

Supporting information

A Broadly Applicable Method for Pd-Catalyzed Carboperfluoro-alkylation of Terminal and Internal Alkynes: A Convenient Route to Tri- and Tetrasubstituted Olefins.

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General Information

All the manipulations were performed in a nitrogen-filled glovebox or under an argon atmosphere using Schlenk techniques, unless mentioned otherwise. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates and visualized with cerium molybdate stain (Hanessian's stain). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F NMR spectra were recorded with a Bruker AV 400 spectrometer. ^1H and ^{13}C chemical shifts are given in ppm relative to TMS. The solvent signals were used as references (CDCl_3 $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.0$ ppm) and the chemical shift converted to the TMS scale. Coupling constants (J) are reported in Hz, and the following abbreviations were used to denote multiplets: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet (denotes complex pattern), dd = doublet of doublets, dt = doublet of triplets and br = broad signal. Infrared spectra were recorded with a Jasco FTIR-6200 spectrometer. Electron ionization high-resolution mass spectra (EI-HR) were recorded with an Autospec Premier (Waters Inc) mass spectrometer using the narrow-range high-voltage scan technique with low-boiling perfluorokerosene (PFK) as internal standard. Samples were introduced by using a heated direct insertion probe. Electrospray ionization high-resolution mass spectra (ESI-HR) were recorded with MALDISynapt G2-S HDMS (Waters Inc) mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyzer. ESI-MS spectra were recorded in the positive ion mode (the source parameters: capillary voltage 3.15 kV, sampling cone 25 V, source temperature 120 °C, desolvation temperature 150 °C). GC analyses were performed on TRACETM Ultra Gas Chromatograph (Thermo Scientific) equipped with FID detector and Restek Rtx-1 column (30m, 0.32 mmID, 0.5 μm df). The following temperature program was used: 100 °C (2 min), 20 °C/min to 310 °C (2 min). Unless otherwise noted, all commercially available compounds (ABCR, Acros, Fluorochem, TCI, Sigma-Aldrich, Strem) were used as received. Phosphine ligands were purchased from Aldrich, $\text{Pd}(\text{OAc})_2$ was purchased Strem. Precatalyst BINAP Pd G3 was prepared following

Buchwald's procedure,¹ and showed similar reactivity to the commercial sample purchased from Strem.

Evaluation of reaction conditions for Pd-catalyzed reaction of perfluorobutyl iodide, 4-methoxyphenylboronic acid and phenylacetylene.

General procedure for evaluation of reaction conditions: Caution, sequence of addition of reagents is important and guarantee reproducibility of results. In a glovebox, to a 4-mL screw-capped vial containing catalyst following reagents were sequentially added: iodoperfluoroalkane, DCE (0.5 mL), acetylene, boronic acid and base. Then, magnetic stirring bar was placed and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 50 °C for 4 h and then cooled to room temperature. The mixture was diluted with MTBE (2 mL) quenched with sat. aqueous NH₄Cl (0.5 mL) and *n*-dodecane (50 µl) was added as a internal standard.

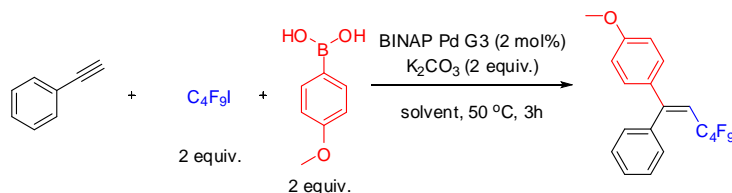
Table S1. Effect of catalyst^a

Entry	Catalyst	Conversion ^b	Yield ^b
1	P(<i>t</i> -Bu) ₃ /Pd(dba) ₂	97%	-
2	XPhos/Pd(dba) ₂	100%	46%
3	CyJohnPhos/Pd(dba) ₂	100%	47%
4	RuPhos/Pd(dba) ₂	100%	40%
5	PAd ₂ (<i>n</i> -Bu)/Pd(dba) ₂	100%	51%
6	<i>t</i> -BuXphos/Pd(dba) ₂	100%	37%
7	SPhos/Pd(dba) ₂	100%	48%
8	DavePhos/Pd(dba) ₂	100%	51%
9	PCy ₃ /Pd(dba) ₂	100%	54%
10	dppf/Pd(dba) ₂	100%	48%
11	BINAP/Pd(dba) ₂	100%	46%
12	2,2'-Bis(di- <i>t</i> -butylphosphino)-1,1'-biphenyl/Pd(dba) ₂	100%	39%
13	Xantphos/Pd(dba) ₂	100%	55%
14	dppb/Pd(dba) ₂	100%	19%
15	Pd(dba) ₂	100%	28%
16	No catalyst	<5%	-
17	SPhos Pd G3	88%	43%
18	Xphos Pd G3	93%	49%
19	RuPhos Pd G3	85%	37%
20	<i>t</i> -BuXphos Pd G3	52%	14%
21	PAd₂(<i>n</i>-Bu) Pd G3	90%	59%
22	BINAP Pd G3	95%	58%
23	dppe Pd G3	23%	16%
24	P(<i>o</i> -tol) ₃ Pd G3	62%	32%
25	JackiePhos Pd G3	92%	43%
26	Pd(PPh ₃) ₄	81%	22%

^aConditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.25 mmol, 2 equiv.), perfluorobutyl iodide (0.25 mmol, 2 equiv.), palladium catalyst 2 mol% (for *in situ* prepared catalysts 2 mol% of Pd(dba)₂ and 2 mol% of bispophosphine or 4 mol% of monophosphine), K₂CO₃ (0.25 mmol, 2 equiv.), dioxane (0.5 mL), 50 °C, 3h. ^bYield was determined by GC with dodecane as a internal standard.

BINAP Pd G3 was chosen as a catalyst due to lower amount of by-product and easier isolation of expected product from the reaction mixture than in case when $\text{PAd}_2(n\text{-Bu})$ Pd G3 was used.

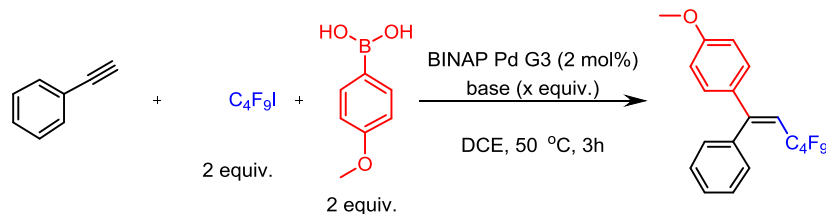
Table S2. Effect of solvent^a



Entry	Solvent	Conversion	Yield ^b
1	Dioxane	95%	58%
2	MeOH	89%	17%
3	DMF	91%	5%
4	Hexane	95%	54%
5	Toluene	100%	46%
6	DCE	100%	67%
7	MeCN	86%	23%
8	DMSO	78%	9%
9	THF	89%	38%

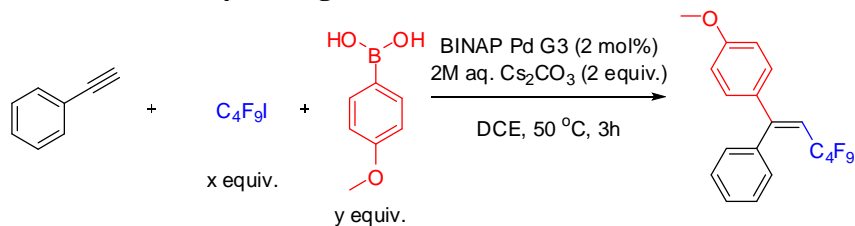
^aConditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.25 mmol, 2 equiv.), perfluorobutyl iodide (0.25 mmol, 2 equiv.), BINAP Pd G3 2 mol%, K_2CO_3 (0.25 mmol, 2 equiv.), solvent (0.5 mL), 50 °C, 4h. ^bYield was determined by GC with dodecane as a internal standard.

Table S3. Effect of base^a



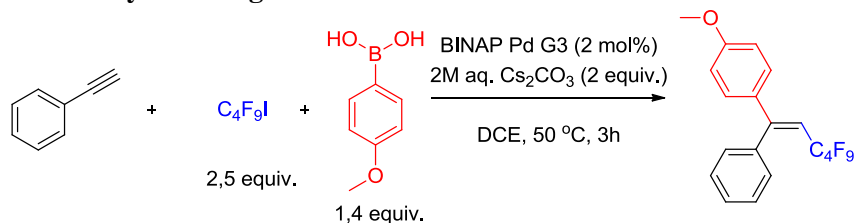
Entry	Base	Conversion ^b	Yield ^b
1	NaF (2 equiv.)	8%	0%
2	MeONa (2 equiv.)	45%	26%
3	EtONa (2 equiv.)	89%	19%
4	K_3PO_4 (2 equiv.)	64%	40%
5	Cs_2CO_3 (2 equiv.)	59%	41%
6	CsF (2 equiv.)	100%	59%
7	2M aqueous K_3PO_4 (2 equiv.)	70%	46%
8	2M aqueous K_2CO_3 (2 equiv.)	100%	68%
9	2M aqueous Cs_2CO_3 (2 equiv.)	100%	72%
10	2M aqueous Cs_2CO_3 (1 equiv.)	84 %	54 %
11	2M aqueous Cs_2CO_3 (1.5 equiv.)	95 %	58 %
12	2M aqueous Cs_2CO_3 (2.5 equiv.)	100 %	65 %
13	2M aqueous Cs_2CO_3 (3.0 equiv.)	100 %	49 %
14	2M aqueous AcONa (2 equiv.)	3%	0%
15	60% aqueous KOH (2 equiv.)	100%	10%
16	NaOMe (2 equiv.) + 0.125mL H_2O	25%	8%
17	NaOtBu (2 equiv.) + 0.125mL H_2O	100%	0%

^aConditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.25 mmol, 2 equiv.), perfluorobutyl iodide (0.25 mmol, 2 equiv.), BINAP Pd G3 2 mol%, base(0.25mmol, 2 equiv.), DCE (0.5 mL), 50 °C, 4h. ^bYield was determined by GC with dodecane as a internal standard.

Table S4. Effect of stoichiometry of reagents^a

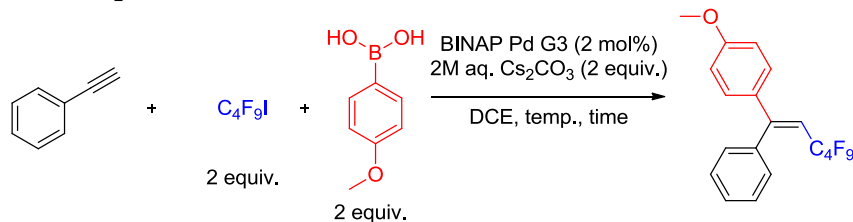
Entry	Amount of $\text{C}_4\text{F}_9\text{I}$ (x equiv.)	Amount of $\text{ArB}(\text{OH})_2$ (y equiv.)	Yield ^b
1	1 equiv.	1.2 equiv.	32%
2	1.5 equiv.	1.2 equiv.	47%
3	2 equiv.	1.2 equiv.	58%
4	2.5 equiv.	1.2 equiv.	65%
5	3 equiv.	1.2 equiv.	72%
6	1 equiv.	1.4equiv.	34%
7	1.5 equiv.	1.4equiv.	47%
8	2 equiv.	1.4equiv.	66%
9	2.5 equiv.	1.4 equiv.	87%
10	3 equiv.	1.4equiv.	88%
11	2.5 equiv.	1.8 equiv.	89%
12	3 equiv.	2equiv.	85%
13	3 equiv.	2.5equiv.	85%
14	3 equiv.	3equiv.	86%

^aConditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (y equiv.), perfluorobutyl iodide (y equiv.), BINAP Pd G3 2 mol%, 2M aqueous Cs_2CO_3 (0.25 mmol, 2 equiv.), DCE (0.5 mL), 50 °C, 4h. ^bYield was determined by GC with dodecane as a internal standard.

Table S5. Effect of catalyst loading^a

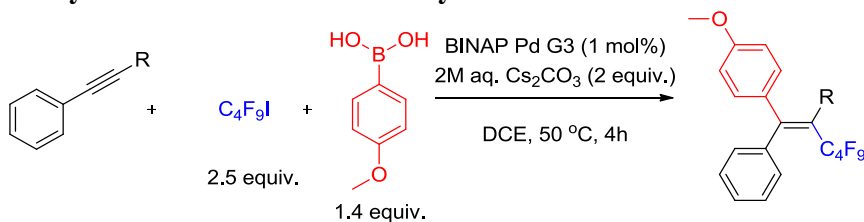
Entry	Catalyst loading	Conversion ^b	Yield ^b
1	4 mol%	100%	89%
2	1 mol%	100%	88%
3	0.5 mol%	94%	43%
4	0.25 mol%	89%	32%

^aConditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.175mmol, 1.4 equiv.), perfluorobutyl iodide (0.3125 mmol, 2.5 equiv.), BINAP Pd G3, 2M aqueous Cs_2CO_3 (0.25 mmol, 2 equiv.), DCE (0.5 mL), 50 °C, 4 h. ^bYield was determined by GC with dodecane as a internal standard.

Table S6. Effect of temperature and reaction time^a

Entry	Rxn. time	Temperature	Conversion ^b	Yield ^b
1	4h	50 °C	100%	88%
2	4h	80 °C	100%	85%
3	4h	60 °C	100%	88%
4	4h	35 °C	68%	41%
5	12h	35 °C	100%	75%
6	12h	rt.	90%	69%
7	4h	rt.	42%	35%

^aStandard conditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.175 mmol, 1.4 equiv.), perfluorobutyl iodide (0.3125 mmol, 2.5 equiv.), BINAP Pd G3 (1 mol%), 2M aqueous Cs_2CO_3 (0.25 mmol, 2 equiv.), DCE (0.5 mL). ^bYield was determined by GC with dodecane as a internal standard.

Table S7. Reactivity of terminal and internal alkynes^a

Entry	R	Variation from standard conditions	Conversion ^b	Yield ^b
1	H	50 °C	100%	88%
2	Me	50 °C	62%	37%
3	Me	60 °C	71%	49%
4	Me	80 °C	100%	78%

^aStandard conditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.175 mmol, 1.4 equiv.), perfluorobutyl iodide (0.3125 mmol, 2.5 equiv.), BINAP Pd G3, 2M aqueous Cs_2CO_3 (0.25 mmol, 2 equiv.), DCE (0.5 mL), 50 °C, 4 h. ^bYield was determined by GC with dodecane as a internal standard.

Table S8. Effect of Pd-source on performance of the catalyst in the model reaction of terminal and internal alkynes^a

Entry	R	Ligand	Conversion ^b	Yield ^b
1	H	BINAP/PdCl ₂	73%	48%
2	H	BINAP/Pd(OAc) ₂	69%	45%
3	H	BINAP/Pd(dba) ₂	66%	42%
4	H	BINAP/Pd(PPh ₃) ₄	92%	38%
5	H	BINAP/Pd-G3-dimer	94%	78%
6	H	BINAP Pd G3	100 %	88 %
7	Me	BINAP/PdCl ₂	85%	0%
8	Me	BINAP/Pd(OAc) ₂	78%	37%
9	Me	BINAP/Pd(dba) ₂	73%	49%
10	Me	BINAP/Pd(PPh ₃) ₄	90%	75%
11	Me	BINAP/ Pd-G3-dimer	91%	77%
12	Me	BINAP Pd G3	100 %	78 %

BINAP-Pd-G3 (commercial)

Pd-G3-dimer

^aStandard conditions: Alkyne (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.175 mmol, 1.4 equiv.), perfluorobutyl iodide (0.3125 mmol, 2.5 equiv.), BINAP (1 mol%), Pd source (1 mol%), 2M aqueous Cs₂CO₃ (0.25 mmol, 2 equiv.), DCE (0.5 mL), 50 °C or 80 °C (for reaction with phenylacetylene or phenylpropyne, respectively), 4 h. ^bYield was determined by GC with dodecane as a internal standard.

Buchwald-type precatalyst BINAP Pd G3 performed in the model reactions with both phenylacetylene and phenylpropyne better than complexes formed in situ from BINAP ligand and various Pd sources (Table S8). However, it is worth mentioning that despite lower efficiency of the process, it is still possible to achieve moderate yields of compound **2** (carboperfluoroalkylation of internal alkyne - phenylpropyne) when combination of BINAP with commonly used Pd sources Pd(dba)₂ or Pd(OAc)₂ were used. The higher efficiency of BINAP Pd G3 could be attributed to fast and clean activation of precatalyst under basic conditions to form Pd(0) species bearing only BINAP ligand, which is postulated to be a active catalytic species in both catalytic cycles, *ie.* iodoperfluoroalkylation of alkyne and Suzuki coupling of vinyl iodide intermediate. On the contrary when combination of ligand and Pd-source was used formation of active Pd(0) species could be inefficient and/or not clean (for Pd(II) salts) or the activity of the species could be modulated by other ligands present in the mixture (eg. dba). Both effects were recalled by Buchwald¹ as plausible reason of exceptionally high activity of these precatalysts in cross-coupling chemistry.

General procedure for carboperfluoroalkylation of alkynes

Conditions A (for reaction of terminal alkyne with iodoperfluoroalkane, boronic acid): Sequence of addition of reagents is important and guarantee reproducibility of results. In a glovebox, to a 4-mL screw-capped vial containing BINAP Pd G3 (1.24 mg, 2.5 μmol) following reagents were sequentially added: iodoperfluoroalkane (0.75 mmol), DCE (1 mL), acetylene (0.25 mmol), boronic acid (0.375 mmol), 2M aqueous Cs₂CO₃ (0.25mL, 0.5 mmol). Then, magnetic stirring bar was placed and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 50 °C for 4 h and then cooled to room temperature. The mixture was quenched with water (5 mL) and extracted with CH₂Cl₂ (3 ×10 mL). Combined organic phases were dried (Na₂SO₄), concentrated and crude product

was purified by column chromatography on silica gel using hexanes/EtOAc or hexanes:tetrachloroethylene(TCE) as a eluent.

Conditions B (for reaction of internal alkyne with iodoperfluoroalkane, boronic acid): Sequence of addition of reagents is important and guarantee reproducibility of results. In a glovebox, to a 4-mL screw-capped vial containing BINAP Pd G3 (1.24 mg, 2.5 μ mol) following reagents were sequentially added: iodoperfluoroalkane (0.75 mmol), DCE (1mL), acetylene (0.25 mmol), boronic acid (0.375 mmol), 2M aqueous Cs₂CO₃ (0.25 mL, 0.5 mmol). Then, magnetic stirring bar was placed and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 80 °C for 4h and then cooled to room temperature. The mixture was quenched with water (5 mL) and extracted with CH₂Cl₂ (3 \times 10 mL). Combined organic phases were dried (Na₂SO₄), concentrated and crude product was purified by column chromatography on silica gel using hexanes/EtOAc or hexanes:tetrachloroethylene (TCE) as a eluent.

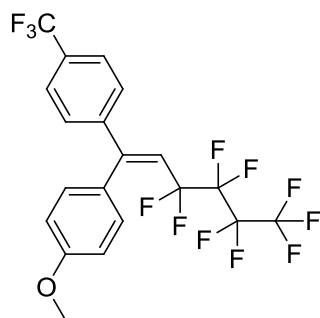
Conditions C (for large scale reaction): Sequence of addition of reagents is important and guarantee reproducibility of results. A 50 ml Shlenck tube containing BINAP Pd G3 (19.2 mg, 0.1 mmol) and stirring bar was evacuated and refilled with argon three times. Then the following reagents were sequentially added: iodoperfluoroalkane (6 mmol), DCE (8 mL), alkyne (2 mmol), boronic acid (3 mmol), 2M aqueous Cs₂CO₃ (2mL, 4 mmol). The reaction mixture was stirred at 50 or 80 °C (for terminal and internal alkyne, respectively) for 4h and then cooled to room temperature. The mixture was quenched with water (5 mL) and extracted with CH₂Cl₂ (3 \times 10 mL). Combined organic phases were dried (Na₂SO₄), concentrated and crude product was purified by column chromatography on silica gel using hexanes/EtOAc or hexanes:tetrachloroethylene (TCE) as a eluent.

Analytical data of isolated compounds –trisubstituted olefins.

(E)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-enyl)benzene (1) Prepared in reaction of phenylacetylene with perfluorobutyl iodide and 4-methoxyphenylboronic acid under **conditions A** (yield: 88 %) or **conditions C** (yield: 78 %). The title compound was isolated as white crystalline solid after chromatography on silica gel (17 g column, TCE:Hexane 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.36 (m, 3H), 7.23 (dd, J = 6.5, 2.9 Hz, 2H), 7.18 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 6.03 (t, J = 14.8 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.8, 153.8 (t, J = 4.6 Hz), 137.7, 133.1, 129.3, 129.0 (t, J = 2.5 Hz), 128.2, 127.8, 113.9, 110.6 (t, J = 21.1 Hz), 55.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (m, 3F), -103.2 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2957, 1606, 1510, 1351, 1236, 1135, 851 cm⁻¹; MS (EI), m/z (%): 428 (M+), 259 (99), 239 (24), 196 (26), 165 (28), 157 (86), 127 (57); HRMS, m/z : calc'd for C₁₉H₁₃F₉O: 428.0823, Found 428.0826.

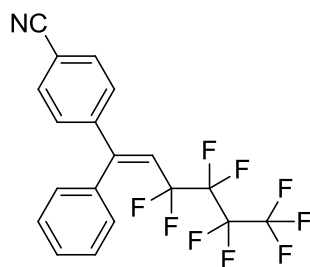
(Z)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzene (3) Prepared in reaction of 4-methoxyphenylacetylene with perfluorobutyl iodide and phenylboronic acid under **conditions A** (yield: 94%). The title compound was isolated as white crystalline solid after chromatography on silica gel (10 g column, TCE:Hexane 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.31 (m, 3H), 7.26 (dd, J = 8.1, 1.5 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.04 (t, J = 14.8 Hz, 1H), 3.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.8, 154.5 (t, J = 4.8 Hz), 141.4, 130.6 (t, J = 2.7 Hz), 129.8, 129.4, 128.4, 128.1, 113.3, 112.2 (t, J = 20.8 Hz), 55.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.3 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2959, 1609, 1513, 1235, 1132, 1035, 879 cm⁻¹; MS (EI), m/z (%): 428 (M+), 259 (95), 239 (20), 165 (20), 157 (72), 127 (47); HRMS, m/z : calcd for: C₁₉H₁₃F₉O: 428.0823, Found 428.0825.

(Z)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(trifluoromethyl)phenyl)hex-1-en-1-yl)benzene (4)



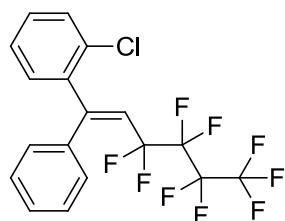
Prepared in reaction of 4-methoxyphenylacetylene with perfluorobutyl iodide and 4-(trifluoromethyl)phenylboronic acid under **conditions A** (yield: 76 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.03 (t, *J* = 14.5 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.1, 153.3 (t, *J* = 4.6 Hz), 144.9, 131.4 (q, *J* = 32.7 Hz), 130.6 (t, *J* = 2.7 Hz), 128.9, 128.5, 125.4 (q, *J* = 3.7 Hz), 113.9 (t, *J* = 20.8 Hz), 113.5, 55.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9 (s, 3F), -81.0 (m, 3F), -103.9 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2939, 1609, 1513, 1327, 1237, 1132, 834 cm⁻¹; MS (EI), *m/z* (%): 496 (M⁺), 477(34), 327 (100), 195 (34), 157 (76); HRMS, *m/z*: calcd for: C₂₀H₁₂F₁₂O: 496.0697, Found 496.0704.

(E)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzonitrile (5)



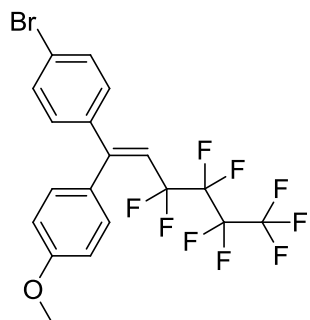
Prepared in reaction of phenylacetylene with perfluorobutyl iodide and 4-cyanophenylboronic acid under **conditions A** (yield: 66 %). The title compound was isolated as bright yellow crystal after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.38 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.18 (dd, *J* = 6.4, 3.1 Hz, 2H), 6.12 (t, *J* = 14.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 152.8 (t, *J* = 4.5 Hz), 144.9, 136.2, 132.3, 128.9, 128.8 (t, *J* = 2.6 Hz), 128.5, 128.2, 118.2, 115.2 (t, *J* = 21.4 Hz), 113.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -104.5 (m, 2F), -125.6 (m, 2F), -125.7 (m, 2F); IR (CH₂Cl₂): 2231, 1639, 1235, 1133, 880, 702 cm⁻¹; MS (EI), *m/z* (%): 423 (M⁺) 254 (100), 234 (50), 152 (43), 127 (77); HRMS, *m/z*: calcd for: C₁₉H₁₀F₉N: 423.0670, Found 423.0662.

(E)-1-chloro-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzene (6)



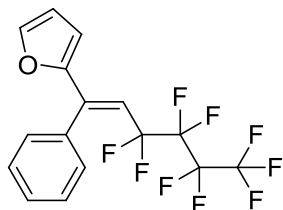
Prepared in reaction of phenylacetylene with perfluorobutyl iodide and 2-chlorophenylboronic acid under **conditions A** (yield: 85 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.33 (m, 1H), 7.32 – 7.27 (m, 5H), 7.26 – 7.21 (m, 3H), 5.88 (t, *J* = 14.8 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 152.6 (t, *J* = 4.8 Hz), 140.6, 137.0, 132.3, 130.4 (t, *J* = 16.2 Hz), 130.3, 129., 128.8 (t, *J* = 2.8 Hz), 128.5 (s, *J* = 19.7 Hz), 127.7, 126.7, 117.20 (t, *J* = 21.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -104.6 (m, 2F), -125.2 (m, 2F), -125.7 (m, 2F); IR (CH₂Cl₂): 2927, 1642, 1353, 1235, 1133, 881 cm⁻¹; MS (EI), *m/z* (%): 432 (M⁺), 397 (33), 263 (100), 243 (34), 227 (20), 207 (24), 161 (33), 127 (89); HRMS, *m/z*: calcd for: C₁₈H₁₀ClF₉: 432.0327, Found 432.0329.

(E)-1-bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene (7)

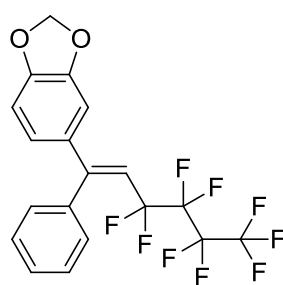


Prepared in reaction of 4-methoxyphenylacetylene with perfluorobutyl iodide and 4-bromophenylboronic acid under **conditions A** (yield: 82 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.98 (t, *J* = 14.6 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.0, 153.4 (t, *J* = 4.3 Hz), 140.3, 131.6, 130.5 (t, *J* = 2.6 Hz), 129.6, 129.1, 123.9, 113.4, 112.4 (t, *J* = 20.9 Hz), 55.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.5 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2959, 1608, 1513, 1353, 1236, 1132, 1035, 880, 822 cm⁻¹; MS (EI), *m/z* (%): 506 (M⁺), 487 (11), 351 (41), 337 (63), 258 (99), 214 (31), 205 (21), 165 (29), 157 (98), 129 (32); HRMS, *m/z*: calcd for: C₁₉H₁₂BrF₉O: 505.9928, Found 505.9931.

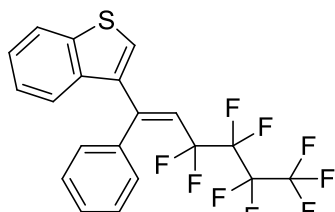
(E)-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)furan (8) Prepared in reaction of phenylacetylene with perfluorobutyl iodide and 2-furanylboronic acid under **conditions A** (yield: 66 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 1H), 7.41 – 7.35 (m, 3H), 7.27 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.95 (s, 1H), 6.58 (d, *J* = 1.1 Hz, 1H), 5.95 (t, *J* = 14.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 145.5 (t, *J* = 4.7 Hz), 144.3 (t, *J* = 1.8 Hz), 144.3, 136.5, 128.2, 128.1, 128.0, 127.8, 109.9 (t, *J* = 21.3 Hz), 107.5; IR (CH₂Cl₂): 2925, 2363, 1354, 1224, 1133, 1032, 738, 712 cm⁻¹; HRMS, *m/z*: calcd for: C₁₆H₉F₉O: 388.0510, Found 388.0505.



(E)-5-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzo[d][1,3]dioxole (9) Prepared in reaction of phenylacetylene with perfluorobutyl iodide and benzo[d][1,3]dioxol-5-ylboronic acid under **conditions A** (yield: 87 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.36 (m, 3H), 7.22 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.75 (s, 1H), 6.74 (s, 2H), 6.06 – 5.96 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 153.9 (t, *J* = 4.4 Hz), 148.9, 148.0, 137.6, 135.0, 129.0 (t, *J* = 2.5 Hz), 128.4, 127.8, 122.6, 111.3 (t, *J* = 21.3 Hz), 108.1, 108.1, 101.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.3 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2901, 1636, 1489, 1353, 1234, 1133, 1041, 936, 867, 702 cm⁻¹; MS (EI), *m/z* (%): 442 (M⁺), 273 (32), 243 (70), 215 (38), 171 (36), 165 (17), 127 (28); HRMS, *m/z*: calcd for: C₁₉H₁₁F₉O₂: 442.0615, Found 442.0618.

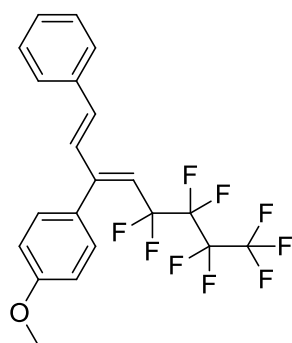


(E)-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzo[b]thiophene (10) Prepared in reaction of phenylacetylene with perfluorobutyl iodide and benzo[b]thiophen-3-ylboronic acid under **conditions A** (yield: 57 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.79 (m, 2H), 7.58 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.43 – 7.30 (m, 9H), 7.28 (s, 1H), 6.18 (t, *J* = 14.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 140.7, 137.6, 137.5, 136.8, 128.8 (t, *J* = 2.7 Hz), 128.8, 128.5, 128.0, 126.2, 124.8 (d, *J* = 6.3 Hz), 124.1 (d, *J* = 5.5 Hz), 123.7 (d, *J* = 22.8 Hz), 122.9 (d, *J* = 15.9 Hz), 122.4, 113.8 (t, *J* = 20.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.3 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 3062, 1630, 1494, 1353, 1234, 1132, 881, 700 cm⁻¹; MS (EI), *m/z* (%): 454 (M⁺), 285 (49), 265 (67), 234 (20), 183 (47), 127 (38); HRMS, *m/z*: calcd for: C₂₀H₁₁F₉S: 454.0438, Found 454.0456.



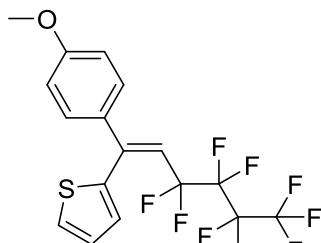
1-methoxy-4-((1E,3Z)-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenylocta-1,3-dien-3-yl)benzene (11)

Prepared in reaction of 4-methoxyphenylacetylene with perfluorobutyl iodide and trans-2-phenylvinylboronic acid under **conditions A** (yield: 55 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 9:1 Hexane:Toluene). ¹H NMR (400 MHz, CDCl₃) δ 7.02 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 3.4 Hz, 2H), 3.84 (s, 3H), 2.97 – 2.90 (m, 2H), 2.66 – 2.54 (m, 2H), 2.10 (s, 3H), 1.64 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 159.4, 152.1 (t, *J* = 5.2 Hz), 137.8, 136.0, 131.5 (t, *J* = 2.1 Hz), 129.9, 128.8, 128.7, 127.2, 127.1, 115.0 (t, *J* = 20.8 Hz), 113.3, 77.3, 77.0, 76.7, 55.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (m, 3F), -103.6 (m, 2F), -123.8 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2906, 1632, 1355, 1237, 890, 744, 703 cm⁻¹; MS (EI), *m/z* (%): 454 (M⁺), 285 (33),



235 (100), 207 (24), 203 (14), 177 (19), 157 (24), 117 (19), 91 (19); HRMS, m/z : calcd for: $C_{21}H_{15}F_9O$: 454.0979, Found 454.0965.

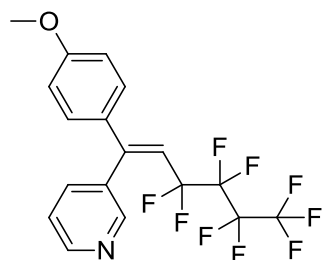
(Z)-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)thiophene (12)



Prepared in reaction of 2-ethynylthiophene with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 76 %). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 99:1→95:5 Hexane:AcOEt). 1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.17 (d, J = 8.8 Hz, 2H), 6.92 (dd, J = 4.8, 0.8 Hz, 1H), 6.83 (d, J = 8.9 Hz, 2H), 5.93 (t, J = 14.7 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 149.0 (t, J = 4.7 Hz), 137.3, 133.0 (t, J = 1.5 Hz), 129.3, 129.0 (t, J = 2.1 Hz), 125.7 (t, J = 3.7 Hz), 124.9, 113.8, 111.1 (t, J = 21.2 Hz), 55.3; ^{19}F NMR (376

MHz, $CDCl_3$) δ -81.0 (m, 3F), -103.2 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH_2Cl_2): 2958, 2934, 1632, 1605, 1511, 1353, 1236, 1132, 1093, 1034, 879, 800, 734 cm^{-1} ; MS (EI), m/z (%): 434 (M^+), 265 (100), 245 (14), 202 (12), 157 (81), 133 (42); HRMS, m/z : calcd for: $C_{17}H_{11}F_9OS$: 434.0387, Found 434.0382.

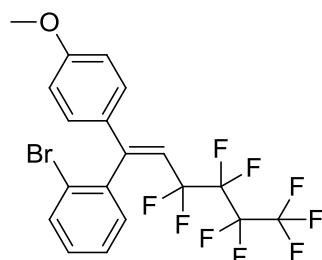
(Z)-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)pyridine (13)



Prepared in reaction of 3-ethynylpyridine with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 70 %). The title compound was isolated as yellow solid crystal after chromatography on silica gel (10 g column, 8:2→7:3 Hexane:AcOEt). 1H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, J = 4.9, 1.6 Hz, 1H), 8.46 (d, J = 1.8 Hz, 1H), 7.50 (dt, J = 7.8, 1.8 Hz, 1H), 7.29 (ddd, J = 7.8, 4.9, 0.7 Hz, 1H), 7.12 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 6.09 (t, J = 14.7 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 150.2 (t, J = 4.8 Hz), 149.6, 149.4 (t, J = 2.7 Hz), 136.4, 133.5, 132.1 (t, J = 1.3 Hz), 129.3, 122.7,

114.1, 112.3 (t, J = 21.5 Hz), 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (m, 3F), -103.0 (m, 2F), -123.8 (m, 2F), -125.6 (m, 2F); IR (CH_2Cl_2): 2961, 1604, 1513, 1237, 1132, 1027, 880, 716 cm^{-1} ; MS (EI), m/z (%): 429 (M^+), 410 (18), 260 (100), 240 (26), 157 (85); HRMS, m/z : calcd for: $C_{18}H_{12}F_9NO$: 429.0775, Found 429.0762.

(Z)-1-bromo-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene (14)



Prepared in reaction of 1-bromo-2-ethynylbenzene with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 46%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). 1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 1H), 7.38 (td, J = 7.3, 1.1 Hz, 1H), 7.27 (d, J = 7.4 Hz, 2H), 7.21 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 6.16 (t, J = 14.6 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 151.6 (t, J = 5.0 Hz), 138.2, 132.7, 130.6 – 130.2 (m), 129.6, 128.7, 126.7, 122.7 (t, J = 2.4 Hz), 114.1, 111.6 (t, J = 21.1

Hz), 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (m, 3F), -106.2 (m, 2F), -123.8 (m, 2F), -125.6 (m, 2F); IR (CH_2Cl_2): 2933, 1639, 1604, 1512, 1353, 1235, 1182, 1132, 1030, 880, 828, 735 cm^{-1} ; MS (EI), m/z (%): 506 (M^+), 337 (60), 258 (100), 243 (28), 227 (22), 214 (33), 208 (17), 165 (27), 157 (76), 129 (29); HRMS, m/z : calcd for: $C_{12}H_{12}BrF_9O$: 505.9928, Found 505.9925.

(Z)-1-bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene (15)

Prepared in reaction of 1-bromo-4-ethynylbenzene with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 76%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.01 (t, *J* = 14.8 Hz, 1H), 3.79 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 161.0, 152.6 (t, *J* = 4.2 Hz), 136.6, 132.4, 131.1, 130.7 (t, *J* = 2.5 Hz), 129.3, 122.6, 114.0, 111.0 (t, *J* = 21.3 Hz), 55.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.1 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2936, 2841, 1604, 1512, 1237, 1132, 1033, 880, 828, 734 cm⁻¹; MS (EI), *m/z* (%): 506 (M⁺), 337 (66), 258 (100), 157 (90), 129 (32); HRMS, *m/z*: calcd for: C₁₉H₁₂BrF₉O: 505.9928, Found 505.9936.

(E)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-nitrophenyl)hex-1-en-1-yl)benzene (16)

Prepared in reaction of 1-ethynyl-4-nitrobenzene with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 55%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 95:5→8:2 Hexane:Toluene). ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.12 (t, *J* = 14.7 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 161.3, 151.5 (t, *J* = 5.4 Hz), 147.8, 144.5, 131.3, 130.0 (t, *J* = 2.5 Hz), 129.2, 123.2, 114.2, 112.0 (t, *J* = 21.5 Hz), 55.4; MS (EI), *m/z* (%): 473 (M⁺), 454 (19), 304 (100), 258 (37), 214 (62), 199 (44), 165 (20), 157 (82), 150 (21); HRMS, *m/z*: calcd for: C₁₉H₁₂F₉NO₃: 473.0673, Found 473.0670.

(Z)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)phenyl 4-methylbenzenesulfonate (17)

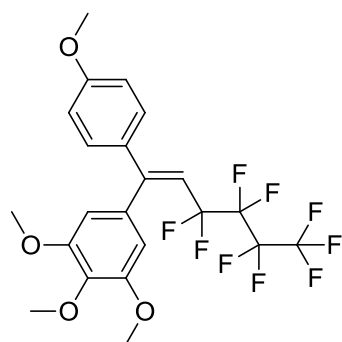
Prepared in reaction of 4-ethynylphenyl 4-methylbenzenesulfonate with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 83%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 9:1→8:2 AcOEt:Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 4H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 5.98 (t, *J* = 14.8 Hz, 1H), 3.78 (s, 3H), 2.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 161.0, 152.4 (t, *J* = 4.9 Hz), 149.6, 145.5, 136.5, 132.2, 132.0 (s, *J* = 17.9 Hz), 130.3 (t, *J* = 2.4 Hz), 129.6, 129.3, 128.6, 121.9, 114.0, 111.1 (t, *J* = 21.1 Hz), 55.4, 21.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.2 (m, 2F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2934, 1603, 1513, 1377, 1237, 1180, 1132, 1093, 864, 553 cm⁻¹; MS (EI), *m/z* (%): 598 (M⁺), 443 (27), 429 (25), 273 (17), 255 (19), 196 (19), 155 (72), 91 (95), 65 (22); HRMS, *m/z*: calcd for: C₂₆H₁₉F₉O₄S: 598.0860, Found 598.0858.

(Z)-1-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)naphthalene (18)

Prepared in reaction of 1-ethynynaphthalene with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 36%). The title compound was isolated as brown oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (t, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.36 (t, *J* = 14.5 Hz, 1H), 3.77 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.8, 152.0 (t, *J* = 5.3 Hz), 134.7, 133.4, 132.1 (t, *J* = 1.7 Hz), 131.4, 128.6, 128.2, 126.6 (t, *J* = 2.6 Hz), 126.3, 125.9, 125.8, 124.9, 114.1, 112.3 (t, *J* = 21.0 Hz), 55.3; ¹⁹F NMR (376 MHz,

CDCl₃) δ -81.0 (m, 3F), -104.6 (m, 1F), -105.7 (m, 1F), -123.9 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2959, 1604, 1511, 1237, 1181, 1132, 1029, 880, 778, 523 cm⁻¹; MS (EI), *m/z* (%): 478 (M⁺), 459 (15), 309 (21), 289 (26), 259 (100), 245 (19), 215 (22), 201 (18), 177 (32), 157 (28), 130 (19); HRMS, *m/z*: calcd for: C₂₃H₁₅F₉O: 478.0979, Found 478.0982.

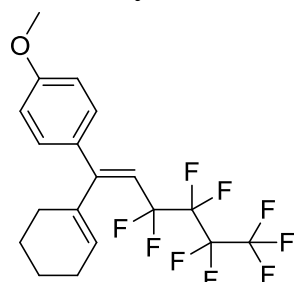
(Z)-1,2,3-trimethoxy-5-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene



(19) Prepared in reaction of 5-ethynyl-1,2,3-trimethoxybenzene with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 89%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.17 (m, 2H), 6.85 – 6.81 (m, 2H), 6.42 (s, 2H), 5.94 (t, *J* = 14.8 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 160.9, 153.7 (t, *J* = 4.6 Hz), 152.7, 138.1, 133.0 (t, *J* = 1.7 Hz), 132.7, 129.4, 113.9, 110.2 (t, *J* = 21.5 Hz), 106.7, 60.9, 56.1, 55.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.3 (m, 2F), -123.8 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 3002, 2940, 2842, 1604, 1583, 1512, 1465,

1415, 1235, 1180, 1130, 1032, 1010, 876, 829, 709, 528 cm⁻¹; MS (EI), *m/z* (%): 518 (M⁺), 502 (21), 498 (11), 349 (26), 318 (16), 259 (14), 217 (16), 157 (19); HRMS, *m/z*: calcd for: C₂₂H₁₉F₉O₄: 518.1140, Found 518.1133.

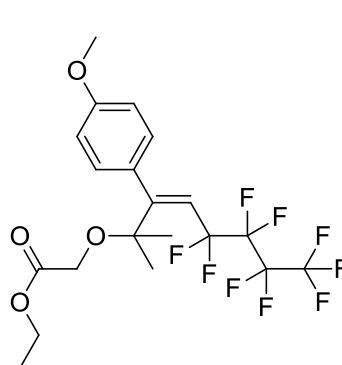
(E)-1-(1-(cyclohex-1-en-1-yl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)-4-methoxybenzene **(20)**



Prepared in reaction of 1-ethynylcyclohex-1-ene with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 75%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 1:1 TCE:Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.74 (s, 1H), 5.65 (t, *J* = 14.7 Hz, 1H), 3.81 (s, 3H), 2.18 (s, 2H), 1.97 – 1.85 (m, 2H), 1.68 – 1.58 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 160.7, 156.6 (t, *J* = 4.4 Hz), 134.2, 130.8, 128.6, 127.8 (t, *J* = 3.4 Hz), 114.0 (s), 109.3 (t, *J* = 20.7 Hz), 55.3, 28.2, 25.2, 22.5, 21.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -103.6

(m, 2F), -124.0 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2935, 2841, 1605, 1511, 1234, 1132, 879 cm⁻¹; MS (EI), *m/z* (%): 432 (M⁺), 351 (31), 263 (30), 213 (65), 199 (25), 171 (31), 121 (23); HRMS, *m/z*: calcd for: C₁₉H₁₇F₉O: 432.1136 Found, 432.1122

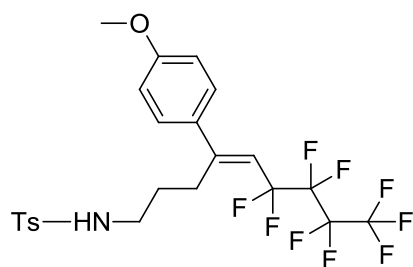
(Z)-ethyl 2-((5,5,6,6,7,7,8,8,8-nonafluoro-3-(4-methoxyphenyl)-2-methyloct-3-en-2-yl)oxy)acetate



(21) Prepared in reaction of ethyl 2-((2-methylbut-3-yn-2-yl)oxy)acetate with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 77%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 6.96 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.18 (t, *J* = 14.6 Hz, 1H), 4.20 (q, *J* = 14.3, 7.2 Hz, 2H), 4.02 (s, 2H), 3.77 (s, 3H), 1.29 – 1.21 (m, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 170.1, 167.5, 159.1, 158.1 (t, *J* = 4.4 Hz), 129.2 (t, *J* = 2.3 Hz), 127.6, 114.0 (t, *J* = 20.8 Hz), 113.0, 79.9, 61.8, 61.0, 55.1, 26.0, 14.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (m, 3F), -105.4 (m, 2F), -124.2 (m, 2F), -125.8 (m, 2F); IR (CH₂Cl₂): 2984, 1760, 1609, 1512, 1236, 1133, 1034, 836, 734

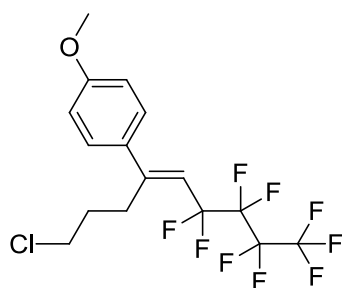
cm⁻¹; MS (EI), *m/z* (%): 393 (23), 217 (29), 145 (100), 87 (27), 59 (33); HRMS, *m/z*: calcd for: C₂₀H₂₁F₉O₄: 496.1296, Found 496.1308.

(E)-4-methyl-N-(6,6,7,7,8,8,9,9,9-nonafluoro-4-(4-methoxyphenyl)non-4-en-1-yl)benzenesulfonamide (22)



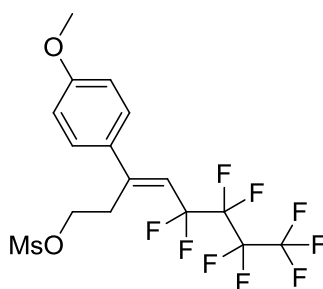
Prepared in reaction of 4-methyl-N-(pent-4-yn-1-yl)benzenesulfonamide of with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 82%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 9:1→8:2 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.22 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.58 (t, *J* = 15.9 Hz, 1H), 4.88 (t, *J* = 6.1 Hz, 1H), 3.82 (s, 3H), 2.85 (dd, *J* = 13.5, 6.8 Hz, 2H), 2.63 (s, 2H), 2.40 (s, 3H), 1.43 – 1.35 (m, 2H), 1.29 – 1.23 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 160.3, 155.7 (t, *J* = 5.0 Hz), 143.3, 137.0, 132.5, 129.6, 127.8, 127.0, 114.0, 113.2, 112.2 (t, *J* = 22.6 Hz), 55.2, 42.9, 30.8, 29.1, 28.1, 26.3, 21.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (m, 3F), -104.6 (m, 2F), -124.2 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 3283, 2938, 1641, 1606, 1513, 1327, 1235, 1160, 1132, 1093, 1036, 880, 816, 663, 552 cm⁻¹; MS (EI), *m/z* (%): 436 (16), 399 (13), 366 (72), 328 (17), 184 (39), 155 (97), 91 (100), 65 (21); HRMS, *m/z*: calcd for: C₂₃H₂₂F₉NO₃S: 563.1177, Found 563.1175.

(E)-1-(1-chloro-6,6,7,7,8,8,9,9,9-nonafluoronon-4-en-4-yl)-4-methoxybenzene (23)



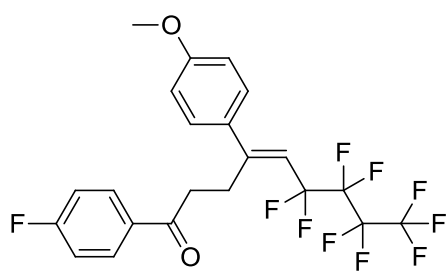
Prepared in reaction of 5-chloropent-1-yne of with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 84%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.65 (t, *J* = 15.8 Hz, 1H), 3.81 (s, 3H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.89 – 2.82 (m, 2H), 1.86 – 1.76 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 160.6, 154.4 (t, *J* = 4.8 Hz), 132.1, 128.0, 114.2, 113.1 (t, *J* = 22.8 Hz), 55.3, 44.4, 31.7, 28.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -104.8 (m, 2F), -124.2 (m, 2F), -125.6 (m, 2F); IR (CH₂Cl₂): 2961, 1607, 1514, 1354, 1236, 1133, 1036, 881, 824, 742 cm⁻¹; MS (EI), *m/z* (%): 428 (M⁺), 393 (16), 366 (100), 259 (22), 133 (23); HRMS, *m/z*: calcd for: C₂₀H₁₃ClF₉O: 428.0589, Found 428.0592.

(E)-5,5,6,6,7,7,8,8,8-nonafluoro-3-(4-methoxyphenyl)oct-3-en-1-yl methanesulfonate (24)



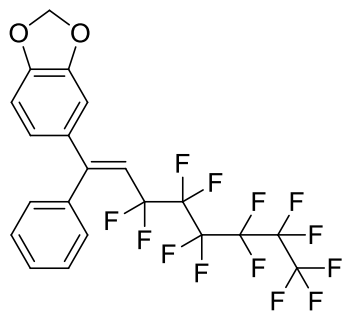
Prepared in reaction of but-3-yn-1-yl methanesulfonate with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 54%) or **conditions C** (yield: 50 %). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 9:1→8:2 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.76 (t, *J* = 15.6 Hz, 1H), 4.15 (t, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.8, 149.7 (t, *J* = 5.1 Hz), 131.2, 128.0, 115.3 (t, *J* = 22.9 Hz), 114.3, 66.9, 55.3, 37.2, 30.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -105.0 (m, 2F), -124.1 (m, 2F), -125.5 (m, 2F); IR (CH₂Cl₂): 2942, 1646, 1607, 1515, 1357, 1235, 1178, 1133, 962 cm⁻¹; MS (EI), *m/z* (%): 474 (M⁺), 359 (28), 209 (100), 189 (50), 159 (35), 146 (19), 133 (27), 79 (39); HRMS, *m/z*: calcd for: C₁₆H₁₅F₉O₄S: 474.0547 Found, 474.0530.

(E)-6,6,7,7,8,8,9,9,9-nonafluoro-1-(4-fluorophenyl)-4-(4-methoxyphenyl)non-4-en-1-one (25)



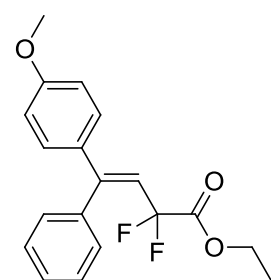
Prepared in reaction of 1-(4-fluorophenyl)pent-4-yn-1-one with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions A** (yield: 83%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 9:1→8:2 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (dd, J = 8.9, 5.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.05 (t, J = 8.6 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.70 (t, J = 15.7 Hz, 1H), 3.80 (s, 3H), 3.18 – 3.10 (m, 2H), 2.95 (dd, J = 9.5, 6.3 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.7, 167.1, 164.5, 160.6, 154.5 (t, J = 4.9 Hz), 132.9 (d, J = 3.0 Hz), 131.8, 130.6 (d, J = 9.3 Hz), 128.0, 115.8, 115.5, 114.3, 113.2 (t, J = 22.8 Hz), 55.3, 37.5, 25.5; ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 (m, 3F), -105.0 (m, 2F), -105.1 (m, 1F), -124.1 (m, 2F), -125.6 (m, 2F); IR (CH_2Cl_2): 2933, 1688, 1601, 1513, 1355, 1235, 1133, 1033, 881, 824 cm^{-1} ; MS (EI), m/z (%): 502 (M^+), 379 (42), 123 (100), 95 (26); HRMS, m/z : calcd for: $\text{C}_{22}\text{H}_{16}\text{F}_{10}\text{O}_2$: 502.0991, Found 502.0978.

(E)-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloct-1-en-1-yl)benzo[d][1,3]dioxole (26)

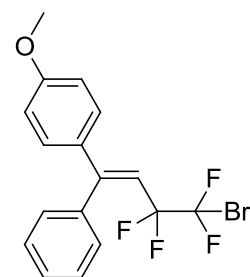


Prepared in reaction of phenylacetylene with perfluorohexyl iodide and benzo[d][1,3]dioxol-5-ylboronic acid under **conditions A** (yield: 72%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.31 (m, 3H), 7.19 (dd, J = 6.5, 2.9 Hz, 2H), 6.75 – 6.68 (m, 3H), 6.03 – 5.92 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.8 (t, J = 4.8 Hz), 148.9, 148.0, 137.6, 134.9, 129.0 (t, J = 2.5 Hz), 128.3, 127.8, 122.6, 111.4 (t, J = 21.1 Hz), 108.1, 108.1 (s, J = 7.8 Hz), 101.5; ^{19}F NMR (376 MHz, CDCl_3) δ -80.8 (m, 3F), -103.1 (m, 2F), -121.5 (m, 2F), -122.8 (m, 2F), -123.0 (m, 2F), -126.1 (m, 2F); IR (CH_2Cl_2): 2900, 1637, 1486, 1240, 1145, 1042, 936, 811, 701 cm^{-1} ; MS (EI), m/z (%): 542 (M^+), 273 (53), 243 (89), 215 (45), 171 (39), 165 (11), 127 (28); HRMS, m/z : calcd for: $\text{C}_{21}\text{H}_{11}\text{F}_{13}\text{O}_2$: 542.0551, Found 542.0549.

(E)-ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-phenylbut-3-enoate (27)



Prepared in reaction of phenylacetylene with ethyl 2,2-difluoro-2-iodoacetate and 4-methoxyphenyl boronic acid under **conditions A** (yield: 59%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.29 (m, 3H), 7.21 – 7.08 (m, 4H), 6.81 (d, J = 8.9 Hz, 2H), 6.18 (t, J = 12.0 Hz, 1H), 3.89 (q, J = 7.2 Hz, 2H), 3.78 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.6, 160.5, 150.4 (t, J = 9.4 Hz), 137.3, 132.9, 129.9 (t, J = 1.8 Hz), 129.2, 128.5, 127.9, 117.6 (t, J = 28.3 Hz), 113.8, 62.7, 55.3, 13.7; ^{19}F NMR (376 MHz, CDCl_3) δ -90.6 (s, 2F); IR (CH_2Cl_2): 2983, 1769, 1605, 1512, 1252, 1100, 1065, 826, 775, 702 cm^{-1} ; MS (EI), m/z (%): 332 (M^+), 259 (100), 239 (16), 196 (12), 157 (61), 127 (41); HRMS, m/z : calcd for: $\text{C}_{19}\text{H}_{18}\text{F}_2\text{O}_3$: 332.1224, Found 332.1227.

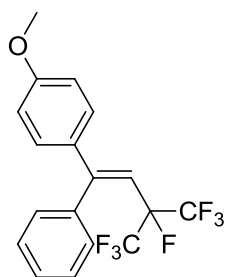


(E)-1-(4-bromo-3,3,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-4-methoxybenzene (28)

Prepared in reaction of phenylacetylene with ethyl 1-bromo-1,1,2,2-tetrafluoro-2-iodoethane and 4-methoxyphenyl boronic acid under **conditions A** (yield: 59%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 99:1→98:2 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.36 (m, 3H), 7.27 – 7.22 (m, 2H), 7.20 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 6.06 (t, J = 14.3 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.7, 153.6 (t, J =

4.0 Hz), 137.8, 133.1 (t, $J = 1.3$ Hz), 129.3, 129.1 (t, $J = 2.6$ Hz), 128.2, 127.78, 113.8, 110.8 (t, $J = 21.7$ Hz), 55.3; ^{19}F NMR (376 MHz, CDCl_3) δ -65.5 (t, $J = 7.0$ Hz, 2F), -100.9 (t, $J = 7.0$ Hz, 2F); IR (CH_2Cl_2): 2935, 1604, 1511, 1254, 1145, 1077, 908, 703 cm^{-1} ; MS (EI), m/z (%): 388 (M+), 259 (100), 239 (17), 157 (62), 127 (40); HRMS, m/z : calcd for: $\text{C}_{17}\text{H}_{13}\text{BrF}_4\text{O}$: 388.0086, Found 388.0078.

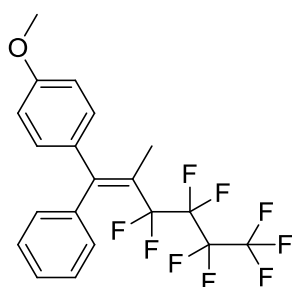
(E)-1-methoxy-4-(3,3,4,4-tetrafluoro-1-phenyl-3-(trifluoromethyl)but-1-en-1-yl)benzene (29)



Prepared in reaction of phenylacetylene with ethyl 1,1,1,2,3,3,3-heptafluoro-2-iodopropane and 4-methoxyphenyl boronic acid under **conditions A** (yield: 59%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 99:1→98:2 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.31 (m, 3H), 7.21 – 7.11 (m, 4H), 6.83 (d, $J = 8.8$ Hz, 2H), 5.88 (d, $J = 26.4$ Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.5, 152.5, 138.0 (d, $J = 2.7$ Hz), 133.6, 129.0, 128.7 (d, $J = 3.4$ Hz), 127.8, 127.7, 113.8, 107.8 (d, $J = 13.7$ Hz), 55.3; ^{19}F NMR (376 MHz, CDCl_3) δ -76.9 (d, $J = 7.7$ Hz, 6F), -184.0 (m, 1F); IR (CH_2Cl_2): 2932, 1604, 1511, 1305, 1225, 1198, 1041, 978, 701 cm^{-1} ; MS (EI), m/z (%): 378 (M+), 309 (92), 289 (25), 207 (21), 196 (19), 165 (15); HRMS, m/z : calcd for: $\text{C}_{18}\text{H}_{13}\text{F}_7\text{O}$: 378.0885, Found 378.0862.

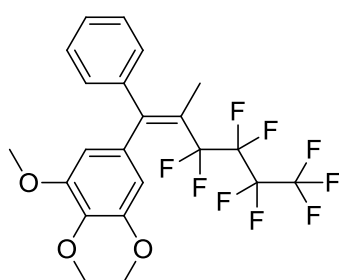
Analytical data of isolated compounds - tetrasubstituted olefins.

