Supporting Information

Photoredox /Copper-Catalyzed

gem-Difluoroalkylation-Cyanation of 1,3-Enynes

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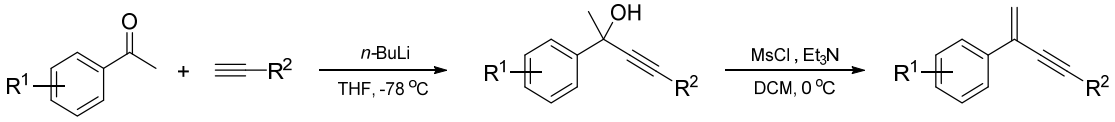
Contents

1. General Information

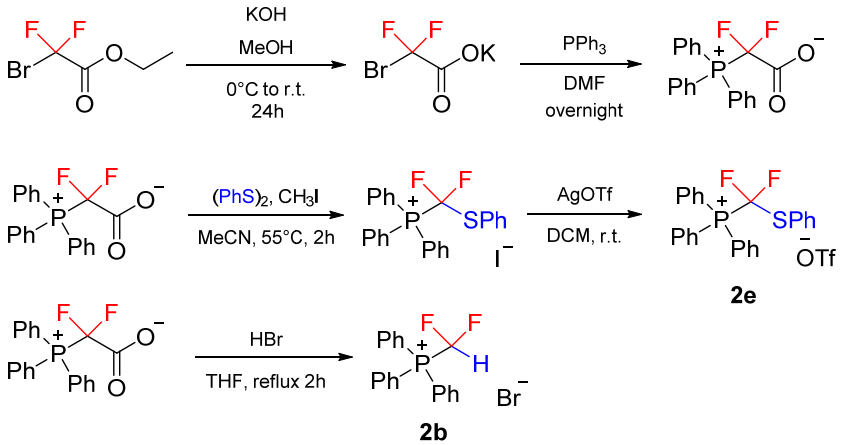
^{1}H NMR (TMS as the internal standard), ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AM400 spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The NMR yield was determined by ^{19}F NMR using trifluorotoluene as an internal standard. IR spectra were recorded on a Thermo Scientific Nicolet iS10 Fourier transform infrared (FT-IR) spectrometer and were reported in terms of wavenumber of absorption (cm^{-1}). Detection of melting point was conducted on the SGW X-4 microscopic melting point meter. HRMS-ESI data was collected by Thermo Fisher Scientific Q Exactive HF Oribitrap-FTMS. LED lights were commercial from Kessil® (KSA 160WE-TB, 40W). Unless otherwise stated, all reactions were carried out under strictly anhydrous conditions and N_2 atmosphere. Unless otherwise noted, all reagents were used as received from commercial sources.

2. Preparation of Substrates and Reagents

Substrates **1a**[1], **1b**[1], **1c**[2], **1d**[3], **1e**[4], **1f**[5], **1g**[3], **1h**[2], **1i**[1], **1j**[1], **1k**[6], **1l**[5], **1m**[3], **1n**[7], **1o**[8], **1p**[9], **1q**[5], **1r**[6], **1s**[10], **1t**[1], **1u**[1], **1v**[11], **1w**[1], **1x**[1], **1y**[7] were prepared according to the reported literatures.

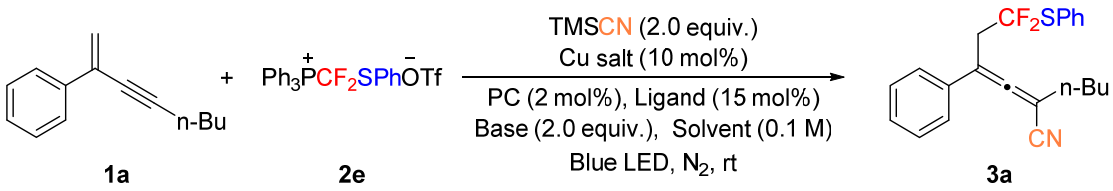


Reagents **2e**[12], **2b**[13] were prepared according to the reported literatures.



3. Optimization of reaction conditions

Table 1. Optimization of reaction conditions[a].



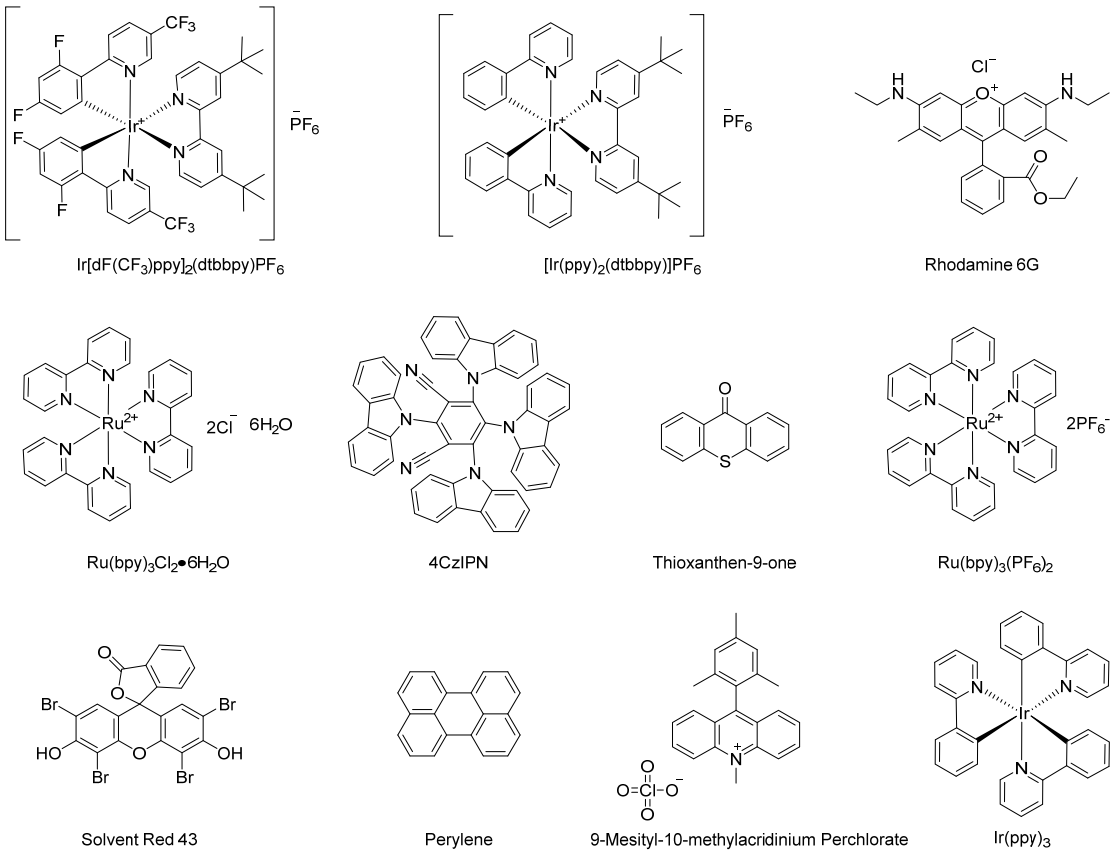
1a **2e** **3a**

Entry	1a	2e	photocatalyst	Ligand	Cu salt	Solvent	Base	Time	Yield (%)[b]
1	1	1.5	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$PF$_6$	MeCN	K_2CO_3	6 h	51
2	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$PF$_6$	MeCN	K_2CO_3	6 h	70
3	1	2	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$PF$_6$	MeCN	K_2CO_3	6 h	65
4	2	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$PF$_6$	MeCN	K_2CO_3	6 h	74
5	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	$(CF_3SO_3)_2Cu$	MeCN	K_2CO_3	6 h	32
6	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	$Cu(OAc)_2$	MeCN	K_2CO_3	6 h	29
7	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	CuI	MeCN	K_2CO_3	6 h	＜5
8	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	CuCl	MeCN	K_2CO_3	6 h	39
9	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	K_2CO_3	6 h	83
10	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	K_3PO_4•3H_2O	6 h	39
11	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	MeONa	6 h	32
12	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CsF	6 h	53
13	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	90, 88[c]
14	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$PF$_6$	MeCN	CH_3CO_2Na	6 h	77
15	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	$Cu(OAc)_2$	MeCN	CH_3CO_2Na	6 h	39
16	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	CuCl	MeCN	CH_3CO_2Na	6 h	50
17	1	1.5	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	71
18	2	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	86
19	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	3 h	60
20	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	12 h	87

21	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	PhCl	CH_3CO_2Na	6 h	＜5
22	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	DMF	CH_3CO_2Na	6 h	＜5
23	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	DCE	CH_3CO_2Na	6 h	＜5
24	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	THF	CH_3CO_2Na	6 h	＜5
25	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	EA	CH_3CO_2Na	6 h	15
26	1.5	1	*fac*-Ir(ppy)$_3$	4,4-d(Me)bpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	62
27	1.5	1	*fac*-Ir(ppy)$_3$	4,4-d(OMe)bpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	68
28	1.5	1	*fac*-Ir(ppy)$_3$	bpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	72
29	1.5	1	*fac*-Ir(ppy)$_3$	1,10-Phen	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	60
30	1.5	1	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	＜5
31	1.5	1	[Ir(ppy)$_2$(dtbbpy)]PF_6	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	＜5
32	1.5	1	Rhodamine 6G	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
33	1.5	1	Ru(bpy)$_3Cl_2$•6H_2O	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
34	1.5	1	4CzIPN	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
35	1.5	1	Thioxanthen-9-one	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
36	1.5	1	Ru(bpy)$_3$(PF_6)$_2$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
37	1.5	1	Solvent Red 43	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
38	1.5	1	Perylene	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	5
39	1.5	1	9-Mesityl-10-methylacridinium Perchlorate	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	7
40	1.5	1	-	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
41	1.5	1	*fac*-Ir(ppy)$_3$	-	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	63
42	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	-	MeCN	CH_3CO_2Na	6 h	0
43	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	-	6 h	36
44[d]	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	0
45[e]	1.5	1	*fac*-Ir(ppy)$_3$	dtbbpy	Cu(MeCN)$_4$BF$_4$	MeCN	CH_3CO_2Na	6 h	＜5

[a] Reaction conditions: **1a** (0.15 mmol), **2e** (0.1 mmol), TMSCN (0.2 mmol), photocatalyst (0.002 mmol), Cu salt (0.01 mmol), ligand (0.015 mmol), base (0.2 mmol), solvent (1 mL), blue LED, under N_2, rt. [b] Yields were determined by ^{19}F NMR spectroscopy with trifluorotoluene as an

internal standard. [c] isolated yield. [d] In the dark. [e] In air.

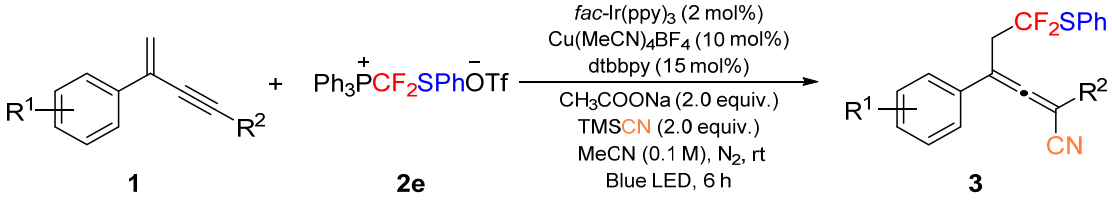


Scheme 1. Common photocatalysts

Our study commenced with oct-1-en-3-yn-2-ylbenzene (**1a**) as the model substrate, its reactivity with difluoro(phenylthio)methyltriphenylphosphonium triflate (**2e**) and TMSCN under photoredox/copper dual catalytic systems[14] was investigated (Table 1). Gratifyingly, the desired 1,4-difunctionalized product **3a** was formed in 51% yield using a catalytic system consisting of *fac*-Ir(ppy)$_3$ and Cu(MeCN)$_4$PF$_6$/dtbbpy with K_2CO_3 as the base in MeCN under irradiation with blue LEDs (entry 1). None of the 1,2-difunctionalized product could be detected. After a series of explorations, it was found that the equivalent ratio of suitable reactants **1a**/**2e** is 1.5/1 (entries 1-4、17-18). Screening of different Cu catalysts revealed that Cu(MeCN)$_4$BF$_4$ was optimal, increasing the yield of **3a** to 83% (entries 5–9、14-16). Subsequently, other bases including $NaHCO_3$, K_3PO_4, MeONa, CsF and NaOAc were evaluated (entries 10-13), and the best result was achieved when NaOAc as the base (entry 13). Studies of reaction duration found that 6 h was more efficient

(entries 19–20). In addition, switching MeCN to other solvents including PhCl, DMF, DCE, THF and EA proved less effective (entries 21–25). The effects of ligands on the reaction were also studied (entries 26-29). Switching the photocatalyst from *fac*-Ir(ppy)$_3$ to Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (entry 30), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (entry 31), Perylene (entry 38) or 9-Mesityl-10-methylacridinium Perchlorate (entry 39) led to lower yields, whereas the employment of Rhodamine 6G, Ru(bpy)$_3$Cl$_2$•6H$_2$O, 4CzIPN, Thioxanthen-9-one, Ru(bpy)$_3$(PF$_6$)$_2$ and Solvent Red 43 as the photocatalyst could not afford any of the desired product (entries 32-37). The control experiments demonstrated that visible light, photocatalyst and Cu catalyst were necessary conditions for the reaction, while ligands and alkalis could promote the reaction (entries 40-45).

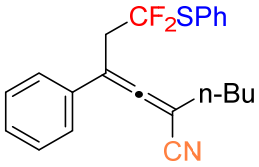
4. Photoredox/copper-Catalyzed Difluoroalkylation of 1,3-enyne



An 8 mL screw-cap vial equipped with a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (2.6 mg, 0.004 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (8.0 mg, 0.03 mmol), Ph$_3$PCF$_2$SPhOTf (114.0 mg, 0.2 mmol), Cu(MeCN)$_4$BF$_4$ (6.3 mg, 0.02 mmol), sodium acetate (32.8 mg, 0.4 mmol) and 1,3- enyne (0.3 mmol, if it is solid). The vial was evacuated and backfilled with nitrogen for three times. Then, MeCN (2.0 mL) and TMSCN (50 μL, 0.4 mmol) were added via a syringe (1,3-enyne is added via a micro syringe if it is liquid). The reaction mixture was placed at a distance of 10 cm from a 40 W blue LEDs and stirred at room temperature for 6 h. Then, saturated NaCl aqueous solution was added and the reaction mixture was extracted with ethyl acetate. The combined organic layers were then dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the

desired product **3**.

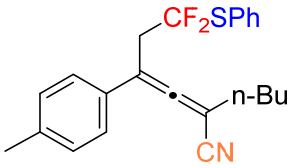
2-butyl-6,6-difluoro-4-phenyl-6-(phenylthio)hexa-2,3-dienenitrile



3a

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3a** (65.0 mg, 88%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.46 – 7.35 (m, 6H), 7.34 – 7.31 (m, 2H), 3.36 (t, *J* = 13.7 Hz, 2H), 2.45 – 2.33 (m, 2H), 1.67 – 1.59 (m, 2H), 1.44 – 1.37 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.9, 136.4, 132.9, 131.1, 129.3, 128.9, 128.8, 128.3 (t, *J* = 282.8 Hz), 126.8, 126.5, 114.8, 103.9, 86.3, 36.6 (t, *J* = 30.3 Hz), 31.4, 29.7, 22.0, 13.8; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -70.76 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2959, 2214, 1442, 1259, 1022, 797, 693 cm^{-1}; **MS** (ESI): *m/z* 392 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{22}H_{21}NF_2NaS$ $[M+Na]^+$: 392.1260; Found: 392.1257.

2-butyl-6,6-difluoro-6-(phenylthio)-4-(p-tolyl)hexa-2,3-dienenitrile

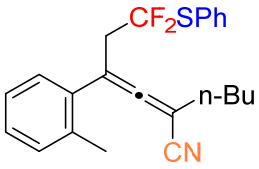


3b

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3b** (68.2 mg, 89%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.47 – 7.35 (m, 3H), 7.23 – 7.17 (m, 4H), 3.33 (t, *J* = 13.7 Hz, 2H), 2.37 (s, 5H), 1.65 – 1.57 (m, 2H), 1.44 – 1.35 (m, 2H), 0.96 – 0.90 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 138.9, 136.4, 130.2, 129.8, 129.7, 129.3, 128.3 (t, *J* = 282.8 Hz), 126.7, 126.5, 115.0, 103.8, 86.2, 39.6 (t, *J* = 30.3 Hz), 31.5, 29.7, 22.1, 21.3, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.72 (AB-t, *J* = 206.8,

15.0 Hz, 2F); **IR** (thin film) ν 2961, 2214, 1328, 1259, 1020, 797 cm^{-1}; **MS** (ESI): *m/z* 406 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{23}H_{23}NF_2NaS$ $[M+Na]^+$: 406.1417; Found: 406.1421.

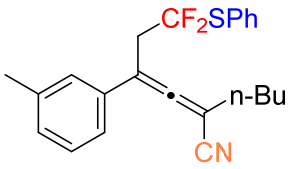
2-butyl-6,6-difluoro-6-(phenylthio)-4-(o-tolyl)hexa-2,3-dienenitrile



3c

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3c** (63.6 mg, 83%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.45 – 7.35 (m, 3H), 7.26 – 7.21 (m, 3H), 7.21 – 7.19 (m, 1H), 3.24 (td, *J* = 13.6, 4.3 Hz, 2H), 2.40 (s, 3H), 2.32 – 2.27 (m, 2H), 1.61 – 1.54 (m, 2H), 1.39 – 1.33 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.9, 136.3, 136.0, 133.7, 131.0, 130.1, 129.3, 128.6, 128.2, 128.2 (t, *J* = 282.8 Hz), 126.5, 126.4, 115.0, 102.3, 83.7, 42.8 (t, *J* = 30.3 Hz), 31.0, 29.7, 22.0, 20.4, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.01 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2925, 2218, 1959, 1446, 1259, 1025, 797 cm^{-1}; **MS** (ESI): *m/z* 406 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{23}H_{23}NF_2NaS$ $[M+Na]^+$: 406.1417; Found: 406.1418.

2-butyl-6,6-difluoro-6-(phenylthio)-4-(m-tolyl)hexa-2,3-dienenitrile

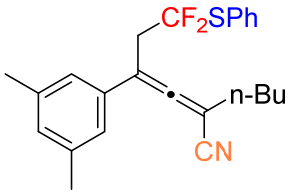


3d

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3d** (61.3 mg, 80%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.44 – 7.33 (m, 3H), 7.25 – 7.22 (m, 1H), 7.14 – 7.06 (m, 3H), 3.31 (t, *J* = 13.7 Hz, 2H), 2.37 – 2.31 (m, 5H), 1.59 (td, *J* = 7.6, 3.5 Hz, 2H), 1.43 – 1.35 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.9, 138.7, 136.4, 132.9, 130.2, 129.6, 129.3, 128.9, 128.3 (t, *J* = 282.8

Hz), 127.5, 126.6, 123.9, 114.9, 103.9, 86.2, 39.7 (t, J = 30.3 Hz), 31.5, 29.8, 22.1, 21.6, 13.8; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -70.79 (AB-t, J = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2968, 2210, 1259, 1023, 797, 693 cm^{-1}; **MS** (ESI): *m/z* 406 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{23}H_{23}NF_2NaS$ $[M+Na]^+$: 406.1417; Found: 406.1415.

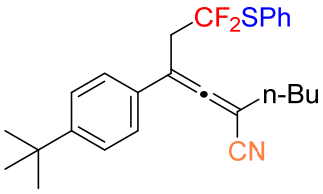
2-butyl-4-(3,5-dimethylphenyl)-6,6-difluoro-6-(phenylthio)hexa-2,3-dienenitrile



3e

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3e** (65.9 mg, 83%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 2H), 7.47 – 7.36 (m, 3H), 7.00 – 6.95 (m, 1H), 6.94 – 6.86 (m, 2H), 3.34 (t, J = 13.7 Hz, 2H), 2.41 – 2.36 (m, 2H), 2.34 (s, 6H), 1.64 (td, J = 7.5, 4.0 Hz, 2H), 1.47 – 1.38 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.9, 138.5, 136.4, 132.7, 130.5, 130.1, 129.2, 128.3 (t, J = 282.8 Hz), 126.6, 124.6, 115.0, 103.9, 86.0, 39.6 (t, J = 30.3 Hz), 31.4, 29.7, 22.0, 21.4, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.69 (AB-t, J = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2961, 2204, 1259, 1020, 797, 694 cm^{-1}; **MS** (ESI): *m/z* 420 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{24}H_{25}NF_2NaS$ $[M+Na]^+$: 420.1573; Found: 420.1577.

2-butyl-4-(4-(tert-butyl)phenyl)-6,6-difluoro-6-(phenylthio)hexa-2,3-dienenitrile

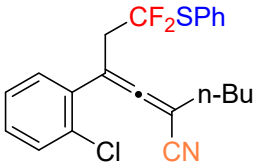


3f

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3f** (79.1 mg, 93%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.45 – 7.35 (m, 5H), 7.26 – 7.24 (m, 1H), 7.24 – 7.21 (m, 1H), 3.33 (t, J = 13.7 Hz, 2H), 2.38 – 2.31 (m, 2H), 1.65 – 1.57 (m, 2H), 1.43 – 1.37 (m, 2H), 1.32 (s, 9H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.0, 152.1, 136.4, 132.2, 130.1, 129.8, 128.6, 128.3 (t, J = 282.8 Hz),

126.5, 126.0, 114.9, 103.6, 39.5 (t, J = 30.3 Hz), 34.8, 31.5, 31.3, 29.8, 22.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.68 (AB-t, J = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2961, 2218, 1259, 1020, 797 cm^{-1}; **MS** (ESI): *m/z* 448 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{26}H_{29}NF_2NaS$ $[M+Na]^+$: 448.1886; Found: 448.1890.

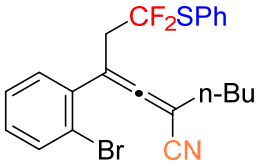
2-butyl-4-(2-chlorophenyl)-6,6-difluoro-6-(phenylthio)hexa-2,3-dienenitrile



3g

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3g** (63.7 mg, 79%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 3.30 (t, J = 13.6 Hz, 2H), 2.35 – 2.29 (m, 2H), 1.62 – 1.54 (m, 2H), 1.40 – 1.32 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.6, 136.4, 133.1, 132.8, 130.5, 130.3, 130.1, 130.0, 129.3, 128.2 (t, J = 282.8 Hz), 127.2, 126.4, 114.8, 101.7 (t, J = 10.1 Hz), 84.4, 41.9 (t, J = 30.3 Hz), 30.9, 29.6, 21.9, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.97 (td, J = 13.5, 2.5 Hz, 2F); **IR** (thin film) ν 2960, 2221, 1259, 1020, 797 cm^{-1}; **MS** (ESI): *m/z* 426 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{22}H_{20}NF_2NaSCl$ $[M+Na]^+$: 426.0871; Found: 426.0874.

4-(2-bromophenyl)-2-butyl-6,6-difluoro-6-(phenylthio)hexa-2,3-dienenitrile

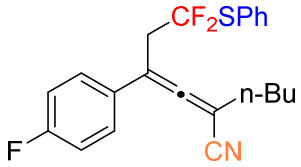


3h

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3h** (59.0 mg, 66%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 3H), 7.46 – 7.29 (m, 5H), 7.24 – 7.18 (m, 1H), 3.28 (t, J = 13.6 Hz, 2H), 2.35 – 2.27 (m, 2H), 1.62 – 1.57 (m, 2H), 1.38 – 1.32 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.4, 136.4, 135.3, 133.5, 130.7, 130.2, 129.3, 128.9, 128.2 (t, J = 282.8 Hz), 127.8, 126.5, 122.6, 114.8,

103.5, 84.6, 42.2 (t, J = 30.3 Hz), 31.0, 29.6, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.93 (td, J = 13.6, 8.8 Hz, 2F); **IR** (thin film) ν 2960, 2221, 1259, 1020, 797, 693 cm^{-1}; **MS** (ESI): *m/z* 470 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{22}H_{20}NF_2NaSBr$ $[M+Na]^+$: 470.0366; Found: 470.0369.

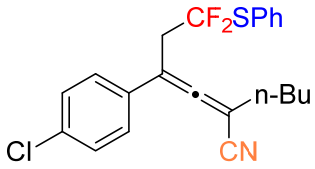
2-butyl-6,6-difluoro-4-(4-fluorophenyl)-6-(phenylthio)hexa-2,3-dienenitrile



3i

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3j** (53.4 mg, 69%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.51 (m, 2H), 7.47 – 7.34 (m, 3H), 7.30 – 7.26 (m, 2H), 7.10 – 7.01 (m, 2H), 3.31 (t, J = 13.6 Hz, 2H), 2.41 – 2.28 (m, 2H), 1.63 – 1.58 (m, 2H), 1.42 – 1.35 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.7, 162.9 (d, J = 121.2 Hz), 136.4, 130.2, 129.3, 128.9 (d, J = 10.1 Hz), 128.8 (d, J = 10.1 Hz), 128.2 (t, J = 282.8 Hz), 126.4, 116.1 (d, J = 10.1 Hz), 114.7, 103.2 (t, J = 10.1 Hz), 86.5, 39.9 (t, J = 30.3 Hz), 31.5, 29.7, 22.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.84 (AB-t, J = 206.8, 15.0 Hz, 2F), -112.47 (ddd, J = 13.3, 8.3, 5.0 Hz); **IR** (thin film) ν 2960, 1945, 1259, 1019, 797, 693 cm^{-1}; **MS** (ESI): *m/z* 410 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{22}H_{20}NF_3NaS$ $[M+Na]^+$: 410.1166; Found: 410.1162.

2-butyl-4-(4-chlorophenyl)-6,6-difluoro-6-(phenylthio)hexa-2,3-dienenitrile

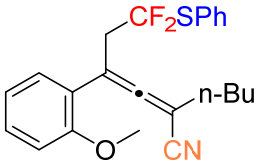


3j

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3j** (53.2 mg, 66%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.47 – 7.42 (m, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.24 – 7.20 (m, 2H), 3.31 (t, J = 13.6 Hz, 2H), 2.40 – 2.30 (m, 2H), 1.59 (dd, J = 7.5, 3.8 Hz, 2H), 1.42 – 1.35 (m, 2H), 0.92 (t, J = 7.4 Hz,

3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 149.3, 136.4, 134.8, 131.4, 130.3, 129.3, 129.2, 128.2 (t, *J* = 282.8 Hz), 128.1, 114.5, 103.1, 86.7, 39.7 (t, *J* = 30.3 Hz), 31.4, 29.7, 22.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ70.68 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2961, 2210, 1259, 1019, 797 cm^{-1}; **MS** (ESI): *m/z* 426 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{22}H_{20}NF_2NaSCl$ $[M+Na]^+$: 426.0871; Found: 426.0875.

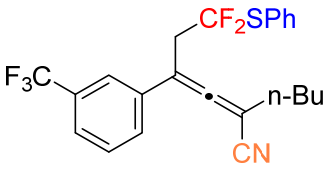
2-butyl-6,6-difluoro-4-(2-methoxyphenyl)-6-(phenylthio)hexa-2,3-dienenitrile



3k

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3k** (61.4 mg, 77%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.44 – 7.29 (m, 4H), 7.23 – 7.16 (m, 1H), 7.01 – 6.93 (m, 1H), 6.93 – 6.87 (m, 1H), 3.83 (s, 3H), 3.35 (td, *J* = 14.1, 6.1 Hz, 2H), 2.31 (t, *J* = 7.7 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.42 – 1.34 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 156.8, 136.3, 130.2,130.0,130.0, 129.2, 128.5 (t, *J* = 282.8 Hz), 126.8, 122.8, 120.9, 115.5, 111.3, 101.5 (t, *J* = 10.1 Hz), 83.0, 55.6, 41.0 (t, *J* = 30.3 Hz), 31.3, 29.7, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.91 (q, *J* = 14.2 Hz, 2F); **IR** (thin film) ν 2961, 2214, 1259, 1020, 797, 694 cm^{-1}; **MS** (ESI): *m/z* 422 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{23}H_{23}NOF_2NaS$ $[M+Na]^+$: 422.1366; Found: 422.1366.

2-butyl-6,6-difluoro-6-(phenylthio)-4-(3-(trifluoromethyl)phenyl)hexa-2,3-dienenitrile

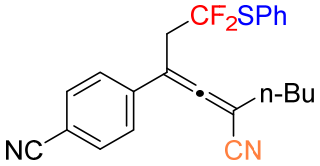


3l

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3l** (76.9 mg, 88%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.6 – 7.6 (m, 3H), 7.5 – 7.5 (m, 3H), 7.5 – 7.4 (m, 2H), 7.4 – 7.4 (m, 1H), 3.4 (t, *J* = 13.6 Hz, 2H), 2.4 (t, *J* = 7.6 Hz, 2H), 1.7

– 1.6 (m, 2H), 1.4 – 1.4 (m, 2H), 0.9 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.9, 136.4, 134.1, 131.4 (q, J = 30.3 Hz), 130.3, 130.1, 129.6, 129.4, 128.1 (t, J = 282.8 Hz), 126.3, 125.5, 123.4, 122.5, 114.3, 103.1, 87.1, 39.6 (t, J = 30.3 Hz), 31.4, 29.7, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.77, -71.02 (AB-t, J = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2961, 2214, 1328, 1259, 1020, 798, 695 cm^{-1}; **MS** (ESI): *m/z* 460 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{23}H_{20}NF_5NaS$ $[M+Na]^+$: 460.1134; Found: 460.1136.

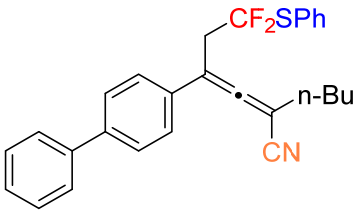
4-(5-cyano-1,1-difluoro-1-(phenylthio)nona-3,4-dien-3-yl)benzonitrile



3m

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3m** (44.9 mg, 57%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 7.0 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.03 (d, J = 8.6 Hz, 2H), 3.29 (t, J = 13.6 Hz, 2H), 2.38 – 2.32 (m, 2H), 1.61 – 1.55 (m, 2H), 1.42 – 1.36 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 138.2, 136.4, 132.6, 130.3, 129.4, 128.5, 128.2 (t, J = 282.8 Hz), 126.4, 124.6, 114.3, 113.7, 94.7, 86.8, 39.6 (t, J = 20.2 Hz), 31.4, 29.7, 22.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.92 (AB-t, J = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2960, 2214, 1328, 1259, 1020, 798, 697 cm^{-1}; **MS** (ESI): *m/z* 395 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{23}H_{21}N_2F_2S$ $[M+H]^+$: 395.1394; Found: 395.1389.

4-([1,1'-biphenyl]-4-yl)-2-butyl-6,6-difluoro-6-(phenylthio)hexa-2,3-dienenitrile

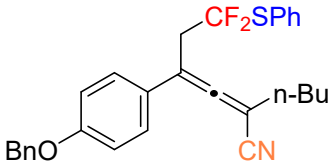


3n

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3n** (60.5 mg, 68%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 5H), 7.50

– 7.42 (m, 4H), 7.41 – 7.36 (m, 5H), 3.38 (t, *J* = 13.7 Hz, 2H), 2.43 – 2.34 (m, 2H), 1.67 – 1.61 (m, 2H), 1.44 – 1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.1, 150.2, 141.6, 140.7, 140.2, 136.4, 131.7, 130.2, 129.3, 129.0, 128.3 (t, *J* = 282.8 Hz), 127.9, 127.7, 127.1, 114.8, 103.7, 86.5, 39.6 (t, *J* = 30.3 Hz), 31.5, 29.8, 22.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.68 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2960, 2221, 1259, 1019, 797, 693 cm^{-1}; **MS** (ESI): *m/z* 468 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{28}H_{25}NF_2NaS$ $[M+Na]^+$: 468.1573; Found: 468.1569.

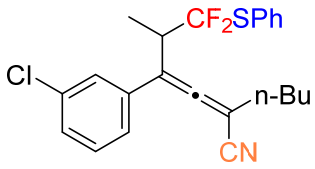
4-(4-(benzyloxy)phenyl)-2-butyl-6,6-difluoro-6-(phenylthio)hexa-2,3-dienenitrile



3o

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3o** (62.7 mg, 66%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 2H), 7.46 – 7.40 (m, 4H), 7.39 – 7.32 (m, 4H), 7.25 – 7.23 (m, 1H), 7.23 – 7.21 (m, 1H), 6.99 – 6.97 (m, 1H), 6.97 – 6.94 (m, 1H), 5.08 (s, 2H), 3.30 (t, *J* = 13.7 Hz, 2H), 2.34 (td, *J* = 7.2, 1.2 Hz, 2H), 1.61 – 1.57 (m, 2H), 1.42 – 1.37 (m, 2H), 1.27 – 1.25 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 159.2, 158.5, 150.8, 136.4, 130.1, 129.3, 128.8, 128.3 (t, *J* = 282.8 Hz), 128.2, 128.1, 127.7, 127.5, 125.1, 115.5, 103.5, 86.2, 70.2, 39.7 (t, *J* = 30.3 Hz), 31.5, 22.6, 22.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.58 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2958, 2217, 1604, 1510, 1255, 1020, 798, 740, 695 cm^{-1}; **MS** (ESI): *m/z* 498 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{29}H_{27}NOF_2NaS$ $[M+Na]^+$: 498.1672; Found: 498.1679.

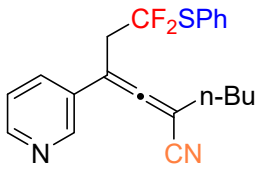
2-butyl-4-(3-chlorophenyl)-6,6-difluoro-5-methyl-6-(phenylthio)hexa-2,3-dienenitrile



3p

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3p** (58.4 mg, 70%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 2H), 7.47 – 7.33 (m, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.20 – 7.13 (m, 1H), 3.44 – 3.34 (m, 1H), 2.41 – 2.31 (m, 2H), 1.62 – 1.58 (m, 2H), 1.45 (dd, *J* = 18.4, 7.1 Hz, 3H), 1.42 – 1.36 (m, 2H), 0.92 (td, J = 7.3, 2.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.3 (d, *J* = 20.2 Hz), 136.5 (d, *J* = 20.2 Hz), 135.7 (d, *J* = 20.2 Hz), 135.0, 130.2 (d, *J* = 10.1 Hz), 130.1 (d, *J* = 10.1 Hz), 129.3 (d, *J* = 10.1 Hz), 128.8 (d, *J* = 10.1 Hz), 128.2 (t, *J* = 282.8 Hz), 127.1, 126.3 (d, *J* = 10.1 Hz), 125.3, 114.5 (d, *J* = 20.2 Hz), 110.3 (d, *J* = 40.4 Hz), 88.1 (d, *J* = 40.4 Hz), 43.7 (q, *J* = 20.2 Hz), 31.4 (d, *J* = 40.4 Hz), 29.8 (d, *J* = 10.1 Hz), 22.1 (d, *J* = 10.1 Hz), 15.6, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -74.20 – -78.61 (m, 2F); **IR** (thin film) ν 2927, 2217, 1639, 1580, 1466, 793, 749, 692 cm^{-1}; **MS** (ESI): *m/z* 440 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{23}H_{22}NF_2NaSCl$ $[M+Na]^+$: 440.1027; Found: 440.1023.

2-butyl-6,6-difluoro-6-(phenylthio)-4-(pyridin-3-yl)hexa-2,3-dienenitrile

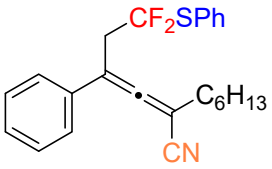


3q

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford **3q** (38.5 mg, 52%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 – 8.56 (m, 1H), 8.56 – 8.52 (m, 1H), 7.65 – 7.55 (m, 3H), 7.47 – 7.36 (m, 3H), 7.33 – 7.28 (m, 1H), 3.33 (t, *J* = 13.6 Hz, 2H), 2.41 – 2.31 (m, 2H), 1.65 – 1.56 (m, 2H), 1.42 – 1.36 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.6, 149.7, 148.0, 136.4, 134.0, 130.3, 129.4, 129.2, 128.1 (t, *J* = 282.8 Hz), 126.2, 123.7, 114.2, 101.4, 87.1, 39.5 (t, *J* = 30.3 Hz), 31.4, 29.7, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.21 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2961, 2204,

1259, 1020, 797, 694 cm^{-1}; **MS** (ESI): *m/z* 371 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{21}H_{21}N_2F_2S$ $[M+H]^+$: 371.1394; Found: 371.1399.

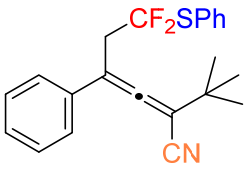
2-(4,4-difluoro-2-phenyl-4-(phenylthio)but-1-en-1-ylidene)octanenitrile



3r

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3r** (72.3 mg, 91%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.47 – 7.29 (m, 8H), 3.34 (t, *J* = 13.7 Hz, 2H), 2.42 – 2.31 (m, 2H), 1.63 – 1.58 (m, 2H), 1.29 – 1.25 (m, 6H), 0.88 – 0.85 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.9, 136.4, 132.9, 130.2, 129.3, 129.0, 128.8, 128.3 (t, *J* = 282.8 Hz), 126.8, 126.5, 114.8, 103.9, 86.4, 39.6 (t, *J* = 30.3 Hz), 31.8, 31.5, 28.6, 27.6, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.90 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2960, 1973, 1259, 1020, 797, 694 cm^{-1}; **MS** (ESI): *m/z* 420 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{24}H_{25}NF_2NaS$ $[M+Na]^+$: 420.1573; Found: 420.1577.

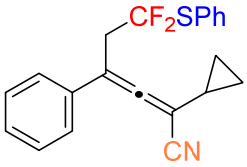
2-(tert-butyl)-6,6-difluoro-4-phenyl-6-(phenylthio)hexa-2,3-dienenitrile



3s

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3s** (58.3 mg, 79%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.51 (m, 2H), 7.48 – 7.27 (m, 8H), 3.52 – 3.21 (m, 2H), 1.26 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.5, 136.4, 133.1, 130.2, 129.3, 129.0, 128.8, 128.3 (t, *J* = 282.8 Hz), 126.6, 126.5, 114.0, 105.0, 97.5, 39.7 (t, *J* = 30.3 Hz), 35.8, 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.47 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2961, 2219, 1453, 1258, 1021, 797, 692 cm^{-1}; **MS** (ESI): *m/z* 392 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{22}H_{21}NF_2NaS$ $[M+Na]^+$: 392.1260; Found: 392.1267.

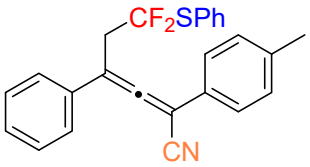
2-cyclopropyl-6,6-difluoro-4-phenyl-6-(phenylthio)hexa-2,3-dienenitrile



3t

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3t** (37.4 mg, 53%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.55 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.32 (m, 5H), 7.32 – 7.28 (m, 2H), 3.34 (td, *J* = 12.0, 4.0 Hz, 2H), 1.64 – 1.59 (m, 1H), 0.92 – 0.88 (m, 2H), 0.79 – 0.73 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.5, 136.5, 133.3, 130.2, 129.3, 129.0, 128.9,128.5, 128.1 (t, *J* = 282.8 Hz), 126.8, 113.9, 105.4, 90.0, 39.6 (t, *J* = 30.3 Hz), 11.6, 6.6, 6.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.11 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2968, 2210, 1259, 1023, 797, 693 cm^{-1}; **MS** (ESI): *m/z* 376 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{21}H_{17}NNaSF_2$ $[M+Na]^+$: 376.0947; Found: 376.0952.

6,6-difluoro-4-phenyl-6-(phenylthio)-2-(p-tolyl)hexa-2,3-dienenitrile

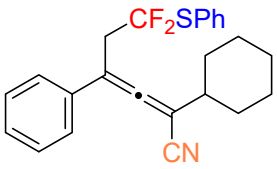


3u

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3u** (33.9 mg, 42%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.43 – 7.38 (m, 2H), 7.35 – 7.33 (m, 1H), 7.31 – 7.27 (m, 6H), 7.18 – 7.13 (m, 3H), 3.41 (td, *J* = 14.1, 13.7, 3.7 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 215.0, 139.6, 136.4, 132.4, 130.2, 130.0, 129.3, 129.3, 129.2, 128.2 (t, *J* = 282.8 Hz), 126.9, 126.5, 126.2, 125.9, 113.5, 107.7 (t, *J* = 10.1 Hz), 90.2, 39.7 (t, *J* = 30.3 Hz), 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.99 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2920, 2224, 1439, 1028, 803, 750, 693 cm^{-1}; **MS** (ESI): *m/z* 426

[M+Na]$^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{25}H_{19}NF_2NaS$ [M+Na]$^+$: 426.1104; Found: 426.1100.

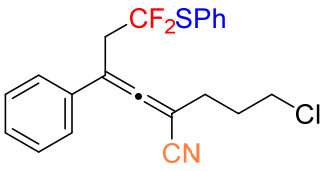
2-cyclohexyl-6,6-difluoro-4-phenyl-6-(phenylthio)hexa-2,3-dienenitrile



3v

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3v** (66.4 mg, 84%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.46 – 7.41 (m, 1H), 7.41 – 7.39 (m, 1H), 7.39 – 7.33 (m, 4H), 7.32 – 7.31 (m, 1H), 7.31 – 7.28 (m, 1H), 3.34 (td, *J* = 14.1, 13.7, 3.7 Hz, 2H), 2.34 – 2.27 (m, 1H), 2.02 – 1.94 (m, 2H), 1.83 – 1.76 (m, 2H), 1.71 – 1.66 (m, 1H), 1.63 – 1.57 (m, 1H), 1.34 – 1.31 (m, 2H), 1.28 – 1.25 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.9, 136.4, 133.0, 130.2, 129.3, 129.0, 128.7, 128.3 (t, *J* = 282.8 Hz), 126.6, 126.4, 114.3, 104.6, 92.1, 40.5, 39.7 (t, *J* = 30.3 Hz), 31.6, 25.9, 25.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.36 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2928, 2218, 1442, 1258, 1025, 797, 753, 692 cm^{-1}; **MS** (ESI): *m/z* 418 [M+Na]$^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{24}H_{23}NF_2NaS$ [M+Na]$^+$: 418.1417; Found: 418.1422.

2-(3-chloropropyl)-6,6-difluoro-4-phenyl-6-(phenylthio)hexa-2,3-dienenitrile

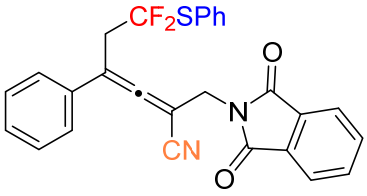


3w

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **3w** (31.9 mg, 41%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.47 – 7.42 (m, 1H), 7.42 – 7.34 (m, 5H), 7.32 – 7.28 (m, 2H), 3.58 (t, *J* = 6.2 Hz, 2H), 3.35 (t, *J* = 13.9 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.14 – 2.05 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.1,

136.4, 132.6, 130.3, 129.4, 129.1, 129.1, 128.2 (t, J = 282.8 Hz), 126.9, 126.4, 114.4, 104.7, 85.0, 43.5, 39.7 (t, J = 30.3 Hz), 30.2, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.95 (AB-t, J = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2968, 2210, 1259, 1023, 797, 693 cm^{-1}; **MS** (ESI): *m/z* 412 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{21}H_{18}NF_2NaSCl$ $[M+Na]^+$: 412.0714; Found: 412.0714.

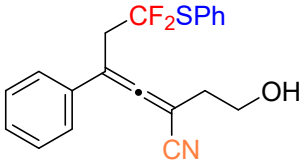
2-((1,3-dioxoisoindolin-2-yl)methyl)-6,6-difluoro-4-phenyl-6-(phenylthio)hexa-2,3-dienenitril e



3x

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford **3x** (28.3 mg, 30%) as yellow waxy solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.77 – 7.69 (m, 2H), 7.53 – 7.49 (m, 2H), 7.43 – 7.39 (m, 1H), 7.39 – 7.33 (m, 4H), 7.33 – 7.28 (m, 3H), 4.68 – 4.51 (m, 2H), 3.32 (td, J = 13.5, 5.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.1, 167.3, 136.4, 134.4, 131.9, 131.6, 130.2, 129.3, 129.3, 129.1, 127.9 (t, J = 282.8 Hz), 127.1, 126.3, 123.8, 112.8, 107.7, 83.1, 39.5 (t, J = 30.3 Hz), 37.6; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -70.91 (td, J = 13.6, 2.4 Hz); **IR** (thin film) ν 2961, 2204, 1690, 1259, 1020, 797, 694 cm^{-1}; **MS** (ESI): *m/z* 473 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{27}H_{19}N_2O_2F_2S$ $[M+H]^+$: 473.1057; Found: 473.1059.

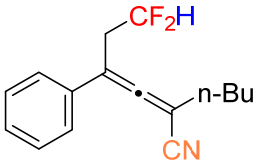
6,6-difluoro-2-(2-hydroxyethyl)-4-phenyl-6-(phenylthio)hexa-2,3-dienenitrile



3y

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 5:1) to afford **3y** (59.3 mg, 83%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.36 (m, 3H), 7.36 – 7.32 (m, 4H), 3.89 (t, *J* = 6.2 Hz, 2H), 3.37 (t, *J* = 13.4 Hz, 2H), 2.60 (t, *J* = 6.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.9, 136.4, 132.5, 130.2, 129.3, 129.1, 129.0, 128.3 (t, *J* = 282.8 Hz), 126.9, 126.4, 114.5, 104.3, 83.4, 60.0, 39.6 (t, *J* = 30.3 Hz), 34.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.68 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 3420, 2951, 2220, 1440, 1258, 1031, 797, 753, 693 cm^{-1}; **MS** (ESI): *m/z* 380 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{20}H_{17}NOF_2NaS$ $[M+Na]^+$: 380.0897; Found: 380.0899.

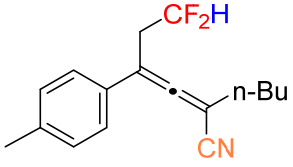
2-butyl-6,6-difluoro-4-phenylhexa-2,3-dienenitrile (4a)



4a

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4a** (46.5 mg, 89 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 5H), 5.97 (tt, *J* = 55.9, 4.6 Hz, 1H), 3.08 (td, *J* = 15.5, 5.2 Hz, 2H), 2.37 – 2.30 (m, 2H), 1.58 (td, *J* = 7.5, 2.0 Hz, 2H), 1.43 – 1.37 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.4, 132.4, 129.2, 129.1, 126.5, 115.1 (t, *J* = 242.4 Hz), 114.9, 103.1, 86.7, 35.4 (t, *J* = 20.2 Hz), 31.6, 29.7, 22.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.87 (dtd, *J* = 56.4, 15.5, 7.0 Hz, 2F); **IR** (thin film) ν 2959, 2214, 1449, 1259, 1021, 797, 695 cm^{-1}; **MS** (ESI): *m/z* 284 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{16}H_{17}NF_2Na$ $[M+Na]^+$: 284.1227; Found: 284.1231.

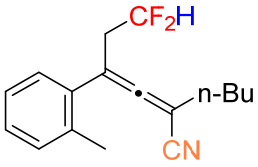
2-butyl-6,6-difluoro-4-(p-tolyl)hexa-2,3-dienenitrile



4b

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4b** (48.4 mg, 88 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 4H), 5.96 (tt, *J* = 56.0, 4.6 Hz, 1H), 3.06 (td, *J* = 15.4, 4.3 Hz, 2H), 2.37 (s, 3H), 2.35 – 2.30 (m, 2H), 1.62 – 1.54 (m, 2H), 1.45 – 1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.4, 139.2, 129.9, 129.3, 126.4, 115.2 (t, *J* = 242.4 Hz), 115.0, 104.2 (t, *J* = 10.1 Hz), 86.4, 35.4 (t, *J* = 20.2 Hz), 31.6, 29.7, 22.1, 21.3, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.83 (dtd, *J* = 56.4, 15.6, 8.3 Hz, 2F); **IR** (thin film) ν 2960, 2214, 1402, 1259, 1022, 798 cm^{-1}; **MS** (ESI): *m/z* 298 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{17}H_{19}NF_2Na$ $[M+Na]^+$: 298.1383; Found: 298.1387.

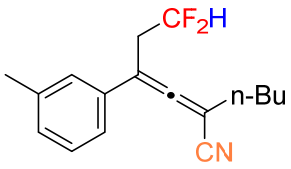
2-butyl-6,6-difluoro-4-(o-tolyl)hexa-2,3-dienenitrile



4c

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4c** (49.0 mg, 89 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 3H), 7.21 – 7.17 (m, 1H), 5.87 (tt, J = 55.9, 4.6 Hz, 1H), 2.96 (tdd, J = 15.6, 4.6, 2.1 Hz, 2H), 2.38 (s, 3H), 2.29 – 2.23 (m, 2H), 1.60 – 1.51 (m, 2H), 1.40 – 1.33 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.5, 136.0, 133.1, 131.2, 128.8, 127.9, 126.5, 115.0, 114.9 (t, *J* = 242.4 Hz), 102.7 (t, *J* = 10.1 Hz), 83.7, 38.7 (t, *J* = 20.2 Hz), 31.1, 29.7, 21.9, 20.3, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.7 (dt, *J* = 55.9, 15.9 Hz, 2F); **IR** (thin film) ν 2961, 2214, 1959, 1259, 1022, 797 cm^{-1}; **MS** (ESI): *m/z* 298 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{17}H_{19}NF_2Na$ $[M+Na]^+$: 298.1383; Found: 298.1381.

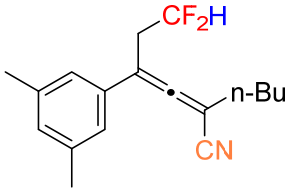
2-butyl-6,6-difluoro-4-(m-tolyl)hexa-2,3-dienenitrile



4d

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4d** (50.6 mg, 92 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 1H), 7.21 – 7.13 (m, 1H), 7.13 – 7.08 (m, 2H), 5.95 (tt, J = 56.0, 4.6 Hz, 1H), 3.05 (tdd, J = 15.7, 4.6, 2.0 Hz, 2H), 2.37 (s, 3H), 2.35 – 2.30 (m, 2H), 1.62 – 1.51 (m, 2H), 1.43 – 1.34 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.4, 139.0, 132.3, 129.9, 128.7, 127.3, 123.6, 115.1 (t, *J* = 242.4 Hz), 114.9, 104.3 (t, *J* = 10.1 Hz), 86.4, 35.5 (t, *J* = 20.2 Hz), 31.6, 29.7, 22.0, 21.6, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.89 (td, *J* =56.4, 15.7, 8.3 Hz, 2F); **IR** (thin film) ν 2959, 2219, 1456, 1259, 1021, 797 cm^{-1}; **MS** (ESI): *m/z* 298 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{17}H_{19}NF_2Na$ $[M+Na]^+$: 298.1383; Found: 298.1387.

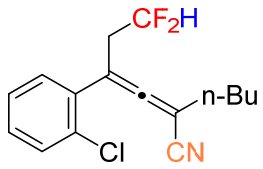
2-butyl-4-(3,5-dimethylphenyl)-6,6-difluorohexa-2,3-dienenitrile



4e

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4e** (54.4 mg, 94 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 – 6.91 (m, 3H), 5.96 (tt, *J* = 56.0, 4.6 Hz, 1H), 3.06 (tdd, *J* = 15.7, 4.6, 2.3 Hz, 2H), 2.36 – 2.32 (m, 8H), 1.59 (dtd, *J* = 13.7, 7.1, 2.8 Hz, 2H), 1.47 – 1.37 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.4, 138.9, 132.2, 130.8, 124.3, 115.2 (t, *J* = 242.4 Hz), 115.0, 104.4 (t, *J* =10.1 Hz), 86.2, 35.5 (t, *J* = 20.2 Hz), 31.6, 29.7, 22.0, 21.4, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.88 (dtd, *J* = 56.4, 15.6, 9.1 Hz, 2F); **IR** (thin film) ν 2961, 2221, 1404, 1260, 1024, 800 cm^{-1}; **MS** (ESI): *m/z* 312 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{18}H_{21}NF_2Na$ $[M+Na]^+$: 312.1540; Found: 312.1544.

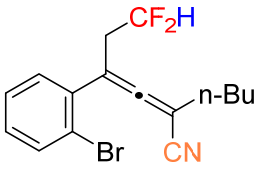
2-butyl-4-(2-chlorophenyl)-6,6-difluorohexa-2,3-dienenitrile



4g

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4g** (31.9 mg, 54 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 1H), 7.32 – 7.25 (m, 3H), 5.89 (tt, *J* = 55.8, 4.5 Hz, 1H), 3.01 (td, *J* = 15.9, 4.5 Hz, 2H), 2.31 – 2.25 (m, 2H), 1.59 – 1.51 (m, 2H), 1.40 – 1.30 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.3, 132.8, 132.8, 130.5, 130.2, 130.1, 127.5, 114.9 (t, *J* = 242.4 Hz), 114.8, 102.0 (t, *J* = 10.1 Hz), 84.7, 37.9 (t, *J* = 20.2 Hz), 31.1, 29.6, 21.9, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.48 (dtd, *J* = 56.4, 15.8, 10.7 Hz, 2F); **IR** (thin film) ν 2961, 2214, 1429, 1259, 1041, 797 cm^{-1}; **MS** (ESI): *m/z* 318 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{16}H_{16}NF_2NaCl$ $[M+Na]^+$: 318.0837; Found: 318.0840.

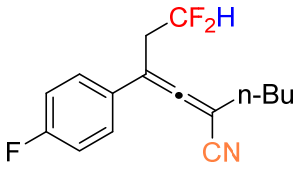
4-(2-bromophenyl)-2-butyl-6,6-difluorohexa-2,3-dienenitrile



4h

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4h** (48.1 mg, 71 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 1H), 7.30 – 7.26 (m, 1H), 7.22 – 7.12 (m, 2H), 5.83 (tt, *J* = 55.8, 4.5 Hz, 1H), 2.93 (td, *J* = 15.9, 4.5 Hz, 2H), 2.24 – 2.17 (m, 2H), 1.53 – 1.44 (m, 2H), 1.29 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 134.9, 133.7, 130.3, 130.2, 128.0, 122.5, 114.8 (t, *J* = 242.4 Hz), 114.7, 103.7 (t, *J* = 10.1 Hz), 84.8, 38.2 (t, *J* = 20.2 Hz), 31.0, 29.6, 21.9, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.43 (dtd, *J* = 56.4, 15.9, 8.8 Hz, 2F); **IR** (thin film) ν 2961, 2221, 1945, 1259, 1021, 797 cm^{-1}; **MS** (ESI): *m/z* 362 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{16}H_{16}NF_2NaBr$ $[M+Na]^+$: 362.0332; Found: 362.0329.

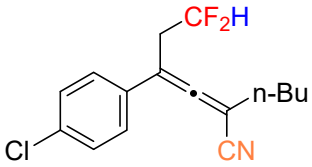
2-butyl-6,6-difluoro-4-(4-fluorophenyl)hexa-2,3-dienenitrile



4i

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4i** (48.6 mg, 87 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.13 – 7.06 (m, 2H), 5.96 (tt, *J* = 55.8, 4.5 Hz, 1H), 3.05 (td, *J* = 15.6, 4.5 Hz, 2H), 2.36 – 2.29 (m, 2H), 1.62 – 1.53 (m, 2H), 1.44 – 1.36 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.2, 164.3, 161.8, 128.4, 128.3, 116.2 (d, *J* = 30.3 Hz), 115.0 (t, *J* = 242.4 Hz), 114.7, 103.4 (t, *J* = 10.1 Hz), 86.9, 35.5 (t, *J* = 20.2 Hz), 31.6, 29.7, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.98 (ddd, *J* = 13.2, 8.4, 5.0 Hz, 1F), -114.87 (dtd, *J* = 56.4, 15.6, 3.7 Hz, 2F); **IR** (thin film) ν 2961, 2221, 1504, 1259, 1020, 797 cm^{-1}; **MS** (ESI): *m/z* 302 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{16}H_{16}NF_3Na$ $[M+Na]^+$: 302.1133; Found: 302.1127.

2-butyl-4-(4-chlorophenyl)-6,6-difluorohexa-2,3-dienenitrile

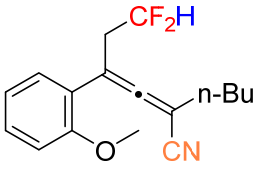


4j

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4j** (31.9 mg, 54 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.28 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 5.96 (tt, *J* = 55.8, 4.5 Hz, 1H), 3.05 (td, *J* = 15.6, 4.5 Hz, 2H), 2.39 – 2.25 (m, 2H), 1.59 – 1.54 (m, 2H), 1.43 – 1.36 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.3, 135.1, 131.0, 129.4, 127.8, 114.9 (t, *J* = 242.4 Hz), 114.6, 103.5, 87.1, 35.3 (t, *J* = 20.2 Hz), 31.6, 29.7, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.88 (dtd, *J* = 56.4, 15.5, 4.0 Hz, 2F); **IR** (thin film) ν 2960, 2217, 1259, 1398, 1020, 797 cm^{-1}; **MS** (ESI): *m/z*

318 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{16}H_{16}NF_2NaCl$ $[M+Na]^+$: 318.0837; Found: 318.0832.

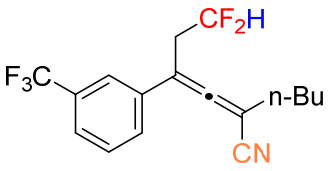
2-butyl-6,6-difluoro-4-(2-methoxyphenyl)hexa-2,3-dienenitrile



4k

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4k** (42.5 mg, 73 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 1H), 7.20 – 7.09 (m, 1H), 7.03 – 6.85 (m, 2H), 5.90 (tt, *J* = 56.2, 4.6 Hz, 1H), 3.86 (s, 3H), 3.04 (ddt, *J* = 16.8, 15.3, 4.9 Hz, 2H), 2.32 – 2.21 (m, 2H), 1.63 – 1.52 (m, 2H), 1.42 – 1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.8, 156.9, 130.4, 129.5, 122.1, 121.0, 115.6, 115.5 (t, *J* = 242.4 Hz), 111.4, 101.5 (t, *J* = 10.1 Hz), 83.1, 55.7, 37.0 (t, *J* = 20.2 Hz), 31.4, 29.7, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.21 (ddd, *J* = 56.4, 33.8, 18.8 Hz, 2F); **IR** (thin film) ν 2961, 2221, 1969, 1258, 1021, 797 cm^{-1}; **MS** (ESI): *m/z* 314 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{17}H_{19}NOF_2Na$ $[M+Na]^+$: 314.1332; Found: 314.1335.

2-butyl-6,6-difluoro-4-(3-(trifluoromethyl)phenyl)hexa-2,3-dienenitrile

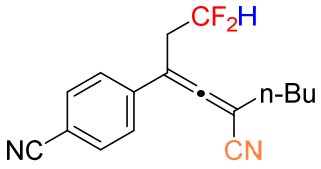


4l

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4l** (59.2 mg, 90 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 1H), 7.57 – 7.47 (m, 3H), 5.99 (tt, *J* = 55.7, 4.4 Hz, 1H), 3.10 (td, *J* = 15.6, 4.4 Hz, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.46 – 1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.4, 133.7, 131.9, 131.6, 129.8 (d, *J* = 10.1 Hz), 125.8, 123.8 (q, *J* = 272.7 Hz), 123.2 (d, *J* = 10.1 Hz), 114.8 (t, *J* = 242.4 Hz), 114.4, 103.4 (t, *J* = 10.1 Hz), 87.6, 35.3 (t, *J* = 20.2 Hz),

31.6, 29.6, 22.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.85 (s, 3F), -115.01 (dtd, 56.4, 15.0, 3.8, 2F); **IR** (thin film) ν 2961, 2221, 1328, 1259, 1020, 797, 697 cm^{-1}; **MS** (ESI): *m/z* 352 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{17}H_{16}NF_5Na$ $[M+Na]^+$: 352.1203; Found: 352.1201.

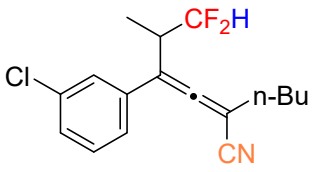
4-(5-cyano-1,1-difluorononona-3,4-dien-3-yl)benzonitrile



4m

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4m** (34.9 mg, 61 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.99 (tt, *J* = 55.5, 4.4 Hz, 1H), 3.09 (td, *J* = 15.7, 4.3 Hz, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.44 – 1.34 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.0, 137.5, 132.9, 127.2, 118.3, 114.7 (t, *J* = 242.4 Hz), 114.0, 112.7, 103.2 (t, *J* = 10.1 Hz), 87.9, 35.1 (t, *J* = 30.3 Hz), 31.5, 29.6, 22.0, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.89 (dtd, *J* = 56.4, 15.6, 4.2 Hz, 2F); **IR** (thin film) ν 2960, 2221, 1969, 1259, 1019, 797, 695 cm^{-1}; **MS** (ESI): *m/z* 309 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{17}H_{16}N_2F_2Na$ $[M+Na]^+$: 309.1282; Found: 309.1287.

2-butyl-4-(3-chlorophenyl)-6,6-difluoro-5-methylhexa-2,3-dienenitrile

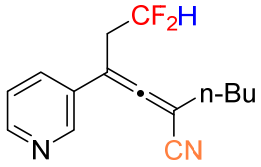


4p

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4p** (53.2 g, 86 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.24 – 7.17 (m, 1H), 5.76 (tdd, *J* = 56.1, 10.0, 3.9 Hz, 1H), 3.26 – 3.08 (m, 1H), 2.33 (td, *J* = 7.8, 3.8 Hz, 2H), 1.64 – 1.53 (m, 2H), 1.45 – 1.35 (m, 2H), 1.29 (dd, *J* = 10.0, 7.0 Hz, 3H), 0.93 (td, *J* = 7.3,

3.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.1 (d, *J* = 10.1 Hz), 135.2, 134.9 (d, *J* = 10.1 Hz), 130.4, 129.0, 127.1, 125.2, 116.7 (td, *J* = 242.4, 10.1 Hz), 114.6, 110.2 (dt, *J* = 20.2, 4.0 Hz), 88.0 (d, *J* = 10.1 Hz), 39.2 (td, *J* = 20.2, 4.0 Hz), 31.5 (d, *J* =20.2 Hz), 29.7 (d, *J* = 10.1 Hz), 22.0, 13.7, 13.0 - 12.8 (m, 1C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.8 – -124.6 (m, 2F). **IR** (thin film) ν 2955, 2217, 1580, 1460, 1259, 1073, 795, 691 cm^{-1}; **MS** (ESI): *m/z* 332 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{17}H_{18}NF_2NaCl$ $[M+Na]^+$: 332.0994; Found: 332.1002.

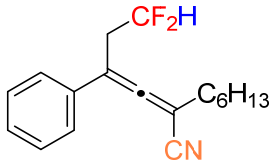
2-butyl-6,6-difluoro-4-(pyridin-3-yl)hexa-2,3-dienenitrile



4q

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4q** (32.0 mg, 61 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 – 8.52 (m, 2H), 7.66 – 7.58 (m, 1H), 7.37 – 7.30 (m, 1H), 5.99 (tt, *J* = 55.7, 4.4 Hz, 1H), 3.08 (td, *J* = 15.7, 4.4 Hz, 2H), 2.38 – 2.27 (m, 2H), 1.62 – 1.52 (m, 2H), 1.43 – 1.34 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.1, 150.0, 147.8, 133.8, 128.8, 123.9, 114.8 (t, *J* = 242.4 Hz), 114.3, 101.7 (t, *J* = 10.1 Hz), 87.5, 35.1 (t, *J* = 20.2 Hz), 31.5, 29.6, 22.0, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.01 (dtd, *J* = 55.6, 15.7, 2.9 Hz, 2F); **IR** (thin film) ν 2962, 2217, 1259, 1085, 1016, 797 cm^{-1}; **MS** (ESI): *m/z* 263 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{15}H_{17}N_2F_2$ $[M+H]^+$: 263.1360; Found: 263.1365.

