Supporting information

Regio- and Stereoselective Radical Perfluoroalkyltriflation of Alkynes Using Phenyl(perfluoroalkyl)iodonium Triflates

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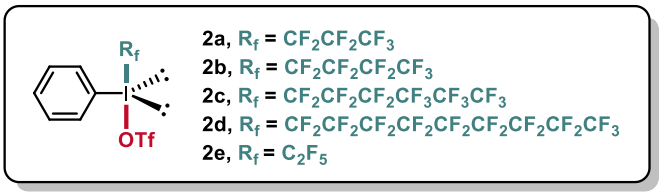
1. General

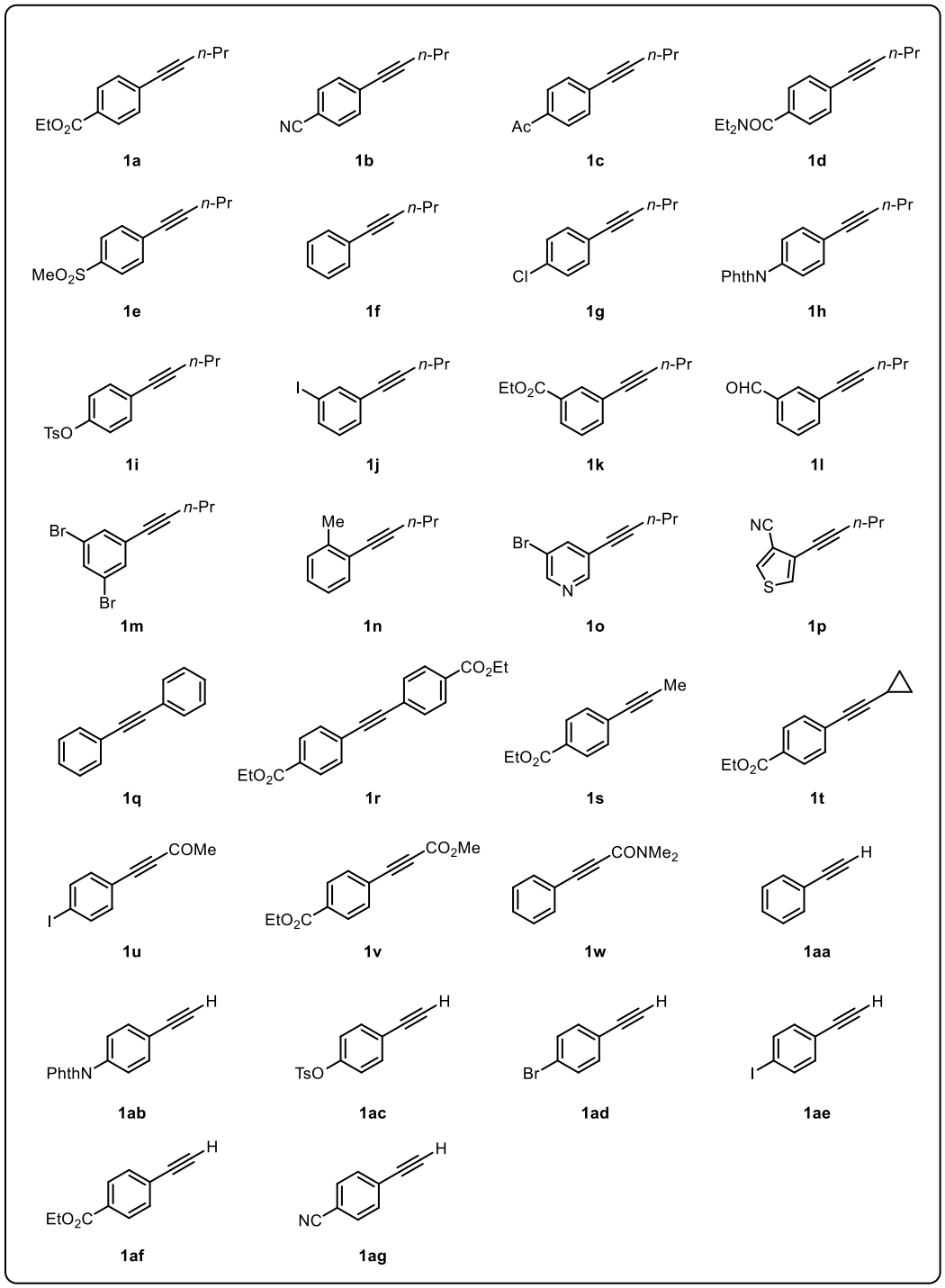
All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard *Schlenk* techniques. THF was freshly distilled from K under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Alfa Aesar, TCI, Aldrich, Fluka, Acros or ABCR. The alkynes were synthesized according to literature procedures. IR spectra were recorded on a *Digilab FTS 4000* with a *Specac MKII Golden Gate Single Refelxtion ART System.* ^{1}H NMR and ^{13}C NMR spectra were recorded on a *DPX* 300, *AV 400 or DD2 600* at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for 13C NMR). TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 µm) applying a pressure of about 0.2 bar. Mass spectra were recorded on a *Finnigan MAT 4200S*, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quatro LCZ* (ESI); peaks are given in *m/z* (% of basis peak).

2. Preparation of starting materials

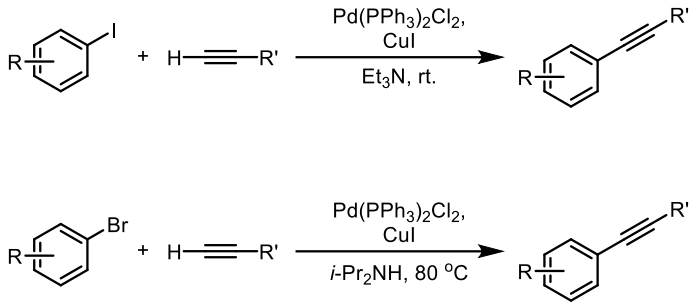
Phenyl(perfluoroalkyl)iodonium triflates **2a**, **2c**, **2d** are commercially available from TCI and were used as received. **2b**, **2e** were prepared according to the previously reported literature procedure.[1]



Alkynes **1f**, **1q**, **1aa**, **1ad**, **1ag** are commercially available from Alfa Aesar and alkyne **1af** is commercially available from ABCR. All commercially available alkynes were used as received. Alkynes **1a,**[2] **1b,**[3] **1c,**[4] **1g,**[5] **1h**,[5] **1k**,[5] **1l**,[5] **1m**,[5] **1r,**[6] **1s**,[7] **1t**,[8] **1u**,[9] **1w**,[10] **1ac**,[11] **1ae**,[12] **1af**,[13] were prepared according to previously reported literature procedures. Alkynes **1d**, **1e**, **1i, 1j, 1n**, **1o**, **1p, 1v, 1ab,** were prepared according to the following procedure.

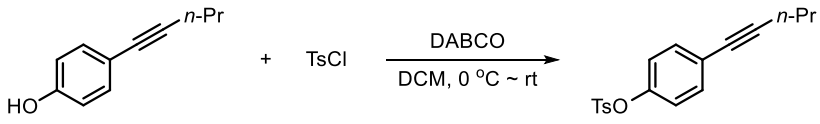


General procedure for the preparation of alkynes 1 from the corresponding aryl iodides or aryl bromides GP1



A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride, copper(I) iodide, aryl iodide or aryl bromide, sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before triethylamine or diisopropylamine was added. The corresponding terminal alkyne was added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature or 80 °C for 12 hours. After the reaction was completed, the reaction mixture was diluted with Et_2O (30 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography to give the corresponding pure alkynes **1**.

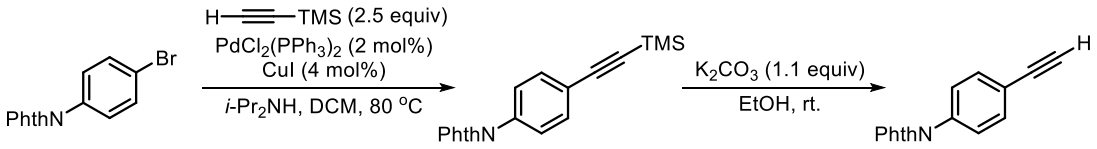
Procedure for the preparation of alkyne 1i



A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with 4-(pent-1-yn-1-yl)phenol (0.787 g, 4.91 mmol, 1.0 equiv),[5] DABCO (0.771 g, 6.87 mmol, 1.4 equiv) in DCM (20 mL). 4-Methylbenzenesulfonyl chloride (1.12 g, 5.89 mmol, 1.2 equiv) in DCM (10 mL) was slowly added to the resulting solution at 0 °C. After addition was completed, the reaction was allowed to warm up to room temperature and stirring was continued for additional 12 h. After the reaction was completed, the reaction mixture was diluted with EtOAc (30 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid

of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane:EtOAc = 80:1) to give pure **1i** as a white solid in 86% yield (1.32 g).

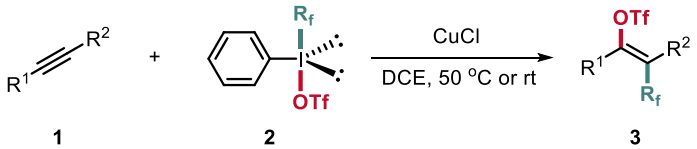
Procedure for the preparation of alkyne 1ab



2-(4-((Trimethylsilyl)ethynyl)phenyl)isoindoline-1,3-dione was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (84.0 mg, 0.120 mmol, 2.0 mol%), CuI (46.0 mg, 0.240 mmol, 4.0 mol%), 2-(4-bromophenyl)isoindoline-1,3-dione (1.81 g, 6.00 mmol, 1.0 equiv), and ethynyltrimethylsilane (1.47 g, 15.0 mmol, 2.5 equiv) in *i*-Pr_2NH (20 mL) and DCM (10 mL) at 80 °C for 12 hours. Purification via silica gel chromatography (pentane:EtOAc = 60:1, then 30:1) gave the desired product as a white solid in 95% yield (1.82 g). **TLC R_f** = 0.3 (pentane:EtOAc = 10:1). To a solution of 2-(4-((trimethylsilyl)ethynyl)phenyl)isoindoline-1,3-dione (1.00 g, 3.13 mmol, 1.0 equiv) in ethanol (20 mL) was added potassium carbonate (0.475 g, 3.45 mmol, 1.1 equiv) at room temperature. After 12 h, water was added and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was purified by silica gel column chromatography (pentane:EtOAc = 25:1, then 15:1) to afford the desired product **1ab** as a white solid in 88% yield (0.681 g).

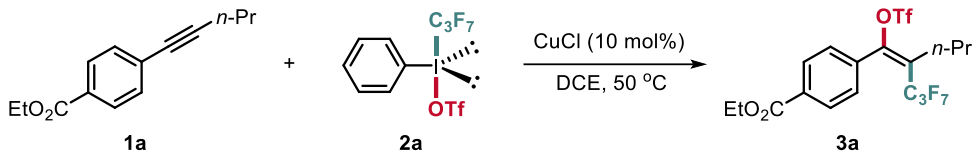
3. General and selective perfluoroalkyltriflation of alkynes using aryl(perfluoroalkyl)iodonium triflates

General procedure for perfluoroalkyltriflation of alkynes (GP2)

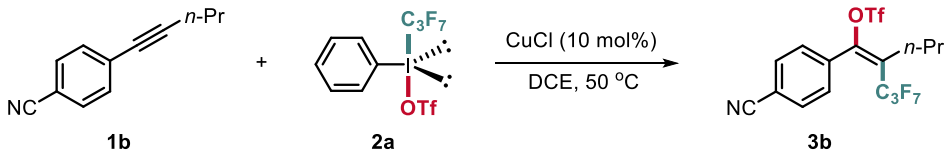


A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with copper(I) chloride (1.0 mg, 10 μmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (1 mL) was added. The corresponding alkyne **1** and phenyl(perfluoropropyl)iodonium triflate **2a** were added successively under a flow of argon. The reaction mixture was then stirred at 50 °C for 15 h or at room temperature for 24 h. After the reaction was completed, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford pure perfluoroalkyltriflated product **3**.

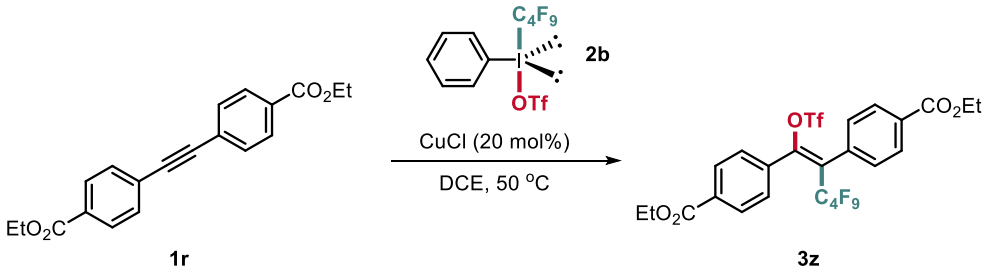
Scale-up experiment



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with copper(I) chloride (58.7 mg, 0.600 mmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (40 mL) was added. Ethyl 4-(pent-1-yn-1-yl)benzoate **1a** (1.30 g, 6.00 mmol, 1.0 equiv) and phenyl(perfluoropropyl)iodonium triflate **2a** (5.33 g, 10.2 mmol, 1.7 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at 50 °C for 30 h. After the reaction was completed, the reaction mixture was diluted with Et_2O (40 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane:EtOAc = 200:1) to afford pure ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifleoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate **3a** as a slight yellow oil in 93% yield (2.97 g).



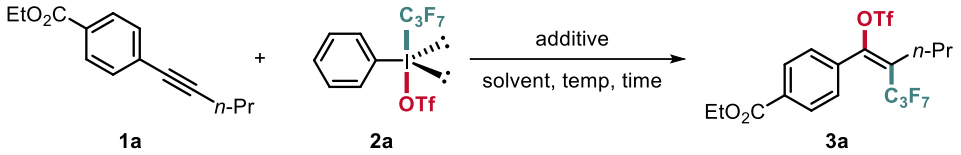
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with copper(I) chloride (19.6 mg, 0.200 mmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (20 mL) was added. 4-(Pent-1-yn-1-yl)benzonitrile **1b** (0.338 g, 2.00 mmol, 1.0 equiv) and phenyl(perfluoropropyl)iodonium triflate **2a** (1.78 g, 3.40 mmol, 1.7 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at 50 °C for 30 h. After the reaction was completed, the reaction mixture was diluted with Et_2O (20 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane:EtOAc = 200:1) to afford pure ethyl (*E*)-1-(4-cyanophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate **3b** as a slight yellow oil in 50% yield (1.71 g).



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with copper(I) chloride (49.0 mg, 0.500 mmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (50 mL) was added. Diethyl 4,4'-(ethyne-1,2-diyl)dibenzoate **1r** (1.61 g, 5.00 mmol, 1.0 equiv) and phenyl(perfluoropropyl)iodonium triflate **2a** (4.86 g, 8.5 mmol, 1.7 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at 50 °C for 15 h. Then further portions of copper(I) chloride (49.0 mg, 0.500 mmol, 10 mol%), and phenyl(perfluoropropyl)iodonium triflate **2a** (4.86 g, 8.5 mmol, 1.7 equiv) were added. The stirring was continued at 50 °C for further 15 h. After the reaction was completed, the reaction mixture was diluted with Et_2O (50 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced

pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane:EtOAc = 200:1, then 150:1) to afford pure Diethyl 4,4'-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(((trifluoromethyl)sulfonyl)oxy)hex-1-ene-1,2-diyl)(*E*) -dibenzoate **3z** as an off-white solid in 50% yield (0.79 g).

Screening of reaction conditions



1a **2a** **3a**

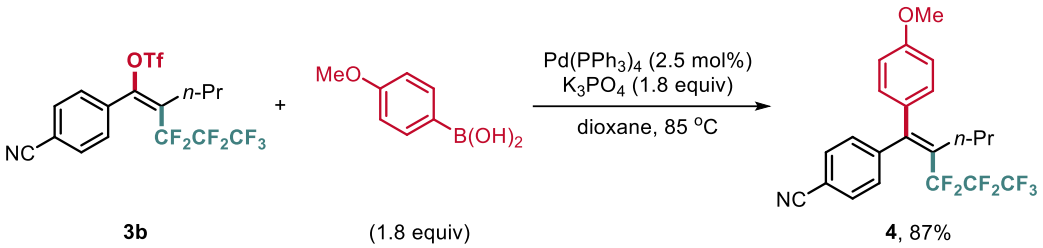
entry[a]	additive	**2a** (equiv)	solvent	temp	time (h)	yield (%)[b]
1	none	1.0	MeOH	rt	4	0
2	none	1.0	Et_2O	rt	4	0
3	none	1.0	MeCN	rt	4	11
4	none	1.0	DCM	rt	4	40
5	none	1.0	$CHCl_3$	rt	4	25
6	none	1.0	DCE	rt	4	49
7	none	1.0	DCE	rt	15	53
8	none	1.7	DCE	rt	15	69
9	pyridine (1.7 equiv)	1.7	DCE	rt	15	86
10	K_2CO_3 (1.7 equiv)	1.7	DCE	rt	15	78
11	$BF_3{\cdot}Et_2O$ (1.7 equiv)	1.7	DCE	rt	15	75
12	TfOH (1.7 equiv)	1.7	DCE	rt	15	53
13	TBAI (10 mol%)	1.7	DCE	rt	15	86
14	CuCl (10 mol%)	1.7	DCE	rt	15	91
15	**CuCl (10 mol%)**	**1.7**	**DCE**	**50 °C**	**15**	**96 (94)[c]**

[a]Reaction condition: **1a** (0.10 mmol, 1.0 equiv), reagent **2a**, additive, solvent (1 mL), room temperature. [b]Yield determined by ^{19}F NMR analysis using $PhCF_3$ as an internal standard; isomer ratio determined by ^{19}F NMR and GC-MS analysis on the crude product, *E*/*Z* > 20:1; [c]Isolated yield.

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with copper(I) chloride (1.0 mg, 10 μmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (50 mL) was added. Ethyl 4-(pent-1-yn-1-yl)benzoate **1a** (21.6 mg, 0.100 mmol, 1.0 equiv) and phenyl(perfluoropropyl)iodonium triflate **2a** were added successively under a flow of argon. The reaction mixture was then stirred at the given temperature for a certain period. After the reaction was completed, the solvent was removed under reduced

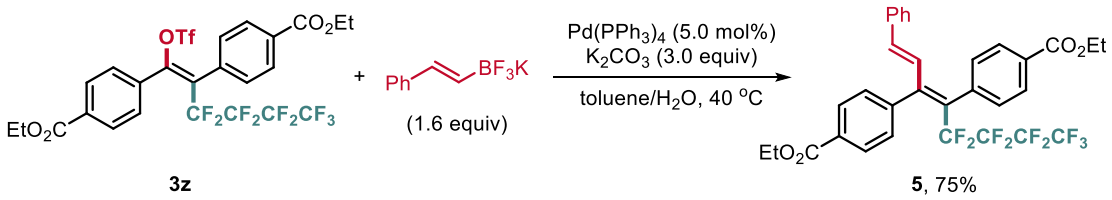
pressure with the aid of a rotary evaporator. The crude residue was analyzed by GC-MS and ^{19}F NMR with *α,α,α*-trifluorotoluene as the internal standard. All other screening experiments were conducted in analogy.

4. Derivatization of vinyl triflates



3b (1.8 equiv) **4**, 87%

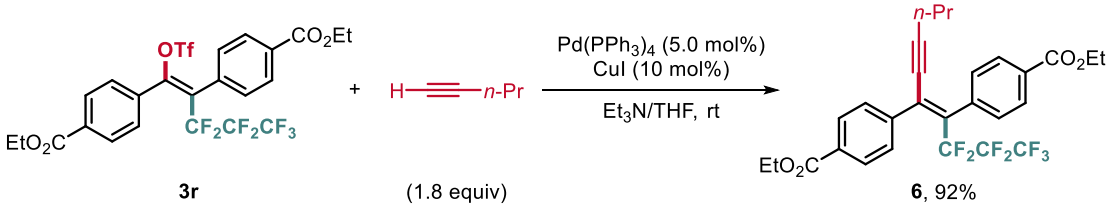
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with tetrakis(triphenylphosphine)palladium(0) (5.8 mg, 5.0 μmol, 2.5 mol%), (4-methoxyphenyl)boronic acid (54.7 mg, 0.360 mmol, 1.8 equiv), tripotassium phosphate (76.4 mg, 0.360 mmol, 1.8 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before dioxane (2 mL) was added. (*E*)-1-(4-Cyanophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate **3b** (97.4 mg, 0.200 mmol, 1.0 equiv, dr > 20:1) was added to the resulting suspension subsequently. The reaction mixture was stirred at 85 °C for 24 hours. After the reaction was completed, the reaction mixture was diluted with Et_2O (10 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane:EtOAc = 200:1, then 150:1) to give pure product **4** as a slight yellow oil in 87% yield (77.4 mg, dr = 20:1).



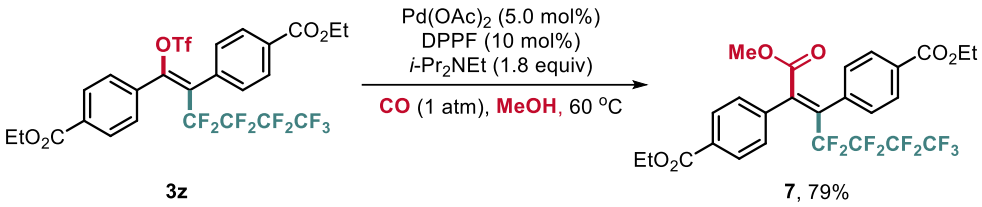
3z (1.6 equiv) **5**, 75%

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with tetrakis(triphenylphosphine)palladium(0) (5.8 mg, 5.0 μmol, 5.0 mol%), potassium

trans-styryltrifluoroborate (33.6 mg, 0.16 mmol, 1.6 equiv), potassium carbonate (41.4 mg, 0.300 mmol, 3.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before toluene (2 mL) and H_2O (0.4 mL) were added. Diethyl 4,4'-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(((trifluoromethyl)sulfonyl)oxy)hex-1-ene-1,2-diyl)(*E*)-dibenzoate **3z** (69.0 mg, 0.100 mmol, 1.0 equiv, dr > 20:1) was added to the resulting suspension subsequently. The reaction mixture was stirred at 40 ºC for 24 hours. After the reaction was completed, the reaction mixture was diluted with Et_2O (10 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a PTLC (pentane:EtOAc = 20:1) to give pure product **5** as a white solid in 75% yield (48.0 mg, dr > 20:1).



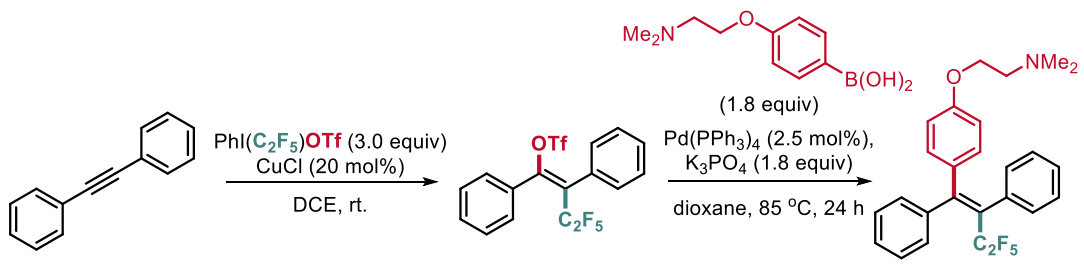
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with tetrakis(triphenylphosphine)palladium(0) (5.8 mg, 5.0 µmol, 5.0 mol%), copper(I) iodide (1.8 mg, 10 µmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before tetrahydrofuran (1 mL) and triethylamine (1 mL) were added. Diethyl 4,4'-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-ene-1,2-diyl)(*E*)-dibenzoate **3r** (64.0 mg, 0.100 mmol, 1.0 equiv, dr > 20:1) and pent-1-yne (12.3 mg, 0.180 mmol, 1.8 equiv) was added to the resulting suspension successively. The reaction mixture was stirred at room temperature for 48 hours. After the reaction was completed, the reaction mixture was diluted with Et_2O (10 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane:EtOAc = 200:1) to give pure product **6** as a pale yellow solid in 92% yield (51.1 mg, dr > 20:1).



3z **7**, 79%

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with palladium(II) acetate (1.1 mg, 5.0 μmol, 5.0 mol%), DPPF (5.5 mg, 10 μmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before methanol (1 mL) was added. *N*,*N*-diisopropylethylamine (23.3 mg, 0.180 mmol, 1.8 equiv) and diethyl 4,4'-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(((trifluoromethyl)sulfonyl)oxy)hex-1-ene-1,2-diyl)(*E*)-dibenzoate **3z** (69.0 mg, 0.100 mmol, 1.0 equiv, dr > 20:1) were then added successively. The flask was fitted with a balloon of carbon monoxide gas and partially evacuated followed by purging with carbon monoxide. This process was repeated three times. The reaction mixture was stirred at 60 °C for 24 hours. After the reaction was completed, the reaction mixture was diluted with Et_2O (10 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a PTLC (pentane:EtOAc = 10:1) to give pure product **7** as a white solid in 79% yield (47.4 mg, dr > 20:1).

5. Synthesis of pentafluorinated Tamoxifen 8



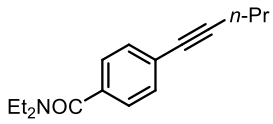
3ah **8 (pentafluoro-Tamoxifen)**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with copper(I) chloride (4.9 mg, 0.50 mmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (5 mL) was added. 1,2-Diphenylethyne **1q** (89.0 mg, 0.500 mmol, 1.0 equiv) and

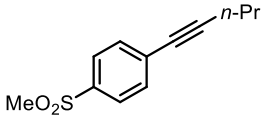
phenyl(pentafluoroethyl)iodonium triflate **2e** (353.9 mg, 750.0 μmol, 1.5 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at room temperature for 24 h. Then further portions of copper(I) chloride (4.9 mg, 0.50 mmol, 10 mol%), phenyl(pentafluoroethyl)iodonium triflate **2e** (353.9 mg, 750.0 μmol, 1.5 equiv), DCE (5 mL) were added. The stirring was continued at room temperature for further 24 h. After the reaction was completed, the solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane) to remove iodobenzene and iodine(III) compound to afford crude pentafluoroethyltriflated product, which was used in the next step. Another flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 12.5 mmol, 2.5 mol%), (4-(2-(dimethylamino)ethoxy)phenyl)boronic acid (188.2 mg, 900.0 μmol, 1.8 equiv),[14] tripotassium phosphate (190.7 mg, 900.0 μmol, 1.8 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before dioxane (5 mL) was added. The resulting crude pentafluoroethyltriflated product was added to the resulting suspension subsequently. The reaction mixture was stirred at 85 ^{o}C for 24 hours. After the reaction was completed, the reaction mixture was diluted with Et_2O (25 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (DCM:MeOH = 60:1, then 30:1) to give pentafluorinated Tamoxifen **8** as a slight yellow oil in 34% yield (77.4 mg, *E*/*Z* = 18:1). The NMR spectrum was obtained with further purification by GPC.

6. Spectral data

Spectral data of alkynes 1

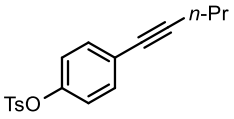


***N*,*N*-Diethyl-4-(pent-1-yn-1-yl)benzamide (1d):** The title compound was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (110 mg, 0.157 mmol, 2.0 mol%), CuI (59.7 mg, 0.313 mmol, 4.0 mol%), 4-bromo-*N*,*N*-diethylbenzamide (2.00 g, 7.84 mmol, 1.0 equiv), and pent-1-yne (1.28 g, 18.8 mmol, 2.4 equiv) in *i*-Pr_2NH (40 mL) at 80 °C for 24 hours. Purification via silica gel chromatography (pentane:EtOAc = 10:1) gave the desired product **1d** as a yellow oil in 86% yield (1.63 g). **TLC** $\mathbf{R_f}$ = 0.30 (pentane:EtOAc = 4:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.34 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.45 (br, 2H), 3.18 (br, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.69 – 1.44 (tq, J^1 = 7.5 Hz, J^2 = 7.2 Hz, 2H), 1.34 – 0.87 (m, 6H), 0.98 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.59, 136.00, 131.33, 126.11, 124.92, 91.45, 80.04, 43.10 (br, C), 39.18 (br, C), 21.96, 21.23, 13.95, 13.35 (br, C), 12.79 (br, C); **HRMS** (ESI) *m*/*z* = 266.1515, calcd. for $C_{16}H_{21}NONa$ $[M+Na]^+$, found: 266.1525; **IR** (neat, cm^{-1}): 2966*m*, 2934*w*, 2873*w*, 1627*s*, 1507*w*, 1457*m*, 1423*s*, 1380*m*, 1364*w*, 1315*m*, 1285*s*, 1220*w*, 1178*w*, 1093*s*, 1019*w*, 942*w*, 876*w*, 876*m*, 841*s*, 789*w*, 764*w*, 741*w*, 652*w*, 575*m*.

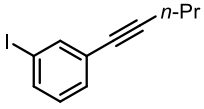


1-(Methylsulfonyl)-4-(pent-1-yn-1-yl)benzene (1e): The title compound was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (56.2 mg, 80.0 µmol, 1.0 mol%), CuI (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-(methylsulfonyl)benzene (1.87 g, 8.00 mmol, 1.0 equiv), and pent-1-yne (0.763 g, 11.2 mmol, 1.4 equiv) in *i*-Pr_2NH (20 mL) at 80 °C for 12 hours. Purification via silica gel chromatography (pentane:EtOAc = 20:1, then 15:1) gave the desired product **1e** as a gray solid in 94% yield (1.67 g). **TLC** $\mathbf{R_f}$ = 0.25 (pentane:EtOAc = 7:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 2.97 (s, 3H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.58 (tq, J^1 = 7.2 Hz, J^2 = 7.2 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 138.96, 132.26, 130.13, 127.23, 95.14, 79.42, 44.49, 21.93, 21.45, 13.51;

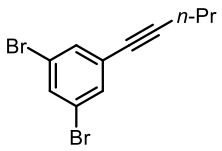
HRMS (ESI) *m*/*z* = 245.0607, calcd. for $C_{12}H_{14}O_2S$ $[M+Na]^+$, found: 245.0612; **IR** (neat, cm^{-1}): 3073*w*, 2961*w*, 2871*w*, 2223*w*, 1592*m*, 1560*w*, 1488*w*, 1466*w*, 1306s 1278*s*, 1181*w*, 1143s, 1087*s*, 1039*w*, 1017*w*, 967*s*, 882*s*, 838*s*, 778*s*, 744*w*, 714*w*.



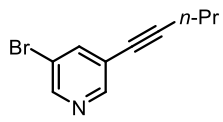
4-(Pent-1-yn-1-yl)phenyl 4-methylbenzenesulfonate (1i): The title compound was prepared according to procedure **1** (**P1**). **TLC** $\mathbf{R_f}$ = 0.30 (pentane:EtOAc = 20:1); **MP**: 34 °C; **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.21 (dd, J^1 = 8.5 Hz, J^2 = 1.6 Hz, 4H), 6.81 (d, *J* = 8.7 Hz, 2H), 2.36 (s, 3H), 2.28 (t, *J* = 7.0 Hz, 2H), 1.53 (h, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 148.67, 145.39, 132.73, 132.27, 129.73, 128.50, 123.20, 122.26, 91.46, 79.47, 22.06, 21.65, 21.30, 13.47; **HRMS** (ESI) *m*/*z* = 337.0869, calcd. for $C_{18}H_{18}O_3SNa$ $[M+Na]^+$, found: 337.0874; **IR** (neat, cm^{-1}): 2963*w*, 2936*w*, 2973*w*, 2238*w*, 1598*w*, 1499*s*, 1463*w*, 1374*s*, 1295*w*, 1198*s*, 1175*s*, 1155*s*, 1093*s*, 1017*w*, 860*s*, 845*s*, 814*m*, 747*m*, 721*w*, 673*m*, 576*s*.



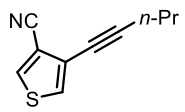
1-Iodo-3-(pent-1-yn-1-yl)benzene (1j): The title compound was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.100 mmol, 1.0 mol%), CuI (38.1 mg, 0.200 mmol, 2.0 mol%), 1,3-diiodobenzene (4.95 g, 15.0 mmol, 1.5 equiv), and pent-1-yne (0.681 g, 10.0 mmol, 1.0 equiv) in Et_3N (20 mL) at room temperature for 12 hours. Purification via silica gel chromatography (pentane) gave the desired product **1j** as a slight yellow oil in 75% yield (2.03 g). **TLC** $\mathbf{R_f}$ = 0.55 (pentane); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.67 (t, *J* = 1.7 Hz, 1H), 7.50 (dt, J^1 = 7.9 Hz, J^2 = 1.4 Hz, 1H), 7.26 (dt, J^1 = 7.7 Hz, J^2 = 1.3 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 2.29 (t, *J* = 7.0 Hz, 2H), 1.54 (tq, J^1 = 7.2 Hz, J^2 = 7.2 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.18, 136.45, 130.62, 129.62, 126.18, 93.57, 91.83, 79.17, 22.06, 21.36, 13.51; **HRMS** (APCI) *m*/*z* = 270.99782, calcd. for $C_{11}H_{12}I$ $[M+H]^+$, found: 270.99756; **IR** (neat, cm^{-1}): 2961*w*, 2932*w*, 2903*w*, 2871*w*, 2835*w*, 2237*w*, 1584*s*, 1549*s*, 1469*s*, 1428*w*, 1397*w*, 1379*w*, 1338*w*, 1299*w*, 1241*w*, 1168*w*, 1066*w*, 994*m*, 961*s*, 881*m*, 778*s*, 753*w*, 719*m*, 681*s*, 653*w*.



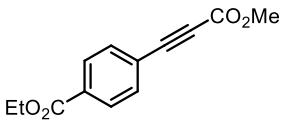
1,3-Dibromo-5-(pent-1-yn-1-yl)benzene (1n): The title compound was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (56.2 mg, 80.0 µmol, 1.0 mol%), CuI (30.5 mg, 0.160 mmol, 2.0 mol%), 1,3,5-tribromobenzene (3.78 g, 12.0 mmol, 1.5 equiv), and pent-1-yne (0.545 g, 8.00 mmol, 1.0 equiv) in *i*-Pr_2NH (16 mL) at 80 °C for 12 hours. Purification via silica gel chromatography (pentane) gave the desired product **1n** as a colorless oil in 67% yield (1.61 g). **TLC R_f** = 0.9 (pentane); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 (t, *J* = 1.8 Hz, 1H), 7.49 (d, *J* = 1.8 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.65 (tq, J^1 = 7.2 Hz, J^2 = 7.2 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 133.18, 133.04, 127.54, 122.42, 93.41, 78.14, 21.95, 21.33, 13.50; **HRMS** (APCI) *m*/*z* = 300.90563, calcd. for $C_{11}H_9Br_2$ $[M]^+$, found: 300.90451; **IR** (neat, cm^{-1}): 2961*w*, 2933*w*, 2872*w*, 2833*w*, 2225*w*, 1580*s*, 1539*s*, 1463*w*, 1429*w*, 1401*m*, 1338*w*, 1250*w*, 1110*w*, 978*w*, 879*w*, 852*s*, 785*w*, 747*s*, 669*s*.



3-Bromo-5-(pent-1-yn-1-yl)pyridine (1o): The title compound was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (84.2 mg, 0.120 mmol, 2.0 mol%), CuI (45.8 mg, 0.240 mmol, 4.0 mol%), 3,5-dibromopyridine (2.11 g, 9.00 mmol, 1.5 equiv), and pent-1-yne (0.408 g, 6.00 mmol, 1.0 equiv) in *i*-Pr_2NH (20 mL) at 80 °C for 12 hours. Purification via silica gel chromatography gave the desired product **1o** as a colorless oil in 76% yield (1.02 g). **TLC R_f** = 0.55 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = δ 8.45 (d, *J* = 4.5 Hz, 2H), 7.73 (t, *J* = 1.9 Hz, 1H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.55 (tq, J^1 = 7.2 Hz, J^2 = 7.2 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.25, 148.96, 140.66, 122.55, 119.86, 95.47, 76.17, 21.83, 21.33, 13.44; **HRMS** (ESI) *m*/*z* = 224.0069, calcd. for $C_{10}H_{11}BrN$ $[M+H]^+$, found: 224.0066; **IR** (neat, cm^{-1}): 3044*w*, 2963*w*, 2933*w*, 2872*w*, 2240*w*, 1574*m*, 1537*w*, 1429*s*, 1405*s*, 1380*w*, 1339*w*, 1308*w*, 1253*w*, 1210*w*, 1162*w*, 1094*w*, 1018*s*, 967*w*, 880*s*, 804*w*, 791*w*, 746*w*, 695*s*, 649*w*.

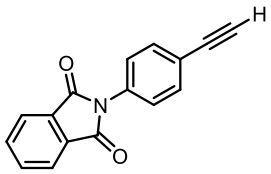


4-(Pent-1-yn-1-yl)thiophene-3-carbonitrile (1p): The title compound was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (56.2 mg, 80.0 µmol, 2.0 mol%), CuI (30.5 mg, 0.160 mmol, 4.0 mol%), 4-bromothiophene-3-carbonitrile (0.752 g, 4.00 mmol, 1.0 equiv), and pent-1-yne (0.763 g, 11.2 mmol, 2.8 equiv) in *i*-Pr_2NH (15 mL) at 80 °C for 12 hours. Purification via silica gel chromatography (pentane:EtOAc = 80:1) gave the desired product **1p** as a brown oil in 65% yield (0.458 g). **TLC R_f** = 0.45 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (d, *J* = 3.2 Hz, 1H), 7.30 (d, *J* = 3.2 Hz, 1H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.58 (tq, J^1 = 7.2 Hz, J^2 = 7.2 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 134.64, 128.11, 125.41, 114.16, 114.07, 94.95, 72.11, 21.88, 21.35, 13.45; **HRMS** (ESI) *m*/*z* = 198.0348, calcd. for $C_{10}H_9NSNa$ $[M+Na]^+$, found: 198.0347; **IR** (neat, cm^{-1}): 3109*m*, 2963*s*, 2934*m*, 2906*w*, 2872*w*, 2832*w*, 2232*s*, 2163*w*, 1517*w*, 1449*w*, 1428*w*, 1381*w*, 1353*w*, 1338*w*, 1276*w*, 1206*w*, 1131*w*, 1091*w*, 1041*w*, 934*w*, 874*m*, 860*w*, 807*s*, 744*w*, 700*w*.



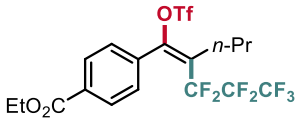
Ethyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate (1v): The title compound was prepared according to general procedure GP1 with $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.100 mmol, 2.0 mol%), CuI (38.2 mg, 0.200 mmol, 4.0 mol%), ethyl 4-iodobenzoate (2.07 g, 7.50 mmol, 1.5 equiv), potassium carbonate (2.07 g, 15.0 mmol, 3.0 equiv), and methyl propiolate (0.420 g, 5.00 mmol, 1.0 equiv) in THF (10 mL) at 65 °C for 12 hours. Purification via silica gel chromatography (pentane:EtOAc = 80:1) gave the desired product **1v** as a white solid in 65% yield (0.754 g). **TLC R_f** = 0.45 (pentane:EtOAc = 0.45); **MP**: 79 °C; **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.98 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.54, 154.10, 132.76, 132.14, 129.58, 123.88, 85.04, 82.25, 61.41, 52.92, 14.26; **HRMS** (ESI) *m*/*z* = 255.0628, calcd. for $C_{13}H_{12}O_4Na$ $[M+Na]^+$, found: 255.0634; **IR** (neat, cm^{-1}): 2991*w*, 2230*m*, 1713*s*,

1607*w*, 1438*m*, 1404*m*, 1364*w*, 1292*m*, 1280*s*, 1210*m*, 1188*m*, 1126*m*, 1104*m*, 1018*m*, 988*w*, 886*w*, 855*m*, 765*m*, 744*m*, 691*m*.

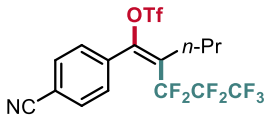


2-(4-Ethynylphenyl)isoindoline-1,3-dione (1ab): The title compound was prepared according to procedure **2** (**P2**). **TLC R_f** = 0.25 (pentane:EtOAc = 7:1); **MP**: 159 °C; **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.96 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.80 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 3.13 (s, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.90, 134.53, 132.81, 132.08, 131.67, 126.15, 123.84, 121.83, 82.89, 78.09; **HRMS** (ESI) *m*/*z* = 270.0525, calcd. for $C_{16}H_9NO_2Na$ $[M+Na]^+$, found: 270.0530; **IR** (neat, cm^{-1}): 3255*m*, 3098*w*, 3031*w*, 2363*w*, 1742*w*, 1703*s*, 1511*w*, 1469*w*, 1389*m*, 1225*w*, 1175*w*, 1110*w*, 1087*w*, 884*m*, 834*m*, 795*w*, 718*s*, 684*w*, 641*w*.

Spectral data of perfluoroalkyltriflation products 3

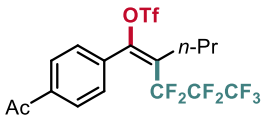


Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate (3a): The title compound was prepared according to general procedure GP2 with CuCl (1.0 mg, 10 μmol, 10 mol%), ethyl 4-(pent-1-yn-1-yl)benzoate **1a** (21.6 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3a** as a colorless oil in 94% yield (50.0 mg). **TLC R_f** = 0.7 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.40 – 2.35 (m, 2H), 1.86 – 1.52 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.55, 151.76 (t, *J* = 5.6 Hz, 1C), 134.74, 132.66, 130.21, 129.09, 127.27 (t, *J* = 21.1 Hz, 1C), 117.92 (q, *J* = 318.5 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 114.92 (t, *J* = 31.7 Hz), 109.07 (t, *J* = 38.2 Hz, 1C), 61.44, 30.00, 22.36, 14.23, 14.13; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.35 (s, 3F), -80.40 (t, *J* = 10.4 Hz, 3F), -106.15 – -106.25 (m, 2F), -123.87 – -124.00 (m, 2F); **HRMS** (ESI) *m*/*z* = 534.0559, calcd. for $C_{18}H_{16}F_{10}O_5SNa$ $[M+Na]^+$, found: 534.0449; **IR** (neat, cm^{-1}): 2974*w*, 1726*m*, 1668*w*, 1611*w*, 1422*m*, 1369*w*, 1348*w*, 1274*s*, 1213*s*, 1181*s*, 1136*s*, 1103*s*, 1072*w*, 1024*w*, 976*m*, 936*w*, 866*s*, 838*s*, 787*w*, 761*w*, 748*w*, 709w, 671*w*, 631*w*.

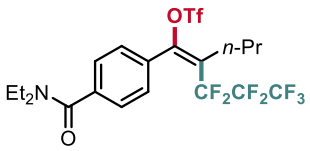


(*E*)-1-(4-Cyanophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpe nt-1-en-1-yl trifluoromethanesulfonate (3b): The title compound was prepared according to general procedure GP2 with CuCl (1.0 mg, 10 μmol, 10 mol%), 4-(pent-1-yn-1-yl)benzonitrile **1b** (16.9 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3b** as a light yellow oil in 88% yield (42.7 mg). **TLC R_f** = 0.5 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 2.41 –

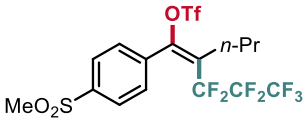
2.36 (m, 2H), 1.72 – 1.59 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.35 (t, *J* = 5.5 Hz, 1C), 135.02, 131.77, 130.90, 128.28 (t, *J* = 21.7 Hz, 1C), 117.89 (q, *J* = 320.6 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 117.59, 114.99, 30.00, 22.34, 14.10; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.31 (s, 3F), -80.38 (t, *J* = 10.4 Hz, 3F), -106.20 – -106.30 (m, 2F), -123.92 – -124.05 (m, 2F); **HRMS** (ESI) *m*/*z* = 510.0192, calcd. for $C_{16}H_{11}F_{10}NO_3SNa$ $[M+Na]^+$, found: 510.0192; **IR** (neat, cm^{-1}): 2922*w*, 2851*w*, 2236*w*, 1670*w*, 1463*w*, 1423*w*, 1348*w*, 1215*s*, 1183*m*, 1136*m*, 1113*m*, 1073*w*, 1030*w*, 980*w*, 936*w*, 880*w*, 853*s*, 790*w*, 747*w*, 674*w*, 646*w*.



(*E*)-1-(4-Acetylphenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpe nt-1-en-1-yl trifluoromethanesulfonate (3c): The title compound was prepared according to general procedure GP2 with CuCl (1.0 mg, 10 μmol, 10 mol%), 1-(4-(pent-1-yn-1-yl)phenyl)ethan-1-one **1c** (18.6 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3c** as a light yellow oil in 87% yield (44.1 mg). **TLC R_f** = 0.3 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.90 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 2.56 (s, 3H), 2.40 – 2.35 (m, 2H), 1.72 – 1.59 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 197.01, 151.59 (t, *J* = 5.5 Hz, C), 127.34 (t, *J* = 21.4 Hz, C), 138.62, 134.93, 130.51, 127.76, 117.92 (q, *J* = 320.5 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 29.99, 26.60, 22.36, 14.10; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.40 (s, 3F), -80.42 (t, *J* = 10.3 Hz, 3F), -106.18 – -106.28 (m, 2F), -122.90 – -124.03 (m, 2F); **HRMS** (ESI) *m*/*z* = 527.0345, calcd. for $C_{17}H_{14}F_{10}O_4SNa$ $[M+Na]^+$, found: 527.0347; **IR** (neat, cm^{-1}): 2970*w*, 2884*w*, 1695*m*, 1669*w*, 1607*w*, 1421*s*, 1405*m*, 1394*m*, 1263*m*, 1215*s*, 1183*s*, 1137*s*, 1113*s*, 1072*m*, 958*w*, 936*w*, 880*m*, 853*s*, 743*w*, 674*w*, 605*s*.

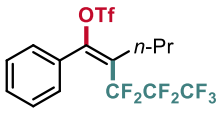


(*E*)-1-(4-(Diethylcarbamoyl)phenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethane sulfonate (3d): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), *N*,*N*-diethyl-4-(pent-1-yn-1-yl)benzamide **1d** (24.3 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 40:1, then 20:1) gave the desired product **3d** as a colorless oil in 79% yield (44.3 mg). **TLC R_f** = 0.7 (pentane:EtOAc = 4:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.38 – 7.31 (m, 4H), 3.48 (br, 2H), 3.09 (br, 2H), 2.40 – 2.34 (m, 2H), 1.72 – 1.59 (m, 2H), 1,19 – 0.96 (m, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.97, 152.12 (t, *J* = 5.6 Hz, 1C), 139.60, 131.35, 130.27, 126.96 (t, *J* = 21.4 Hz, 1C), 125.98, 117.92 (q, *J* = 320.7 Hz, OSO_2CF_3), 125.00 – 105.00 (m, $CF_2CF_2CF_3$), 43.25, 39.52, 29.97, 22.33, 14.09, 14.03, 12.85; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.47 (s, 3F), -80.46 (t, *J* = 11.1 Hz, 3F), -106.06 – -106.18 (m, 2F), -123.88 – -124.01 (m, 2F); **HRMS** (ESI) *m*/*z* = 584.0924, calcd. for $C_{20}H_{21}F_{10}NO_4SNa$ $[M+Na]^+$, found: 584.0924; **IR** (neat, cm^{-1}): 2975*w*, 2938*w*, 2881*w*, 1638*s*, 1420*s*, 1384*w*, 1349*m*, 1317*w*, 1289*m*, 1212*s*, 1182*s*, 1136*s*, 1112*s*, 1095*s*, 1071*s*, 1024*w*, 973*m*, 937*m*, 878*s*, 851*s*, 788*w*, 748m, 675*w*, 605*s*.

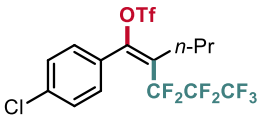


(*E*)-3,3,4,4,5,5,5-Heptafluoro-1-(4-(methylsulfonyl)phenyl)-2-propylpent-1-en-1-yl trifluoromethanesulfonate (3e): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 1-(methylsulfonyl)-4-(pent-1-yn-1-yl)benzene **1e** (22.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (104 mg, 0.200 mmol, 2.0 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 30:1, then 15:1) gave the desired product **3e** as a colorless oil in 90% yield (48.4 mg). **TLC R_f** = 0.4 (pentane:EtOAc = 7:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.89 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 2.98 (s, 3H), 2.39

– 2.33 (m, 2H), 1.64 (tq, J^1 = 7.8 Hz, J^2 = 7.5 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.32 (t, J = 5.6 Hz, C), 142.79, 135.97, 131.23, 128.31 (t, J = 21.5 Hz, C), 127.09, 117.86 (q, J = 320.5 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 44.29, 30.01, 22.34, 14.10; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.36 (s, 3F), -80.35 (t, J = 10.3 Hz, 3F), -106.27 (q, J = 8.5 Hz, 2F), -124.93 – -124.07 (m, 2F); **HRMS** (ESI) *m*/*z* = 563.0015, calcd. for $C_{16}H_{14}F_{10}O_5S_2Na$ $[M+Na]^+$, found: 563.0022; **IR** (neat, cm^{-1}): 2973*w*, 2937*w*, 2885*w*, 1670*m*, 1422*m*, 1349*w*, 1320*m*, 1213*s*, 1184*s*, 1153*s*, 1135*s*, 1113*s*, 1090*m*, 1072*m*, 979*m*, 957*m*, 936*m*, 890*m*, 879*m*, 853*s*, 789*w*, 749*m*, 731*w*, 701*w*, 673*w*, 604*s*.

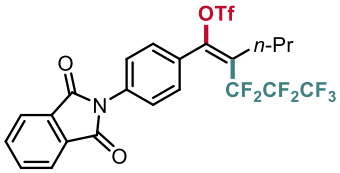


(*E*)-3,3,4,4,5,5,5-Heptafluoro-1-phenyl-2-propylpent-1-en-1-yl trifluoromethanesulfonate (3f): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), pent-1-yn-1-ylbenzene **1f** (14.4 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. The desired product **3f** could not be separated from the perfluoropropylated by-products resulting from arene perfluoroalkylation. The yield (88%) is based on ^{19}F NMR analysis with $PhCF_3$ as internal standard. **TLC R_f** = 0.8 (pentane); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.50 (s, 3F), -80.44 (t, J = 10.3 Hz, 3F), -106.06 (q, J = 9.1 Hz, 2F), -123.83 – -123.96 (m, 2F); **HRMS** (ESI) *m*/*z* = 485.0240, calcd. for $C_{15}H_{12}F_{10}O_3SNa$ $[M+Na]^+$, found: 485.0252.

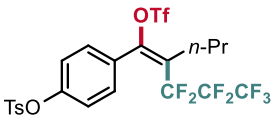


(*E*)-1-(4-Chlorophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propyl pent-1-en-1-yl trifluoromethanesulfonate (3g): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 1-chloro-4-(pent-1-yn-1-yl)benzene **1g** (17.8 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. The desired product **3g** could not be separated from the perfluoropropylated by-products resulting from arene perfluoroalkylation. The yield (79%) is based on ^{19}F NMR analysis with $PhCF_3$ as internal standard. **TLC R_f** = 0.75 (pentane); **^{19}F NMR** (282 MHz, $CDCl_3$, 300

K): δ (ppm) = -74.39 (s, 3F), -80.36 (t, *J* = 10.3 Hz, 3F), -106.23 (q, *J* = 9.9 Hz, 2F), -124.05 – -124.09 (m, 2F); **EI-MS** (m/z, relative intensity): 496 (M+, 6), 447 (4), 383 (6), 311 (6), 139 (100), 111 (24), 75 (8), 69 (18).

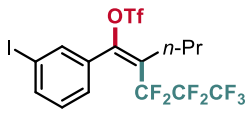


(*E*)-1-(4-(1,3-Dioxoisoindolin-2-yl)phenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate (3h): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 2-(4-(pent-1-yn-1-yl)phenyl)isoindoline-1,3-dione **1h** (28.9 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. The desired product **3h** could not be separated from the perfluoropropylated by-products. The yield (93%) is based on ^{19}F NMR analysis with $PhCF_3$ as internal standard. **TLC** $\mathbf{R_f}$ = 0.3 (pentane:EtOAc = 20:1); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.35 (s, 3F), -80.28 (t, *J* = 10.3 Hz, 3F), -106.19 (q, *J* = 9.9 Hz, 2F), -123.96 – -124.00 (m, 2F); **HRMS** (ESI) *m/z* = 630.0403, calcd. for $C_{23}H_{15}F_{10}NO_5SNa$ $[M+Na]^+$, found: 630.0403.

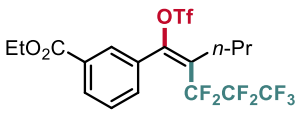


(*E*)-4-(3,3,4,4,5,5,5-Heptafluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzenesulfonate (3i): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 4-(pent-1-yn-1-yl)phenyl 4-methylbenzenesulfonate **1i** (31.4 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Purification via silica gel chromatography (pentane:EtOAc = 150:1) gave the desired product **3i** as a colorless oil in 90% yield (56.9 mg). **TLC** $\mathbf{R_f}$ = 0.4 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 2.35 (s, 3H), 2.36 – 2.31 (m, 2H), 1.68 – 1.55 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.48 (t, *J* = 5.6 Hz, 1C), 151.33, 145.75, 131.74, 131.67, 129.70, 129.45, 128.55, 127.25 (t,

J = 21.2 Hz, 1C), 122.17, 117.90 (q, *J* = 318.5 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 29.96, 22.33, 21.59, 14.09; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.39 (s, 3F), -80.47 (t, *J* = 10.4 Hz, 3F), -106.06 (q, *J* = 9.6 Hz, 2F), -123.91 – -123.91 (m, 2F); **HRMS** (ESI) *m/z* = 655.0277, calcd. for $C_{22}H_{18}F_{10}NaO_6S_2Na$ $[M+Na]^+$, found: 655.0296; **IR** (neat, cm^{-1}): 2973*w*, 1669*w*, 1600*w*, 1501*w*, 1421*m*, 1383*m*, 1349*w*, 1213*s*, 1201*s*, 1179*s*, 1159*s*, 1136*s*, 1113*s*, 1093*s*, 1072*m*, 1020*w*, 975*m*, 936*w*, 860*s*, 838*s*, 814*m*, 744*s*, 720*m*, 667*m*, 604*s*.

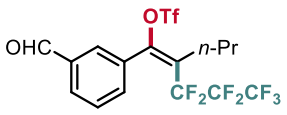


(*E*)-3,3,4,4,5,5,5-Heptafluoro-1-(3-iodophenyl)-2-propylpen -1-en-1-yl trifluoromethanesulfonate (3j): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 1-iodo-3-(pent-1-yn-1-yl)benzene **1j** (27.0 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Purification via silica gel chromatography (pentane) gave the desired product **3j** as a colorless oil in 83% yield (48.6 mg). **TLC R_f** = 0.8 (pentane); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74 (dt, J^1 = 8.0 Hz, J^2 = 1.4 Hz, 1H), 7.67 (s, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 2.38 – 2.32 (m, 2H), 1.70 – 1.58 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): 151.00 (t, *J* = 5.5 Hz, 1C), 139.89, 138.60, 132.44, 129.52, 129.28, 127.22 (t, *J* = 21.3 Hz, 1C), 117.91 (q, *J* = 320.5 Hz, OSO_2CF_3), 125.00 –100.00 (m, $CF_2CF_2CF_3$), 92.83, 29.99, 22.35, 14.17; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.35 (s, 3F), -80.39 (t, *J* = 10.1 Hz, 3F), -106.27 (q, *J* = 10.3 Hz, 2F), -123.85 – -123.97 (m, 2F); **HRMS** (ESI) *m/z* = 610.9206, calcd. for $C_{15}H_{11}F_{10}IO_3SNa$ $[M+Na]^+$, found: 610.9179; **IR** (neat, cm^{-1}): 2975*w*, 2881*w*, 1560*w*, 1471*w*, 1421*s*, 1348*m*, 1211*s*, 1182*s*, 1136*s*, 1113*s*, 1070*m*, 1029*w*, 978*m*, 944*w*, 890*m*, 880*s*, 844*s*, 795*m*, 749*w*, 762*m*, 699*m*, 673*m*, 605*s*.



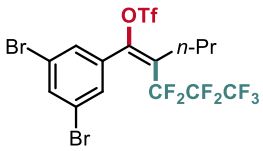
Ethyl (*E*)-3-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate (3k): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), ethyl 3-(pent-1-yn-1-

yl)benzoate **1k** (21.6 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3k** as a slight yellow oil in 95% yield (50.9 mg). **TLC** $\mathbf{R_f}$ = 0.7 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.08 (dt, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 8.00 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.40 – 2.35 (m, 2H), 1.73 – 1.60 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.37, 151.82 (t, *J* = 5.4 Hz, C), 134.17, 131.86, 131.22, 131.03, 130.63, 128.13, 127.19 (t, *J* = 21.6 Hz, C), 117.94 (q, *J* = 320.5 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 61.43, 30.03 (t, *J* = 2.6 Hz, C), 22.38, 14.20, 14.15; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.40 (s, 3F), -80.43 (t, *J* = 10.3 Hz, 3F), -106.16 – -106.26 (m, 2F), -123.88 – -124.01 (m, 2F); **HRMS** (ESI) *m*/*z* = 557.0451, calcd. for $C_{18}H_{16}F_{10}O_5SNa$ $[M+Na]^+$, found: 557.0462; **IR** (neat, cm^{-1}): 2924*w*, 2854*w*, 1728*m*, 1670*w*, 1422*m*, 1370*w*, 1349*w*, 1272*m*, 1207*s*, 1183*s*, 1137*s*, 1114*s*, 1028*w*, 987*w*, 958*w*, 924*w*, 883*w*, 863*w*, 840*m*, 764*w*, 749*w*, 704w, 620*w*, 607*w*.