(E)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzene (2)



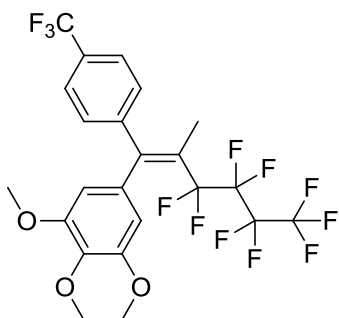
Prepared in reaction of phenylpropyne with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 78%) or **conditions C** (yield: 75 %). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 1:1 Hexane:TCE). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.22 (m, 3H), 7.15 (d, $J = 6.9$ Hz, 2H), 7.10 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 3.80 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.0, 150.3 (t, $J = 4.2$ Hz), 141.3, 134.5, 129.5, 127.9 (t, $J = 2.5$ Hz), 127.6, 127.0, 121.8 (t, $J = 19.5$ Hz), 113.9, 55.2, 16.7; ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 (m, 3F), -104.3 (m, 2F), -120.2 (m, 2F), -126.1 (m, 2F); IR (CH_2Cl_2): 2937, 1606, 1510, 1236, 1135, 851 cm^{-1} ; MS (EI), m/z (%): 442 (M+), 273(73), 253(30), 157(87), 127(47); HRMS, m/z : calcd for: $\text{C}_{20}\text{H}_{15}\text{F}_9\text{O}$: 442.0979, Found 442.0984.

(Z)-1,2,3-trimethoxy-5-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzene (30)



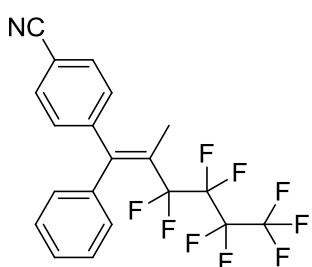
Prepared in reaction of 1,2,3-trimethoxy-5-(prop-1-yn-1-yl)benzene with perfluorobutyl iodide and phenyl boronic acid under **conditions B** (yield: 83%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.31 (m, 2H), 7.29 – 7.25 (m, 1H), 7.19 – 7.15 (m, 2H), 6.35 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 1.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.6, 150.4 (t, $J = 4.2$ Hz), 141.8, 137.3, 136.2, 128.6, 127.7, 127.7, 122.4 (t, $J = 19.8$ Hz), 105.5, 60.8, 56.1, 16.5; ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 (m, 3F), -104.8 (m, 2F), -119.8 (m, 2F), -126.0 (m, 2F); IR (CH_2Cl_2): 2940, 1581, 1504, 1411, 1343, 1236, 1130, 1011, 704 cm^{-1} ; MS (EI), m/z (%): 502 (M+), 487 (28), 425 (12), 333 (13), 302 (24), 206 (11); HRMS, m/z : calcd for: $\text{C}_{22}\text{H}_{19}\text{F}_9\text{O}_3$: 502.1190, Found 502.1199.

(Z)-1,2,3-trimethoxy-5-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-(4-(trifluoromethyl)phenyl)hex-1-en-1-yl)benzene (31)



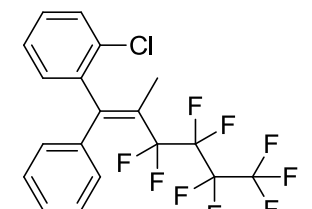
Prepared in reaction of 1,2,3-trimethoxy-5-(prop-1-yn-1-yl)benzene with perfluorbutyl iodide and (4-(trifluoromethyl)phenyl)boronic acid under **conditions B** (yield: 79%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.34 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 1.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 152.8, 149.1 (t, *J* = 4.1 Hz), 145.3, 137.6, 135.2, 129.9 (q, *J* = 32.7 Hz), 128.1, 125.7 (q, *J* = 3.7 Hz), 123.7 (t, *J* = 19.8 Hz), 105.4, 60.8, 56.1, 16.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.8(m, 3F), -81.0 (m, 3F), -105.1 (m, 2F), -119.8 (m, 2F), -126.0 (m, 2F); IR (CH₂Cl₂): 2943, 1615, 1583, 1504, 1414, 1325, 1238, 1129, 1068, 1016, 863 cm⁻¹; MS (EI), *m/z* (%): 570 (M⁺), 555 (21), 425 (11), 370 (23); HRMS, *m/z*: calcd for: C₂₃H₁₈F₁₂O₃: 570.1064, Found 570.1064.

(E)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzonitrile (32)



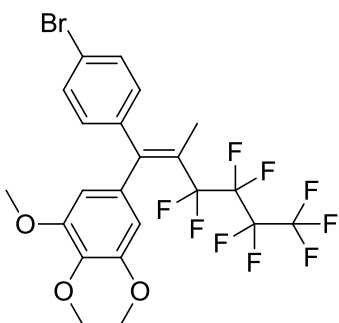
Prepared in reaction of phenylpropyne with perfluorbutyl iodide and 4-cyanophenylboronic acid under **conditions B** (yield: 62%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.13 (d, *J* = 6.9 Hz, 2H), 1.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.8 (t, *J* = 4.4 Hz), 146.5, 139.3, 132.5, 128.6, 127.9, 127.7 (s, *J* = 7.4 Hz), 127.6, 124.0 (t, *J* = 19.8 Hz), 118.3, 111.6, 16.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -104.9 (m, 2F), -120.3 (m, 2F), -126.0 (m, 2F); IR (CH₂Cl₂): 2230, 1605, 1351, 1235, 1135, 855 cm⁻¹; MS (EI), *m/z* (%): 437 (M⁺), 268 (84), 248 (69), 190 (25), 152 (44), 127(92);HRMS, *m/z*: calcd for: C₂₀H₁₂F₉N: 437.0826, Found 437.0821

(E)-1-chloro-2-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzene (33)



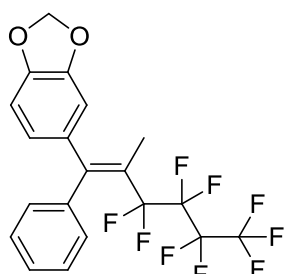
Prepared in reaction of phenylpropyne with perfluorbutyl iodide and 2-chlorophenylboronic acid under **conditions B** (yield: 82%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.38 (m, 1H), 7.35 – 7.33 (m, 1H), 7.33 – 7.31 (m, 1H), 7.29 – 7.16 (m, 6H), 1.78 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.9(t, *J* = 4.7 Hz), 131.3, 131.2, 130.1, 129.5, 129.2, 128.9, 128.8, 127.6, 127.4, 126.5 (t, *J* = 19.6 Hz), 16.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -105.0(m, 2F), -120.3 (m, 2F), -126.1 (m, 2F); IR (CH₂Cl₂): 2931, 1645, 1358, 1235, 1133, 882 cm⁻¹; HRMS, *m/z*: calcd for: C₁₉H₁₂ClF₉: 446.0484, Found 446.0485.

(Z)-5-(1-(4-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluoro-2-methylhex-1-en-1-yl)-1,2,3-trimethoxybenzene (34)



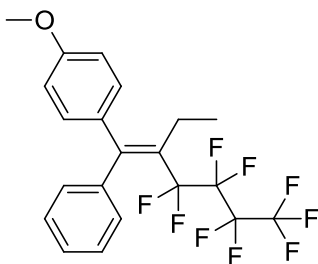
Prepared in reaction of 1,2,3-trimethoxy-5-(prop-1-yn-1-yl)benzene with perfluorbutyl iodide and 4-bromophenylboronic acid under **conditions B** (yield: 76%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 1.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 149.2 (t, *J* = 4.4 Hz), 140.6, 137.5, 135.6, 131.8, 129.6, 122.9 (t, *J* = 19.7 Hz), 121.9, 105.5, 60.8, 56.1, 16.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -104.9 (m, 2F), -119.7 (m, 2F), -126.1 (m, 2F); IR (CH₂Cl₂): 2940, 1583, 1505, 1412, 1340, 1237, 1130, 1011, 860 cm⁻¹; MS (EI), *m/z* (%): 580 (M⁺), 565 (16), 380 (15), 165 (11); HRMS, *m/z*: calcd for: C₂₂H₁₈BrF₉O₃: 580.0296, Found 580.0272.

(E)-5-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzo[d][1,3]dioxole (35)



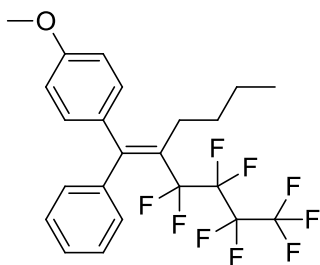
Prepared in reaction of phenylpropyne with perfluorbutyl iodide and benzo[d][1,3]dioxol-5-ylboronic acid under **conditions B** (yield: 92%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.22 (m, 3H), 7.14 (d, J = 6.9 Hz, 2H), 6.78 (d, J = 7.9 Hz, 1H), 6.68 – 6.61 (m, 2H), 5.93 (s, 2H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.2 (t, J = 4.1 Hz), 147.8, 147.0, 141.0, 134.0, 127.8, 127.6, 127.1, 122.4 (t, J = 19.8 Hz), 121.6, 108.6, 108.4, 101.2, 16.7; ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 (m, 3F), -104.4 (m, 2F), -120.2 (m, 2F), -126.1 (m, 2F); IR (CH_2Cl_2): 2898, 1488, 1351, 1235, 1134, 1041, 937, 839, 702 cm^{-1} ; HRMS, m/z : calcd for: $\text{C}_{20}\text{H}_{13}\text{F}_9\text{O}_2$: 456.0772, Found 456.0769.

(E)-1-(2-ethyl-3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)-4-methoxybenzene (36)



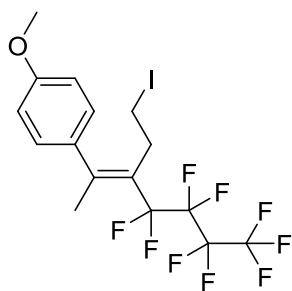
Prepared in reaction of but-1-yn-1-ylbenzene with perfluorbutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 77%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.19 (m, 3H), 7.16 – 7.10 (m, 4H), 6.88 – 6.84 (m, 2H), 3.78 (s, 3H), 2.33 (q, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.8, 151.5 (t, J = 4.6 Hz), 141.4, 134.7, 128.7, 127.7, 127.5, 126.8, 114.0 (t, J = 21.4 Hz), 55.2, 22.9, 14.3; ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 (m, 3F), -103.0 (m, 2F), -120.2 (m, 2F), -126.0 (m, 2F); IR (CH_2Cl_2): 2974, 2939, 1606, 1509, 1351, 1237, 1134, 1109, 1036, 829, 806, 744, 700 cm^{-1} ; MS (EI), m/z (%): 456 (M^+), 441 (33), 363 (21), 333 (30), 287 (35), 222 (20), 207 (17), 178 (19), 157 (49), 127 (28), 91 (22); HRMS, m/z : calcd for: $\text{C}_{21}\text{H}_{17}\text{F}_9\text{O}$: 456.1136, Found 456.1148.

(E)-1-(2-butyl-3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)-4-methoxybenzene (37)



Prepared in reaction of hex-1-yn-1-ylbenzene with perfluorbutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 75%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.20 (m, 1H), 7.16 – 7.08 (m, 2H), 6.90 – 6.83 (m, 1H), 3.78 (s, 1H), 2.33 – 2.26 (m, 1H), 1.45 – 1.35 (m, 1H), 1.15 (dq, J = 14.6, 7.4 Hz, 1H), 0.74 (t, J = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.8, 151.1, 141.4, 134.8, 128.8, 127.8, 127.5, 126.8, 113.9, 55.2, 31.9, 22.6, 13.5; ^{19}F NMR (376 MHz, CDCl_3) δ -80.9 (m, 3F), -102.9 (m, 2F), -120.2 (m, 2F), -126.0 (m, 2F); IR (CH_2Cl_2): 2960, 1606, 1509, 1351, 1234, 1134, 831, 700 cm^{-1} ; MS (EI), m/z (%): 484 (M^+), 441 (100), 421 (26), 363 (39), 333 (61), 315 (15), 271 (19), 222 (35), 207 (25), 164 (24), 157 (29), 121 (30), 91 (32); HRMS, m/z : calcd for: $\text{C}_{23}\text{H}_{21}\text{F}_9\text{O}$: 484.1449, Found 484.1461.

(E)-1-methoxy-4-(5,5,6,6,7,7,8,8,8-nonafluoro-1-iodo-4-methyloct-3-en-3-yl)benzene (38)



Prepared in reaction of 5-iodopent-2-yne with perfluorbutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 55 %, 5:3 inseparable mixture of regioisomers). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ^1H NMR (400 MHz, CDCl_3) Major regioisomer: δ 7.02 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 3.4 Hz, 2H), 3.84 (s, 3H), 2.96 (t, J = 8.0 Hz, 2H), 2.65 – 2.54 (m, 2H), 2.10 (s, 3H); Indicative signals of minor isomer: δ 3.83 (s, 3H), 3.06 (t, J = 7.6 Hz, 2H), 1.63 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.1, 151.8 (t, J = 5.0 Hz), 135.1, 127.3, 125.0 (t, J = 20.7 Hz), 114.4, 77.3, 77.0, 76.7, 55.23, 35.2 (t, J = 4.1 Hz), 24.0 – 23.8 (m), 1.53; ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 (m, 2F), -105.2 (m, 2F), -122.2 (m,

2F), -125.9 (m, 2F); IR (CH₂Cl₂): 2929, 1607, 1482, 1354, 1233, 1133, 1041, 936, 835, 732; HRMS, m/z: calcd for: C₁₆H₁₄F₉IO: 519.9946, Found 519.9942.

(E)-3-(4-methoxyphenyl)-2-(perfluorobutyl)hex-2-en-1-ol (39) Prepared in reaction of hex-2-yn-1-ol with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 57 %, 5:1 inseparable mixture of regioisomers). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 9:1→7:3 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) Major regioisomer: δ 7.16 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 2H), 3.80 (s, 3H), 2.45 (t, *J* = 7.7 Hz, 2H), 1.27 – 1.20 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H); Indicative signals of minor isomer: δ 6.83 (d, *J* = 8.7 Hz, 2H), 4.36 (s, 2H), 3.81 (s, 3H), 2.55 (dd, *J* = 8.7, 7.0 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 159.4, 158.8 (t, *J* = 4.7 Hz), 132.5, 128.8, 124.7 (t, *J* = 21.6 Hz), 113.8, 55.3, 37.9, 21.5, 13.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -104.8 (m, 2F), -121.9 (m, 2F), -125.9 (m, 2F); IR (CH₂Cl₂): 3247, 2964, 1608, 1511, 1350, 1236, 1134, 838, 744 cm⁻¹; MS (EI), m/z (%): 424 (M⁺), 381 (73), 363 (33), 237 (44), 195 (32), 161 (55), 121 (54), 108 (32); HRMS, m/z: calcd for: C₁₇H₁₇F₉O₂: 424.1085, Found 424.1075.

(E)-4-methyl-N-(7,7,8,8,9,9,10,10,10-nonafluoro-5-(4-methoxyphenyl)-6-methyldec-5-en-1-yl)benzenesulfonamide (40) Prepared in reaction of N-(hept-5-yn-1-yl)-4-methylbenzenesulfonamide with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 68 %, 1:1 inseparable mixture of regioisomers). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 8:2→7:3 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) Major regioisomer: δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.94 – 6.89 (m, 4H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.39 (t, *J* = 6.1 Hz, 1H), 4.01 (t, *J* = 5.9 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.83 (d, *J* = 6.9 Hz, 2H), 2.64 (q, *J* = 6.6 Hz, 2H), 2.41 (s, 9H), 2.07 (s, 3H), 1.96 – 1.90 (m, 2H), 1.60 (s, *J* = 6.5 Hz, 3H), 1.46 – 1.40 (m, *J* = 14.9, 7.5 Hz, 2H); Indicative signals of minor isomer: δ 7.63 (d, *J* = 8.2 Hz, 2H), 4.01 (t, *J* = 5.9 Hz, 1H), 3.80 (d, *J* = 6.9 Hz, 3H), 2.83 (dd, *J* = 13.7, 6.9 Hz, 2H), 1.60 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.9, 158.9, 158.9, 150.0, 149.6, 143.3, 143.3, 143.3, 136.9, 136.9, 135.5, 133.4, 129.6, 129.6, 128.6, 127.6, 127.1, 127.0, 127.0, 114.2, 114.0, 55.3, 55.2, 42.9, 42.7, 32.7, 30.0, 29.7, 28.5, 28.3, 26.9, 23.6, 21.0, 16.6, 16.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -105.3 (m, 2F), -122.1 (m, 2F), -122.4 (m, 2F), -125.9 (m, 2F); IR (CH₂Cl₂): 3282, 2927, 1608, 1511, 1327, 1235, 1201, 1161, 1133, 1092, 835, 815, 742, 663, 552 cm⁻¹; MS (EI), m/z (%): 577 (M⁺), 422 (68), 405 (35), 380 (84), 359 (48), 314 (70), 184 (55), 155 (82), 121 (28), 91 (100), 56 (25); HRMS, m/z: calcd for: C₂₄H₂₄F₉NO₃S: 577.1333, Found 577.1356.

(E)-5,5,6,6,7,7,8,8,8-nonafluoro-3-(4-methoxyphenyl)-4-methyloct-3-en-1-yl methanesulfonate (41) Prepared in reaction of pent-3-yn-1-yl methanesulfonate with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under **conditions B** (yield: 51 %, 2:1 inseparable mixture of regioisomers) or **conditions C** (yield: 50 %, 2:1 inseparable mixture of regioisomers). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 9:1→8:2 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) Major regioisomer: δ 7.01 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 6.2 Hz, 2H), 3.79 (s, 3H), 2.79 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.12 (bs, 3H); Indicative signals of minor isomer: δ 3.83 (s, 3H), 2.95 (d, *J* = 6.8 Hz, 2H), 2.89 (s, 3H), 1.67 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 153.5 (t, *J* = 5.2 Hz), 134.9, 127.4, 114.4, 67.8, 55.3, 37.1, 24.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -105.1 (m, 2F), -122.1 (m, 2F), -125.9 (m, 2F); IR (CH₂Cl₂): 2941, 1609, 1512, 1354, 1237, 1177, 1134, 958, 835 cm⁻¹; MS (EI), m/z (%): 488 (M⁺), 379 (100), 223 (48), 203 (36), 173 (53), 160 (57), 145 (22), 79 (33); HRMS, m/z: calcd for: C₁₇H₁₇F₉O₃S: 488.0704, Found 488.0702.

(E)-1-(4-ethyl-5,5,6,7,7,8,8,8-nonafluorooct-3-en-3-yl)-4-methoxybenzene (42) Prepared in reaction of 3-hexyne perfluorobutyl iodide and 4-methoxyphenylboronic acid under **conditions B** (yield: 62%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 2.44 (q, *J* = 7.2 Hz, 2H), 1.97 (q, *J* = 7.3 Hz, 2H), 0.92 – 0.85 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 158.6, 154.0 (t, *J* = 4.9 Hz), 133.8, 128.6, 126.5 (t, *J* = 19.8 Hz), 113.6, 77.3, 77.0, 76.7, 55.2, 29.2, 15.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -105.1 (m, 2F), -122.1 (m, 2F), -125.9 (m, 2F); 2929, 1609, 1488, 1342, 1231, 1133, 1045, 942, 839; HRMS, *m/z*: calcd for: C₂₂H₁₅F₁₃O: 408.1136, Found 408.1129.

(E)-5-(5,5,6,6,7,7,8,8,8-nonafluoro-2,4-dimethyloct-3-en-3-yl)benzo[d][1,3]dioxole (43) Prepared in reaction of 4-methylpent-2-yne with perfluorobutyl iodide and benzo[d][1,3]dioxol-5-ylboronic acid under **conditions B** (yield: 47 %, 5:3 inseparable mixture of regioisomers). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, Hexane). ¹H NMR (400 MHz, CDCl₃) Major regioisomer: δ 6.80 (d, *J* = 6.6 Hz, 1H), 6.47 (d, *J* = 1.5 Hz, 1H), 6.41 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.98 (s, 2H), 3.22 (hept, 1H), 1.51 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 6H); Indicative signals of minor isomer: δ 6.57 (d, *J* = 1.6 Hz, 1H), 6.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.97 (s, 2H), 2.73 (hept, *J* = 14.3, 7.2 Hz, 1H), 2.08 – 1.99 (m, 3H), 1.01 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 156.6 (t, *J* = 3.8 Hz), 147.8, 147.4, 146.5, 132.0, 121.5, 109.1, 108.4, 108.0, 101.0, 32.1 (t, *J* = 1.9 Hz), 21.3, 16.5 (t, *J* = 6.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -104.5 (m, 2F), -122.9 (m, 2F), -126.0 (m, 2F); IR (CH₂Cl₂): 2927, 1606, 1486, 1350, 1232, 1136, 1042, 941, 835, 734; HRMS, *m/z*: calcd for: C₁₇H₁₅F₉O₂: 422.0928, Found 422.0915.

(E)-5-(5,5,6,6,7,7,8,8,8-nonafluoro-2,2,4-trimethyloct-3-en-3-yl)benzo[d][1,3]dioxole (44) Prepared in reaction of 4,4-dimethylpent-2-yne with perfluorobutyl iodide and 4-methoxyphenylboronic acid under **conditions B** (yield: 15%, 5:1 inseparable mixture of regioisomers). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) Major regioisomer: δ 6.77 (d, *J* = 7.9 Hz, 1H), 6.39 (d, *J* = 1.4 Hz, 1H), 6.32 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.94 (s, 2H), 1.46 (s, 3H), 1.09 (s, 9H); Indicative signals of minor isomer: δ 7.10 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 2H), 1.53 (s, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 159.8 (t, *J* = 3.0 Hz), 147.8, 145.9, 138.1, 119.5, 108.4, 107.6, 102.0, 101.0, 36.8, 32.2 (t, *J* = 5.7 Hz), 29.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -101.9 (m, 2F), -117.6 (m, 2F), -125.9 (m, 2F); IR (CH₂Cl₂): 2930, 1610, 1488, 1356, 1237, 1134, 1042, 945, 835, 734; HRMS, *m/z*: calcd for: C₁₈H₁₇F₉O₂: 436.1085, Found 436.1081.

(E)-1-methoxy-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-methyl-1-phenyloct-1-en-1-yl)benzene (45) Prepared in reaction of prop-1-yn-1-yl benzene with perfluorohexyl iodide and 4-methoxyphenylboronic acid under **conditions B** (yield: 69%). The title compound was isolated as white solid crystal after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.23 (m, 3H), 7.15 (d, *J* = 6.9 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 1.96 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 150.3 (t, *J* = 4.3 Hz), 141.3, 134.5, 129.5, 127.9, 127.6, 127.0, 121.9 (t, *J* = 19.7 Hz), 113.88, 55.18, 16.68; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 (m, 3F), -104.08 (m, 2F), -119.3 (m, 2F), -

122.0 (m, 2F), -122.7 (m, 2F), -126.2 (m, 2F); IR (CH₂Cl₂): 2935, 1606, 1510, 1244, 1144, 1037, 834, 707 cm⁻¹; MS (EI), m/z (%): 542 (M⁺), 273 (75), 253 (40), 157 (71), 127 (48); HRMS, m/z: calcd for: C₁₇H₁₇F₉O: 542.0915, Found 542.0909.

(E)-ethyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-4-phenylbut-3-enoate (46) Prepared in reaction of prop-1-yn-1-yl benzene with 2,2-difluoro-2-iodoacetate and 4-methoxyphenylboronic acid under **conditions B** (yield: 53%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 95:5→9:1 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.22 (m, 3H), 7.15 – 7.09 (m, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.84 – 3.75 (m, 5H), 1.99 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 163.7 (t, *J* = 33.6 Hz), 159.0, 146.0 (t, *J* = 7.3 Hz), 140.2, 134.0, 130.46, 130.02 (t, *J* = 1.7 Hz), 127.78 (d, *J* = 4.9 Hz), 126.49 (t, *J* = 23.9 Hz), 113.5, 62.5, 55.2, 16.1, 13.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -93.9 (s, 2F); IR (CH₂Cl₂): 2930, 1770, 1605, 1510, 1302, 1248, 1110, 1051, 833, 702 cm⁻¹; MS (EI), m/z (%): 346 (M⁺), 273 (100), 253 (32), 157 (69), 127 (36); HRMS, m/z: calcd for: C₂₀H₂₀F₂O₃: 346.1381, Found 346.1385.

(E)-1-(4-bromo-3,3,4,4-tetrafluoro-2-methyl-1-phenylbut-1-en-1-yl)-4-methoxybenzene (47) Prepared in reaction of prop-1-yn-1-yl benzene with 1-bromo-1,1,2,2-tetrafluoro-2-iodoethane and 4-methoxyphenylboronic acid under **conditions B** (yield: 39%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.21 (m, 3H), 7.14 (d, *J* = 7.0 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 1.94 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.9, 150.2 (t, *J* = 3.8 Hz), 141.5, 134.7, 128.0 (t, *J* = 2.4 Hz), 127.5, 126.9, 121.5 (t, *J* = 20.9 Hz), 113.8, 55.2, 17.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -61.2 (t, *J* = 5.1 Hz, 2F), -100.5 (t, *J* = 5.1 Hz, 2F); IR (CH₂Cl₂): 2934, 1605, 1509, 1248, 1149, 1106, 855, 701 cm⁻¹; MS (EI), m/z (%): 401 (M⁺), 273 (100), 253 (48), 157 (86), 127 (58); HRMS, m/z: calcd for: C₁₈H₁₅BrF₄O: 402.0242, Found 402.0247.

(E)-1-methoxy-4-(3,3,4,4-tetrafluoro-2-methyl-1-phenyl-3-(trifluoromethyl)but-1-en-1-yl)benzene (48) Prepared in reaction of prop-1-yn-1-ylbenzene with 1,1,1,2,3,3,3-heptafluoro-2-iodopropane and 4-methoxyphenyl boronic acid under **conditions B** (yield: 44%). The title compound was isolated as colorless oil after chromatography on silica gel (10 g column, 98:2→95:5 Hexane:AcOEt). ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.20 (m, 3H), 7.14 – 7.10 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 1.91 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.8, 150.0, 142.2 (d, *J* = 5.1 Hz), 135.0 (d, *J* = 2.2 Hz), 129.2, 127.7, 127.1 (d, *J* = 4.7 Hz), 126.5, 118.4 (d, *J* = 12.8 Hz), 114.0, 55.2, 16.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -76.9 (d, *J* = 7.7 Hz, 6F), -184.1 (m, 1F); IR (CH₂Cl₂): 2935, 1607, 1509, 1246, 1118, 1010, 962, 833, 701 cm⁻¹; MS (EI), m/z (%): 392 (M⁺), 323 (78), 239 (16), 207 (15) HRMS, m/z: calcd for: C₁₉H₁₅F₇O: 392.1011 Found 392.1010.

(E)-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-ene-1,2-diyl)dibenzene (53) Prepared in reaction of 1,2-diphenylethyne with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under modified (run at 100 °C) **conditions B** (yield: 28%). The title compound was isolated as yellow oil after chromatography on silica gel (10 g column, 8:2 Hexane:Toluene). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.17 (m, 11H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 3.65 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.5, 152.9 (t, *J* = 3.9 Hz), 141.1, 135.5, 134.1, 132.0, 131.0, 127.9, 127.8, 127.7, 127.3, 113.1, 55.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (m, 3F), -101.3 (m, 2F), -117.6 (m, 2F), -126.1 (m, 2F).

Assignment of the structure of products of carboperfluoroalkylation of alkynes

Products of carboperfluoroalkylation of terminal alkynes. Products of carboperfluoroalkylation of terminal alkynes (**1**, **3-29**) were isolated as a single regioisomer with high stereoselectivity (>95:5). Their structures were determined based on the literature precedence. Compounds **1** and **11** were previously reported in the literature and their ^1H , ^{19}F , and ^{13}C NMR spectra were in agreement with those reported by Nevado.² Structure of several other compounds (eq.) are closely related to those reported by Nevado, which is reflected in their NMR spectra. Structures of other compounds were assigned by analogy, and their spectra were in agreement with expectations.

Products of carboperfluoroalkylation of internal alkynes. Products of the reaction involving aryl alkyl substituted alkynes (**2**, **30-37**, **45-48**) were isolated as a single regioisomer with high stereoselectivity (>95:5). Structure (regio- and stereochemistry) of **34** was determined based on NOE experiment (Figure S1). Structures of other compounds were assigned by analogy, and their spectra were in agreement with expectations. Generally, carboperfluoroalkylation of dialkylsubstituted alkynes gave products isolated as a mixture of regioisomer (**37-44**), except of compound **42**, resulting from reaction of symmetrical alkyne, that was isolated as a single isomer. NOESY 1D experiment performed on **42** (Figure S1) proved *anti* addition of perfluoroalkyl (from perfluoroalkyl iodide) and aryl (from boronic acid) groups. The stereoselectivity is in agreement with previously discussed stereoselectivity of terminal alkynes as well as the aryl alkyl substituted internal alkynes. Similar stereoselectivity was assumed for others products of reactions involving dialkyl substituted internal alkynes.

Regioisomer ratio, and the structure of major and minor isomers was determined based on careful analysis of NMR spectra (involving 2D). For instance methyl groups at vinyl positions were shifted more downfield for isomer in which it is closer to aryl then to perfluoroalkyl substituent. Moreover, in the ^1H - ^{13}C HMBC experiment signals representing coupling of protons of methyl group with two vinyl and one aryl carbons (all quaternary) are present; For the other isomer only two couplings with vinyl carbons are present. Analogical observations were taken for methylene at vinyl positions. Representative example of analysis of ^1H - ^{13}C HMBC spectrum is presented in Figure S2.

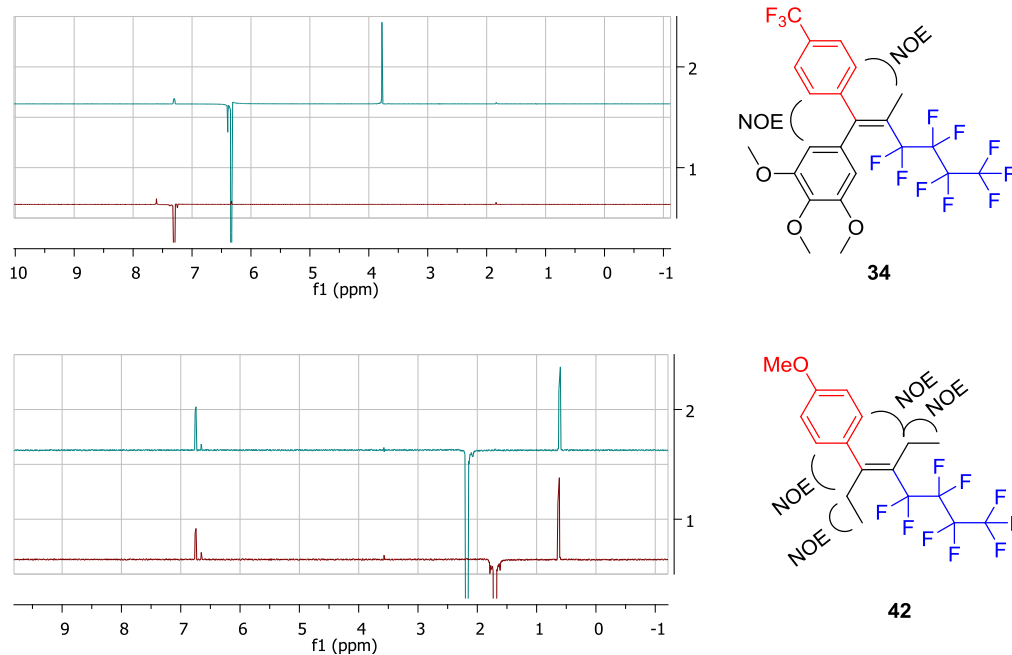


Figure S1. NOESY 1D experiment of representative examples of the functionalisation of internal alkynes (compounds **34** and **42**)

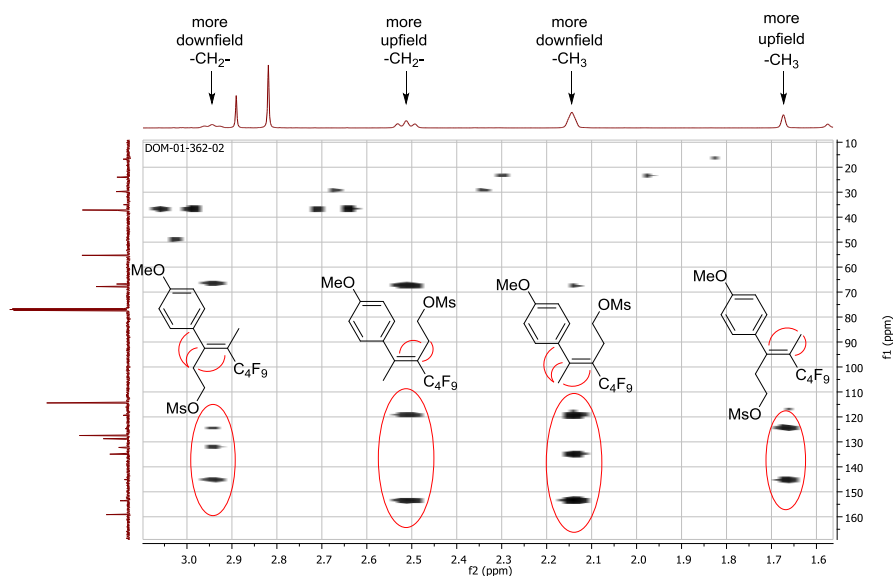


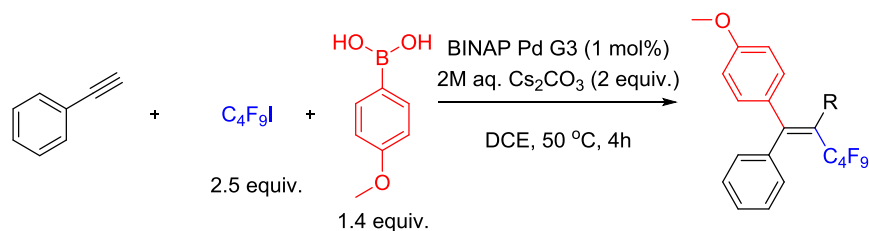
Figure S2. Assignment of the structure based on analysis of chemical shifts in ^1H NMR and ^1H - ^{13}C HMBC correlations of substituents at vinyl positions, exemplified on compound **41**.

Mechanistic Studies

• Radical inhibition experiment

A series of reactions in a presence of radical inhibitors were run. Reactions were run for 4h under standard conditions following general procedure for evaluation of reaction conditions (page S5). Additive was introduced to reaction mixture as a last component.

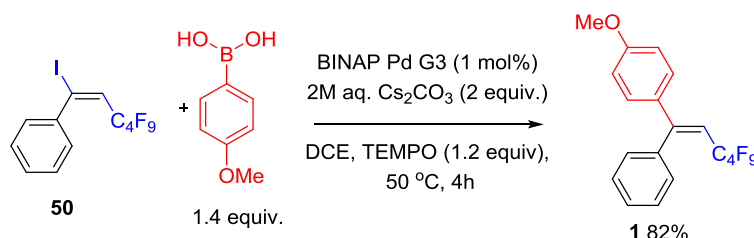
Table S9. Effect of addition of radical inhibitors.



Entry	Additive	Conversion ^b	Yield ^b
1	None	100%	88%
2	Hydroquinone (40 mol%)	100%	84%
3	Hydroquinone (80 mol%)	100%	87%
4	BHT (80 mol%)	100%	72%
5	Ascorbic acid (80 mol%)	93%	75%
6	TEMPO (40 mol%)	31%	21%
7	TEMPO (80 mol%)	18%	5%
8	TEMPO (100 mol%)	10%	0%

^aStandard conditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.175 mmol, 1.4 equiv.), perfluorobutyl iodide (0.3125 mmol, 2.5 equiv.), BINAP Pd G3, 2M aqueous Cs_2CO_3 (0.25 mmol, 2 equiv.), DCE (0.5 mL), additive, 50 °C, 4 h. ^bGC yield with dodecane as internal standard.

Detrimental effect of addition of radical inhibitors on the reaction outcome was observed. TEMPO was the most efficient inhibitor, causing significant reduction in yield when 40 mol% of TEMPO was added to the reaction mixture (table S9, entry 6). At higher loadings of TEMPO almost no product of the reaction was observed (table S9, entries 7-8). The observations are consistent with literature reports on radical character of Pd-catalyzed additions of iodoperfluoroalkanes to C-C multiple bonds. In particular, it also matches reported by Nevado² mechanistic investigations of carboperfluoroalkylations of terminal acetylenes. It is worth mentioning that addition of tempo exerts no effect on Suzuki coupling of independently obtained vinyl iodide **50** (Scheme S1).



Scheme S1. Influence of addition of TEMPO on Suzuki coupling.

- **Accumulation of vinyl iodide and homocoupling product during of reaction**

Composition of the reaction mixture was investigated at various points of reaction progress. A series of model reactions were run following general procedure for evaluation of reaction conditions. Individual reactions were stopped after 0.5, 1, 2 and 4 h, and the composition of reaction was investigated by GC.

Table S10. Composition of reaction mixture at various stages of reaction progress.^a

Entry	Rxn. time	Conversion ^b	Yield of 1 ^b	Yield of 50 ^b	Yield of 52 ^b
1	0.5h	23%	8%	13%	<1%
2	1h	34%	21%	9%	2%
3	2h	54%	38%	12%	6%
4	4h	100%	85%	<1%	10%

^aStandard conditions: Phenylacetylene (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.175 mmol, 1.4 equiv.), perfluorobutyl iodide (0.3125 mmol, 2.5 equiv.), BINAP Pd G3 (1 mol%), 2M aqueous Cs₂CO₃ (0.25 mmol, 2 equiv.), DCE (0.5 mL), 50 °C, 0.5-4 h. ^byields and conversions were determined by GC with dodecane as a internal standard.

Formation of significant amount of vinyl iodide **50** was observed during initial stage of the reaction (table S10, entry 1). Then the amount of **50** remains constant during reaction progress, when rate of formation and consumption of intermediate vinyl iodide **50** remains equal (table S10, entries 2-3). At the final stage, when alkyne was consumed stopping delivery of **50**, the accumulated vinyl iodide **50** was almost completely coupled with boronic acid. The above presented results supports proposed reaction mechanism involving two catalytic cycles, one responsible for formation of vinyl iodide **50** intermediate, and the other involving Suzuki coupling of **50** with boronic acid.

Formation of biaryl **52** was observed and the amount **52** of increased steadily during reaction progress (Table S10). Formation of **52** results from Pd(II) mediated reductive homocoupling of arylboronic acid, providing possibility of reduction of Pd(II) back to Pd(0) species. For further discussion, see following chapter.

- **Pd-catalyzed iodoperfluoroarylation of phenylacetylene - effect of boronic acid**

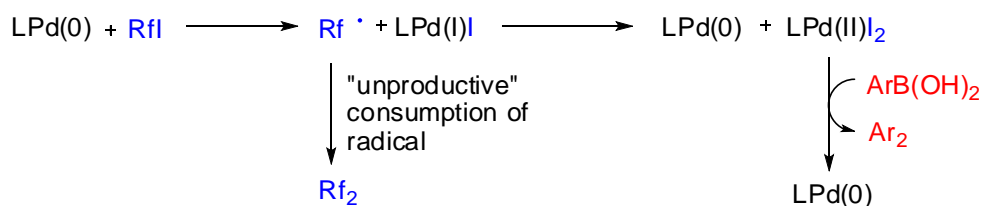
The role of arylboronic acid in the reaction was investigated. Reactions were run for 4h under standard conditions, following general procedure for evaluation of reaction conditions (table S11, entries 1-3) or for 2h, after which time additional reagent was added and the reaction was carried out for further 2h (table S11, entries 4-6).

Table S11. The role of arylboronic acid in the reaction

Entry	ArB(OH) ₂ added at the beginning	Added after 2h	Rxn. time	Yield (2h) ^b		Yield (4h) ^b	
				1	50	1	50
1	-	-	4h	-	-	0%	24%
2	53 (10 mol%)	-	4h	-	-	7%	61%
3	53 (1.3 equiv.)	-	4h	-	-	87%	<1%
4	53 (10 mol%)	53 (1.3 equiv.)	2h+2h	6 ^c	59%	74%	<1%
5	54 (10 mol%)	53 (1.3 equiv.)	2h+2h	0 ^c	58%	65%	<1%
6	53 (10 mol%)	54 (1.3 equiv.)	2h+2h	7	62%	61% ^c	<1%

^aStandard conditions: Phenylacetylene (0.125 mmol, 1 equiv.), boronic acid, perfluorobutyl iodide (0.3125 mmol, 2.5 equiv.), BINAP Pd G3 (1 mol%), 2M aqueous Cs₂CO₃ (0.25 mmol, 2 equiv.), DCE (0.5 mL), 50 °C, ^byields and conversions were determined by GC with dodecane as a internal standard. ^c yield of compound **3** (coupling with phenylboronic acid).

We found that Pd-BINAP species are capable to catalyze addition of iodoperfluoroalkanes across triple bond of phenylacetylene, however, the efficiency of the process is low (table S11, Entry 1). The observation is consistent with Okada's³ report on Pd-catalyzed iodoprefluorination of acetylenes and explains high catalyst loadings needed to provide efficient addition. Interestingly, in the presence of arylboronic acid, even in catalytic quantities, addition of iodoperfluorobutane to phenylacetylene is more efficient (table S11, Entry 2). The effect could be attributed to Pd(II) mediated reductive homocoupling of arylboronic acid, providing possibility of reduction of Pd(II) back to Pd(0) species. Formation of LPd(II)I₂ is a consequence of “unproductive” reactions of perfluoroalkyl radicals formed in Pd-catalyzed atom transfer process. Above discussed processes are summarized in Scheme S2. Stone⁴ reported formation of considerable amounts of L_nPdI₂ was observed during oxidative addition of iodoperfluoroalkanes to Pd(0) species. “Unproductive” reactions of radicals are typical for atom transfer radical additions (and polymerizations) and are responsible for accumulation of oxidized state of catalyst (also called activator in polymerization chemistry).⁵ Constant reduction of Pd(II) to Pd(0) with the aid of boronic acid is conceptually similar to ATRA (or ATRAP) reaction setup involving activator regeneration (for instance ICAR or ARGET). It also explains more effective Pd-catalyzed addition of iodoperfluoroalkane across acetylene moiety in the presence of catalytic amount boronic acid (*cf.* table S11, entries 1 and 2).



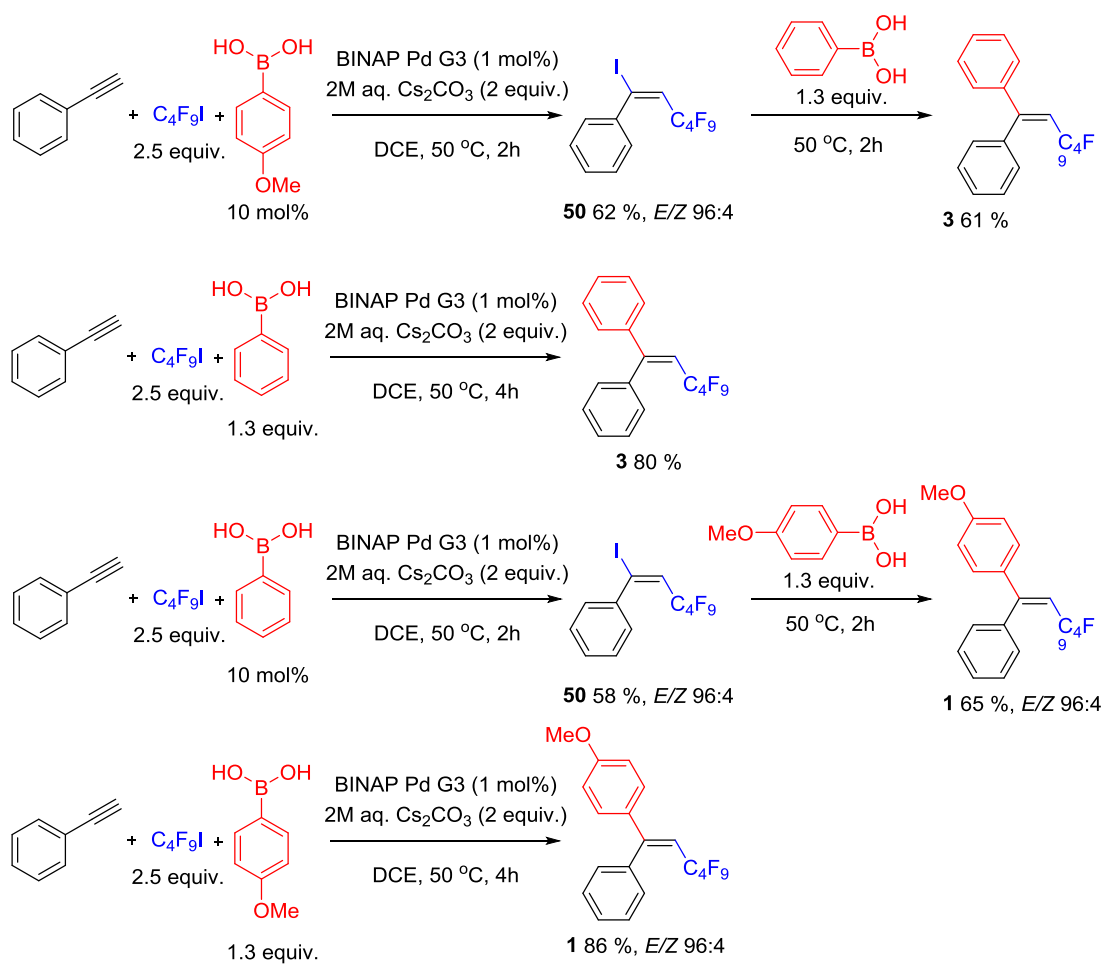
Scheme S2. Role of boronic acid in regeneration of Pd(0).

Efficient formation of vinyl iodide **50** in the reaction between phenylacetylene and iodoperfluorobutane catalyzed by Pd G3 BINAP in the presence of arylboronic acid could also suggest vinyl iodides as a credible intermediate in the carboperfluoroalkylation of alkynes. This concept is further supported by experiments in which formation of **50** is resolved in time from Suzuki coupling (table S11, entries 4-6). Firstly, vinyl iodide was formed in the presence of catalytic amount of arylboronic acid, then it was effectively coupled with boronic acid added later to the reaction mixture. The observation strongly supports mechanism involving two separate catalytic cycles, one responsible for formation of intermediate **50**, and the other for its coupling with boronic acid.

- **Stereoselectivity of the reaction.**

The aspect of stereoselectivity of the reaction was investigated (Scheme S3). Stereochemical outcome of the reactions with phenylboronic and p-methoxyphenylboronic acids run under standard reaction conditions were compared with analogous reactions with steps of addition of RfI and Suzuki coupling resolved in time (scheme S3, see also table S10 entries 5 and 6). In the latter case additions of iodoperfluorobutane was carried out for 2h in the presence of 10 mol% of boronic acid; after that time 1.3 equiv. of other boronic acid was introduced and the reaction was carried out for further 2h. To avoid change in composition of isomers during isolation and purification of products, stereoselectivities were determined by GC analysis of crude reaction mixtures (Figure S3).

Results depicted in Scheme 2 clearly showed that composition of isomers of initially formed vinyl iodide intermediate **50** was further reflected in Suzuki coupling products **1** and **3**. Moreover stereoselectivities were also identical to those observed for tandem process run under standard conditions, and were independent on boronic acid used. Reactions run with other sterically and electronically varied boronic acids led to corresponding products with *E/Z* selectivities similar to those presented in Scheme 2. These results shows that stereoselectivity is achieved during addition of iodoperfluoroalkane to acetylene and is conserved in the second step of Suzuki coupling. The observation is also consistent with proposed mechanistic picture involving two separate catalytic cycles linked with common reaction intermediate **50**.



Scheme S3. Stereoselectivity of the reaction.

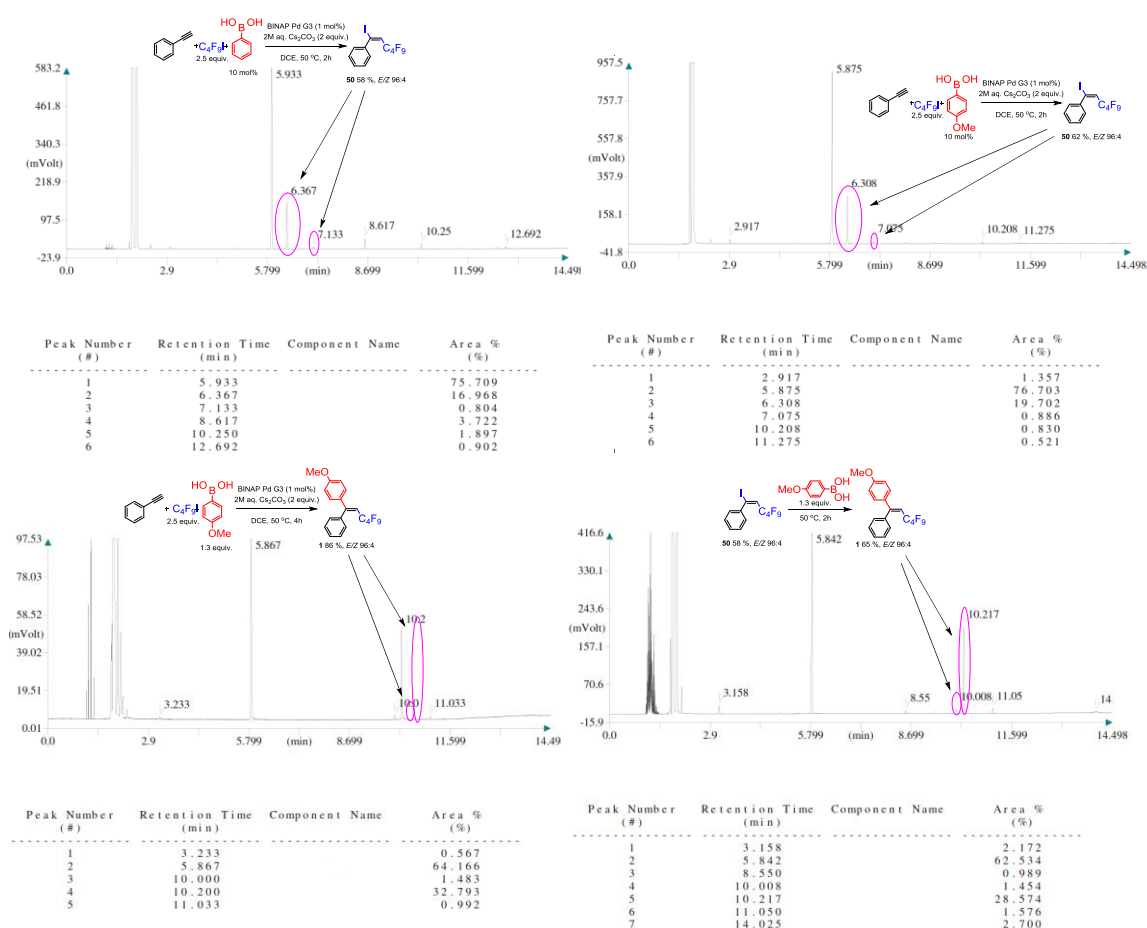


Figure S3. GC traces of selected reactions from Scheme S2.

- Suzuki reaction of independently prepared vinyl iodide **50**.**

Suzuki coupling of independently prepared vinyl iodide **50** were run under conditions analogues to general conditions for carboperfluoroalkylation.

Table S12. Suzuki coupling of vinyl iodide **50.**

Entry	Rxn. time	Conversion ^b	Yield ^b
1	0.5h	22%	18%
2	1h	45%	38%

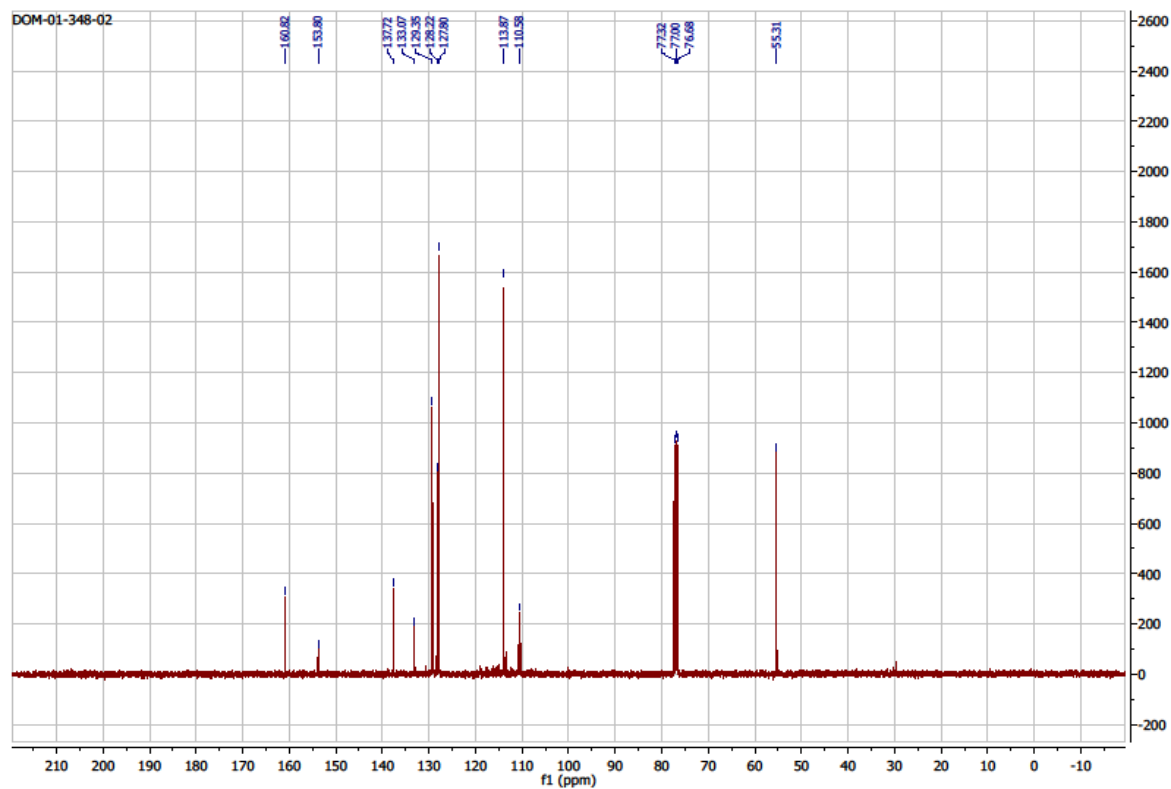
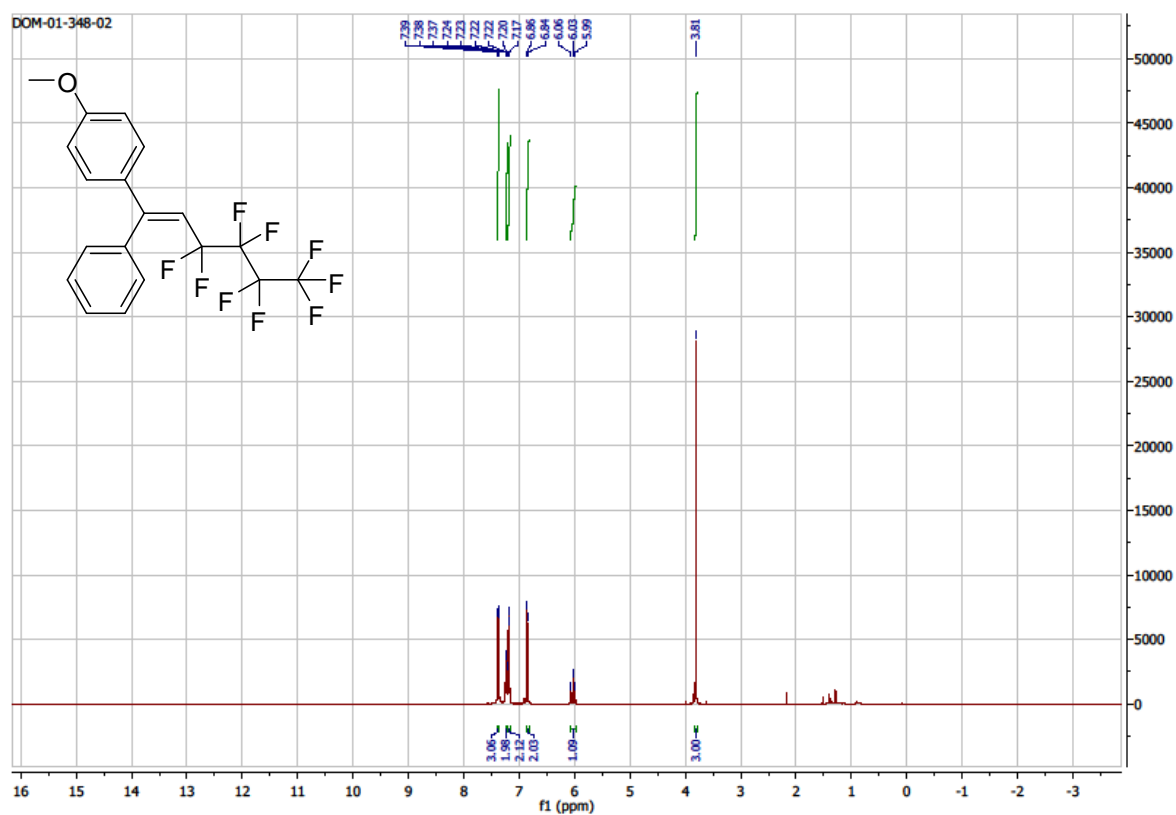
^aStandard conditions: **50** (0.125 mmol, 1 equiv.), 4-methoxyphenyl boronic acid (0.175 mmol, 1.4 equiv.), BINAP Pd G3 (1 mol%), 2M aqueous Cs₂CO₃ (0.25 mmol, 2 equiv.), DCE (0.5 mL), 50 °C.