2-(4,4-difluoro-2-phenylbut-1-en-1-ylidene)octanenitrile

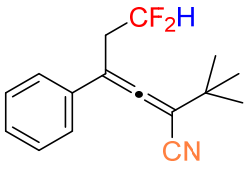


4r

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4r** (43.4 g, 75 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 5H), 5.97 (tt, *J* = 55.9, 4.6 Hz, 1H), 3.17 – 2.98 (m, 2H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.53 (m, 2H), 1.36 (t, *J*

= 5.4 Hz, 2H), 1.29 – 1.24 (m, 4H), 0.91 – 0.84 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.4, 132.4, 129.2, 129.0, 126.6, 115.1 (t, *J* = 242.4 Hz), 114.8, 104.2 (t, *J* = 10.1 Hz), 86.6, 35.4 (t, *J* = 20.2 Hz), 31.9, 31.5, 28.6, 27.6, 22.6, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.86 (dtd, *J* = 55.7, 15.6, 6.7 Hz, 2F); **IR** (thin film) ν 2959, 2217, 1952, 1259, 1019, 797, 694 cm^{-1}; **MS** (ESI): *m/z* 312 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{18}H_{21}NF_2Na$ $[M+Na]^+$: 312.1540; Found: 312.1534.

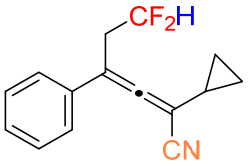
2-(tert-butyl)-6,6-difluoro-4-phenylhexa-2,3-dienenitrile



4s

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4s** (44.4 g, 85 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.39 – 7.29 (m, 3H), 5.99 (tt, *J* = 55.8, 4.6 Hz, 1H), 3.16 – 3.04 (m, 2H), 1.26 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.0, 132.5, 129.2, 129.0, 126.3, 115.1 (t, *J* = 242.4 Hz), 113.9, 105.2, 97.7, 35.7, 35.4 (t, *J* = 20.2 Hz), 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.37 (dtd, *J* = 56.4, 15.4, 2.9 Hz, 2F). **IR** (thin film) ν 2961, 2217, 1401, 1259, 1020, 798 cm^{-1}; **MS** (ESI): *m/z* 284 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{16}H_{17}NF_2Na$ $[M+Na]^+$: 284.1227; Found: 284.1226.

2-cyclopropyl-6,6-difluoro-4-phenylhexa-2,3-dienenitrile

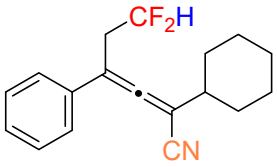


4t

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4t** (44.4 g, 50 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.38 – 7.30 (m, 3H), 5.96 (tt, J = 55.9, 4.6 Hz, 1H), 3.20 – 2.93 (m, 2H), 1.56 (td, J = 8.2, 4.9 Hz, 1H), 0.94 – 0.87 (m, 2H), 0.78 – 0.68 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.8, 132.4, 129.2, 129.2, 126.6, 115.1 (t, *J* = 242.4 Hz), 113.8, 105.8, 90.3, 35.5 (t, *J* = 20.2 Hz), 11.7, 6.7, 6.6;

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.94 (dtd, *J* = 56.0, 15.4, 3.0 Hz). **IR** (thin film) ν 2963, 2215, 1411, 1261, 1018, 797 cm^{-1}; **MS** (ESI): *m/z* 268 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{15}H_{13}NF_2Na$ $[M+Na]^+$: 268.1017; Found: 268.1016.

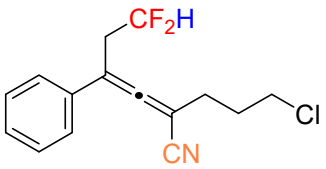
2-cyclohexyl-6,6-difluoro-4-phenylhexa-2,3-dienenitrile



4v

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4v** (47.7 g, 83 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.37 – 7.29 (m, 3H), 5.98 (tt, *J* = 55.9, 4.6 Hz, 1H), 3.08 (tt, *J* = 15.2, 4.2 Hz, 2H), 2.32 – 2.23 (m, 1H), 2.02 – 1.93 (m, 2H), 1.84 – 1.75 (m, 2H), 1.73 – 1.66 (m, 1H), 1.61 – 1.56 (m, 1H), 1.33 – 1.25 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.4, 132.5, 129.2, 129.0, 126.4, 115.2 (t, *J* = 242.4 Hz), 114.3, 105.1 (t, *J* = 10.1 Hz), 92.4, 40.5, 35.4 (t, *J* = 20.2 Hz), 31.6, 25.9, 25.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.50 (dq, *J* = 56.1, 16.1 Hz, 2F); **IR** (thin film) ν 2929, 2214, 1942, 1448, 1056, 762, 693 cm^{-1}; **MS** (ESI): *m/z* 310 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{18}H_{19}NF_2Na$ $[M+Na]^+$: 310.1383; Found: 310.1387.

2-(3-chloropropyl)-6,6-difluoro-4-phenylhexa-2,3-dienenitrile

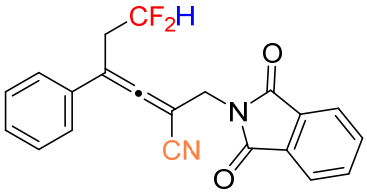


4w

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4w** (49.5 g, 88 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 5.99 (tt, *J* = 55.8, 4.5 Hz, 1H), 3.60 (t, *J* = 6.2 Hz, 2H), 3.19 – 3.01 (m, 2H), 2.58 – 2.49 (m, 2H), 2.12 – 2.02 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.6, 132.1, 129.3, 128.5, 126.6, 115.0 (t, *J* = 242.4 Hz), 114.4, 105.1, 85.2, 43.5, 35.4 (t, *J* = 20.2 Hz), 30.0, 29.1; **^{19}F NMR** (376 MHz, $CDCl_3$)

δ -114.91 (dtd, *J* = 55.7, 15.7, 7.1 Hz, 2F); **IR** (thin film) ν 2958, 2228, 1259, 1024, 797, 698 cm^{-1}; **MS** (ESI): *m/z* 304 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{15}H_{14}NF_2NaCl$ $[M+Na]^+$: 304.0681; Found: 304.0685.

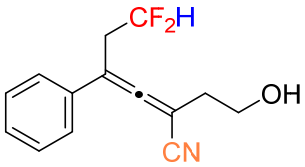
2-((1,3-dioxoisoindolin-2-yl)methyl)-6,6-difluoro-4-phenylhexa-2,3-dienenitrile



4x

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4x** (24.0 mg, 33 %) as yellow waxy solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.77 – 7.67 (m, 3H), 7.42 – 7.33 (m, 3H), 7.29 – 7.27 (m, 1H), 5.94 (tt, *J* = 55.8, 4.6 Hz, 1H), 4.57 (s, 2H), 3.04 (td, *J* = 15.5, 15.0, 5.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.5, 167.3, 134.6, 131.8, 131.1, 129.6, 129.2, 126.8, 123.8, 114.8 (t, *J* = 242.4 Hz), 112.4, 108.2, 83.4, 37.7, 35.3 (t, *J* = 20.2 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.09 (dt, *J* = 56.4, 15.4 Hz, 2F); **IR** (thin film) ν 2958, 2228, 1679, 1259, 1024, 797, 698 cm^{-1}; **MS** (ESI): *m/z* 365 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{21}H_{15}N_2O_2F_2$ $[M+H]^+$: 365.1023; Found: 365.1025.

6,6-difluoro-2-(2-hydroxyethyl)-4-phenylhexa-2,3-dienenitrile

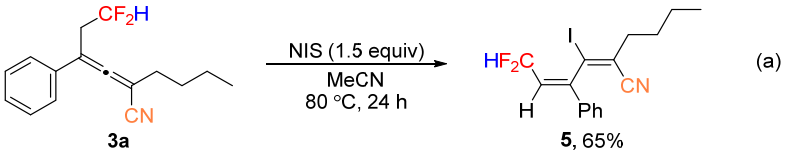


4y

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4y** (35.4 mg, 71 %) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 6.04 (tt, *J* = 55.9, 4.5 Hz, 1H), 3.88 (t, *J* = 5.9 Hz, 2H), 3.09 (td, *J* = 15.6, 15.1, 4.6 Hz, 2H), 2.56 (t, *J* = 6.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.3, 131.0, 128.1, 128.1, 125.5, 114.0 (t, *J* = 242.4 Hz), 113.4, 103.5 (t, *J* = 10.1 Hz), 82.6, 58.7, 34.1(t, *J* = 20.2 Hz), 33.8; **^{19}F NMR** (376 MHz,

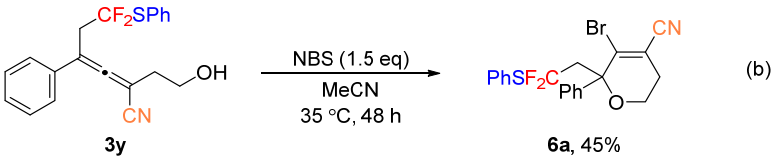
$CDCl_3$) δ -115.04 (dtd, *J* = 55.7, 15.7, 3.8 Hz, 2F); **IR** (thin film) ν 2960, 2214, 1259, 1020, 797, 695 cm^{-1}; **MS** (ESI): *m/z* 250 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{14}H_{14}NOF_2$ $[M+H]^+$: 250.1043; Found: 250.1040.

5. Transformation of difluoroalkylated allenes

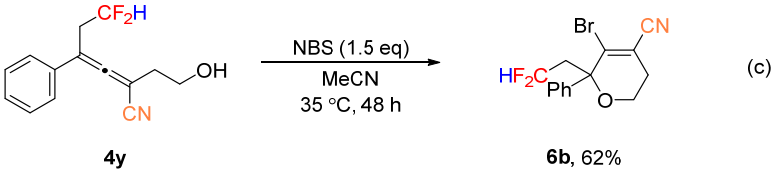


3a **5**, 65% (a)

In an 8 mL screw-cap vial was charged with allene (**3a**, 52.2 mg, 0.2 mmol), NIS (67.5 mg, 0.3 mmol) and CH_3CN (2.0 mL). The resulting suspension was stirred at 80℃ for 24 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **5** (50.3 mg, 65%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 5H), 6.31 (tdd, *J* = 54.8, 11.6, 7.0 Hz, 1H), 6.07 (td, *J* = 8.4, 6.7 Hz, 1H), 2.67 – 2.54 (m, 1H), 2.26 – 2.17 (m, 1H), 1.78 – 1.65 (m, 1H), 1.52 – 1.44 (m, 1H), 1.02 (t, *J* = 7.3 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5 (d, *J* = 20.2 Hz), 133.6, 130.6, 130.3, 129.4, 129.2, 127.0, 126.6, 121.3, 119.5, 112.0 (t, *J* = 242.4 Hz), 38.9, 33.7, 29.6 (d, *J* = 50.5 Hz), 22.2, 13.8 (d, *J* = 30.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.05 (ddd, *J* = 54.7, 15.3, 8.1 Hz, 2F); **IR** (thin film) ν 2960, 2214, 1259, 1083, 1020, 797, 696 cm^{-1}; **MS** (ESI): *m/z* 388 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{16}H_{17}NF_2I$ $[M+H]^+$: 388.0374; Found: 388.0370.



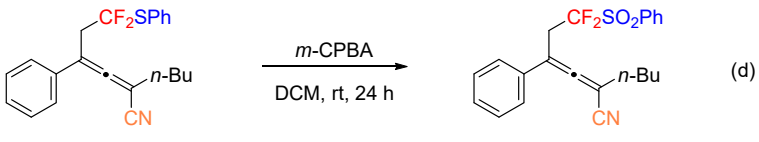
3y **6a**, 45% (b)



4y **6b**, 62% (c)

In an 8 mL screw-cap vial was charged with allene (**3y**, 71.4 mg, 0.2 mmol), NBS (53.4 mg, 0.3 mmol) and CH_3CN (2.0 mL). The resulting suspension was stirred at 35℃ for 24 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 5:1) to afford **6a** (39.2 mg, 45%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H), 7.49 – 7.36 (m, 8H), 4.12 (q, J = 7.2 Hz, 1H), 3.84 (ddd, J = 12.0, 6.0, 2.0 Hz, 1H), 3.48 (ddd, J = 12.0, 10.4, 3.7 Hz, 1H), 3.23 – 3.17 (m, 1H), 2.81 (ddd, J = 16.7, 10.4, 6.0 Hz, 1H), 2.30 (ddd, J = 17.0, 3.8, 2.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 139.4, 136.7, 130.1, 129.2, 129.1, 128.8, 127.7 (t, *J* = 282.8 Hz), 127.5, 117.0, 116.0, 81.0, 58.2, 53.6, 47.3 (t, *J* = 20.2 Hz), 30.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.10 (AB-t, *J* = 206.8, 15.0 Hz, 2F); **IR** (thin film) ν 2960, 2214, 1956, 1259, 1020, 797, 695 cm^{-1}; **MS** (ESI): *m/z* 458 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{20}H_{16}NOF_2SNaBr$ $[M+Na]^+$: 458.0104; Found: 458.0107.

In an 8 mL screw-cap vial was charged with allene (**4y**, 49.8 mg, 0.2 mmol), NBS (53.4 mg, 0.3 mmol) and CH_3CN (2.0 mL). The resulting suspension was stirred at 35℃ for 24 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 5:1) to afford **6b** (40.6 mg, 62%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.44 – 7.36 (m, 3H), 6.07 (tt, *J* = 56.0, 4.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.80 (ddd, *J* = 12.1, 6.0, 2.4 Hz, 1H), 3.53 (ddd, *J* = 12.1, 10.0, 4.0 Hz, 1H), 2.86 (dd, *J* = 4.5, 2.1 Hz, 1H), 2.71 (ddd, *J* = 17.3, 10.0, 6.0 Hz, 1H), 2.36 (ddd, *J* = 17.3, 4.0, 2.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 138.9, 129.3, 128.9, 127.5, 116.9, 116.4, 115.0 (t, *J* = 242.4 Hz), 80.5 (t, *J* = 10.1 Hz), 58.1, 43.5 (t, *J* = 20.2 Hz), 30.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.36 (ddt, *J* = 56.4, 15.0, 3.8 Hz, 2F); **IR** (thin film) ν 2922, 2214, 1463, 1259, 1084, 1020, 797 cm^{-1}; **MS** (ESI): *m/z* 350 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{14}H_{12}NOF_2NaBr$ $[M+Na]^+$: 349.9968; Found: 349.9962.

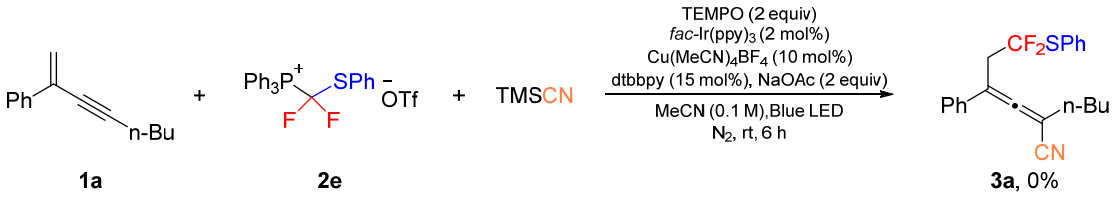


3a **7**, 65% (d)

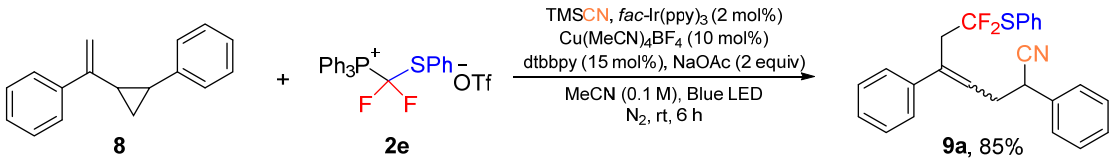
In an 8 mL screw-cap vial was charged with allene (**3a**, 52.2 mg, 0.2 mmol), *m*-CPBA (103.5 mg, 0.6 mmol) and DCM (2.0 mL). The resulting suspension was stirred at room temperature for 24 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford **7** (52.1 mg, 65%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 8.00 (m, 2H), 7.80 – 7.77 (m, 1H), 7.66 - 7.62 (m, 2H), 7.42 – 7.34 (m, 5H), 3.62 (t, *J* = 16.0 Hz, 2H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.40 – 1.34 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.6, 135.8, 132.4, 131.7, 131.0, 129.6, 129.1, 129.1, 126.8, 122.8 (t, *J* = 282.8 Hz), 114.5, 101.6, 86.7, 31.5, 30.4 (t, *J* = 20.2 Hz), 29.6, 22.0, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.85 (t, *J* = 17.9 Hz, 2F); **IR** (thin film) ν 2960, 2214, 1259, 1086, 1019, 797, 690 cm^{-1}; **MS** (ESI): *m/z* 424 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{22}H_{21}NO_2F_2SNa$ $[M+Na]^+$: 424.1159; Found: 424.1156.

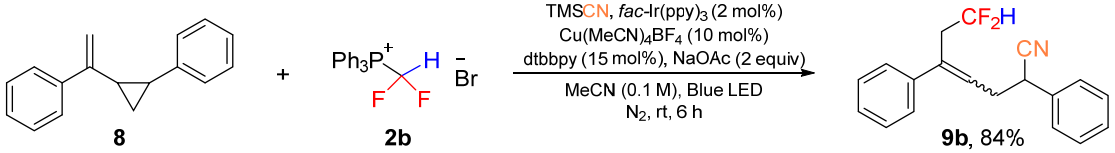
6. Mechanistic Studies

Radical Inhibition Experiment



Radical Clock Experiment





An 8 mL screw-cap vial equipped with a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (2.6 mg, 0.004 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (8.0 mg, 0.03 mmol), $Ph_3PCF_2SPhOTf$ (114.0 mg, 0.2 mmol), $Cu(MeCN)_4BF_4$ (6.3 mg, 0.02 mmol) and sodium acetate (32.8 mg, 0.4 mmol). The vial was evacuated and backfilled with nitrogen for three times. Then, MeCN (2.0 mL), TMSCN (50 μL, 0.4 mmol) and **8** (44.0 mg, 0.2 mmol) were added via a syringe. The reaction mixture was placed at a distance of 10 cm from a 40 W blue LEDs and stirred at room temperature for 6h. Then, saturated NaCl aqueous solution was added and the reaction mixture was extracted with ethyl acetate. The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column

chromatography to give the desired product **9a** (68.9 mg, 85%) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.12 (m, 9H), 6.96 – 6.91 (m, 2H), 5.70 (t, *J* = 7.4 Hz, 1H), 3.73 (t, *J* = 7.1 Hz, 1H), 3.12 (t, *J* = 14.2 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.0, 136.9 (t, *J* = 10.1 Hz), 136.2, 135.0, 129.8, 129.1, 129.0, 128.5, 128.4, 128.3, 128.3 (t, *J* = 282.8 Hz), 127.5, 127.0, 120.4, 48.1 (t, *J* = 20.2 Hz), 37.4, 35.2, 29.8, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -69.89 (t, *J* = 14.2 Hz, 2F); **IR** (thin film) ν 2961, 2214, 1259, 1021, 1019, 797, 697 cm^{-1}; **MS** (ESI): *m/z* 428 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{25}H_{21}NF_2NaS$ $[M+Na]^+$: 428.1260; Found: 428.1264.

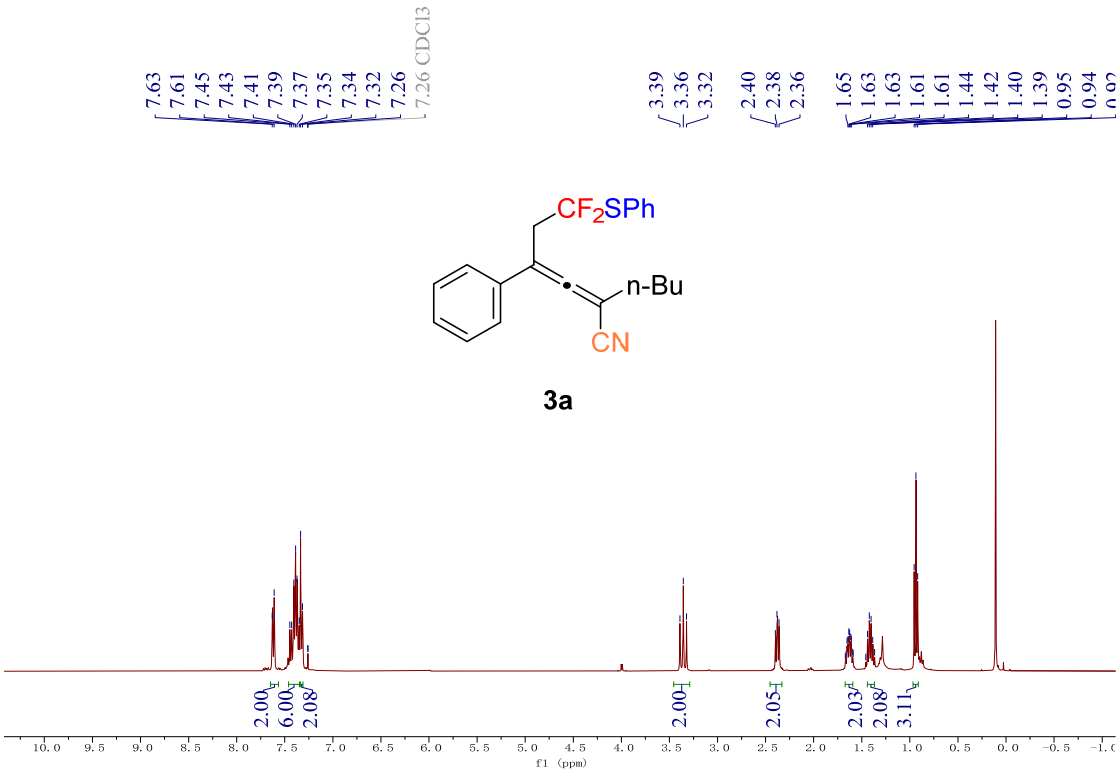
9b (49.9 mg, 84%), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 6H), 7.16 – 7.12 (m, 2H), 6.91 – 6.83 (m, 2H), 5.62 (t, *J* = 7.4 Hz, 1H), 5.56 (t, *J* = 4.9 Hz, 1H), 3.72 (t, *J* = 7.1 Hz, 1H), 2.79 (td, *J* = 16.3, 4.9 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.6, 137.5 (t, *J* = 10.1 Hz), 135.0, 129.1, 128.7, 128.3, 128.1, 127.8, 127.5, 126.5, 120.4, 115.5 (t, *J* = 242.4 Hz), 44.2 (t, *J* = 20.2 Hz), 37.4, 35.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.98 (dt, *J* = 56.4, 16.3 Hz, 2F); **IR** (thin film) ν 2922, 2214, 1259, 1021, 797, 699 cm^{-1}; **MS** (ESI): *m/z* 320 $[M+Na]^+$; **HRMS** (ESI-TOF): *m/z* Calculated for $C_{19}H_{17}NF_2Na$ $[M+Na]^+$: 320.1227; Found: 320.1228.

7. References

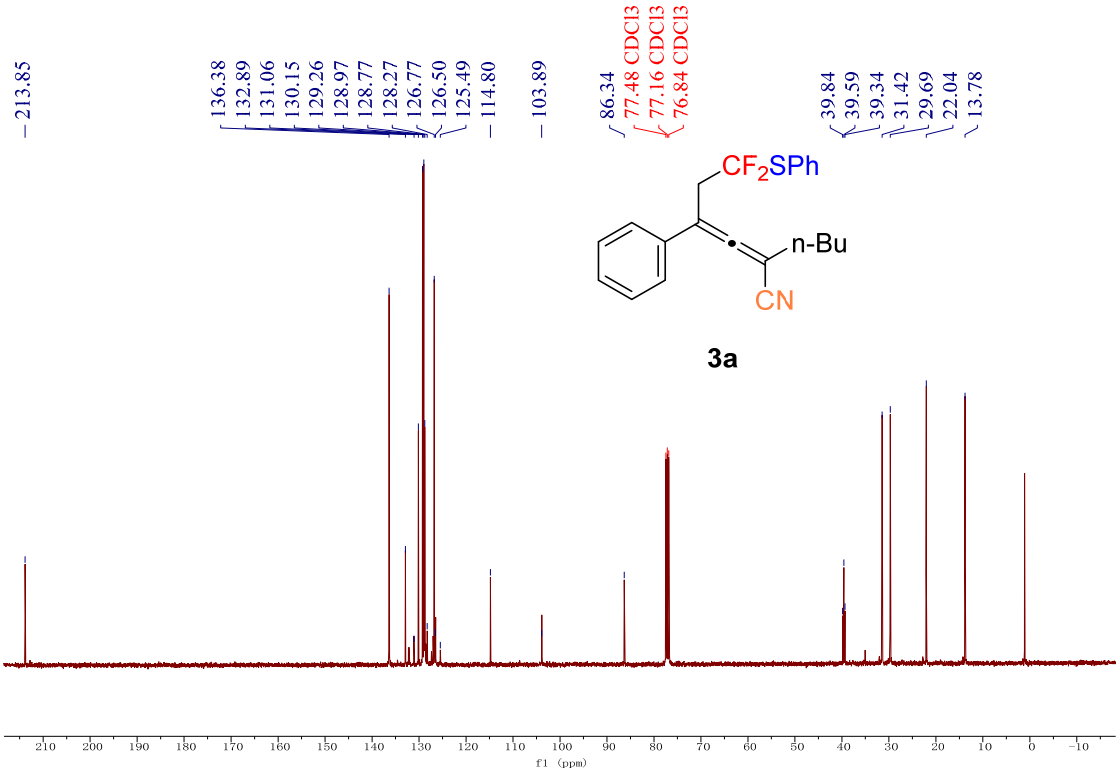
1. Y. L. Song, C. L. Fu and S. M. Ma, *ACS Catal.*, 2021, **11**, 10007-10013.
2. L. H. Wang, R. Y. Ma, J. Q. Sun, G. F. Zheng and Q. Zhang, *Chem. Sci.*, 2022, **13**, 3169-3175.
3. H. Y. Chen, J. Zhang and D. Z. Wang, *Org. Lett.*, 2015, **17**, 2098-2101.
4. M. Taj Muhammad, Y. H. Jiao, C. Q. Ye, M. F. Chiou, M. Israr, X. T. Zhu, Y. J. Li, Z. H. Wen, A. Studer and H. L. Bao, *Nat. Commun.*, 2020, **11**, 8.
5. S. Liu, Y. G. Huang, F. L. Qing and X. H. Xu, *Eur. J. Org. Chem.*, 2023, **26**, 5.
6. H. Y. Chen, X. R. Shao, H. F. Wang and H. B. Zhai, *Org. Chem. Front.*, 2017, **4**, 409-412.
7. X. Y. Dong, T. Y. Zhan, S. P. Jiang, X. D. Liu, L. Ye, Z. L. Li, Q. S. Gu and X. Y. Liu, *Angew. Chem. Int. Ed.*, 2021, **60**, 2160-2164.
8. F. L. Sun, J. Ni, G. J. Cheng and X. J. Fang, *Chem. Eur. J.*, 2020, **26**, 5956-5960.
9. Q. Zhang, M. T. Muhammad, M. F. Chiou, Y. H. Jiao, H. L. Bao and Y. J. Li, *Org. Lett.*, 2020, **22**, 5261-5265.
10. L. Chen, C. Lin, S. M. Zhang, X. J. Zhang, J. M. Zhang, L. J. Xing, Y. G. Guo, J. Feng, J. Gao and D. Du, *ACS Catal.*, 2021, **11**, 13363-13373.
11. X. T. Zhu, W. L. Deng, M. F. Chiou, C. Q. Ye, W. J. Jian, Y. H. Zeng, Y. H. Jiao, L. Ge, Y. J. Li, X. H. Zhang and H. L. Bao, *J. Am. Chem. Soc.*, 2019, **141**, 548-559.
12. (a)Y. Y. Zhu, S. Liu, Y. E. Huang, F. L. Qing and X. H. Xu, *J. Fluor. Chem.*, 2022, **257**, 10; (b)A. L. Trifonov, L. I. Panferova, V. V. Levin, A. D. Volodin, A. A. Korlyukov and A. D. Dilman, *J. Fluor. Chem.*, 2019, **220**, 78-82.
13. N. B. Heine and A. Studer, *Org. Lett.*, 2017, **19**, 4150-4153.
14. T. Besset, P. Jubault, X. Pannecoucke and T. Poisson, *Org. Chem. Front.*, 2016, **3**, 1004-1010.

8. Copies of ^{1}H, ^{19}F, and ^{13}C NMR Spectra for the Products

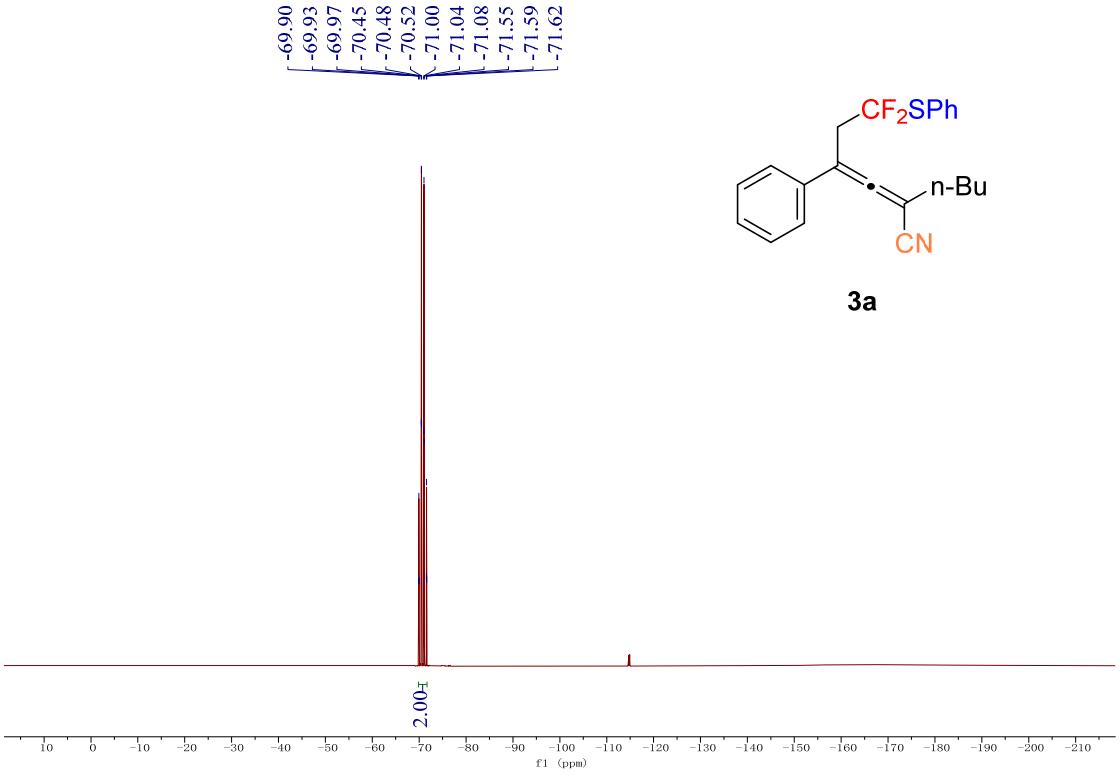
^{1}H NMR (400 MHz, $CDCl_3$)



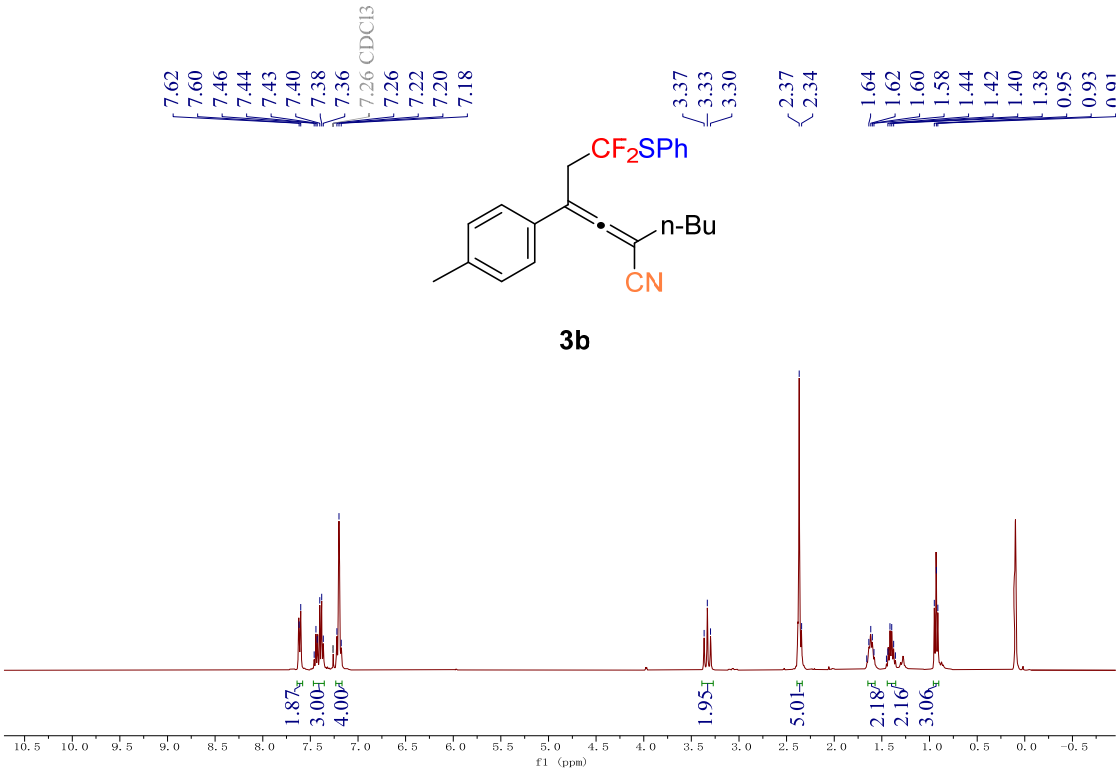
^{13}C NMR (101 MHz, $CDCl_3$)



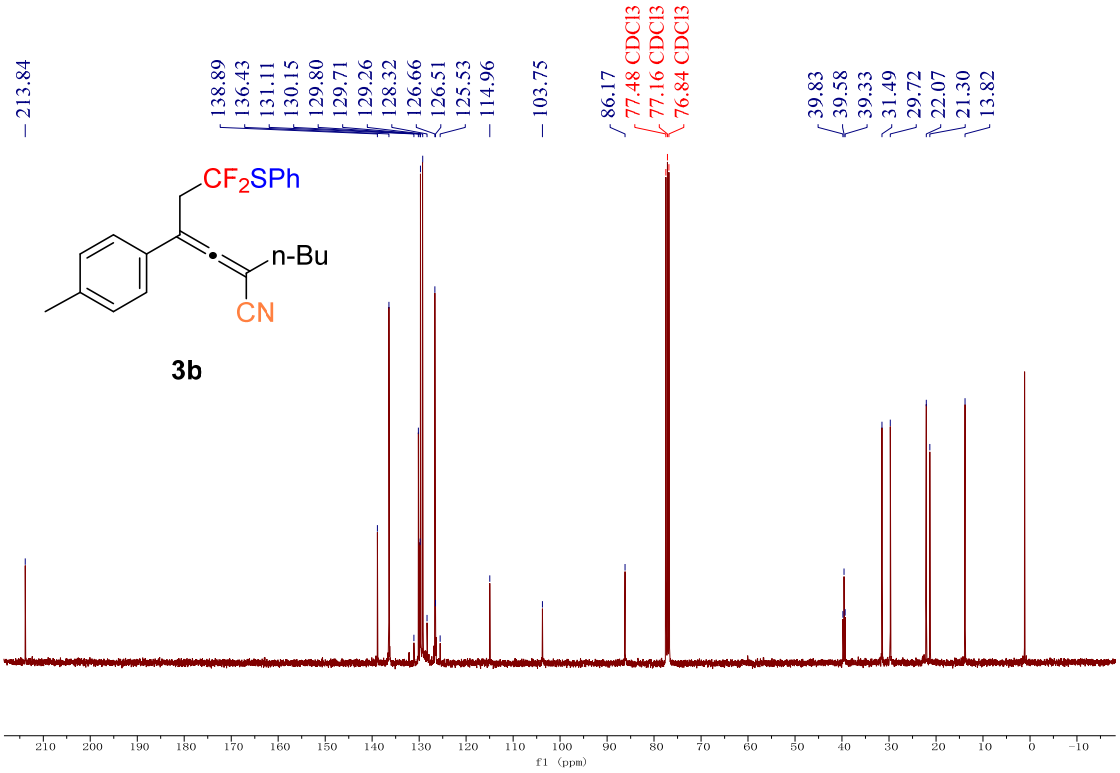
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

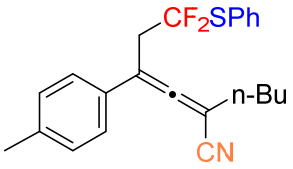


^{13}C NMR (101 MHz, $CDCl_3$)

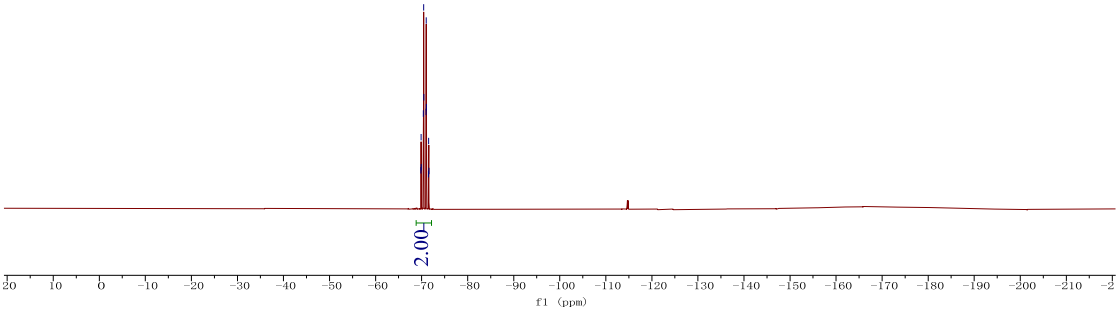


^{19}F NMR (376 MHz, $CDCl_3$)

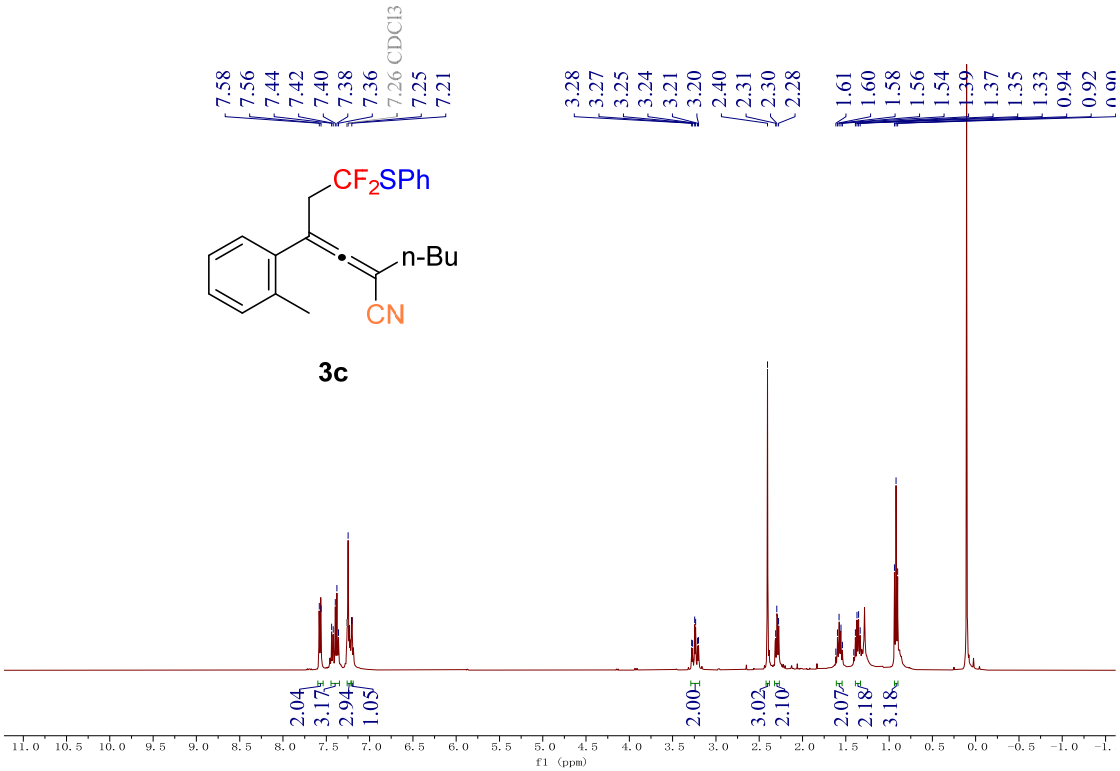

-69.85
-69.89
-69.91
-70.39
-70.43
-70.46
-70.95
-70.99
-71.03
-71.49
-71.53
-71.58


CF2SPh
n-Bu
CN

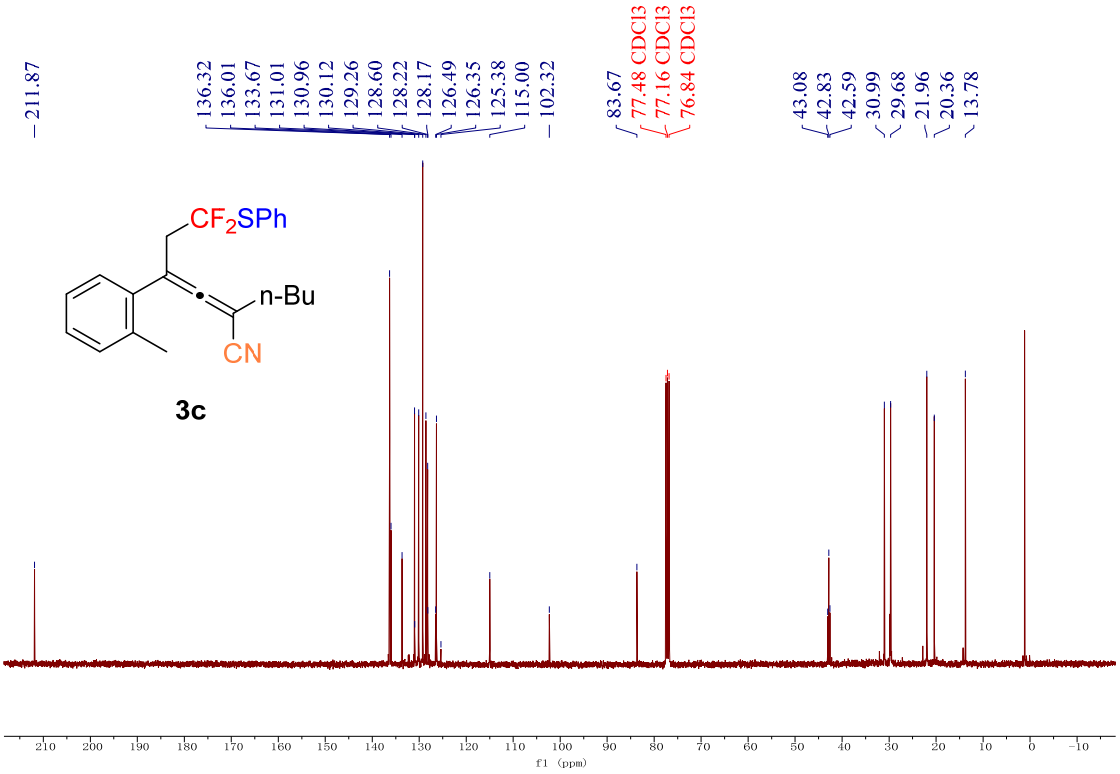
3b


2.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

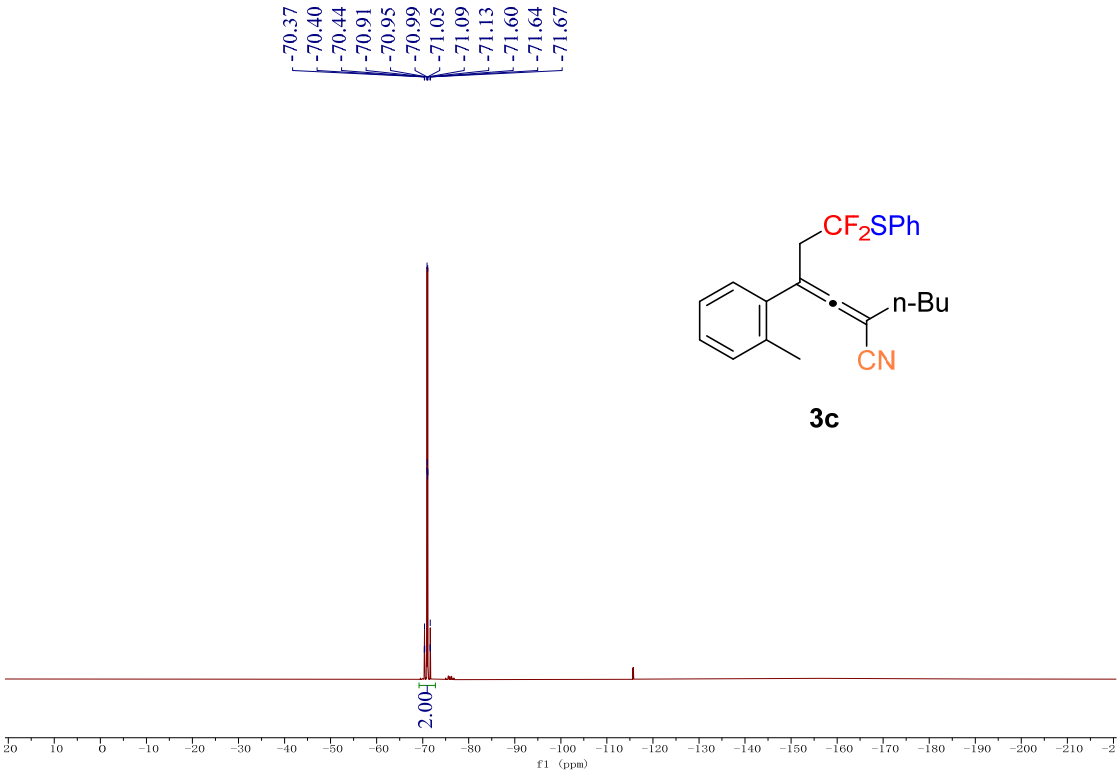
^{1}H NMR (400 MHz, $CDCl_3$)



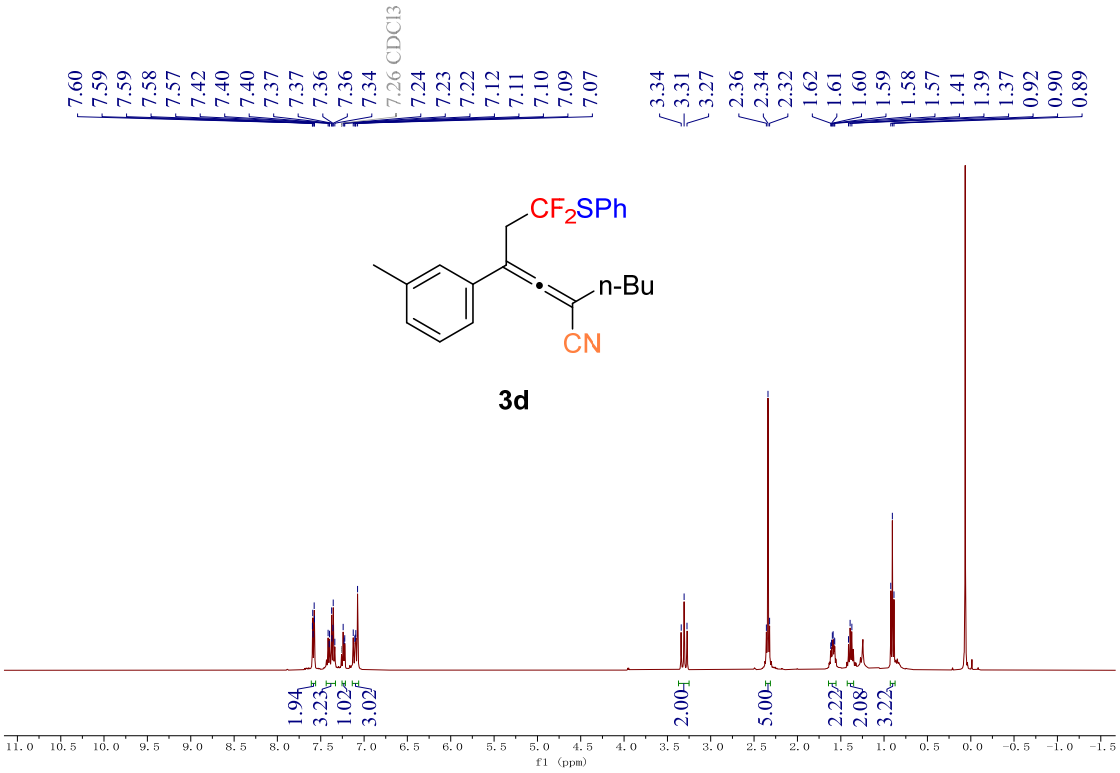
^{13}C NMR (101 MHz, $CDCl_3$)


211.87
136.32
136.01
133.67
131.01
130.96
130.12
129.26
128.60
128.22
128.17
126.49
126.35
125.38
115.00
102.32
83.67
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
43.08
42.83
42.59
30.99
29.68
21.96
20.36
13.78
CF2SPh
n-Bu
CN
3c
f1 (ppm)

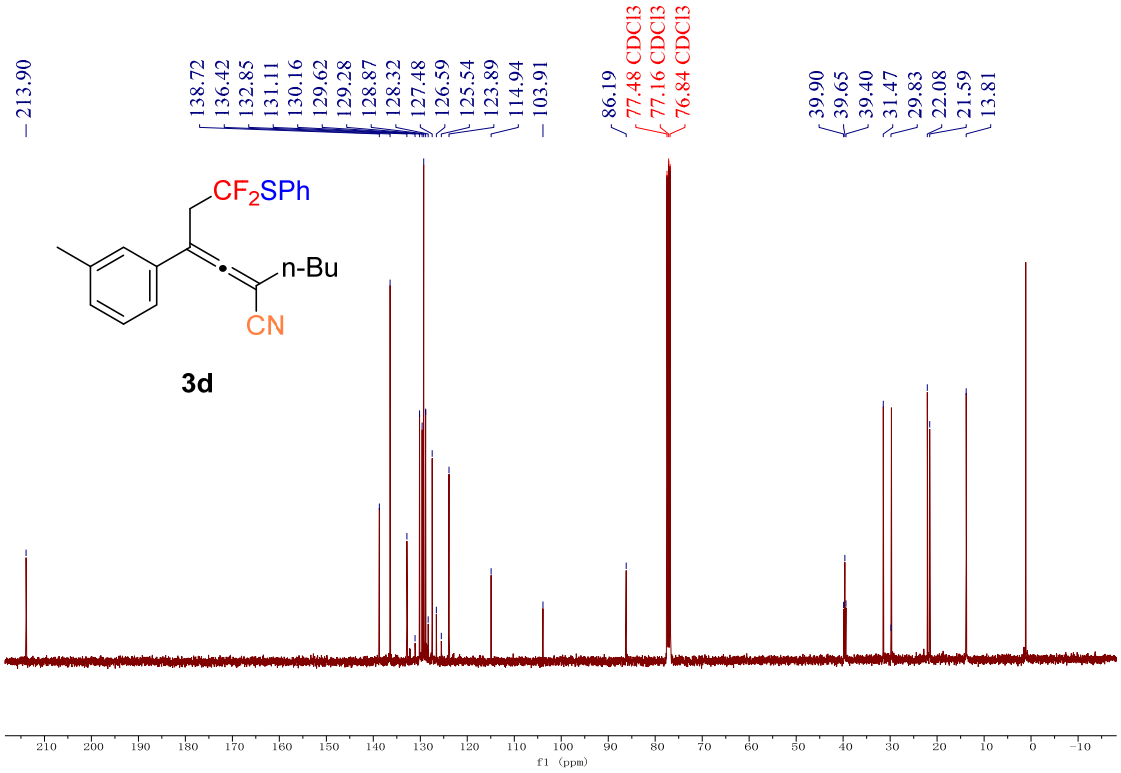
^{19}F NMR (376 MHz, $CDCl_3$)



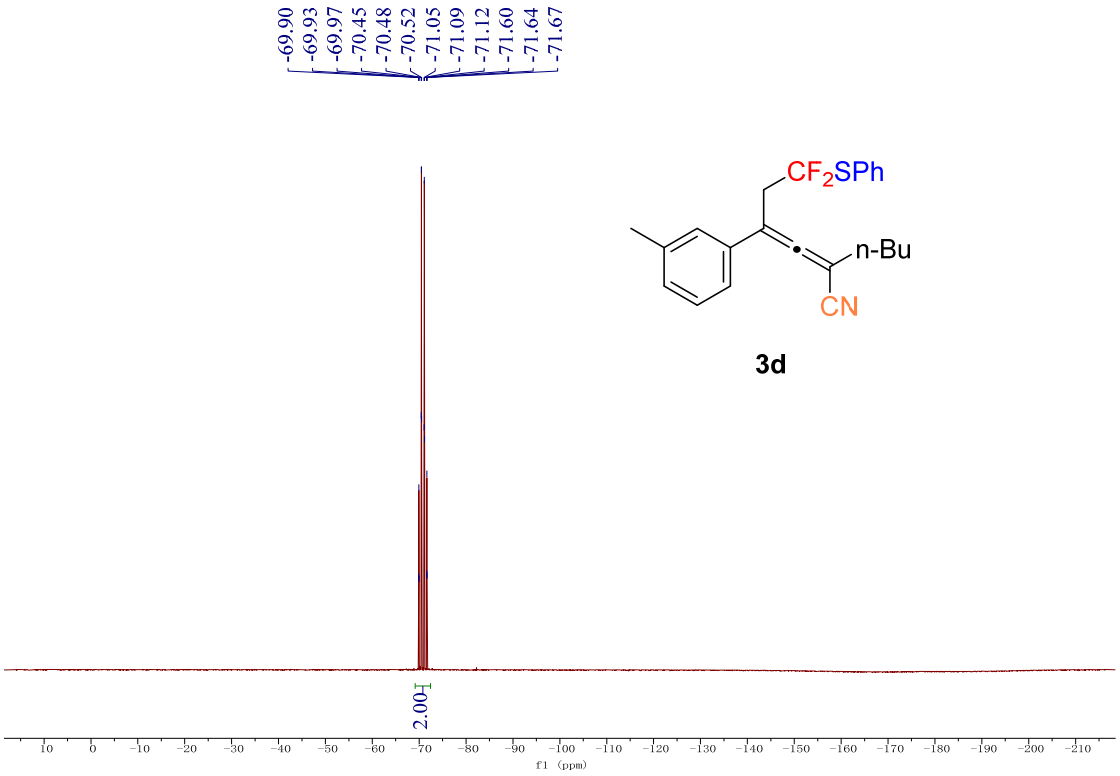
^{1}H NMR (400 MHz, $CDCl_3$)



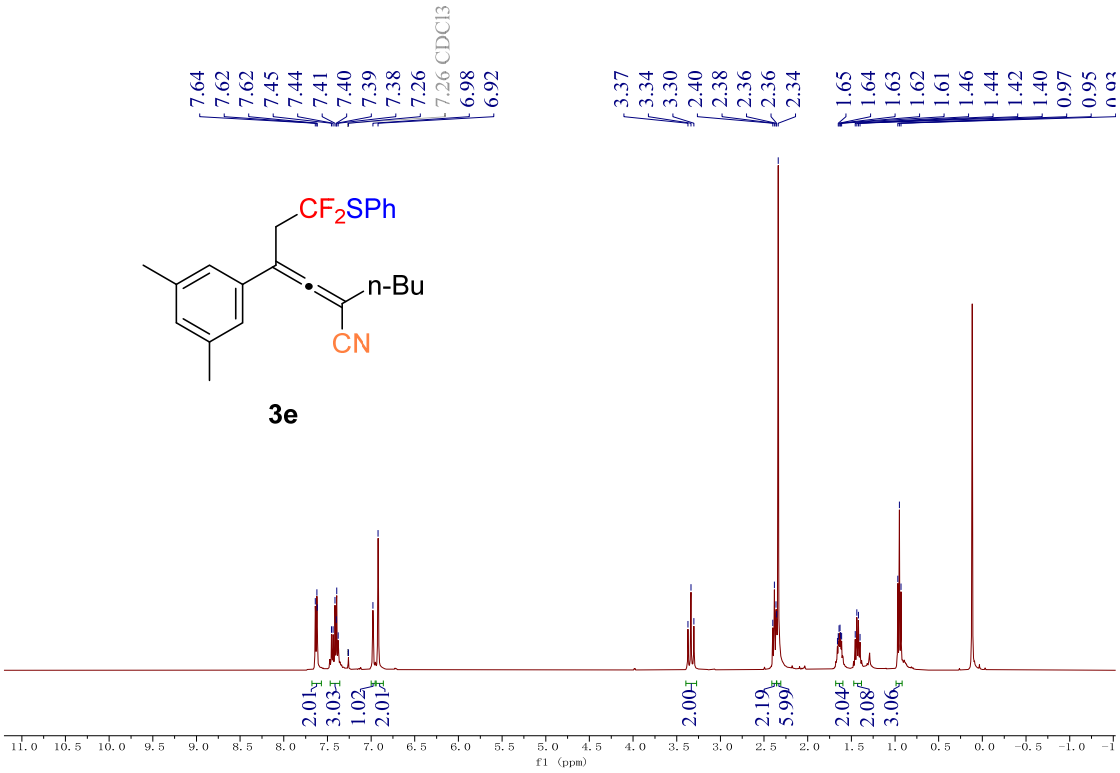
^{13}C NMR (101 MHz, $CDCl_3$)



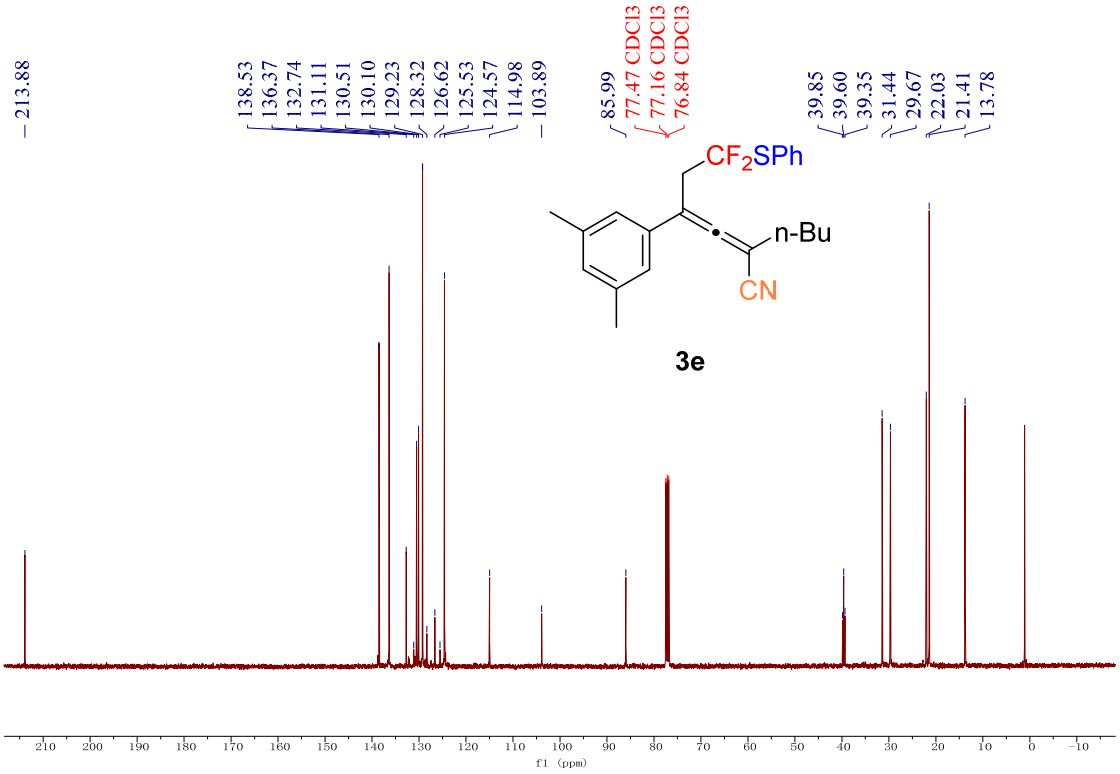
^{19}F NMR (376 MHz, $CDCl_3$)


-69.90
-69.93
-69.97
-70.45
-70.48
-70.52
-71.05
-71.09
-71.12
-71.60
-71.64
-71.67
CF2SPh
n-Bu
CN
3d
2.00
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

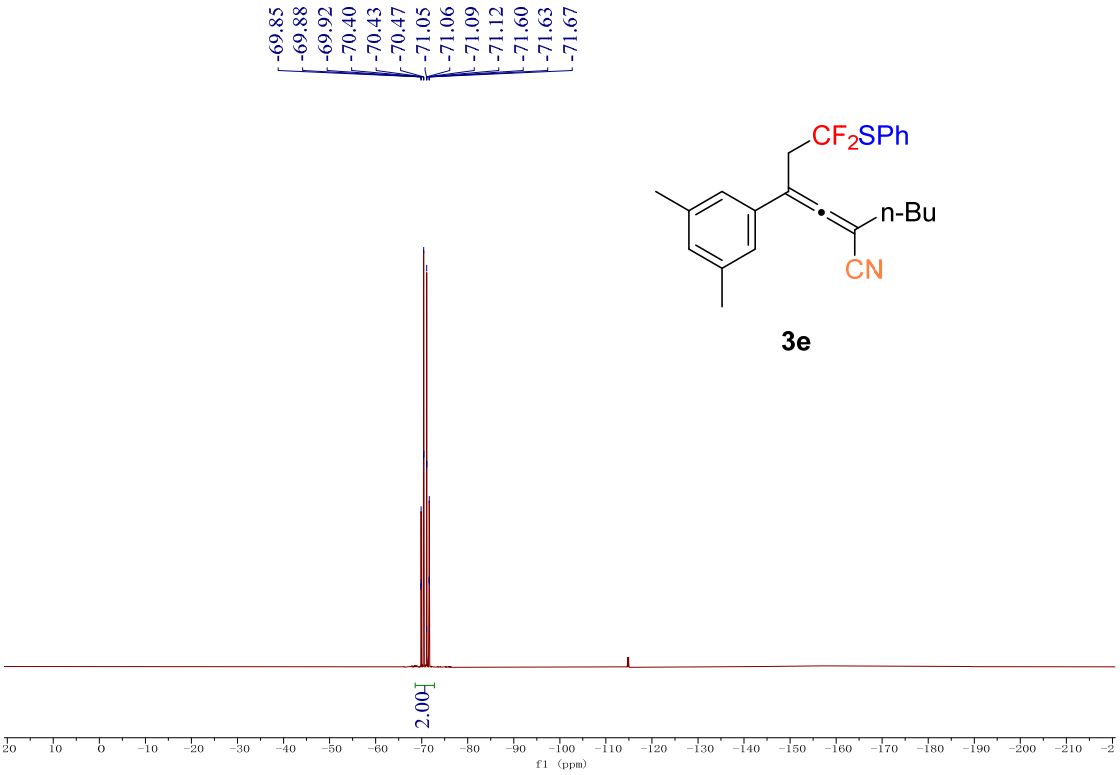
^{1}H NMR (400 MHz, $CDCl_3$)



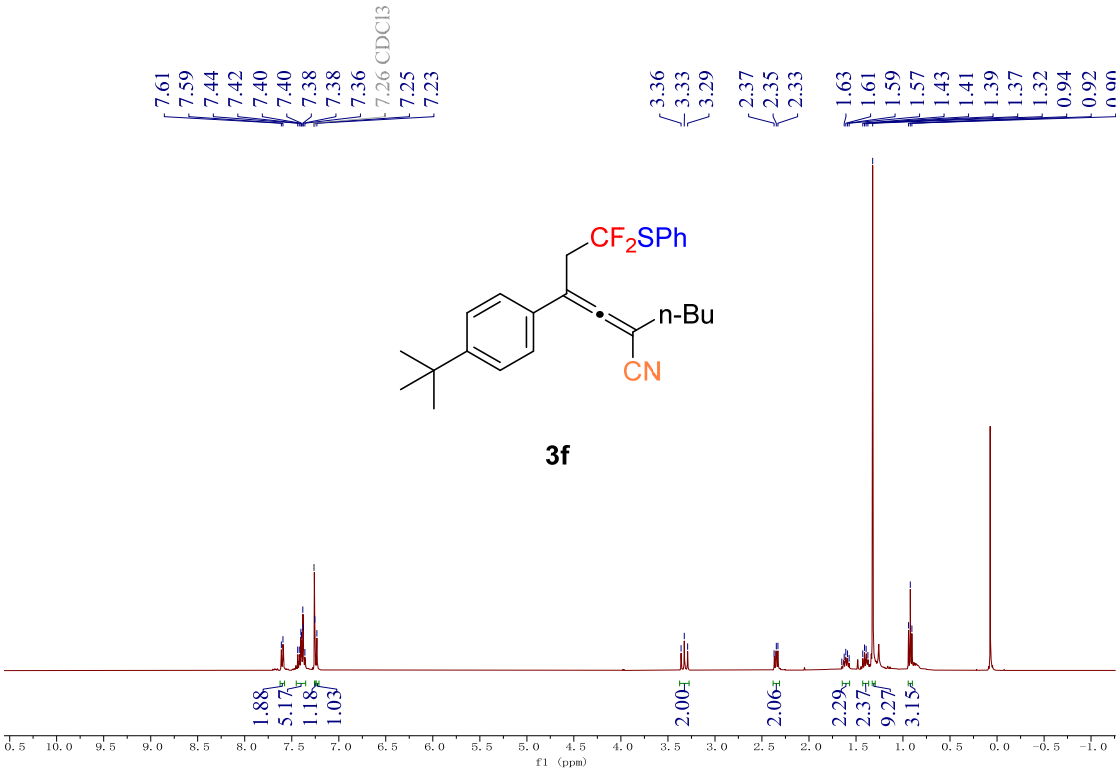
^{13}C NMR (101 MHz, $CDCl_3$)