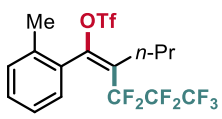


(*E*)-3,3,4,4,5,5,5-Heptafluoro-1-(3-formylphenyl)-2-propylpent-1-en-1-yl trifluoromethanesulfonate (3l): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), 3-(pent-1-yn-1-yl)benzaldehyde **1l** (17.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1, then 150:1) gave the desired product **3l** as a slight yellow oil in 82% yield (40.1 mg). **TLC** $\mathbf{R_f}$ = 0.5 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.96 (s, 1H), 7.93 (dt, J^1 = 7.4 Hz, J^2 = 1.6 Hz, 1H), 7.83 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 2.42 – 2.36 (m, 2H), 1.67 (tq, J^1 = 7.8 Hz, J^2 = 7.5 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.77, 151.22 (t, *J* = 5.6 Hz, C), 136.13, 135.66, 131.83, 131.64, 131.39, 128.87, 127.72 (t, *J* = 21.2 Hz, C), 117.92 (q, *J* = 318.5 Hz,

OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$) 30.03, 22.40, 14.14; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.42 (s, 3F), -80.43 (t, *J* = 10.3 Hz, 3F), -106.18 (q, *J* = 8.5 Hz, 2F), -124.00 – -124.12 (m, 2F); **HRMS** (ESI) *m*/*z* = 513.0189, calcd. for $C_{16}H_{12}F_{10}O_4SNa$ $[M+Na]^+$, found: 513.0187; **IR** (neat, cm^{-1}): 2358*w*, 1707*w*, 1420*w*, 1349*w*, 1227*w*, 1184*w*, 1137*w*, 1072*w*, 997*w*, 904*s*, 828*w*, 724*s*, 649*m*, 606*w*.

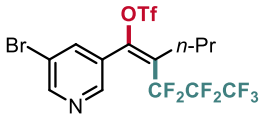


(*E*)-1-(3,5-Dibromophenyl)-3,3,4,4,5,5,5-heptafluoro-2-pro pylpent-1-en-1-yl trifluoromethanesulfonate (3m): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 1,3-dibromo-5-(pent-1-yn-1-yl)benzene **1m** (30.0 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Purification via silica gel chromatography (pentane) gave the desired product **3m** as a colorless oil in 81% yield (50.1 mg). **TLC R_f** = 0.85 (pentane); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.73 – 7.71 (m, 1H), 7.43 – 7.41 (m, 2H), 2.40 – 2.32 (m, 2H), 1.69 – 1.57 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 149.40 (t, *J* = 5.5 Hz, C), 136.62, 133.75, 131.65, 122.42, 117.98 (q, *J* = 320.6 Hz, OSO_2CF_3), 128.39 (t, *J* = 21.3 Hz, C); 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 30.04, 22.29, 14.11; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.21 – -74.32 (m, 3F), -80.29 – -80.50 (m, 3F), -106.39 – -106.53 (m, 2F), -123.88 – -123.93 (m, 2F); **HRMS** (ESI) *m*/*z* = 642.8430, calcd. for $C_{15}H_{10}Br_2F_{10}O_3SNa$ $[M+Na]^+$, found: 642.8425; **IR** (neat, cm^{-1}): 2973*w*, 2882*w*, 1670*w*, 1583*w*, 1552*m*, 1423*m*, 1348*w*, 1212*s*, 1181*s*, 1135*s*, 1113*s*, 1073*w*, 1000*w*, 987*w*, 957*w*, 898*m*, 846*s*, 868*s*, 791*s*, 748*w*, 666*m*, 606s.

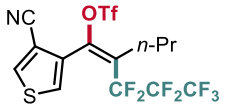


(*E*)-3,3,4,4,5,5,5-Heptafluoro-2-propyl-1-(*o*-tolyl)pent-1-en-1-yl trifluoromethanesulfonate (3n): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 1-methyl-2-(pent-1-yn-1-yl)benzene **1n** (15.8 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. The desired product **3n** could not

be separated from the perfluoropropylated by-products resulting from arene perfluoroalkylation. The yield (70%) is based on ^{19}F NMR analysis with $PhCF_3$ as internal standard. **TLC** $\mathbf{R_f}$ = 0.75 (pentane); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.82 (s, 3F), -80.42 (t, *J* = 10.4 Hz, 3F), -105.04 – -106.17 (m, 1F), -108.74 – -109.88 (m, 1F), -123.99 – -124.01 (m, 1F), -124.34 – -124.40 (m, 1F); **HRMS** (ESI) *m*/*z* = 499.0396, calcd. for $C_{16}H_{14}F_{10}O_3SNa$ $[M+Na]^+$, found: 499.0393.

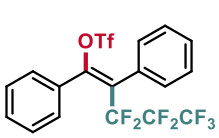


(*E*)-1-(5-Bromopyridin-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate (3o): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), 3-bromo-5-(pent-1-yn-1-yl)pyridine **1o** (17.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1, then 150:1) gave the desired product **3o** as a slight yellow oil in 47% yield (25.4 mg). **TLC** $\mathbf{R_f}$ = 0.5 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.71 (s, 1H), 8.48 (s, 1H), 7.80 (s, 1H), 2.42 – 2.37 (m, 2H), 1.65 (tq, J^1 = 7.8 Hz, J^2 = 7.5 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.92, 148.32, 148.04 (t, *J* = 5.5 Hz, 1C), 139.74, 129.88 (t, *J* = 21.4 Hz, C), 128.41, 119.75, 117.90 (q, *J* = 318.4 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 30.12, 22.41, 14.13; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): -74.17 (s, 3F), -80.30 (q, *J* = 9.8 Hz, 3F), -106.27 – -106.30 (m, 2F), -124.11 – -124.24 (m, 2F); **HRMS** (ESI) *m*/*z* = 565.9277; calcd. For $C_{14}H_{10}BrF_{10}NO_3SNa$ $[M+Na]^+$, found: 565.9287; **IR** (neat, cm^{-1}): 2974*w*, 2364*w*, 1669*w*, 1578*w*, 1548*w*, 1424*m*, 1349*w*, 1215*s*, 1182*m*, 1135*s*, 1114*s*, 1100*w*, 1073*m*, 1024*w*, 985*m*, 896*m*, 880*w*, 846*s*, 781*w*, 757*w*, 746*w*, 704*w*, 675*w*, 606*m*.



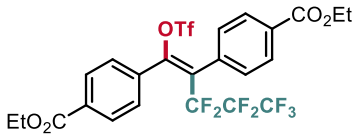
(*E*)-1-(4-Cyanothiophen-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate (3p): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), 4-(pent-1-yn-1-yl)thiophene-3-carbonitrile **1p** (17.5 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7

equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3p** as a colorless oil in 85% yield (42.0 mg). **TLC** $\mathbf{R_f}$ = 0.55 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.91 (d, *J* = 3.1 Hz, 1H), 7.56 (d, *J* = 3.1 Hz, 1H), 2.41 (m, 2H), 1.75 – 1.61 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.59 (t, *J* = 5.5 Hz, C), 135.88, 131.80, 131.90 – 131.24 (m, C), 131.44, 118.01 (q, *J* = 320.6 Hz, OSO_2CF_3), 112.53, 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 30.27, 22.42, 14.06; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.46 (s, 3F), -80.32 (t, *J* = 10.3 Hz, 3F), -105.32 – -106.41 (m, 1F), -108.47 – -109.45 (m, 1F), -124.48 (br, 1F), -124.67 (br, 1F); **HRMS** (ESI) *m*/*z* = 515.9756; calcd. For $C_{14}H_9F_{10}NO_3S_2Na$ $[M+Na]^+$, found: 515.9758; **IR** (neat, cm^{-1}): 2974*w*, 2881*w*, 2238*w*, 1671*w*, 1422*m*, 1347*w*, 1283*w*, 1216*s*, 1184*s*, 1135*s*, 1117*s*, 1092*w*, 1071*m*, 1029*w*, 972*m*, 919*m*, 863*s*, 835*s*, 783*w*, 746*m*, 736*m*, 703*w*, 652*w*, 604*m*.

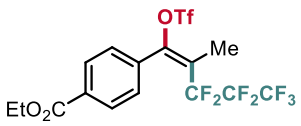


(*E*)-3,3,4,4,5,5,5-Heptafluoro-1,2-diphenylpent-1-en-1-yl trifle oromethanesulfonate (3q): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), 1,2-diphenylethyne **1q** (17.8 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Then further portions of CuCl (1.0 mg, 10 μmol, 10 mol%), phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) and DCE (1 mL) were added. The stirring was continued at room temperature for 24 h. Purification via silica gel chromatography (pentane) gave the desired product **3q** as a white solid in 69% yield (34.2 mg). **MP**: 79 °C; **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.62 – 7.33 (m, 10H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.64 (t, *J* = 4.1 Hz, C), 131.19, 130.14, 129.80, 129.65, 128.53, 128.16, 117.67 (q, *J* = 320.7 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.88 (s, 3F), -80.40 (t, *J* = 10.5 Hz, 2F), -103.92 (q, *J* =9.9 Hz, 2F), -122.35 – -122.48 (m, 2F); **HRMS** (ESI) *m*/*z* = 519.0083, calcd. for $C_{18}H_{10}F_{10}O_3SNa$ $[M+Na]^+$, found: 519.0091; **IR** (neat, cm^{-1}): 2923*w*, 2851*w*, 1659*w*,

1494*w*, 1424*m*, 1345*m*, 1250*s*, 1183*s*, 1135*s*, 1112*s*, 1076*w*, 1037*w*, 1001*w*, 981*w*, 933*w*, 896*w*, 864*m*, 847*m*, 798*m*, 766*m*, 742*m*, 697*m*, 678*m*, 601*m*, 559*m*.

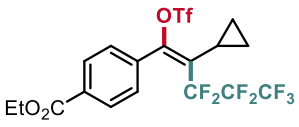


Diethyl 4,4'-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-ene-1,2-diyl)(*E*)-dibenzoate (3r): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), diethyl 4,4'-(ethyne-1,2-diyl)dibenzoate **1r** (32.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Then further portions of CuCl (1.0 mg, 10 μmol, 10 mol%), phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) and DCE (1 mL) were added. The stirring was continued at 50 °C for further 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3r** as a white solid in 64% yield (41.1 mg). **MP**: 99 °C; **TLC** $\mathbf{R_f}$ = 0.55 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 (d, *J* = 5.0 Hz, 2H), 8.07 (d, *J* = 4.9 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.72, 152.65 (t, *J* = 4.3 Hz, C), 165.40, 134.29, 133.23, 133.15, 131.91, 130.22, 129.84, 129.76, 129.37, 126.56 (t, *J* = 21.8 Hz, C), 117.58 (q, *J* = 318.8 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 61.55, 61.35, 14.25, 14.25; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.51 (s, 3F), -80.32 (t, *J* = 10.5 Hz, 3F), -103.93 (q, *J* = 11.3 Hz, 2F), -122.37 – -122.50 (m, 2F); **HRMS** (ESI) *m*/*z* = 663.0506, calcd. for $C_{24}H_{18}F_{10}O_7SNa$ $[M+Na]^+$, found: 663.0506; **IR** (neat, cm^{-1}): 2988*w*, 1723*s*, 1662*w*, 1611*w*, 1427*w*, 1408*w*, 1369*w*, 1345*w*, 1272*s*, 1225*s*, 1208*s*, 1183*s*, 1136*s*, 1104*s*, 1025*m*, 1005*w*, 987*w*, 883*m*, 852*m*, 835*m*, 796*w*, 770*m*, 746*w*, 711*m*, 677*w*, 602*m*, 567*w*.



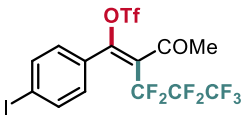
Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-methyl-1-(((trifleoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate (3s): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), ethyl 4-(prop-1-yn-1-

yl)benzoate **1s** (18.8 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3s** as a colorless oil in 95% yield (48.2 mg). **TLC R_f** = 0.6 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.12 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.53, 151.14 (t, *J* = 4.8 Hz, C), 134.84, 132.68, 129.88, 129.19, 122.97 (t, *J* = 22.0 Hz, C), 117.94 (q, *J* = 318.4 Hz, OSO_2CF_3), 120.00 – 100.00 (m, $CF_2CF_2CF_3$), 61.44, 14.22, 13.48 (p, *J* = 3.5 Hz, C); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.33 (s, 3F), -80.50 (t, *J* = 10.1 Hz, 3F), -107.26 (q, *J* = 10.1 Hz, 2F), -124.31 – -124.45 (m, 2F); **HRMS** (ESI) *m*/*z* = 529.0138, calcd. for $C_{16}H_{12}F_{10}O_5SNa$ $[M+Na]^+$, found: 529.0172; **IR** (neat, cm^{-1}): 2992*w*, 1726*m*, 1679*w*, 1423*m*, 1370*w*, 1348*w*, 1273*s*, 1207*s*, 1182*s*, 1137*s*, 1104*s*, 1120*s*, 1024*s*, 972*m*, 938*w*, 912*s*, 867*s*, 840*s*, 783*w*, 759*m*, 740*m*, 710*m*, 672*s*, 631*w*, 602*s*, 579*w*.

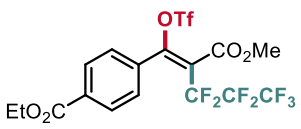


Ethyl (*E*)-4-(2-cyclopropyl-3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate (3t): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), ethyl 4-(cyclopropylethynyl)benzoate **1t** (21.4 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3t** as a colorless oil in 64% yield (34.1 mg). **TLC R_f** = 0.5 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.58 (tt, J^1 = 8.4 Hz, J^2 = 5.7 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.07 – 1.00 (m, 2H), 0.92 – 0.86 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) =165.55, 154.28 (t, *J* = 4.5 Hz, 1C), 135.47, 132.51, 129.56, 129.19, 127.13 (t, *J* = 20.1 Hz, C), 117.94 (q, *J* = 318.5 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 61.43, 14.23, 9.78 (p, *J* = 2.8 Hz, C), 7.65; **^{19}F NMR**

(282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.43 (s, 3F), -80.46 (t, *J* = 10.9 Hz, 3F), -103.20 – -103.37 (m, 2F), -123.23 – -123.37 (m, 2F); **HRMS** (ESI) *m*/*z* = 555.0294, calcd. for $C_{18}H_{14}F_{10}O_5SNa$ $[M+Na]^+$, found: 555.0287; **IR** (neat, cm^{-1}): 2988*w*, 1724*m*, 1424*m*, 1347*w*, 1274*s*, 1210*s*, 1183*s*, 1138*s*, 1113*s*, 1045*w*, 1023*w*, 983*m*, 954*w*, 904*w*, 875*s*, 856*m*, 835*m*, 760*w*, 745*w*, 708*w*, 603*m*.

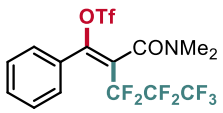


(*E*)-2-Acetyl-3,3,4,4,5,5,5-heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate (3u): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), 4-(4-iodophenyl)but-3-yn-2-one **1u** (27.0 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3u** as a white solid in 43% yield (25.5 mg). **MP**: 55 °C; **TLC** $\mathbf{R_f}$ = 0.6 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 1.95 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.08, 152.43 (t, *J* = 5.9 Hz, C), 138.59, 130.87, 129.13, 124.88 – 124.23 (m, C), 117.94 (q, *J* = 318.9 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 100.00, 31.35; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.24 (s, 3F), -80.19 – -80.29 (m, 3F), -106.88 – -106.98 (m, 2F), -124.48 – -124.53 (m, 2F); **HRMS** (ESI) *m*/*z* = 610.8842, calcd. for $C_{14}H_7F_{10}IO_4SNa$ $[M+Na]^+$, found: 610.8854; **IR** (neat, cm^{-1}): 2922*w*, 2854*w*, 1720*m*, 1645*w*, 1584*w*, 1483*w*, 1420*m*, 1395*m*, 1345*m*, 1287*m*, 1213*s*, 1131*s*, 1117*w*, 1062*m*, 1010*m*, 991*s*, 960*w*, 900*m*, 836*m*, 804*s*, 756*s*, 747*s*, 731*m*, 708*m*, 675*m*, 662*m*, 626*m*, 602*s*.



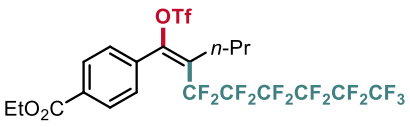
Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-(methoxycarbonyl)-1-(((trifluoromethyl)sulfonyl)oxy) pent-1-en-1-yl)benzoate (3v): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), ethyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate **1v** (23.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE

(1 mL) at 50 °C for 15 h. Then further portions of CuCl (1.0 mg, 10 μmol, 10 mol%), phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) and DCE (1 mL) were added. The stirring was continued at 50 °C for further 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1) gave the desired product **3v** as a colorless oil in 64% yield (35.3 mg). **TLC R_f** = 0.5 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) =165.22, 159.97 (t, *J* = 3.2 Hz, 1C), 155.02 (t, *J* = 5.2 Hz, 1C), 133.71, 132.52, 129.74, 129.35, 117.86 (q, *J* = 318.8 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 61.63, 53.74, 14.21; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.93 (s, 3F), -80.30 (t, *J* = 10.2 Hz, 3F), -104.13 (q, *J* = 10.2 Hz, 2F), -123.79 – -123.88 (m, 2F); **HRMS** (ESI) *m*/*z* = 573.0046, calcd. for $C_{17}H_{12}F_{10}O_7SNa$ $[M+Na]^+$, found: 573.0046; **IR** (neat, cm^{-1}): 2851*w*, 2361*w*, 1753*m*, 1726*m*, 1667*w*, 1431*m*, 1370*w*, 1347*w*, 1274*s*, 1212*s*, 1134*s*, 1119*s*, 1105*s*, 1063*m*, 1023*m*, 992*m*, 961*m*, 898*w*, 865*s*, 798*s*, 761*m*, 703*w*, 677*w*, 601*s*.

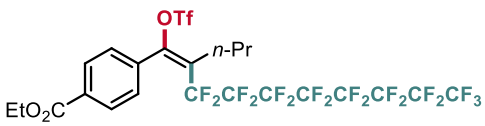


(*E*)-2-(Dimethylcarbamoyl)-3,3,4,4,5,5,5-heptafluoro-1-phenyl pent-1-en-1-yl trifluoromethanesulfonate (3w): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), *N*,*N*-dimethyl-3-phenylpropiolamide **1w** (17.3 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Then further portions of CuCl (1.0 mg, 10 μmol, 10 mol%), phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) and DCE (1 mL) were added. The stirring was continued at 50 °C for further 15 h. Purification via silica gel chromatography (pentane:EtOAc = 80:1) gave the desired product **3w** as a colorless oil in 64% yield (31.6 mg). **TLC R_f** = 0.65 (pentane:EtOAc = 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.50 – 7.34 (m, 5H), 3.12 (s, 3H), 3.01 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.36, 153.23 – 152.07 (m, 2C), 131.90, 129.77, 129.02, 128.25, 117.86 (q, *J* = 318.7 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 38.00, 34.79; **^{19}F NMR** (282 MHz,

$CDCl_3$, 300 K): δ (ppm) = -74.35 (s, 3F), -80.32 (t, *J* = 10.8 Hz, 3F), -100.18 – -101.33 (m, 1F), -104.50 – -105.58 (m, 1F), -123.42 – -123.53 (m, 2F); **HRMS** (ESI) *m*/*z* = 514.0141, calcd. for $C_{15}H_{11}F_{10}NO_4SNa$ $[M+Na]^+$, found: 514.0137; **IR** (neat, cm^{-1}): 2932*w*, 2360*w*, 1658*m*, 1497*w*, 1423*w*, 1344*w*, 1275*w*, 1212*s*, 1195*s*, 1162*m*, 1133*s*, 1115*s*, 1047*w*, 978*w*, 944*w*, 864*s*, 835*w*, 801*m*, 765*w*, 748*w*, 697*m*, 603*m*, 558*w*.

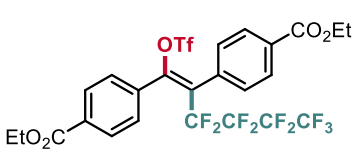


Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)oct-1-en-1-yl)benzoate (3x): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), ethyl 4-(pent-1-yn-1-yl)benzoate **1a** (21.6 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluorohexyl)iodonium triflate **2c** (144 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1, then 150:1) gave the desired product **3x** as a colorless oil in 94% yield (64.1 mg). **TLC** $\mathbf{R_f}$ = 0.5 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.40 – 2.35 (m, 2H), 1.72 – 1.59 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) =165.55, 151.90 (t, *J* = 5.6 Hz, 1C), 134.78, 132.67, 130.19, 129.10, 127.49 (t, *J* = 21.4 Hz), 117.94 (q, *J* = 320.5 Hz, OSO_2CF_3), 125.00 –100.00 (m, $CF_2CF_2CF_2CF_2CF_2CF_3$), 61.44, 30.05, 22.39, 14.20, 14.11; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.45 (3F), -80.94 (tt, J^1 = 10.3 Hz, J^2 = 3.0 Hz, 3F), -105.41 – -105.55 (m, 2F), -119.44 – -119.56 (m, 2F), -121.92 (br, 2F), -122.82 (br, 2F), -126.14 – -126.28 (m, 2F); **HRMS** (ESI) *m*/*z* = 707.0355, calcd. for $C_{21}H_{16}F_{16}O_5SNa$ $[M+Na]^+$, found: 707.0447; **IR** (neat, cm^{-1}): 2981*w*, 2884*w*, 2849*w*, 1727*m*, 1668*w*, 1611*w*, 1423*m*, 1407*w*, 1366*w*, 1275*m*, 1211*s*, 1136*s*, 1104*s*, 1023*w*, 967*m*, 893*w*, 866*m*, 844*m*, 809*m*, 791*m*, 736*m*, 709*m*, 689*m*, 602*s*.



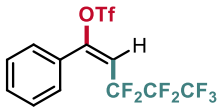
Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)dec-1-en-1-yl)benzoate (3y): The title compound was prepared according to general procedure **GP2** with CuCl

(1.0 mg, 10 μmol, 10 mol%), ethyl 4-(pent-1-yn-1-yl)benzoate **1a** (21.6 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluorooctyl)iodonium triflate **2d** (1.31 g, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 300:1, then 250:1) gave the desired product **3y** as a colorless oil in 81% yield (63.6 mg). **TLC** $\mathbf{R_f}$ = 0.6 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.40 – 2.35 (m, 2H), 1.72 – 1.59 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.54 (d, *J* = 1.6 Hz, C), 151.86 (d, *J* = 5.5 Hz, 1C), 134.79, 132.67, 130.18, 129.09, 127.50 (t, *J* = 21.4 Hz, C), 117.94 (q, *J* = 320.4 Hz, OSO_2CF_3), 125.00 –100.00 (m, $CF_2CF_2CF_2CF_2CF_2CF_2CF_3$), 61.43 (d, *J* = 1.9 Hz), 30.04, 22.38, 14.18 (d, *J* = 3.5 Hz, 1C), 14.08 (d, *J* = 4.4 Hz, C); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.40 – -76.60 (m, 3F), -80.85 – -81.16 (m, 3F), -105.50 (br, 2F), -119.50 (br, 2F), -121.67 – -122.04 (m, 6F), -122.85 (br, 2F), -126.28 (br, 2F); **HRMS** (ESI) *m*/*z* = 807.0291, calcd. for $C_{23}H_{16}F_{20}O_5SNa$ $[M+Na]^+$, found: 807.0300; **IR** (neat, cm^{-1}): 2983*w*, 1728*w*, 1668*w*, 1611*w*, 1423*m*, 1369*w*, 1275*m*, 1243*s*, 1206*s*, 1135*s*, 1104*s*, 1057*w*, 1024*w*, 978*w*, 950*m*, 905*w*, 866*m*, 839*m*, 821*m*, 790*w*, 735*w*, 709*m*, 692*w*, 659*w*, 603*m*, 558*w*.

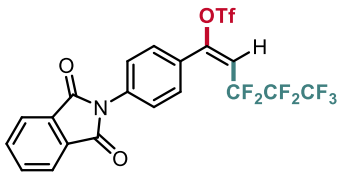


Diethyl 4,4'-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(((trifluoromethyl)sulfonyl)oxy)hex-1-ene-1,2-diyl)(*E*)-dibenzoate (3z): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), diethyl 4,4'-(ethyne-1,2-diyl)dibenzoate **1r** (32.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluorobutyl)iodonium triflate **2b** (97.2 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Then further portions of CuCl (1.0 mg, 10 μmol, 10 mol%), phenyl(perfluorobutyl)iodonium triflate **2b** (9 7.2 mg, 0.170 mmol, 1.7 equiv) and DCE (1 mL) were added. The stirring was continued at 50 °C for further 15 h. Purification via silica gel chromatography (pentane:EtOAc = 200:1, then 150:1) gave the desired product **3z** as an off-white solid in 55% yield (37.7 mg). **MP**: 78 °C; **TLC** $\mathbf{R_f}$ = 0.4

(pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = δ 8.12 – 8.05 (m, 4H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) =165.70, 165.40, 152.71 (t, *J* = 4.3 Hz, C), 134.31, 133.23, 133.15, 131.92, 130.24, 129.82, 129.76, 129.38, 126.79 (t, *J* = 21.9 Hz, C), 117.58 (q, *J* = 318.8 Hz, OSO_2CF_3), 125.00 – 100.00 (m, $CF_2CF_2CF_2CF_3$) 61.54, 61.34, 14.24, 14.24; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -74.53 (s, 3F), -80.79 – -81.06 (m, 3F), -103.42 (t, *J* = 15.1 Hz, 2F), -118.81 – -118.90 (m, 2F), -125.86 – -126.02 (m, 2F); **HRMS** (ESI) *m/z* = 713.0474, calcd. for $C_{25}H_{18}F_{12}O_7SNa$ $[M+Na]^+$, found: 713.0488; **IR** (neat, cm^{-1}): 2988*w*, 2363*w*, 1722*s*, 1661*w*, 1612*w*, 1571*w*, 1427*m*, 1408*m*, 1369*m*, 1352*w*, 1272*s*, 1209*s*, 1182*s*, 1134*s*, 1103*s*, 1068*w*, 1022*s*, 997*m*, 946*w*, 912*w*, 879*m*, 863*m*, 820*s*, 769*s*, 739*s*, 710*s*, 691*m*, 605*s*.

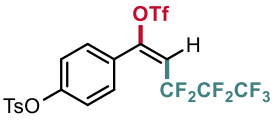


(*E*)-3,3,4,4,5,5,5-Heptafluoro-1-phenylpent-1-en-1-yl trifluoro methanesulfonate (3aa): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), ethynylbenzene **1aa** (10.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 e quiv) in DCE (1 mL) at room temperature for 24 h. The desired product **3aa** could not be separated from the perfluoropropylated by-products resulting from arene perfluoroalkylation. The yield (51%) is based on ^{19}F NMR analysis with $PhCF_3$ as internal standard. **TLC R_f** = 0.75 (pentane); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.68 (s, 3F), -80.19 (t, *J* = 9.0 Hz, 3F), -106.91 (q, *J* = 9.2 Hz, 2F), -127.18 – -127.27 (m, 2F); **EI-MS** (m/z, relative intensity): 420 (M+, 9), 271 (7), 237 (10), 171 (18), 151 (14), 140 (11), 119 (10), 105 (13), 91 (11), 77 (21), 69 (100), 51 (11).



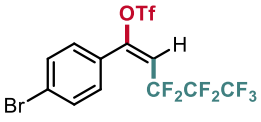
(*E*)-1-(4-(1,3-Dioxoisoindolin-2-yl)phenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate (3ab): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 2-(4-ethynylphenyl)isoindoline-1,3-dione **1ab** (24.7 mg, 0.100 mmol, 1.0

equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Purification via silica gel chromatography (Pentane:Aceton = 7:1) gave the desired product **3ab** as a white solid in 72% yield (40.5 mg). **MP**: 116 °C; **TLC** $\mathbf{R_f}$ = 0.3 (pentane:acetone = 7:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.83 (dd, J^1 = 5.5 Hz, J^2 = 3.0 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 6.10 (t, J = 13.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.60, 156.44 (t, J = 4.6 Hz, C), 135.27, 134.76, 131.49, 129.84 (t, J = 2.5 Hz, C), 128.61, 125.68, 124.00, 118.31 (q, J = 318.6 Hz, OSO_2CF_3), 110.52 (t, J = 23.2 Hz, C), 125.00 –100.00 (m, $CF_2CF_2CF_3$); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.53 (s, 3F), -80.13 (t, J = 9.2 Hz, 3F), -106.80 (q, J = 9.3 Hz, 2F), -127.13 – -127.21 (m, 2F); **HRMS** (ESI) m/z = 587.9934, calcd. for $C_{20}H_9F_{10}NO_5SNa$ $[M+Na]^+$, found: 587.9951; **IR** (neat, cm^{-1}): 2363*w*, 1742*w*, 1715*s*, 1606*w*, 1515*w*, 1424*m*, 1374*m*, 1279*w*, 1212*s*, 1183*m*, 1138*s*, 1120*s*, 1096*m*, 1080*m*, 1026*w*, 1003*w*, 953*w*, 907*s*, 884*m*, 866*m*, 830*w*, 789*w*, 792*s*, 716*s*, 687*w*, 651*w*, 667*w*, 627*w*, 602*m*.

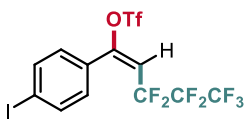


(*E*)-4-(3,3,4,4,5,5,5-Heptafluoro-1-(((trifluoromethyl)sulfon yl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzenesulfonate (3ac): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), 4-ethynylphenyl 4-methylbenzenesulfonate **1ac** (27.2 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Purification via PTCL (pentane:acetone = 15:1) gave the desired product **3ac** as a colorless oil in 82% yield (48.4 mg). **TLC** $\mathbf{R_f}$ = 0.35 (pentane:acetone = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 5.97 (t, J = 13.0 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.90 (t, J = 5.0 Hz, C), 152.06, 145.91, 131.80, 130.77 (t, J = 2.8 Hz, C), 129.82, 128.50, 128.41, 122.70, 118.22 (q, J = 318.7 Hz, OSO_2CF_3), 110.97 (t, J = 23.5 Hz, C), 125.00 –100.00 (m, $CF_2CF_2CF_3$). 21.61; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm)

= -73.59 – -73.62 (m, 3F), -80.24 – -80.30 (m, 3F), -107.03 (q, *J* = 8.5 Hz, 2F), -127.21 – -127.23 (m, 2F); **HRMS** (ESI) *m*/*z* = 612.9808, calcd. for $C_{19}H_{12}F_{10}O_6S_2Na$ $[M+Na]^+$, found: 612.9830; **IR** (neat, cm^{-1}): 3091*w*, 1681*w*, 1601*w*, 1503*w*, 1429*m*, 1381*m*, 1203*s*, 1158*s*, 1179*s*, 1137*s*, 1117*s*, 1092*s*, 1021*w*, 992*m*, 957*m*, 862*s*, 814*m*, 759*m*, 735*m*, 694*m*, 655*m*, 600*m*, 581*m*.

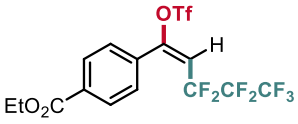


(*E*)-1-(4-Bromophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate (3ad): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 1-bromo-4-ethynylbenzene **1ad** (18.1 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Purification via silica gel chromatography (pentane) gave the desired product **3ad** as a colorless oil in 60% yield (29.7 mg). **TLC** $\mathbf{R_f}$ = 0.6 (pentane); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.55 (dt, J^1 = 9.0 Hz, J^2 = 2.3 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.98 (t, *J* = 13.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 156.22 (t, *J* = 4.9 Hz, 1C), 131.99, 130.55 (t, *J* = 2.7 Hz, 1C), 128.63, 126.91, 118.27 (q, *J* = 318.7 Hz, OSO_2CF_3), 110.79 (t, *J* = 23.5 Hz, 1C), 125.00 –100.00 (m, $CF_2CF_2CF_3$); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.59 (s, 3F), -80.13 – -80.24 (m, 3F), -106.98 (q, *J* = 8.5 Hz, 2F), -127.18 – -127.25 (m, *J* = 8.0 Hz, 2F); **HRMS** (EI) *m*/*z* = 497.89831, calcd. for $C_{12}H_5BrF_{10}O_3S$ $[M]^+$, found: 497.89886; **IR** (neat, cm^{-1}): 3101*w*, 2920*w*, 1680*w*, 1592*w*, 1490*w*, 1431*m*, 1398*w*, 1366*s*, 1350*w*, 1209*s*, 1182*s*, 1137*s*, 1117*s*, 1096*m*, 1073*m*, 1018*m*, 991*s*, 956*m*, 856*s*, 787*w*, 756*m*, 731*m*, 720*m*, 665*w*, 660*s*, 559*w*.

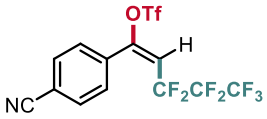


(*E*)-3,3,4,4,5,5,5-Heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate (3ae): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 1-ethynyl-4-iodobenzene **1ae** (22.8 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (78.3 mg, 0.150 mmol, 1.5 equiv) in DCE (1 mL) at room temperature for 24 h. Purification via silica gel

chromatography (pentane) gave the desired product **3ae** as a colorless oil in 60% yield (32.9 mg). **TLC** $\mathbf{R_f}$ = 0.75 (pentane); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.97 (t, *J* = 13.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 156.39 (t, *J* = 4.8 Hz, C), 137.92, 130.41 (t, *J* = 2.5 Hz, C), 118.27 (q, *J* = 320.7 Hz, OSO_2CF_3), 110.71 (t, *J* = 23.5 Hz, C), 129.20, 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 99.11; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.61 (s, 3F), -80.23 (t, *J* = 9.0 Hz, 3F), -106.98 (q, *J* = 9.6 Hz, 2F), -127.23 – -127.27 (m, 2F); **HRMS** (ESI) *m*/*z* = 568.8737, calcd. for $C_{12}H_5F_{10}IO_3SNa$ $[M+Na]^+$, found: 568.8723; **IR** (neat, cm^{-1}): 3097*w*, 1680*w*, 1587*w*, 1486*w*, 1430*m*, 1394*w*, 1350*w*, 1210*s*, 1183*s*, 1137*s*, 1116*s*, 1061*w*, 1014*m*, 990*s*, 951*m*, 855*s*, 787*w*, 755*m*, 731*w*, 718*w*, 668*w*, 598*s*.

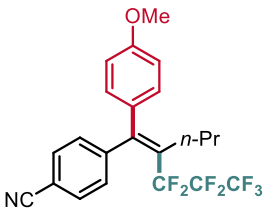


Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate (3af): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 μmol, 10 mol%), ethyl 4-ethynylbenzoate **1af** (17.4 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via PTLC (pentane:acetone = 40:1) gave the desired product **3af** as a slight yellow oil in 65% yield (31.9 mg). **TLC** $\mathbf{R_f}$ = 0.6 (pentane:EtOAc = 40:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 6.03 (t, *J* = 13.0 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.29, 156.20 (t, *J* = 5.0 Hz, 1C), 137.90, 133.59 (d, *J* = 1.5 Hz, 1C), 129.62, 129.18, 118.26 (q, *J* = 318.5 Hz, OSO_2CF_3), 111.29 (t, *J* = 23.7 Hz, 1C), 125.00 –100.00 (m, $CF_2CF_2CF_3$), 61.57, 14.24; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.54 (s, 3F), -80.21 (t, *J* = 9.3 Hz, 3F), -107.06 (q, *J* = 9.4 Hz, 2F), -127.13 – -127.21 (m, 2F); **HRMS** (ESI) *m*/*z* = 514.9981, calcd. for $C_{15}H_{10}F_{10}O_5SNa$ $[M+Na]^+$, found: 514.9975; **IR** (neat, cm^{-1}): 2999*w*, 1724*m*, 1682*w*, 1431*m*, 1369*w*, 1351*w*, 1275*s*, 1245*s*, 1210*s*, 1182*s*, 1138*s*, 1104*s*, 1024*m*, 994*s*, 955*m*, 872*s*, 843*m*, 779*w*, 759*m*, 733*m*, 706*s*, 599s.



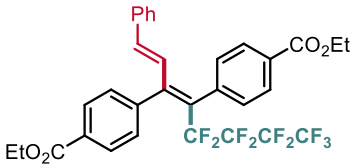
(*E*)-1-(4-Cyanophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate (3ag): The title compound was prepared according to general procedure **GP2** with CuCl (1.0 mg, 10 µmol, 10 mol%), 4-ethynylbenzonitrile **1ag** (12.7 mg, 0.100 mmol, 1.0 equiv), and phenyl(perfluoropropyl)iodonium triflate **2a** (88.8 mg, 0.170 mmol, 1.7 equiv) in DCE (1 mL) at 50 °C for 15 h. Purification via PTLC (pentane:EtOAc = 20:1) gave the desired product **3ag** as a colorless oil in 34% yield (15.1 mg). **TLC R_f** = 0.5 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.71 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 6.08 (t, *J* = 13.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.88 (t, *J* = 5.1 Hz, C), 133.88, 132.31, 129.83 (t, *J* = 2.5 Hz, C), 118.23 (q, *J* = 318.7 Hz, OSO_2CF_3), 117.36, 112.19 (t, *J* = 24.0 Hz, C), 115.91, 125.00 –100.00 (m, $CF_2CF_2CF_3$); **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -73.33 (s, 3F), -80.13 (t, *J* = 9.2 Hz, 3F), -107.07 (q, *J* = 9.4 Hz, 2F), -127.04 – -127.12 (m, 2F); **HRMS** (ESI) *m*/*z* = 467.9723, calcd. for $C_{13}H_5F_{10}NO_3SNa$ $[M+Na]^+$, found: 467.9722; **IR** (neat, cm^{-1}): 2920*w*, 2237*w*, 1682*w*, 1505*w*, 1432*m*, 1351*w*, 1212*s*, 1182*s*, 1136*s*, 1117*s*, 1025*w*, 997*s*, 956*m*, 861*s*, 828*w*, 786*w*, 758*m*, 732*s*, 668*w*, 660*s*, 566*m*.

Spectral data of follow-up products 4, 5, 6, 7

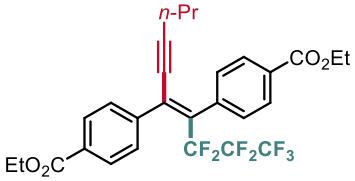


(*E*)-4-(3,3,4,4,5,5,5-Heptafluoro-1-(4-methoxyphenyl)-2-propylpent-1-en-1-yl)benzonitrile (4): TLC R_f = 0.50 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.45 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.70 (s, 3H), 2.21 – 2.15 (m, 2H), 1.34 (tq, J^1 = 7.8 Hz, J^2 = 7.2 Hz, 2H), 0.67 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.22, 149.53 (t, *J* = 4.9 Hz, C), 146.15, 133.15, 131.43, 128.79, 128.62, 118.61, 114.27, 110.92, 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 55.19, 31.60, 22.95, 14.02; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -80.45 (t, *J* = 10.2 Hz, 3F), -103.90 (q, *J* = 10.0 Hz, 2F), -123.93 – -124.08 (m, 2F); **HRMS** (ESI) *m*/*z* = 468.1169, calcd. for $C_{22}H_{18}F_7NONa$ $[M+Na]^+$, found: 468.1176; **IR** (neat, cm^{-1}):

2965*w*, 2876*w*, 2842*w*, 2230*w*, 1605*m*, 1509*m*, 1467*w*, 1345*m*, 1289*w*, 1247*s*, 1223*s*, 1195*s*, 1174*s*, 1129*m*, 1107*s*, 1061*w*, 1033*m*, 951*w*, 926*m*, 874*w*, 843*w*, 828*m*, 806*w*, 767*w*, 748*m*, 691*m*, 573*s*.

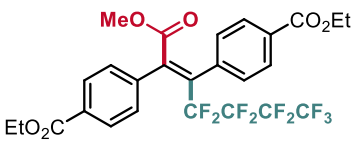


Diethyl 4,4'-((1E,3Z)-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenylocta-1,3-diene-3,4-diyl)dibenzoate (5): MP > 105 °C decomp.**;** $\mathbf{R_f}$ = 0.45 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.08 (d, *J* = 12.6 Hz, 2H), 8.06 (d, *J* = 12.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.04 (m, 3H), 7.02 – 6.82 (m, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 5.87 (d, *J* = 15.9 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.34, 166.16, 148.60 (t, *J* = 4.3 Hz, C), 141.45, 139.28, 138.66, 135.68, 131.55, 130.83, 129.95, 129.54, 129.04, 128.93, 128.66, 128.37, 127.16, 126.65 (t, *J* = 19.9 Hz, C), 125.00 – 100.00 (m, $CF_2CF_2CF_2CF_3$), 61.26, 61.12, 14.32, 14.32; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -81.01 (t, *J* = 9.7 Hz, 3F), -101.30 (t, *J* = 14.8 Hz, 3F), -118.24 (q, *J* = 9.1 Hz, 2F), -125.94 – -126.11 (m, 2F); **HRMS** (ESI) *m*/*z* = 667.1501, calcd. For $C_{32}H_{25}F_9O_4Na$ $[M+Na]^+$, found: 667.1511; **IR** (neat, cm^{-1}): 2983*w*, 1717*s*, 1608*w*, 1580*w*, 1449*w*, 1406*w*, 1368*w*, 1351*w*, 1310*w*, 1270*s*, 1232*s*, 1204*s*, 1174*s*, 1133*s*, 1101*s*, 1083*m*, 1022*m*, 966*w*, 954*w*, 935*w*, 912*w*, 889*m*, 850*w*, 825*w*, 800*w*, 768*w*, 757*w*, 726*m*, 714*s*, 693*m*, 638*w*.



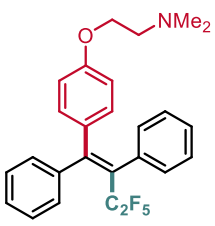
Diethyl 4,4'-(1,1,1,2,2,3,3-heptafluorodec-4-en-6-yne-4,5-diyl)(*E*)-dibenzoate (6): MP: 91 °C; $\mathbf{R_f}$ = 0.5 (pentane:EtOAc = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (d, *J* = 8.3 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.96 (t, *J* = 6.9 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H) , 1.12 (tq, J^1 = 7.2 Hz, J^2 = 7.2 Hz, 2H), 0.54 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.18, 166.12, 142.17, 139.67 (t, *J* = 2.9 Hz, C), 135.61 (t, *J* = 4.8 Hz, C), 132.90 (t, *J* = 20.2 Hz, C), 130.60, 130.14, 129.24, 129.19,

127.61 (t, J =3.1 Hz, C), 105.54, 125.00 – 100.00 (m, $CF_2CF_2CF_3$), 80.47 (t, J = 2.6 Hz, C), 61.09, 61.04, 21.58, 21.29, 14.29, 13.00; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -80.38 (t, J = 10.5 Hz, 3F), -102.61 – -102.70 (m, 2F), -122.13 – -122.27 (m, 2F); **HRMS** (ESI) m/z = 581.1533, calcd. For $C_{28}H_{25}F_7O_4Na$ $[M+Na]^+$, found: 581.1547; **IR** (neat, cm^{-1}): 2970*w*, 2937*w*, 2875*w*, 2214*w*, 1718*s*, 1610*w*, 1407*w*, 1368*w*, 1345*m*, 1310*w*, 1270*s*, 1227*s*, 1213*s*, 1178*s*, 1147*m*, 1100*s*, 1021*m*, 996*m*, 911*w*, 879*w*, 836*w*, 769*w*, 741*m*, 713*s*, 638*w*.



Diethyl 4,4'-(4,4,5,5,6,6,7,7,7-nonafluoro-1-methoxy-1-oxohept-2-ene-2,3-diyl)(*E*)-dibenzoate (7): MP: 109 °C; **R_f** = 0.4 (pentane:EtOAc = 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 (d, J = 8.2 Hz, 4H), 7.42 (d, J = 8.1 Hz, 4H), 4.33 (q, J = 7.1 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.28 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.40, 165.93, 165.86, 145.97 (t, J = 4.2 Hz), 137.35, 136.97, 131.34, 130.95, 130.27, 129.30, 129.24, 127.80, 125.00 – 100.00 (m, $CF_2CF_2CF_2CF_3$), 61.26, 61.18, 52.58, 14.28, 14.28; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -81.01 (t, J = 9.7 Hz, 3F), -103.98 (t, J = 14.1 Hz, 2F), -118.96 (tt, J^1 = 12.5 Hz, J^2 = 6.5 Hz, 2F), -125.90 – -126.11 (m, 2F); **HRMS** (ESI) m/z = 623.1087, calcd. For $C_{26}H_{21}F_9O_6Na$ $[M+Na]^+$, found: 623.1096; **IR** (neat, cm^{-1}): 2988*w*, 1722*s*, 1610*w*, 1435*w*, 1407*w*, 1369*w*, 1354*w*, 1311*w*, 1273*s*, 1235*s*, 1219*s*, 1180*m*, 1135*s*, 1104*s*, 1022*m*, 897*w*, 814*w*, 774*w*, 744*w*, 712*w*.

Spectral data of pentafluorinated Tamoxifen 8



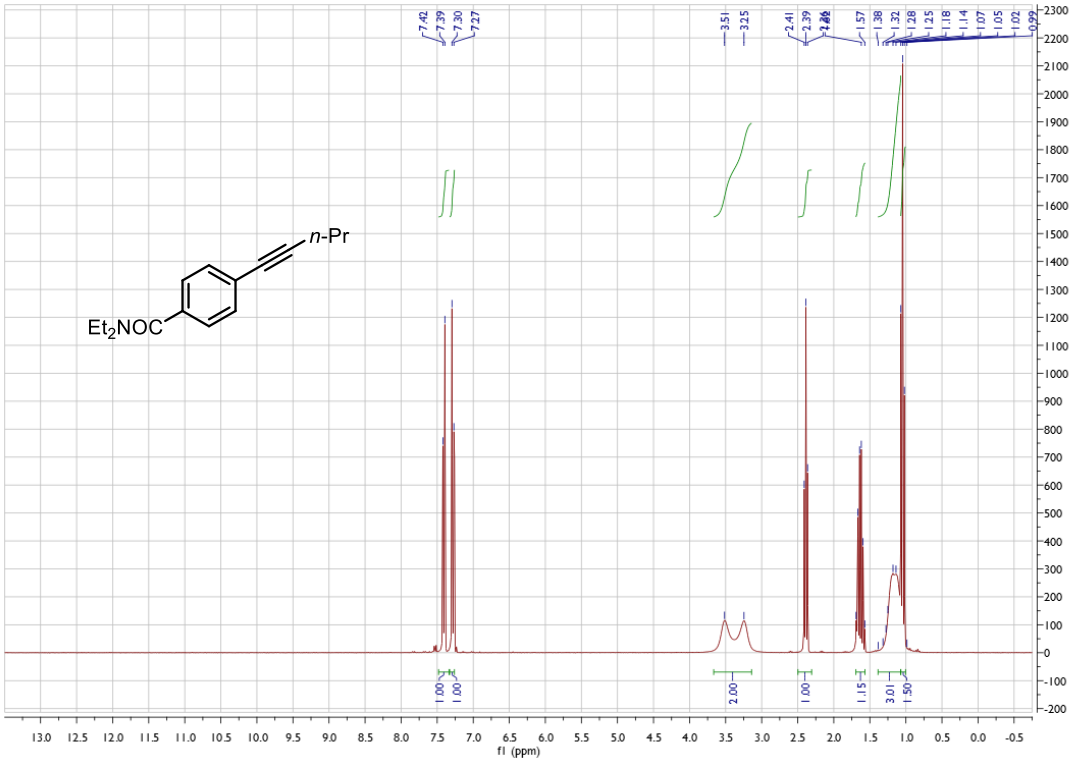
(*E*)-*N*,*N*-dimethyl-2-(4-(3,3,4,4,4-pentafluoro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethan-1-amine (8): R_f = 0.3 (DCM:MeOH = 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 – 7.19 (m, 2H), 7.17 – 7.10 (m, 4H), 6.72 (d, J = 8.8 Hz, 6H), 6.47 (d, J = 8.8 Hz, 2H), 3.85 (t, J = 5.6 Hz, 2H), 2.59 (t, J = 5.5 Hz, 2H), 2.23 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.69, 152.72 – 152.44 (m, C), 141.10, 135.42, 134.16, 131.78, 130.91, 127.92, 127.86, 127.76, 127.68, 127.30, 113.65, 130.00 – 100.00 (m, CF_2CF_3), 65.63, 58.09, 45.73; **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm)

= -80.76 (t, *J* = 3.1 Hz, 3F), -104.92 (s, 2F); **HRMS** (EI) *m*/*z* = 462.1851, calcd. for $C_{26}H_{25}F_5NO^+$ $[M+H]^+$, found: 462.1844; **IR** (neat, cm^{-1}): 2974*w*, 2943*w*, 2934*w*, 2825*w*, 2775*w*, 1606*w*, 1509*m*, 1466*w*, 1445*w*, 1325*w*, 1287*w*, 1208*s*, 1196*s*, 1158*m*, 1109*w*, 1077*w*, 1046*m*, 1029*m*, 965*w*, 912*w*, 840*w*, 760*w*, 724*w*, 705*m*, 671*w*.

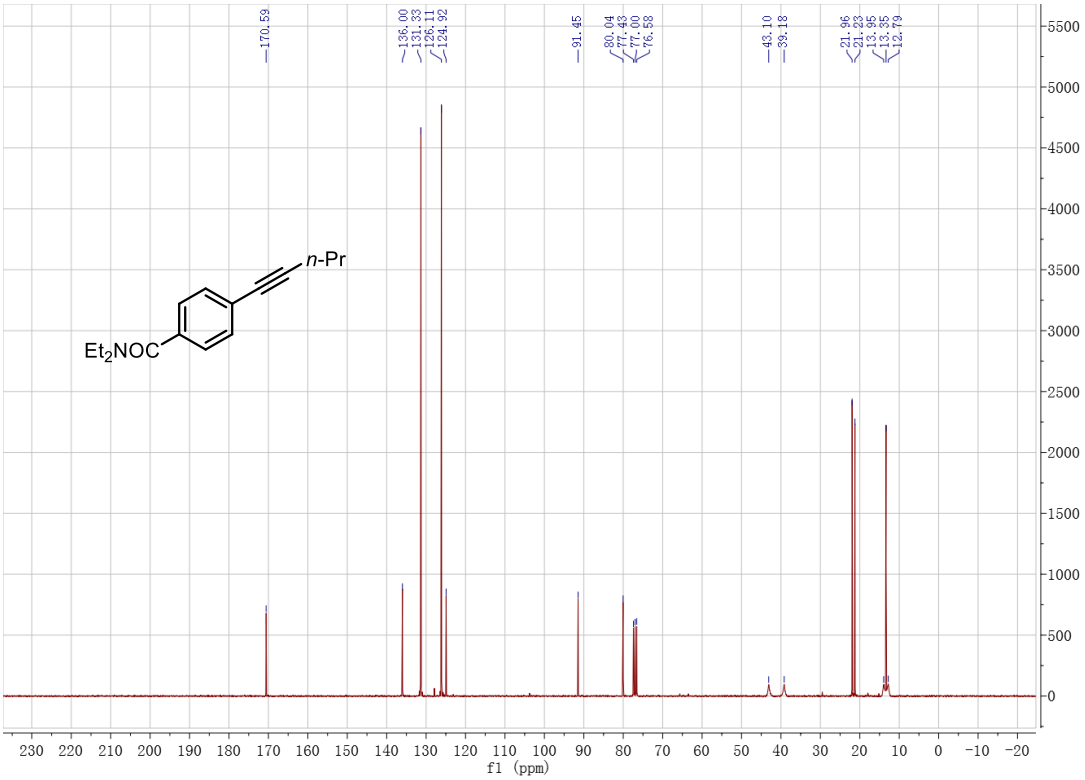
7. Spectra

Spectra of alkynes 1

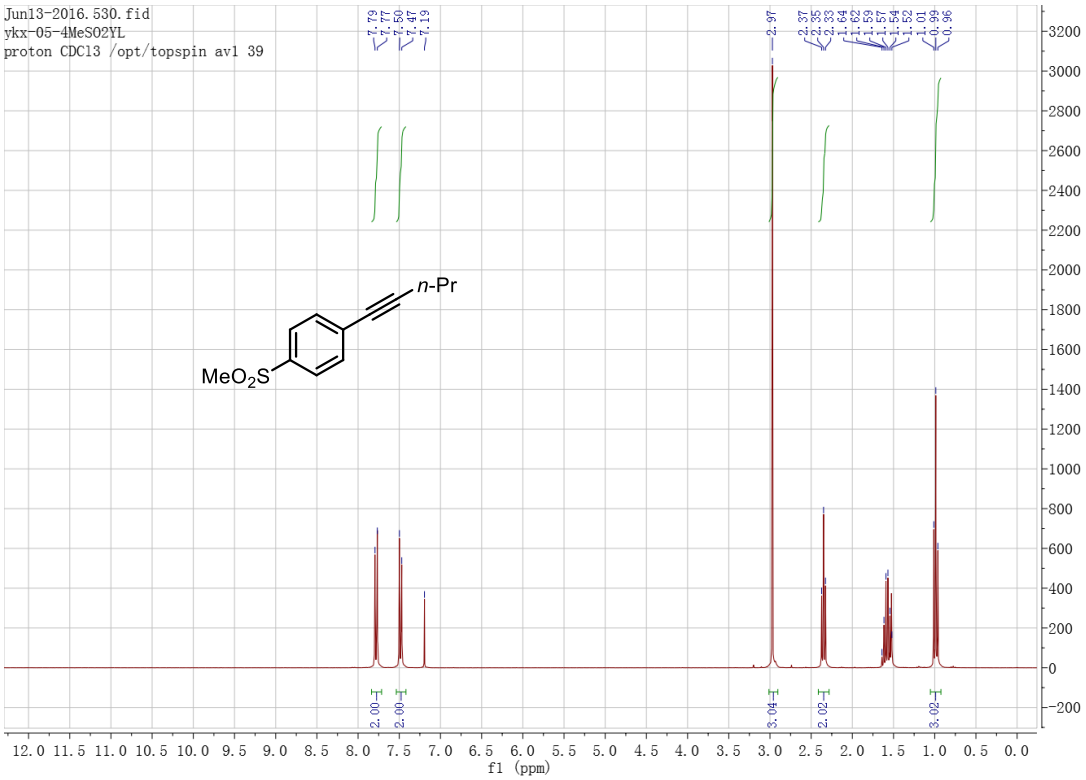
^{1}H NMR Spectrum of *N*,*N*-diethyl-4-(pent-1-yn-1-yl)benzamide 1d



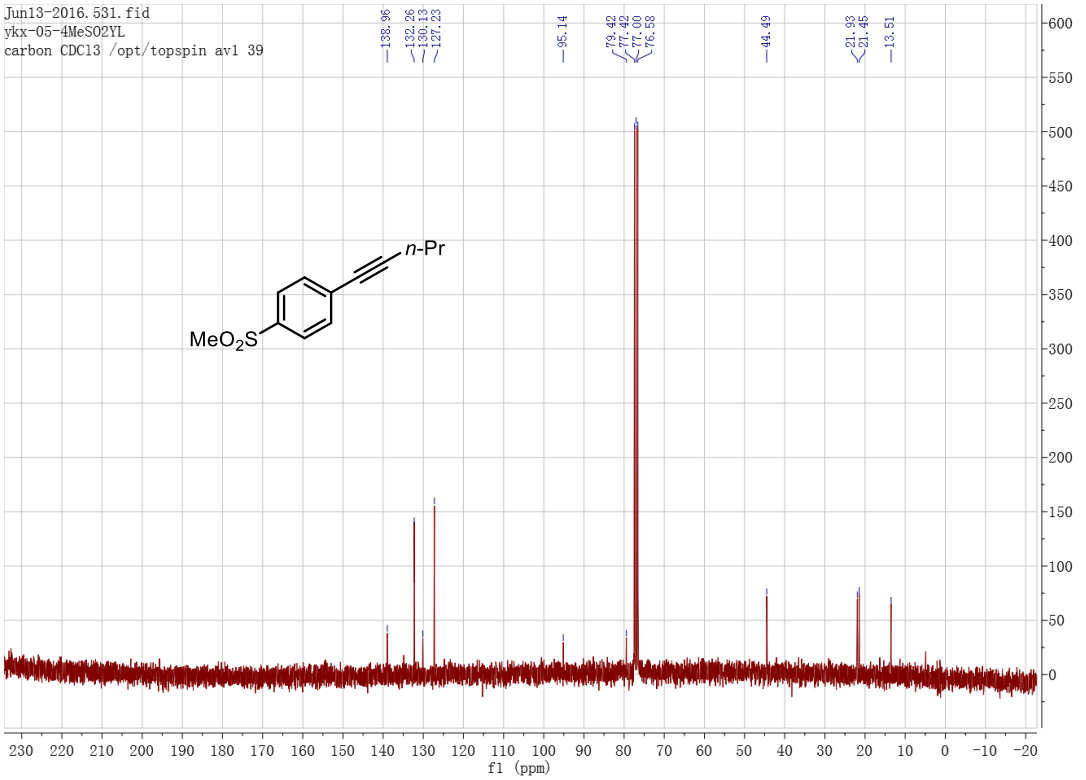
^{13}C NMR Spectrum of *N*,*N*-diethyl-4-(pent-1-yn-1-yl)benzamide 1d



