

Supporting Information

Visible-Light-Induced Photocatalyst-Free Activation of Alkynyl Triflones for Trifluoromethylalkynylation of Unactivated 1,6-Dialkenes

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Table of Contents

1. General Information.....	2
1.1. Materials and Instruments	2
2. Experimental Procedures	3
2.1 Preparation of Starting Materials.....	3
2.2 General Procedure for the Synthesis of Products	5
2.3 The Gram-scale Synthesis	5
2.4 The Application under the Sunlight.....	6
2.5 Synthetic Transformations.....	7
2.6 Set of Experiments.....	7
2.7 Mechanistic Study	8
3. Characterization Data	13
3.1 Characterization Data for Substrates	13
3.2 Characterization Data for Products.....	14
4. NMR Copies of Products.....	26

1. General Information

1.1. Materials and instruments

All the chemicals were purchased from commercial suppliers, all commercially available reagents were directly used without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All the ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz spectrometer operating at 400 MHz, 101 MHz, and 376 MHz, respectively. Proton chemical shifts δ were given in ppm using tetramethylsilane as the internal standard. All NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ at room temperature (20 ± 3 °C). High-resolution mass spectroscopy (HRMS) was taken with a 3000-mass spectrometer, using Waters Q-ToF MS/MS system with the ESI technique.

The spectrum of our lamp and the visible-light irradiation instrument

Photochemical reaction was carried out under visible light irradiation by a blue LED at 25 °C. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. Eight 10 W blue LED were equipped in this Photo reactor. The blue LED's energy peak wavelength is 430 nm, peak width at half-height is 18.4 nm, irradiance@10 W is 237.57 mW/cm^2 (Figure S1). The reaction vessel is borosilicate glass test tube and the distance between it and the lamp is 15 mm, no filter is applied. More details are showed in Figures S1-S4.

Name of parameter	Parameter value	Name of parameter	Parameter value	Name of parameter	Parameter value
Ultraviolet harmful irradiation (mW/cm^2)	0.000	Coordinate (u, v)	0.2384, 0.0209	CIE1931 Y	35322.906
UVC (mW/cm^2)	0.000	Coordinate (u', v')	0.2384, 0.0313	CIE1931 Z	3006587.250
UVB (mW/cm^2)	0.000	SDCM	100.0	TLCI-2012	0
UVA (mW/cm^2)	0.2275	Color render index	-80.4	Integral time (ms)	0.1
Euv (mW/cm^2)	0.23	Ee (mW/cm^2)	237.57027	Peak signal (ms)	51818
Eb (mW/cm^2)	236.28	S/P	36.907	Dark signal	2434
Eg (mW/cm^2)	0.00	WLD (nm)	437.20	Level compensation	2892
Er (mW/cm^2)	0.00	Color purity (%)	99.9		
Eir (mW/cm^2)	1.41	Half width (nm)	18.4		
Illuminance (lx)	24125.55	Peak wavelength (nm)	429.7		
Candlepower (fc)	2241.32	Central wavelength (nm)	429.5		
CCT (K)	100000	Centroid wavelength (nm)	433.4		
DUV	-0.11668	RGB	0.0, 0.0, 100.0		
Coordinate (x, y)	0.1659, 0.0097	CIE1931 X	605200.438		

Figure S1. Parameter list

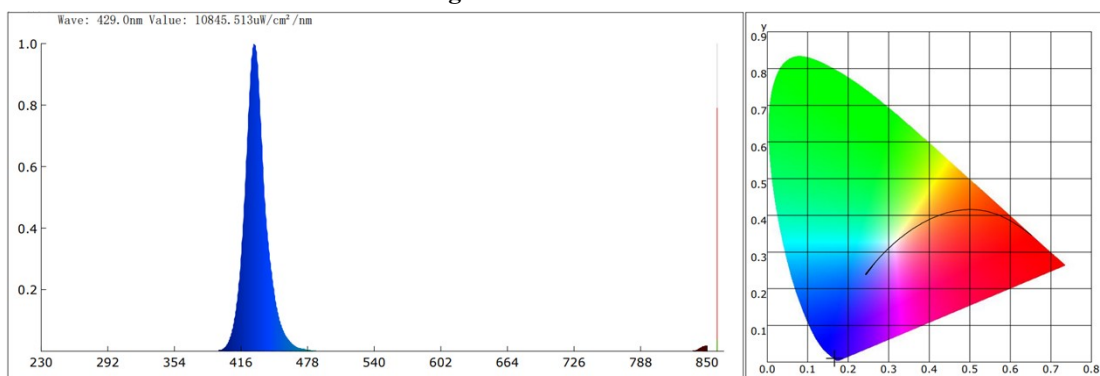


Figure S2. The spectrum of our lamp (blue LED)

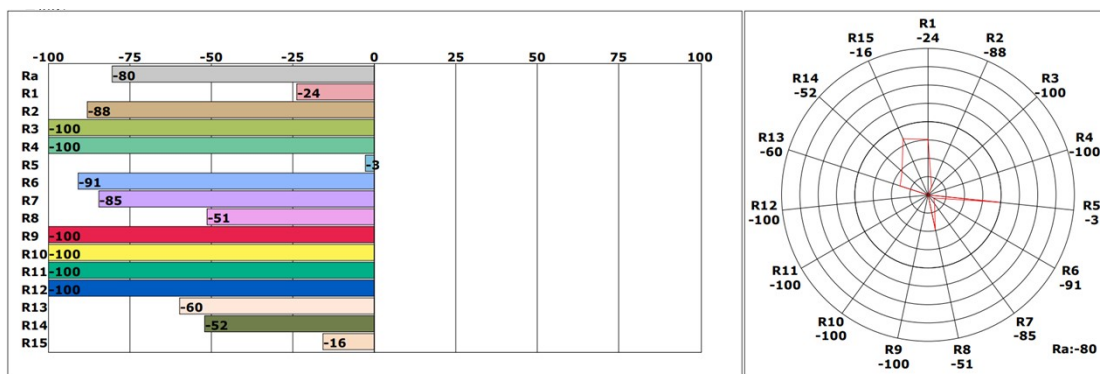


Figure S3. Color render index

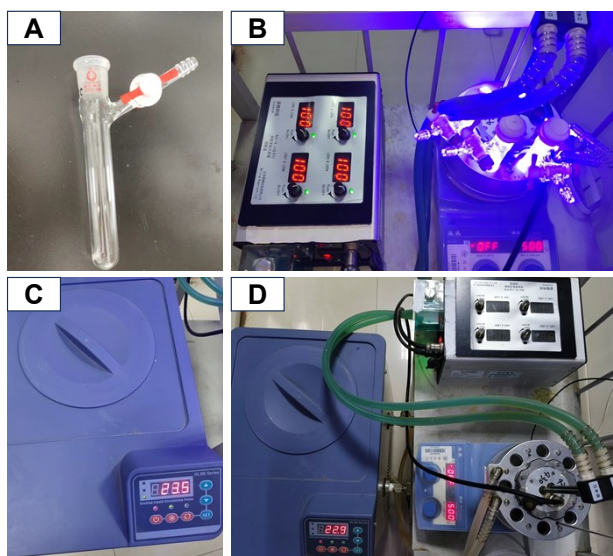
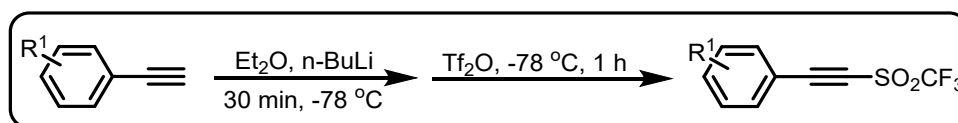


Figure S4. A: Schlenk tube; B: Photoreactor; C: Cooling water circuit; D: Total reaction system.

2. Experimental Procedures

2.1 Preparation of starting materials

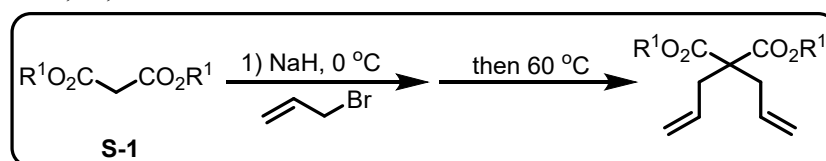
Preparation of **2a-2o**



Scheme S1. General experimental procedures for substrate **2a-2o**

2a-2o were synthesized according to the literature report.¹ To a stirring solution of alkynes (1.0 equiv) in ether was added n-BuLi (1.1 equiv) over 30 min at -78 °C under a nitrogen atmosphere. After stirring at -78 °C for half an hour, the corresponding lithium acetylide was slowly transferred via cannula to a solution of triflic anhydride (1.0 equiv) in ether at -78 °C. The reaction was stirred at -78 °C for 1 h before being quenched with water. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford **2a-2o**.

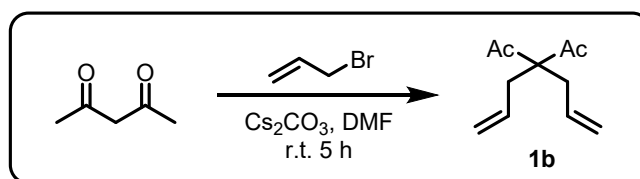
Preparation of **1a**, **1c**, **1d** and **1f**



Scheme S2. General experimental procedures for substrate **1a**, **1c**, **1d** and **1f**

1a, **1c**, **1d**, and **1f** were synthesized according to the literature report.² To a suspension of NaH (420 mg, 60% dispersion in mineral oil, 10.5 mmol, 2.1 equiv) in dry THF (20 mL) was added dropwise **S-1** (5.0 mmol, 1.0 equiv) at 0 °C under nitrogen atmosphere for 30 min. After stirring at 0 °C for half an hour, a solution of allyl bromide (11.0 mmol, 2.2 equiv) in THF (6 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was quenched by the addition of saturated aqueous NH₄Cl solution and H₂O, and extracted with EtOAc. The combined organics were washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford **1a**, **1c**, **1d**, and **1f**.

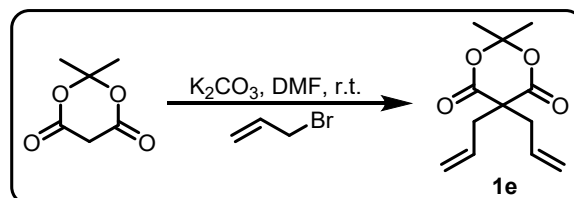
Preparation of **1b**



Scheme S3. General experimental procedures for substrate **1b**

1b was synthesized according to the literature report.³ The allyl bromide (10 mmol, 2.5 equiv) was added to a mixture of acetyl acetone (4 mmol, 1 equiv), cesium carbonate (10 mmol, 2.5 equiv) and DMF (20 mL) at room temperature, then the mixture was stirred for 5 h. Finally, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na₂SO₄, filtered and the filtrate was evaporated and purified by column chromatography to afford **1b**.

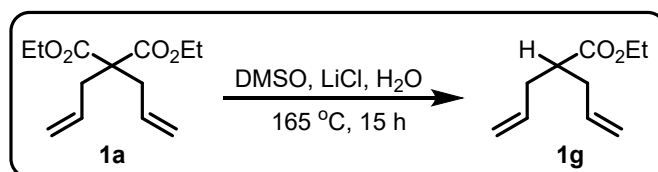
Preparation of **1e**



Scheme S4. General experimental procedures for substrate **1e**

1e was synthesized according to the literature report.⁴ To a dry 50 mL round bottom flask equipped with a stir bar, Meldrum's acid (5 mmol, 1 equiv), allyl bromide (11 mmol, 2.2 equiv), DMF (20 mL), and K₂CO₃ (15 mmol, 3 equiv) were combined. The reaction mixture was allowed to stir at room temperature overnight. The reaction was quenched upon pouring into 30 mL of 1 M HCl, extracted with EtOAc, dried with Na₂SO₄, filtered and the filtrate was evaporated and purified by column chromatography to afford **1e**.

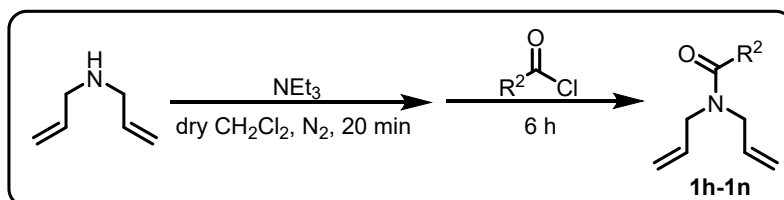
Preparation of **1g**



Scheme S5. General experimental procedures for substrate **1g**

1g was synthesized according to the literature report.⁵ The commercial **1a** (5 mmol, 1 equiv) was dissolved in DMSO (15 mL) and H₂O (5 mL), followed by the addition of LiCl (15.5 mmol, 3.1 equiv). The mixture was placed into a preheated 165 °C oil bath and refluxed for 15 hours (monitored by TLC). After cooling to room temperature, H₂O was added, and the solution was extracted by EtOAc, dried with Na₂SO₄, filtered and the filtrate was evaporated and purified by column chromatography to afford **1g**.

Preparation of **1h-1n**



Scheme S6. General experimental procedures for substrate **1h-1n**

1f was synthesized according to the literature report.⁶ Diallylamine (5.0 mmol, 1 equiv) was added dropwise to a stirred solution of triethylamine in dry CH₂Cl₂ (10.0 mL) at 0 °C. Then, the formyl chloride (6.00 mmol) was slowly added to the mixture for 30 min. The solution was warmed up to room temperature and stirred for 6 h. After completion of the reaction, aqueous NaHCO₃ (25 mL) was added. The crude product was extracted with CH₂Cl₂. The combined organic layers were washed with 1 M HCl (3 × 20 mL) and brine (3 × 20 mL), and then dried over Na₂SO₄ and concentrated. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford **1h-1n**.

2.2 General procedure for the synthesis of products

In a 25 mL Schlenk tube, a mixture of 1,6-dialkene **1** (0.1 mmol), alkynyl triflone **2** (0.2 mmol, 2.0 equiv), and BPO (20 mol%) in 1 mL TBME was allowed to stir with irradiation of 10 W 430 nm blue LED under N₂ at rt for 12 h. The reaction was monitored by TLC. The reaction mixture was quenched with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product **3**.

2.3 The gram-scale synthesis

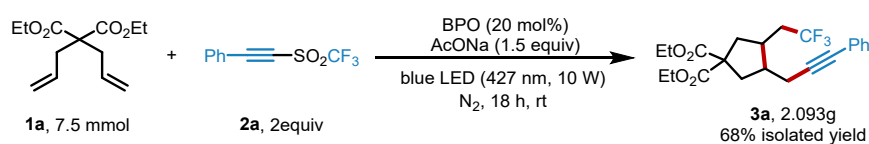




Figure S5. The reactor for the gram-scale synthesis

The reactor for the gram-scale synthesis: Gram-scale synthesis of **3a** with blue LEDs light irradiation under N₂ atmosphere: **1a** (1.8023 g, 7.5 mmol), **2a** (3.512 g, 15 mmol), BPO (363 mg, 1.5 mmol) in 75 mL TBME at room temperature for 18 h with the assistance of designed reactor. The distance from the reaction vessel to the light source is 5.2 cm. The reaction was monitored by TLC. The reaction mixture was extracted with ethyl acetate (3×25 mL). The combined organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford an isolated yield of **3a** (1.21 g, 55% yield).

2.4 The application under the sunlight

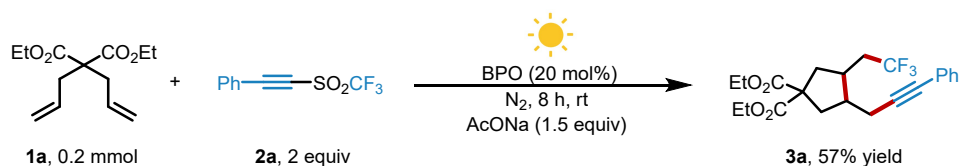
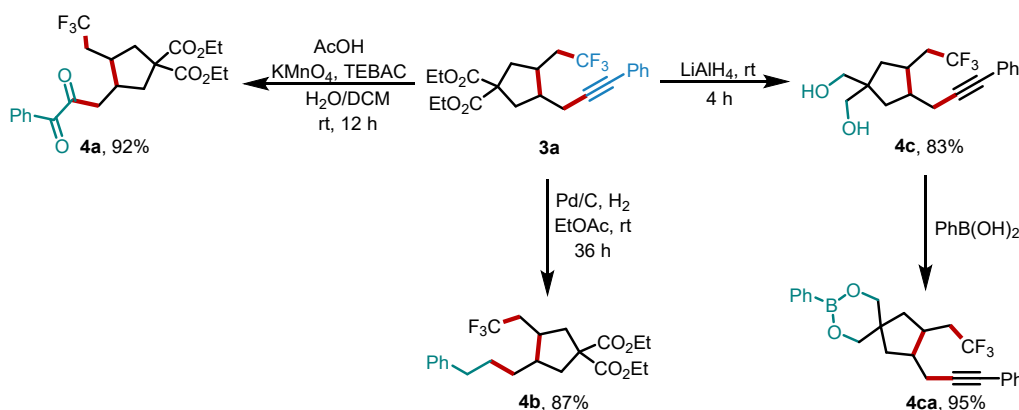


Figure S6. The synthesis of **3a** under the sunlight

The mixture of substrates **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, equiv), BPO (20 mol%), AcONa (2 equiv) and TBME (2 mL) were sequentially added into a reaction tube, then the reaction system was irradiated under sunlight in N₂ atmosphere for 8 h (from 9:00 to 17:00, 2023/03/28, Zhengzhou, China. Temperature: 9 °C – 23 °C). The isolated yield of **3a** (57%) was given.

2.5 Synthetic transformations



Scheme S7. General experimental procedures for synthetic transformations of **3a**

Synthesis of product 4a: In a 25 mL round-bottom flask, **3a** (0.2 mmol, 1.0 equiv), AcOH (0.6 mL) and TEBAC (0.1 mmol, 50 mol%) were dissolved in 3.0 mL CH_2Cl_2 . Then a solution of KMnO_4 (0.6 mmol, 3 equiv) in H_2O (3.0 mL) was added. The reaction mixture was stirred at room temperature for 8 h. Then the excess of KMnO_4 and formed MnO_2 were destroyed by the addition of small portions of Na_2SO_3 . Finally, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in CH_2Cl_2 and the mixture was washed with water, brine, dried with Na_2SO_4 , filtered and the filtrate was evaporated and purified by column chromatography to afford **4a**.

Synthesis of product 4b: In a flame-dried sealed tube, to a solution of **3a** (0.1 mmol, 1 equiv) and 10 wt% Pd/C (0.005 mmol, 5 mol %) in EA (1 mL), the hydrogenation with a hydrogen balloon was performed at rt for 36 h. After filtration through a short pad of celite, the organic solvent was removed under vacuum. The filtrate was evaporated and purified by column chromatography to afford **4b**.

Synthesis of product 4c: In a flame-dried sealed tube, a dry THF (2 mL) solution of **3a** (0.2 mmol, 1 equiv) was added dropwise over a period of 30 min to a suspension of LiAlH_4 (0.6 mmol, 3 equiv) in dry THF (0.5 mL) at 0 °C. After completion of the reaction as detected by TLC, the reaction was quenched with saturated aqueous NH_4Cl (4 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over MgSO_4 and filtered. The filtrate was evaporated and purified by column chromatography to afford **4c**.

Synthesis of product 4ca: In a flame-dried flask, phenylboronic acid (0.1 mmol, 1 equiv) was added to the solution of **4c** (0.1 mmol, 1 equiv), dry MgSO_4 (0.2 mmol, 2 equiv) and dry THF (1 mL). The reaction was stirred in at room temperature for 4 hours. Finally, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4 , filtered and the filtrate was evaporated and purified by column chromatography to afford **4ca**.

2.6 Set of Experiments

A set of experiments that employed **1a** and **2a** were performed to evaluate the reaction-condition-based sensitivity of this conversion, which will be valuable in increasing the insight of this new synthetic method and reproducibility. Various parameters, including concentration, temperature, oxygen level, water level, light intensity, and scale, were chosen with positive and

negative direction relative to the standard reaction conditions. Each experiment only deliberately changed one parameter, while keeping others at standard levels.

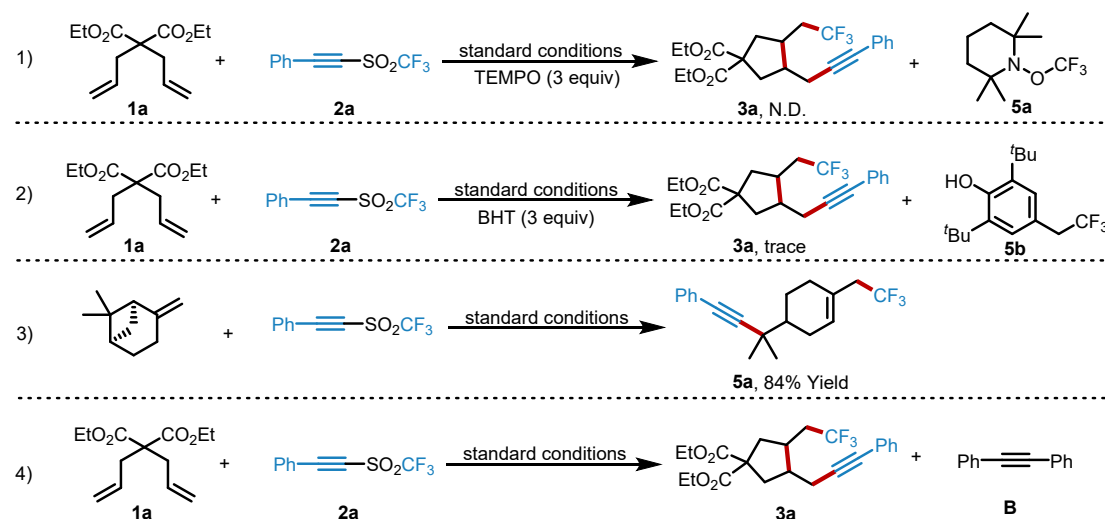
Table S1. Set of Experiments^a

Parameter	Variation		Description	Yield ^b	Deviation ^c
Concentration (<i>c</i>)	High <i>c</i>	<i>c</i> + 10% <i>c</i>	0.9 ml TBME	72%	-3%
	Low <i>c</i>	<i>c</i> - 10% <i>c</i>	1.1 ml TBME	70%	-5%
H ₂ O level	High H ₂ O	+ H ₂ O; V _{H₂O} = 1% V _{rxn}	10 μL H ₂ O in 1 mL TBME	72%	-3%
O ₂ level	-	Air	Air instead of N ₂	0%	-100%
Temperature (<i>T</i>)	High <i>T</i>	<i>T</i> + 10 °C	35 °C	76%	+3%
	Low <i>T</i>	<i>T</i> - 10 °C	15 °C	43%	-34%
Light intensity (<i>W</i>)	Low <i>W</i>	<i>W</i> /16	0.625 W	0%	-100%
Scale	Big scale	n·15	3 mmol of 2a	68%	-8%

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), BPO (20 mol%), AcONa (1.5 equiv), solvent (1 mL), 430 nm blue LED (10 W) with N₂ protection at rt for 12 h. ^b The average yield of three parallel reactions. ^c Deviation from the yield of standard reaction.

2.7 Mechanistic study

2.7.1 Radical-trapping experiments



Scheme S8. General experimental procedures for radical-trapping experiment

Experimental process 1: To a 25 mL reaction tube, 1,6-dialkene **1a** (24 mg, 0.1 mmol), alkynyl triflone **2a** (47 mg, 0.2 mmol), AcONa (13 mg, 0.15 mmol), BPO (20 mol%), 2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl (TEMPO) (3 equiv) and TBME (1 mL) were added. This mixture was stirred for 12 h at room temperature under a N₂ atmosphere.

Experimental process 2: To a 25 mL reaction tube, 1,6-dialkene **1a** (24 mg, 0.1 mmol), alkynyl triflone **2a** (47 mg, 0.2 mmol), AcONa (13 mg, 0.15 mmol), BPO (20 mol%), TBME (1 mL), and 2,6-di-tert-butyl-4-methylphenol (BHT) (3 equiv) were added. This mixture was stirred for 12 h at room temperature under a N₂ atmosphere.

Experimental process 3: To a 25 mL reaction tube, β -pinene (0.2 mmol), alkynyl triflone **2a** (94 mg, 0.2 mmol), AcONa (26 mg, 0.3 mmol), BPO (20 mol%) and TBME (2 mL) were added. This mixture was stirred for 12 h at room temperature under a N₂ atmosphere.

Experimental process 4: To a 25 mL reaction tube, 1,6-dialkene **1a** (24 mg, 0.1 mmol), alkynyl triflone **2a** (47 mg, 0.2 mmol), AcONa (13 mg, 0.15 mmol), BPO (20 mol%), TBME (1 mL) were added. This mixture was stirred for 12 h at room temperature under a N₂ atmosphere.

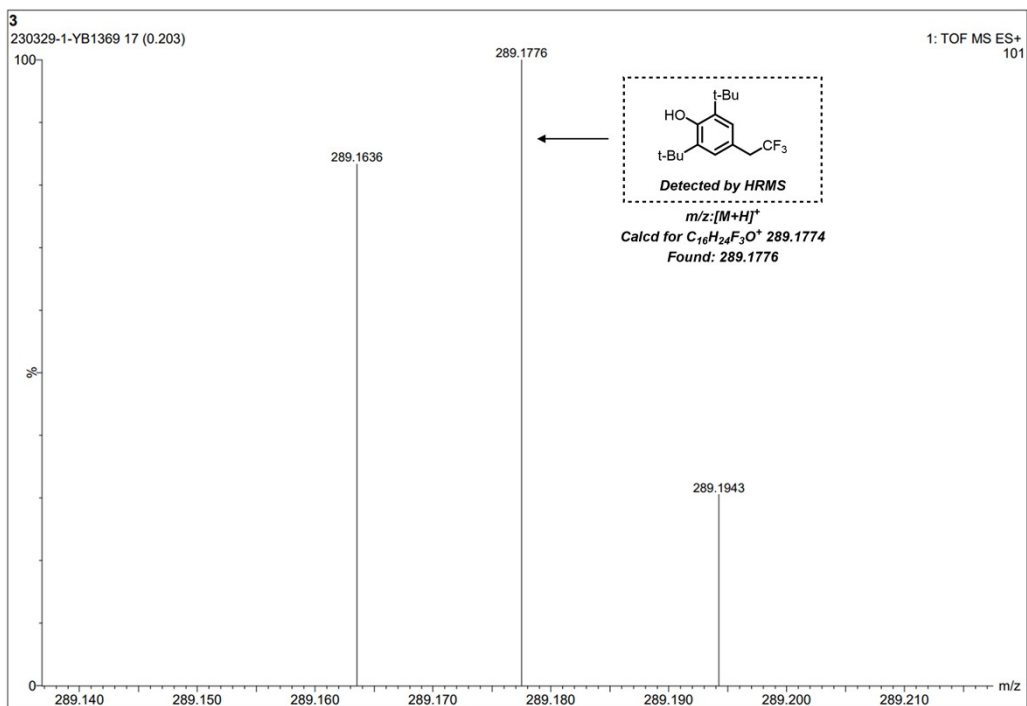


Figure S7. HR-MS of 5a

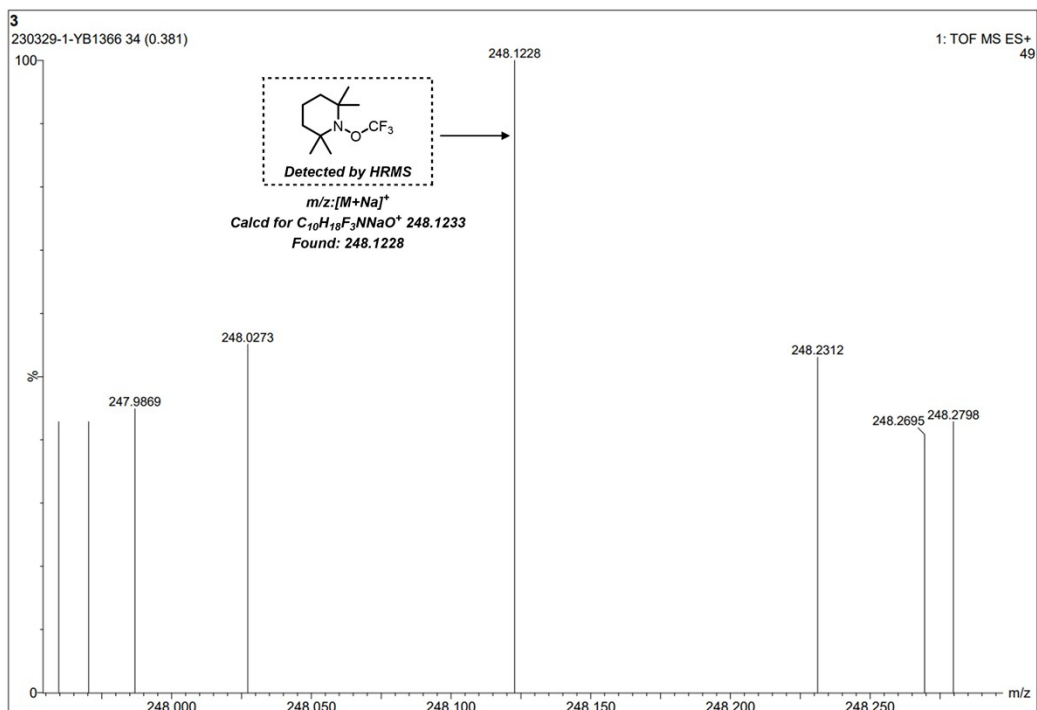


Figure S8. HR-MS of 5b

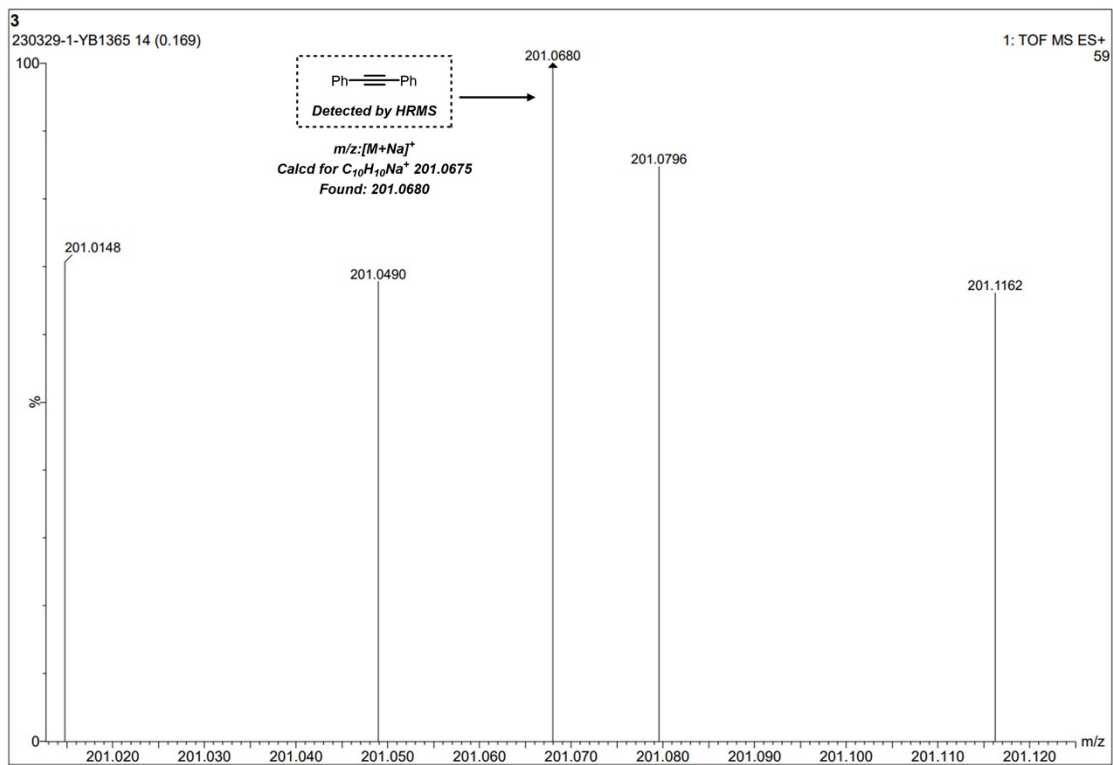


Figure S9. HR-MS of B

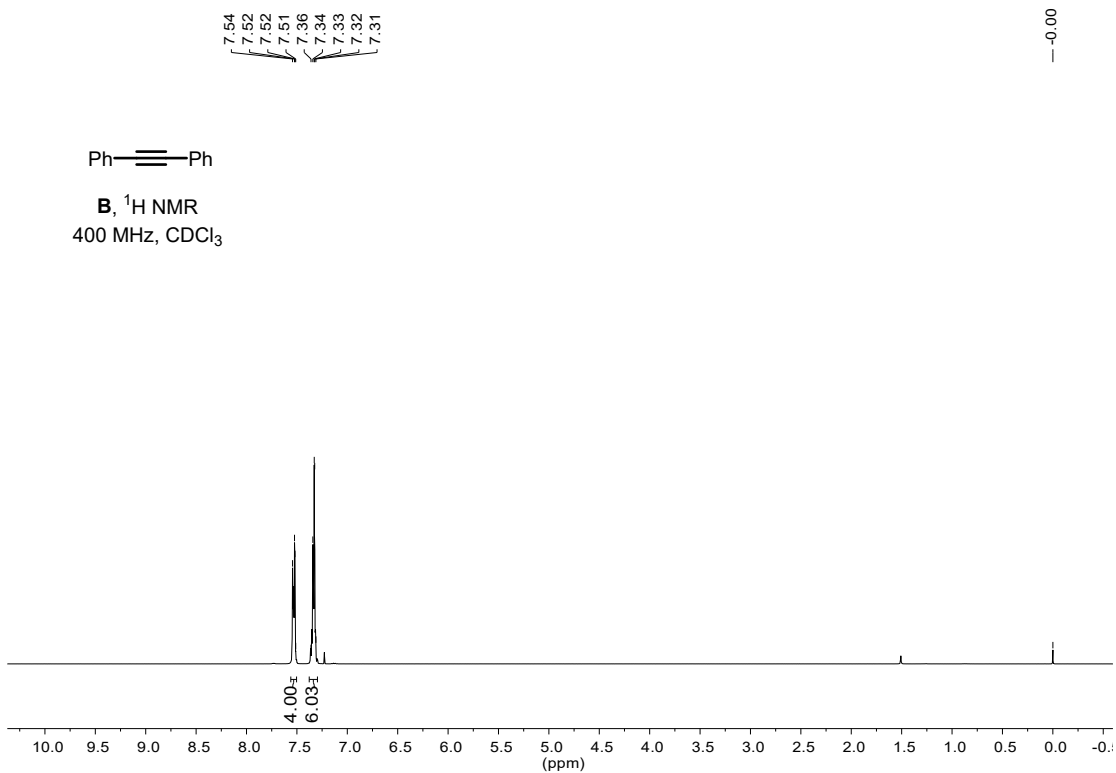


Figure S10. 1H NMR spectra of B

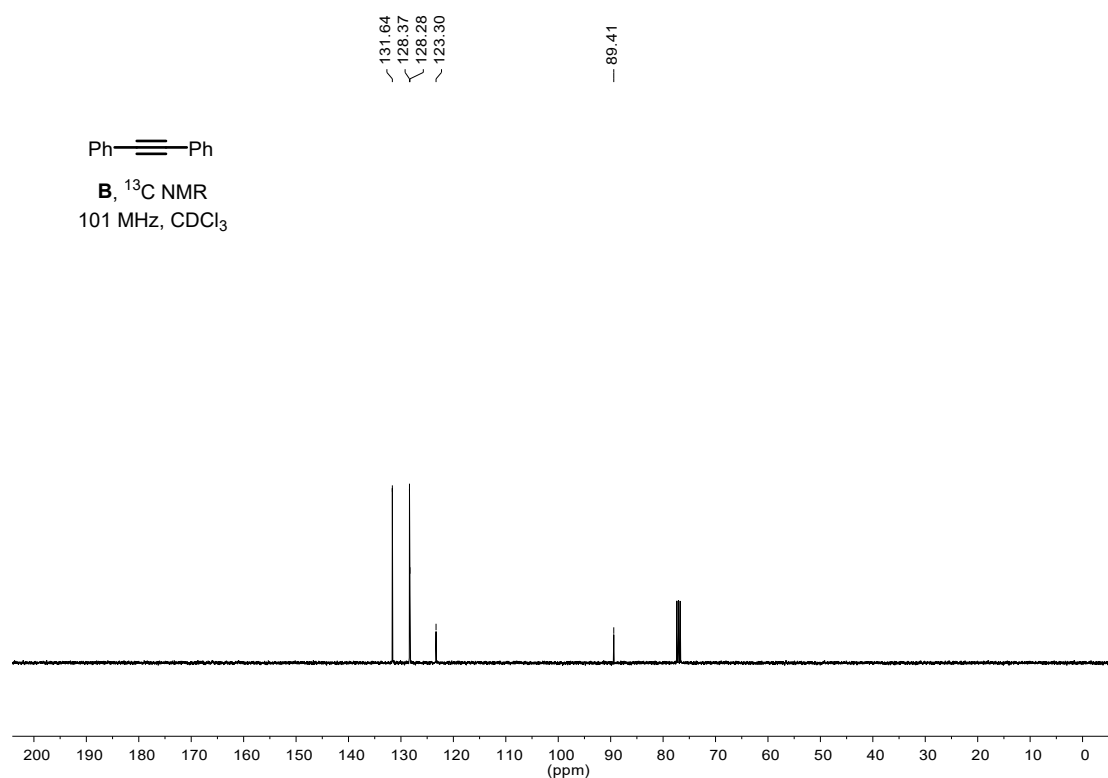


Figure S11. ^{13}C NMR spectra of **B**

2.7.2 Light ON/OFF control experiment

To 6 identical 25 mL reaction tubes, 1,6-dialkene **1a** (24 mg, 0.1 mmol), alkynyl triflone **2a** (47 mg, 0.2 mmol), AcONa (13 mg, 0.15 mmol), BPO (20 mol%) and TBME (1 mL) were added. The tubes were sealed, then irradiated with 10 W blue LEDs. All the reactions were stirred under blue light irradiation at ambient temperature for 2 h. Then the light was turned off. Remove one of the tubes. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The yield of product was determined by ^{19}F NMR using benzotrifluoride as the internal standard. The remaining mixture was stirred in the absence of light for an additional 2 h. Then remove one of the tubes. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. ^{19}F NMR analysis was performed every 2 h until the reaction time reached 12 h.



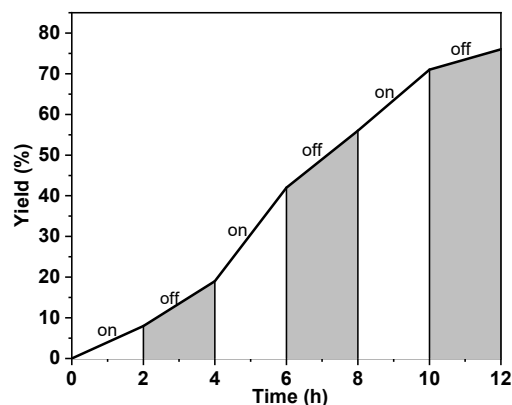


Figure S12. Light ON/OFF control experiment

2.7.3 ^{19}F NMR spectra of reaction mixtures

Experimental process 1: To a 25 mL reaction tube, BPO (0.05 mmol), **2a** (0.1 mmol) and TBME (1 mL) were added. This mixture was stirred for 3 h under the irradiation of a 10 W blue LED (430 nm) at room temperature under a N_2 atmosphere. The reaction mixture was analyzed by ^{19}F NMR.

Experimental process 2: To a 25 mL reaction tube, **2a** (0.1 mmol) and TBME (1 mL) were added. This mixture was stirred for 3 h under the irradiation of a 10 W blue LED (430 nm) at room temperature under a N_2 atmosphere. The reaction mixture was analyzed by ^{19}F NMR.

As can be shown in Figure S13, a signal at -49.82 ppm corresponding to compound **5d** was expressly observed,⁷ which was higher than that in the solvent of alkynyl triflone **2a** under the irradiation of a 10 W blue LED (430 nm) for 3 h. The results indicated the important role of BPO in the production of CF_3 radical.

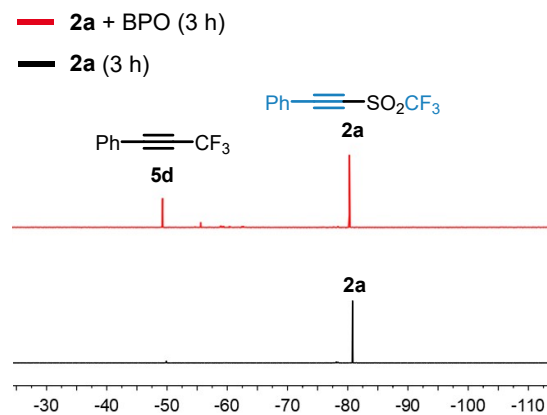
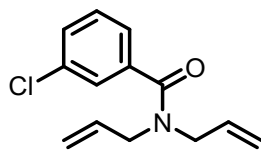


Figure S13. ^{19}F NMR spectra of reaction mixtures

3. Characterization Data

3.1 Characterization data for substrates

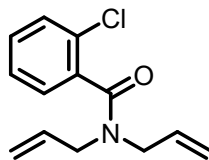
N,N-diallyl-3-chlorobenzamide (**1v**)



Purification by flash column chromatography (PE:EA, v/v = 100:10) to provide **1v**. Colorless oil (1.08

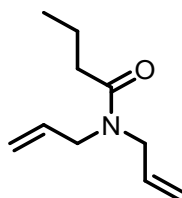
g, 92% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 1H), 7.39 – 7.35 (m, 1H), 7.35 – 7.28 (m, 2H), 5.79 (d, *J* = 53.0 Hz, 2H), 5.28 – 5.16 (m, 4H), 4.12 (s, 2H), 3.82 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.1, 137.9, 134.4, 132.6 (d, *J* = 37.2 Hz), 129.7 (d, *J* = 1.1 Hz), 126.8, 124.6, 117.9, 50.7, 47.1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₃H₁₅ClNO, 236.0837, found: 236.0838.

***N,N*-diallyl-2-chlorobenzamide (1w)**



Purification by flash column chromatography (PE:EA, v/v = 10:1) to provide **1w**. Colorless oil (1.05 g, 90% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.39 (m, 2H), 7.42 – 7.32 (m, 3H), 5.80 (d, *J* = 60.9 Hz, 2H), 5.27 – 5.14 (m, 4H), 4.13 (s, 2H), 3.83 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.7, 136.2, 133.2, 132.8, 129.6, 128.3, 126.5, 117.6, 50.7, 46.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₃H₁₅ClNO, 236.0837, found: 236.0839.

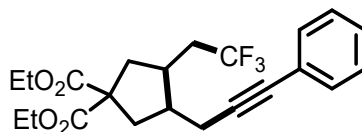
***N,N*-diallylbutyramide (1x)**



Purification by flash column chromatography (PE:EA, v/v = 10:1) to provide **1x**. Colorless oil (743 mg, 89% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 5.82 – 5.70 (m, 2H), 5.23 – 5.08 (m, 4H), 3.99 (d, *J* = 5.9 Hz, 2H), 3.88 (d, *J* = 4.8 Hz, 2H), 2.32 – 2.27 (m, 2H), 1.76 – 1.59 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.9, 133.5, 133.0, 117.0, 116.4, 49.1, 47.7, 34.9, 18.7, 13.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₀H₁₈NO, 168.1383, found: 168.1382.

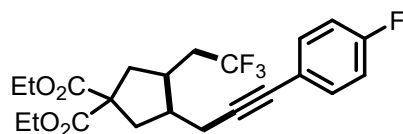
3.2 Characterization data for Products

diethyl-3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3a)



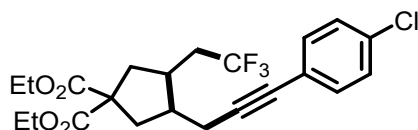
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3a**. Colorless oil (54 mg, 65% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.32 – 7.24 (m, 3H), 4.25 – 4.13 (m, 4H), 2.61 – 2.45 (m, 4H), 2.44 – 2.20 (m, 5H), 2.20 – 2.08 (m, 1H), 1.28 – 1.20 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.25, 172.19, 131.5, 128.2, 127.8, 127.1 (q, *J* = 277.0 Hz), 123.5, 87.7, 82.1, 61.7, 58.8, 40.9, 38.5, 38.4, 35.8 (q, *J* = 2.2 Hz), 33.6 (q, *J* = 28.2 Hz), 20.2, 14.0 (d, *J* = 1.7 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.44. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₂₆F₃O₄, 411.1778, found: 411.1784.

diethyl-3-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3b)



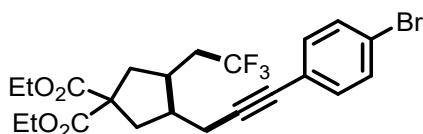
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3b**. Colorless oil (54 mg, 63% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.31 (m, 2H), 7.03 – 6.93 (m, 2H), 4.24 – 4.15 (m, 4H), 2.59 – 2.42 (m, 4H), 2.41 – 1.98 (m, 6H), 1.30 – 1.19 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 172.2, 162.2 (d, J = 248.6 Hz), 133.3 (d, J = 8.3 Hz), 128.4 (q, J = 277.0 Hz), 119.5 (d, J = 3.5 Hz), 115.5 (d, J = 22.0 Hz), 87.3, 81.0, 61.7, 58.7, 40.8, 38.5, 38.4, 35.8 (q, J = 2.3 Hz), 33.6 (q, J = 28.1 Hz), 20.1, 14.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.44, -111.78. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{F}_4\text{O}_4$, 429.1683, found: 429.1686.

diethyl-3-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3c)



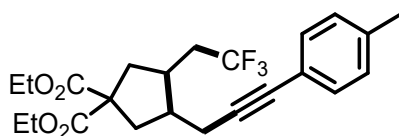
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3c**. Colorless oil (56 mg, 64% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 4.27 – 4.15 (m, 4H), 2.60 – 2.43 (m, 4H), 2.40 – 1.89 (m, 6H), 1.32 – 1.21 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 133.8, 132.7, 128.6, 127.0 (q, J = 277.1 Hz), 122.0, 88.8, 81.0, 61.7, 58.7, 40.8, 38.5, 38.3, 35.8 (q, J = 2.2 Hz), 33.6 (q, J = 28.3 Hz), 20.2, 14.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.37. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{ClF}_3\text{O}_4$, 445.1388, found: 445.1386.

diethyl-3-(3-(4-bromophenyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3d)



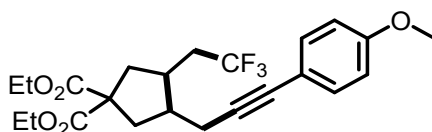
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3d**. Colorless oil (74 mg, 76% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 4.23 – 4.15 (m, 4H), 2.60 – 2.43 (m, 4H), 2.40 – 2.00 (m, 6H), 1.27 – 1.21 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 133.0, 131.5, 127.0 (q, J = 277.1 Hz), 122.4, 122.0, 89.0, 81.1, 61.7, 58.6, 40.7, 38.5, 38.3, 35.8 (q, J = 2.3 Hz), 33.6 (q, J = 28.2 Hz), 20.2, 14.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.43. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{BrF}_3\text{O}_4$, 489.0883, found: 489.0879.

diethyl-3-(3-(*p*-tolyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3e)



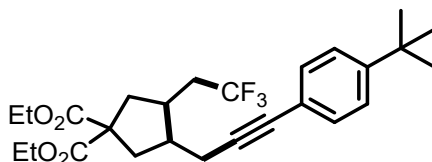
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3e**. Colorless oil (50 mg, 58% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.24 – 4.14 (m, 4H), 2.58 – 2.35 (m, 7H), 2.33 (s, 3H), 2.32 – 1.88 (m, 3H), 1.29 – 1.19 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 172.2, 137.8, 131.4, 129.0, 127.1 (q, *J* = 277.0 Hz), 120.4, 86.9, 82.1, 61.7, 58.7, 40.9, 38.5, 38.3, 35.8 (q, *J* = 2.3 Hz), 33.6 (q, *J* = 28.1 Hz), 21.4, 20.2, 14.0 (d, *J* = 1.4 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.39. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₃H₂₈F₃O₄, 425.1934, found: 425.1935.

diethyl-3-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3f)



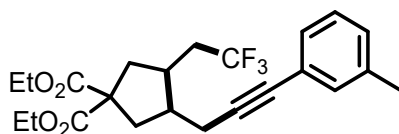
Purification by flash column chromatography (PE:EA, v/v = 5:1) to provide **3f**. Colorless oil (44 mg, 51% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.25 – 4.15 (m, 4H), 3.86 (s, 3H), 3.49 – 3.21 (m, 2H), 2.96 – 2.74 (m, 1H), 2.64 – 2.55 (m, 3H), 2.53 – 2.29 (m, 1H), 2.27 – 2.02 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 171.7, 162.4, 134.9, 126.6 (q, *J* = 277.3 Hz), 114.6, 108.9, 94.2, 82.7, 62.1, 61.9, 58.1, 57.6, 55.5, 38.3, 38.0, 37.0, 36.6 (q, *J* = 2.2 Hz), 33.4 (q, *J* = 28.4 Hz), 14.0 (d, *J* = 2.8 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.05, -64.40. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₃H₂₈F₃O₅, 441.1883, found: 441.1881.

diethyl-3-(3-(4-(tert-butyl)phenyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3g)



Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3g**. Colorless oil (58 mg, 63% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 (s, 4H), 4.28 – 4.14 (m, 4H), 2.60 – 2.44 (m, 4H), 2.42 – 1.88 (m, 6H), 1.32 (s, 9H), 1.29 – 1.23 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 172.2, 151.0, 131.2, 127.1 (q, *J* = 277.2 Hz), 125.2, 120.5, 86.9, 82.1, 61.7, 58.8, 40.8, 38.5, 38.4, 35.7 (q, *J* = 2.3 Hz), 34.7, 33.6 (q, *J* = 28.0 Hz), 31.2, 20.3, 14.0 (d, *J* = 1.4 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.39. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₆H₃₄F₃O₄, 467.2404, found: 467.2402.

