Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Regio- and Stereo-selective Coupling Reactions of Homoallenylboronates

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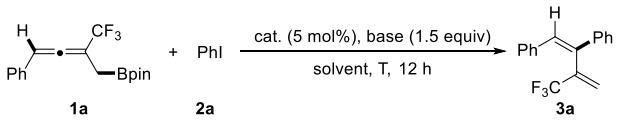
I. General Experimental Information

Unless otherwise noted, all the reactions were carried out under argon atmosphere using standard Schlenk technique. For reactions that require heating, oil bath equipped with a magnetic stir bar was used. And all reagents were used as supplied commercially without further purification. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded at 25 ^{o}C on a Bruker Advance 400 M NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts of ^{1}H, ^{19}F and ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as a *J* value in Hertz (Hz). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF or Thermo Scientific Q Exactive GC Orbitrap, GCT Premier. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

II. Optimization of the Coupling Reaction Conditions

Table S1. Optimization of Reaction Conditions for the Coupling of Homoallenylboronate **1a** with Iodobenzene **2a**.



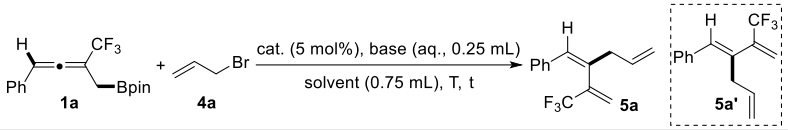
1a **2a** **3a**

entry	2a (equiv)	cat. (5 mol%)	base (1.5 equiv)	solvent (mL)	T (°C)	yield (%)[c]
1	1.1	$Pd_2(dba)_3$	K_3PO_4	THF (1)	70	23
2	1.1	$Pd(PPh_3)_4$	K_3PO_4	THF (1)	70	62
3	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4	THF (1)	70	70
4	1.1	$PdCl_2(PPh_3)_2$	K_3PO_4	THF (1)	70	65
5	1.1	$PdCl_2(dppf)•CH_2Cl_2$	NaOH	THF (1)	70	33
6	1.1	$PdCl_2(dppf)•CH_2Cl_2$	Cs_2CO_3	THF (1)	70	62
7	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_2CO_3	THF (1)	70	15
8	1.1	$PdCl_2(dppf)•CH_2Cl_2$	CsOPiv	THF (1)	70	46
9	1.1	$PdCl_2(dppf)•CH_2Cl_2$	NaOAc	THF (1)	70	1
10	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	THF (0.75)	70	88
11	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	MTBE (0.75)	70	80
12	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	Dioxane (0.75)	70	55
13	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	DME (0.75)	70	79
14	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	MeOH (0.75)	70	79
15	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	EtOH (0.75)	70	80
16	1.2	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	THF (0.75)	70	87
17	1.3	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	THF (0.75)	70	85
18	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	THF (0.75)	80	87
19	**1.1**	**$PdCl_2(dppf)•CH_2Cl_2$**	**K_3PO_4 (aq.)**	**THF (0.75)**	**60**	**90 (92[d])**
20	1.1	$PdCl_2(dppf)•CH_2Cl_2$	K_3PO_4 (aq.)	THF (0.75)	50	83

[a] The reactions were run under the following reaction conditions: the mixture of **1a** (0.1 mmol), **2a** (0.11 mmol), palladium catalyst (5 mol%), and base (1.5 equiv) was stirred in the solvent as shown under argon atmosphere for

12 h. [b] For entries 10~20, K_3PO_4 was dissolved in 0.25 mL H_2O and added into the reaction. [c] Determined by ^1H NMR analysis using mesitylene as the internal standard. [d] Isolated yield.

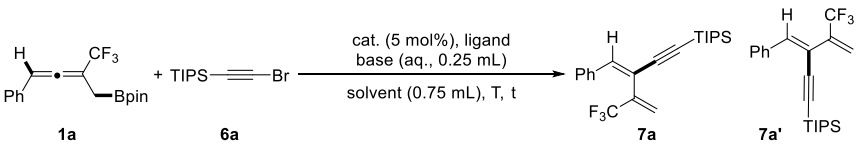
Table S2. Optimization of Reaction Conditions for the Coupling of Homoallenylboronate **1a** with Allyl Bromide **4a**.



entry	cat. (5 mol%)	base (equiv, aq.)	solvent	t (h)	T (ºC)	5a (%)[b]	5a' (%)[b]
1	$Pd_2(dba)_3$	K_3PO_4 (1.5)	THF	12	60	55	5
2	$Pd(CH_3CN)_2Cl_2$	K_3PO_4 (1.5)	THF	12	60	56	6
3	$Pd(cod)Cl_2$	K_3PO_4 (1.5)	THF	12	60	53	6
4	$Pd(CH_3CN)_4(BF_4)_2$	K_3PO_4 (1.5)	THF	12	60	77	7
5	$Pd(TFA)_2$	K_3PO_4 (1.5)	THF	12	60	82	6
6	$Pd(TFA)_2$	K_2HPO_4 (1.5)	THF	12	60	74	12
7	$Pd(TFA)_2$	Na_3PO_4 (1.5)	THF	12	60	85	7
8	$Pd(TFA)_2$	K_2CO_3 (1.5)	THF	12	60	75	7
9	$Pd(TFA)_2$	Na_2CO_3 (1.5)	THF	12	60	79	7
10	$Pd(TFA)_2$	Na_3PO_4 (1.2)	THF	12	60	85	7
11	$Pd(TFA)_2$	Na_3PO_4 (1.2)	MTBE	12	60	67	7
12	$Pd(TFA)_2$	Na_3PO_4 (1.2)	Dioxane	12	60	87	5
13	**$Pd(TFA)_2$**	**Na_3PO_4 (1.2)**	**MeOH**	**12**	**60**	**91 (90[c])**	**3**
14	$Pd(TFA)_2$	Na_3PO_4 (1.2)	EtOH	12	60	86	3
15	$Pd(TFA)_2$	Na_3PO_4 (1.2)	^{i}PrOH	12	60	81	4
16	$Pd(TFA)_2$	Na_3PO_4 (1.2)	MeOH	12	50	89	3
17	$Pd(TFA)_2$	Na_3PO_4 (1.2)	MeOH	12	70	89	3
18	$Pd(TFA)_2$	Na_3PO_4 (1.2)	MeOH	6	60	87	3

[a] The reactions were run under the following reaction conditions: the mixture of homoallenylboronate **1a** (0.2 mmol), **4a** (0.22 mmol), palladium catalyst (5 mol%), and base (aq., 0.25 mL) was stirred in the solvent as shown (0.75 mL) under argon atmosphere for 12 h. [b] Determined by ^1H NMR analysis using mesitylene as the internal standard. [c] Isolated yield, **5a**:**5a'** = 97:3 (determined by ^1H NMR analysis).

Table S3. Optimization of Reaction Conditions for the Coupling of Homoallenylboronate **1a** with Alkynyl Bromides **6a**.

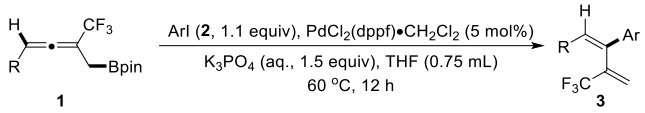


entry	6a (equiv)	cat. (5 mol%)	ligand (mol%)	base (equiv, aq.)	solvent	T (ºC)	7a (%)[b]	7a' (%)[b]
1	1.1	$Pd_2(dba)_3$	-	Na_3PO_4 (1.2)	THF	60	13	15
2	1.1	$Pd(OAc)_2$	-	Na_3PO_4 (1.2)	THF	60	14	14
3	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.2)	THF	60	62	9
4	1.1	$PdCl_2(PPh_3)_2$	-	Na_3PO_4 (1.2)	THF	60	23	1
5	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.2)	Dioxane	60	71	6
6	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.2)	MeOH	60	62	9
7	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.2)	^{i}PrOH	60	73	9
8	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	K_3PO_4 (1.2)	^{i}PrOH	60	70	11
9	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	K_2CO_3 (1.2)	^{i}PrOH	60	38	44

10	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.5)	^{i}PrOH	60	73	7
11	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.2)	^{i}PrOH	50	61	10
12	1.1	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.2)	^{i}PrOH	70	69	12
13	1.5	$PdCl_2(dppf)•CH_2Cl_2$	-	Na_3PO_4 (1.2)	^{i}PrOH	60	74	7
14	1.1	$Pd(OAc)_2$	dppf (5)	Na_3PO_4 (1.2)	^{i}PrOH	60	62	12
15	1.1	$Pd(OAc)_2$	dcypf (5)	Na_3PO_4 (1.2)	^{i}PrOH	60	39	20
16	1.1	$Pd(OAc)_2$	xantphos (5)	Na_3PO_4 (1.2)	^{i}PrOH	60	52	8
17	1.1	$Pd(OAc)_2$	Ph_3P (10)	Na_3PO_4 (1.2)	^{i}PrOH	60	86	2
18	1.1	$Pd(OAc)_2$	$(4\text{-}FPh)_3P$ (10)	Na_3PO_4 (1.2)	^{i}PrOH	60	76	8
19	1.1	$Pd(OAc)_2$	$(4\text{-}MePh)_3P$ (10)	Na_3PO_4 (1.2)	^{i}PrOH	60	84	3
20[c]	**1.1**	**$Pd(OAc)_2$**	**Ph_3P (10)**	**Na_3PO_4 (1.2)**	**^{i}PrOH**	**60**	**86 (80[d])**	**3**

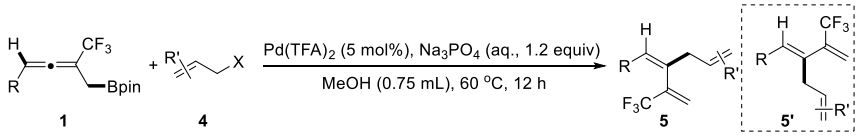
[a] The reactions were run under the following reaction conditions: the mixture of homoallenylboronate **1a** (0.2 mmol), **6a** (0.22 mmol), palladium catalyst (5 mol%), ligand, and base (aq., 0.25 mL) was stirred in the solvent as shown (0.75 mL) under argon atmosphere for 12 h. [b] Determined by ^{1}H NMR analysis using mesitylene as the internal standard. [c] Reacted for 8 h. [d] Isolated yield.

III. General Method for the Coupling Reactions



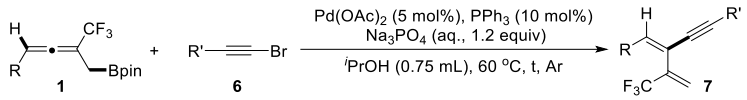
Scheme S1. The Coupling between Homoallenylboronates and Aryl Iodides for Products **3**.

Under argon atmosphere, $PdCl_2(dppf)•CH_2Cl_2$ (0.0082 g, 5 mol%) was added into a Schlenk tube. Then, K_3PO_4 (0.0637 g, 0.3 mmol, 1.5 equiv) dissolved in 0.25 mL H_2O was added into the reaction tube. THF (0.75 mL), corresponding 2,3-butadien-1-ylboronate (0.2 mmol, 1.0 equiv) and ArI (0.22 mmol, 1.1 equiv) were added sequentially. The mixture was stirred at 60 °C for 12 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-300 mesh) using ethyl acetate/petroleum ether as eluent.



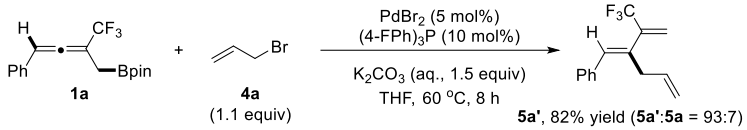
Scheme S2. The Coupling between Homoallenylboronates and Allyl Halides for Products **5**.

Under argon atmosphere, $Pd(TFA)_2$ (0.0033 g, 5 mol%) was added into a Schlenk tube. Then, Na_3PO_4 (0.0393 g, 0.24 mmol, 1.2 equiv) dissolved in 0.25 mL H_2O was added into the reaction tube. MeOH (0.75 mL), corresponding 2,3-butadien-1-ylboronate (0.2 mmol, 1.0 equiv) and substituted allyl halide (0.22 mmol, 1.1 equiv) were added sequentially. The mixture was stirred at 60 °C for 12 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by preparative thin layer chromatography using ethyl acetate/hexane as eluent.



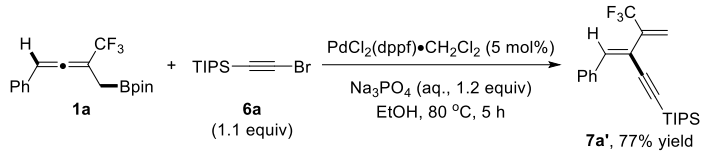
Scheme S3. The Coupling between Homoallenylboronates and Alkynyl Bromides for Products **7**.

Under argon atmosphere, $Pd(OAc)_2$ (0.0022 g, 5 mol%) and PPh_3 (0.0053 g, 10 mol%) were added into a Schlenk tube. Then, ^{i}PrOH (0.75 mL) was added and stirred at room temperature for 30 min. Na_3PO_4 (0.0393 g, 0.24 mmol, 1.2 equiv) dissolved in 0.25 mL H_2O was added into the reaction tube. Corresponding 2,3-butadien-1-ylboronate (0.2 mmol, 1.0 equiv) and substituted alkynyl bromide (0.22 mmol, 1.1 equiv) were added sequentially. The mixture was stirred at 60 °C for indicated time, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by preparative thin layer chromatography using ethyl acetate/hexane as eluent.



Scheme S4. The Coupling between **1a** and **4a** for Products **5a'**.

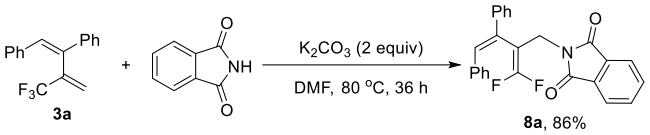
Under argon atmosphere, $PdBr_2$ (0.0027 g, 5 mol%) and $(4\text{-FPh})_3P$ (0.0063 g, 10 mol%) were added into a Schlenk tube. Then, THF (0.75 mL) was added and stirred at room temperature for 30 min. K_2CO_3 (0.0415 g, 0.3 mmol, 1.5 equiv) dissolved in 0.25 mL H_2O was added into the reaction tube. Homoallenylboronate **1a** (0.0648 g, 0.2 mmol, 1.0 equiv) and allyl bromide **4a** (0.0266 g, 0.22 mmol, 1.1 equiv) were added sequentially. The mixture was stirred at 60 °C for 8 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by preparative thin layer chromatography using hexane as eluent, the aim product **5a'** was obtained as colorless oil (0.0389 g, 82% yield, **5a'**:**5a** = 93:7).



Scheme S5. The Coupling between **1a** and **6a** for Products **7a'**.

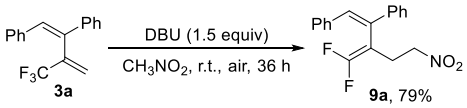
Under argon atmosphere, $PdCl_2(dppf)\bullet CH_2Cl_2$ (0.0082 g, 5 mol%) was added into a Schlenk tube. Then, Na_3PO_4 (0.0393 g, 0.24 mmol, 1.2 equiv) was dissolved in 0.25 mL H_2O and added into the reaction tube. EtOH (0.75 mL), homoallenylboronate **1a** (0.0648 g, 0.2 mmol, 1.0 equiv) and alkynyl bromide **6a** (0.0575 g, 0.22 mmol, 1.1 equiv) were added sequentially. The mixture was stirred at 80 °C for 5 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by preparative thin layer chromatography using hexane as eluent, the aim product **7a'** was obtained as colorless oil (0.0583 g, 77% yield).

IV. General Method for the Derivatization of the Products



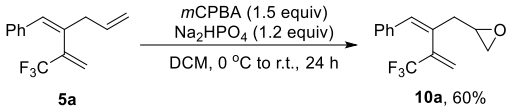
Scheme S6. Defluorophthalimidation of 1,3-Diene **3a**.

Under argon atmosphere, K_2CO_3 (0.0276 g, 2 equiv) and phthalimide (0.0294 g, 2 equiv) were added into a Schlenk tube. Then, DMF (1 mL) and 1,3-diene **3a** (0.0274 g, 0.1 mmol, 1 equiv) were added sequentially. The mixture was stirred at 80 °C for 36 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by preparative thin layer chromatography using ethyl acetate/hexane = 1:10 as eluent, the aim product **8a** was obtained as pale yellow solid (0.0345 g, 86% yield).



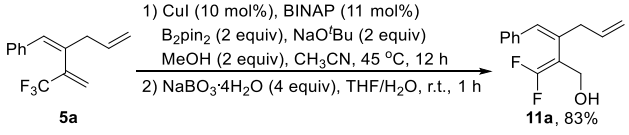
Scheme S7. Defluoronitromethanation of 1,3-Diene **3a**.

1,3-Diene **3a** (0.0274 g, 0.1 mmol, 1 equiv) and CH_3NO_2 (1 mL) were added into reaction tube. Then, DBU (0.0228 g, 1.5 equiv) was added and stirred at r.t. for 36 h. After concentration under vacuum, the residue was diluted with DCM, washed by 1 M HCl (aq.) and dried over anhydrous Na_2SO_4. Concentrated again and the crude product was purified by preparative thin layer chromatography using ethyl acetate/hexane = 1:50 as eluent, the aim product **9a** was obtained as pale yellow oil (0.0249 g, 79% yield).



Scheme S8. Epoxidation of 1,3-Diene **5a**.

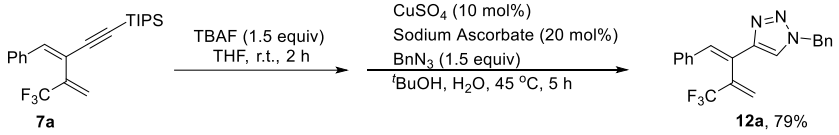
1,3-Diene **5a** (0.0238 g, 0.1 mmol, 1 equiv) in DCM (1 mL) was cooled to 0 °C. *m*CPBA (0.0259 g, 1.5 equiv) and Na_2HPO_4 (0.0170 g, 1.2 equiv) were added. The reaction was warmed to r.t. and stirred for 24 h. The mixture was diluted with DCM, washed by saturated aqueous Na_2CO_3, saturated aqueous $Na_2S_2O_3$ and 2 mol/L NaOH (aq.) sequentially. The combined organic phase was dried over anhydrous Na_2SO_4. After concentration under vacuum, the crude product was purified by preparative thin layer chromatography using ethyl acetate/hexane = 1:20 as eluent, the aim product **10a** was obtained as colorless oil (0.0152 g, 60% yield).



Scheme S9. Defluoroborylation of 1,3-Diene **5a**.

Under argon atmosphere, CuI (0.0019 g, 10 mol%), BINAP (0.0068 g, 11 mol%), B_2pin_2 (0.0508 g,

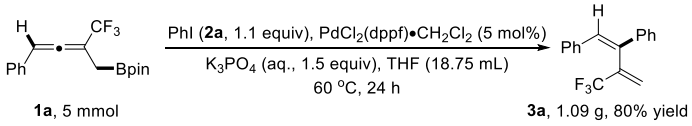
2 equiv), NaO^{t}Bu (0.0192 g, 2 equiv), 1,3-Diene **5a** (0.0238 g, 0.1 mmol, 1 equiv) and MeOH (0.0064 g, 2 equiv) were added into a Schlenk tube, diluted with degassed anhydrous CH_3CN (1 mL). The mixture was stirred at 45 °C for 12 h. The mixture was diluted with DCM and filtrated through silica gel. After concentration under vacuum, the residue was diluted with THF (1 mL). H_2O (1 mL) and $NaBO_3 \cdot 4H_2O$ (0.0615 g, 4 equiv) were added and stirred for 1 h at room temperature. After extracted with DCM, dried over anhydrous Na_2SO_4, the concentrated crude product was purified by preparative thin layer chromatography using ethyl acetate/hexane = 1:10 as eluent, the aim product **11a** was obtained as colorless oil (0.0197 g, 83% yield).



Scheme S10. Desilylation and Click Reaction of 1,3-Diene **7a**.

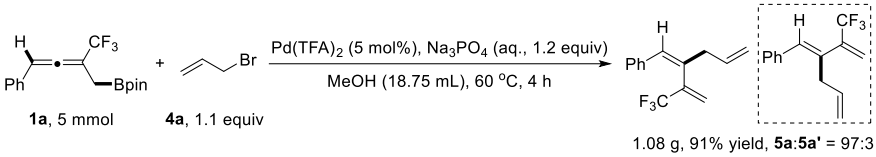
To a solution of 1,3-diene **7a** (0.0379 g, 0.1 mmol, 1 equiv) in THF (1 mL), TBAF (1 mol/L in THF, 1.5 mL, 1.5 equiv) was added dropwise and the resulting mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (4 mL) and extracted with DCM (10 mL X 3'). The combined organic phase was dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue and BnN_3 (0.0200 g, 1.5 equiv) were dissolved into ^{t}BuOH (3 mL). To the above solution, H_2O (240 μL) and $CuSO_4$ (0.1 mol/L in H_2O, 10 mol%), sodium ascorbate (0.1 mol/L in H_2O, 20 mol%) were added sequentially. The reaction was stirred at 45 °C for 5 h, and then cooled to room temperature, quenched with $NH_3 \cdot H_2O$, extracted with DCM (10 mL X 3'). The combined organic phase was dried over anhydrous Na_2SO_4. After concentration under vacuum, the crude product was purified by preparative thin layer chromatography using ethyl acetate/hexane = 1:4 as eluent, the aim product **12a** was obtained as pale yellow oil (0.0279 g, 79% yield).

V. Gram-Scale Synthesis of the Coupling Products



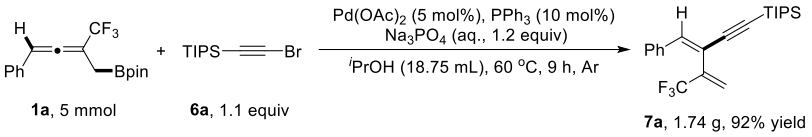
Scheme S11. Gram-Scale Synthesis of 1,3-Diene **3a**.

Under argon atmosphere, $PdCl_2(dppf) \bullet CH_2Cl_2$ (0.205 g, 5 mol%) and K_3PO_4 (1.59 g, 7.5 mmol, 1.5 equiv, in 6.25 mL H_2O) were added into a Schlenk flask. Then, THF (18.75 mL), **1a** (1.62 g, 5 mmol, 1.0 equiv) and PhI (1.12 g, 0.63 mL, 1.1 equiv) were added sequentially. The mixture was stirred at 60 °C for 24 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-300 mesh) using petroleum ether as eluent to give the aim product (1.09 g, 80% yield).



Scheme S12. Gram-Scale Synthesis of 1,3-Diene **5a**.

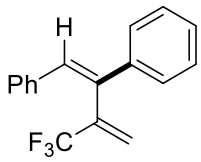
Under argon atmosphere, $Pd(TFA)_2$ (0.0831 g, 5 mol%) and Na_3PO_4 (0.9836 g, 6 mmol, 1.2 equiv, in 6.25 mL H_2O) were added into a Schlenk flask. Then, MeOH (18.75 mL), **1a** (1.62 g, 5 mmol, 1.0 equiv) and **4a** (0.6654 g, 0.5 mL, 1.1 equiv) were added sequentially. The mixture was stirred at 60 °C for 4 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-300 mesh) using petroleum ether as eluent to give the aim product (1.08 g, 91% yield).



Scheme S13. Gram-Scale Synthesis of 1,3-Diene **7a**.

Under argon atmosphere, $Pd(OAc)_2$ (0.0561 g, 5 mol%) and PPh_3 (0.1311 g, 10 mol%) were added into a Schlenk flask. Then, ^{i}PrOH (18.75 mL) was added and stirred at room temperature for 30 min. Na_3PO_4 (0.9836 g, 6 mmol, 1.2 equiv, in 6.25 mL H_2O), **1a** (5 mmol, 1.0 equiv) and **6a** (1.437 g, 1.3 mL, 1.1 equiv) were added sequentially. The mixture was stirred at 60 °C for 9 h, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-300 mesh) using petroleum ether as eluent to give the aim product (1.74 g, 92% yield).

VI. Characterization Data and Spectrum of Compounds



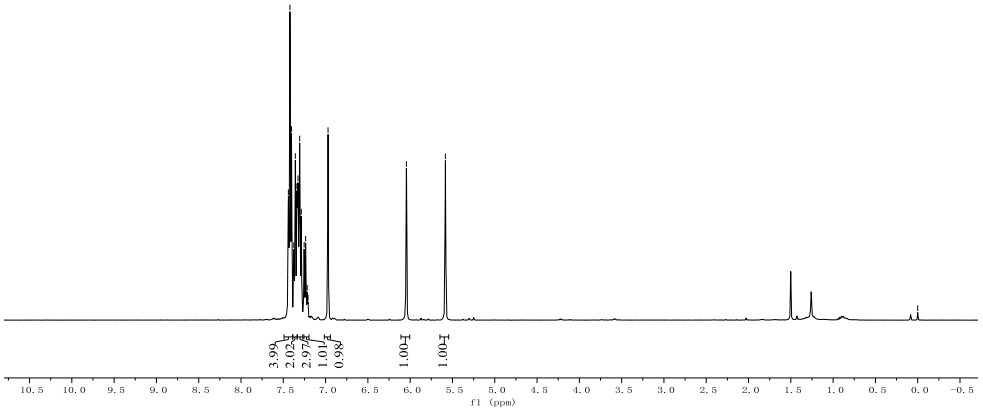
(*Z*)-(3-(trifluoromethyl)buta-1,3-diene-1,2-diyl)dibenzene (**3a**): Colorless oil, yield = 92% (using petroleum ether as eluent).

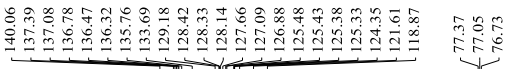
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 7.3 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.23 (dd, *J* = 12.9, 5.6 Hz, 1H), 6.97 (s, 1H), 6.04 (s, 1H), 5.58 (s, 1H).

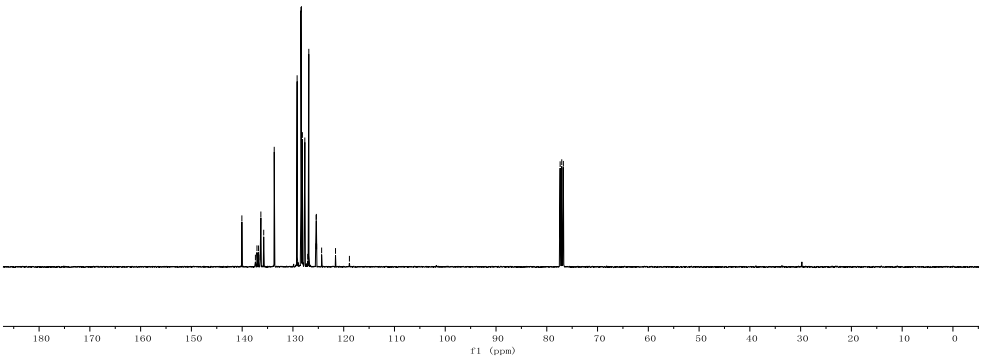
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.78.

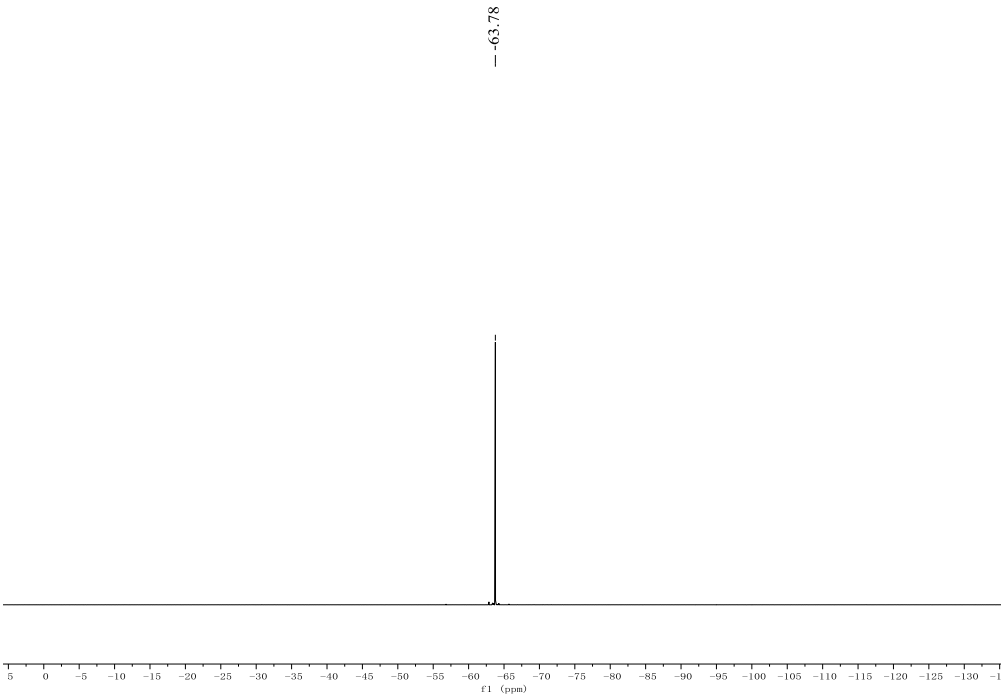
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.06, 136.93 (q, *J* = 31.0 Hz), 136.32, 135.76, 133.69, 129.18, 128.42, 128.33, 128.14, 127.66, 126.88, 125.41 (q, *J* = 4.9 Hz), 122.98 (q, *J* = 275.4 Hz).

HRMS (EI) m/z calcd for $C_{17}H_{13}F_3$ $[M]^+$: 274.0964, found: 274.0961.

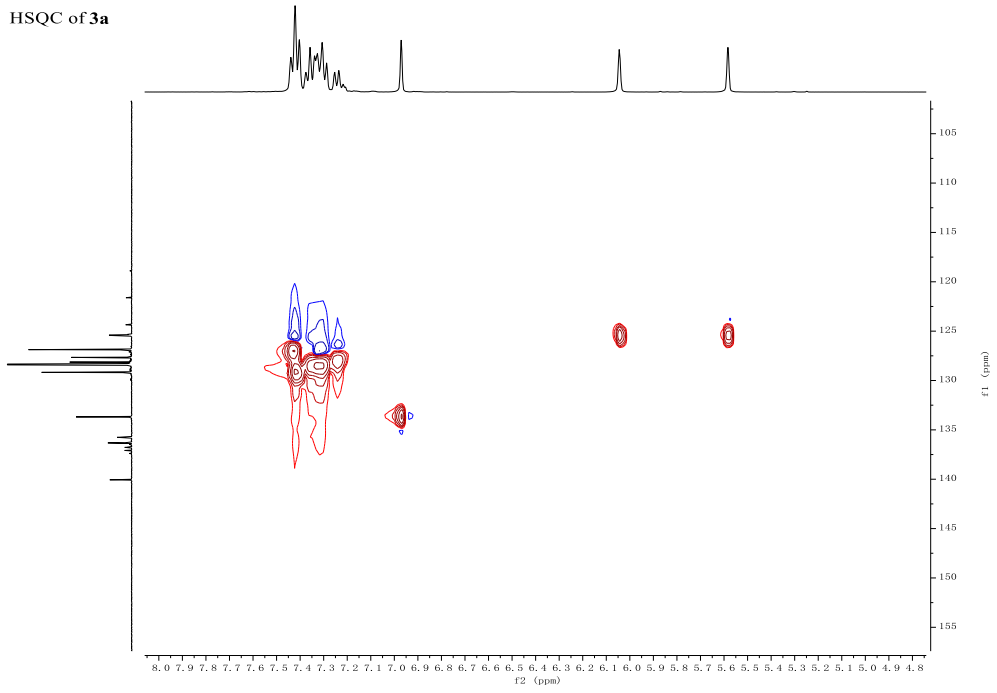




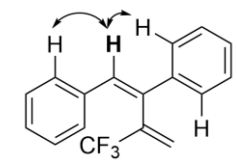


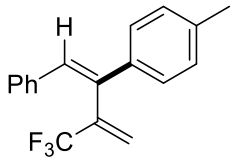


HSQC of **3a**



1D NOESY of **3a**





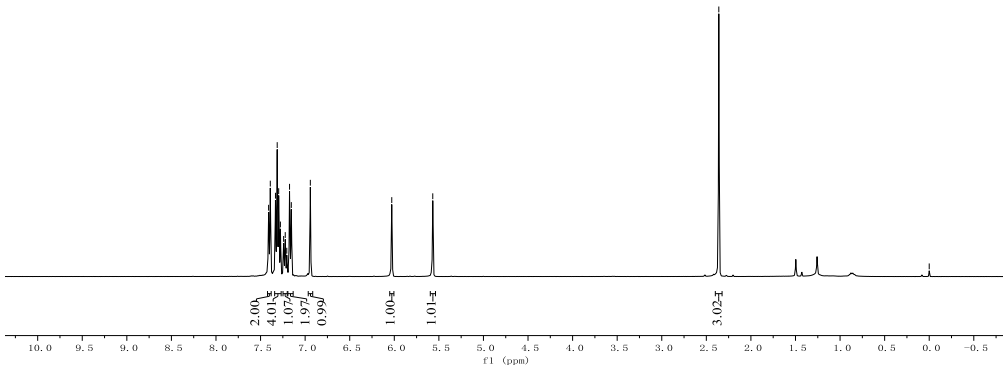
(*Z*)-1-methyl-4-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene (**3b**): Colorless oil, yield = 93% (using petroleum ether as eluent).

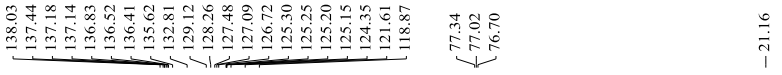
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.94 (s, 1H), 6.03 (s, 1H), 5.57 (s, 1H), 2.36 (s, 3H).

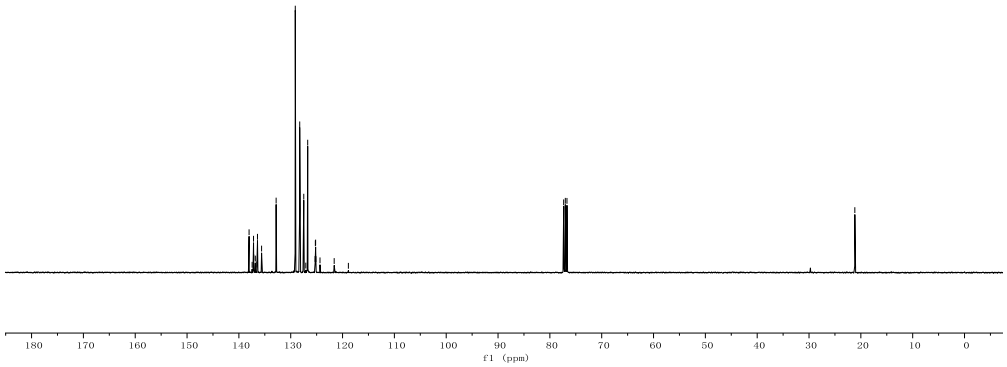
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.73.

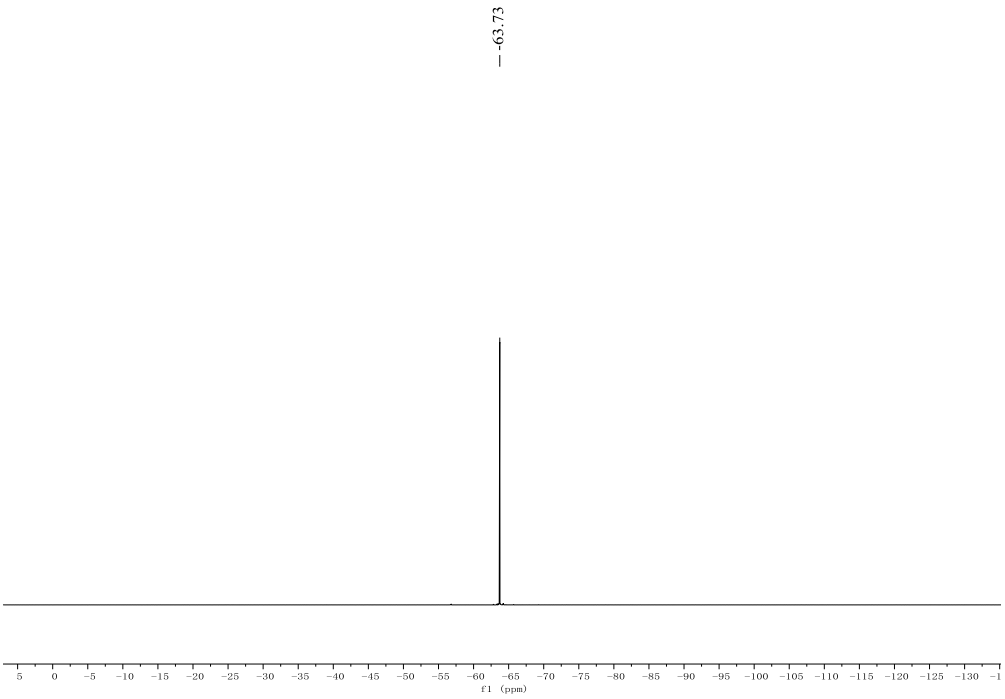
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.03, 137.18, 136.98 (q, *J* = 30.9 Hz), 136.41, 135.62, 132.81, 129.12, 128.26, 127.48, 126.72, 125.22 (q, *J* = 5.0 Hz), 122.98 (q, *J* = 275.5 Hz), 21.16.

HRMS (EI) m/z calcd for $C_{18}H_{15}F_3$ $[M]^+$: 288.1120, found: 288.1116.








-63.73
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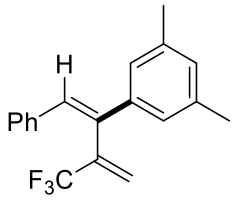
f1 (ppm)



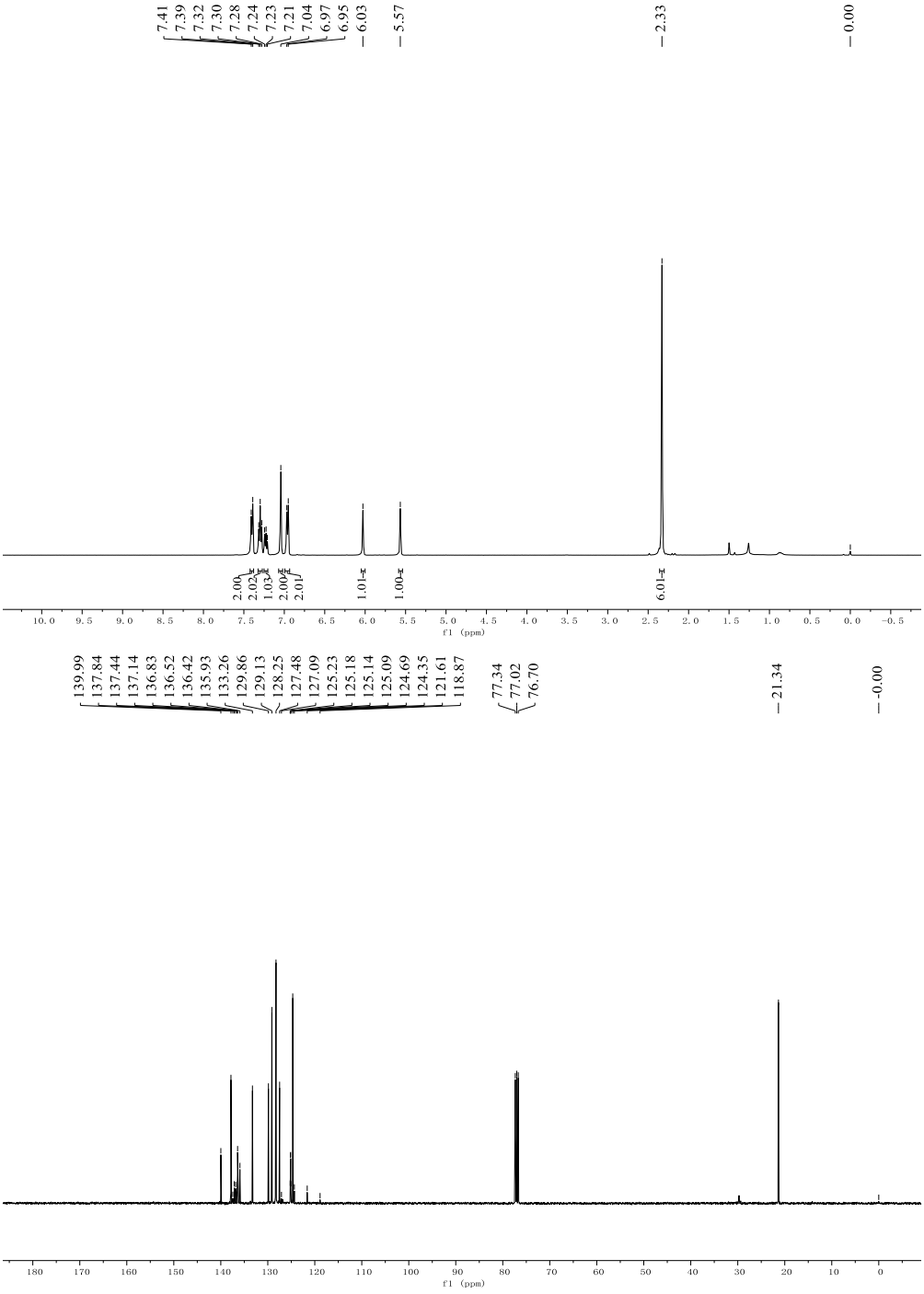
(*Z*)-1,3-dimethyl-5-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene (**3c**): Colorless oil, yield = 91% (using petroleum ether as eluent).

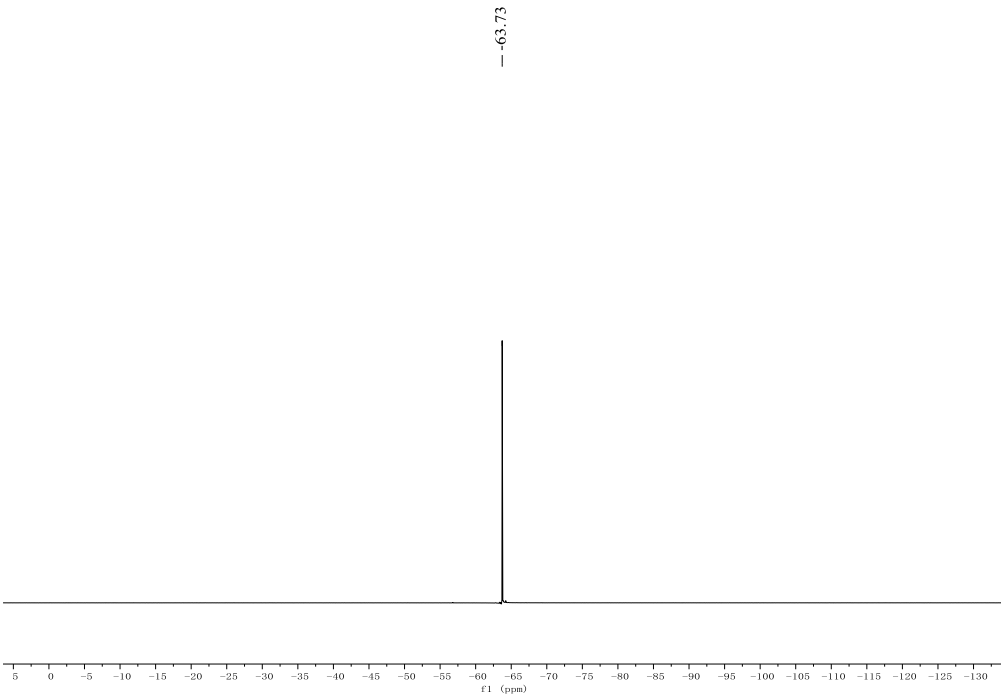
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.04 (s, 2H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.03 (s, 1H), 5.57 (s, 1H), 2.33 (s, 6H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.73.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.99, 137.84, 136.98 (q, *J* = 31.0 Hz), 136.42, 135.93, 133.26, 129.86, 129.13, 128.25, 127.48, 125.16 (q, *J* = 5.0 Hz), 124.69, 122.98 (q, *J* = 275.4 Hz), 21.34.

HRMS (EI) m/z calcd for $C_{19}H_{17}F_3$ $[M]^+$: 302.1277, found: 302.1272.




-63.73
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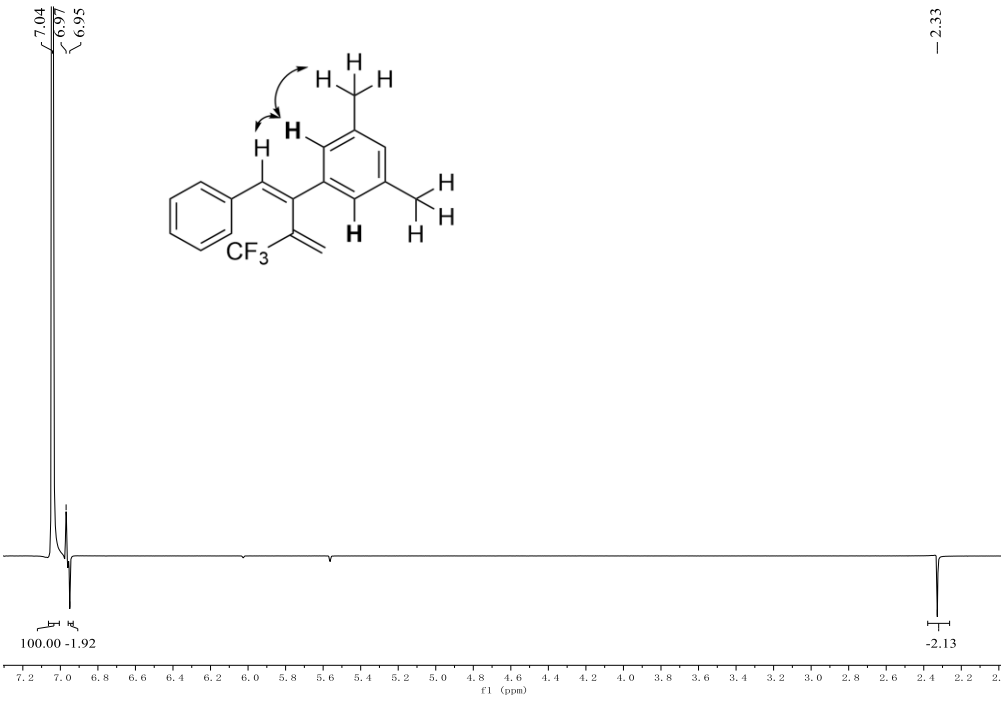
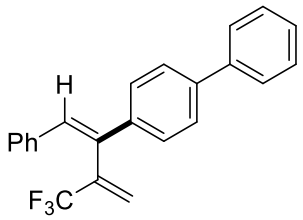
f1 (ppm)


7.04
6.97
6.95
2.33
H
H
H
H
H
H
H
H
CF3
100.00
-1.92
-2.13
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.
f1 (ppm)



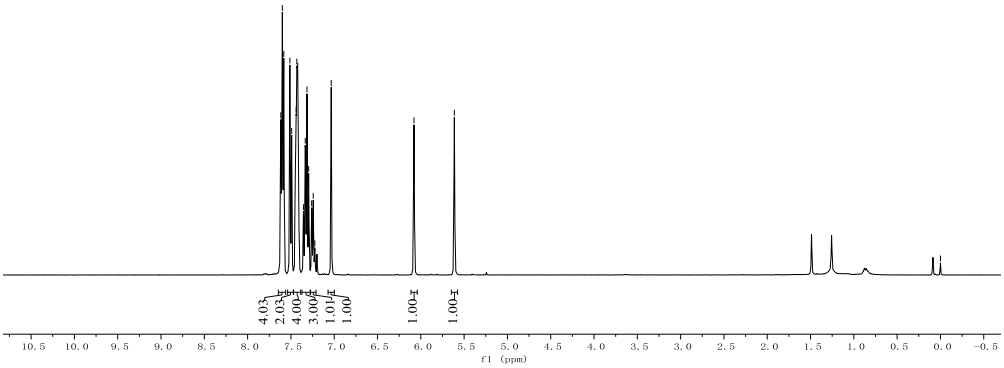
(*Z*)-4-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)-1,1'-biphenyl (**3d**): White solid, yield = 94% (using petroleum ether as eluent).

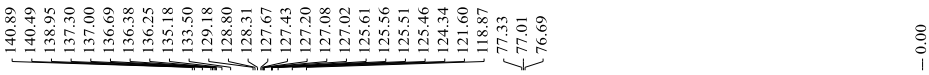
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.56 (m, 4H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.37 – 7.28 (m, 3H), 7.27 – 7.21 (m, 1H), 7.03 (s, 1H), 6.08 (s, 1H), 5.61 (s, 1H).

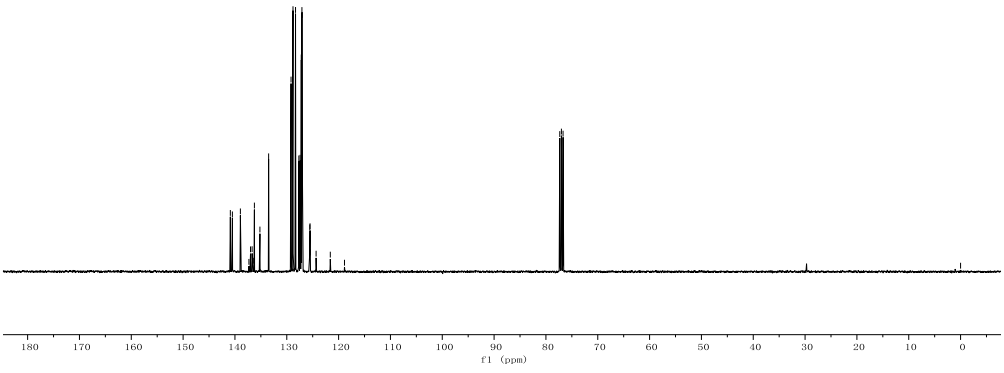
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.69.

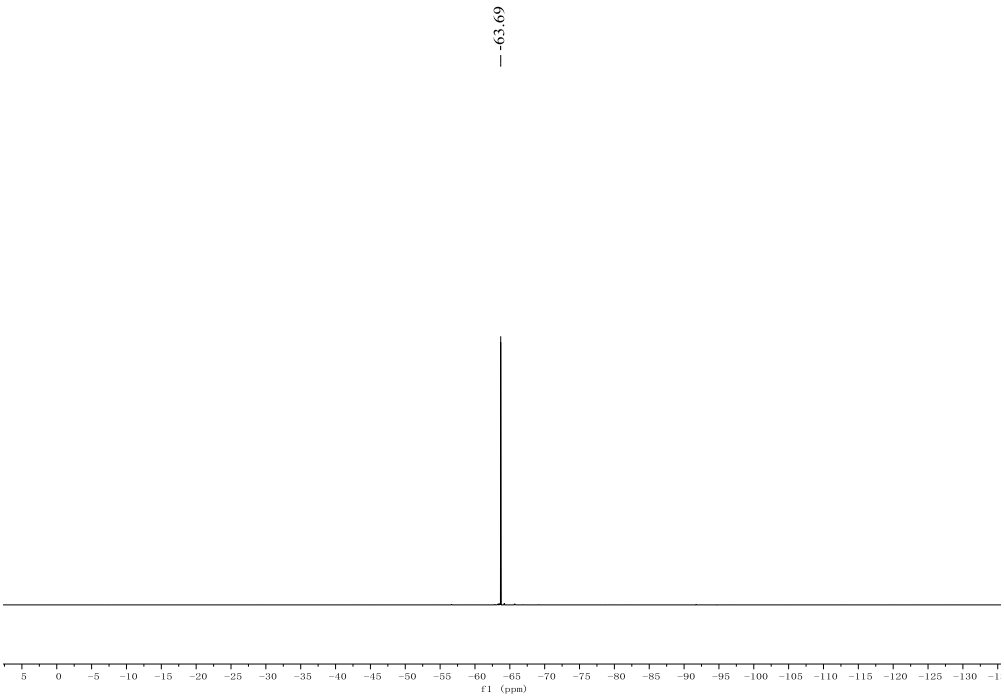
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.89, 140.49, 138.95, 136.84 (q, *J* = 31.0 Hz), 136.25, 135.18, 133.50, 129.18, 128.80, 128.31, 127.67, 127.43, 127.20, 127.08, 127.02, 125.54 (q, *J* = 5.0 Hz), 122.97 (q, *J* = 275.4 Hz).

HRMS (EI) m/z calcd for $C_{23}H_{17}F_3$ $[M]^+$: 350.1277, found: 350.1271.








-63.69
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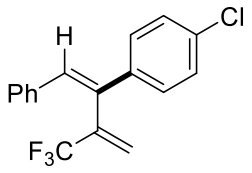
f1 (ppm)



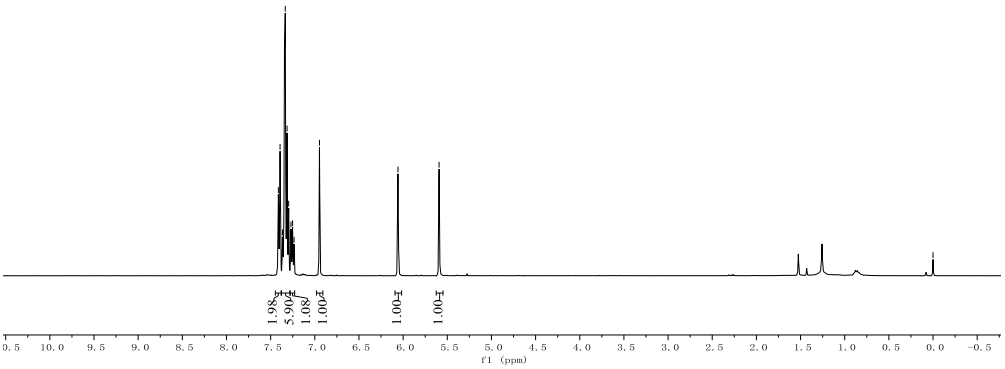
(*Z*)-1-chloro-4-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene (**3e**): Colorless oil, yield = 96% (using petroleum ether as eluent).

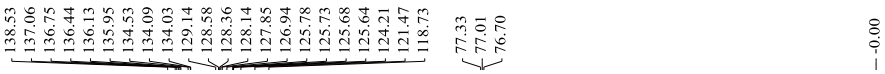
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.28 (m, 6H), 7.28 – 7.23 (m, 1H), 6.95 (s, 1H), 6.06 (s, 1H), 5.59 (s, 1H).

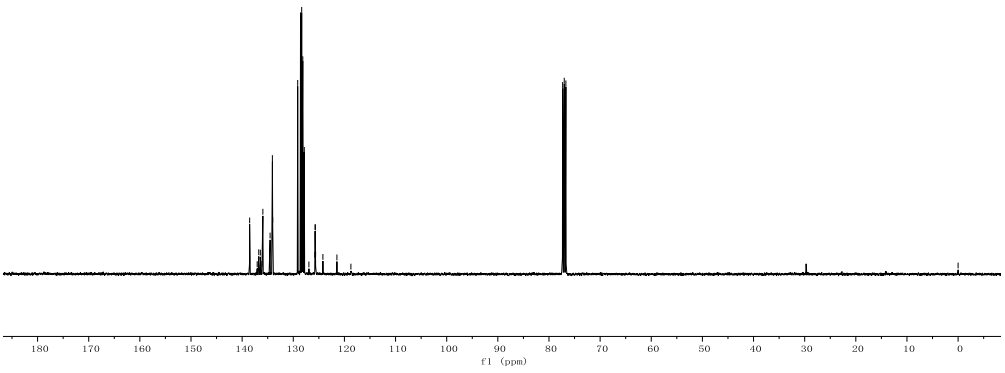
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.84.

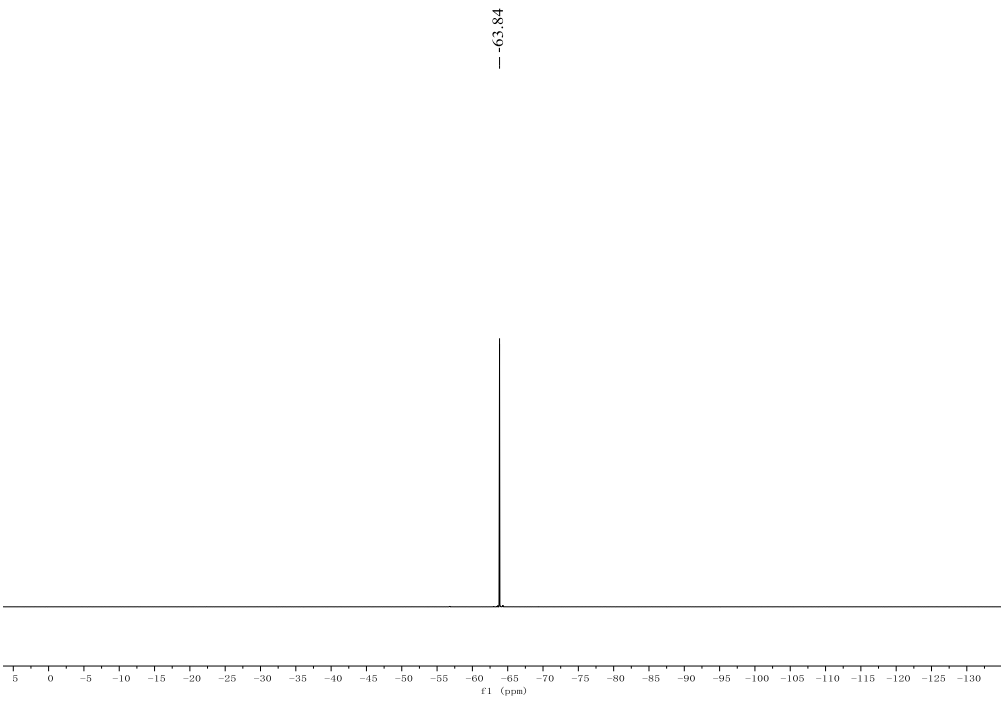
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.53, 136.60 (q, *J* = 31.0 Hz), 135.95, 134.53, 134.09, 134.03, 129.14, 128.58, 128.36, 128.14, 127.85, 125.71 (q, *J* = 4.9 Hz), 122.84 (q, *J* = 275.4 Hz).

HRMS (EI) m/z calcd for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0574, found: 308.0567.








-63.84
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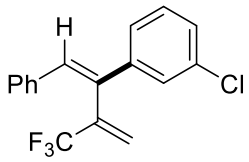
f1 (ppm)



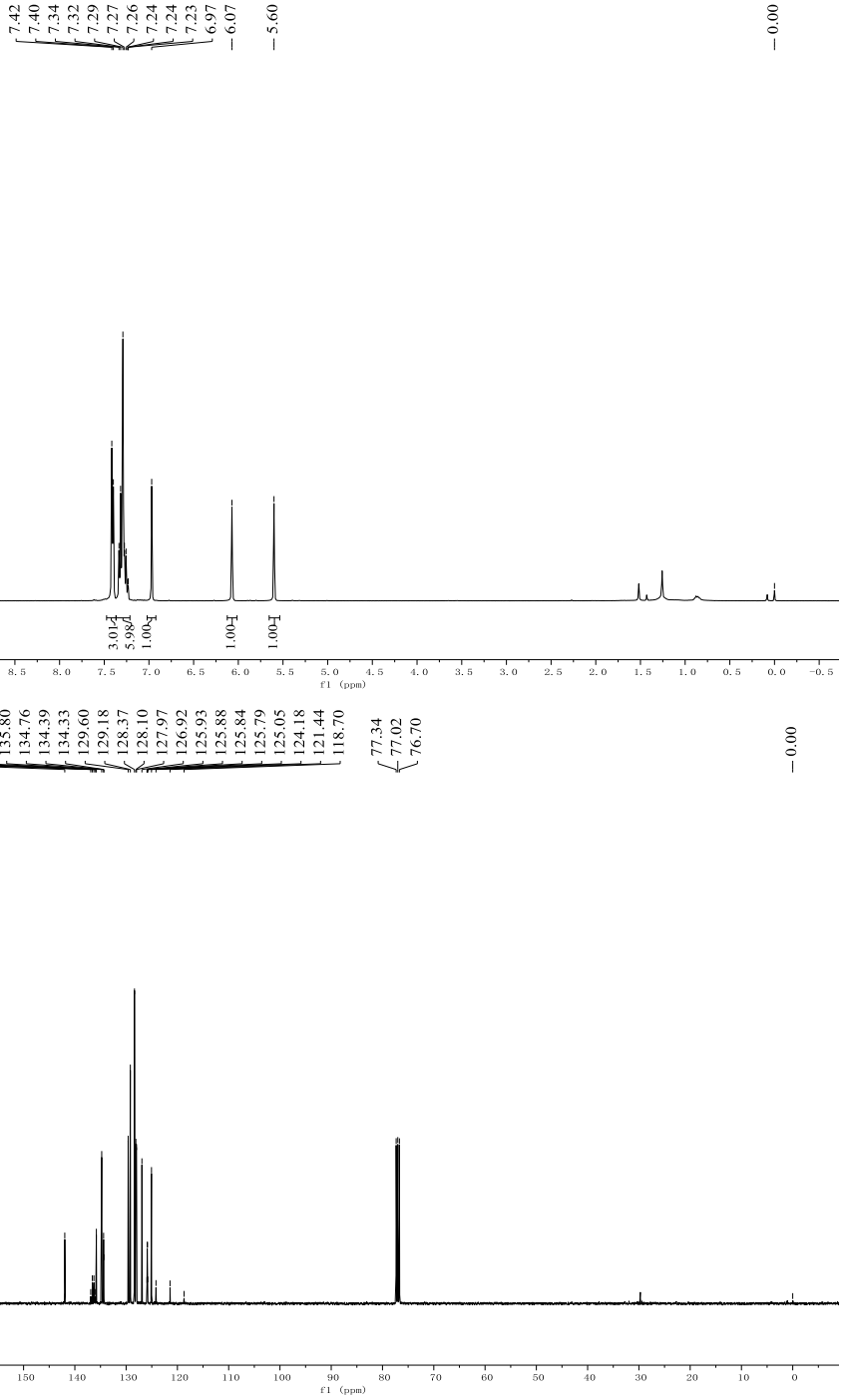
(*Z*)-1-chloro-3-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene (**3f**): Colorless oil, yield = 97% (using petroleum ether as eluent).