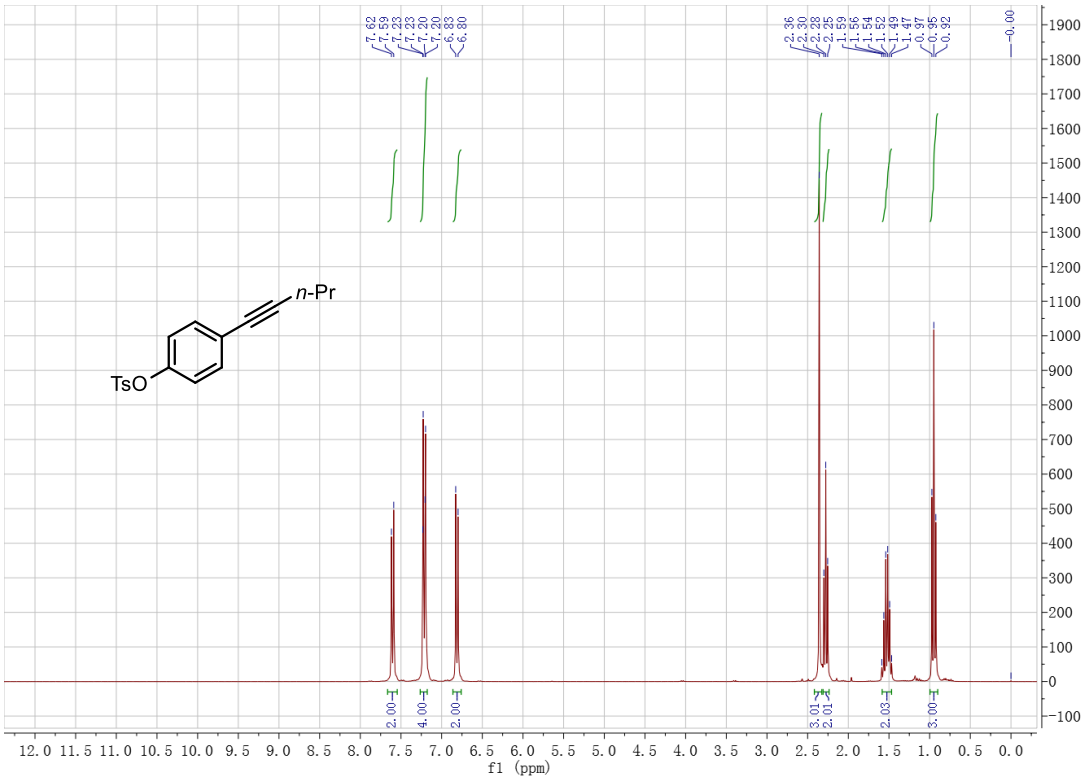
^{1}H NMR Spectrum of 1-(Methylsulfonyl)-4-(pent-1-yn-1-yl)benzene 1e



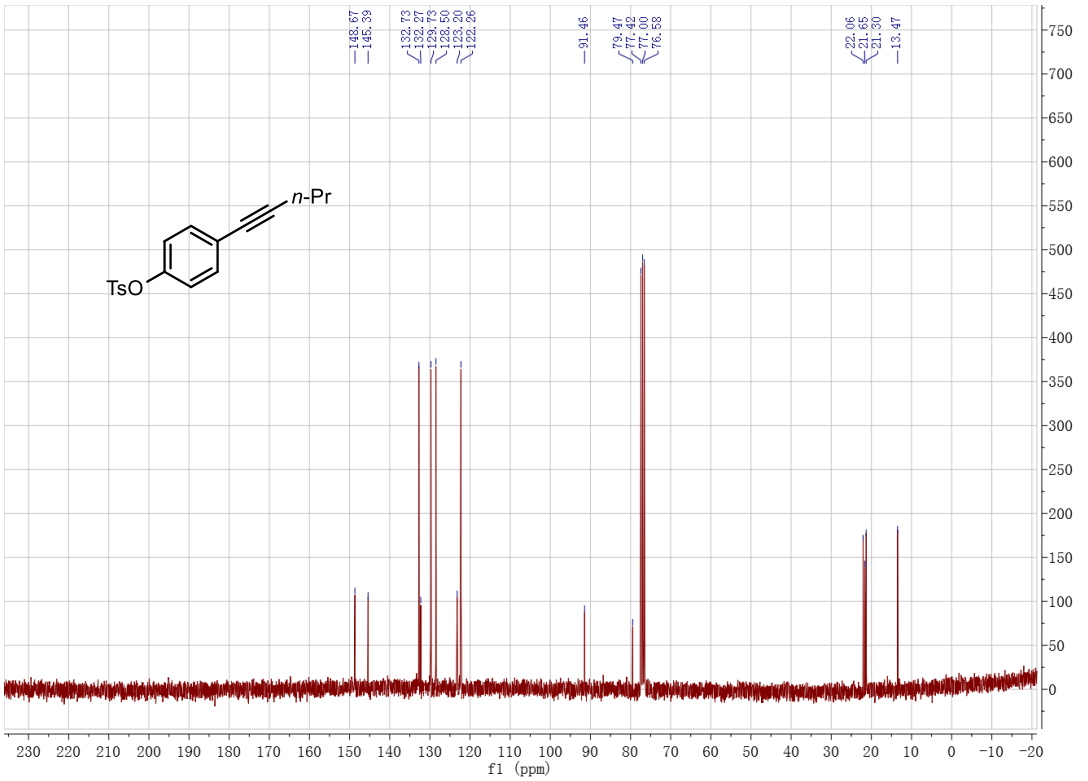
^{13}C NMR Spectrum of 1-(Methylsulfonyl)-4-(pent-1-yn-1-yl)benzene 1e



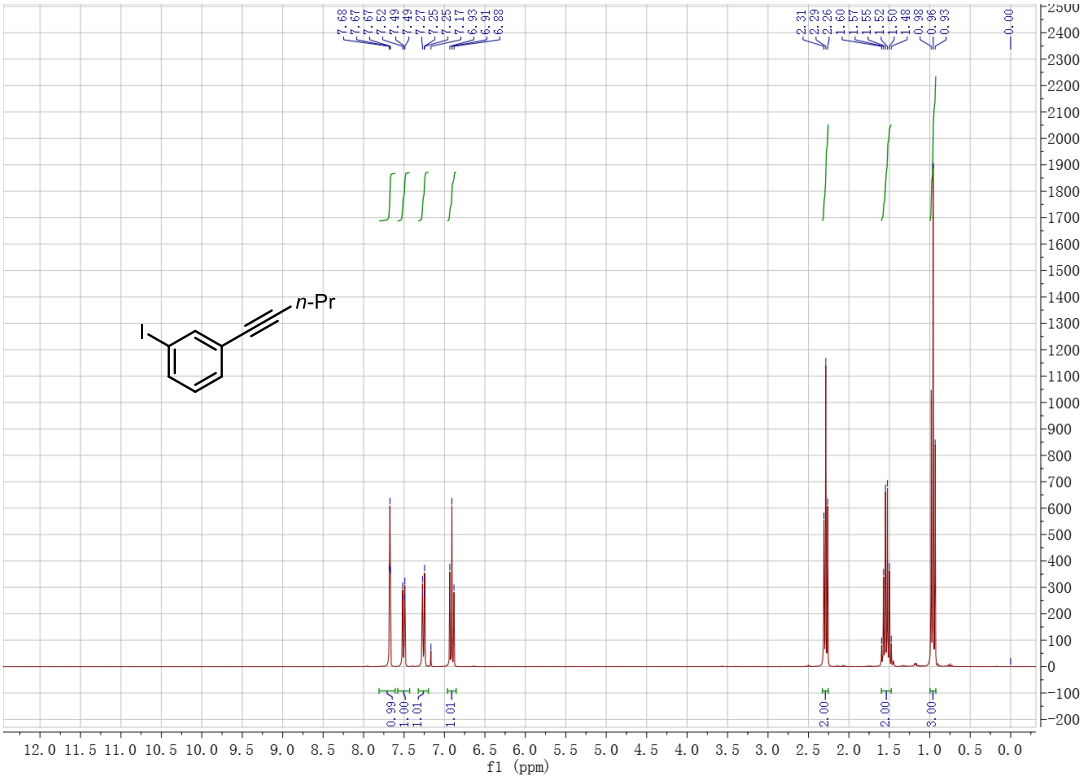
^{1}H NMR Spectrum of 4-(Pent-1-yn-1-yl)phenyl 4-methylbenzenesulfonate 1i:



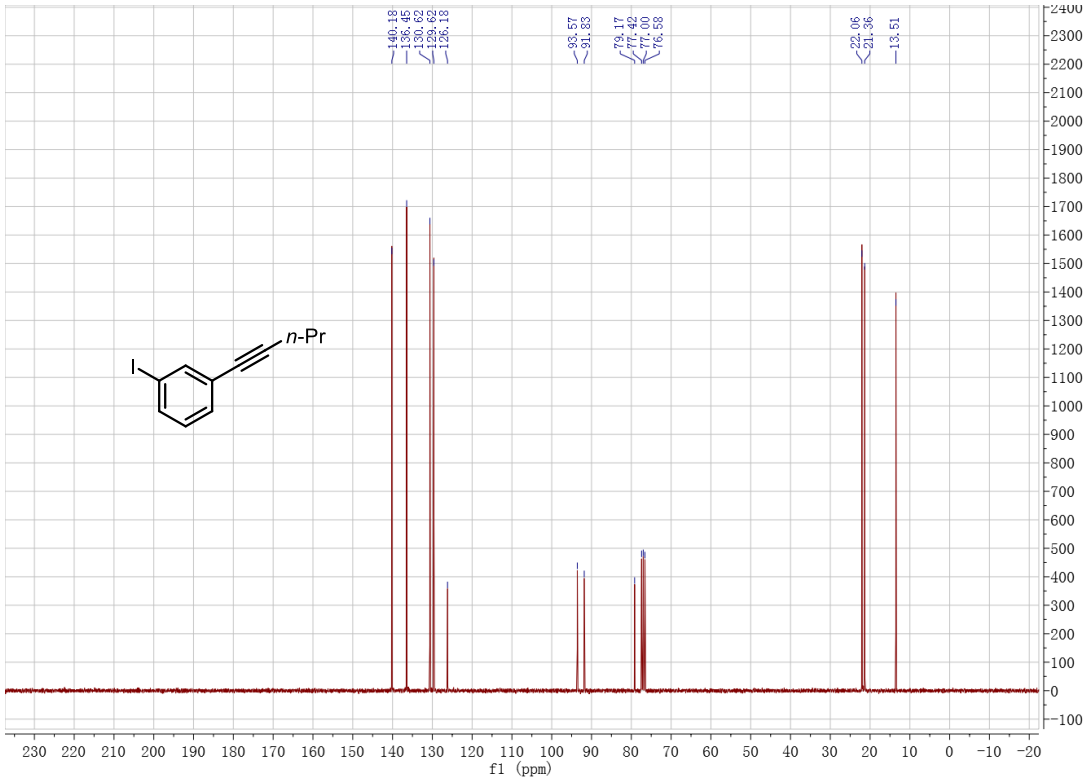
^{13}C NMR Spectrum of 4-(Pent-1-yn-1-yl)phenyl 4-methylbenzenesulfonate 1i:



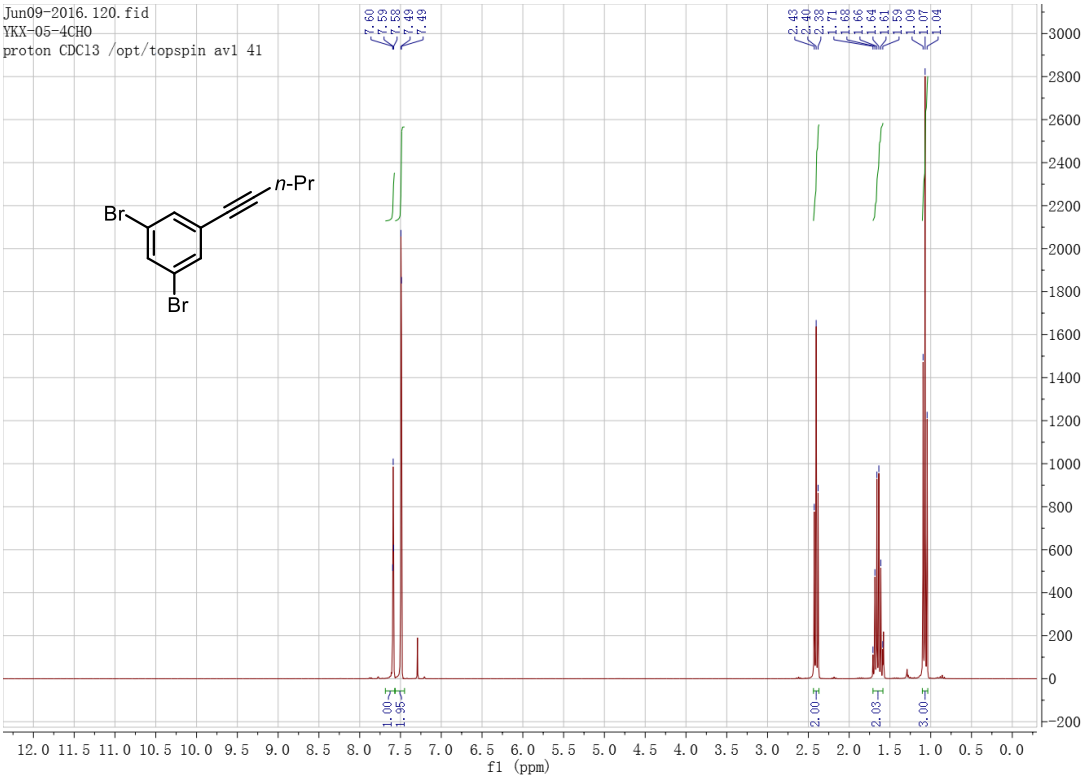
^{1}H NMR Spectrum of 1-Iodo-3-(pent-1-yn-1-yl)benzene 1j



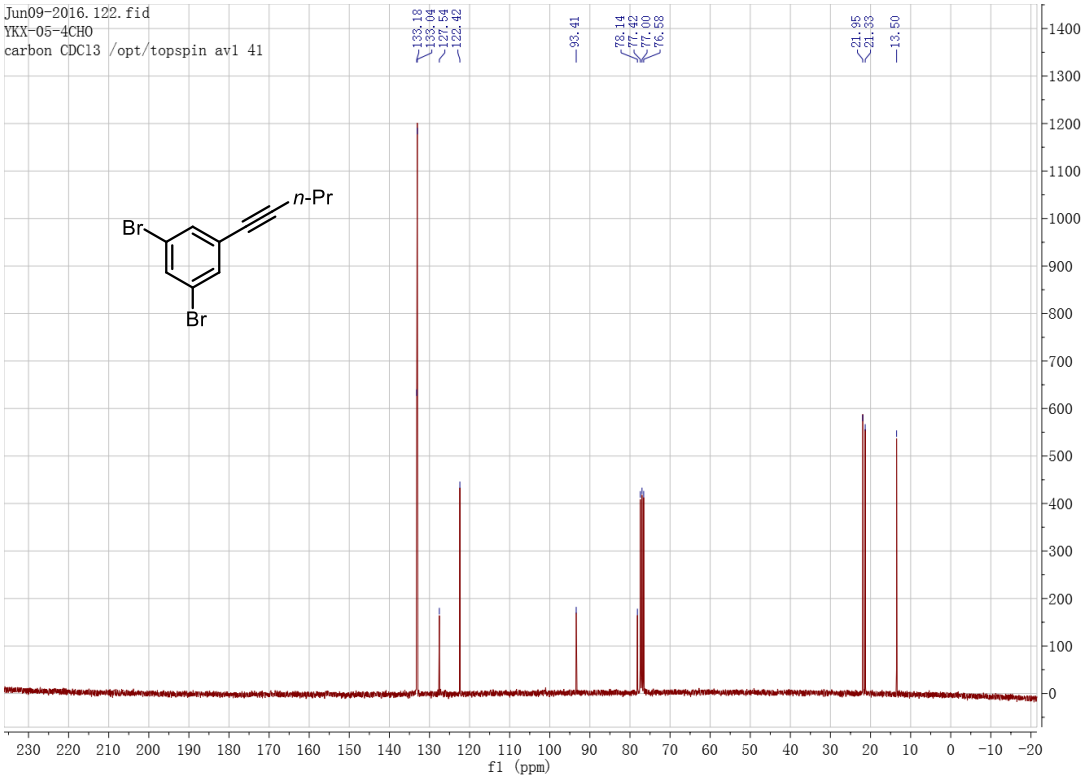
^{13}C NMR Spectrum of 1-Iodo-3-(pent-1-yn-1-yl)benzene 1j



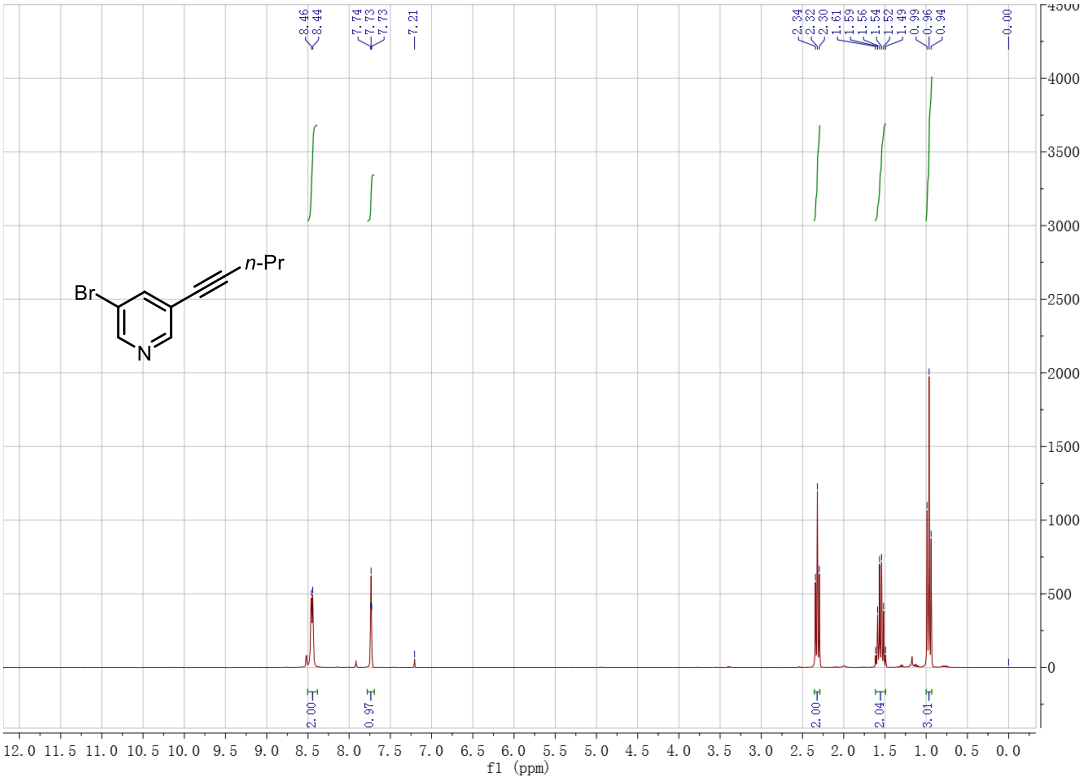
^{1}H NMR Spectrum of 1,3-Dibromo-5-(pent-1-yn-1-yl)benzene 1n



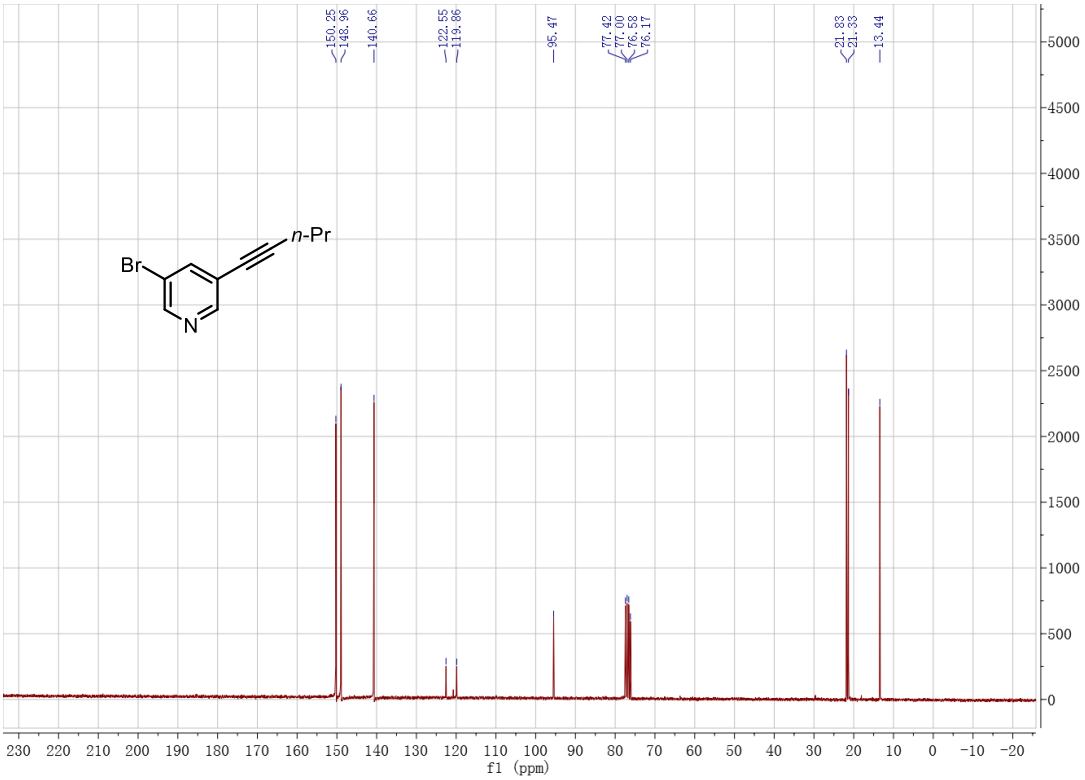
^{13}C NMR Spectrum of 1,3-Dibromo-5-(pent-1-yn-1-yl)benzene 1n



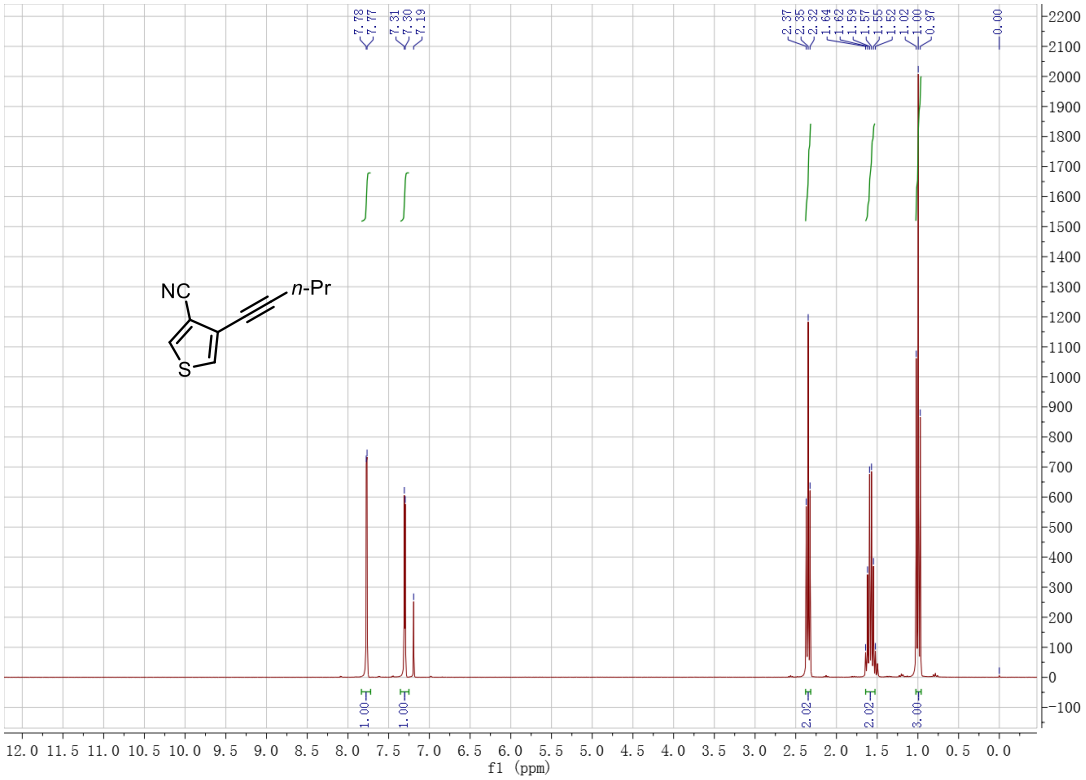
^{1}H NMR Spectrum of 3-Bromo-5-(pent-1-yn-1-yl)pyridine 1o



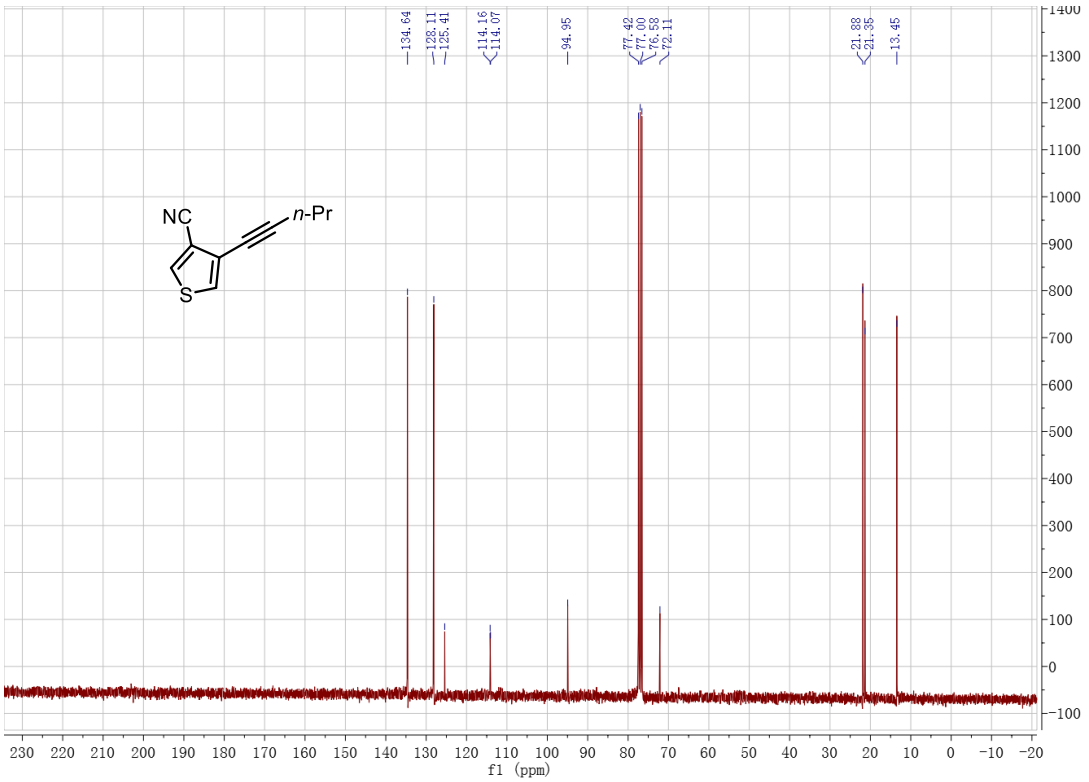
^{13}C NMR Spectrum of 3-Bromo-5-(pent-1-yn-1-yl)pyridine 1o



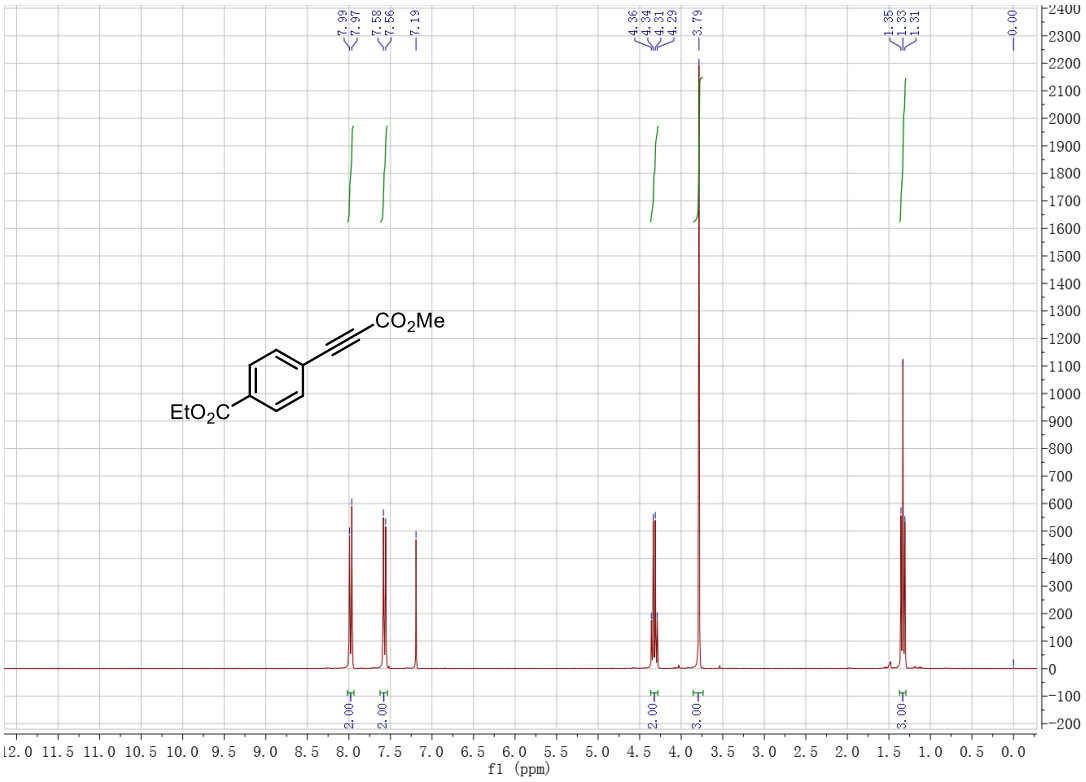
^{1}H NMR Spectrum of 4-(Pent-1-yn-1-yl)thiophene-3-carbonitrile 1p



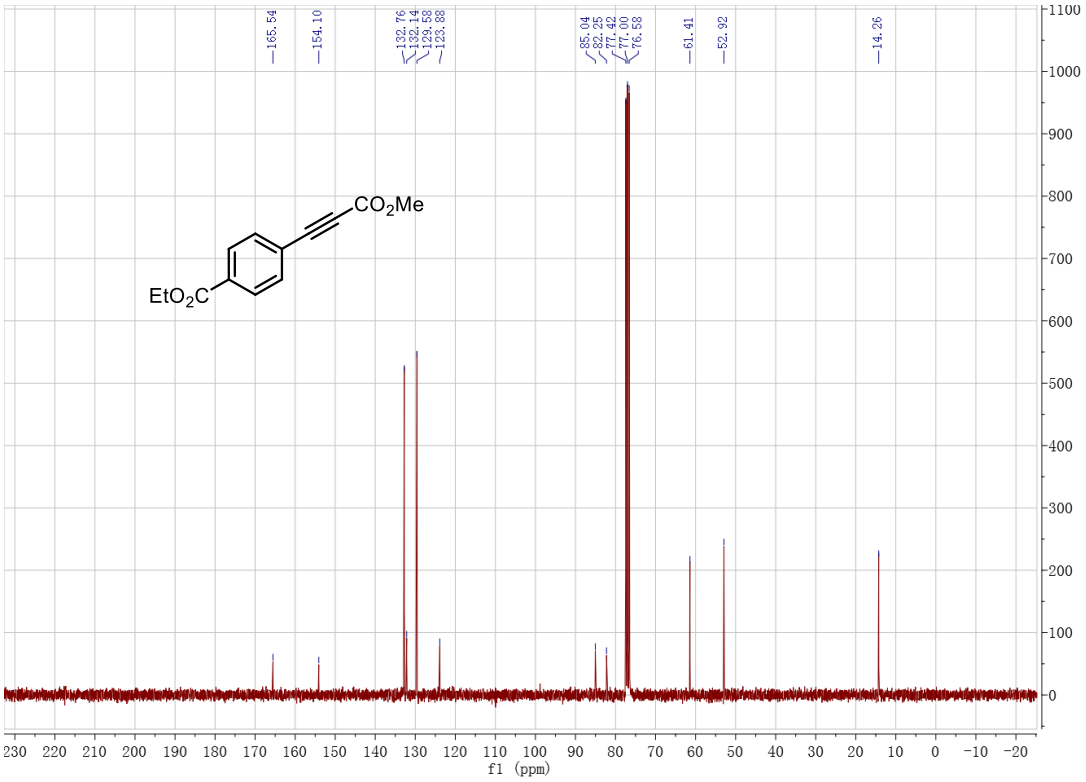
^{13}C NMR Spectrum of 4-(Pent-1-yn-1-yl)thiophene-3-carbonitrile 1p



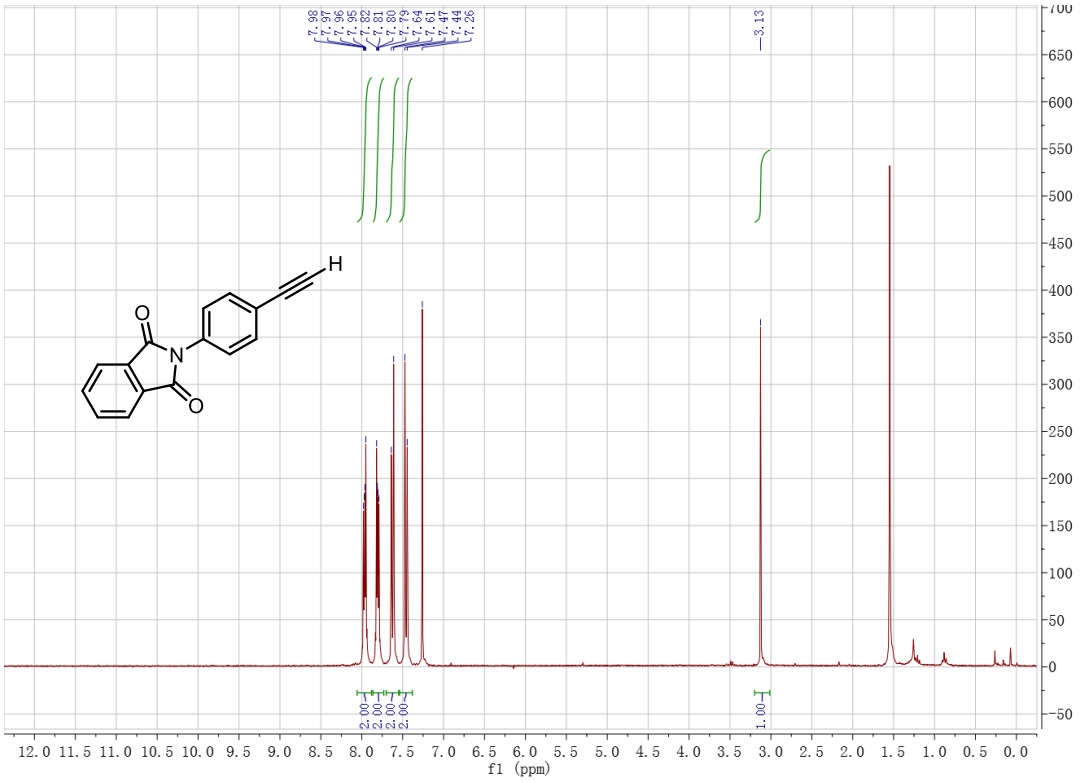
^{1}H NMR Spectrum of Ethyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate 1v



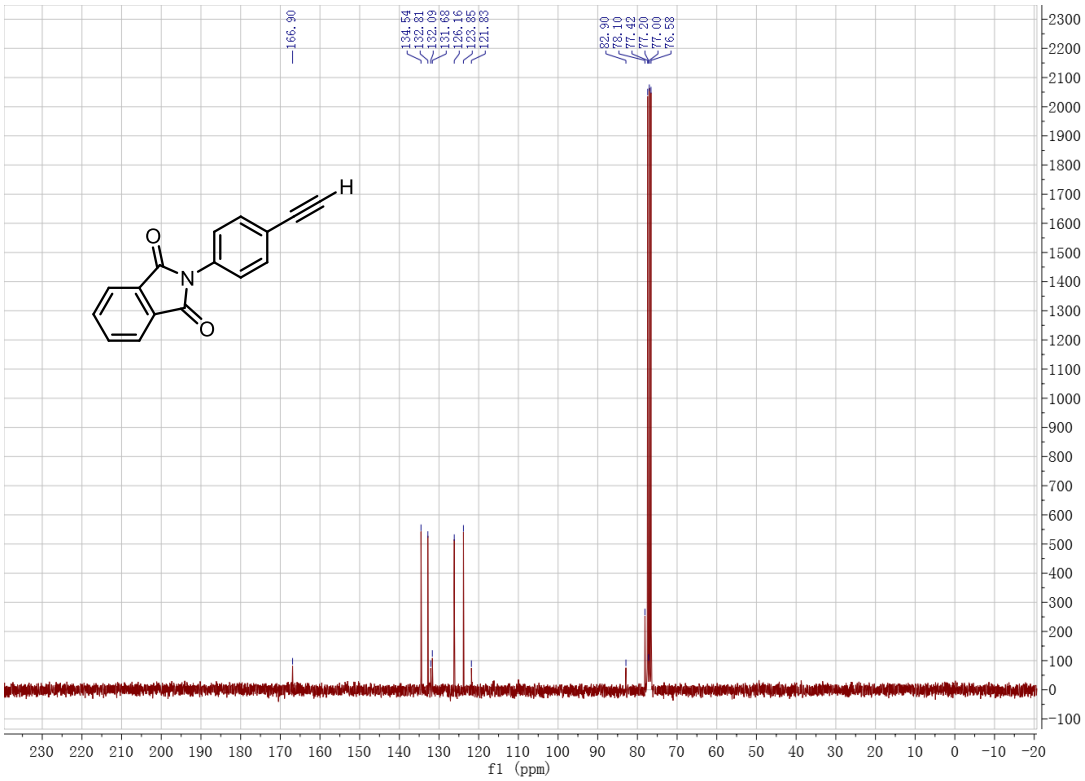
^{13}C NMR Spectrum of Ethyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate 1v



^{1}H NMR Spectrum of 2-(4-Ethynylphenyl)isoindoline-1,3-dione 1ab

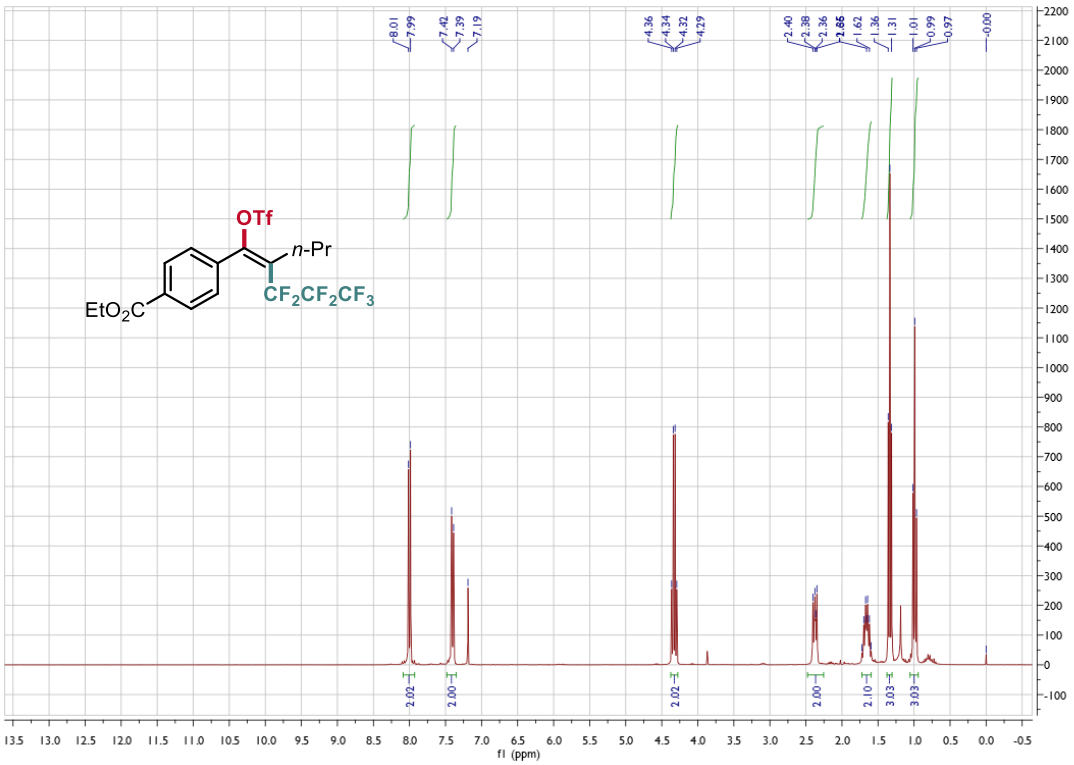


^{13}C NMR Spectrum of 2-(4-Ethynylphenyl)isoindoline-1,3-dione 1ab

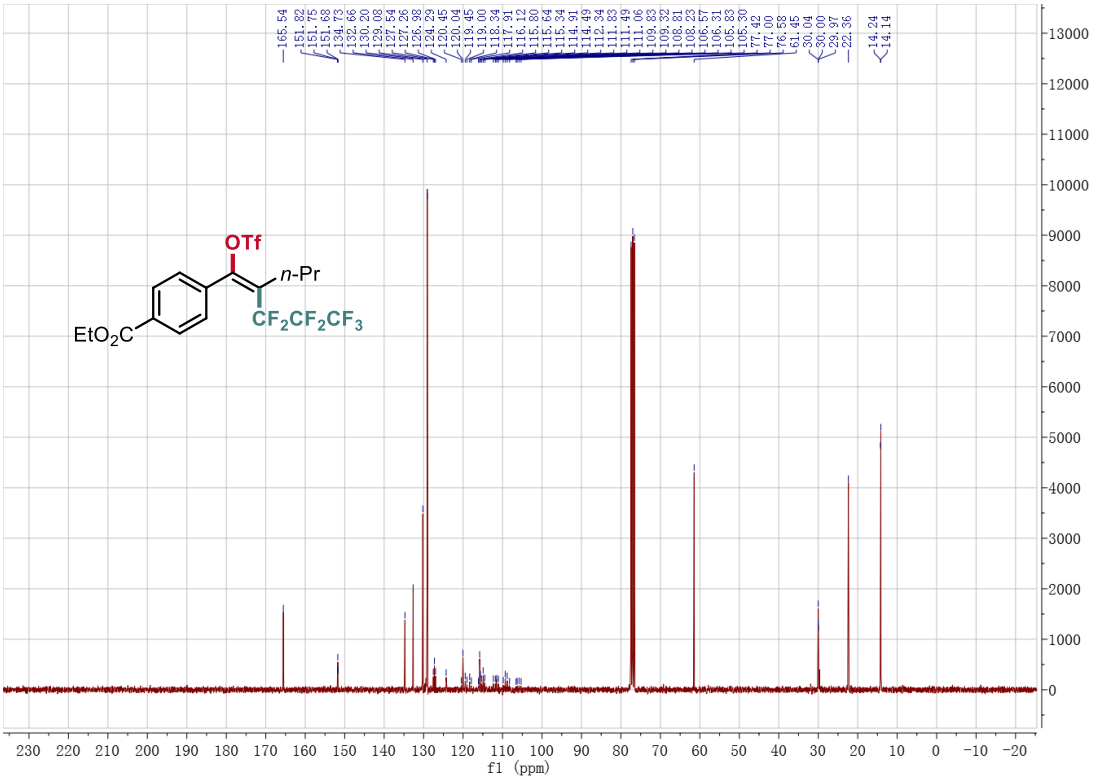


Spectral of perfluoroalkyltriflation products 3

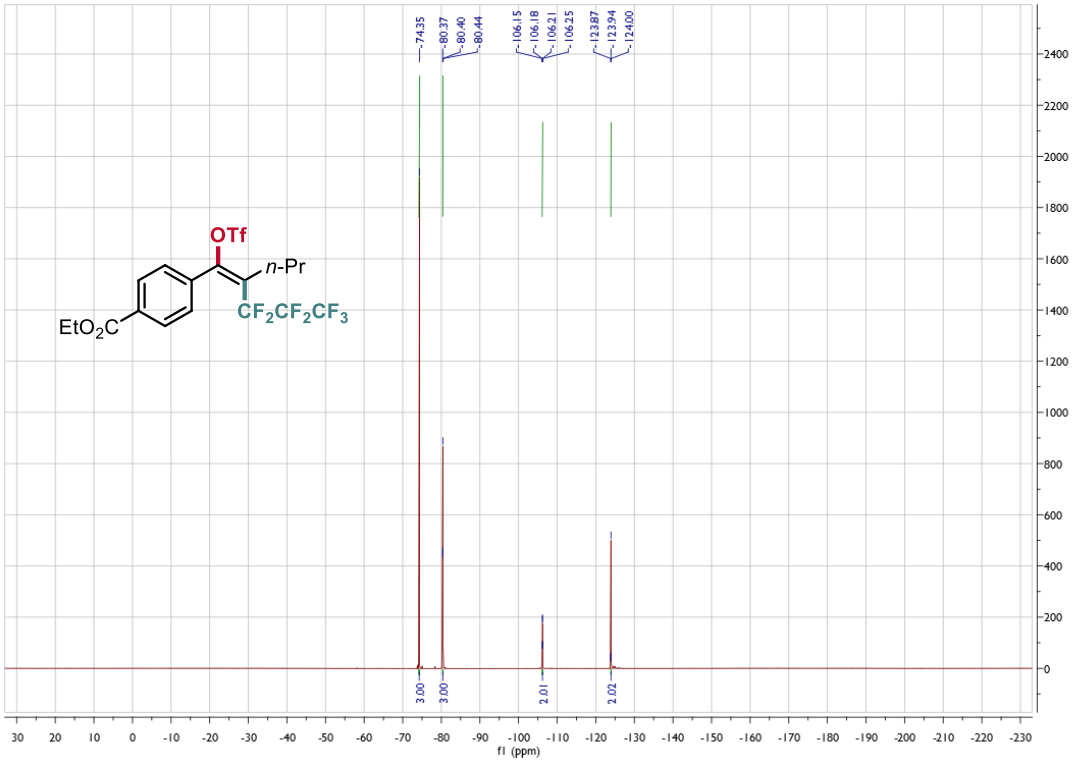
^{1}H NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3a



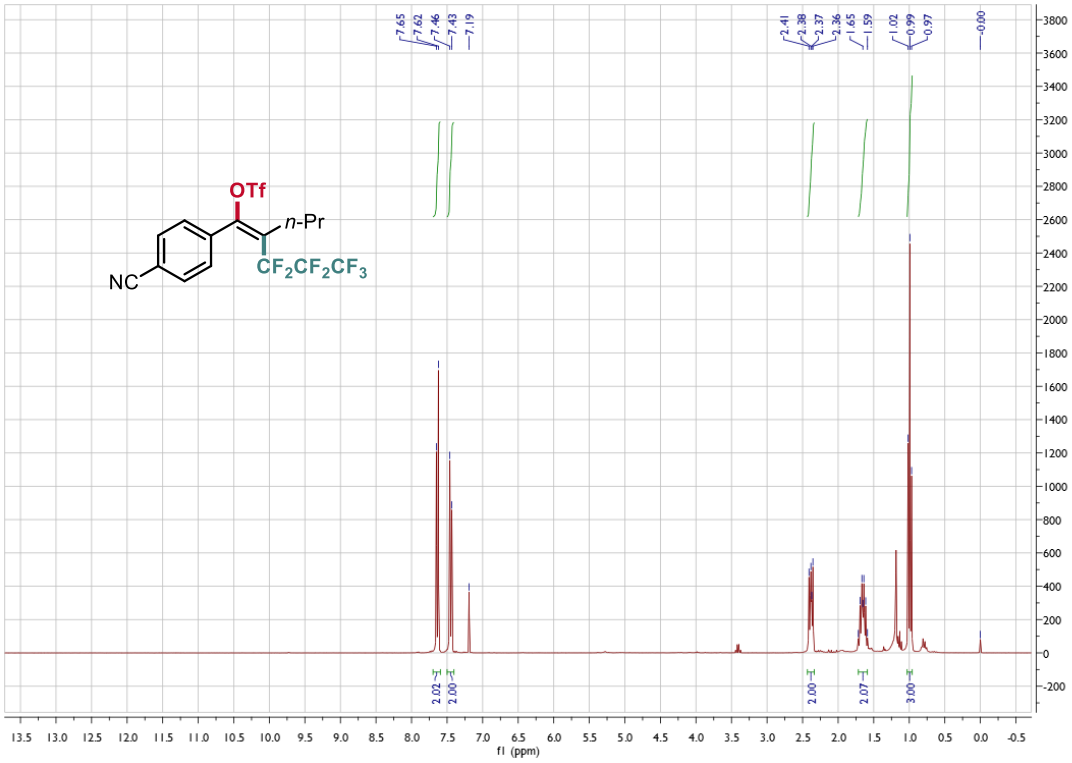
^{13}C NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3a



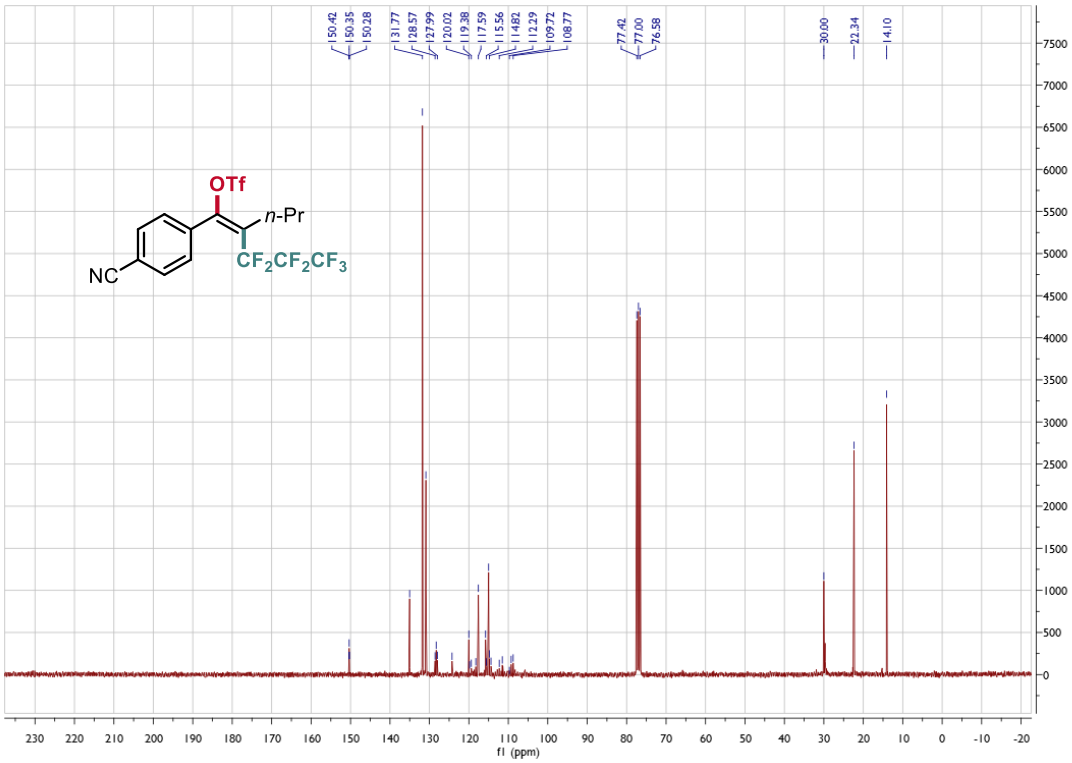
^{19}F NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3a



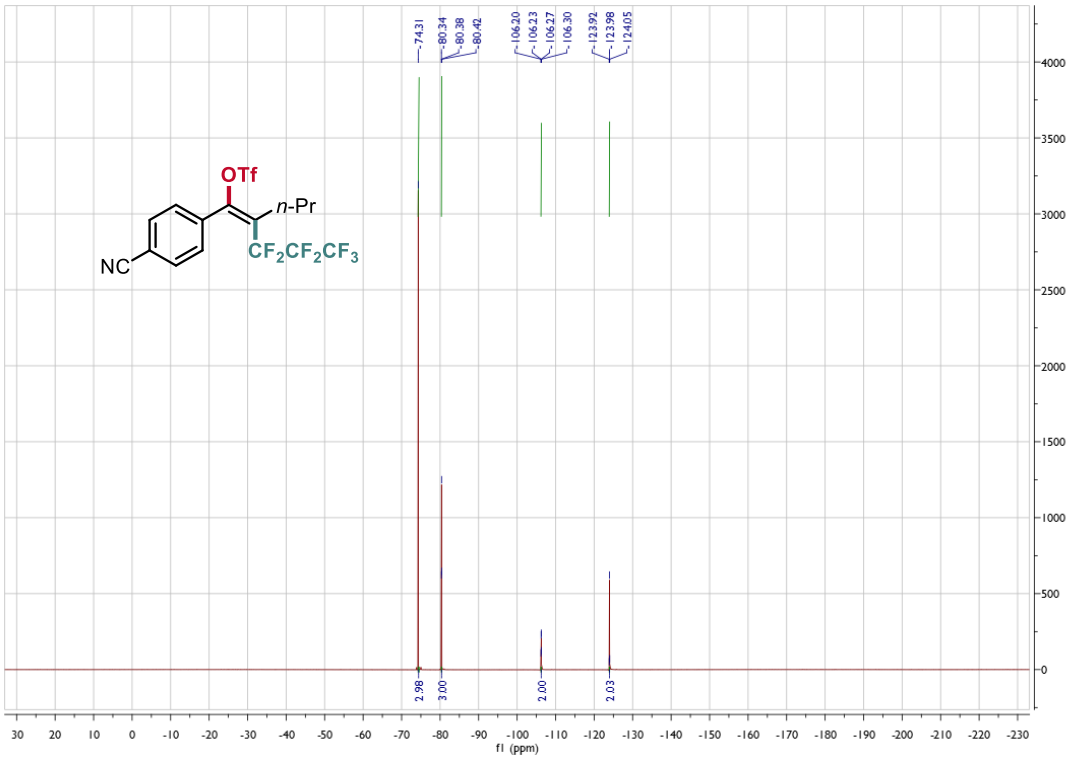
^{1}H NMR Spectrum of (*E*)-1-(4-cyanophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3b



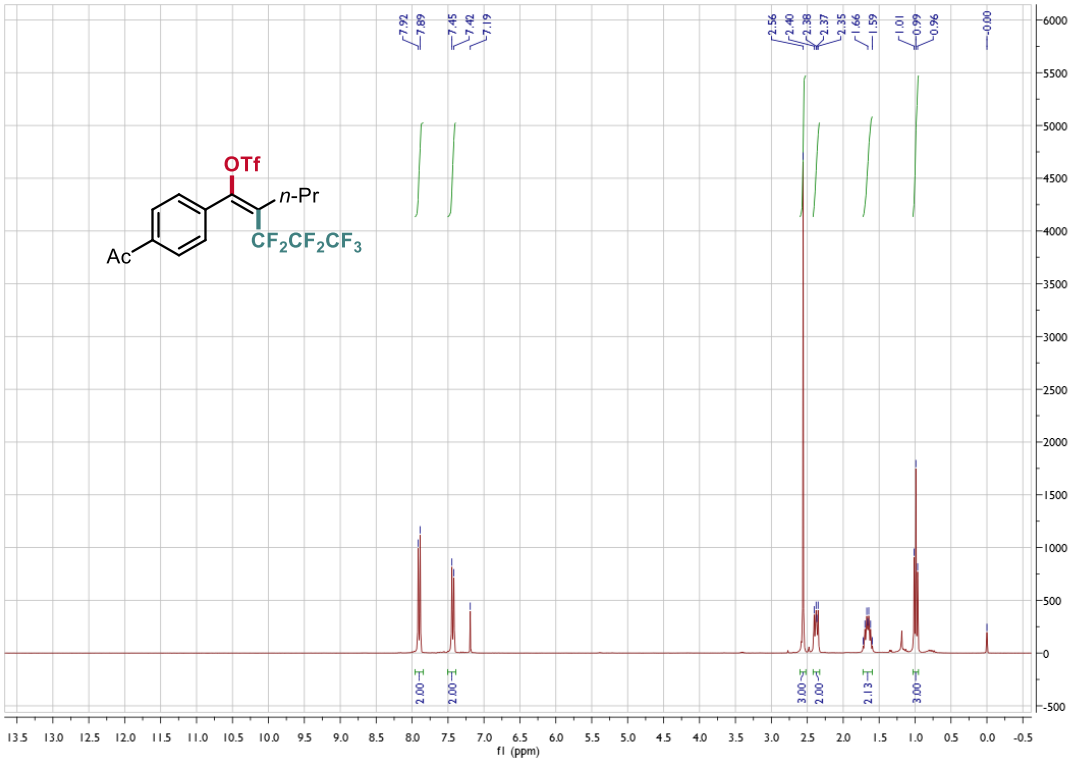
^{13}C NMR Spectrum of (*E*)-1-(4-cyanophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3b