213.88
138.53
136.37
132.74
131.11
130.51
130.10
129.23
128.32
126.62
125.53
124.57
114.98
103.89
85.99
77.47 CDCl3
77.16 CDCl3
76.84 CDCl3
39.85
39.60
39.35
31.44
29.67
22.03
21.41
13.78
CF2SPh
n-Bu
CN
3e
f1 (ppm)

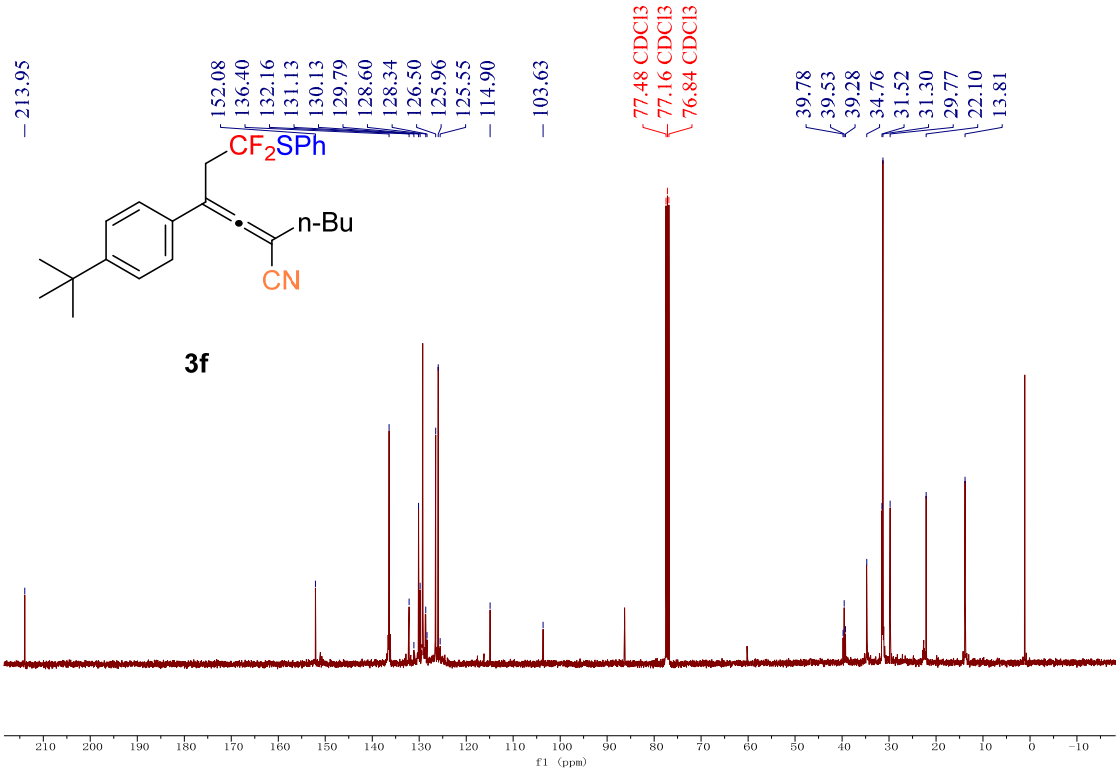
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

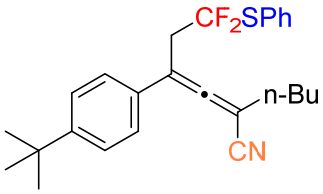


^{13}C NMR (101 MHz, $CDCl_3$)

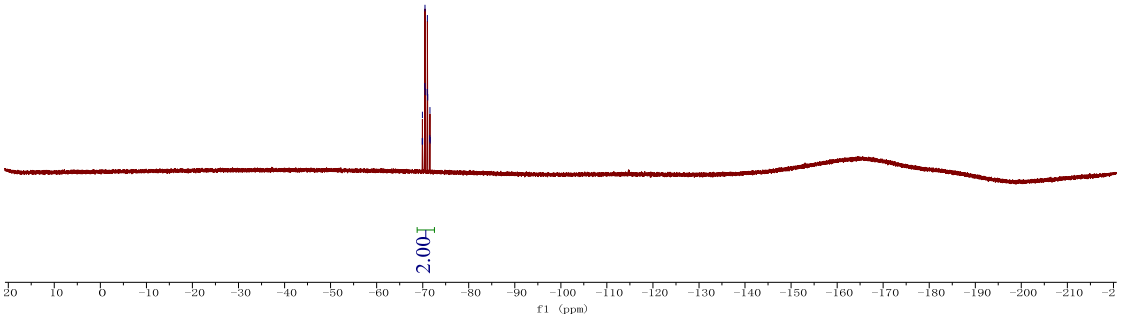


^{19}F NMR (376 MHz, $CDCl_3$)

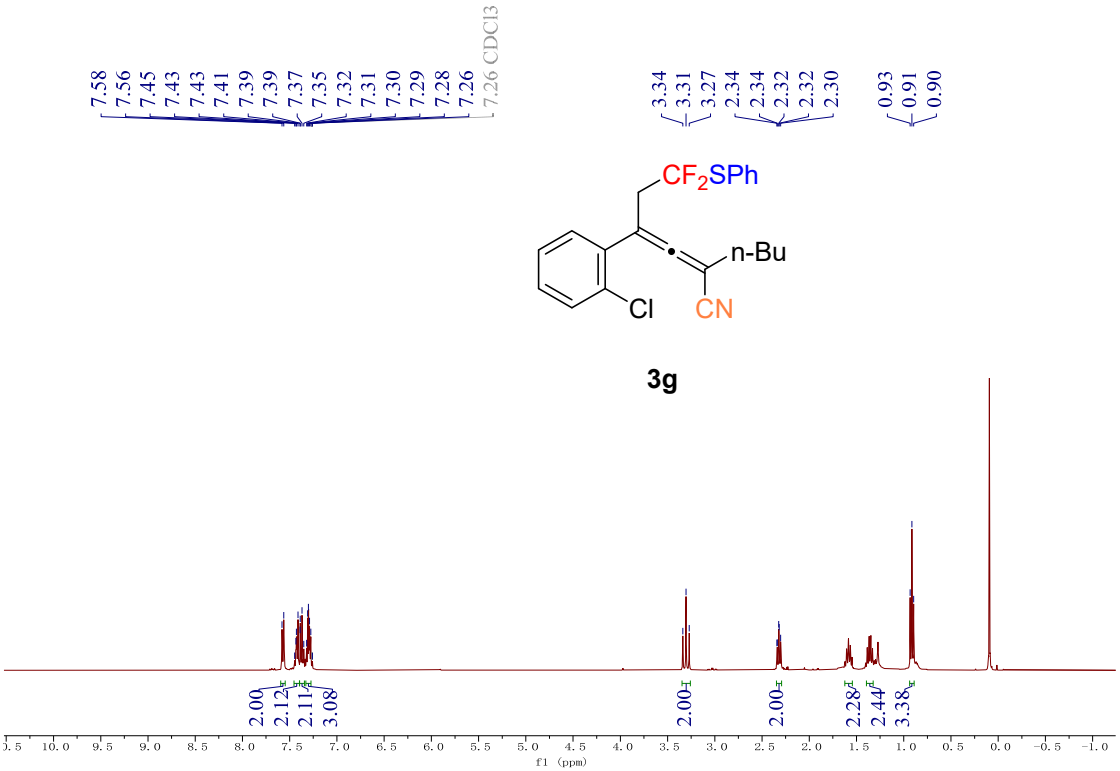

-69.92
-69.95
-69.99
-70.46
-70.50
-70.53
-71.00
-71.04
-71.08
-71.55
-71.59
-71.62


CF2SPh
n-Bu
CN

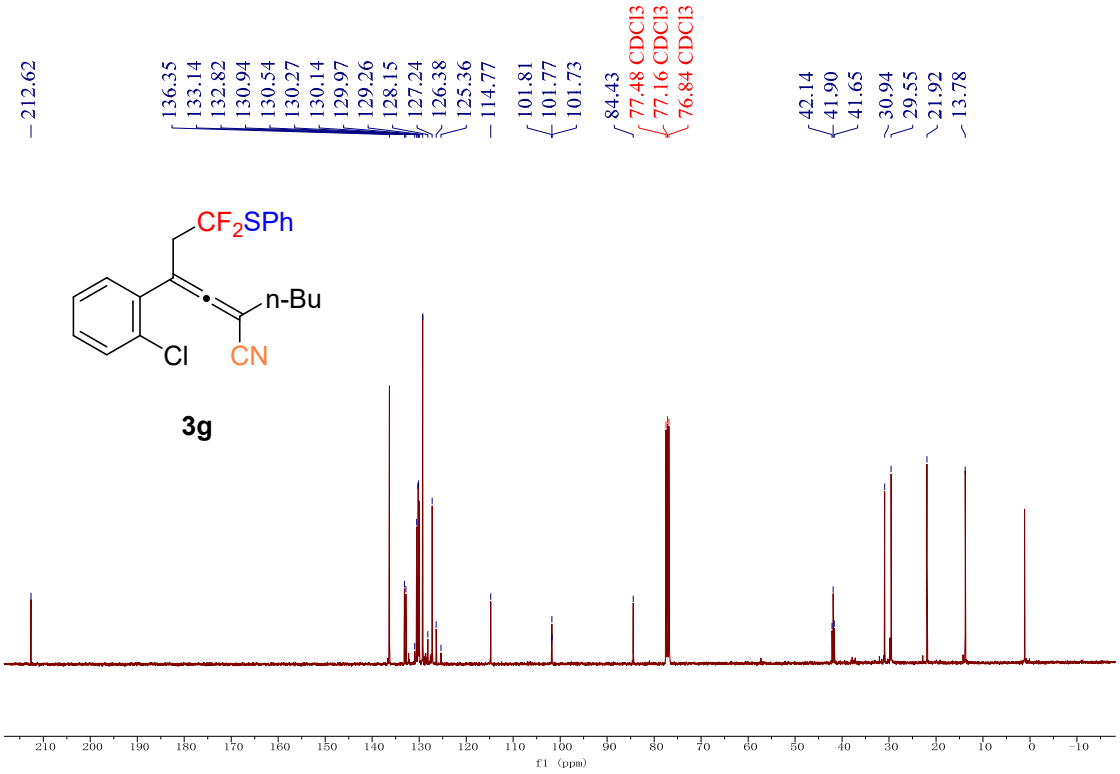
3f


2.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

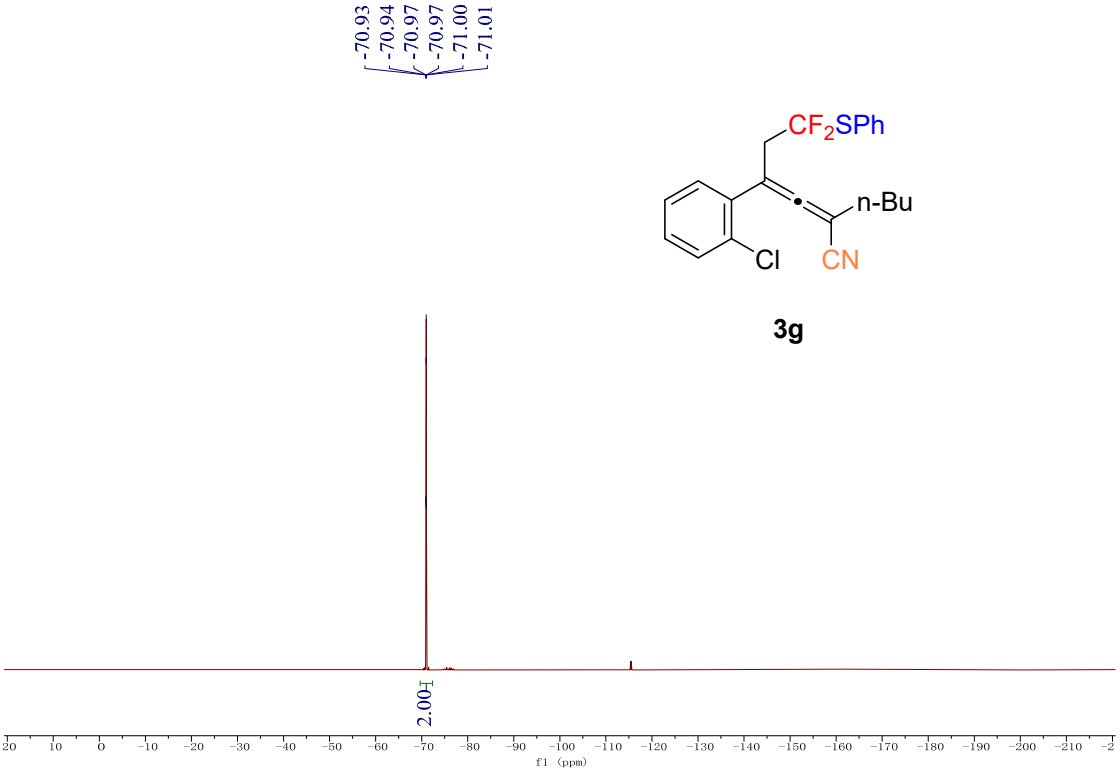
^{1}H NMR (400 MHz, $CDCl_3$)



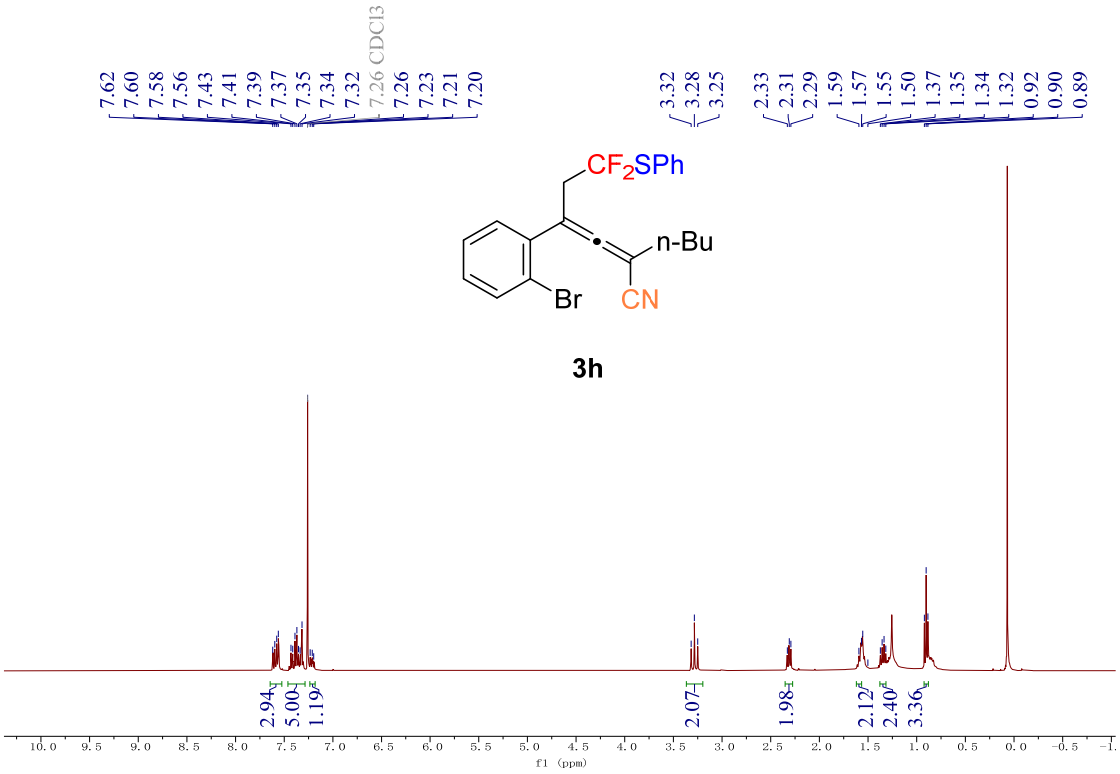
^{13}C NMR (101 MHz, $CDCl_3$)


212.62
136.35
133.14
132.82
130.94
130.54
130.27
130.14
129.97
129.26
128.15
127.24
126.38
125.36
114.77
101.81
101.77
101.73
84.43
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.14
41.90
41.65
30.94
29.55
21.92
13.78
CF2SPh
n-Bu
Cl
CN
3g
f1 (ppm)

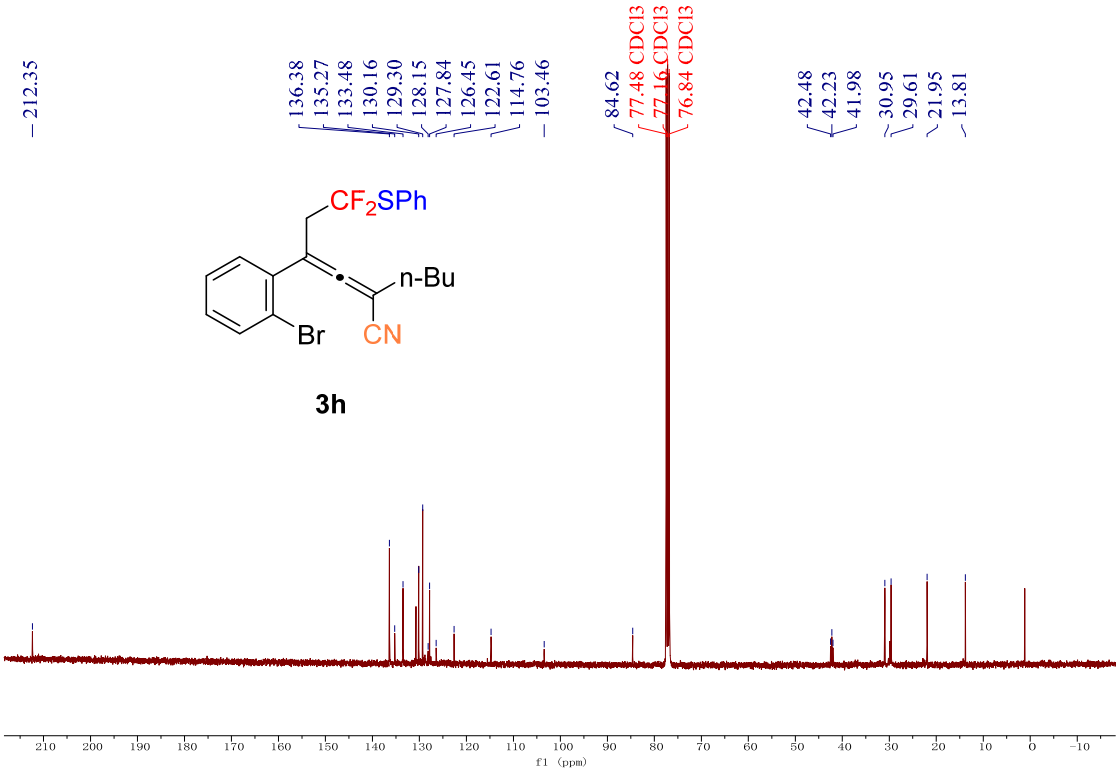
^{19}F NMR (376 MHz, $CDCl_3$)



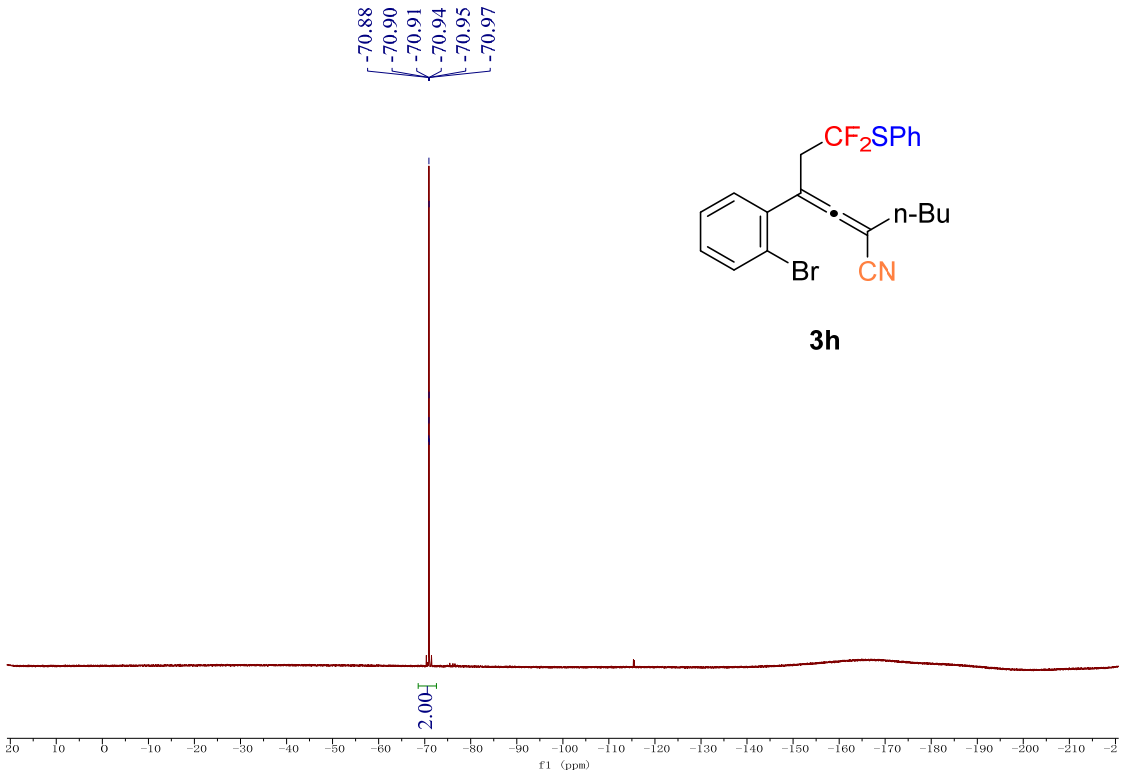
^{1}H NMR (400 MHz, $CDCl_3$)


7.62
7.60
7.58
7.56
7.43
7.41
7.39
7.37
7.35
7.34
7.32
7.26 CDCl3
7.26
7.23
7.21
7.20
3.32
3.28
3.25
2.33
2.31
2.29
1.59
1.57
1.55
1.50
1.37
1.35
1.34
1.32
0.92
0.90
0.89
CF2SPh
n-Bu
Br
CN
3h
2.94
5.00
1.19
2.07
1.98
2.12
2.40
3.36
f1 (ppm)

^{13}C NMR (101 MHz, $CDCl_3$)

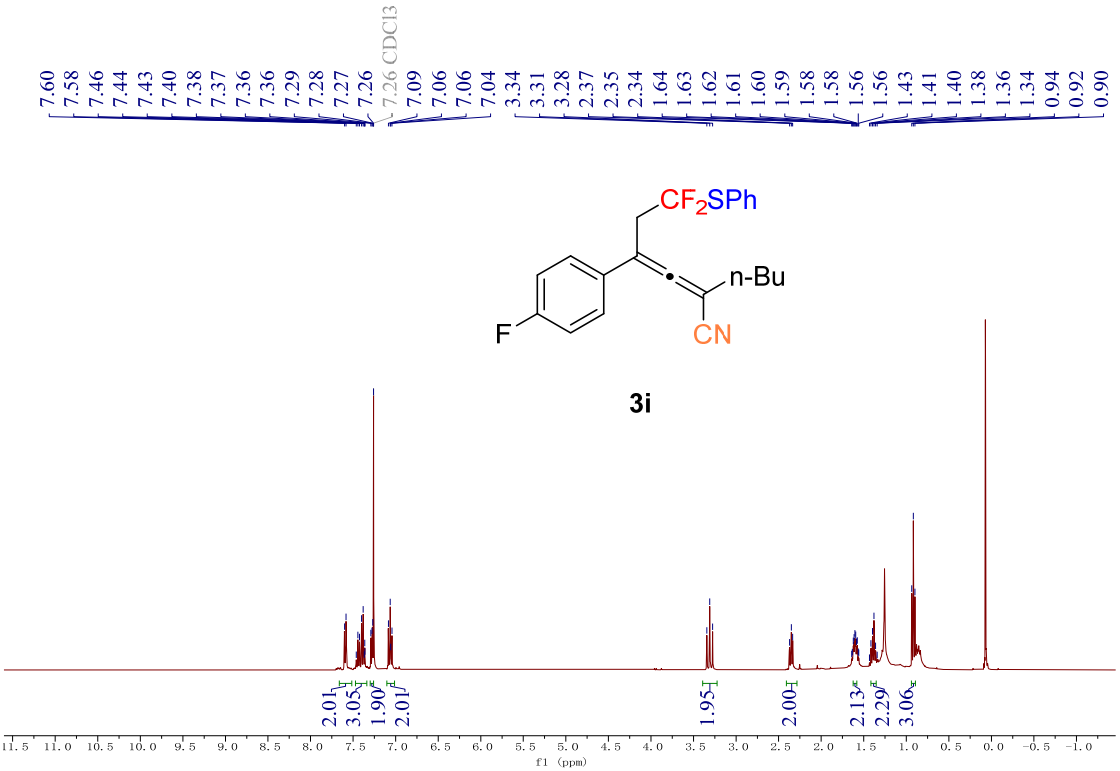


^{19}F NMR (376 MHz, $CDCl_3$)

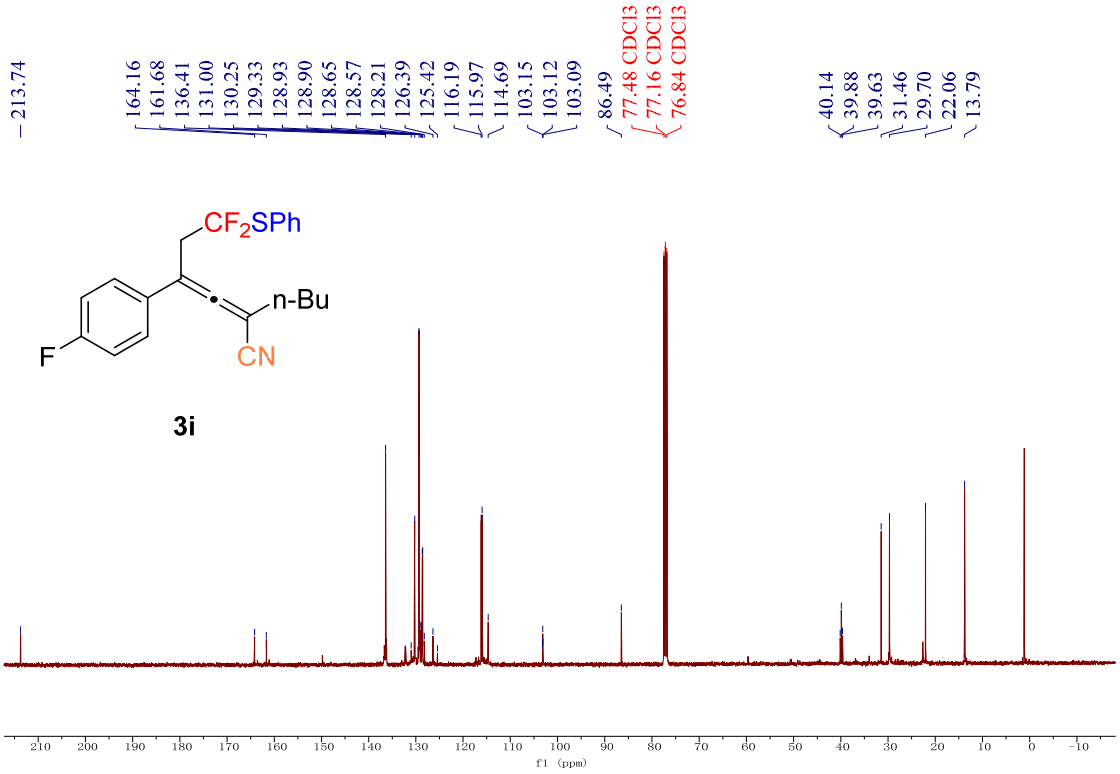


3h

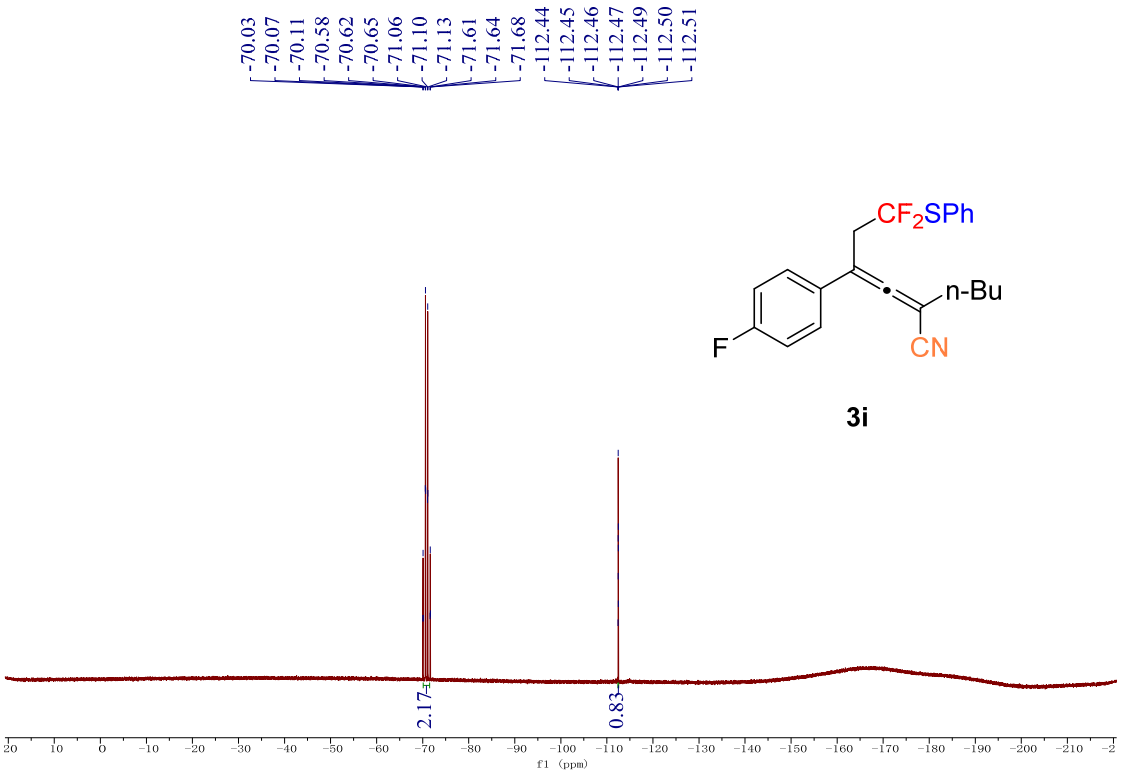
^{1}H NMR (400 MHz, $CDCl_3$)



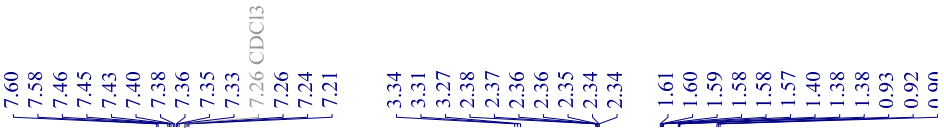
^{13}C NMR (101 MHz, $CDCl_3$)

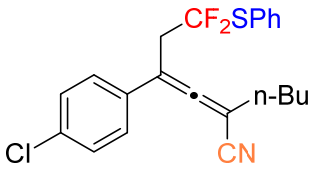

213.74
164.16
161.68
136.41
131.00
130.25
129.33
128.93
128.90
128.65
128.57
128.21
126.39
125.42
116.19
115.97
114.69
103.15
103.12
103.09
86.49
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
40.14
39.88
39.63
31.46
29.70
22.06
13.79
CF2SPh
n-Bu
CN
F
3i
f1 (ppm)

^{19}F NMR (376 MHz, $CDCl_3$)

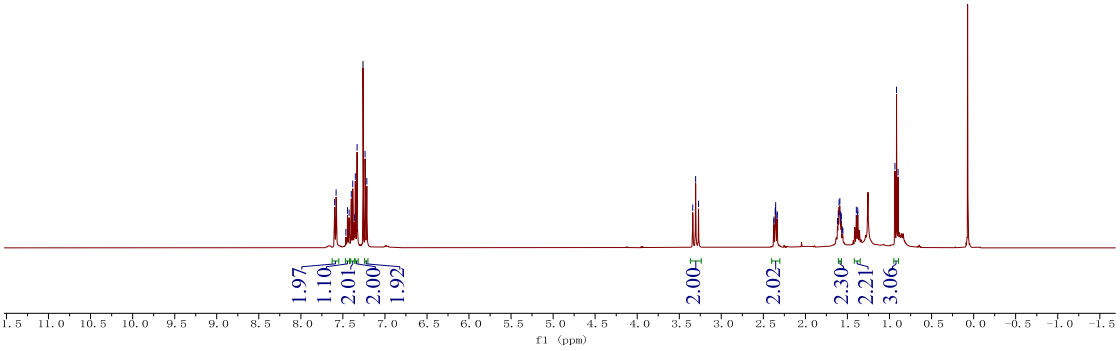


^{1}H NMR (400 MHz, $CDCl_3$)

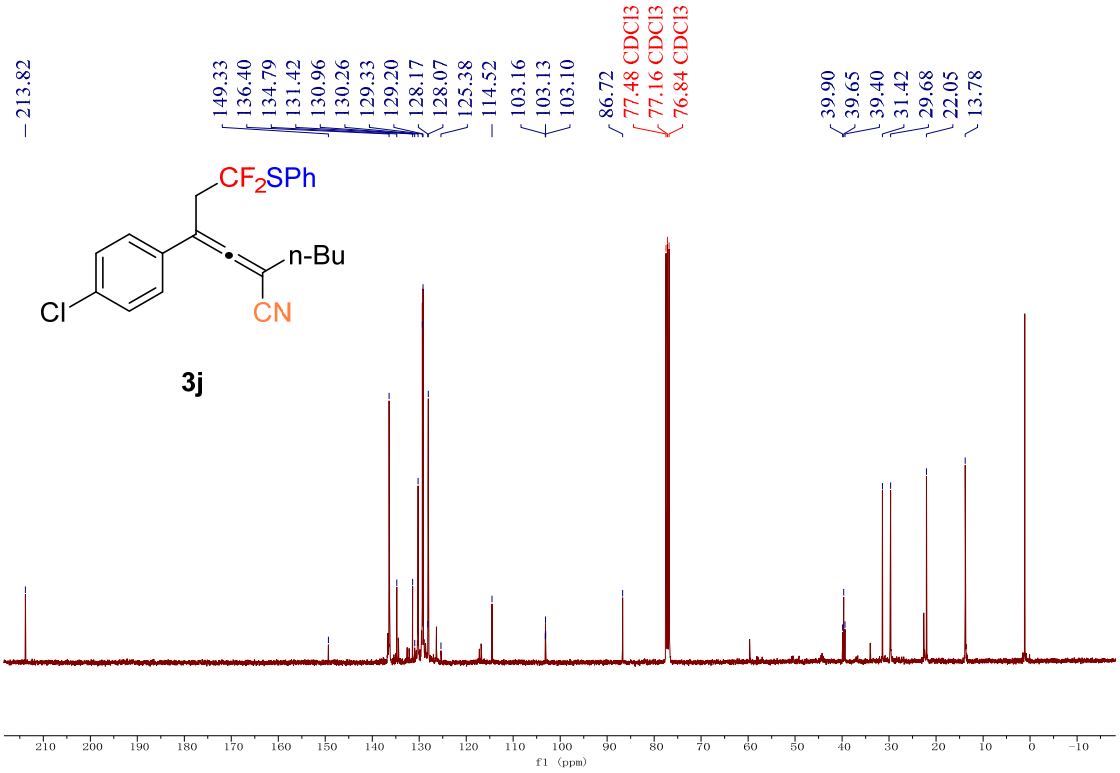

7.60
7.58
7.46
7.45
7.43
7.40
7.38
7.36
7.35
7.33
7.26 CDCl3
7.26
7.24
7.21
3.34
3.31
3.27
2.38
2.37
2.36
2.36
2.35
2.34
2.34
1.61
1.60
1.59
1.58
1.58
1.57
1.40
1.38
1.38
0.93
0.92


CF2SPh
n-Bu
Cl
CN

3j

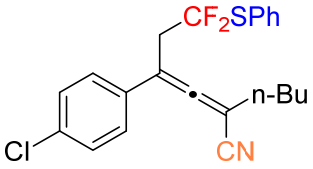

1.97
1.10
2.01
2.00
1.92
2.00
2.02
2.30
2.21
3.06
f1 (ppm)

^{13}C NMR (101 MHz, $CDCl_3$)

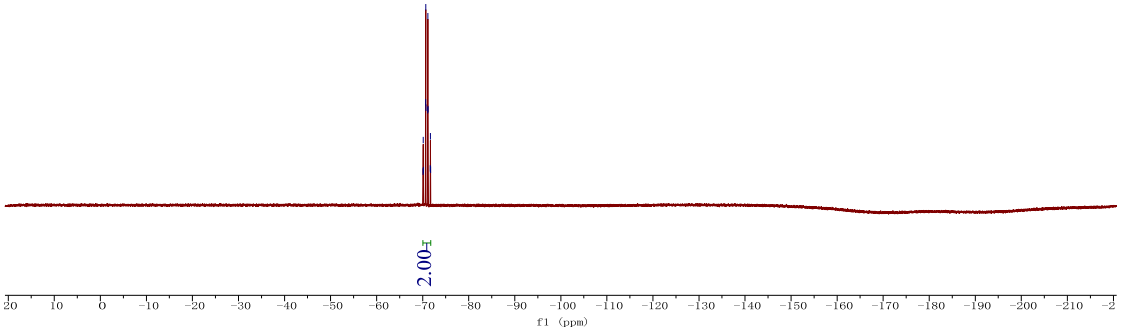


^{19}F NMR (376 MHz, $CDCl_3$)

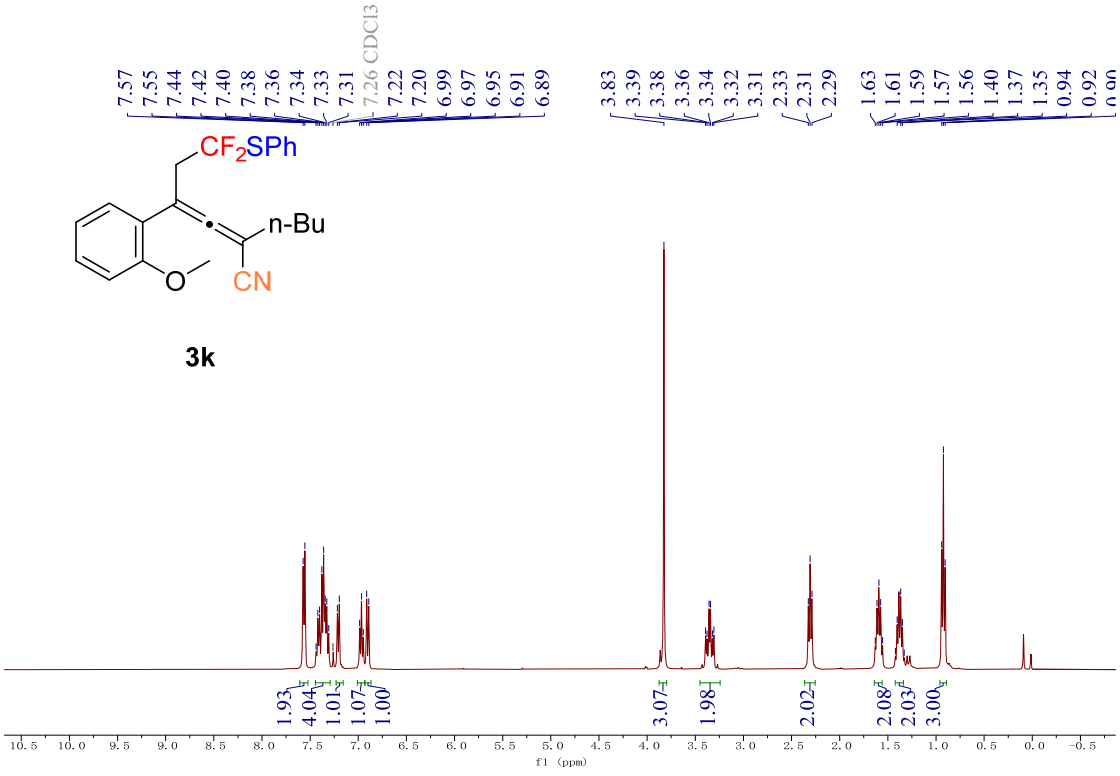

-70.07
-70.11
-70.15
-70.62
-70.66
-70.69
-71.10
-71.14
-71.18
-71.65
-71.69
-71.73


CF2SPh
n-Bu
Cl
CN

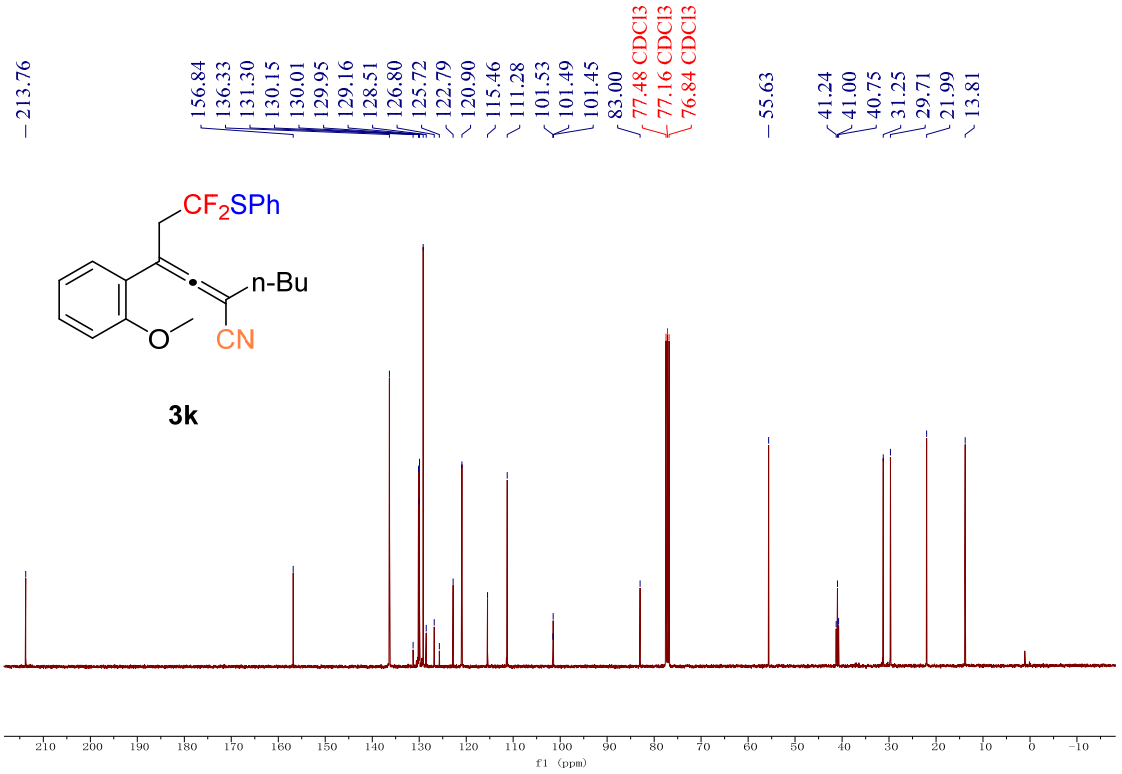
3j


2.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

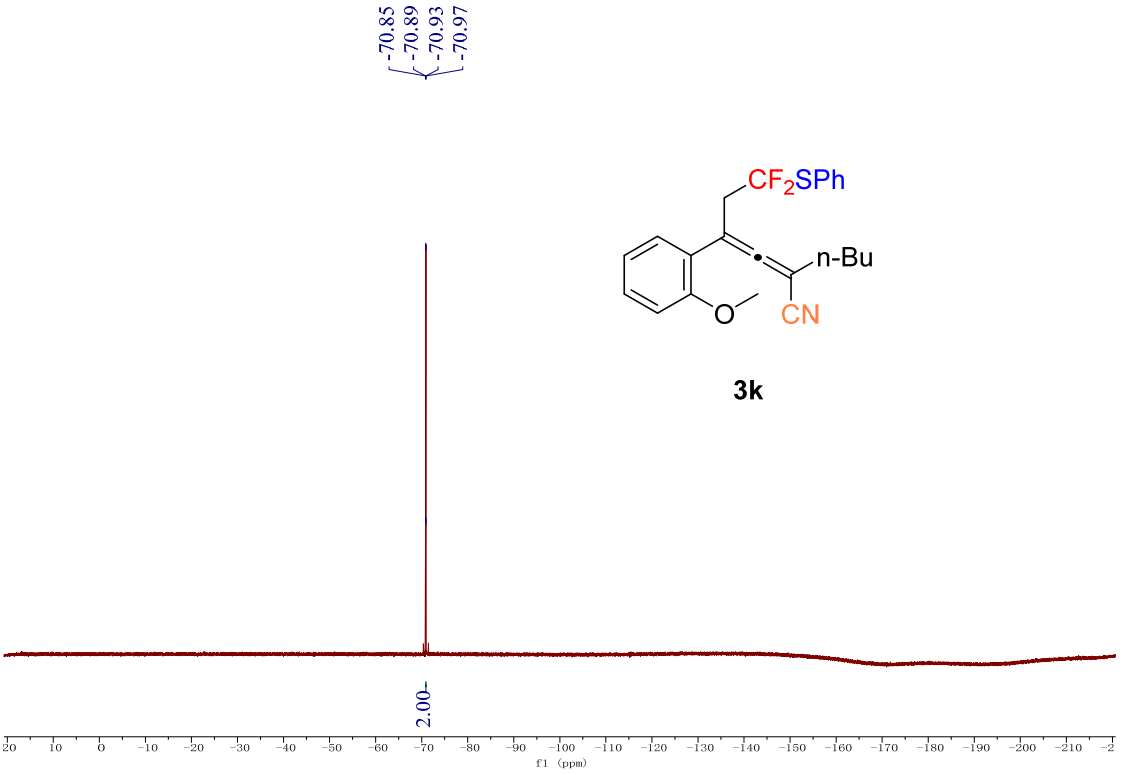
^{1}H NMR (400 MHz, $CDCl_3$)



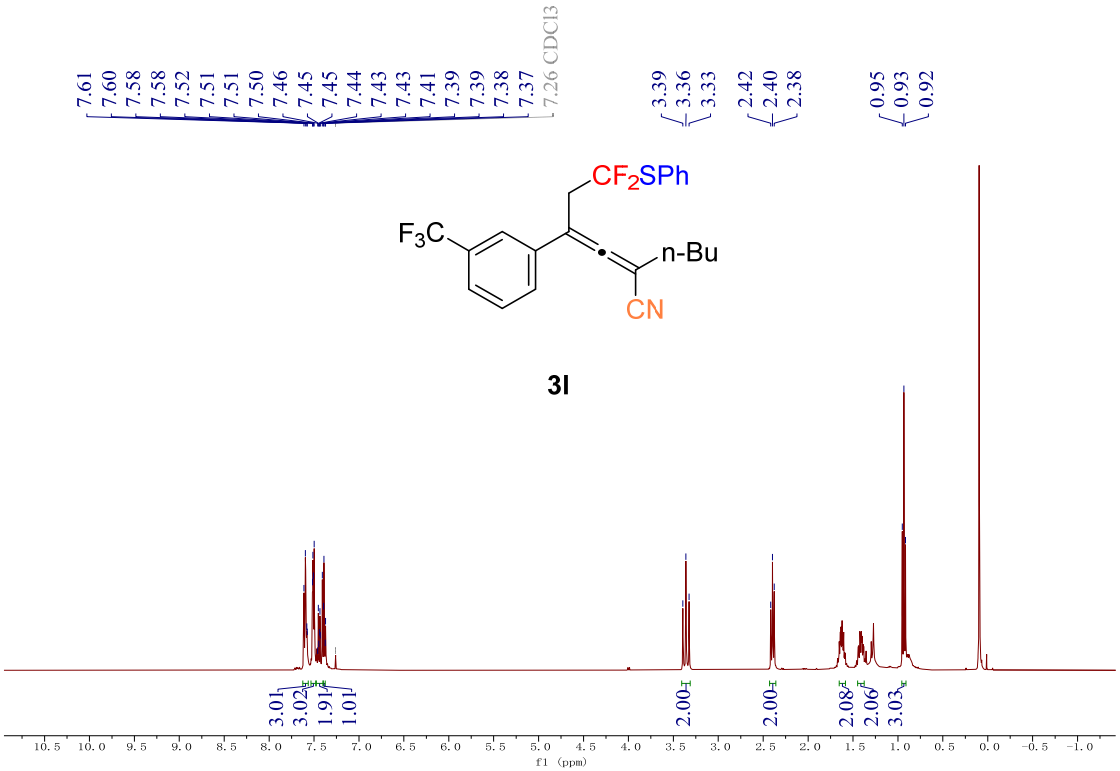
^{13}C NMR (101 MHz, $CDCl_3$)



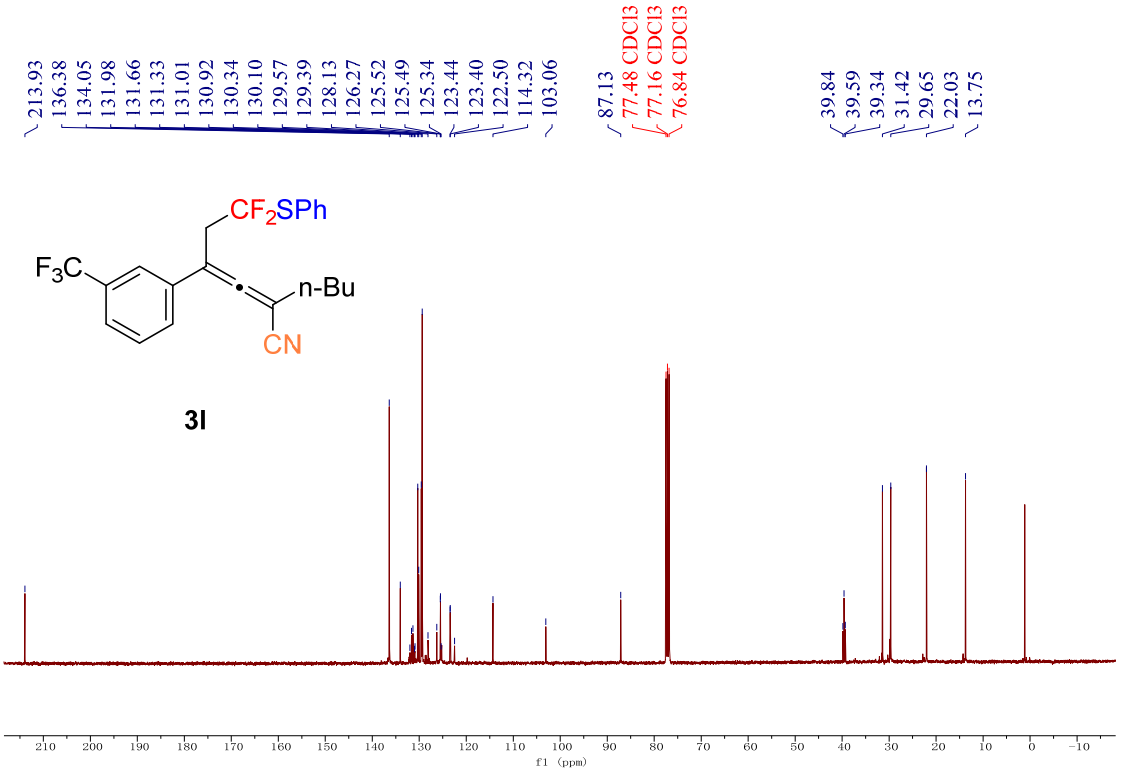
^{19}F NMR (376 MHz, $CDCl_3$)



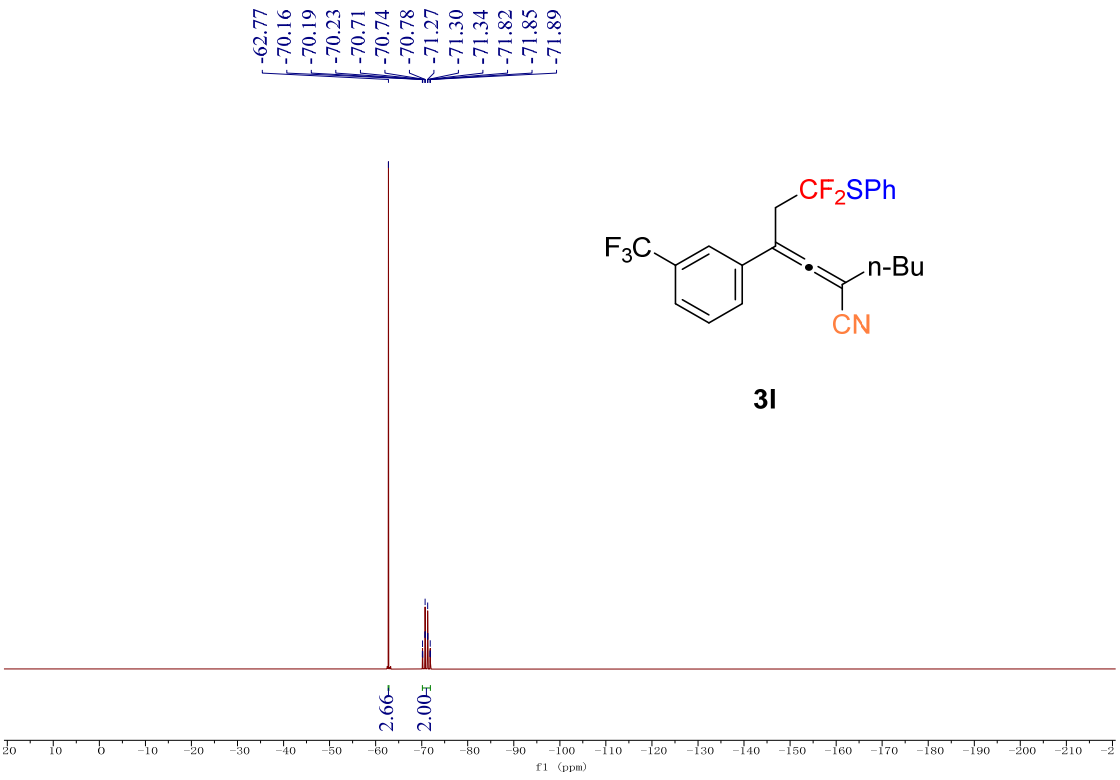
^{1}H NMR (400 MHz, $CDCl_3$)



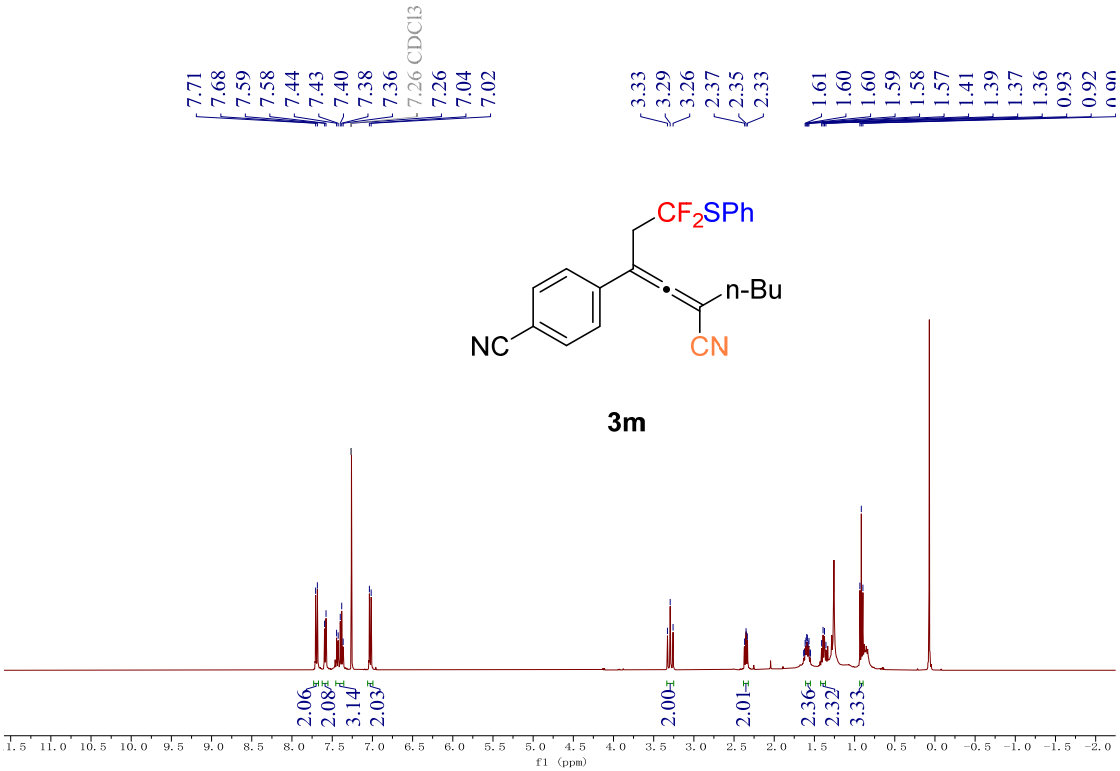
^{13}C NMR (101 MHz, $CDCl_3$)



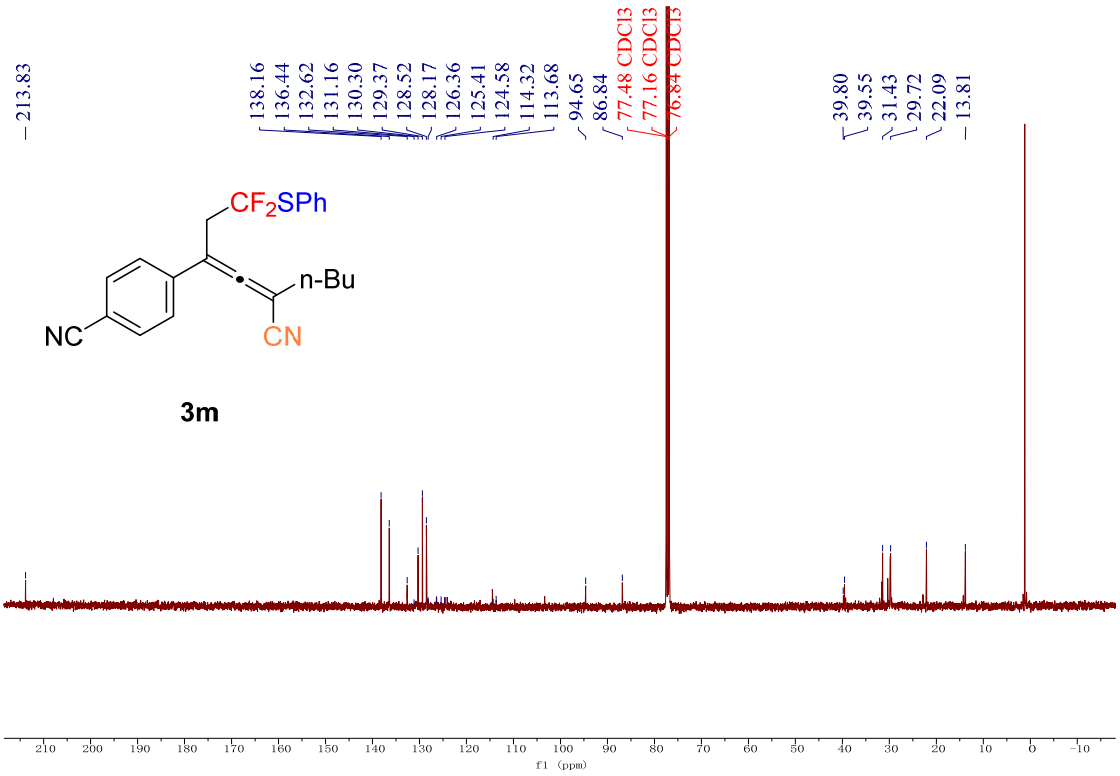
^{19}F NMR (376 MHz, $CDCl_3$)


-62.77
-70.16
-70.19
-70.23
-70.71
-70.74
-70.78
-71.27
-71.30
-71.34
-71.82
-71.85
-71.89
CF2SPh
F3C
n-Bu
CN
3l
2.66
2.00
f1 (ppm)

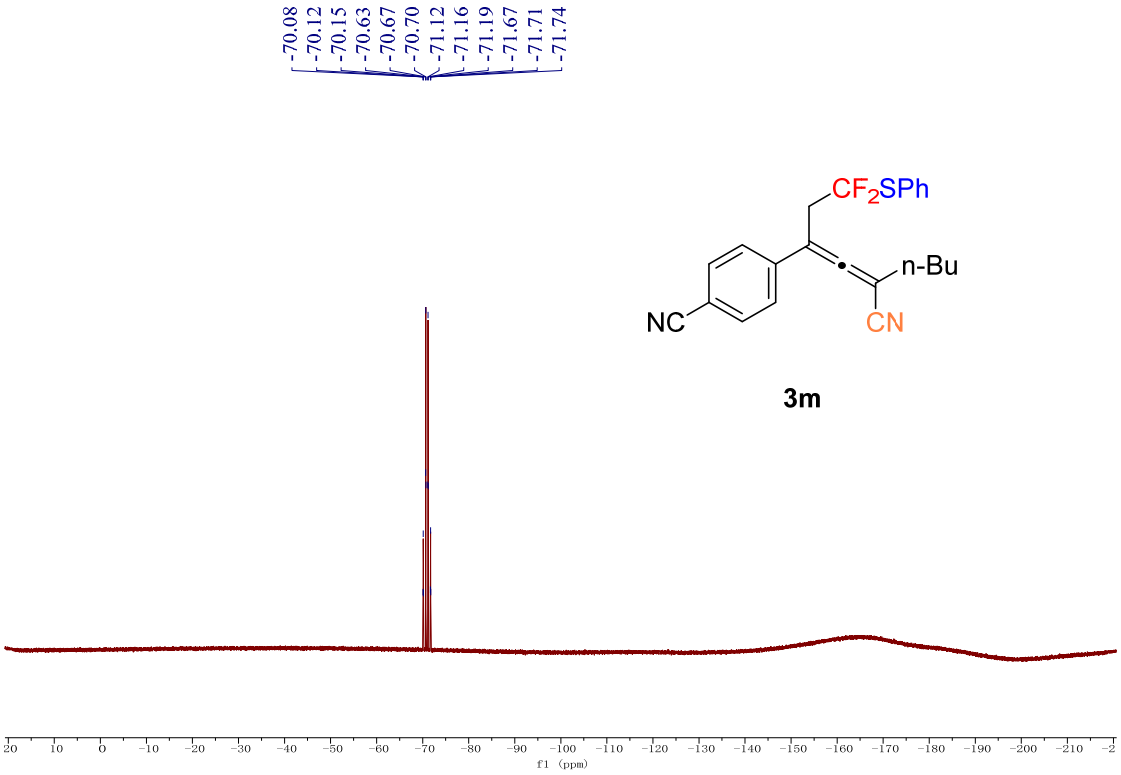
^{1}H NMR (400 MHz, $CDCl_3$)