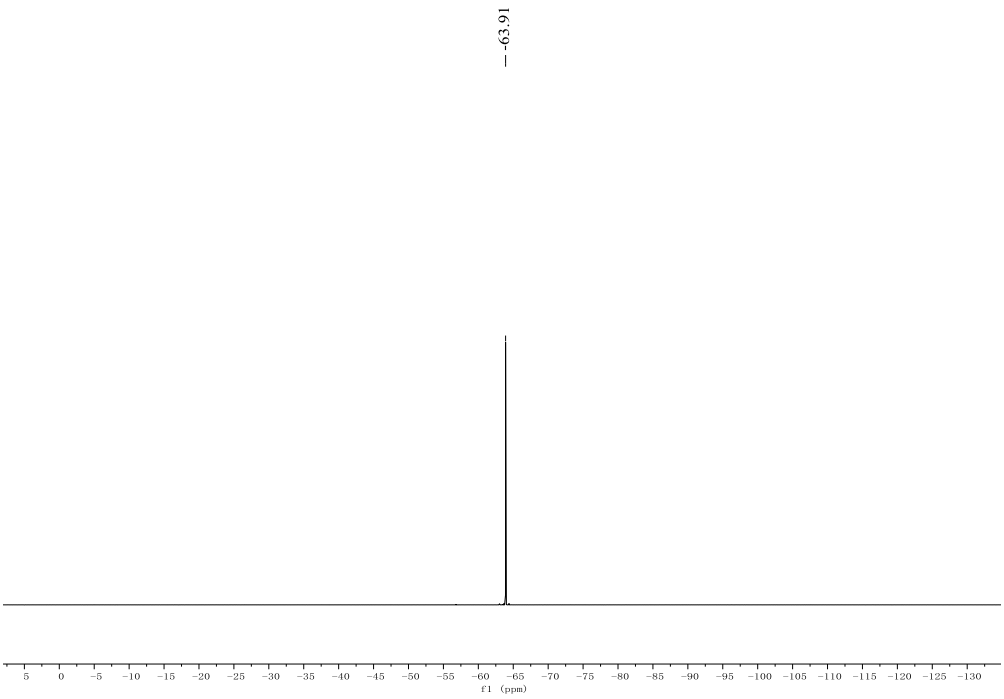
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 6.9 Hz, 3H), 7.37 – 7.21 (m, 6H), 6.97 (s, 1H), 6.07 (s, 1H), 5.60 (s, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.91.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.97, 136.44 (q, *J* = 31.2 Hz), 135.80, 134.76, 134.39, 134.33, 129.60, 129.18, 128.37, 128.10, 127.97, 126.92, 125.86 (q, *J* = 4.9 Hz), 125.05, 122.81 (q, *J* = 275.4 Hz).

HRMS (EI) m/z calcd for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0574, found: 308.0565.




-63.91
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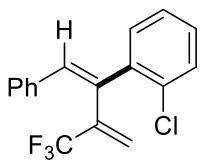
f1 (ppm)



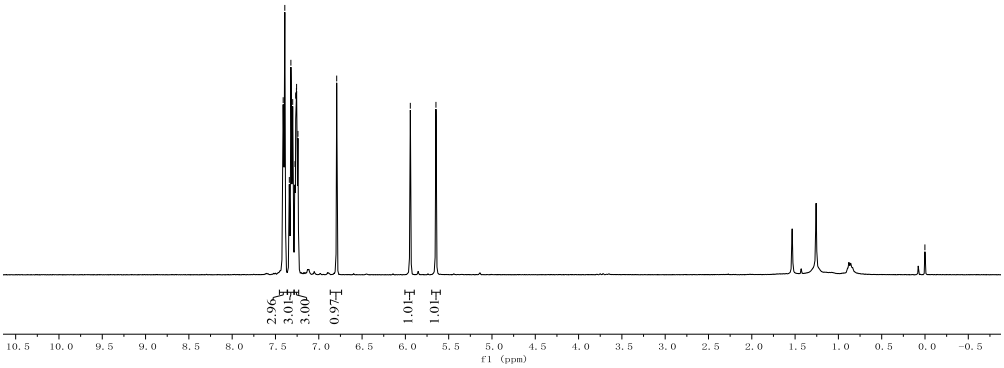
(*E*)-1-chloro-2-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene (**3g**): Colorless oil, yield = 70% (isolated with preparative thin layer chromatography and using hexane as eluent).

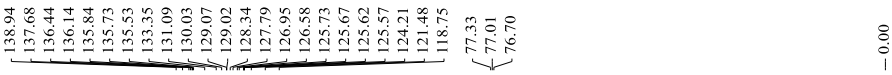
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.5 Hz, 3H), 7.32 (t, *J* = 7.8 Hz, 3H), 7.28 – 7.23 (m, 3H), 6.79 (s, 1H), 5.94 (s, 1H), 5.65 (s, 1H).

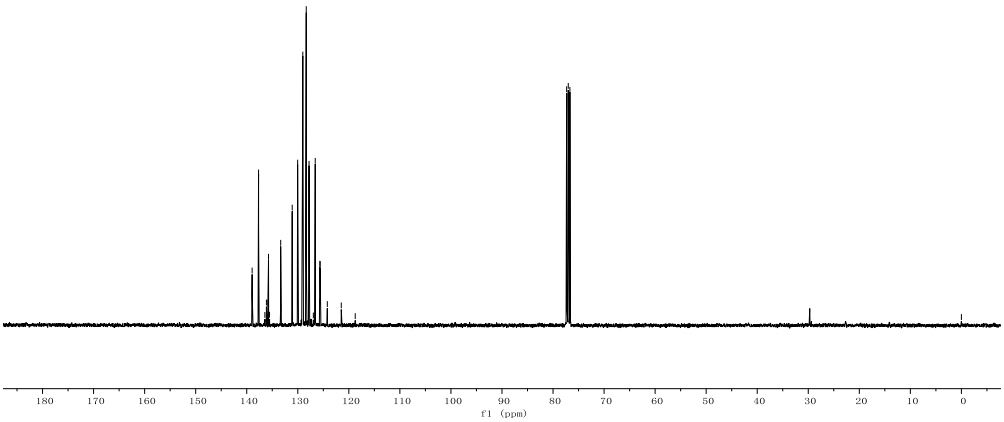
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.29.

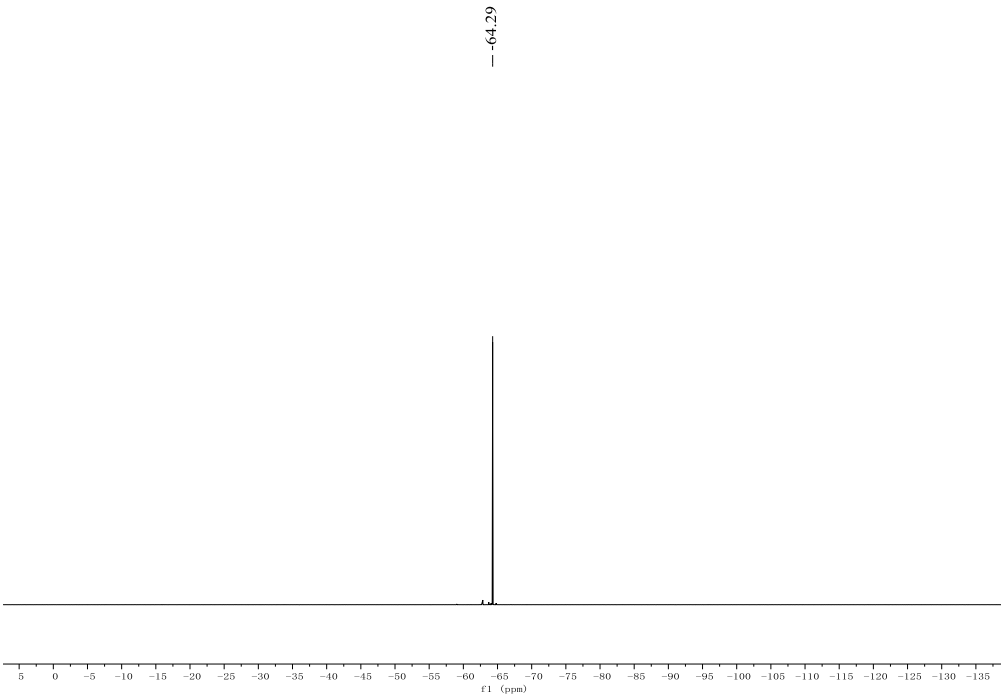
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.94, 137.68, 135.99 (q, *J* = 30.4 Hz), 135.73, 133.35, 131.09, 130.03, 129.07, 129.02, 128.34, 127.79, 126.58, 125.65 (q, *J* = 5.2 Hz), 122.85 (q, *J* = 275.1 Hz).

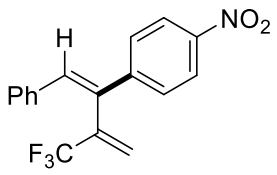
HRMS (EI) m/z calcd for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0574, found: 308.0567.








-64.29
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)



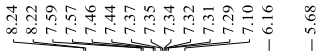
(*Z*)-1-nitro-4-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene (**3h**): Yellow solid, yield = 98% (using ethyl acetate/petroleum ether = 1:50 as eluent).

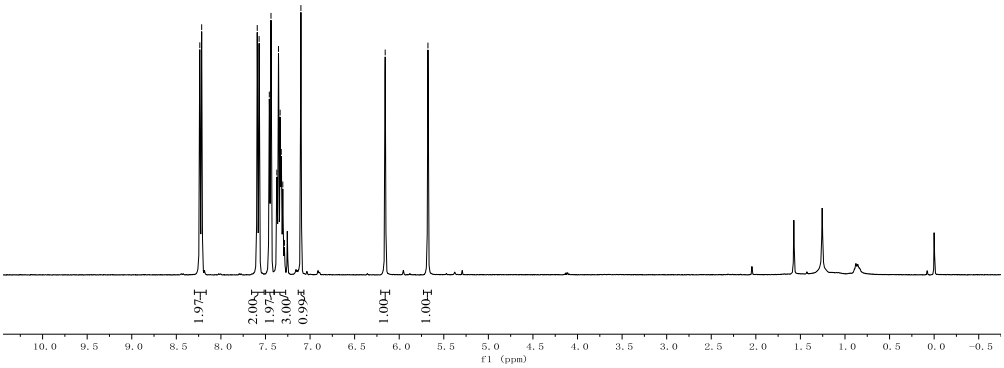
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.27 (m, 3H), 7.10 (s, 1H), 6.16 (s, 1H), 5.68 (s, 1H).

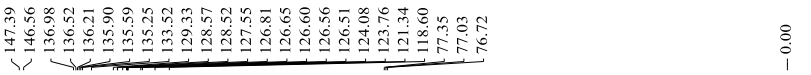
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.01.

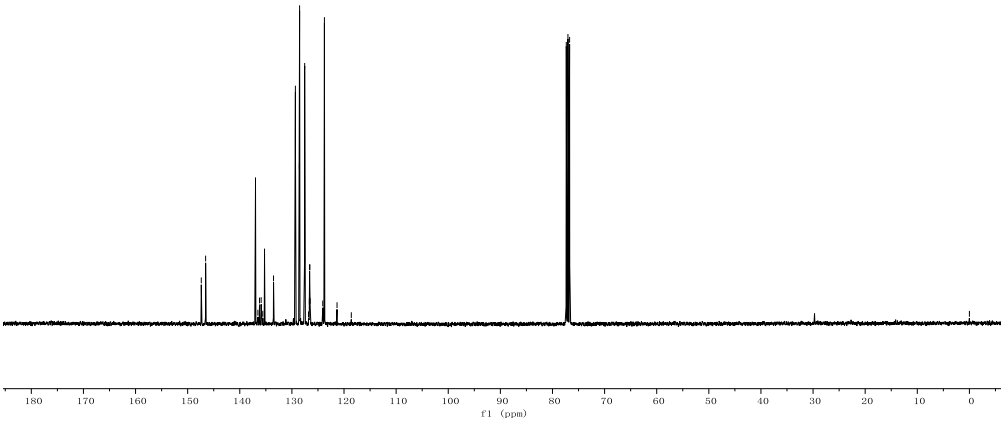
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.39, 146.56, 136.98, 136.06 (q, *J* = 31.4 Hz), 135.25, 133.52, 129.33, 128.57, 128.52, 127.55, 126.58 (q, *J* = 5.0 Hz), 123.76, 122.71 (q, *J* = 276.5 Hz).

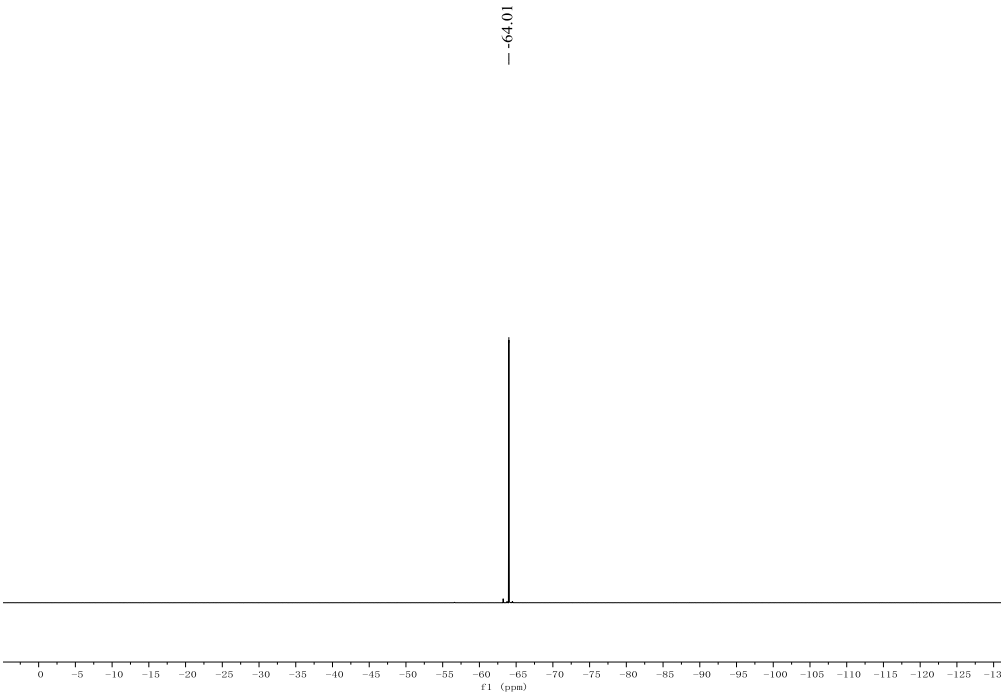
HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3NO_2$ $[M+H]^+$: 320.0898, found: 320.0898.

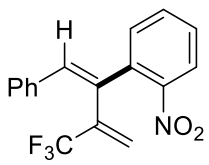









-64.01
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -13
f1 (ppm)



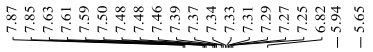
(*Z*)-1-nitro-2-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene (**3i**): Yellow oil, yield = 70% (isolated with preparative thin layer chromatography and using ethyl acetate/petroleum ether = 1:50 as eluent, at the same time, (*E*)-1-nitro-2-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzene **3i'** was obtained in 18% yield).

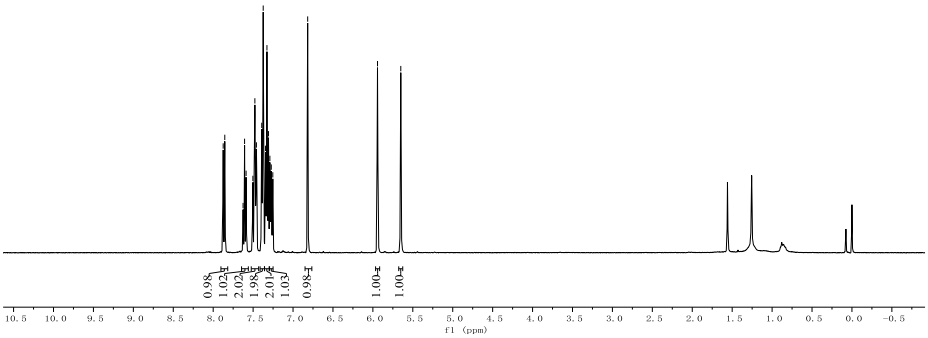
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.29 – 7.25 (m, 1H), 6.82 (s, 1H), 5.94 (s, 1H), 5.65 (s, 1H).

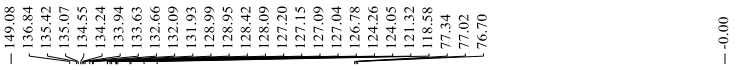
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.08.

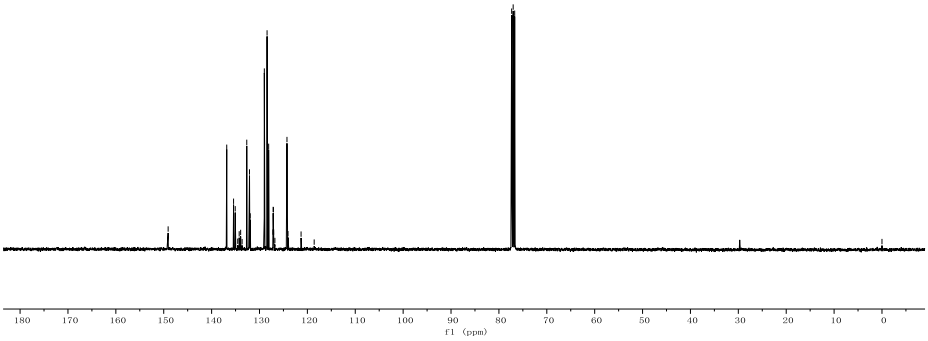
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.08, 136.84, 135.42, 135.07, 134.09 (q, *J* = 30.7 Hz), 132.66, 132.09, 131.93, 128.99, 128.95, 128.42, 128.09, 127.12 (q, *J* = 5.3 Hz), 124.26, 122.68 (q, *J* = 275.1 Hz).

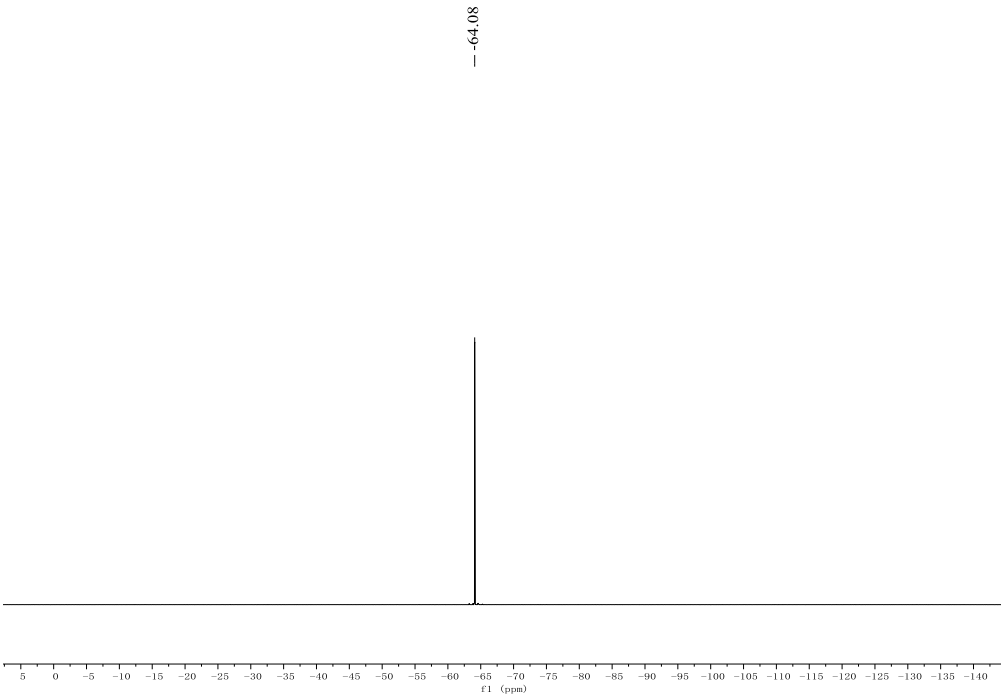
HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3NO_2$ $[M+H]^+$: 320.0898, found: 320.0899.

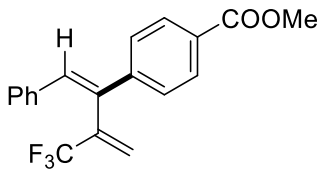









-64.08
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)



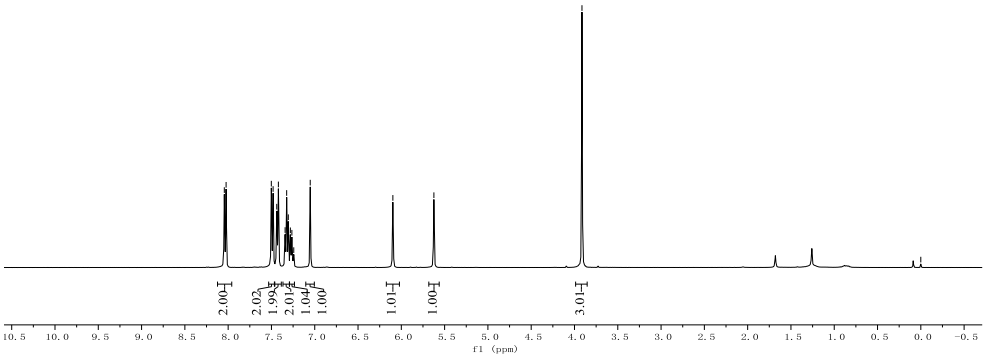
methyl (*Z*)-4-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)benzoate (**3j**): White solid, yield = 96% (using ethyl acetate/petroleum ether = 1:50 as eluent).

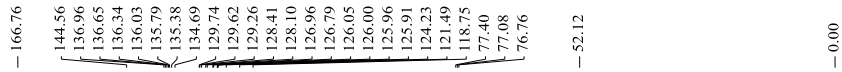
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.05 (s, 1H), 6.10 (s, 1H), 5.62 (s, 1H), 3.91 (s, 3H).

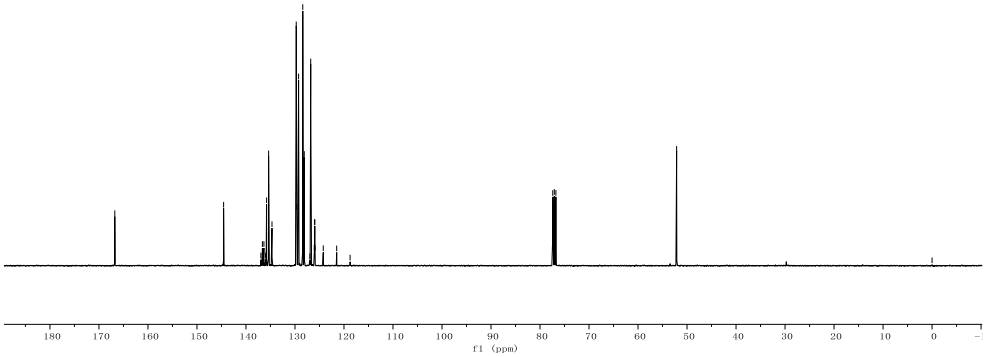
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.94.

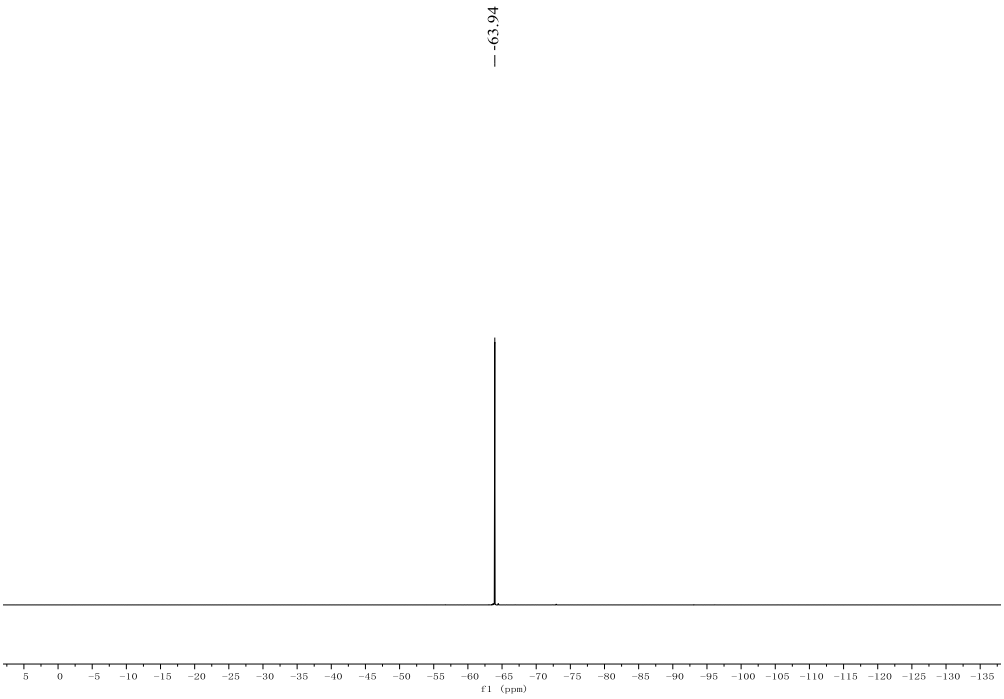
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.76, 144.56, 136.49 (q, *J* = 31.1 Hz), 135.79, 135.38, 134.69, 129.74, 129.62, 129.26, 128.41, 128.10, 126.79, 125.98 (q, *J* = 5.0 Hz), 122.86 (q, *J* = 275.4 Hz), 52.12.

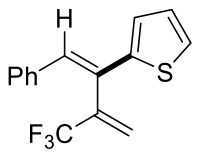
HRMS (ESI) m/z calcd for $C_{19}H_{16}F_3O_2$ $[M+H]^+$: 333.1102, found: 333.1097.








-63.94
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)



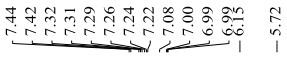
(*E*)-2-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)thiophene (**3k**): Colorless oil, yield = 69% (isolated with preparative thin layer chromatography and using hexane as eluent).

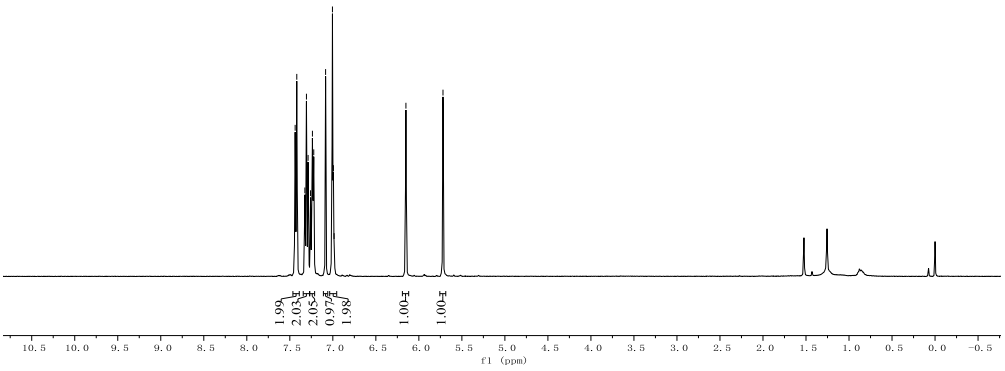
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.08 (s, 1H), 7.04 – 6.95 (m, 2H), 6.15 (s, 1H), 5.72 (s, 1H).

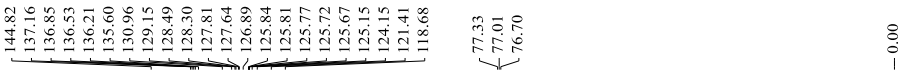
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.96.

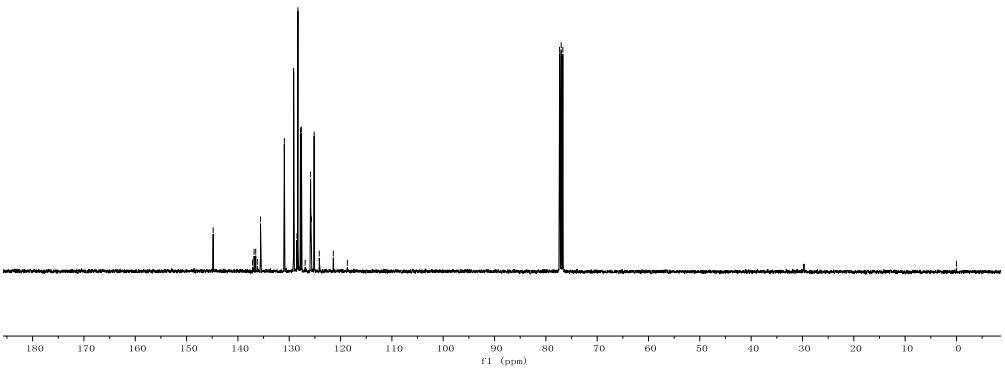
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.82, 136.69 (q, *J* = 31.7 Hz), 135.60, 130.96, 129.15, 128.49, 128.30, 127.81, 127.64, 125.84, 125.74 (q, *J* = 4.9 Hz), 125.15, 122.78 (q, *J* = 275.4 Hz).

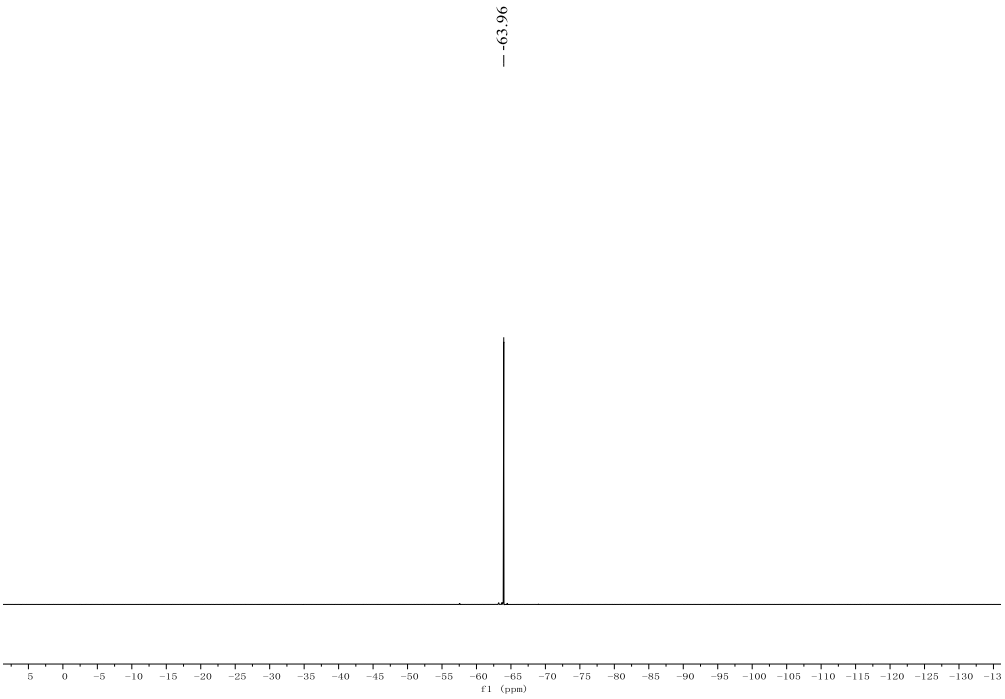
HRMS (APCI) m/z calcd for $C_{15}H_{12}F_3S$ $[M+H]^+$: 281.0612, found: 281.0603.

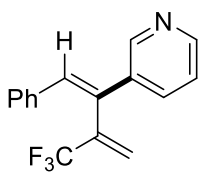









-63.96
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -13
f1 (ppm)



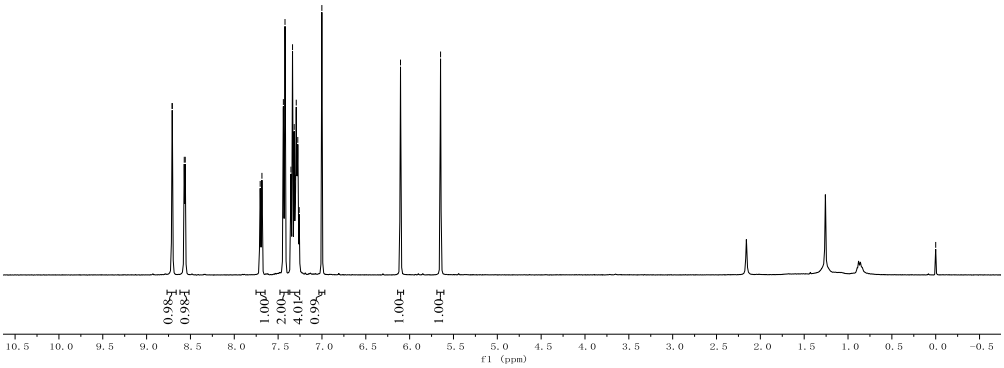
(*Z*)-3-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)pyridine (**3l**): Colorless oil, yield = 88% (using ethyl acetate/petroleum ether = 1:5 as eluent).

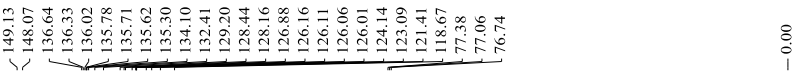
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.66 (m, 1H), 8.56 (d, *J* = 4.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 – 7.25 (m, 4H), 7.00 (s, 1H), 6.10 (s, 1H), 5.65 (s, 1H).

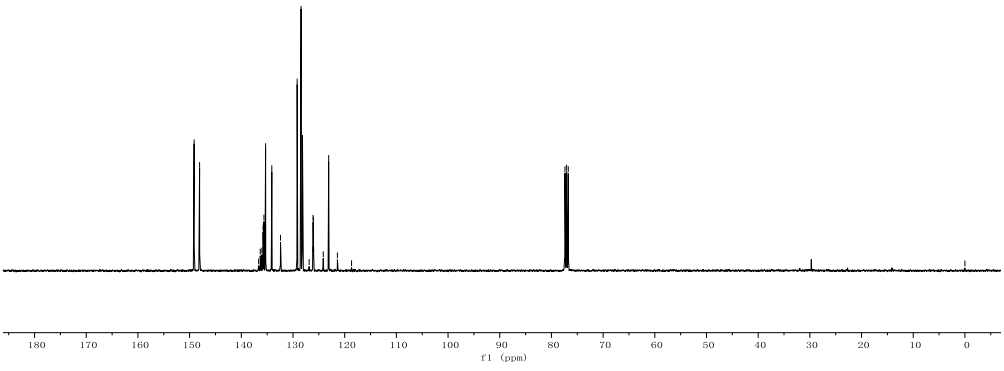
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.98.

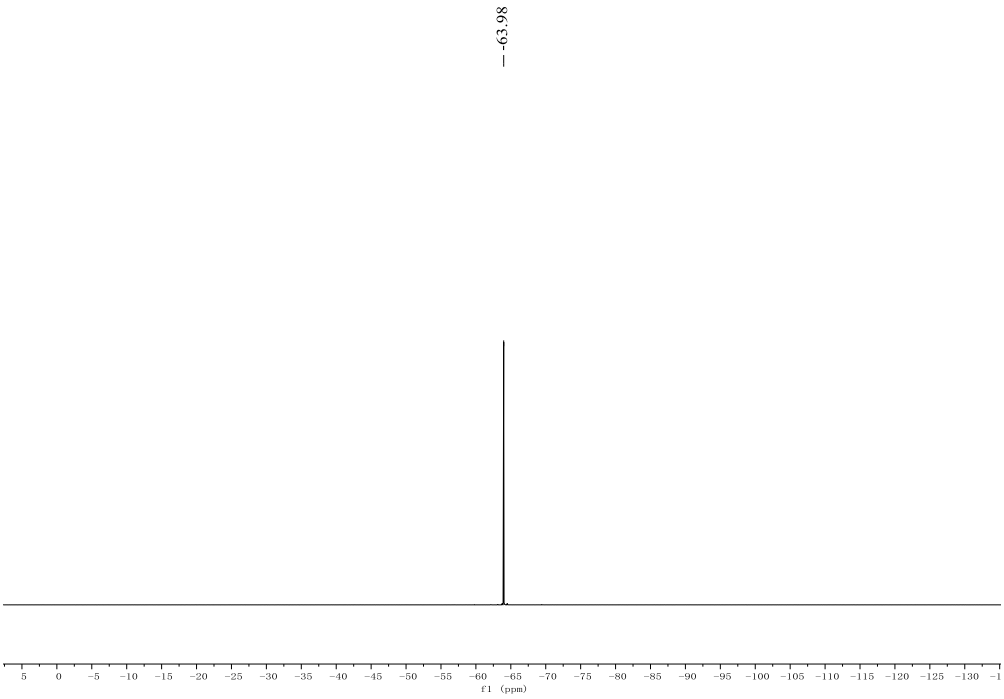
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.13, 148.07, 136.18 (q, *J* = 31.2 Hz), 135.78, 135.62, 135.30, 134.10, 132.41, 129.20, 128.44, 128.16, 126.09 (q, *J* = 5.0 Hz), 123.09, 122.78 (q, *J* = 276.3 Hz).

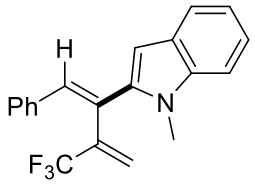
HRMS (ESI) m/z calcd for $C_{16}H_{13}F_3N$ $[M+H]^+$: 276.1000, found: 276.1001.








-63.98
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -1
f1 (ppm)



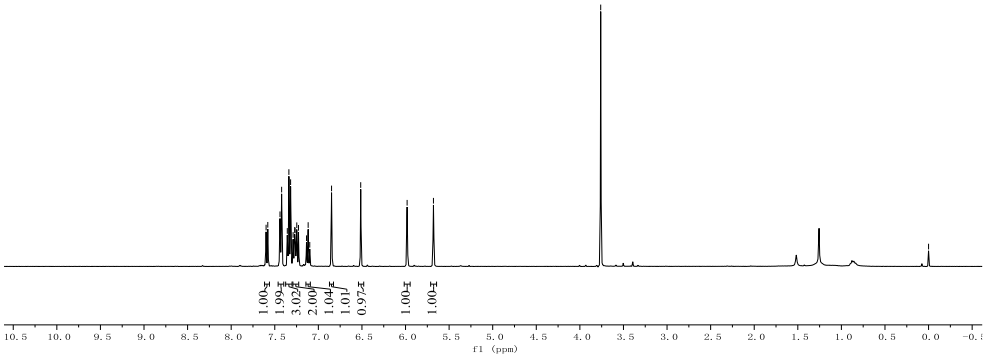
(*E*)-1-methyl-2-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)-1*H*-indole (**3m**): Pale red oil, yield = 45% (isolated with thin layer chromatography and using ethyl acetate/petroleum ether = 1:50 as eluent).

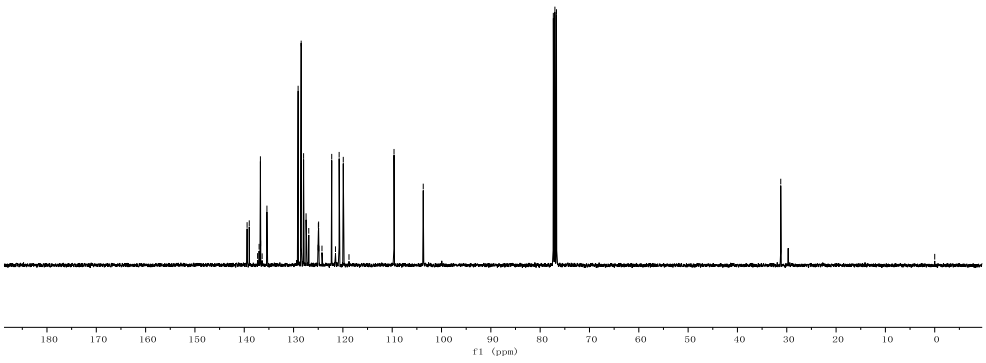
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 2H), 7.34 (t, *J* = 7.6 Hz, 3H), 7.29 – 7.23 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 6.51 (s, 1H), 5.98 (s, 1H), 5.68 (s, 1H).

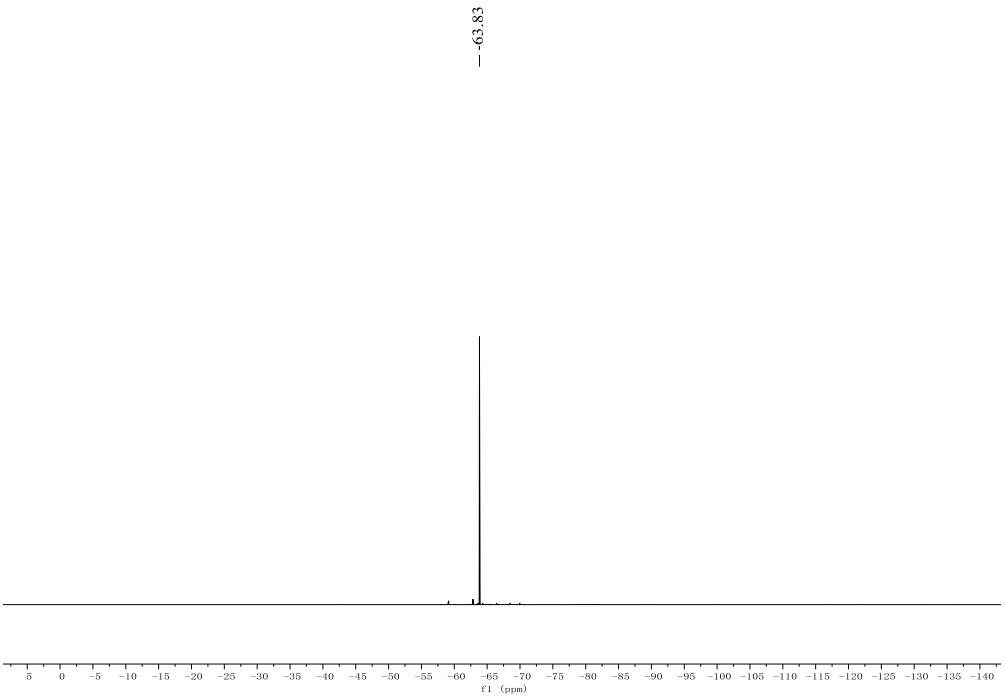
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.83.

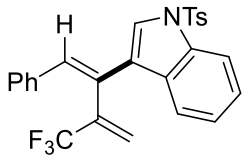
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.42, 138.98, 136.72, 135.40, 134.34 (q, *J* = 31.0 Hz), 129.08, 128.46, 127.97, 127.46, 126.92, 124.95 (q, *J* = 4.9 Hz), 122.87 (q, *J* = 276.4 Hz), 122.26, 120.76, 119.92, 109.63, 103.71, 31.22.

HRMS (ESI) m/z calcd for $C_{20}H_{17}F_3N$ $[M+H]^+$: 328.1313, found: 328.1308.






-63.83
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)



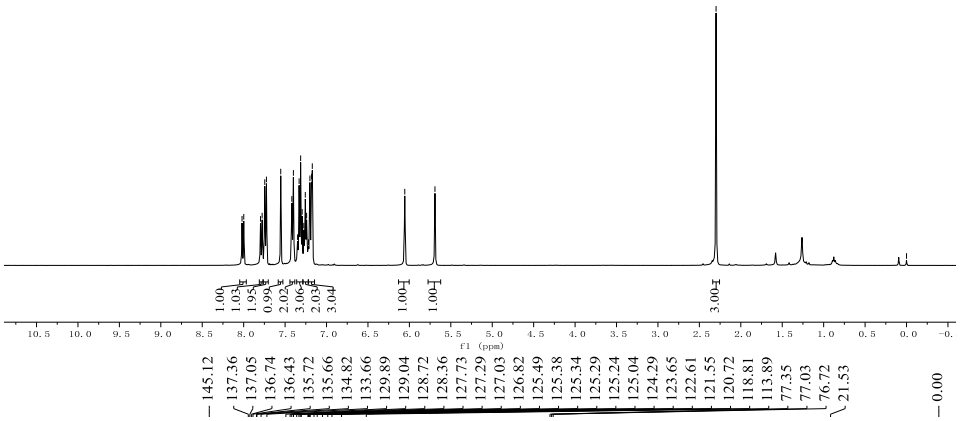
(*Z*)-3-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)-1-tosyl-1*H*-indole (**3n**): White solid, yield = 83% (using ethyl acetate/petroleum ether = 1:50 as eluent).

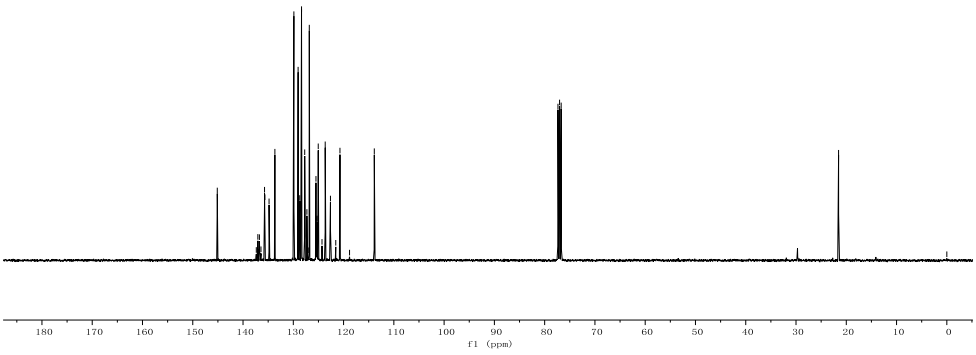
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.55 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.26 (t, *J* = 6.8 Hz, 2H), 7.22 – 7.14 (m, 3H), 6.06 (s, 1H), 5.69 (s, 1H), 2.30 (s, 3H).

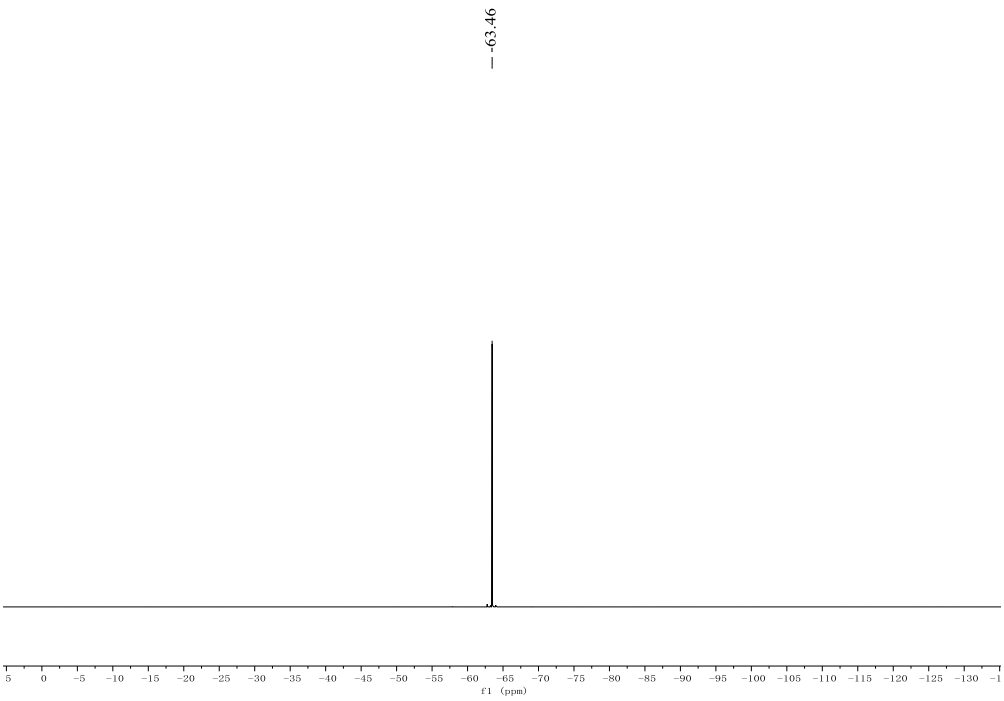
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.46.

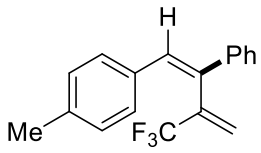
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.12, 136.90 (q, *J* = 31.1 Hz), 135.72, 135.66, 134.82, 133.66, 129.89, 129.04, 128.72, 128.36, 127.73, 127.29, 126.82, 125.49, 125.31 (q, *J* = 4.8 Hz), 125.04, 123.65, 122.92 (q, *J* = 276.6 Hz), 122.61, 120.72, 113.89, 21.53.

HRMS (ESI) m/z calcd for $C_{26}H_{21}F_3NO_2S$ $[M+H]^+$: 468.1245, found: 468.1249.






-63.46
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -1
f1 (ppm)



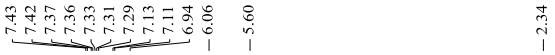
(*Z*)-1-methyl-4-(2-phenyl-3-(trifluoromethyl)buta-1,3-dien-1-yl)benzene (**3o**): Colorless oil, yield = 88% (isolated with preparative thin layer chromatography and using hexane as eluent).

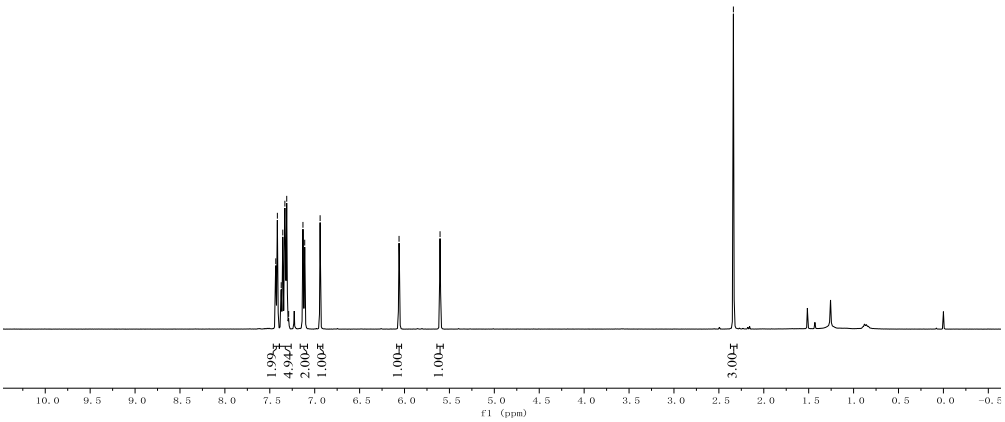
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.26 (m, 5H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.94 (s, 1H), 6.06 (s, 1H), 5.60 (s, 1H), 2.34 (s, 3H).

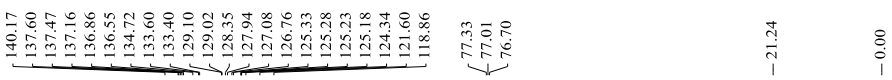
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.85.

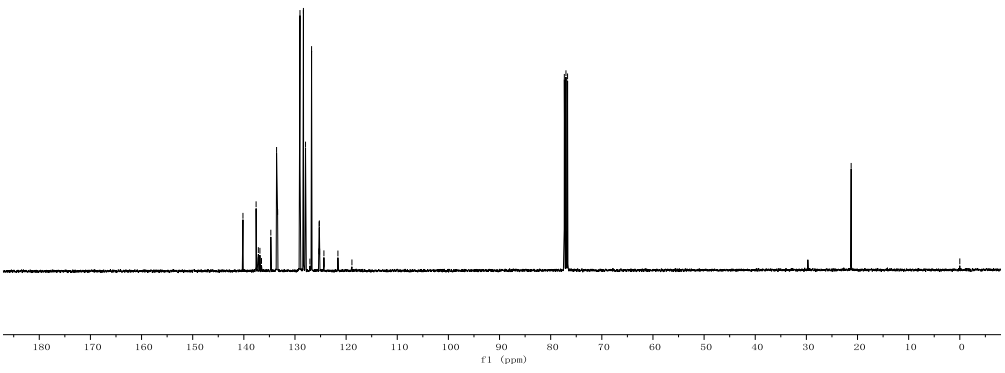
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.17, 137.60, 137.01 (q, *J* = 30.8 Hz), 134.72, 133.60, 133.40, 129.10, 129.02, 128.35, 127.94, 126.76, 125.25 (q, *J* = 5.0 Hz), 122.97 (q, *J* = 275.4 Hz), 21.24.

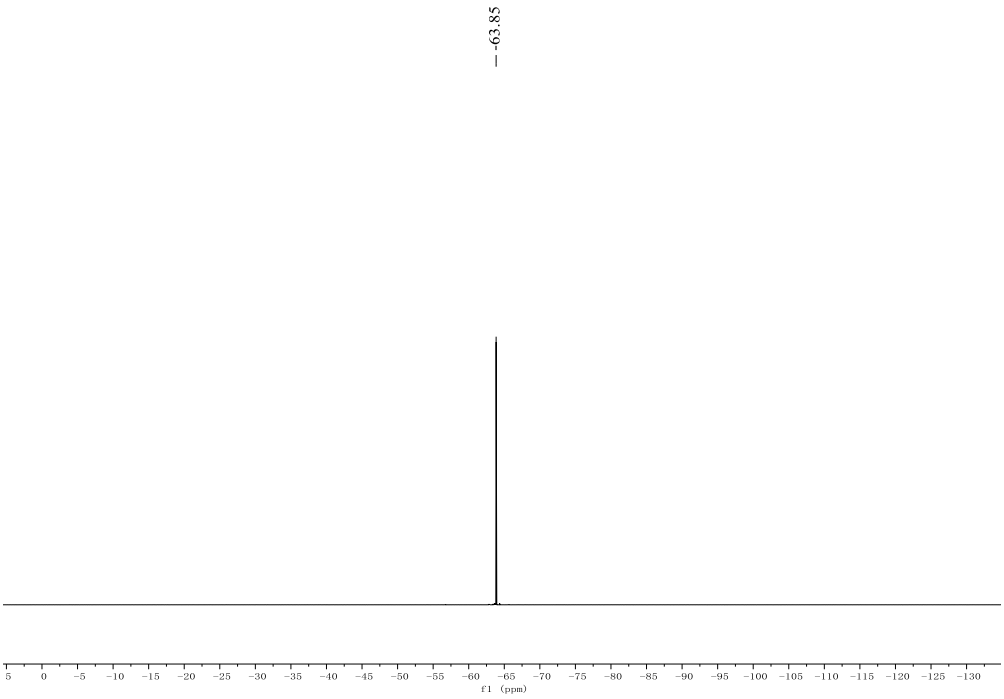
HRMS (EI) m/z calcd for $C_{18}H_{15}F_3$ $[M]^+$: 288.1120, found: 288.1115.

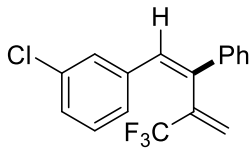









-63.85
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)



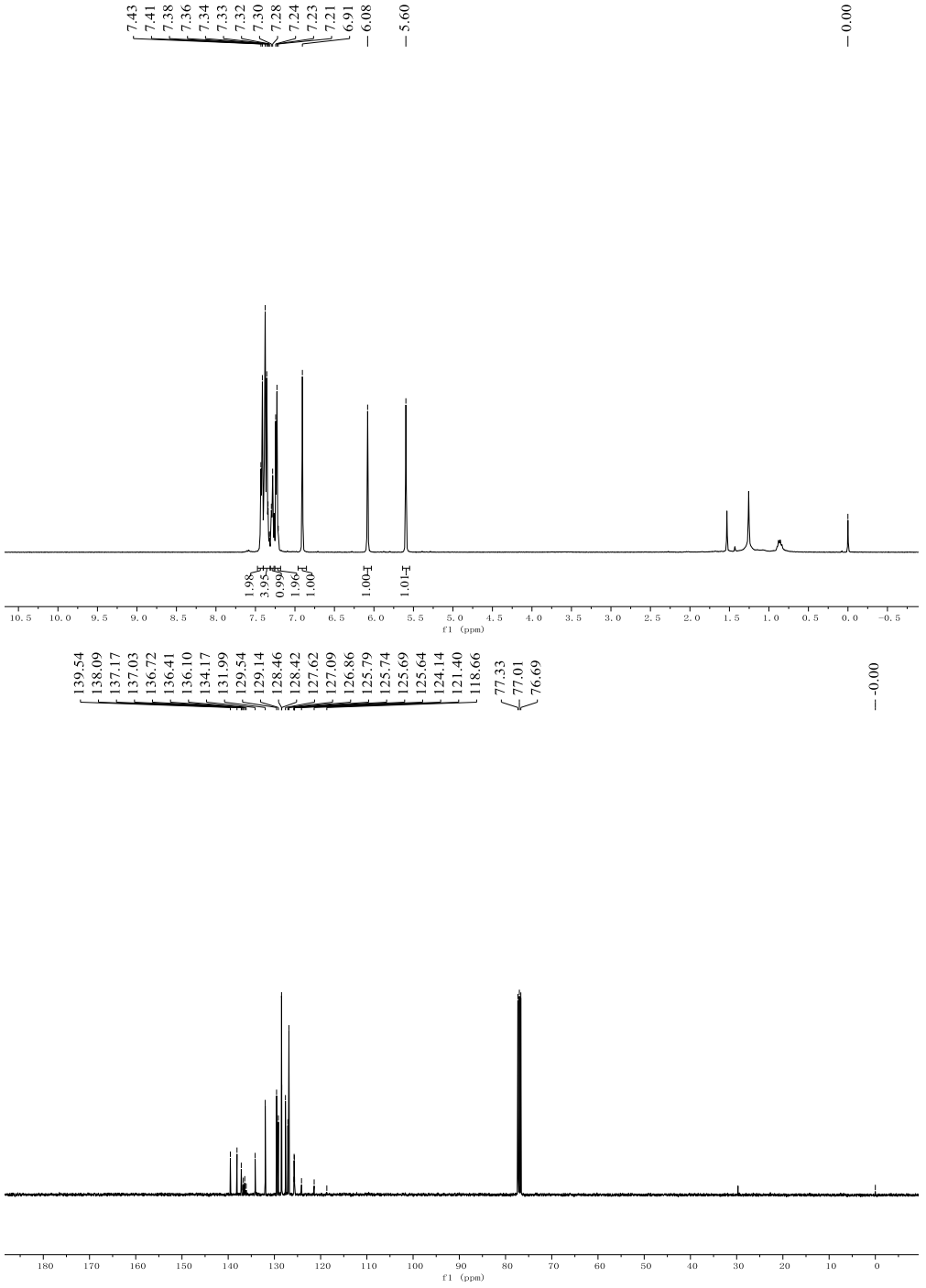
(*Z*)-1-chloro-3-(2-phenyl-3-(trifluoromethyl)buta-1,3-dien-1-yl)benzene (**3p**): Colorless oil, yield = 82% (isolated with preparative thin layer chromatography and using hexane as eluent).

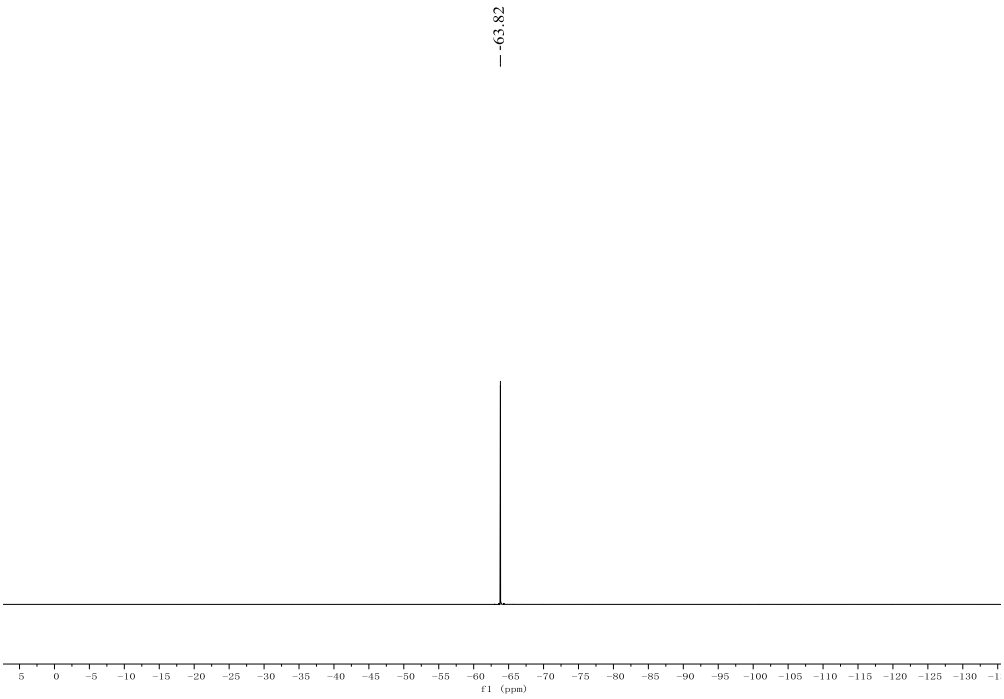
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.29 (d, *J* = 6.4 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.91 (s, 1H), 6.08 (s, 1H), 5.60 (s, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.82.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.54, 138.09, 137.17, 136.57 (q, *J* = 31.1 Hz), 134.17, 131.99, 129.54, 129.14, 128.46, 128.42, 127.62, 127.09, 126.86, 125.72 (q, *J* = 4.9 Hz), 122.77 (q, *J* = 275.3 Hz).

