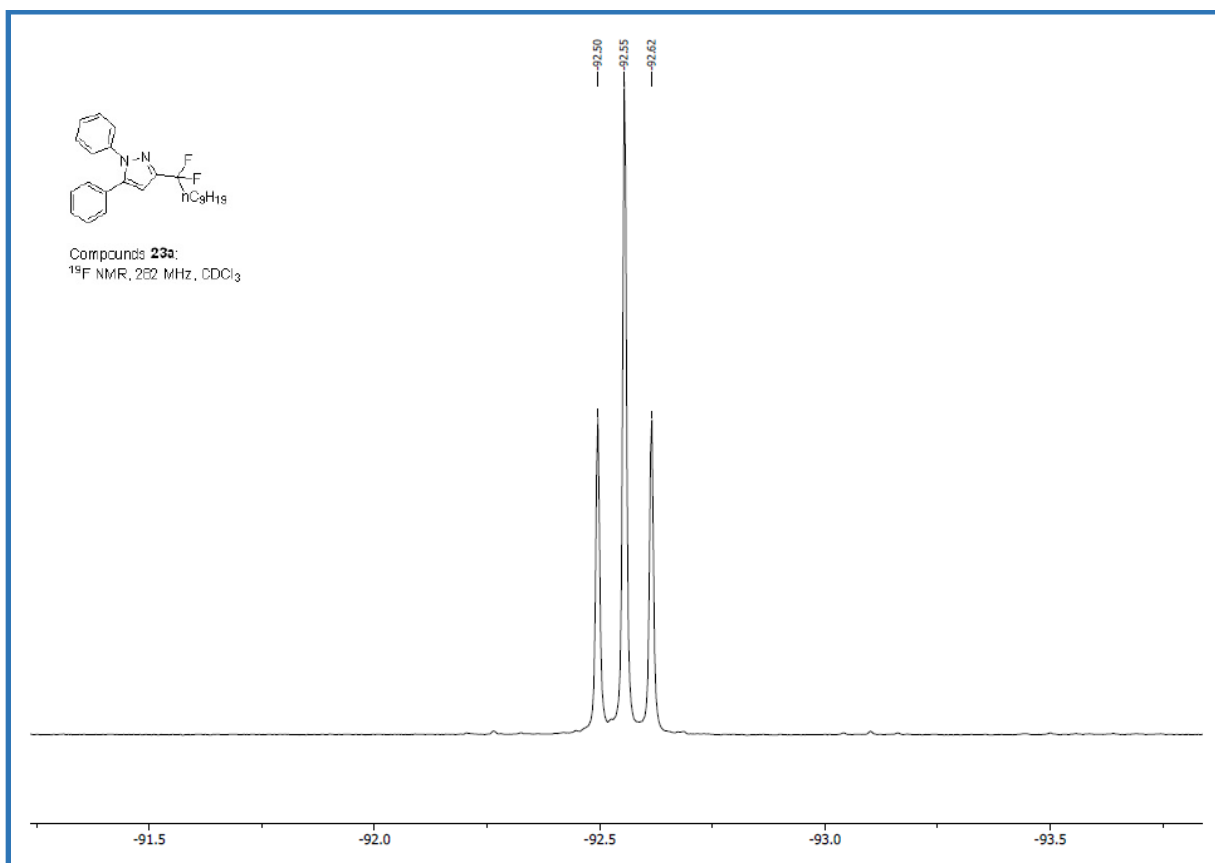


Figure: ^{19}F NMR spectra indicating the intermediacy of an intermediate (postulated structure **22a**) along the formation of **23a**