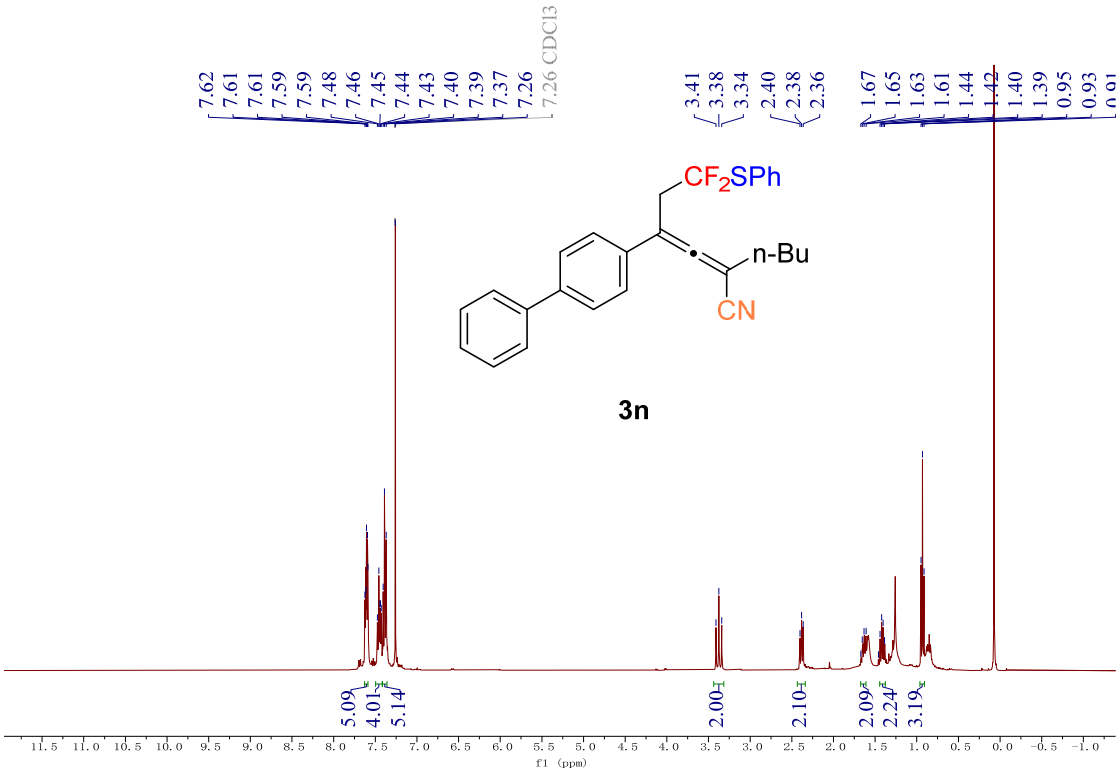
^{13}C NMR (101 MHz, $CDCl_3$)


213.83
138.16
136.44
132.62
131.16
130.30
129.37
128.52
128.17
126.36
125.41
124.58
114.32
113.68
94.65
86.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.80
39.55
31.43
29.72
22.09
13.81
CF2SPh
n-Bu
NC
CN
3m
f1 (ppm)

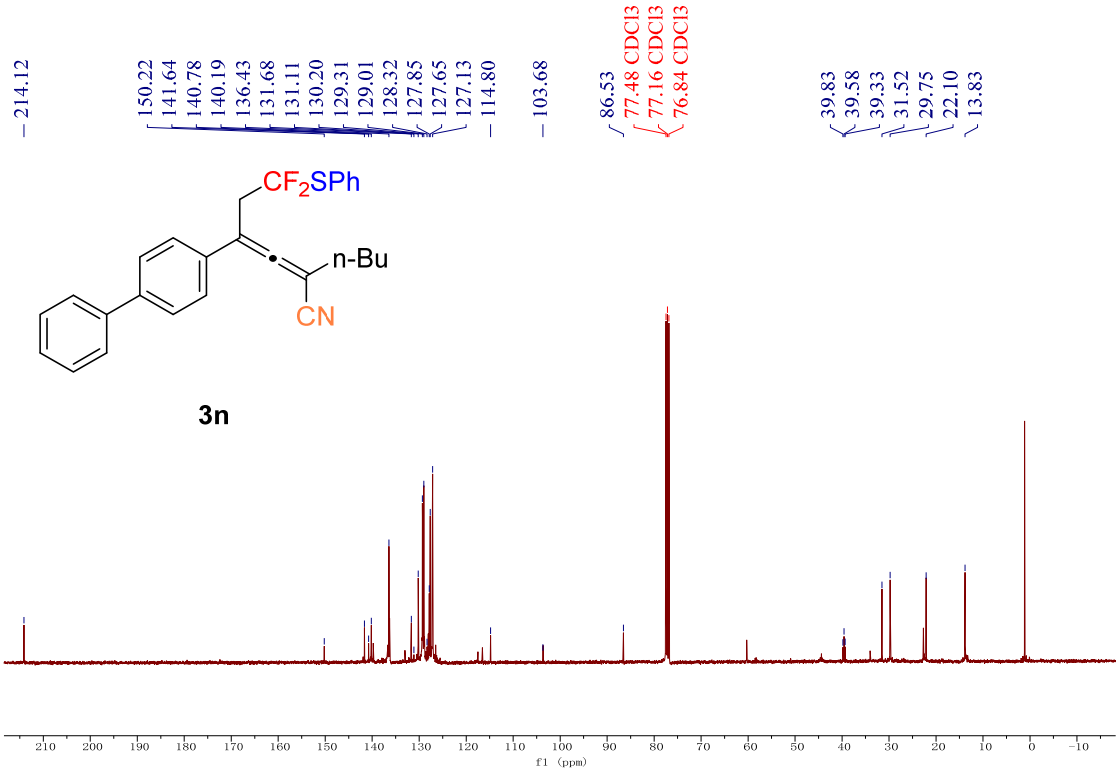
^{19}F NMR (376 MHz, $CDCl_3$)



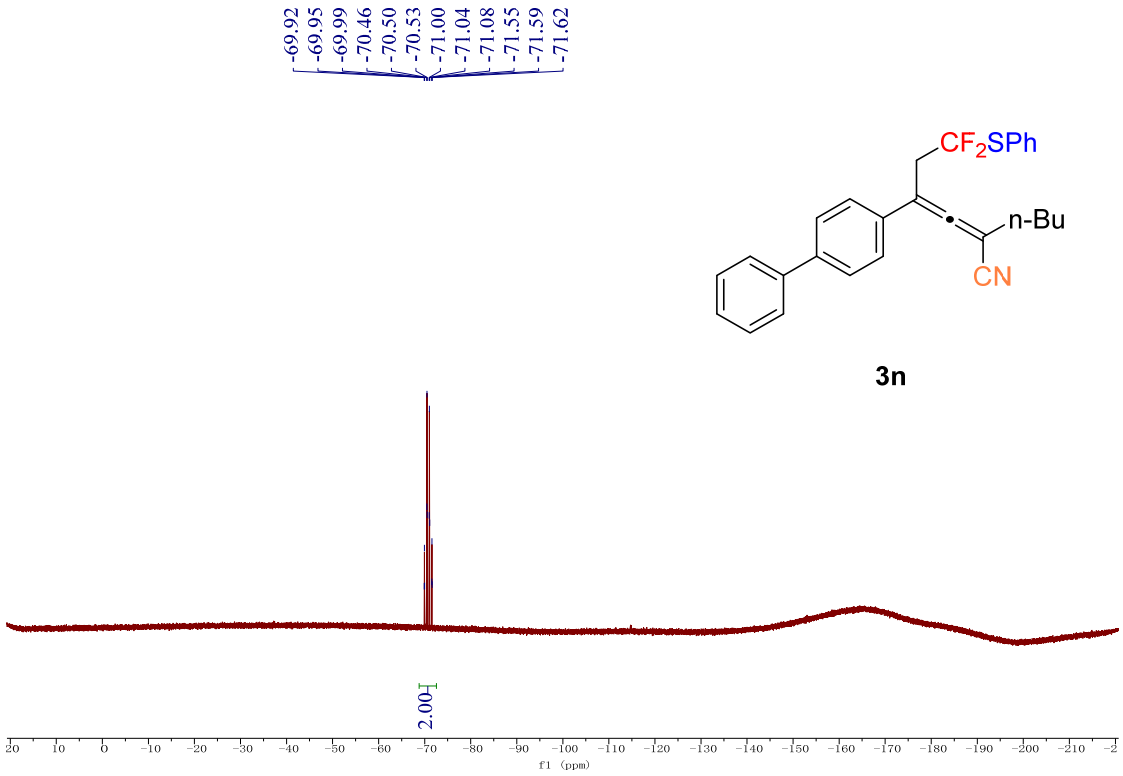
^{1}H NMR (400 MHz, $CDCl_3$)


7.62
7.61
7.61
7.59
7.59
7.48
7.46
7.45
7.44
7.43
7.40
7.39
7.37
7.26
7.26 CDCl3
3.41
3.38
3.34
2.40
2.38
2.36
1.67
1.65
1.63
1.61
1.44
1.42
1.40
1.39
0.95
0.93
CF2SPh
n-Bu
CN
3n
5.09
4.01
5.14
2.00
2.10
2.09
2.24
3.19
f1 (ppm)

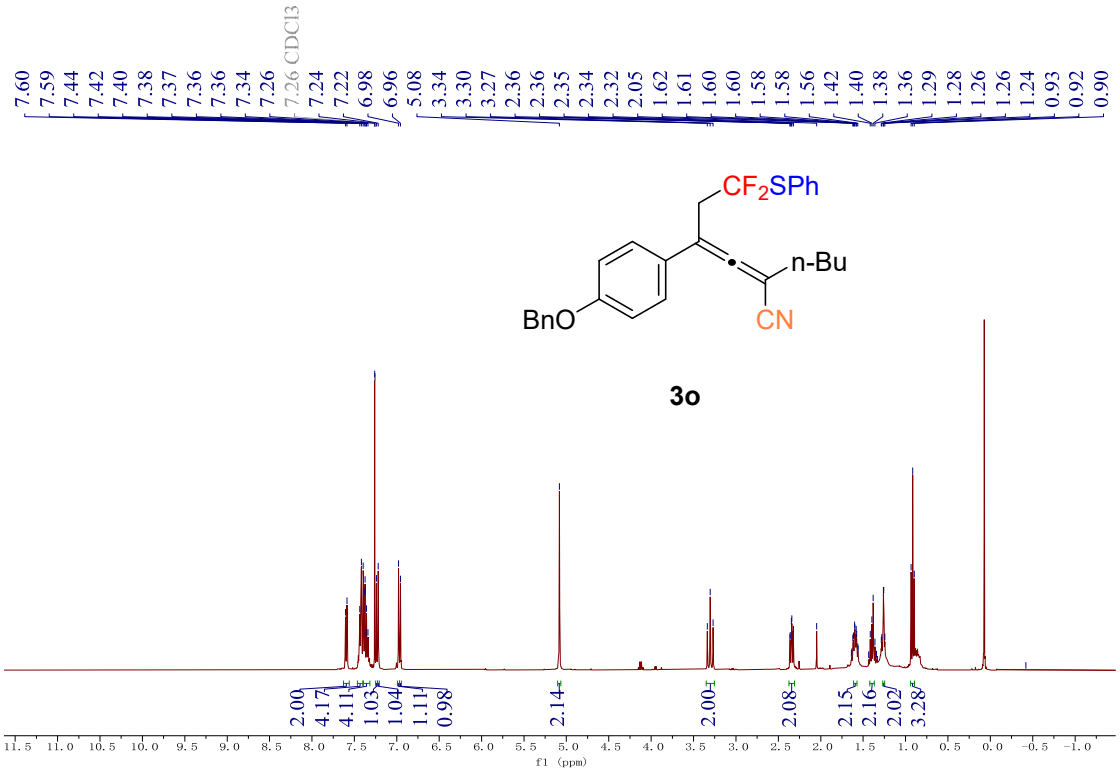
^{13}C NMR (101 MHz, $CDCl_3$)



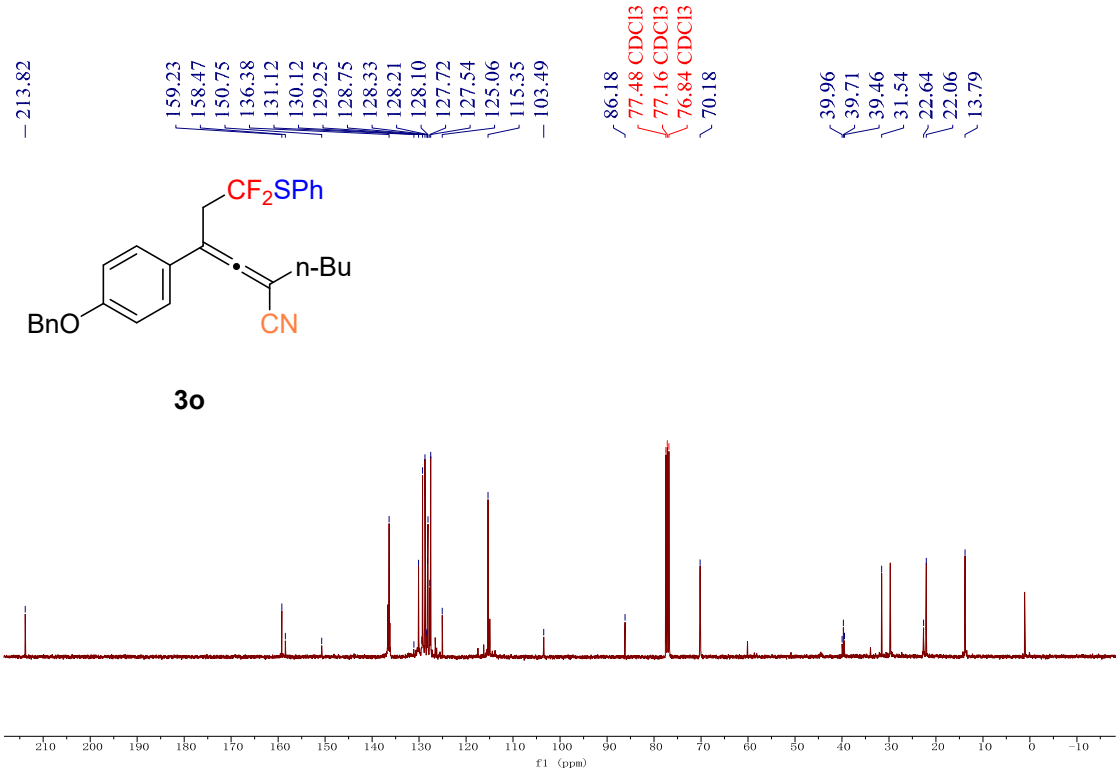
^{19}F NMR (376 MHz, $CDCl_3$)


-69.92
-69.95
-69.99
-70.46
-70.50
-70.53
-71.00
-71.04
-71.08
-71.55
-71.59
-71.62
CF2SPh
n-Bu
CN
3n
2.00
f1 (ppm)

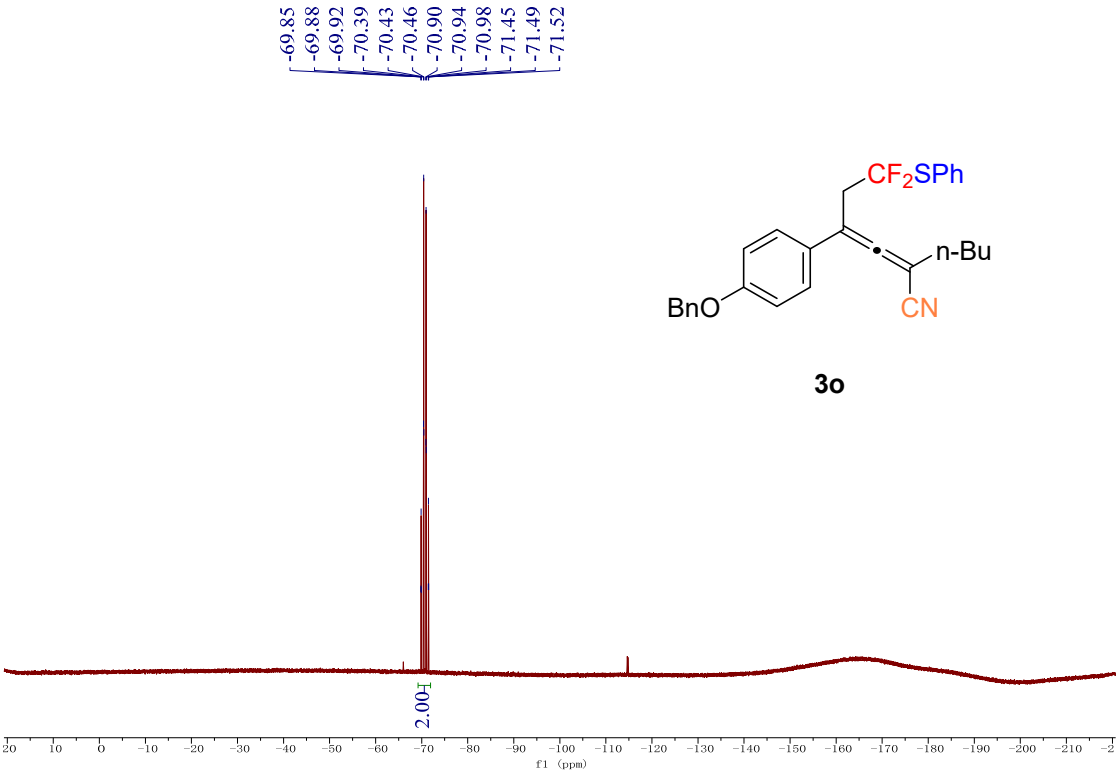
^{1}H NMR (400 MHz, $CDCl_3$)



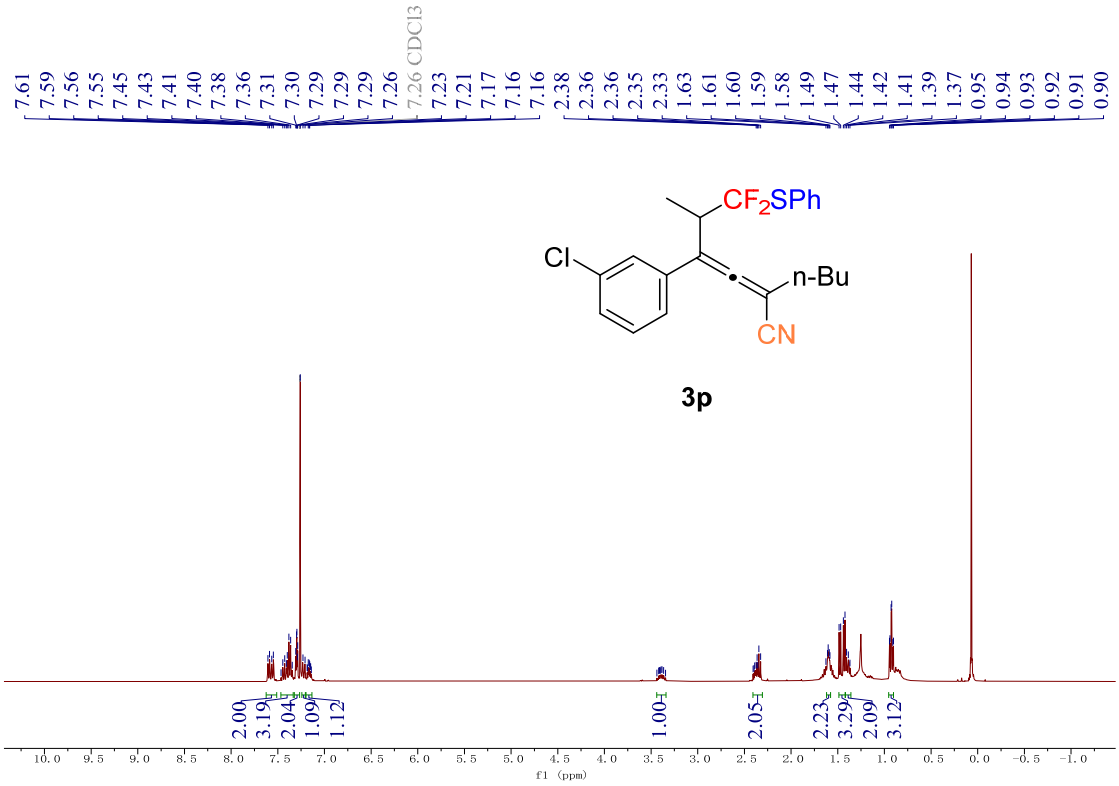
^{13}C NMR (101 MHz, $CDCl_3$)


213.82
159.23
158.47
150.75
136.38
131.12
130.12
129.25
128.75
128.33
128.21
128.10
127.72
127.54
125.06
115.35
103.49
86.18
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.18
39.96
39.71
39.46
31.54
22.64
22.06
13.79
CF2SPh
n-Bu
BnO
CN
3o
f1 (ppm)

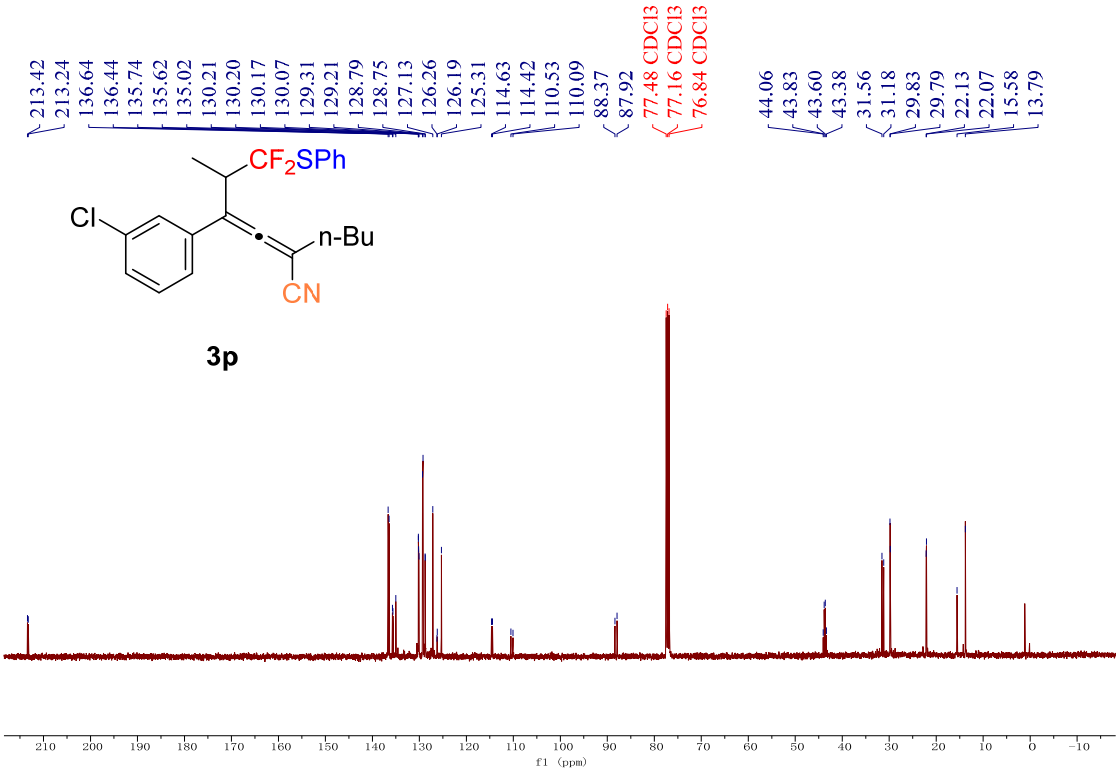
^{19}F NMR (376 MHz, $CDCl_3$)



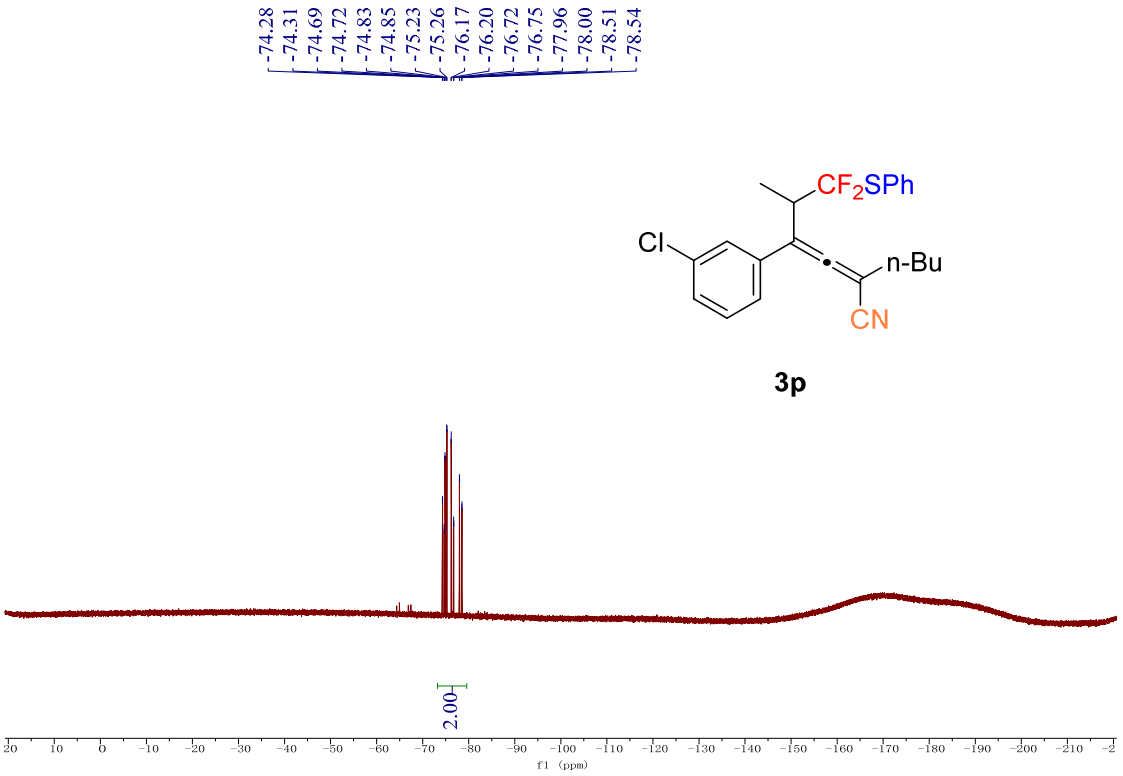
^{1}H NMR (400 MHz, $CDCl_3$)


7.61 7.59 7.56 7.55 7.45 7.43 7.41 7.40 7.38 7.36 7.31 7.30 7.29 7.29 7.29 7.26 7.26 CDCl3 7.23 7.21 7.17 7.16 7.16
2.38 2.36 2.36 2.35 2.33 1.63 1.61 1.60 1.59 1.58 1.49 1.47 1.44 1.42 1.41 1.39 1.37 0.95 0.94 0.93 0.92 0.91 0.90
CF2SPh
Cl
n-Bu
CN
3p
2.00 3.19 2.04 1.09 1.12 1.00 2.05 2.23 3.29 2.09 3.12
f1 (ppm)

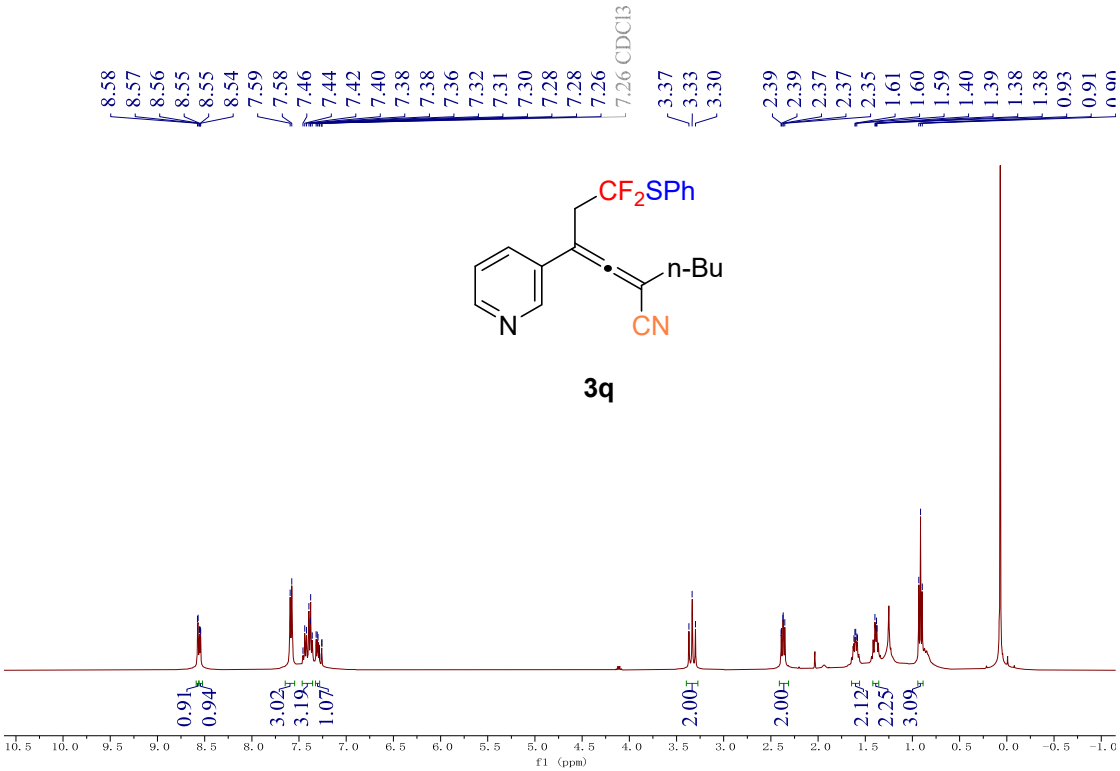
^{13}C NMR (101 MHz, $CDCl_3$)



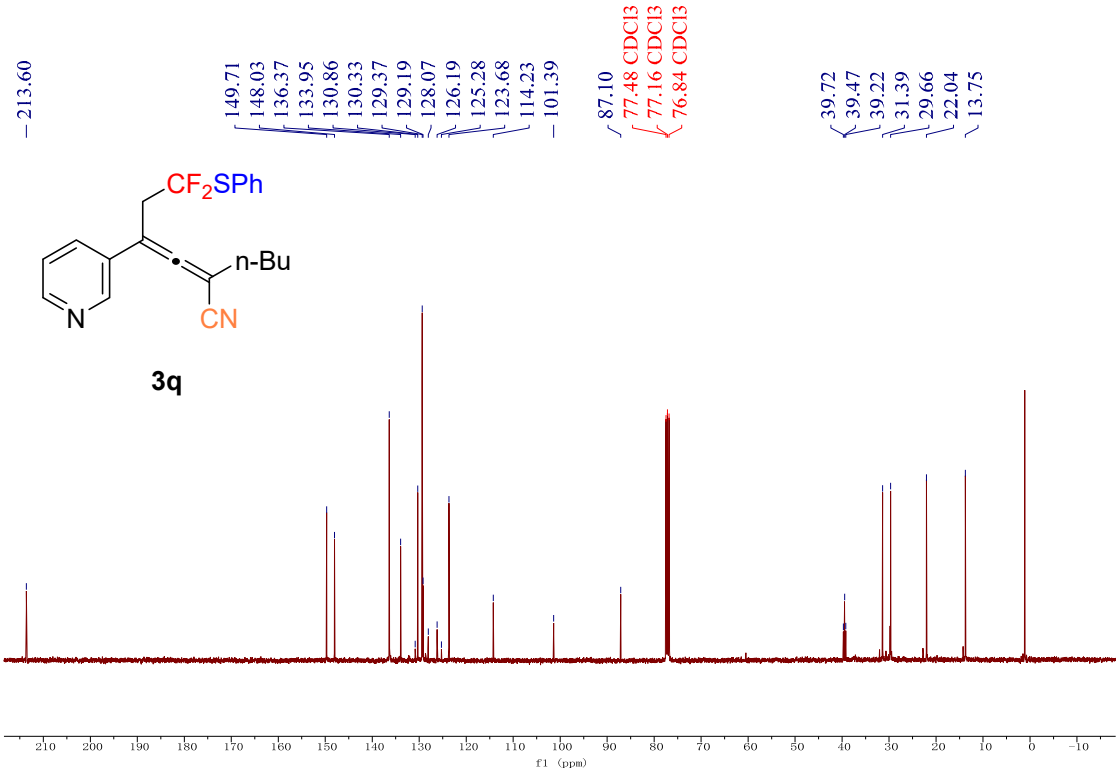
^{19}F NMR (376 MHz, $CDCl_3$)


-74.28
-74.31
-74.69
-74.72
-74.83
-74.85
-75.23
-75.26
-76.17
-76.20
-76.72
-76.75
-77.96
-78.00
-78.51
-78.54
CF2SPh
Cl
n-Bu
CN
3p
2.00
f1 (ppm)

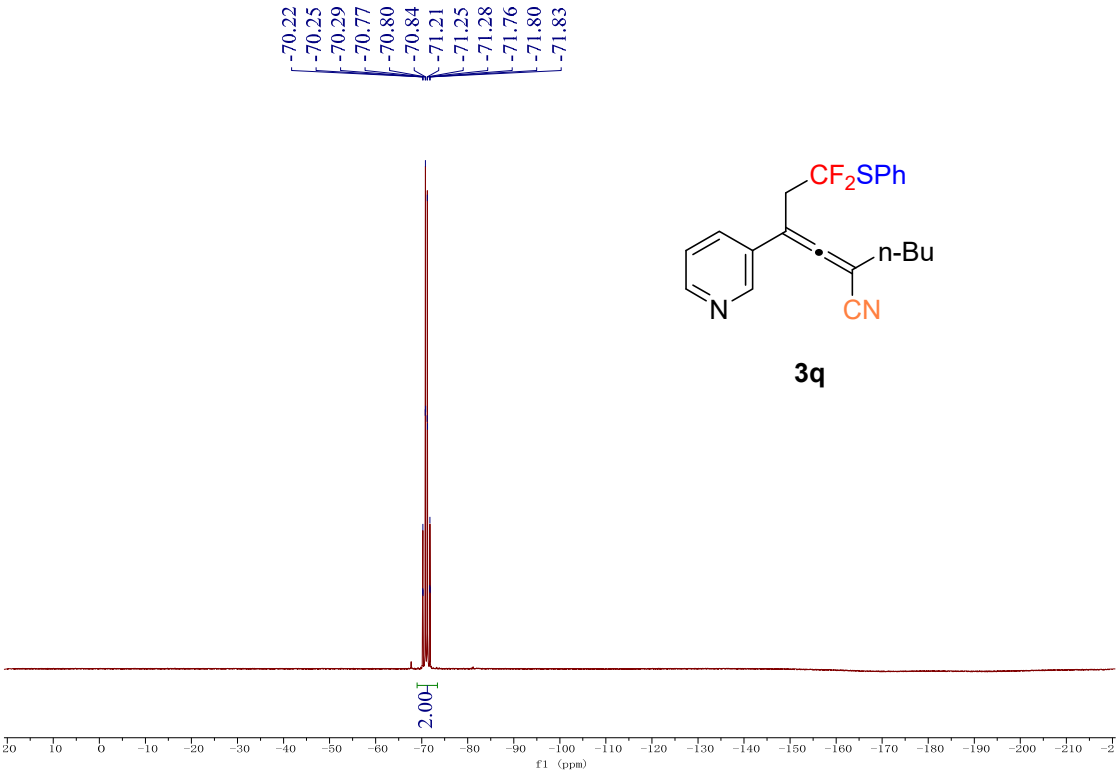
^{1}H NMR (400 MHz, $CDCl_3$)



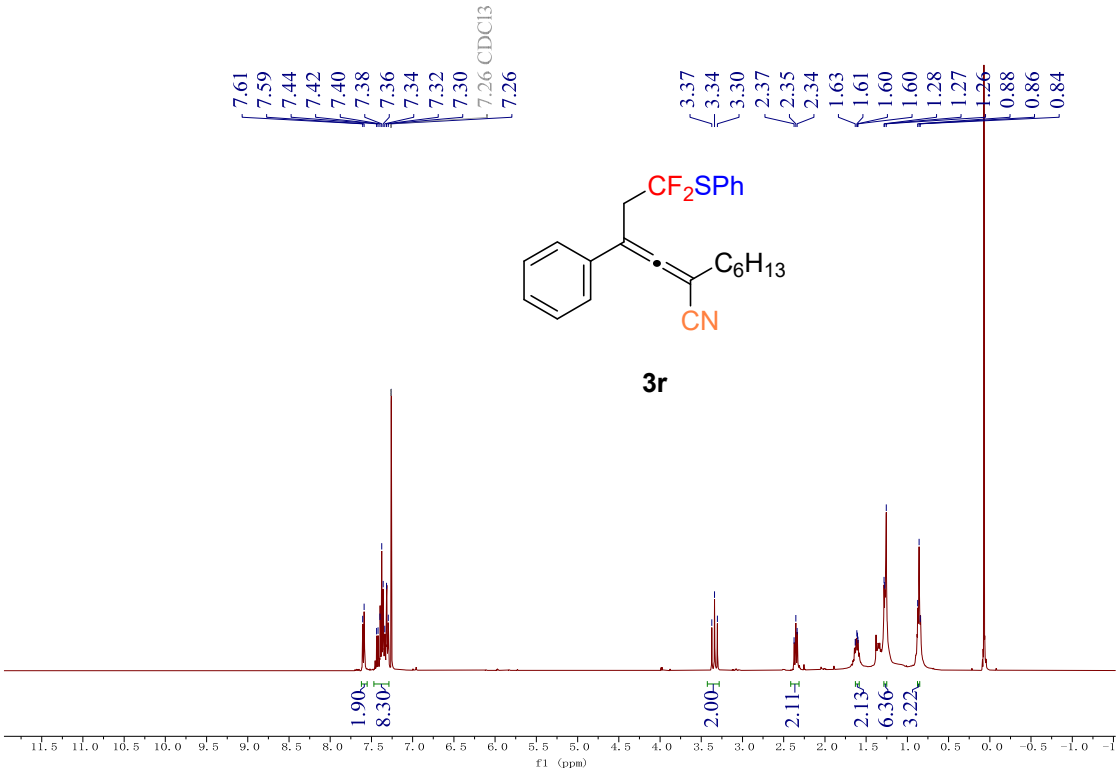
^{13}C NMR (101 MHz, $CDCl_3$)


213.60
149.71
148.03
136.37
133.95
130.86
130.33
129.37
129.19
128.07
126.19
125.28
123.68
114.23
101.39
87.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.72
39.47
39.22
31.39
29.66
22.04
13.75
CF2SPh
n-Bu
CN
N
3q
f1 (ppm)

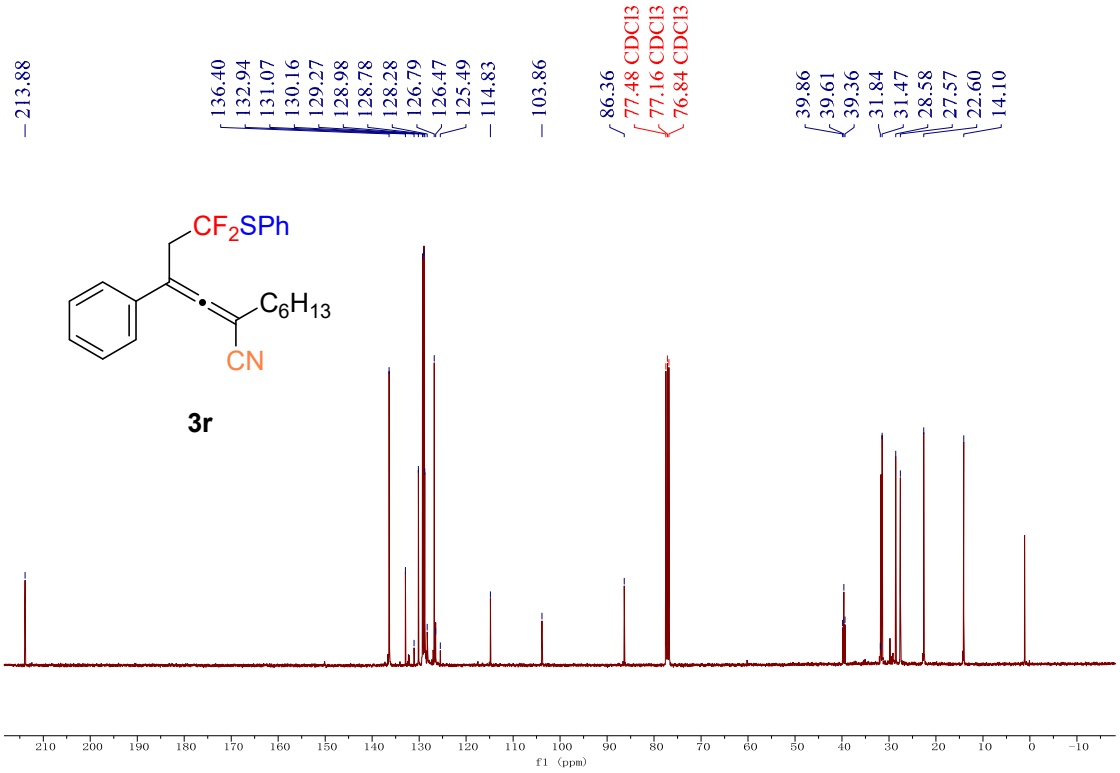
[19]F NMR (376 MHz, $CDCl_3$)



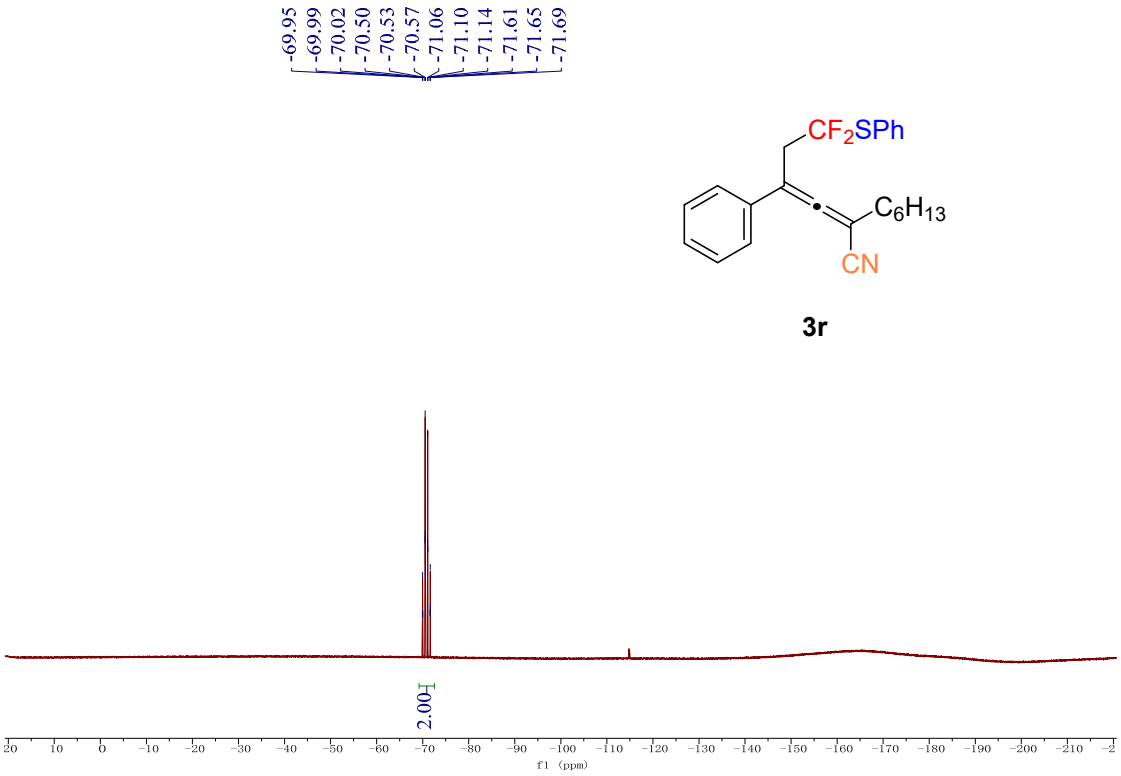
[1]H NMR (400 MHz, $CDCl_3$)


7.61
7.59
7.44
7.42
7.40
7.38
7.36
7.34
7.32
7.30
7.26 CDCl3
7.26
3.37
3.34
3.30
2.37
2.35
2.34
1.63
1.61
1.60
1.60
1.28
1.27
1.26
0.88
0.86
0.84
CF2SPh
C6H13
CN
3r
1.90
8.30
2.00
2.11
2.13
6.36
3.22
f1 (ppm)

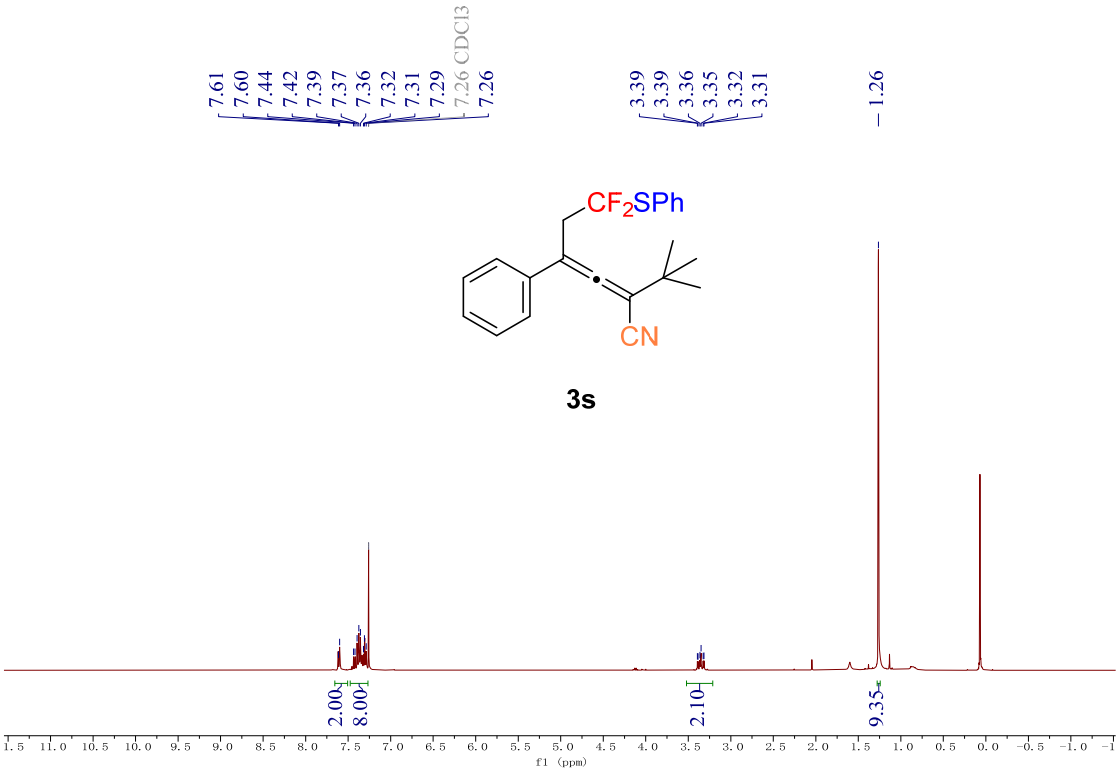
^{13}C NMR (101 MHz, $CDCl_3$)



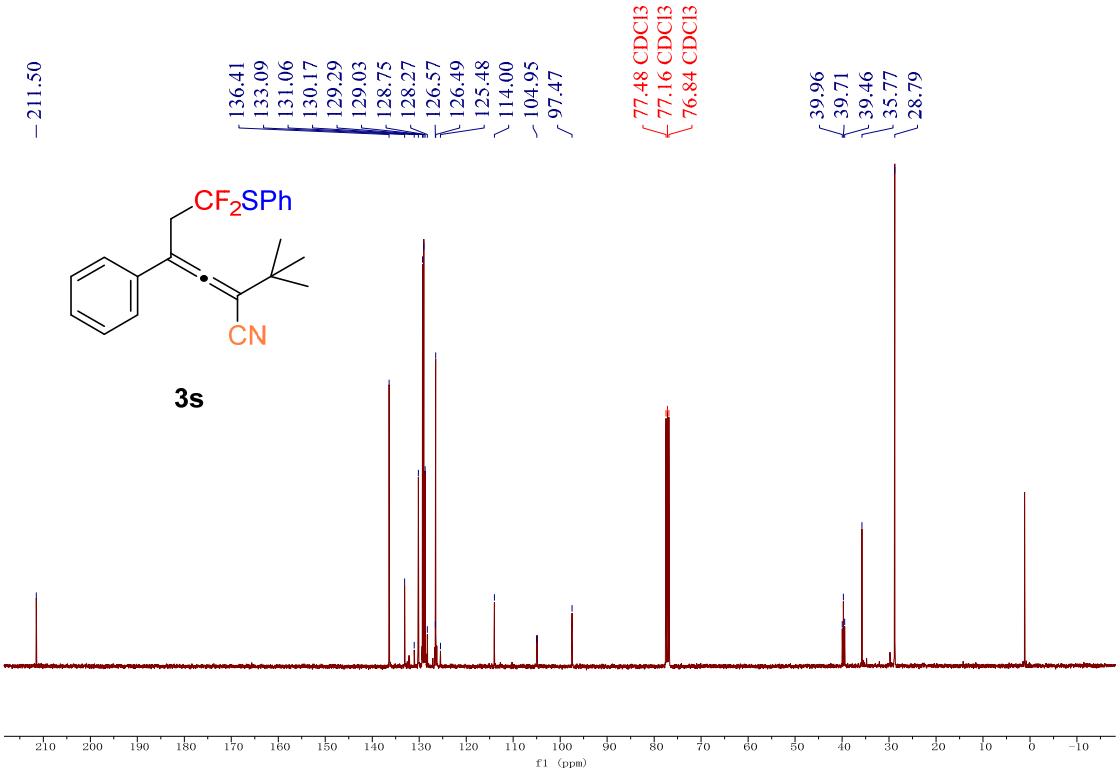
^{19}F NMR (376 MHz, $CDCl_3$)


-69.95
-69.99
-70.02
-70.50
-70.53
-70.57
-71.06
-71.10
-71.14
-71.61
-71.65
-71.69
CF2SPh
C6H13
CN
3r
2.00
f1 (ppm)

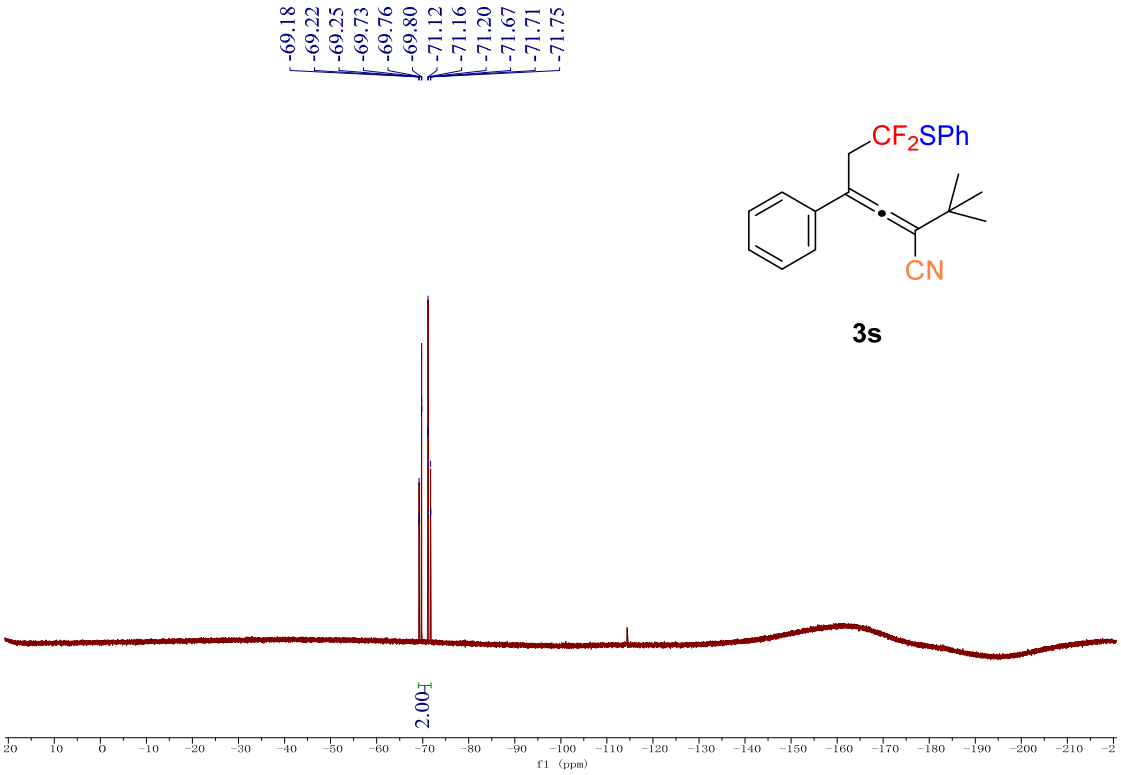
^{1}H NMR (400 MHz, $CDCl_3$)



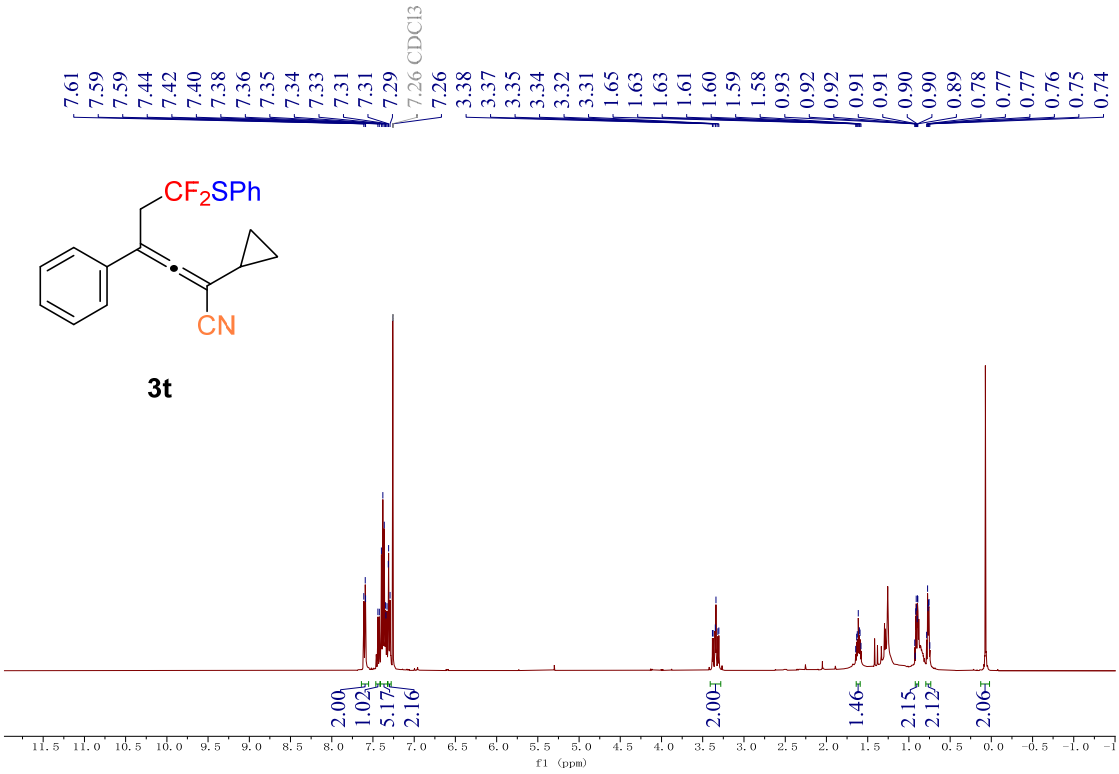
^{13}C NMR (101 MHz, $CDCl_3$)


211.50
136.41
133.09
131.06
130.17
129.29
129.03
128.75
128.27
126.57
126.49
125.48
114.00
104.95
97.47
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.96
39.71
39.46
35.77
28.79
CF2SPh
CN
3s
f1 (ppm)

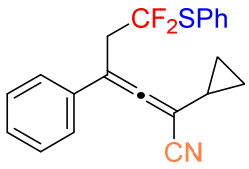
^{19}F NMR (376 MHz, $CDCl_3$)



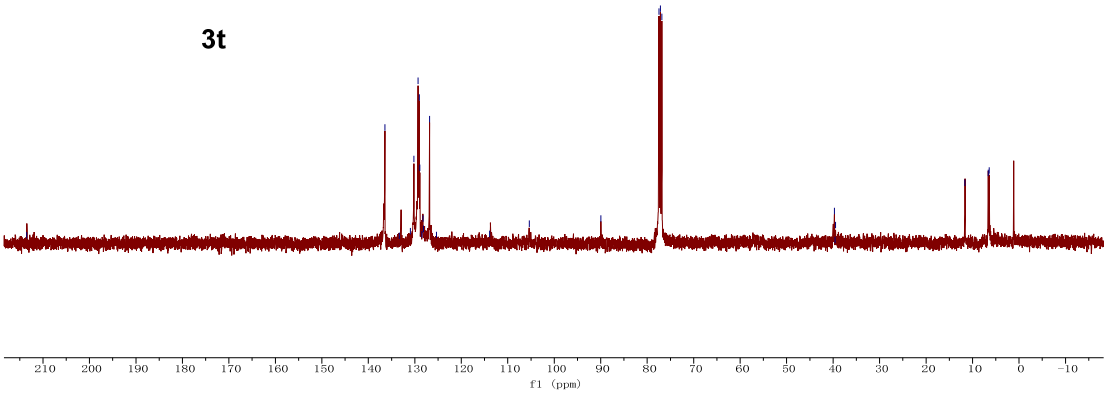
^{1}H NMR (400 MHz, $CDCl_3$)


7.61
7.59
7.59
7.44
7.42
7.40
7.38
7.36
7.35
7.34
7.33
7.31
7.31
7.29
7.26 CDCl3
7.26
3.38
3.37
3.35
3.34
3.32
3.31
1.65
1.63
1.63
1.61
1.60
1.59
1.58
0.93
0.92
0.92
0.91
0.91
0.90
0.90
0.89
0.78
0.77
0.77
0.76
0.75
0.74
CF2SPh
CN
3t
2.00
1.02
5.17
2.16
2.00
1.46
2.15
2.12
2.06
f1 (ppm)

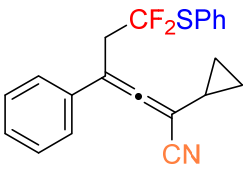
^{13}C NMR (101 MHz, $CDCl_3$)



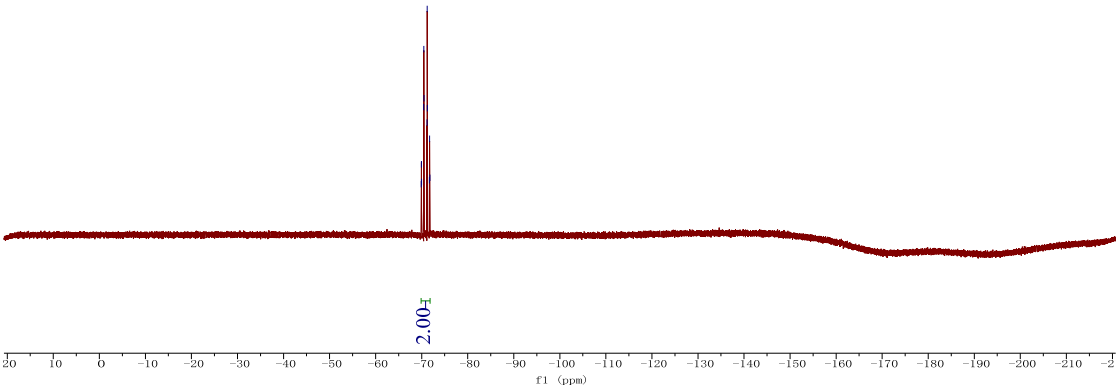
3t



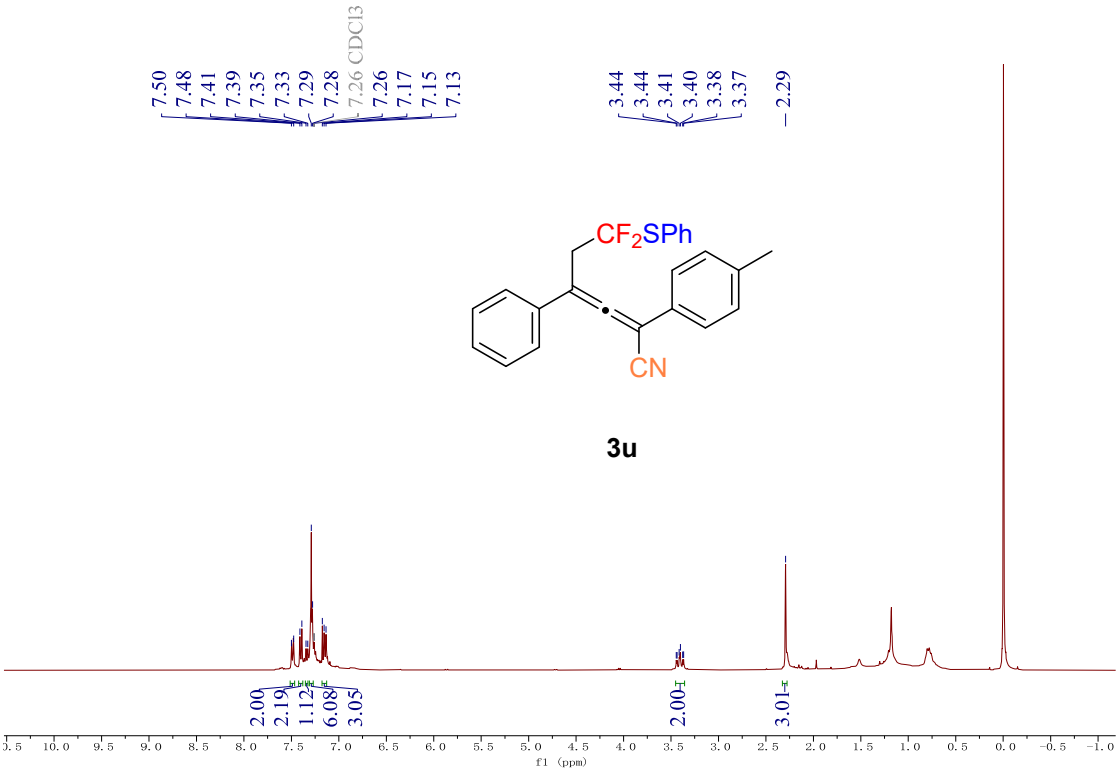
^{19}F NMR (376 MHz, $CDCl_3$)