HRMS (EI) m/z calcd for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0574, found: 308.0568.




-63.82
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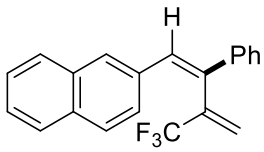
f1 (ppm)



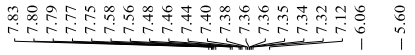
(*Z*)-2-(2-phenyl-3-(trifluoromethyl)buta-1,3-dien-1-yl)naphthalene (**3q**): White solid, yield = 82% (isolated with preparative thin layer chromatography and using hexane as eluent).

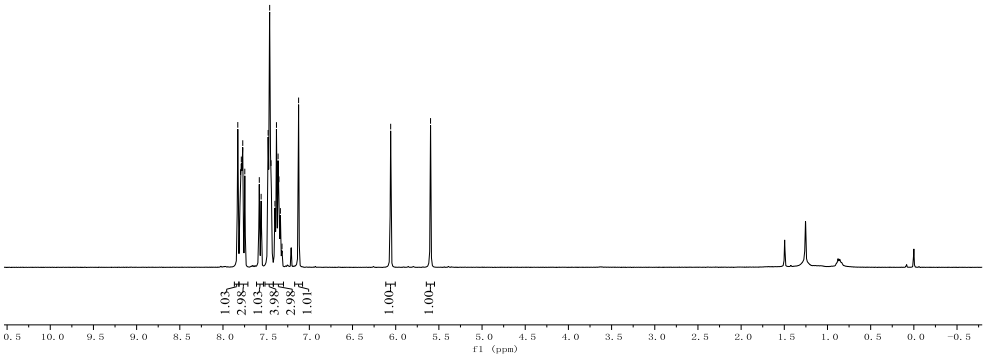
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.81 – 7.71 (m, 3H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.42 – 7.30 (m, 3H), 7.12 (s, 1H), 6.06 (s, 1H), 5.60 (s, 1H).

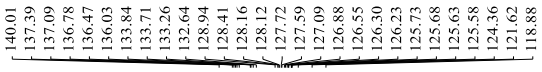
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.56.

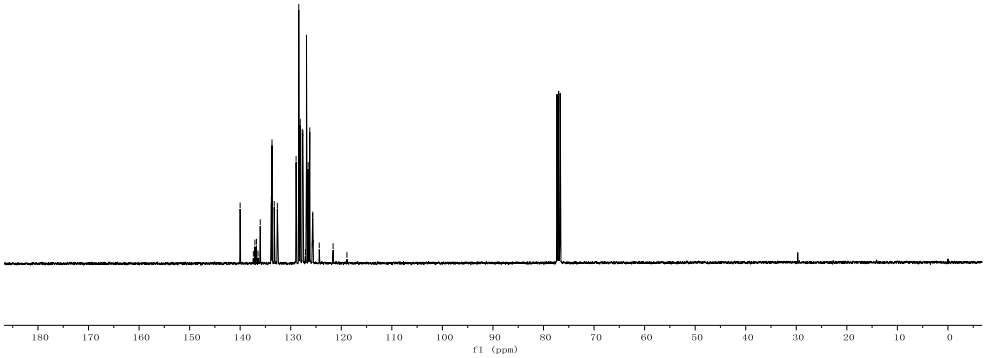
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.01, 136.93 (q, *J* = 31.0 Hz), 136.03, 133.84, 133.71, 133.26, 132.64, 128.94, 128.41, 128.16, 128.12, 127.72, 127.59, 126.88, 126.55, 126.30, 126.23, 125.65 (q, *J* = 4.9 Hz), 122.99 (q, *J* = 275.5 Hz).

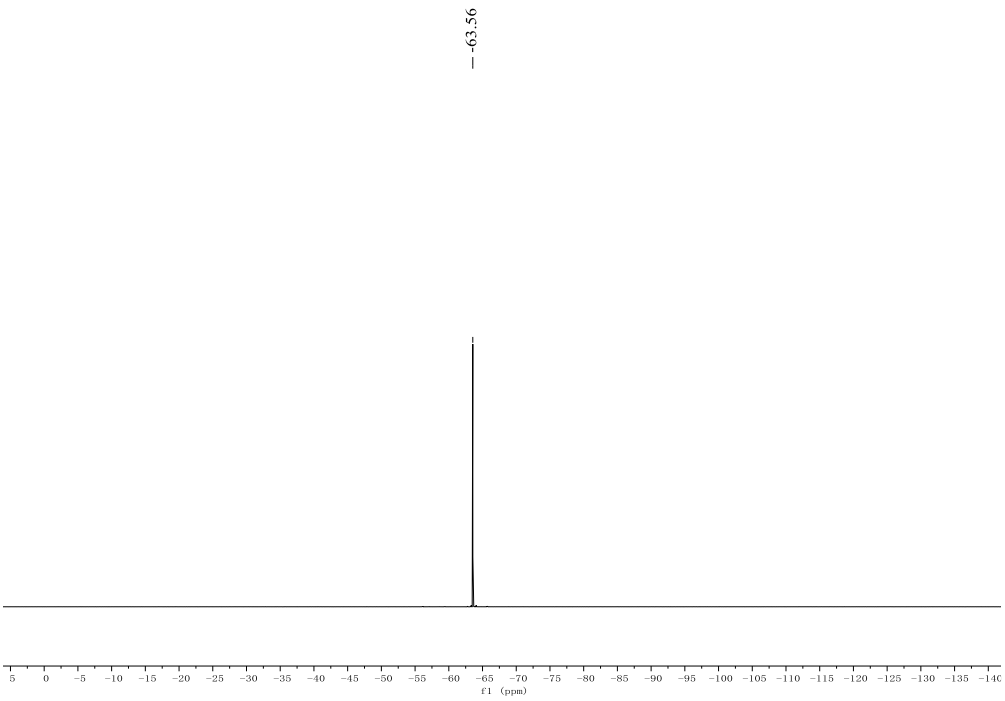
HRMS (EI) m/z calcd for $C_{21}H_{15}F_3$ $[M]^+$: 324.1120, found: 324.1114.

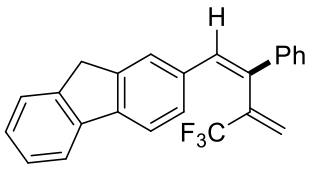









-63.56
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)



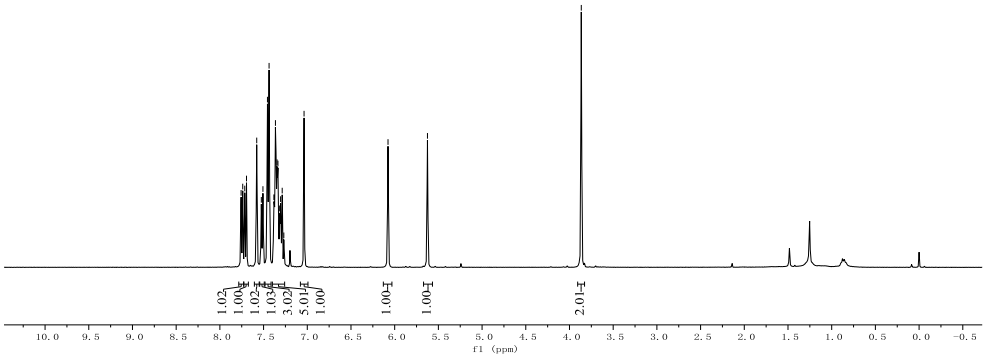
(*Z*)-2-(2-phenyl-3-(trifluoromethyl)buta-1,3-dien-1-yl)-9*H*-fluorene (**3r**): White solid, yield = 80% (isolated with preparative thin layer chromatography and using hexane as eluent).

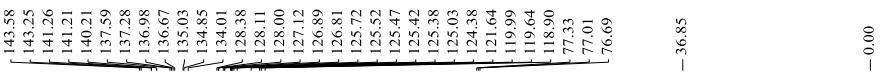
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.58 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 3H), 7.40 – 7.26 (m, 5H), 7.04 (s, 1H), 6.08 (s, 1H), 5.62 (s, 1H), 3.86 (s, 2H).

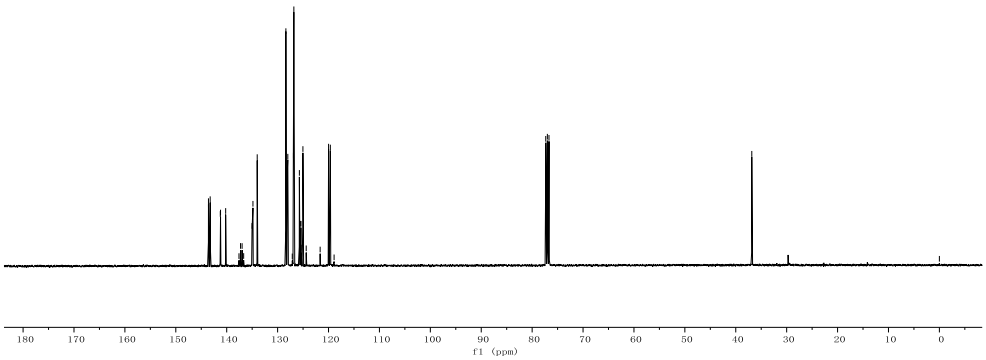
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.59.

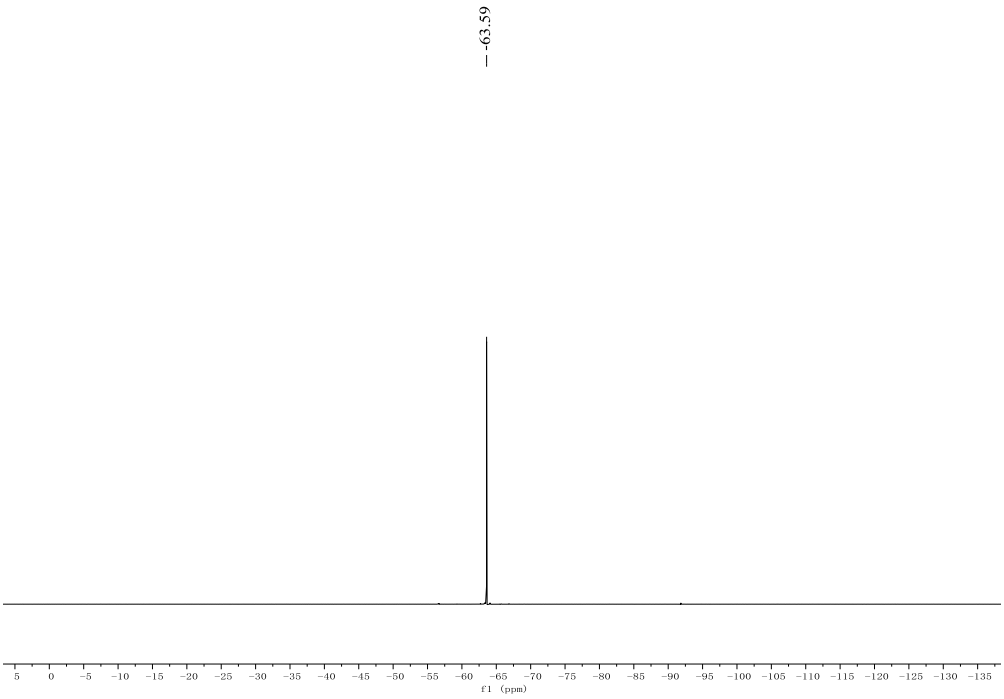
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.58, 143.25, 141.26, 141.21, 140.21, 137.13 (q, *J* = 30.9 Hz), 135.03, 134.85, 134.01, 128.38, 128.11, 128.00, 126.89, 126.81, 125.72, 125.45 (q, *J* = 4.9 Hz), 125.03, 123.01 (q, *J* = 275.5 Hz), 119.99, 119.64, 36.85.

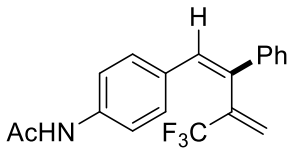
HRMS (EI) m/z calcd for $C_{24}H_{17}F_3$ $[M]^+$: 362.1277, found: 362.1270.








-63.59
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)



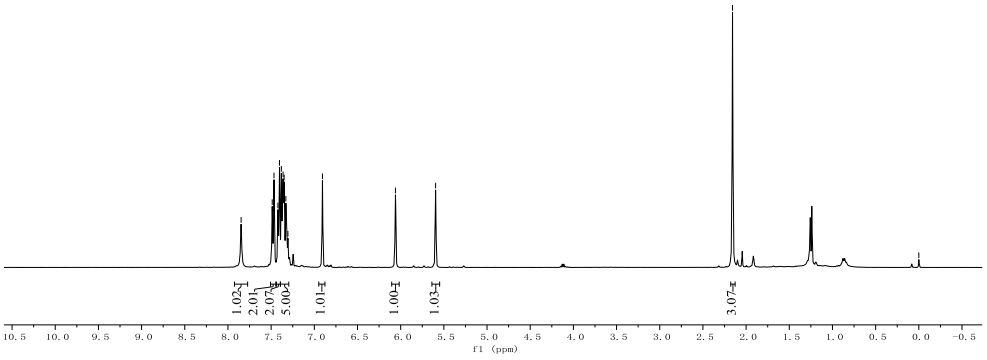
(*Z*)-*N*-(4-(2-phenyl-3-(trifluoromethyl)buta-1,3-dien-1-yl)phenyl)acetamide (**3s**): White solid, yield = 79% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:1 as eluent).

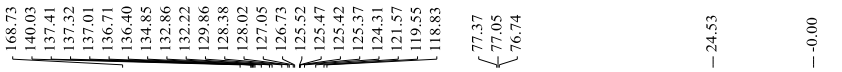
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.30 (m, 5H), 6.91 (s, 1H), 6.06 (s, 1H), 5.60 (s, 1H), 2.16 (s, 3H).

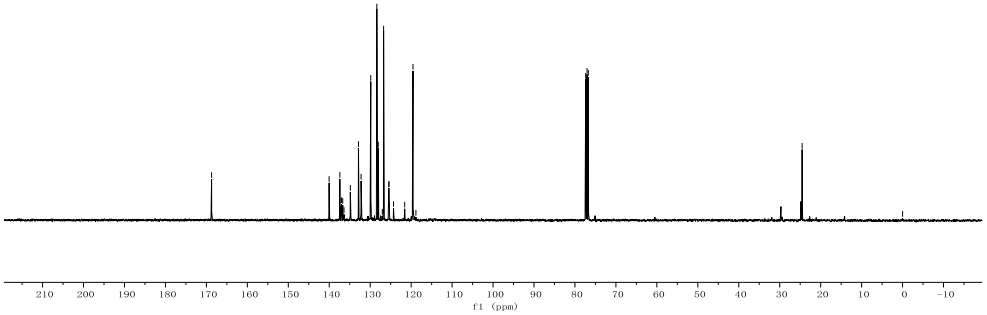
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.85.

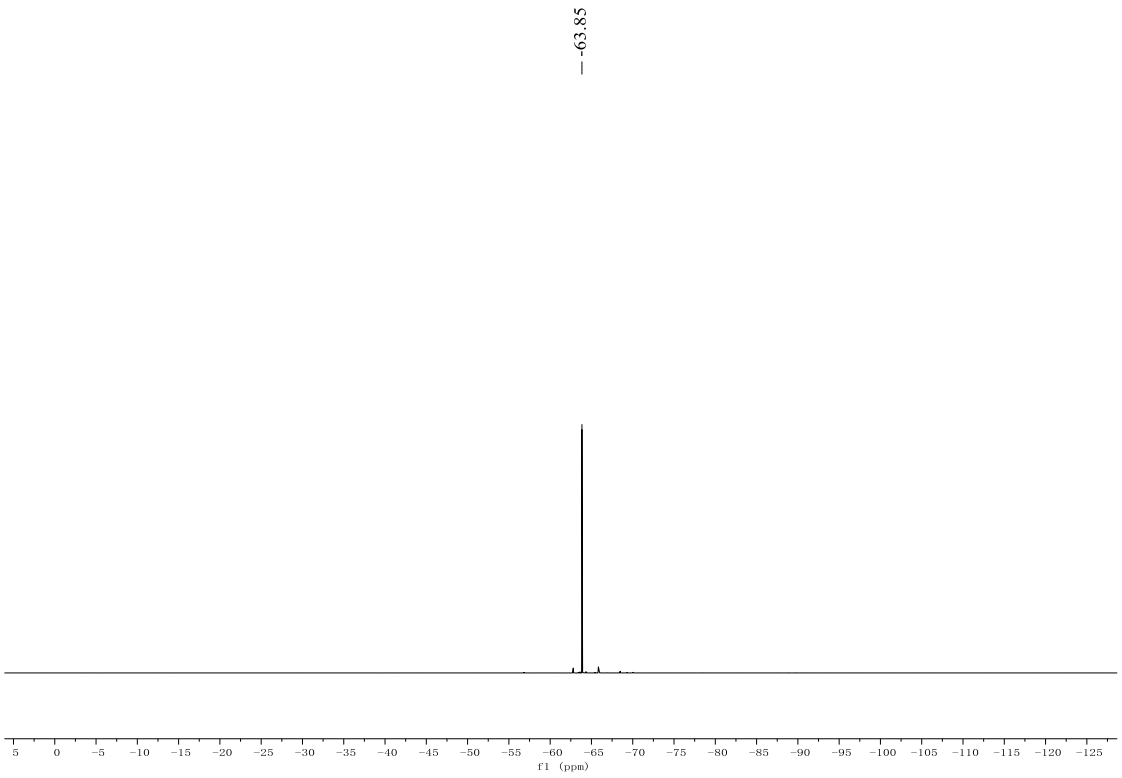
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.73, 140.03, 137.41, 136.86 (q, *J* = 31.0 Hz), 134.85, 132.86, 132.22, 129.86, 128.38, 128.02, 126.73, 125.44 (q, *J* = 4.9 Hz), 122.94 (q, *J* = 275.4 Hz), 119.55, 24.53.

HRMS (ESI) m/z calcd for $C_{19}H_{17}F_3NO$ $[M+H]^+$: 332.1262, found: 332.1263.








-63.85
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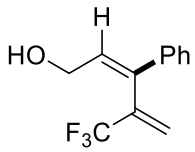
f1 (ppm)



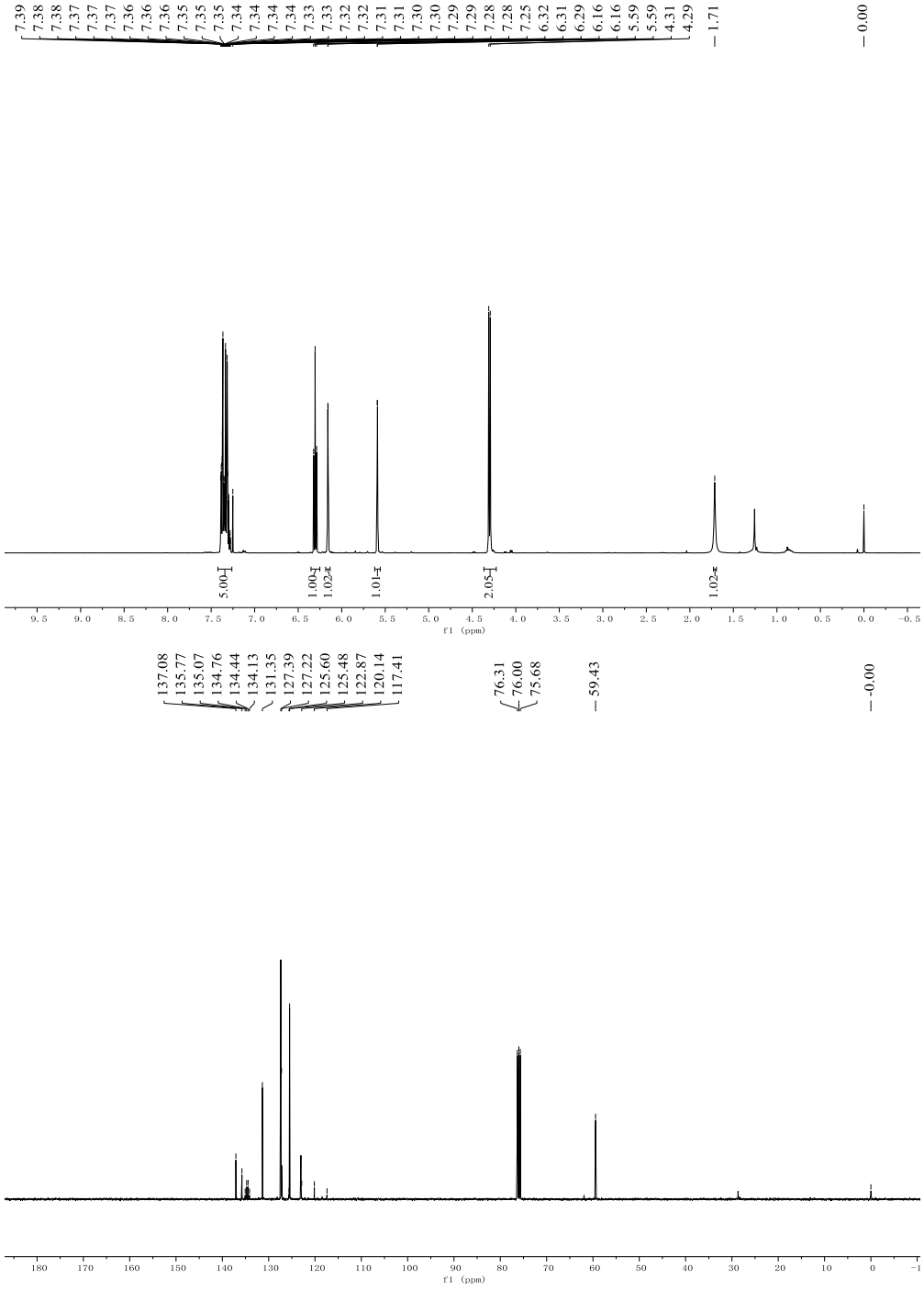
(*Z*)-3-phenyl-4-(trifluoromethyl)penta-2,4-dien-1-ol (**3t**): Pale yellow oil, yield = 71% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:5 as eluent, at the same time, (*E*) -3-phenyl-4-(trifluoromethyl)penta-2,4-dien-1-ol **3t'** was obtained in 13% yield).

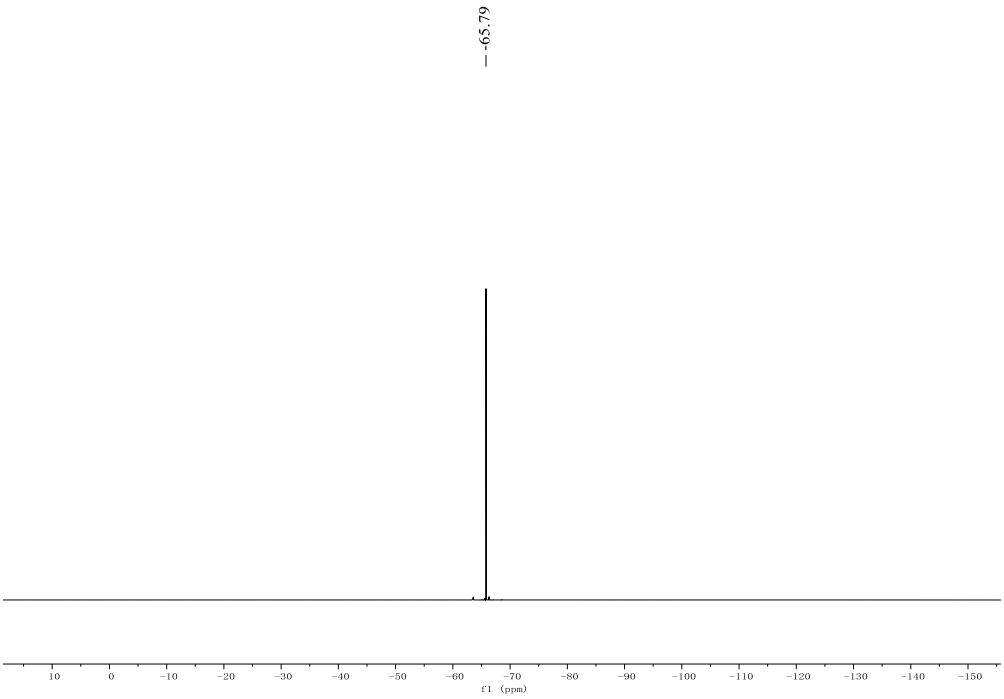
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.26 (m, 5H), 6.31 (t, *J* = 6.9 Hz, 1H), 6.16 (d, *J* = 1.3 Hz, 1H), 5.59 (d, *J* = 1.1 Hz, 1H), 4.30 (d, *J* = 6.9 Hz, 2H), 1.71 (s, 1H).

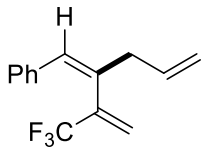
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.79.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.08, 135.77, 134.60 (q, *J* = 31.3 Hz), 131.35, 127.39, 127.22, 125.48, 123.06 (q, *J* = 5.1 Hz), 121.50 (d, *J* = 274.7 Hz), 59.43.

HRMS (ESI) m/z calcd for $C_{12}H_{12}F_3O$ $[M+H]^+$: 229.0840, found: 229.0853.




-65.79
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)



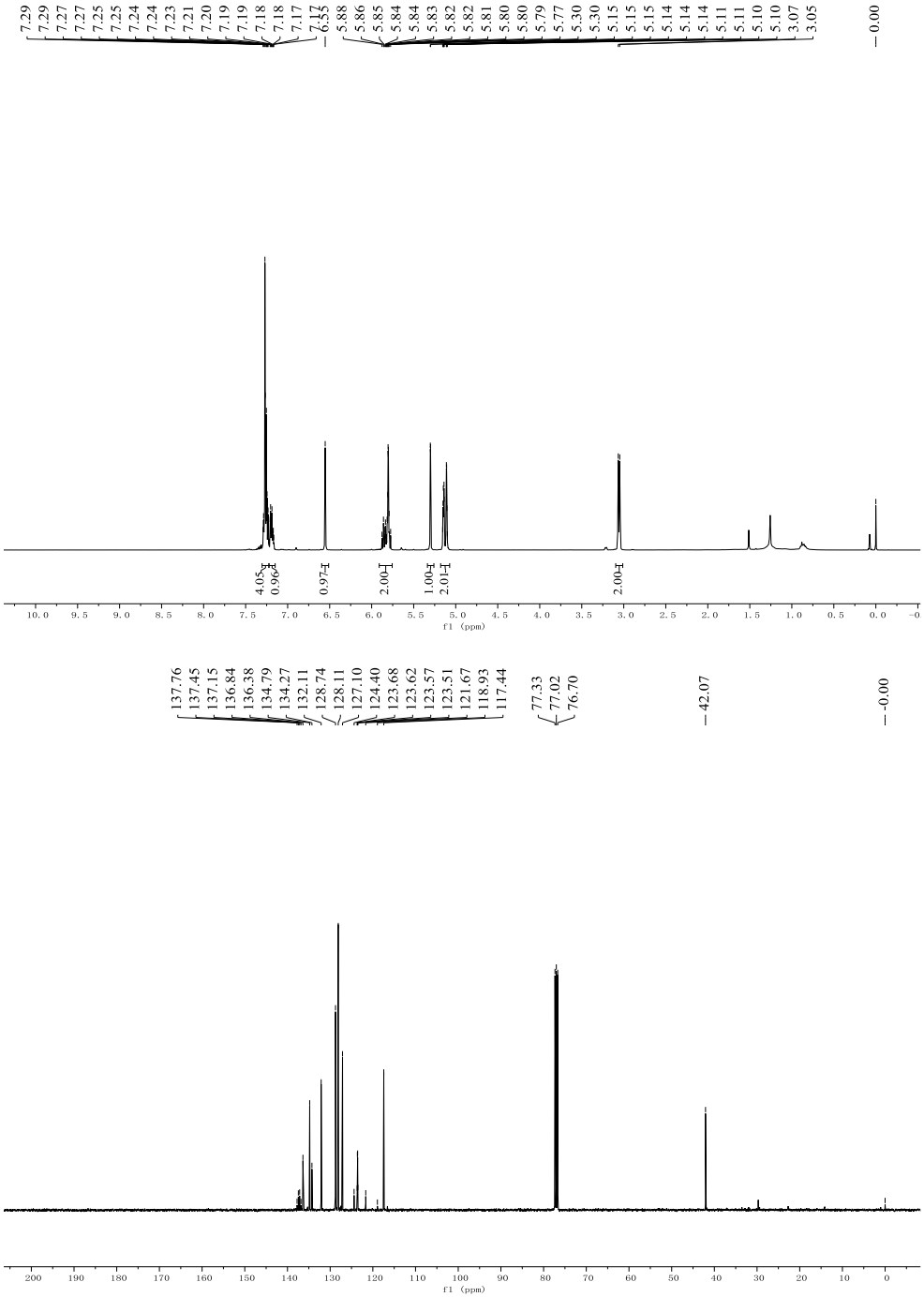
(*Z*)-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)benzene (**5a**): Colorless oil, yield = 90% (**5a**:**5a'** = 97:3, isolated with preparative thin layer chromatography and using hexane as eluent).

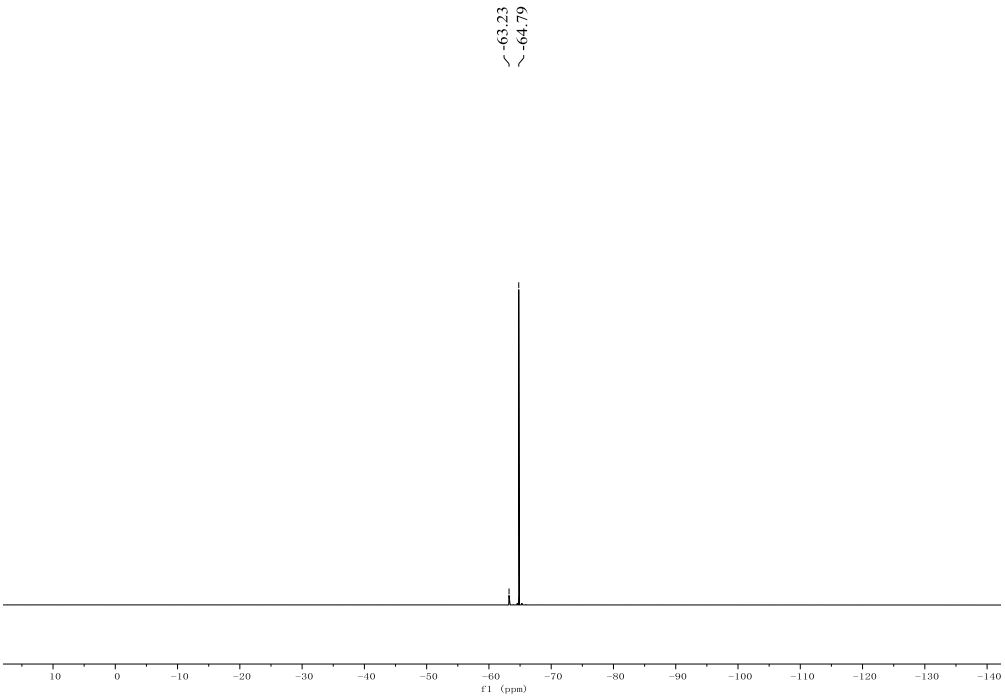
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 4H), 7.2 – 7.15 (m, 1H), 6.55 (s, 1H), 5.91 – 5.76 (m, 2H), 5.34 – 5.26 (m, 1H), 5.17 – 5.12 (m, 1H), 5.12 – 5.08 (m, 1H), 3.06 (d, *J* = 6.9 Hz, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.79.

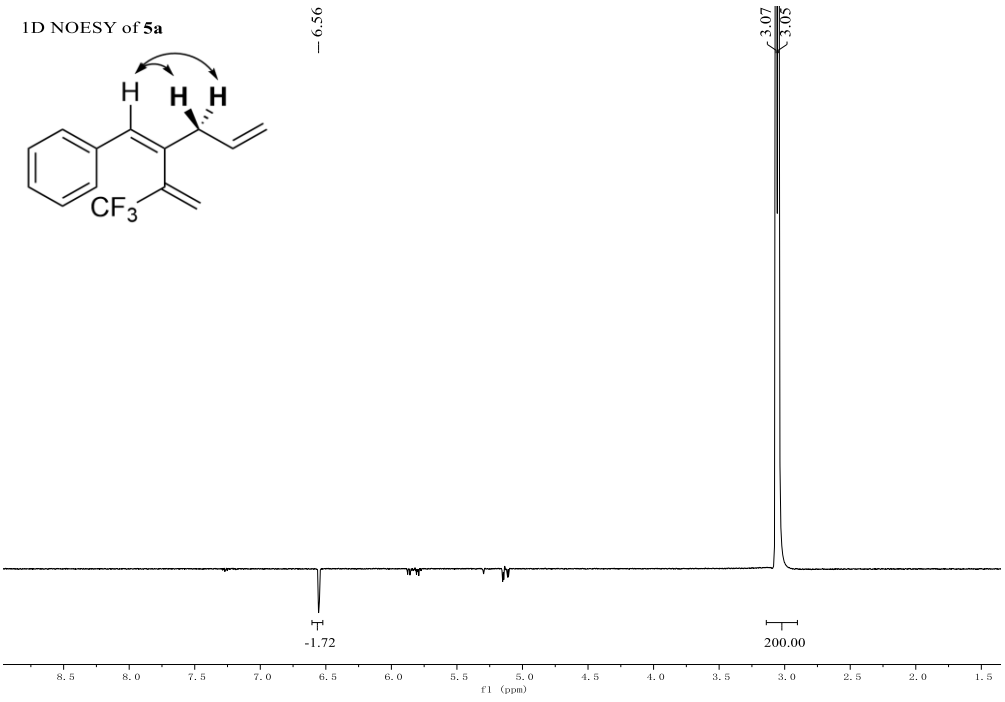
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.30 (q, *J* = 30.6 Hz), 136.38, 134.79, 134.27, 132.11, 128.74, 128.11, 127.10, 123.59 (q, *J* = 5.4 Hz), 123.03 (q, *J* = 276.0 Hz), 117.44, 42.07.

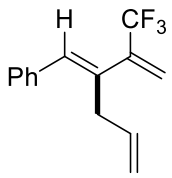
HRMS (EI) m/z calcd for $C_{14}H_{13}F_3$ $[M]^+$: 238.0964, found: 238.0962





1D NOESY of **5a**





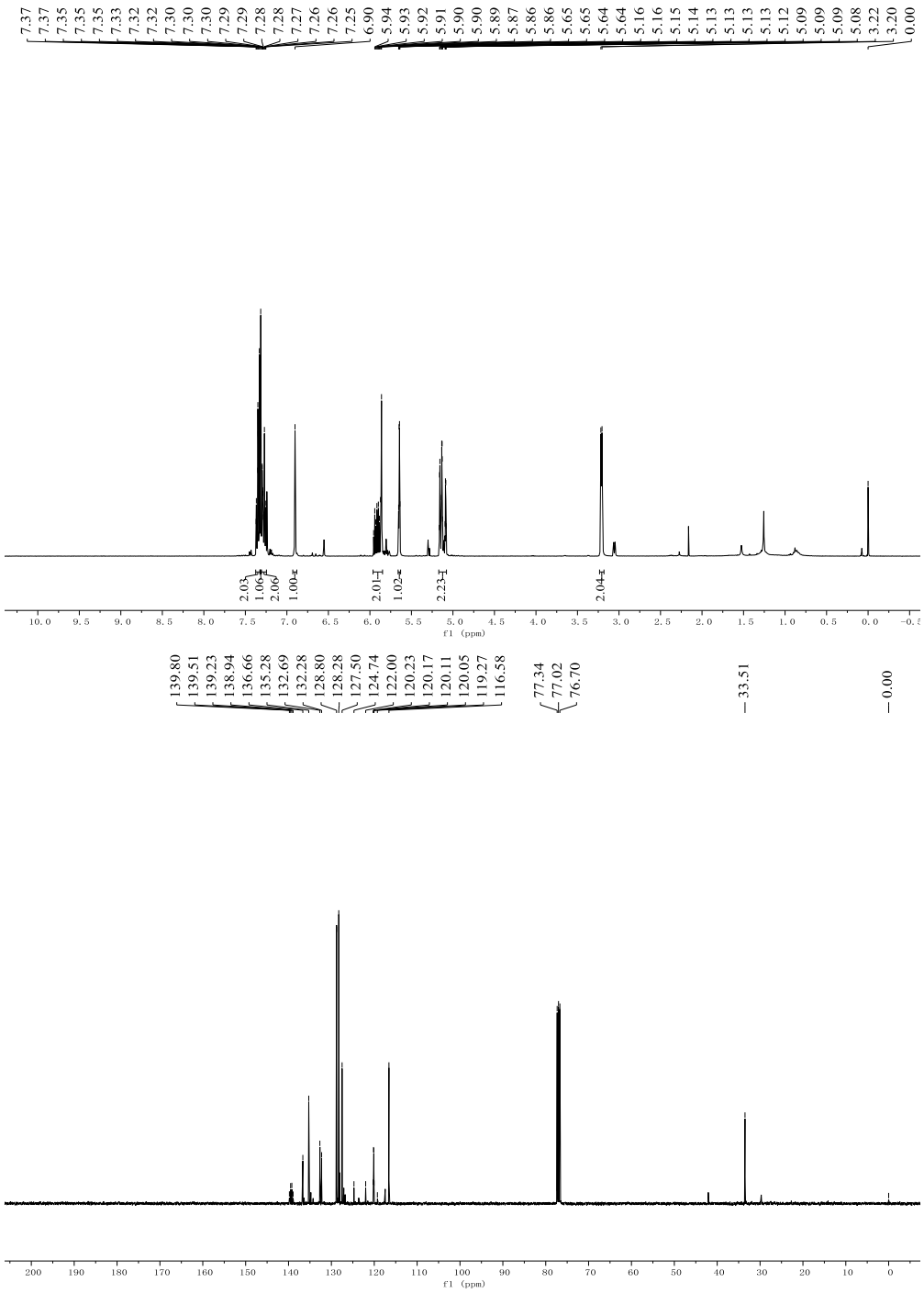
(*E*)-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)benzene (**5a'**): Colorless oil, yield = 82% (**5a'**:**5a** = 93:7, isolated with preparative thin layer chromatography and using hexane as eluent).

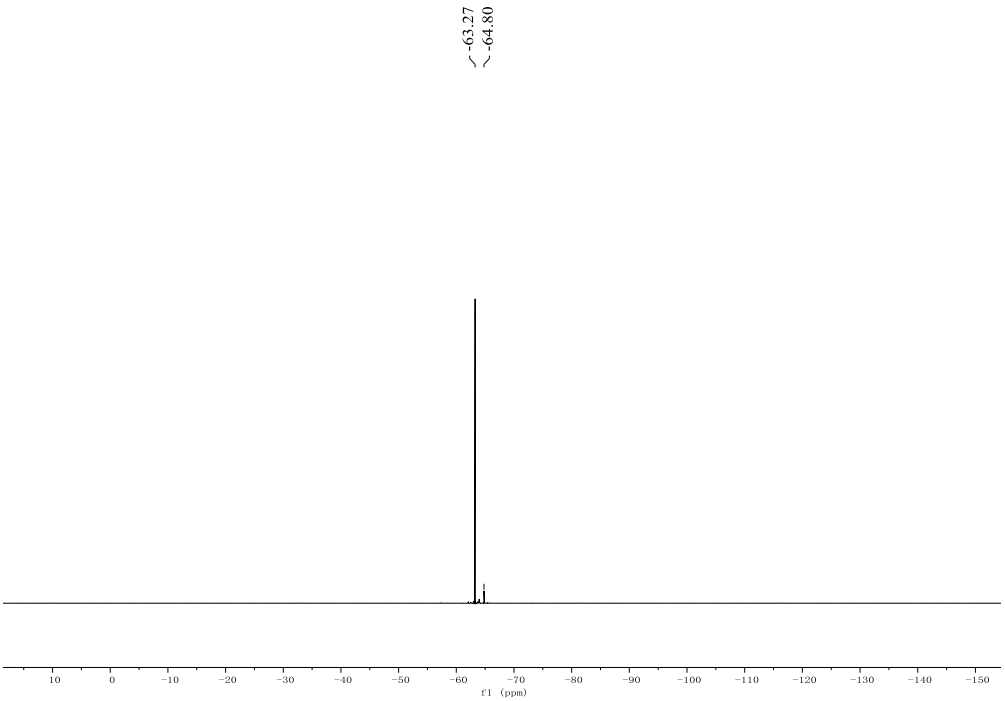
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.31 (m, 1H), 7.31 – 7.25 (m, 2H), 6.90 (s, 1H), 5.96 – 5.85 (m, 2H), 5.65 (q, *J* = 2.1 Hz, 1H), 5.17 – 5.08 (m, 2H), 3.21 (d, *J* = 5.5 Hz, 2H).

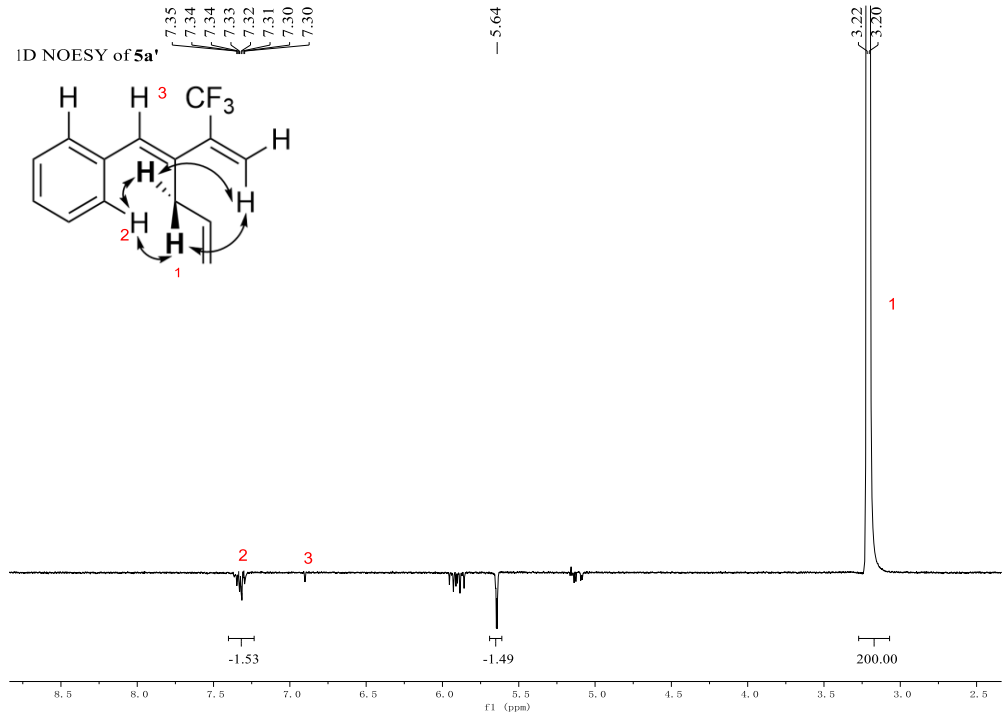
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.27.

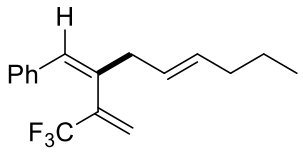
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.37 (q, *J* = 28.7 Hz), 136.66, 135.28, 132.69, 132.28, 128.80, 128.28, 127.50, 123.37 (q, *J* = 275.1 Hz), 120.14 (q, *J* = 6.0 Hz), 116.58, 33.51.

HRMS (EI) m/z calcd for $C_{14}H_{13}F_3$ $[M]^+$: 238.0964, found: 238.0959.




-63.27
-64.80
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


1D NOESY of 5a'
7.35
7.34
7.34
7.33
7.32
7.31
7.30
7.30
5.64
3.22
3.20
H
H
3
CF3
H
H
H
H
2
H
1
2
3
1
-1.53
-1.49
200.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)



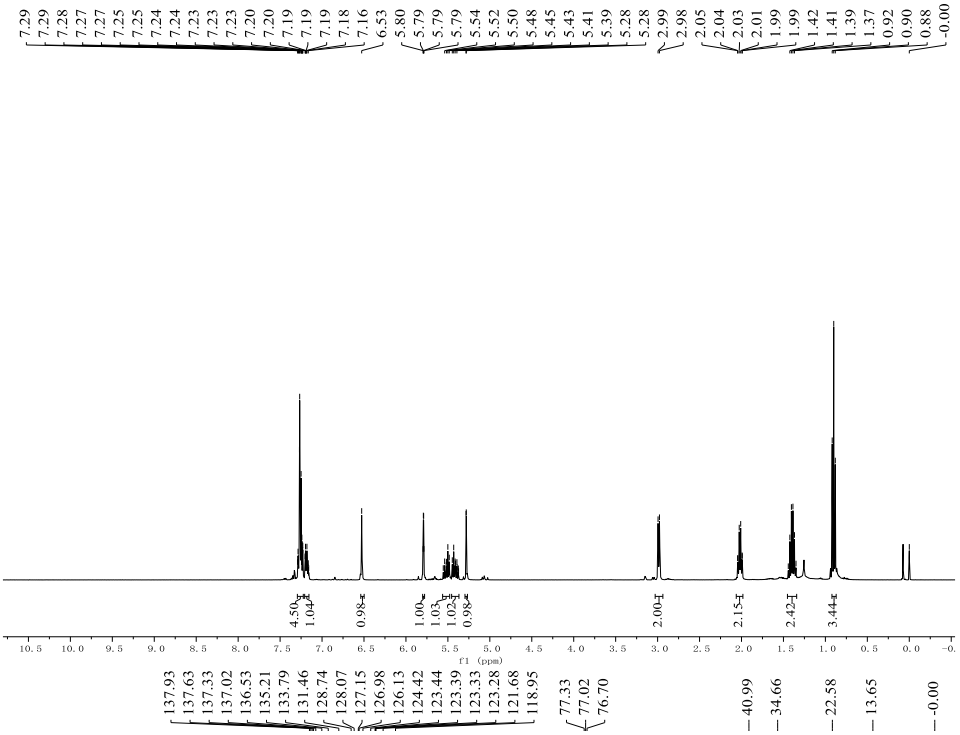
((1*Z*,4*E*)-2-(3,3,3-trifluoroprop-1-en-2-yl)octa-1,4-dien-1-yl)benzene (**5b**): Colorless oil, yield = 78% (**5b**:**5b'** = 96:4, isolated with preparative thin layer chromatography and using hexane as eluent).

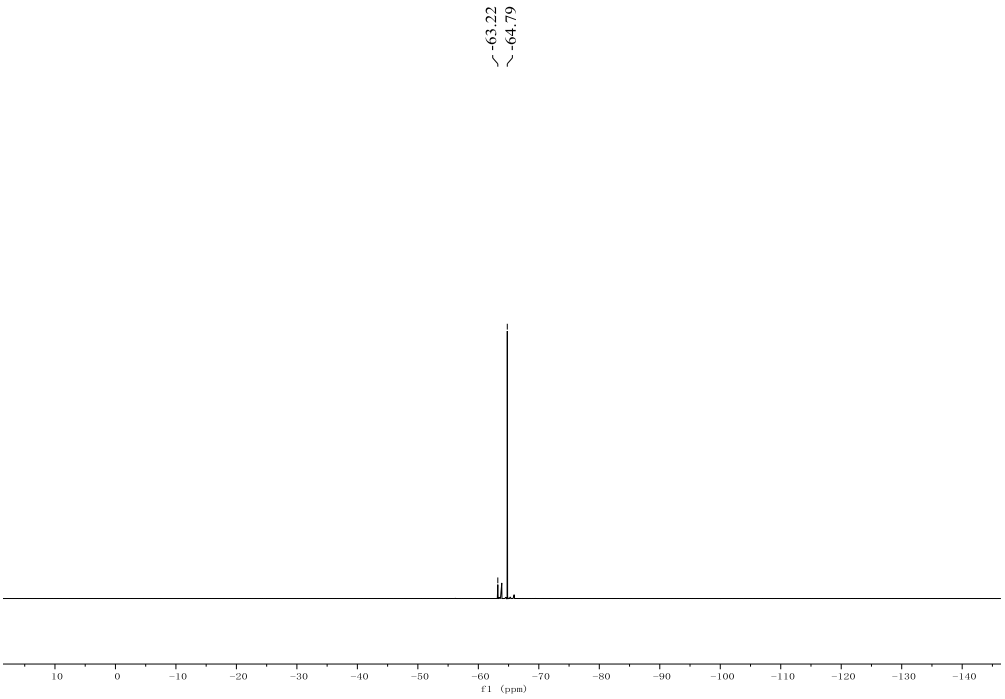
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 4H), 7.21 – 7.16 (m, 1H), 6.53 (s, 1H), 5.80 – 5.78 (m, 1H), 5.56 – 5.48 (m, 1H), 5.46 – 5.37 (m, 1H), 5.30 – 5.27 (m, 1H), 2.99 (d, *J* = 6.7 Hz, 2H), 2.06 – 1.98 (m, 2H), 1.40 (h, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

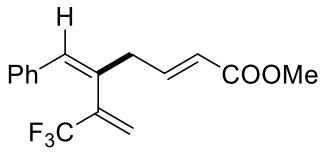
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.79.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.48 (q, *J* = 30.5 Hz), 136.53, 135.21, 133.79, 131.46, 128.74, 128.07, 126.98, 126.13, 123.36 (q, *J* = 5.4 Hz), 123.05 (q, *J* = 276.2 Hz), 40.99, 34.66, 22.58, 13.65.

HRMS (EI) m/z calcd for $C_{17}H_{19}F_3$ $[M]^+$: 280.1433, found: 280.1429.




-63.22
-64.79
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)



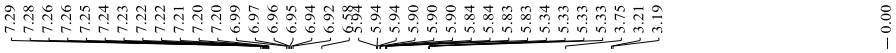
methyl (*E*)-5-((*Z*)-benzylidene)-6-(trifluoromethyl)hepta-2,6-dienoate (**5c**): Colorless oil, yield = 43% (**5c**:**5c'** = 83:17, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:50 as eluent).

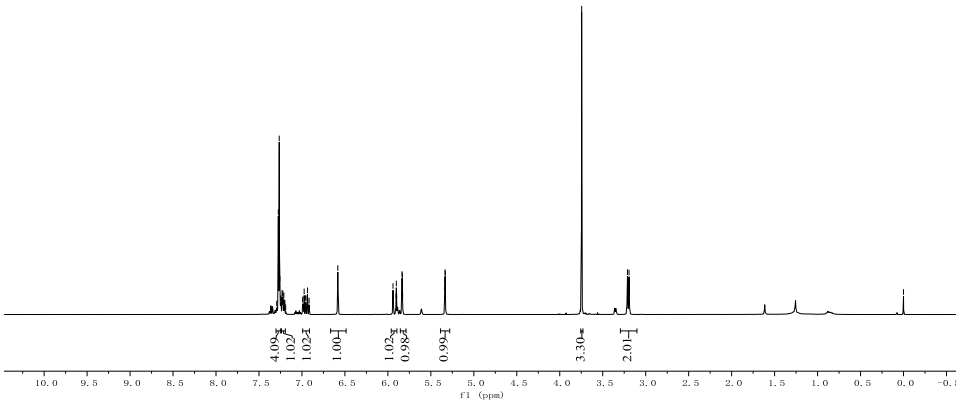
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 4H), 7.24 – 7.19 (m, 1H), 6.95 (dt, *J* = 15.6, 7.2 Hz, 1H), 6.58 (s, 1H), 5.92 (dt, *J* = 15.7, 1.4 Hz, 1H), 5.83 (d, *J* = 1.4 Hz, 1H), 5.39 – 5.28 (m, 1H), 3.75 (s, 3H), 3.20 (d, *J* = 7.3 Hz, 2H).

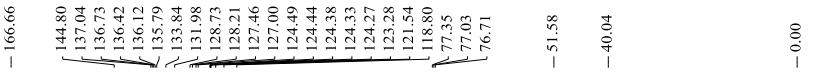
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.78.

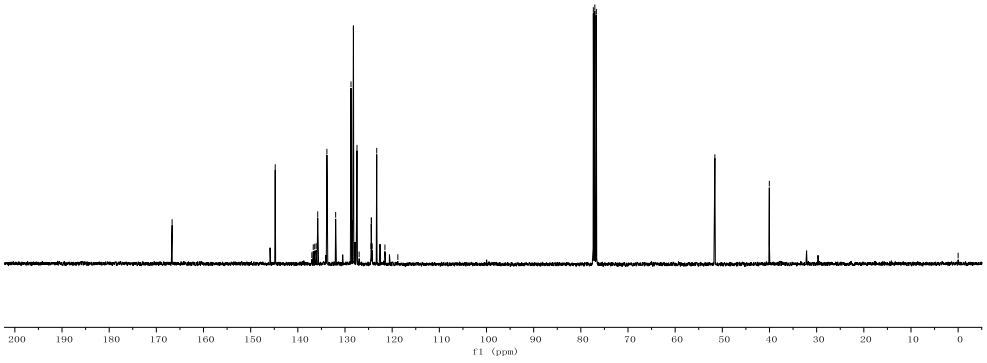
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.66, 144.80, 136.58 (q, *J* = 30.9 Hz), 135.79, 133.84, 131.98, 128.73, 128.21, 127.46, 124.41 (q, *J* = 5.4 Hz), 123.28, 122.90 (q, *J* = 276.1 Hz), 51.58, 40.04.

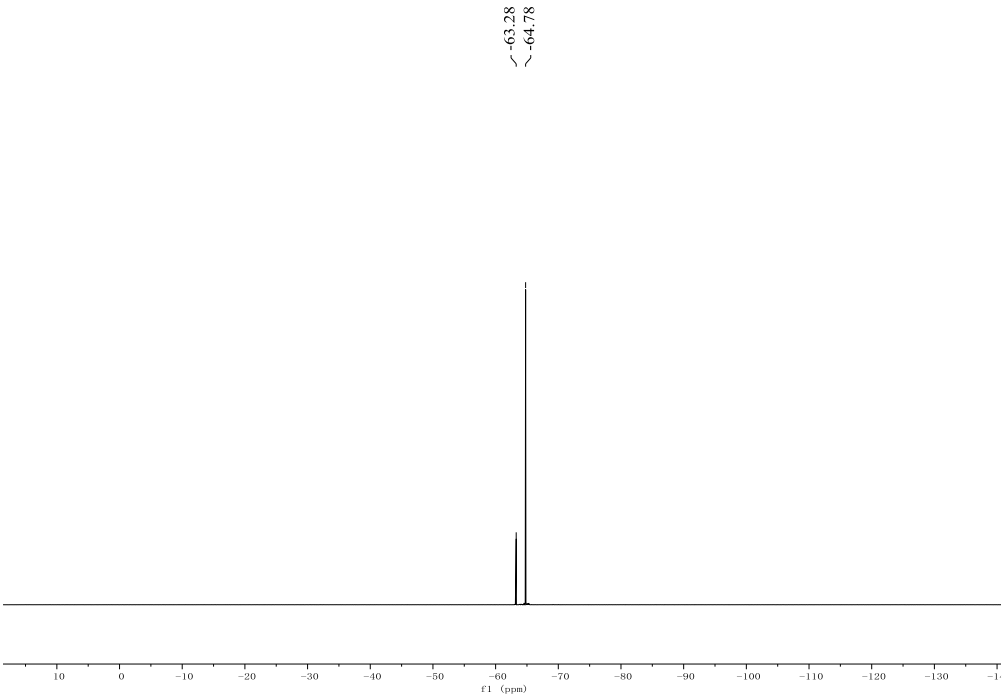
HRMS (ESI) m/z calcd for $C_{16}H_{15}F_3O_2Na$ $[M+Na]^+$: 319.0922, found: 319.0923.










-63.28
-64.78
10
0
-10
-20
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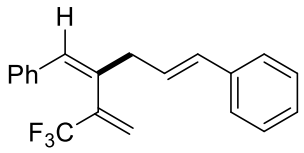
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
f1 (ppm)



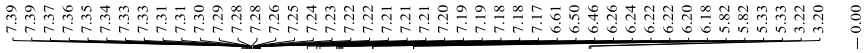
((1*Z*,4*E*)-2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-diene-1,5-diyl)dibenzene (**5d**): White solid, yield = 49% (**5d**:**5d'** = 90:10, isolated with preparative thin layer chromatography and using hexane as eluent).

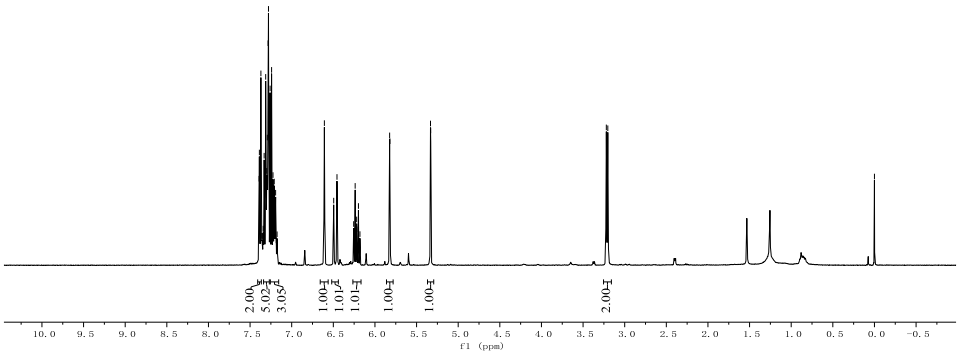
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.27 (m, 5H), 7.26 – 7.16 (m, 3H), 6.61 (s, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.7, 7.2 Hz, 1H), 5.82 (d, *J* = 1.3 Hz, 1H), 5.37 – 5.29 (m, 1H), 3.21 (d, *J* = 7.2 Hz, 2H).

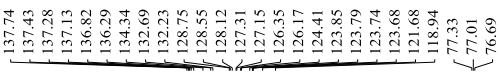
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.71.

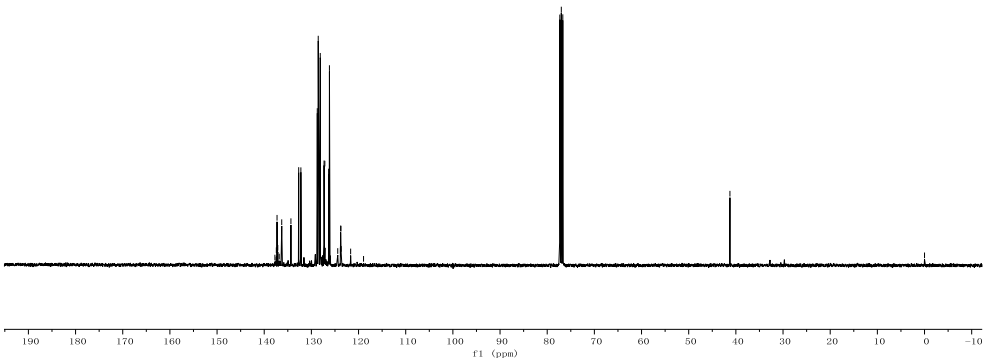
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.28, 137.28 (q, *J* = 30.8 Hz), 136.29, 134.34, 132.69, 132.23, 128.75, 128.55, 128.12, 127.31, 127.15, 126.35, 126.17, 123.77 (q, *J* = 5.4 Hz), 123.04 (q, *J* = 276.3 Hz), 41.26.

