Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-Catalyzed Endo-type trifluoromethylarylation of Alkynes

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I. General Information

1. Materials:

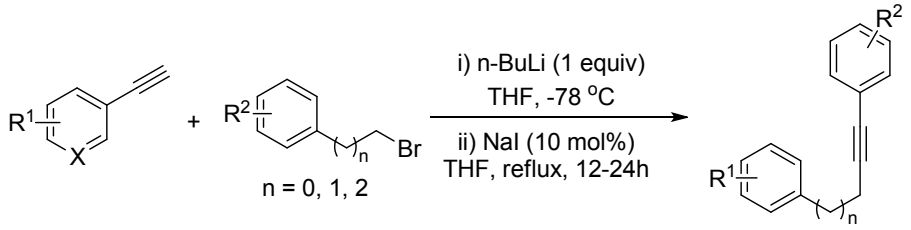
All reagents were used as received from commercial sources unless specified otherwise, or prepared as described in the literature. DMF was purchased from ACROS, and used without further purification. **Cu powder (-100 mash, 99.999% metal base)** was purchased from Alfa Aesar. Trifluoromethyl electrophilic reagents **2a**, **2b** was purchased from Aldrich. All other reagents were purchased from commercial sources without further purification.

2. Analytical Methods:

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts of ^{19}F NMR spectra ($CFCl_3$ as outside standard and low field is positive) were recorded with ^{1}H-coupling on a Bruker 376 MHz spectrometer. ^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Brucker 100 MHz spectrometer. Chemical shifts (δ) are reported in ppm and referenced to residual solvent peaks. Coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI mode unless otherwise stated. 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). Sartorius CPA225D (Repeatability $\leqslant \pm 0.05$ mg) was used to weight the catalysts and reagents.

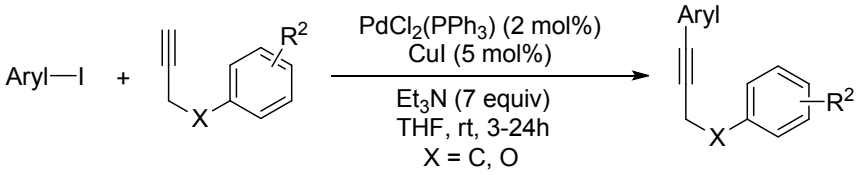
II. Preparation of Substrates

1.General Procedure A for the Synthesis of Alkynes (1) [1]



A solution of alkyne (1.0 equiv.) in tetrahydrofuran (0.25 M) was cooled to -78 °C and a solution of *n*-butyllithium (1.0 equiv., 1.6 M in hexanes) was added. The reaction mixture was allowed to warm to room temperature. Sodium iodide (0.1 equiv.) and the corresponding bromoethylbenzene (1.2 equiv.) were added. The mixture was heated to reflux for the specified length of time. The reaction mixture was cooled to room temperature and quenched by addition of ammonium chloride solution. The aqueous layer was separated and extracted with diethyl ether. The combined organics were washed (brine), dried ($MgSO_4$) and the solvent removed in vacuo. The crude residue was purified by flash chromatography to yield the corresponding alkyne (**1**).

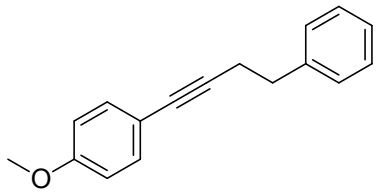
2.General Procedure B for the Synthesis of Alkynes (1) [1]



To a suspension of *trans*-dichloro-*bis*-(triphenylphosphine)palladium(II) (1-5 mol%) and copper(I) iodine (2-10 mol%) in tetrahydrofuran (0.2 M) was added the appropriate iodoarene (1.0 equiv.) and triethylamine (7.0 equiv.). The corresponding alkyne (1.1 equiv.) was added and the reaction mixture stirred at room temperature for the specified length of time. The reaction mixture was concentrated in vacuo and filtered through a plug of celite and silica, eluting with diethyl ether. The solvent was removed in vacuo and the crude residue was purified by flash chromatography to yield the corresponding alkyne (**1**).

3. Substrates Spectra data

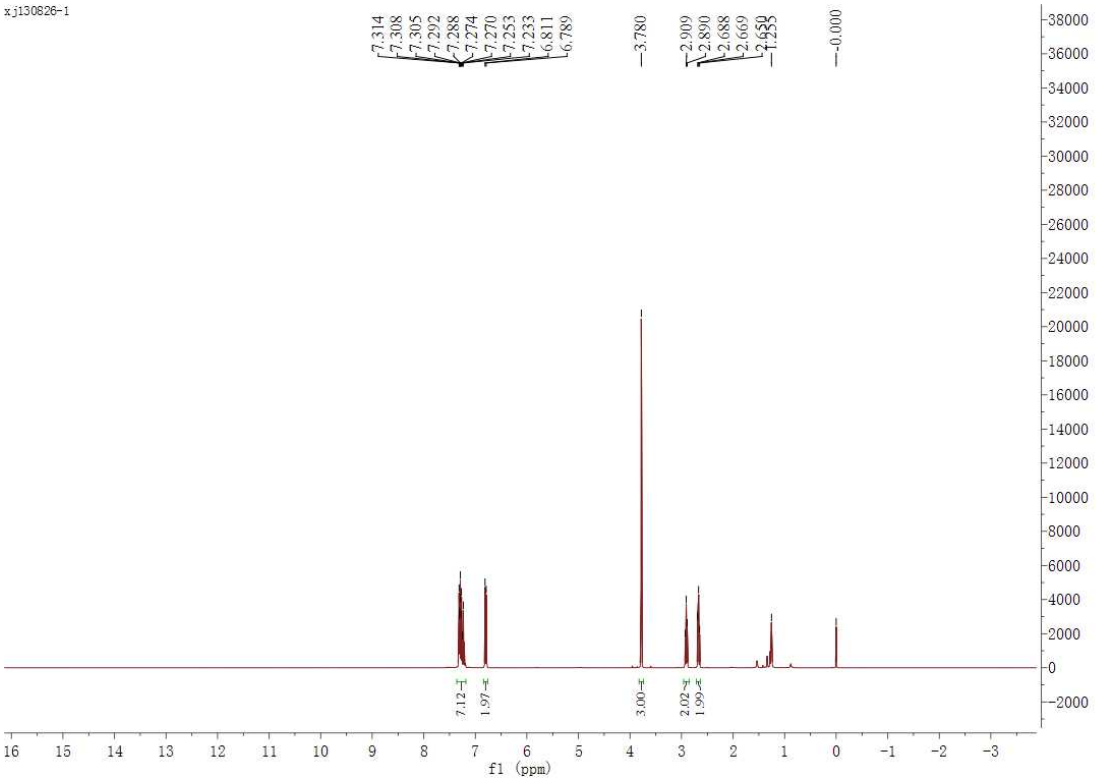
1-methoxy-4-(4-phenylbut-1-yn-1-yl)benzene **(1a)**

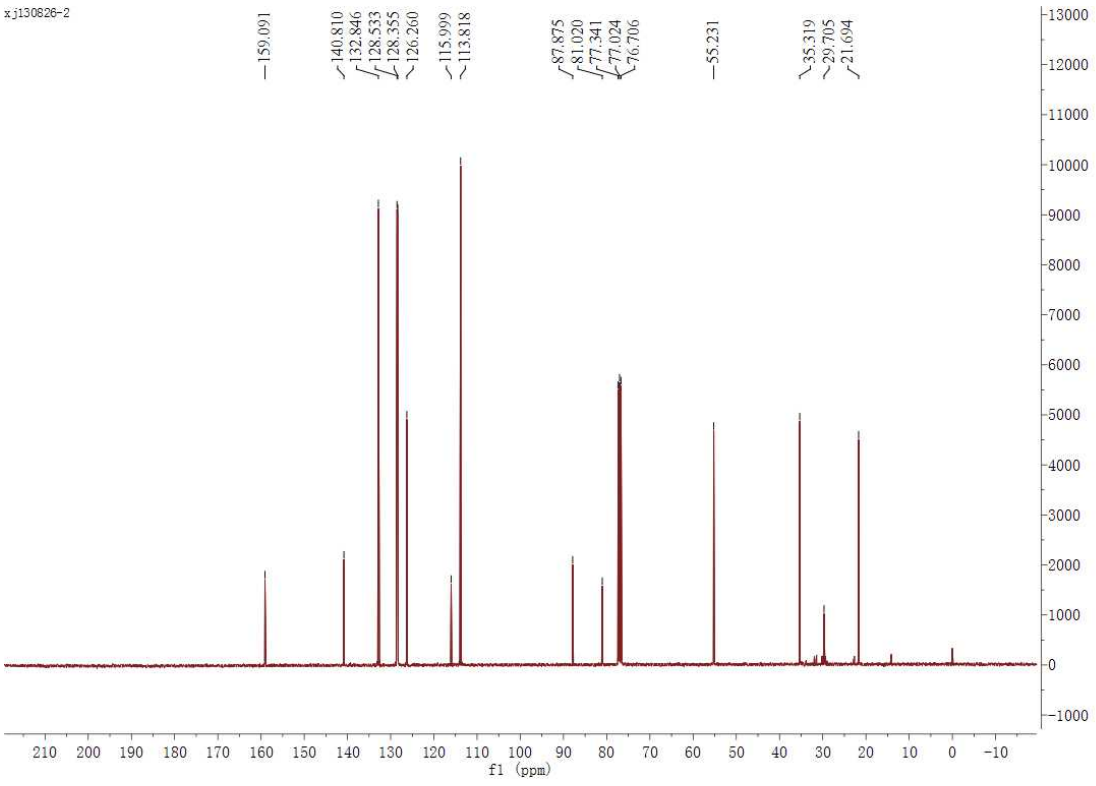


Prepared according to General Procedure **A.**

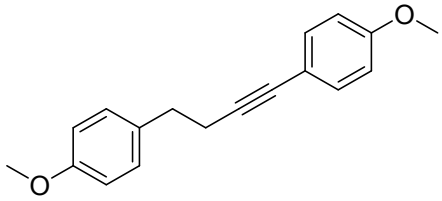
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 7H), 6.80 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.09, 140.81, 132.85, 128.533, 128.355, 126.26, 116.00, 113.82, 87.87, 81.02, 55.23, 35.32, 21.69.





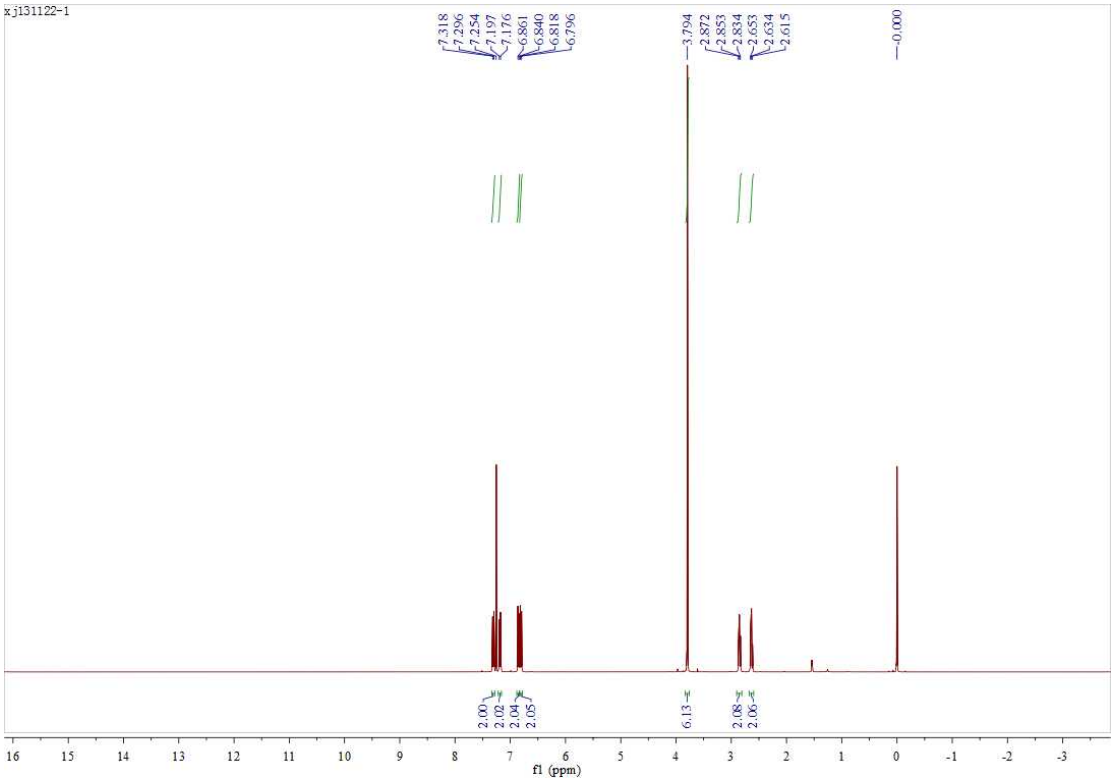
4,4'-(but-1-yne-1,4-diyl)bis(methoxybenzene) **(1b)**

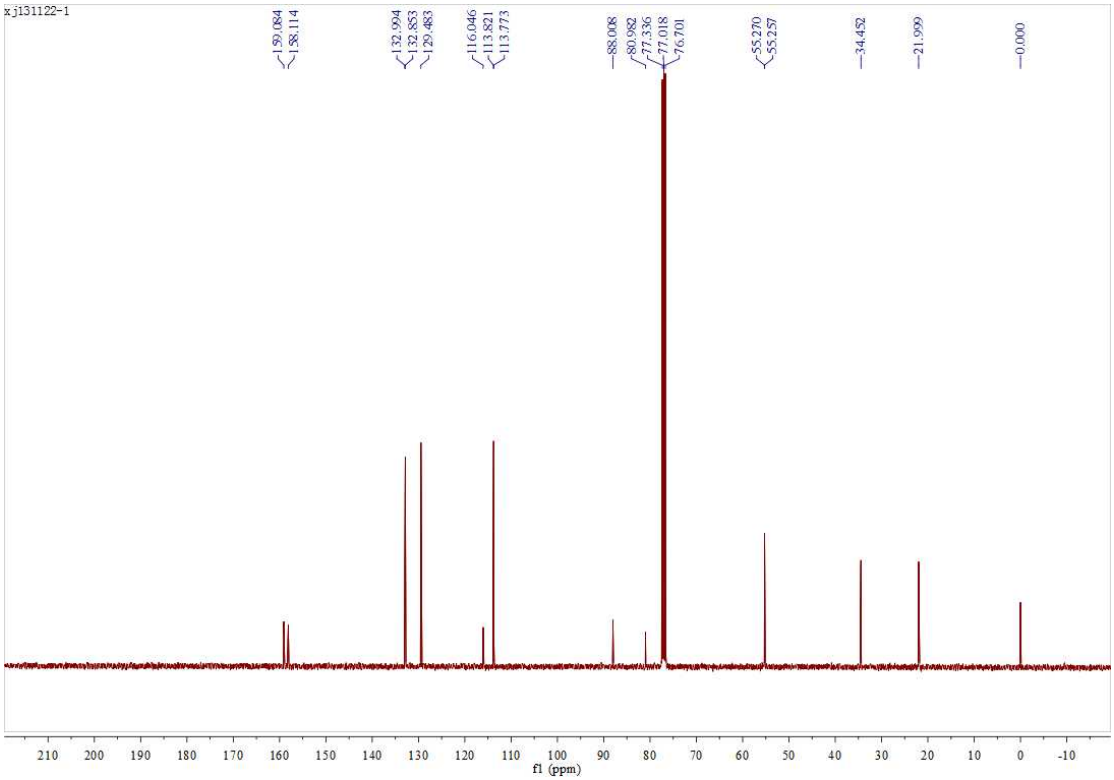


Prepared according to General Procedure **A.**

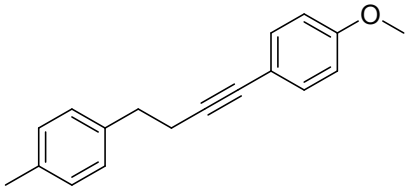
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 6H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.08, 158.11, 132.99, 132.85, 129.48, 116.05, 113.82, 113.77, 88.01, 80.98, 55.27, 55.25, 34.45, 22.00.





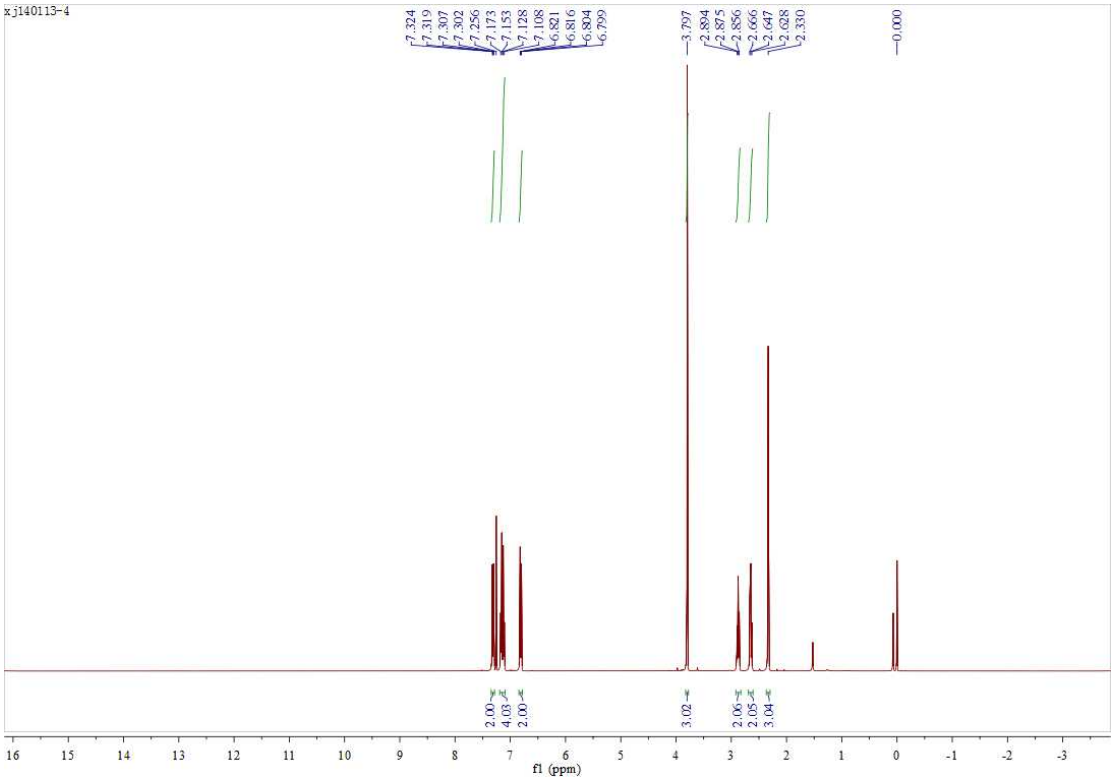
1-methoxy-4-(4-(p-tolyl)but-1-yn-1-yl)benzene **(1c)**

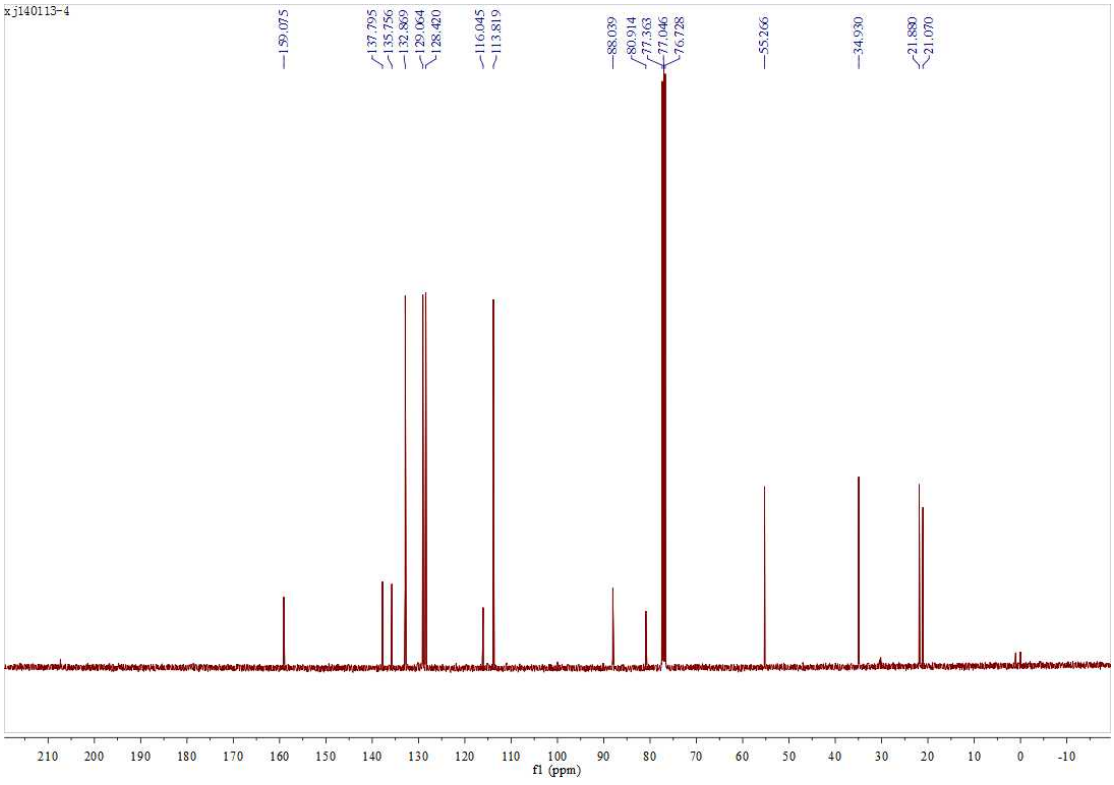


Prepared according to General Procedure **A.**

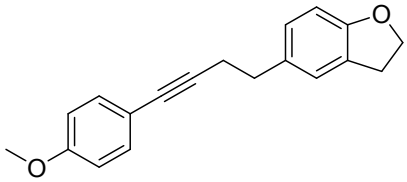
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (d, *J* = 8.8 Hz, 2H), 7.14 (dd, *J* = 18.1, 8.0 Hz, 4H), 6.84 – 6.78 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.08, 137.80, 135.76, 132.87, 129.06, 128.42, 116.04, 113.82, 88.04, 80.91, 55.27, 34.93, 21.88, 21.07.


xj140113-4
7.324
7.319
7.307
7.302
7.256
7.173
7.153
7.128
7.108
6.821
6.816
6.804
6.799
3.797
2.894
2.875
2.856
2.666
2.647
2.628
2.330
0.000
2.00
4.03
2.00
3.02
2.06
2.05
3.04
f1 (ppm)


xj140113-4
159.075
137.795
135.756
132.869
129.064
128.420
116.045
113.819
88.039
80.914
77.363
77.046
76.728
55.266
34.930
21.880
21.070
f1 (ppm)

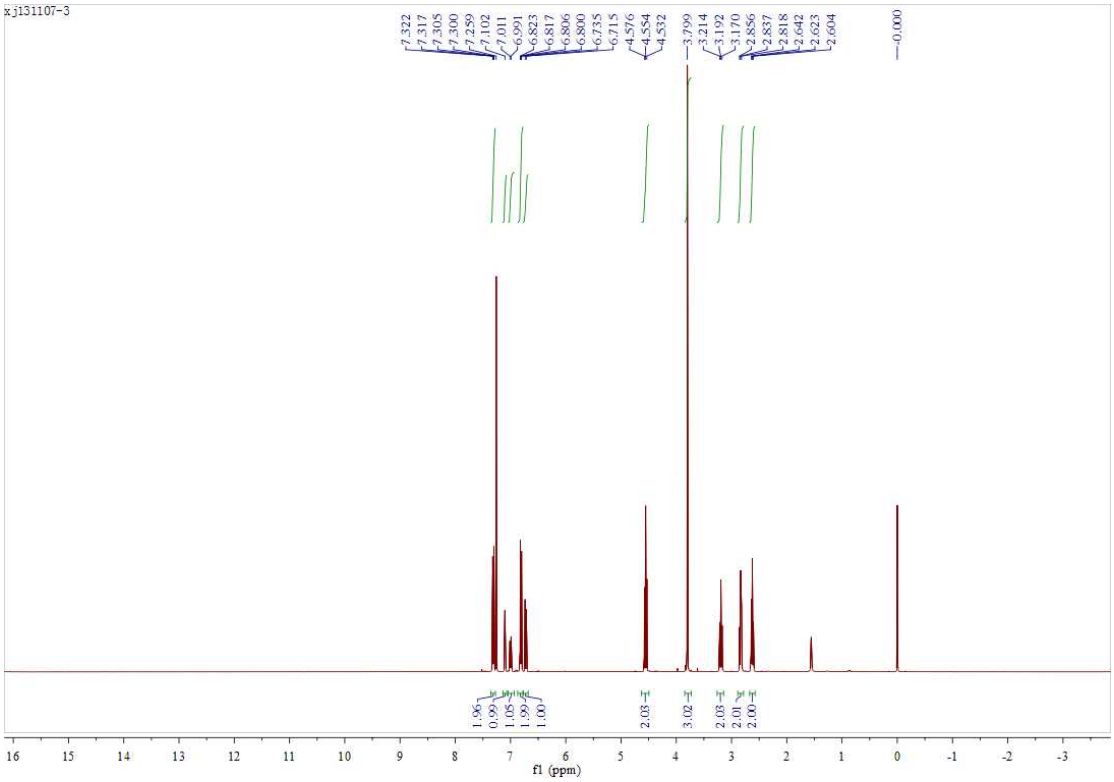
5-(4-(4-methoxyphenyl)but-3-yn-1-yl)-2,3-dihydrobenzofuran **(1d)**

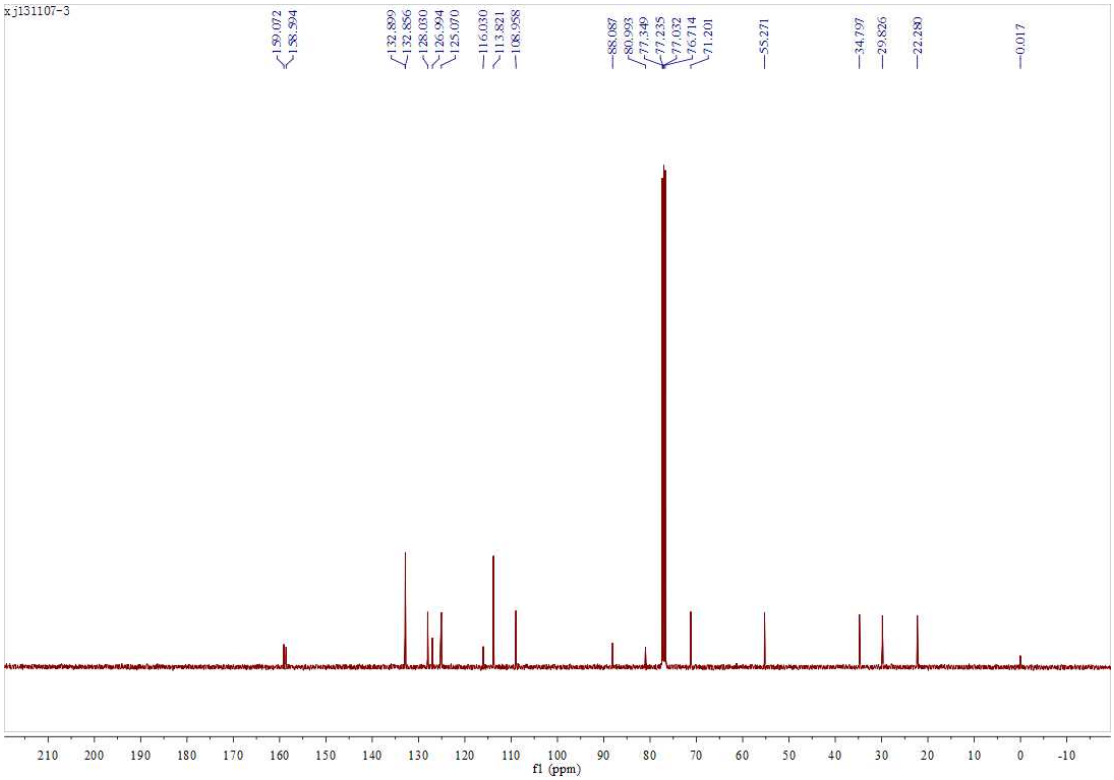


Prepared according to General Procedure **A.**

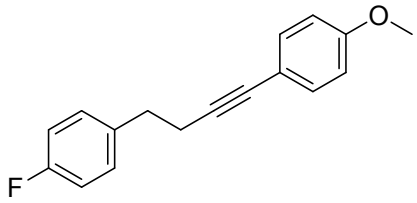
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.10 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.87 – 6.77 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 4.55 (t, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.19 (t, *J* = 8.7 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.07, 158.60, 132.90, 132.86, 128.03, 126.99, 125.07, 116.03, 113.82, 108.96, 88.09, 80.99, 71.20, 55.27, 34.80, 29.83, 22.28.





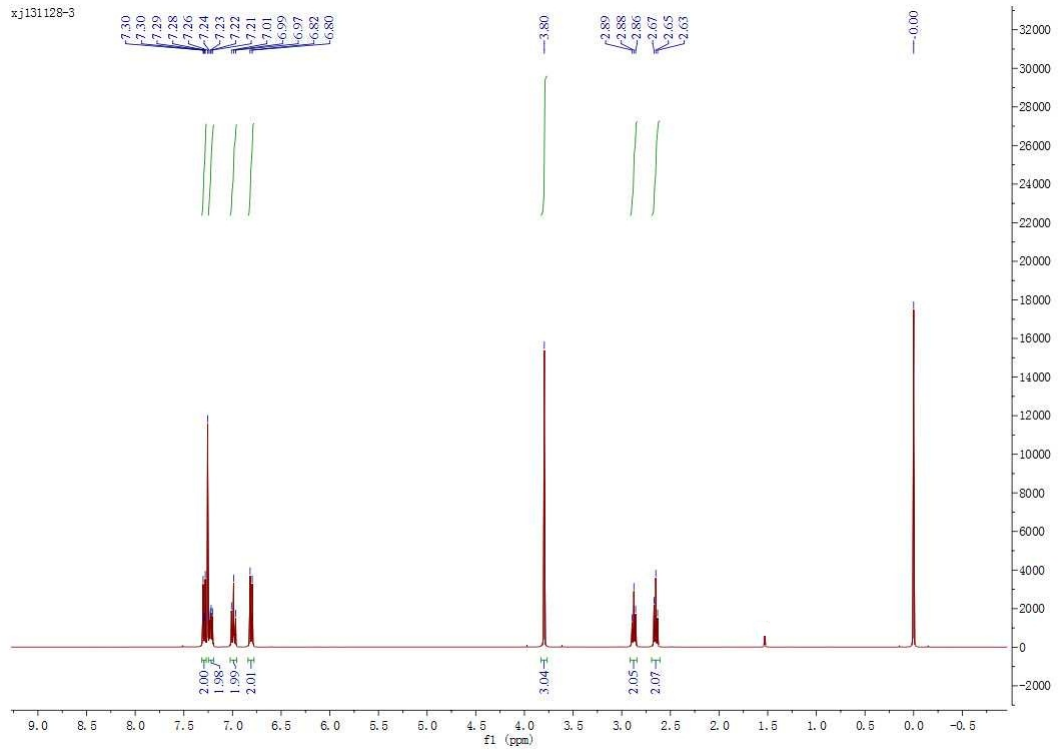
1-fluoro-4-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene **(1e)**

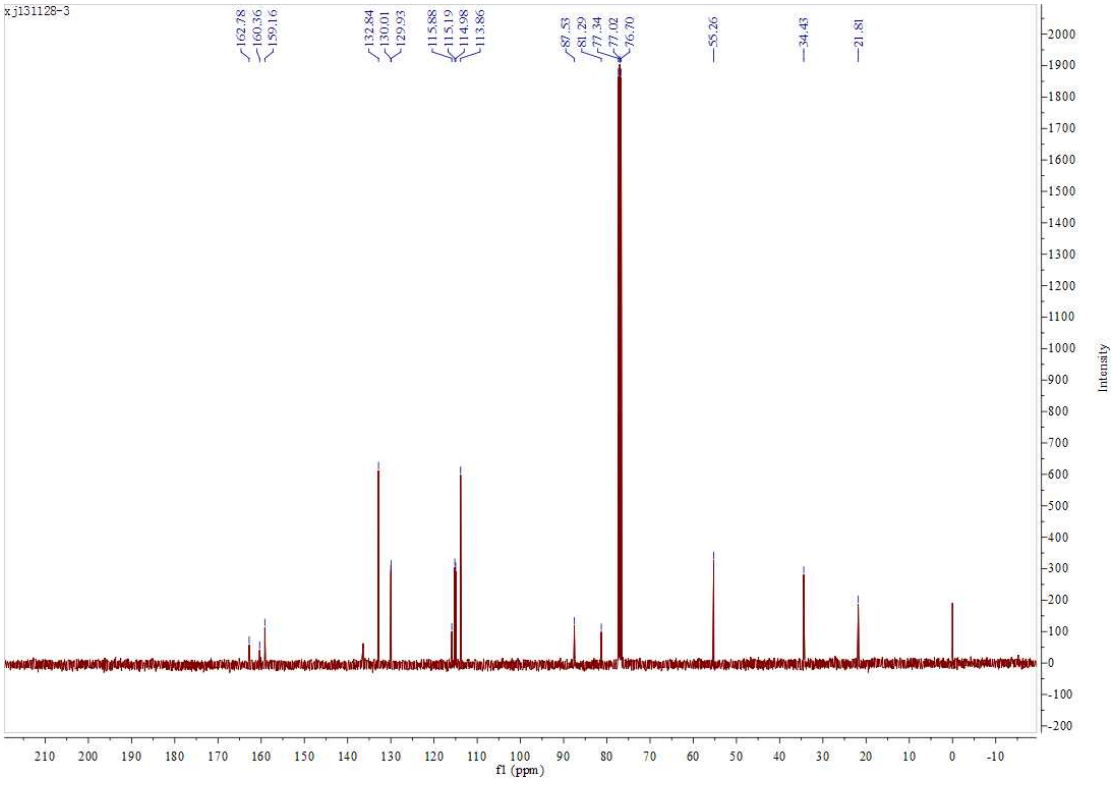


Prepared according to General Procedure **A.**

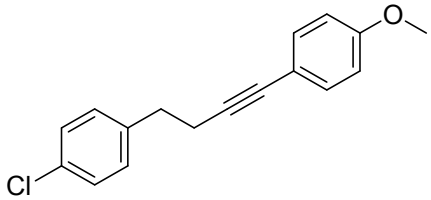
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (d, *J* = 8 Hz, 2H), 7.25 – 7.19 (m, 2H), 6.99 (t, *J* = 8 Hz, 2H), 6.81 (d, *J* = 8 Hz, 2H), 3.80 (s, 3H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.52 (d, *J* = 242 Hz), 159.16, 136.42 (d, *J* = 4 Hz) 132.84, 129.97 (d, *J* = 8 Hz), 115.88, 115.08 (d, *J* = 21 Hz), 113.86, 87.53, 81.29, 55.26, 34.43, 21.81.


xj131128-3
7.30
7.30
7.29
7.28
7.26
7.24
7.23
7.22
7.21
7.01
6.99
6.97
6.82
6.80
3.80
2.89
2.88
2.86
2.67
2.65
2.63
0.00
2.00
1.98
1.99
2.01
3.04
2.05
2.07
f1 (ppm)


xj131128-3
162.78
160.36
159.16
132.84
130.01
129.93
115.88
115.19
114.98
113.86
87.53
81.29
77.34
77.02
76.70
55.26
34.43
21.81
Intensity
f1 (ppm)

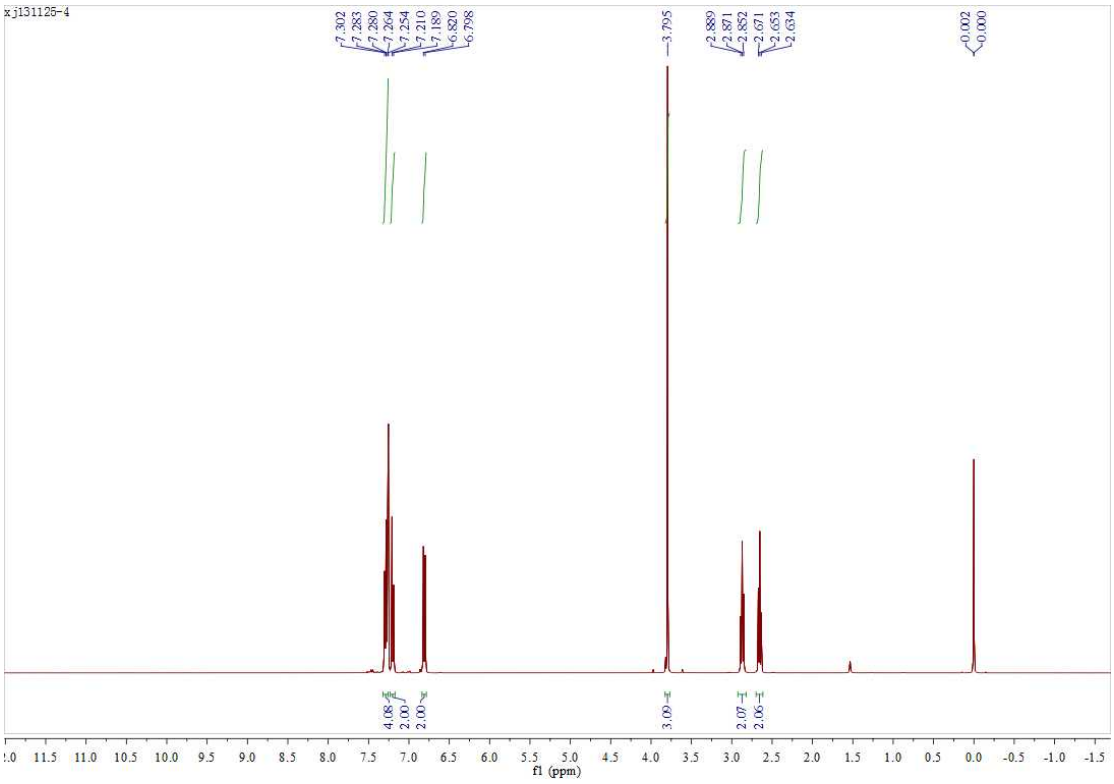
1-chloro-4-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene **(1f)**

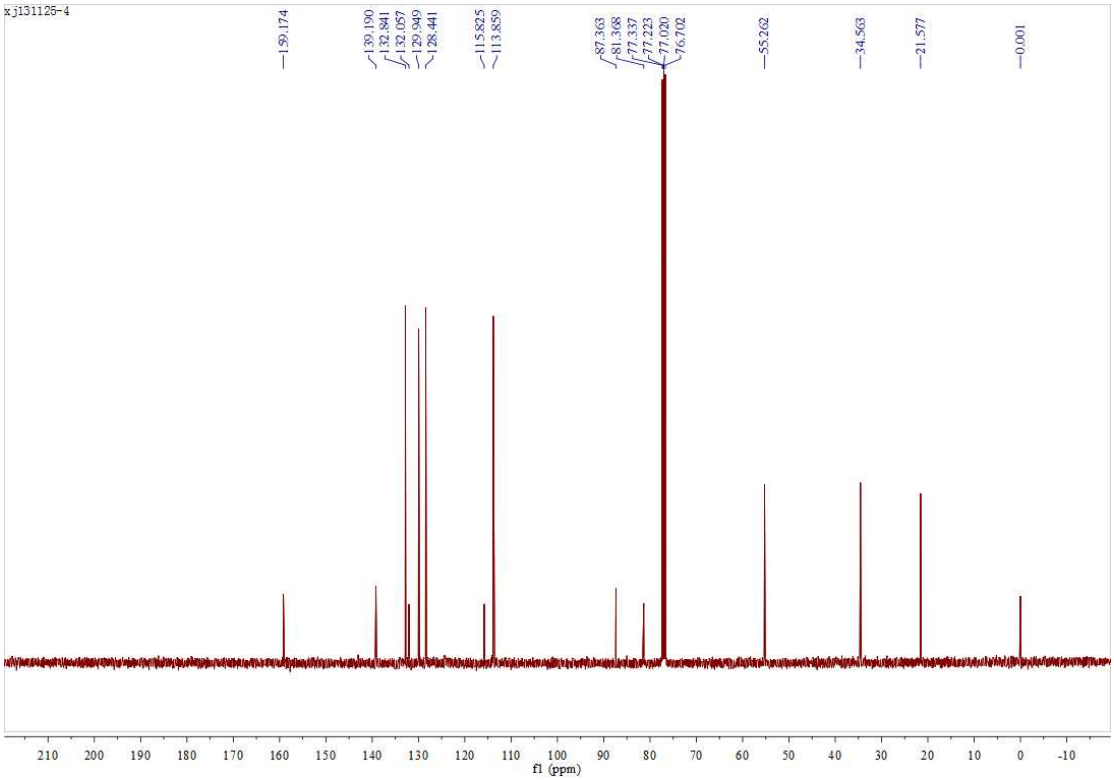


Prepared according to General Procedure **A.**

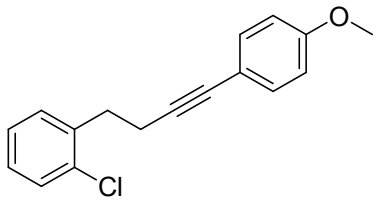
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 7.1 Hz, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.17, 139.19, 132.84, 132.06, 129.95, 128.44, 115.82, 113.86, 87.36, 81.37, 55.26, 34.56, 21.58.