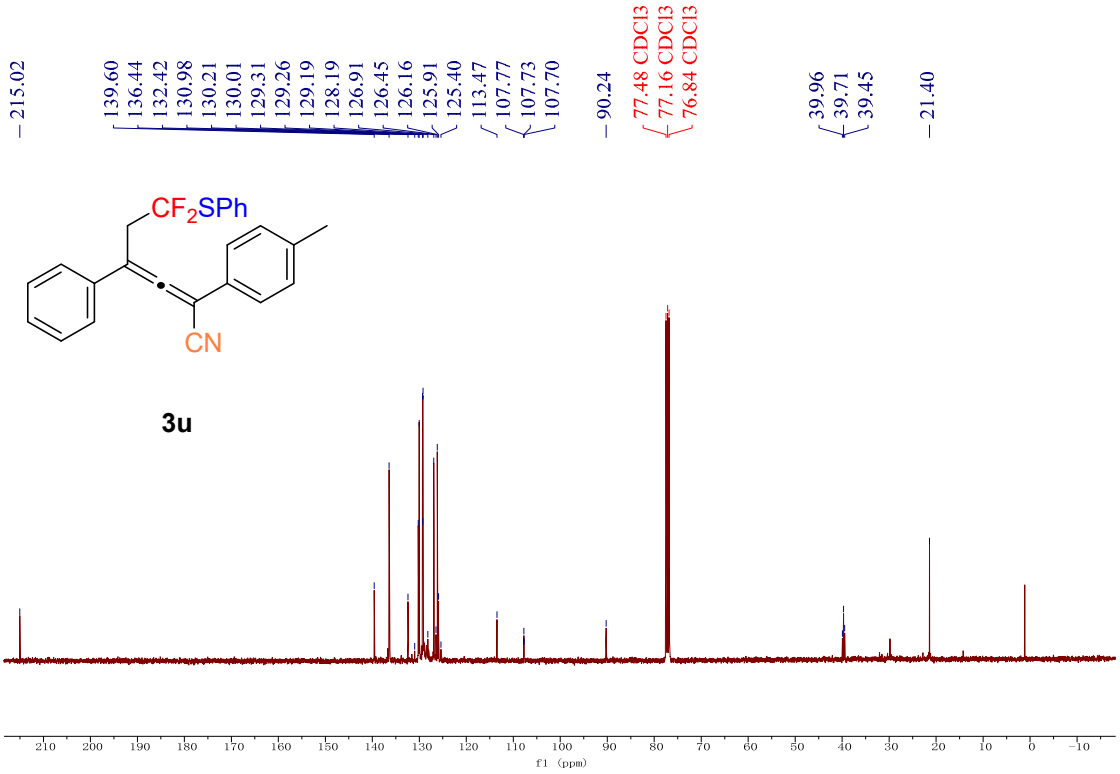
3t



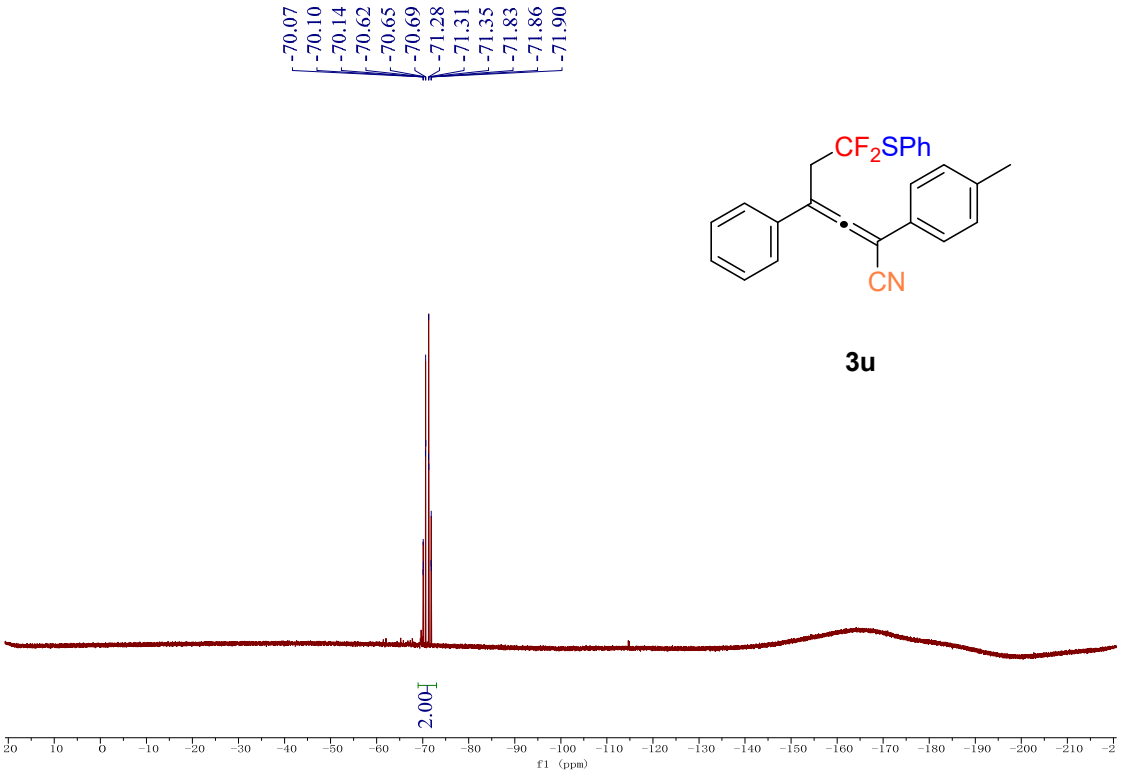
^{1}H NMR (400 MHz, $CDCl_3$)



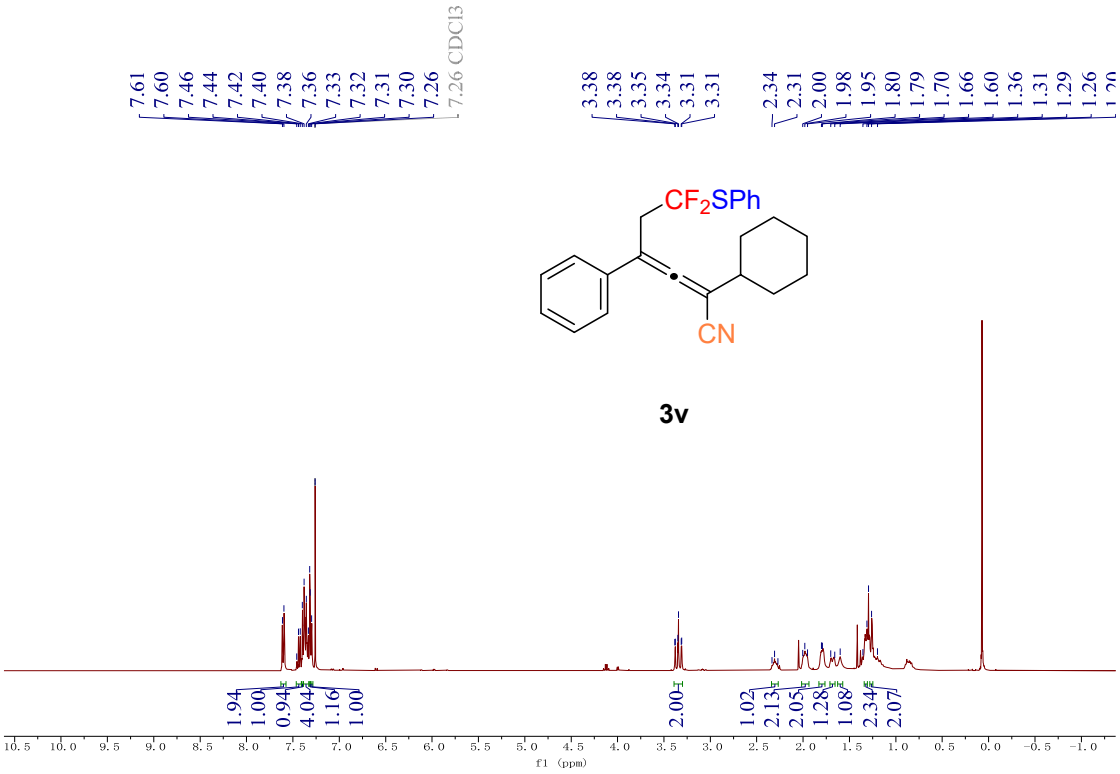
^{13}C NMR (101 MHz, $CDCl_3$)


215.02
139.60
136.44
132.42
130.98
130.21
130.01
129.31
129.26
129.19
128.19
126.91
126.45
126.16
125.91
125.40
113.47
107.77
107.73
107.70
90.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.96
39.71
39.45
21.40
CF2SPh
CN
3u
f1 (ppm)

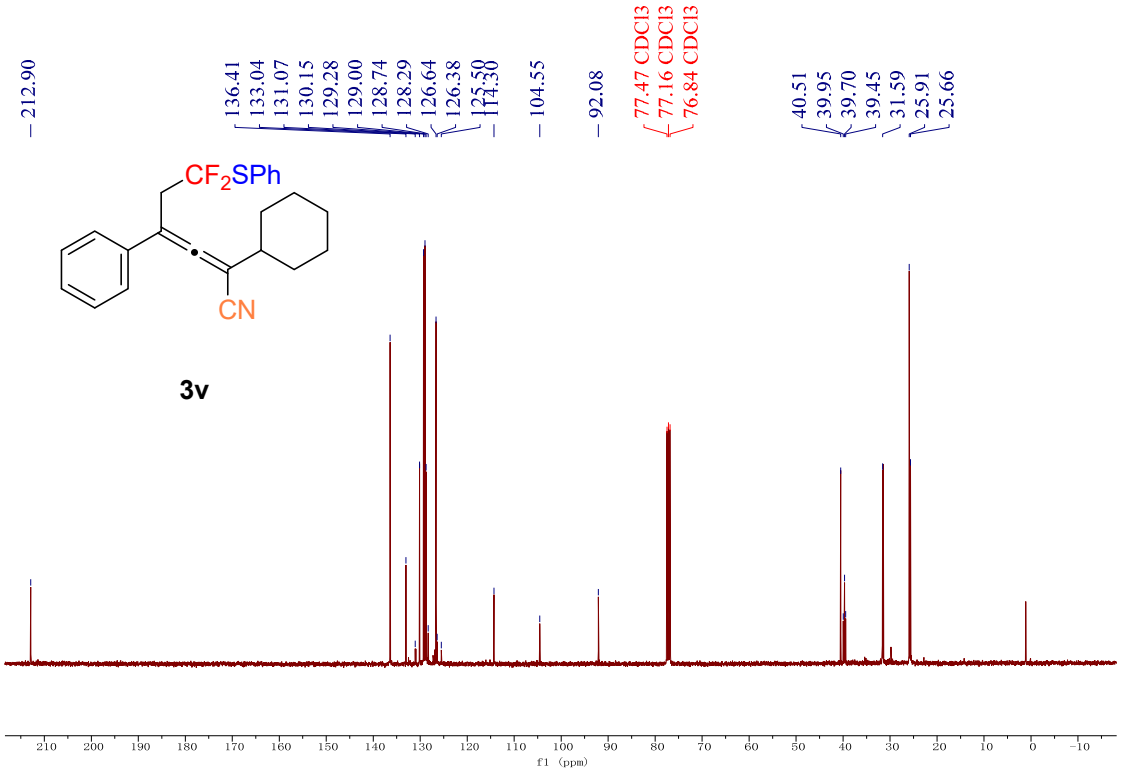
^{19}F NMR (376 MHz, $CDCl_3$)



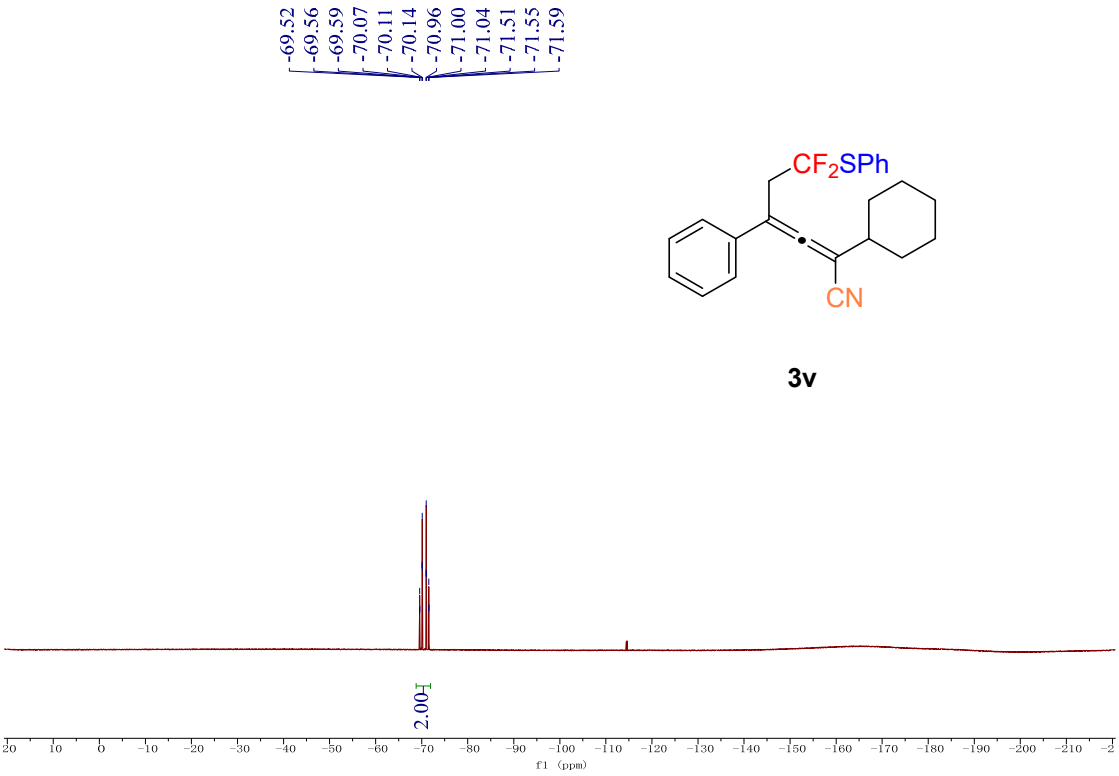
^{1}H NMR (400 MHz, $CDCl_3$)


7.61
7.60
7.46
7.44
7.42
7.40
7.38
7.36
7.33
7.32
7.31
7.30
7.26
7.26 CDCl3
3.38
3.38
3.35
3.34
3.31
3.31
2.34
2.31
2.00
1.98
1.95
1.80
1.79
1.70
1.66
1.60
1.36
1.31
1.29
1.26
CF2SPh
CN
3v
1.94
1.00
0.94
4.04
1.16
1.00
2.00
1.02
2.13
2.05
1.28
1.08
2.34
2.07
f1 (ppm)

^{13}C NMR (101 MHz, $CDCl_3$)

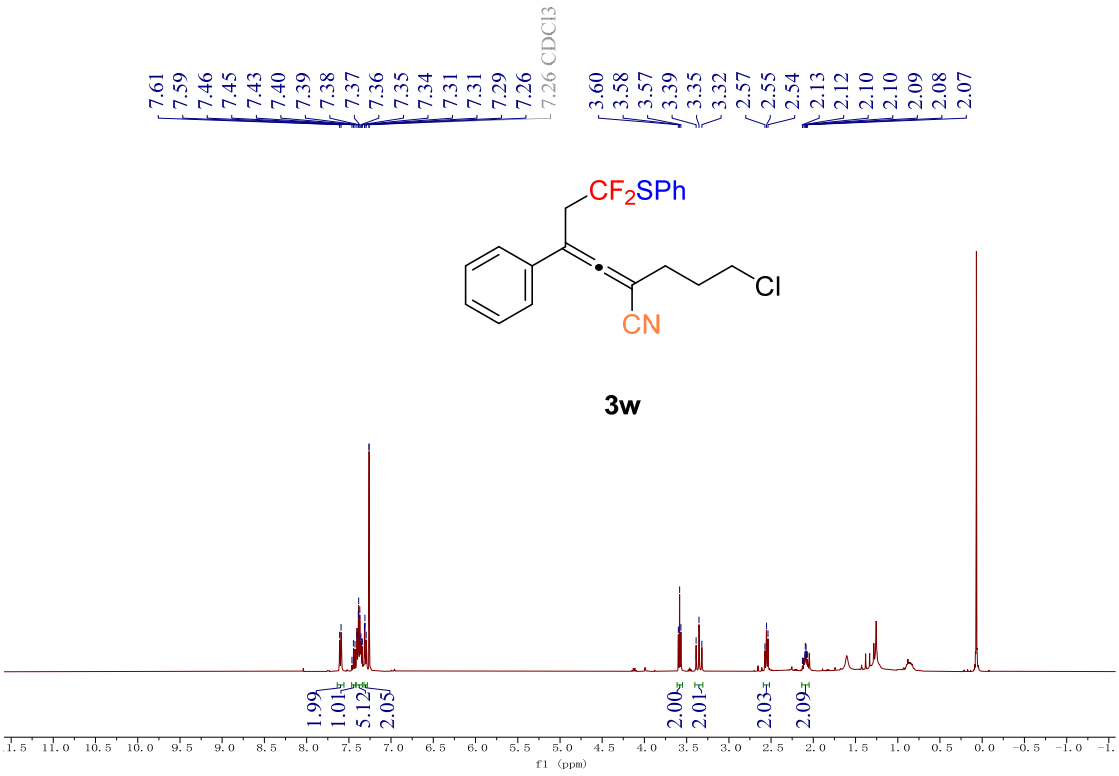


^{19}F NMR (376 MHz, $CDCl_3$)



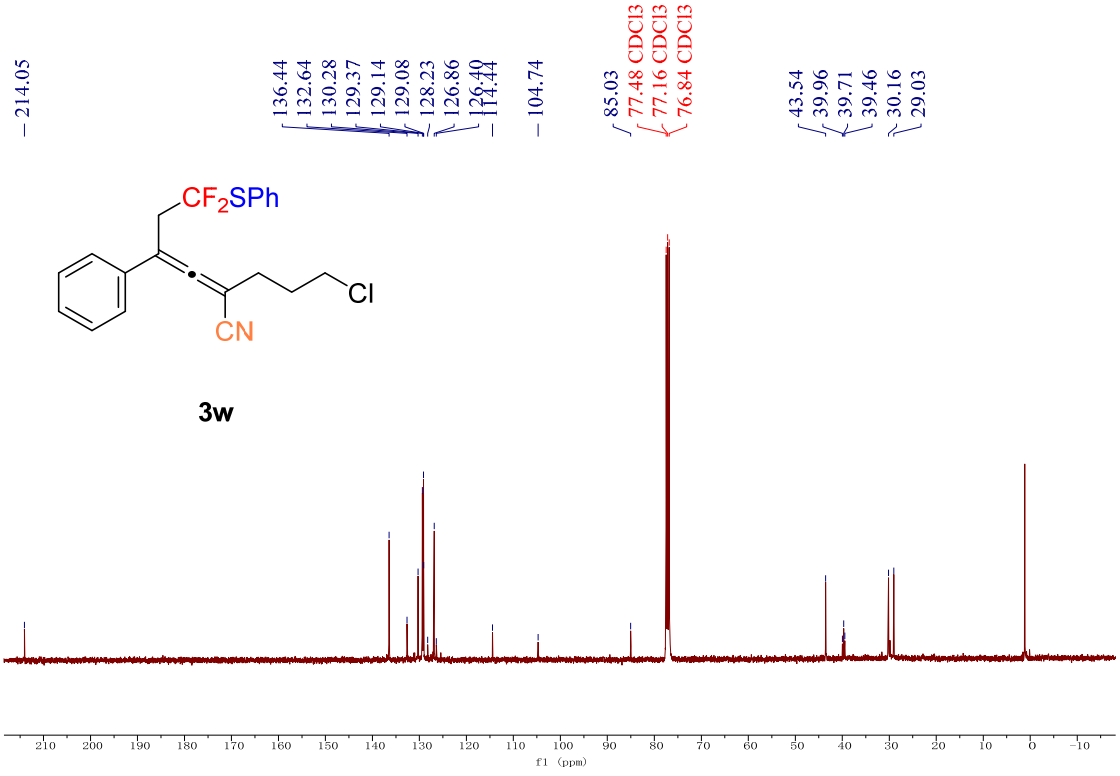
3v

^{1}H NMR (400 MHz, $CDCl_3$)

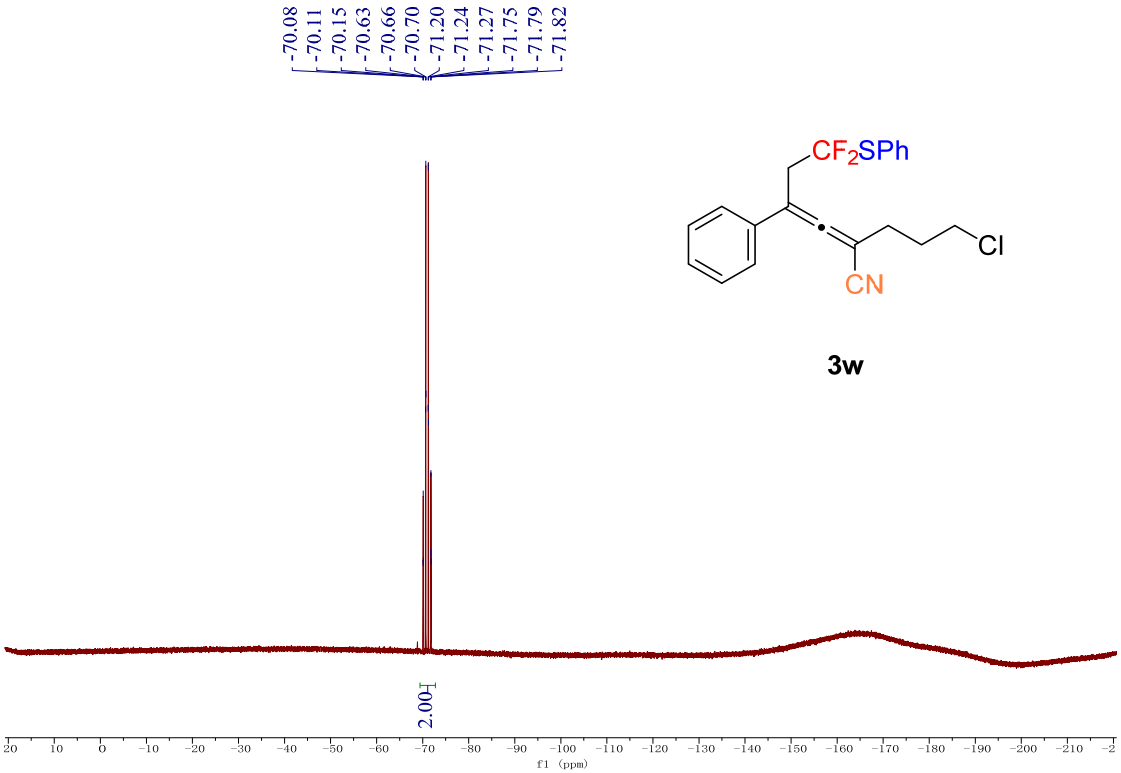


3w

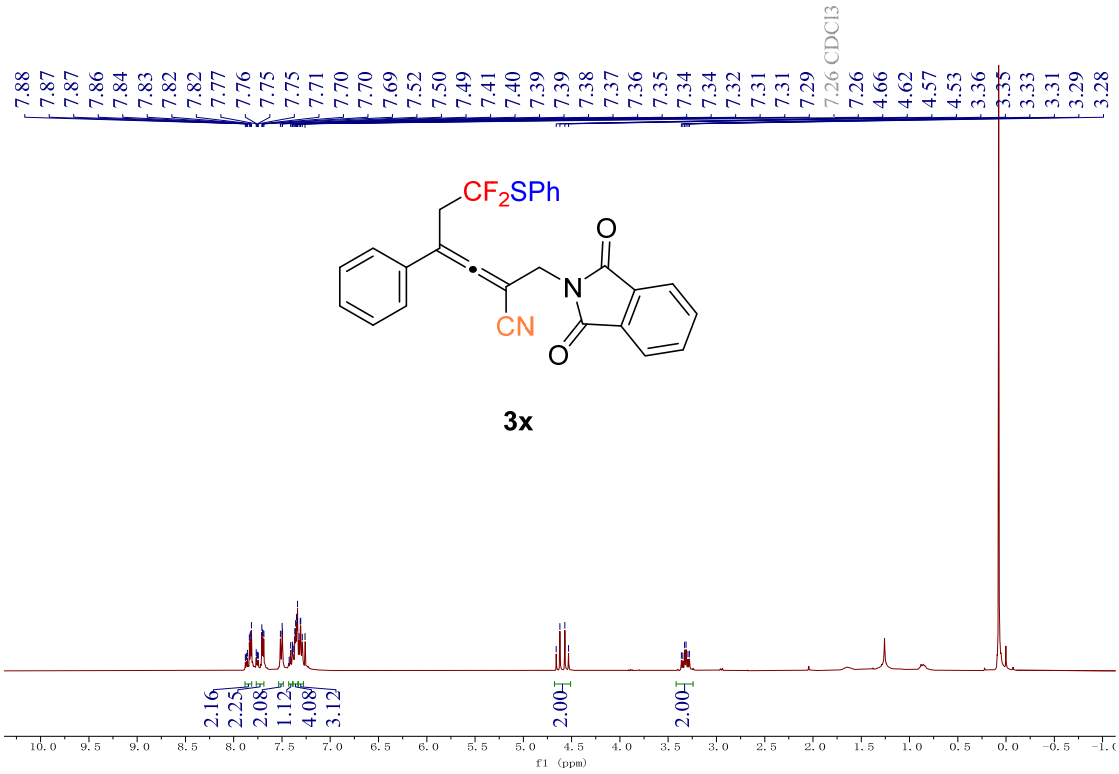
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

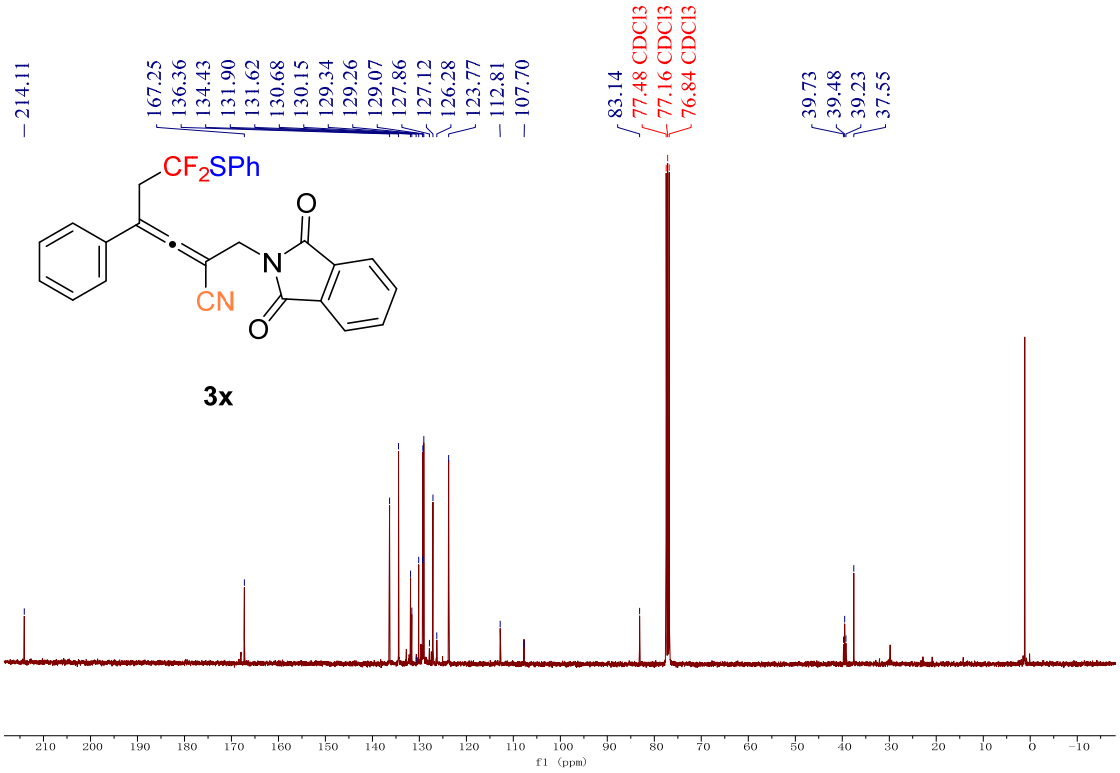


^{1}H NMR (400 MHz, $CDCl_3$)

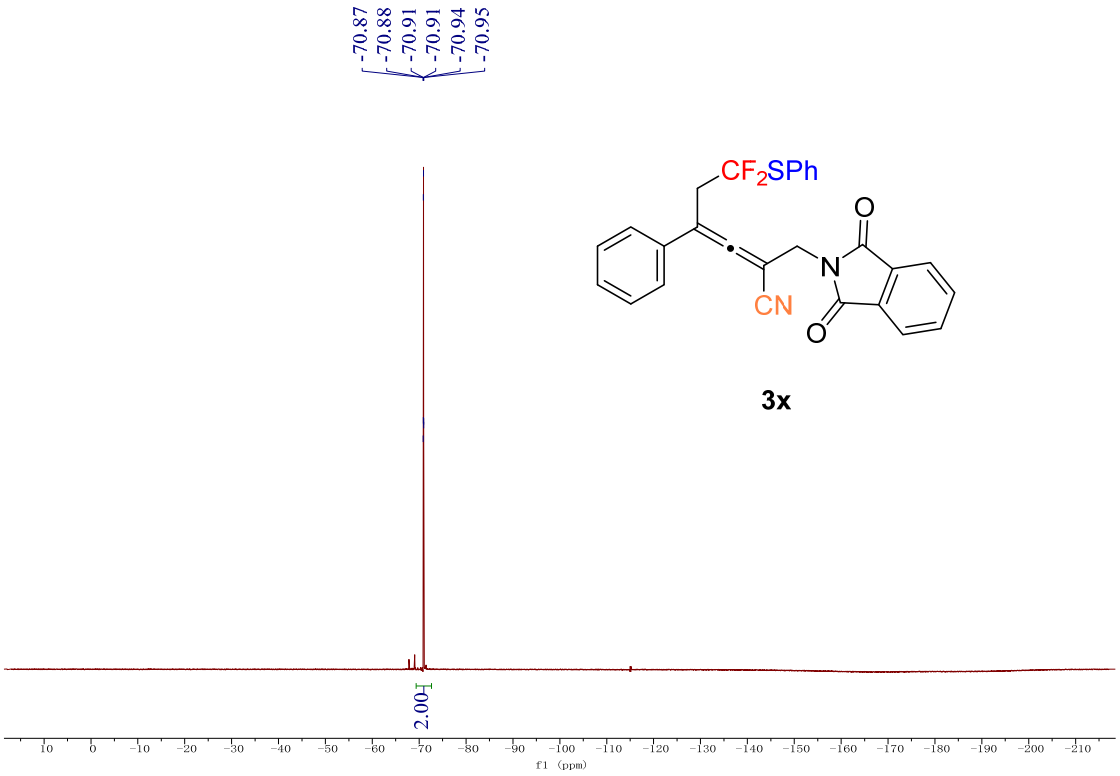

7.88
7.87
7.87
7.86
7.84
7.83
7.82
7.82
7.77
7.76
7.75
7.75
7.71
7.70
7.70
7.69
7.52
7.50
7.49
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.35
7.34
7.34
7.32
7.31
7.31
7.29
7.26 CDCl3
7.26
4.66
4.62
4.57
4.53
3.36
3.35
3.33
3.31
3.29
3.28
CF2SPh
O
N
CN
O
2.16
2.25
2.08
1.12
4.08
3.12
2.00
2.00
f1 (ppm)

3x

^{13}C NMR (101 MHz, $CDCl_3$)

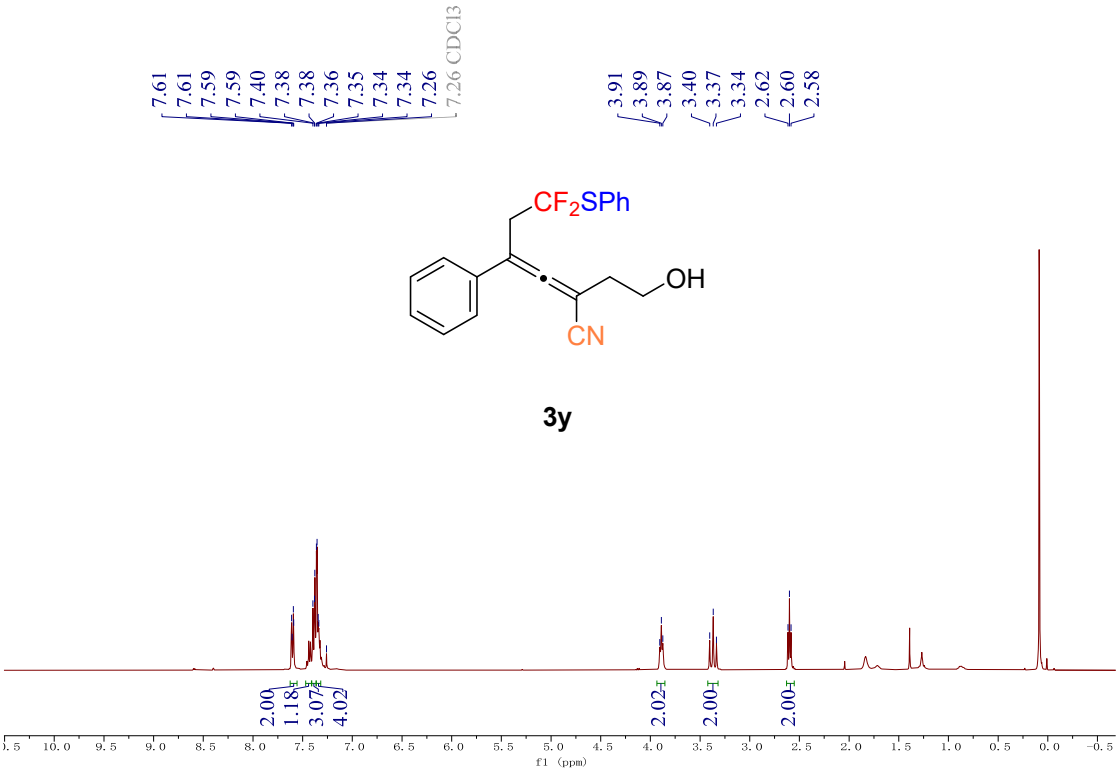


^{19}F NMR (376 MHz, $CDCl_3$)

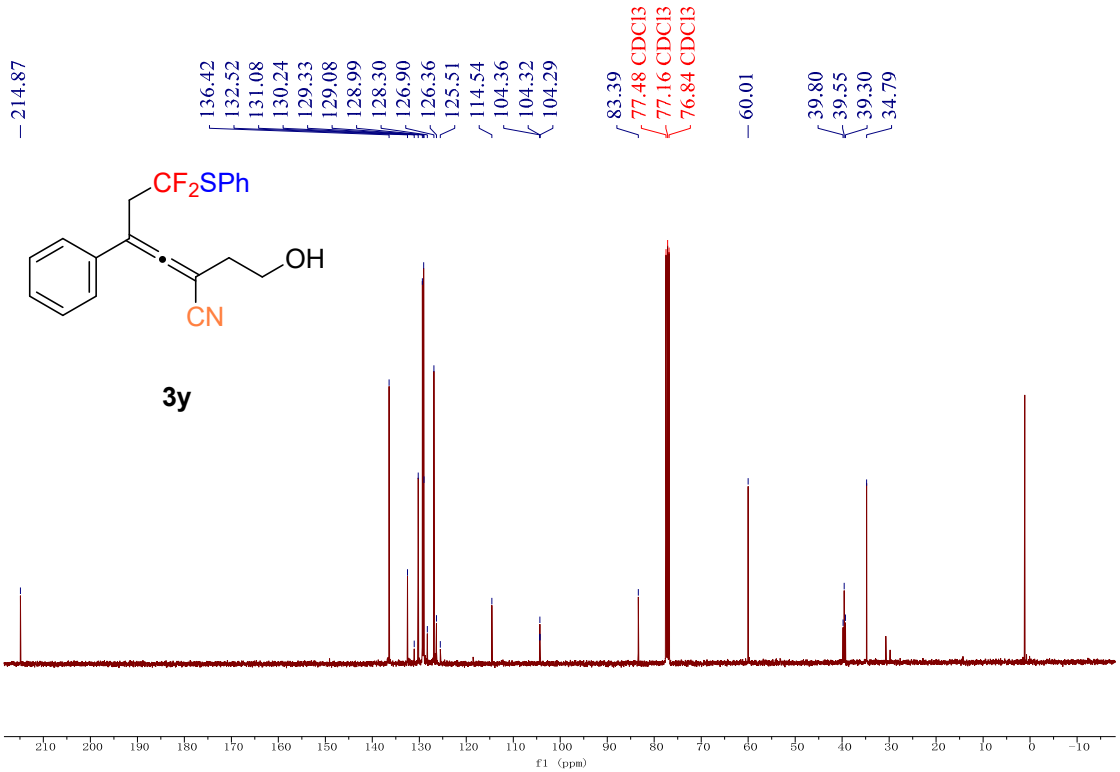

-70.87
-70.88
-70.91
-70.91
-70.94
-70.95
CF2SPh
O
N
CN
O
2.00
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

3x

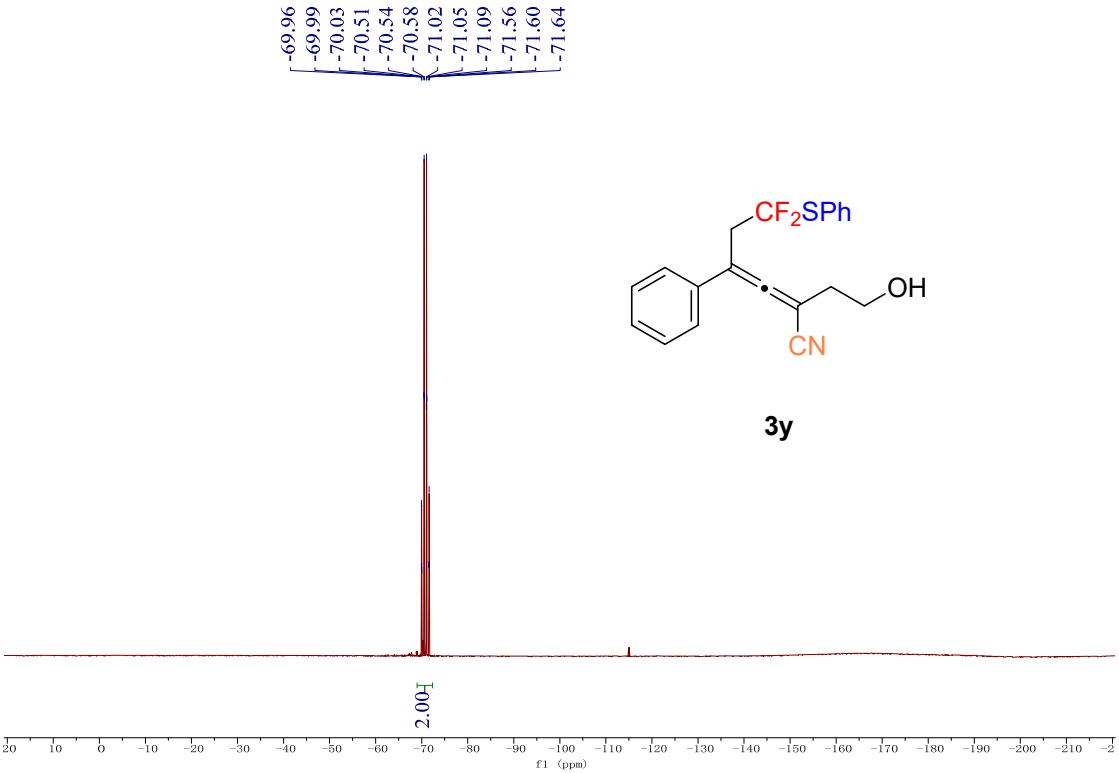
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

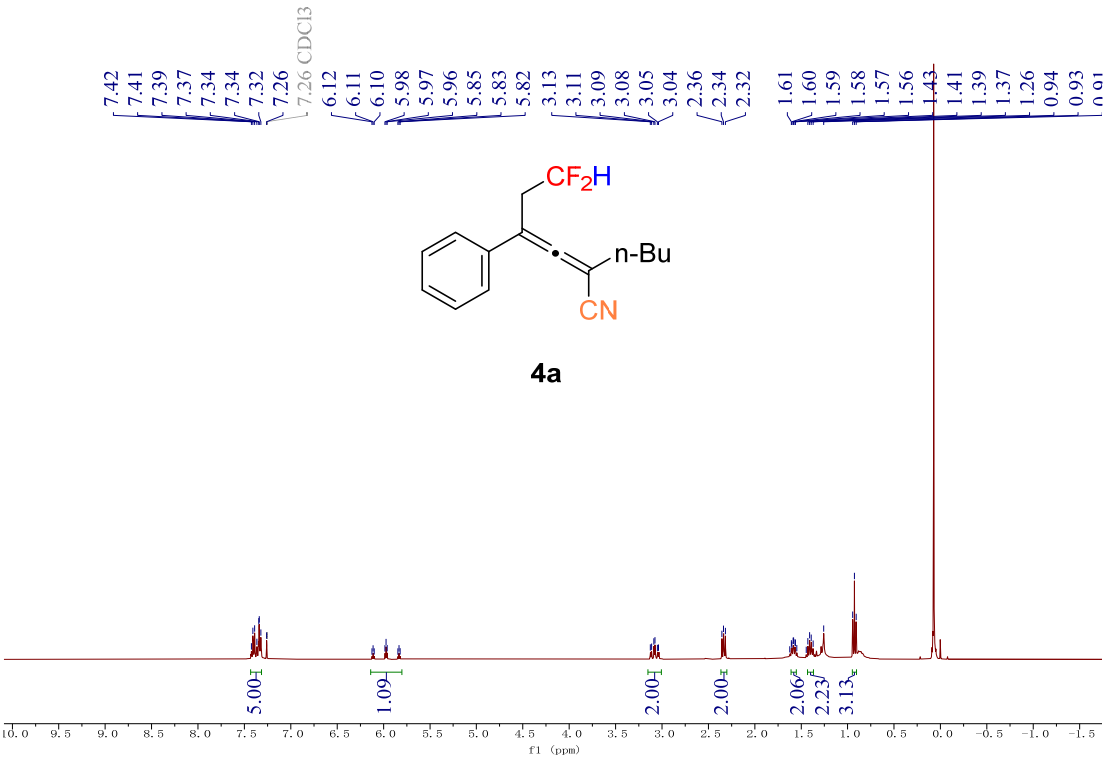


^{19}F NMR (376 MHz, $CDCl_3$)



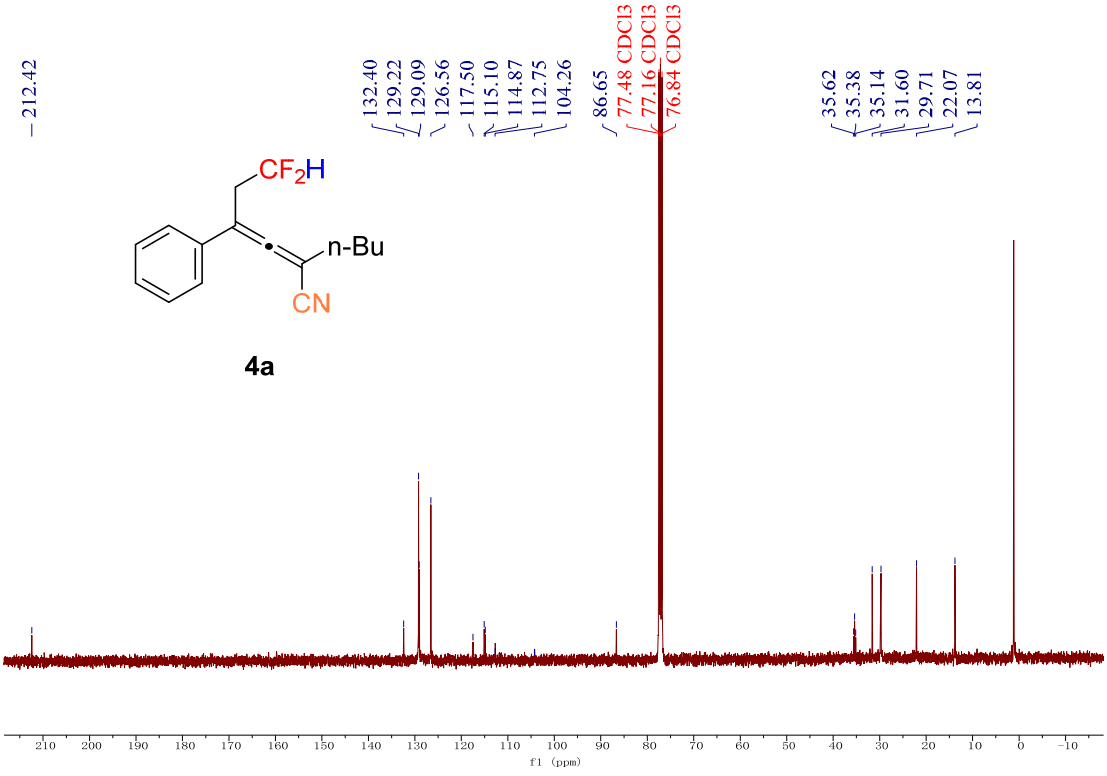
3y

^{1}H NMR (400 MHz, $CDCl_3$)

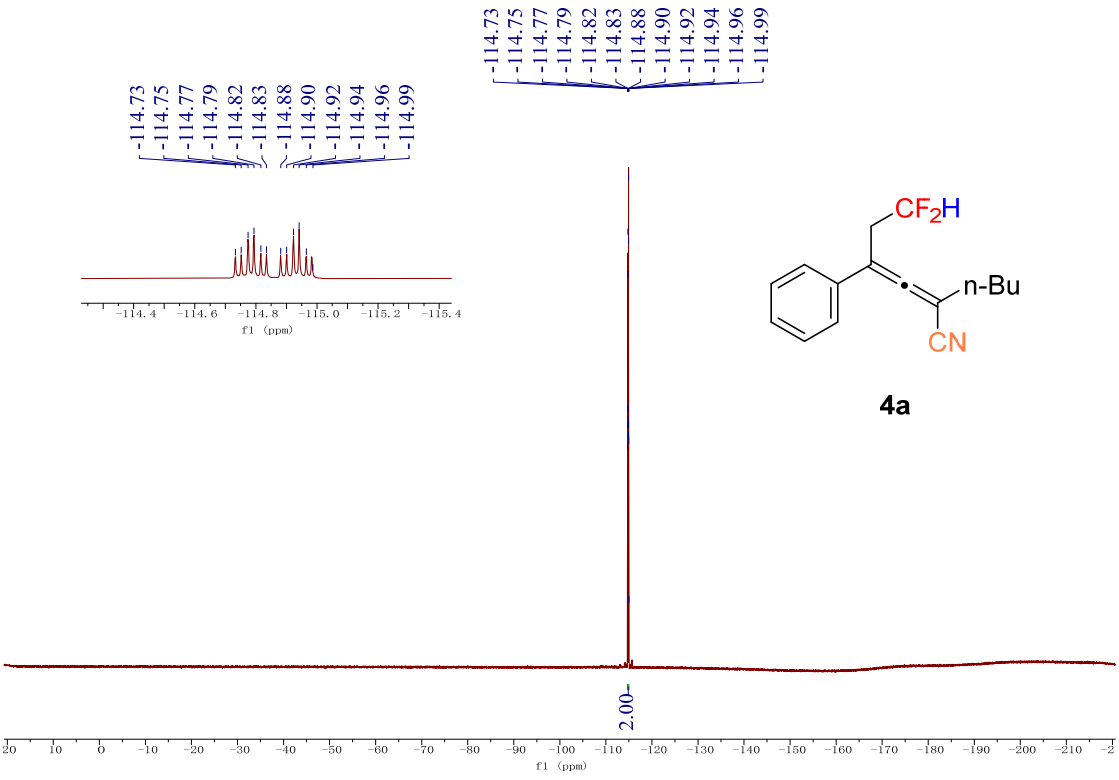


4a

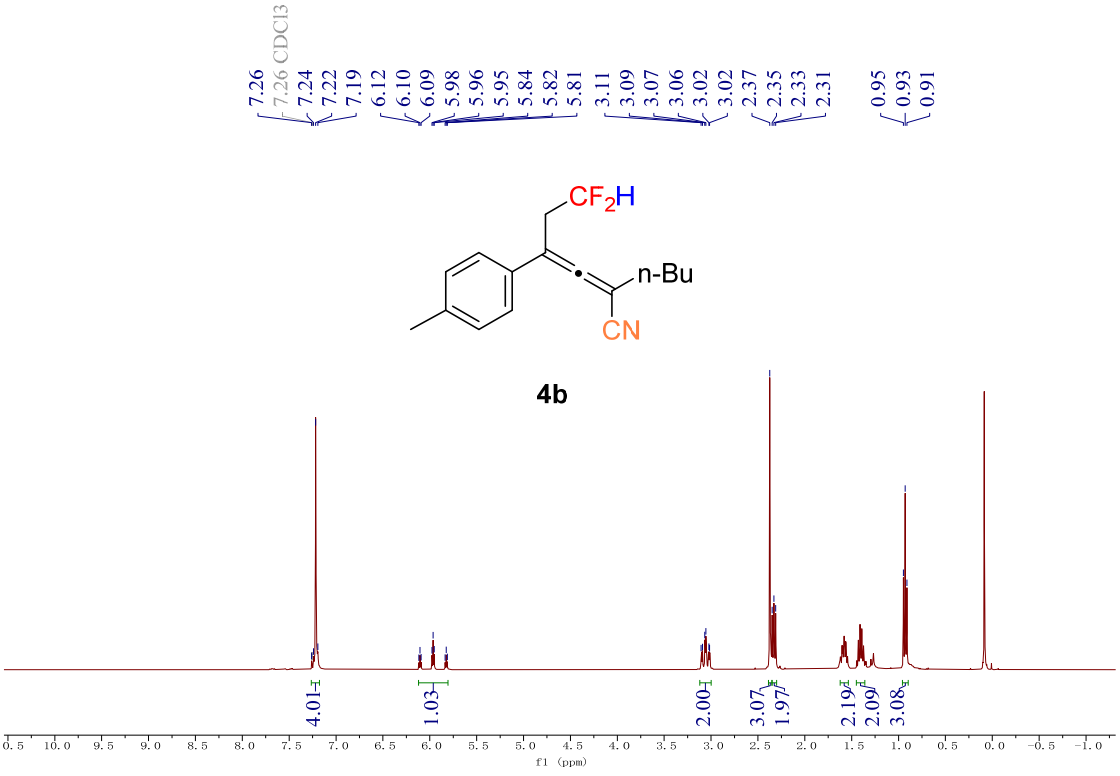
^{13}C NMR (101 MHz, $CDCl_3$)



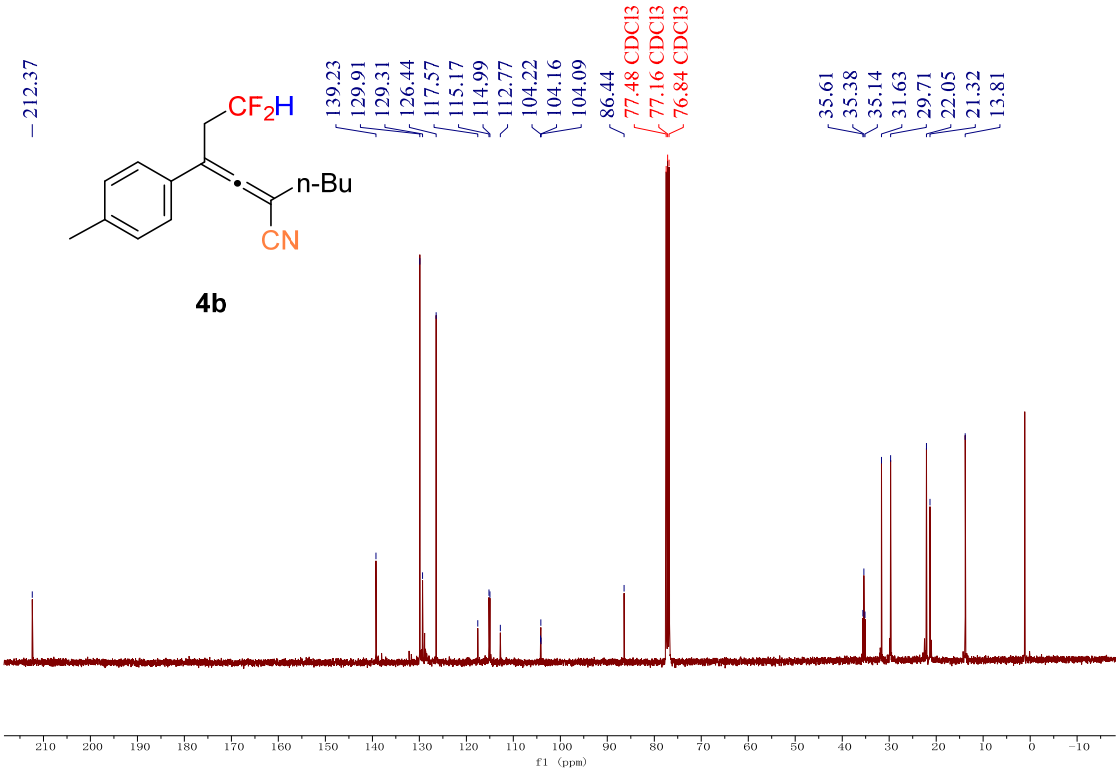
^{19}F NMR (376 MHz, $CDCl_3$)



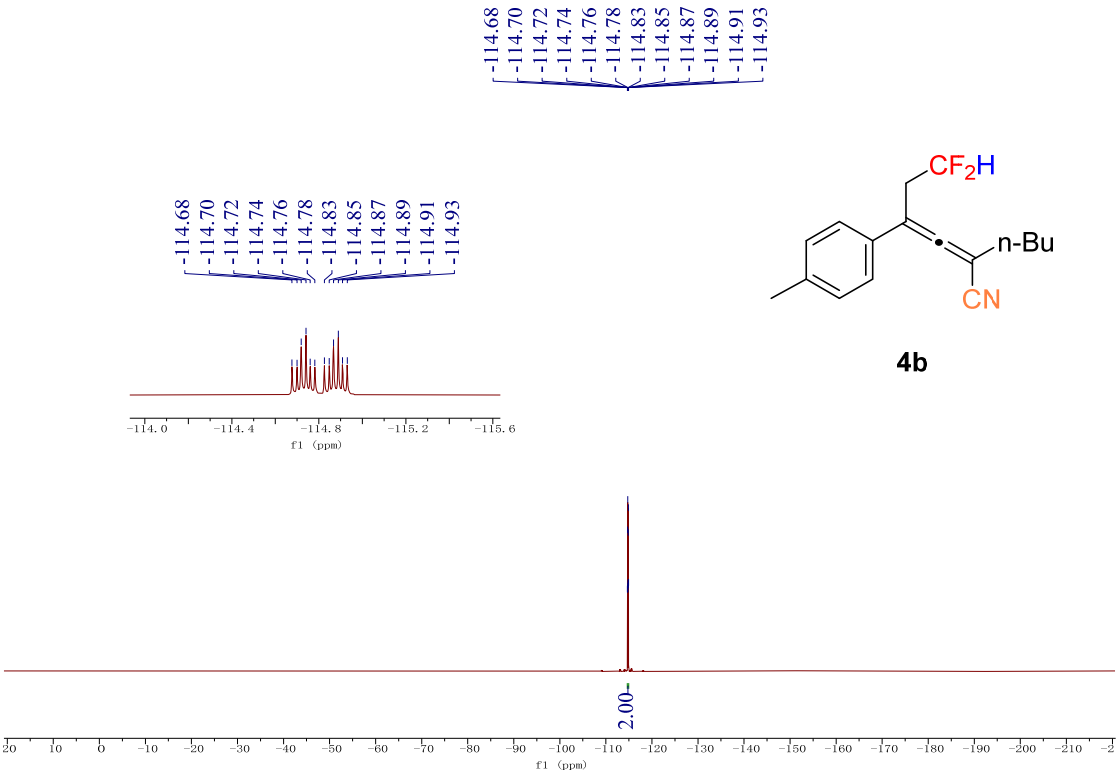
^{1}H NMR (400 MHz, $CDCl_3$)



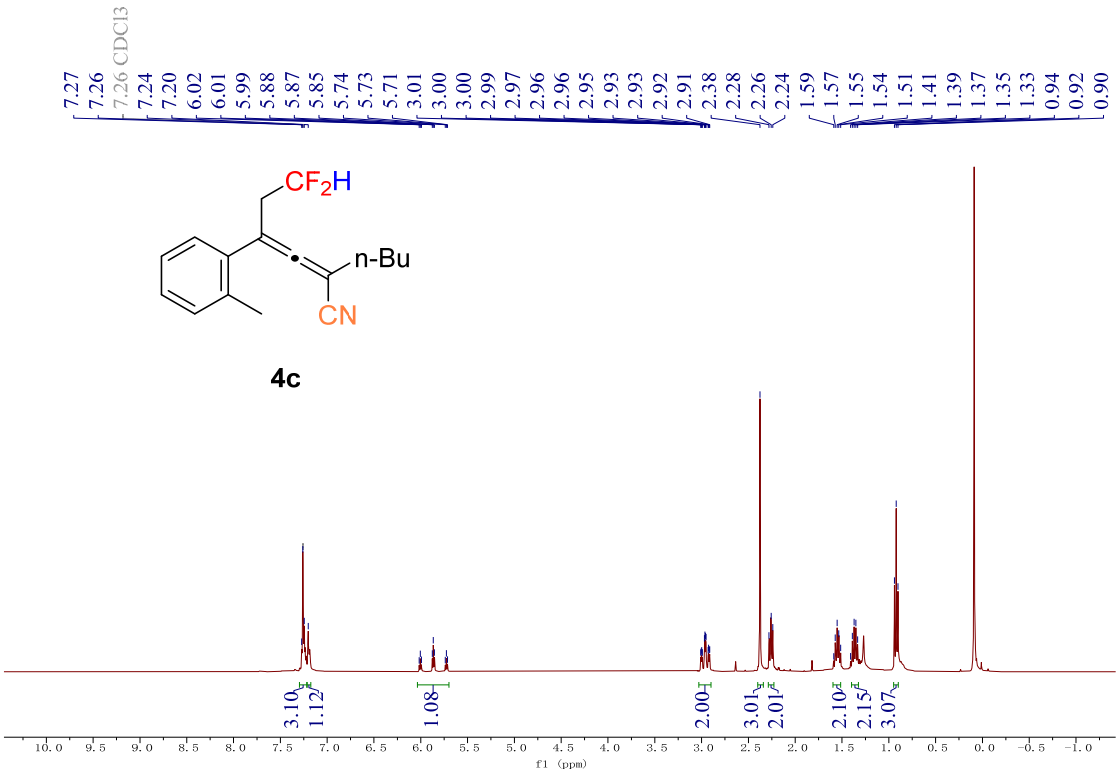
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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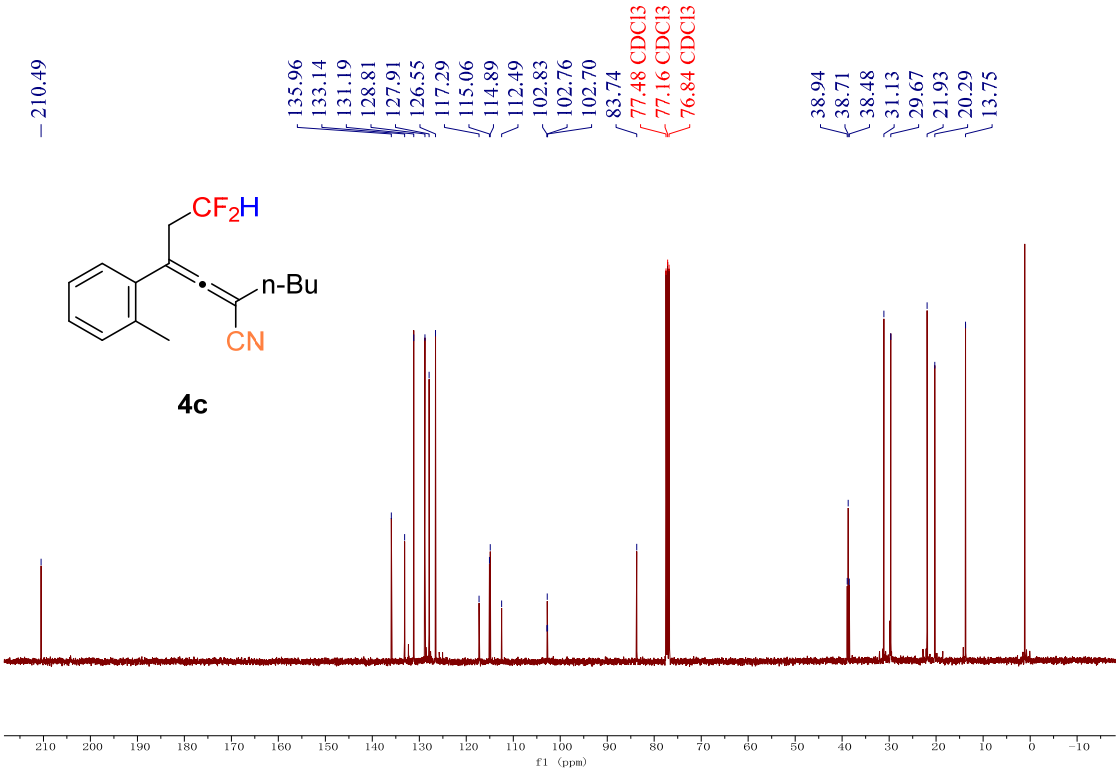

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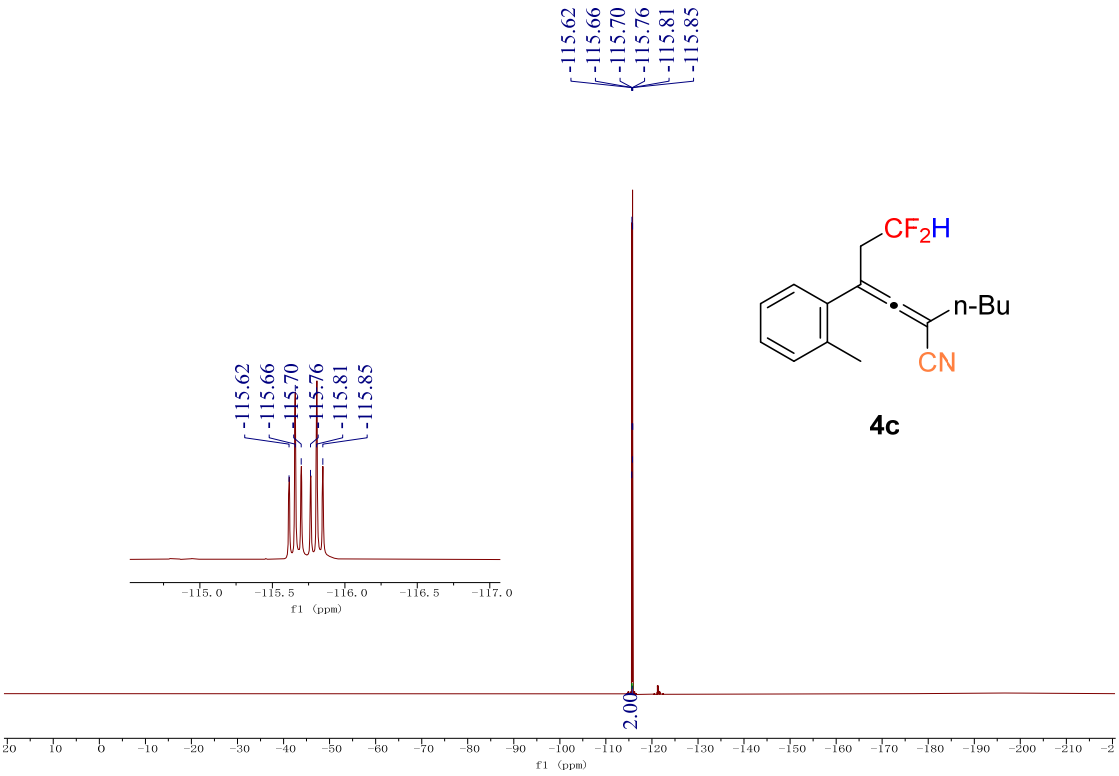

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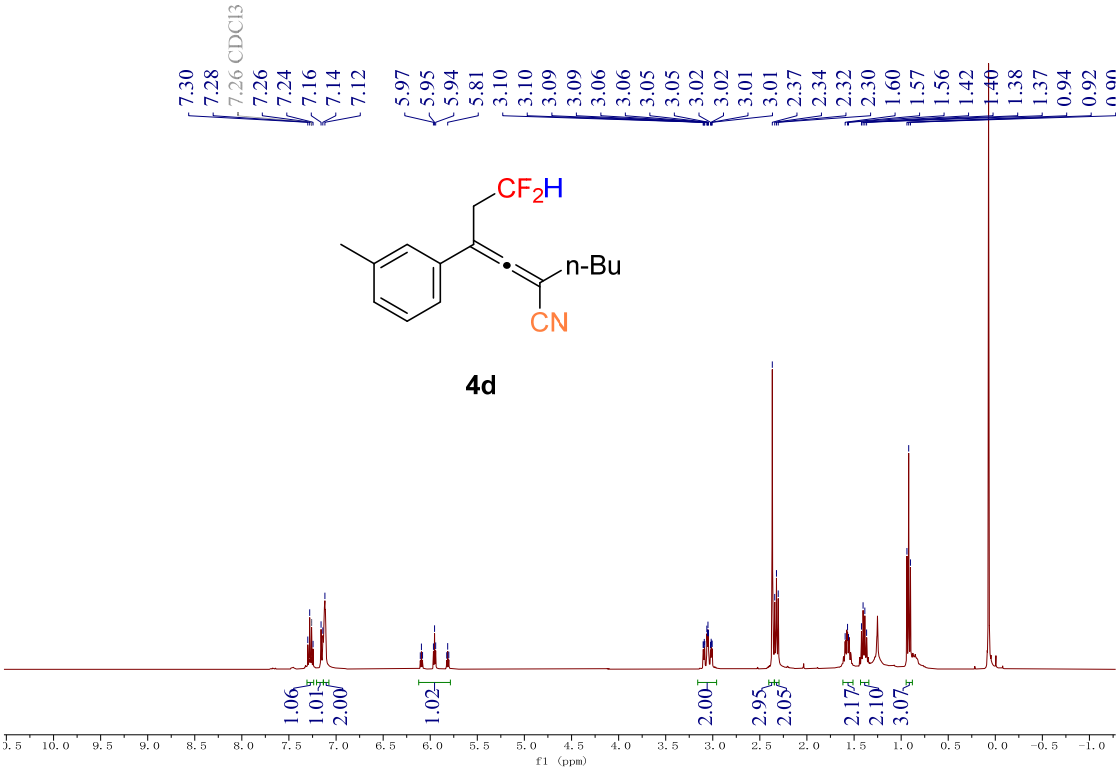

