Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

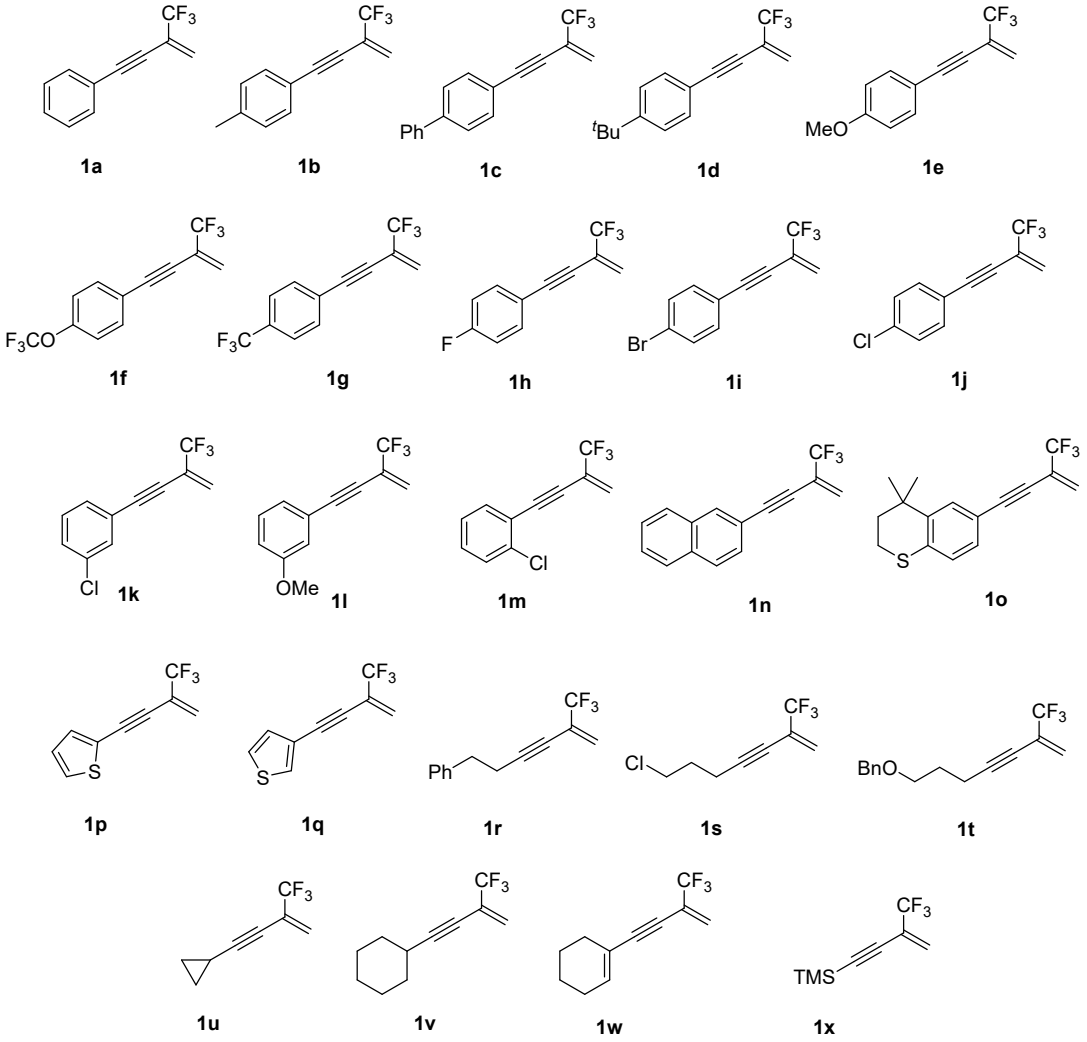
Synthesis of Conjugated Bisallenes by Cooperative Cu/Pd Catalysed Borylallenylation of 2-Trifluoromethyl-1,3-Enynes

Shang-Hai Yu, Tian-Jun Gong* and Yao Fu*

I. General Information

A. Materials

All solvents were purchased and used without further purification. The following Chemicals were purchased and used as received: IMesCuCl (Sigma-Aldrich), IPrCuCl (Sigma-Aldrich), Pd(dppf)Cl_2 (*J&K*), Pd(dppe)Cl_2 (*J&K*), LiOMe (99%, *J&K*), LiO^{t}Bu (99%, Acros), NaO^{t}Bu (99%, Acros), dry THF (J&K). The 2-trifluoromethyl-1,3-enynes **1a-1x** were prepared according to standard procedures[1-4].



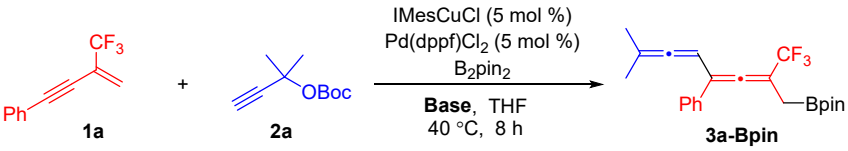
B. Analytical Methods

^{1}H-NMR, ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient

temperature in $CDCl_3$ unless otherwise noted; Data for ^{1}H-NMR arereported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatography (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Acquity UPLC-Xevo G2 QTof mass spectrometer. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

II. General Experimental Procedures

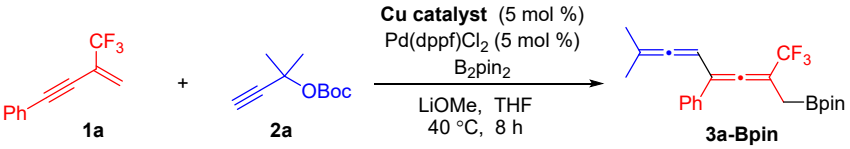
Table S1. Screening of base[a]



entry	**Base**	conv. of **1a** (%)	yield (%) [b]
1	LiO^{t}Bu	> 99	trace
2	NaO^{t}Bu	> 99	7
3	KO^{t}Bu	78	trce
4	**LiOMe**	**> 99**	**24**
5	NaOMe	93	trace

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), B_2pin_2 (0.15 mmol), Base (0.2 mmol), IMesCuCl (5 mol %), and $Pd(dppf)Cl_2$ (5 mol %) in THF (1.5 mL) at 40 °C for 8 h, the conversion ratio of **1a** was determined by GC. [b]Yield was determined by ^{1}H NMR using Ph_3CH as internal standard.

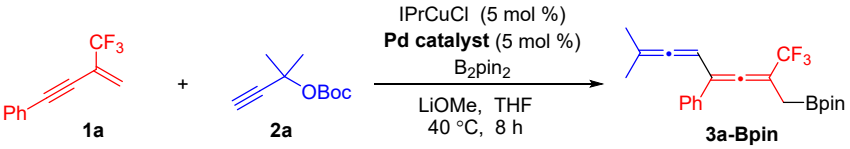
Table S2. Screening of Cu catalyst[a]



entry	**Cu catalyst**	conv. of **1a** (%)	yield (%) [b]
1	$CuCl/PCy_3$	> 99	11
2	ICyCuCl	64	trace
3	SIMeCuCl	> 99	20
4	SIPrCuCl	> 99	45
5	**IPrCuCl**	**> 99**	**47**

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), B_2pin_2 (0.15 mmol), LiOMe (0.2 mmol), Cu catalyst (5 mol %), and $Pd(dppf)Cl_2$ (5 mol %) in THF (1.5 mL) at 40 °C for 8 h, the conversion ratio of **1a** was determined by GC. [b]Yield was determined by ^1H NMR using Ph_3CH as internal standard.

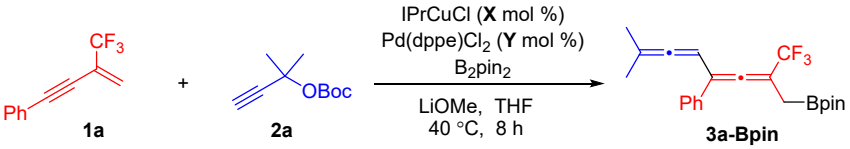
Table S3. Screening of Pd catalyst[a]



entry	**Pd catalyst**	conv. of **1a** (%)	yield (%) [b]
1	$Pd(dba)_2/dppf$	> 99	38
2	**$Pd(dppe)Cl_2$**	**87**	**66**
3	$Pd(dppp)Cl_2$	92	60
4	$Pd(dppm)Cl_2$	> 99	51
5	Pd-XPhos-G3	> 99	trace
6	Pd-SPhos-G3	> 99	18

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), B_2pin_2 (0.15 mmol), LiOMe (0.2 mmol), IPrCuCl (5 mol %), and Pd catalyst (5 mol %) in THF (1.5 mL) at 40 °C for 8 h, the conversion ratio of **1a** was determined by GC. [b]Yield was determined by ^1H NMR using Ph_3CH as internal standard.

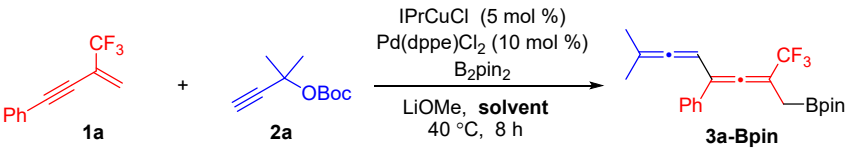
Table S4. Screening of the loadings of Cu and Pd catalysts[a]



entry	**X** (mol %)	**Y** (mol %)	conv. of **1a** (%)	yield (%) [b]
1	2	2	74	51
2	5	5	87	66
3[c]	5	5	95	68
4	**5**	**10**	**> 99**	**72**
5	5	15	> 99	71

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), B_2pin_2 (0.15 mmol), LiOMe (0.2 mmol), IPrCuCl (X mol %), and $Pd(dppe)Cl_2$ (Y mol %) in THF (1.5 mL) at 40 °C for 8 h, the conversion ratio of **1a** was determined by GC. [b]Yield was determined by ^1H NMR using Ph_3CH as internal standard. [c]Reaction time: 12 h.

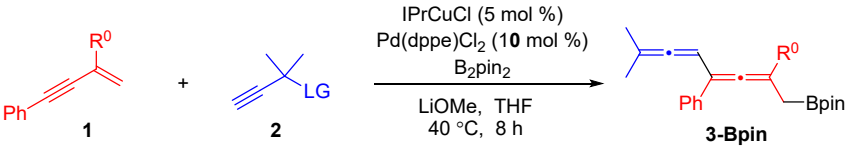
Table S5. Screening of the solvent[a]



entry	**solvent**	conv. of **1a** (%)	yield (%) [b]
1[c]	**THF**	**> 99**	**57**
2	2-MeTHF	33	trace
3	Toluene	92	14
4	Dioxane	> 99	35
5	MeCN	41	trace
6	DME	55	trace

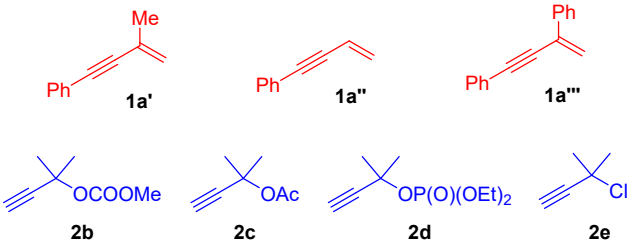
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), B_2pin_2 (0.15 mmol), LiOMe (0.2 mmol), IPrCuCl (5 mol %), and $Pd(dppe)Cl_2$ (10 mol %) in solvent (1.5 mL) at 40 °C for 8 h, the conversion ratio of **1a** was determined by GC. [b]Yield was determined by ^1H NMR using Ph_3CH as internal standard. [c]Reaction temperature: 60 °C.

Table S6. Screening of the types of substrates[a]



1 2 3-Bpin

entry	1	2	conv. of **1a** (%)	yield (%) [b]
1	**1a**	**2b**	**95**	**64**
2	1a	2c	73	28
3	1a	2d	77	34
4	1a	2e	> 99	43
5	1a'	2a	18	trace
6	1a''	2a	92	trace
7	1a'''	2a	40	trace

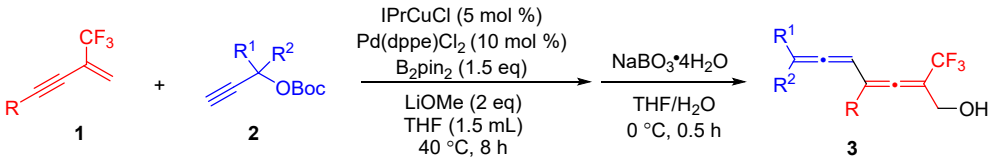


1a' 1a'' 1a''' 2b 2c 2d 2e

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol), B_2pin_2 (0.15 mmol), LiOMe (0.2 mmol), IPrCuCl (5 mol %), and $Pd(dppe)Cl_2$ (10 mol %) in THF (1.5 mL) at 40 °C for 8 h, the conversion ratio of **1a** was determined by GC. [b]Yield was determined by ^1H NMR using Ph_3CH as internal standard.

III. General Experimental Procedures

A. General Experimental Procedures of Cu/Pd Catalysed Borylallenylation of 1,3-Enynes

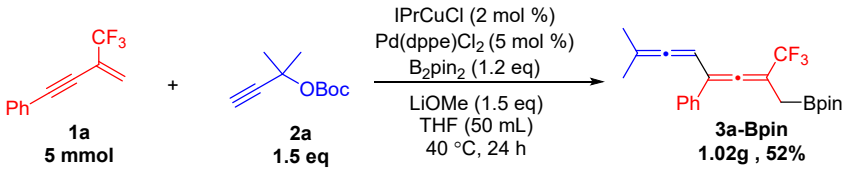


1 2 3

In the glove box, A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with IPrCuCl (5 mol %), B_2pin_2 (1.5 eq) and LiOMe (2 eq), then the mixture was stirred for 2 minutes in THF (0.5 mL) at room temperature. In a separate vial, $Pd(dppe)Cl_2$ (10 mol %), enyne **1** (0.1 mmol) and propargylic carbonate **2** (0.2 mmol) were stirred in THF (1mL) for 5 minutes at room temperature, this solution was finally

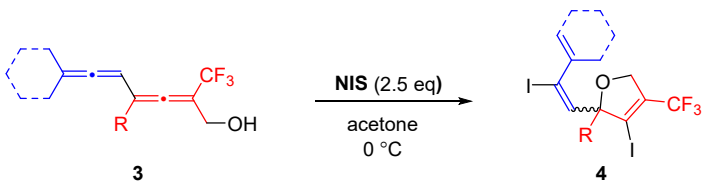
added to the reaction tube and heated at 40 ºC (oil bath) for 8 h (while the aliphatic substituted enyne was used, corresponding solution was heated at 50 ºC for 10 h). After this time, the reaction mixture was filtrated through a celite pad and concentrated under vacuum. Then the residue passed through a short column of deactivated silica gel to afford the product containing Bpin. Then a 10 mL vial with a stir bar was charged the product containing Bpin, 1.0 mL THF, 1.0 mL H_2O and $NaBO_3 \cdot 4H_2O$ (4 eq) was added. After stirring at 0 °C for 0.5 h, the mixture was extracted with EtOAc, dried over Na_2SO_4. The combined organic phase was evaporated under vacuum, purified by flash column chromatography on silica gel to give the target product.

Gram Scale Experiment for Synthesis of 3a-Bpin:



A 100 mL Schlenk tube equipped with a magnetic stirrer was charged with IMesCuCl (2 mol %), Pd(dppe)Cl_2 (5 mol %), B_2pin_2 (1.2 eq) and LiOMe (1.5 eq). The tube was evacuated and backfilled with argon for three times, and then THF (50 mL) was added. After stirring for 5 min, the enyne **1a** (5 mmol) and propargylic carbonate **2a** (1.5 eq) were added by syringes under Ar. The reaction mixture was stirred and heated at 40 ºC (oil bath) for 24 h. Then EtOAc and water were added and the layers were separated. The aqueous phase was extracted with EtOAc (x 2) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on deactivated silica gel to give the product.

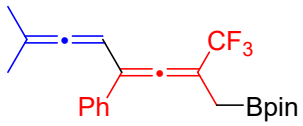
B. General Experimental Procedures of Iodination of Conjugated Bisallenes



A 10 mL Schlenk tube equipped with magnetic stir bar was charged with NIS (2.5

eq) and 1.0 mL dry acetone, then cooled to 0 °C under argon atmosphere. The bisallene **3** (0.2 mmol) in 1.0 mL dry acetone was added. The mixture was stirred at 0 °C for one hour. Purification of the reaction mixture by flash chromatography (PE/EA 50:1) afforded the title compound **4**.

IV. NMR Data and Spectra



4,4,5,5-tetramethyl-2-(7-methyl-4-phenyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-yl)-1,3,2-dioxaborolane (3a-Bpin)

After isolated and purified procedure, this compound was obtained 1.02g (52% yield on the scale of 5 mmol) as colorless oil. (Petroleum ether: EtOAc = 15 : 1)

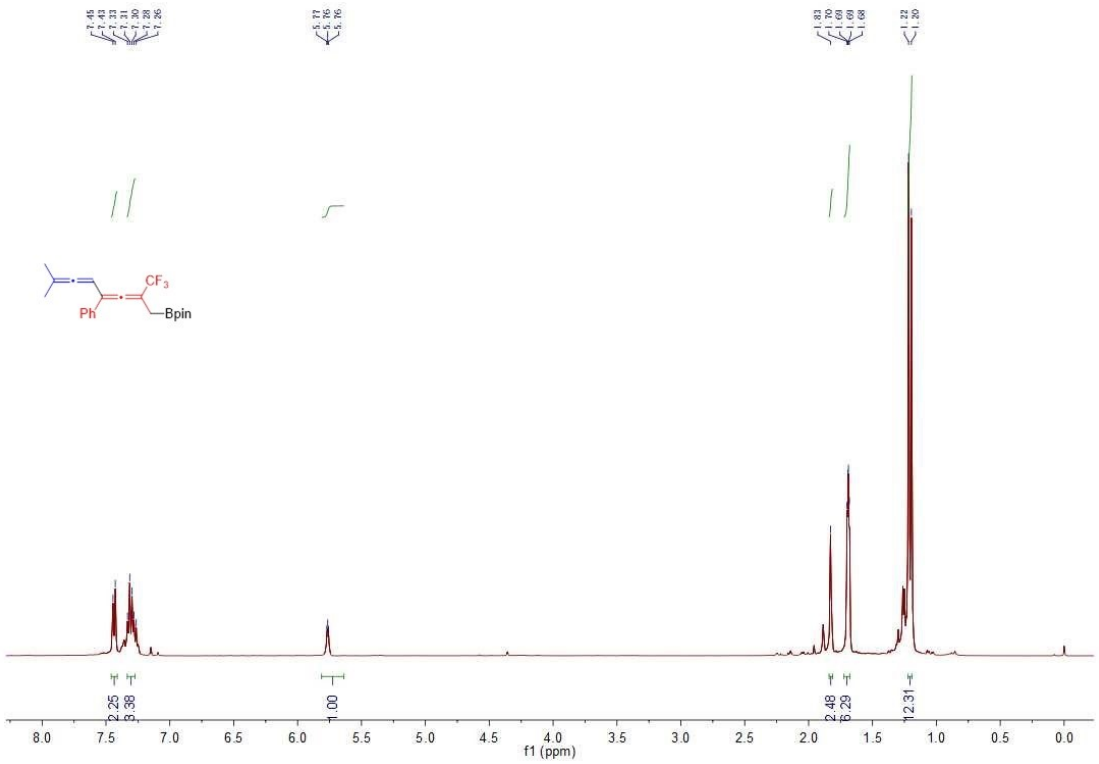
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.37 (m, 2H), 7.35-7.20 (m, 3H), 5.83-5.65 (m, 1H), 1.83 (s, 1H), 1.69 (dd, J = 4.3, 3.2 Hz, 6H), 1.21 (d, J = 8.8 Hz, 12H).

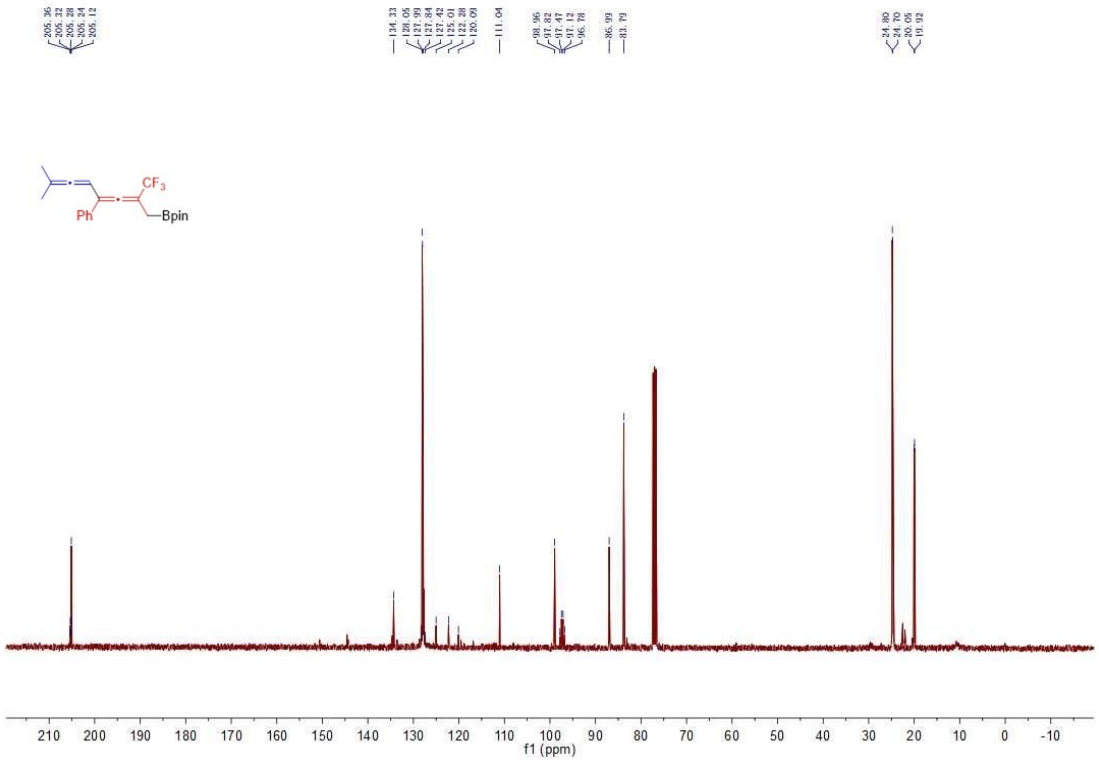
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3 (q, J = 4.0 Hz), 205.1, 134.3, 128.1, 128.0, 127.8, 123.6 (q, J = 274.6 Hz), 111.0, 99.0, 97.3 (q, J = 35.0 Hz), 87.0, 83.8, 24.8, 24.7, 20.1, 19.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.98.

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.30.

HRMS (ESI) calculated for $C_{22}H_{27}BF_3O_2^+$ $[M+H]^+$ 391.2051; found 391.2062.


7.45
7.43
7.33
7.31
7.30
7.28
7.26
5.17
5.16
5.76
1.83
1.70
1.69
1.68
1.32
1.30
CF3
Ph
Bpin
2.25
3.38
1.00
2.48
6.29
12.31
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


205.36
205.32
205.28
205.24
205.12
134.33
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127.99
127.84
127.42
125.01
122.28
120.69
111.04
98.95
97.82
97.47
97.12
96.78
96.99
93.79
24.80
24.70
20.05
19.92
CF3
Ph
Bpin
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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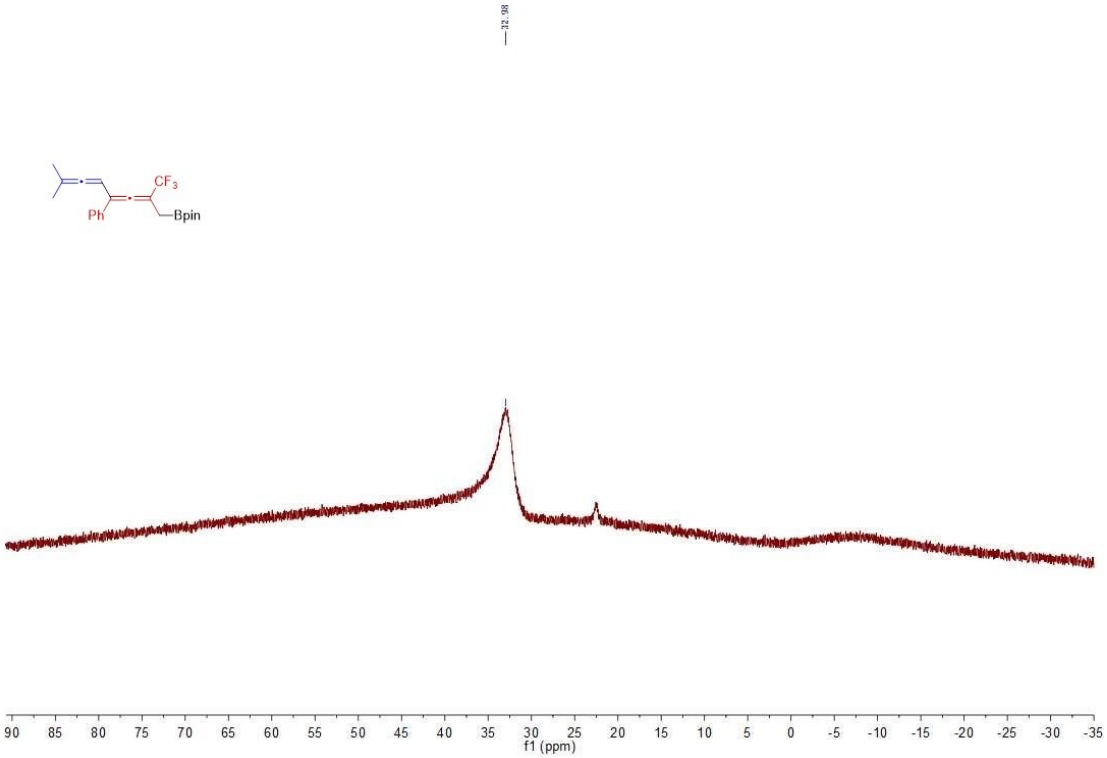
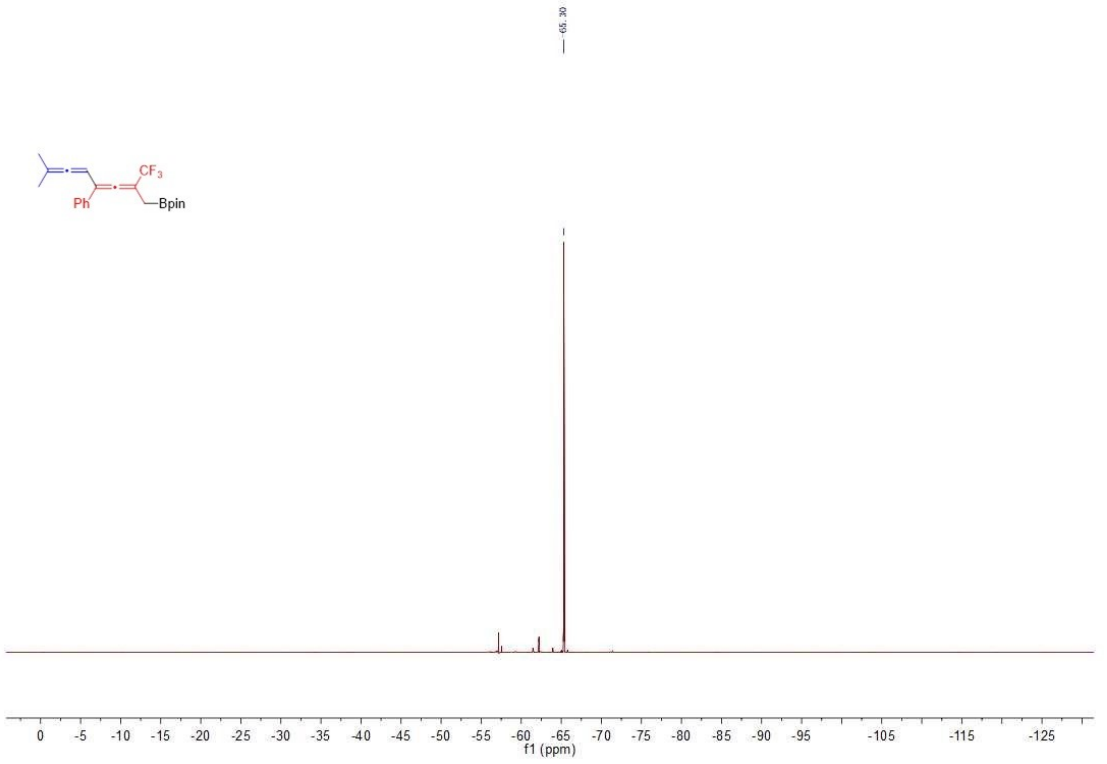
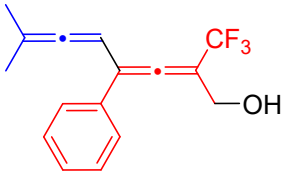
f1 (ppm)







7-methyl-4-phenyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3a)

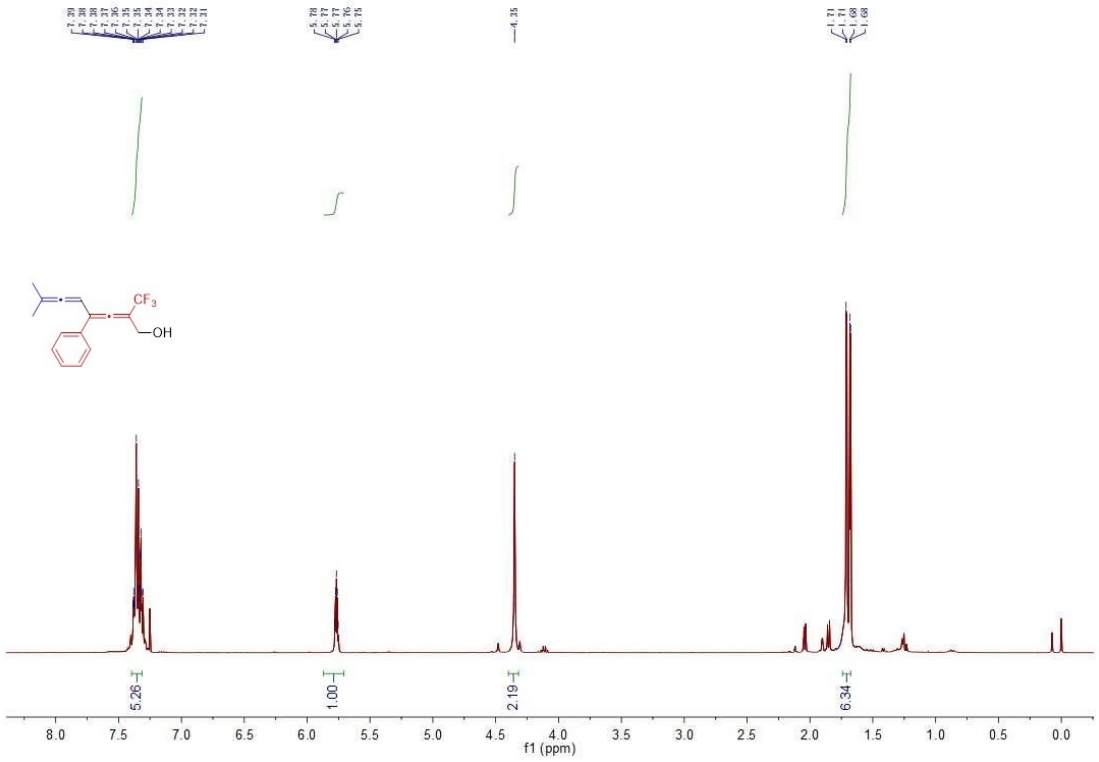
After isolated and purified procedure, this compound was obtained 18.2 mg (65% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

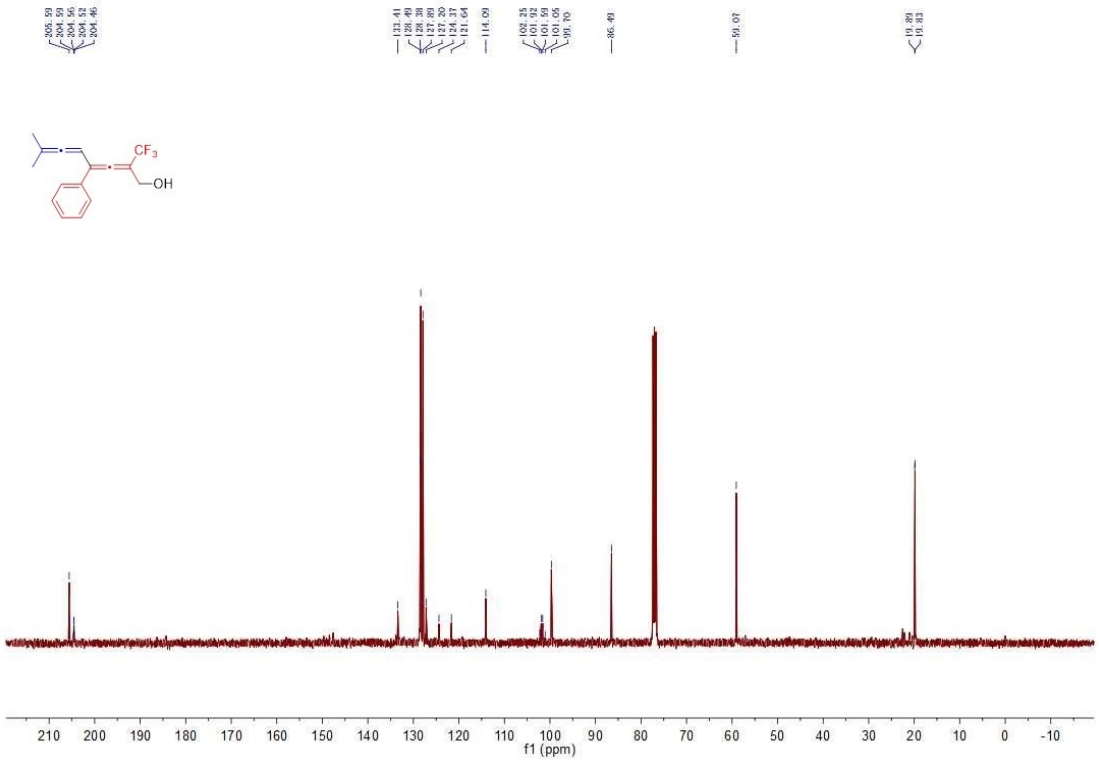
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.27 (m, 5H), 5.77 (dt, *J* = 5.6, 2.8 Hz, 1H), 4.35 (s, 2H), 1.69 (dd, *J* = 12.0, 2.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.6 (q, *J* = 4.2 Hz), 133.4, 128.5, 128.4, 127.9, 127.2, 123.0 (q, *J* = 274.9 Hz), 114.1, 101.7 (q, *J* = 33.3 Hz), 99.7, 86.5, 59.1, 19.9, 19.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22.

HRMS (ESI) calculated for $C_{16}H_{16}F_3O^+$ $[M+H]^+$ 281.1148; found 281.1153.

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204.59
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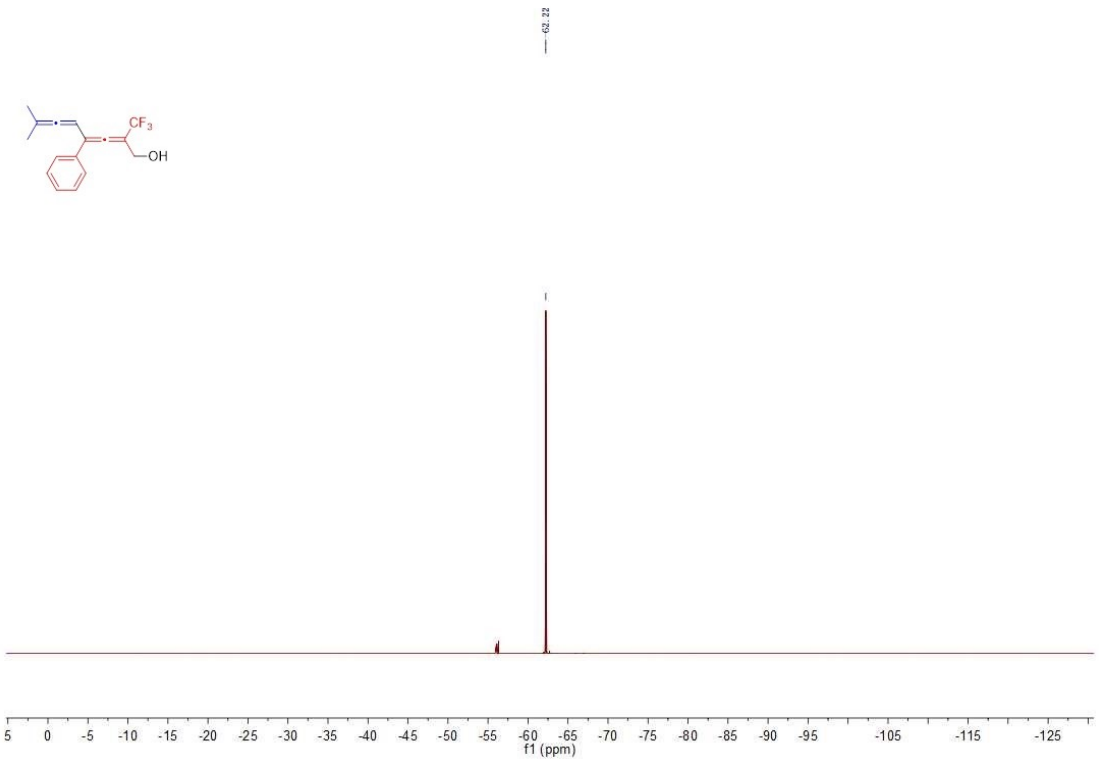
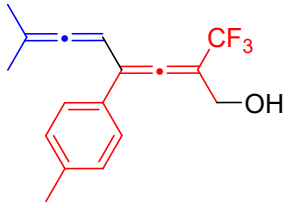
204.52
204.46
133.41
128.49
128.38
127.89
127.30
124.37
121.64
114.09
102.25
101.92
101.59
101.05
99.70
86.49
59.07
19.89
19.83
CF3
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.22
CF3
OH
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH

7-methyl-4-(p-tolyl)-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3b)

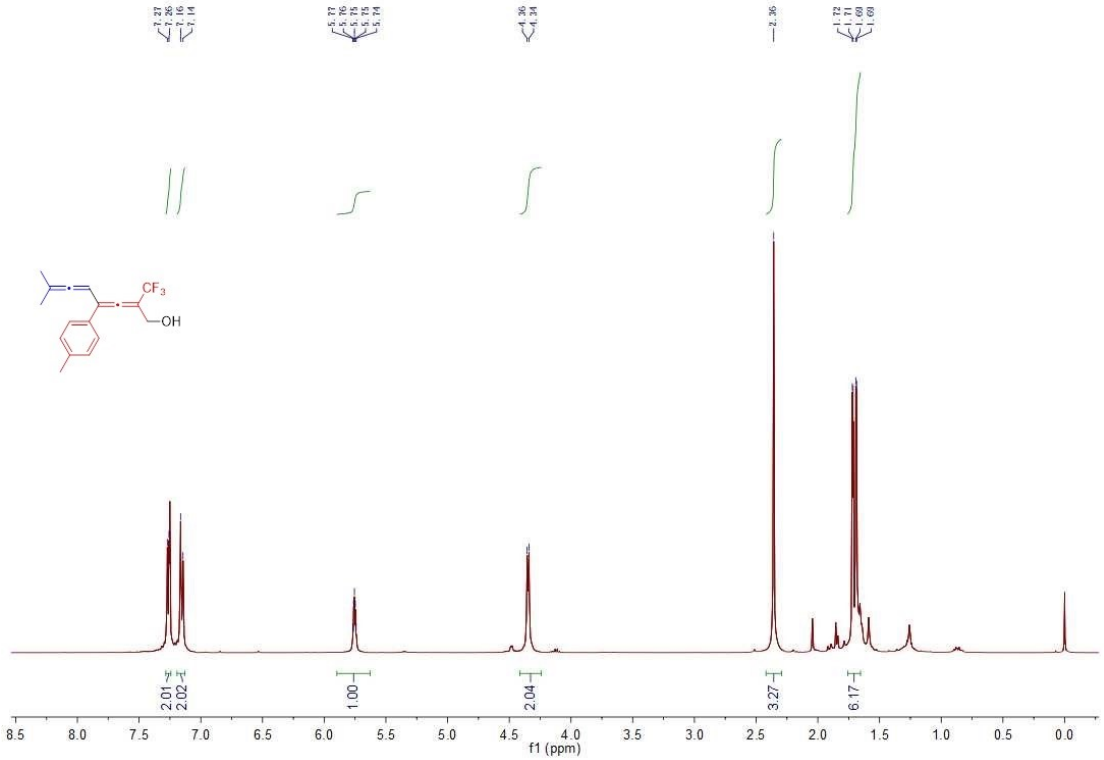
After isolated and purified procedure, this compound was obtained 20.0 mg (68% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

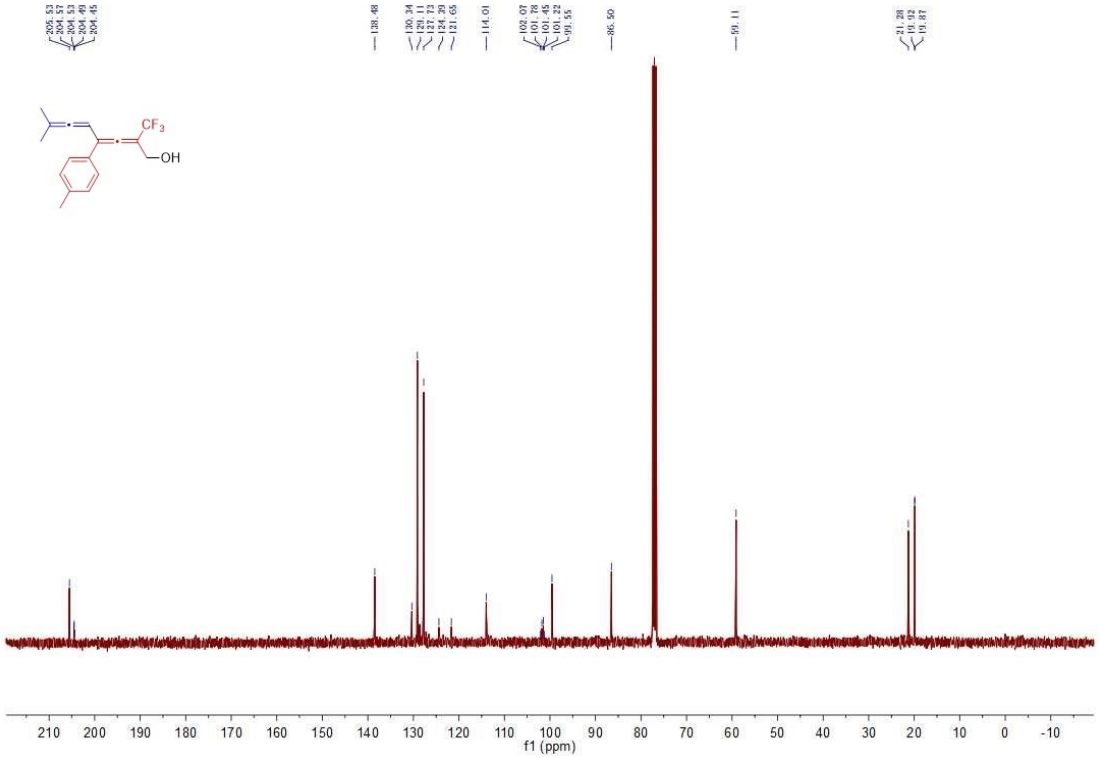
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 5.3 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.75 (dt, *J* = 5.6, 2.8 Hz, 1H), 4.35 (d, *J* = 5.8 Hz, 2H), 2.36 (s, 3H), 1.70 (dd, *J* = 11.3, 2.8 Hz, 6H).