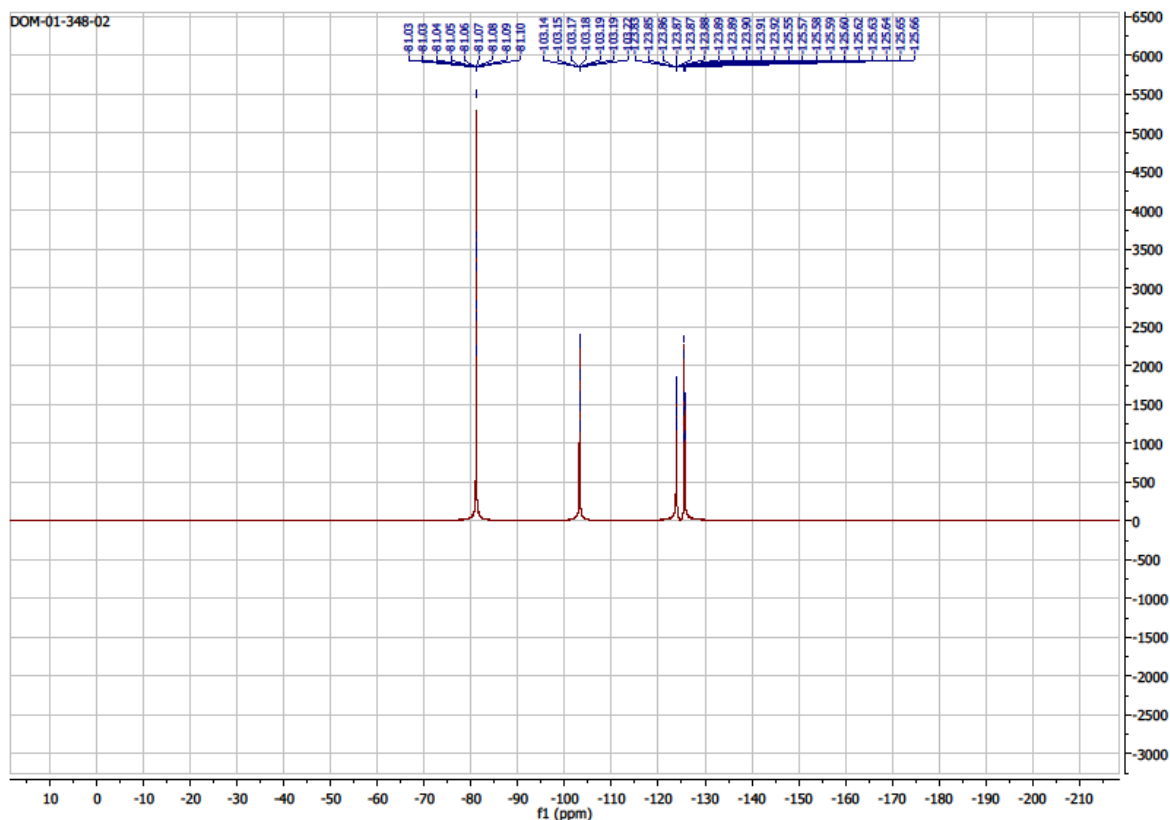
^byields and conversions were determined by GC with dodecane as a internal standard.

It is not surprising that vinyl iodide **50** undergoes Suzuki coupling under reaction condition developed for carboperfluoroalkylation of alkynes. Crude analysis of the reaction outcome demonstrate that the rate of coupling is roughly similar to the rate of overall process of carboperfluoroalkylation (cf. table S12 with table 10). The observation is consistent with results presented in table S9 and discussed thereafter.

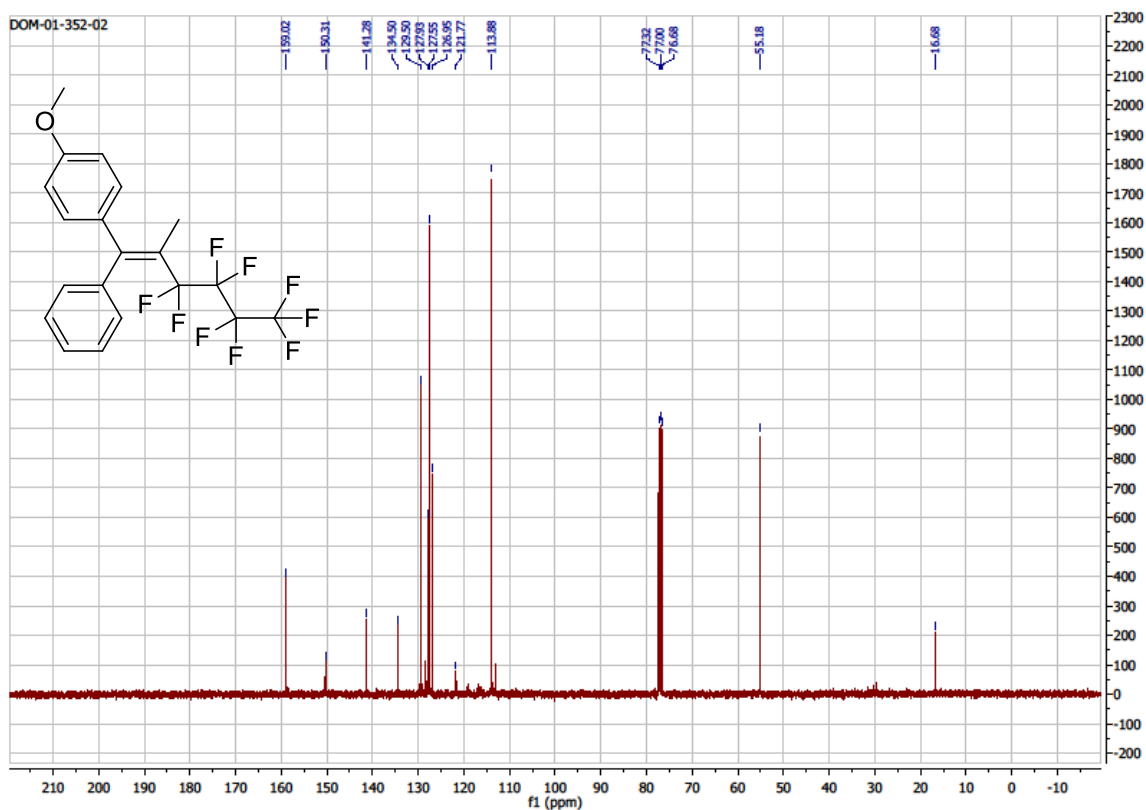
Copies of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of isolated compounds

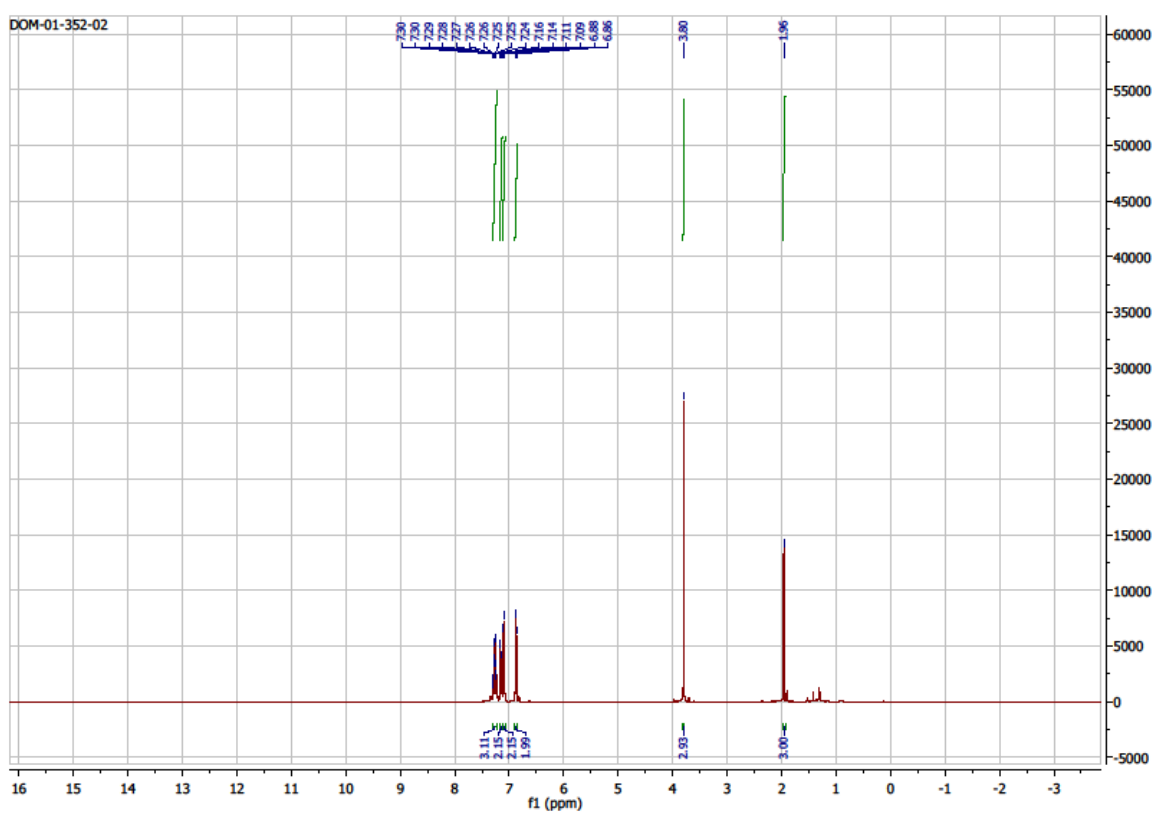
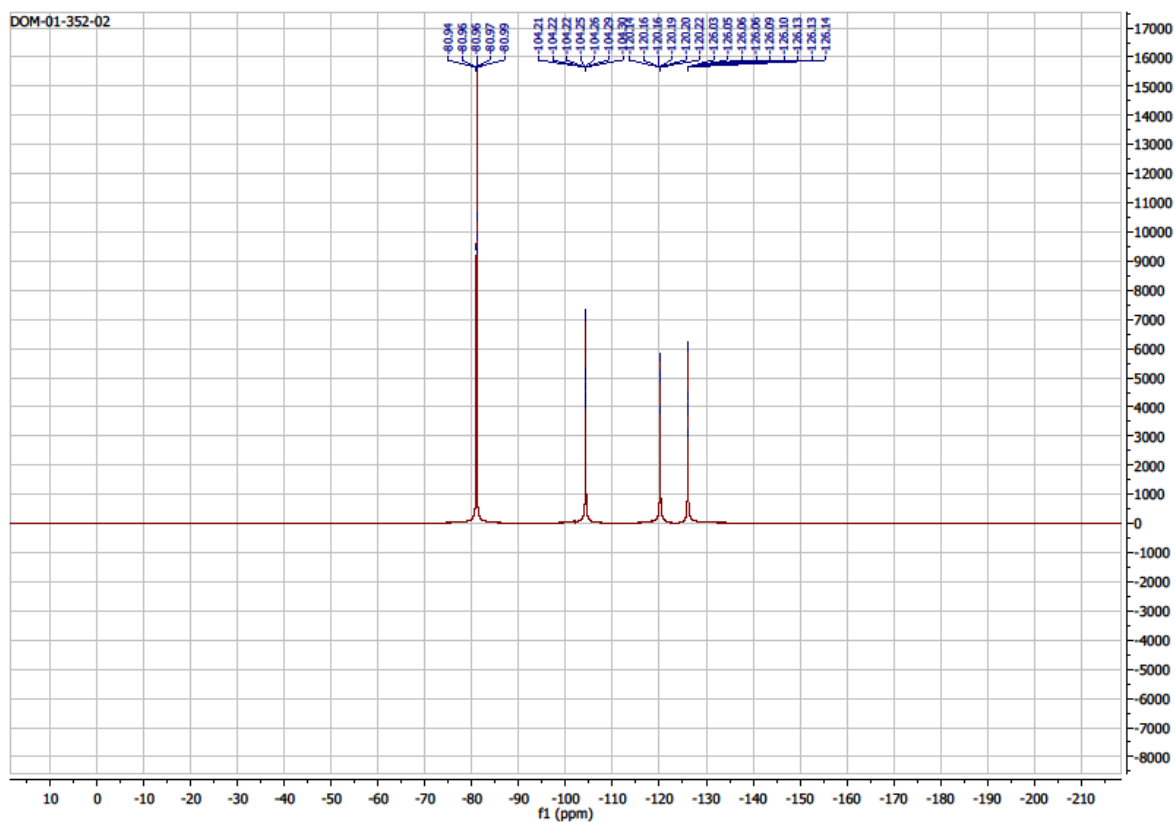
(*E*)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-enyl)benzene (1)



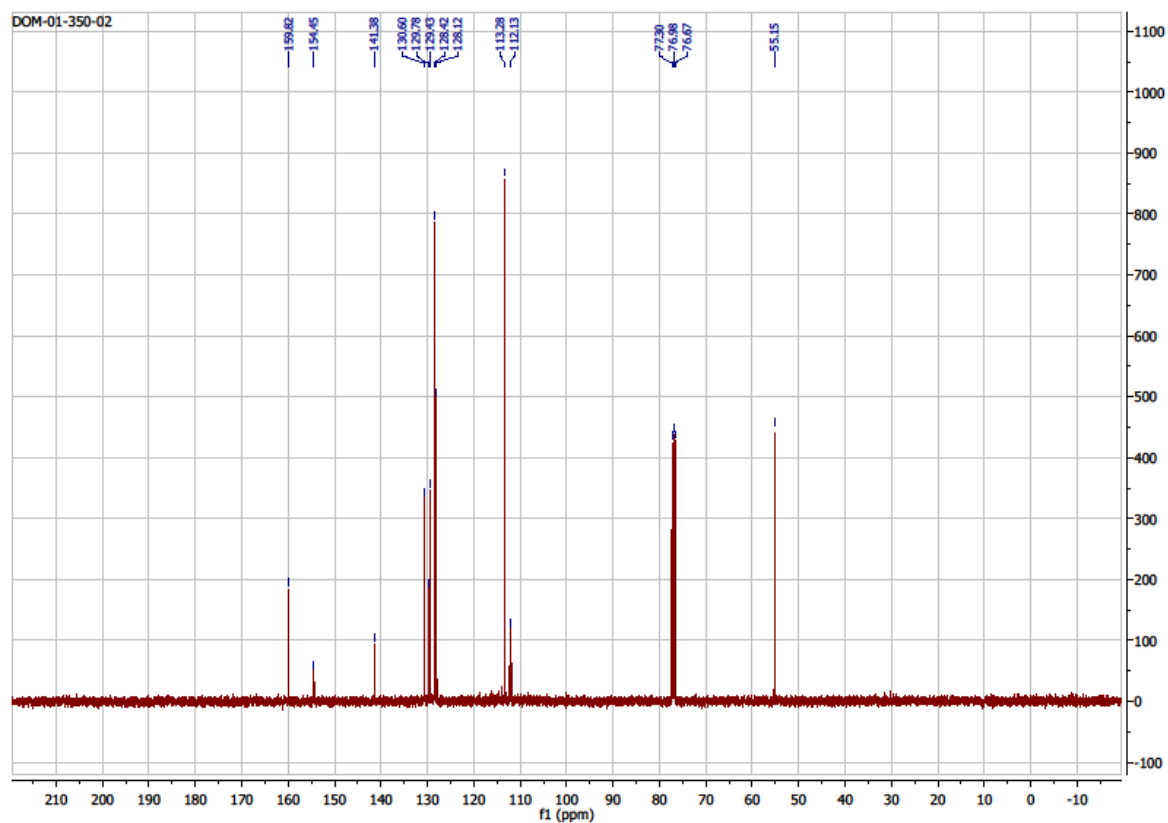
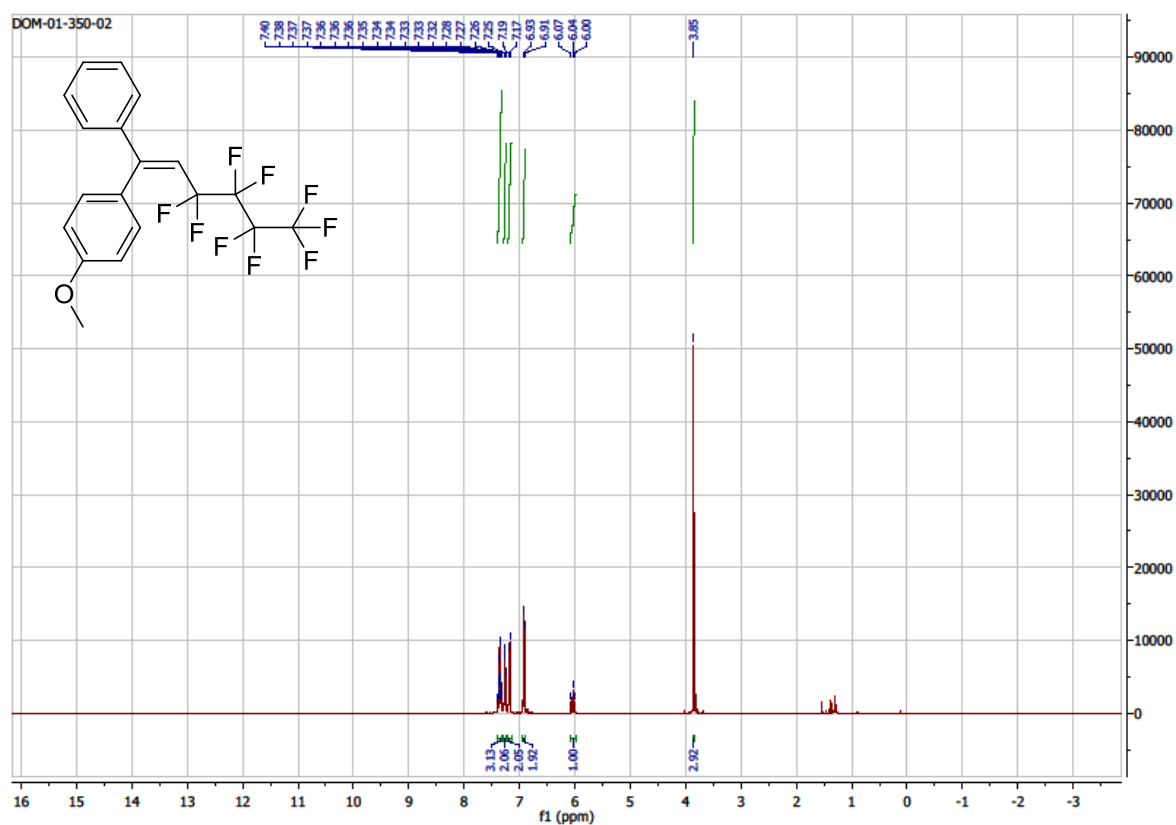


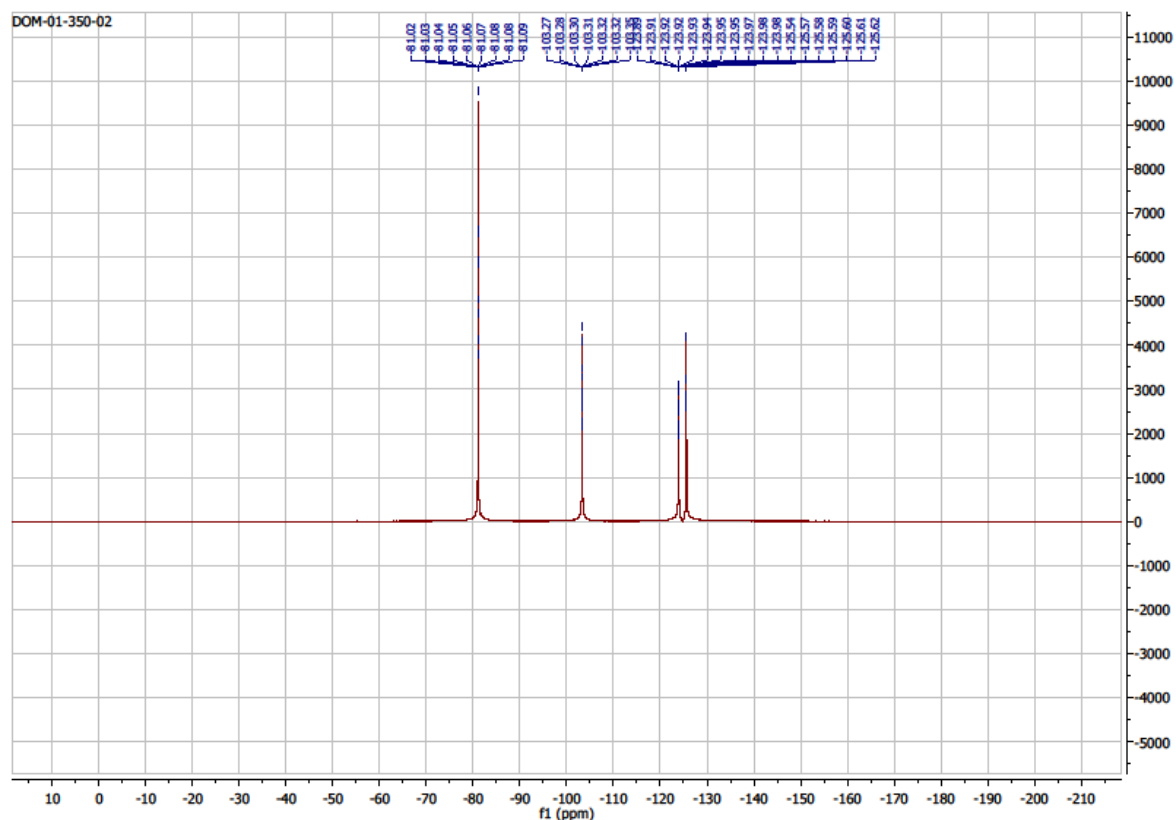
(*E*)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzene (2)



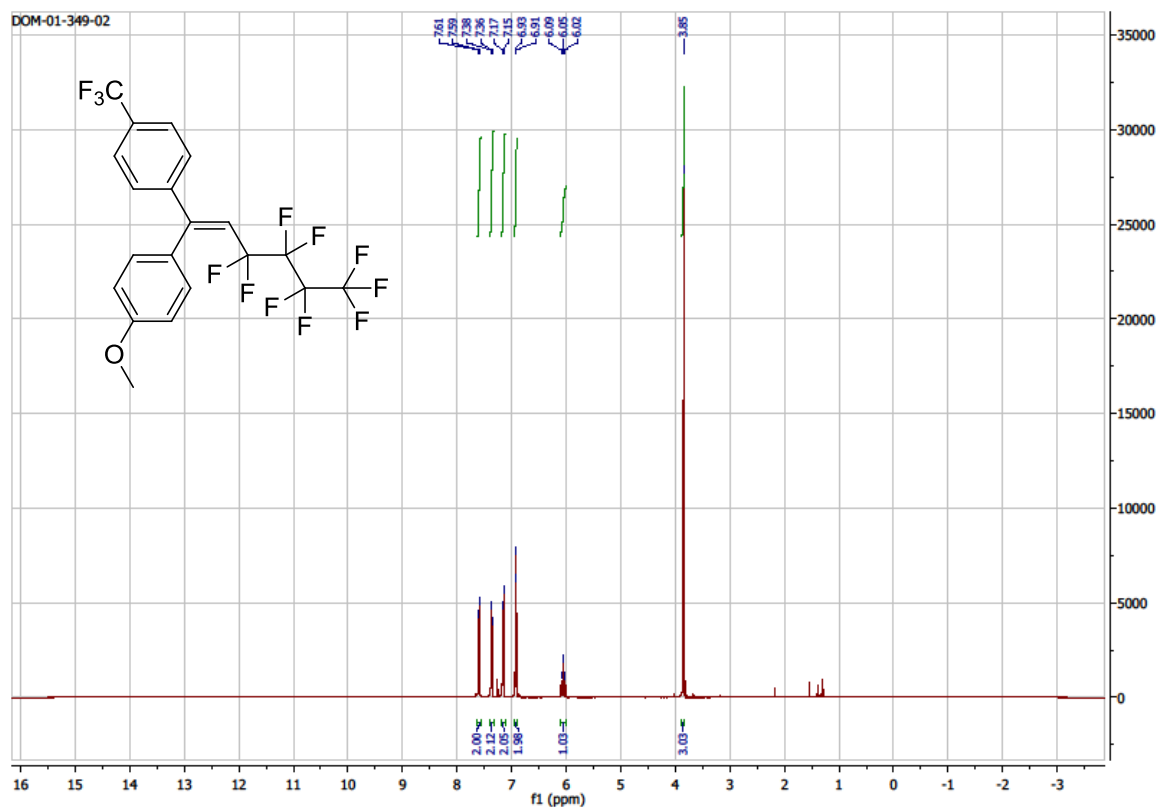


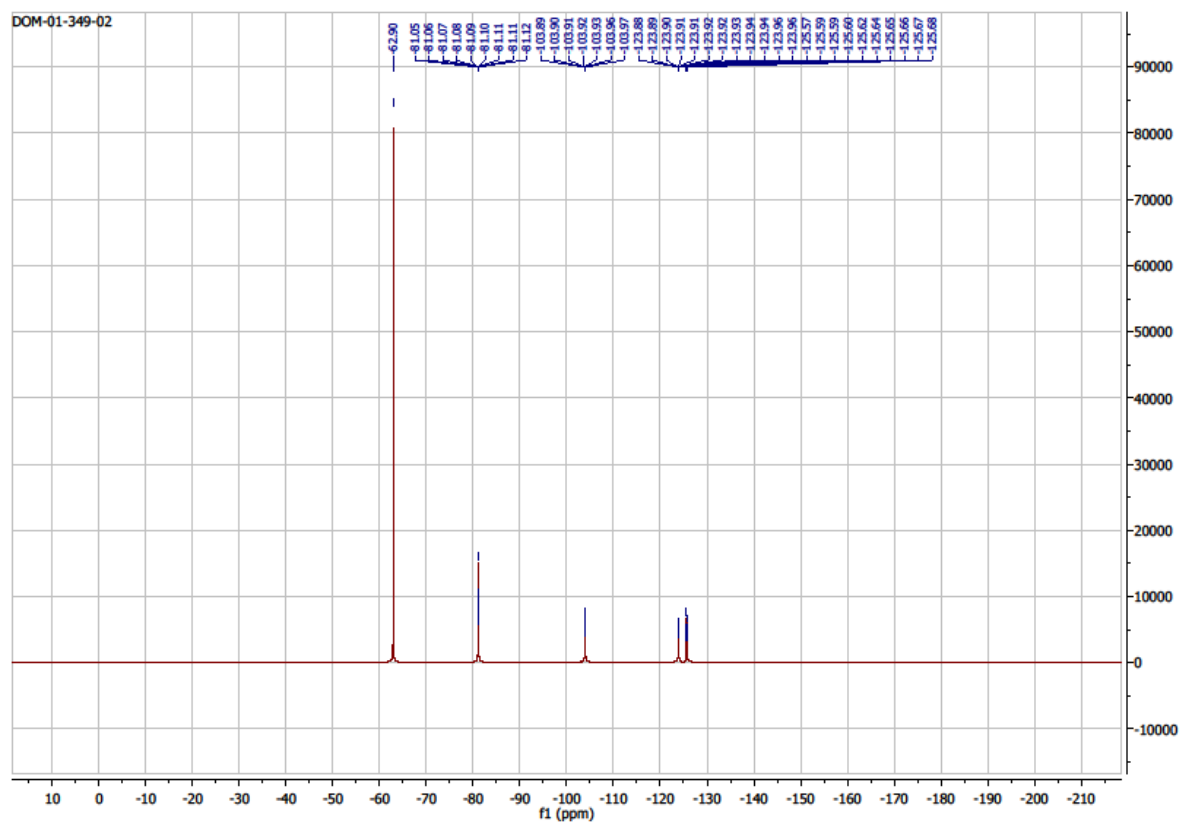
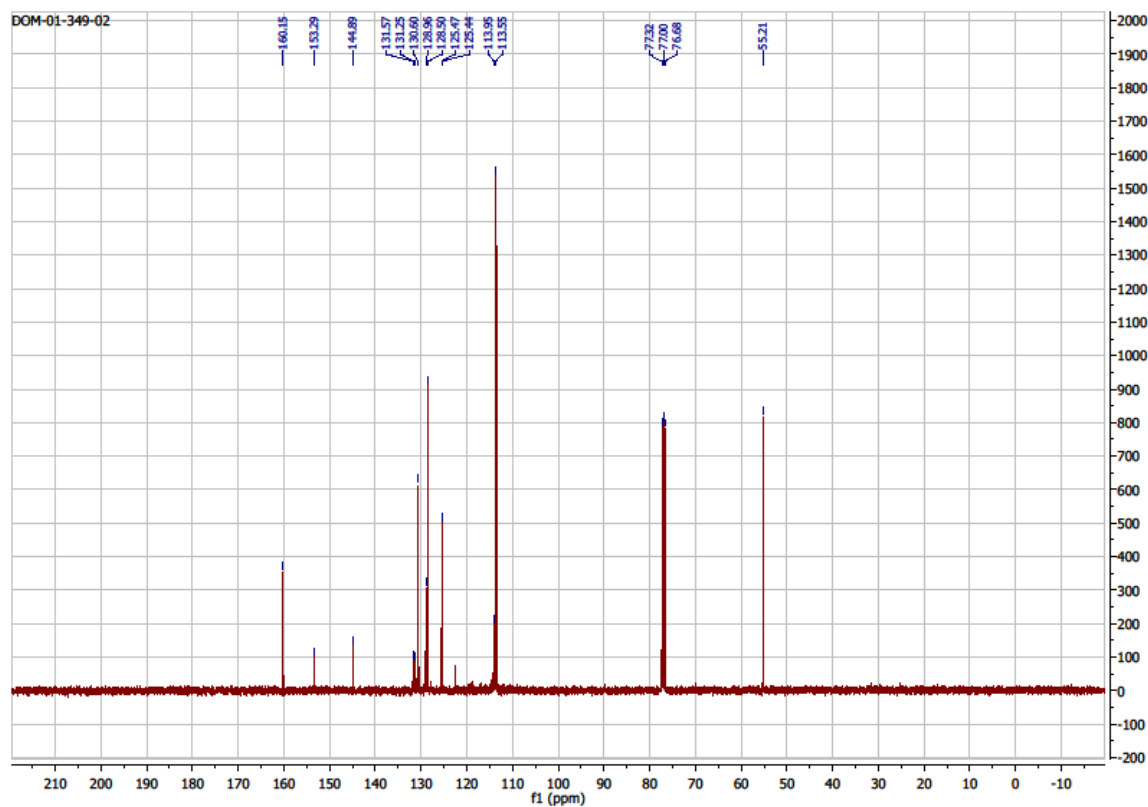
(Z)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzene (3)



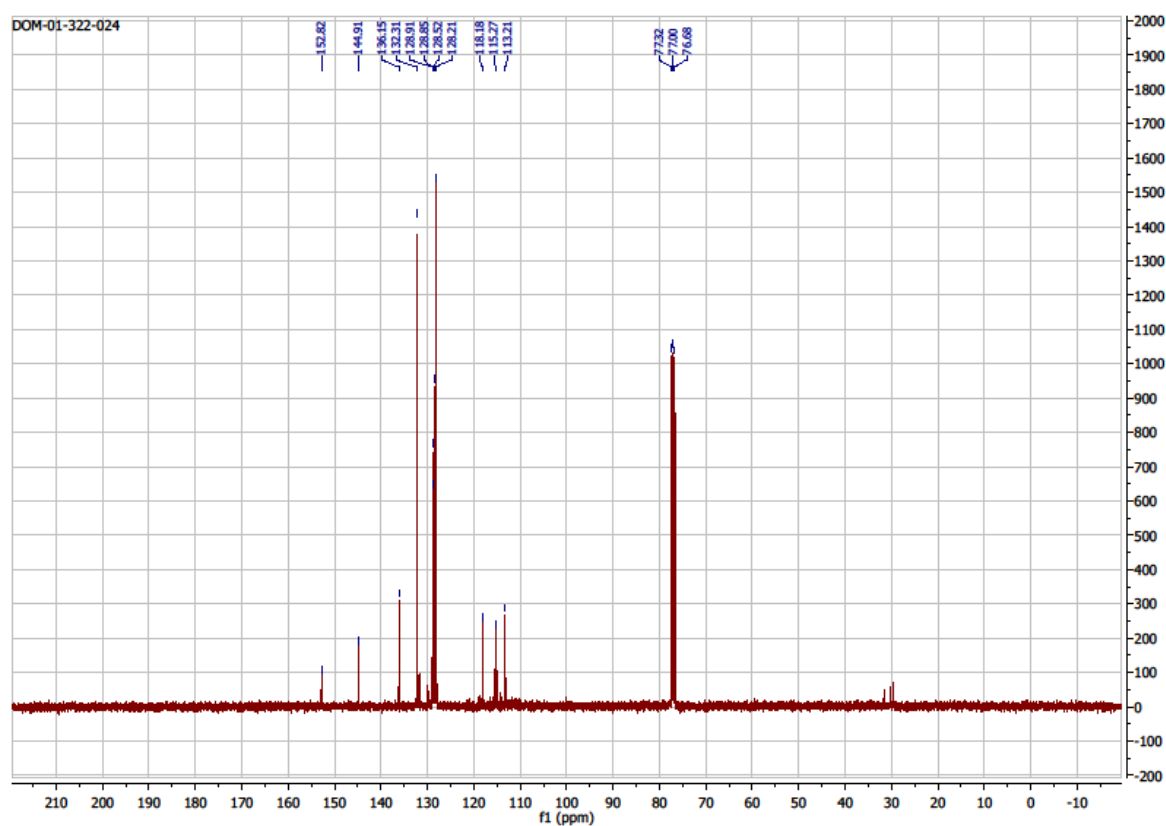
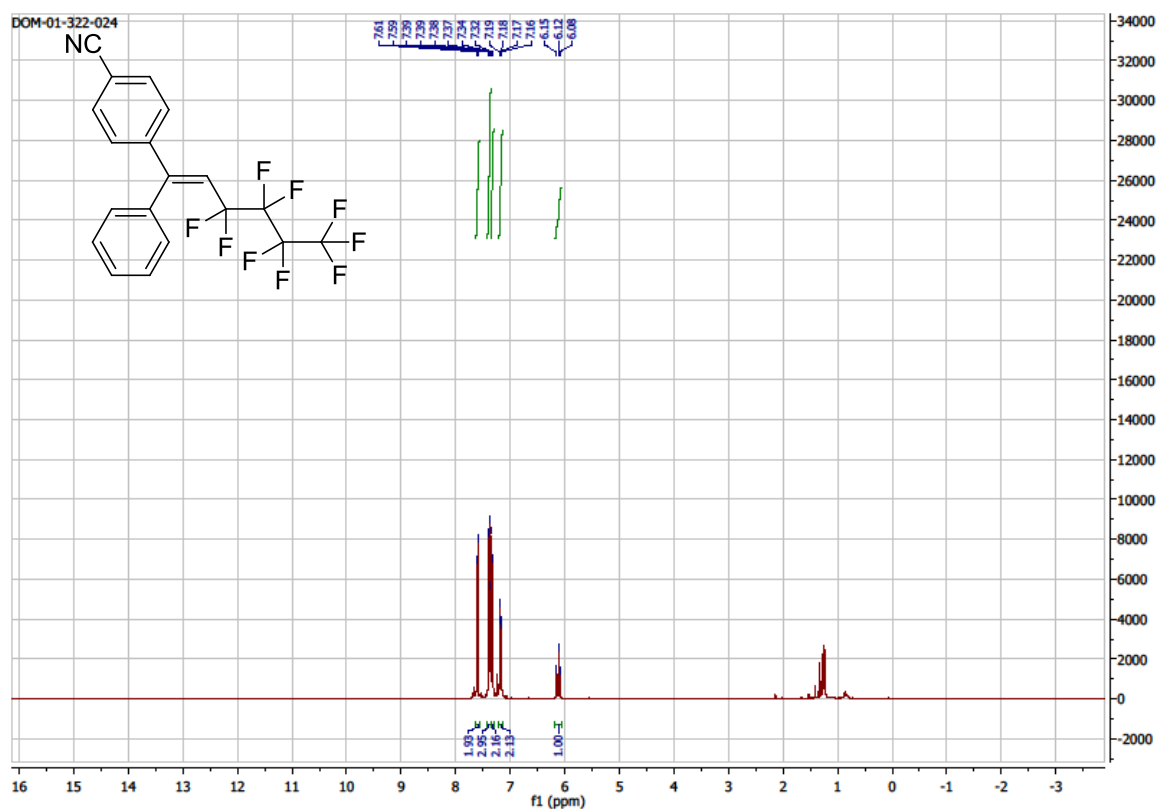


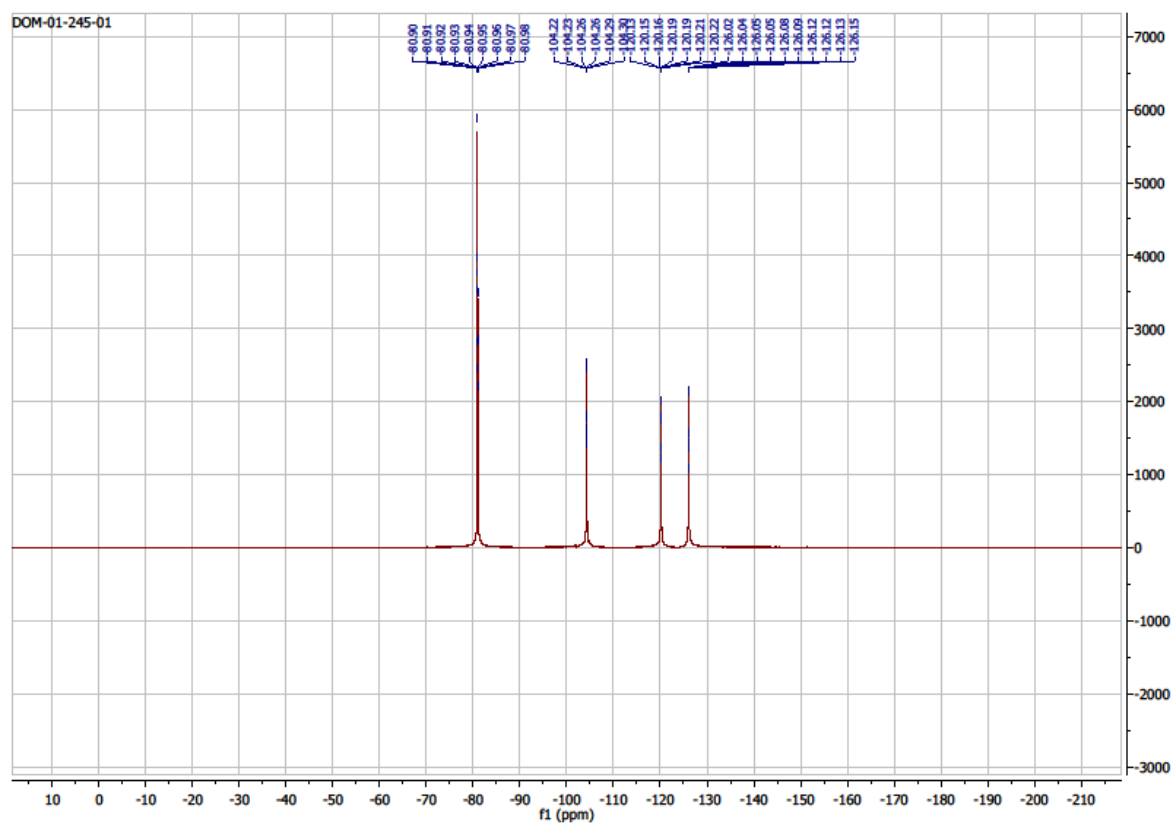
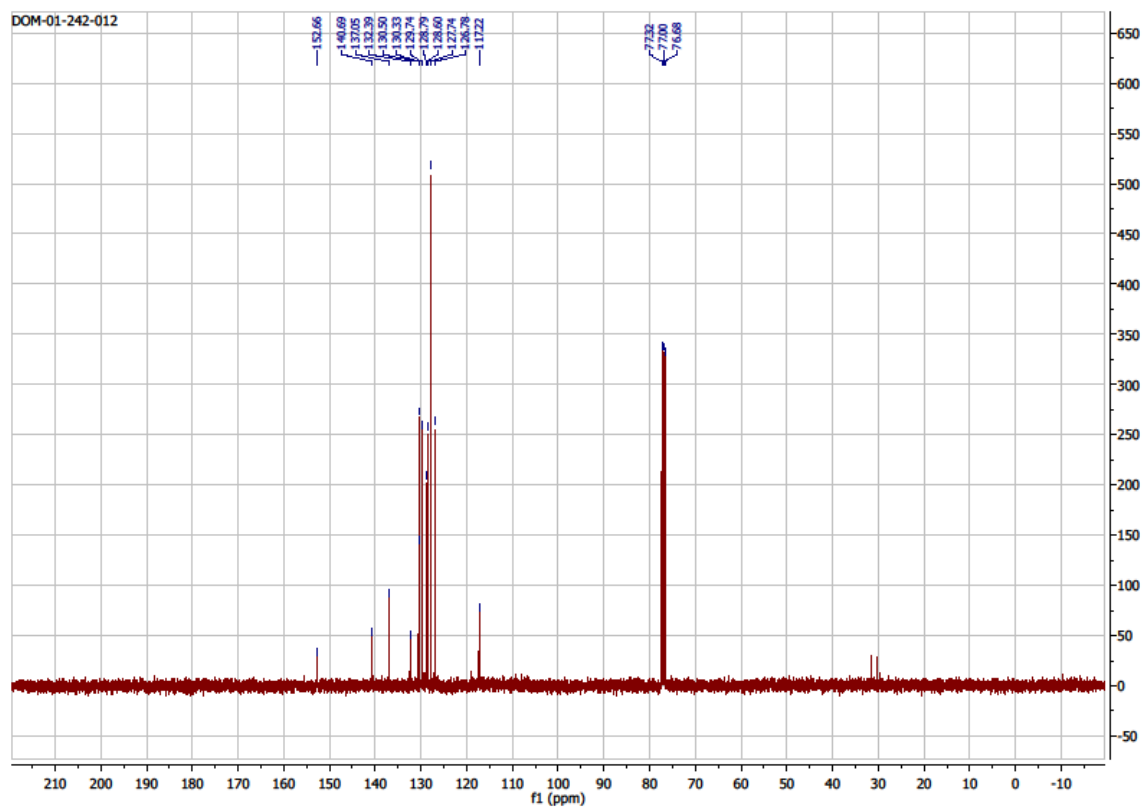
(Z)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(trifluoromethyl)phenyl)hex-1-en-1-yl)benzene (4)



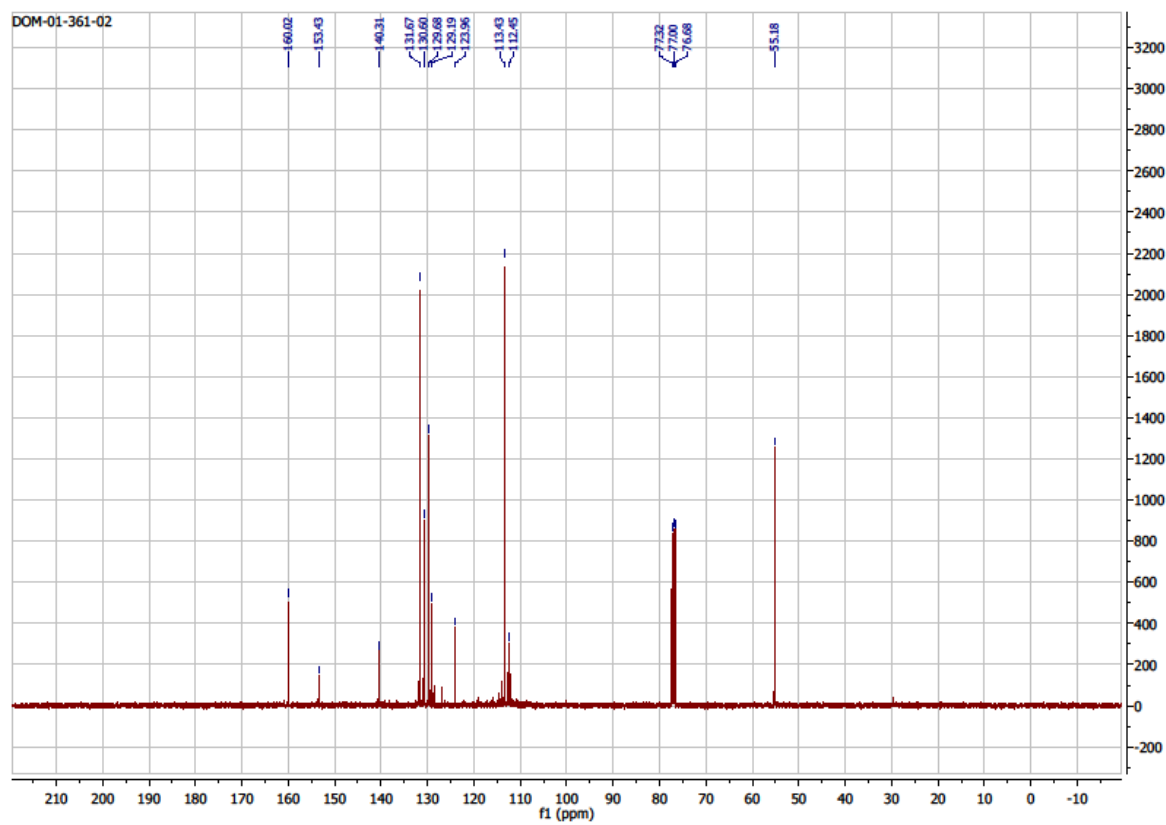
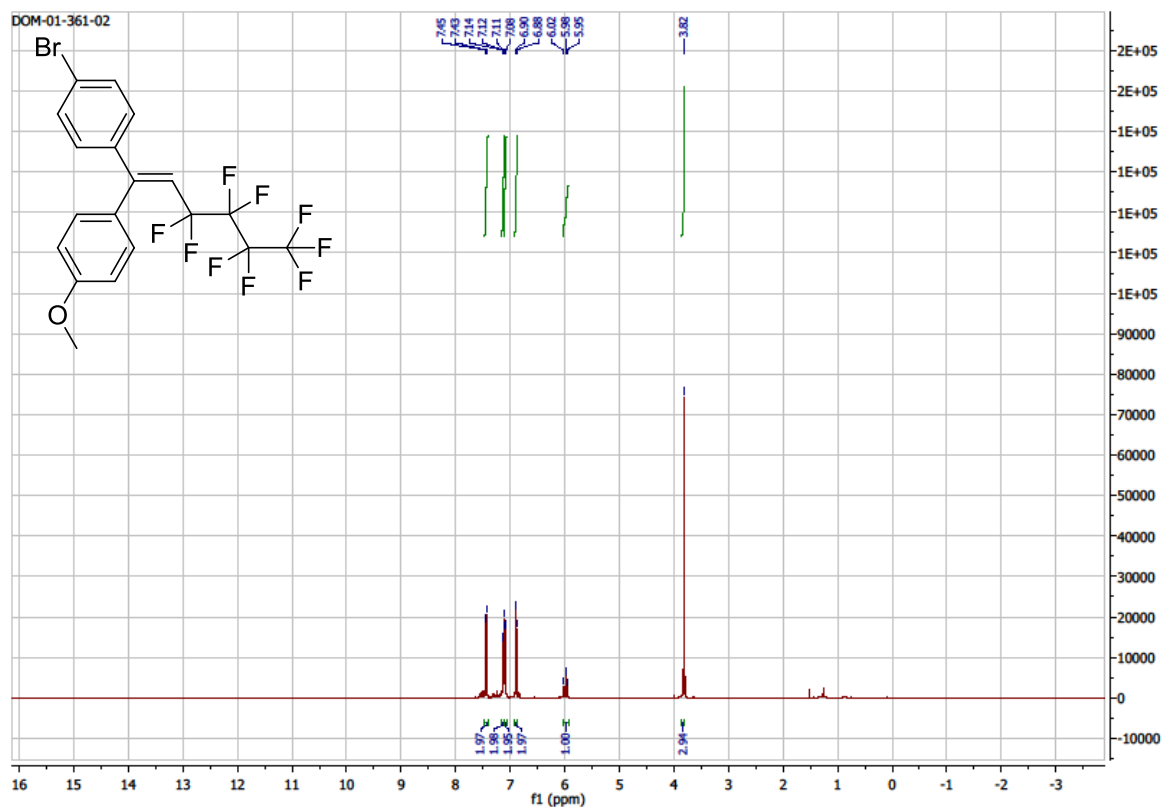


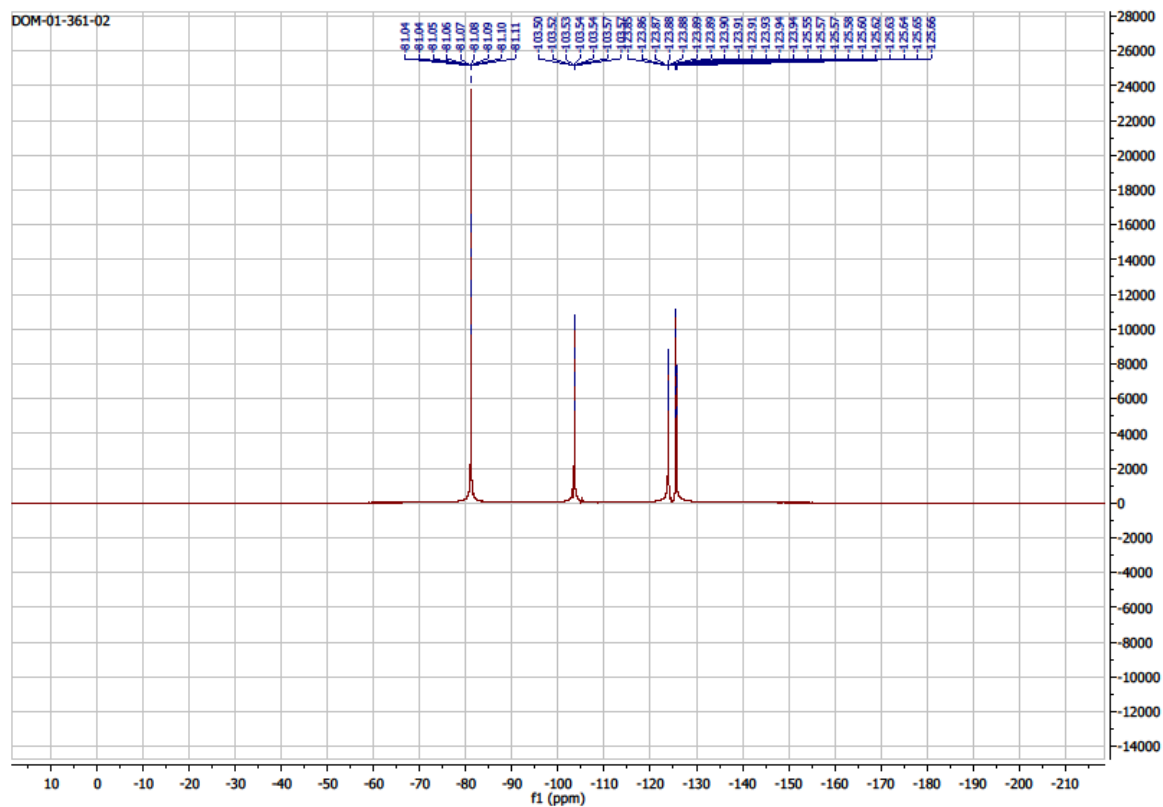
(*E*)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzonitrile (5)

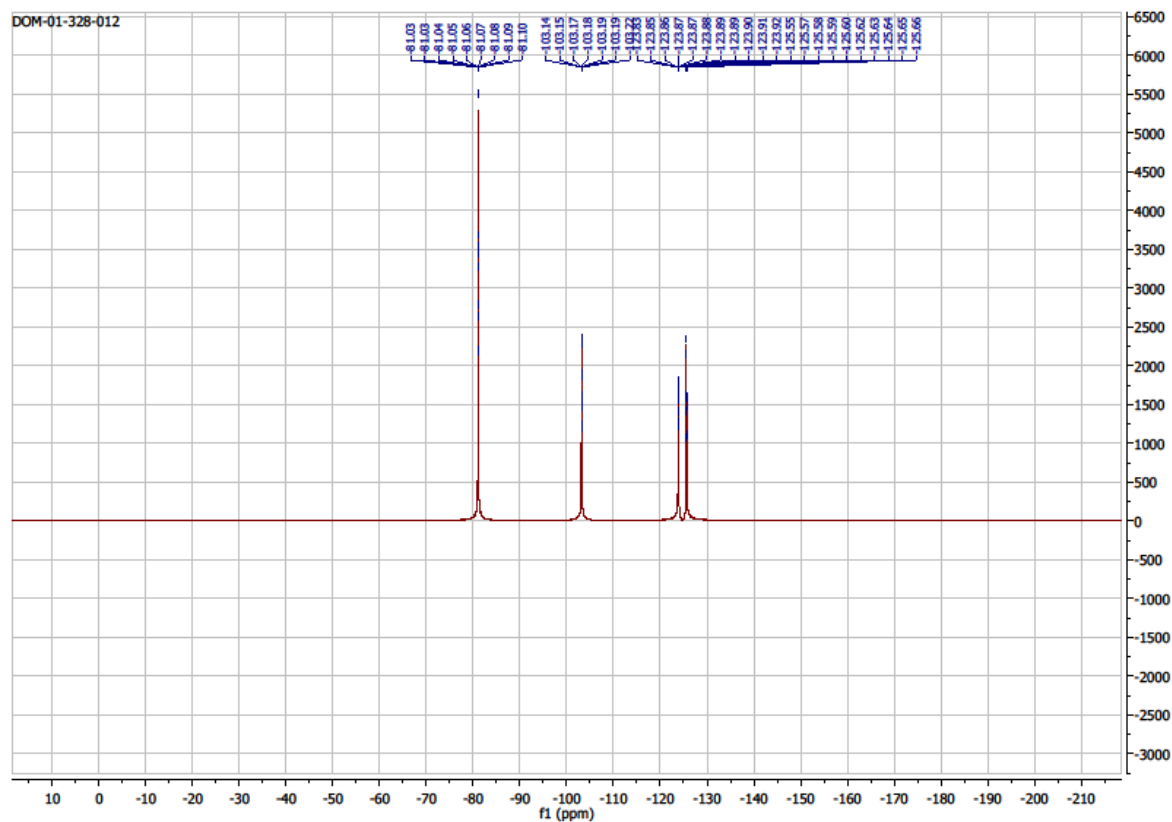
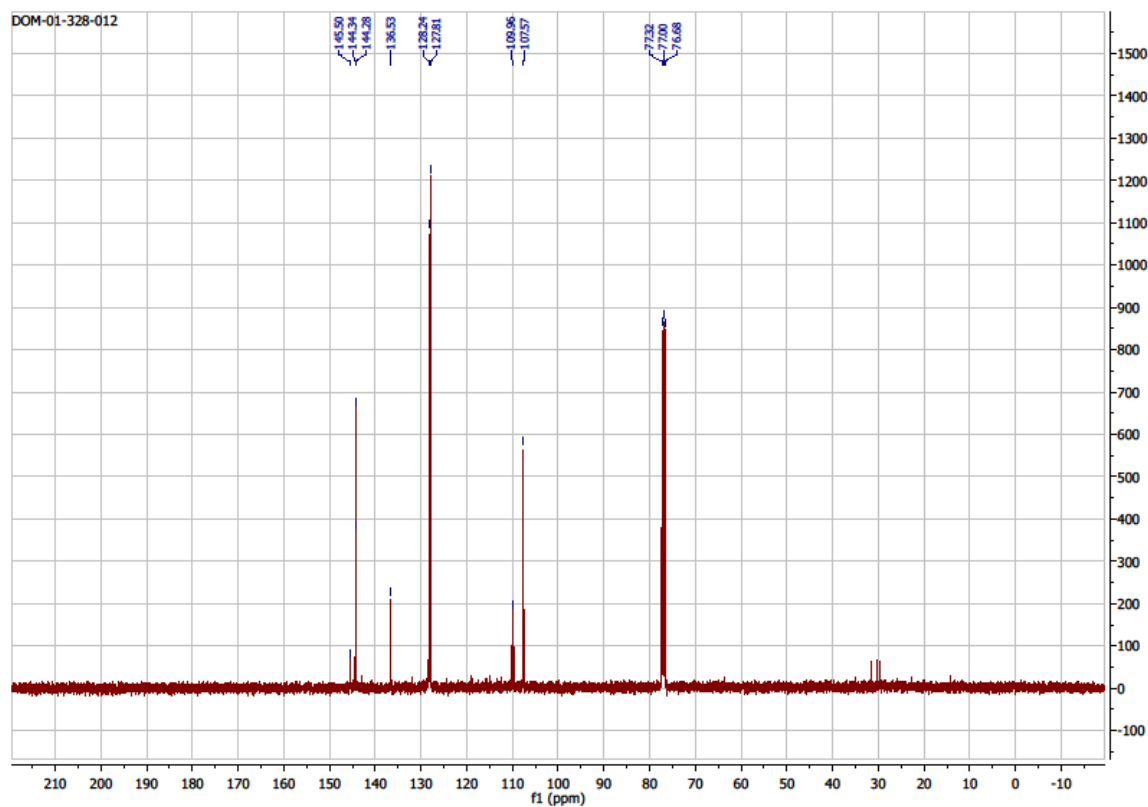