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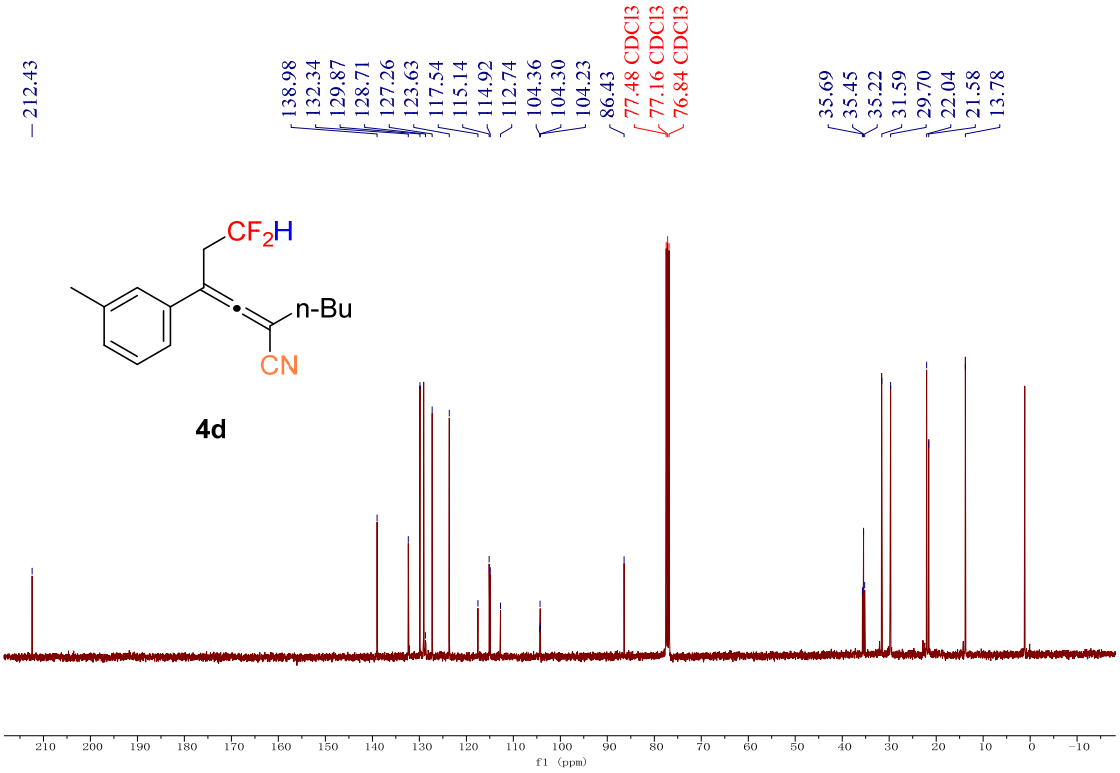

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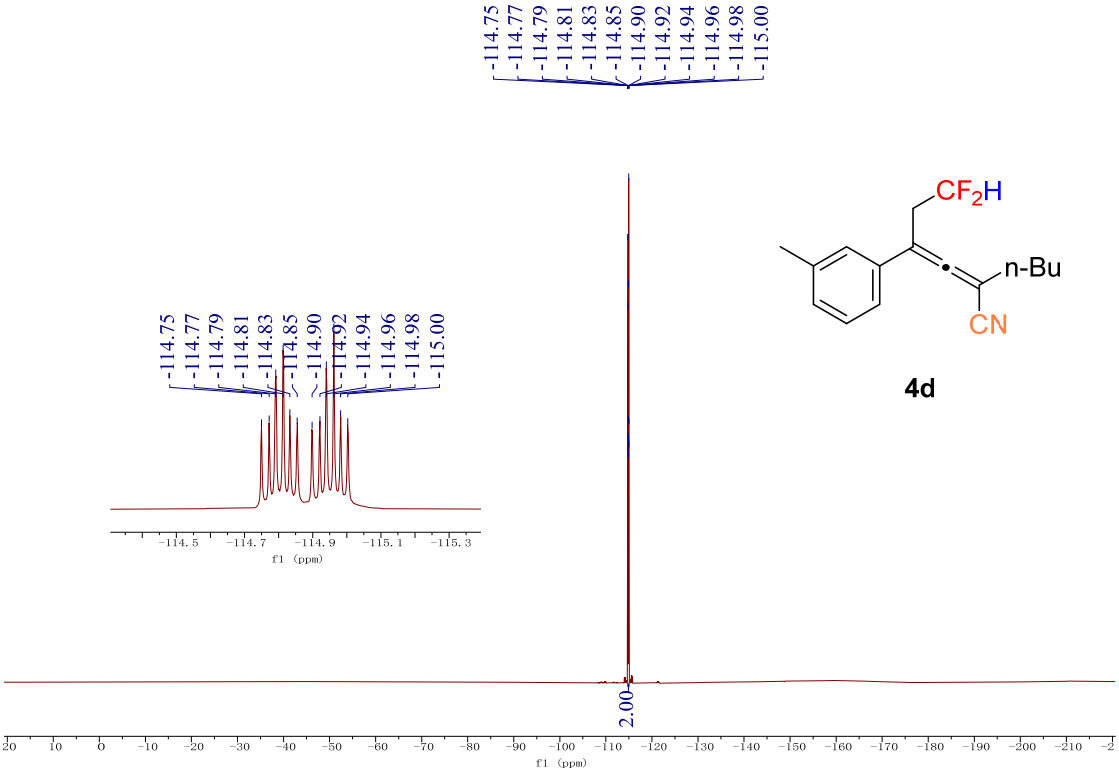

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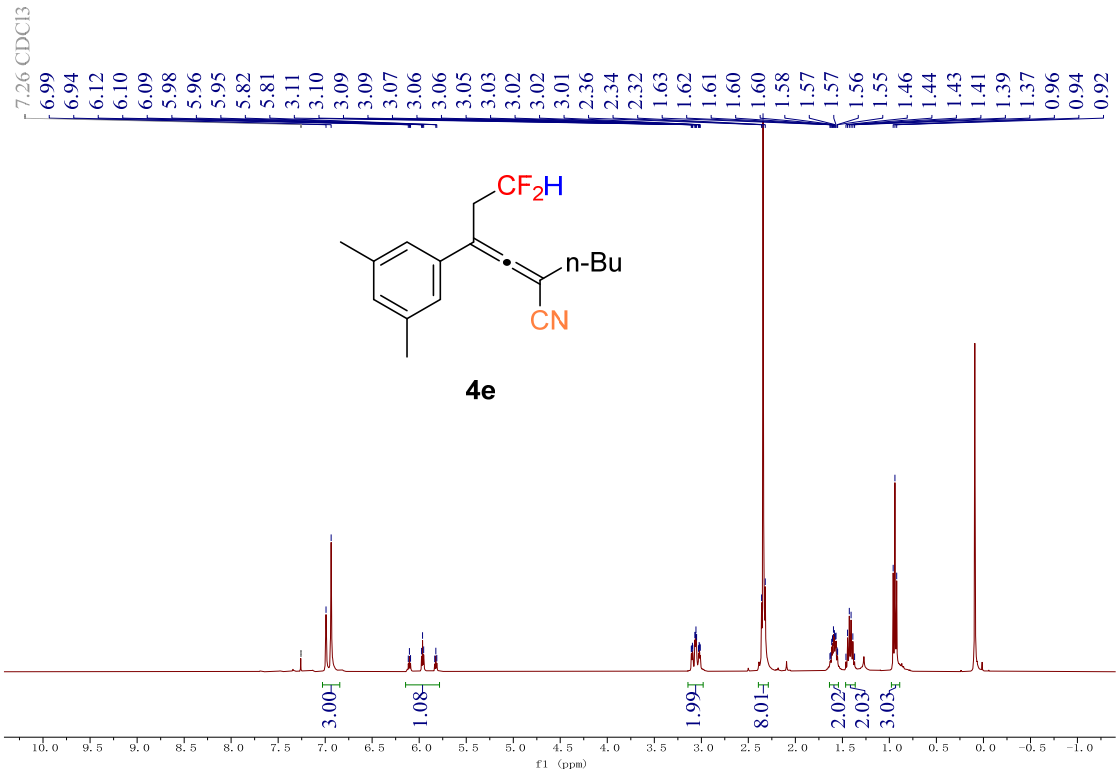

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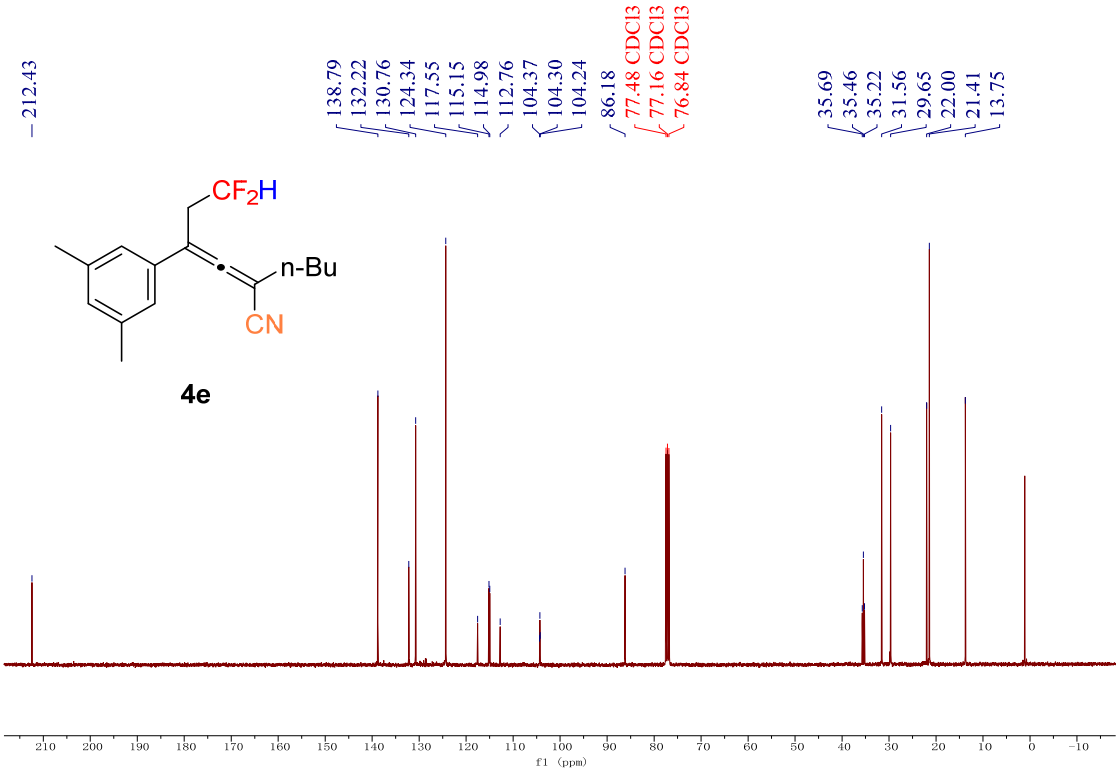

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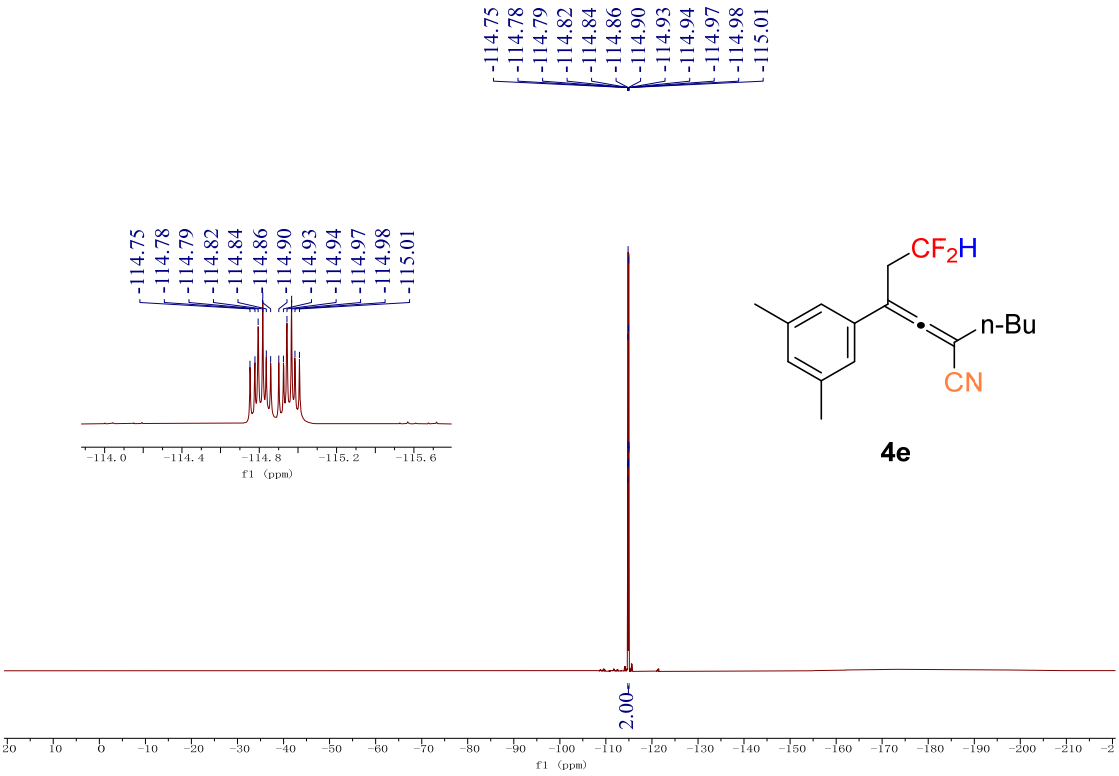

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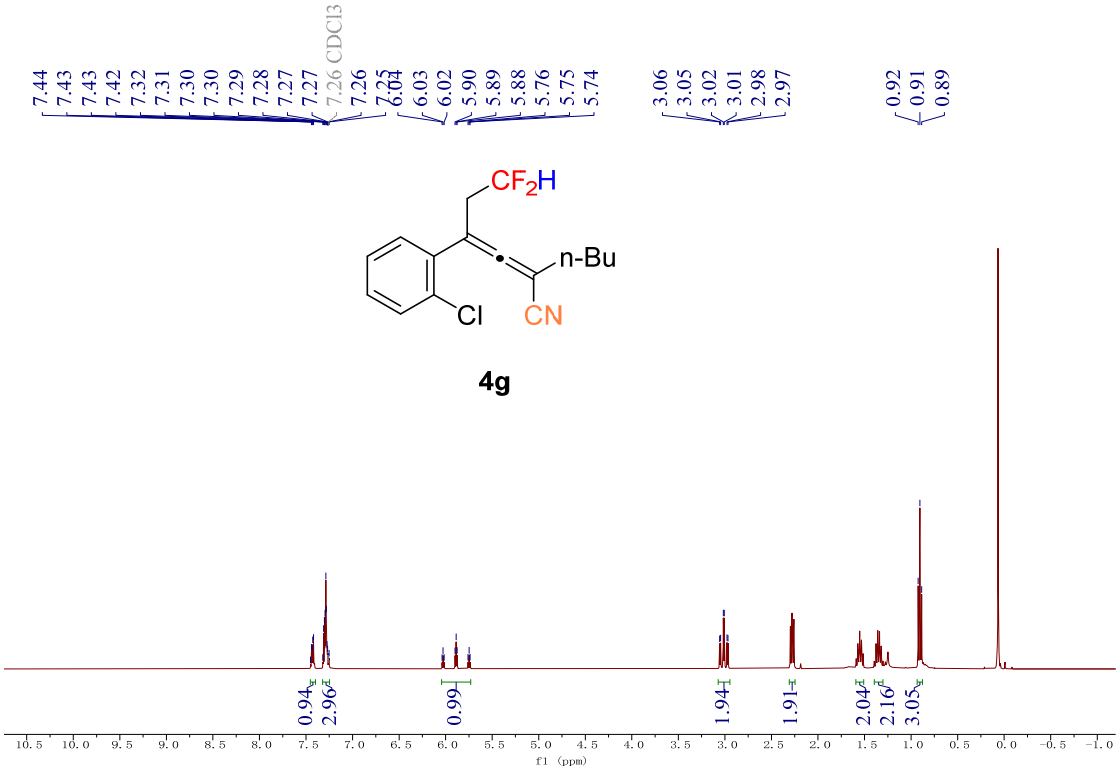

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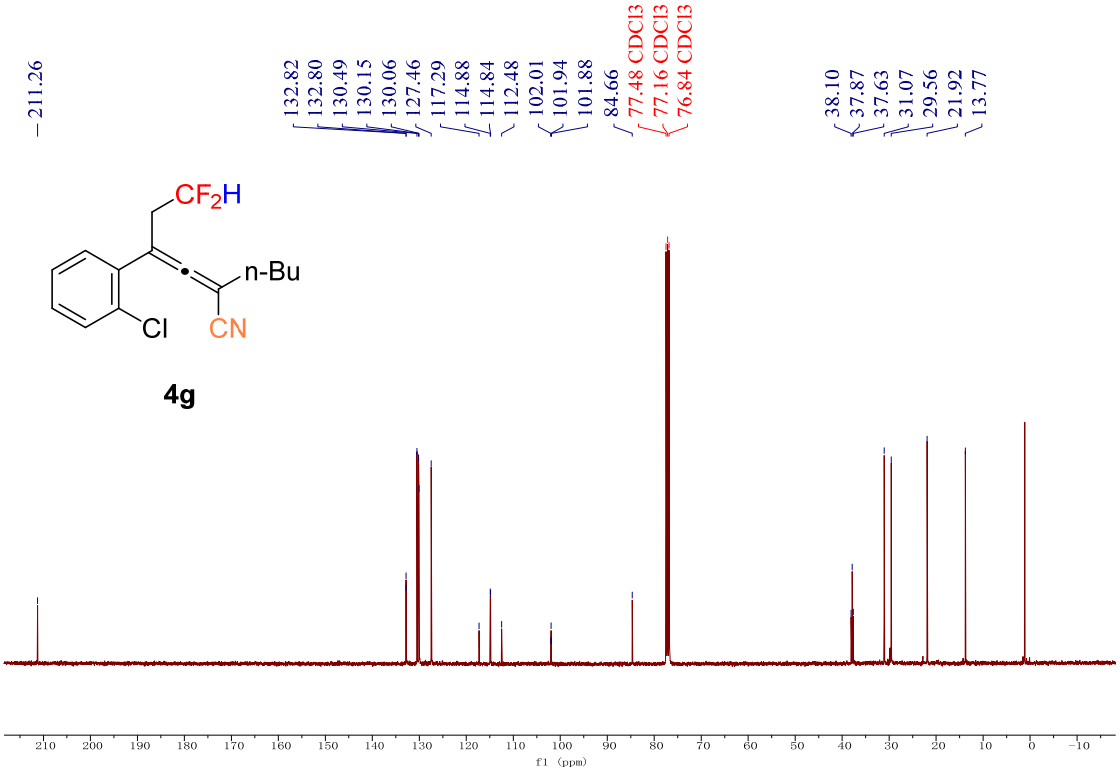

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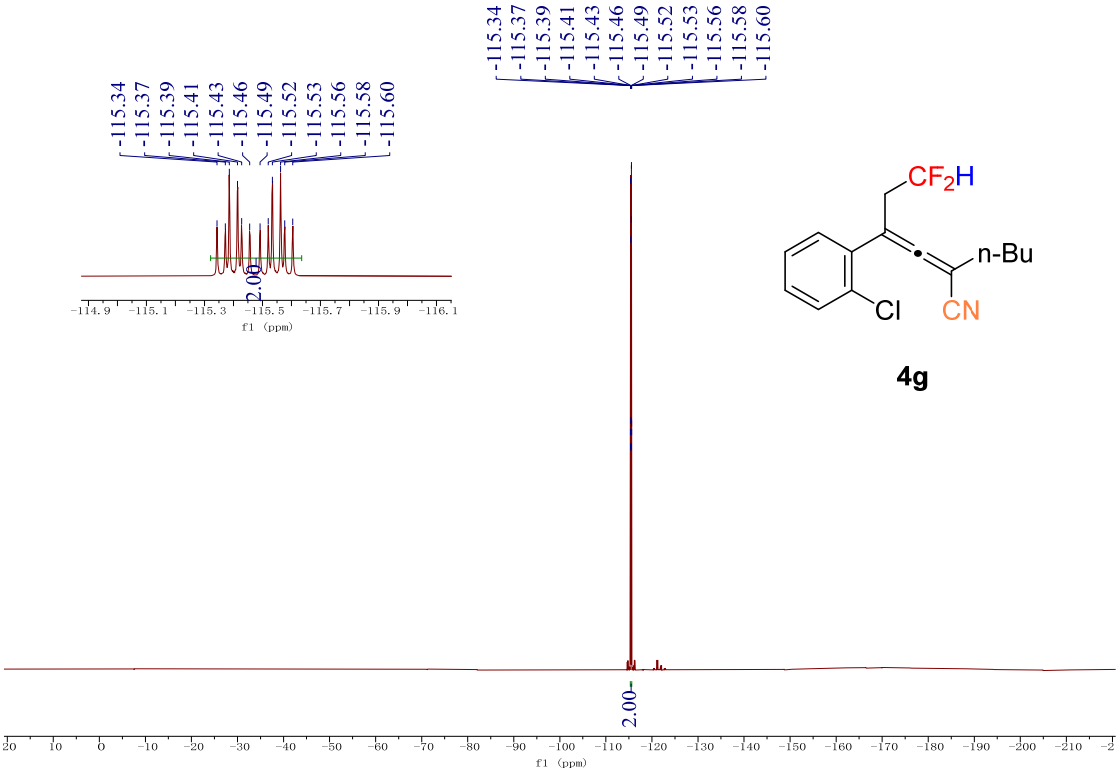

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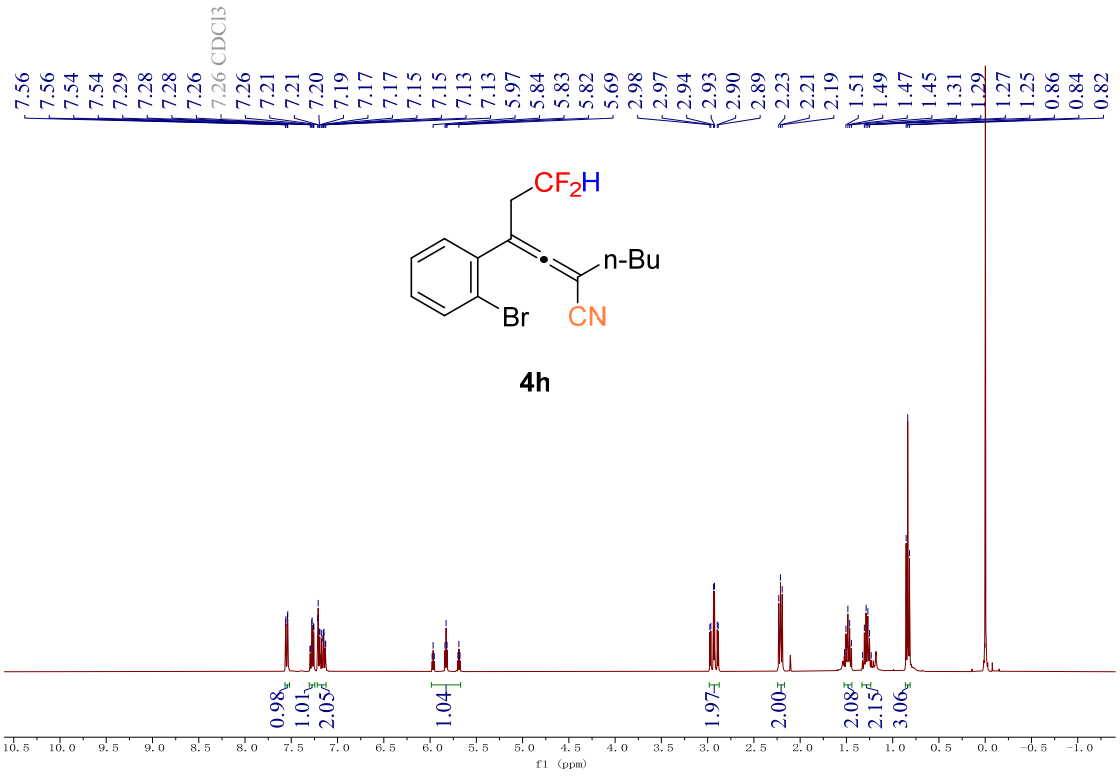

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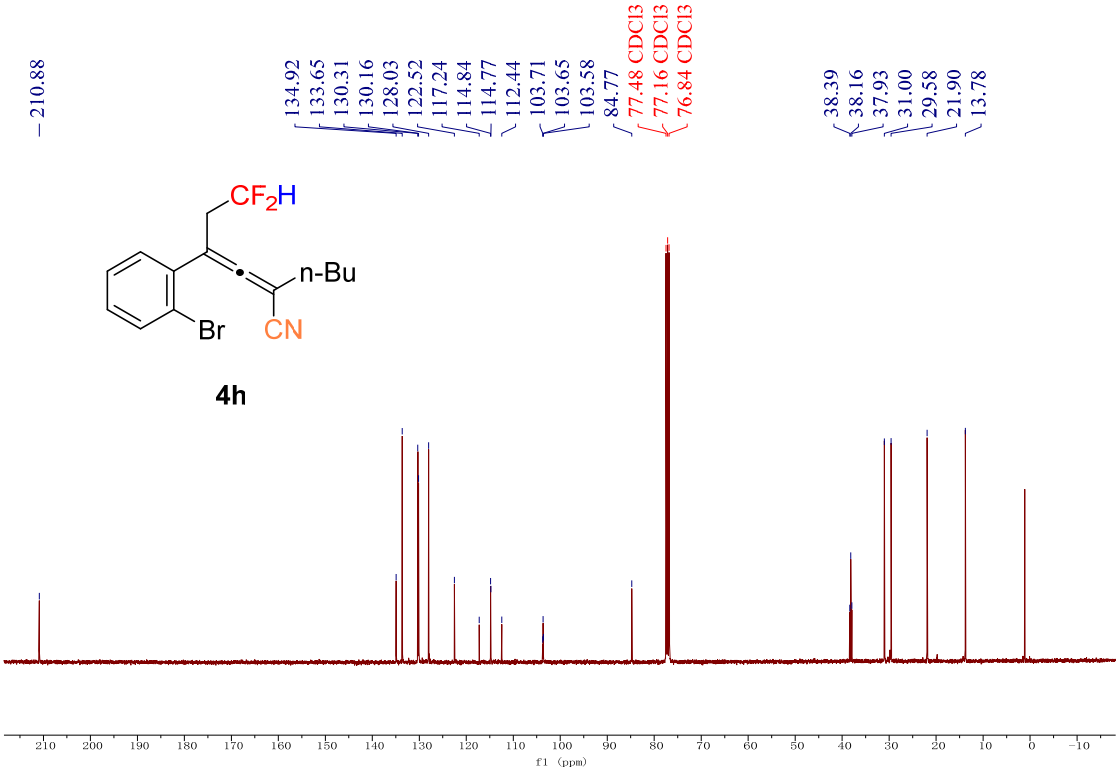

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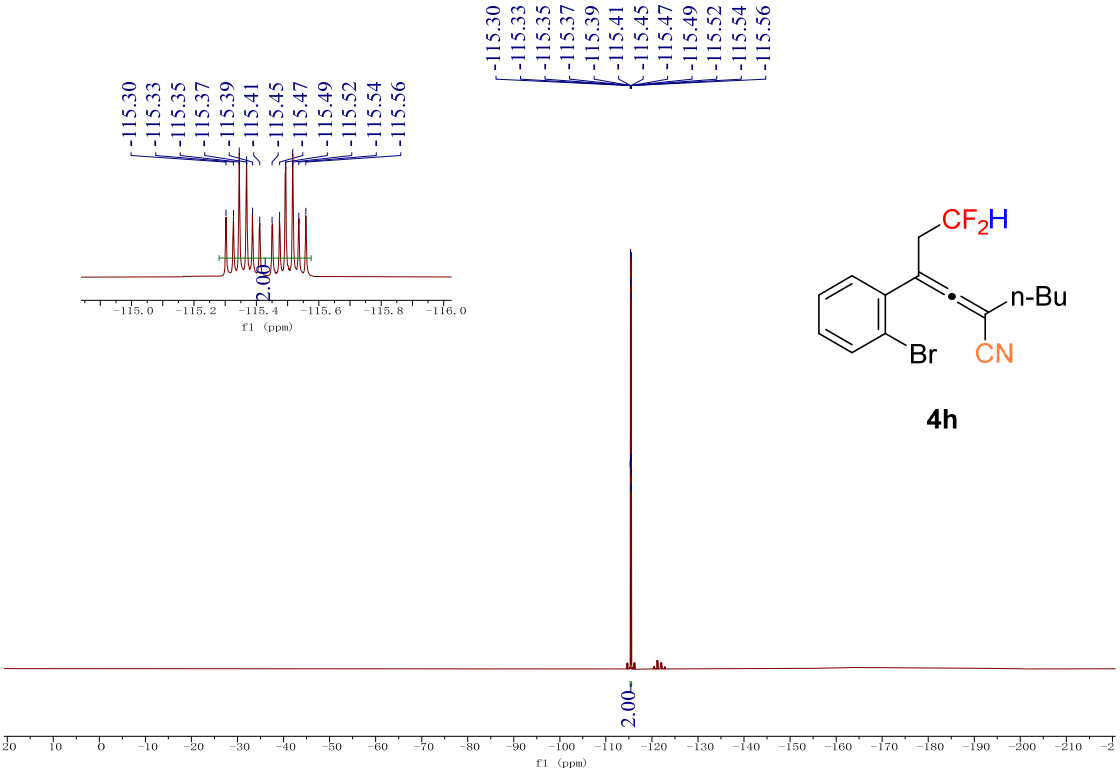

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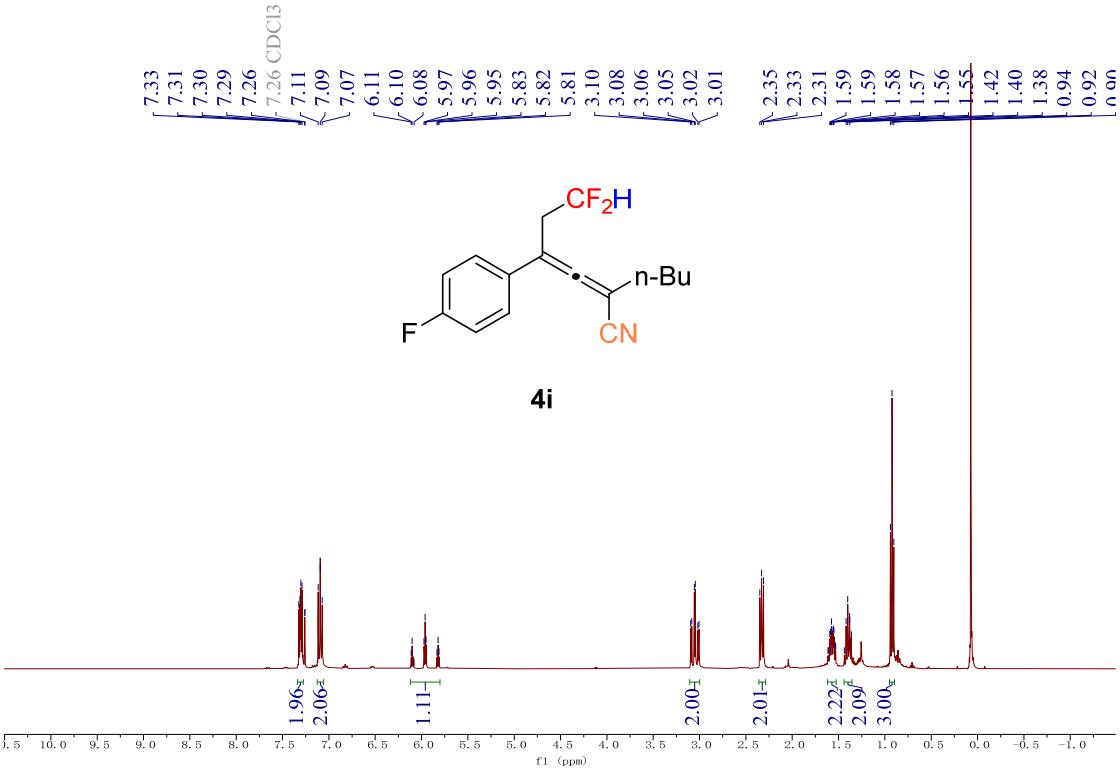

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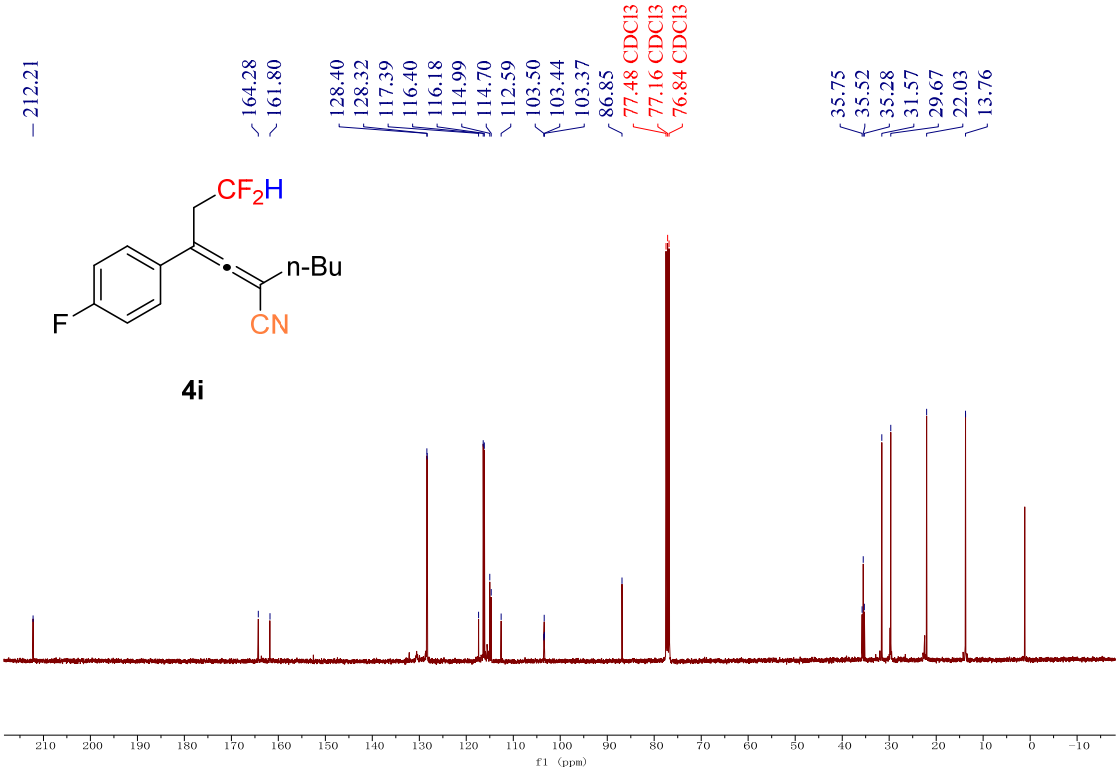

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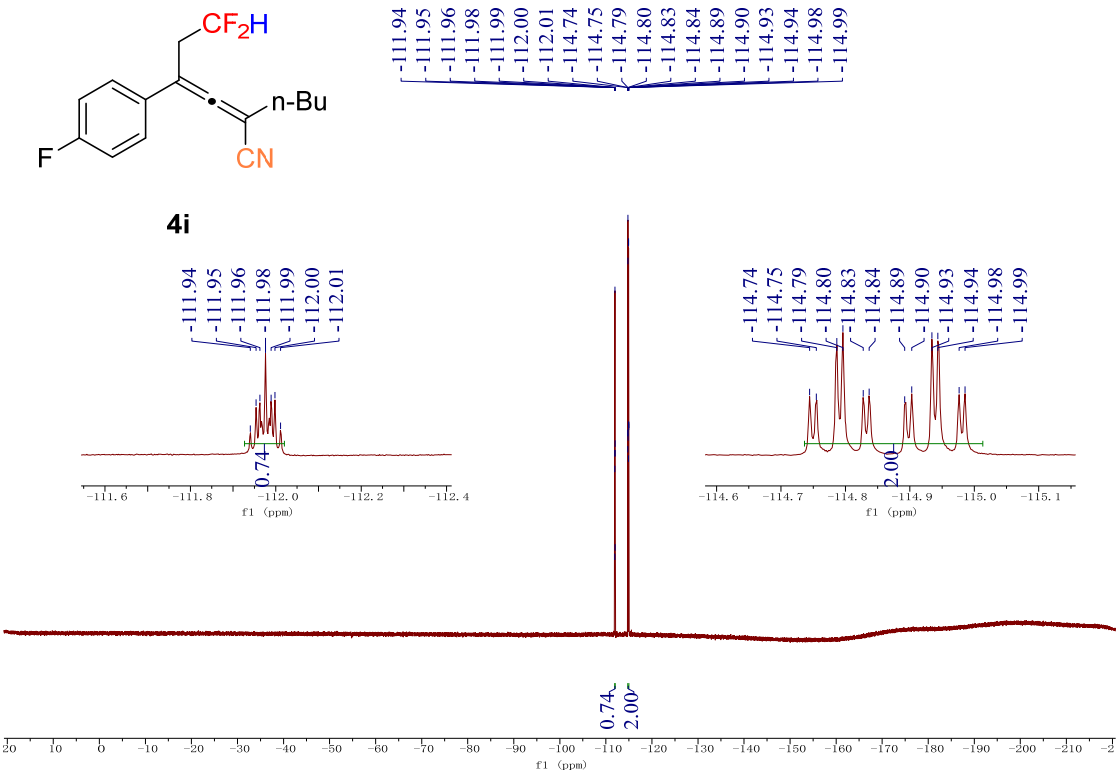

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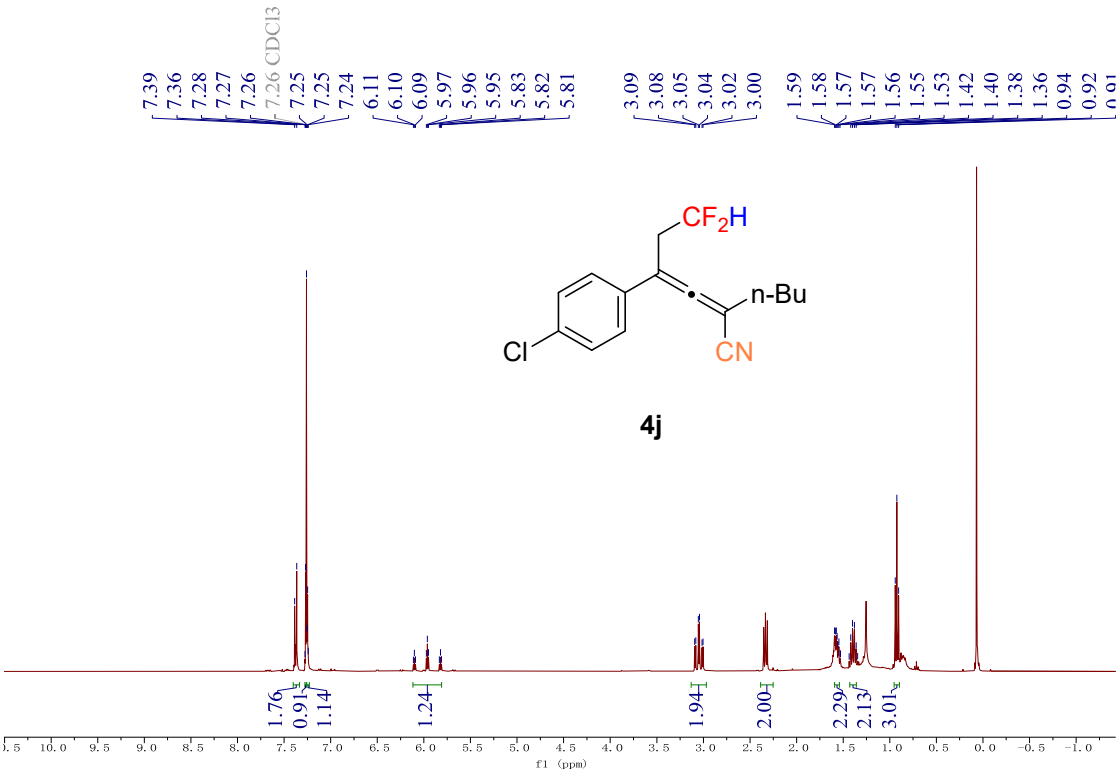

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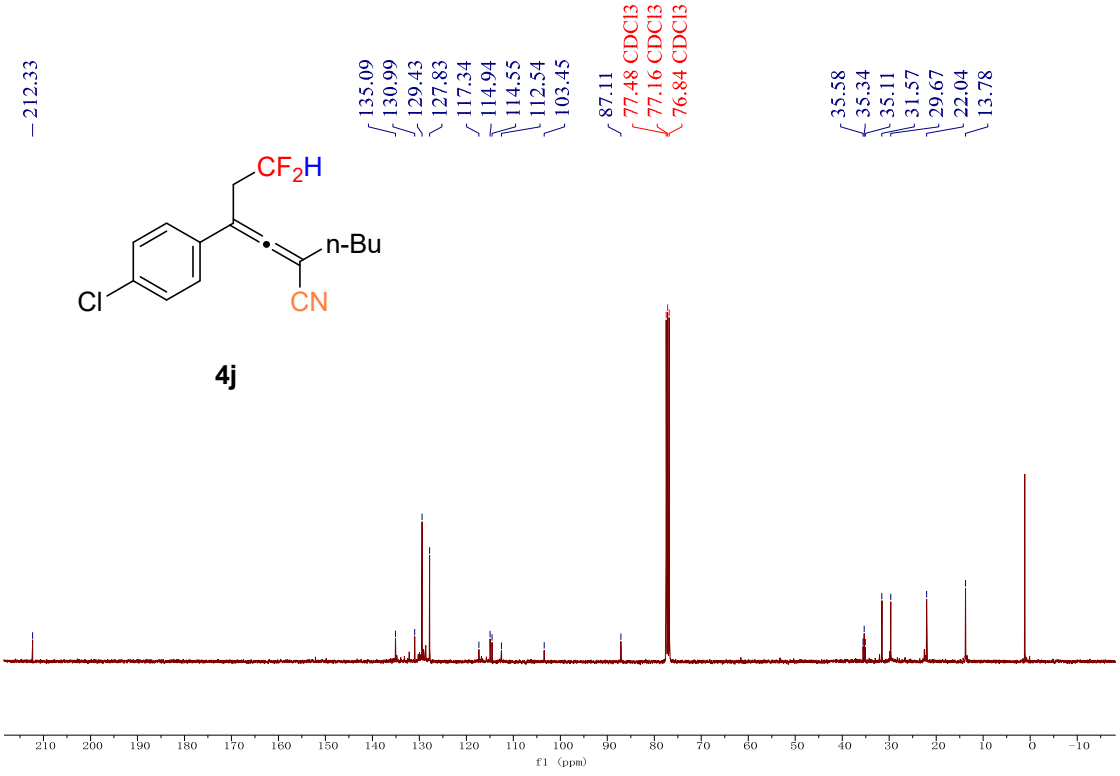

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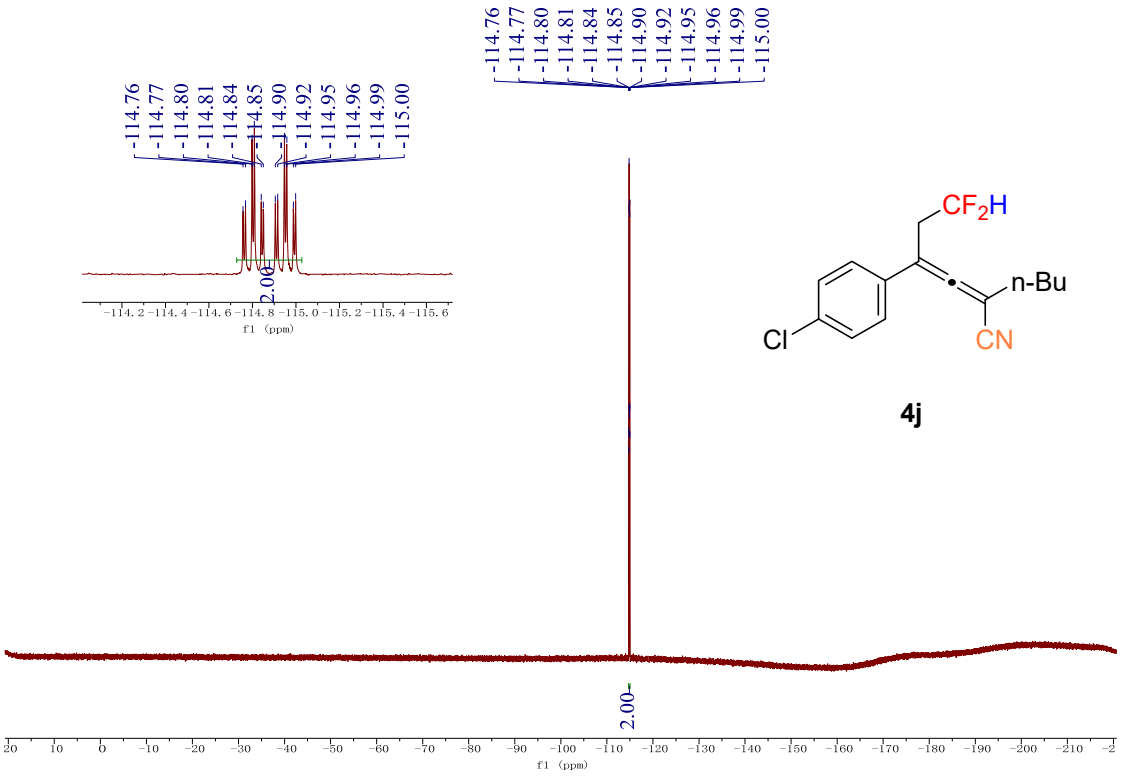

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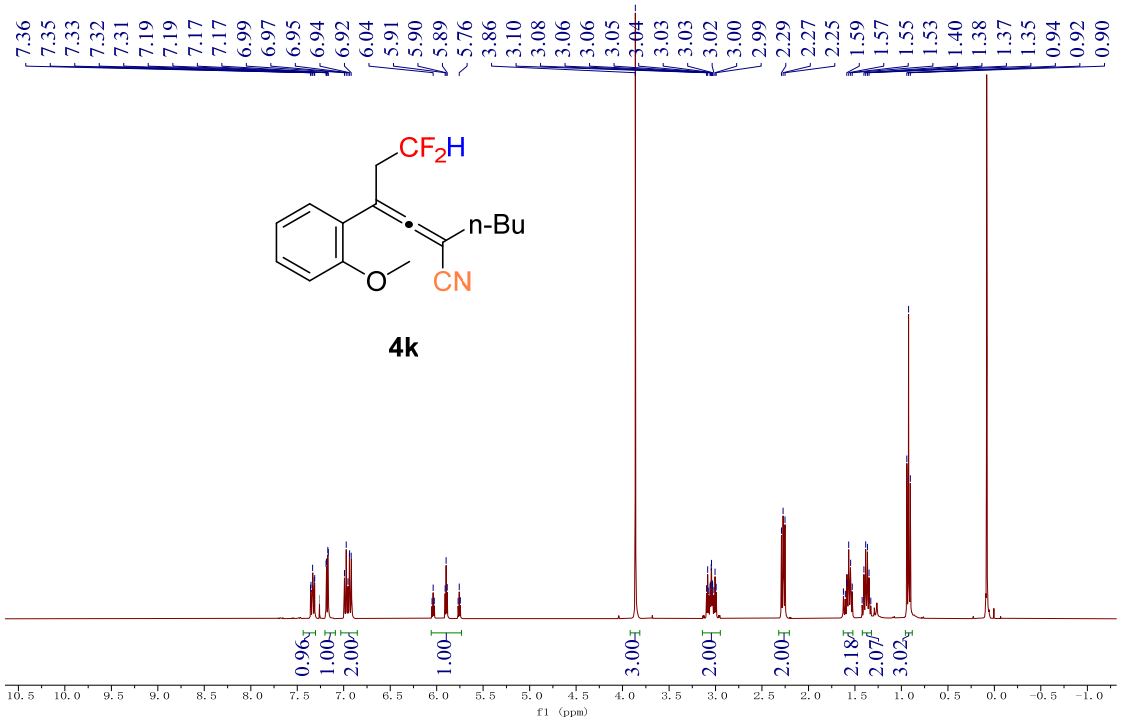

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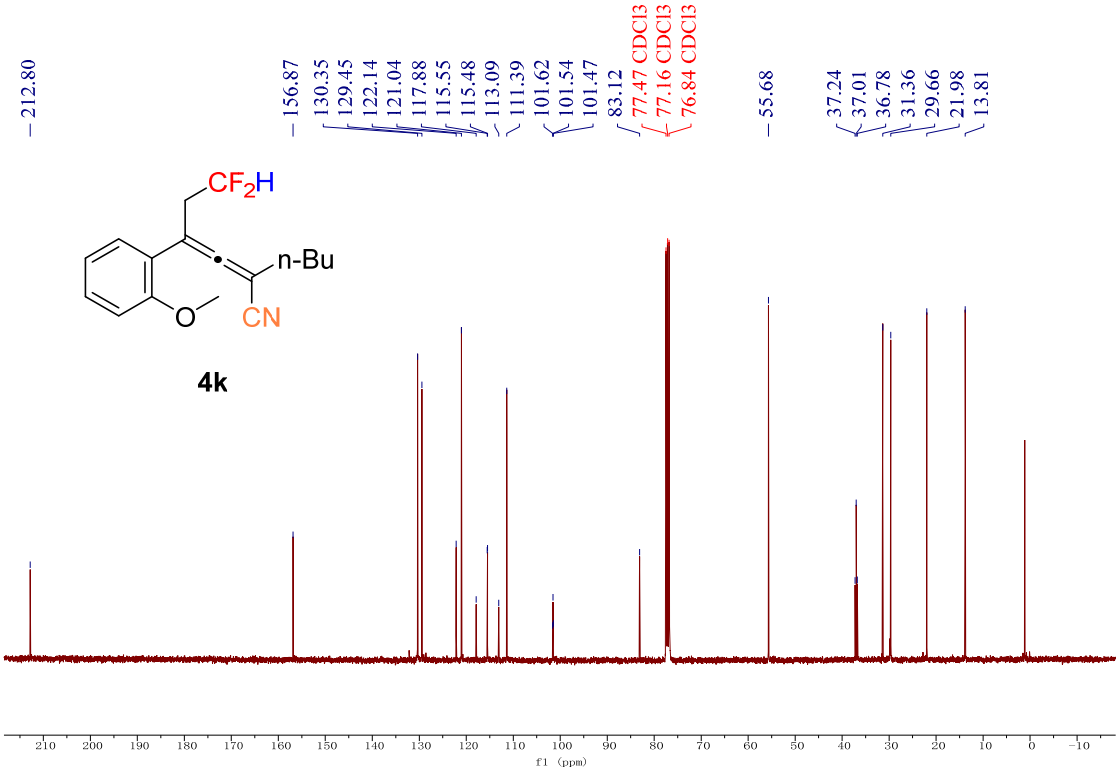

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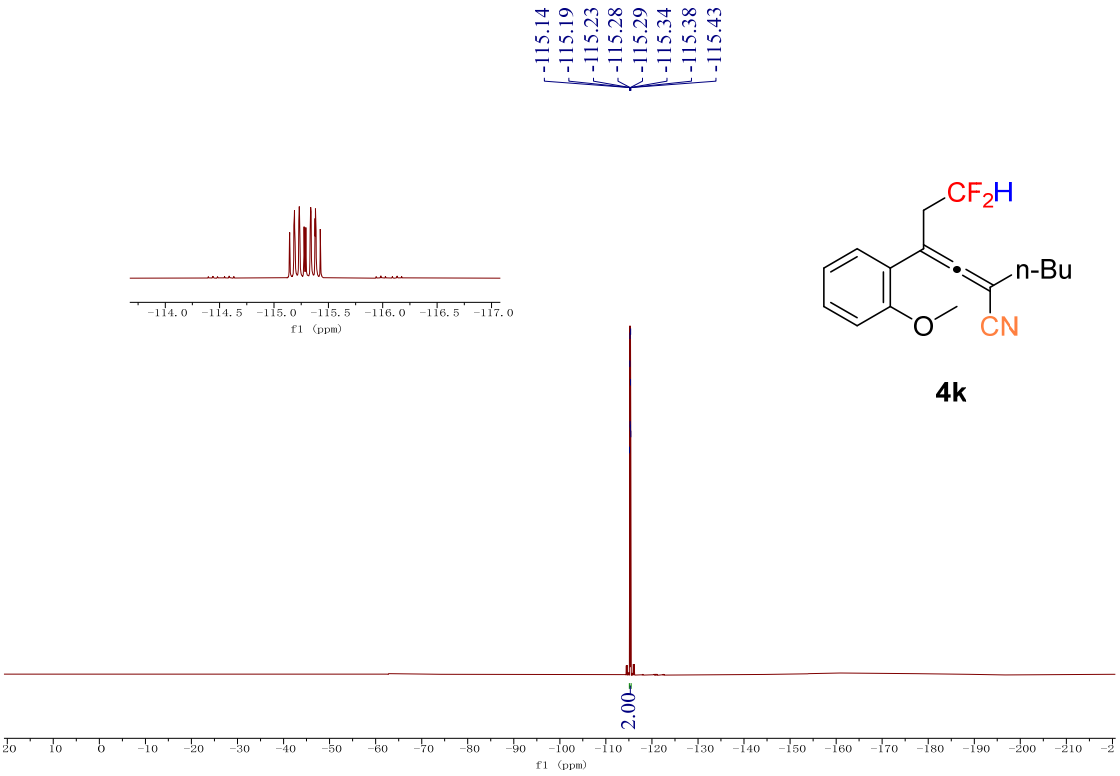

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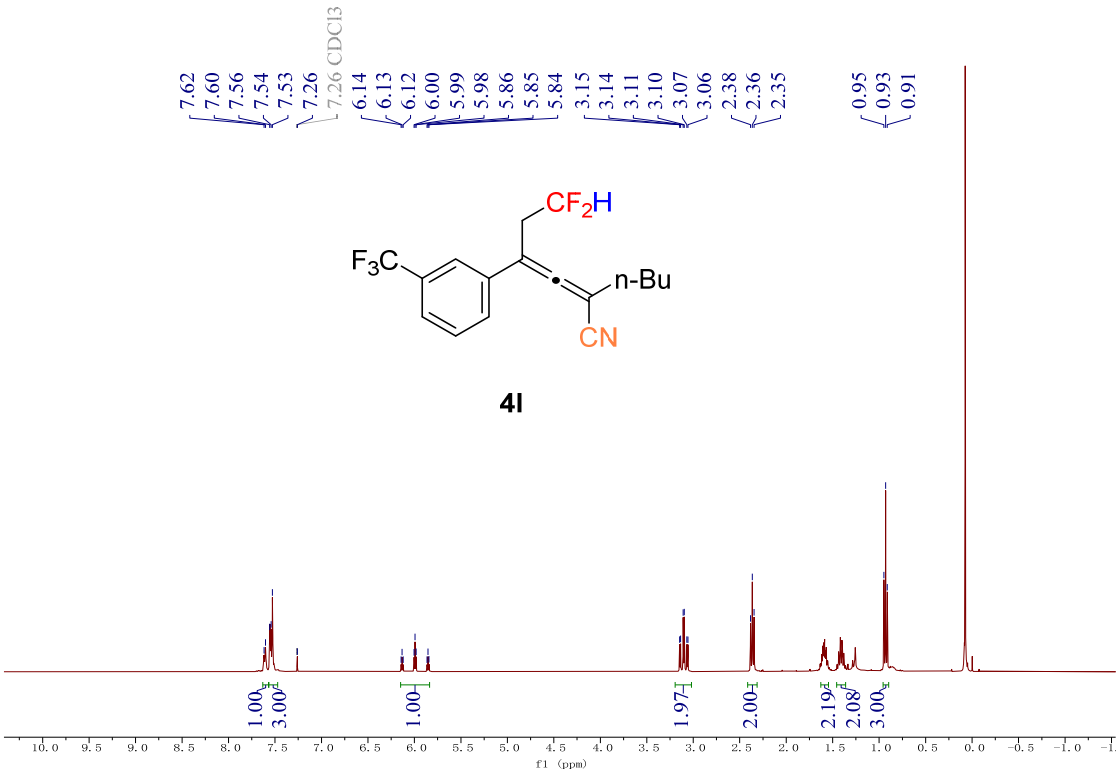

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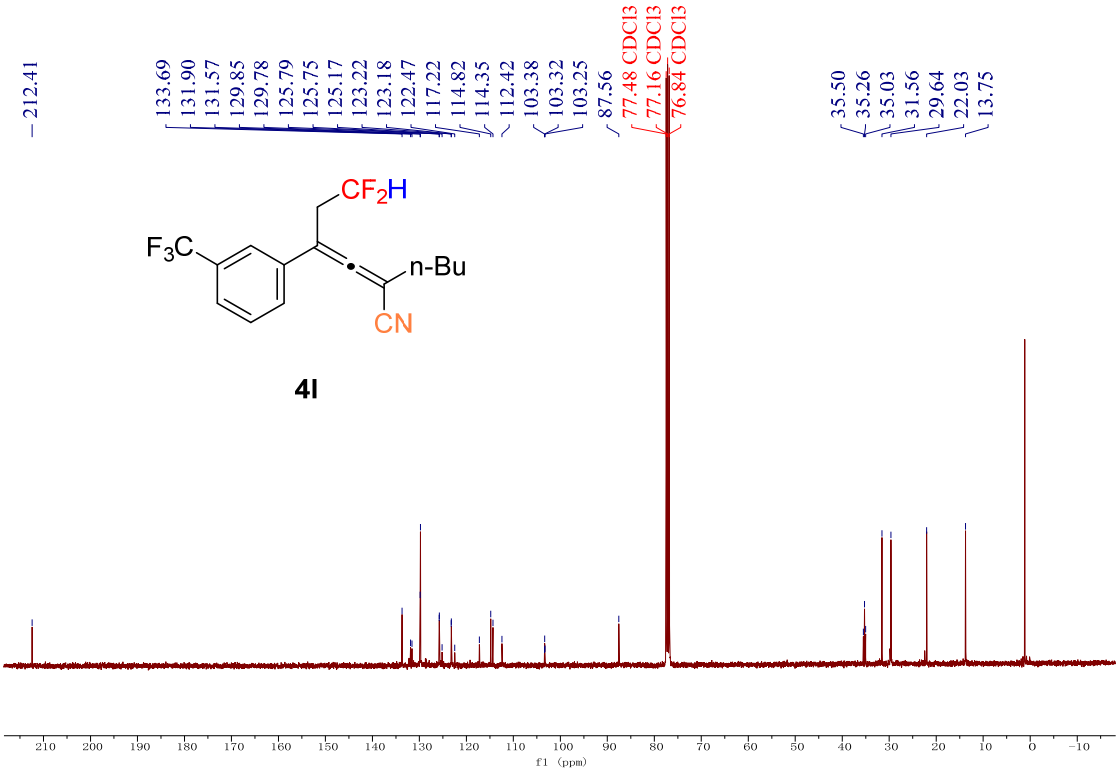

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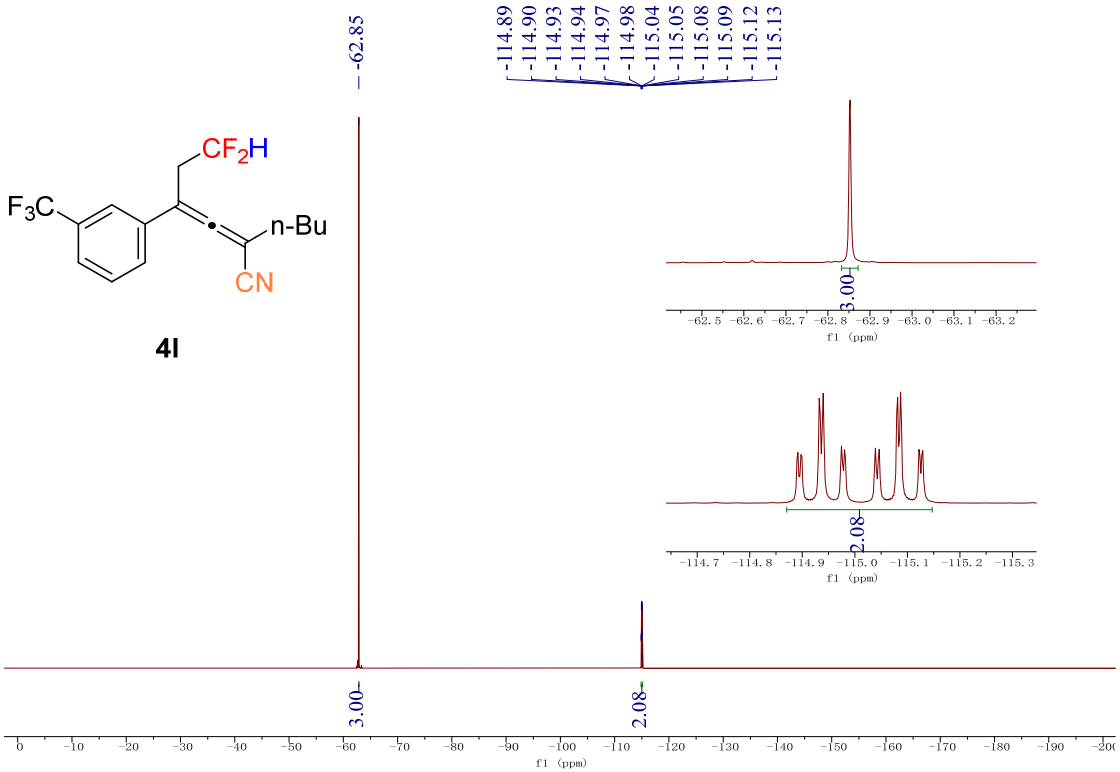