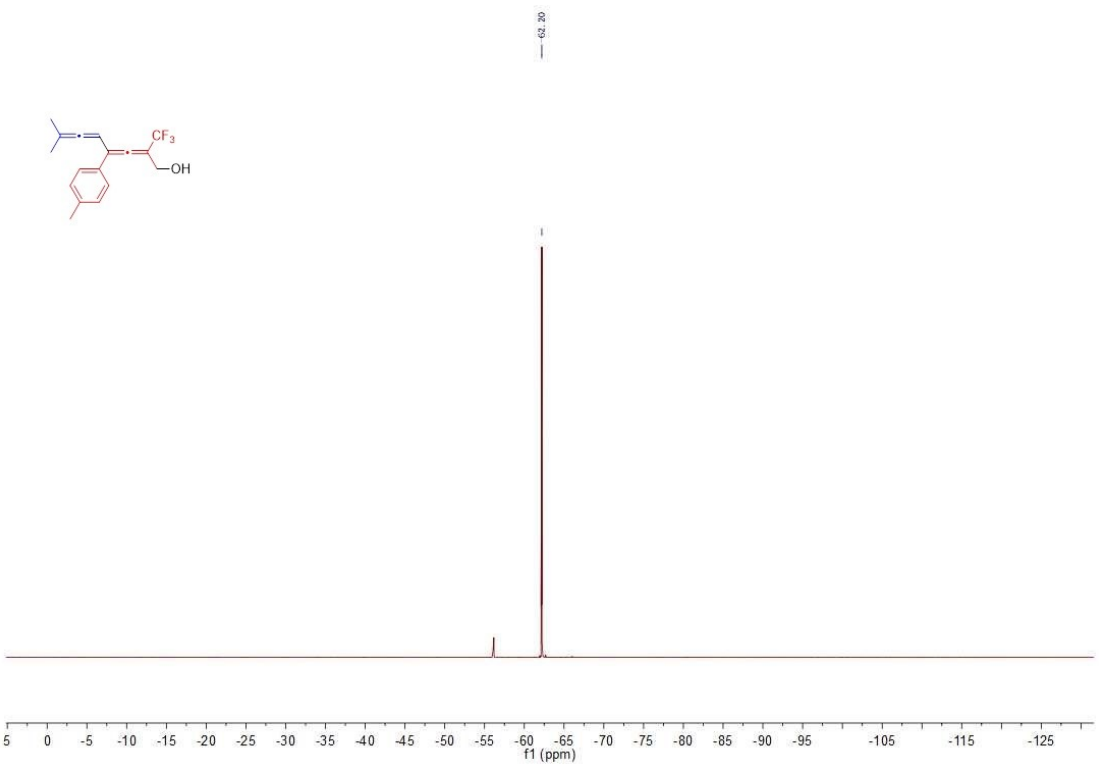
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5, 204.5 (q, *J* = 4.0 Hz), 138.5, 130.3, 129.1, 127.7, 123.0 (q, *J* = 275.0 Hz), 114.0, 101.6 (q, *J* = 33.2 Hz), 99.6, 86.5, 59.1, 21.3, 19.9, 19.87.

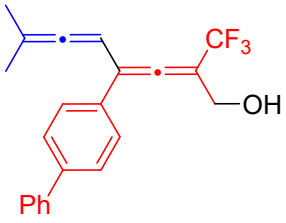
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.20.

HRMS (ESI) calculated for $C_{17}H_{18}F_3O^+$ $[M+H]^+$ 295.1304; found 295.1308.




205.53
204.57
204.53
204.49
204.45
138.48
130.34
129.11
127.73
124.20
121.65
114.01
102.07
101.78
101.45
101.22
99.55
86.50
59.11
21.28
19.92
19.87
CF3
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.20
CF3
OH
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
Ph

4-([1,1'-biphenyl]-4-yl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3c)

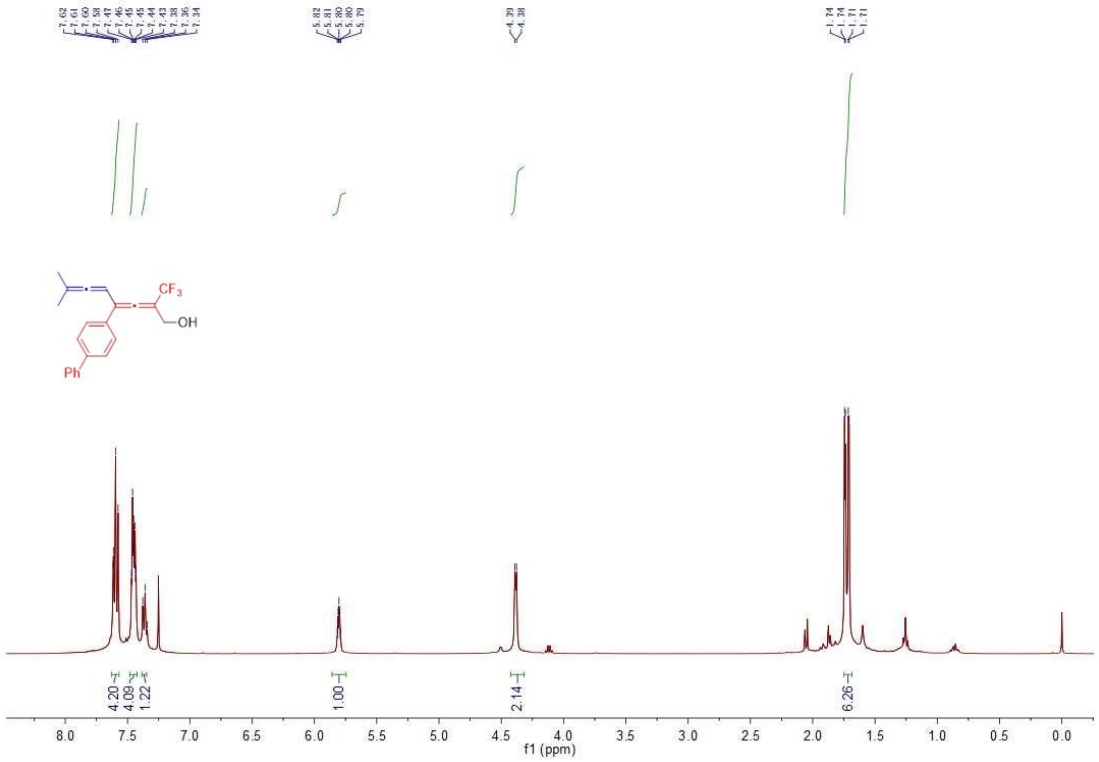
After isolated and purified procedure, this compound was obtained 25.3 mg (71% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

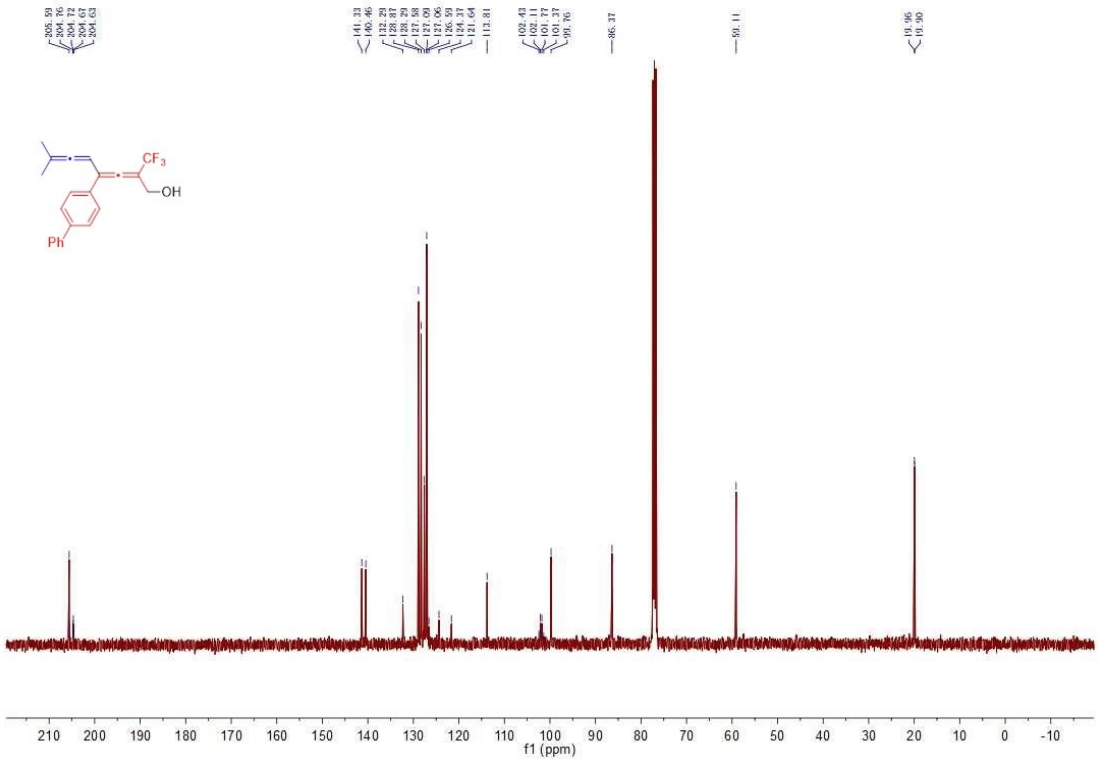
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 4H), 7.47-7.44 (m, 4H), 7.43-7.34 (m, 1H), 5.80 (dt, *J* = 5.6, 2.8 Hz, 1H), 4.38 (d, *J* = 5.2 Hz, 2H), 1.73 (dd, *J* = 12.0, 2.8 Hz, 6H).

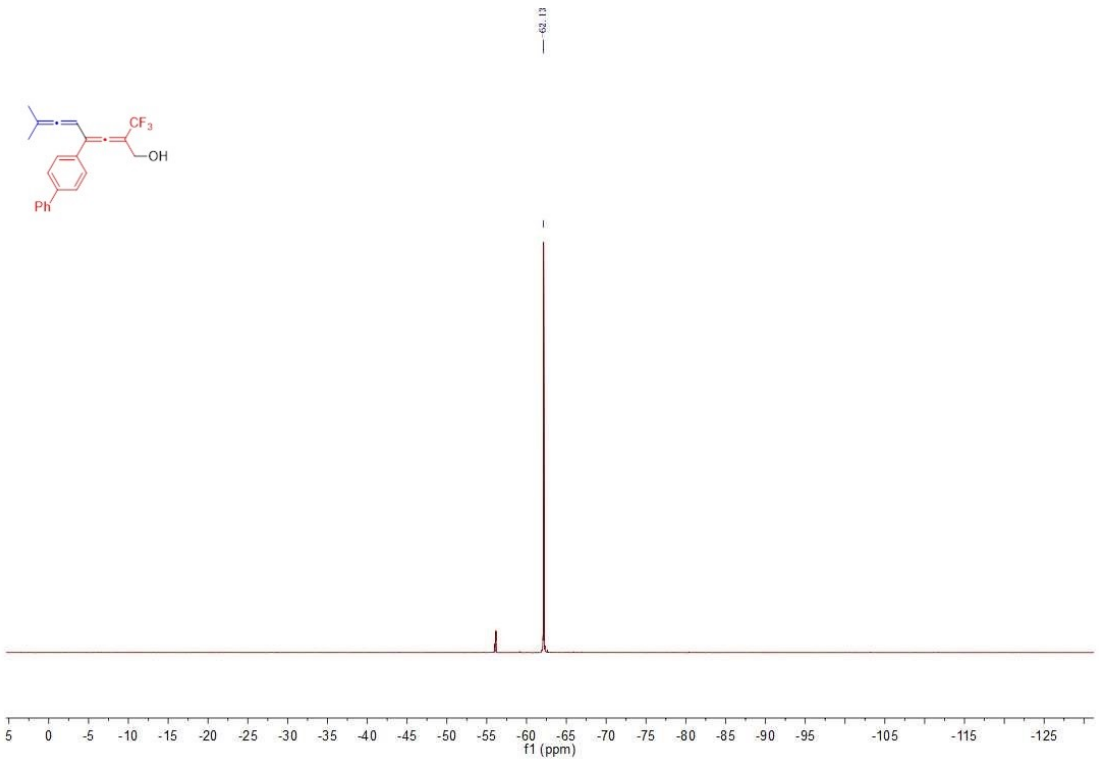
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.7 (q, *J* = 4.1 Hz), 141.3, 140.5, 132.3, 128.9, 128.3, 127.6, 127.1, 127.1, 126.6, 123.0 (q, *J* = 275.2 Hz), 113.8, 101.9 (d, *J* = 33.5 Hz), 99.8, 86.4, 59.1, 20.0, 19.9.

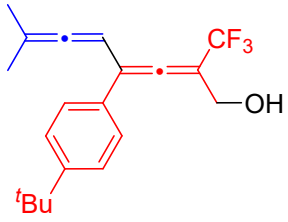
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.13.

HRMS (ESI) calculated for $C_{22}H_{20}F_3O^+$ $[M+H]^+$ 357.1461; found 357.1465.




205.59
204.76
204.72
204.67
204.63
141.33
140.46
132.29
128.87
128.29
127.58
127.20
127.06
125.59
124.37
121.64
113.81
102.43
102.11
101.17
101.37
99.76
86.37
69.11
19.96
19.90
CF3
OH
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.13
CF3
OH
Ph
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
tBu

4-(4-(tert-butyl)phenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3d)

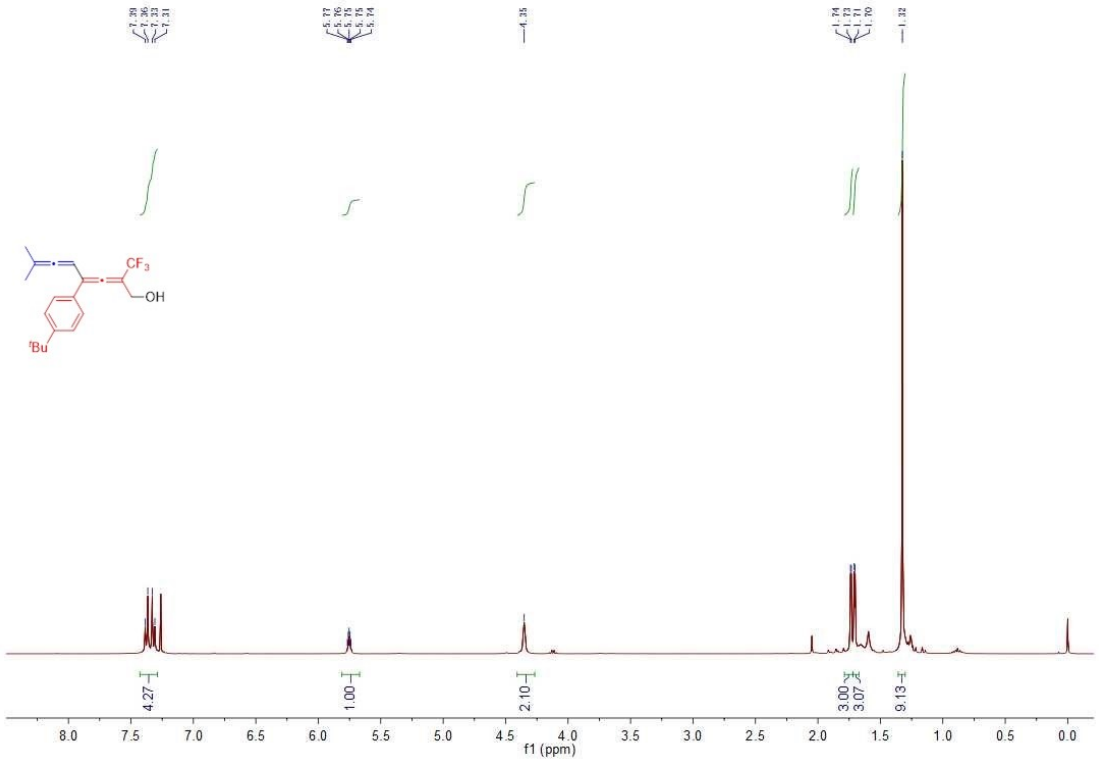
After isolated and purified procedure, this compound was obtained 23.5 mg (70% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

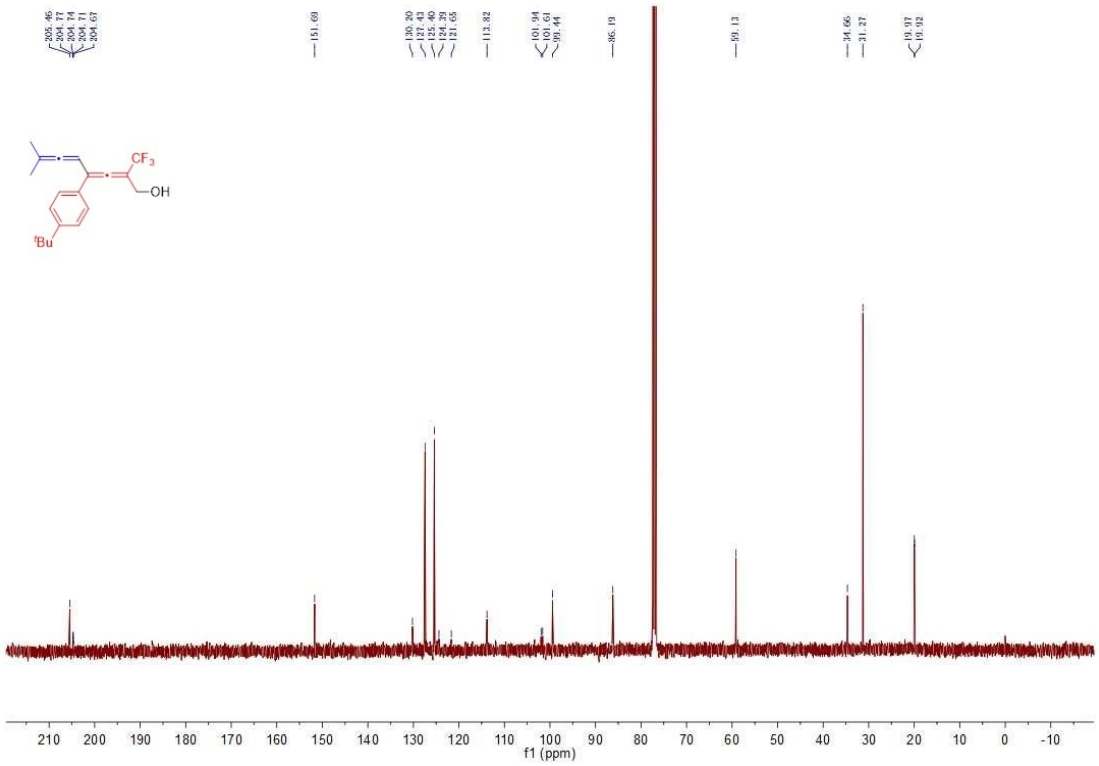
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 22.6, 8.5 Hz, 4H), 5.75 (dt, *J* = 5.6, 2.8 Hz, 1H), 4.35 (s, 2H), 1.72 (dd, *J* = 12.0, 2.8 Hz, 6H), 1.32 (s, 3H).

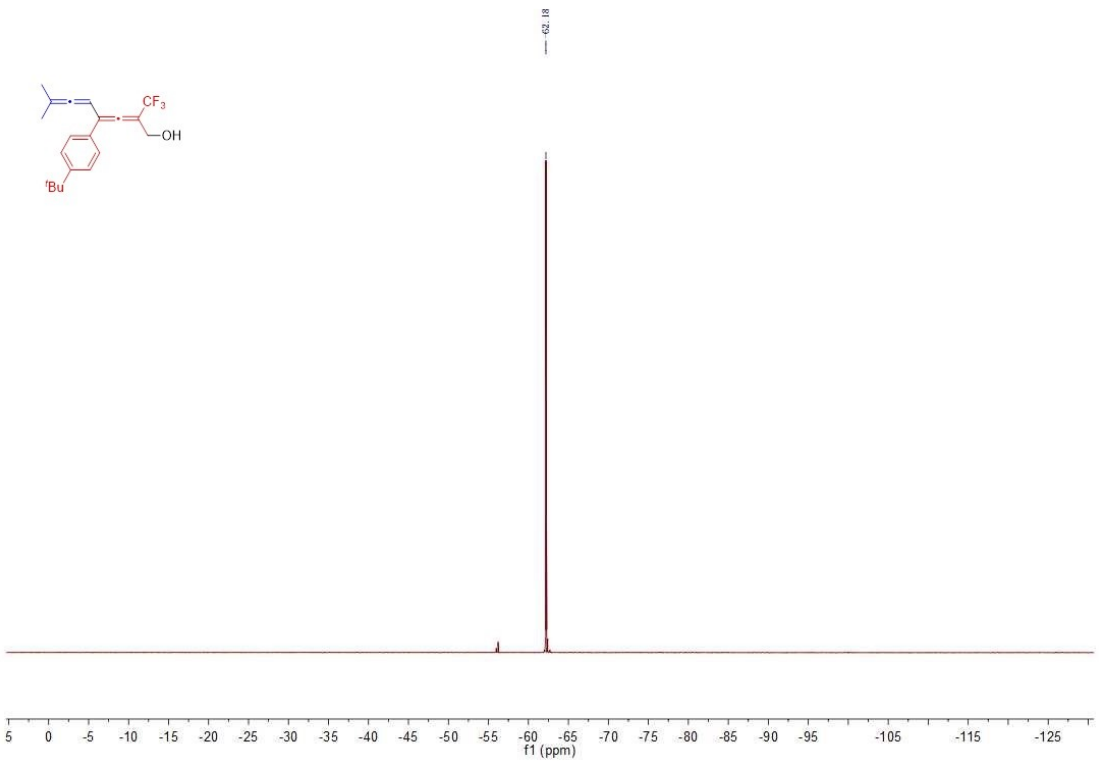
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5, 204.7 (q, *J* = 3.5 Hz), 151.7, 130.2, 127.4, 125.4, 123.0 (q, *J* = 275.0 Hz), 113.9, 101.8 (q, *J* = 33.4 Hz), 99.4, 86.2, 59.1, 34.7, 31.3, 20.0, 19.9.

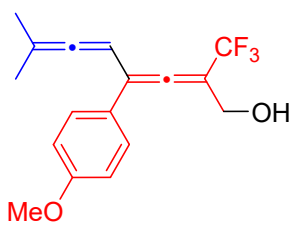
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.18.

HRMS (ESI) calculated for $C_{20}H_{24}F_3O^+$ $[M+H]^+$ 337.1774; found 337.1781.




205.46
204.17
204.14
204.11
204.07
151.69
130.20
127.43
125.40
124.28
121.05
113.82
101.94
101.61
99.44
86.19
59.13
34.66
31.27
19.97
19.92
CF3
OH
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.18
CF3
OH
tBu
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
MeO

4-(4-methoxyphenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3e)

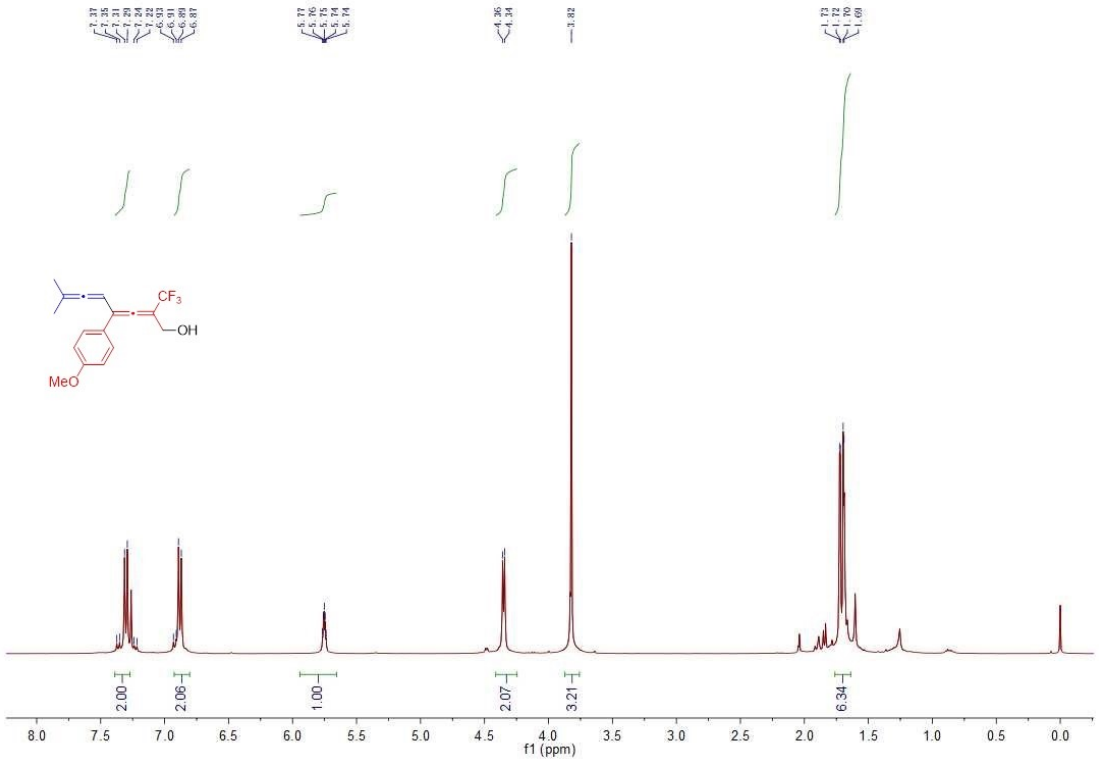
After isolated and purified procedure, this compound was obtained 17.9 mg (58% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

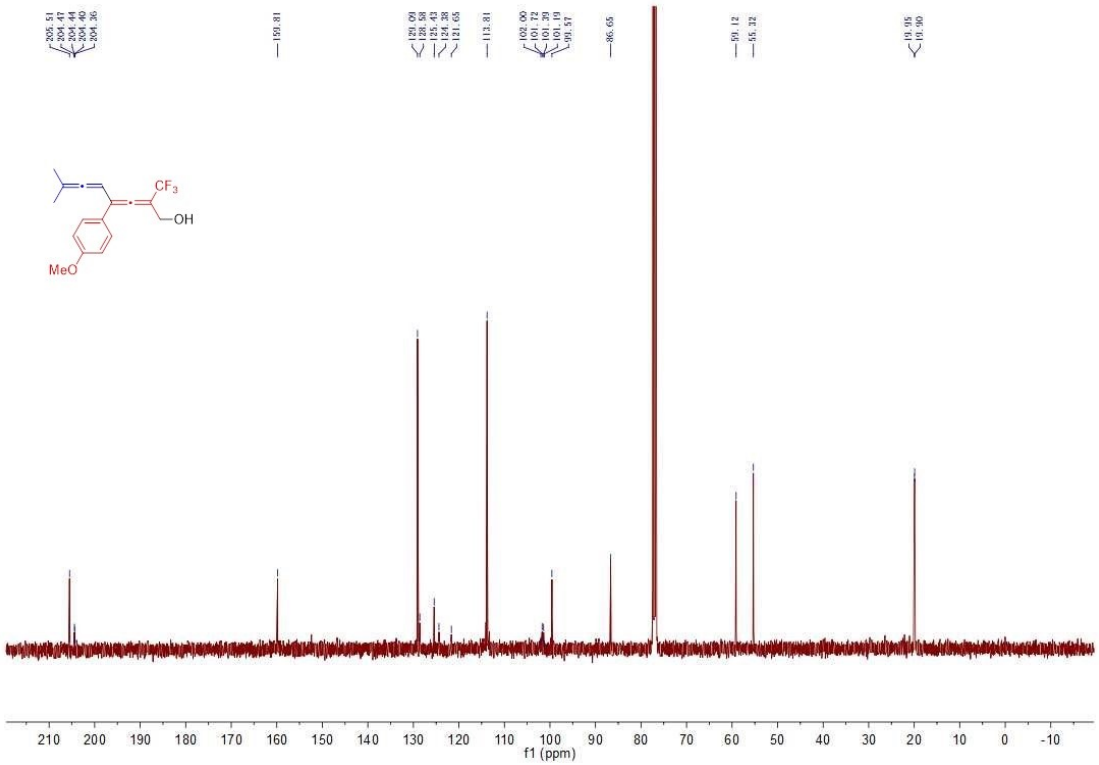
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.17 (m, 2H), 6.90 (dd, *J* = 15.8, 8.8 Hz, 2H), 5.75 (dt, *J* = 5.6, 2.7 Hz, 1H), 4.35 (d, *J* = 6.3 Hz, 2H), 3.82 (s, 3H), 1.71 (dd, *J* = 11.4, 2.8 Hz, 6H).

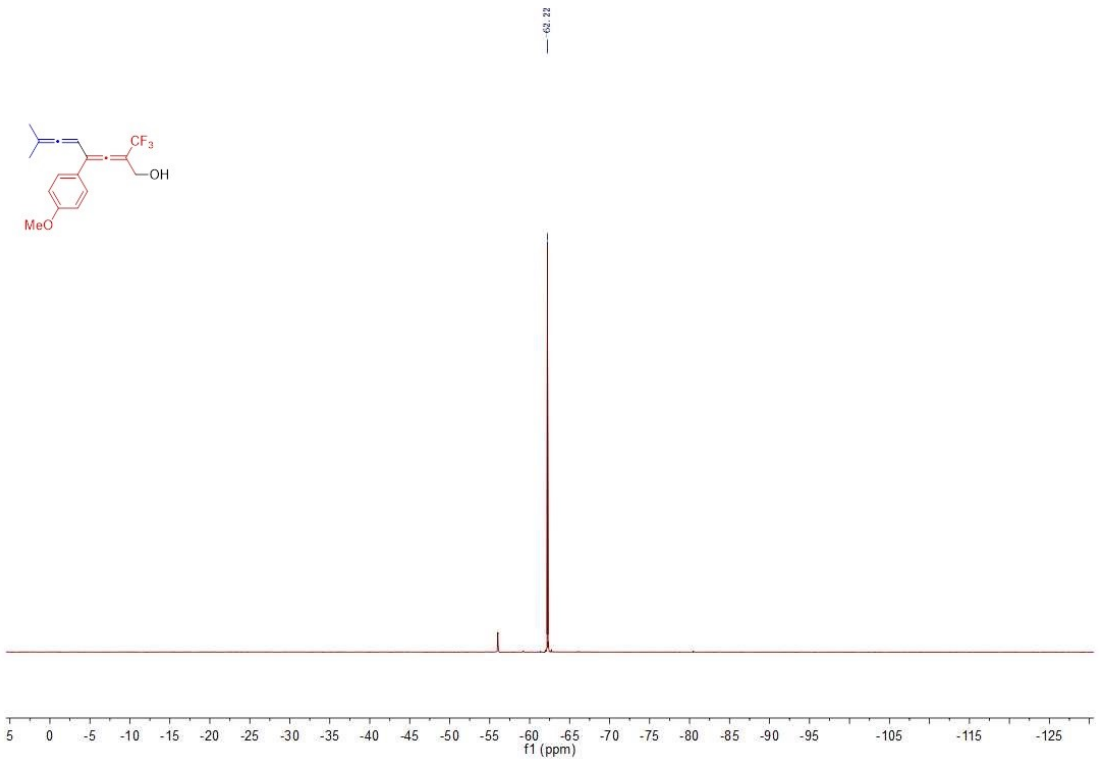
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5, 204.4 (q, *J* = 4.1 Hz), 159.8, 129.1, 128.6, 125.4, 123.0 (q, *J* = 275.1 Hz), 113.8, 101.6 (q, *J* = 33.1 Hz), 99.6, 86.7, 59.1, 55.3, 20.0, 19.9.

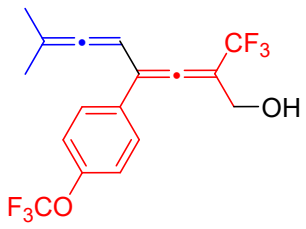
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22.

HRMS (ESI) calculated for $C_{17}H_{18}F_3O_2^+$ $[M+H]^+$ 311.1253; found 311.1255.




205.51
204.47
204.44
204.40
204.36
159.81
129.09
128.58
125.43
124.38
121.65
113.81
102.00
101.72
101.39
101.19
99.57
86.65
59.12
55.32
19.95
16.90
CF3
OH
MeO
f1 (ppm)


-62.22
CF3
OH
MeO
f1 (ppm)


CF3
OH
F3CO

7-methyl-4-(4-(trifluoromethoxy)phenyl)-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3f)

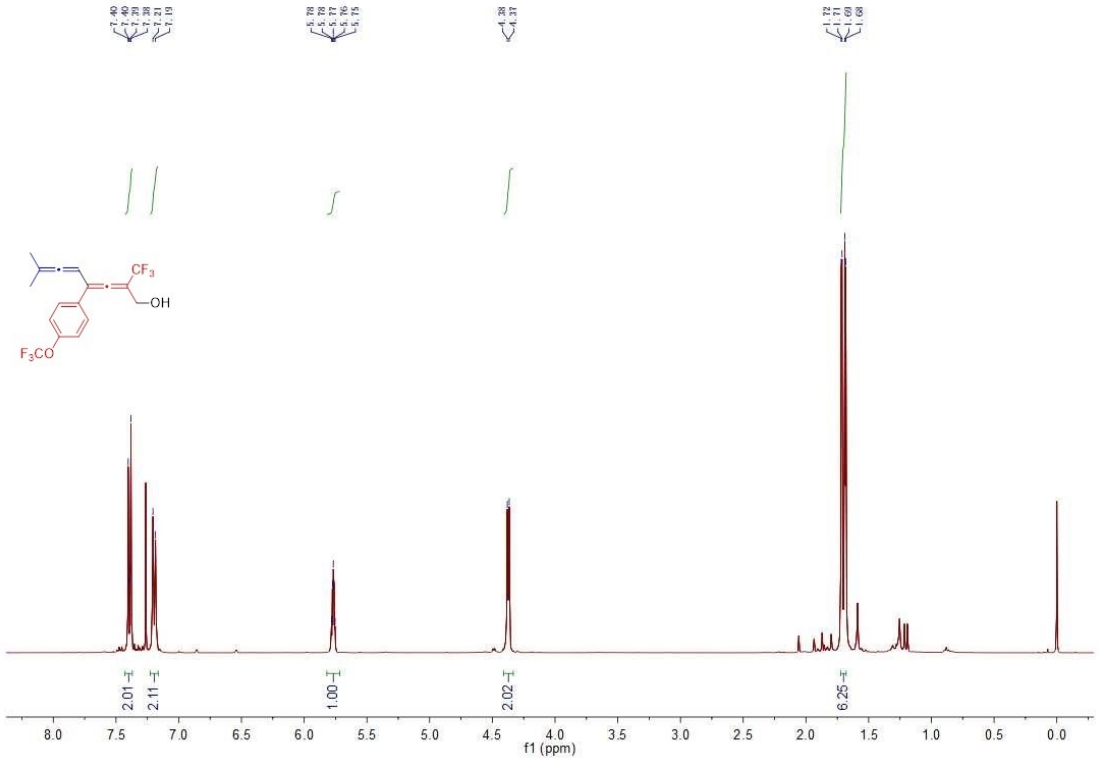
After isolated and purified procedure, this compound was obtained 21.8 mg (60% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

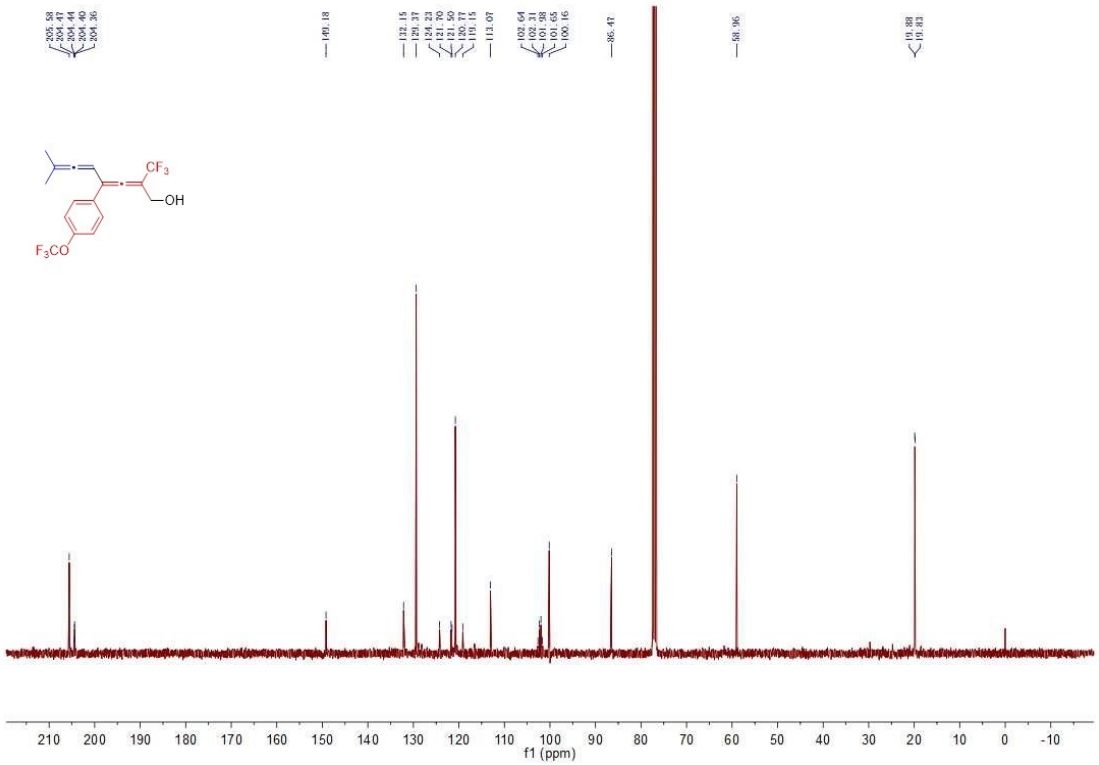
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.77 (dt, *J* = 5.7, 2.8 Hz, 1H), 4.37 (d, *J* = 6.2 Hz, 2H), 1.70 (dd, *J* = 11.9, 2.9 Hz, 6H).

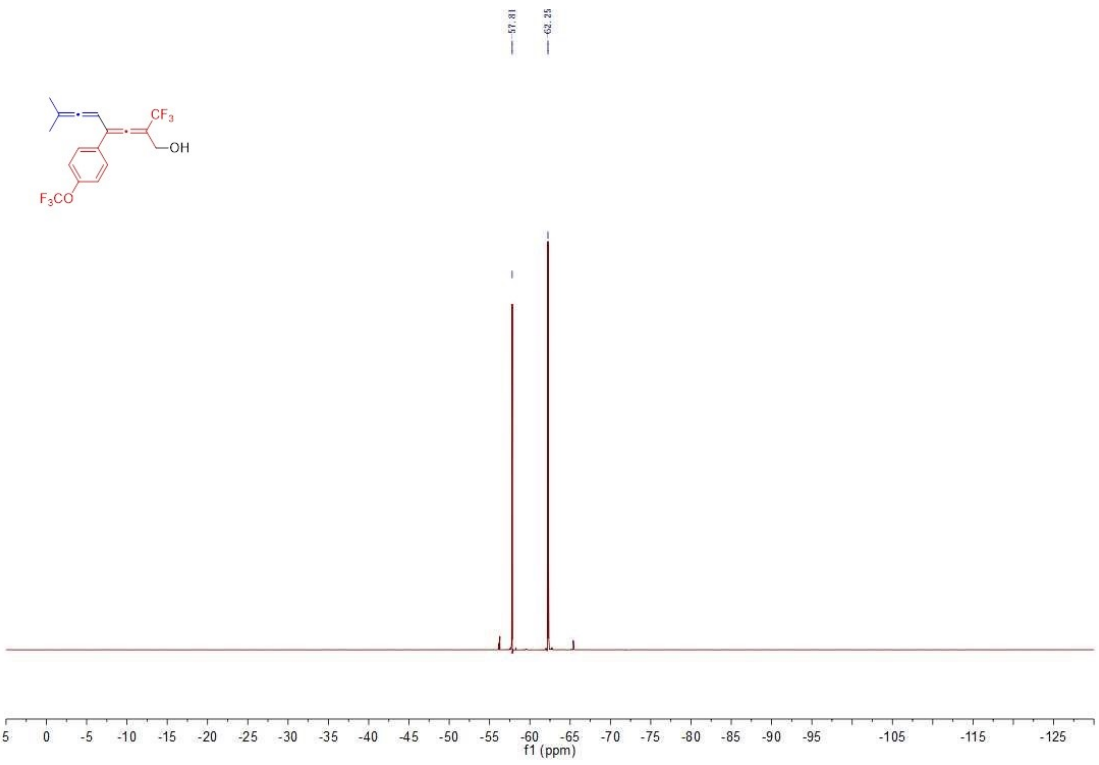
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.42 (q, *J* = 4.1 Hz), 149.2, 132.2, 129.4, 122.9 (q, *J* = 275.1 Hz), 120.8, 120.4 (q, *J* = 257.5 Hz), 113.1, 102.1 (q, *J* = 33.4 Hz), 100.2, 86.5, 59.0, 19.9, 19.8.

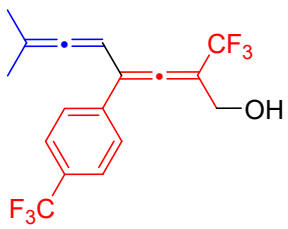
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.81, -62.25.

HRMS (ESI) calculated for $C_{17}H_{15}F_6O_2^+$ $[M+H]^+$ 365.0971; found 365.0974.




205.58
204.47
204.44
204.40
204.35
149.18
132.15
129.37
124.33
121.50
121.50
120.77
119.15
113.07
102.64
102.31
101.98
101.65
100.16
86.47
58.96
19.88
19.83
CF3
OH
F3CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


57.81
62.25
CF3
OH
F3CO
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
F3C

7-methyl-2-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)octa-2,3,5,6-tetraen-1-ol (3g)

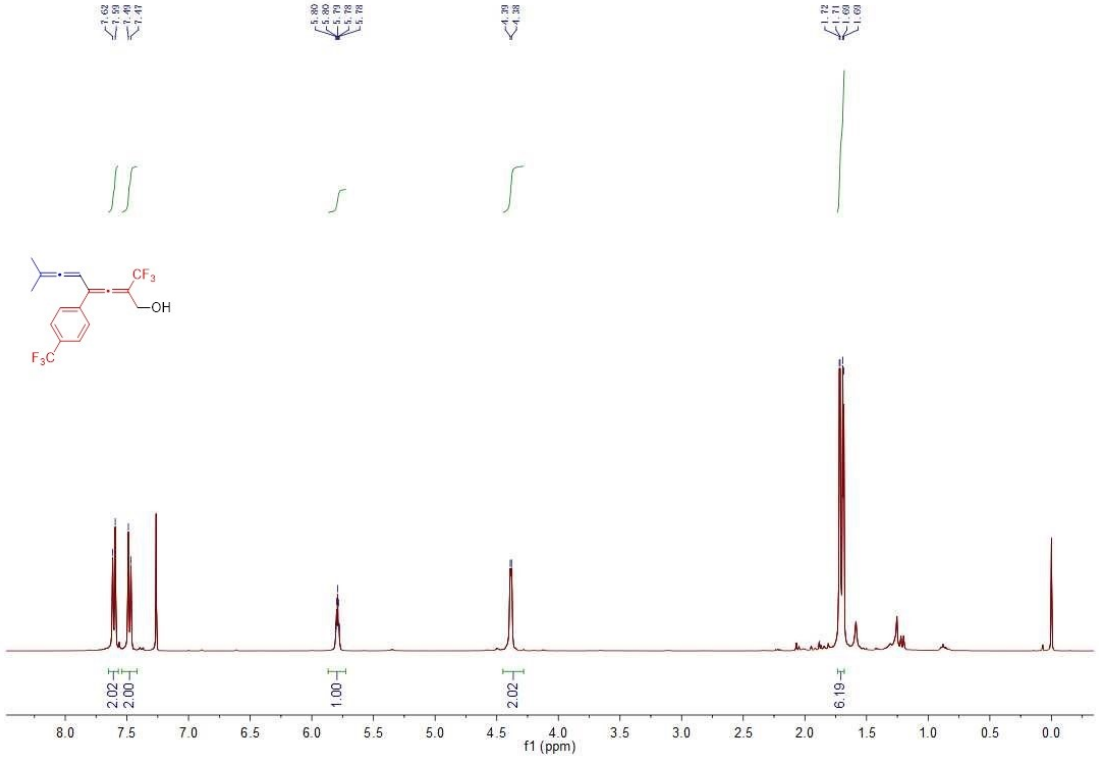
After isolated and purified procedure, this compound was obtained 19.1 mg (55% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

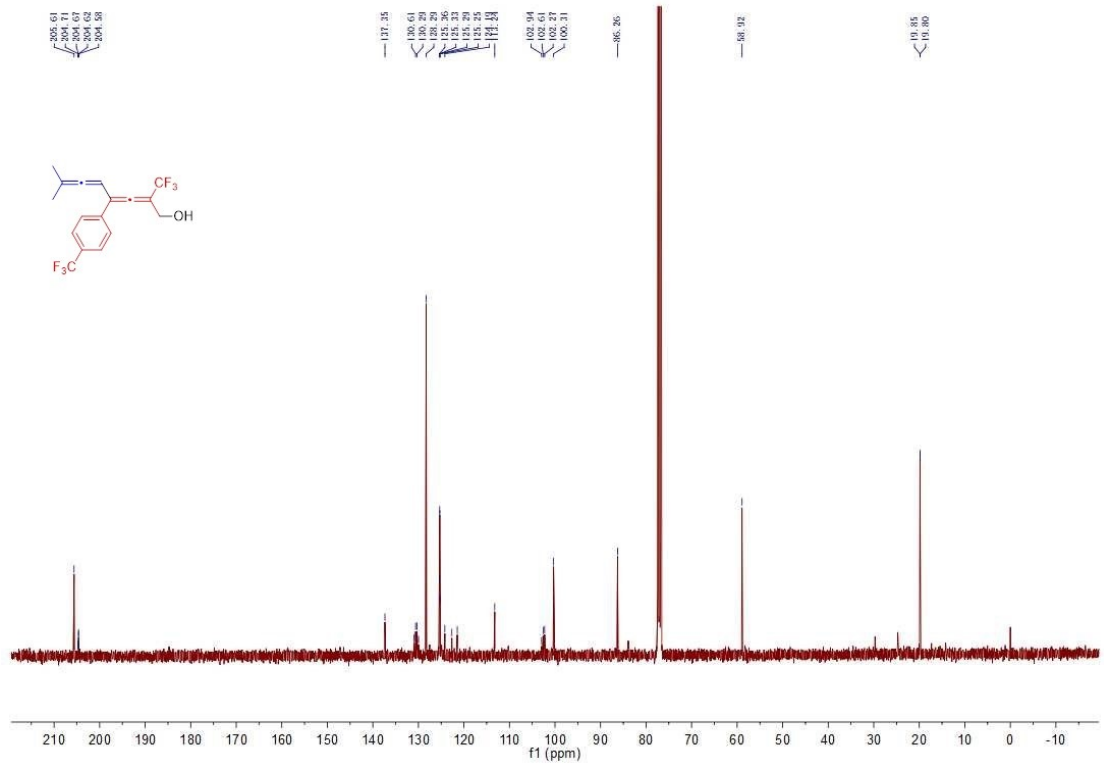
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 5.79 (dt, *J* = 5.7, 2.8 Hz, 1H), 4.38 (d, *J* = 4.1 Hz, 2H), 1.70 (dd, *J* = 11.5, 2.8 Hz, 6H).