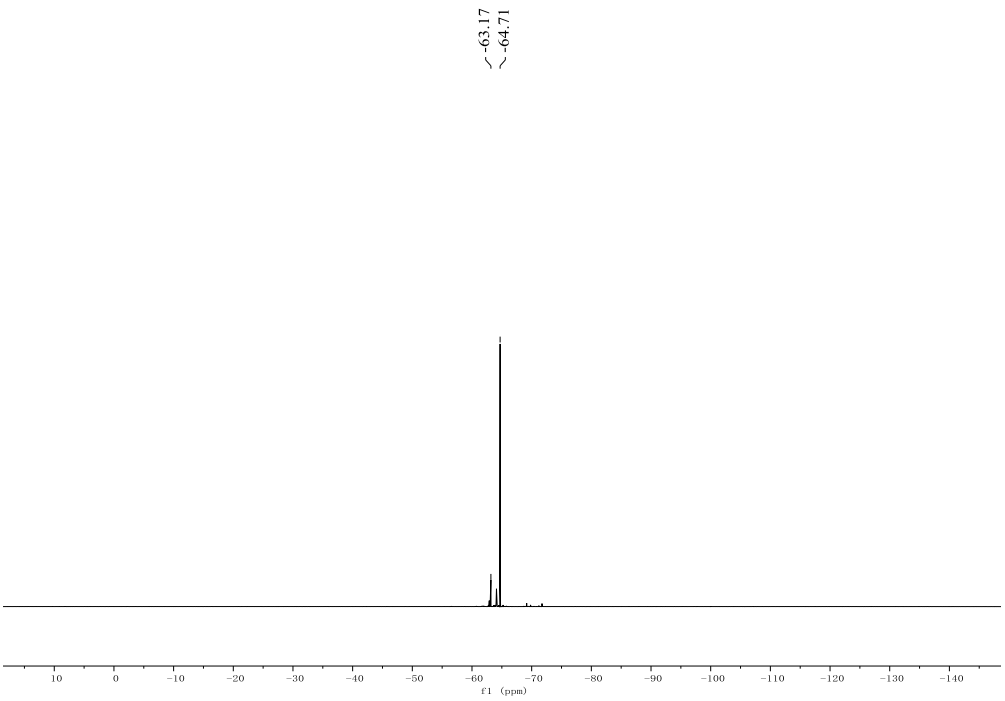
HRMS (EI) m/z calcd for $C_{20}H_{17}F_3$ $[M]^+$: 314.1277, found: 314.1273.










-63.17
-64.71
10
0
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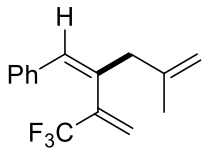
-90
-100
-110
-120
-130
-140
f1 (ppm)



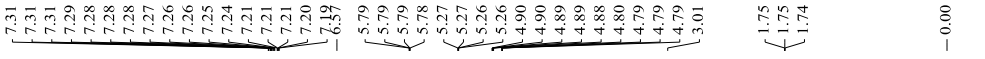
(*Z*)-(4-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)benzene (**5e**): Colorless oil, yield = 61% (**5e**:**5e'** = 94:6, isolated with preparative thin layer chromatography and using hexane as eluent).

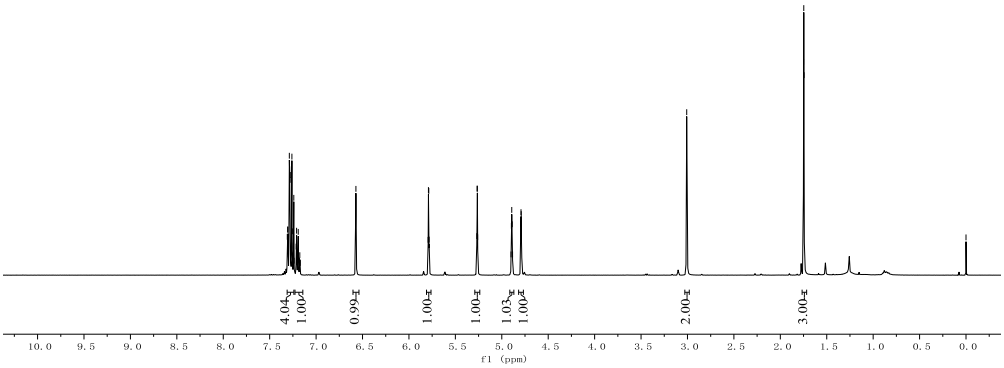
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 4H), 7.23 – 7.14 (m, 1H), 6.57 (s, 1H), 5.79 (q, *J* = 1.4 Hz, 1H), 5.26 (q, *J* = 1.1 Hz, 1H), 4.89 (p, *J* = 1.5 Hz, 1H), 4.82 – 4.77 (m, 1H), 3.01 (s, 2H), 1.77 – 1.72 (m, 3H).

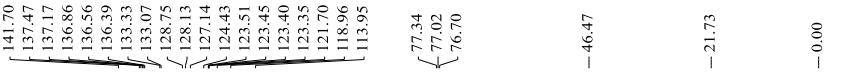
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.55.

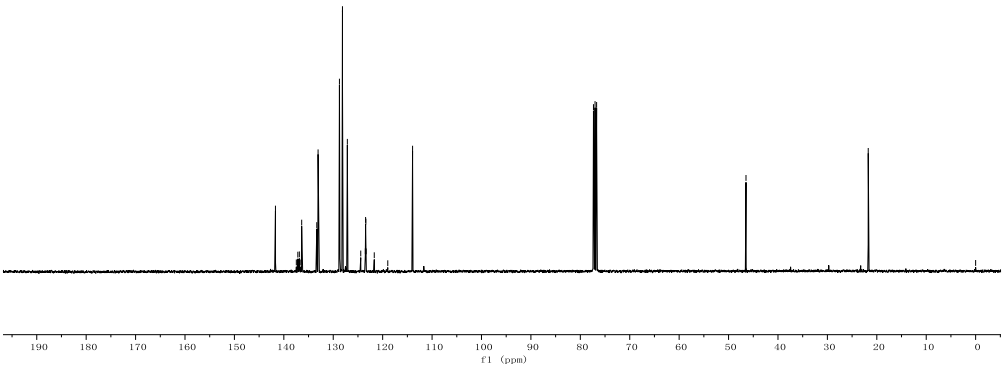
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.70, 137.01 (q, *J* = 30.6 Hz), 136.39, 133.33, 133.07, 128.75, 128.13, 127.14, 123.43 (q, *J* = 5.4 Hz), 123.07 (q, *J* = 276.3 Hz), 113.95, 46.47, 21.73.

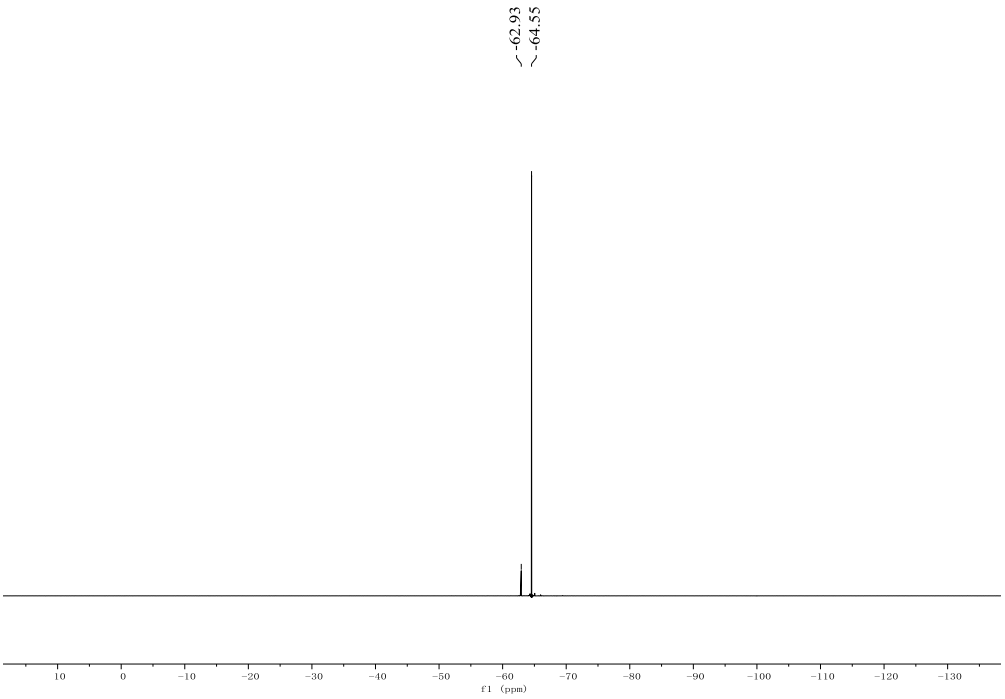
HRMS (EI) m/z calcd for $C_{15}H_{15}F_3$ $[M]^+$: 252.1120, found: 252.1116.







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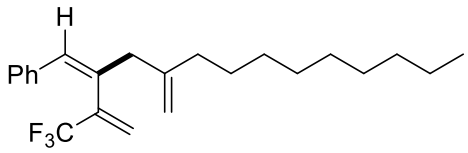
-80
-90
-100
-110
-120
-130
f1 (ppm)



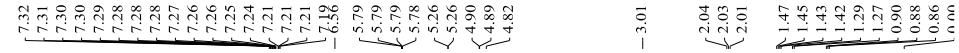
(*Z*)-(4-methylene-2-(3,3,3-trifluoroprop-1-en-2-yl)tridec-1-en-1-yl)benzene (**5f**): Colorless oil, yield = 71% (**5f**:**5f'** = 96:4, isolated with preparative thin layer chromatography and using hexane as eluent).

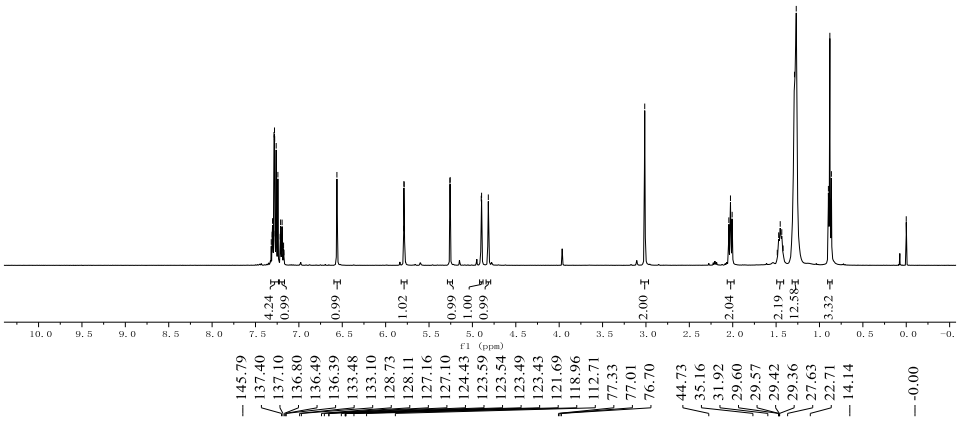
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 6.56 (s, 1H), 5.82 – 5.75 (m, 1H), 5.26 (d, *J* = 1.1 Hz, 1H), 4.90 (d, *J* = 1.6 Hz, 1H), 4.82 (s, 1H), 3.01 (s, 2H), 2.03 (t, *J* = 6.6 Hz, 2H), 1.45 (p, *J* = 6.2 Hz, 2H), 1.32 – 1.24 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H).

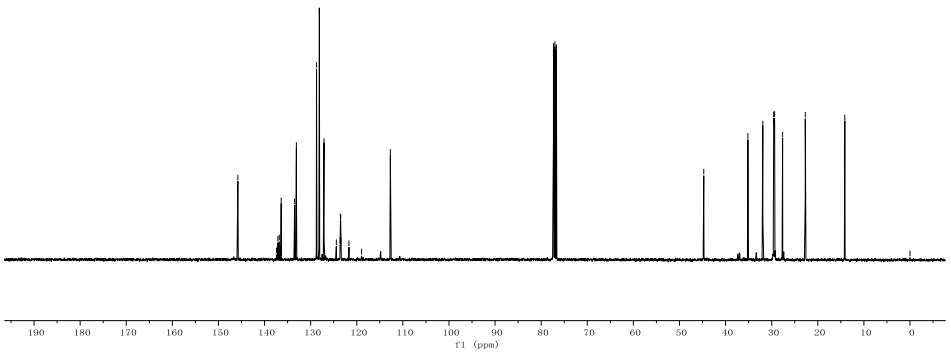
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.53.

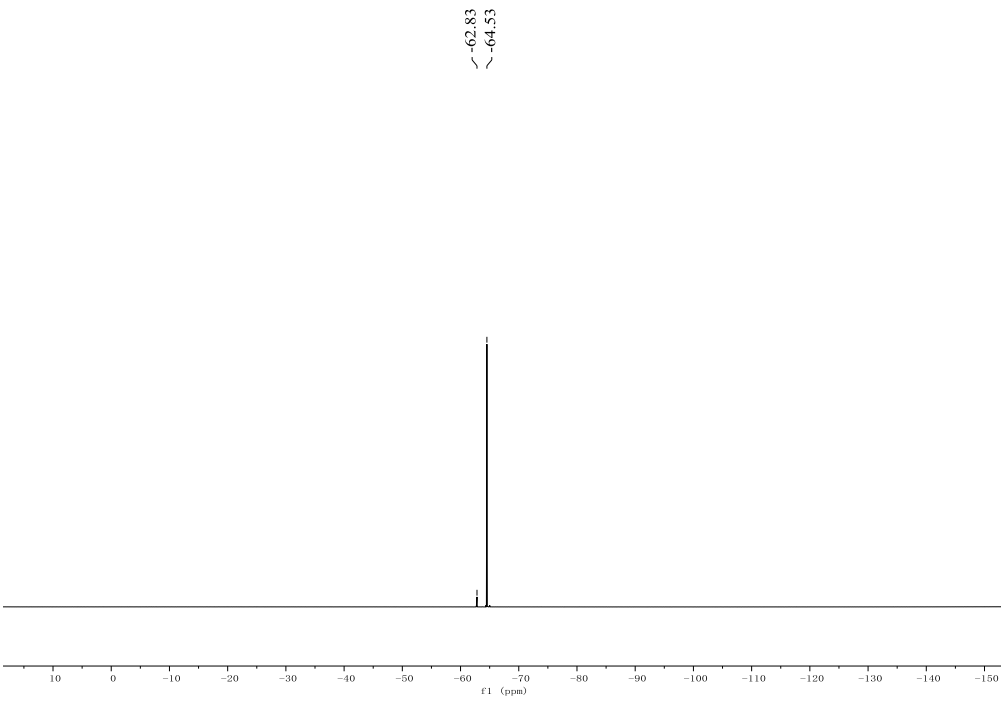
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.79, 136.95 (q, *J* = 30.5 Hz), 136.39, 133.48, 133.10, 128.73, 128.11, 127.10, 123.51 (q, *J* = 5.4 Hz), 123.06 (q, *J* = 276.3 Hz), 112.71, 44.73, 35.16, 31.92, 29.60, 29.57, 29.42, 29.36, 27.63, 22.71, 14.14.

HRMS (EI) m/z calcd for $C_{23}H_{31}F_3$ $[M]^+$: 364.2372, found: 364.2367.








-62.83
-64.53
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-120
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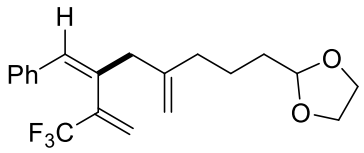
-140
-150
f1 (ppm)



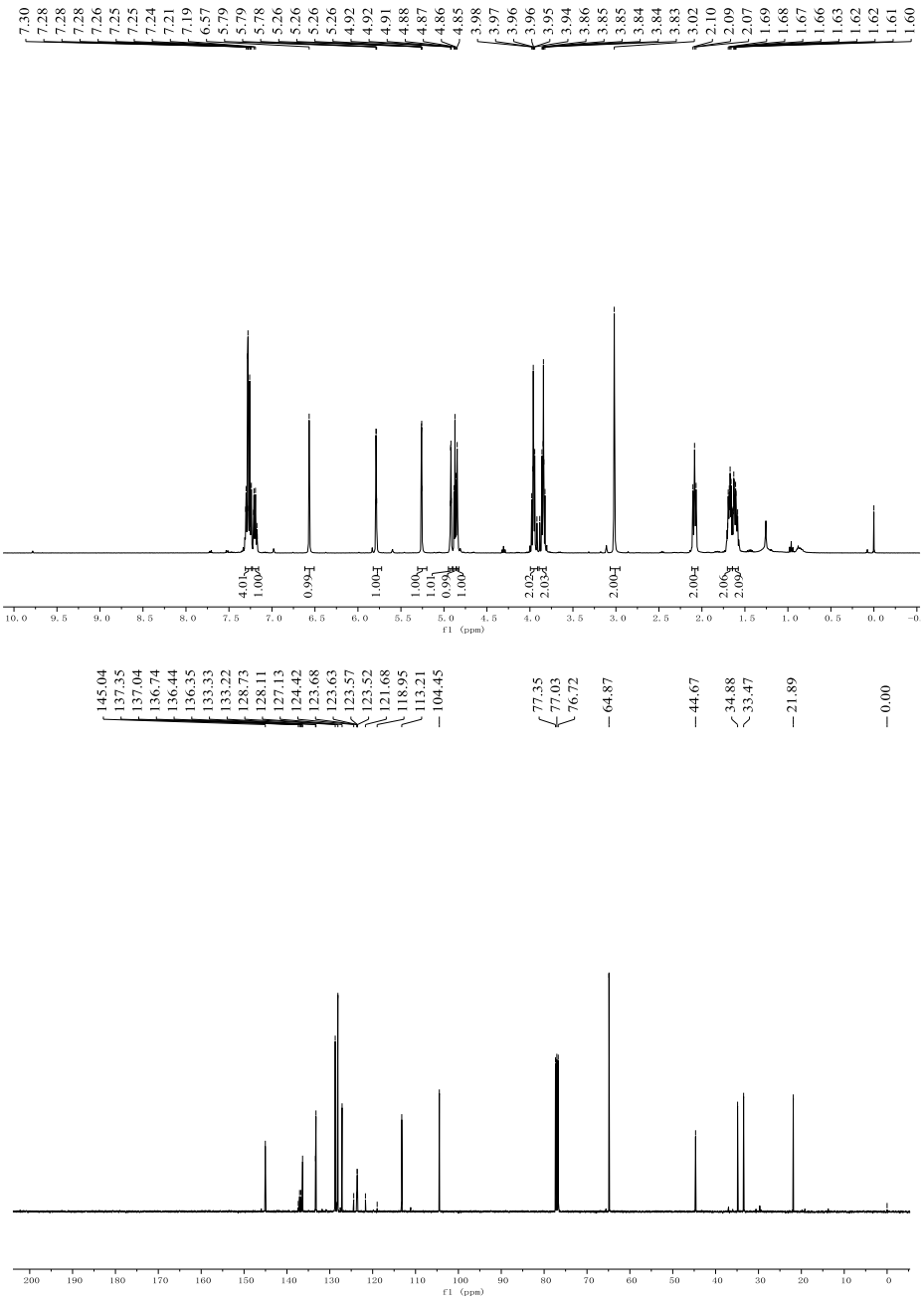
(*Z*)-2-(6-benzylidene-4-methylene-7-(trifluoromethyl)oct-7-en-1-yl)-1,3-dioxolane (**5g**): Colorless oil, yield = 72% (**5g**:**5g'** = 96:4, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:20 as eluent).

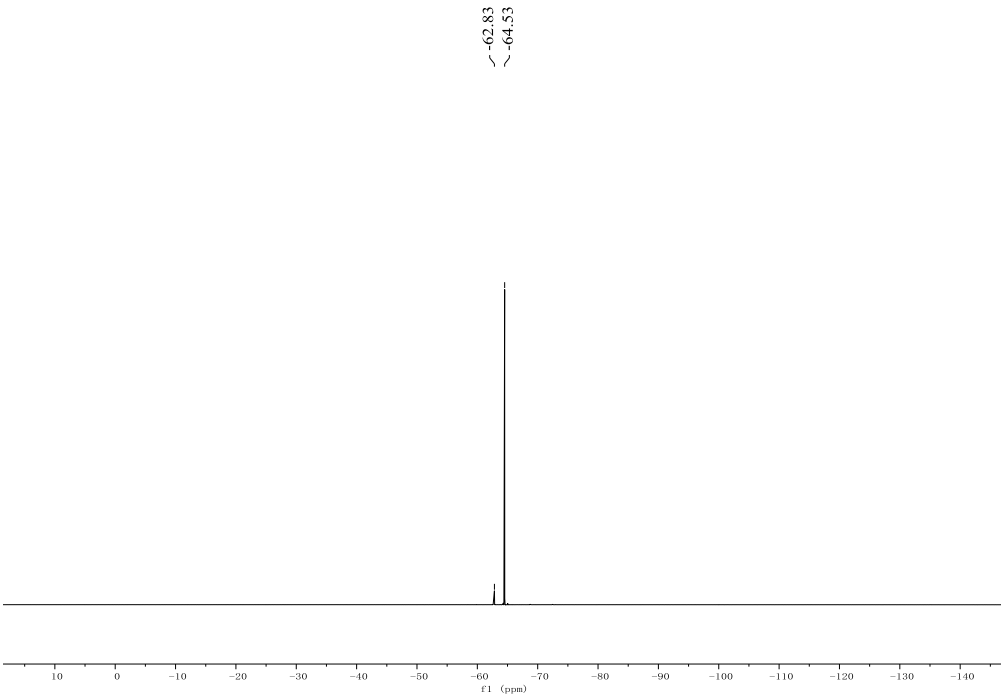
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 4H), 7.23 – 7.16 (m, 1H), 6.57 (s, 1H), 5.79 (d, *J* = 1.4 Hz, 1H), 5.31 – 5.20 (m, 1H), 4.92 (d, *J* = 1.4 Hz, 1H), 4.87 (t, *J* = 4.5 Hz, 1H), 4.85 (s, 1H), 3.99 – 3.91 (m, 2H), 3.89 – 3.81 (m, 2H), 3.02 (s, 2H), 2.09 (t, *J* = 7.3 Hz, 2H), 1.70 – 1.64 (m, 2H), 1.88 – 1.64 (m, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.53.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.04, 136.89 (q, *J* = 30.5 Hz), 136.35, 133.33, 133.22, 128.73, 128.11, 127.13, 123.60 (q, *J* = 5.4 Hz), 123.05 (q, *J* = 276.3 Hz), 113.21, 104.45, 64.87, 44.67, 34.88, 33.47, 21.89.

HRMS (ESI) m/z calcd for $C_{20}H_{23}F_3O_2Na$ $[M+Na]^+$: 375.1548, found: 375.1548.

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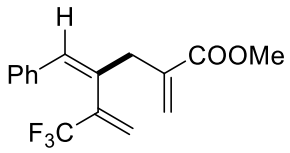
f1 (ppm)



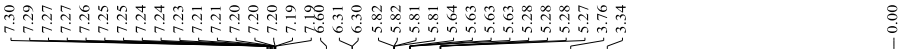
methyl (*Z*)-4-benzylidene-2-methylene-5-(trifluoromethyl)hex-5-enoate (**5h**): Colorless oil, yield = 90% (**5h**:**5h'** = 94:6, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:50 as eluent).

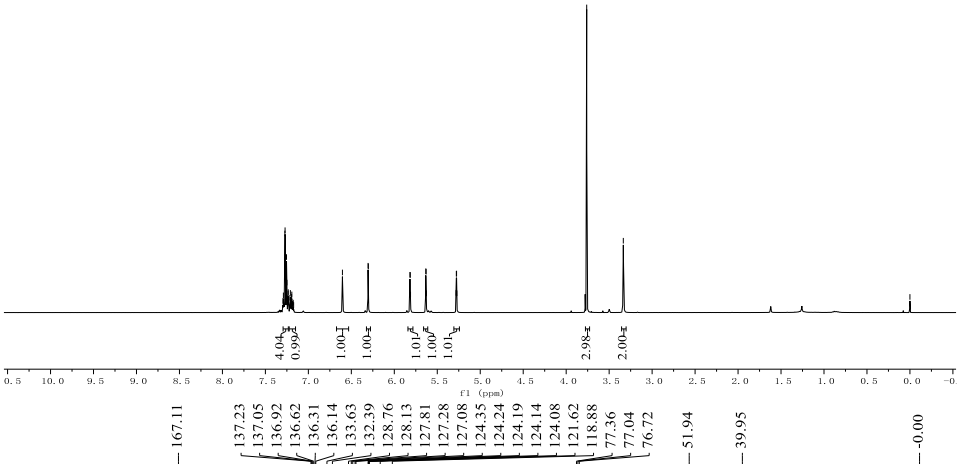
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 4H), 7.22 – 7.15 (m, 1H), 6.60 (s, 1H), 6.30 (d, *J* = 1.3 Hz, 1H), 5.82 (q, *J* = 1.3 Hz, 1H), 5.63 (d, *J* = 1.2 Hz, 1H), 5.28 (d, *J* = 1.1 Hz, 1H), 3.76 (s, 3H), 3.34 (s, 2H).

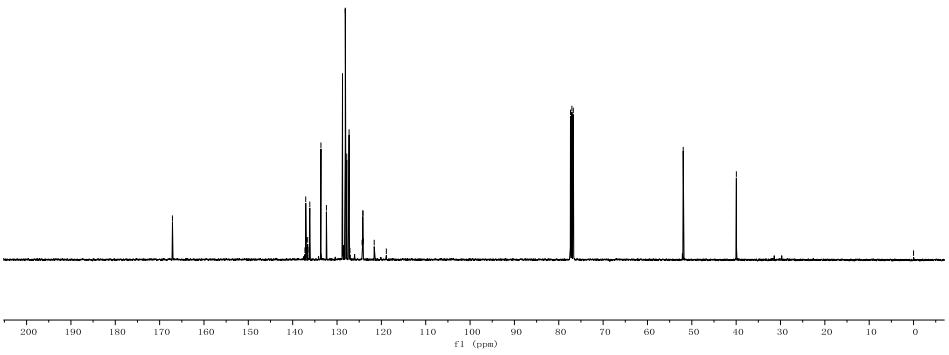
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.72.

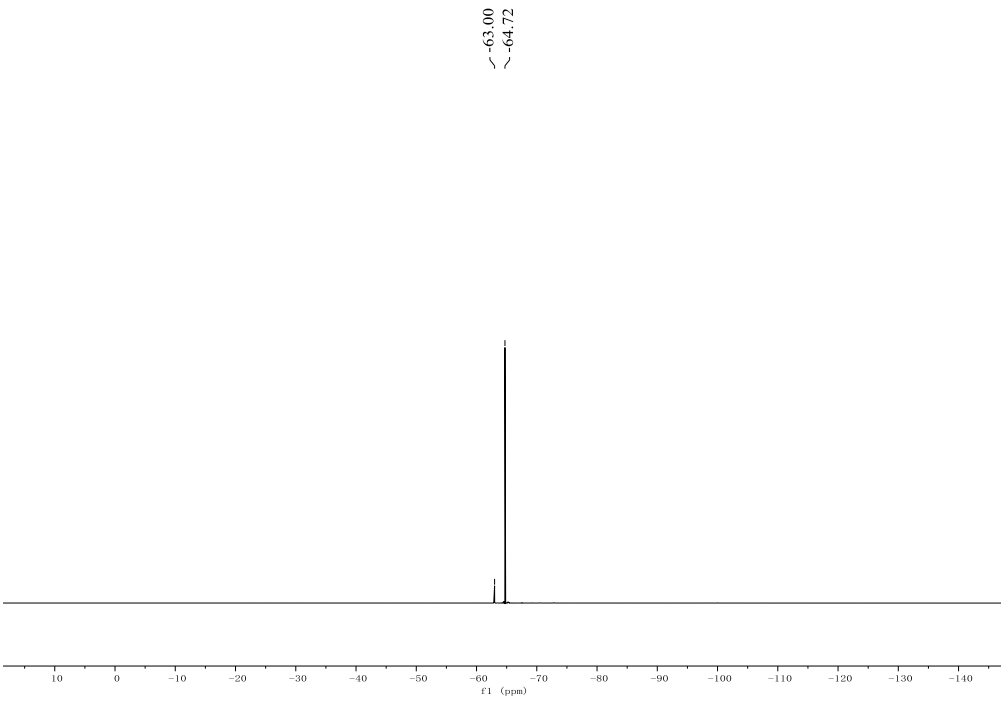
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.11, 137.05, 136.77 (q, *J* = 30.7 Hz), 136.14, 133.63, 132.39, 128.76, 128.13, 127.81, 127.28, 124.16 (q, *J* = 5.4 Hz), 122.98 (q, *J* = 276.2 Hz), 51.94, 39.95.

HRMS (ESI) m/z calcd for $C_{16}H_{15}F_3O_2Na$ $[M+Na]^+$: 319.0922, found: 319.0925.





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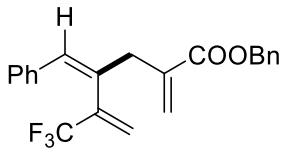
f1 (ppm)



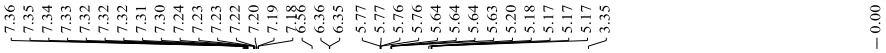
benzyl (Z)-4-benzylidene-2-methylene-5-(trifluoromethyl)hex-5-enoate (**5i**): Colorless oil, yield = 90% (**5i**:**5i'** = 91:9, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:50 as eluent).

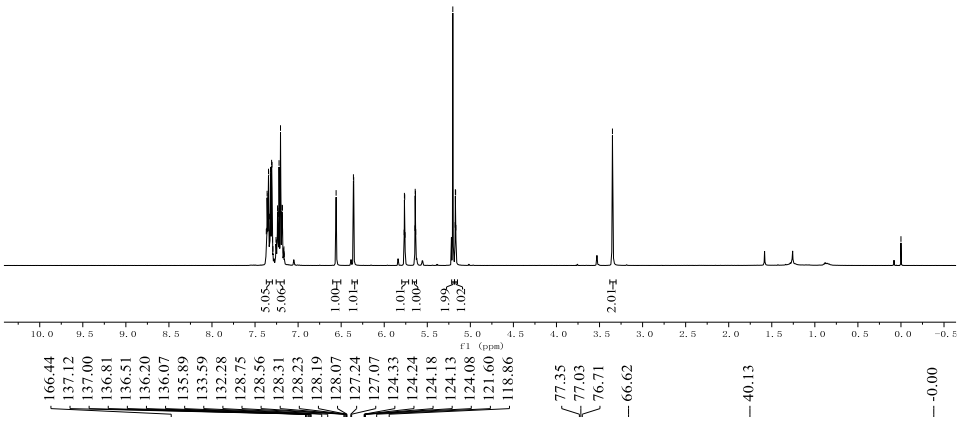
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 5H), 7.25 – 7.16 (m, 5H), 6.56 (s, 1H), 6.36 (d, *J* = 1.3 Hz, 1H), 5.80 – 5.72 (m, 1H), 5.64 (d, *J* = 1.2 Hz, 1H), 5.20 (s, 2H), 5.17 (d, *J* = 1.1 Hz, 1H), 3.35 (s, 2H).

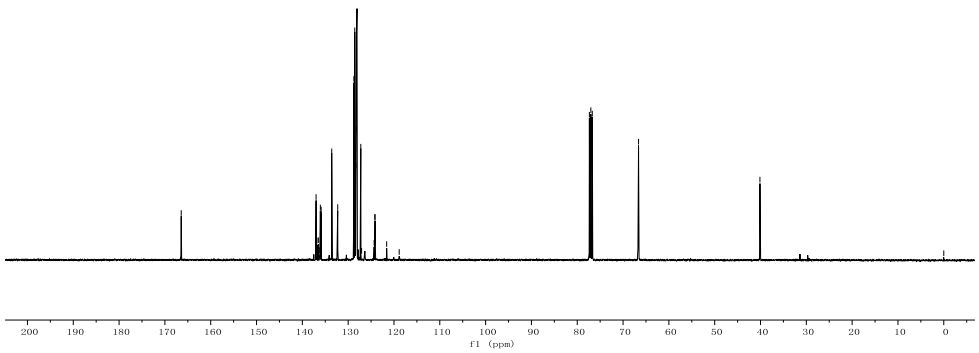
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.69.

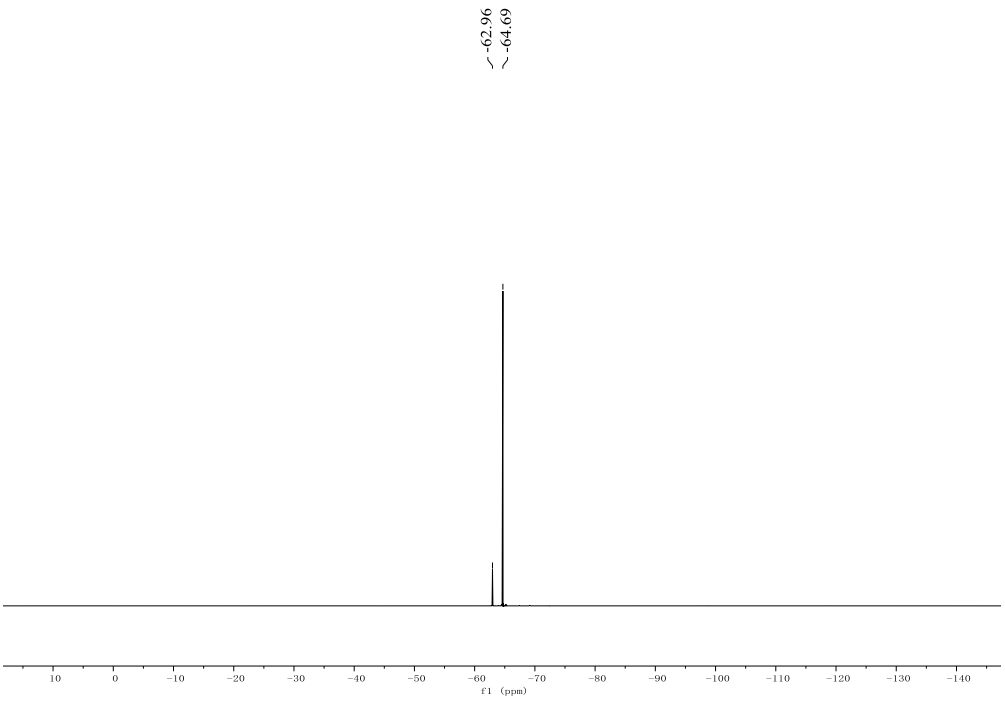
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.44, 137.00, 136.66 (q, *J* = 30.7 Hz), 136.07, 135.89, 133.59, 132.28, 128.75, 128.56, 128.31, 128.23, 128.19, 128.07, 127.24, 124.16 (q, *J* = 5.4 Hz), 122.96 (q, *J* = 276.2 Hz), 66.62, 40.13.

HRMS (ESI) m/z calcd for $C_{22}H_{19}F_3O_2Na$ $[M+Na]^+$: 395.1235, found: 395.1236.





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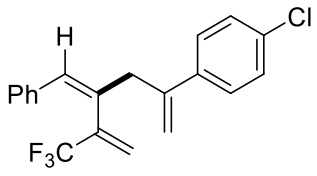
f1 (ppm)



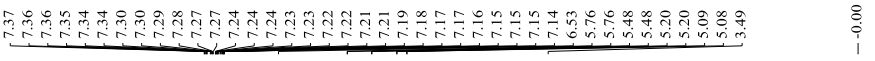
(*Z*)-1-(4-benzylidene-5-(trifluoromethyl)hexa-1,5-dien-2-yl)-4-chlorobenzene (**5j**): Colorless oil, yield = 77% (**5j**:**5j'** = 95:5, isolated with preparative thin layer chromatography and using hexane as eluent).

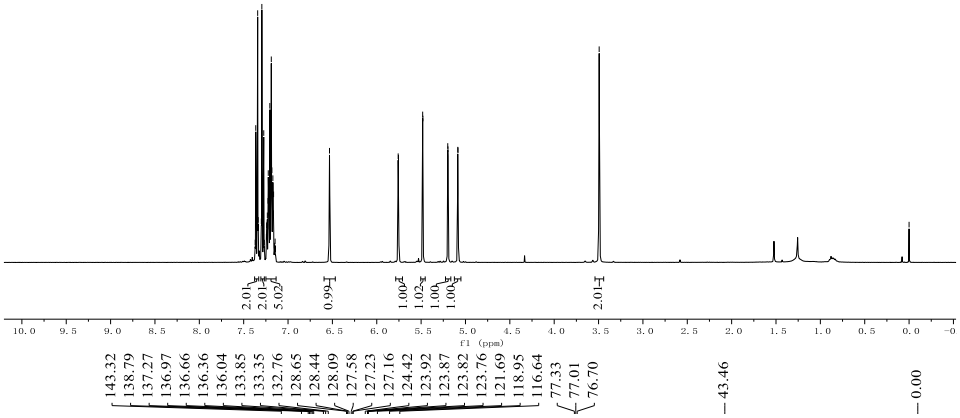
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.13 (m, 5H), 6.53 (s, 1H), 5.76 (d, *J* = 1.4 Hz, 1H), 5.48 (d, *J* = 1.0 Hz, 1H), 5.22 – 5.17 (m, 1H), 5.13 – 5.05 (m, 1H), 3.49 (s, 2H).

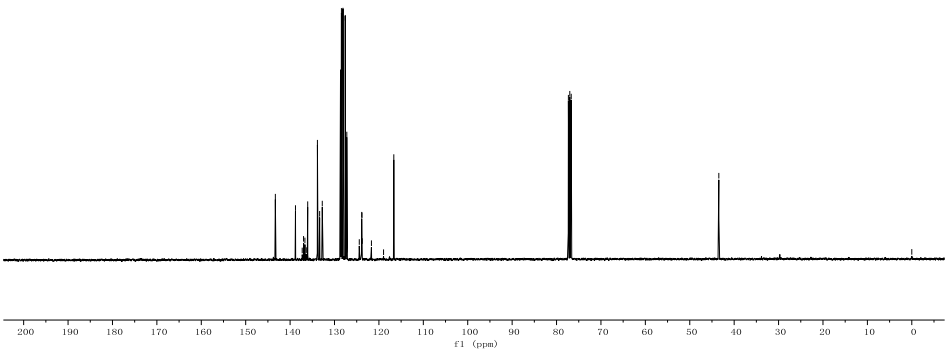
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.53.

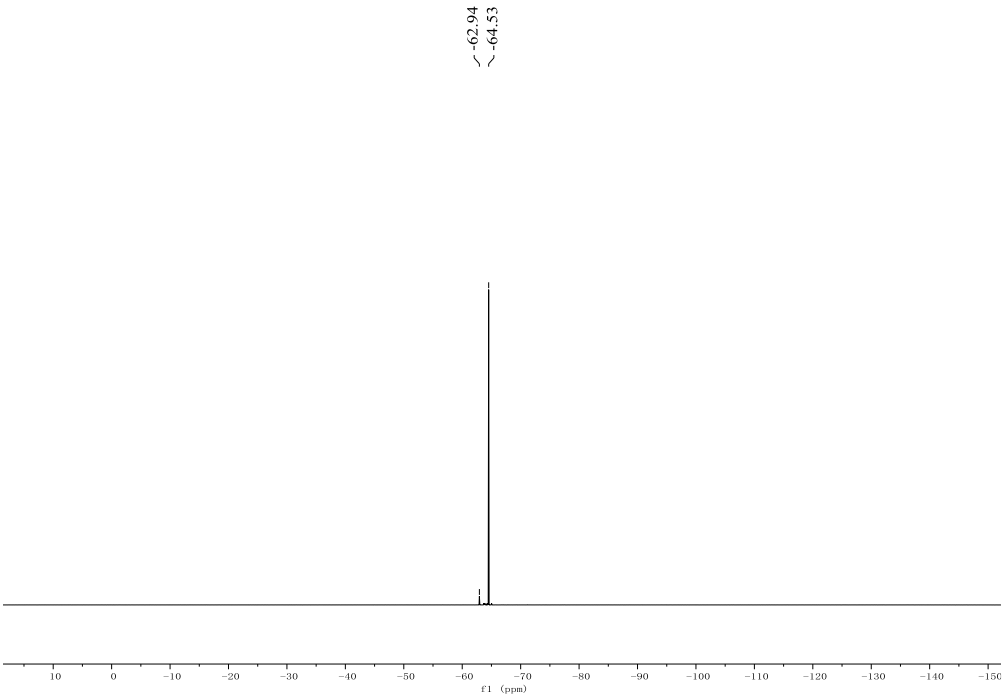
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.32, 138.79, 136.82 (q, *J* = 30.6 Hz), 136.04, 133.85, 133.35, 132.76, 128.65, 128.44, 128.09, 127.58, 127.23, 123.84 (q, *J* = 5.4 Hz), 123.05 (q, *J* = 276.3 Hz), 116.64, 43.46.

HRMS (EI) m/z calcd for $C_{20}H_{16}ClF_3$ $[M]^+$: 348.0887, found: 348.0883.





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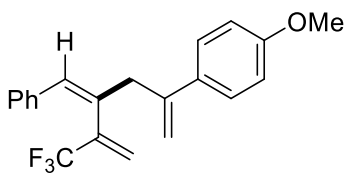
f1 (ppm)



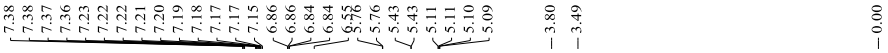
(*Z*)-1-(4-benzylidene-5-(trifluoromethyl)hexa-1,5-dien-2-yl)-4-methoxybenzene (**5k**): Colorless oil, yield = 58% (**5k**:**5k'** = 96:4, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:50 as eluent).

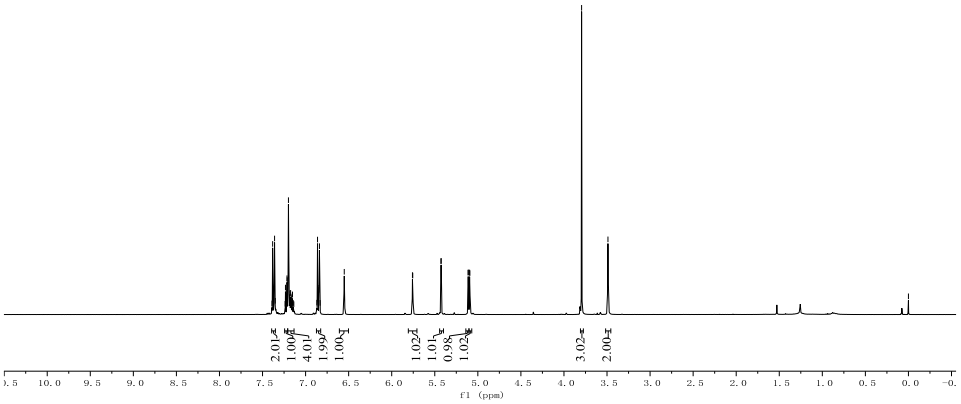
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.24 – 7.21 (m, 1H), 7.21 – 7.13 (m, 4H), 6.87 – 6.82 (m, 2H), 6.55 (s, 1H), 5.76 (d, *J* = 1.4 Hz, 1H), 5.43 (d, *J* = 1.4 Hz, 1H), 5.14 – 5.10 (m, 1H), 5.10 – 5.07 (m, 1H), 3.80 (s, 3H), 3.49 (s, 2H).

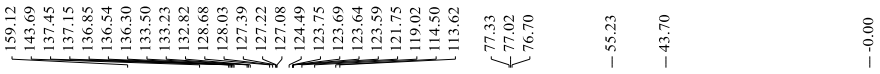
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.56.

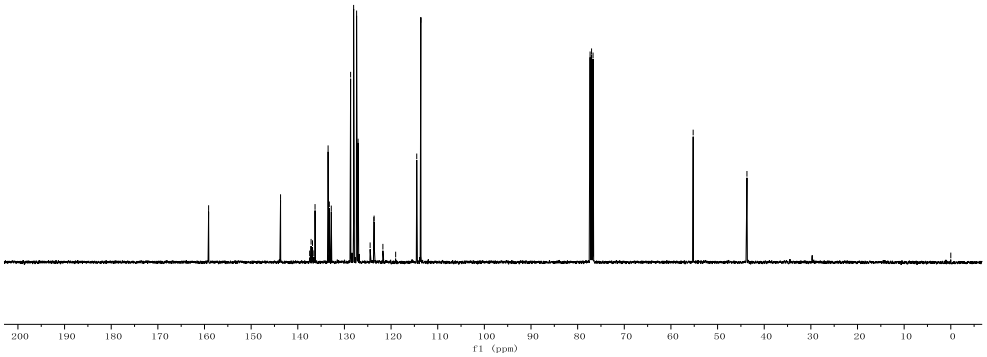
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.12, 143.69, 137.00 (q, *J* = 30.6 Hz), 136.30, 133.50, 133.23, 132.82, 128.68, 128.03, 127.39, 127.08, 123.67 (q, *J* = 5.4 Hz), 123.12 (q, *J* = 276.2 Hz), 114.50, 113.62, 55.23, 43.70.

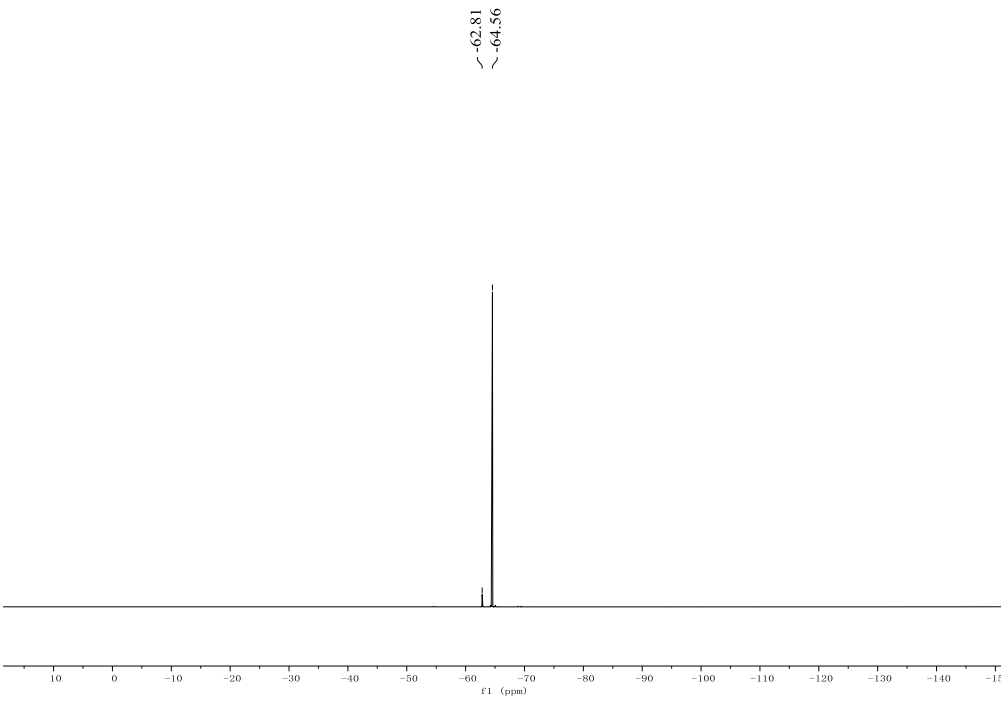
HRMS (ESI) m/z calcd for $C_{21}H_{20}F_3O$ $[M+H]^+$: 345.1466, found: 345.1462.







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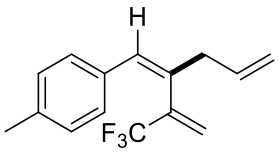
f1 (ppm)



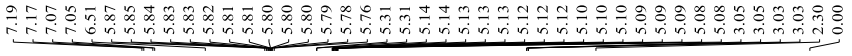
(*Z*)-1-methyl-4-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)benzene (**5l**): Colorless oil, yield = 91% (**5l**:**5l'** = 97:3, isolated with preparative thin layer chromatography and using hexane as eluent).

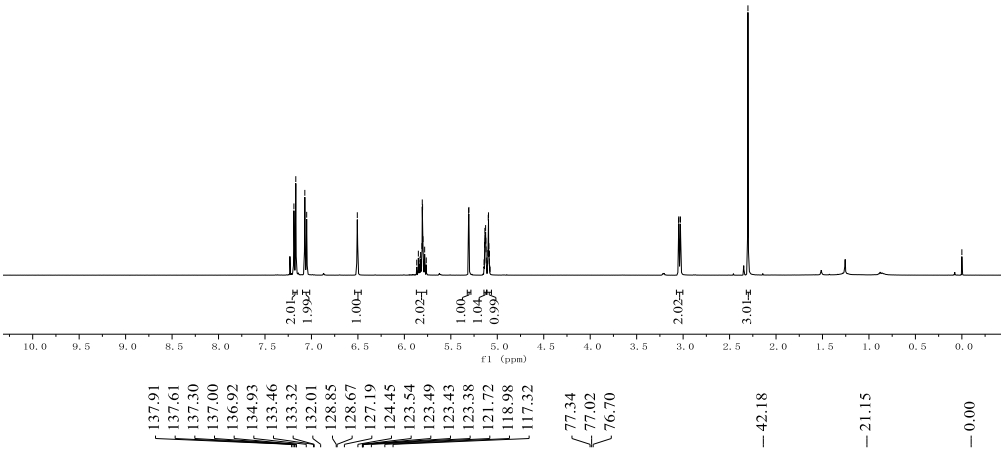
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 5.87 – 5.76 (m, 2H), 5.31 (d, *J* = 1.1 Hz, 1H), 5.14 – 5.12 (m, 1H), 5.11 – 5.06 (m, 1H), 3.07 – 3.00 (m, 2H), 2.30 (s, 3H).

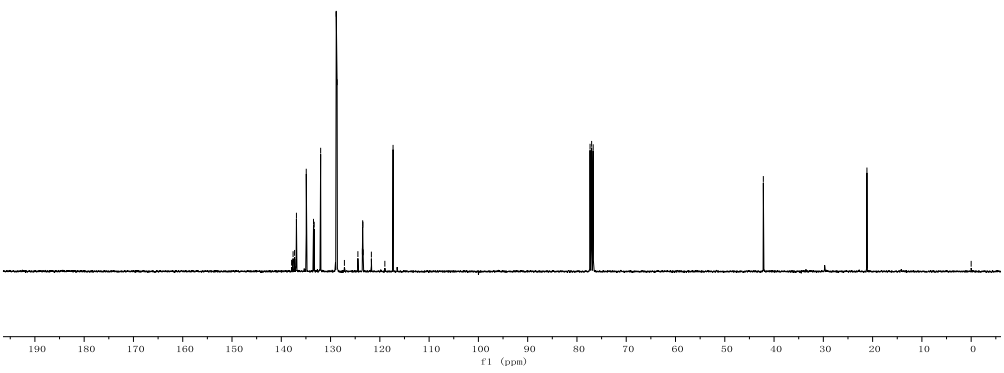
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.80.

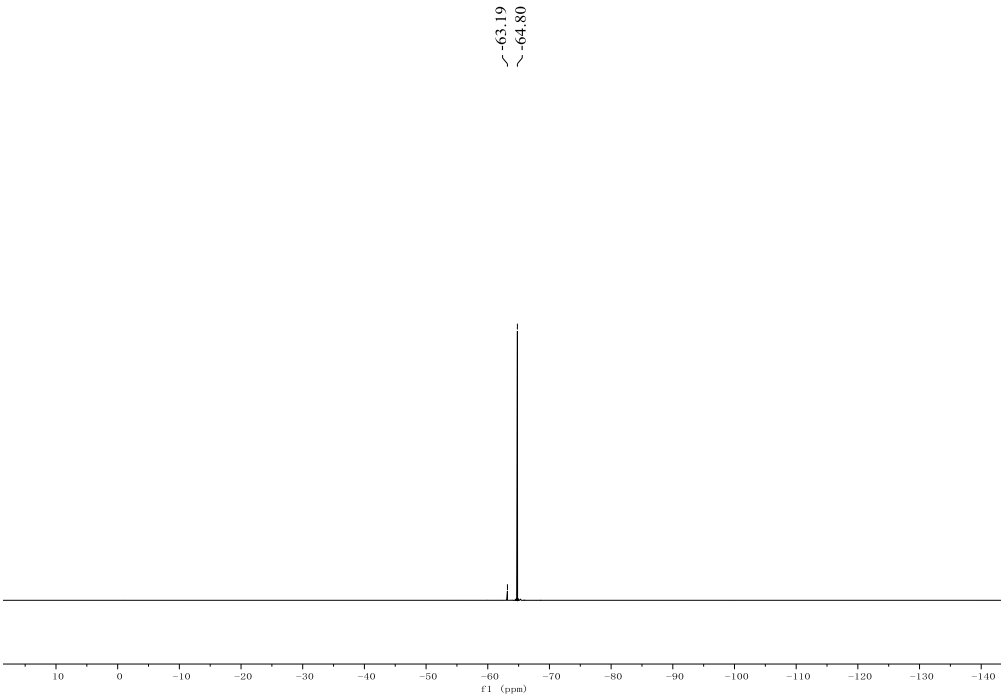
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.45 (q, *J* = 30.6 Hz), 136.92, 134.93, 133.46, 133.32, 132.01, 128.85, 128.67, 123.46 (q, *J* = 5.4 Hz), 123.08 (q, *J* = 276.2 Hz), 117.32, 42.18, 21.15.

HRMS (EI) m/z calcd for $C_{15}H_{15}F_3$ $[M]^+$: 252.1120, found: 252.1116.





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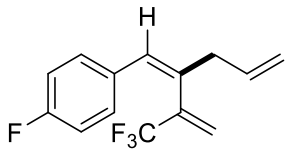


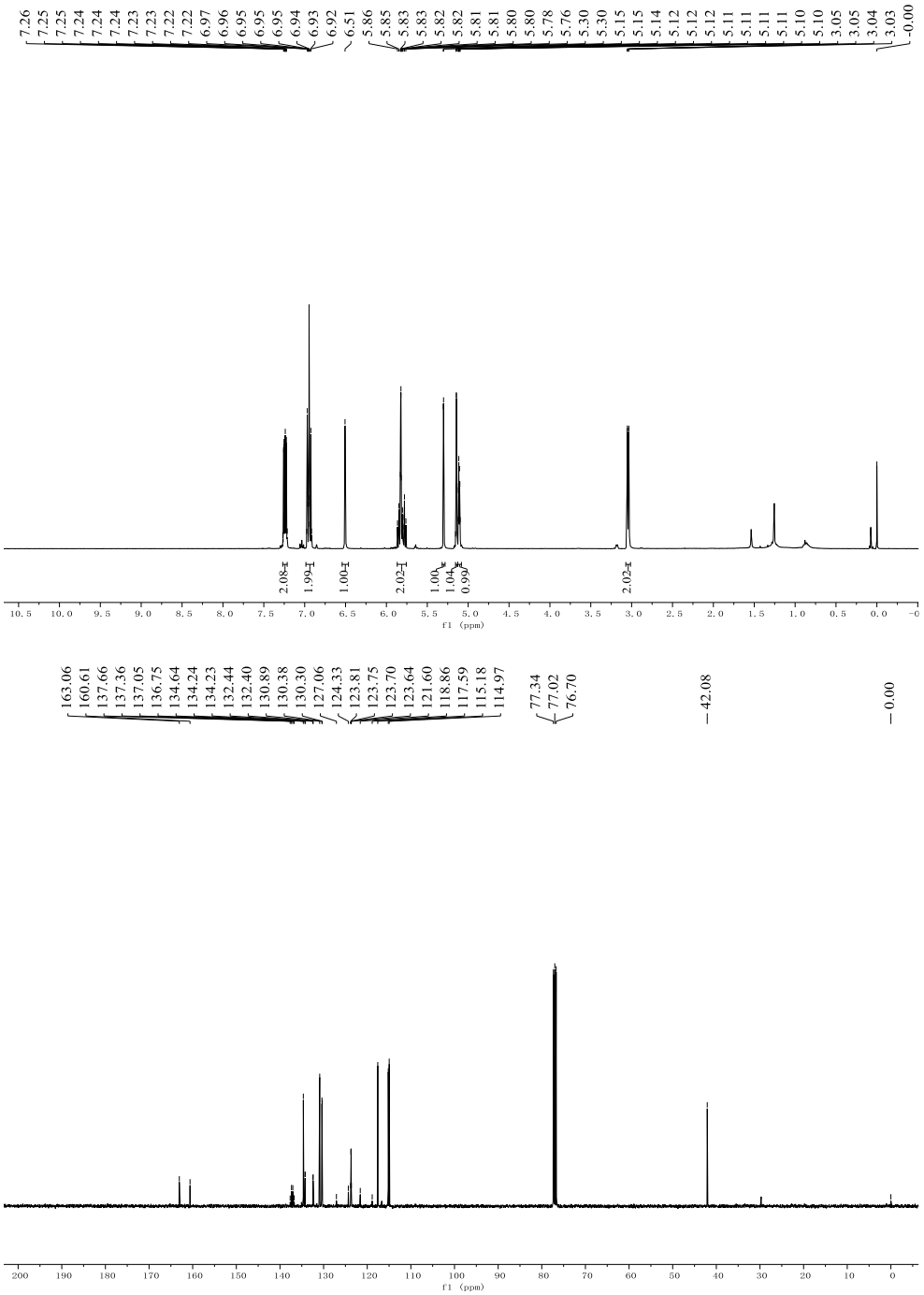
(*Z*)-1-fluoro-4-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)benzene (**5m**): Colorless oil, yield = 78% (**5m**:**5m'** = 96:4, isolated with preparative thin layer chromatography and using hexane as eluent).

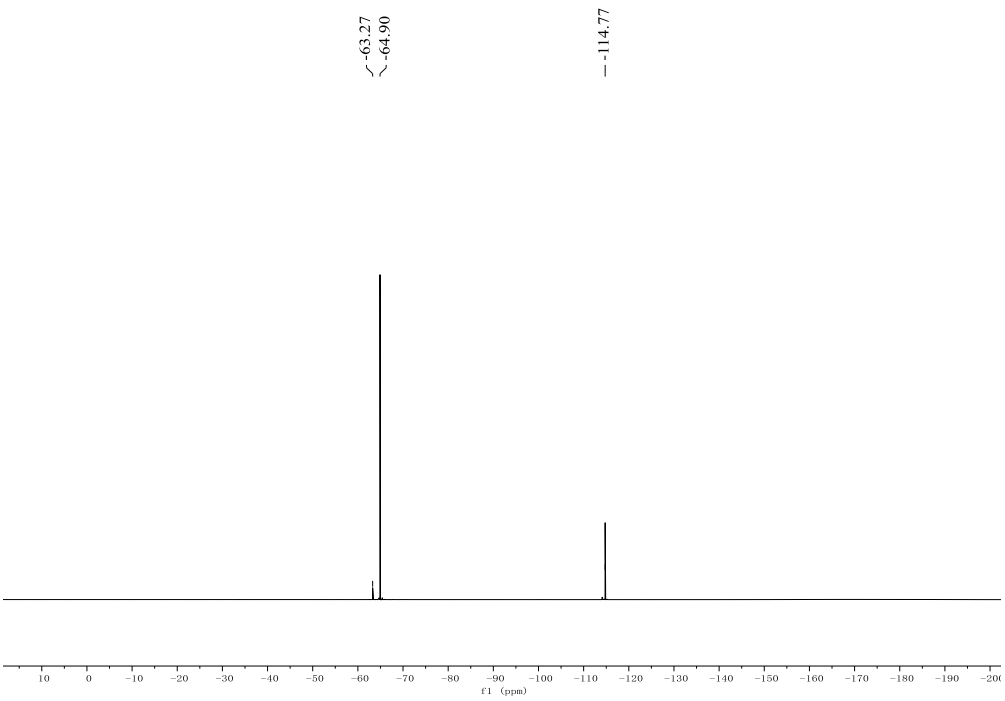
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 2H), 6.98 – 6.89 (m, 2H), 6.51 (s, 1H), 5.87 – 5.76 (m, 2H), 5.30 (d, *J* = 1.2 Hz, 1H), 5.15 – 5.13 (m, 1H), 5.13 – 5.08 (m, 1H), 3.04 (d, *J* = 6.9 Hz, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.90, -114.77.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.84 (d, *J* = 246.9 Hz), 137.21 (q, *J* = 30.7 Hz), 134.64, 134.24 (d, *J* = 1.2 Hz), 132.42 (d, *J* = 3.4 Hz), 130.89, 130.34 (d, *J* = 7.9 Hz), 123.73 (q, *J* = 5.4 Hz), 122.96 (q, *J* = 276.1 Hz), 117.59, 115.08 (d, *J* = 21.4 Hz), 42.08.

HRMS (EI) m/z calcd for $C_{14}H_{12}F_4$ $[M]^+$: 256.0870, found: 256.0866.