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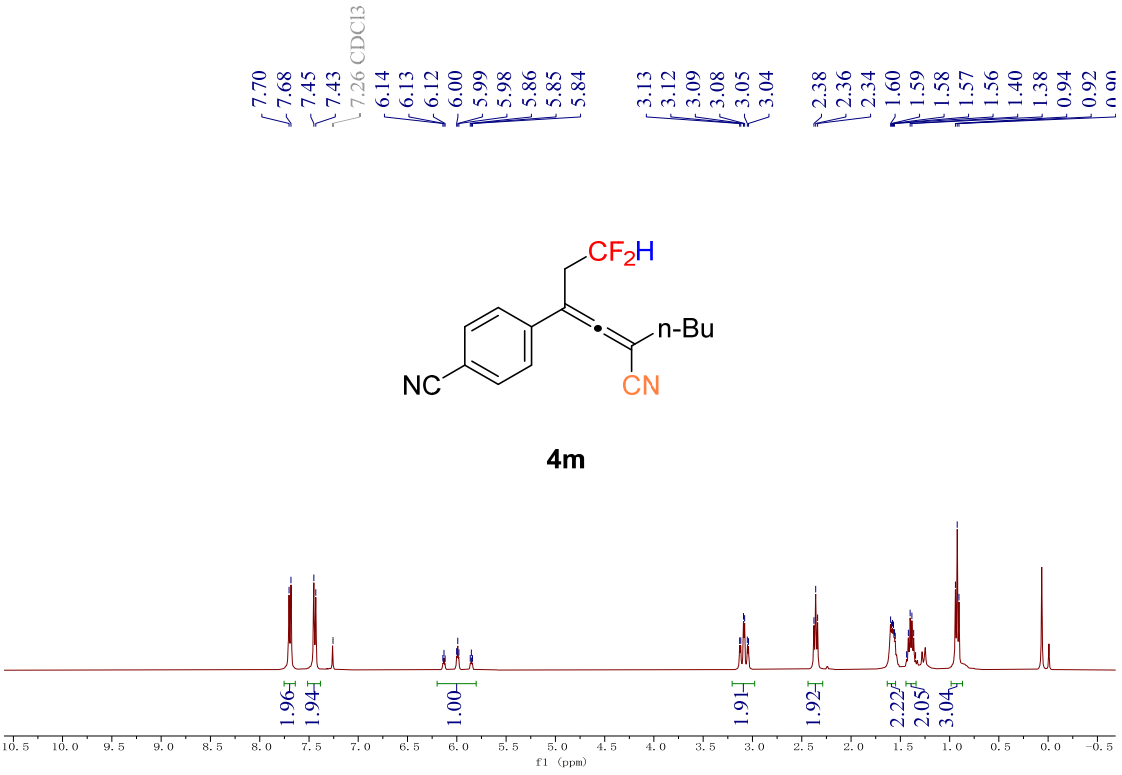
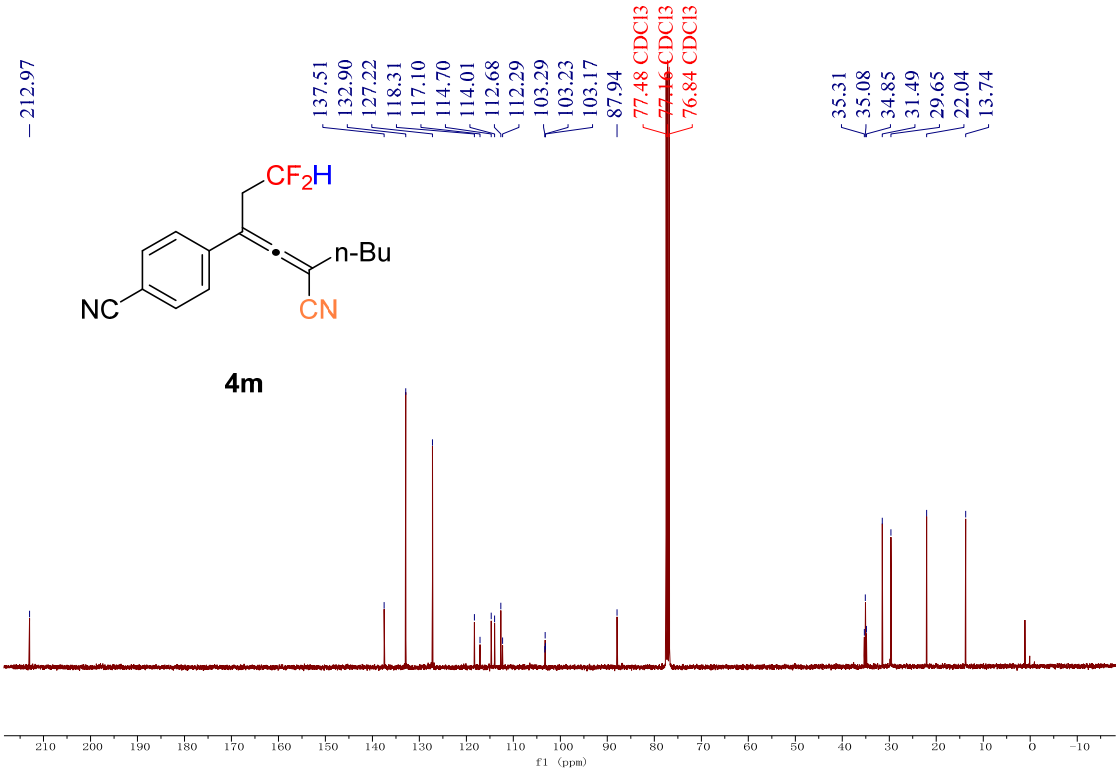
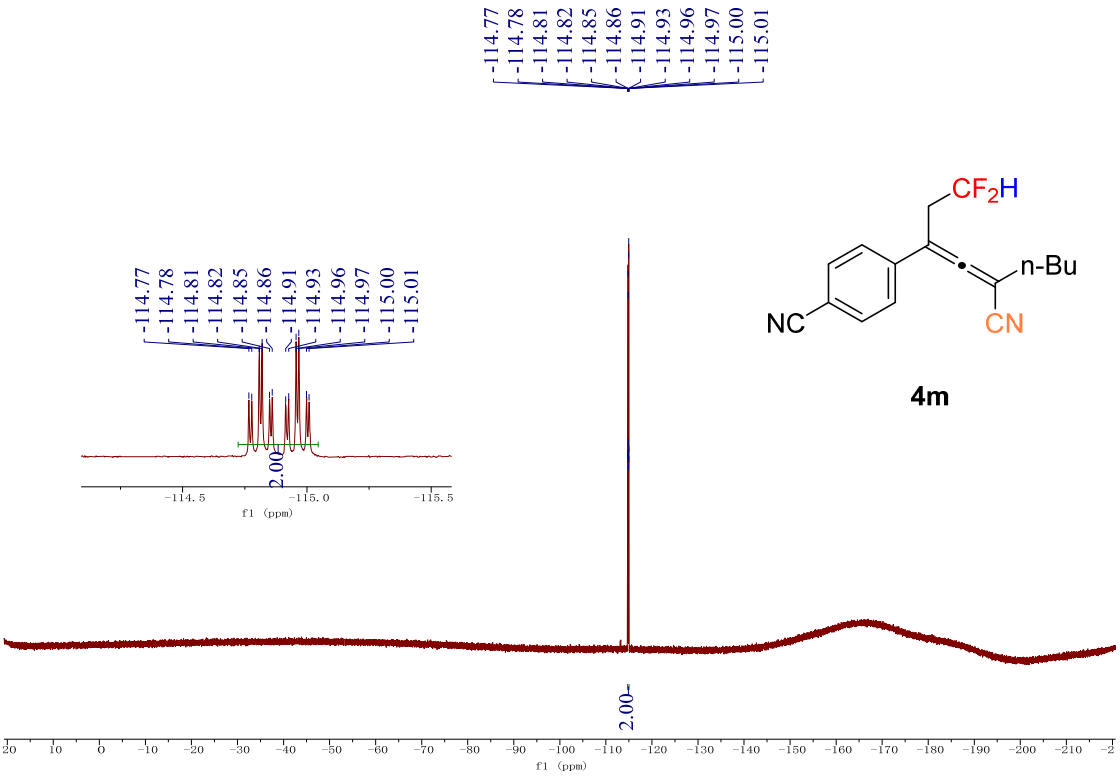


4m

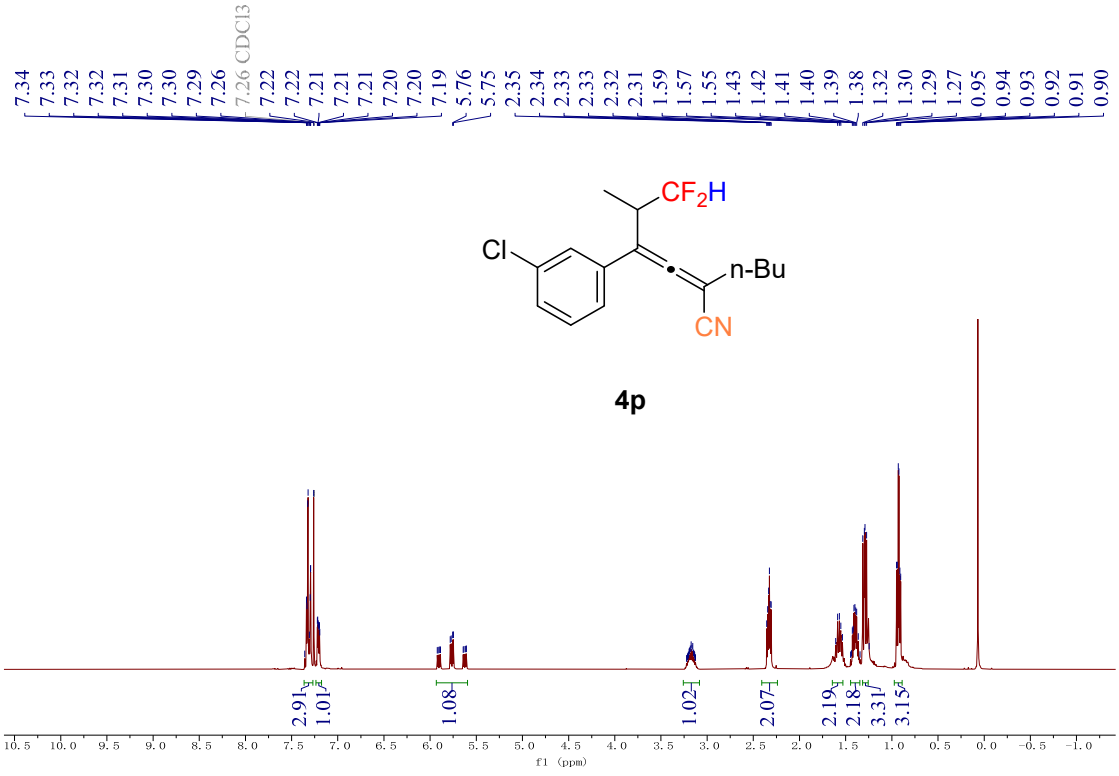
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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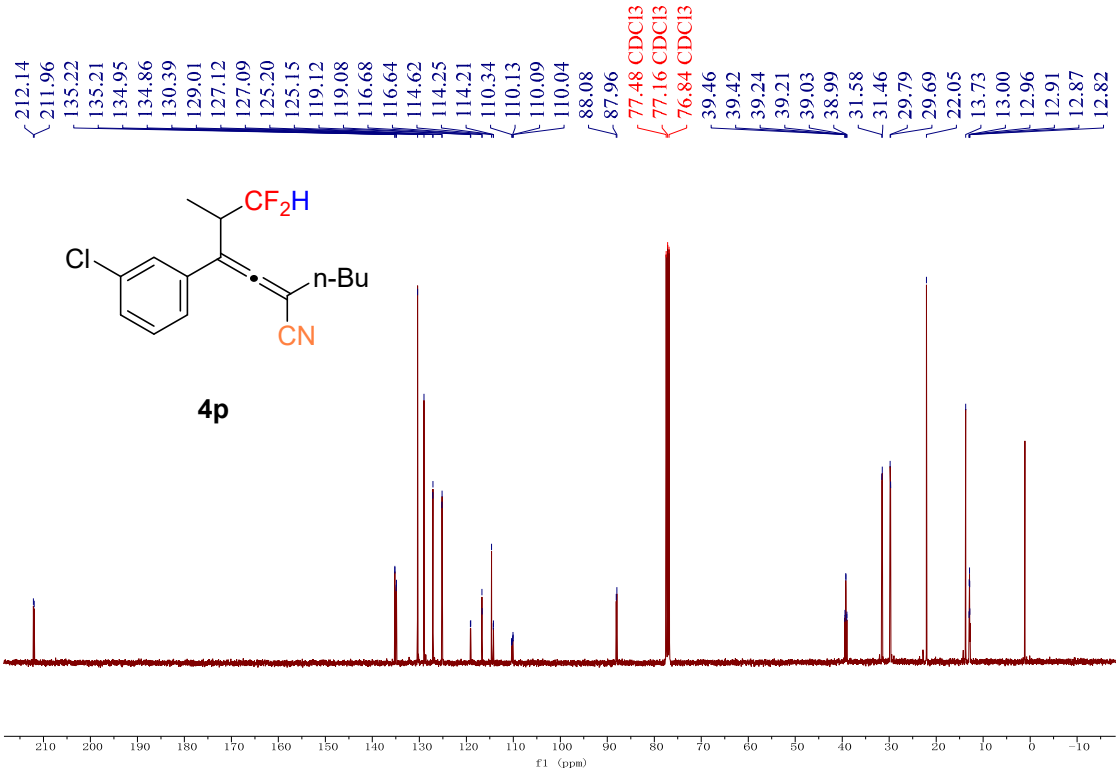

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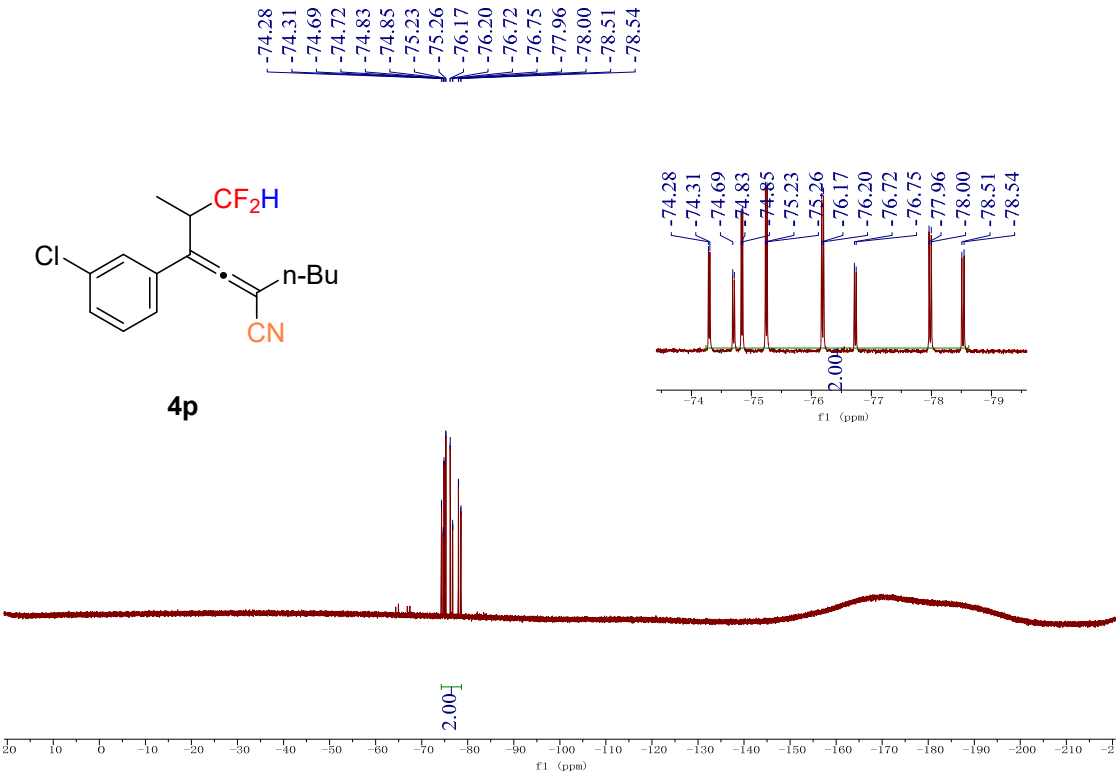
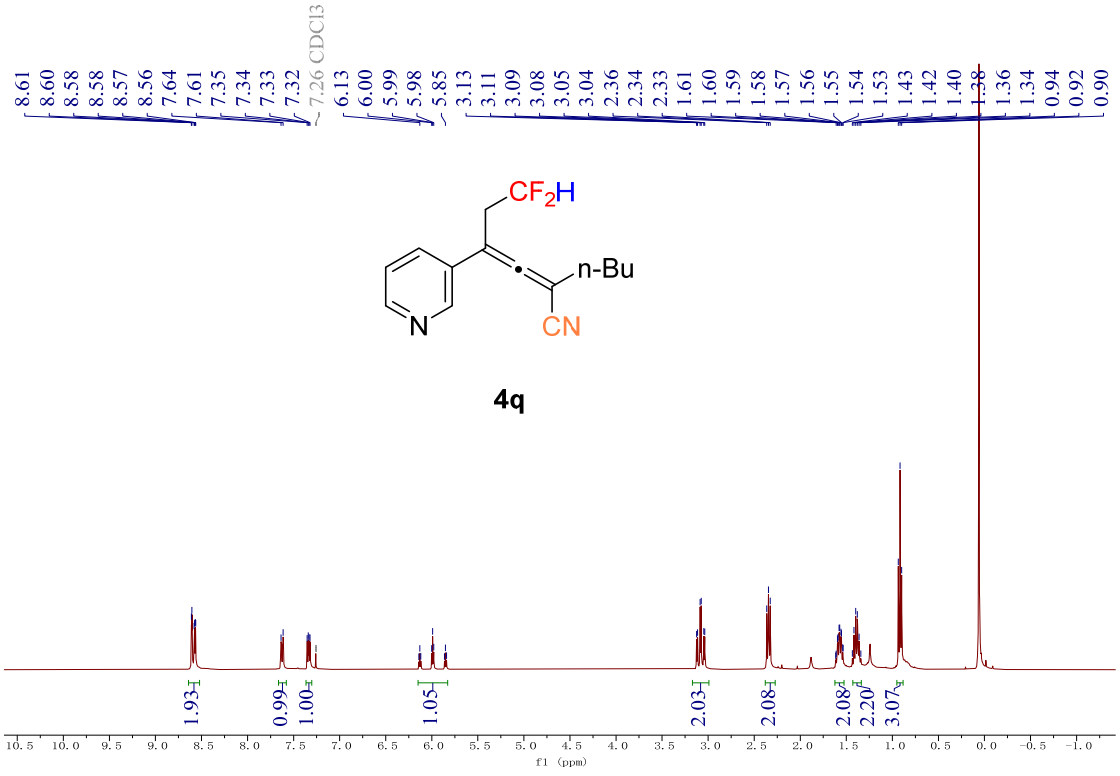


^{1}H NMR (400 MHz, $CDCl_3$)



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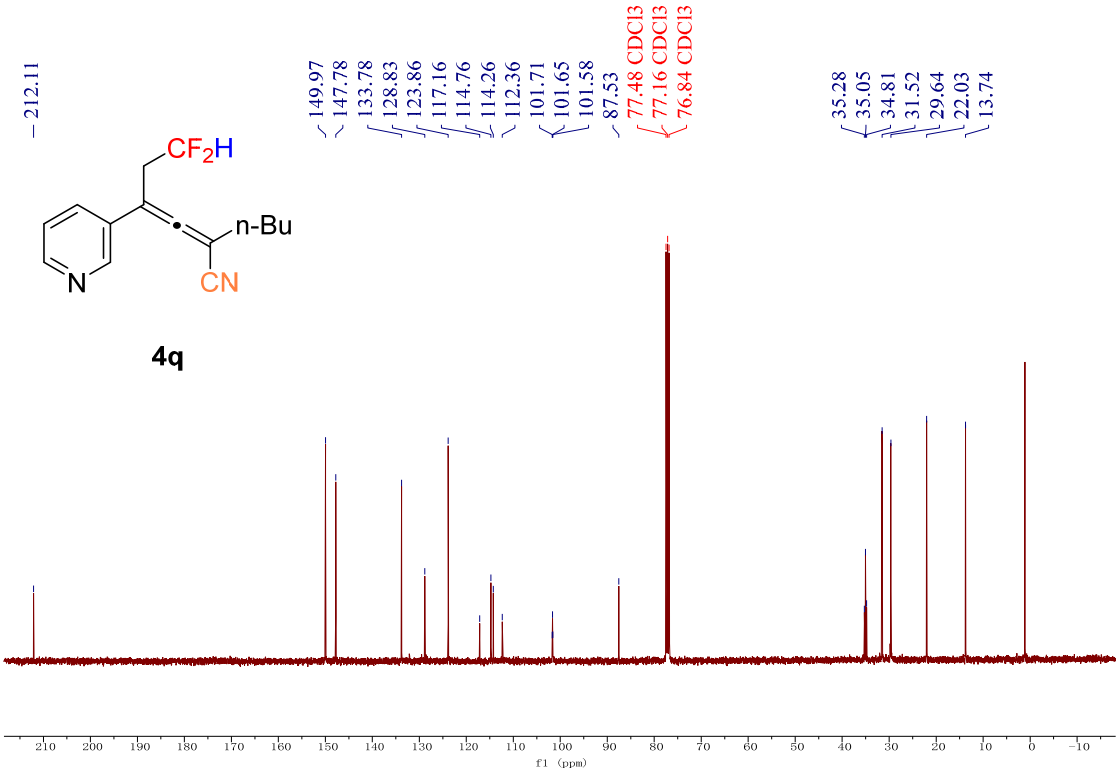
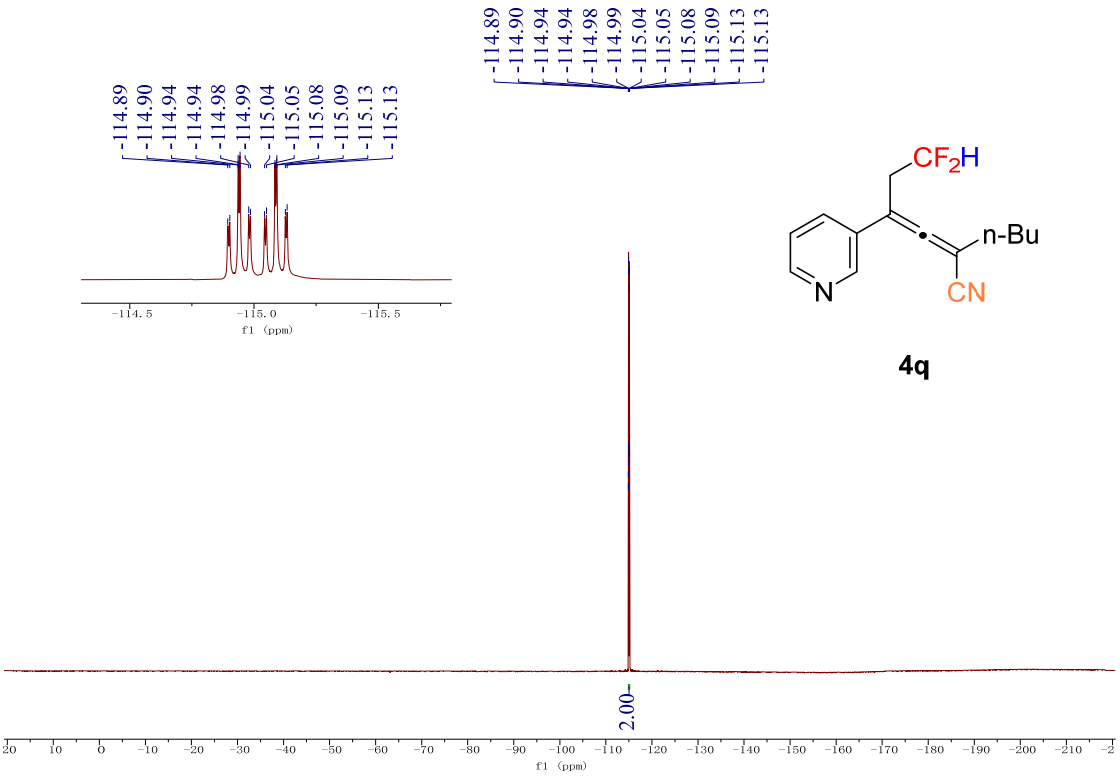


^{19}F NMR (376 MHz, $CDCl_3$)



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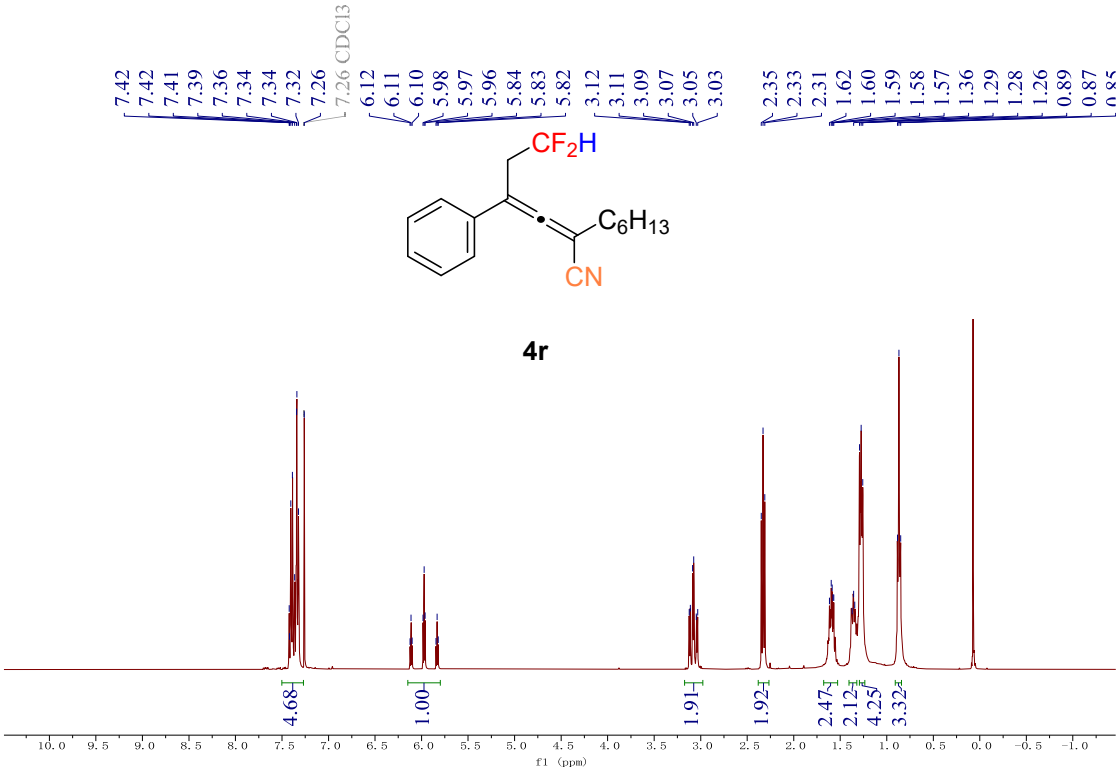
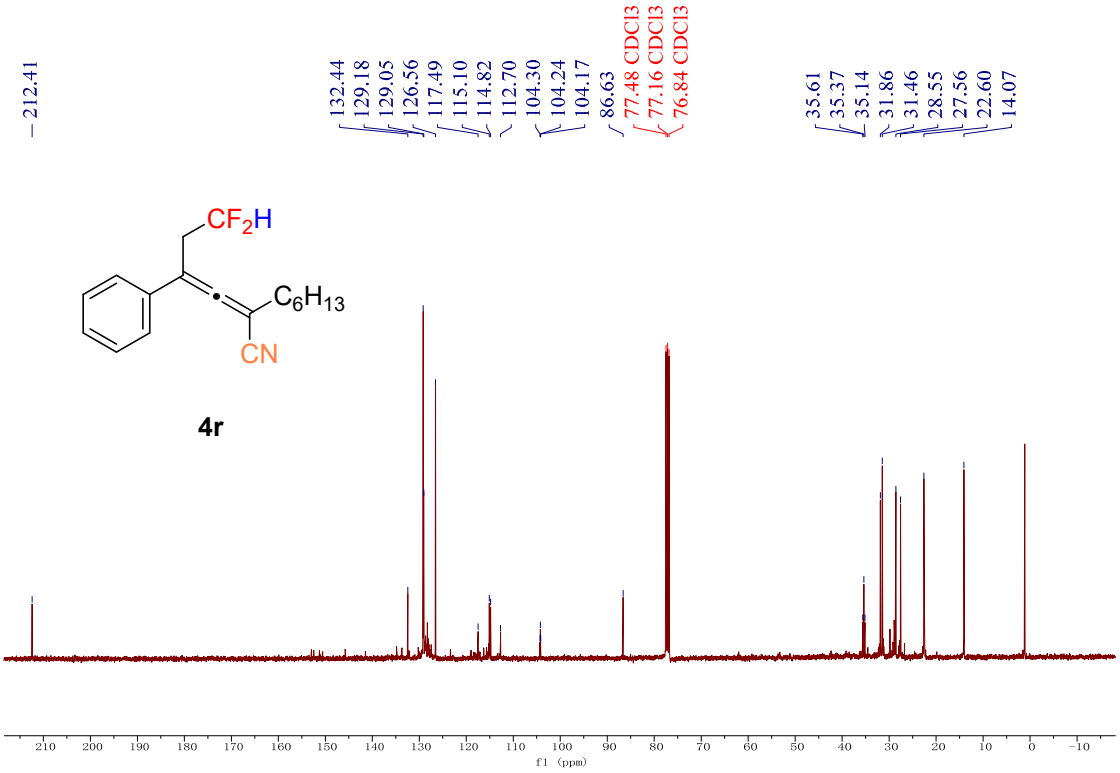
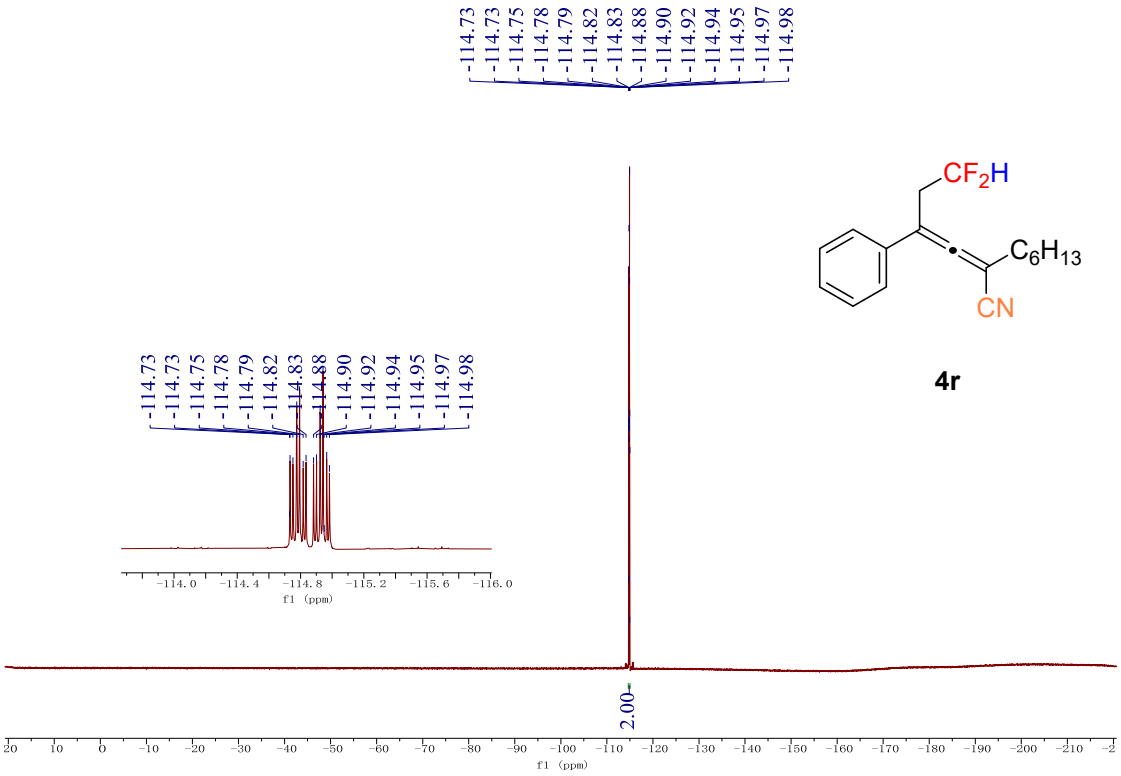


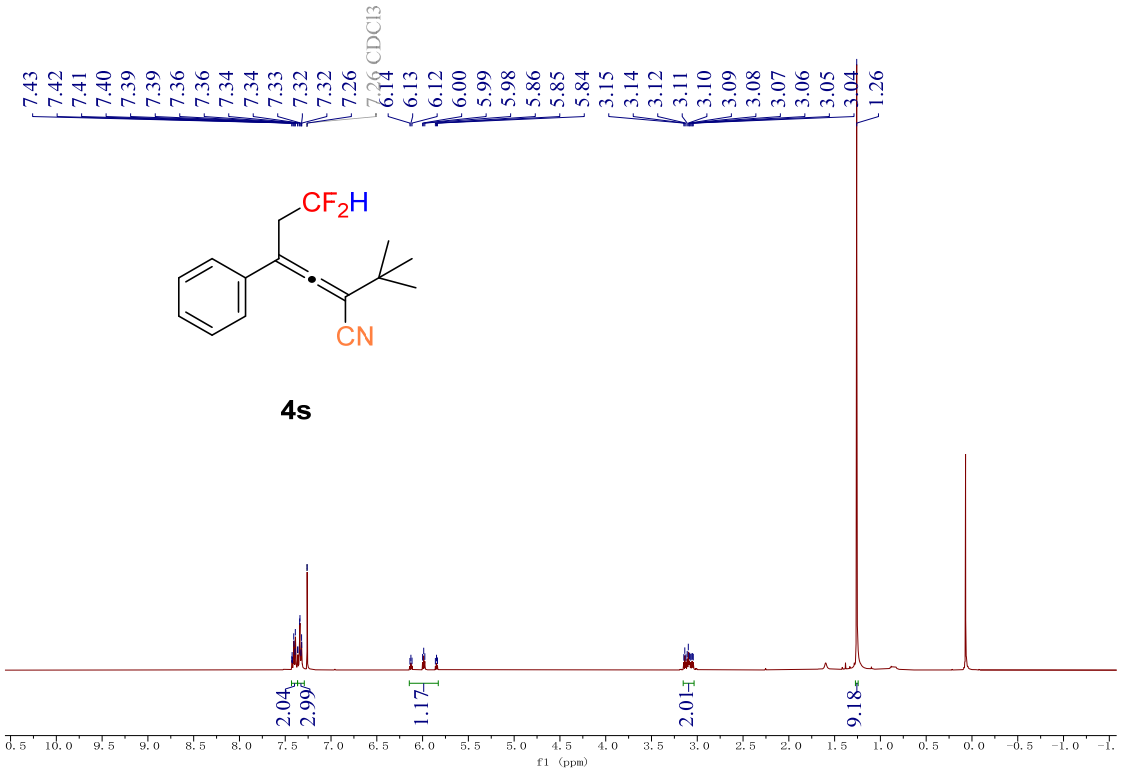
^{13}C NMR (101 MHz, $CDCl_3$)



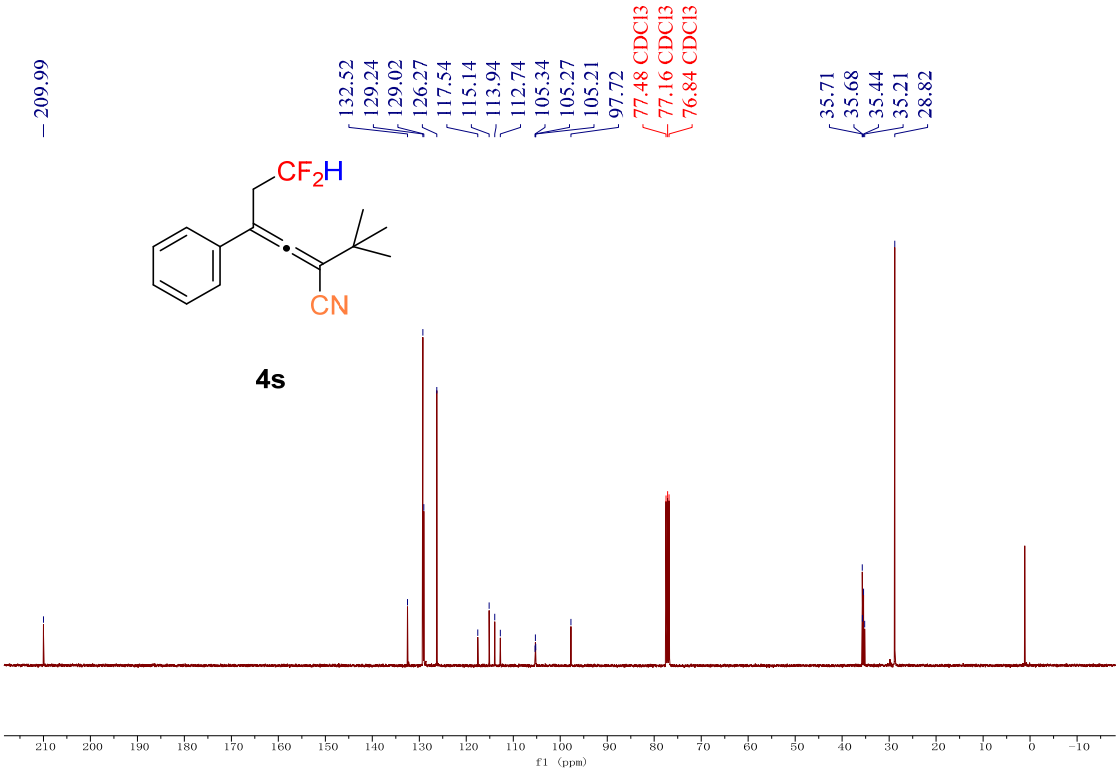
^{19}F NMR (376 MHz, $CDCl_3$)



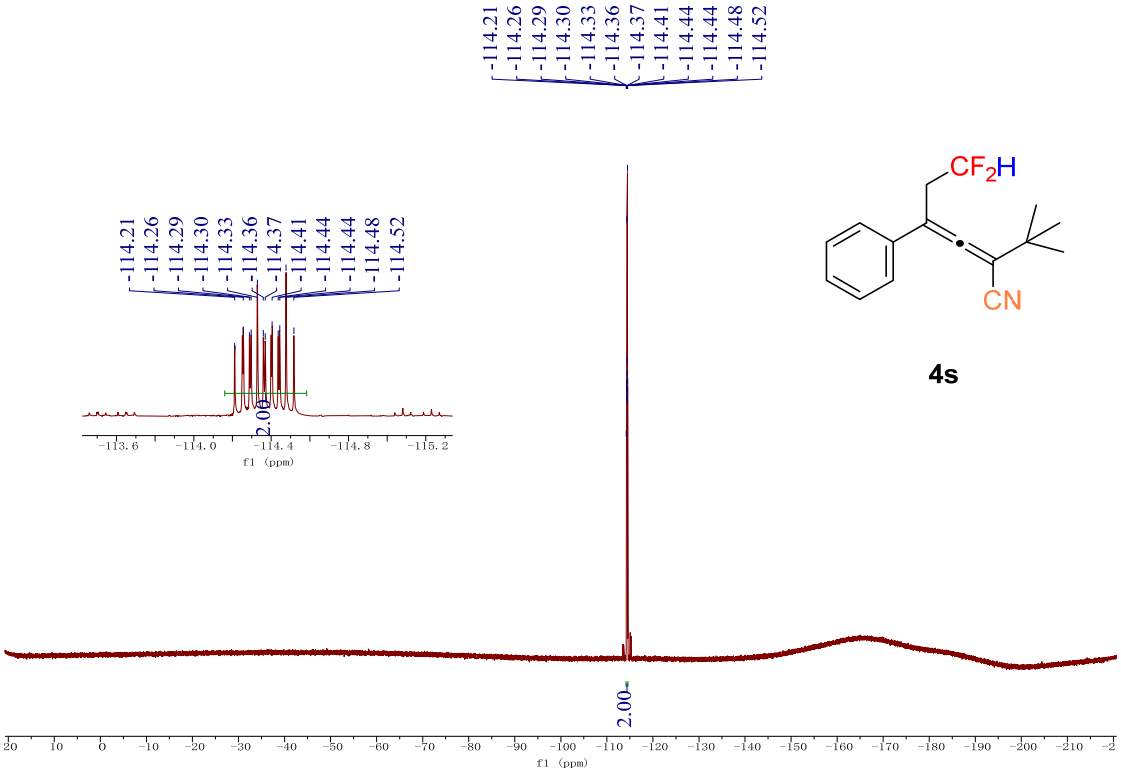
^{1}H NMR (400 MHz, $CDCl_3$)



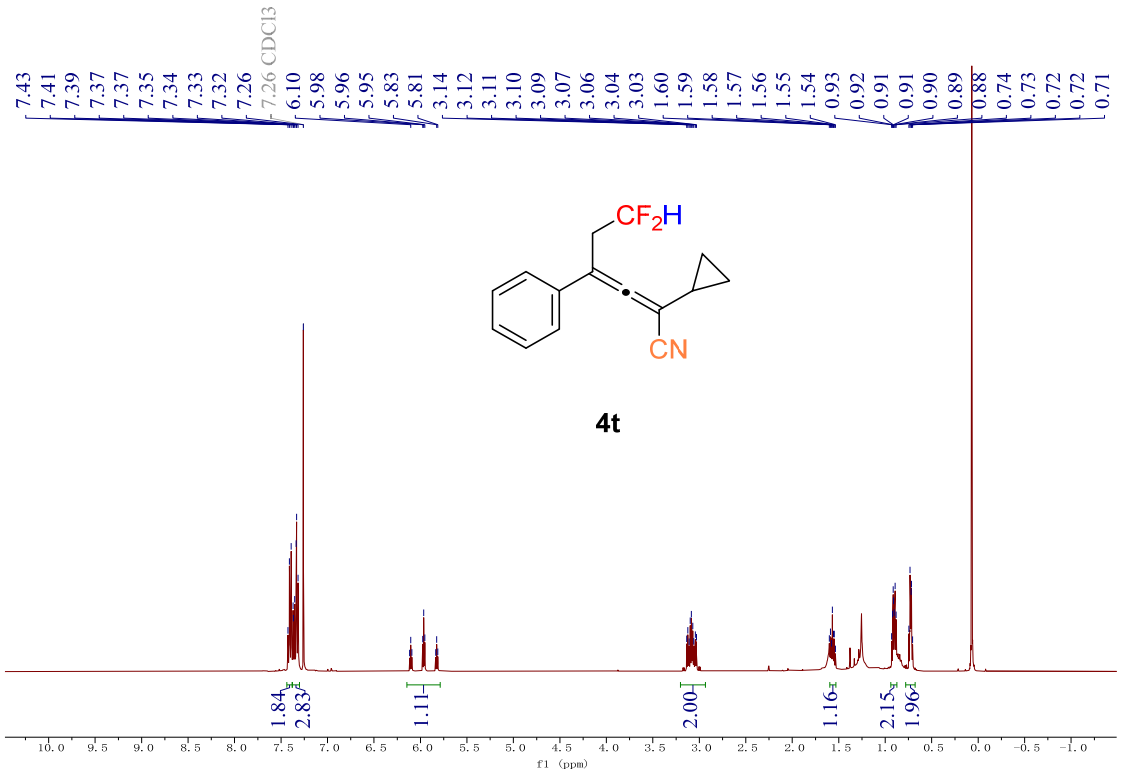
^{13}C NMR (101 MHz, $CDCl_3$)



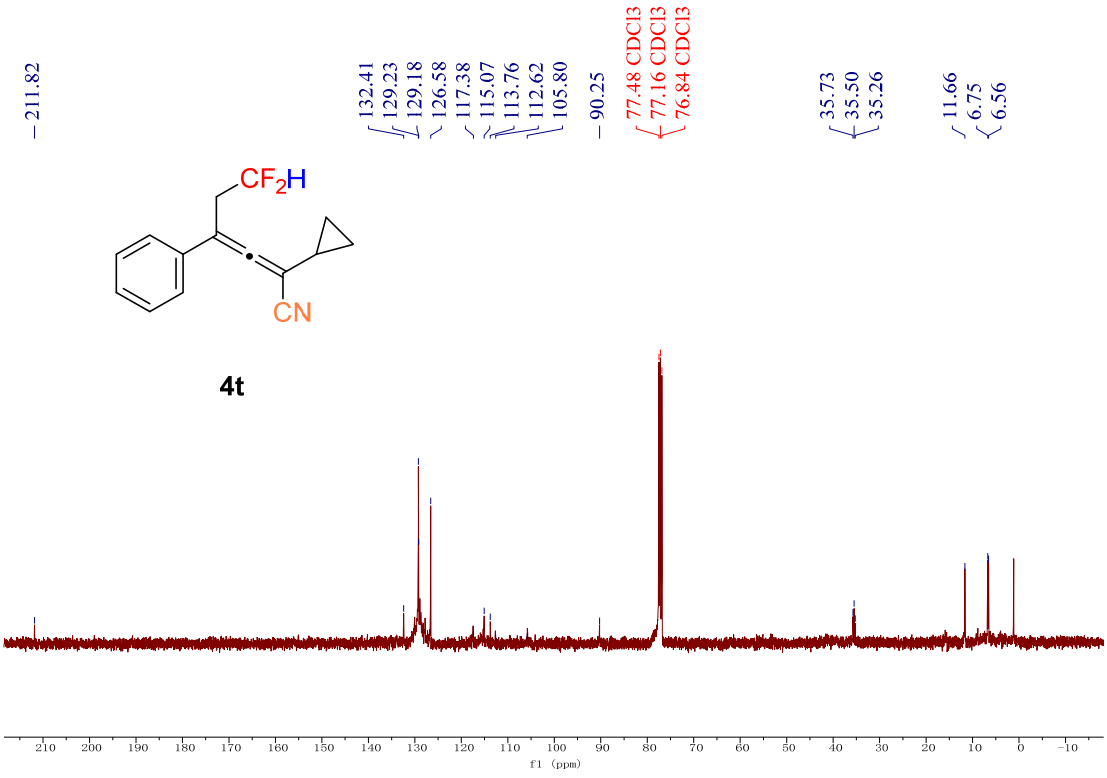
^{19}F NMR (376 MHz, $CDCl_3$)



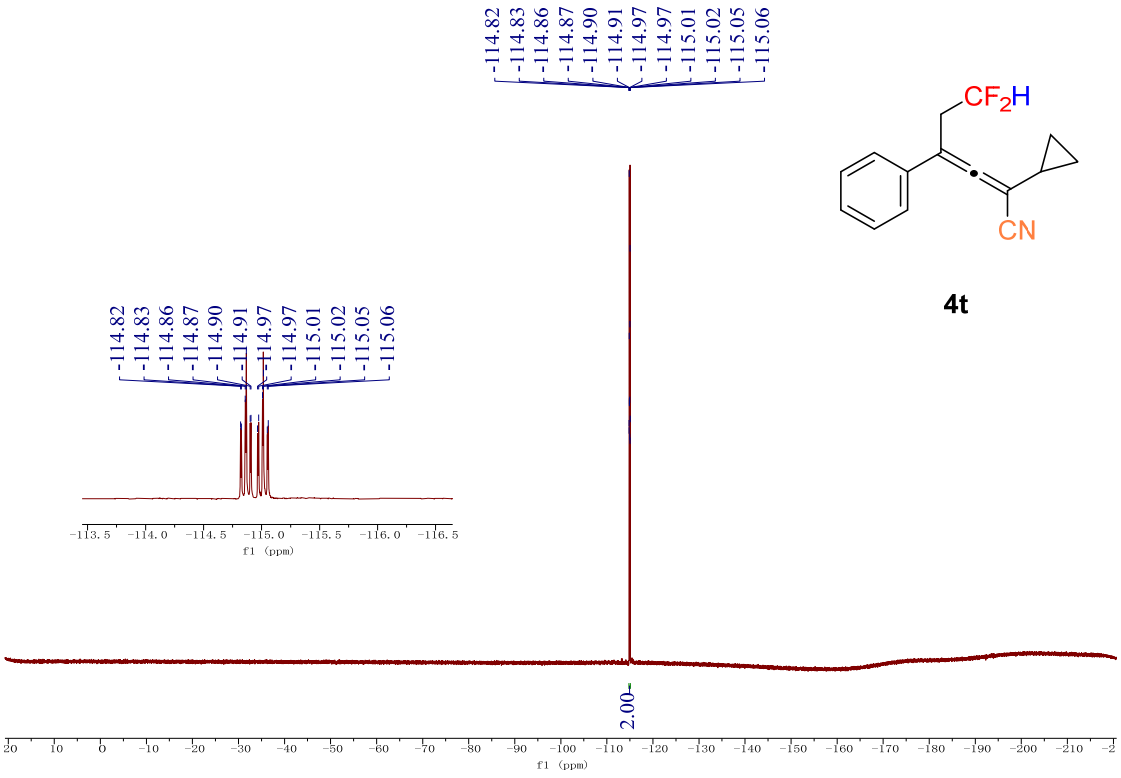
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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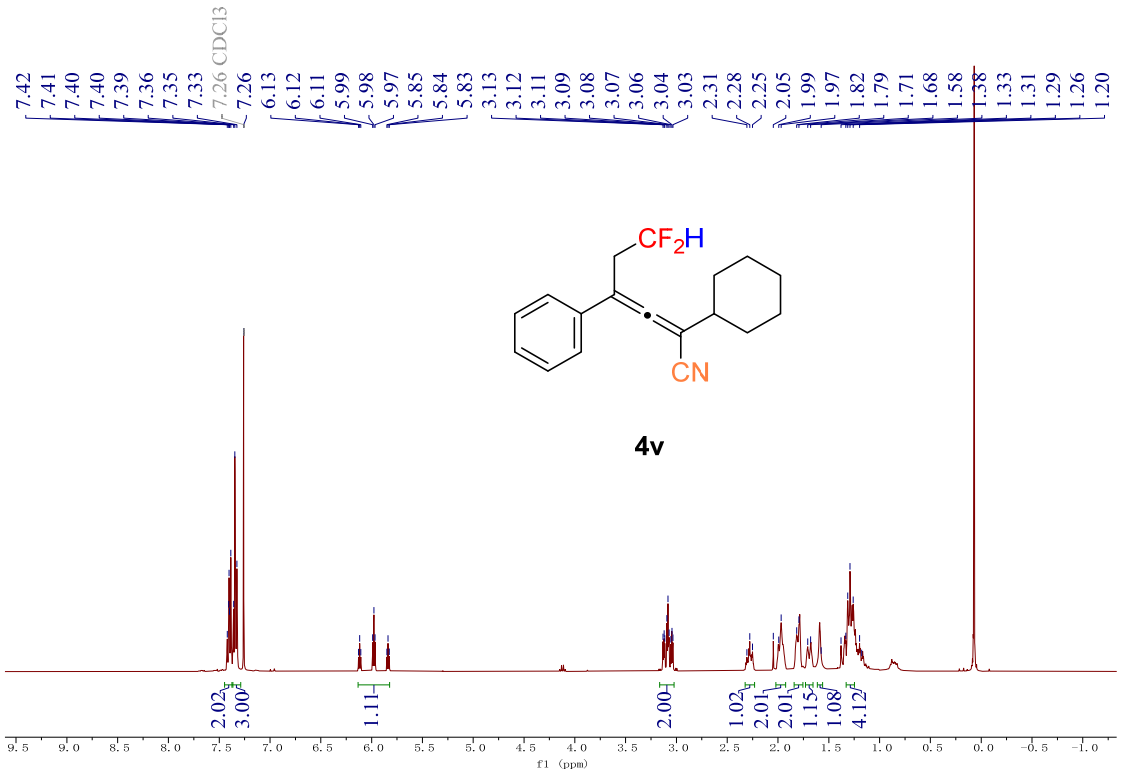
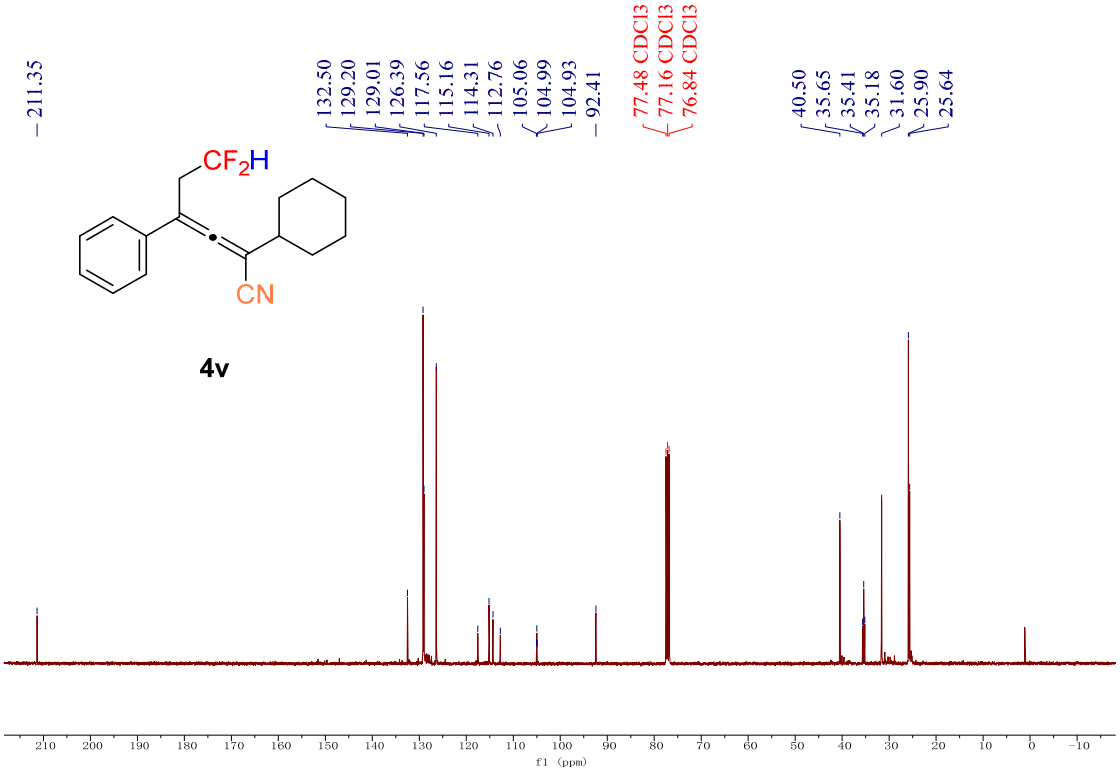


^{13}C NMR (101 MHz, $CDCl_3$)



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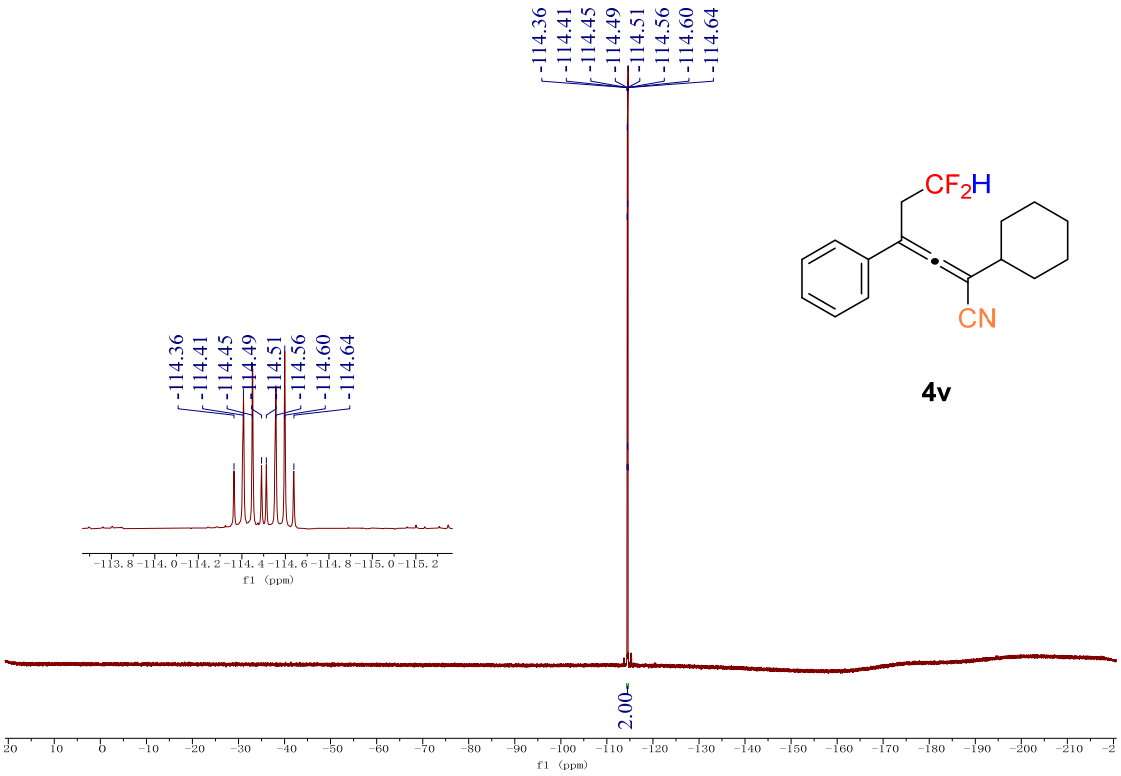

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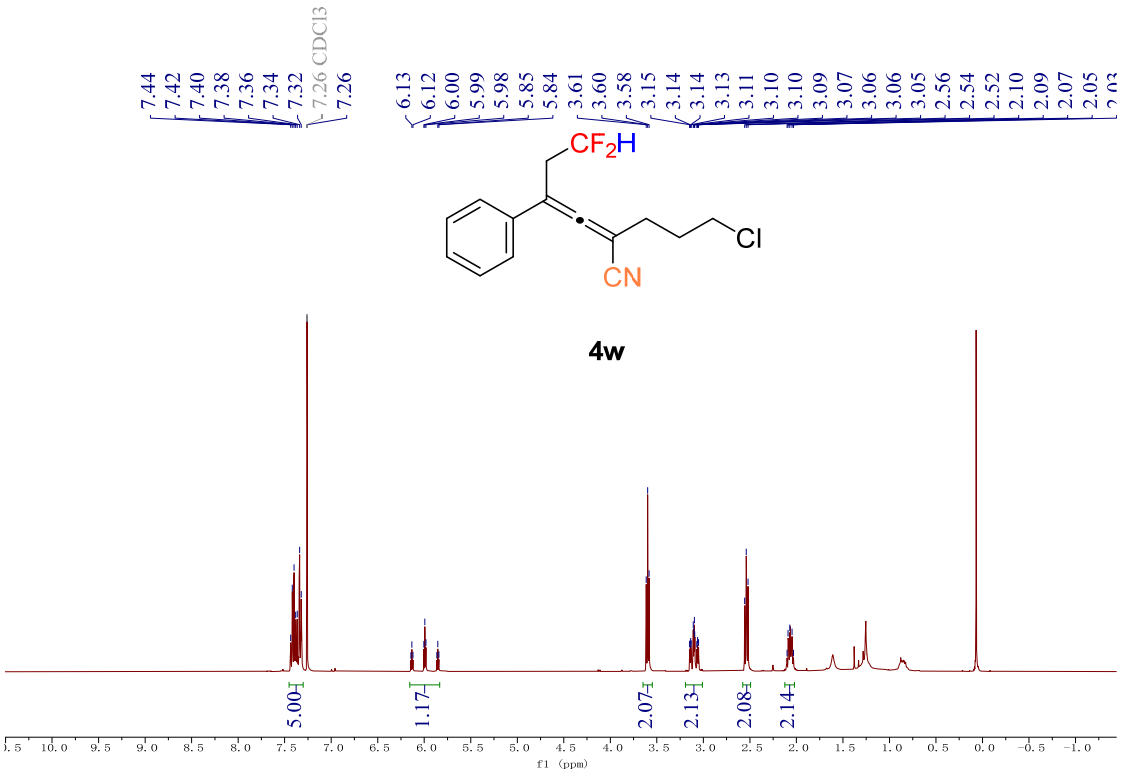

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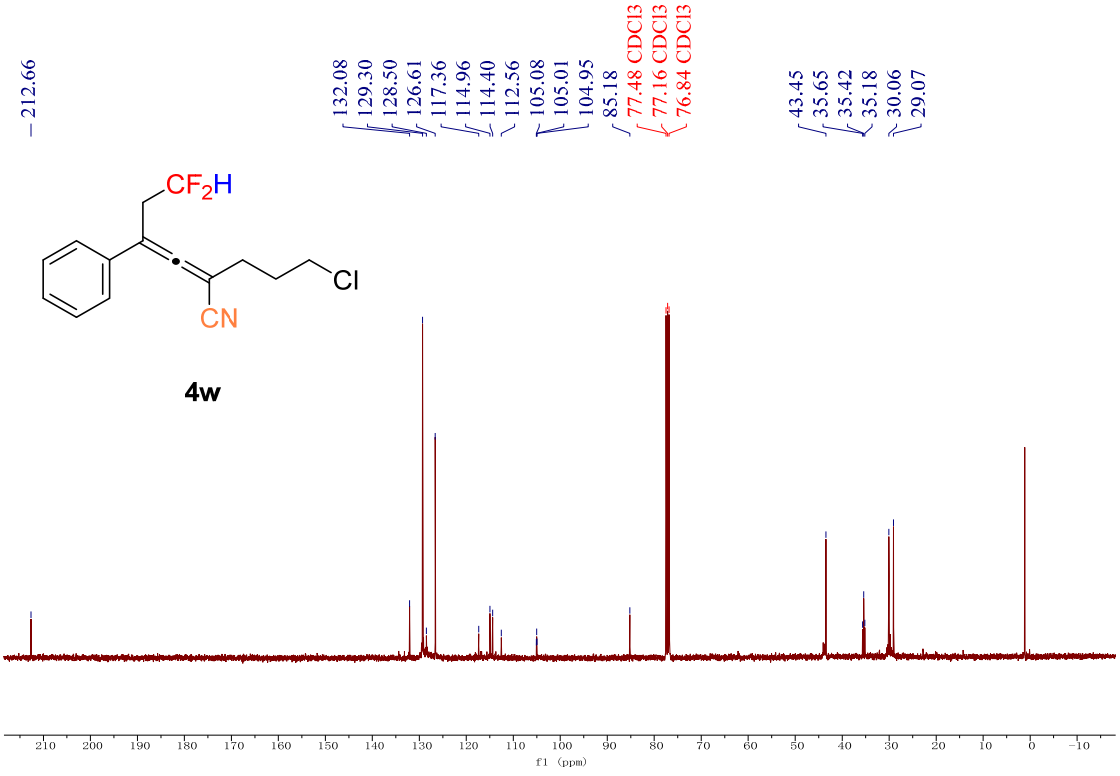