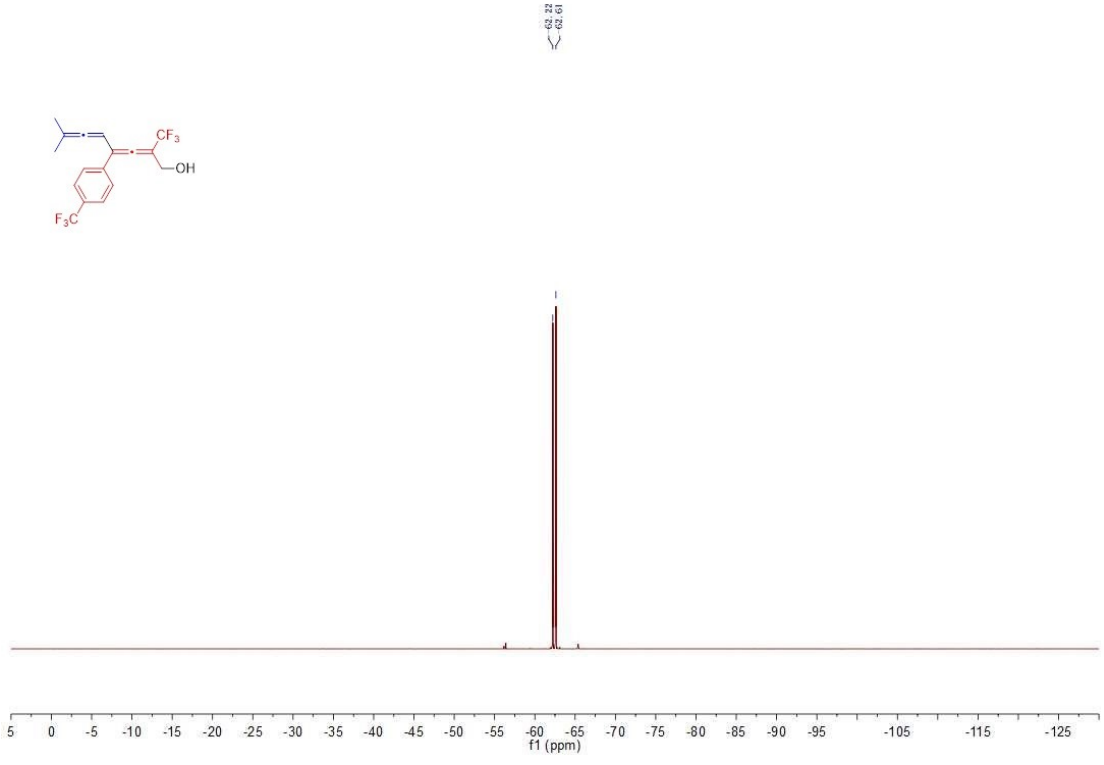
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.6 (d, *J* = 4.4 Hz), 137.4, 130.5 (q, *J* = 32.7 Hz), 128.3, 125.3 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 275.0 Hz), 122.7, 113.2, 102.4 (q, *J* = 33.3 Hz), 100.3, 86.3, 58.9, 19.9, 19.8.

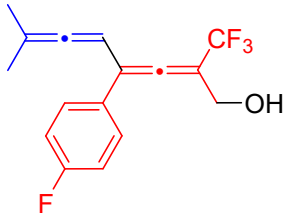
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22, -62.61.

HRMS (ESI) calculated for $C_{17}H_{15}F_6O^+$ $[M+H]^+$ 349.1022; found 349.1024.




CF3
OH
F3C
f1 (ppm)


CF3
OH
F3C
f1 (ppm)


CF3
OH
F

4-(4-fluorophenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3h)

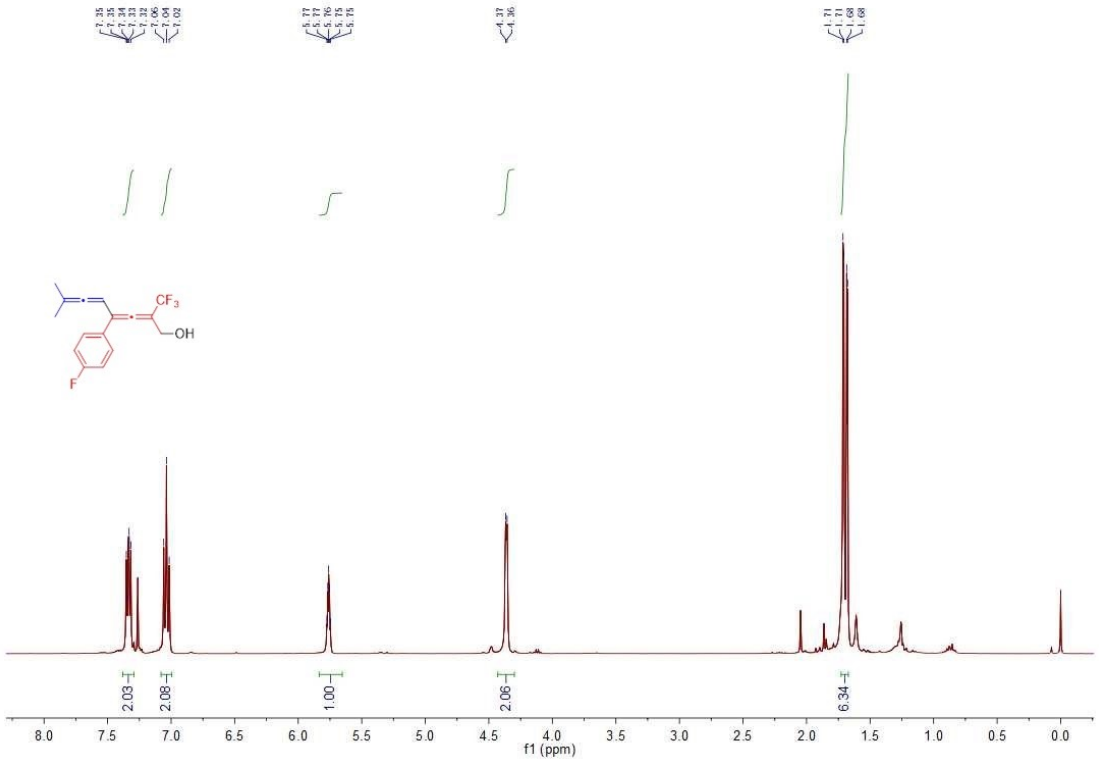
After isolated and purified procedure, this compound was obtained 17.9 mg (60% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

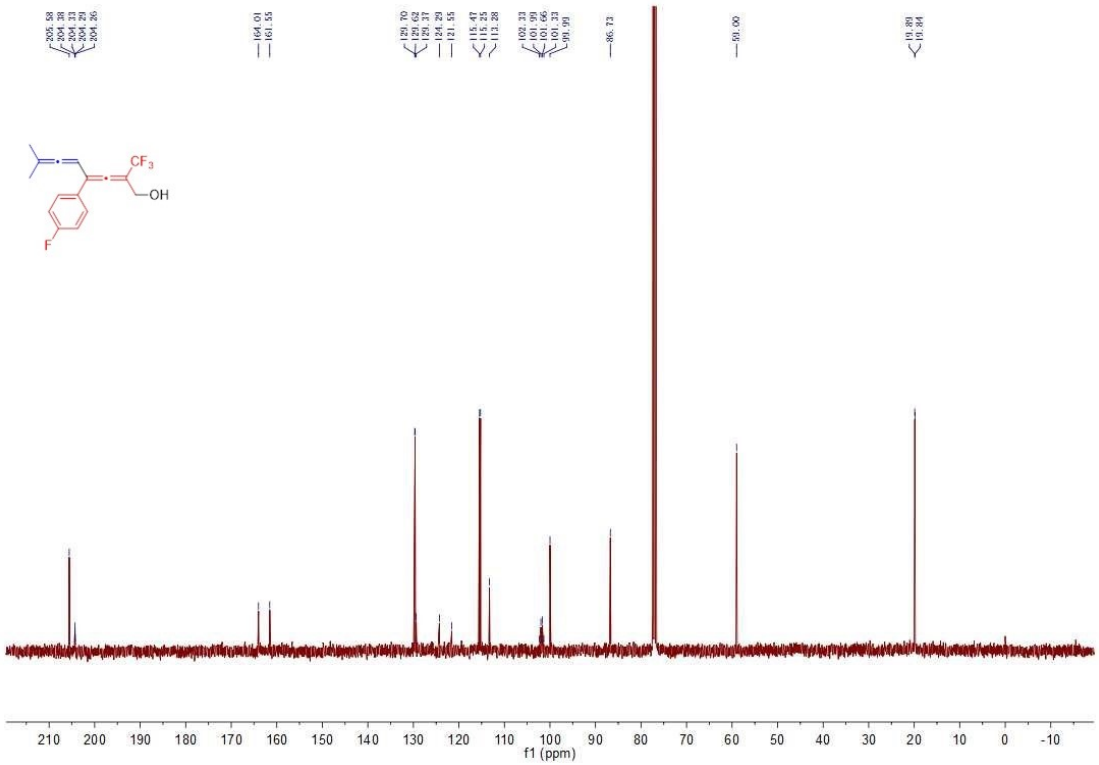
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.30 (m, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 5.76 (dt, *J* = 5.6, 2.7 Hz, 1H), 4.36 (d, *J* = 4.5 Hz, 2H), 1.69 (dd, *J* = 11.6, 2.8 Hz, 6H).

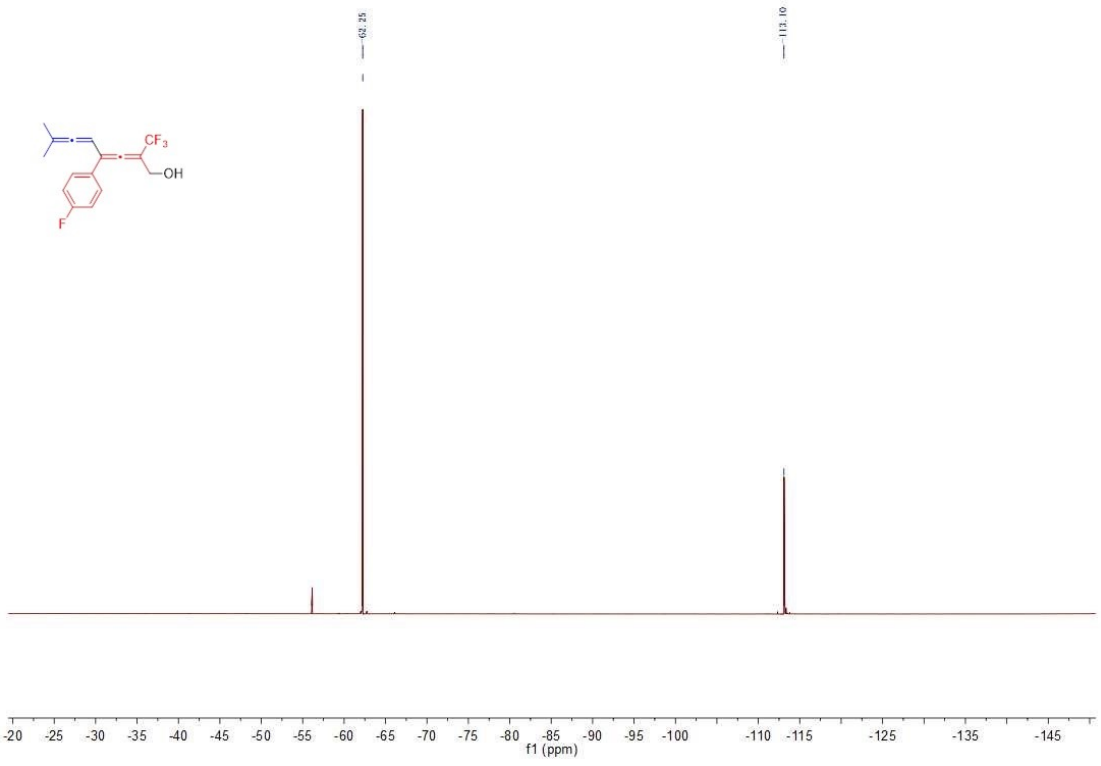
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.3 (q, *J* = 3.9 Hz), 162.8 (d, *J* = 248.0 Hz), 129.7 (d, *J* = 8.2 Hz), 129.4, 122.9 (q, *J* = 275.0 Hz), 115.4 (d, *J* = 21.7 Hz), 113.3, 101.8 (q, *J* = 33.3 Hz), 100.0, 86.7, 59.0, 19. 9, 19.8.

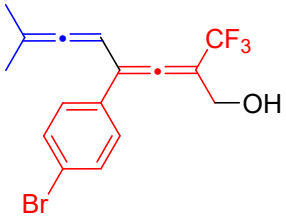
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.25, -113.10.

HRMS (ESI) calculated for $C_{16}H_{15}F_4O^+$ $[M+H]^+$ 299.1054; found 299.1050.




CF3
OH
F
f1 (ppm)


CF3
OH
F
f1 (ppm)


CF3
OH
Br

4-(4-bromophenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3i)

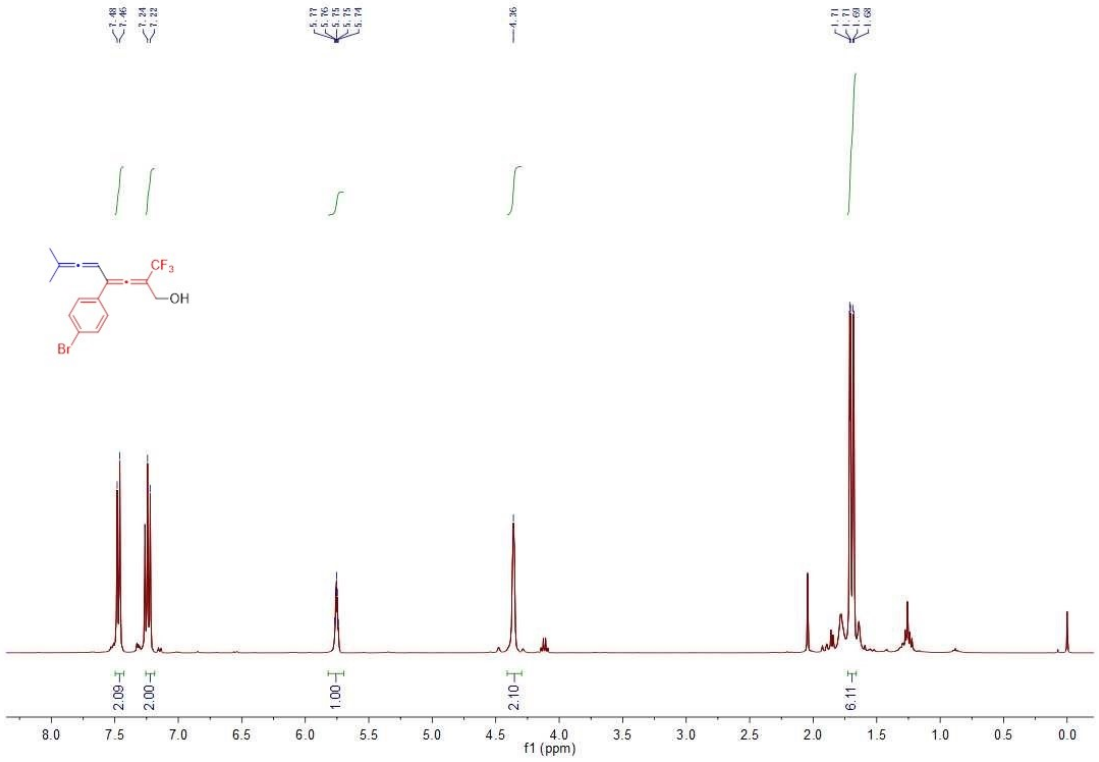
After isolated and purified procedure, this compound was obtained 22.9 mg (64% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

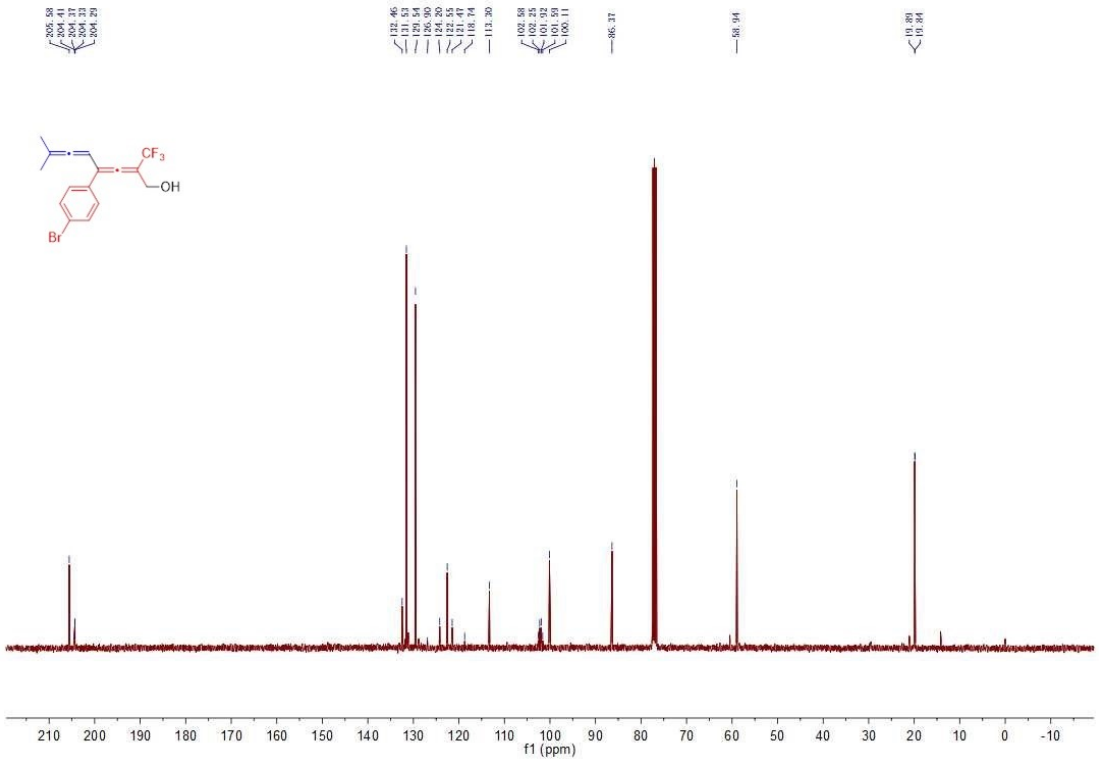
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.75 (dt, *J* = 5.6, 2.7 Hz, 1H), 4.36 (s, 2H), 1.70 (dd, *J* = 10.2, 2.8 Hz, 6H).

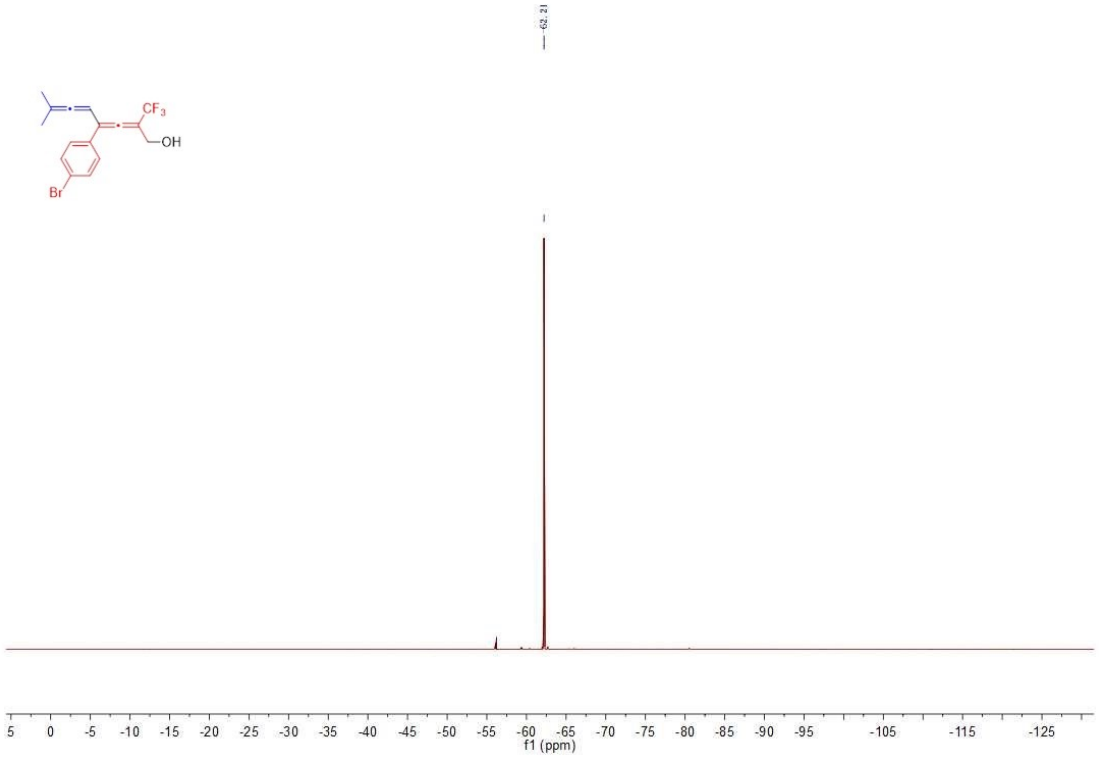
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.4 (q, *J* = 4.0 Hz), 132.5, 131.5, 129.5, 122.8 (q, *J* = 275.0 Hz), 122.6, 113.3, 102.1 (q, *J* = 33.3 Hz), 100.1, 86.4, 58.9, 19.9, 19.8.

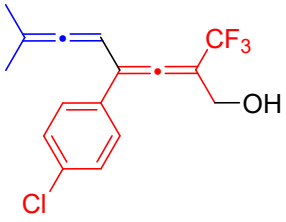
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.21.

HRMS (ESI) calculated for $C_{16}H_{15}BrF_3O^+$ $[M+H]^+$ 359.0253; found 359.0257.




205.58
204.41
204.37
204.33
204.29
132.46
131.53
129.54
126.90
124.20
122.55
121.47
118.74
113.30
102.58
102.25
101.92
101.59
100.11
86.37
58.94
19.80
19.84
CF3
OH
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.21
CF3
OH
Br
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
Cl

4-(4-chlorophenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3j)

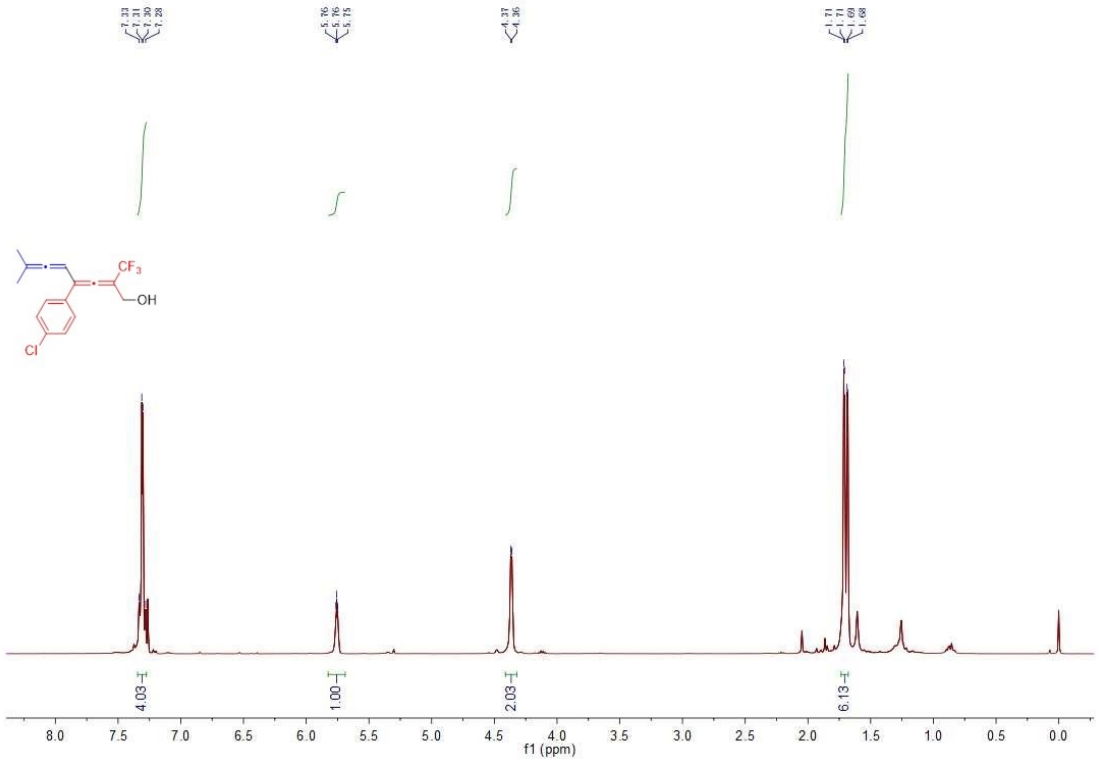
After isolated and purified procedure, this compound was obtained 20.7 mg (66% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

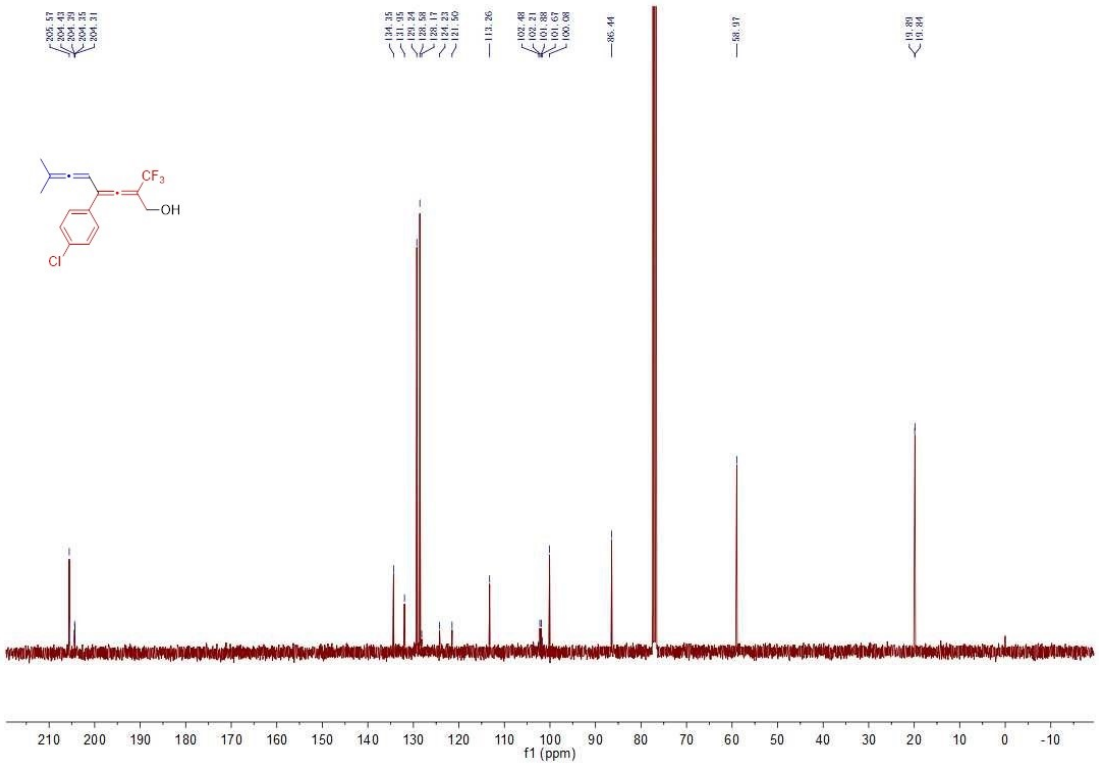
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 4H), 5.75 (dt, *J* = 5.7, 2.9 Hz, 1H), 4.36 (d, *J* = 3.4 Hz, 2H), 1.70 (dd, *J* = 10.6, 2.7 Hz, 6H).

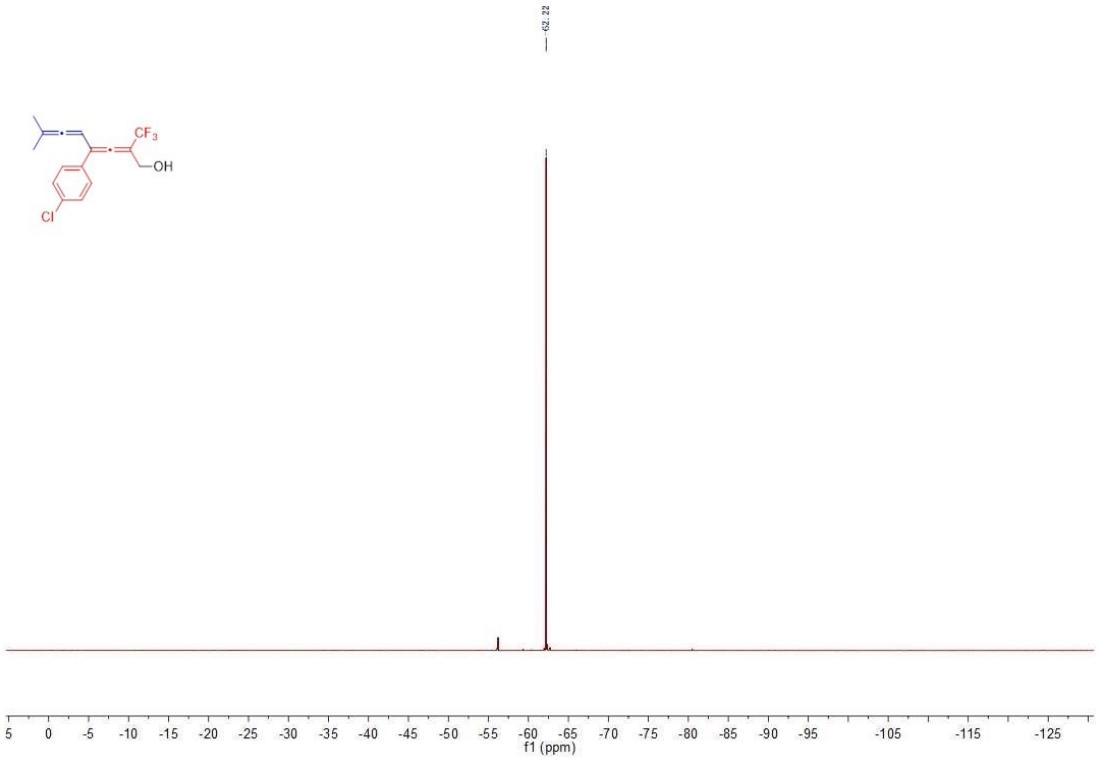
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.4 (q, *J* = 4.0 Hz), 134.4, 132.0, 129.2, 128.6, 128.2, 122.9 (q, *J* = 275.1 Hz), 113.3, 102.1 (q, *J* = 33.3 Hz), 100.1, 86.4, 59.0, 19.9, 19.8.

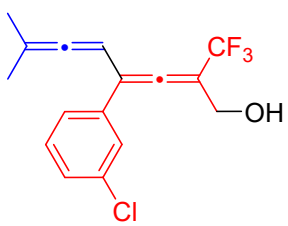
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22.

HRMS (ESI) calculated for $C_{16}H_{15}ClF_3O^+$ $[M+H]^+$ 315.0758; found 315.0755.




205.67
204.43
204.39
204.35
204.31
134.35
131.95
131.24
128.58
128.17
124.23
121.90
113.26
102.48
102.21
101.88
101.67
100.98
86.44
58.97
19.89
19.84
CF3
OH
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.22
CF3
OH
Cl
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
Cl

4-(3-chlorophenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3k)

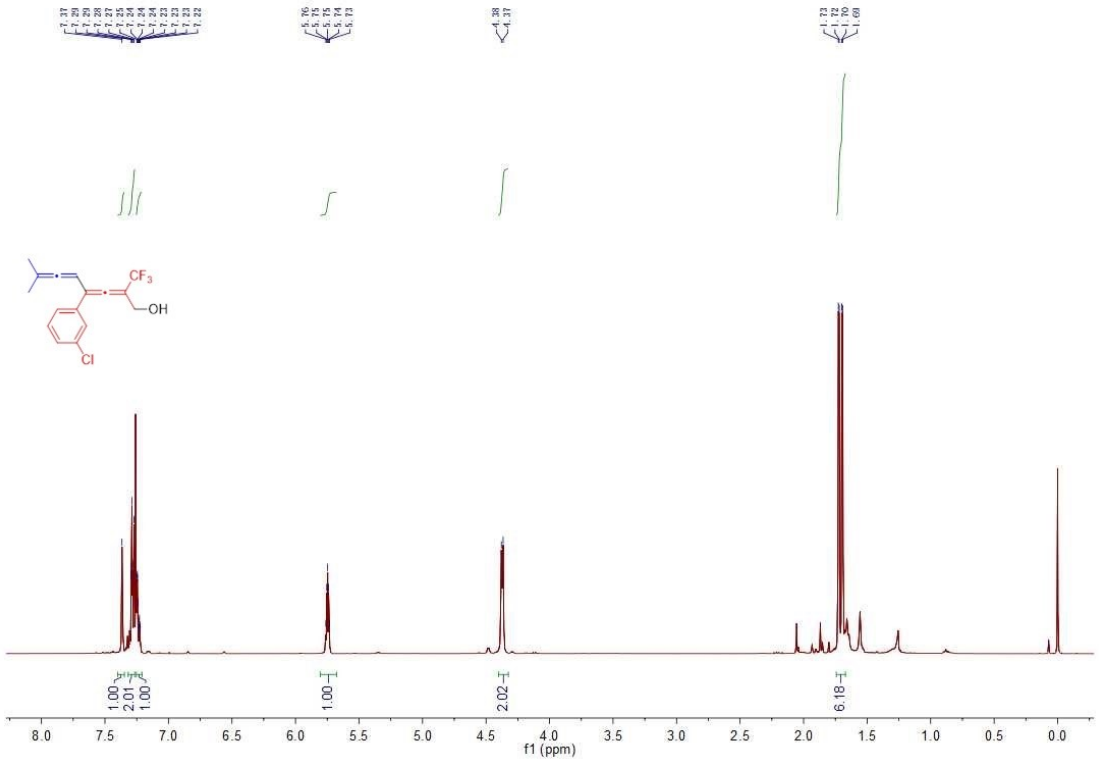
After isolated and purified procedure, this compound was obtained 19.5 mg (62% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

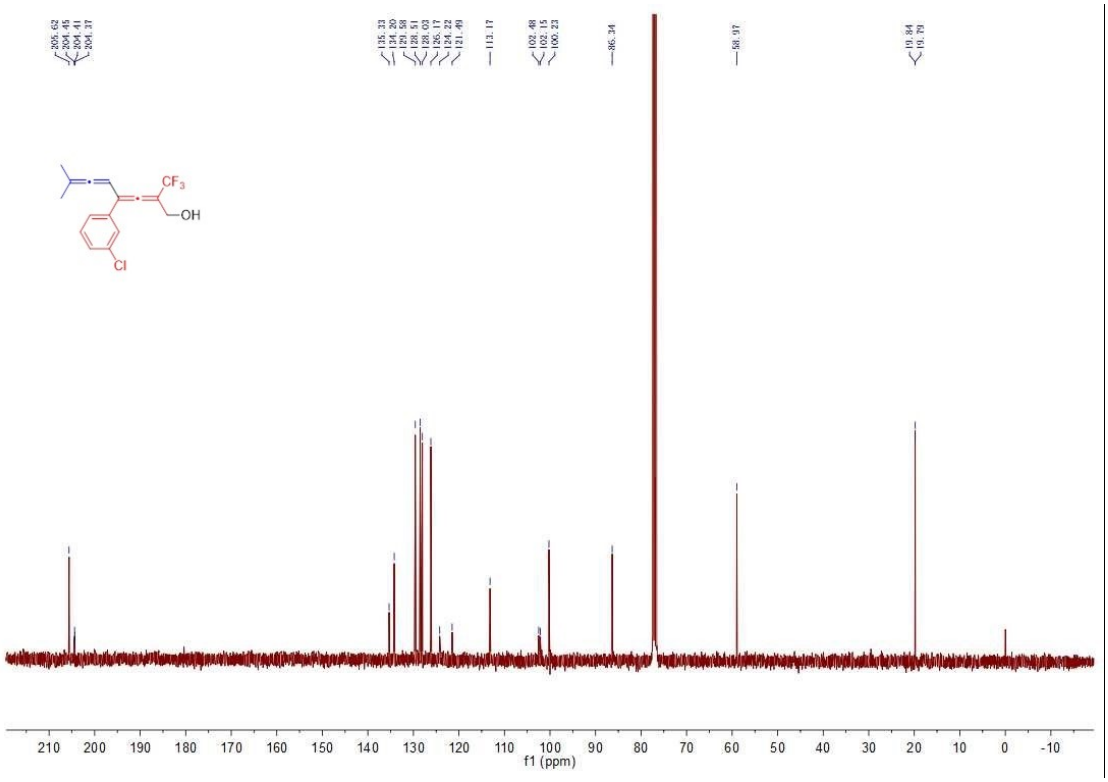
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.30-7.27 (m, 2H), 7.25-7.21 (m, 1H), 5.75 (dt, *J* = 5.7, 2.8 Hz, 1H), 4.37 (d, *J* = 5.6 Hz, 2H), 1.71 (dd, *J* = 11.0, 2.8 Hz, 6H).

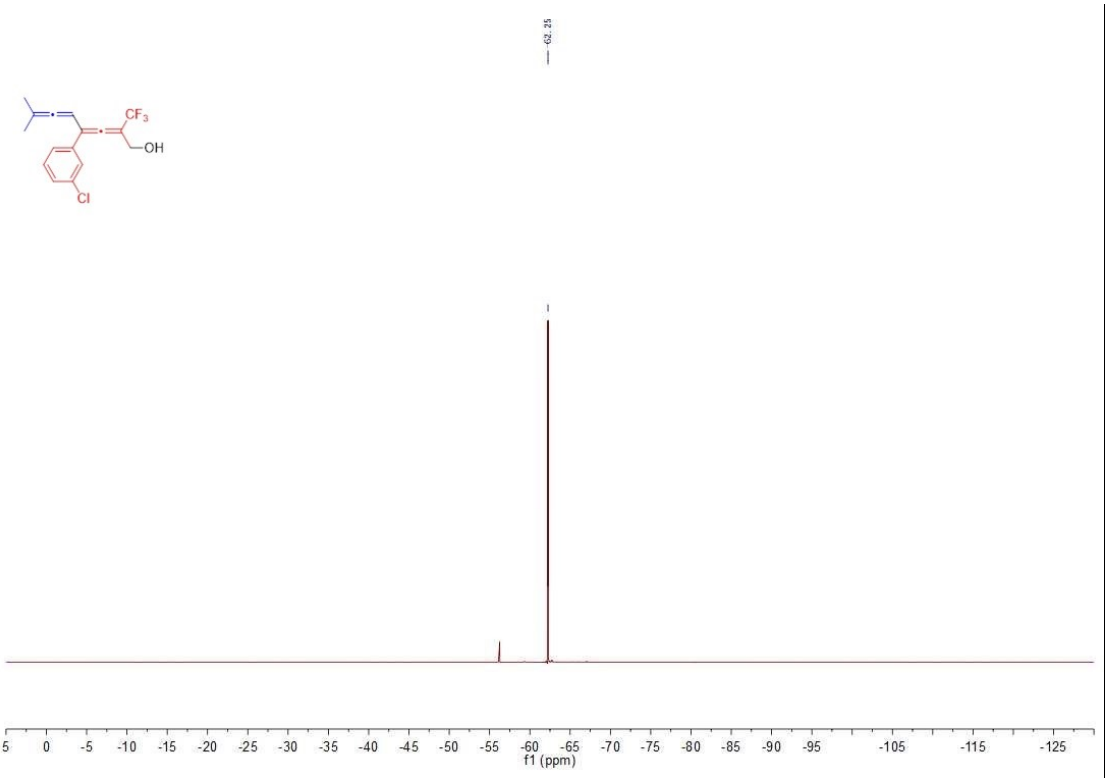
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 204.4 (q, *J* = 4.1 Hz), 135.3, 134.2, 129.6, 128.5, 128.0, 126.2, 122.9 (q, *J* = 275.0 Hz), 113.2, 102.3 (q, *J* = 33.4 Hz), 100.2, 86.3, 59.0, 19.8, 19.8.

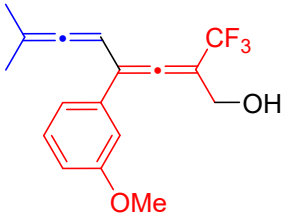
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.25.