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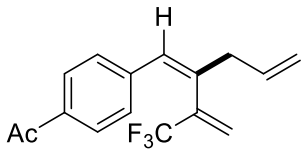
f1 (ppm)



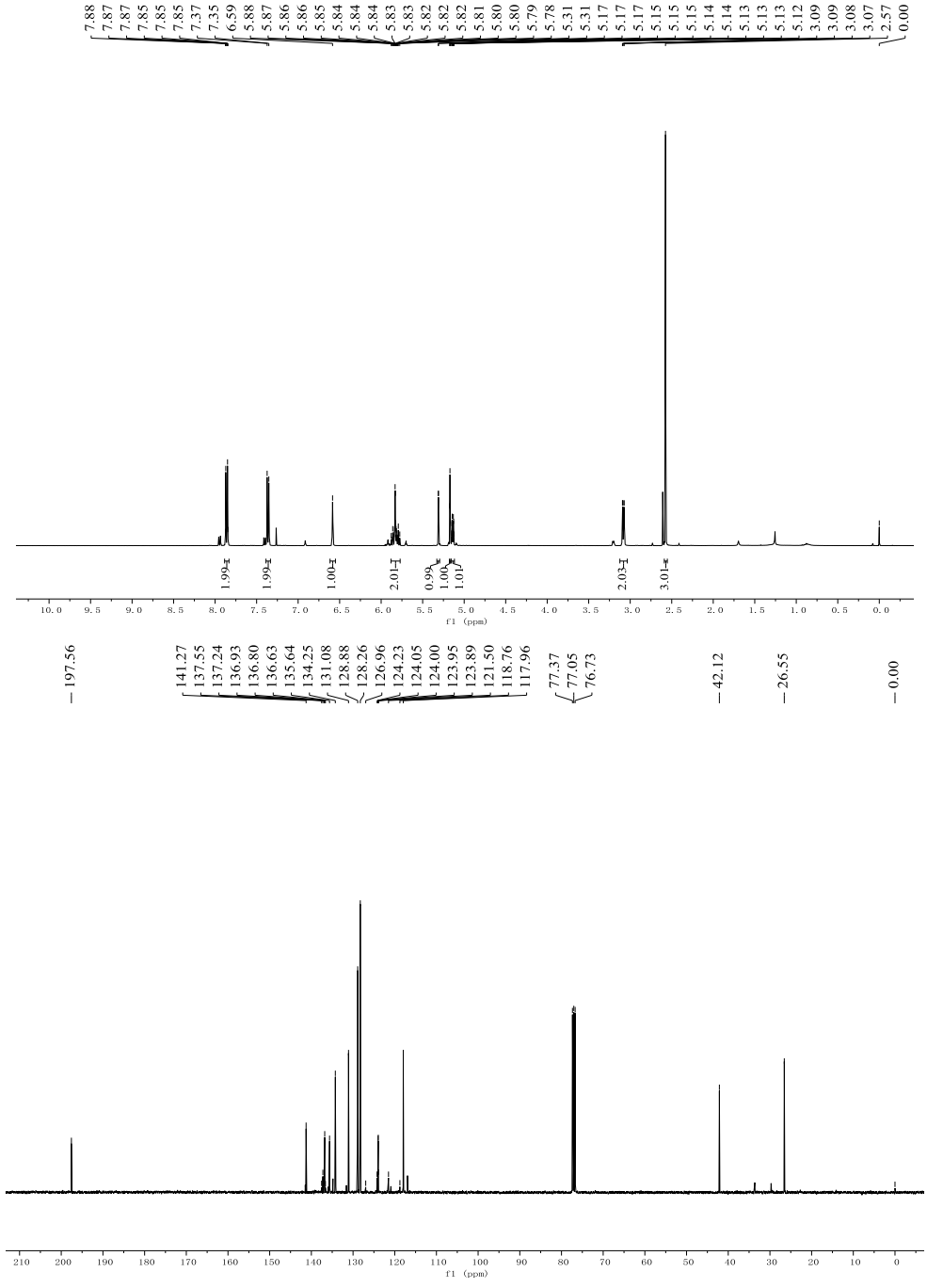
(*Z*)-1-(4-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)phenyl)ethan-1-one (**5n**): Colorless oil, yield = 85% (**5n**:**5n'** = 90:10, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:20 as eluent).

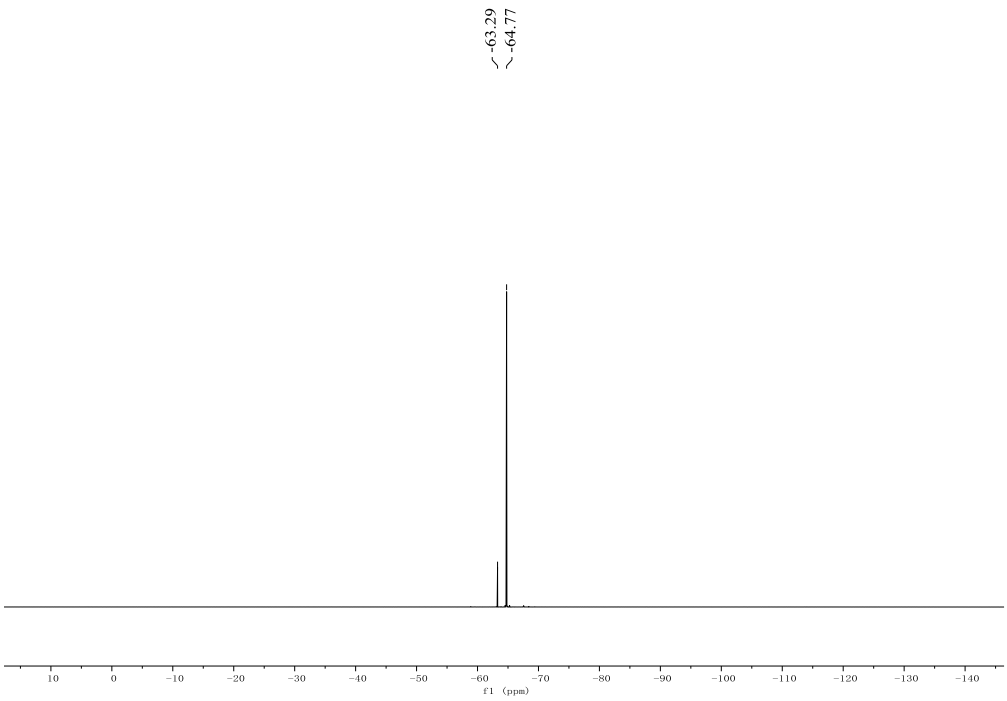
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.39 – 7.33 (m, 2H), 6.59 (s, 1H), 5.88 – 5.77 (m, 2H), 5.31 (d, *J* = 1.2 Hz, 1H), 5.17 (t, *J* = 1.2 Hz, 1H), 5.15 – 5.12 (m, 1H), 3.12 – 3.04 (m, 2H), 2.57 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64. 77.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.56, 141.27, 137.09 (q, *J* = 30.8 Hz), 136.80, 135.64, 134.25, 131.08, 128.88, 128.26, 123.97 (q, *J* = 5.4 Hz), 122.86 (q, *J* = 276.1 Hz), 117.96, 42.12, 26.55.

HRMS (ESI) m/z calcd for $C_{16}H_{15}F_3ONa$ $[M+Na]^+$: 303.0973, found: 303.0971.

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0
-10
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-80
-90
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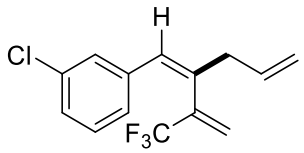
-110
-120
-130
-140
f1 (ppm)



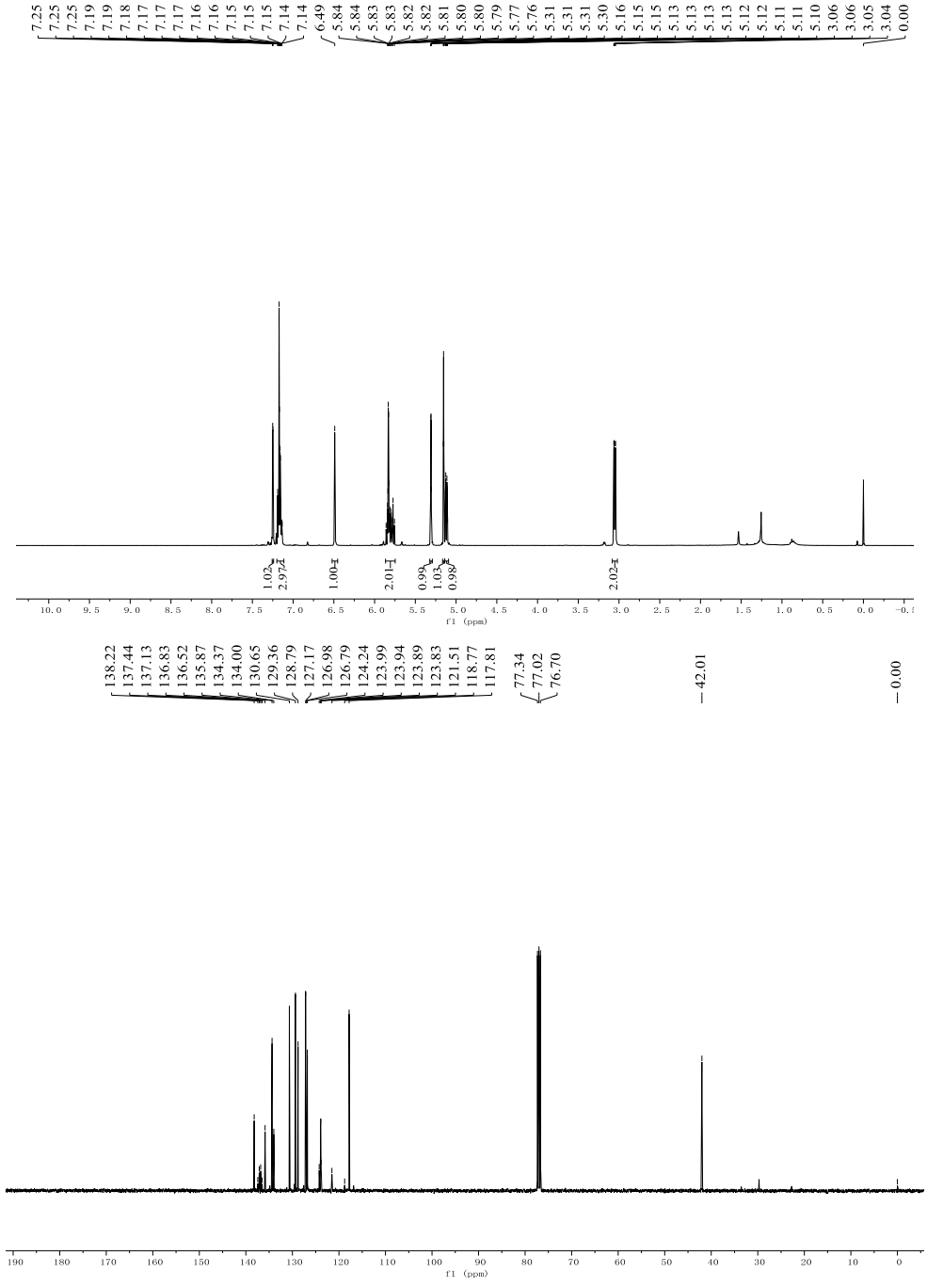
(*Z*)-1-chloro-3-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)benzene (**5o**): Colorless oil, yield = 73% (**5o**:**5o'** = 96:4, isolated with preparative thin layer chromatography and using hexane as eluent).

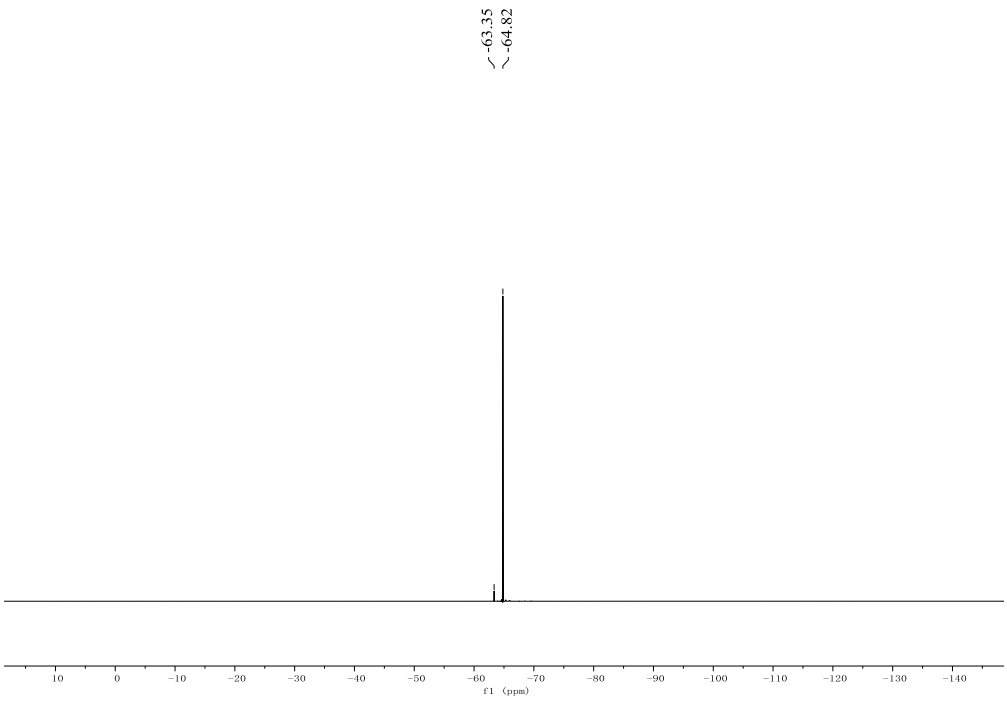
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.24 (m, 1H), 7.20 – 7.11 (m, 3H), 6.49 (s, 1H), 5.87 – 5.75 (m, 2H), 5.32 – 5.29 (m, 1H), 5.15 (t, *J* = 1.2 Hz, 1H), 5.14 – 5.09 (m, 1H), 3.08 – 3.02 (m, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64. 82.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.22, 136.98 (q, *J* = 30.8 Hz), 135.87, 134.37, 134.00, 130.65, 129.36, 128.79, 127.17, 126.79, 123.91 (q, *J* = 5.4 Hz), 122.87 (q, *J* = 276.1 Hz), 117.81, 42.01.

HRMS (EI) m/z calcd for $C_{14}H_{12}ClF_3$ $[M]^+$: 272.0574, found: 272.0570.

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-64.82
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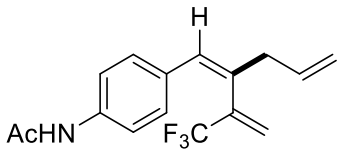
f1 (ppm)



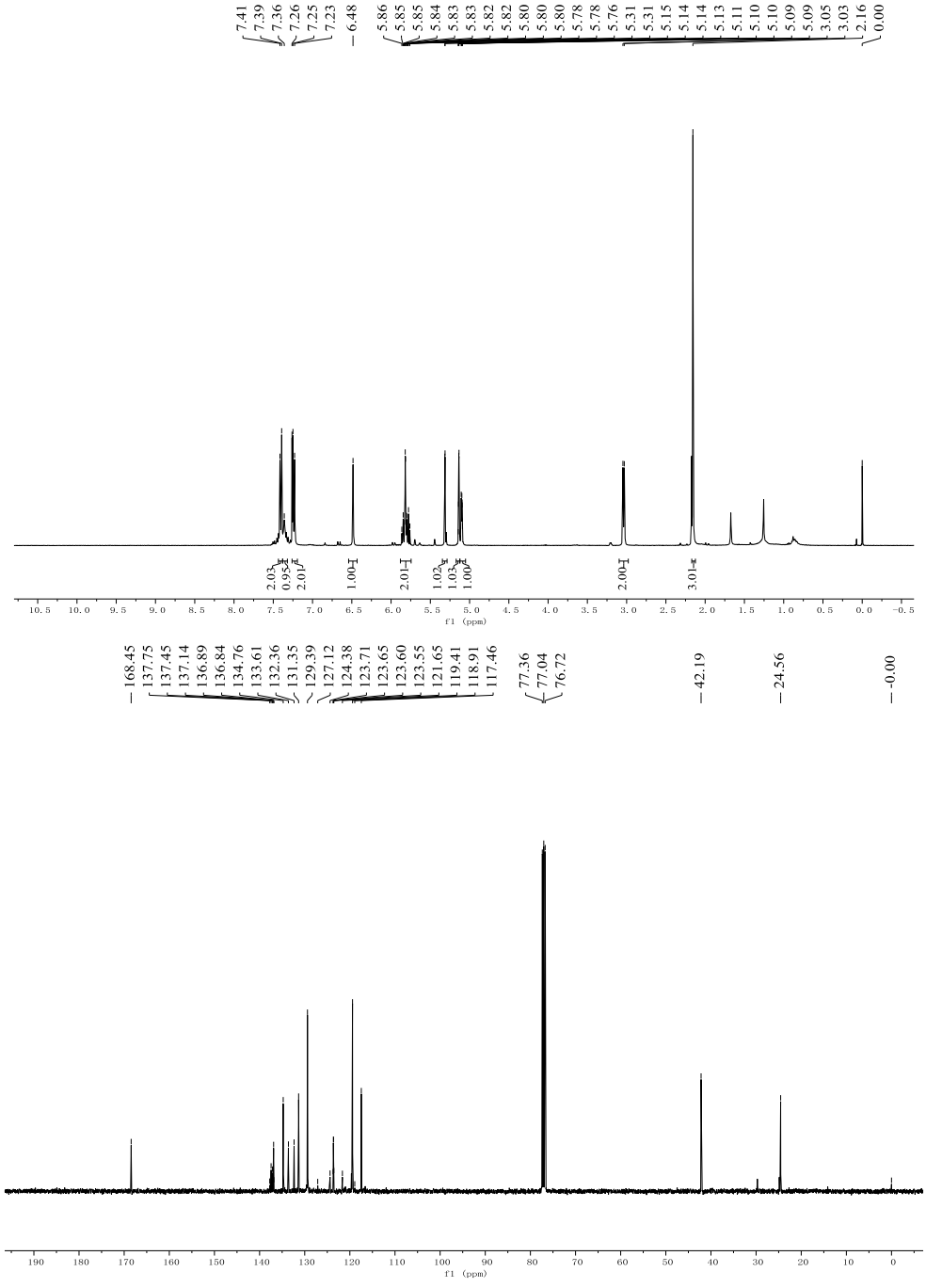
(*Z*)-*N*-(4-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)phenyl)acetamide (**5p**): Colorless oil, yield = 51% (**5p**:**5p'** = 96:4, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:2 as eluent).

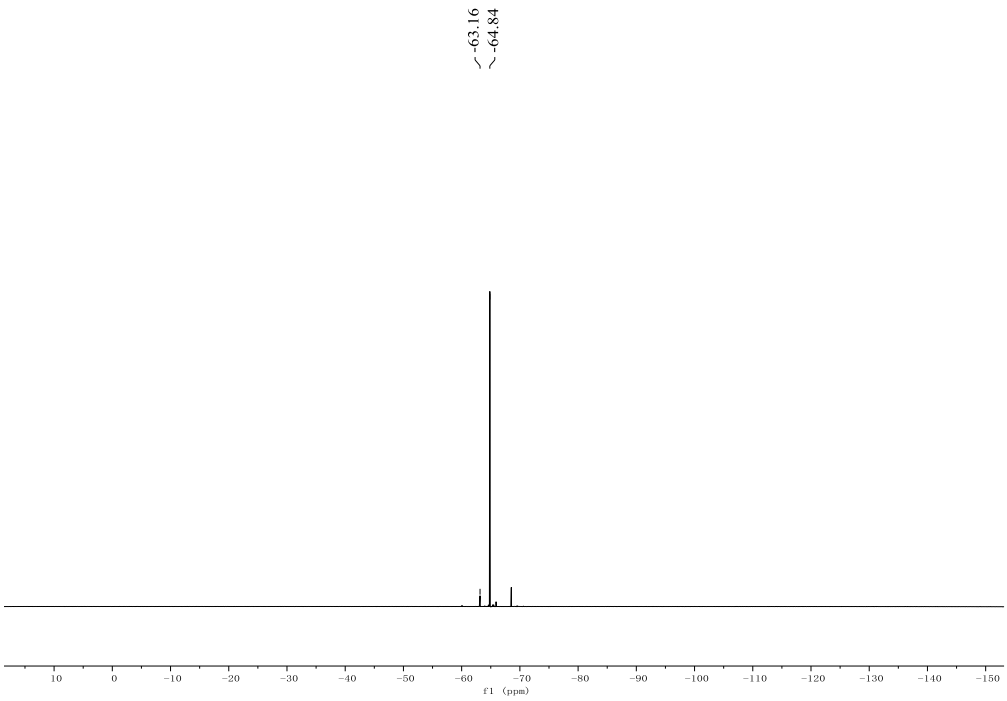
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.36 (s, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.48 (s, 1H), 5.88 – 5.74 (m, 2H), 5.35 – 5.29 (m, 1H), 5.17 – 5.12 (m, 1H), 5.12 – 5.05 (m, 1H), 3.04 (d, *J* = 6.9 Hz, 2H), 2.16 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64. 84.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.45, 137.30 (q, *J* = 30.7 Hz), 136.89, 134.76, 133.61, 132.36, 131.35, 129.39, 123.63 (q, *J* = 5.4 Hz), 123.02 (q, *J* = 276.3 Hz), 119.41, 117.46, 42.19, 24.56.

HRMS (ESI) m/z calcd for $C_{16}H_{16}F_3NONa$ $[M+Na]^+$: 318.1082, found: 318.1083.

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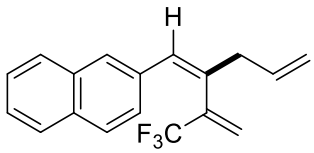
f1 (ppm)



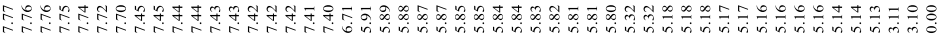
(*Z*)-2-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)naphthalene (**5q**): Colorless oil, yield = 85% (**5q**:**5q'** = 97:3, isolated with preparative thin layer chromatography and using hexane as eluent).

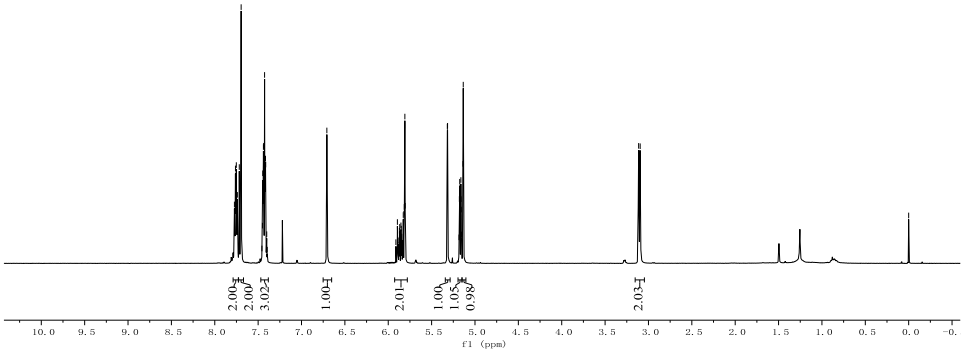
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 2H), 7.73 – 7.67 (m, 2H), 7.47 – 7.38 (m, 3H), 6.71 (s, 1H), 5.93 – 5.78 (m, 2H), 5.32 (d, *J* = 1.1 Hz, 1H), 5.20 – 5.15 (m, 1H), 5.14 (t, *J* = 1.2 Hz, 1H), 3.10 (d, *J* = 7.1 Hz, 2H).

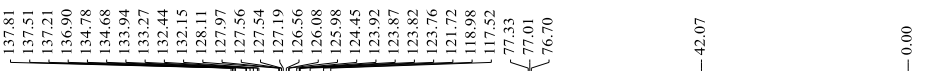
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64. 58.

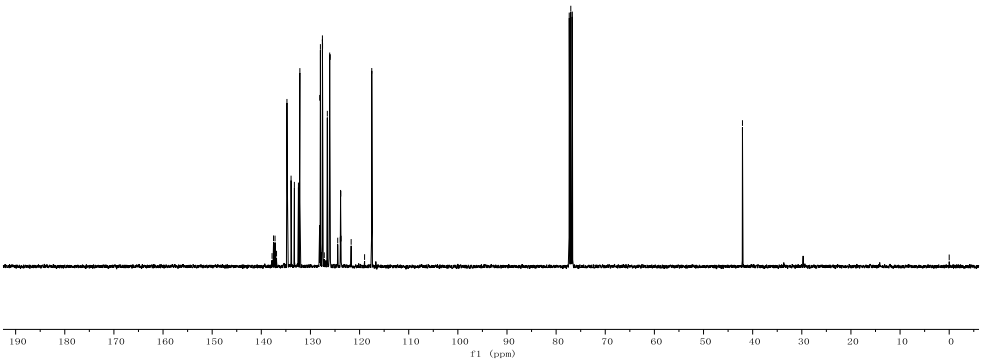
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.36 (q, *J* = 30.6 Hz), 134.78, 134.68, 133.94, 133.27, 132.44, 132.15, 128.11, 127.97, 127.56, 127.54, 126.56, 126.08, 125.98, 123.84 (q, *J* = 5.4 Hz), 123.08 (q, *J* = 276.2 Hz), 117.52, 42.07.

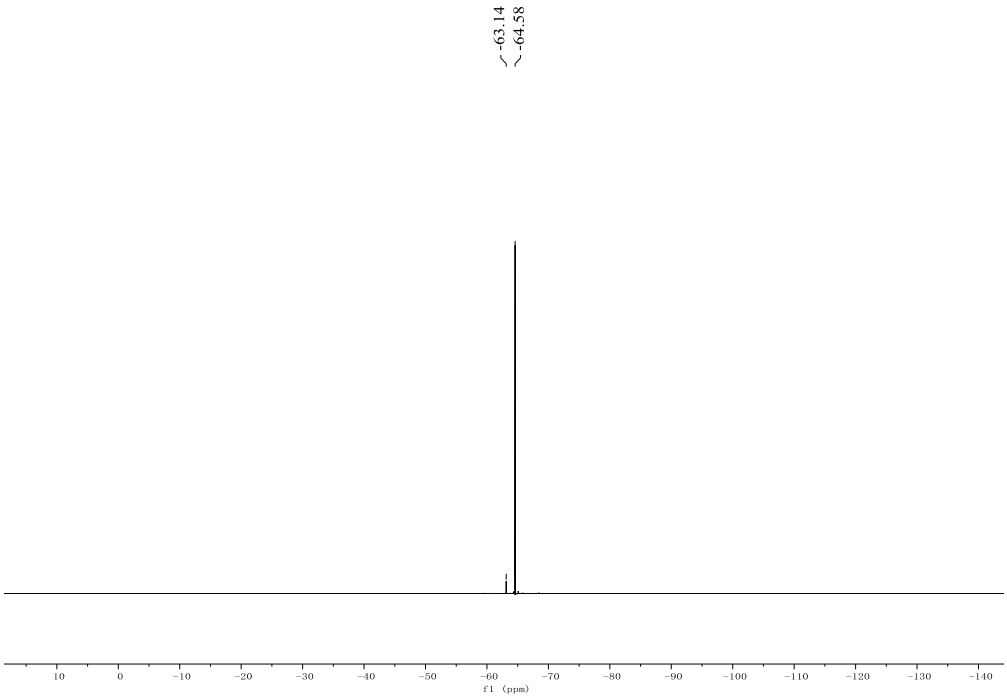
HRMS (EI) m/z calcd for $C_{18}H_{15}F_3$ $[M]^+$: 288.1120, found: 288.1116.







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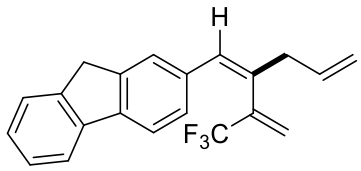
f1 (ppm)



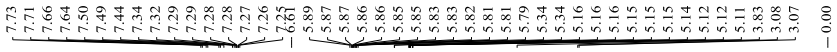
(*Z*)-2-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)-9*H*-fluorene (**5r**): White solid, yield = 84% (**5r**:**5r'** = 95:5, isolated with preparative thin layer chromatography and using hexane as eluent).

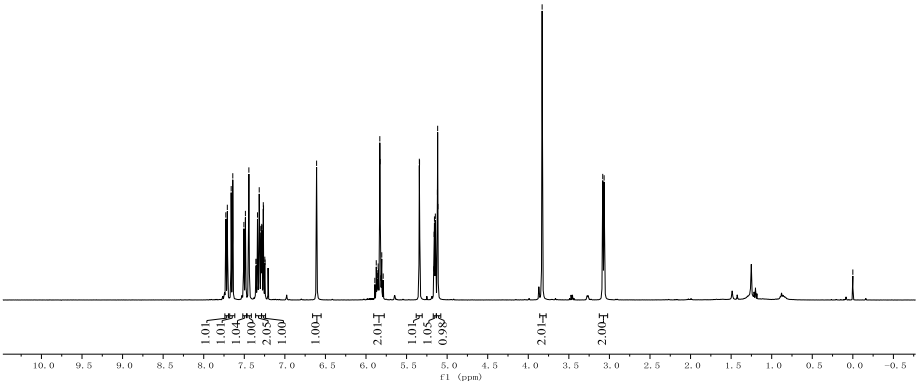
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.44 (s, 1H), 7.36 – 7.29 (m, 2H), 7.26 (td, *J* = 7.4, 1.2 Hz, 1H), 6.61 (s, 1H), 5.90 – 5.78 (m, 2H), 5.38 – 5.31 (m, 1H), 5.17 – 5.13 (m, 1H), 5.12 (t, *J* = 1.1 Hz, 1H), 3.83 (s, 2H), 3.07 (d, *J* = 6.8 Hz, 2H).

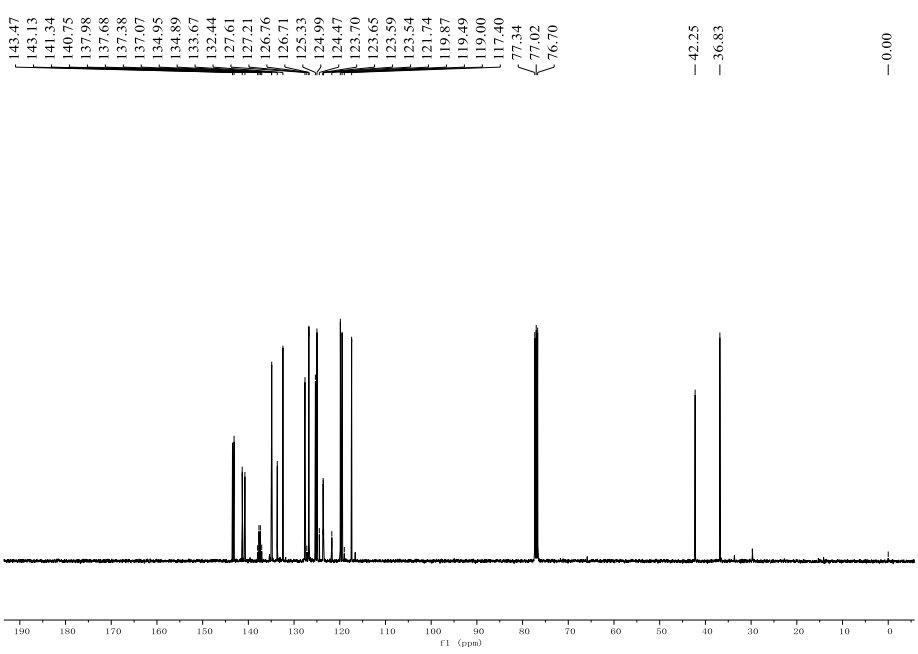
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64. 60.

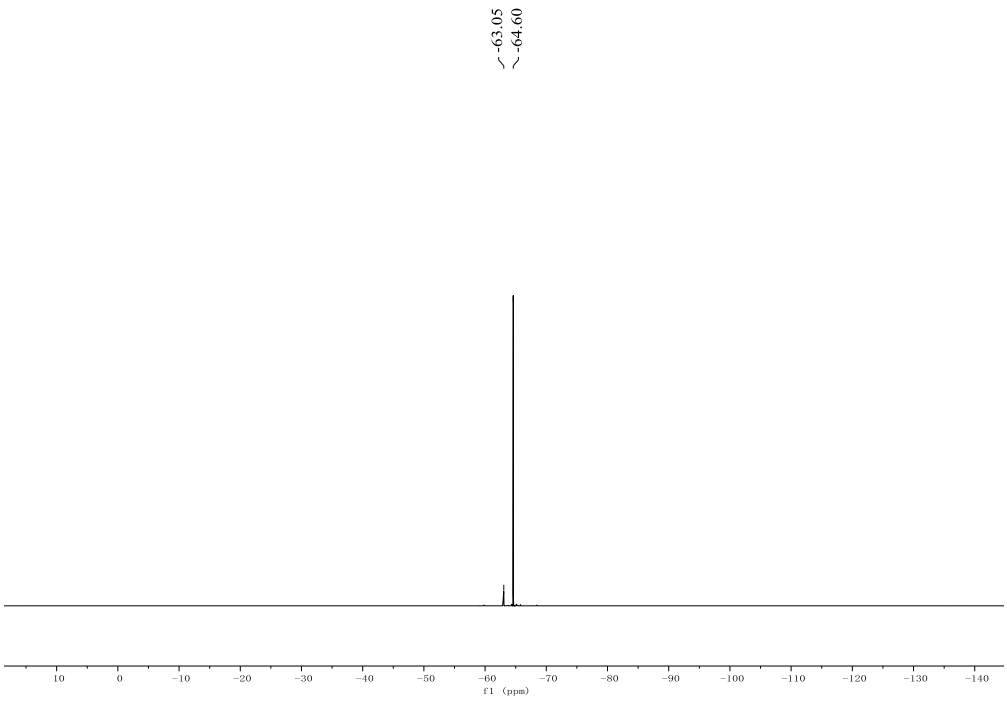
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.47, 143.13, 141.34, 140.75, 137.53 (q, *J* = 30.6 Hz), 134.95, 134.89, 133.67, 132.44, 127.61, 126.76, 126.71, 125.33, 124.99, 123.62 (q, *J* = 5.4 Hz), 123.11 (q, *J* = 276.2 Hz), 119.87, 119.49, 117.40, 42.25, 36.83.

HRMS (EI) m/z calcd for $C_{21}H_{17}F_3$ $[M]^+$: 326.1277, found: 326.1271.





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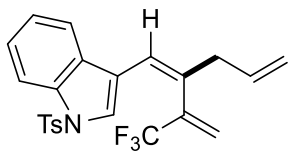
f1 (ppm)



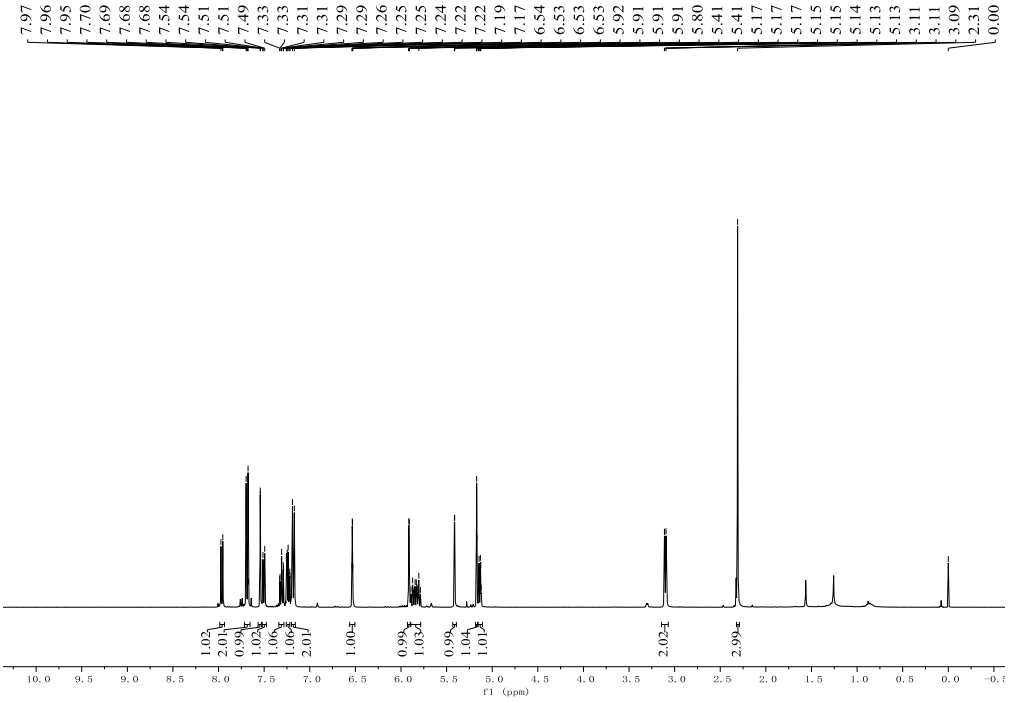
(*Z*)-1-tosyl-3-(2-(3,3,3-trifluoroprop-1-en-2-yl)penta-1,4-dien-1-yl)-1*H*-indole (**5s**): Pale yellow solid, yield = 54% (**5s**:**5s'** = 93:7, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:10 as eluent).

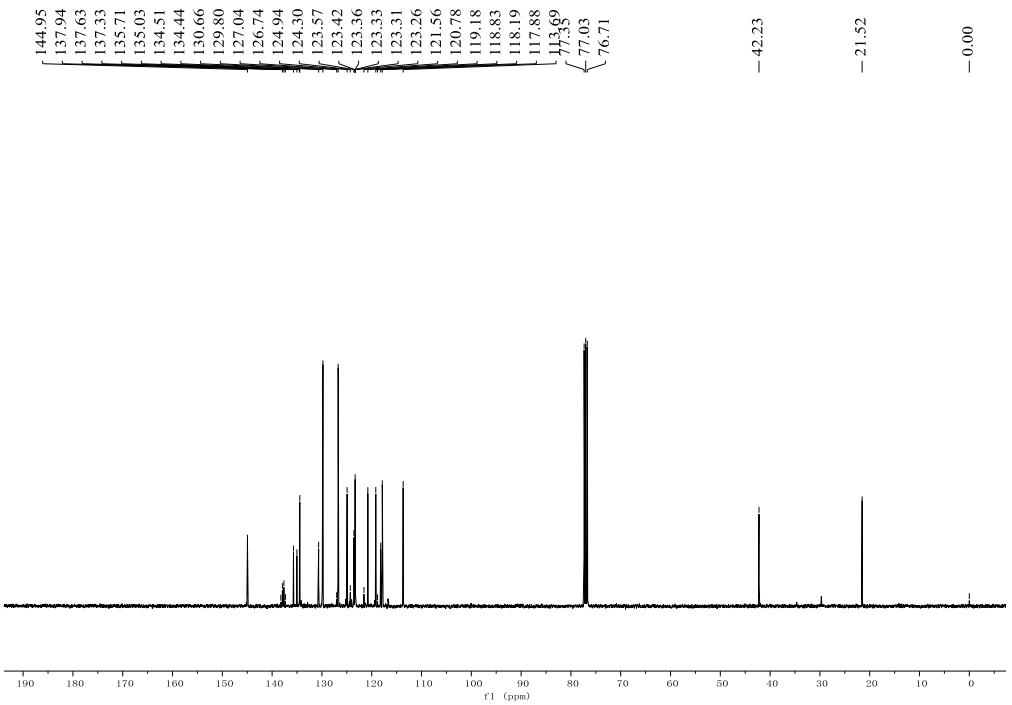
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.94 (m, 1H), 7.72 – 7.65 (m, 2H), 7.57 – 7.53 (m, 1H), 7.52 – 7.48 (m, 1H), 7.34 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 7.20 – 7.16 (m, 2H), 6.53 (d, *J* = 1.2 Hz, 1H), 5.91 (q, *J* = 1.4 Hz, 1H), 5.84 (ddt, *J* = 15.9, 11.0, 7.0 Hz, 1H), 5.41 (d, *J* = 1.1 Hz, 1H), 5.17 (t, *J* = 1.1 Hz, 1H), 5.16 – 5.11 (m, 1H), 3.14 – 3.07 (m, 2H), 2.31 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65. 00.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.95, 137.79 (q, *J* = 31.0 Hz), 135.71, 135.03, 134.51, 134.44, 130.66, 129.80, 126.74, 124.94, 123.57, 123.34 (q, *J* = 5.3 Hz), 123.33, 122.93 (q, *J* = 276.4 Hz), 120.78, 119.18, 118.19, 117.88, 113.69, 42.23, 21.52.

HRMS (ESI) m/z calcd for $C_{23}H_{20}F_3NO_2SNa$ $[M+Na]^+$: 454.1065, found: 454.1064.




144.95
137.94
137.63
137.33
135.71
135.03
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134.44
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124.30
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123.33
123.31
123.26
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117.88
113.69
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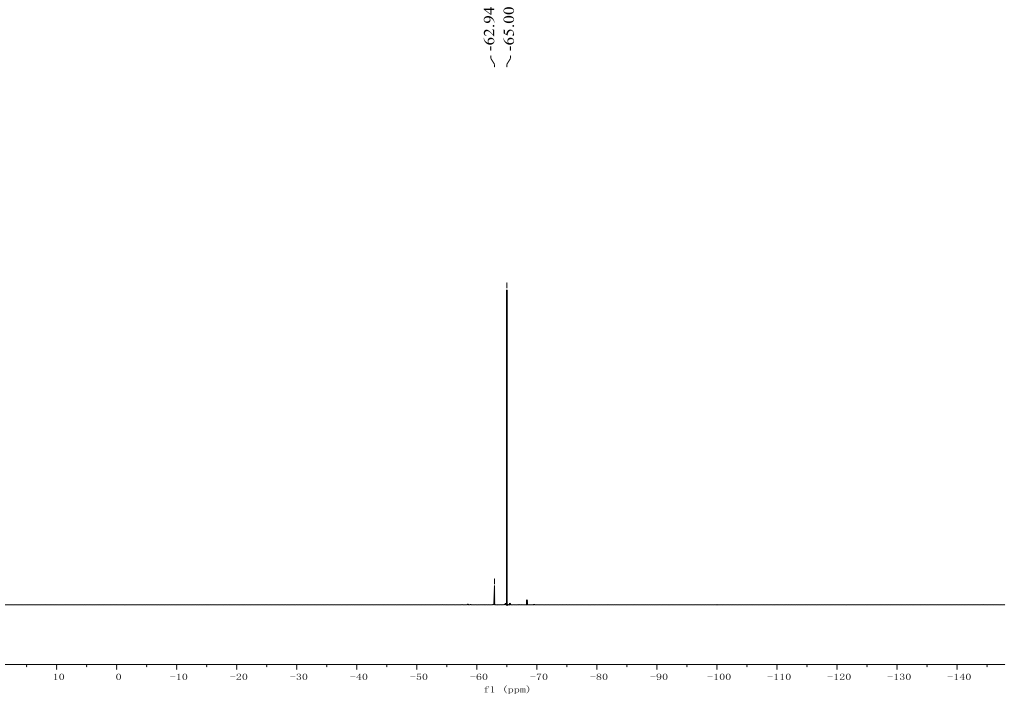
42.23
21.52
0.00
f1 (ppm)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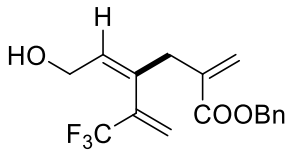
f1 (ppm)



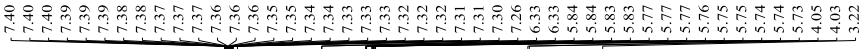
benzyl (*Z*)-6-hydroxy-2-methylene-4-(3,3,3-trifluoroprop-1-en-2-yl)hex-4-enoate (**5t**): Pale yellow oil, yield = 76% (**5t**:**5t'** = 80:20, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:5 as eluent).

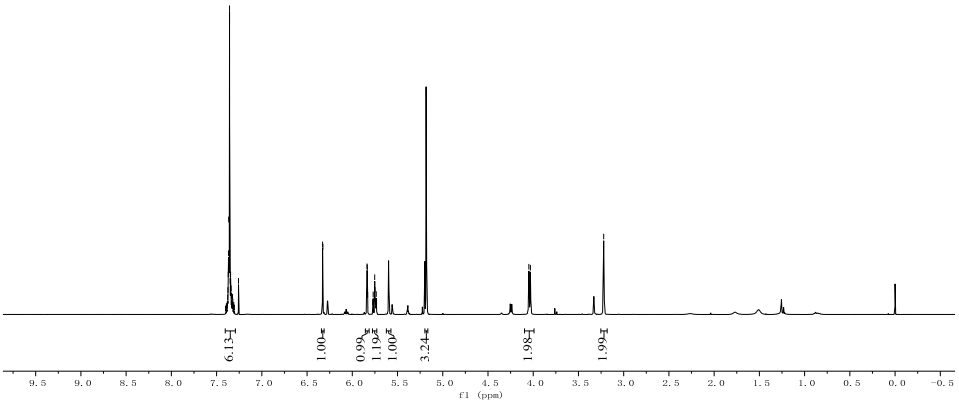
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 5H), 6.33 (d, *J* = 1.3 Hz, 1H), 5.84 (q, *J* = 1.4 Hz, 1H), 5.75 (tt, *J* = 6.8, 1.4 Hz, 1H), 5.60 (q, *J* = 1.2 Hz, 1H), 5.20 – 5.16 (m, 3H), 4.04 (d, *J* = 6.8 Hz, 2H), 3.22 (s, 2H).

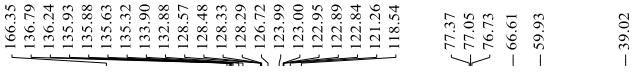
^{19}F NMR (376 MHz, Chloroform-*d*) δ -66.17.

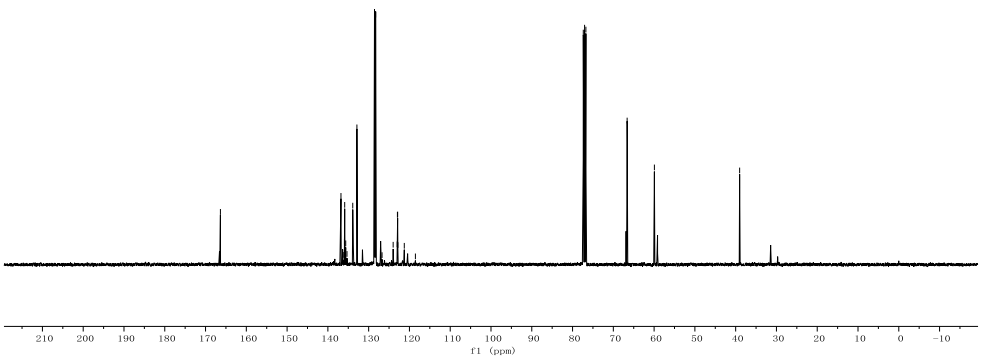
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.35, 136.79, 135.88, 135.78 (q, *J* = 31.1 Hz), 133.90, 132.88, 128.57, 128.48, 128.33, 128.29, 122.92 (q, *J* = 5.4 Hz), 122.63 (q, *J* = 275.5 Hz), 66.61, 59.93, 39.02.

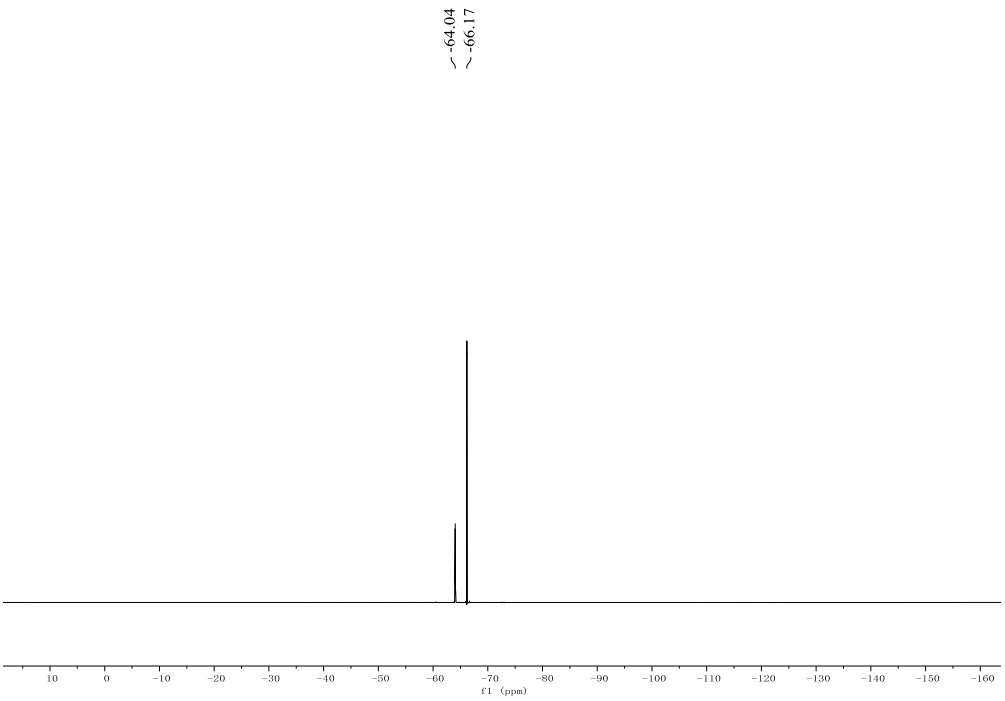
HRMS (ESI) m/z calcd for $C_{17}H_{17}F_3O_3Na$ $[M+Na]^+$: 349.1028, found: 349.1028.







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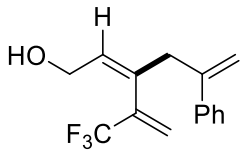
f1 (ppm)



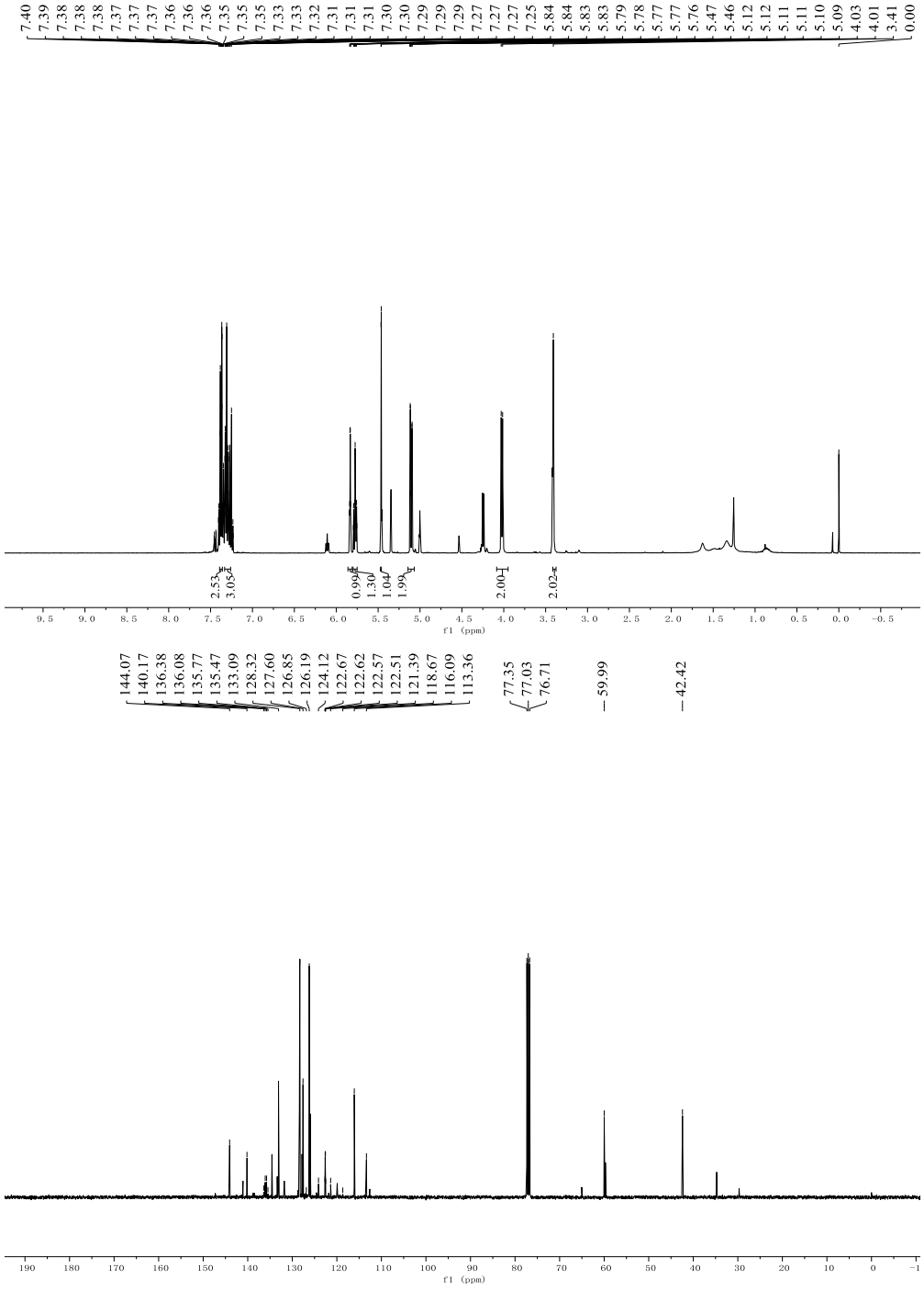
(*Z*)-5-phenyl-3-(3,3,3-trifluoroprop-1-en-2-yl)hexa-2,5-dien-1-ol (**5u**): Pale yellow oil, yield = 68% (**5u**:**5u'** = 72:28, isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:5 as eluent).

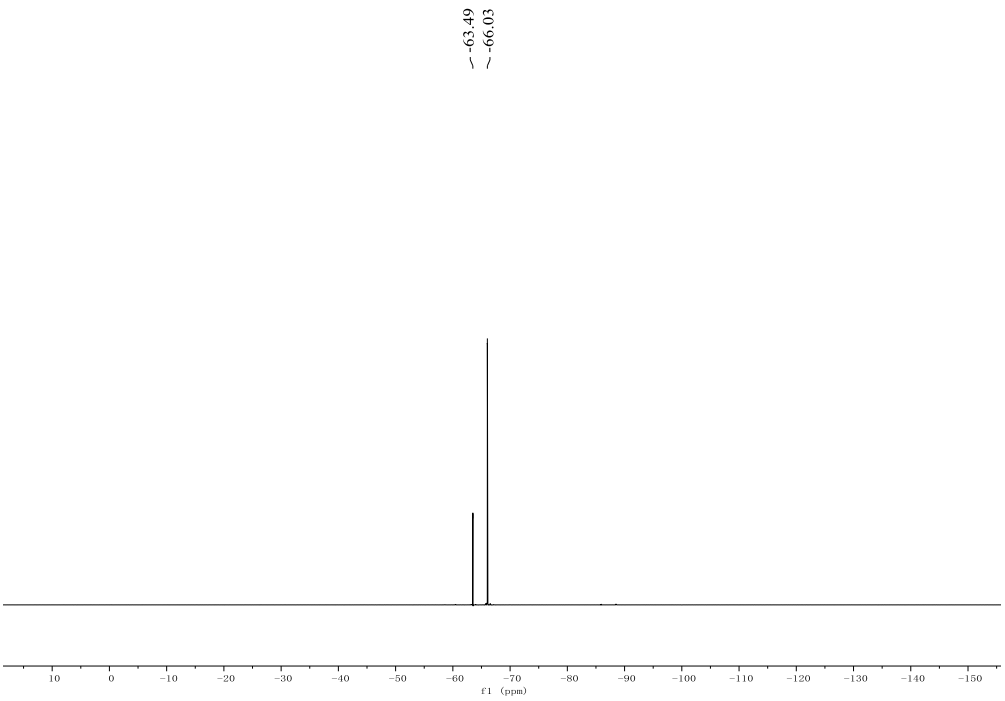
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.36 (m, 2H), 7.33 – 7.26 (m, 3H), 5.83 (q, *J* = 1.4 Hz, 1H), 5.77 (tt, *J* = 6.8, 1.4 Hz, 1H), 5.46 (d, *J* = 1.3 Hz, 1H), 5.14 – 5.07 (m, 2H), 4.02 (d, *J* = 6.8 Hz, 2H), 3.41 (s, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -66.03.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.07, 140.17, 135.92 (q, *J* = 30.8 Hz), 133.09, 128.32, 127.60, 126.19, 122.76 (q, *J* = 275.5 Hz), 122.59 (q, *J* = 5.5 Hz), 116.09, 113.36, 59.99, 42.42.

HRMS (ESI) m/z calcd for $C_{15}H_{15}F_3ONa$ $[M+Na]^+$: 291.0973, found: 291.0971.

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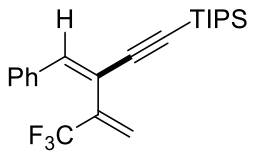
-150
f1 (ppm)



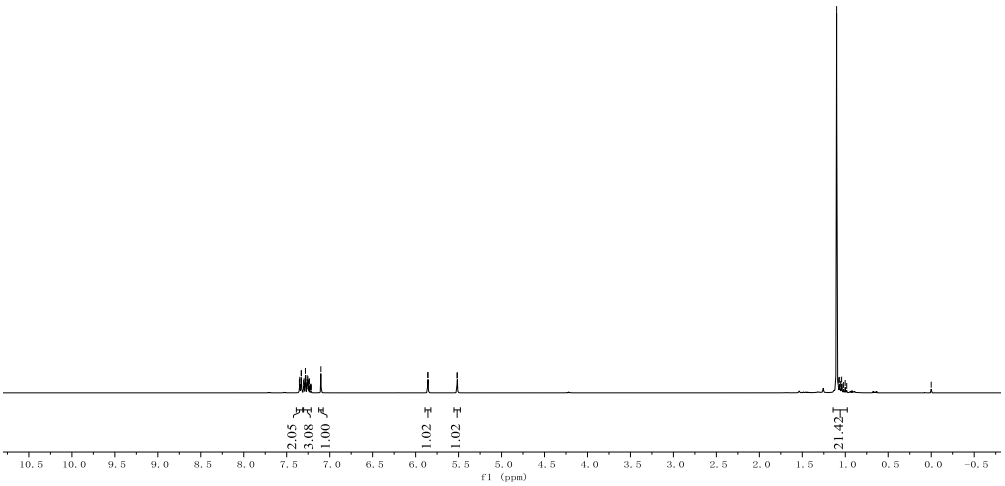
(*E*)-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)triisopropylsilane (**7a**)[1]: Colorless oil, yield = 80% (isolated with preparative thin layer chromatography and using hexane as eluent).

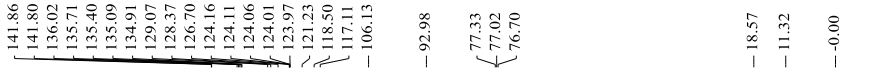
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 2H), 7.31 – 7.21 (m, 3H), 7.10 (s, 1H), 5.86 (d, *J* = 1.3 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 1.14 – 0.97 (m, 21H).

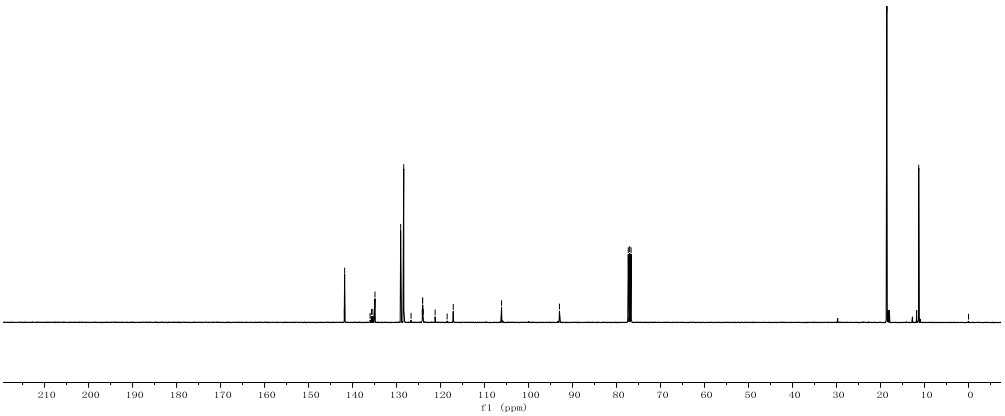
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.89.

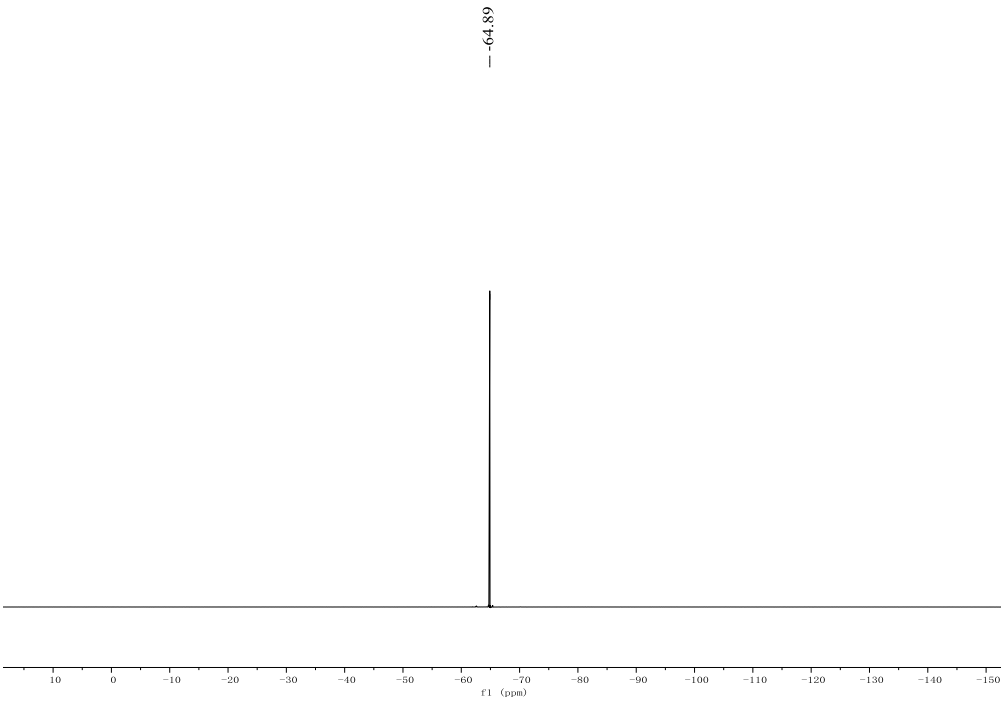
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.86, 141.80, 135.55 (q, *J* = 31.2 Hz), 134.91, 129.07, 128.37, 124.08 (q, *J* = 5.1 Hz), 122.60 (q, *J* = 274.9 Hz), 117.11, 106.13, 92.98, 18.57, 11.32.