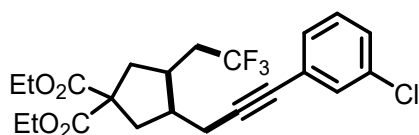
diethyl-3-(3-(*m*-tolyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3h)



Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3h**. Colorless oil (46 mg, 55% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 (s, 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.09 (m,

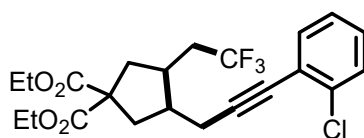
1H), 4.28 – 4.15 (m, 4H), 2.60 – 2.33 (m, 8H), 2.31 (s, 3H), 2.28 – 2.11 (m, 2H), 1.30 – 1.21 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 172.2, 137.9, 132.1, 128.7, 128.6, 128.1, 127.1 (q, *J* = 277.0 Hz), 123.3, 87.3, 82.2, 61.7, 58.7, 40.9, 38.5, 38.3, 35.8 (q, *J* = 2.2 Hz), 33.6 (q, *J* = 28.1 Hz), 21.2, 20.2, 14.0 (d, *J* = 1.8 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.39. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₃H₂₈F₃O₄, 425.1934, found: 425.1941.

diethyl-3-(3-(3-chlorophenyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3i)



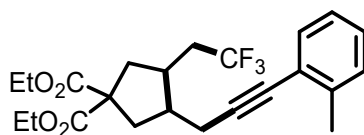
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3i**. Colorless oil (62 mg, 70% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 1.6 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.25 – 7.18 (m, 2H), 4.23 – 4.16 (m, 4H), 2.60 – 2.44 (m, 4H), 2.40 – 2.07 (m, 6H), 1.27 – 1.22 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.2, 134.0, 131.4, 129.7, 129.5, 128.1, 127.0 (q, *J* = 277.0 Hz), 125.2, 89.2, 80.8, 61.7, 58.6, 40.7, 38.5, 38.3, 35.8 (q, *J* = 2.3 Hz), 33.6 (q, *J* = 28.2 Hz), 20.1, 14.0. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.45. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₂₅ClF₃O₄, 445.1388, found: 445.1388.

diethyl-3-(3-(2-chlorophenyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3j)



Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3j**. Colorless oil (60 mg, 67% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H), 7.28 – 7.15 (m, 2H), 4.32 – 4.10 (m, 4H), 2.78 – 1.95 (m, 10H), 1.31 – 1.20 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 172.2, 135.9, 133.3, 129.1, 128.9, 127.1 (q, *J* = 277.1 Hz), 126.4, 123.3, 93.3, 79.0, 61.7 (d, *J* = 1.1 Hz), 58.7, 40.8, 38.5, 38.3, 35.7 (q, *J* = 2.3 Hz), 33.7 (q, *J* = 28.1 Hz), 20.4, 14.0 (d, *J* = 3.0 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.40. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₂₅ClF₃O₄, 445.1388, found: 445.1391.

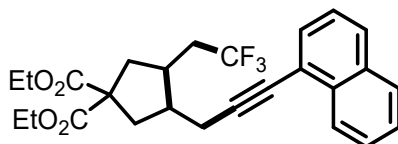
diethyl-3-(3-(*o*-tolyl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3k)



Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3k**. Colorless oil (58 mg, 69% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.10 (m, 3H), 4.28 – 4.15 (m, 4H), 2.66 – 2.43 (m, 6H), 2.43 (s, 3H), 2.41 – 2.16 (m, 4H), 1.32 – 1.21 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.27, 172.25, 140.0, 131.9, 129.3, 127.8, 127.1 (q, *J* = 277.0 Hz), 125.5, 123.3, 91.6, 80.9, 61.7, 58.7, 41.1, 38.5, 38.3, 35.7 (q, *J* = 2.3 Hz), 33.6 (q, *J* = 28.1 Hz), 20.7, 20.3,

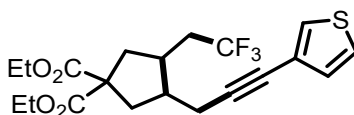
14.0 (d, $J = 2.8$ Hz). ^{19}F NMR (376 MHz, Chloroform- d) δ -64.41. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{28}\text{F}_3\text{O}_4$, 425.1934, found: 425.1935.

diethyl-3-(3-(naphthalen-1-yl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3l)



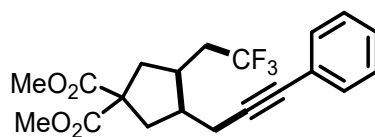
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3l**. Colorless oil (44 mg, 48% yield). ^1H NMR (400 MHz, Chloroform- d) δ 7.90 (s, 1H), 7.83 – 7.72 (m, 3H), 7.52 – 7.40 (m, 3H), 4.26 – 4.12 (m, 4H), 2.64 – 2.48 (m, 4H), 2.47 – 1.92 (m, 6H), 1.28 – 1.19 (m, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 172.30, 172.26, 132.8, 132.4, 131.0, 128.3, 127.7, 127.5, 127.4, 126.9 (q, $J = 277.1$ Hz), 126.3, 120.6, 87.9, 82.3, 61.5, 58.5, 40.7, 38.3, 38.2, 35.7 (q, $J = 2.3$ Hz), 33.4 (q, $J = 28.0$ Hz), 20.1, 13.8 (d, $J = 1.2$ Hz). ^{19}F NMR (376 MHz, Chloroform- d) δ -64.45. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{F}_3\text{O}_4$, 461.1934, found: 461.1937.

diethyl-3-(3-(thiophen-3-yl)prop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3m)



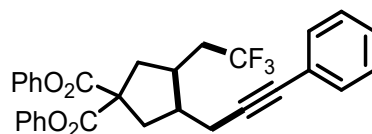
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3m**. Colorless oil (38 mg, 46% yield). ^1H NMR (400 MHz, Chloroform- d) δ 7.36 (dd, $J = 2.9, 1.0$ Hz, 1H), 7.24 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.06 (dd, $J = 5.0, 1.1$ Hz, 1H), 4.25 – 4.13 (m, 4H), 2.60 – 2.45 (m, 4H), 2.39 – 1.97 (m, 6H), 1.27 – 1.22 (m, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 172.3, 172.2, 129.9, 128.0, 127.0 (q, $J = 277.0$ Hz), 125.1, 122.4, 87.2, 77.2, 61.7, 58.7, 40.8, 38.5, 38.4, 35.8 (q, $J = 2.4$ Hz), 33.6 (q, $J = 28.1$ Hz), 20.2, 14.0. ^{19}F NMR (376 MHz, Chloroform- d) δ -64.43. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{24}\text{F}_3\text{O}_4\text{S}$, 417.1342, found: 417.1346.

dimethyl-3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3n)



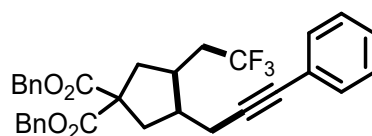
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3n**. Colorless oil (50 mg, 66% yield). ^1H NMR (400 MHz, Chloroform- d) δ 7.44 – 7.37 (m, 2H), 7.33 – 7.29 (m, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 2.61 – 2.46 (m, 4H), 2.42 – 2.00 (m, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 172.7, 172.6, 131.5, 128.3, 127.9, 127.0 (q, $J = 277.1$ Hz), 123.4, 87.6, 82.2, 58.6, 53.0 (d, $J = 6.5$ Hz), 40.7, 38.7, 38.5, 35.7 (q, $J = 2.3$ Hz), 33.6 (q, $J = 28.2$ Hz), 20.3. ^{19}F NMR (376 MHz, Chloroform- d) δ -64.42. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{O}_4$, 383.1465, found: 383.1467.

diphenyl-3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3o)



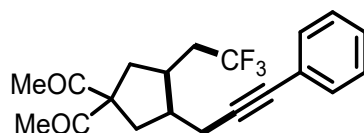
Purification by flash column chromatography (PE:EA, v/v = 50:1) to provide **3o**. Colorless oil (42 mg, 41% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.31 (m, 6H), 7.30 – 7.20 (m, 5H), 7.11 (dd, *J* = 13.4, 7.6 Hz, 4H), 3.02 – 2.74 (m, 2H), 2.73 – 2.53 (m, 4H), 2.50 – 2.07 (m, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.70, 170.66, 150.6 (d, *J* = 2.0 Hz), 131.6, 129.6 (d, *J* = 4.4 Hz), 128.3, 128.0, 127.0 (q, *J* = 276.8 Hz), 126.3 (d, *J* = 3.7 Hz), 123.4, 121.1 (d, *J* = 5.2 Hz), 87.4, 82.5, 58.9, 41.0, 38.7, 38.5, 36.1 (q, *J* = 2.2 Hz), 33.6 (q, *J* = 28.3 Hz), 20.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.36. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₃₀H₂₆F₃O₄, 507.1778, found: 507.1779.

dibenzyl-3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3p)



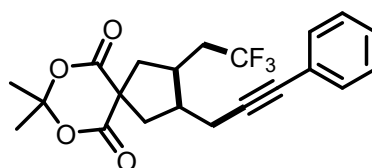
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3p**. Colorless oil (68 mg, 63% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.37 (m, 2H), 7.39 – 7.23 (m, 13H), 5.20 – 5.08 (m, 4H), 2.65 – 2.42 (m, 4H), 2.41 – 1.95 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.93, 171.87, 135.4 (d, *J* = 5.0 Hz), 131.6, 128.6 (d, *J* = 4.5 Hz), 128.4 (d, *J* = 4.5 Hz), 128.3, 128.1 (d, *J* = 3.7 Hz), 127.9, 127.1 (q, *J* = 277.2 Hz), 123.5, 87.6, 82.2, 67.5 (d, *J* = 3.3 Hz), 58.9, 40.8, 38.6, 38.5, 35.8 (q, *J* = 2.2 Hz), 33.6 (q, *J* = 28.4 Hz), 20.3. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.35. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₃₂H₃₀F₃O₄, 535.2091, found: 535.2092.

3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-diylbis(ethan-1-one) (3q)



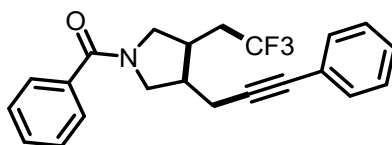
Purification by flash column chromatography (PE:EA, v/v = 50:1) to provide **3q**. Colorless oil (38 mg, 54% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.29 (m, 3H), 2.62 – 2.13 (m, 9H), 2.11 (s, 6H), 2.09 – 1.90 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 204.7, 204.1, 131.5, 128.3, 127.9, 127.0 (q, *J* = 277.2 Hz), 123.3, 87.5, 82.3, 74.0, 40.6, 35.7 (q, *J* = 2.3 Hz), 35.0, 34.8, 33.7 (q, *J* = 28.0 Hz), 26.8, 26.0, 20.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.44, -111.78. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₀H₂₂F₃O₂, 351.1566, found: 351.1569.

8,8-dimethyl-2-(3-phenylprop-2-yn-1-yl)-3-(2,2,2-trifluoroethyl)-7,9-dioxaspiro[4.5]decane-6,10-dione (3r)



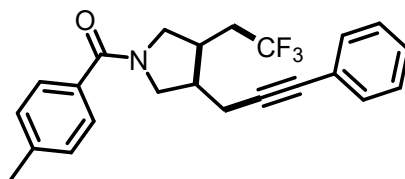
Purification by flash column chromatography (PE:EA, v/v = 20:1) to provide **3r**. Colorless oil (38 mg, 47% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.34 – 7.24 (m, 3H), 2.97 – 2.68 (m, 2H), 2.66 – 2.31 (m, 8H), 1.76 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.44, 171.31, 131.6, 128.27, 127.9, 127.0 (d, *J* = 277.0 Hz), 123.4, 105.1, 87.3, 82.2, 52.1, 43.8, 43.2, 42.7, 37.2 (q, *J* = 2.3 Hz), 33.1 (q, *J* = 28.3 Hz), 28.9 (d, *J* = 6.4 Hz), 19.8. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.33. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₁H₂₂F₃O₄, 395.1465, found: 395.1467.

phenyl(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)methanone (3t)



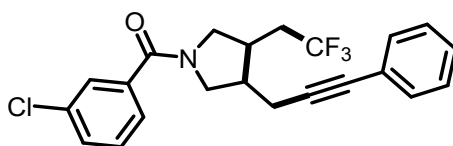
Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3t**. Colorless oil (32 mg, 42% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 2H), 7.44 – 7.26 (m, 8H), 3.95 – 3.46 (m, 4H), 2.84 – 2.51 (m, 3H), 2.51 – 2.34 (m, 2H), 2.34 – 2.02 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.0, 136.5, 136.3, 131.6, 131.5, 130.2, 130.0, 128.39, 128.35, 128.3, 128.2, 128.1, 127.1, 126.6 (q, *J* = 277.0 Hz), 123.1, 122.9, 86.5, 86.1, 82.63, 82.57, 53.9, 52.6, 50.7, 49.5, 40.5, 38.9, 35.9 (q, *J* = 1.8 Hz), 34.4 (q, *J* = 2.1 Hz), 32.8 (q, *J* = 29.0 Hz), 32.2 (q, *J* = 28.9 Hz), 19.4, 18.5. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.67, -64.87. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₂₁F₃NO, 372.1570, found: 372.1574.

(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)(*p*-tolyl)methanone (3u)



Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3u**. Colorless oil (40 mg, 53% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 3H), 7.32 – 7.26 (m, 4H), 7.17 (t, *J* = 7.8 Hz, 2H), 3.94 – 3.49 (m, 4H), 2.82 – 2.38 (m, 5H), 2.37 (s, 3H), 2.33 – 2.12 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.1, 140.4, 140.2, 133.5, 133.4, 131.5, 129.0, 128.32, 128.26, 128.11, 128.06, 127.3, 126.6 (q, *J* = 276.6 Hz), 123.1, 123.0, 86.5, 86.2, 82.60, 82.56, 53.9, 52.7, 50.7, 49.5, 40.5, 38.9, 35.9 (q, *J* = 2.0 Hz), 34.4 (q, *J* = 2.2 Hz), 32.8 (q, *J* = 29.4 Hz), 32.2 (q, *J* = 28.9 Hz), 21.4, 19.4, 18.5. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.65, -64.85. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₃H₂₂F₃NNaO, 408.1546, found: 408.1548.

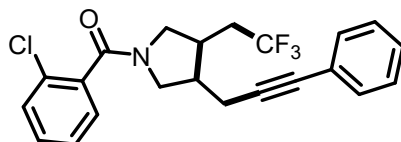
(3-chlorophenyl)(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)methanone (3v)



Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3v**. Colorless oil (48 mg, 59% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 16.2 Hz, 1H), 7.43 – 7.27 (m, 8H), 3.92 – 3.50 (m, 4H), 2.84 – 2.52 (m, 3H), 2.50 – 2.15 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.4,

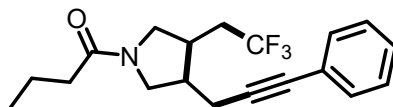
138.1, 138.0, 134.5, 131.6, 131.5, 130.3, 130.2, 129.81, 129.78, 128.4, 128.3, 128.23, 128.19, 127.4, 126.5 (q, $J = 276.4$ Hz), 125.21, 125.16, 122.9, 122.8, 86.3, 85.9, 82.7, 82.6, 77.4, 53.8, 52.6, 50.8, 49.5, 40.4, 38.7, 36.0 (q, $J = 2.2$ Hz), 34.3 (q, $J = 2.7$ Hz), 32.8 (q, $J = 29.1$ Hz), 32.2 (q, $J = 28.7$ Hz), 19.4, 18.5. ^{19}F NMR (376 MHz, Chloroform- d) δ -64.66, -64.88. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{20}\text{ClF}_3\text{NO}$, 406.1180, found: 406.1184.

(2-chlorophenyl)(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)methanone (3w)



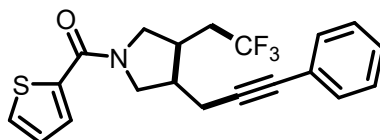
Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3w**. Colorless oil (50 mg, 62% yield). ^1H NMR (400 MHz, Chloroform- d) δ 7.53 – 7.49 (m, 1H), 7.48 – 7.43 (m, 1H), 7.44 – 7.33 (m, 3H), 7.36 – 7.25 (m, 4H), 4.17 – 3.28 (m, 4H), 2.87 – 2.50 (m, 3H), 2.50 – 1.96 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 170.0, 136.5, 136.4, 131.6, 131.5, 130.2, 130.0, 128.39, 128.37, 128.35, 128.3, 128.2, 128.1, 127.1, 126.6 (q, $J = 276.4$ Hz), 123.1, 122.9, 86.5, 86.1, 82.64, 82.57, 53.9, 52.6, 50.7, 49.5, 40.5, 38.9, 36.0 (q, $J = 2.0$ Hz), 34.3 (q, $J = 2.7$ Hz), 32.8 (q, $J = 29.0$ Hz), 32.2 (q, $J = 29.0$ Hz), 19.4, 18.5. ^{19}F NMR (376 MHz, Chloroform- d) δ -64.64, -64.85. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{20}\text{ClF}_3\text{NO}$, 406.1180, found: 406.1181.

1-(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)butan-1-one (3x)



Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3x**. Colorless oil (32 mg, 46% yield). ^1H NMR (400 MHz, Chloroform- d) δ 7.41 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 3.82 – 3.56 (m, 3H), 3.48 – 3.28 (m, 1H), 2.80 – 2.50 (m, 3H), 2.50 – 2.33 (m, 2H), 2.29 – 2.15 (m, 3H), 1.68 (dt, $J = 14.8, 7.4$ Hz, 2H), 0.95 (dt, $J = 12.2, 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 172.0, 171.9, 131.53, 131.52, 128.34, 128.28, 128.13, 128.06, 126.6 (q, $J = 277.0$ Hz), 123.1, 123.0, 86.5, 86.4, 82.5, 82.4, 51.0, 50.0, 48.8, 40.6, 38.9, 36.50, 36.48, 35.7 (q, $J = 2.1$ Hz), 34.2 (q, $J = 2.4$ Hz), 32.5 (qd, $J = 28.8, 3.1$ Hz), 19.2, 18.7, 18.4, 18.2, 14.0, 13.9. ^{19}F NMR (376 MHz, Chloroform- d) δ -64.58, -64.87. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{F}_3\text{NNaO}$, 360.1546, found: 360.1548.

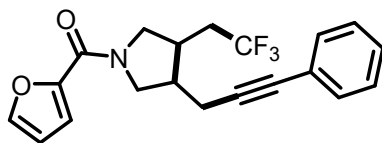
(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)(thiophen-2-yl)methanone (3y)



Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3y**. Colorless oil (44 mg, 58% yield). ^1H NMR (400 MHz, Chloroform- d) δ 7.49 (dd, $J = 5.0, 0.8$ Hz, 2H), 7.38 – 7.25 (m, 5H), 7.07 (s, 1H), 4.05 – 3.59 (m, 4H), 2.83 – 2.40 (m, 5H), 2.32 – 2.18 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 162.1, 138.7, 131.6, 130.0, 129.9, 128.3, 128.1, 127.2, 126.6 (q, $J = 276.9$ Hz), 123.0, 86.3, 86.2, 82.68, 82.67, 53.2, 52.1, 51.7, 50.4, 41.0, 38.5, 36.3 (q, $J = 2.5$ Hz), 33.9 (q, $J = 2.4$ Hz), 32.5 (q, $J = 28.9$ Hz), 19.2, 18.7. ^{19}F NMR (376 MHz, Chloroform- d) δ -64.69, -64.78. HRMS (ESI-

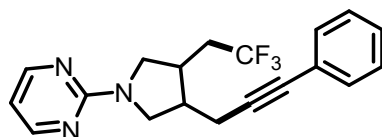
TOF) m/z : $[M + Na]^+$ calcd for $C_{20}H_{18}F_3NNaOS$, 400.0953, found: 400.0952.

furan-2-yl(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)methanone (3z)



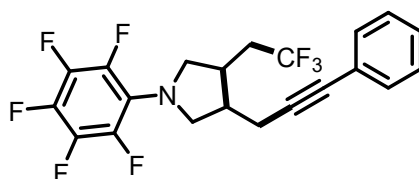
Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3z**. Colorless oil (24 mg, 33% yield). 1H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, $J = 4.7$ Hz, 1H), 7.44 – 7.27 (m, 5H), 7.13 (dd, $J = 5.7, 3.5$ Hz, 1H), 6.52 (q, $J = 3.4$ Hz, 1H), 4.16 – 3.60 (m, 4H), 2.83 – 2.23 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.23, 158.17, 148.4, 144.3, 131.6, 131.5, 128.3, 128.2, 128.1, 128.0, 126.6 (d, $J = 277.4$ Hz), 123.0, 116.5, 116.4, 111.5, 86.42, 86.35, 82.6, 82.5, 52.1, 51.4, 51.0, 50.1, 41.0, 38.1, 36.1 (q, $J = 2.1$ Hz), 33.4 (q, $J = 2.4$ Hz), 32.6 (q, $J = 29.2$ Hz), 32.4 (q, $J = 28.6$ Hz), 19.1, 18.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.69, -64.75. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{20}H_{19}F_3NO_2$, 362.1362, found: 362.1368.

2-(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidin-1-yl)pyrimidine (3aa)



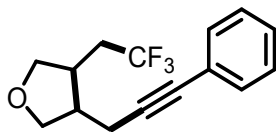
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3aa**. Colorless oil (22 mg, 32% yield). 1H NMR (400 MHz, Chloroform-*d*) δ 8.32 (dd, $J = 4.7, 1.9$ Hz, 2H), 7.42 – 7.35 (m, 1H), 7.34 – 7.32 (m, 1H), 7.28 – 7.24 (m, 3H), 6.50 (t, $J = 4.8$ Hz, 1H), 4.33 – 3.81 (m, 2H), 3.75 – 3.31 (m, 2H), 2.82 – 2.63 (m, 2H), 2.62 – 2.39 (m, 3H), 2.30 – 2.17 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 157.8, 131.6, 131.5, 128.3, 128.2, 128.0, 127.9, 126.8 (q, $J = 277.1$ Hz) 123.3, 123.2, 109.6, 87.0, 86.0, 82.7, 82.2, 52.1, 51.1, 50.8, 50.0, 42.4, 40.2, 36.9 (q, $J = 2.2$ Hz), 35.2 (q, $J = 2.2$ Hz), 32.7 (q, $J = 28.7$ Hz) 21.1, 19.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.63, -64.69. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{19}H_{19}F_3N_3$, 346.1526, found: 346.1531.

1-(perfluorophenyl)-3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)pyrrolidine (3ab)



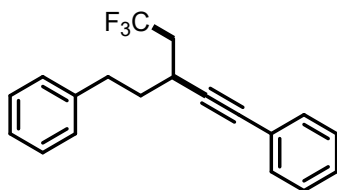
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3ab**. Colorless oil (23 mg, 27% yield). 1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.26 (m, 3H), 3.88 – 3.79 (m, 1H), 3.68 – 3.53 (m, 3H), 2.77 – 2.67 (m, 1H), 2.67 – 2.59 (m, 1H), 2.56 – 2.38 (m, 3H), 2.33 – 2.14 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7 – 140.6 (m), 140.0 – 139.3 (m), 139.0 – 138.0 (m), 137.4 – 136.7 (m), 131.5, 128.3, 128.0, 126.8 (q, $J = 276.9$ Hz), 123.2, 86.9, 82.3, 55.4 (t, $J = 5.2$ Hz), 54.4 (t, $J = 4.5$ Hz), 40.5, 35.3 (d, $J = 2.0$ Hz), 32.5 (q, $J = 28.7$ Hz), 18.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.75 (s, 3F), -154.05 – -155.37 (m, 2F), -164.40 (t, $J = 22.0$ Hz, 2F), -168.90 – -172.88 (m, 1F). HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{21}H_{16}F_8N$, 434.1150, found: 434.1154.

3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)tetrahydrofuran (3ac)



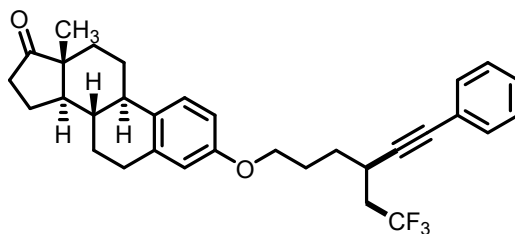
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3ac**. Colorless oil (44 mg, 81% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.35 – 7.30 (m, 3H), 4.18 – 3.99 (m, 2H), 3.90 – 3.54 (m, 2H), 2.74 – 2.34 (m, 5H), 2.25 – 2.14 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 131.54, 131.51, 128.3, 128.0, 126.9 (q, *J* = 278.0 Hz), 123.28, 123.26, 87.2, 86.7, 82.2, 82.1, 73.4, 72.4, 72.3, 71.5, 44.0, 40.8, 38.7 (q, *J* = 2.3 Hz), 37.1, 36.8, 35.9 (q, *J* = 2.2 Hz), 31.9 (q, *J* = 28.7 Hz), 22.1, 18.7. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.99, -65.03. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₅H₁₆F₃O, 269.1148, found: 269.1149.

(3-(2,2,2-trifluoroethyl)pent-1-yne-1,5-diyl)dibenzene (3ad)⁸



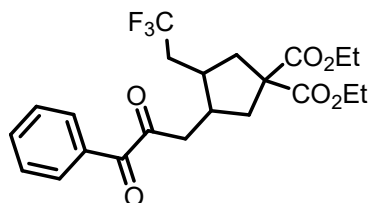
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **3ad**. Colorless oil (50 mg, 83% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.34 – 7.26 (m, 5H), 7.26 – 7.19 (m, 3H), 3.00 – 2.88 (m, 2H), 2.86 – 2.77 (m, 1H), 2.53 – 2.38 (m, 1H), 2.37 – 2.22 (m, 1H), 2.00 – 1.84 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.1, 131.7, 128.5 (d, *J* = 1.8 Hz), 128.3, 128.1, 126.17 (q, *J* = 277.6 Hz), 126.16, 123.3, 89.6, 83.3, 39.2 (q, *J* = 27.8 Hz), 36.5, 33.3, 26.1 (q, *J* = 3.0 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -63.95.

(8*S*,9*R*,13*R*,14*R*)-13-methyl-3-((6-phenyl-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3ae)⁸



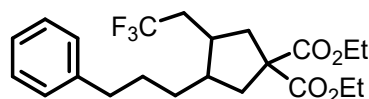
Purification by flash column chromatography (PE:EA, v/v = 5:1) to provide **3ae**. Colorless oil (71 mg, 68% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.43 (m, 2H), 7.35 – 7.32 (m, 3H), 6.77 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.70 (d, *J* = 2.3 Hz, 1H), 4.05 (t, *J* = 6.1 Hz, 2H), 3.06 (tt, *J* = 9.5, 5.2 Hz, 1H), 2.99 – 2.84 (m, 2H), 2.60 – 2.48 (m, 2H), 2.46 – 2.34 (m, 2H), 2.33 – 2.23 (m, 1H), 2.24 – 1.93 (m, 7H), 1.96 – 1.85 (m, 1H), 1.83 – 1.74 (m, 1H), 1.70 – 1.60 (m, 2H), 1.58 – 1.44 (m, 4H), 0.94 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.0, 137.8, 132.1, 131.6, 128.3, 128.1, 126.4, 126.2 (d, *J* = 277.5 Hz), 123.2, 114.6, 112.1, 89.6, 83.1, 67.2, 50.4, 48.0, 44.0, 39.2 (q, *J* = 27.7 Hz), 38.4, 35.9, 31.6, 31.5, 29.7, 26.9, 26.6, 26.4 (q, *J* = 2.9 Hz), 26.0, 21.6, 13.9. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -63.98.

diethyl 3-(2,3-dioxo-3-phenylpropyl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (4a)



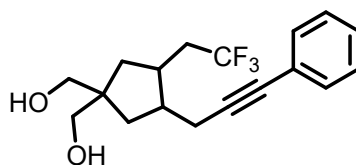
Purification by flash column chromatography (PE:EA, v/v = 25:1) to provide **4a**. Yellow oil (82 mg, 92% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.93 (m, 2H), 7.68 – 7.61 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 4.25 – 4.12 (m, 4H), 2.98 – 2.75 (m, 3H), 2.64 – 2.46 (m, 3H), 2.26 – 2.04 (m, 4H), 1.27 – 1.20 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 201.3, 191.5, 172.4, 172.0, 134.7, 131.7, 130.3, 128.9, 126.8 (q, *J* = 277.1 Hz), 61.8 (d, *J* = 9.1 Hz), 58.3, 38.8, 38.3, 37.9, 36.7, 36.0 (q, *J* = 2.2 Hz), 33.8 (q, *J* = 28.2 Hz), 14.0 (d, *J* = 3.6 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.35. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₂₆F₃O₆, 443.1676, found: 443.1678.

diethyl 3-(3-phenylpropyl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (4b)



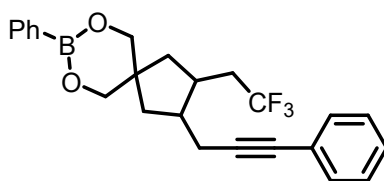
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **4b**. Colorless oil (68 mg, 81% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 3H), 4.20 – 4.13 (m, 4H), 2.66 – 2.56 (m, 2H), 2.49 – 2.31 (m, 3H), 2.22 – 1.93 (m, 5H), 1.75 – 1.65 (m, 1H), 1.60 – 1.51 (m, 1H), 1.37 – 1.27 (m, 1H), 1.23 (td, *J* = 7.1, 1.5 Hz, 6H), 1.20 – 1.12 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.6, 172.5, 142.2, 128.3 (d, *J* = 1.9 Hz), 127.3 (q, *J* = 277.1 Hz), 125.8, 61.6 (q, *J* = 1.5 Hz), 58.6, 42.0, 38.4, 38.2, 35.9, 33.2 (q, *J* = 27.7 Hz), 29.7, 28.5, 14.0. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.25. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₃₀F₃O₄, 415.2091, found: 415.2108.

(3-(3-phenylprop-2-yn-1-yl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-diyl)dimethanol (4c)



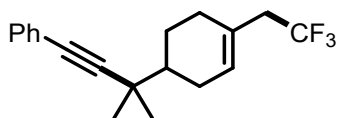
Purification by flash column chromatography (PE:EA, v/v = 50:1) to provide **4c**. Colorless oil (54 mg, 83% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.25 (m, 3H), 3.63 (s, 2H), 3.52 (s, 2H), 3.41 (d, *J* = 12.0 Hz, 2H), 2.44 – 1.96 (m, 6H), 1.85 – 1.37 (m, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 131.5, 128.3, 127.9, 127.2 (q, *J* = 277.2 Hz), 123.5, 88.5, 82.0, 70.9, 69.2, 47.2, 40.4, 36.4, 36.2, 35.2 (q, *J* = 2.0 Hz), 34.1 (q, *J* = 27.9 Hz), 20.8. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.25. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₈H₂₂F₃O₂, 327.1566, found: 327.1572.

8-phenyl-2-(3-phenylprop-2-yn-1-yl)-3-(2,2,2-trifluoroethyl)-7,9-dioxa-8-borospiro[4.5]decane (4ca)



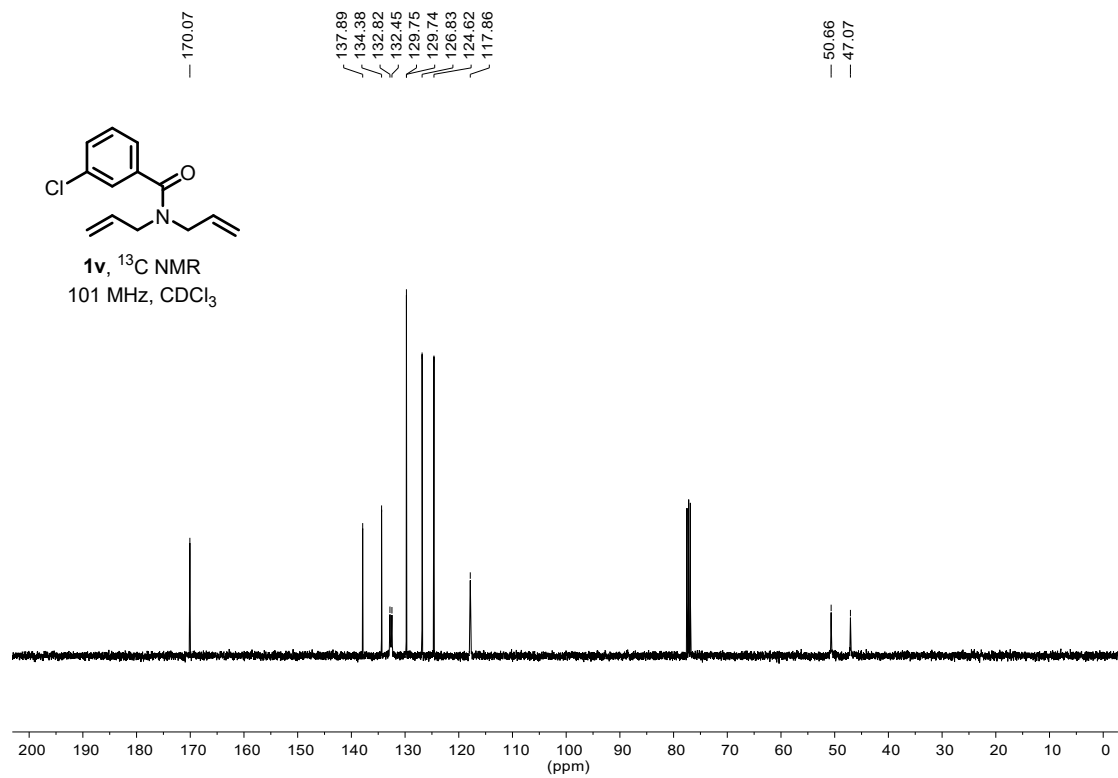
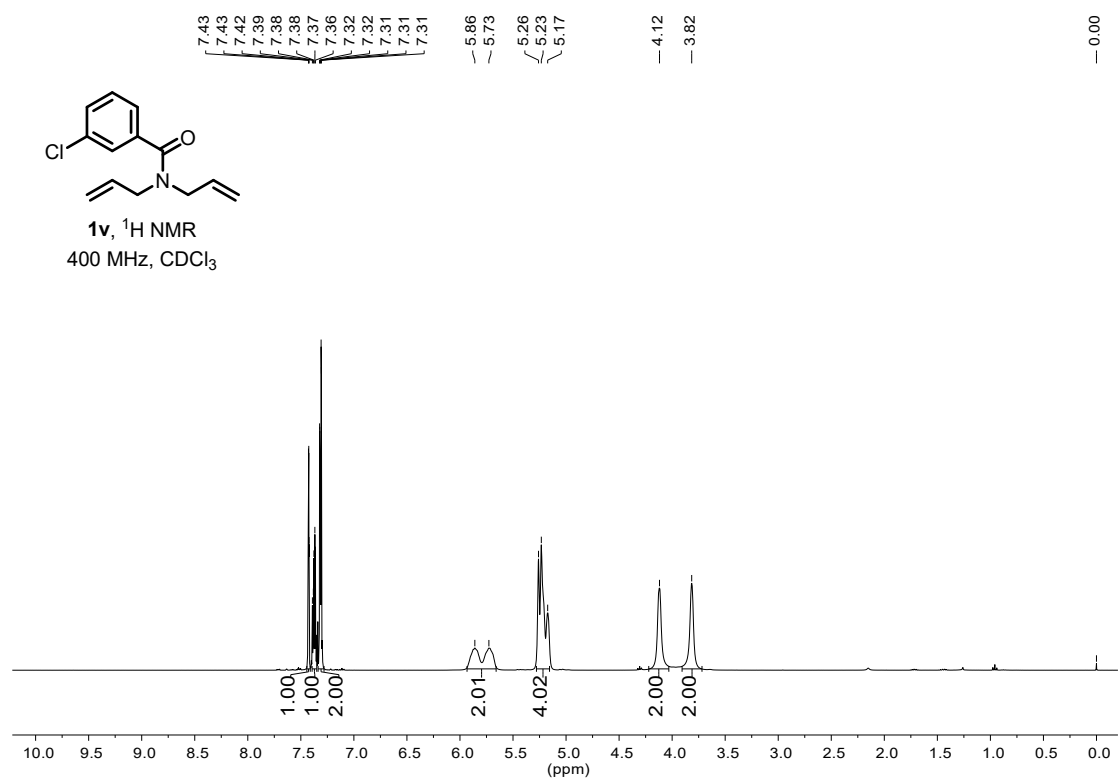
Purification by flash column chromatography (PE:EA, v/v = 10:1) to provide **4c**. Colorless oil (78 mg, 95% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 2H), 7.44 – 7.33 (m, 5H), 7.33 – 7.25 (m, 3H), 3.97 (s, 2H), 3.85 (s, 2H), 2.50 – 2.33 (m, 5H), 2.19 – 2.08 (m, 1H), 1.96 – 1.78 (m, 2H), 1.71 (dd, $J = 14.3, 3.9$ Hz, 1H), 1.64 – 1.54 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.9, 131.5, 130.8, 128.3, 128.0, 127.6, 127.1 (q, $J = 277.3$ Hz), 123.4, 87.9, 82.3, 72.3, 70.8, 42.6, 40.3, 37.6, 37.4, 35.5 (q, $J = 2.1$ Hz), 34.2 (q, $J = 28.1$ Hz), 20.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.34. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{BF}_3\text{O}_2$, 413.1894, found: 413.1898.

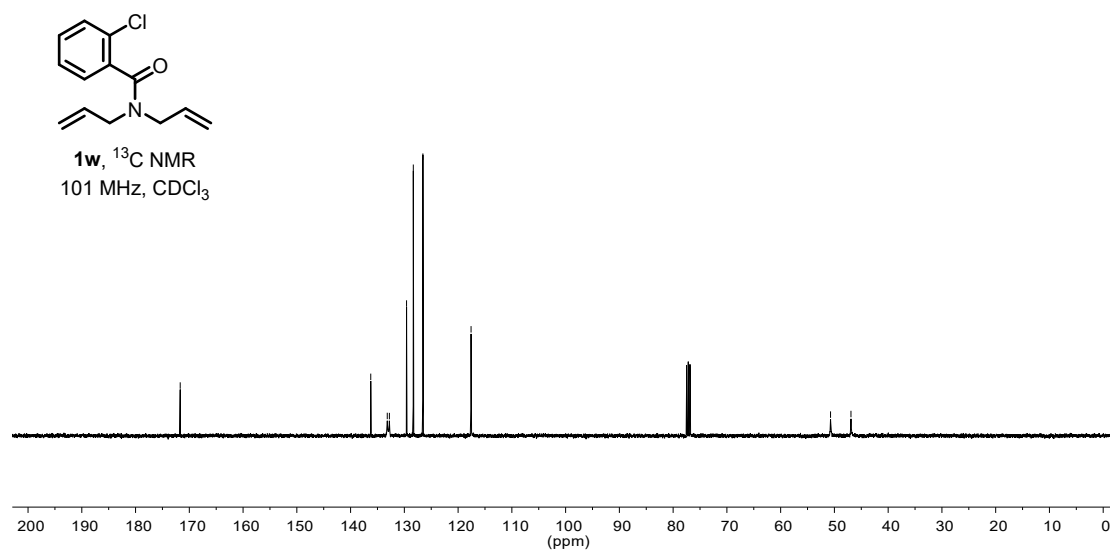
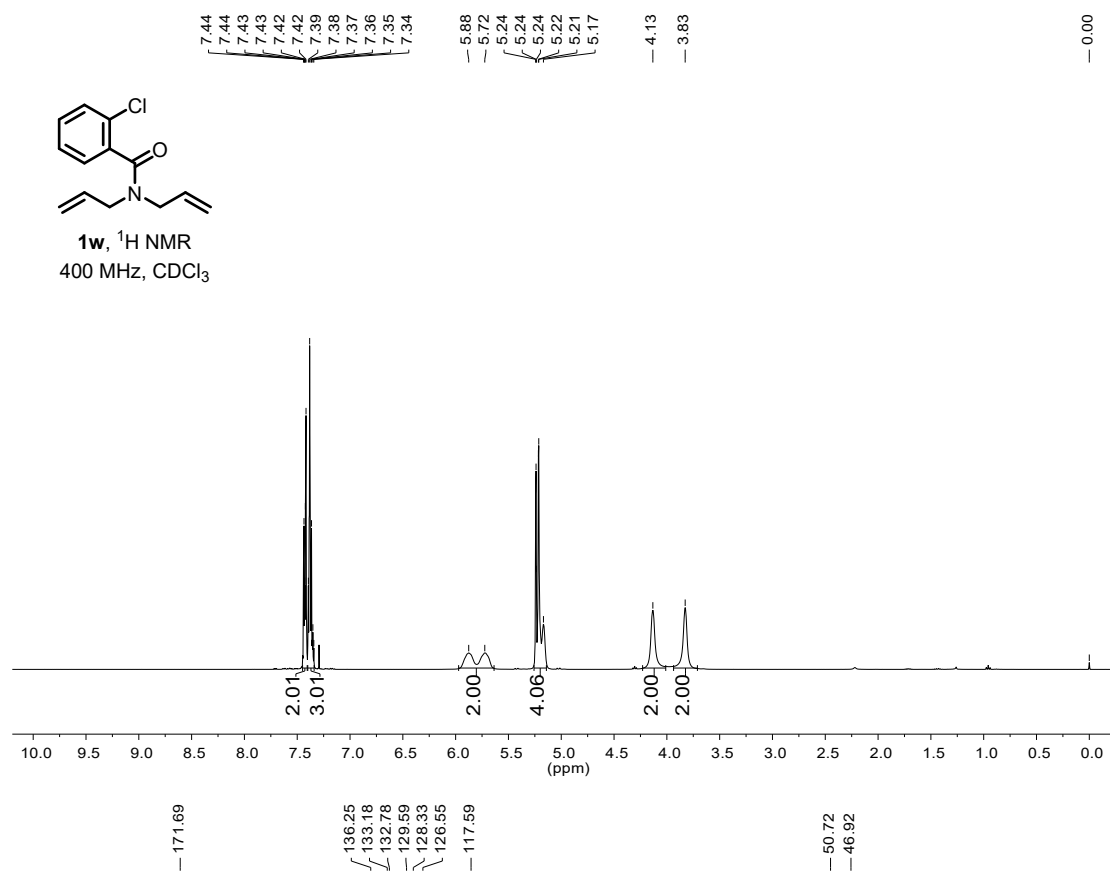
*(3-methyl-3-(4-(2,2-trifluoroethyl)cyclohex-3-en-1-yl)but-1-yn-1-yl)benzene (5c)*⁹