HRMS (ESI) calculated for $C_{16}H_{15}ClF_3O^+$ $[M+H]^+$ 315.0758; found 315.0757




205.62
204.45
204.41
204.37
135.33
134.20
129.58
128.61
128.03
125.17
124.22
121.49
113.17
102.48
102.15
100.23
86.34
58.97
19.84
19.79
CF3
OH
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.25
CF3
OH
Cl
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
OMe

4-(3-methoxyphenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3l)

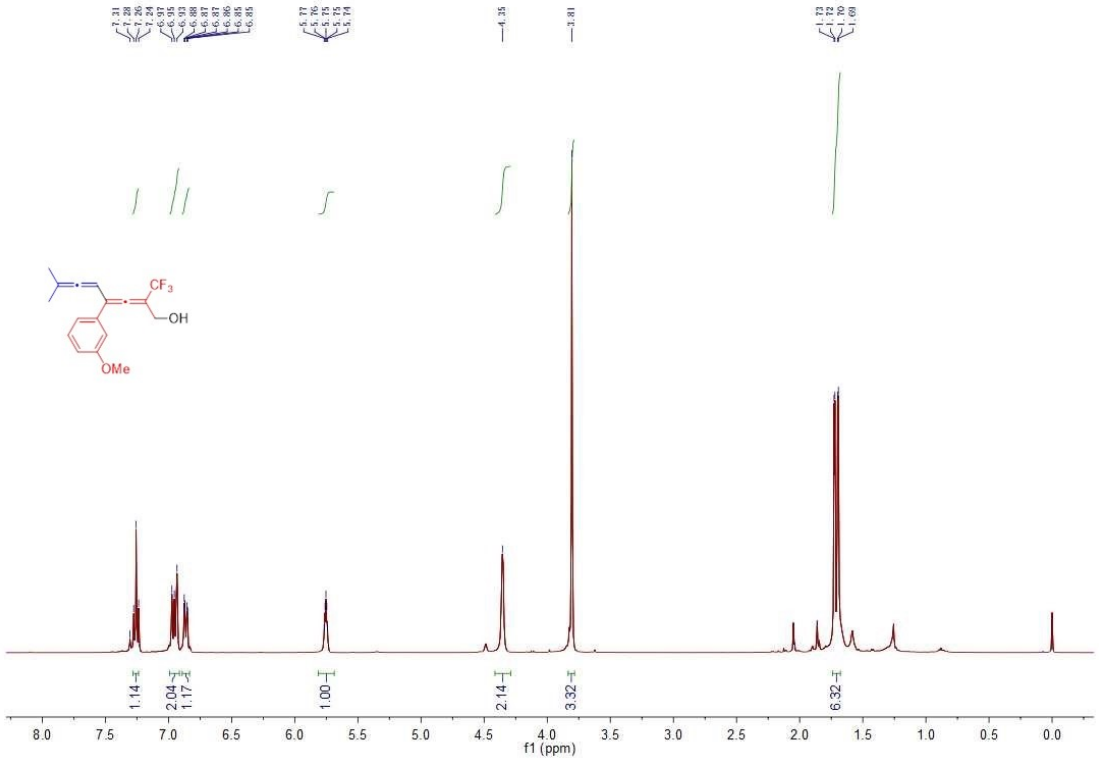
After isolated and purified procedure, this compound was obtained 15.8 mg (51% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

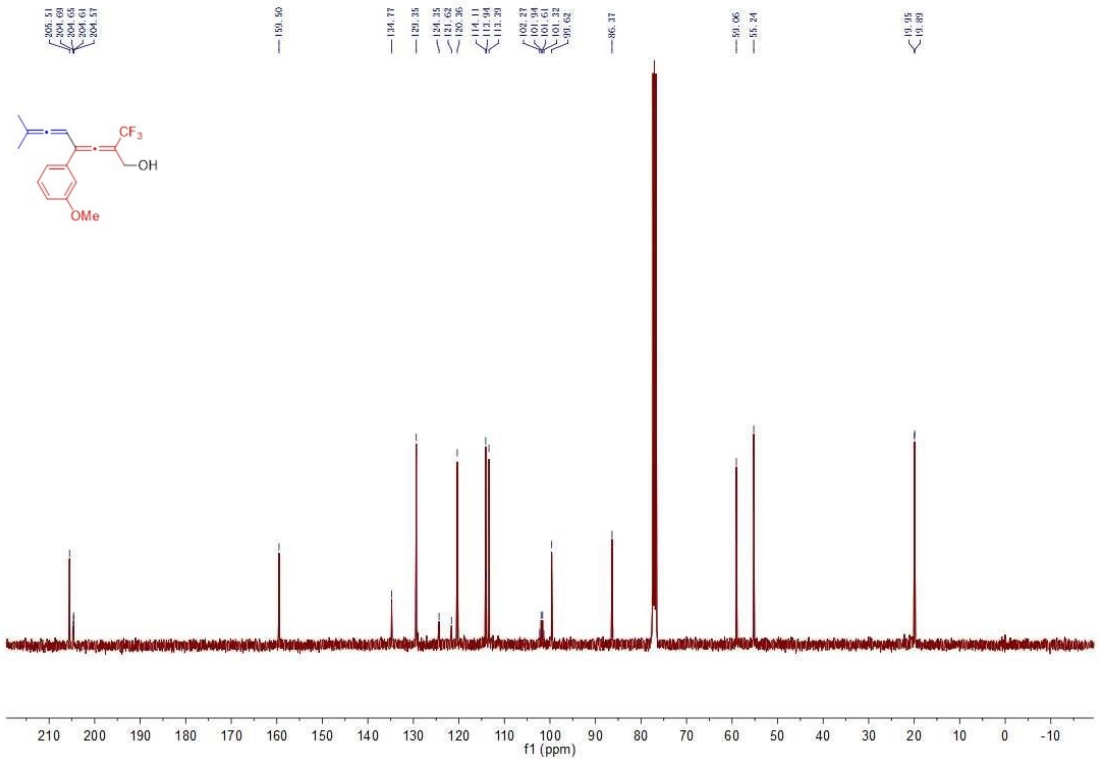
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 1H), 7.03-6.92 (m, 2H), 6.89-6.82 (m, 1H), 5.75 (dt, *J* = 5.6, 2.8 Hz, 1H), 4.35 (s, 2H), 3.81 (s, 3H), 1.71 (dd, *J* = 11.1, 2.7 Hz, 6H).

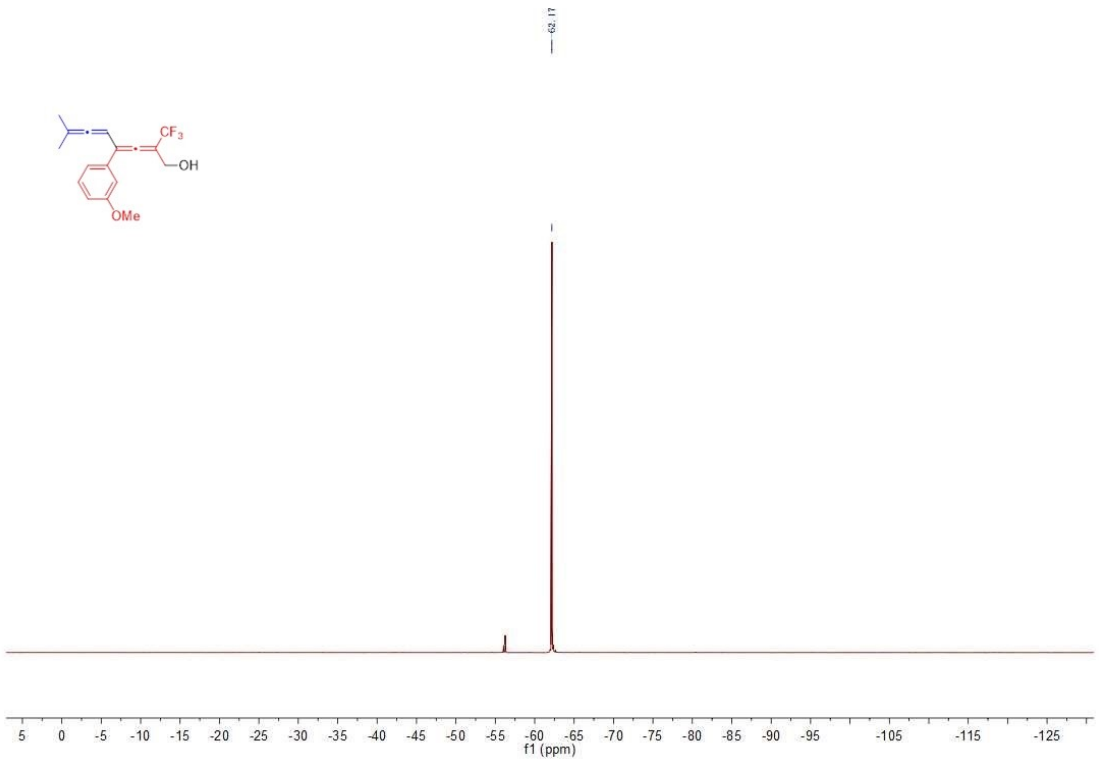
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5, 204.6 (q, *J* = 4.2 Hz), 159.5, 134.8, 129.4, 123.0 (q, *J* = 275.1 Hz), 121.6, 120.4, 114.1, 114.0, 113.4, 101.8 (q, *J* = 33.2 Hz), 99.6, 86.4, 59.1, 55.2, 20.0, 19.9.

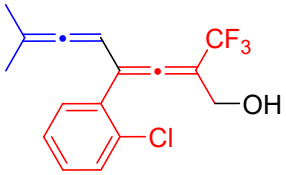
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.17.

HRMS (ESI) calculated for $C_{17}H_{18}F_3O_2^+$ $[M+H]^+$ 311.1253; found 311.1256.









4-(2-chlorophenyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3m)

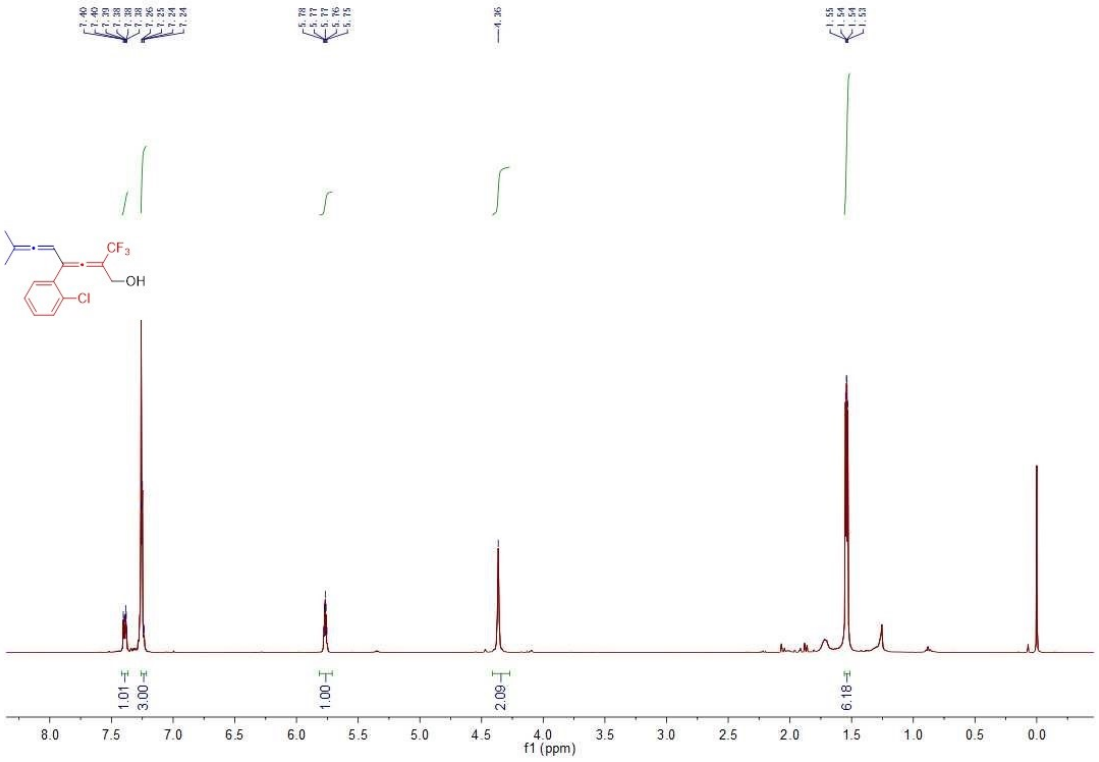
After isolated and purified procedure, this compound was obtained 17.9 mg (57% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

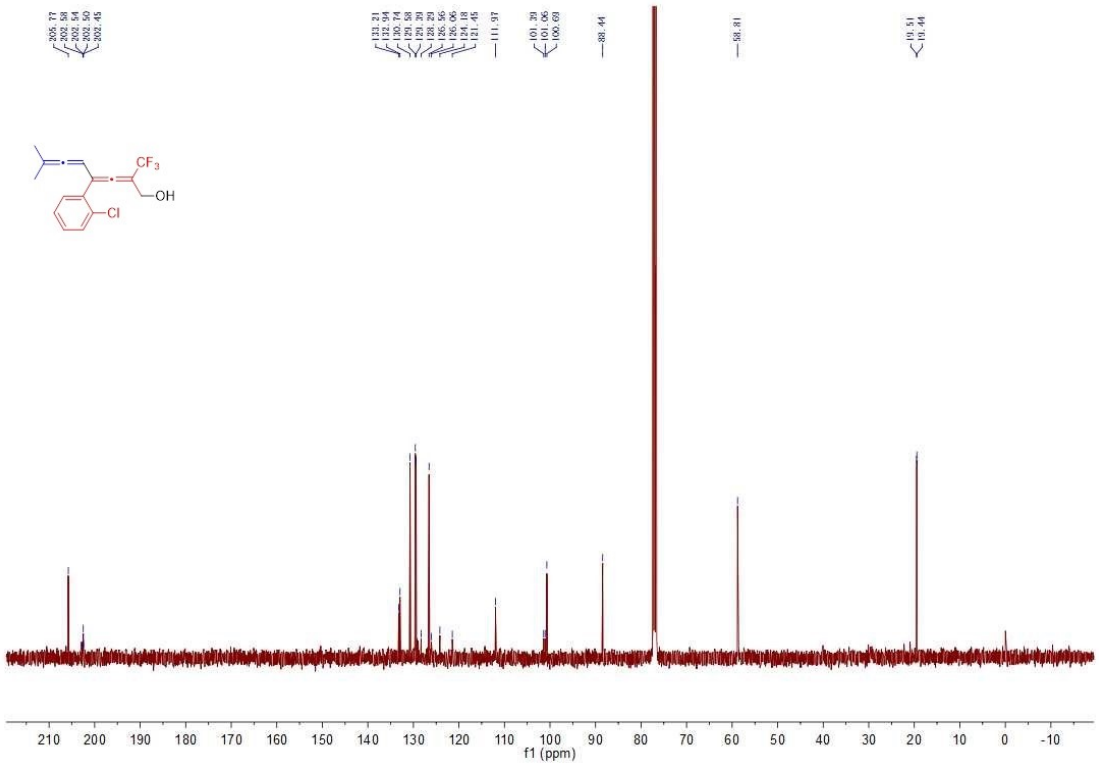
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.32 (m, 1H), 7.25-7.23 (m, 3H), 5.77 (dt, *J* = 5.5, 2.7 Hz, 1H), 4.36 (s, 2H), 1.54 (dd, *J* = 4.7, 2.8 Hz, 6H).

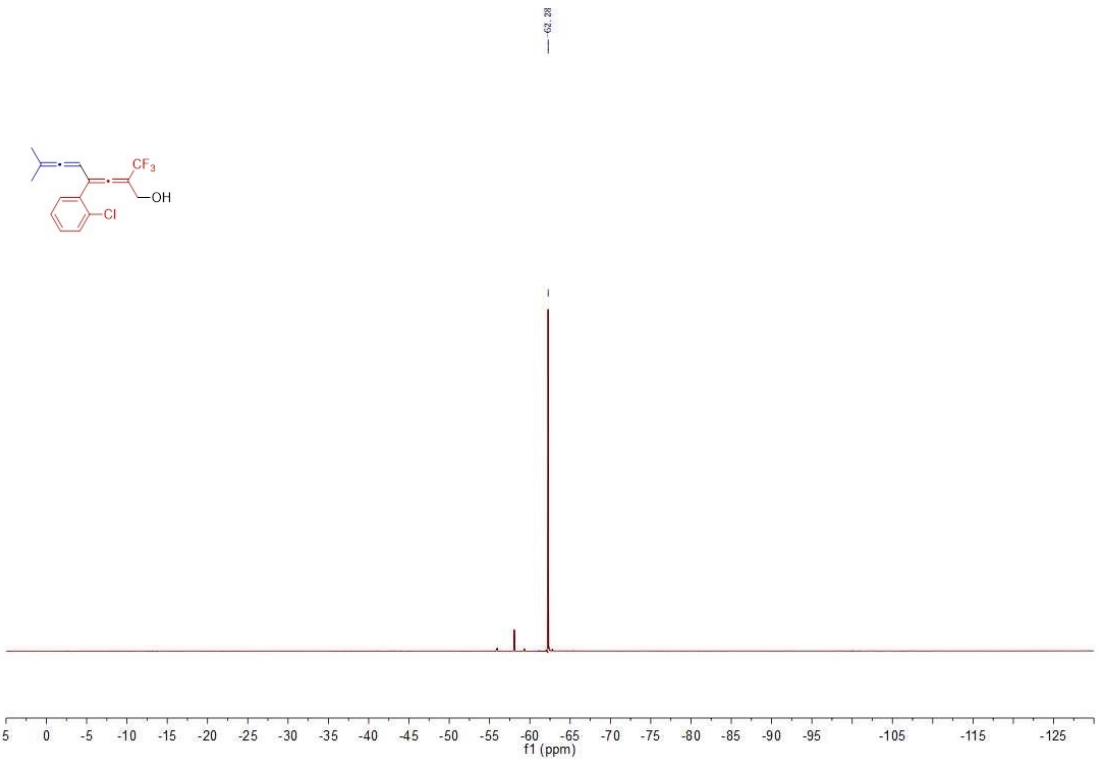
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 202.5 (q, *J* = 4.2 Hz), 133.2, 132.9, 130.7, 129.6, 129.4, 126.6, 122.8 (q, *J* = 274.7 Hz), 112.0, 101.2 (q, *J* = 33.3 Hz), 100.7, 88.4, 58.8, 19.5, 19.4.

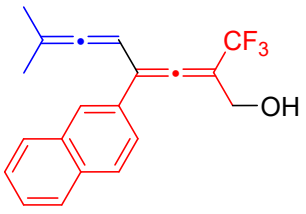
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28.

HRMS (ESI) calculated for $C_{16}H_{15}ClF_3O^+$ $[M+H]^+$ 315.0758; found 315.0751




205.17
202.98
202.84
202.50
202.45
133.31
132.94
130.74
129.58
129.39
128.29
125.66
125.06
124.18
121.45
111.97
101.39
101.06
100.69
88.44
58.81
19.51
19.44
CF3
OH
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.28
CF3
OH
Cl
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH

7-methyl-4-(naphthalen-2-yl)-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3n)

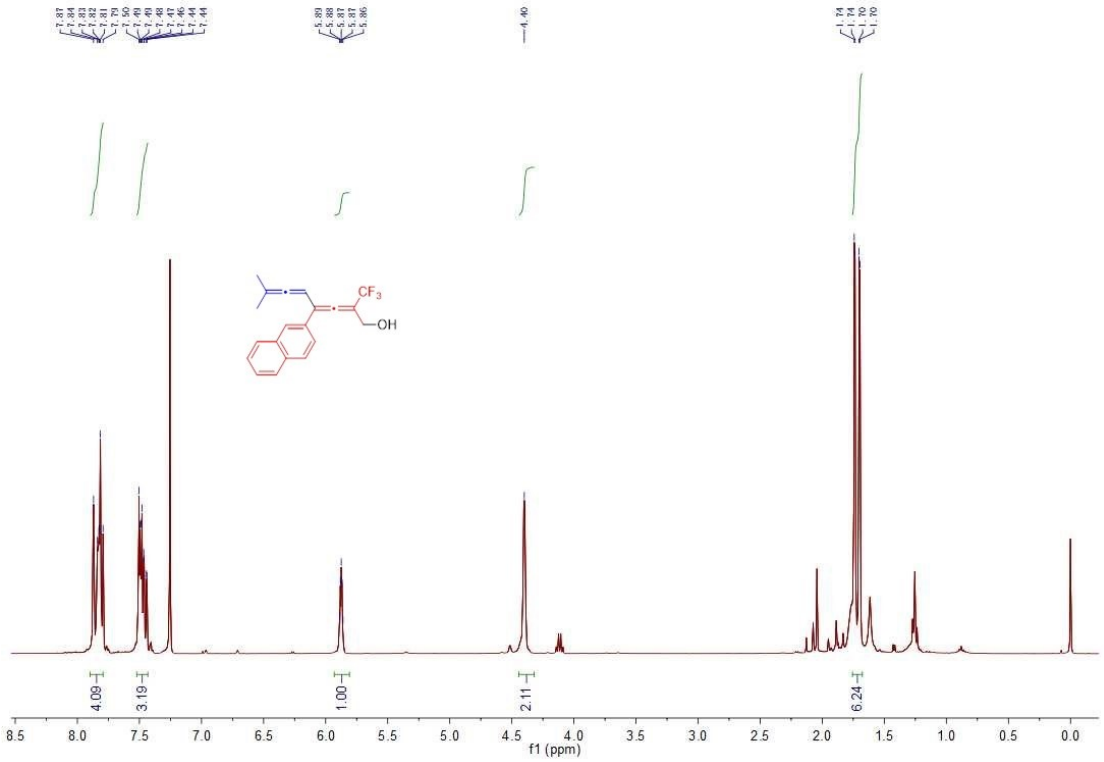
After isolated and purified procedure, this compound was obtained 20.8 mg (63% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

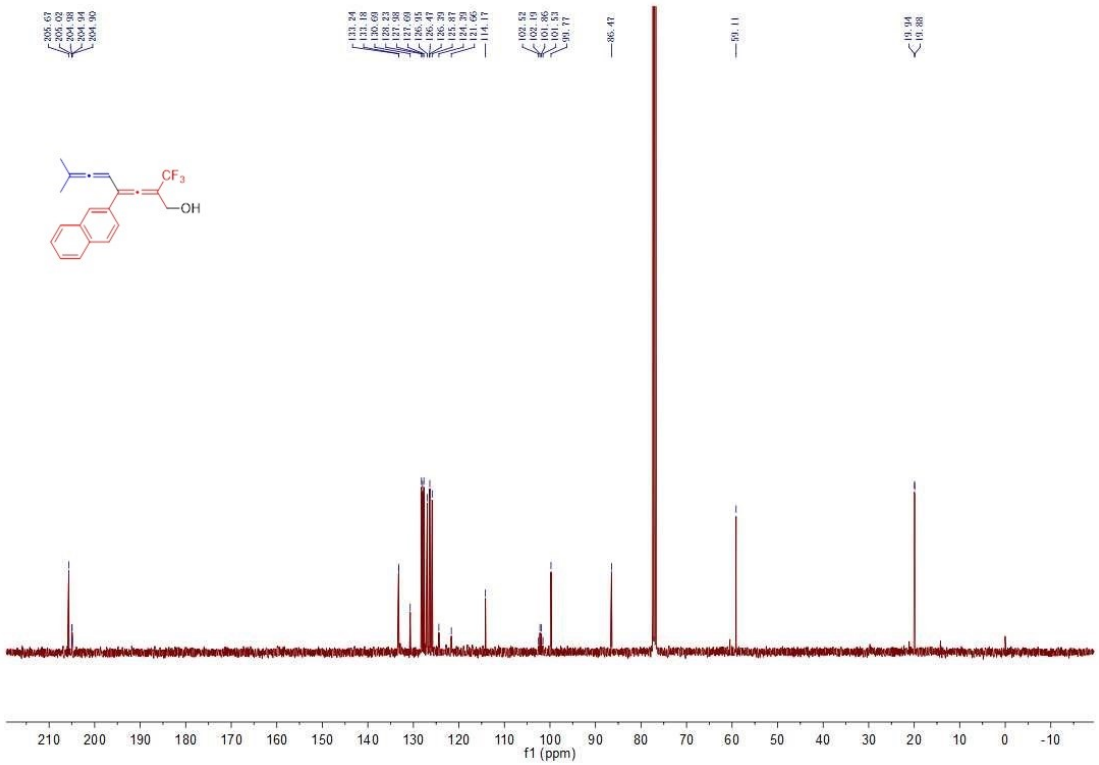
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-7.65 (m, 4H), 7.61-7.38 (m, 3H), 5.87 (dt, *J* = 5.6, 2.7 Hz, 1H), 4.40 (s, 2H), 1.72 (dd, *J* = 15.5, 2.7 Hz, 6H).

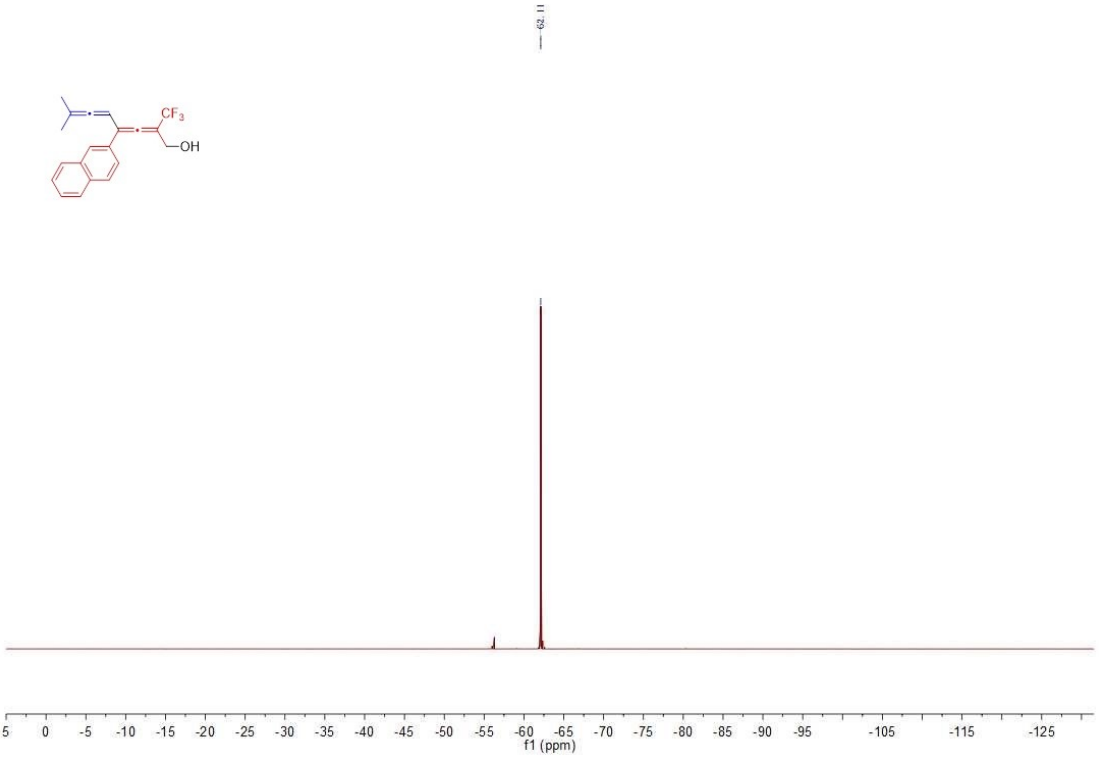
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7, 205.0 (q, *J* = 4.0 Hz), 133.2, 133.2, 130.7, 128.2, 128.0, 127.7, 126.9, 126.5, 126.4, 125.9, 123.0 (q, *J* = 275.1 Hz), 114.2, 102.0 (q, *J* = 33.2 Hz), 99.8, 86.5, 59.1, 19.9, 19.9.

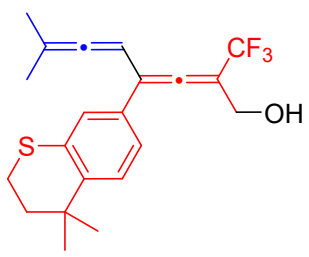
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.11.

HRMS (ESI) calculated for $C_{20}H_{18}F_3O^+$ $[M+H]^+$ 331.1304; found 331.1302.




205.67
205.02
204.98
204.94
204.90
133.24
133.18
130.69
128.23
127.58
127.69
126.95
126.47
126.29
125.87
124.39
121.66
114.17
102.52
102.19
101.86
101.53
90.77
86.47
59.11
19.94
19.88
CF3
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.11
CF3
OH
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH
S

4-(4,4-dimethylthiochroman-7-yl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3o)

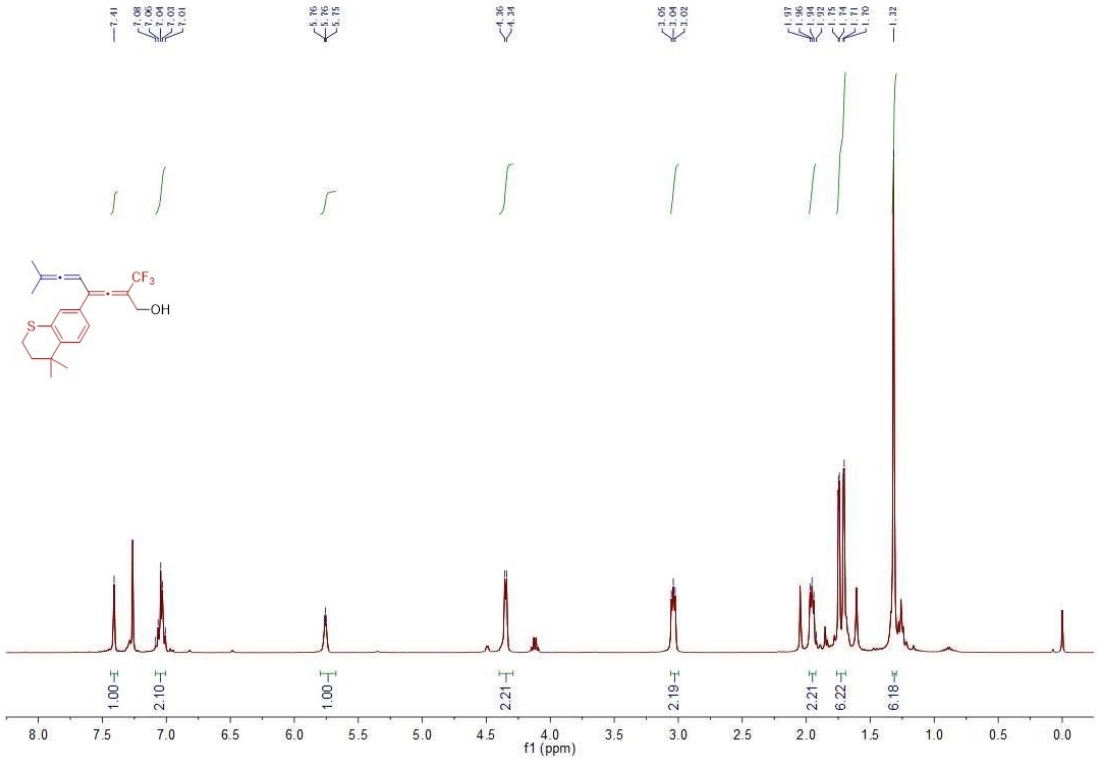
After isolated and purified procedure, this compound was obtained 25.4 mg (67% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

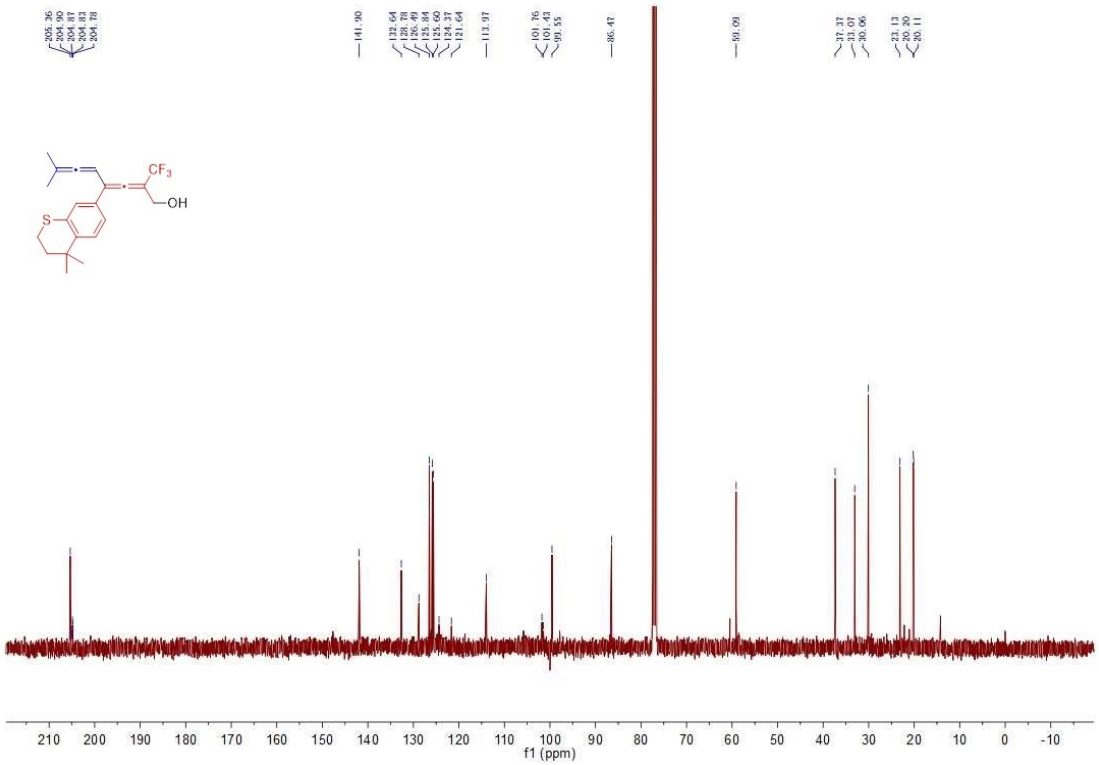
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.17-6.93 (m, 2H), 5.88-5.53 (m, 1H), 4.35 (d, *J* = 5.6 Hz, 2H), 3.10-2.97 (m, 2H), 2.00-1.89 (m, 2H), 1.73 (dd, *J* = 15.2, 2.6 Hz, 6H), 1.32 (s, 6H).

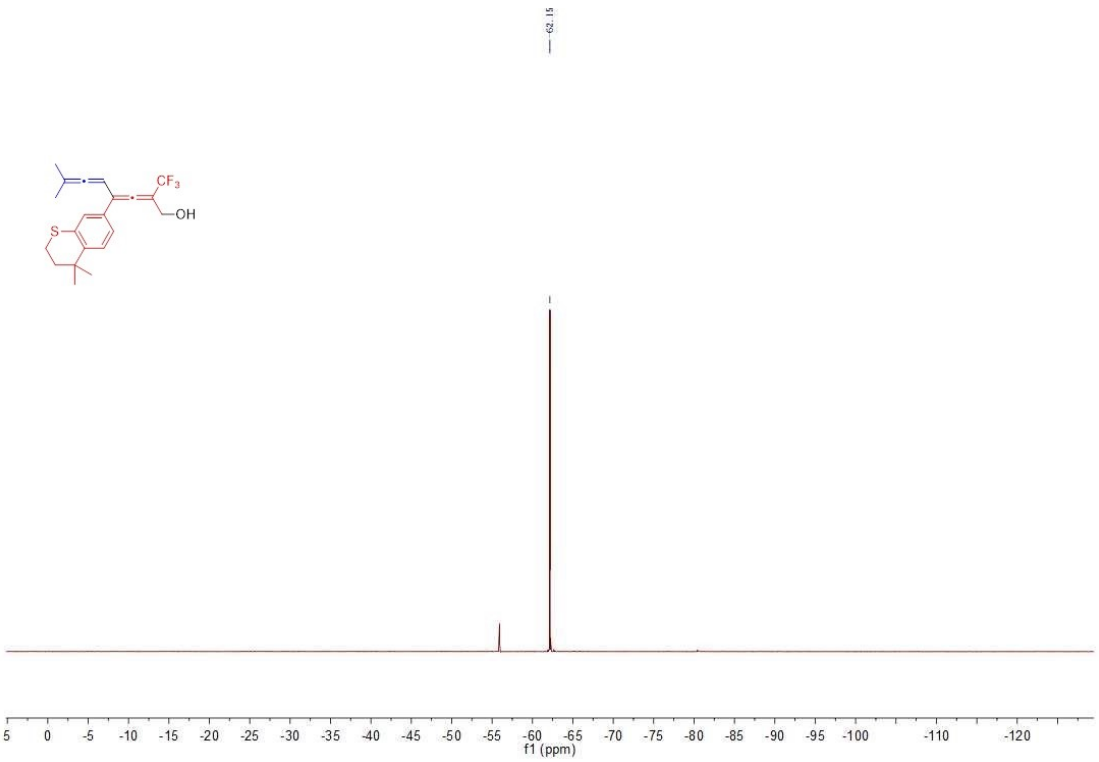
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4, 204.9 (q, *J* = 4.0 Hz), 141.9, 132.6, 128.8, 126.5, 125.8, 125.6, 123.0 (q, *J* = 275.1 Hz), 101.6 (q, *J* = 33.1 Hz), 99.6, 86.5, 59.1, 37.4, 33.1, 30.1, 23.1, 20.2, 20.1.

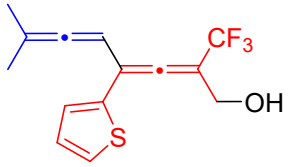
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.15.

HRMS (ESI) calculated for $C_{21}H_{24}F_3OS^+$ $[M+H]^+$ 381.1494; found 381.1489.









7-methyl-4-(thiophen-2-yl)-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3p)

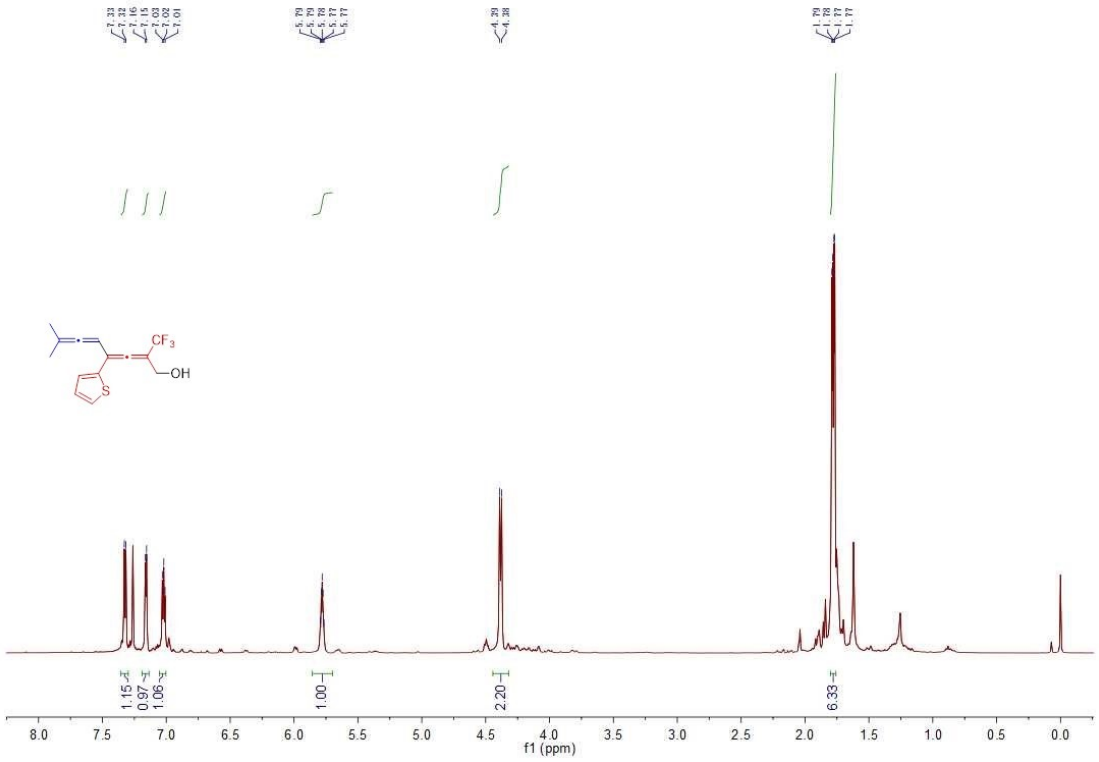
After isolated and purified procedure, this compound was obtained 12.8 mg (45% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

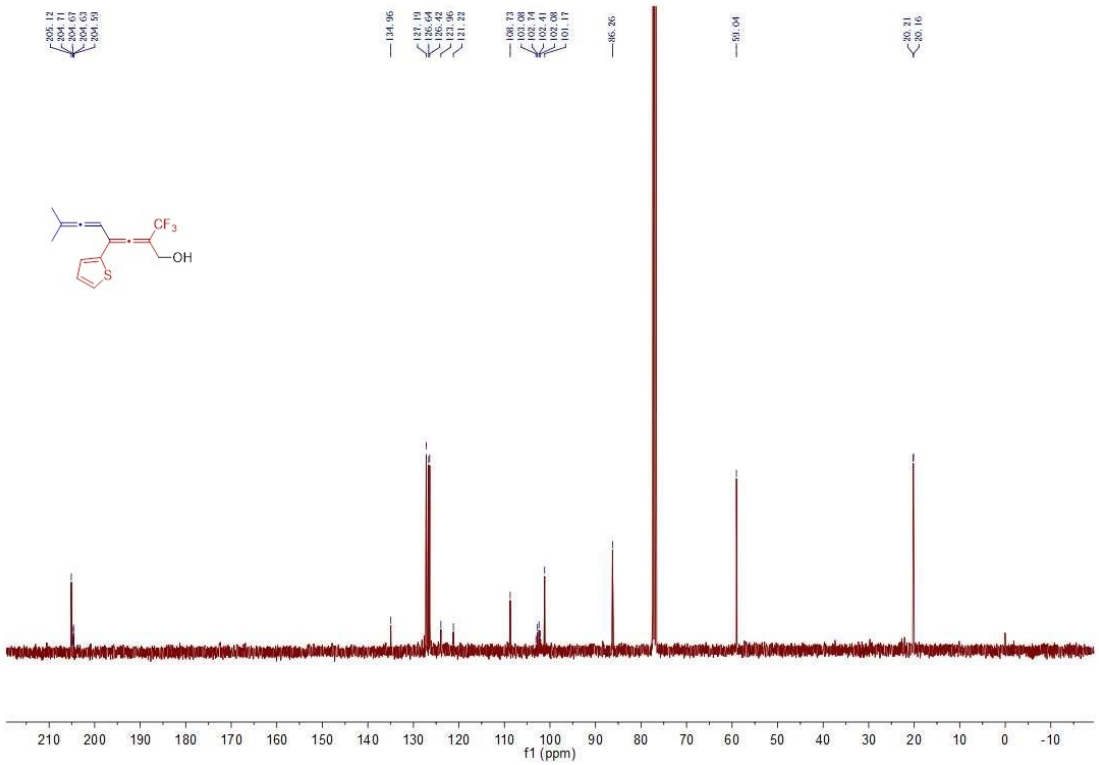
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 7.06-6.97 (m, 1H), 5.78 (dt, *J* = 5.5, 2.7 Hz, 1H), 4.38 (d, *J* = 6.2 Hz, 2H), 1.78 (dd, *J* = 6.3, 2.8 Hz, 6H).

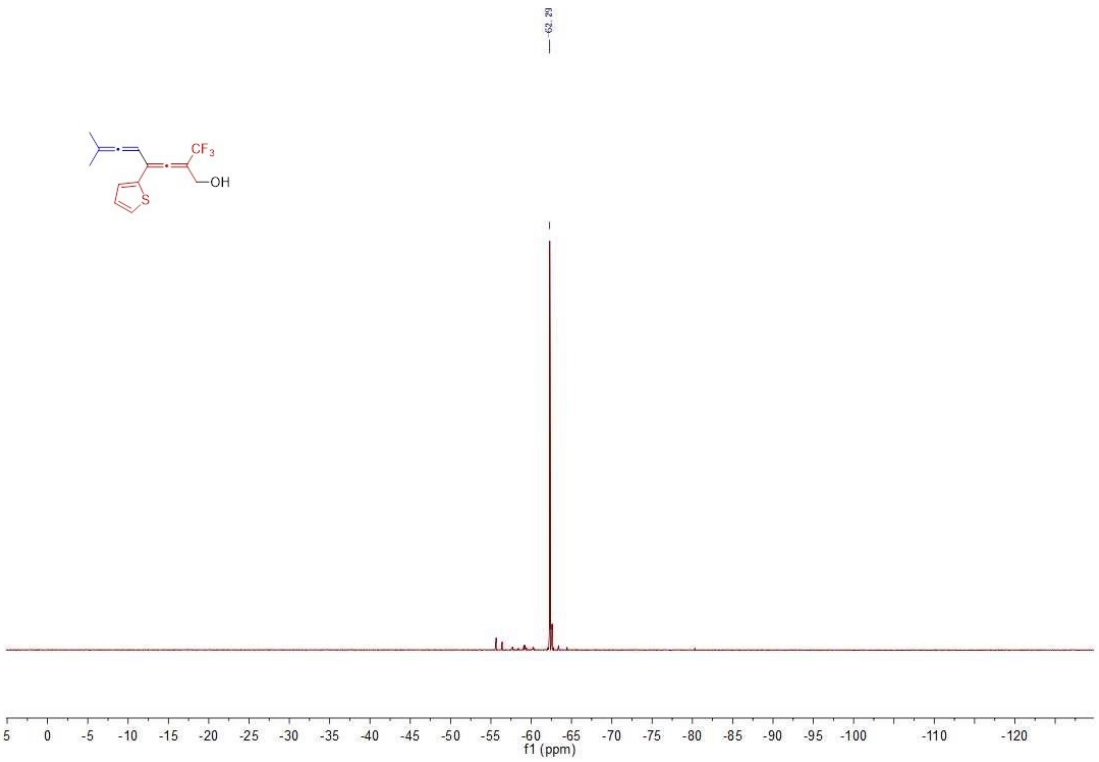
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.1, 204.7 (q, *J* = 4.1 Hz), 135.0, 127.2, 126.6, 126.4, 122.6 (q, *J* = 275.5 Hz), 108.7, 102.6 (q, *J* = 33.4 Hz), 101.2, 86.3, 59.0, 20.2, 20.2.

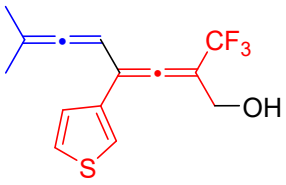
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.29.

HRMS (ESI) calculated for $C_{14}H_{14}F_3OS^+$ $[M+H]^+$ 287.0712; found 287.0713.