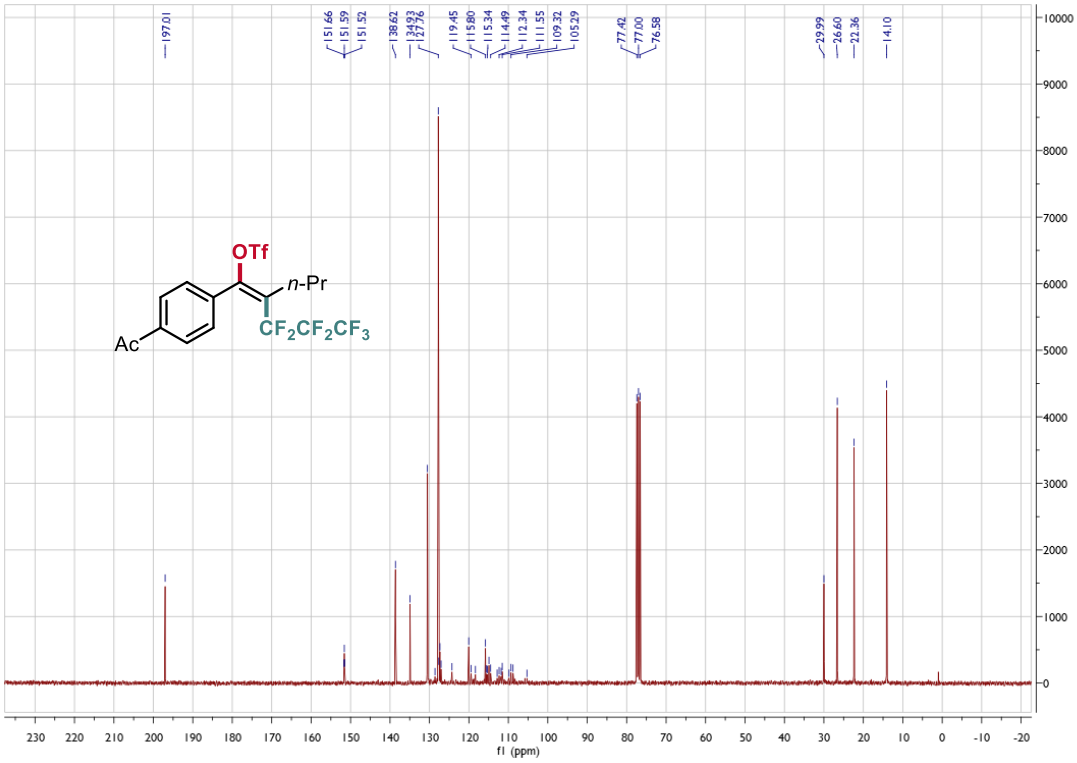
^{19}F NMR Spectrum of (*E*)-1-(4-cyanophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3b



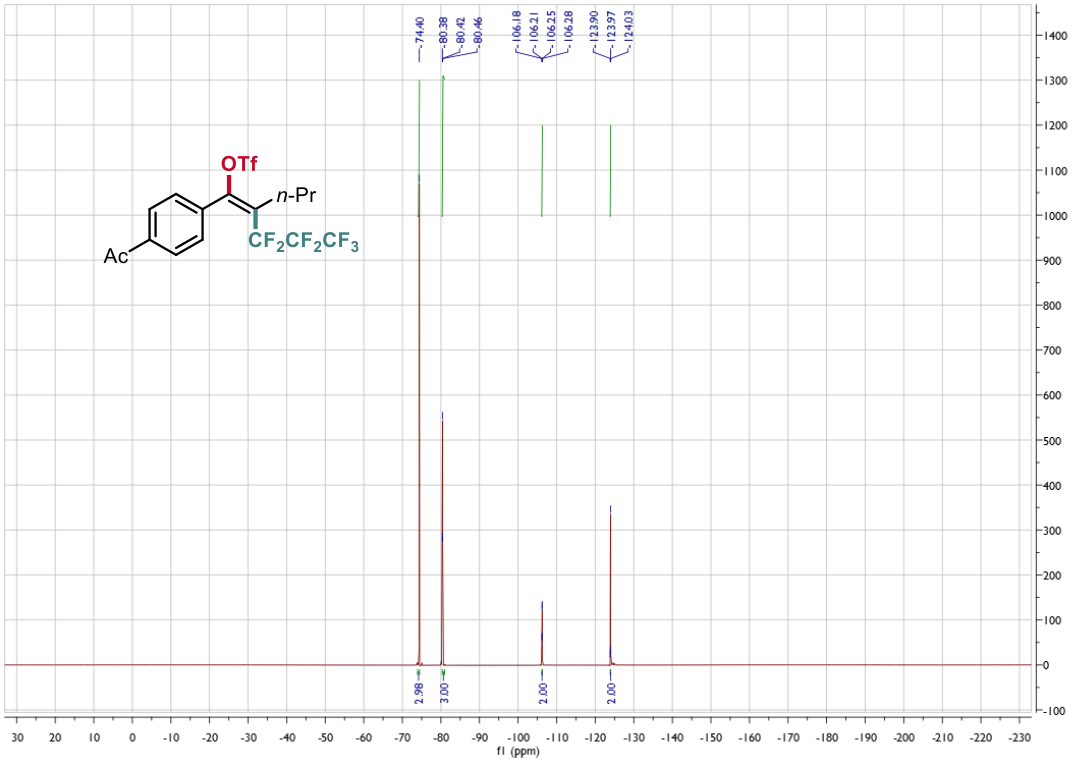
^{1}H NMR Spectrum of (*E*)-1-(4-acetylphenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3c



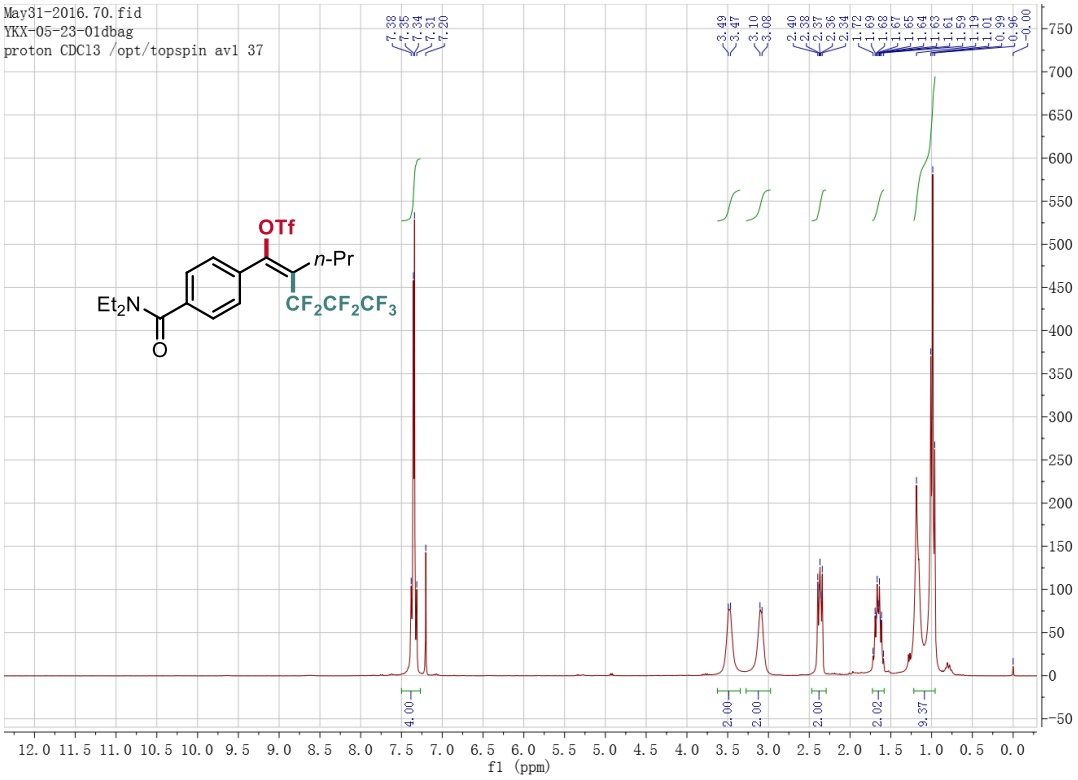
^{13}C NMR Spectrum of (*E*)-1-(4-acetylphenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3c



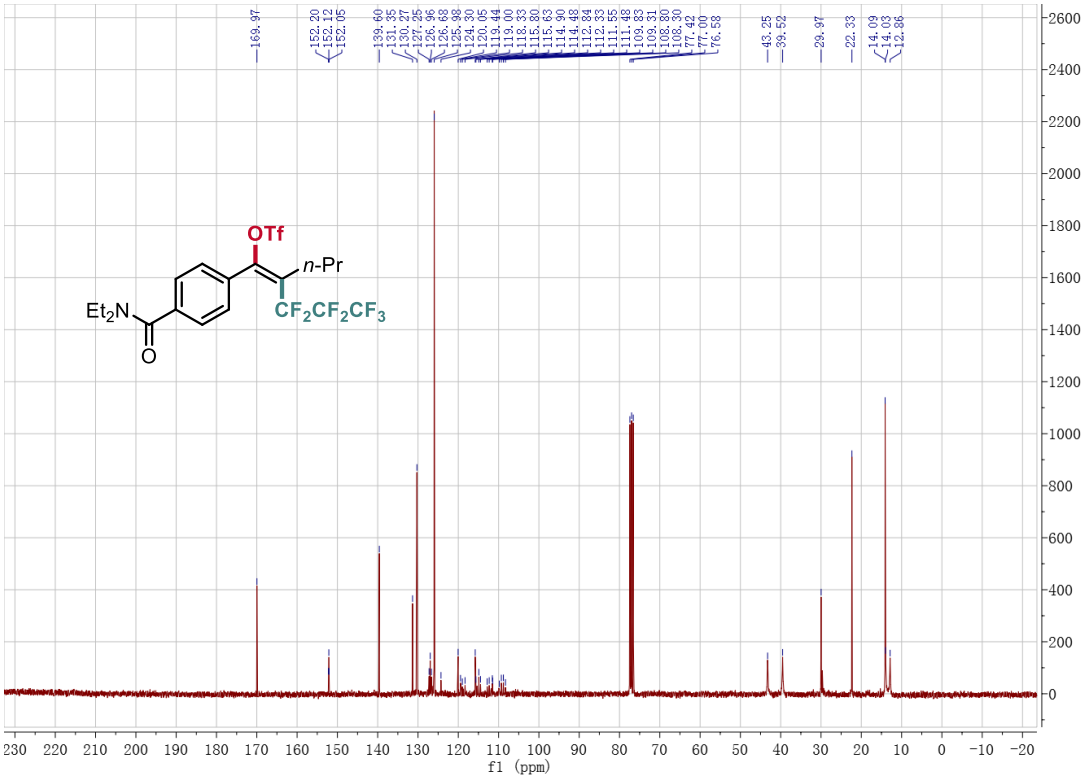
^{19}F NMR Spectrum of (*E*)-1-(4-acetylphenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3c



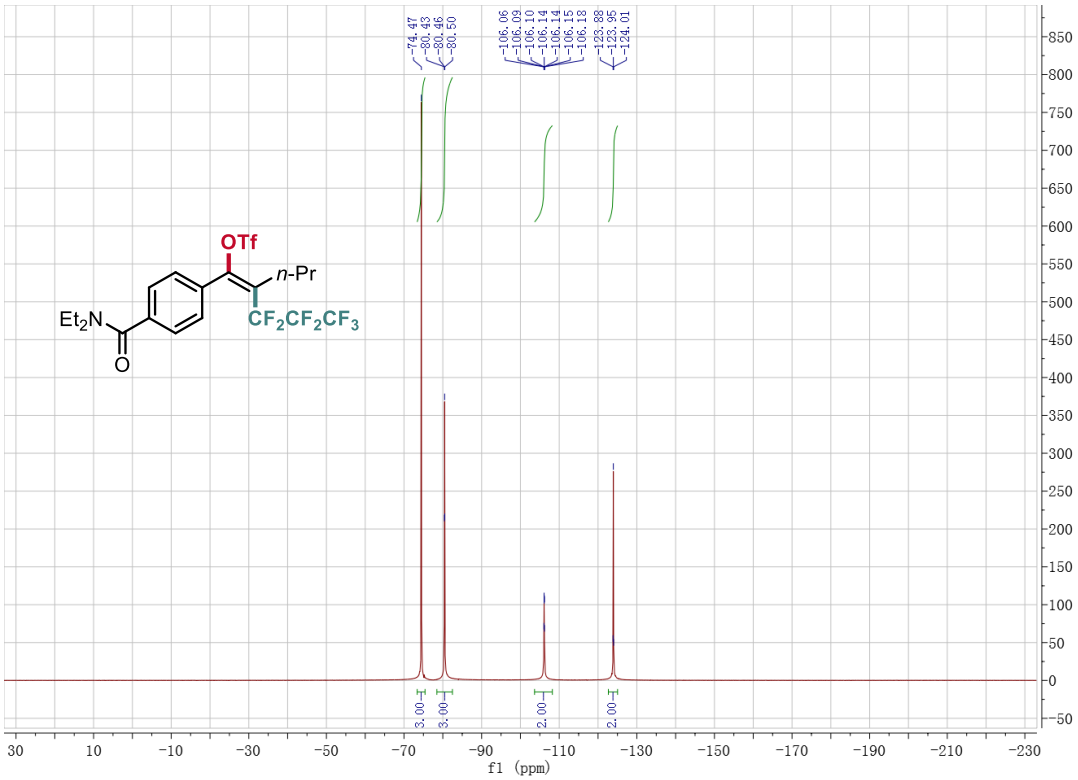
^{1}H NMR Spectrum of (*E*)-1-(4-(diethylcarbamoyl)phenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethane sulfonate 3d



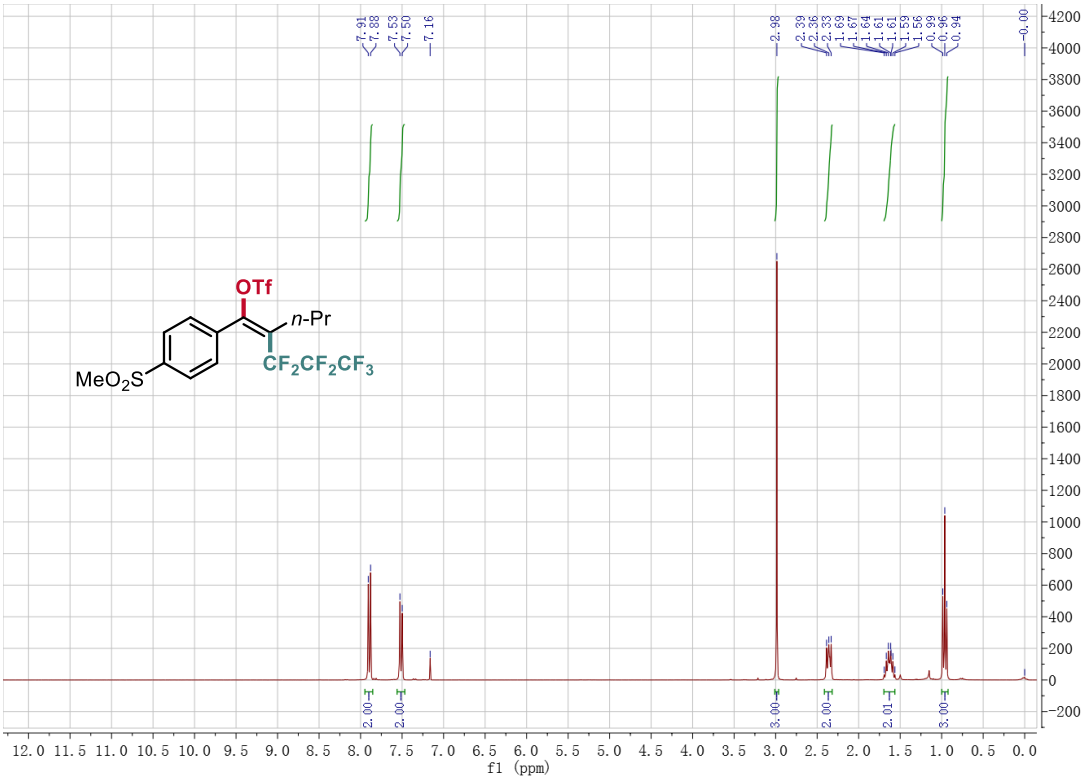
^{13}C NMR Spectrum of (*E*)-1-(4-(diethylcarbamoyl)phenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethane sulfonate 3d



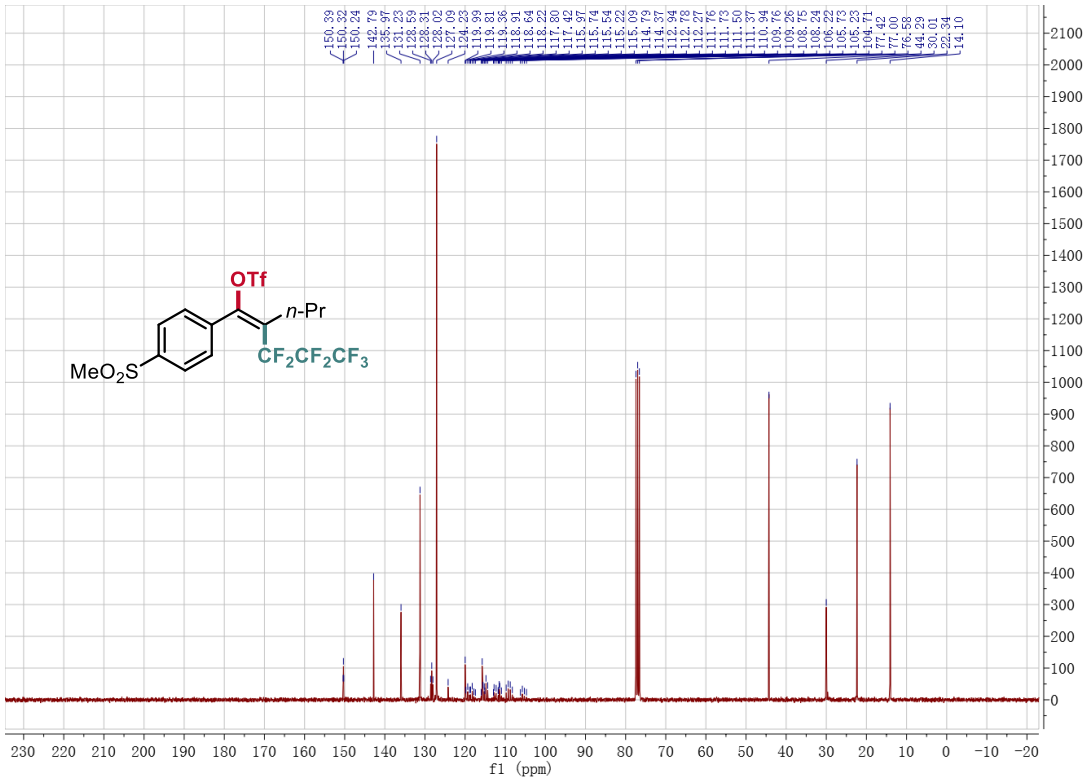
^{19}F NMR Spectrum of (*E*)-1-(4-(diethylcarbamoyl)phenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethane sulfonate 3d



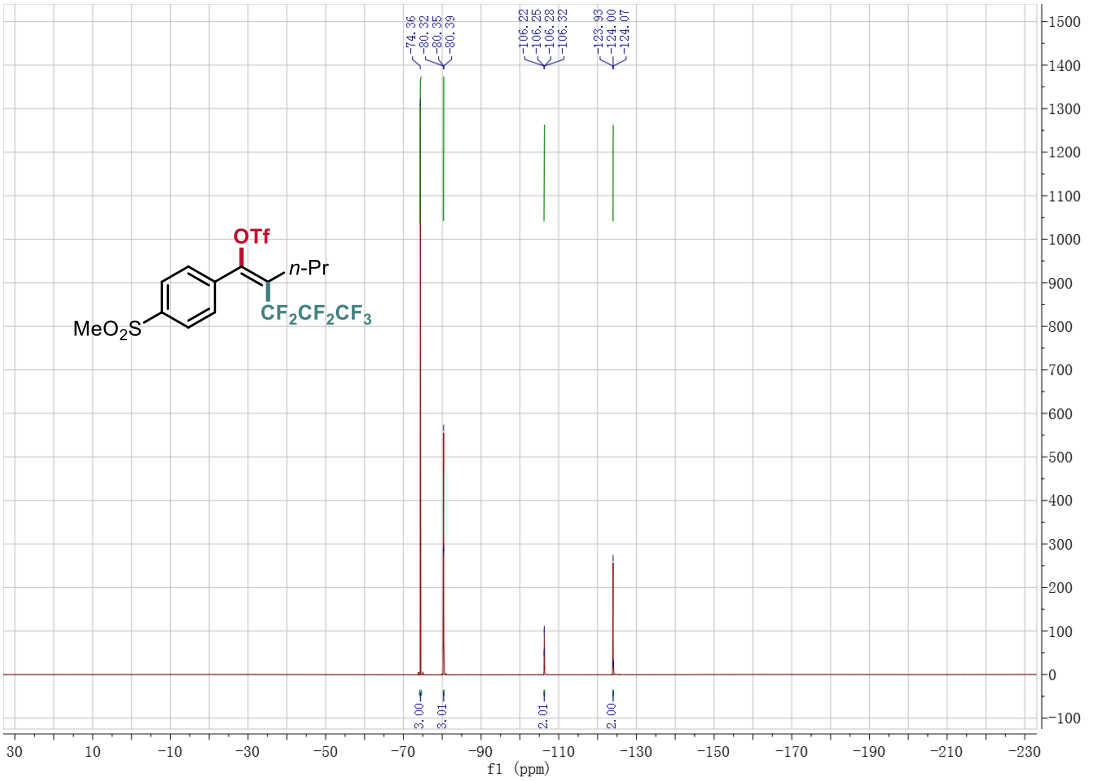
^{1}H NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(4-(methylsulfonyl)phen yl)-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3e



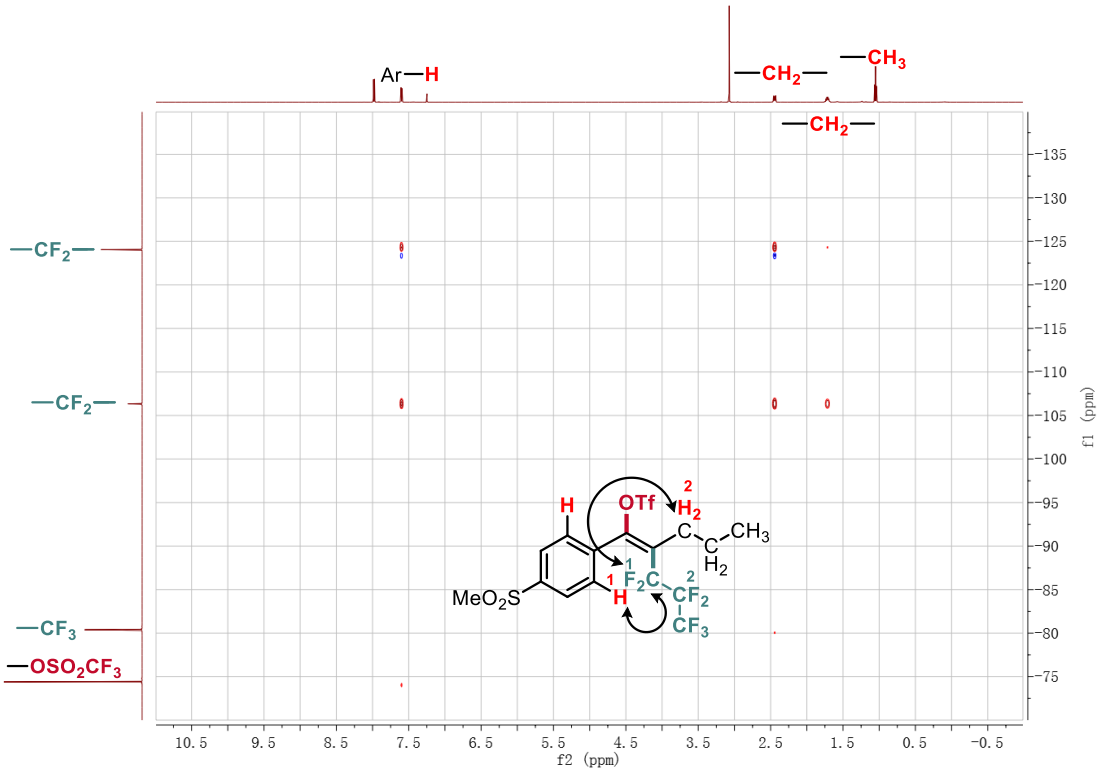
^{13}C NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(4-(methylsulfonyl)phen yl)-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3e



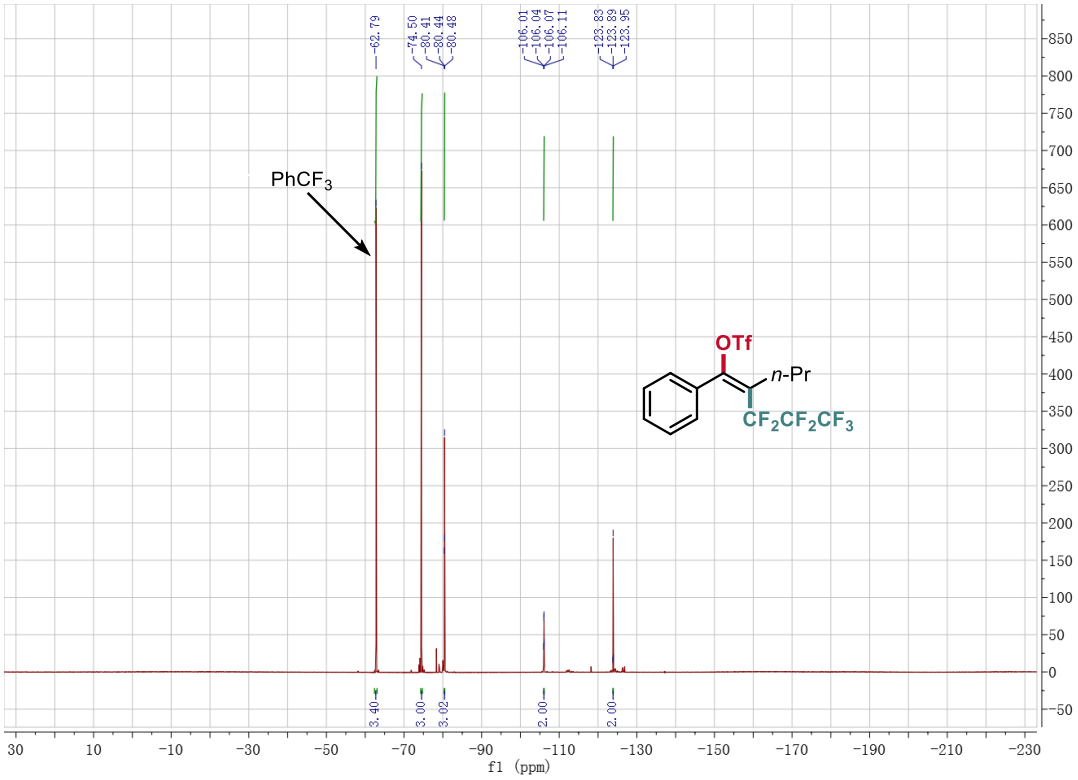
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(4-(methylsulfonyl)phen yl)-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3e



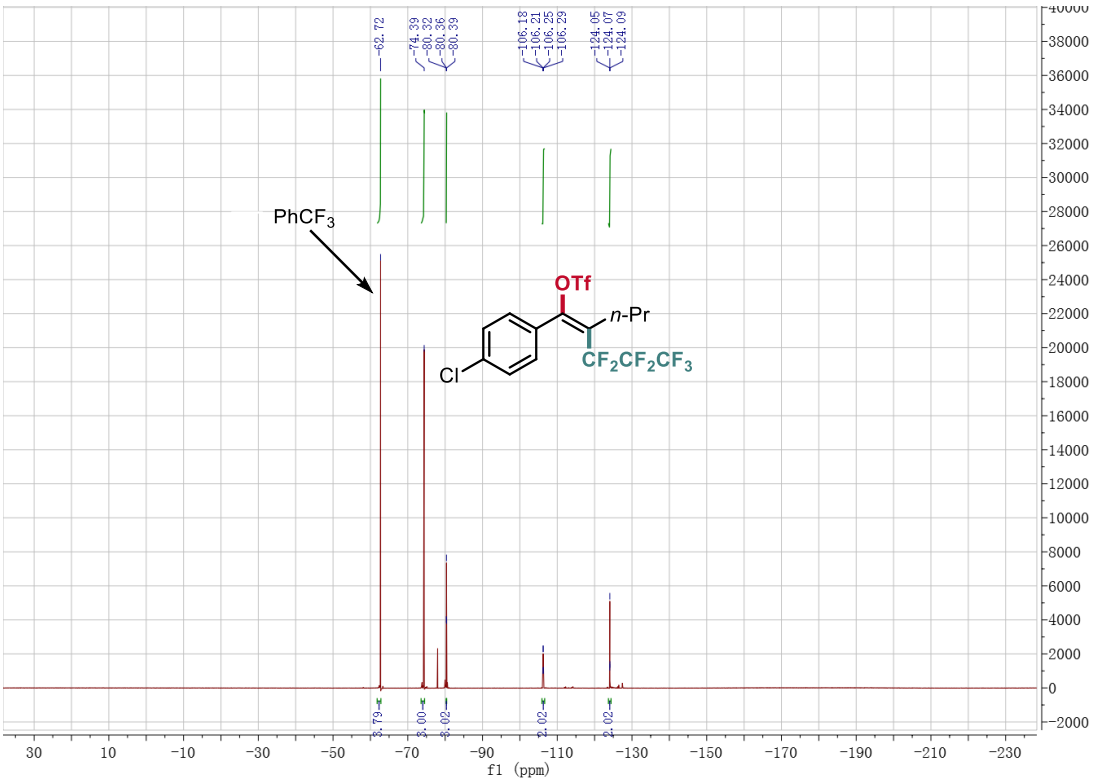
^{19}F-^{1}H HOESY NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(4-(methylsulfonyl)phen yl)-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3e



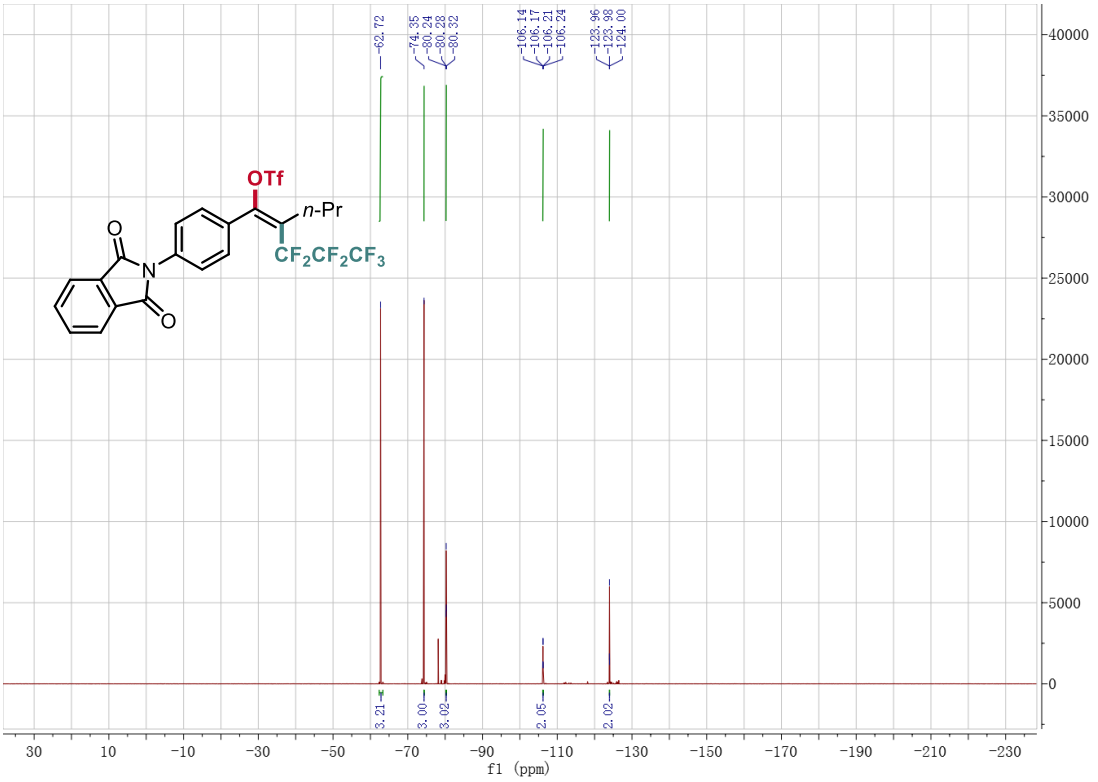
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-phenyl-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3f



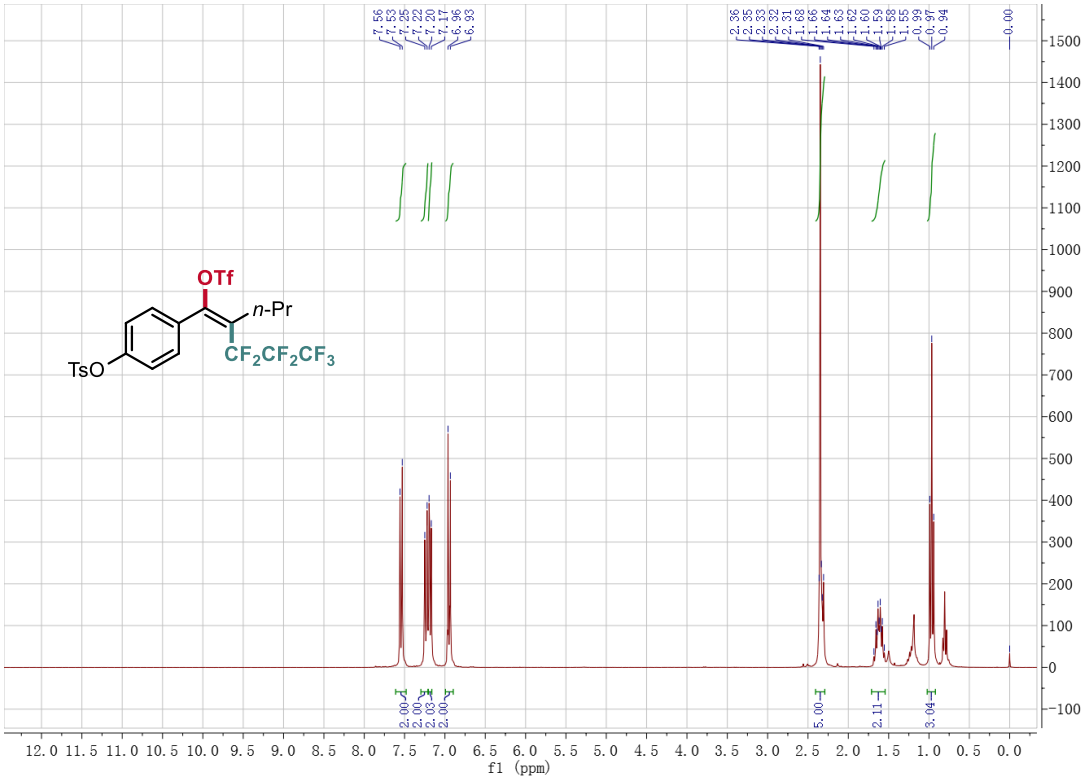
^{19}F NMR Spectrum of (*E*)-1-(4-chlorophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propyl pent-1-en-1-yl trifluoromethanesulfonate 3g



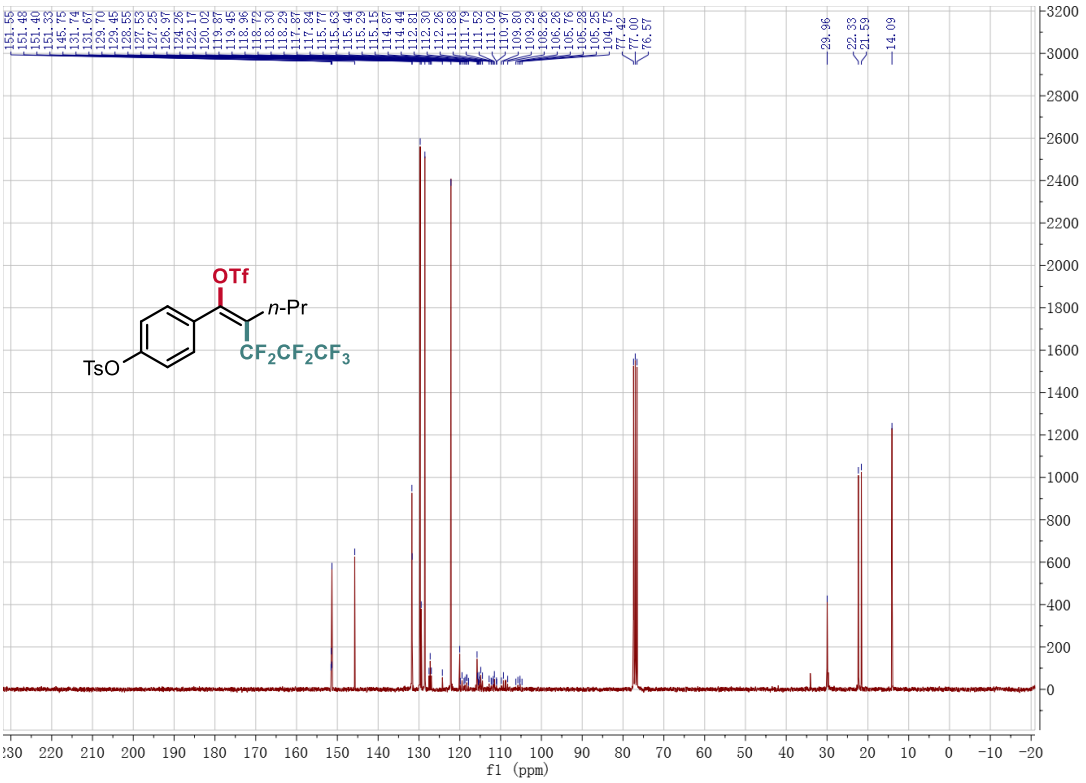
^{19}F NMR Spectrum of (*E*)-1-(4-(1,3-dioxoisoindolin-2-yl)phenyl)-3,3,4,4,5, 5,5-heptafluoro-2-propylpent-1-en-1-yl trifluorome thanesulfonate 3h



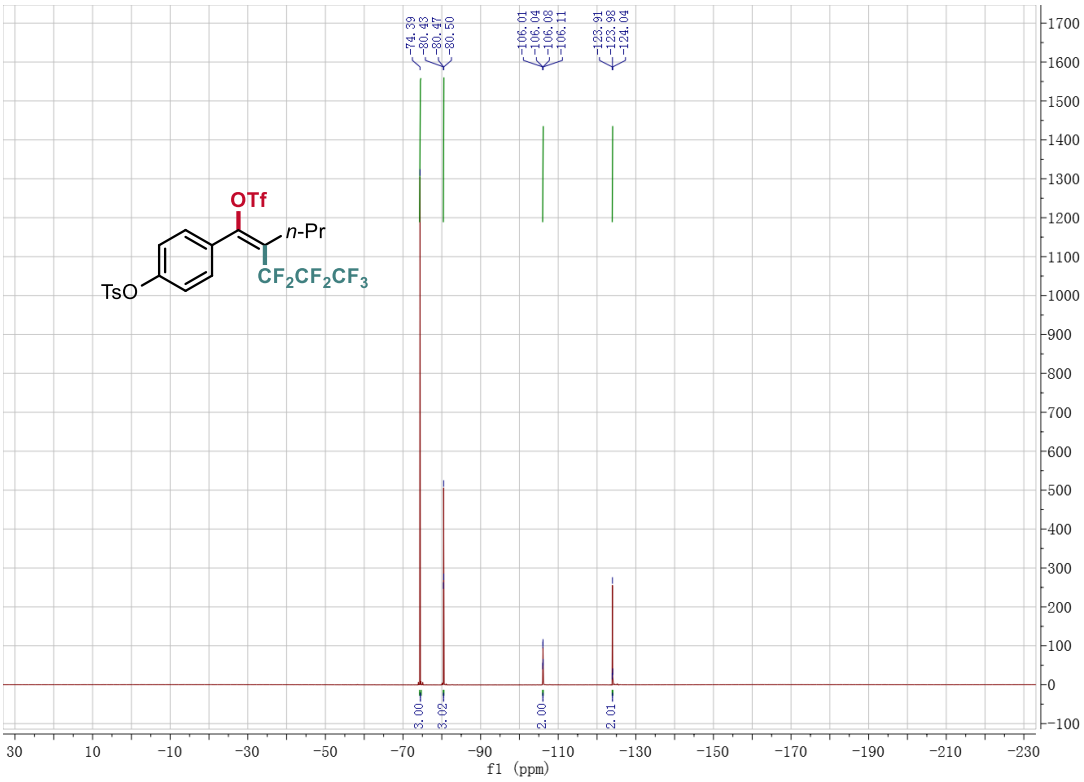
^{1}H NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzene sulfonate 3i



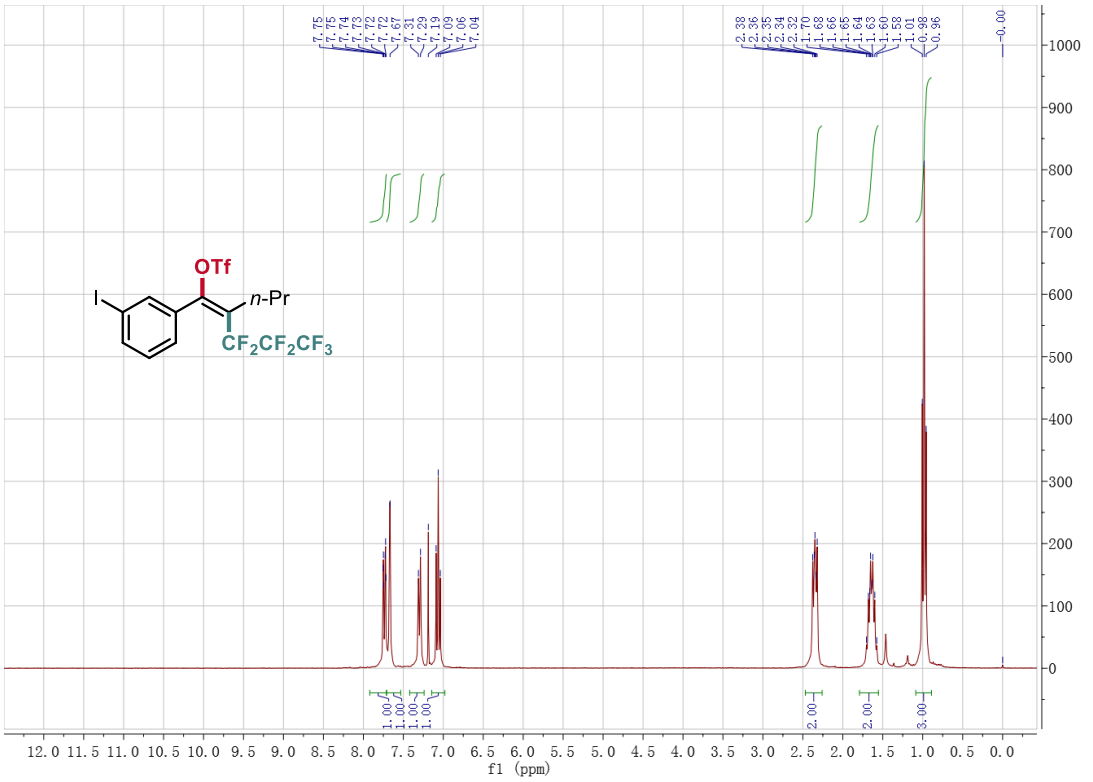
^{13}C NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzene sulfonate 3i



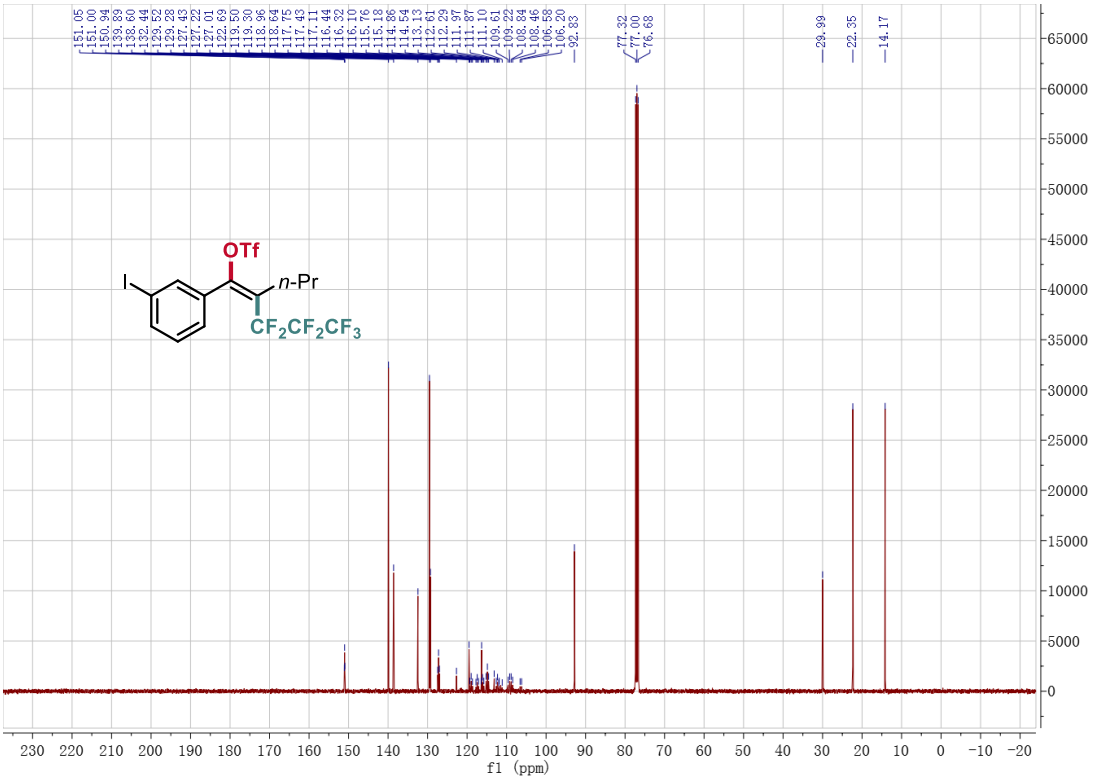
^{19}F NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzene sulfonate 3i



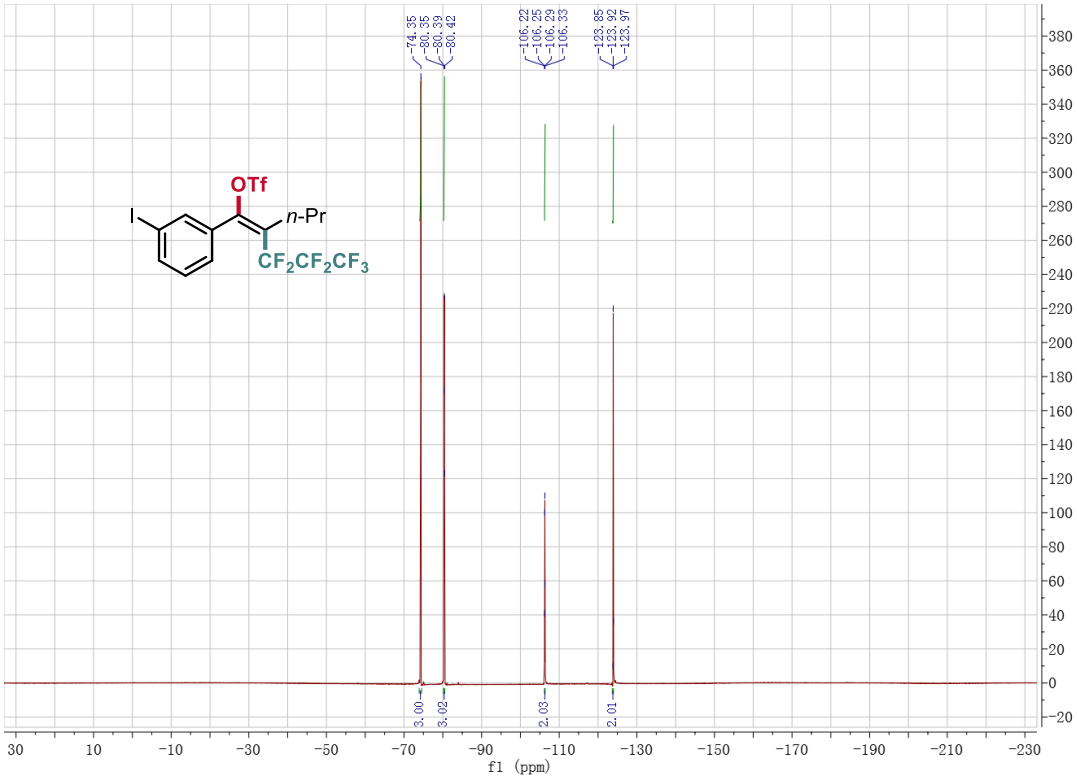
^{1}H NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(3-iodophenyl)-2-propylpen -1-en-1-yl trifluoromethanesulfonate 3j



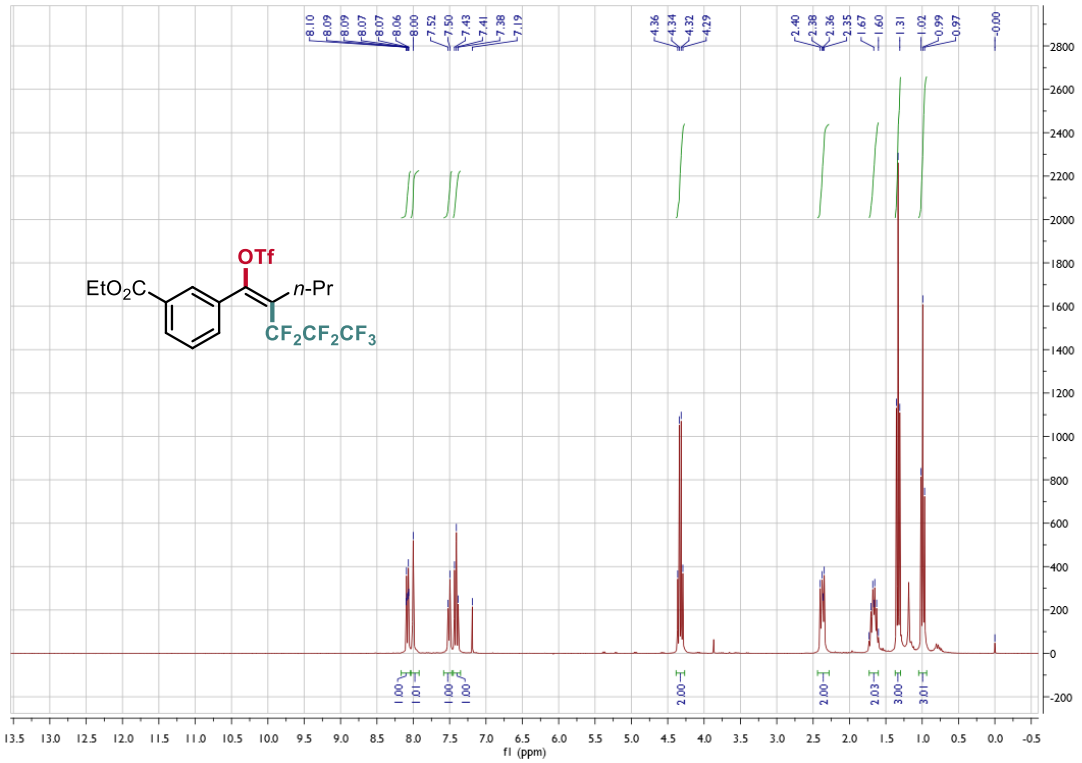
^{13}C NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(3-iodophenyl)-2-propylpen -1-en-1-yl trifluoromethanesulfonate 3j



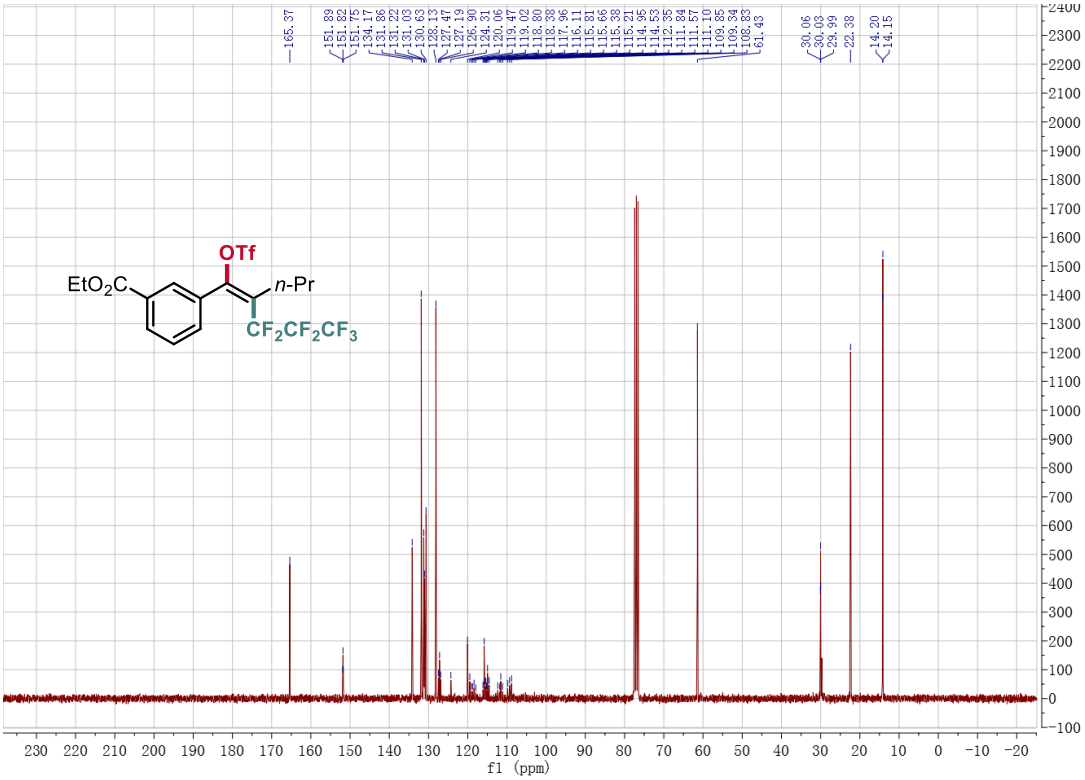
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(3-iodophenyl)-2-propylpen -1-en-1-yl trifluoromethanesulfonate 3j



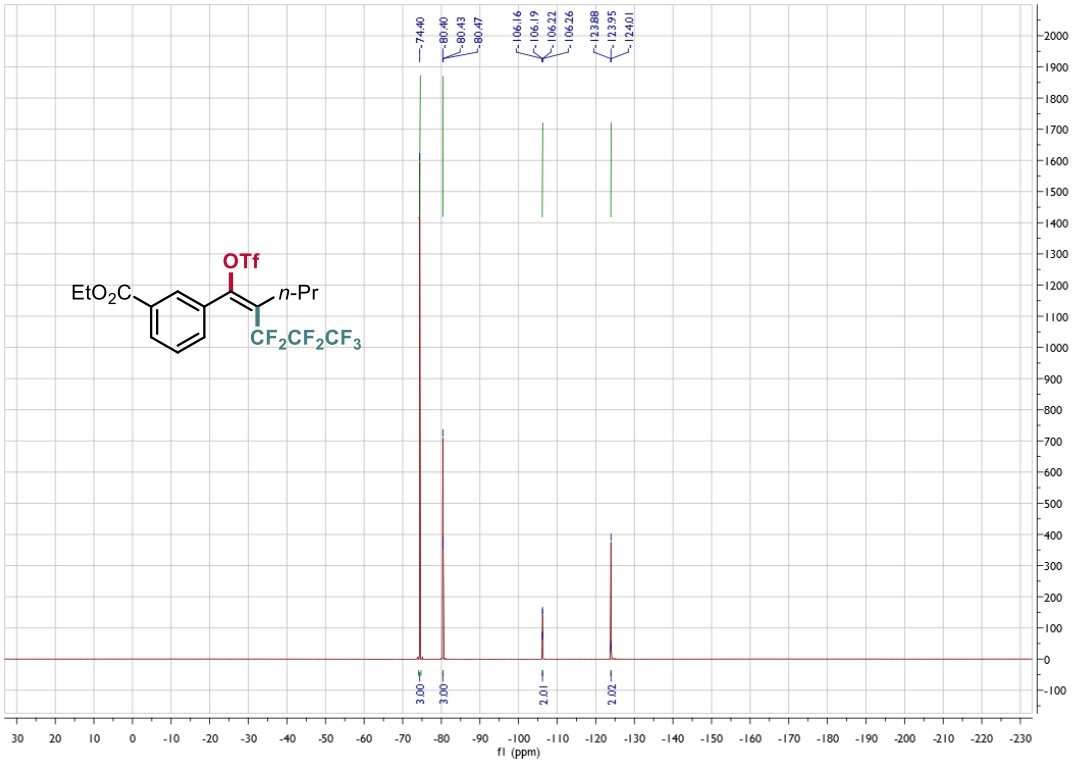
^{1}H NMR Spectrum of Ethyl (*E*)-3-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3k



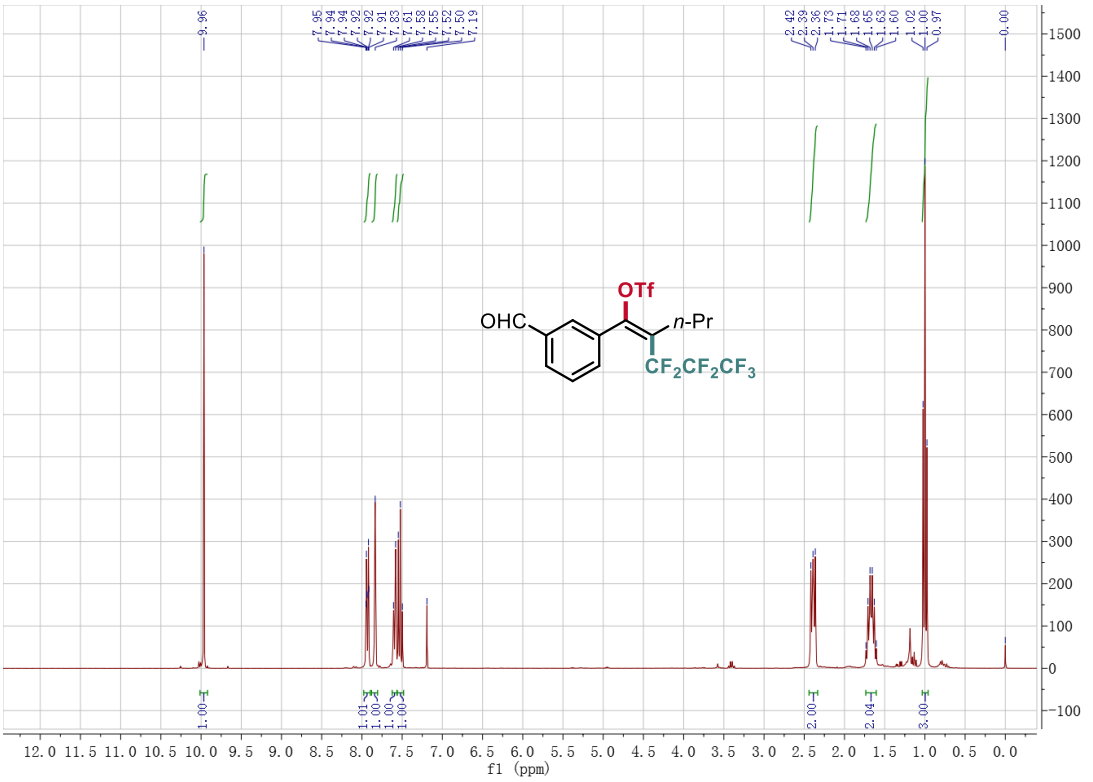
^{13}C NMR Spectrum of Ethyl (*E*)-3-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3k