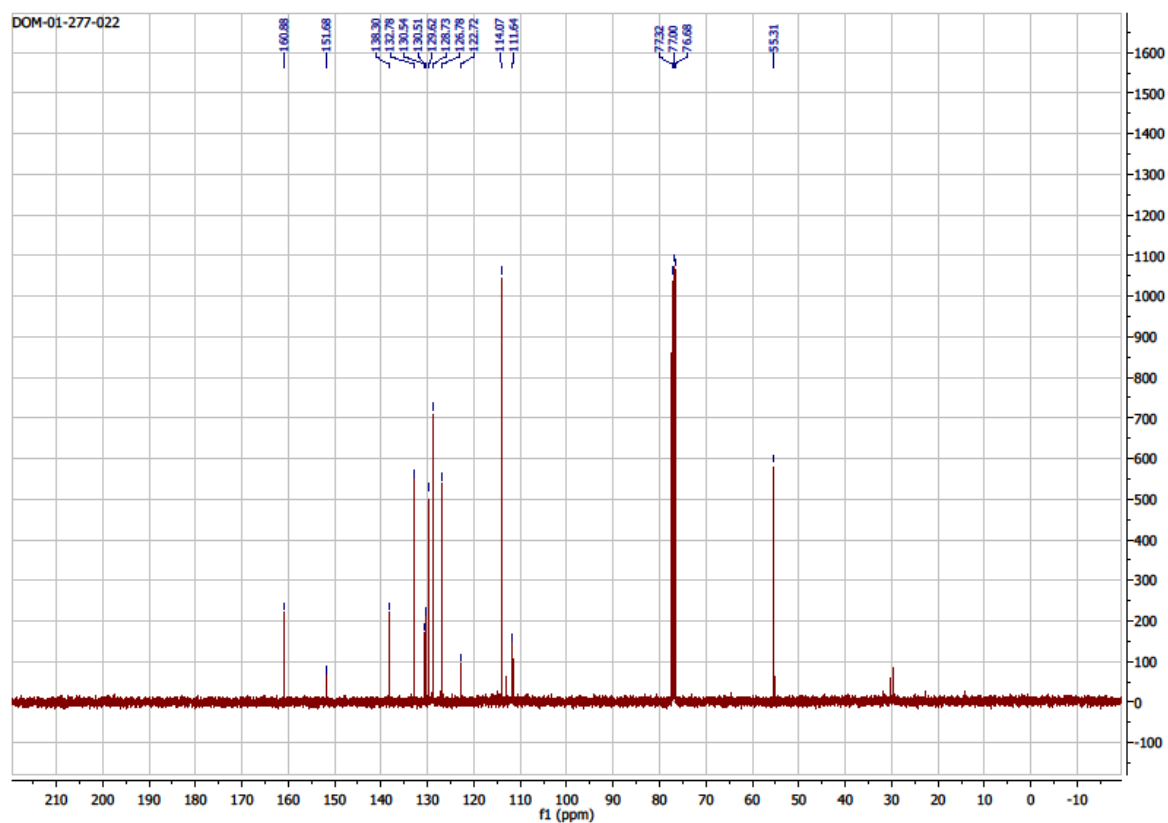
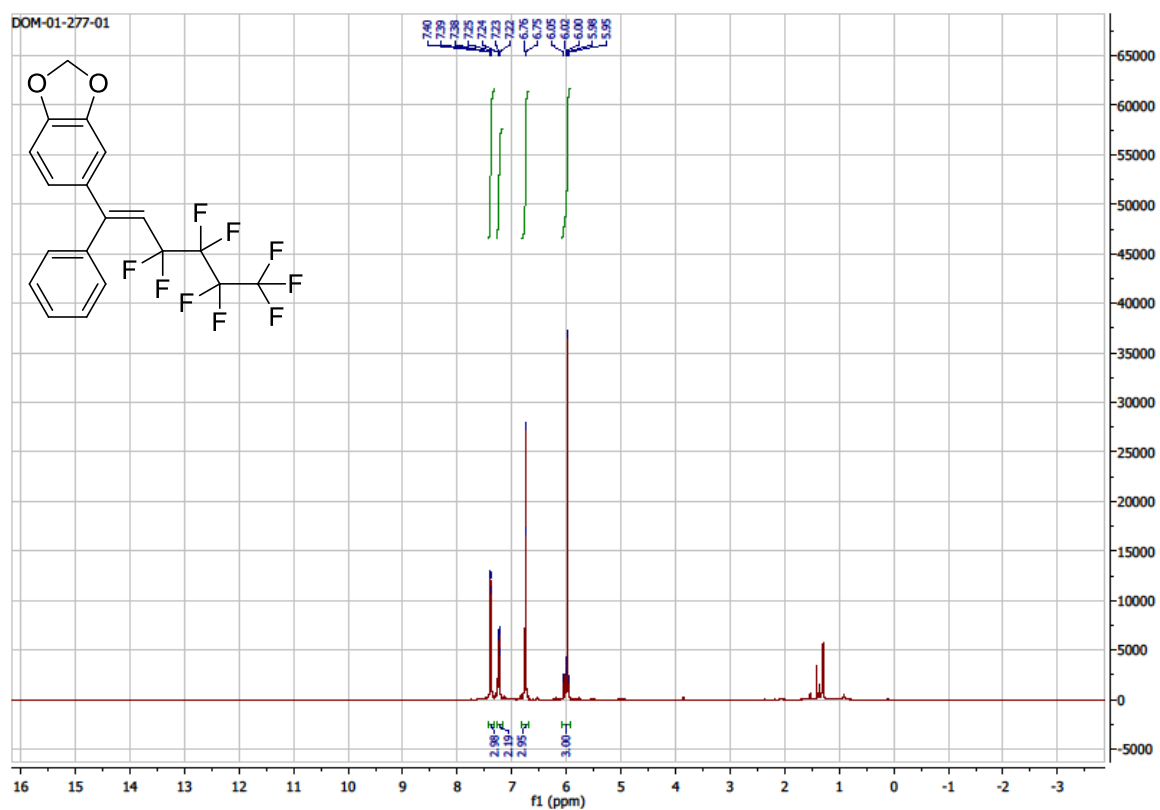
(E)-1-bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene (7)

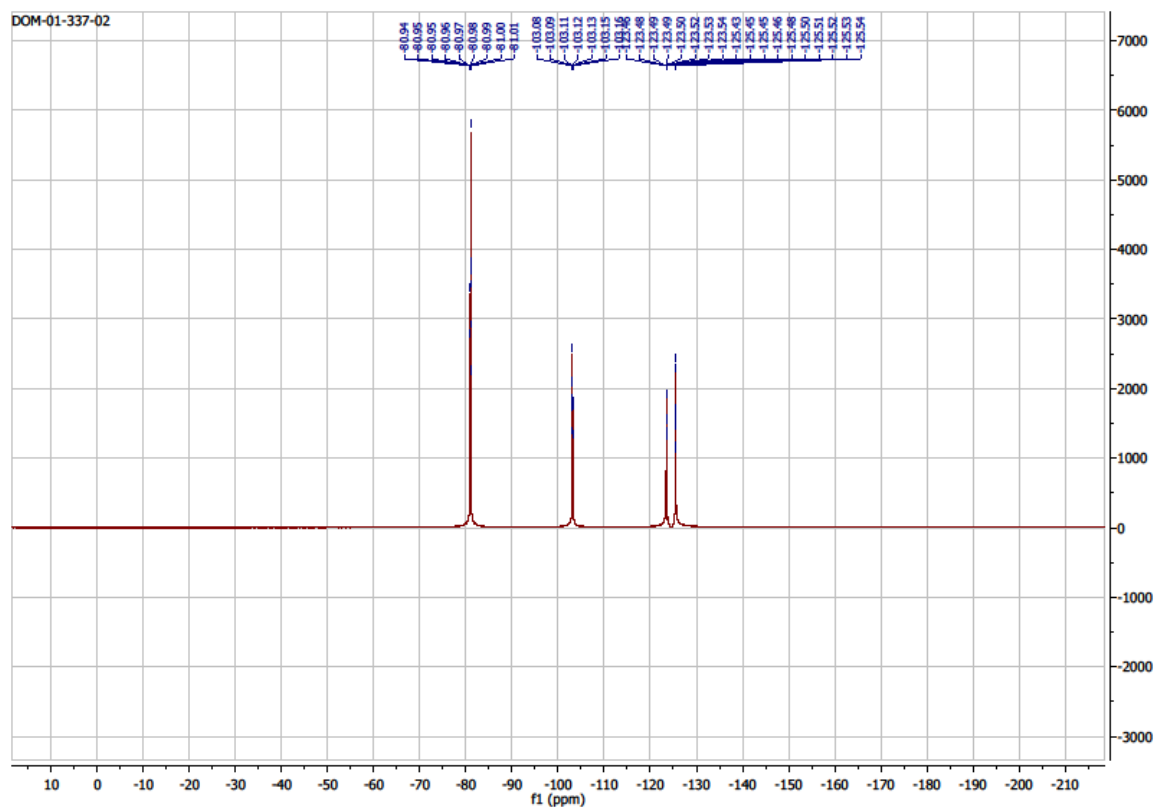
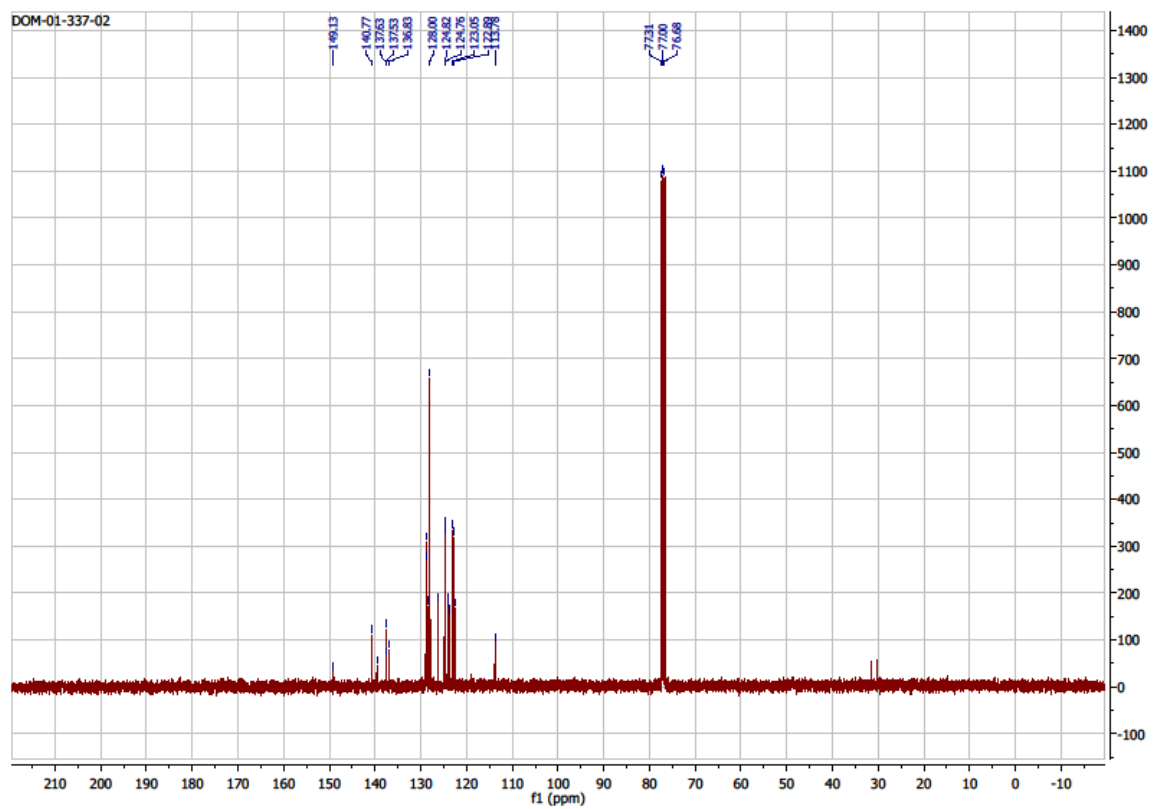




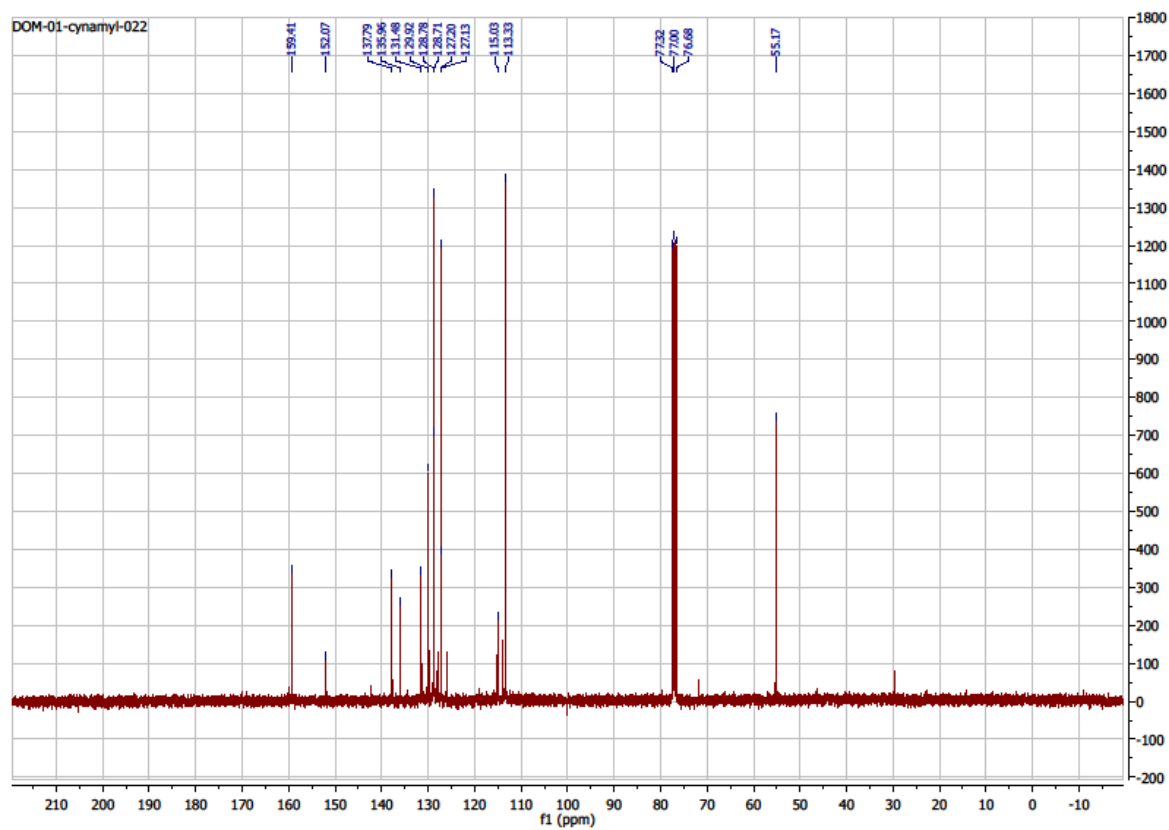
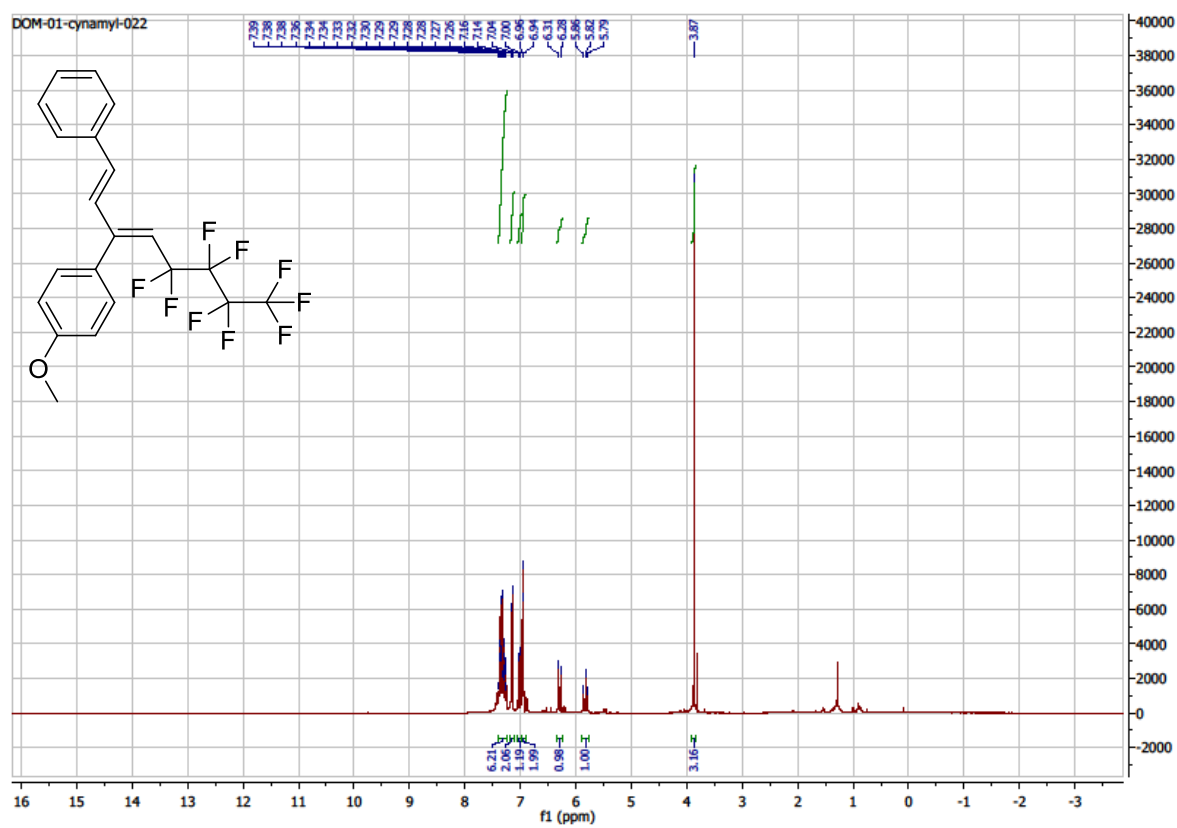


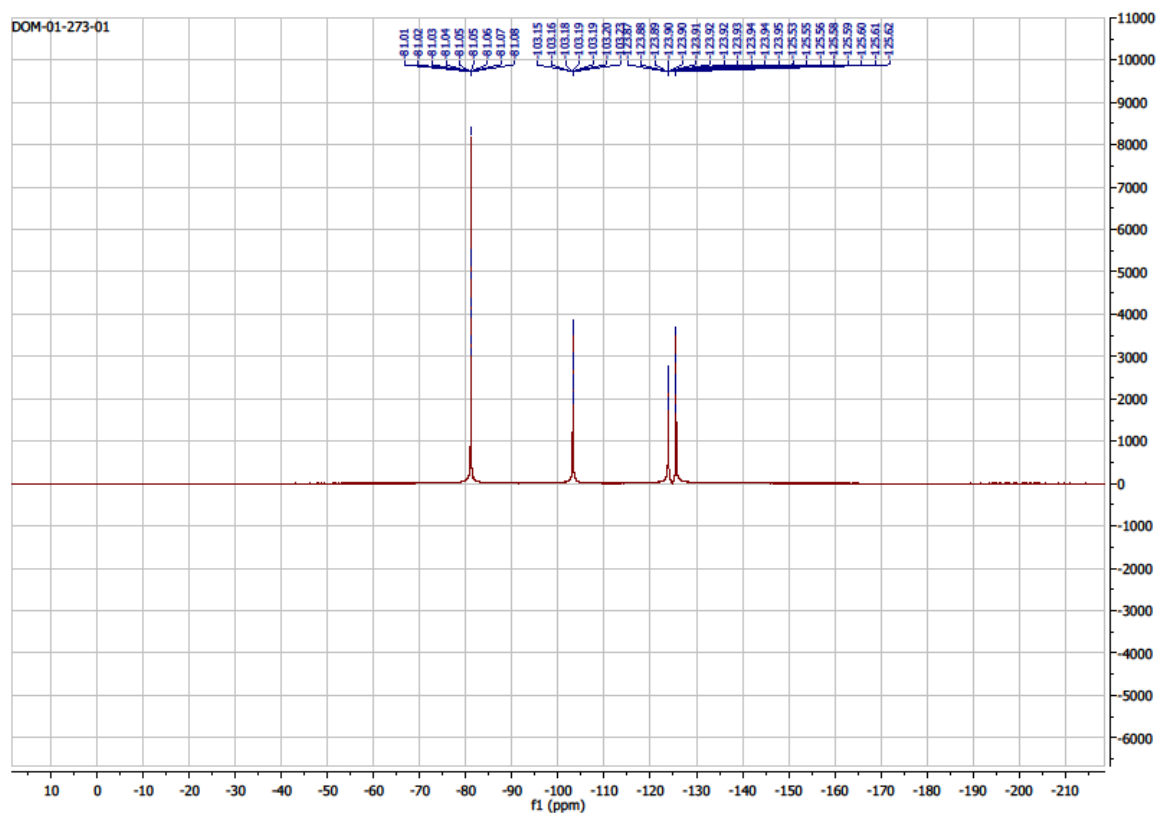
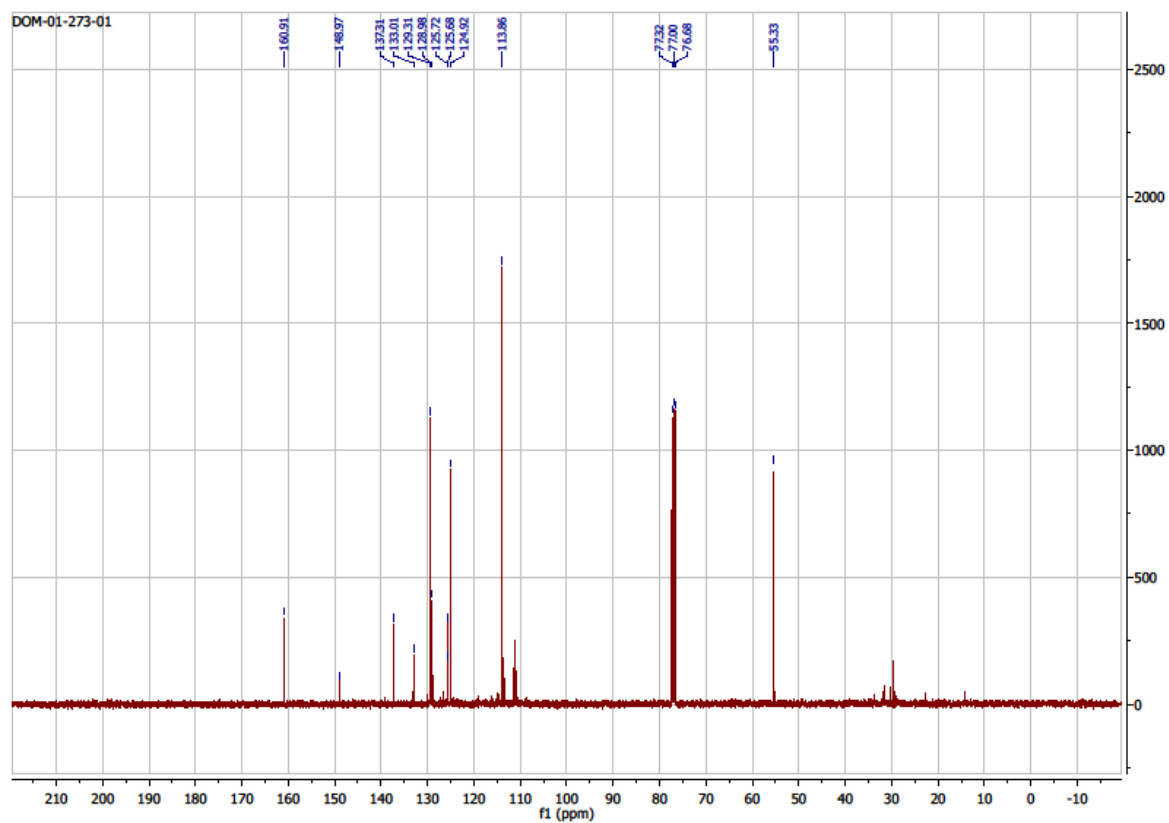
(E)-5-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)benzo[d][1,3]dioxole (9)



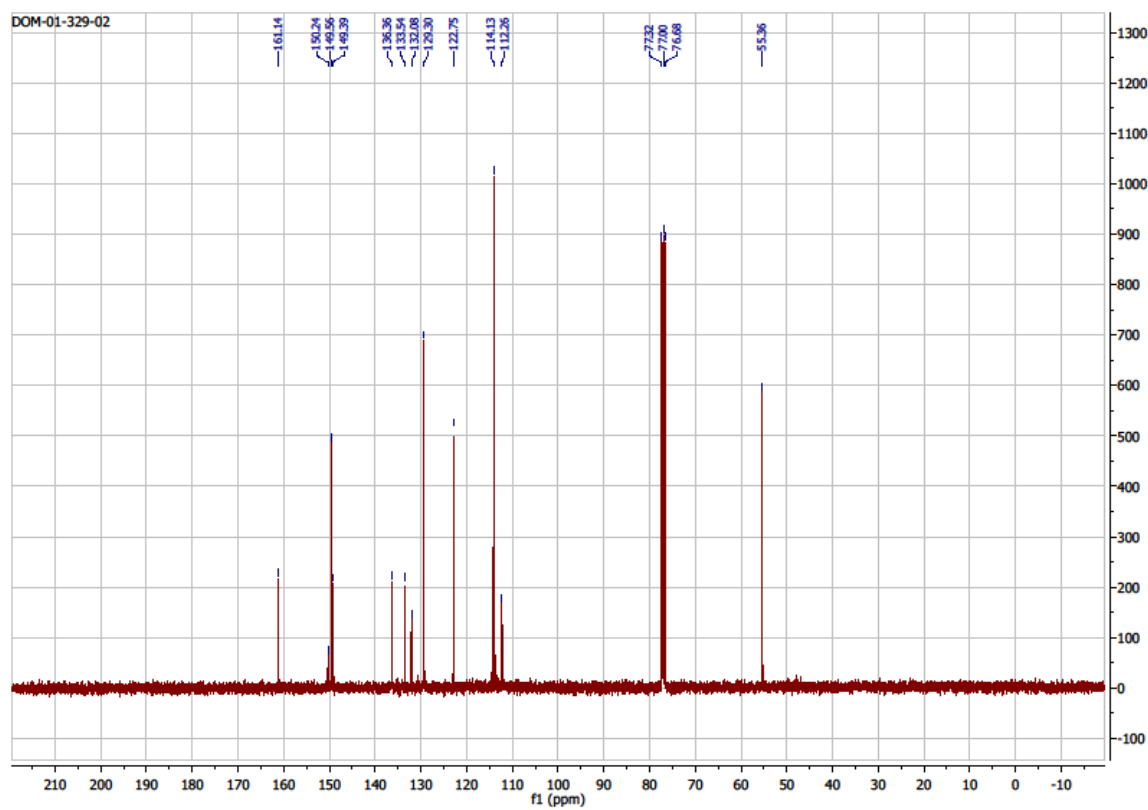
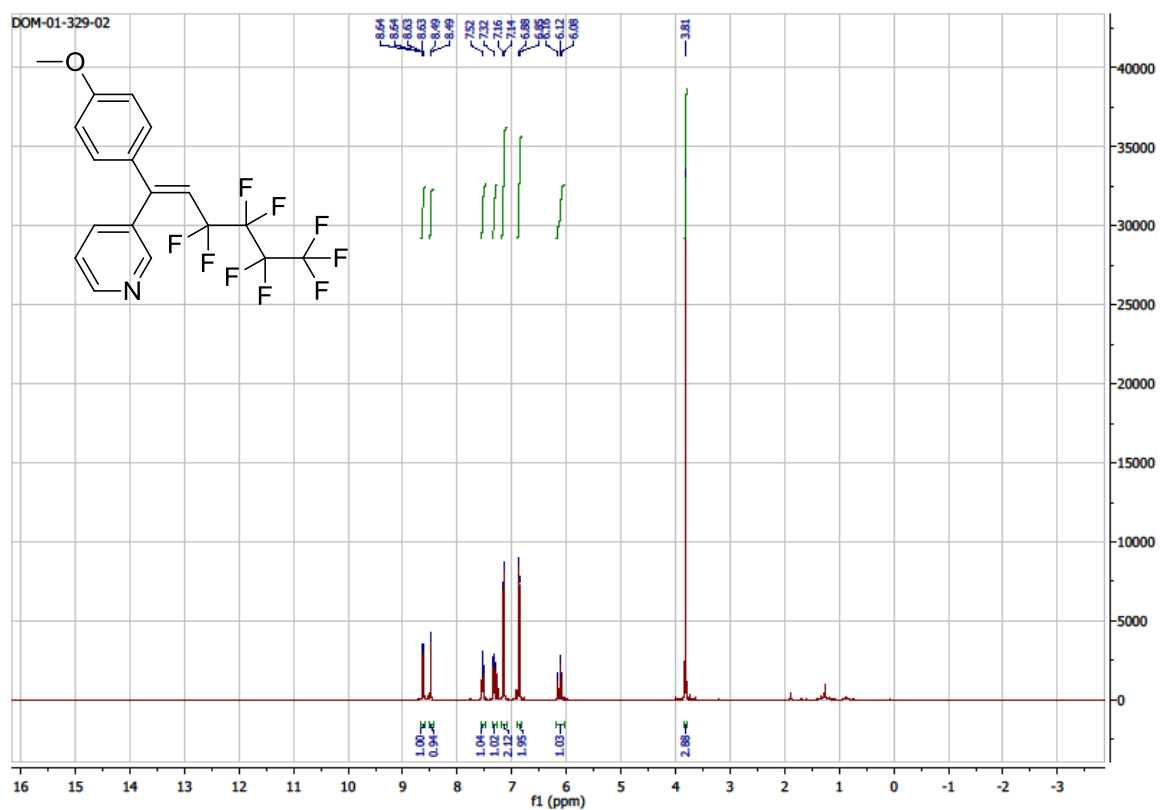


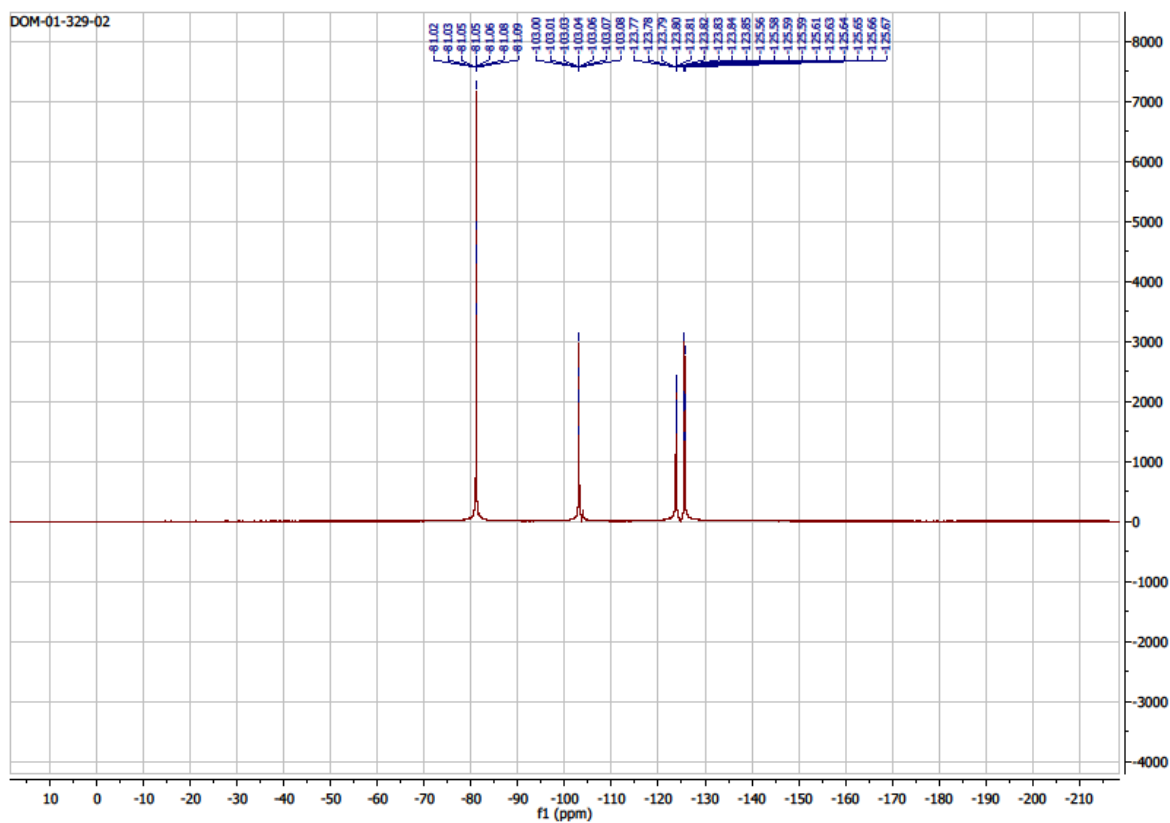
1-methoxy-4-((1E,3Z)-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenylocta-1,3-dien-3-yl)benzene (11)



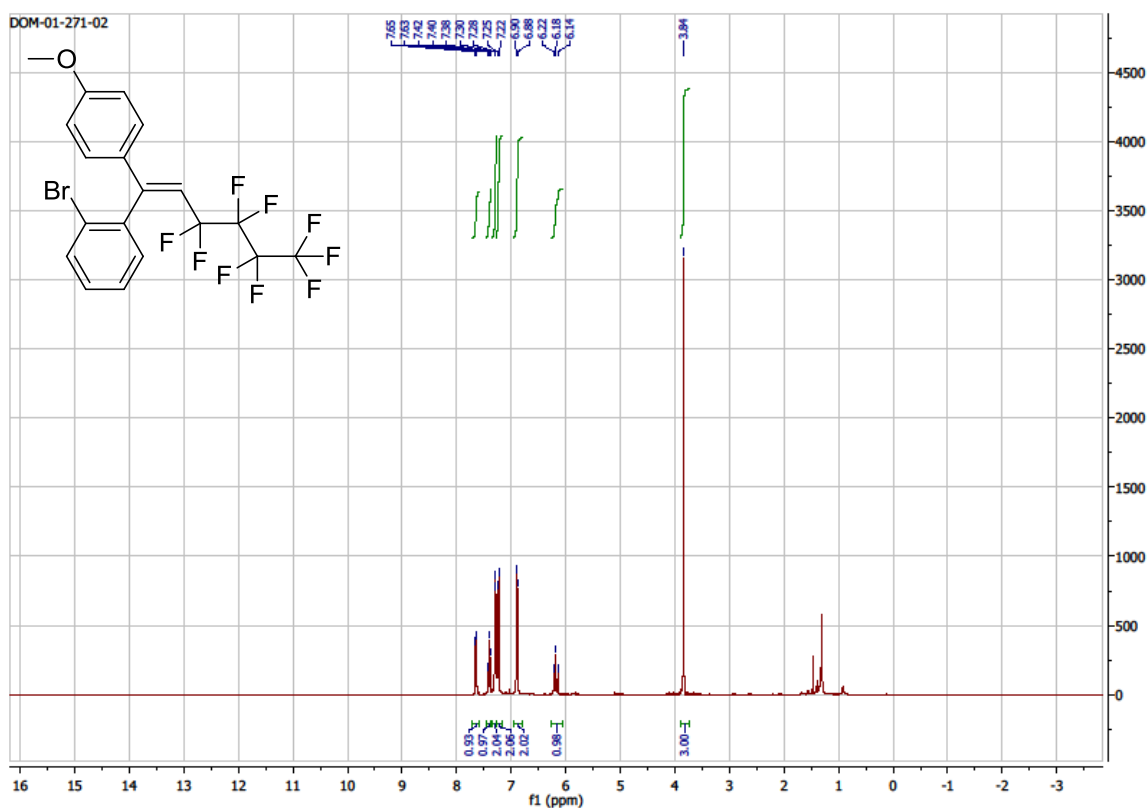


(Z)-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)pyridine (13)

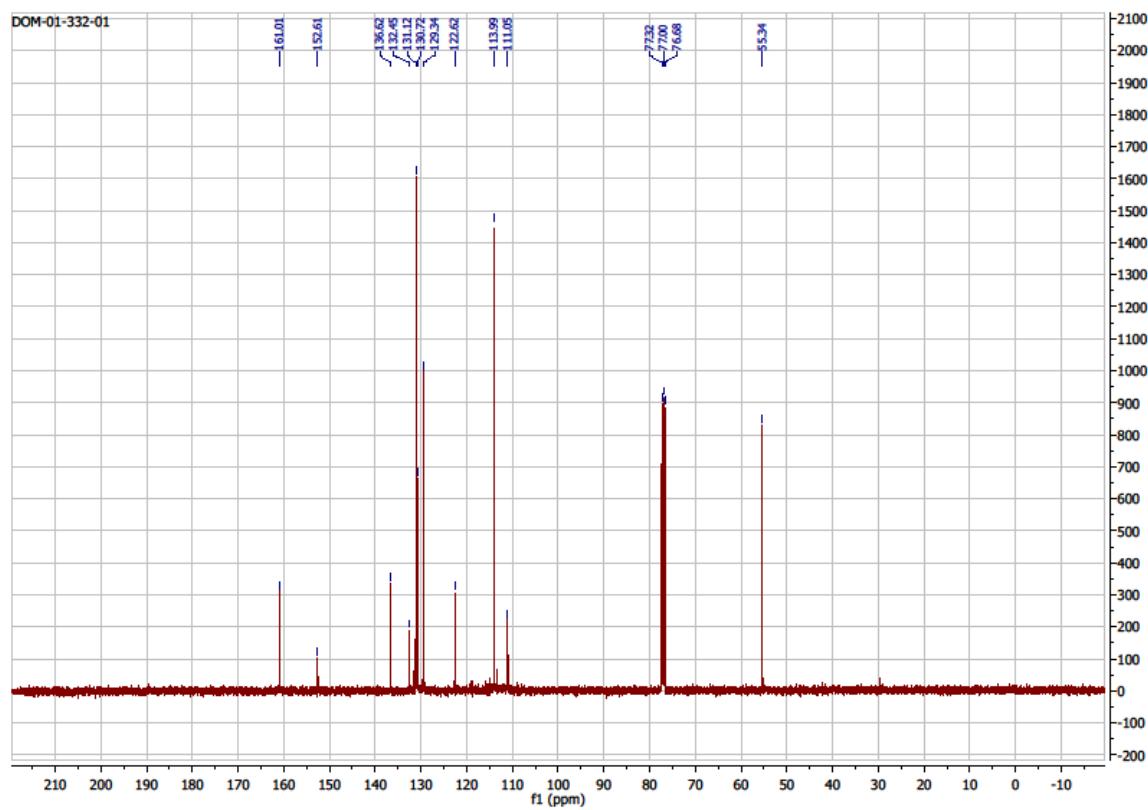
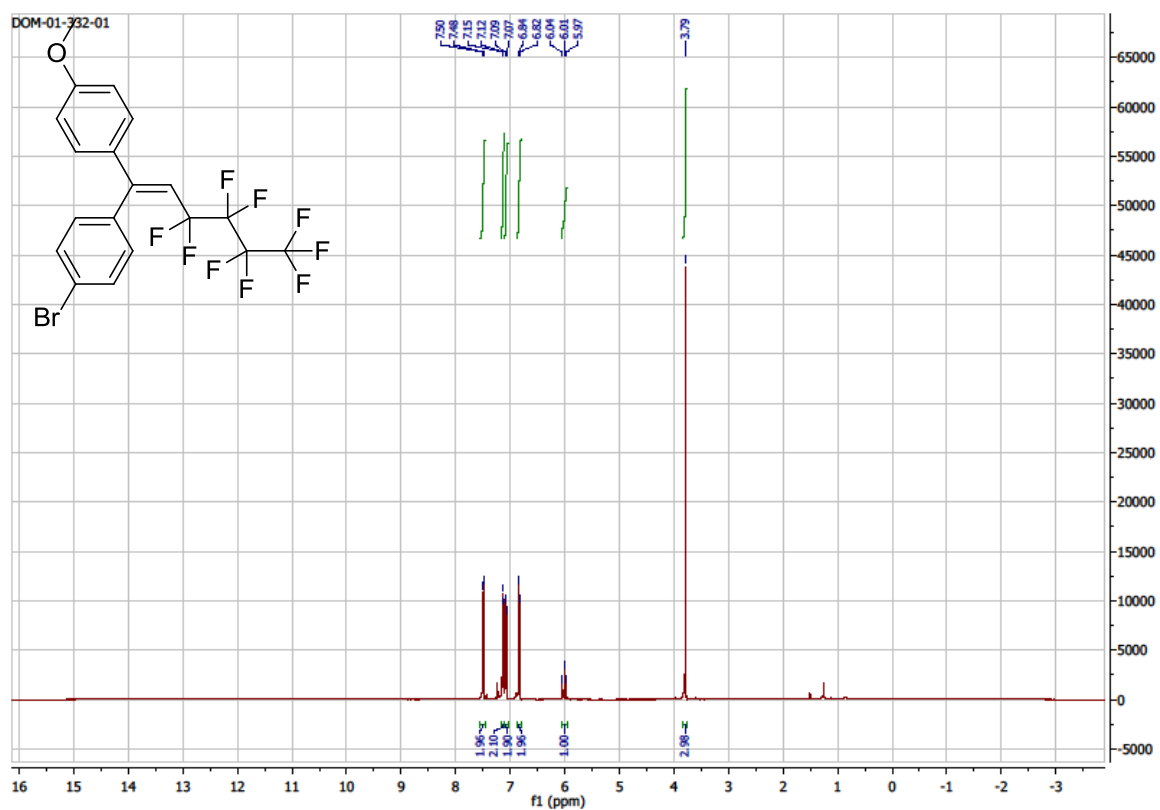


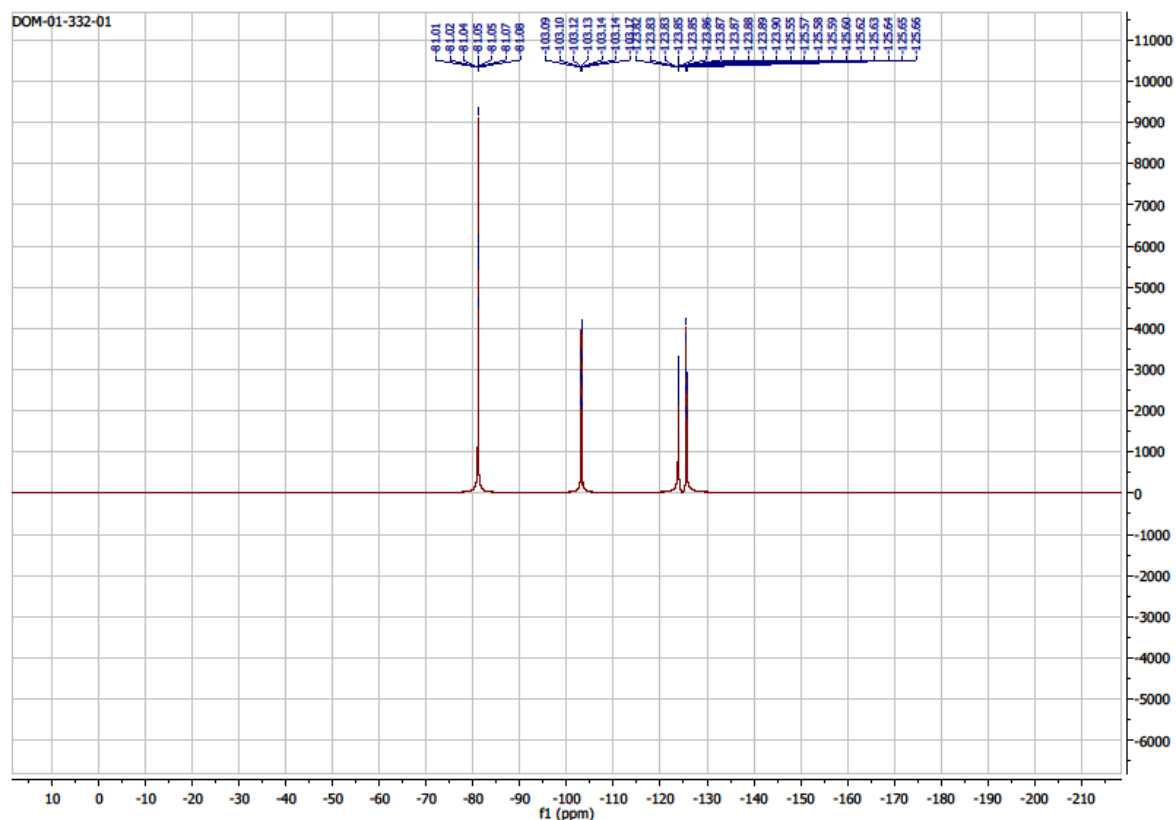


(Z)-1-bromo-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene (14)

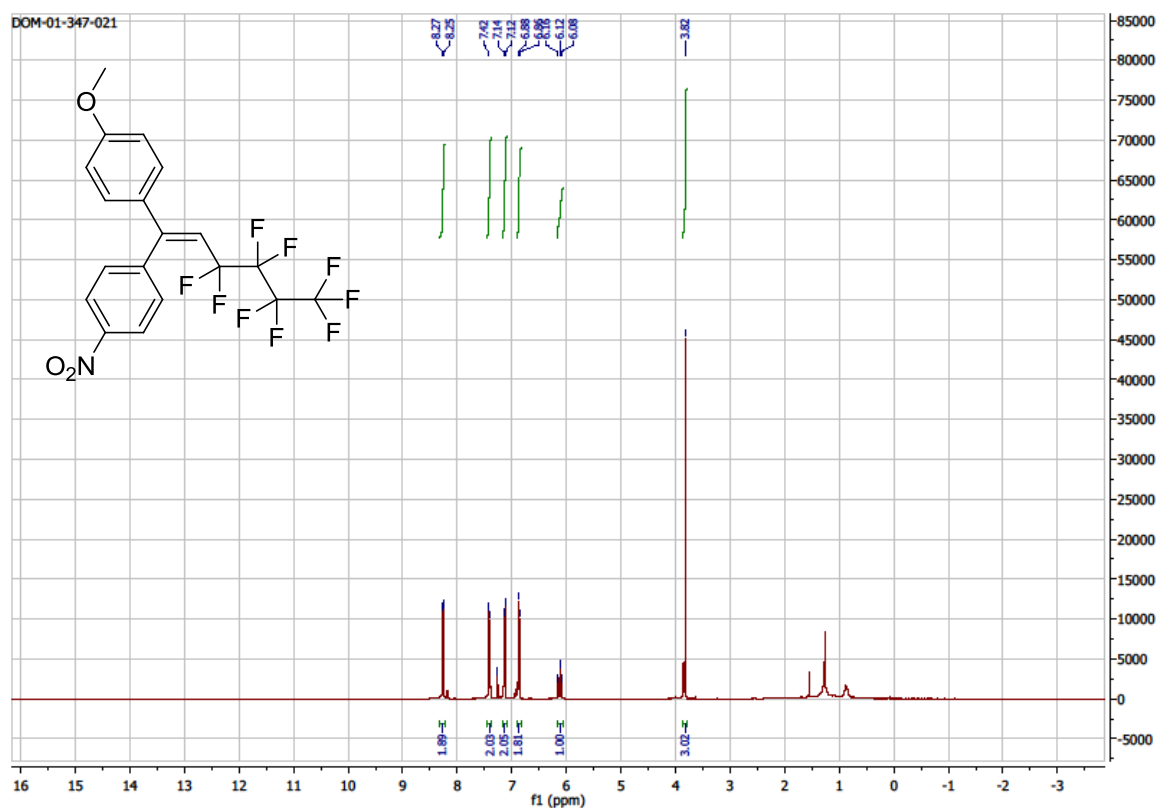


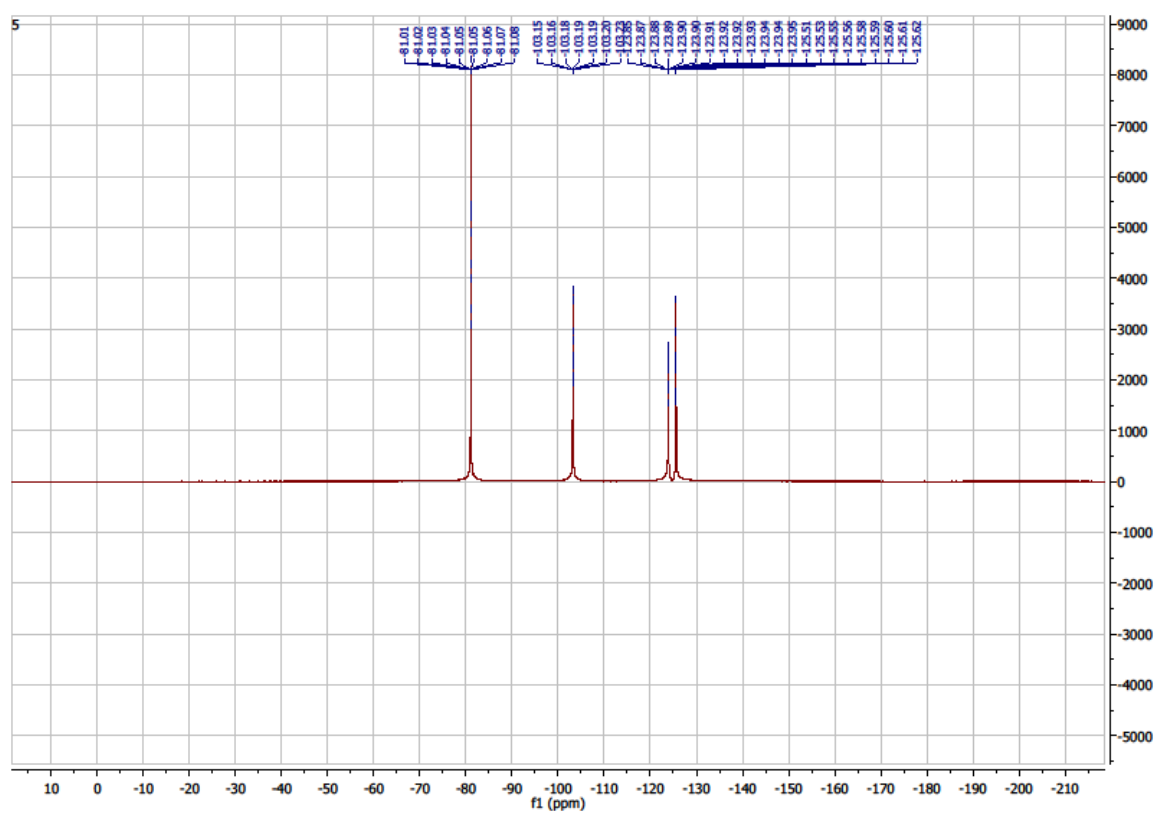
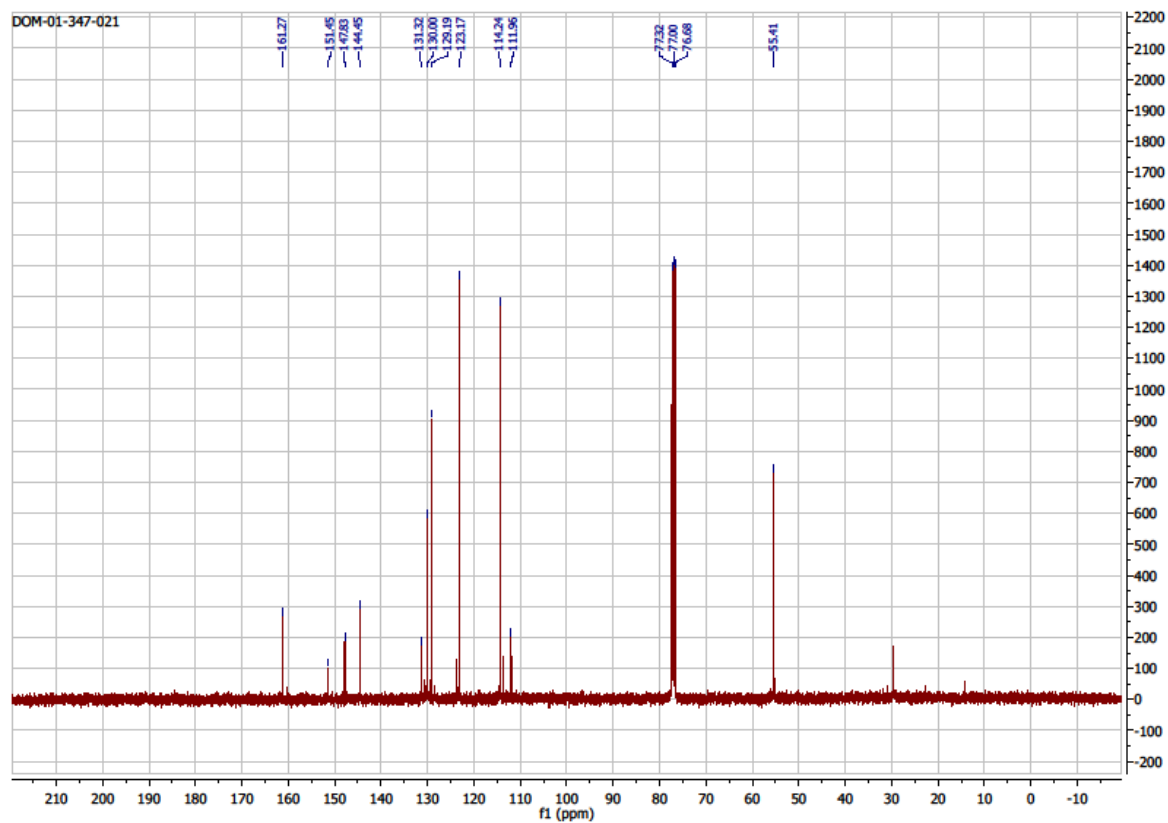
(Z)-1-bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene (15)



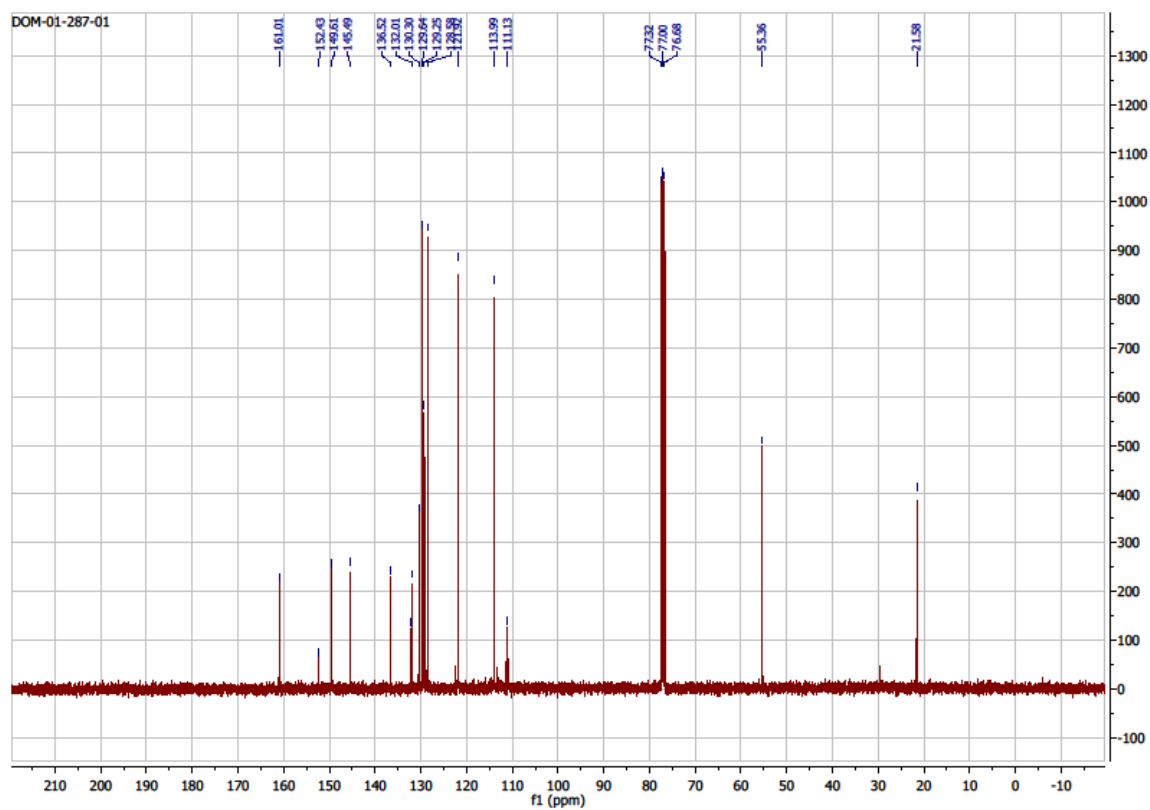
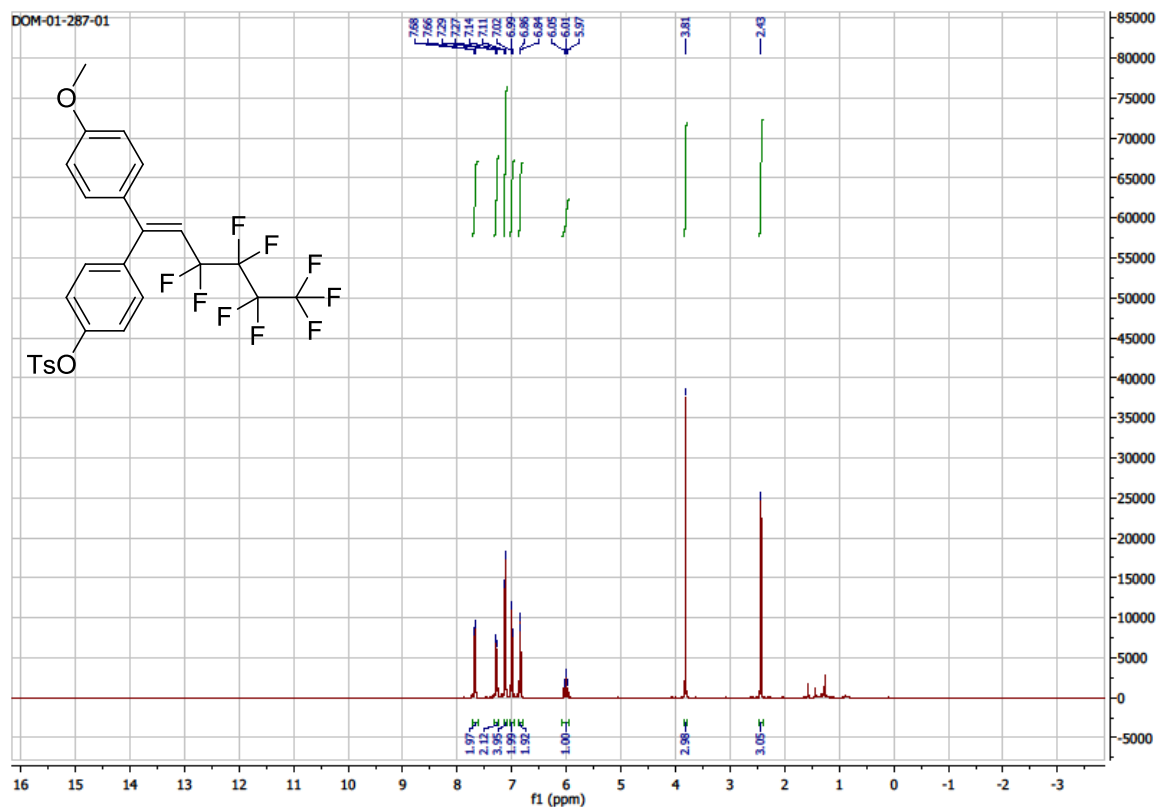