7-methyl-4-(thiophen-3-yl)-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3q)

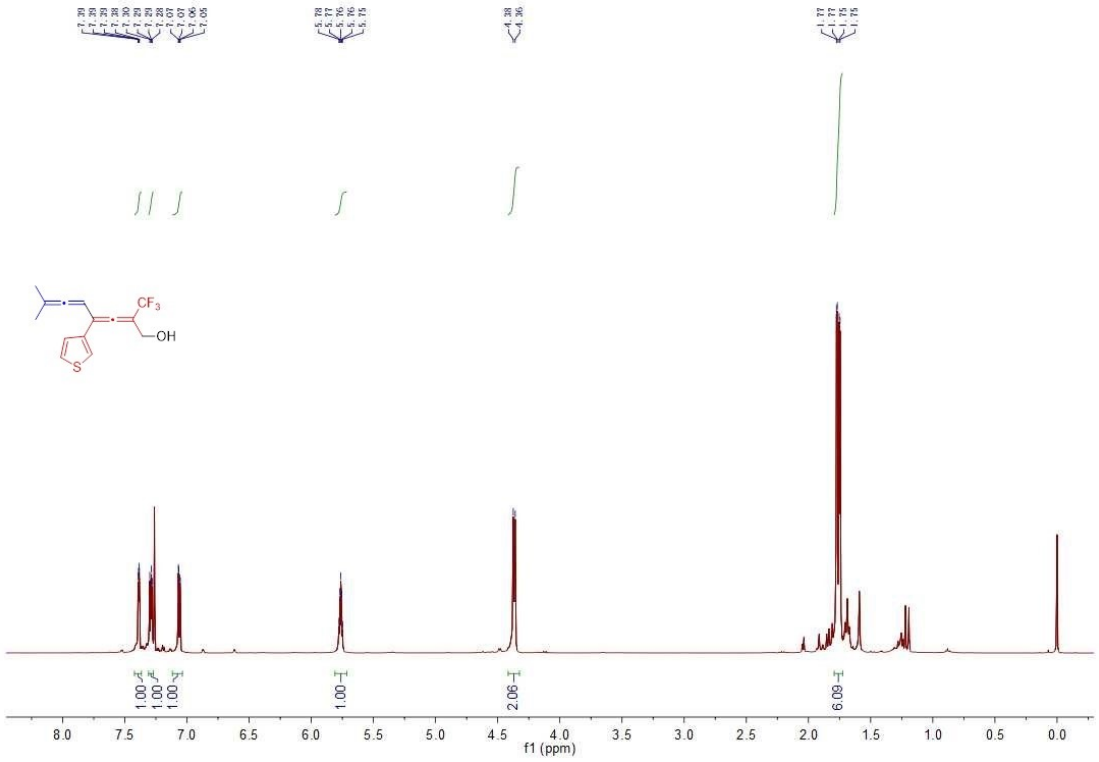
After isolated and purified procedure, this compound was obtained 16.6 mg (58% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

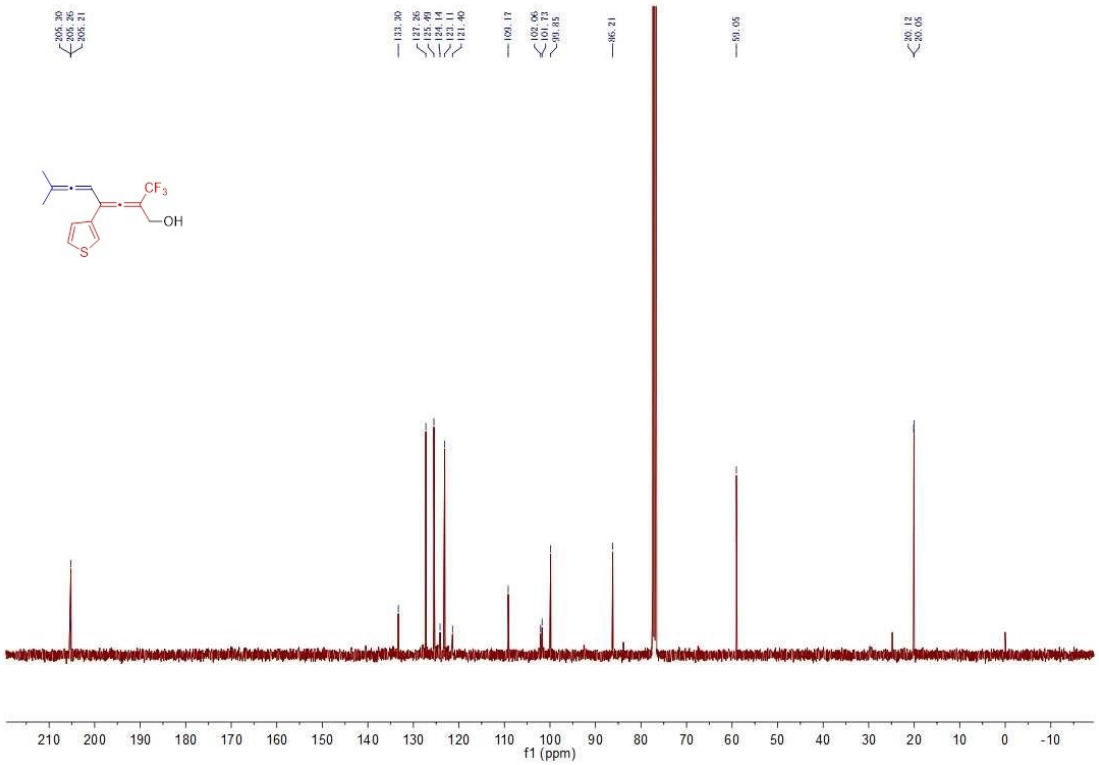
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.29 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.06 (dd, *J* = 5.0, 1.1 Hz, 1H), 5.76 (dt, *J* = 5.8, 2.9 Hz, 1H), 4.37 (d, *J* = 6.3 Hz, 2H), 1.76 (dd, *J* = 8.8, 2.9 Hz, 6H).

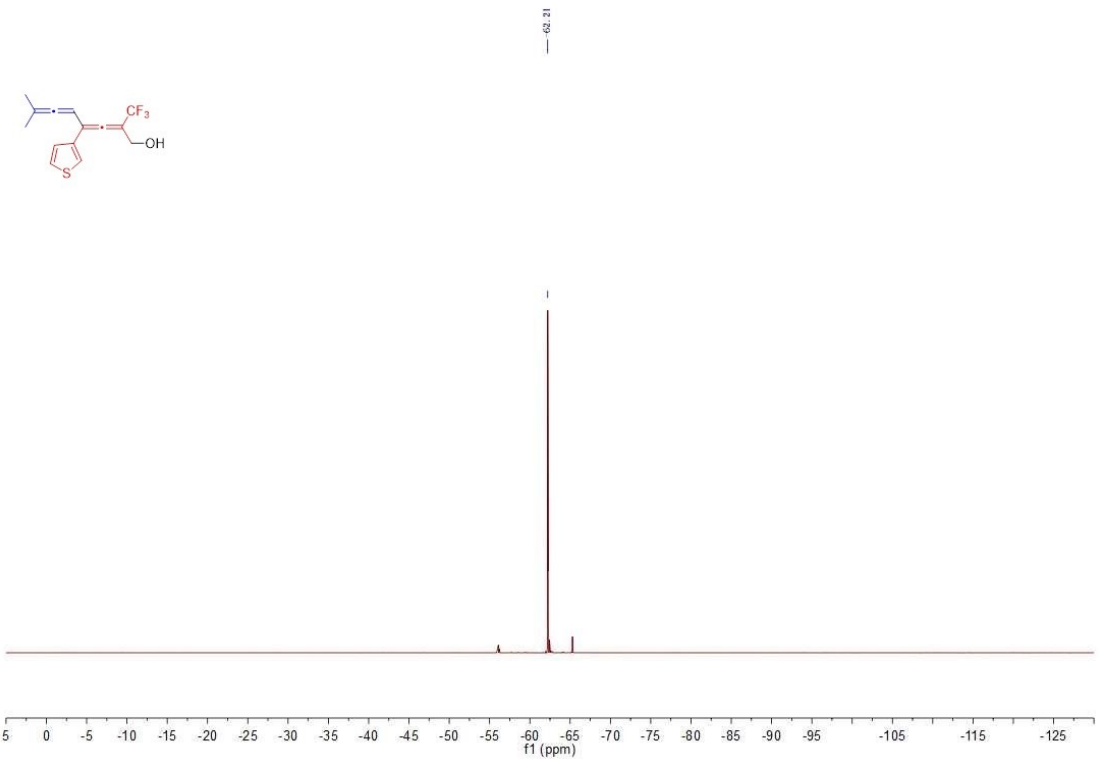
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3 (q, *J* = 4.3 Hz), 205.2, 133.3, 127.3, 125.5, 123.1, 122.8 (q, *J* = 275.2 Hz), 109.2, 101.9 (q, *J* = 33.4 Hz), 99.9, 86.2, 59.1, 20.1, 20.1.

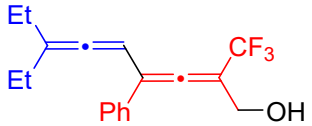
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.21.

HRMS (ESI) calculated for $C_{14}H_{14}F_3OS^+$ $[M+H]^+$ 287.0712; found 287.0715.









7-ethyl-4-phenyl-2-(trifluoromethyl)nona-2,3,5,6-tetraen-1-ol (3aa)

After isolated and purified procedure, this compound was obtained 20.3 mg (66% yield)

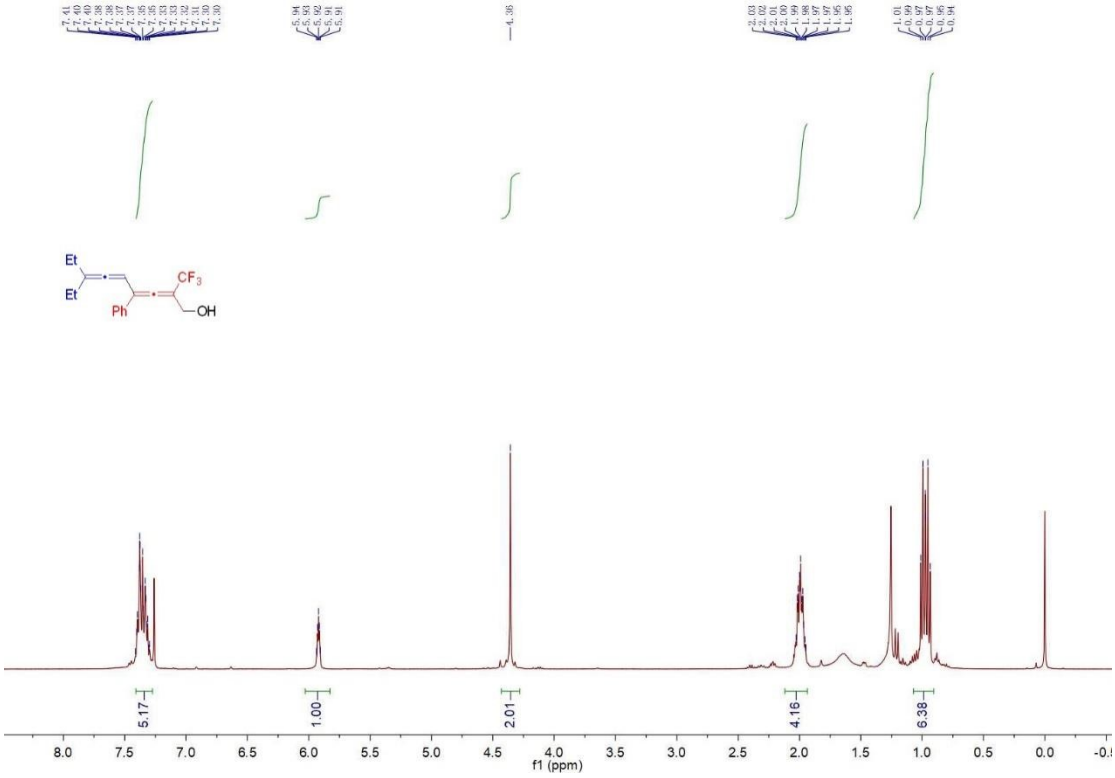
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

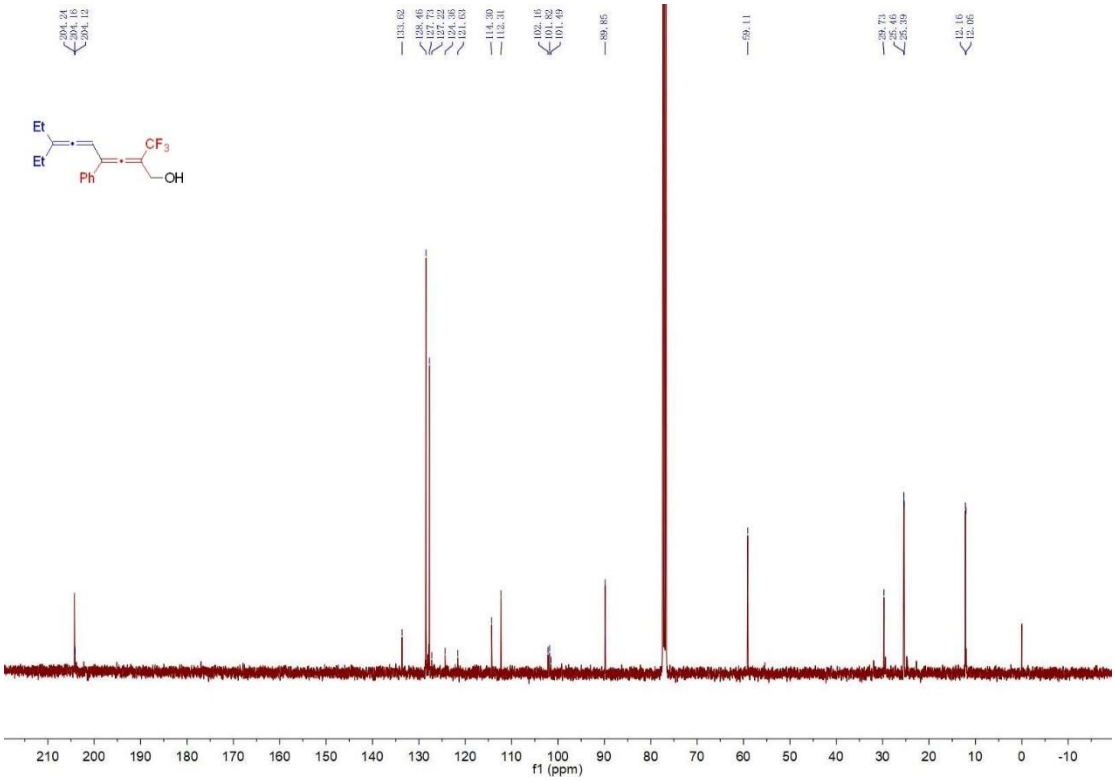
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.25 (m, 5H), 5.92 (t, *J* = 3.1 Hz, 1H), 4.36 (s, 2H), 1.99 (tt, *J* = 6.5, 3.1 Hz, 4H), 1.16-0.49 (m, 6H).

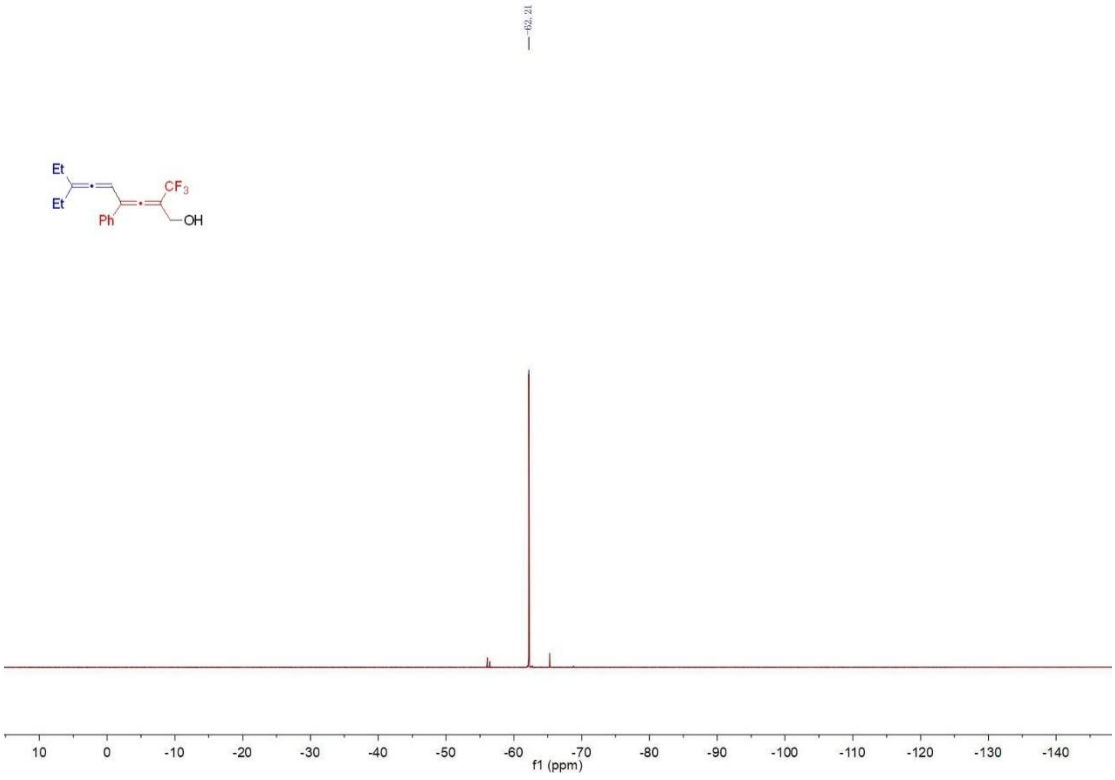
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 204.1 (q, *J* = 4.4 Hz), 133.6, 128.5, 127.7, 127.2, 123.0 (q, *J* = 274.8 Hz), 114.3, 112.3, 102.0 (q, *J* = 33.5 Hz), 89.9, 59.1, 29.7, 25.5, 25.4, 12.2, 12.1.

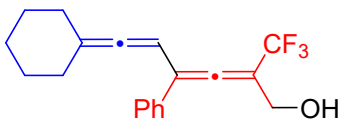
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.21.

HRMS (ESI) calculated for $C_{18}H_{20}F_3O^+$ $[M+H]^+$ 309.1461; found 309.1467.









6-cyclohexylidene-4-phenyl-2-(trifluoromethyl)hexa-2,3,5-trien-1-ol (3ab)

After isolated and purified procedure, this compound was obtained 22.4 mg (70% yield)

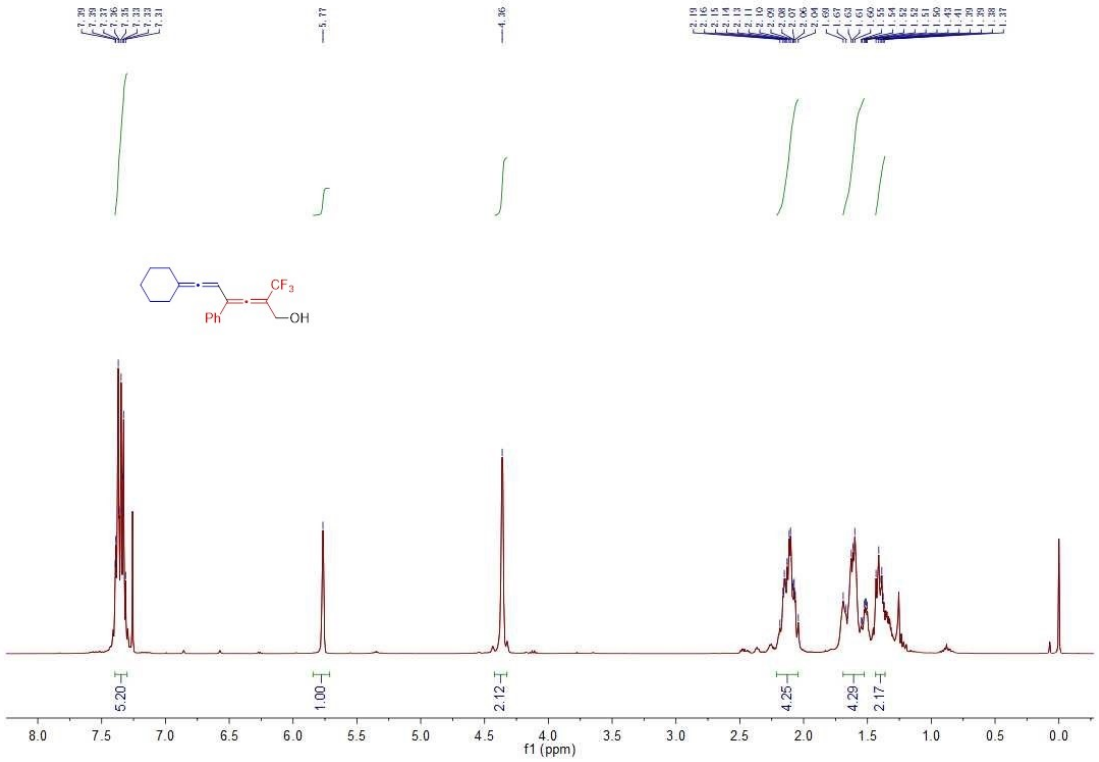
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

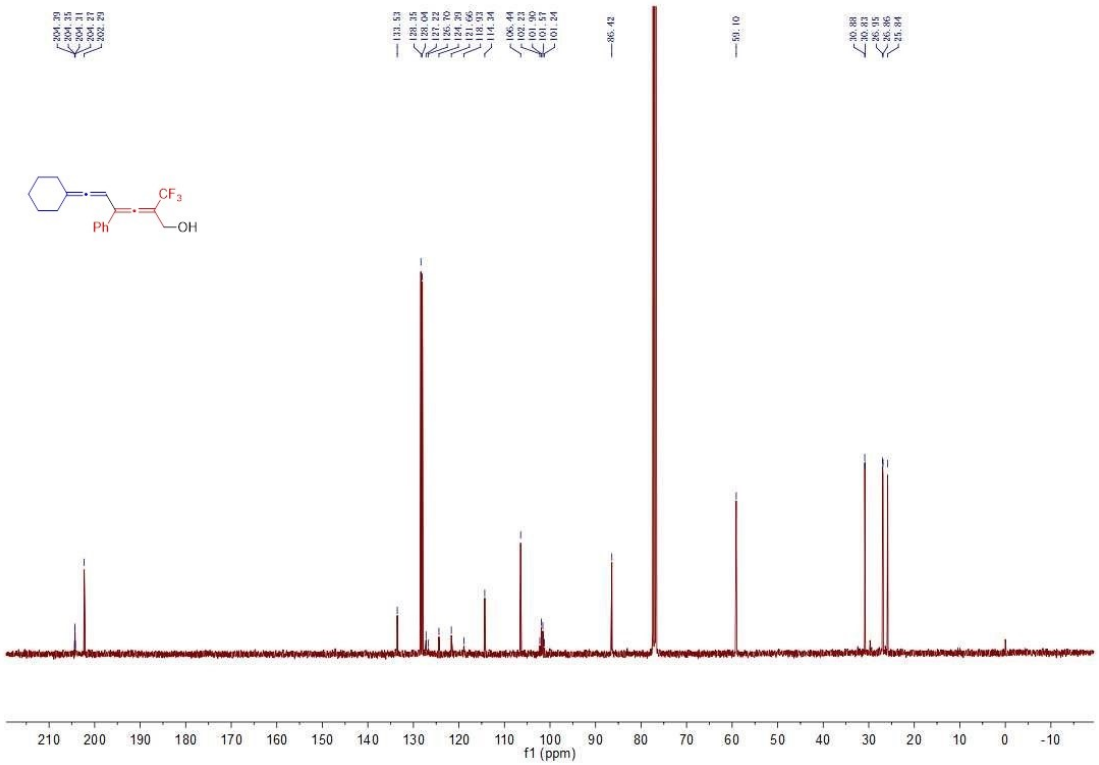
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.30 (m, 5H), 5.77 (s, 1H), 4.36 (s, 2H), 2.24-1.98 (m, 4H), 1.73-1.47 (m, 4H), 1.44-1.33 (m, 2H).

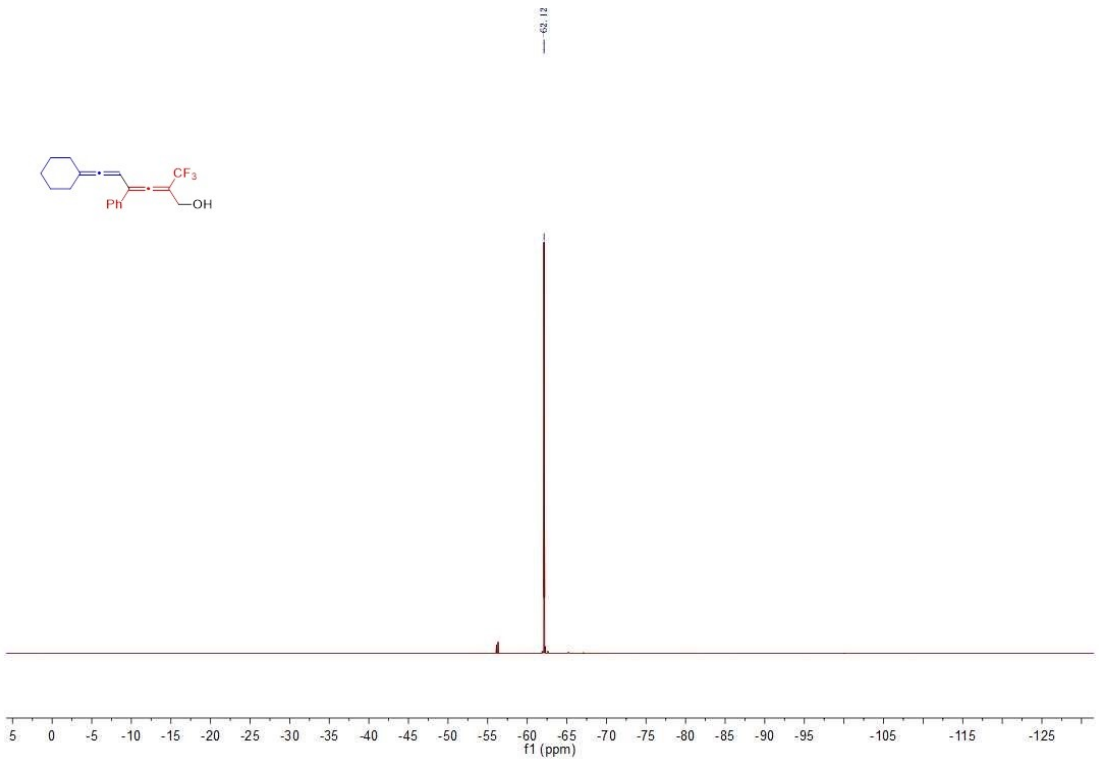
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3 (q, J = 4.2 Hz), 202.3, 133.5, 128.4, 128.0, 127.2, 123.0 (q, J = 275.0 Hz), 114.3, 106.4, 101.7 (q, J = 33.3 Hz), 86.4, 59.1, 30.9, 30.8, 27.0, 26.9, 25.8.

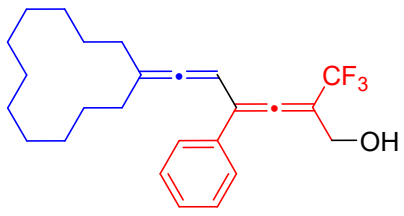
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.12.

HRMS (ESI) calculated for $C_{19}H_{20}F_3O^+$ $[M+H]^+$ 321.1461; found 321.1467.




204.39
204.35
204.31
204.27
202.29
133.53
128.35
128.04
127.22
125.70
124.29
121.66
118.93
114.24
106.44
102.23
101.90
101.57
101.24
86.42
59.10
30.88
30.83
26.95
26.86
25.84
CF3
Ph
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.12
CF3
Ph
OH
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


CF3
OH

6-cyclododecylidene-4-phenyl-2-(trifluoromethyl)hexa-2,3,5-trien-1-ol (3ac)

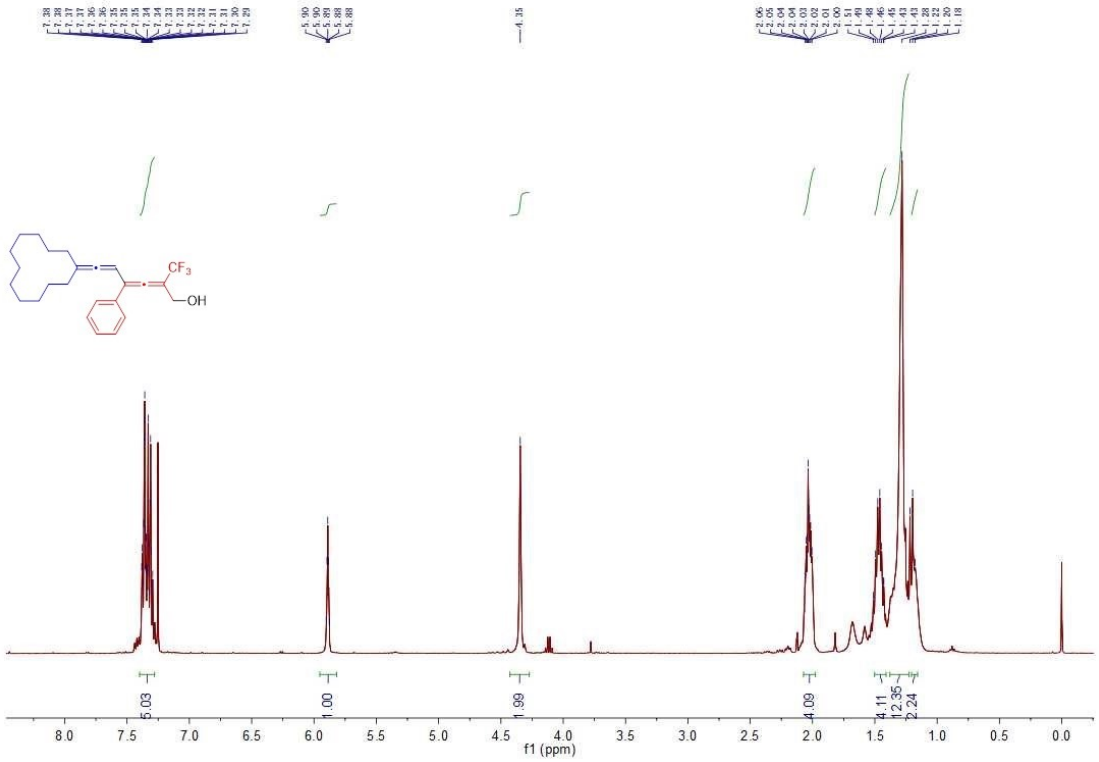
After isolated and purified procedure, this compound was obtained 29.9 mg (74% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

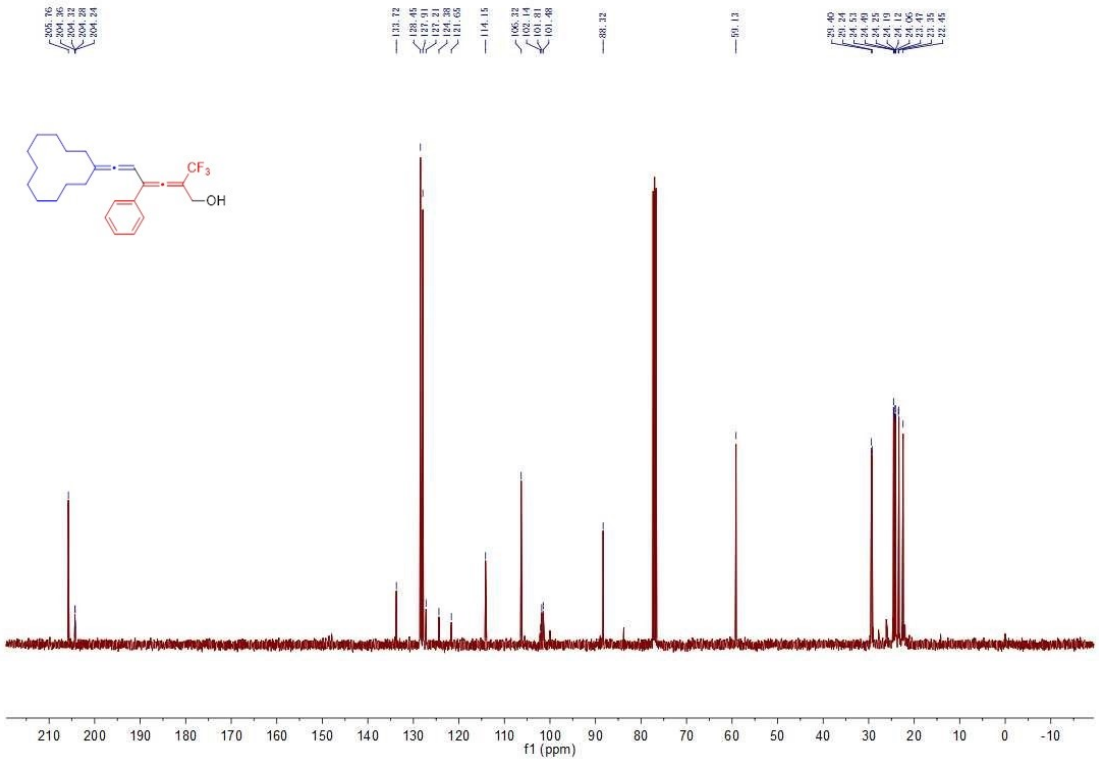
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 5.90-5.88 (m, 1H), 4.35 (s, 2H), 2.06-1.99 (m, 4H), 1.53-1.39 (m, 4H), 1.28 (s, 12H), 1.22-1.11 (m, 2H).

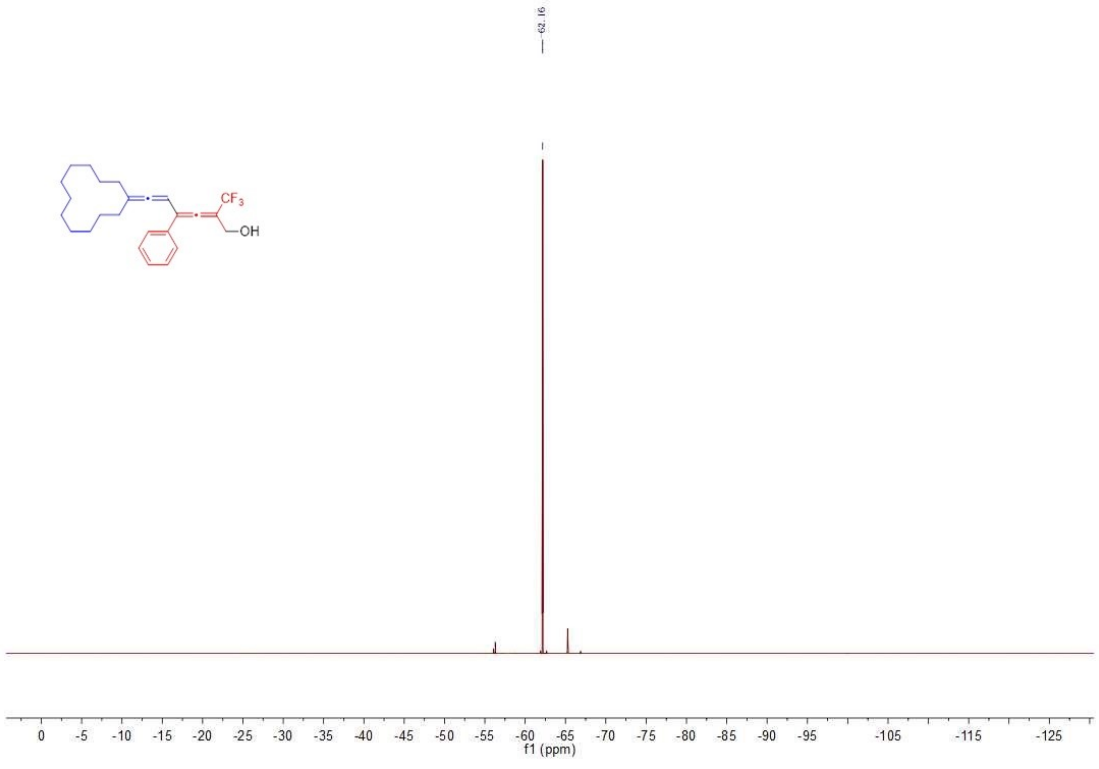
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 204.3 (q, J = 4.2 Hz), 133.7, 128.5, 127.9, 127.2, 123.0 (q, J = 275.0 Hz), 114.2, 101.7 (q, J = 33.2 Hz), 88.3, 59.1, 29.4, 29.2, 24.5, 24.5, 24.3, 24.2, 24.1, 24.1, 23.5, 23.4, 22.5.

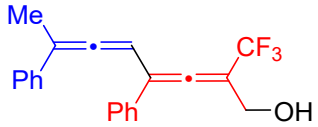
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.16.

HRMS (ESI) calculated for $C_{25}H_{32}F_3O^+$ $[M+H]^+$ 405.2400; found 405.2405.









4,7-diphenyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3ad)

After isolated and purified procedure, this unstable compound was obtained (55% NMR

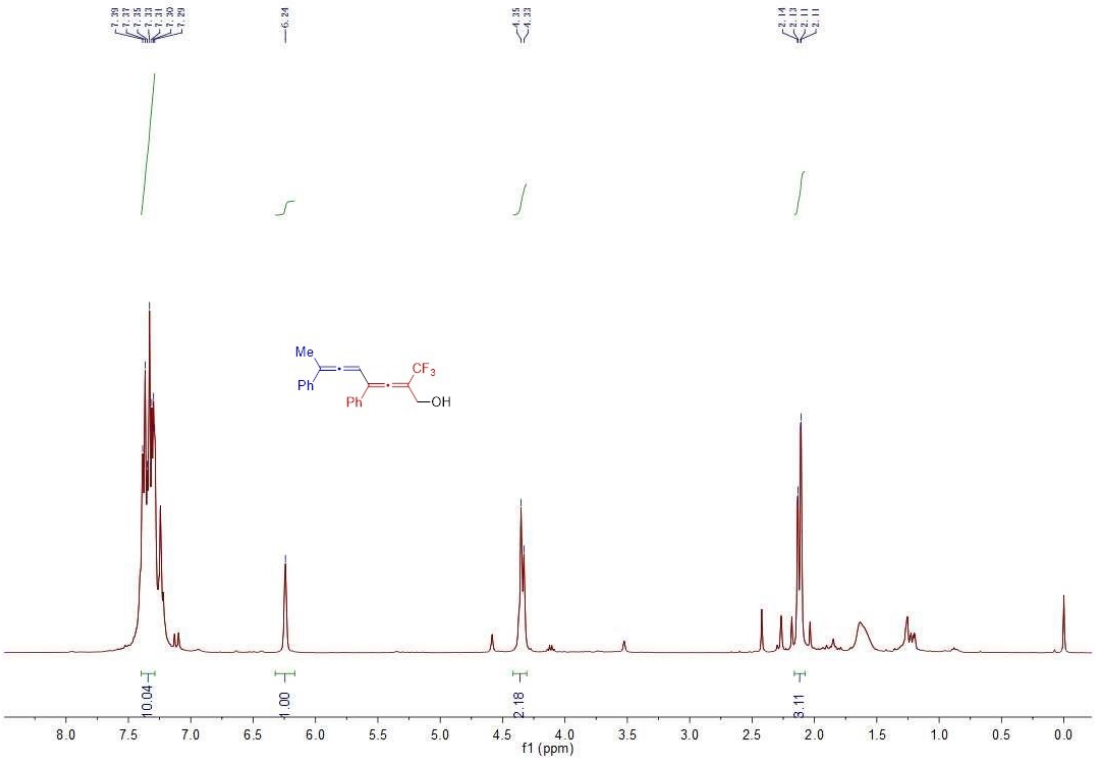
yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

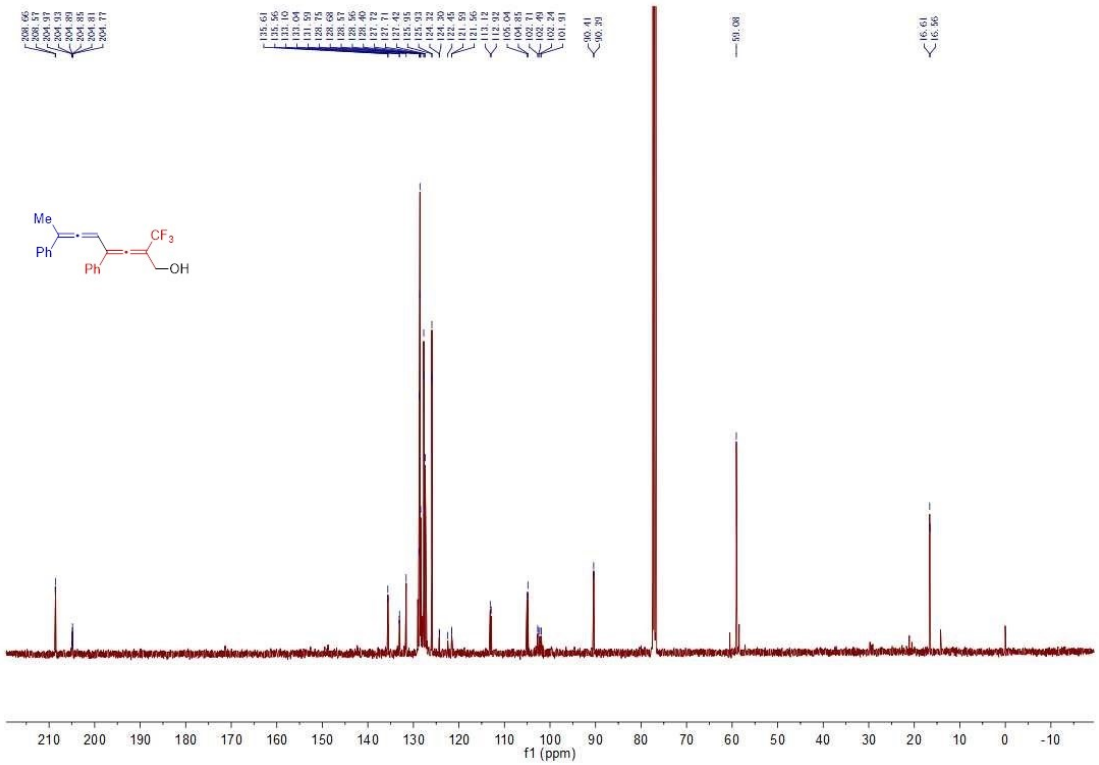
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.23 (m, 10H), 6.24 (s, 1H), 4.34 (d, *J* = 9.2 Hz, 2H), 2.12 (dd, *J* = 10.0, 2.0 Hz, 3H).

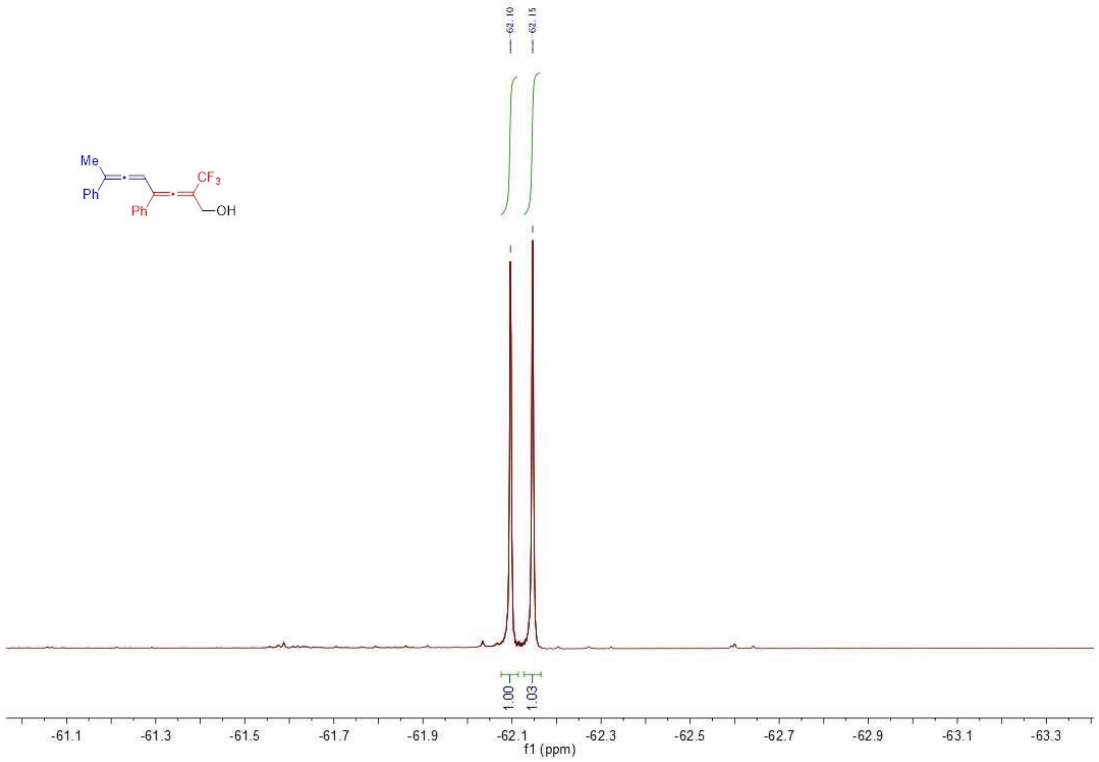
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 208.6, 204.9 (dq, *J* = 7.5, 4.0 Hz), 135.6, 135.6, 133.1, 133.0, 131.6, 128.8, 128.7, 128.6, 128.6, 128.4, 127.7, 127.7, 127.4, 122.9 (dq, *J* = 275.1, 2.4 Hz), 113.1, 112.9, 105.0, 104.9, 102.3 (dq, *J* = 52.1, 27.6 Hz), 90.4, 90.4, 59.1, 16.6, 16.6.