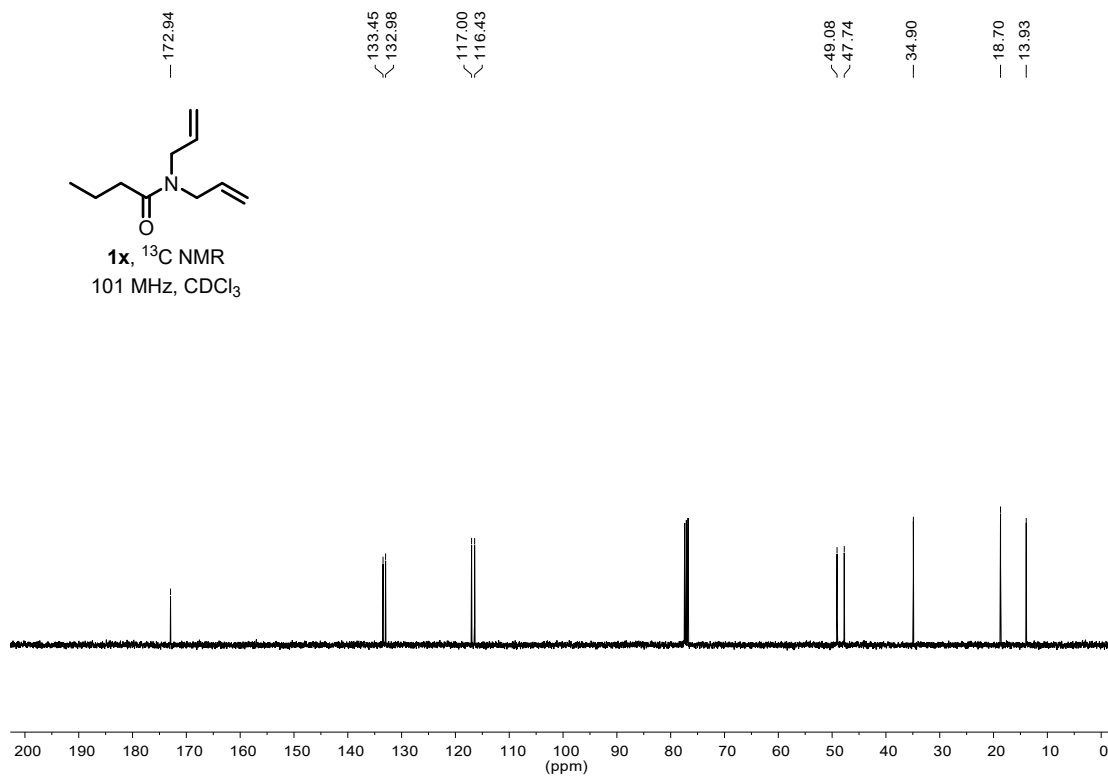
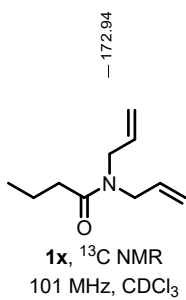
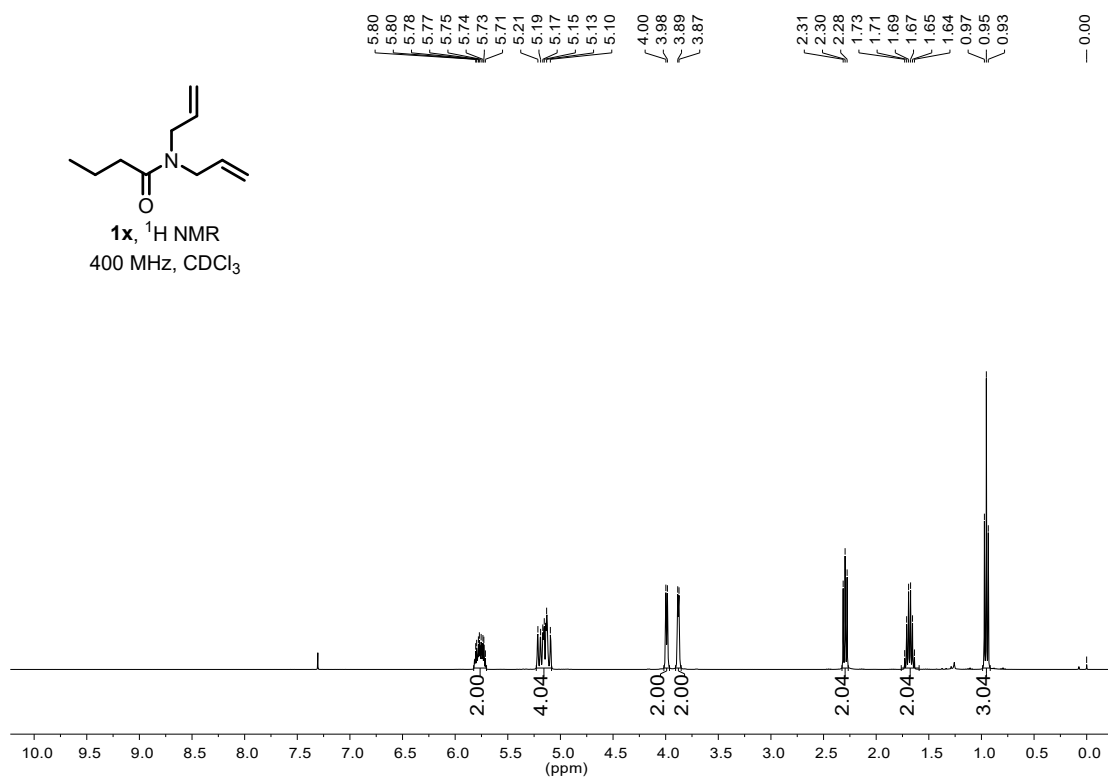
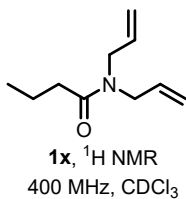


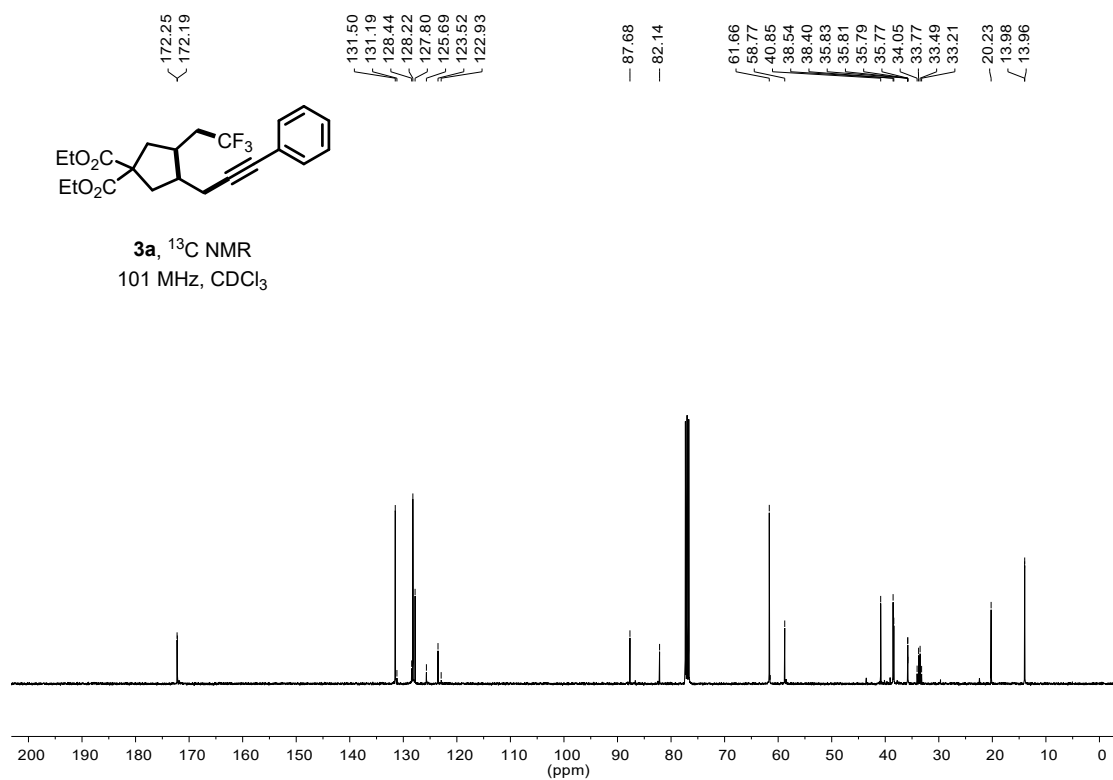
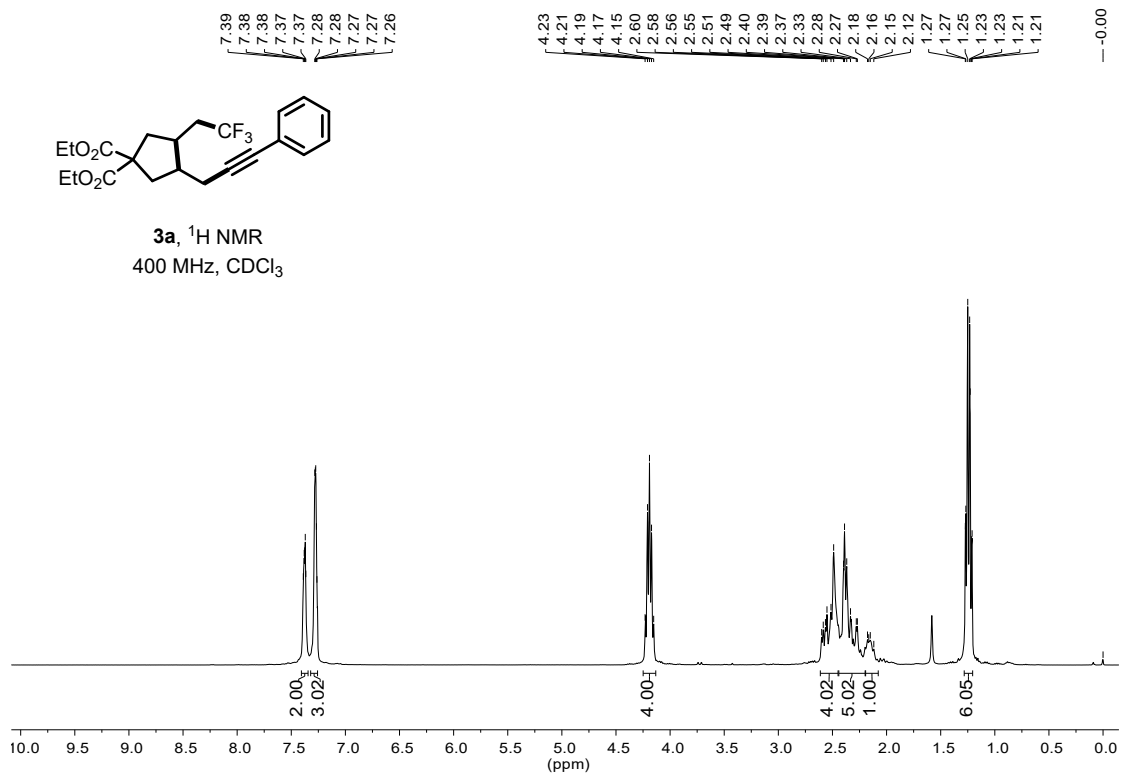
Purification by flash column chromatography (PE:EA, v/v = 100:1) to provide **5c**. Colorless oil (52 mg, 84% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.29 – 7.23 (m, 3H), 5.73 – 5.65 (m, 1H), 2.72 (q, $J = 11.5$ Hz, 2H), 2.28 – 2.00 (m, 5H), 1.53 – 1.41 (m, 2H), 1.30 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.6, 128.9, 128.1, 127.5, 127.4 (q, $J = 2.6$ Hz), 126.3 (q, $J = 277.7$ Hz), 124.0, 96.1, 81.2, 43.3, 41.8 (q, $J = 28.7$ Hz), 34.6, 29.7, 27.8, 27.2, 27.0, 24.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.76.

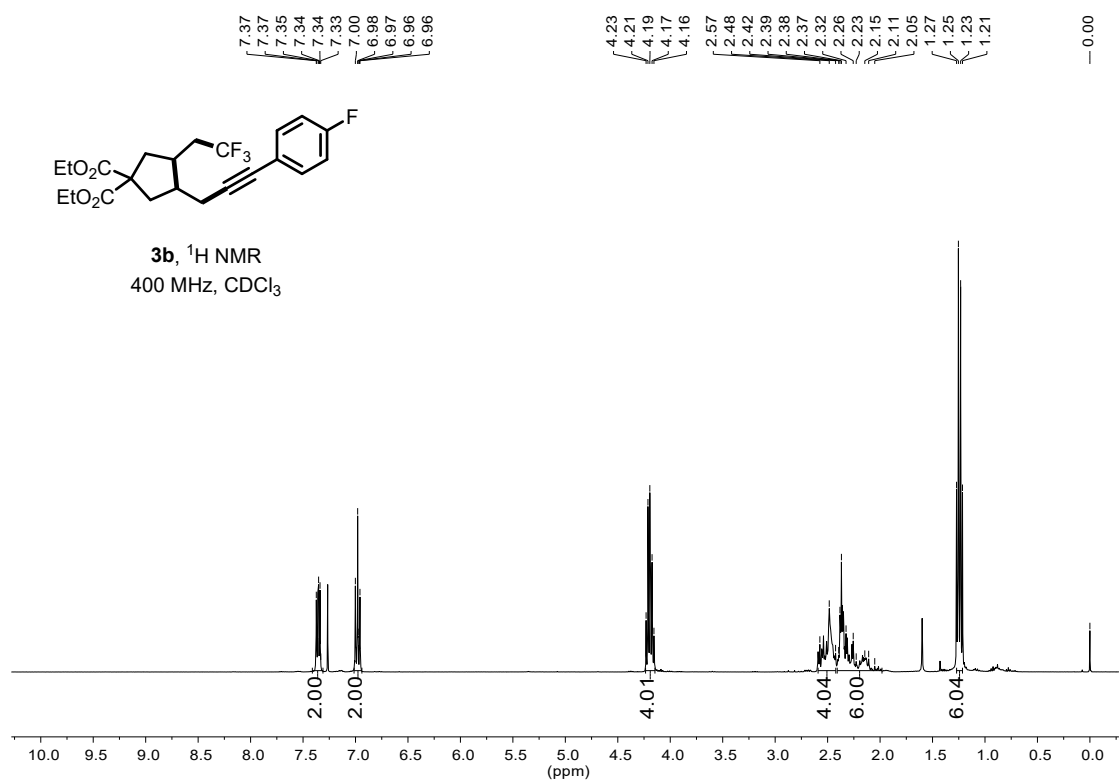
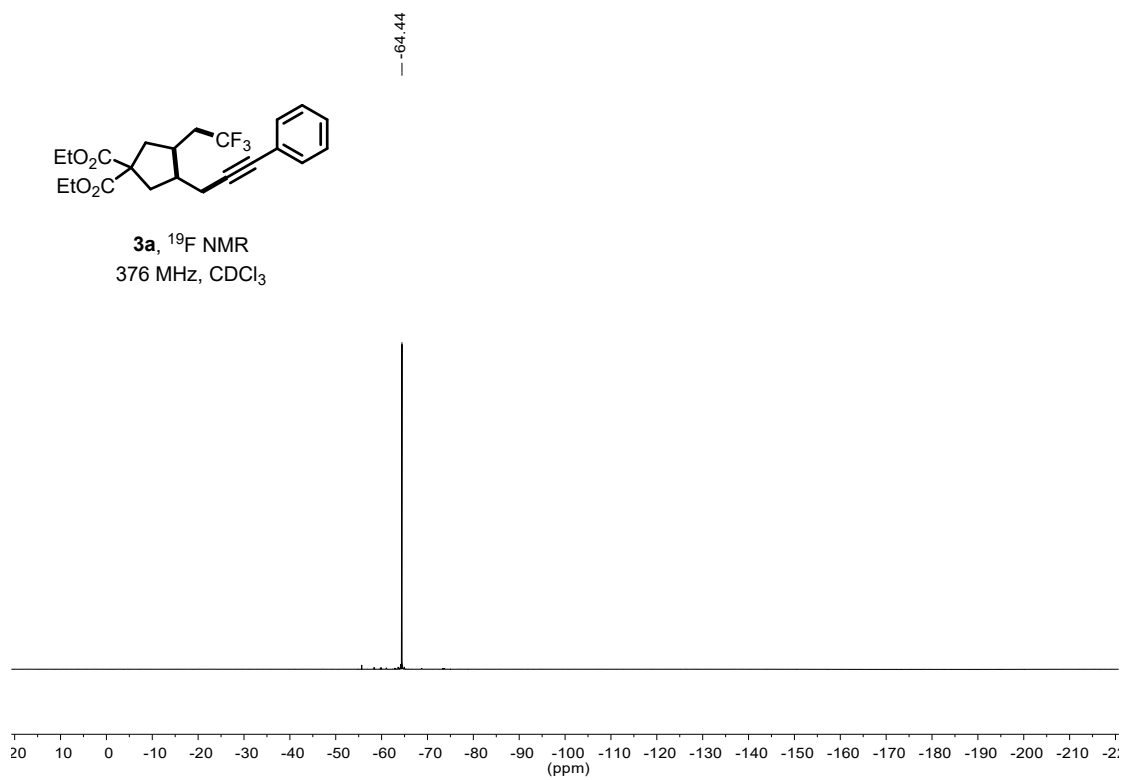
4. NMR Copies of Products

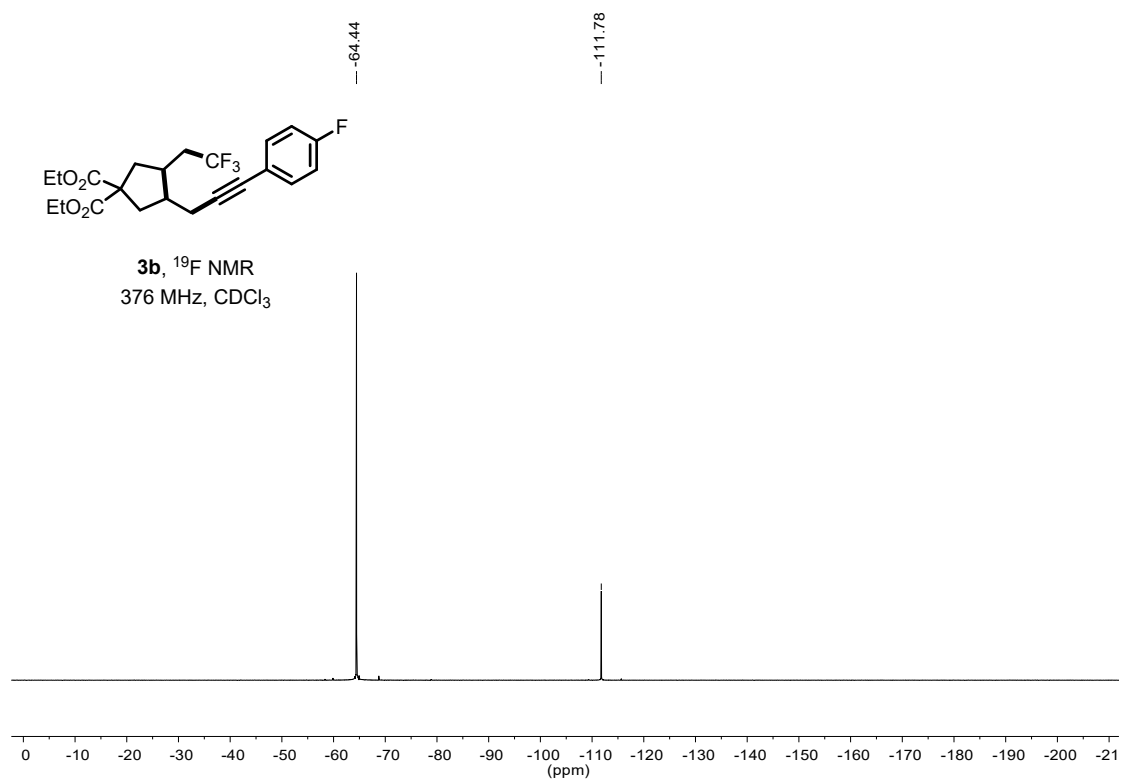
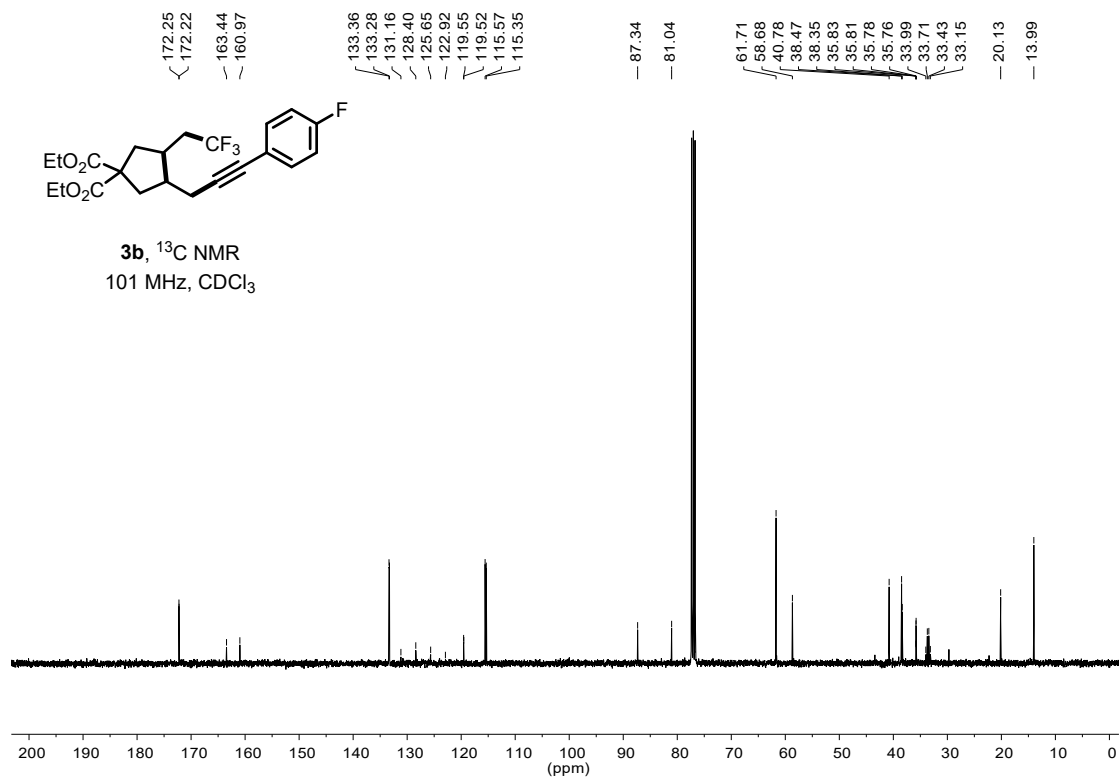


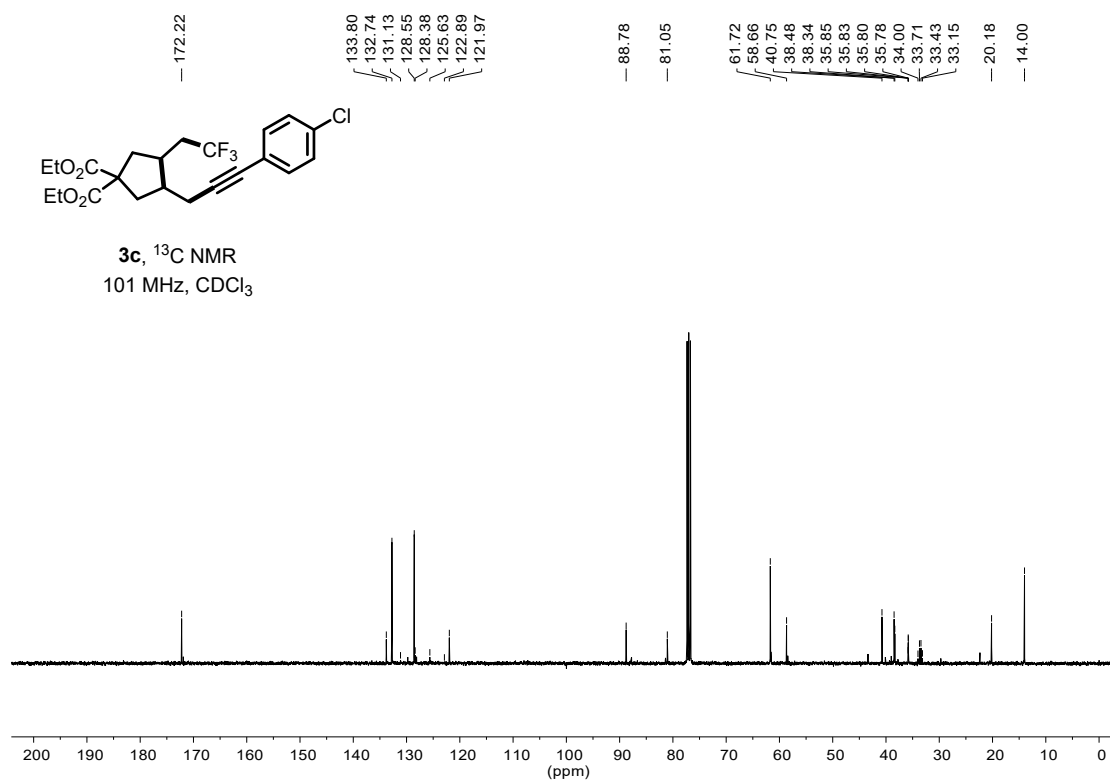
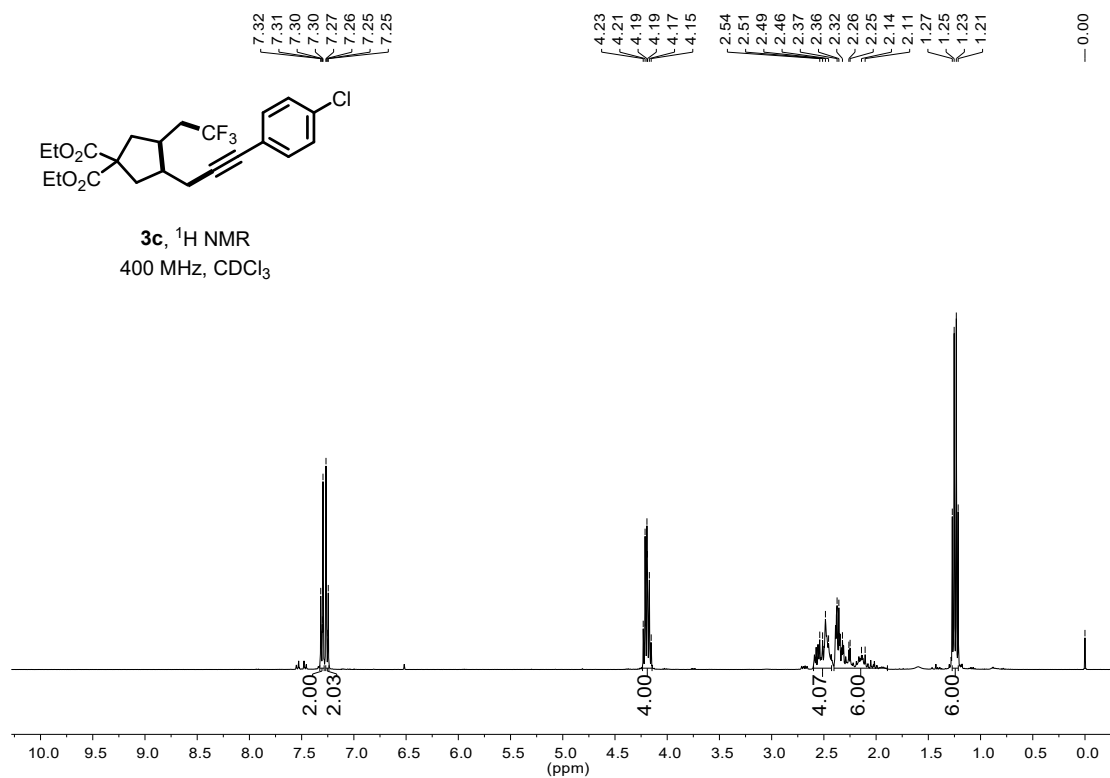


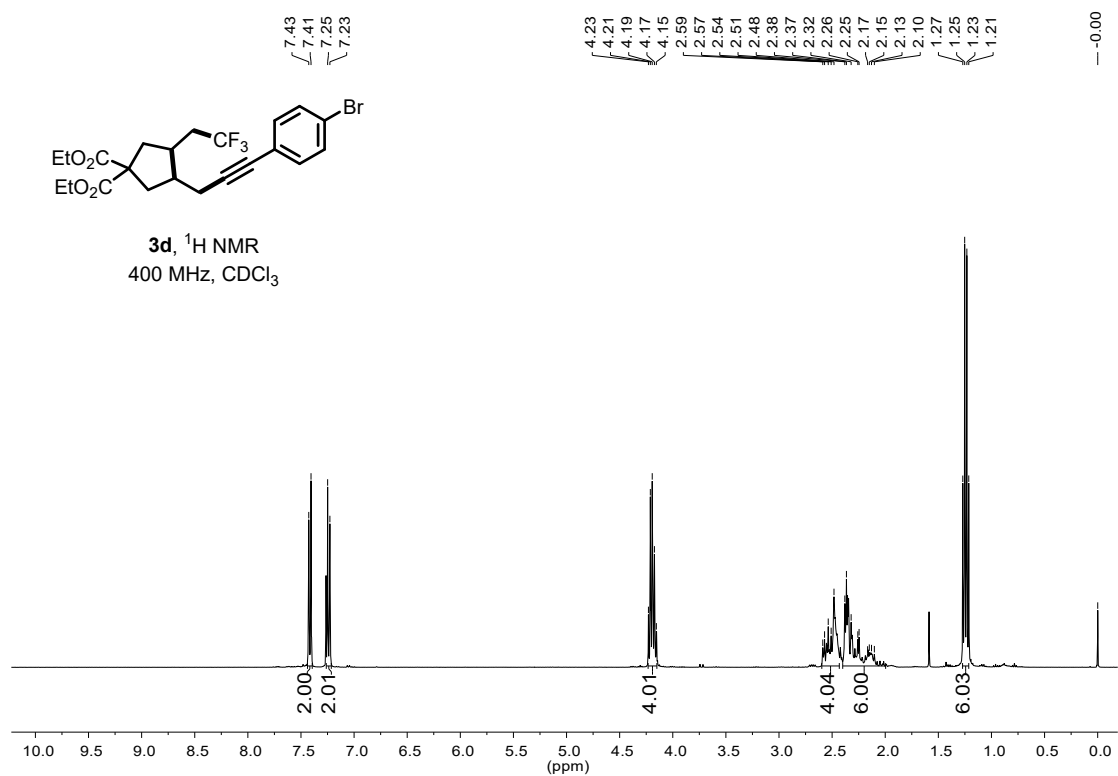
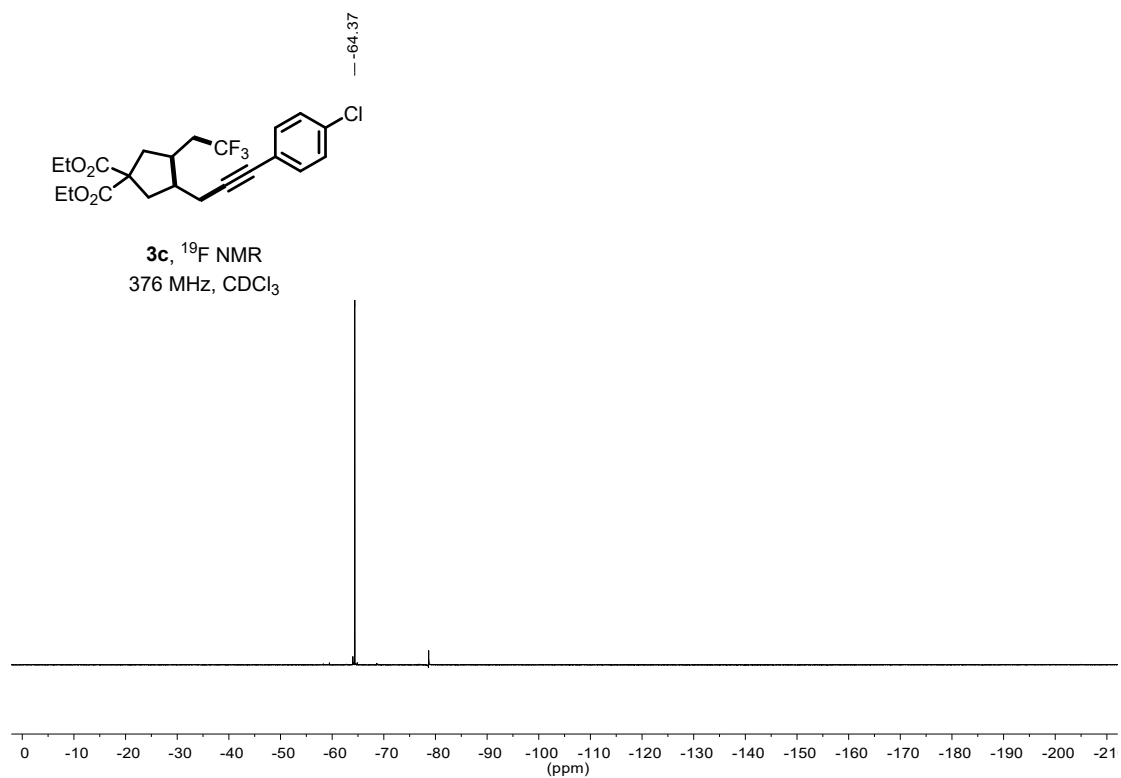


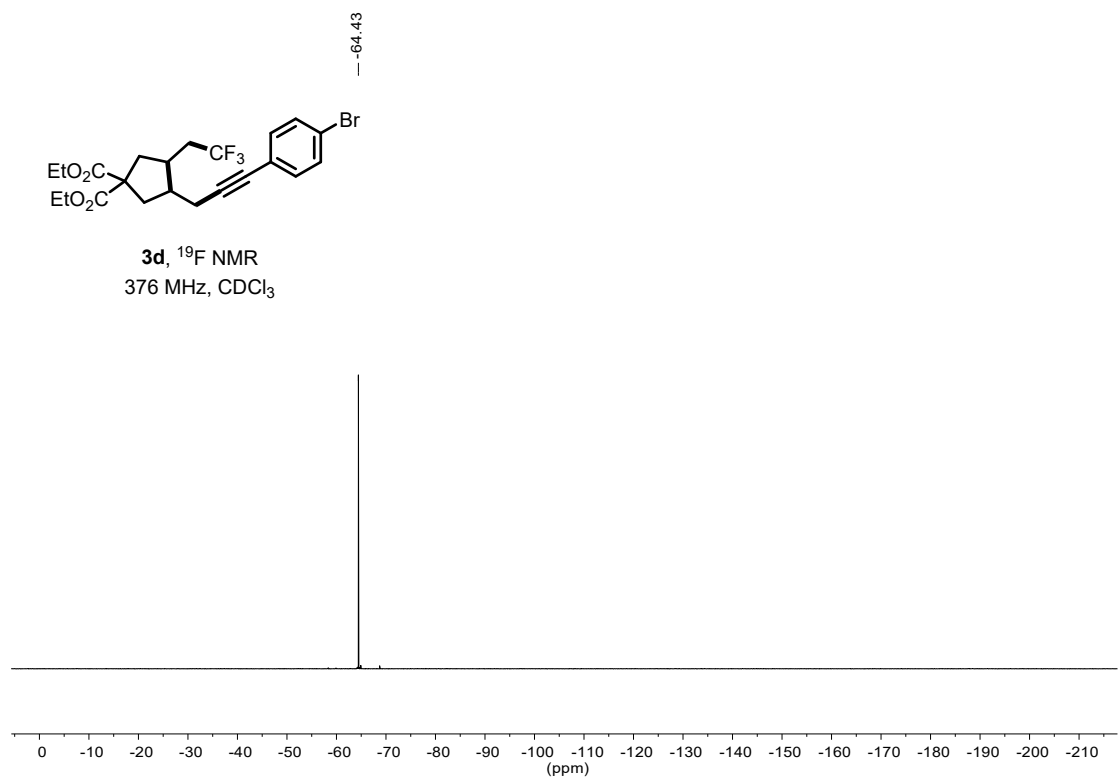
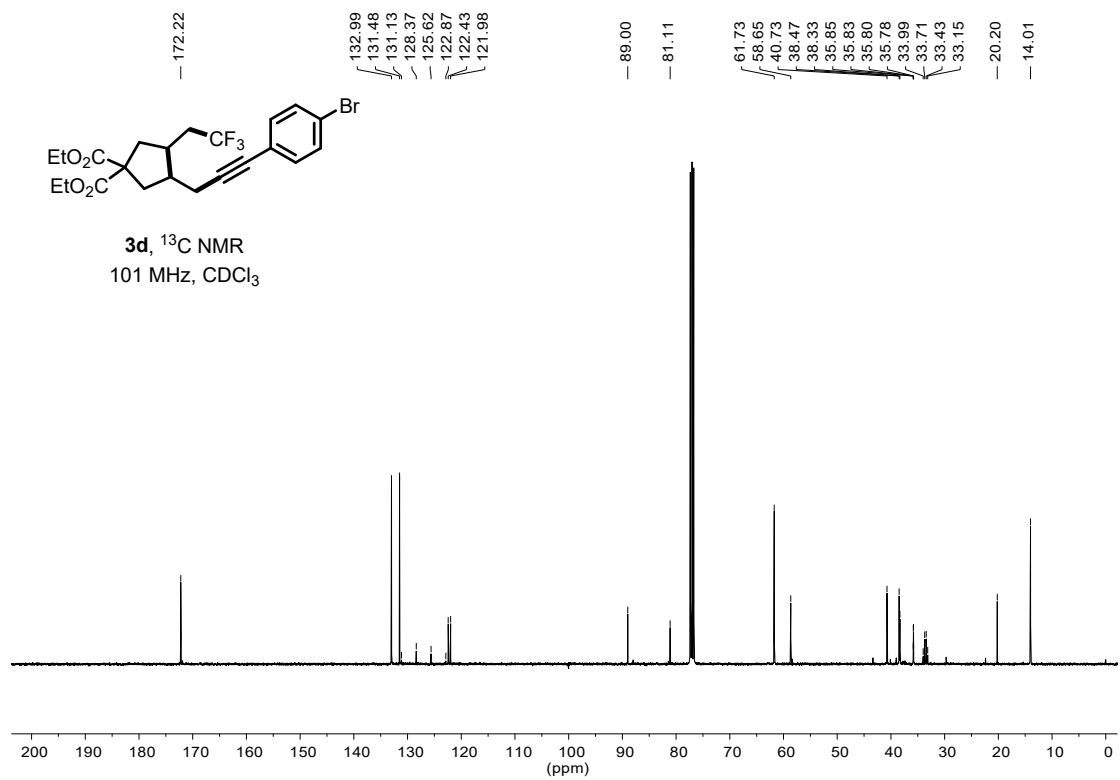


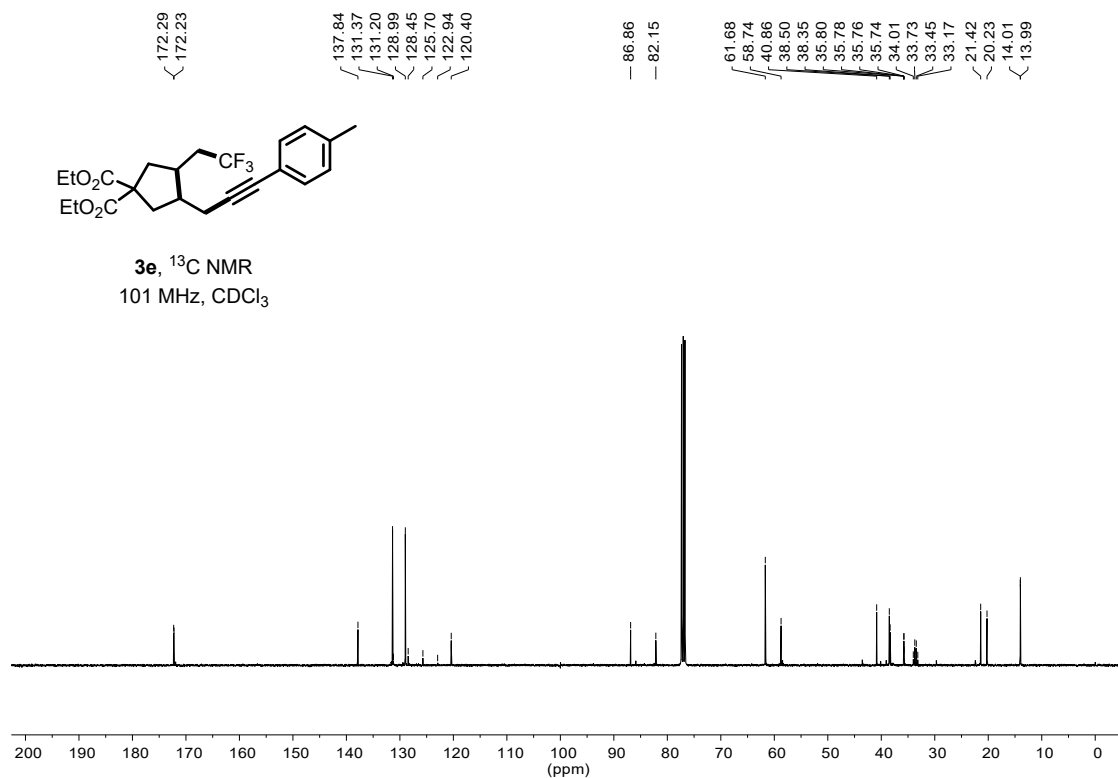
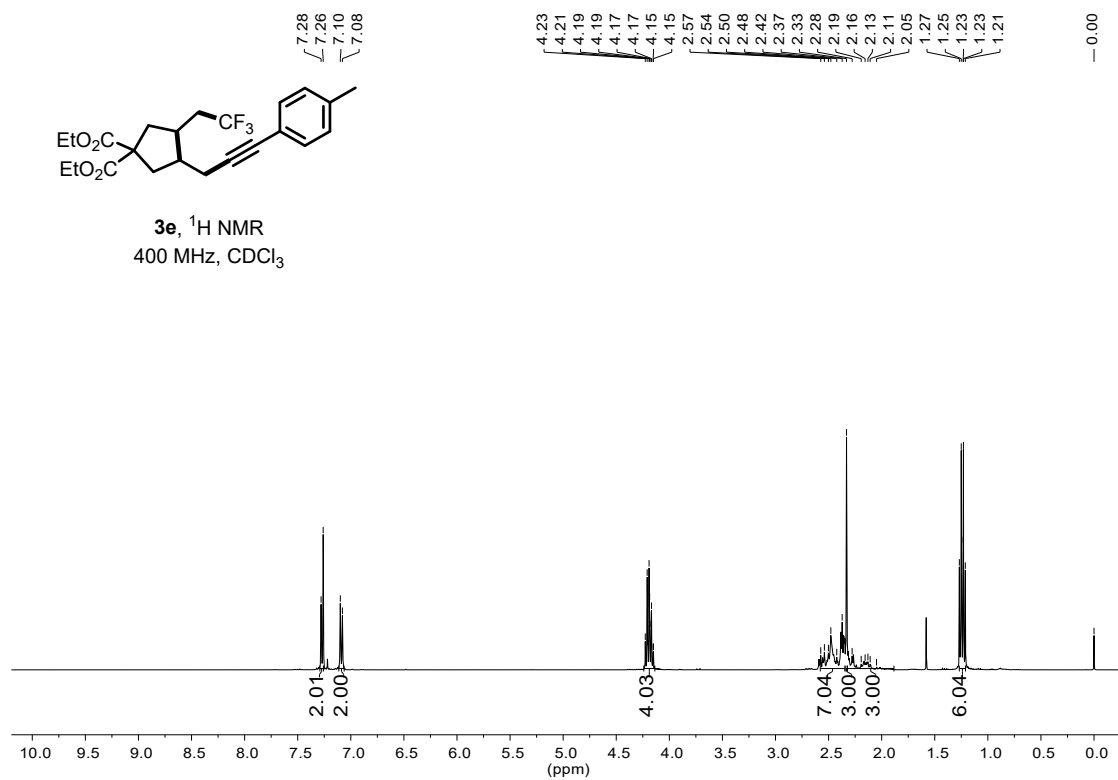


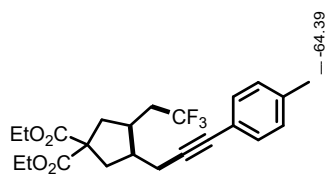




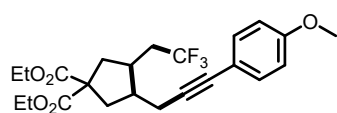
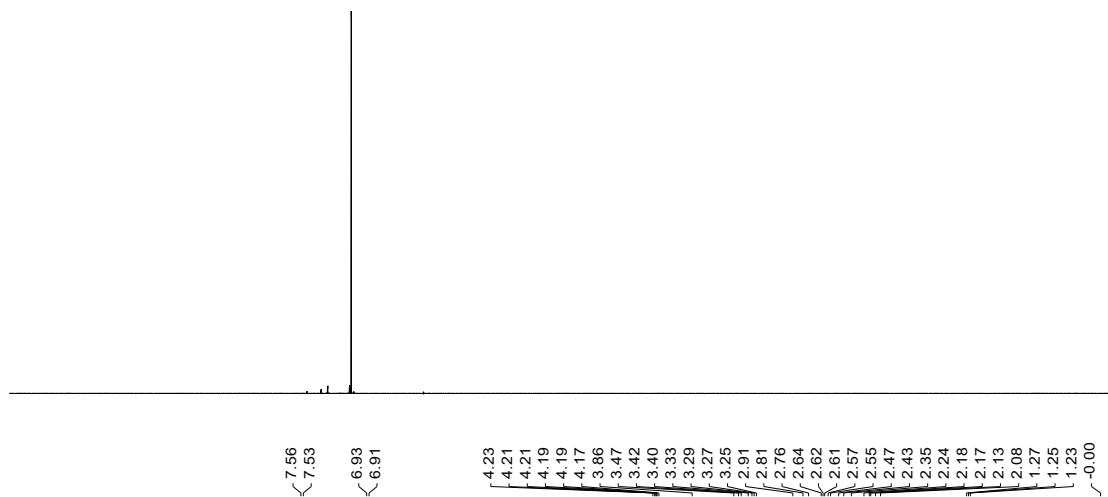




