

Supporting Information

for

Palladium-catalyzed Heck-type reaction of secondary trifluoromethylated alkyl bromides

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General experimental information, experimental details on the synthesis of compounds 2–4 and 6; full characterization data as well as ¹H, ¹⁹F and ¹³C NMR spectra of all products.

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General information

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AM 400, Agilent MR 400 and Agilent MR 500 spectrometers. ^{19}F NMR was recorded on an Agilent MR 400 spectrometer (CFCl_3 as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air, and refilled with an inert atmosphere of N_2 at room temperature.

Screening of Pd-catalyzed cross-coupling of 2a with styrene 1a (Tables S1 – S4). To a 25 mL of Schlenk tube were added [Pd] (5 mol %), ligand (7.5–10 mol %) and base (2.0 equiv) under air. The mixture was then evacuated and backfilled with N_2 for three times. Styrene (**1a**, 0.2 mmol), 2-bromo-1,1,1-trifluorohexane (**2a**, 2.0 equiv) and solvent (3 mL) were then added. The reaction mixture was heated to 80 °C (oil bath). After stirring for 16 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (2 mL). The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. If necessary, the reaction mixture was filtered with a pad of celite. The filtrate was concentrated, and the residue was purified with silica gel chromatography to give product **3a**.

Table S1. Screening of bases.^a

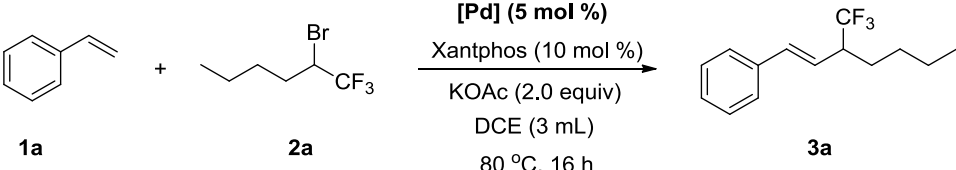
Entry	Base	Yield 3a (%) ^b
1	Na ₂ CO ₃	5
2	K ₂ CO ₃	27
3	Cs ₂ CO ₃	26
4	KOAc	84 (83)
5	NaOAc	42
6	K ₃ PO ₄	75
7	KF	37
8	<i>t</i> -BuOLi	27

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (2.0 equiv), DCE (3 mL).^bDetermined by ¹⁹F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield.**Table S2.** Screening of solvents.^a

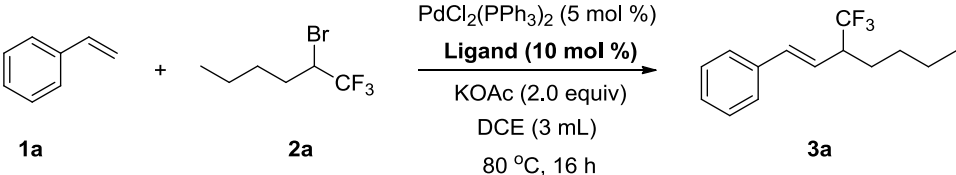
Entry	Solvent	Yield (%) ^b
1	1,4-Dioxane	26
2	DMSO	69
3	THF	35
4	DMA	49
5	MeCN	61
6	DCE	84 (83)
7	Toluene	74

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (2.0 equiv), Solvent (3 mL).^bDetermined by ¹⁹F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield.

Table S3. Screening of palladium sources.^a

		
Entry	[Pd]	Yield (%) ^b
1	Pd(PPh ₃) ₄	64
2	PdCl ₂	18
3	Pd(OAc) ₂	51
4	PdCl ₂ ·dppp	trace
5	PdCl ₂ ·dppf	69
6	PdCl₂(PPh₃)₂	84 (83)

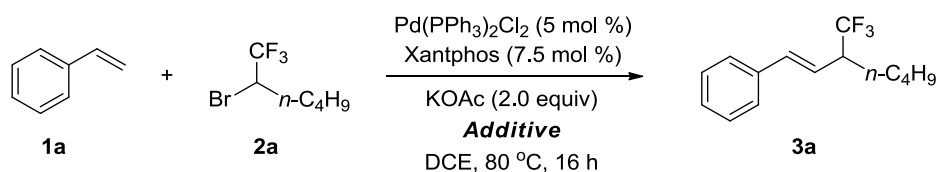
^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (2.0 equiv), DCE (3 mL).^bDetermined by ¹⁹F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield.**Table S4.** Screening of ligands.^a

		
Entry	Ligand (x)	Yield (%) ^b
1	Xantphos (10)	84 (83)
2	Dppe (10)	0
3	Dppp (10)	0
4	Dppb (10)	0
5	Dppf (10)	0
6	Sphos (10)	0
7	Ruphos (10)	0
8	Davephos (10)	0
9	Dpephos (10)	45
10	Binap (10)	0
11^c	Xantphos (7.5)	95 (88)

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (2.0 equiv), DCE (3 mL).^bDetermined by ¹⁹F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield. ^c**1a** (0.4 mmol, 1.0 equiv), **2a** (2.0 equiv), KOAc (2.0 equiv), DCE (3 mL) were used.

Mechanistic studies

Table S5. Radical inhibition experiments ^a



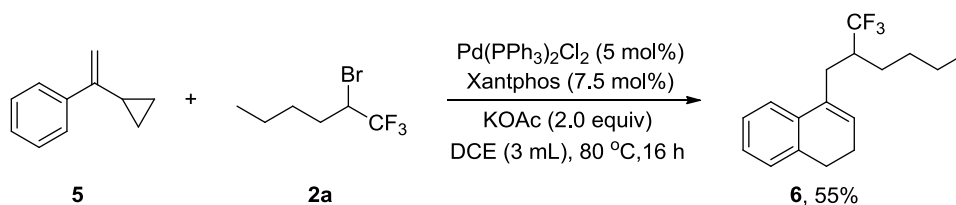
Entry	Additive (equiv)	3a Yield(%) ^a
1	none	95 (88)
2	1,4-dinitrobenzene (0.2)	22
3	1,4-dinitrobenzene (1.0)	5
4	Hydroquinone (0.2)	0

^aReaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (2.0 equiv), DCE (3 mL).

^bDetermined by ¹⁹F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield.

Procedure for radical inhibition experiments: To a 25 mL of Schlenk tube were added PdCl₂(PPh₃)₂ (5 mol%), Xantphos (7.5 mol %), KOAc (2.0 equiv) and additive (0–1.0 equiv) under air, the mixture was then evacuated and backfilled with N₂ for three times. **1a** (0.4 mmol, 1.0 equiv), **2a** (2.0 equiv) and DCE (3 mL) were added subsequently. The reaction mixture was heated to 80 °C (oil bath). After stirring for 16 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (2 mL). The yield was determined by ¹⁹F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield.

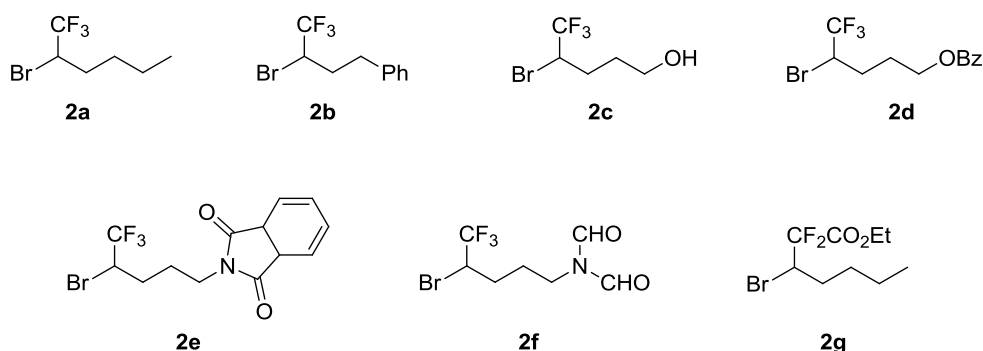
Radical clock experiments



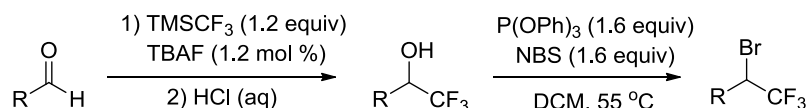
To a 25 mL of Schlenk tube were added PdCl₂(PPh₃)₂ (5 mol %), Xantphos (7.5 mol %) and KOAc (2.0 equiv) under air, the mixture was then evacuated and backfilled with N₂ for three times. **5** (0.4

mmol), **2a** (2.0 equiv) and DCE (3 mL) were added subsequently. The reaction mixture was heated to 80 °C (oil bath). After stirring for 16 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (2 mL). The reaction mixture was filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleum ether) to give product **6** (62 mg, 55%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.15 (m, 4H), 5.94 (t, *J* = 4.4 Hz, 1H), 2.96 (d, *J* = 11.2 Hz, 1H), 2.75 (t, *J* = 7.8 Hz, 2H), 2.41 – 2.21 (m, 4H), 1.65 – 1.44 (m, 2H), 1.43 – 1.33 (m, 1H), 1.32 – 1.19 (m, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -70.2 (d, *J* = 9.0 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 137.0, 133.8, 133.0, 128.7 (q, *J* = 282.0 Hz), 128.1, 127.8, 126.9, 126.5, 122.4, 40.8 (q, *J* = 24.5 Hz), 32.0 (q, *J* = 2.8 Hz), 28.9, 28.3, 27.4 (q, *J* = 1.9 Hz), 23.2, 22.7, 13.8. MS (EI): *m/z* (%) 282 (M⁺), 129 (100). HRMS: Calculated for C₁₇H₂₁F₃: 282.1595; Found: 282.1594.

Preparation of secondary fluoroalkylated alkyl halides.



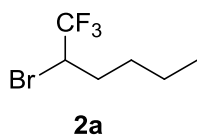
General procedure for the preparation of secondary fluoroalkylated alkyl bromides.



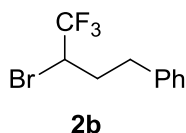
Trifluoromethylation of the aldehyde.¹ A solution of TBAF (1.0 M in THF, 1.8 mL, 1.8 mmol, 0.012 equiv) was added over 20 min to a solution of aldehyde (150 mmol) and trifluoromethyltrimethylsilane (26.6 mL, 180 mmol, 1.2 equiv) in anhydrous THF (400 mL) at 0 °C (Caution: very exothermic!). After stirring for 30 min at 0 °C, the reaction mixture was allowed to warm to room temperature, and stirred for 2 hours at room temperature. An aqueous solution of 1 N

HCl (200 mL) was added slowly, and the reaction mixture was allowed to stir at room temperature for another 2 hours. Then, the mixture was extracted with ethyl acetate (3×150 mL), and the combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated. The crude product was purified with flash chromatography on silica gel to give trifluoromethylated alcohol.

Bromination of the alcohol.² A solution of triphenylphosphite (74.5 g, 63.0 mL, 1.6 equiv) in DCM (50 mL) was added over 30 min to a solution of *N*-bromosuccinimide (42.7 g, 240 mmol, 1.6 equiv) in DCM (300 mL) at 0 °C. Then a solution of the prepared alcohol (150 mmol) in DCM (100 mL) was added over 20 min to the mixture at 0 °C. The reaction mixture was stirred at 0 °C for 20 min, and then allowed to heat to 55 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature and concentrated. The residue was purified by flash chromatography on silica gel to give product **2**. For compound **2a**, the product was purified by reduced pressure distillation of the reaction mixture.

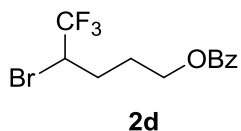


2-Bromo-1,1,1-trifluorohexane (2a). The product as a colorless oil (13.1 g, 40% yield, 2 steps) was purified by reduced pressure distillation. ^1H NMR (400 MHz, CDCl_3) δ 4.12 – 3.99 (m, 1H), 2.12 – 1.97 (m, 1H), 1.92 – 1.79 (m, 1H), 1.71 – 1.57 (m, 1H), 1.48 – 1.27 (m, 3H), 0.94 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -72.4 (d, $J = 7.2$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 124.1 (q, $J = 277.9$ Hz), 47.7 (q, $J = 32.5$ Hz), 31.1 (q, $J = 1.4$ Hz), 28.9, 21.8, 13.7. MS (EI): m/z (%) 218 (M^+), 203 (100). HRMS: Calculated for $\text{C}_6\text{H}_{10}\text{BrF}_3$: 217.9918; Found: 217.9927.

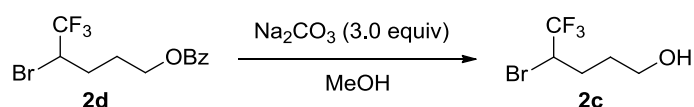


(3-Bromo-4,4,4-trifluorobutyl)benzene (2b). The product as a light yellow oil (20.4 g, 51% yield, 2 steps) was purified with silica gel chromatography (petroleum ether). This compound is known.² ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, $J = 7.2$ Hz, 2H), 7.25 – 7.20 (m, 3H), 4.05 – 3.89 (m, 1H), 3.07 – 2.92 (m, 1H), 2.81 – 2.67 (m, 1H), 2.40 – 2.27 (m, 1H), 2.25 – 2.10 (m, 1H). ^{19}F NMR (376 MHz,

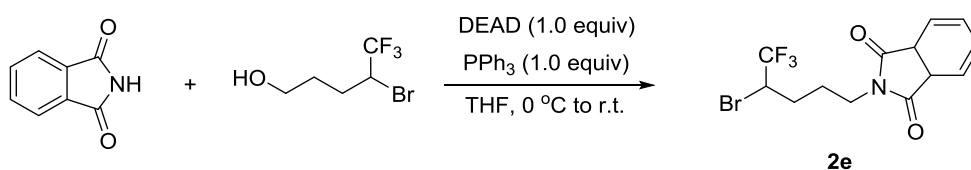
CDCl₃) δ -72.2 (d, J = 7.1 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 139.2, 128.8, 128.5, 126.7, δ 124.1 (q, J = 278.7 Hz), 46.7 (q, J = 32.8 Hz), 32.9, 32.5.



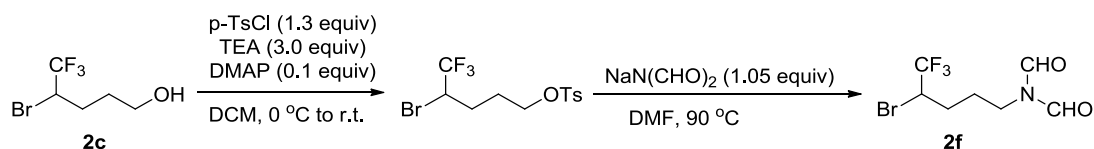
4-Bromo-5,5,5-trifluoropentyl benzoate (2d). The product as a light yellow oil (17.5 g, 30% yield, 2 steps) was synthesized according to the literature.¹ ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 4.47 – 4.31 (m, 2H), 4.25 – 4.13 (m, 1H), 2.36 – 2.21 (m, 1H), 2.16 – 2.10 (m, 1H), 2.08 – 1.88 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -72.3 (d, J = 7.1 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 133.1, 129.9, 129.5, 128.4, 123.9 (q, J = 278.8 Hz), 63.5, 46.9 (q, J = 32.9 Hz), 28.4 (q, J = 1.5 Hz), 26.2.



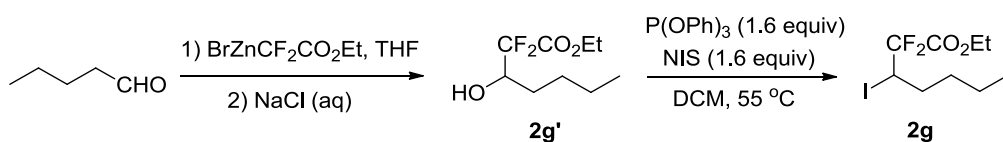
4-Bromo-5,5,5-trifluoropentanol (2c). The product as a light yellow oil (12.1 g, 88% yield) was synthesized according to the literature.¹ ¹H NMR (400 MHz, CDCl₃) δ 4.21 – 4.10 (m, 1H), 3.75 – 3.63 (m, 2H), 2.30 – 2.13 (m, 2H), 2.00 – 1.82 (m, 2H), 1.75 – 1.59 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -72.4 (d, J = 6.9 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 124.0 (q, J = 278.7 Hz), 61.5, 47.5 (q, J = 32.8 Hz), 29.6, 28.2 (d, J = 1.6 Hz).



2-(4-Bromo-5,5,5-trifluoropentyl)-3a,7a-dihydro-1H-isoindole-1,3(2H)-dione (2e). The product as a yellow oil (882 mg, 84% yield) was synthesized according to the literature.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.73 (m, 2H), 7.72 – 7.63 (m, 2H), 4.28 – 4.08 (m, 1H), 3.68 (t, J = 6.2 Hz, 2H), 2.17 – 1.93 (m, 2H), 1.93 – 1.69 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -72.3 (d, J = 7.1 Hz). ¹³C NMR (126 MHz, CDCl₃) δ 168.3, 134.1, 131.9, 123.8 (q, J = 278.2 Hz), 123.3, 46.6 (q, J = 32.8 Hz), 36.5, 28.6, 26.0.



N-(4-Bromo-5,5,5-trifluoropentyl)-N-formylformamide (2f)³ *p*-TsCl (1.49 g, 7.8 equiv) was slowly added to a solution of **2c** (1.33 g, 6.0 mmol), DMAP (74 mg, 0.1 equiv) and TEA (2.5 mL, 18 mmol, 3.0 equiv) in DCM (15 mL) at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for another 5 hours, the reaction mixture was washed with water (2 × 10 mL), and the aqueous layers were extracted with DCM (15 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified with flash chromatography on silica gel (petroleum ether / ethyl acetate 10:1) to give a light yellow oil. The crude product and diformylimide sodium salt (599 mg, 1.05 equiv) were dissolved in DMF (5 mL), then the reaction mixture was allowed to heated to 90 °C and stirred for 8 h. The reaction mixture was then cooled to room temperature and the solvent was evaporated to give a solid residue. The solid residue was washed with CHCl₃ (3 × 10 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified with flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to give **2f** as a light yellow oil (1.07 g, 65% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.87 (s, 2H), 4.19 – 4.08 (m, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.07 – 1.81 (m, 3H), 1.80 – 1.69 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -72.3 (d, *J* = 7.7 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 164.1, 123.8 (q, *J* = 278.9 Hz), 46.4 (q, *J* = 33.0 Hz), 37.3, 28.5, 24.9. MS (EI): *m/z* (%) 275 (M⁺), 58 (100). HRMS: Calculated for C₇H₉BrF₃NO₂: 274.9769; Found: 274.9774.



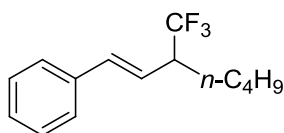
Ethyl 2, 2-difluoro-3-iodoheptanoate (2g)² Under the atmosphere of argon, preactivated zinc powder (3.33 g, 51.0 mmol, 3.0 equiv) was added into anhydrous THF (10 mL) at room temperature, followed by 2, 2, 2-trifluoroacetic acid (0.19 mL, 2.55 mmol, 0.15 equiv). After the mixture was stirred for 10 min at room temperature, anhydrous THF (15 mL) was added and then ethyl 2-bromo-2, 2 -difluoroacetate (3.27 mL, 25.5 mmol, 1.5 equiv) was added by dropwise. After stirring

for 15 min, another anhydrous THF (20 mL) was added and the reaction was then stirred for another 3 hours. The supernatant of prepared zinc reagents was transferred into a solution of valeraldehyde (1.81 mL, 17 mmol, 1.0 equiv) in anhydrous THF (10 mL). After stirring for 12 hours at room temperature, the reaction was quenched by saturated NaCl solution (100 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified with flash chromatography on silica gel (petroleum ether / ethyl acetate = 10/1) to give compound **2g'**, as a light yellow oil (1.72 g, 48% yield).

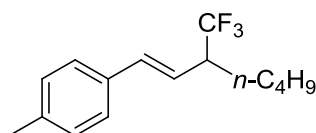
The preparation of compound **2g** from alcohol **2g'** is according to the procedure of the preparation of compound **2b**. The product as a light yellow oil (1.3 g, 50 % yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate 10:1). *N*-iodosuccinimide was used instead of *N*-bromosuccinimide. ¹H NMR (400 MHz, CDCl₃) δ 4.37 (q, *J* = 7.2 Hz, 2H), 4.33 – 4.23 (m, 1H), 1.90 – 1.74 (m, 2H), 1.68 – 1.57 (m, 1H), 1.47 – 1.27 (m, 6H), 0.93 (t, *J* = 6.6 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.1 (dd, *J* = 252.3 Hz, 12.2 Hz), -106.65 (dd, *J* = 252.3 Hz, 12.0 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 162.0 (t, *J* = 32.4 Hz), 114.1 (t, *J* = 255.6 Hz), 63.3, 31.2, 31.1, 28.8 (t, *J* = 25.0 Hz), 21.6, 13.9, 13.8. MS (EI): *m/z* (%) 320 (*M*⁺), 85 (100). HRMS: Calculated for C₉H₁₅F₂IO₂: 320.0085; Found: 320.0094.

General Procedure for Pd-Catalyzed cross-coupling of secondary fluorinated alkyl halides with alkenes.

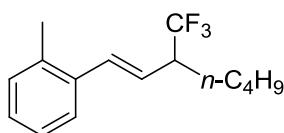
To a 25 mL of Schlenk tube were added PdCl₂(PPh₃)₂ (5 mol %), Xantphos (7.5 mol %) and KOAc (2.0 equiv) under air. The mixture was then evacuated and backfilled with N₂ for three times. Alkene **1** (0.4 mmol), secondary fluoroalkylated alkyl halide **2** (0.8 mmol, 2.0 equiv) and DCE (3 mL) were added subsequently. The reaction mixture was heated to 80 °C (oil bath). After stirring for 16 h, the reaction mixture was cooled to room temperature, diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography to give product.



(E)-(3-(Trifluoromethyl)hept-1-en-1-yl)benzene (3a). The product (86 mg, 88% yield) as a colorless oil was purified by silica gel chromatography (petroleum ether). ^1H NMR (500 MHz, CDCl_3) δ 7.42 (d, $J = 7.5$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.29 (t, $J = 7.3$ Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 5.99 (dd, $J = 16.0$ Hz, 9.5 Hz, 1H), 2.94 – 2.78 (m, 1H), 1.90 – 1.80 (m, 1H), 1.63 – 1.53 (m, 1H), 1.48 – 1.24 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.9 (d, $J = 8.6$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 136.3, 135.6, 128.6, 128.0, 127.0 (q, $J = 280.4$ Hz), 126.5, 123.1 (q, $J = 2.6$ Hz), 47.91 (q, $J = 26.5$ Hz), 28.7, 27.6 (q, $J = 2.0$ Hz), 22.4, 13.8. MS (EI): m/z (%) 242 (M^+), 242 (100). HRMS: Calculated for $\text{C}_{14}\text{H}_{17}\text{F}_3$: 242.1282; Found: 242.1285.

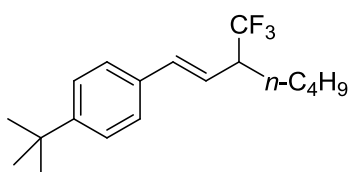


(E)-1-Methyl-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3b). The product (94 mg, 91% yield) as colorless oil was purified by silica gel chromatography (petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.56 (d, $J = 15.6$ Hz, 1H), 5.95 (dd, $J = 16.0$ Hz, 9.2 Hz, 1H), 3.01 – 2.68 (m, 1H), 2.39 (s, 3H), 1.98 – 1.75 (m, 1H), 1.63 – 1.53 (m, 1H), 1.48 – 1.21 (m, 4H), 0.94 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.9 (d, $J = 9.0$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 137.9, 135.5, 133.6, 129.3, 127.1 (q, $J = 280.4$ Hz), 126.4, 122.08 (q, $J = 2.6$ Hz), 47.9 (q, $J = 26.5$ Hz), 28.7, 27.7 (q, $J = 2.0$ Hz), 22.4, 21.2, 13.8. MS (EI): m/z (%) 256 (M^+), 105 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_{19}\text{F}_3$: 256.1439; Found: 256.1433.

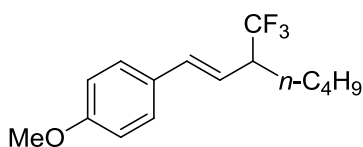


(E)-1-Methyl-2-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3c). The product (93 mg, 90% yield) as a colorless oil was purified by silica gel chromatography (petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.46 (m, 1H), 7.25 – 7.19 (m, 3H), 6.82 (d, $J = 15.6$ Hz, 1H), 5.87 (dd, $J = 15.8$ Hz, 9.4 Hz, 1H), 3.01 – 2.78 (m, 1H), 2.40 (s, 3H), 1.92 – 1.83 (m, 1H), 1.67 – 1.55 (m, 1H), 1.51 – 1.29

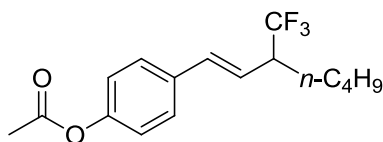
(m, 4H), 0.96 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.9 (d, $J = 9.0$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 135.7, 135.4, 133.7, 130.3, 127.9, 127.0 (q, $J = 280.0$ Hz), 126.2, 125.9, 124.7 (q, $J = 2.5$ Hz), 48.1 (q, $J = 26.4$ Hz), 28.7, 27.5 (q, $J = 2.0$ Hz), 22.3, 19.7, 13.8. MS (EI): m/z (%) 256 (M^+), 129 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_{19}\text{F}_3$: 256.1439; Found: 256.1428.



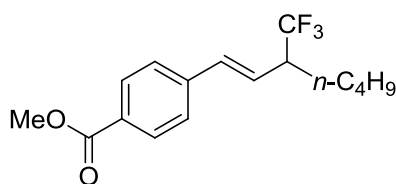
(*E*)-1-(*tert*-Butyl)-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3d). The product (108 mg, 90% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.34 (m, 4H), 6.55 (d, $J = 16.0$ Hz, 1H), 5.95 (dd, $J = 16.0$ Hz, 9.2 Hz, 1H), 2.96 – 2.72 (m, 1H), 1.87 – 1.76 (m, 1H), 1.65 – 1.48 (m, 1H), 1.48 – 1.22 (m, 13H), 0.91 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.8 (d, $J = 8.6$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 151.2, 135.4, 133.6, 127.1 (q, $J = 280.0$ Hz), 126.2, 125.6, 122.31 (q, $J = 3.1$ Hz), 48.0 (q, $J = 26.6$ Hz), 34.6, 31.2, 28.7, 27.7 (q, $J = 1.9$ Hz), 22.4, 13.8. MS (EI): m/z (%) 298 (M^+), 283 (100). HRMS: Calculated for $\text{C}_{18}\text{H}_{25}\text{F}_3$: 298.1908; Found: 298.1902.



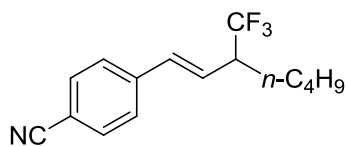
(*E*)-1-Methoxy-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3e). The product (106 mg, 97% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether/ethyl acetate 20/1). ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.53 (d, $J = 16.0$ Hz, 1H), 5.86 (dd, $J = 15.6$ Hz, 9.6 Hz, 1H), 3.84 (s, 3H), 2.90 – 2.74 (m, 1H), 1.92 – 1.77 (m, 1H), 1.62 – 1.52 (m, 1H), 1.49 – 1.25 (m, 4H), 0.94 (t, $J = 6.9$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.9 (d, $J = 9.0$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 159.5, 135.0, 129.1, 127.1 (q, $J = 280.0$ Hz), 127.1, 120.8 (q, $J = 2.6$ Hz), 114.0, 55.2, 47.9 (q, $J = 26.5$ Hz), 28.7, 27.7 (q, $J = 2.0$ Hz), 22.4 13.8. MS (EI): m/z (%) 272 (M^+), 121 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{O}$: 272.1388; Found: 272.1393.



(E)-4-(3-(Trifluoromethyl)hept-1-en-1-yl)phenyl acetate (3f). The product (114 mg, 95% yield) as a pale yellow oil was purified with silica gel chromatography (petroleum ether/dichloromethane 2:1). ^1H NMR (500 MHz, CDCl_3) δ 7.42 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 15.8 Hz, 1H), 5.94 (dd, J = 15.8 Hz, 9.2 Hz, 1H), 2.92 – 2.74 (m, 1H), 2.31 (s, 3H), 1.96 – 1.69 (m, 1H), 1.60 – 1.53 (m, 1H), 1.48 – 1.22 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.9 (d, J = 8.6 Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 169.3, 150.3, 134.6, 134.1, 127.4, 126.9 (q, J = 280.3 Hz), 123.3 (q, J = 2.5 Hz), 121.7, 47.8 (q, J = 26.5 Hz), 28.6, 27.5 (q, J = 1.8 Hz), 22.3, 21.0, 13.7. MS (EI): m/z (%) 300 (M^+), 258 (100). HRMS: Calculated for $\text{C}_{16}\text{H}_{19}\text{F}_3\text{O}_2$: 300.1337; Found: 300.1338.

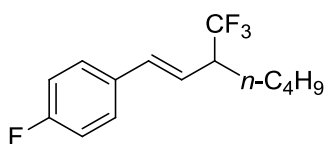


Methyl (E)-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzoate (3g). The product (76 mg, 63% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 16.0 Hz, 1H), 6.09 (dd, J = 16.0 Hz, 9.4 Hz, 1H), 3.91 (s, 3H), 2.92 – 2.77 (m, 1H), 1.91 – 1.76 (m, 1H), 1.62 – 1.51 (m, 1H), 1.45 – 1.24 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.7 (d, J = 8.6 Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 140.6, 134.7, 129.9, 129.4, 126.8 (q, J = 281.1 Hz), 126.3, 125.9 (q, J = 2.5 Hz), 52.1, 47.9 (q, J = 26.6 Hz), 28.7, 27.5 (q, J = 1.9 Hz), 22.3, 13.8. MS (EI): m/z (%) 300 (M^+), 191 (100). HRMS: Calculated for $\text{C}_{16}\text{H}_{19}\text{F}_3\text{O}_2$: 300.1337; Found: 300.1333.

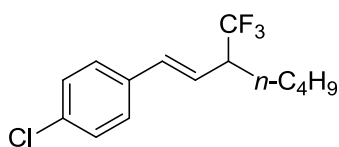


(E)-4-(3-(Trifluoromethyl)hept-1-en-1-yl)benzonitrile (3h). The product (77 mg, 72% yield) as a

colorless oil was purified with silica gel chromatography (petroleum ether/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 6.57 (d, $J = 15.8$ Hz, 1H), 6.10 (dd, $J = 15.8$ Hz, 9.4 Hz, 1H), 2.97 – 2.74 (m, 1H), 1.92 – 1.74 (m, 1H), 1.61 – 1.52 (m, 1H), 1.43 – 1.22 (m, 4H), 0.90 (t, $J = 6.4$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.6 (d, $J = 8.7$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 140.6, 134.0, 132.4, 127.2 (q, $J = 2.5$ Hz), 126.9, 126.7 (q, $J = 281.2$ Hz), 118.7, 111.3, 47.9 (q, $J = 26.8$ Hz), 28.7, 27.4 (q, $J = 2.0$ Hz), 22.3, 13.7. MS (EI): m/z (%) 267 (M^+), 129 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}$: 267.1235; Found: 267.1241.

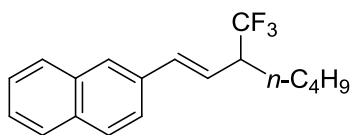


(*E*)-1-Fluoro-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3i). The product (90 mg, 86% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.32 (m, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 6.53 (d, $J = 15.8$ Hz, 1H), 5.90 (dd, $J = 15.8$ Hz, 9.3 Hz, 1H), 2.92 – 2.71 (m, 1H), 1.93 – 1.76 (m, 1H), 1.62 – 1.50 (m, 1H), 1.49 – 1.20 (m, 4H), 0.92 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.9 (d, $J = 9.0$ Hz, 3F), -113.8 – -113.9 (m, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 162.6 (d, $J = 248.0$ Hz), 134.4, 132.5 (d, $J = 3.4$ Hz), 128.0 (d, $J = 8.0$ Hz), 127.0 (q, $J = 280.4$ Hz), 123.0-122.8 (m), 115.5 (d, $J = 21.6$ Hz), 47.9 (q, $J = 26.6$ Hz), 28.7, 27.6 (q, $J = 2.0$ Hz), 22.4, 13.8. MS (EI): m/z (%) 260 (M^+), 122 (100). HRMS: Calculated for $\text{C}_{14}\text{H}_{16}\text{F}_4$: 260.1188; Found: 260.1184.

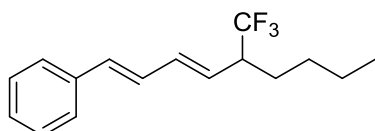


(*E*)-1-Chloro-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3j). The product (89 mg, 80% yield) as a white solid was purified with silica gel chromatography (petroleum ether). m.p. 48~50 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.28 (m, 4H), 6.51 (d, $J = 16.0$ Hz, 1H), 5.94 (dd, $J = 15.8$ Hz, 9.2 Hz, 1H), 2.91 – 2.74 (m, 1H), 1.86 – 1.77 (m, 1H), 1.61 – 1.50 (m, 1H), 1.44 – 1.22 (m, 4H), 0.91 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.8 (d, $J = 9.0$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ

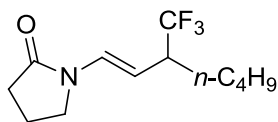
134.8, 134.4, 133.7, 128.8, 127.7, 126.9 (q, $J = 280.4$ Hz), 123.9 (q, $J = 2.6$ Hz), 47.9 (q, $J = 26.6$ Hz), 28.7, 27.6 (q, $J = 2.0$ Hz), 22.4, 13.8. MS (EI): m/z (%) 276 (M^+), 138 (100). HRMS: Calculated for $C_{14}H_{16}ClF_3$: 276.0893; Found: 276.0890.



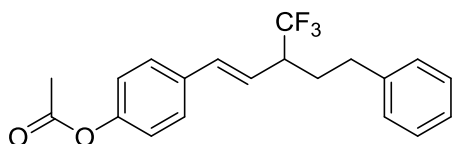
(*E*)-2-(3-(Trifluoromethyl)hept-1-en-1-yl)naphthalene (3k). The product (95 mg, 81% yield) as a white solid was purified with silica gel chromatography (petroleum ether). m.p. 86~88 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 3H), 7.76 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.53 – 7.44 (m, 2H), 6.73 (d, $J = 15.6$ Hz, 1H), 6.11 (dd, $J = 15.6$ Hz, 9.2 Hz, 1H), 3.00 – 2.81 (m, 1H), 1.99 – 1.79 (m, 1H), 1.73 – 1.55 (m, 1H), 1.51 – 1.21 (m, 4H), 0.93 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.8 (d, $J = 8.6$ Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 133.8, 133.5, 133.1, 128.3, 128.0, 127.7, 127.1 (q, $J = 280.4$ Hz), 126.5, 126.4, 126.1, 123.5 (q, $J = 2.5$ Hz), 123.4, 48.0 (q, $J = 26.5$ Hz), 28.7, 27.7 (q, $J = 1.9$ Hz), 22.4, 13.8. MS (EI): m/z (%) 292 (M^+), 199 (100). HRMS: Calculated for $C_{18}H_{19}F_3$: 292.1439; Found: 292.1444.



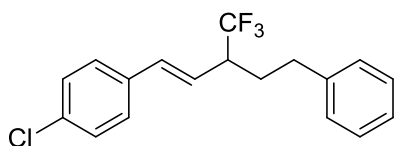
((1*E*,3*E*)-5-(Trifluoromethyl)nona-1,3-dien-1-yl)benzene (3l). The product (90 mg, 83% yield) as a white semi-solid was purified with silica gel chromatography (petroleum ether). 1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.2$ Hz, 1H), 6.81 (dd, $J = 15.6$ Hz, 10.4 Hz, 1H), 6.60 (d, $J = 15.6$ Hz, 1H), 6.40 (dd, $J = 15.2$ Hz, 10.4 Hz, 1H), 5.60 (dd, $J = 15.2$ Hz, 9.2 Hz, 1H), 2.90 – 2.66 (m, 1H), 1.92 – 1.75 (m, 1H), 1.60 – 1.48 (m, 1H), 1.45 – 1.21 (m, 4H), 0.95 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.8 (d, $J = 9.0$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 135.9, 133.2, 128.6, 127.9, 127.8, 126.97 (q, $J = 281.1$ Hz), 126.95 (q, $J = 2.4$ Hz), 126.4, 47.6 (q, $J = 26.4$ Hz), 28.7, 27.6 (q, $J = 1.9$ Hz), 22.4, 13.8. MS (EI): m/z (%) 268 (M^+), 104 (100). HRMS: Calculated for $C_{16}H_{19}F_3$: 268.1439; Found: 268.1432.



(E)-1-(3-(Trifluoromethyl)hept-1-en-1-yl)pyrrolidin-2-one (3m). The reaction was conducted at 100 °C. The product (61 mg, 61% yield) as a pale yellow solid was purified with silica gel chromatography (petroleum ether/ethyl acetate 2:1). m.p. 66~69 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.00 (d, *J* = 14.4 Hz, 1H), 4.62 (dd, *J* = 14.4 Hz, 9.6 Hz, 1H), 3.51 (t, *J* = 7.2 Hz, 2H), 2.76 – 2.55 (m, 1H), 2.48 (t, *J* = 8.2 Hz, 2H), 2.19 – 2.03 (m, 2H), 1.80 – 1.66 (m, 1H), 1.48 – 1.14 (m, 5H), 0.86 (t, *J* = 6.8 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -71.6 (d, *J* = 8.6 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 173.3, 128.2, 127.0 (q, *J* = 280.9 Hz), 104.6 (q, *J* = 2.8 Hz), 45.6 (q, *J* = 27.0 Hz), 45.0, 31.0, 28.6, 27.8 (q, *J* = 1.9 Hz), 22.2, 17.3, 13.8. MS (EI): *m/z* (%) 249 (M⁺), 86 (100). HRMS: Calculated for C₁₂H₁₈F₃NO: 249.1340; Found: 249.1332.

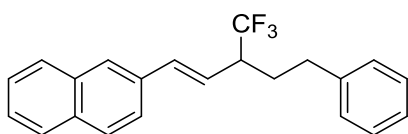


(E)-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)phenyl acetate (4a). The product (129 mg, 92% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether/ethyl acetate 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.03 (dd, *J* = 15.8 Hz, 9.2 Hz, 1H), 3.00 – 2.79 (m, 2H), 2.69 – 2.58 (m, 1H), 2.37 (s, 3H), 2.30 – 2.17 (m, 1H), 2.02 – 1.89 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -70.7 (d, *J* = 8.6 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 169.4, 150.5, 140.6, 135.3, 134.0, 128.5, 128.4, 127.5, 126.8 (q, *J* = 280.6 Hz), 126.2, 122.8 (q, *J* = 2.4 Hz), 121.8, 47.1 (q, *J* = 26.8 Hz), 32.4, 29.3, 21.1. MS (EI): *m/z* (%) 348 (M⁺), 107 (100). HRMS: Calculated for C₂₀H₁₉F₃O₂: 348.1337; Found: 348.1344.

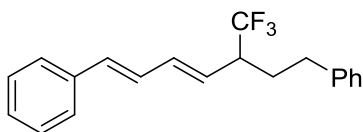


(E)-1-Chloro-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene (4b). The product (123 mg, 94% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether/ethyl

acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.29 (m, 6H), 7.27 – 7.21 (m, 1H), 7.19 (d, J = 7.6 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.00 (dd, J = 15.8 Hz, 9.4 Hz, 1H), 2.97 – 2.73 (m, 2H), 2.69 – 2.52 (m, 1H), 2.26 – 2.13 (m, 1H), 2.02 – 1.84 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.6 (d, J = 8.6 Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 140.5, 135.1, 134.7, 133.9, 128.8, 128.6, 128.4, 127.7, 126.8 (q, J = 280.7 Hz), 126.3, 123.3 (q, J = 2.4 Hz), 47.1 (q, J = 26.9 Hz), 32.4, 29.3. MS (EI): m/z (%) 324 (M^+), 91 (100). HRMS: Calculated for $\text{C}_{18}\text{H}_{16}\text{ClF}_3$: 324.0893; Found: 324.0883.

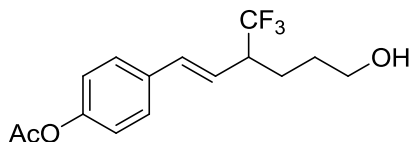


(*E*)-2-(5-Phenyl-3-(trifluoromethyl)pent-1-en-1-yl)naphthalene (4c). The product (123 mg, 90% yield) as a white semi-solid was purified by silica gel chromatography (petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 8.8 Hz, 3H), 7.78 (s, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 7.2 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 15.8 Hz, 9.2 Hz, 1H), 3.04 – 2.78 (m, 2H), 2.72 – 2.57 (m, 1H), 2.32 – 2.16 (m, 1H), 2.06 – 1.89 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.6 (d, J = 9.0 Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 136.4, 133.6, 133.5, 133.2, 128.6, 128.4, 128.3, 128.0, 127.7, 126.9 (q, J = 280.8 Hz), 126.7, 126.4, 126.2, 126.1, 123.4, 122.9 (q, J = 2.5 Hz), 47.3 (q, J = 26.8 Hz), 32.5, 29.4. MS (EI): m/z (%) 340 (M^+), 141 (100). HRMS: Calculated for $\text{C}_{22}\text{H}_{19}\text{F}_3$: 340.1439; Found: 340.1441.

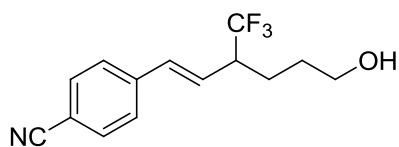


((1*E*, 3*E*)-5-(Trifluoromethyl)hepta-1,3-diene-1,7-diyl)dibenzene (4d). The product (90 mg, 71% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 7.4 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.33 – 7.26 (m, 2H), 7.23 (d, J = 7.1 Hz, 2H), 6.85 (dd, J = 15.6 Hz, 10.4 Hz, 1H), 6.64 (d, J = 15.7 Hz, 1H), 6.42 (dd, J = 15.2 Hz, 10.4 Hz, 1H), 5.66 (dd, J = 15.2 Hz, 9.4 Hz, 1H), 2.94 – 2.76 (m, 2H), 2.65 – 2.57 (m, 1H), 2.24 – 2.12 (m, 1H), 1.95 – 1.84 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.6 (d, J = 8.6 Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 136.8, 136.6, 133.5, 128.6, 128.5, 128.4, 127.8, 127.7, 126.8 (q, J = 281.1

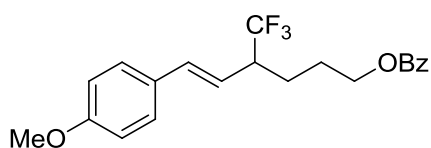
Hz), 126.5, 126.3 (q, $J = 2.5$ Hz), 126.2, 46.9 (q, $J = 26.8$ Hz), 32.4, 29.4 (q, $J = 1.7$ Hz). MS (EI): m/z (%) 316 (M^+), 212 (100). HRMS: Calculated for $C_{20}H_{19}F_3$: 316.1439; Found: 316.1442.



(E)-4-(6-Hydroxy-3-(trifluoromethyl)hex-1-en-1-yl)phenyl acetate (4e). The product (118 mg, 97% yield) as a yellow oil was purified with silica gel chromatography (petroleum ether/ethyl acetate 5:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, $J = 8.4$ Hz, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 6.55 (d, $J = 16.0$ Hz, 1H), 5.92 (dd, $J = 16.0$ Hz, 9.2 Hz, 1H), 3.69 – 3.62 (m, 2H), 2.94 – 2.78 (m, 1H), 2.30 (s, 3H), 1.99 – 1.86 (m, 1H), 1.75 – 1.48 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.9 (d, $J = 8.6$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 150.4, 135.0, 133.9, 127.4, 126.8 (q, $J = 280.8$ Hz), 123.0 (q, $J = 2.5$ Hz), 121.8, 62.2, 47.7 (q, $J = 26.8$ Hz), 29.5, 24.4 (q, $J = 1.8$ Hz), 21.0. MS (EI): m/z (%) 302 (M^+), 107 (100). HRMS: Calculated for $C_{15}H_{17}F_3O_3$: 302.1130; Found: 302.1126.

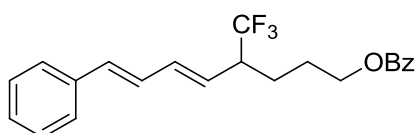


(E)-4-(6-hydroxy-3-(trifluoromethyl)hex-1-en-1-yl)benzonitrile (4f). The product (92 mg, 85% yield) as a yellow oil was purified with silica gel chromatography (petroleum ether/ethyl acetate 5:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 6.60 (d, $J = 16.0$ Hz, 1H), 6.11 (dd, $J = 16.0$ Hz, 9.6 Hz, 1H), 3.69 (t, $J = 6.2$ Hz, 2H), 3.07 – 2.82 (m, 1H), 2.01 – 1.91 (m, 1H), 1.74 – 1.51 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.6 (d, $J = 8.6$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 134.3, 132.4, 126.9, 126.8 (q, $J = 2.5$ Hz), 126.6 (q, $J = 280.9$ Hz), 118.7, 111.3, 62.1, 47.7 (q, $J = 27.0$ Hz), 29.4, 24.4 (q, $J = 2.0$ Hz). MS (EI): m/z (%) 269 (M^+), 154 (100). HRMS: Calculated for $C_{14}H_{14}F_3NO$: 269.1027; Found: 269.1033.

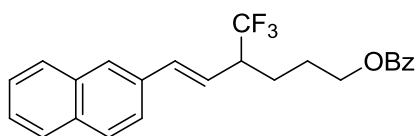


(E)-6-(4-Methoxyphenyl)-4-(trifluoromethyl)hex-5-en-1-yl benzoate (4g). The product (105 mg,

69% yield) as a pale yellow oil was purified with silica gel chromatography (petroleum ether/acetone 20:1). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 7.2$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.33 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.78$ Hz, 2H), 6.54 (d, $J = 16.0$ Hz, 1H), 5.85 (dd, $J = 15.8$ Hz, 9.4 Hz, 1H), 4.35 (t, $J = 6.2$ Hz, 2H), 3.82 (s, 3H), 2.96 – 2.82 (m, 1H), 2.06 – 1.87 (m, 2H), 1.82 – 1.62 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.9 (d, $J = 8.6$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 166.5, 159.6, 135.7, 132.9, 130.2, 129.5, 128.8, 128.4, 127.7, 126.8 (q, $J = 280.4$ Hz), 119.9 (q, $J = 2.5$ Hz), 114.0, 64.2, 55.3, 47.6 (q, $J = 26.8$ Hz), 25.9, 24.7 (q, $J = 2.0$ Hz). MS (EI): m/z (%) 378 (M^+), 105 (100). HRMS: Calculated for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{O}_3$: 378.1443; Found: 378.1436.