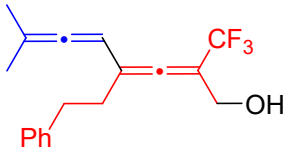
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.10, -62.15.

HRMS (ESI) calculated for $C_{21}H_{18}F_3O^+$ $[M+H]^+$ 343.1304; found 343.1300.









7-methyl-4-phenethyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3r)

After isolated and purified procedure, this compound was obtained 19.1 mg (62% yield)

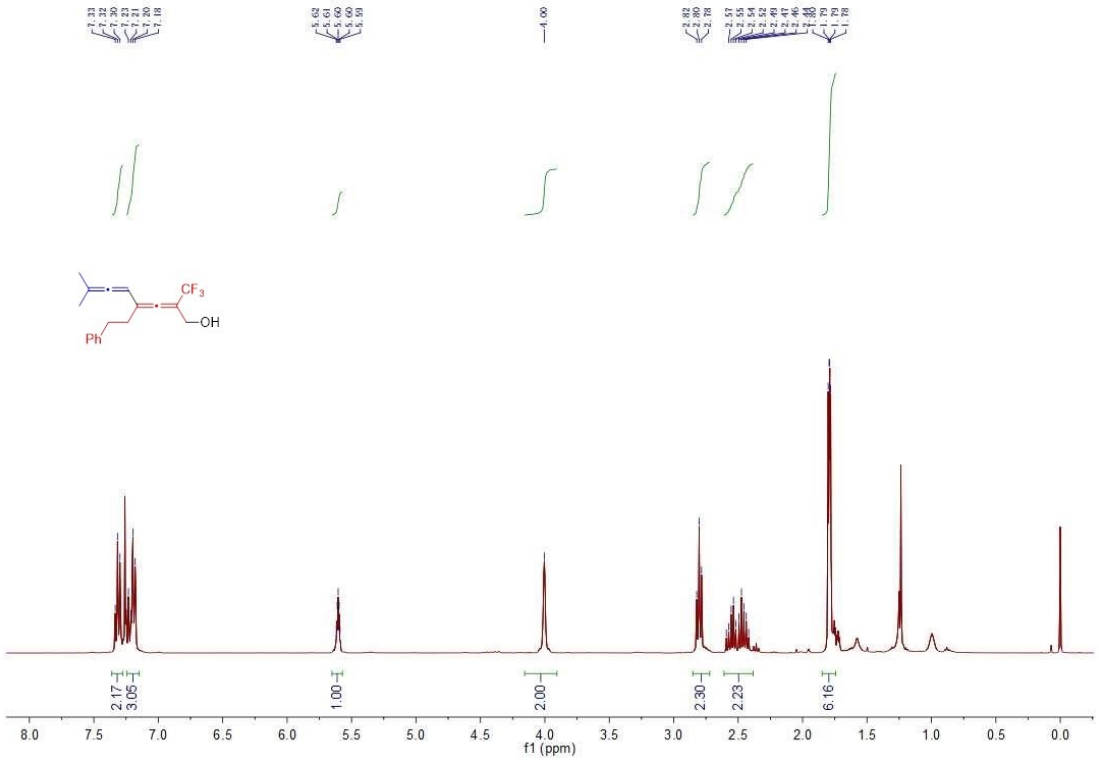
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

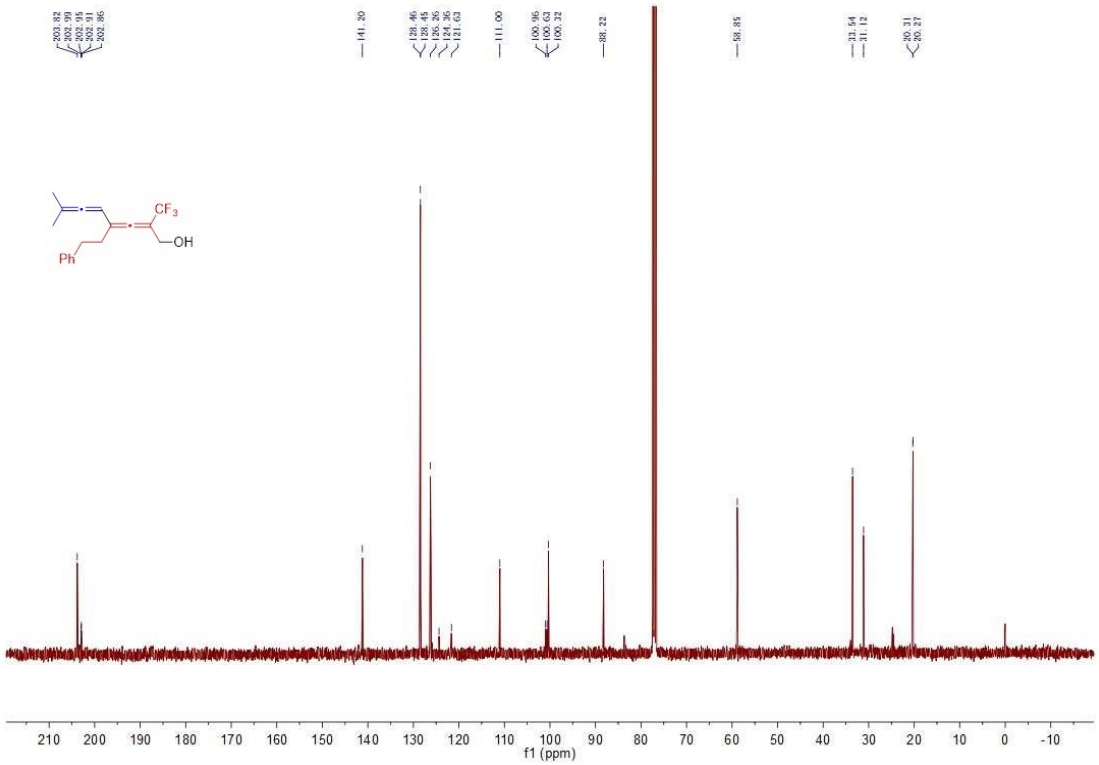
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2H), 7.25-7.15 (m, 3H), 5.60 (dt, *J* = 5.7, 2.8 Hz, 1H), 4.00 (s, 2H), 2.80 (t, *J* = 7.4 Hz, 2H), 2.51 (ddt, *J* = 40.0, 15.1, 7.4 Hz, 2H), 1.79 (dd, *J* = 4.9, 2.9 Hz, 6H).

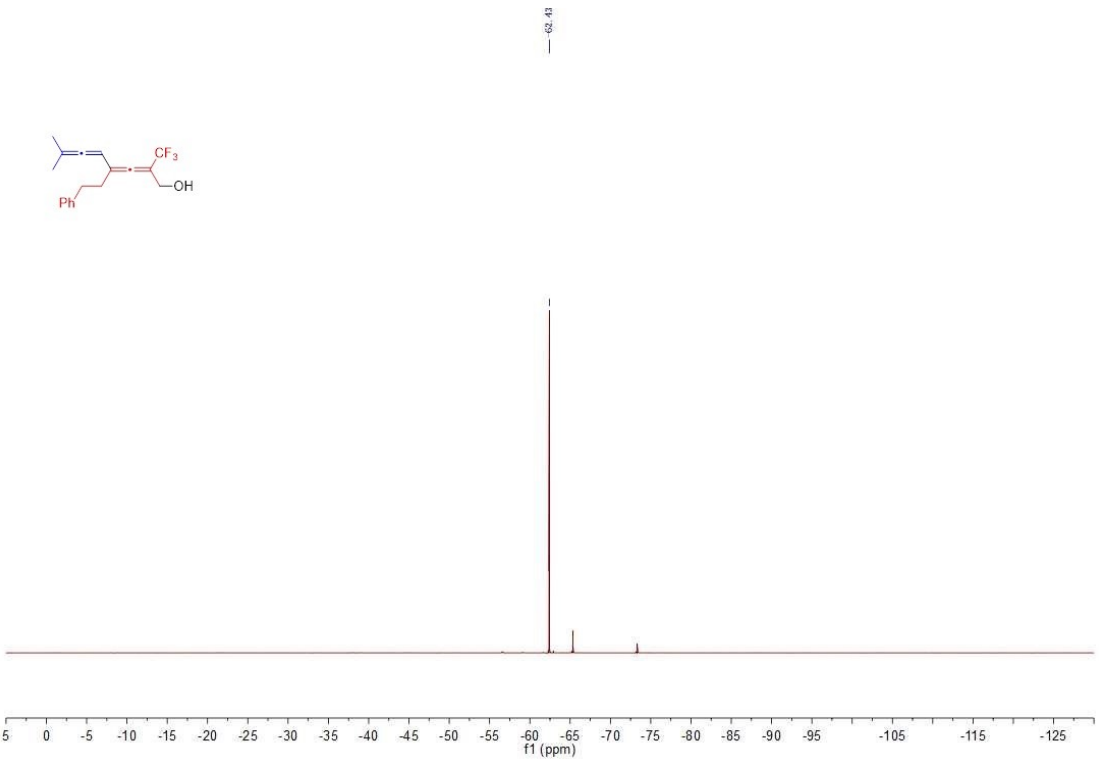
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 202.9 (q, *J* = 4.2 Hz), 141.2, 128.5, 128.5, 126.3, 123.0 (q, *J* = 274.6 Hz), 111.0, 100.8 (q, *J* = 33.1 Hz), 100.3, 88.2, 58.9, 33.5, 31.1, 20.3, 20.3.

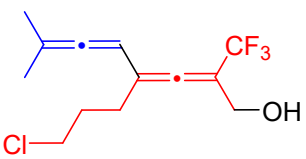
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43.

HRMS (ESI) calculated for $C_{18}H_{20}F_3O^+$ $[M+H]^+$ 309.1461; found 309.1464.









4-(3-chloropropyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3s)

After isolated and purified procedure, this compound was obtained 18.2 mg (65% yield)

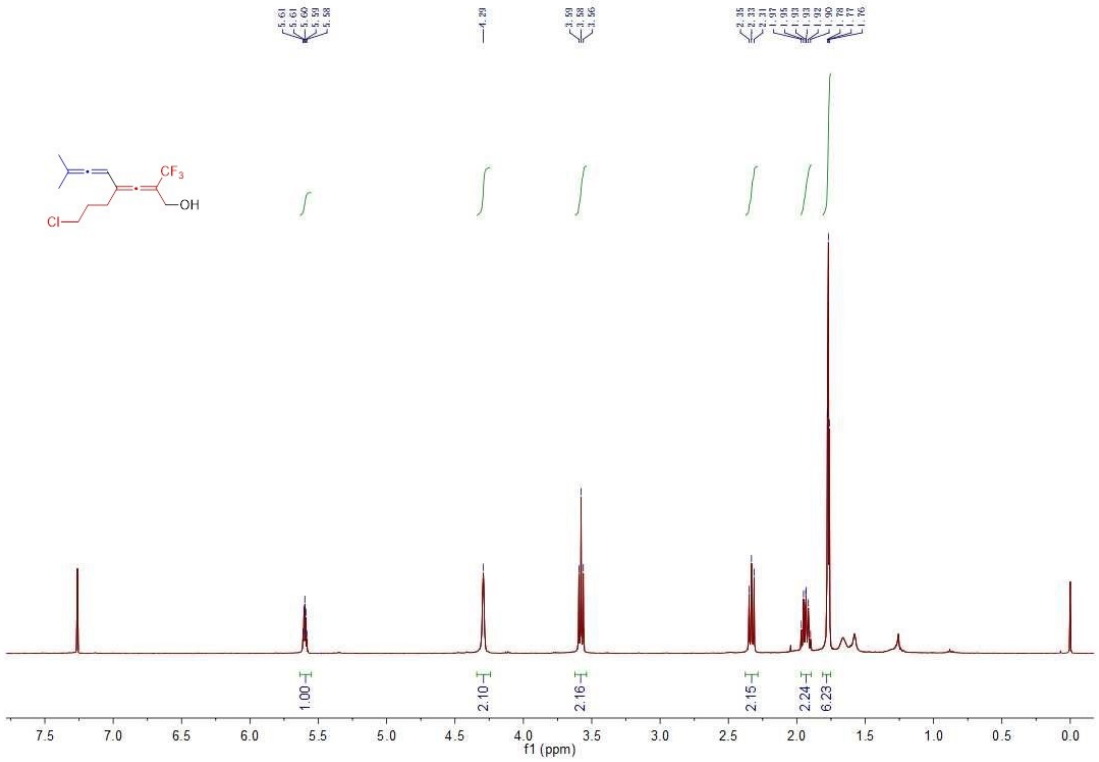
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

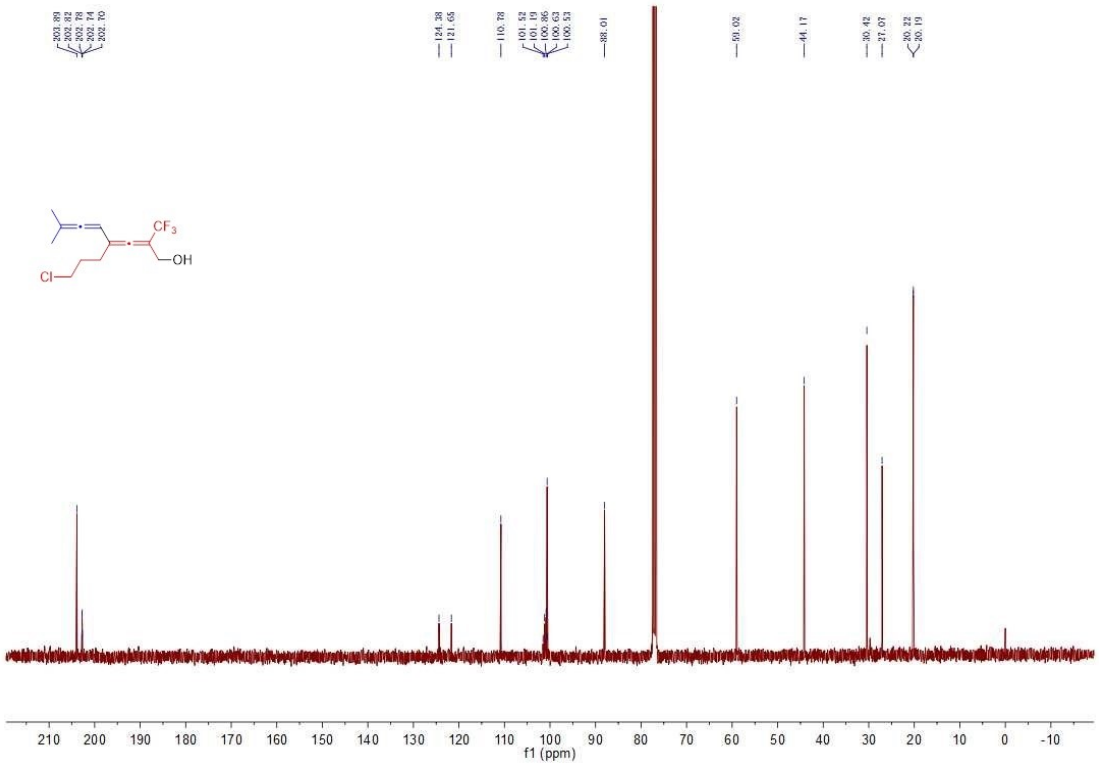
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (dt, *J* = 5.7, 2.8 Hz, 1H), 4.29 (s, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.46-2.13 (m, 2H), 1.93 (dq, *J* = 12.8, 6.4 Hz, 2H), 1.77 (t, *J* = 3.0 Hz, 6H).

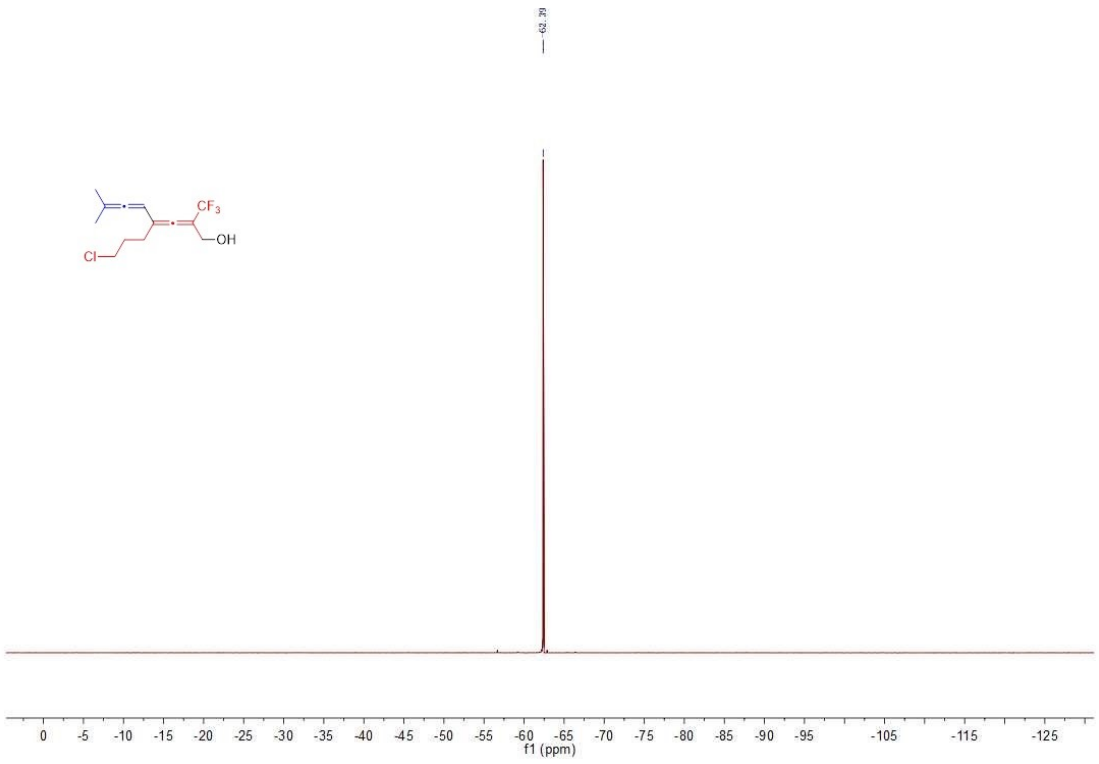
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 202.8 (q, *J* = 4.1 Hz), 123.0 (q, *J* = 274.7 Hz), 101.0 (q, *J* = 33.1 Hz), 100.9, 88.0, 59.0, 44.2, 30.4, 27.1, 20.2, 20.2.

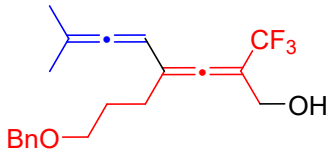
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.39.

HRMS (ESI) calculated for $C_{13}H_{17}ClF_3O^+$ $[M+H]^+$ 281.0915; found 281.0914.









4-(3-(benzyloxy)propyl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3t)

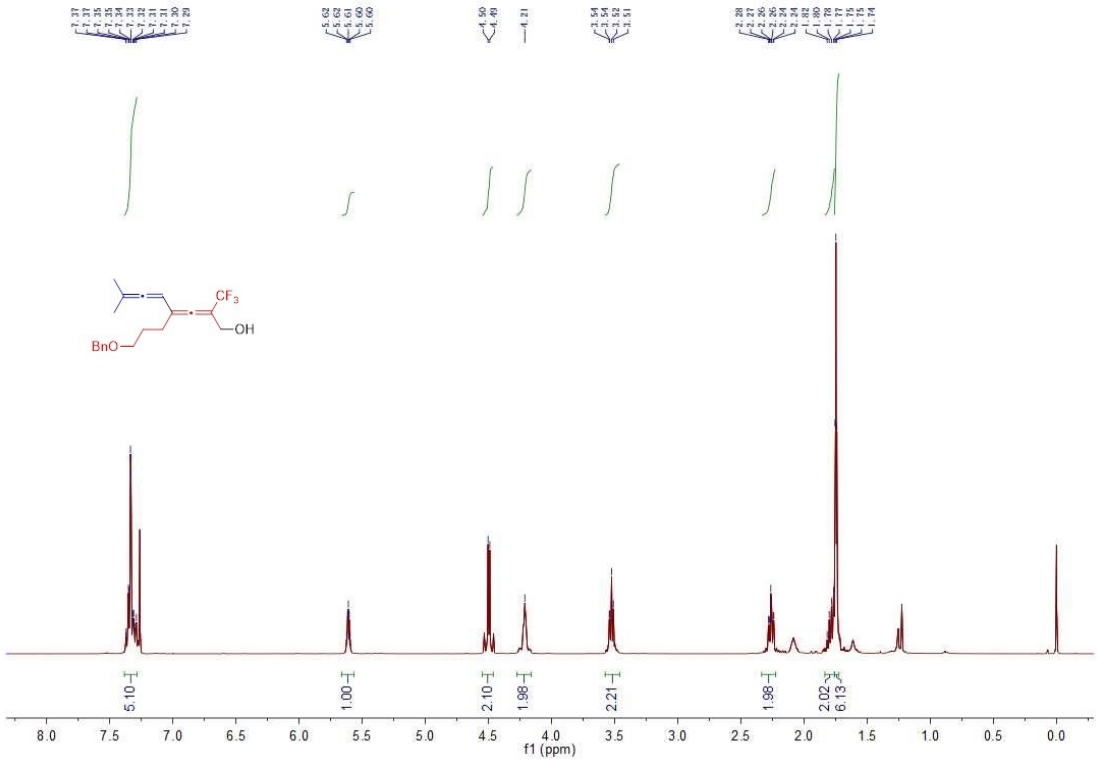
After isolated and purified procedure, this compound was obtained 21.1 mg (60% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

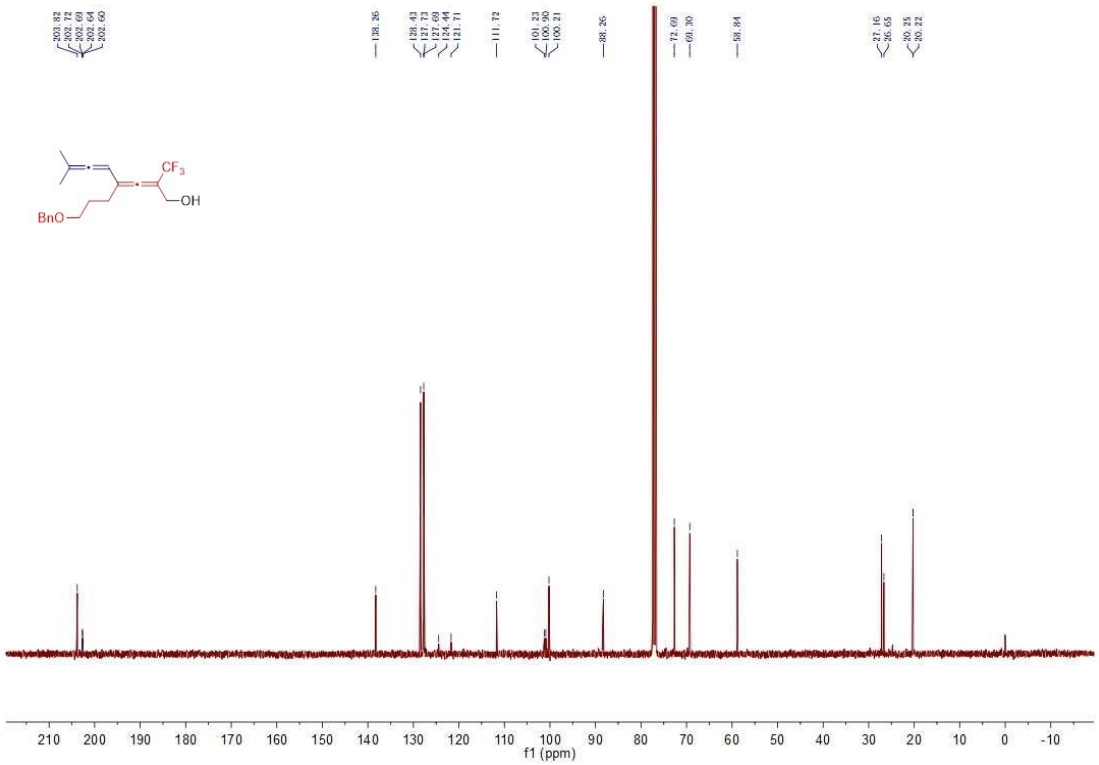
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.26 (m, 5H), 5.61 (dt, *J* = 5.7, 2.8 Hz, 1H), 4.50 (d, *J* = 5.5 Hz, 2H), 4.21 (s, 2H), 3.53 (dd, *J* = 9.6, 3.6 Hz, 2H), 2.26 (td, *J* = 7.3, 2.6 Hz, 2H), 1.82-1.76 (m, 2H), 1.75 (dd, *J* = 6.7, 3.8 Hz, 6H).

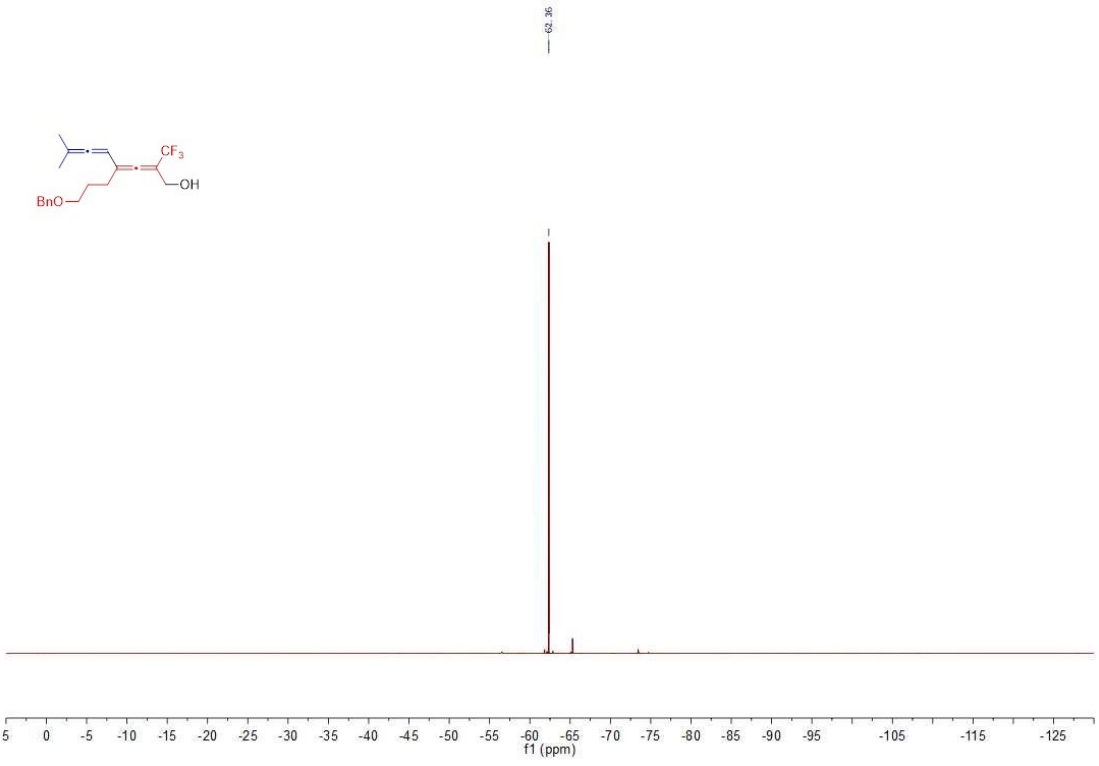
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 202.7 (q, *J* = 4.3 Hz), 138.3, 128.4, 127.7, 127.7, 123.1 (q, *J* = 274.6 Hz), 111.7, 101.1 (q, *J* = 33.1 Hz), 100.2, 88.3, 72.7, 69.3, 58.8, 27.2, 26.7, 20.3, 20.2.

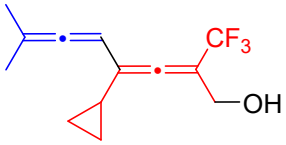
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.36.

HRMS (ESI) calculated for $C_{20}H_{24}F_3O_2^+$ $[M+H]^+$ 353.1723; found 353.1725.









4-cyclopropyl-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3u)

After isolated and purified procedure, this compound was obtained 14.2 mg (58% yield)

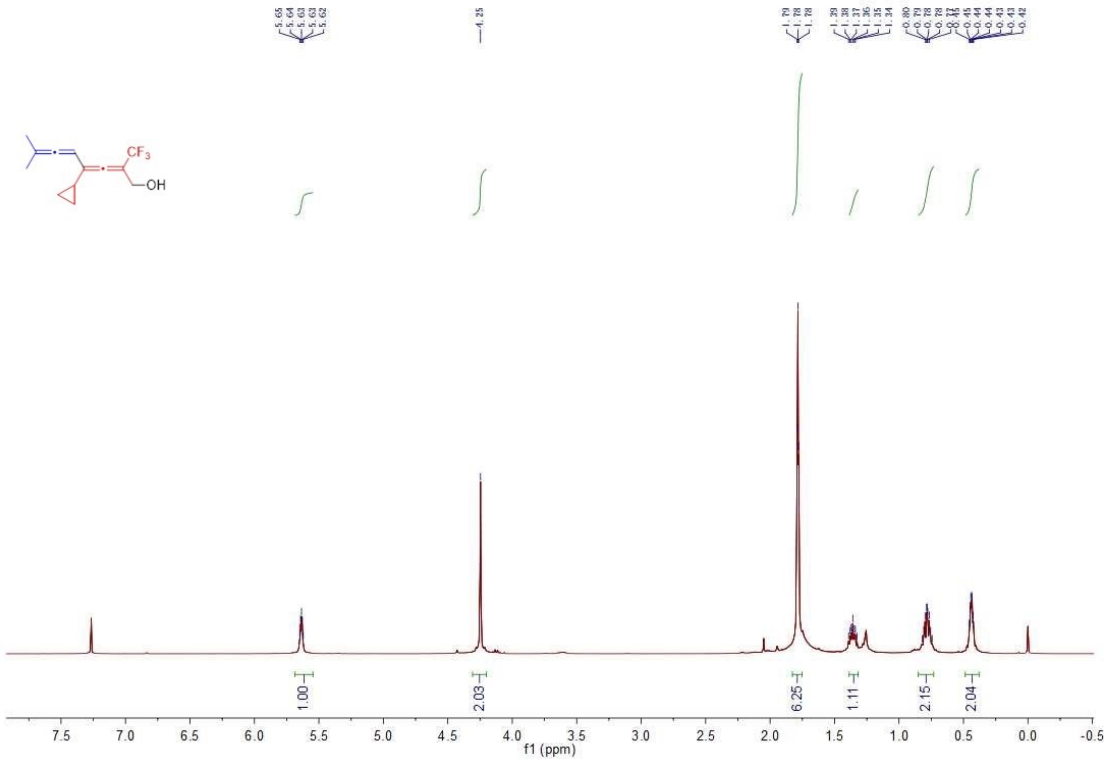
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

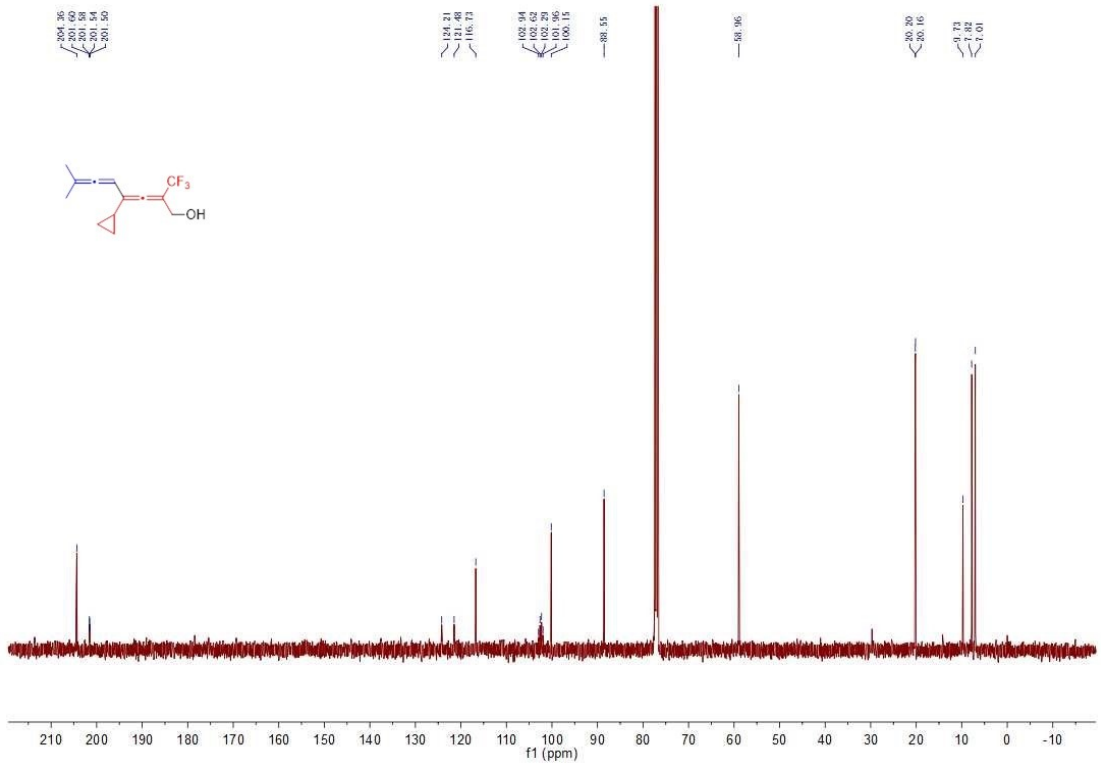
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (dt, *J* = 5.5, 2.7 Hz, 1H), 4.25 (s, 2H), 1.78 (t, *J* = 2.5 Hz, 6H), 1.42-1.30 (m, 1H), 0.84-0.67 (m, 2H), 0.52-0.22 (m, 2H).

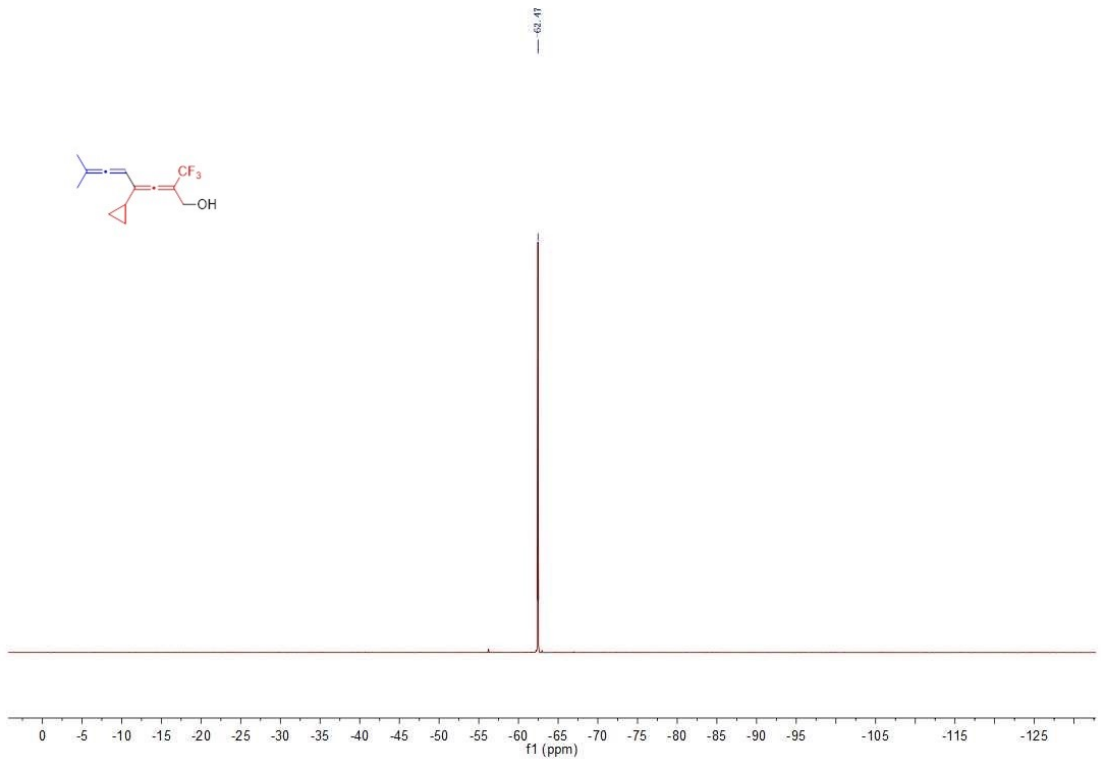
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 201.6 (q, *J* = 4.1 Hz), 122.9 (q, *J* = 274.7 Hz), 116.7, 102.5 (q, *J* = 33.1 Hz), 100.2, 88.6, 59.0, 20.2, 20.2, 9.7, 7.8, 7.0.

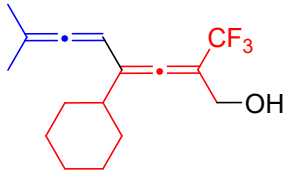
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47.

HRMS (ESI) calculated for $C_{13}H_{16}F_3O^+$ $[M+H]^+$ 245.1148; found 245.1154.









4-cyclohexyl-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3v)

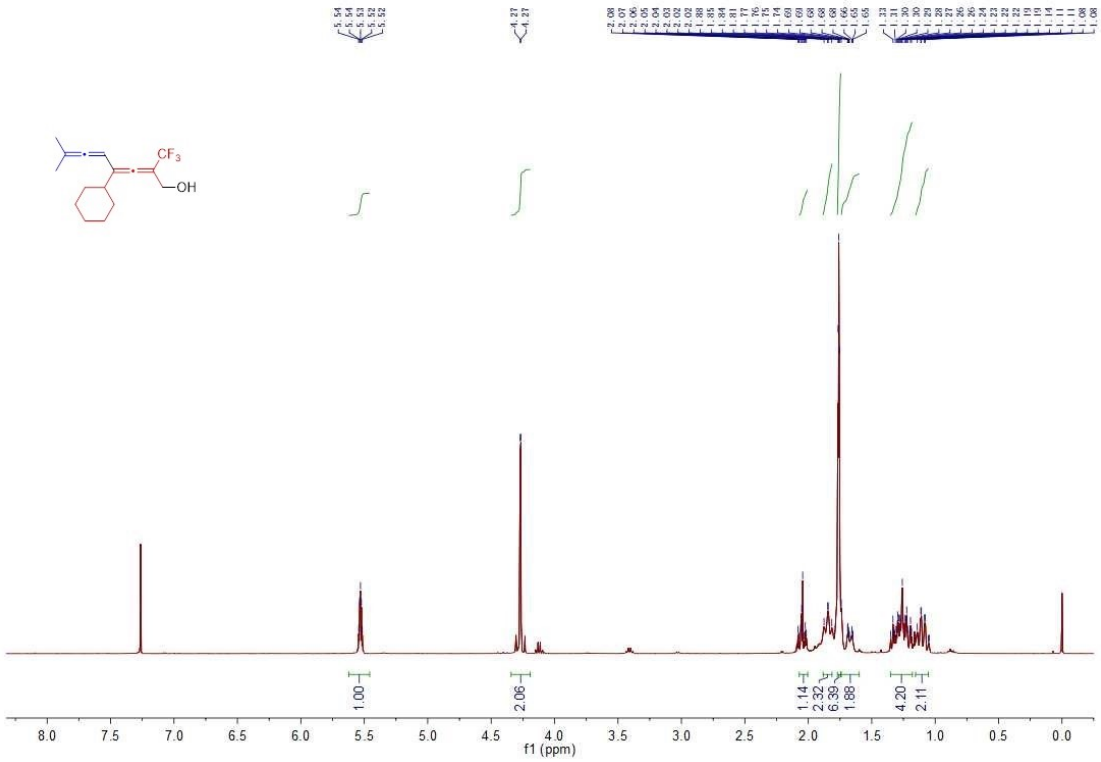
After isolated and purified procedure, this compound was obtained 15.7 mg (55% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

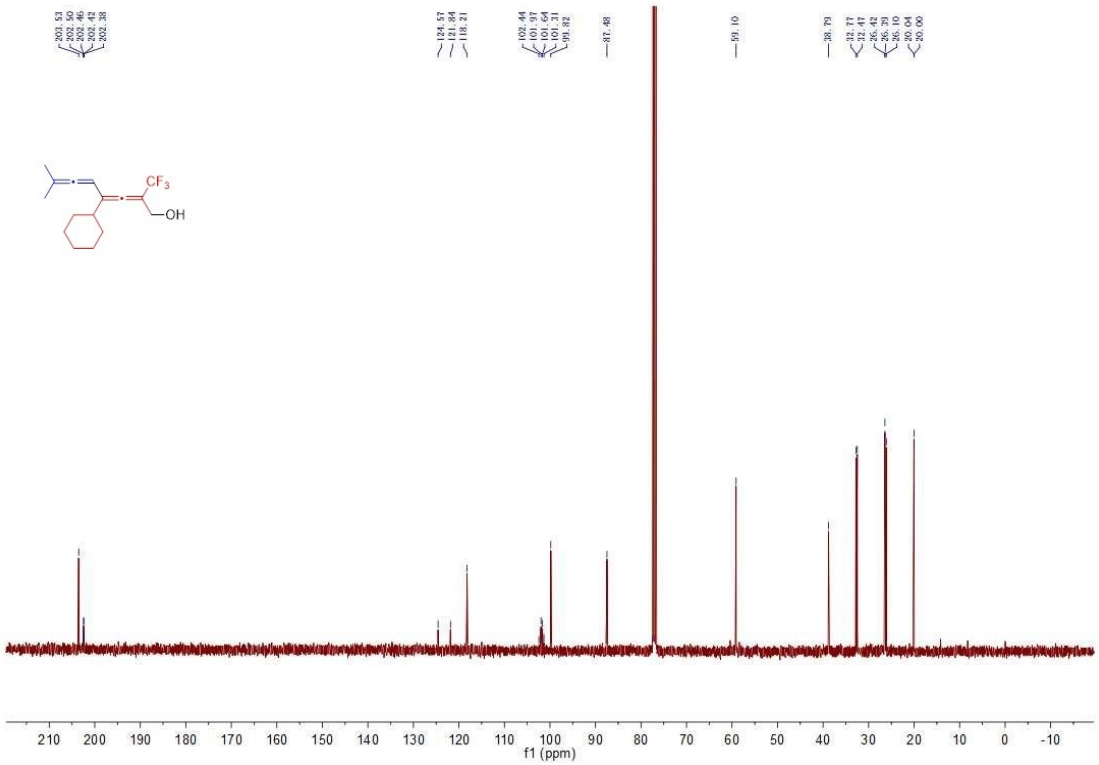
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dt, *J* = 5.7, 2.9 Hz, 1H), 4.27 (d, *J* = 2.1 Hz, 2H), 2.12-1.98 (m, 1H), 1.90-1.80 (m, 2H), 1.77-1.75 (m, 6H), 1.72-1.61 (m, 2H), 1.34-1.18 (m, 4H), 1.17-0.98 (m, 2H).