HRMS (EI) m/z calcd for $C_{22}H_{29}F_3Si$ $[M]^+$: 378.1985, found: 378.1983.





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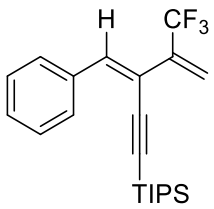
f1 (ppm)



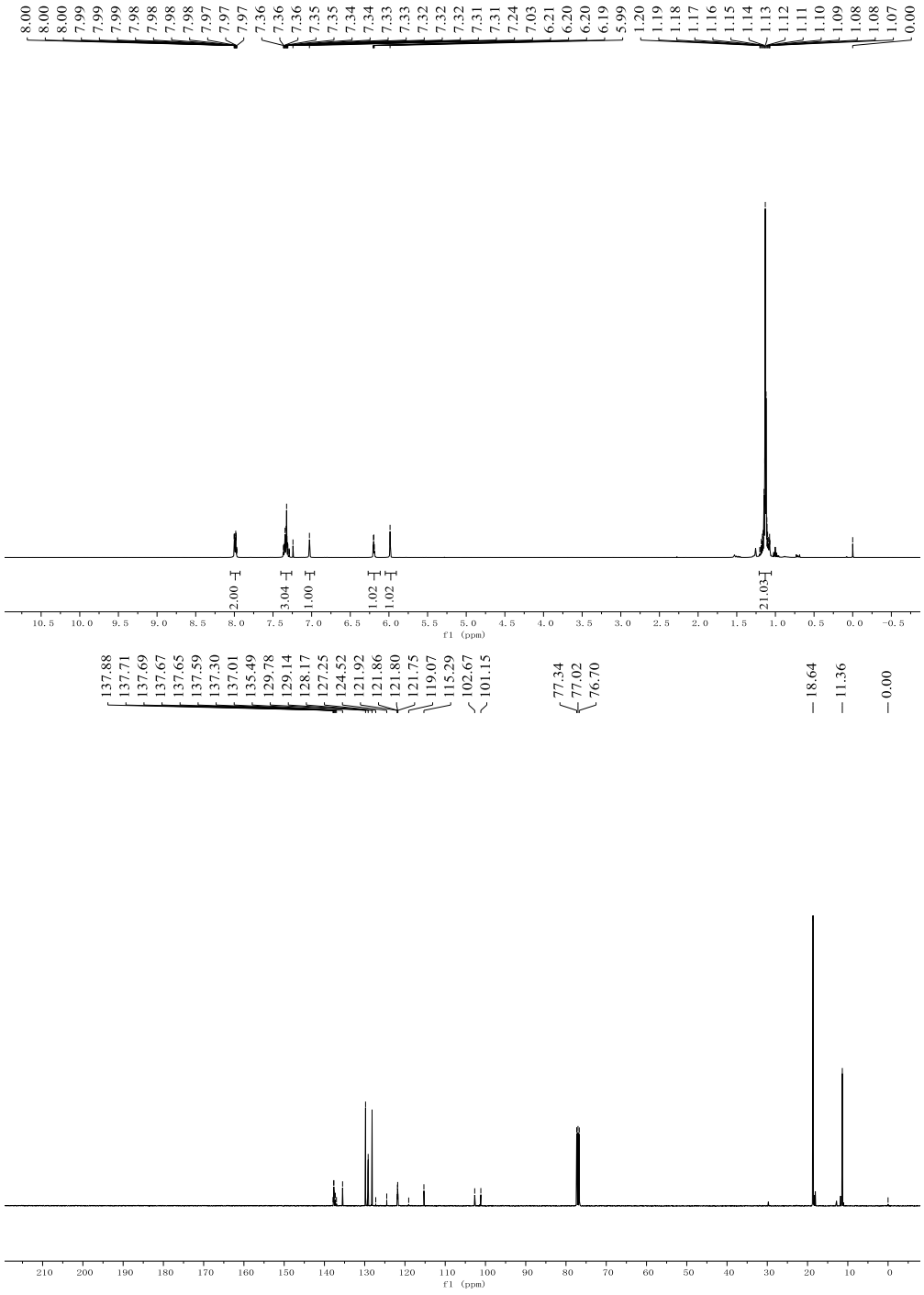
(*Z*)-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)triisopropylsilane (**7a'**)[2]: Colorless oil, yield = 77% (isolated with preparative thin layer chromatography and using hexane as eluent).

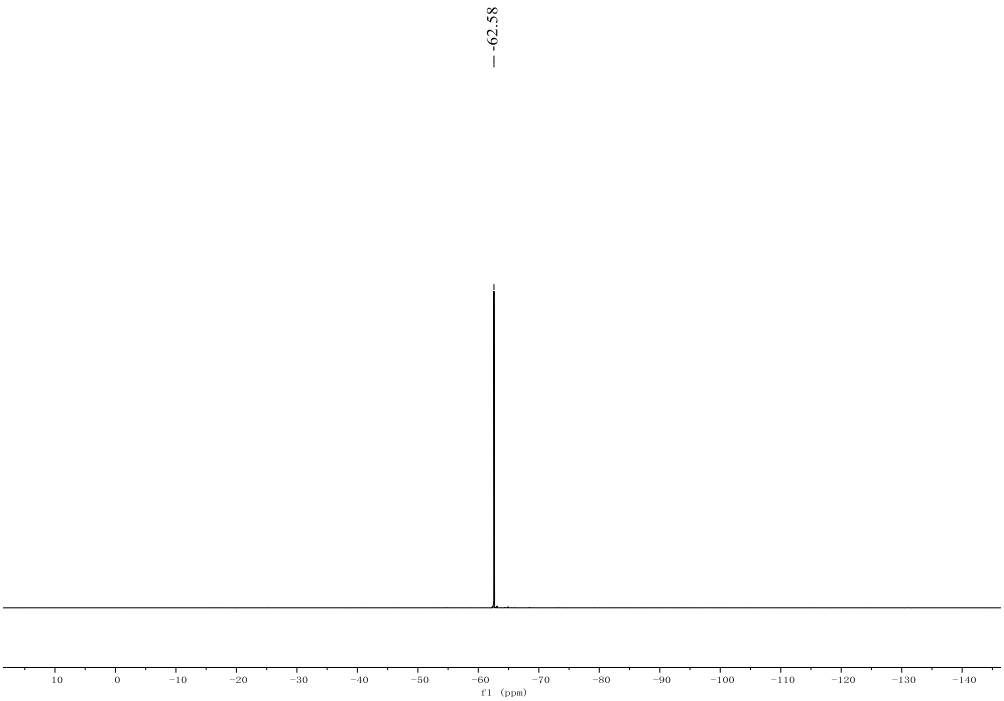
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.93 (m, 2H), 7.40 – 7.26 (m, 3H), 7.03 (s, 1H), 6.20 (q, *J* = 2.1 Hz, 1H), 5.99 (s, 1H), 1.21 – 1.05 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.58.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.68 (q, *J* = 1.9 Hz), 137.44 (q, *J* = 29.3 Hz), 135.49, 129.78, 129.14, 128.17, 123.16 (q, *J* = 275.5 Hz), 121.83 (q, *J* = 5.6 Hz), 115.29, 102.67, 101.15, 18.64, 11.36.

HRMS (EI) m/z calcd for $C_{22}H_{29}F_3Si$ $[M]^+$: 378.1985, found: 378.1979.

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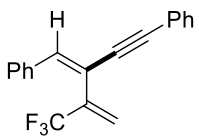
f1 (ppm)



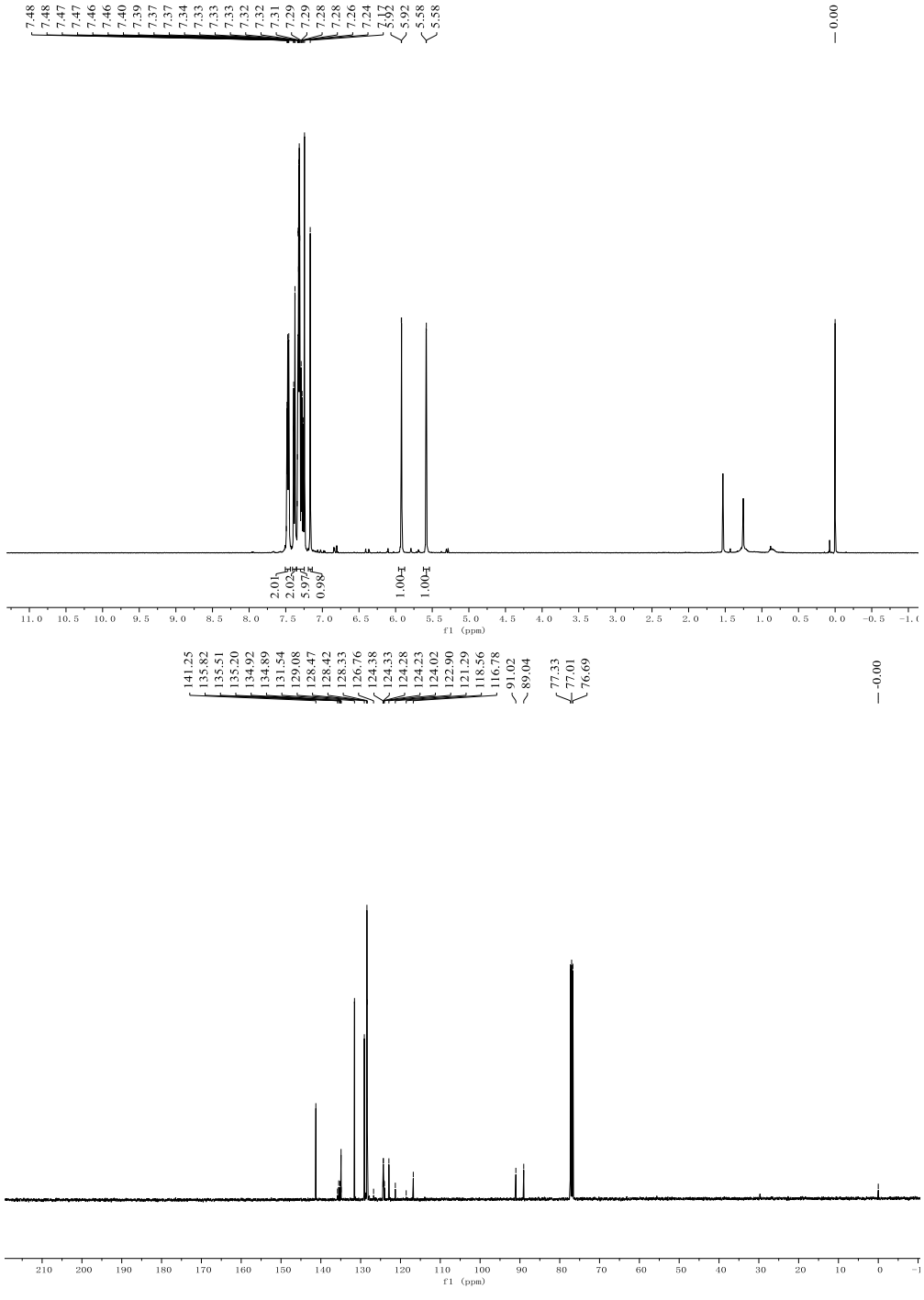
(*Z*)-(2-(3,3,3-trifluoroprop-1-en-2-yl)but-1-en-3-yne-1,4-diyl)dibenzene (**7b**): Colorless oil, yield = 64% (isolated with preparative thin layer chromatography and using hexane as eluent).

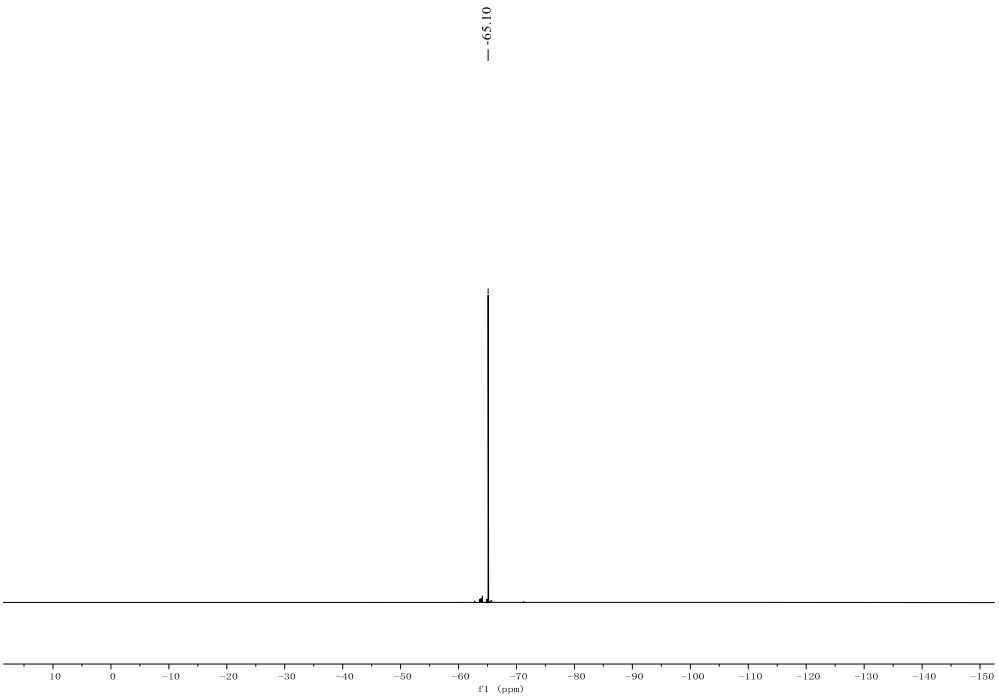
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.25 (m, 6H), 7.17 (s, 1H), 5.92 (d, *J* = 1.3 Hz, 1H), 5.58 (d, *J* = 1.3 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.10.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.25, 135.35 (q, *J* = 31.2 Hz), 134.92, 131.54, 129.08, 128.47, 128.42, 128.33, 124.31 (q, *J* = 5.1 Hz), 122.90, 122.60 (q, *J* = 275.9 Hz), 116.78, 91.02, 89.04.

HRMS (EI) m/z calcd for $C_{19}H_{13}F_3$ $[M]^+$: 298.0964, found: 298.0962.

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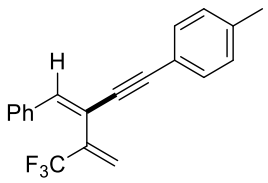
f1 (ppm)



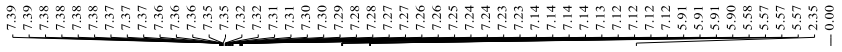
(*Z*)-1-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)-4-methylbenzene (**7c**): Colorless oil, yield = 61% (isolated with preparative thin layer chromatography and using hexane as eluent).

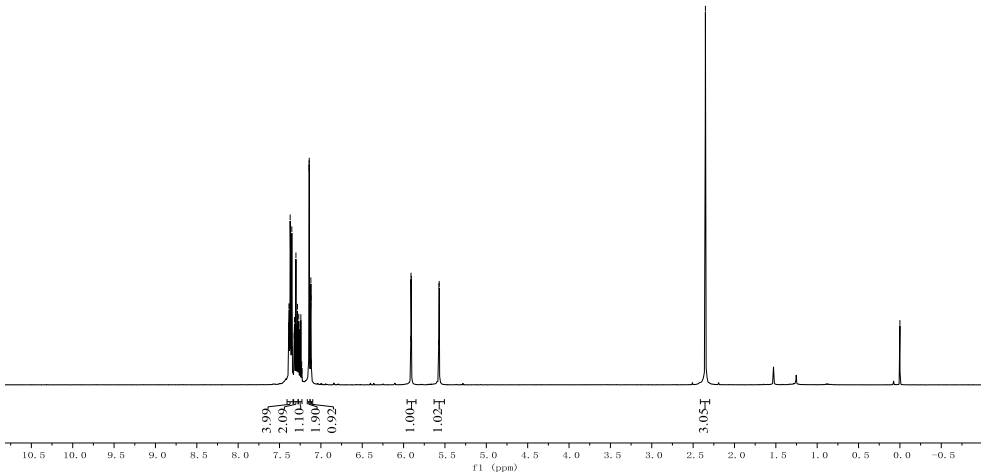
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 4H), 7.33 – 7.27 (m, 2H), 7.27 – 7.22 (m, 1H), 7.16 – 7.13 (m, 2H), 7.13 – 7.10 (m, 1H), 5.91 (q, *J* = 1.3 Hz, 1H), 5.57 (q, *J* = 1.3 Hz, 1H), 2.35 (s, 3H).

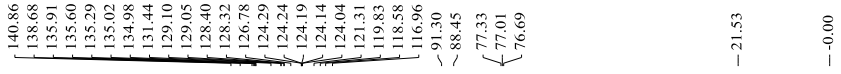
^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.09.

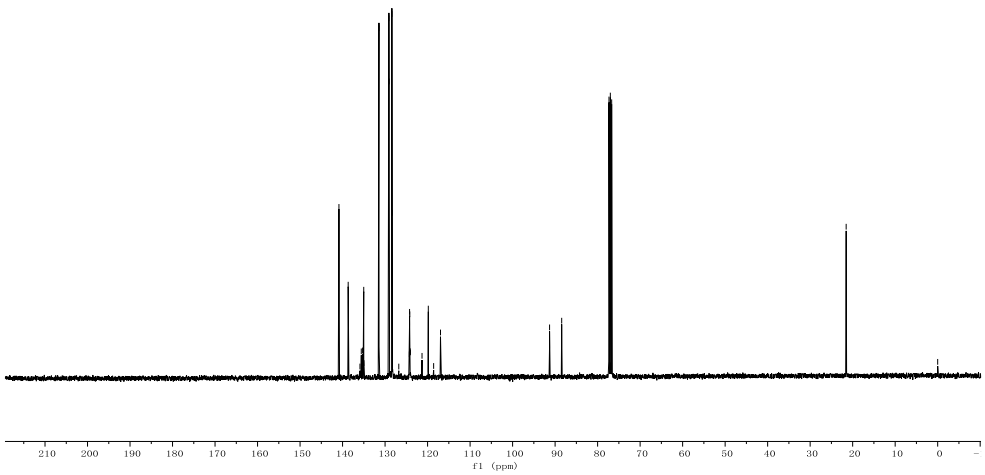
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.86, 138.68, 135.44 (q, *J* = 31.2 Hz), 135.02, 131.44, 129.10, 129.05, 128.40, 128.32, 124.21 (q, *J* = 5.1 Hz), 122.68 (q, *J* = 274.8 Hz), 119.83, 116.96, 91.30, 88.45, 21.53.

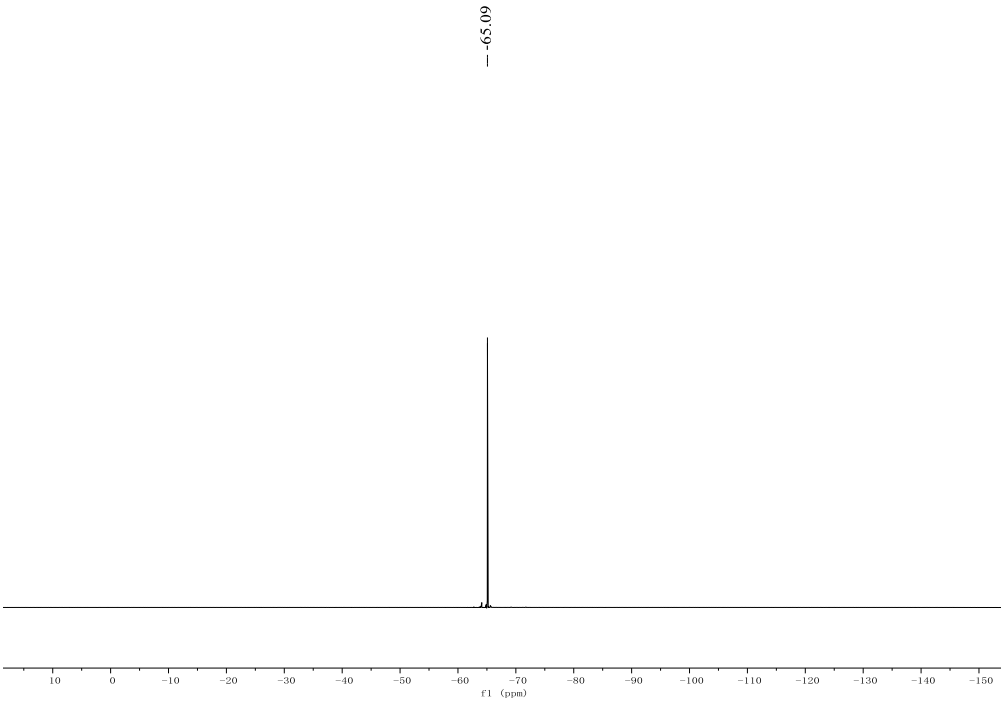
HRMS (EI) m/z calcd for $C_{20}H_{15}F_3$ $[M]^+$: 312.1120, found: 312.1121.







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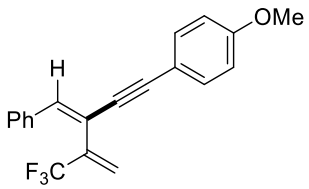
f1 (ppm)



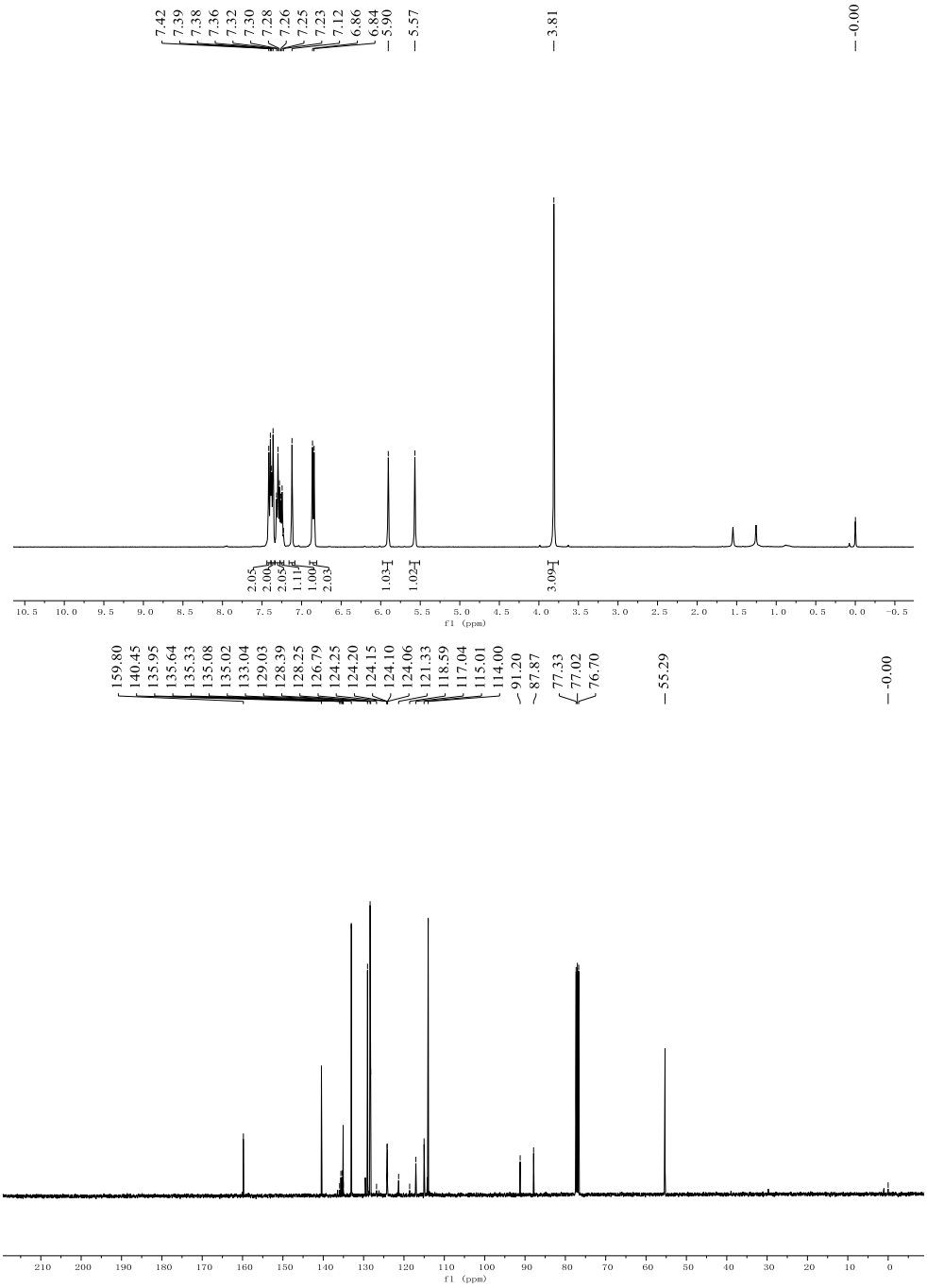
(*Z*)-1-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)-4-methoxybenzene (**7d**): Pale yellow oil, yield = 59% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:100 as eluent).

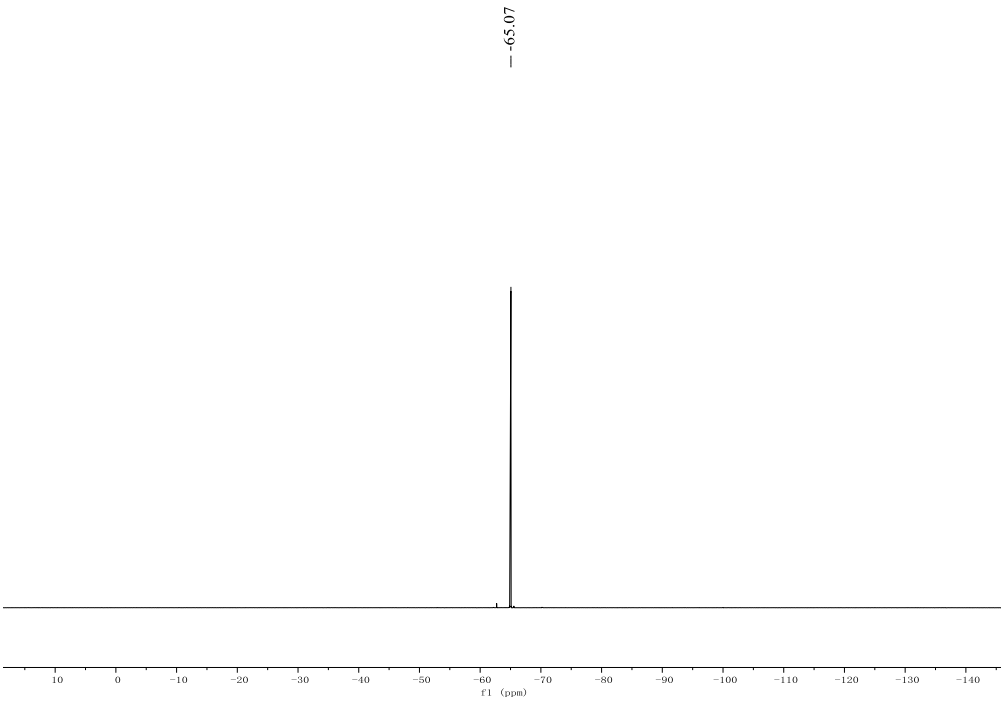
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.12 (s, 1H), 6.85 (d, *J* = 8.1 Hz, 2H), 5.90 (s, 1H), 5.57 (s, 1H), 3.81 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.07.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.80, 140.45, 135.48 (q, *J* = 31.1 Hz), 135.08, 133.04, 129.03, 128.39, 128.25, 124.17 (q, *J* = 5.1 Hz), 122.69 (q, *J* = 274.8 Hz), 117.04, 115.01, 114.00, 91.20, 87.87, 55.29.

HRMS (EI) m/z calcd for $C_{20}H_{15}F_3O$ $[M]^+$: 328.1070, found: 328.1070.

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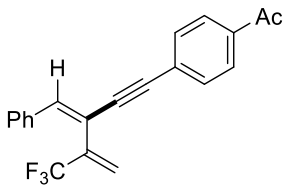
f1 (ppm)



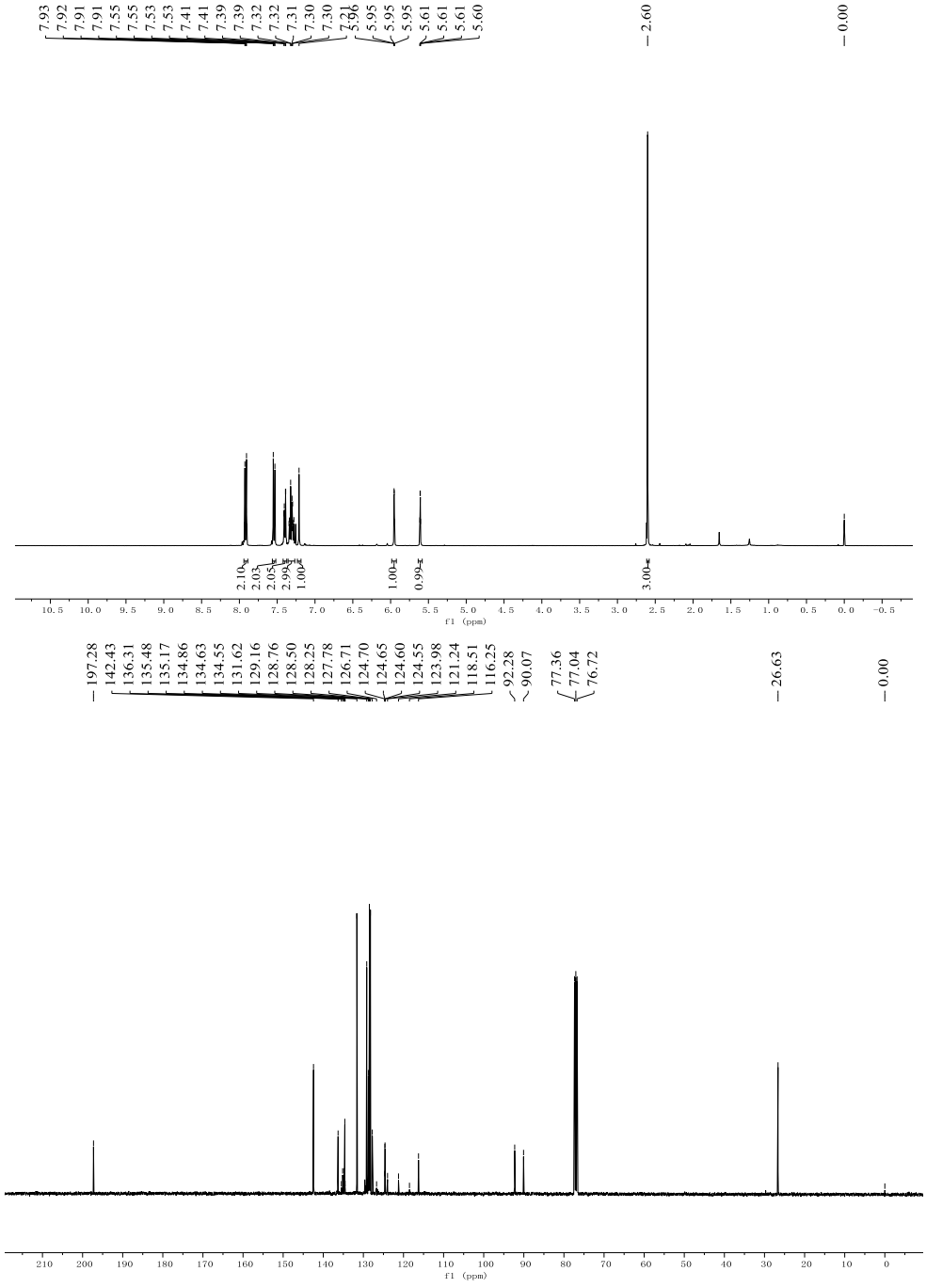
(*Z*)-1-(4-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)phenyl)ethan-1-one (**7e**): White solid, yield = 69% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:20 as eluent).

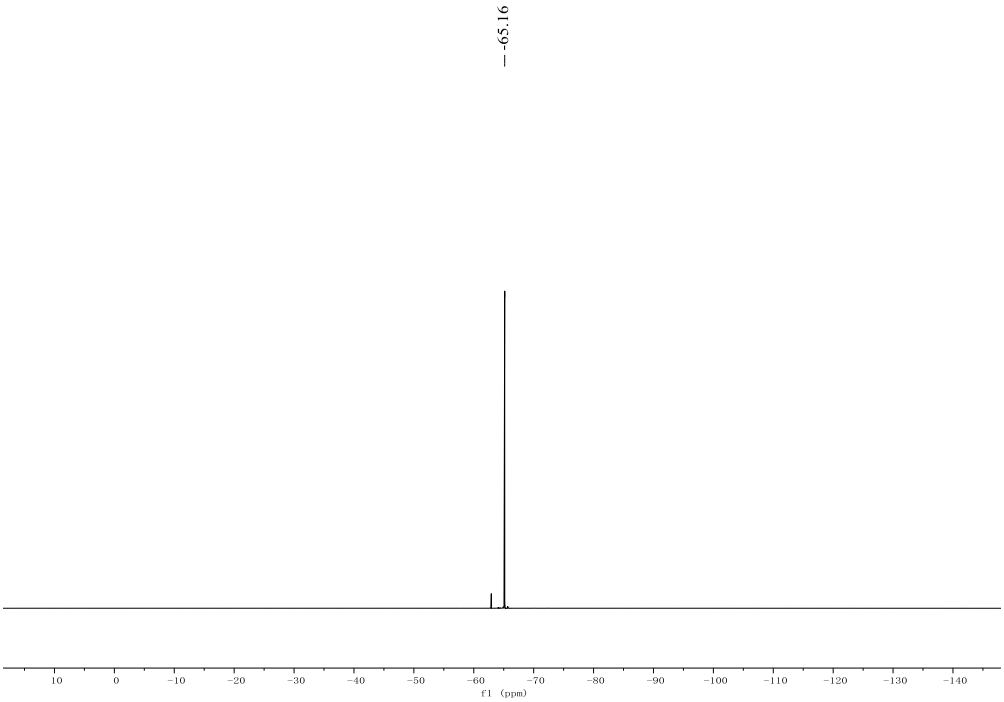
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.89 (m, 2H), 7.57 – 7.52 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 7.21 (s, 1H), 5.95 (q, *J* = 1.3 Hz, 1H), 5.61 (q, *J* = 1.2 Hz, 1H), 2.60 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.16.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.28, 142.43, 136.31, 135.01 (q, *J* = 31.2 Hz), 134.63, 131.62, 129.16, 128.76, 128.50, 128.25, 127.78, 124.62 (q, *J* = 5.0 Hz), 122.61 (q, *J* = 274.8 Hz), 116.25, 92.28, 90.07, 26.63.

HRMS (ESI) m/z calcd for $C_{21}H_{16}F_3O$ $[M+H]^+$: 341.1153, found: 341.1151.

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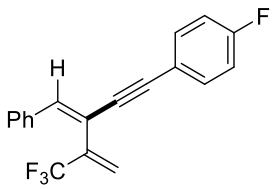
f1 (ppm)



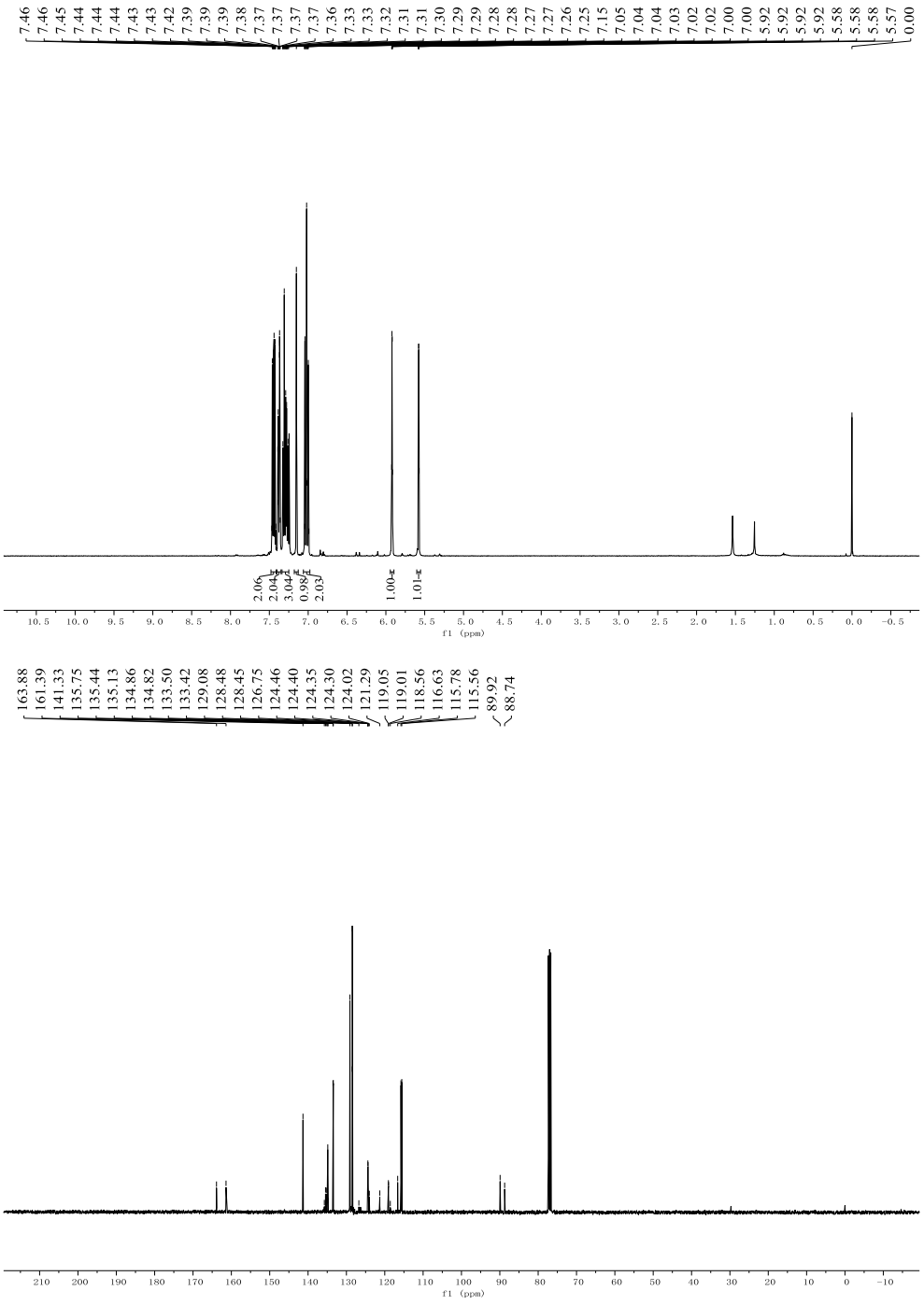
(*Z*)-1-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)-4-fluorobenzene (**7f**): Pale yellow oil, yield = 66% (isolated with preparative thin layer chromatography and using hexane as eluent).

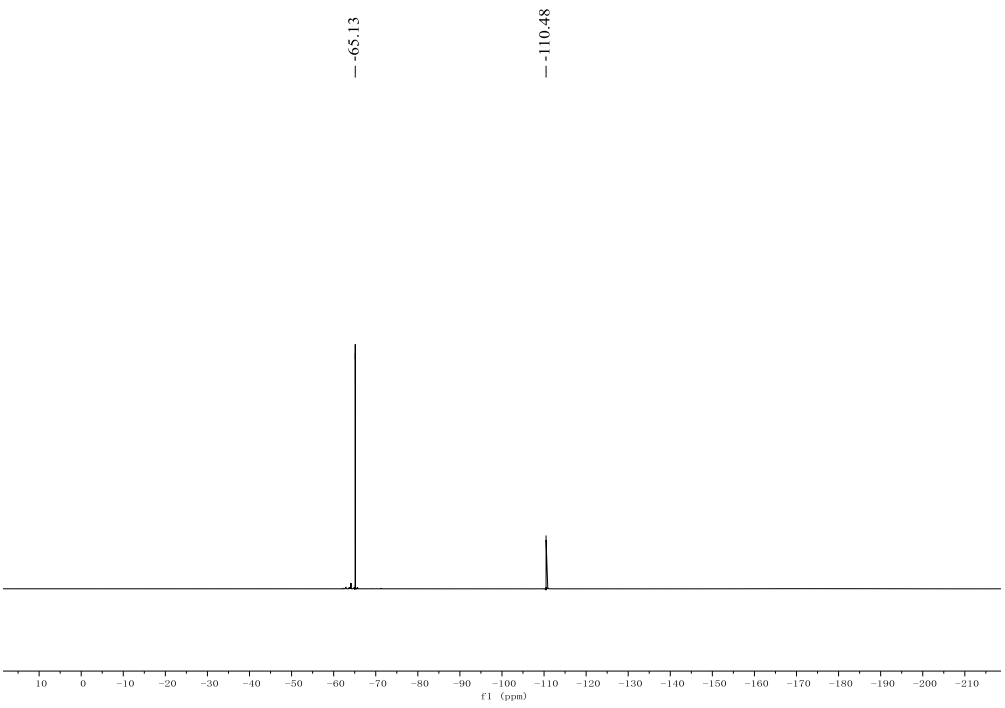
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.25 (m, 3H), 7.15 (s, 1H), 7.06 – 6.98 (m, 2H), 5.92 (q, *J* = 1.3 Hz, 1H), 5.58 (q, *J* = 1.2 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.13, -110.48.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.63 (d, *J* = 250.0 Hz), 141.33, 135.29 (q, *J* = 31.1 Hz), 134.86, 133.46 (d, *J* = 8.4 Hz), 129.08, 128.48, 128.45, 124.38 (q, *J* = 5.1 Hz), 122.66 (q, *J* = 274.8 Hz), 119.03 (d, *J* = 3.5 Hz), 116.63, 115.67 (d, *J* = 22.2 Hz), 89.92, 88.74.

HRMS (EI) m/z calcd for $C_{19}H_{12}F_4$ $[M]^+$: 316.0870, found: 316.0872.




-65.13
-110.48
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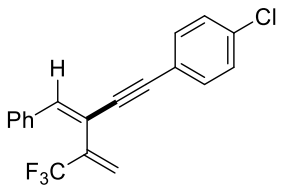
f1 (ppm)



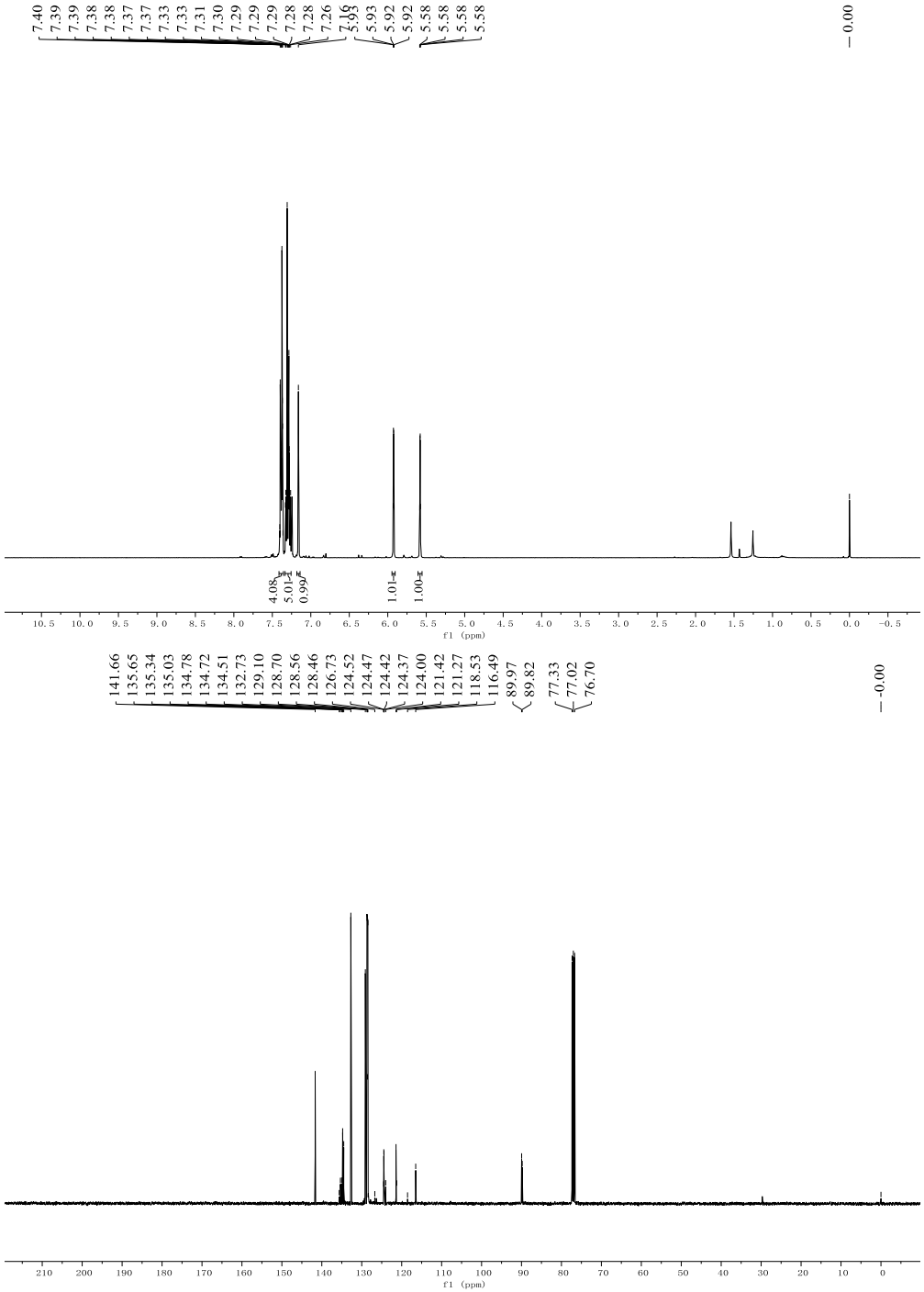
(*Z*)-1-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)-4-chlorobenzene (**7g**): Pale yellow oil, yield = 65% (isolated with preparative thin layer chromatography and using hexane as eluent).

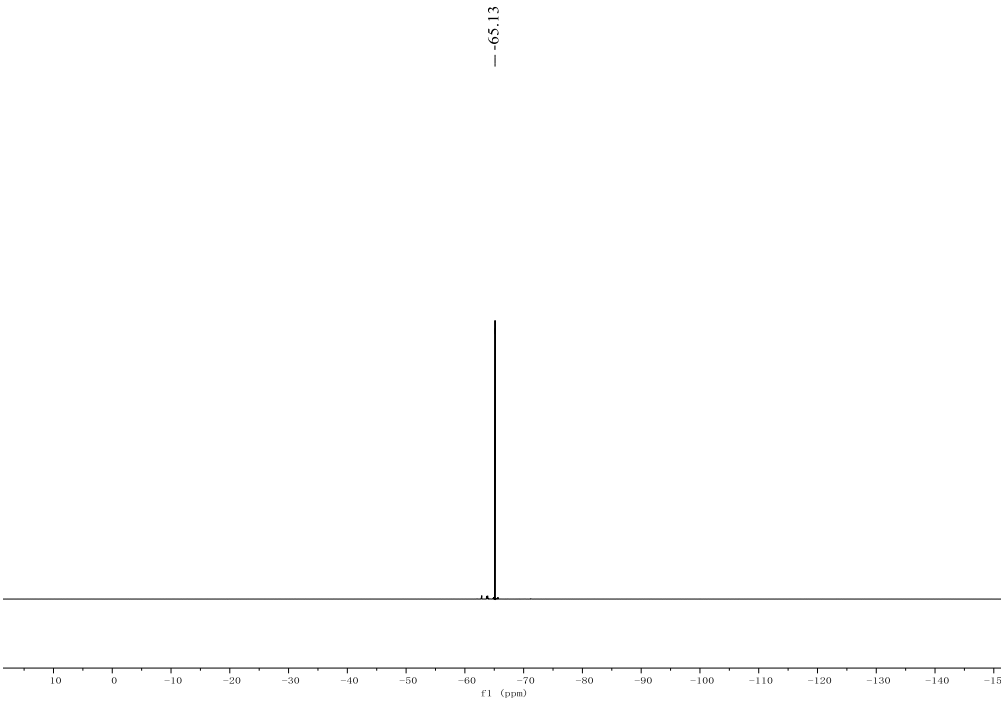
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 4H), 7.33 – 7.26 (m, 5H), 7.16 (s, 1H), 5.92 (q, *J* = 1.3 Hz, 1H), 5.58 (q, *J* = 1.2 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.13.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.66, 135.19 (q, *J* = 31.2 Hz), 134.78, 134.51, 132.73, 129.10, 128.70, 128.56, 128.46, 124.45 (q, *J* = 5.1 Hz), 122.63 (q, *J* = 274.8 Hz), 121.42, 116.49, 89.97, 89.82.

HRMS (EI) m/z calcd for $C_{19}H_{12}F_3Cl$ $[M]^+$: 332.0874, found: 332.0871.

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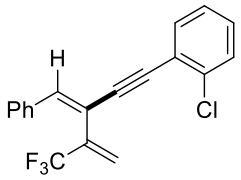
f1 (ppm)



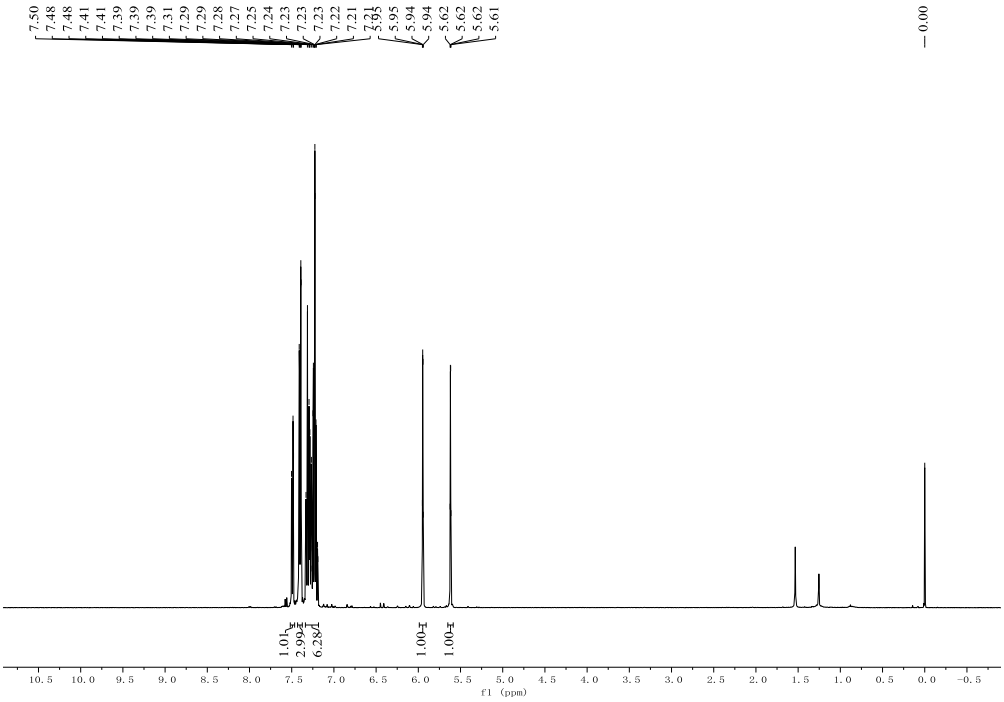
(*Z*)-1-(3-benzylidene-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)-2-chlorobenzene (**7h**): Pale yellow oil, yield = 75% (isolated with preparative thin layer chromatography and using hexane as eluent).

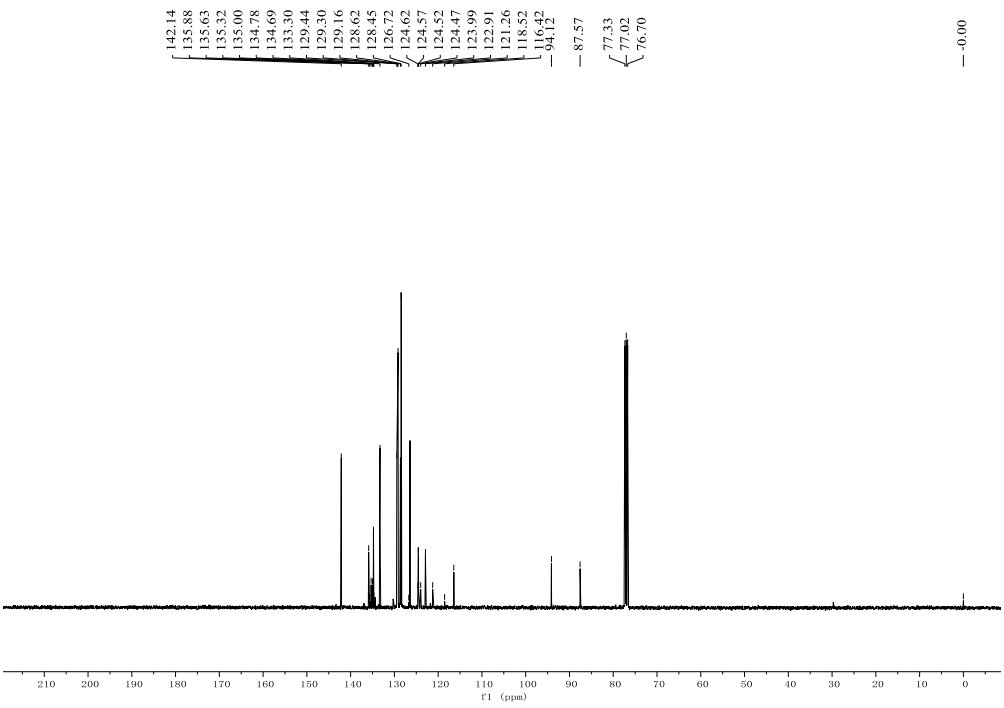
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 1H), 7.43 – 7.37 (m, 3H), 7.34 – 7.18 (m, 6H), 5.95 (q, *J* = 1.3 Hz, 1H), 5.62 (q, *J* = 1.2 Hz, 1H).

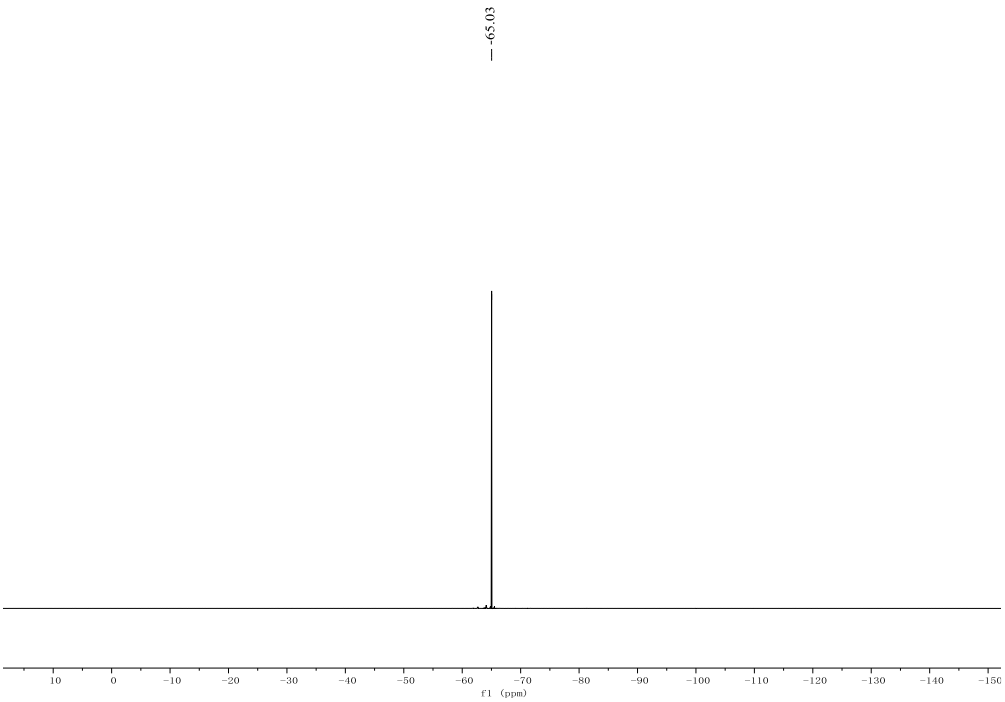
^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.03.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.14, 135.88, 135.16 (q, *J* = 31.4 Hz), 134.78, 133.30, 129.44, 129.30, 129.16, 128.62, 128.45, 126.43, 124.55 (q, *J* = 5.1 Hz), 122.91, 122.62 (q, *J* = 274.9 Hz), 116.42, 94.12, 87.57.

HRMS (EI) m/z calcd for $C_{19}H_{12}F_3Cl$ $[M]^+$: 332.0874, found: 332.0875.



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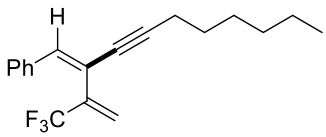
f1 (ppm)



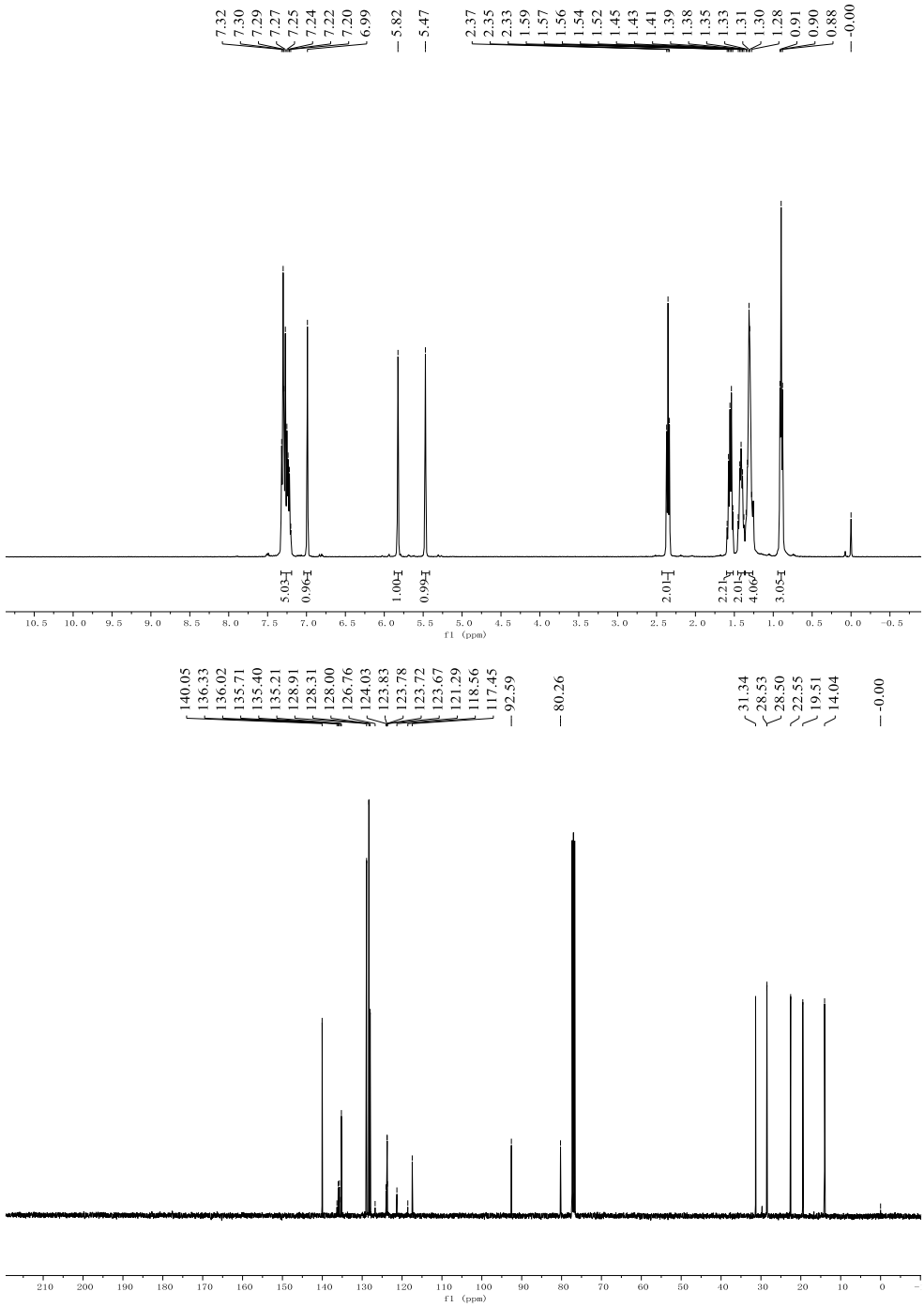
(*Z*)-(2-(3,3,3-trifluoroprop-1-en-2-yl)dec-1-en-3-yn-1-yl)benzene (**7i**): Pale yellow oil, yield = 48% (isolated with preparative thin layer chromatography and using hexane as eluent).