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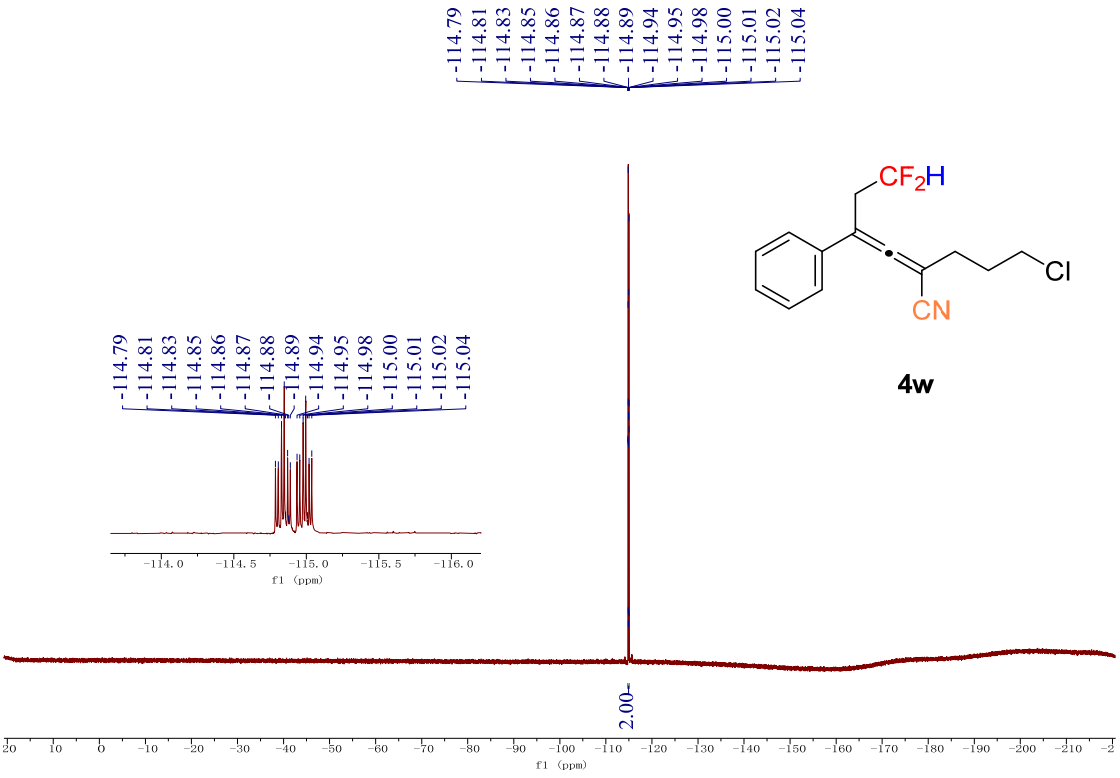
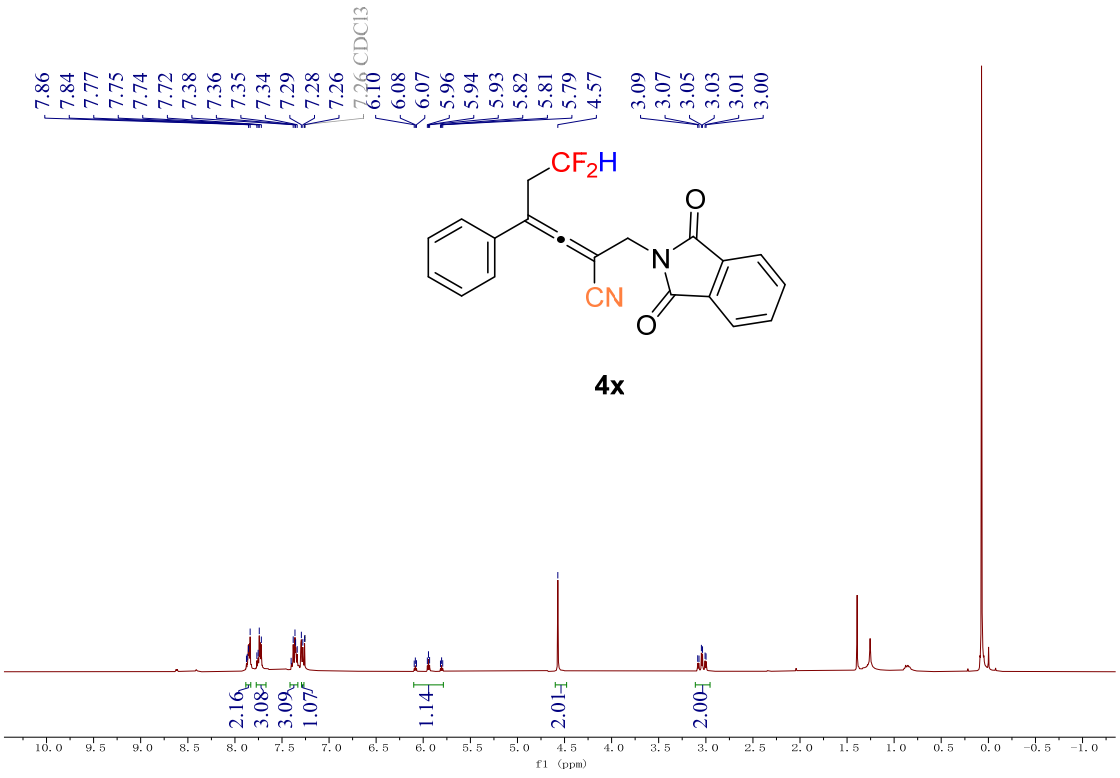
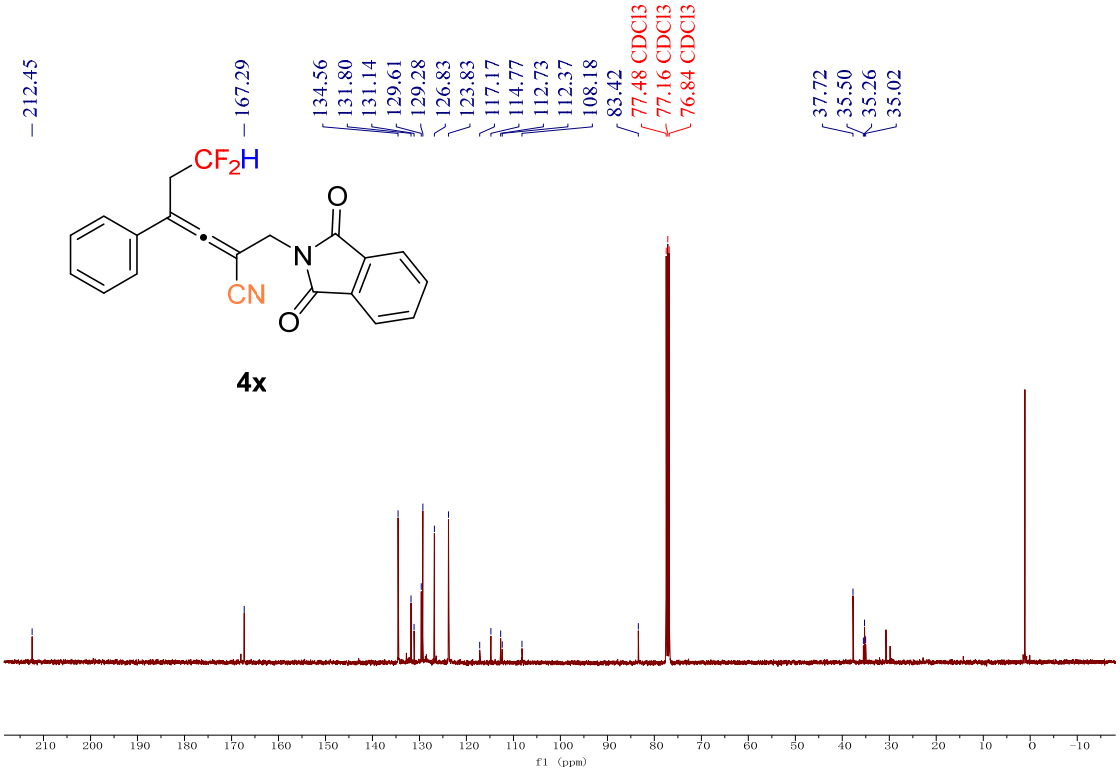


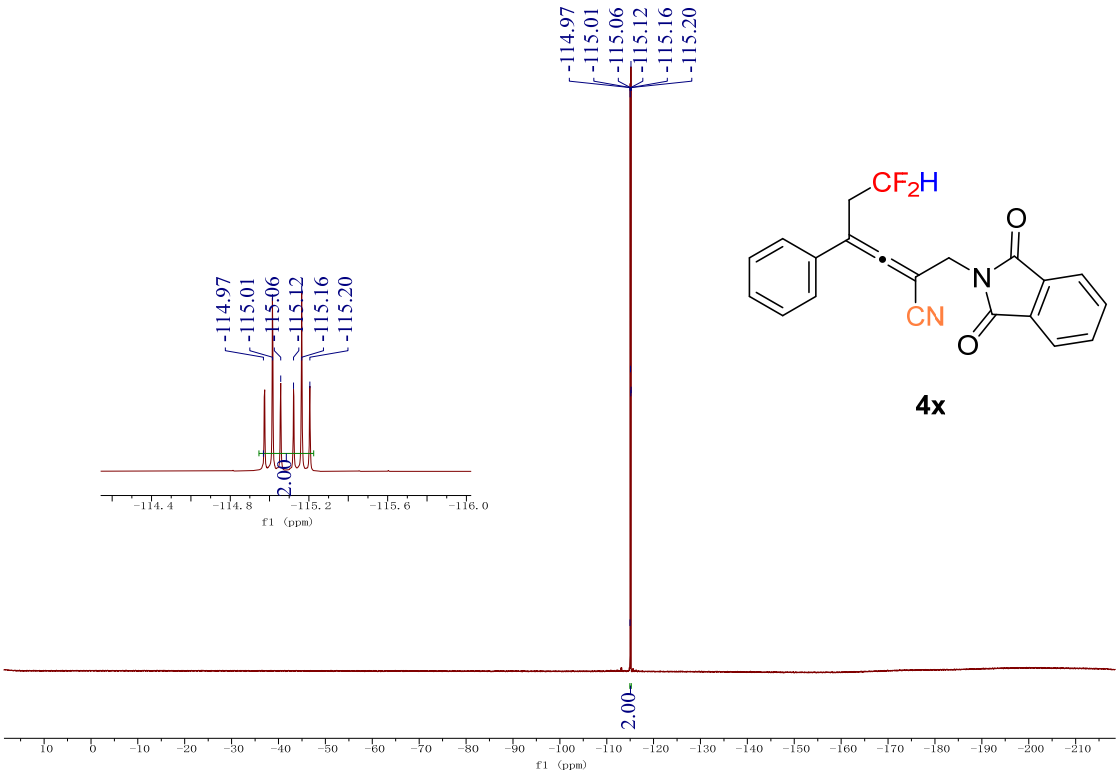
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

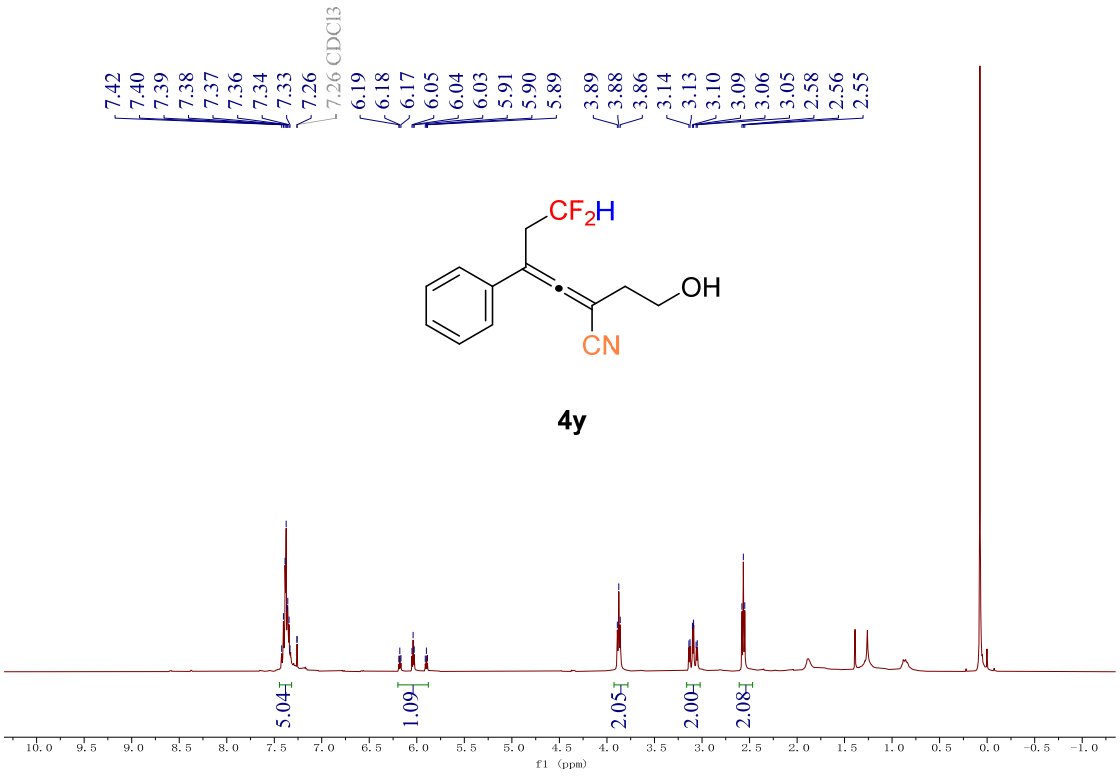


^{19}F NMR (377 MHz, $CDCl_3$)



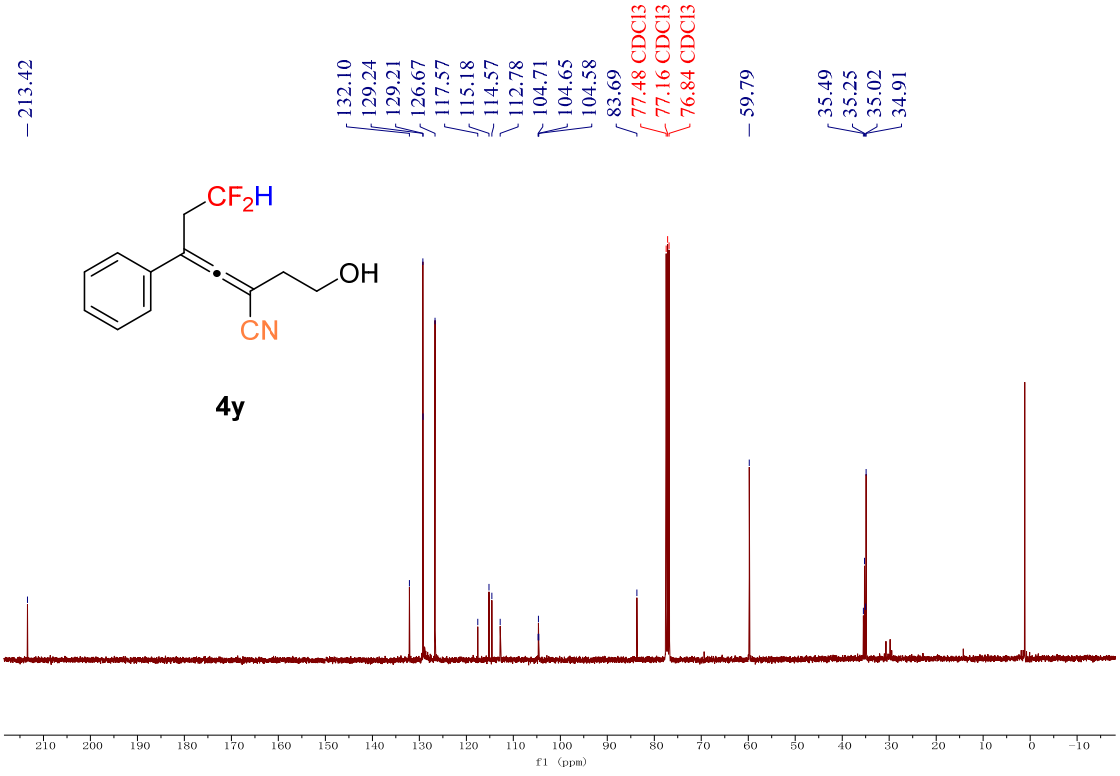
4x

[1]H NMR (400 MHz, $CDCl_3$)

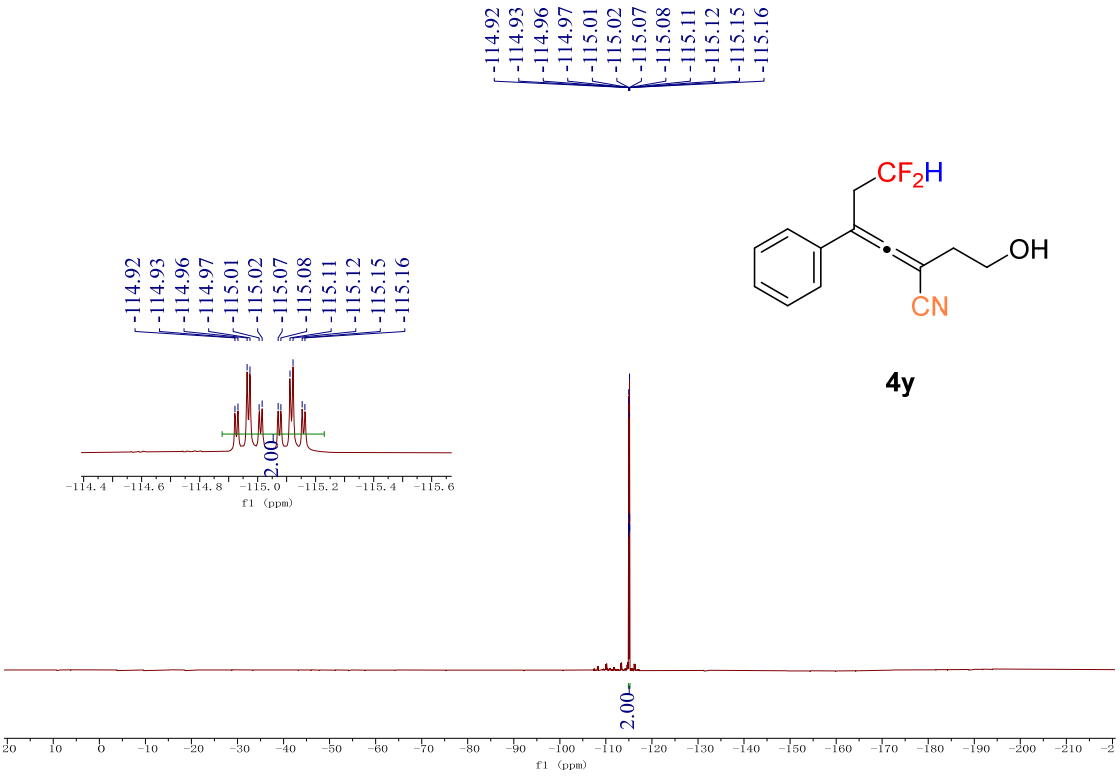


4y

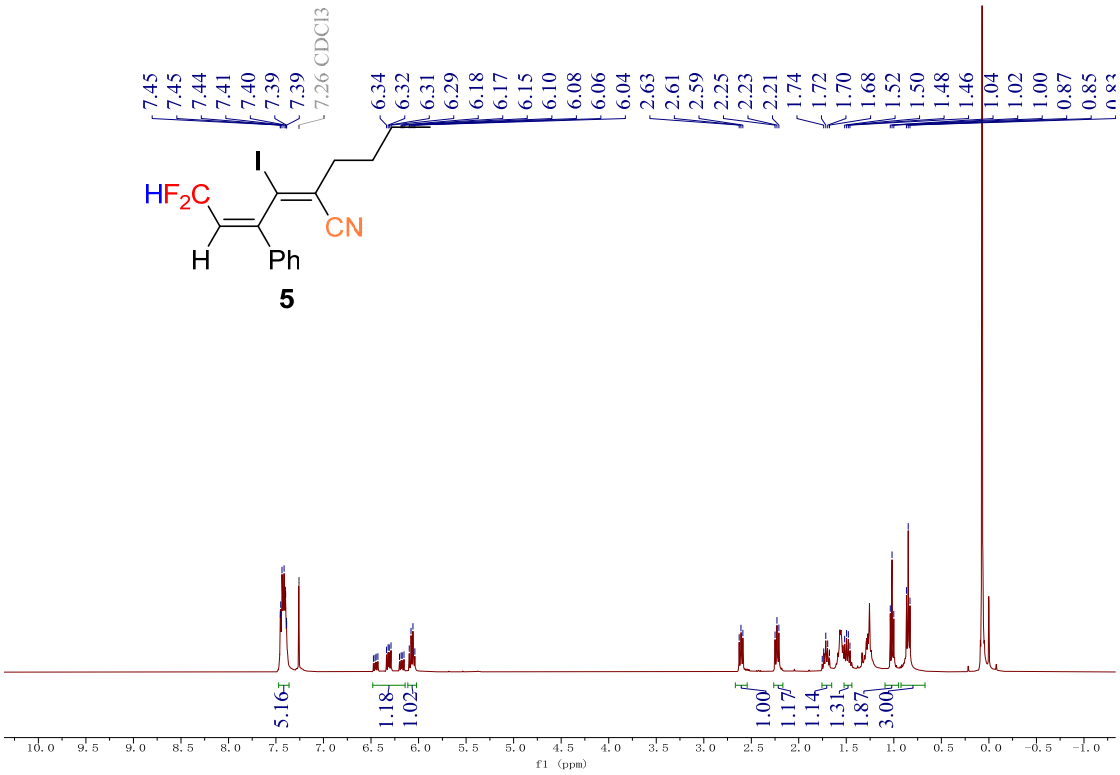
^{13}C NMR (101 MHz, $CDCl_3$)



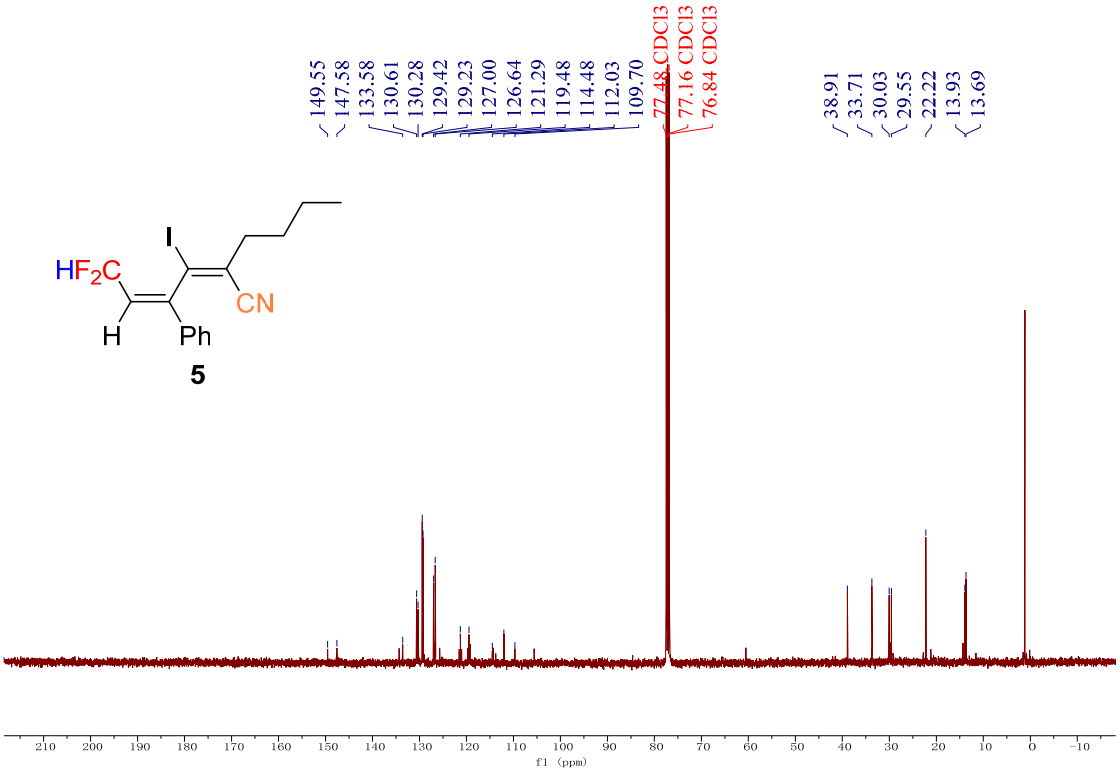
^{19}F NMR (376 MHz, $CDCl_3$)



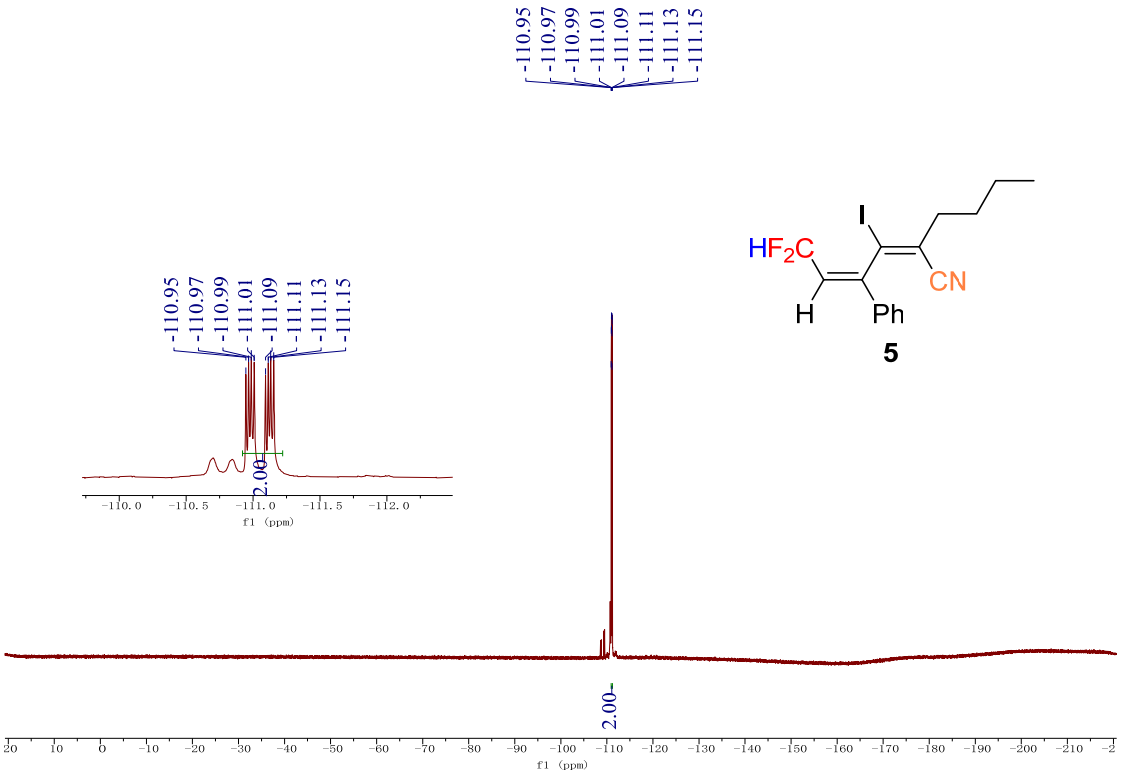
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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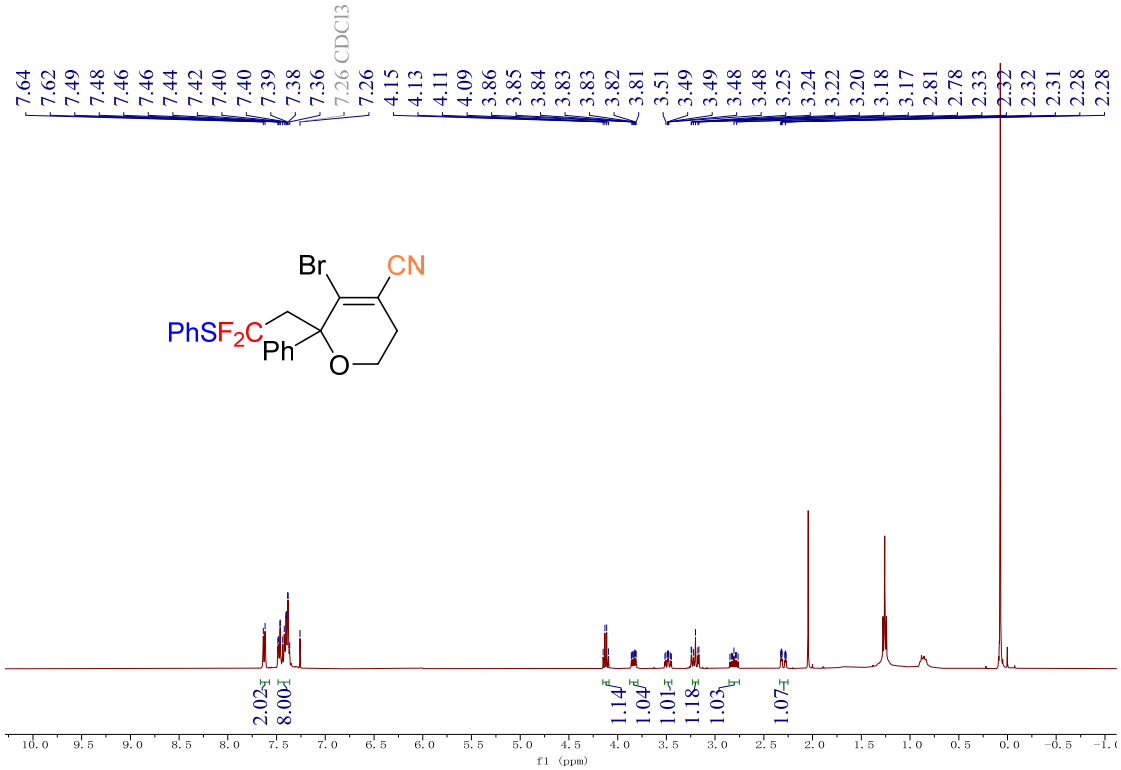
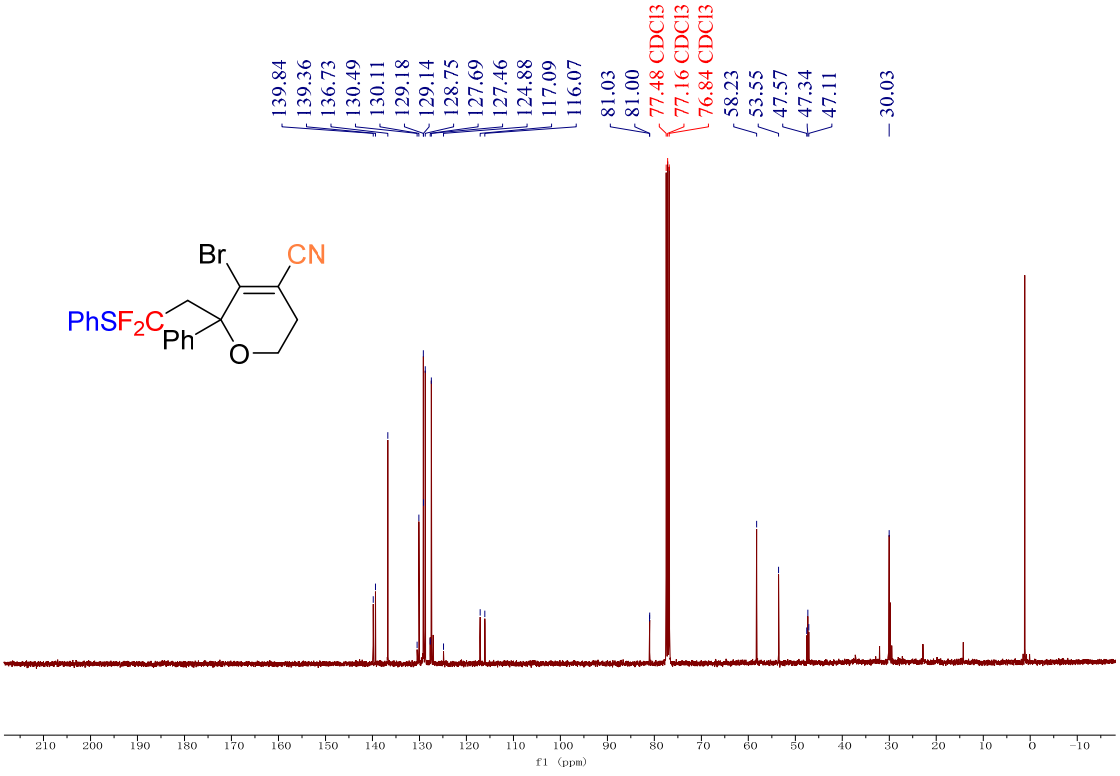


^{13}C NMR (101 MHz, $CDCl_3$)



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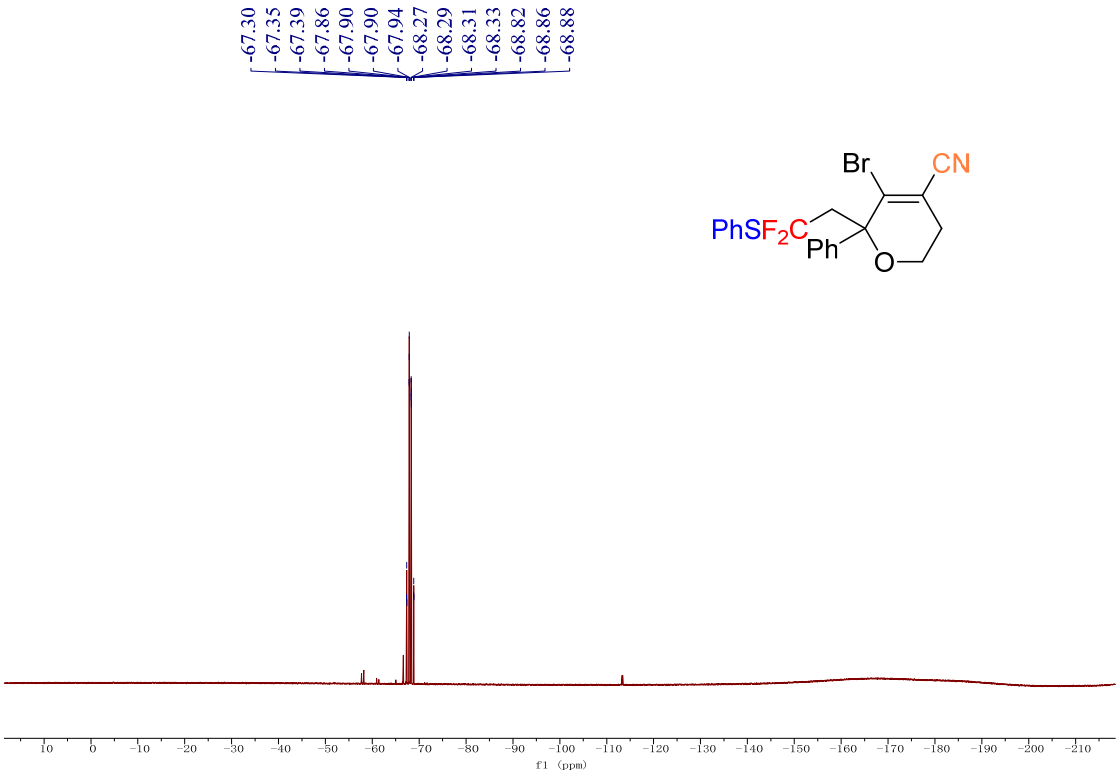

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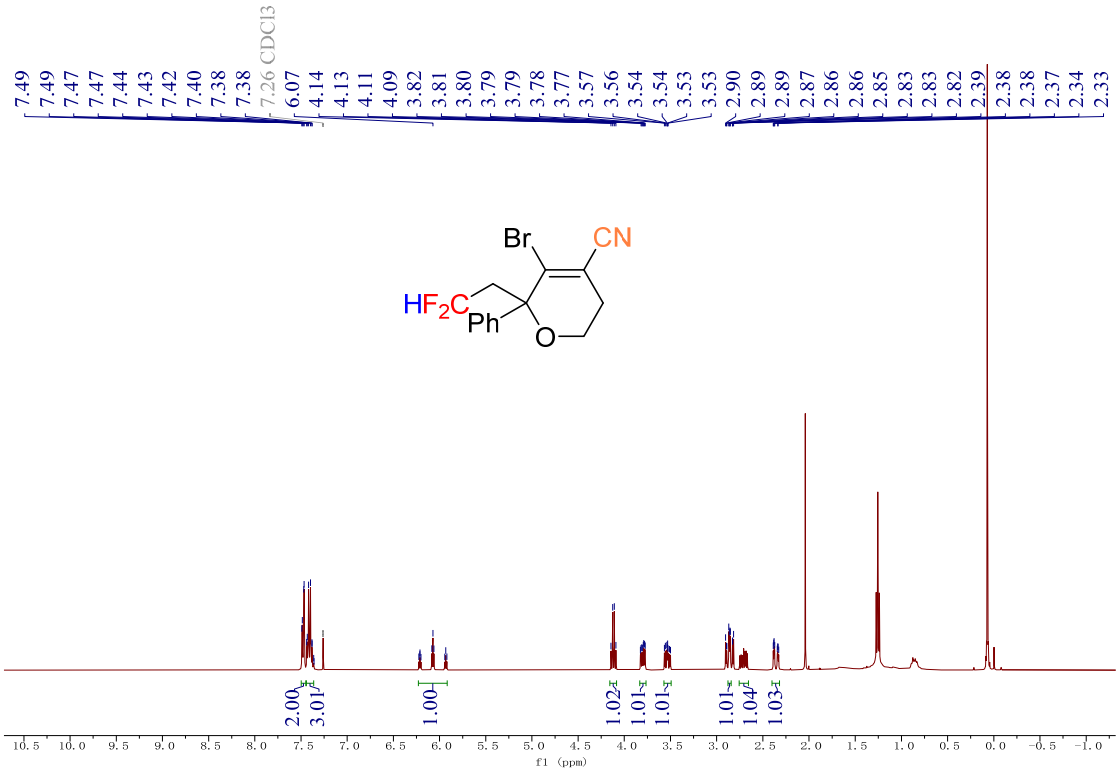

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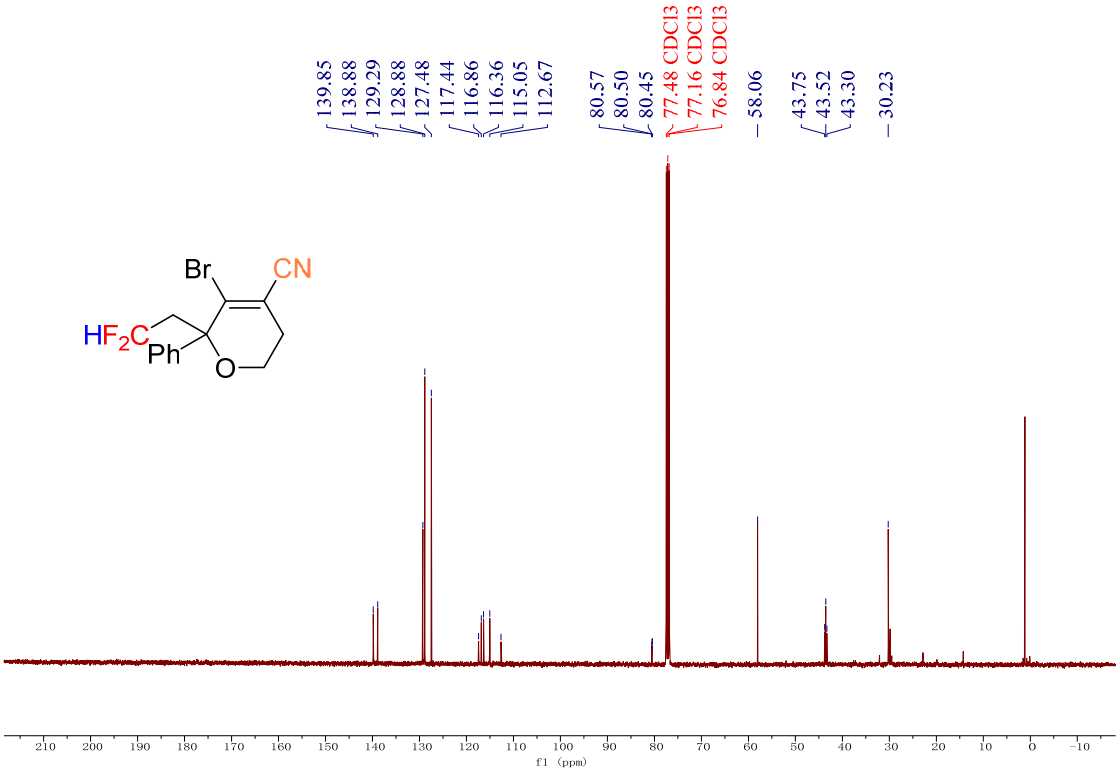
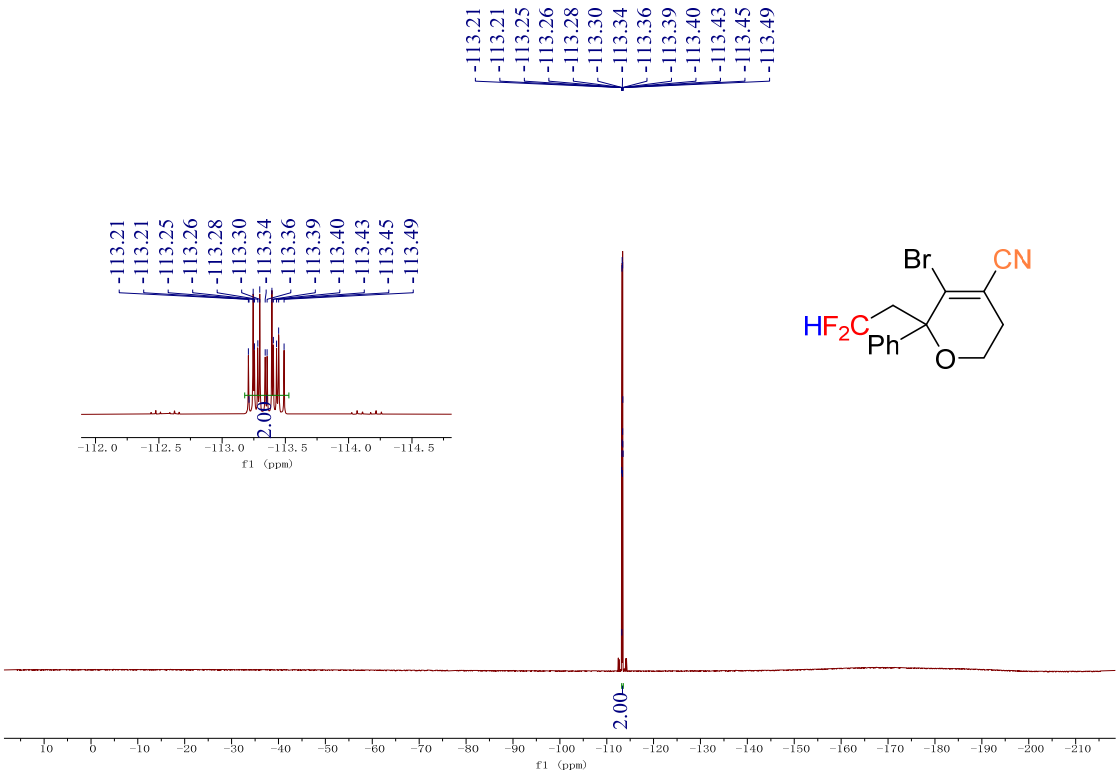
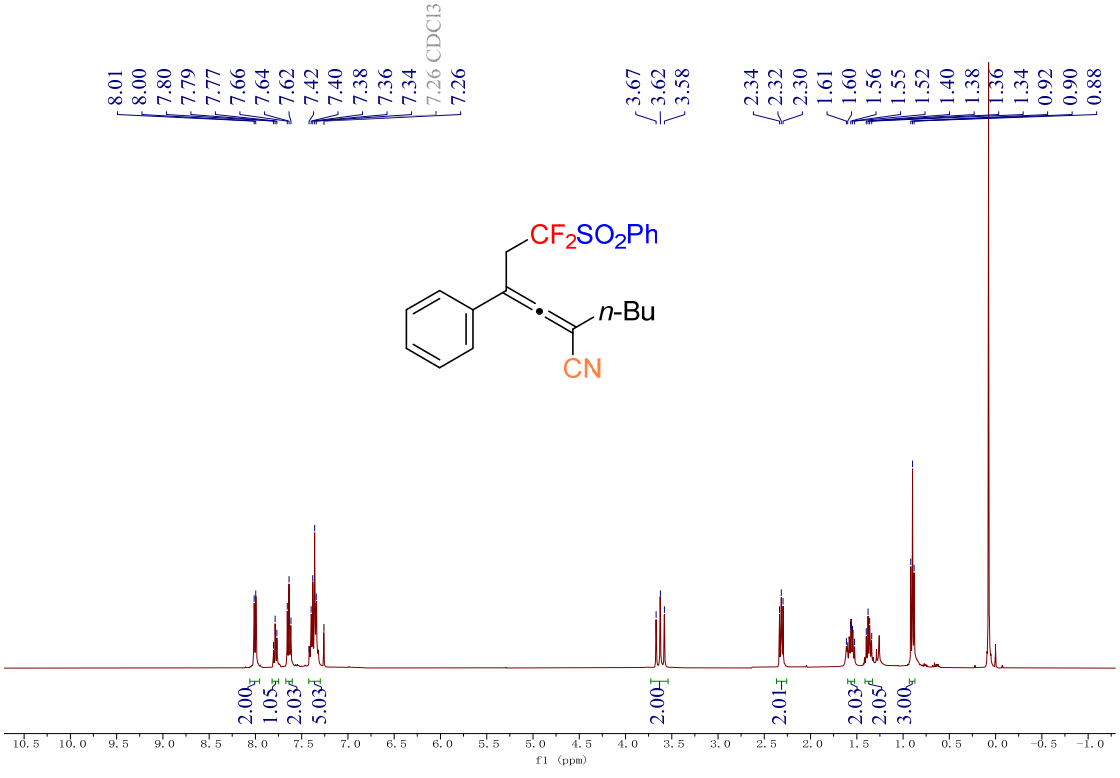


^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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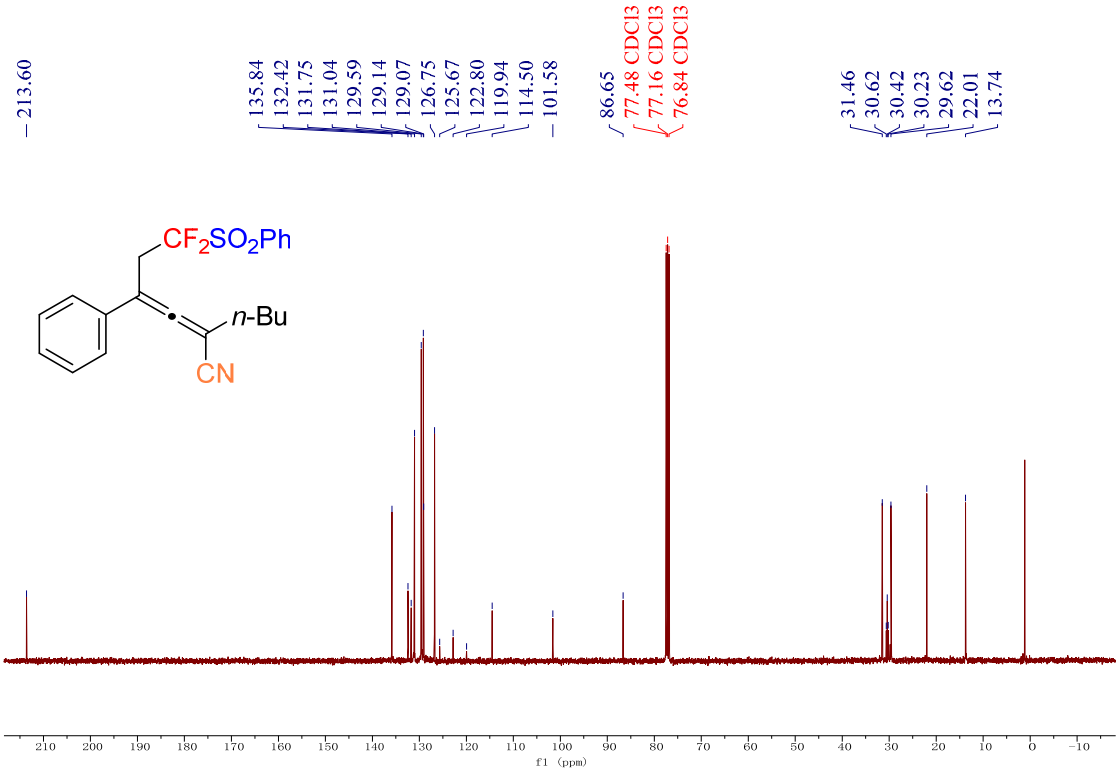

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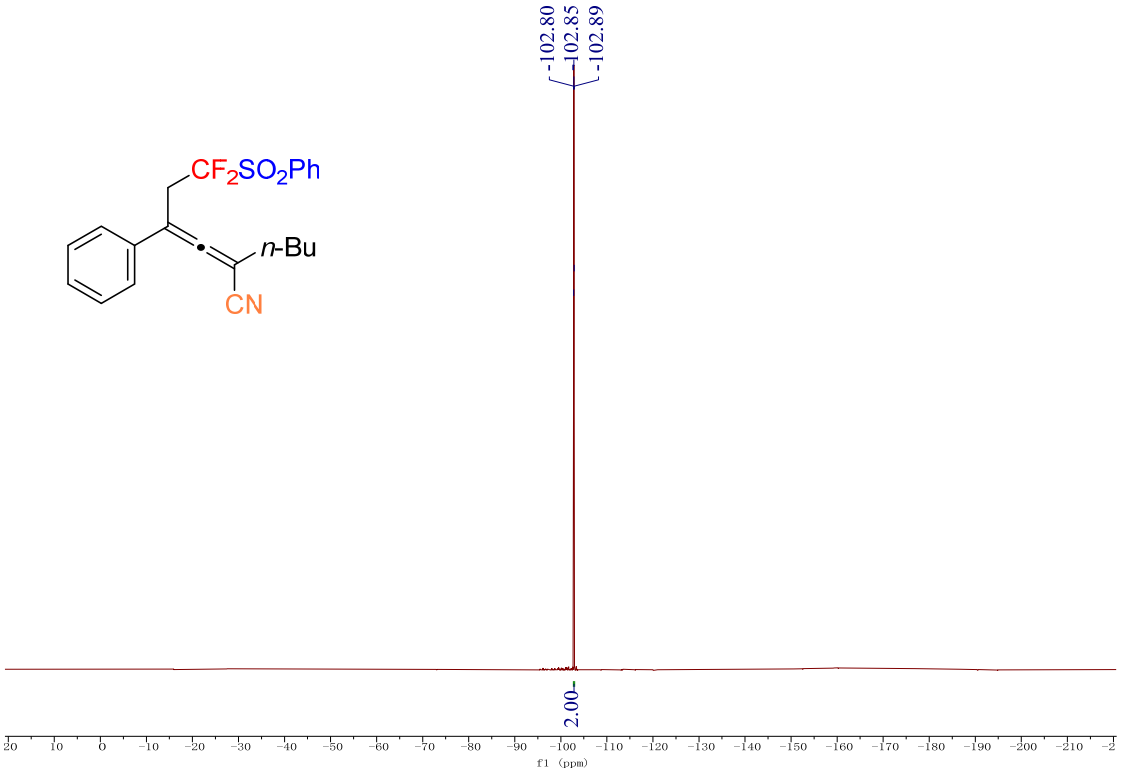

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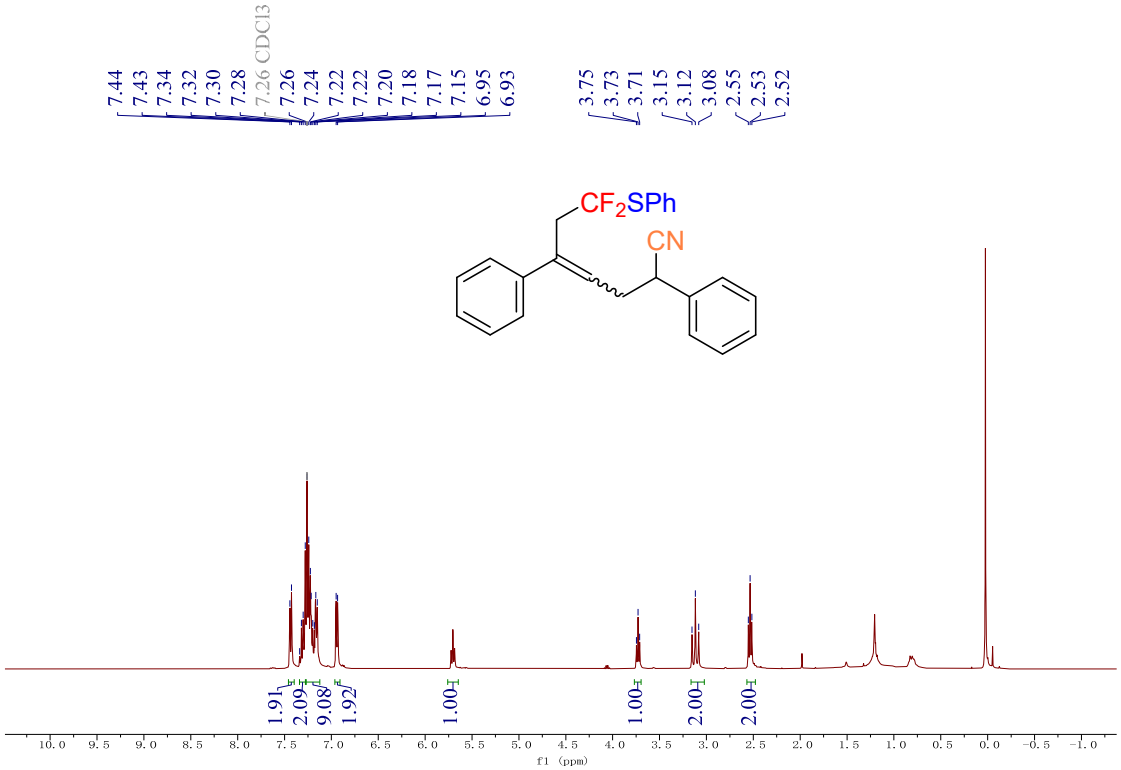

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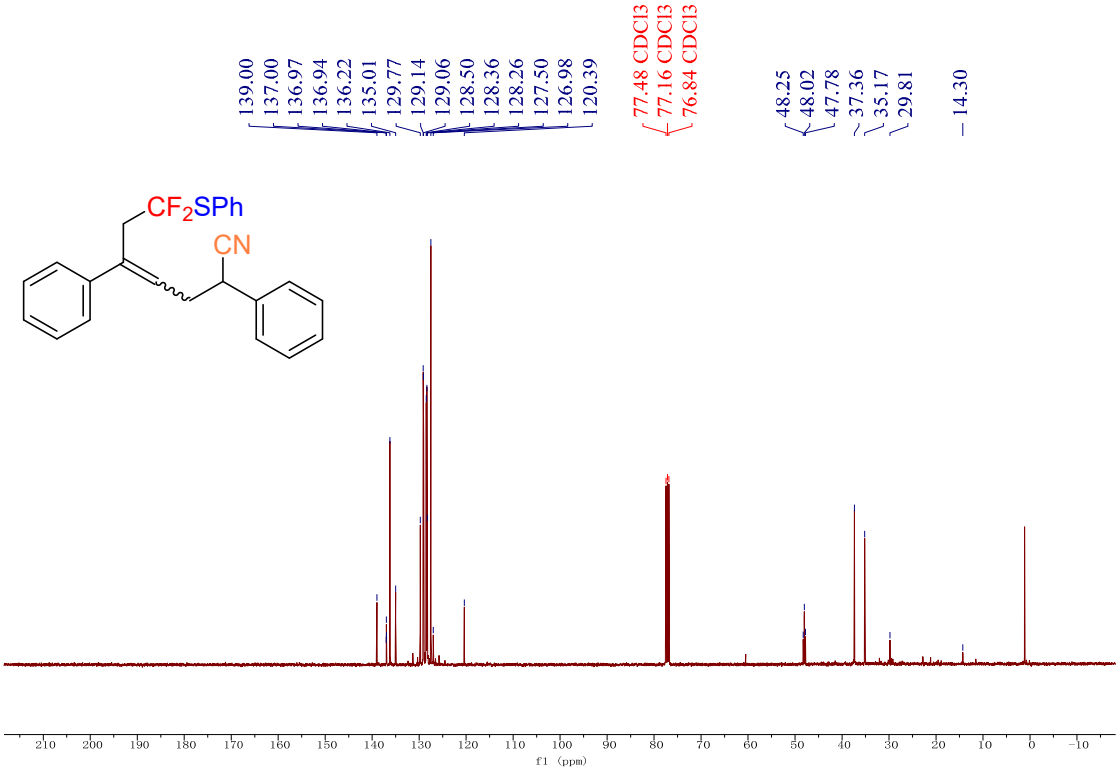

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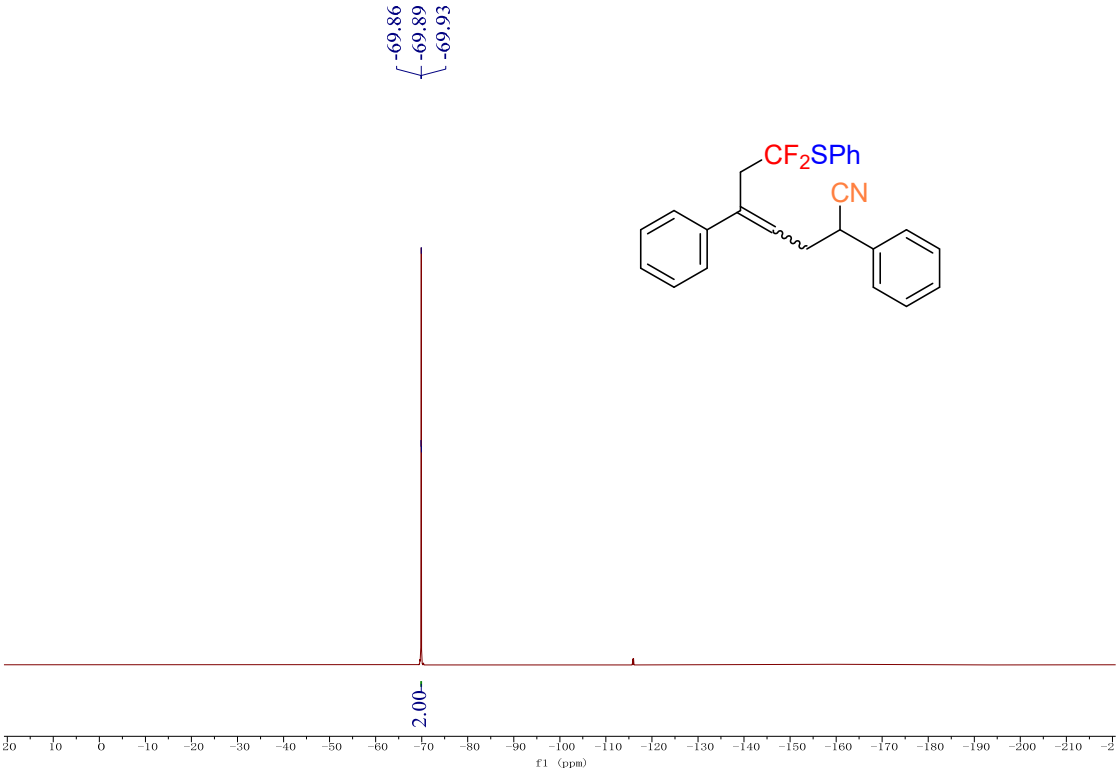

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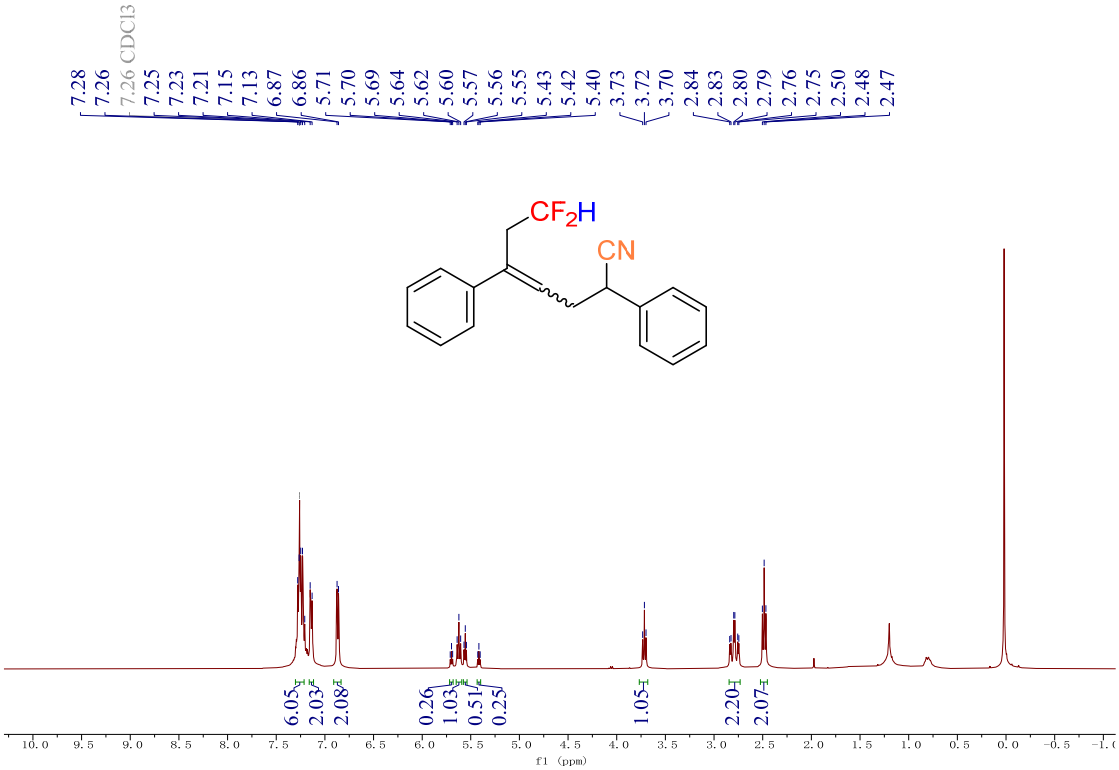

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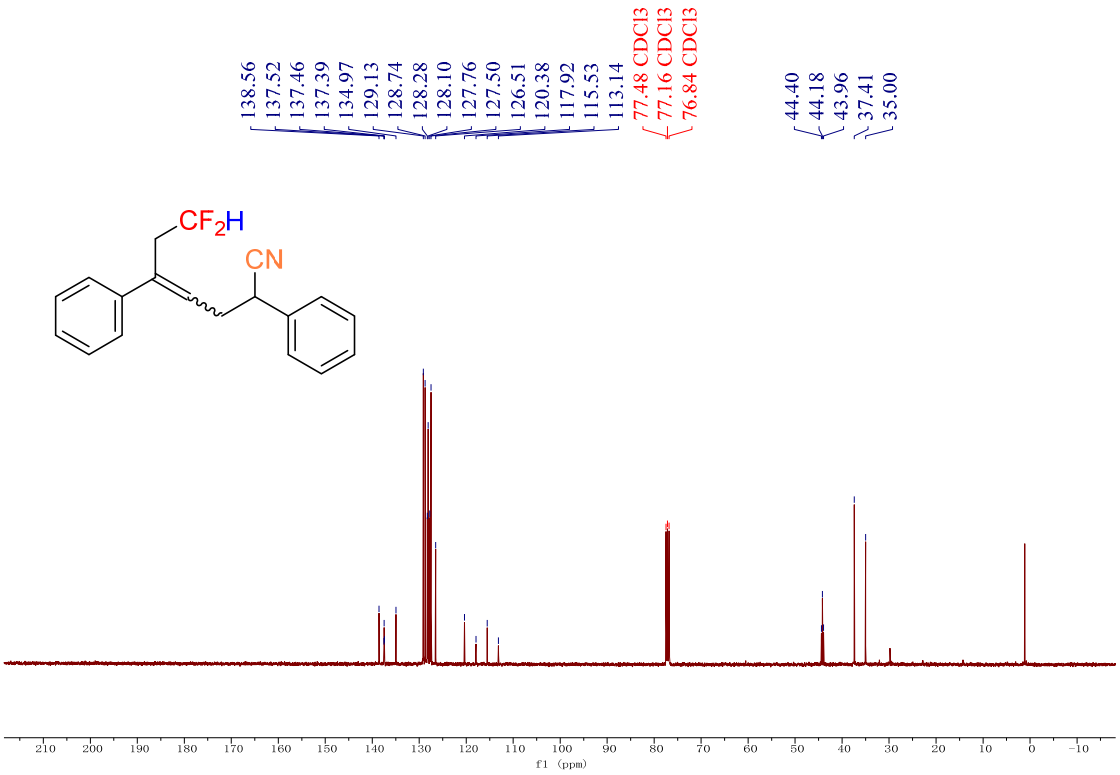

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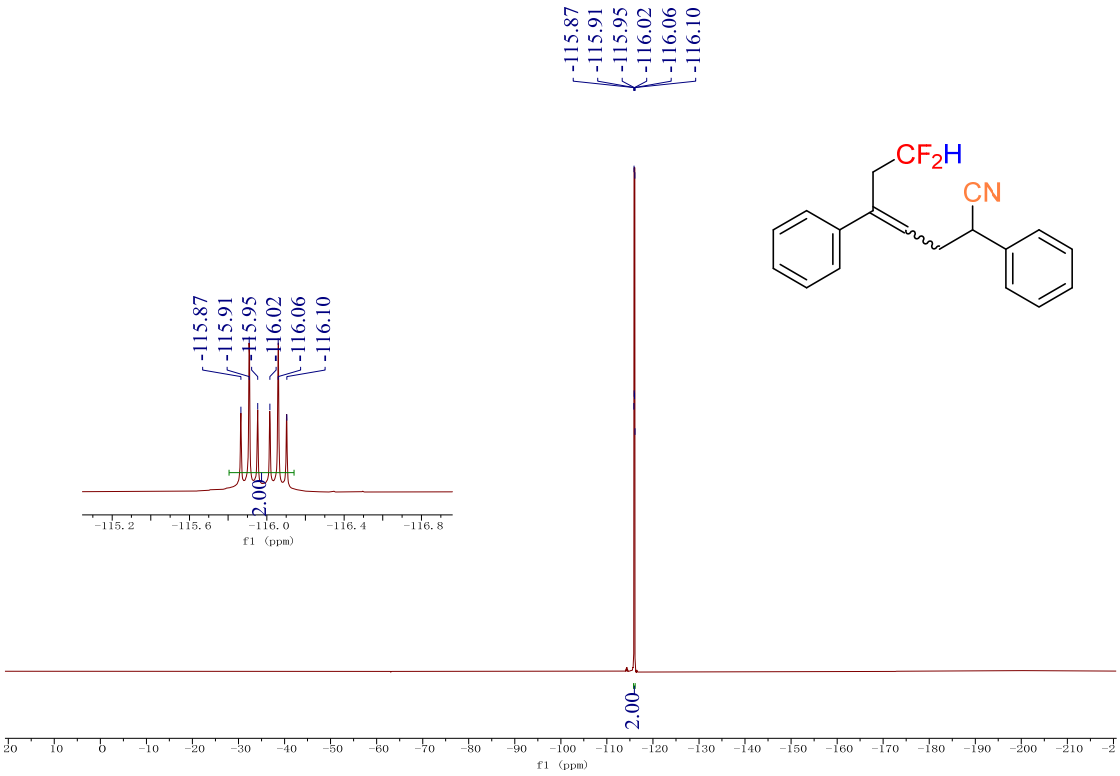
-115.87
-115.91
-115.95
-116.02
-116.06
-116.10
CF2H
CN
2.00
2.00
f1 (ppm)
f1 (ppm)