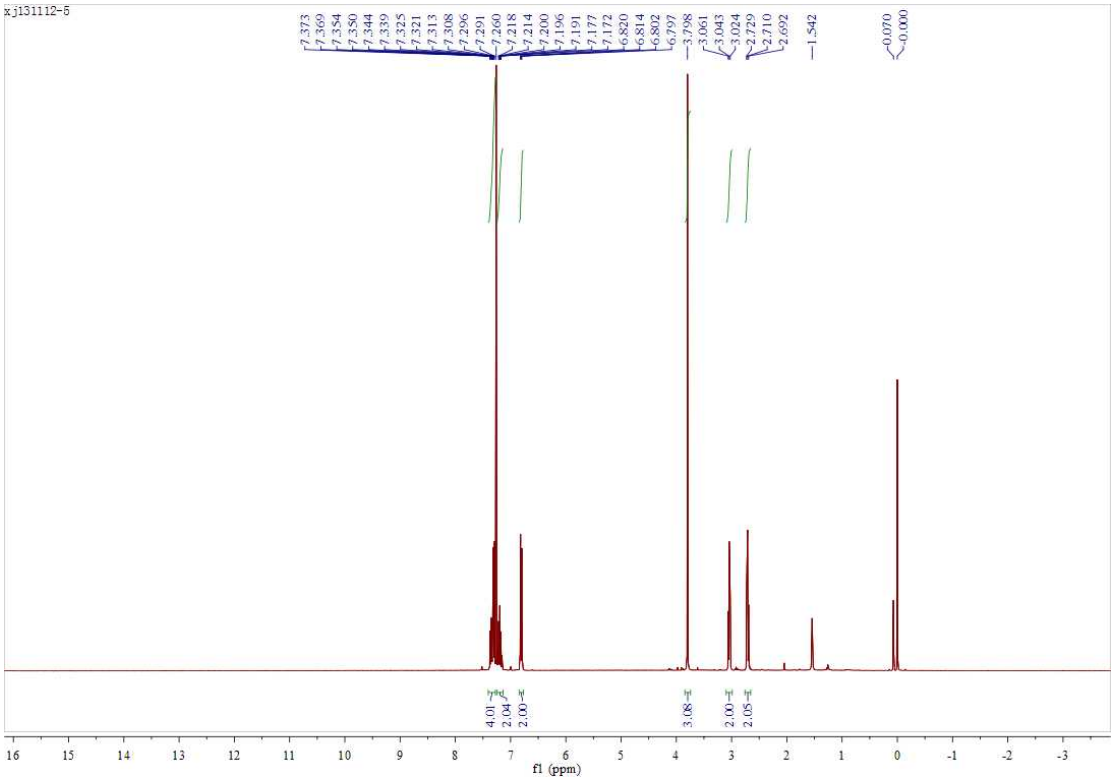
1-chloro-2-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene **(1g)**

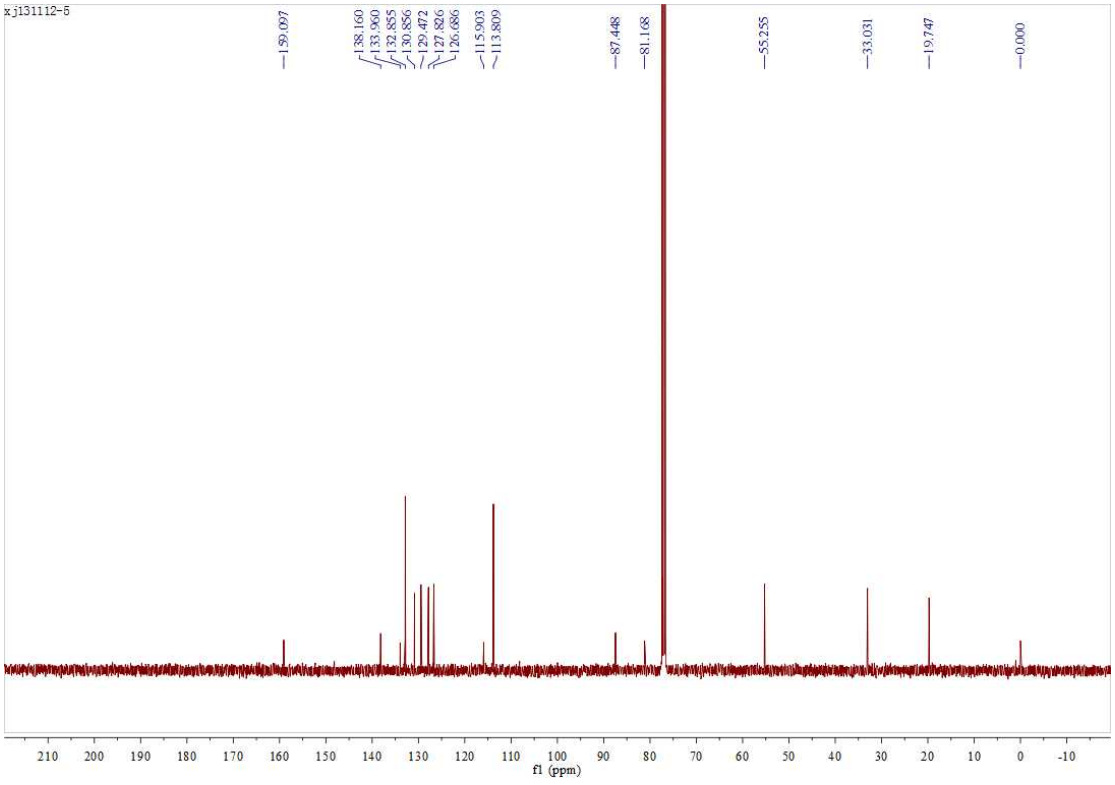


Prepared according to General Procedure **A.**

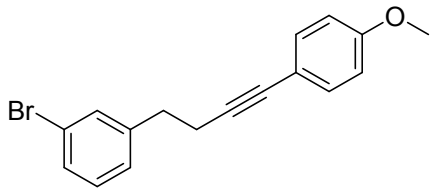
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 4H), 7.24 – 7.14 (m, 2H), 6.81 (d, J = 9.2 Hz,, 2H), 3.80 (s, 3H), 3.04 (t, J = 7.4 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.10, 138.16, 133.96, 132.86, 130.86, 129.47, 127.83, 126.69, 115.90, 113.81, 87.45, 81.17, 55.25, 33.03, 19.75.


xj131112-5
7.373
7.369
7.354
7.350
7.344
7.339
7.325
7.321
7.313
7.308
7.296
7.291
7.260
7.218
7.214
7.200
7.196
7.191
7.177
7.172
6.820
6.814
6.802
6.797
3.798
3.061
3.043
3.024
2.729
2.710
2.692
1.542
0.070
0.000
4.01
2.04
2.00
3.08
2.00
2.05
f1 (ppm)


xj131112-5
159.097
138.160
133.960
132.855
130.856
129.472
127.826
126.686
115.903
113.809
87.448
81.168
55.255
33.031
19.747
0.000
f1 (ppm)

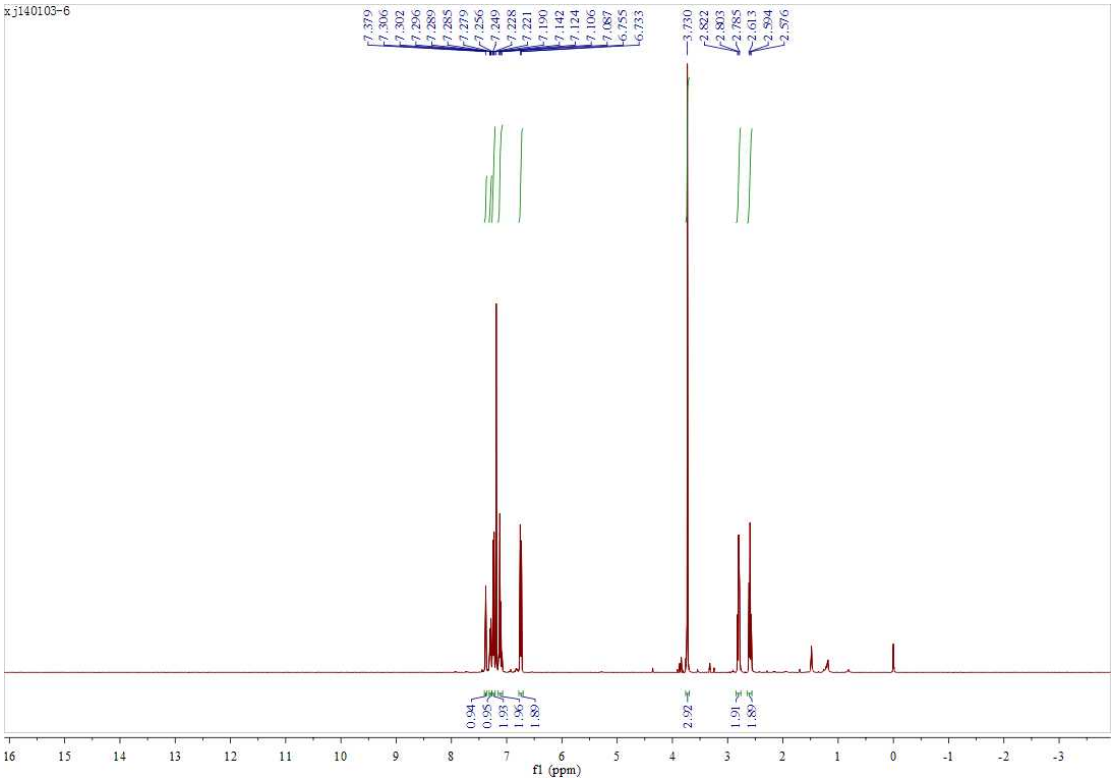
1-bromo-3-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene **(1h)**

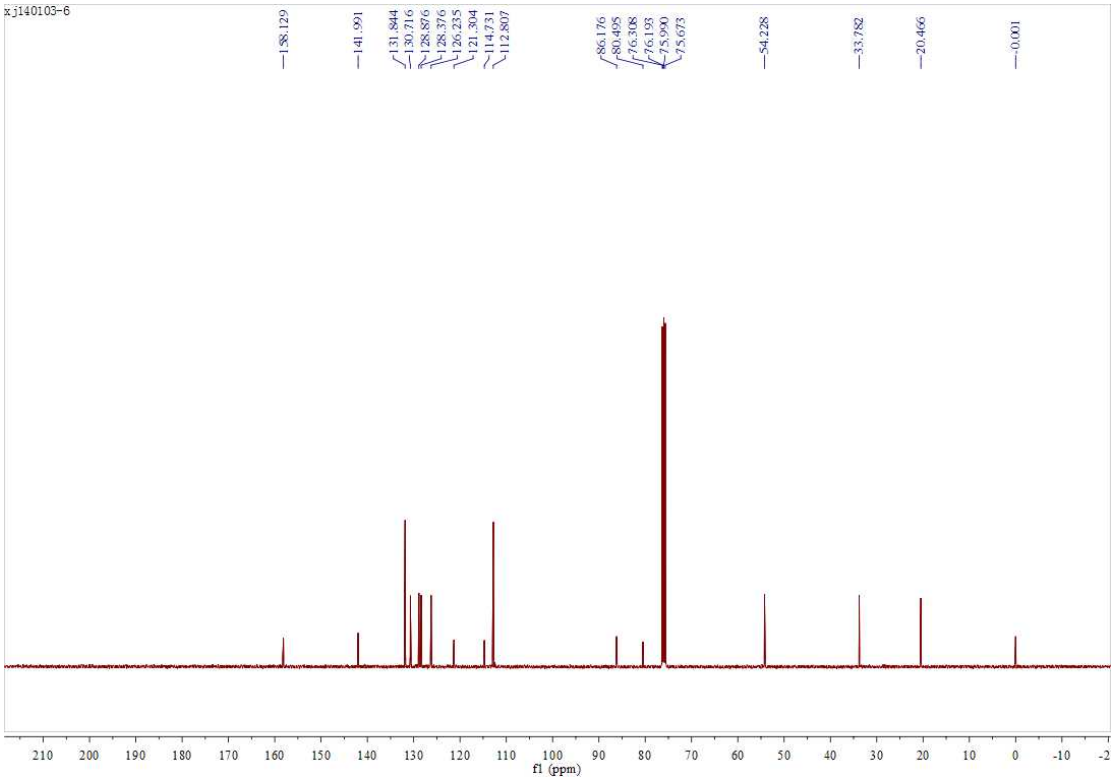


Prepared according to General Procedure **A.**

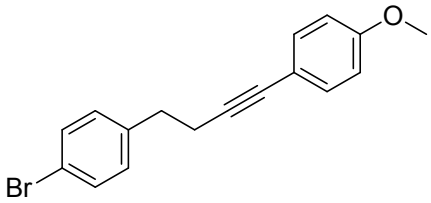
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz,, 2H), 7.15 – 7.07 (m, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.13, 141.99, 131.84, 130.72, 128.88, 128.38, 126.23, 121.30, 114.73, 112.81, 86.18, 80.49, 54.23, 33.78, 20.47.





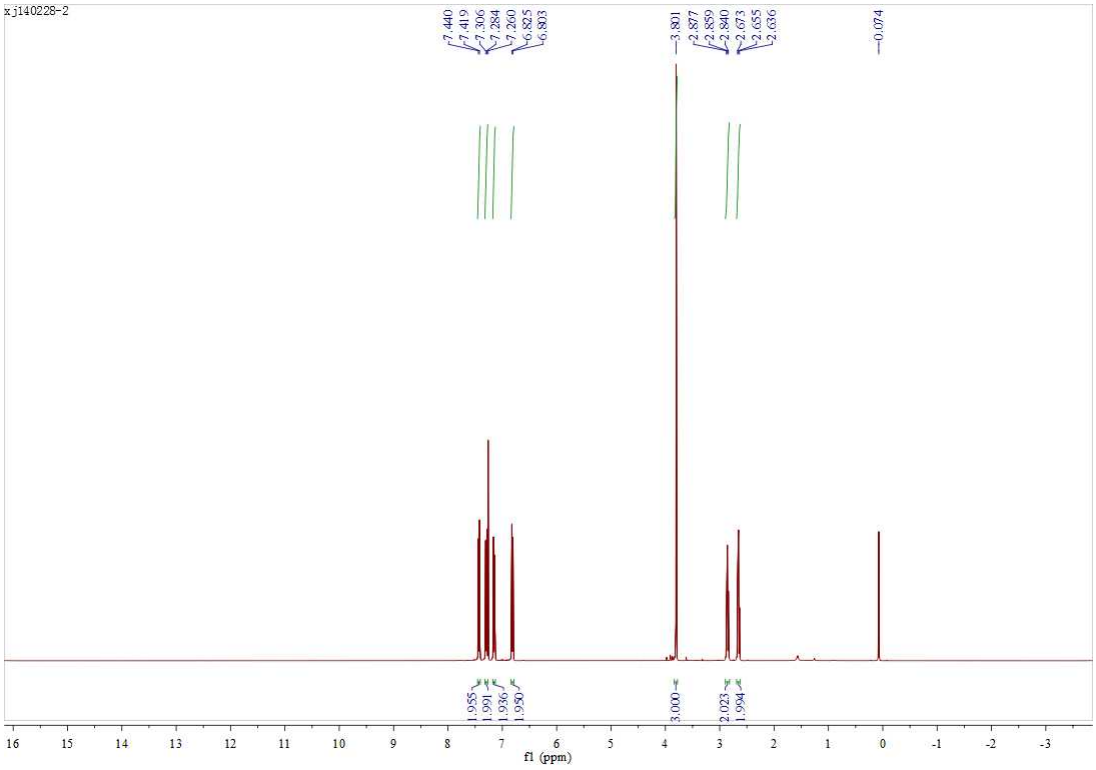
1-bromo-4-(4-(4-methoxyphenyl)but-3-yn-1-yl)benzene **(1i)**

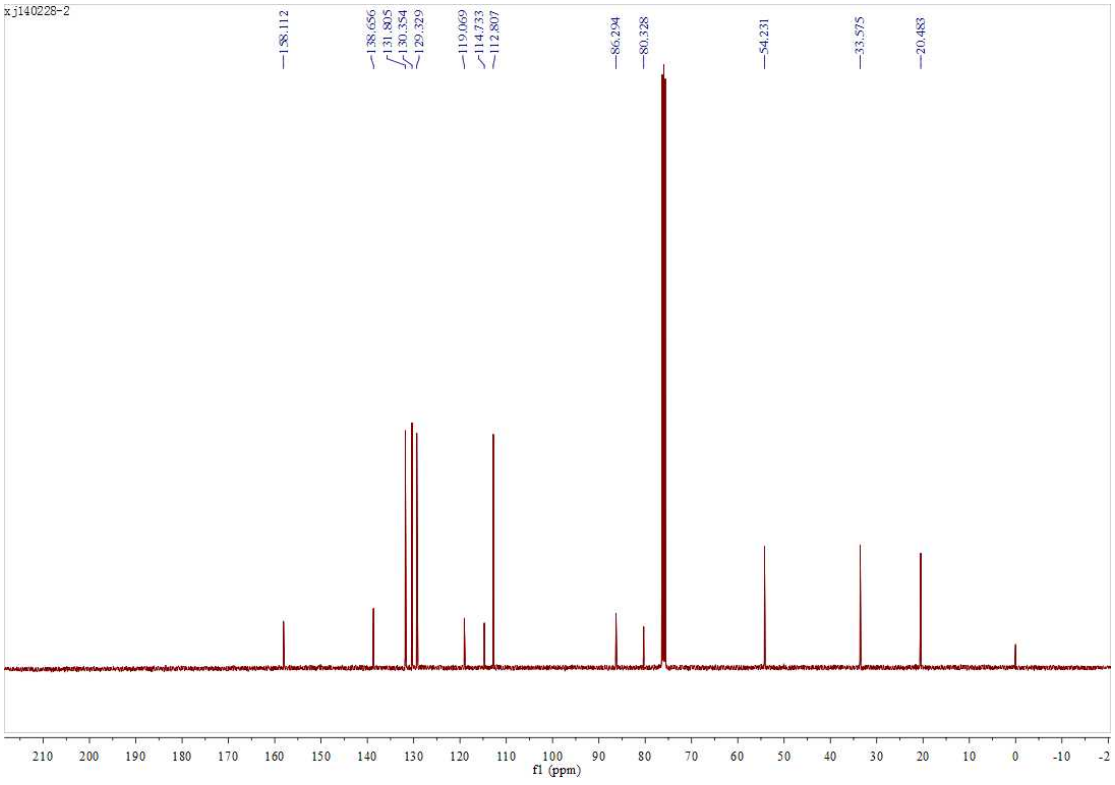


Prepared according to General Procedure **A.**

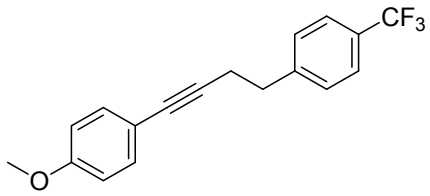
^{1}H NMR (400 MHz, $CDCl_3$) δ7.43 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.86 (t, *J* = 7.8 Hz,, 2H), 2.65 (t, *J* = 7.8 Hz,, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.11, 138.66, 131.80, 130.35, 129.33, 119.07, 114.73, 112.81, 86.29, 80.33, 54.23, 33.57, 20.48.


xj140228-2
7.440
7.419
7.306
7.284
7.260
6.825
6.803
3.801
2.877
2.859
2.840
2.673
2.655
2.636
0.074
1.955
1.991
1.936
1.990
3.000
2.023
1.994
f1 (ppm)


xj140228-2
158.112
138.656
131.805
130.354
129.329
119.069
114.733
112.807
86.294
80.328
54.231
33.575
20.483
f1 (ppm)

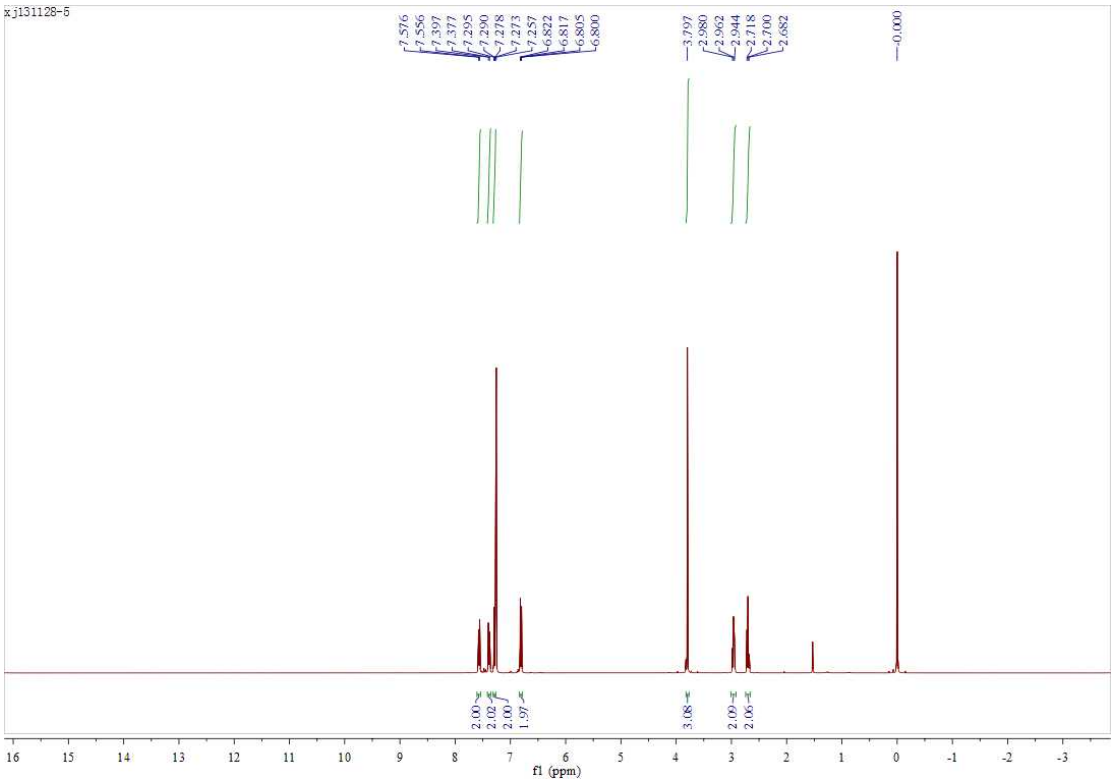
1-methoxy-4-(4-(4-(trifluoromethyl)phenyl)but-1-yn-1-yl)benzene **(1j)**

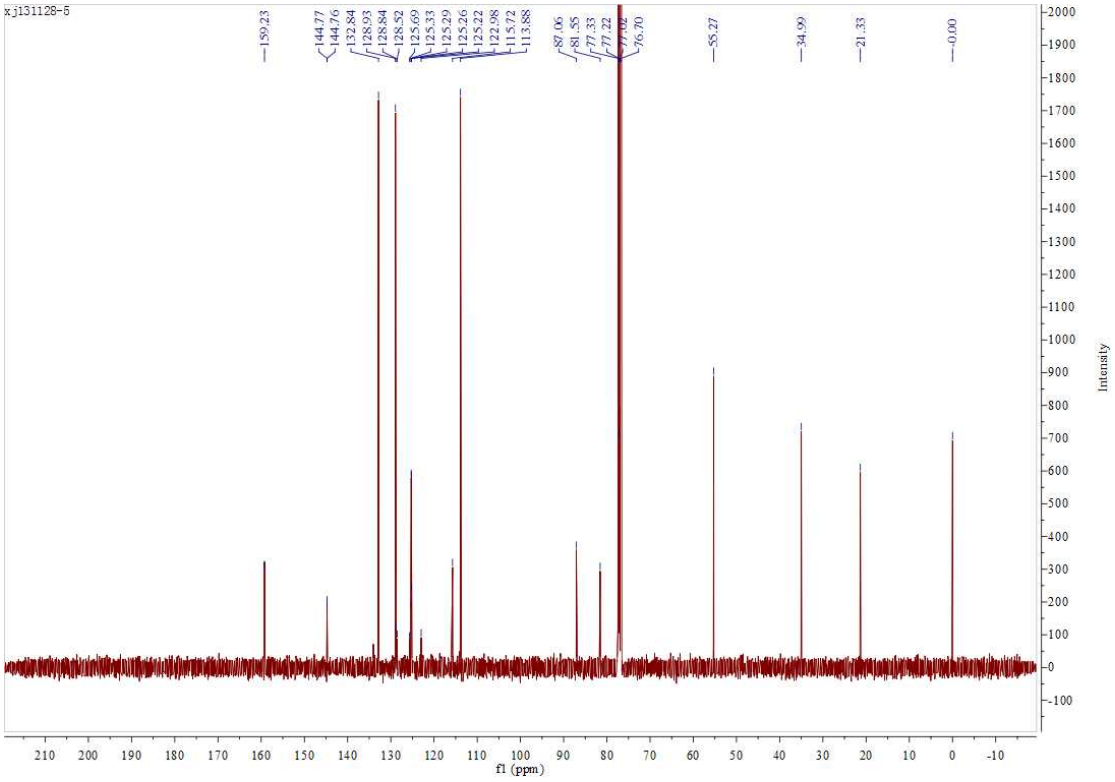


Prepared according to General Procedure **B.**

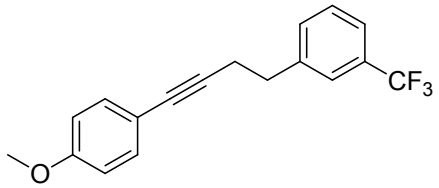
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.8 Hz,, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.23, 144.76, 132.84, 128.93, 128.68 (q, *J* = 32 Hz), 125.28 (q, *J* = 3 Hz), 124.33 (q, *J* = 271 Hz), 115.72, 113.88, 87.06, 81.55, 55.27, 34.99, 21.33.





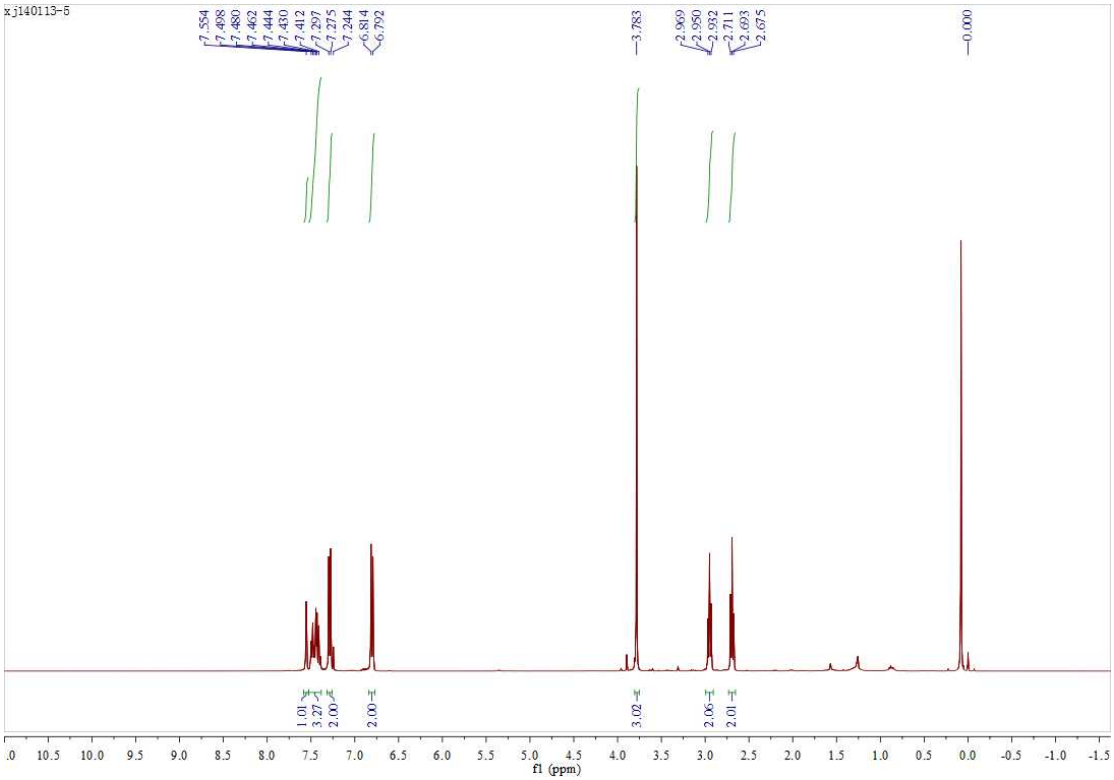
1-(4-(4-methoxyphenyl)but-3-yn-1-yl)-3-(trifluoromethyl)benzene **(1k)**

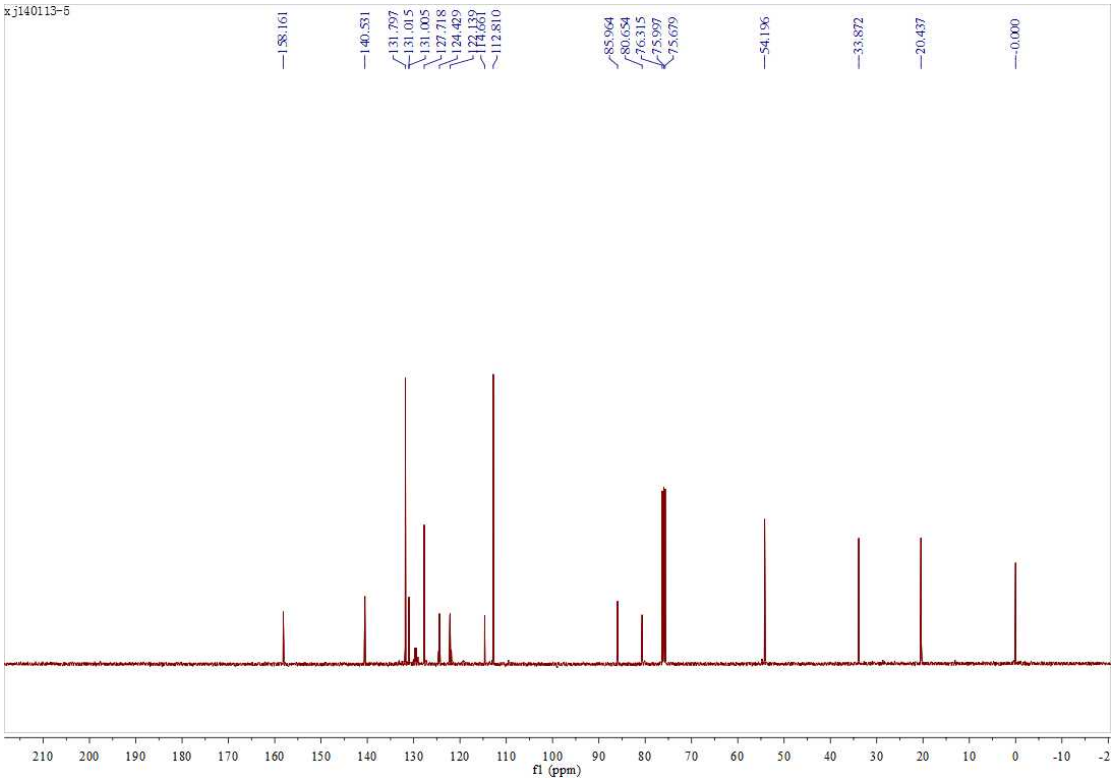


Prepared according to General Procedure **B.**

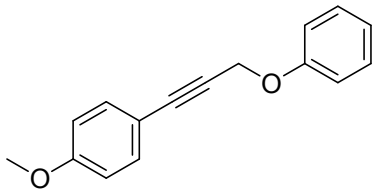
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.53 – 7.38 (m, 3H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.16, 140.53, 131.80, 131.01, 129.55 (q, *J* = 31 Hz), 127.72, 124.41 (q, *J* = 4 Hz), 123.23 (q, *J* = 270 Hz), 122.16 (q, *J* = 4 Hz), 114.66, 112.81, 85.96, 80.65, 54.20, 33.87, 20.44.


xj140113-6
7.554
7.498
7.480
7.462
7.444
7.430
7.412
7.297
7.275
7.244
6.814
6.792
3.783
2.969
2.950
2.932
2.711
2.693
2.675
0.000
1.01
3.27
2.00
2.00
3.02
2.06
2.01
f1 (ppm)


xj140113-6
158.161
140.531
131.797
131.015
131.005
127.718
124.429
122.139
114.681
112.810
85.964
80.654
76.315
75.997
75.679
54.196
33.872
20.437
0.000
f1 (ppm)

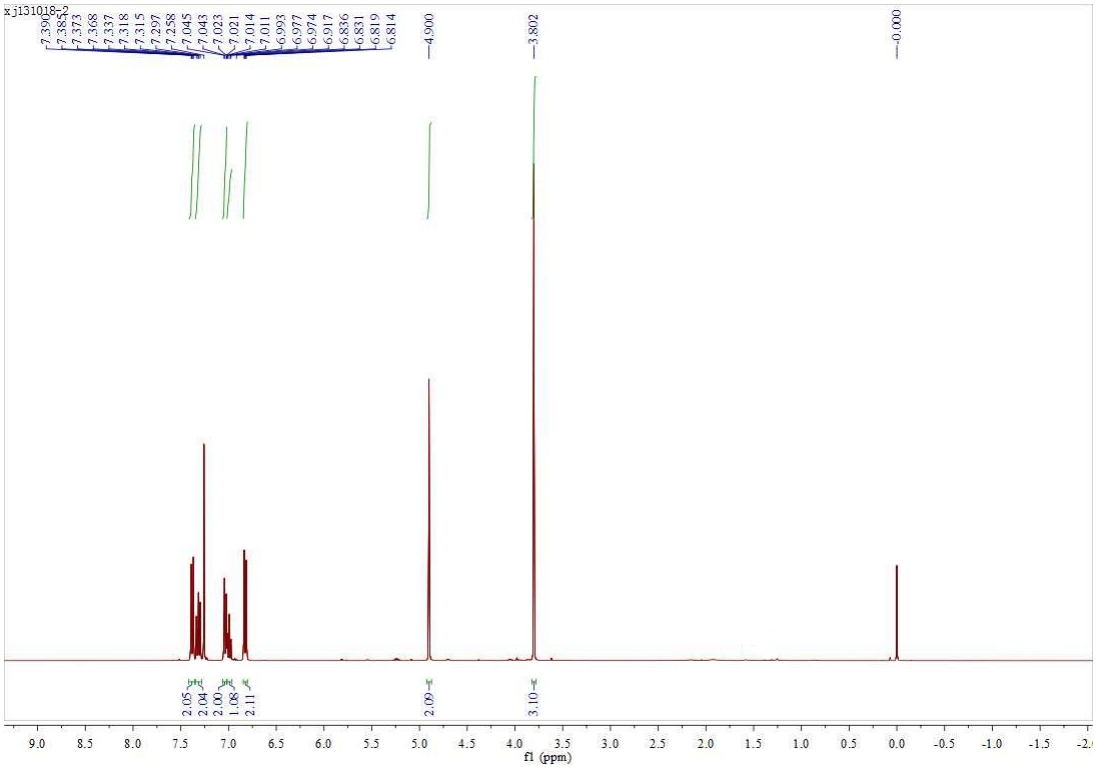
1-methoxy-4-(3-phenoxyprop-1-yn-1-yl)benzene **(1l)**

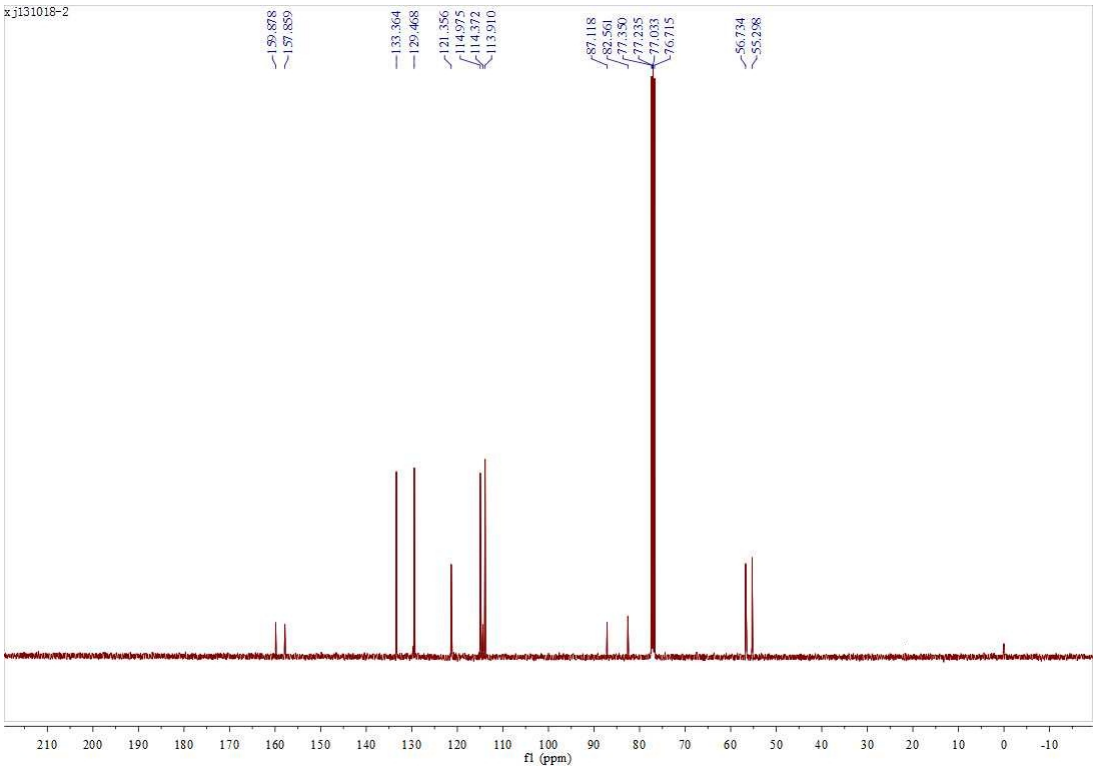


Prepared according to General Procedure **B.**

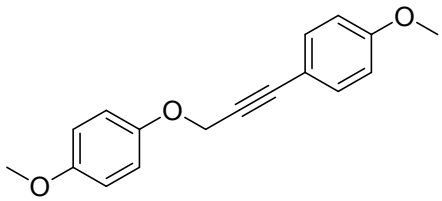
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.99 (t, *J* = 7.8 Hz,1H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.90 (s, 2H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.88, 157.86, 133.36, 129.47, 121.36, 114.98, 114.37, 113.91, 87.12, 82.56, 56.73, 55.30.





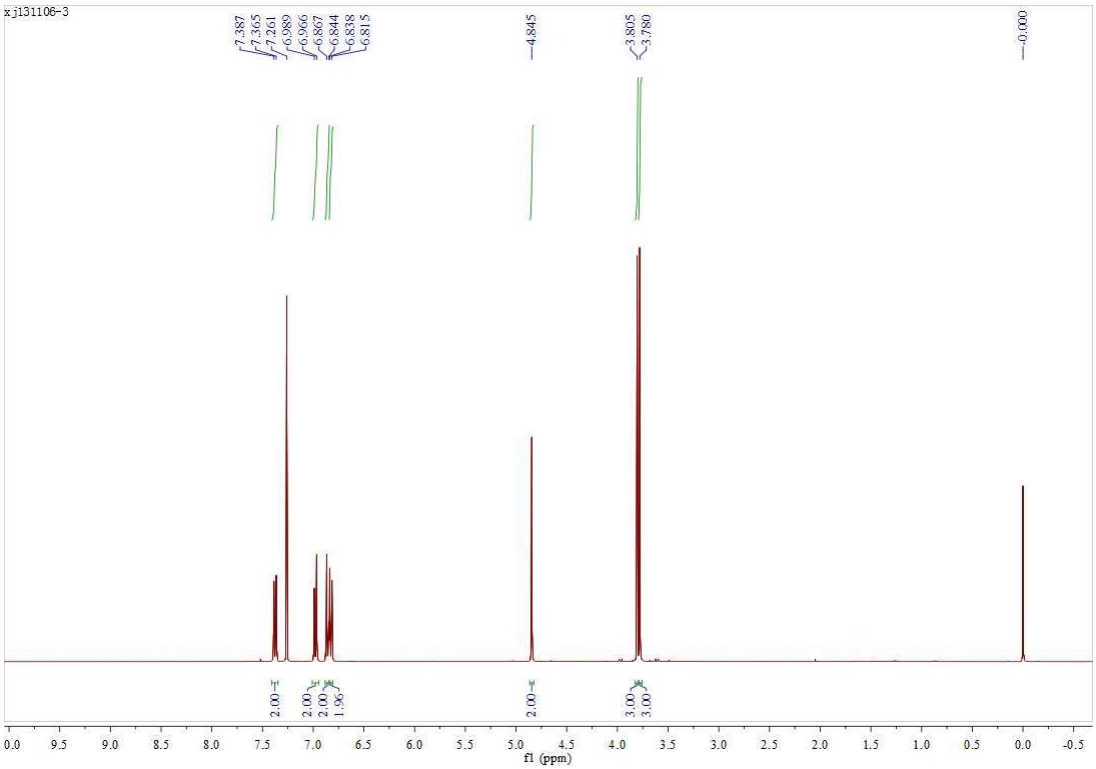
1-methoxy-4-(3-(4-methoxyphenoxy)prop-1-yn-1-yl)benzene **(1m)**

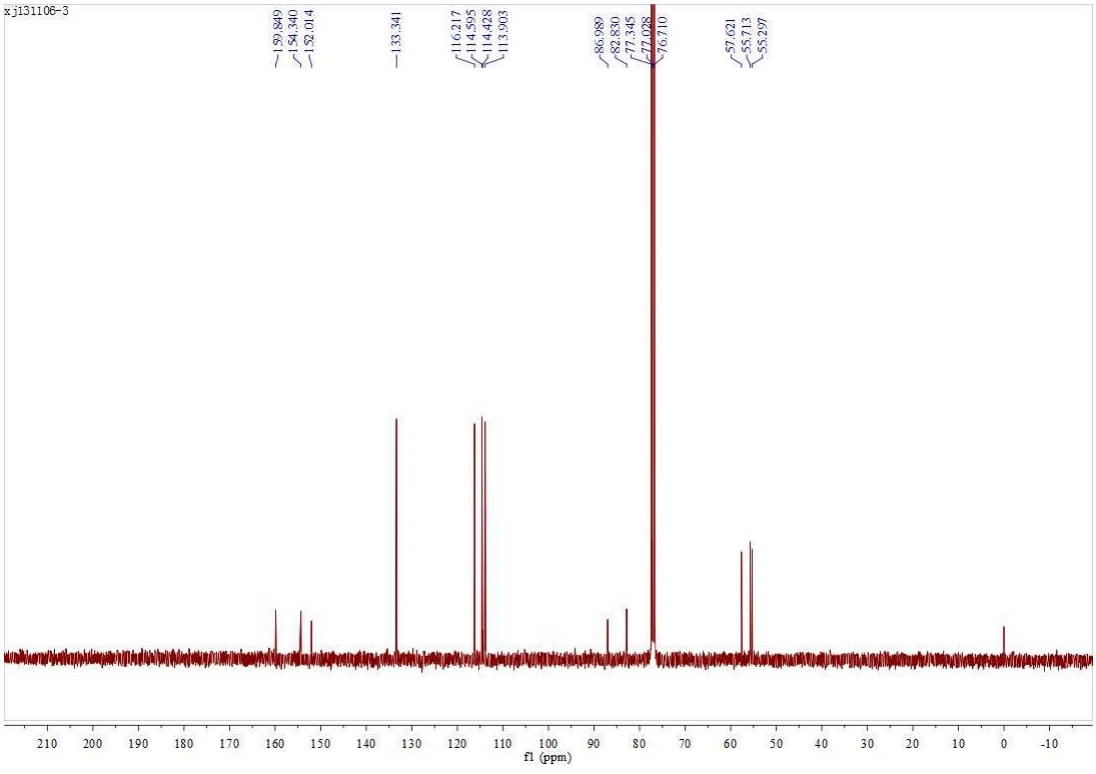


Prepared according to General Procedure **B.**

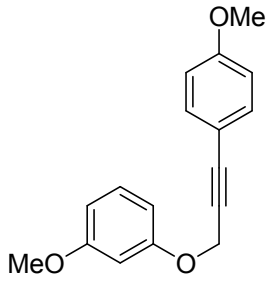
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 9.1 Hz, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 6.82 (d, *J* = 9.2 Hz, 2H), 4.84 (s, 2H), 3.81 (s, 3H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.85, 154.34, 152.01, 133.34, 116.22, 114.60, 114.43, 113.90, 86.99, 82.83, 57.62, 55.71, 55.30.


xj131106-3
7.387
7.365
7.261
6.989
6.966
6.867
6.844
6.838
6.815
4.845
3.805
3.780
0.000
2.00
2.00
2.00
1.96
2.00
3.00
3.00
f1 (ppm)


xj131106-3
159.849
154.340
152.014
133.341
116.217
114.595
114.428
113.903
86.989
82.830
77.345
77.028
76.710
57.621
55.713
55.297
f1 (ppm)

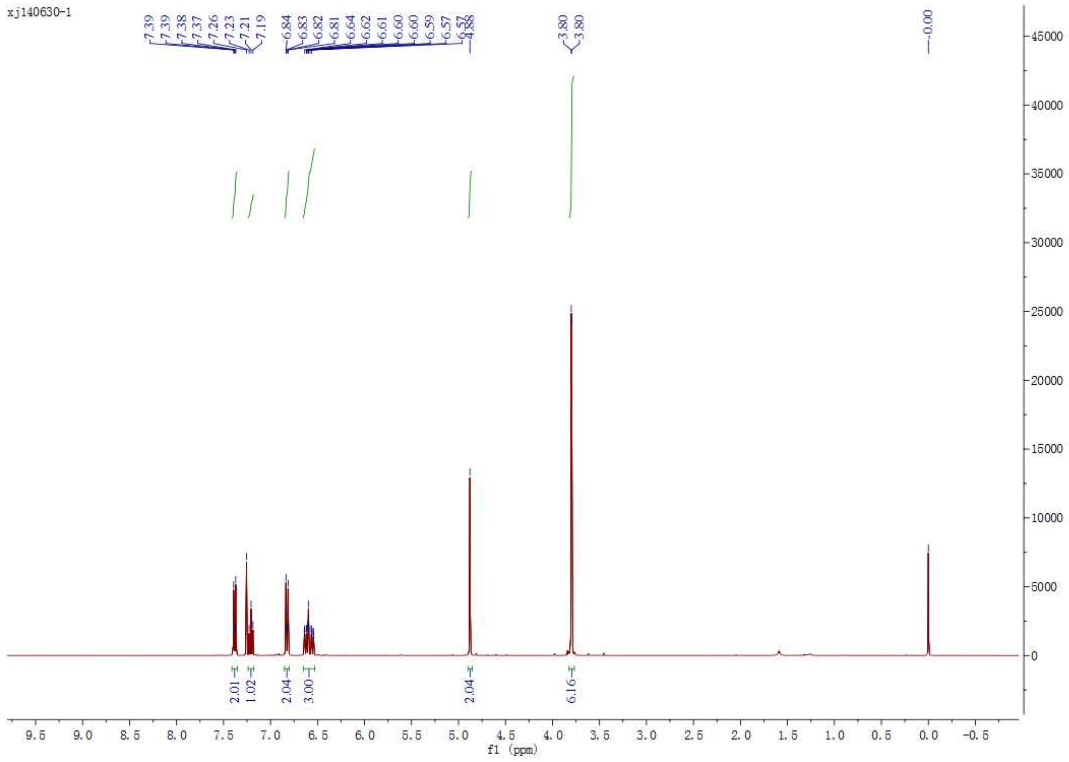
1-methoxy-3-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzene (**1n**)

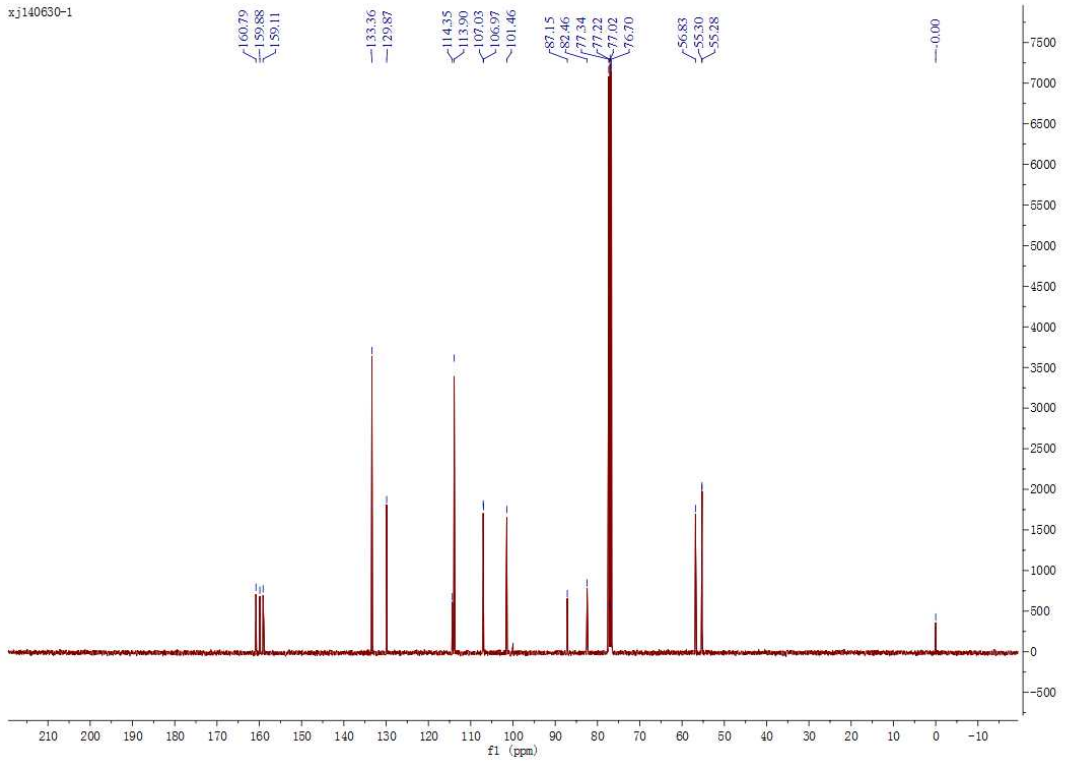


Prepared according to General Procedure **B.**

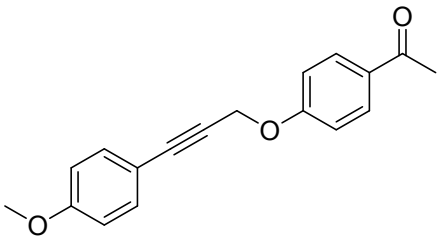
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 2H), 6.65 – 6.53 (m, 3H), 4.88 (s, 2H), 3.80 (d, *J* = 1.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.79, 159.88, 159.11, 133.36, 129.87, 114.35, 113.90, 107.03, 106.97, 101.46, 87.15, 82.46, 56.83, 55.30, 55.28.