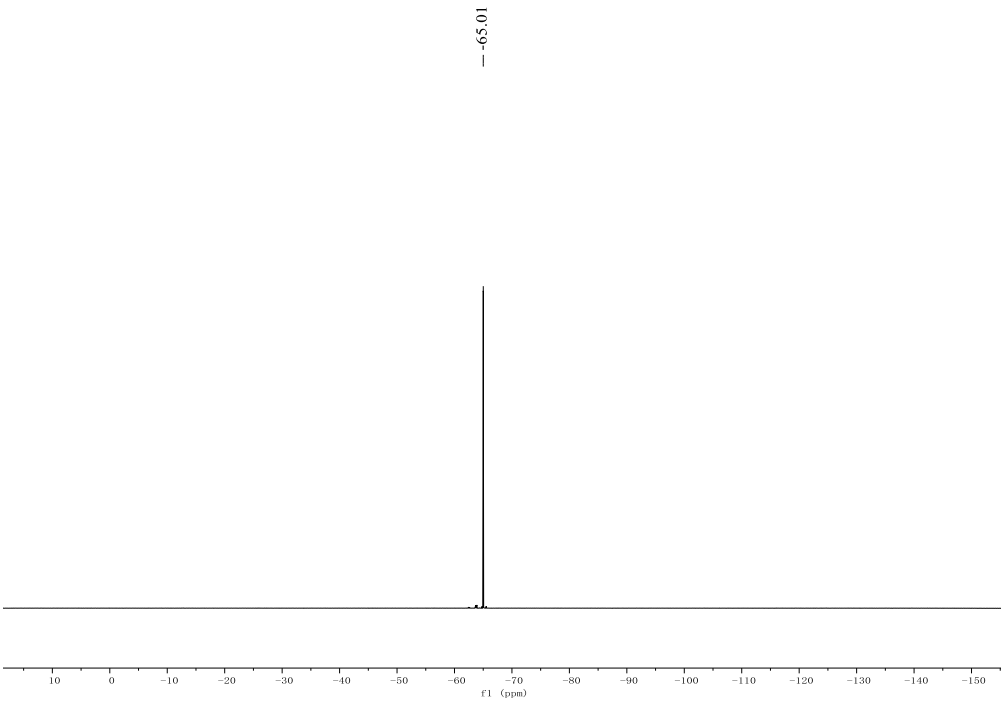
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.17 (m, 5H), 6.99 (s, 1H), 5.82 (s, 1H), 5.47 (s, 1H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.46 – 1.37 (m, 2H), 1.36 – 1.26 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.01.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.05, 135.86 (q, *J* = 30.9 Hz), 135.21, 128.91, 128.31, 128.00, 123.75 (q, *J* = 5.0 Hz), 122.66 (q, *J* = 275.0 Hz), 117.45, 92.59, 80.26, 31.34, 28.53, 28.50, 22.55, 19.51, 14.04.

HRMS (EI) m/z calcd for $C_{19}H_{21}F_3$ $[M]^+$: 306.1590, found: 306.1589.

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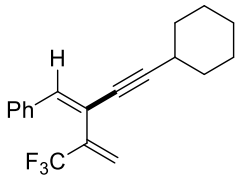
f1 (ppm)



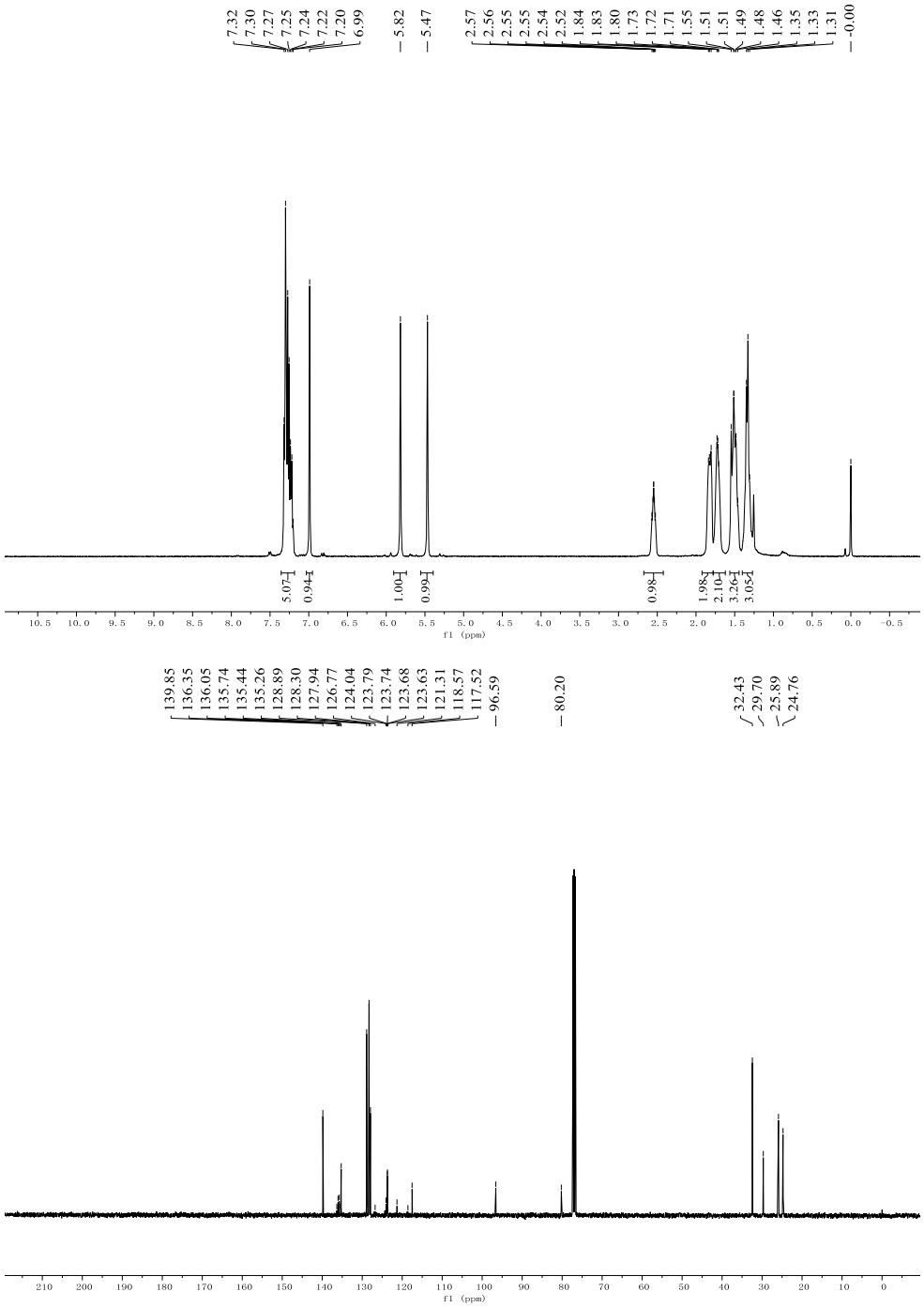
(*Z*)-(2-(cyclohexylethynyl)-3-(trifluoromethyl)buta-1,3-dien-1-yl)benzene (**7j**): Pale yellow oil, yield = 57% (isolated with preparative thin layer chromatography and using hexane as eluent).

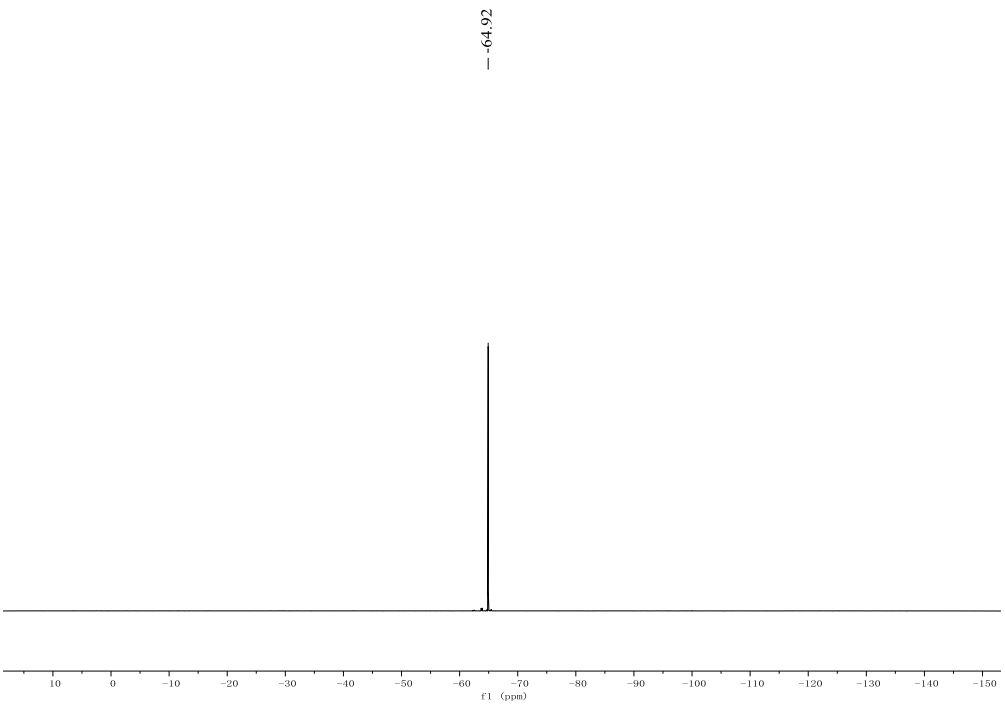
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.19 (m, 5H), 6.99 (s, 1H), 5.82 (s, 1H), 5.47 (s, 1H), 2.67 – 2.42 (m, 1H), 1.92 – 1.78 (m, 2H), 1.78 – 1.63 (m, 2H), 1.57 – 1.44 (m, 3H), 1.40 – 1.27 (m, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.92.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.85, 135.90 (q, *J* = 30.7 Hz), 135.26, 128.89, 128.30, 127.94, 123.71 (q, *J* = 5.0 Hz), 122.67 (q, *J* = 275.0 Hz), 117.52, 96.59, 80.20, 32.43, 29.70, 25.89, 24.76.

HRMS (EI) m/z calcd for $C_{19}H_{19}F_3$ $[M]^+$: 304.1433, found: 304.1434.

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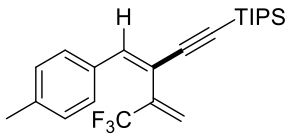
f1 (ppm)



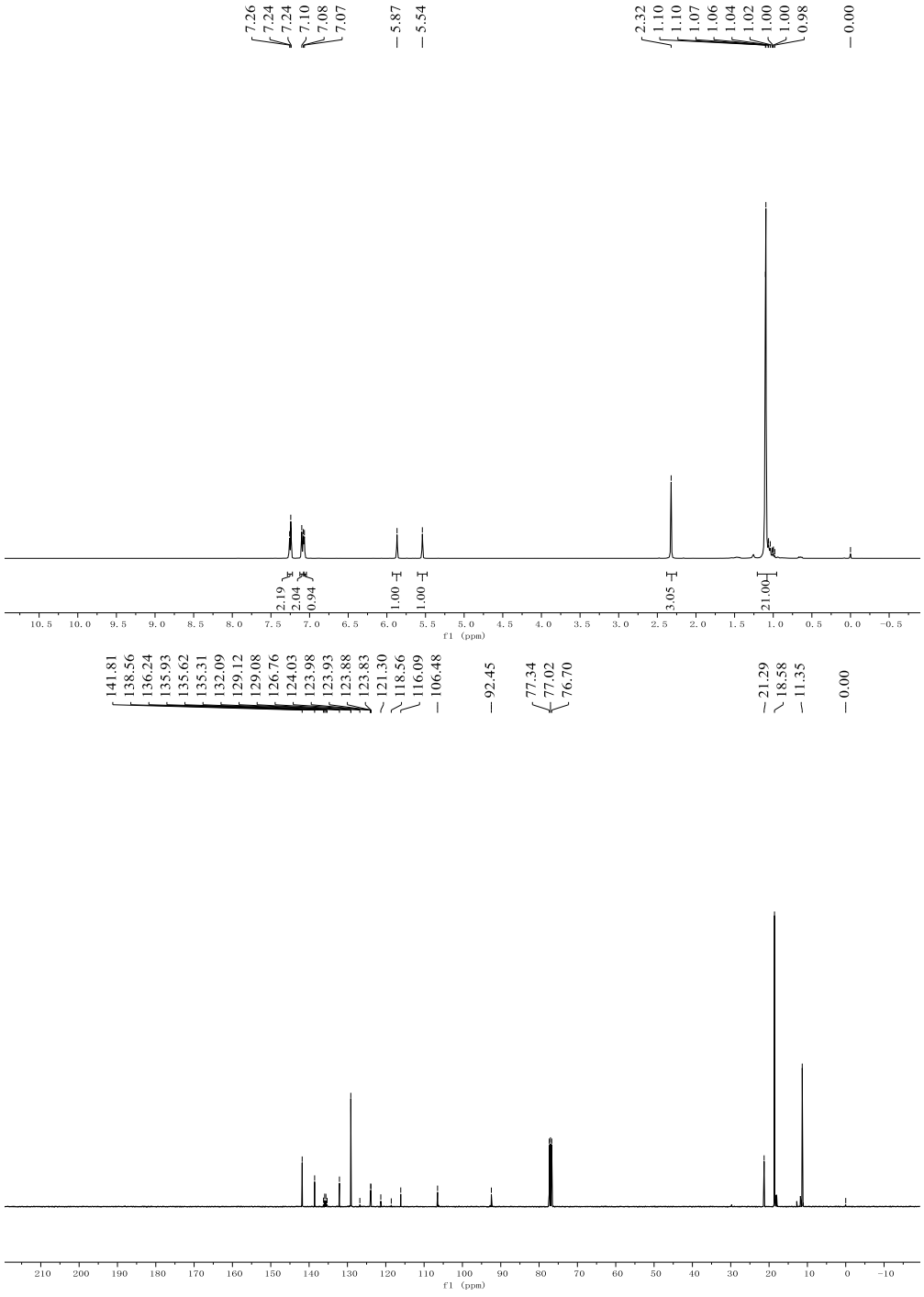
(*E*)-triisopropyl(3-(4-methylbenzylidene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)silane (**7k**): Colorless oil, yield = 78% (isolated with preparative thin layer chromatography and using hexane as eluent).

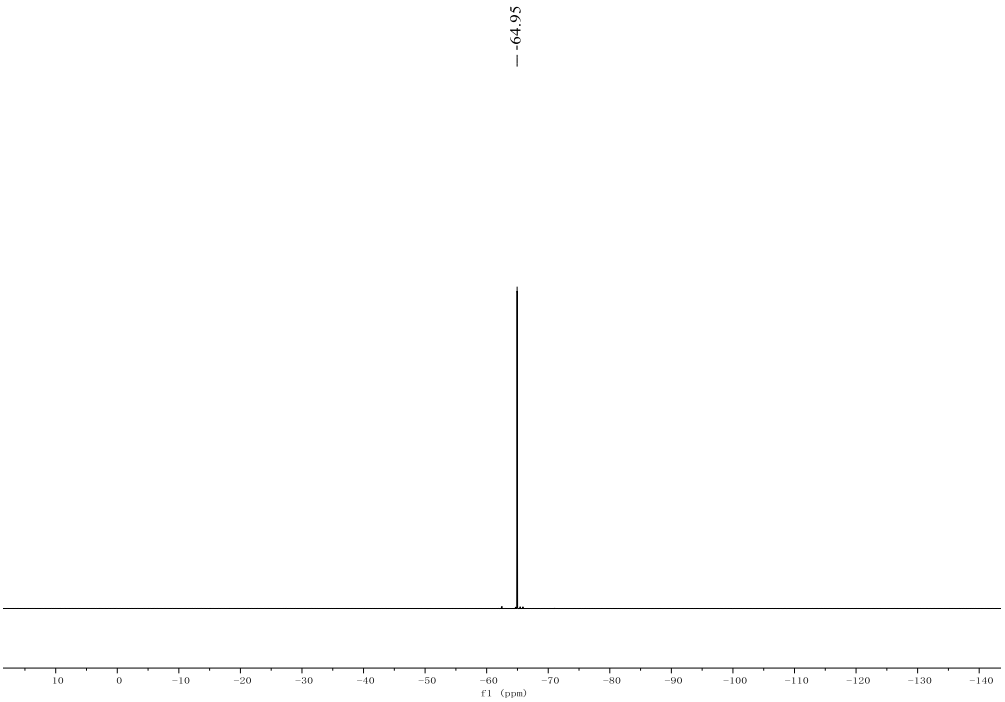
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 1H), 5.87 (s, 1H), 5.54 (s, 1H), 2.32 (s, 3H), 1.18 – 0.96 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.95.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.81, 138.56, 135.77 (q, *J* = 31.2 Hz), 132.09, 129.12, 129.08, 123.90 (q, *J* = 5.0 Hz), 122.66 (q, *J* = 276.1 Hz), 116.09, 106.48, 92.45, 21.29, 18.58, 11.35.

HRMS (EI) m/z calcd for $C_{23}H_{31}F_3Si$ $[M]^+$: 392.2142, found: 392.2145.

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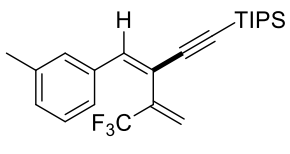


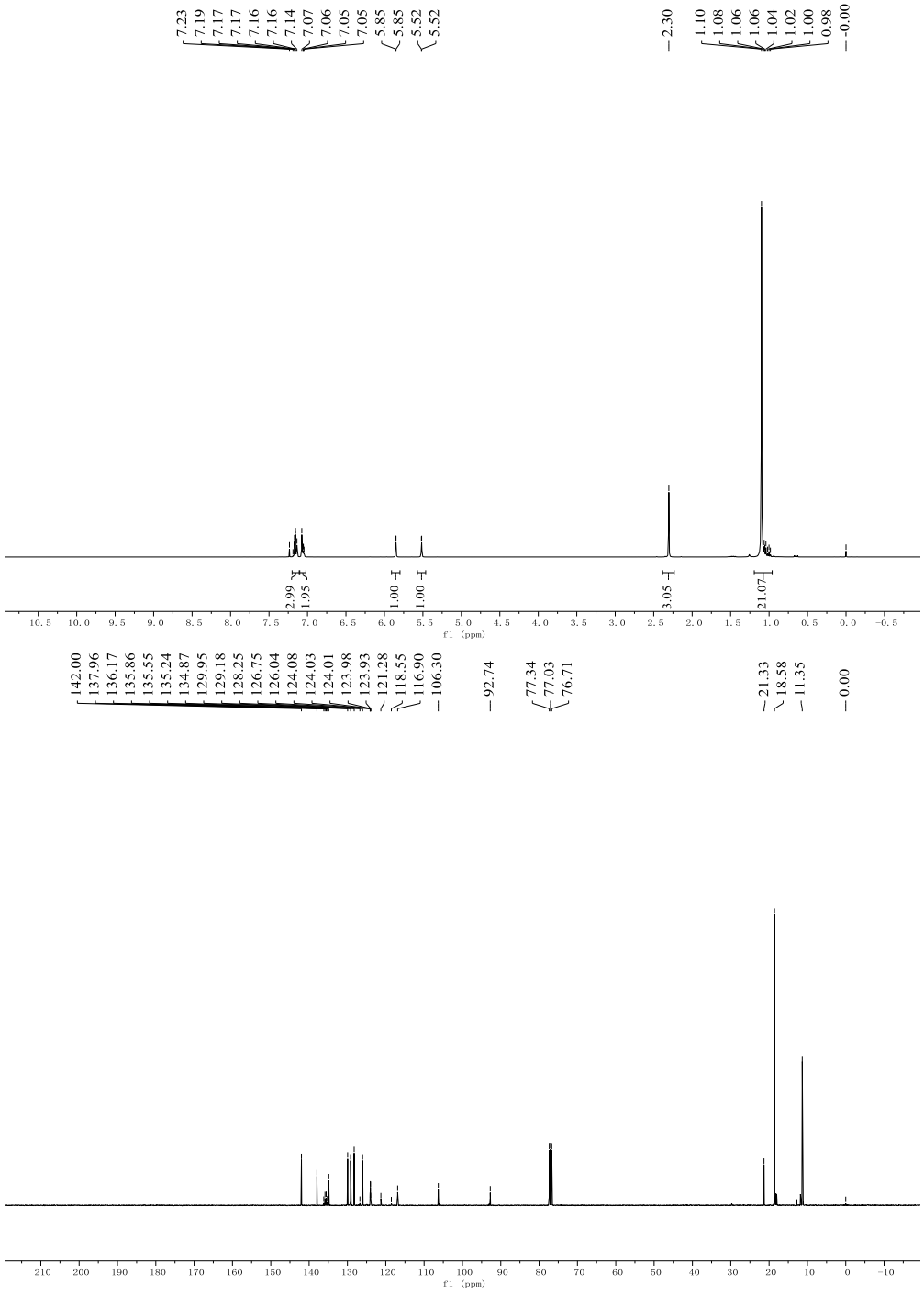
(*E*)-triisopropyl(3-(3-methylbenzylidene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)silane (**7l**): Colorless oil, yield = 83% (isolated with preparative thin layer chromatography and using hexane as eluent).

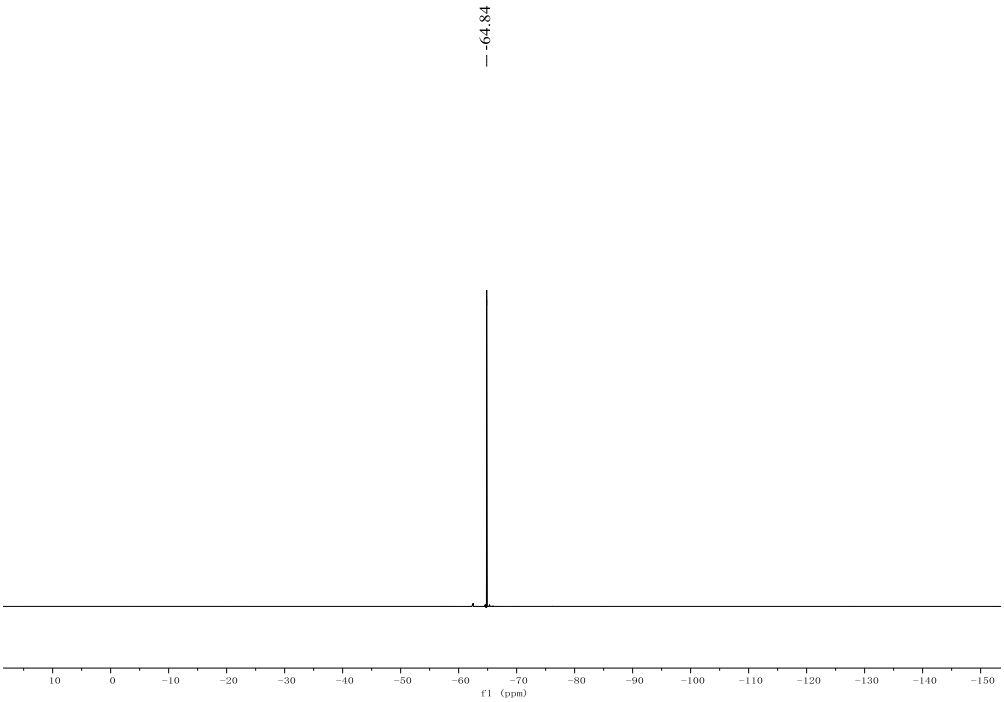
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.11 (m, 3H), 7.10 – 7.02 (m, 2H), 5.85 (d, *J* = 1.3 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 2.30 (s, 3H), 1.17 – 0.97 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.84.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.00, 137.96, 135.70 (q, *J* = 31.2 Hz), 134.87, 129.95, 129.18, 128.25, 126.04, 124.01 (q, *J* = 5.1 Hz), 122.65 (q, *J* = 276.0 Hz), 116.90, 106.30, 92.74, 21.33, 18.58, 11.35.

HRMS (EI) m/z calcd for $C_{23}H_{31}F_3Si$ $[M]^+$: 392.2140, found: 392.2144.

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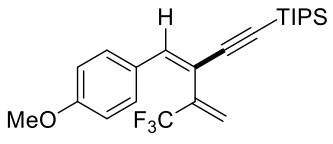
f1 (ppm)



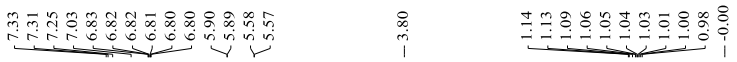
(*E*)-triisopropyl(3-(4-methoxybenzylidene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)silane (**7m**): Colorless oil, yield = 70% (isolated with preparative thin layer chromatography and using hexane as eluent).

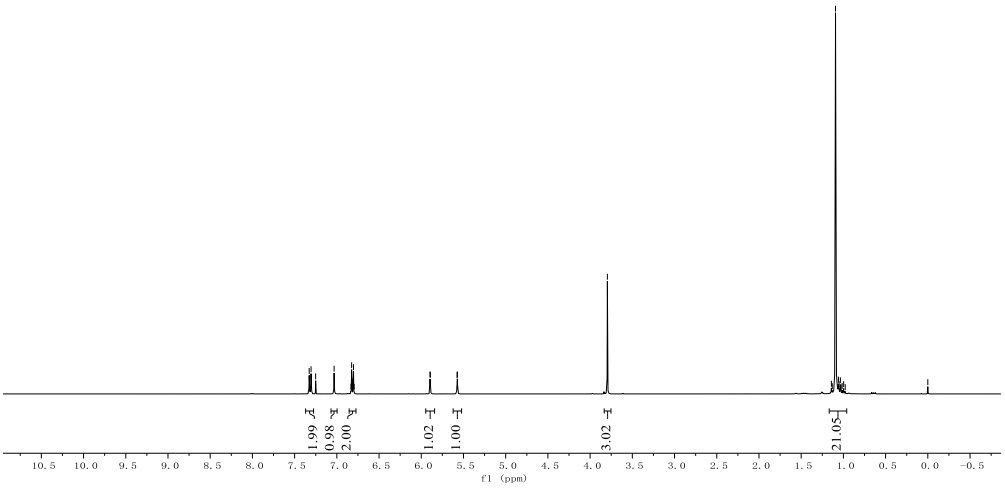
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.03 (s, 1H), 6.85 – 6.78 (m, 2H), 5.89 (d, *J* = 1.2 Hz, 1H), 5.57 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 1.17 – 0.97 (m, 21H).

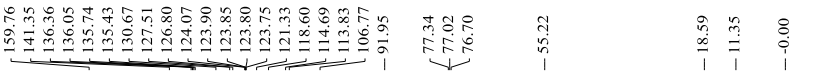
^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.05.

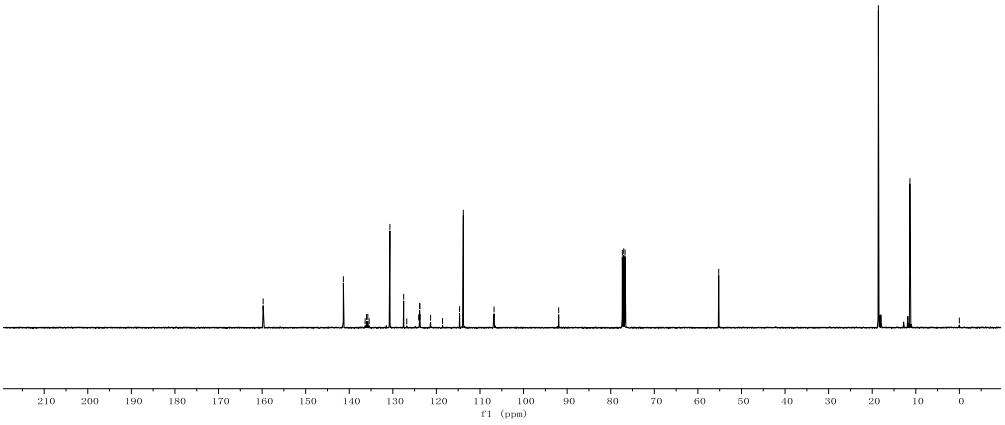
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.76, 141.35, 135.89 (q, *J* = 31.2 Hz), 130.67, 127.51, 123.82 (q, *J* = 5.0 Hz), 122.70 (q, *J* = 276.2 Hz), 114.69, 113.83, 106.77, 91.95, 55.22, 18.59, 11.35.

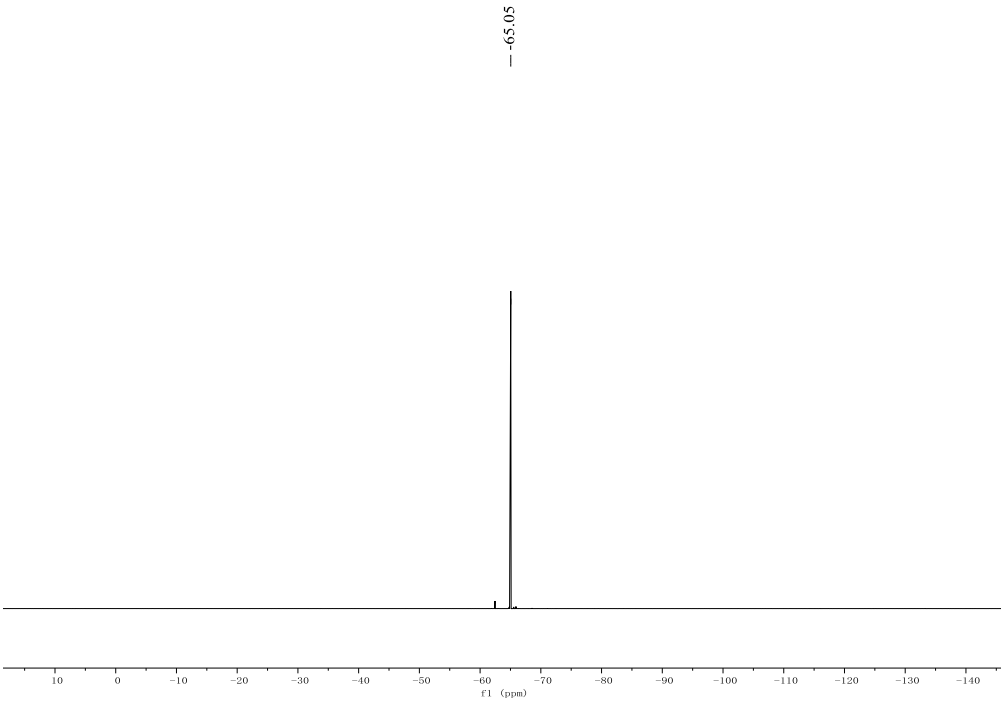
HRMS (EI) m/z calcd for $C_{23}H_{31}F_3SiO$ $[M]^+$: 408.2091, found: 408.2093.







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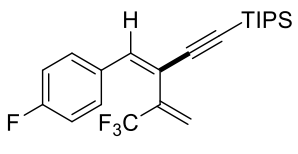
f1 (ppm)



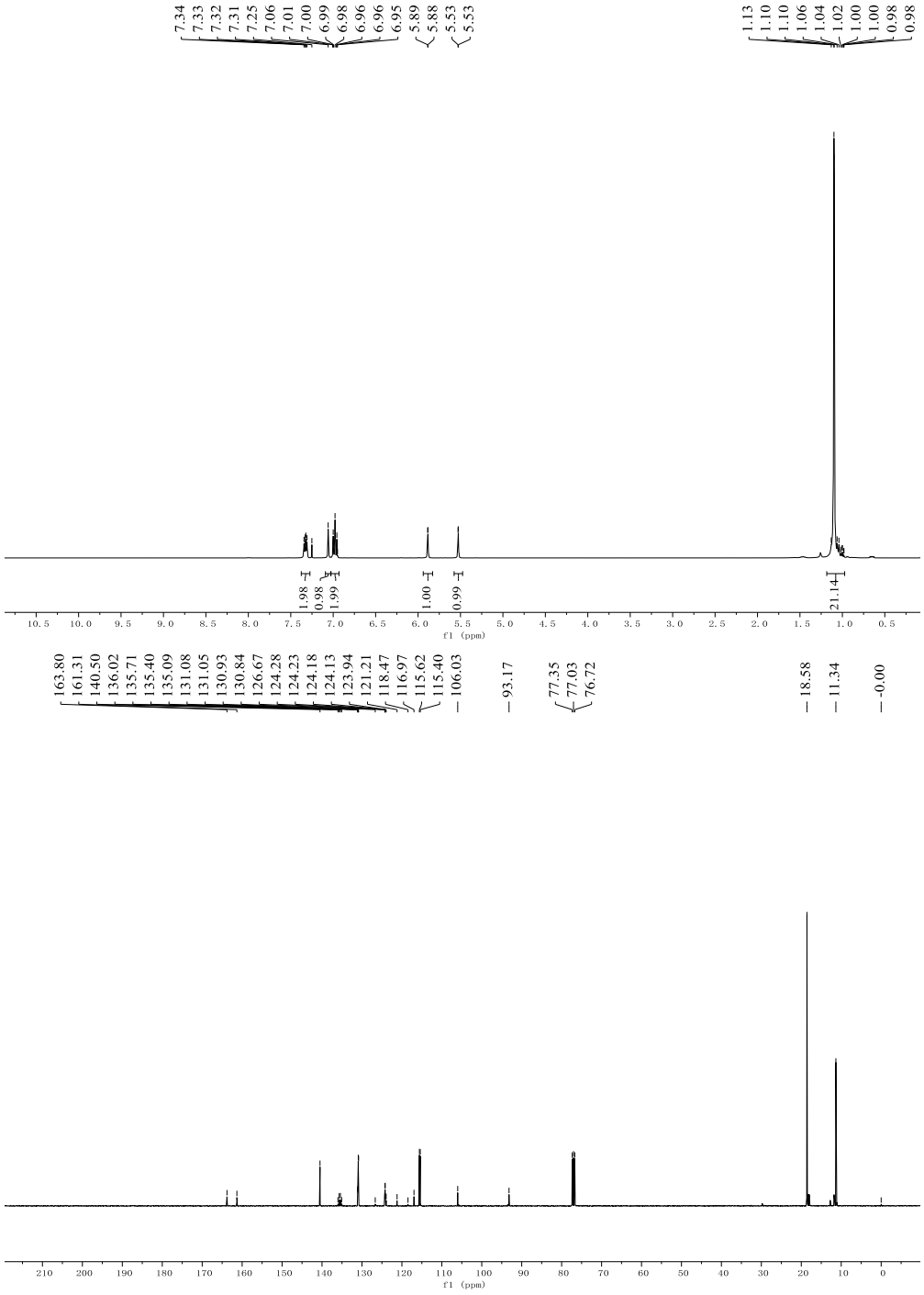
(*E*)-(3-(4-fluorobenzylidene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)triisopropylsilane (**7n**): Colorless oil, yield = 78% (isolated with preparative thin layer chromatography and using hexane as eluent).

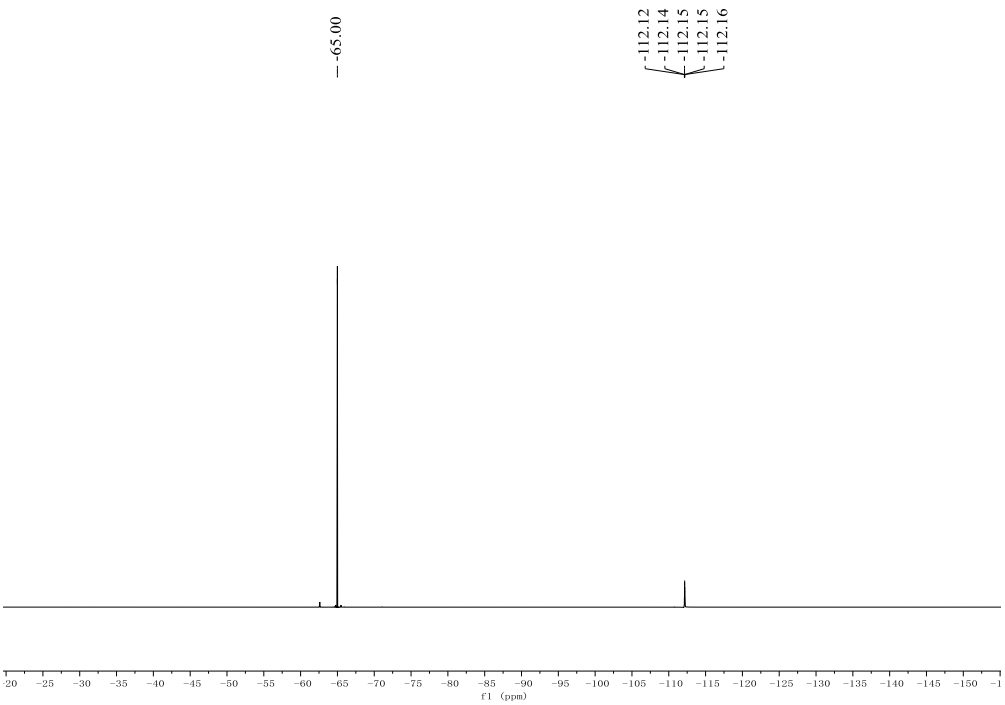
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.06 (s, 1H), 7.02 – 6.94 (m, 2H), 5.91 – 5.86 (m, 1H), 5.56 – 5.50 (m, 1H), 1.16 – 0.97 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.00, -112.07 – -112.20 (m).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.56 (d, *J* = 249.6 Hz), 140.50, 135.55 (q, *J* = 31.3 Hz), 131.07 (d, *J* = 3.5 Hz), 130.88 (d, *J* = 8.1 Hz), 124.21 (q, *J* = 5.0 Hz), 122.57 (q, *J* = 274.9 Hz), 116.97, 115.51 (d, *J* = 21.7 Hz), 106.03, 93.17, 18.58, 11.34.

HRMS (EI) m/z calcd for $C_{22}H_{28}F_4Si$ $[M]^+$: 396.1891, found: 396.1890.

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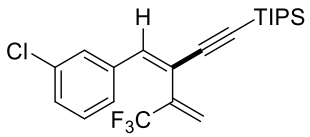
-112.16
-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -1
f1 (ppm)



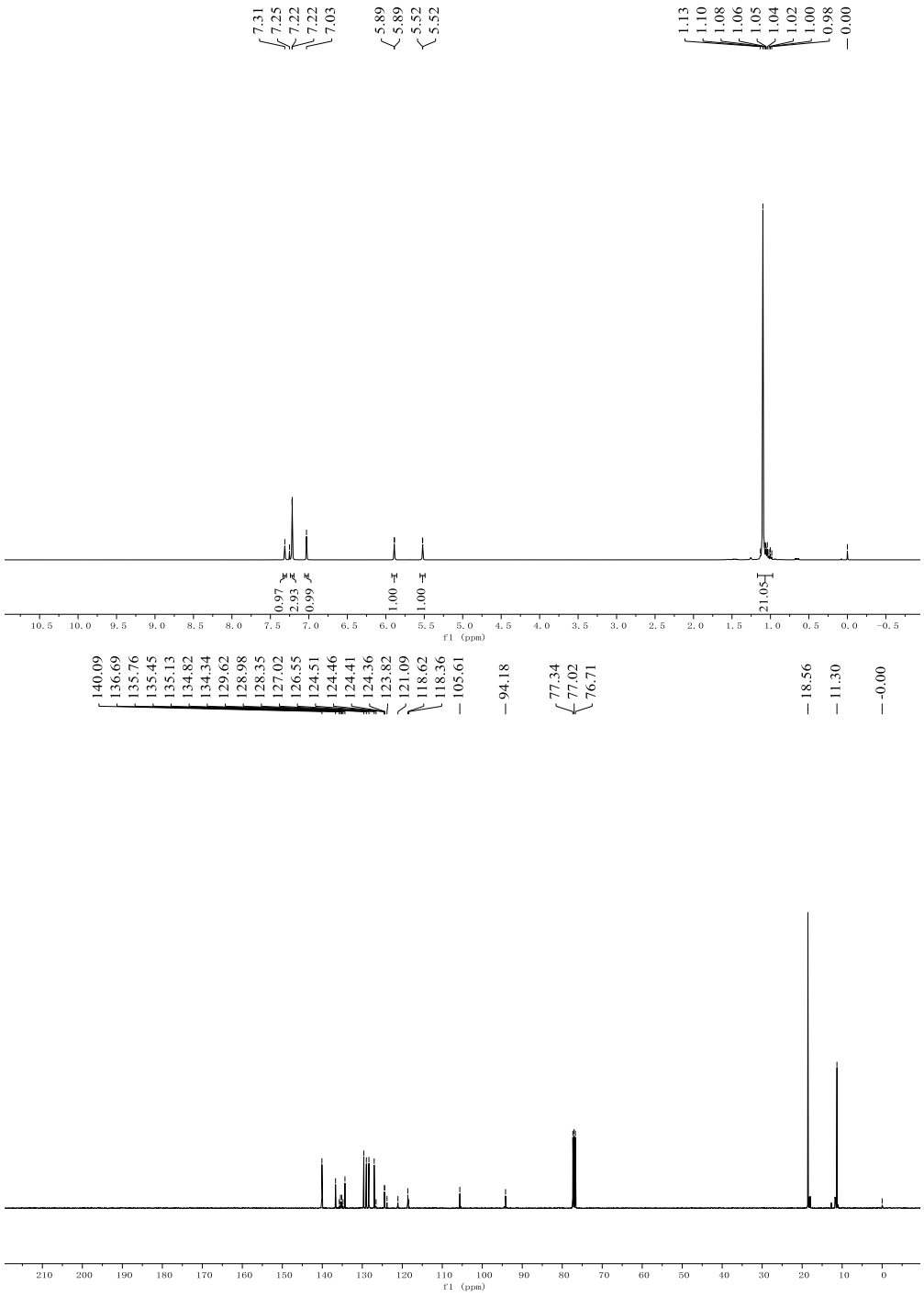
(*E*)-(3-(3-chlorobenzylidene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)triisopropylsilane (**7o**): Colorless oil, yield = 73% (isolated with preparative thin layer chromatography and using hexane as eluent).

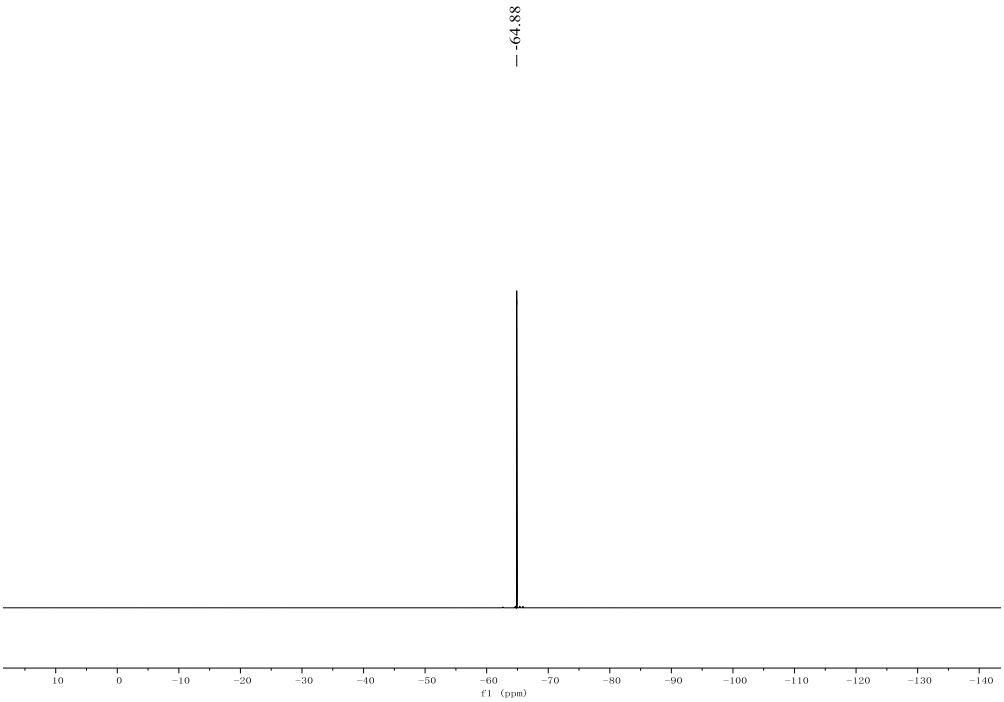
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (s, 1H), 7.22 (d, *J* = 1.2 Hz, 3H), 7.03 (s, 1H), 5.92 – 5.86 (m, 1H), 5.55 – 5.48 (m, 1H), 1.17 – 0.97 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.88.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.09, 136.69, 135.29 (q, *J* = 31.4 Hz), 134.34, 129.62, 128.98, 128.35, 127.02, 124.44 (q, *J* = 5.0 Hz), 122.46 (q, *J* = 274.9 Hz), 118.62, 105.61, 94.18, 18.56, 11.30.

HRMS (EI) m/z calcd for $C_{22}H_{28}F_3ClSi$ $[M]^+$: 412.1595, found: 412.1599.

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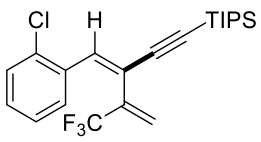
f1 (ppm)



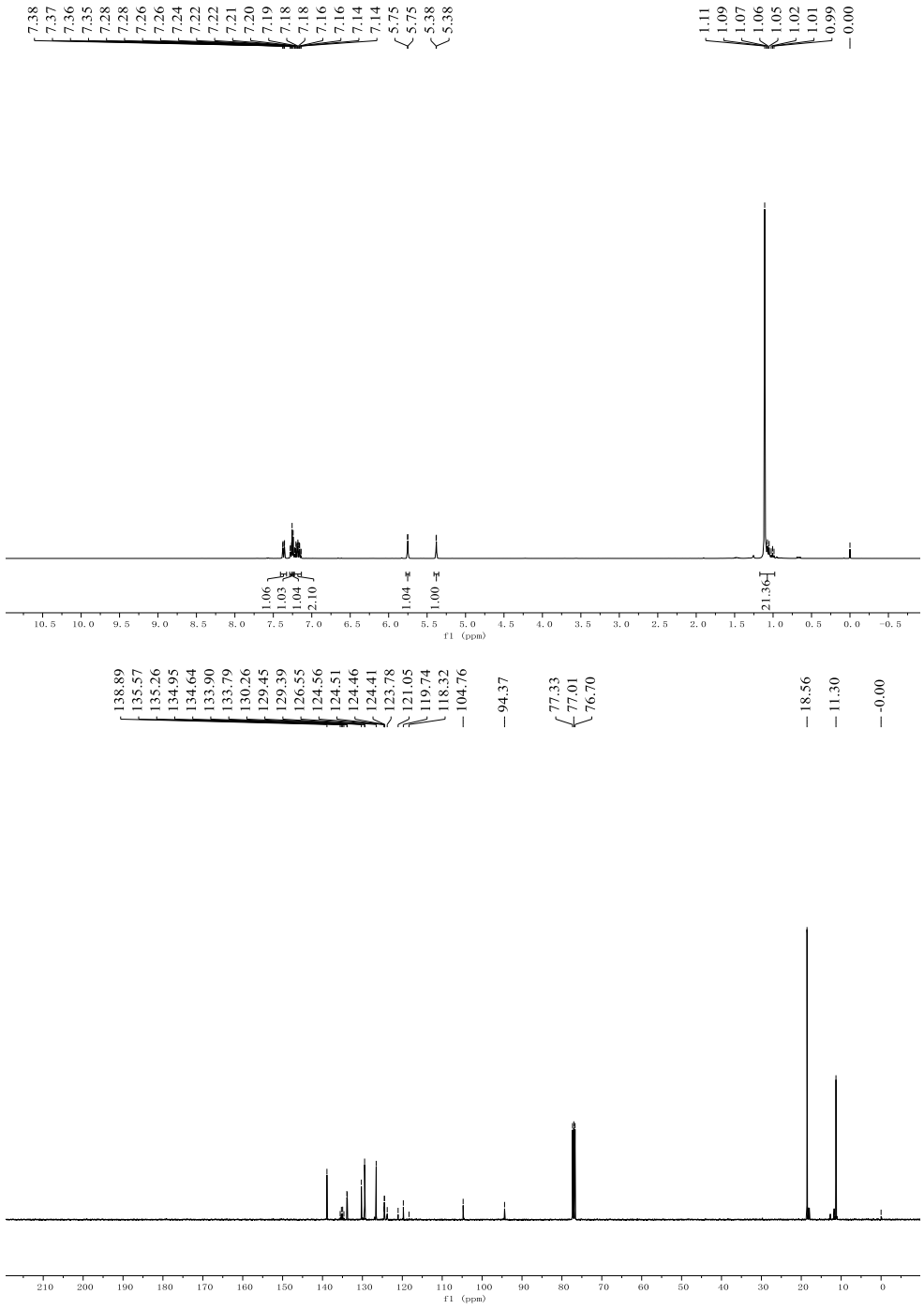
(*E*)-(3-(2-chlorobenzylidene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)triisopropylsilane (**7p**): Pale yellow oil, yield = 58% (isolated with preparative thin layer chromatography and using hexane as eluent).

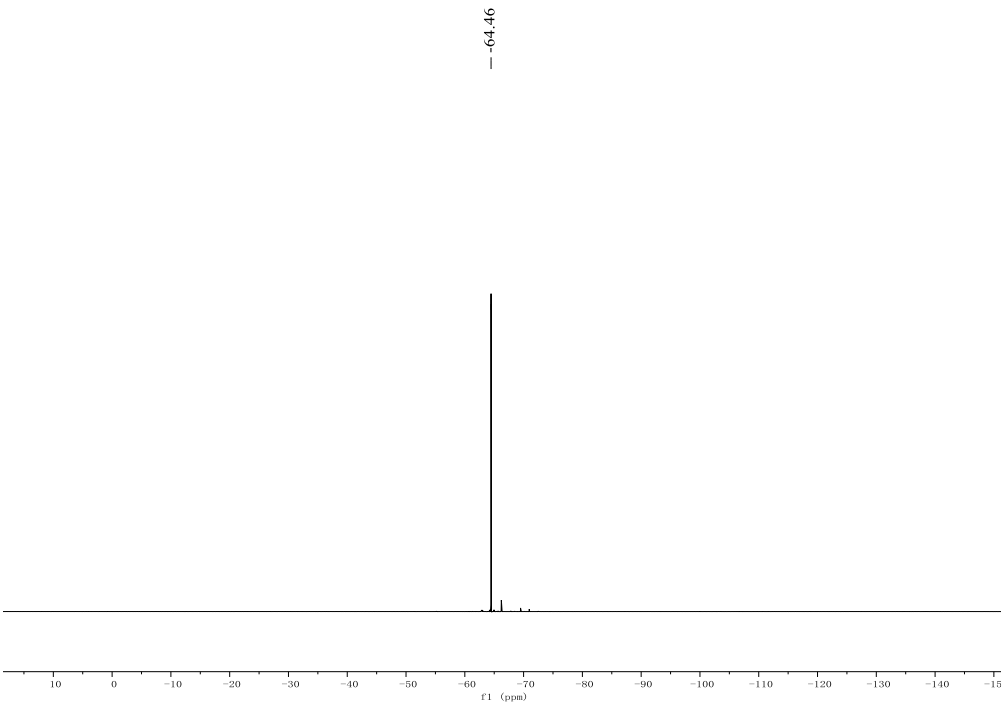
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.24 (s, 1H), 7.23 – 7.13 (m, 2H), 5.75 (d, *J* = 1.2 Hz, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 1.18 – 0.98 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.46.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.89, 135.11 (q, *J* = 31.2 Hz), 133.90, 133.79, 130.26, 129.45, 129.39, 126.55, 124.49 (q, *J* = 5.1 Hz), 122.42 (q, *J* = 274.8 Hz), 119.74, 104.76, 94.37, 18.56, 11.30.

HRMS (EI) m/z calcd for $C_{22}H_{28}F_3ClSi$ $[M]^+$: 412.1595, found: 412.1599.

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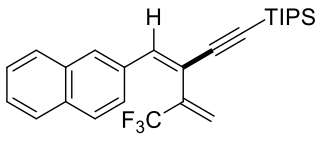
f1 (ppm)



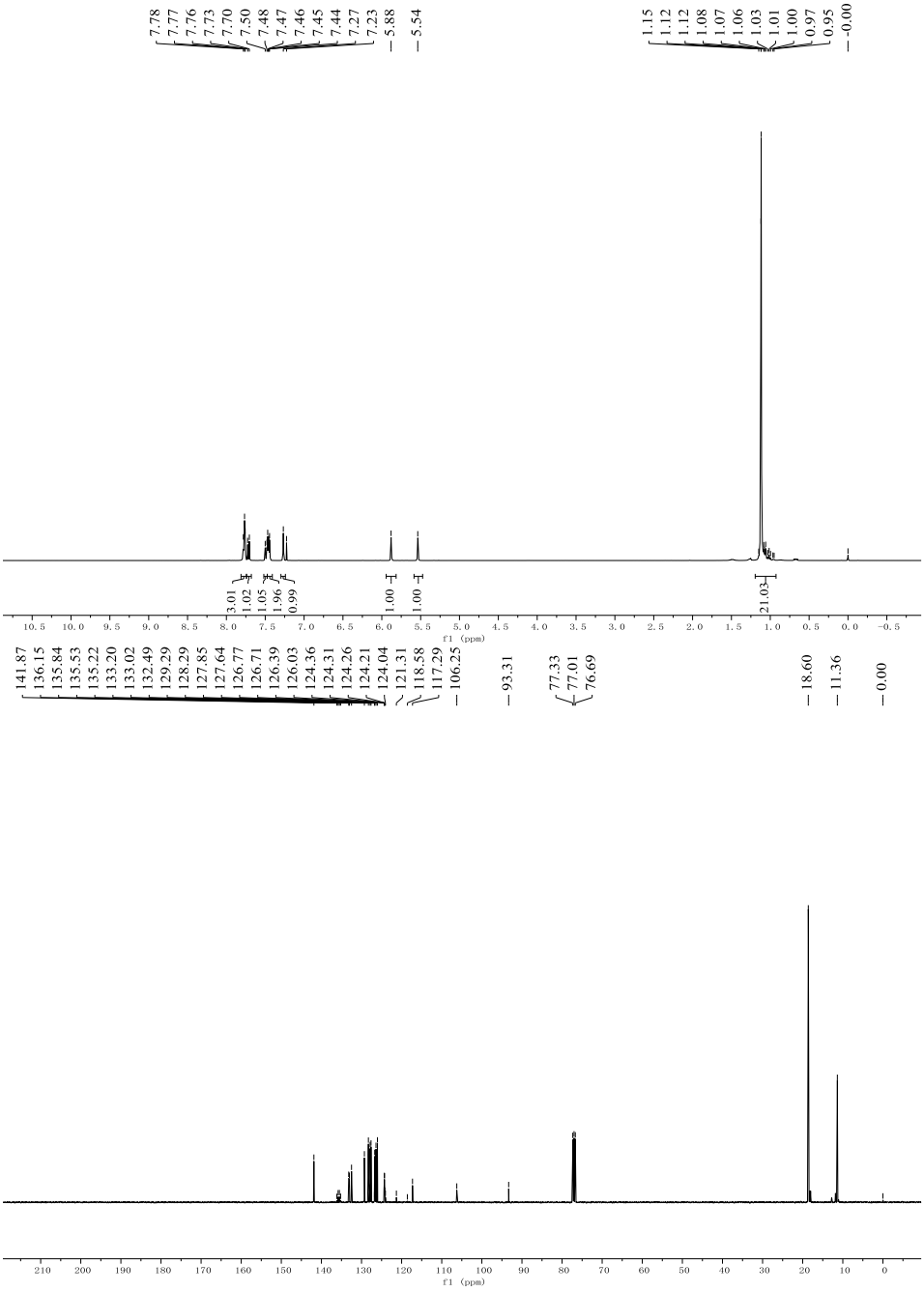
(*E*)-triisopropyl(3-(naphthalen-2-ylmethylene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)silane (**7q**): Colorless oil, yield = 77% (isolated with preparative thin layer chromatography and using hexane as eluent).

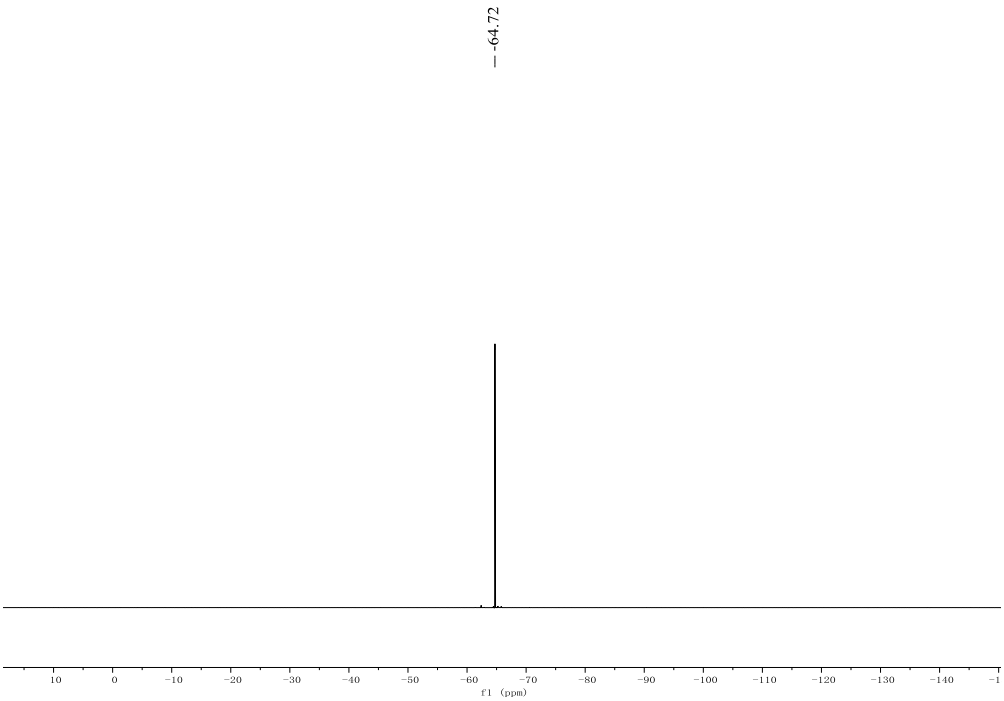
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 3H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.46 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.27 (s, 1H), 5.88 (s, 1H), 5.54 (s, 1H), 1.18 – 0.92 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.72.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.87, 135.68 (q, *J* = 31.4 Hz), 133.20, 133.02, 132.49, 129.29, 128.29, 127.85, 127.64, 126.71, 126.39, 126.03, 124.29 (q, *J* = 4.9 Hz), 122.67 (d, *J* = 274.9 Hz), 117.29, 106.25, 93.31, 18.60, 11.36.

HRMS (EI) m/z calcd for $C_{26}H_{31}F_3Si$ $[M]^+$: 428.2142, found: 428.2143.




-64.72
10
0
-10
-20
-30
-40
-50
-60
-70
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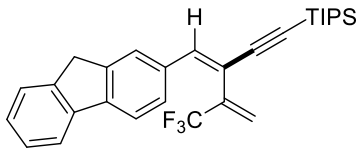
-90
-100
-110
-120
-130
-140
f1 (ppm)



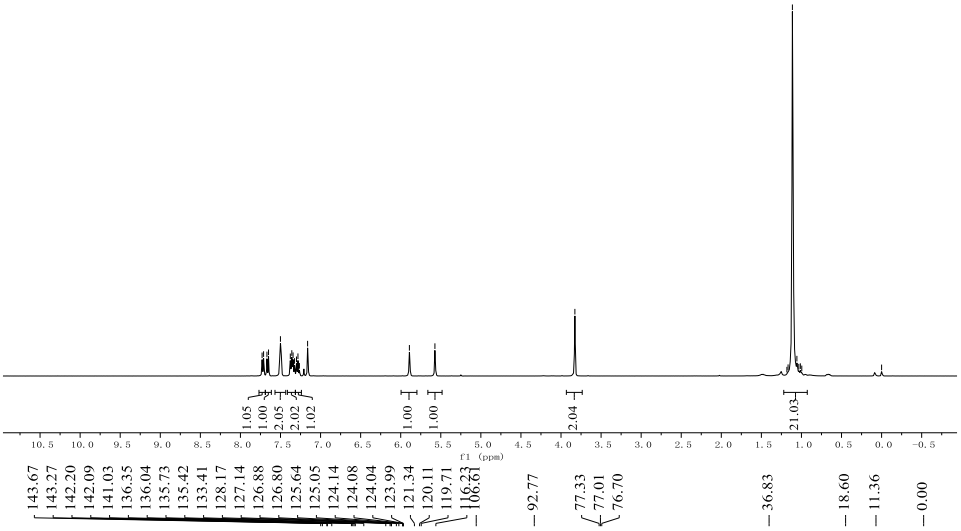
(*E*)-(3-((9H-fluoren-2-yl)methylene)-4-(trifluoromethyl)pent-4-en-1-yn-1-yl)triisopropylsilane (**7r**): White solid, yield = 87% (isolated with preparative thin layer chromatography and using hexane as eluent).

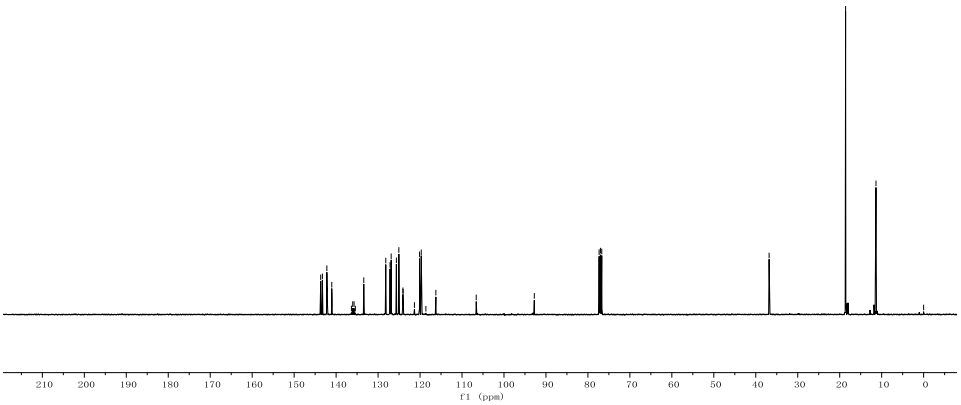
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 2H), 7.35 (dd, *J* = 13.7, 7.4 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.16 (s, 1H), 5.89 (s, 1H), 5.57 (s, 1H), 3.83 (s, 2H), 1.11 (s, 21H).