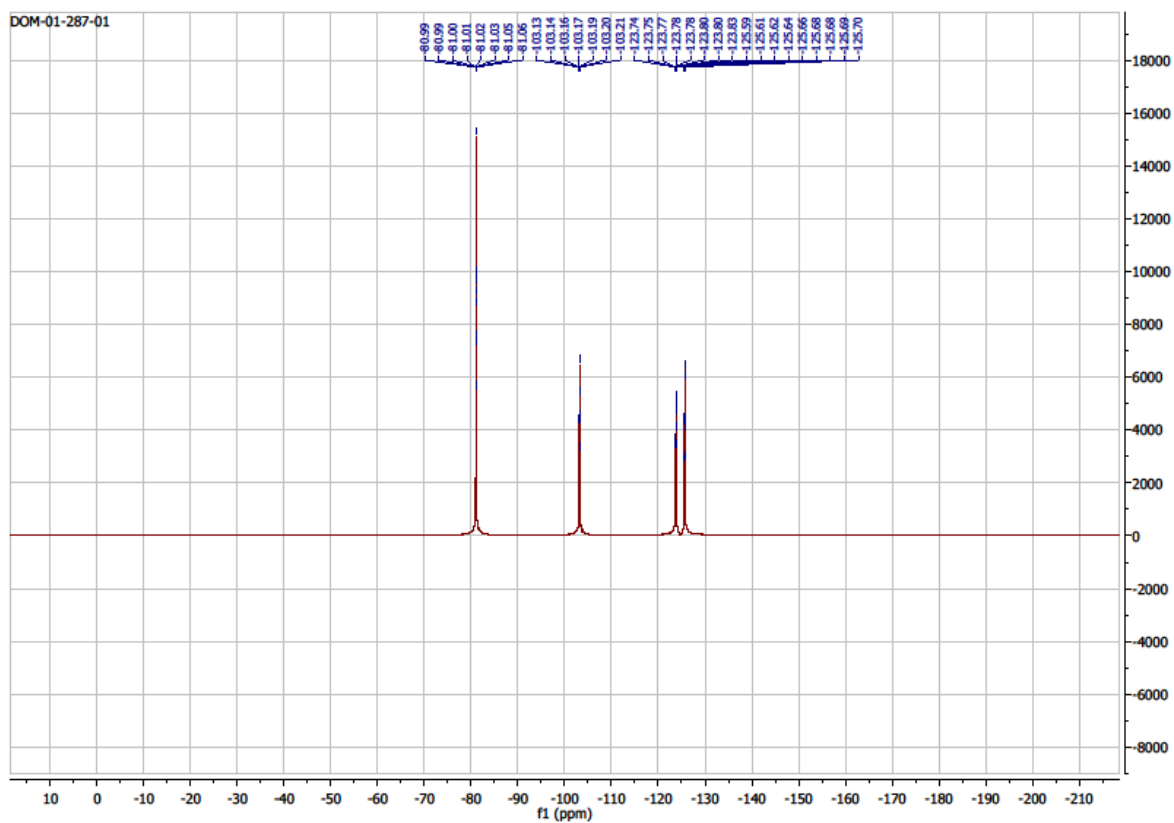
(*E*)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-nitrophenyl)hex-1-en-1-yl)benzene (16)



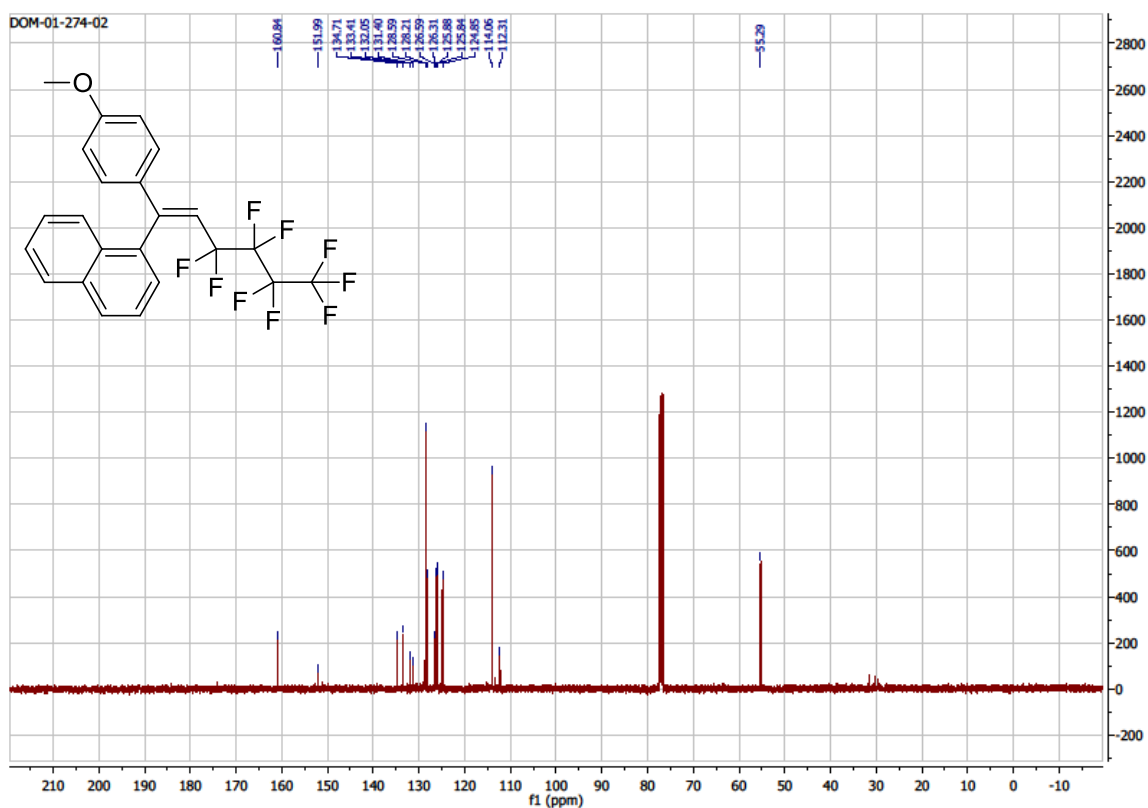


(Z)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)phenyl 4-methylbenzenesulfonate

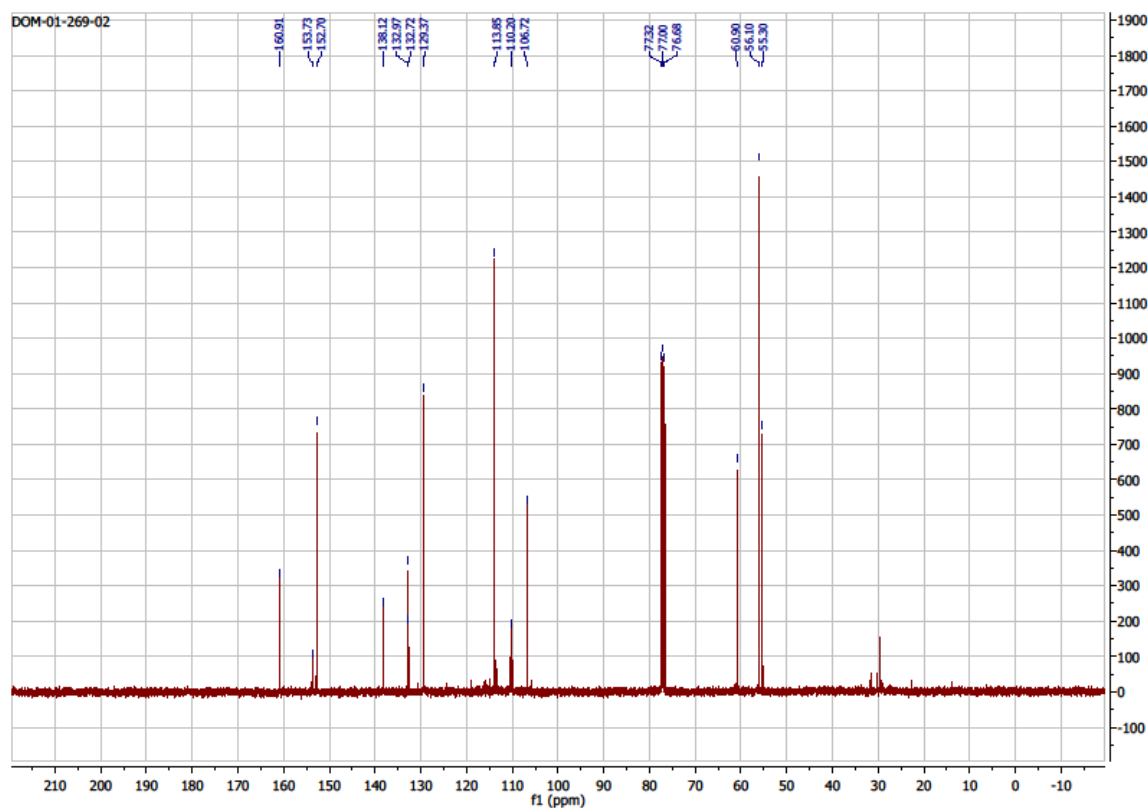
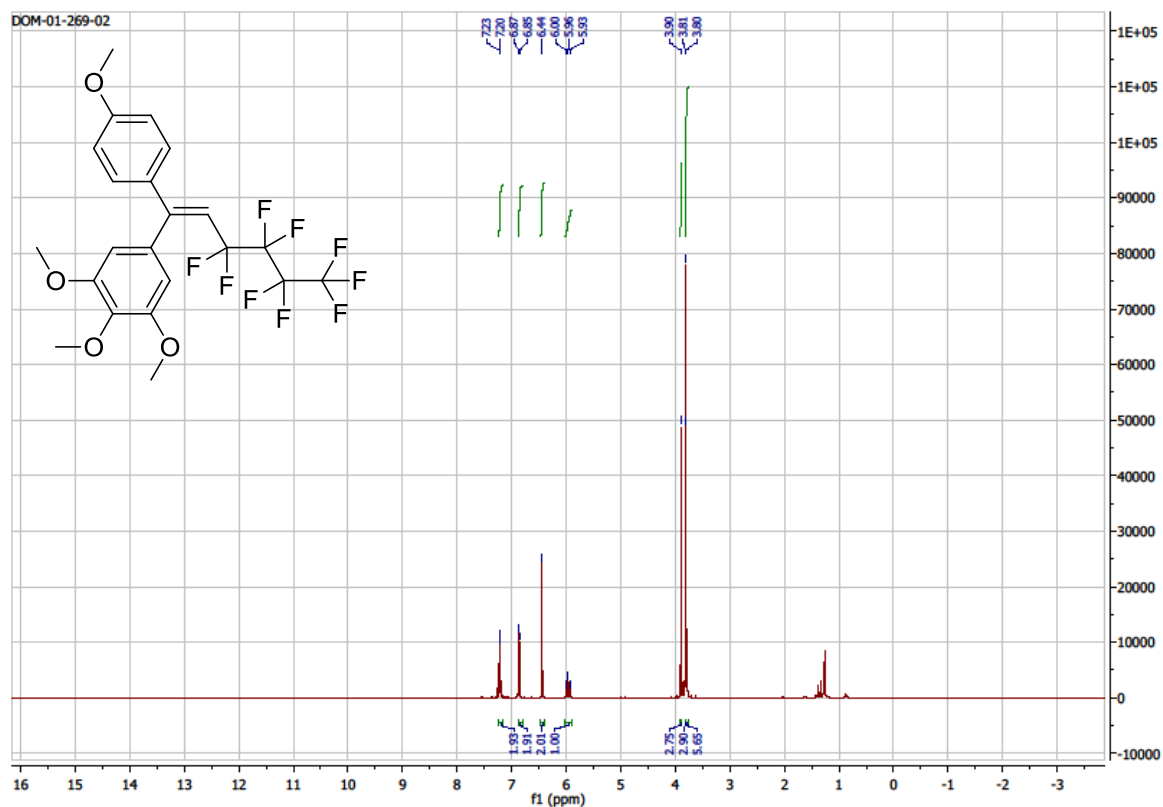


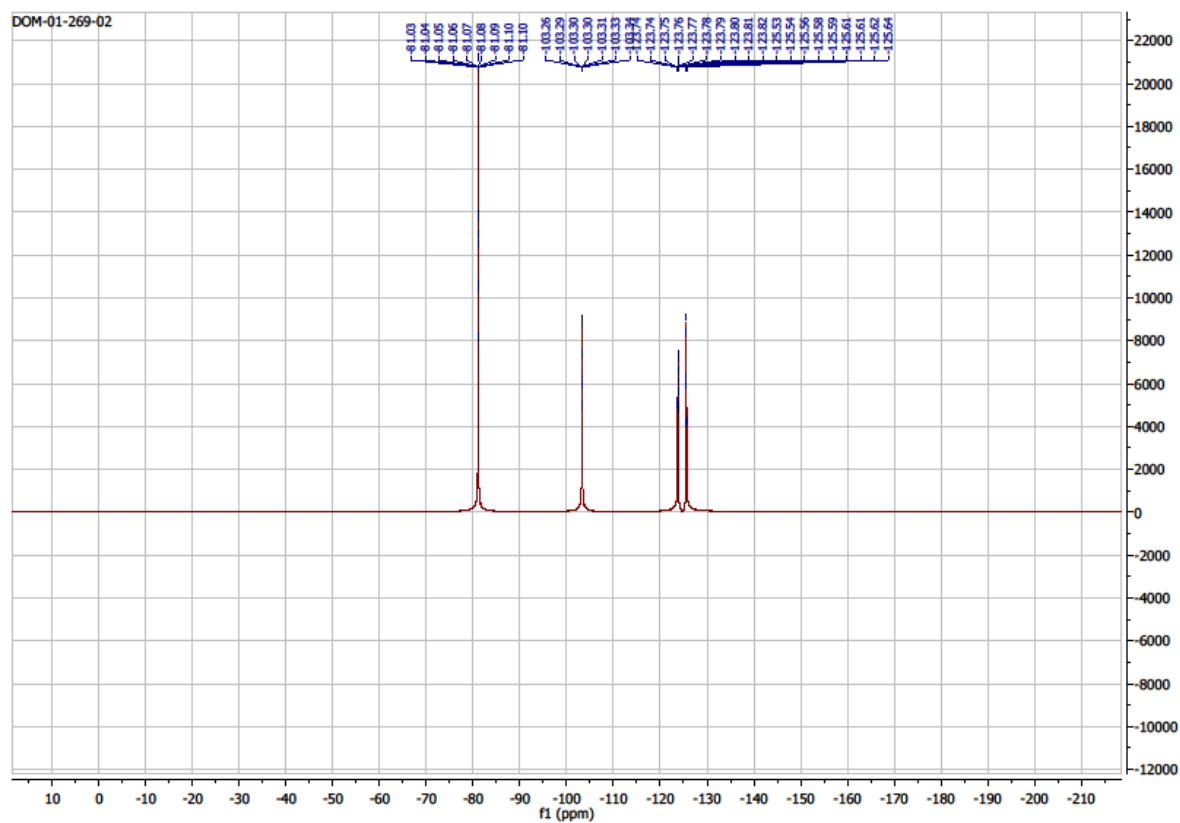


(Z)-1-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)naphthalene (18)

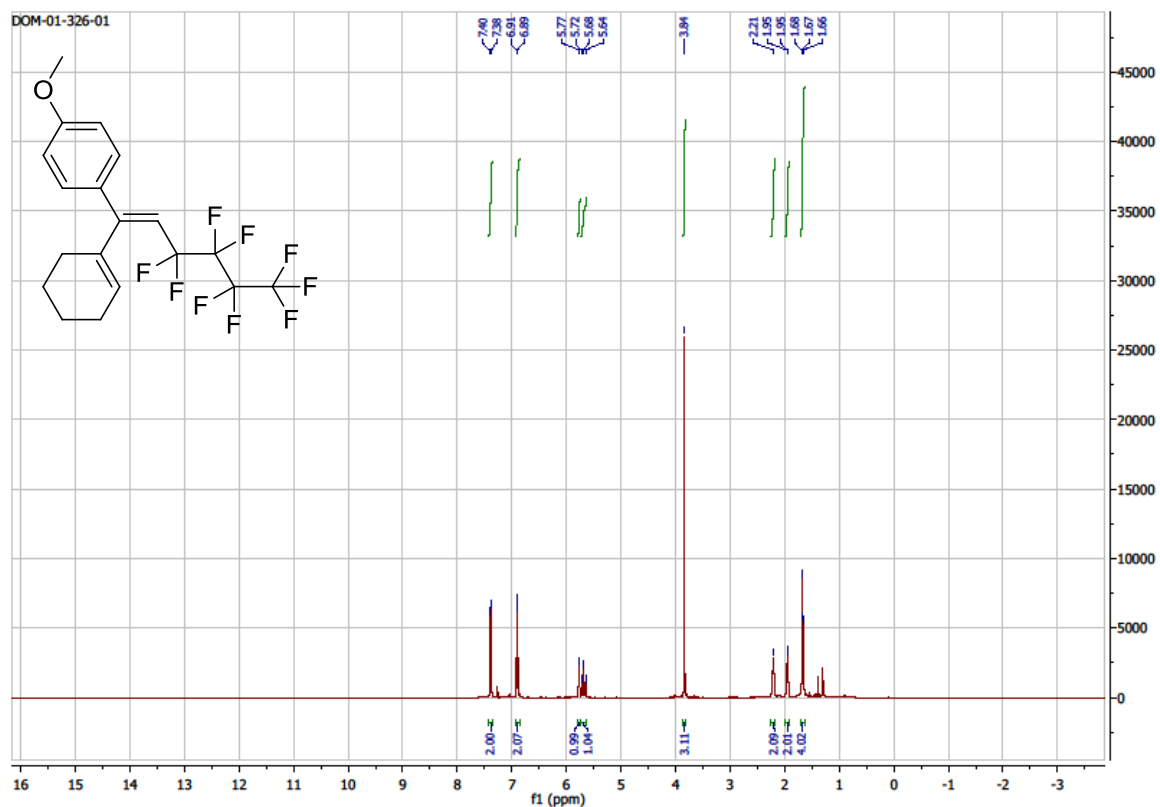


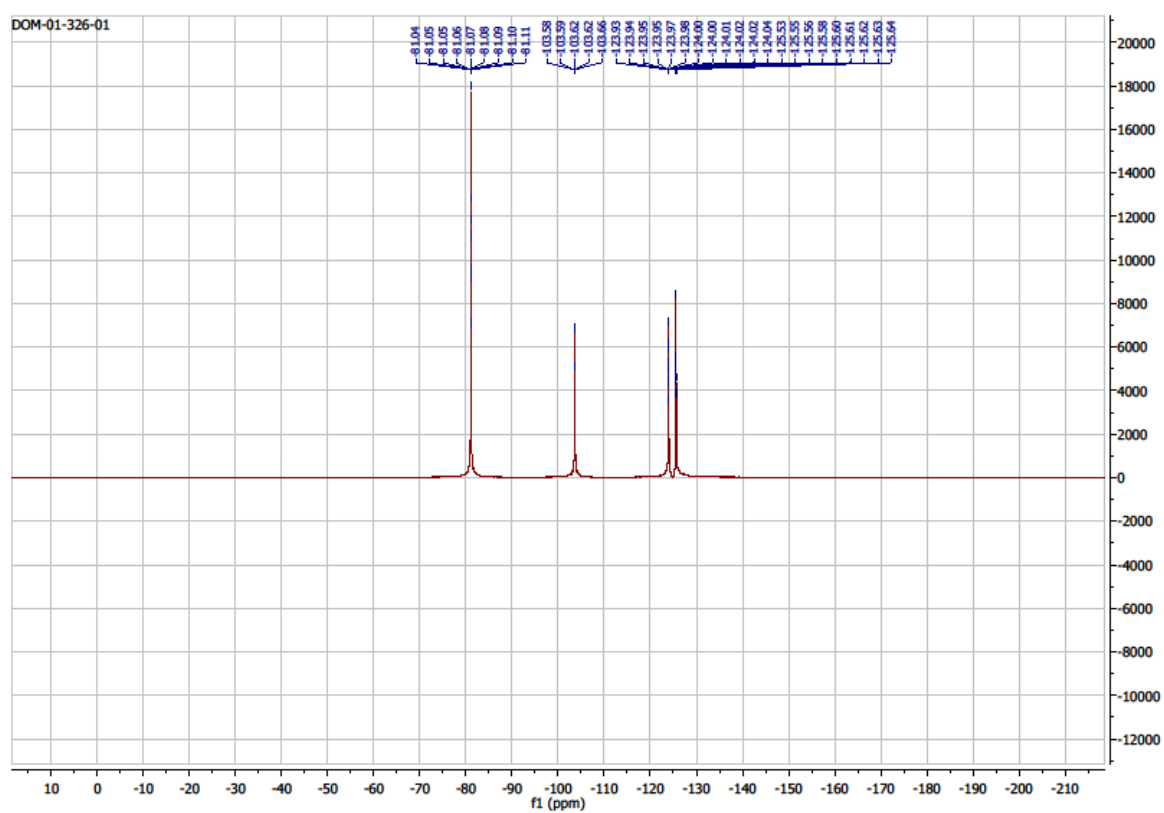
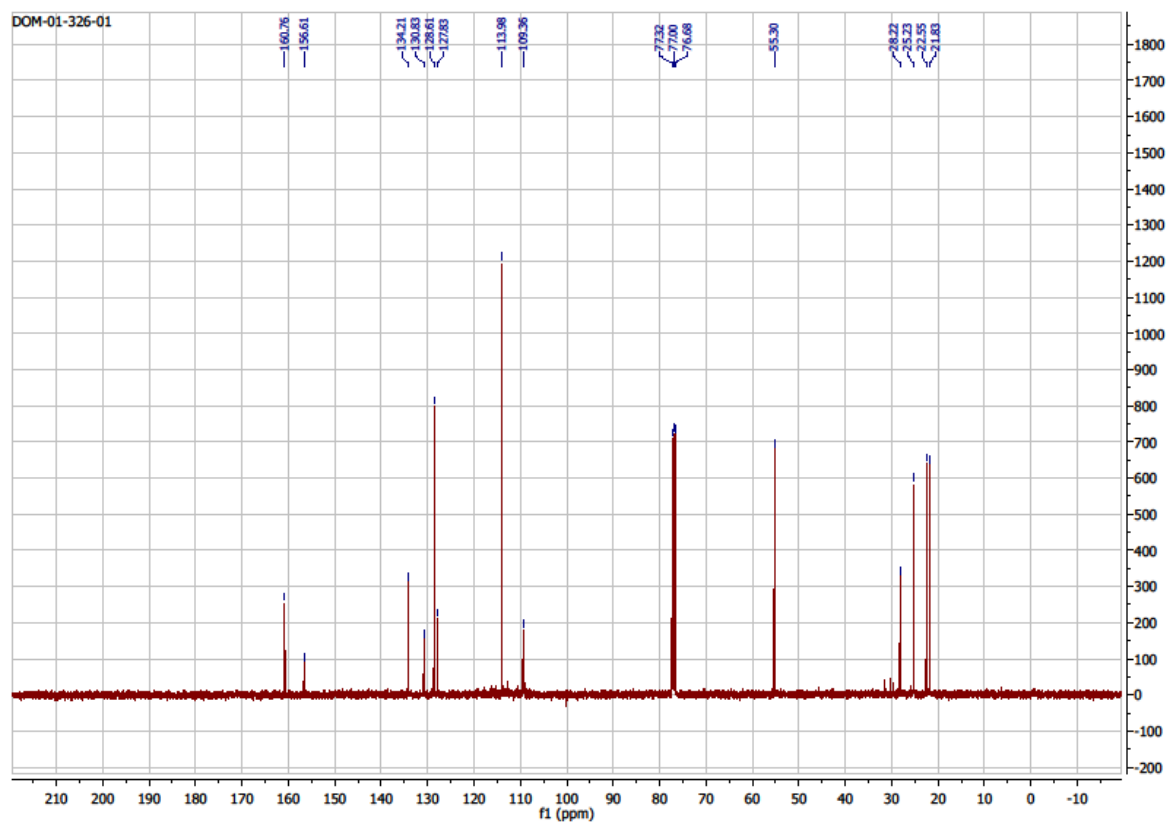
(Z)-1,2,3-trimethoxy-5-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)benzene
(19)



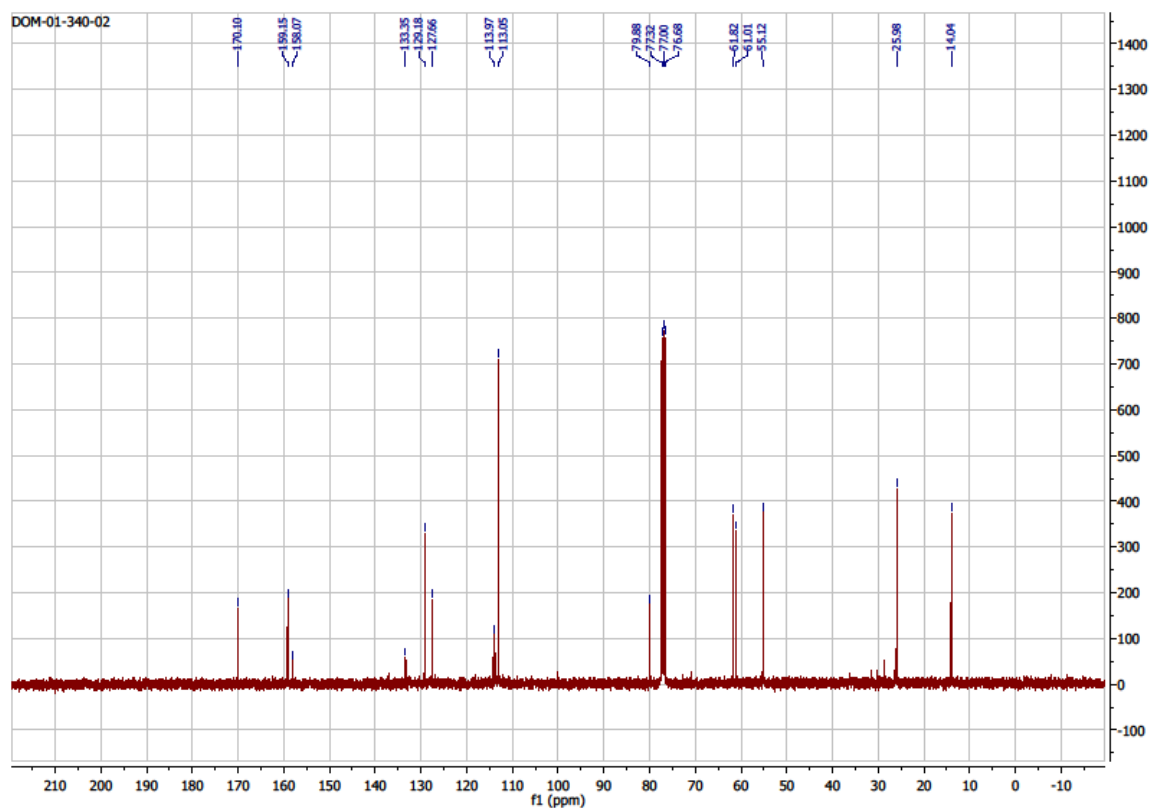
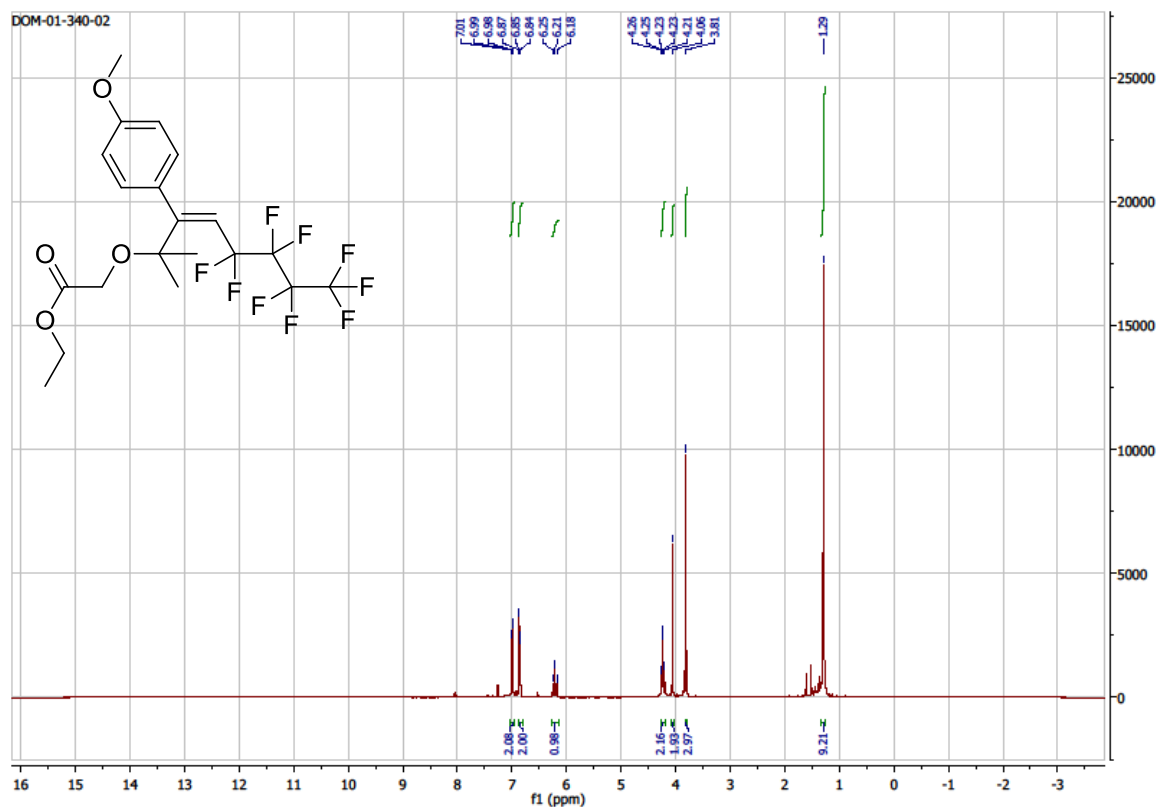


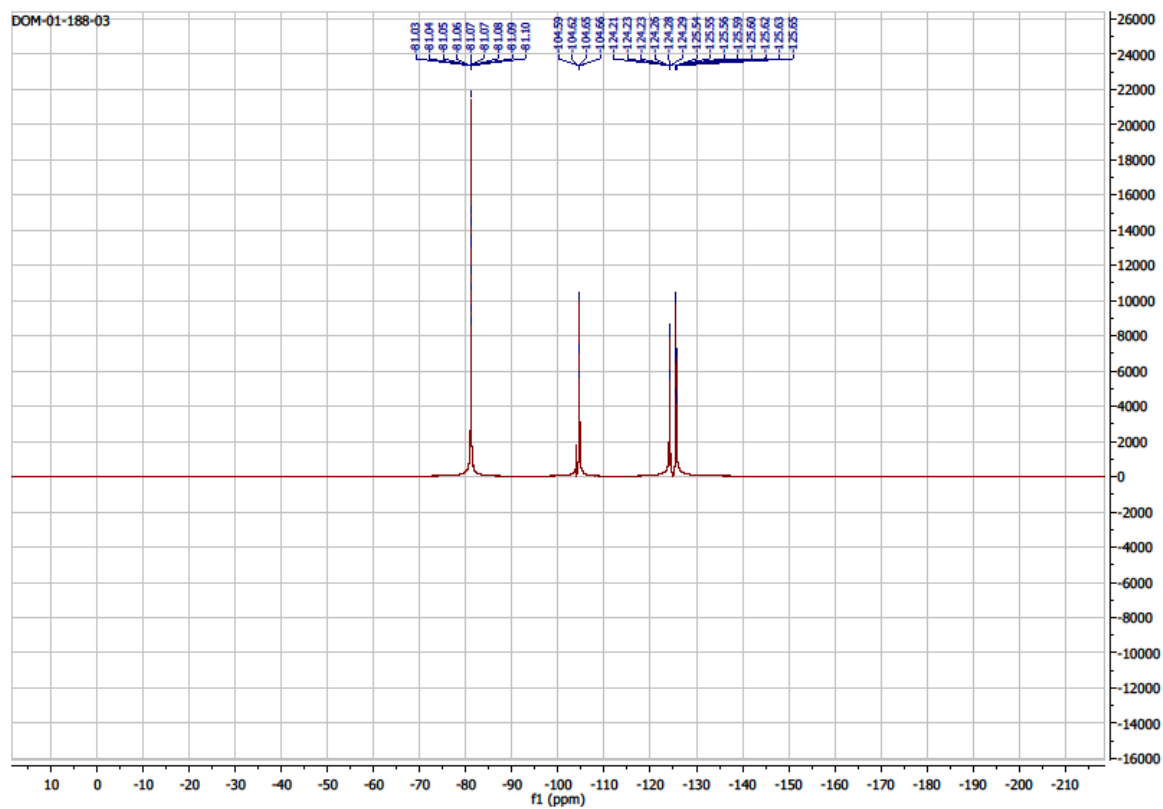
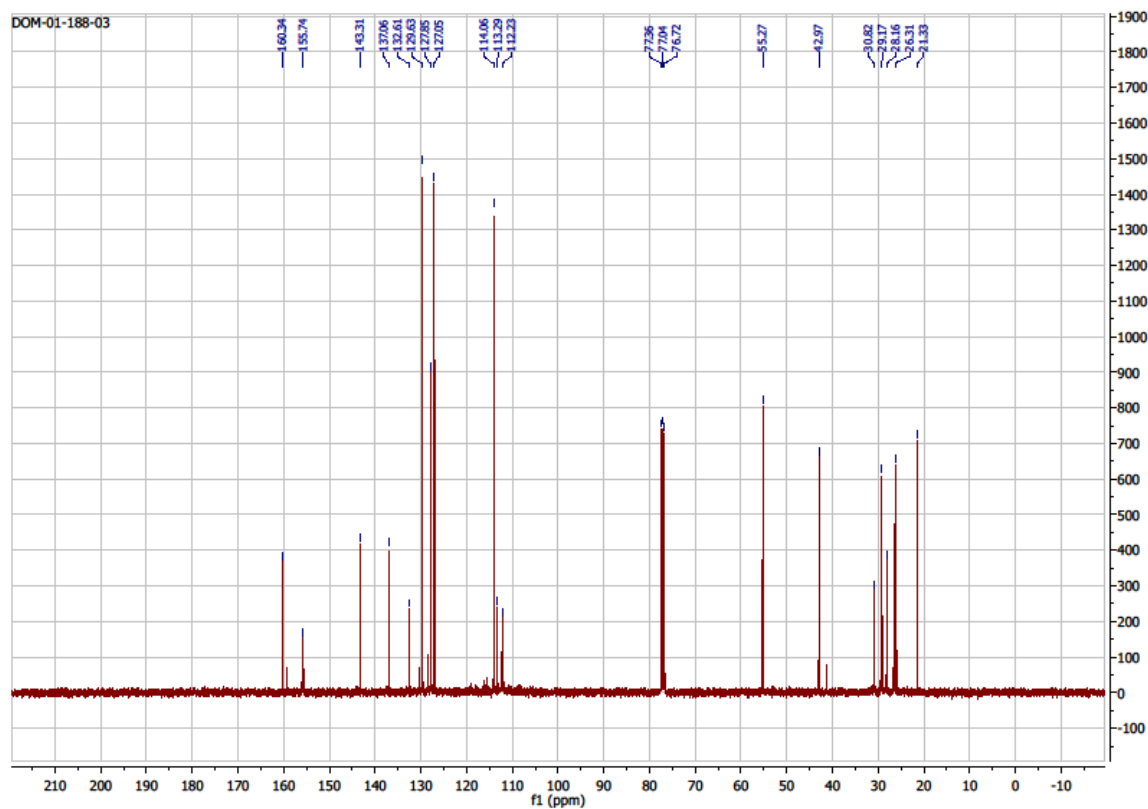
(E)-1-(1-(cyclohex-1-en-1-yl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)-4-methoxybenzene (20)



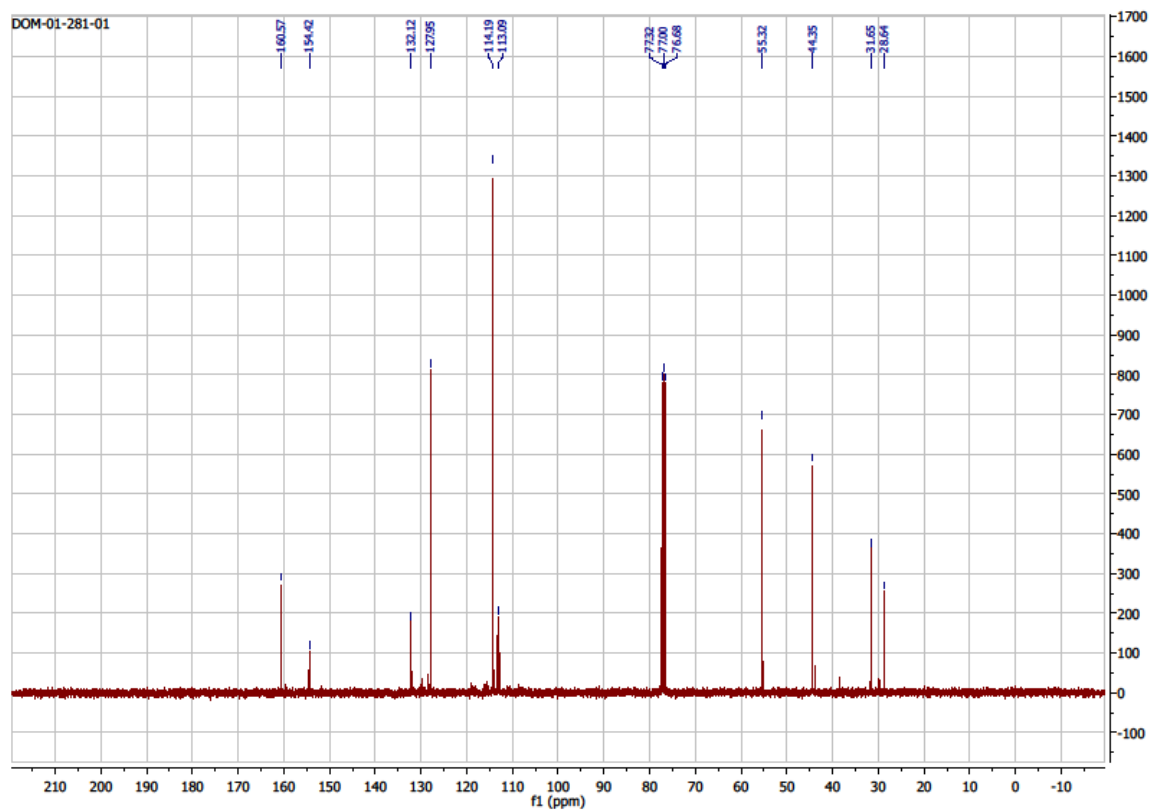
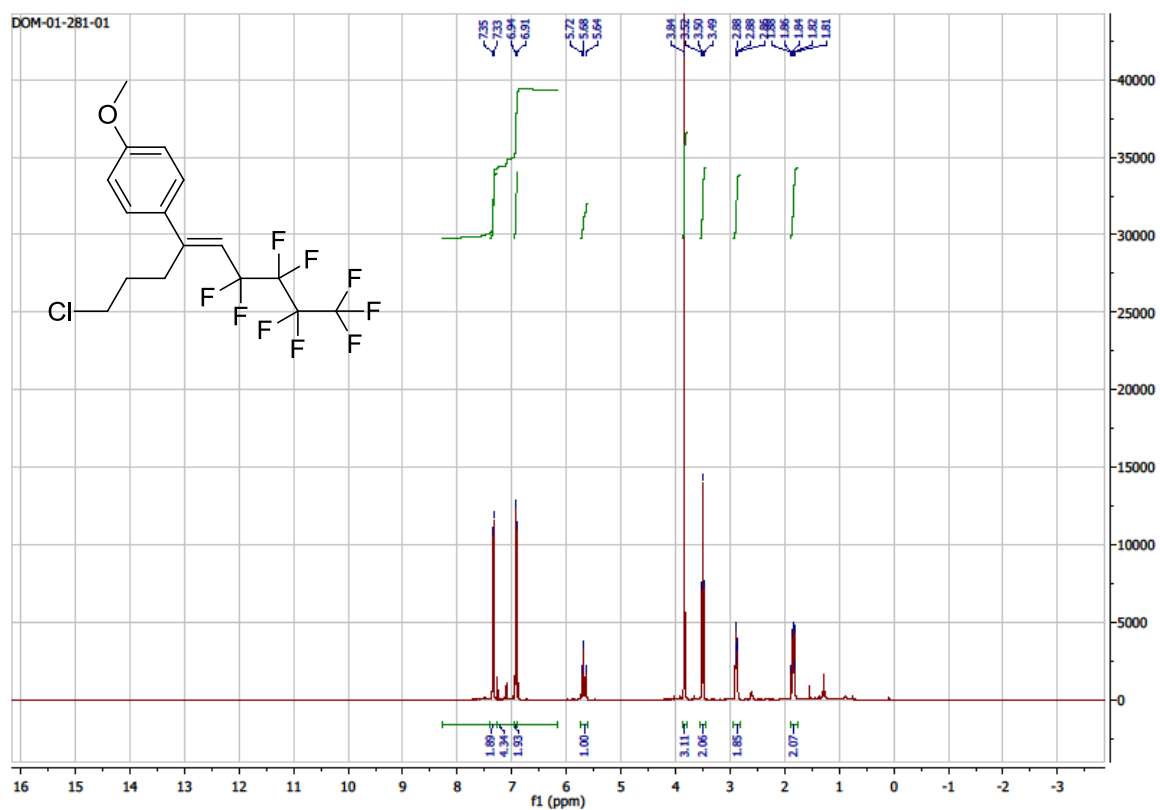


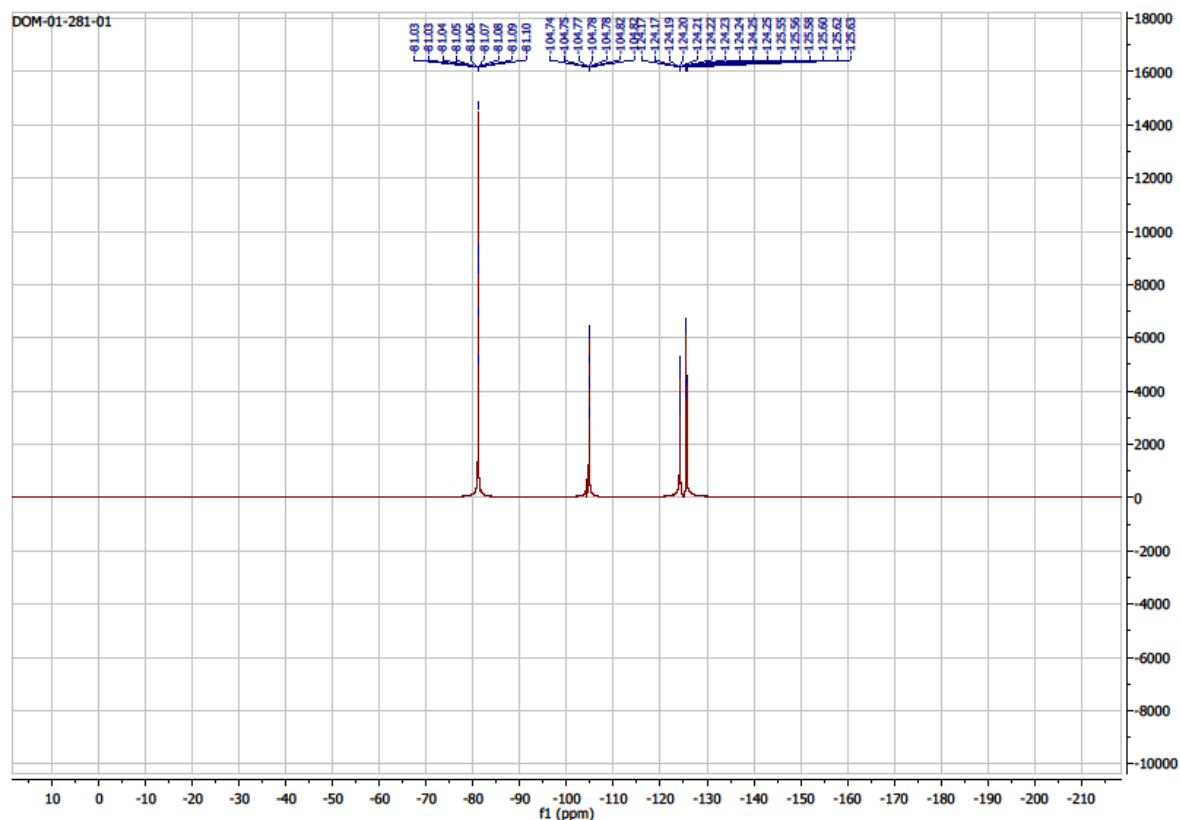
**(Z)-ethyl 2-((5,5,6,6,7,7,8,8,8-nonafluoro-3-(4-methoxyphenyl)-2-methyloct-3-en-2-yl)oxy)acetate
(21)**



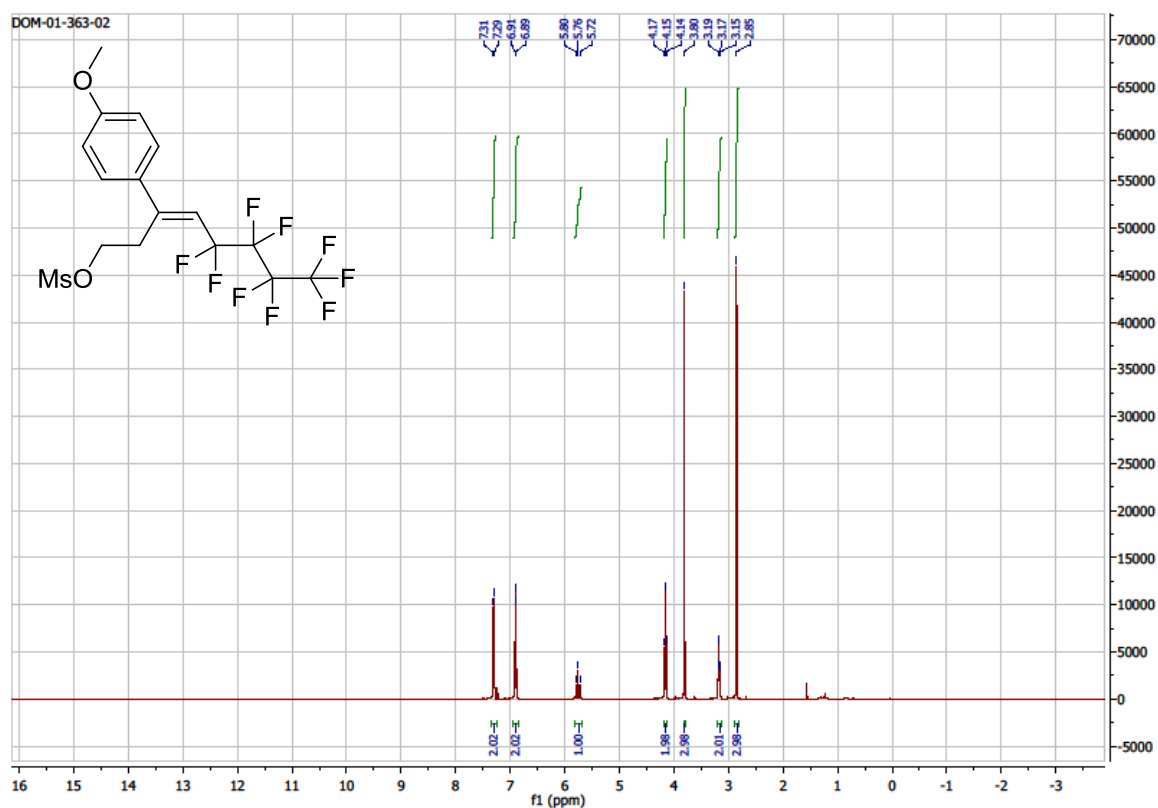


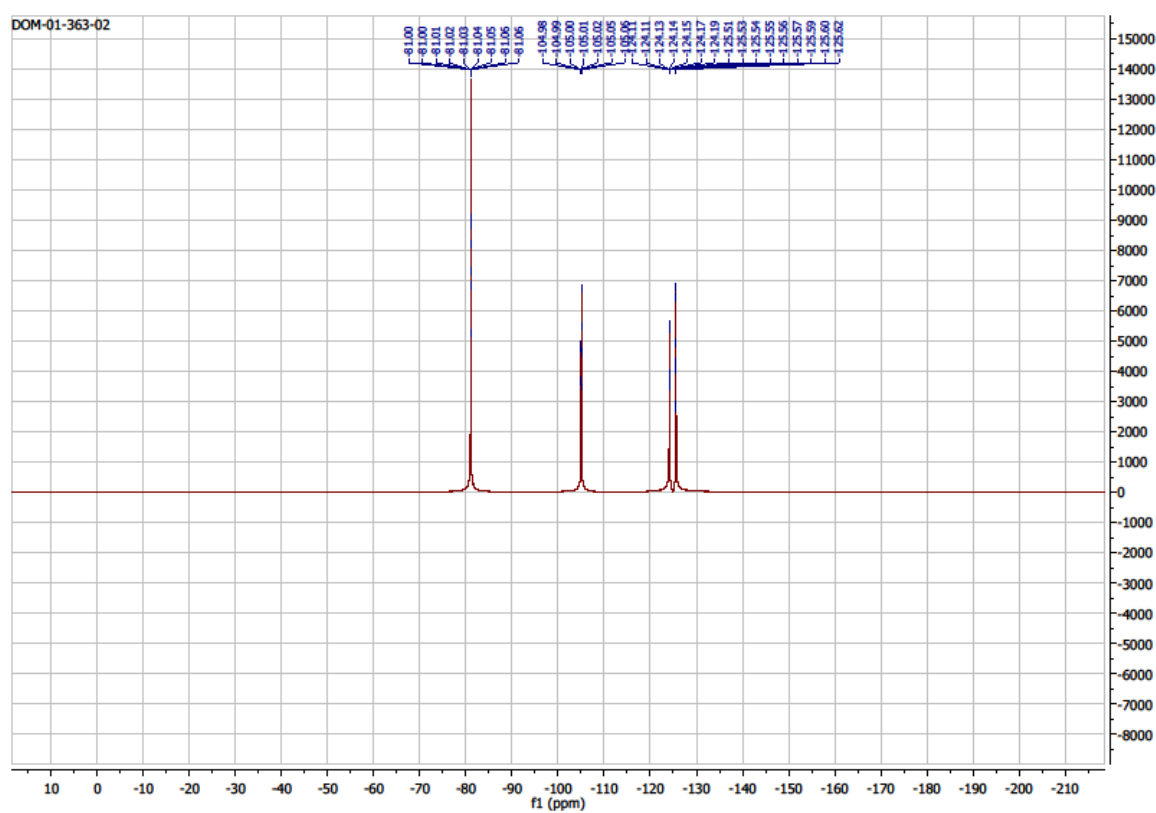
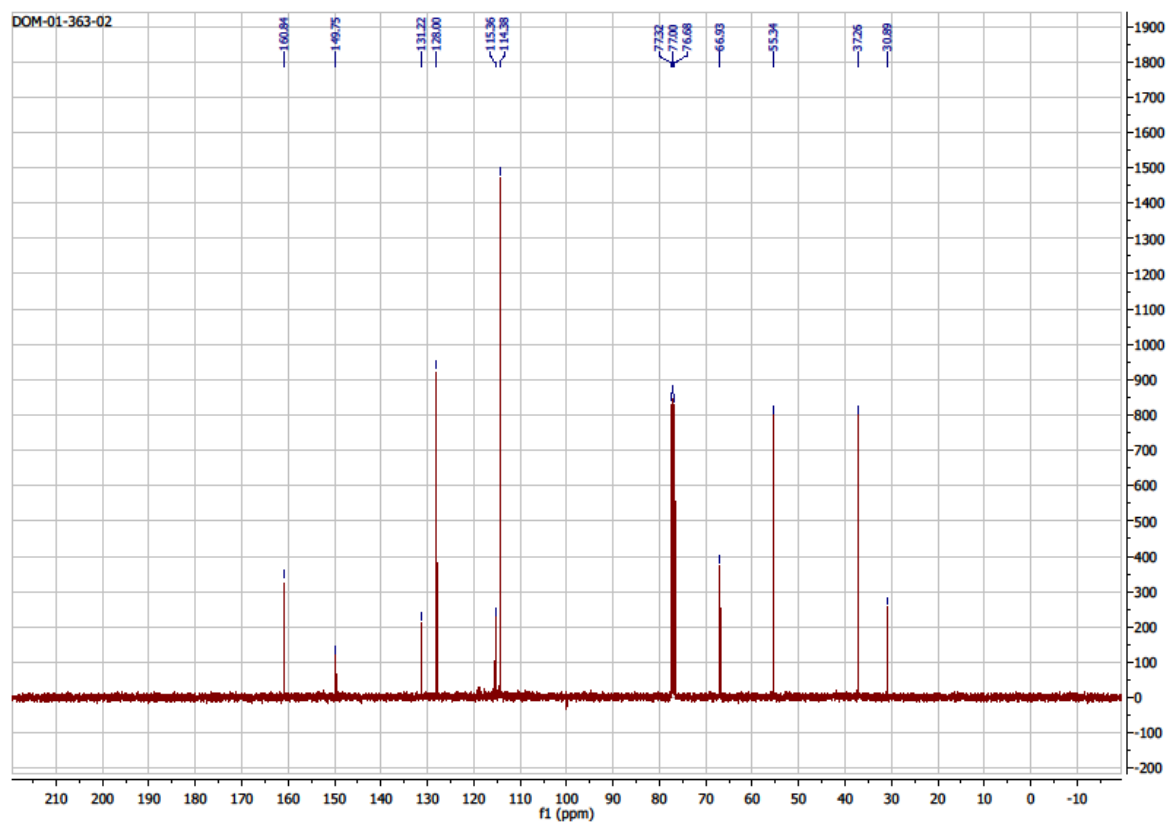
(E)-1-(1-chloro-6,6,7,7,8,9,9,9-nonafluoronon-4-en-4-yl)-4-methoxybenzene (23)



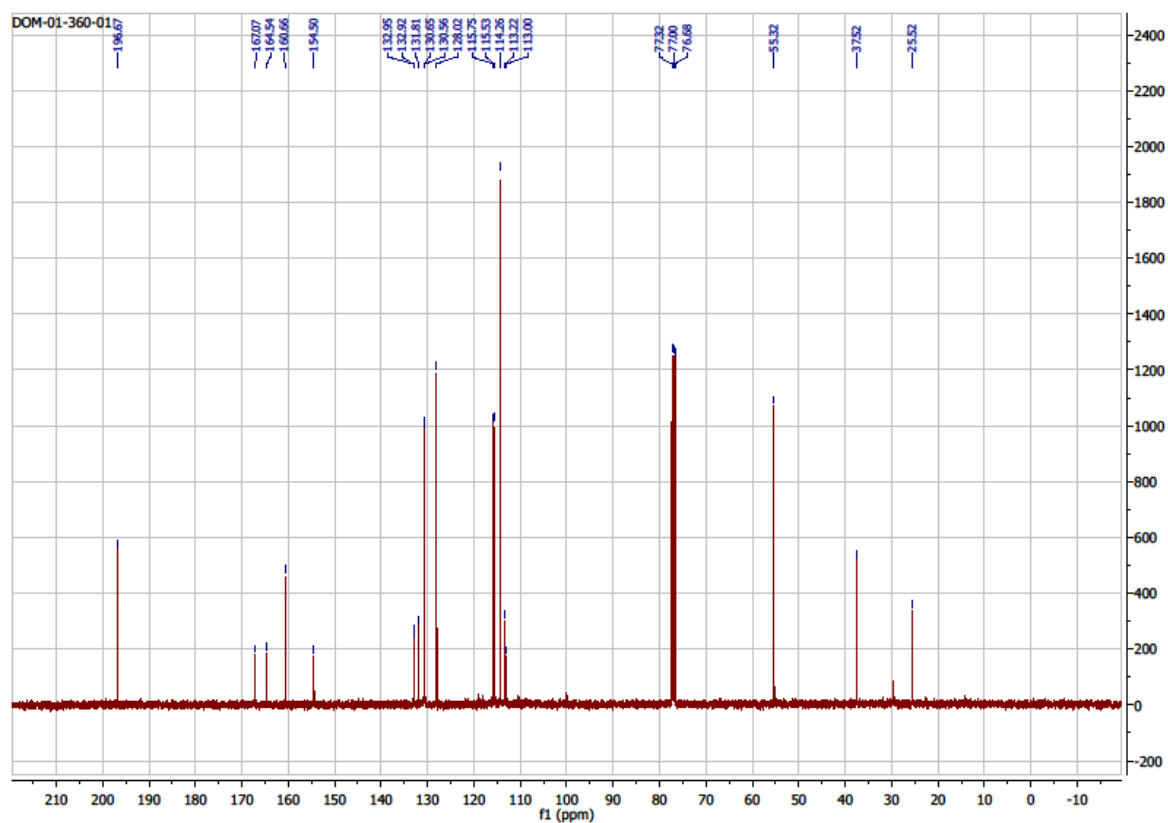
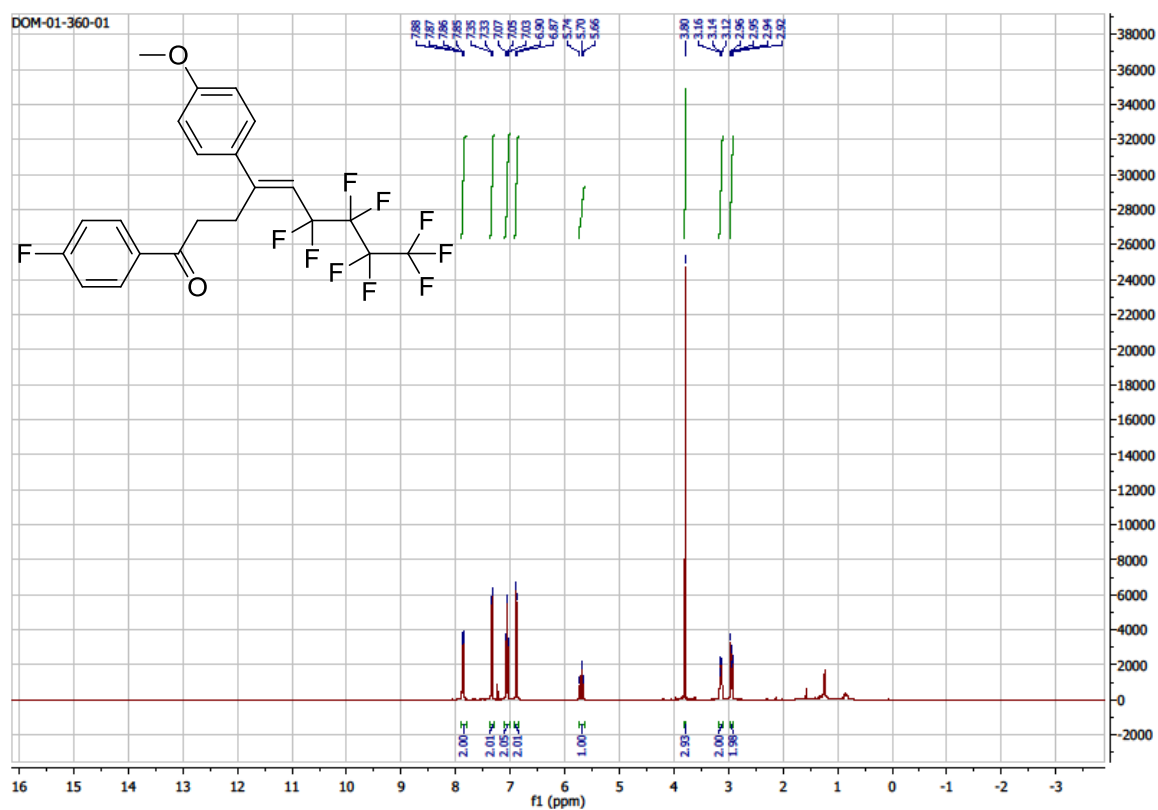