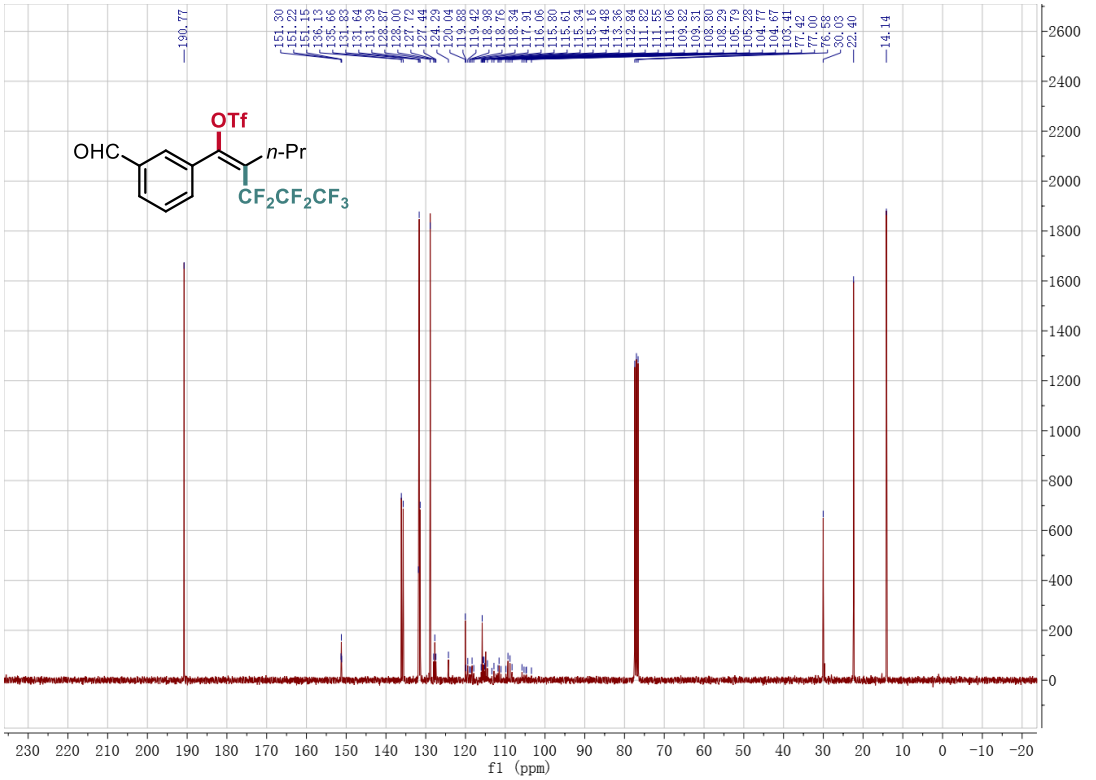
^{19}F NMR Spectrum of Ethyl (*E*)-3-(3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(((trifle oromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3k



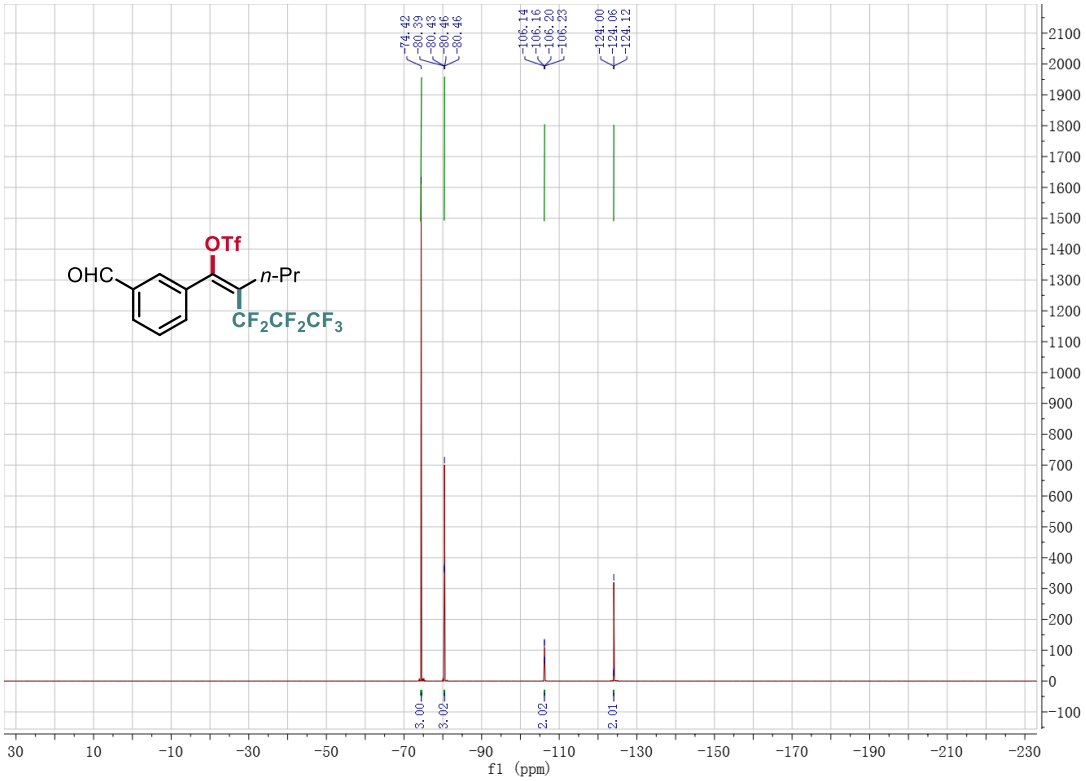
^{1}H NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(3-formylphenyl)-2-propyl pent-1-en-1-yl trifluoromethanesulfonate 3l



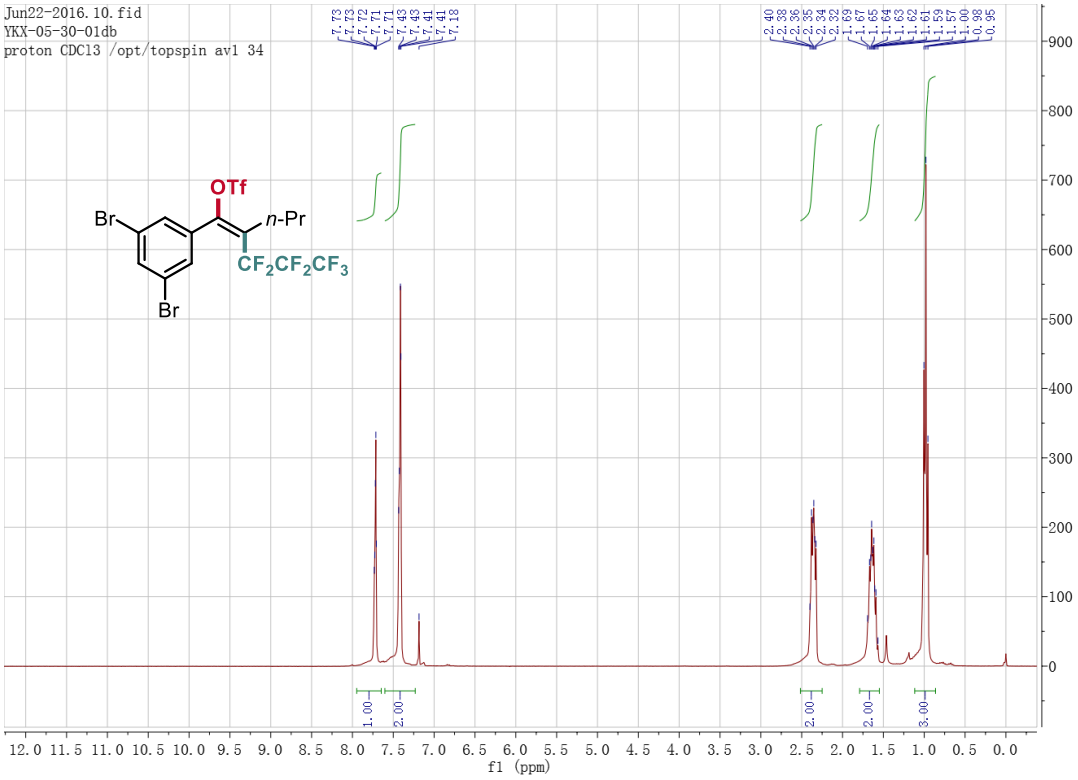
^{13}C NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(3-formylphenyl)-2-propyl pent-1-en-1-yl trifluoromethanesulfonate 3l



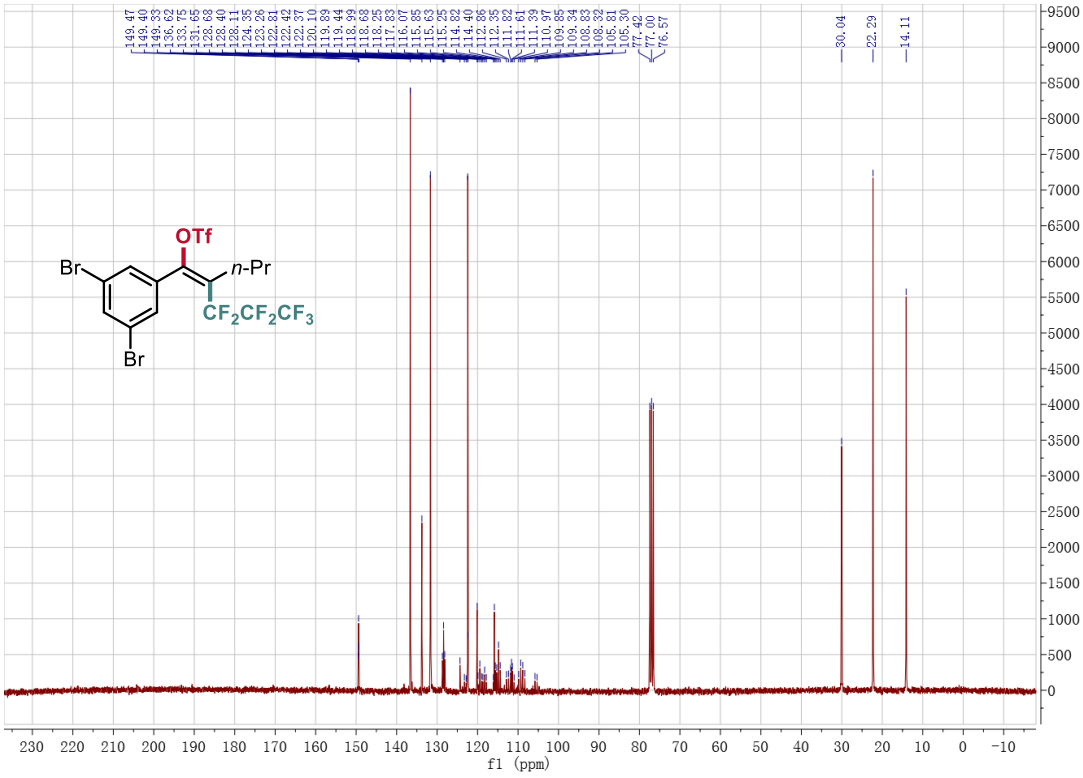
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(3-formylphenyl)-2-propyl pent-1-en-1-yl trifluoromethanesulfonate 3l



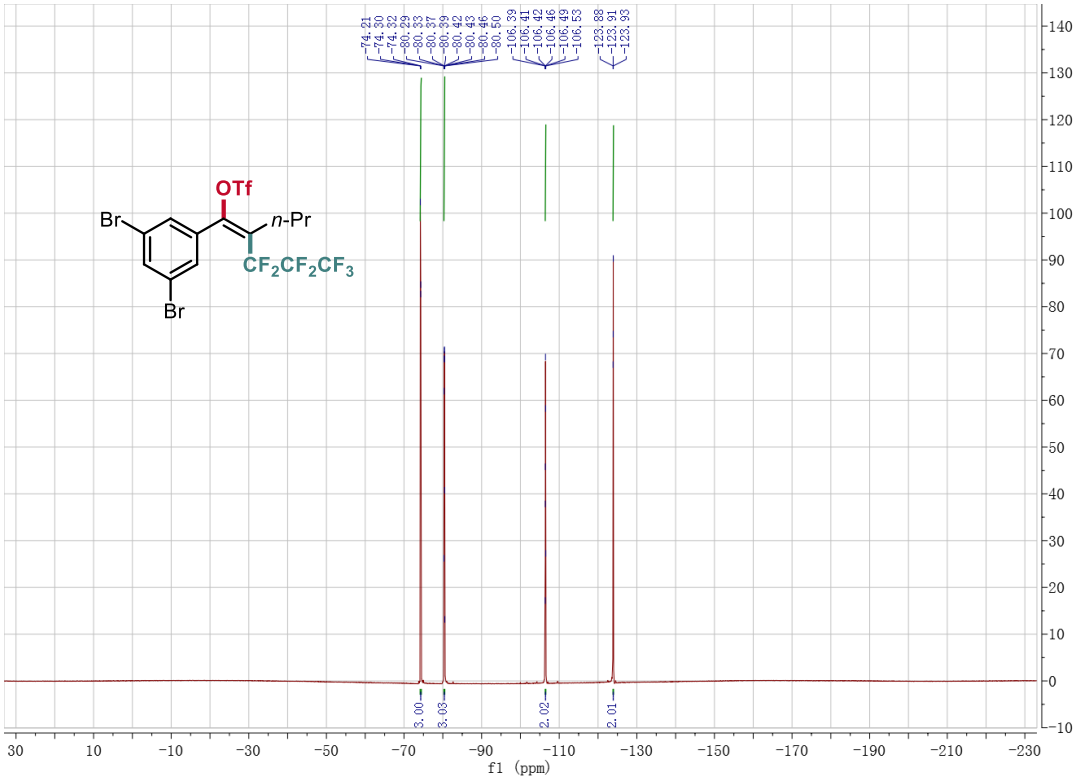
^{1}H NMR Spectrum of (*E*)-1-(3,5-dibromophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3m



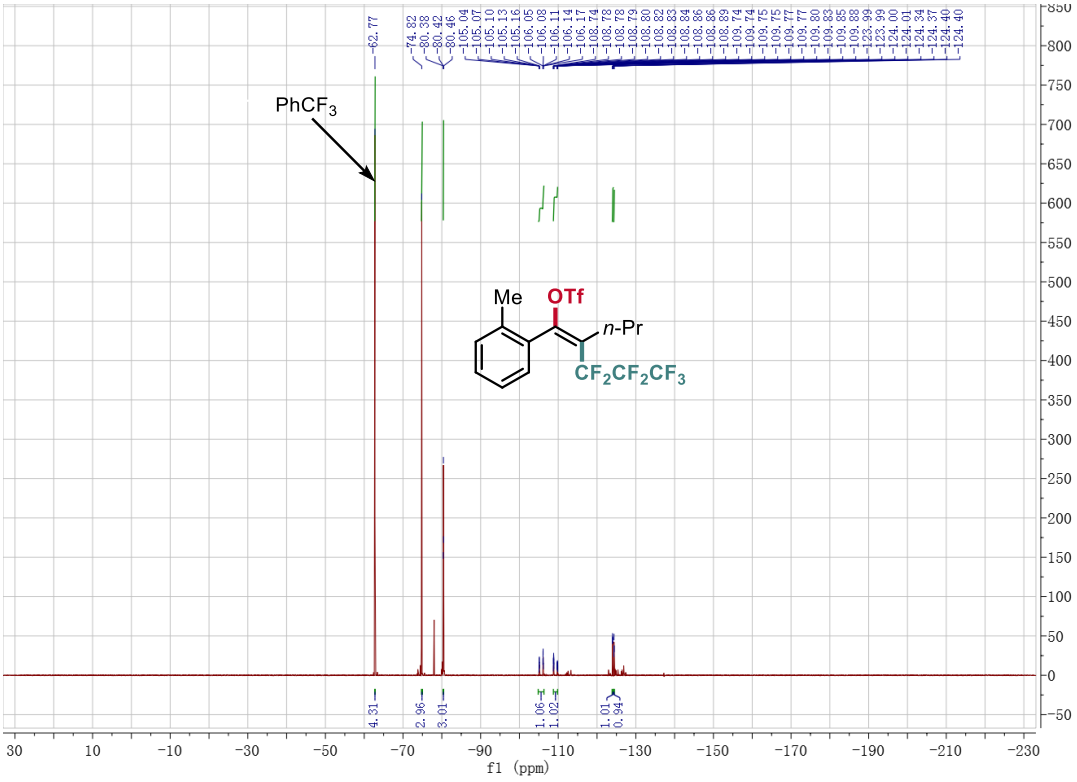
^{13}C NMR Spectrum of (*E*)-1-(3,5-dibromophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3m



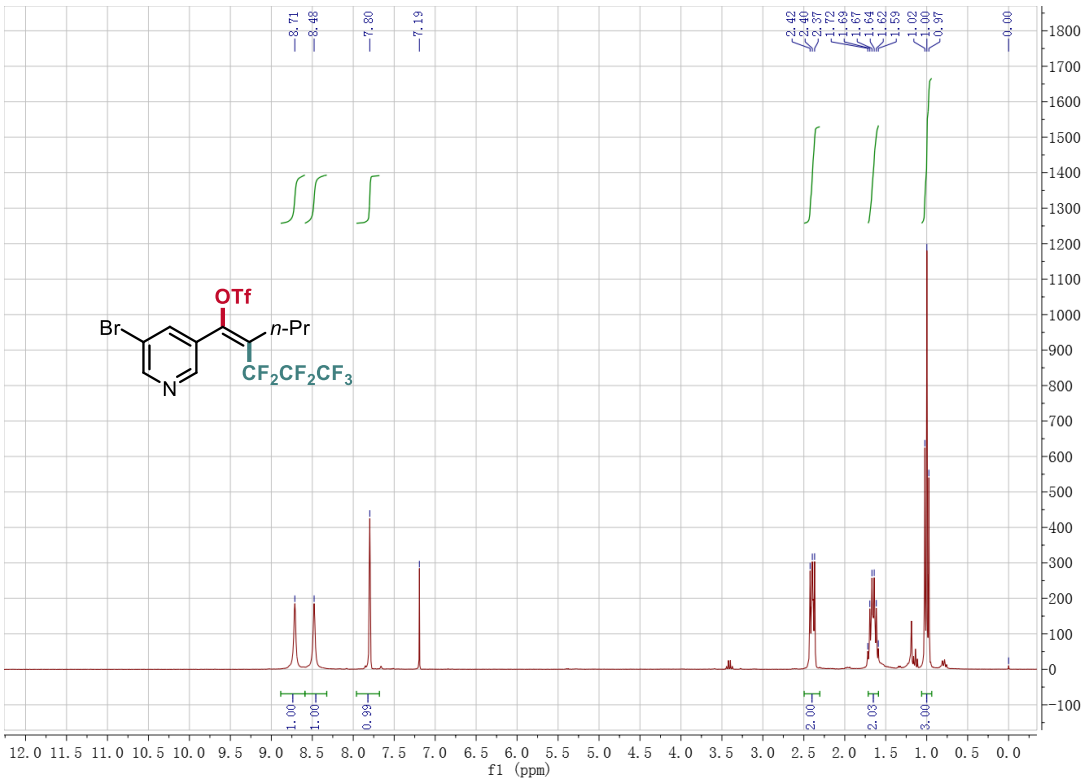
^{19}F NMR Spectrum of (*E*)-1-(3,5-dibromophenyl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3m



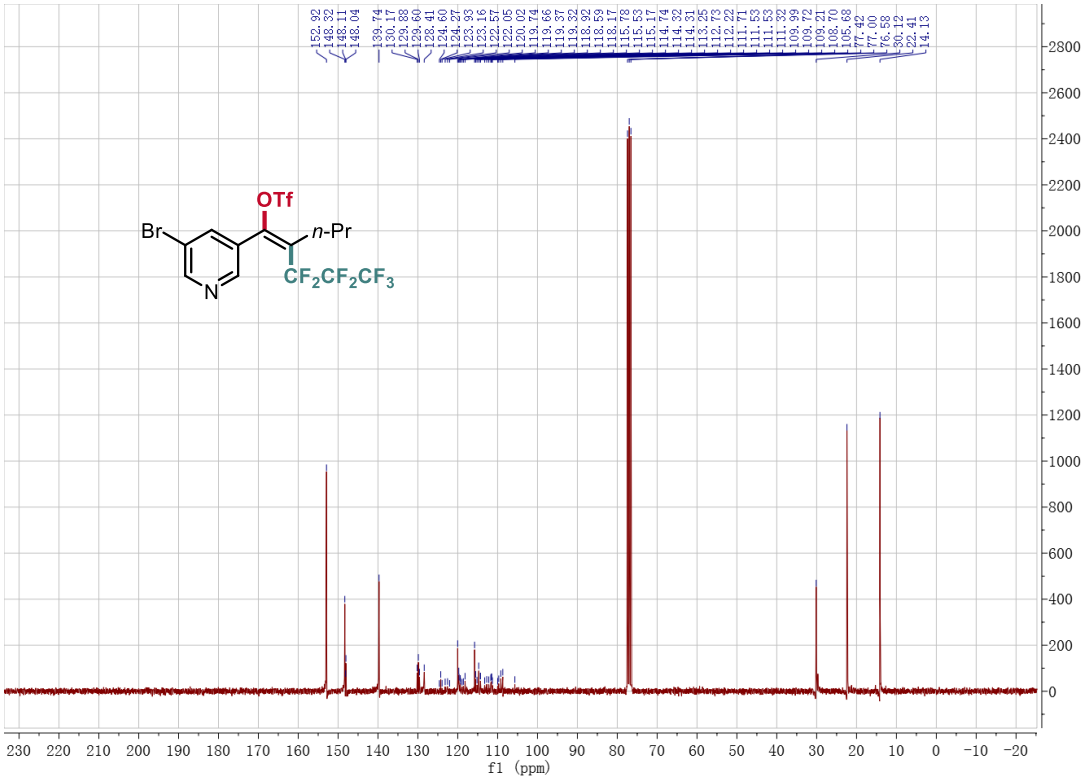
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-2-propyl-1-(*o*-tolyl)pent-1-en-1-yl trifluoromethanesulfonate 3n



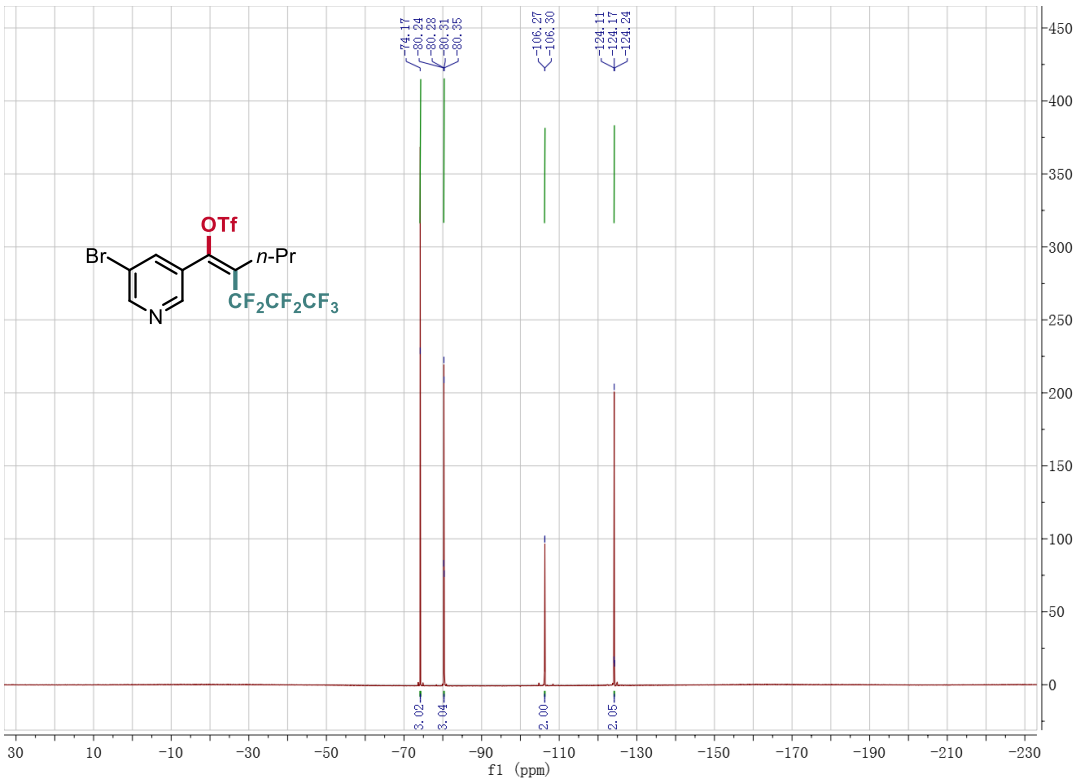
^{1}H NMR Spectrum of (*E*)-1-(5-bromopyridin-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3o



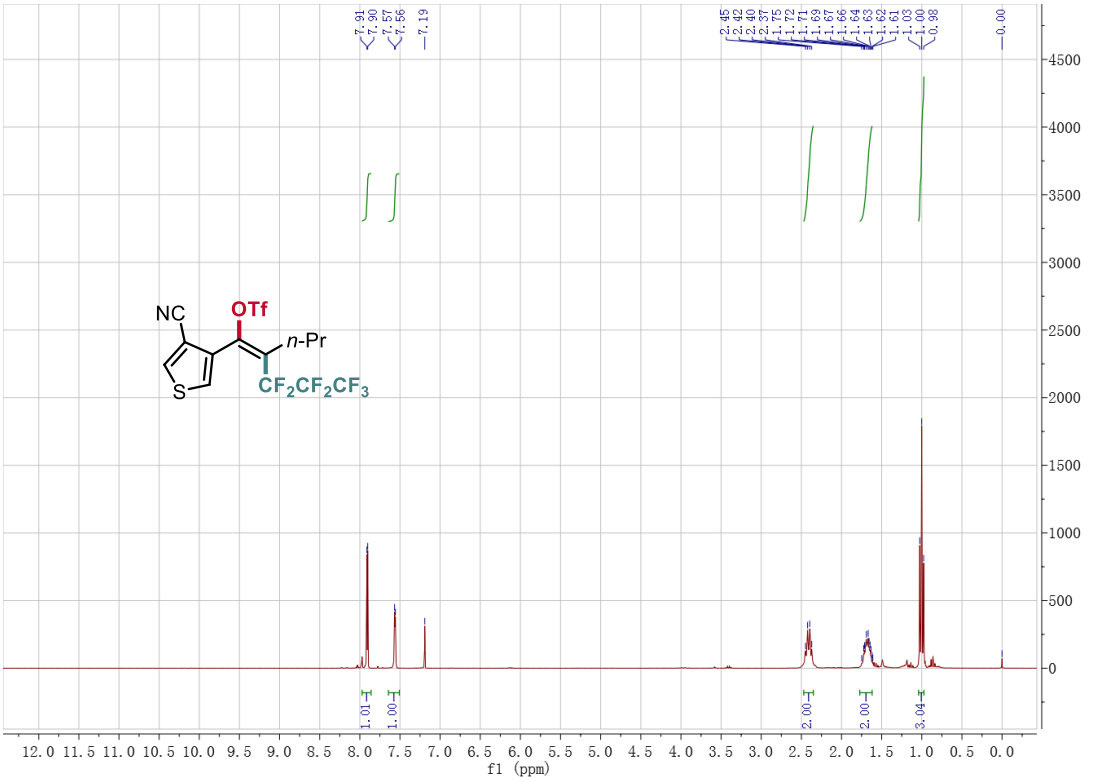
^{13}C NMR Spectrum of (*E*)-1-(5-bromopyridin-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3o



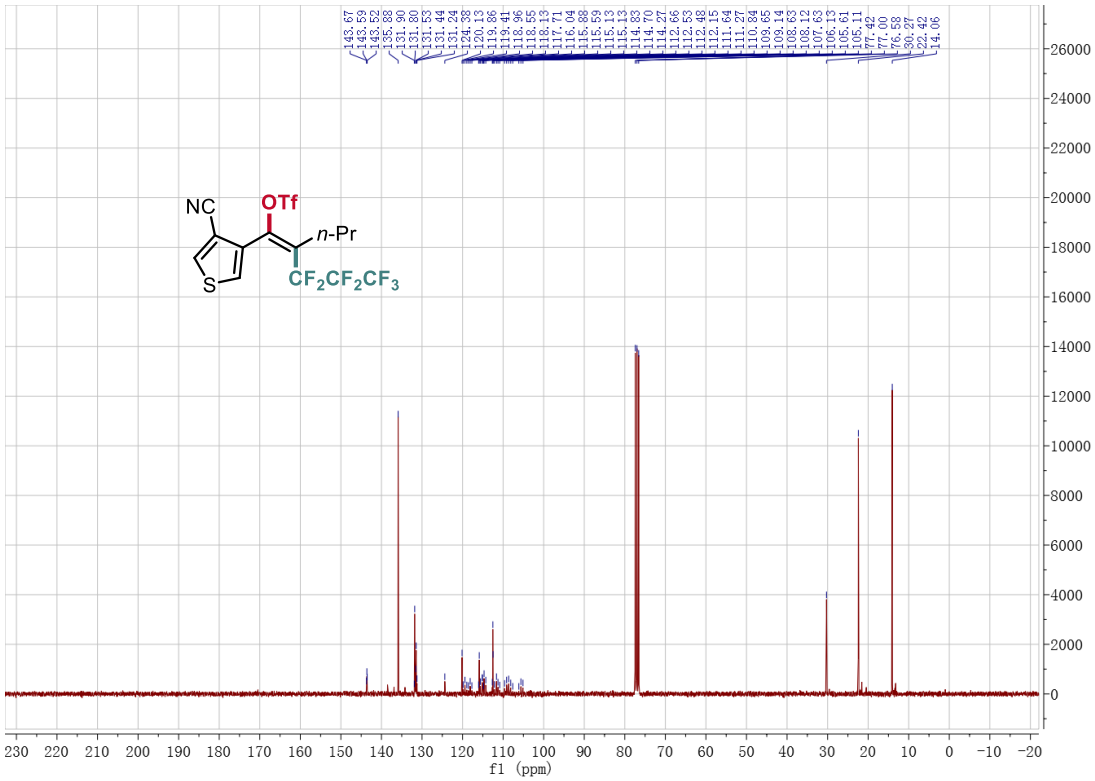
^{19}F NMR Spectrum of (*E*)-1-(5-bromopyridin-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3o



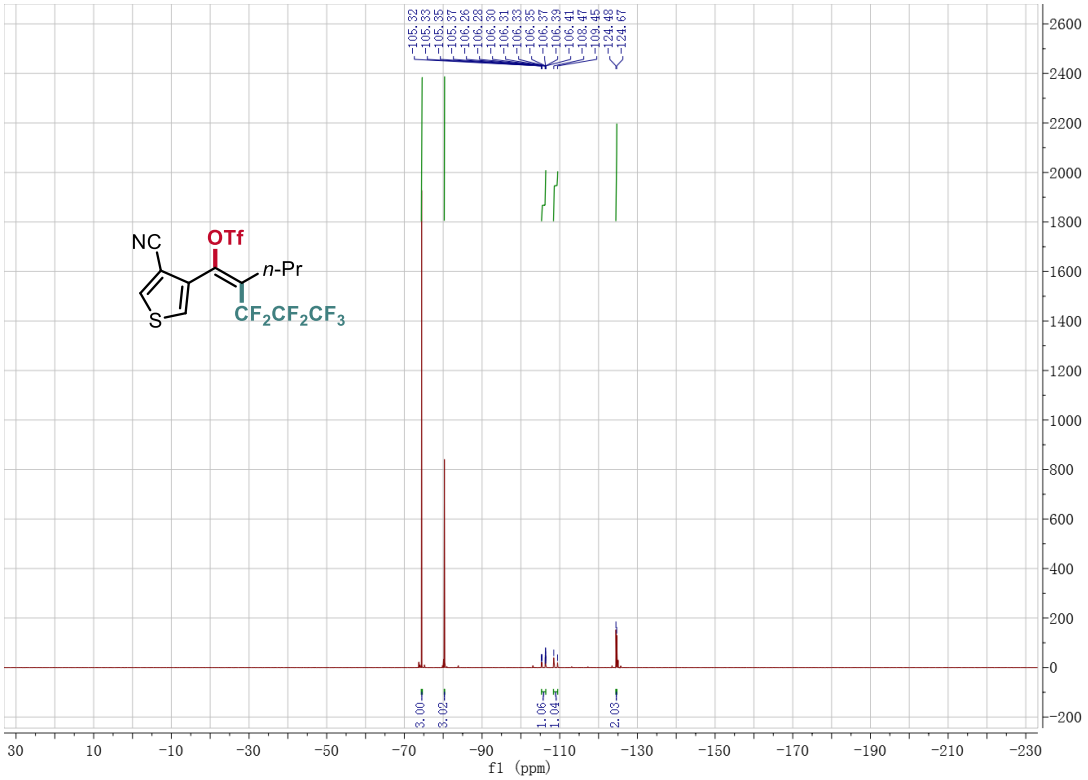
^{1}H NMR Spectrum of (*E*)-1-(4-cyanothiophen-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3p



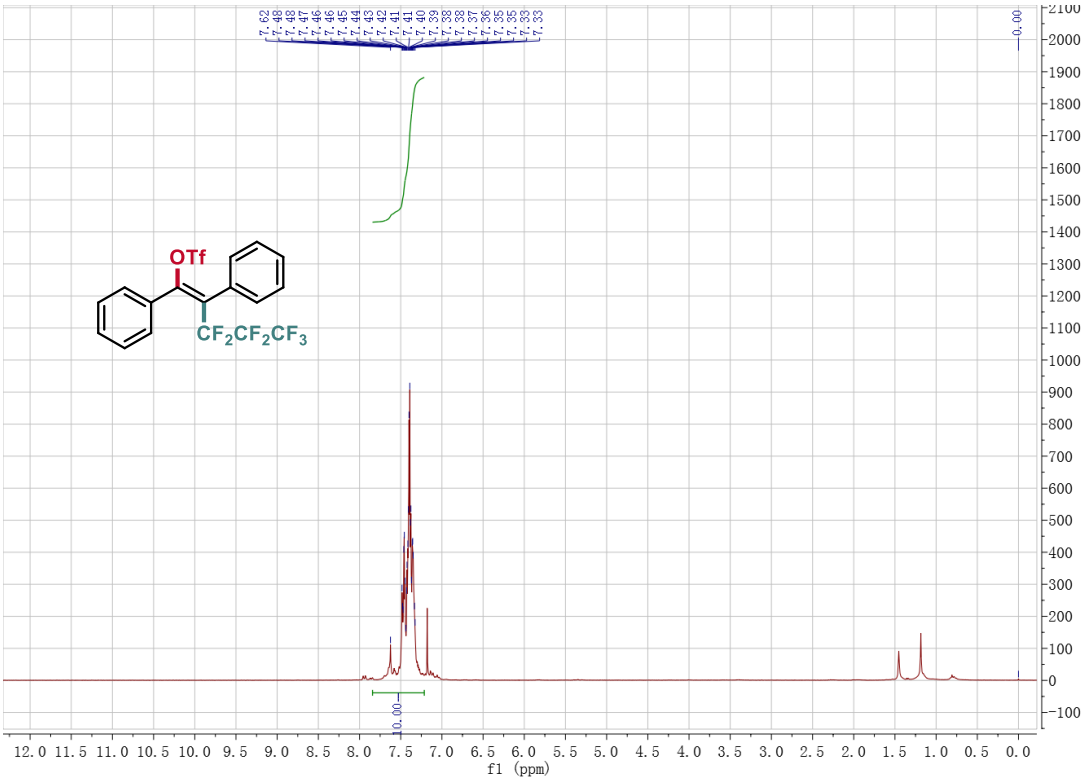
^{13}C NMR Spectrum of (*E*)-1-(4-cyanothiophen-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3p



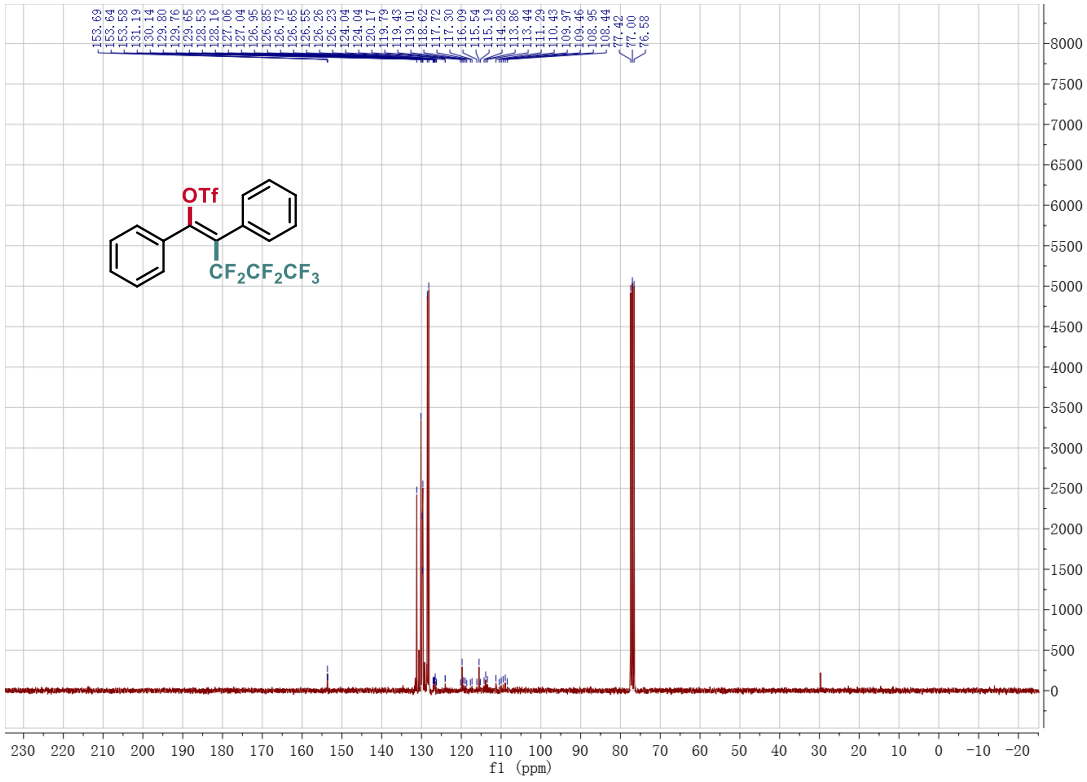
^{19}F NMR Spectrum of (*E*)-1-(4-cyanothiophen-3-yl)-3,3,4,4,5,5,5-heptafluoro-2-propylpent-1-en-1-yl trifluoromethanesulfonate 3p



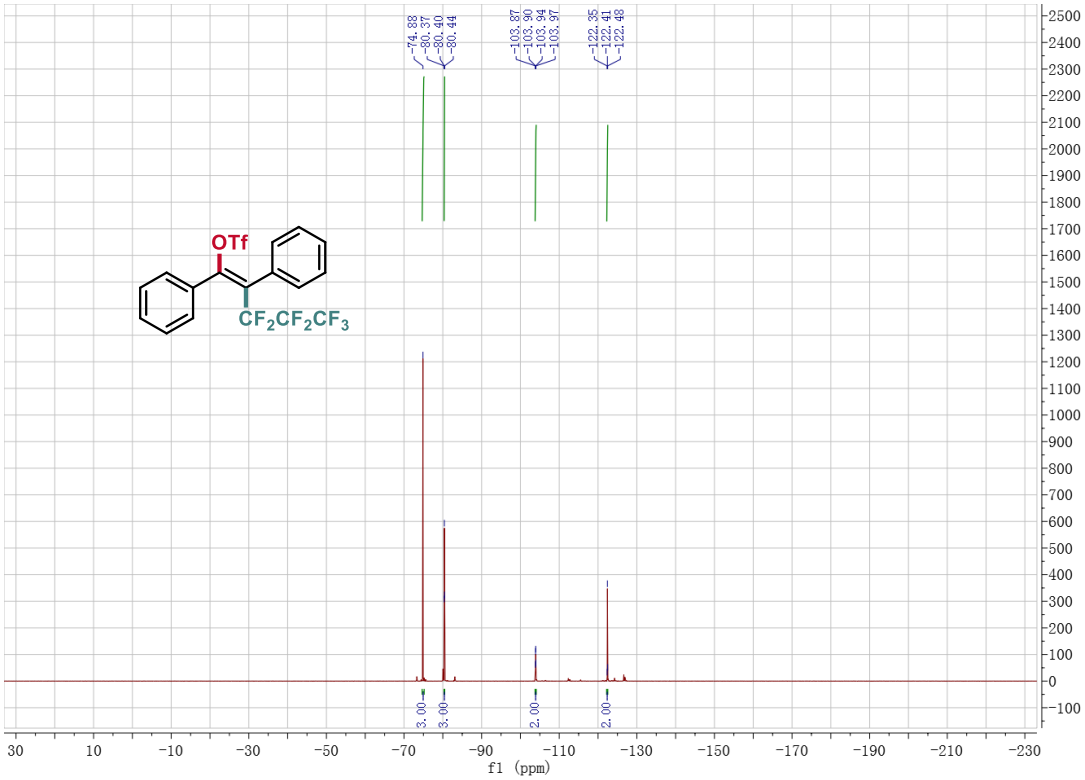
^{1}H NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1,2-diphenylpent-1-en-1-yl trifluoromethanesulfonate 3q



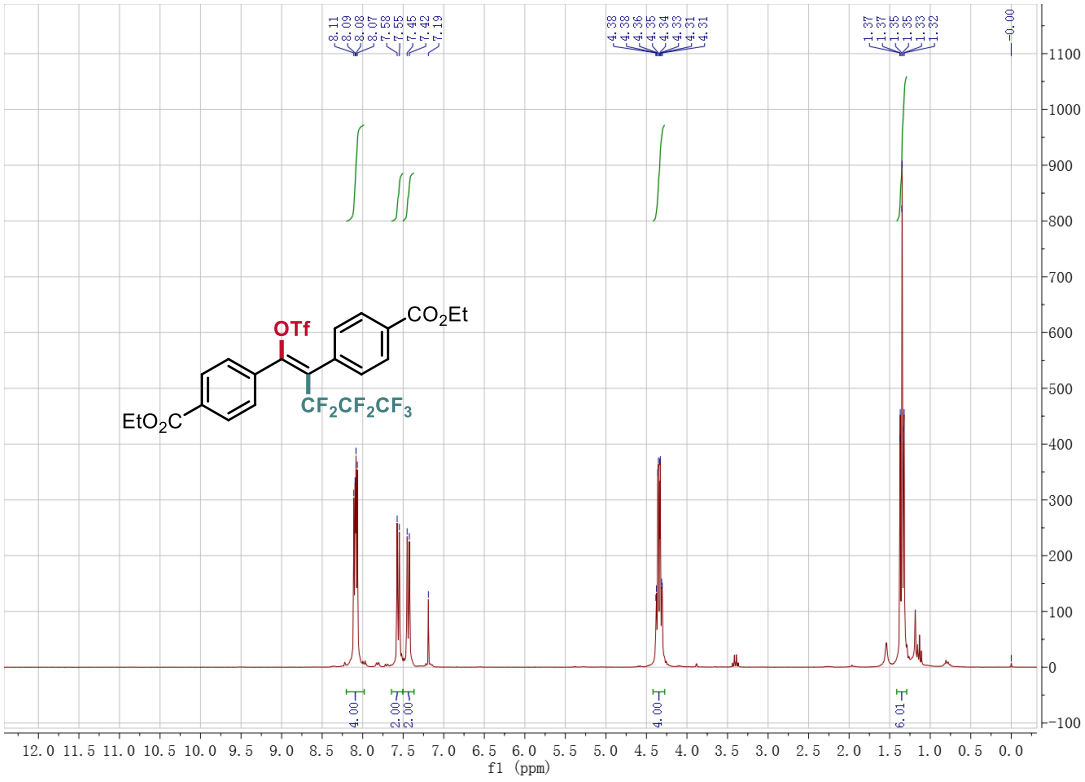
^{13}C NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1,2-diphenylpent-1-en-1-yl trifluoromethanesulfonate 3q



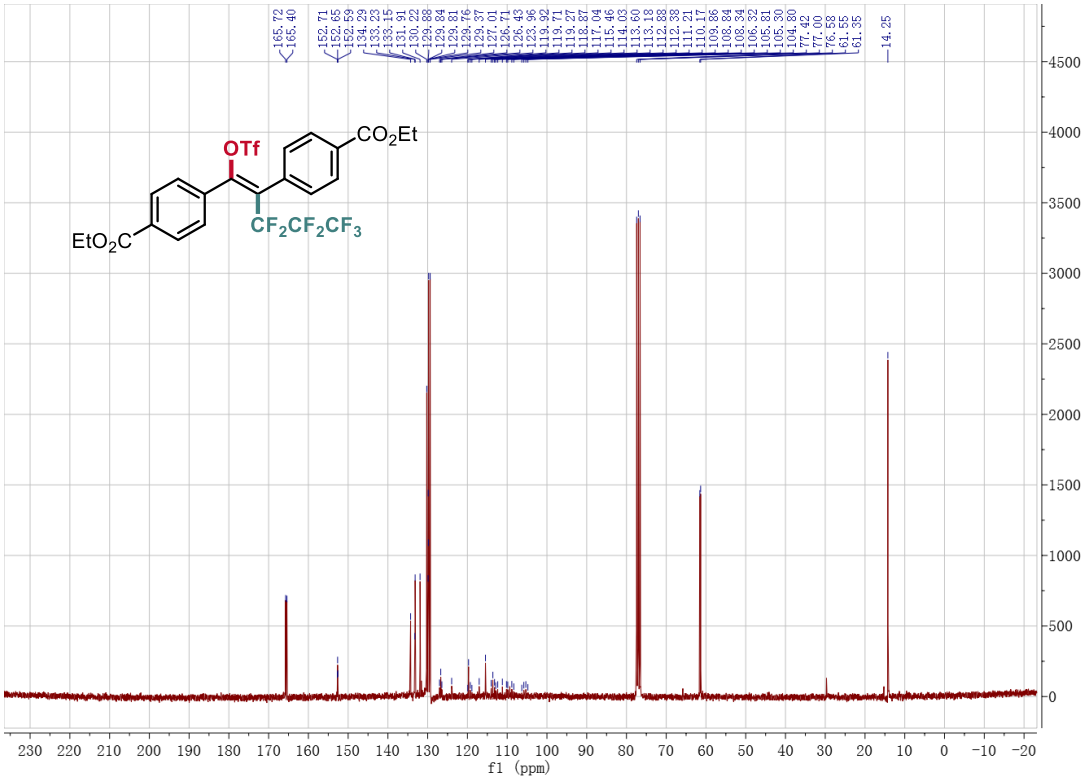
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1,2-diphenylpent-1-en-1-yl trifluoromethanesulfonate 3q



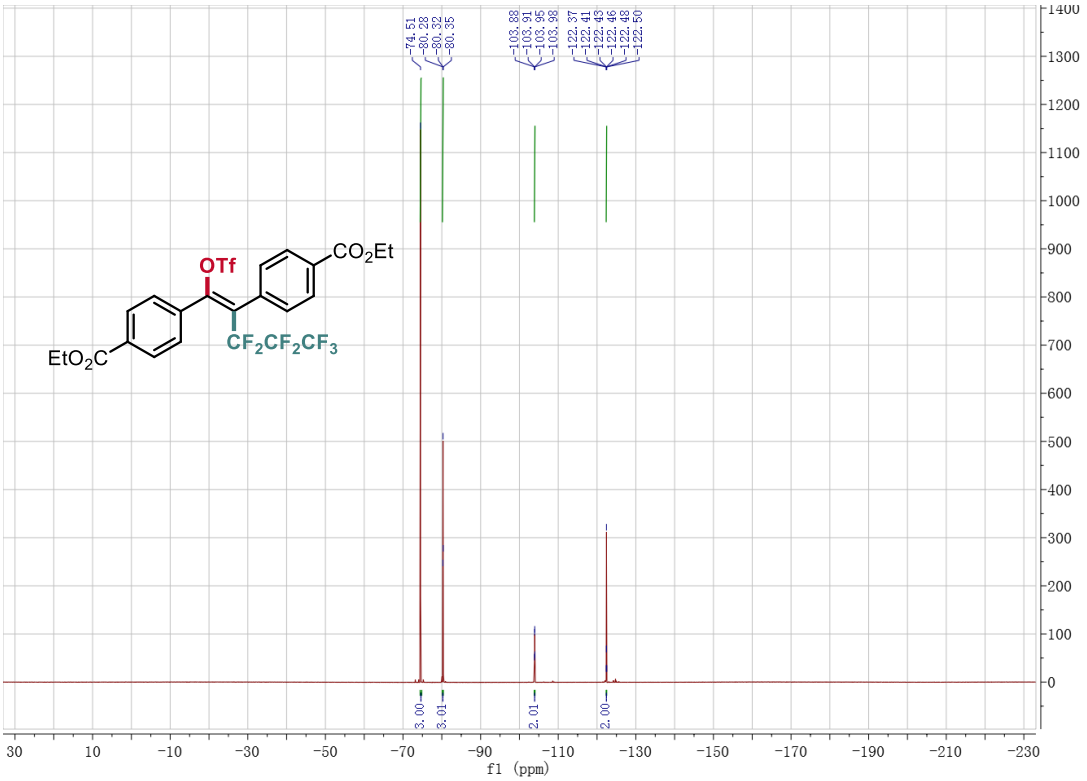
^{1}H NMR Spectrum of Diethyl 4,4'-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-ene-1,2-diyl)(*E*)-dibenzoate 3r



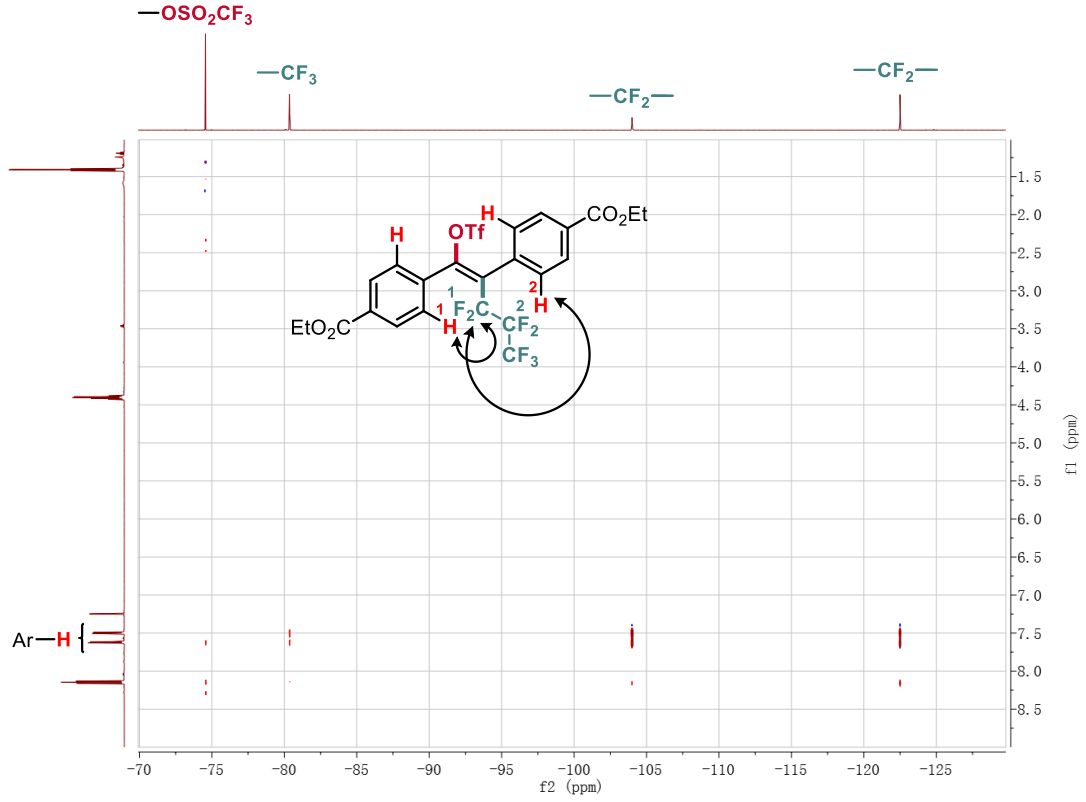
^{13}C NMR Spectrum of Diethyl 4,4'-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-ene-1,2-diyl)(*E*)-dibenzoate 3r



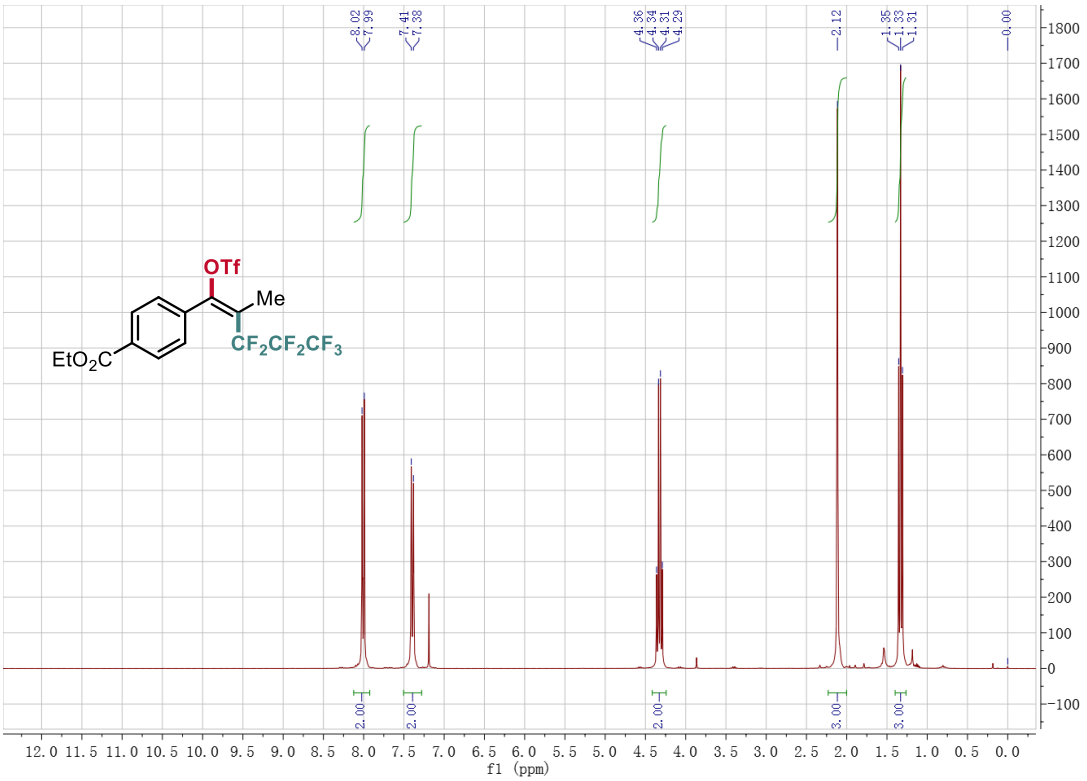
^{19}F NMR Spectrum of Diethyl 4,4'-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluor omethyl)sulfonyl)oxy)pent-1-ene-1,2-diyl)(*E*)-dibenzoate 3r



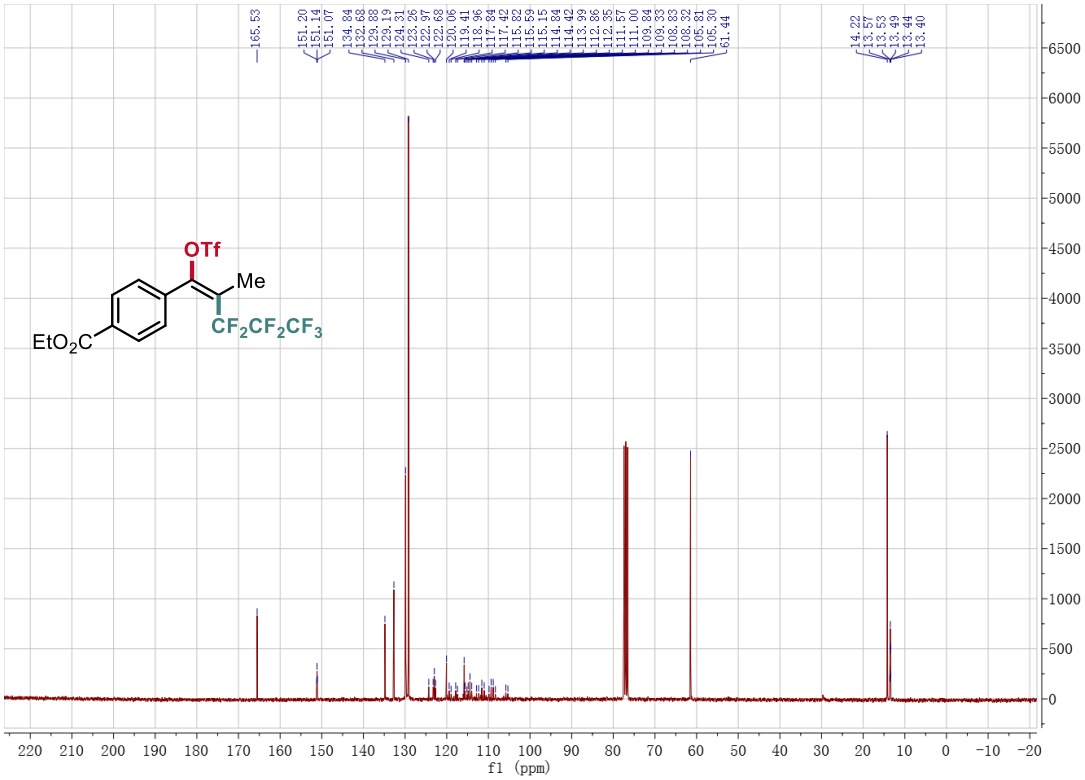
^{19}F-^{1}H HOESY NMR Spectrum of Diethyl 4,4'-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluor omethyl)sulfonyl)oxy)pent-1-ene-1,2-diyl)(*E*)-dibenzoate 3r