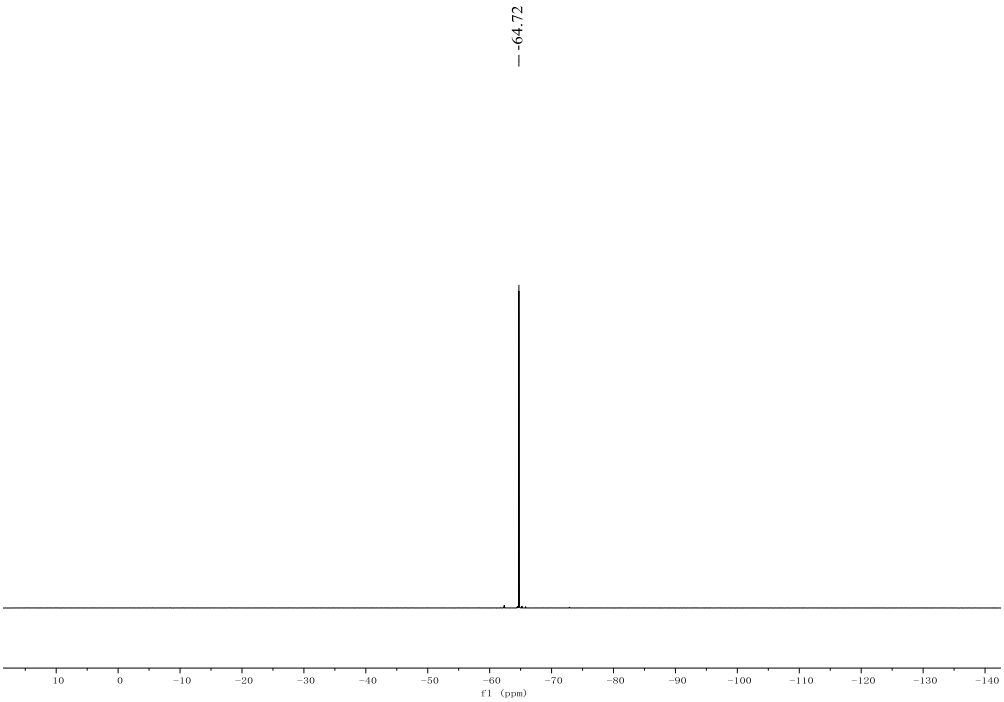
^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.72.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.67, 143.27, 142.20, 142.09, 141.03, 135.88 (q, *J* = 31.0 Hz), 133.41, 128.17, 127.14, 126.88, 125.64, 125.05, 124.06 (q, *J* = 5.1 Hz), 122.71 (q, *J* = 275.7 Hz), 120.11, 119.71, 116.23, 106.61, 92.77, 36.83, 18.60, 11.36.

HRMS (EI) m/z calcd for $C_{29}H_{33}F_3Si$ $[M]^+$: 466.2298, found: 466.2299.






-64.72
10
0
-10
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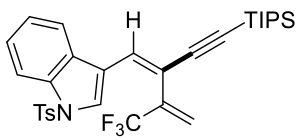
f1 (ppm)



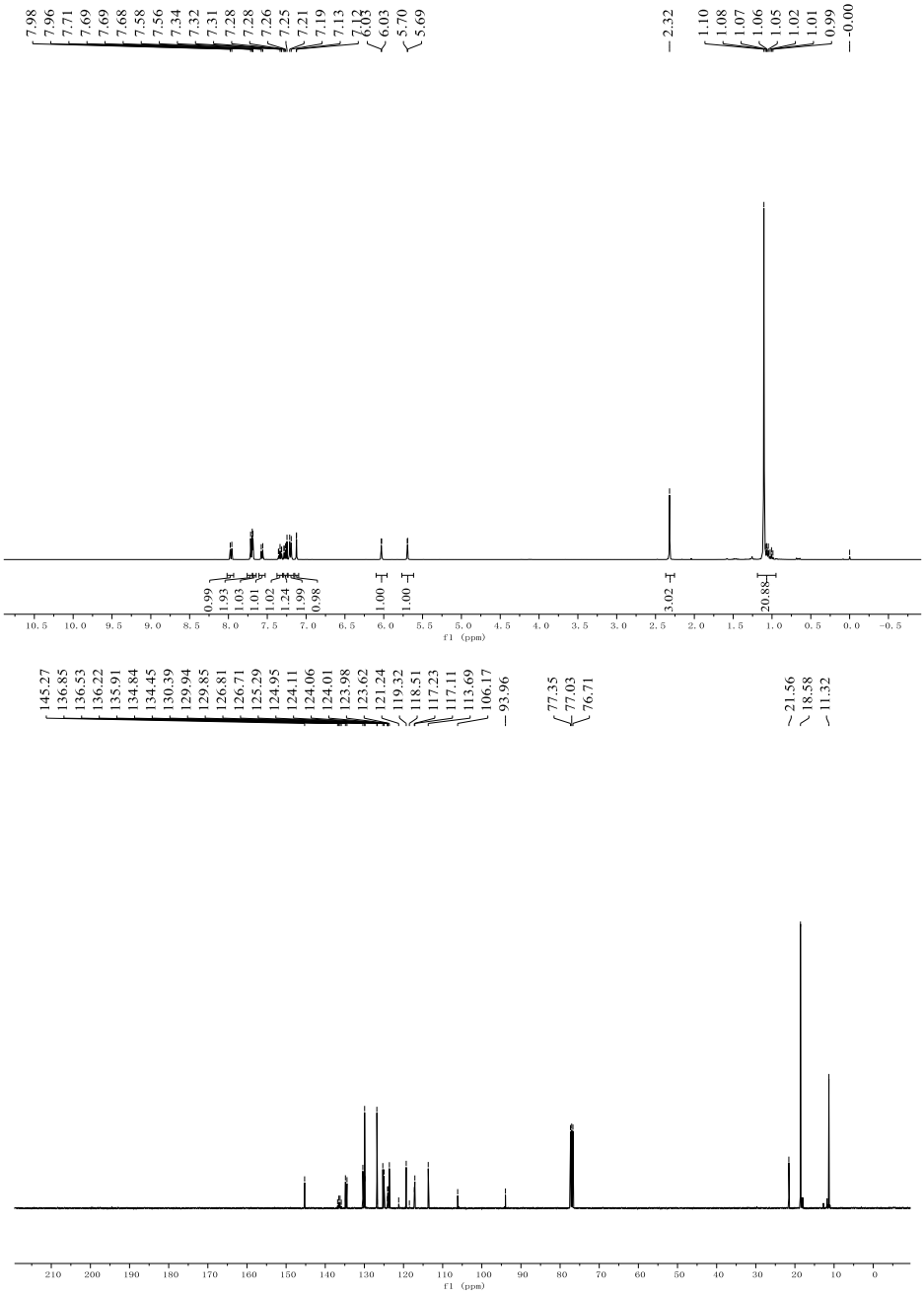
(*E*)-1-tosyl-3-(3-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)buta-1,3-dien-1-yl)-1*H*-indole (**7s**): Pale yellow solid, yield = 77% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:10 as eluent).

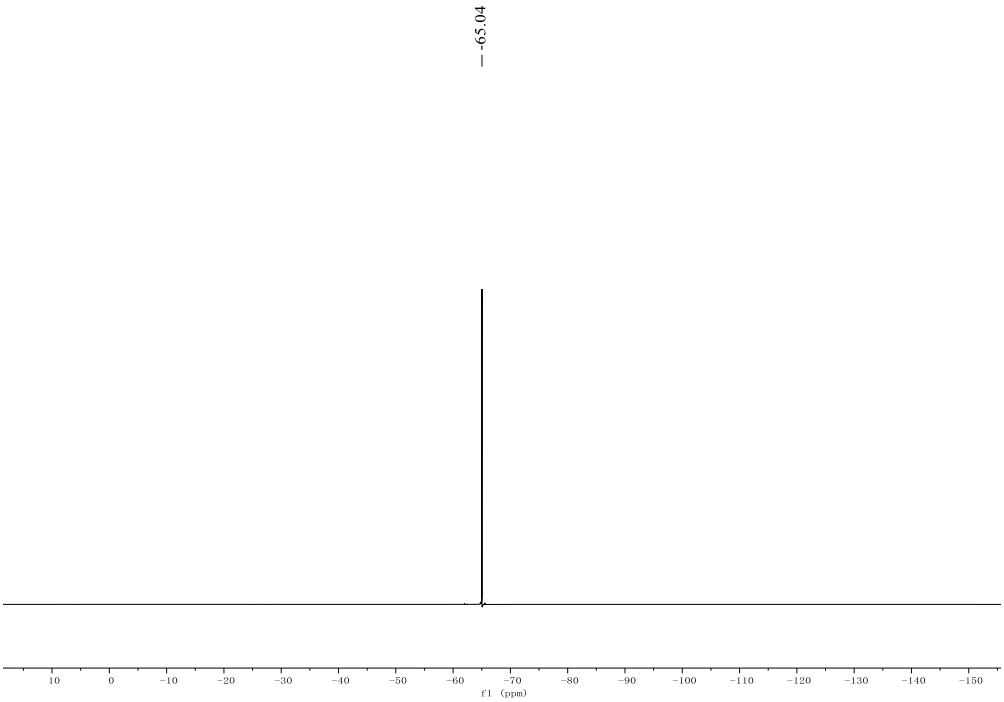
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.67 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.30 – 7.24 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.10 (m, 1H), 6.03 (d, *J* = 1.3 Hz, 1H), 5.69 (d, *J* = 1.1 Hz, 1H), 2.32 (s, 3H), 1.19 – 0.95 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.04.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.27, 136.38 (q, *J* = 31.6 Hz), 134.84, 134.45, 130.39, 129.94, 129.85, 126.81, 125.29, 124.95, 124.04 (q, *J* = 5.0 Hz), 123.62, 122.61 (q, *J* = 275.2 Hz), 119.32, 117.23, 117.11, 113.69, 106.17, 93.96, 21.56, 18.58, 11.32.

HRMS (ESI) m/z calcd for $C_{31}H_{37}F_3NO_2SSi$ $[M+H]^+$: 572.2266, found: 572.2272.




-65.04
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-10
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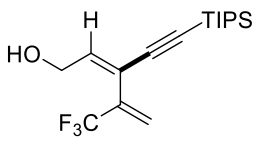
-140
-150
f1 (ppm)



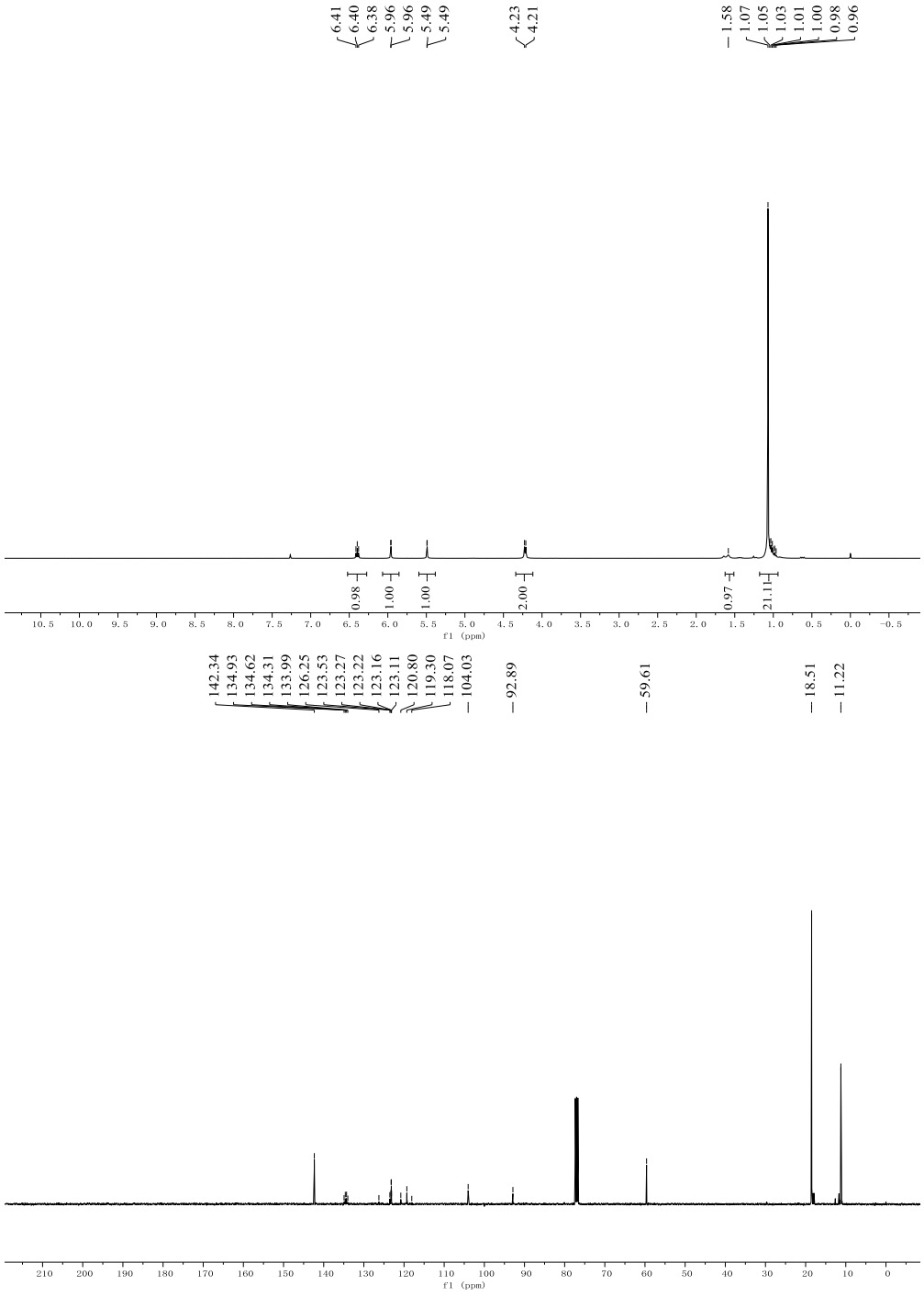
(*E*)-4-(trifluoromethyl)-3-((triisopropylsilyl)ethynyl)penta-2,4-dien-1-ol (**7t**): Pale yellow oil, yield = 53% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:10 as eluent).

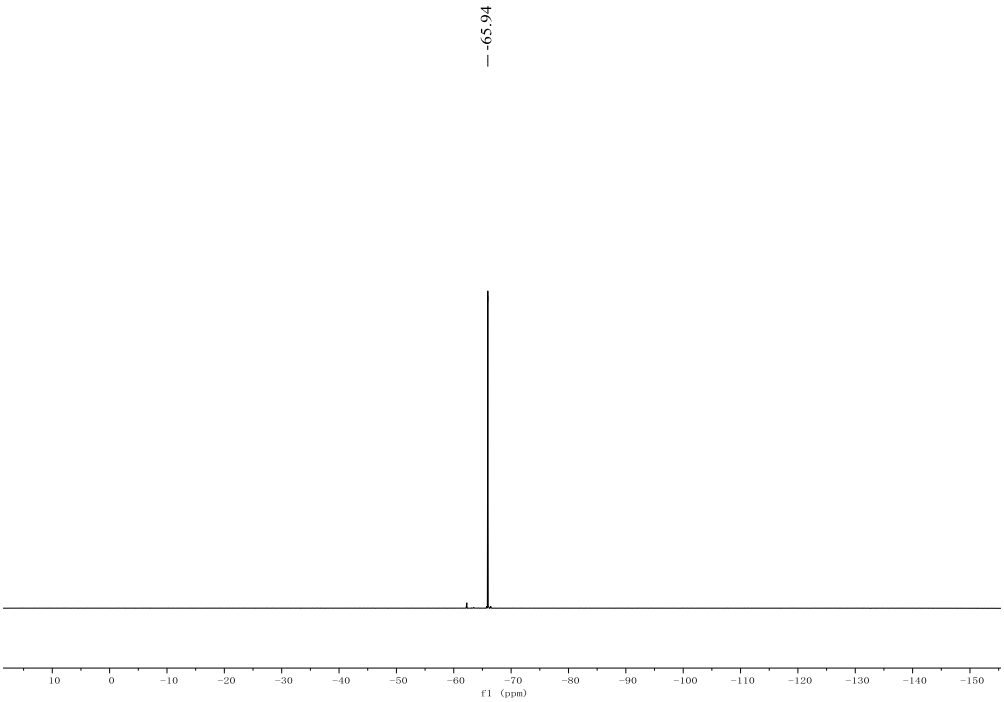
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.40 (t, *J* = 6.9 Hz, 1H), 6.09 – 5.85 (m, 1H), 5.60 – 5.38 (m, 1H), 4.22 (d, *J* = 6.8 Hz, 2H), 1.58 (s, 1H), 1.17 – 0.94 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.94.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.34, 134.46 (q, *J* = 31.4 Hz), 123.19 (q, *J* = 5.2 Hz), 122.16 (q, *J* = 274.4 Hz), 119.30, 104.03, 92.89, 59.61, 18.51, 11.22.

HRMS (ESI) m/z calcd for $C_{17}H_{27}F_3OSiNa$ $[M+Na]^+$: 355.1681, found: 355.1676.

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-110
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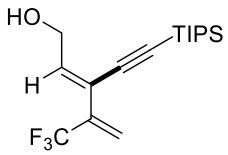
-130
-140
-150
f1 (ppm)



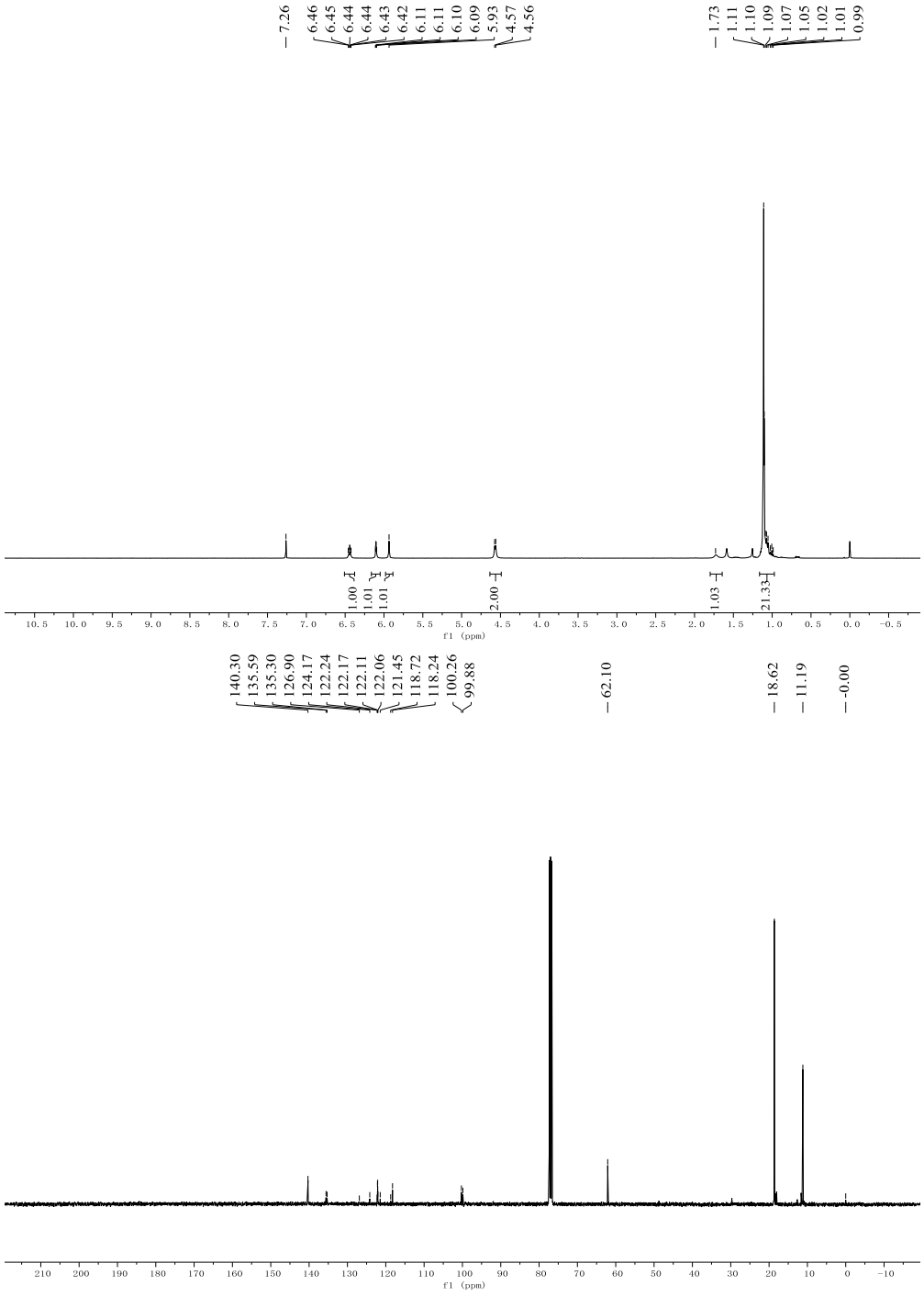
(*Z*)-4-(trifluoromethyl)-3-((triisopropylsilyl)ethynyl)penta-2,4-dien-1-ol (**7t'**): Pale yellow oil, yield = 17% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:10 as eluent).

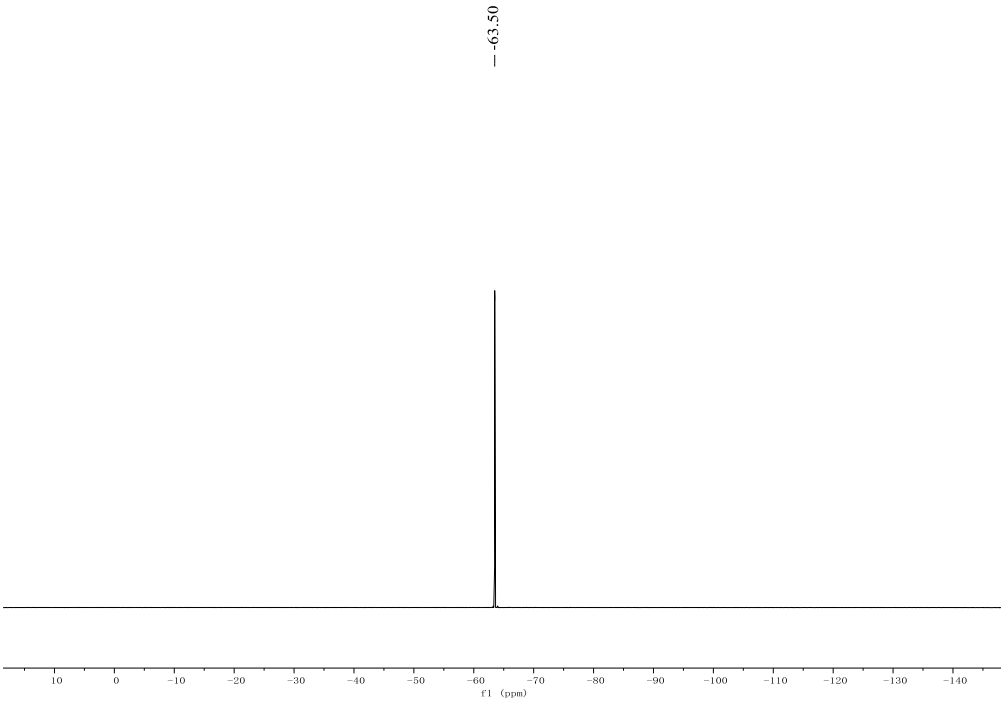
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.44 (ddq, *J* = 6.2, 3.7, 1.9 Hz, 1H), 6.10 (q, *J* = 2.4 Hz, 1H), 5.93 (s, 1H), 4.57 (d, *J* = 6.1 Hz, 2H), 1.73 (s, 1H), 1.16 – 0.97 (m, 21H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.50.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.30, 135.44 (q, *J* = 29.8 Hz), 122.81 (q, *J* = 274.2 Hz), 122.14 (q, *J* = 6.3, 5.5 Hz), 118.24, 100.26, 99.88, 62.10, 18.62, 11.19.

HRMS (ESI) m/z calcd for $C_{17}H_{28}F_3OSi$ $[M+H]^+$: 333.1862, found: 333.1862.




-63.50
10
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-70
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-90
-100
-110
-120
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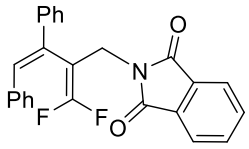
-140
f1 (ppm)



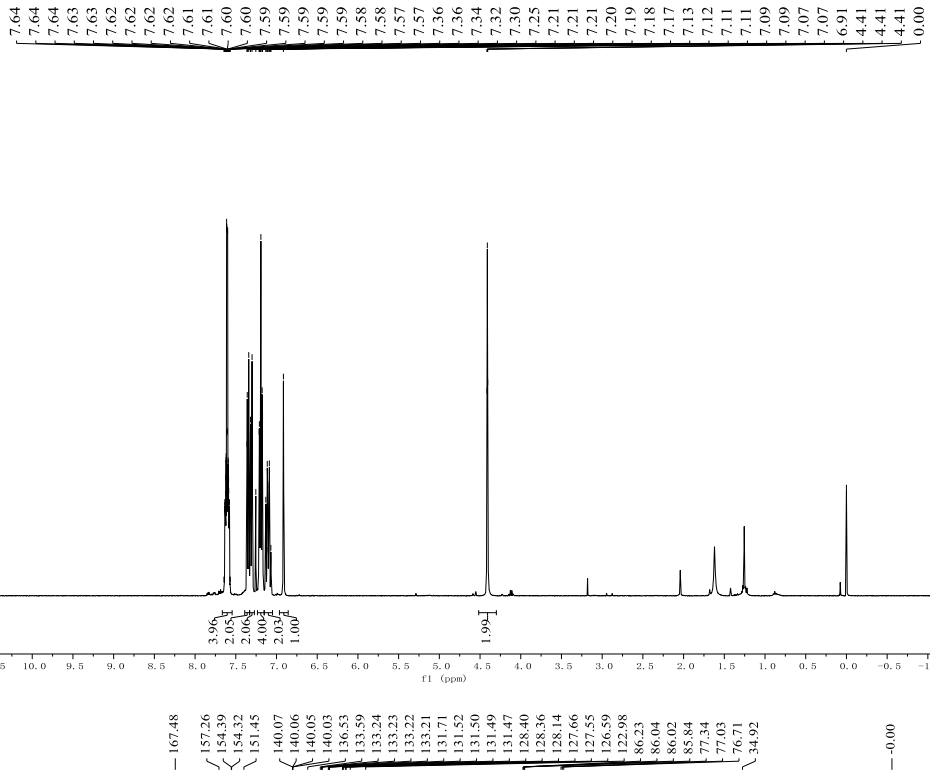
(*Z*)-2-(2-(difluoromethylene)-3,4-diphenylbut-3-en-1-yl)isoindoline-1,3-dione (**8a**): Pale yellow solid, yield = 86% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:10 as eluent).

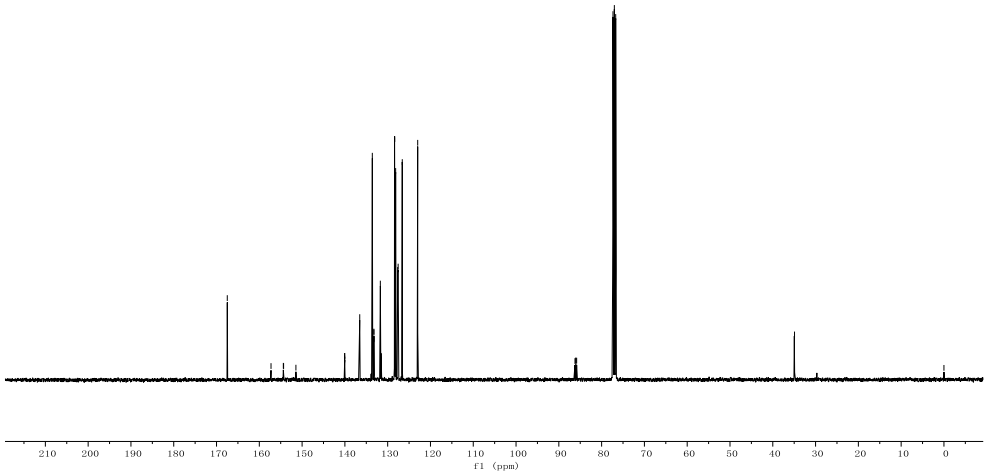
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.54 (m, 4H), 7.39 – 7.33 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.15 – 7.05 (m, 2H), 6.91 (s, 1H), 4.41 (t, *J* = 1.8 Hz, 2H).

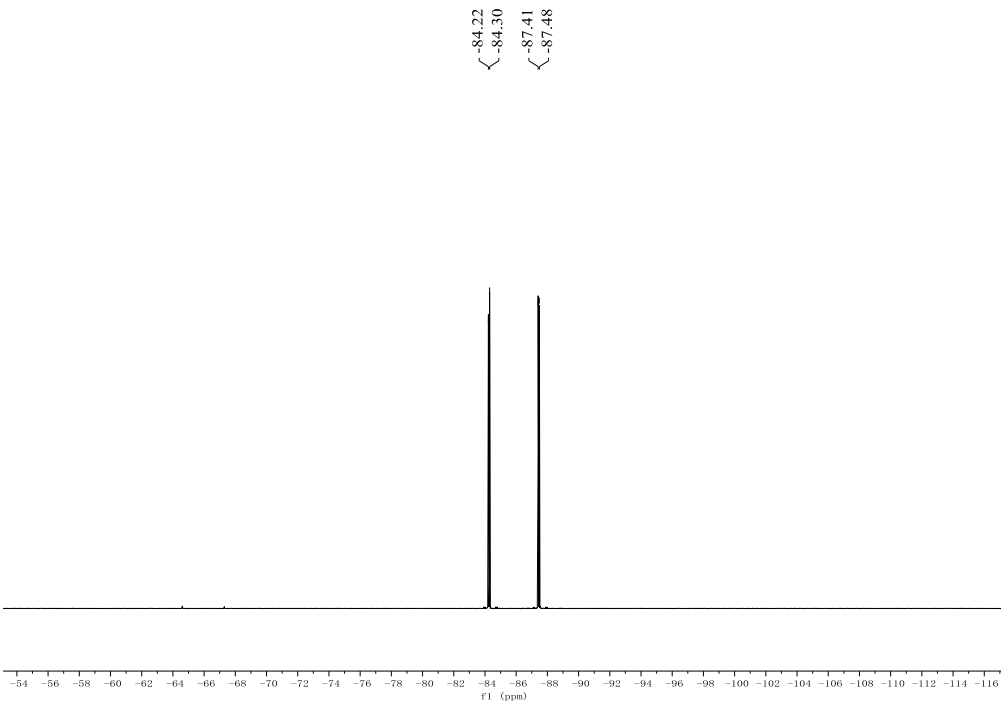
^{19}F NMR (376 MHz, Chloroform-*d*) δ -84.26 (d, *J* = 28.5 Hz), -87.45 (d, *J* = 28.5 Hz).

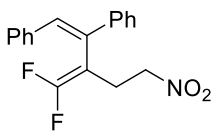
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.48, 154.36 (dd, *J* = 295.8, 289.6 Hz), 140.05 (dd, *J* = 2.8, 1.5 Hz), 136.53, 133.59, 133.23 (dd, *J* = 2.3, 1.2 Hz), 131.71, 131.50 (dd, *J* = 3.1, 1.9 Hz), 128.40, 128.36, 128.14, 127.66, 127.55, 126.59, 122.98, 86.03 (dd, *J* = 20.6, 18.5 Hz), 34.92.

HRMS (ESI) m/z calcd for $C_{25}H_{18}F_2NO_2$ $[M+H]^+$: 402.1306, found: 402.1314.






-84.22
-84.30
-87.41
-87.48
-54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116
f1 (ppm)



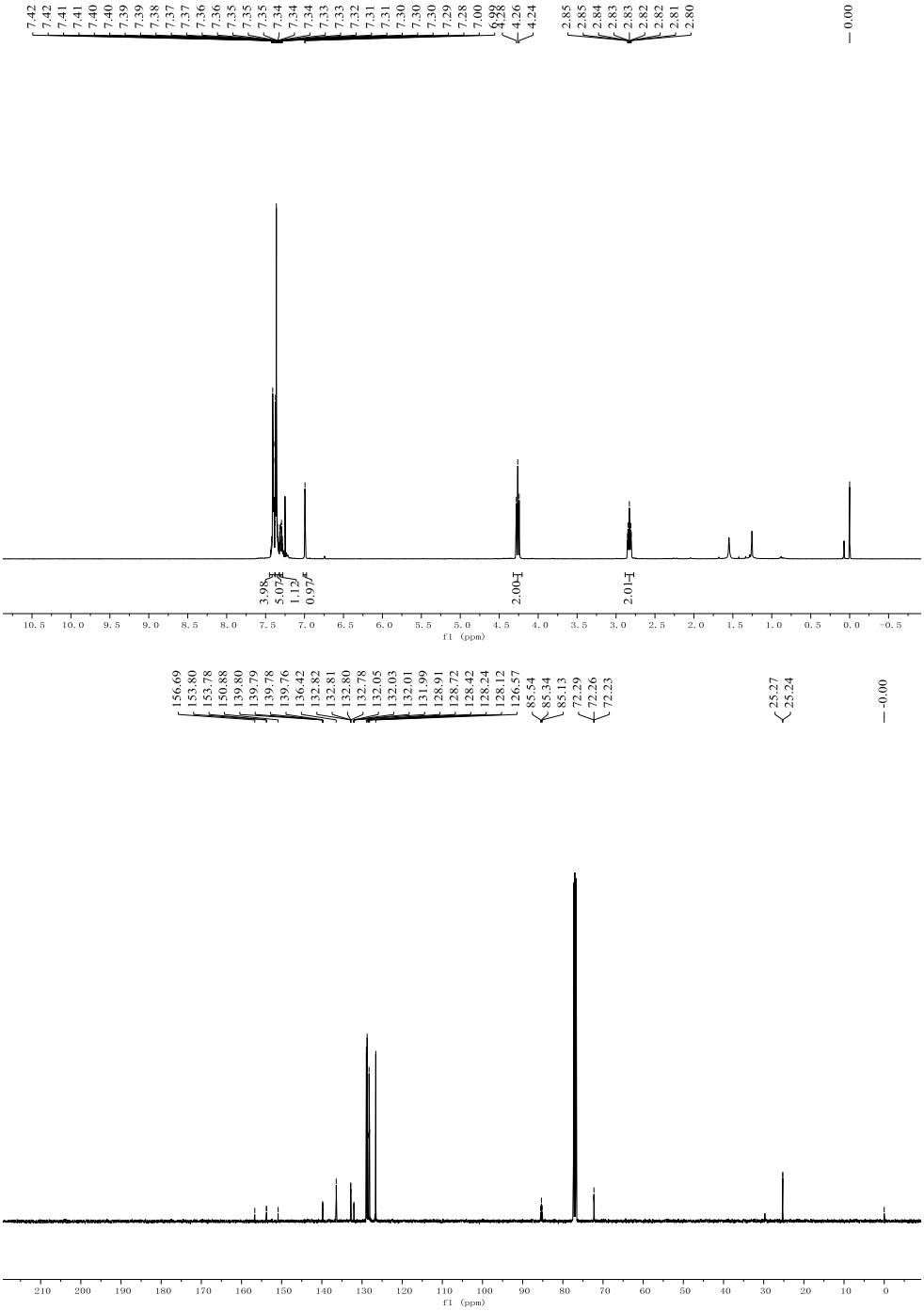
(*Z*)-(3-(difluoromethylene)-5-nitropent-1-ene-1,2-diyl)dibenzene (**9a**): Pale yellow oil, yield = 79% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:50 as eluent).

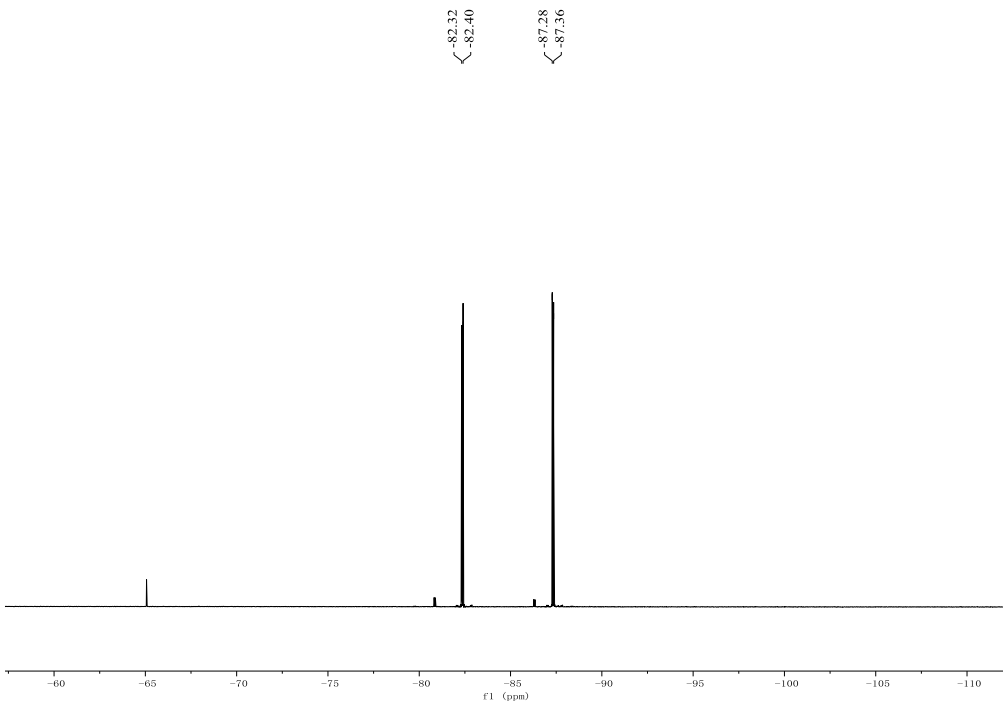
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 4H), 7.38 – 7.32 (m, 5H), 7.32 – 7.28 (m, 1H), 7.00 (d, *J* = 1.0 Hz, 1H), 4.26 (t, *J* = 7.4 Hz, 2H), 2.83 (tt, *J* = 7.4, 2.1 Hz, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -82.36 (d, *J* = 28.9 Hz), -87.32 (d, *J* = 28.8 Hz).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.79 (dd, *J* = 293.3, 291.6 Hz), 139.78 (dd, *J* = 2.7, 1.6 Hz), 136.42, 132.80 (dd, *J* = 2.6, 1.4 Hz), 132.02 (dd, *J* = 3.7, 2.2 Hz), 128.91, 128.72, 128.42, 128.24, 128.12, 126.57, 85.34 (t, *J* = 20.4 Hz), 72.26 (m), 25.26 (d, *J* = 2.7 Hz).

HRMS (ESI) m/z calcd for $C_{18}H_{16}F_2NO_2$ $[M+H]^+$: 316.1149, found: 316.1149.




-82.32
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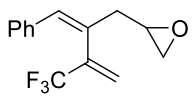
-110
f1 (ppm)



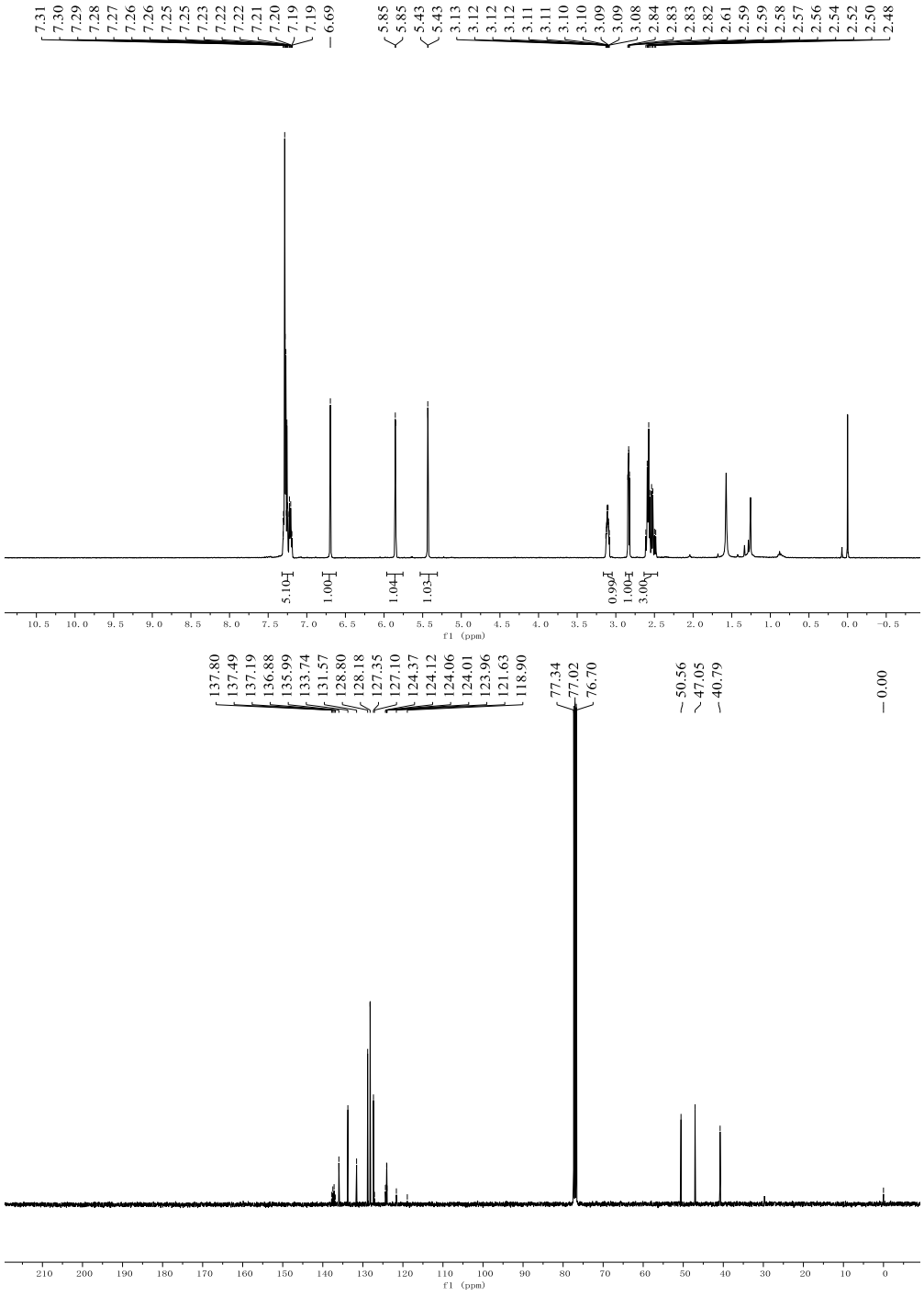
(*Z*)-2-(2-benzylidene-3-(trifluoromethyl)but-3-en-1-yl)oxirane (**10a**): Colorless oil, yield = 60% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:20 as eluent).

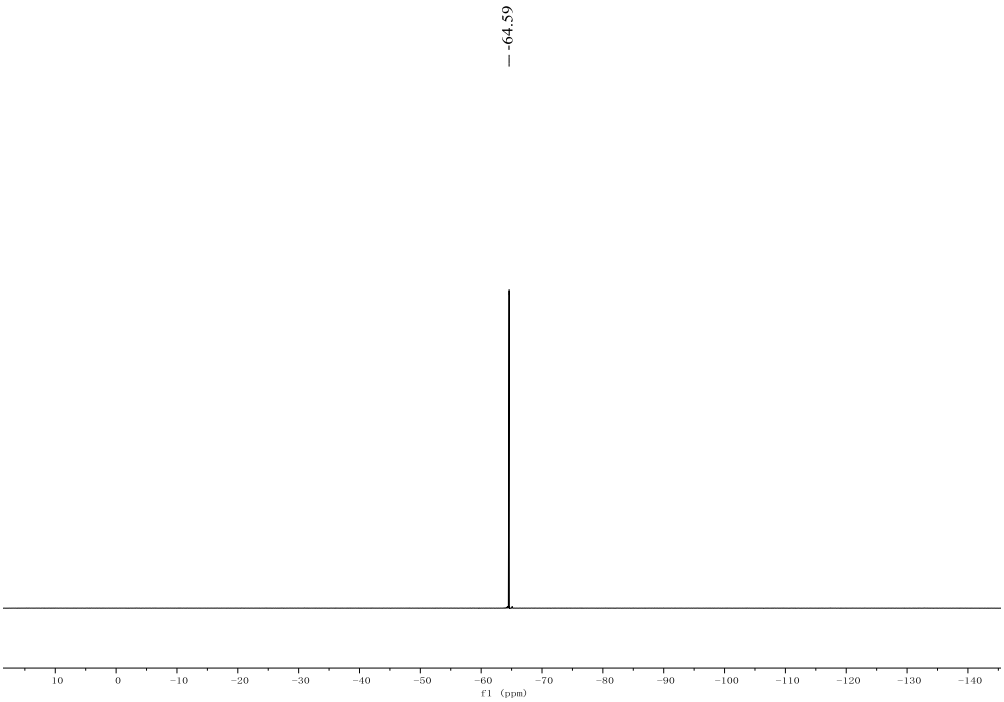
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.18 (m, 5H), 6.69 (s, 1H), 5.85 (d, *J* = 1.4 Hz, 1H), 5.54 – 5.35 (m, 1H), 3.16 – 3.05 (m, 1H), 2.88 – 2.79 (m, 1H), 2.64 – 2.46 (m, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.59.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.34 (q, *J* = 30.8 Hz), 135.99, 133.74, 131.57, 128.80, 128.18, 127.35, 124.04 (q, *J* = 5.4 Hz), 123.00 (q, *J* = 275.1 Hz), 50.56, 47.05, 40.79.

HRMS (ESI) m/z calcd for $C_{14}H_{14}F_3O$ $[M+H]^+$: 255.0997, found: 255.0989.

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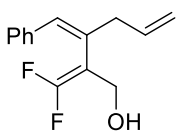
-140
f1 (ppm)



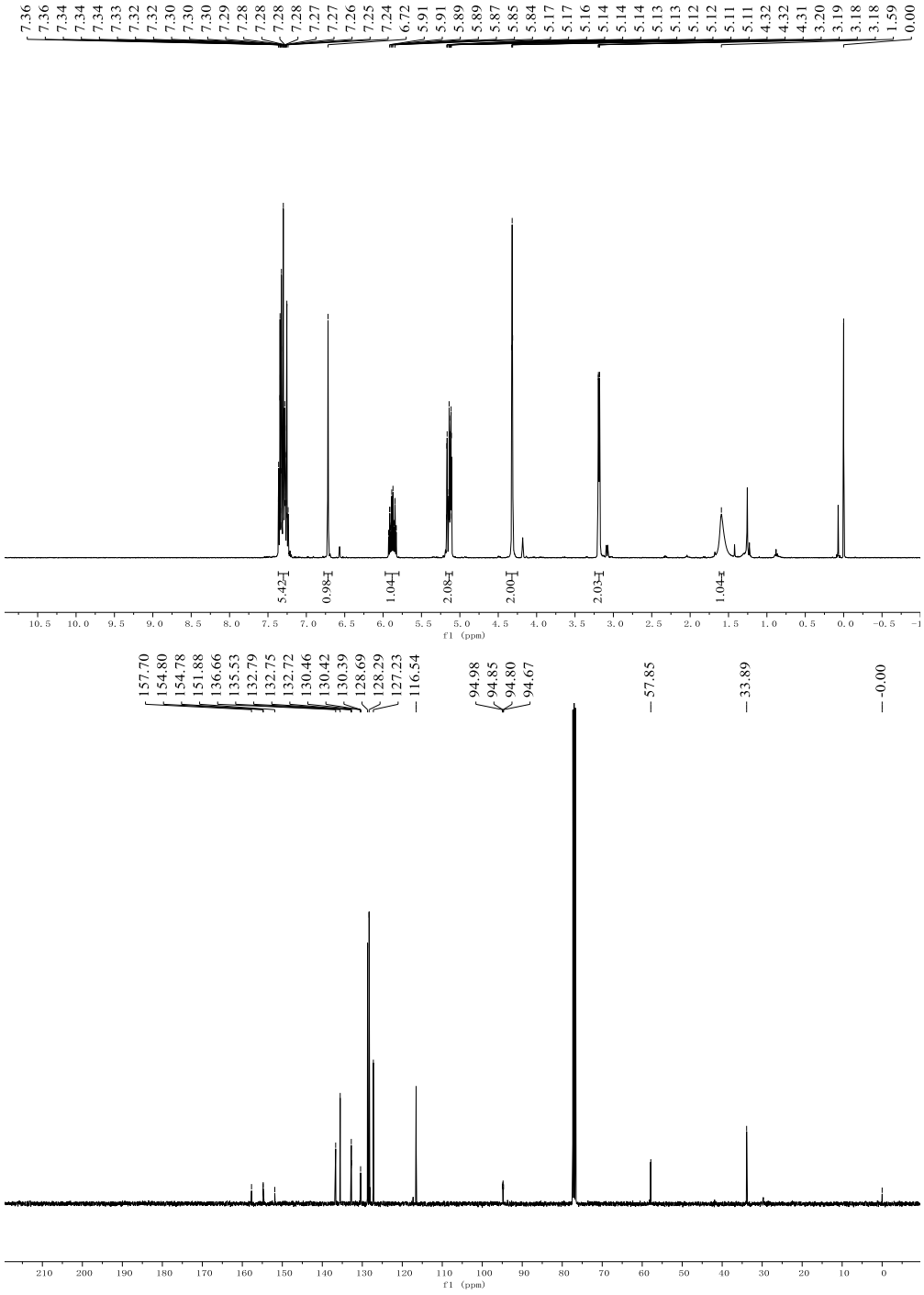
(*Z*)-3-benzylidene-2-(difluoromethylene)hex-5-en-1-ol (**11a**): Colorless oil, yield = 83% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:10 as eluent).

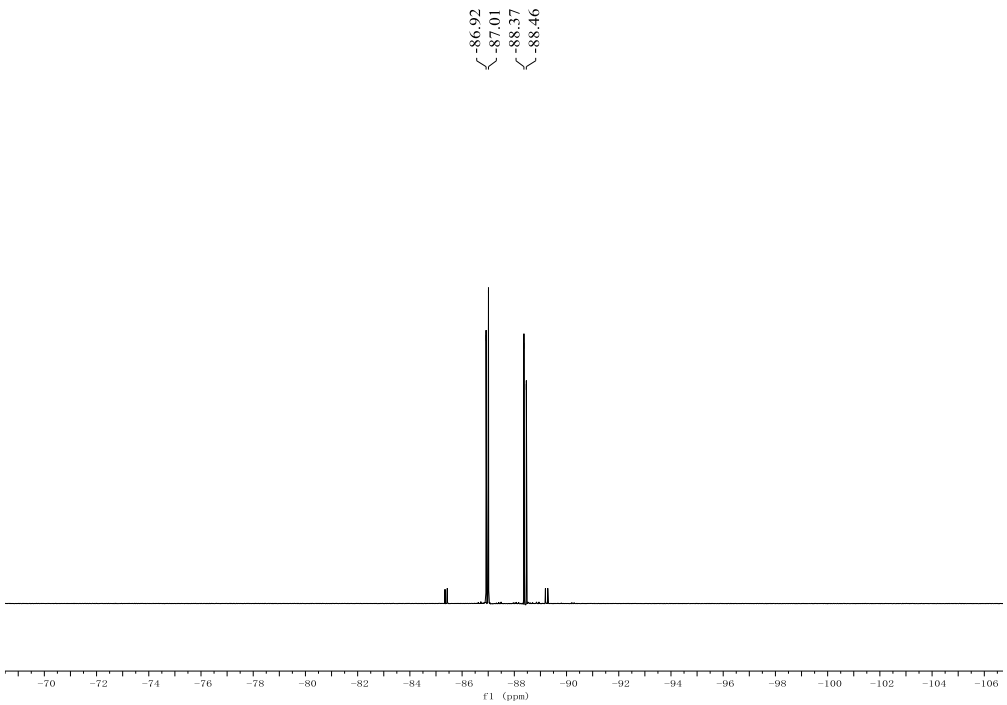
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.22 (m, 5H), 6.72 (s, 1H), 6.01 – 5.75 (m, 1H), 5.22 – 5.04 (m, 2H), 4.32 (t, *J* = 2.4 Hz, 2H), 3.28 – 3.12 (m, 2H), 1.59 (s, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -86.96 (d, *J* = 34.7 Hz), -88.41 (d, *J* = 34.7 Hz).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.79 (dd, *J* = 293.6, 291.8 Hz), 136.66, 135.53, 132.75 (t, *J* = 3.4 Hz), 130.42 (t, *J* = 3.3 Hz), 128.69, 128.29, 127.23, 116.54, 94.82 (dd, *J* = 18.0, 12.6 Hz), 57.85, 33.89.

HRMS (ESI) m/z calcd for $C_{14}H_{15}F_2O$ $[M+H]^+$: 237.1091, found: 237.1102.

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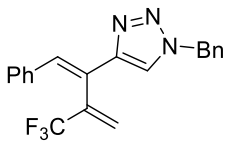
-106
f1 (ppm)



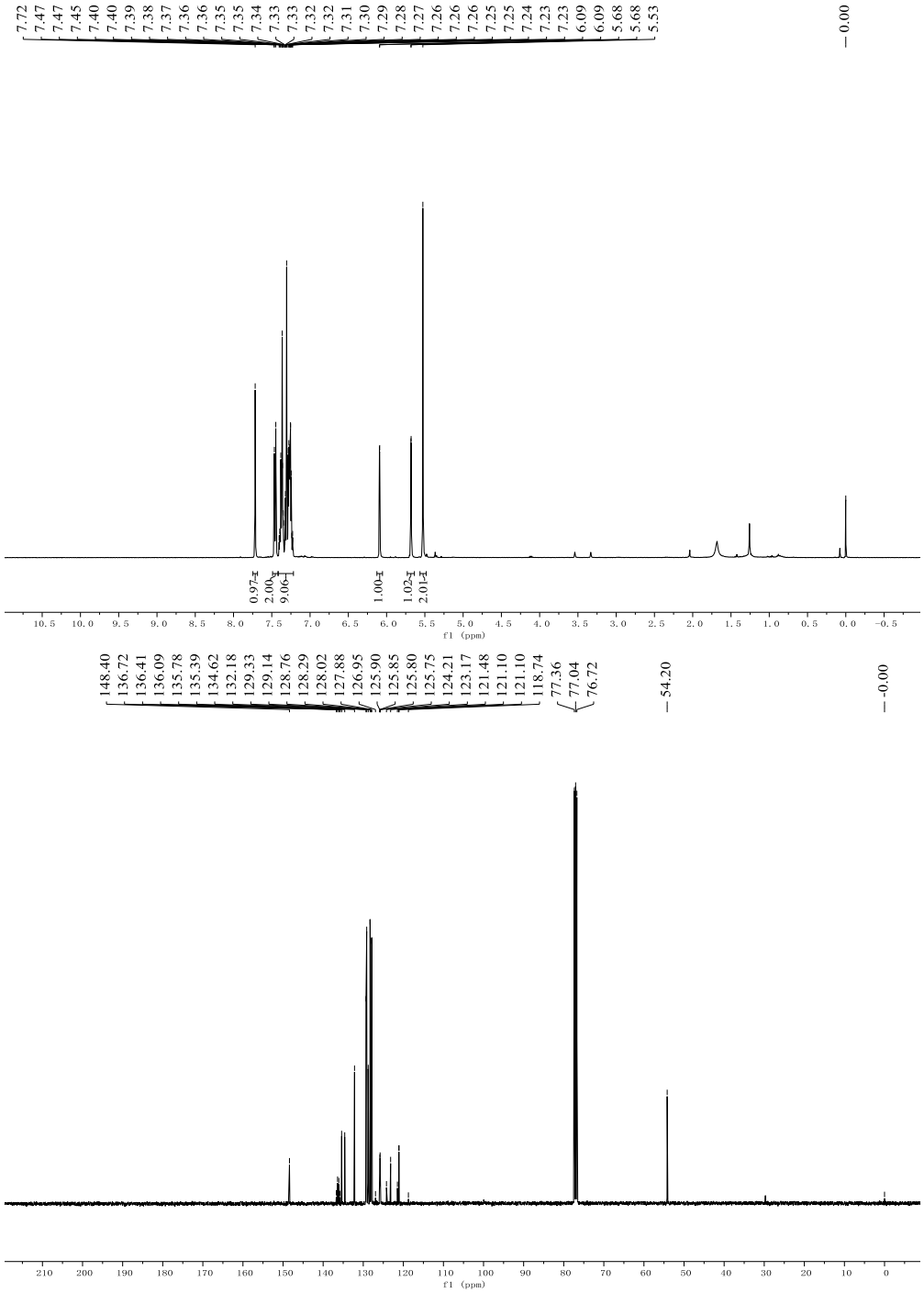
(*E*)-1-benzyl-4-(1-phenyl-3-(trifluoromethyl)buta-1,3-dien-2-yl)-1*H*-1,2,3-triazole (**12a**): Pale yellow oil, yield = 79% (isolated with preparative thin layer chromatography and using ethyl acetate/hexane = 1:4 as eluent).

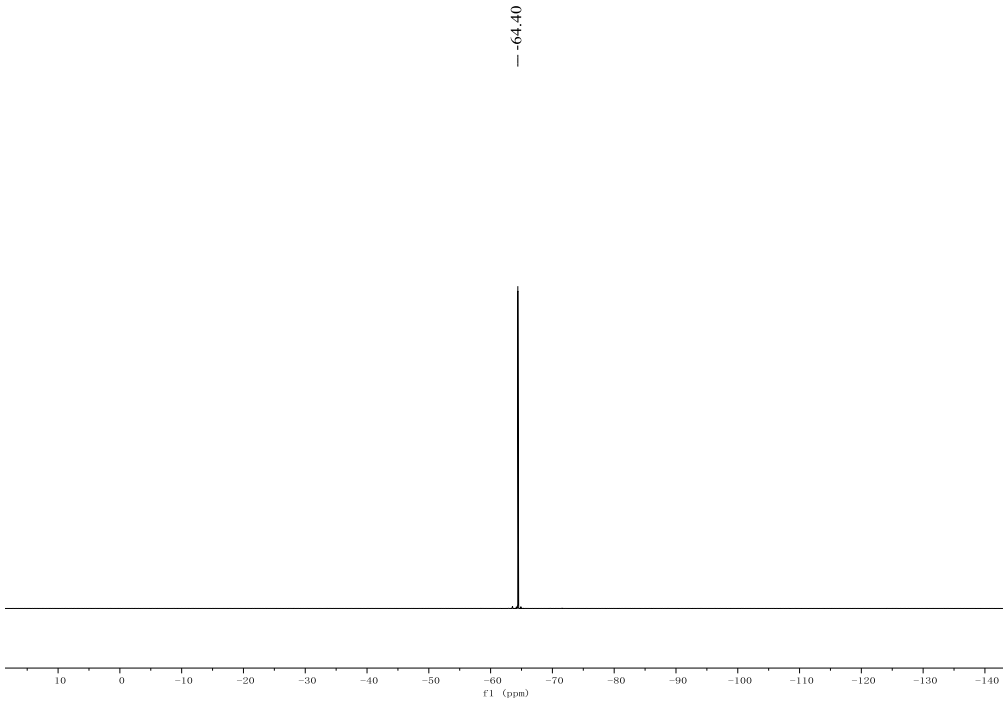
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.22 (m, 9H), 6.09 (d, *J* = 1.3 Hz, 1H), 5.73 – 5.64 (m, 1H), 5.53 (s, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.40.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.40, 136.25 (q, *J* = 31.7 Hz), 135.39, 134.62, 132.18, 129.33, 129.14, 128.76, 128.29, 128.02, 127.88, 125.82 (q, *J* = 4.9 Hz), 123.17, 122.84 (q, *J* = 275.3 Hz), 121.10 (m), 54.20.

HRMS (ESI) m/z calcd for $C_{20}H_{17}F_3N_3$ $[M+H]^+$: 356.1375, found: 356.1378.





VII. Reference:

1. Azpíroz, R.; Rubio-Pérez, L.; Castarlenas, R.; Pérez-Torrente, J. J.; Oro, L. A. Gem-Selective Cross-Dimerization and Cross-Trimerization of Alkynes with Silylacetylenes Promoted by a Rhodium-Pyridine-N-Heterocyclic Carbene Catalyst. *ChemCatChem* **2014**, *6*, 2587–2592.
2. Wu, Y.-T.; Lin, W.-C.; Liu, C.-J.; Wu, C.-Y. Palladium-Catalyzed Trimerizations of Terminal Arylalkynes: Synthesis of 1,3-Diaryl-2-Arylethynyl-1,3-Butadienes. *Adv. Synth. Catal.* **2008**, *350*, 1841–1849.