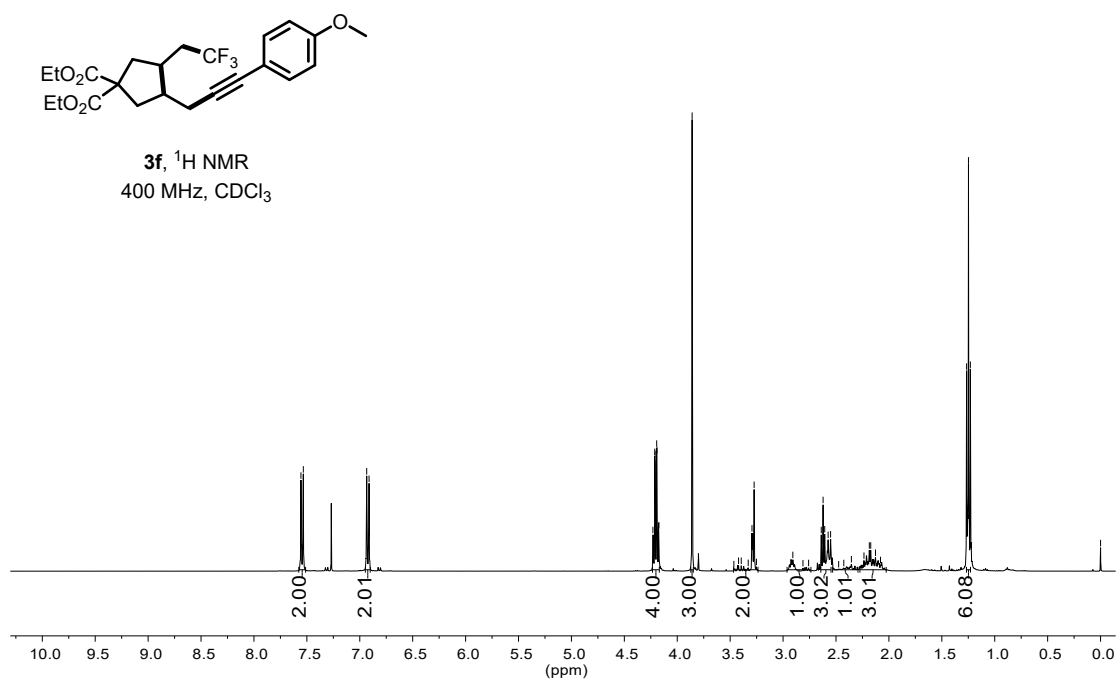


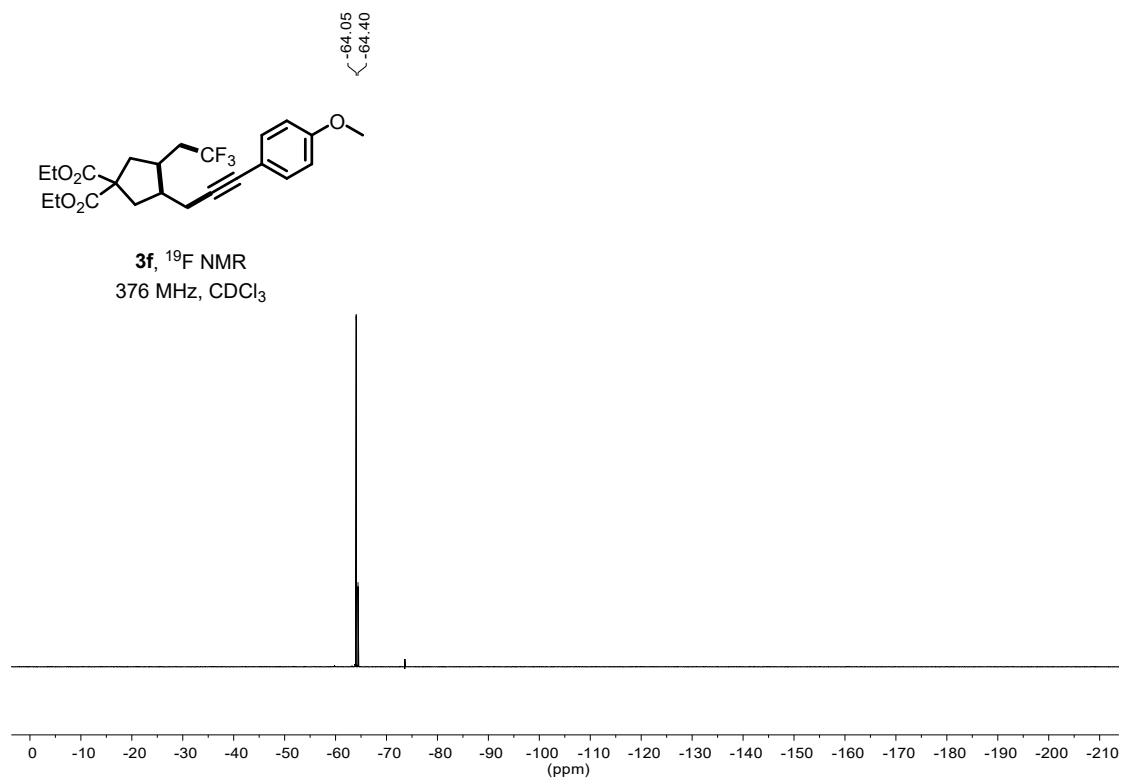
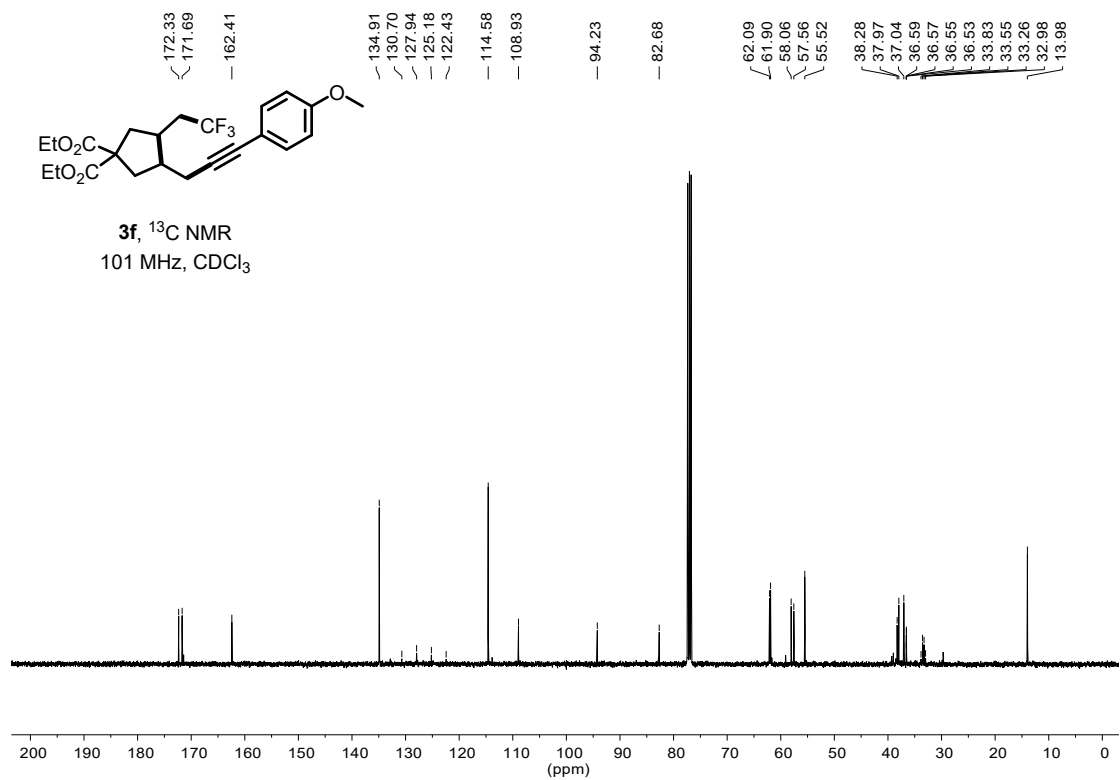


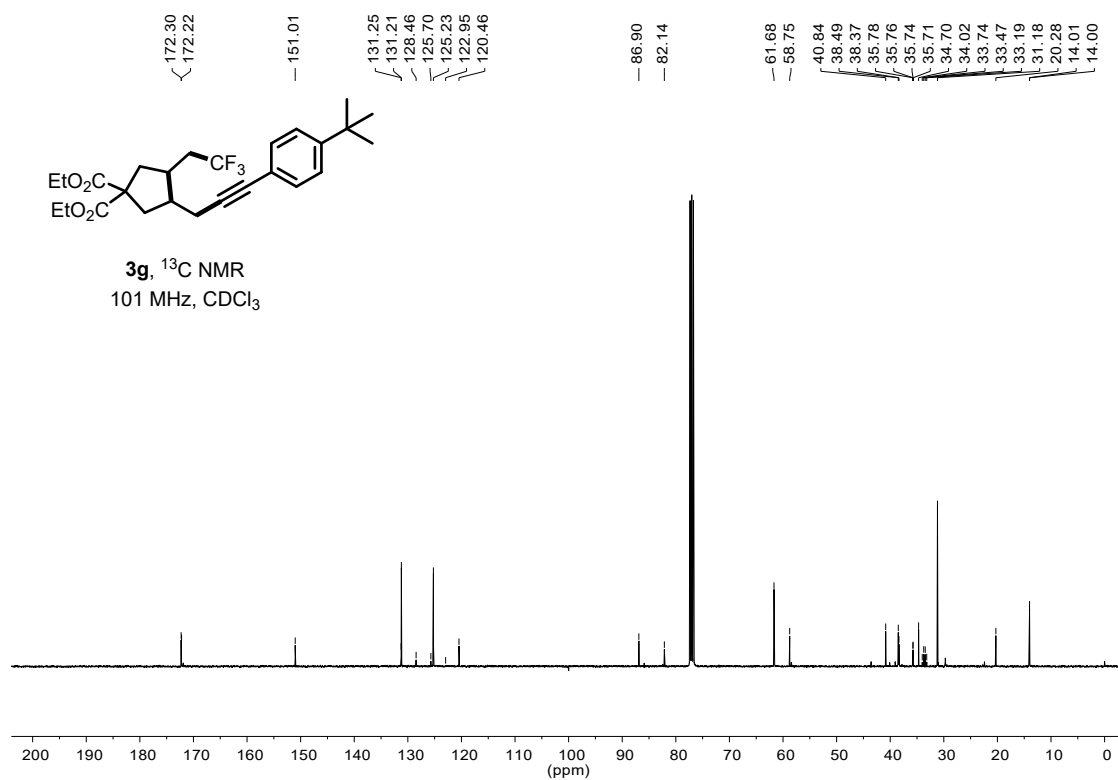
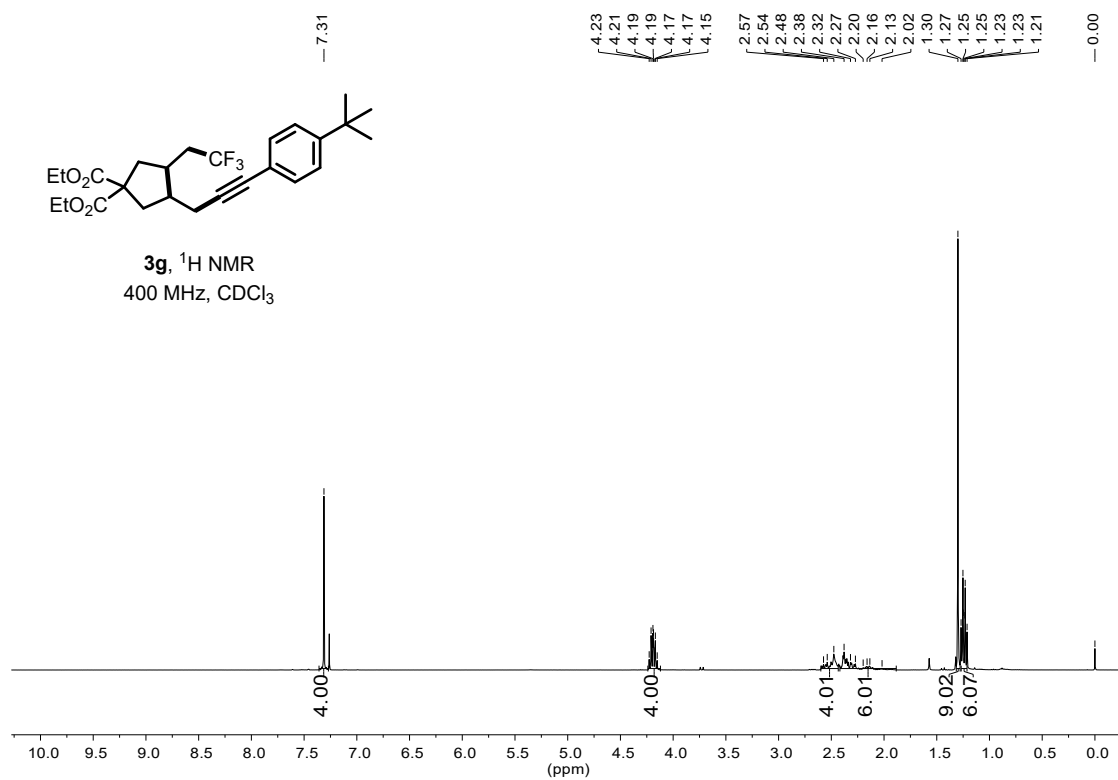
3e, ¹⁹F NMR
376 MHz, CDCl₃

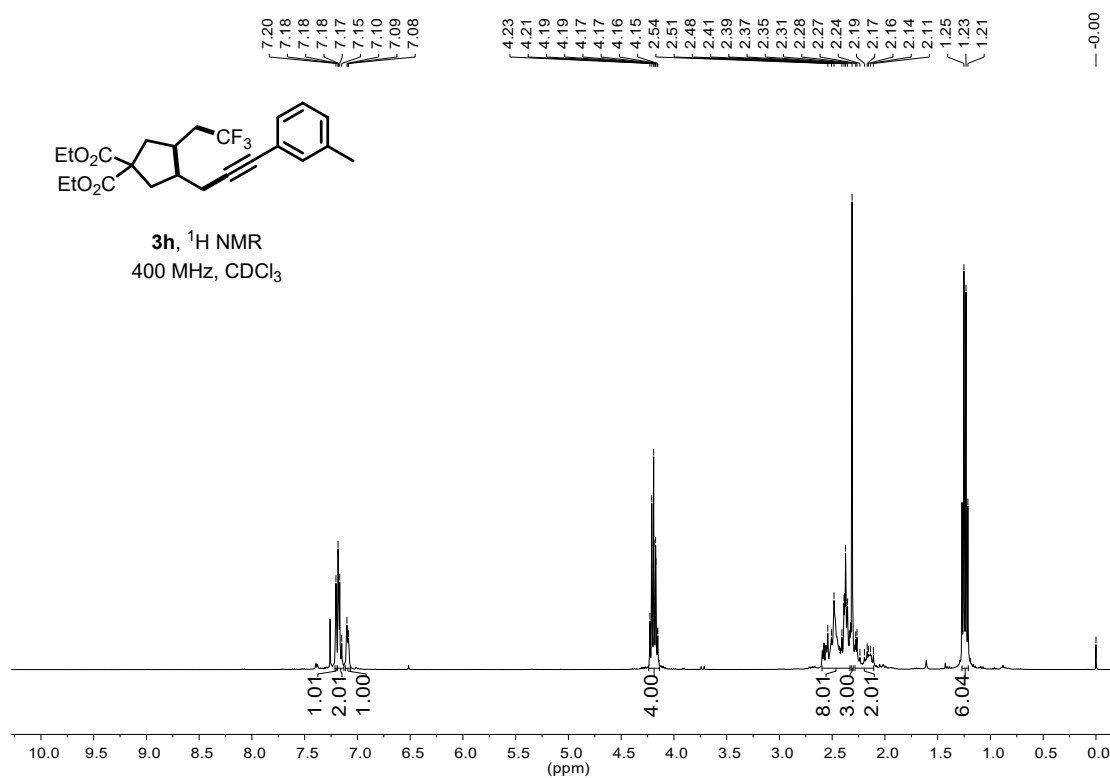
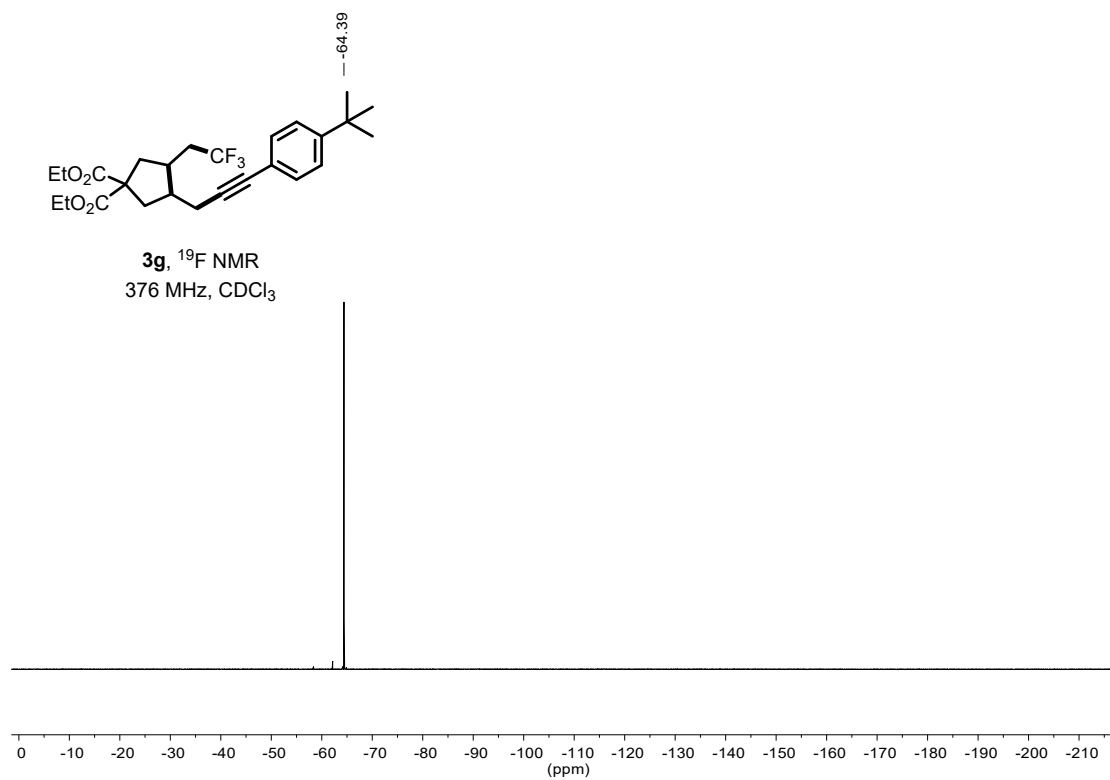


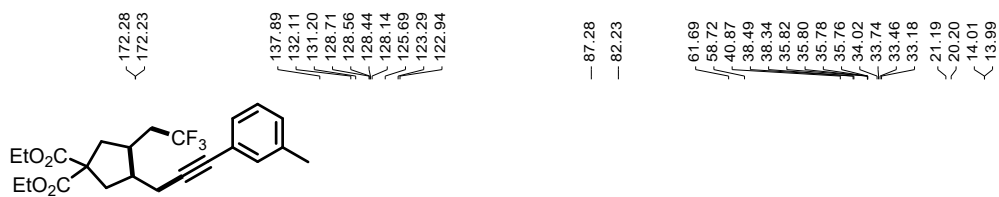
3f, ¹H NMR
400 MHz, CDCl₃



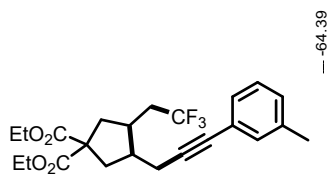
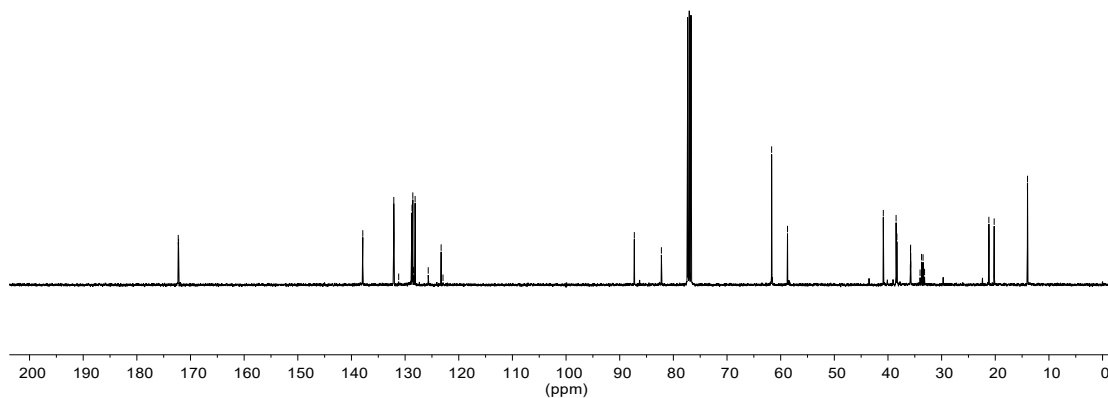




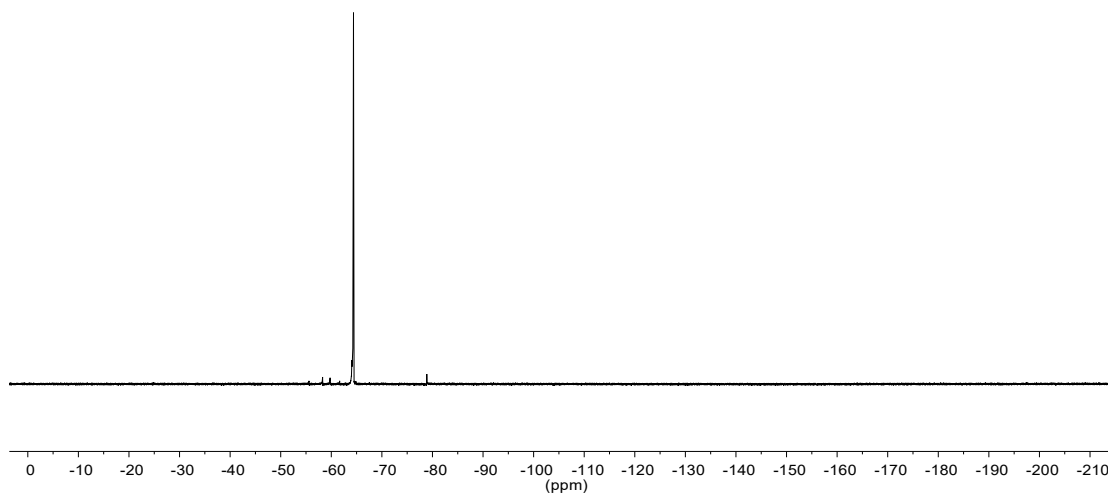


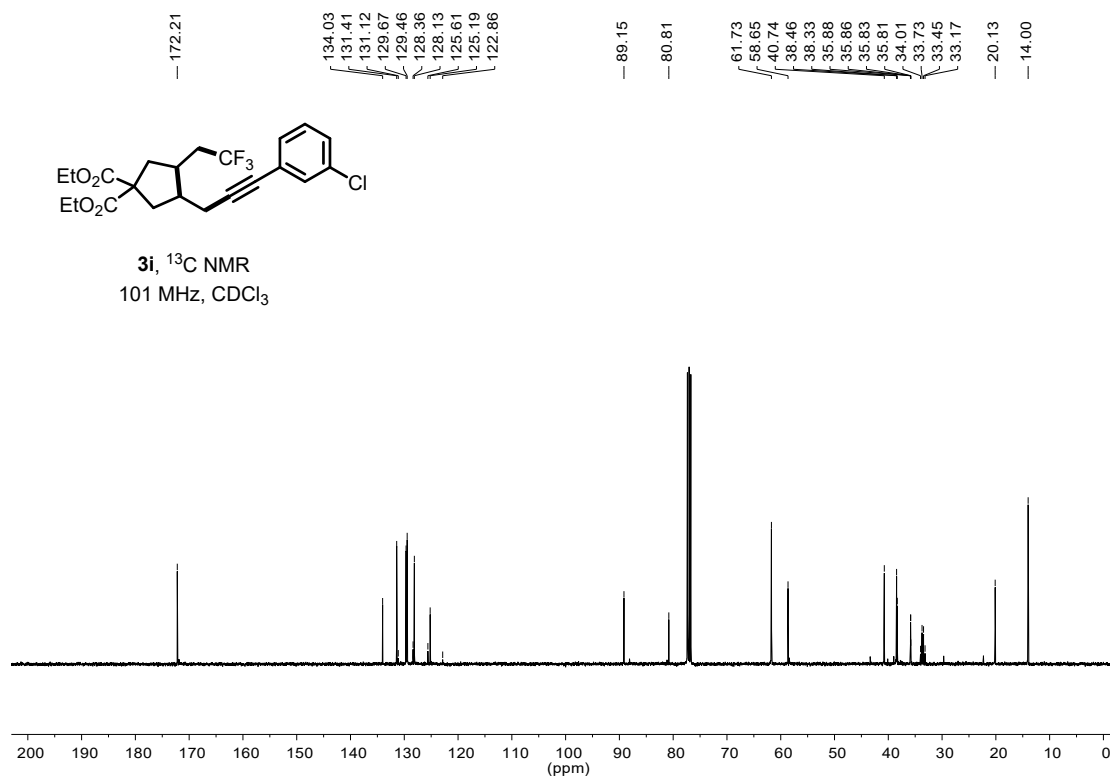
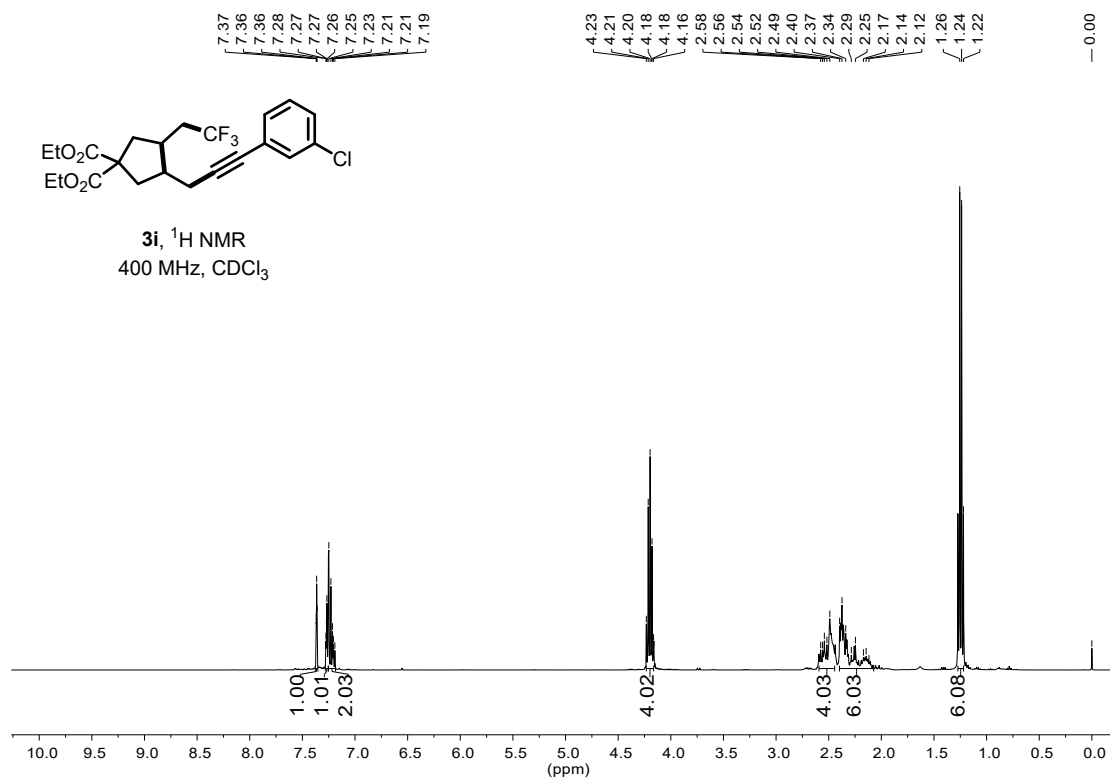


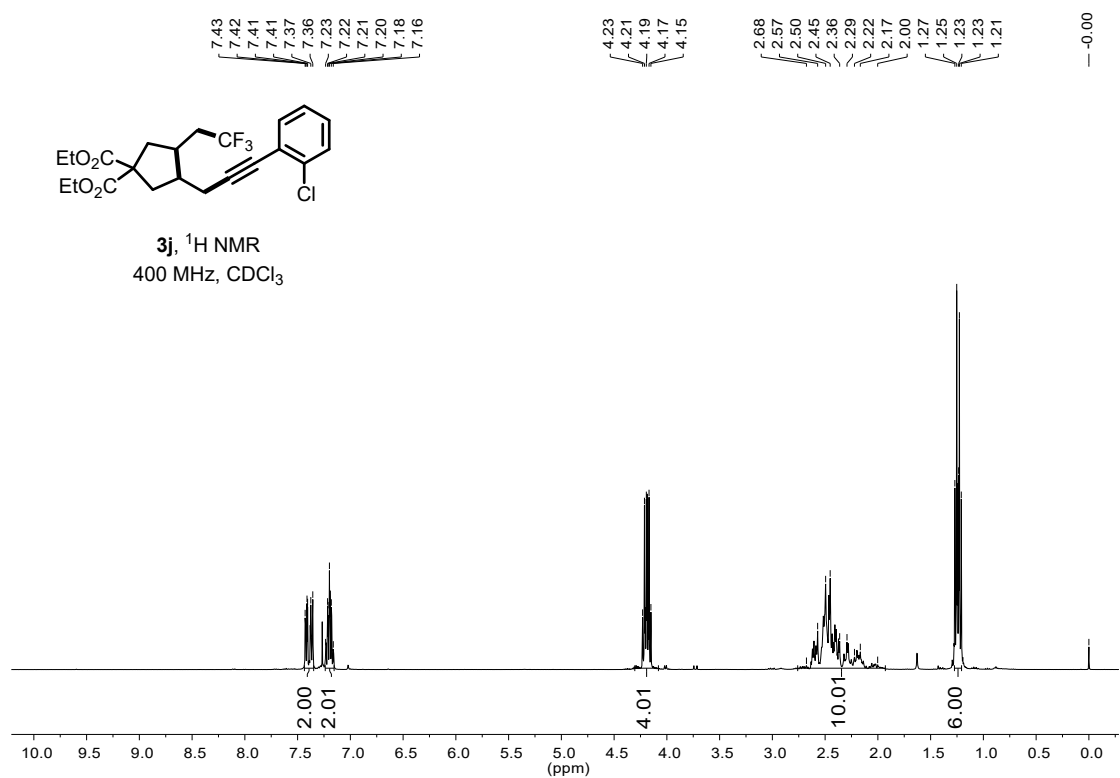
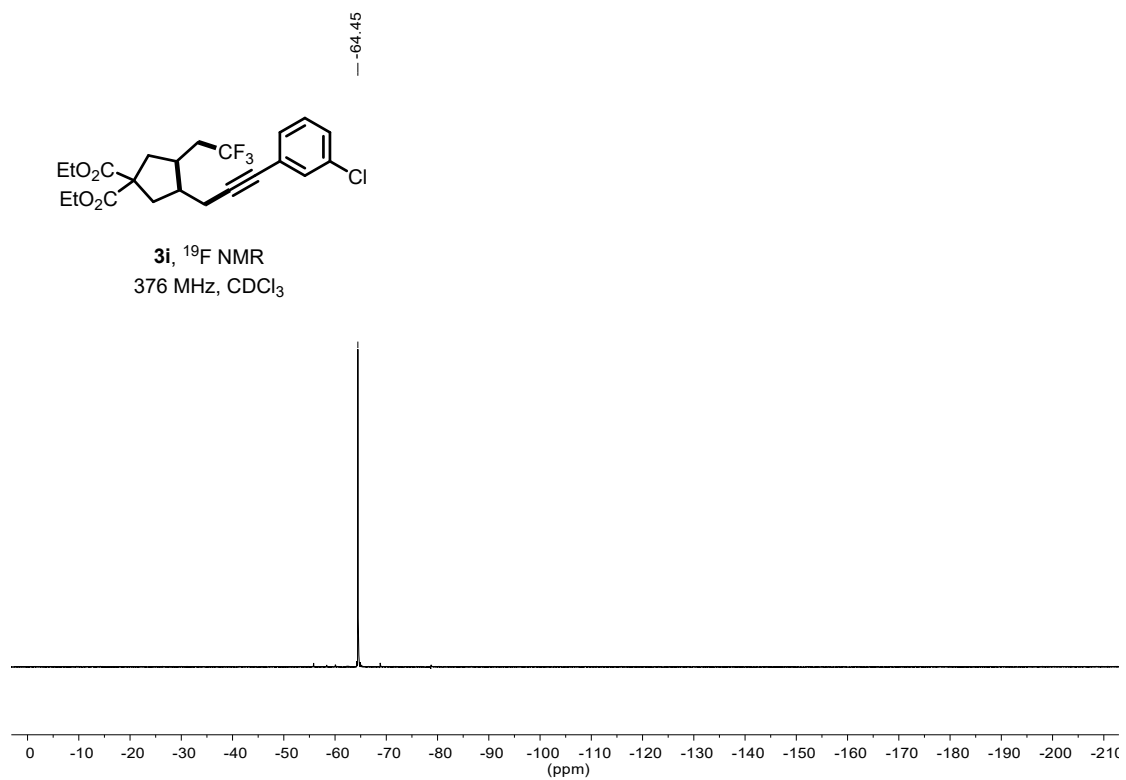
3h, ^{13}C NMR
101 MHz, CDCl_3

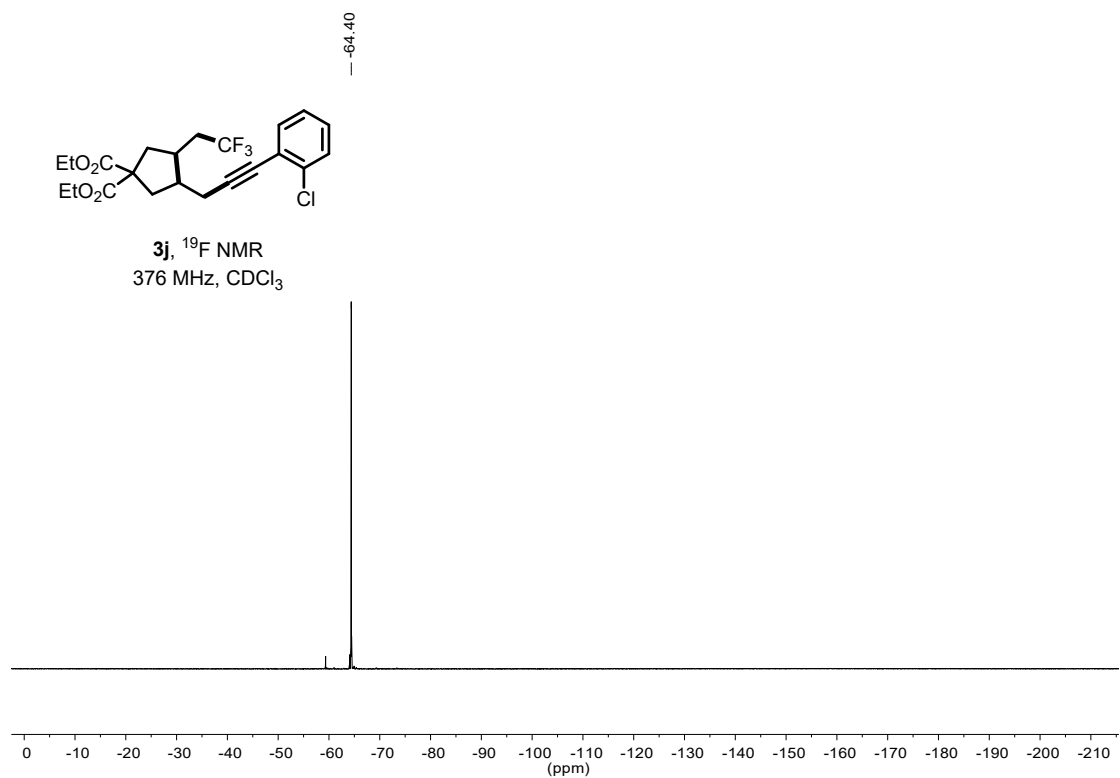
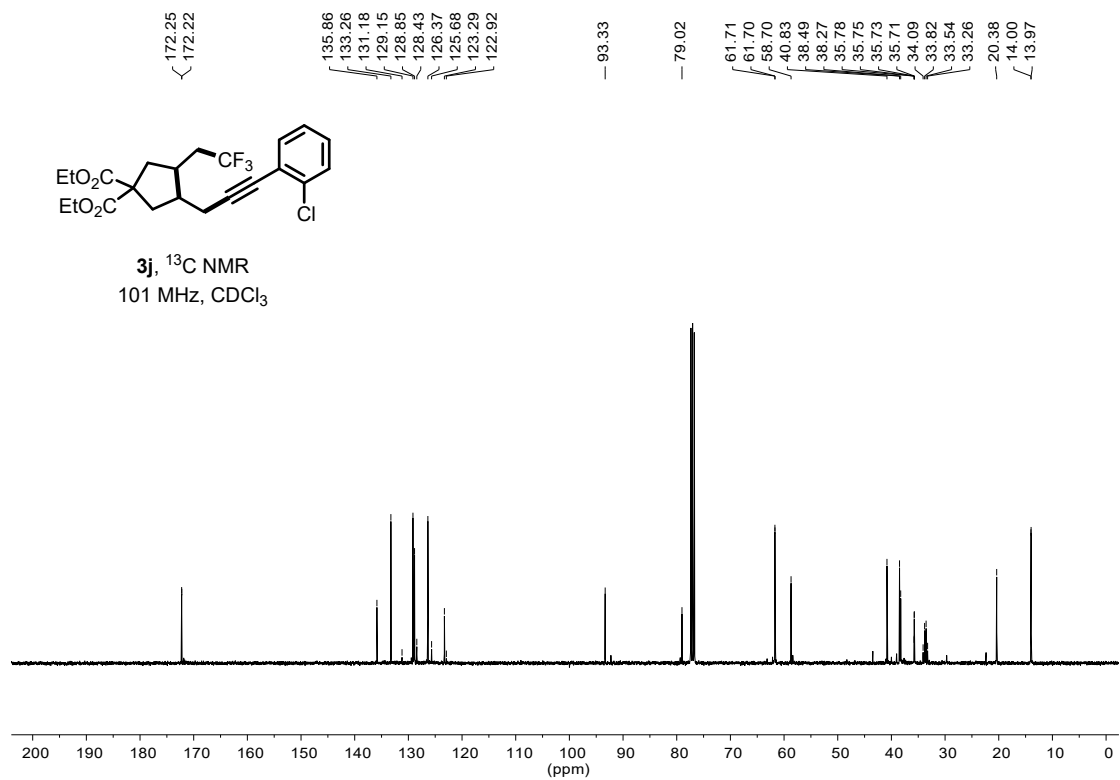


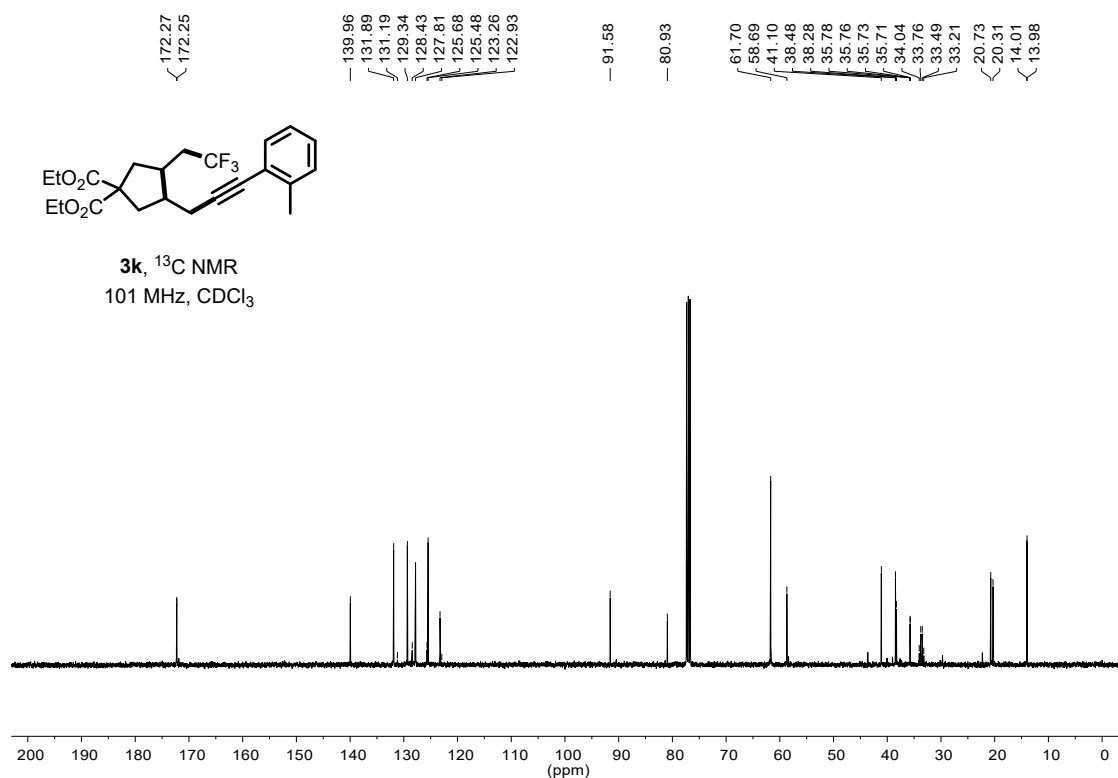
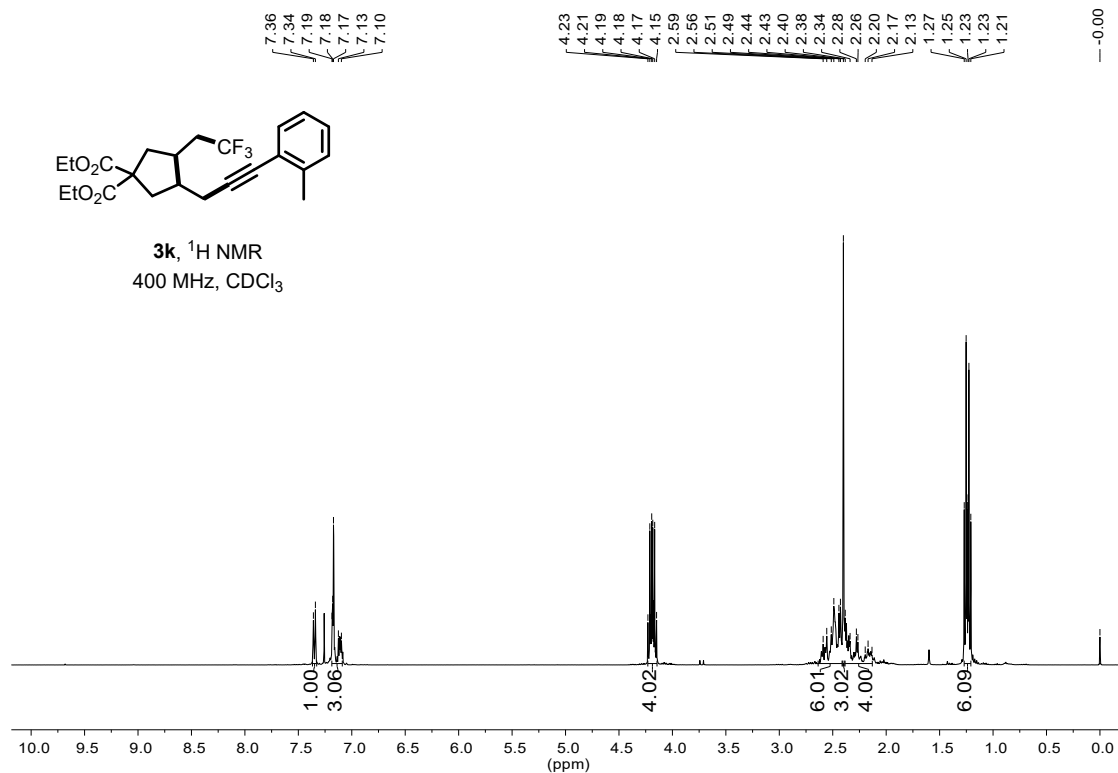
3h, ^{19}F NMR
376 MHz, CDCl_3

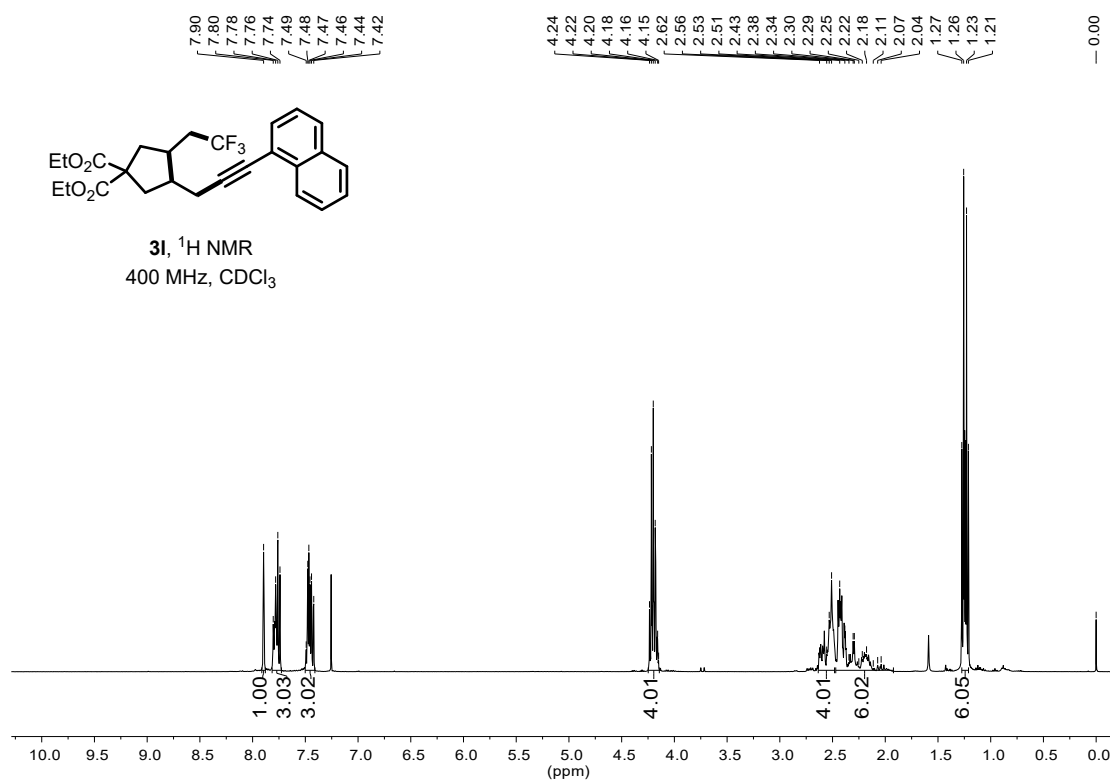
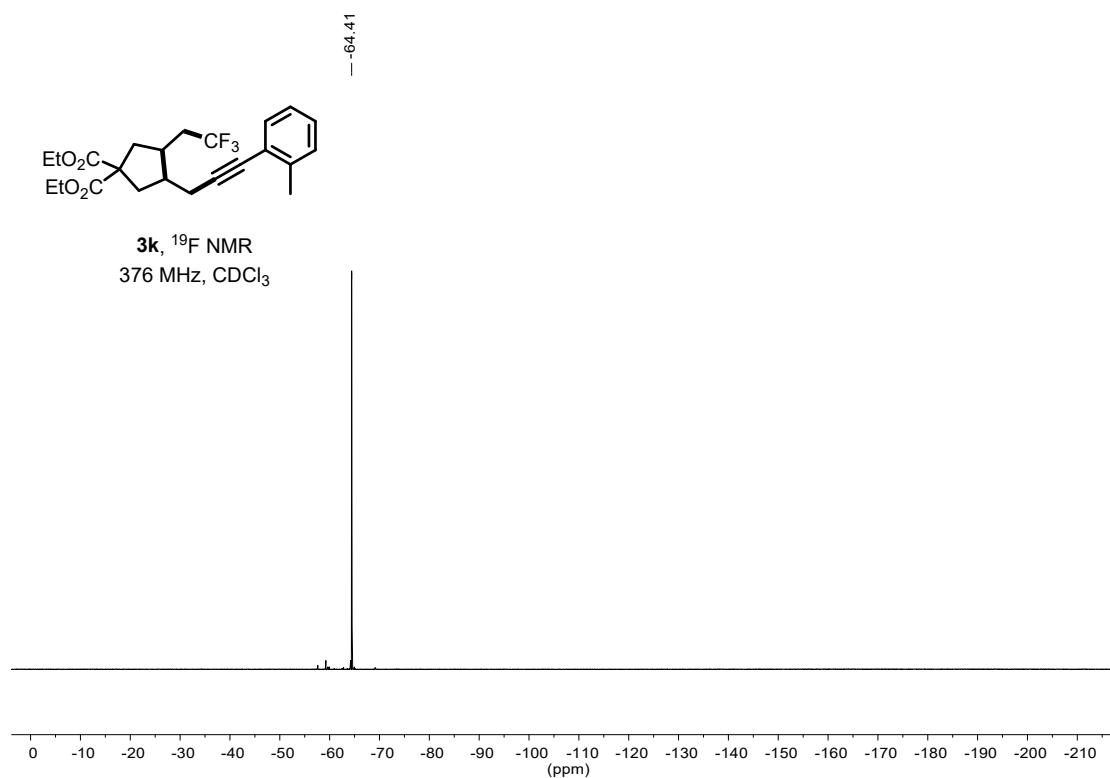