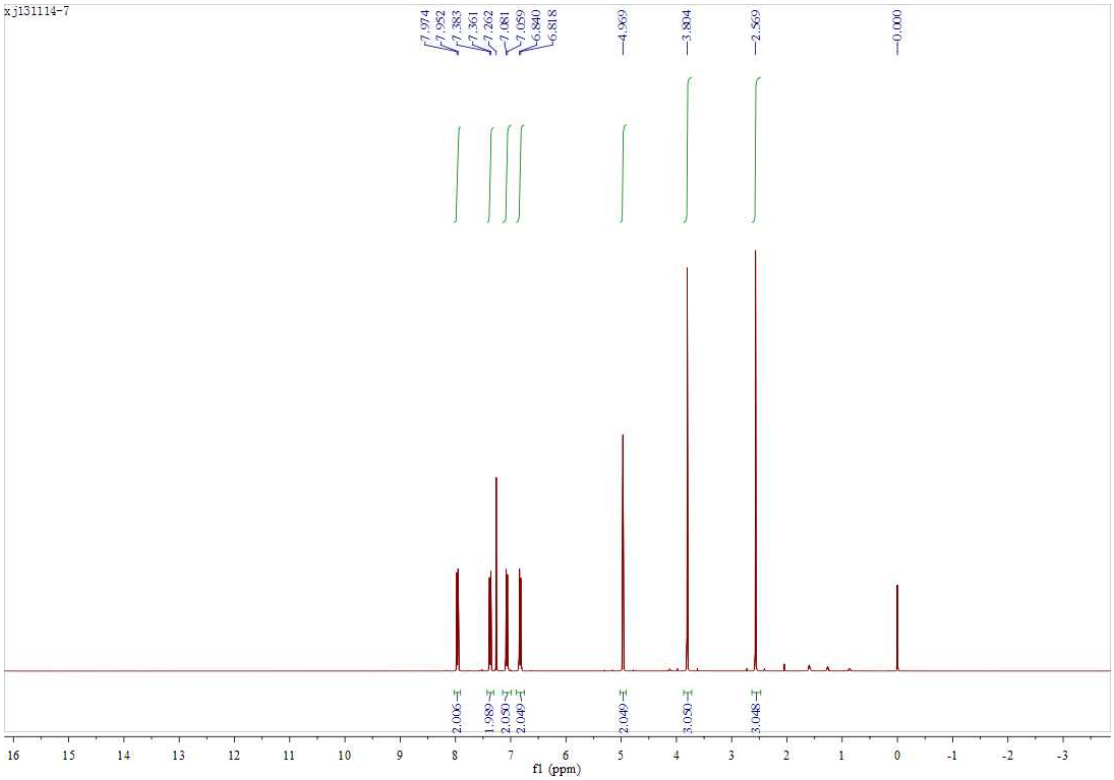
1-(4-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl)ethanone **(1o)**

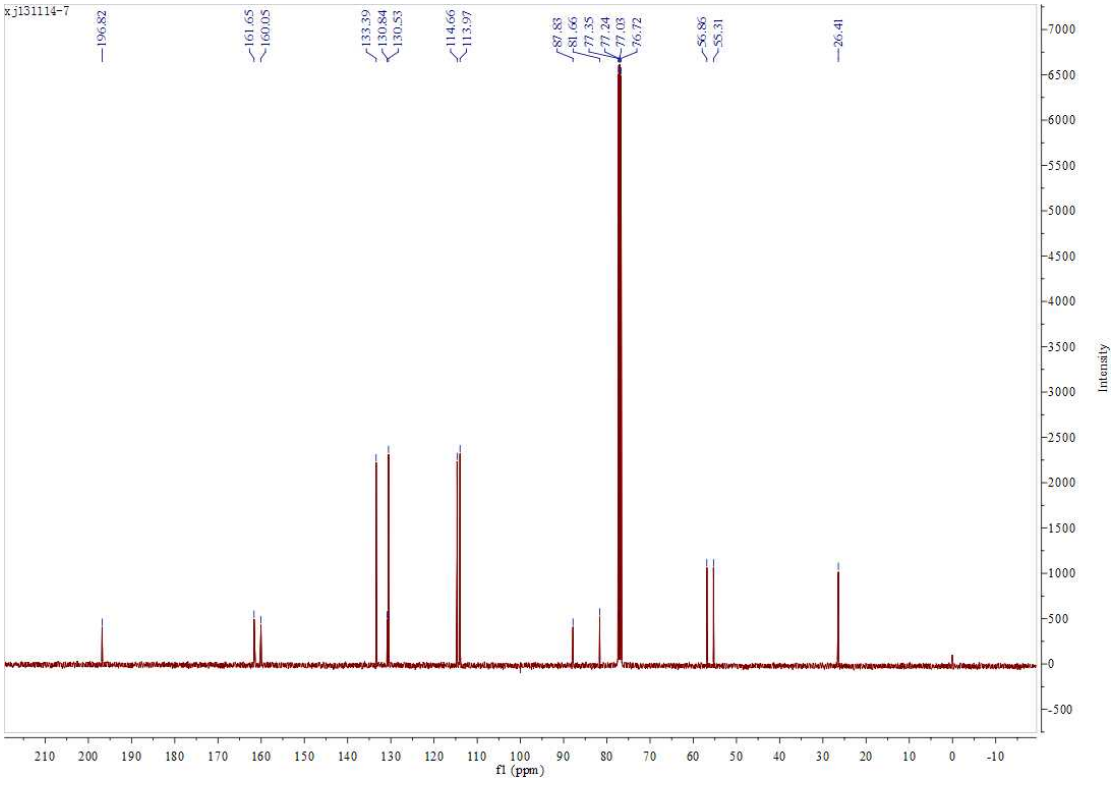


Prepared according to General Procedure **B.**

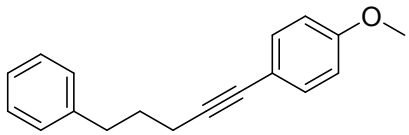
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 3.80 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.82, 161.65, 160.05, 133.39, 130.84, 130.53, 114.66, 113.97, 87.83, 81.66, 56.86, 55.31, 26.41.


xj131114-7
7.974
7.952
7.383
7.361
7.262
7.081
7.059
6.840
6.818
4.969
3.804
2.569
0.000
2.006
1.989
2.030
2.049
2.049
3.030
3.048
f1 (ppm)


xj131114-7
196.82
161.65
160.05
133.39
130.84
130.53
114.66
113.97
87.88
81.66
77.35
77.24
77.03
76.72
56.86
55.31
26.41
Intensity
f1 (ppm)

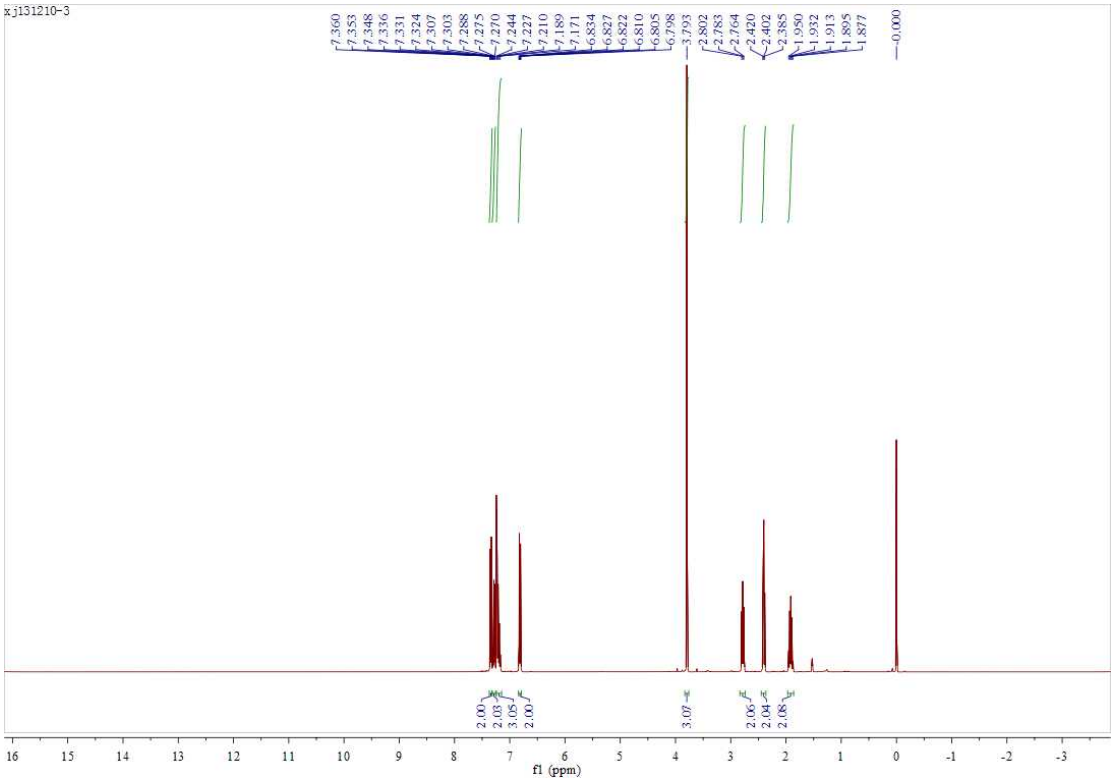
1-methoxy-4-(5-phenylpent-1-yn-1-yl)benzene **(1p)**

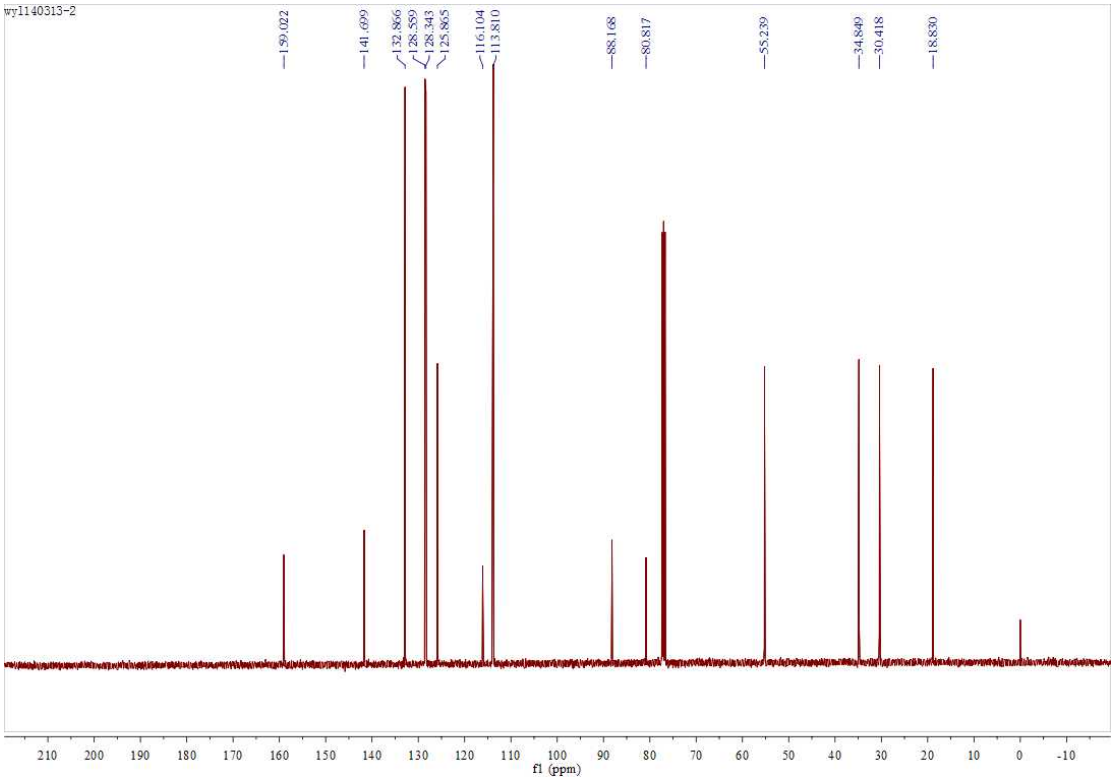


Prepared according to General Procedure **B.**

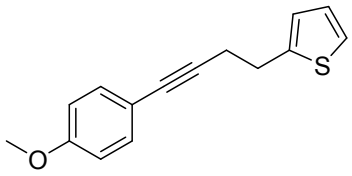
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.20 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.83 (t, *J* = 7.8 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.97 – 1.86 (m, 2H).

^{13}C NMR(100 MHz, $CDCl_3$) δ 159.02, 141.70, 132.87, 128.56, 128.34, 125.87, 116.10, 113.81, 88.17, 80.82, 55.24, 34.85, 30.42, 18.83.





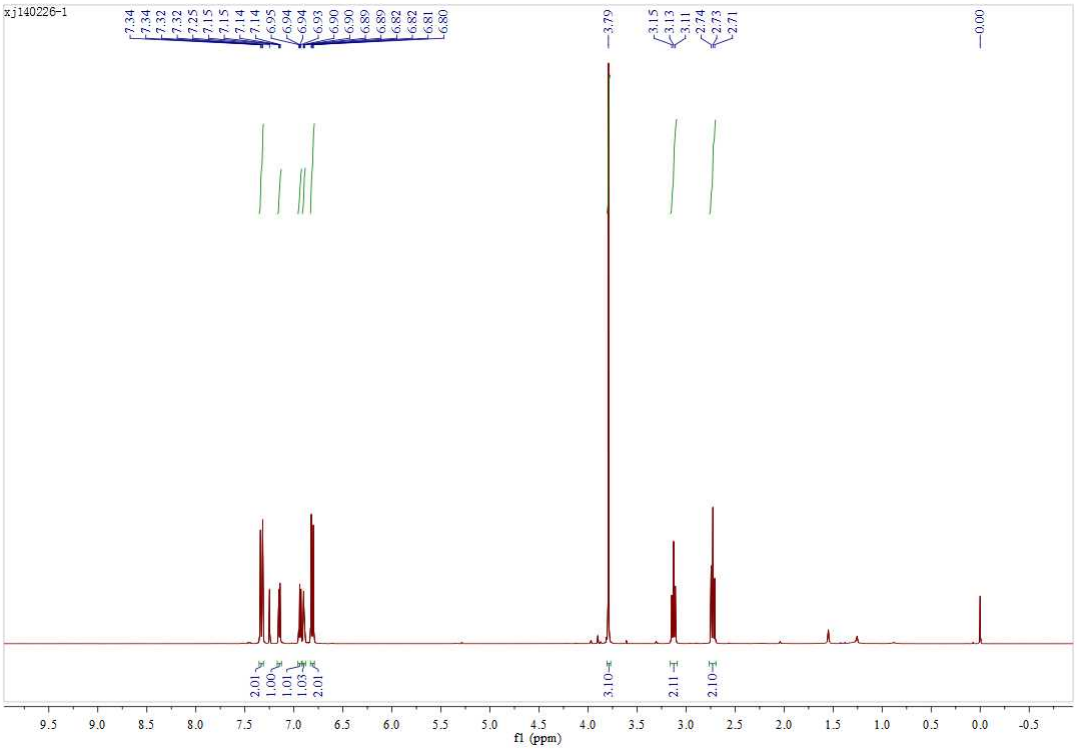
2-(4-(4-methoxyphenyl)but-3-yn-1-yl)thiophene **(1r)**

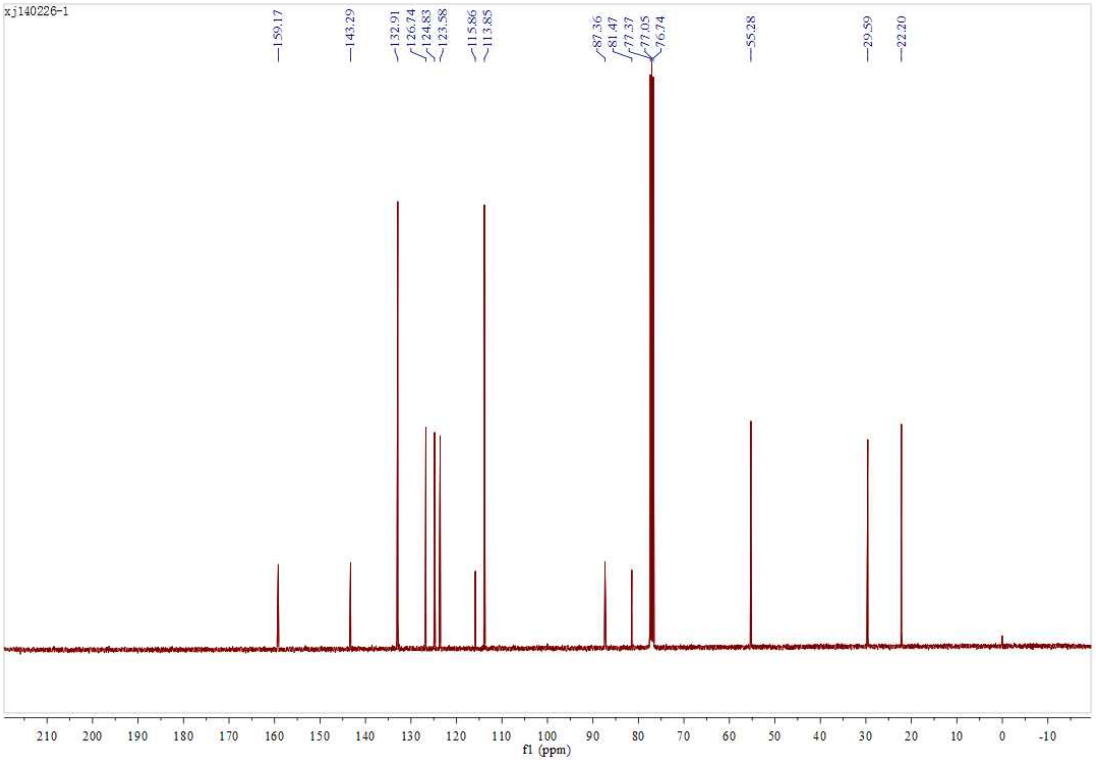


Prepared according to General Procedure **A.**

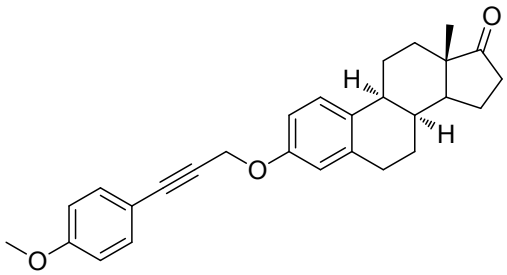
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8 Hz, 2H), 7.15 (dd, *J* = 5.1, 1.2 Hz, 4H), 6.97 – 6.93 (m, 1H), 6.91 – 6.89 (m, 1H), 6.81(d, *J* = 8 Hz, 2H), 3.79 (s, 3H), 3.13 (t, *J* = 7.3 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.17, 143.29, 132.91, 126.74, 124.83, 123.58, 115.86, 113.85, 87.36, 81.47, 55.28, 29.59, 22.20 .


xj140226-1
7.34
7.34
7.32
7.32
7.25
7.15
7.14
7.14
6.95
6.94
6.94
6.93
6.90
6.90
6.89
6.82
6.82
6.81
6.80
3.79
3.15
3.13
3.11
2.74
2.73
2.71
0.00
2.01
1.00
1.01
1.03
2.01
3.10
2.11
2.10
f1 (ppm)


xj140226-1
159.17
143.29
132.91
126.74
124.83
123.58
115.86
113.85
87.36
81.47
77.37
77.05
76.74
55.28
29.59
22.20
f1 (ppm)

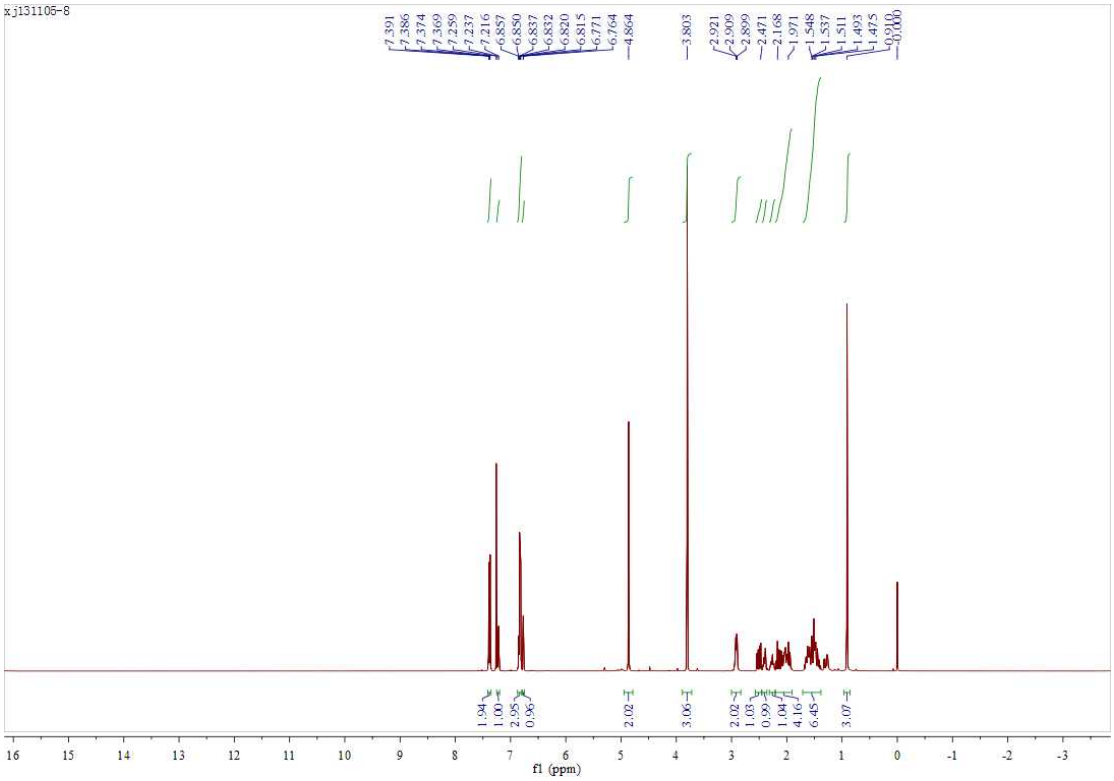
(8S,9S,13S)-3-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one **(1s)**

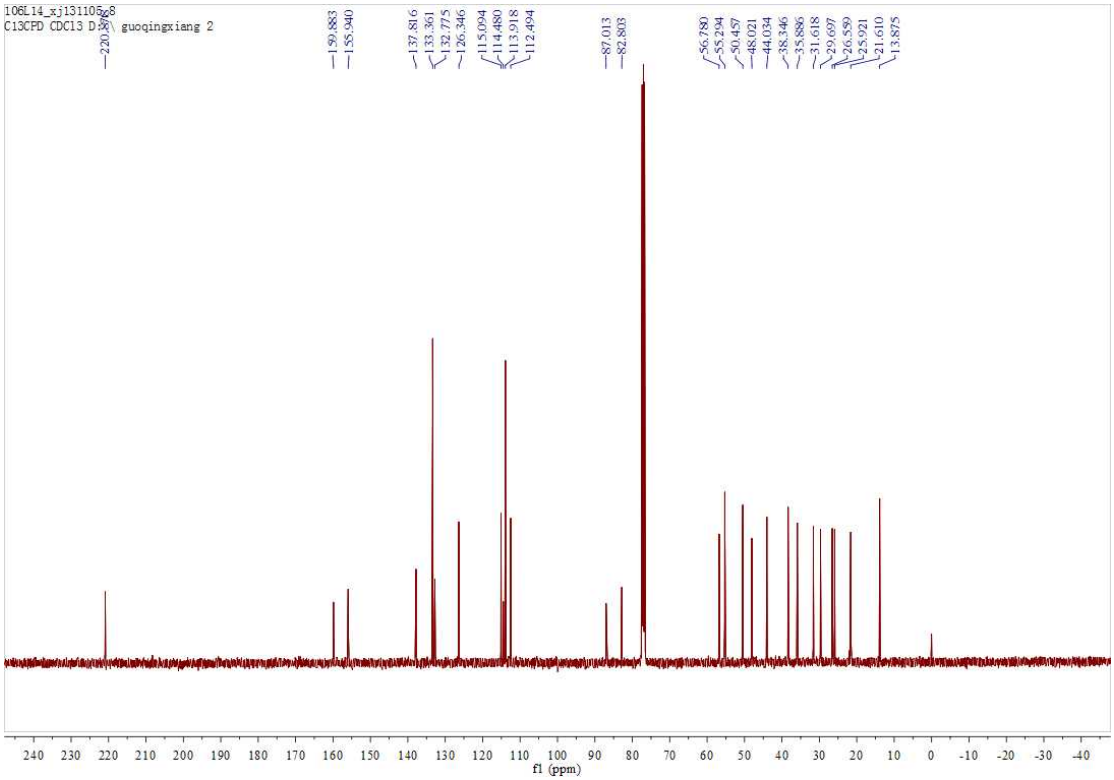


Prepared according to General Procedure **B.**

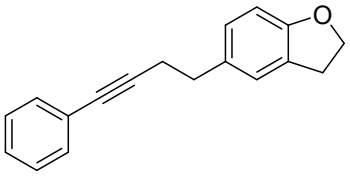
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 6.87 – 6.80 (m, 3H), 6.77 (d, *J* = 2.7 Hz, 1H), 4.86 (s, 2H), 3.80 (s, 3H), 2.94 – 2.89 (m, 2H), 2.54 – 2.47 (m, 1H), 2.43 – 2.36 (m, 1H), 2.32 – 2.22 (m, 1H), 2.21 – 1.90 (m, 4H), 1.71 – 1.38 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 220.88, 159.88, 155.94, 137.82, 133.36, 132.77, 126.35, 115.09, 114.48, 113.92, 112.49, 87.01, 82.80, 56.78, 55.29, 50.46, 48.02, 44.03, 38.35, 35.89, 31.62, 29.70, 26.56, 25.92, 21.61, 13.88.





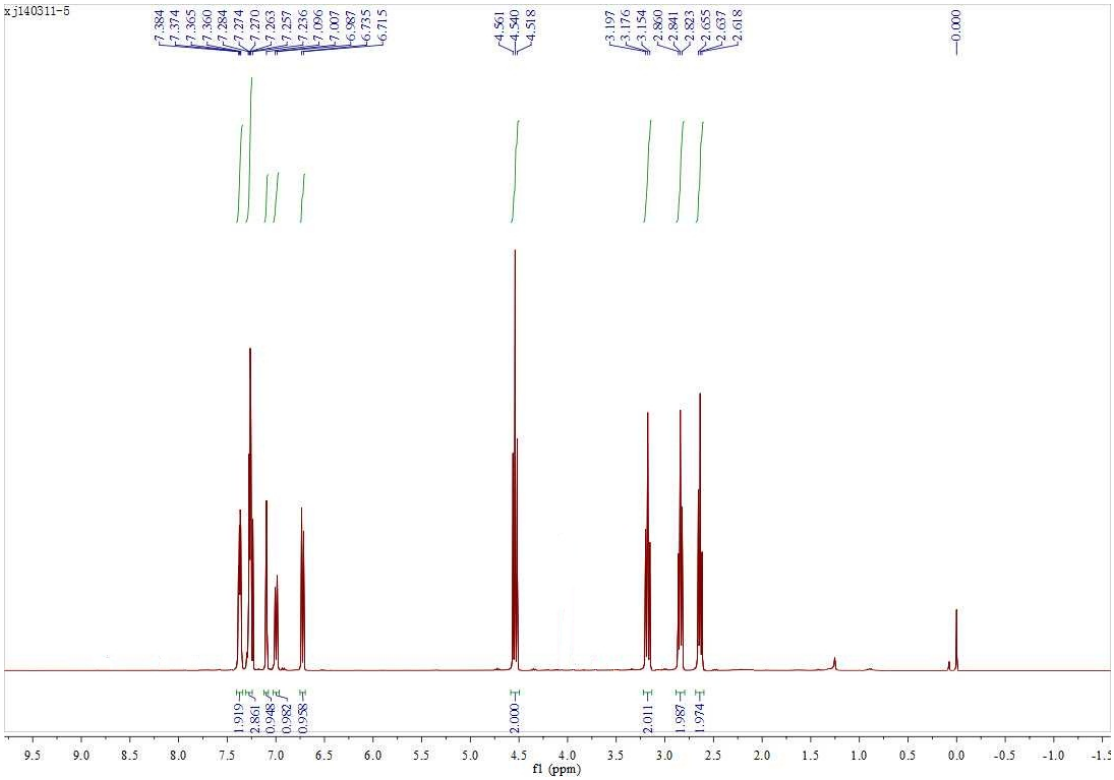
5-(4-phenylbut-3-yn-1-yl)-2,3-dihydrobenzofuran **(1t)**

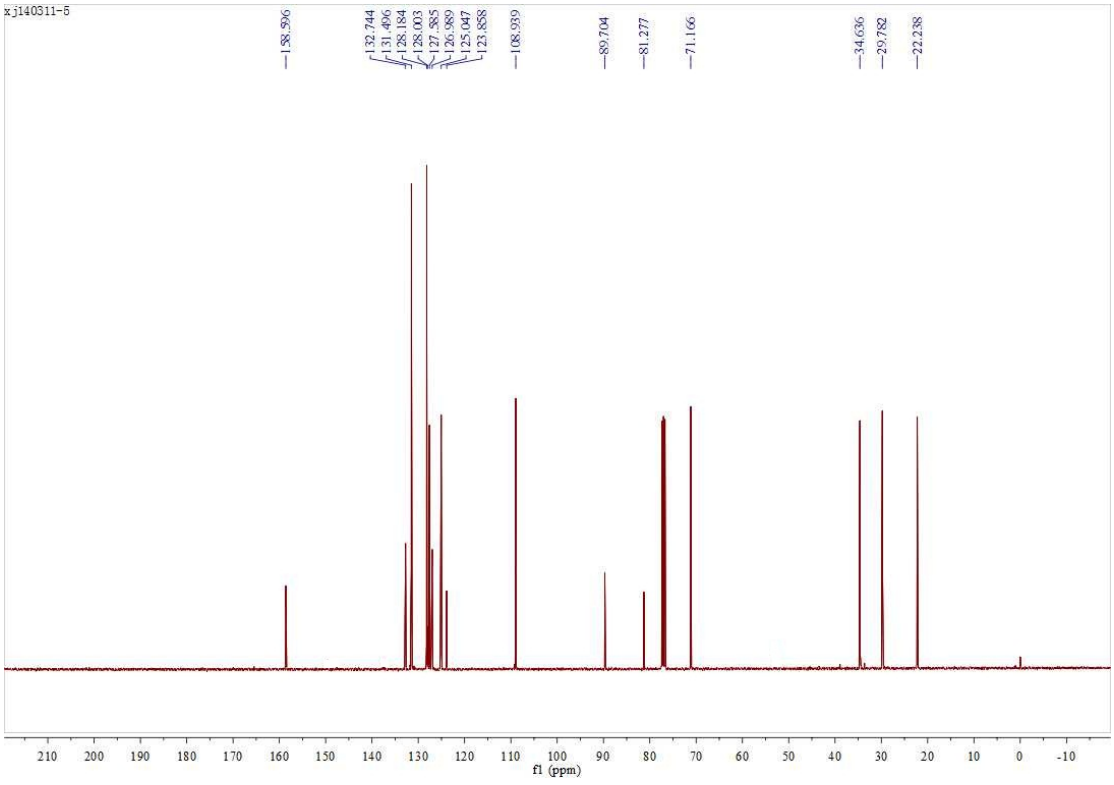


Prepared according to General Procedure **A.**

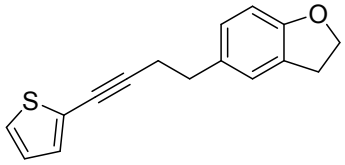
^{1}H NMR (400 MHz, $CDCl_3$) δ7.41 – 7.35 (m, 2H), 7.31 – 7.24 (m, 3H), 7.10 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.54 (t, *J* = 8.7 Hz, 2H), 3.18 (t, *J* = 8.7 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.60, 132.74, 131.50, 128.18, 128.00, 127.59, 126.99, 125.05, 123.86, 108.94, 89.70 , 81.28, 71.17, 34.64, 29.78, 22.24.


xj140311-5
7.384
7.374
7.365
7.360
7.284
7.274
7.270
7.263
7.257
7.236
7.096
7.007
6.987
6.735
6.715
4.561
4.540
4.518
3.197
3.176
3.154
2.860
2.841
2.823
2.655
2.637
2.618
0.000
1.919
2.861
0.948
0.982
0.958
2.000
2.011
1.987
1.974
f1 (ppm)


xj140311-5
158.596
132.744
131.496
128.184
128.003
127.885
126.989
125.047
123.858
108.939
89.704
81.277
71.166
34.636
29.782
22.238
f1 (ppm)

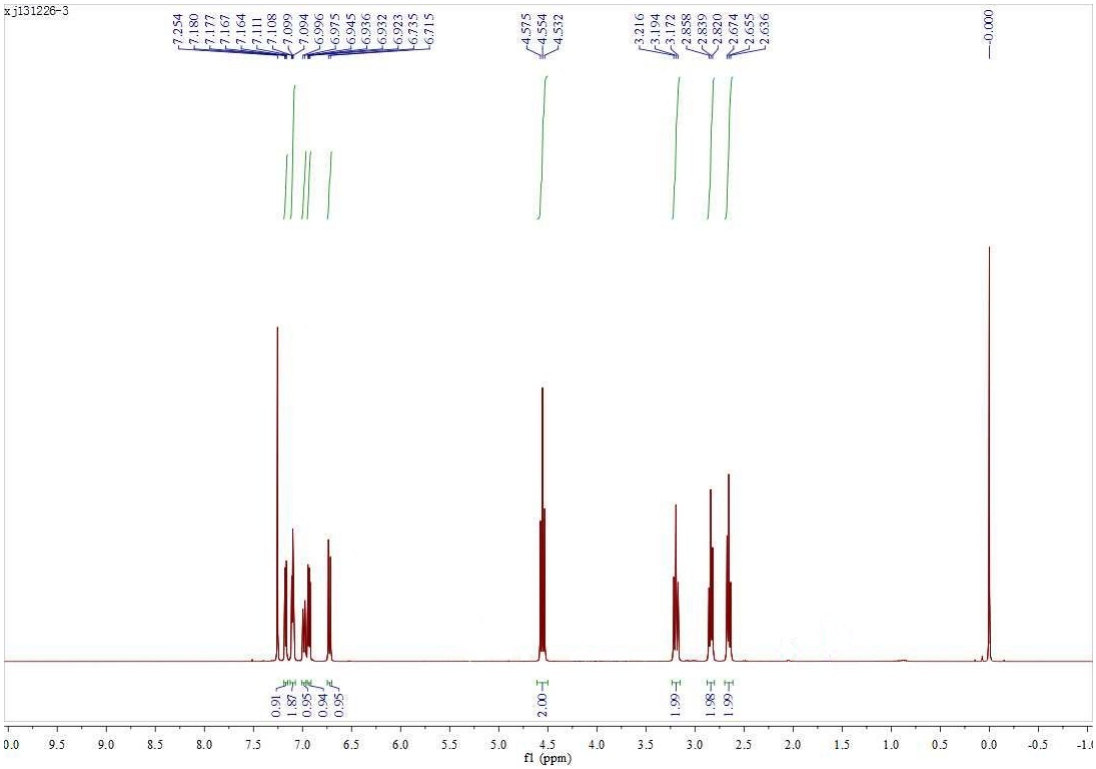
5-(4-(thiophen-2-yl)but-3-yn-1-yl)-2,3-dihydrobenzofuran **(1u)**

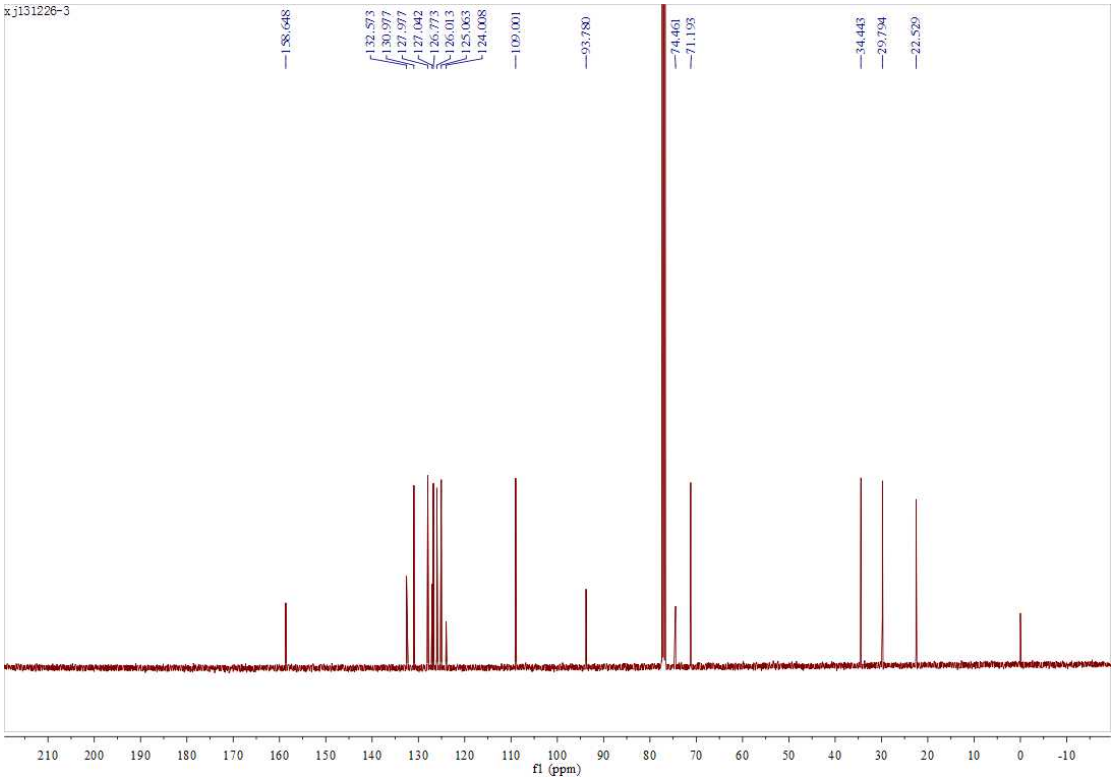


Prepared according to General Procedure **A.**

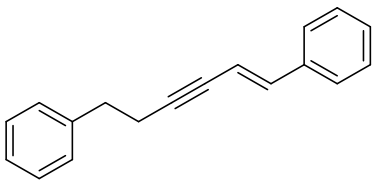
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.10 (dd, *J* = 5.1, 1.4 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.93 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.55 (t, *J* = 8.7 Hz, 2H), 3.19 (t, *J* = 8.7 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.65, 132.57, 130.98, 127.98, 127.04, 126.77, 126.01, 125.06, 124.01, 109.00, 93.78, 74.46, 71.19, 34.44, 29.79, 22.53.



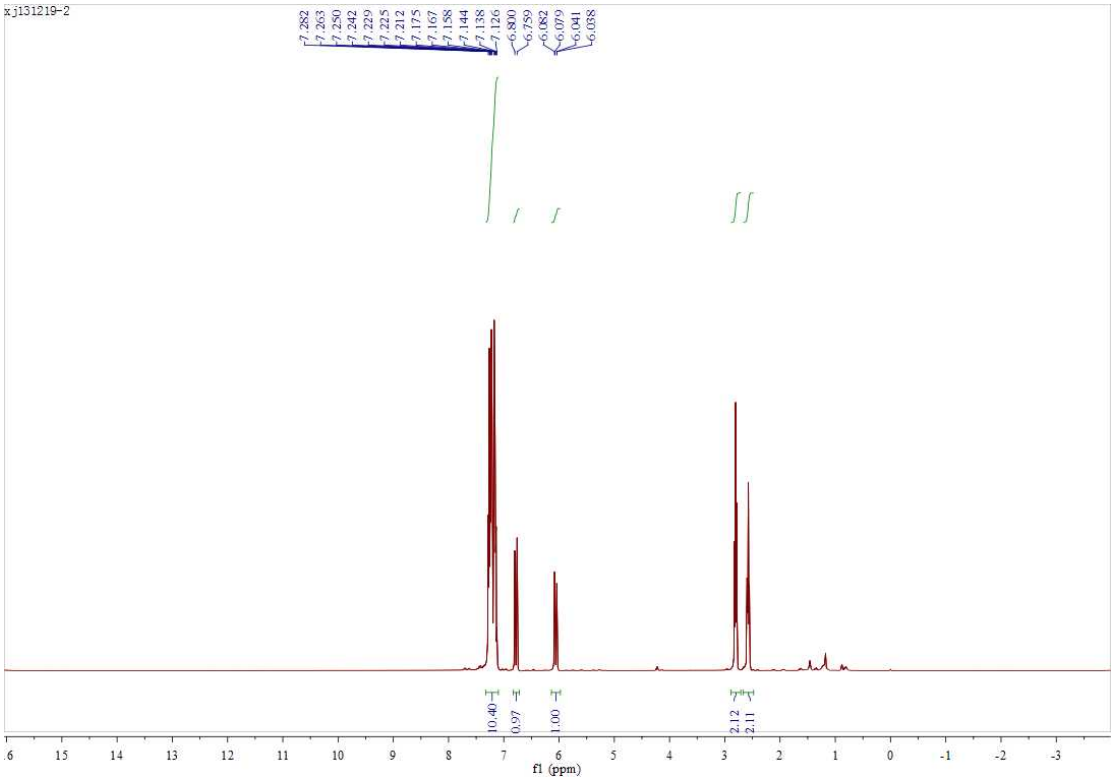


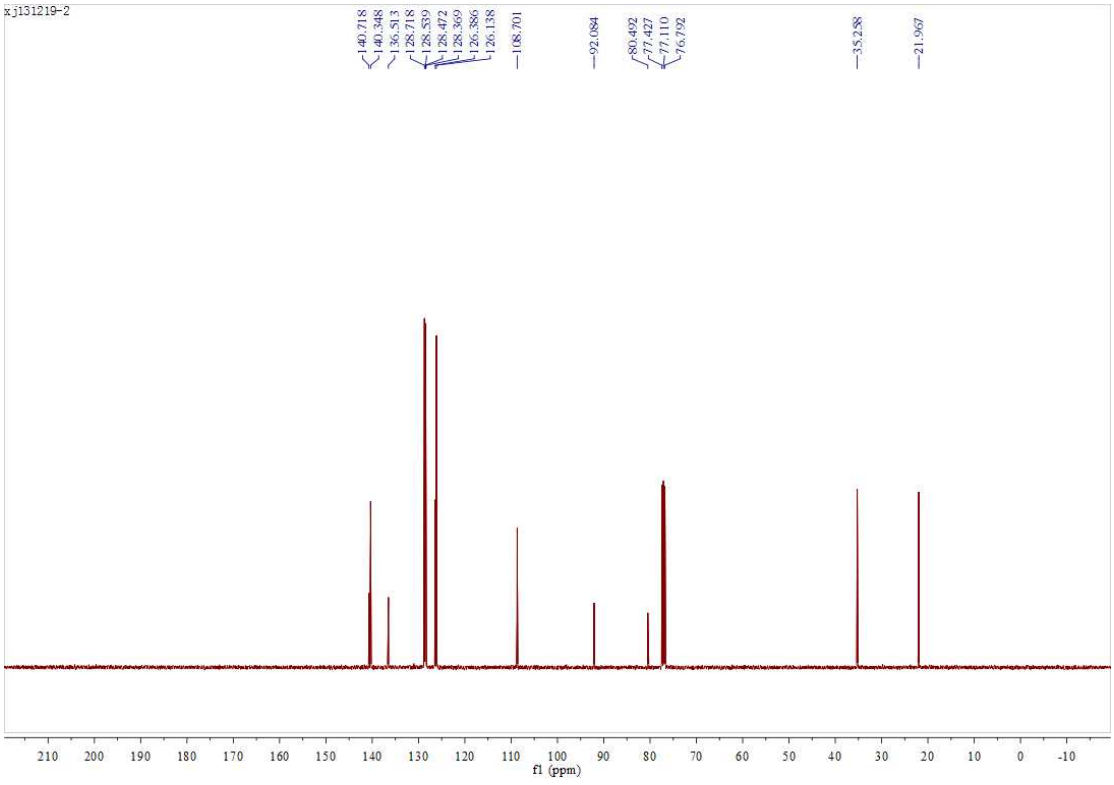
(E)-hex-1-en-3-yne-1,6-diyldibenzene **(1v)**[1]



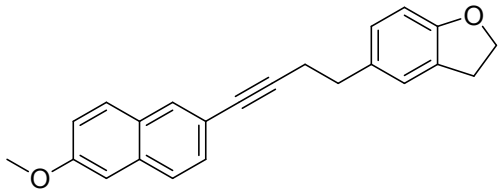
To a suspension of tetrakis(triphenylphosphine)palladium(0) (0.29 mmol) and (*E*)-styrylboronic acid (5 mmol) in dioxane (50 mL) was added (4-bromobut-3-yn-1-yl)benzene (7 mmol) and 3.0 M aqueous potassium hydroxide (10 mL) and the mixture stirred at 90 °C for 14 h. The reaction mixture was concentrated in vacuo and filtered through a plug of silica, eluting with diethyl ether (3×10 mL). The solvent was removed in vacuo and the crude residue was purified by flash chromatography to give compound **1u** as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.10 (m, 10H), 6.78 (d, *J* = 16.2 Hz, 1H), 6.06 (d, *J* = 16.2, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.72, 140.35, 136.51, 128.72, 128.54, 128.47, 128.37, 126.39, 126.14, 108.70, 92.08, 80.49, 35.26, 21.97.


xj131219-2
7.282
7.263
7.250
7.242
7.229
7.225
7.212
7.175
7.167
7.158
7.144
7.138
7.126
6.800
6.759
6.082
6.079
6.041
6.038
10.40
0.97
1.00
2.12
2.11
f1 (ppm)


xj131219-2
140.718
140.348
136.513
128.718
128.539
128.472
128.369
126.386
126.138
108.701
92.084
80.492
77.427
77.110
76.792
35.238
21.967
f1 (ppm)

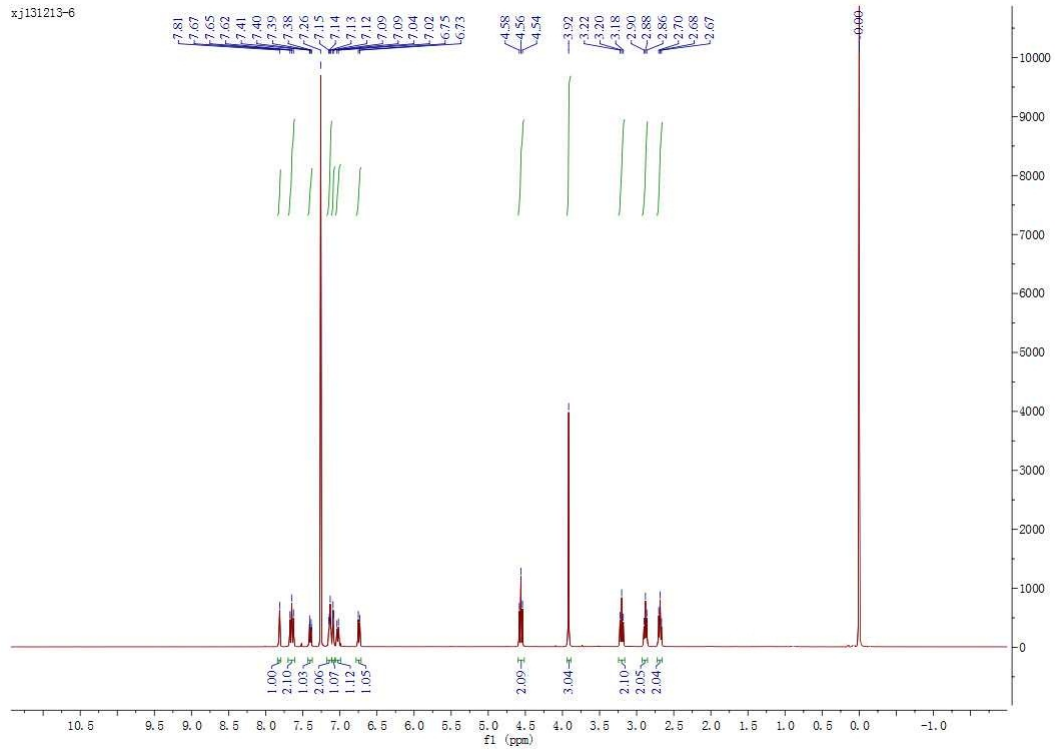
5-(4-(6-methoxynaphthalen-2-yl)but-3-yn-1-yl)-2,3-dihydrobenzofuran **(1w)**

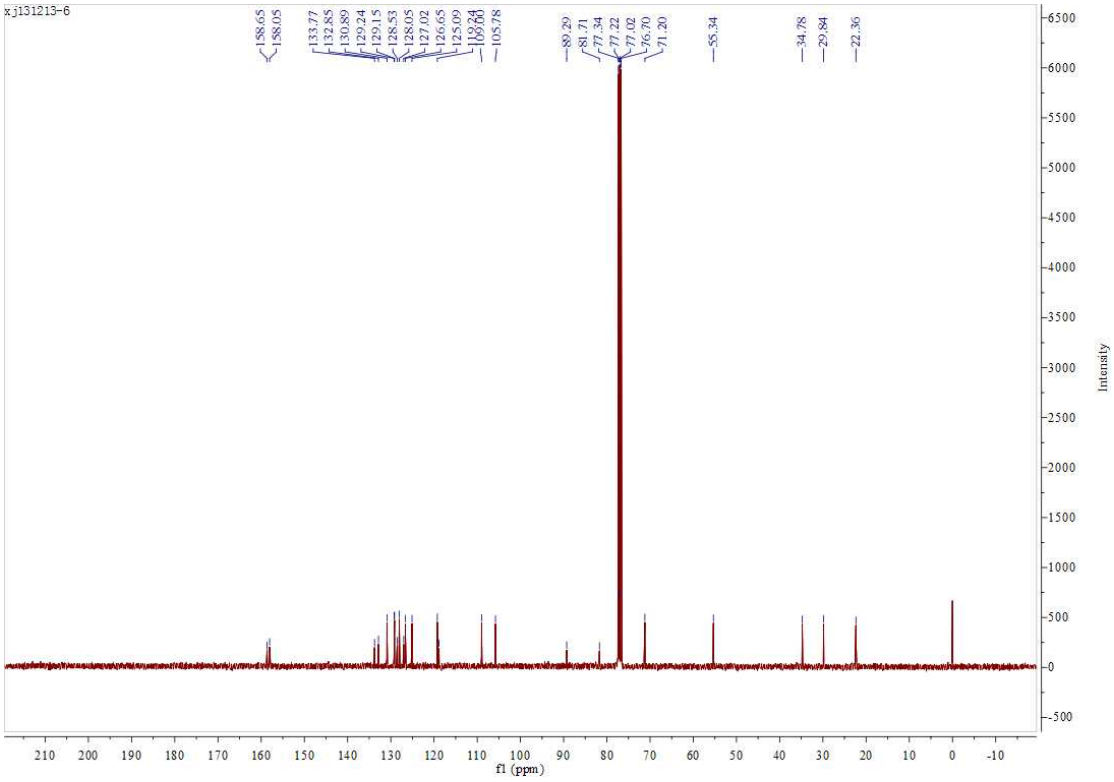


Prepared according to General Procedure **A.**

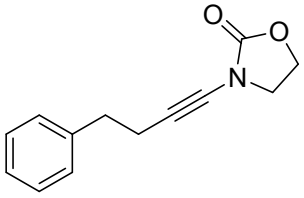
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.65 (t, *J* = 9.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.09 (s, 1H), 7.02 (d, *J* = 8 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.56 (t, *J* = 8.7 Hz, 2H), 3.93 (s, 3H), 3.20 (t, *J* = 8.6 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.65, 158.05, 133.77, 132.85, 130.89, 129.24, 129.15, 128.53, 128.05, 127.02, 126.65, 125.09, 119.24, 118.84, 109.00, 105.78, 89.29, 81.71, 71.20, 55.34, 34.78, 29.84, 22.36.