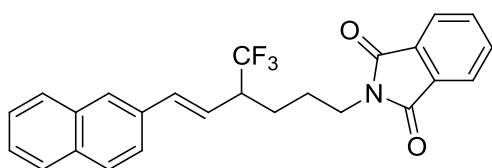


(5E,7E)-8-Phenyl-4-(trifluoromethyl)octa-5,7-dien-1-yl benzoate (4h). The product (120 mg, 80% yield) as a pale yellow oil was purified with silica gel chromatography (petroleum ether/acetone 20:1). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.39 (d, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.24 (t, $J = 7.2$ Hz, 1H), 6.76 (dd, $J = 15.6$ Hz, 10.4 Hz, 1H), 6.55 (d, $J = 15.6$ Hz, 1H), 6.39 (dd, $J = 15.1$ Hz, 10. Hz, 1H), 5.58 (dd, $J = 15.2$ Hz, 9.4 Hz, 1H), 4.34 (t, $J = 6.2$ Hz, 2H), 2.92 – 2.77 (m, 1H), 2.02 – 1.85 (m, 2H), 1.80 – 1.63 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.8 (d, $J = 8.6$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 166.5, 136.8, 136.5, 133.7, 133.0, 130.2, 129.5, 128.6, 128.4, 127.9, 127.5, 126.7 (q, $J = 280.6$ Hz), 126.5, 125.9 (q, $J = 2.4$ Hz), 64.2, 47.4 (q, $J = 26.9$ Hz), 25.9, 24.7 (q, $J = 2.0$ Hz). MS (EI): m/z (%) 374 (M^+), 105 (100). HRMS: Calculated for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{O}_2$: 374.1494; Found: 374.1505.

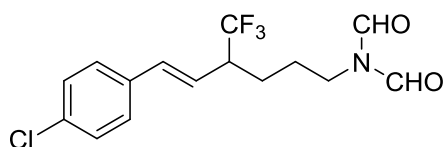


(E)-6-(Naphthalen-2-yl)-4-(trifluoromethyl)hex-5-en-1-yl benzoate (4i). The product (145 mg, 91% yield) as a pale yellow solid was purified with silica gel chromatography (petroleum ether/ethyl acetate 30:1). m.p. 79~82 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 7.2$ Hz, 2H), 7.85 – 7.80 (m, 3H), 7.75 (s, 1H), 7.65 – 7.55 (m, 2H), 7.52 – 7.42 (m, 4H), 6.78 (d, $J = 15.6$ Hz, 1H), 6.14 (dd, $J =$

15.8 Hz, 9.2 Hz, 1H), 4.39 (t, $J = 6.0$ Hz, 2H), 3.08 – 2.93 (m, 1H), 2.10 – 2.02 (m, 1H), 2.01 – 1.91 (m, 1H), 1.89 – 1.75 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.7 (d, $J = 8.6$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 136.4, 133.42, 133.39, 133.2, 132.9, 130.1, 129.5, 128.4, 128.3, 128.0, 127.6, 126.9 (q, $J = 281.3$ Hz), 126.7, 126.4, 126.1, 123.3, 122.5 (q, $J = 2.4$ Hz), 64.2, 47.7 (q, $J = 27.0$ Hz), 25.9, 24.7 (q, $J = 2.0$ Hz). MS (EI): m/z (%) 398 (M^+), 105 (100). HRMS: Calculated for $\text{C}_{24}\text{H}_{21}\text{F}_3\text{O}_2$: 398.1494; Found: 398.1491.

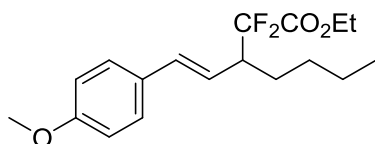


(*E*)-2-(6-(Naphthalen-2-yl)-4-(trifluoromethyl)hex-5-en-1-yl)isoindoline-1,3-dione (4j). The reaction was carried out in the presence of 2-vinylnaphthalene (0.2 mmol), **1e** (0.4 mmol, 2.0 equiv), $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol %), Xantphos (7.5 mol %), and KOAc (2.0 equiv) in DCE (3 mL). The product (72 mg, 85% yield) as a white solid was purified with silica gel chromatography (petroleum ether/ethyl acetate 10:1). m.p. 156~159 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.75 (m, 5H), 7.75 – 7.64 (m, 3H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.51 – 7.41 (m, 2H), 6.74 (d, $J = 16.0$ Hz, 1H), 6.07 (dd, $J = 15.8$ Hz, 9.4 Hz, 1H), 3.73 (t, $J = 6.6$ Hz, 2H), 3.07 – 2.91 (m, 1H), 1.94 – 1.80 (m, 2H), 1.78 – 1.63 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.7 (d, $J = 8.6$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 168.3, 136.4, 133.9, 133.42, 133.41, 133.2, 132.0, 128.3, 128.0, 127.6, 126.7 (q, $J = 280.6$ Hz), 126.69, 126.3, 126.1, 123.4, 123.2, 122.5 (q, $J = 2.3$ Hz), 47.6 (q, $J = 26.9$ Hz), 37.3, 25.7, 25.2 (q, $J = 1.6$ Hz). MS (EI): m/z (%) 423 (M^+), 165 (100). HRMS: Calculated for $\text{C}_{25}\text{H}_{20}\text{F}_3\text{NO}_2$: 423.1446; Found: 423.1447.

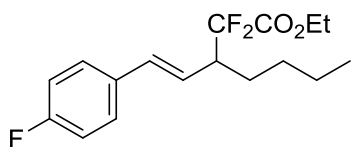


(*E*)-N-(6-(4-chlorophenyl)-4-(trifluoromethyl)hex-5-en-1-yl)-N-formylformamide (4k). The product (122 mg, 91% yield) as a white solid was purified with silica gel chromatography (petroleum ether/ethyl acetate 5:1). m.p. 57~60 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.83 (s, 2H), 7.36 – 7.27 (m, 4H), 6.54 (d, $J = 16.0$ Hz, 1H), 5.90 (dd, $J = 15.8$ Hz, 9.4 Hz, 1H), 3.67 (t, $J = 6.6$ Hz, 2H), 2.94 –

2.80 (m, 1H), 1.85 – 1.52 (m, 4H). ^{19}F NMR (376 MHz, CDCl_3) δ -70.8 (d, J = 8.6 Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 163.9, 135.2, 134.4, 133.9, 128.8, 127.7, 126.6 (q, J = 280.7 Hz), 122.6, 47.4 (q, J = 27.1 Hz), 38.1, 25.0, 24.6. MS (EI): m/z (%) 333 (M^+), 313 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_{15}\text{ClF}_3\text{NO}_2$: 333.0743; Found: 333.0746.



Ethyl (*E*)-2,2-difluoro-3-(4-methoxystyryl)heptanoate (4l). The product (107 mg, 82% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether/ethyl acetate 30:1). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.43 (d, J = 16.0 Hz, 1H), 5.77 (dd, J = 15.8 Hz, 9.6 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.05 – 2.73 (m, 1H), 1.81 – 1.69 (m, 1H), 1.41 – 1.20 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -109.3 (dd, J = 251.9 Hz, 11.1 Hz, 1F), -114.46 (dd, J = 251.2 Hz, 19.2 Hz, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 164.2 (t, J = 33.0 Hz), 159.4, 134.9, 129.2, 127.6, 121.6 (dd, J = 6.2 Hz, 1.4 Hz), 116.7 (t, J = 255.7 Hz), 113.9, 62.5, 55.2, 48.2 (t, J = 22.1 Hz), 28.9, 26.5, 22.4, 14.0, 13.8. MS (EI): m/z (%) 326 (M^+), 203 (100). HRMS: Calculated for $\text{C}_{18}\text{H}_{24}\text{F}_2\text{O}_3$: 326.1694; Found: 326.1696.



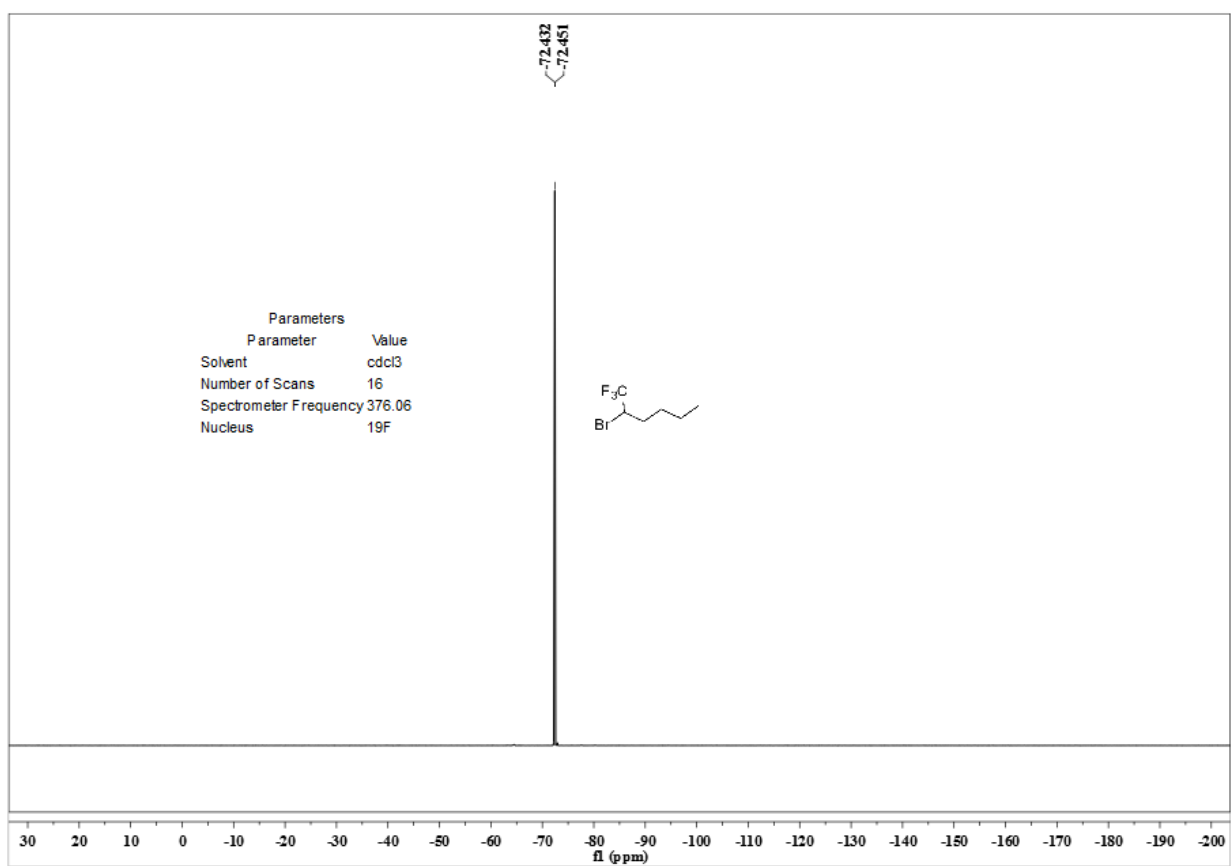
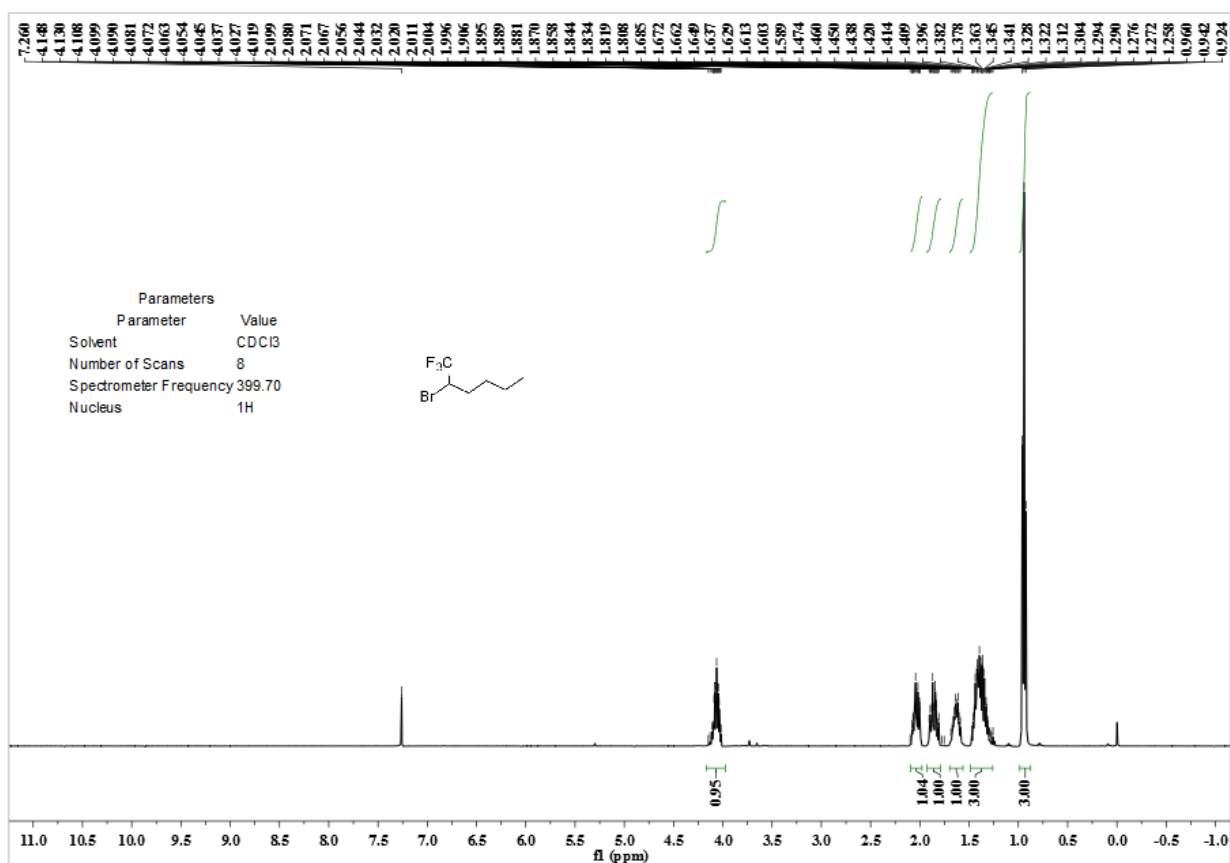
Ethyl (*E*)-2,2-difluoro-3-(4-fluorostyryl)heptanoate (4m). The product (96 mg, 76% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether/acetone 150:1). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.29 (m, 2H), 7.00 (t, J = 8.2 Hz, 2H), 6.46 (d, J = 16.0 Hz, 1H), 5.84 (dd, J = 15.5 Hz, 10.0 Hz, 1H), 4.28 (q, J = 7.0 Hz, 2H), 2.96 – 2.79 (m, 1H), 1.81 – 1.67 (m, 1H), 1.61 – 1.47 (m, 1H), 1.42 – 1.20 (m, 7H), 0.89 (t, J = 6.4 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -109.7 (dd, J = 252.5 Hz, 11.5 Hz, 1F), -113.13 – -114.26 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 164.2 (t, J = 33.0 Hz), 162.5 (d, J = 248.2 Hz), 134.3, 132.6 (d, J = 3.1 Hz), 128.0 (d, J = 8.0 Hz), 123.7 (d, J = 6.2 Hz), 116.6 (t, J = 255.8 Hz), 115.5 (d, J = 21.7 Hz), 62.6, 48.2 (t, J = 22.3 Hz), 28.9, 26.5 (t, J = 2.4 Hz), 22.4, 14.0, 13.8. MS (EI): m/z (%) 314 (M^+), 135 (100). HRMS: Calculated for

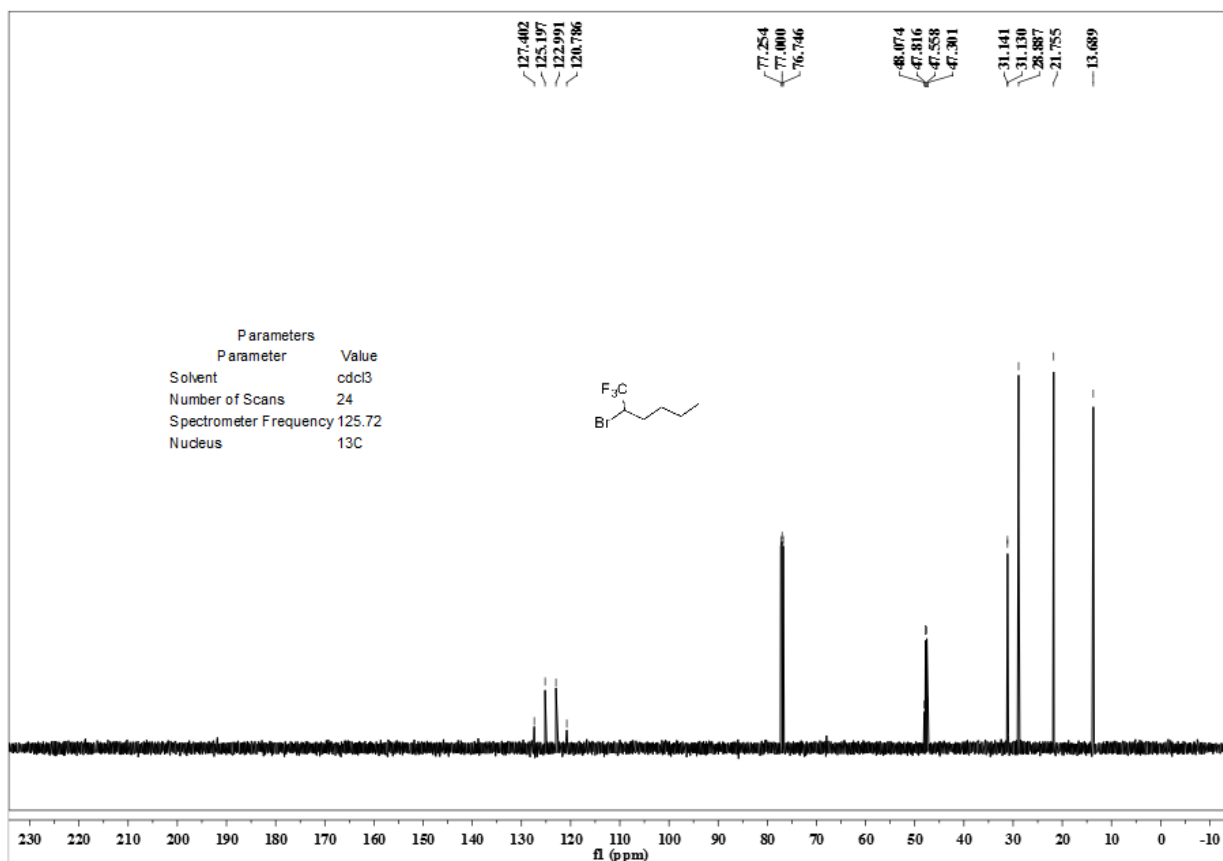
C₁₇H₂₁F₃O₂: 314.1494; Found: 314.1504.

REFERENCES.

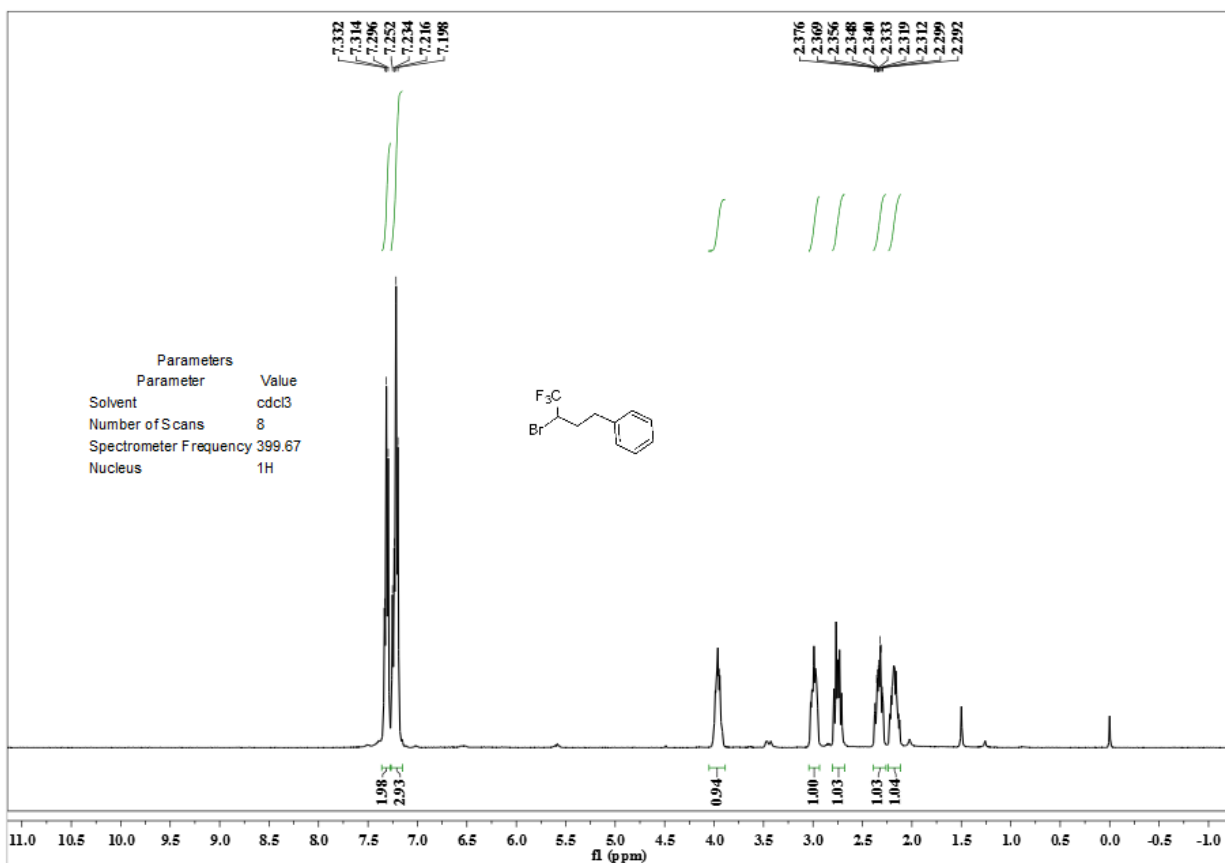
1. Li, X. -F.; Feng, Z.; Jiang, Z.; Zhang, X. *Org. Lett.* **2015**, *17*, 5570.
2. Liang, Y.; Fu, G. C. *J. Am. Chem. Soc.* **2015**, *137*, 9523.
3. Han, Y.-L, Hu, H, *Synthesis* **1990**, *2*, 122.

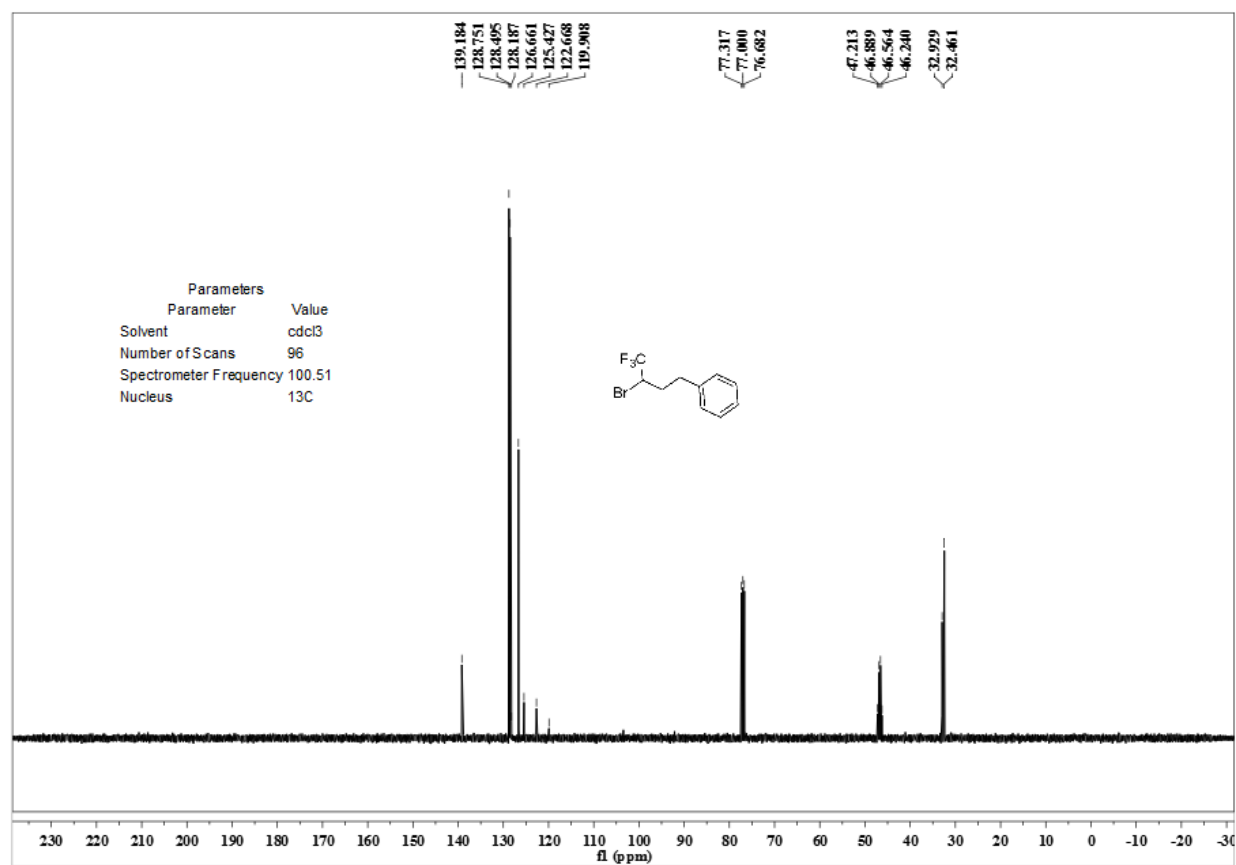
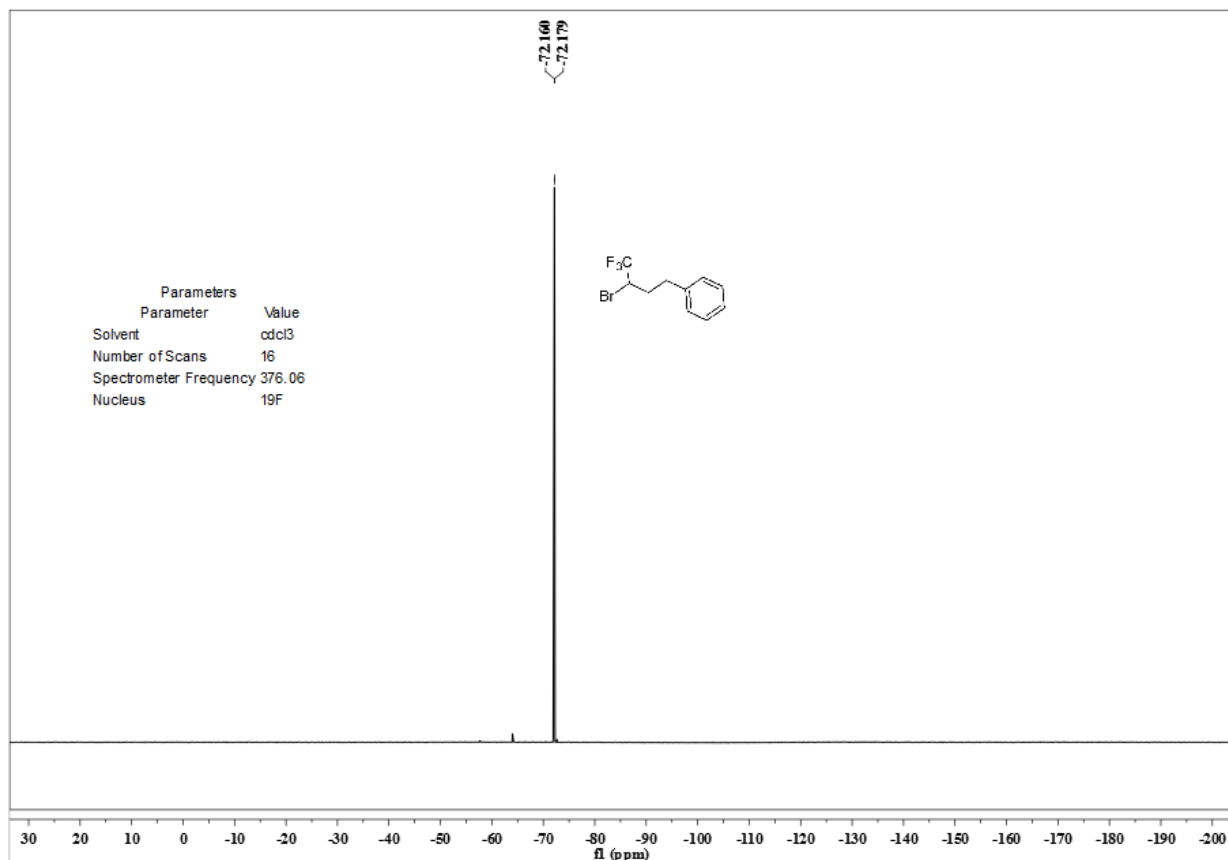
2-Bromo-1,1,1-trifluorohexane (2a).



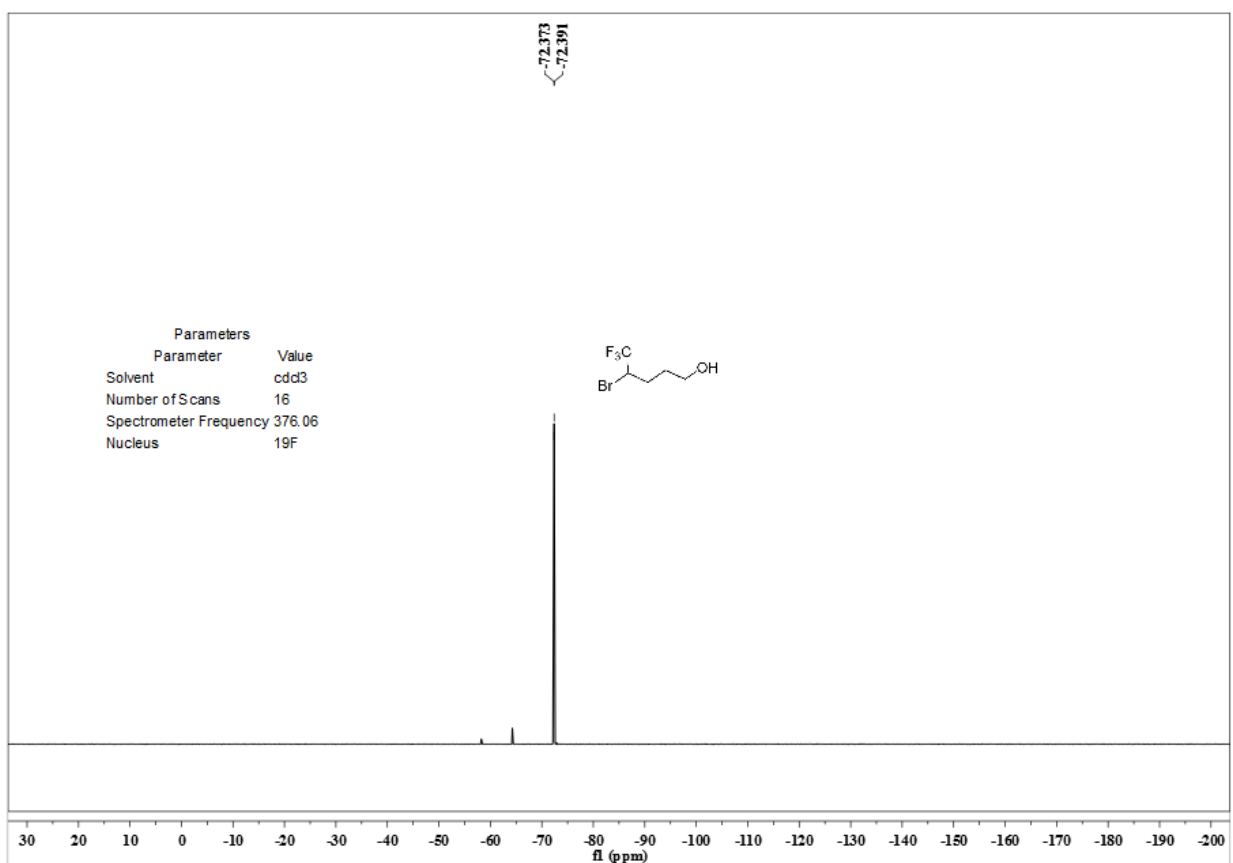
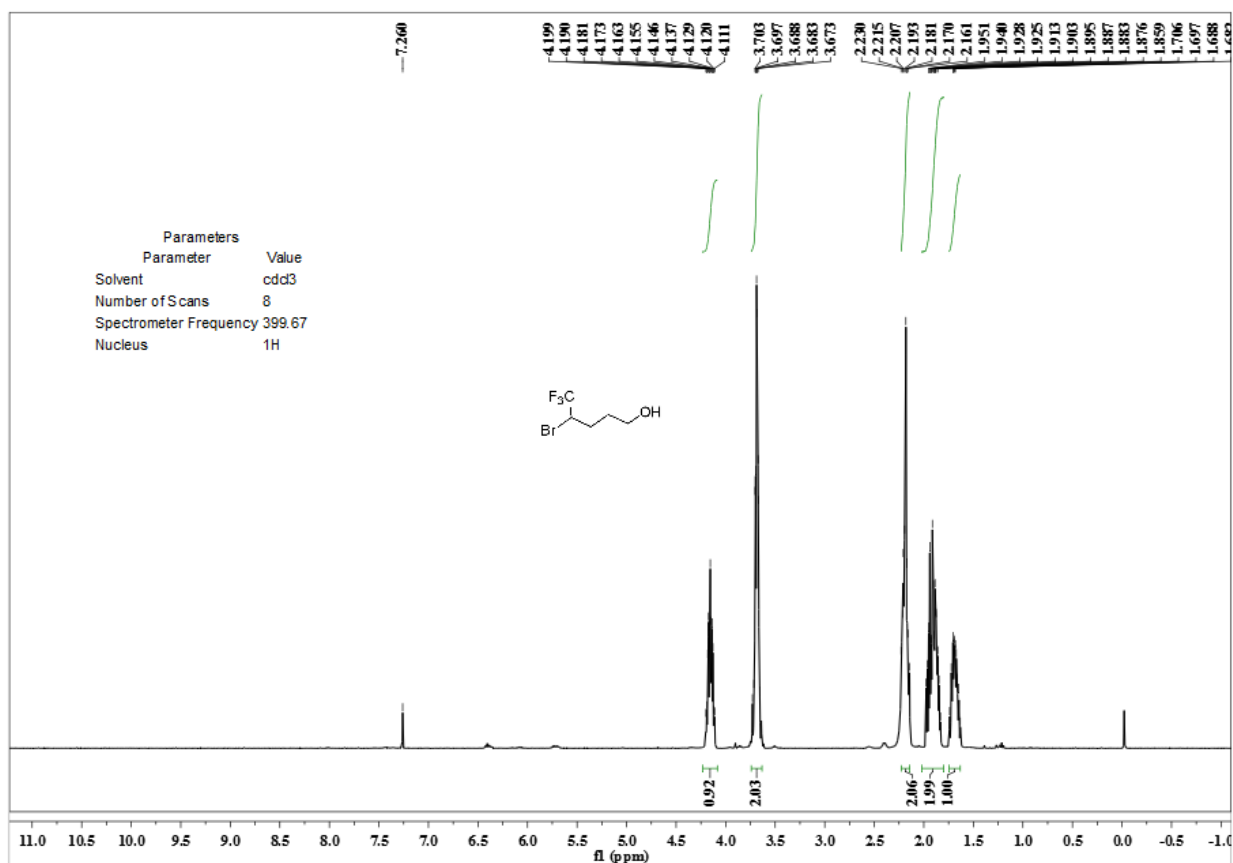


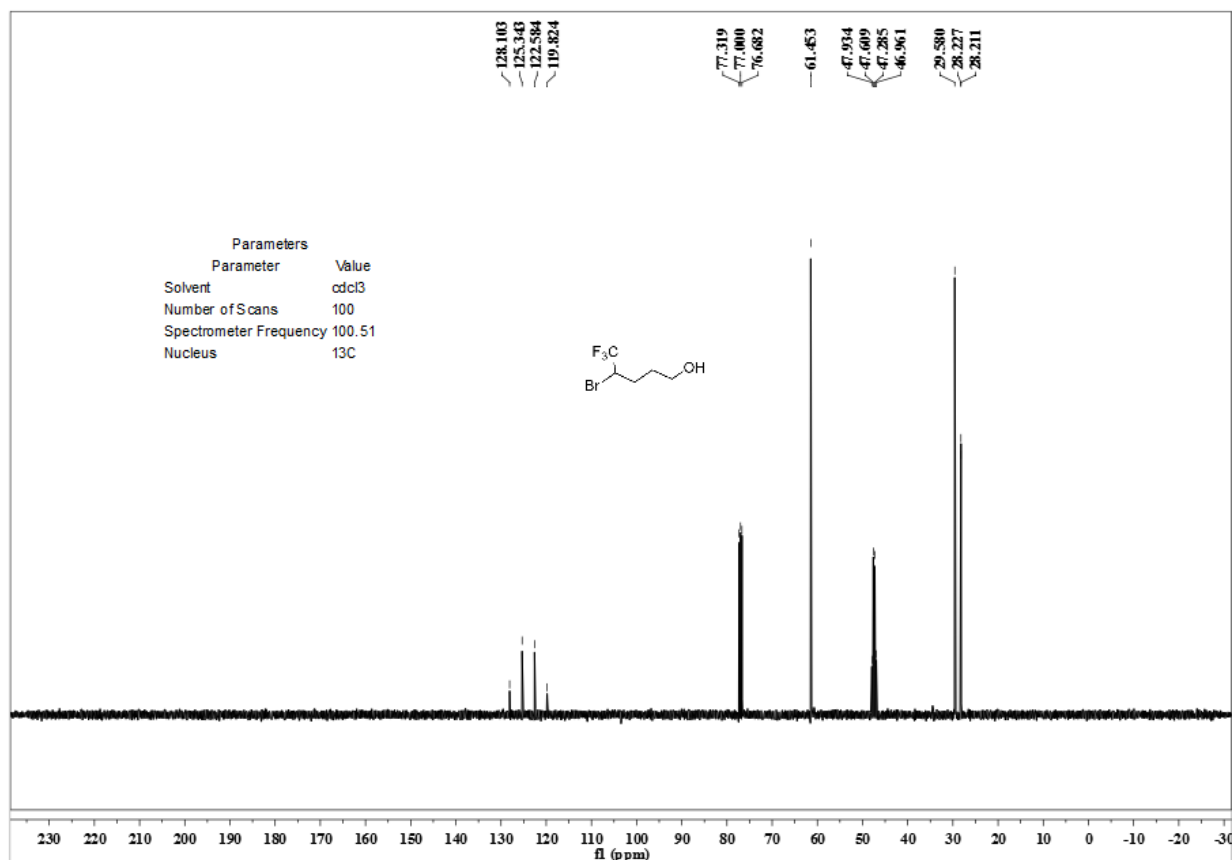
(3-Bromo-4,4,4-trifluorobutyl)benzene (2b).



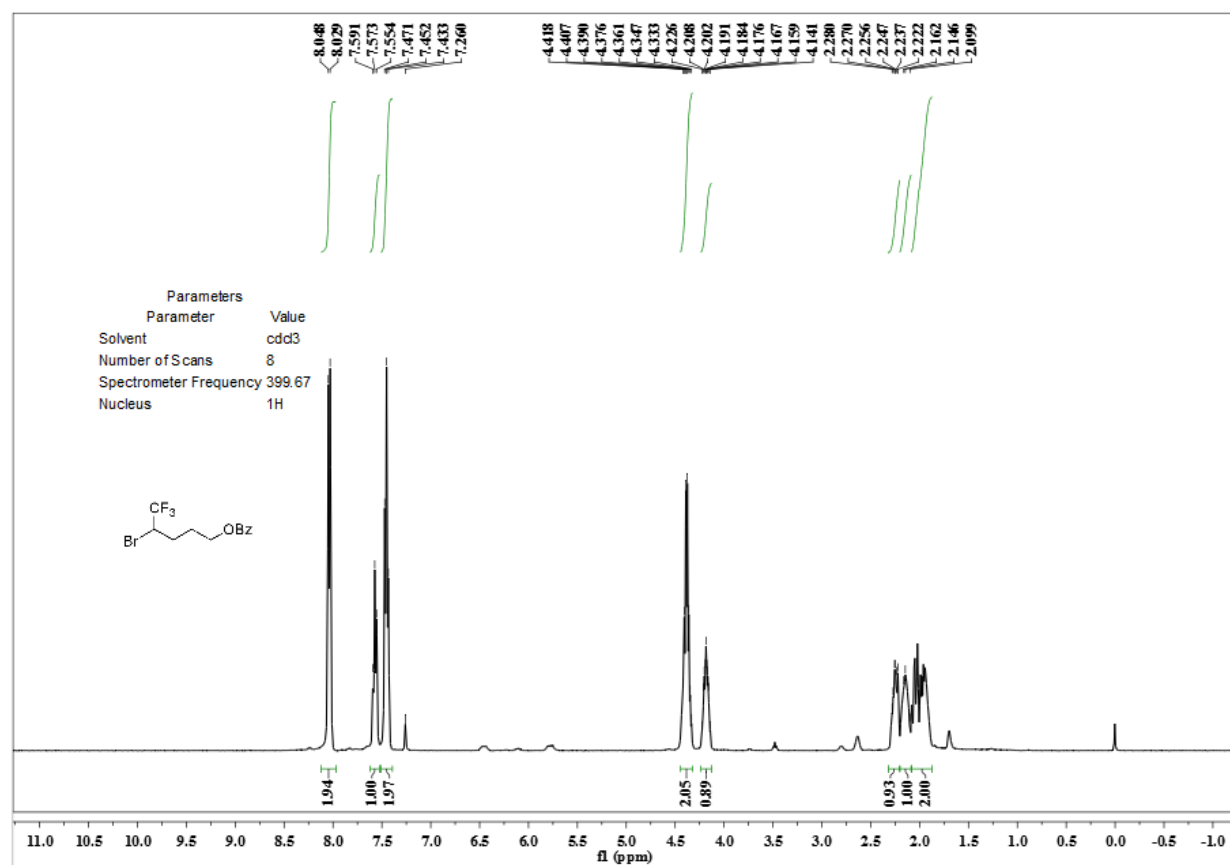


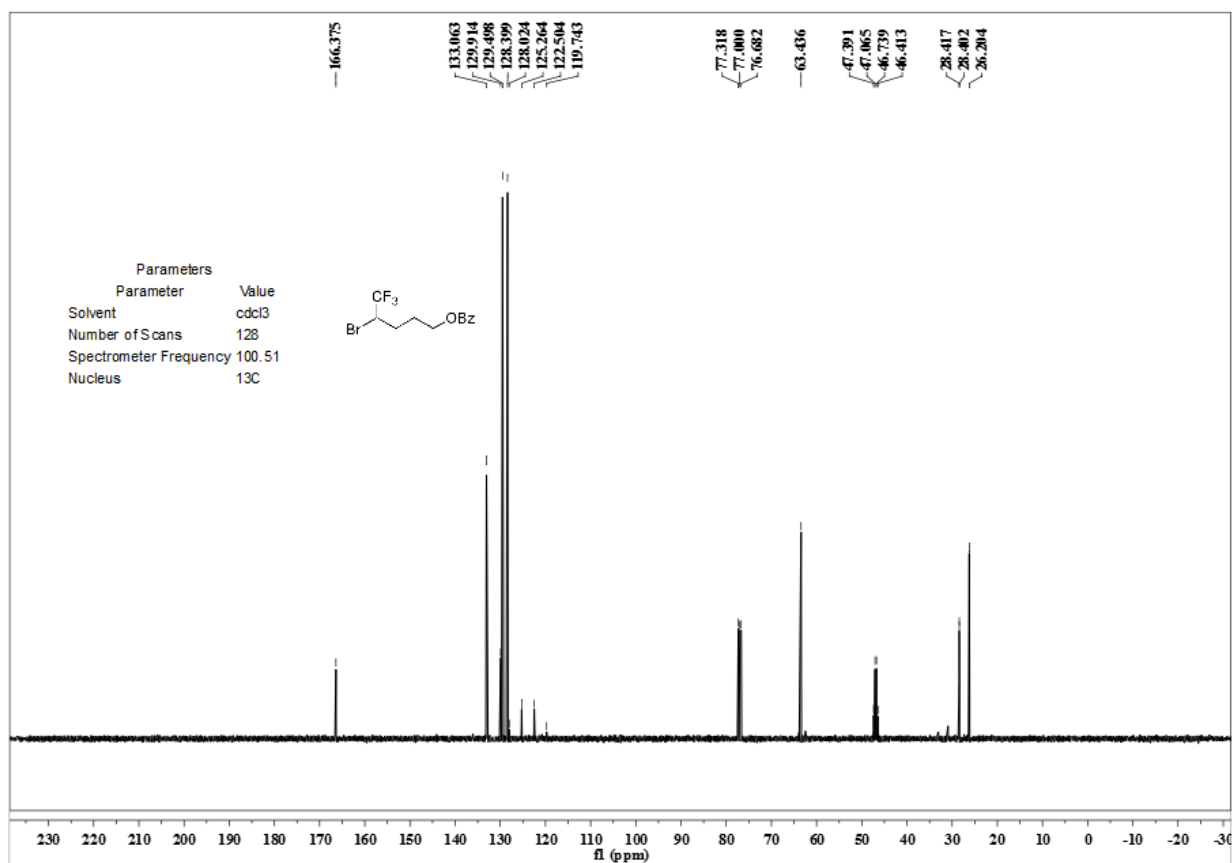
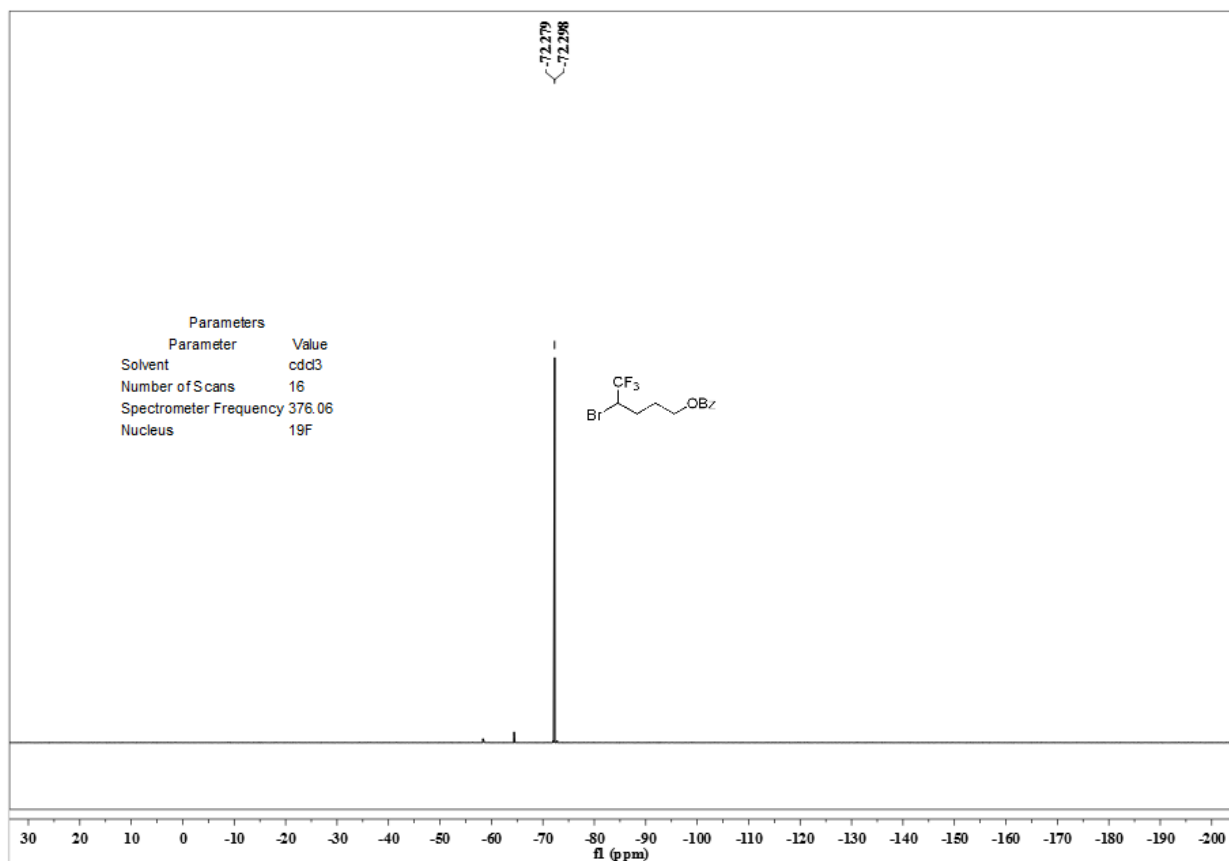
4-Bromo-5,5,5-trifluoropentan-1-ol (2c).