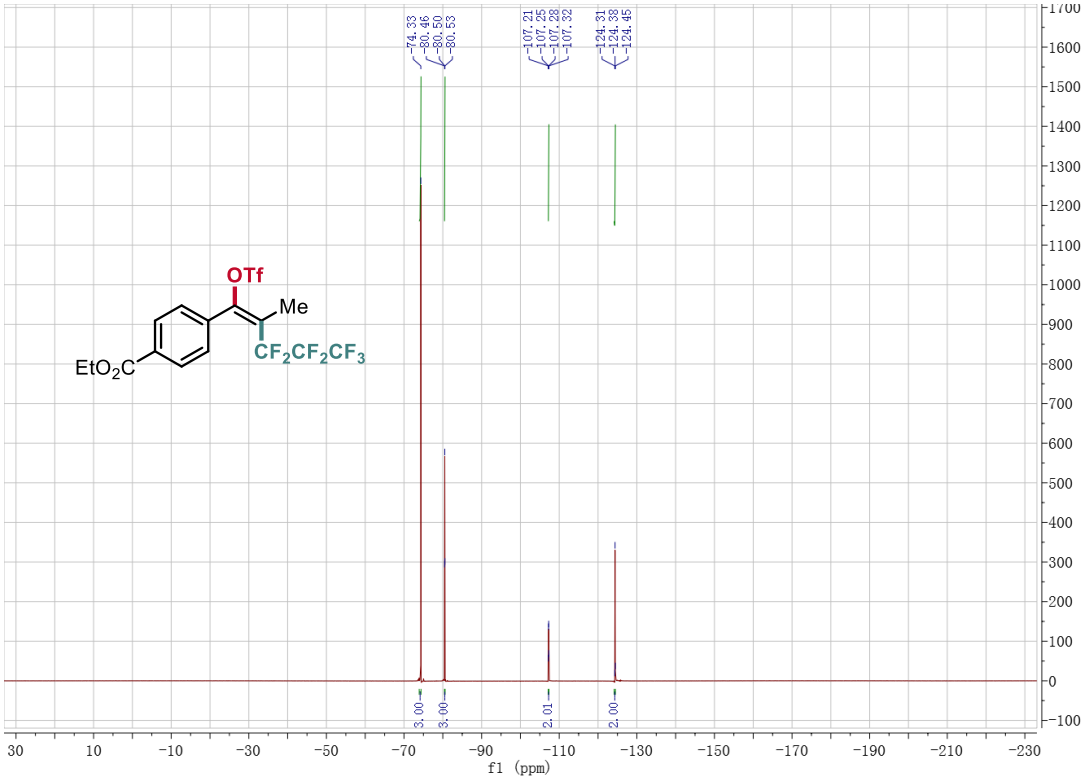
^{1}H NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-methyl-1-(((trifleoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3s



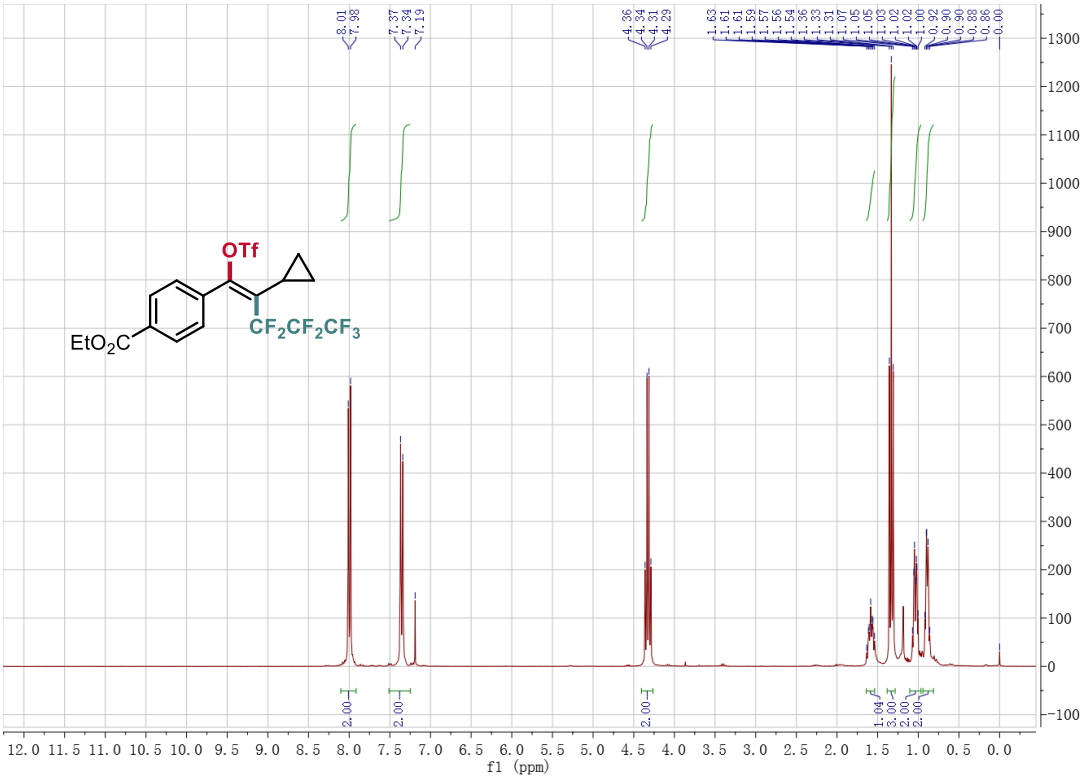
^{13}C NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-methyl-1-(((trifleoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3s



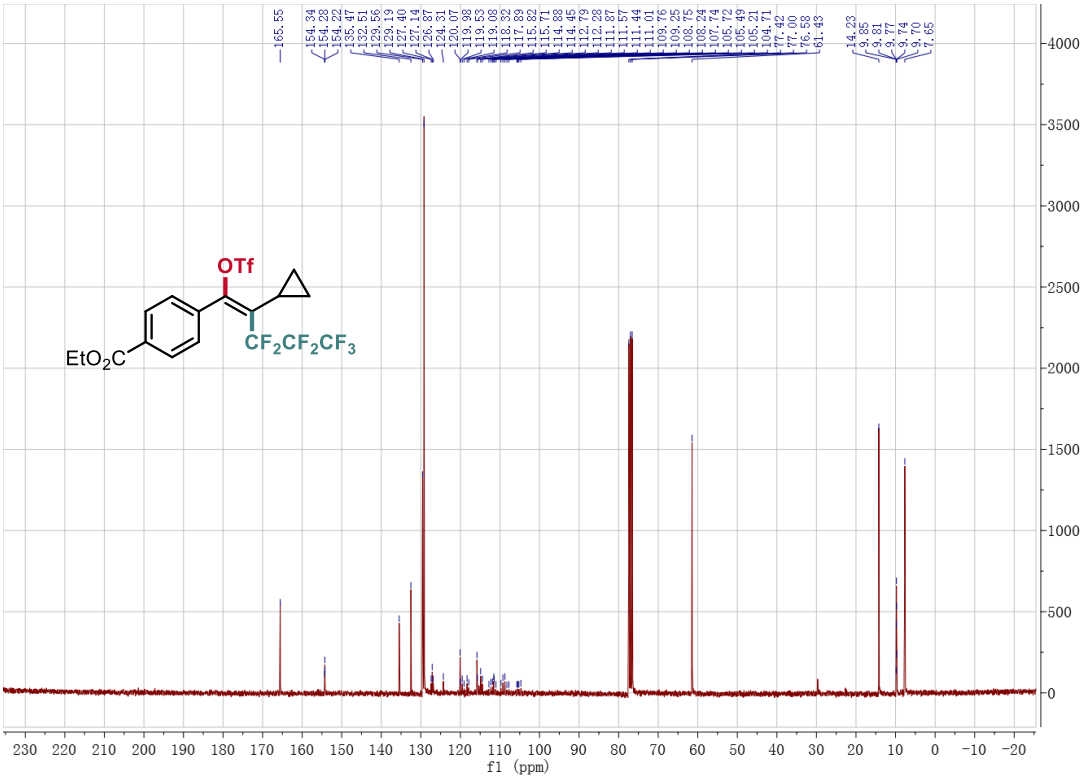
^{19}F NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-methyl-1-(((trifleoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3s



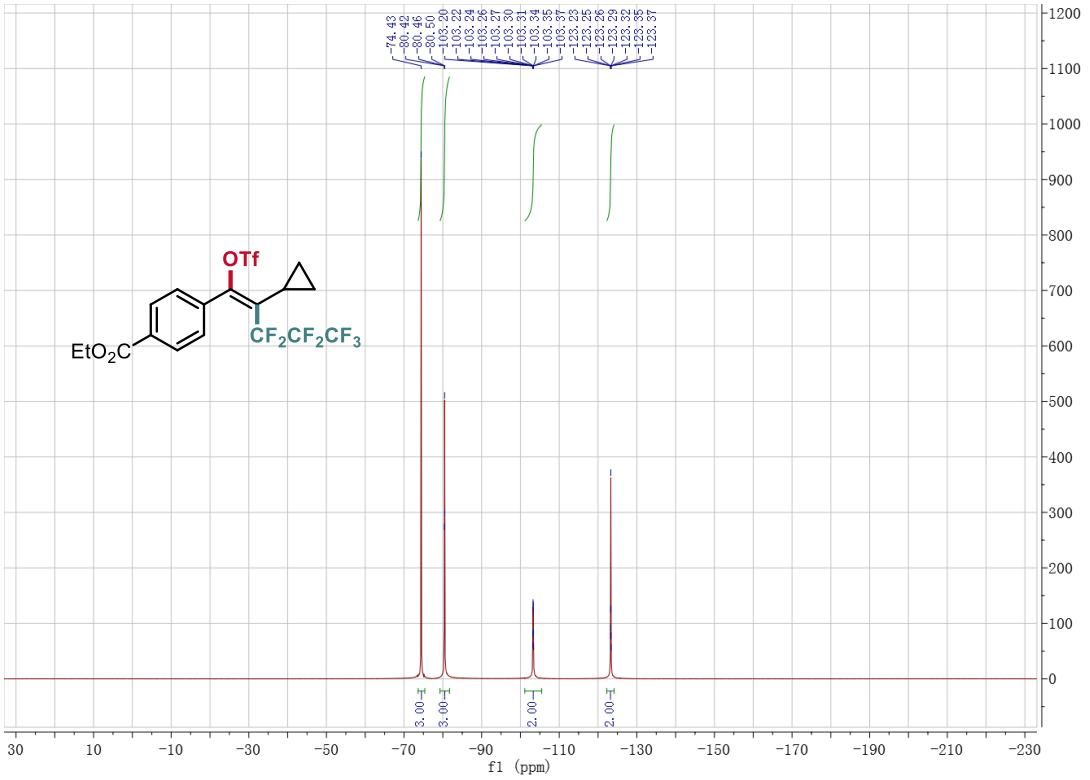
^{1}H NMR Spectrum of Ethyl (*E*)-4-(2-cyclopropyl-3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3t



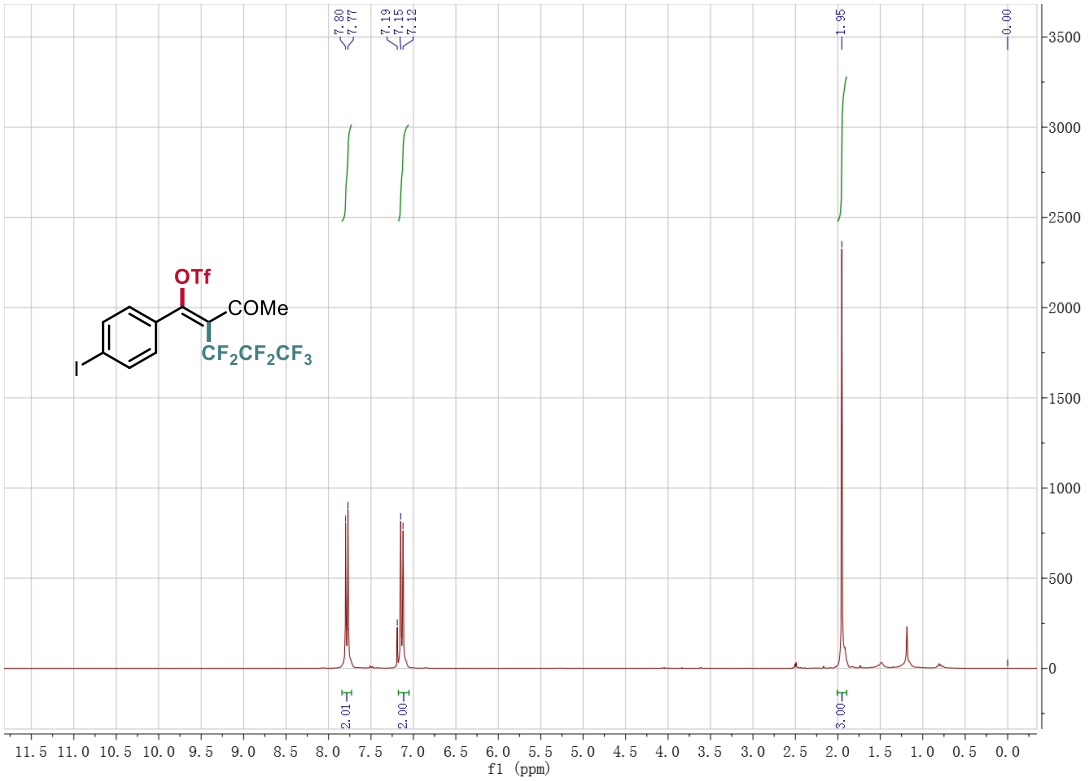
^{13}C NMR Spectrum of Ethyl (*E*)-4-(2-cyclopropyl-3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3t



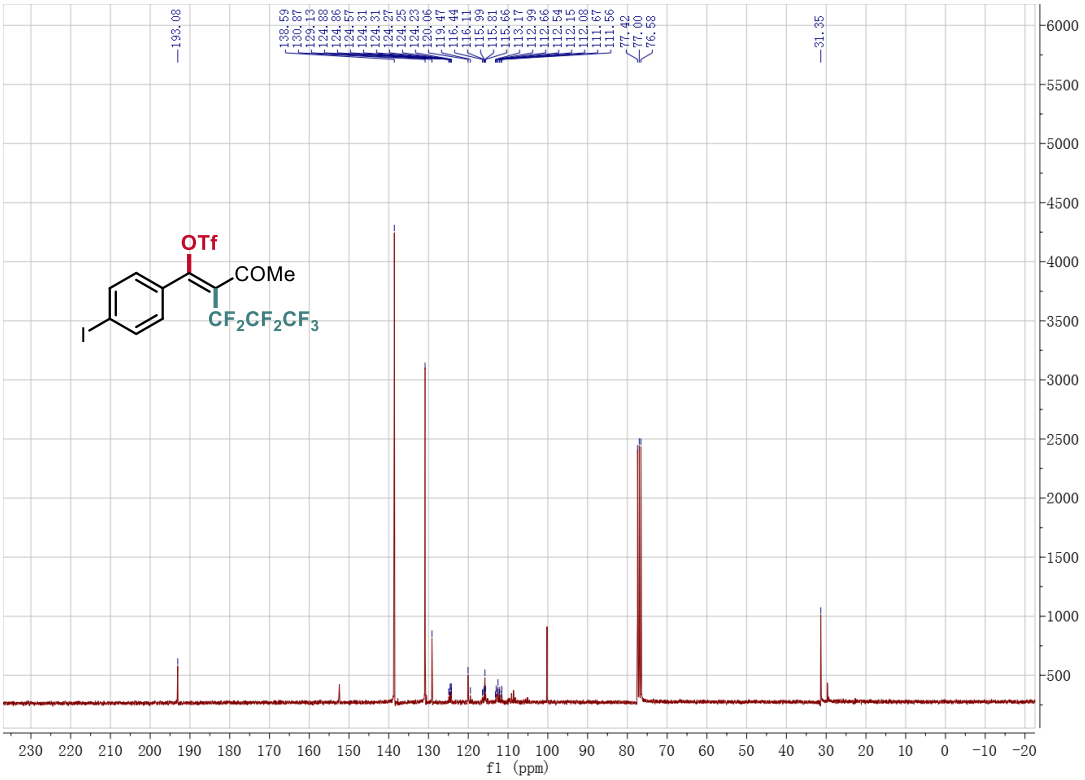
^{19}F NMR Spectrum of Ethyl (*E*)-4-(2-cyclopropyl-3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3t



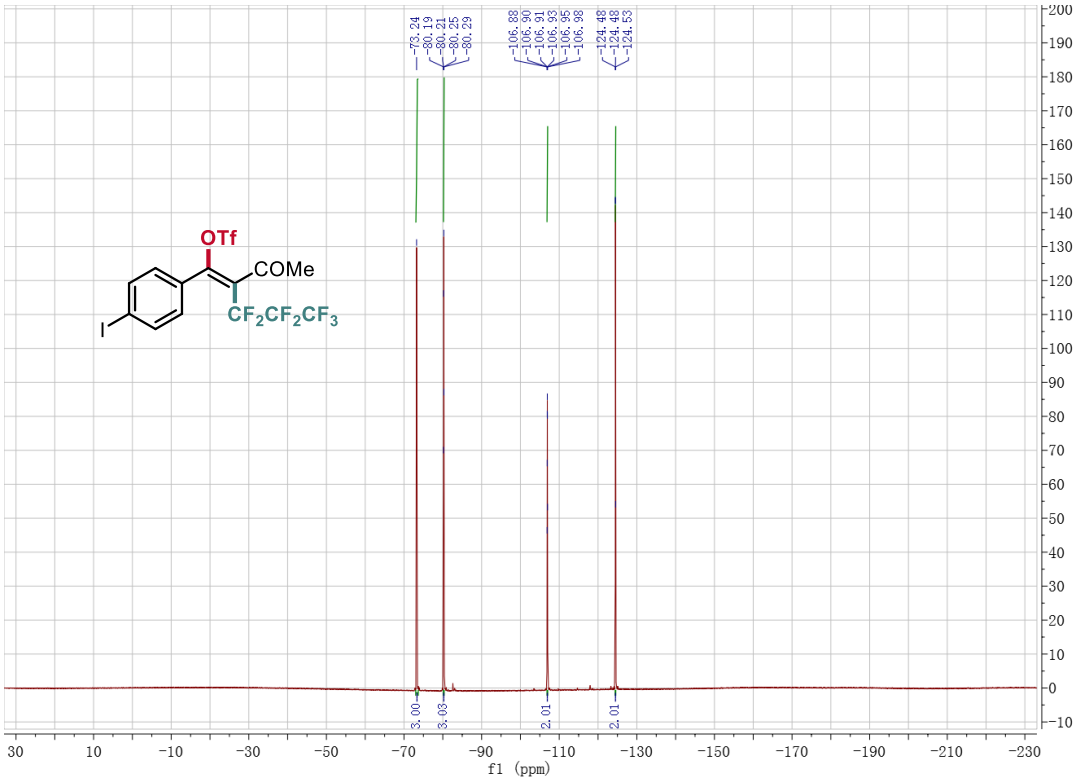
^{1}H NMR Spectrum of (*E*)-2-acetyl-3,3,4,4,5,5,5-heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate 3u



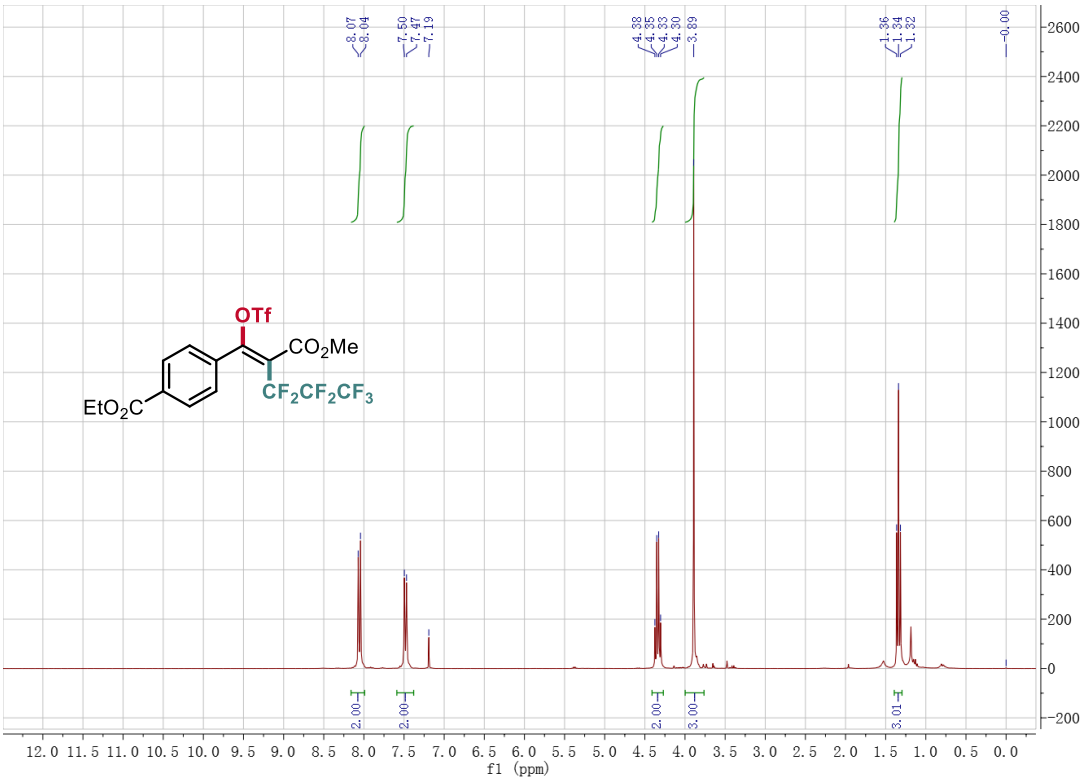
^{13}C NMR Spectrum of (*E*)-2-acetyl-3,3,4,4,5,5,5-heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate 3u



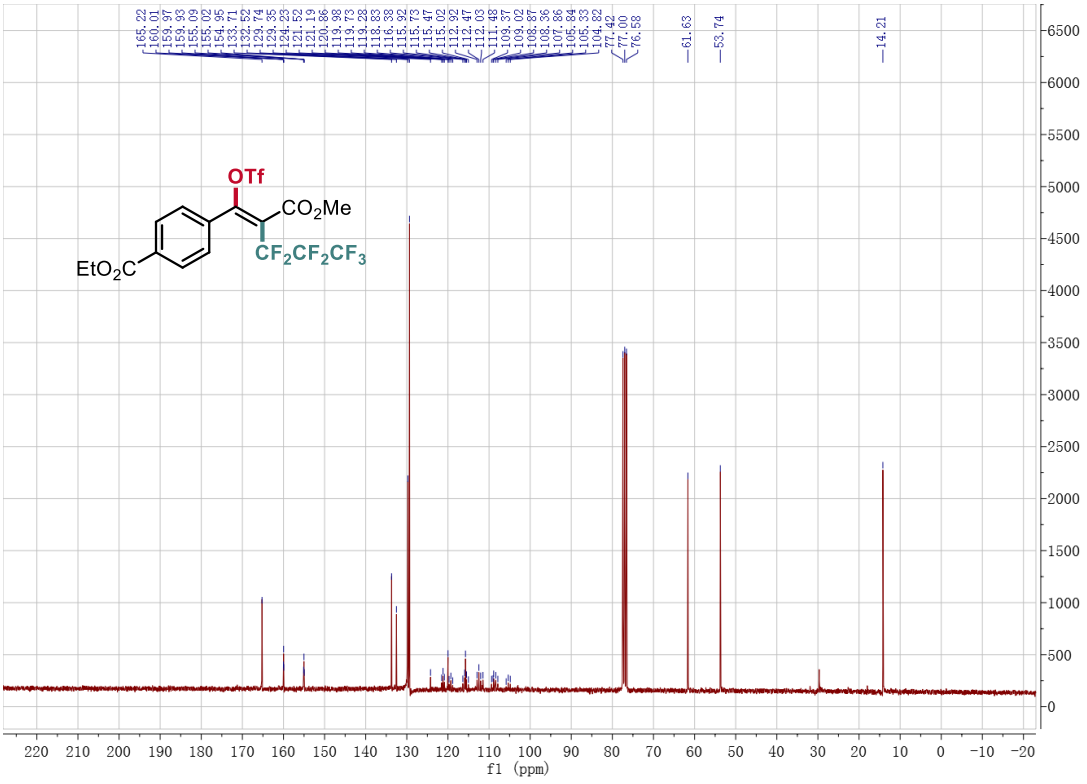
^{19}F NMR Spectrum of (*E*)-2-acetyl-3,3,4,4,5,5,5-heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate 3u



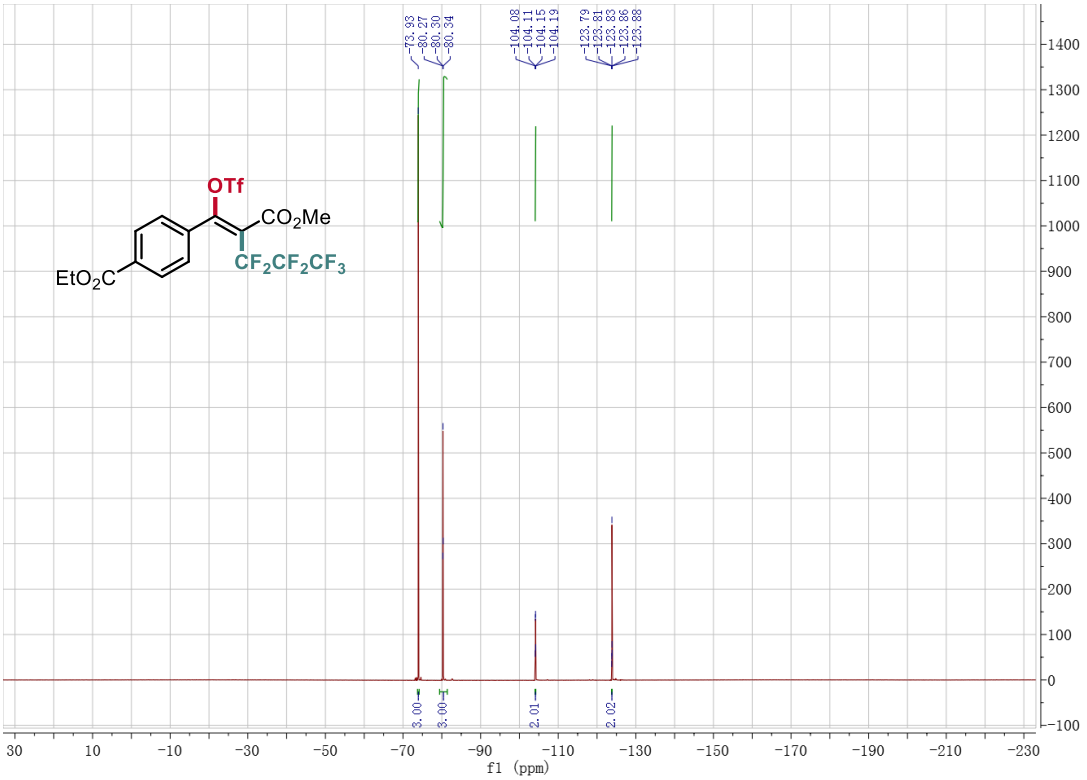
^{1}H NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-(methoxycarbonyl)-1-(((trifluoromethyl)sulfonyl)oxy) pent-1-en-1-yl)benzoate 3v



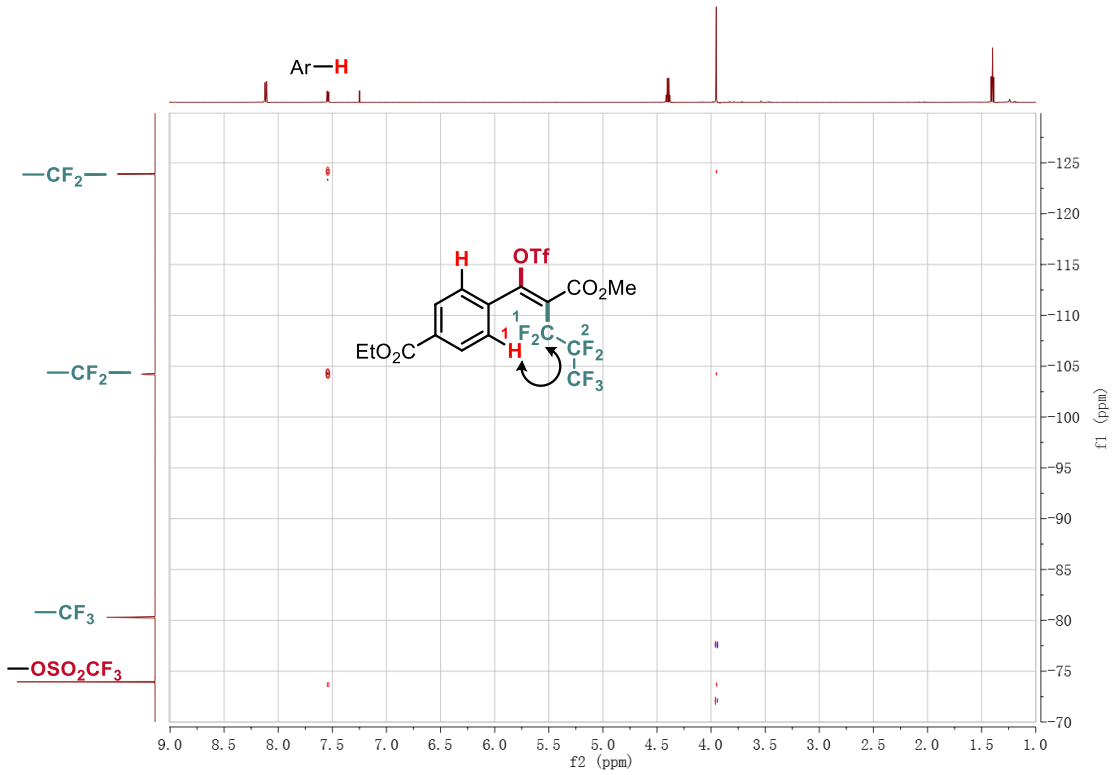
^{13}C NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-(methoxycarbonyl)-1-(((trifluoromethyl)sulfonyl)oxy) pent-1-en-1-yl)benzoate 3v



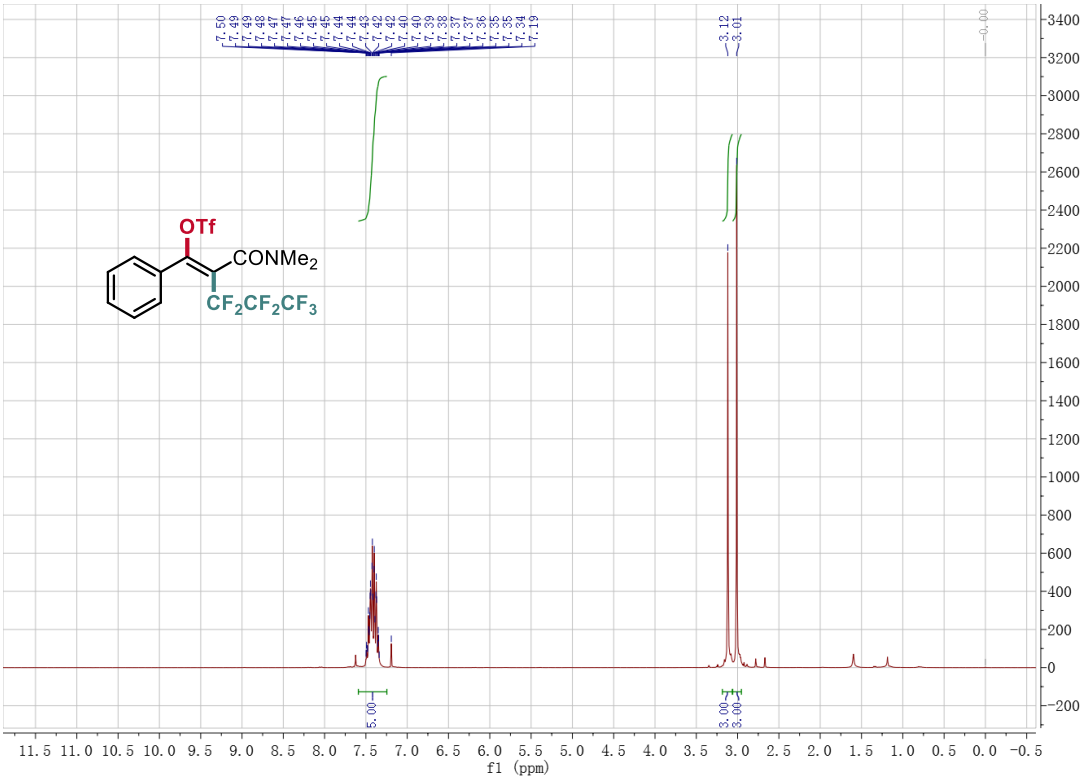
^{19}F NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-(methoxycarbon yl)-1-(((trifluoromethyl)sulfonyl)oxy) pent-1-en-1-yl)benzoate 3v



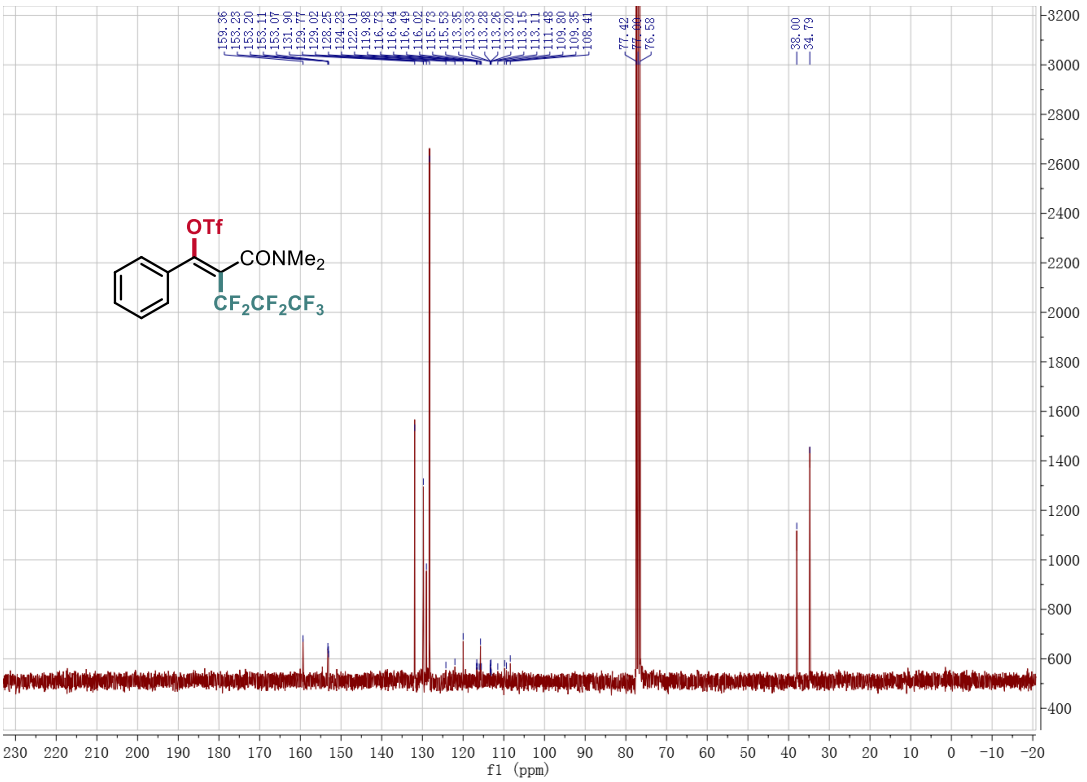
^{19}F-^{1}H HOESY NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-2-(methoxycarbon yl)-1-(((trifluoromethyl)sulfonyl)oxy) pent-1-en-1-yl)benzoate 3v:



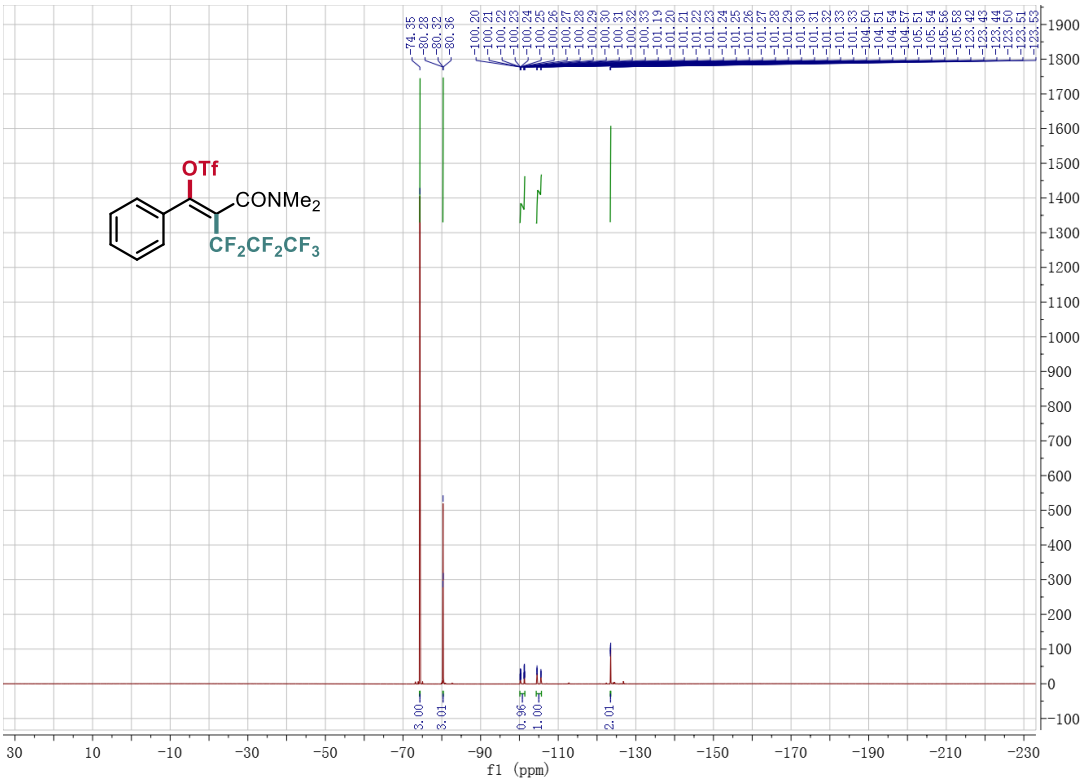
^{1}H NMR Spectrum of (*E*)-2-(dimethylcarbamoyl)-3,3,4,4,5,5,5-heptafluoro-1-phenyl pent-1-en-1-yl trifluoromethanesulfonate 3w



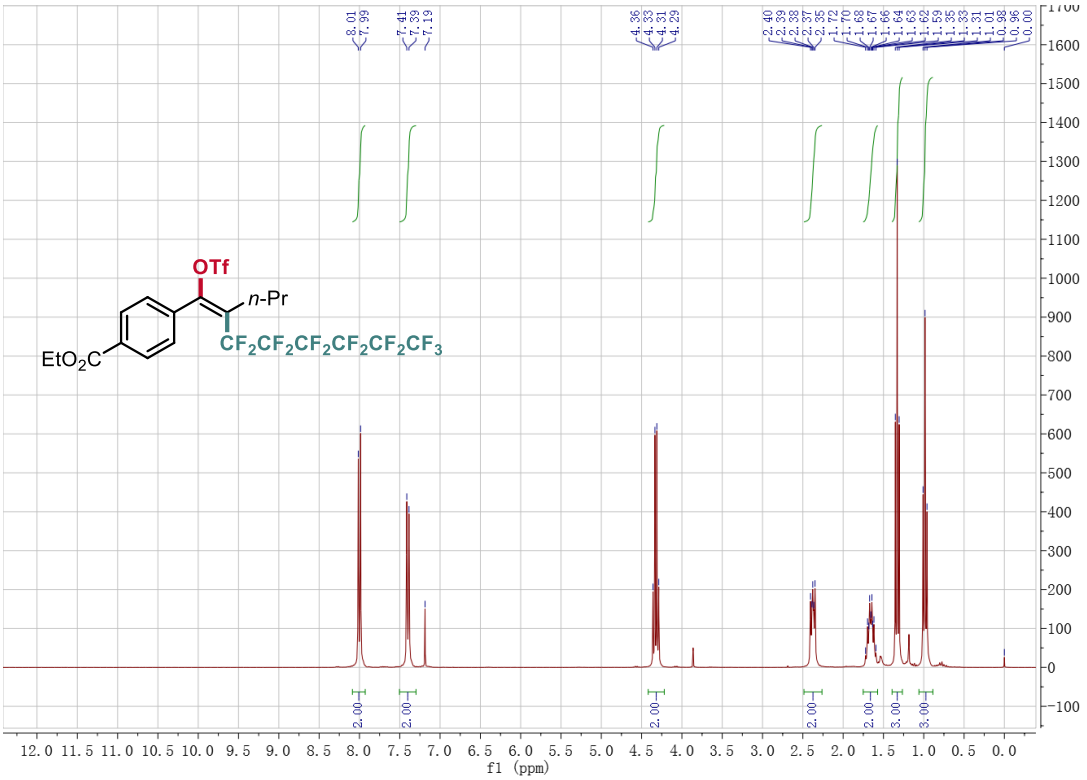
^{13}C NMR Spectrum of (*E*)-2-(dimethylcarbamoyl)-3,3,4,4,5,5,5-heptafluoro-1-phenyl pent-1-en-1-yl trifluoromethanesulfonate 3w



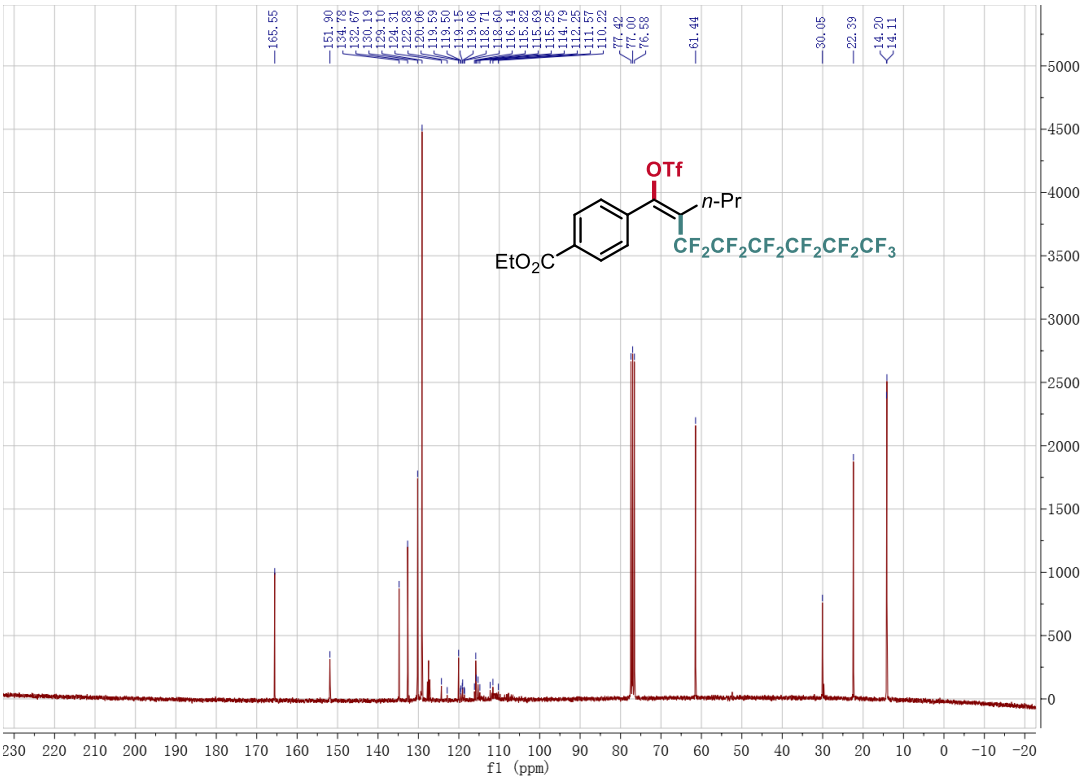
^{19}F NMR Spectrum of (*E*)-2-(dimethylcarbamoyl)-3,3,4,4,5,5,5-heptafluoro-1-phenyl pent-1-en-1-yl trifluoromethanesulfonate 3w



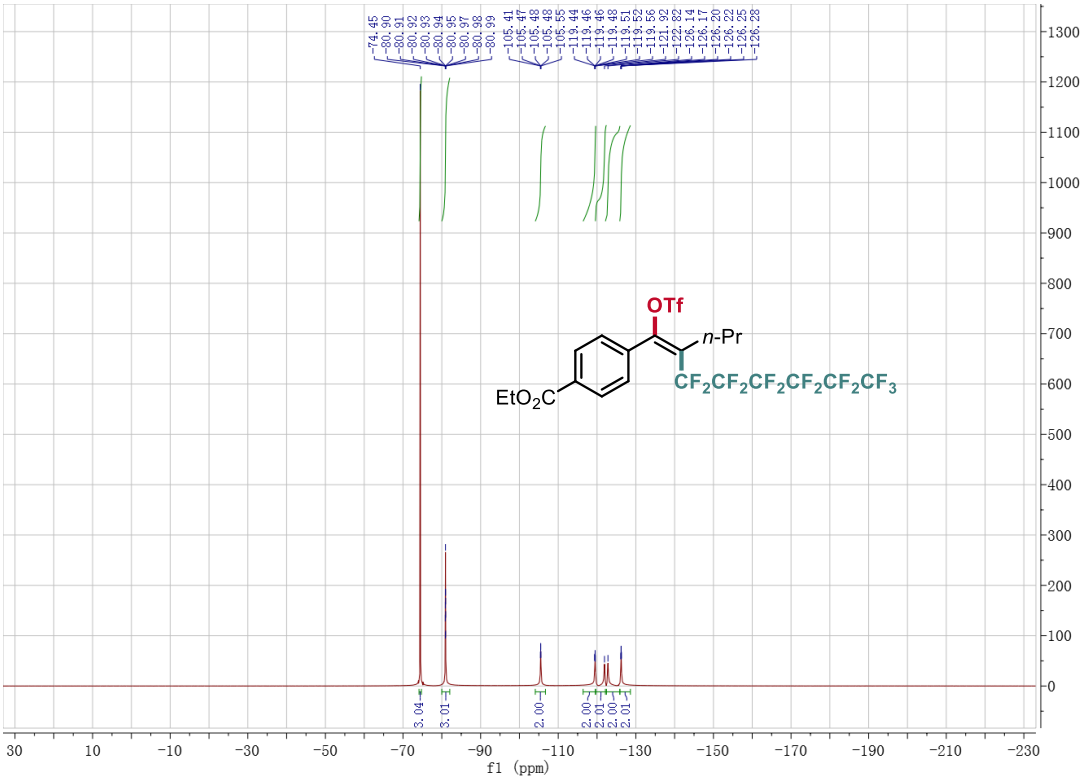
^{1}H NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluo ro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)oct-1-en-1-yl)benzoate 3x



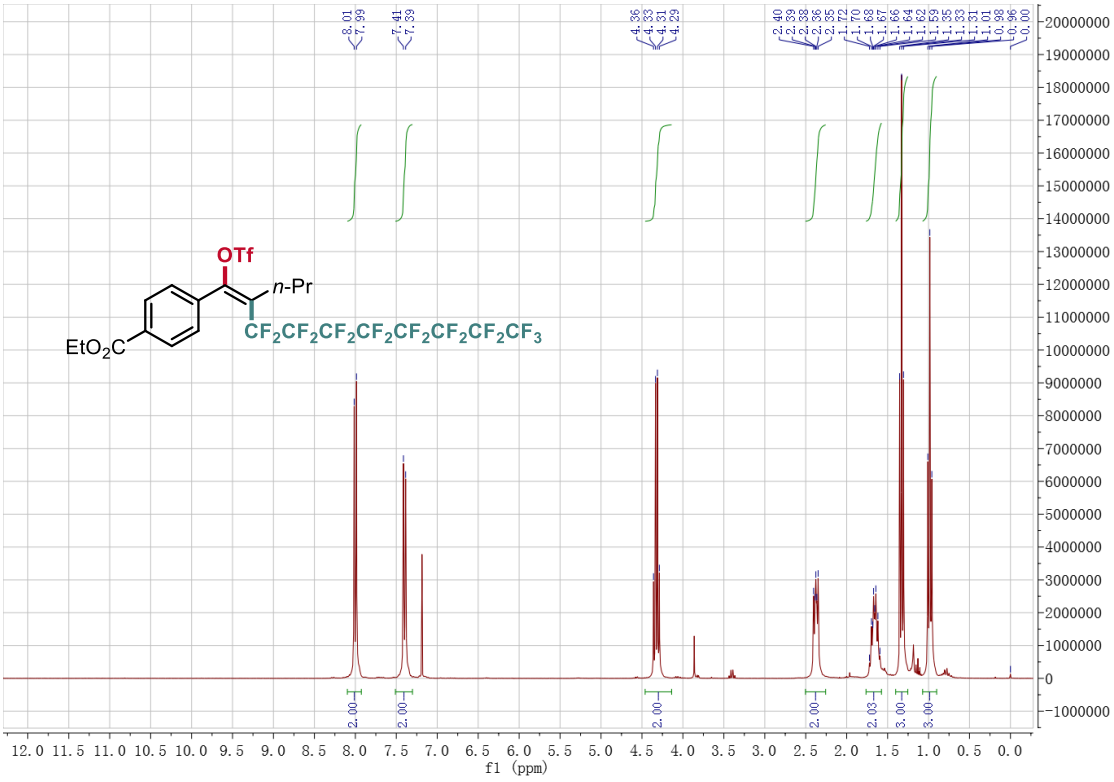
^{13}C NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluo ro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)oct-1-en-1-yl)benzoate 3x



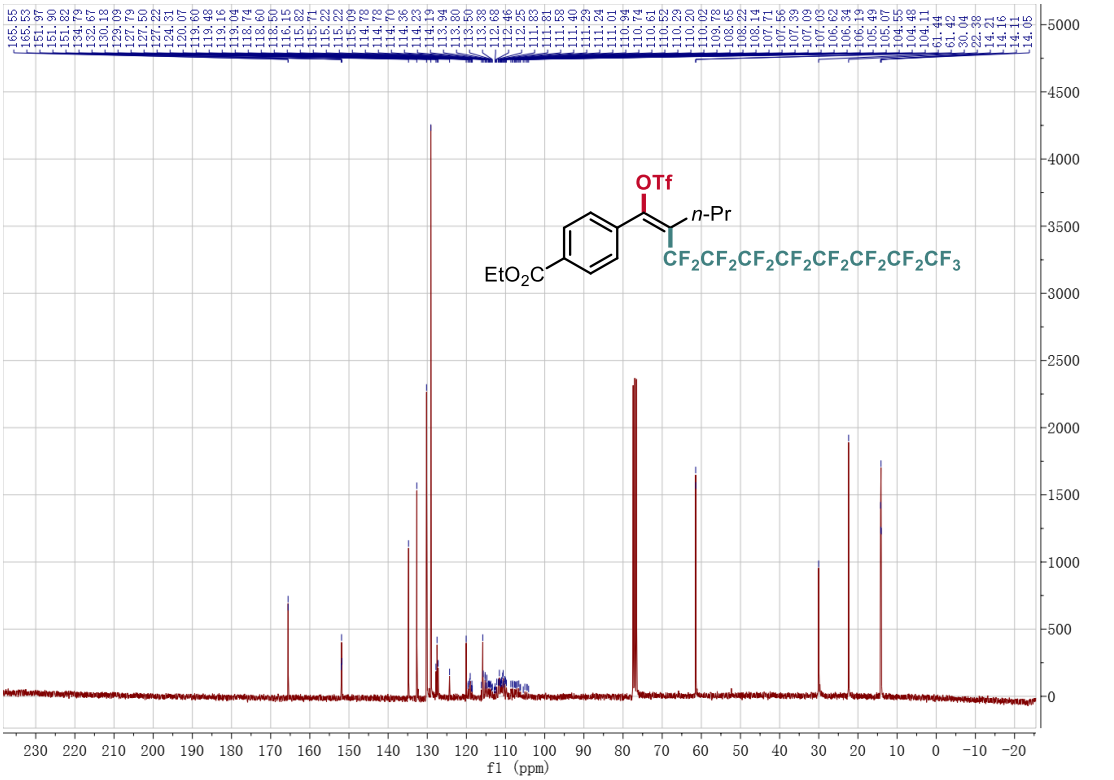
^{19}F NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluo ro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)oct-1-en-1-yl)benzoate 3x



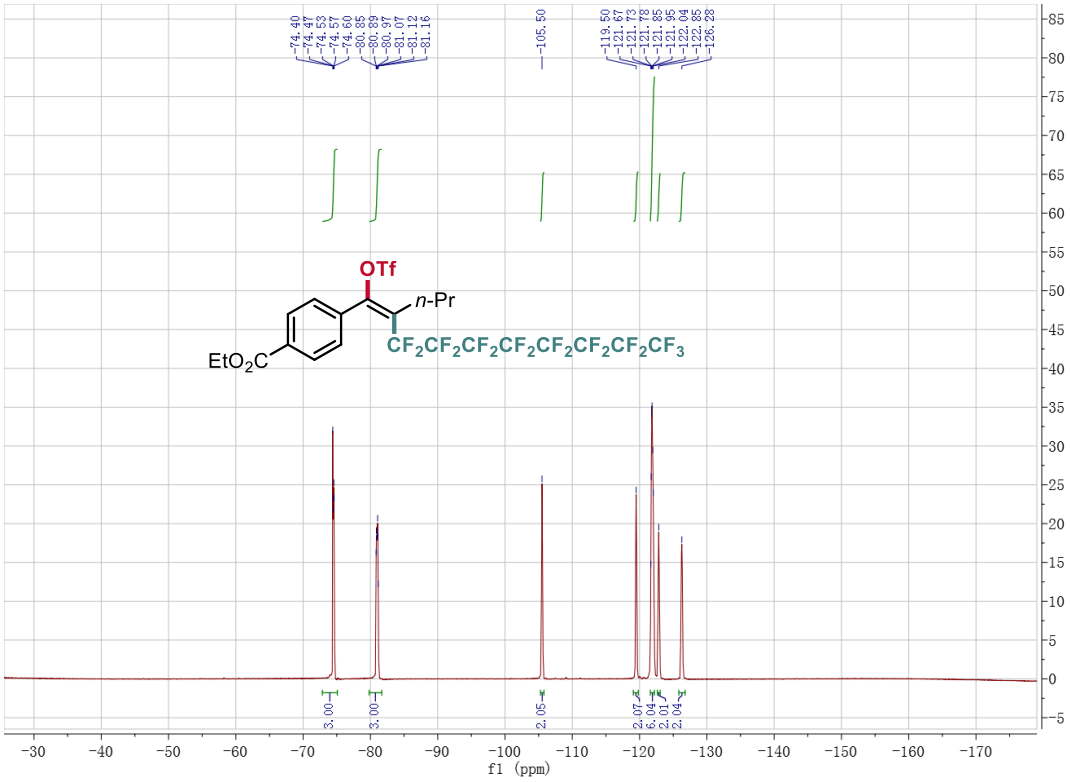
^{1}H NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadeca fluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)dec-1-en-1-yl)benzoate 3y