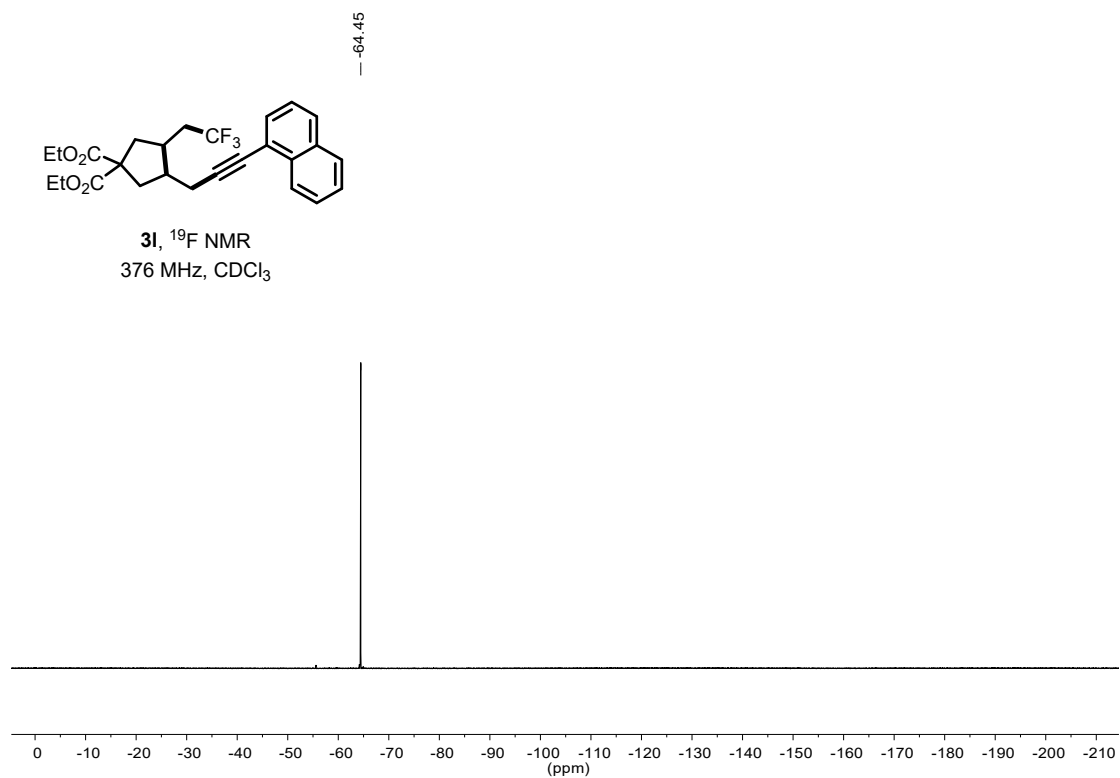
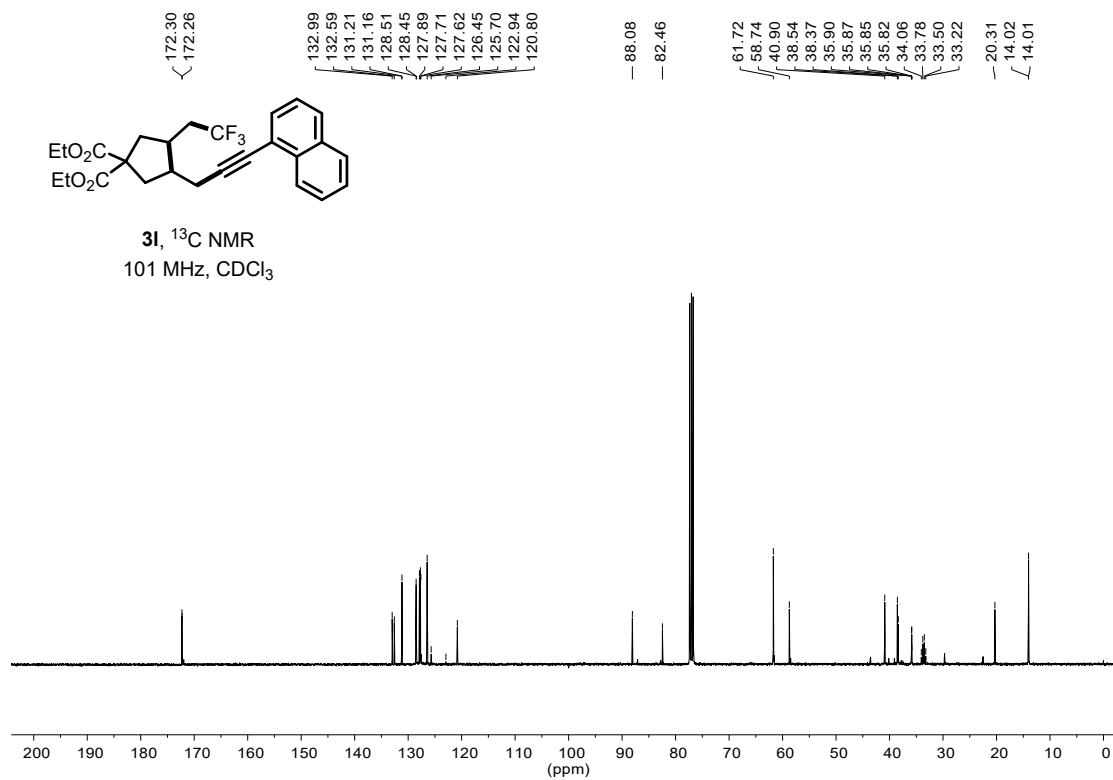


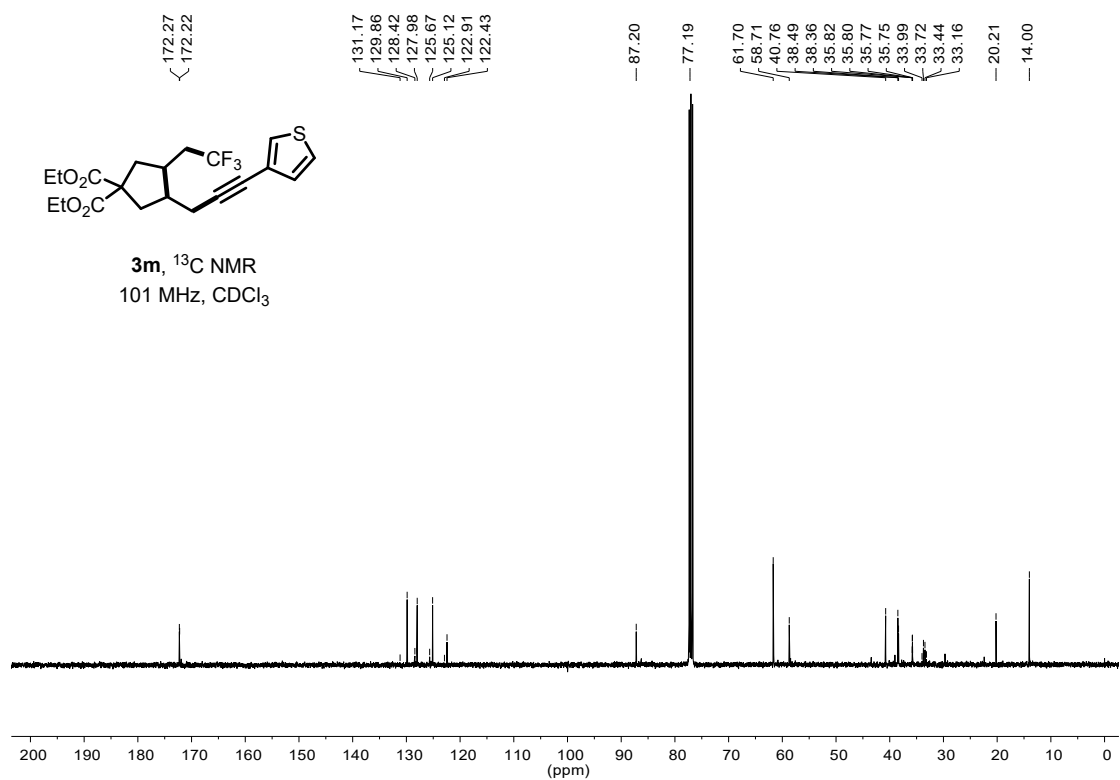
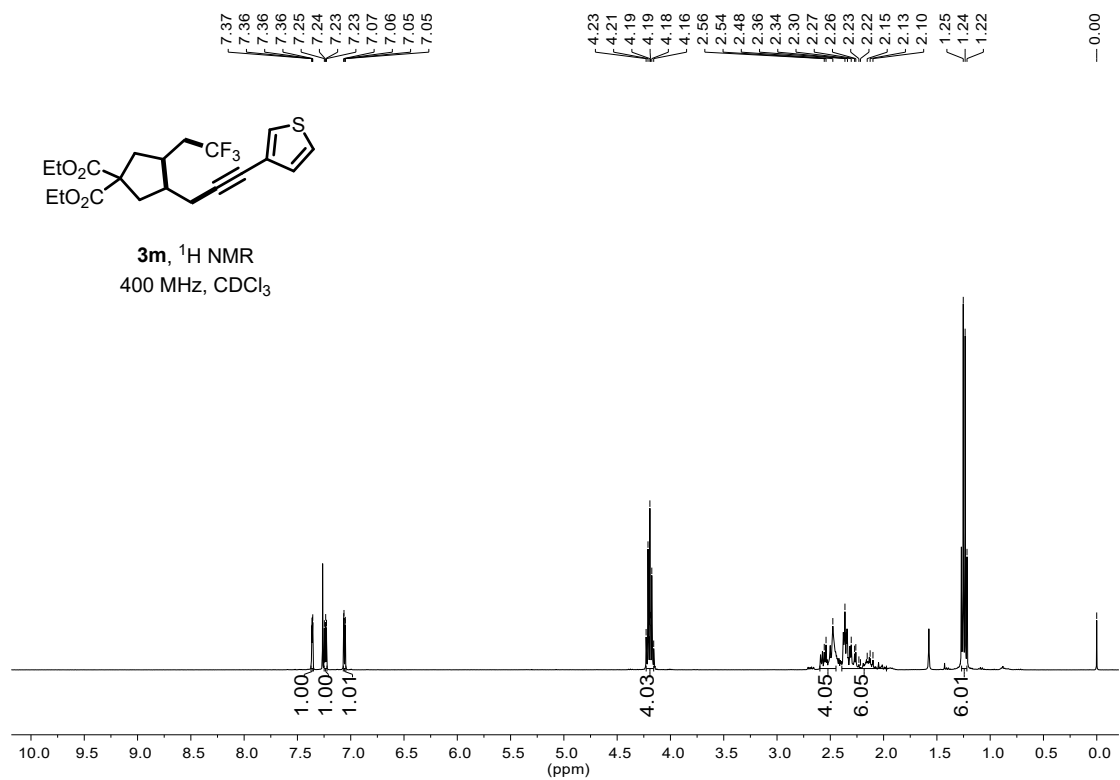


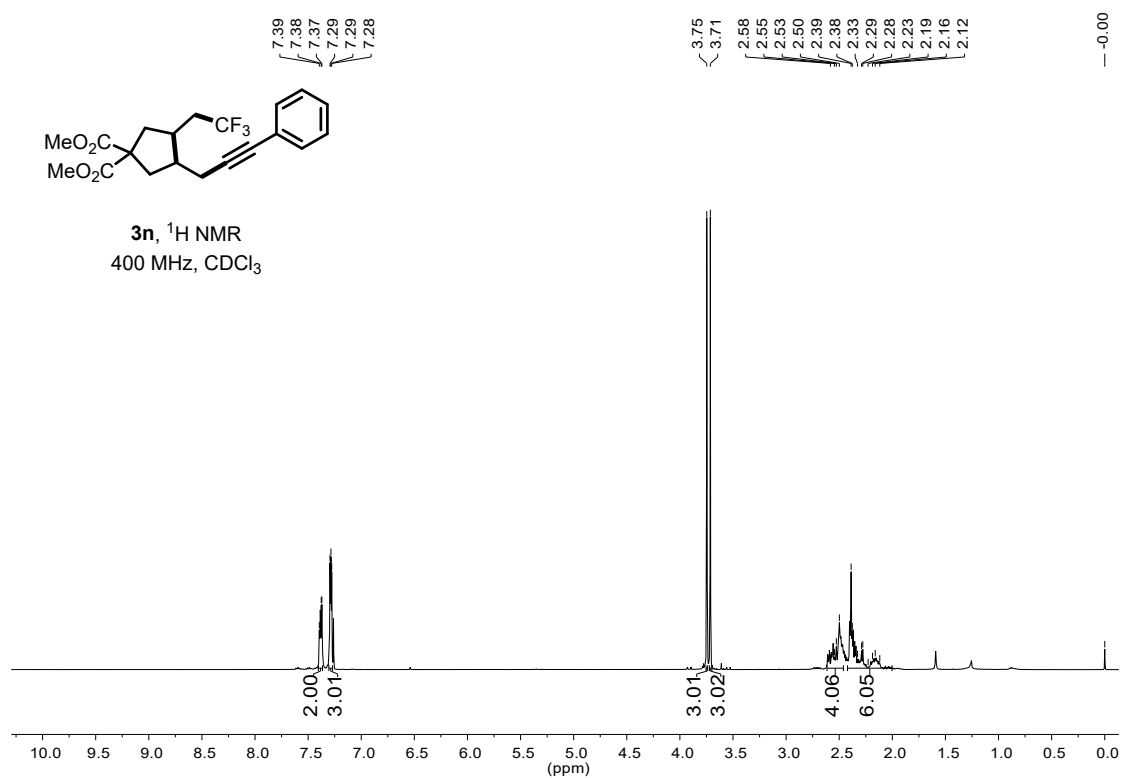
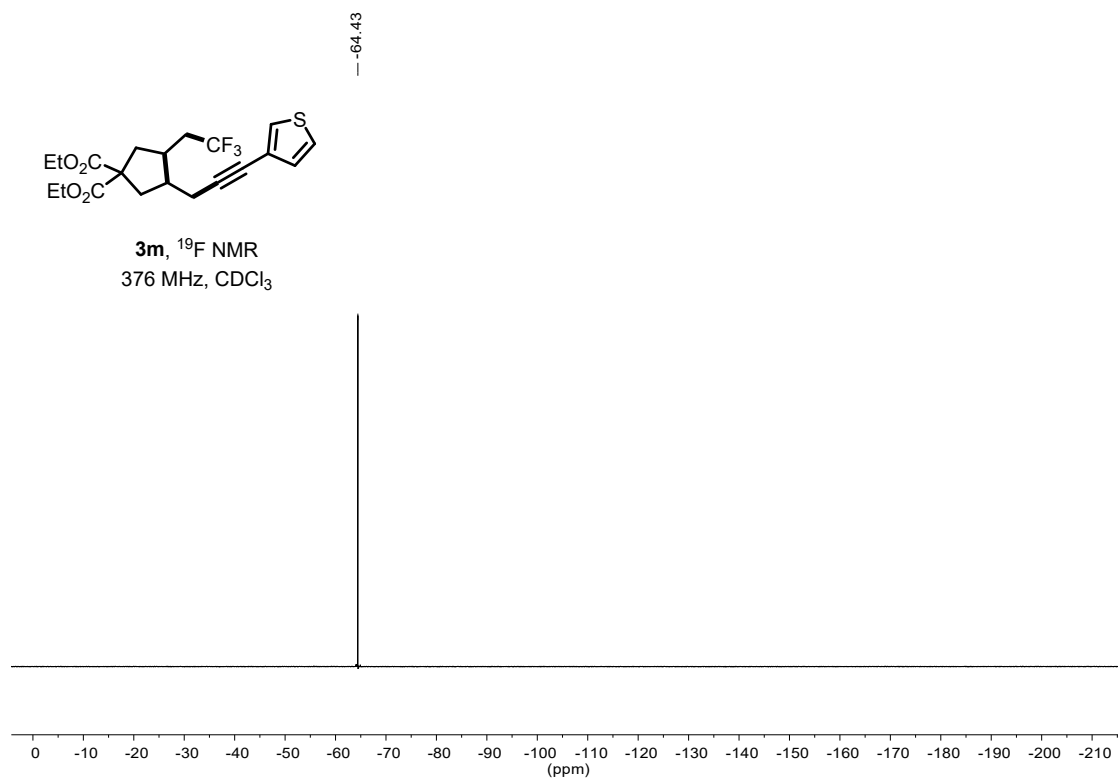


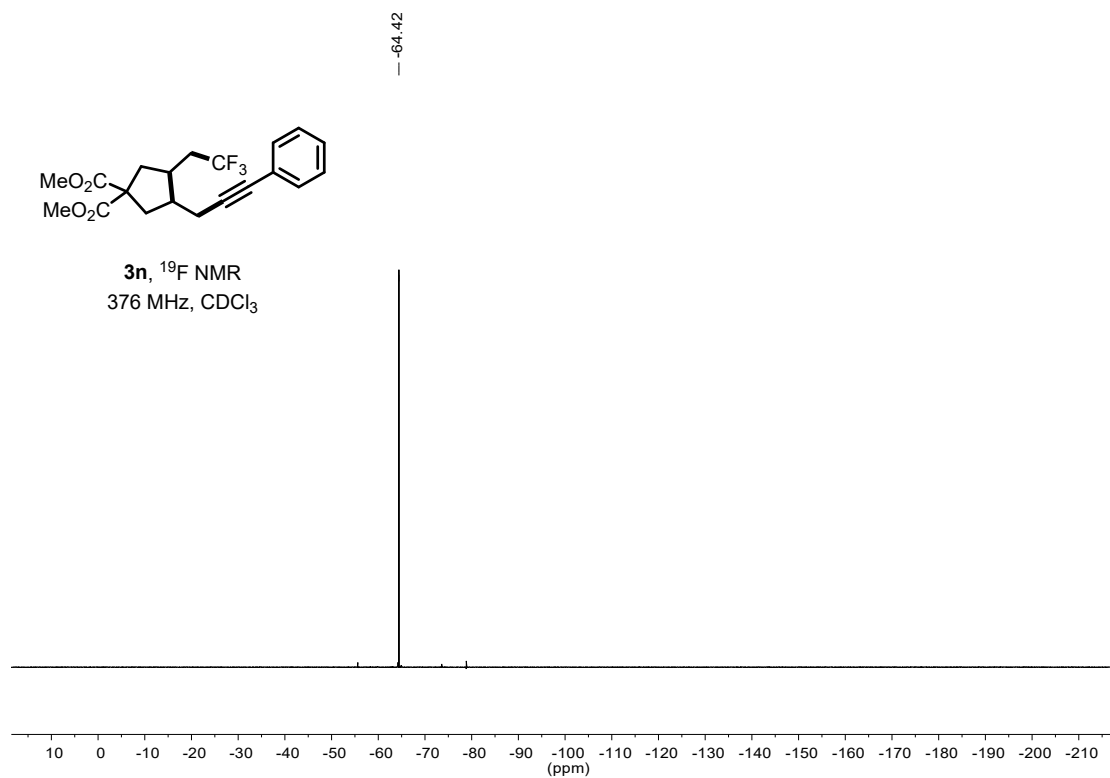
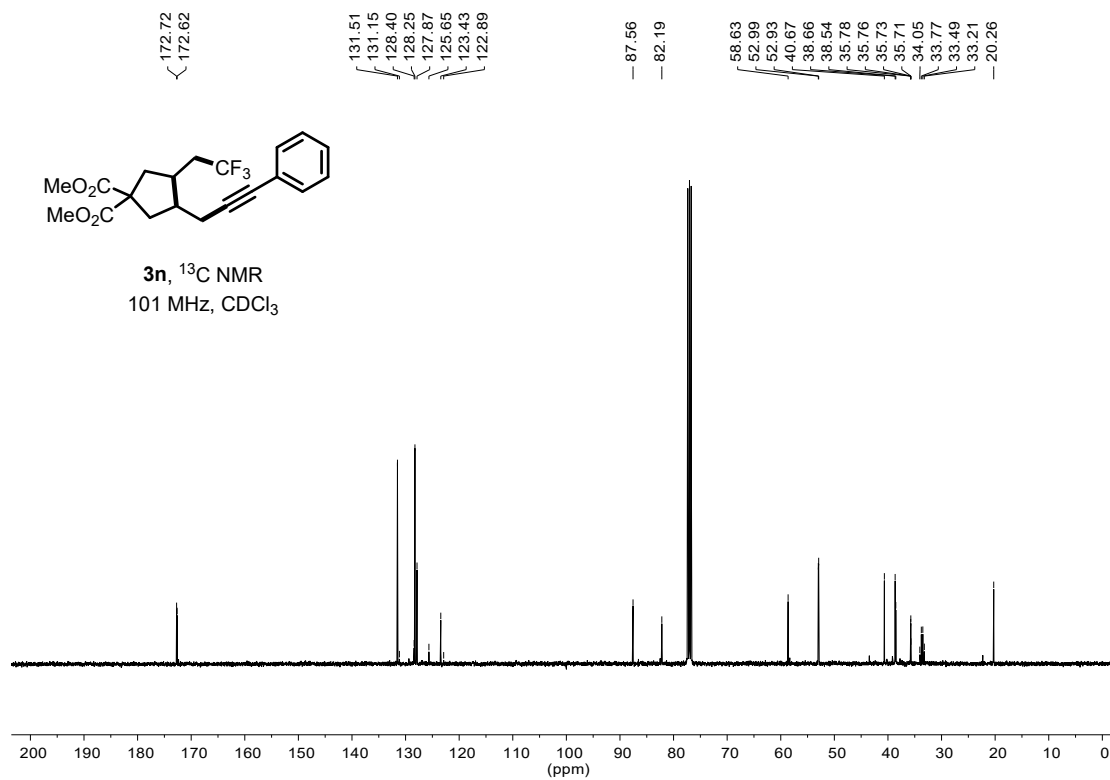


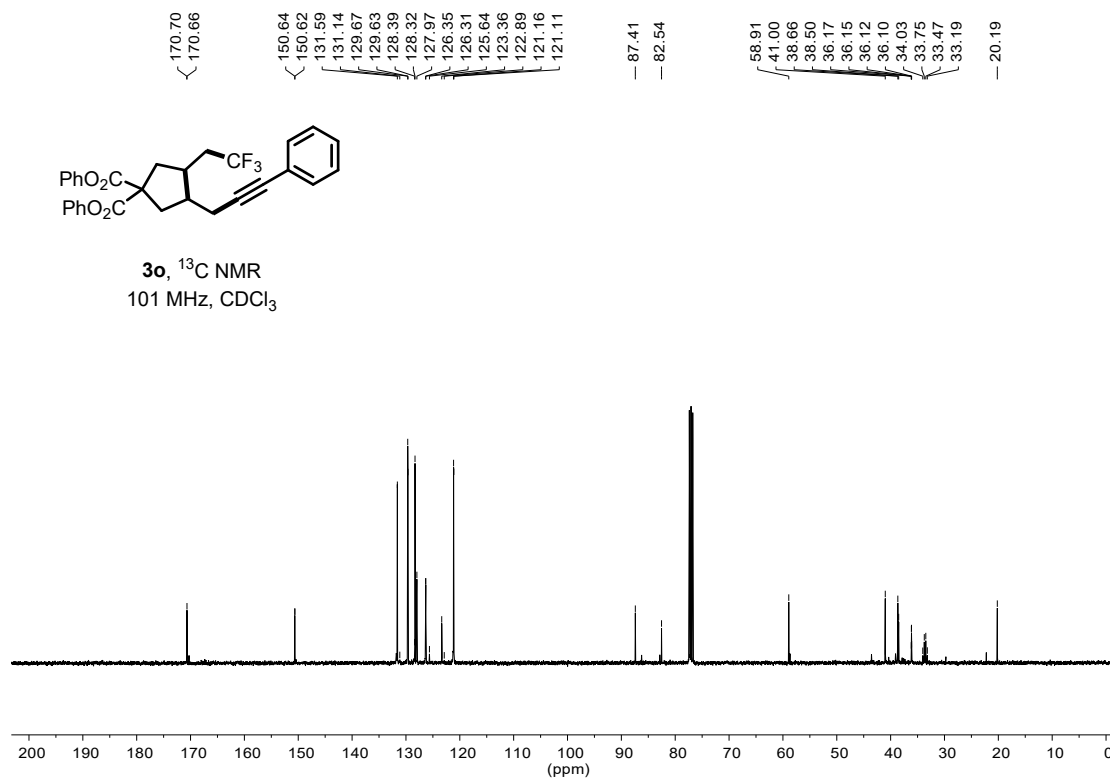
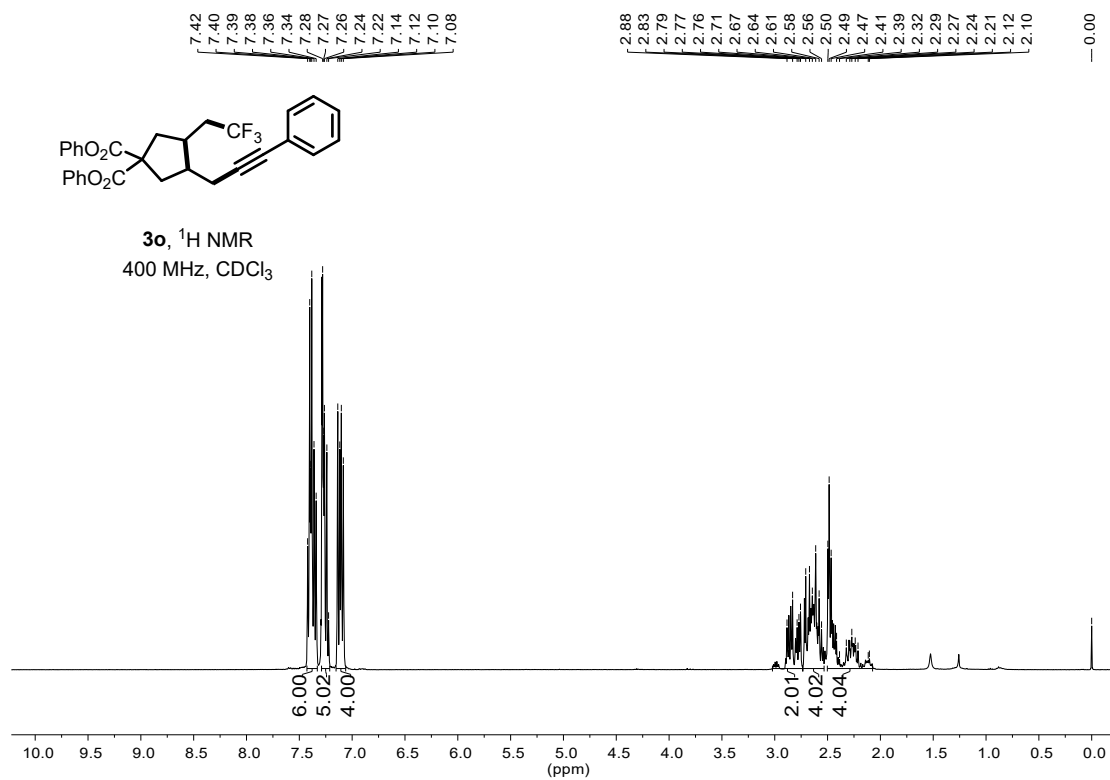


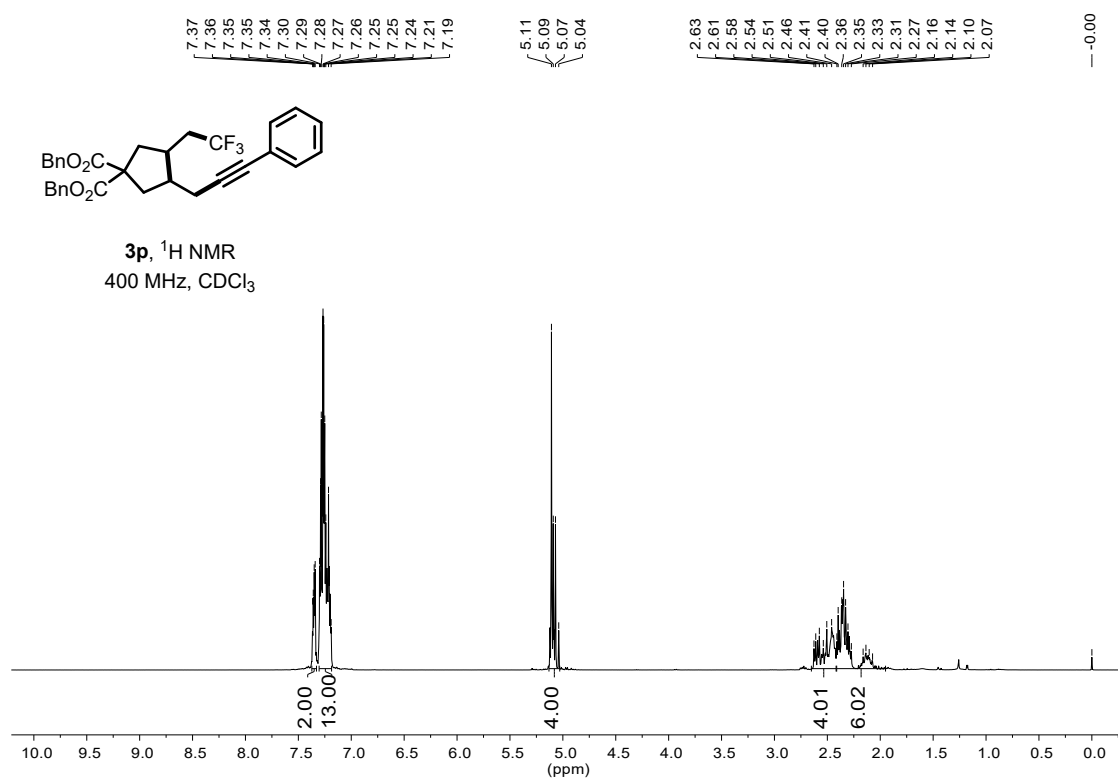
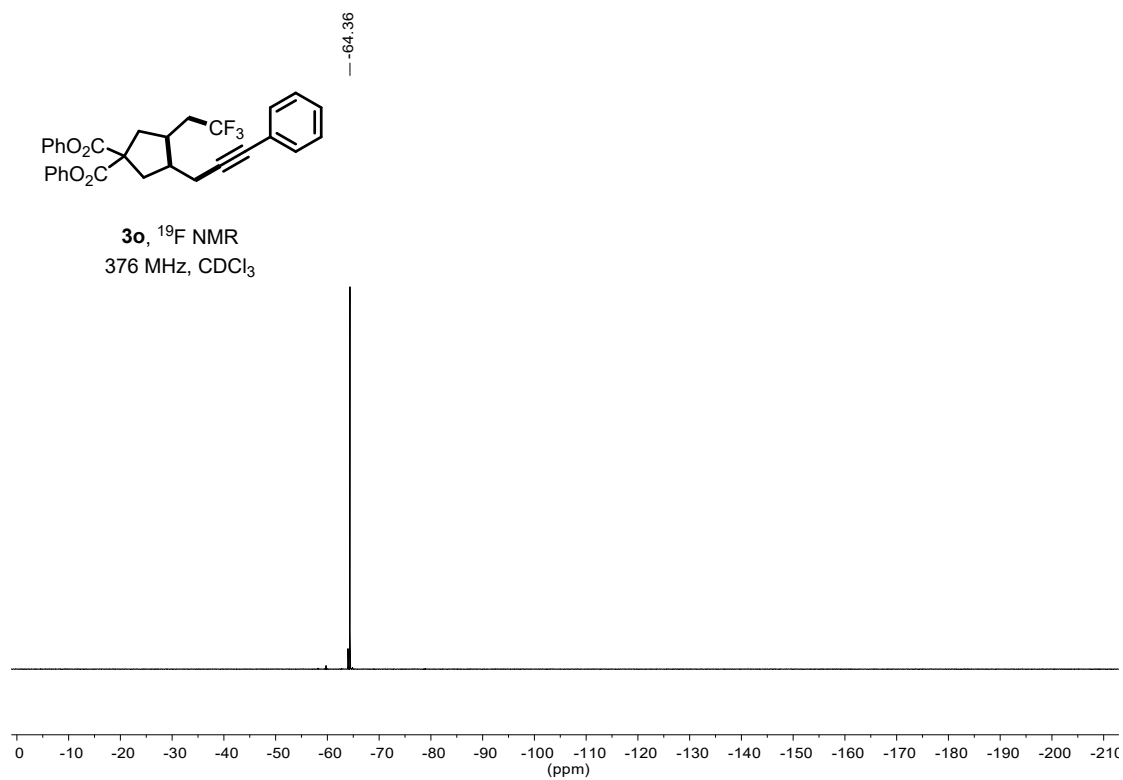


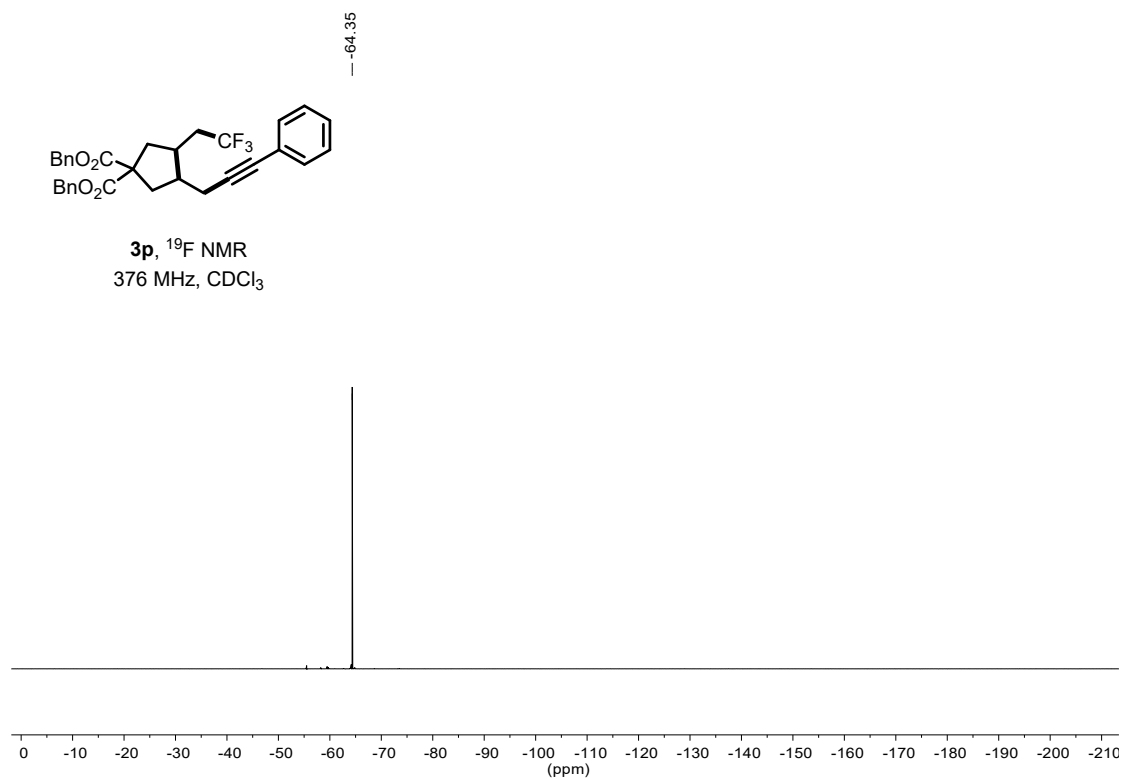
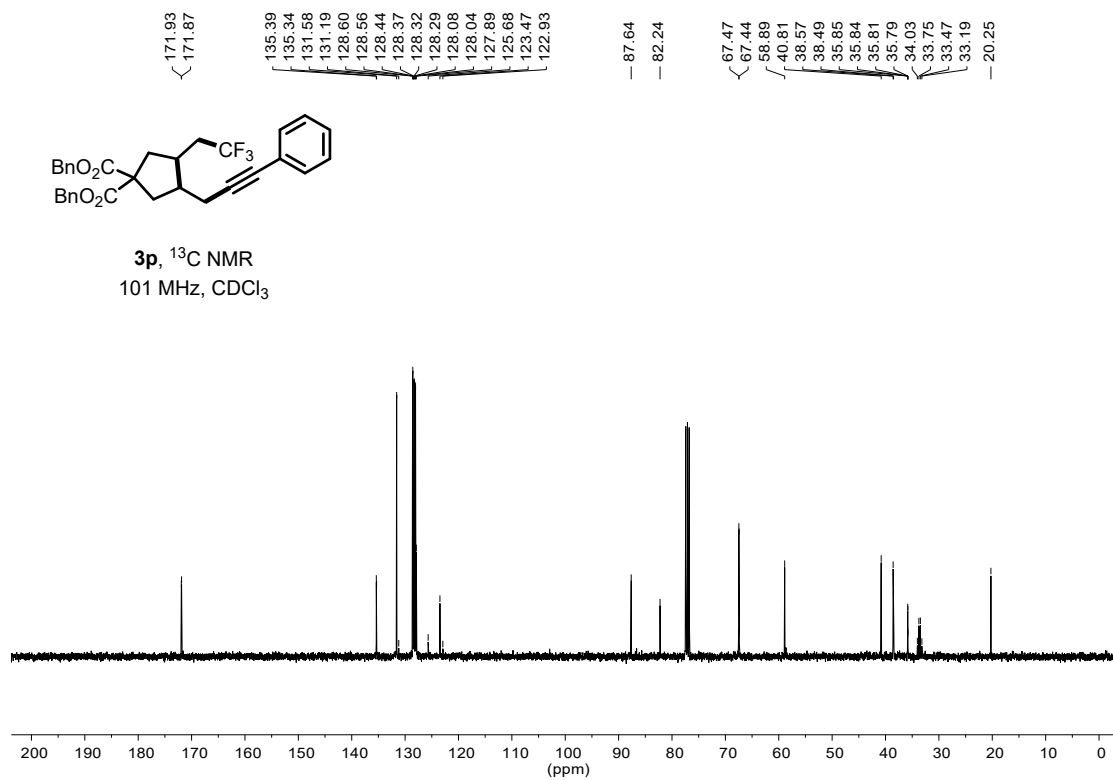


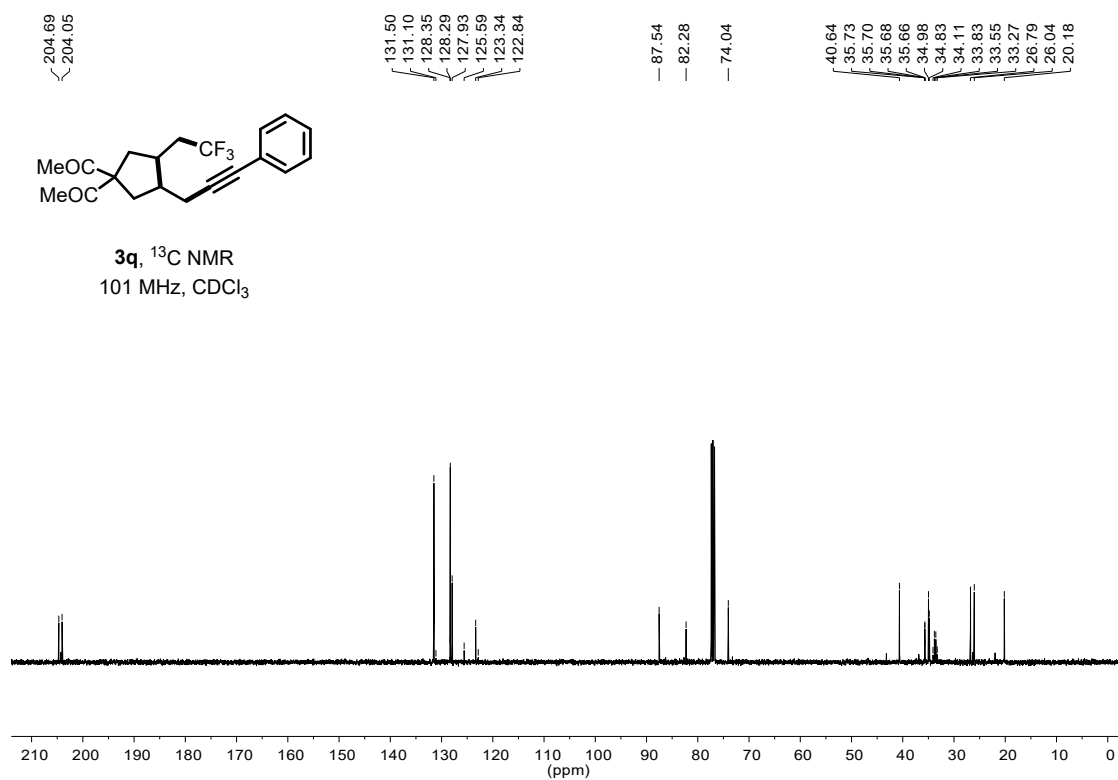
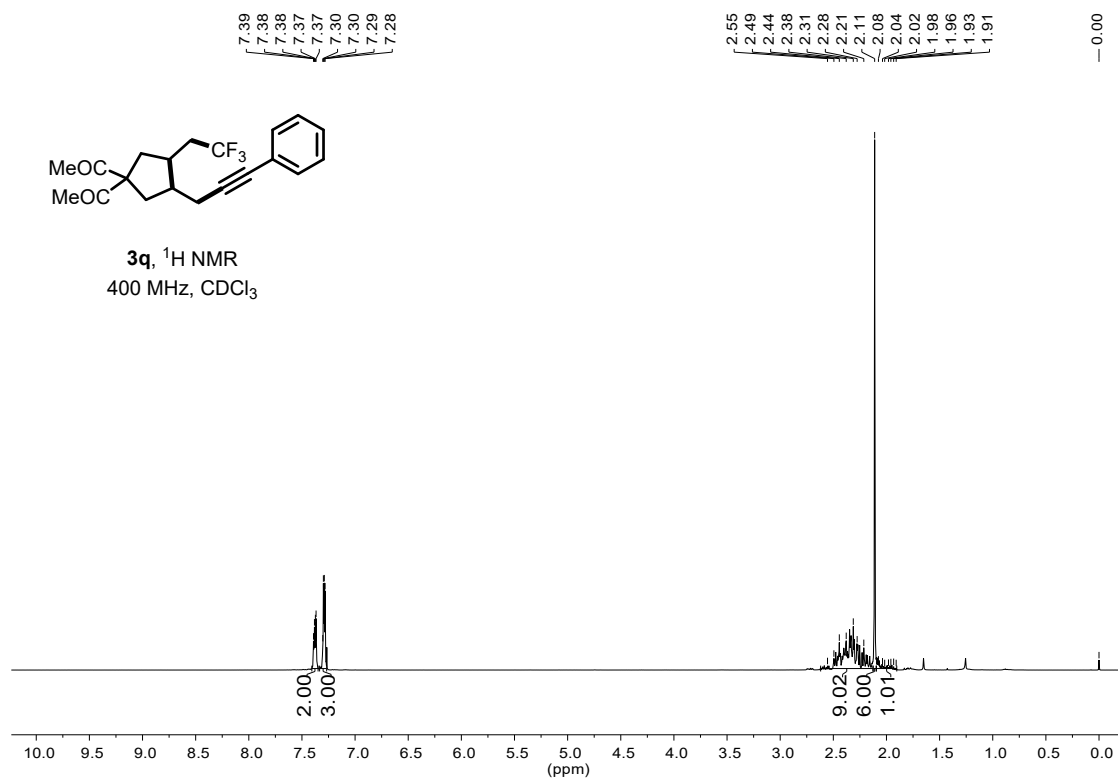


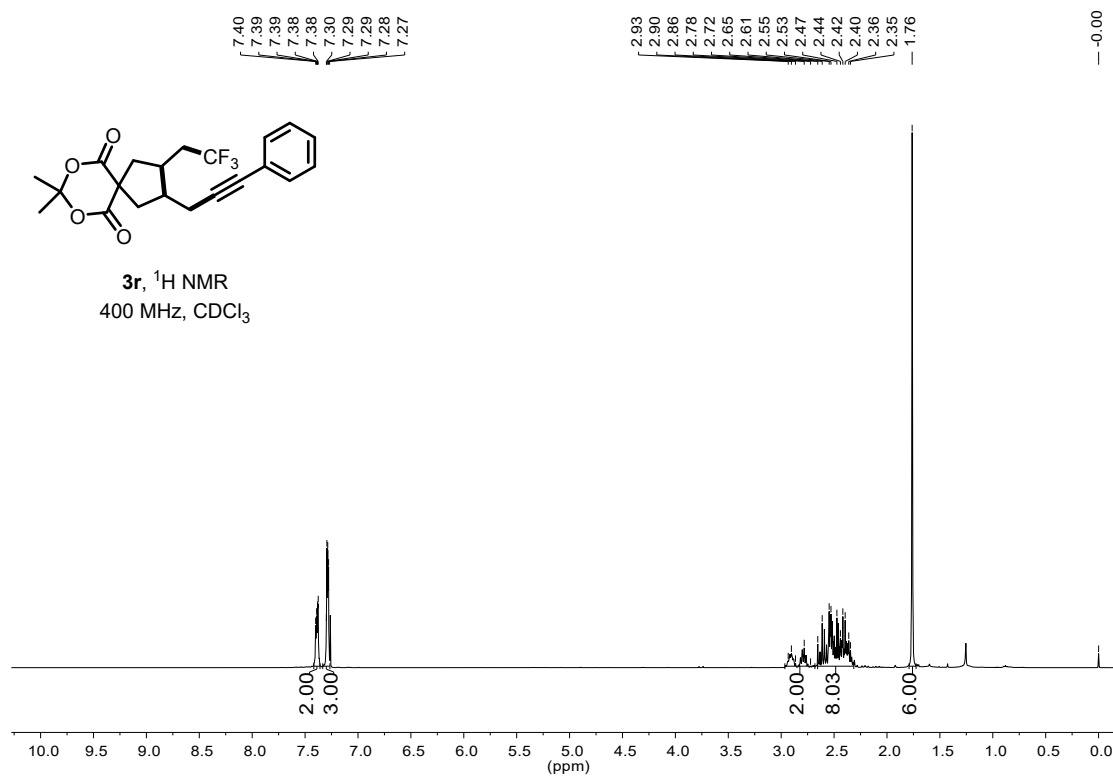
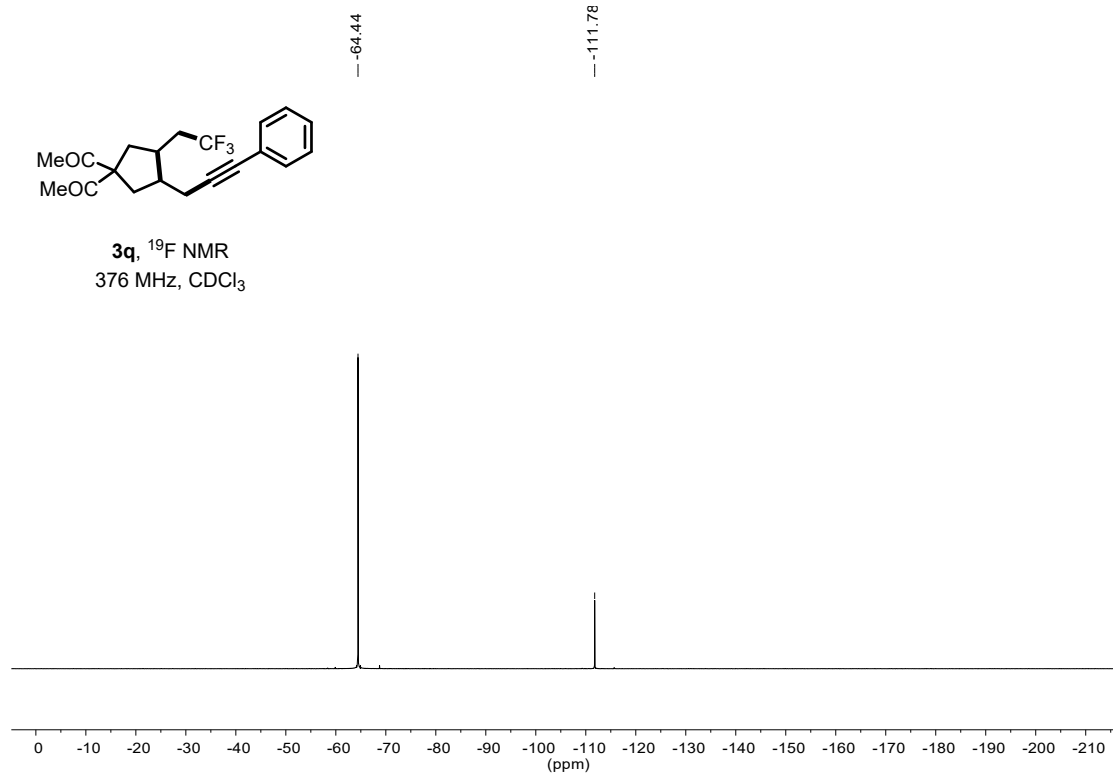