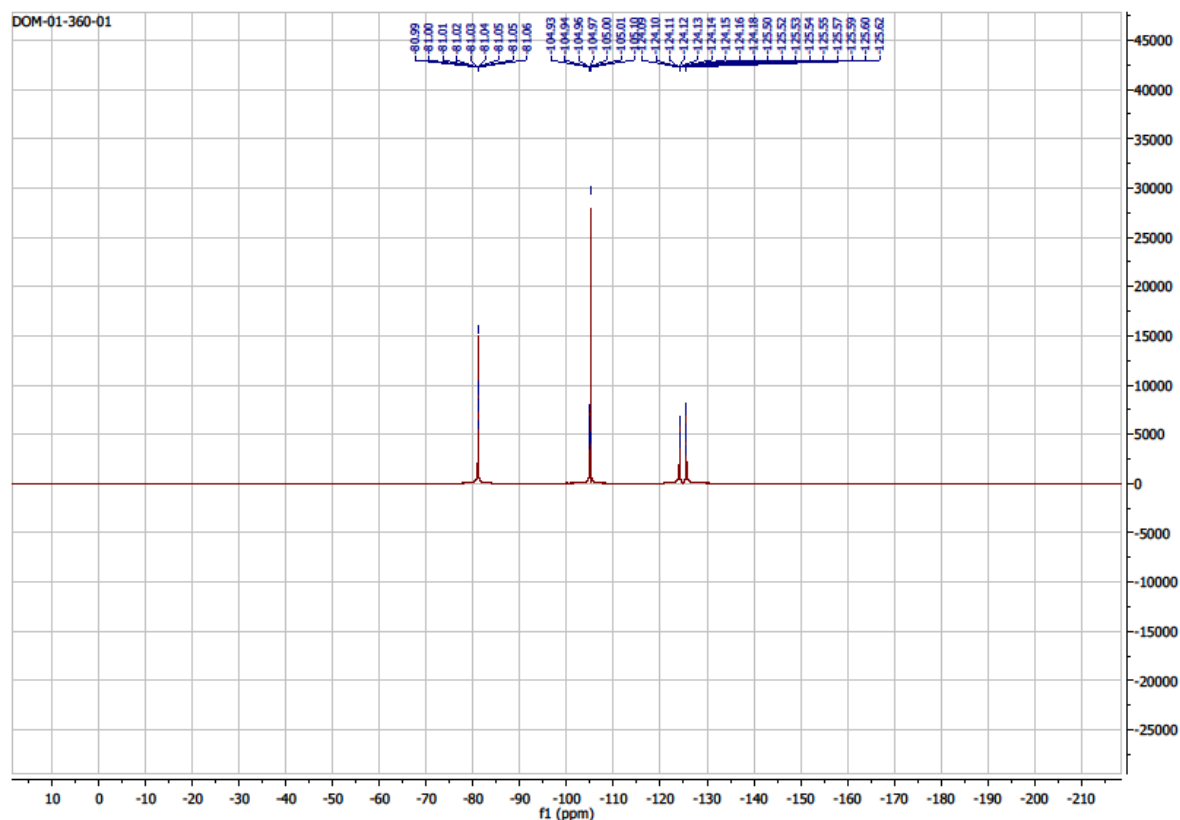
(*E*)-5,5,6,6,7,7,8,8,8-nonafluoro-3-(4-methoxyphenyl)oct-3-en-1-yl methanesulfonate (24)



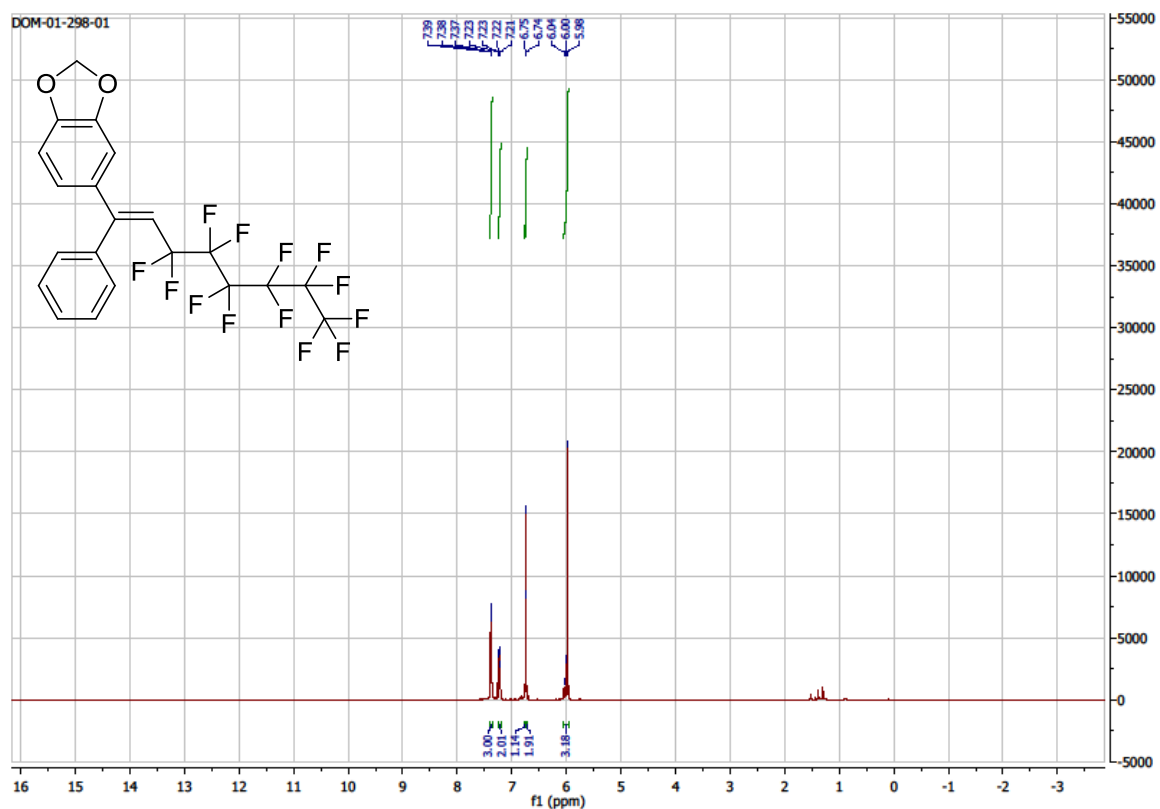


(E)-6,6,7,7,8,8,9,9,9-nonafluoro-1-(4-fluorophenyl)-4-(4-methoxyphenyl)non-4-en-1-one (25)

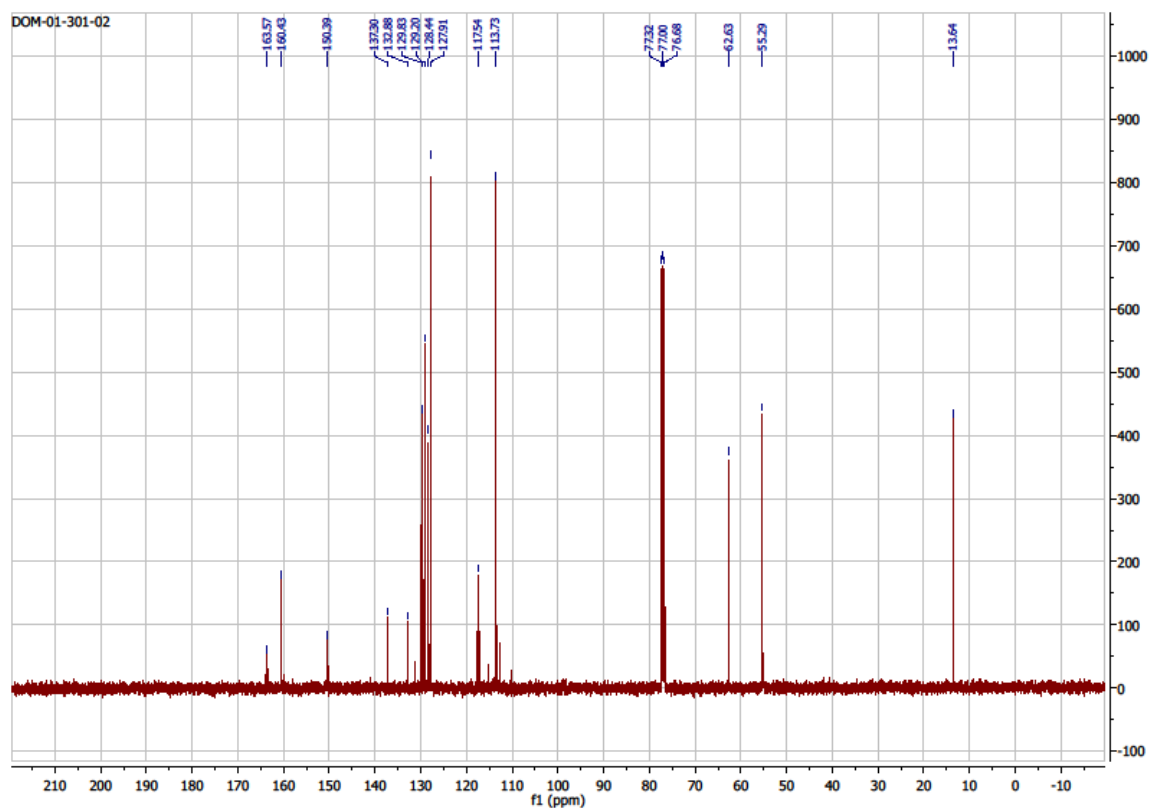
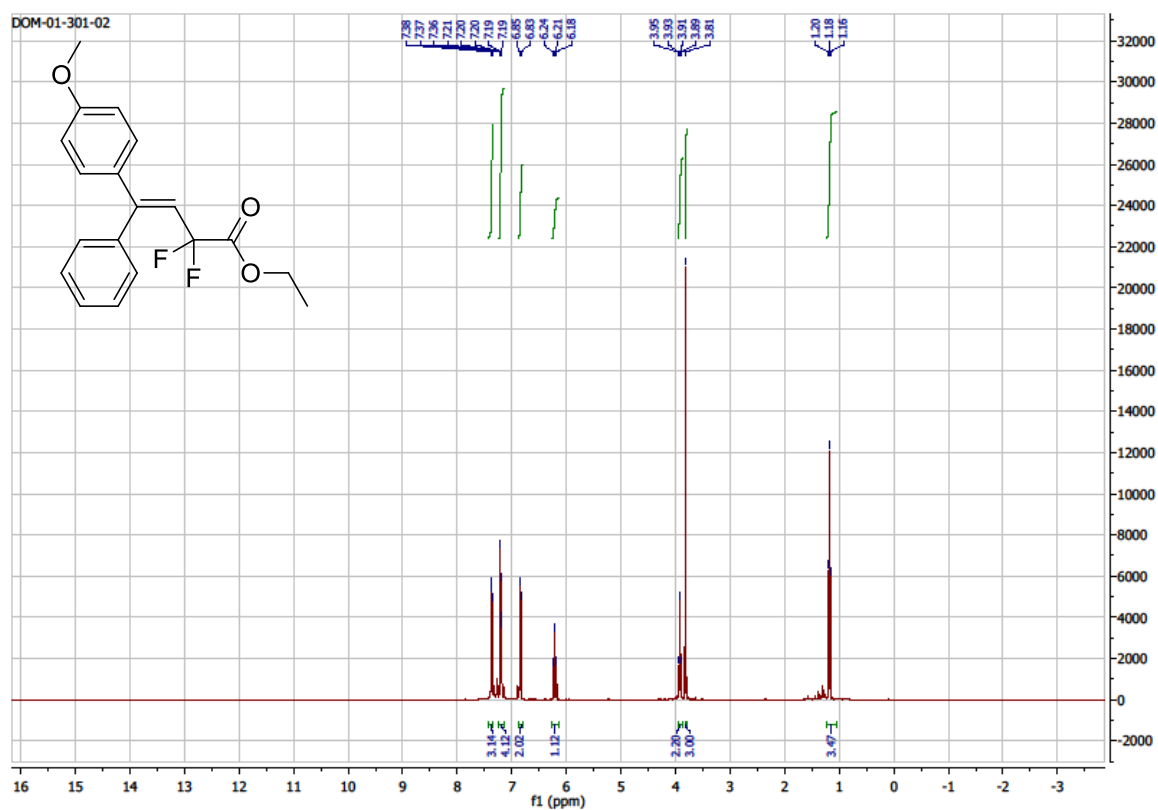


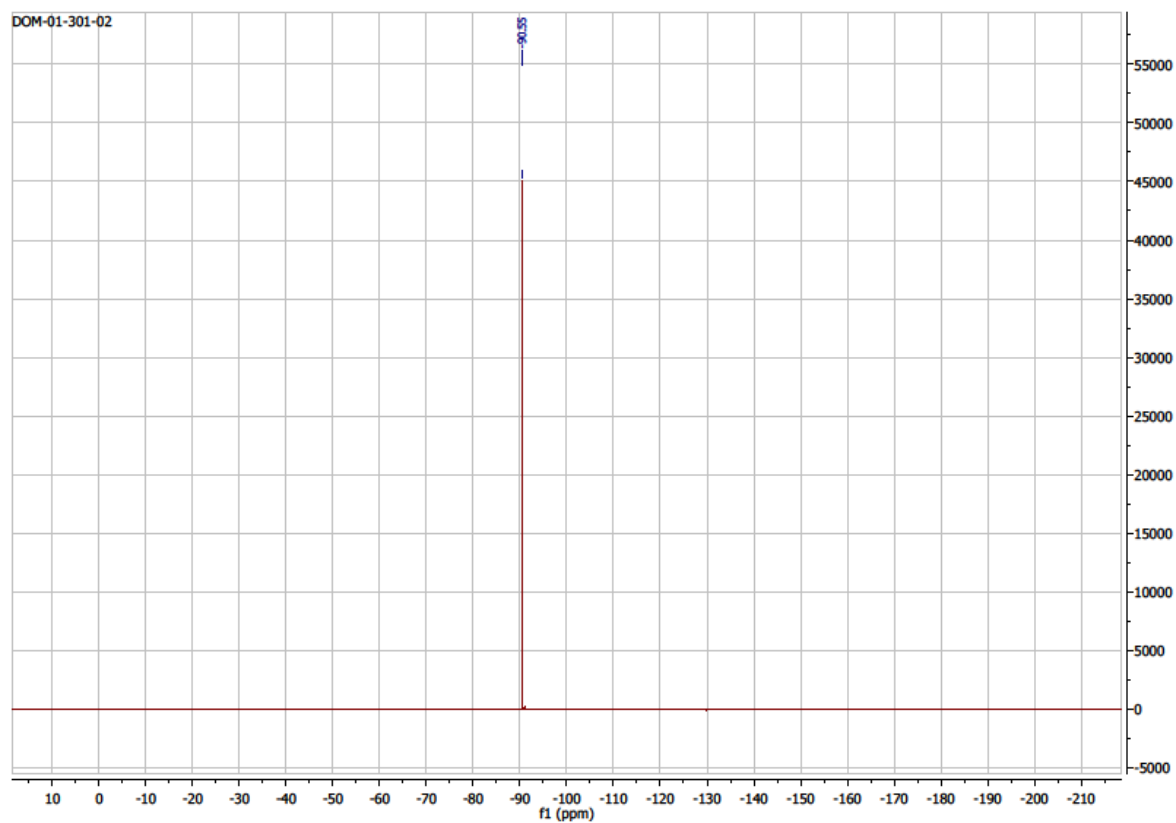


(*E*)-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloct-1-en-1-yl)benzo[d][1,3]dioxole (26)

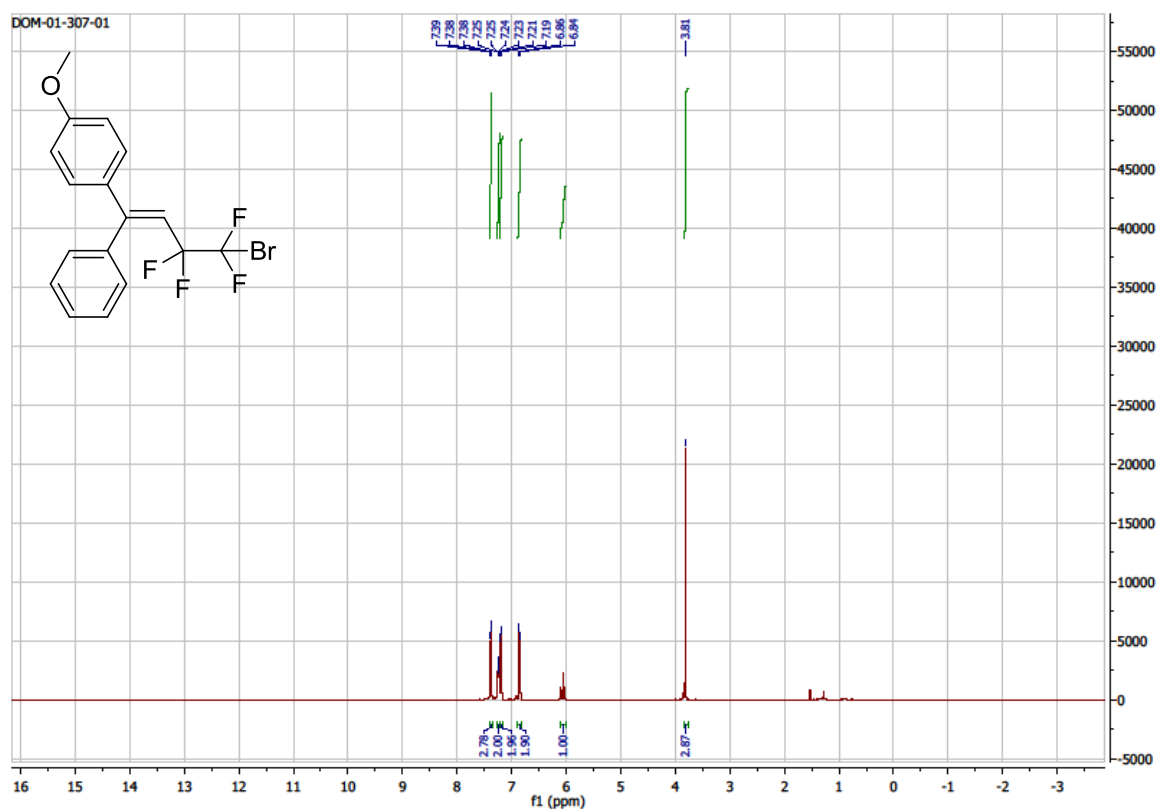


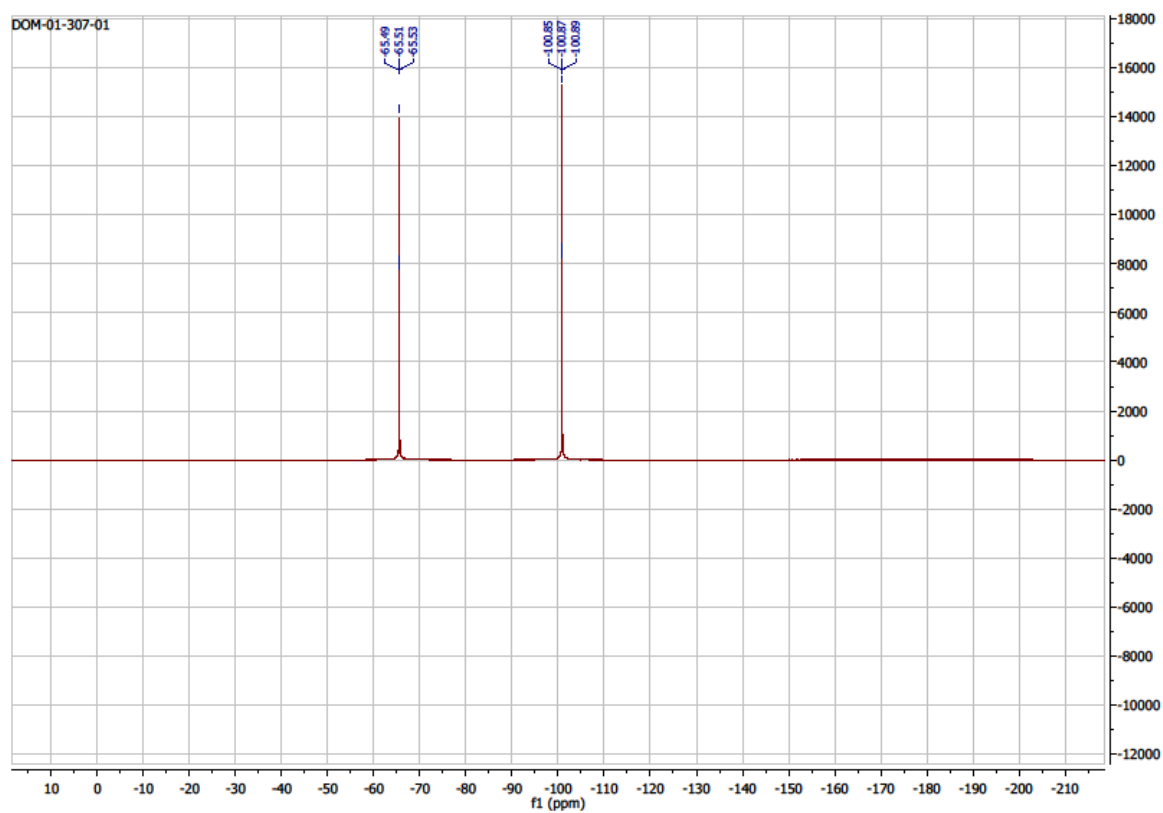
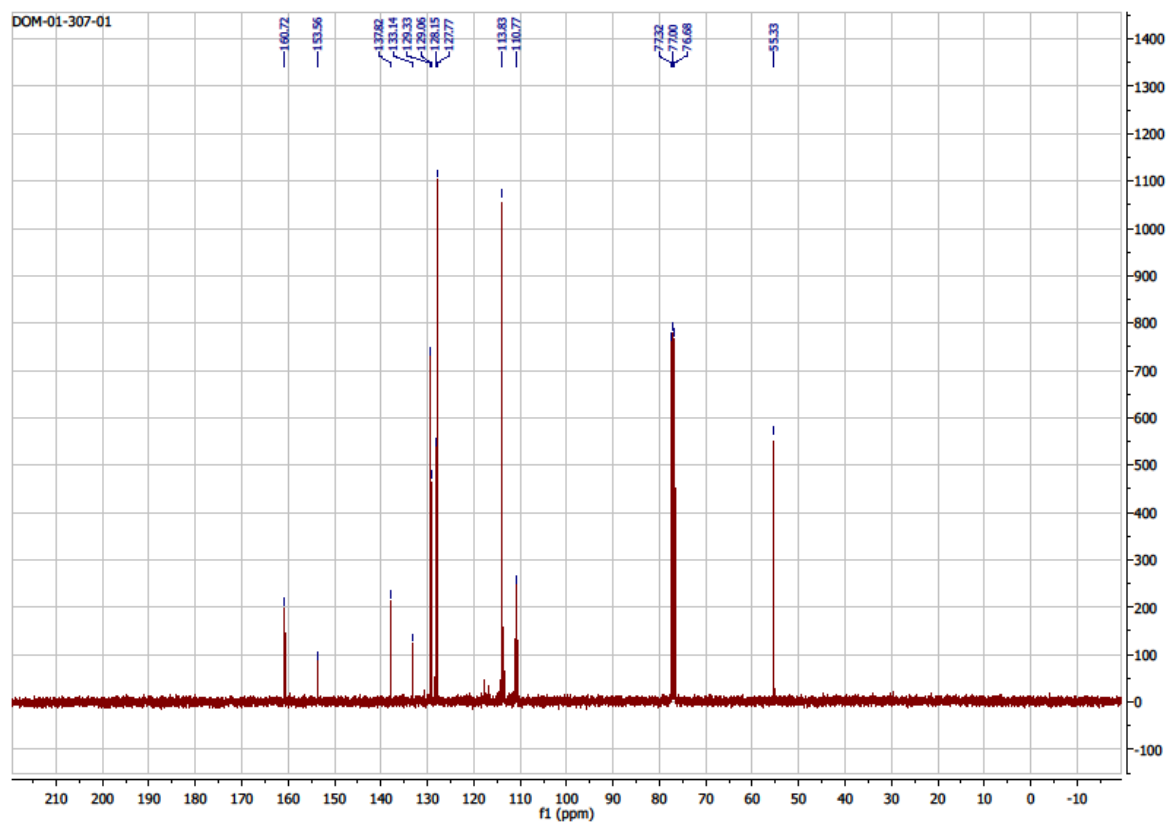
(E)-ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-phenylbut-3-enoate (27)



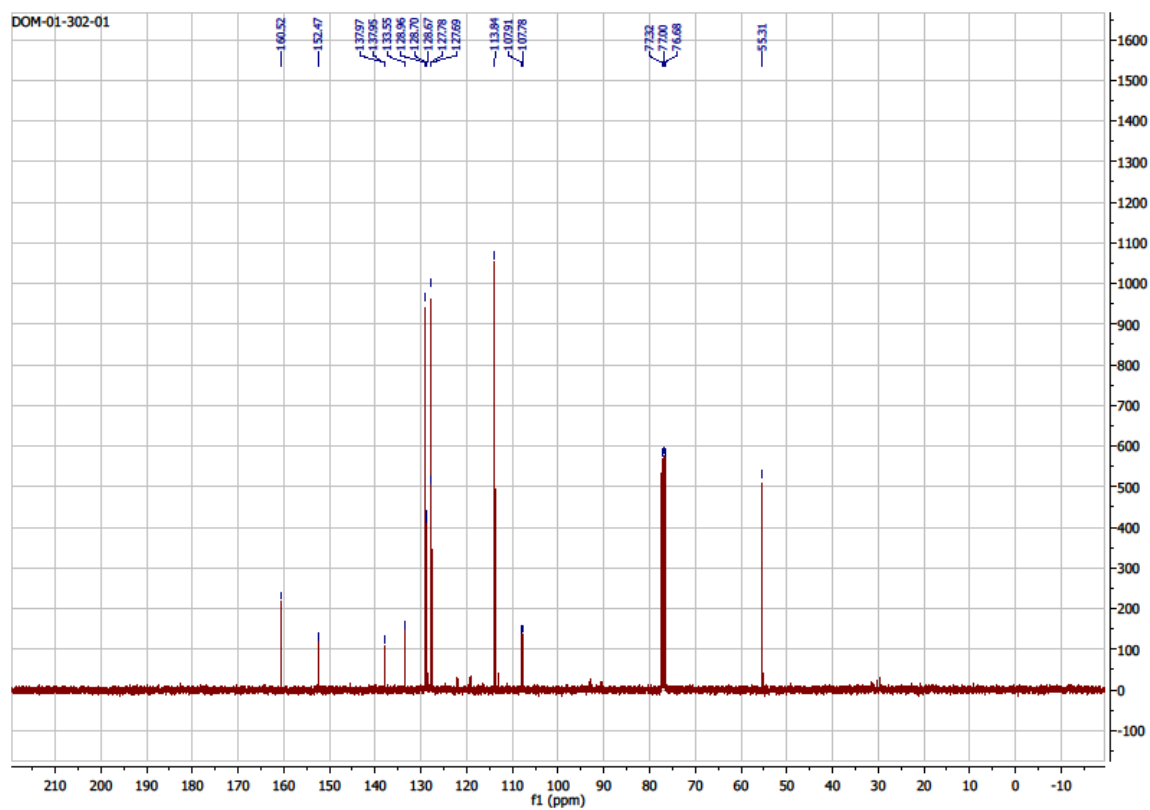
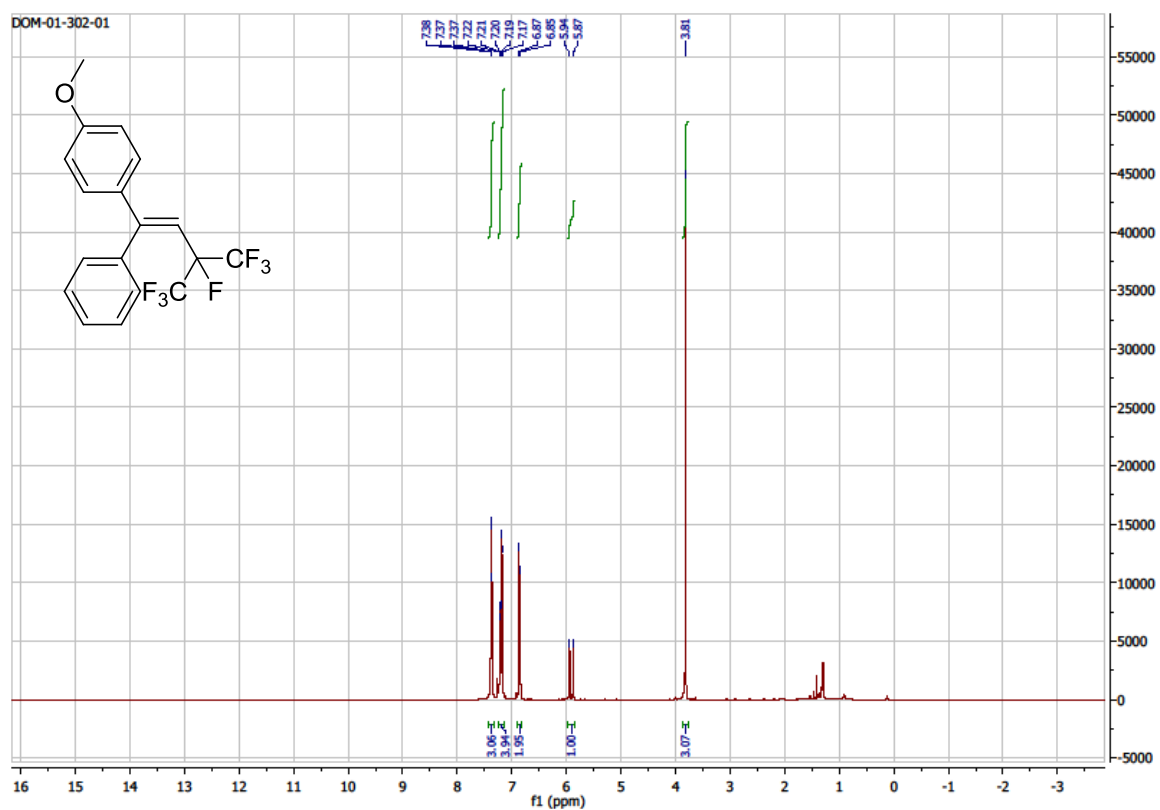


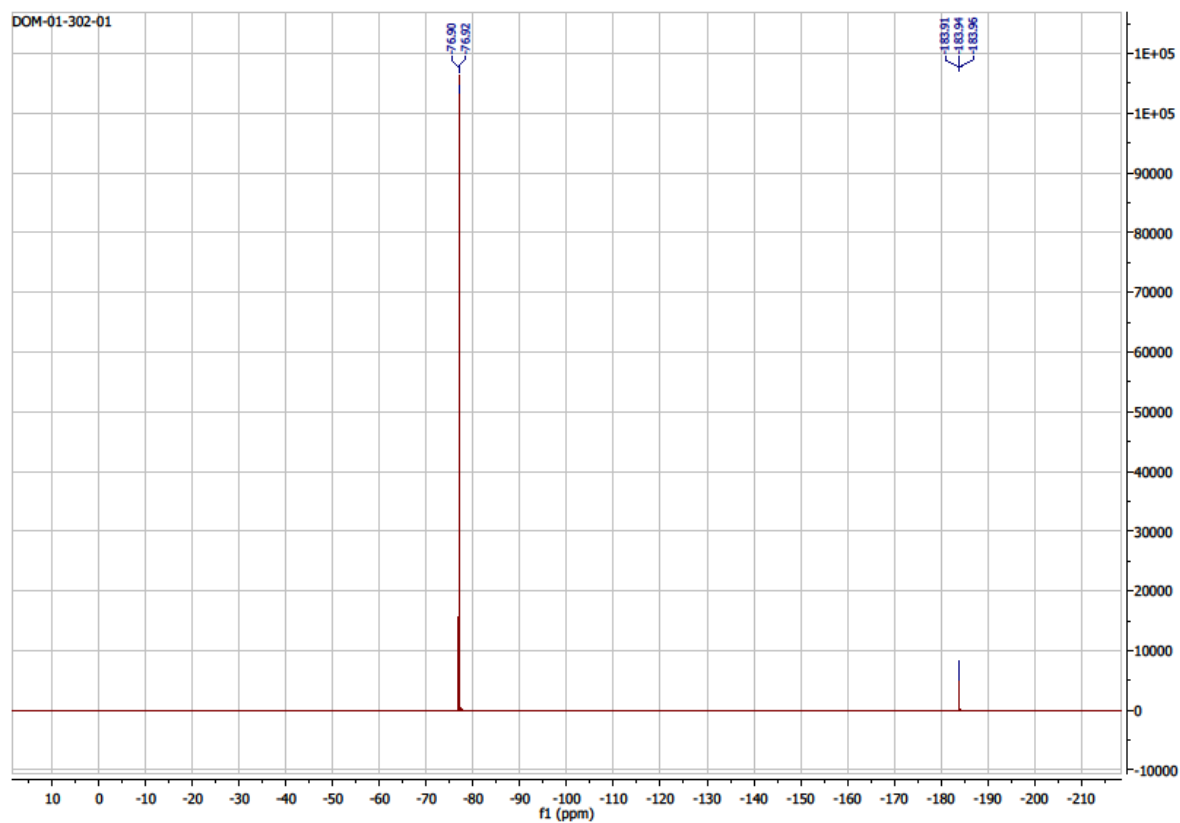
(*E*)-1-(4-bromo-3,3,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-4-methoxybenzene (28)



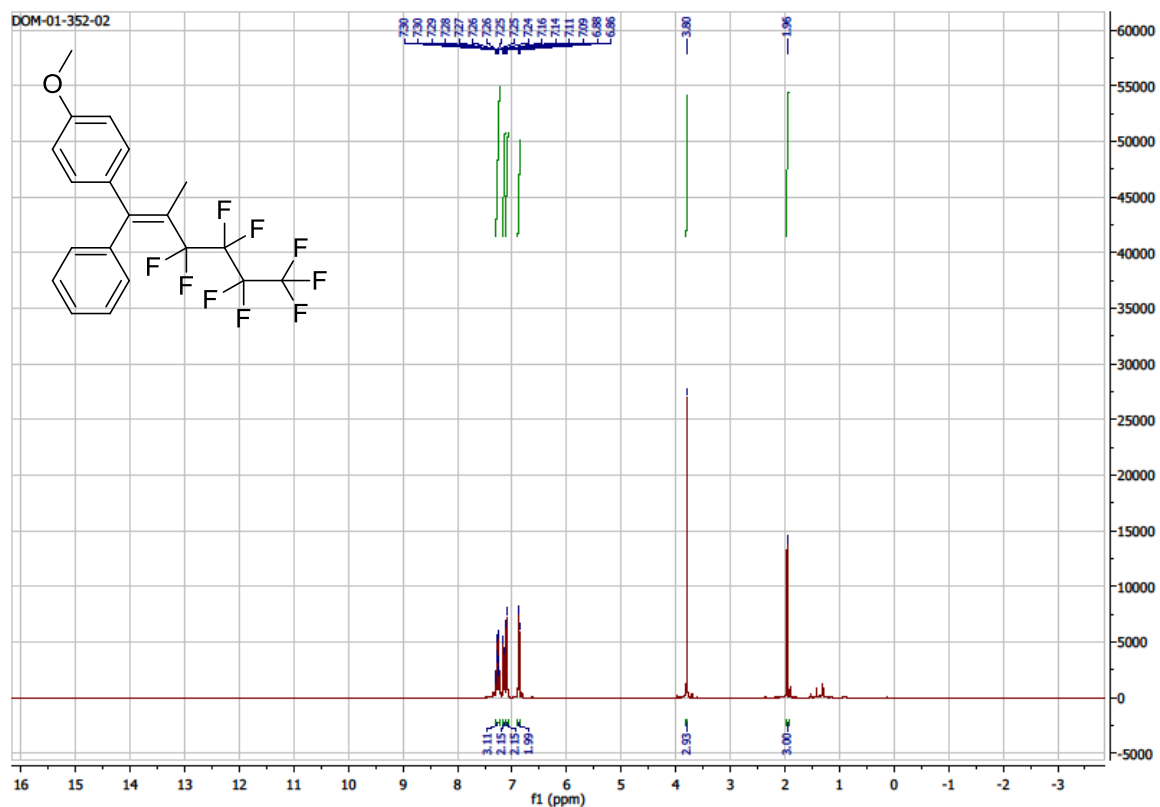


(E)-1-methoxy-4-(3,4,4,4-tetrafluoro-1-phenyl-3-(trifluoromethyl)but-1-en-1-yl)benzene (29)

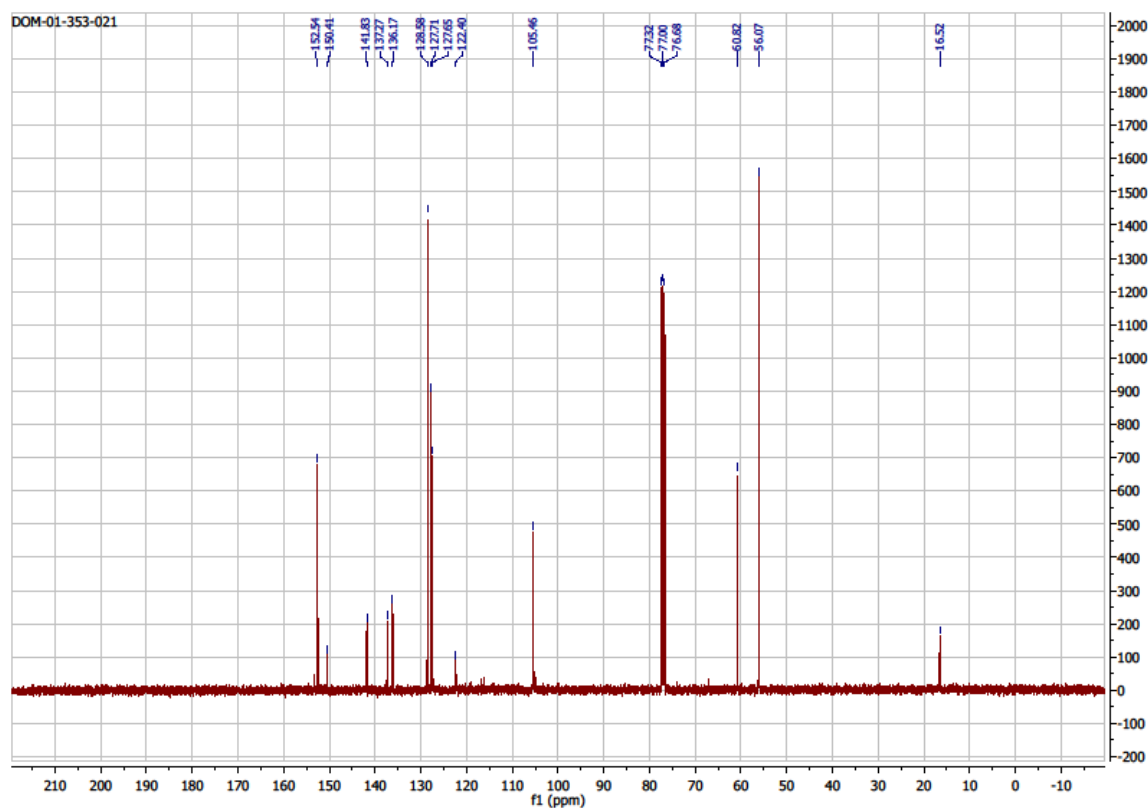
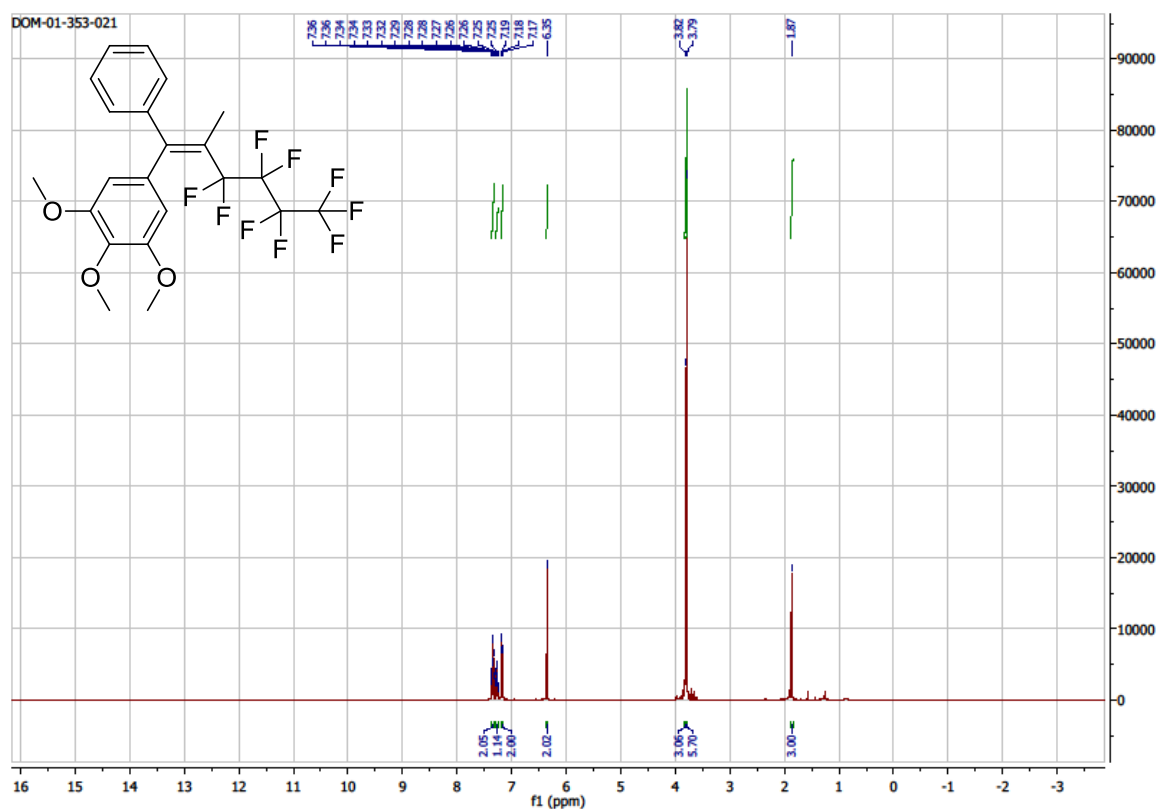


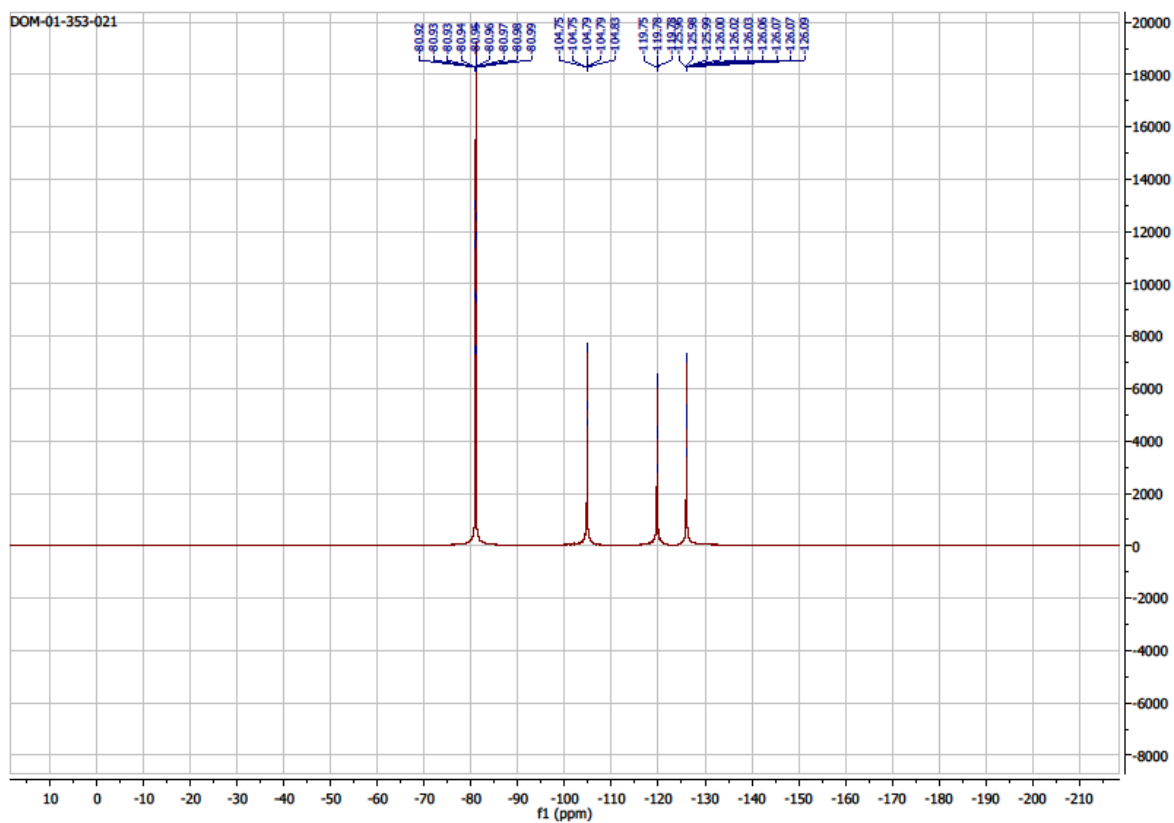


(E)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzene (2)

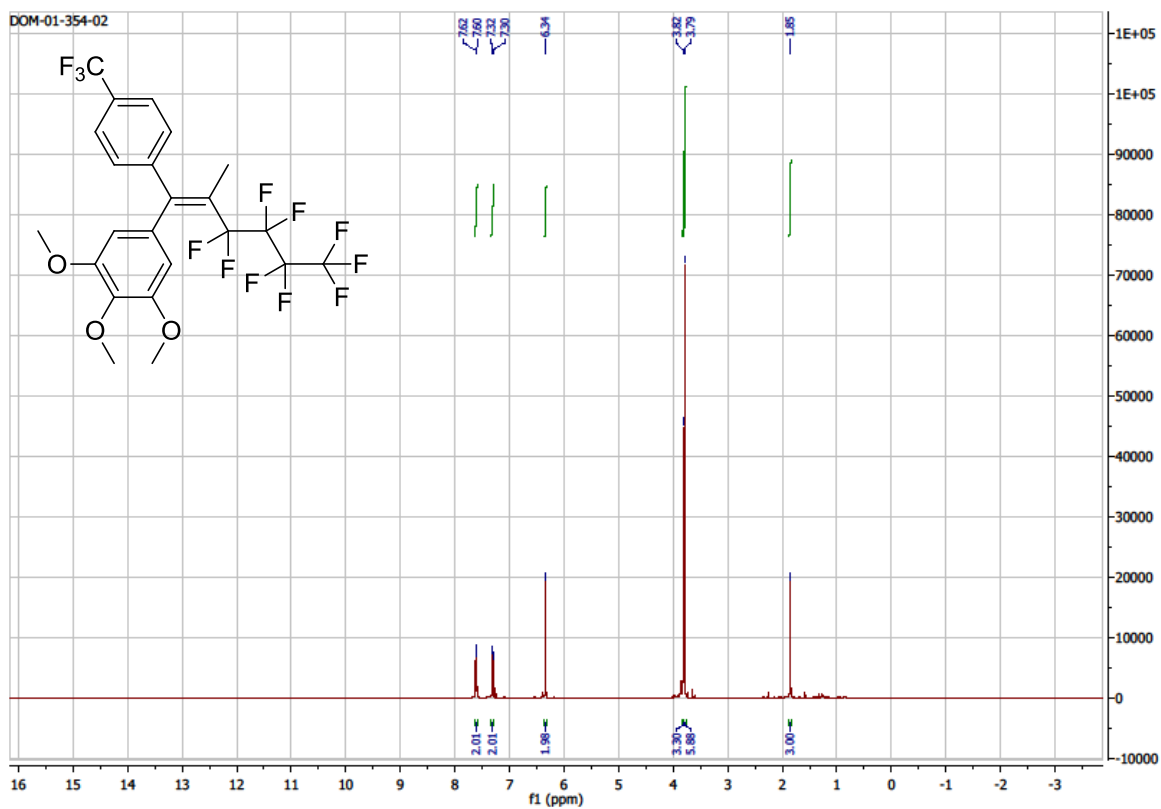


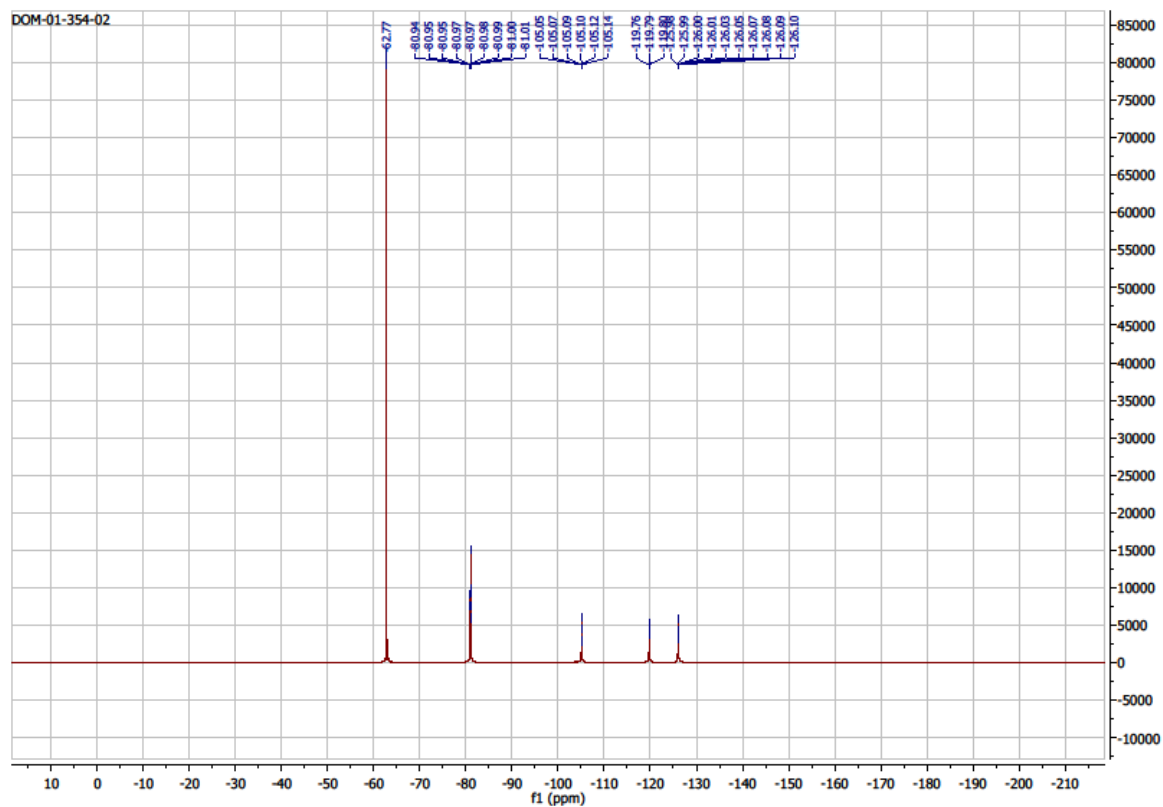
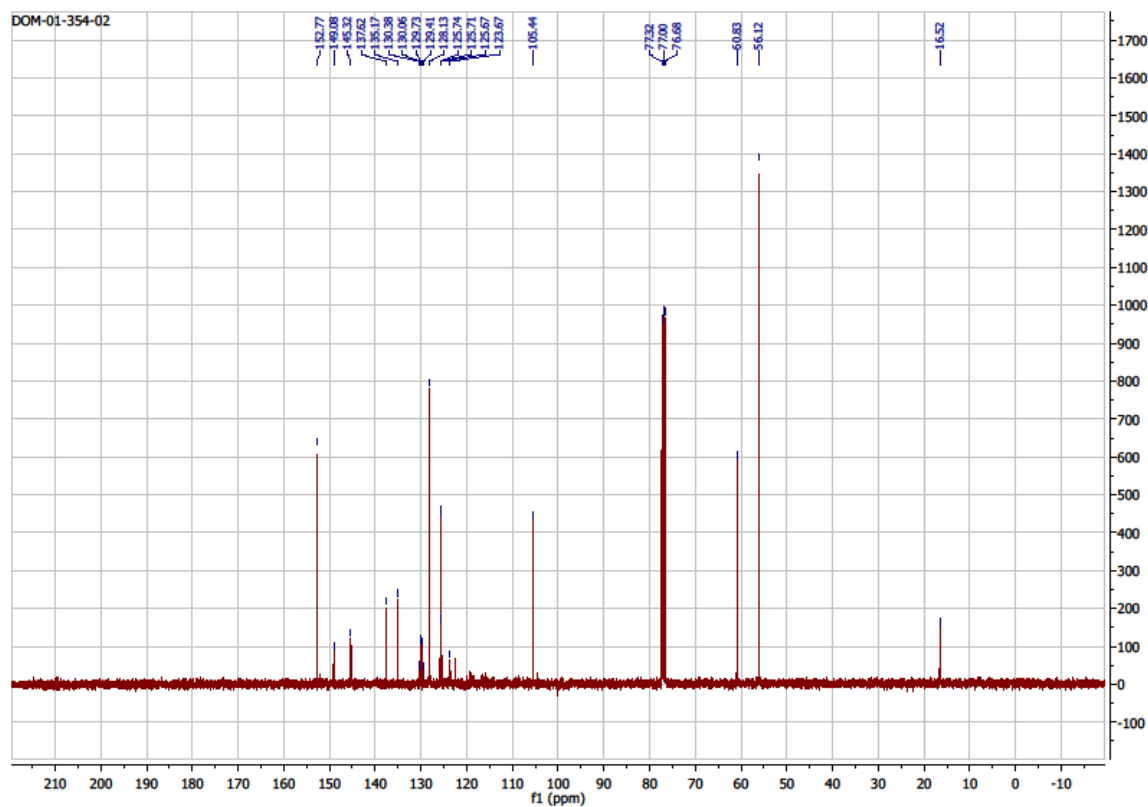
(Z)-1,2,3-trimethoxy-5-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzene (30)



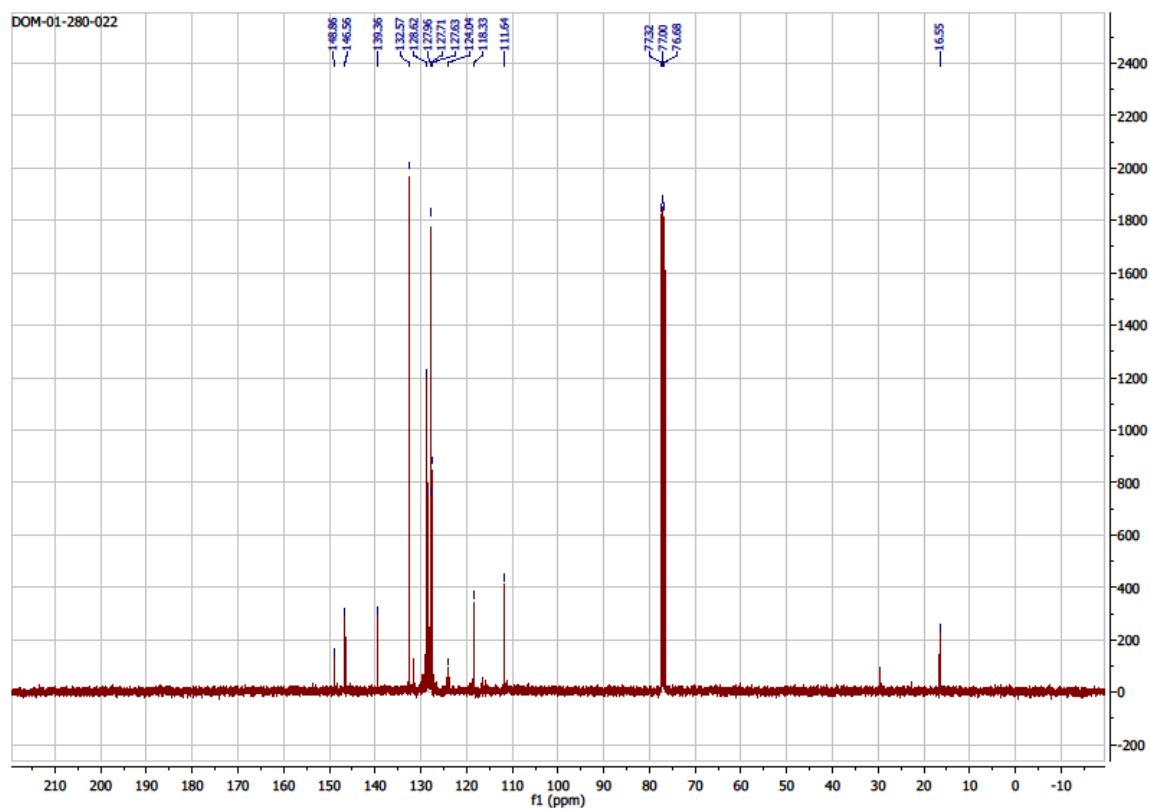
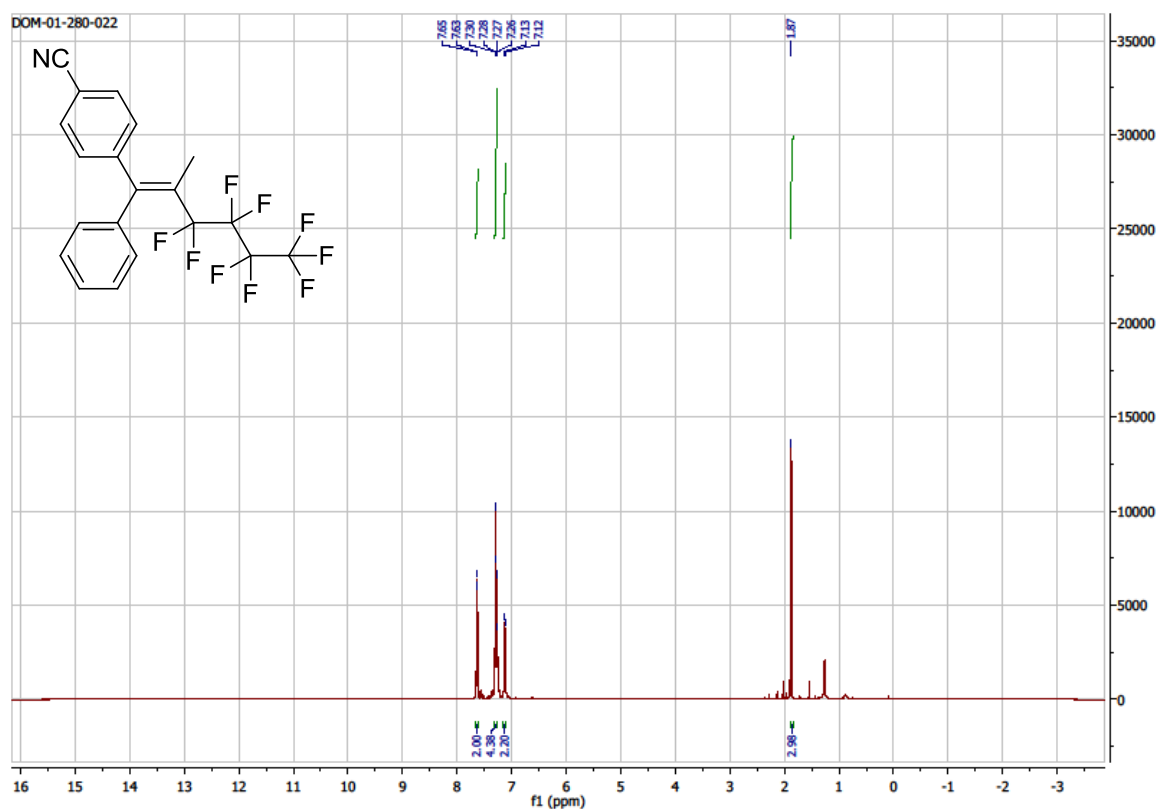