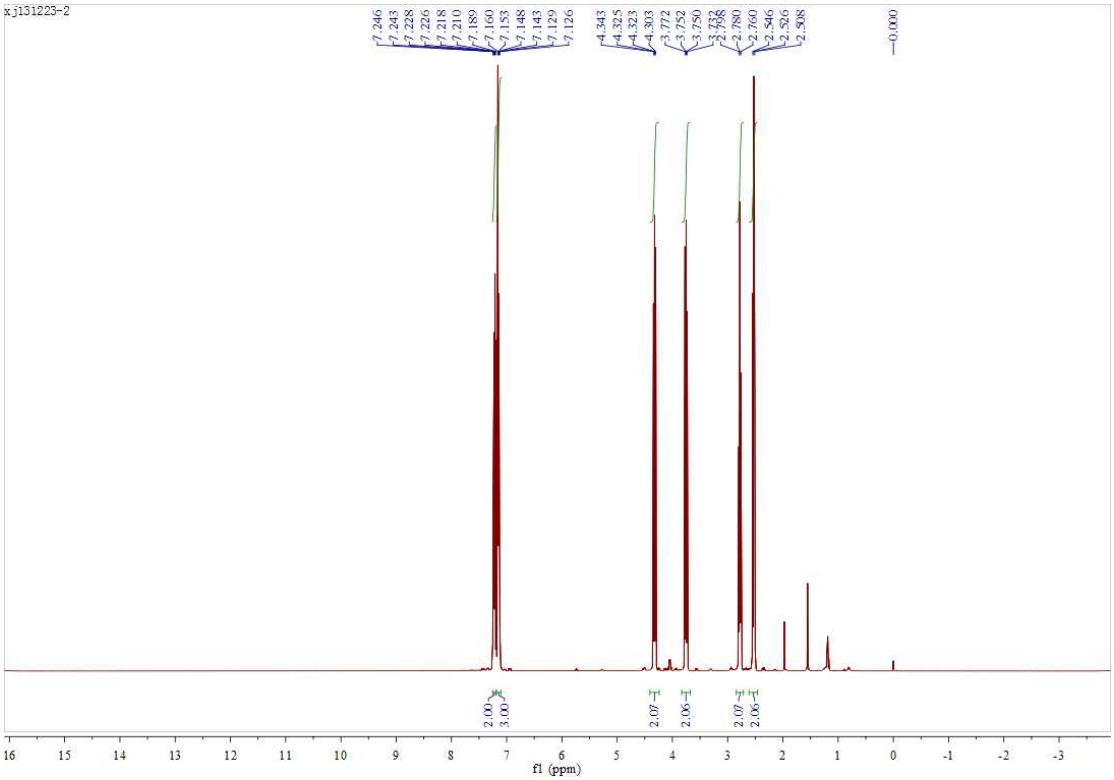


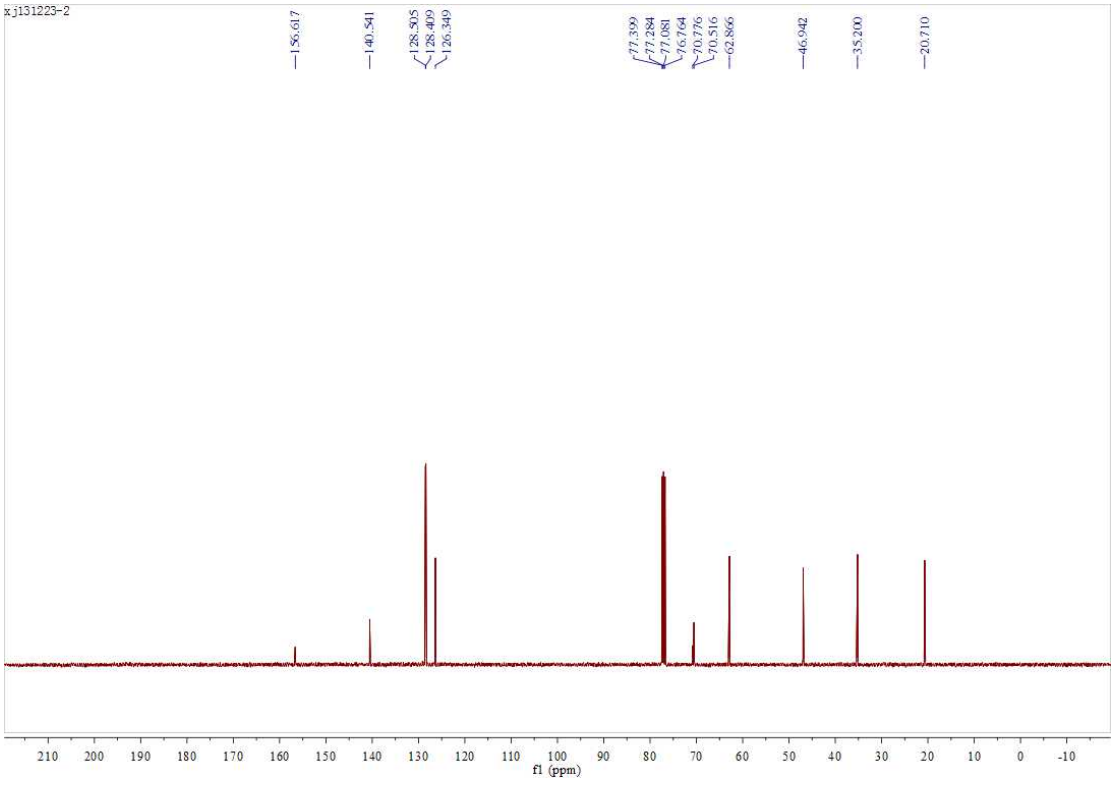
3-(4-phenylbut-1-yn-1-yl)oxazolidin-2-one **(1x)**[1]



To a solution of oxazolidin-2-one (10 mmol), $CuCl_2$ (0.4 mmol) and sodium carbonate (4 mmol) in toluene (20 mL) was added pyridine (4 mmol). Oxygen was bubbled through the reaction mixture (20 min). The reaction was heated to 70 °C under an atmosphere of oxygen. A solution of but-3-yn-1-ylbenzene (2 mmol) in toluene (20 mL) was added dropwise over 4 h, by use of a syringe pump. Once the addition was complete, the reaction mixture was stirred at 70 °C for a further 12 h. The reaction mixture was cooled to room temperature and filtered through a plug of celite, eluting with dichloromethane (3 × 25 mL). The solvent was removed in vacuo and the crude residue was purified by flash chromatography to give compound **1w** as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.19 – 7.10 (m, 3H), 4.41 – 4.24 (m, 2H), 3.83 – 3.68 (m, 2H), 2.78 (t, J = 7.6 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.62, 140.54, 128.50, 128.41, 126.35, 70.78, 70.52, 62.87, 46.94, 35.20, 20.71.


xj131223-2
7.246
7.243
7.228
7.226
7.218
7.210
7.189
7.160
7.153
7.148
7.143
7.129
7.126
4.343
4.325
4.323
4.303
3.772
3.752
3.750
3.732
3.708
2.780
2.760
2.546
2.526
2.308
0.000
2.00
3.00
2.07
2.06
2.07
2.06
f1 (ppm)


xj131223-2
156.617
140.541
128.505
128.409
126.349
77.399
77.284
77.081
76.764
70.776
70.516
62.866
46.942
35.200
20.710
f1 (ppm)

III. General Procedure for Copper-Catalyzed Trifluoromethylaryl-ation of Alkynes.

1. General Procedure C for Copper-Catalyzed Trifluoromethylarylation of Alkynes.

A reaction tube was charged with Cu (1.28 mg, 10 mmol%), **1** (0.2 mmol) and **2a** (0.24 mmol, 81.6 mg), the vessel was sealed before being evacuated and filled with argon (three times). DMF (0.4 mmol, 30.8 μL), and DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 24 h at the specified temperature. At the conclusion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with brine for once and then dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **3**.

2. General Procedure D for Copper-Catalyzed Trifluoromethylarylation of Alkynes.

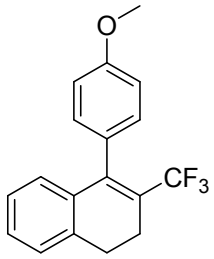
A reaction tube was charged with Cu (1.28 mg, 10 mmol%), **1** (0.2 mmol) and **2a** (0.4 mmol, 136 mg), the vessel was sealed before being evacuated and filled with argon (three times). DMF (0.4 mmol, 30.8 μL), and DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 24 h at the specified temperature. At the conclusion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with brine for once and then dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **3**.

3. General Procedure E for Copper-Catalyzed Trifluoromethylarylation of Alkynes.

A reaction tube was charged with Cu (0.32 mg, 2.5 mmol%), **1** (0.4 mmol) and **2b** (0.2 mmol, 80.4 mg), the vessel was sealed before being evacuated and filled with argon (three times). DMF (0.4 mmol, 30.8 μL), and DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 24 h at the specified temperature. At the conclusion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with brine for once and then dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **3**.

4. Copper-Catalyzed Trifluoromethylarylation of Alkynes.

4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3a**)



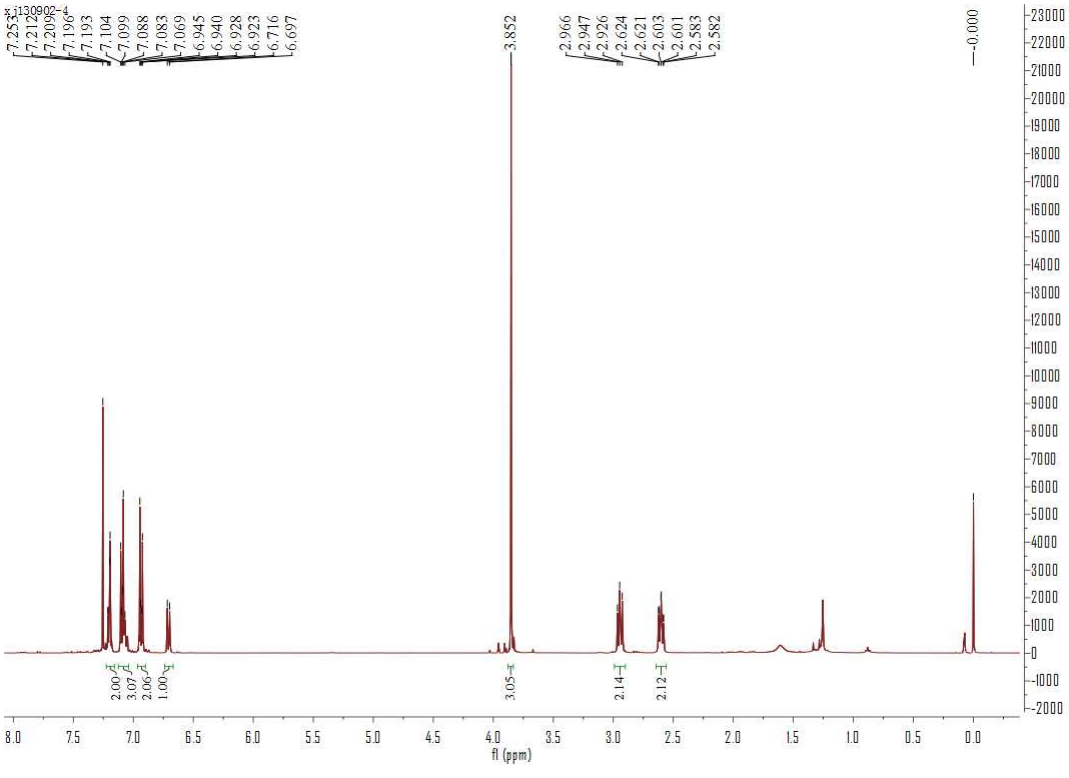
Prepared according to General Procedure **C.**

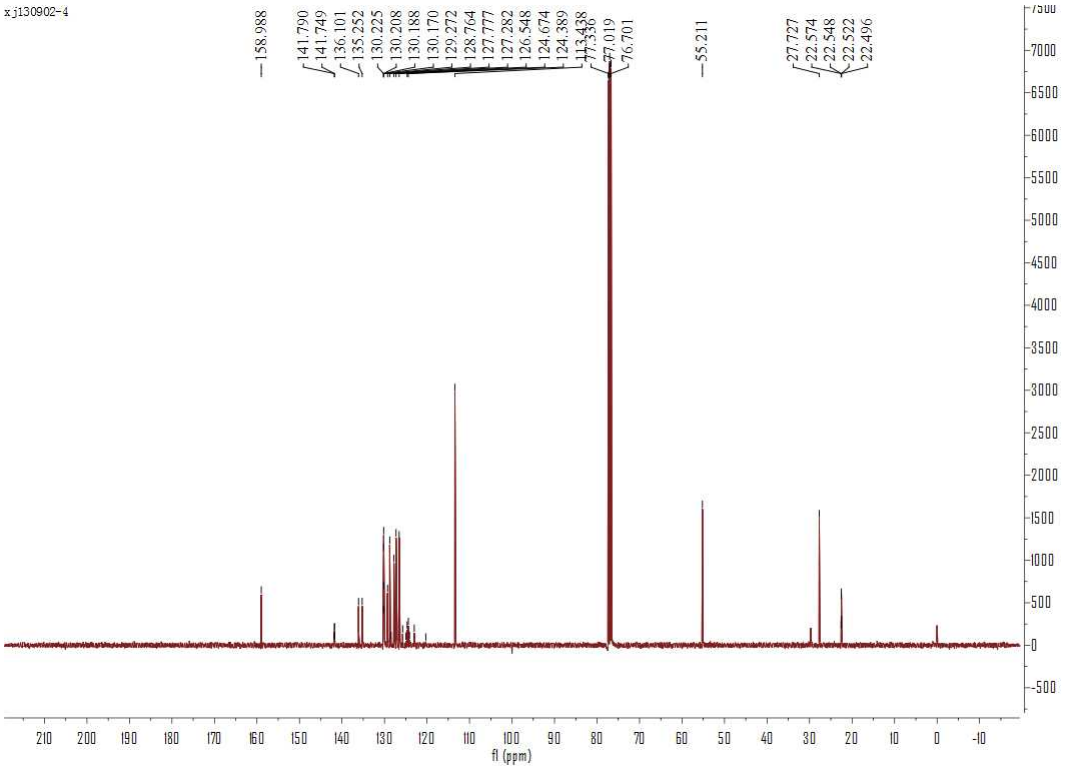
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22– 7.19 (m, 2H), 7.12 – 7.04 (m, 3H), 6.94 (d, *J* = 8.8Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 7.9, 2H).

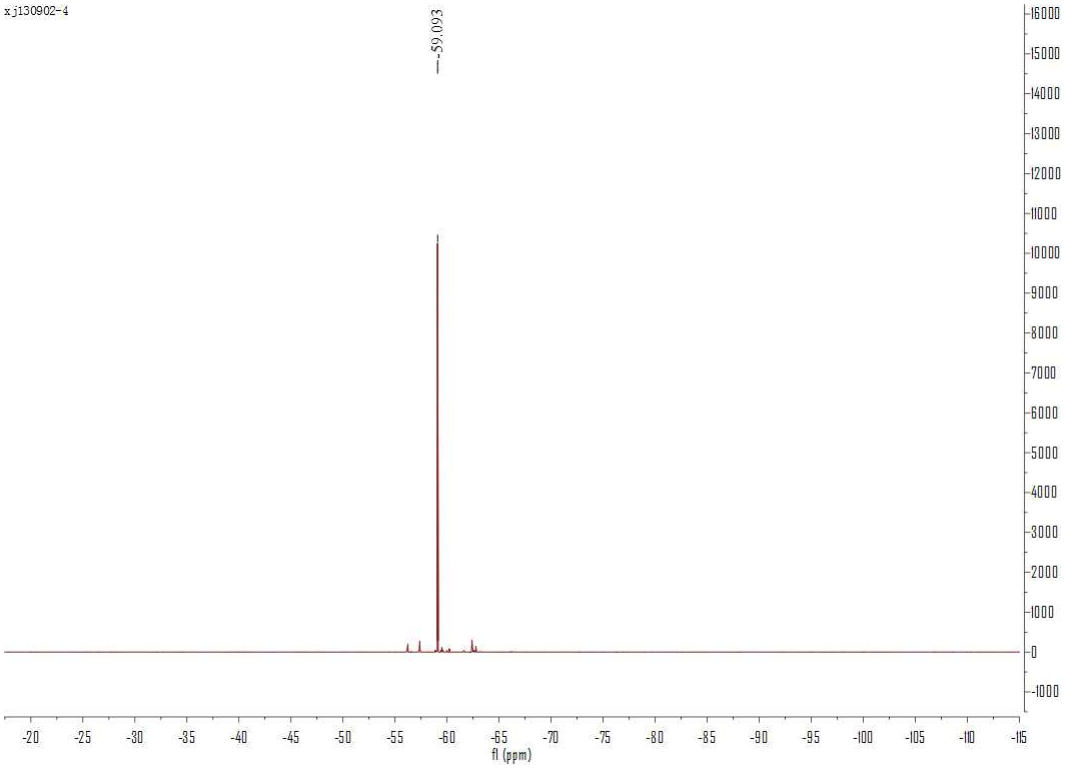
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.99, 141.77 (q, *J* = 4.0 Hz), 136.10, 135.25, 130.20 (q, *J* = 2.0, Hz), 129.27, 128.76, 127.78, 127.28, 126.55, 124.50 (q, *J* = 28.5 Hz) , 124.36 (q, *J* = 271 Hz), 113.44, 55.21, 27.73, 22.54 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.09.

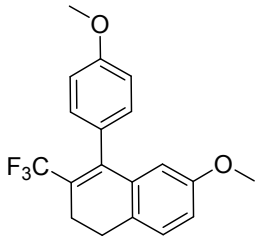
HRMS calcd for $C_{18}H_{15}F_3O$ ([M]$^+$): 304.1075; found: 304.1071.




xj130902-4
158.988
141.790
141.749
136.101
135.252
130.225
130.208
130.188
130.170
129.272
128.764
127.777
127.282
126.548
124.674
124.389
113.438
77.336
77.019
76.701
55.211
27.727
22.574
22.548
22.522
22.496
f1 (ppm)


xj130902-4
-59.093
f1 (ppm)

6-methoxy-4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3b**)



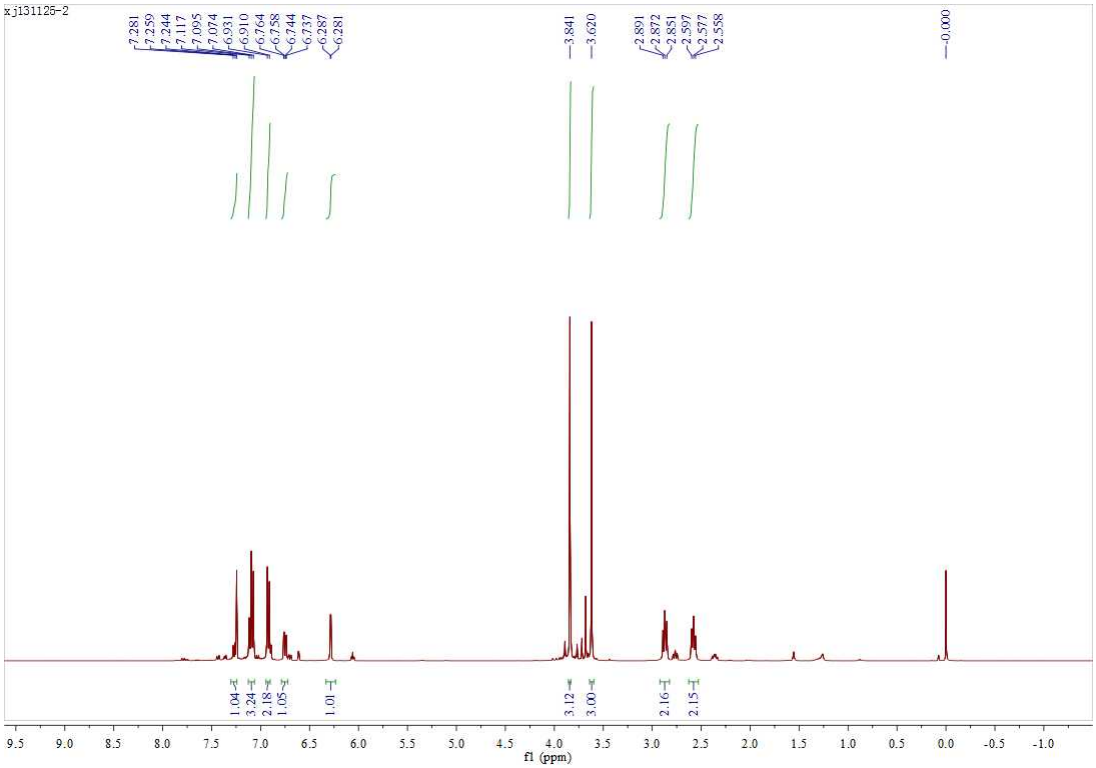
Prepared according to General Procedure **C.**

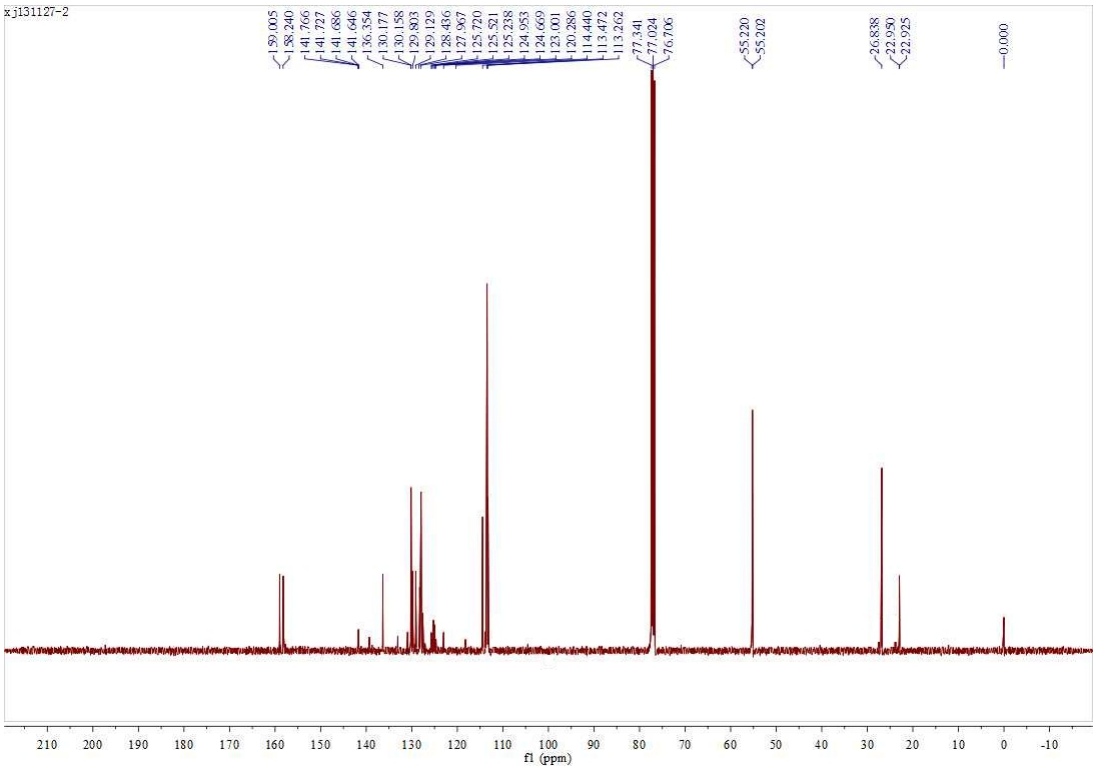
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.75 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.28 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 3H), 3.62 (s, 3H), 2.87 (t, *J* = 7.9 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H).

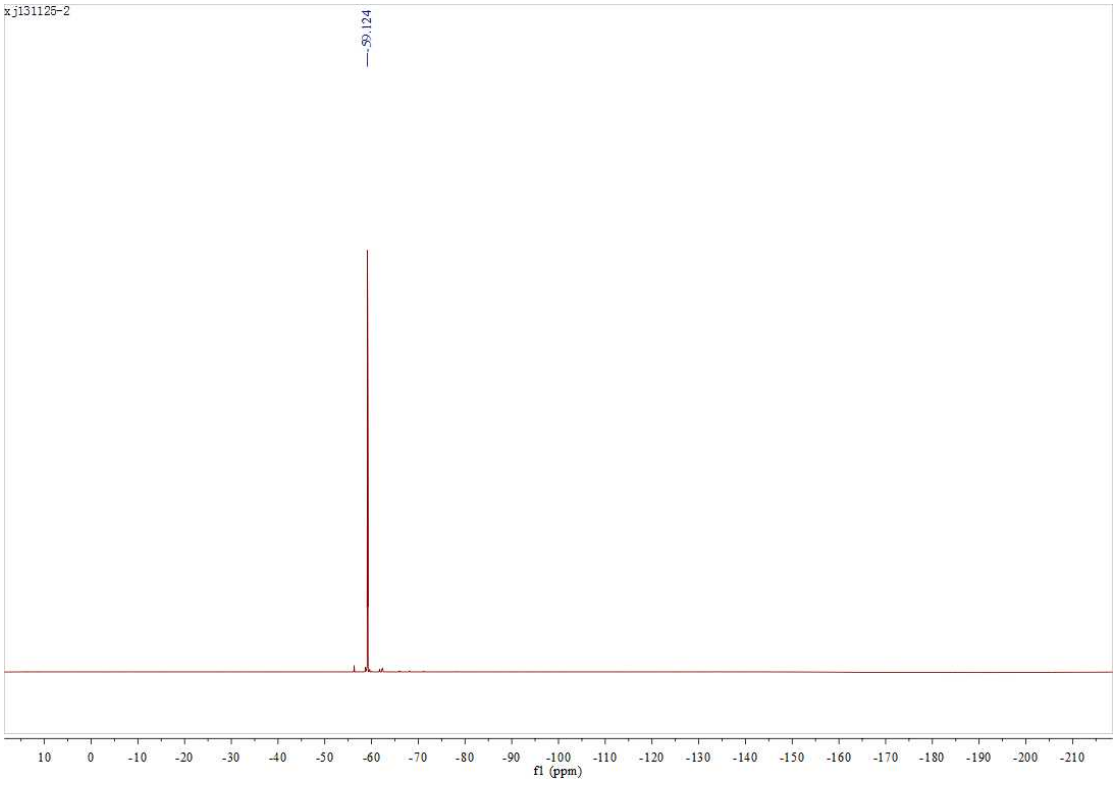
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.01, 158.25, 141.72 (q, *J* = 4.0 Hz), 136.36, 130.17 (q, *J* = 1.9 Hz), 129.81, 129.14, 127.98, 125.10 (q, *J* = 28.4 Hz), 124.37 (q, *J* = 272 Hz), 114.44, 113.48, 113.27, 55.24, 26.84, 22.94 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.13.

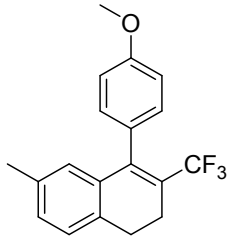
HRMS calcd for $C_{19}H_{17}F_3O_2$ ([M]$^+$): 334.1181; found: 334.1184.




xj131127-2
159.005
158.240
141.766
141.727
141.686
141.646
136.354
130.177
130.158
129.803
129.129
128.436
127.957
125.720
125.521
125.238
124.953
124.669
123.001
120.286
114.440
113.472
113.262
77.341
77.024
76.706
55.220
55.202
26.838
22.950
22.925
0.000
f1 (ppm)


xj131126-2
-59.124
f1 (ppm)

4-(4-methoxyphenyl)-6-methyl-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3c**)



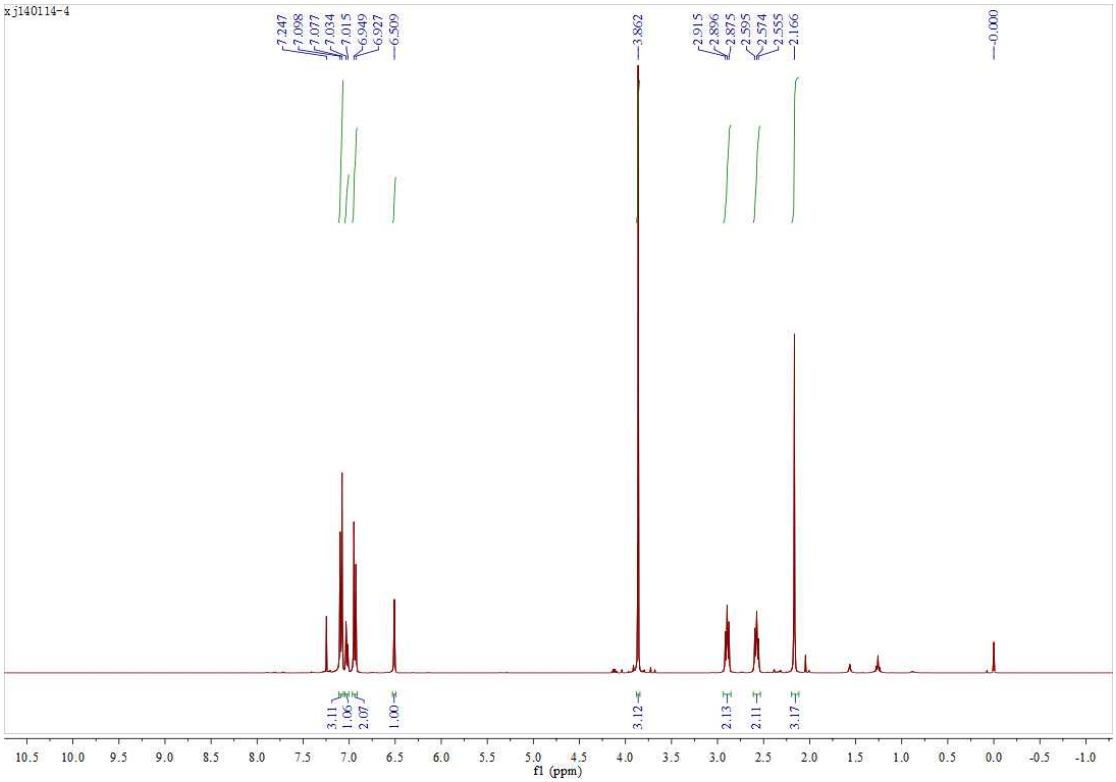
Prepared according to General Procedure **C.**

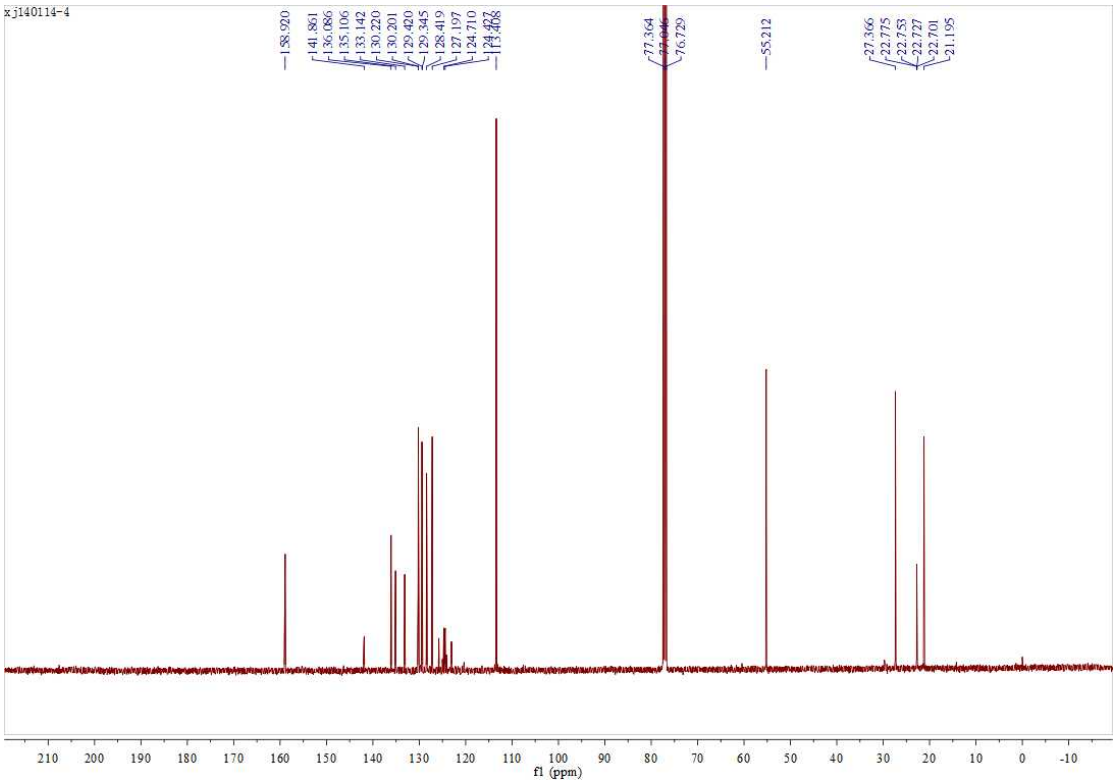
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 3H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.51 (s, 1H), 3.86 (s, 3H), 2.9O (t, *J* = 8.0 Hz, 2H), 2.57 (t, *J* = 8.0 Hz, 2H), 2.17 (s, 3H).

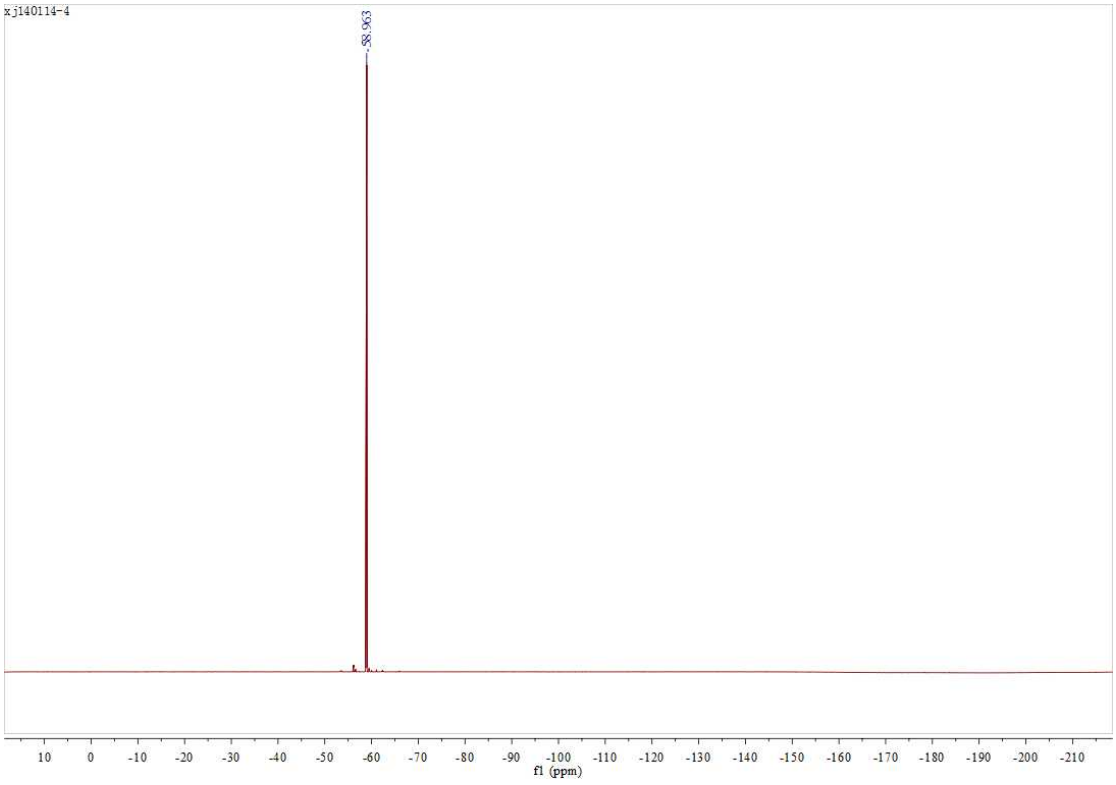
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.92, 141.88 (q, *J* = 4.0 Hz), 136.09, 135.11, 133.14, 130.21 (q, *J* = 1.9 Hz), 129.42, 129.35, 128.42, 127.20, 124.56 (q, *J* = 28.3 Hz), 124.42 (q, *J* = 272 Hz), 113.41, 55.21, 27.37, 22.74 (q, *J* = 2.6 Hz), 21.20.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.96.

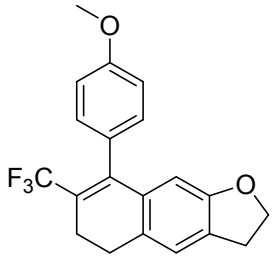
HRMS calcd for $C_{19}H_{17}F_3O$ ([M]$^+$): 318.1231; found: 318.1228.




xj140114-4
158.920
141.861
136.086
135.106
133.142
130.220
130.201
129.420
129.345
128.419
127.197
124.710
114.468
77.364
77.046
76.729
55.212
27.366
22.775
22.753
22.727
22.701
21.195
f1 (ppm)


xj140114-4
-58.963
f1 (ppm)

8-(4-methoxyphenyl)-7-(trifluoromethyl)-2,3,5,6-tetrahydronaphtho[2,3-b]furan (**3d**)



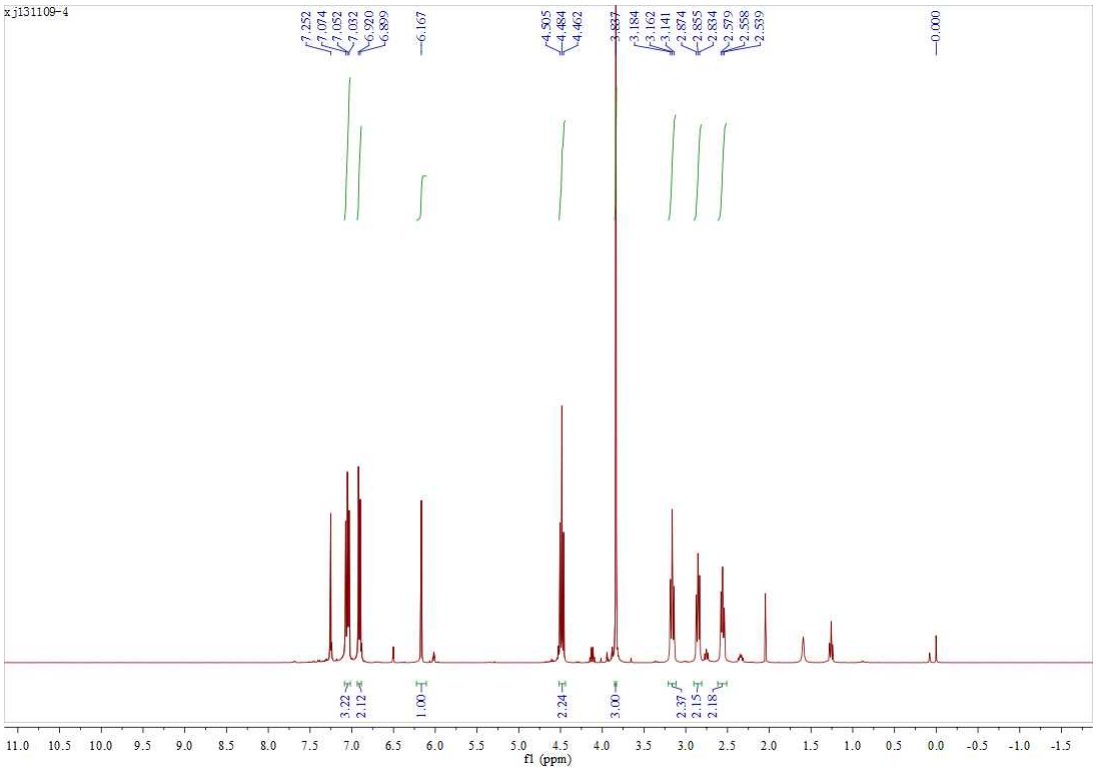
Prepared according to General Procedure **C.**

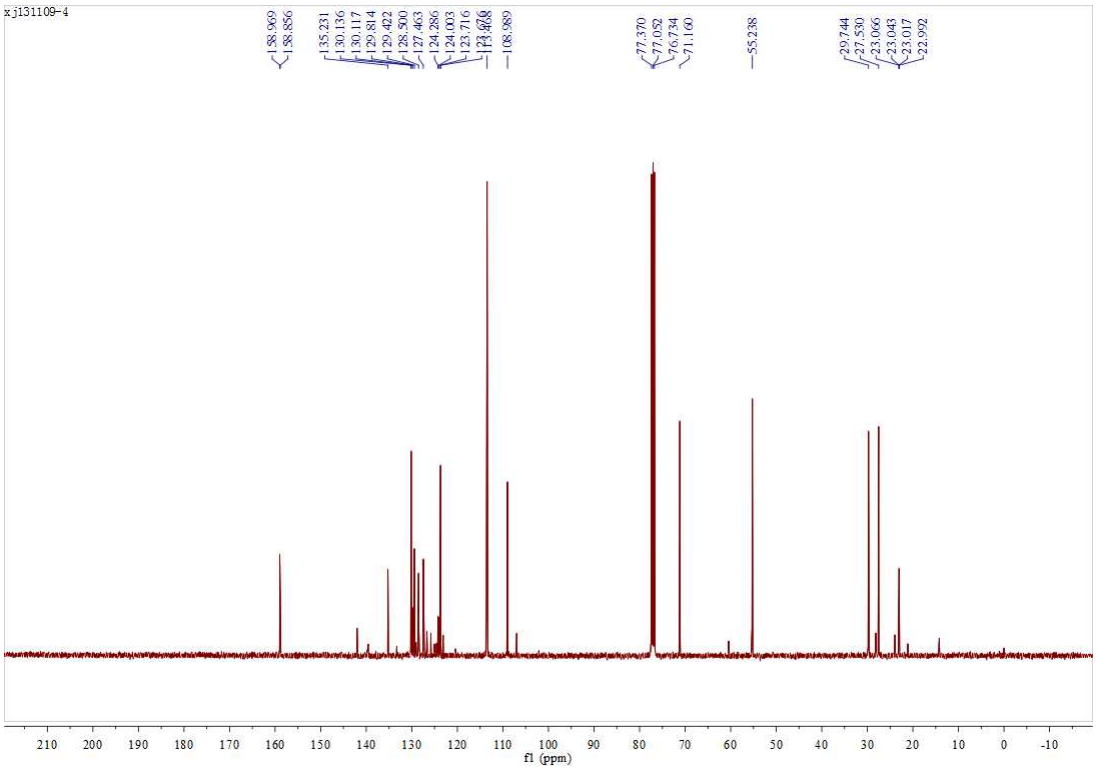
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.02 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.17 (s, 1H), 4.48 (t, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.16 (t, *J* = 8.6 Hz, 2H), 2.86 (t, *J* = 8.3 Hz,, 2H), 2.56 (t, *J* = 7.9 Hz, 2H).

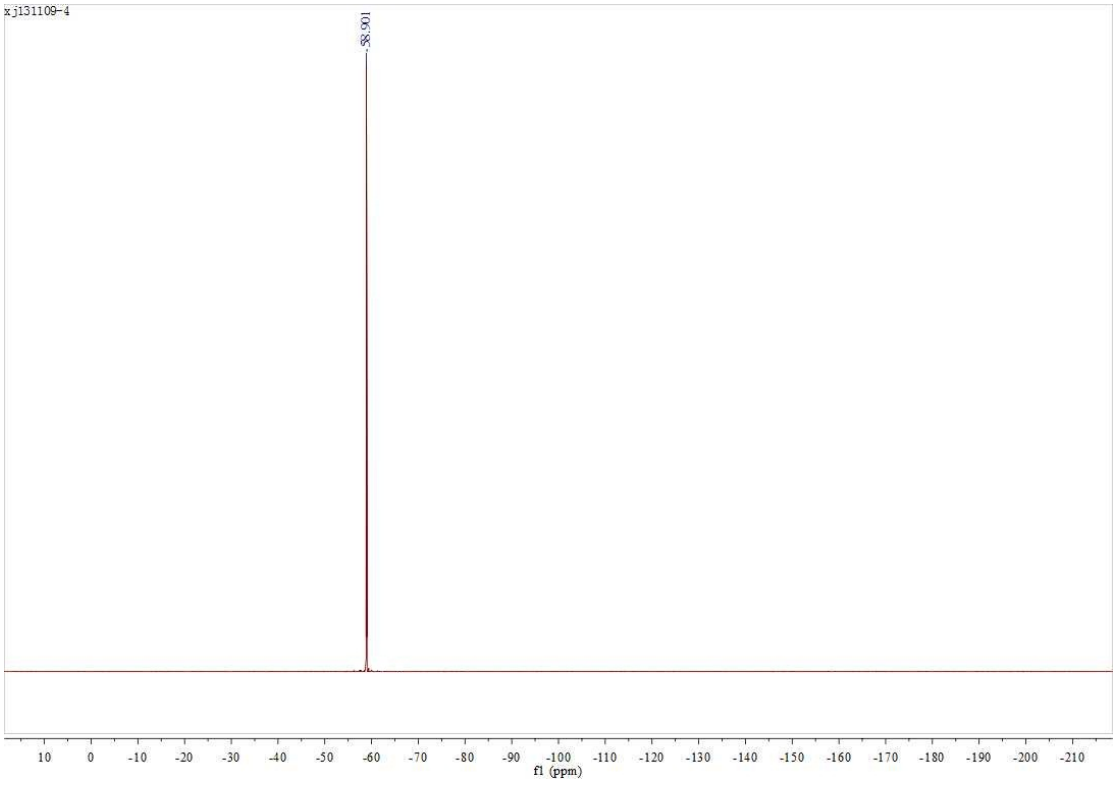
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.91, 141.99 (q, *J* = 4.0 Hz), 135.23, 130.13 (q, *J* = 1.9 Hz), 129.81, 129.42, 128.50, 127.46, 124.47 (q, *J* = 272 Hz), 124.15 (q, *J* = 28.3 Hz), 123.68, 113.47, 108.99, 71.16, 55.24, 29.74, 27.53, 23.03 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.90.