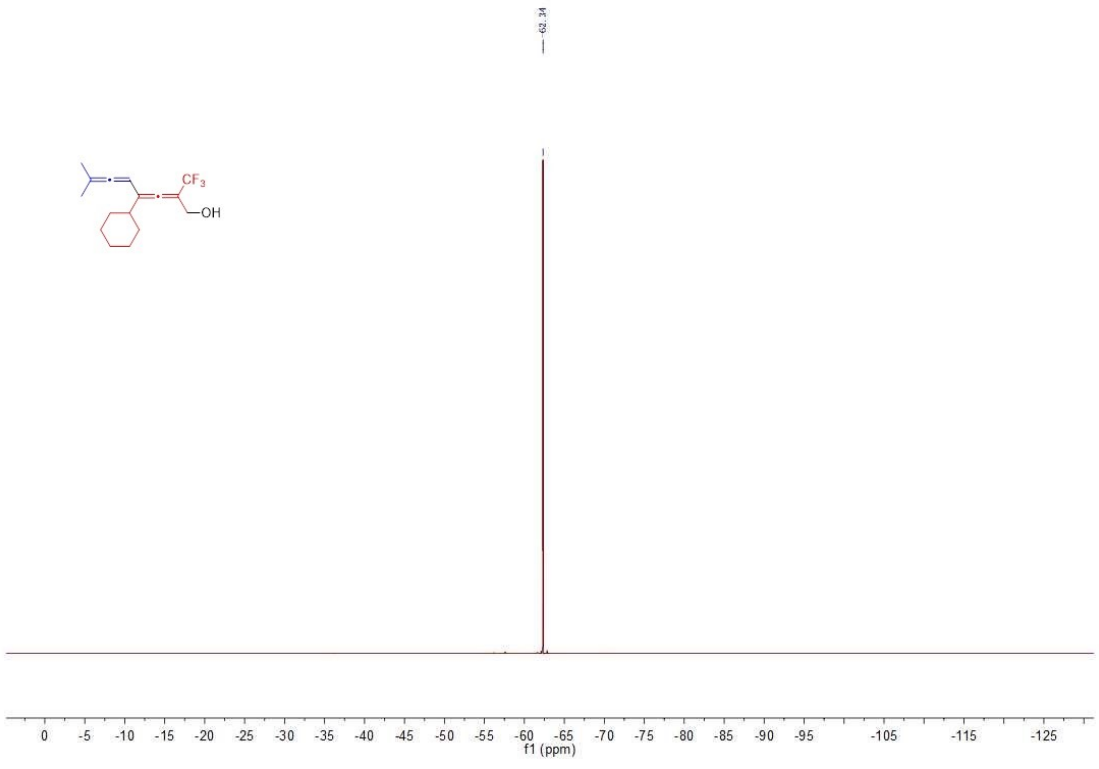
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 202.4 (q, *J* = 4.1 Hz), 123.2 (q, *J* = 274.6 Hz), 118.2, 101.8 (q, *J* = 33.0 Hz), 99.8, 87.5, 59.1, 38.8, 32.8, 32.5, 26.4, 26.4, 26.1, 20.0, 20.0.

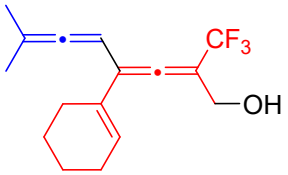
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.34.

HRMS (ESI) calculated for $C_{16}H_{22}F_3O^+$ $[M+H]^+$ 287.1617; found 287.1621.









4-(cyclohex-1-en-1-yl)-7-methyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3w)

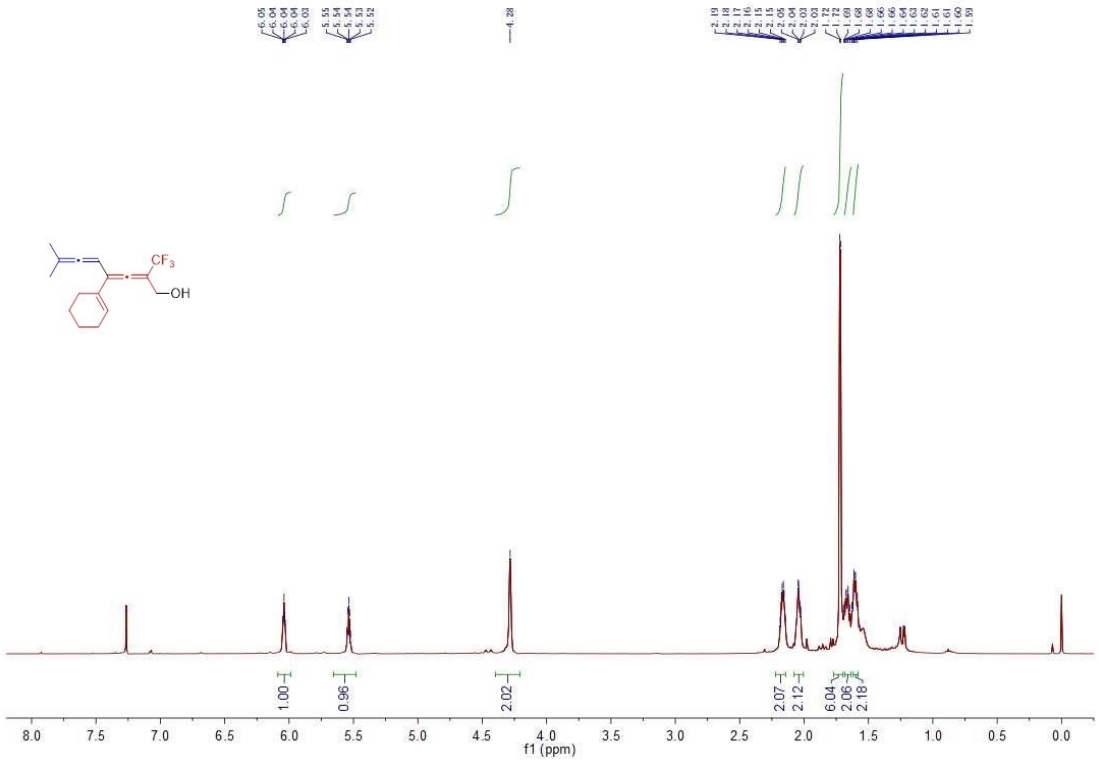
After isolated and purified procedure, this compound was obtained 17.0 mg (60% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

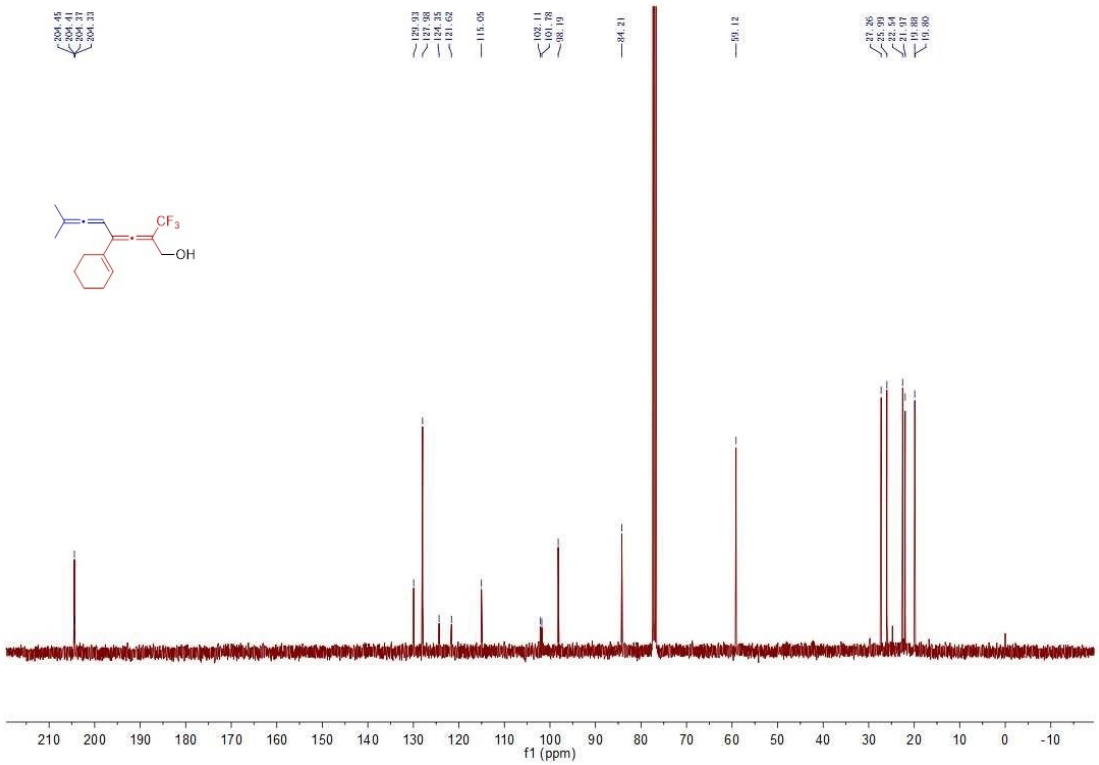
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (dd, *J* = 3.6, 2.0 Hz, 1H), 5.54 (dt, *J* = 5.6, 2.8 Hz, 1H), 4.28 (s, 2H), 2.26-2.07 (m, 2H), 2.07-1.94 (m, 2H), 1.72 (d, *J* = 2.6 Hz, 6H), 1.69-1.64 (m, 2H), 1.63-1.56 (m, 2H).

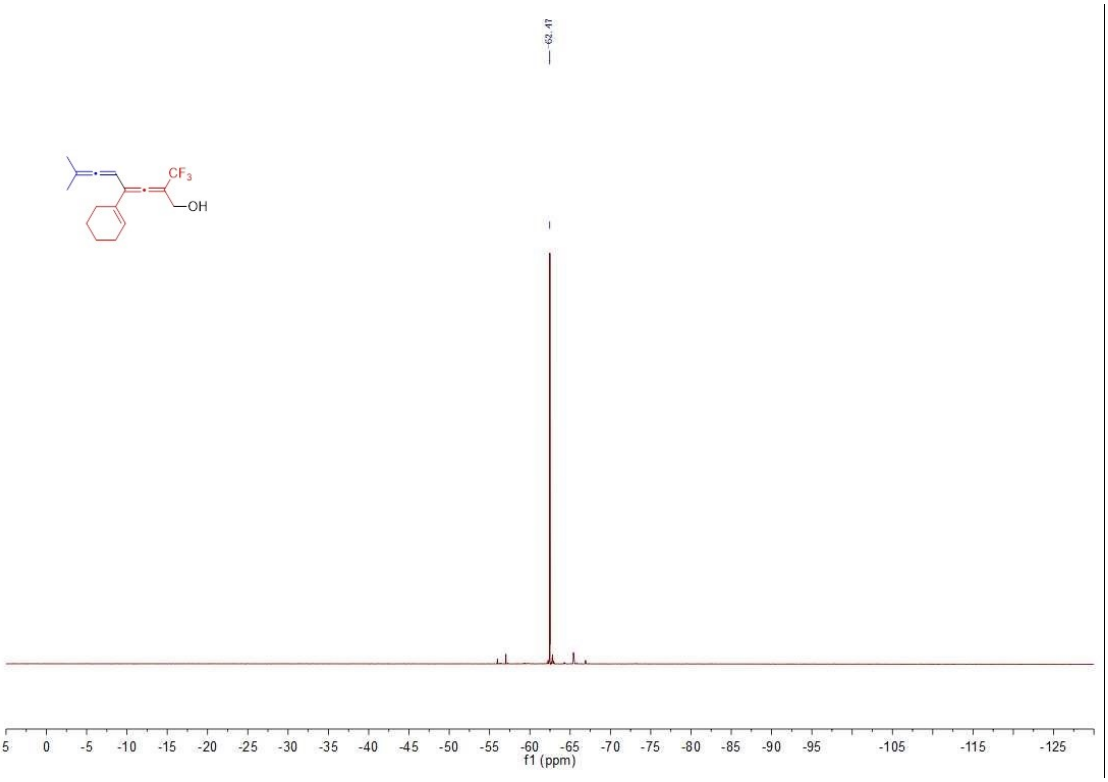
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 204.4 (q, *J* = 4.2 Hz), 129.9, 128.0, 123.0 (q, *J* = 274.7 Hz), 115.1, 102.0 (q, *J* = 33.2 Hz), 98.2, 84.2, 59.1, 27.3, 26.0, 22.5, 22.0, 19.9, 19.8.

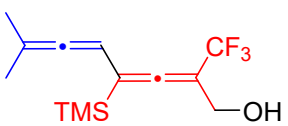
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47.

HRMS (ESI) calculated for $C_{16}H_{20}F_3O^+$ $[M+H]^+$ 285.1461; found 285.1466.









7-methyl-2-(trifluoromethyl)-4-(trimethylsilyl)octa-2,3,5,6-tetraen-1-ol (3x)

After isolated and purified procedure, this compound was obtained 6.9 mg (25% yield)

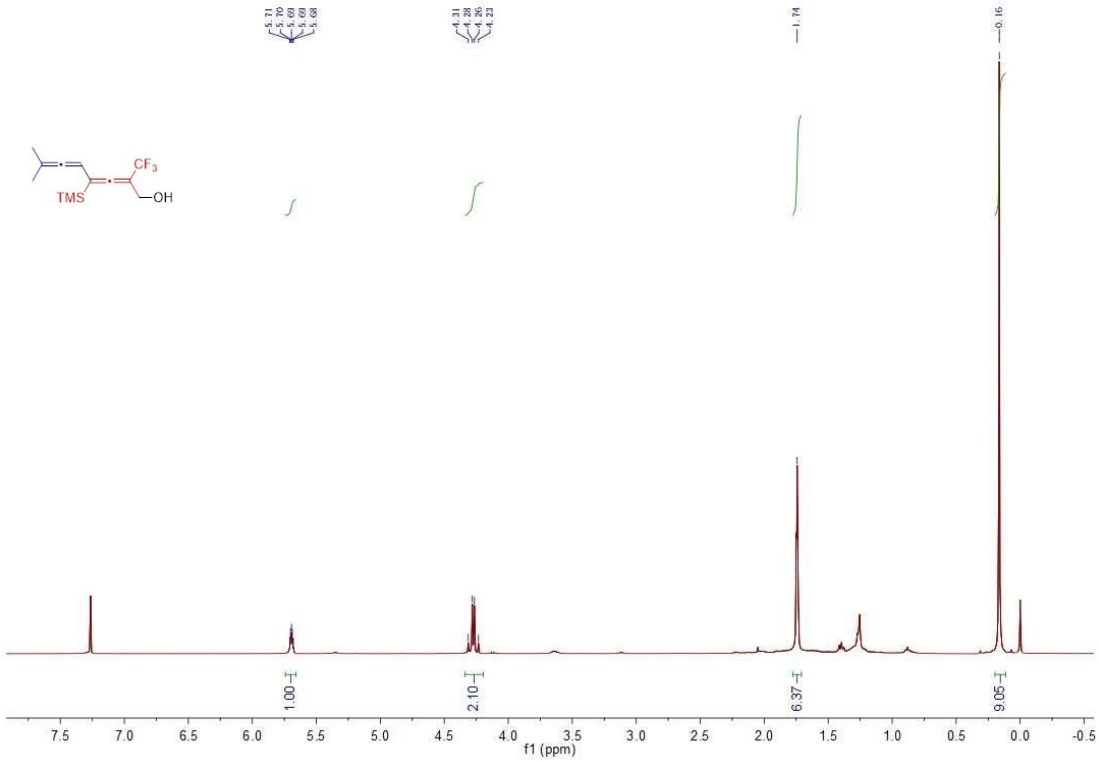
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

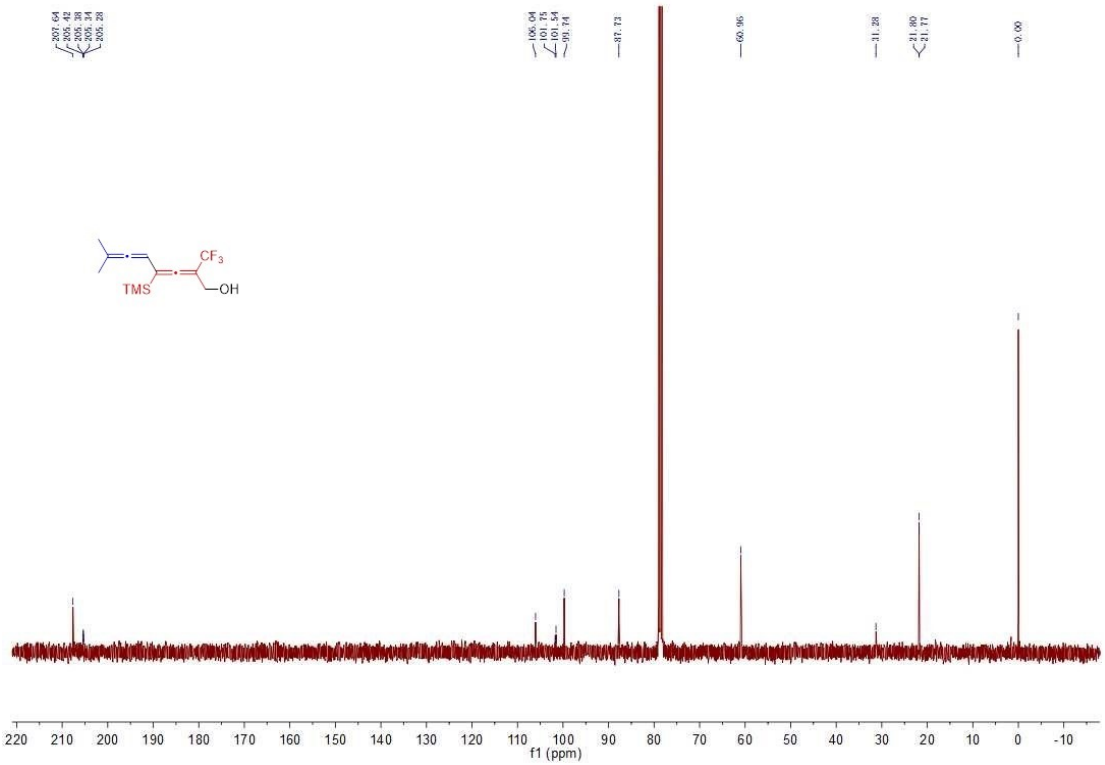
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (dt, *J* = 5.7, 2.9 Hz, 1H), 4.27 (d, *J* = 6.5 Hz, 2H), 1.74 (s, 8H), 0.16 (s, 9H).

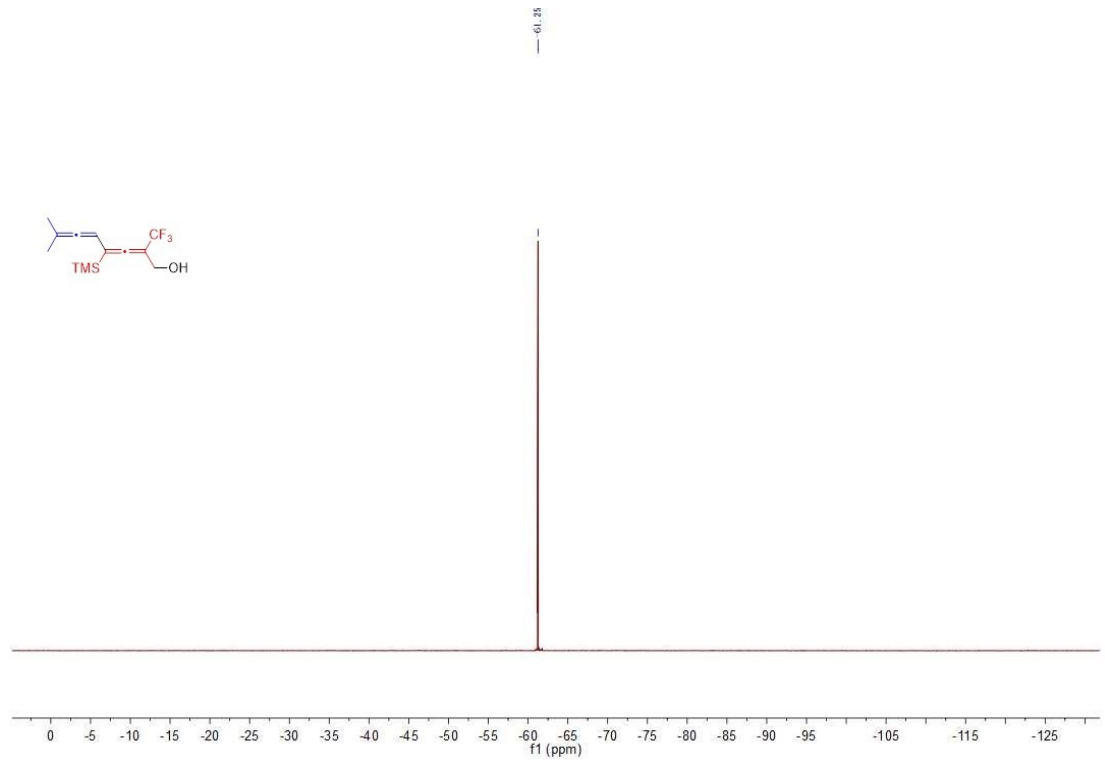
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 205.4 (q, *J* = 3.5 Hz), 106.0, 101.6 (q, *J* = 20.7 Hz), 99.7, 87.7, 61.0, 31.3, 21.8, 21.8, 0.00.

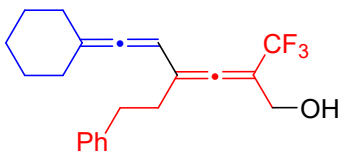
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.25.

HRMS (ESI) calculated for $C_{13}H_{20}F_3OSi^+$ $[M+H]^+$ 277.1230; found 277.1225.









6-cyclohexylidene-4-phenethyl-2-(trifluoromethyl)hexa-2,3,5-trien-1-ol (3ra)

After isolated and purified procedure, this compound was obtained 22.3 mg (64% yield)

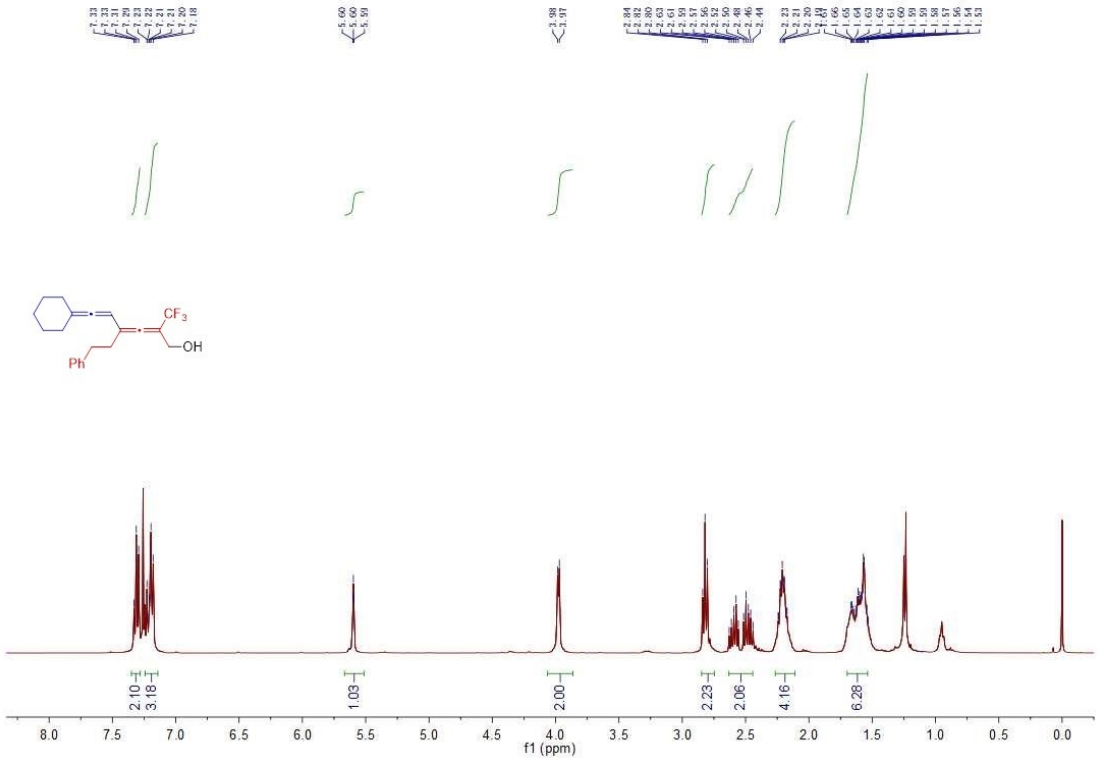
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

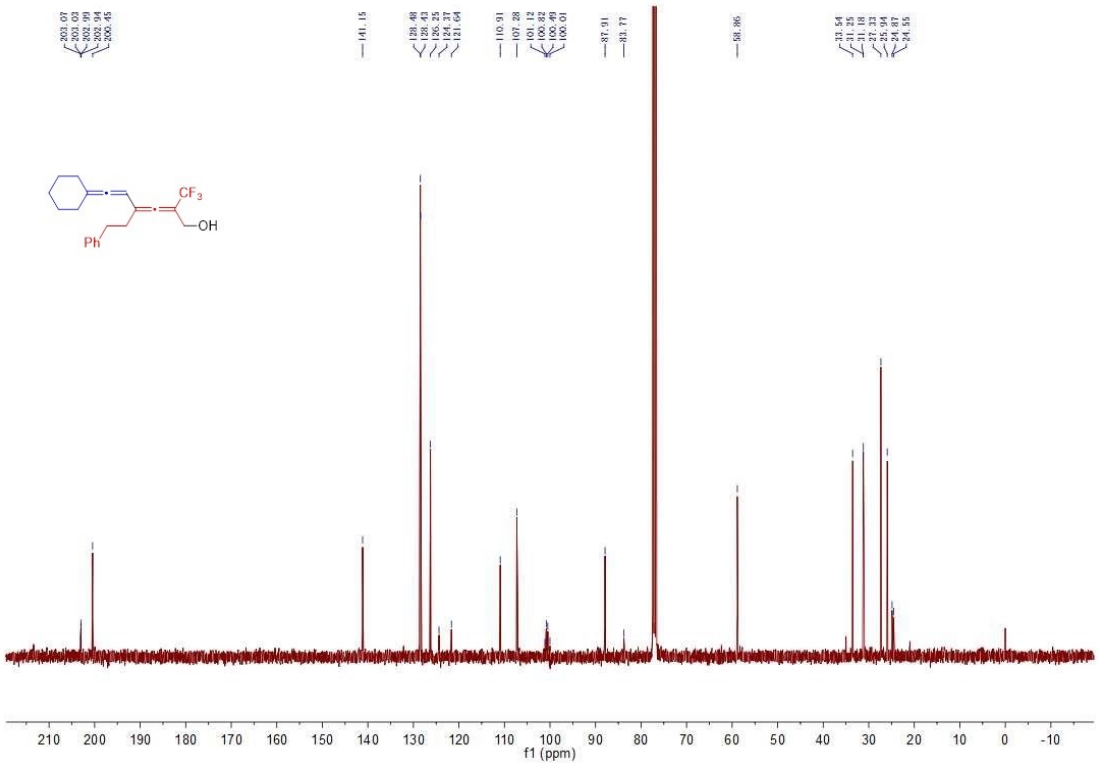
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 10.1, 4.5 Hz, 2H), 7.25-7.10 (m, 3H), 5.99-5.33 (m, 1H), 3.98 (d, *J* = 5.6 Hz, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.54 (ddt, *J* = 29.8, 14.8, 7.2 Hz, 2H), 2.30-2.09 (m, 4H), 1.73-1.41 (m, 6H).

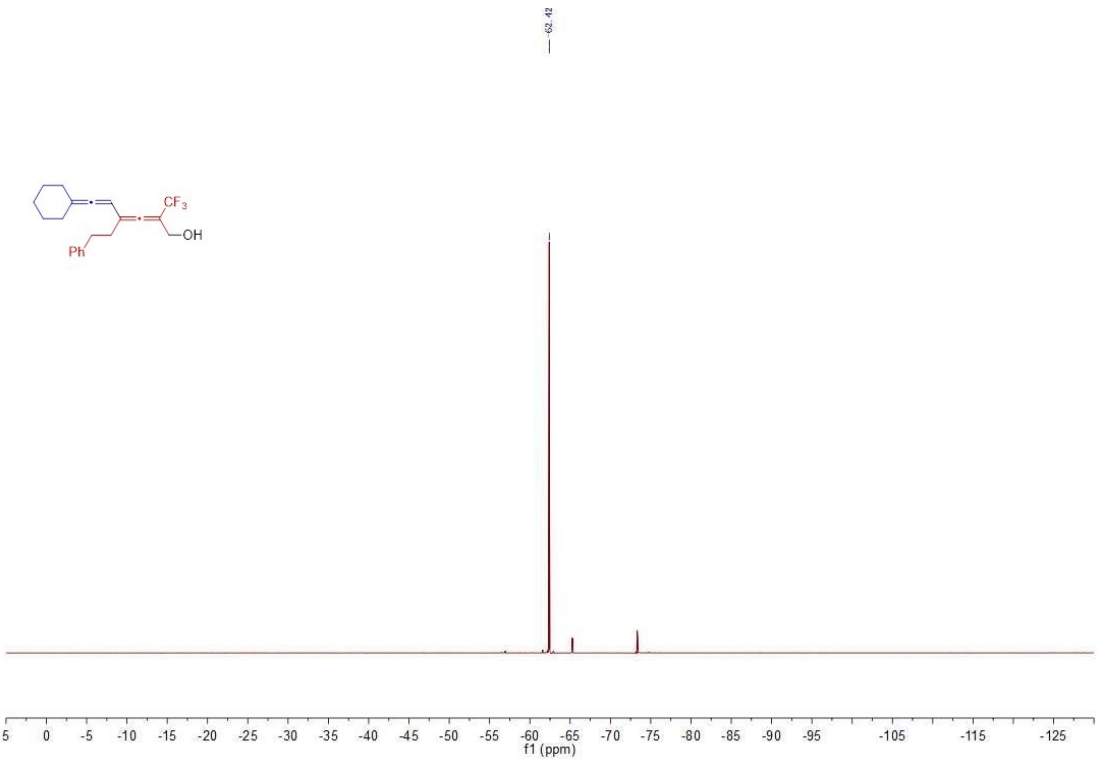
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0 (q, *J* = 4.2 Hz), 200.5, 141.2, 128.5, 128.4, 126.3, 123.0 (q, *J* = 274.7 Hz), 110.9, 107.3, 100.7 (q, *J* = 33.0 Hz), 87.9, 83.8, 58.9, 33.5, 31.3, 31.2, 27.3, 25.9, 24.9, 24.6.

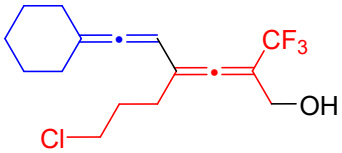
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.42.

HRMS (ESI) calculated for $C_{21}H_{24}F_3O^+$ $[M+H]^+$ 349.1774; found 349.1771.









7-chloro-4-(2-cyclohexylidenevinyl)-2-(trifluoromethyl)hepta-2,3-dien-1-ol (3sa)

After isolated and purified procedure, this compound was obtained 21.1 mg (66% yield)

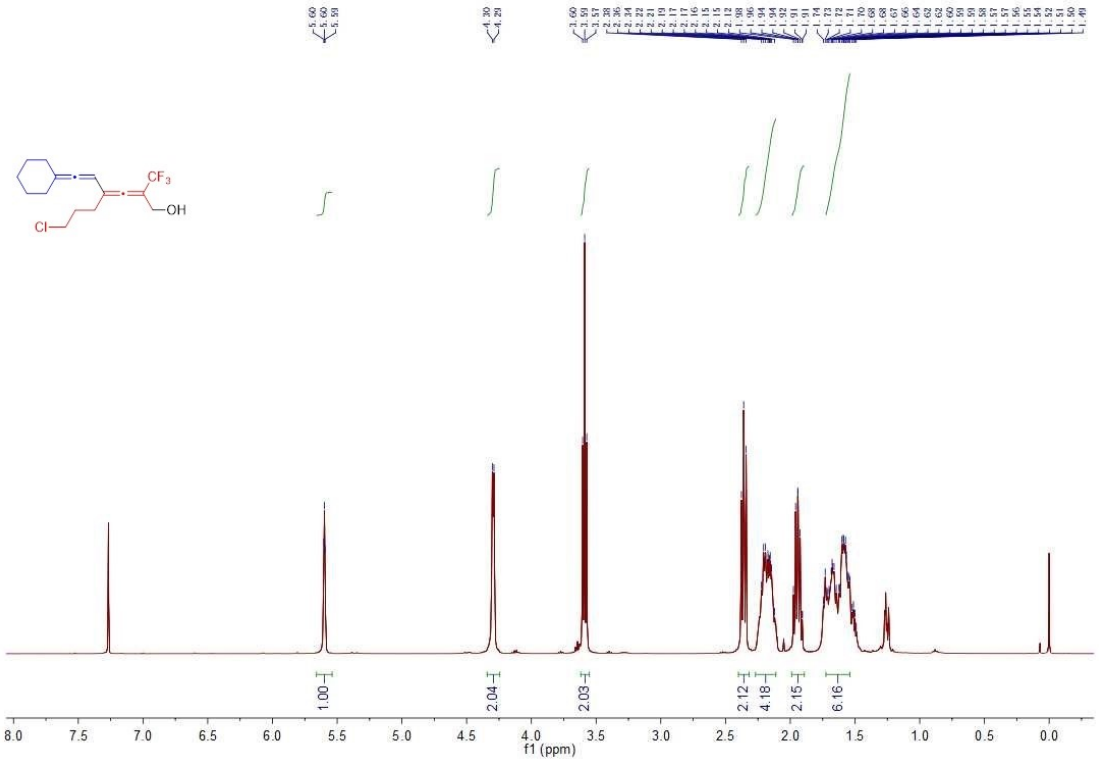
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

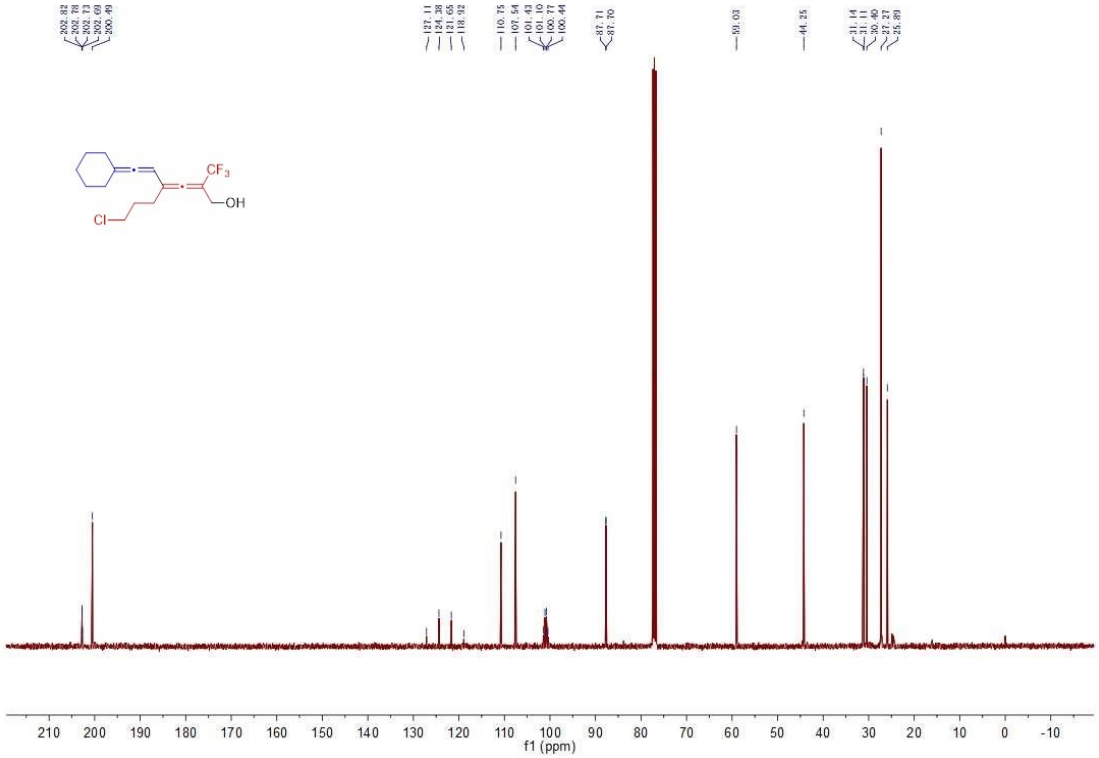
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77-5.35 (m, 1H), 4.30 (d, *J* = 5.1 Hz, 2H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.42-2.31 (m, 2H), 2.26-2.11 (m, 4H), 2.02-1.85 (m, 2H), 1.76-1.10 (m, 6H).

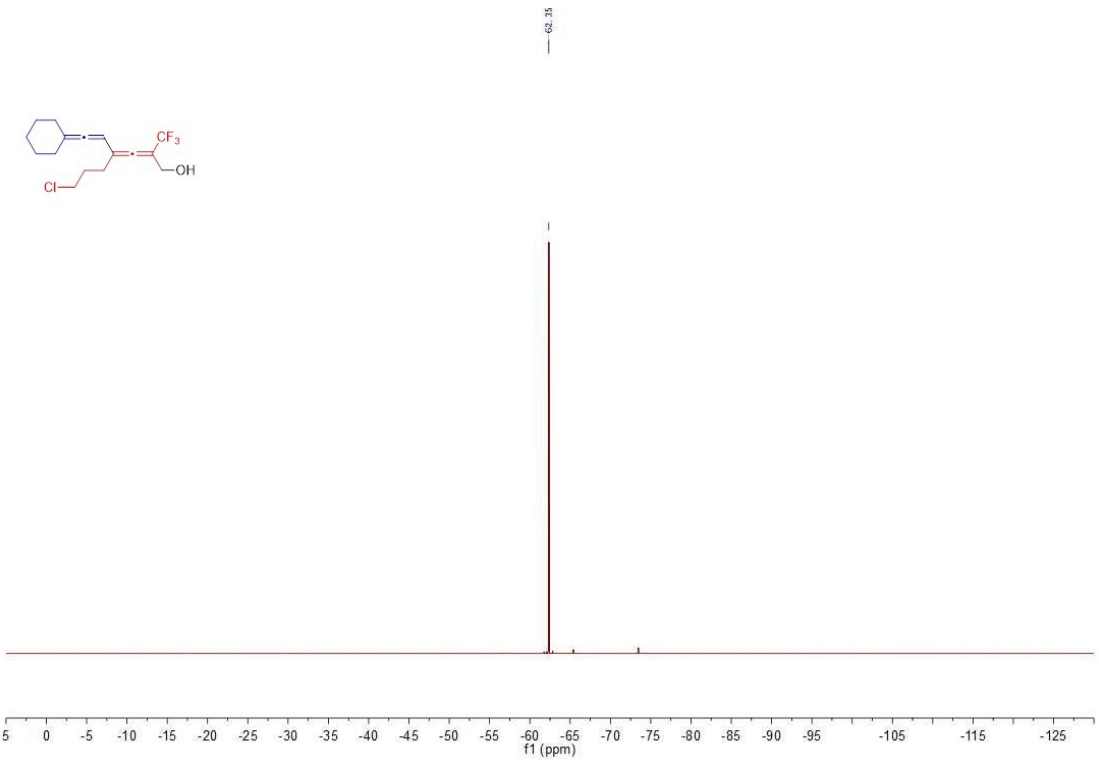
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8 (q, *J* = 4.1 Hz), 200.5, 123.0 (q, *J* = 274.7 Hz), 110.8, 107.5, 100.9 (q, *J* = 33.1 Hz), 87.7, 87.7, 59.0, 44.3, 31.1, 31.1, 30.4, 27.3, 25.9.

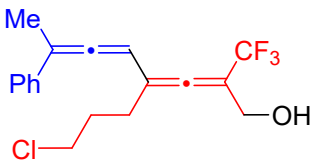
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35.

HRMS (ESI) calculated for $C_{16}H_{21}ClF_3O^+$ $[M+H]^+$ 321.1228; found 321.1221.









4-(3-chloropropyl)-7-phenyl-2-(trifluoromethyl)octa-2,3,5,6-tetraen-1-ol (3sd)

After isolated and purified procedure, this compound was obtained 18.1 mg (53% yield)

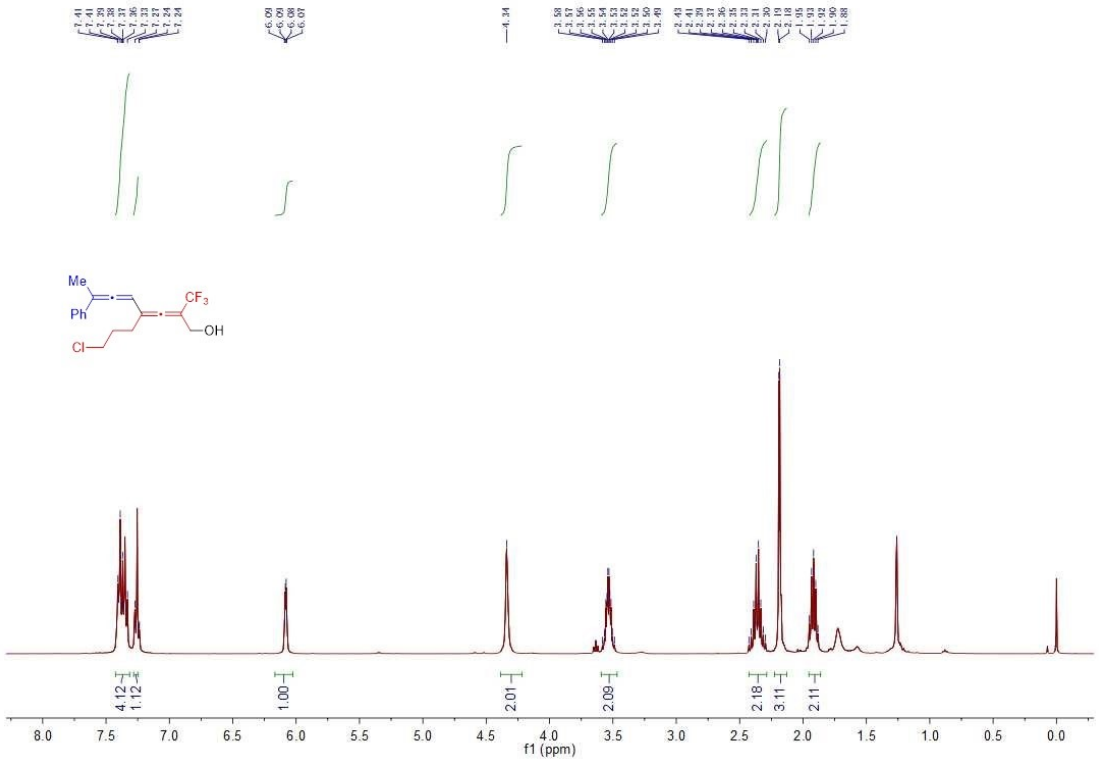
as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.32 (m, 4H), 7.29-7.20 (m, 1H), 6.12-6.03 (m, 1H), 4.34 (s, 2H), 3.59-3.48 (m, 2H), 2.45-2.27 (m, 2H), 2.19 (d, J = 2.9 Hz, 3H), 1.96-1.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 203.2 (dq, J = 8.1, 4.1 Hz), 135.6, 128.6, 127.5, 125.9, 123.0 (q, J = 274.8 Hz), 110.0, 105.8, 101.5 (q, J = 33.2 Hz), 92.2, 59.0, 43.9, 30.3, 27.2, 16.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.30, -62.32.

HRMS (ESI) calculated for $C_{18}H_{19}ClF_3O^+$ $[M+H]^+$ 343.1071; found 343.1075.