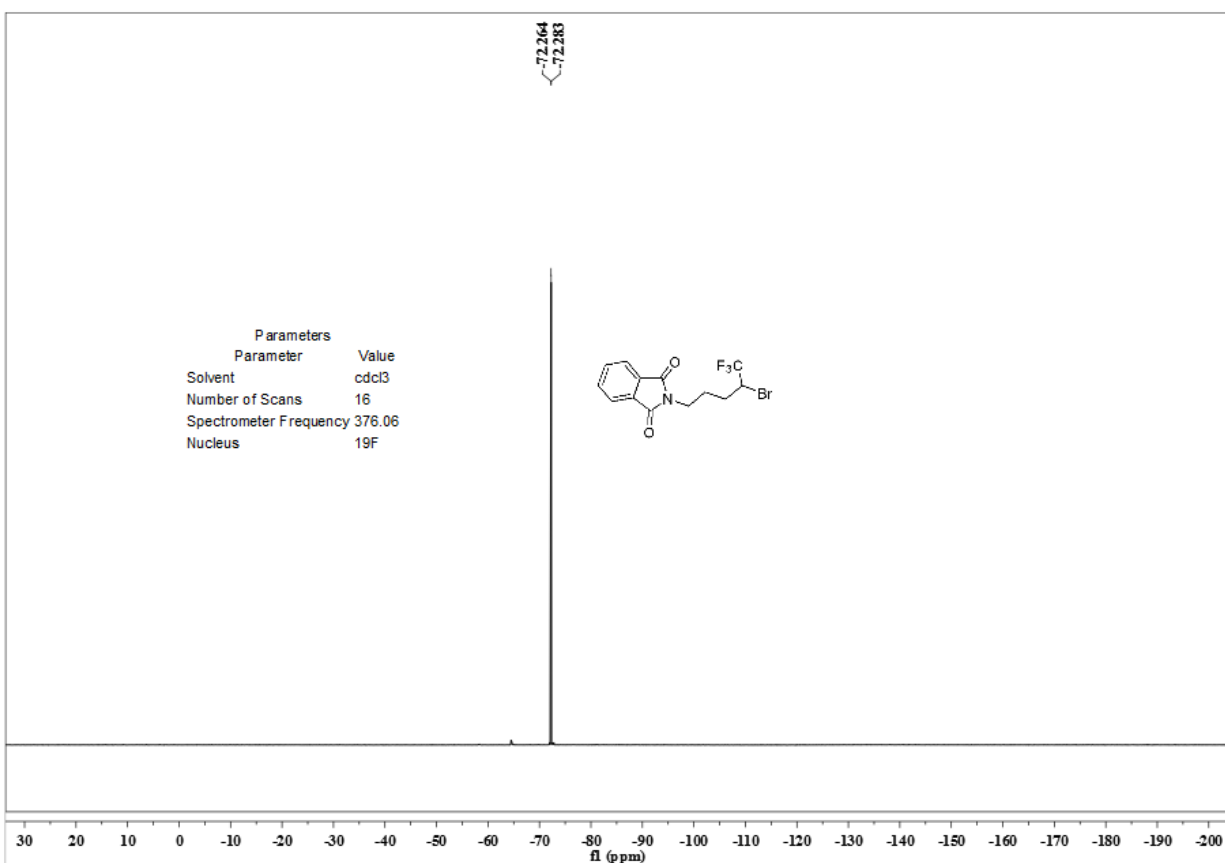
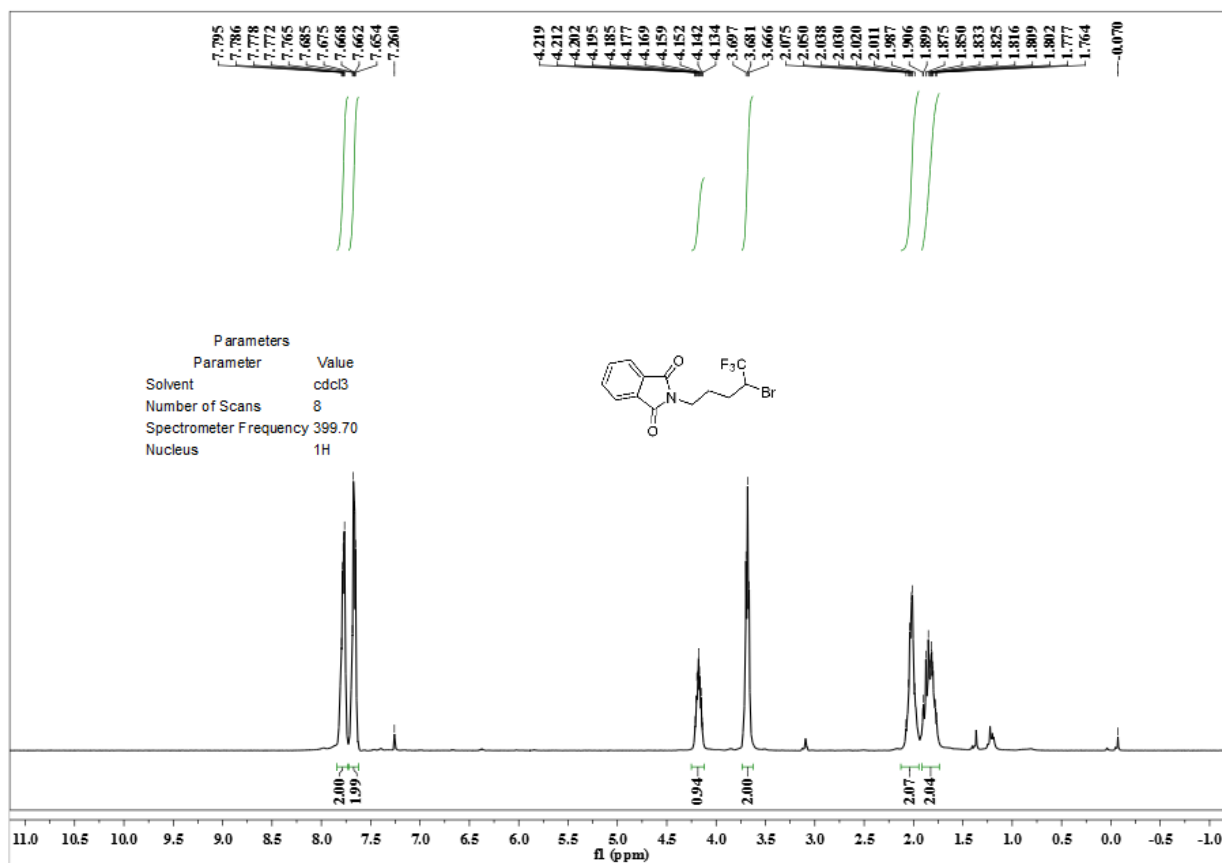


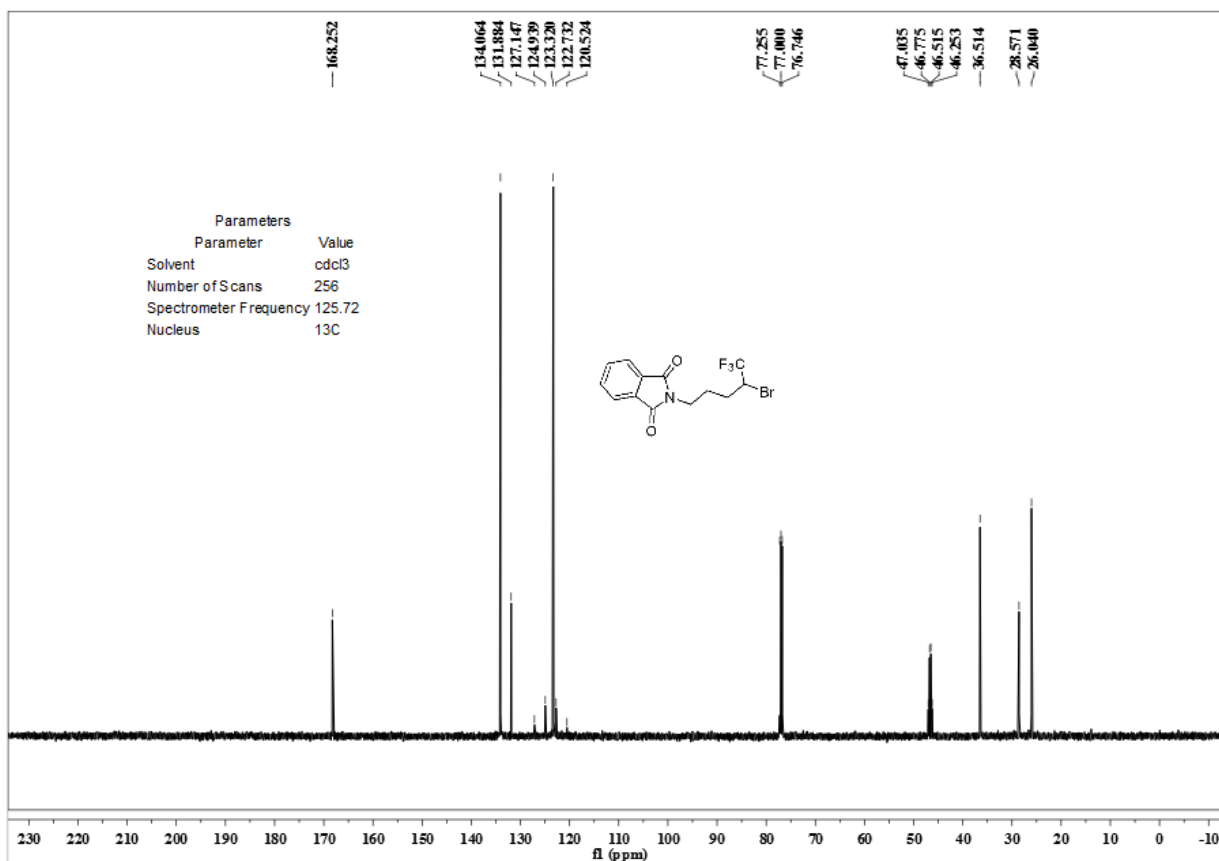
4-Bromo-5,5,5-trifluoropentyl benzoate (2d).



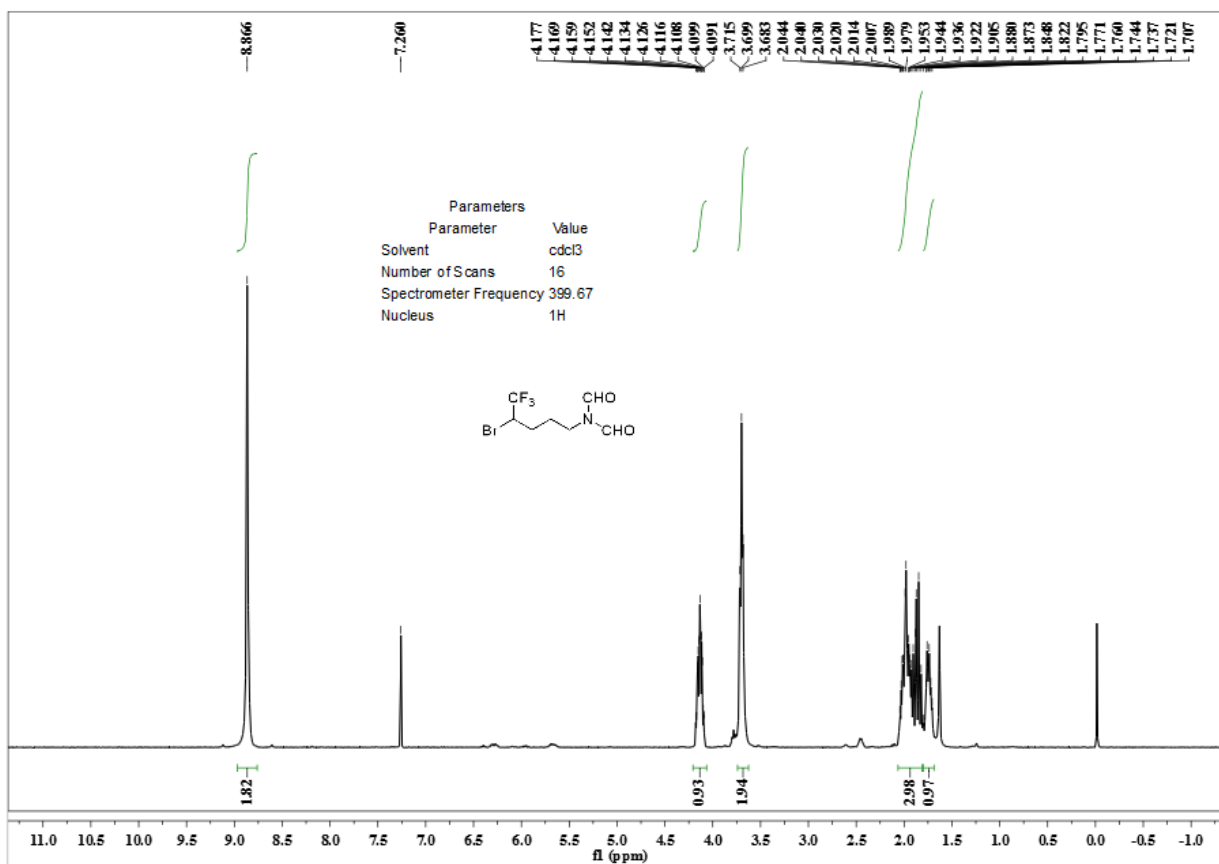


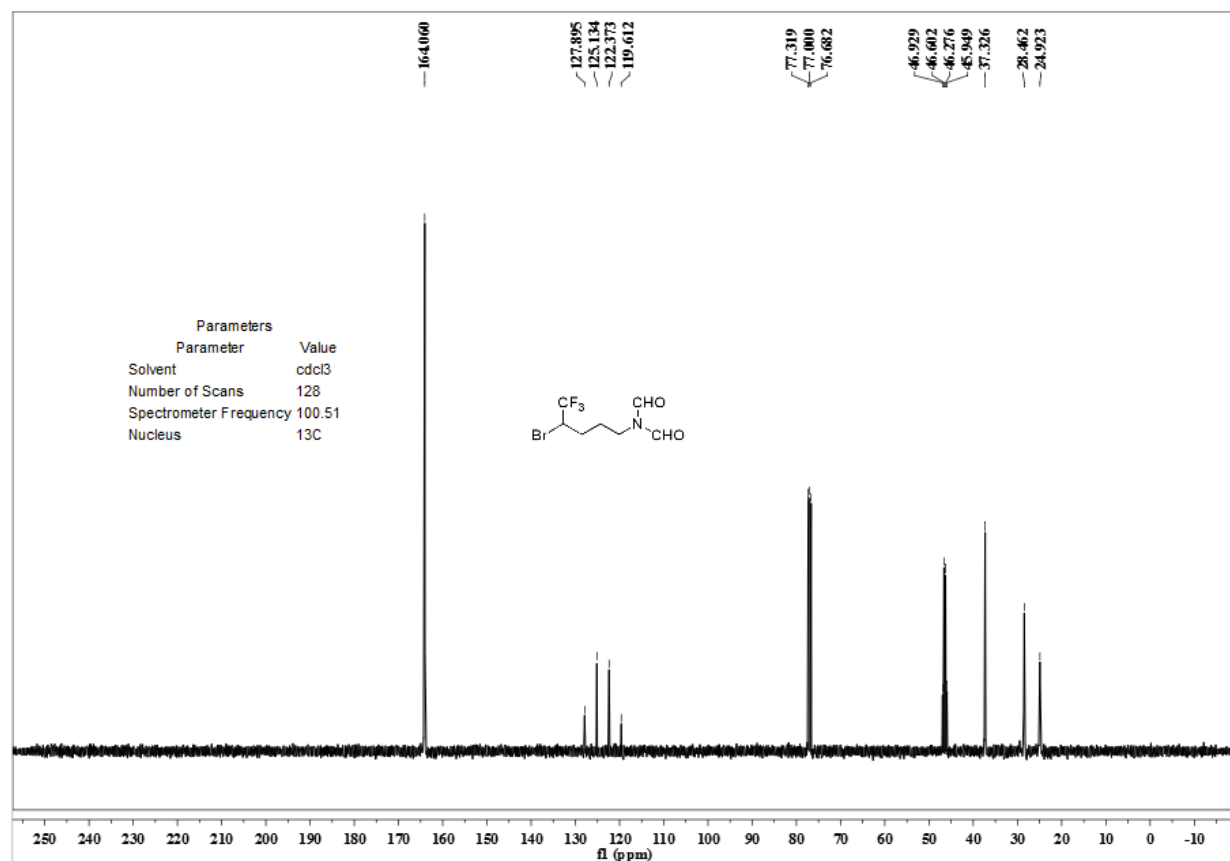
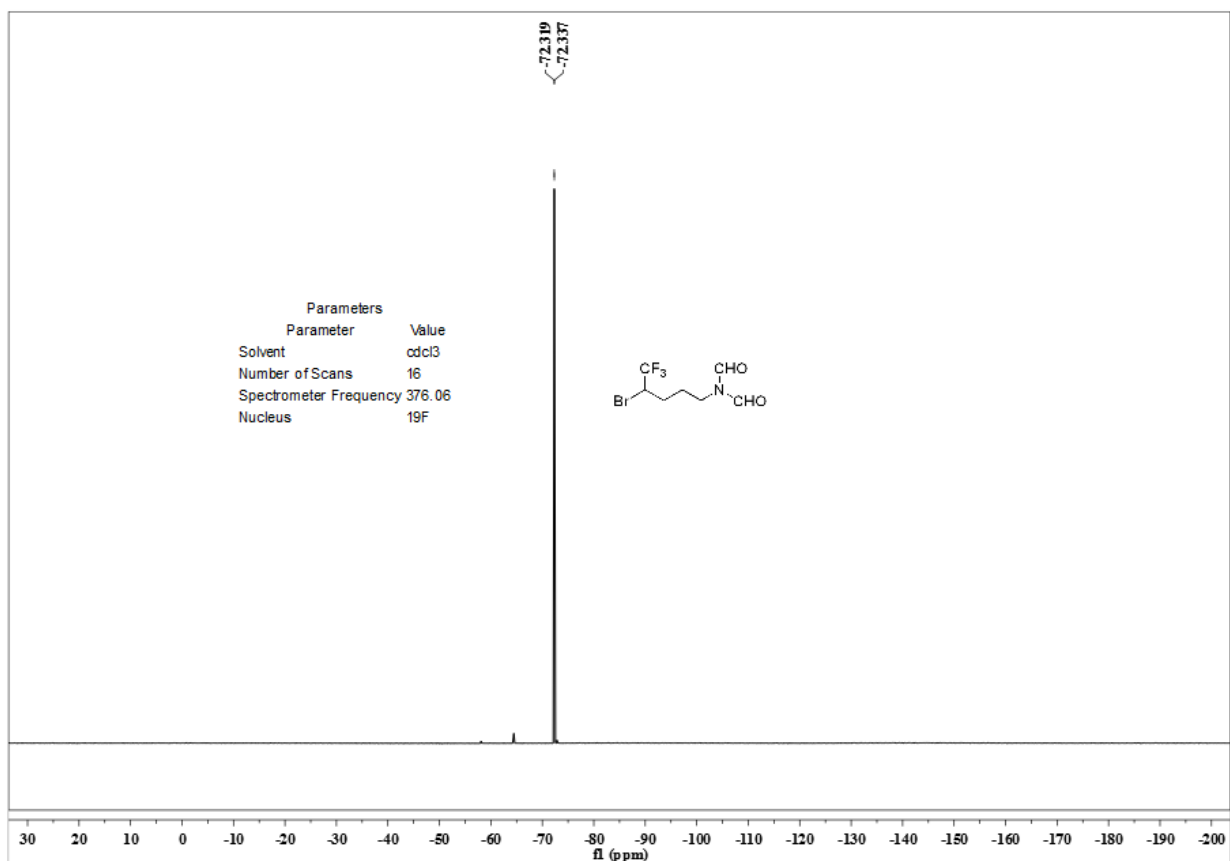
2-(4-Bromo-5,5,5-trifluoropentyl)-3a,7a-dihydro-1*H*-isoindole-1,3(2*H*)-dione (2e).



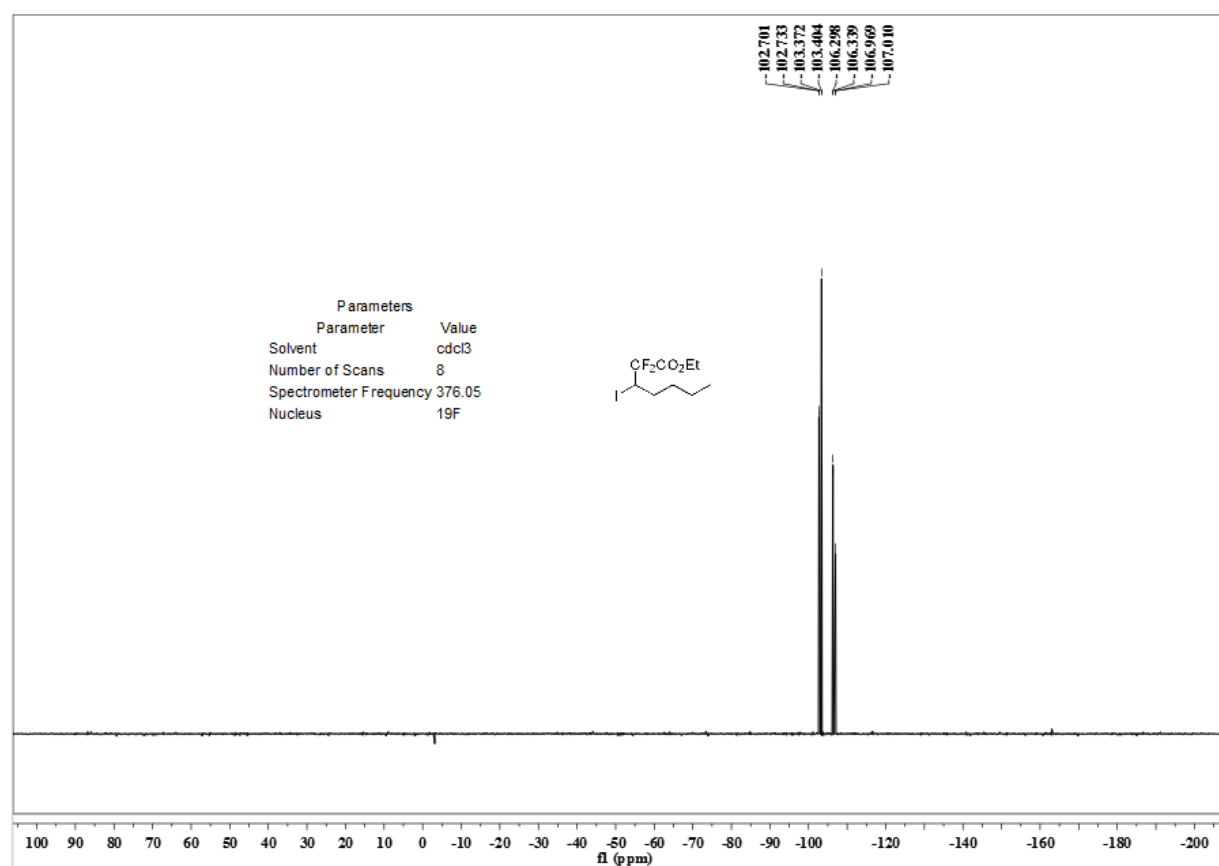
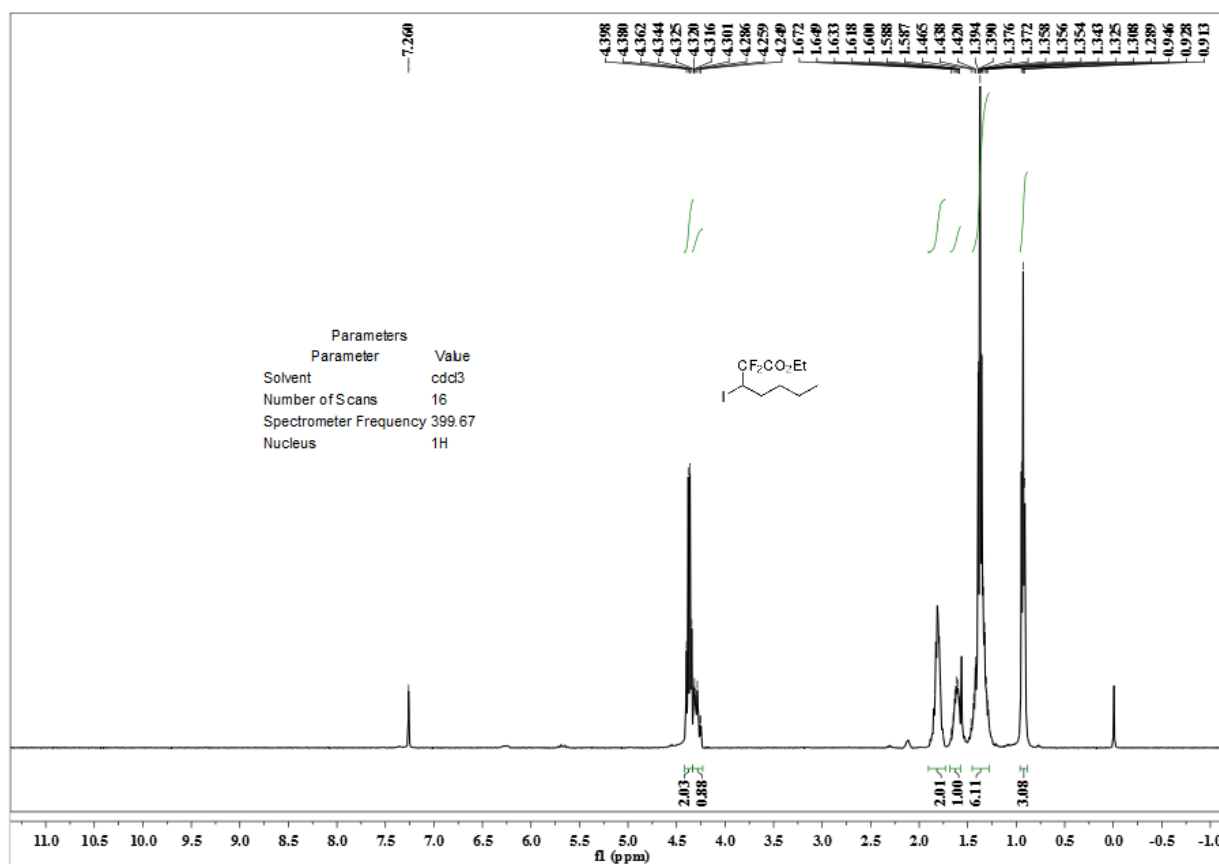


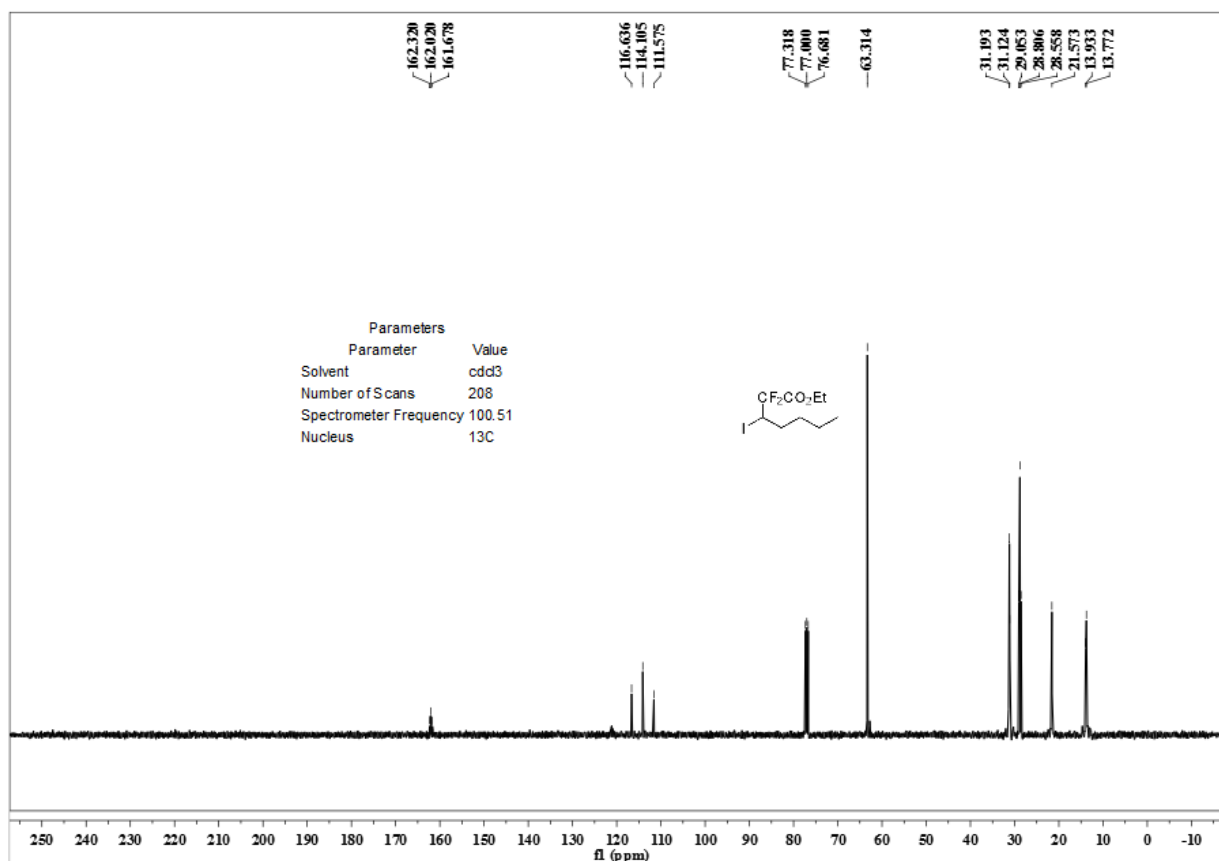
N-(4-Bromo-5, 5, 5-trifluoropentyl)-N-formylformamide (2f)



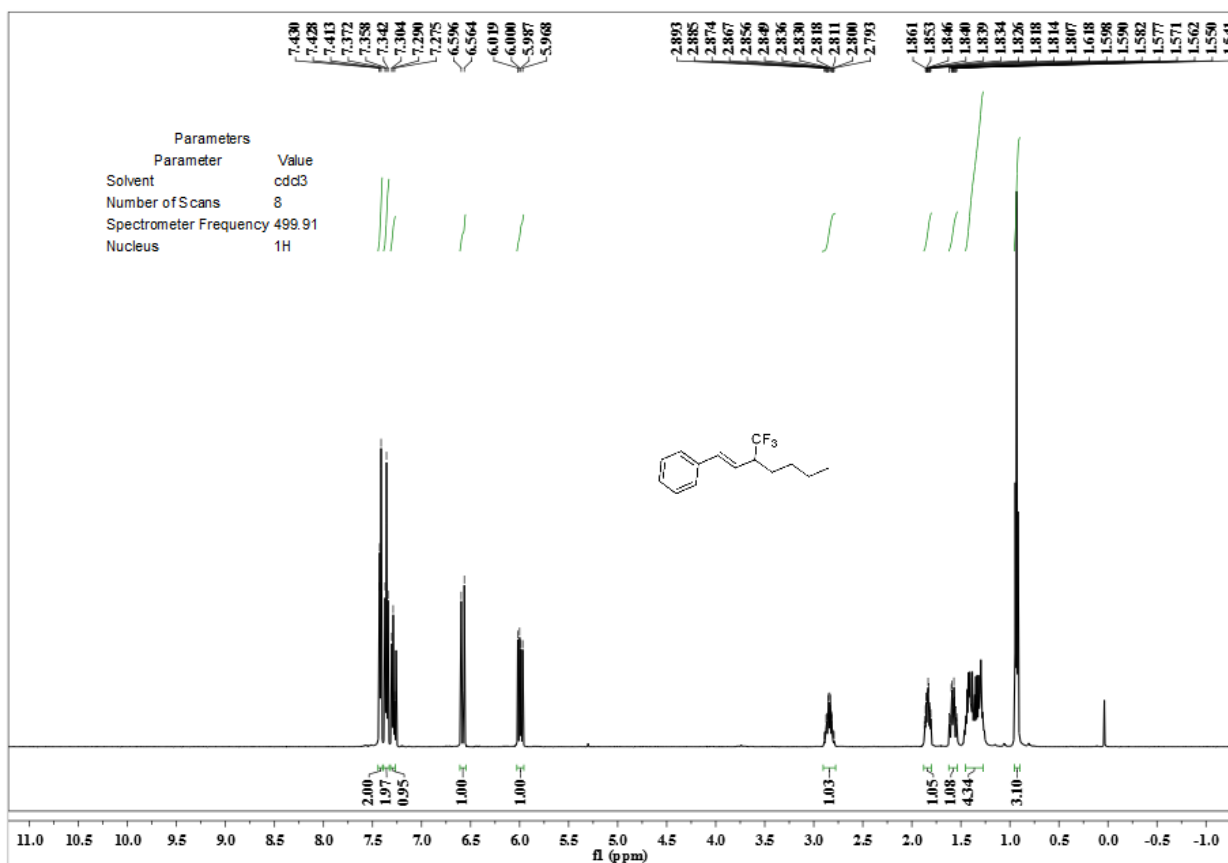


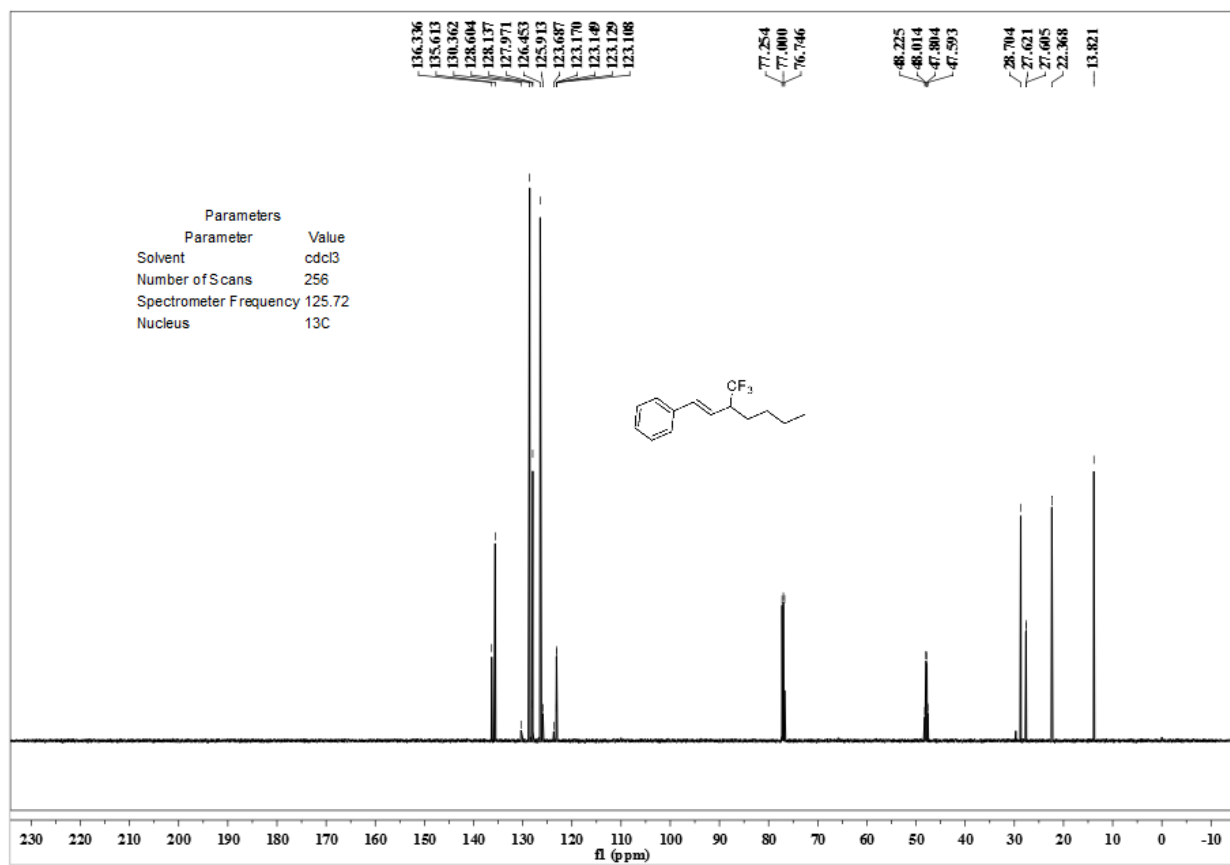
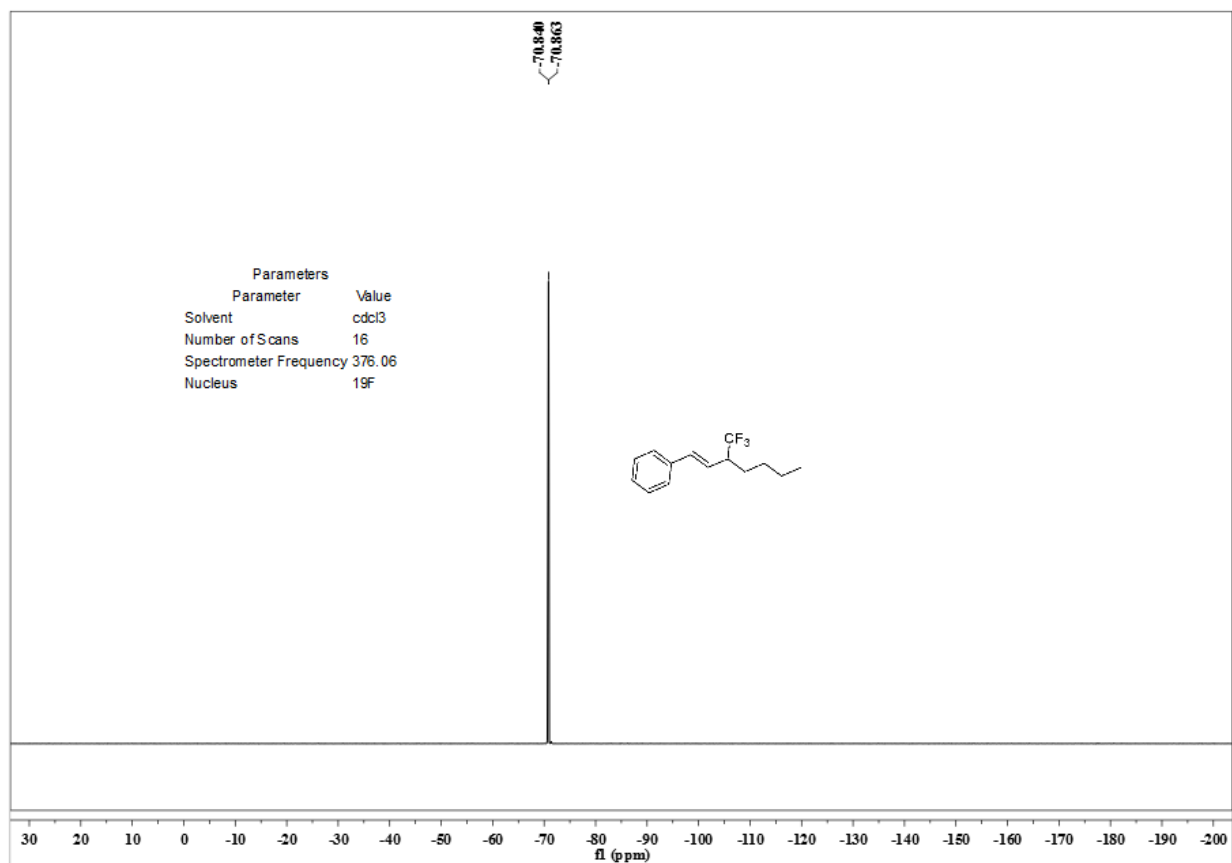
Ethyl 2, 2-difluoro-3-iodoheptanoate (2g).