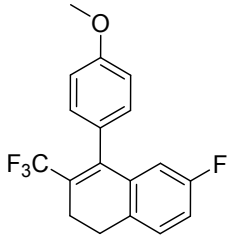
HRMS calcd for $C_{20}H_{17}F_3O_2$ ([M]$^+$): 346.1181; found: 346.1180.




xj131109-4
158.969
158.856
135.231
130.136
130.117
129.814
129.422
128.500
127.463
124.286
124.033
123.716
108.989
77.370
77.052
76.734
71.160
55.238
29.744
27.530
23.066
23.043
23.017
22.992
f1 (ppm)


xj131109-4
-58.901
f1 (ppm)

6-fluoro-4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3e**)



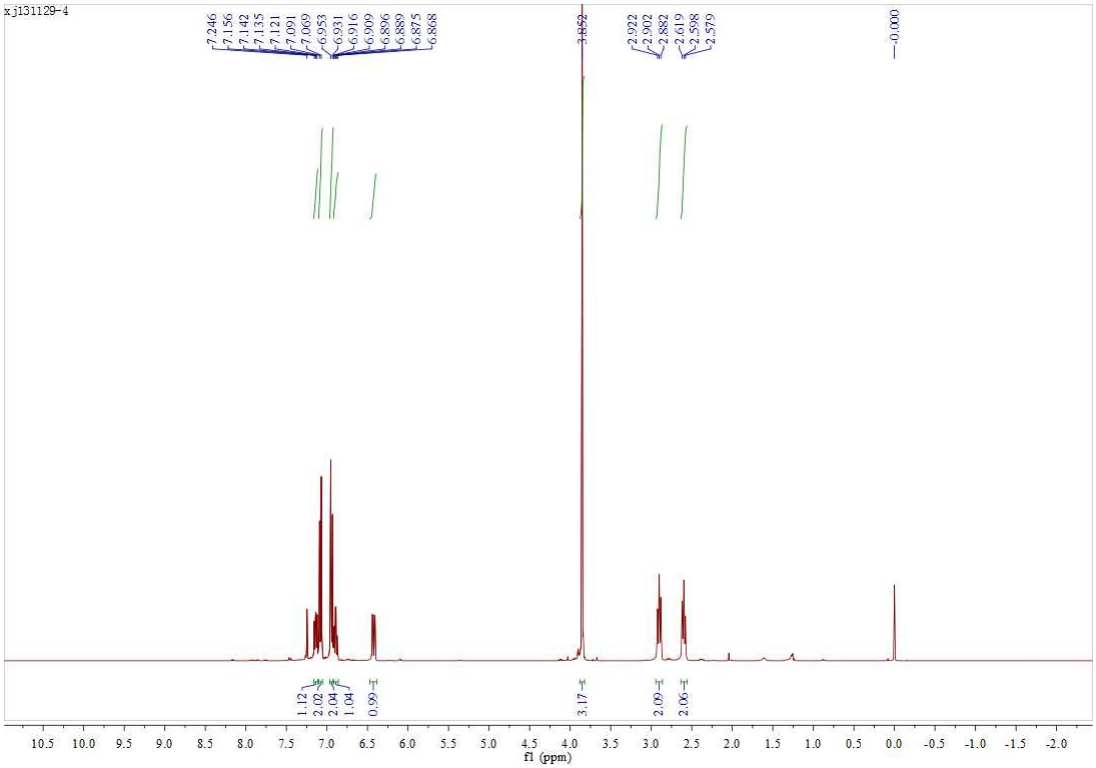
Prepared according to General Procedure **C.**

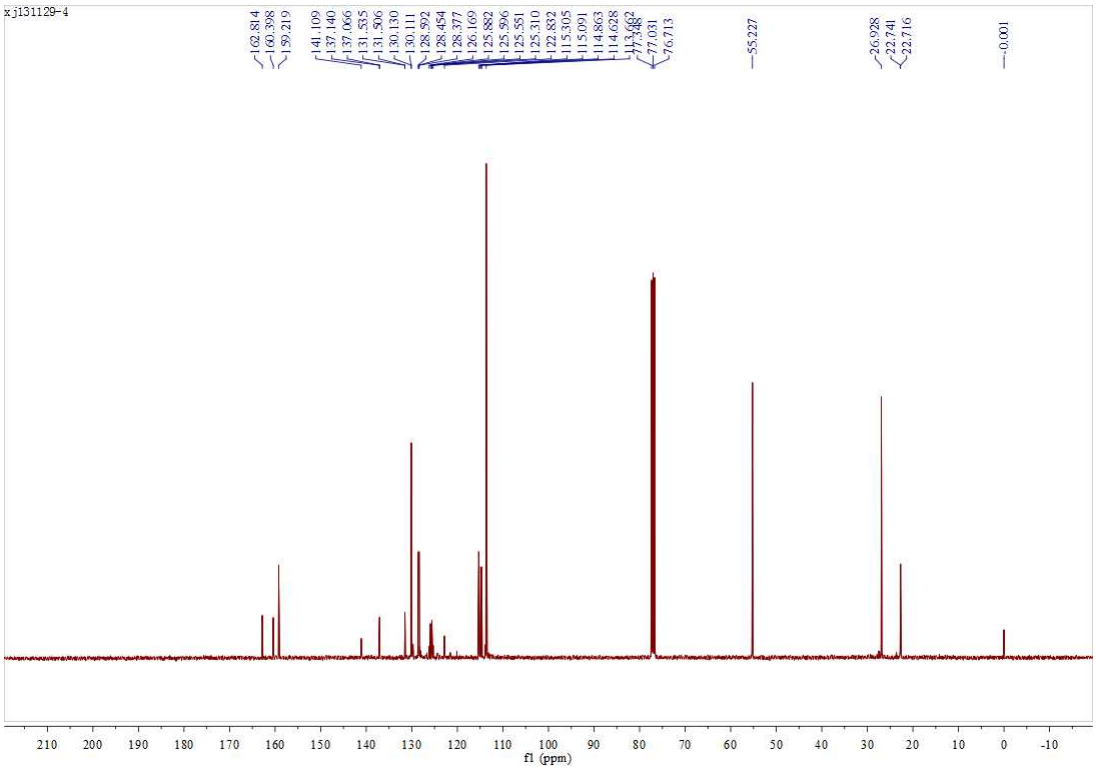
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.2, 5.7 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.89 (td, *J* = 8.3, 2.7 Hz, 1H), 6.42 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.85 (s, 3H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H).

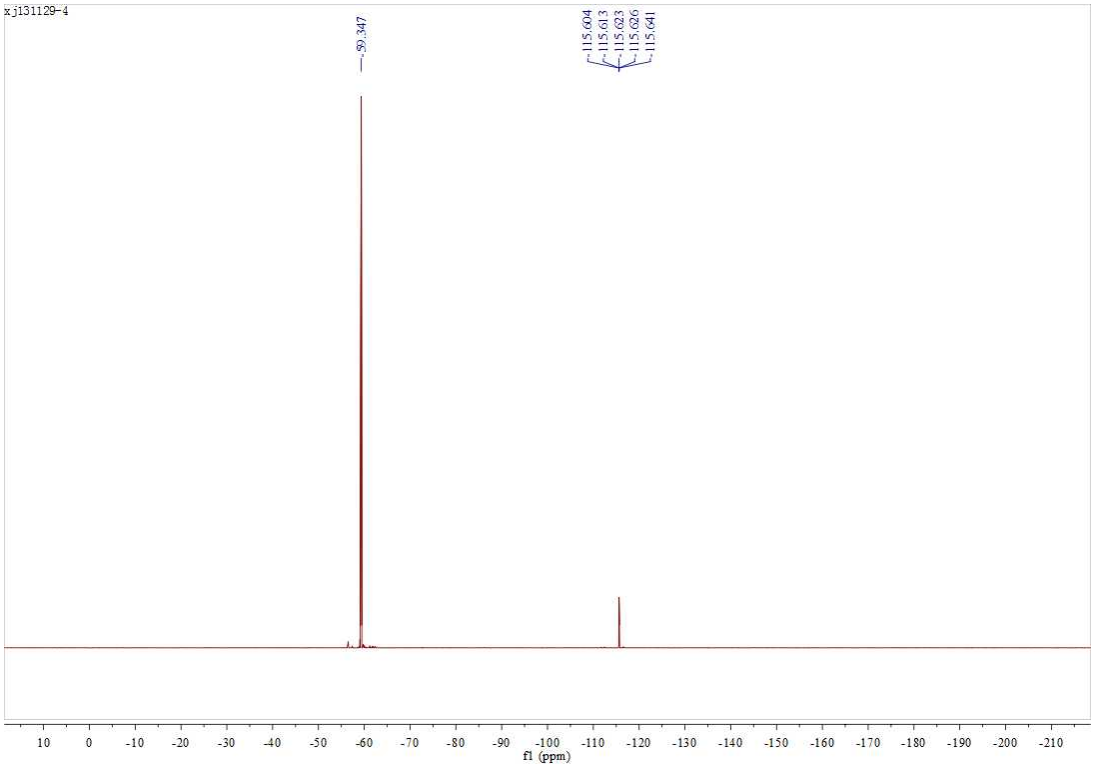
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, *J* = 242 Hz), 159.22, 141.11, 137.10 (d, *J* = 7.4 Hz), 131.52 (d, *J* = 2.9 Hz), 130.12 (q, *J* = 1.9 Hz), 128.60, 128.42 (d, *J* = 7.7 Hz), 125.74 (q, *J* = 28.6 Hz), 124.19 (q, *J* = 272 Hz), 115.20 (d, *J* = 21.4 Hz), 114.75 (d, *J* = 23.5 Hz), 113.66, 55.23, 26.93, 22.73 (q, *J* = 2.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.35 (s), -115.37 – -115.70 (m).

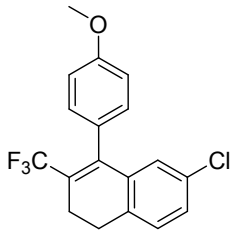
HRMS calcd for $C_{18}H_{14}F_4O$ ([M]$^+$): 322.0981; found: 322.0978.




xj131129-4
162.814
160.398
159.219
141.109
137.140
137.066
131.535
131.506
130.130
130.111
128.592
128.454
128.377
126.169
125.882
125.906
125.551
125.310
122.852
115.305
115.091
114.863
114.628
113.662
77.348
77.031
76.713
55.227
26.928
22.741
22.716
0.001
fl (ppm)


xj131129-4
-59.347
115.604
115.613
115.623
115.626
115.641
fl (ppm)

6-chloro-4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3f**)



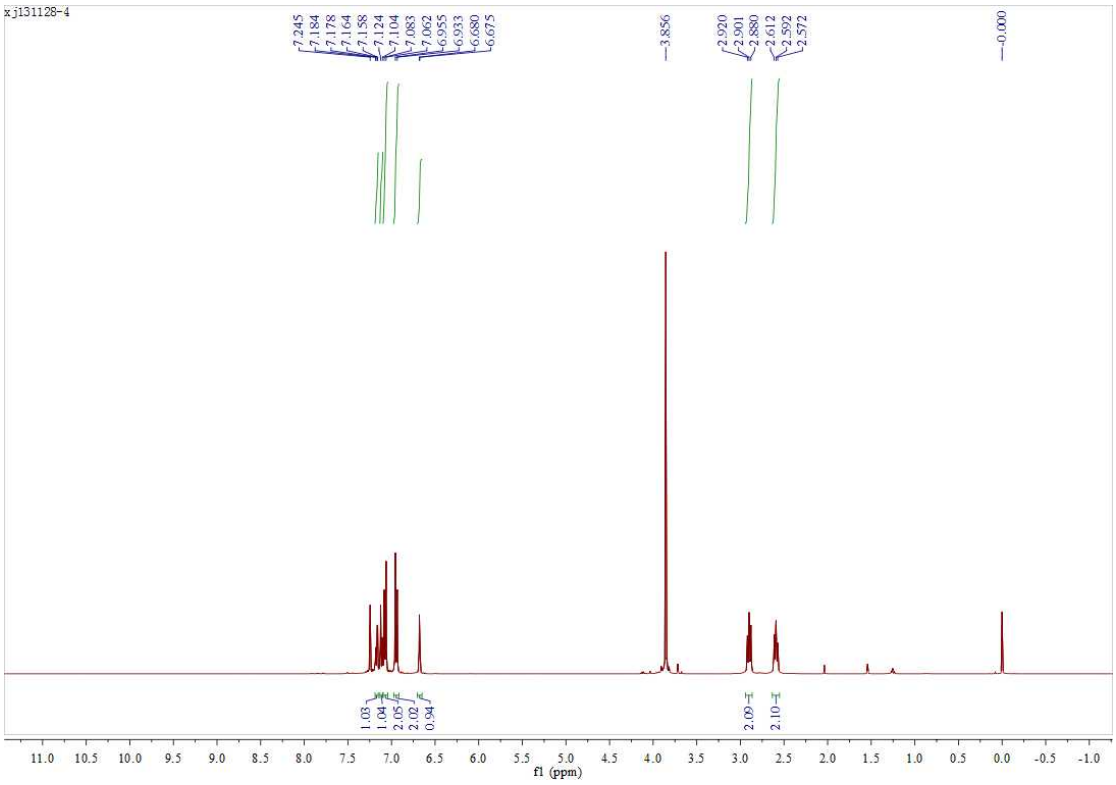
Prepared according to General Procedure **C.**

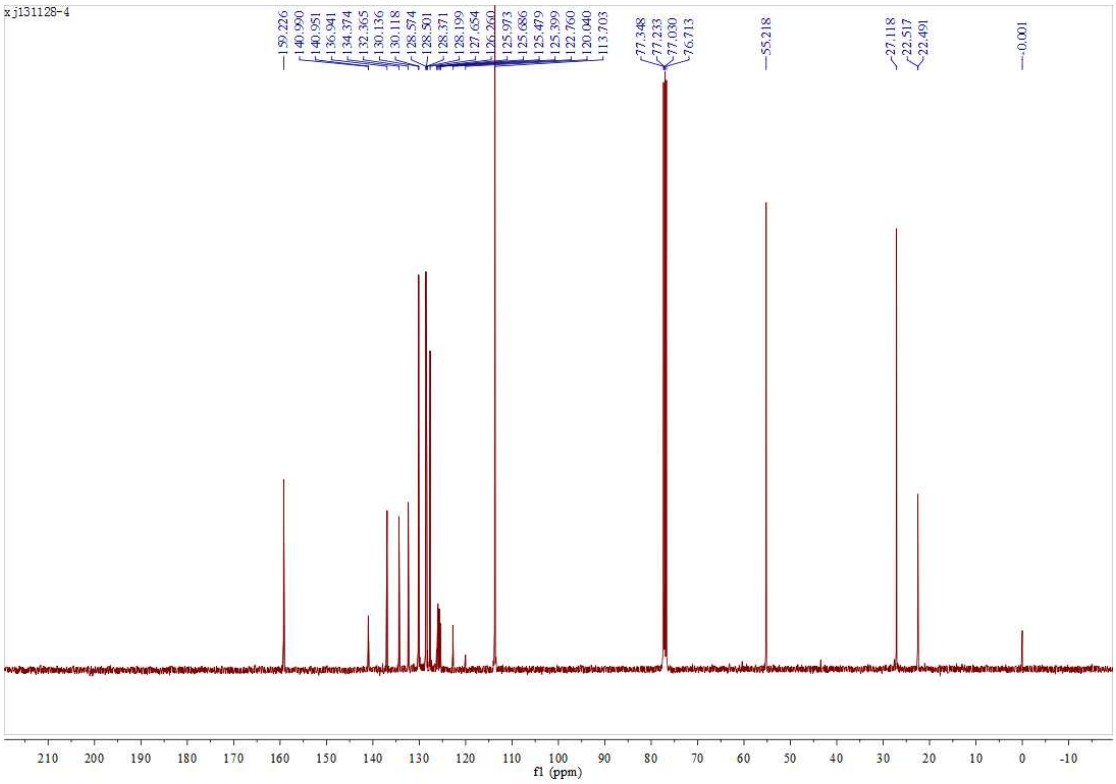
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.0, 1H), 7.11 (d, *J* = 8.0, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 2 Hz, 1H), 3.86 (s, 3H), 2.900 (t, *J* = 8.0, 2H), 2.59 (t, *J* = 8.0 Hz, 2H).

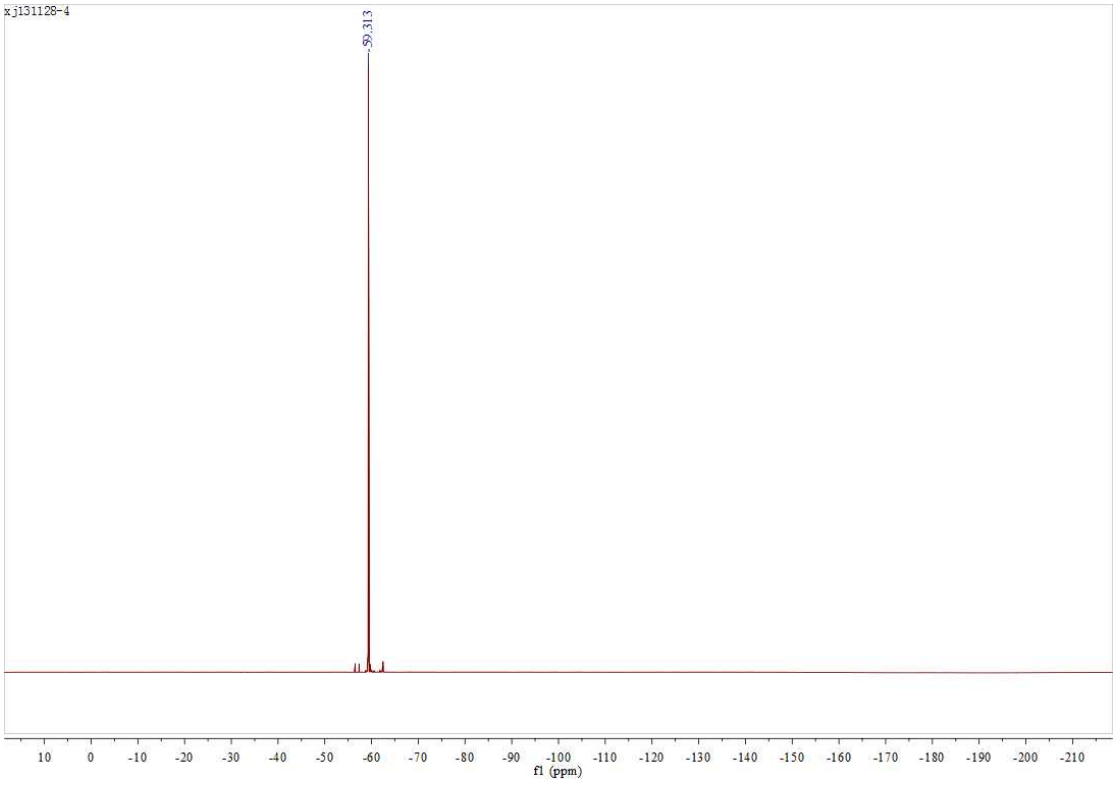
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.23, 140.97 (q, *J* = 4.0 Hz), 136.94, 134.37, 132.37, 130.13 (q, *J* = 1.9 Hz), 128.57, 128.50, 128.37, 127.65, 125.88 (q, *J* = 28.7 Hz), 124.12 (q, *J* = 271 Hz), 113.70, 55.22, 27.12, 22.50 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.31.

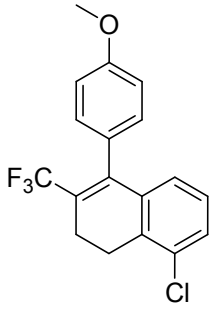
HRMS calcd for $C_{18}H_{14}ClF_3O$ ($[M]^+$): 338.0685; found: 338.0683.




xj131128-4
199.226
140.990
140.951
136.941
134.374
132.365
130.136
130.118
128.574
128.501
128.371
128.199
127.654
126.260
125.973
125.686
125.479
125.399
122.760
120.040
113.703
77.348
77.233
77.030
76.713
55.218
27.118
22.517
22.491
-0.001
f1 (ppm)


xj131128-4
-59.313
f1 (ppm)

8-chloro-4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3g**)



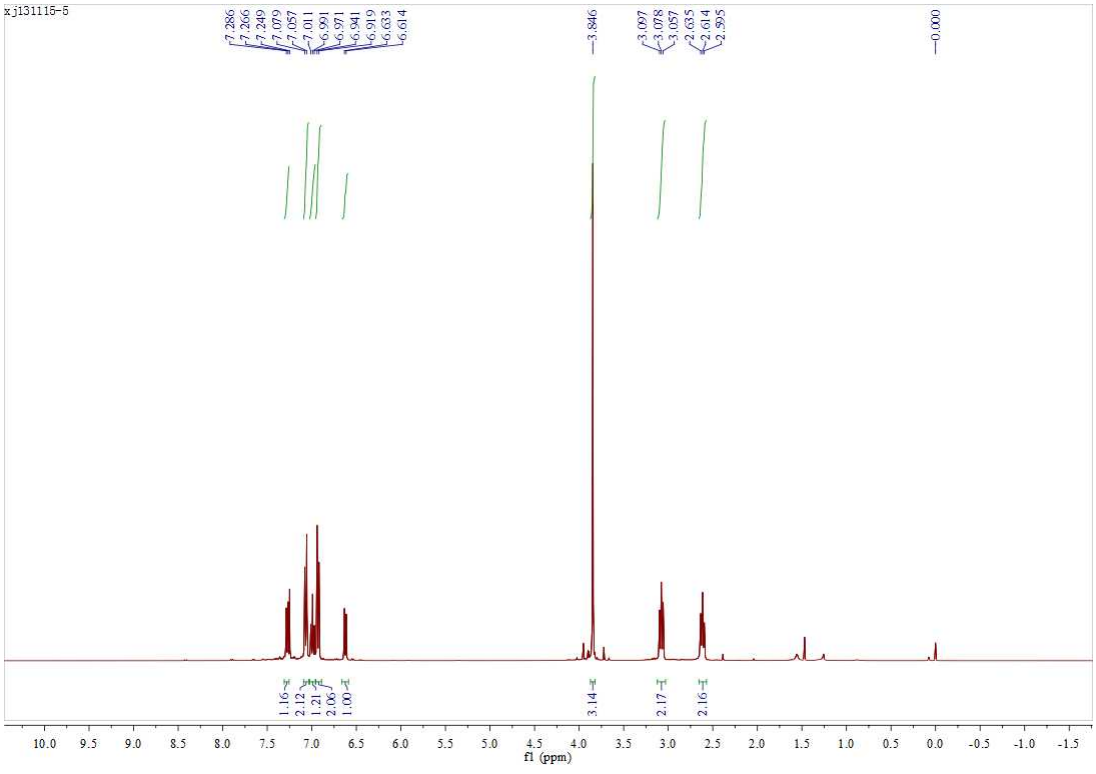
Prepared according to General Procedure **D.**

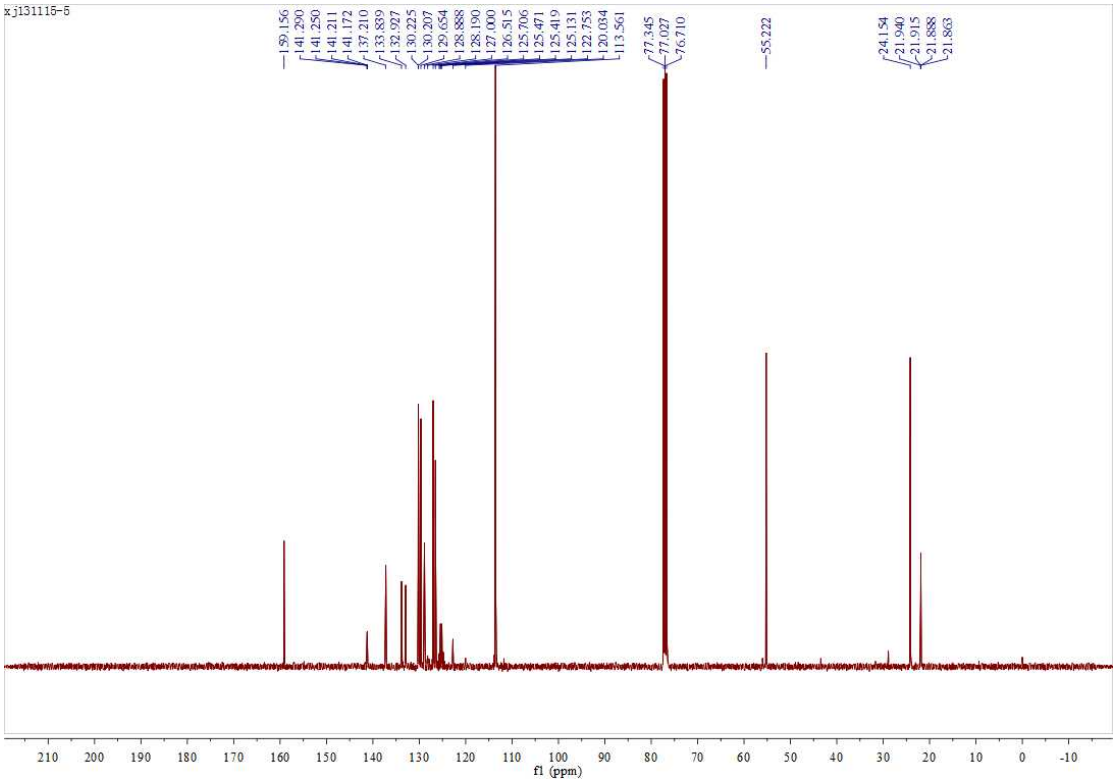
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H).

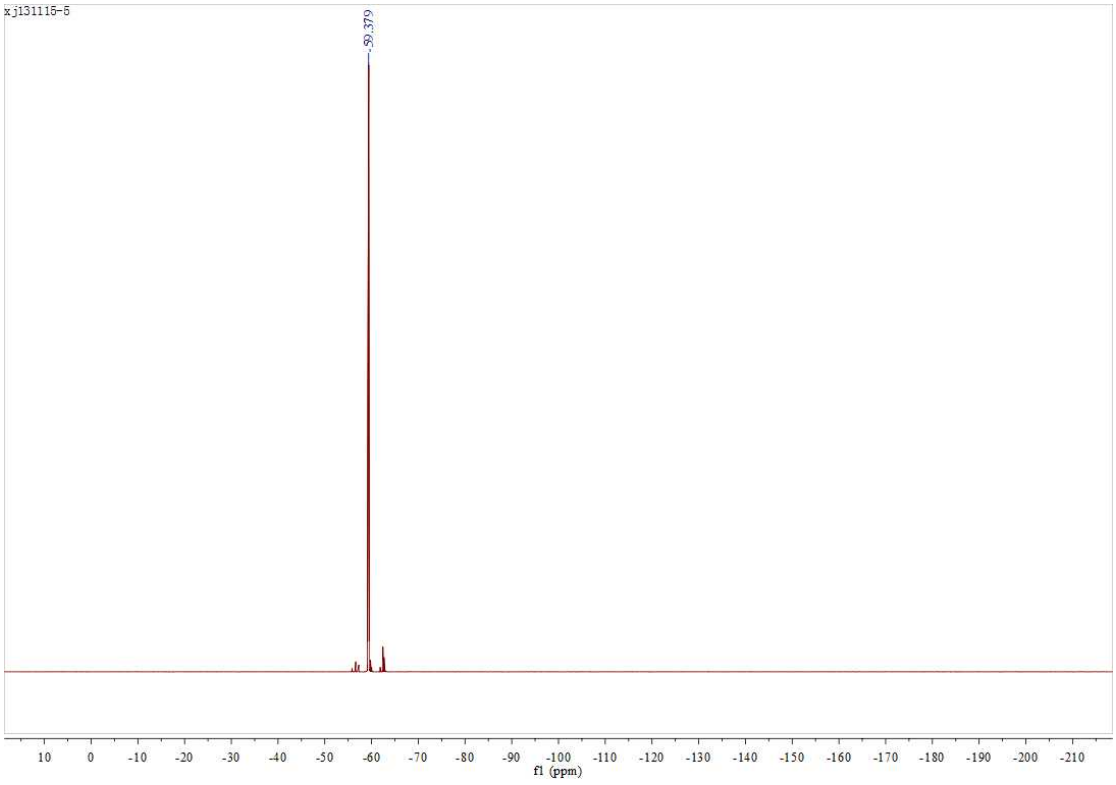
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.16, 141.23 (q, *J* = 4.0 Hz), 137.21, 133.84, 132.93, 130.22 (q, *J* = 1.9 Hz), 129.65, 128.89, 127.00, 126.52, 125.28 (q, *J* = 28.8 Hz), 124.11 (q, *J* = 272 Hz), 113.56, 55.22, 24.15, 21.90 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.38.

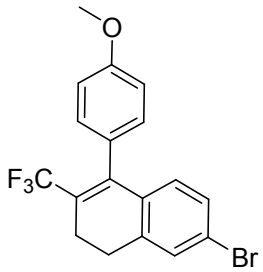
HRMS calcd for $C_{18}H_{14}ClF_3O$ ($[M]^+$): 338.0685; found: 338.0686.




xj131115-5
199.156
141.290
141.250
141.211
141.172
137.210
133.889
132.927
130.225
130.207
129.654
128.888
128.190
127.000
126.515
125.706
125.471
125.419
125.131
122.753
120.034
113.561
77.345
77.027
76.710
55.222
24.154
21.940
21.915
21.888
21.863
f1 (ppm)


xj131115-5
-59.379
f1 (ppm)

7-bromo-4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3h**)



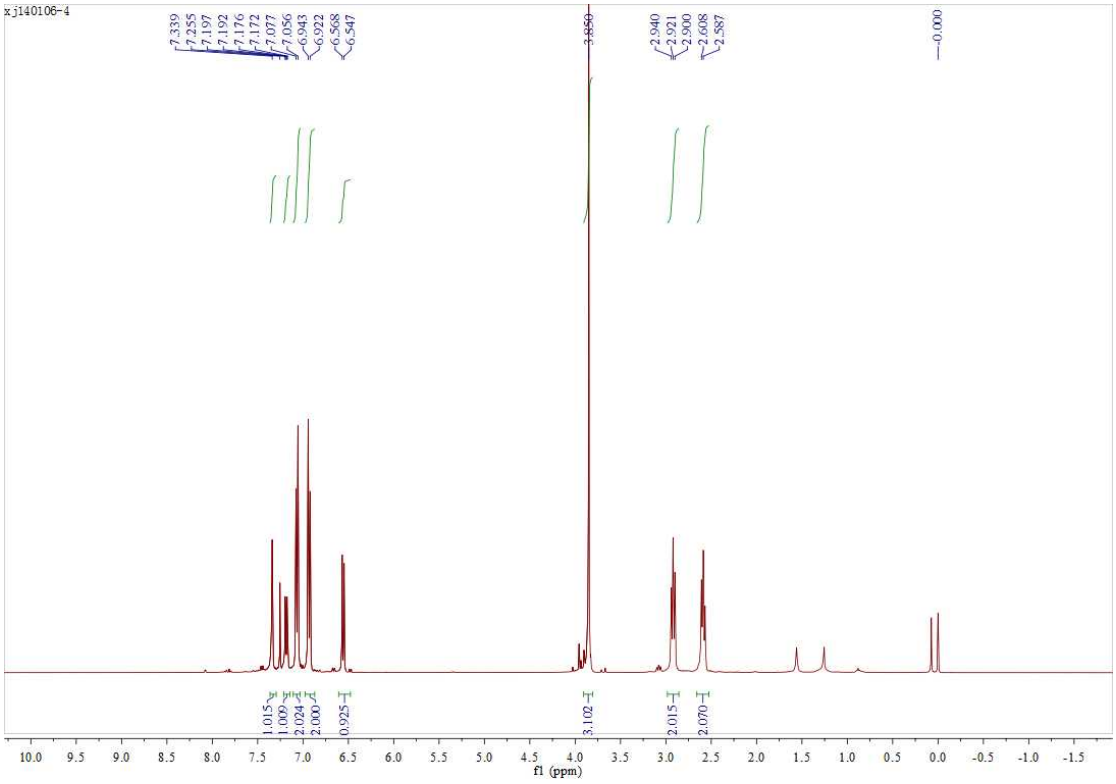
Prepared according to General Procedure **C.**

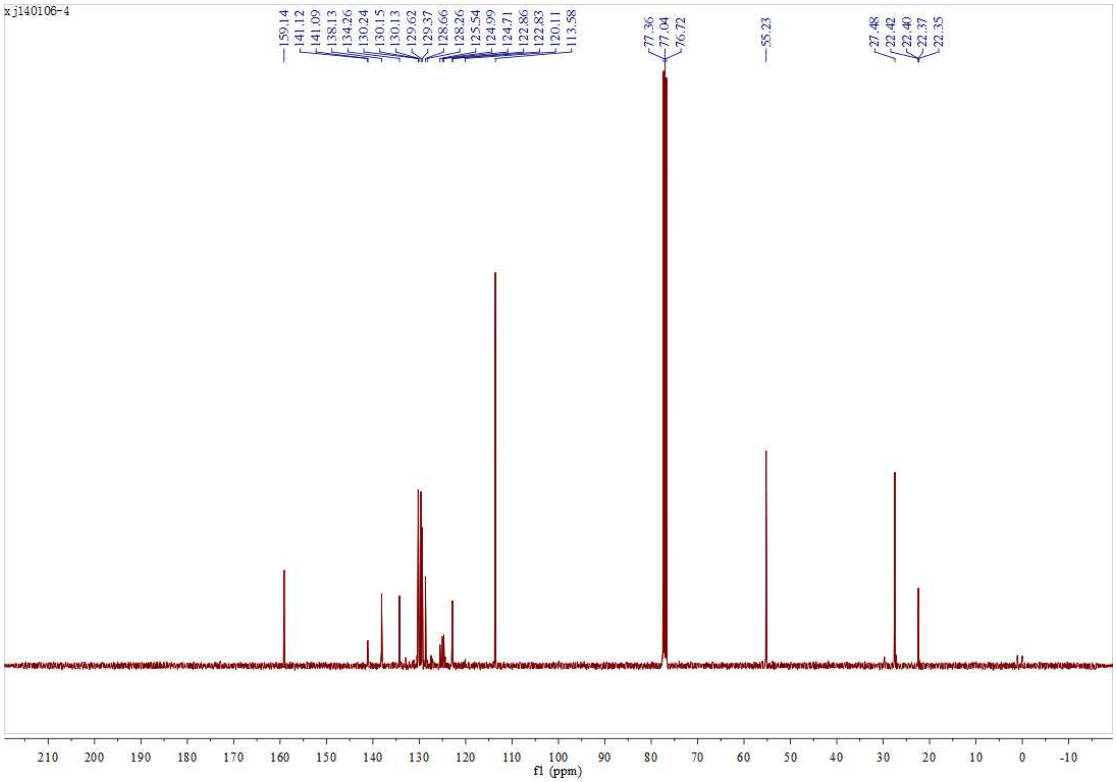
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.18 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 2.92 (t, *J* = 8.4 Hz,, 2H), 2.60 (d, *J* = 8.1 Hz, 2H).

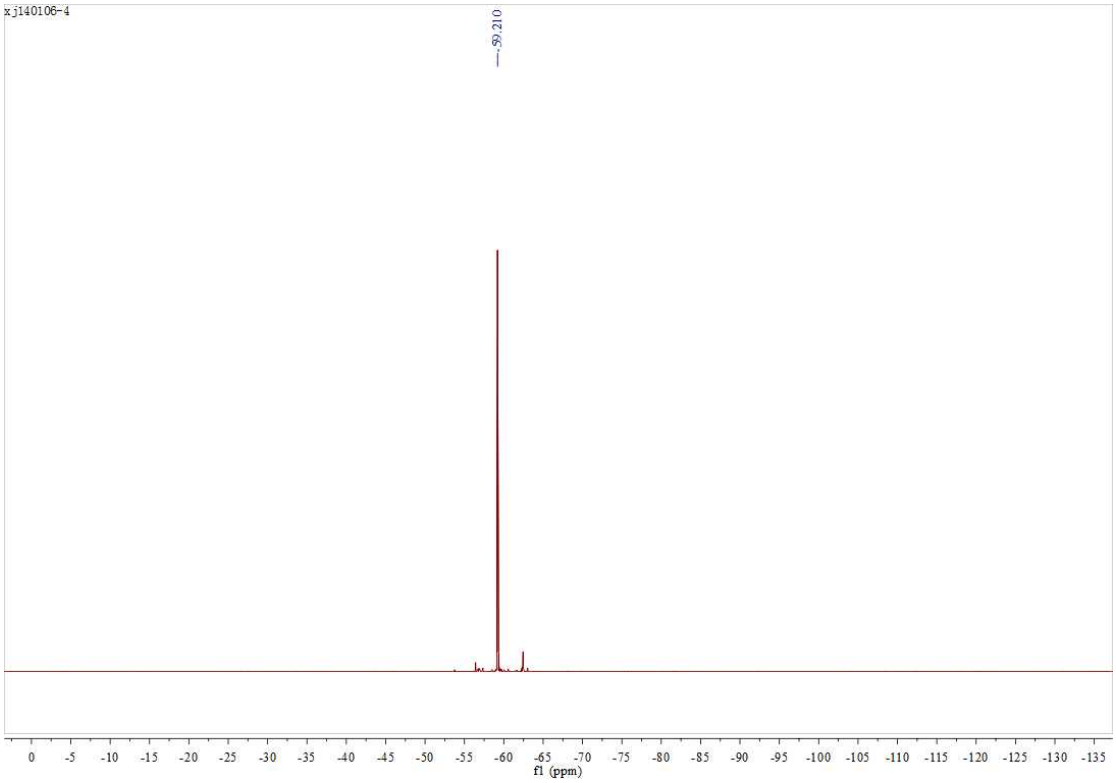
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.14, 141.11 (q, *J* = 3.9 Hz), 138.13, 134.26, 130.24, 130.14 (q, *J* = 2.0 Hz), 129.62, 129.37, 128.66, 124.19 (q, *J* = 271 Hz), 124.85 (q, *J* = 28.6 Hz), 122.86, 113.58, 55.23, 27.48, 22.39 (q, *J* = 2.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.21.

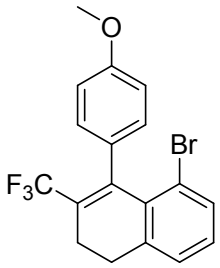
HRMS calcd for $C_{18}H_{14}BrF_3O$ ([M]$^+$): 382.0180; found: 382.0183.




xj140106-4
159.14
141.12
141.09
138.13
134.26
130.24
130.15
130.13
129.62
129.37
128.66
128.26
125.54
124.99
124.71
122.86
122.83
120.11
113.58
77.36
77.04
76.72
55.23
27.48
22.42
22.40
22.37
22.35
f1 (ppm)


xj140106-4
-59.210
f1 (ppm)

5-bromo-4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3h'**)



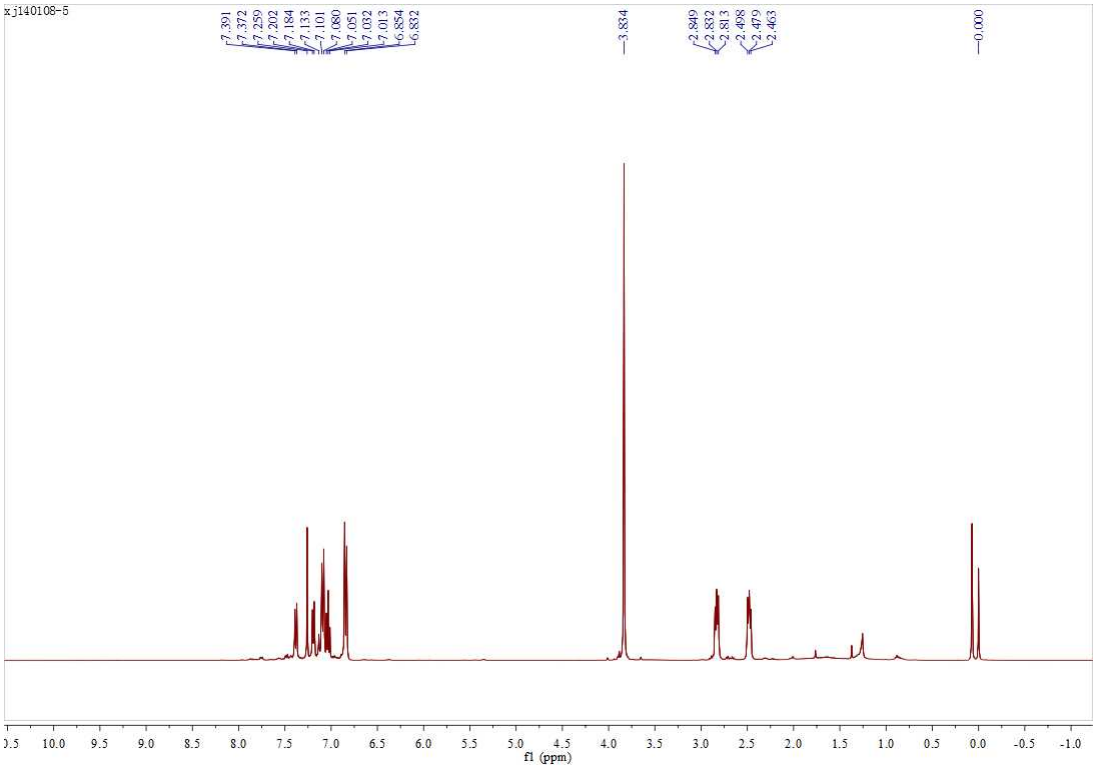
Prepared according to General Procedure **C.**

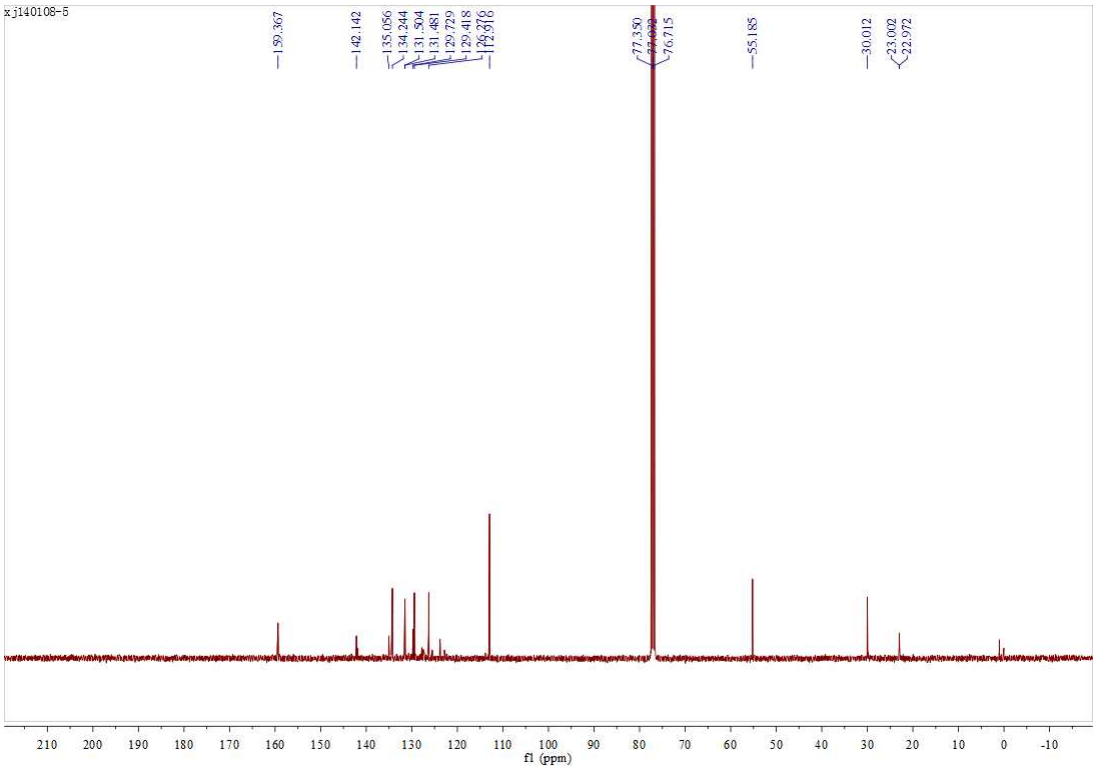
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 2.83(t, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 6.4 Hz, 2H).

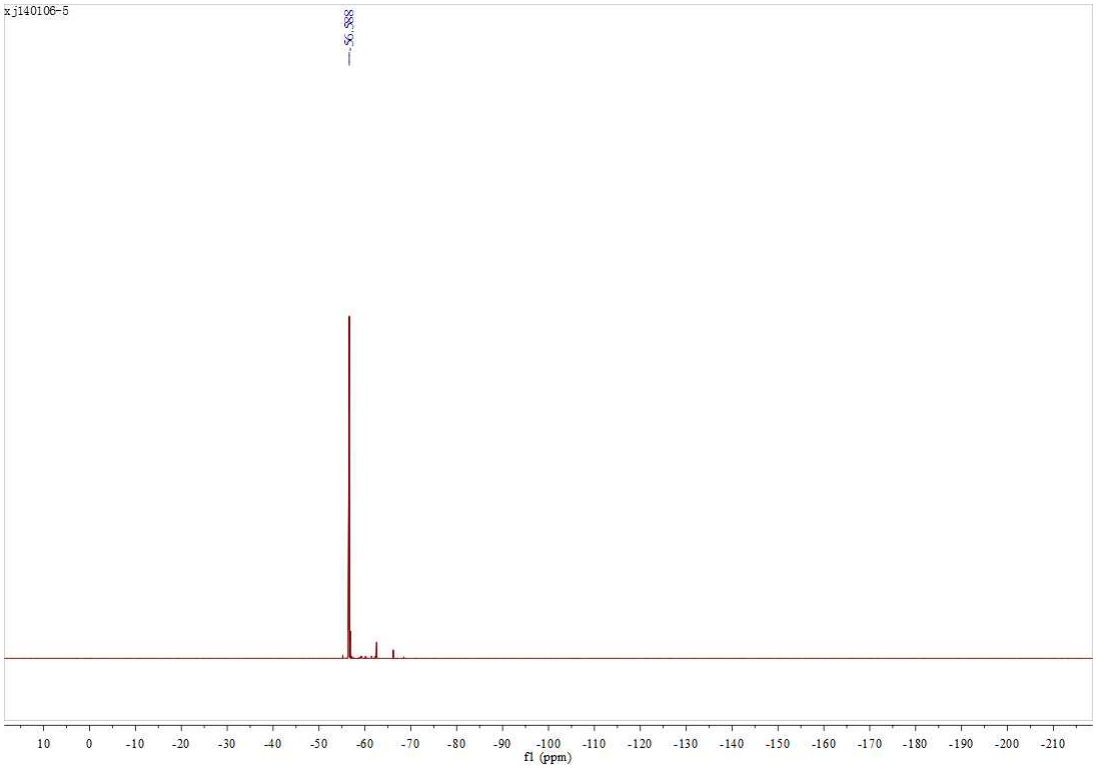
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.35, 142.13, 141.88 (q, *J* = 4.2 Hz), 135.04, 134.23, 131.48 (q, *J* = 2.3 Hz), 129.72, 129.41, 127.66 (q, *J* = 29.4 Hz), 126.26, 124.15 (q, *J* = 271 Hz), 123.79, 112.90, 55.17, 30.00, 22.96 (q, *J* = 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -56.59.