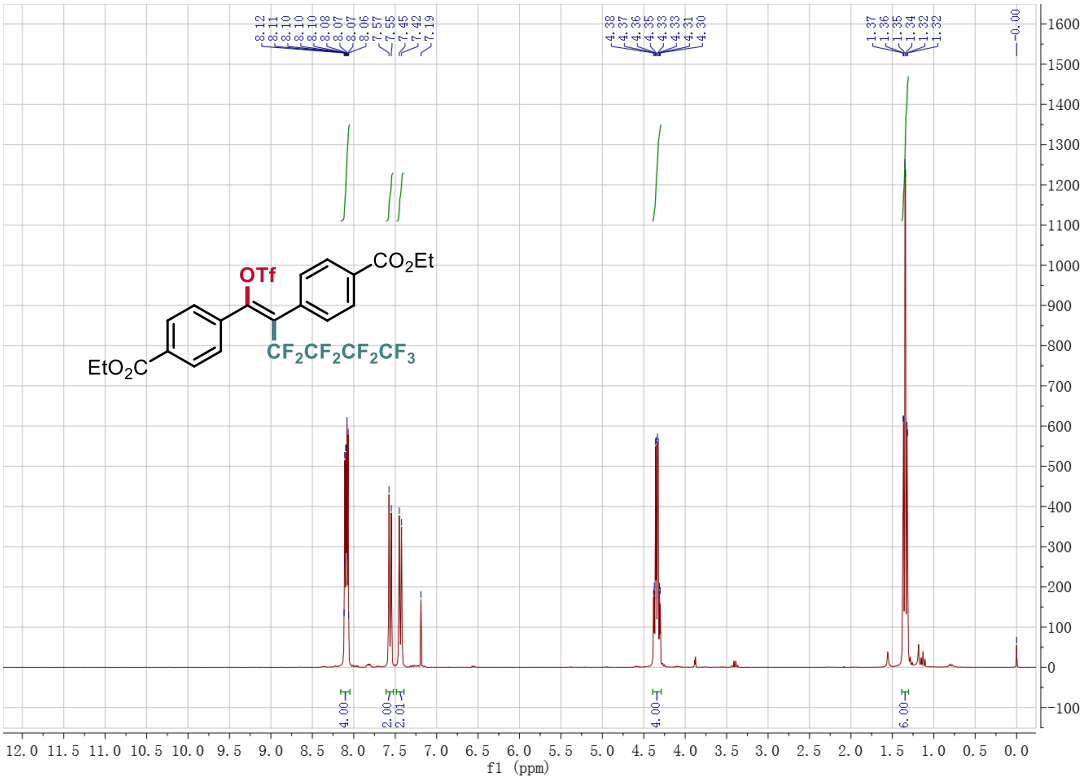
^{13}C NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadeca fluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)dec-1-en-1-yl)benzoate 3y



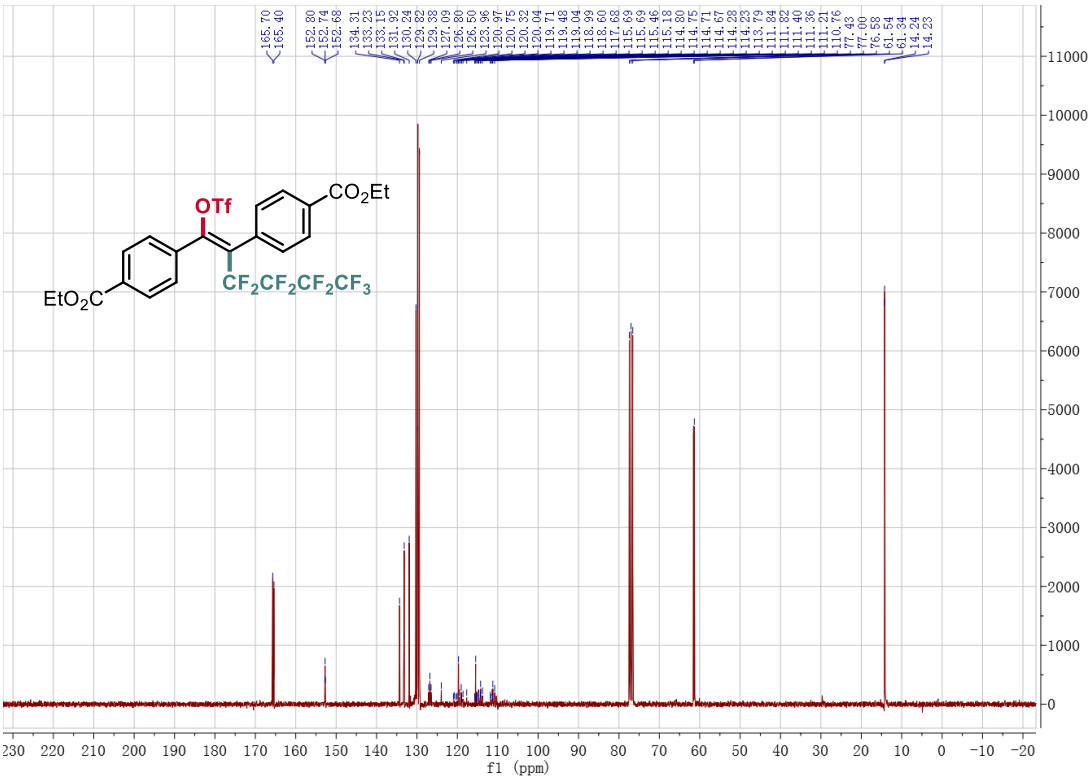
^{19}F NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadeca fluoro-2-propyl-1-(((trifluoromethyl)sulfonyl)oxy)dec-1-en-1-yl)benzoate 3y



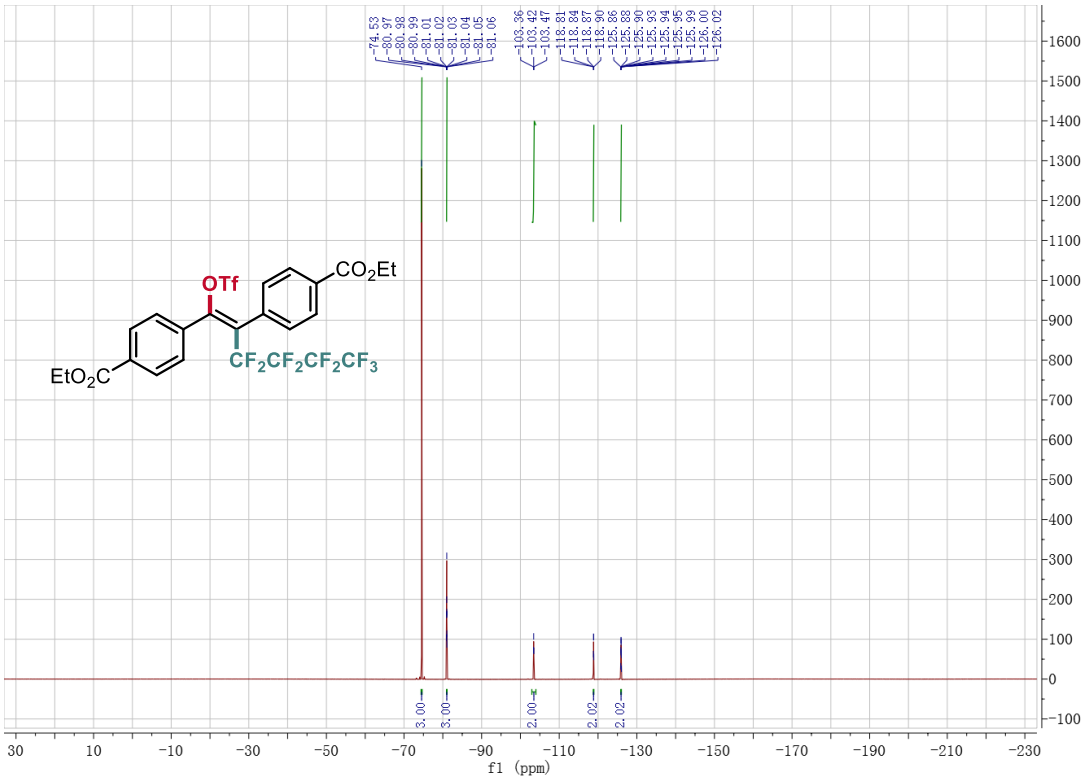
^{1}H NMR Spectrum of Diethyl 4,4'-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(((trifluoromethyl)sulfonyl)oxy)hex-1-ene-1,2-diyl)(*E*)-dibenzoate 3z



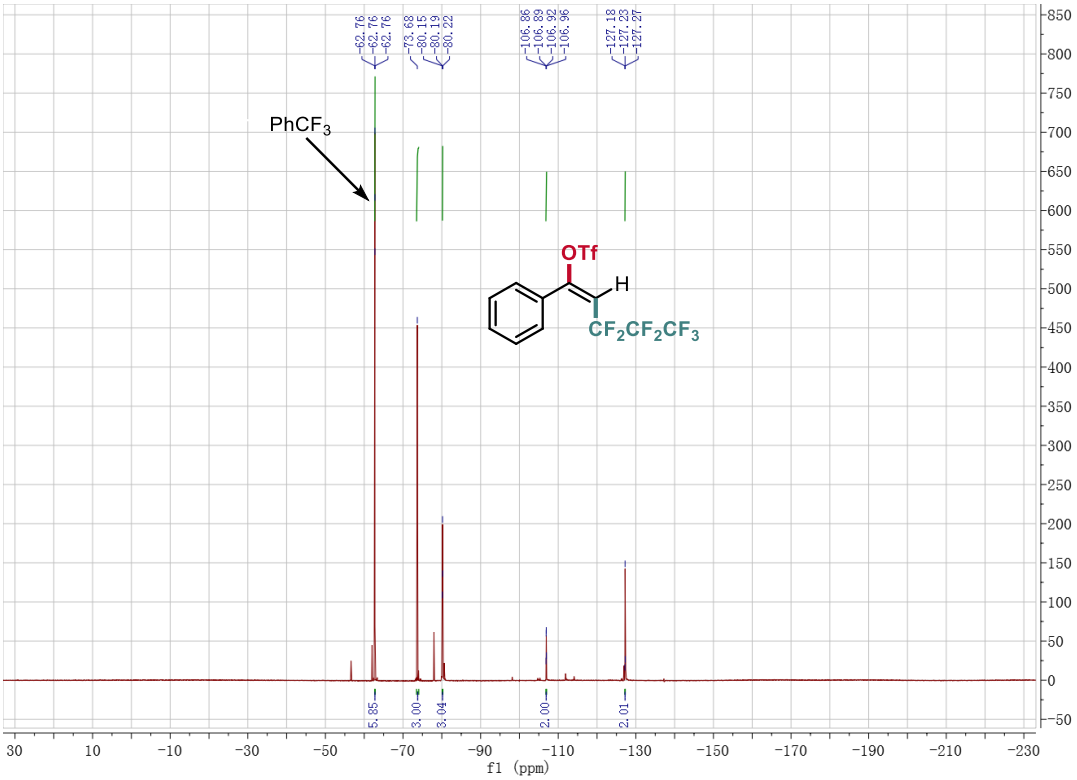
^{13}C NMR Spectrum of Diethyl 4,4'-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(((trifluoromethyl)sulfonyl)oxy)hex-1-ene-1,2-diyl)(*E*)-dibenzoate 3z



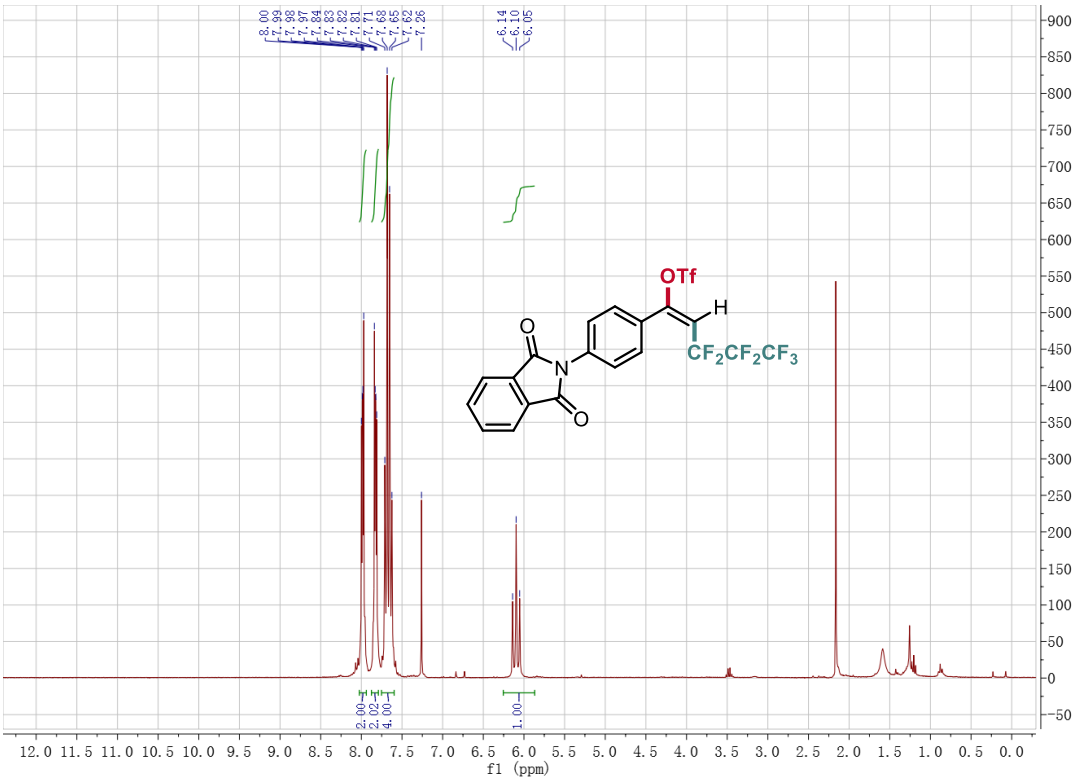
^{19}F NMR Spectrum of Diethyl 4,4'-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(((trifluoromethyl)sulfonyl)oxy)hex-1-ene-1,2-diyl)(*E*)-dibenzoate 3z



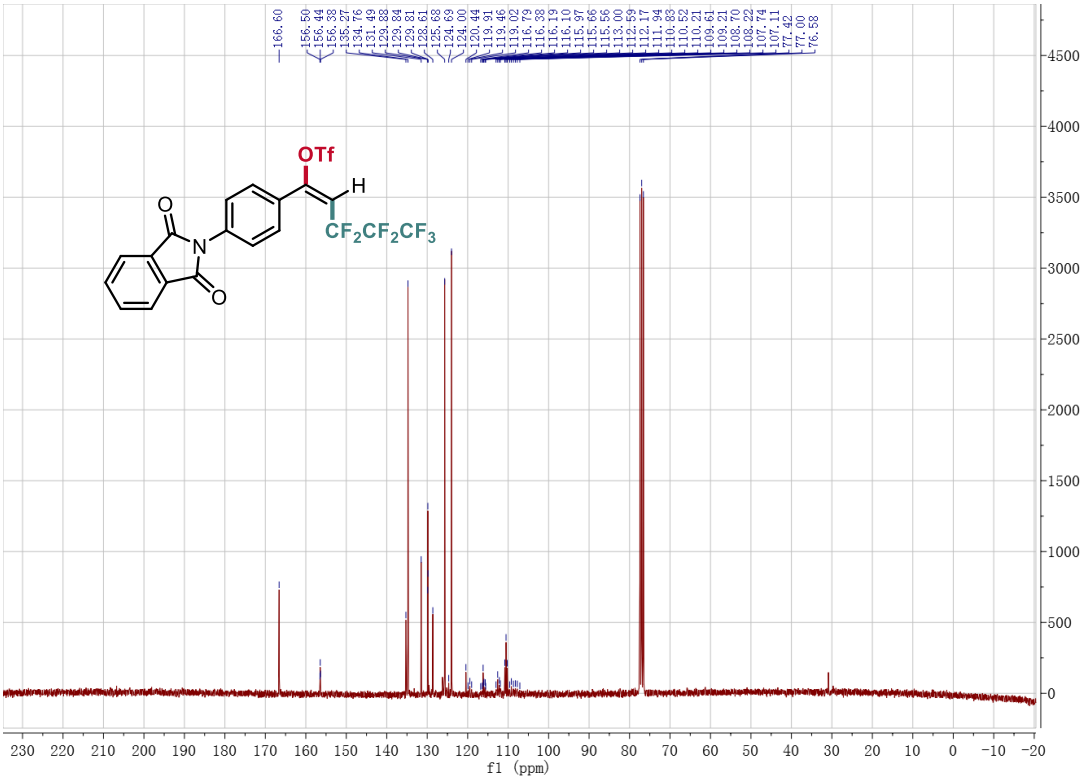
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-phenylpent-1-en-1-yl trifluoromethanesulfonate 3aa



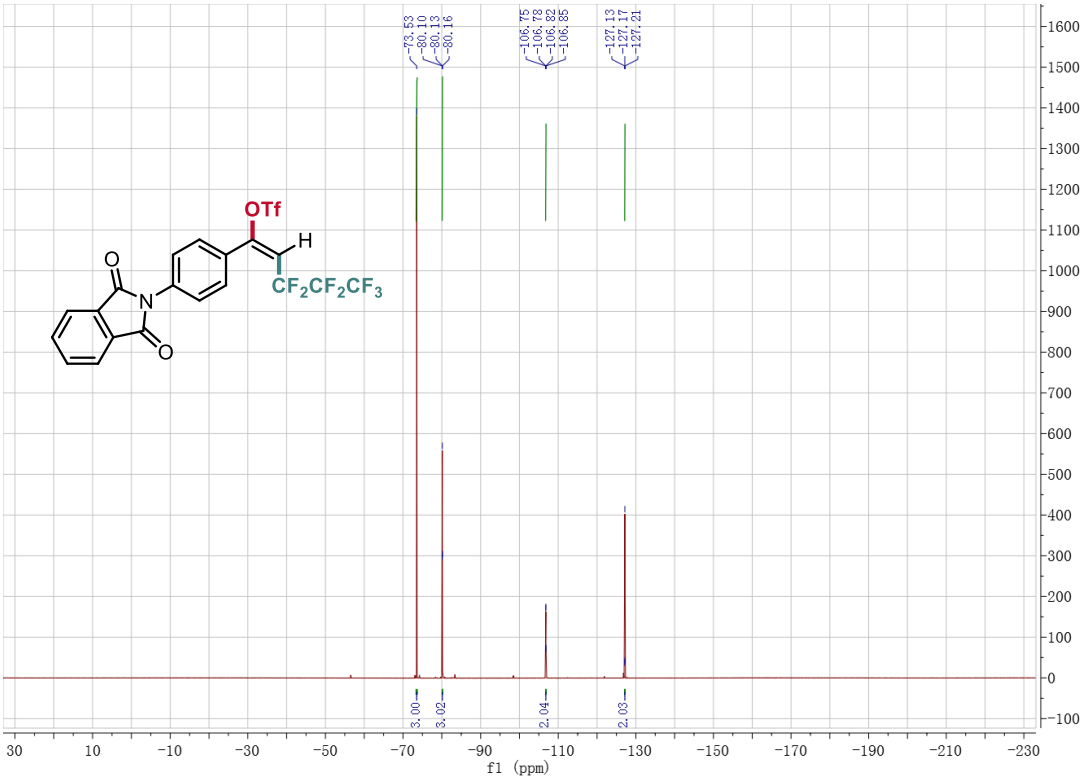
^{1}H NMR Spectrum of (*E*)-1-(4-(1,3-dioxoisoindolin-2-yl)phenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ab



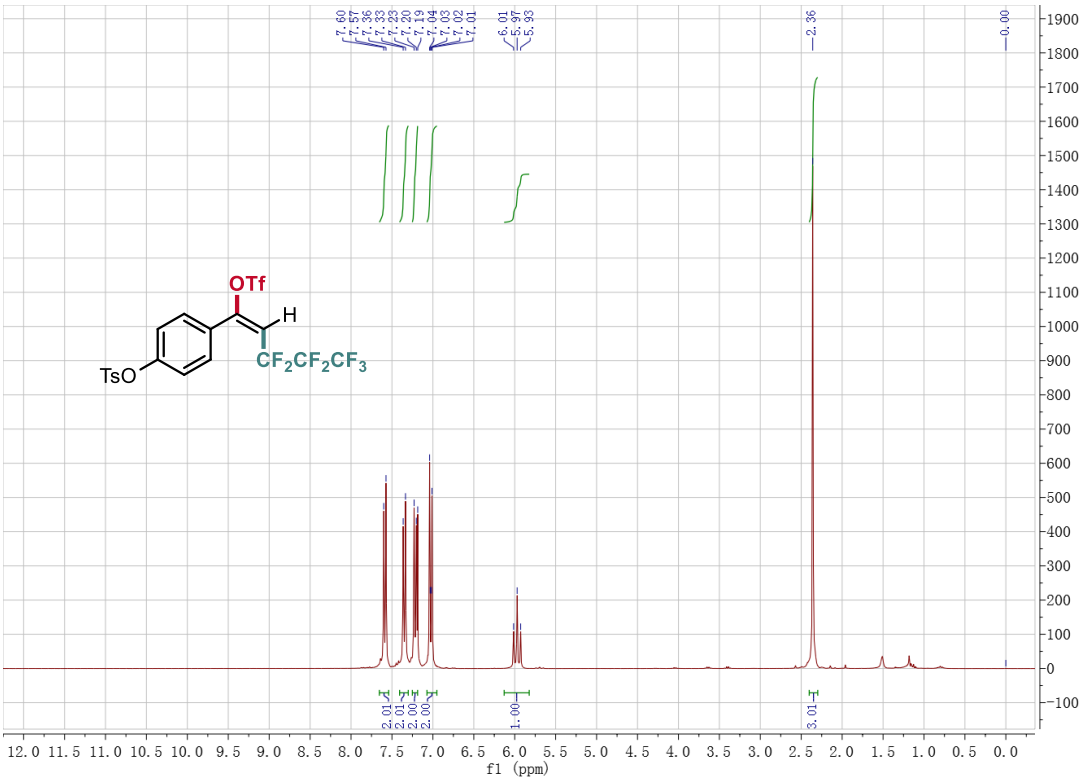
^{13}C NMR Spectrum of (*E*)-1-(4-(1,3-dioxoisoindolin-2-yl)phenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ab



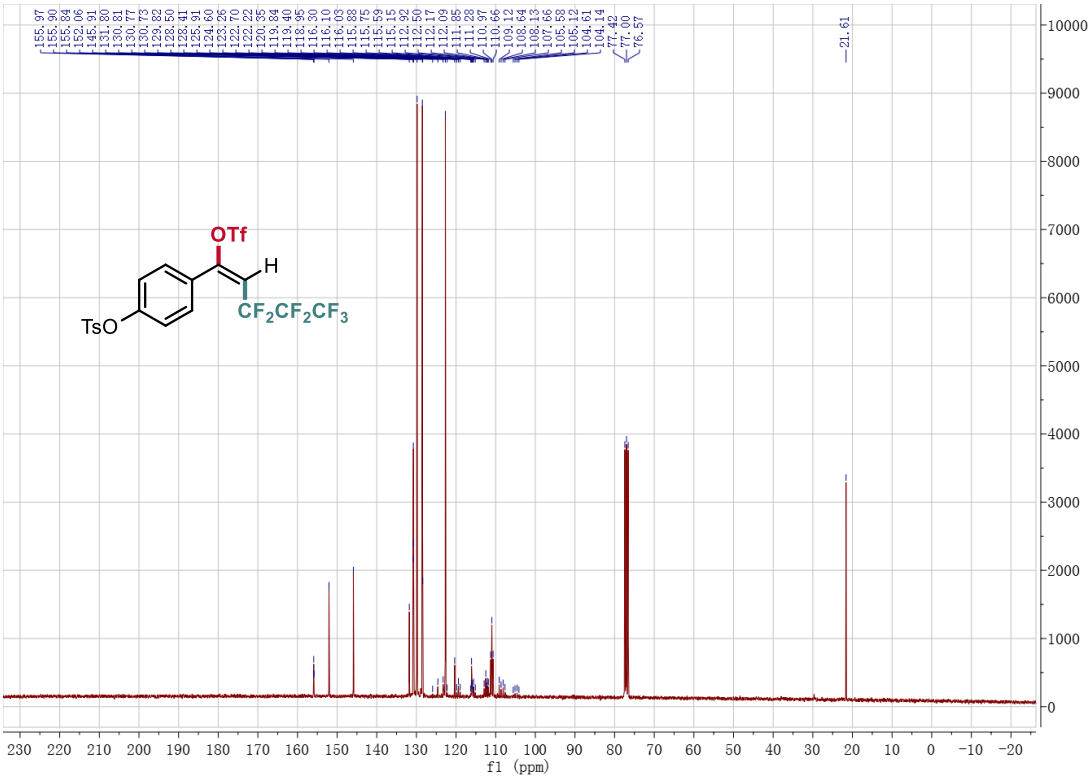
^{19}F NMR Spectrum of (*E*)-1-(4-(1,3-dioxoisoindolin-2-yl)phenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ab



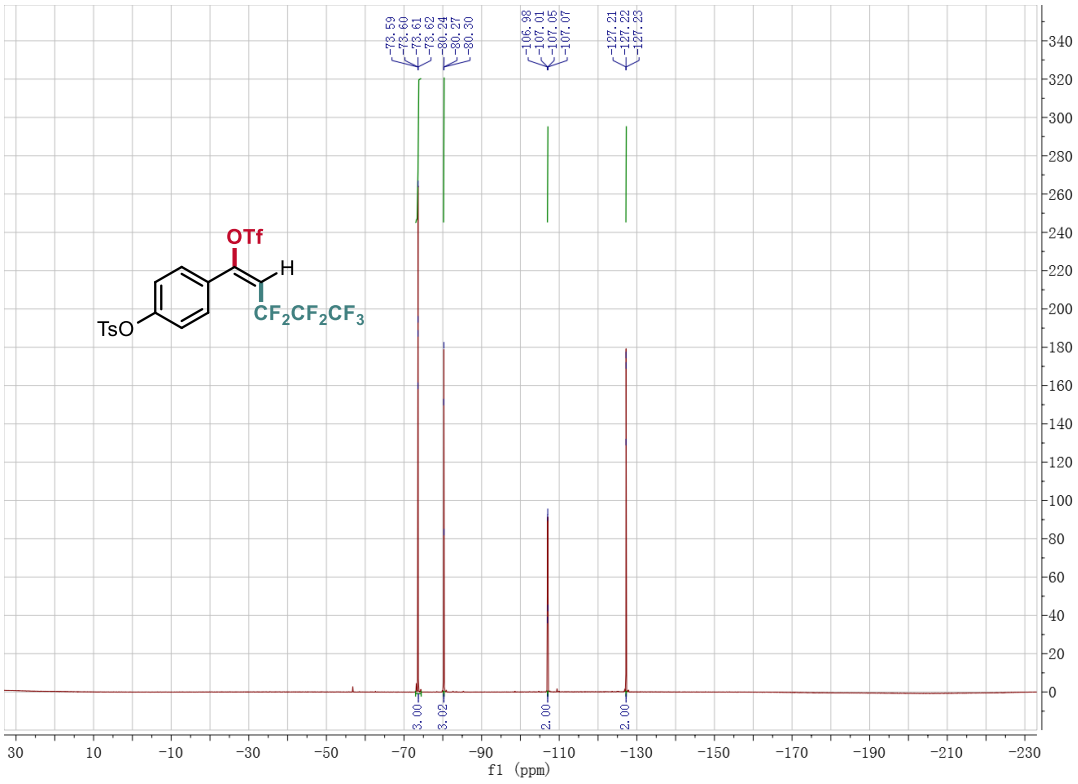
^{1}H NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzenesulfonate 3ac



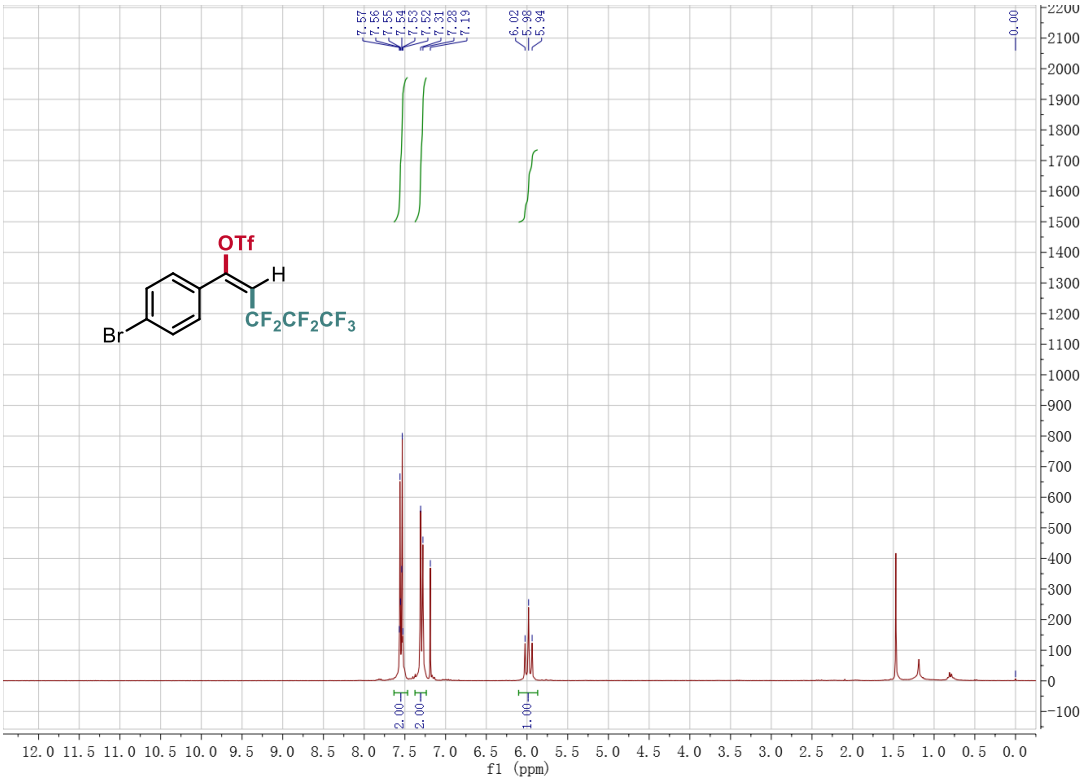
^{13}C NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzenesulfonate 3ac



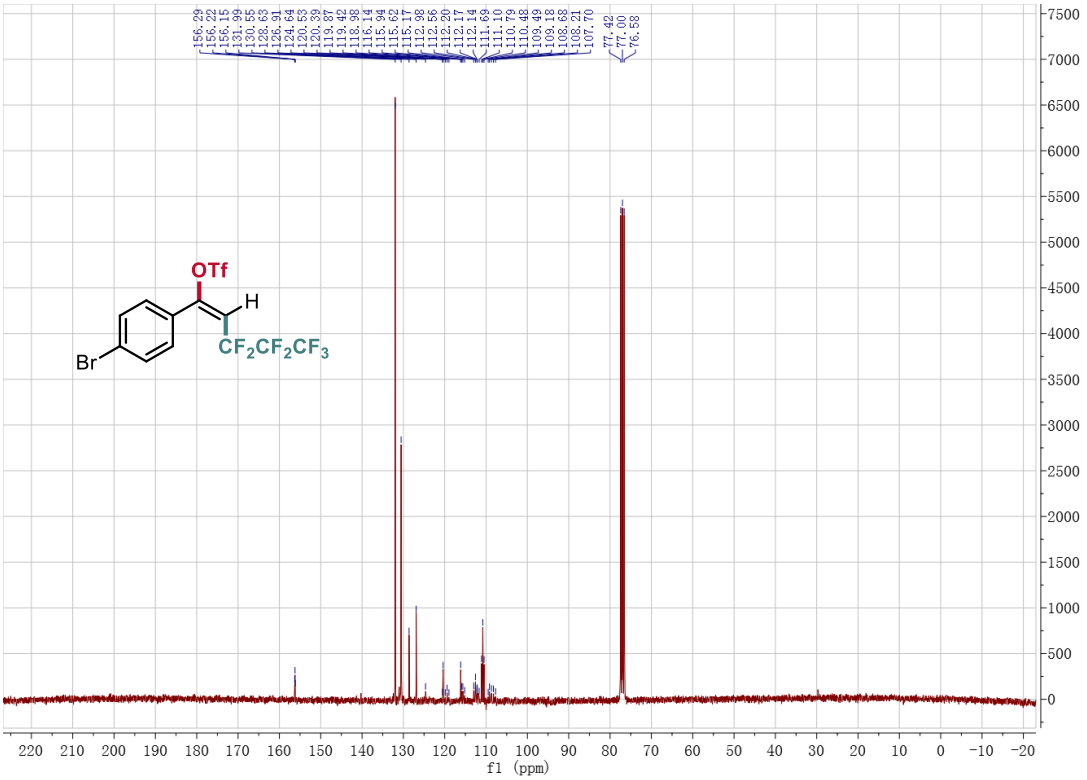
^{19}F NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzenesulfonate 3ac



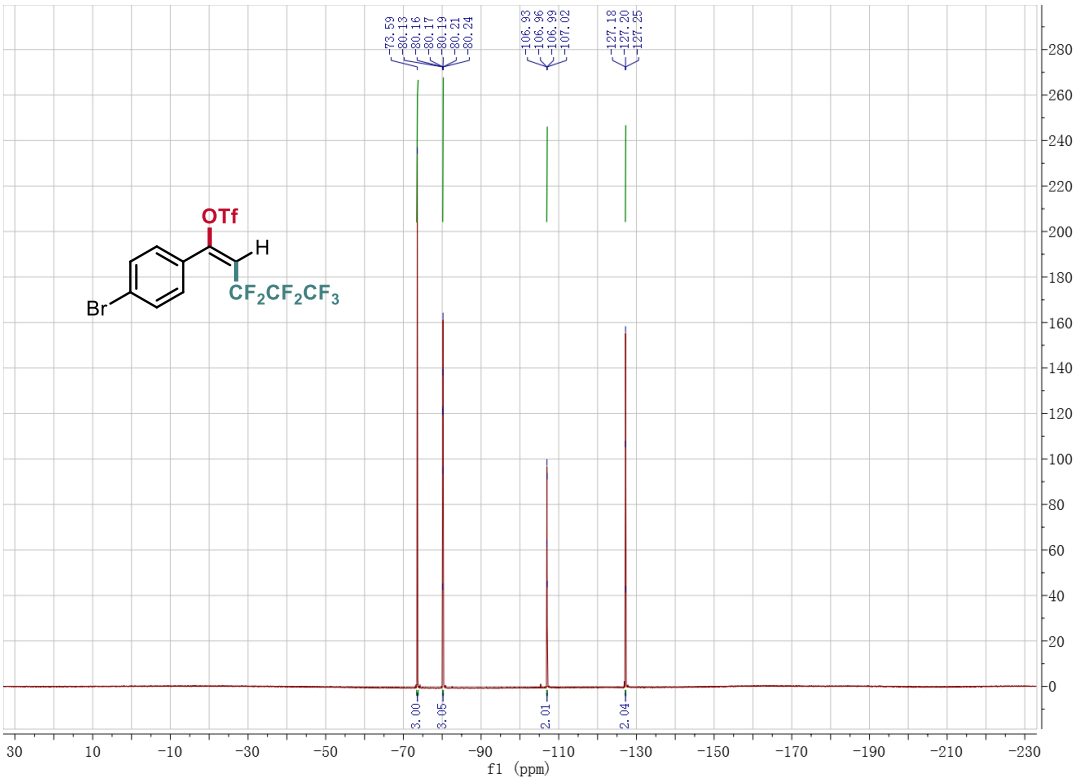
^{1}H NMR Spectrum of (*E*)-1-(4-bromophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ad



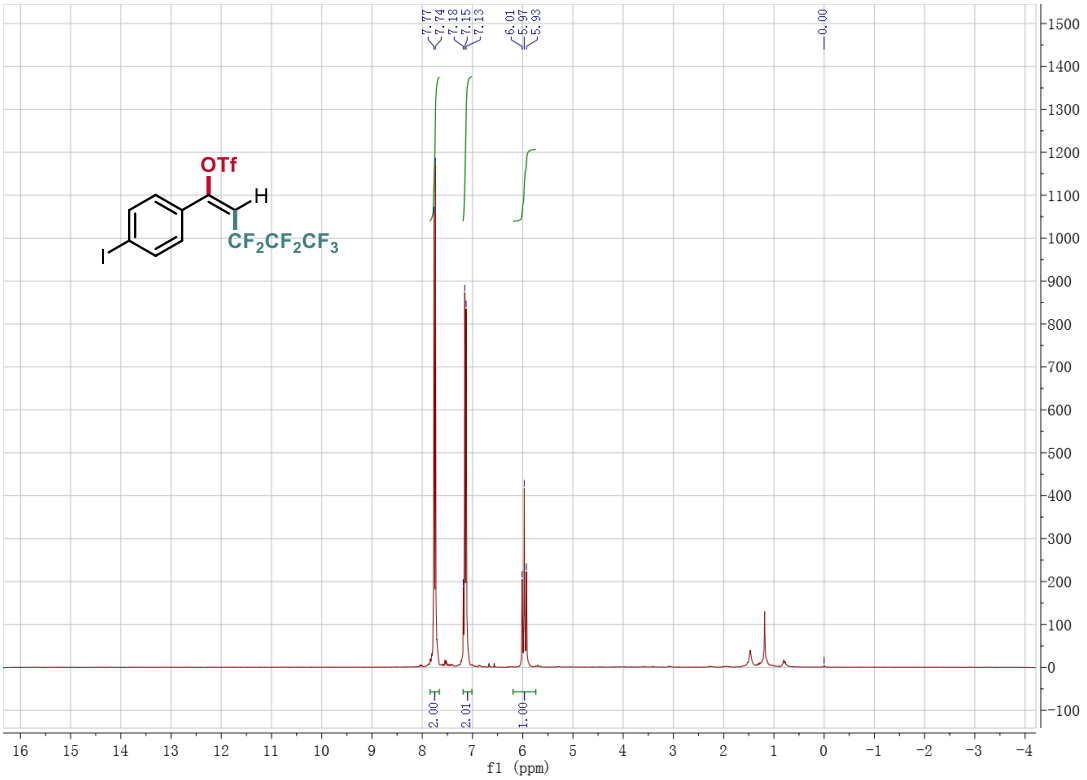
^{13}C NMR Spectrum of (*E*)-1-(4-bromophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ad



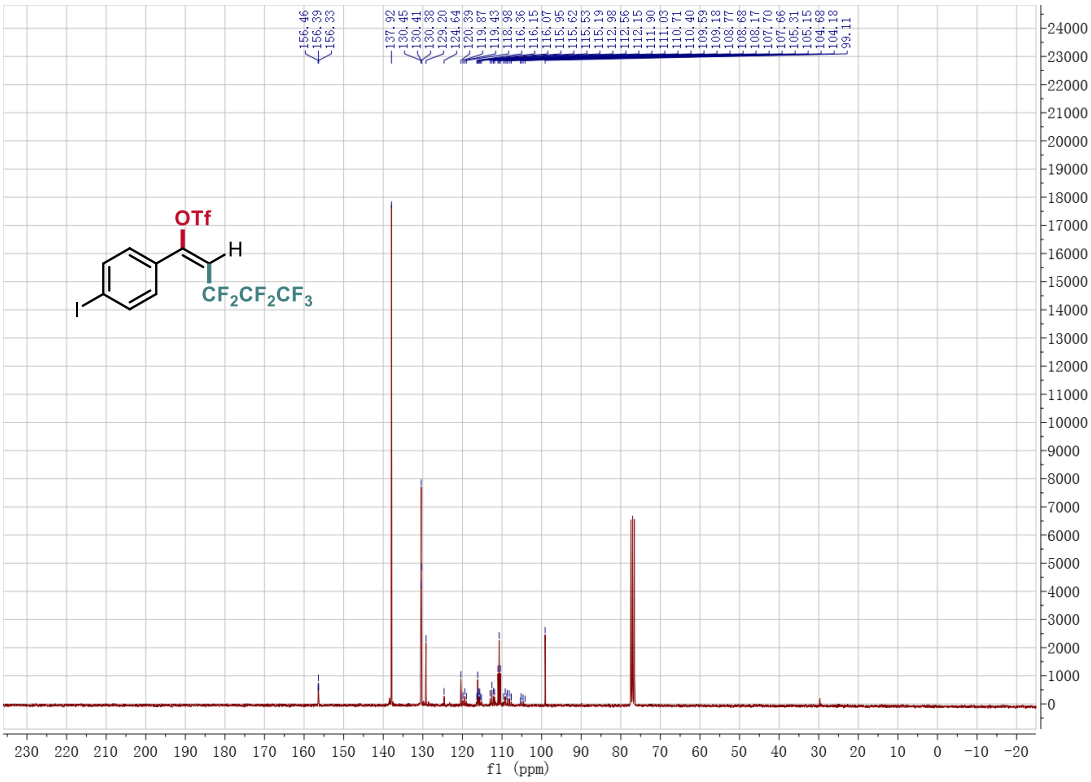
^{19}F NMR Spectrum of (*E*)-1-(4-bromophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ad



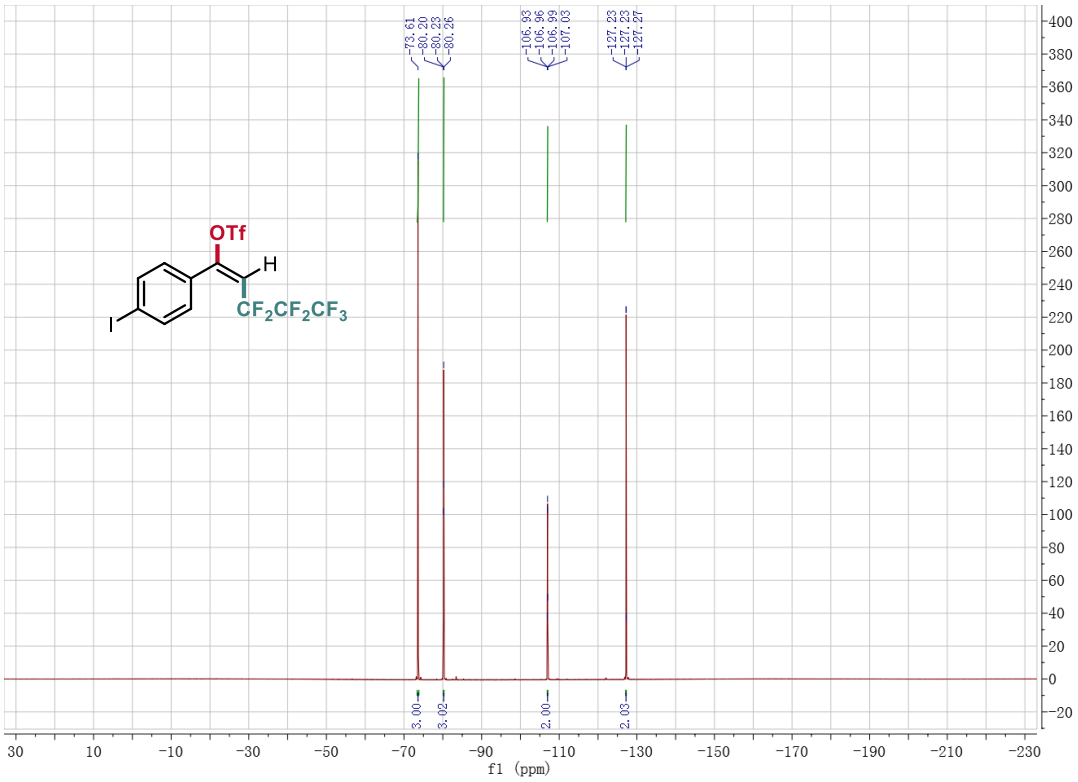
^{1}H NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate 3ae



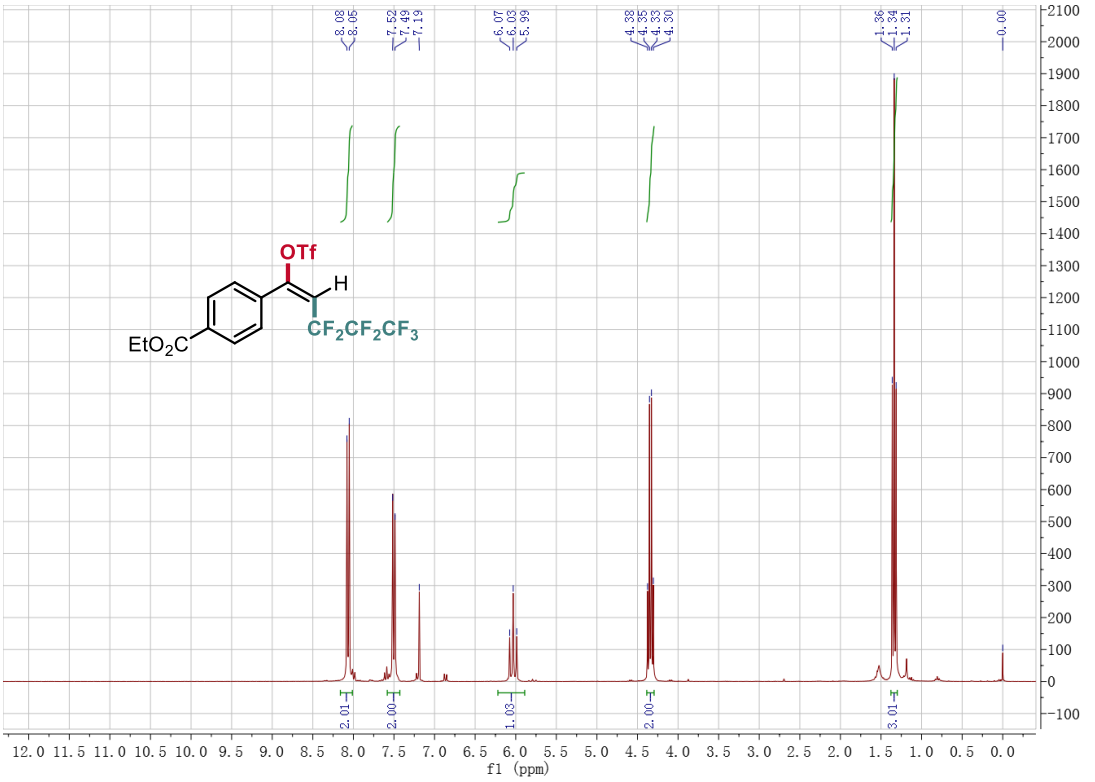
^{13}C NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate 3ae



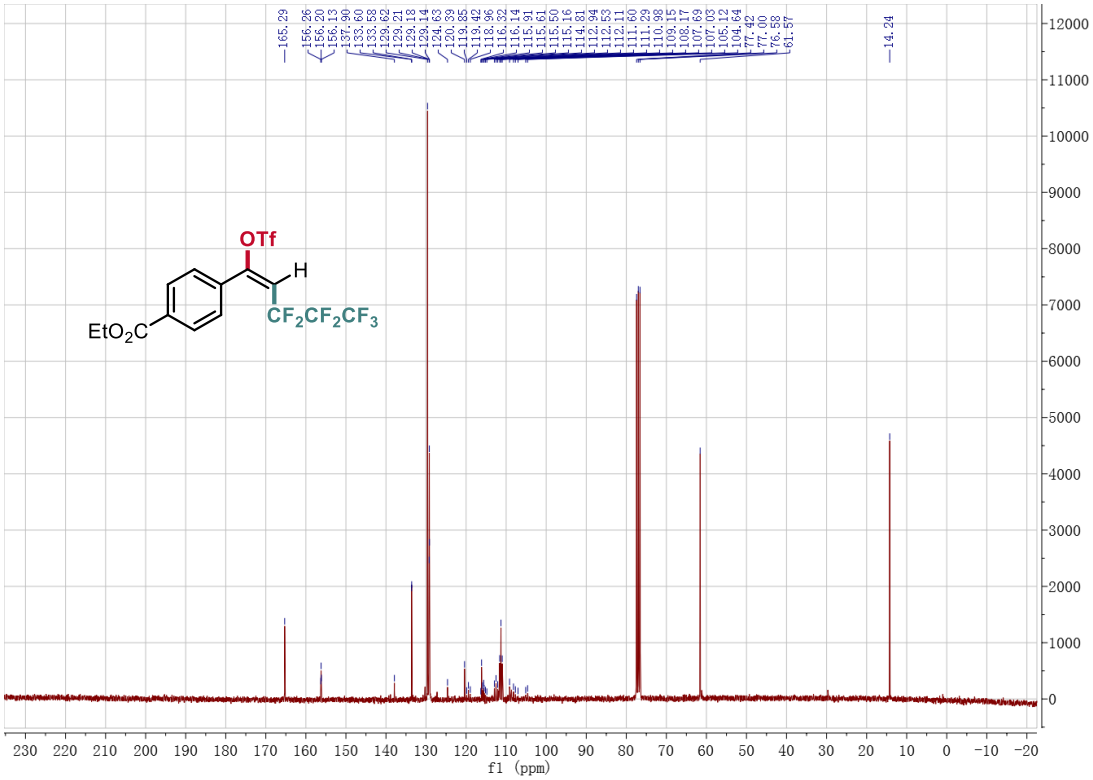
^{19}F NMR Spectrum of (*E*)-3,3,4,4,5,5,5-heptafluoro-1-(4-iodophenyl)pent-1-en-1-yl trifluoromethanesulfonate 3ae



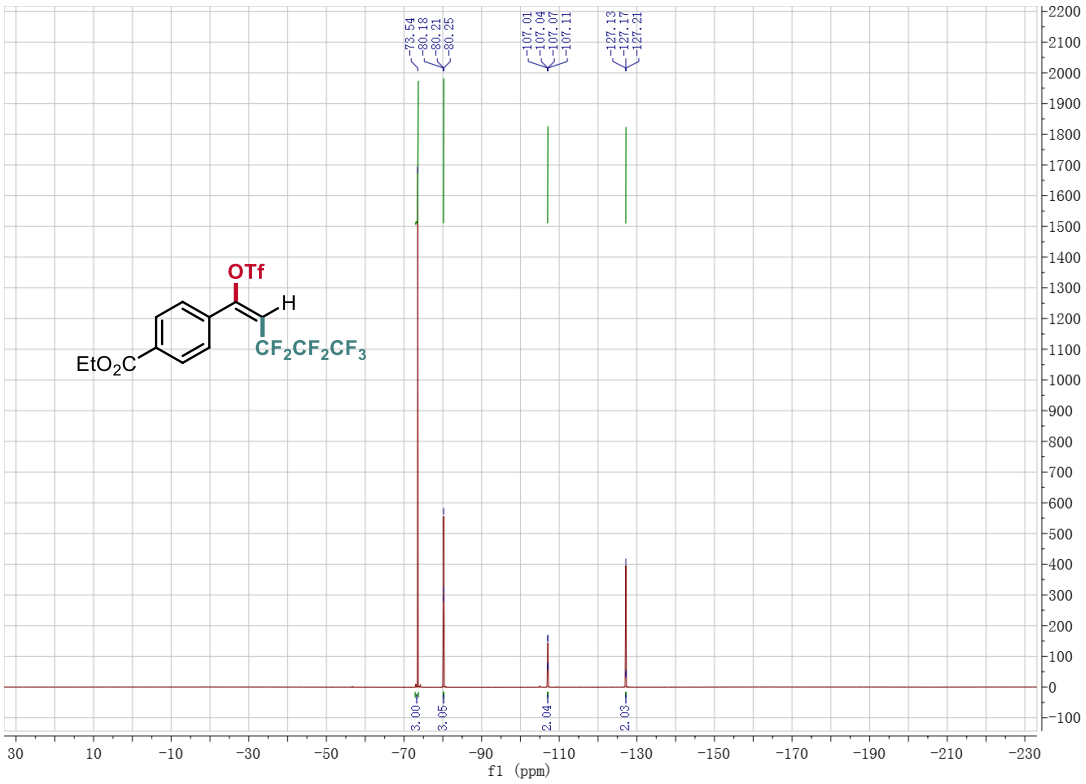
^{1}H NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3af



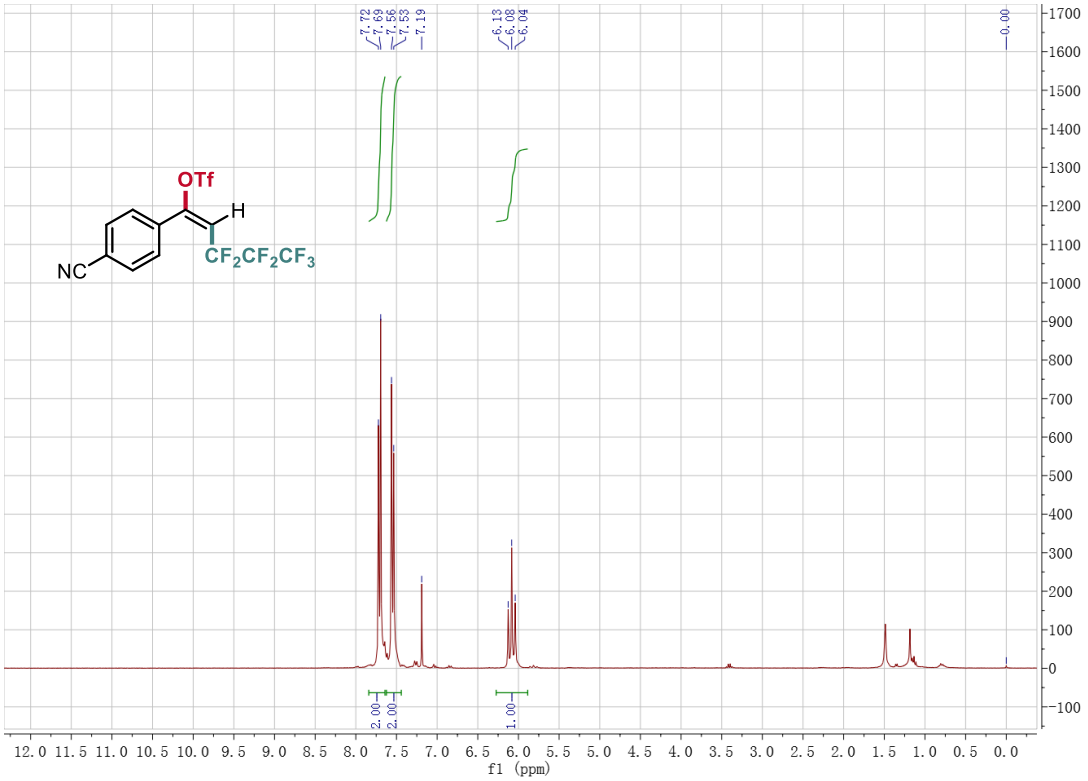
^{13}C NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3af



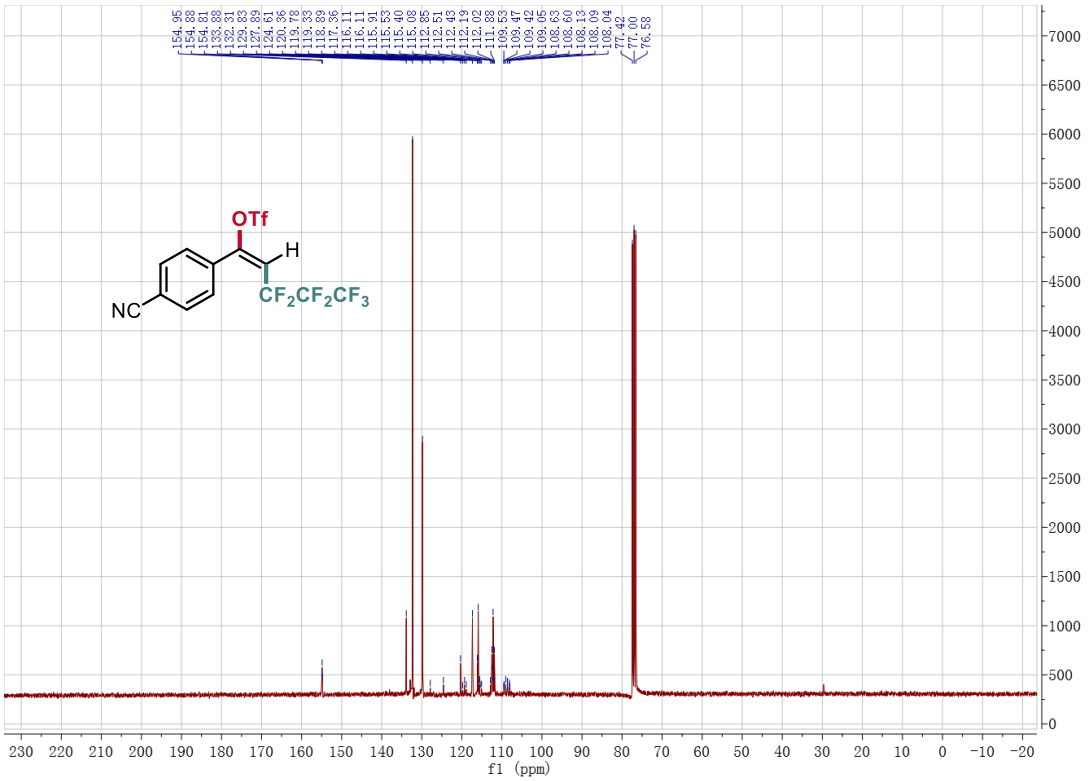
^{19}F NMR Spectrum of Ethyl (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)benzoate 3af



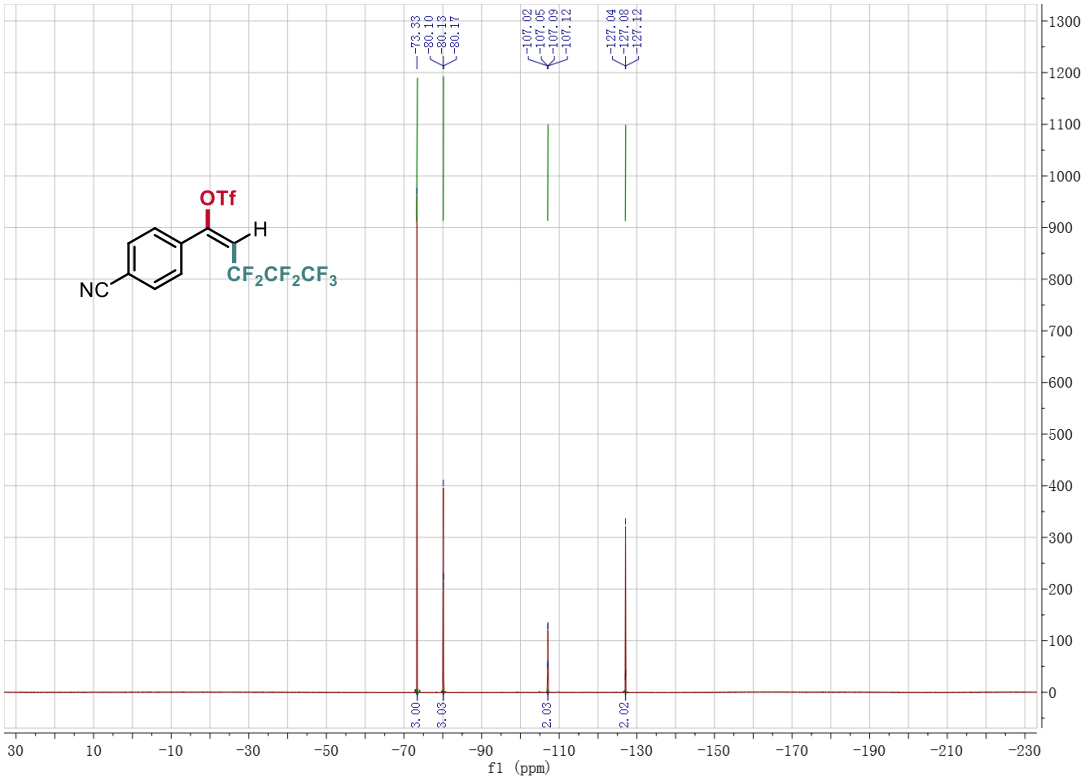
^{1}H NMR Spectrum of (*E*)-1-(4-cyanophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ag