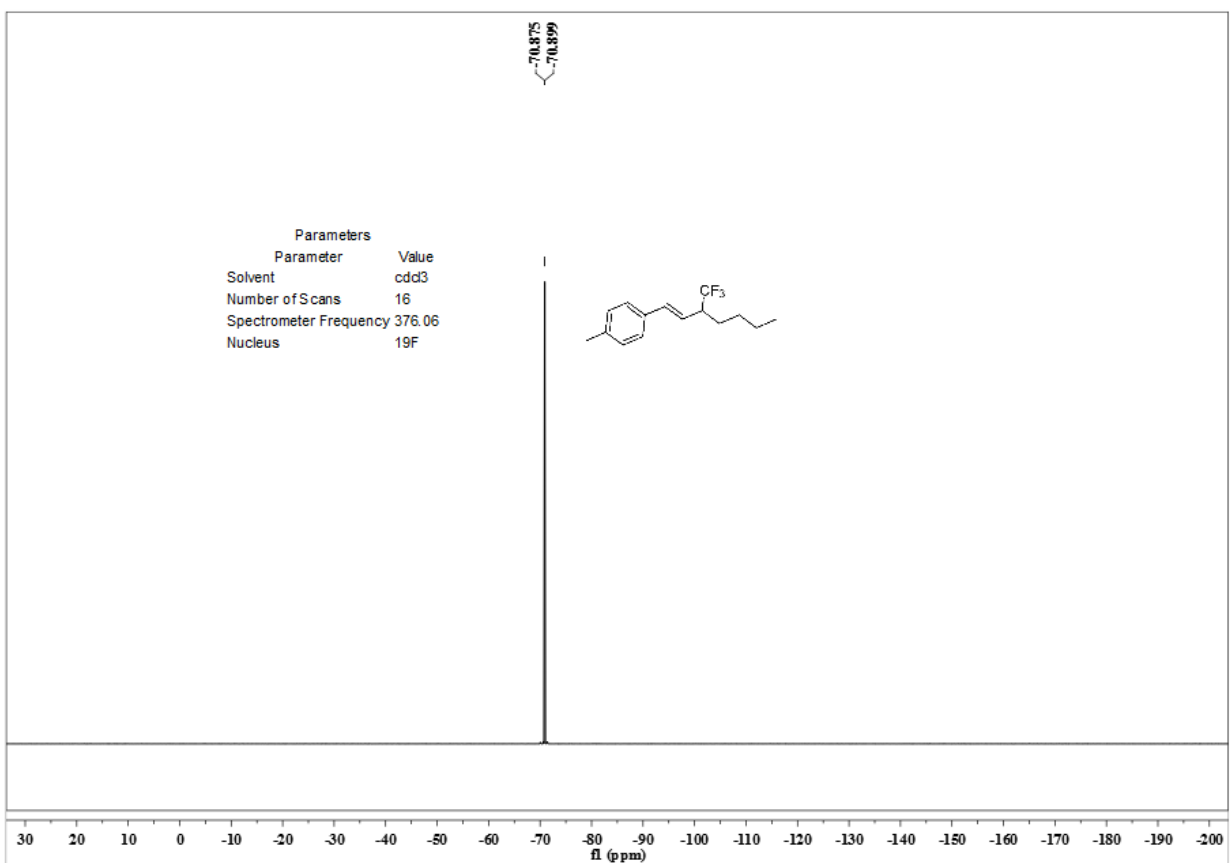
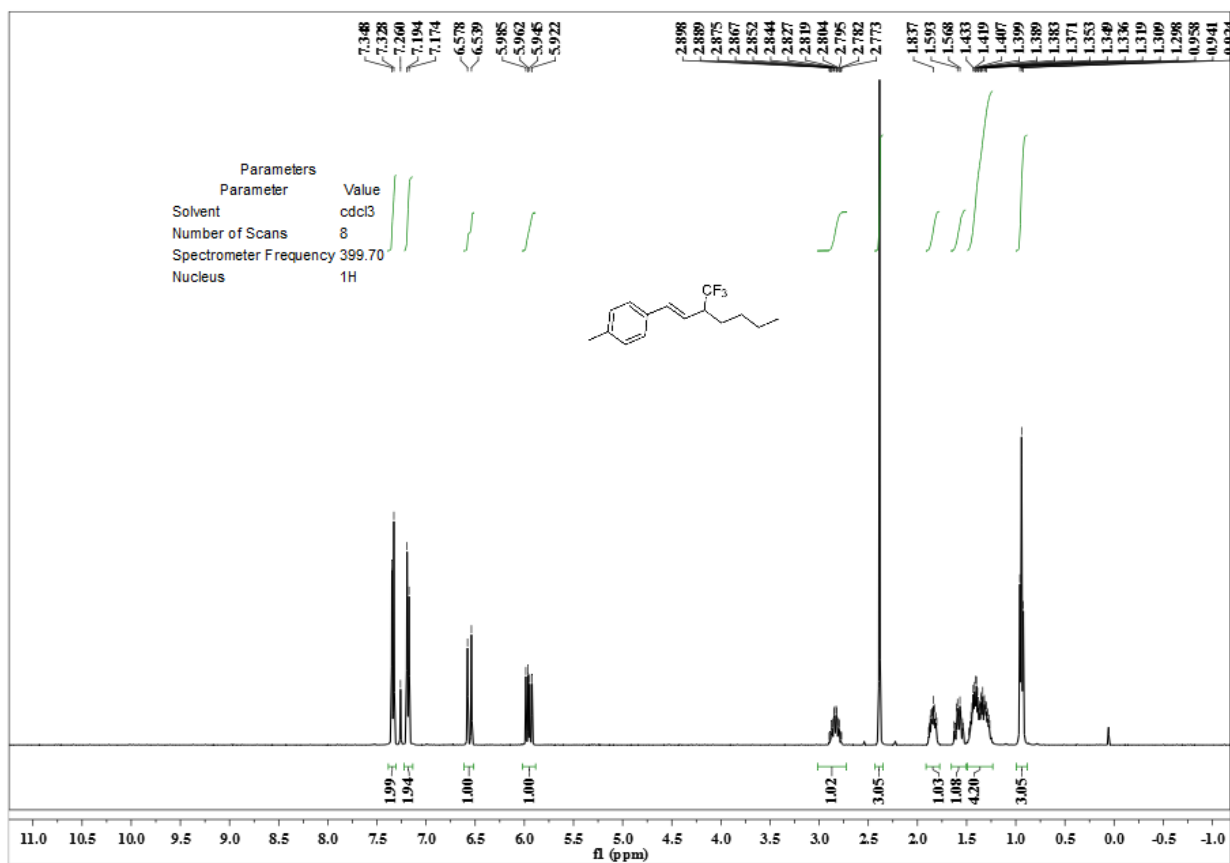


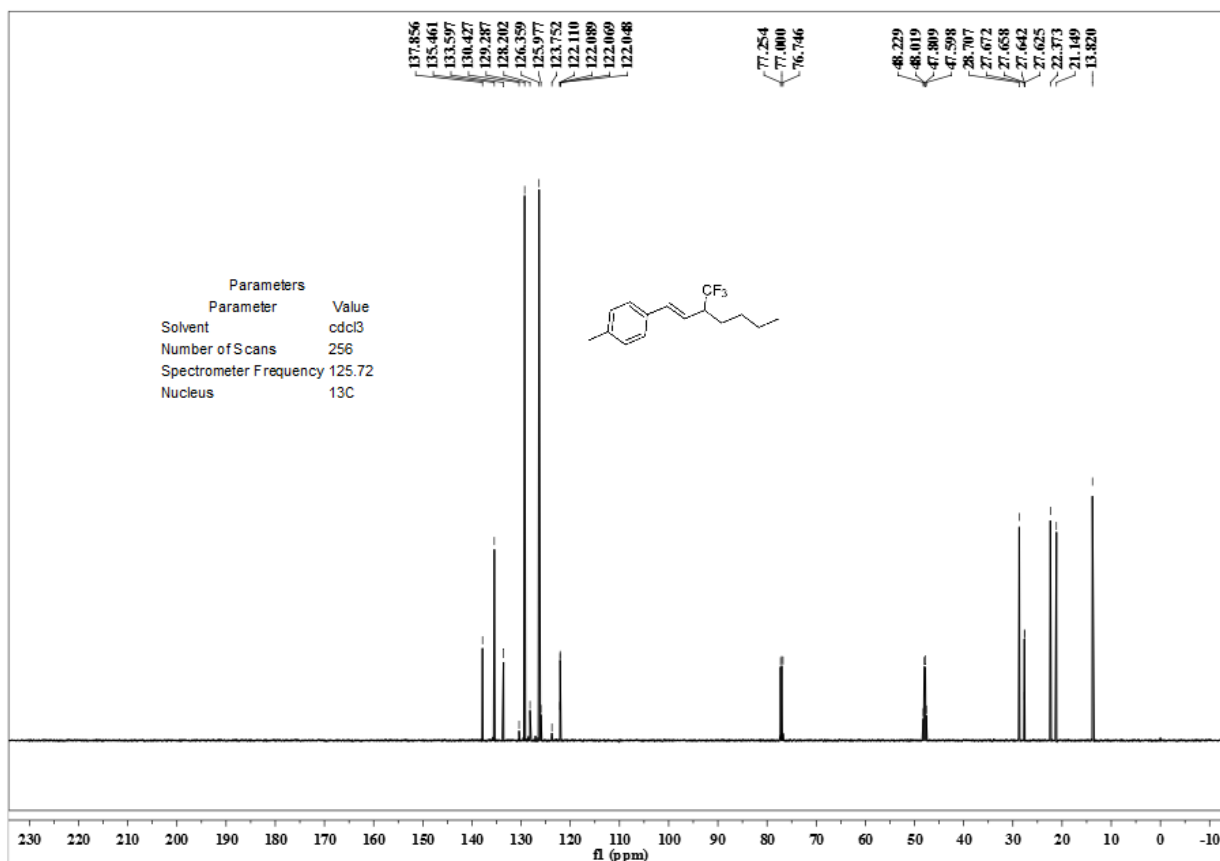
(*E*)-(3-(Trifluoromethyl)hept-1-en-1-yl)benzene (3a).



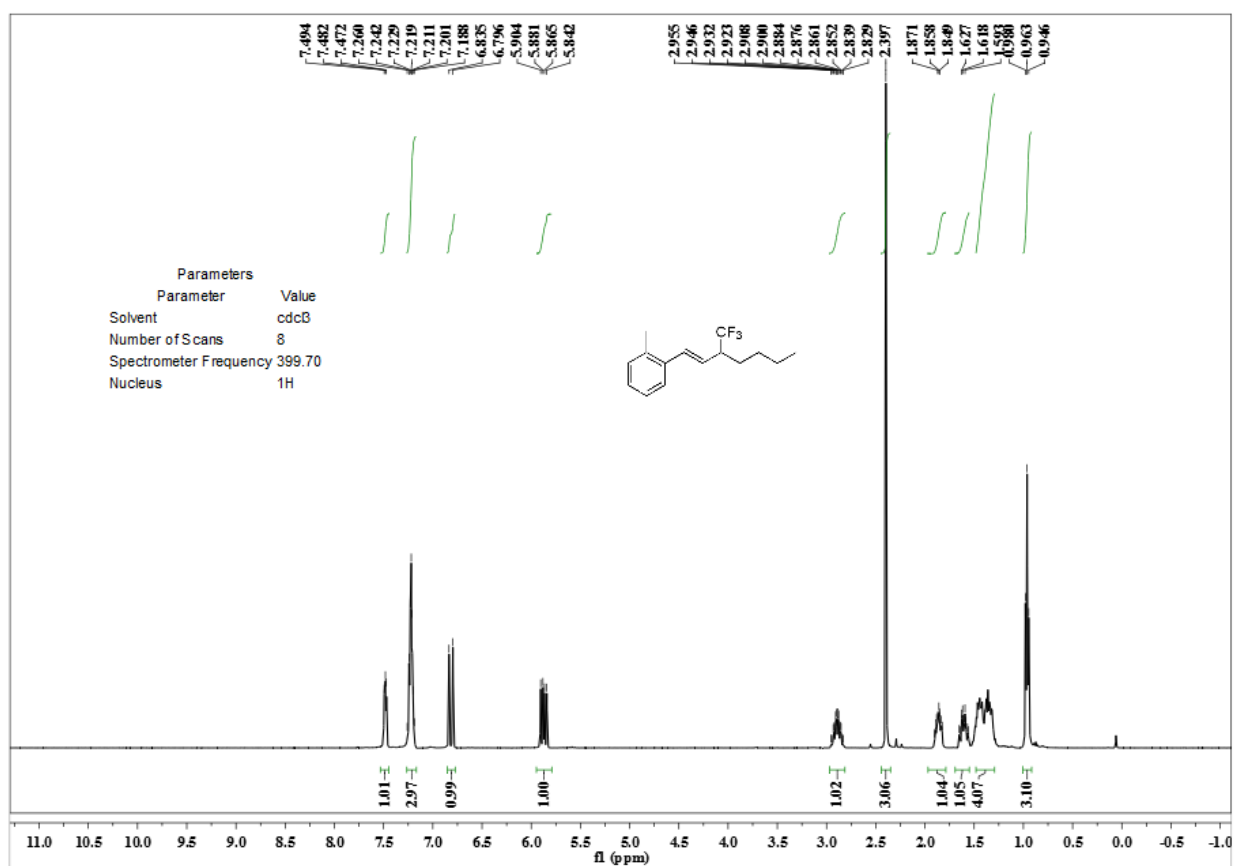


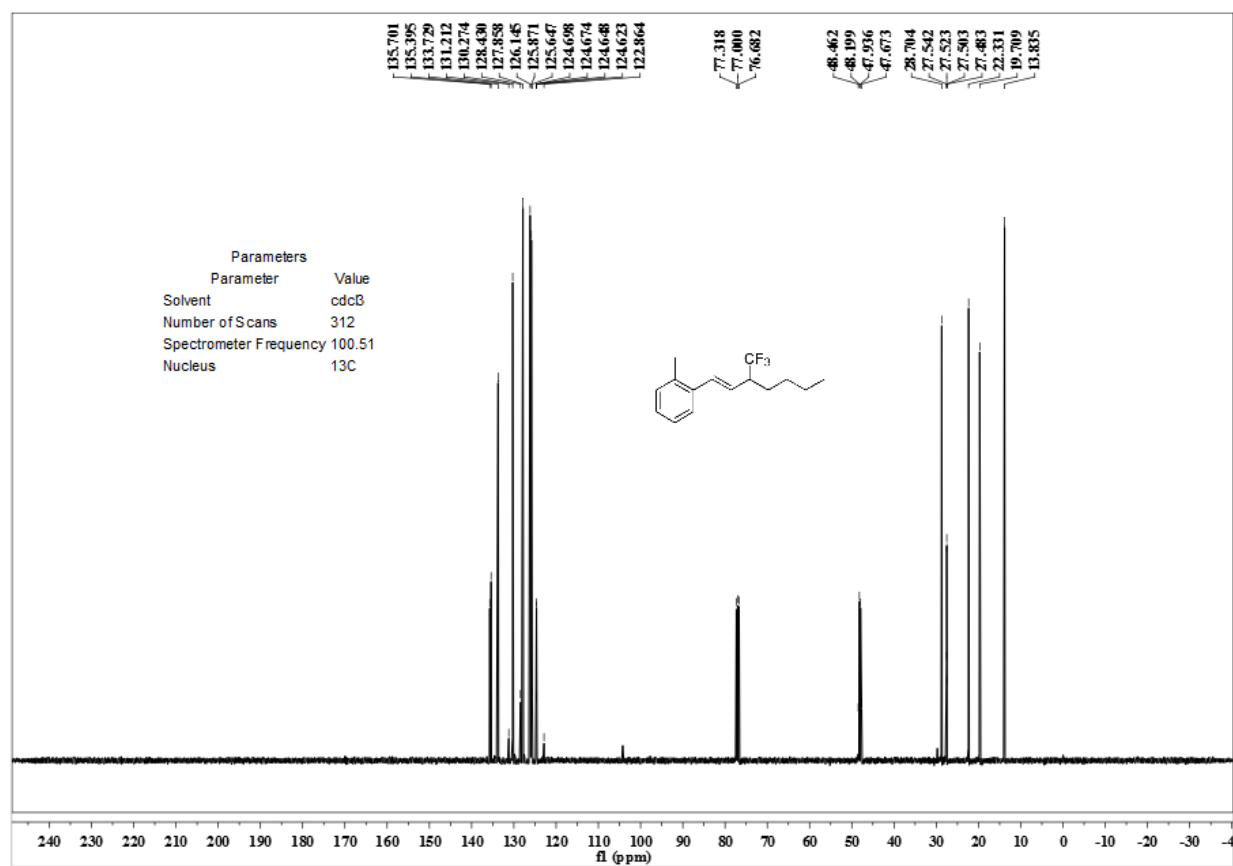
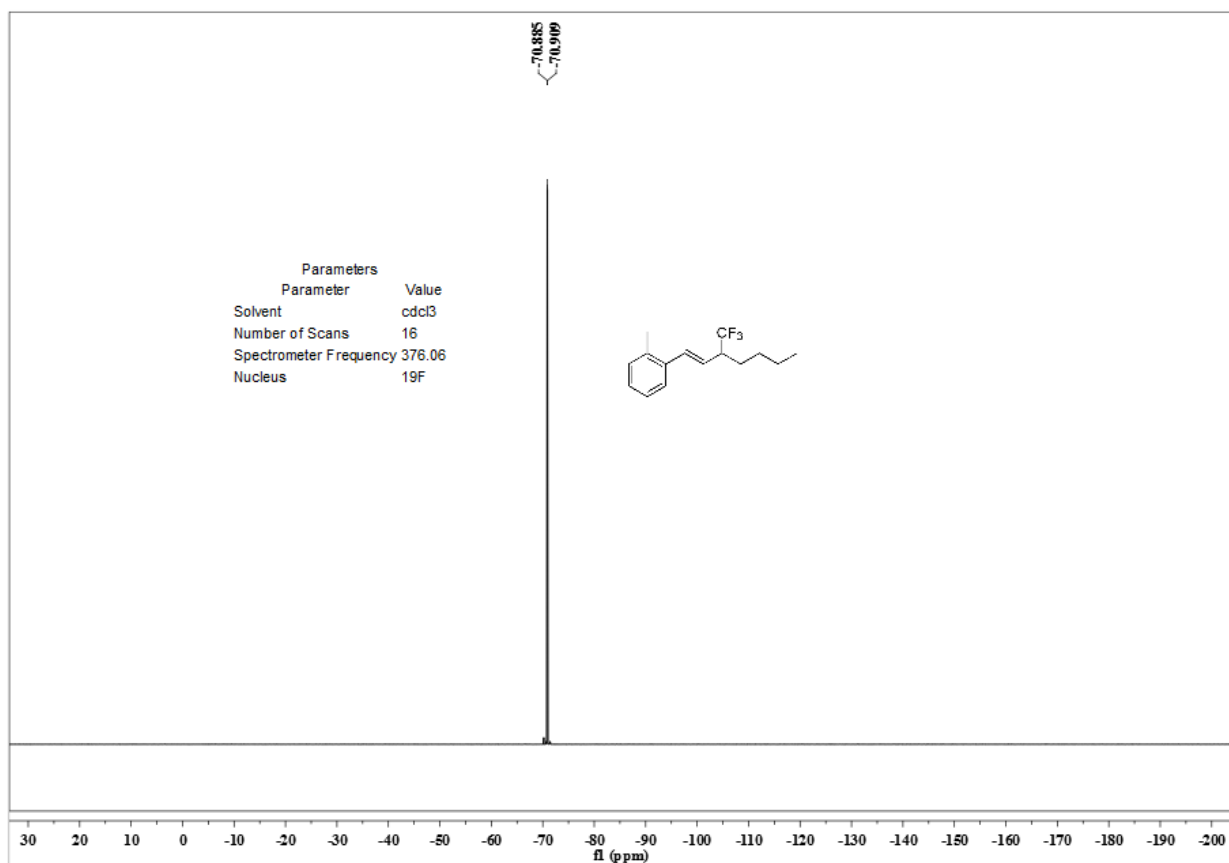
(E)-1-Methyl-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3b).



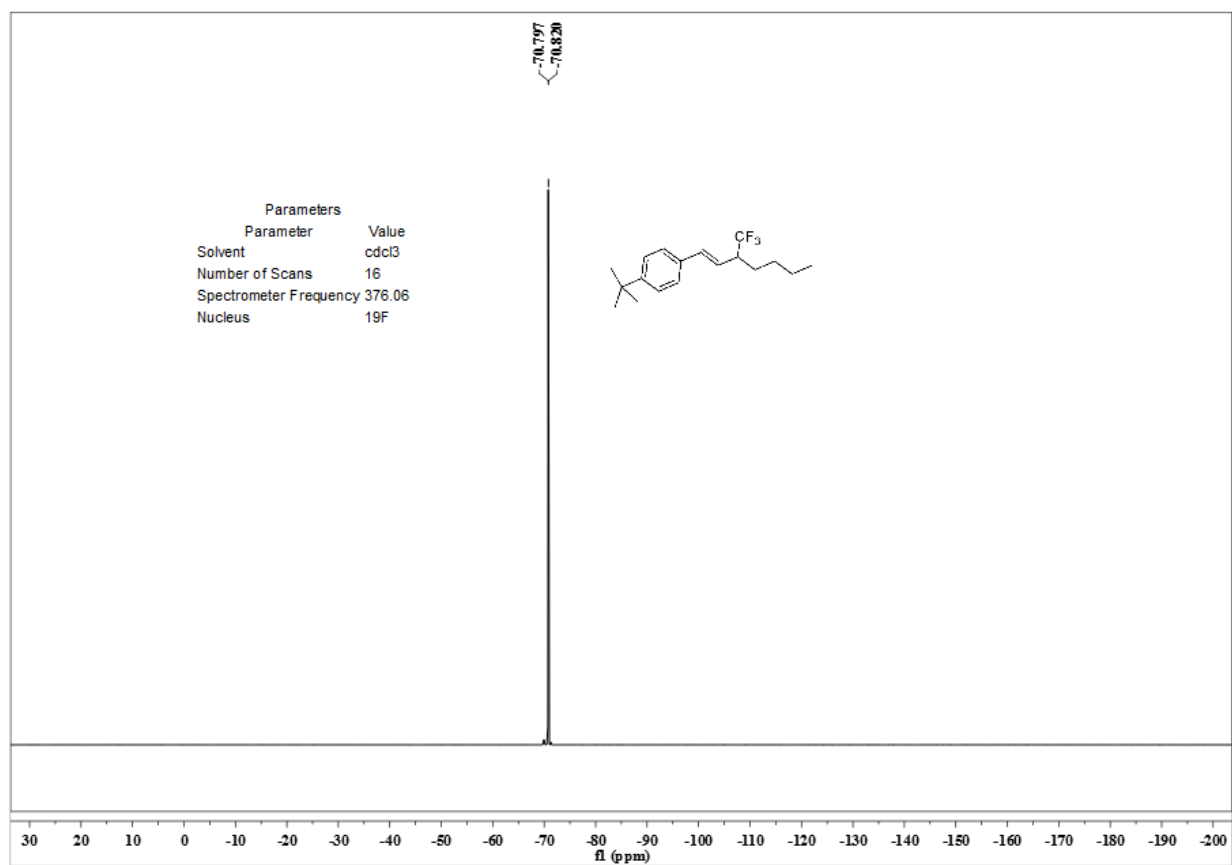
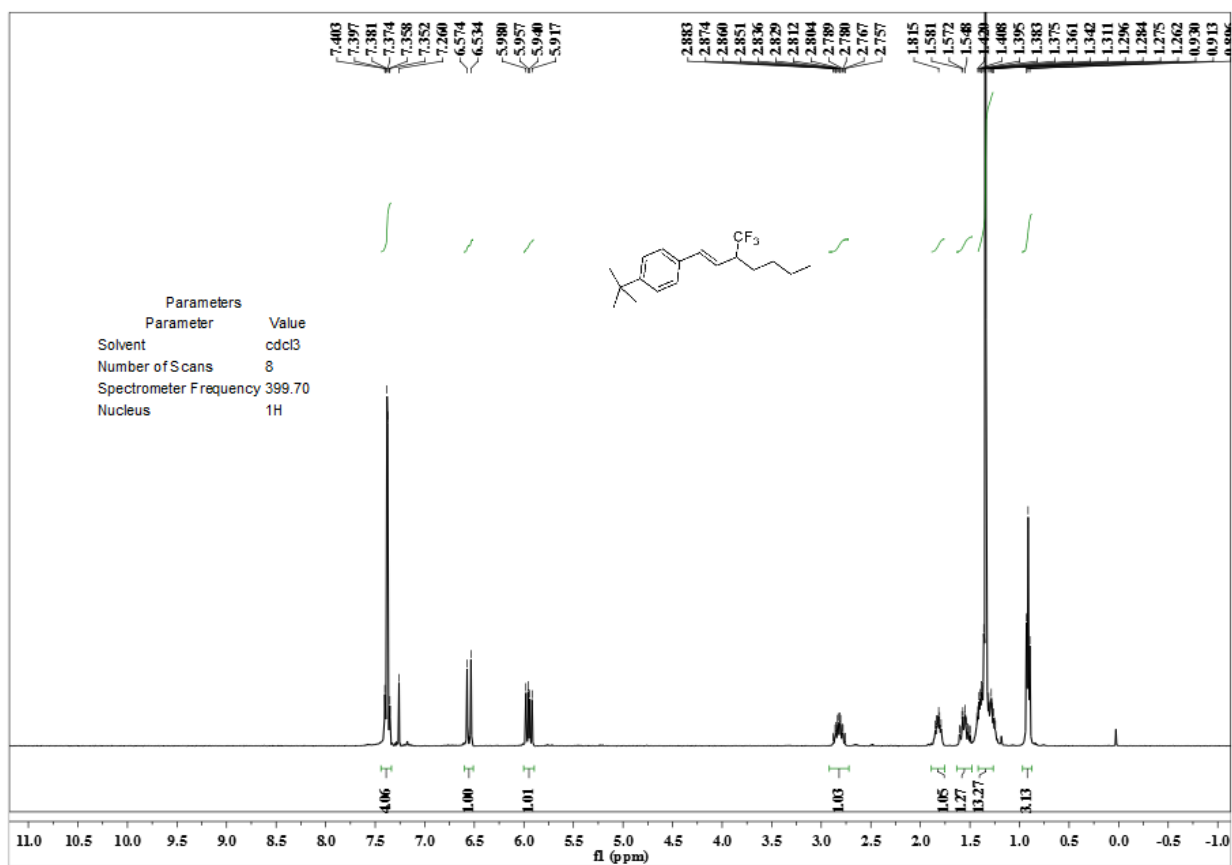


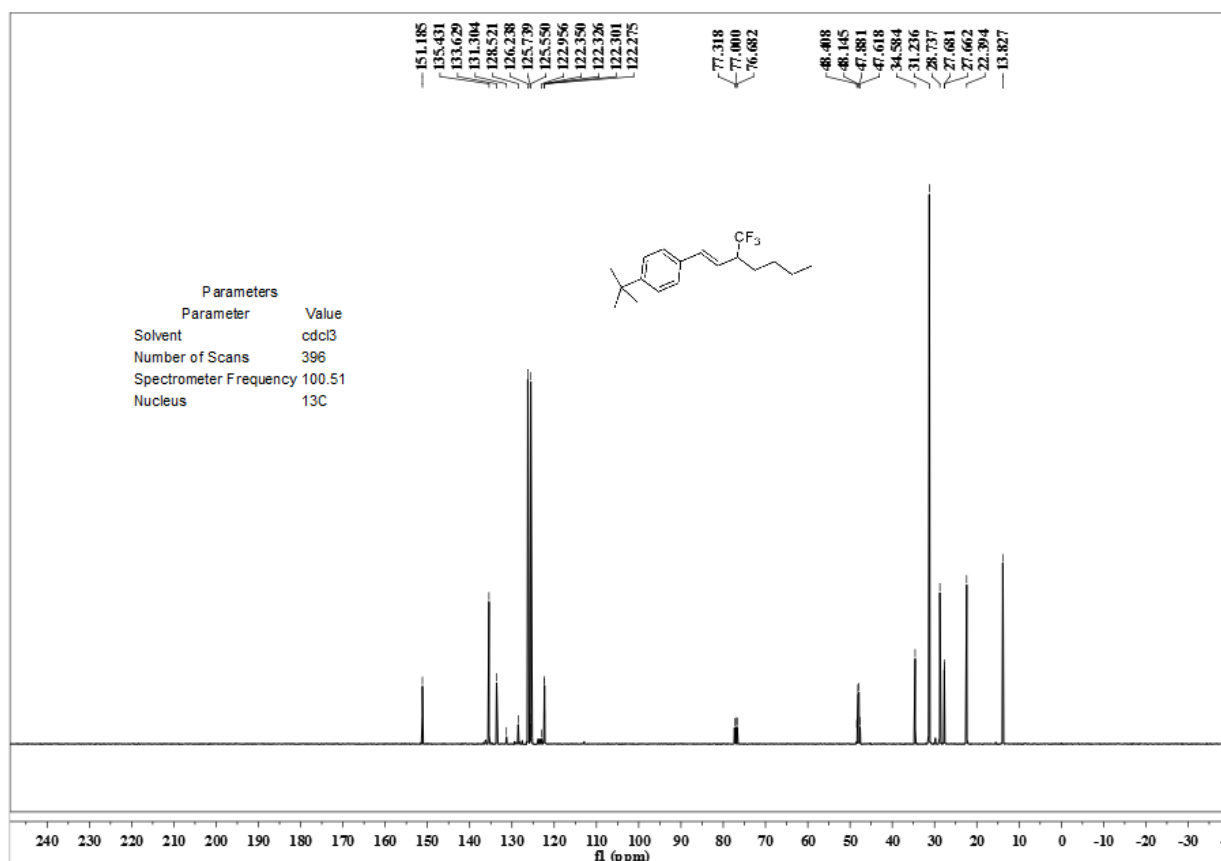
(*E*)-1-Methyl-2-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3c).



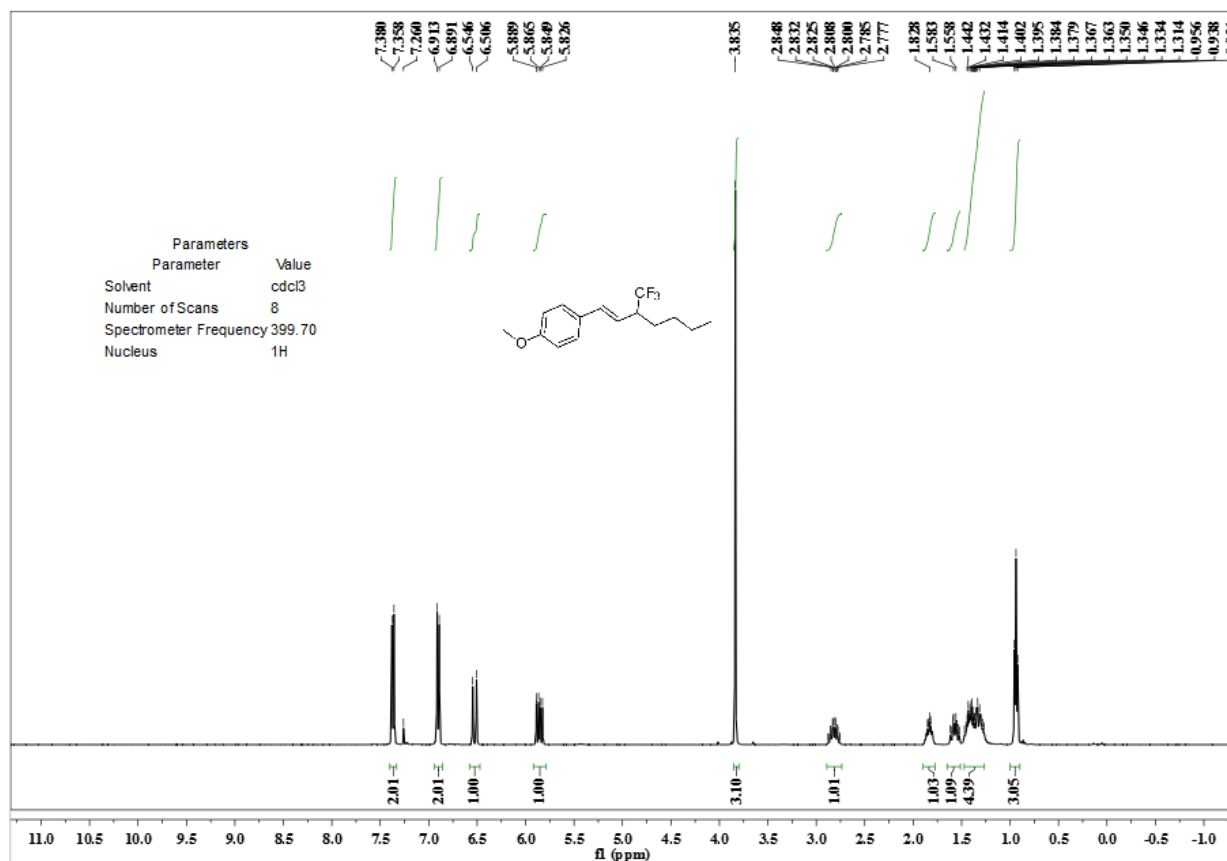


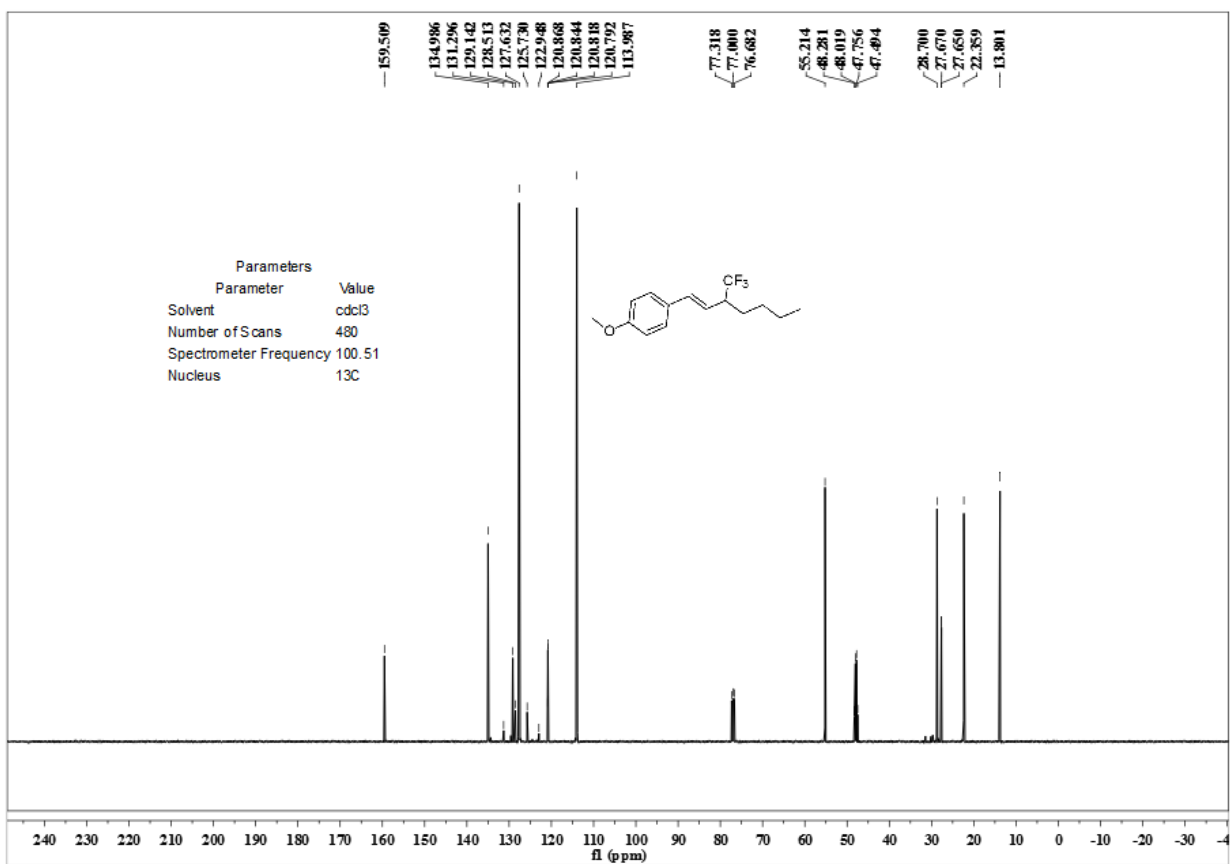
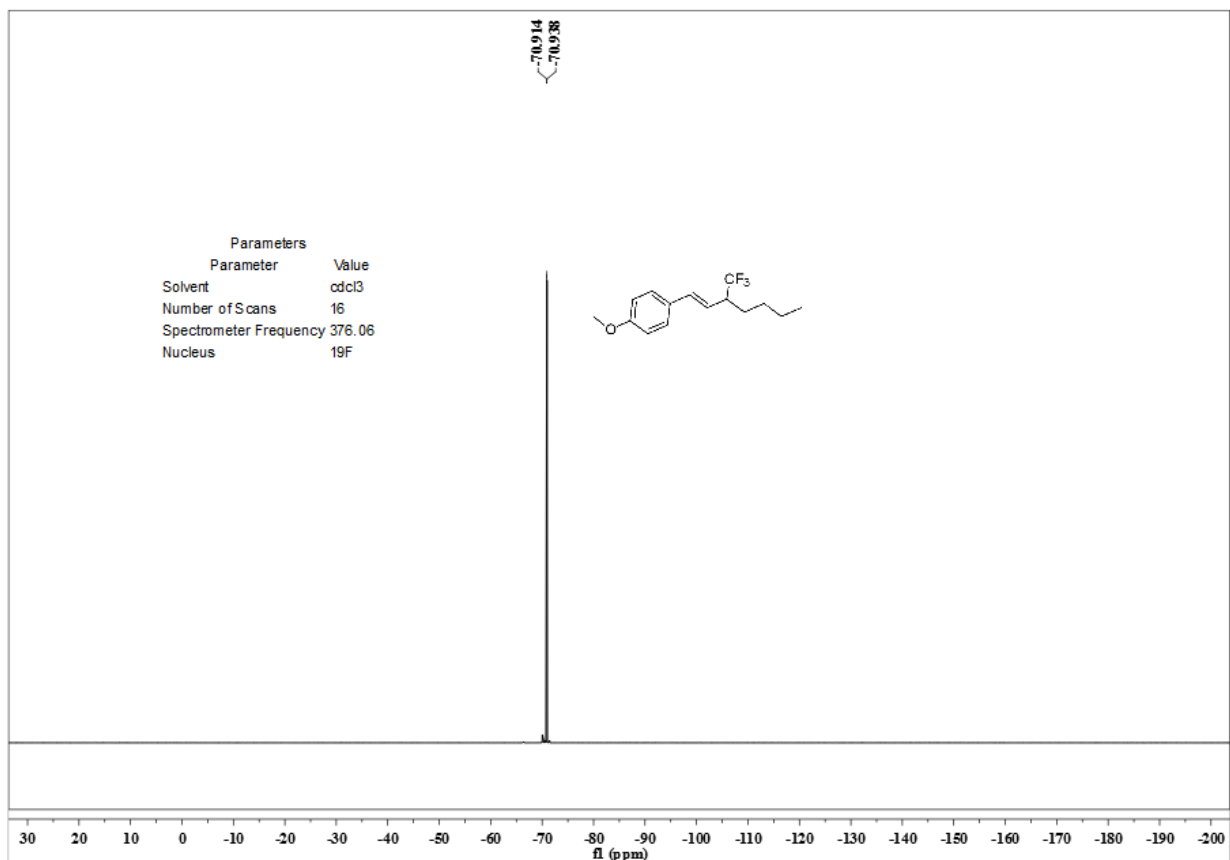
(E)-1-(tert-Butyl)-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3d).



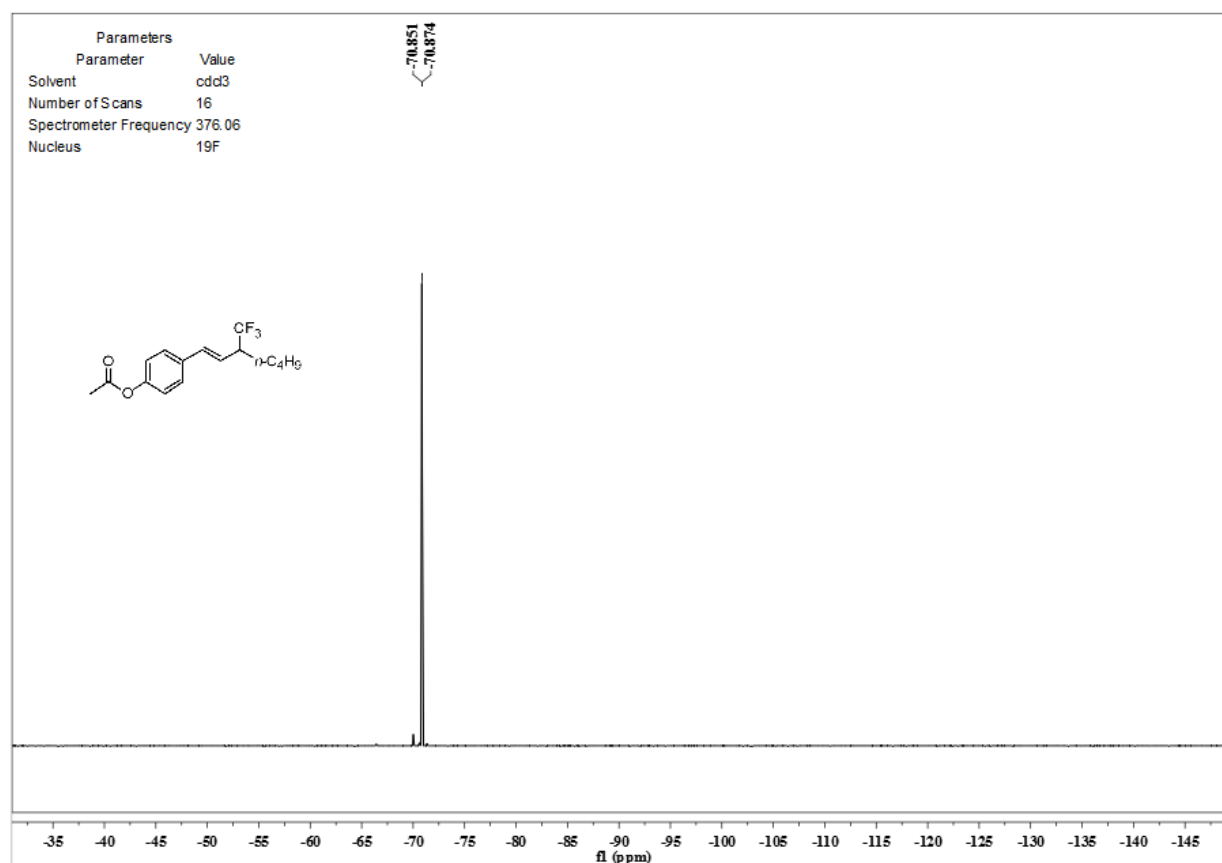
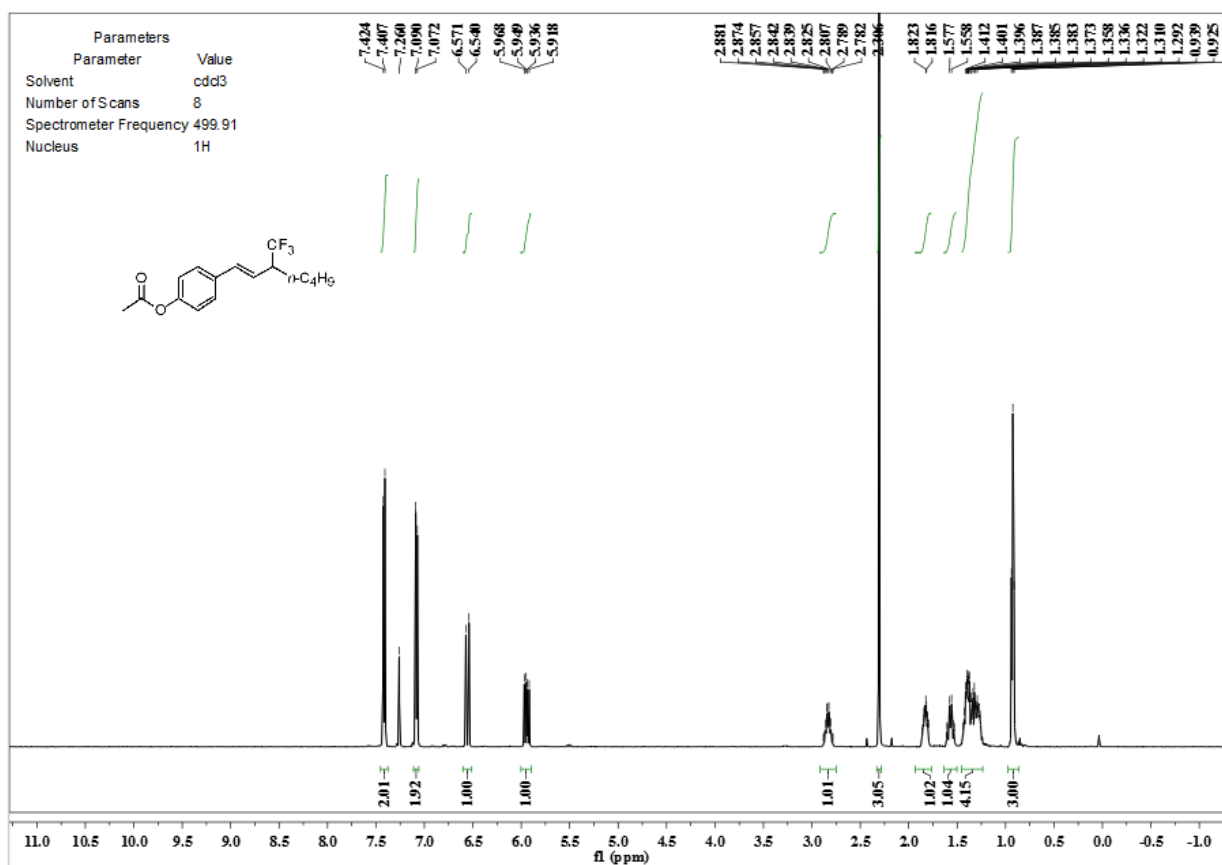


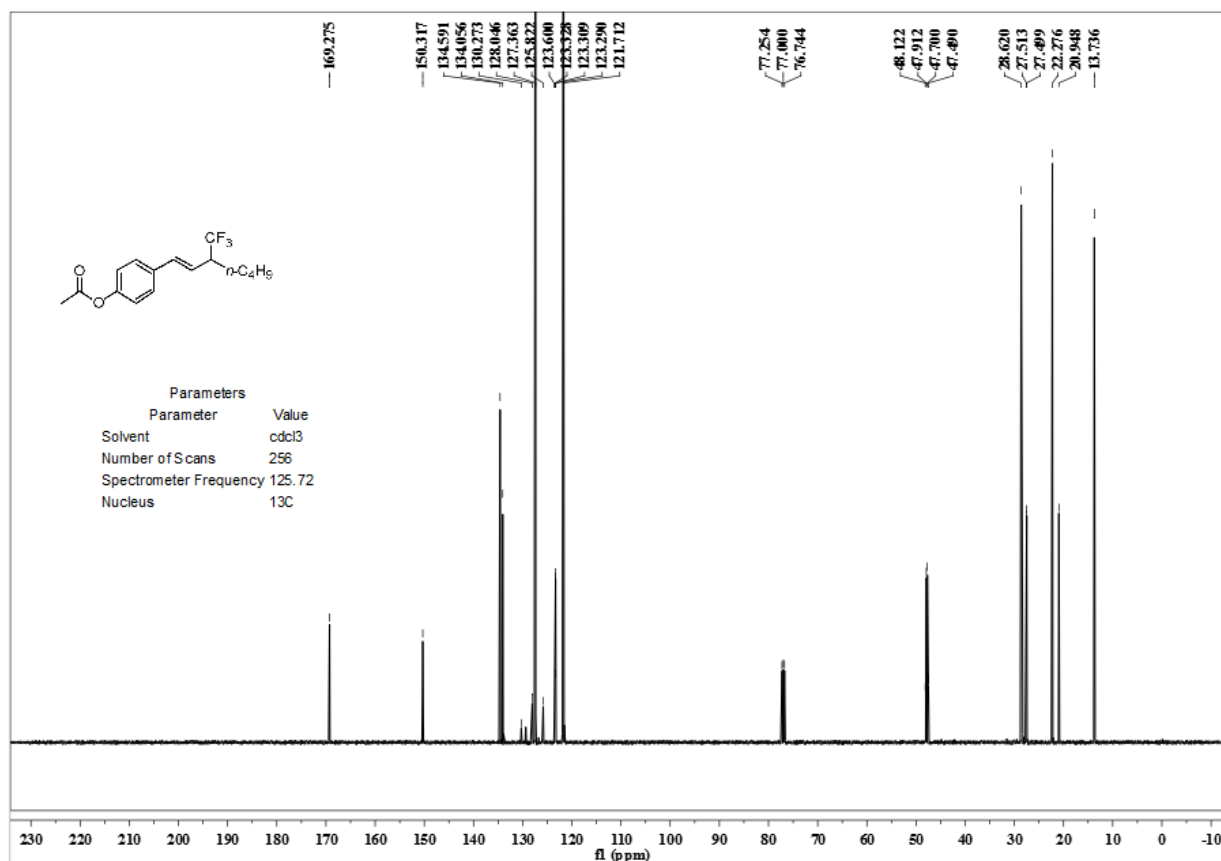
(E)-1-Methoxy-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3e).