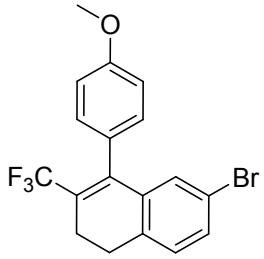
HRMS calcd for $C_{18}H_{14}BrF_3O$ ([M]$^+$): 382.0180; found: 382.0181.




xj140108-5
159.367
142.142
135.056
134.244
131.504
131.481
129.729
129.418
126.376
112.910
77.350
77.033
76.715
55.185
30.012
23.002
22.972
f1 (ppm)


xj140106-5
56.888
f1 (ppm)

6-bromo-4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3i**)



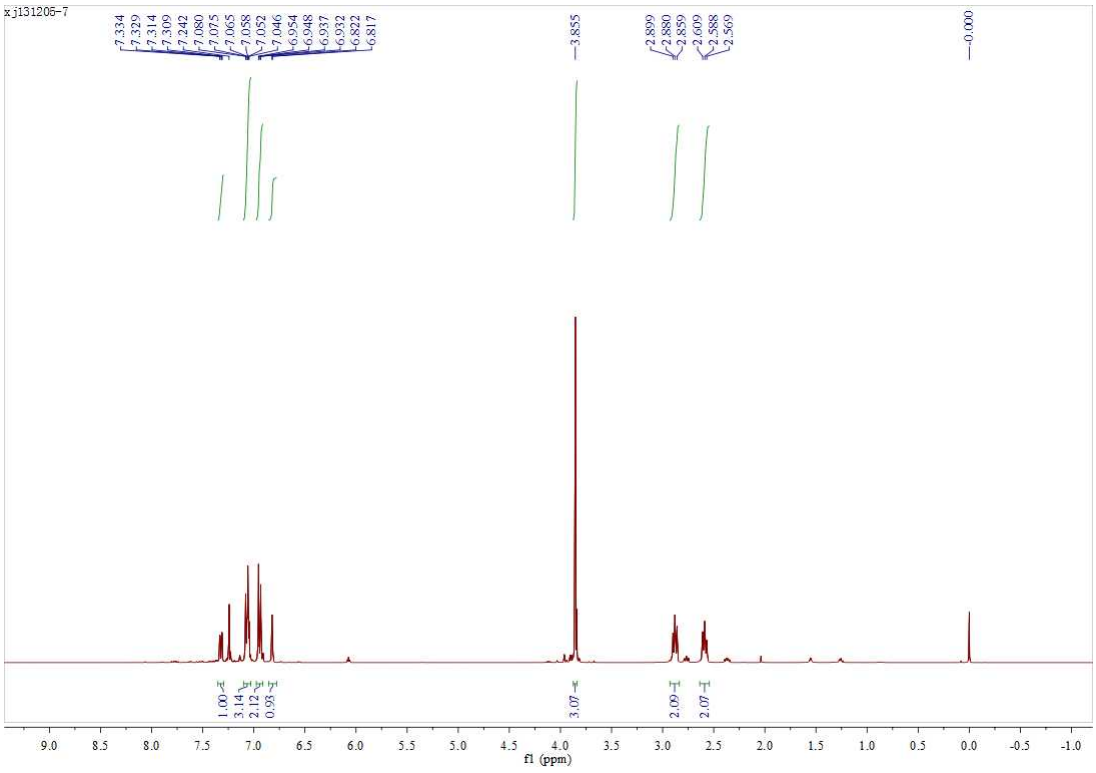
Prepared according to General Procedure **C.**

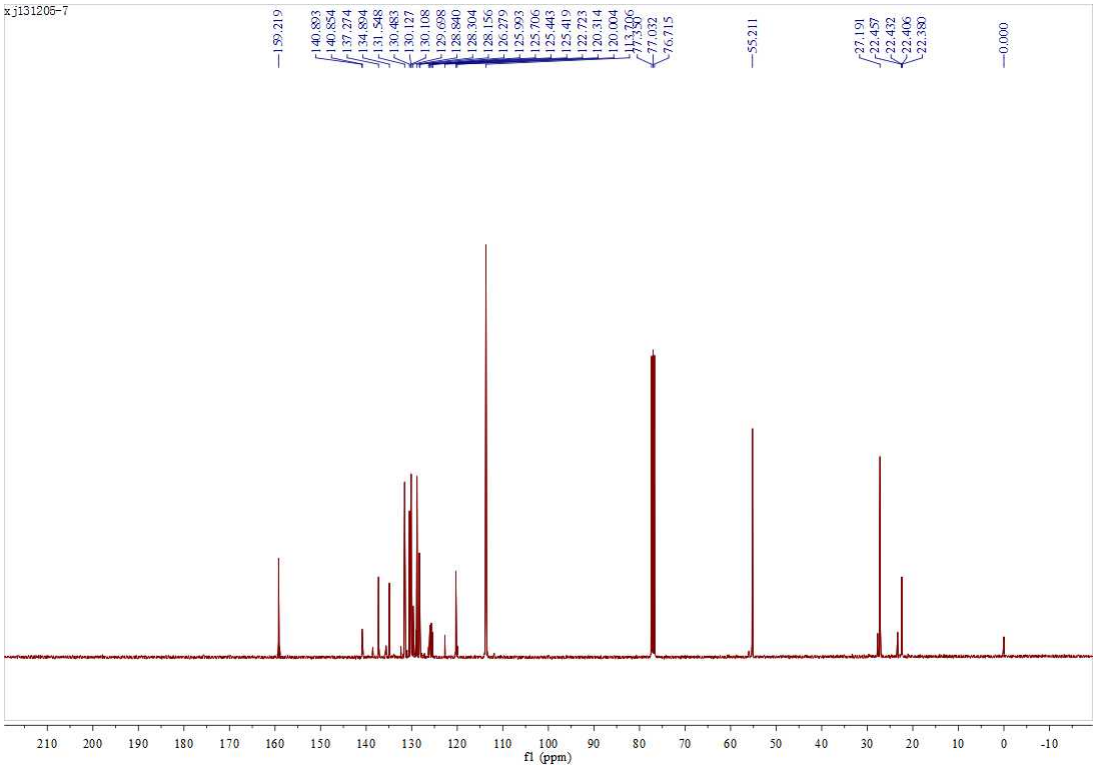
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.10 – 7.03 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 1.8 Hz, 1H), 3.85 (s, 3H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 2H).

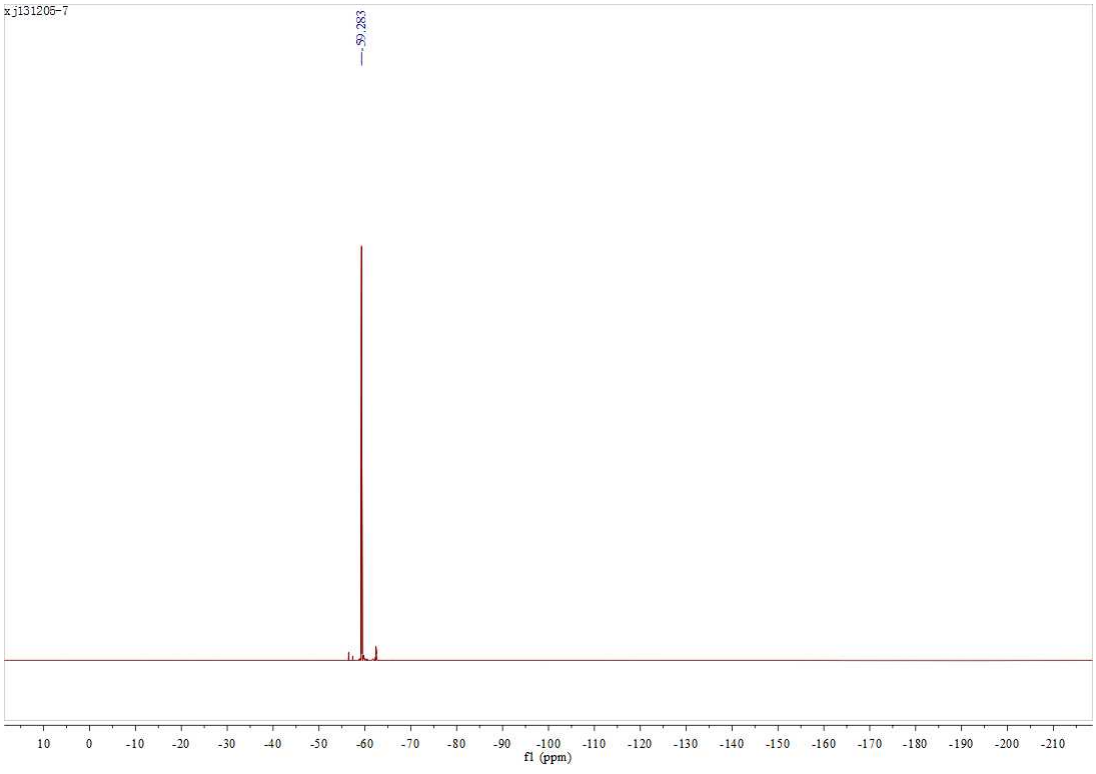
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.22, 140.87 (q, *J* = 4.0 Hz), 137.27, 134.89, 131.55, 130.48, 130.12 (q, *J* = 1.9 Hz), 128.84, 128.30, 125.85 (q, *J* = 28.7 Hz), 124.08 (q, *J* = 272 Hz), 120.31, 113.71, 55.21, 27.19, 22.42 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.28.

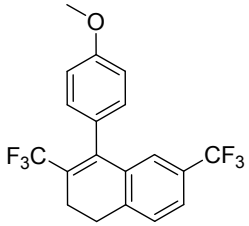
HRMS calcd for $C_{18}H_{14}BrF_3O$ ([M]$^+$): 382.0180; found: 382.0182.




xji31206-7
159.219
140.893
140.854
137.274
134.894
131.548
130.483
130.127
130.108
129.698
128.840
128.304
128.156
126.279
125.993
125.706
125.443
125.419
122.723
120.314
120.004
113.706
77.350
77.032
76.715
55.211
27.191
22.457
22.432
22.406
22.380
0.000
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)


xji31206-7
59.283
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-(4-methoxyphenyl)-3,6-bis(trifluoromethyl)-1,2-dihydronaphthalene (**3j**)



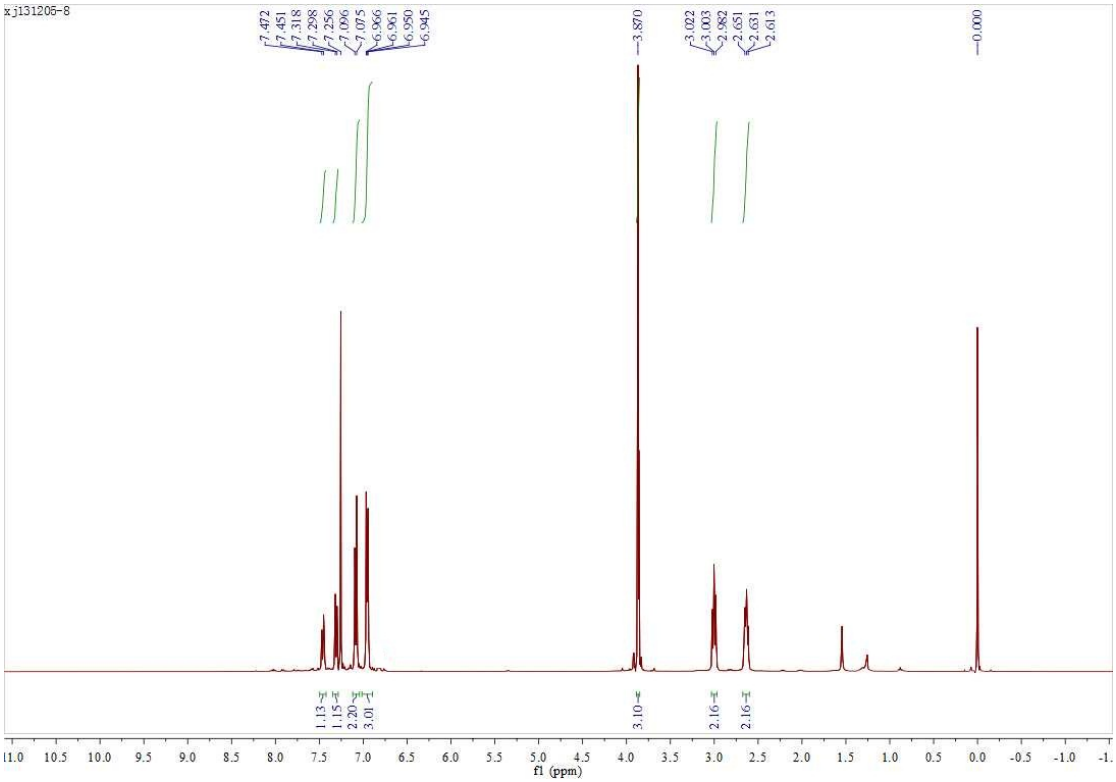
Prepared according to General Procedure **E.**

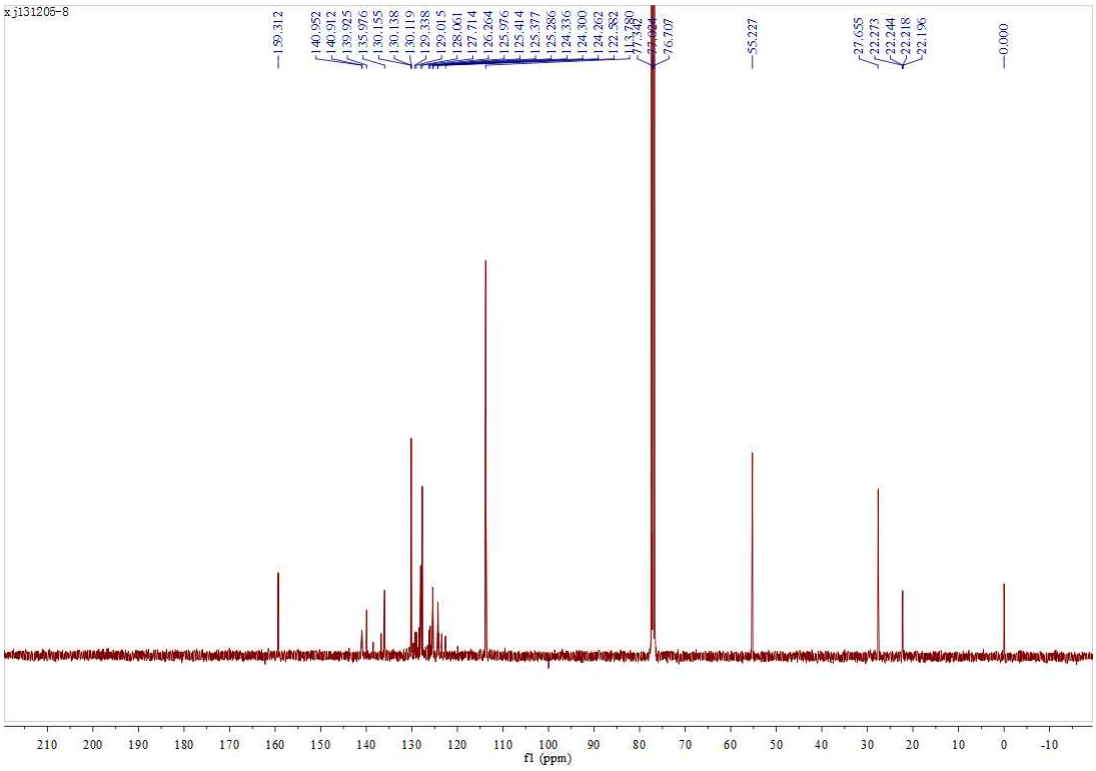
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.96 (m, 3H), 3.87 (s, 3H), 3.00 (t, *J* = 8.0 Hz, 2H), 2.63 (t, *J* = 8.0 Hz, 2H).

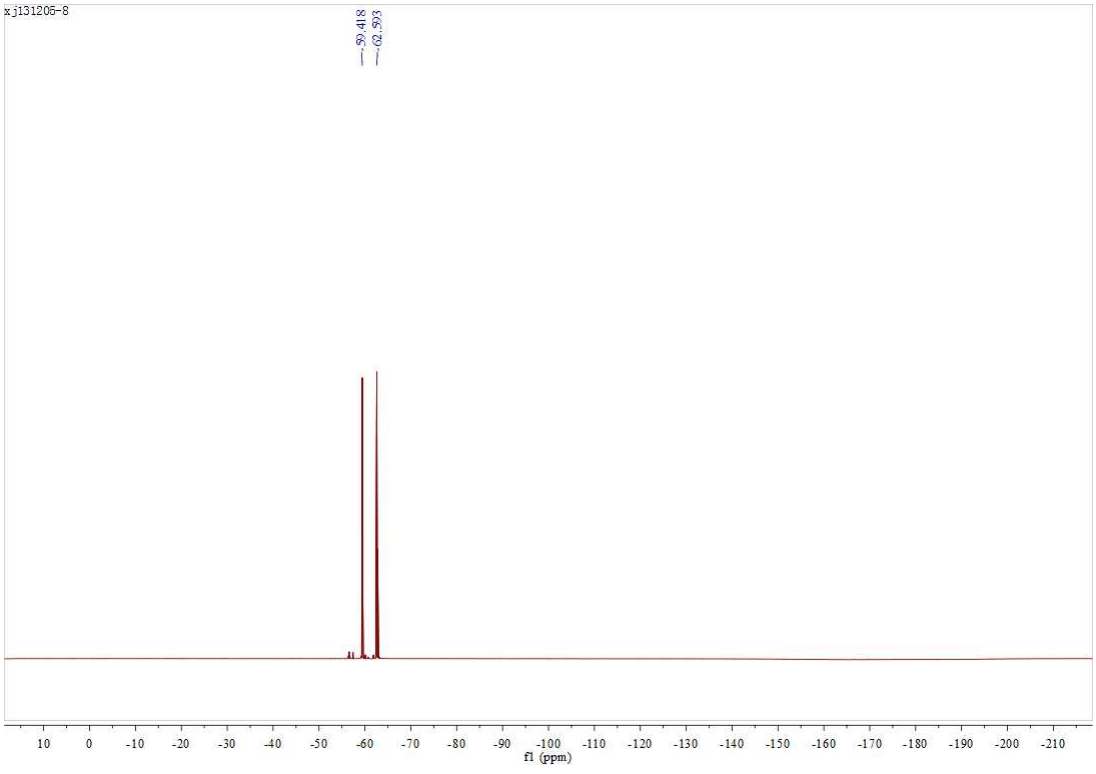
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.31, 140.93 (q, *J* = 4.2 Hz), 139.93, 135.98, 130.14 (q, *J* = 1.9 Hz), 129.17 (q, *J* = 32.3 Hz), 128.06, 127.71, 126.12 (q, *J* = 28.8 Hz), 125.40 (q, *J* = 3.7 Hz), 124.28 (q, *J* = 3.6 Hz), 121.32 (q, *J* = 272 Hz), 121.23 (q, *J* = 272 Hz), 113.78, 55.23, 27.65, 22.23 (q, *J* = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.42, -62.59.

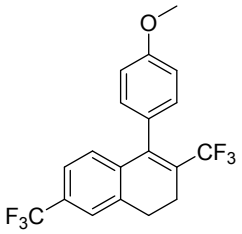
HRMS calcd for $C_{19}H_{14}F_6O$ ([M]$^+$): 372.0949; found: 372.0946.




xj131206-8
159.312
140.952
140.912
139.925
135.976
130.155
130.138
130.119
129.338
129.015
128.061
127.714
126.264
125.976
125.414
125.377
125.286
124.336
124.300
124.262
122.582
113.780
77.342
77.024
76.707
55.227
27.655
22.273
22.244
22.218
22.196
0.000
f1 (ppm)


xj131206-8
59.418
62.593
f1 (ppm)

4-(4-methoxyphenyl)-3,7-bis(trifluoromethyl)-1,2-dihydronaphthalene (**3k**)



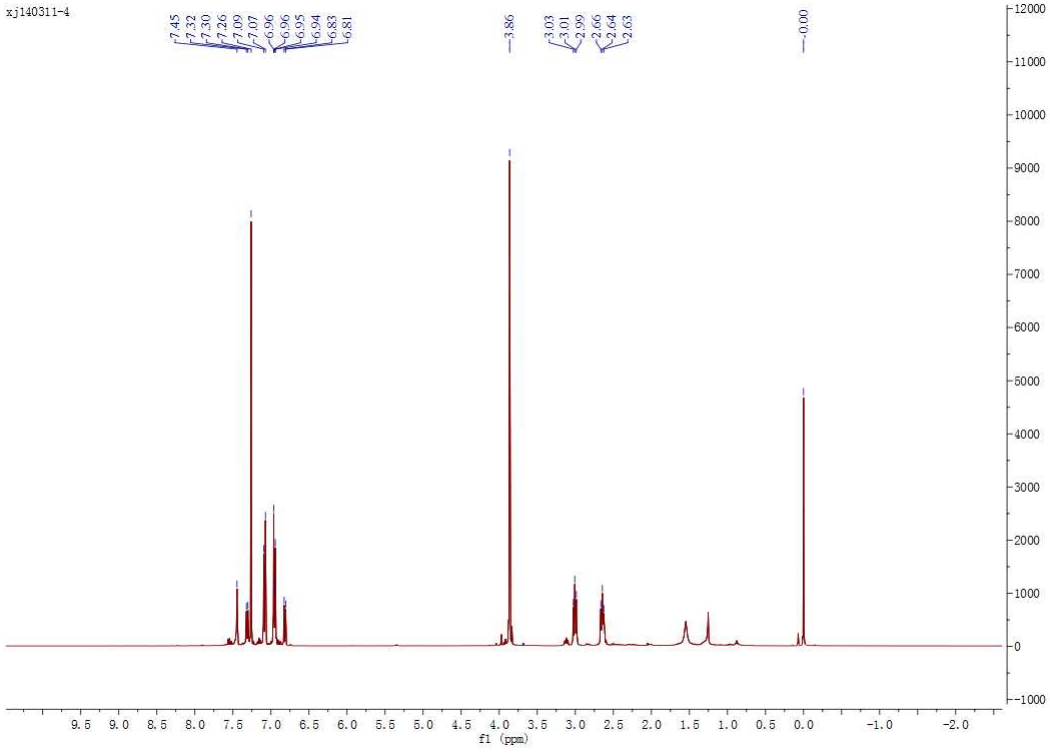
Prepared according to General Procedure **E.**

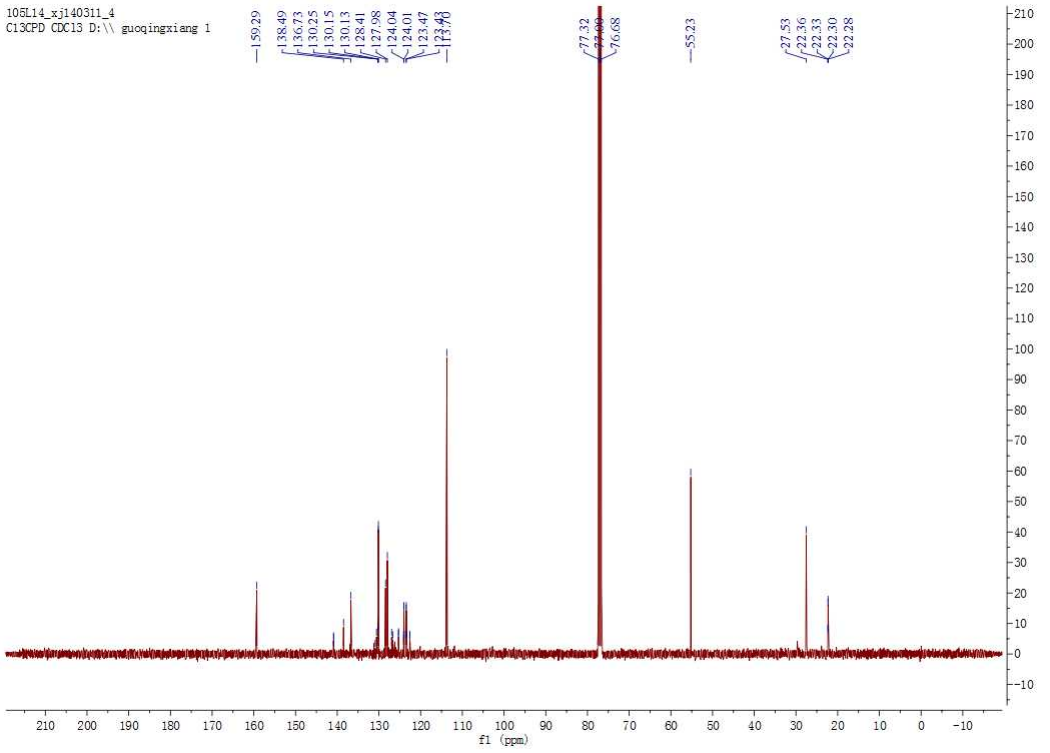
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.00 (t, *J* = 7.9 Hz, 2H), 2.64 (t, *J* = 7.9 Hz, 2H).

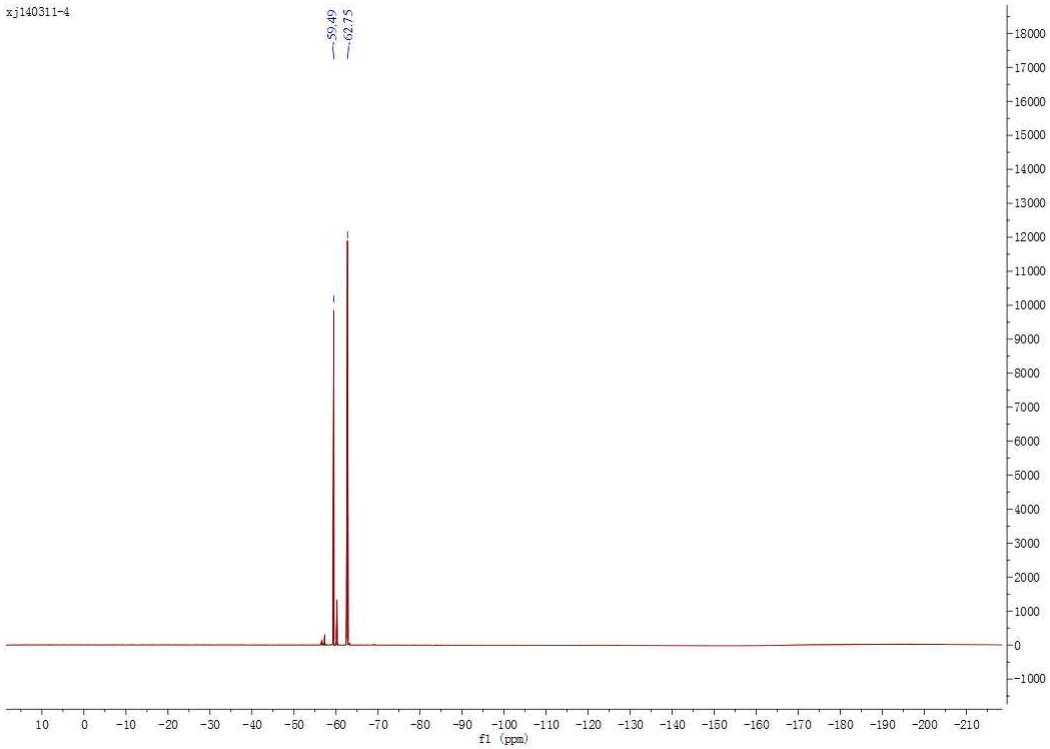
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.29, 140.88 (q, *J* = 5.0 Hz), 138.49, 136.73, 130.42 (q, *J* = 33.1 Hz), 130.14 (q, *J* = 1.8 Hz), 128.41, 127.98, 126.82 (q, *J* = 29.0 Hz), 124.03 (q, *J* = 3.6 Hz), 123.98 (q, *J* = 272 Hz), 123.92 (q, *J* = 271 Hz), 123.45 (q, *J* = 4.0 Hz), 113.68, 55.23, 27.53, 22.31 (q, *J* = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.49, -62.75.

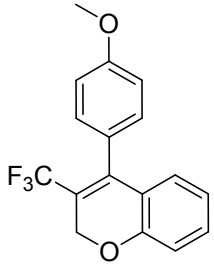
HRMS calcd for $C_{19}H_{14}F_6O$ ([M]$^+$): 372.0949; found: 372.0954.




105L14_xj140311_4
C13CPD CDCl3 D:\\ guoqingxiang 1
159.29
138.49
136.73
130.25
130.15
130.13
128.41
127.98
124.04
124.01
123.47
123.43
113.90
77.32
77.00
76.68
55.23
27.53
22.36
22.33
22.30
22.28
f1 (ppm)


xj140311-4
59.49
62.75
f1 (ppm)

4-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-chromene (**3l**)



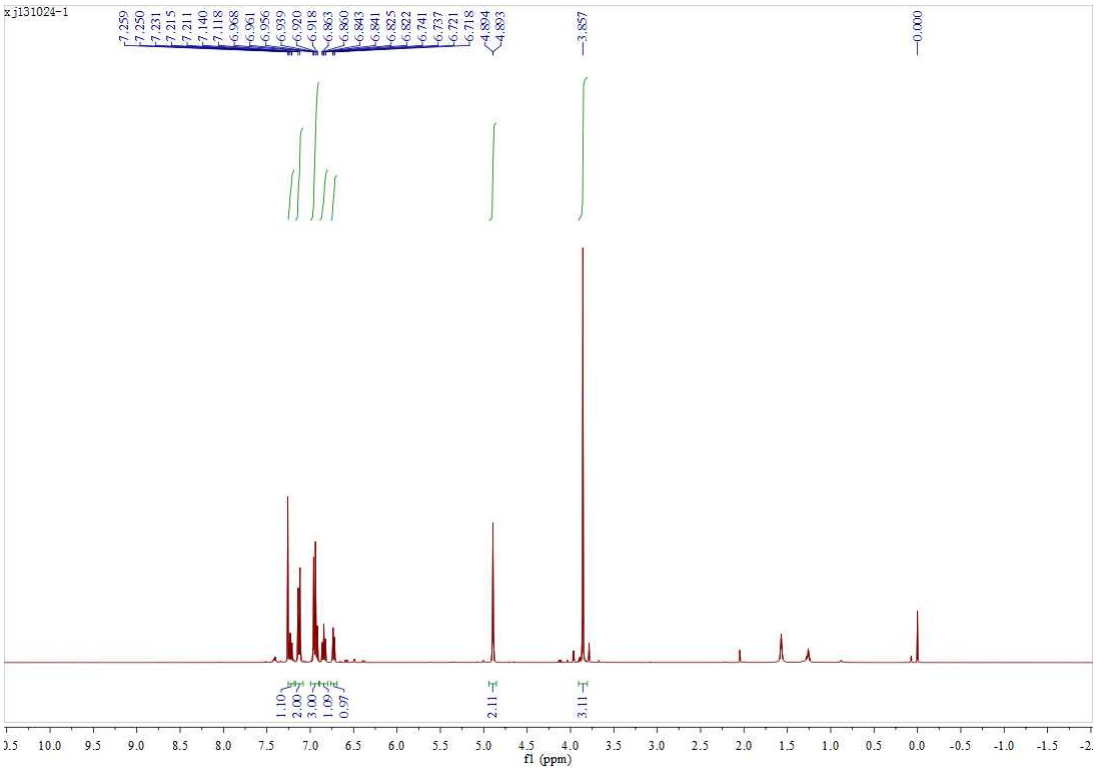
Prepared according to General Procedure **E.**

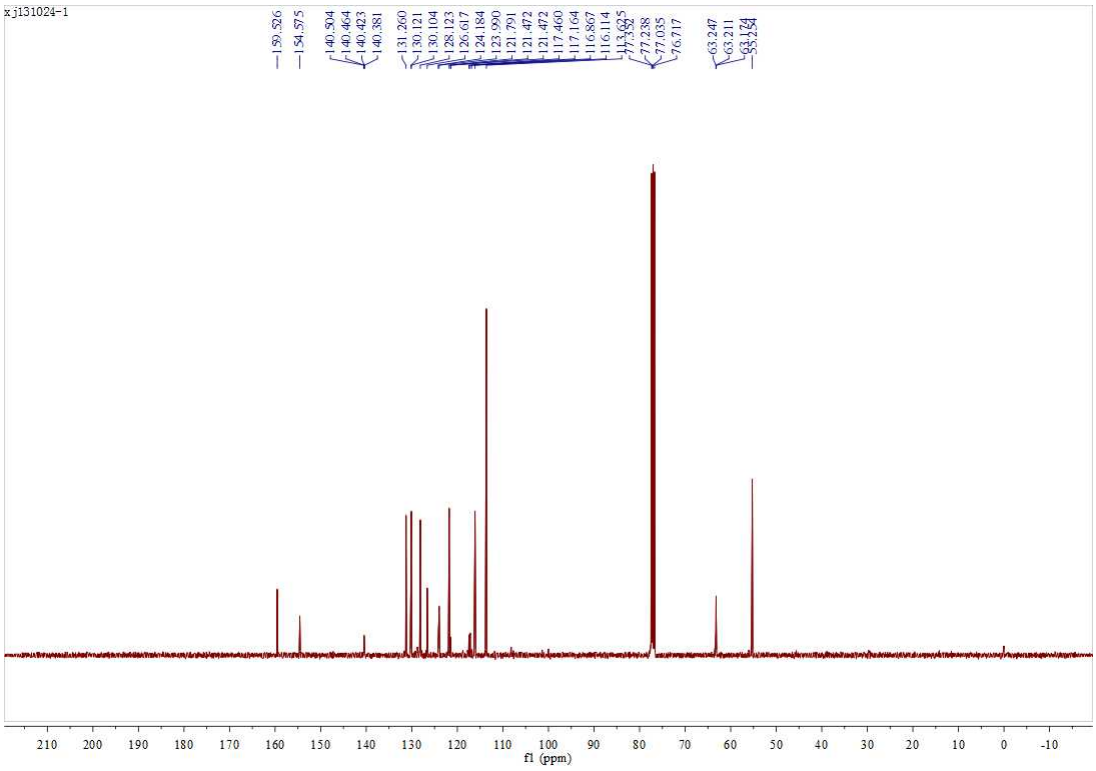
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 11.1, 4.5 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.90 (m, 3H), 6.84 (t, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 7.8, 1H), 4.89 (s, 2H), 3.86 (s, 3H).

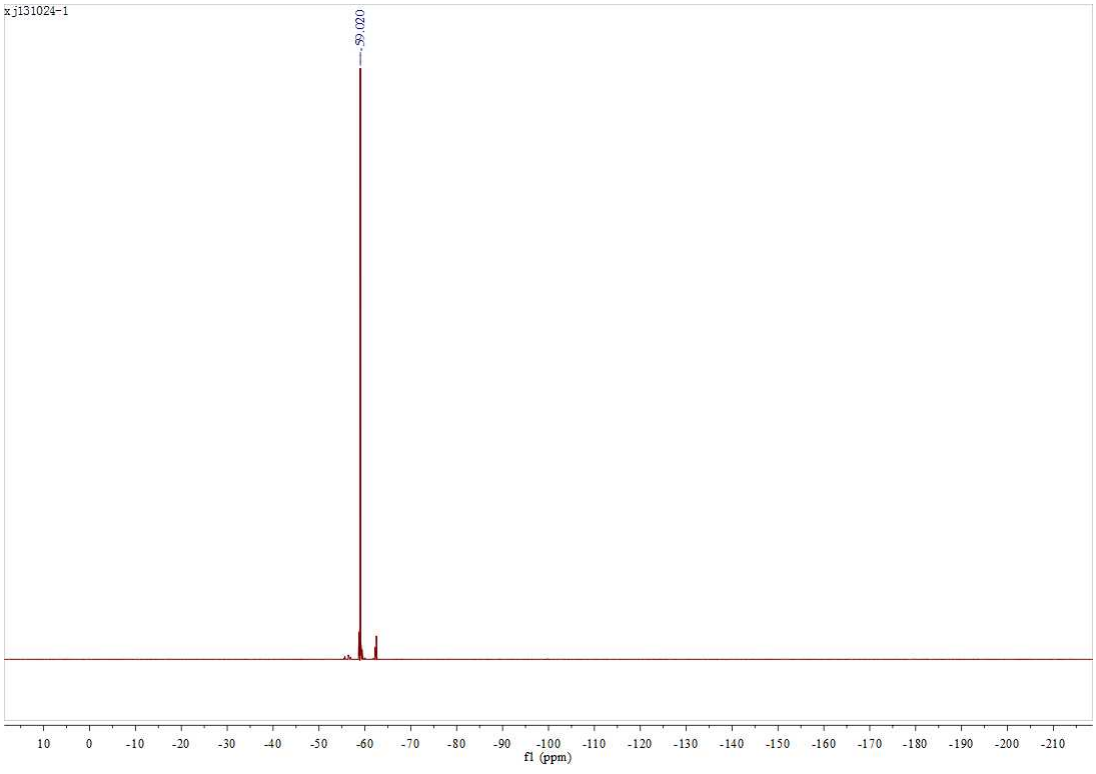
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.53, 154.57, 140.44 (q, *J* = 4.1 Hz), 131.26, 130.11 (q, *J* = 1.7 Hz), 128.12, 126.62, 123.99, 122.82 (q, *J* = 271 Hz), 121.79, 117.31 (q, *J* = 29.6 Hz), 116.11, 113.62, 63.19 (q, *J* = 3.7 Hz), 55.25.

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.02.

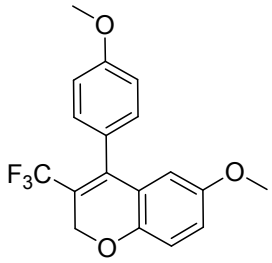
HRMS calcd for $C_{17}H_{13}F_3O_2$ ([M]$^+$): 306.0868; found: 306.0871.




xji31024-1
159.526
154.575
140.504
140.464
140.423
140.381
131.260
130.121
130.104
128.123
126.617
124.184
123.990
121.791
121.472
121.472
117.460
117.164
116.867
116.114
77.592
77.238
77.035
76.717
63.247
63.211
53.454
53.424
f1 (ppm)


xji31024-1
-59.020
f1 (ppm)

6-methoxy-4-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-chromene (**3m**)



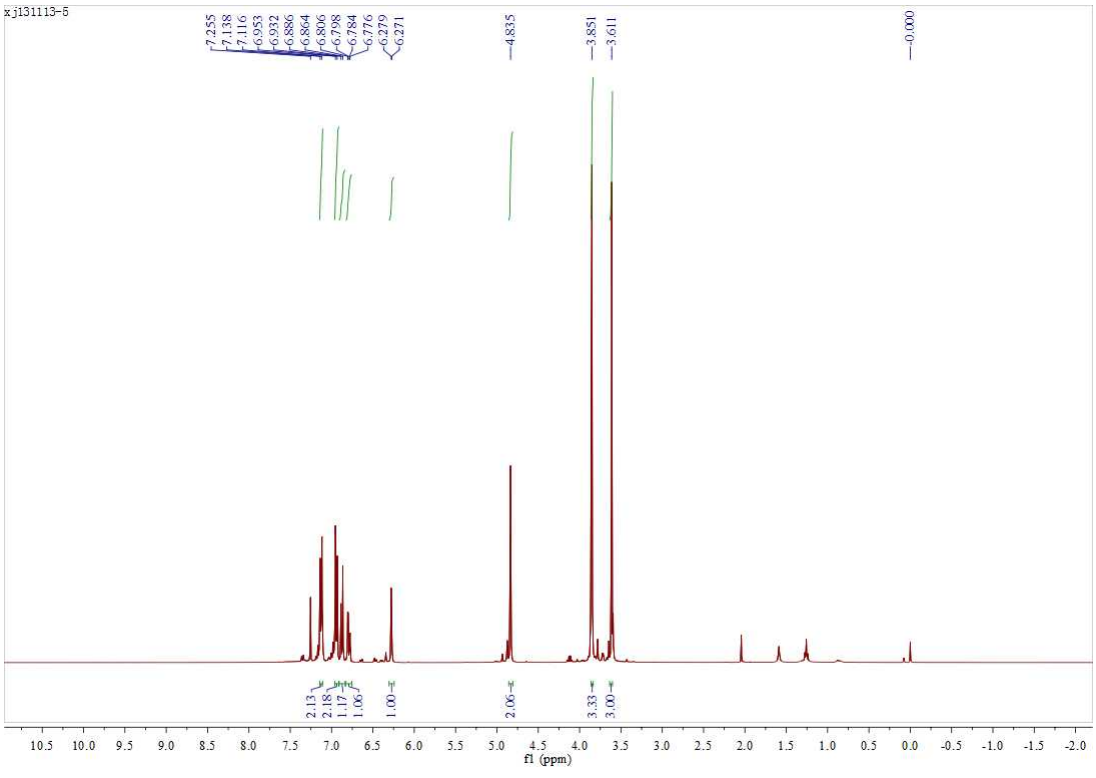
Prepared according to General Procedure **E.**

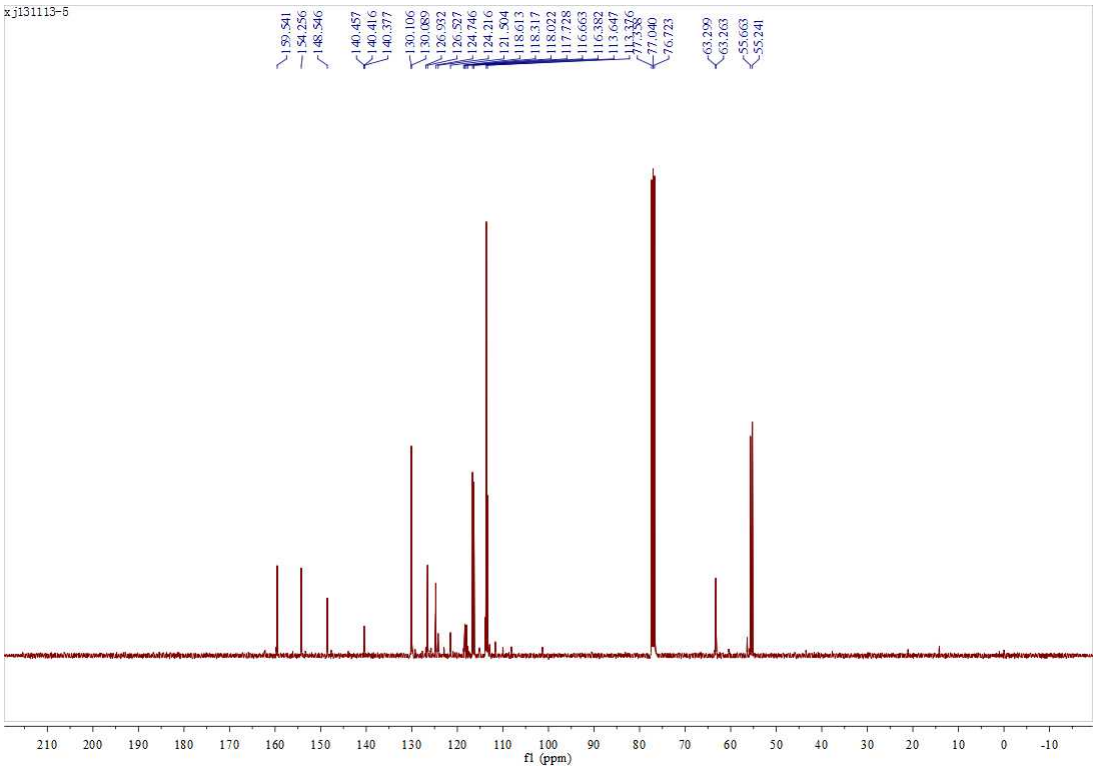
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.28 (d, *J* = 2.9 Hz, 1H), 4.83 (s, 2H), 3.85 (s, 3H), 3.61 (s, 3H).

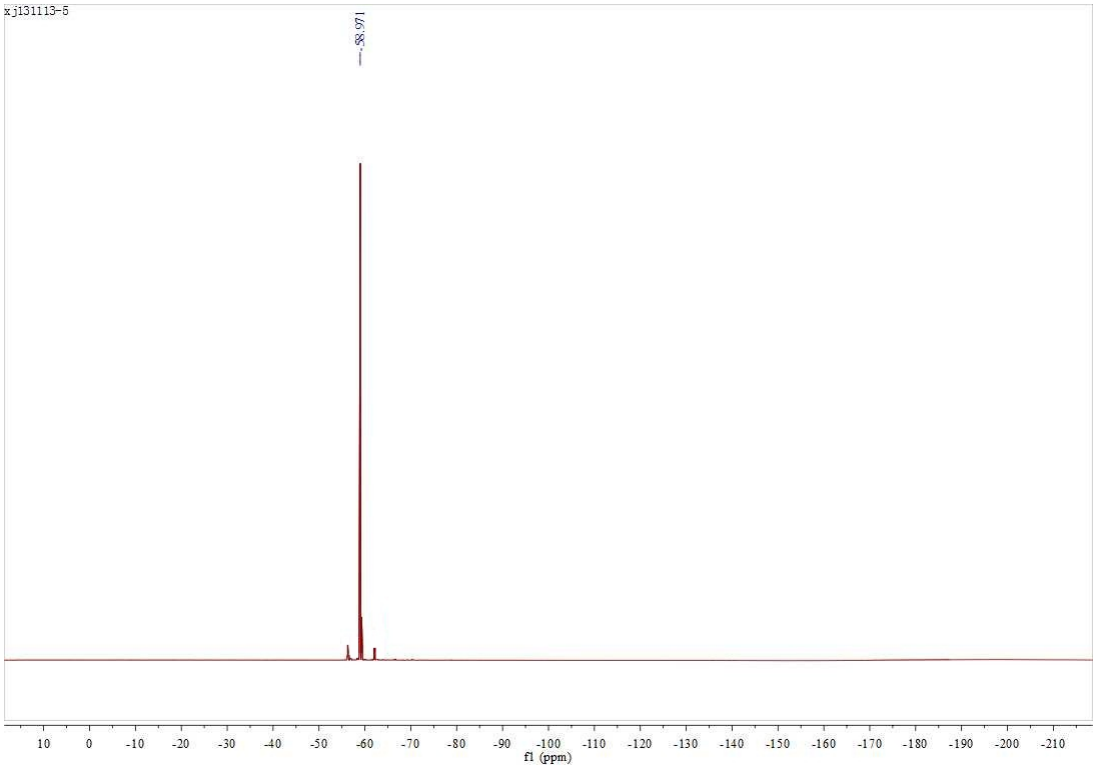
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.54, 154.26, 148.55, 140.44 (q, *J* = 4.0 Hz), 130.10 (q, *J* = 1.7 Hz), 126.53, 124.75, 122.85 (q, *J* = 271 Hz), 118.17 (q, *J* = 29.5 Hz), 116.66, 116.38, 113.65, 113.38, 63.28 (q, *J* = 3.6 Hz), 55.66, 55.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.97.