^{13}C NMR Spectrum of (*E*)-1-(4-cyanophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ag

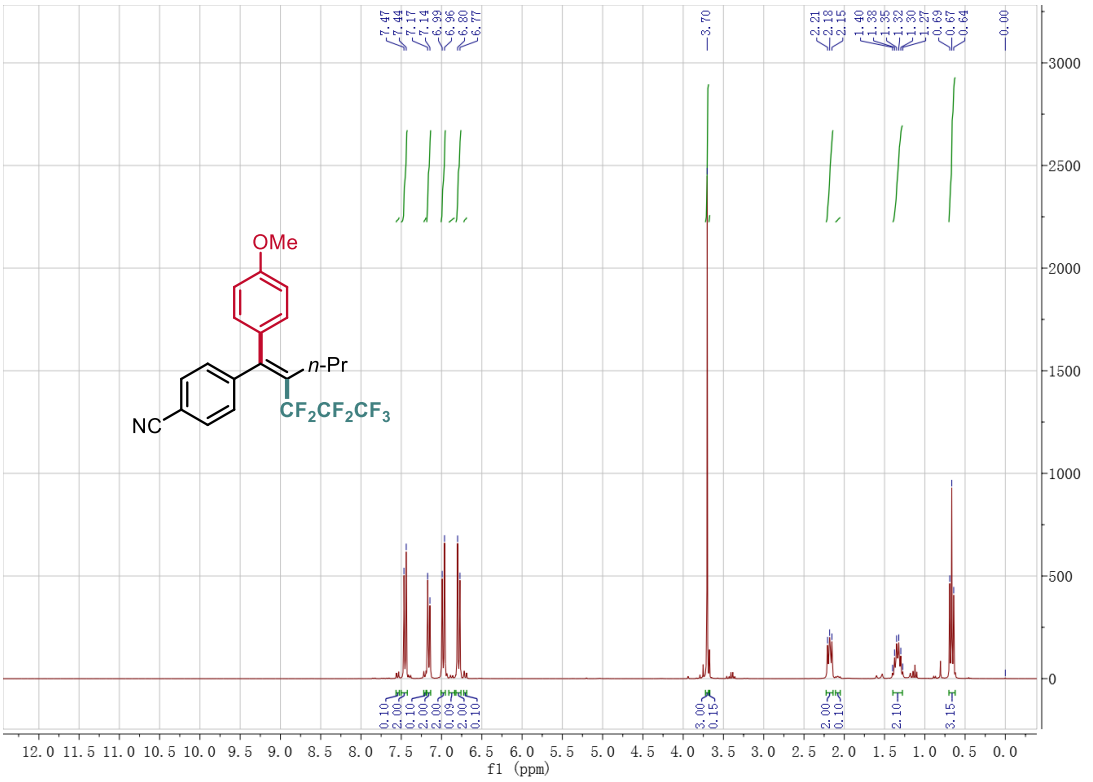


^{19}F NMR Spectrum of (*E*)-1-(4-cyanophenyl)-3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl trifluoromethanesulfonate 3ag

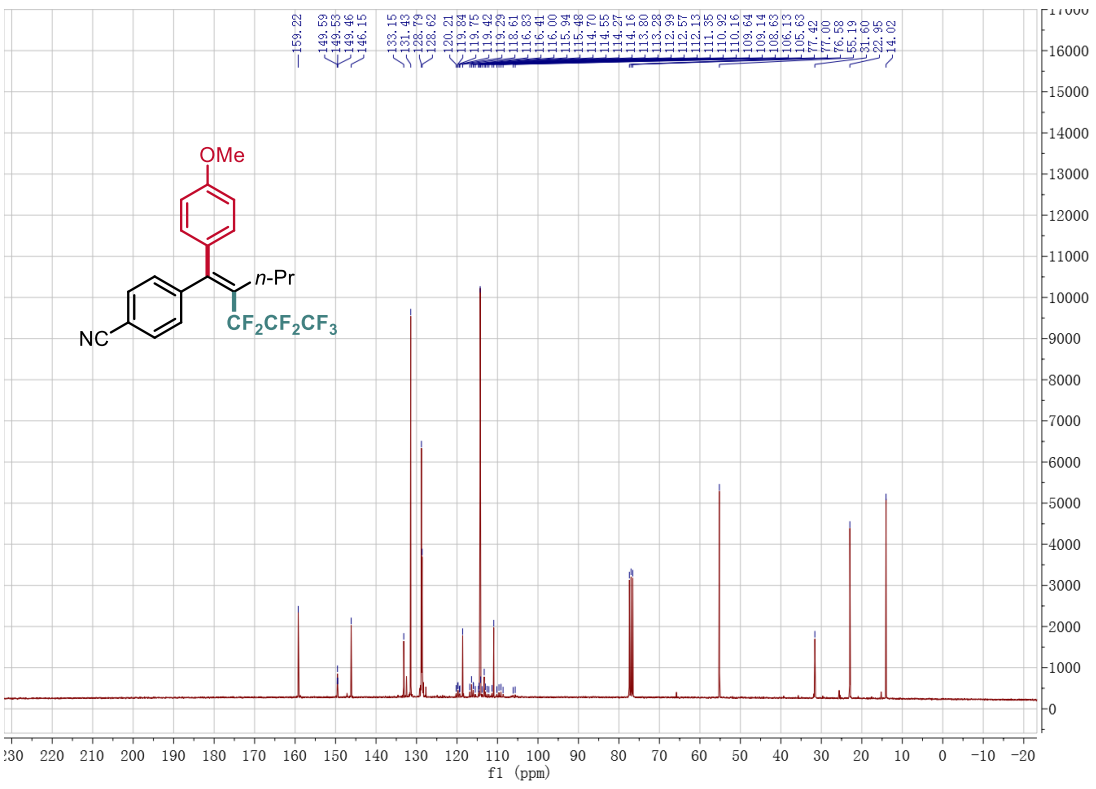


Spectral data of follow-up chemistry products 4, 5, 6, 7

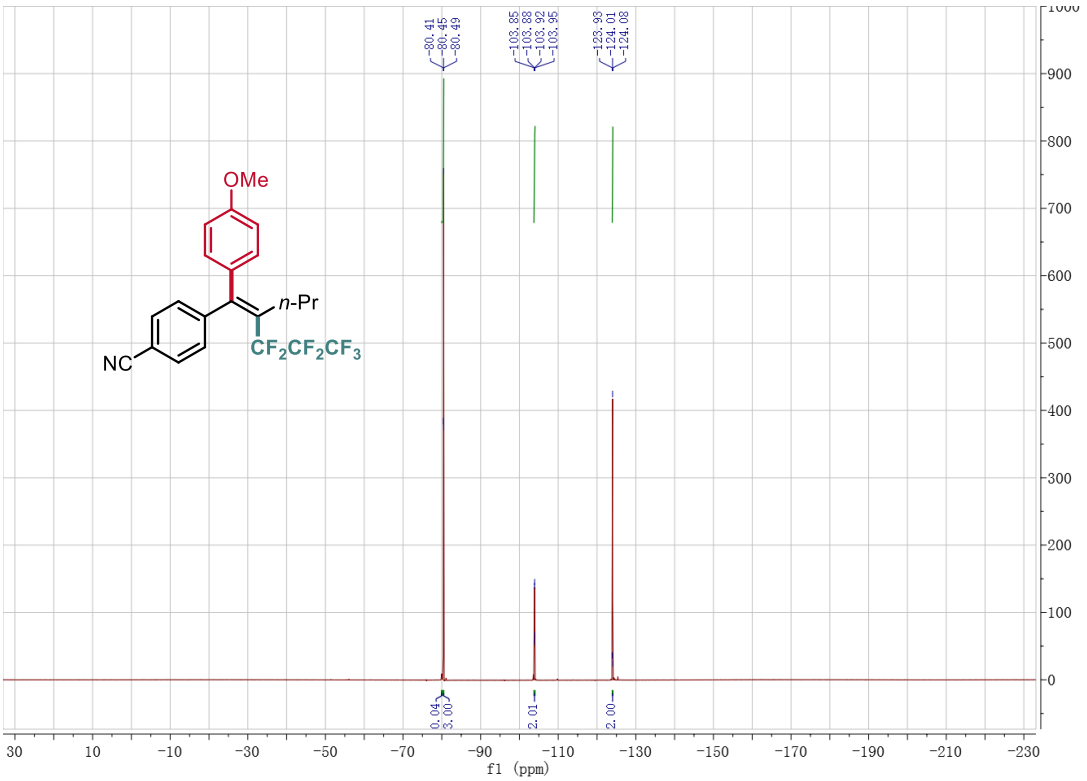
^{1}H NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(4-methoxyphenyl)-2-propylpent-1-en-1-yl)benzonitrile 4



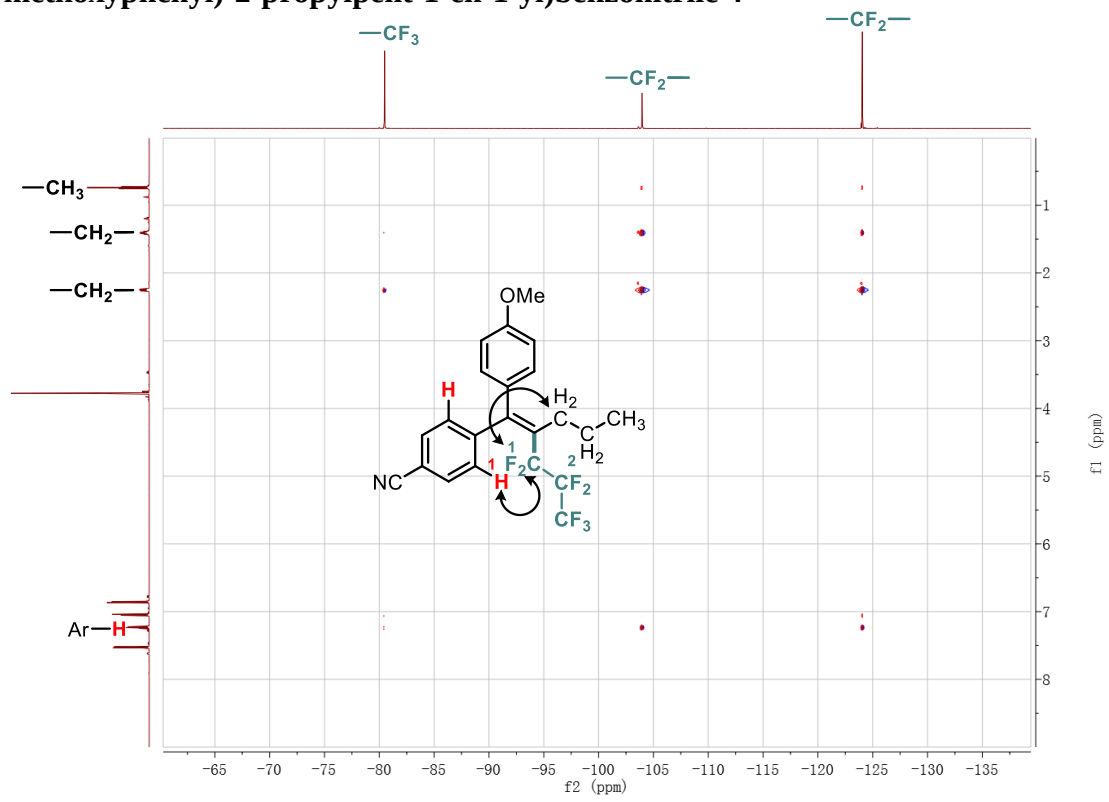
^{13}C NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(4-methoxyphenyl)-2-propylpent-1-en-1-yl)benzonitrile 4



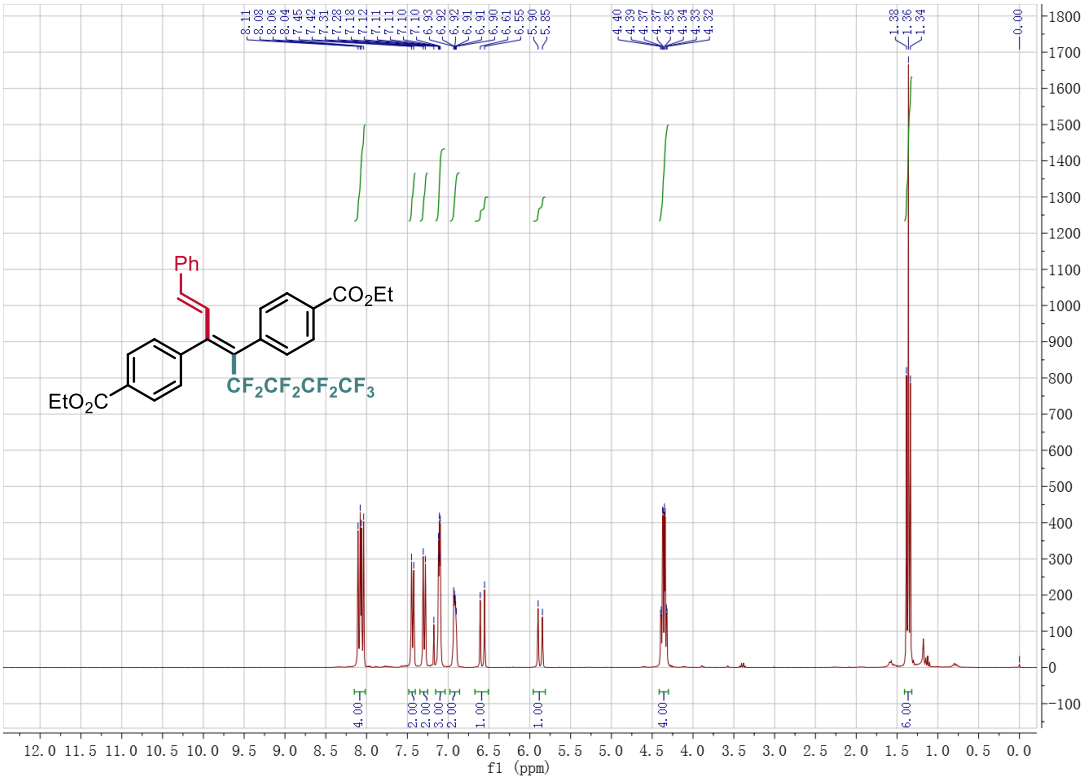
^{19}F NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(4-methoxyphenyl)-2-propylpent-1-en-1-yl)benzonitrile 4



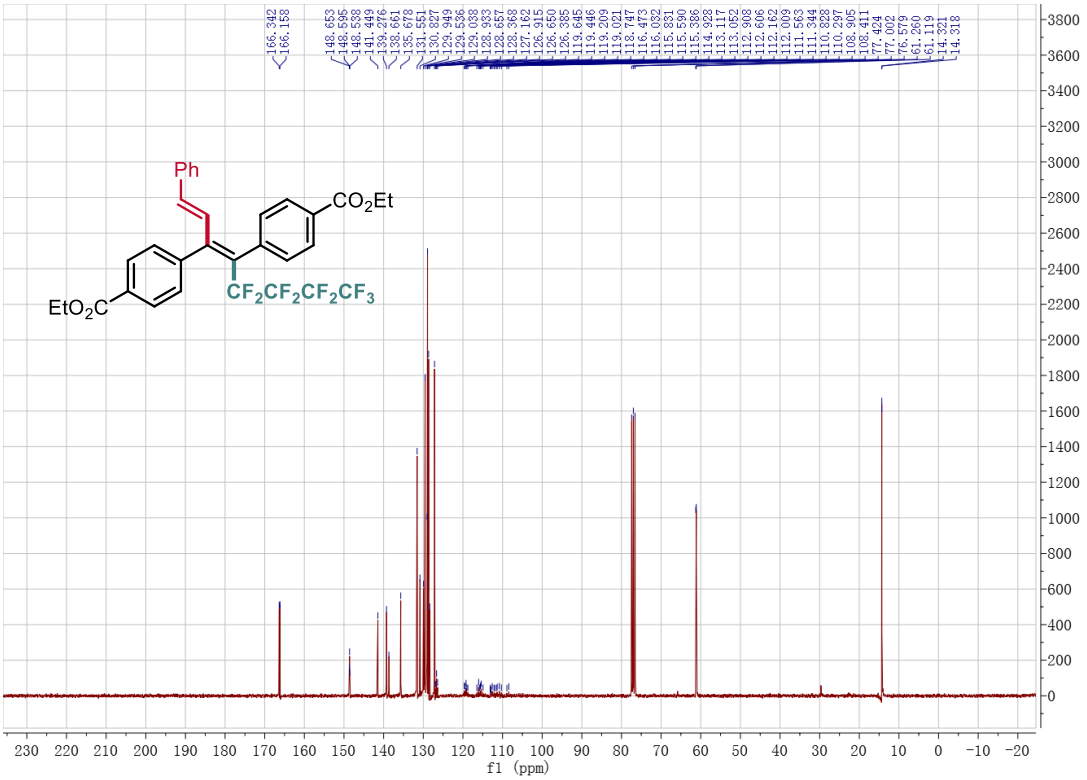
^{19}F-^{1}H HOESY NMR Spectrum of (*E*)-4-(3,3,4,4,5,5,5-heptafluoro-1-(4-methoxyphenyl)-2-propylpent-1-en-1-yl)benzonitrile 4



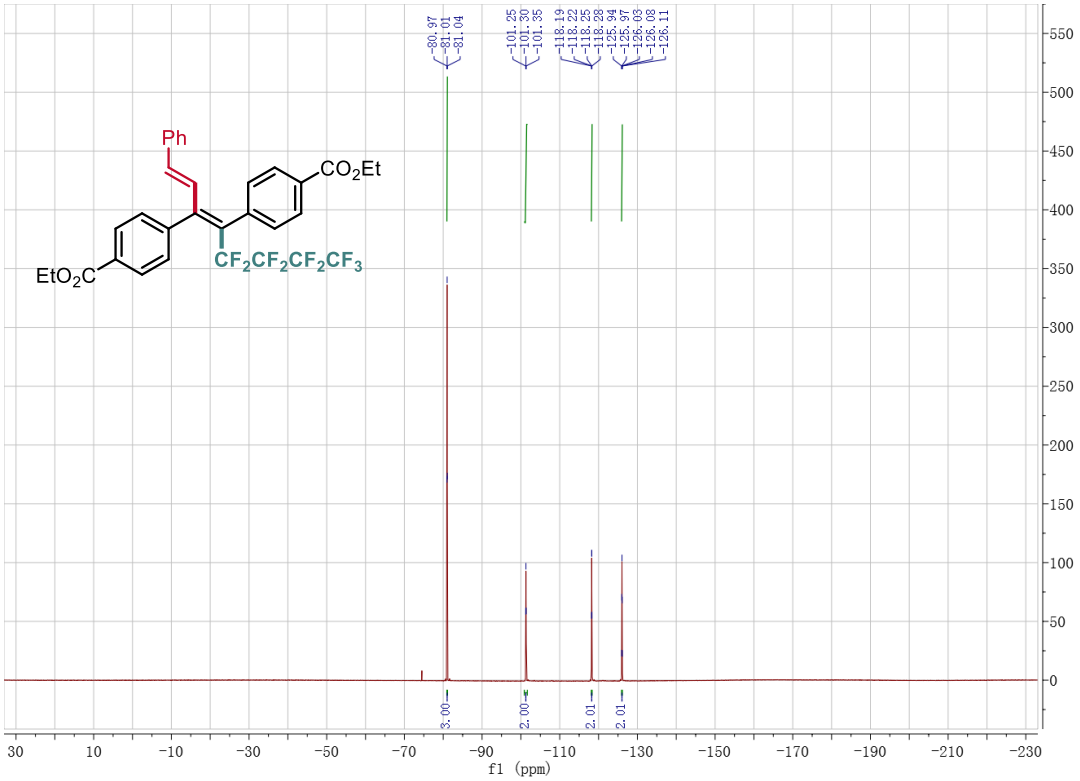
^{1}H NMR Spectrum of Diethyl 4,4'-((1*E*,3*Z*)-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenylocta-1,3-diene-3,4-diyl)dibenzoate 5



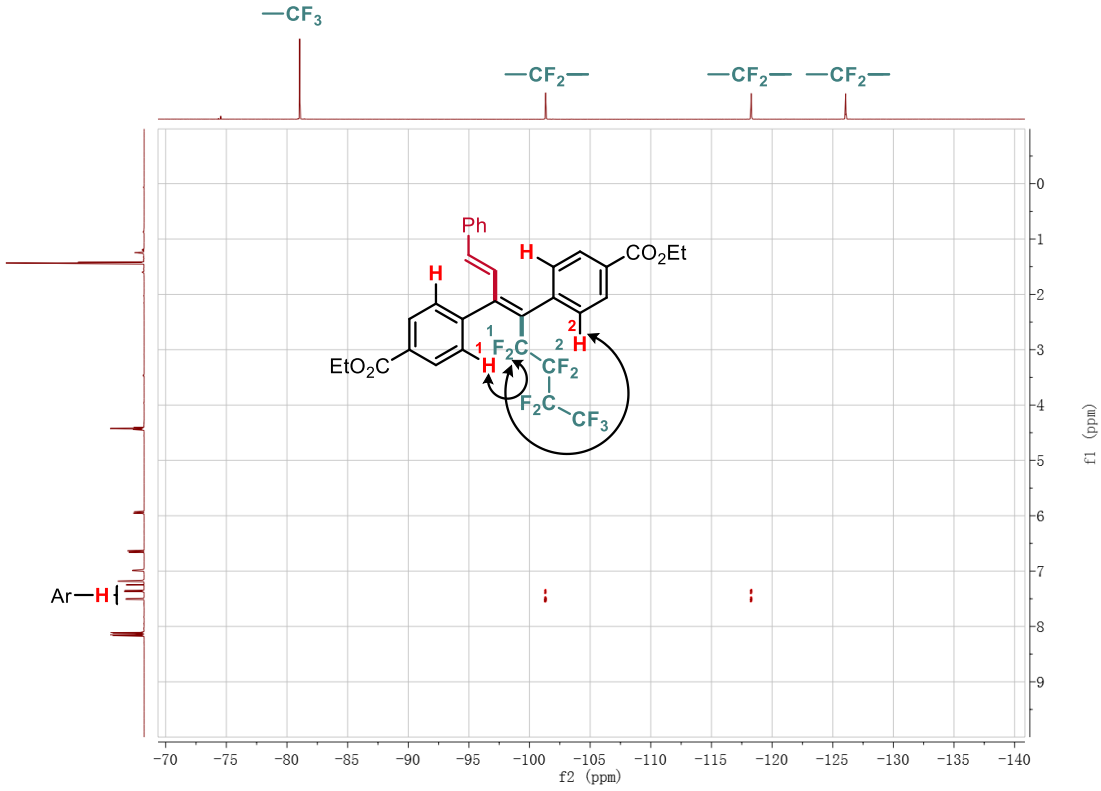
^{13}C NMR Spectrum of Diethyl 4,4'-((1*E*,3*Z*)-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenylocta-1,3-diene-3,4-diyl)dibenzoate 5



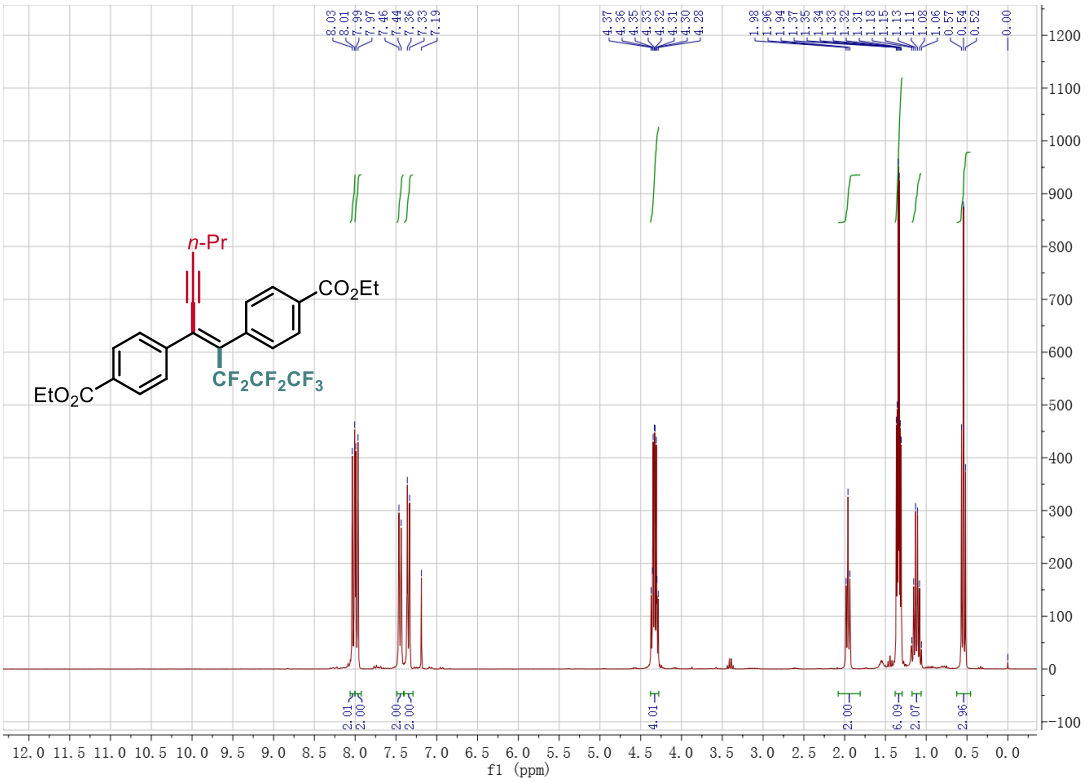
^{19}F NMR Spectrum of Diethyl 4,4'-((1*E*,3*Z*)-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenylocta-1,3-diene-3,4-diyl)dibenzoate 5



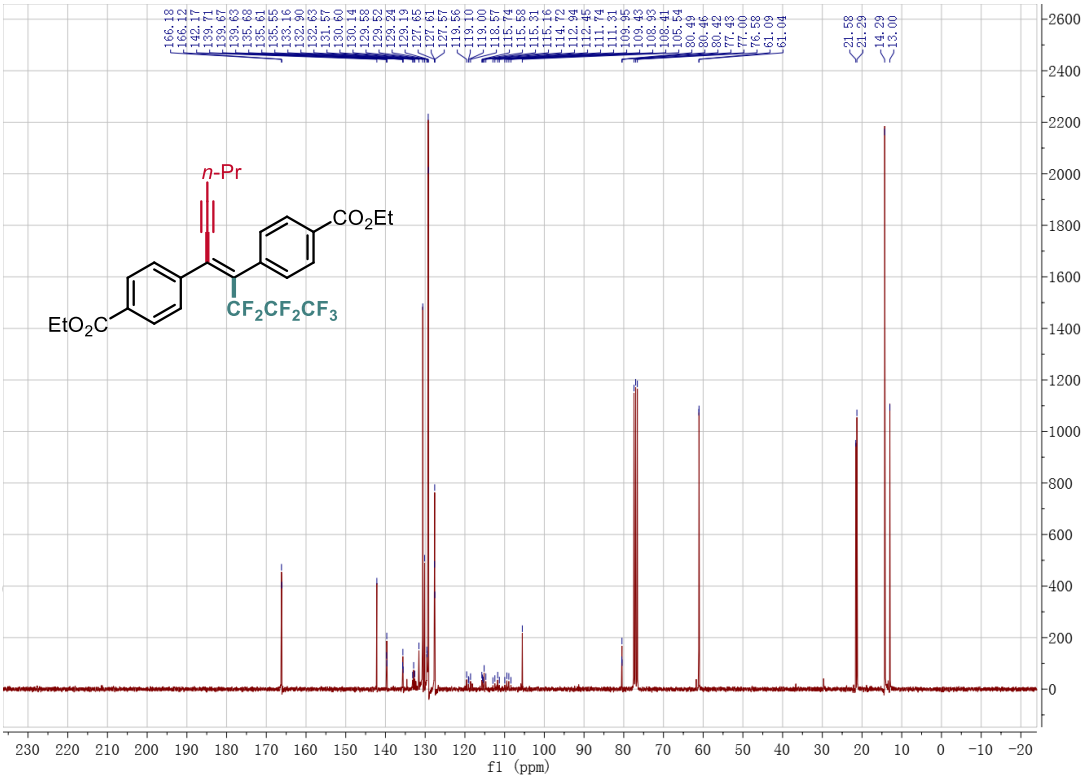
^{19}F-^{1}H HOESY NMR Spectrum of Diethyl 4,4'-((1*E*,3*Z*)-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenylocta-1,3-diene-3,4-diyl)dibenzoate 5



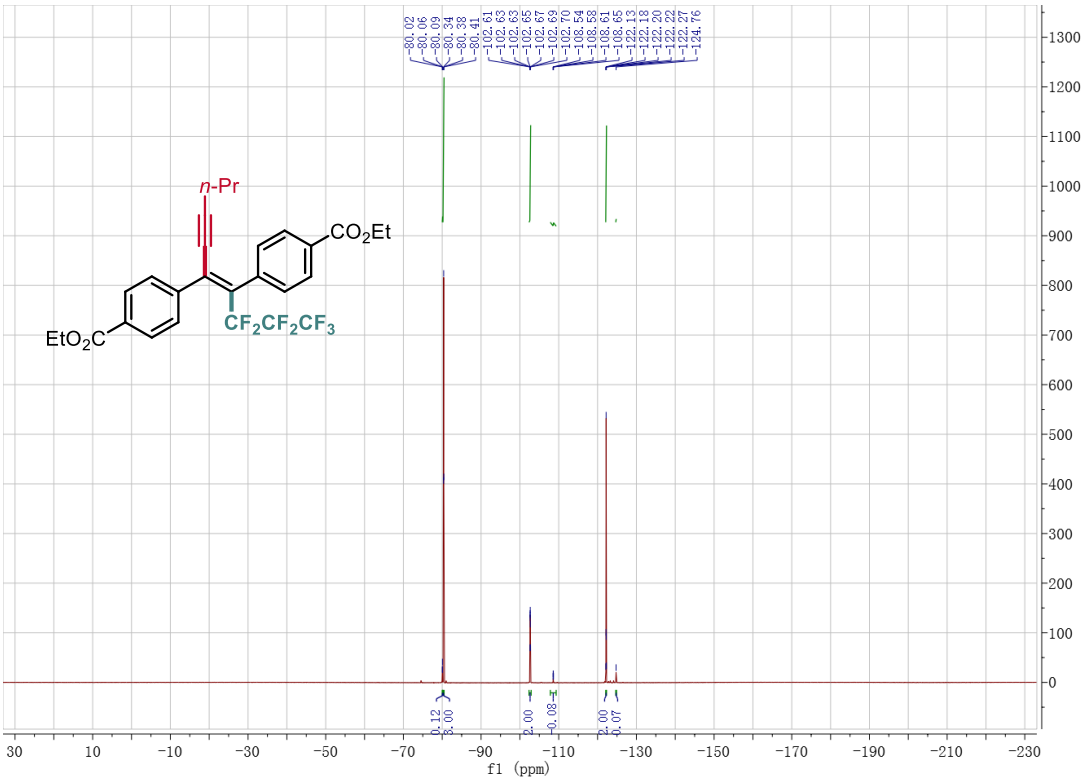
^{1}H NMR Spectrum of Diethyl 4,4'-(1,1,1,2,2,3,3-heptafluorodec-4-en-6-yne-4,5-diyl)(*E*)-dibenzoate 6



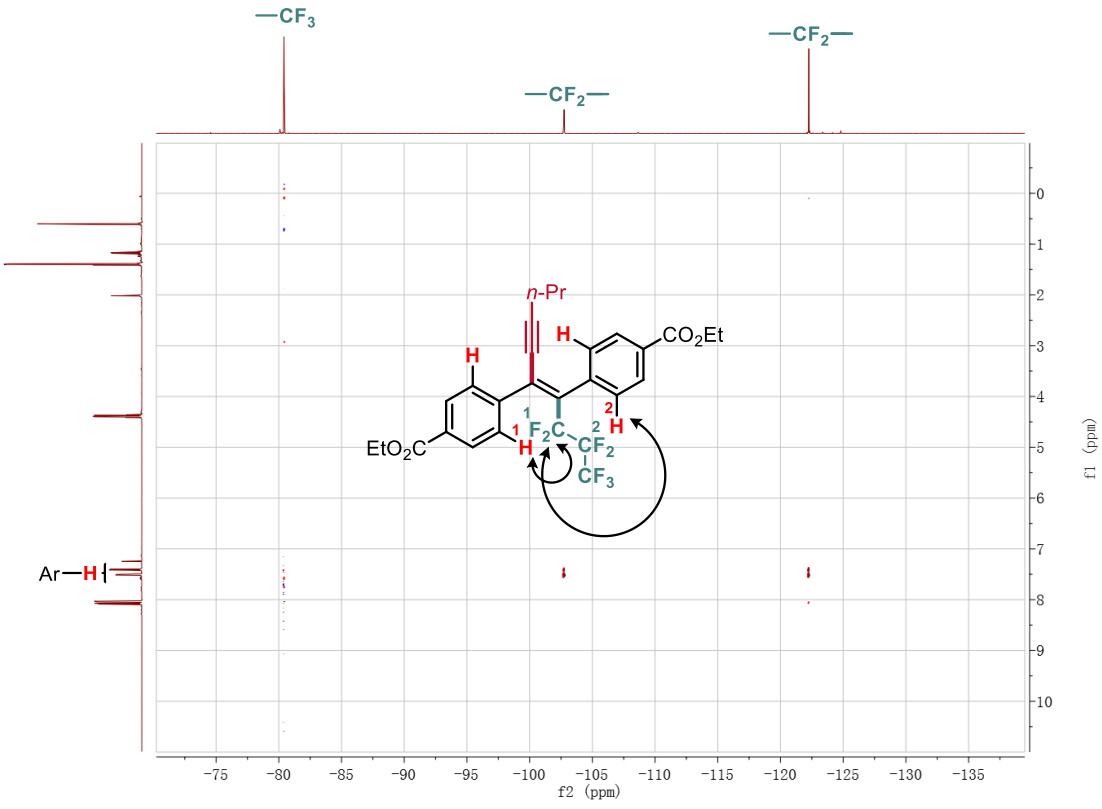
^{13}C NMR Spectrum of Diethyl 4,4'-(1,1,1,2,2,3,3-heptafluorodec-4-en-6-yne-4,5-diyl)(*E*)-dibenzoate 6



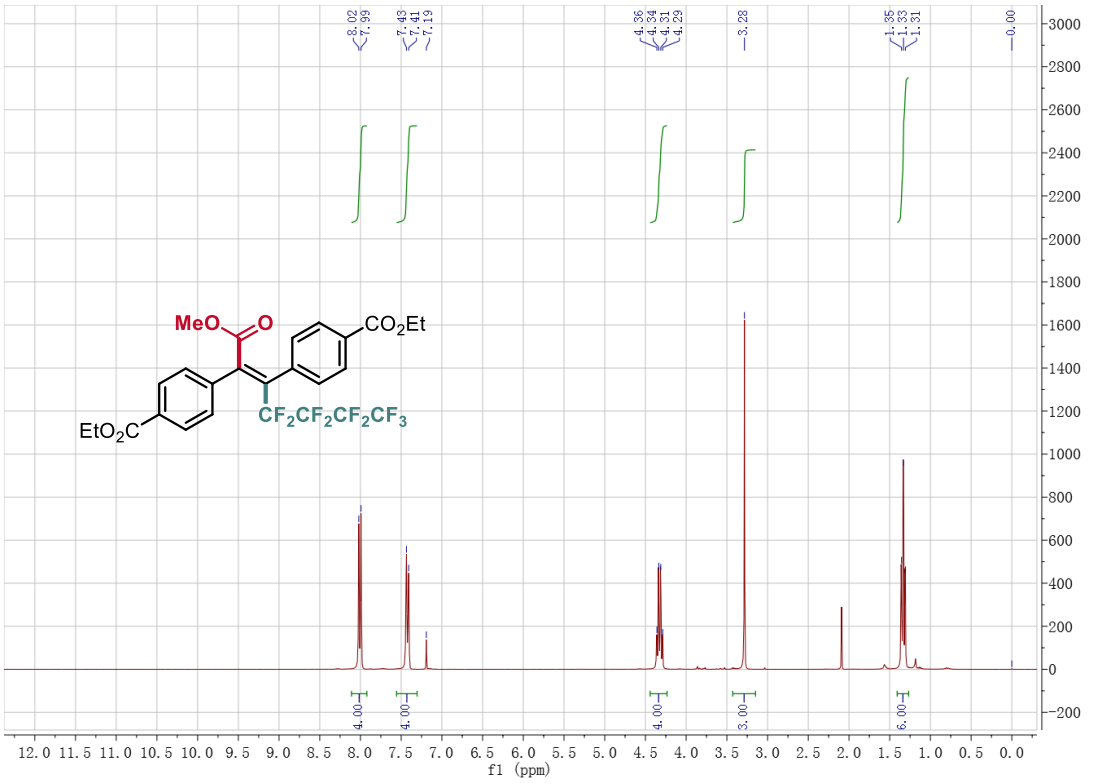
^{19}F NMR Spectrum of Diethyl 4,4'-(1,1,1,2,2,3,3-heptafluorodec-4-en-6-yne-4,5-diyl)(*E*)-dibenzoate 6



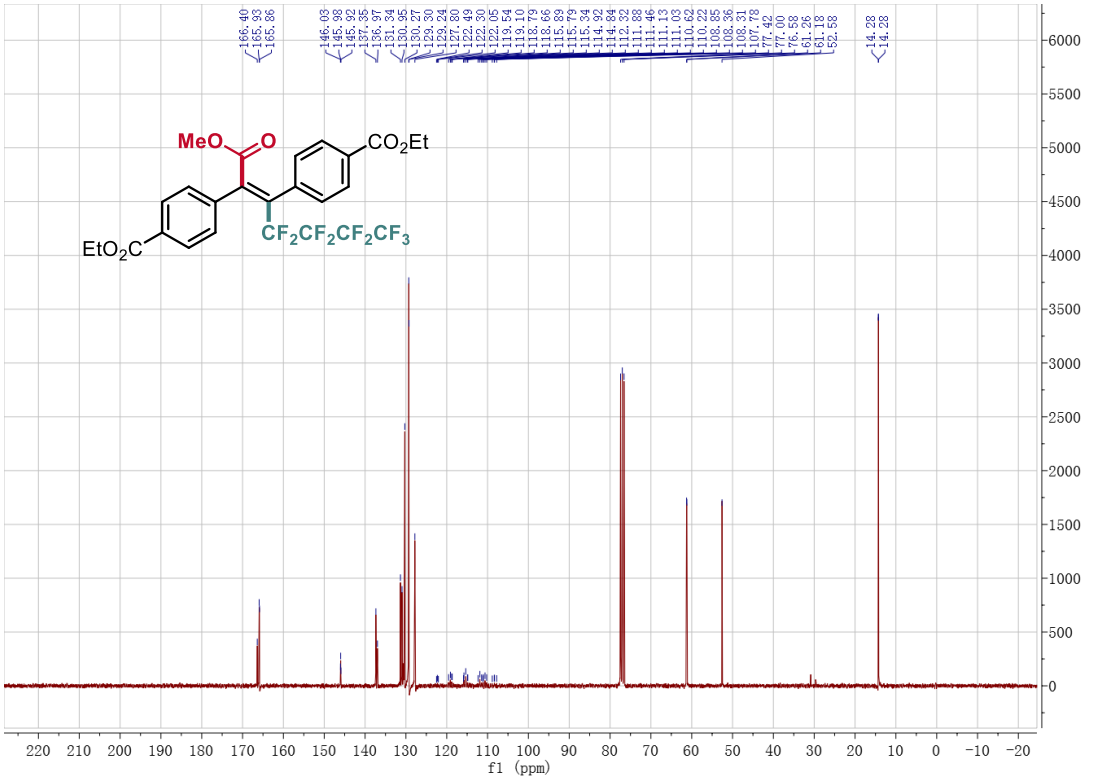
^{19}F-^{1}H HOESY NMR Spectrum of Diethyl 4,4'-(1,1,1,2,2,3,3-heptafluorodec-4-en-6-yne-4,5-diyl)(*E*)-dibenzoate 6



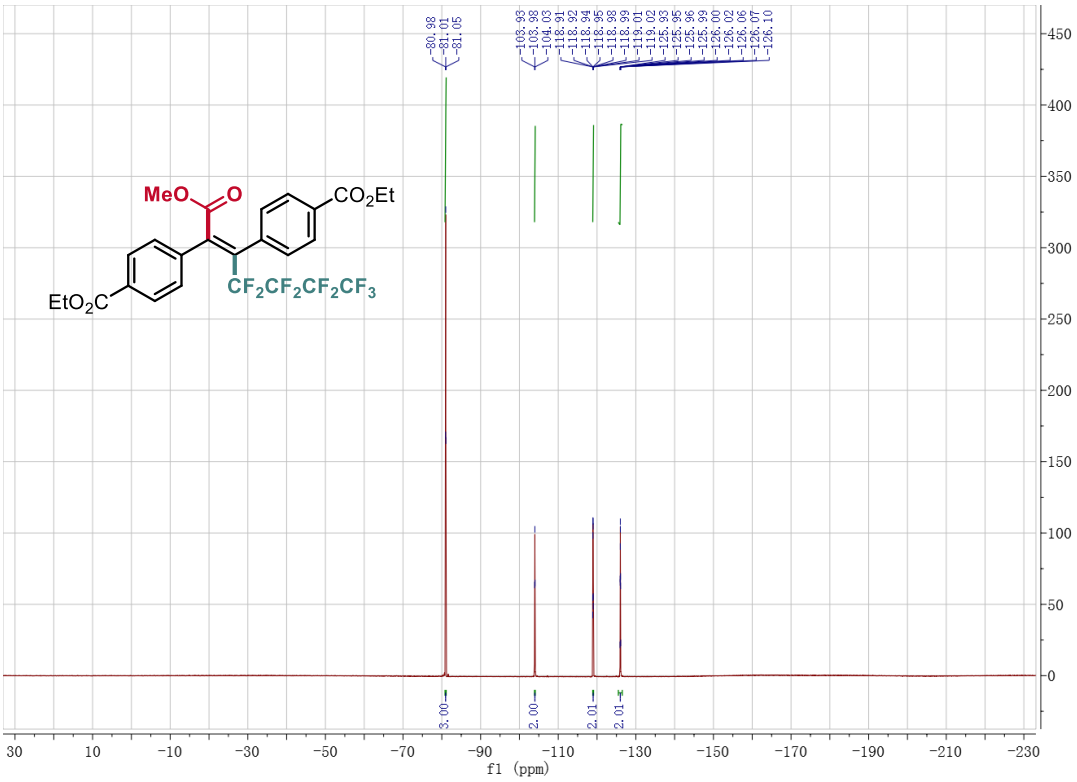
^{1}H NMR Spectrum of Diethyl 4,4'-(4,4,5,5,6,6,7,7,7-nonafluoro-1-methoxy-1-oxohept-2-ene-2,3-diyl)(*E*)-dibenzoate 7



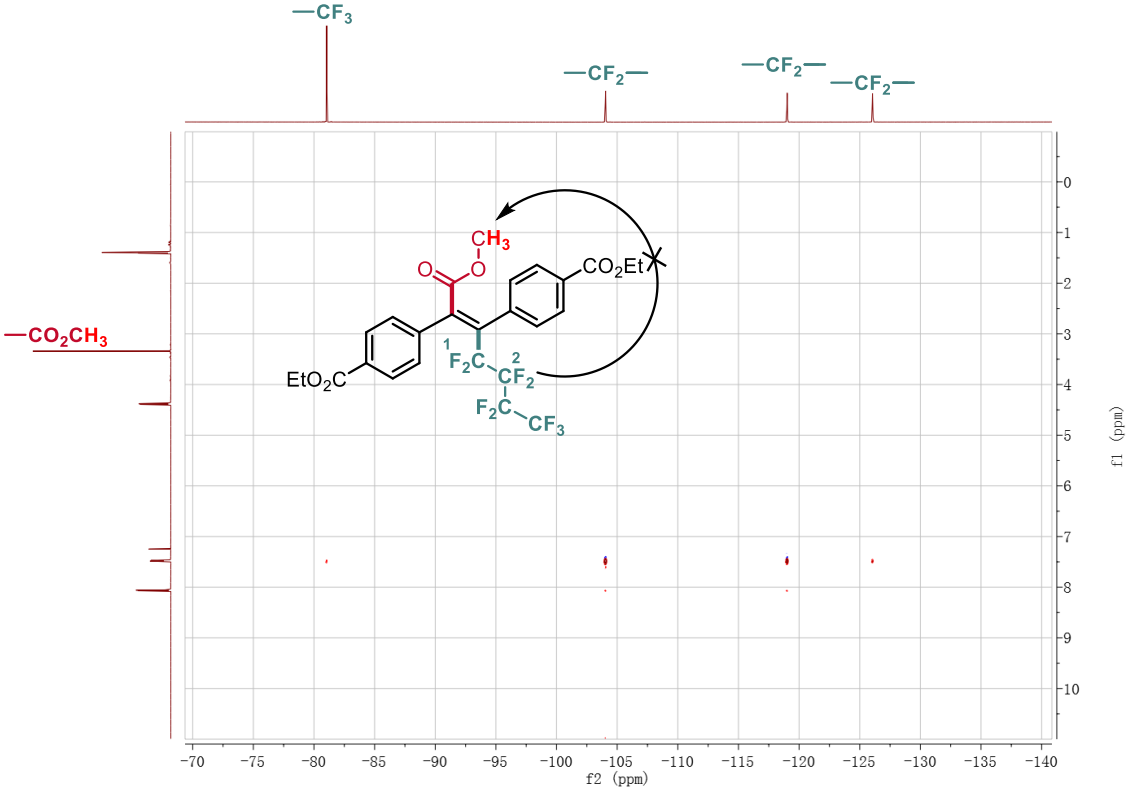
^{13}C NMR Spectrum of Diethyl 4,4'-(4,4,5,5,6,6,7,7,7-nonafluoro-1-methoxy-1-oxohept-2-ene-2,3-diyl)(*E*)-dibenzoate 7



^{19}F NMR Spectrum of Diethyl 4,4'-(4,4,5,5,6,6,7,7,7-nonafluoro-1-methoxy-1-oxohept-2-ene-2,3-diyl)(*E*)-dibenzoate 7

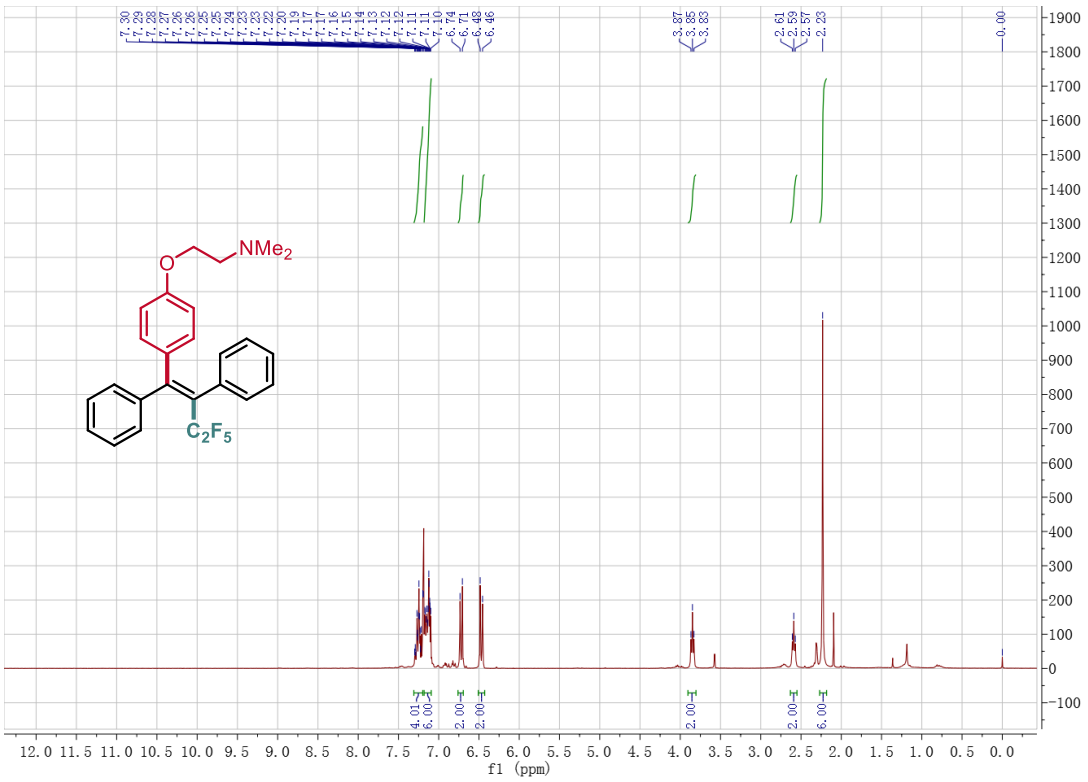


^{19}F-^{1}H HOESY NMR Spectrum of Diethyl 4,4'-(4,4,5,5,6,6,7,7,7-nonafluoro-1-methoxy-1-oxohept-2-ene-2,3-diyl)(*E*)-dibenzoate 7

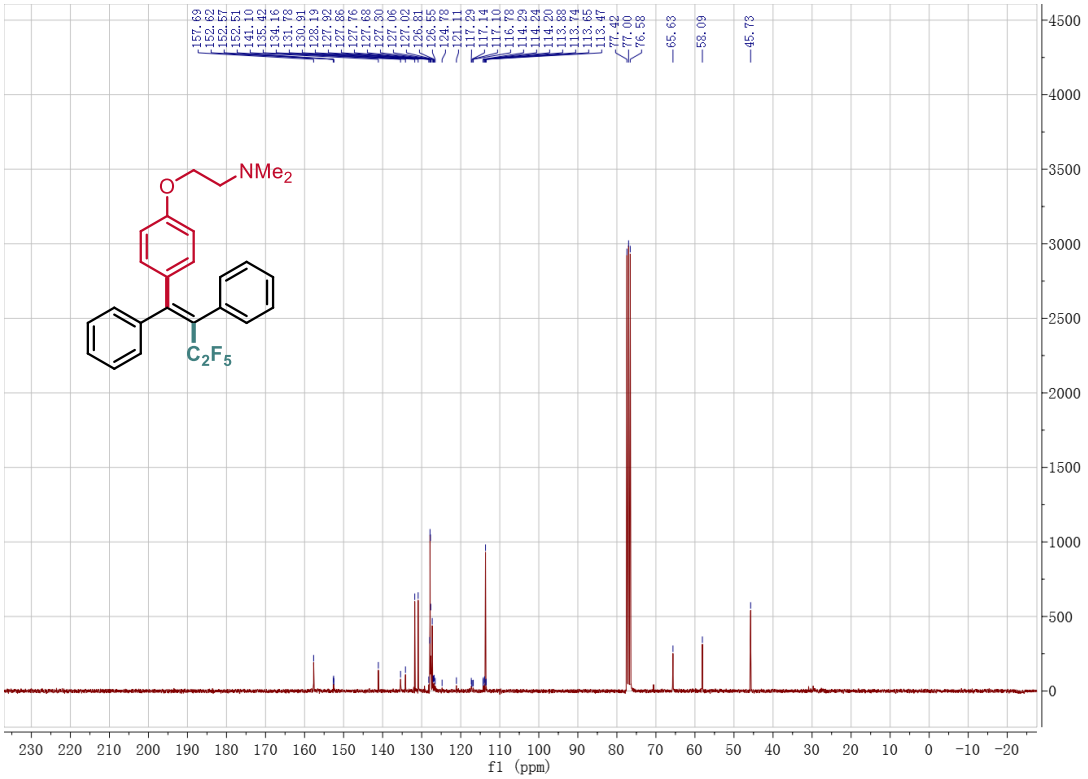


Spectra of Pentafluorinated-Tamoxifen 8

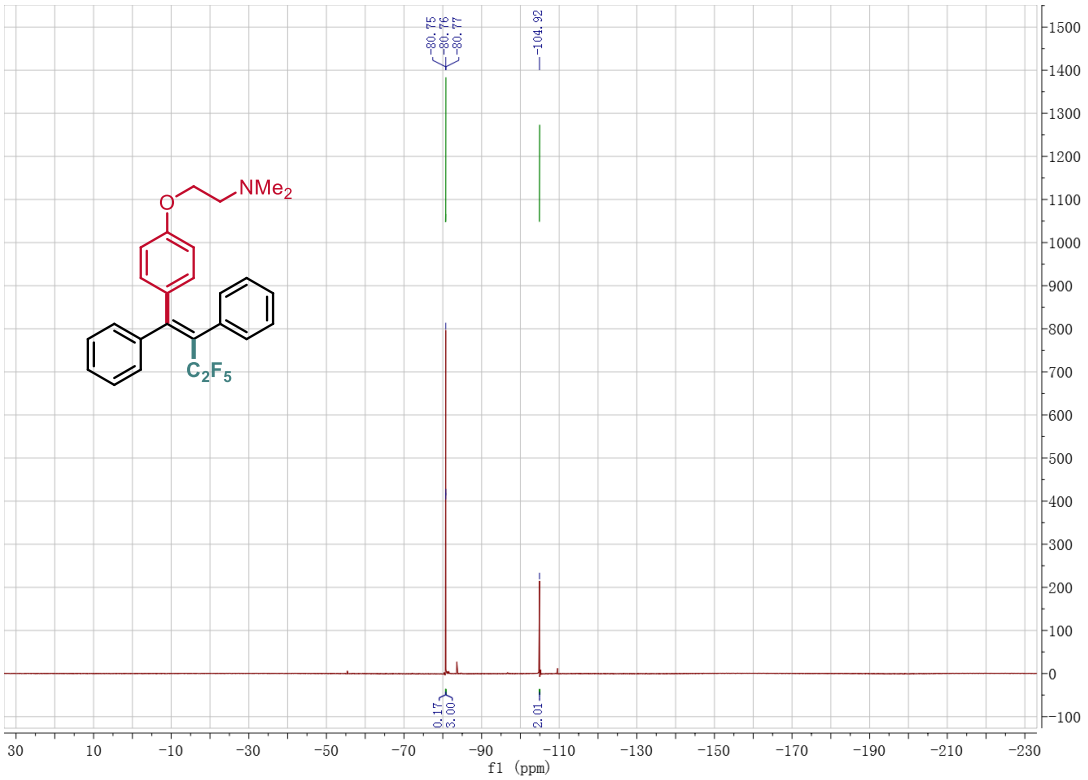
^{1}H NMR Spectrum of (*E*)-*N*,*N*-dimethyl-2-(4-(3,3,4,4,4-pentafluoro-1,2-diphenyl but-1-en-1-yl)phenoxy)ethan-1-amine 8



^{13}C NMR Spectrum of (E)-N,N-dimethyl-2-(4-(3,3,4,4,4-pentafluoro-1,2-diphenyl but-1-en-1-yl)phenoxy)ethan-1-amine 8



^{19}F NMR Spectrum of (E)-N,N-dimethyl-2-(4-(3,3,4,4,4-pentafluoro-1,2-diphenyl but-1-en-1-yl)phenoxy)ethan-1-amine 8



8. References

[1] Umemoto, T.; Kuriu, Y.; Shuyama, H.; Miyano, O.; Nakayama, S.-I. *J. Fluorine. Chem*, **1982**, *20*, 695–698.

[2] Ichitsuka, T.; Fujita, T.; Ichikawa, J. *ACS Catal*. **2015**, *5*, 5947−5950.

[3] Chu, Y.-T.; Chanda, K.; Lin, P.-H.; Huang, M. H. *Langmuir*, **2012**, *28*, 11258–11264.

[4] Gallagher, W. P.; Maleczka, Jr. R. E. *J. Org. Chem*. **2003**, *68*, 6775–6779.

[5] Wang, X.; Studer, A. *J. Am. Chem. Soc*. **2016**, *138*, 2977–2980.

[6] Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc*. **2010**, *132*, 9585–9587.

[7] Jiang, T.; Quan, X.; Zhu, C.; Andersson, P. G.; Bäckvall, J.-E. *Angew. Chem. Int. Ed*. **2016**, *55*, 5824 –5828.

[8] Flipo, M.; Charton, J.; Hocine, A.; Dassonneville, S.; Deprez, B.; Deprez-Poulain, R. *J. Med. Chem*. **2009**, *52*, 6790–6802.

[9] Liu, J.; Xie, X.; Ma, S. *Synthesis* **2012**, *44*, 1569–1576.

[10] Mo, F.; Lim, N.; Dong, G. *J. Am. Chem. Soc*. **2015**, *137*, 15518−15527.

[11] Woźniak, Ł.; Staszewska-Krajewska, O.; Michalak, M. *Chem. Commun*. **2015**, *51*, 1933−1936.

[12] Aakerçy, C. B.; Baldrighi, M.; Desper, J.; Metrangolo, P.; Resnati, G. *Chem. Eur. J*. **2013**, *19*, 16240–16247.

[13] Liu, T.-F.; Feng, D.; Chen, Y.-P.; Zou, L.; Bosch, M.; Yuan, S.; Wei, Z.; Fordham, S.; Wang, K.; Zhou, H.-C.

[14] Zhou, C.; Larock, R. C. *J. Org. Chem*. **2005**, *70*, 3765–3777.