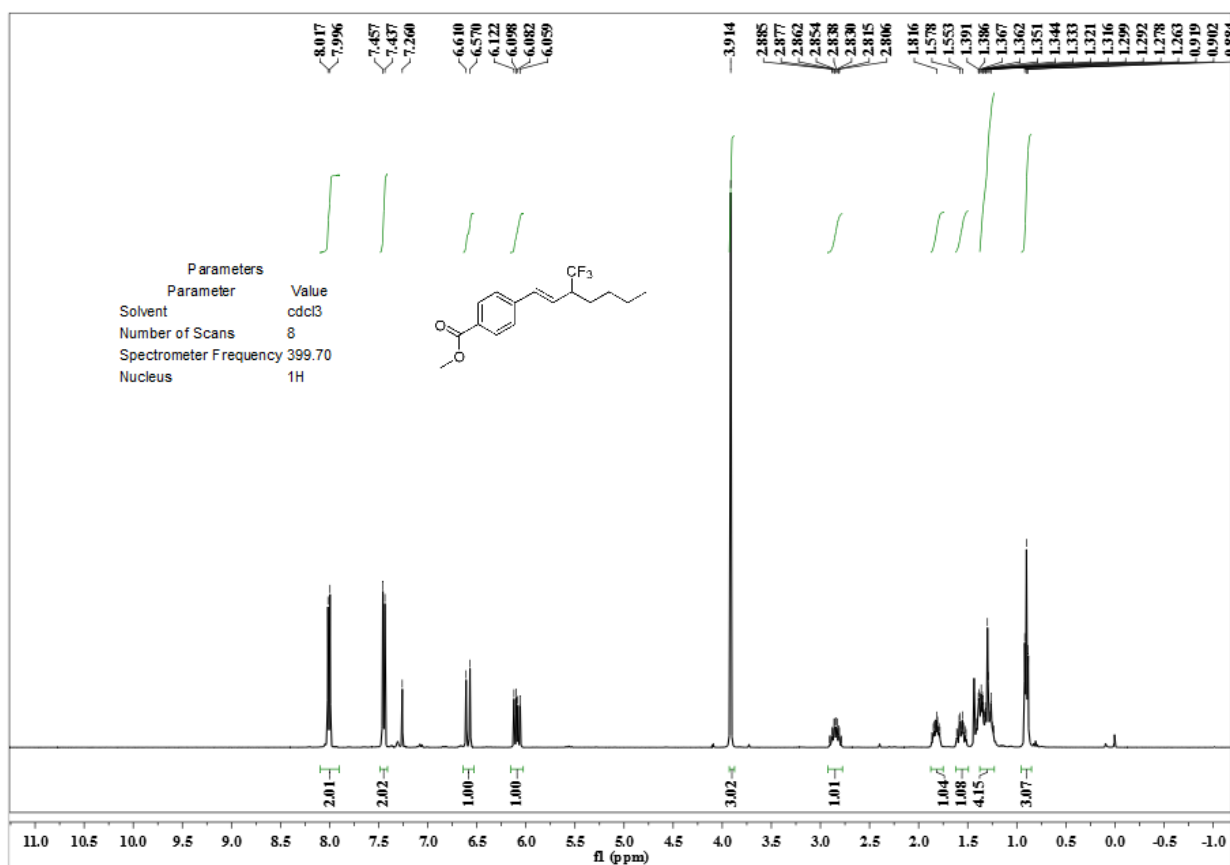


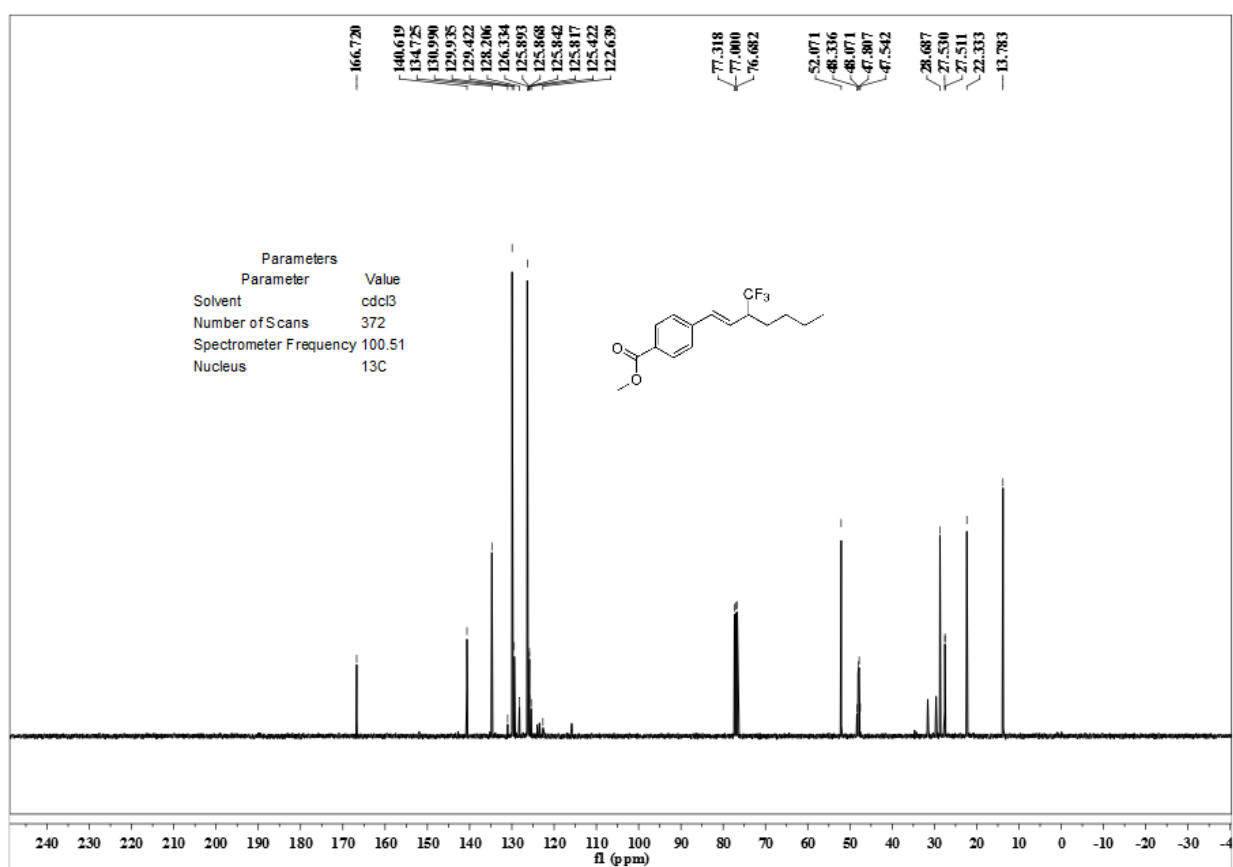
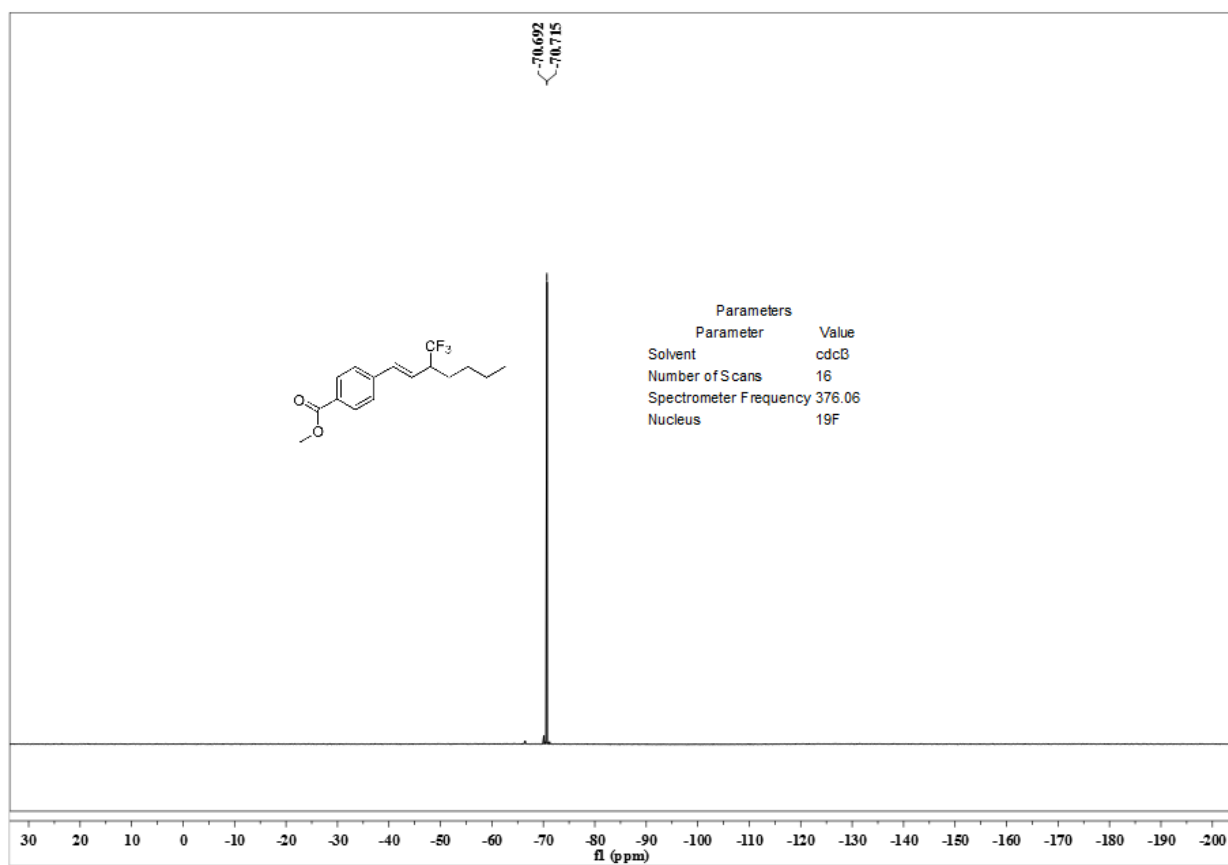
(E)-4-(3-(Trifluoromethyl)hept-1-en-1-yl)phenyl acetate (3f).



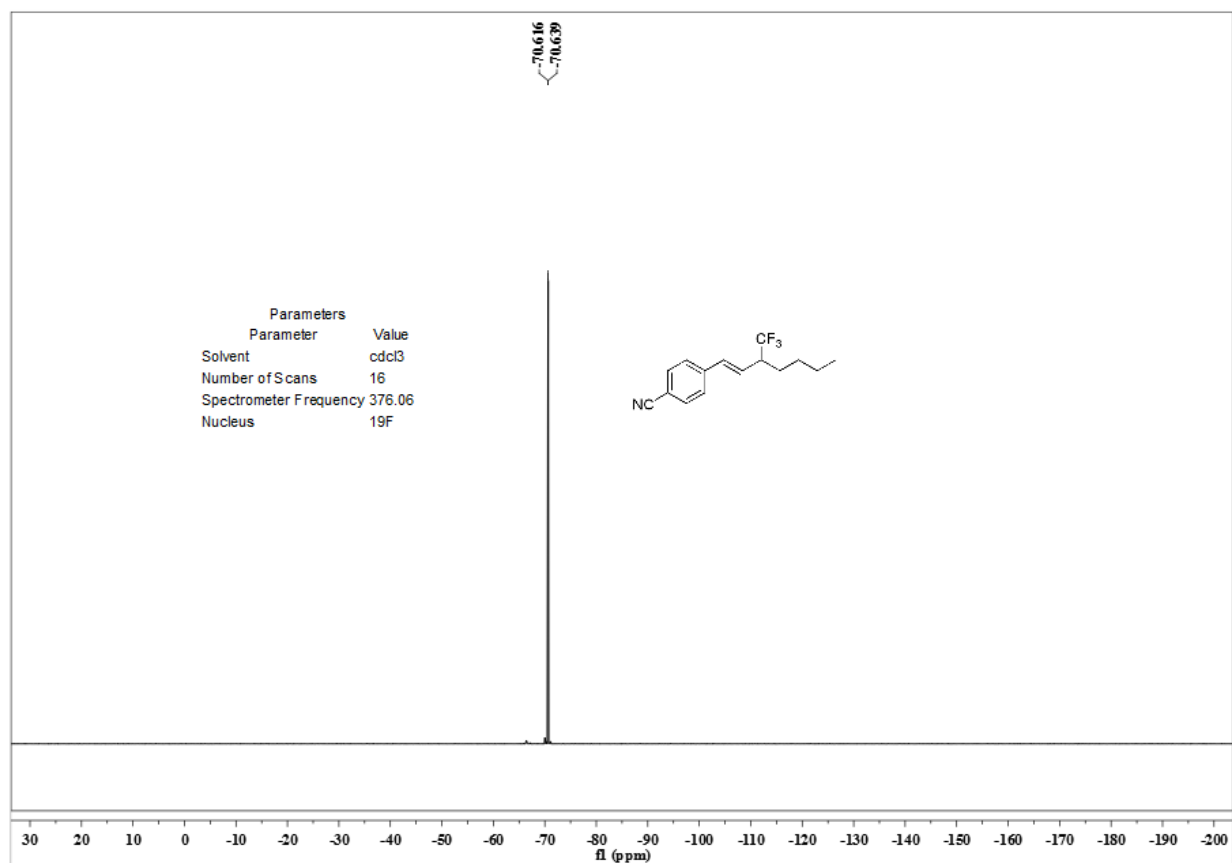
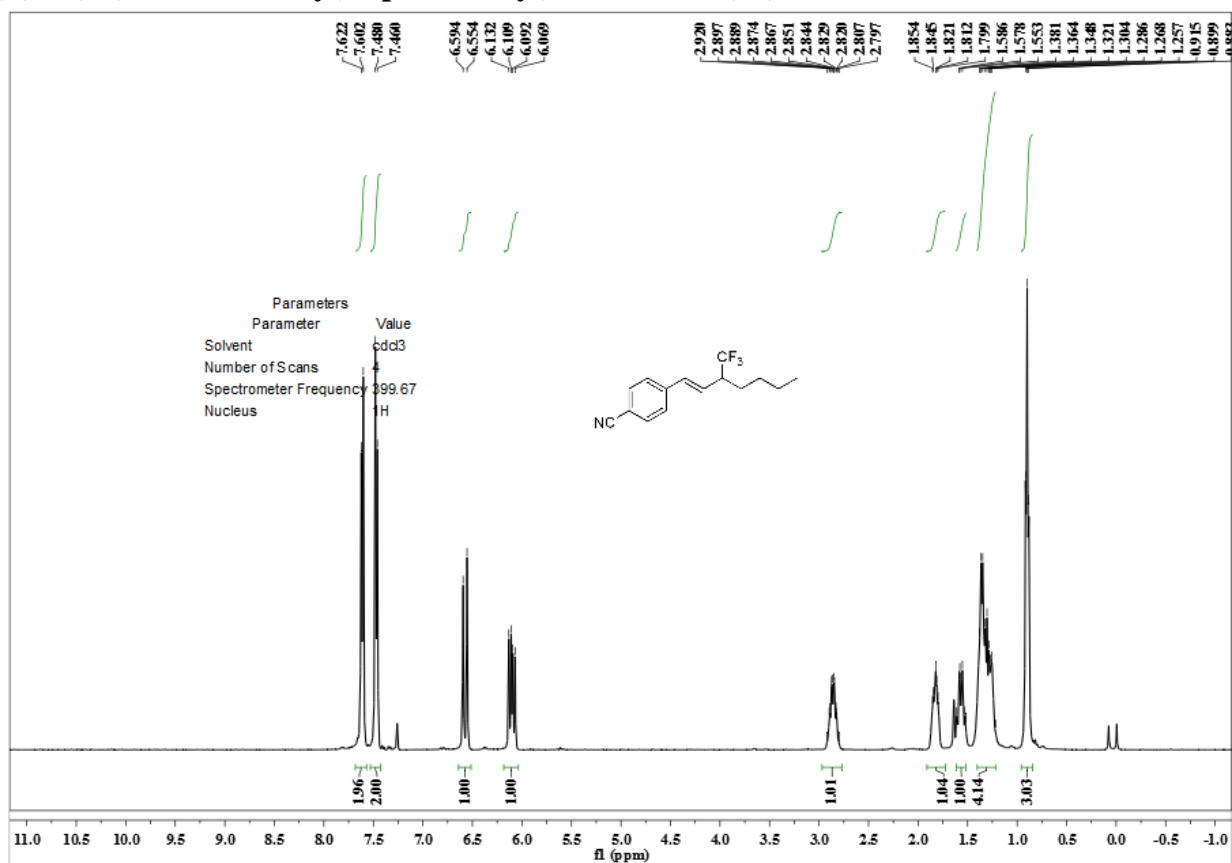


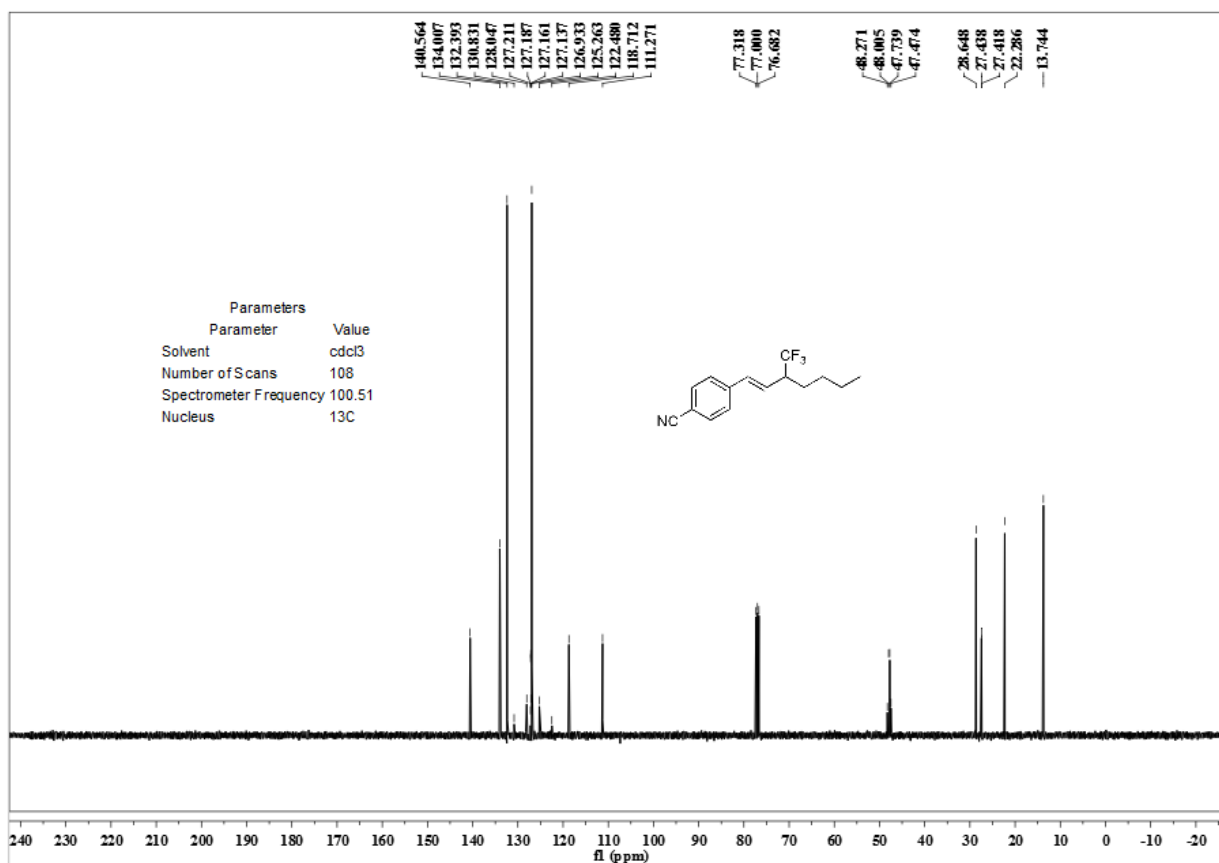
Methyl (*E*)-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzoate (3g).



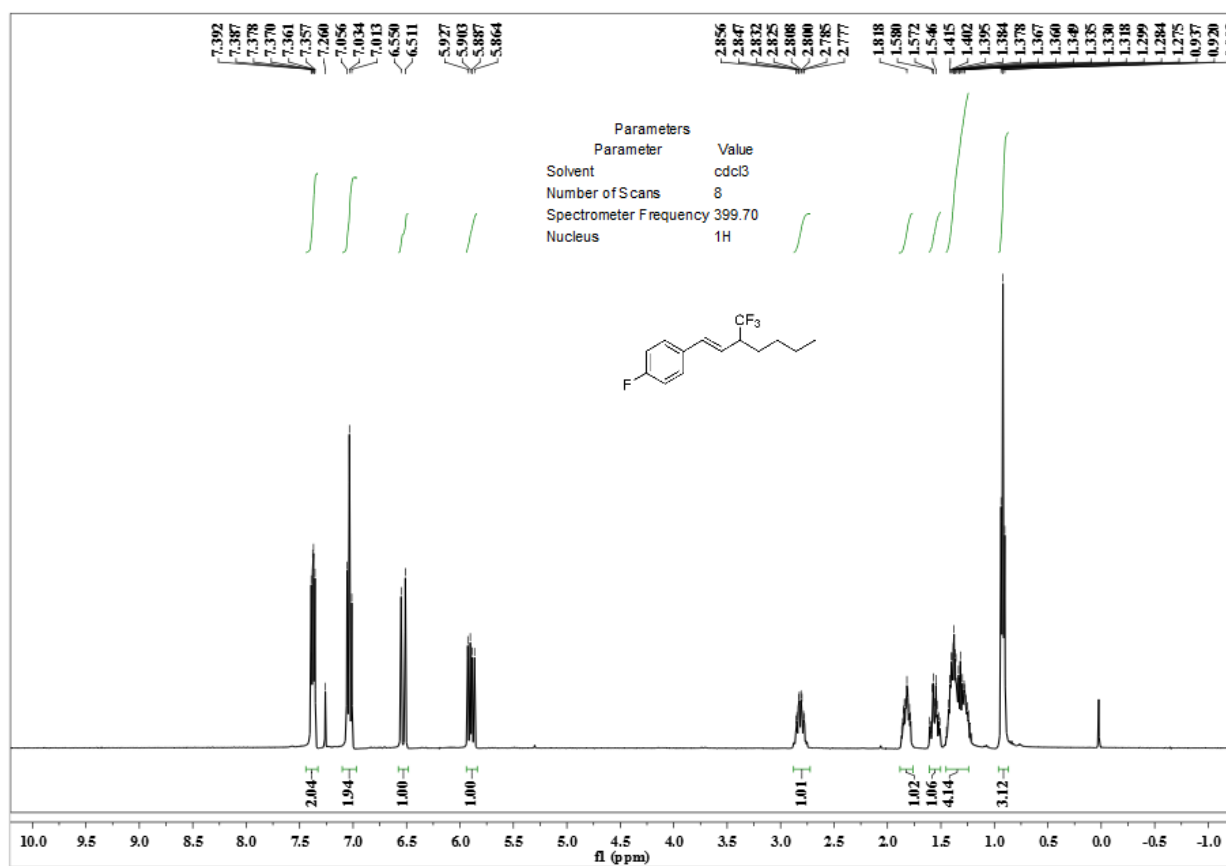


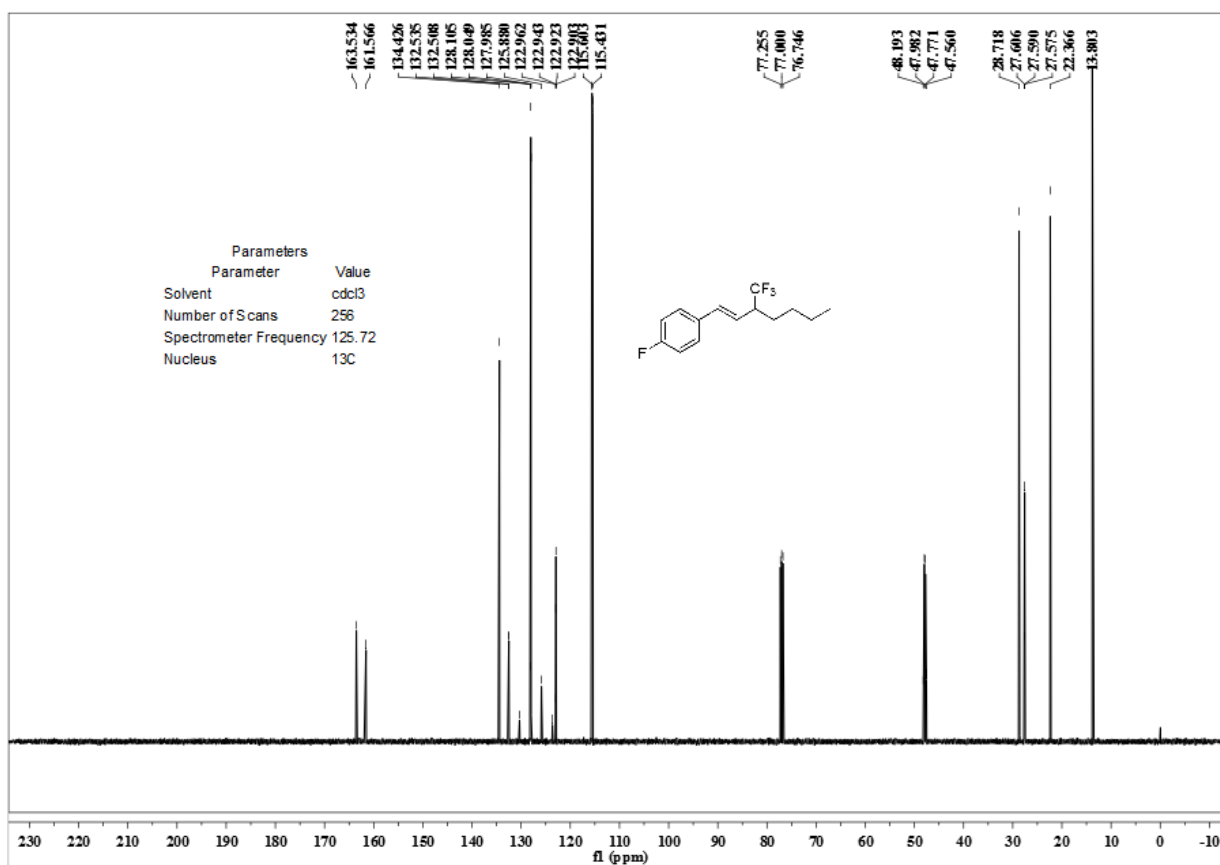
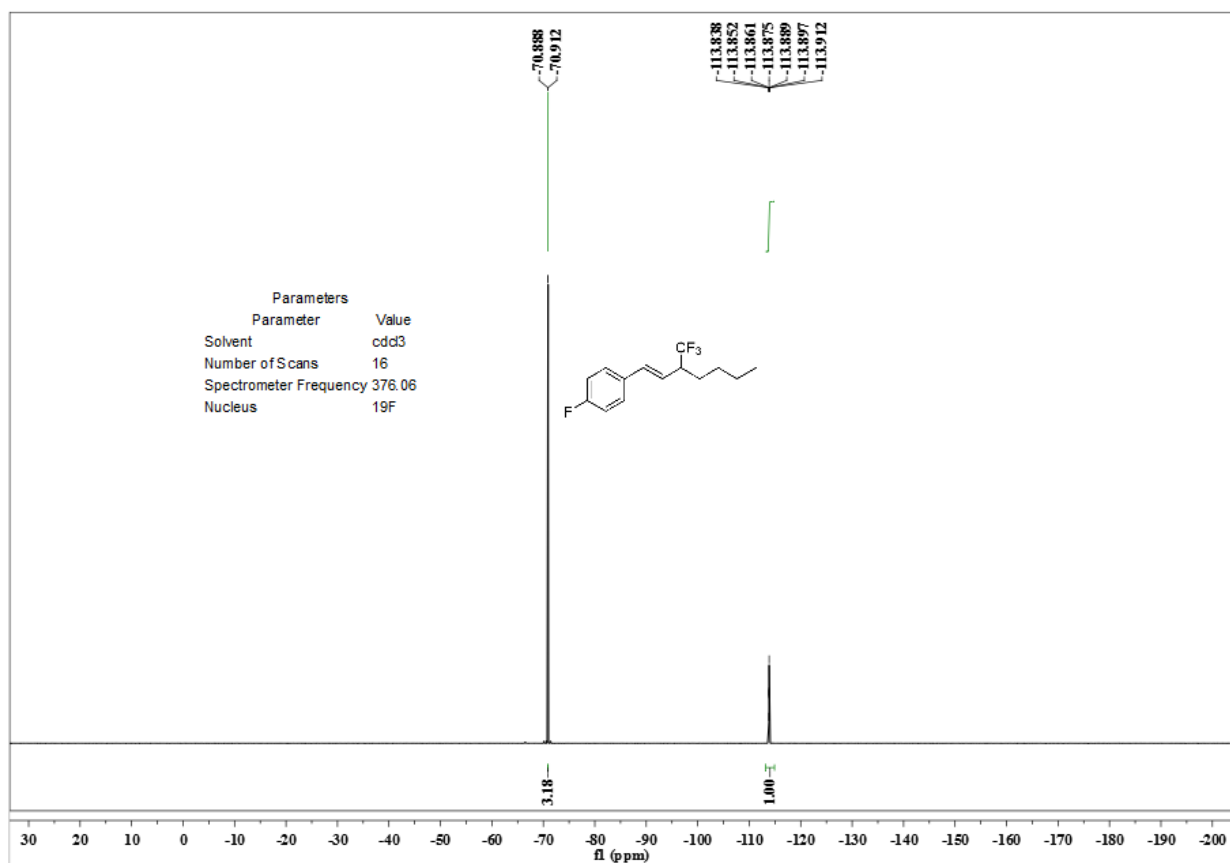
(E)-4-(3-(Trifluoromethyl)hept-1-en-1-yl)benzonitrile (3h).



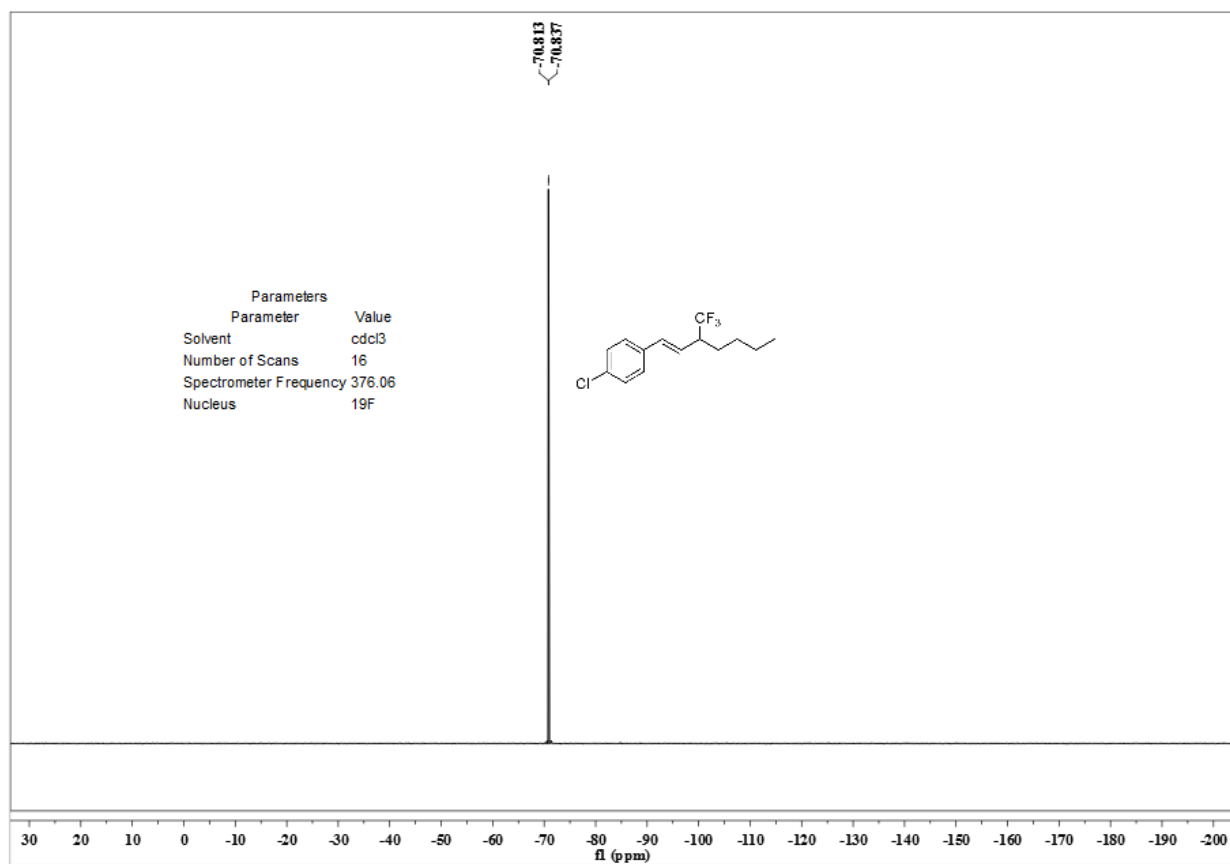
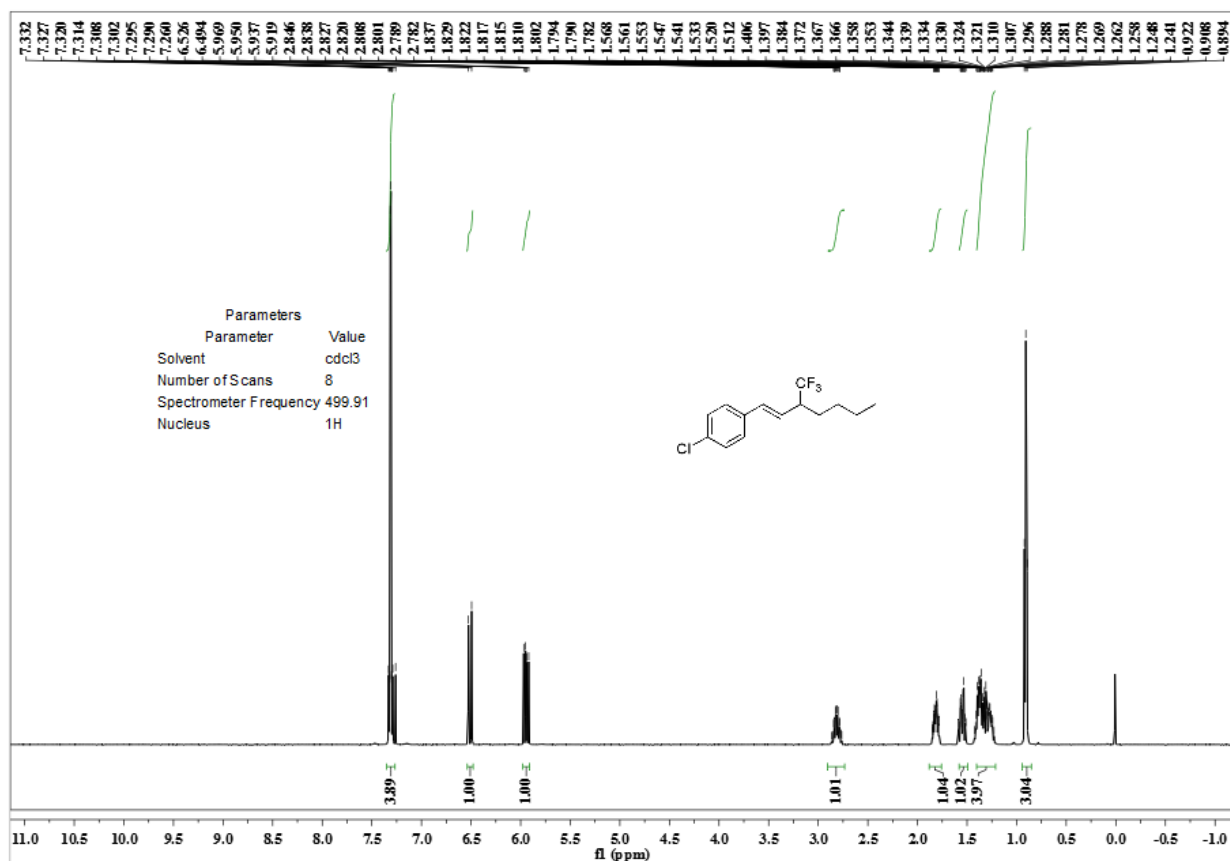


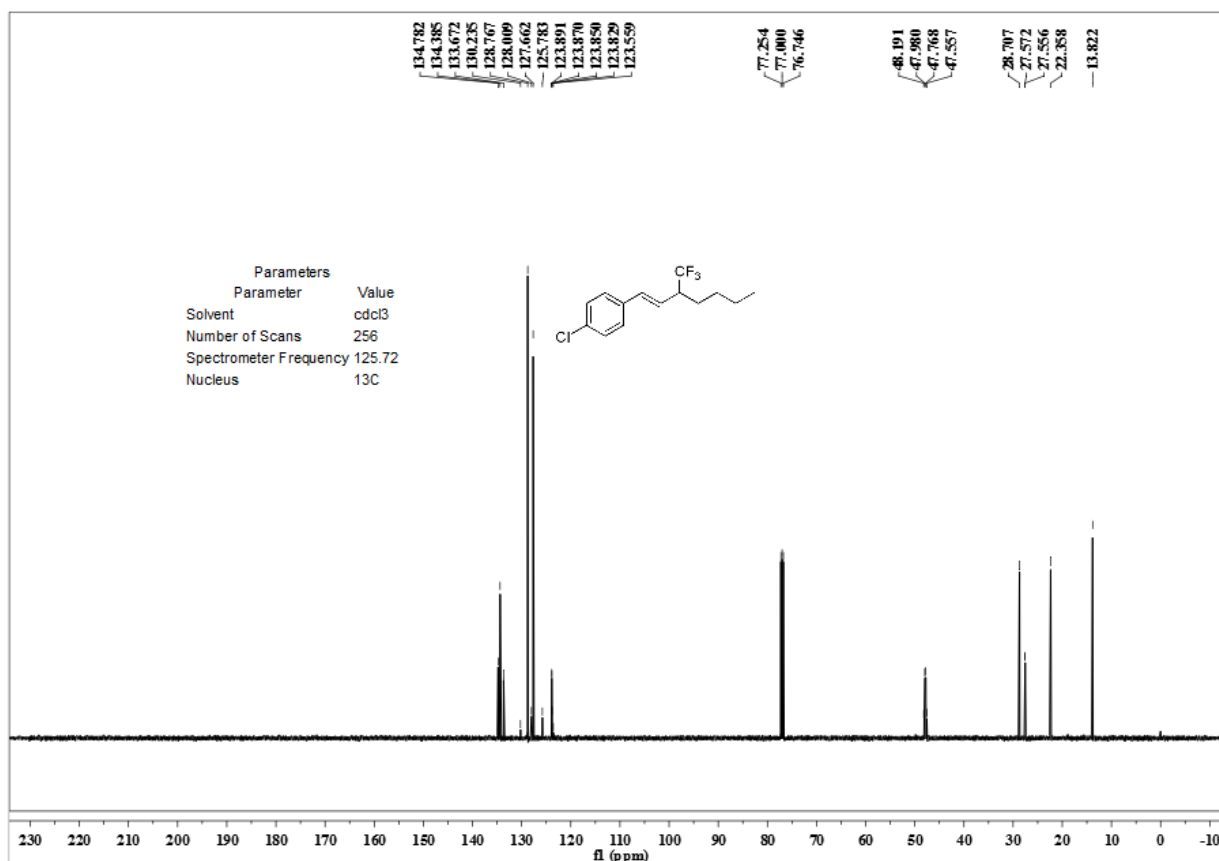
(*E*)-1-Fluoro-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3i).



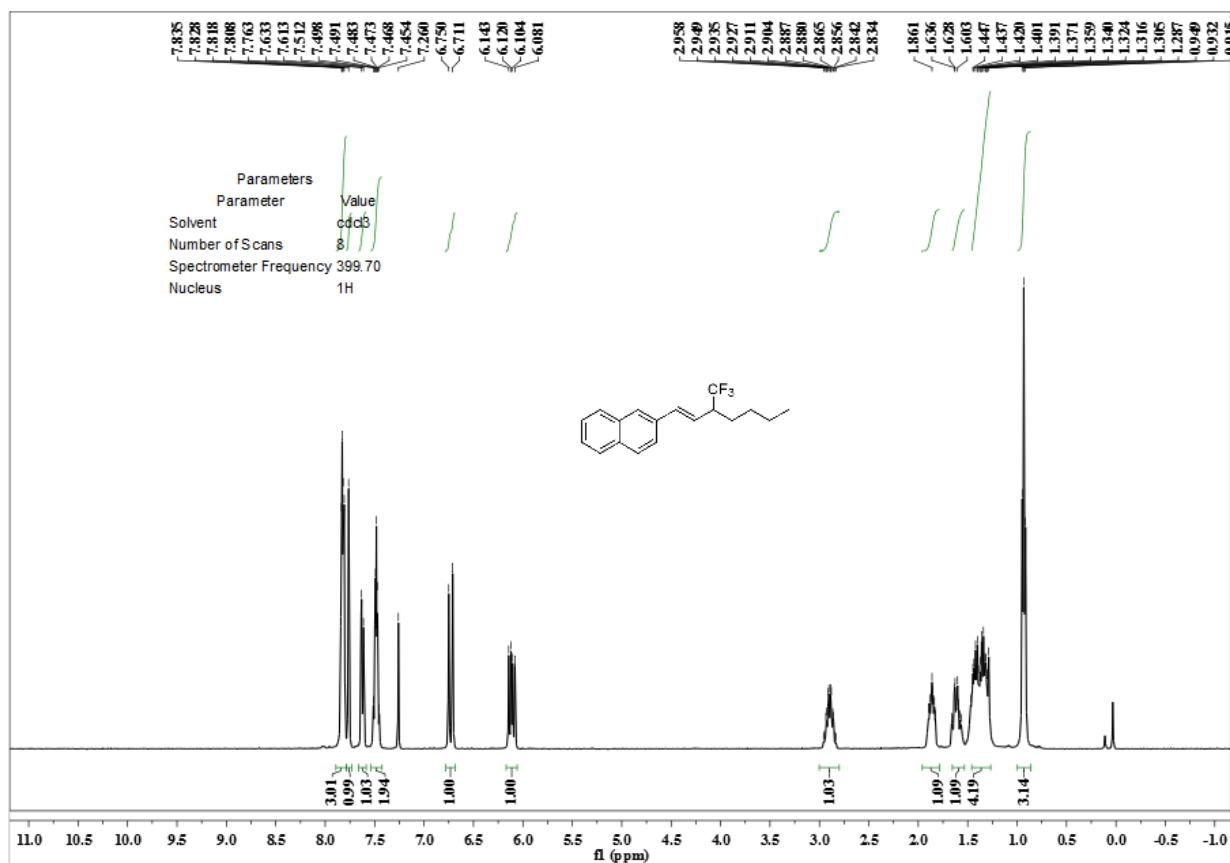


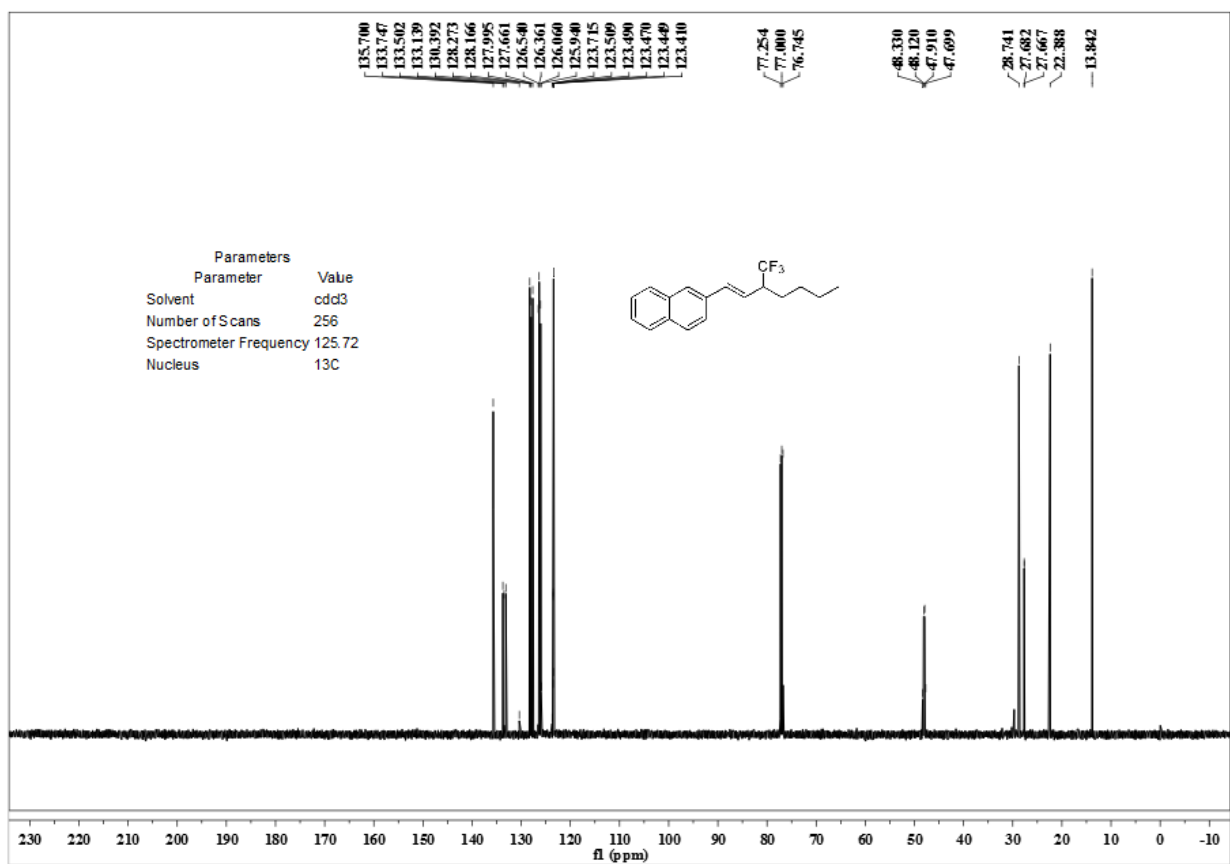
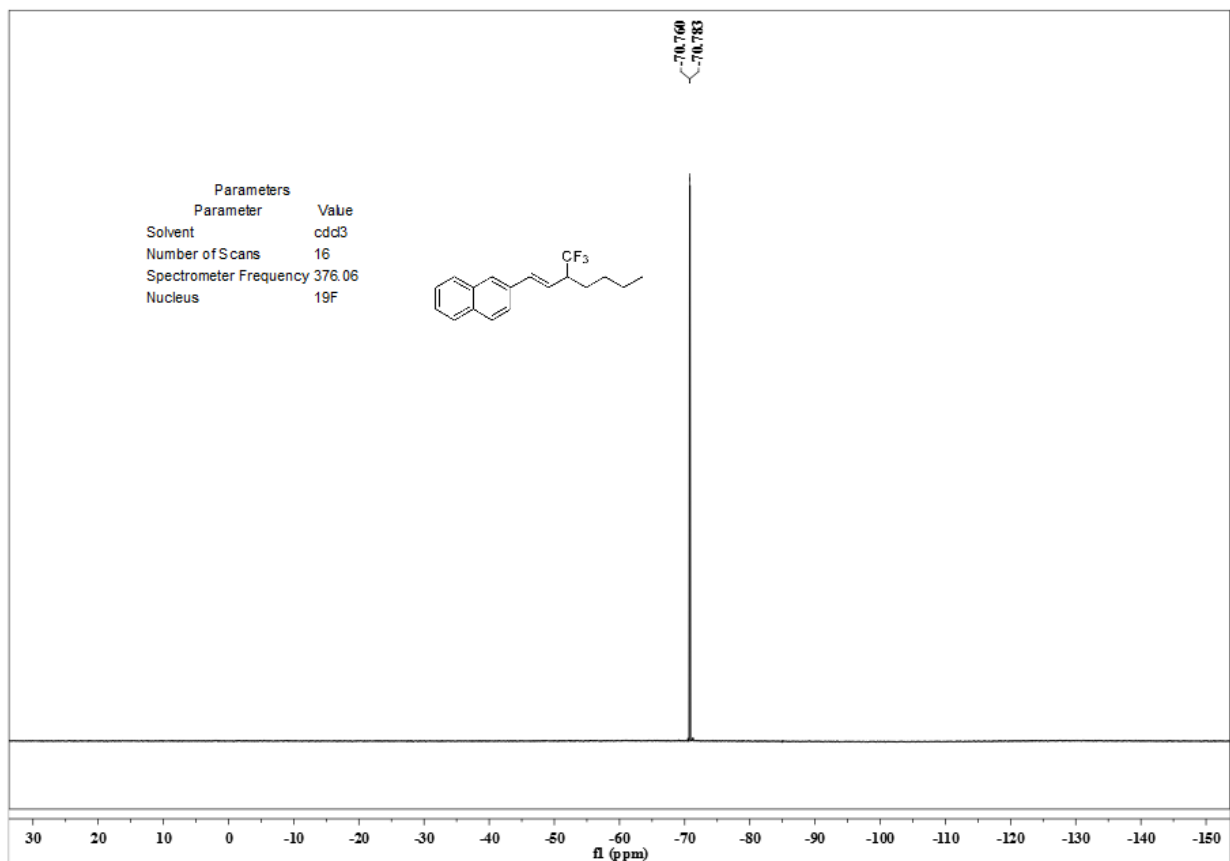
(E)-1-Chloro-4-(3-(trifluoromethyl)hept-1-en-1-yl)benzene (3j).