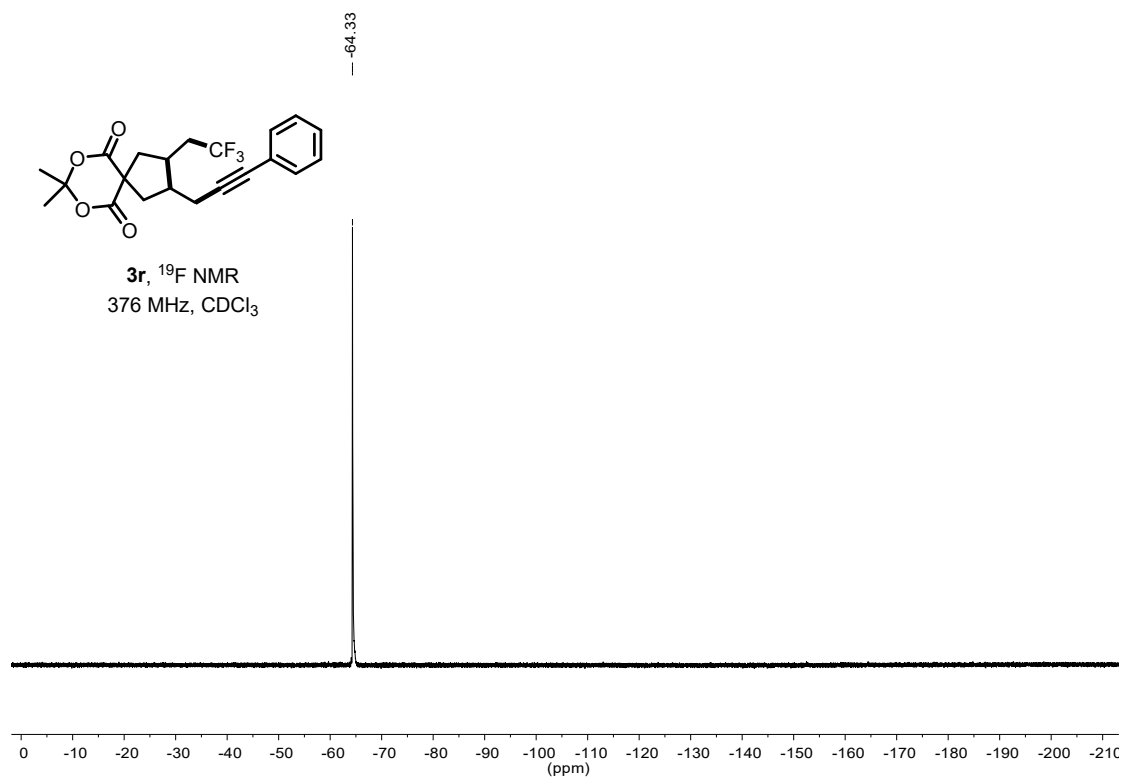
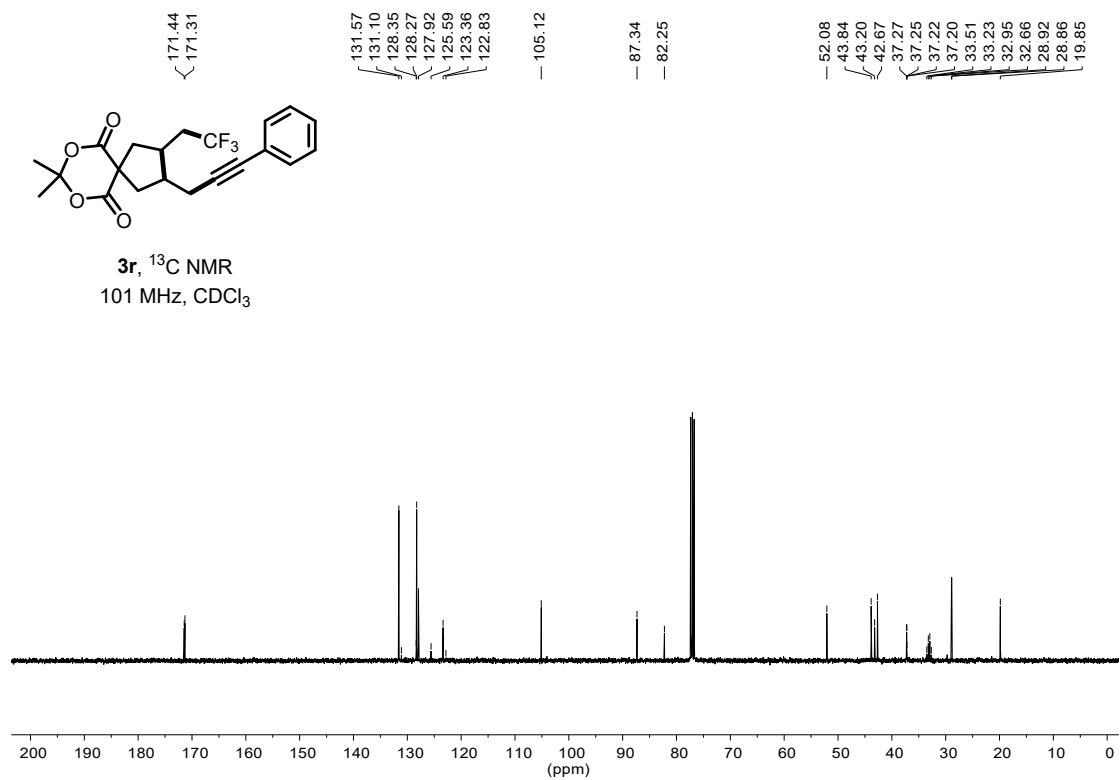


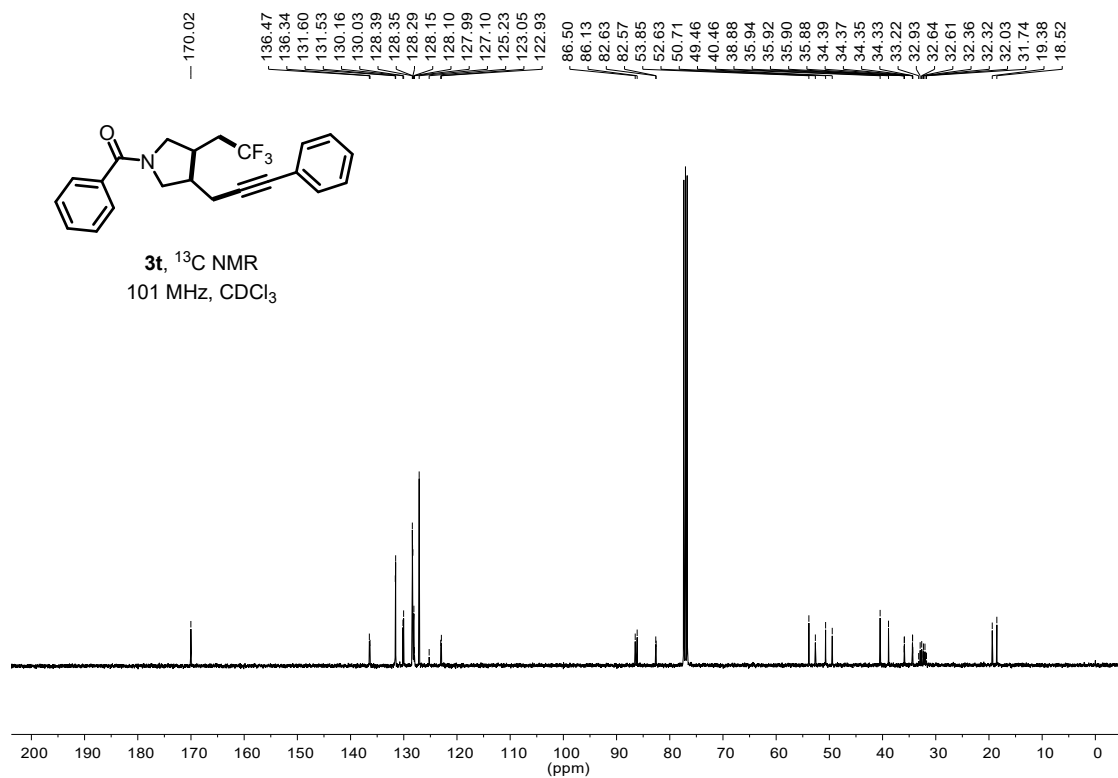
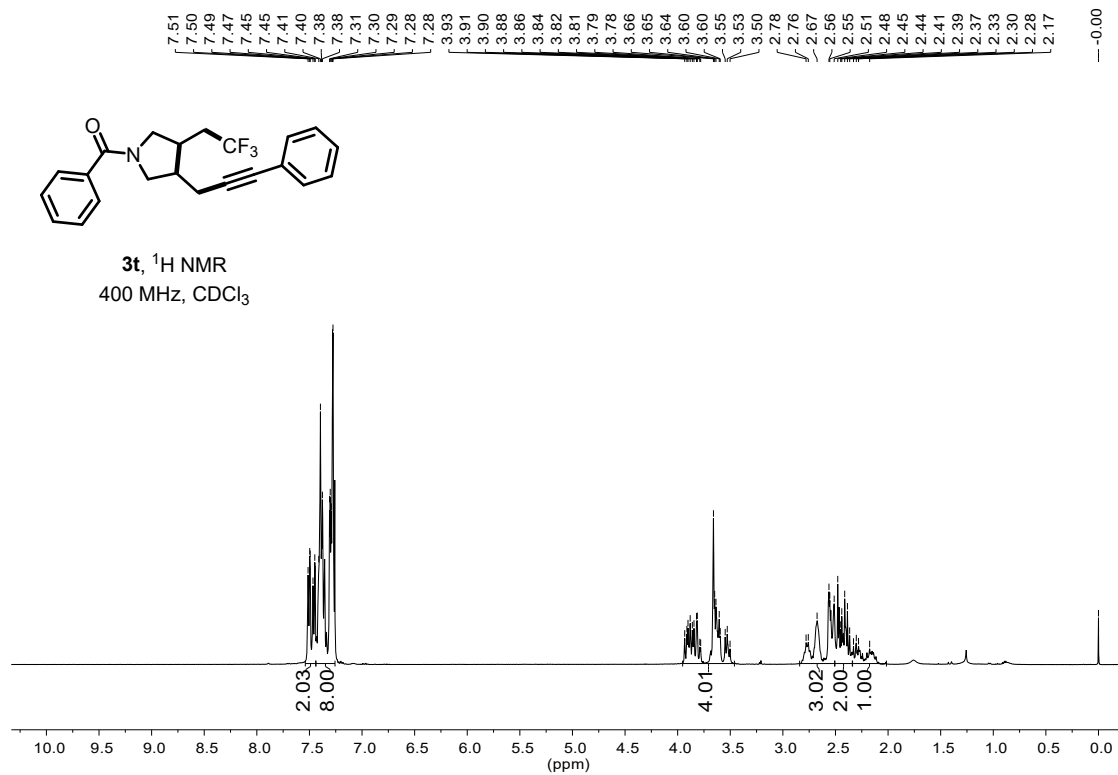


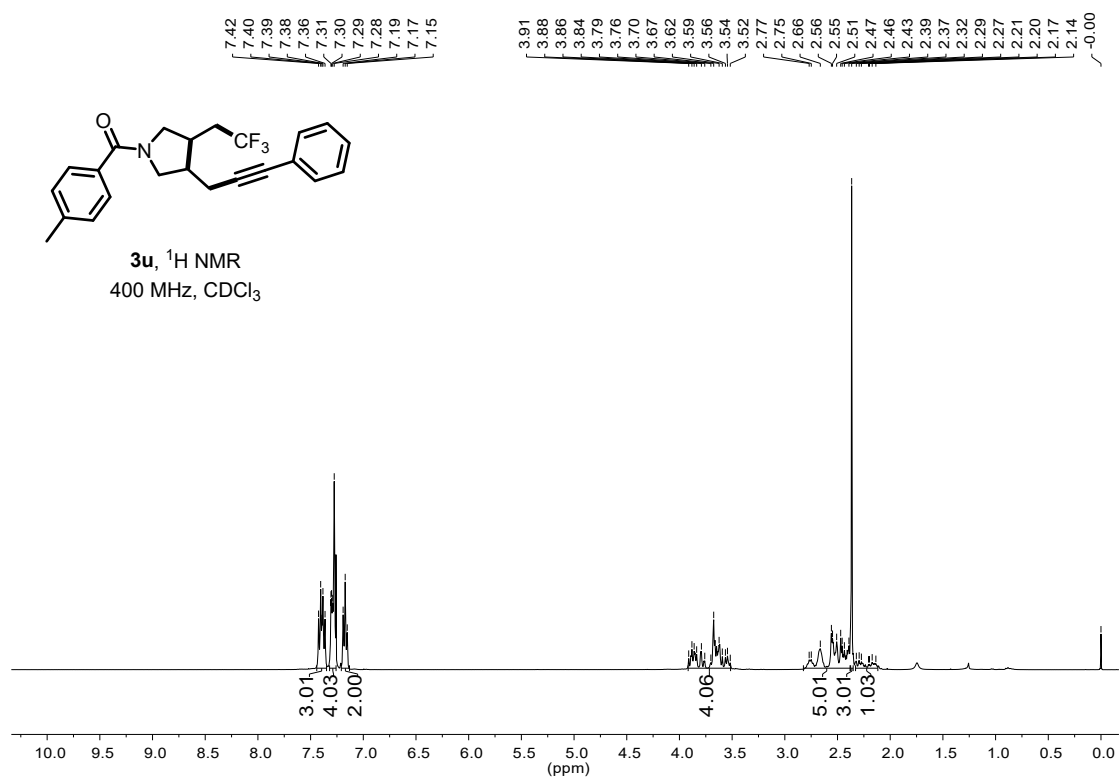
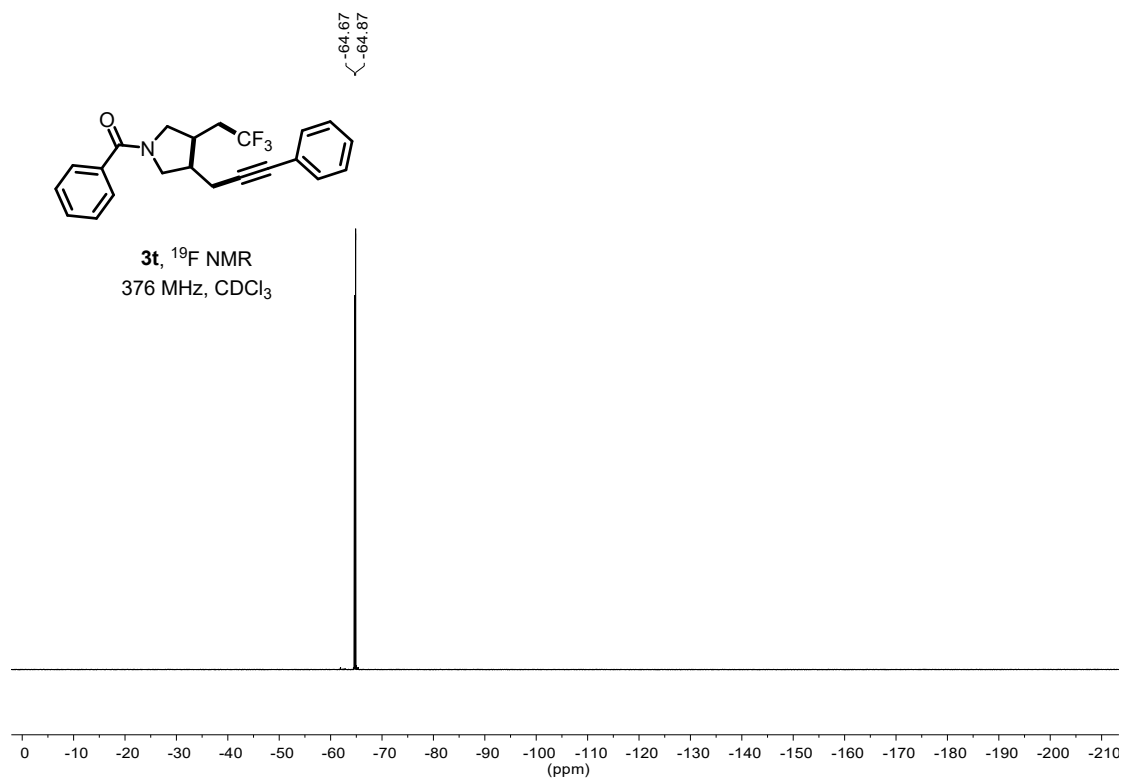


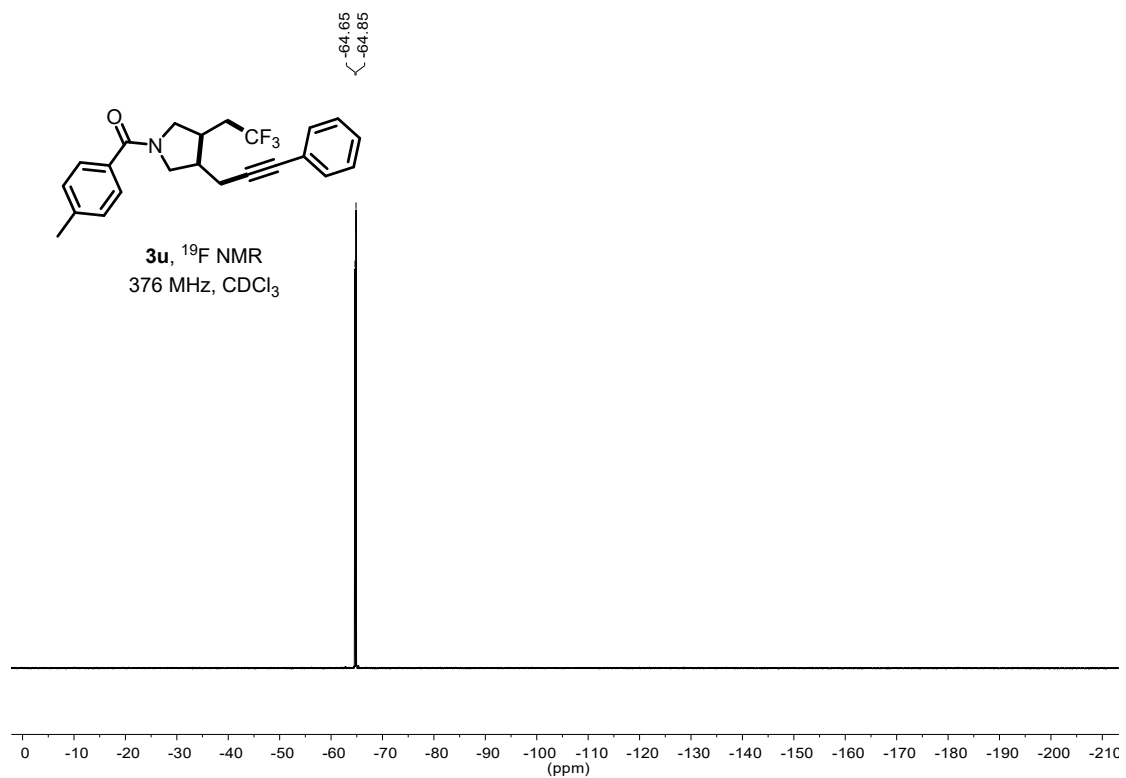
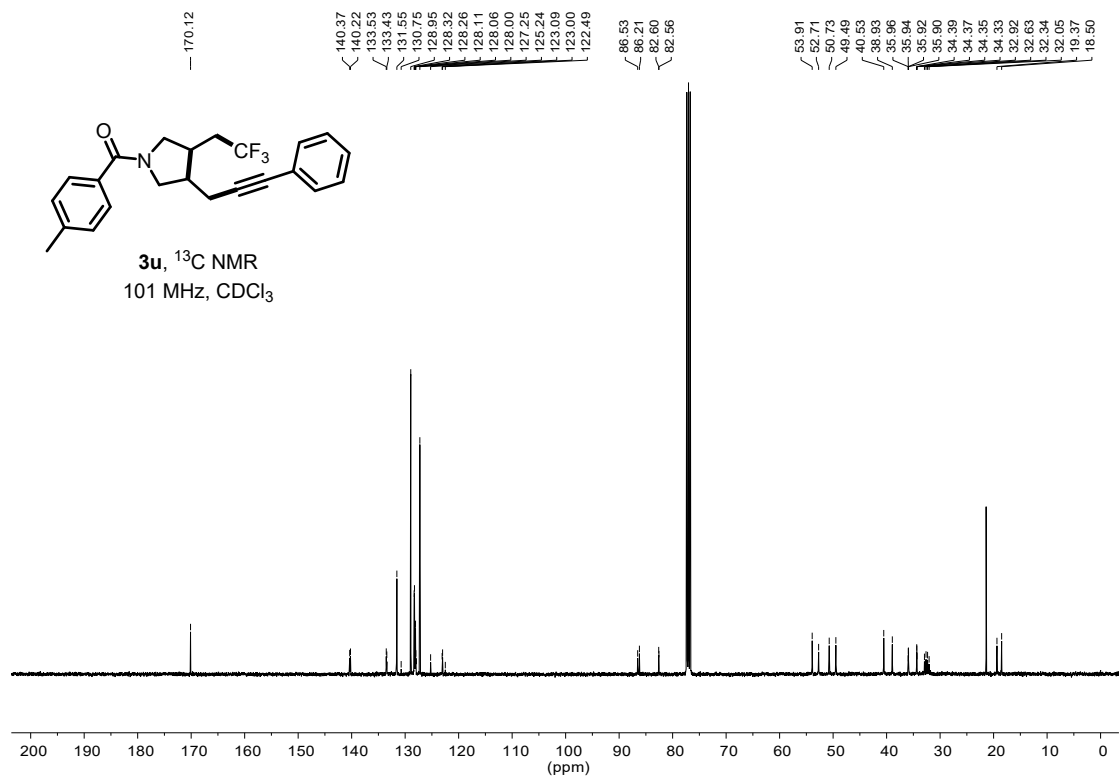


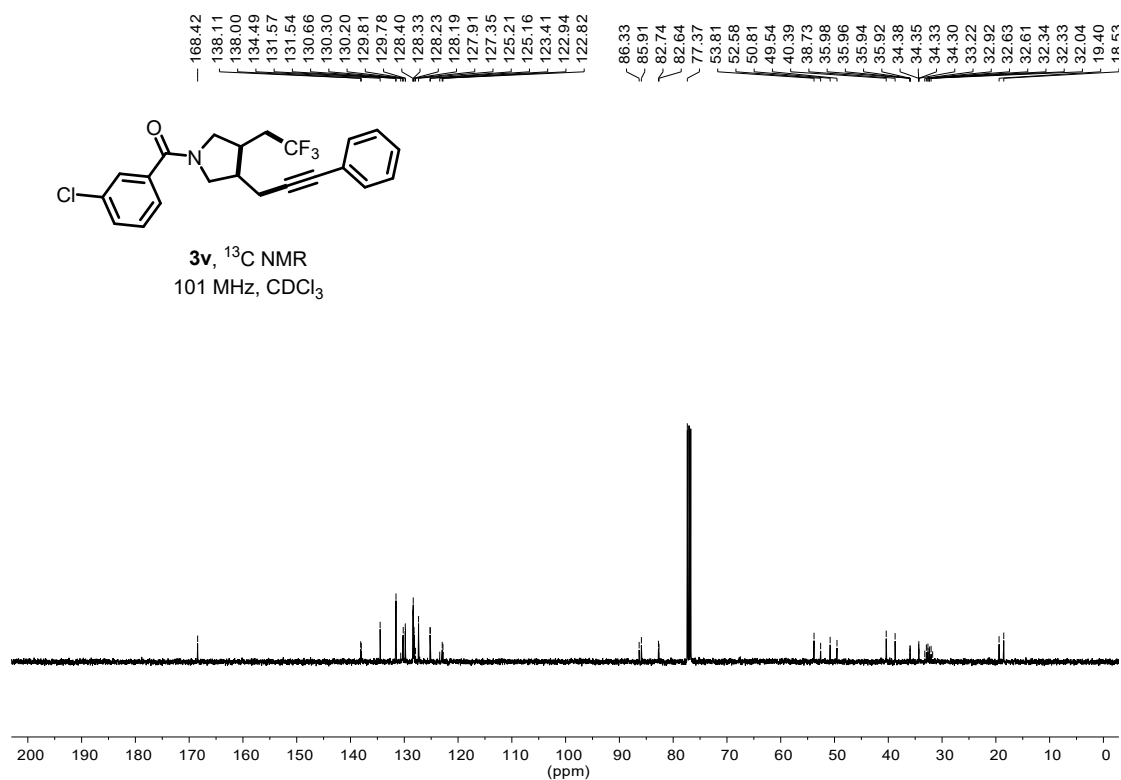
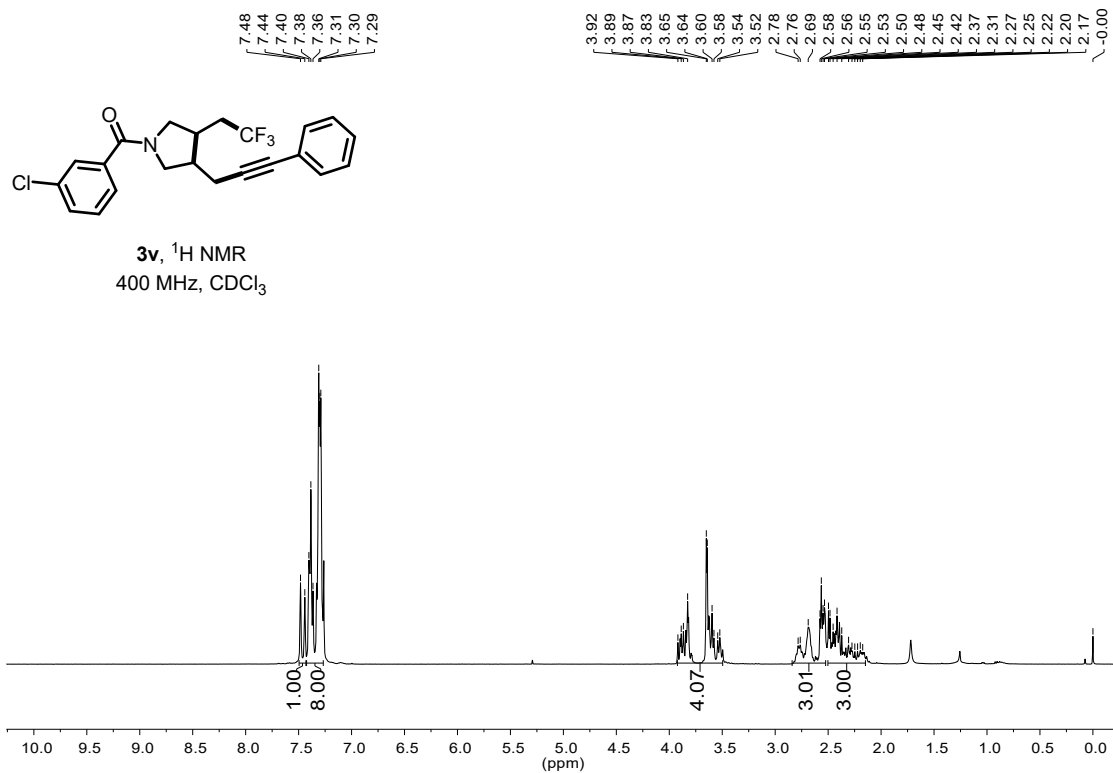


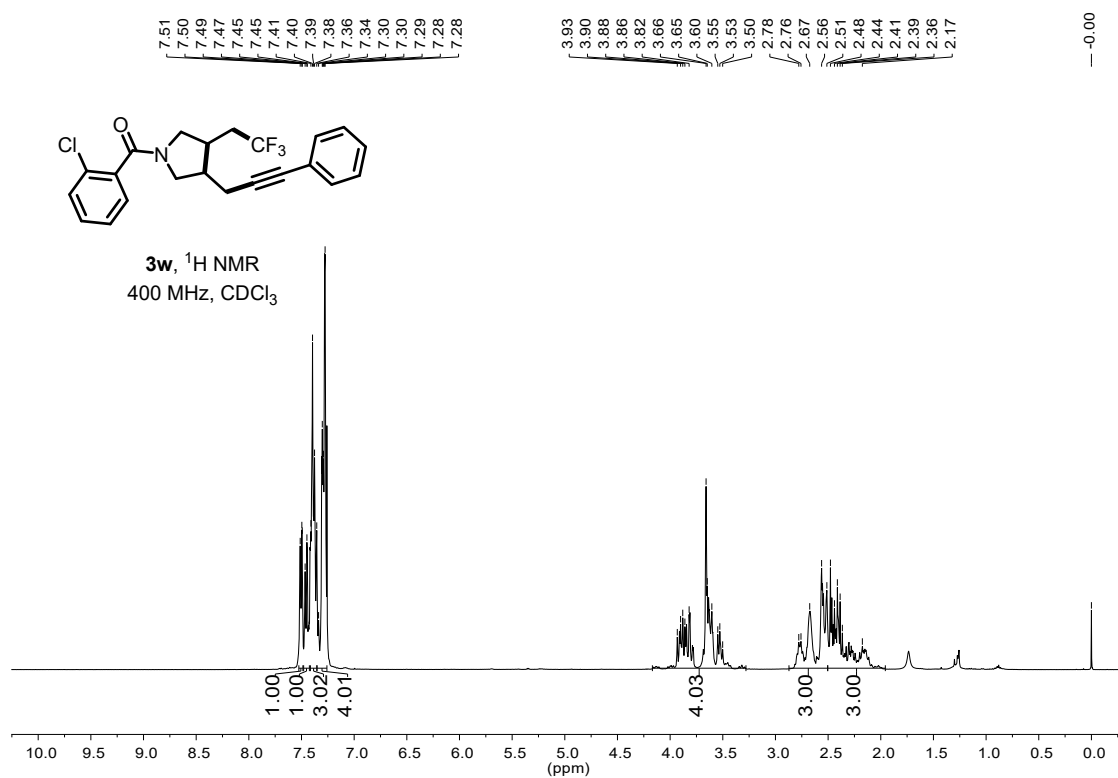
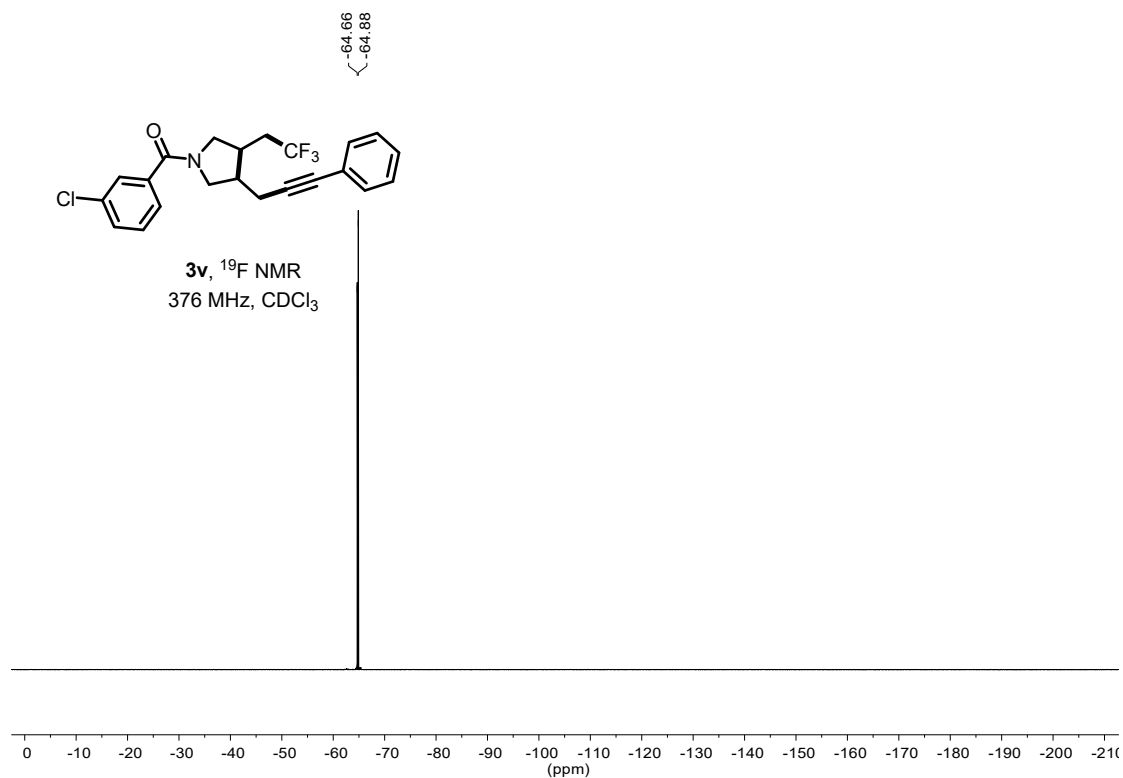


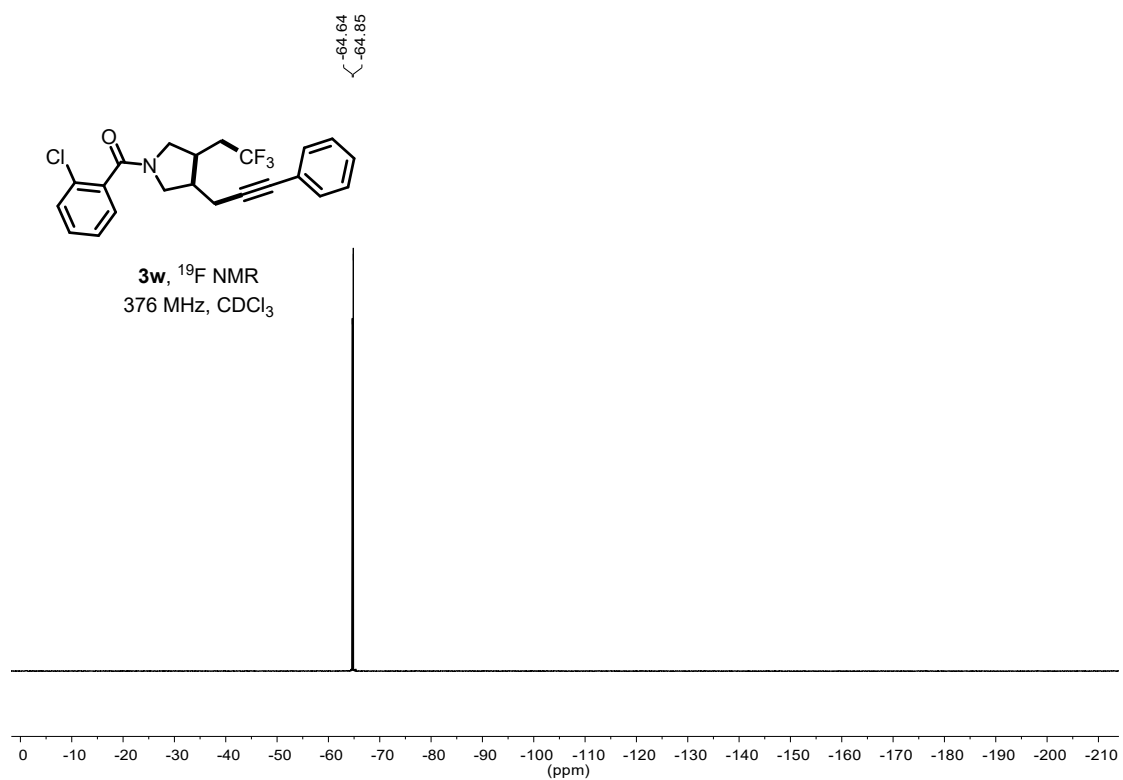
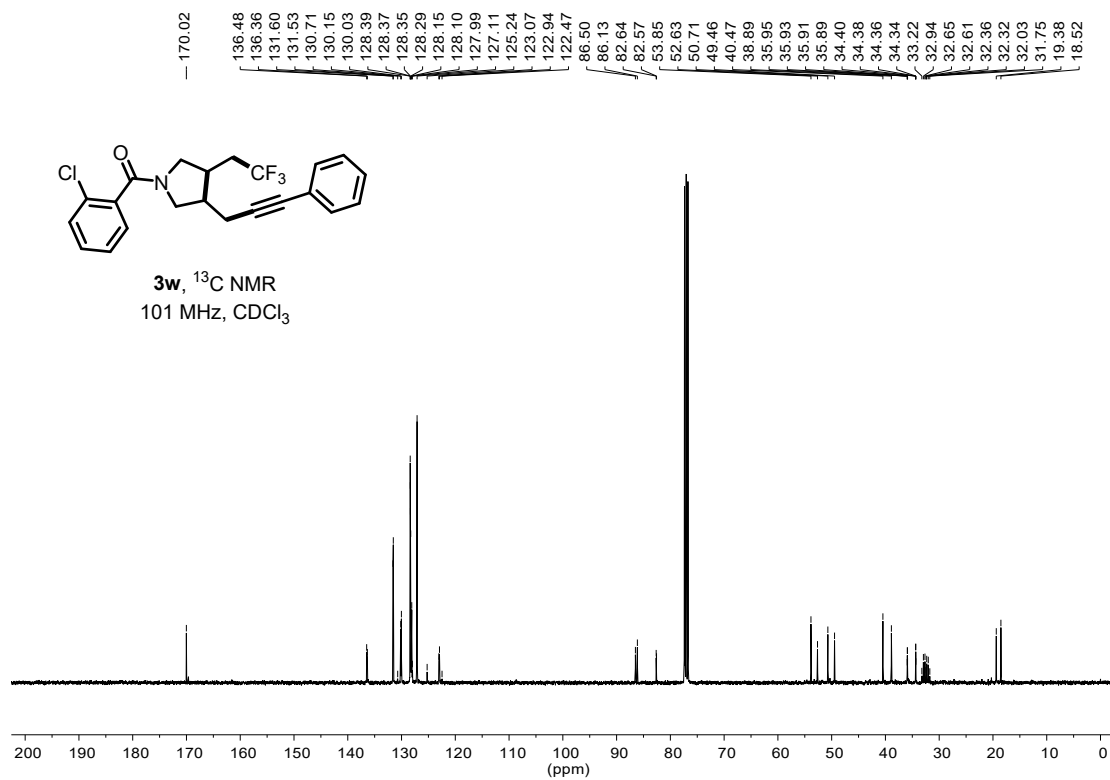


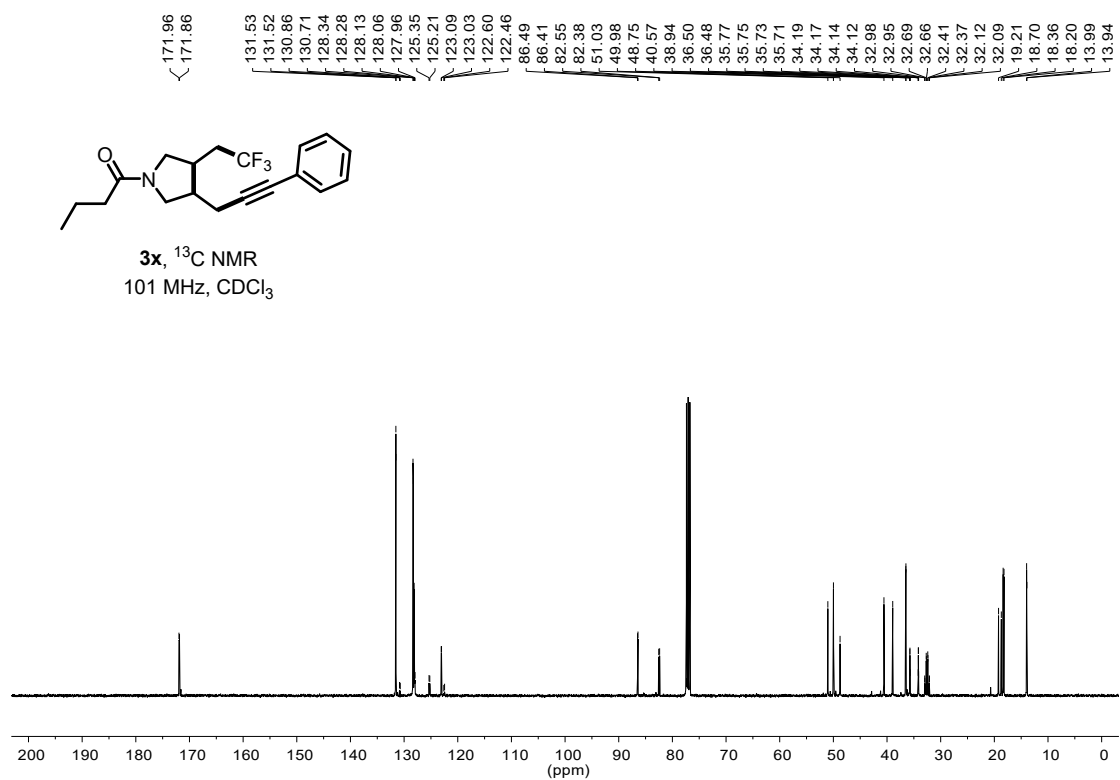
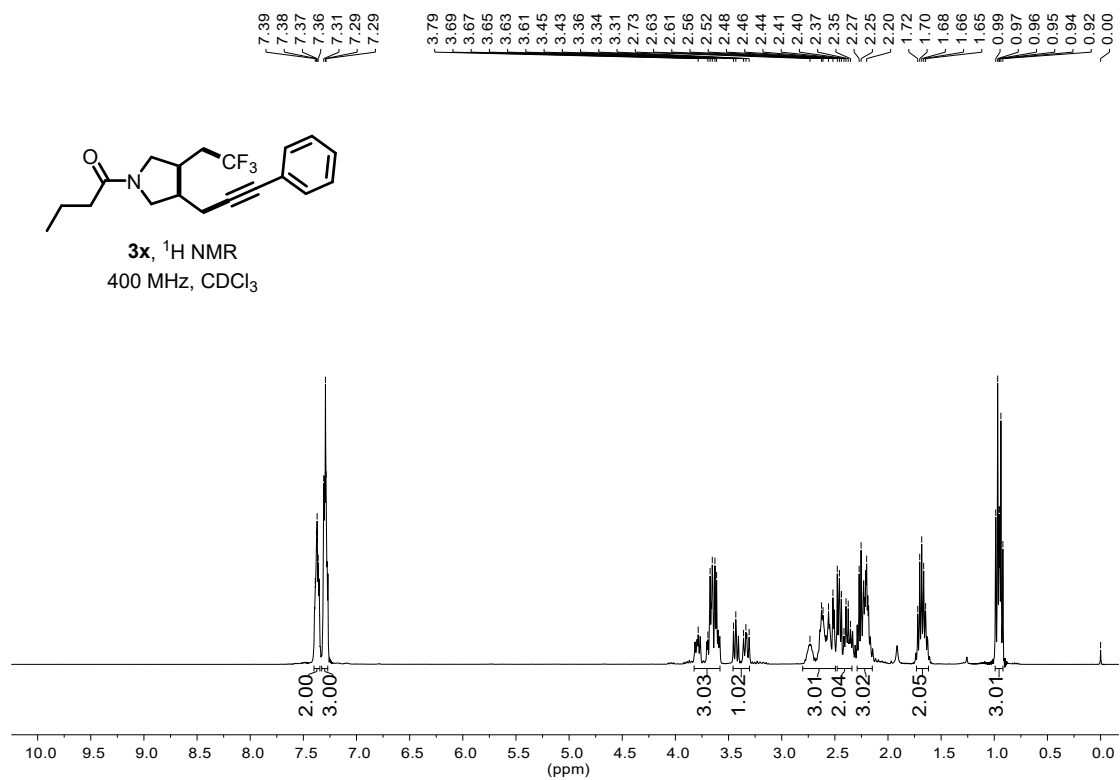


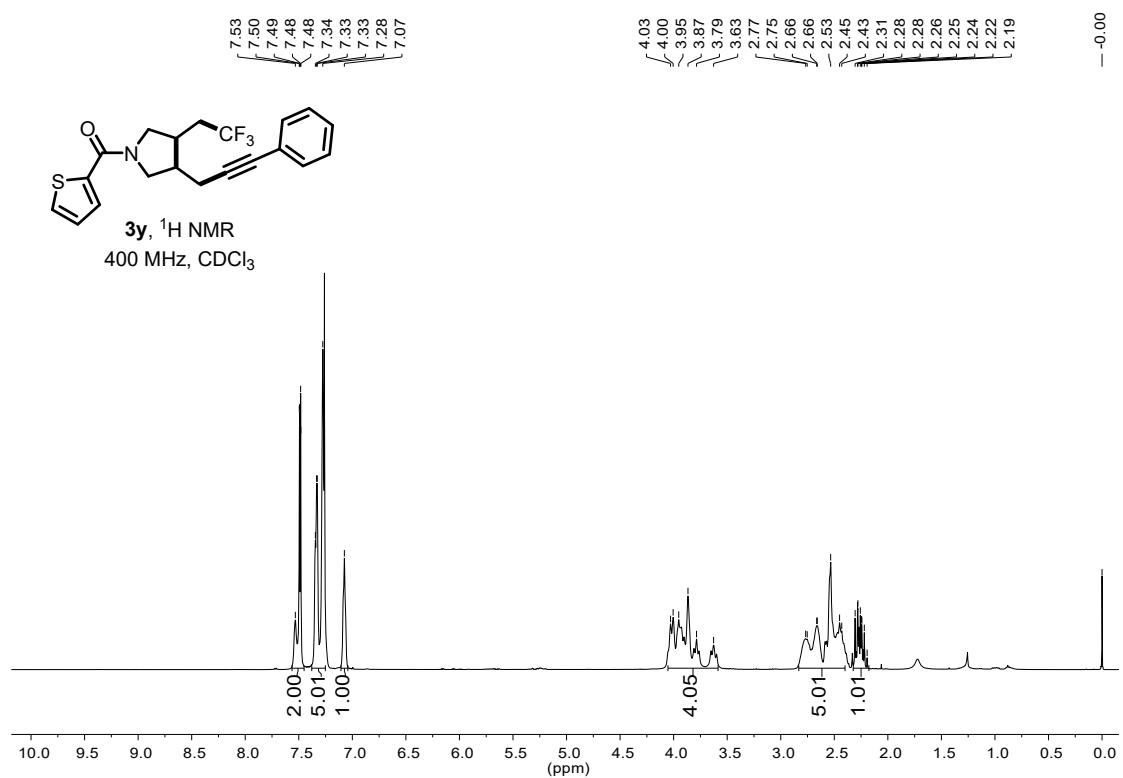
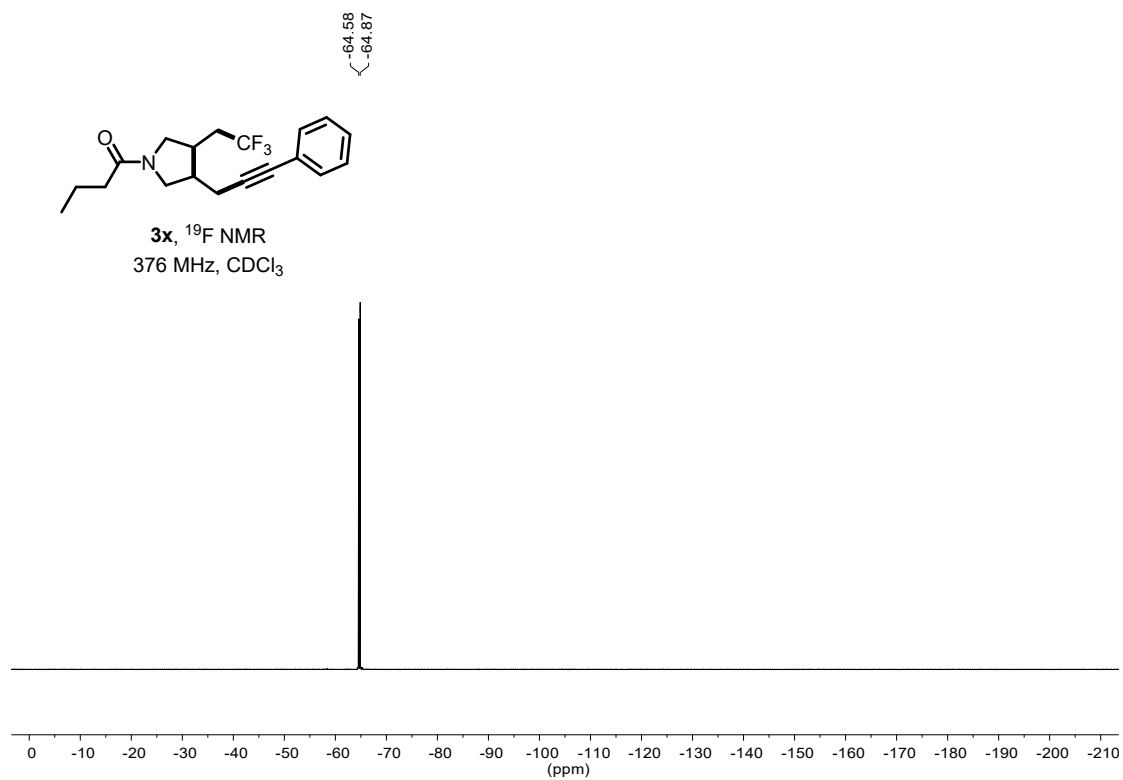