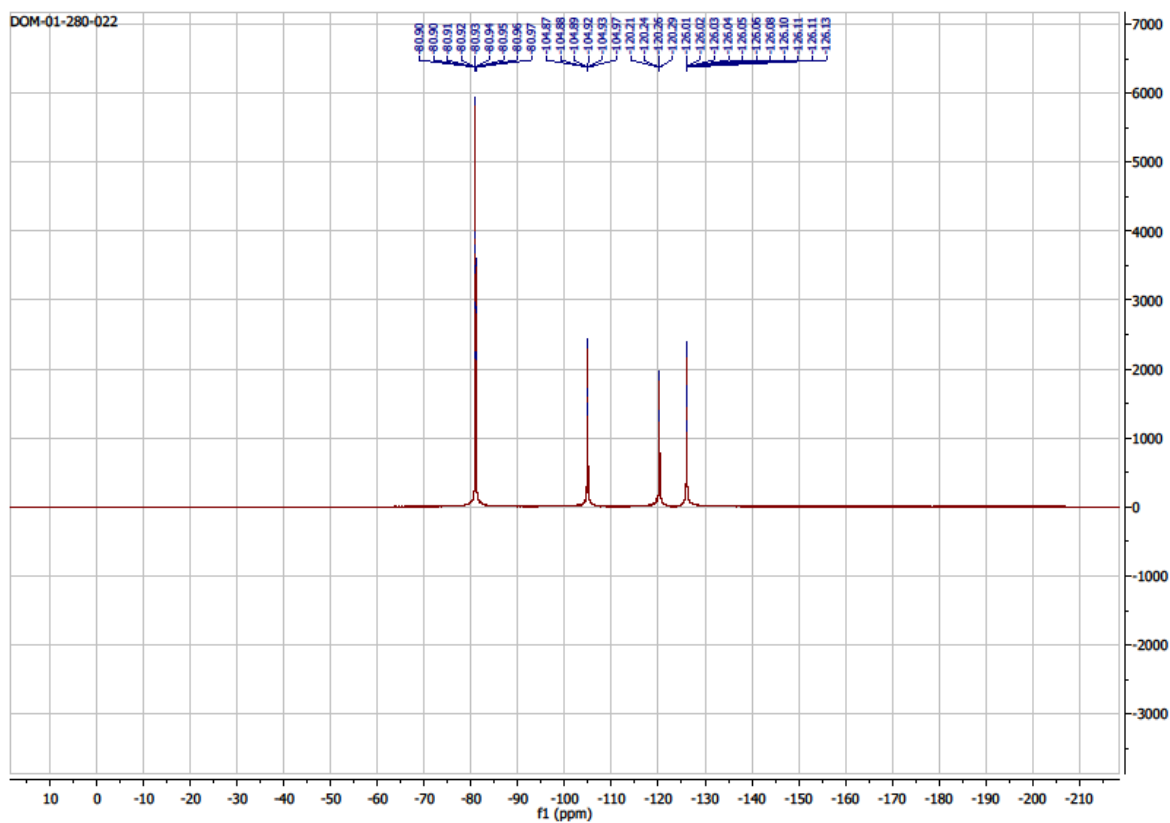
(Z)-1,2,3-trimethoxy-5-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-(4-(trifluoromethyl)phenyl)hex-1-en-1-yl)benzene (31)



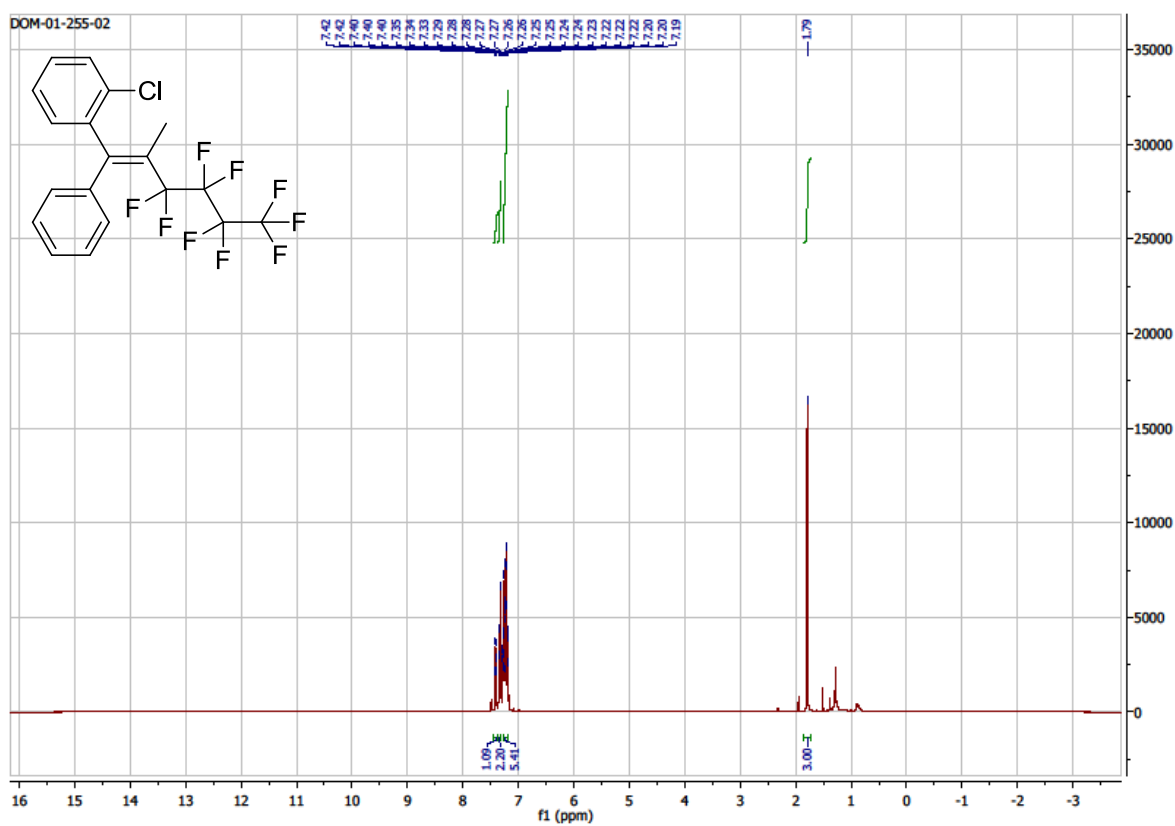


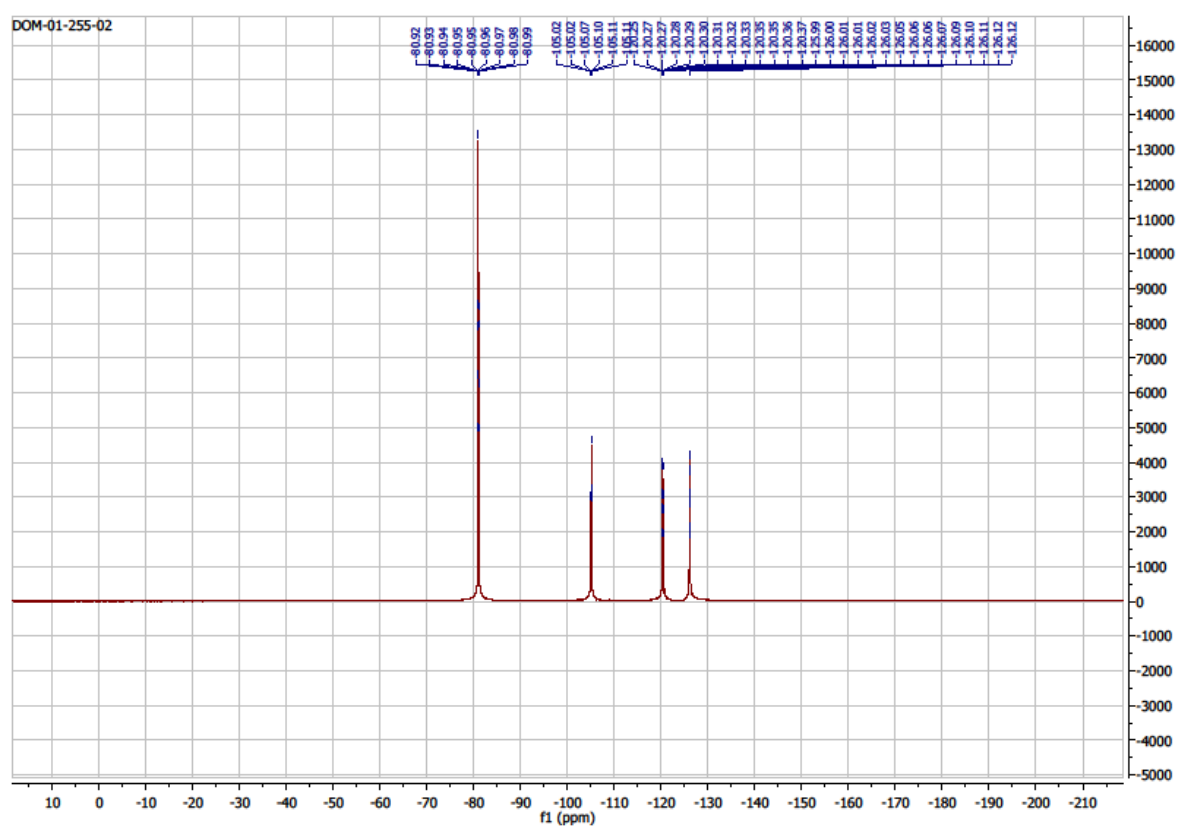
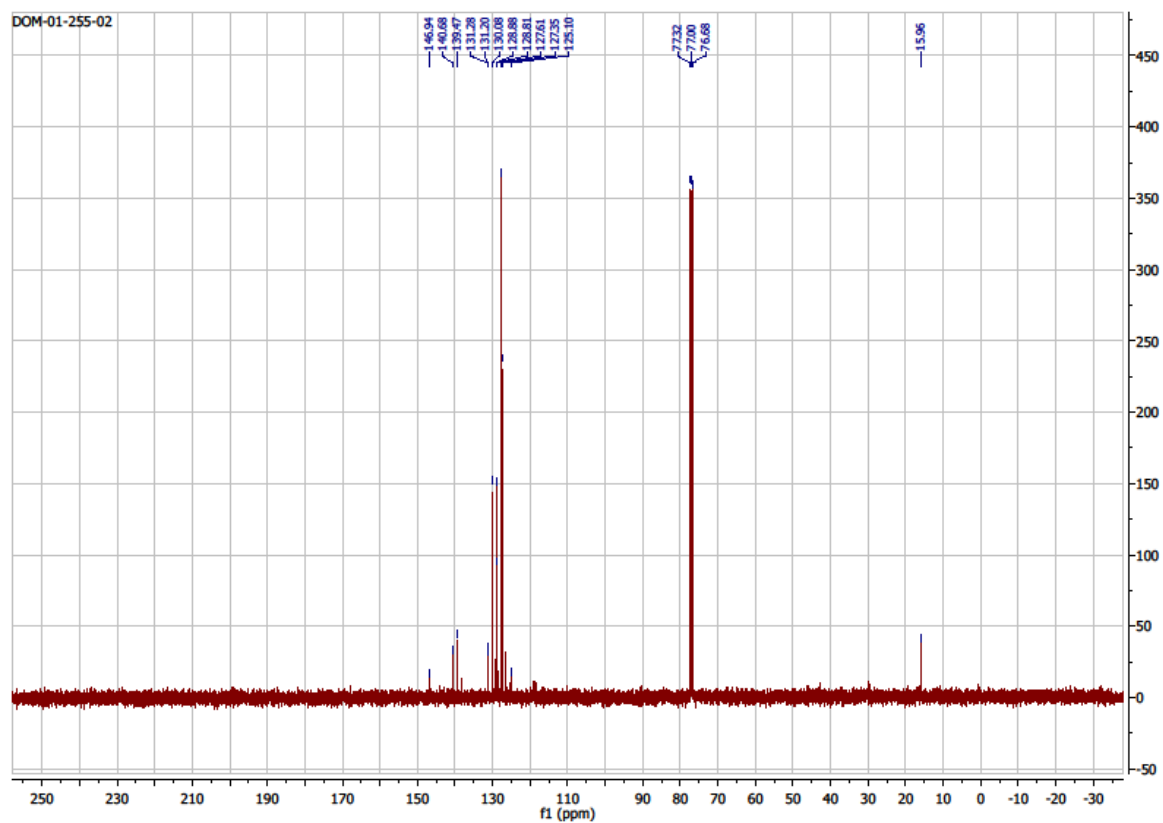
(E)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzonitrile (32)



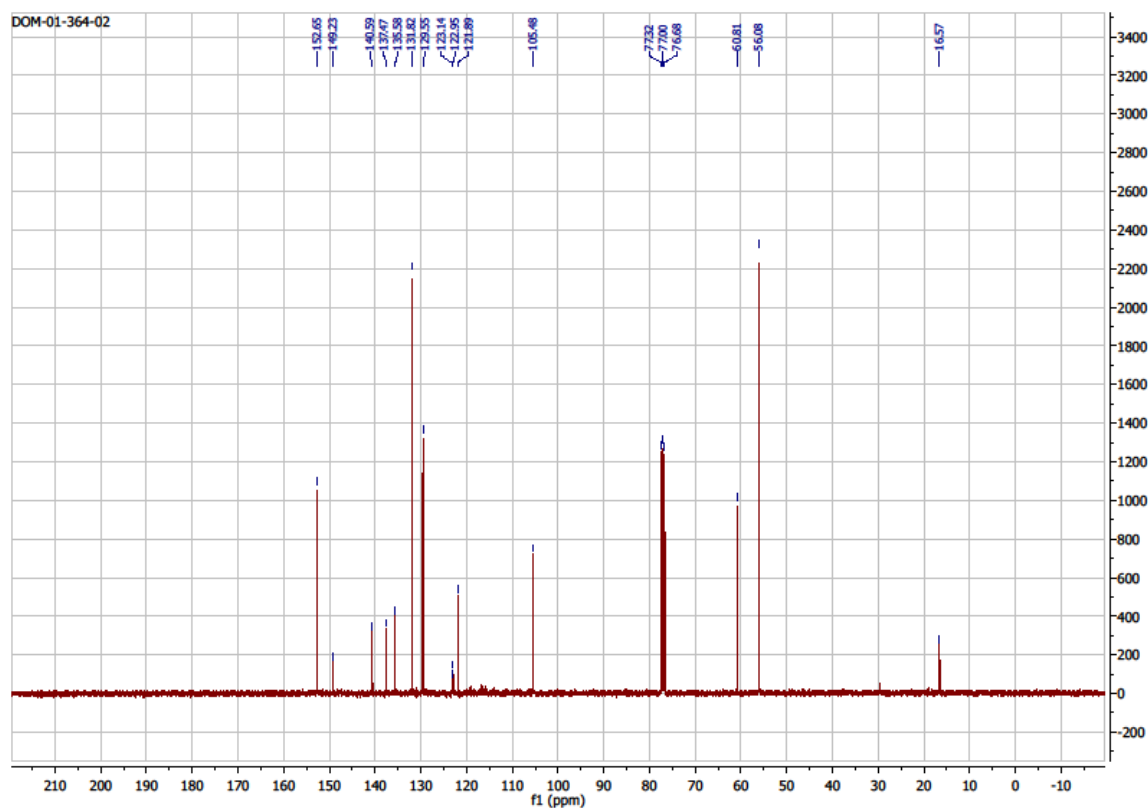
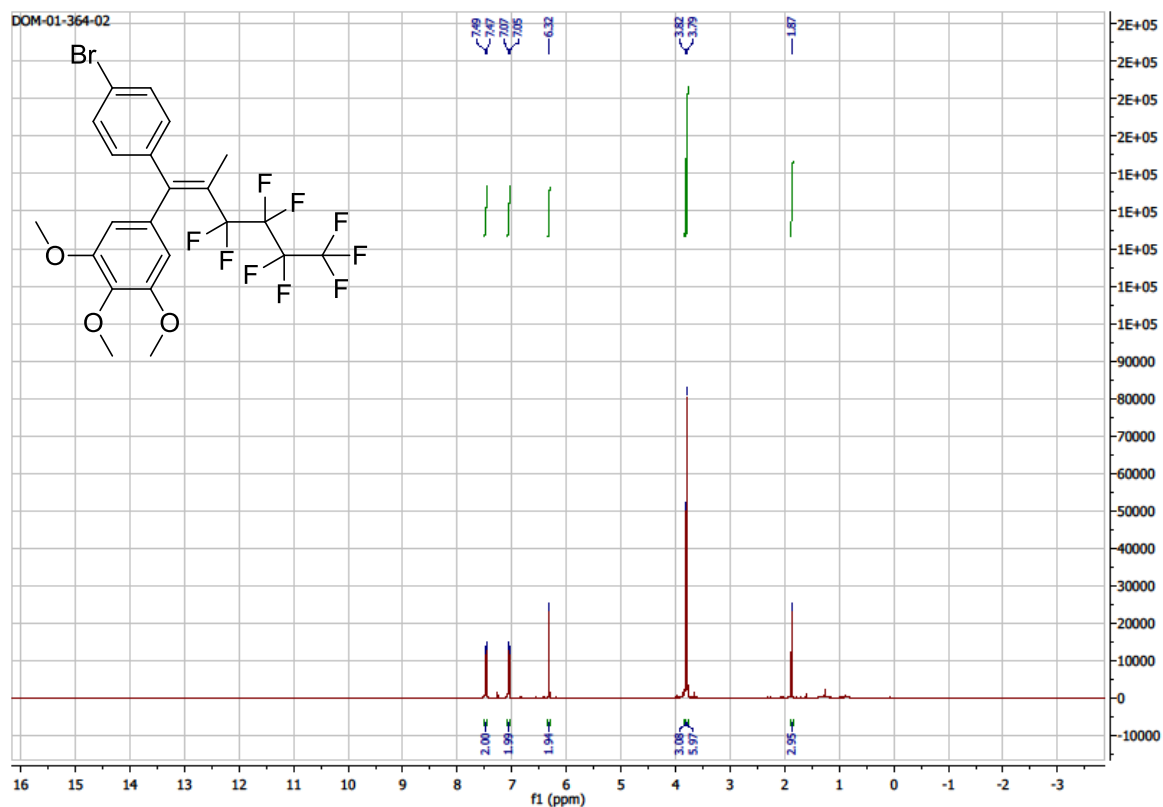


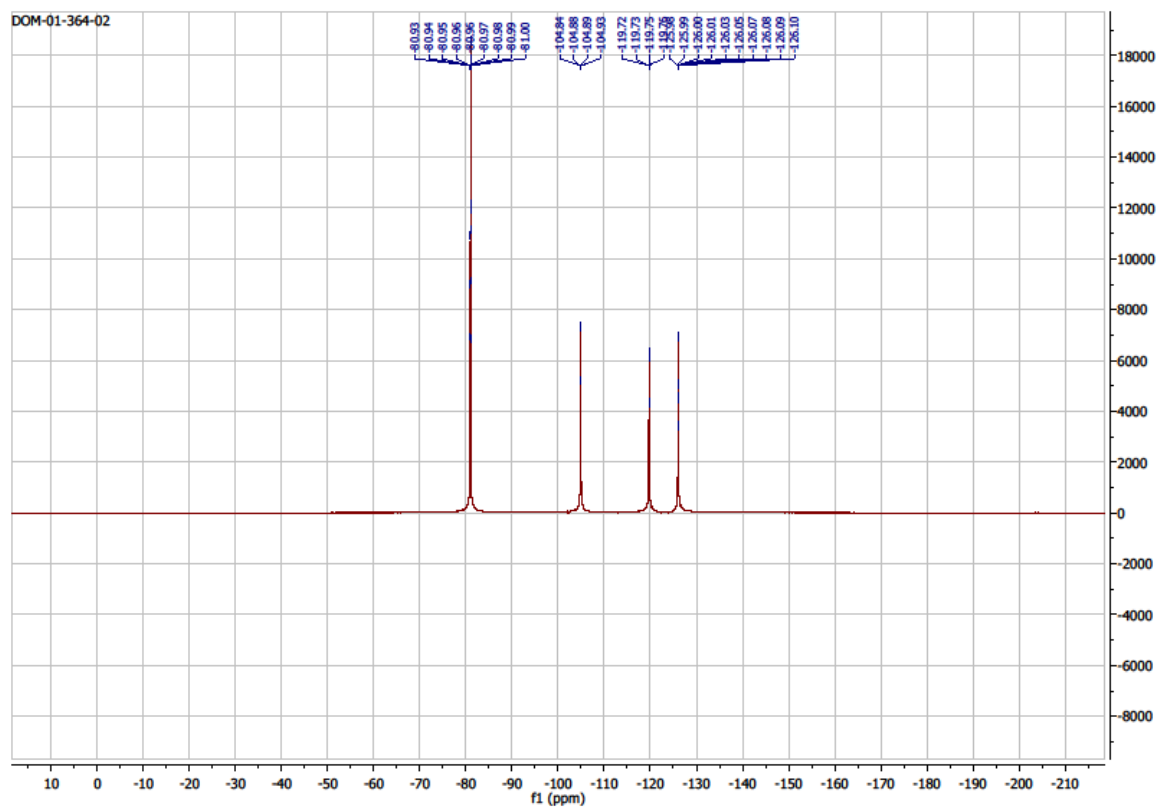
(*E*)-1-chloro-2-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzene (33)



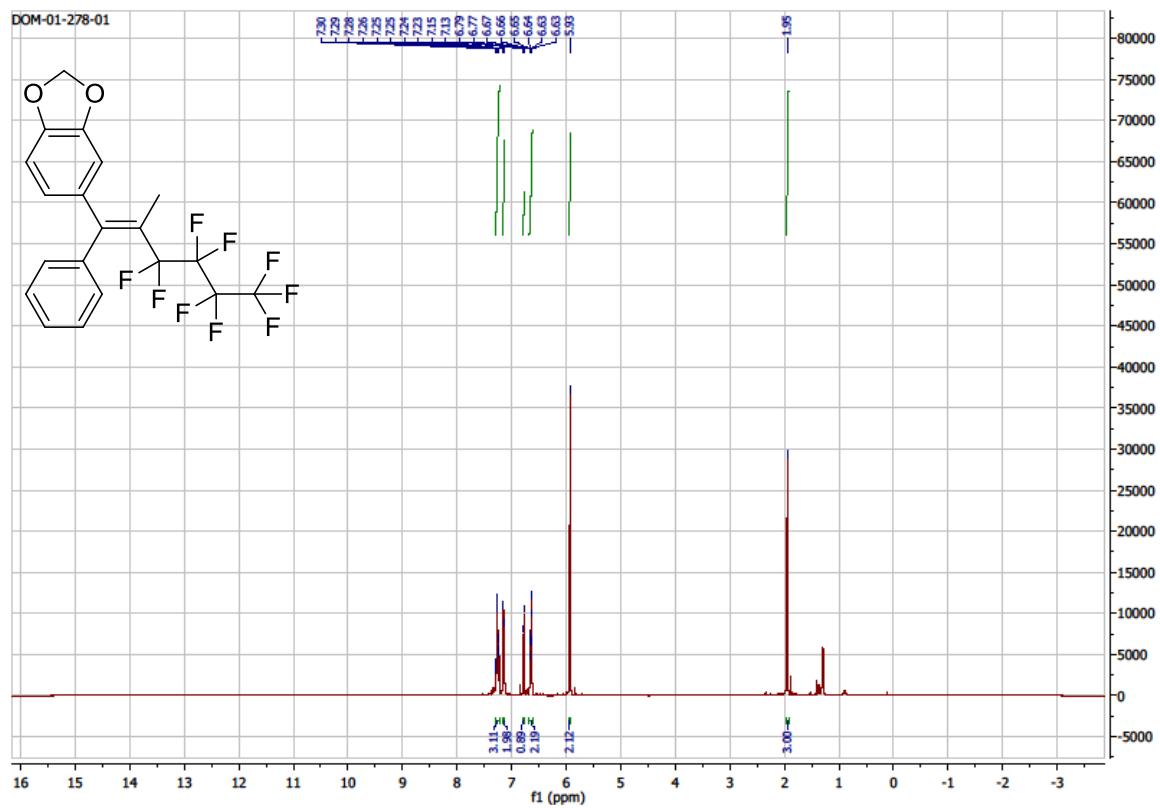


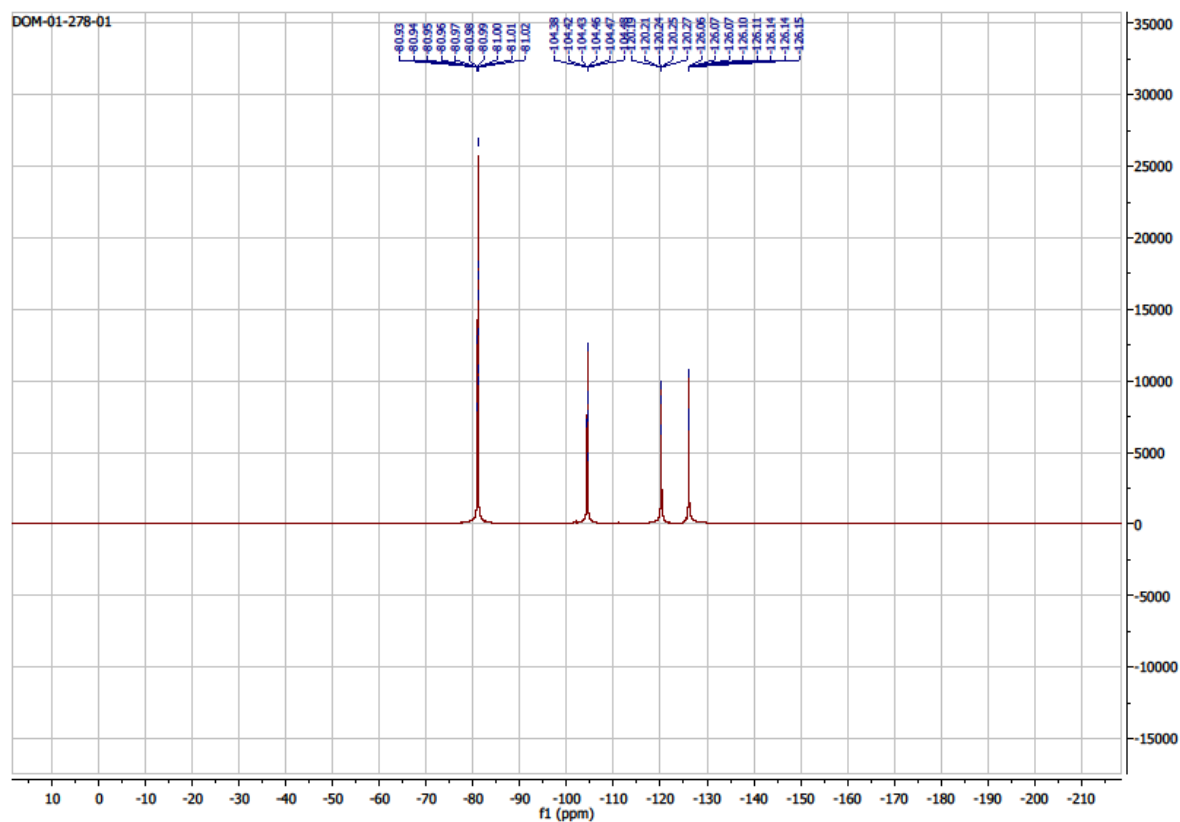
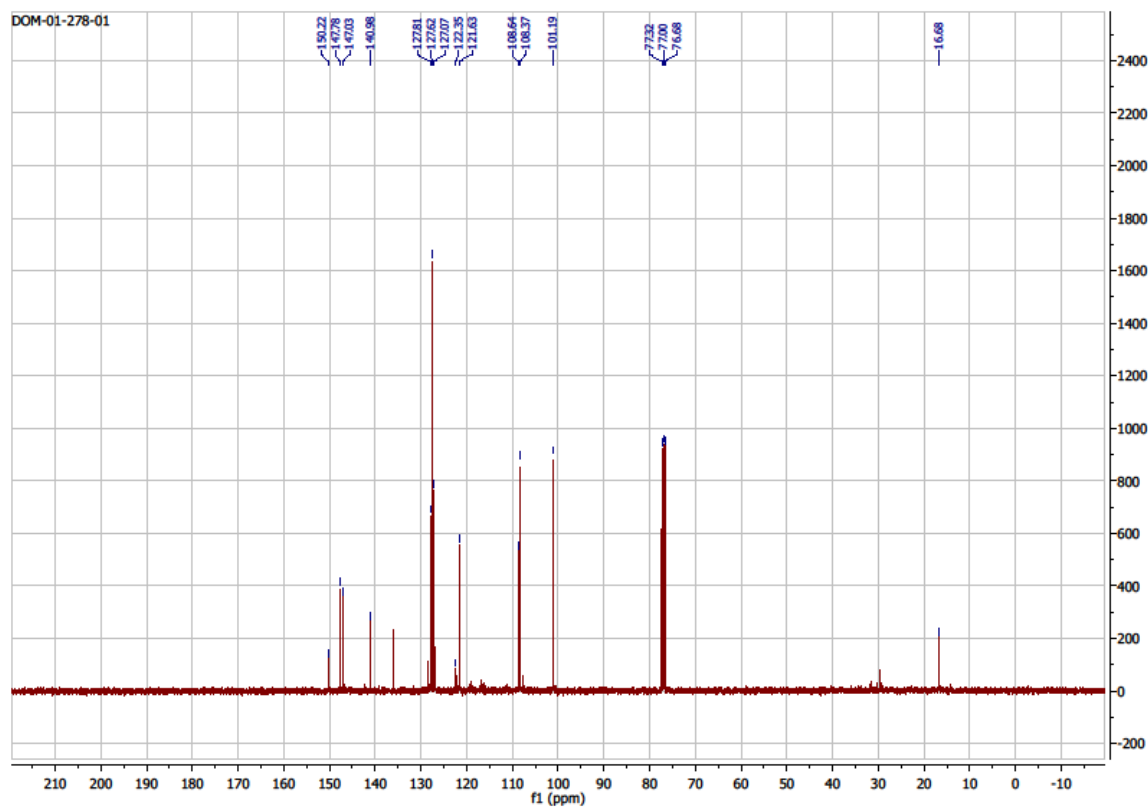
(Z)-5-(1-(4-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluoro-2-methylhex-1-en-1-yl)-1,2,3-trimethoxybenzene (34)



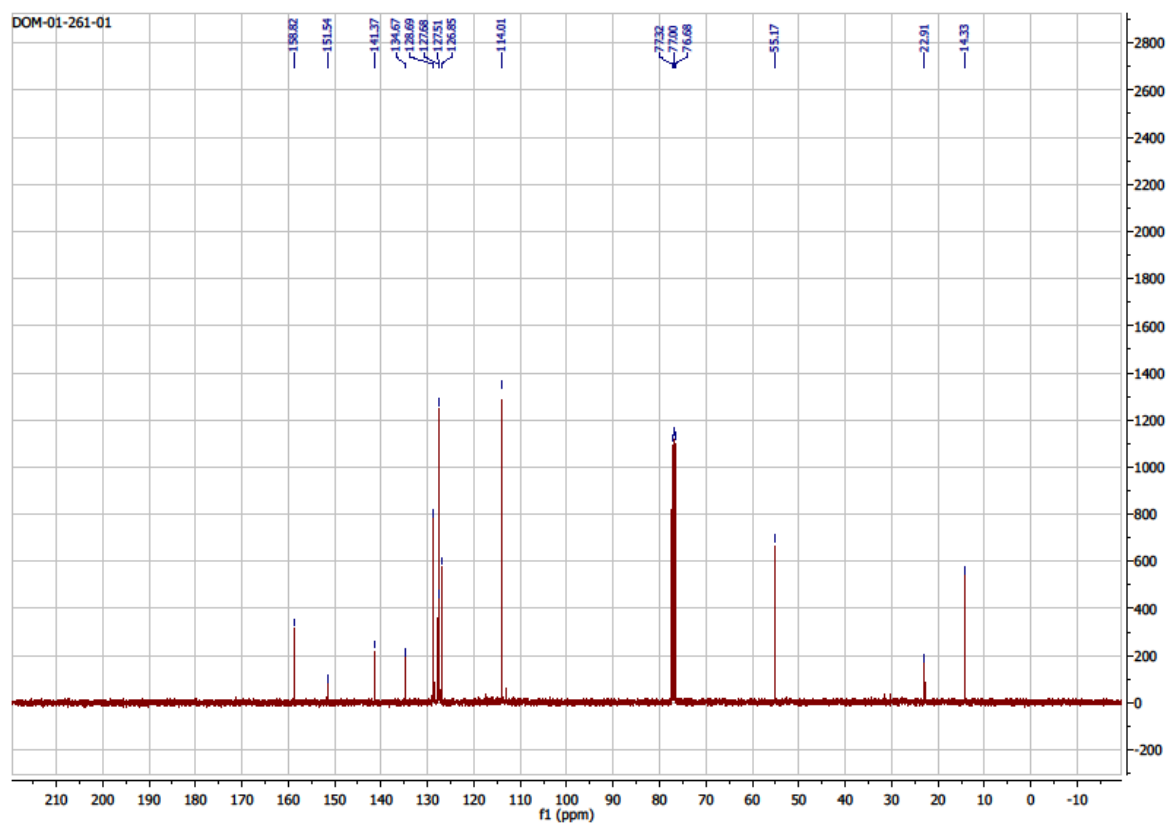
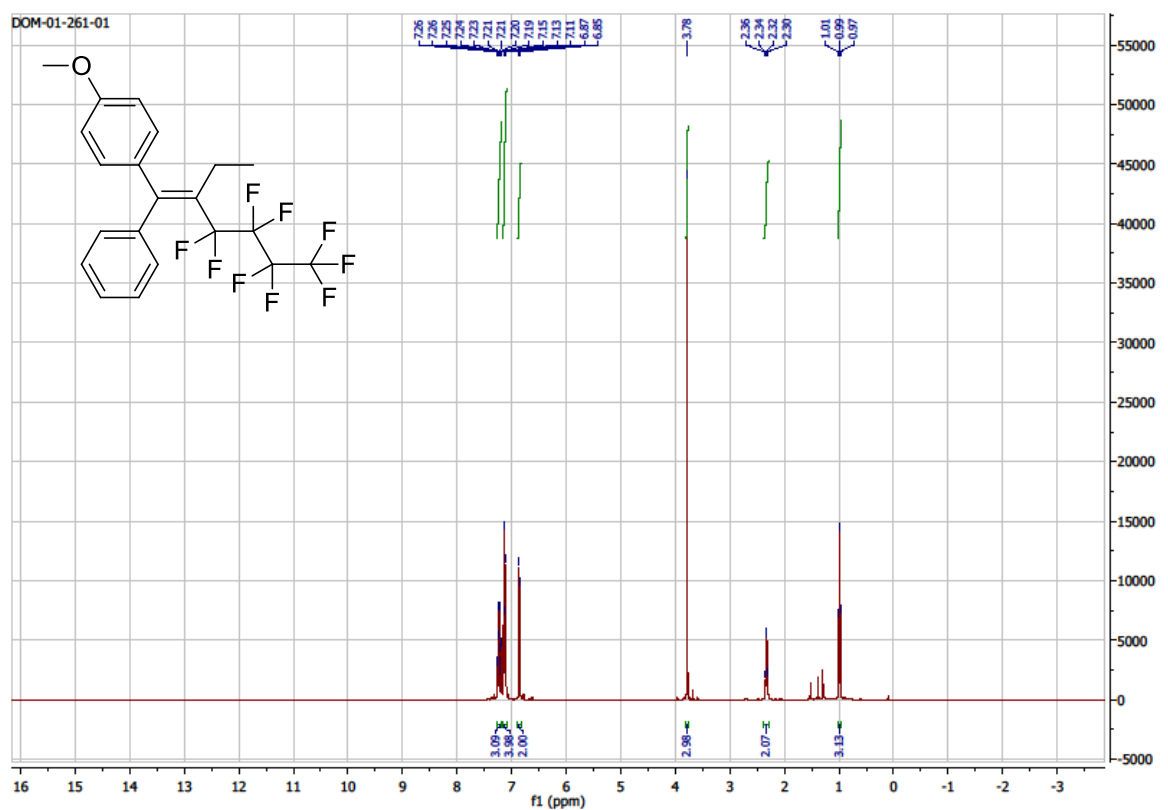


(E)-5-(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-phenylhex-1-en-1-yl)benzo[d][1,3]dioxole (35)

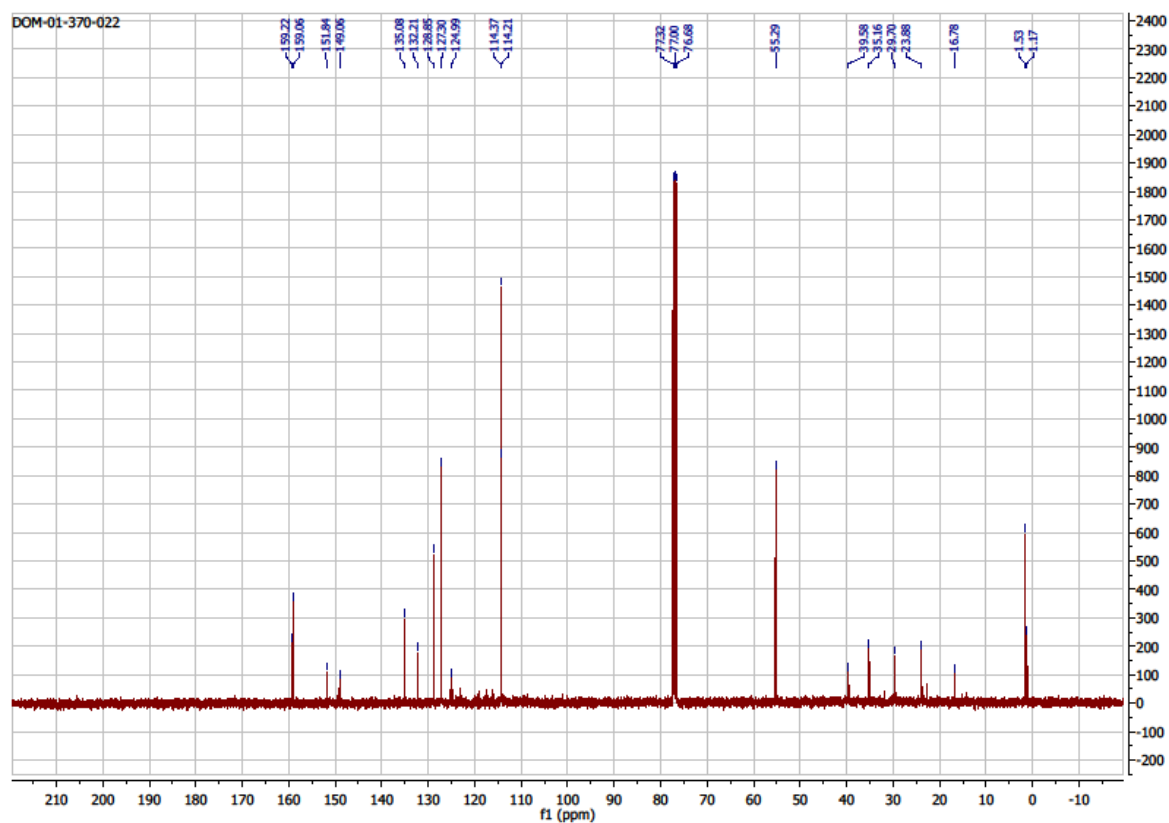
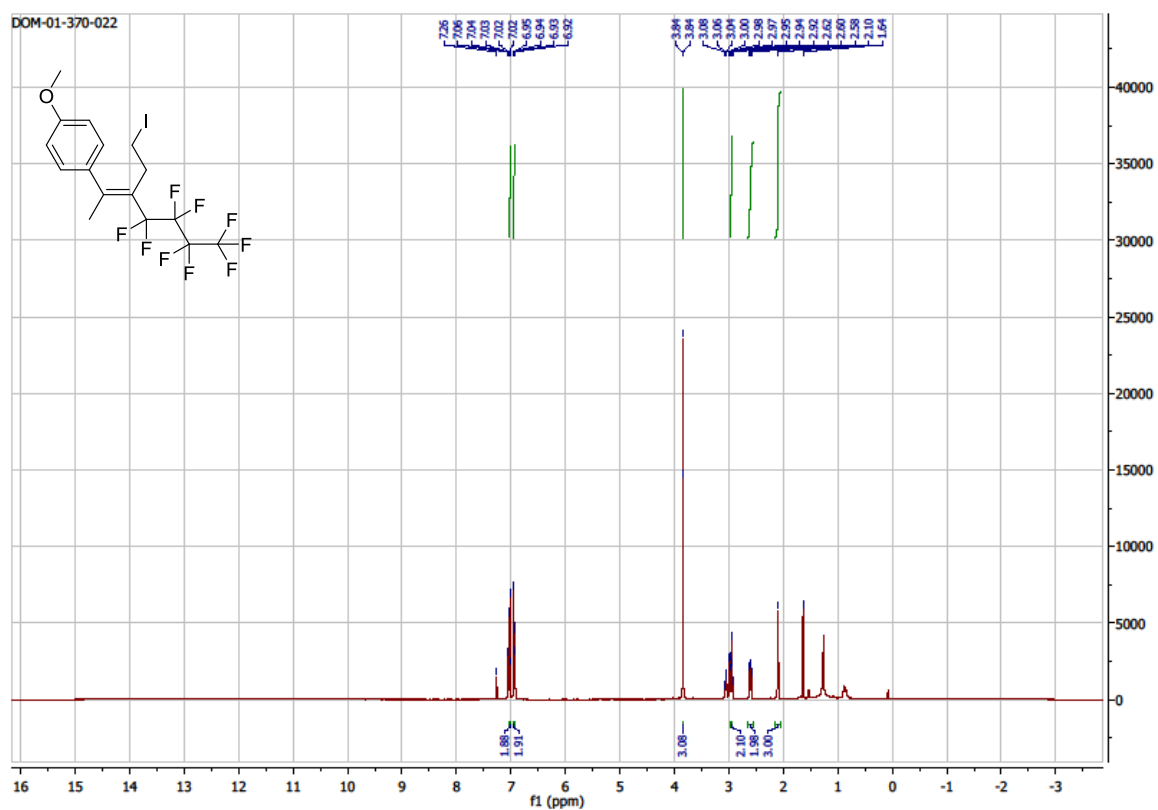


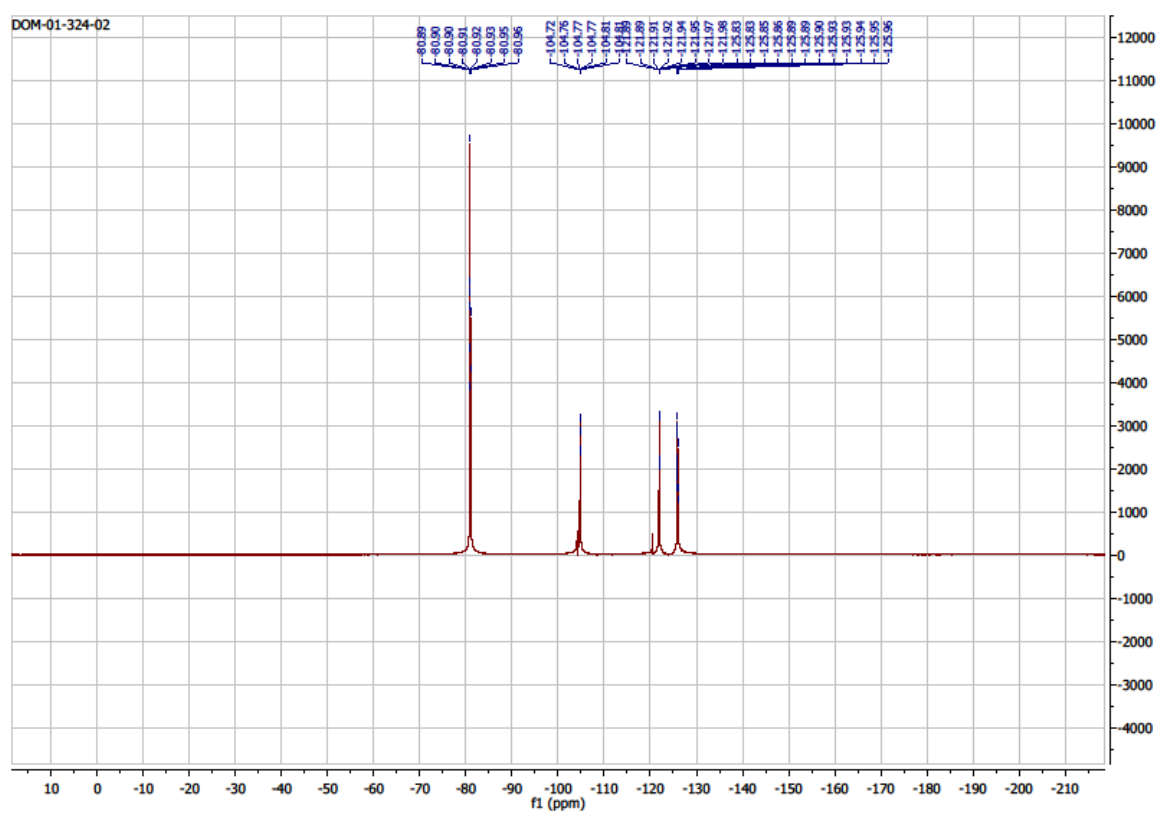
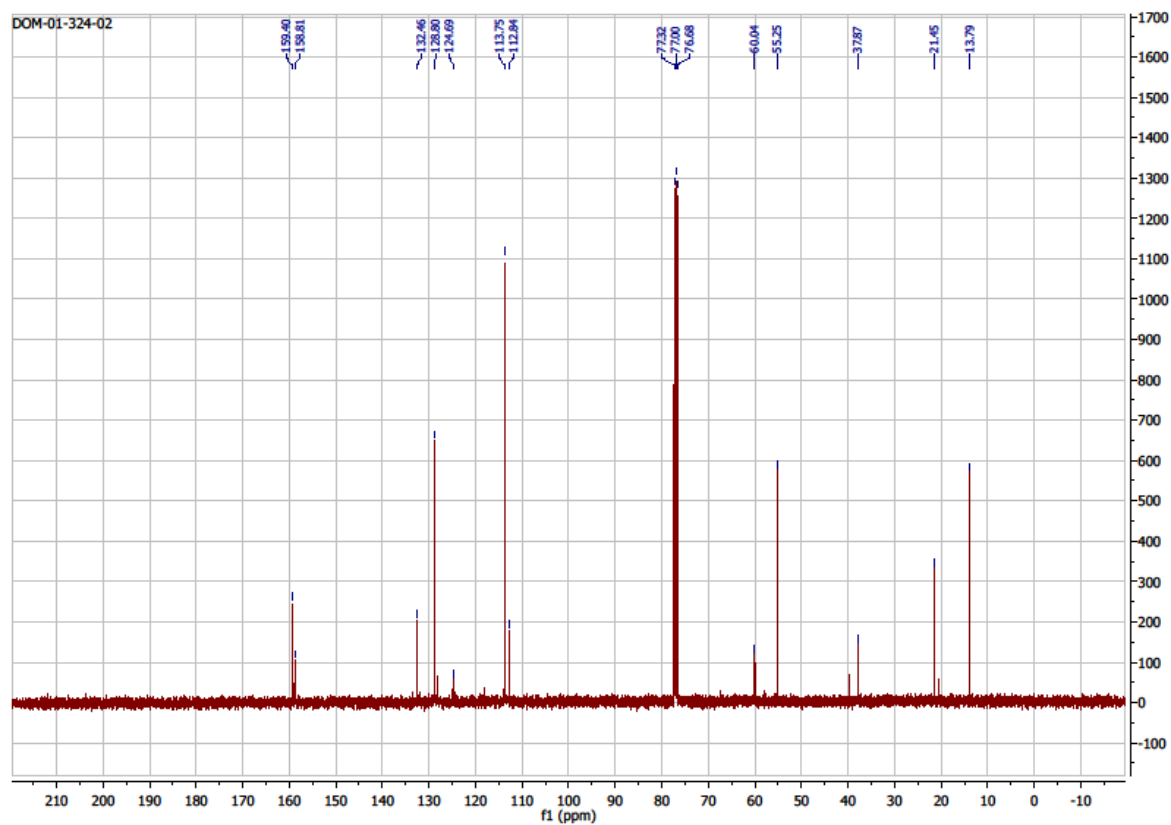


(E)-1-(2-ethyl-3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)-4-methoxybenzene (36)

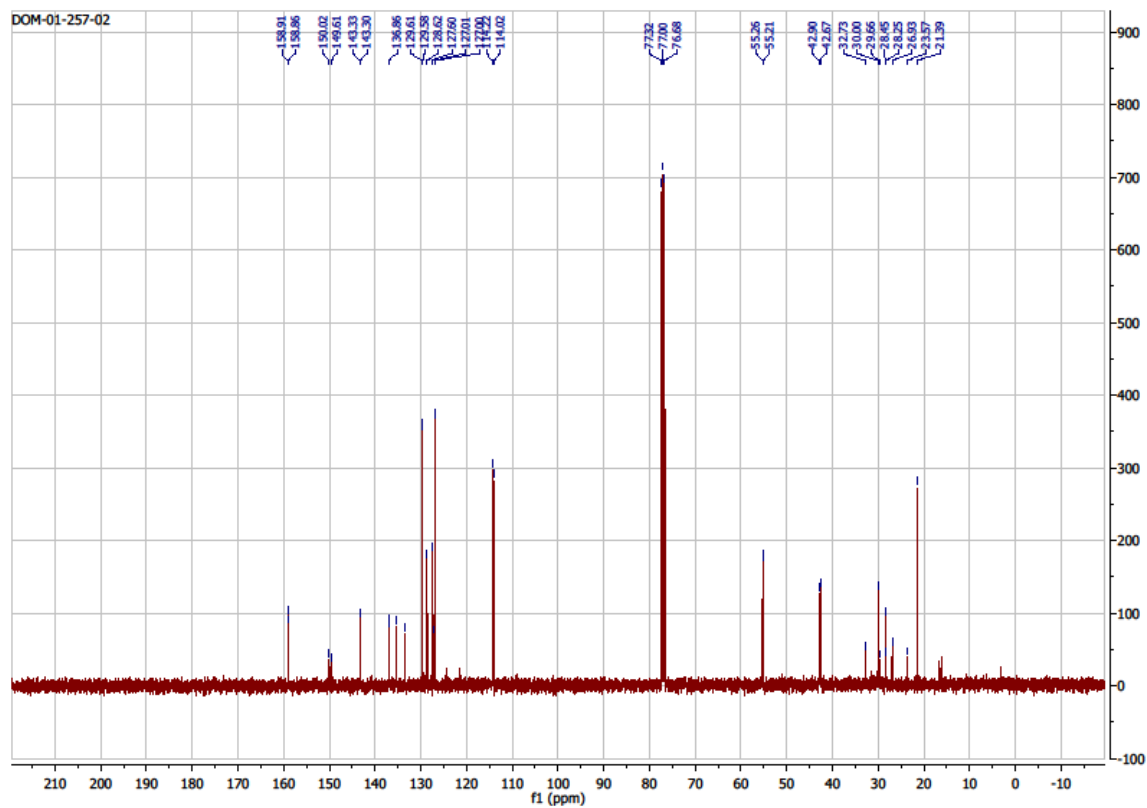
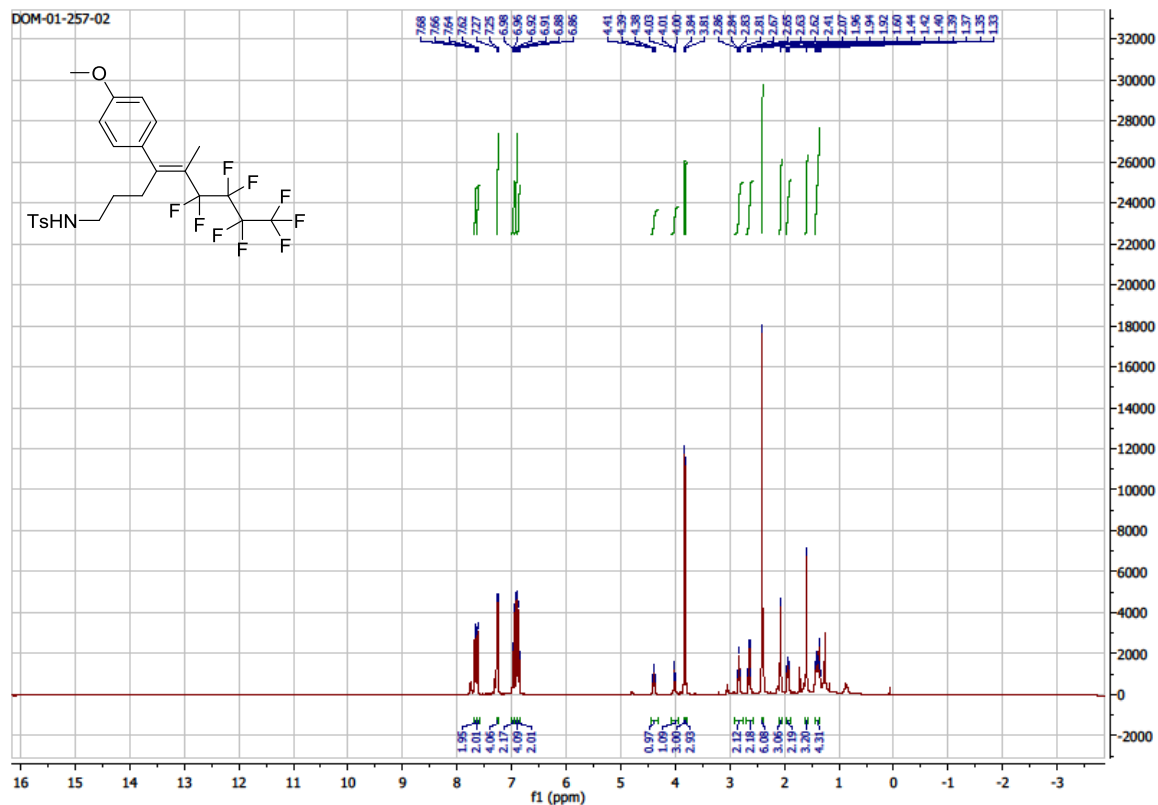