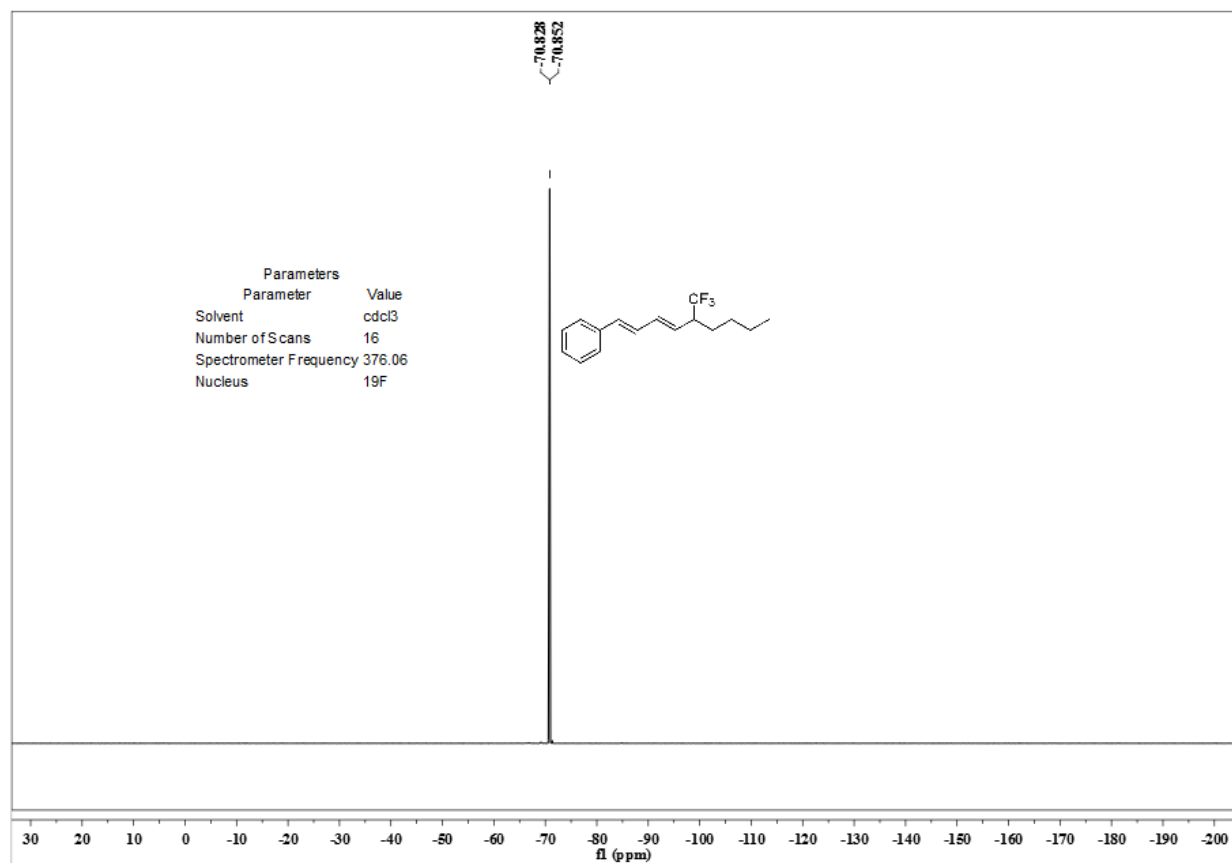
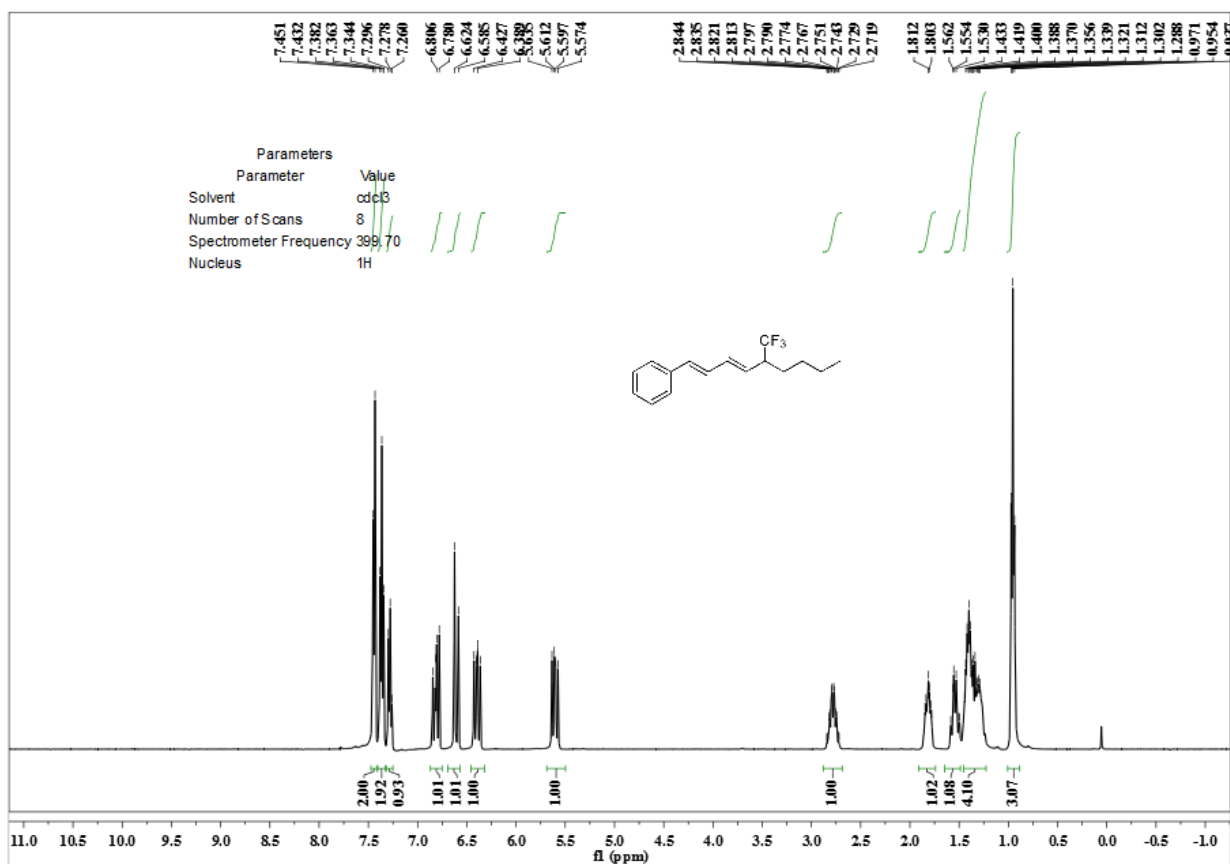


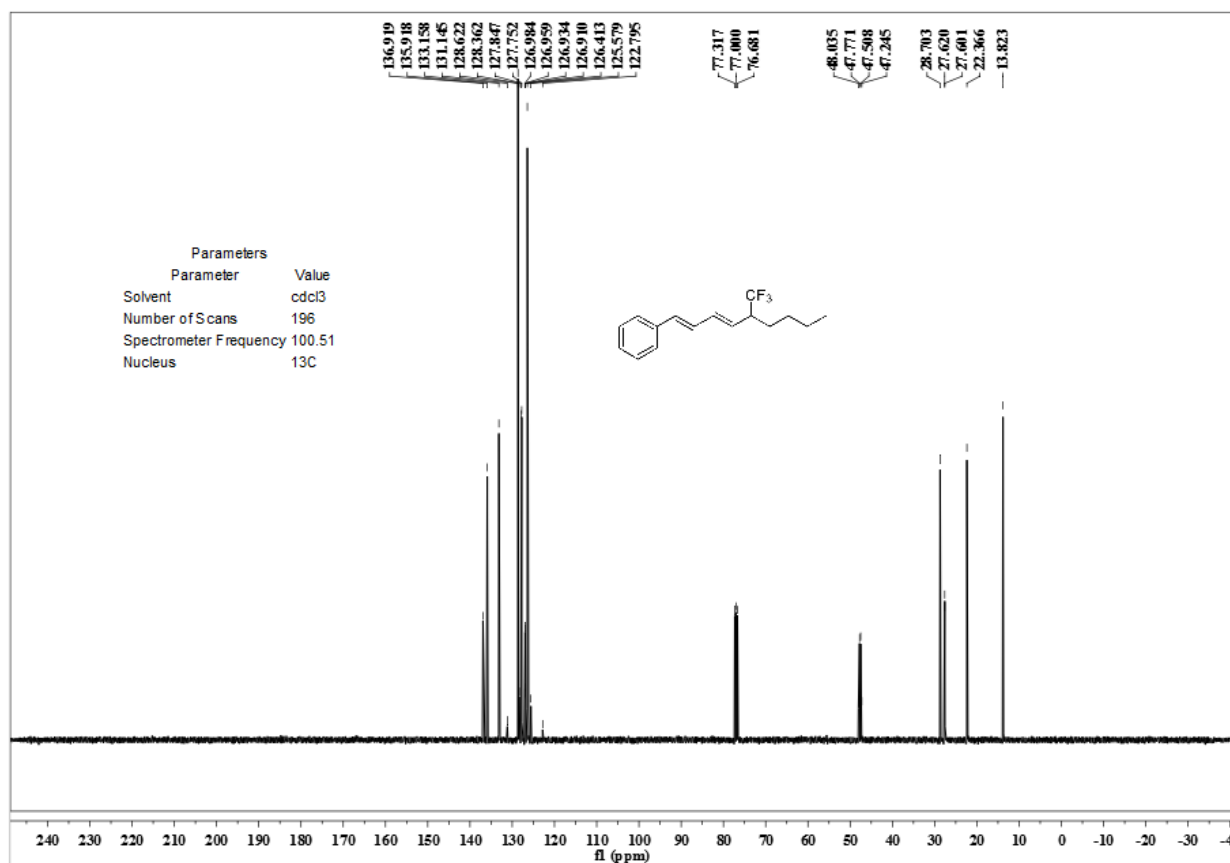
(*E*)-2-(3-(Trifluoromethyl)hept-1-en-1-yl)naphthalene (3k).



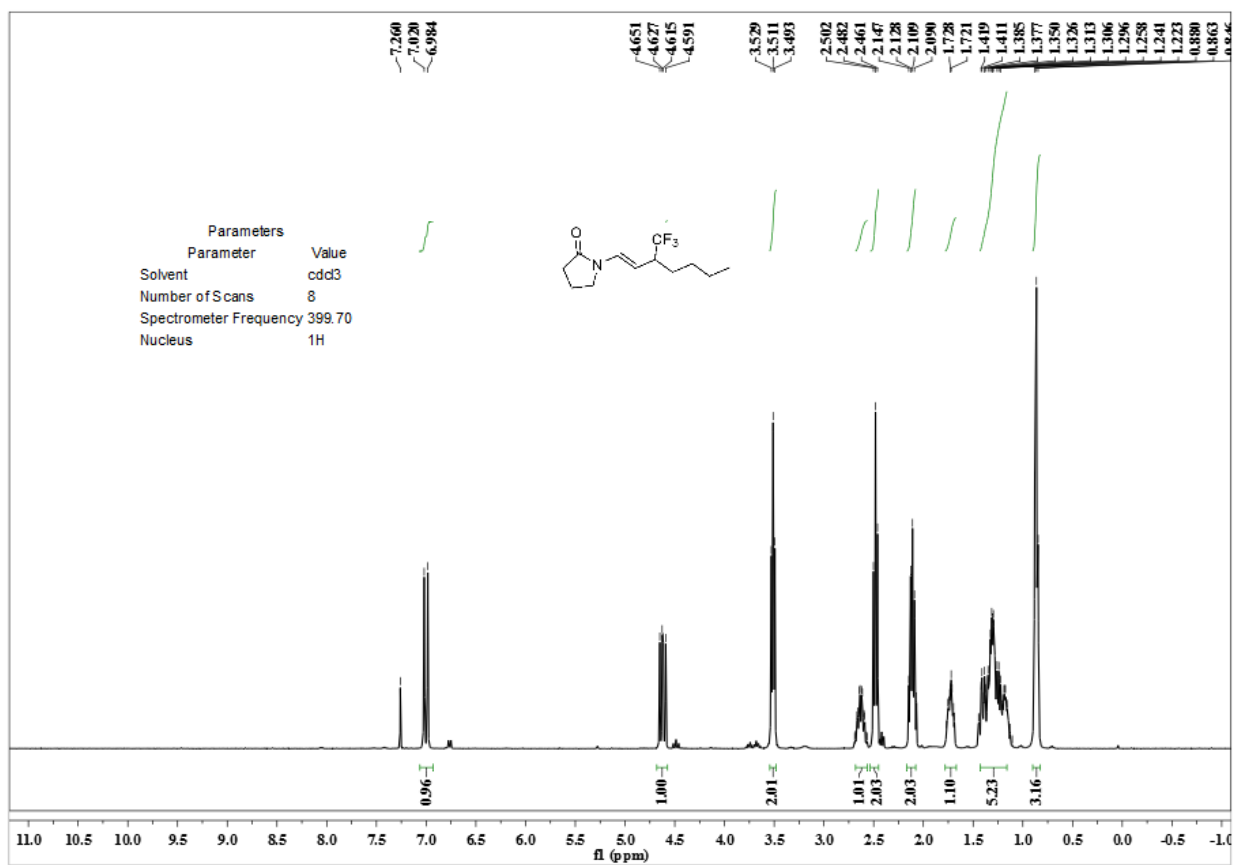


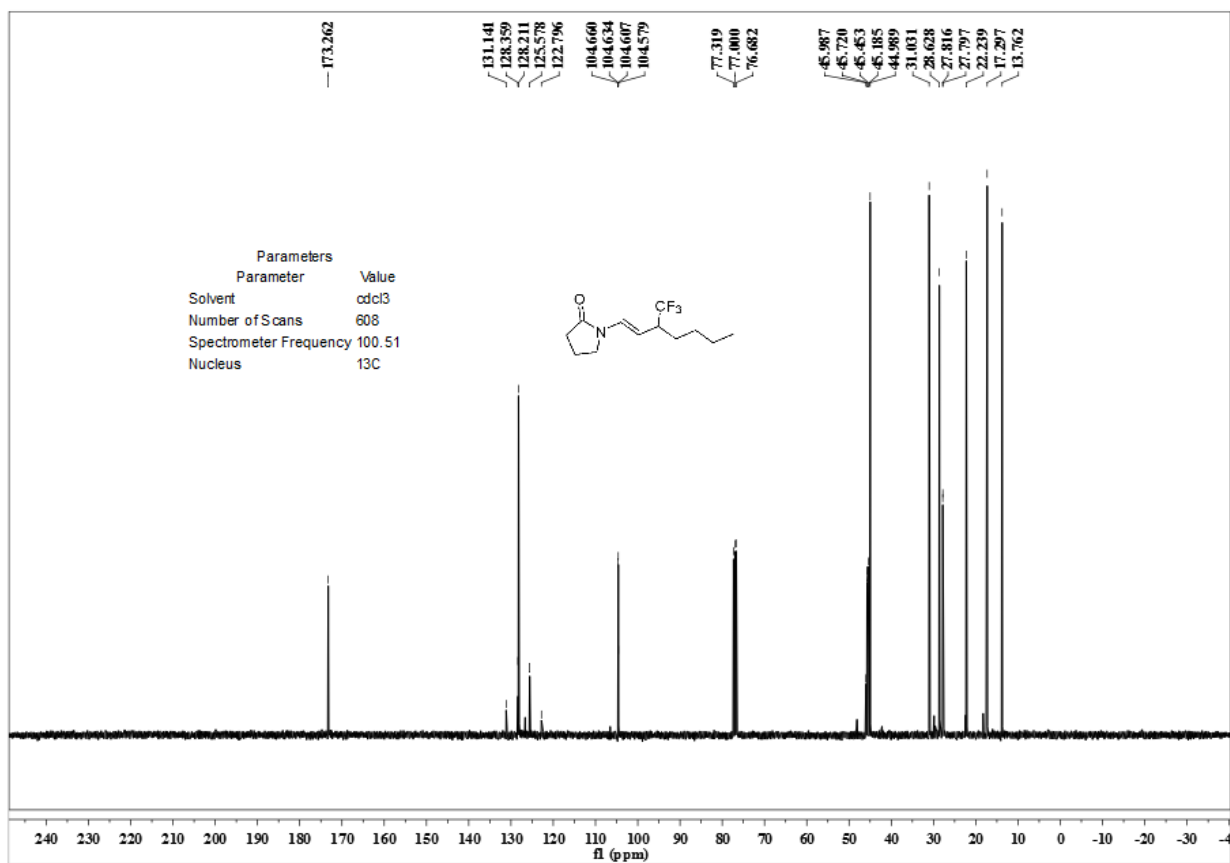
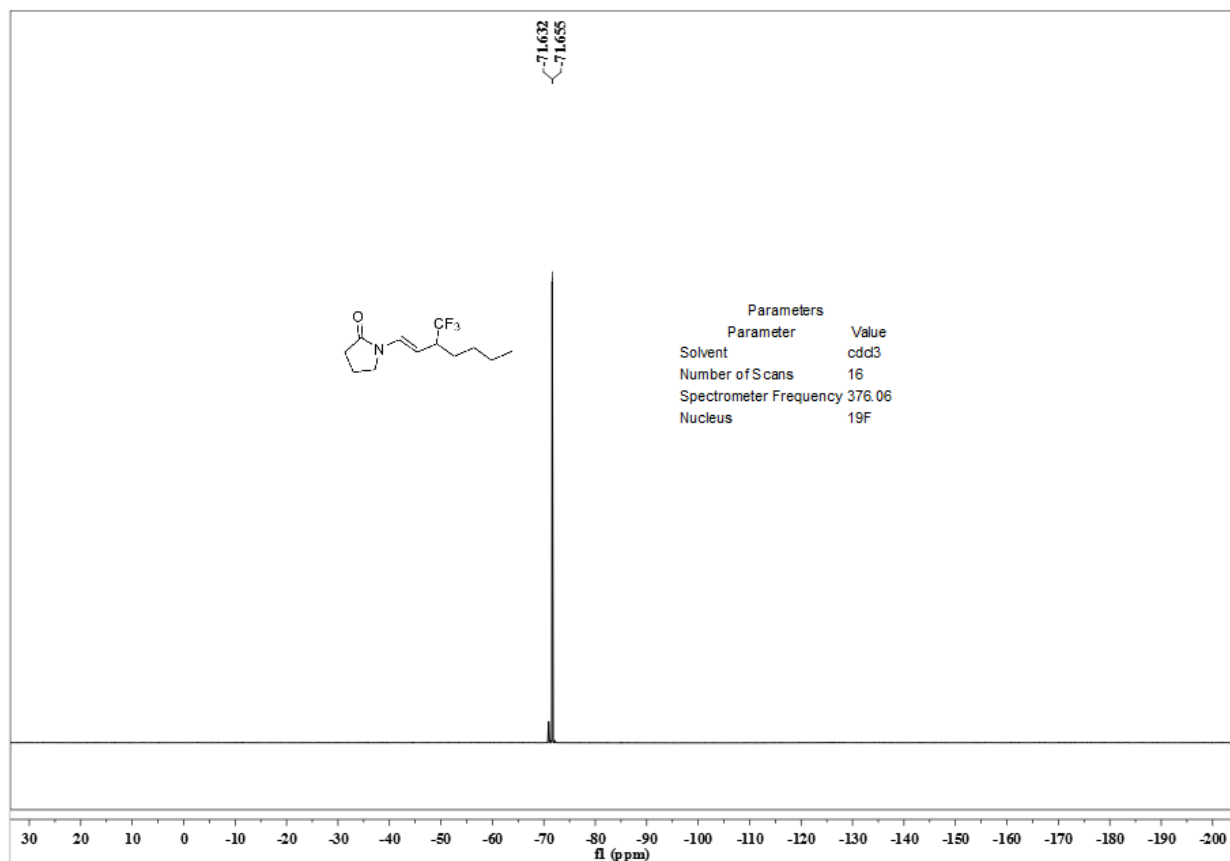
((1*E*,3*E*)-5-(Trifluoromethyl)nona-1,3-dien-1-yl)benzene (3l).



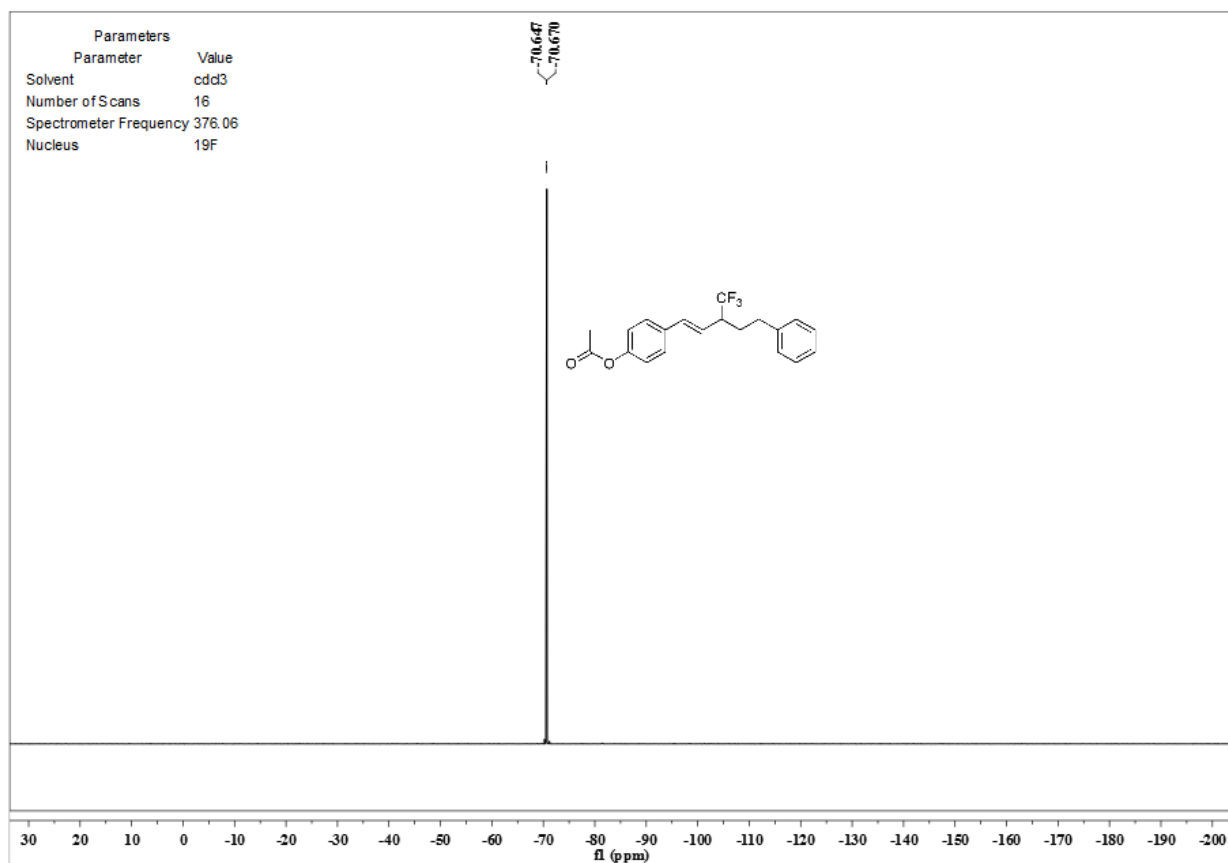
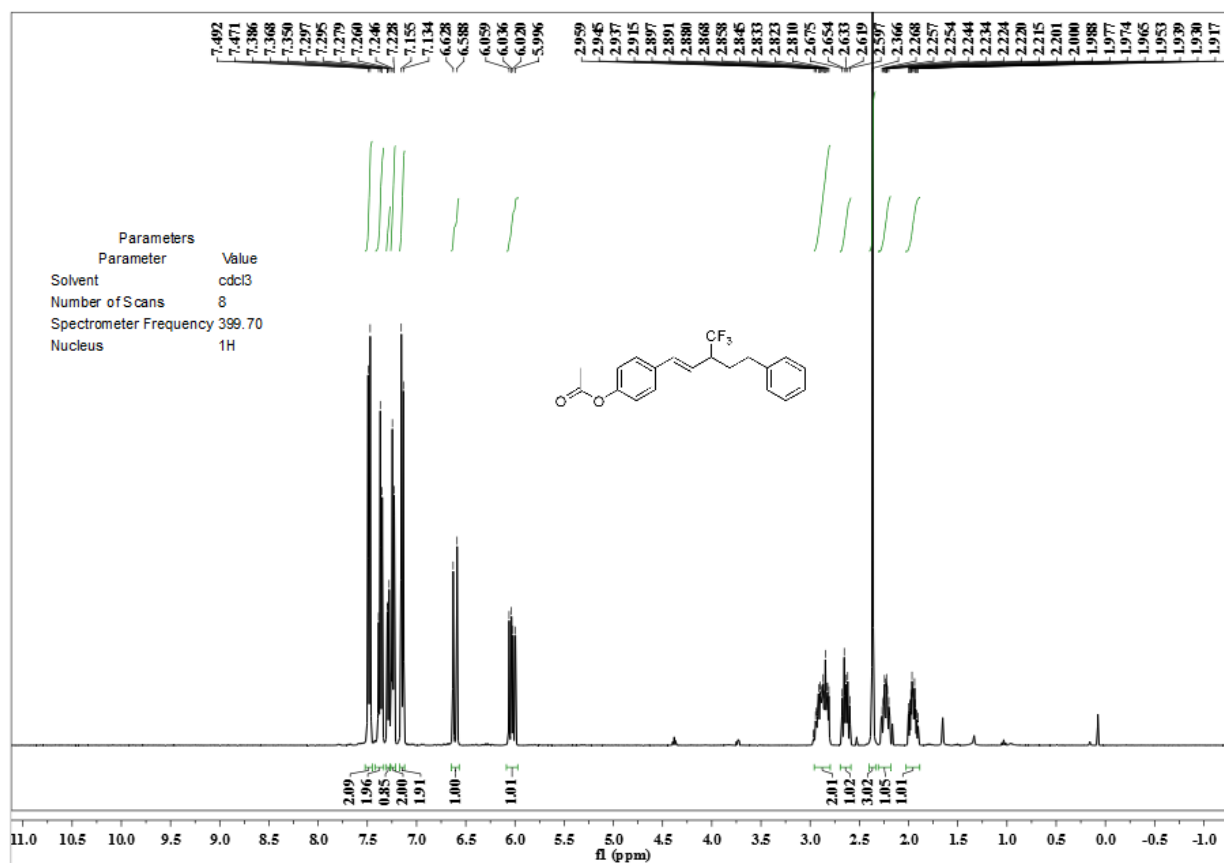


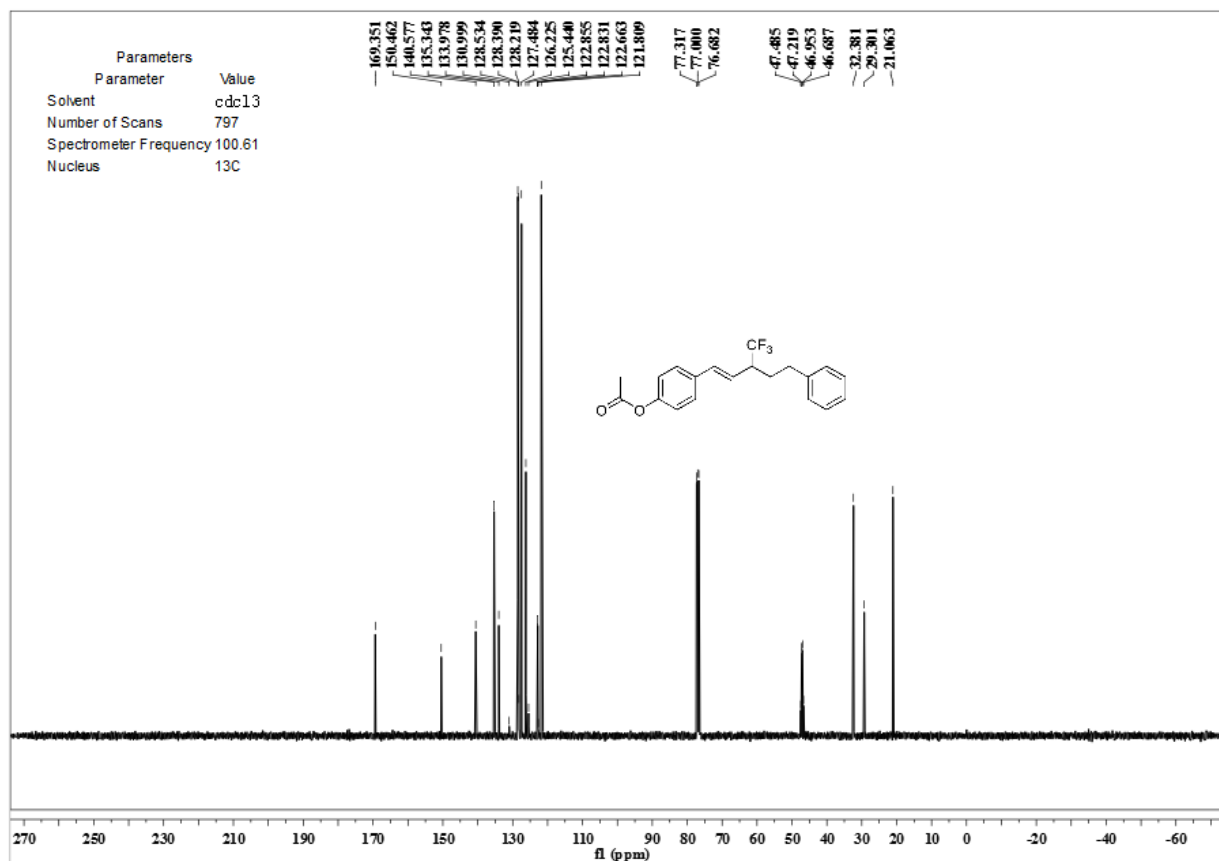
(E)-1-(3-(Trifluoromethyl)hept-1-en-1-yl)pyrrolidin-2-one (3m).



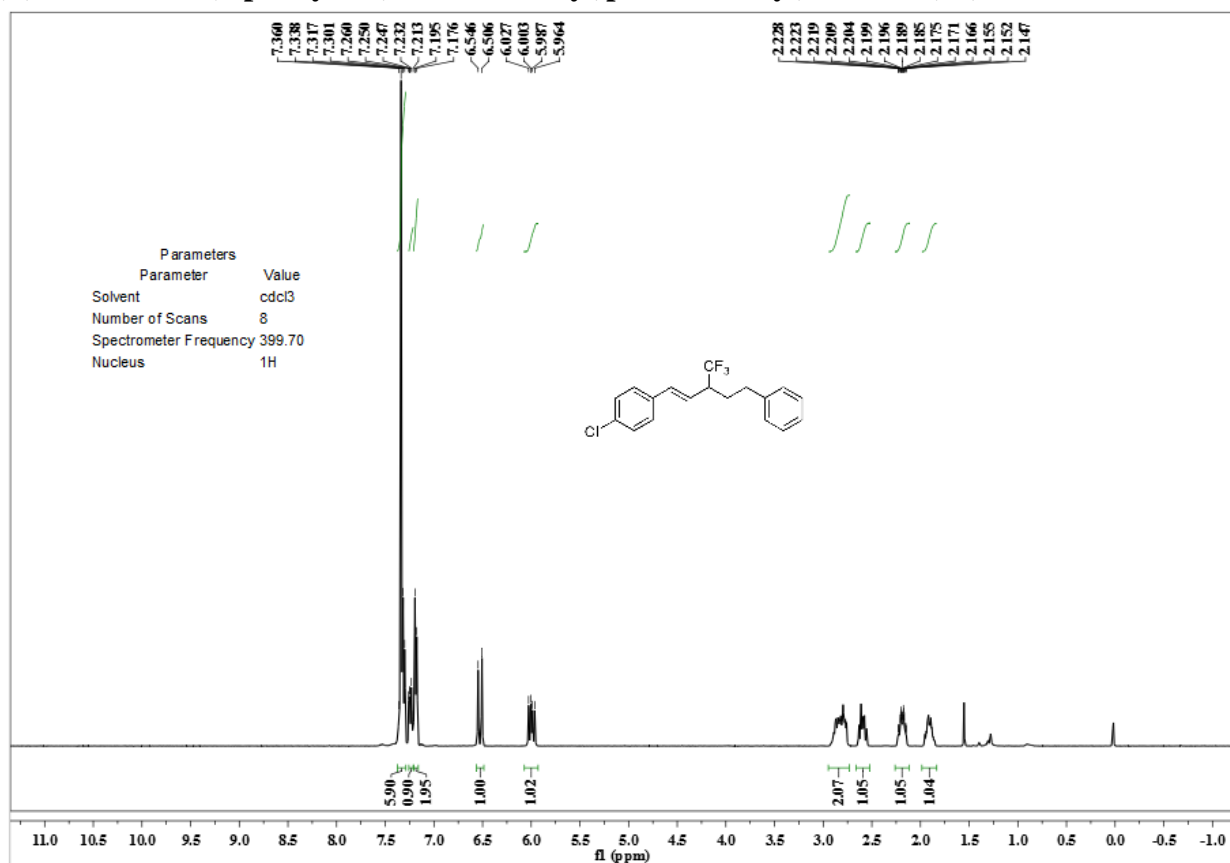


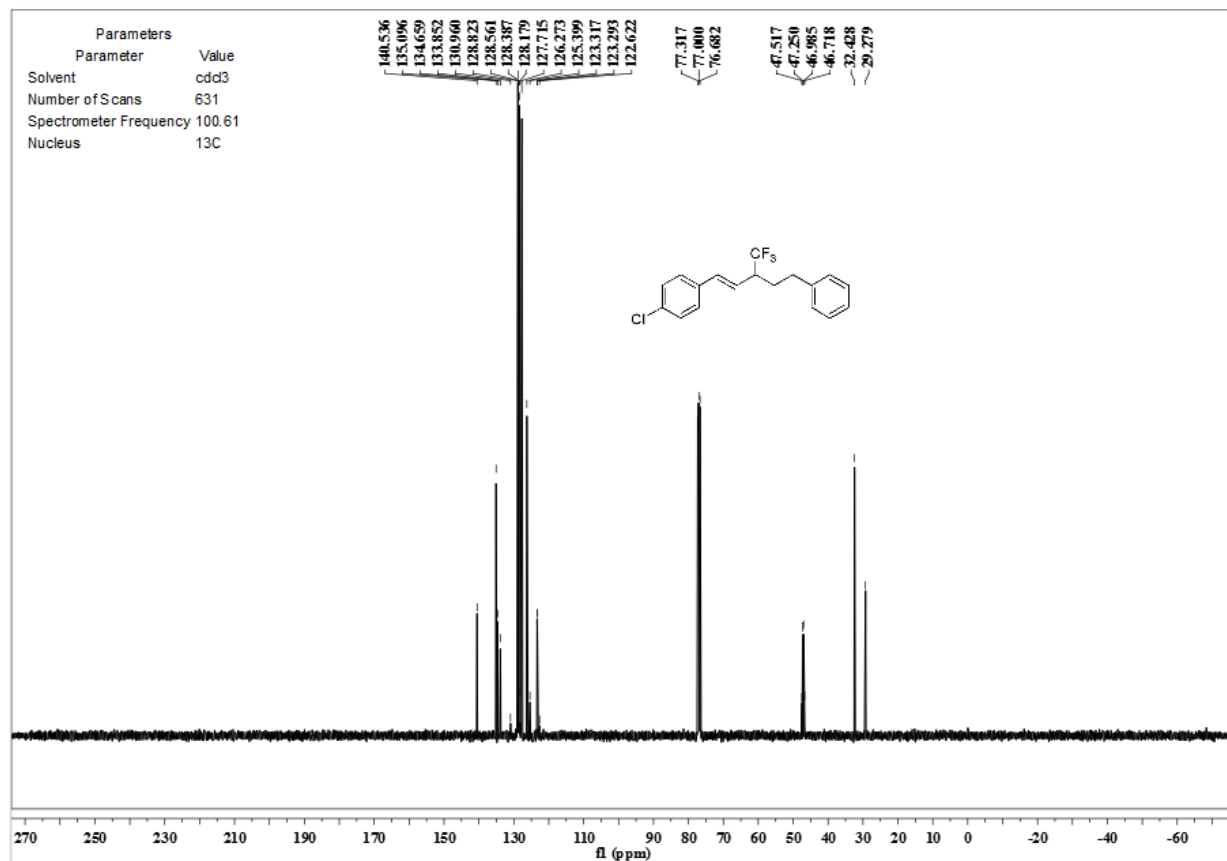
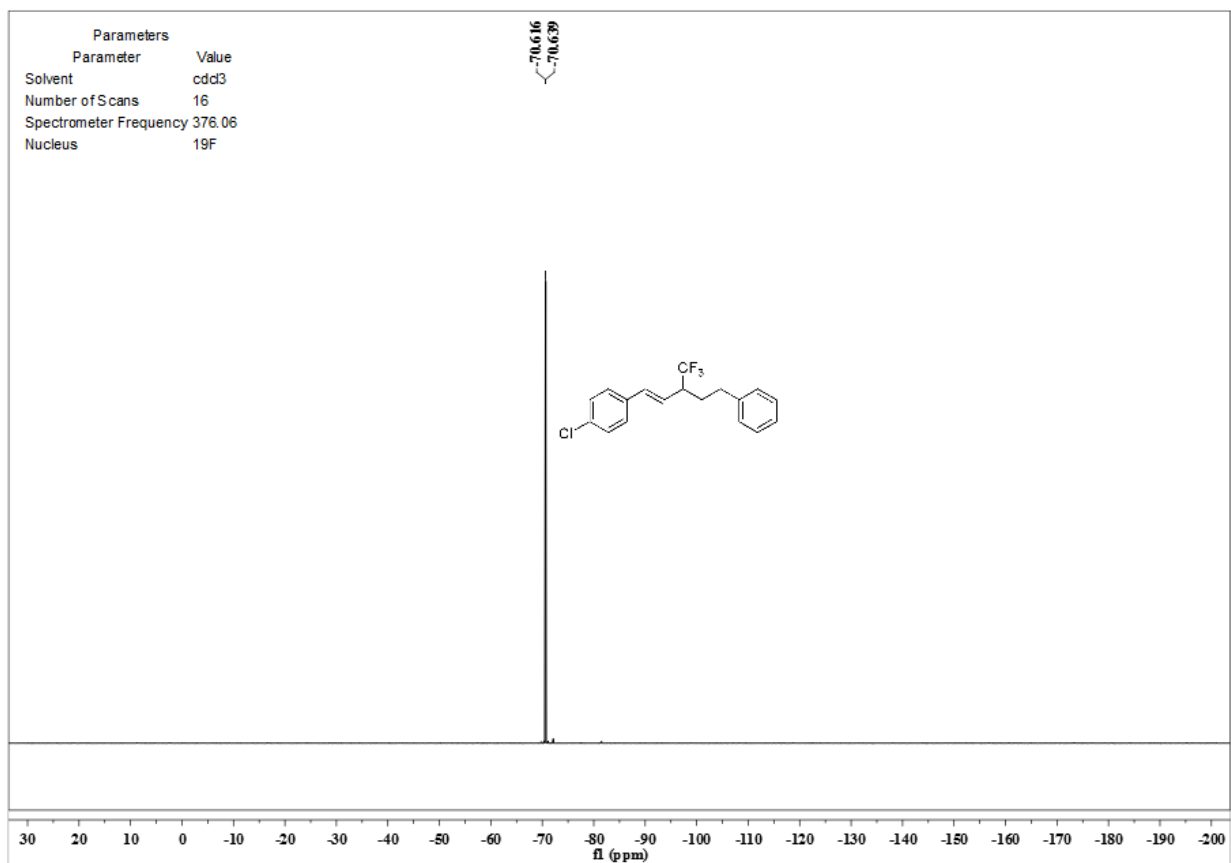
(*E*)-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)phenyl acetate (4a).