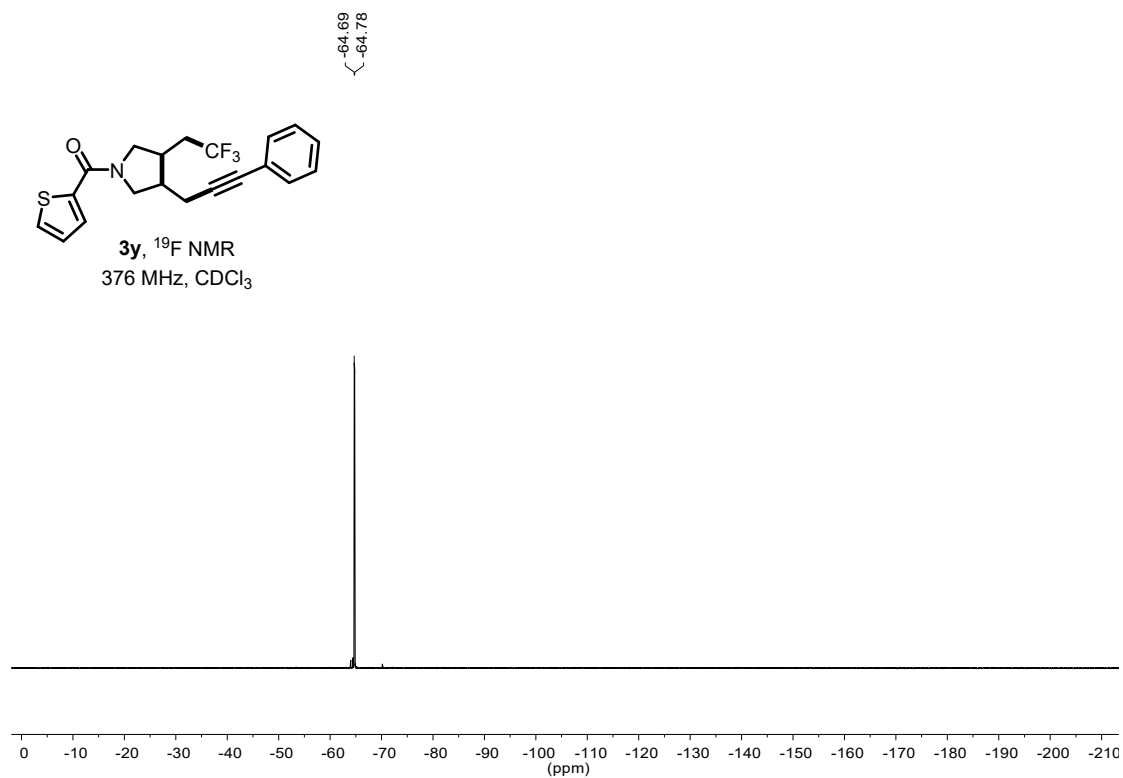
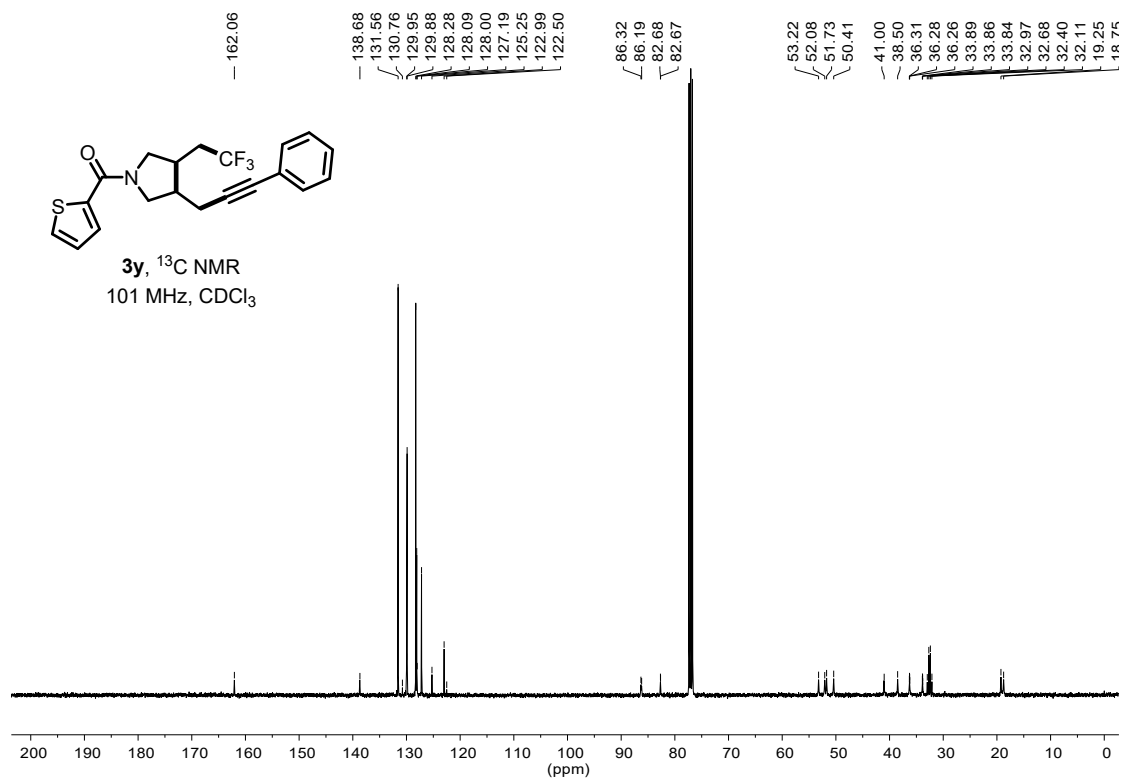


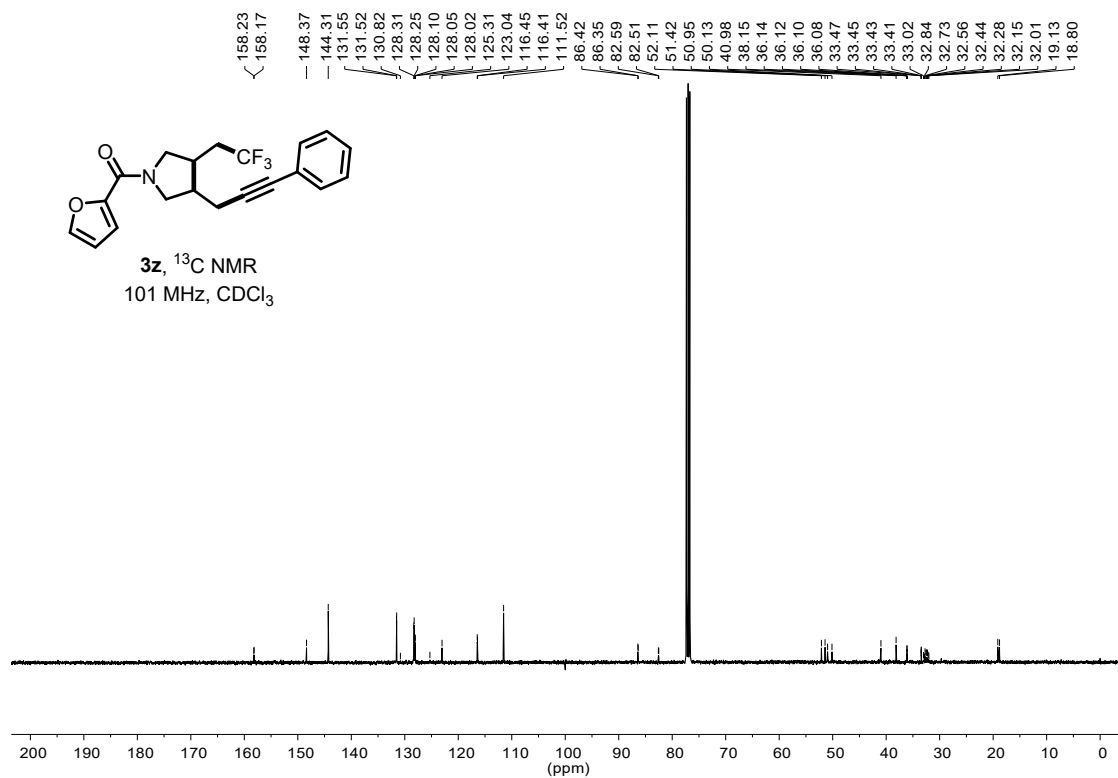
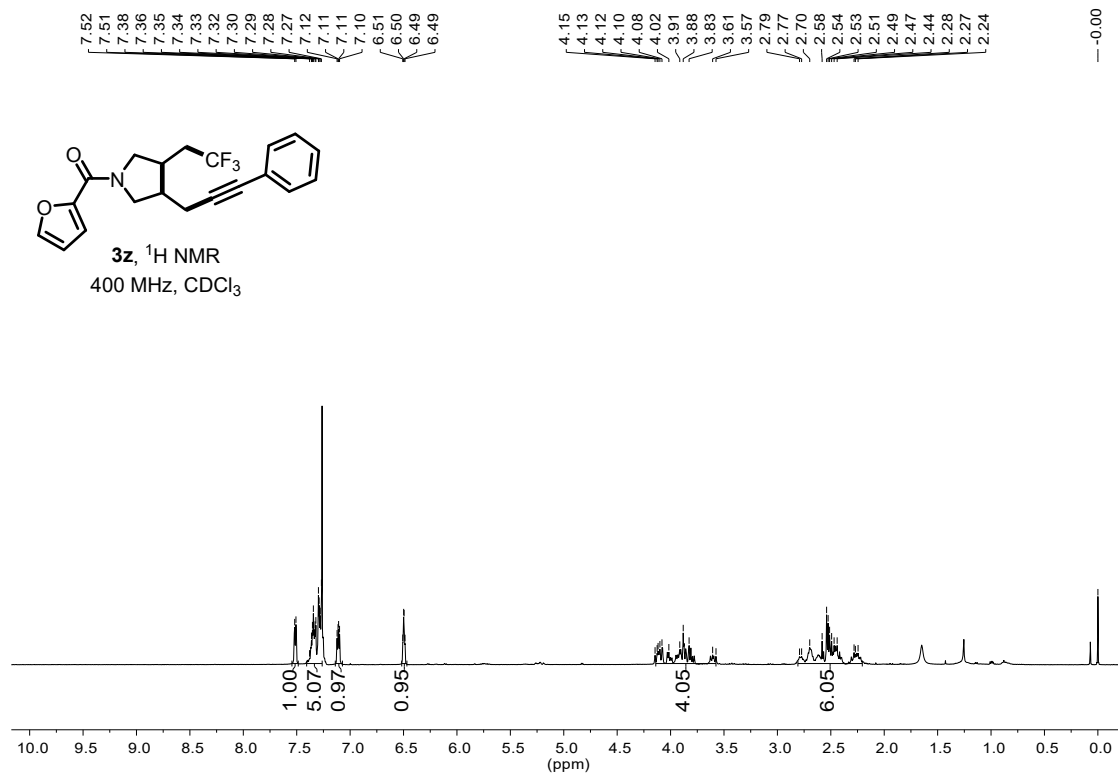


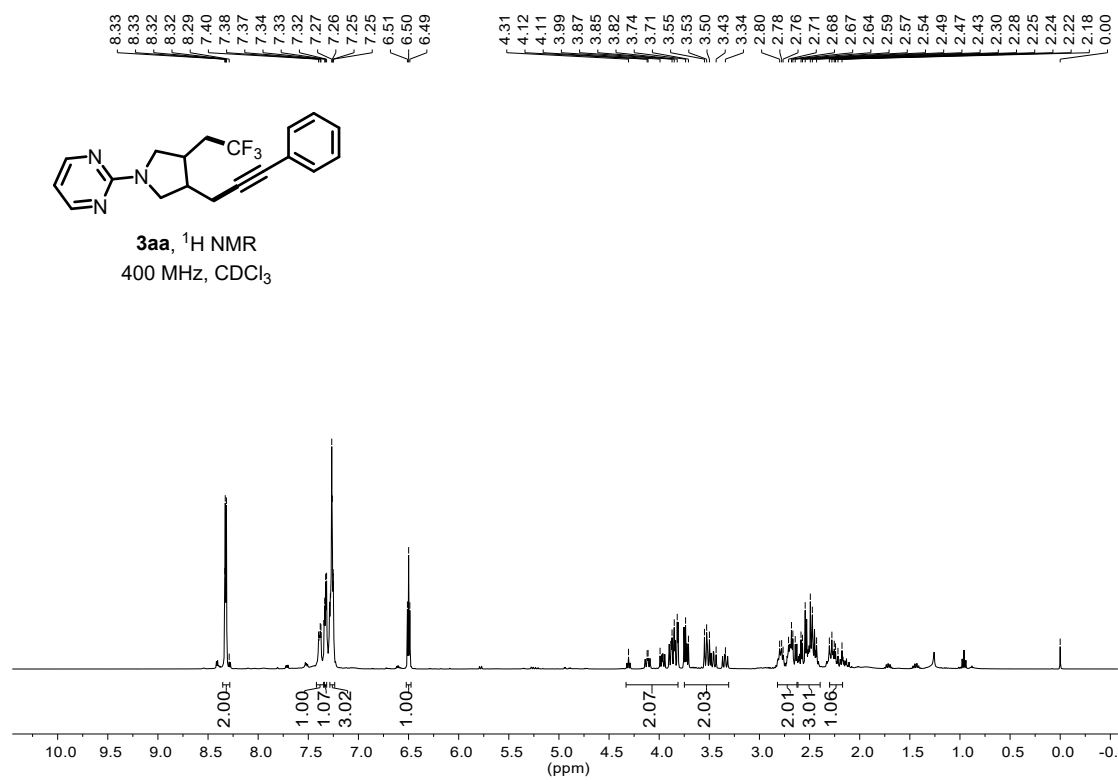
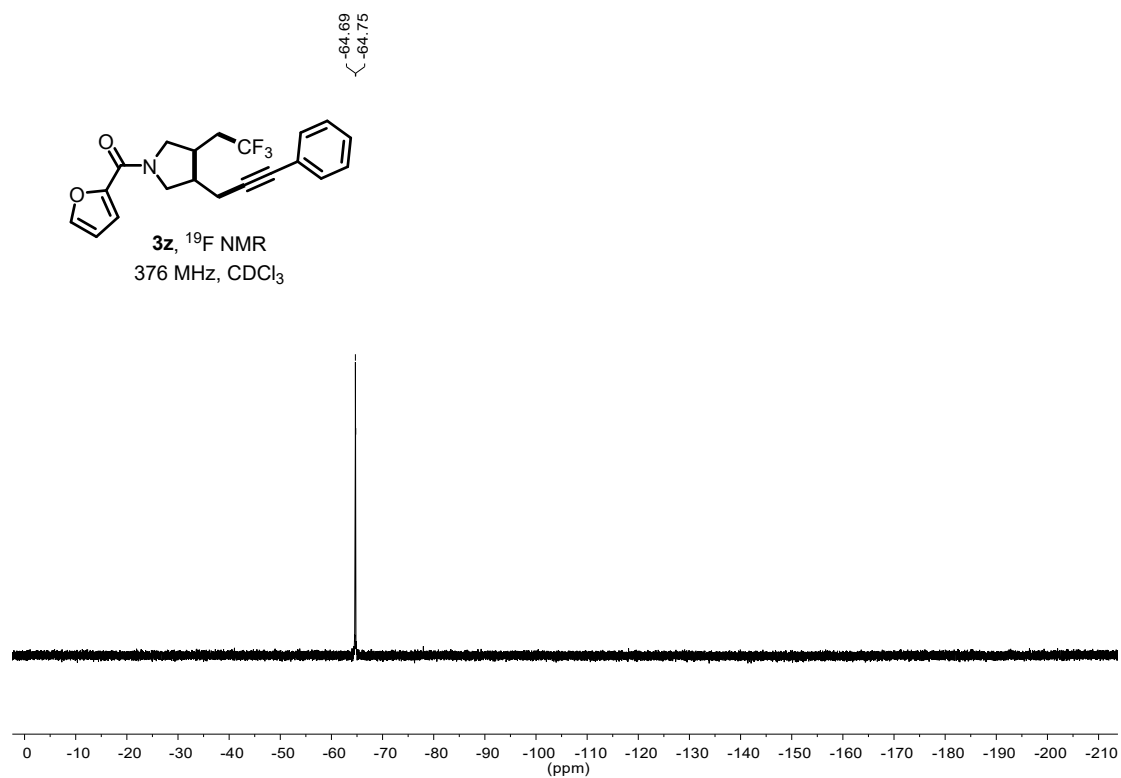


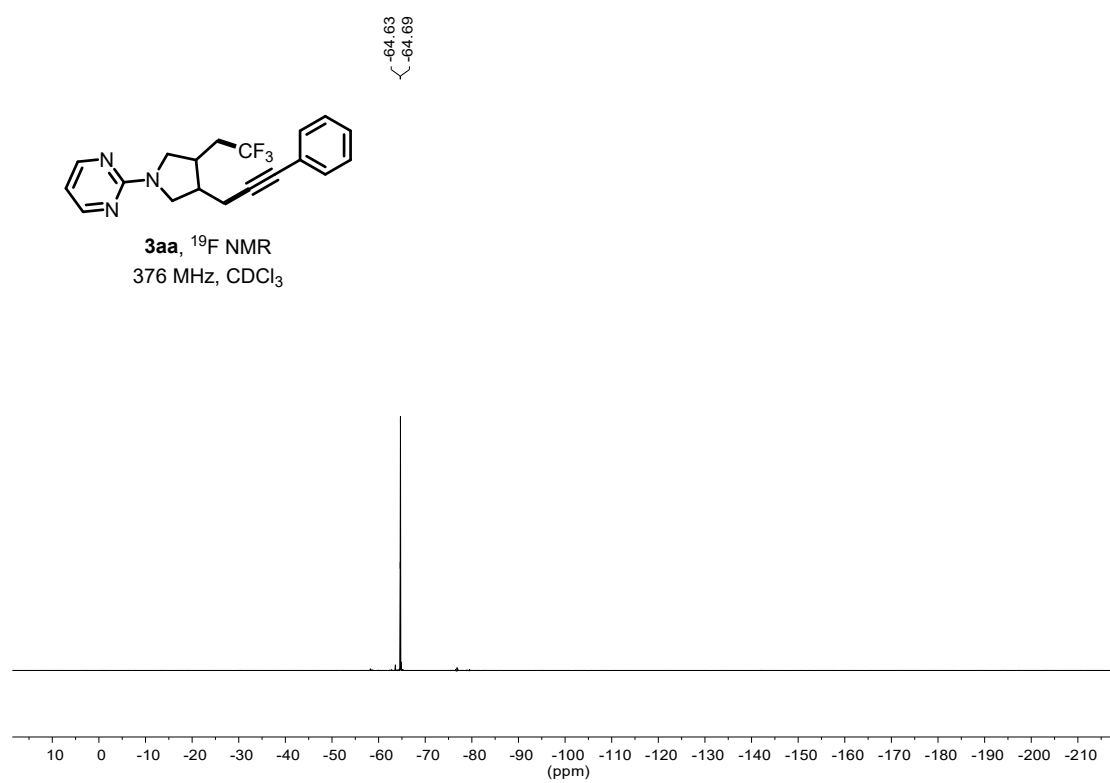
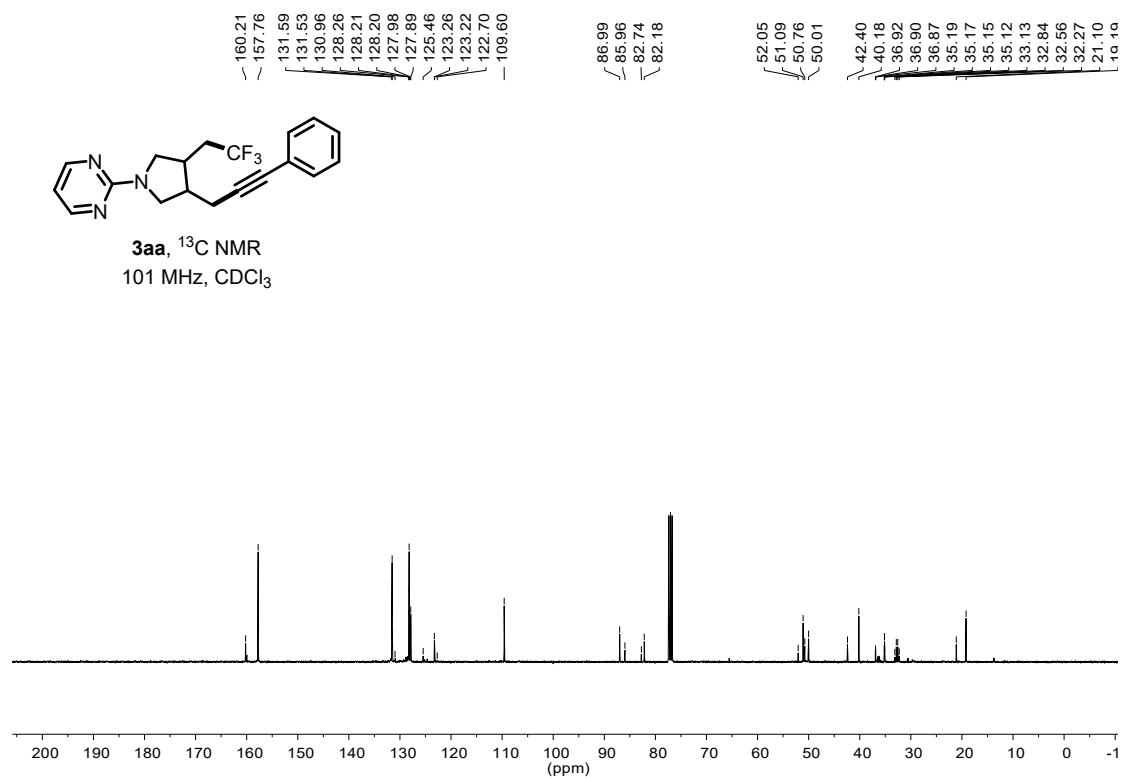


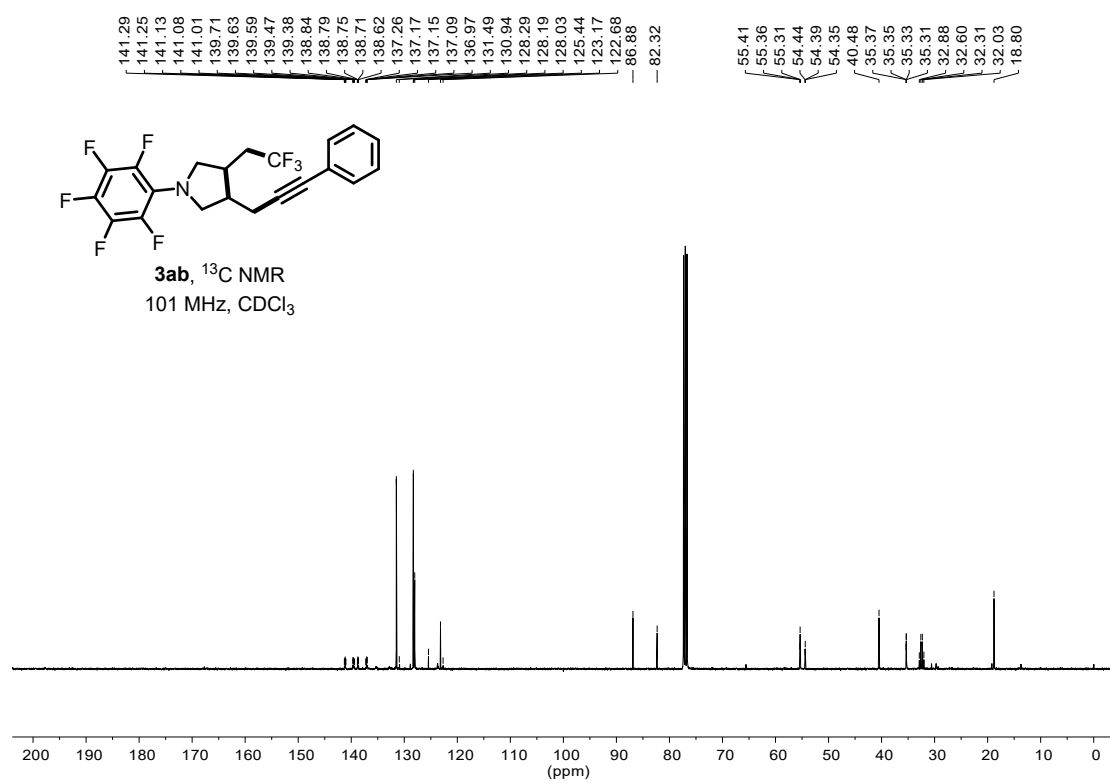
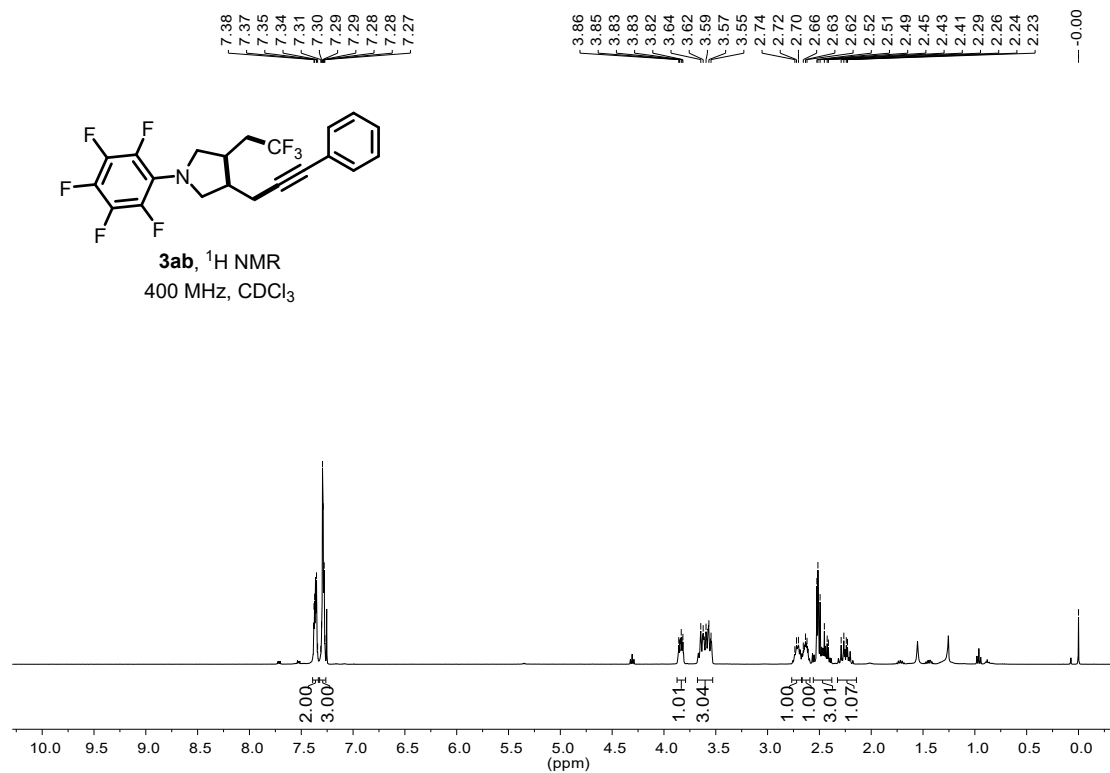


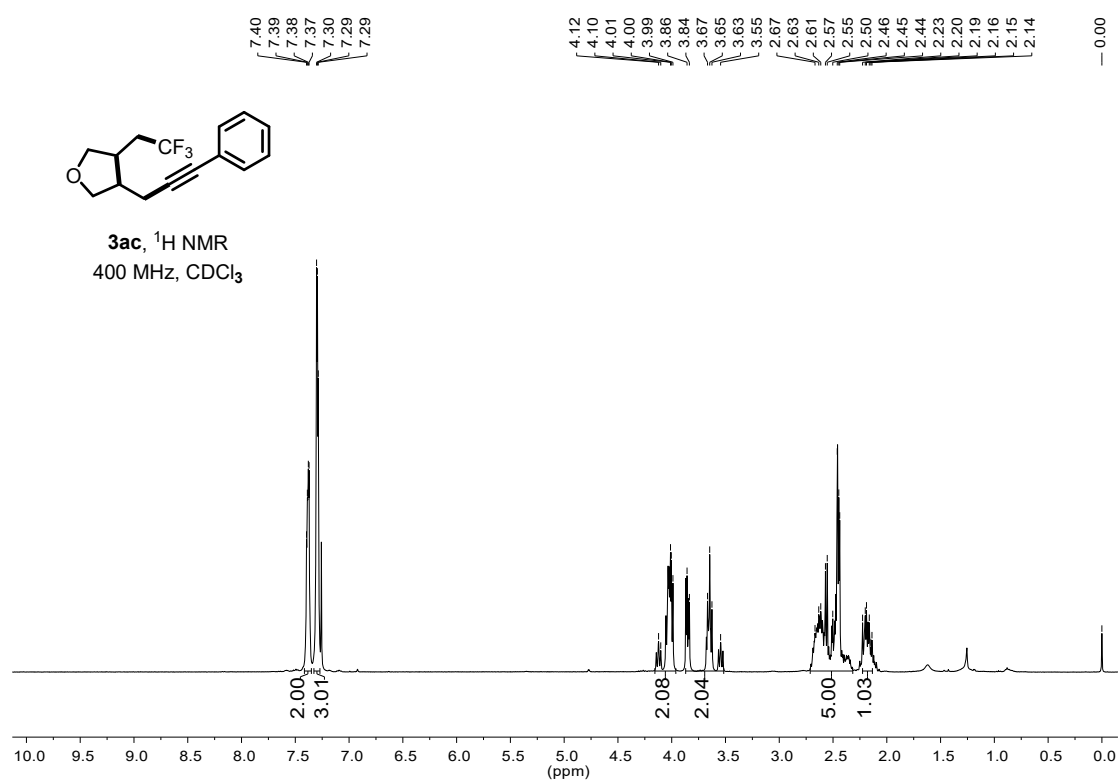
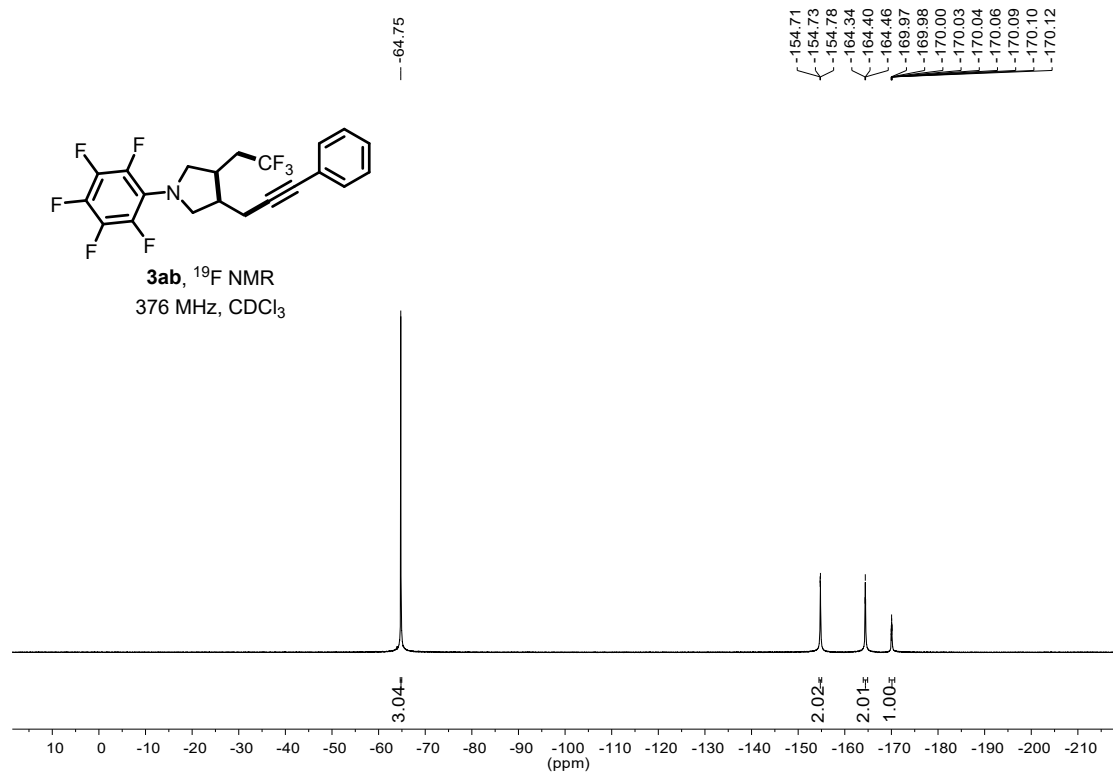


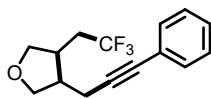




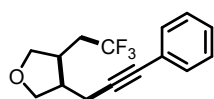
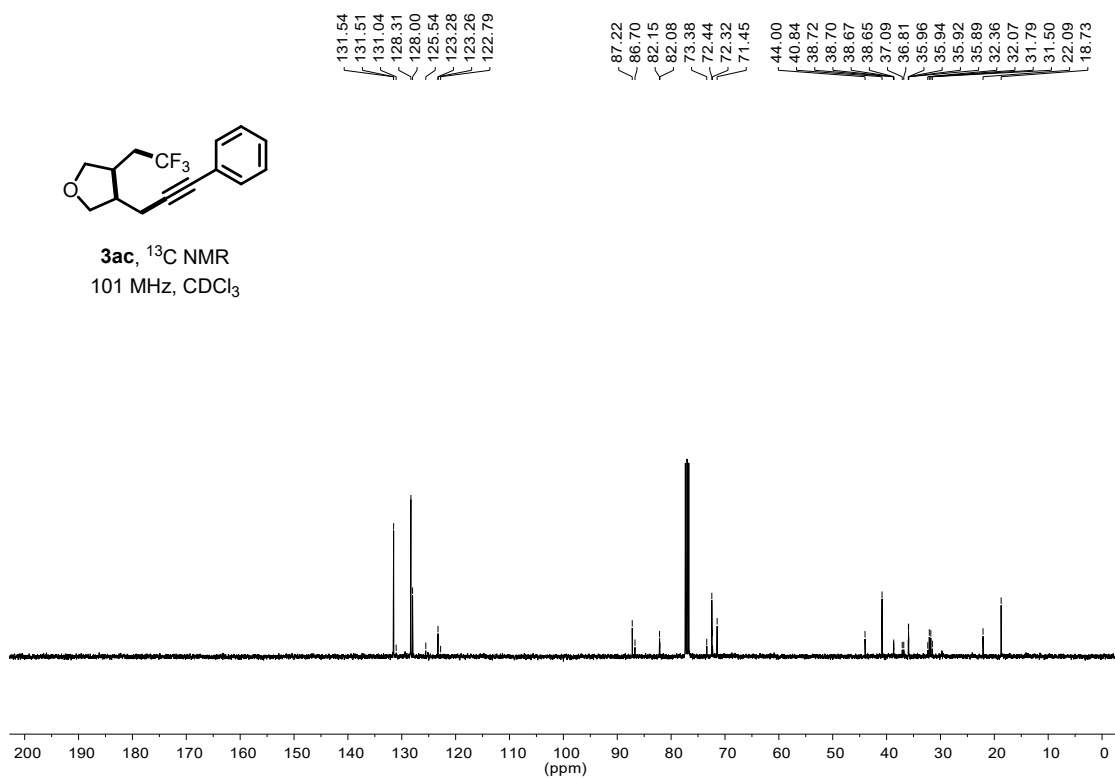




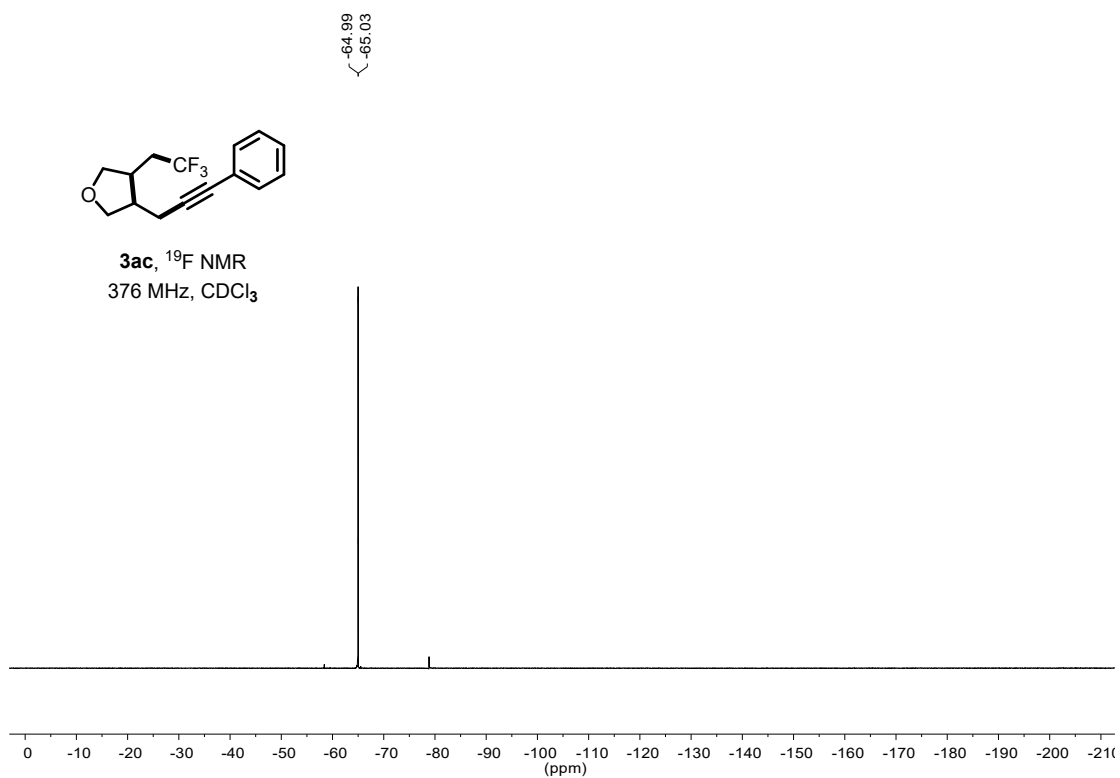


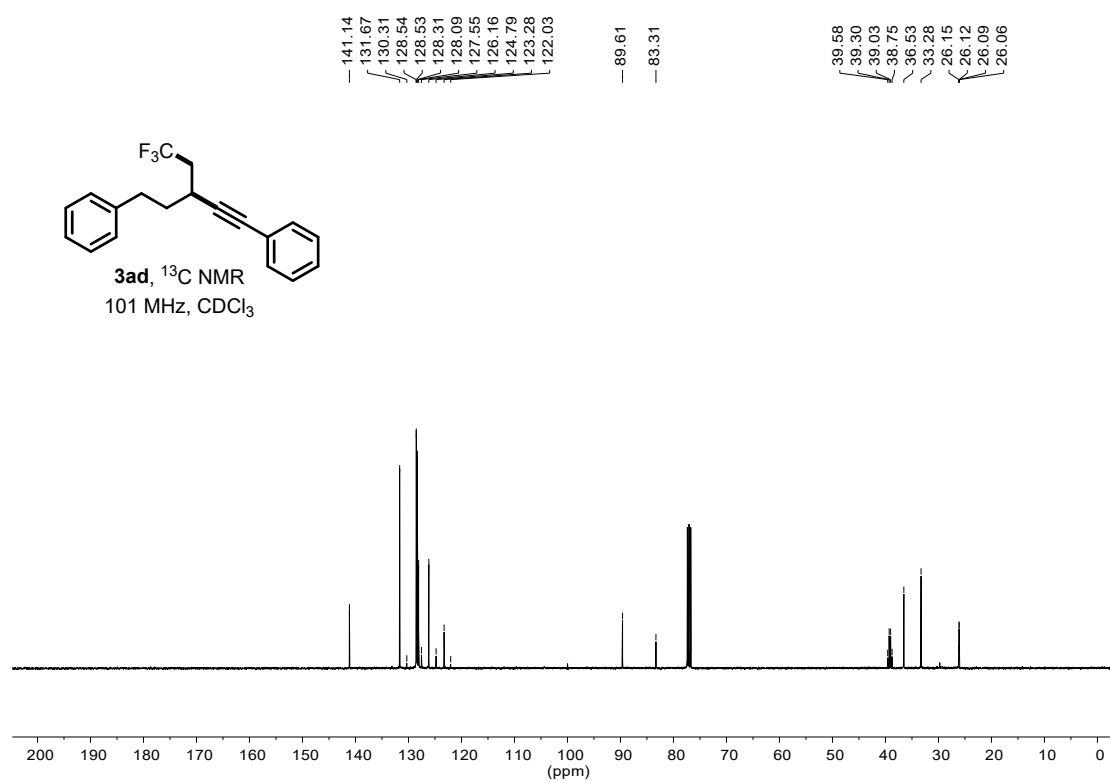
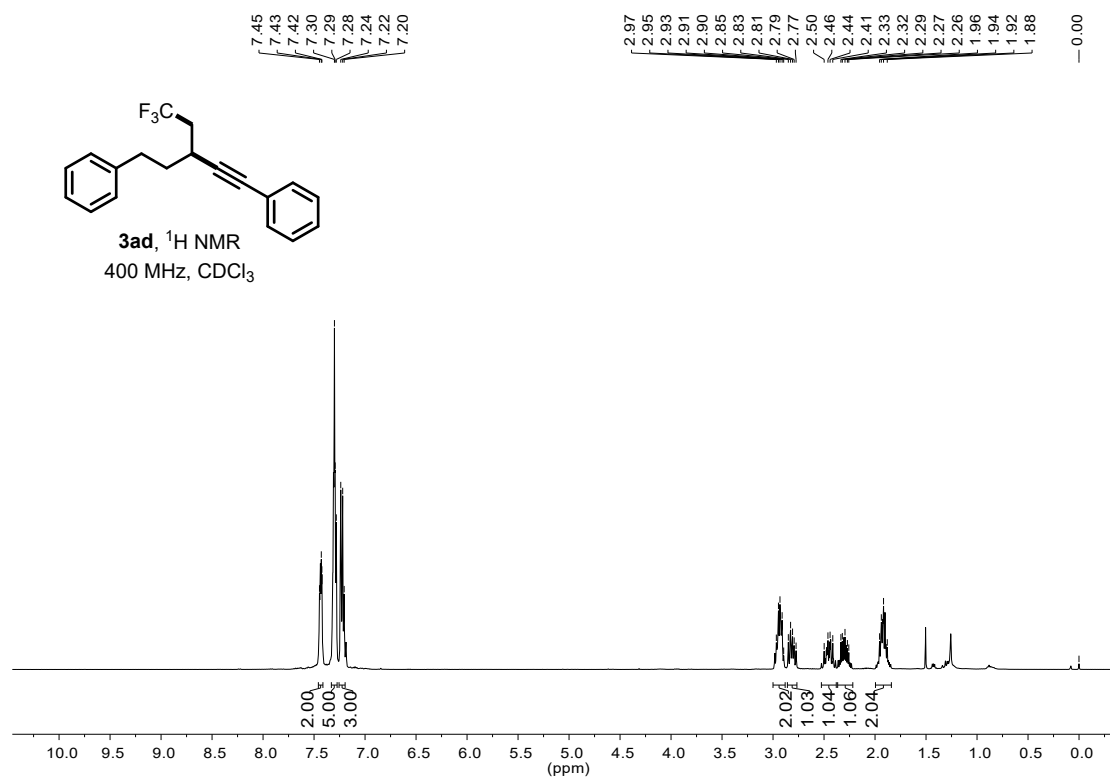


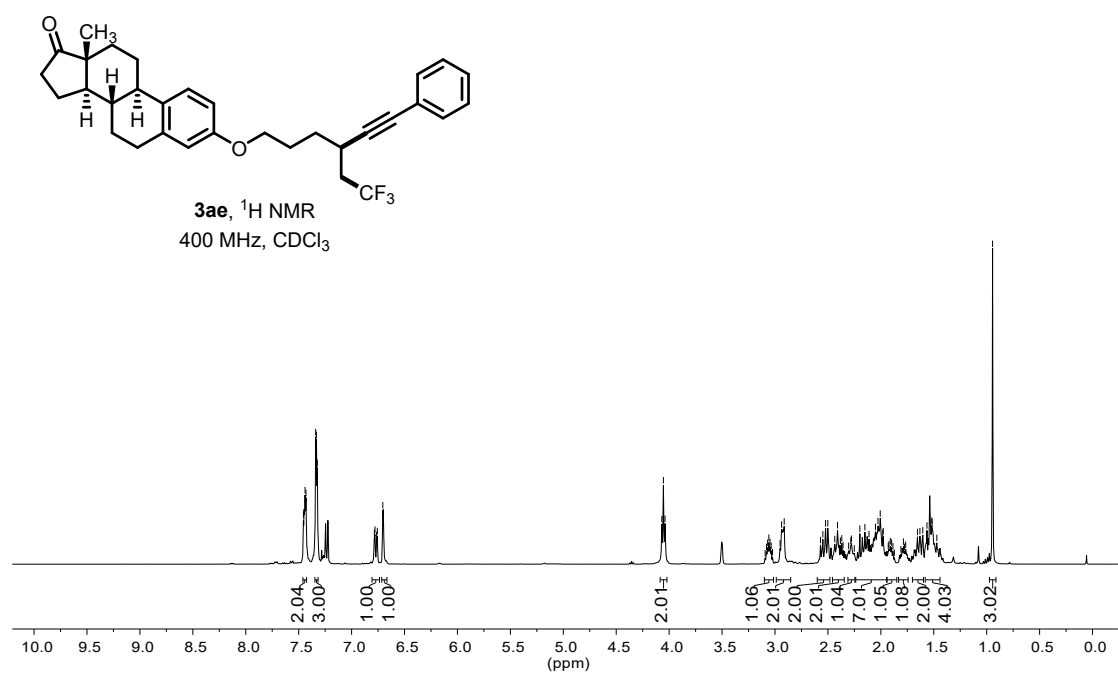
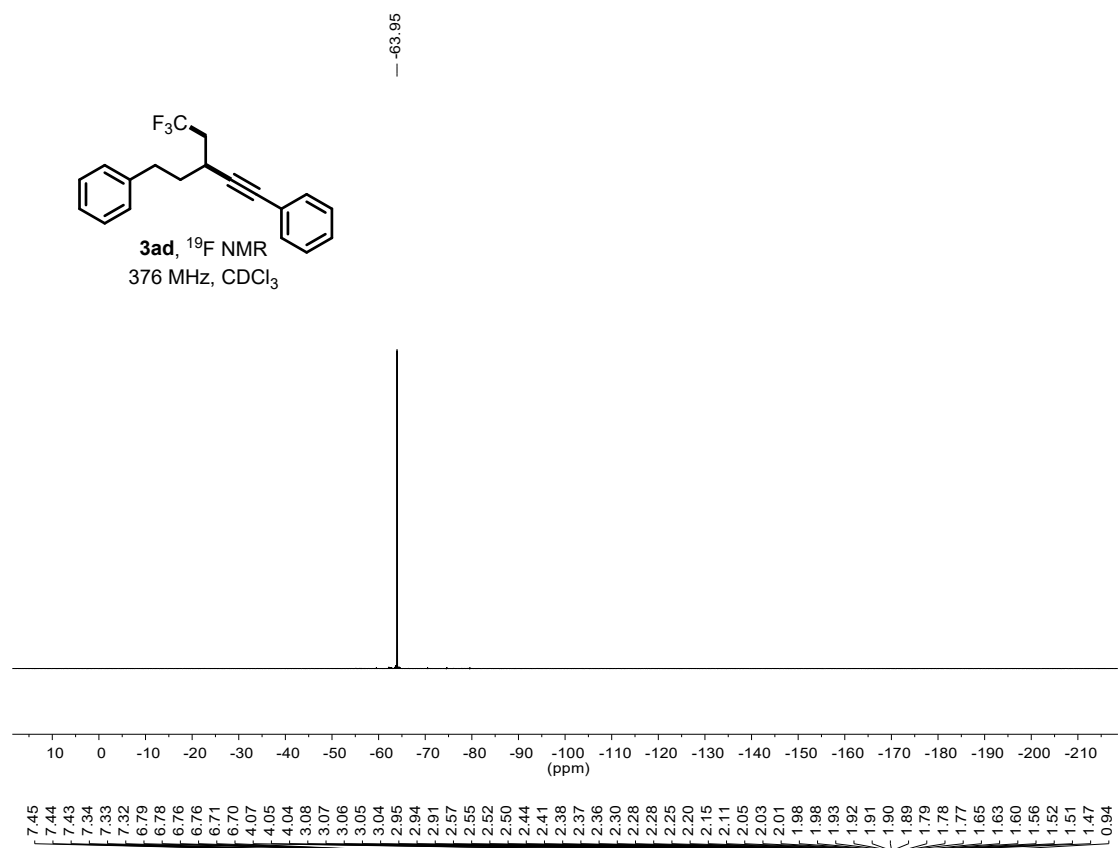
3ac, ^{13}C NMR
101 MHz, CDCl_3