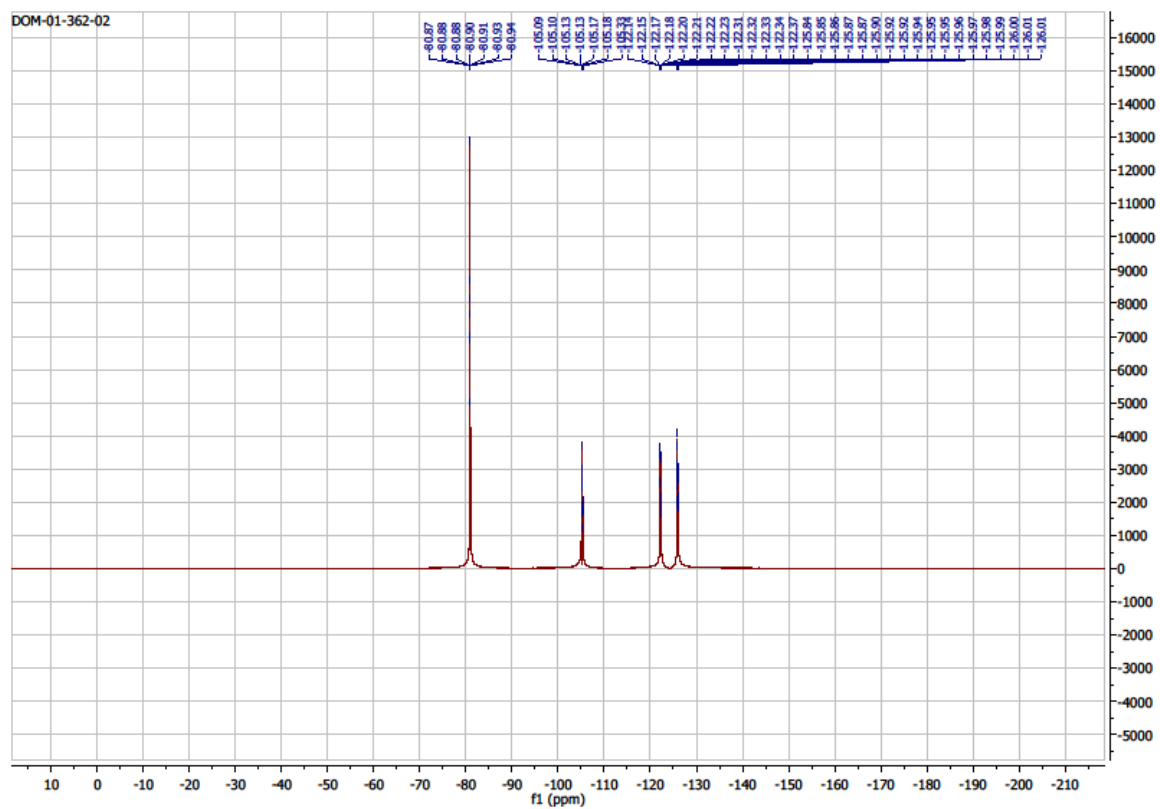
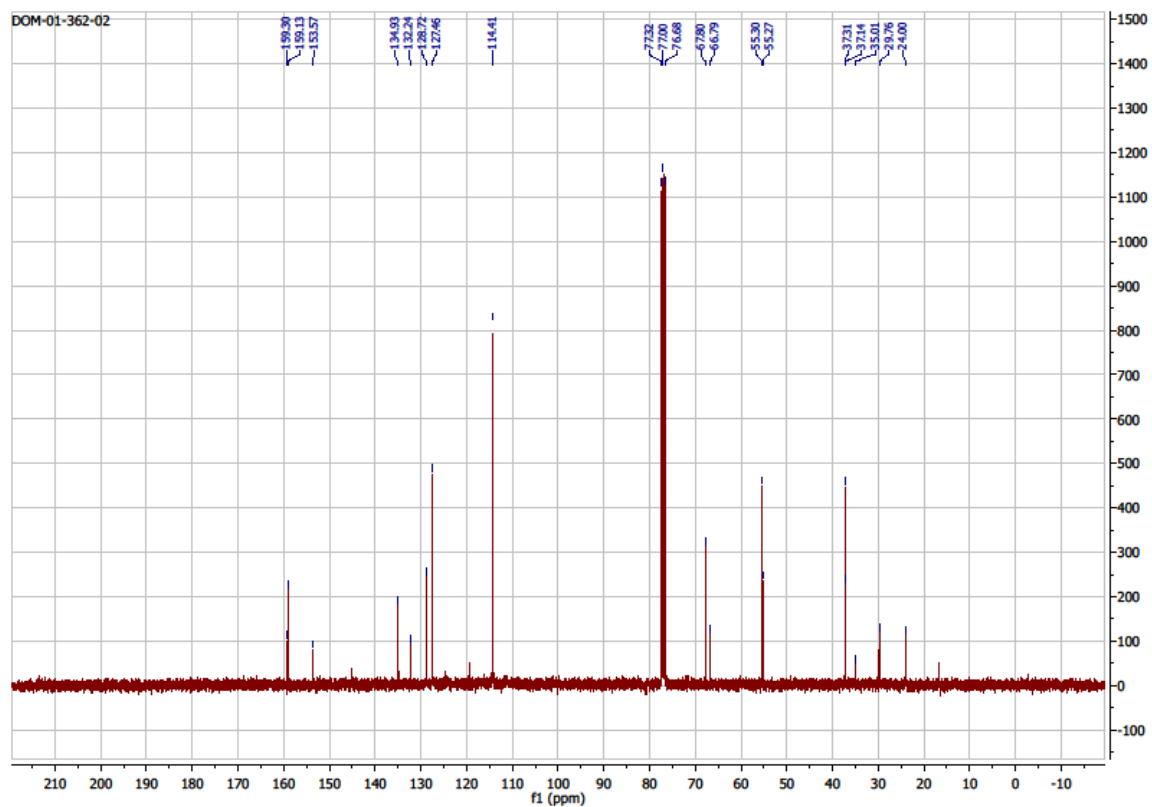
(E)-1-methoxy-4-(5,5,6,6,7,7,8,8,8-nonafluoro-1-iodo-4-methyloct-3-en-3-yl)benzene (38)



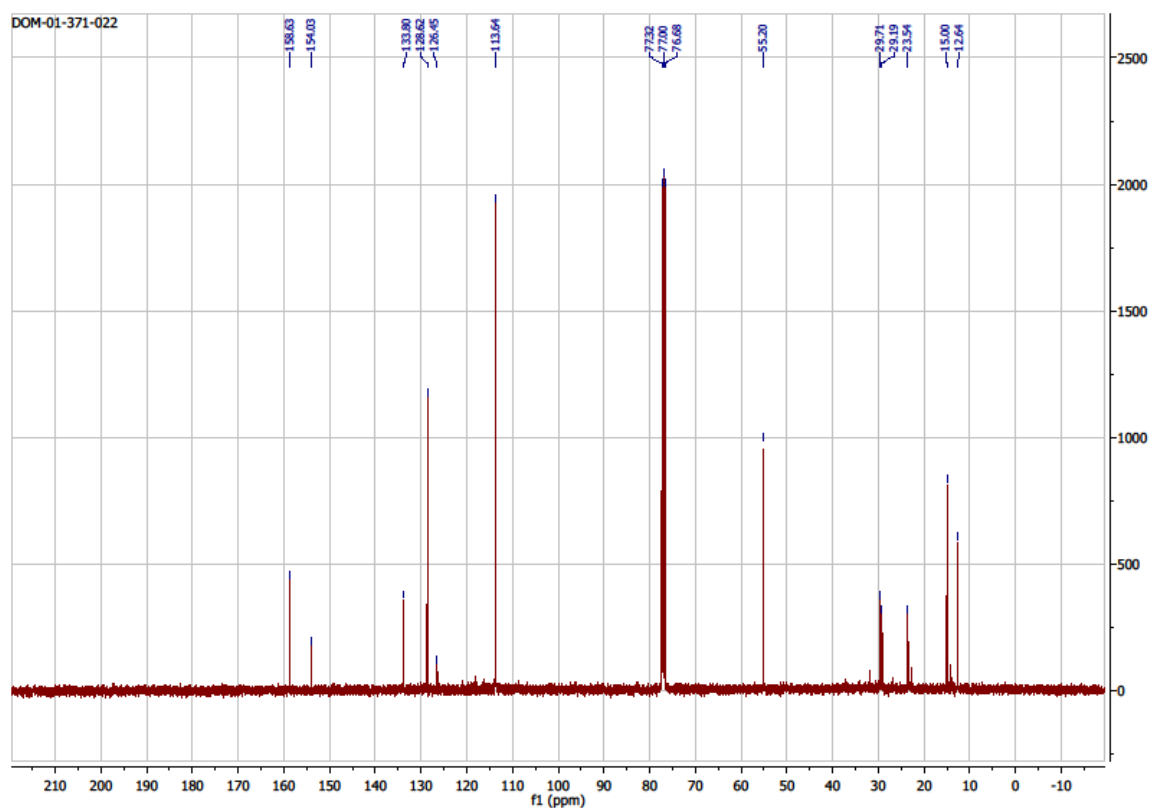
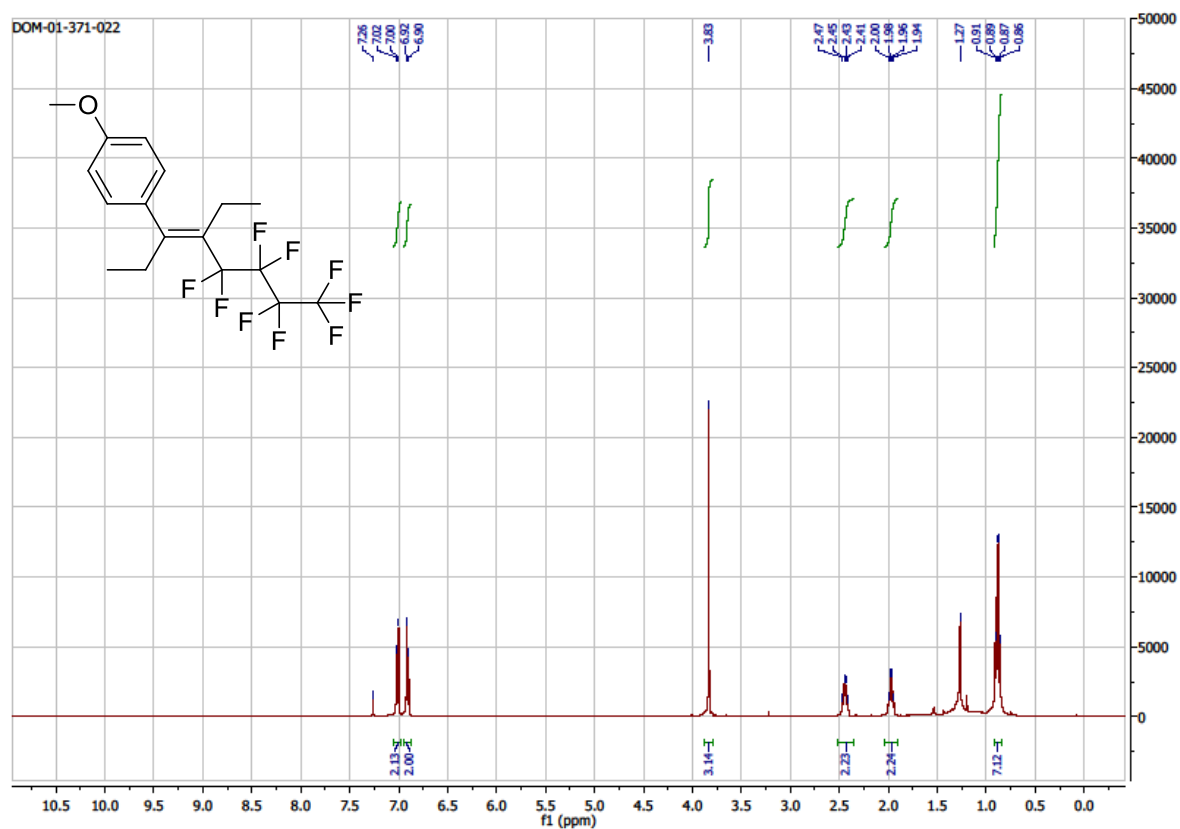


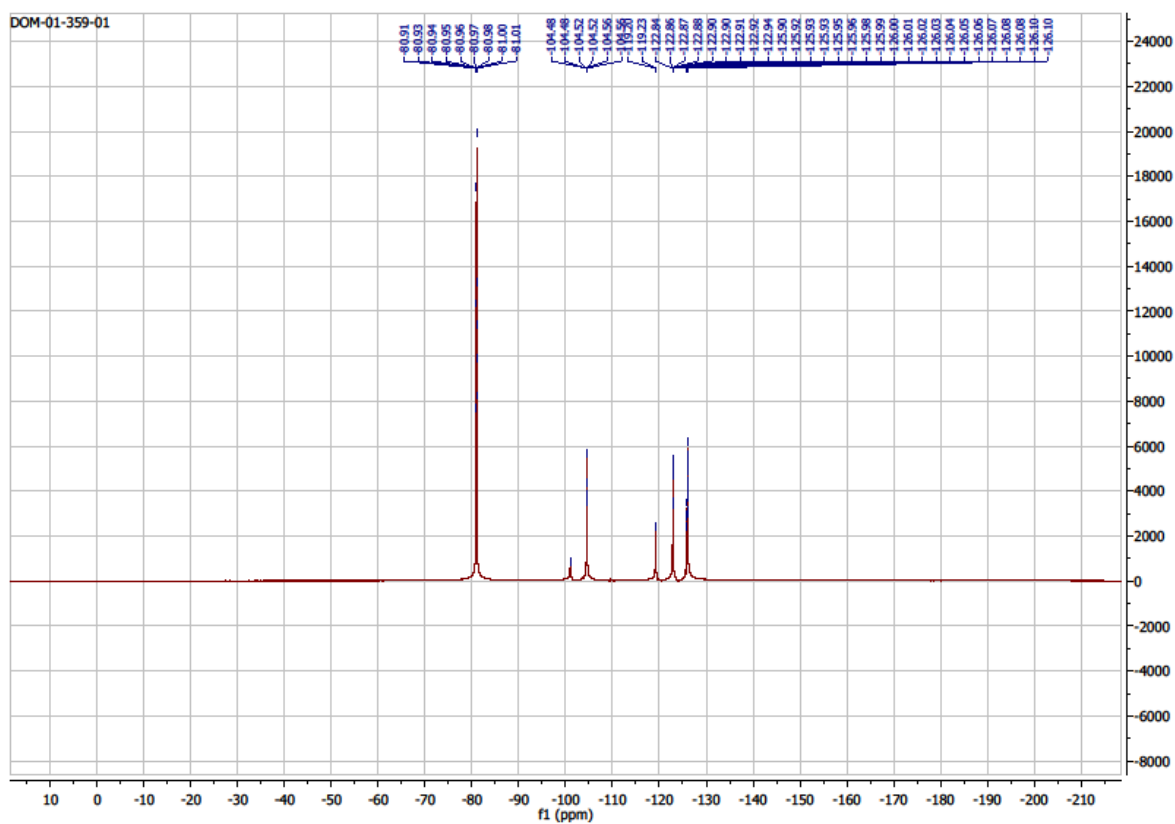
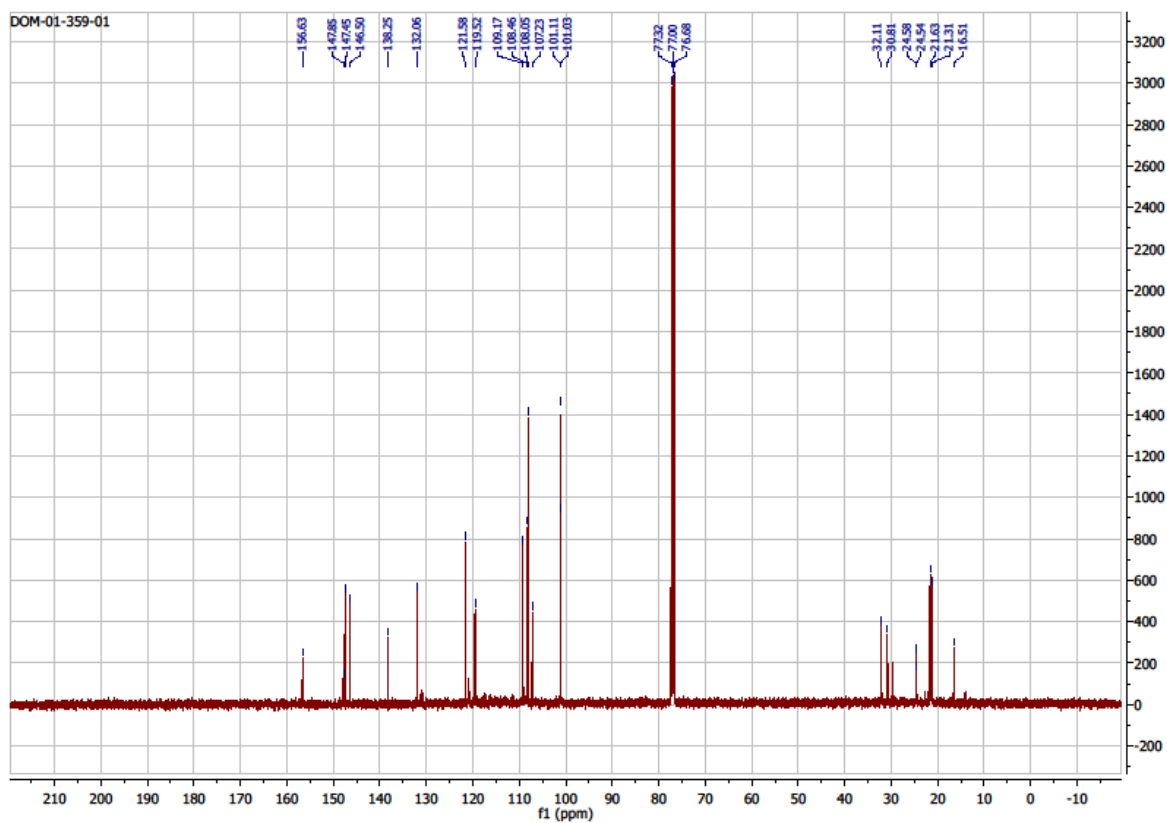
(E)-4-methyl-N-(7,7,8,8,9,9,10,10,10-nonafluoro-5-(4-methoxyphenyl)-6-methyldec-5-en-1-yl)benzenesulfonamide (40)



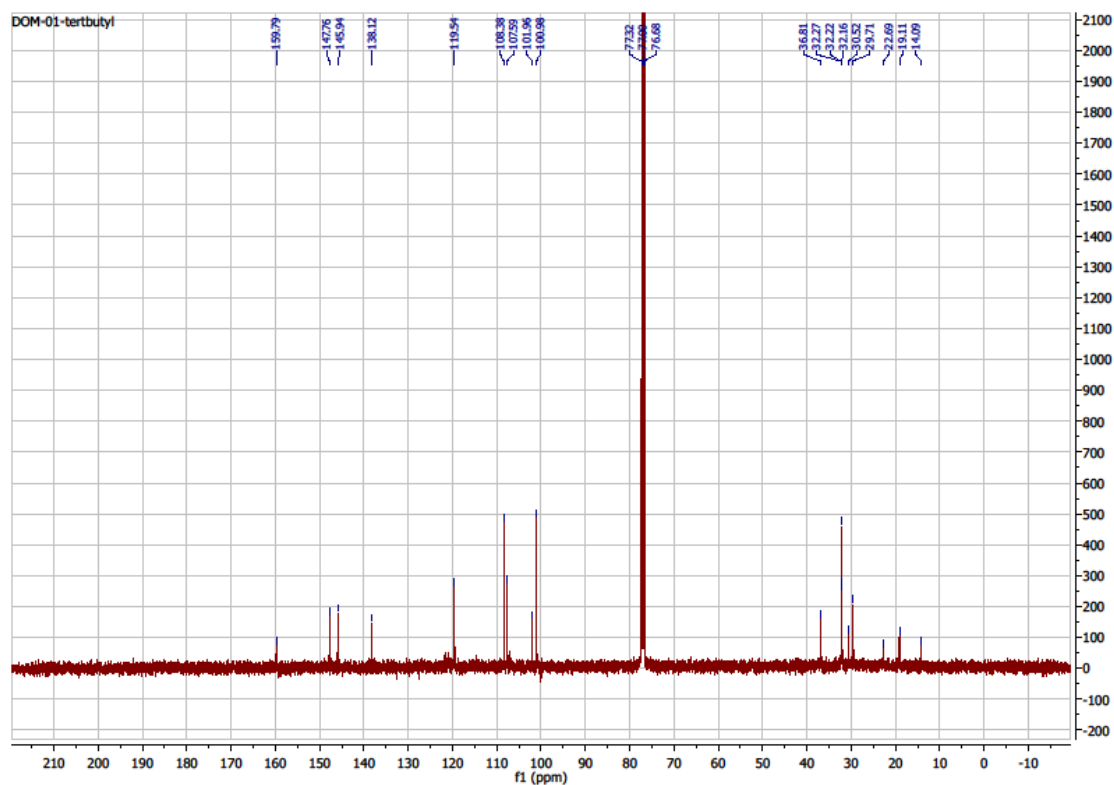
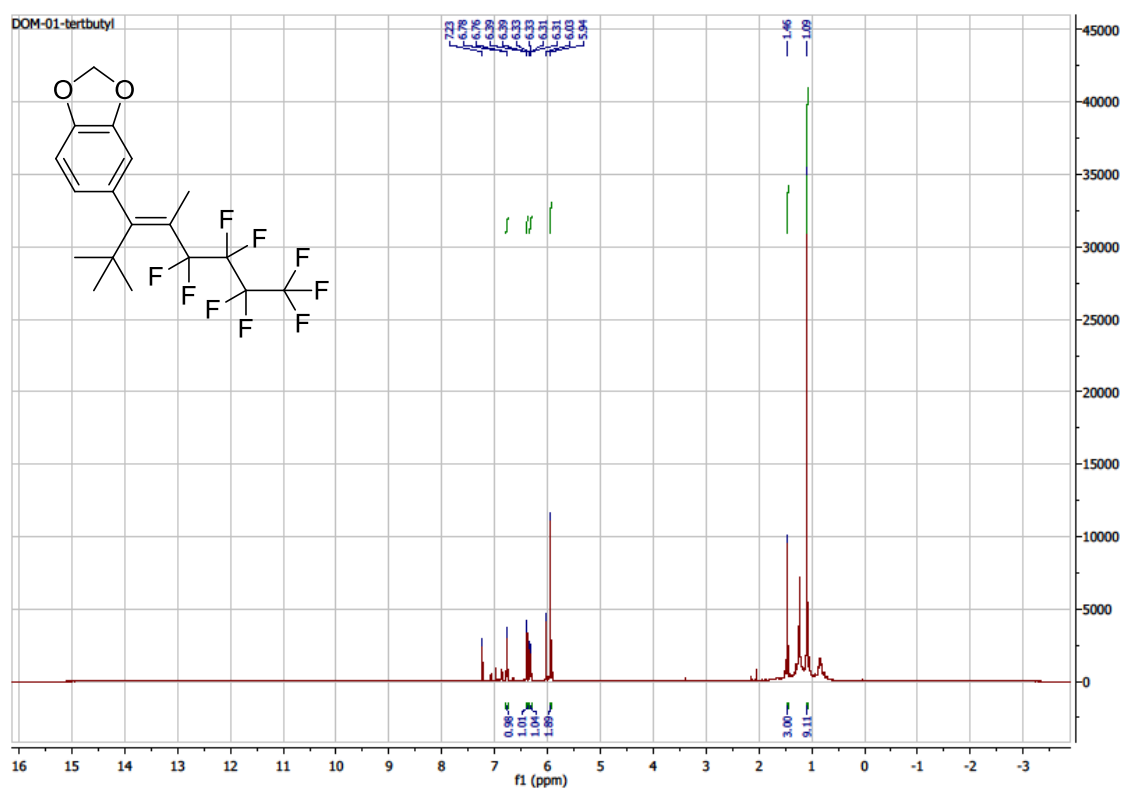


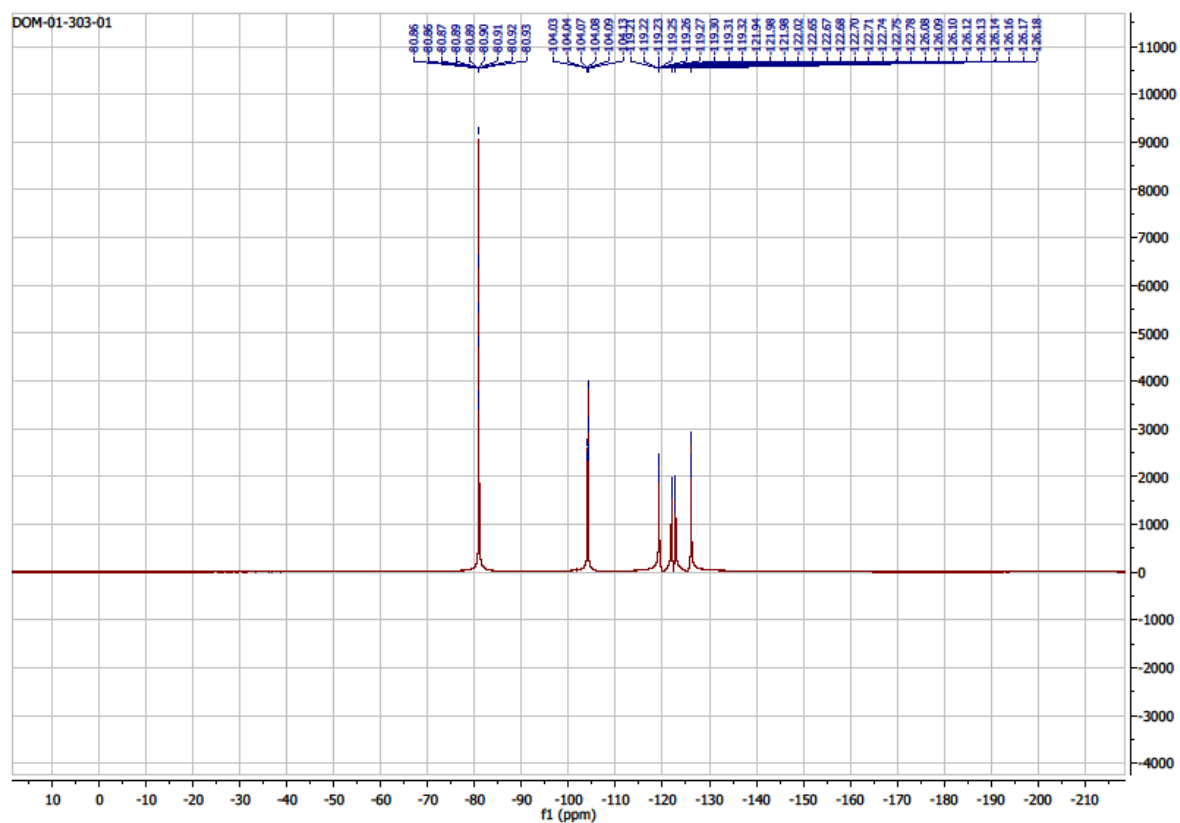
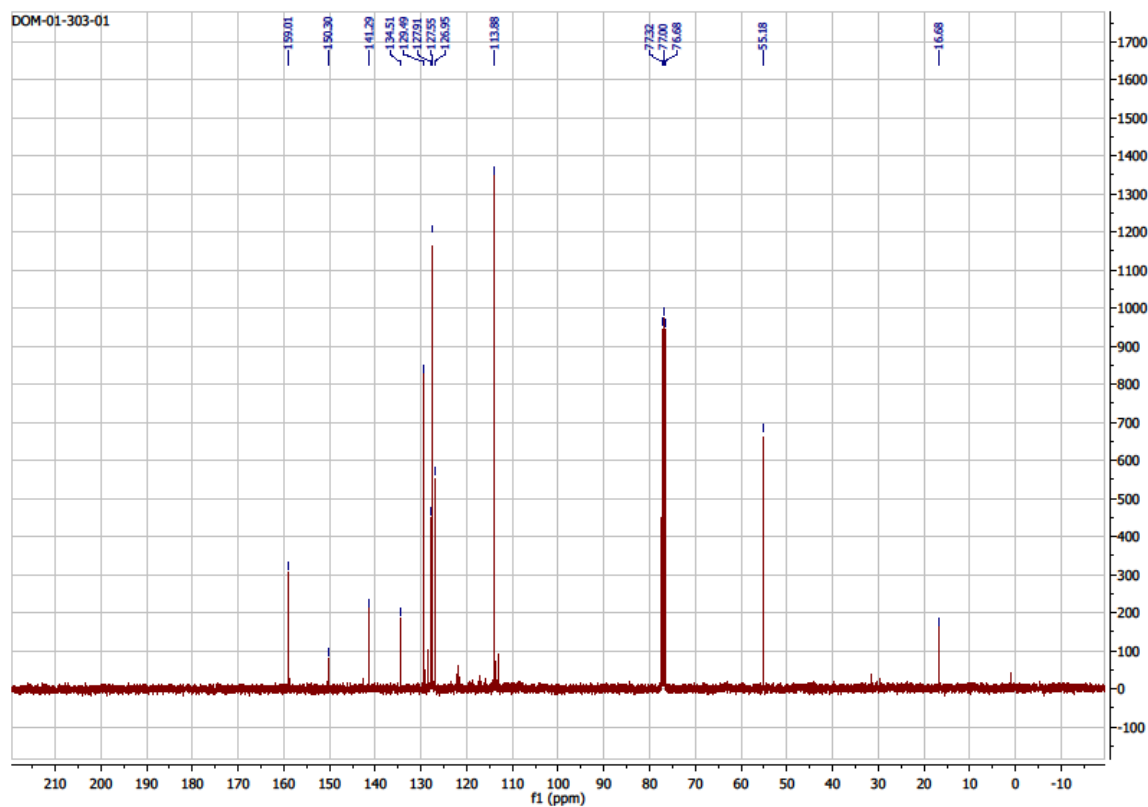
(E)-1-(4-ethyl-5,5,6,6,7,7,8,8,8-nonafluorooct-3-en-3-yl)-4-methoxybenzene (42)



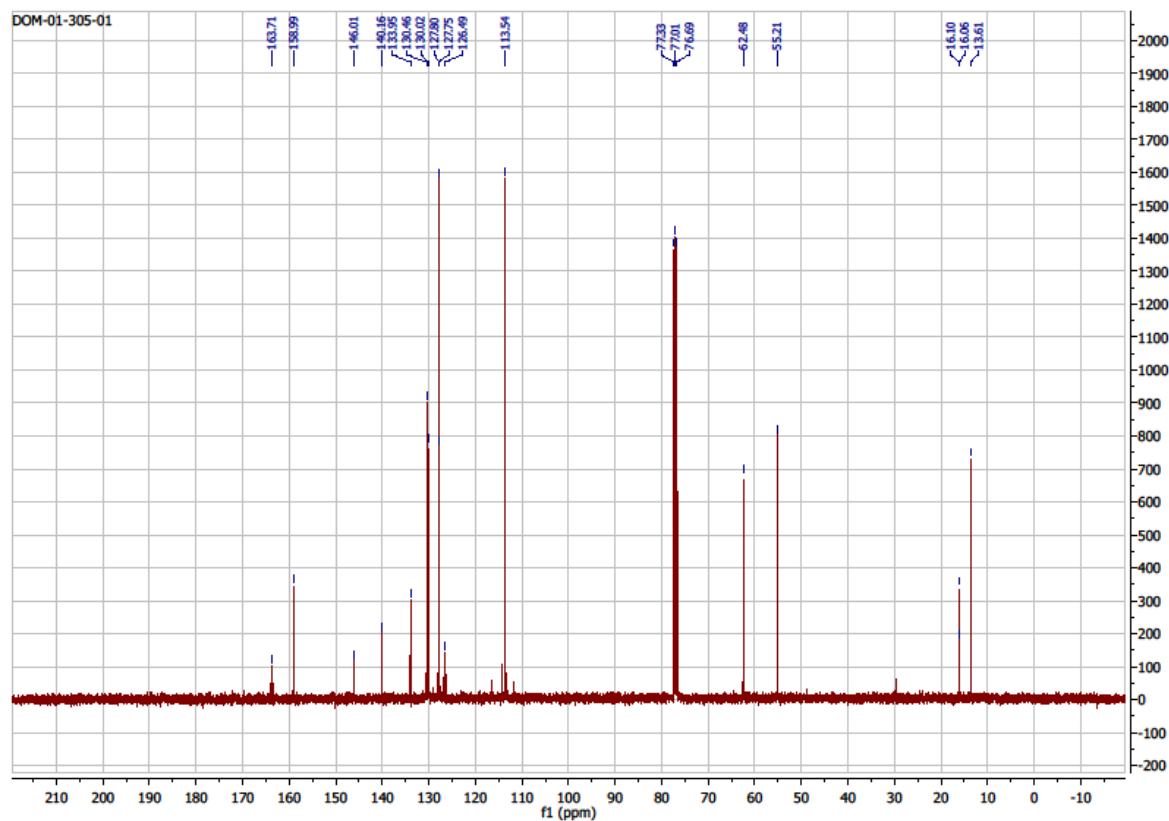
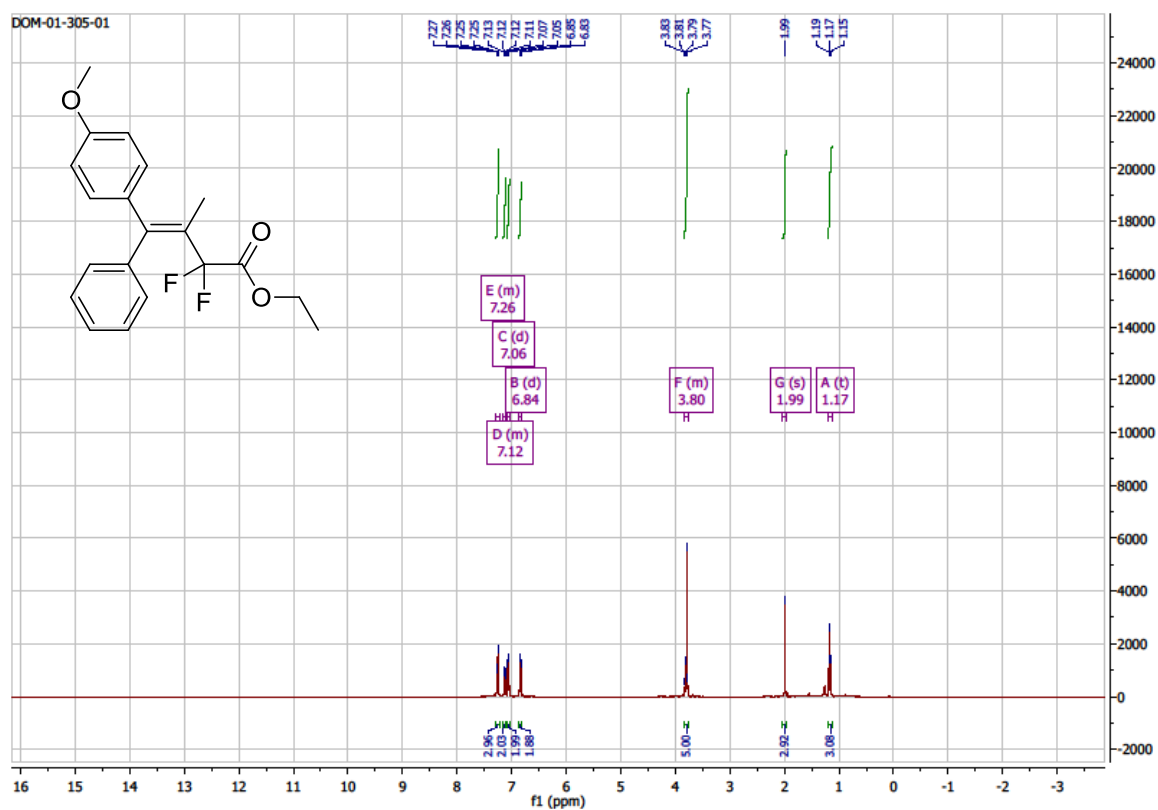


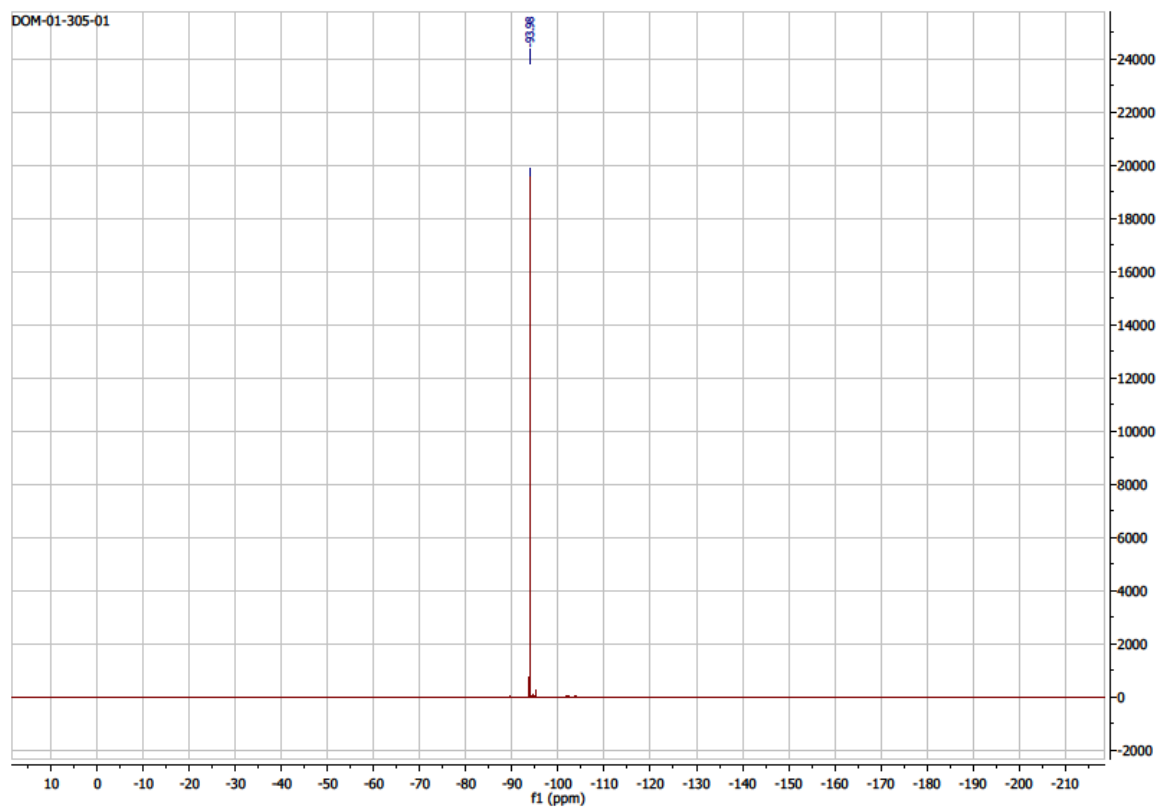
(E)-5-(5,5,6,6,7,7,8,8,8-nonafluoro-2,2,4-trimethyloct-3-en-3-yl)benzo[d][1,3]dioxole (44)



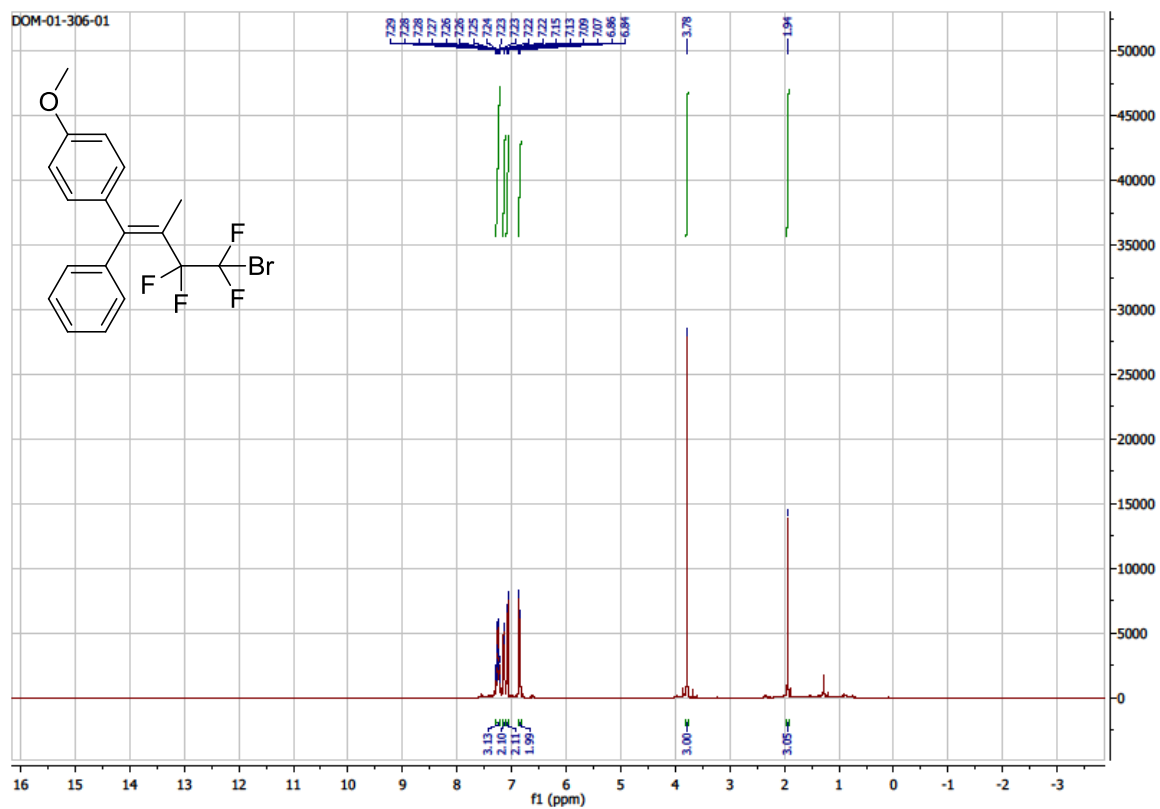


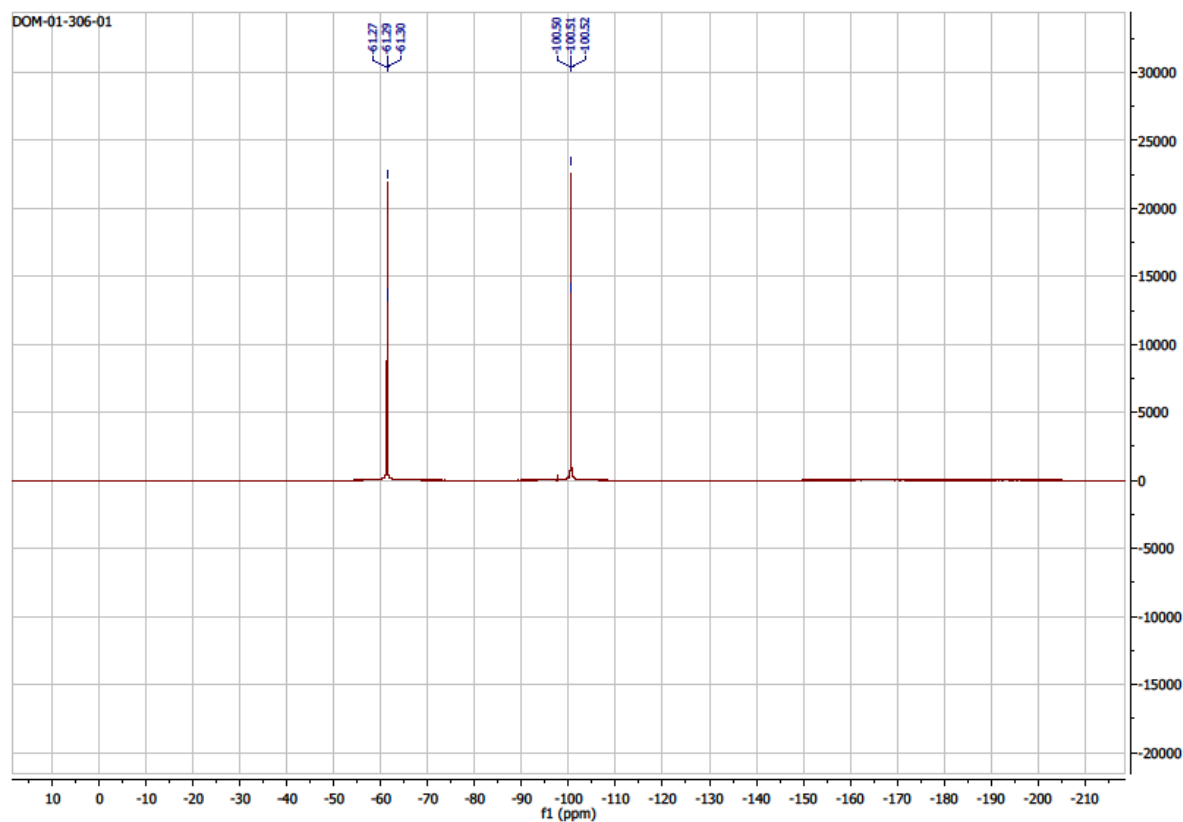
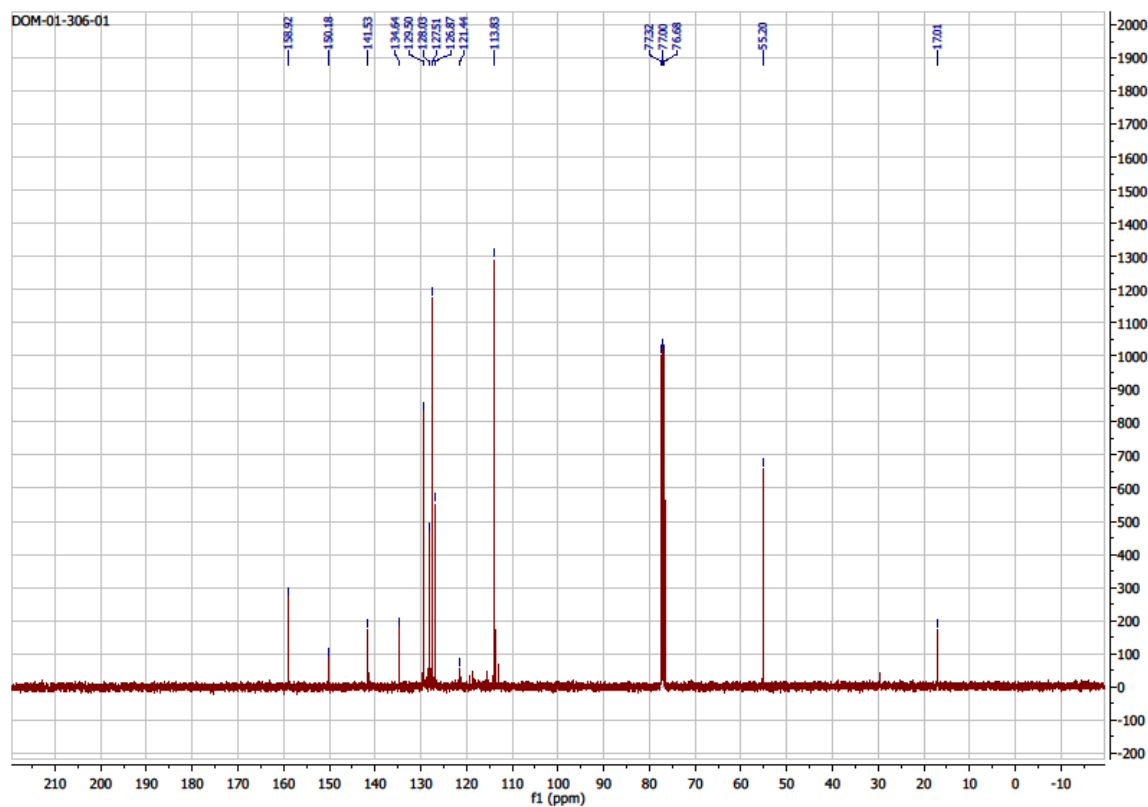
(E)-ethyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-4-phenylbut-3-enoate (46)



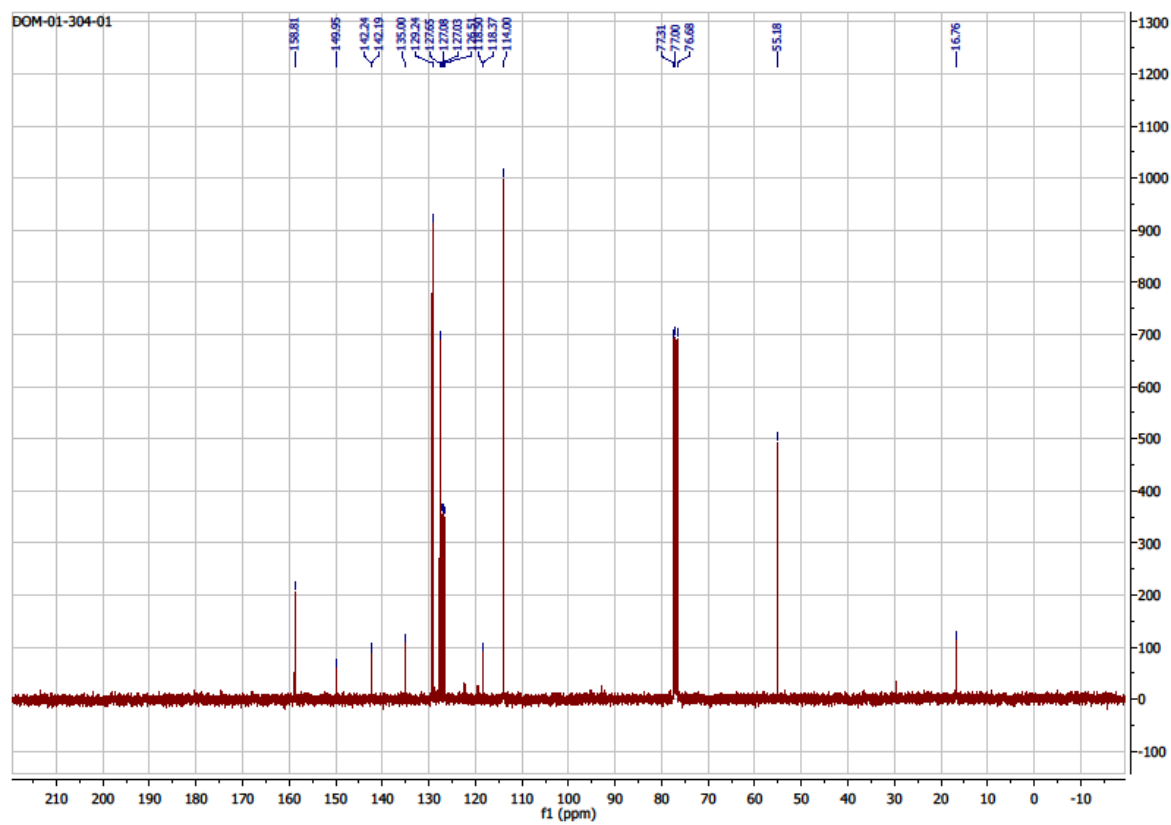
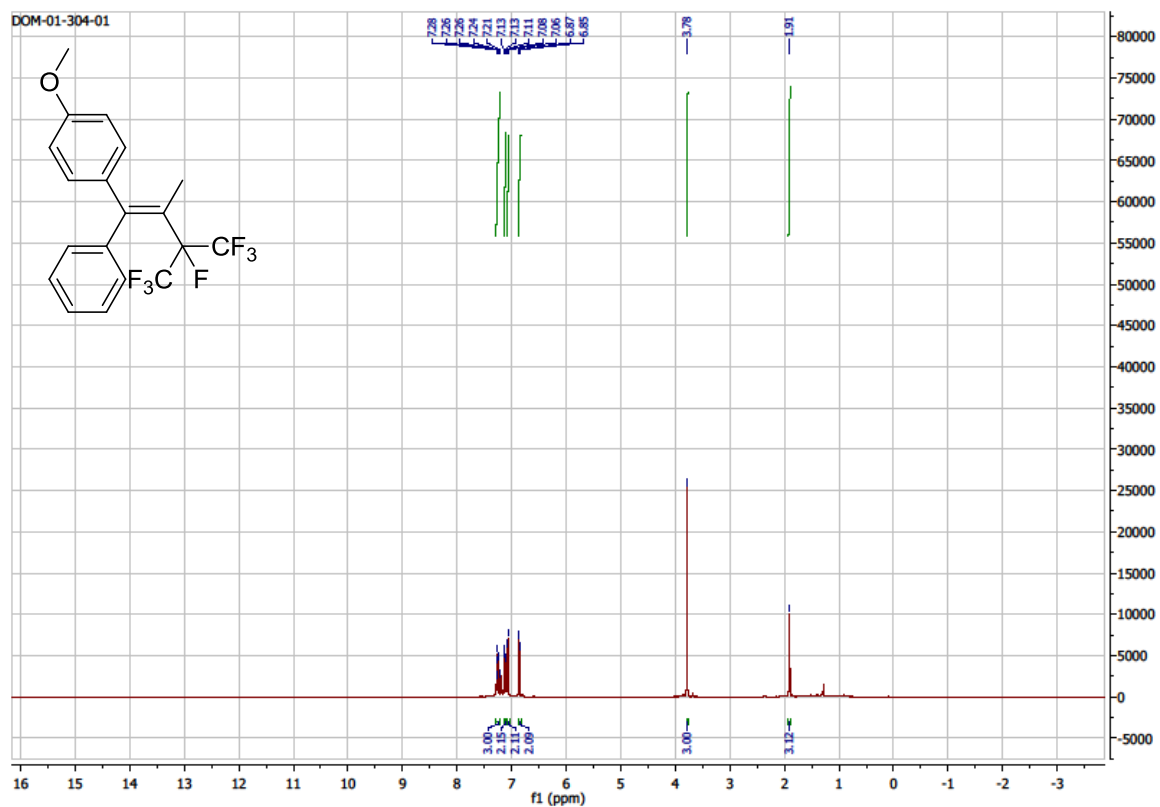


(*E*)-1-(4-bromo-3,3,4-tetrafluoro-2-methyl-1-phenylbut-1-en-1-yl)-4-methoxybenzene (47)

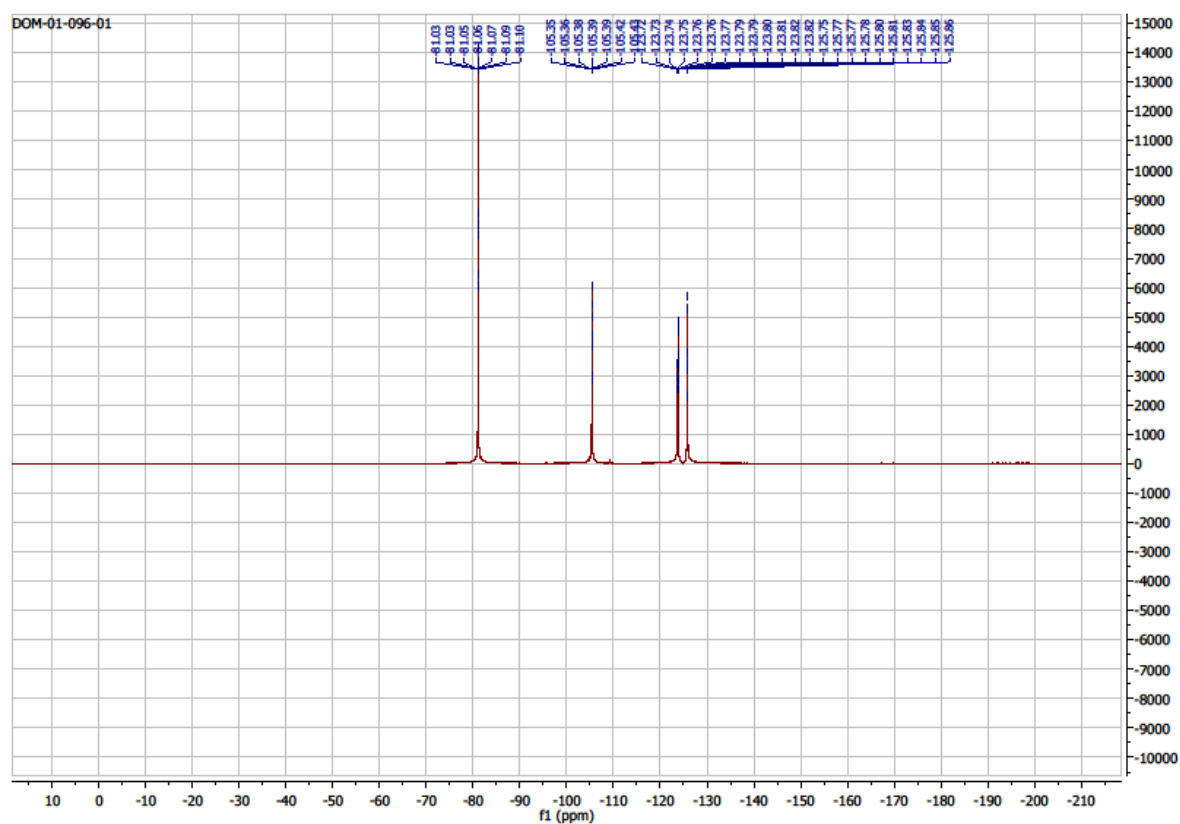
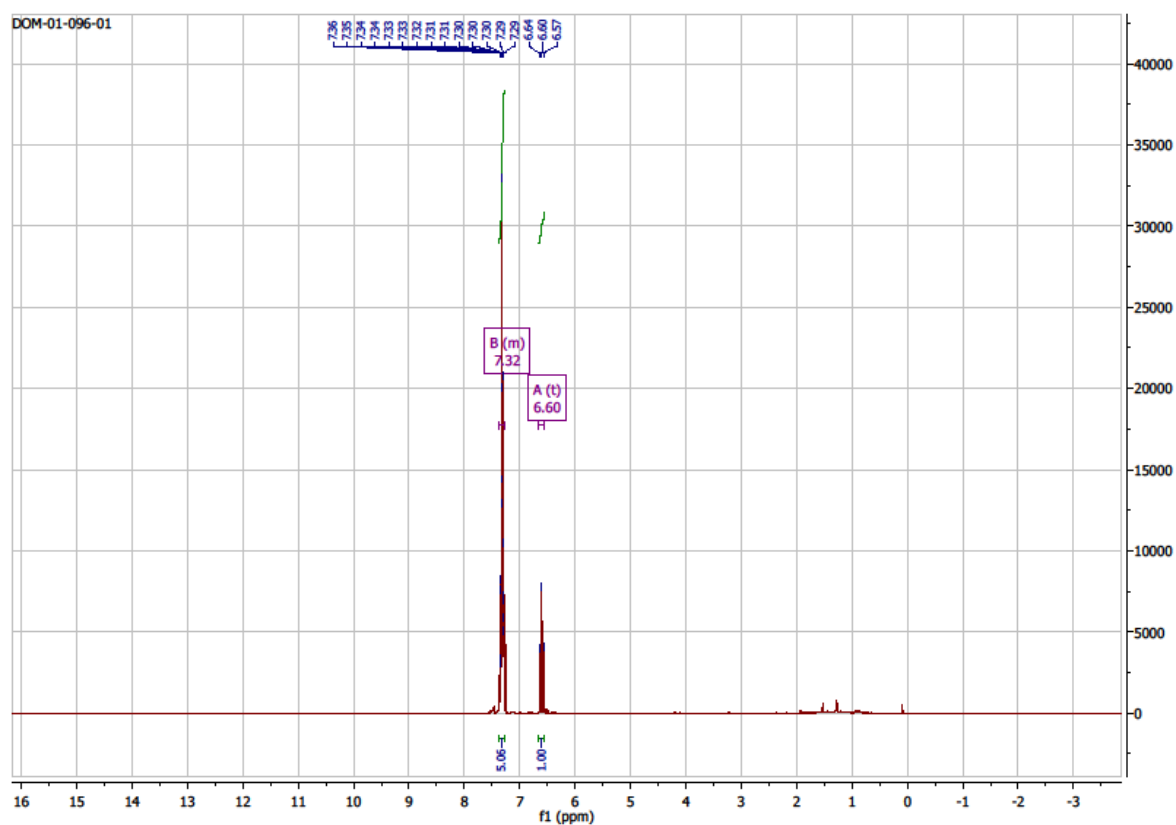




(*E*)-1-methoxy-4-(3,4,4,4-tetrafluoro-2-methyl-1-phenyl-3-(trifluoromethyl)but-1-en-1-yl)benzene (48)



(E)-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (50)



References

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- ⁵ For review, see: Pintauer, T.; Matyjaszewski, K. *Chem. Soc. Rev.* 2008, **37**, 1087-1097.