Me
Ph
CF3
OH
Cl
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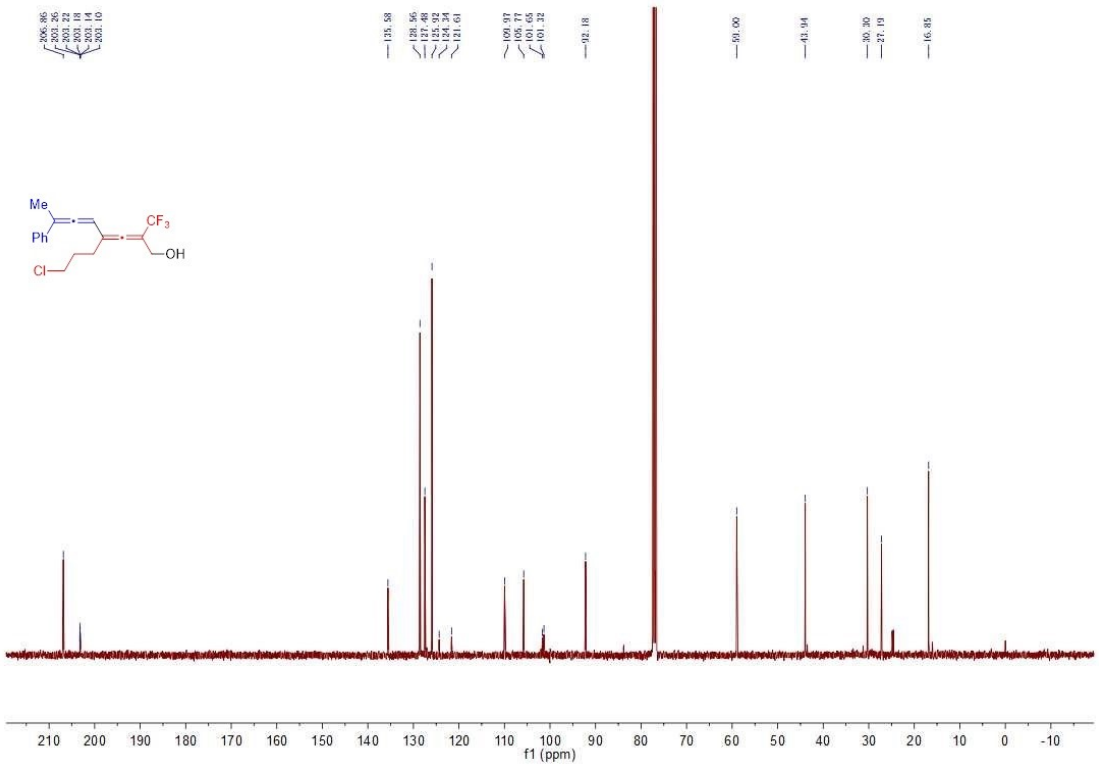
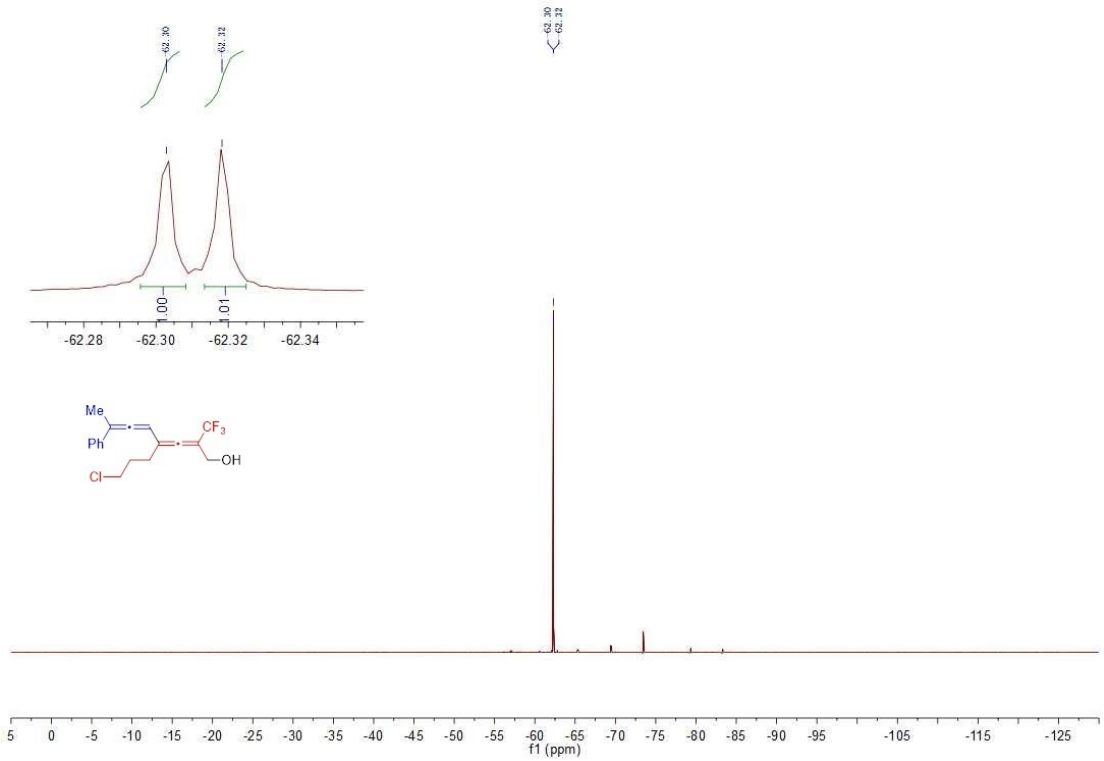
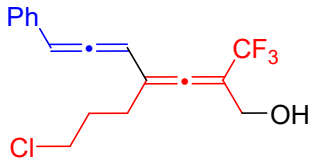
1.12
1.00
2.01
2.09
2.18
3.11
2.11
f1 (ppm)


Me
Ph
CF3
OH
Cl
f1 (ppm)





4-(3-chloropropyl)-7-phenyl-2-(trifluoromethyl)hepta-2,3,5,6-tetraen-1-ol (3se)

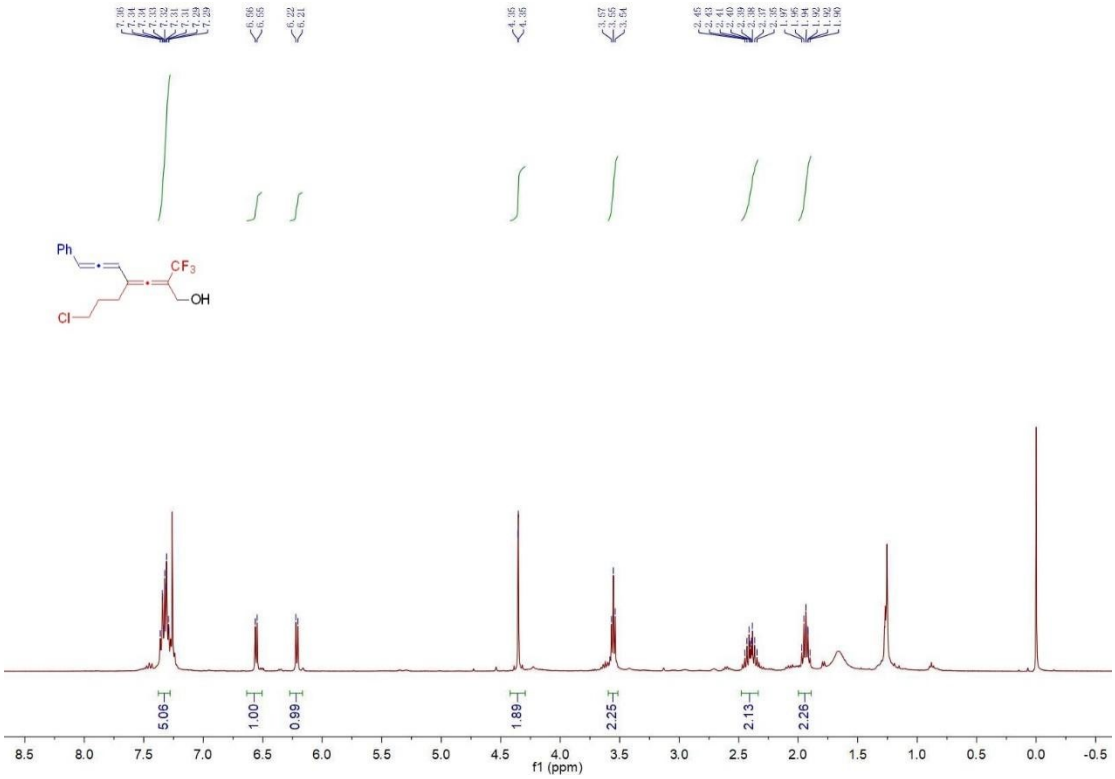
After isolated and purified procedure, this compound was obtained 14.4 mg (44% yield) as colorless oil. (Petroleum ether : EtOAc = 5 : 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-6.82 (m, 5H), 6.56 (d, J = 6.4 Hz, 1H), 6.21 (d, J = 6.5 Hz, 1H), 4.35 (d, J = 1.1 Hz, 2H), 3.55 (t, J = 6.3 Hz, 2H), 2.48-2.29 (m, 2H), 2.03 -1.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 203.2 (q, J = 4.2 Hz), 132.8, 128.9, 127.8, 127.1, 122.9 (q, J = 274.8 Hz), 109.2, 101.7 (q, J = 33.4 Hz), 99.3, 94.3, 58.9, 43.9, 30.1, 27.01.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.29, -62.36.

HRMS (ESI) calculated for $C_{17}H_{17}ClF_3O^+$ $[M+H]^+$ 329.0915; found 329.0920.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Cl
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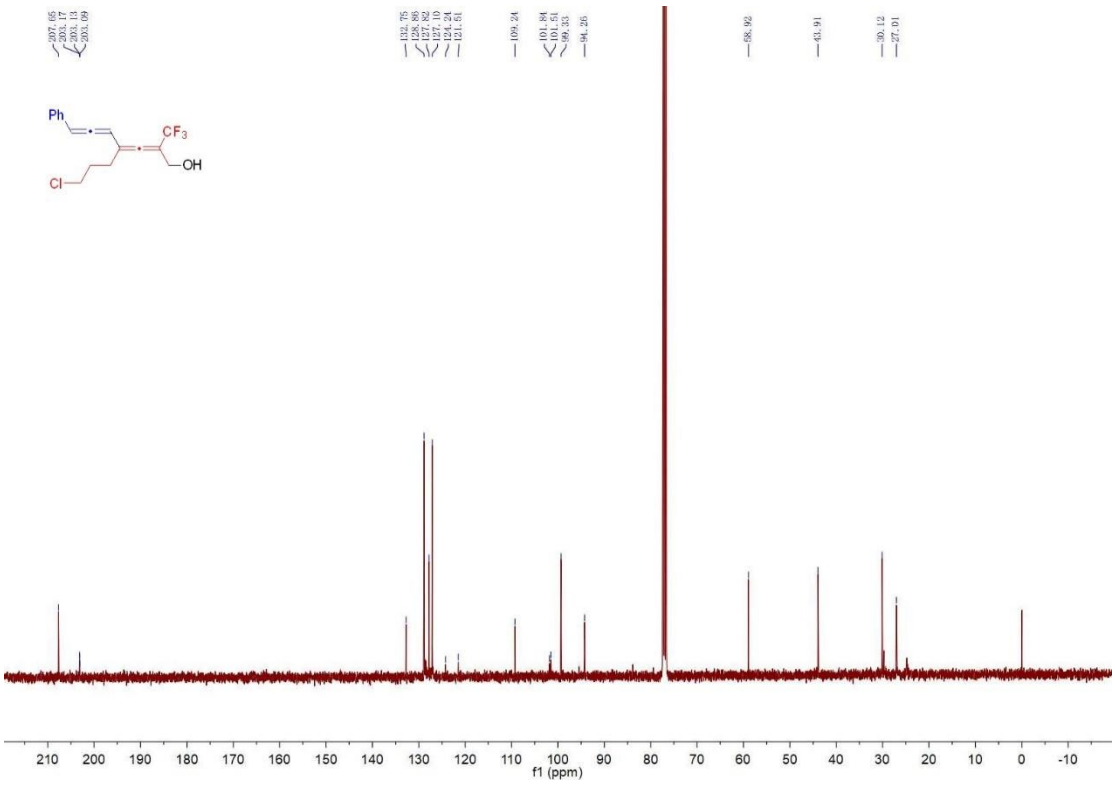
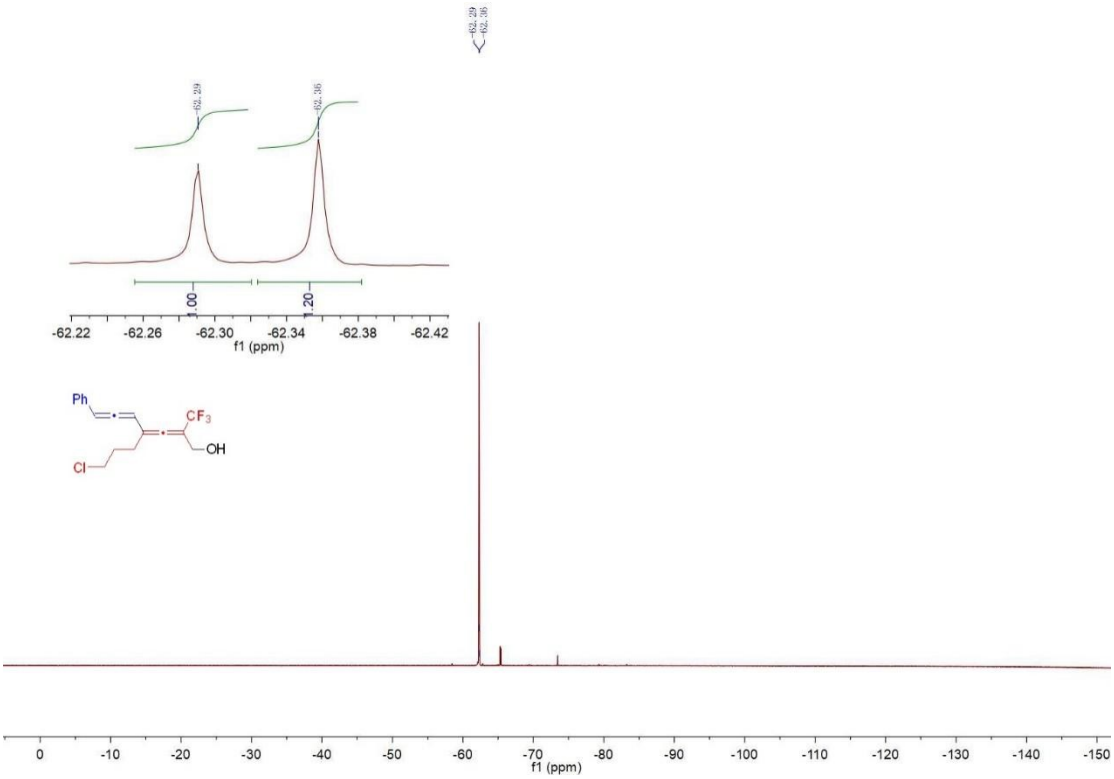
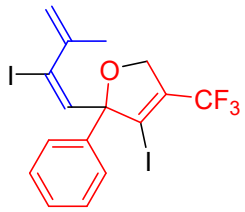
0.99
1.89
2.25
2.13
2.26
f1 (ppm)


Ph
CF3
OH
Cl
f1 (ppm)





(*E*)-3-iodo-2-(2-iodo-3-methylbuta-1,3-dien-1-yl)-2-phenyl-4-(trifluoromethyl)-2,5-dihydrofuran (4a)

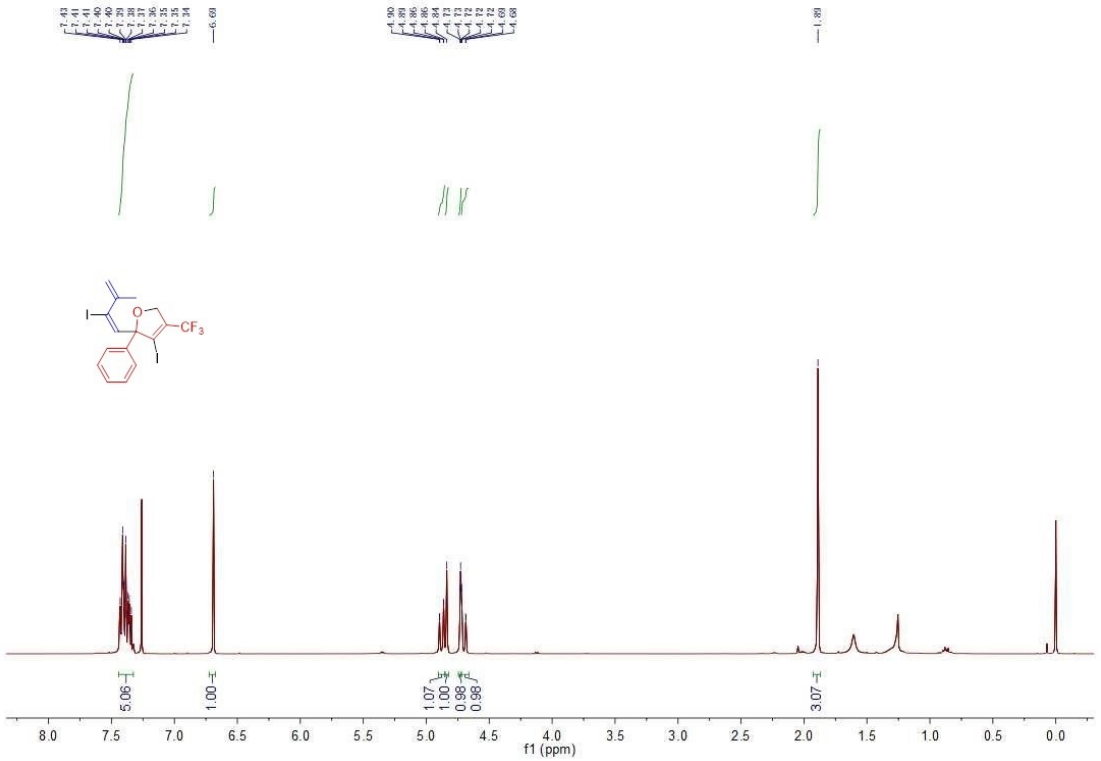
After isolated and purified procedure, this compound was obtained 32.4 mg (61% yield) as colorless oil. (Petroleum ether : EtOAc = 50 : 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H), 6.69 (s, 1H), 4.88 (dd, J = 13.0, 1.2 Hz, 1H), 4.84 (s, 1H), 4.73-4.72 (m, 1H), 4.70 (dd, J = 13.1, 1.2 Hz, 1H), 1.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 141.0, 138.6, 133.7 (q, J = 34.8 Hz), 128.5, 126.6, 120.5 (q, J = 271.3 Hz), 113.3, 107.2, 103.1 (q, J = 4.4 Hz), 98.5, 74.6, 74.6, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.05.

HRMS (ESI) calculated for $C_{16}H_{14}F_3I_2O^+$ $[M+H]^+$ 532.9081; found 532.9088.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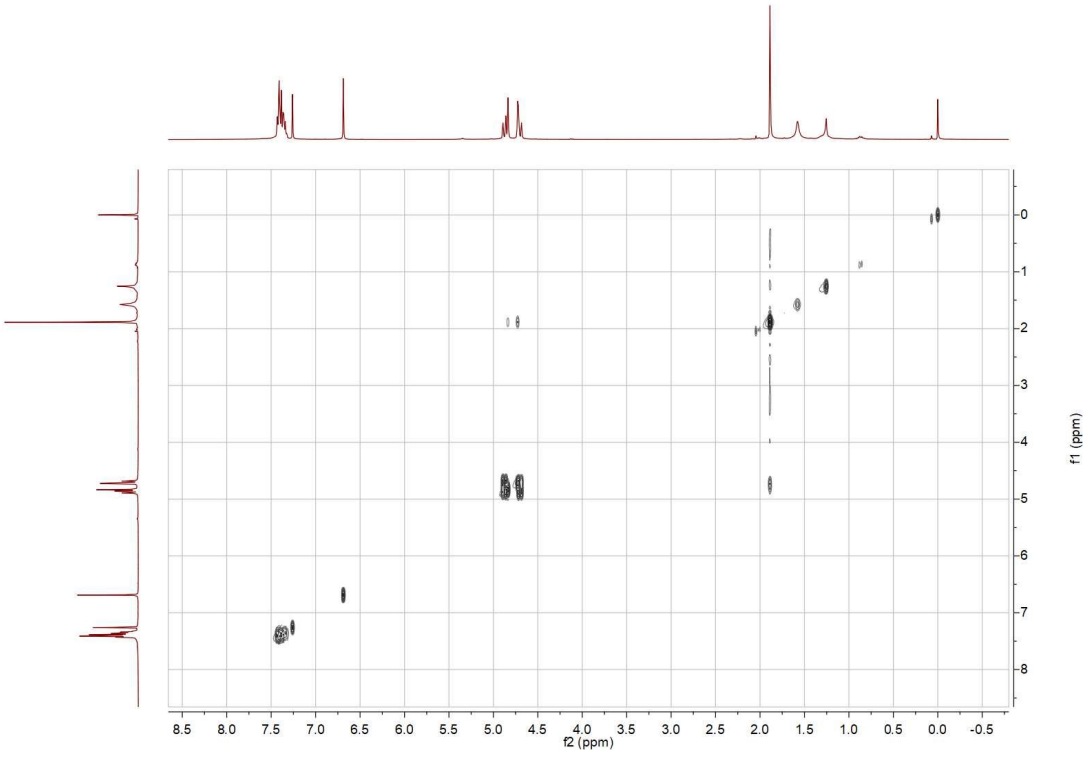
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.34
6.69
4.90
4.89
4.86
4.85
4.84
4.73
4.73
4.72
4.72
4.69
4.68
1.89
I
O
CF3
I
5.06
1.00
1.07
1.00
0.98
0.99
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


0
1
2
3
4
5
6
7
8
f1 (ppm)
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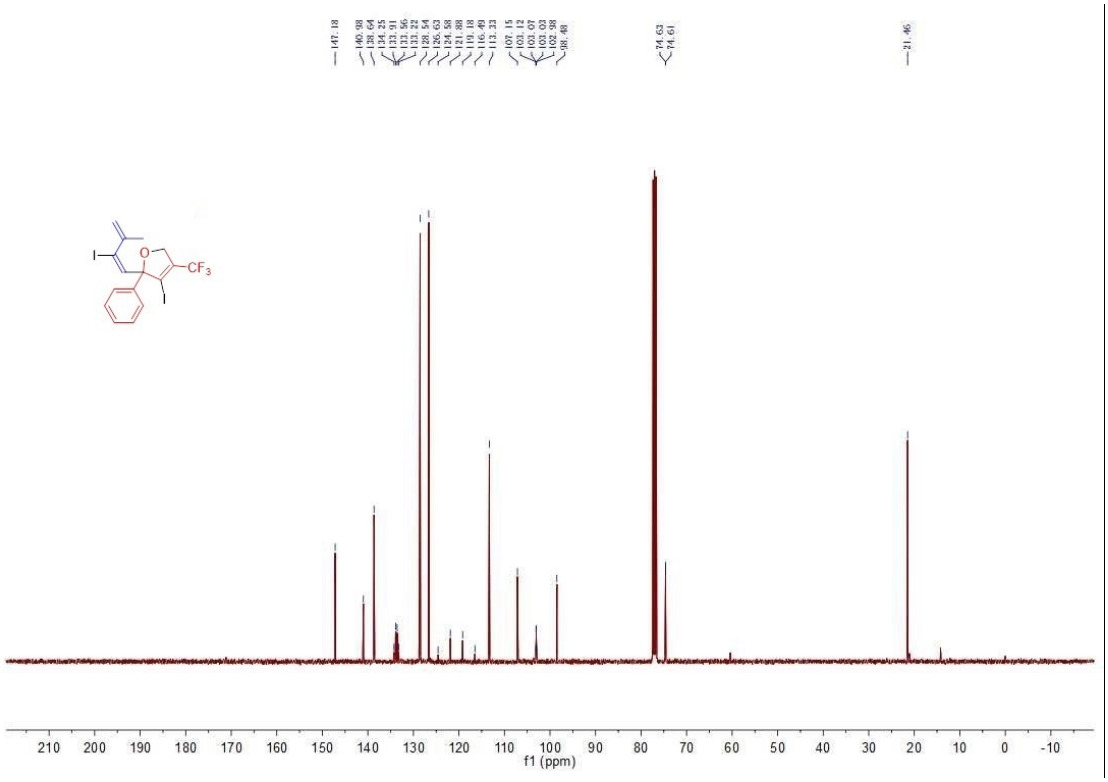
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)


147.18
140.98
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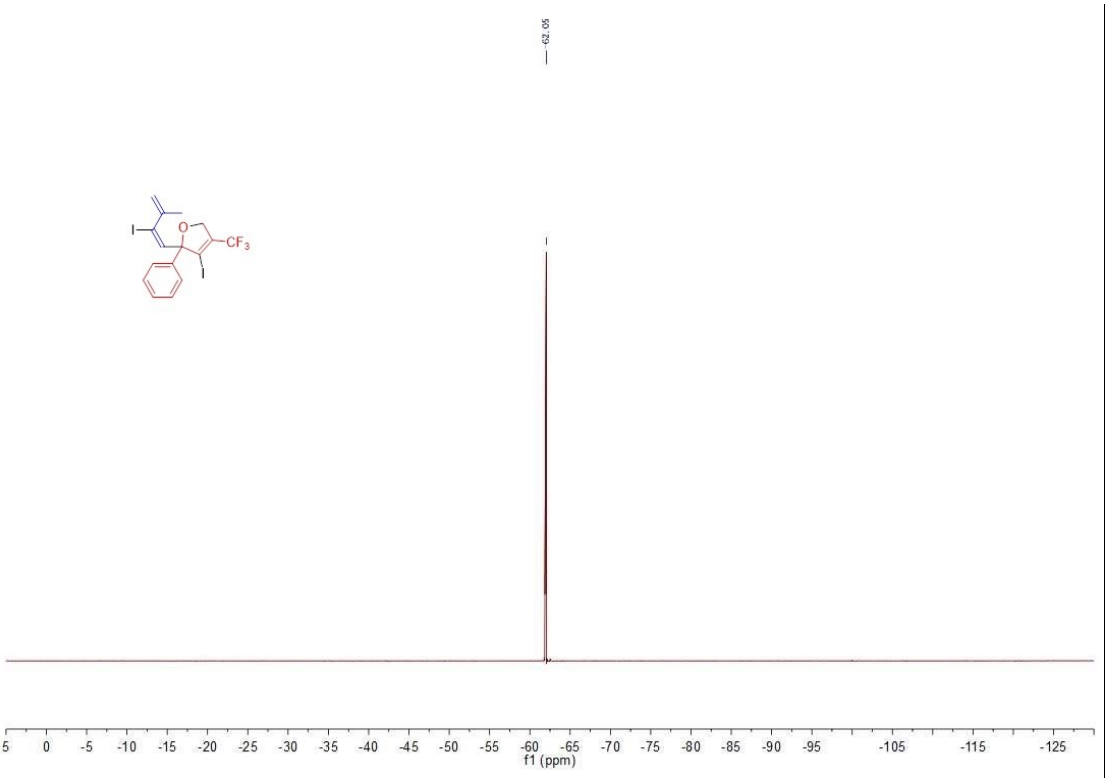
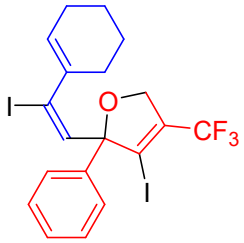
133.56
133.22
128.54
126.63
124.58
121.98
119.18
116.40
113.33
107.15
103.12
103.07
103.03
102.98
98.48
74.63
74.61
21.46
O
I
CF3
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.05
O
I
CF3
I
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)



(*E*)-2-(2-(cyclohex-1-en-1-yl)-2-iodovinyl)-3-iodo-2-phenyl-4-(trifluoromethyl)-2,5-dihydrofuran (4b)

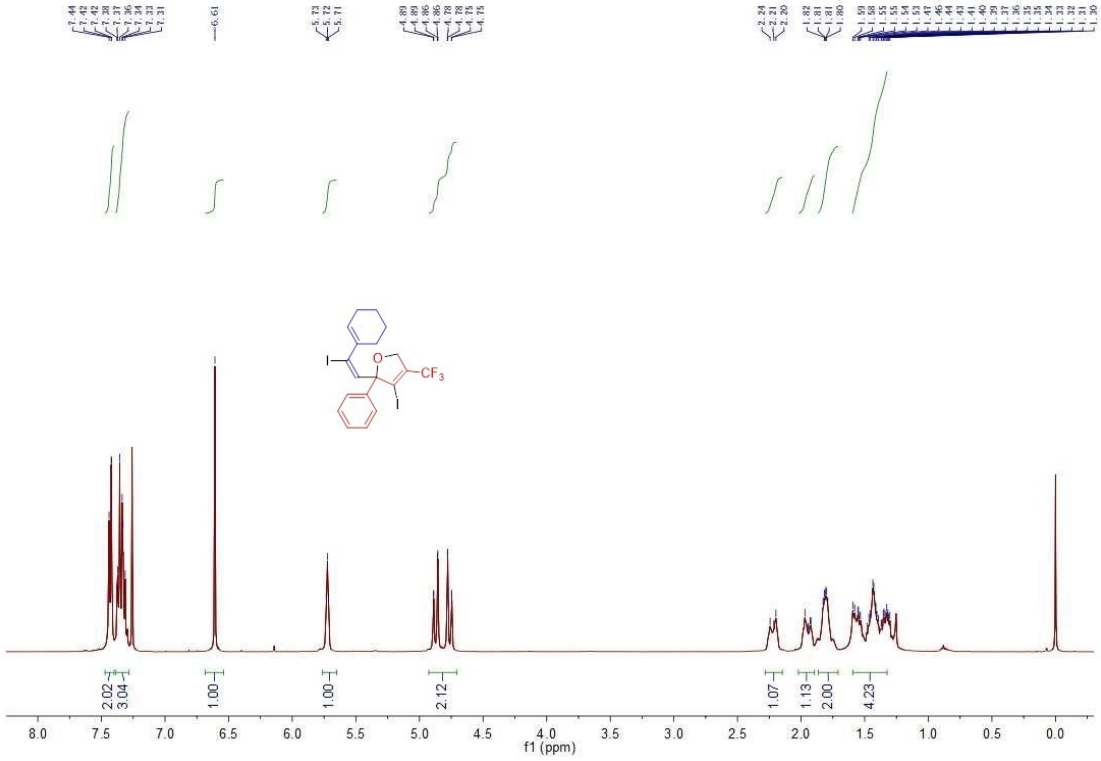
After isolated and purified procedure, this compound was obtained 37.7 mg (66% yield) as colorless oil. (Petroleum ether : EtOAc = 50 : 1)

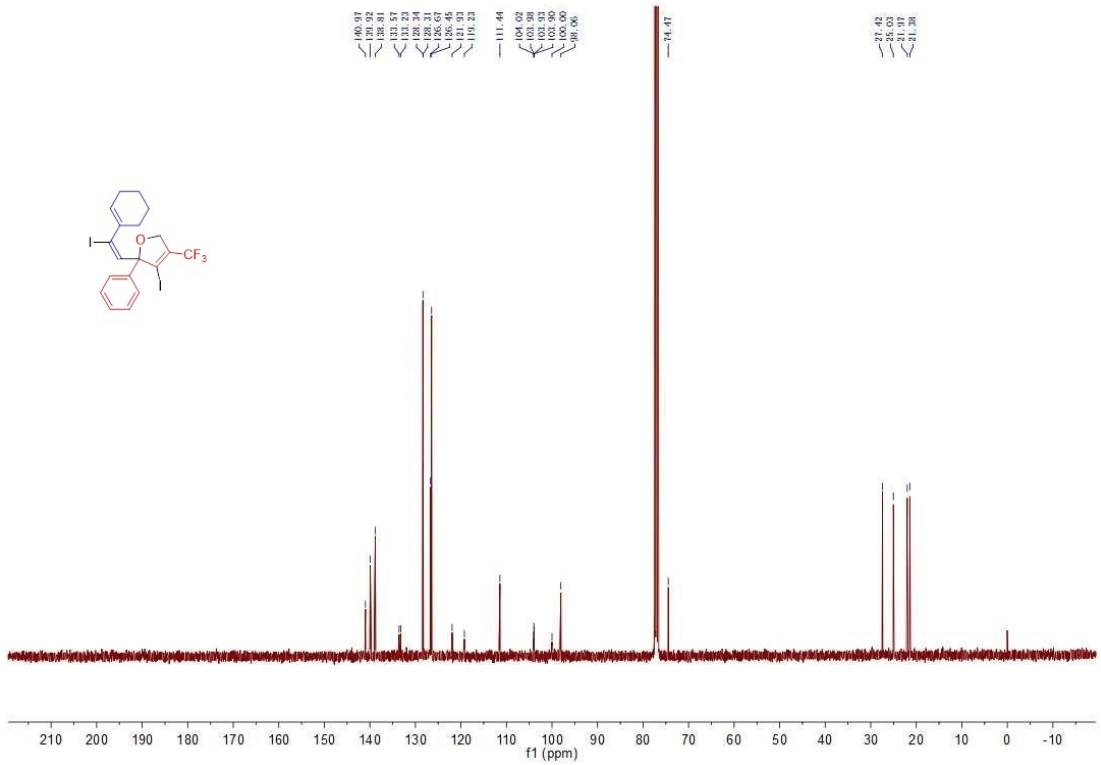
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.40 (m, 2H), 7.38-7.30 (m, 3H), 6.61 (s, 1H), 5.72 (t, *J* = 3.7 Hz, 1H), 4.82 (ddd, *J* = 44.0, 12.9, 1.0 Hz, 2H), 2.31-2.15 (m, 1H), 1.99-1.91 (m, 1H), 1.87-1.75 (m, 2H), 1.59-1.14 (m, 4H).

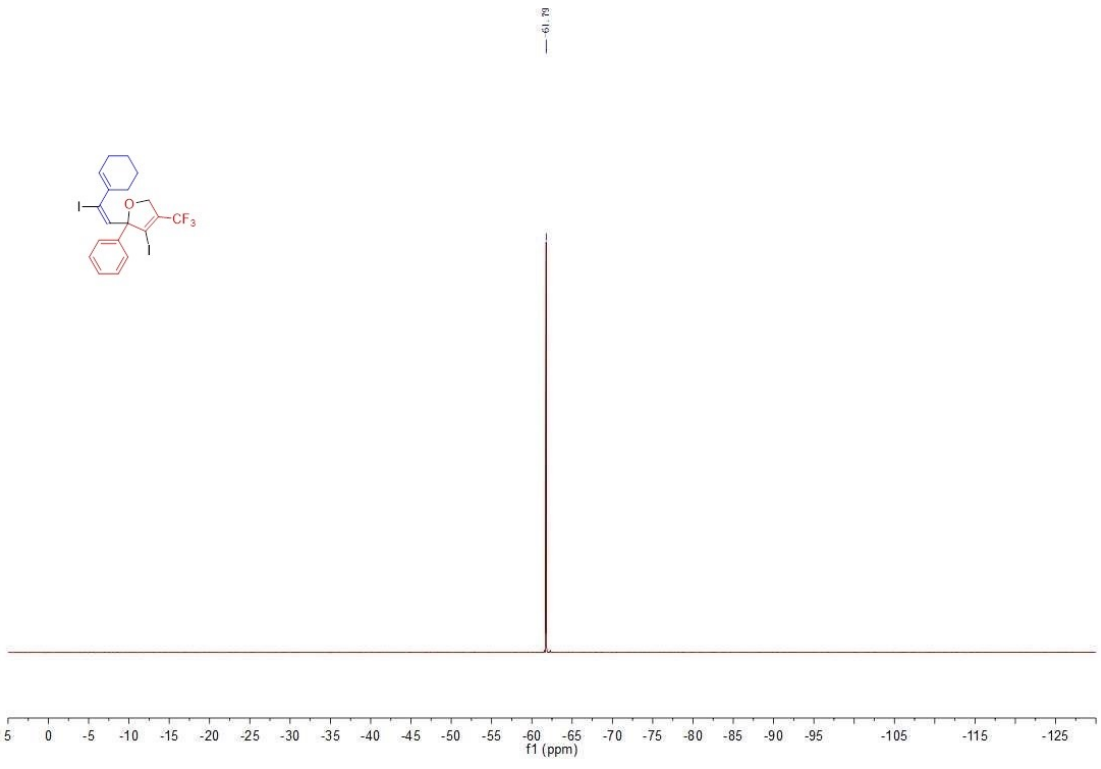
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.9, 138.8, 133.4 (q, *J* = 34.7 Hz), 128.3, 128.3, 126.7, 126.5, 120.6 (q, *J* = 271.3 Hz), 111.4, 104.0 (q, *J* = 4.3 Hz), 100.0, 98.1, 74.5, 27.4, 25.0, 22.0, 21.4.

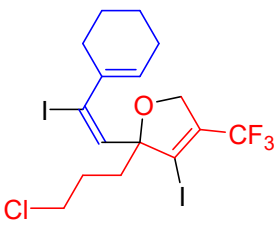
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.79.

HRMS (ESI) calculated for $C_{19}H_{18}F_3I_2O^+$ $[M+H]^+$ 572.9394; found 572.9391.




140.97
139.92
138.81
133.57
133.23
128.34
128.21
125.67
125.45
121.93
119.23
111.44
104.02
103.98
103.33
102.90
100.00
98.06
74.47
27.42
25.03
21.97
21.38
I
O
CF3
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-61.79
I
O
CF3
I
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)


I
O
CF3
I
Cl

(*E*)-2-(3-chloropropyl)-2-(2-(cyclohex-1-en-1-yl)-2-iodovinyl)-3-iodo-4-(trifluoromethyl)-2,5-dihydrofuran (4c)

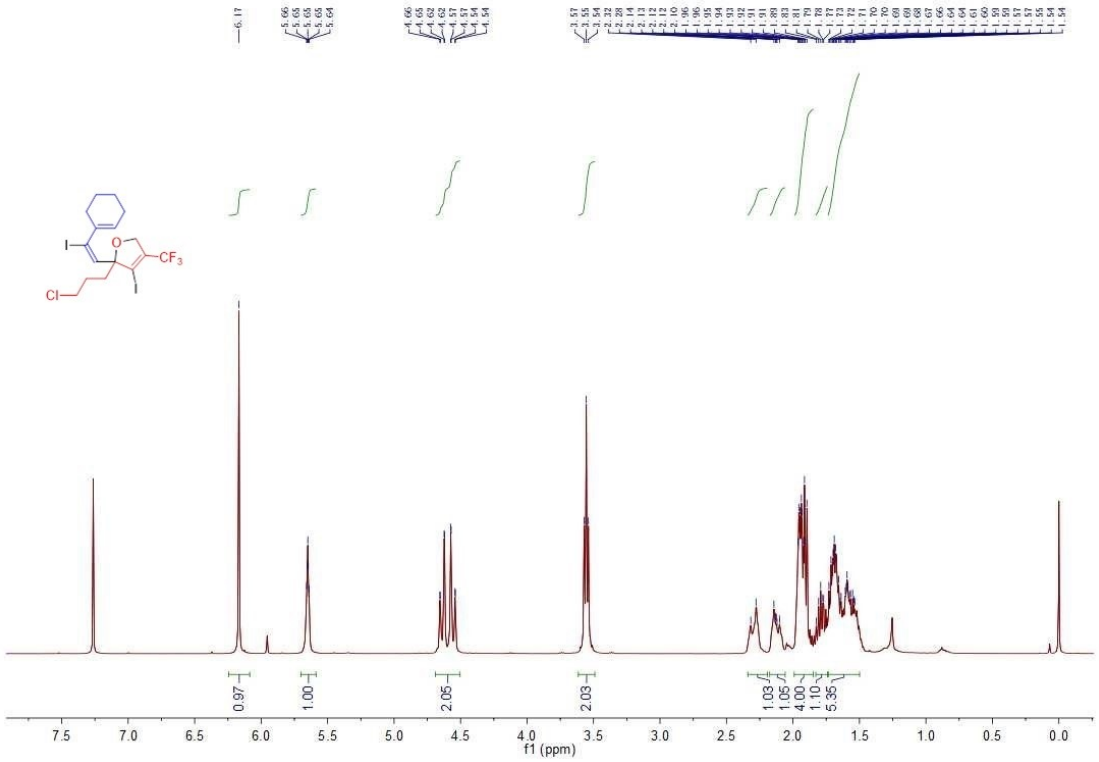
After isolated and purified procedure, this compound was obtained 33.1 mg (58% yield) as colorless oil. (Petroleum ether : EtOAc = 50 : 1)

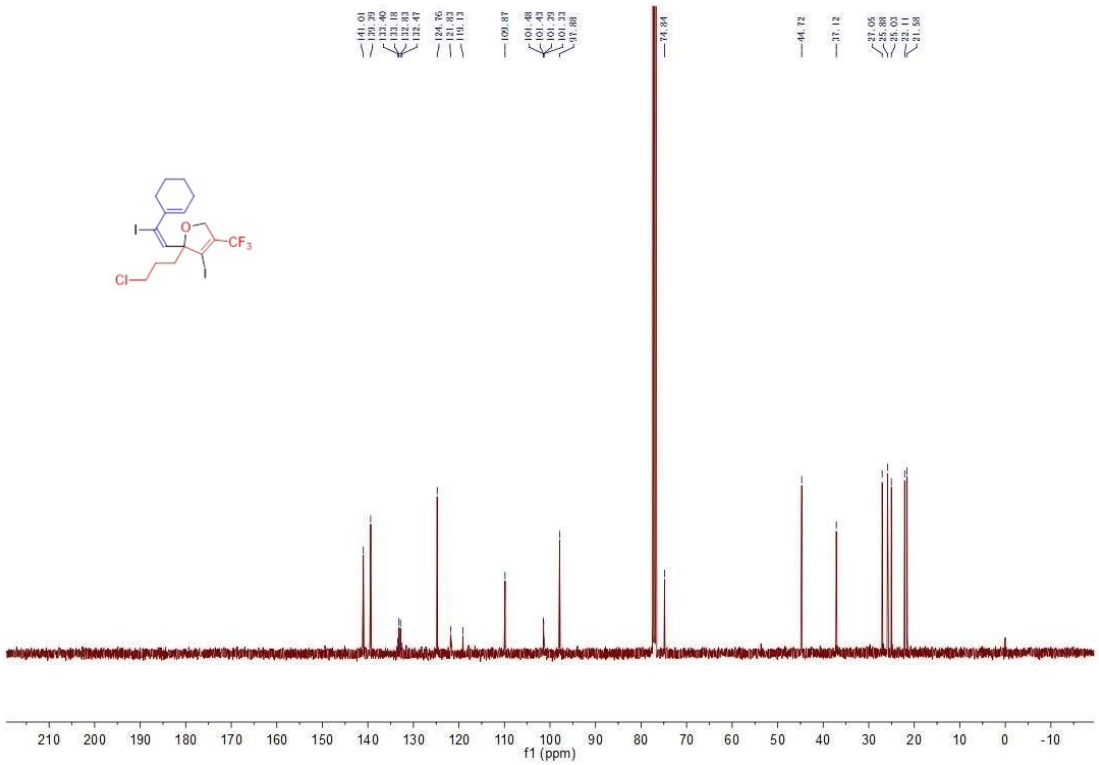
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 5.80-5.33 (m, 1H), 4.60 (ddd, *J* = 33.0, 12.8, 1.2 Hz, 2H), 3.55 (t, *J* = 6.2 Hz, 2H), 2.40-2.25 (m, 1H), 2.18-2.04 (m, 1H), 1.99-1.85 (m, 4H), 1.83-1.76 (m, 1H), 1.80-1.46 (m, 5H).

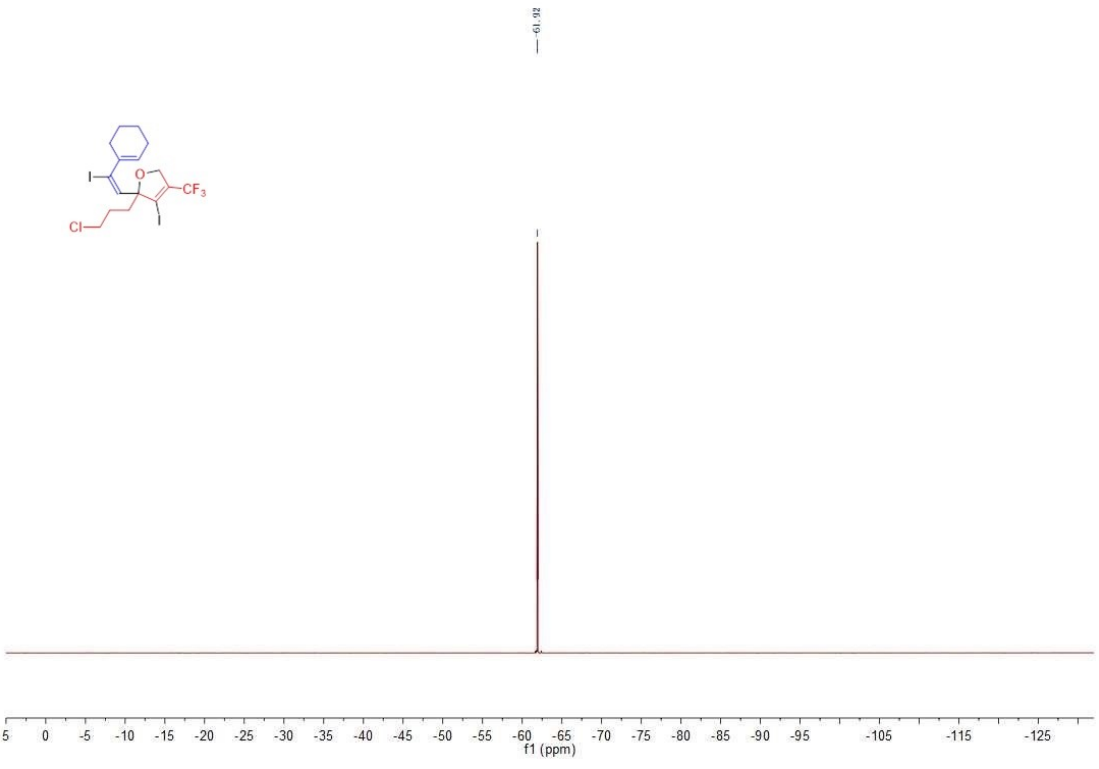
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.4, 133.0 (q, *J* = 34.7 Hz), 124.8, 120.5 (q, *J* = 271.3 Hz), 109.9, 101.4 (q, *J* = 4.6 Hz), 97.9, 74.8, 44.7, 37.1, 27.1, 25.9, 25.0, 22.1, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.92.

HRMS (ESI) calculated for $C_{16}H_{19}ClF_3I_2O^+$ $[M+H]^+$ 572.9160; found 572.9166.




141.91
139.78
133.40
133.18
132.93
132.47
124.76
121.83
119.13
109.87
101.48
101.43
101.39
101.33
97.88
74.84
44.72
37.12
27.05
25.88
25.03
22.11
21.58
I
O
CF3
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-61.92
I
O
CF3
Cl
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)

References

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