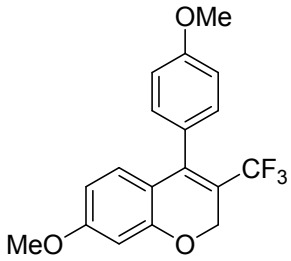
HRMS calcd for $C_{18}H_{15}F_3O_3$ ([M]$^+$): 336.0973; found: 336.0975.




xji31113-5
159.541
154.256
148.546
140.457
140.416
140.377
130.106
130.089
126.932
126.527
124.746
124.216
121.504
118.613
118.317
118.022
117.728
116.663
116.382
113.647
113.376
77.358
77.040
76.723
63.299
63.263
55.663
55.241
f1 (ppm)


xji31113-5
58.971
f1 (ppm)

7-methoxy-4-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-chromene (3**n**)

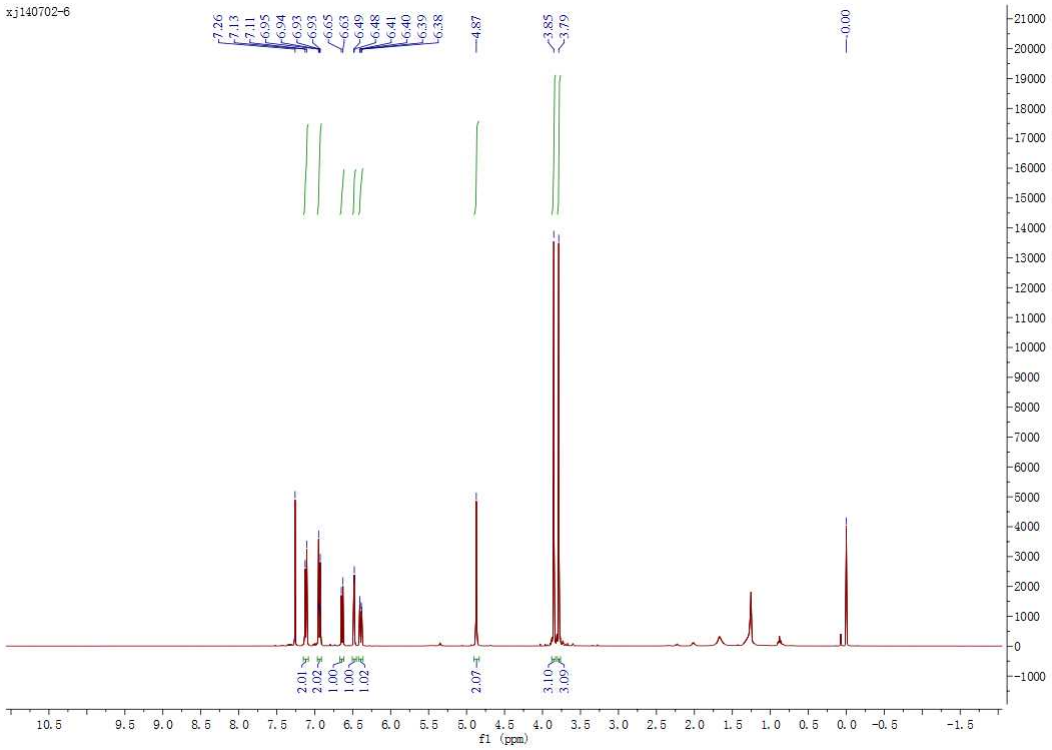


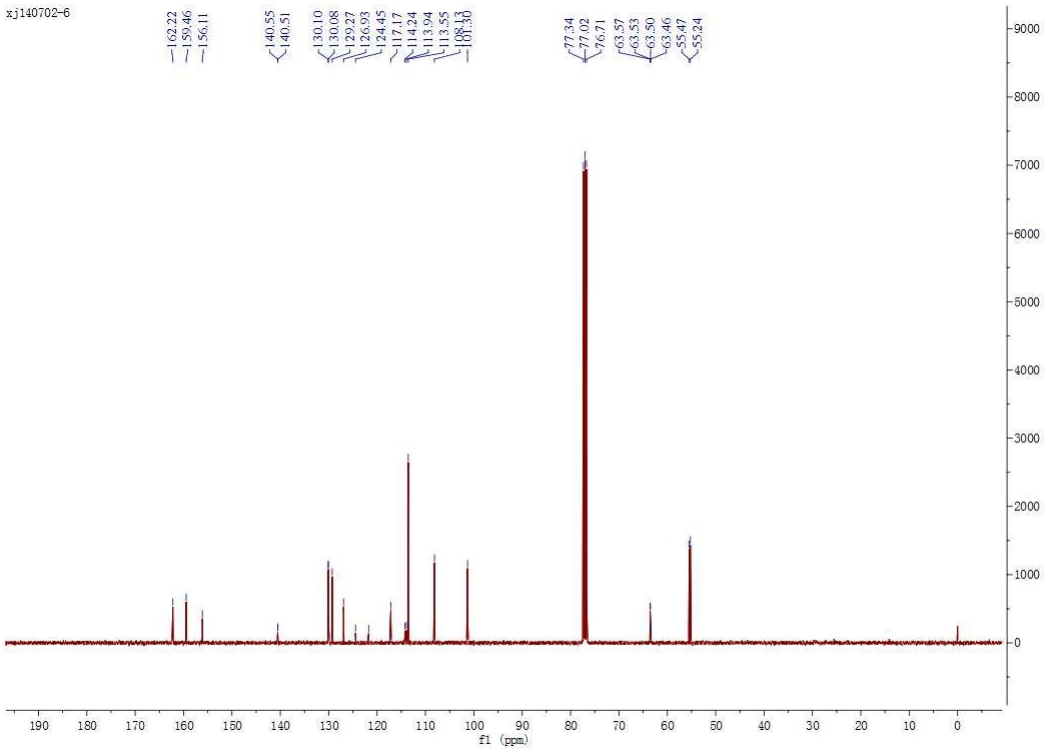
Prepared according to General Procedure **E.**

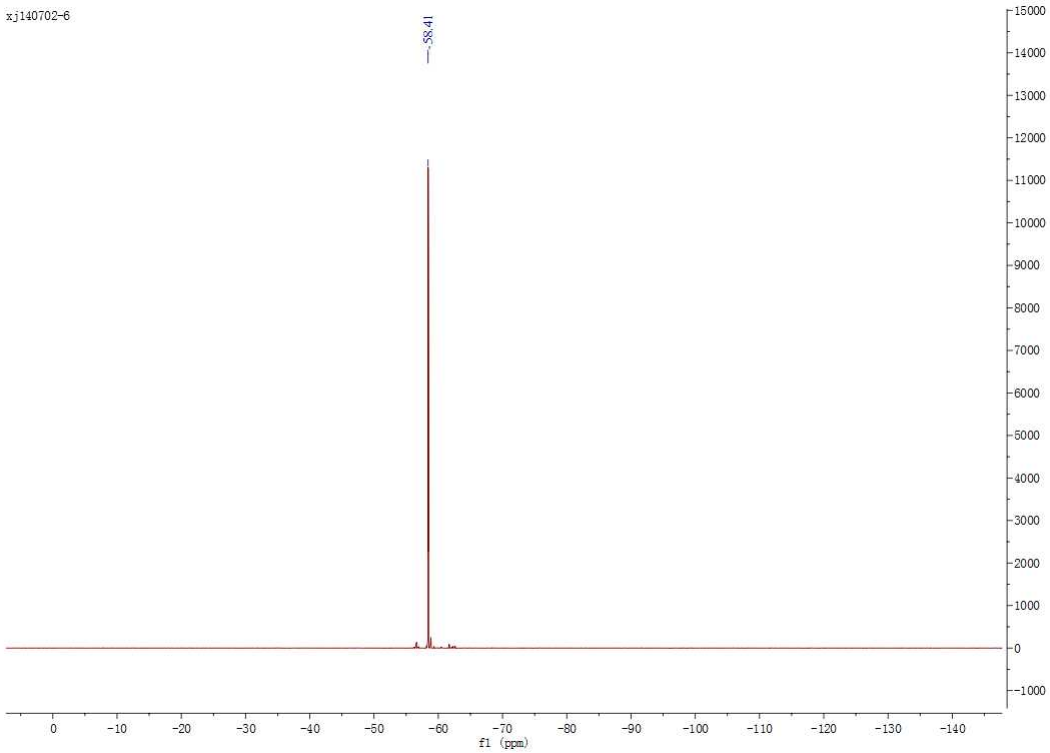
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.39 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.87 (s, 2H), 3.85 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.22, 159.46, 156.11, 140.53 (q, *J* = 4.1 Hz), 130.09 (q, *J* = 1.7 Hz), 129.27, 126.93, 123.10 (q, *J* = 271 Hz), 117.17, 114.09 (q, *J* = 30 Hz), 113.55, 108.13, 101.30, 63.51 (q, *J* = 3.6 Hz), 55.47, 55.24.

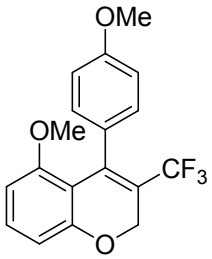
^{19}F NMR (376 MHz, $CDCl_3$) δ -58.41.




xj140702-6
162.22
159.46
156.11
140.55
140.51
130.10
130.08
129.27
126.93
124.45
117.17
114.24
113.94
113.55
108.13
101.50
77.34
77.02
76.71
63.57
63.53
63.50
63.46
55.47
55.24
f1 (ppm)


xj140702-6
-58.41
f1 (ppm)

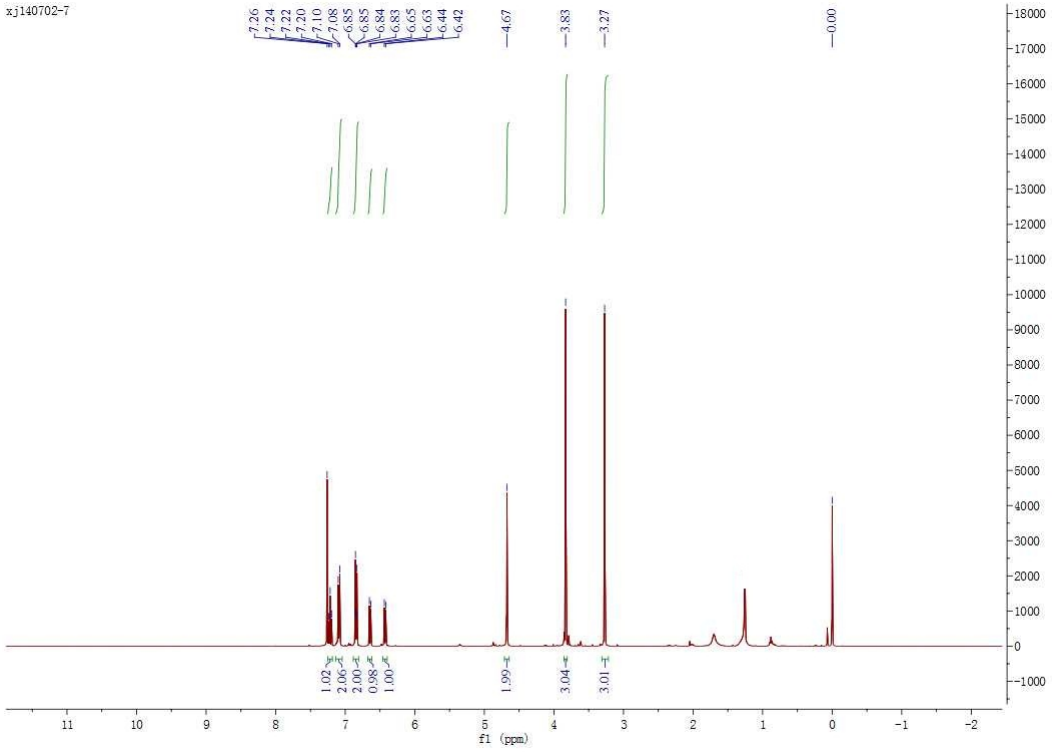
5-methoxy-4-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-chromene (**3n'**)

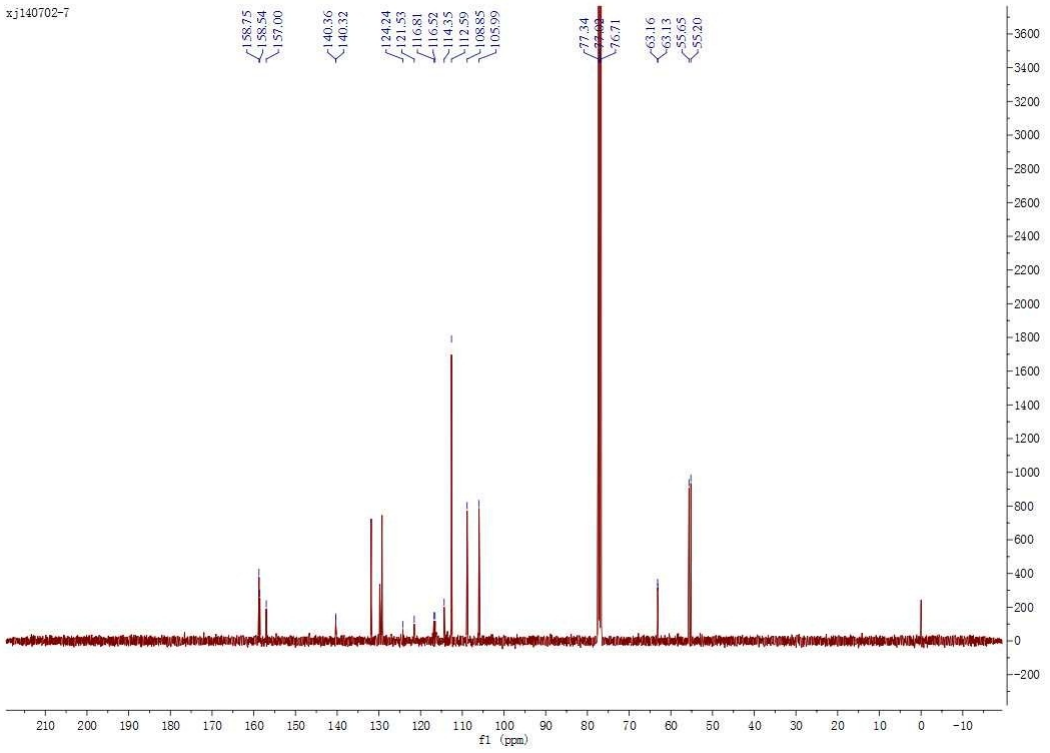


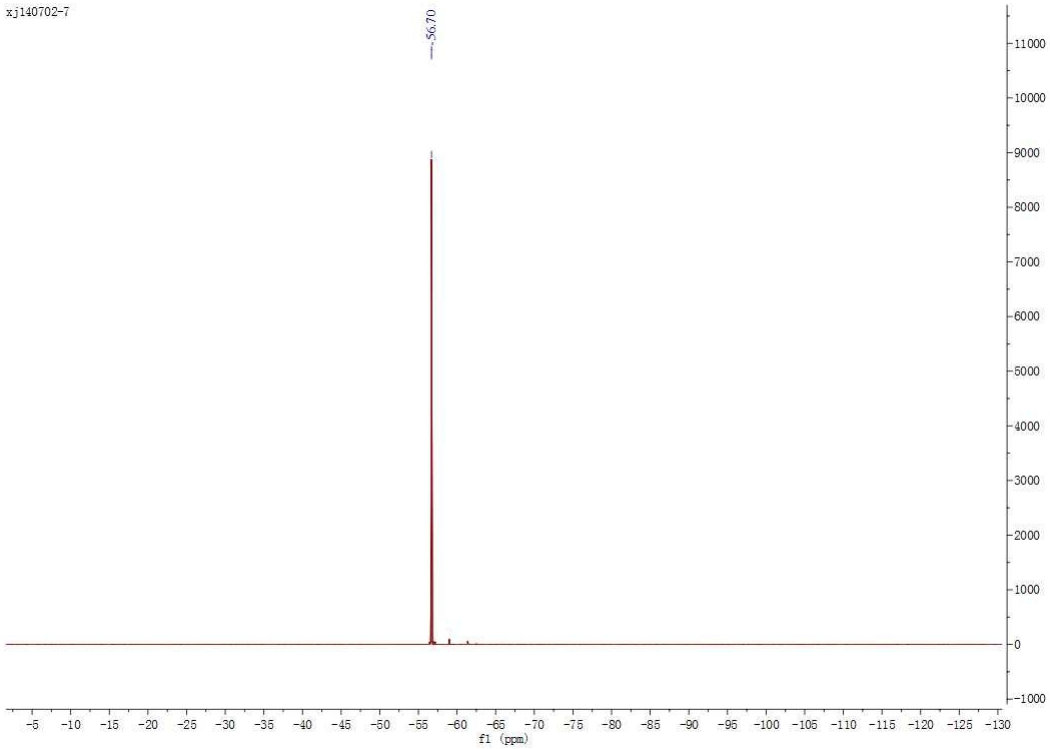
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 4.67 (s, 1H), 3.83 (s, 2H), 3.27 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.75, 158.54, 157.00, 140.34 (q, *J* = 4.1 Hz), 131.85, 129.80, 129.24 (q, *J* = 1.9 Hz), 122.88(q, *J* = 271 Hz), 116.67(q, *J* = 29 Hz), 114.35, 112.59, 108.85, 105.99, 63.15 (q, *J* = 3.7 Hz), 55.65, 55.20.

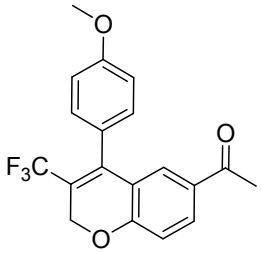
^{19}F NMR (376 MHz, $CDCl_3$) δ -56.70.




xj140702-7
158.75
158.54
157.00
140.36
140.32
124.24
121.53
116.81
116.52
114.35
112.59
108.85
105.99
77.34
77.08
76.71
63.16
63.13
55.65
55.20
f1 (ppm)


xj140702-7
56.70
f1 (ppm)

1-(4-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-chromen-6-yl)ethanone (**3o**)



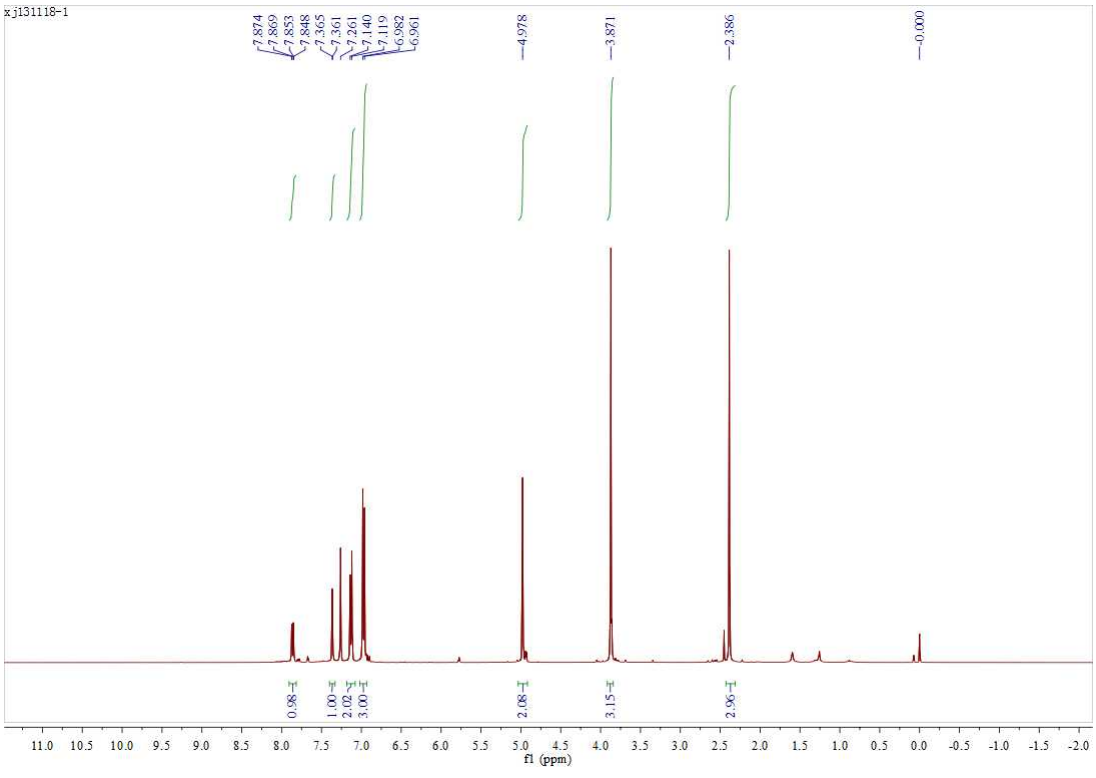
Prepared according to General Procedure **E.**

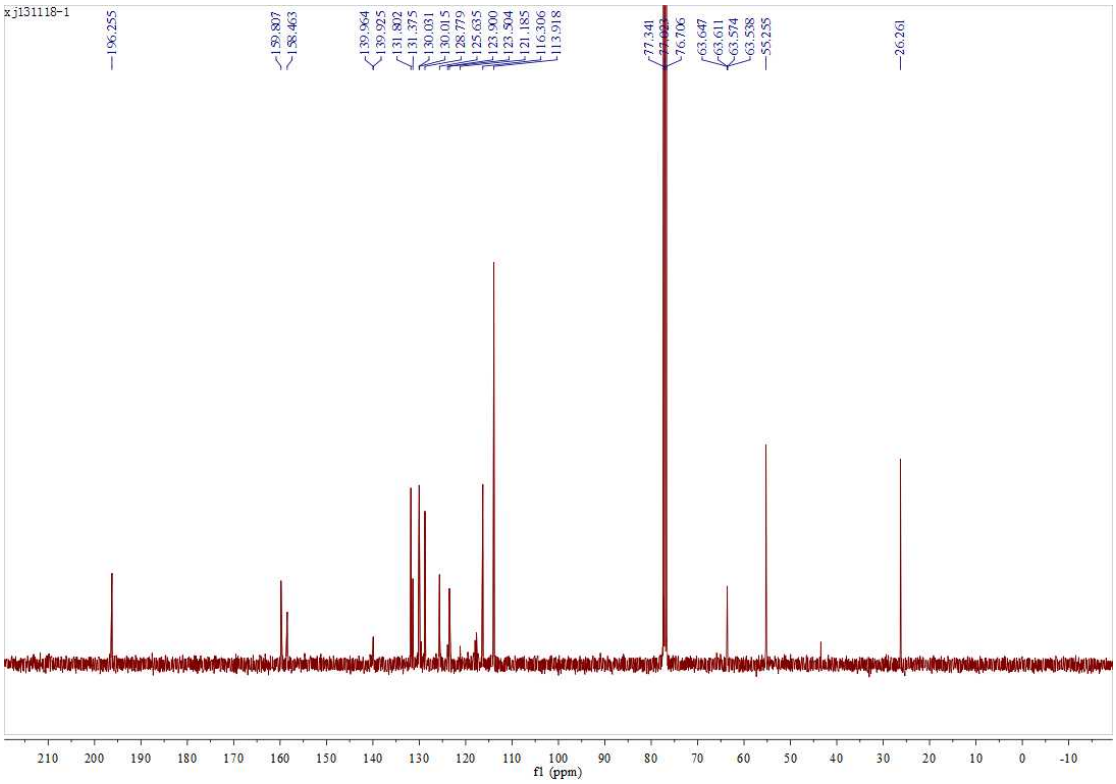
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 3H), 4.98 (s, 2H), 3.87 (s, 3H), 2.39 (s, 3H).

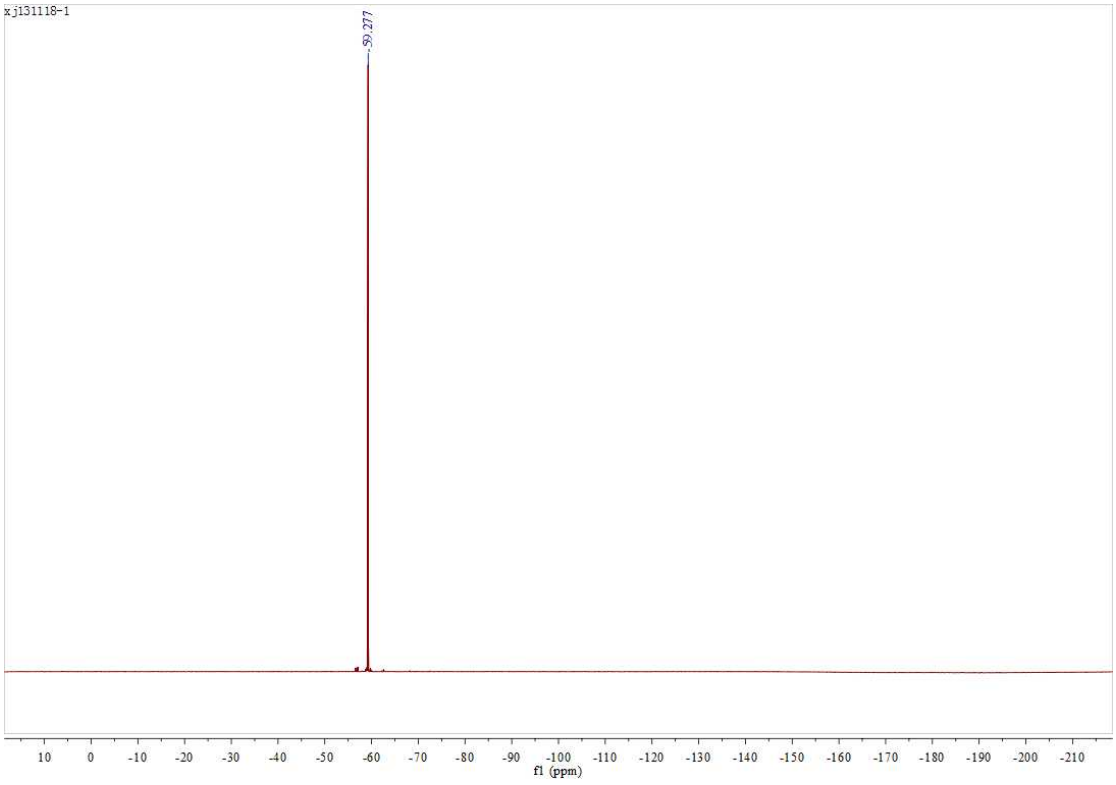
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.25, 159.81, 158.46, 139.94 (q, *J* = 4.0 Hz), 131.80, 131.38, 130.02 (q, *J* = 1.7 Hz), 128.78, 125.63, 123.50, 122.54 (q, *J* = 271 Hz), 116.31, 113.92, 63.59 (q, *J* = 3.6 Hz), 55.26, 26.26.

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.28.

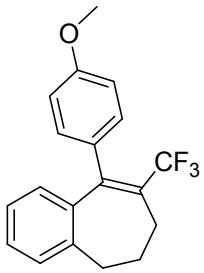
HRMS calcd for $C_{19}H_{15}F_3O_3$ ([M]$^+$): 348.0973; found: 348.0976.




xj131118-1
196.255
159.807
158.463
139.964
139.925
131.802
131.375
130.031
130.015
128.779
125.635
123.900
123.504
121.185
116.306
113.918
77.341
77.033
76.706
63.647
63.611
63.574
63.538
55.255
26.261
f1 (ppm)


xj131118-1
59.277
f1 (ppm)

9-(4-methoxyphenyl)-8-(trifluoromethyl)-6,7-dihydro-5H-benzo[7]annulene (**3p**)



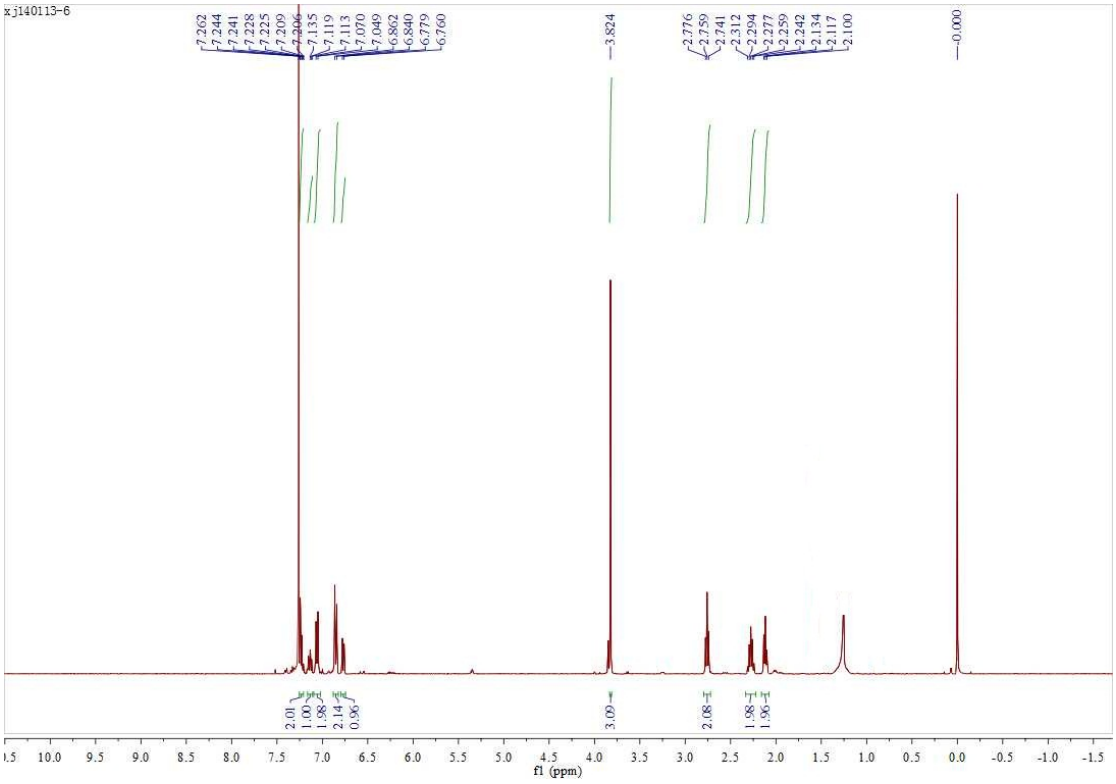
Prepared according to General Procedure **E.**

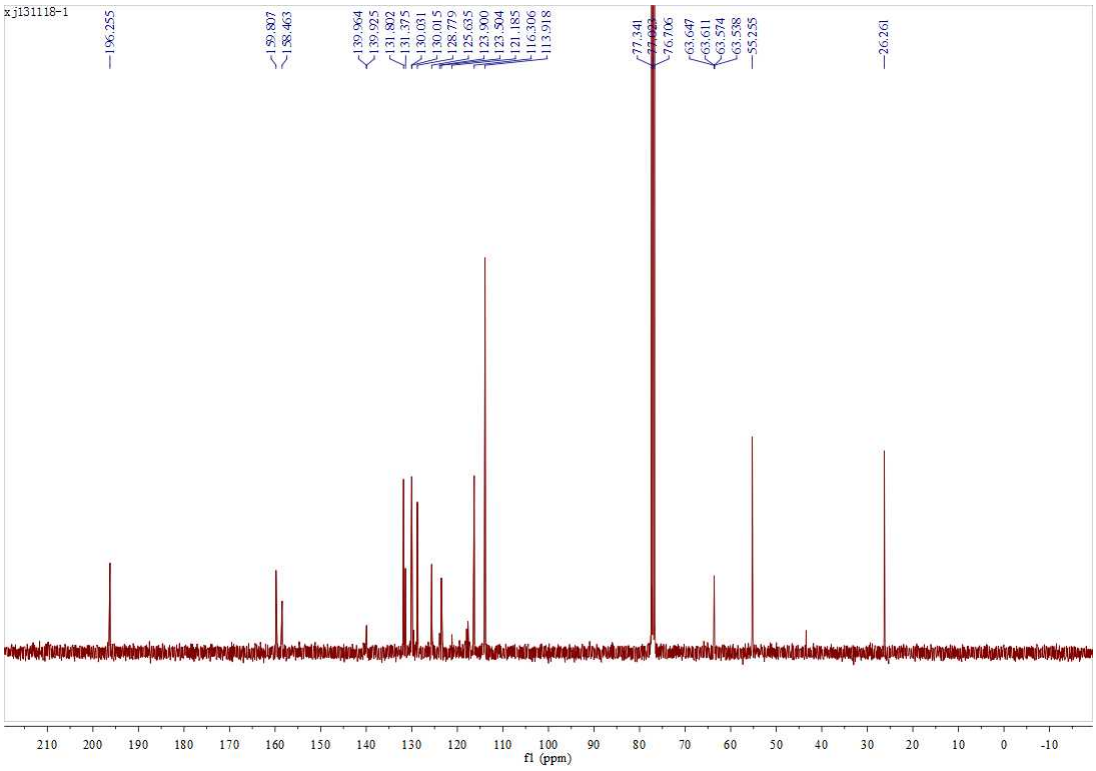
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.16 – 7.11 (m, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.32 – 2.24 (m, 2H), 2.12 (t, *J* = 6.9 Hz, 2H).

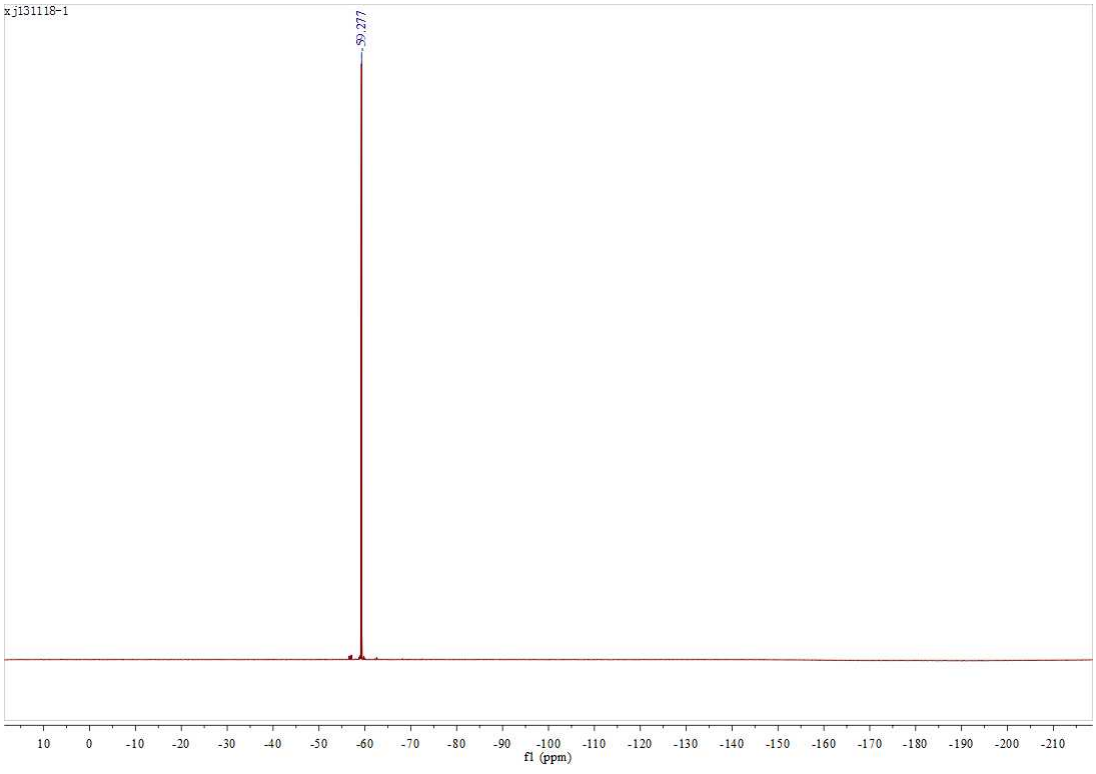
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.29, 146.47 (q, *J* = 2.5 Hz), 141.20, 141.04, 132.60, 130.77 (q, *J* = 2.1 Hz), 130.24, 128.55, 128.33, 126.20, 126.12 (q, *J* = 31.3 Hz), 124.88 (q, *J* = 274 Hz), 113.18, 55.21, 35.69, 31.81, 26.38 (q, *J* = 2.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.49.

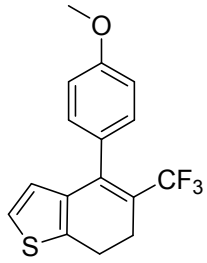
HRMS calcd for $C_{19}H_{17}F_3O$ ([M]$^+$): 318.1231; found: 318.1234.




xji31118-1
196.255
159.807
158.463
139.964
139.925
131.802
131.375
130.031
130.015
128.779
125.635
123.900
123.504
121.185
116.306
113.918
77.341
77.003
76.706
63.647
63.611
63.574
63.538
55.255
26.261
f1 (ppm)


xji31118-1
59.277
f1 (ppm)

4-(4-methoxyphenyl)-5-(trifluoromethyl)-6,7-dihydrobenzo[b]thiophene (**3r**)



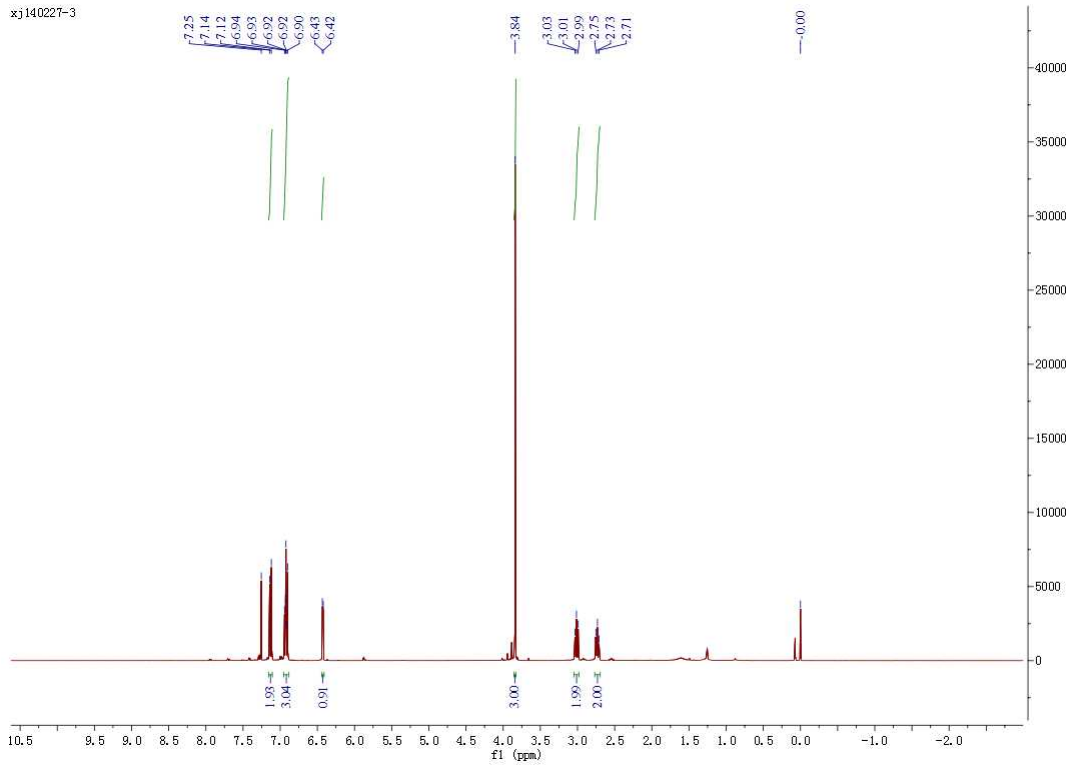
Prepared according to General Procedure **E.**

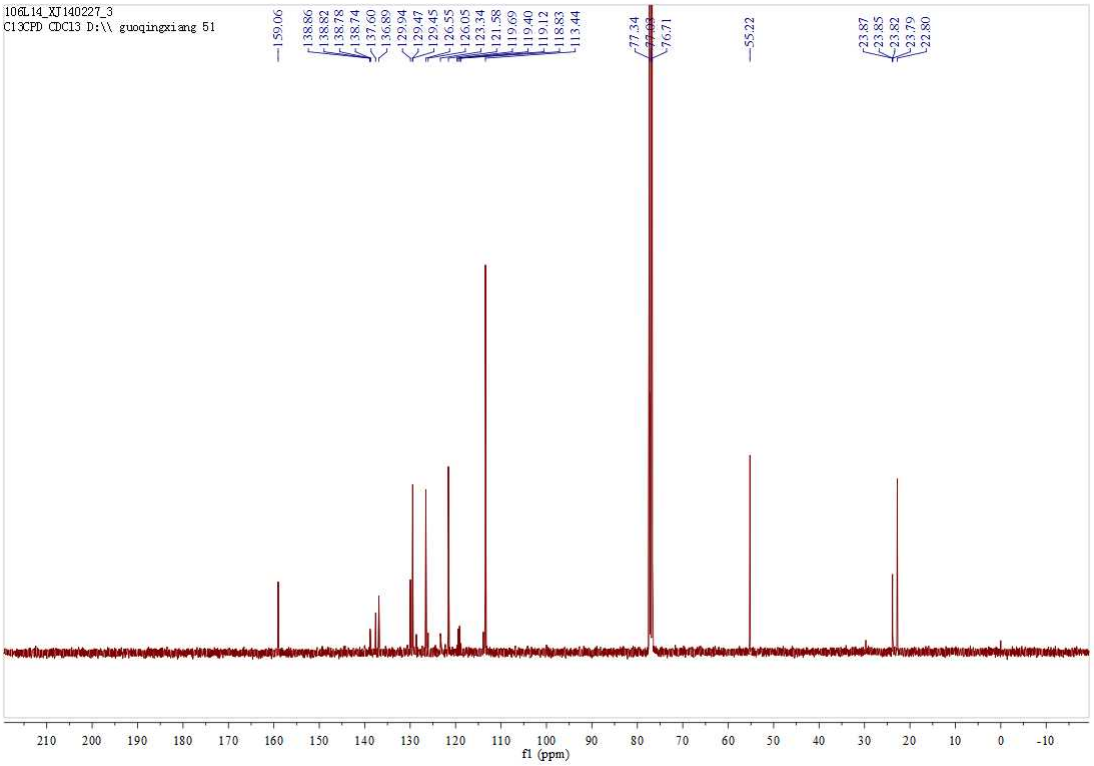
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 2H), 6.95 – 6.88 (m, 3H), 6.43 (d, *J* = 5.2 Hz, 1H), 3.84 (s, 3H), 3.01 (t, *J* = 8.7 Hz, 2H), 2.73 (t, *J* = 8.5 Hz, 2H).

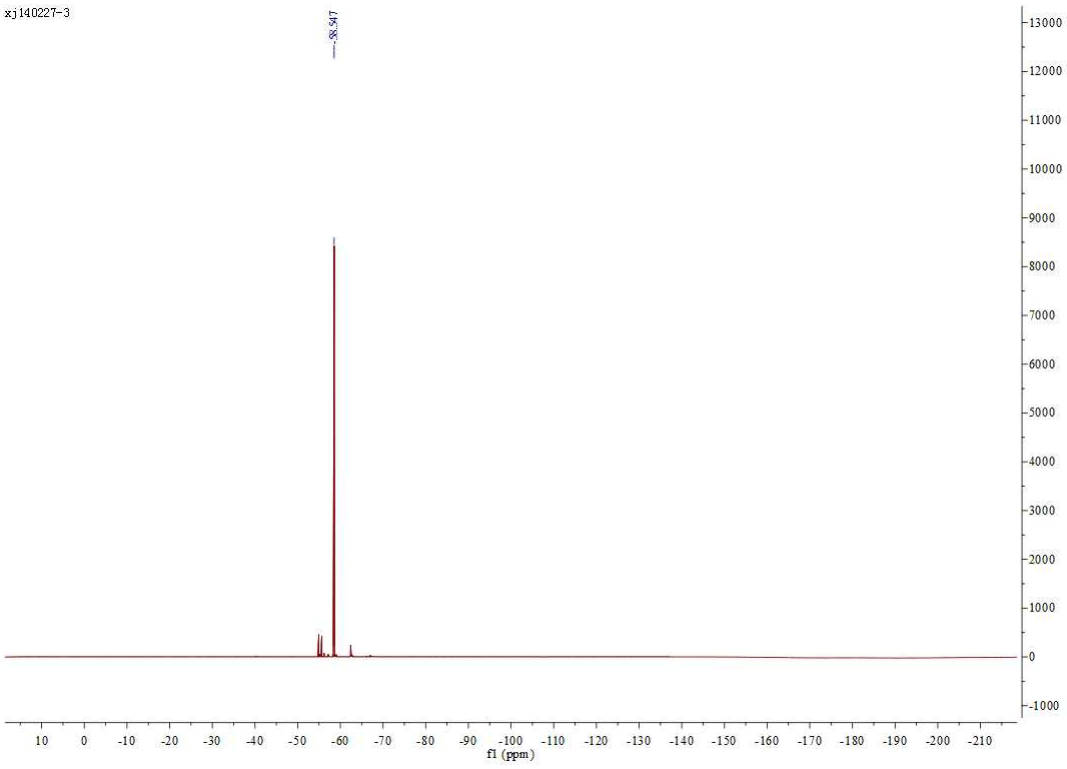
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.06, 138.80 (q, *J* = 4.2 Hz), 137.60, 136.89, 129.94, 129.46 (q, *J* = 2.0 Hz), 126.55, 124.70 (q, *J* = 271 Hz), 121.58, 119.29 (q, *J* = 28.6 Hz), 113.44, 55.22, 23.83 (q, *J* = 3 Hz), 22.80.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.55.

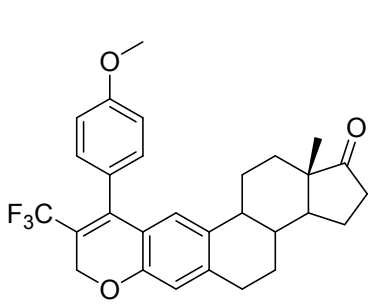
HRMS calcd for $C_{16}H_{13}F_3OS$ ([M]$^+$): 310.0639; found: 310.06341.