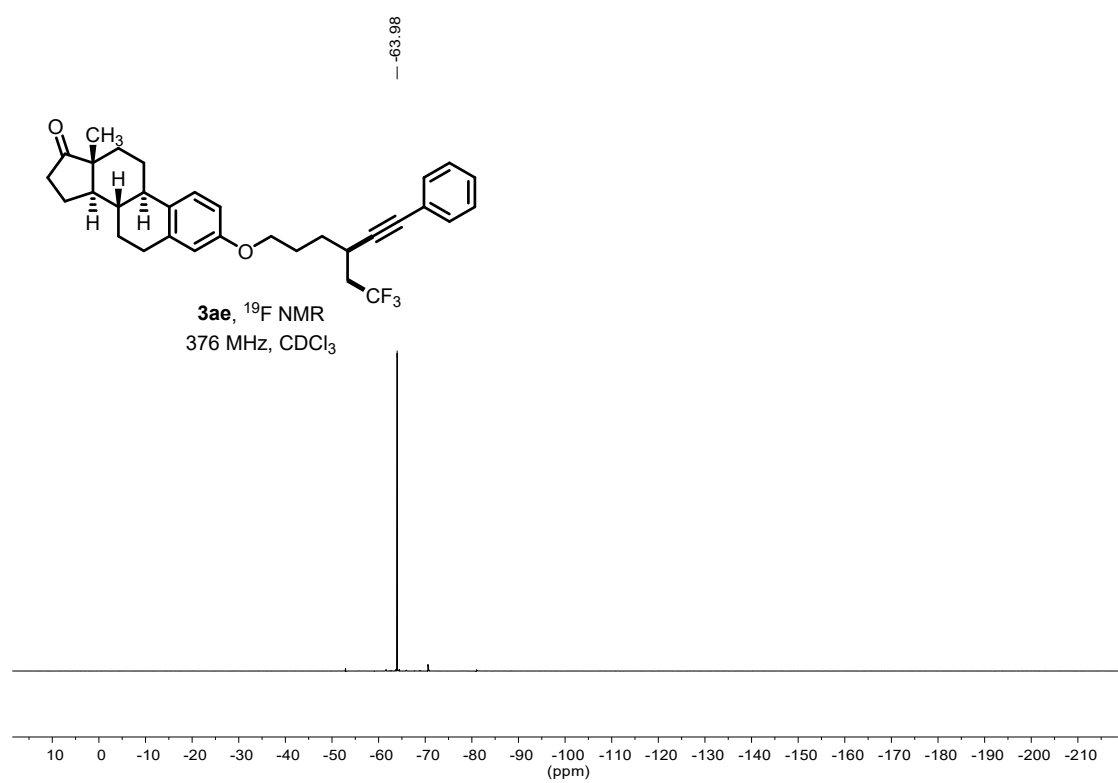
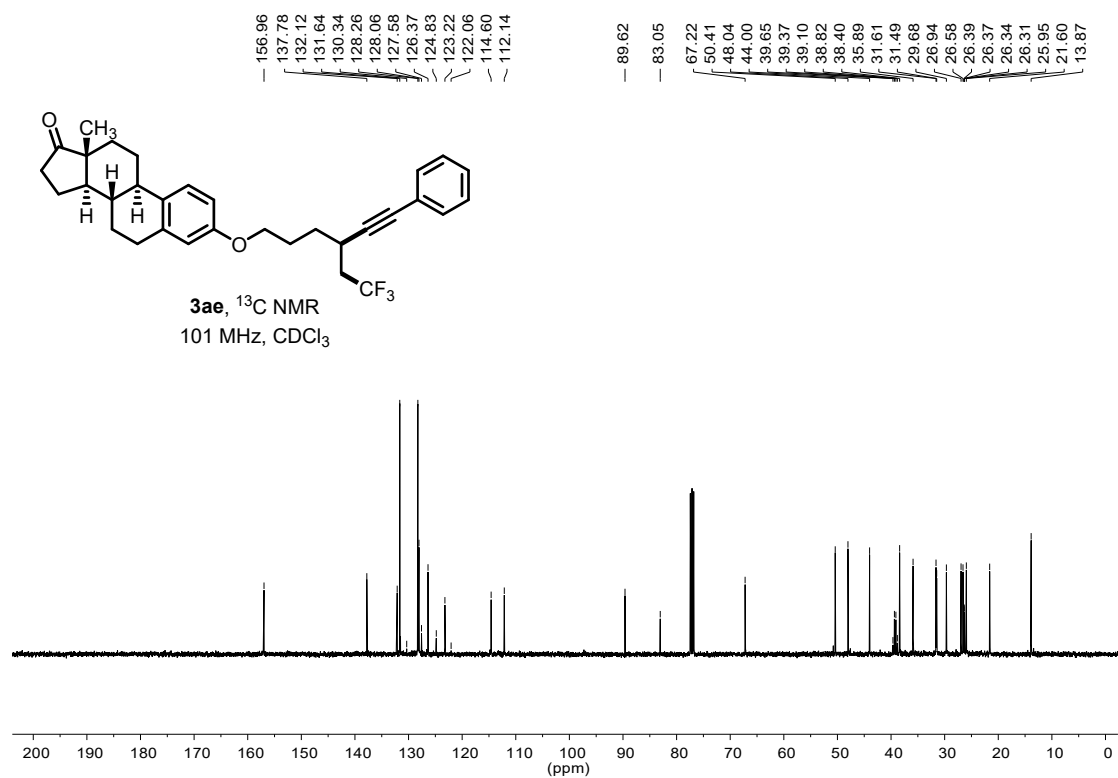


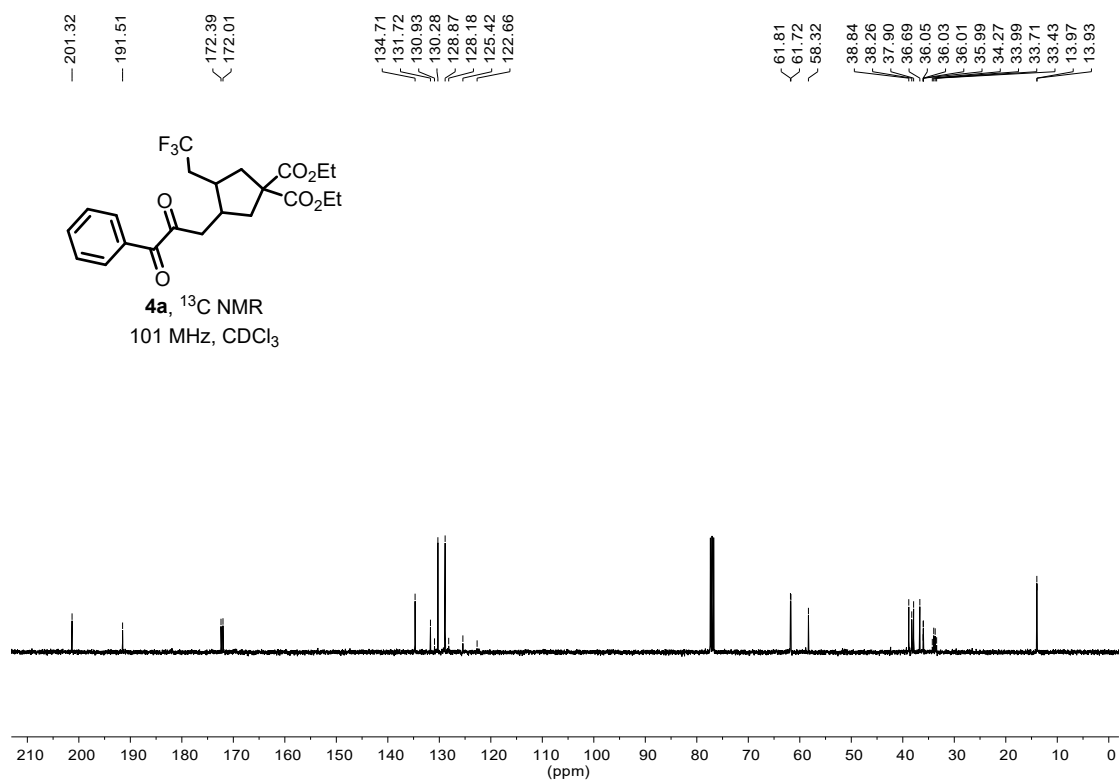
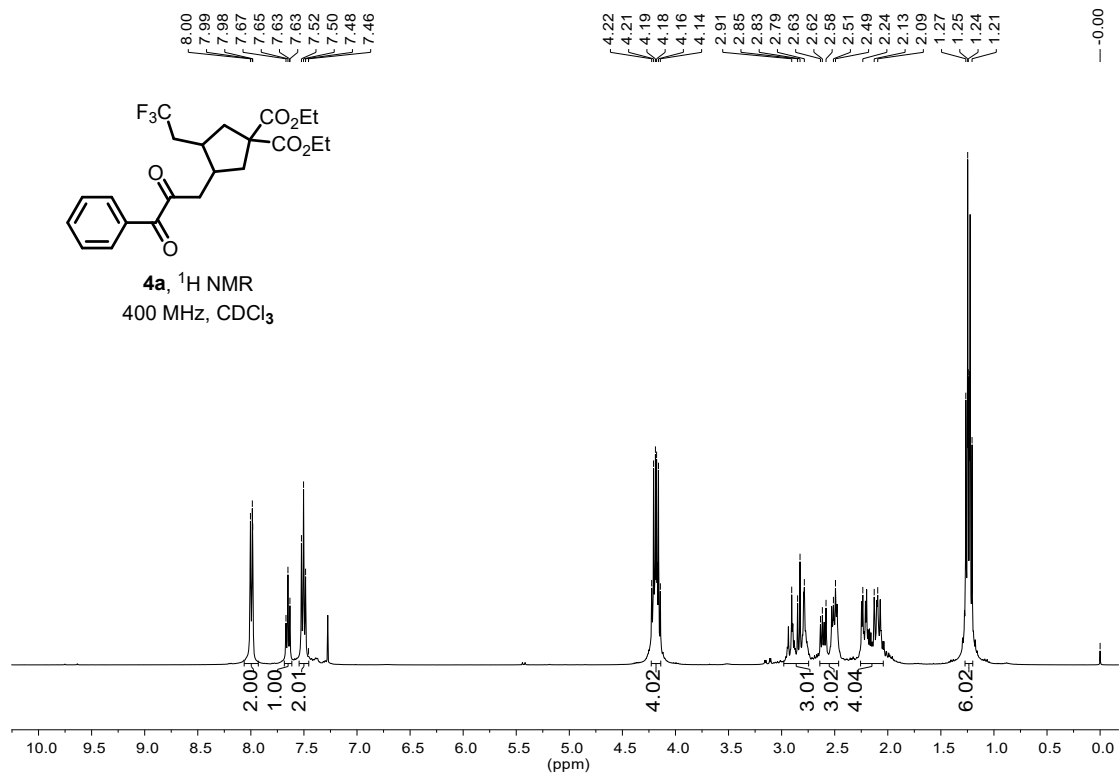
3ac, ^{19}F NMR
376 MHz, CDCl_3

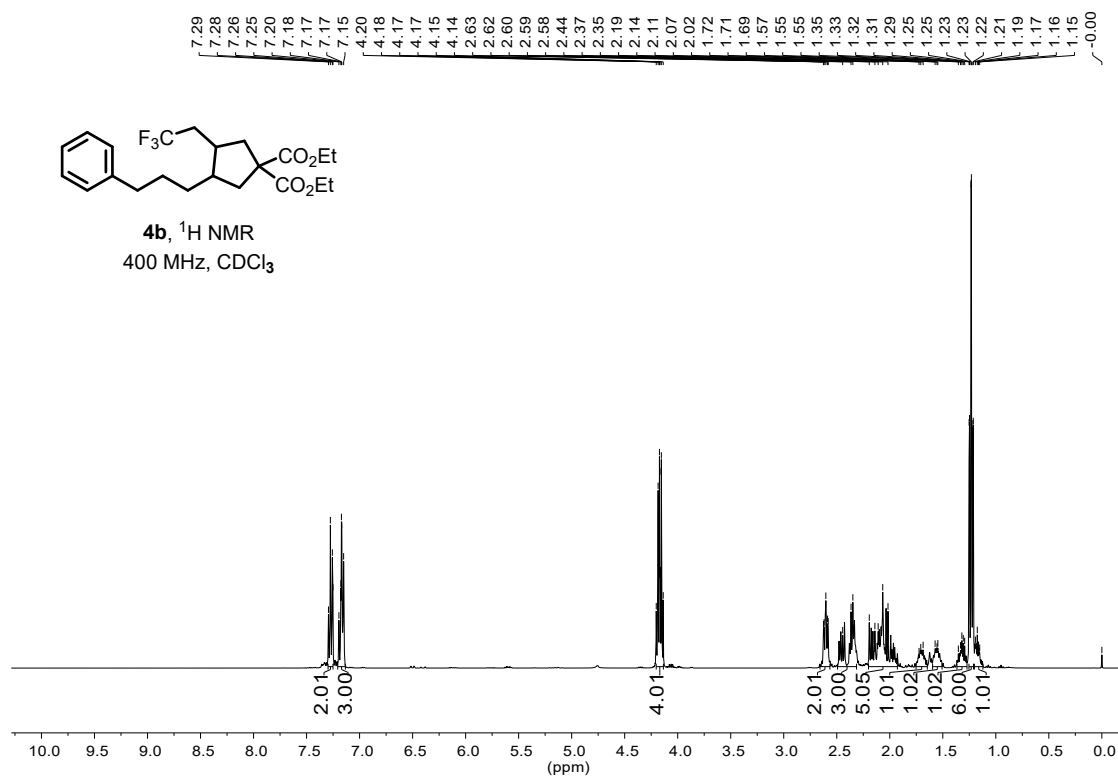
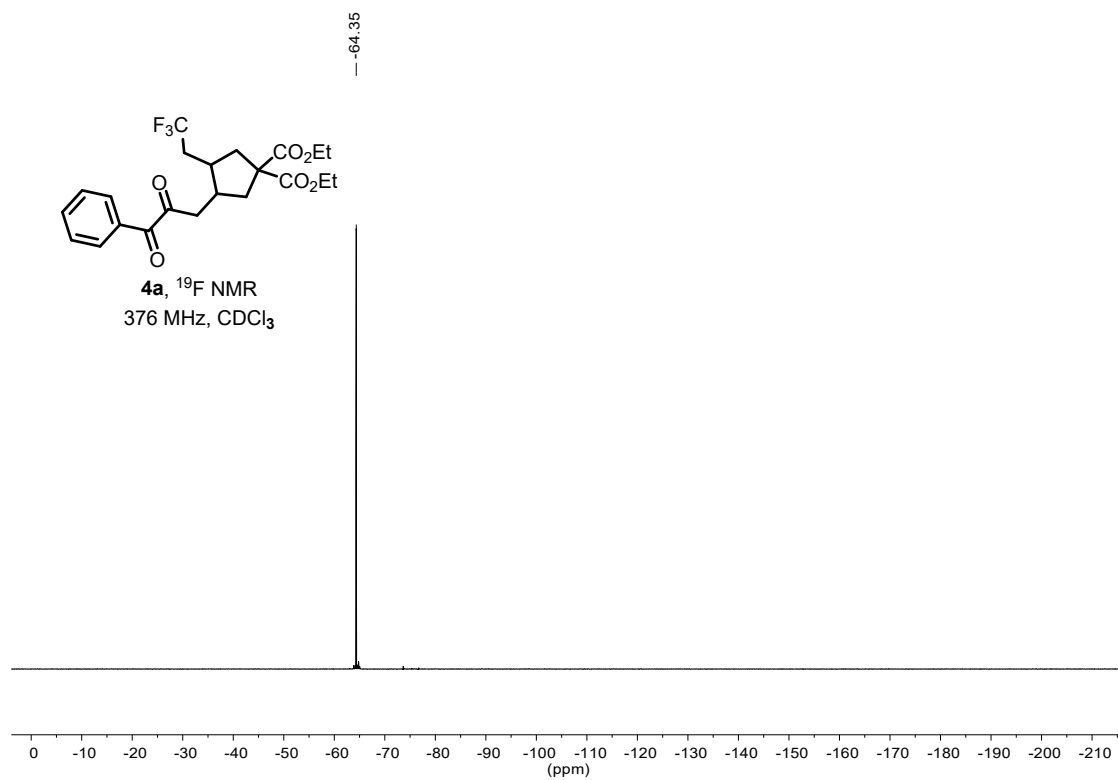


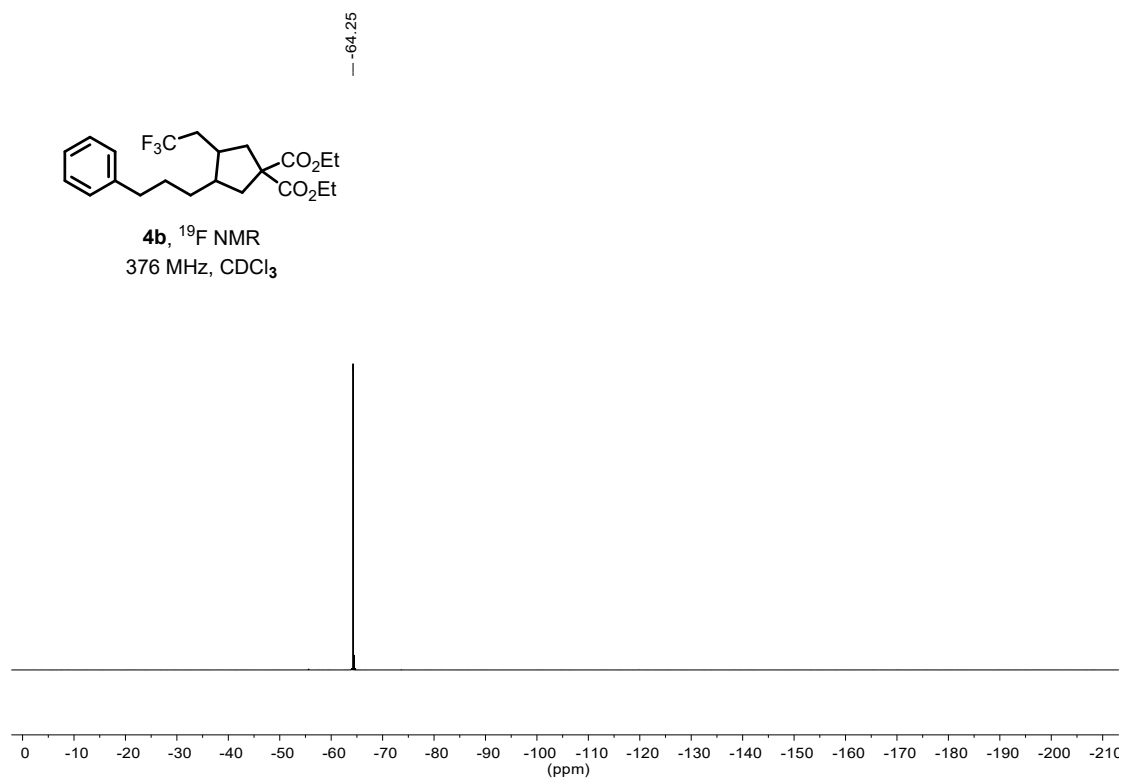
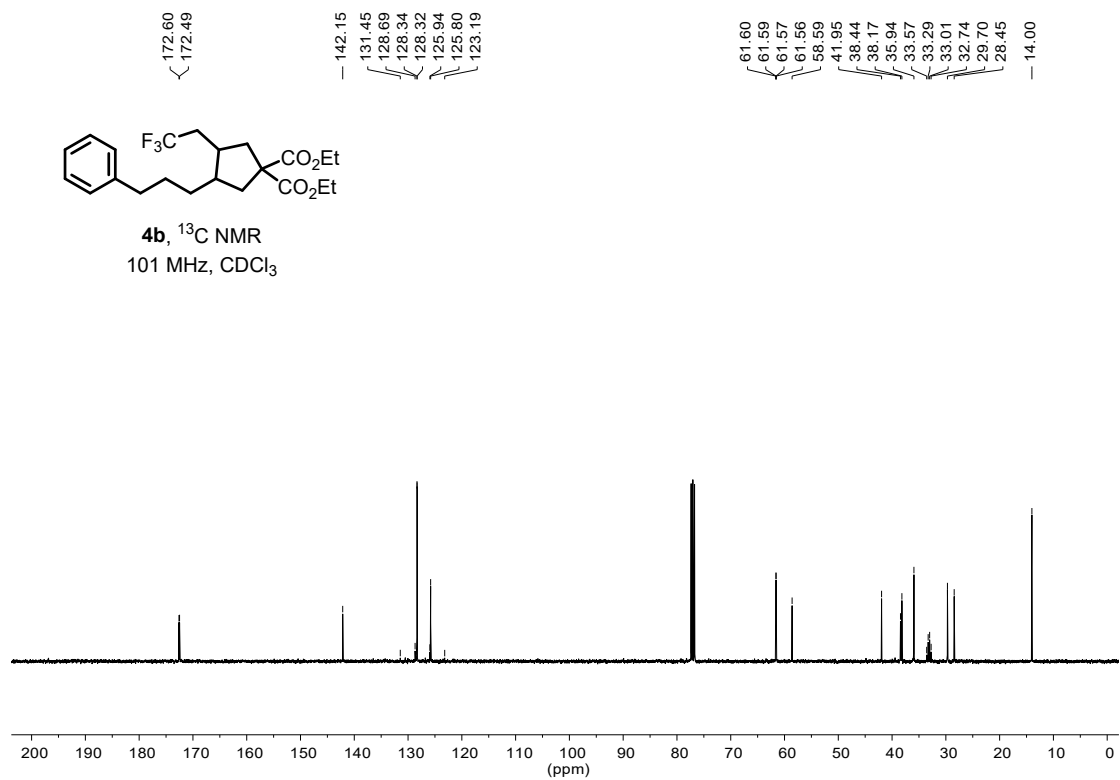


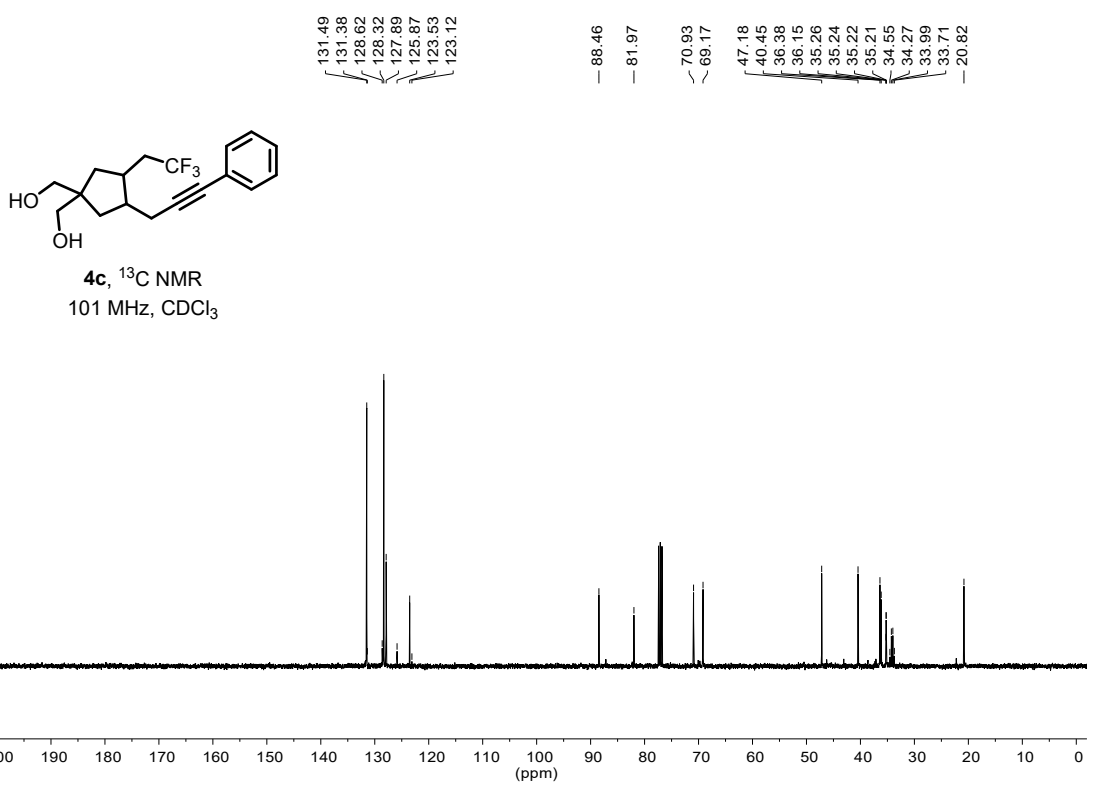
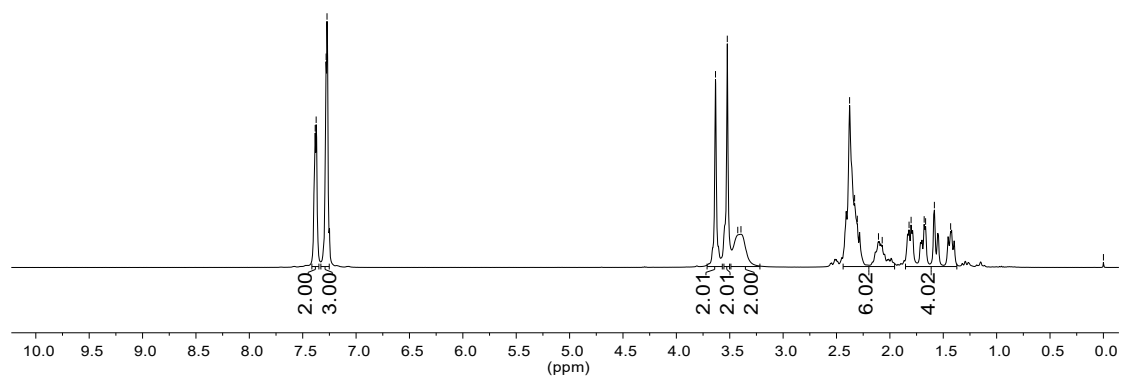


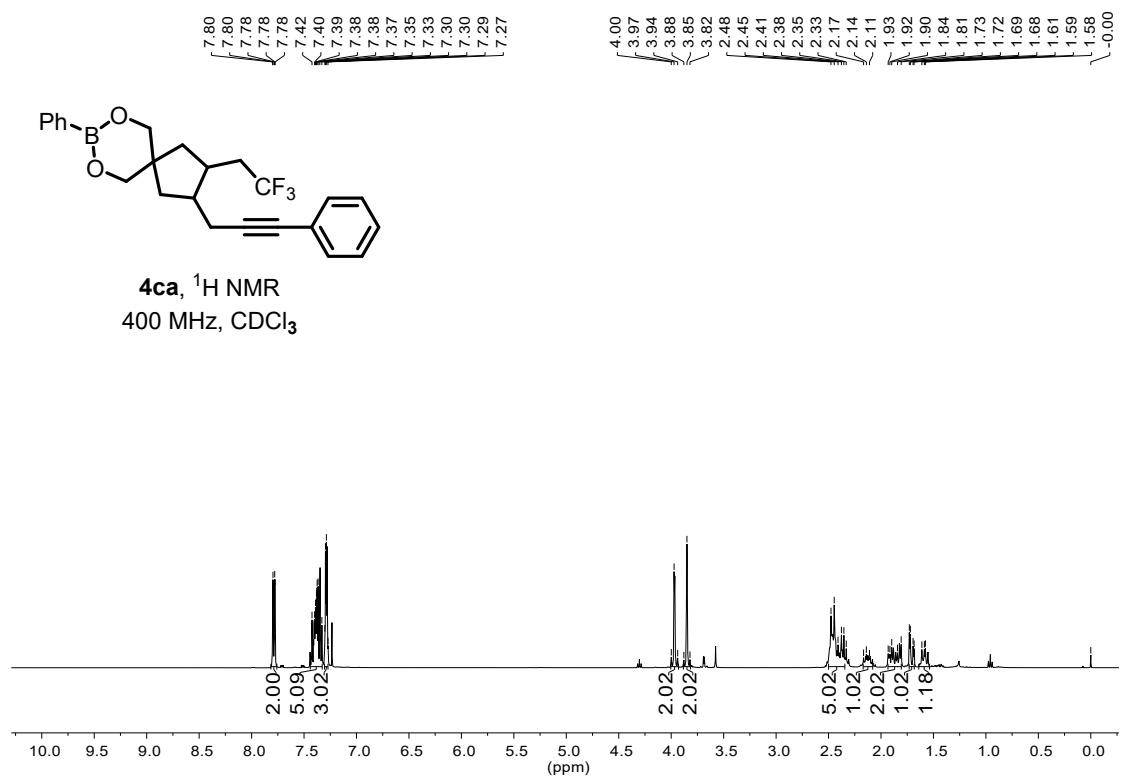
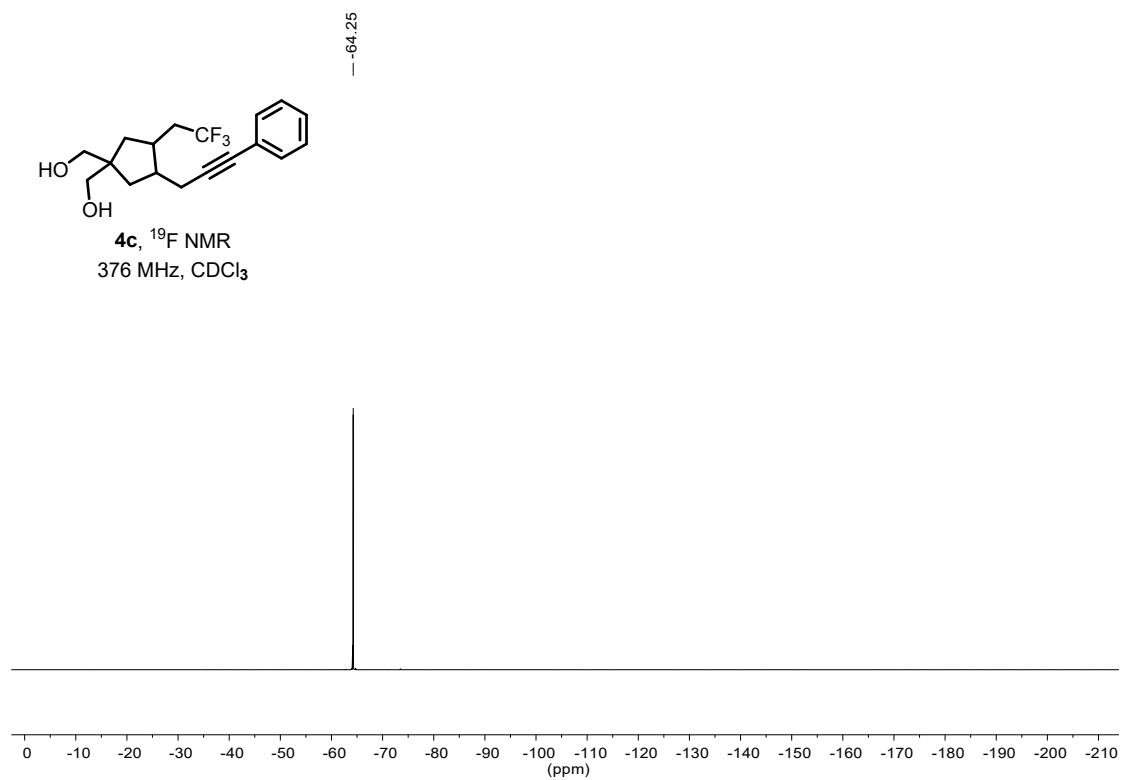


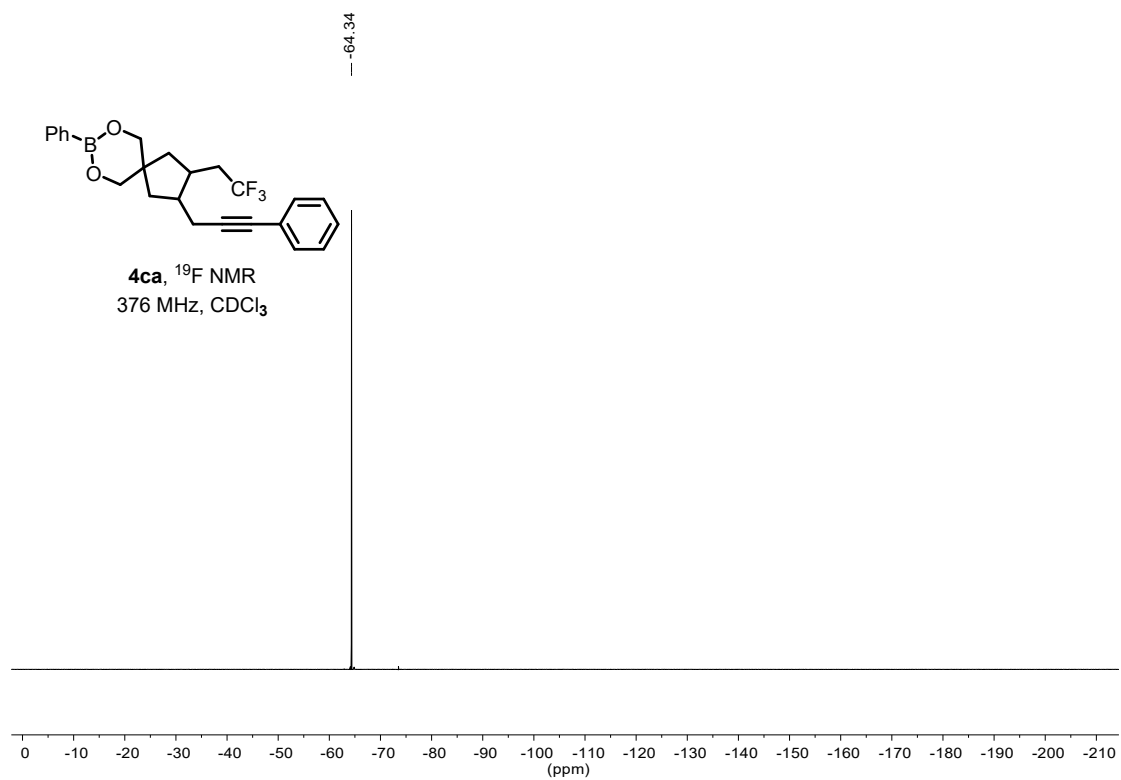
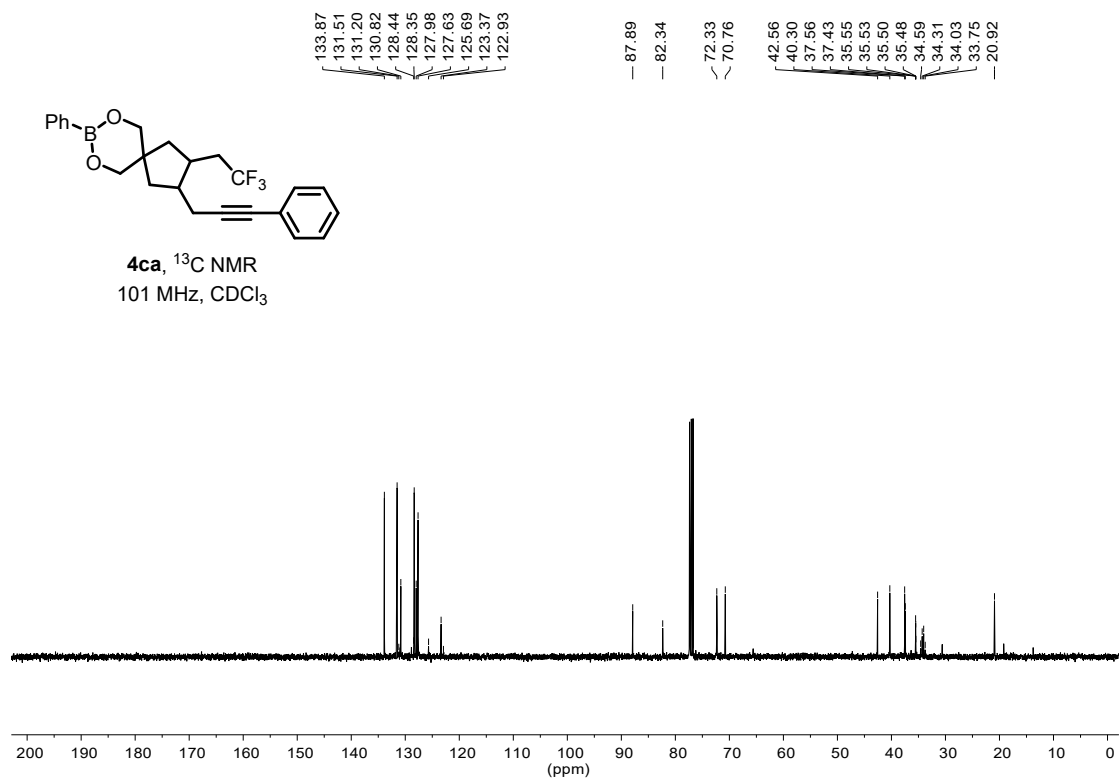


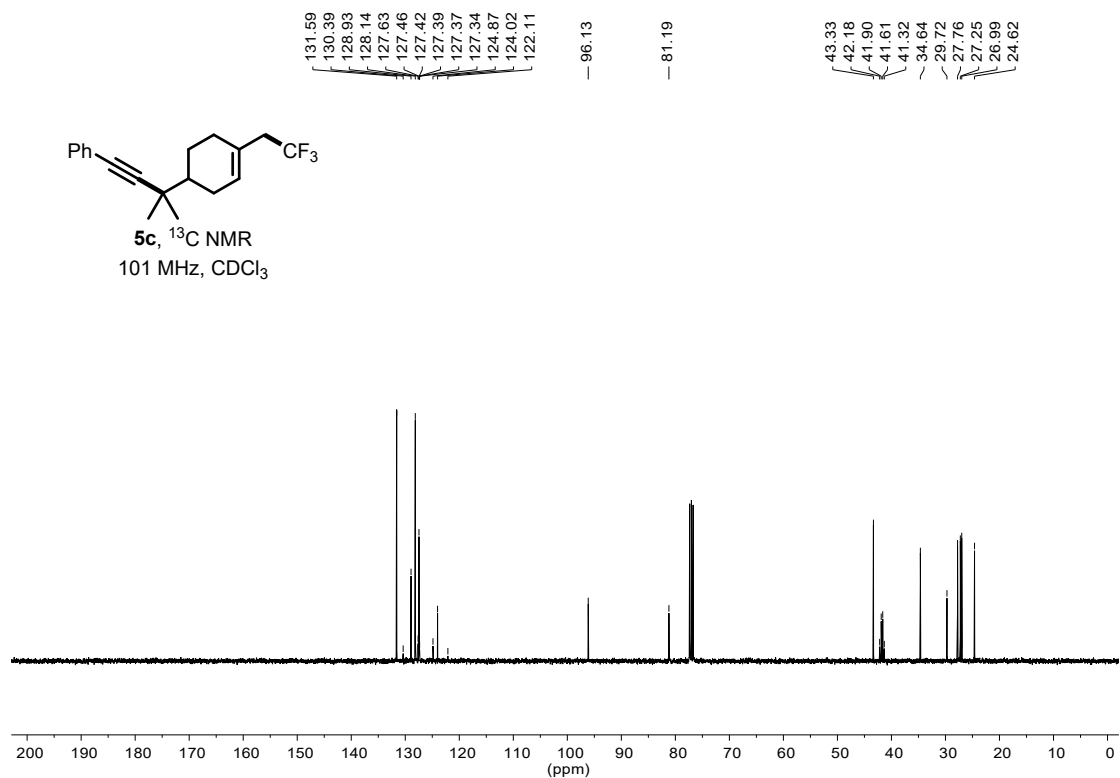
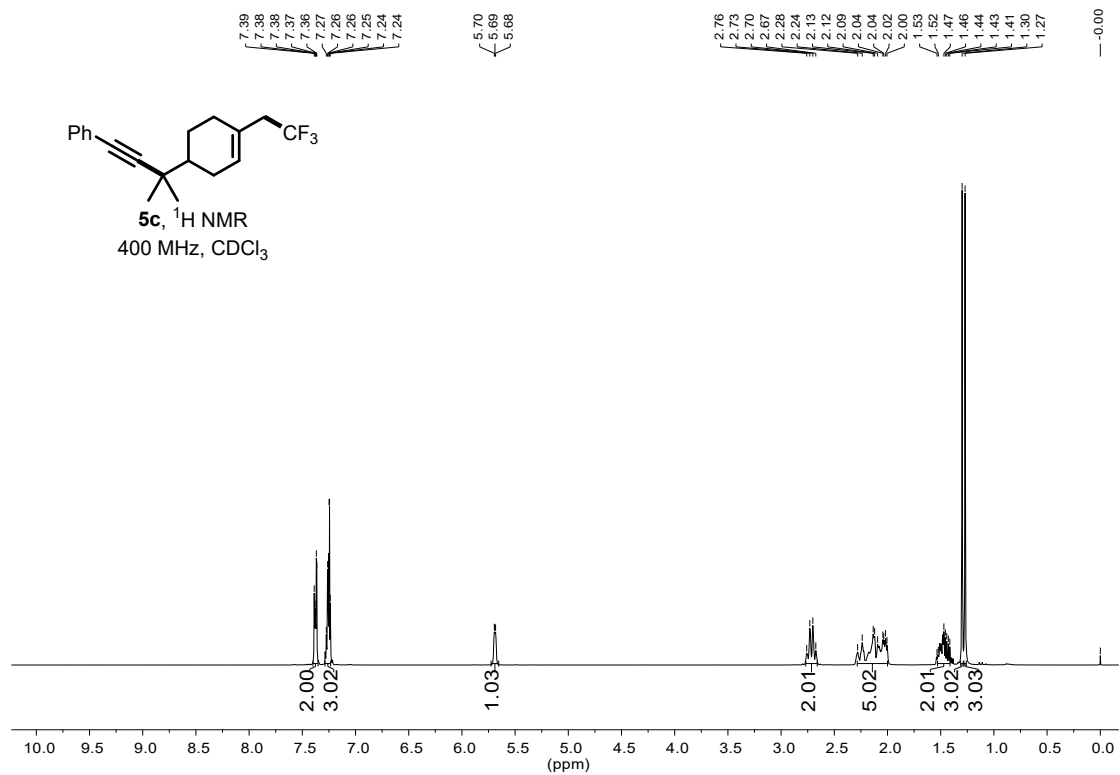


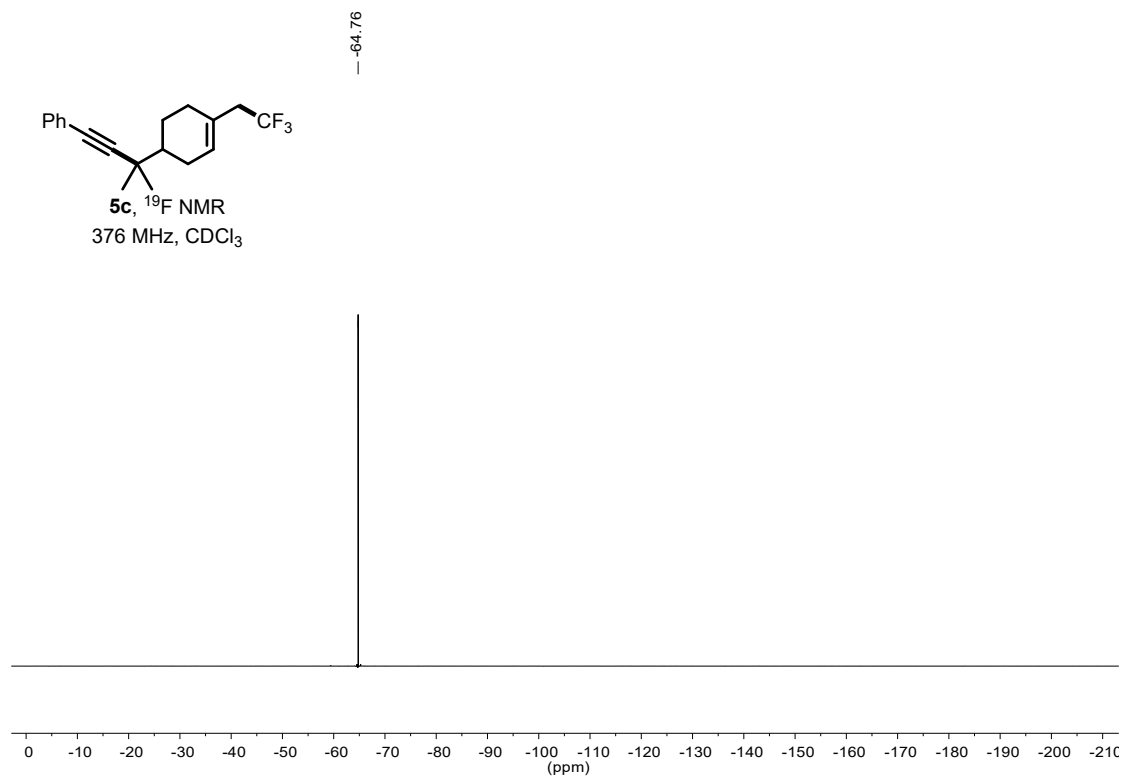












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