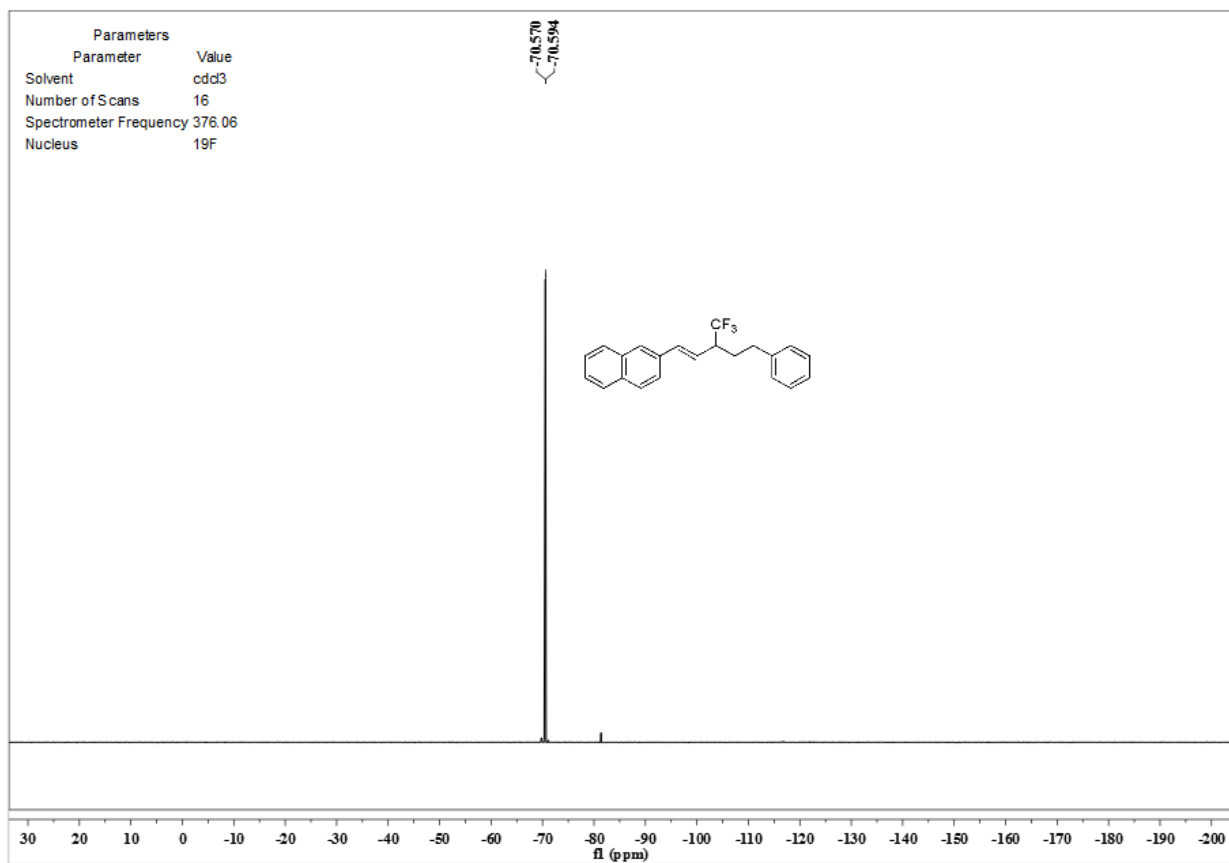
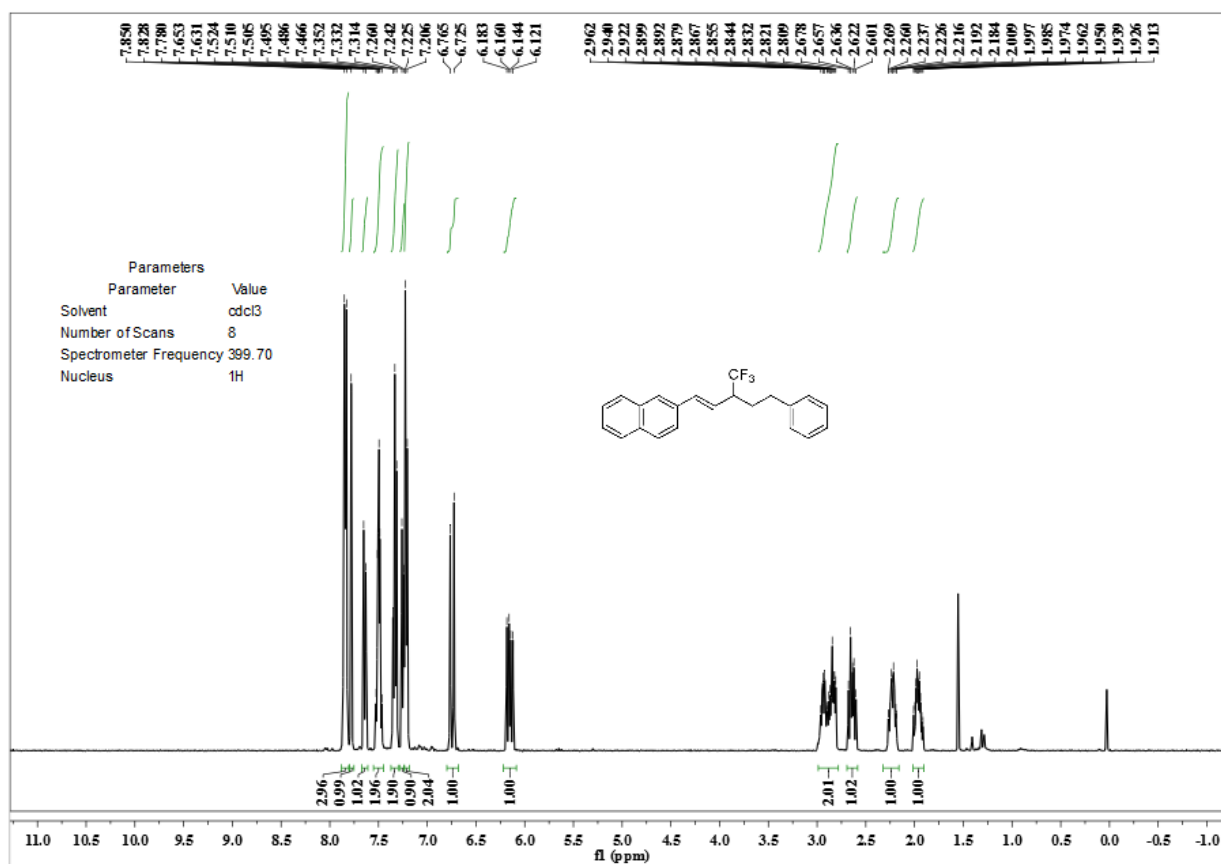


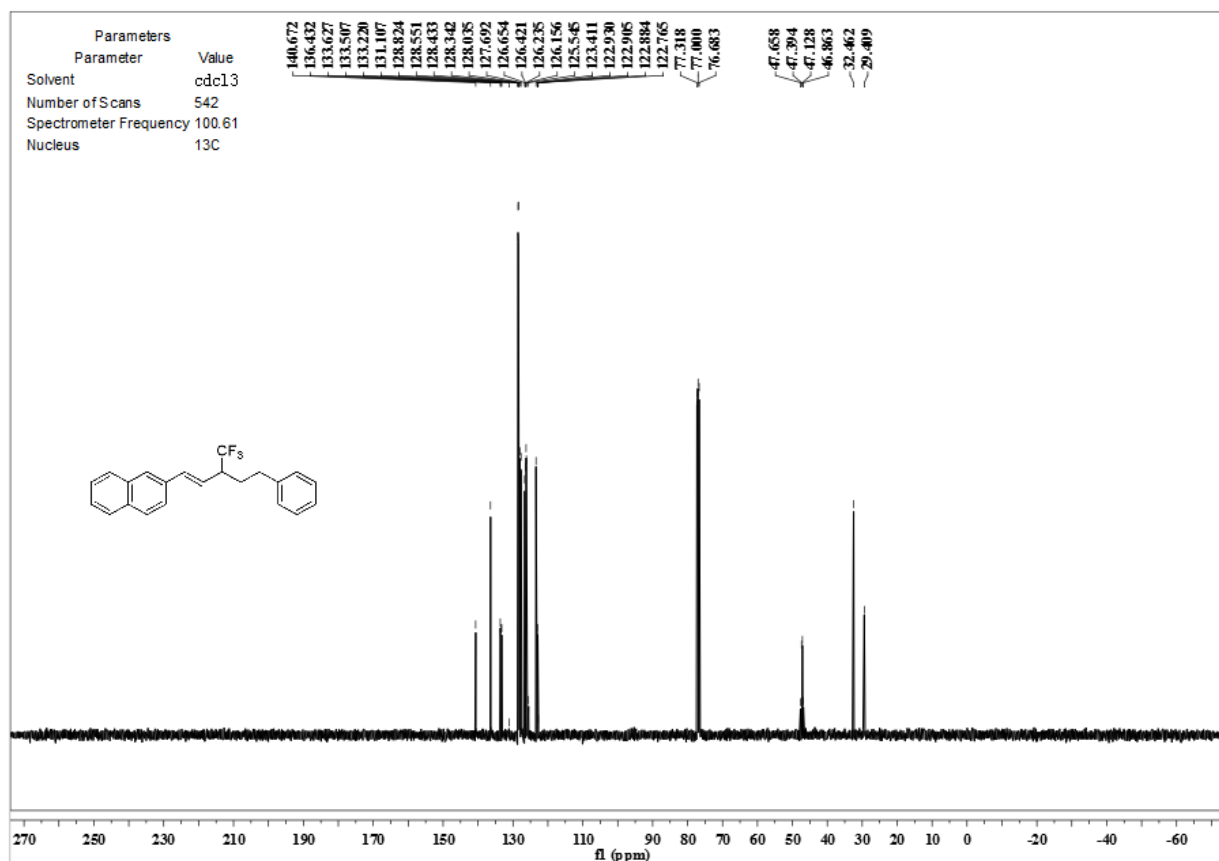
(*E*)-1-Chloro-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene (4b).



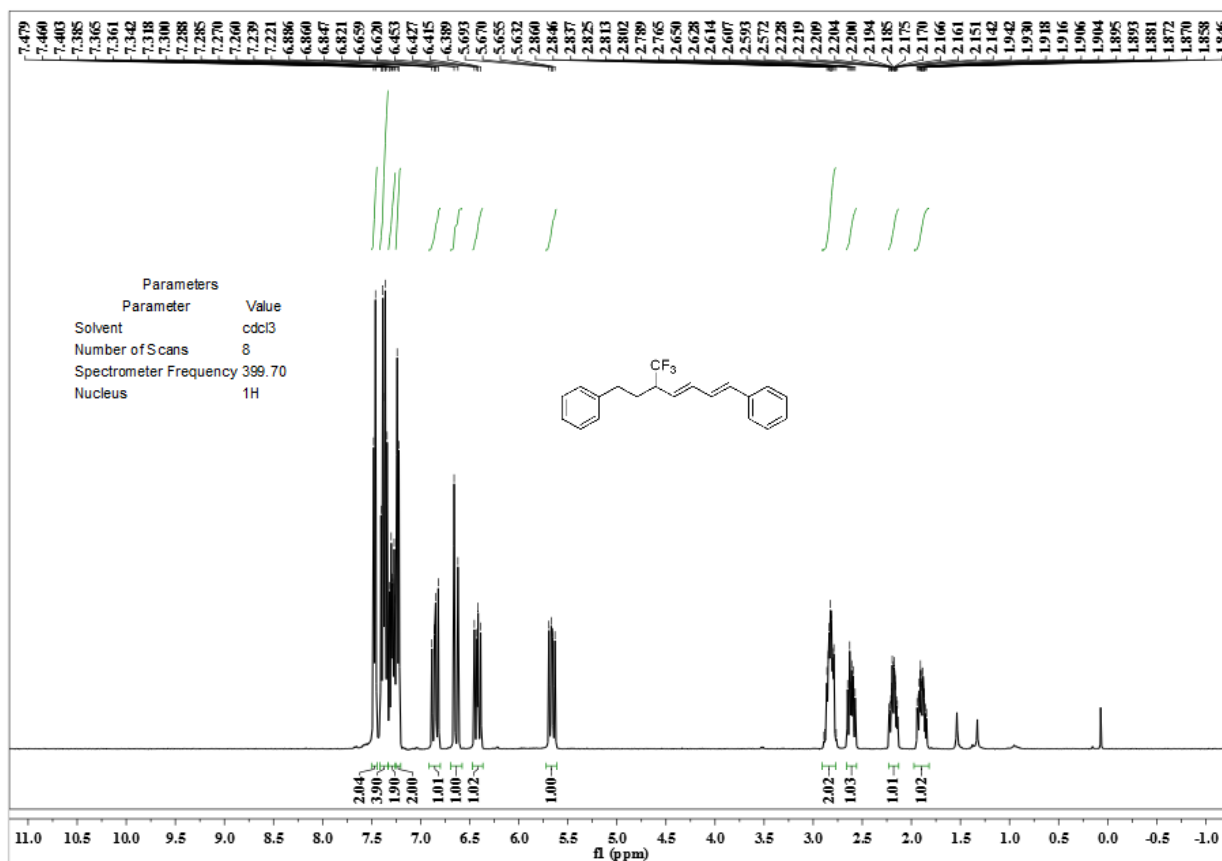


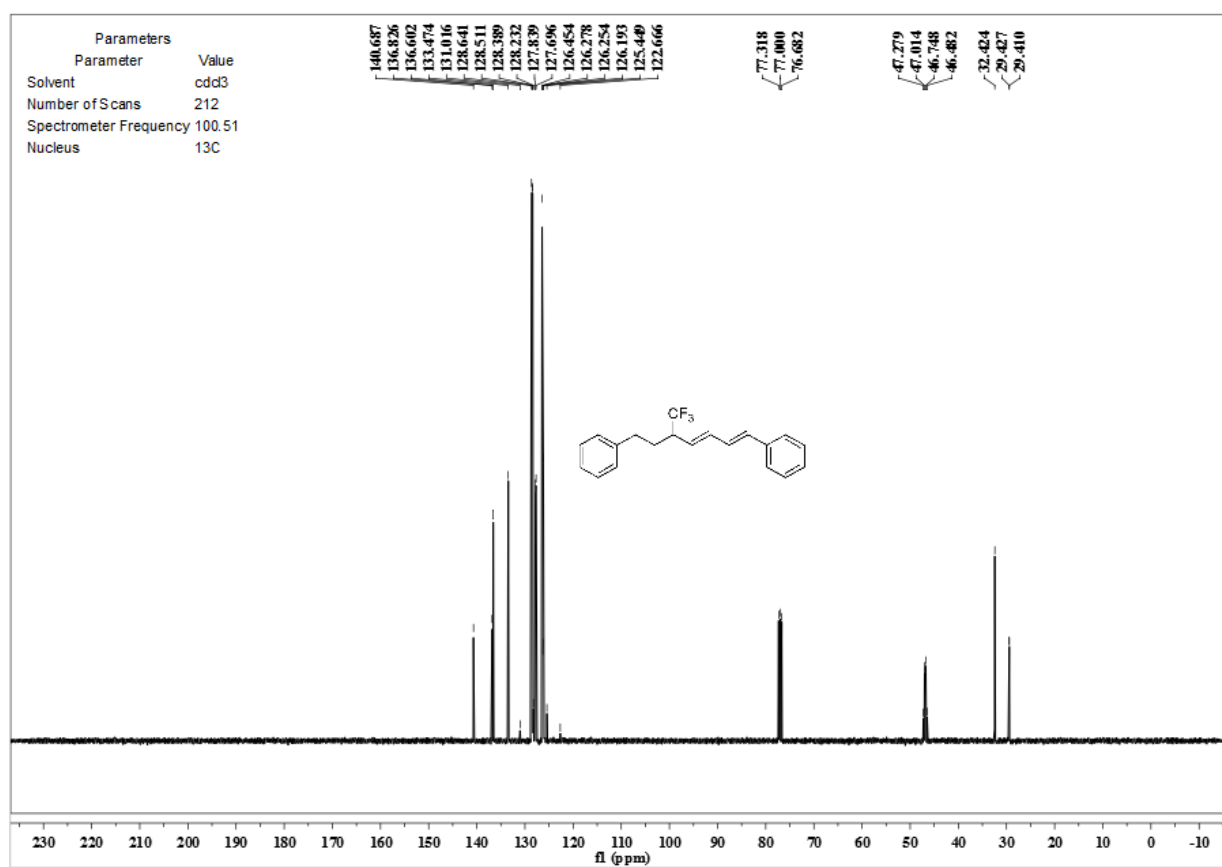
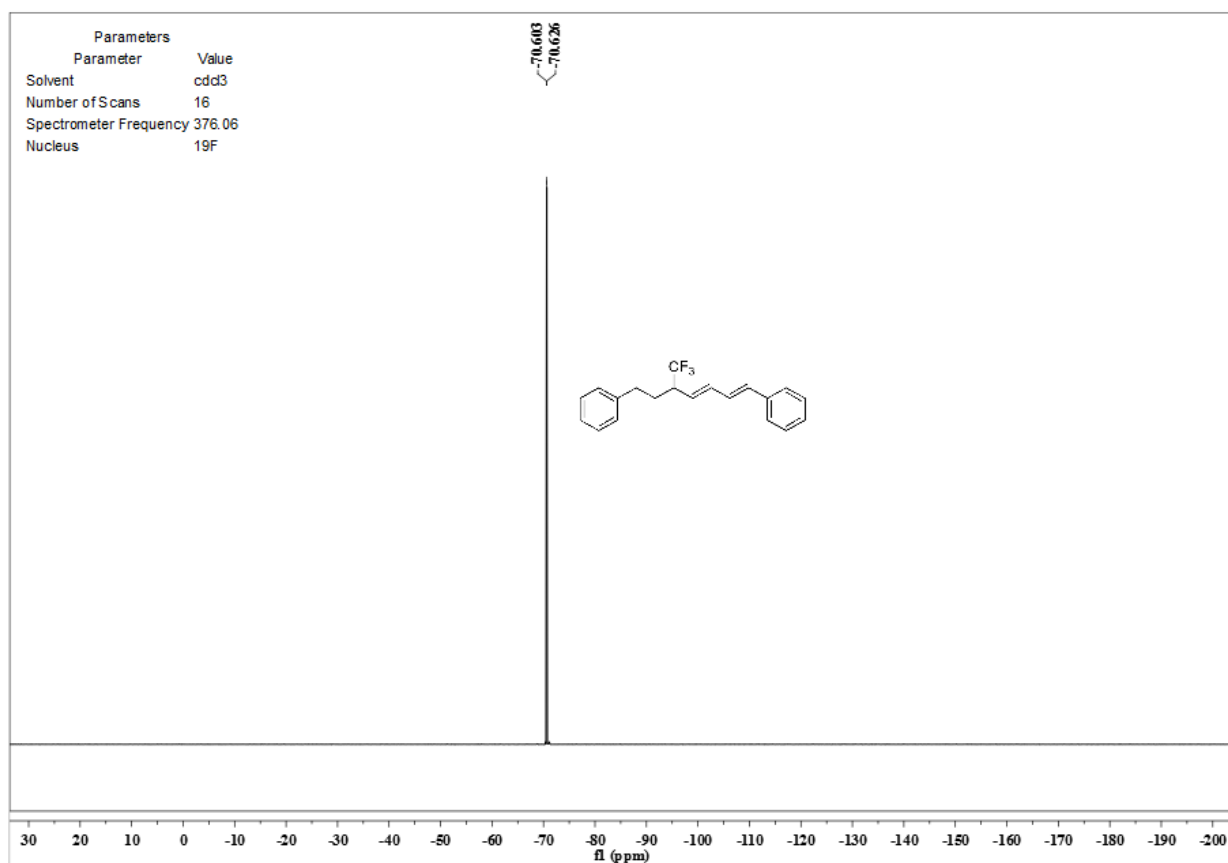
(E)-2-(5-Phenyl-3-(trifluoromethyl)pent-1-en-1-yl)naphthalene (4c).



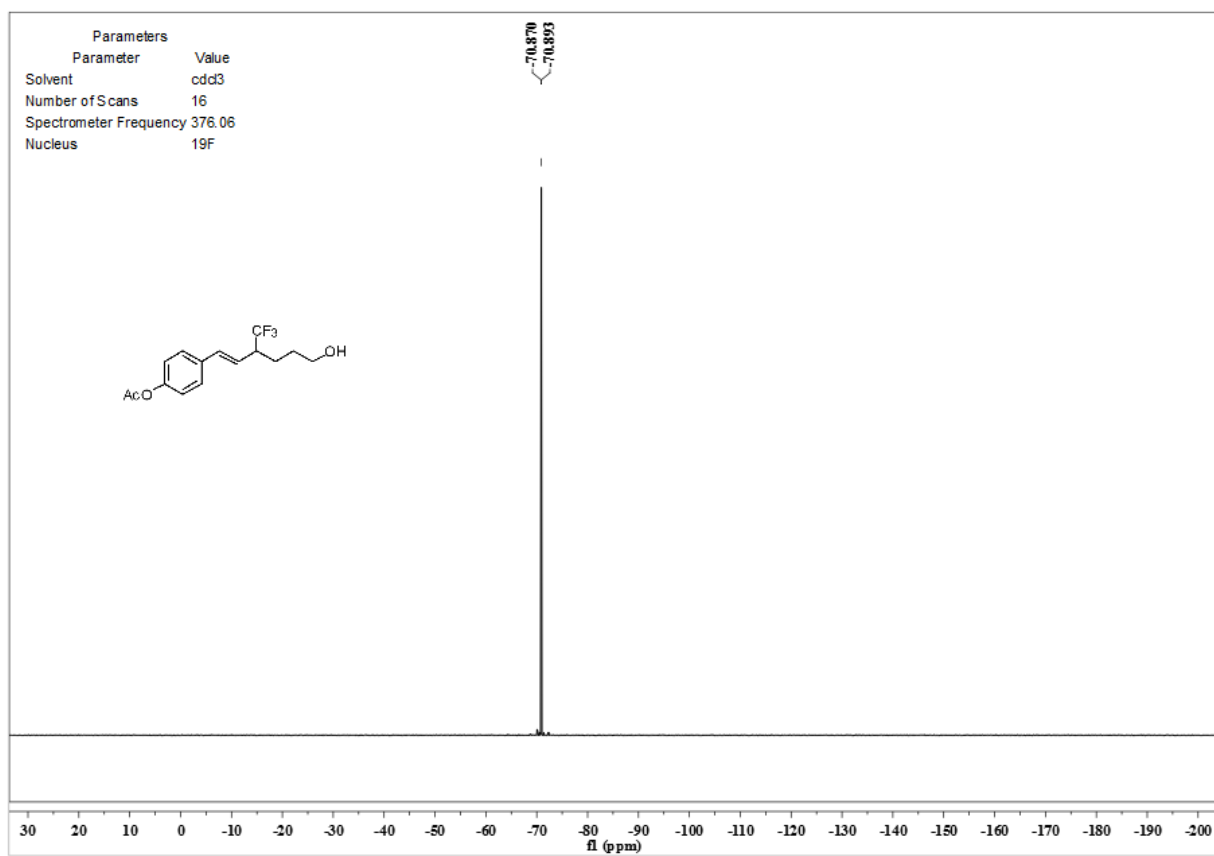
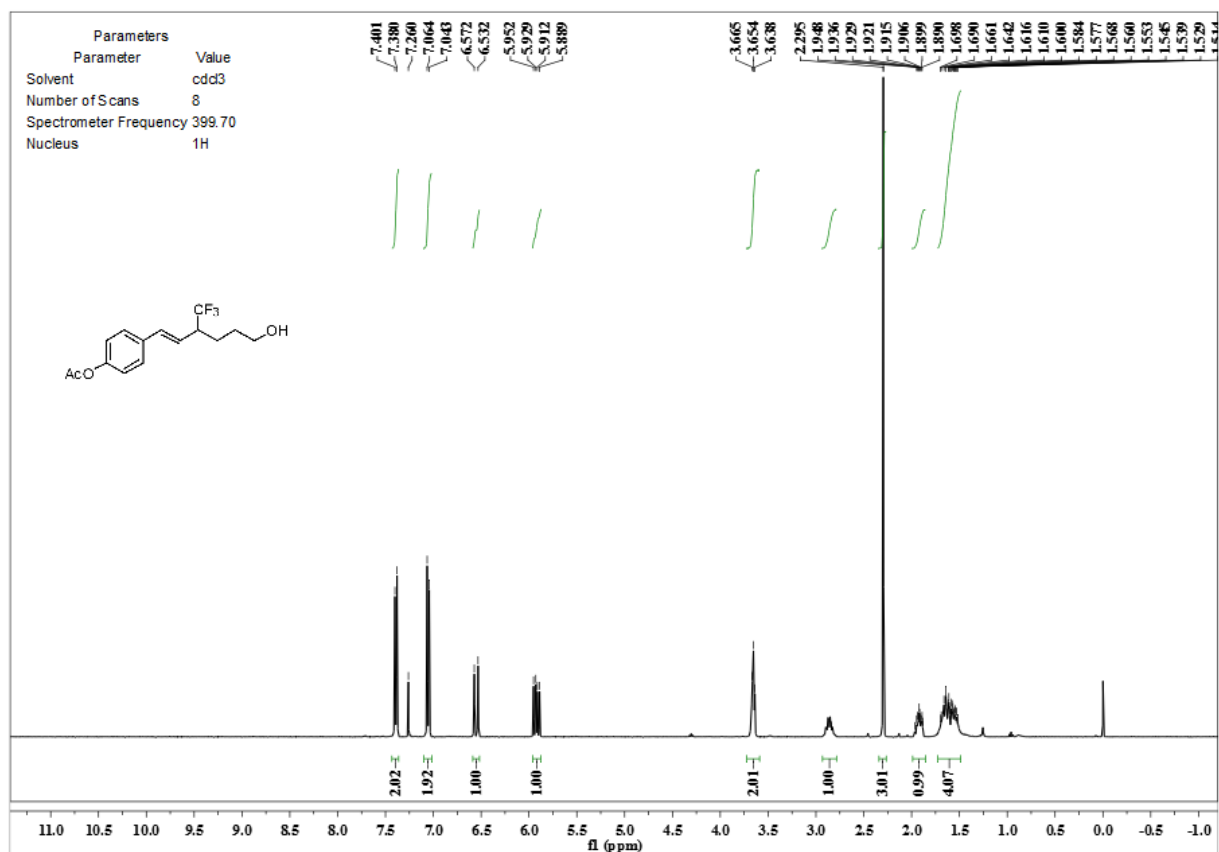


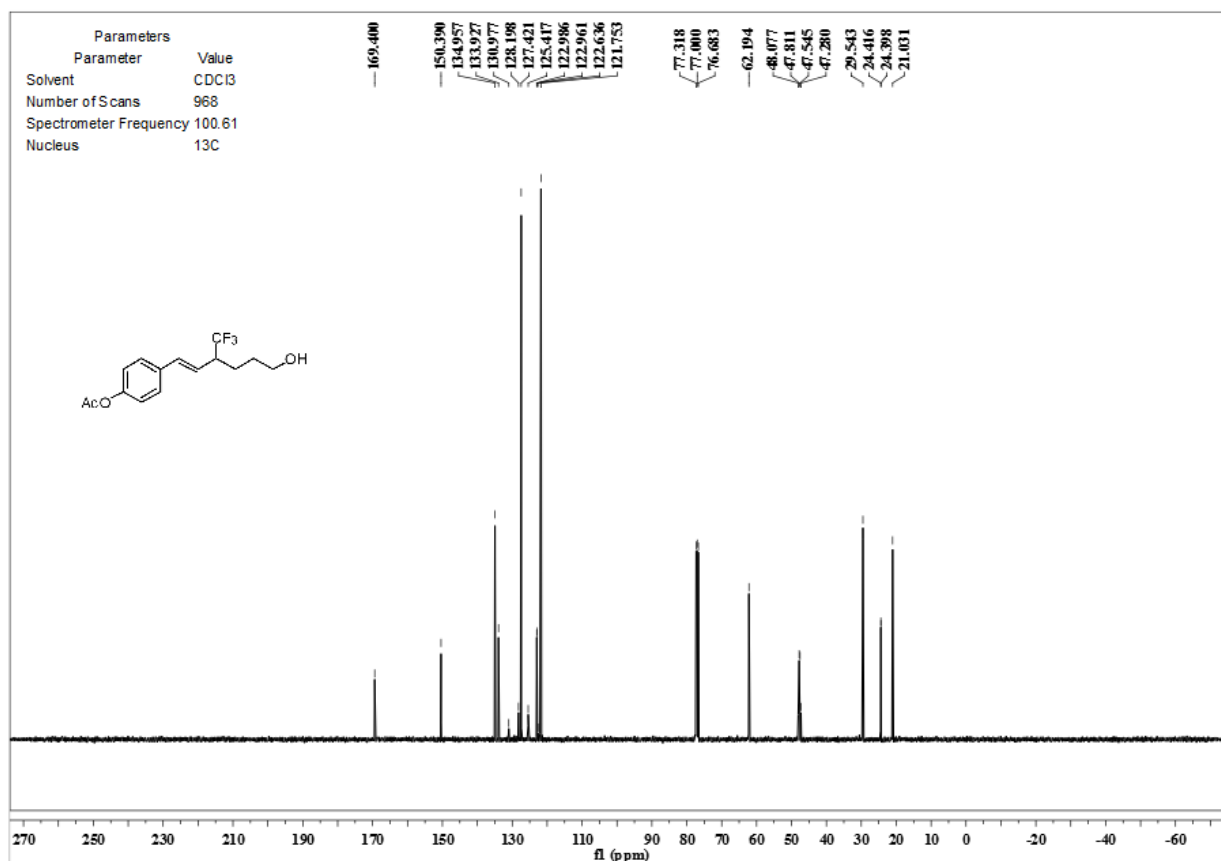
((1E,3E)-5-(trifluoromethyl)hepta-1,3-diene-1,7-diyl)dibenzene (4d).



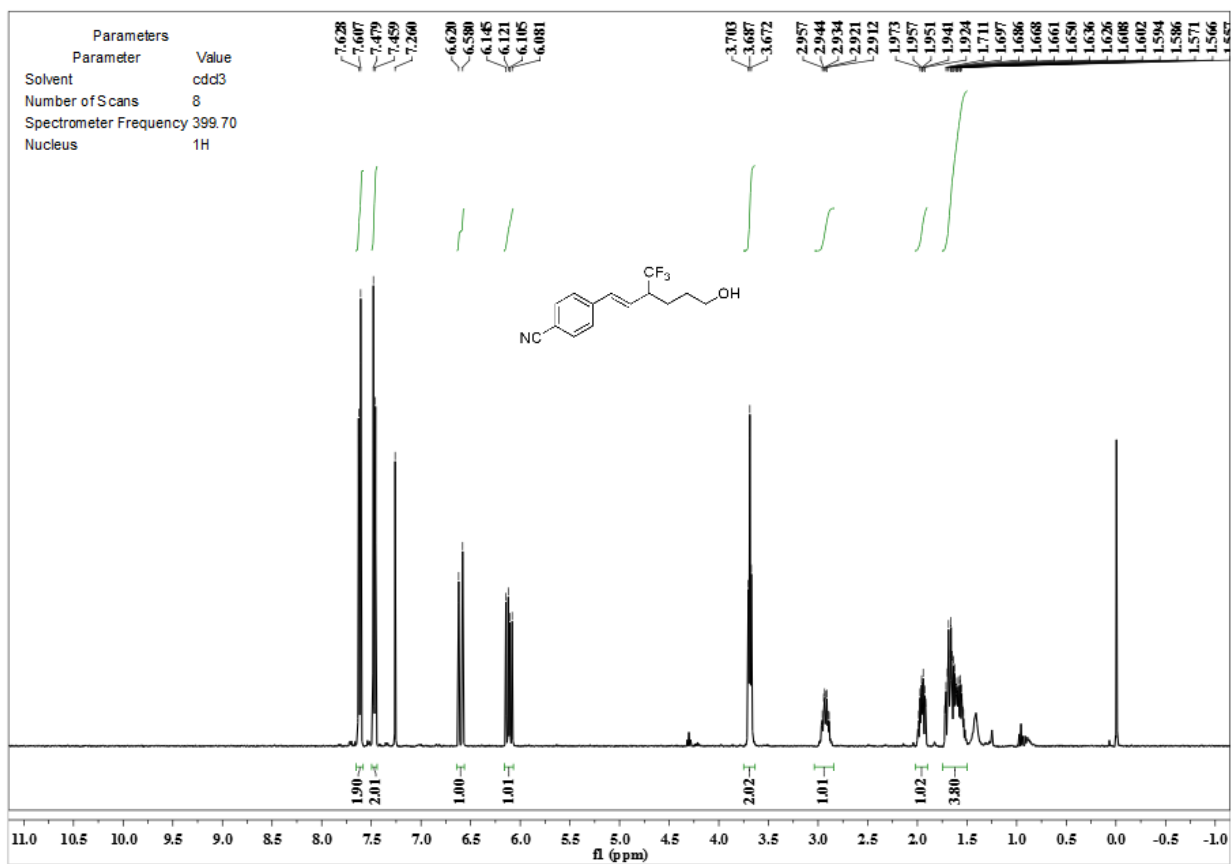


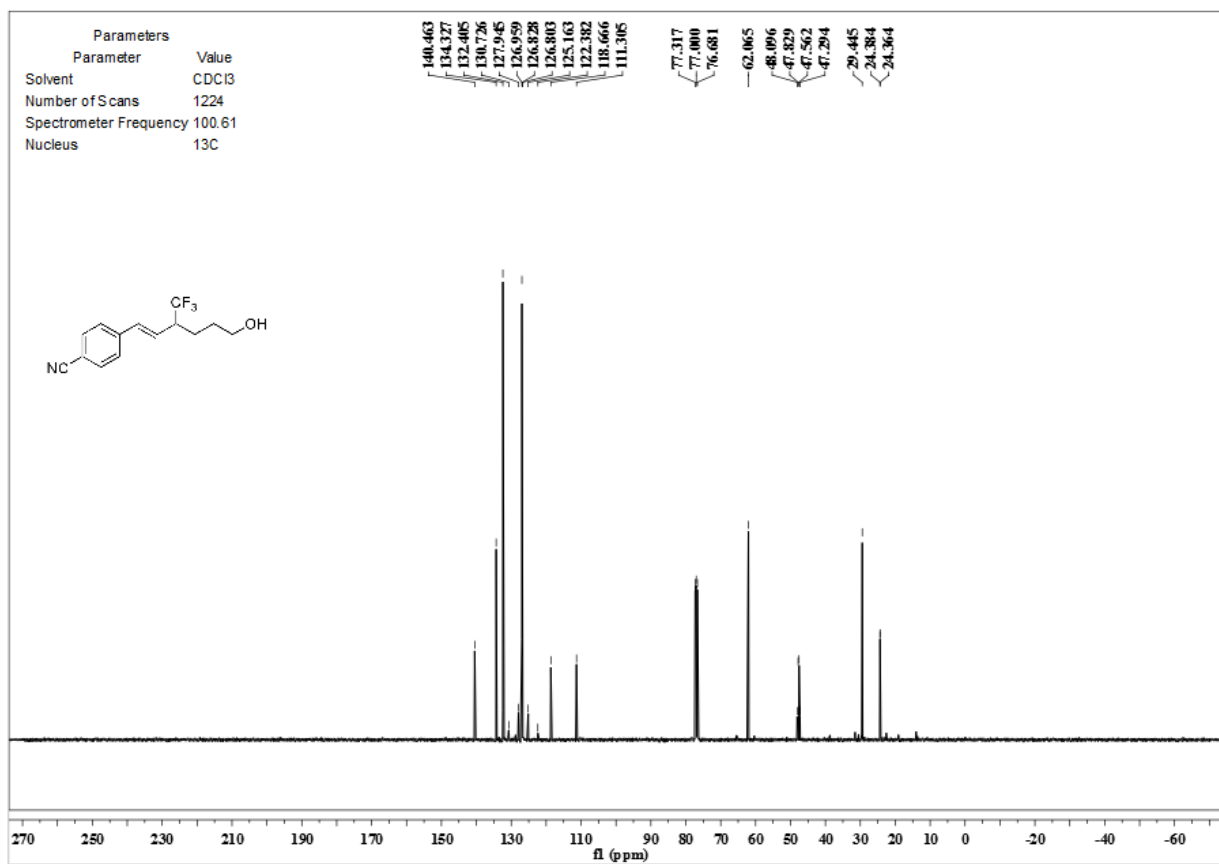
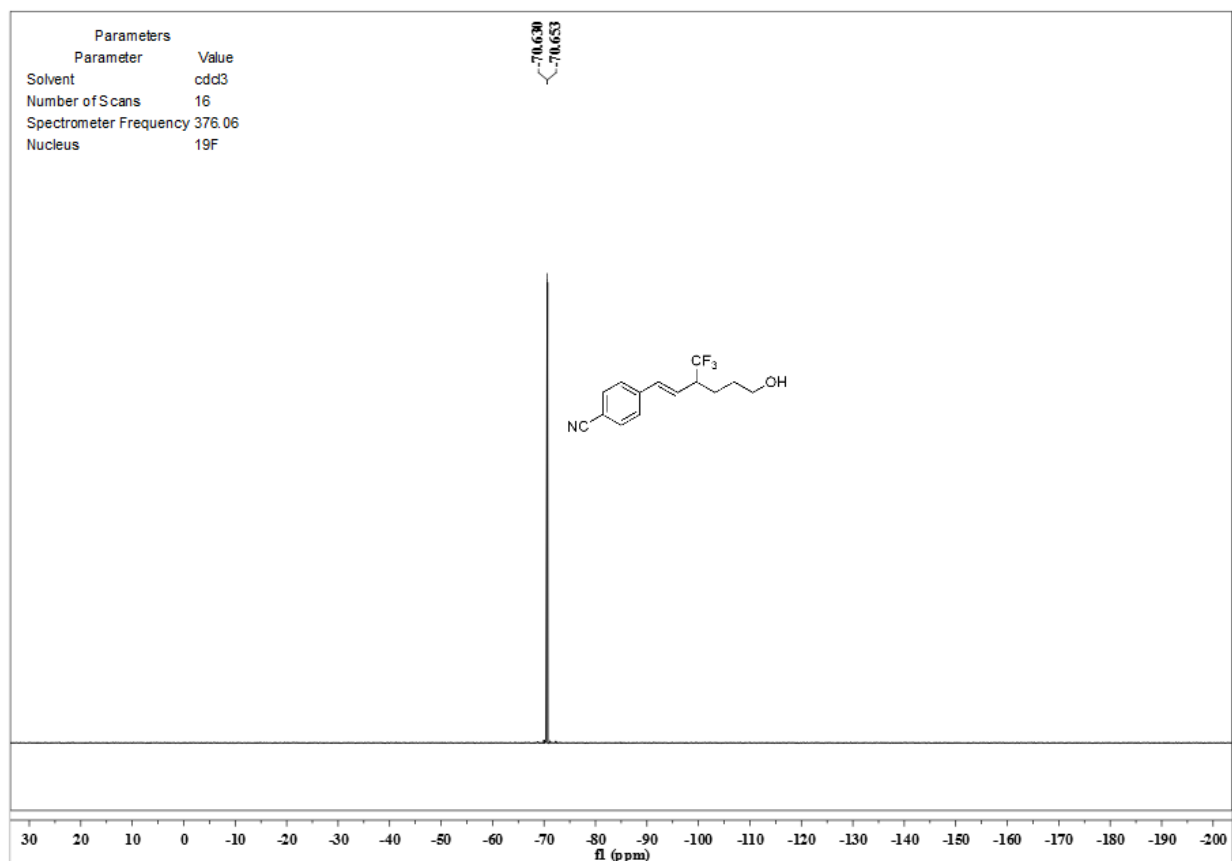
(E)-4-(6-Hydroxy-3-(trifluoromethyl)hex-1-en-1-yl)phenyl acetate (4e).



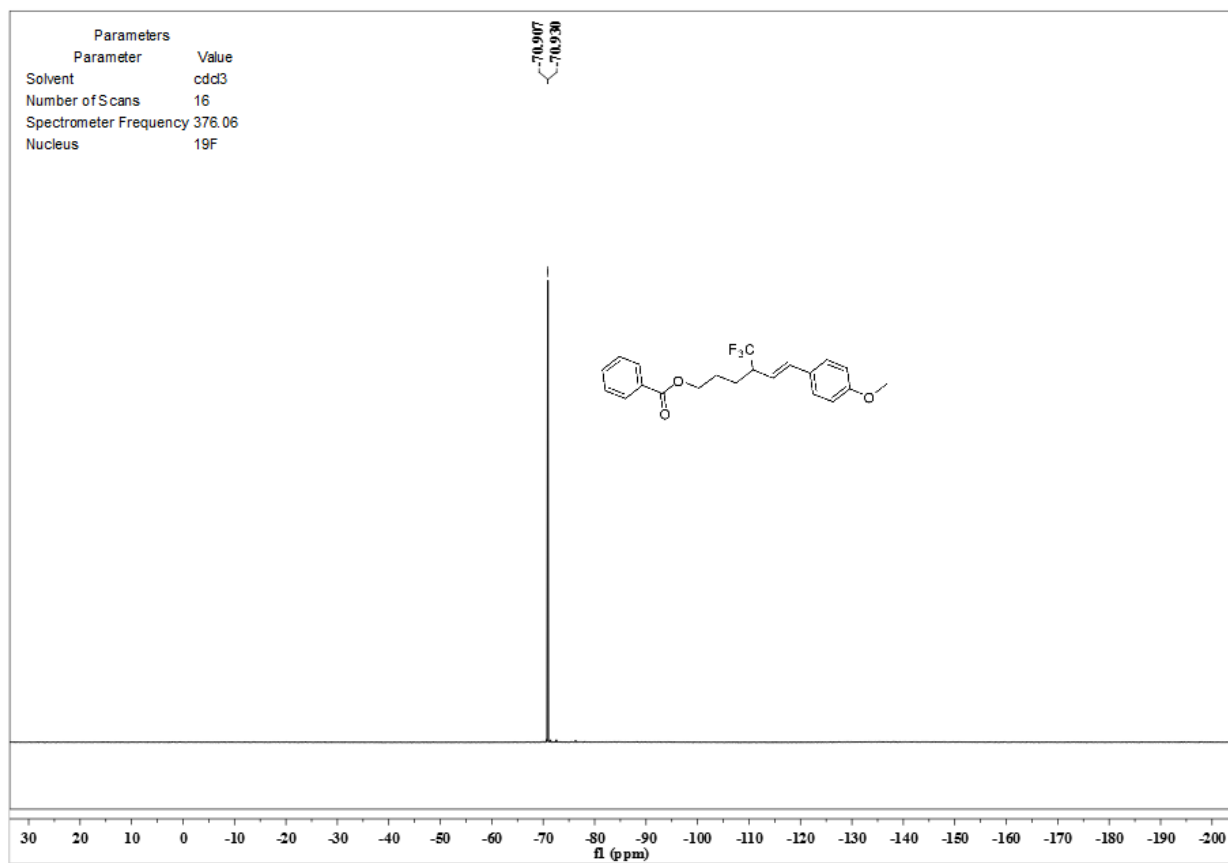
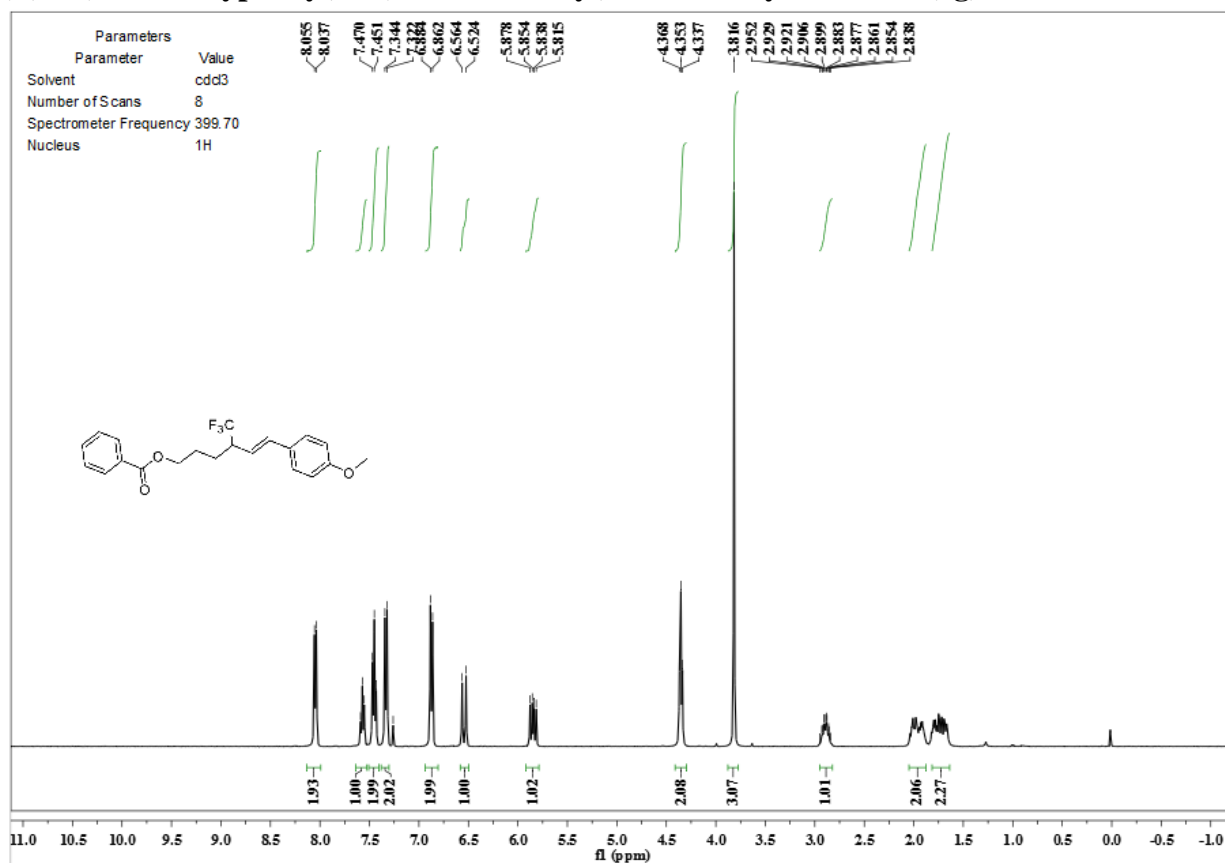


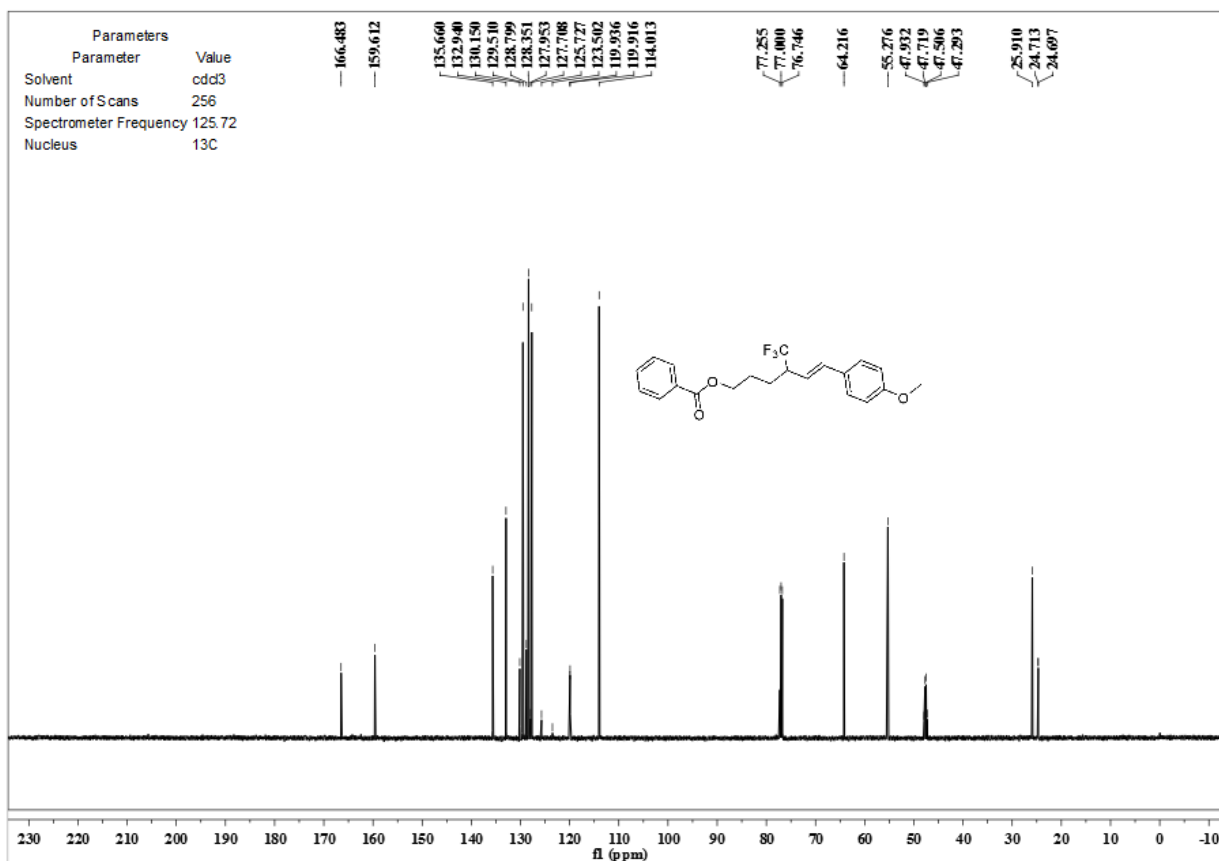
(E)-4-(6-hydroxy-3-(trifluoromethyl)hex-1-en-1-yl)benzonitrile (4f).



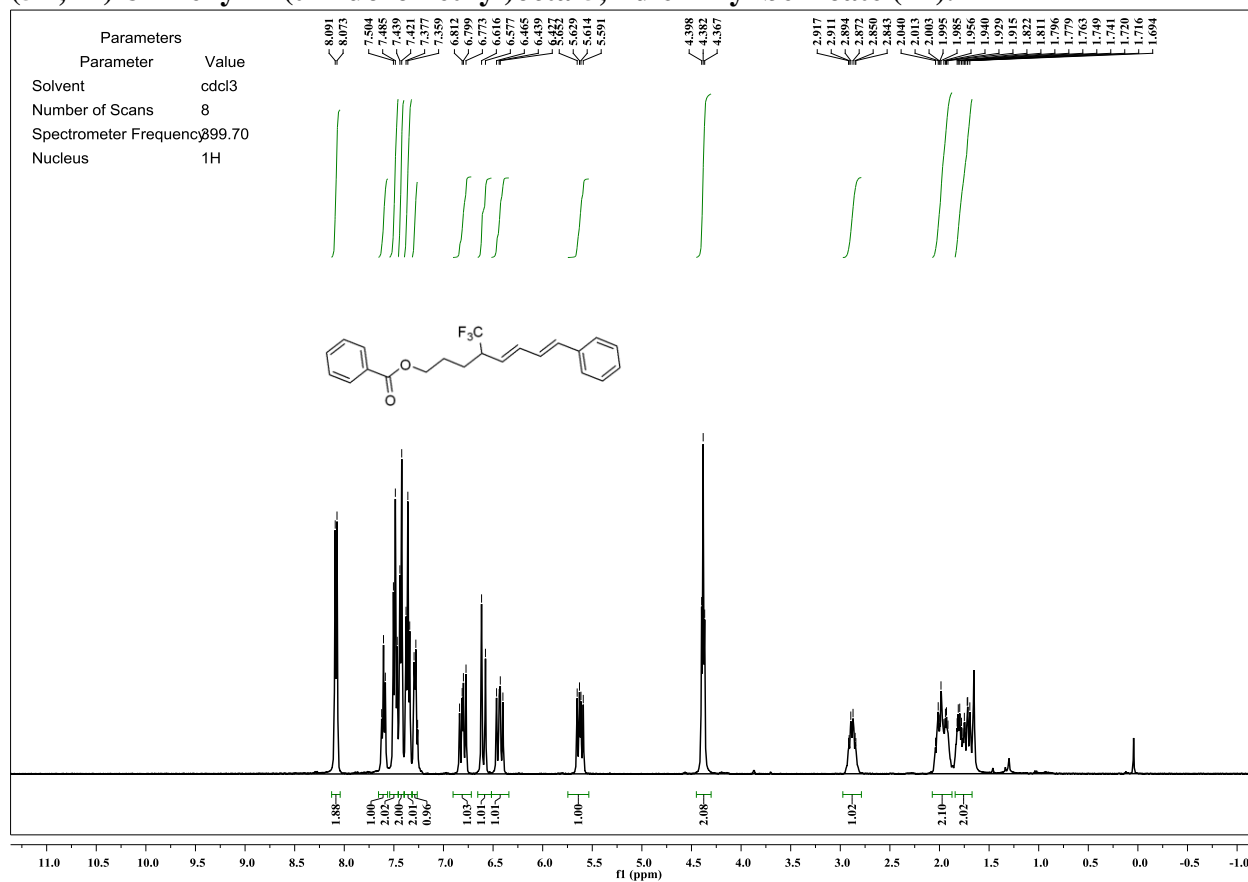


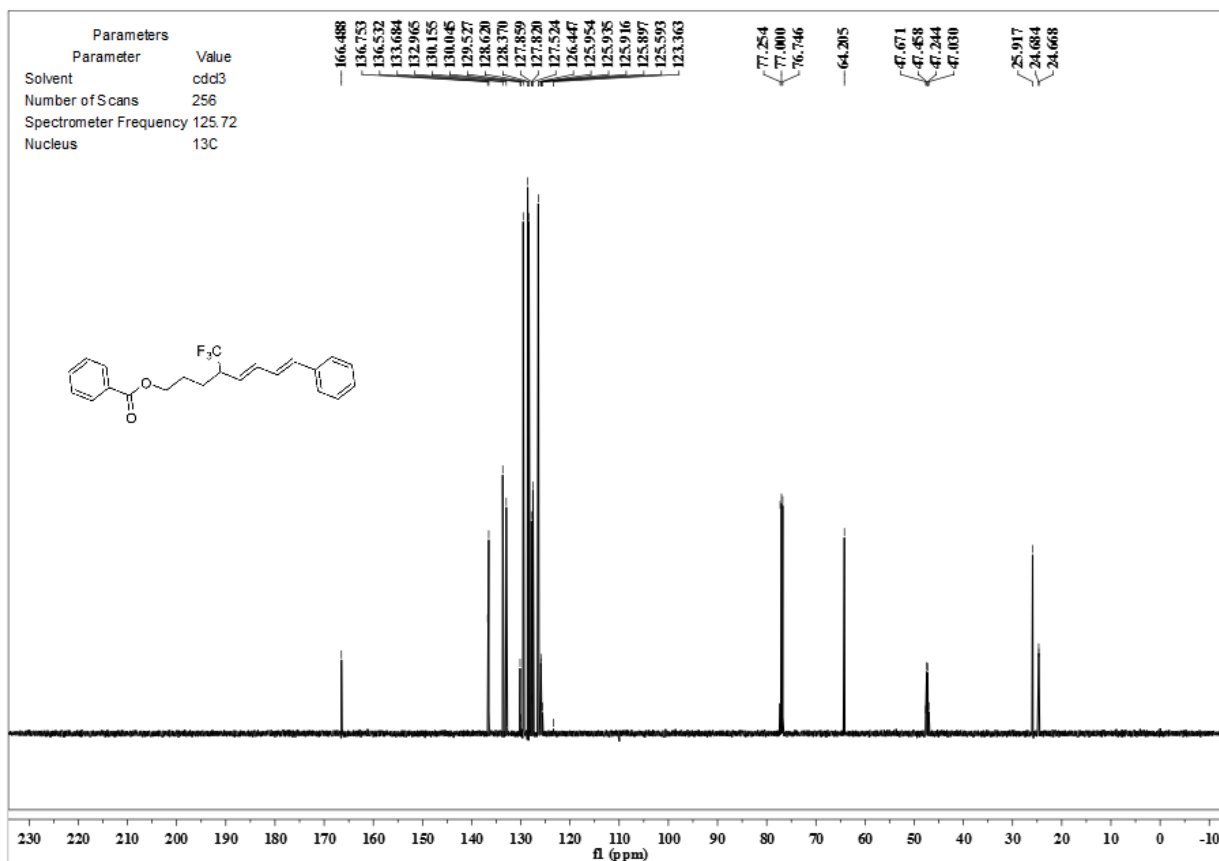
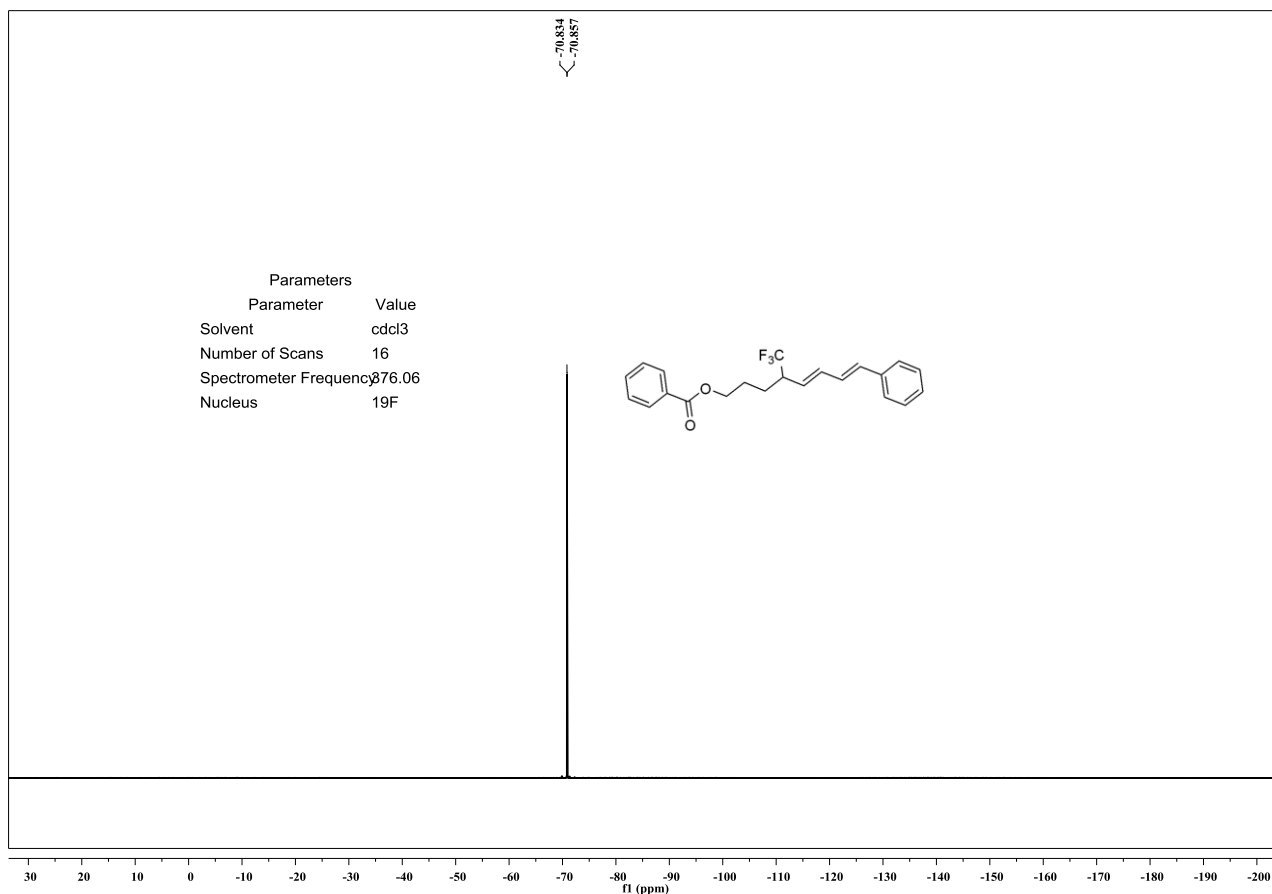
(E)-6-(4-Methoxyphenyl)-4-(trifluoromethyl)hex-5-en-1-yl benzoate (4g).



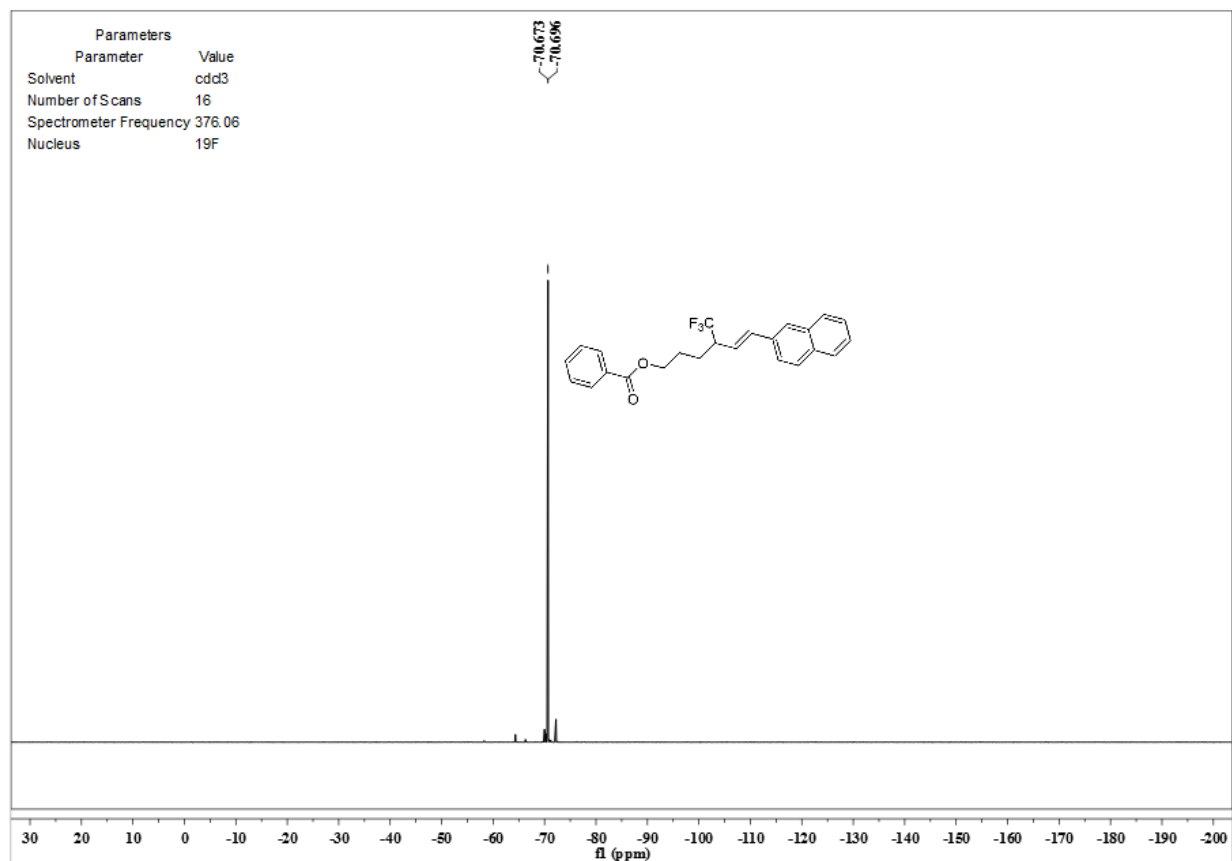
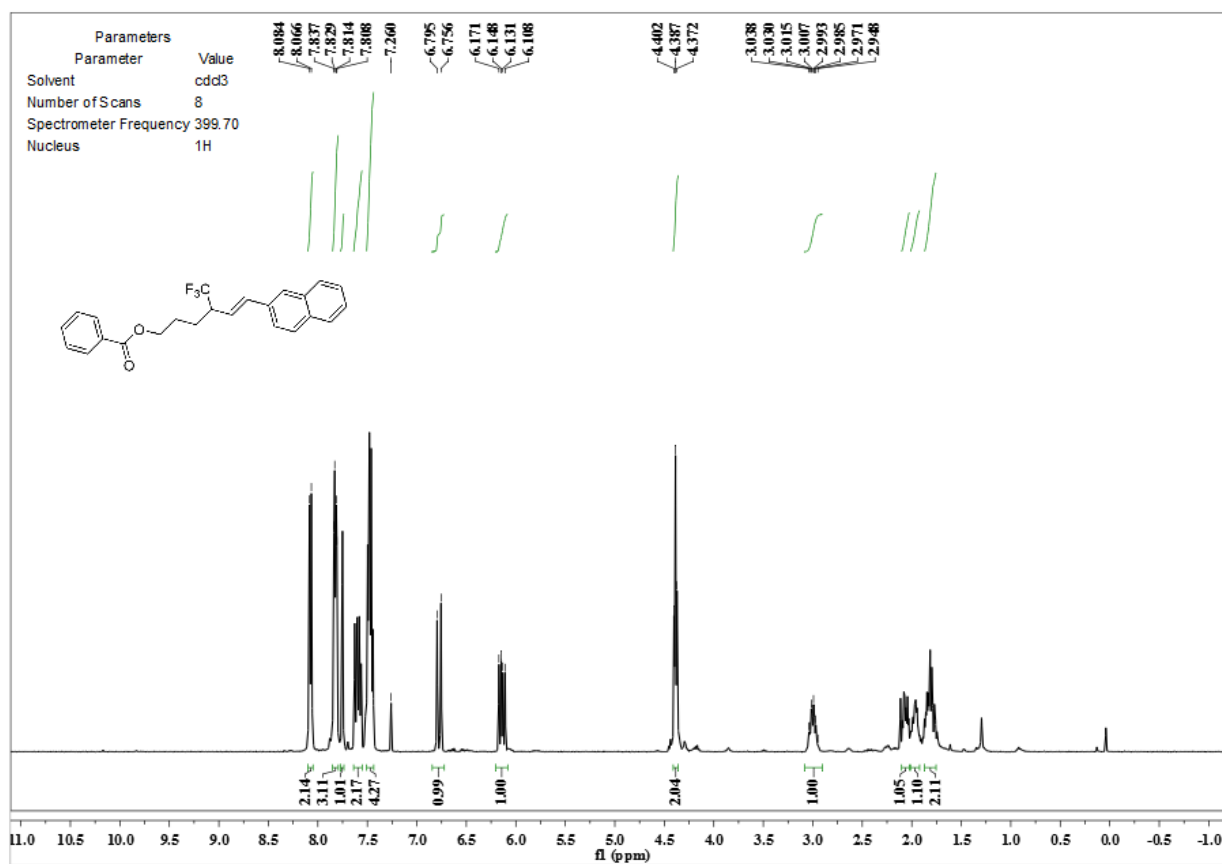


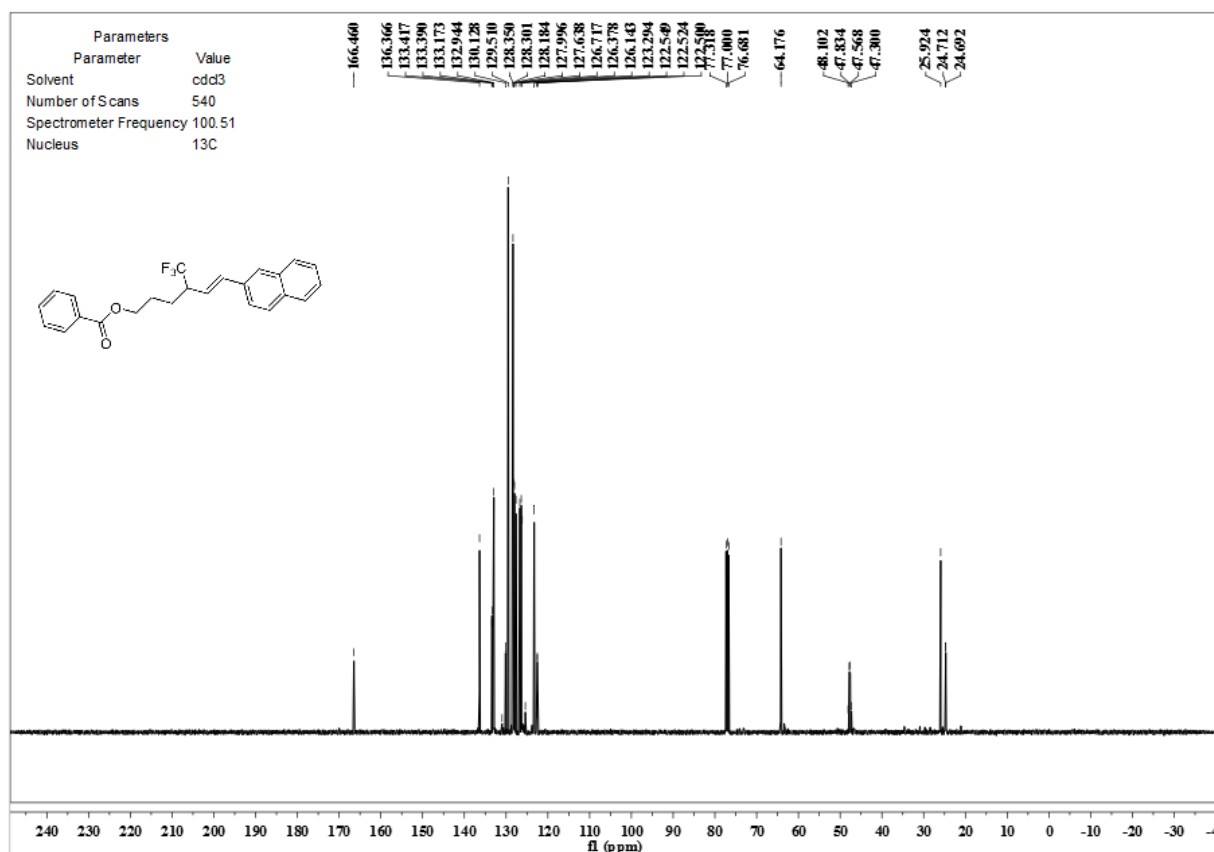
(5E,7E)-8-Phenyl-4-(trifluoromethyl)octa-5,7-dien-1-yl benzoate (4h).



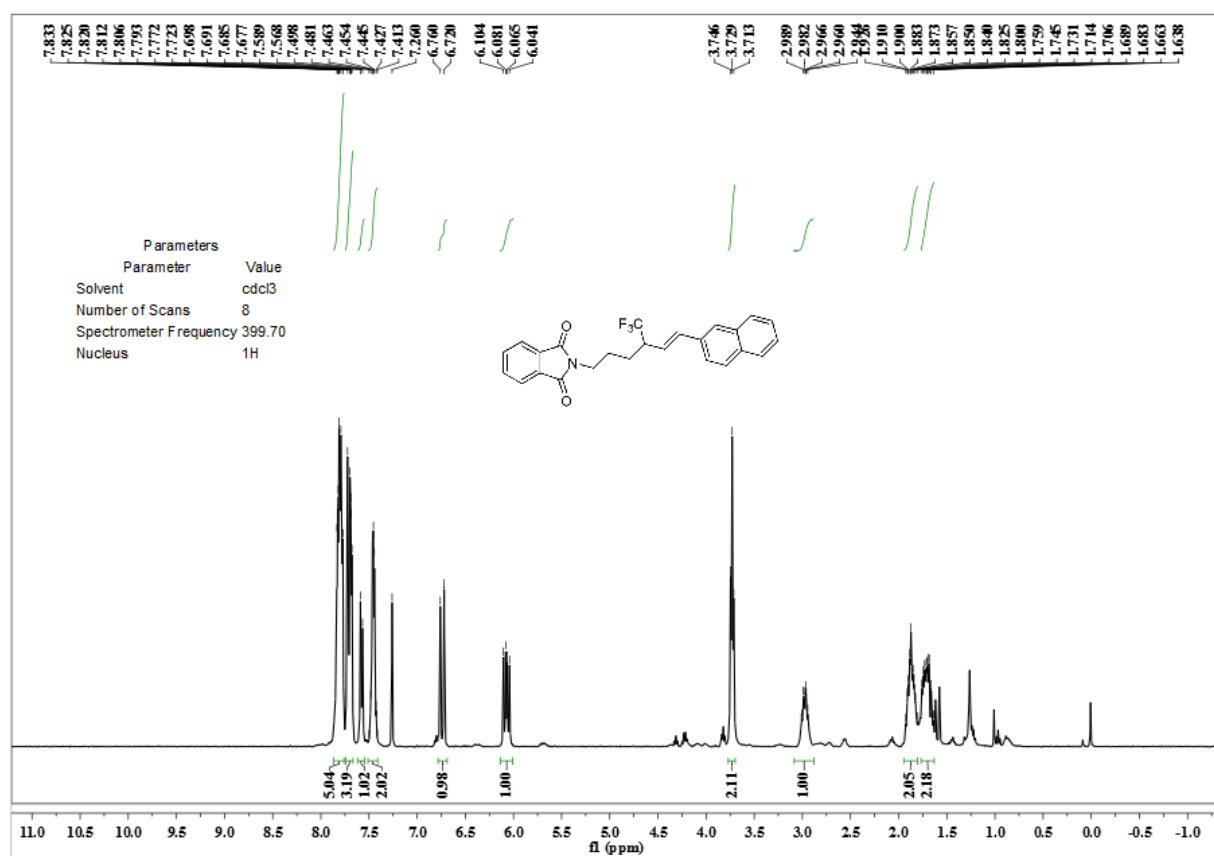


(*E*)-6-(Naphthalen-2-yl)-4-(trifluoromethyl)hex-5-en-1-yl benzoate (4i).

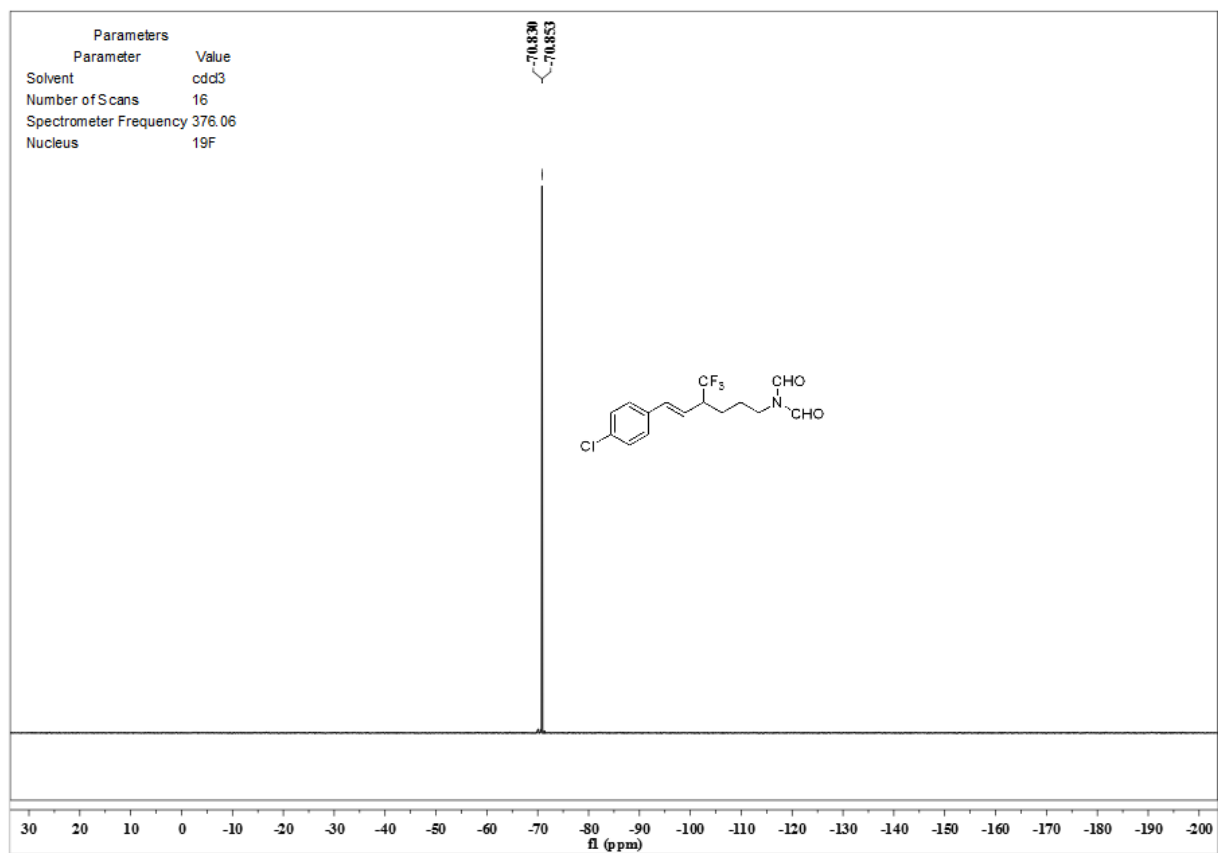
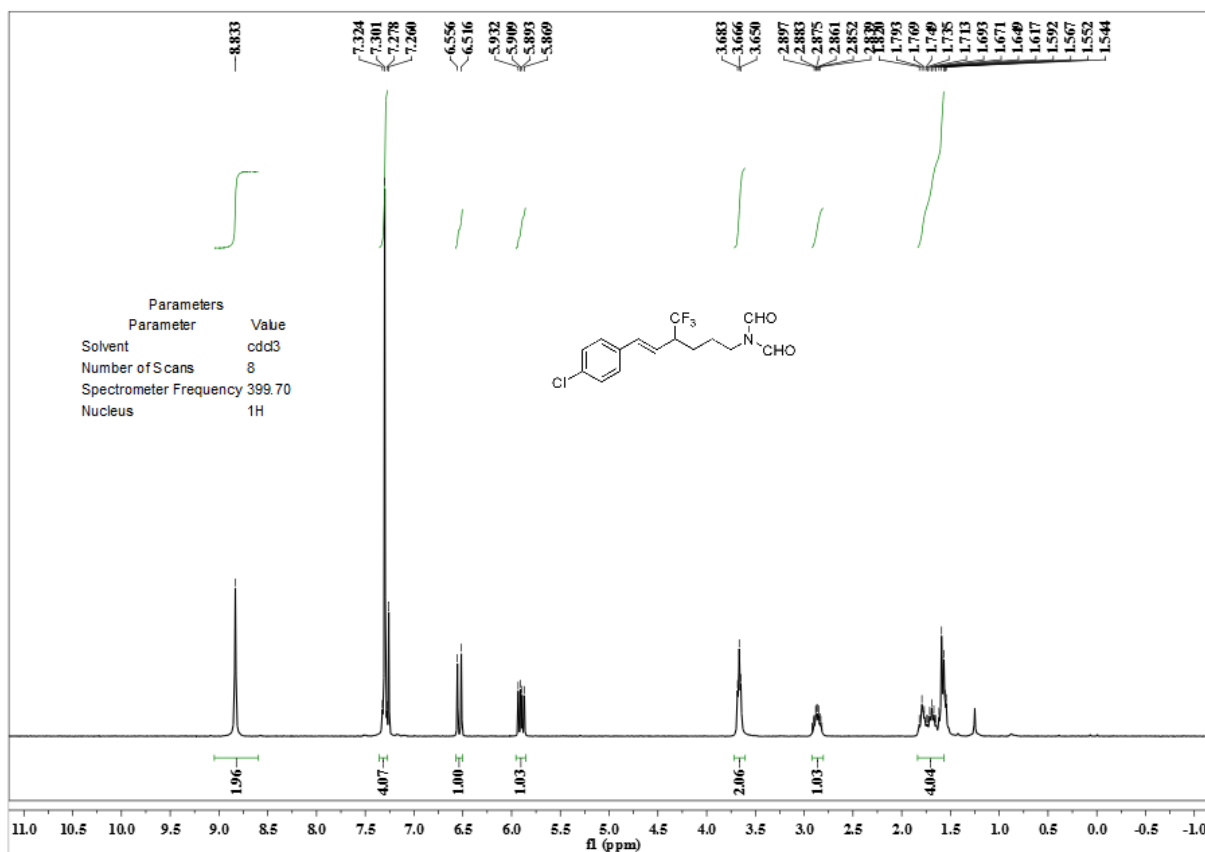


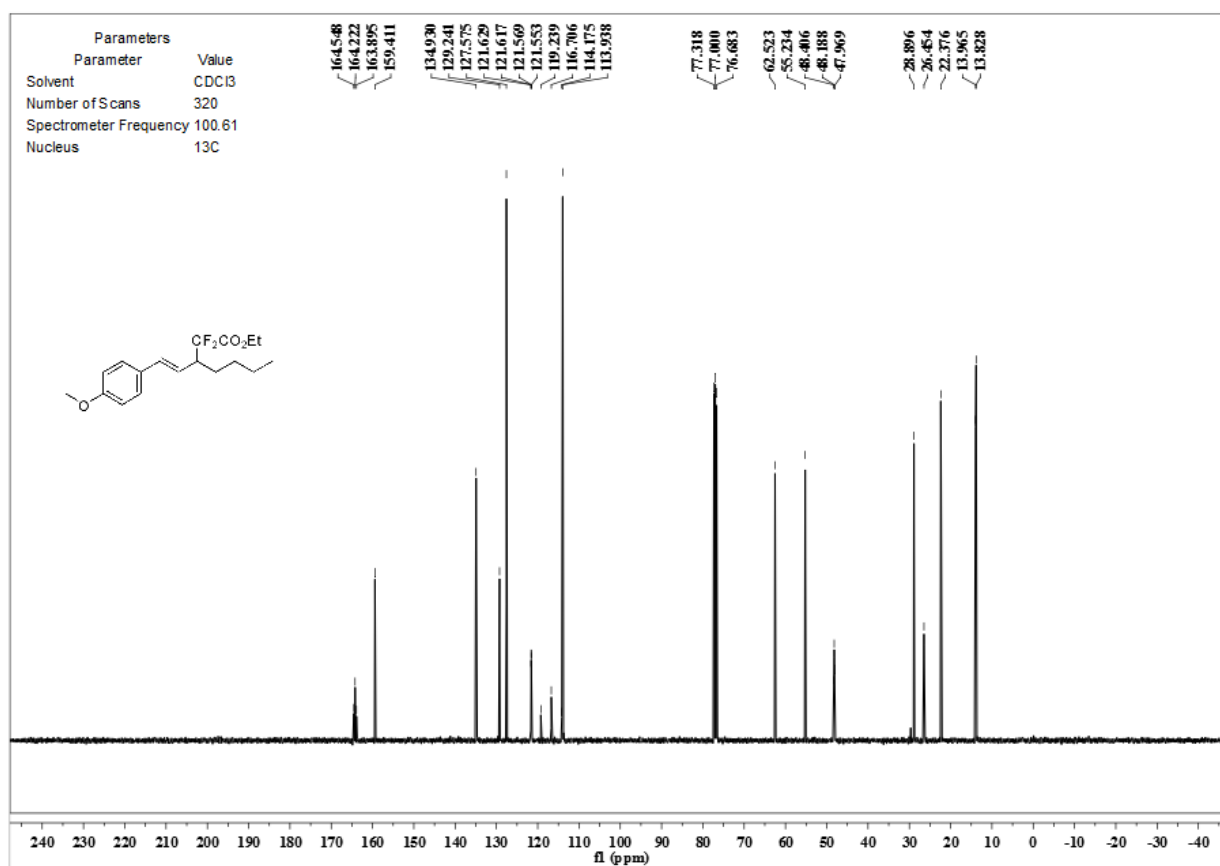
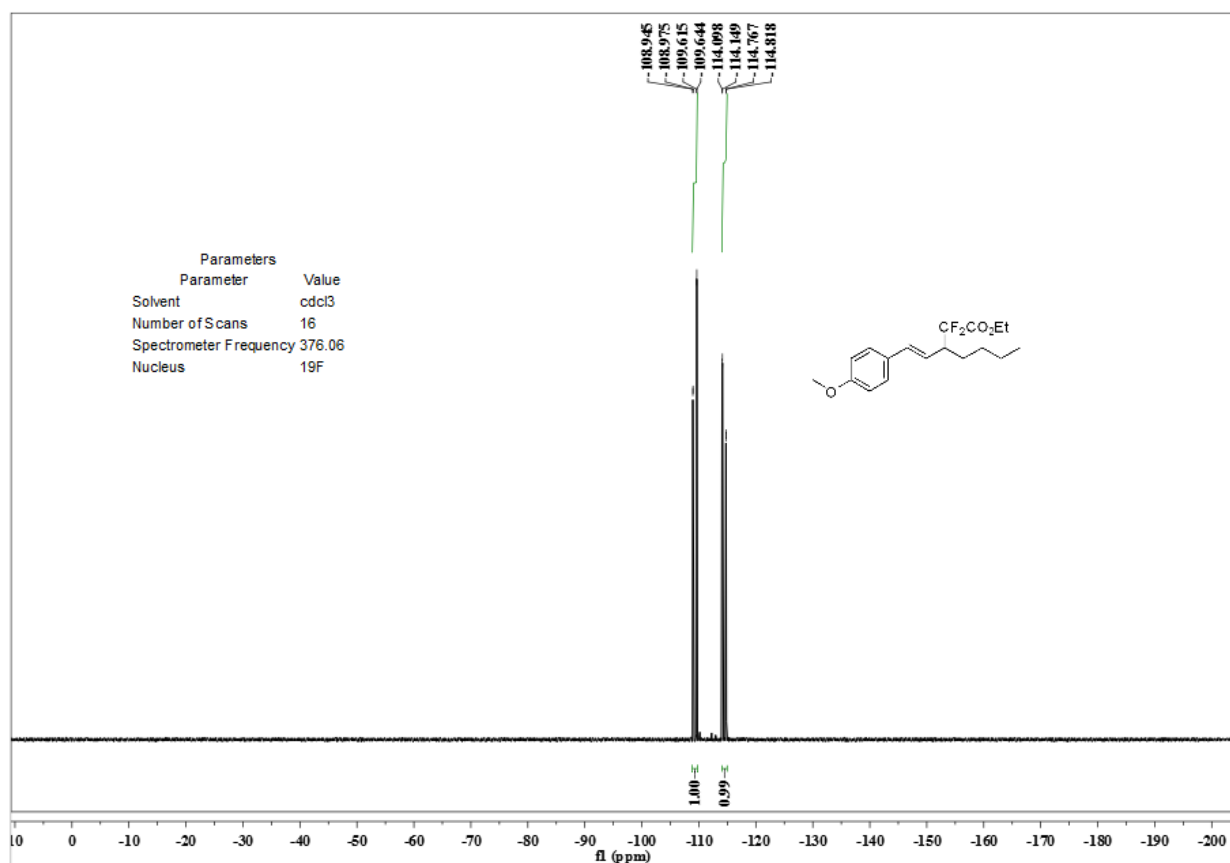


(E)-2-(6-(Naphthalen-2-yl)-4-(trifluoromethyl)hex-5-en-1-yl)isoindoline-1,3-dione (4j).

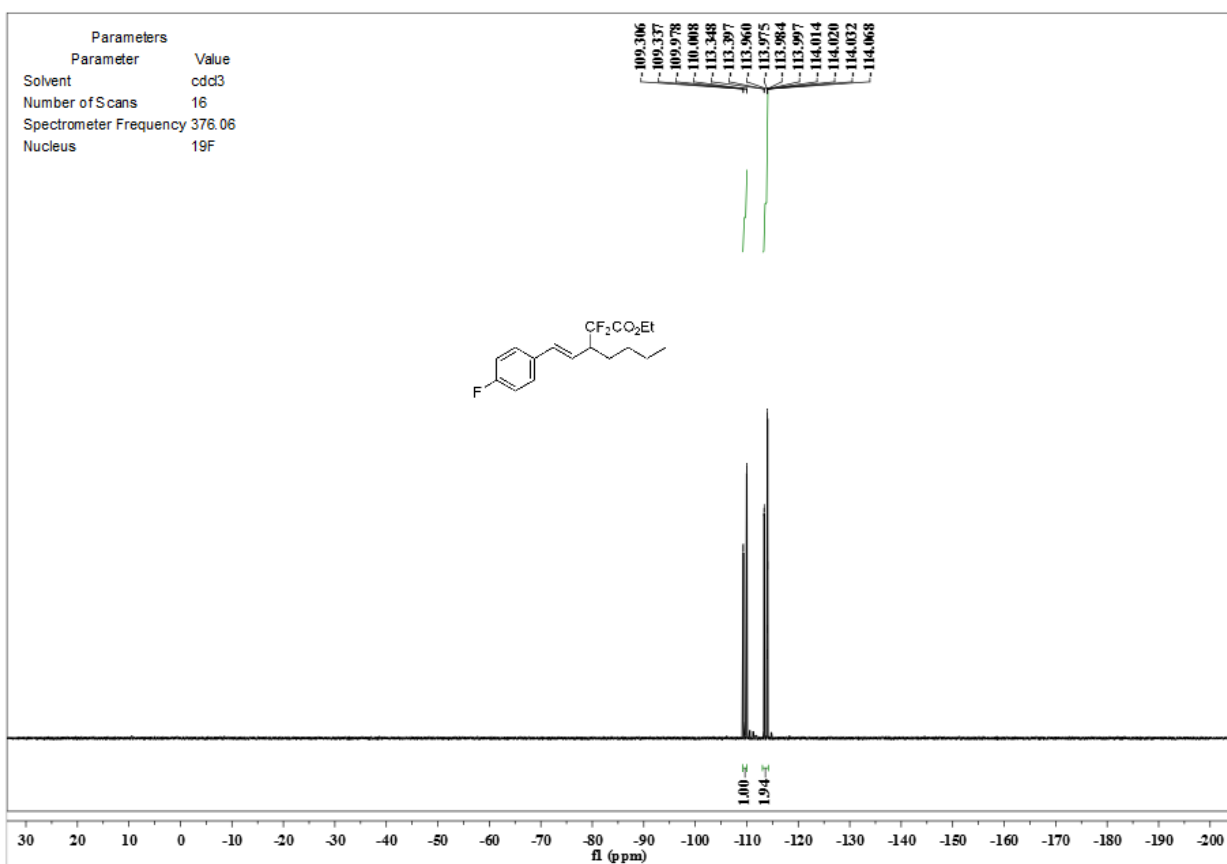
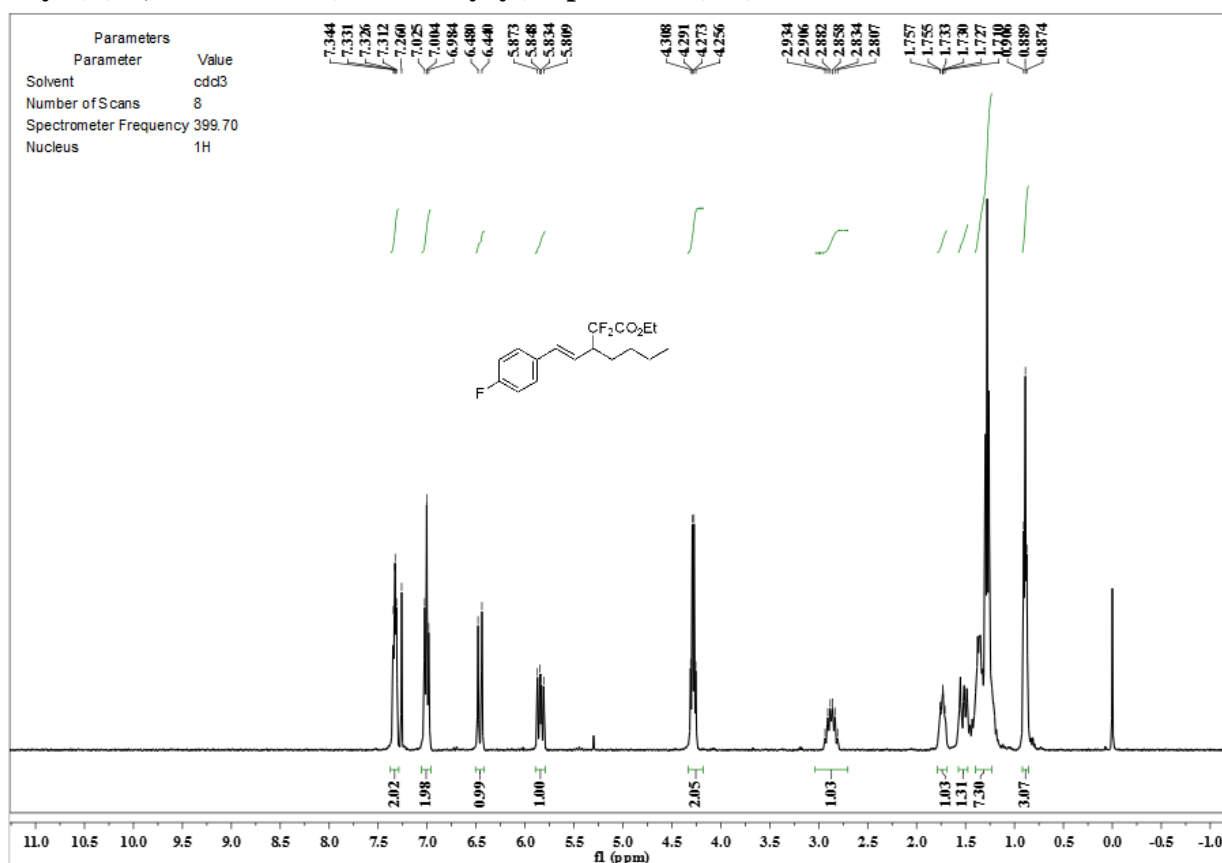


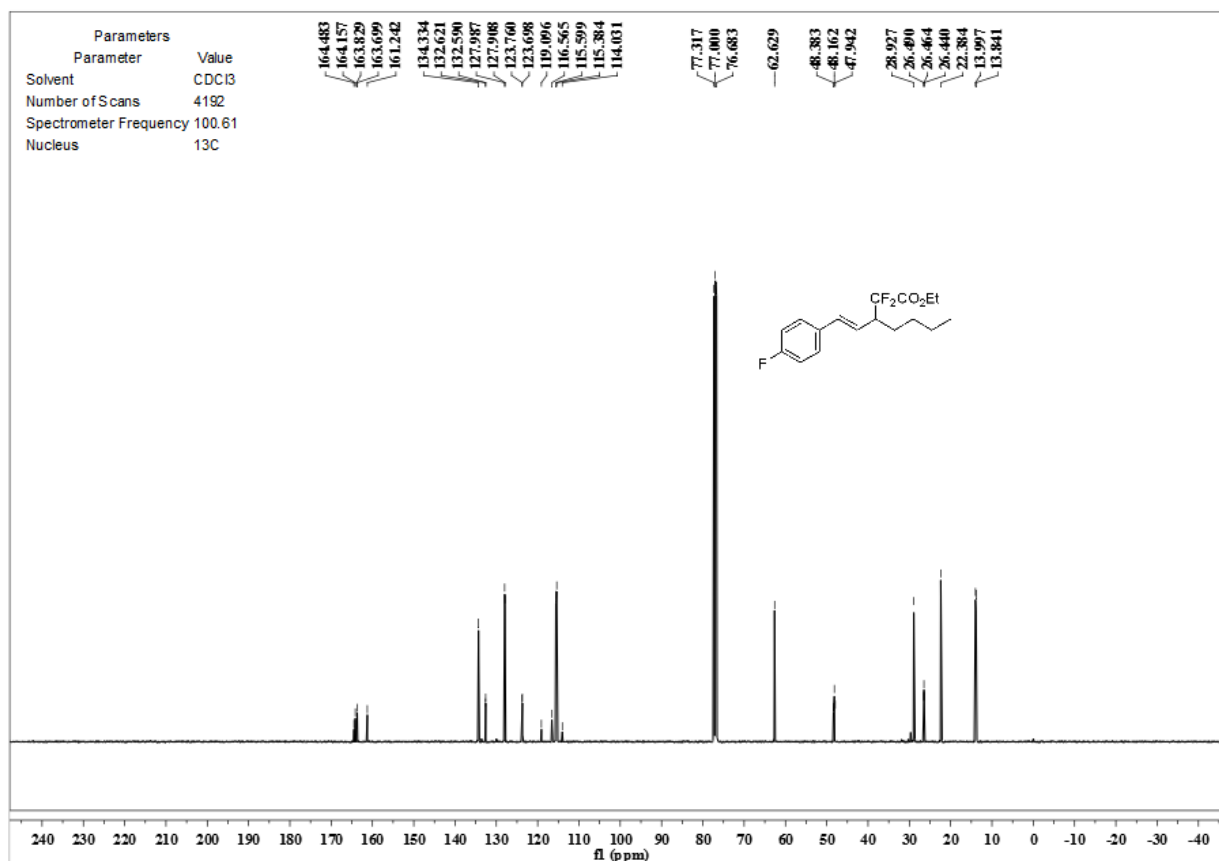
(*E*)-N-(6-(4-chlorophenyl)-4-(trifluoromethyl)hex-5-en-1-yl)-N-formylformamide (4k).





Ethyl (*E*)-2,2-difluoro-3-(4-fluorostyryl)heptanoate (4m).





4-(2-(trifluoromethyl)hexyl)-1,2-dihydronaphthalene (6).