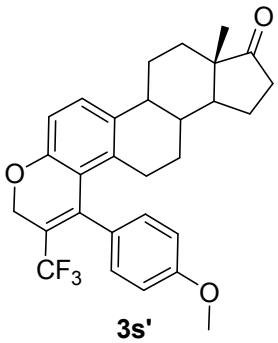

106L14_XJ140227_3
C13CPD CDCl3 D:\\ guoqingxiang 51
159.06
138.86
138.82
138.78
138.74
137.60
136.89
129.94
129.47
129.45
126.55
126.05
123.34
121.58
119.69
119.40
119.12
118.83
113.44
77.34
77.03
76.71
55.22
23.87
23.85
23.82
23.79
22.80
f1 (ppm)


xj140227-3
-58.547
f1 (ppm)

(13aS)-10-(4-methoxyphenyl)-13a-methyl-9-(trifluoromethyl)-3,3a,3b,4,5,8,11b,12,13,13a-decahydrocyclopenta[5,6]naphtho[1,2-g]chromen-1(2H)-one (**3r**) and (8aS)-1-(4-methoxyphenyl)-8a-methyl-2-(trifluoromethyl)-6b,7,8,8a,10,11,11a,11b,12,13-decahydrocyclopenta[5,6]naphtho[2,1-f]chromen-9(3H)-one (**3s'**)



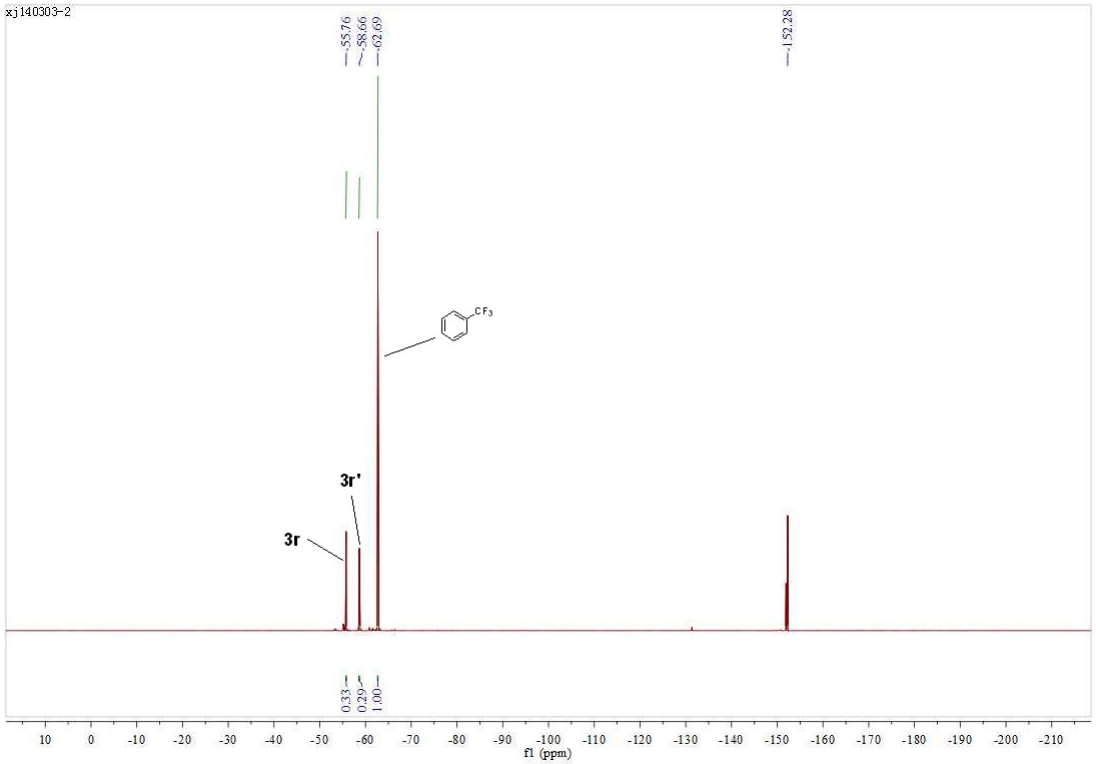
3s

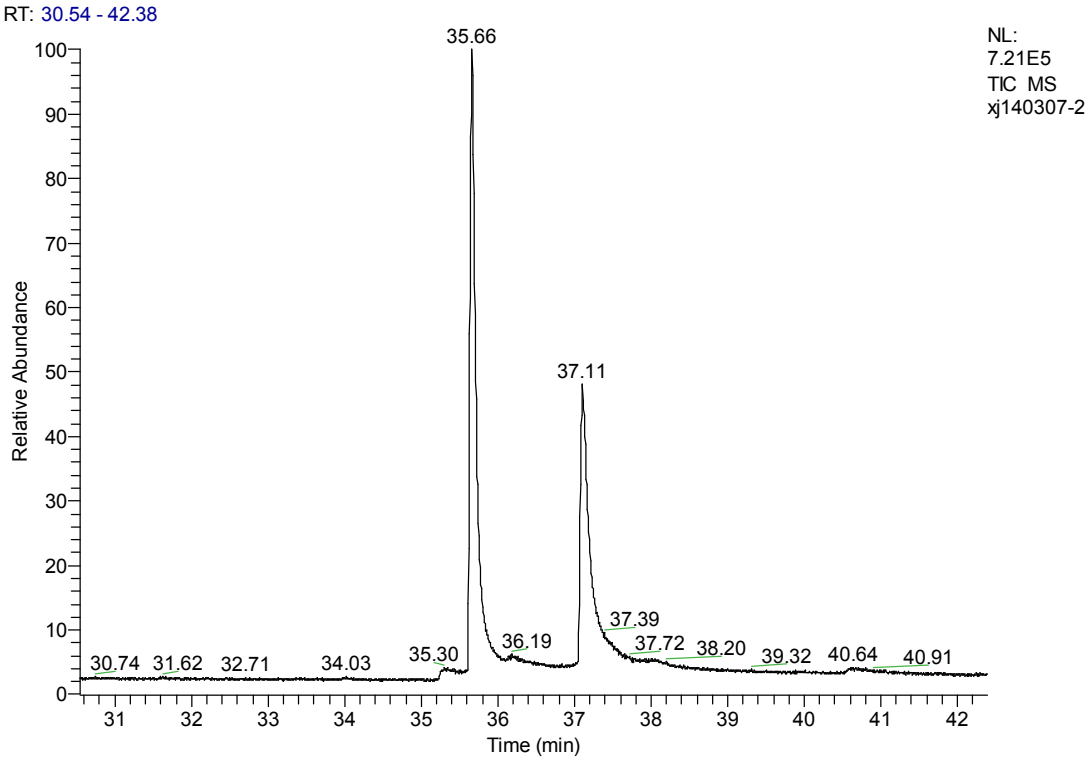


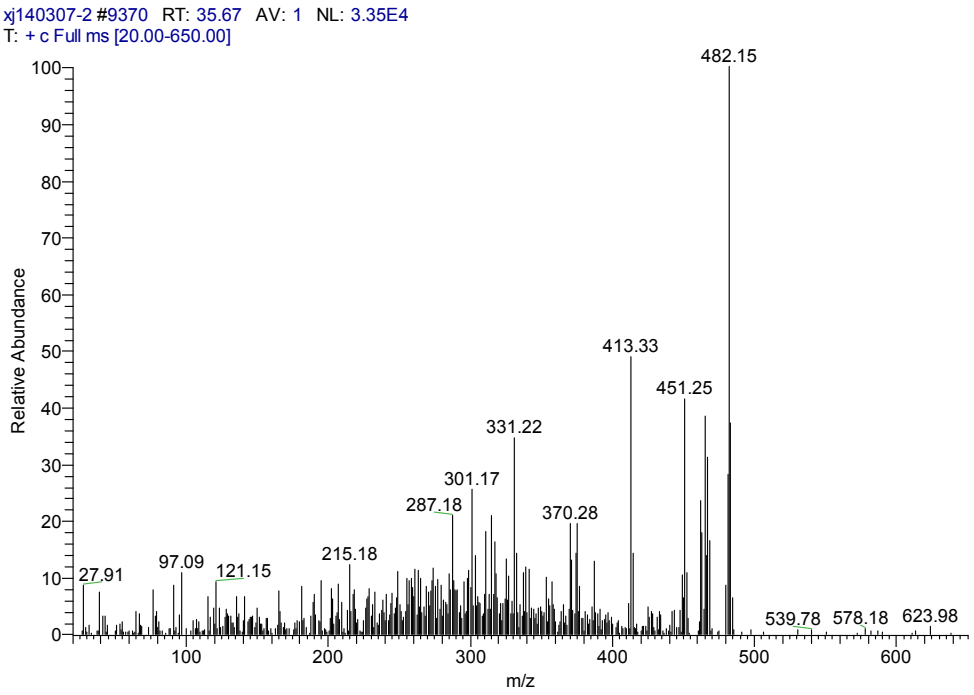
3s'

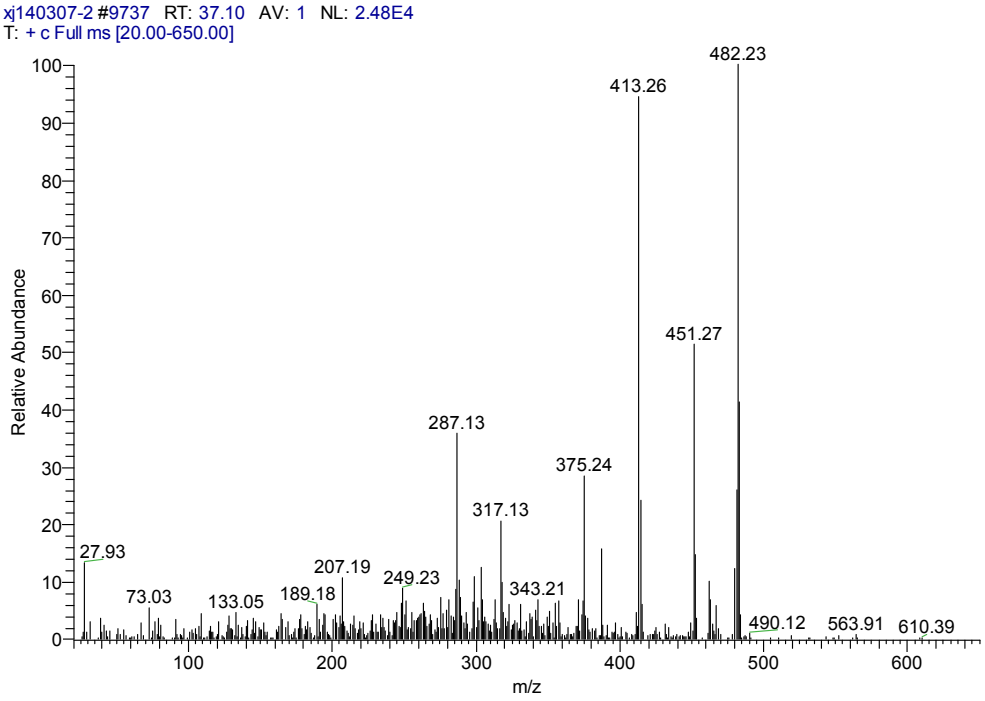
Note：Prepared according to General Procedure **E,** and the yield and ratio were determined by ^{19}F NMR with $PhCF_3$ as internal stansard. The two products can not be separated from each other by column chromatographic for the similar polarity, and the molecular weight and structures was determined by GC-MS and HRMS (calcd for $C_{29}H_{30}F_3O_3$ ($[M+H]^+$): 483.2147; found: 483.2145.

.

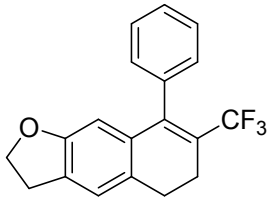



RT: 30.54 - 42.38
NL:
7.21E5
TIC MS
xj140307-2
Relative Abundance
Time (min)
35.66
37.11
37.39
30.74
31.62
32.71
34.03
35.30
36.19
37.72
38.20
39.32
40.64
40.91


xj140307-2 #9370 RT: 35.67 AV: 1 NL: 3.35E4
T: + c Full ms [20.00-650.00]
Relative Abundance
m/z
482.15
413.33
451.25
331.22
301.17
287.18
370.28
215.18
97.09
121.15
27.91
539.78
578.18
623.98



8-phenyl-7-(trifluoromethyl)-2,3,5,6-tetrahydronaphtho[2,3-b]furan (**3t**)



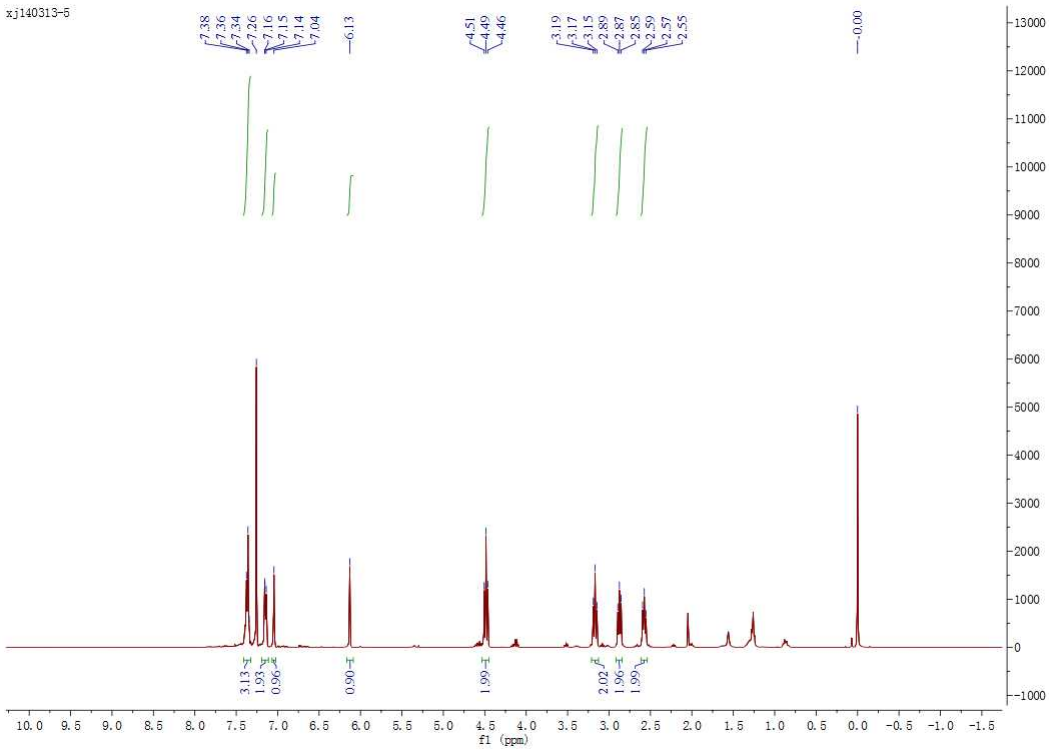
Prepared according to General Procedure **E.**

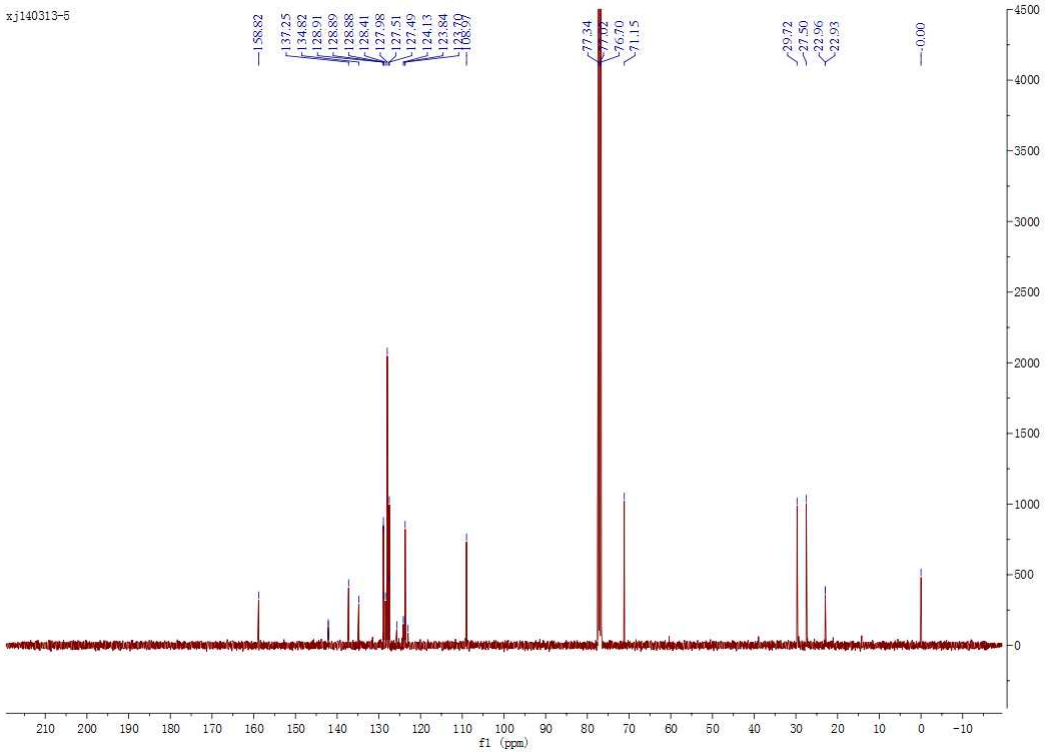
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 3H), 7.15 (d, *J* = 8 Hz, 2H), 7.04 (s, 1H), 6.13 (s, 1H), 4.49 (t, *J* = 8.7 Hz, 2H), 3.17 (t, *J* = 8.7 Hz, 2H), 2.87 (t, *J* = 8 Hz, 2H), 2.57 (t, *J* = 7.9 Hz, 2H).

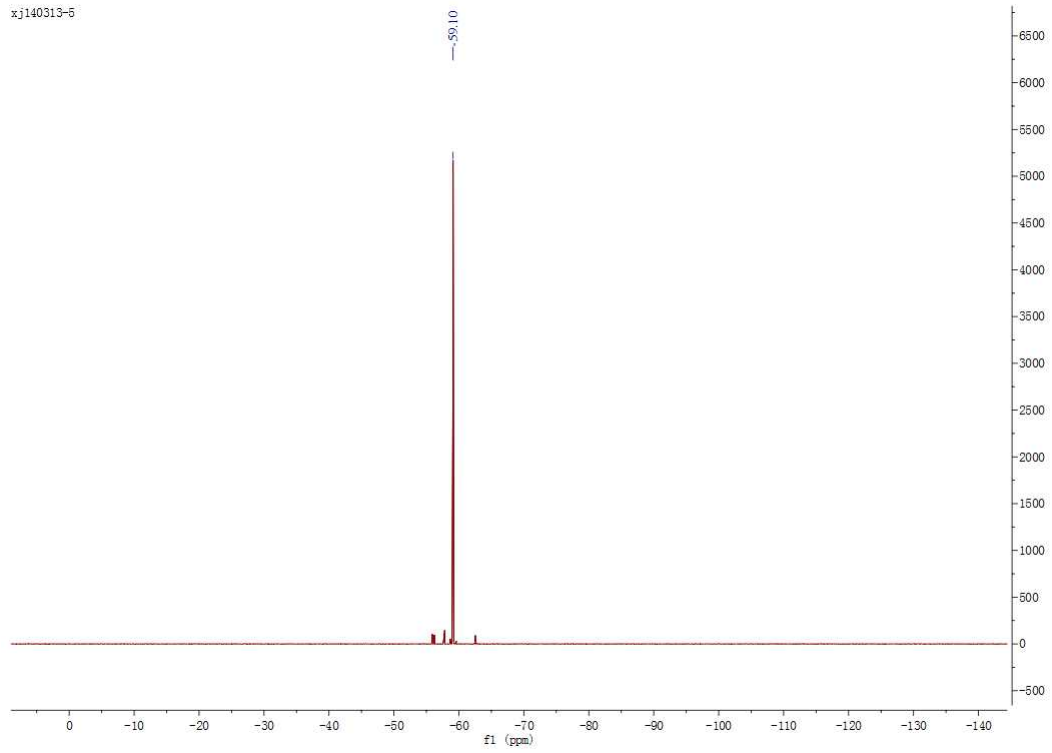
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.82, 142.12 (q, *J* = 2 Hz), 137.25, 134.82, 128.90 (q, *J* = 2 Hz), 128.41, 127.98, 127.51, 127.49, 124.35 (q, *J* = 271 Hz), 123.98 (q, *J* = 29 Hz), 123.70, 108.97, 71.15, 29.72, 27.50, 22.95 (q, *J* = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.10.

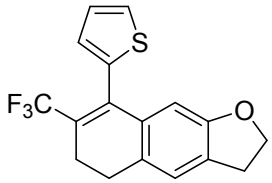
HRMS calcd for $C_{19}H_{15}F_3O$ ([M]$^+$): 316.1075; found: 316.1078.


xj140313-5
7.38
7.36
7.34
7.26
7.16
7.15
7.14
7.04
6.13
4.51
4.49
4.46
3.19
3.17
3.15
2.89
2.87
2.85
2.59
2.57
2.55
0.00
3.13
1.93
0.96
0.90
1.99
2.02
1.96
1.99
f1 (ppm)


xj140313-5
158.82
137.25
134.82
128.91
128.89
128.88
128.41
127.98
127.51
127.49
124.13
123.84
77.34
77.02
76.70
71.15
29.72
27.50
22.96
22.93
0.00
f1 (ppm)



8-(thiophen-2-yl)-7-(trifluoromethyl)-2,3,5,6-tetrahydronaphtho[2,3-b]furan (**3u**)



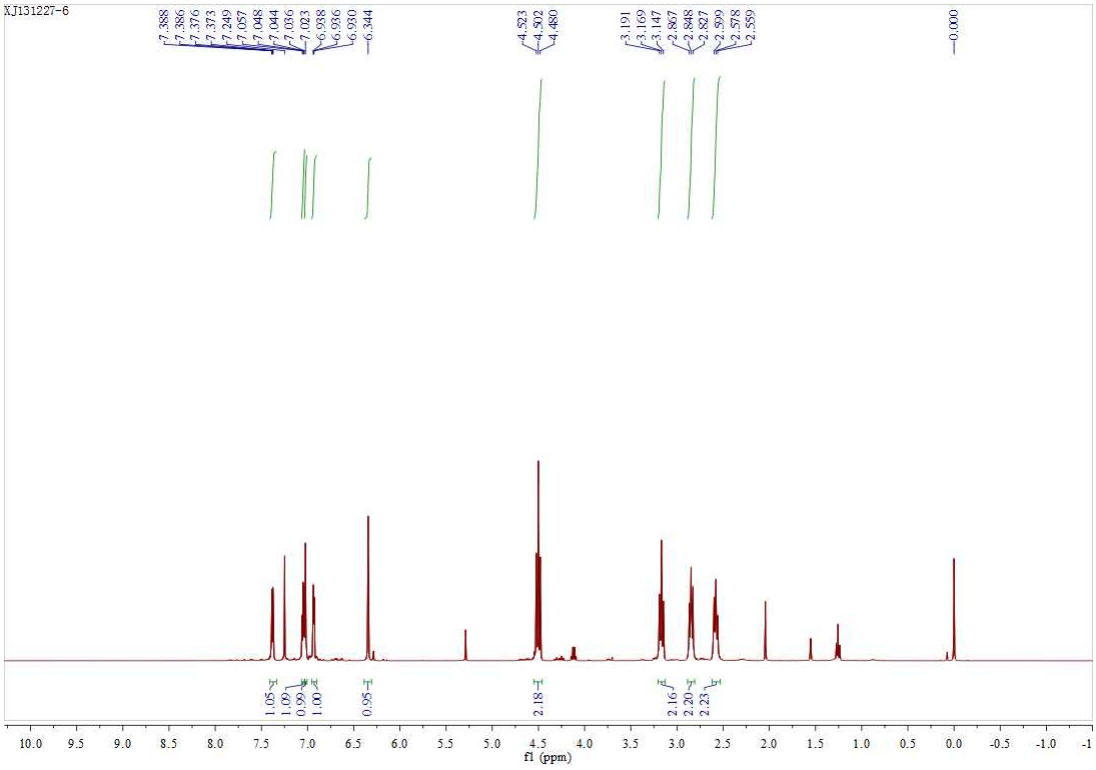
Prepared according to General Procedure **E.**

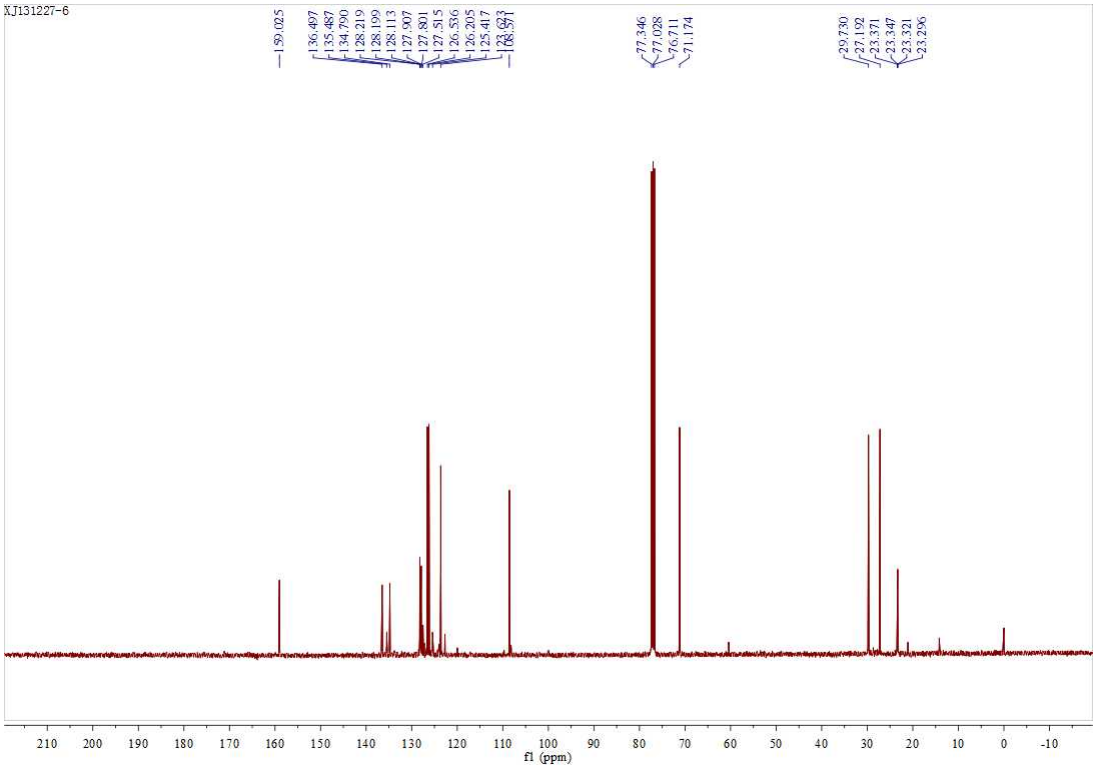
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.04 (m, 1H), 7.02 (s, 1H), 6.93 (d, *J* = 3.2 Hz, 1H), 6.34 (s, 1H), 4.50 (t, *J* = 8.7 Hz, 2H), 3.17 (t, *J* = 8.6 Hz, 2H), 2.85 (t, *J* = 8.4 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H).

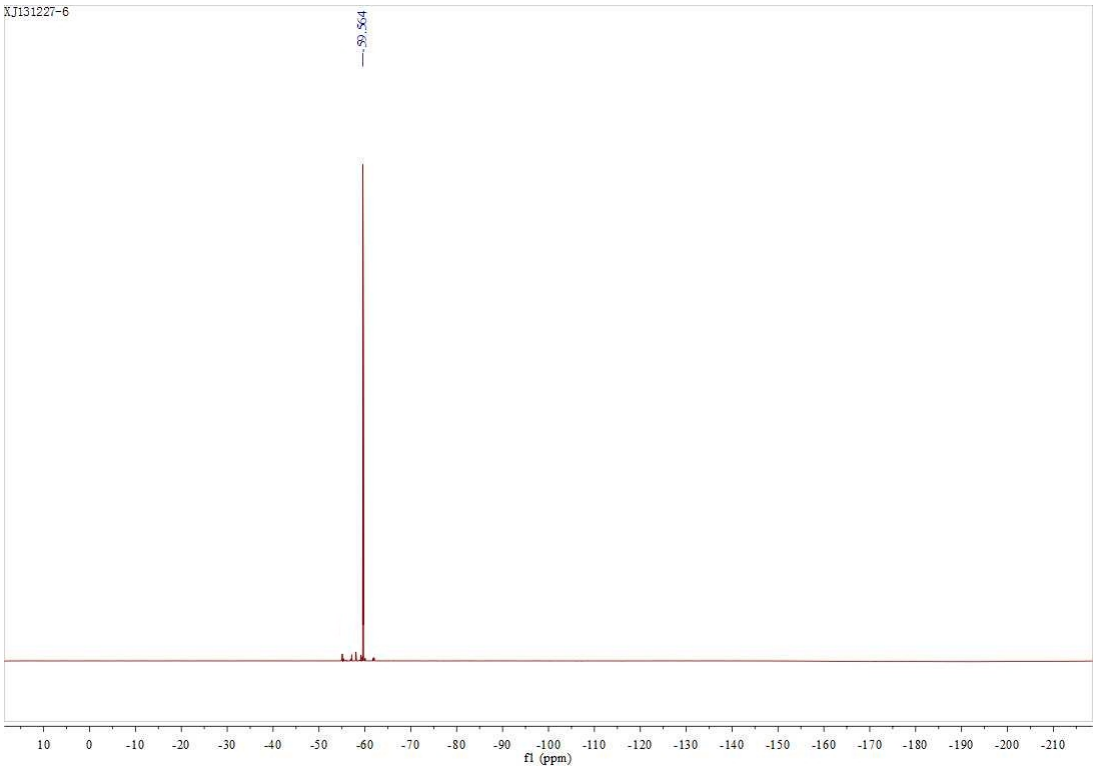
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.03, 136.50, 135.47 (q, *J* = 4.0 Hz), 134.79, 128.21 (q, *J* = 2.0 Hz), 128.11, 127.90, 127.66 (q, *J* = 28.6 Hz), 126.54, 126.20, 124.06 (q, *J* = 271 Hz), 123.62, 108.57, 71.17, 29.73, 27.19, 23.33 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.56.

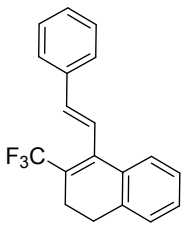
HRMS calcd for $C_{17}H_{13}F_3OS$ ($[M]^+$): 322.0639; found: 322.0642.


XJ131227-6
7.388
7.386
7.376
7.373
7.249
7.057
7.048
7.044
7.036
7.023
6.938
6.936
6.930
6.344
4.523
4.502
4.480
3.191
3.169
3.147
2.867
2.848
2.827
2.599
2.578
2.559
0.000
1.05
1.09
0.99
1.00
0.95
2.18
2.16
2.20
2.23
f1 (ppm)


XJ131227-6
159.025
136.497
135.487
134.790
128.219
128.199
128.113
127.907
127.801
127.515
126.556
126.205
125.417
123.693
118.571
77.346
77.028
76.711
71.174
29.730
27.192
23.371
23.347
23.321
23.296
f1 (ppm)



(E)-4-styryl-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3v**)



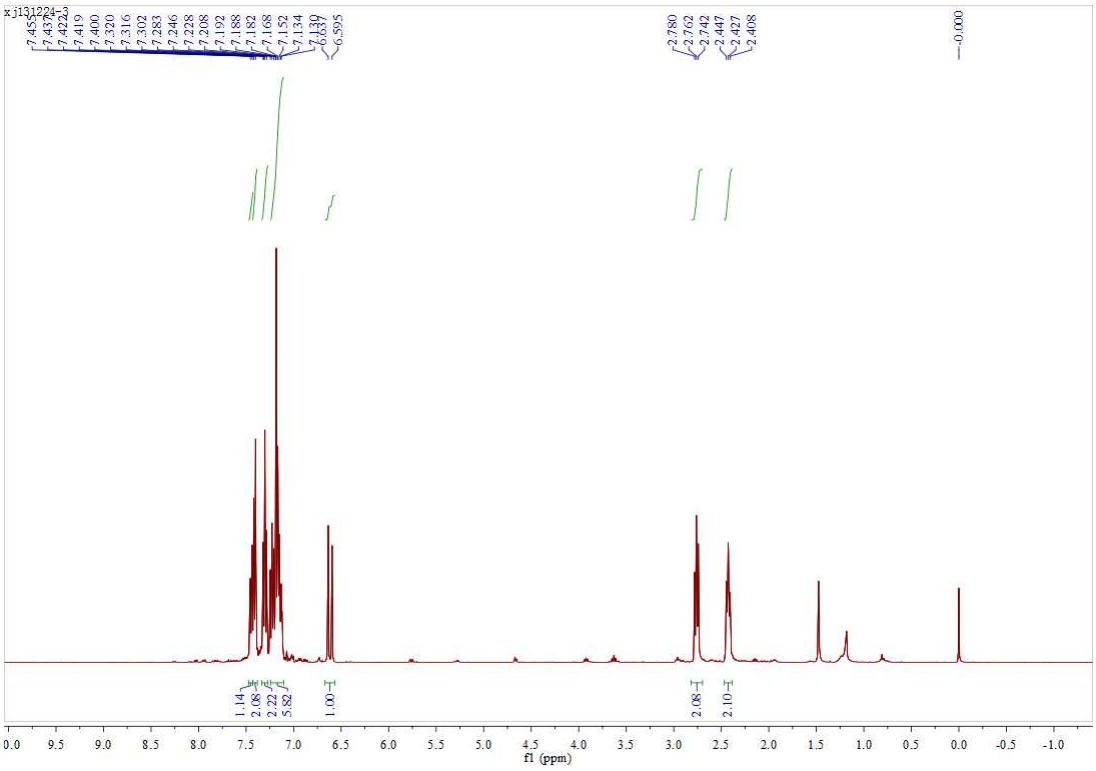
Prepared according to General Procedure **E.**

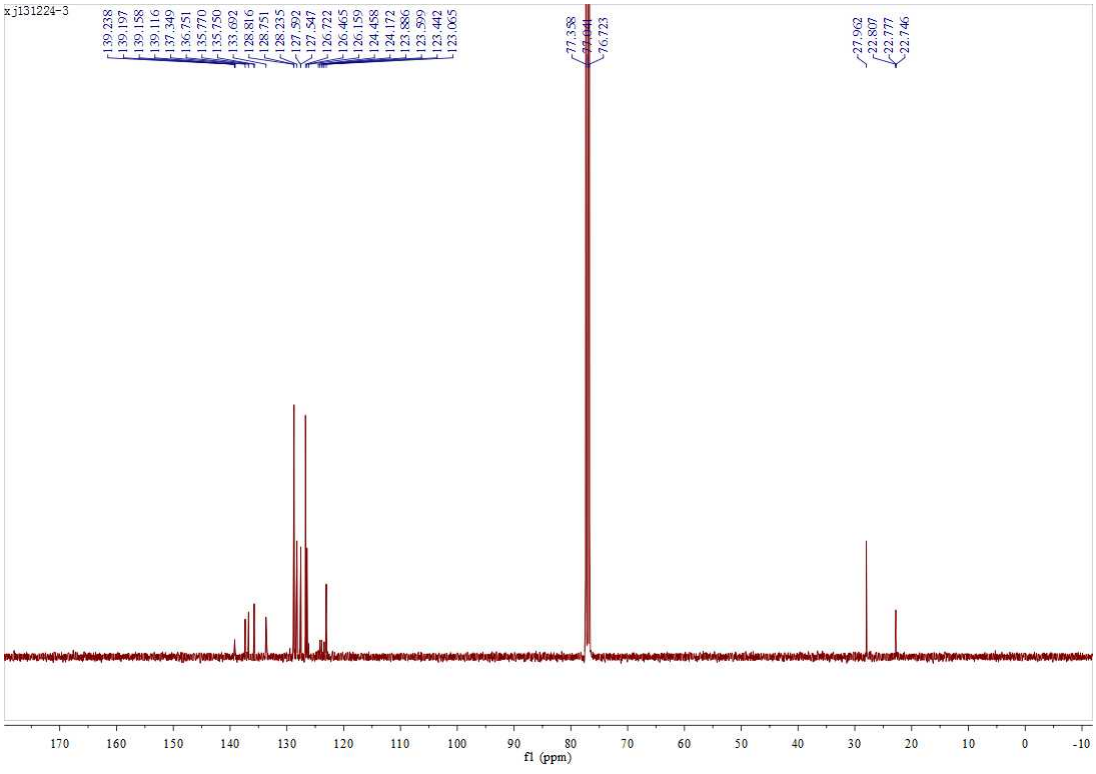
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.2 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.31 (t, *J* = 5.6 Hz, 2H), 7.24 – 7.10 (m, 5H), 6.62 (d, *J* = 16.5 Hz, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.43 (t, *J* = 7.7 Hz, 2H).

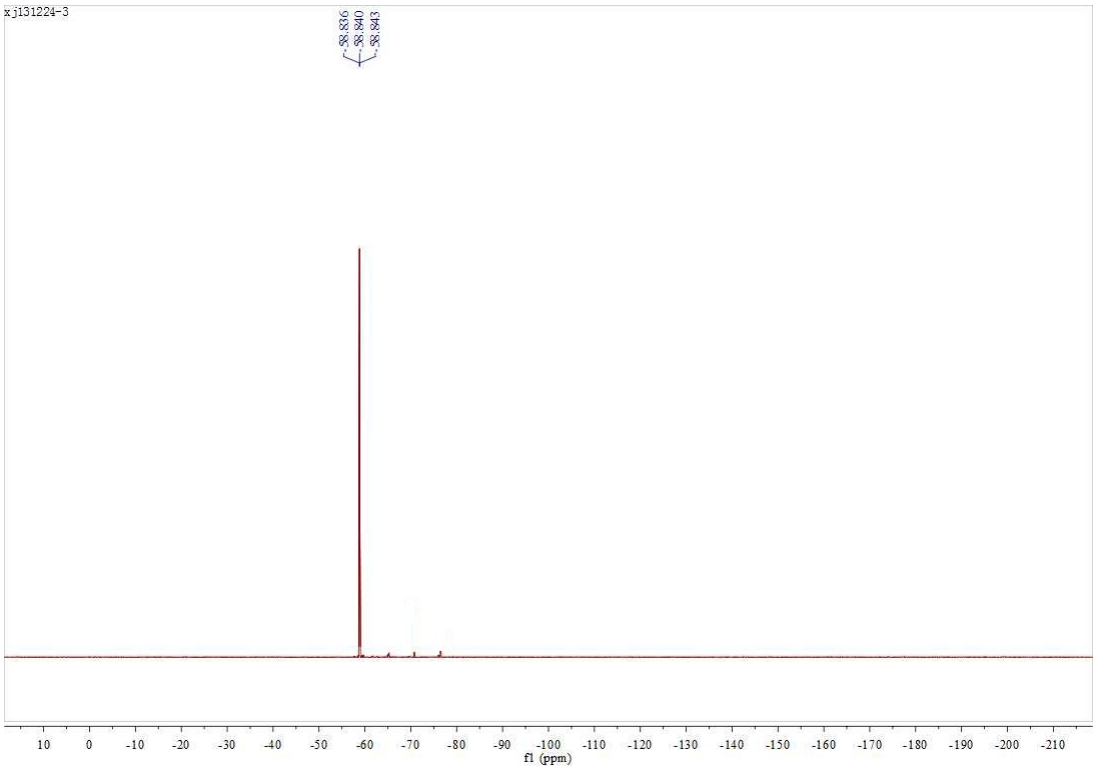
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.18 (q, *J* = 4.2 Hz), 137.35, 136.75, 135.76 (q, *J* = 2.0 Hz), 133.69, 128.81, 128.75, 128.24, 127.59, 127.55, 126.72, 126.46, 124.80 (q, *J* = 271 Hz), 124.03 (q, *J* = 28.6 Hz), 123.07, 27.96, 22.79 (q, *J* = 3.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.84.

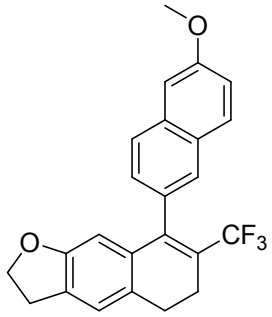
HRMS calcd for $C_{19}H_{15}F_3$ ($[M]^+$): 300.1126; found: 300.1129.


xj131224-3
7.455
7.437
7.422
7.419
7.400
7.320
7.316
7.302
7.283
7.246
7.228
7.208
7.192
7.188
7.182
7.168
7.152
7.134
7.139
7.137
6.595
2.780
2.762
2.742
2.447
2.427
2.408
-0.000
1.14
2.08
2.22
5.82
1.00
2.08
2.10
f1 (ppm)


xj131224-3
139.238
139.197
139.158
139.116
137.349
136.751
135.770
135.750
133.692
128.816
128.751
128.235
127.892
127.547
126.722
126.465
126.159
124.458
124.172
123.886
123.599
123.442
123.065
77.388
77.041
76.723
27.962
22.807
22.777
22.746
f1 (ppm)



8-(6-methoxynaphthalen-2-yl)-7-(trifluoromethyl)-2,3,5,6-tetrahydronaphtho[2,3-b]furan (**3w**)



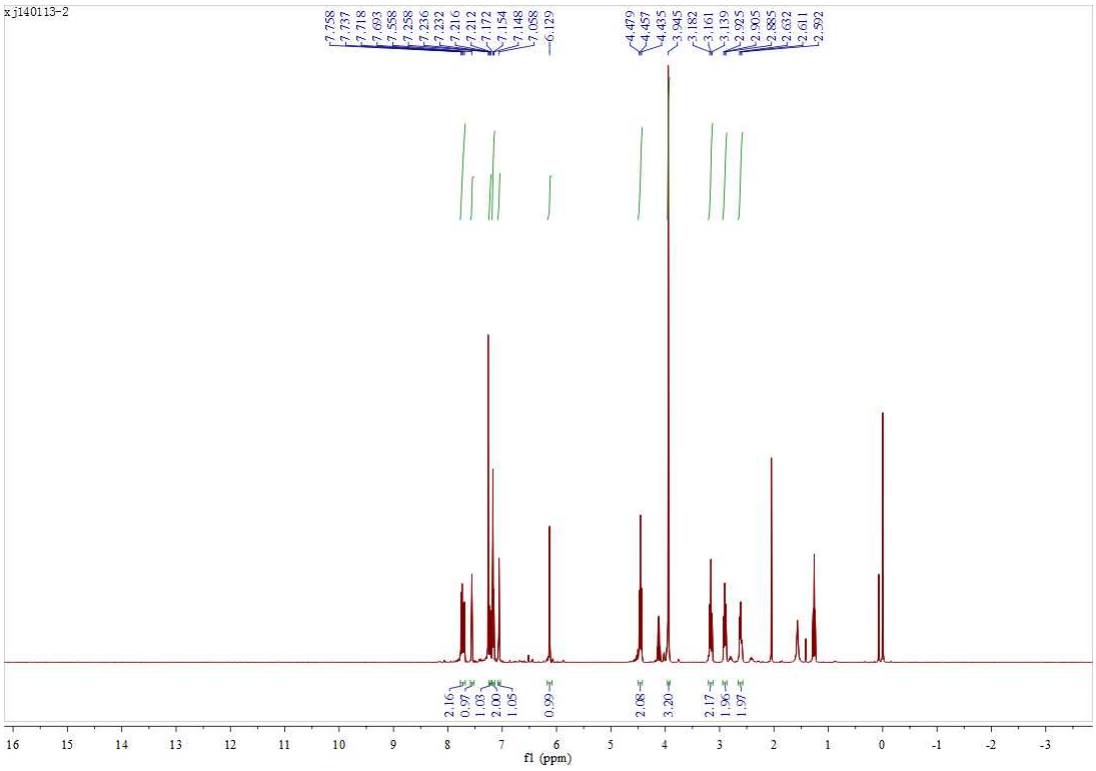
Prepared according to General Procedure **E.**

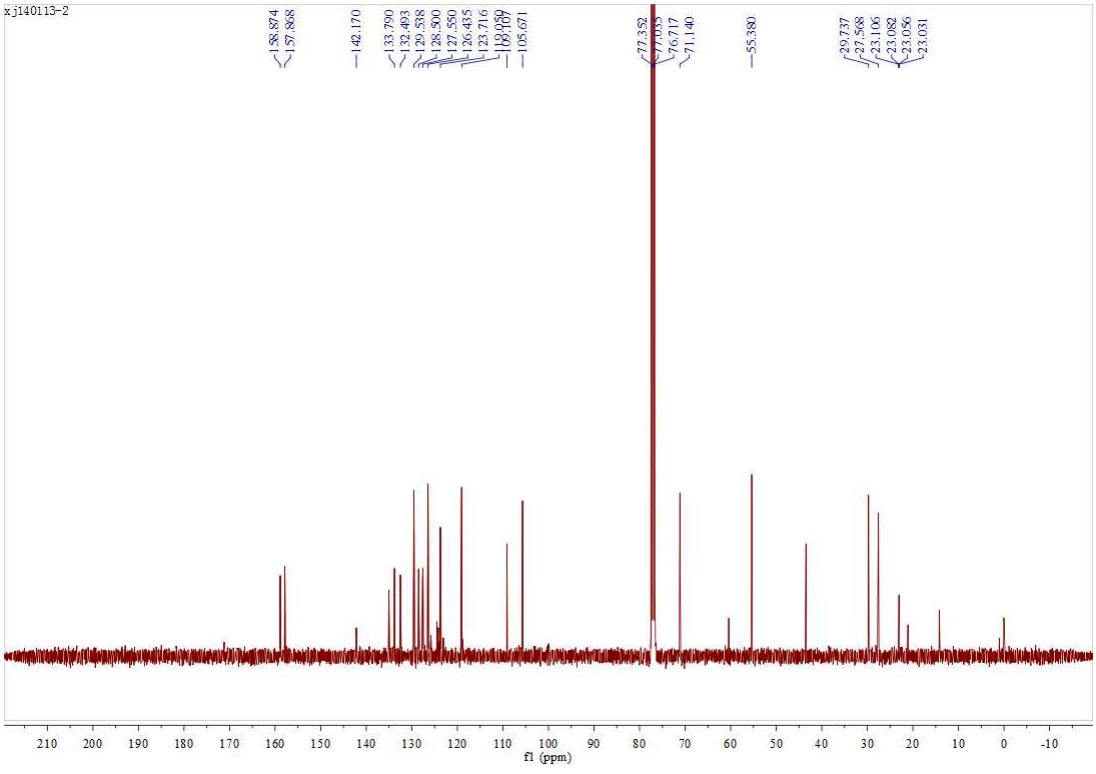
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 10 Hz, 1H),7.56 (s, 1H), 7.22 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.06 (s, 1H), 6.13 (s, 1H), 4.46 (t, *J* = 8.7 Hz, 2H), 3.94 (s, 3H), 3.16 (t, *J* = 8.7 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 7.9 Hz, 2H).

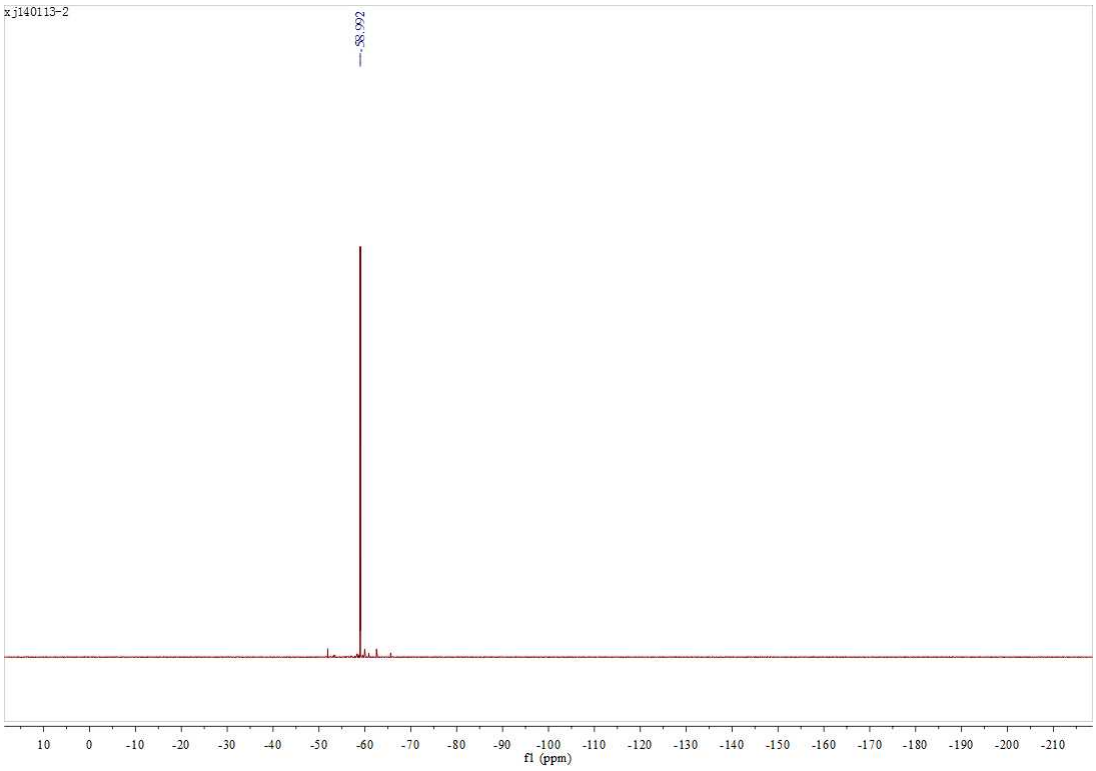
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.87, 157.87, 142.17, 135.04, 133.79, 132.49, 129.54, 128.50, 128.45, 127.68, 127.63, 127.45, 126.44, 124.44 (q, *J* = 272 Hz), 124.33 (q, *J* = 28.5 Hz) , 123.72, 119.05, 109.11, 105.67, 71.14, 55.38, 29.74, 27.57, 23.07 (q, *J* = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.99.

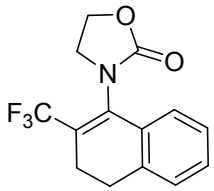
HRMS calcd for $C_{24}H_{19}F_3O_2$ ($[M]^+$): 396.1337; found: 396.1334.


xj140113-2
7.758
7.737
7.718
7.693
7.558
7.258
7.236
7.232
7.216
7.212
7.172
7.154
7.148
7.058
6.129
4.479
4.457
4.435
3.945
3.182
3.161
3.139
2.925
2.905
2.885
2.632
2.611
2.592
2.16
0.97
1.03
2.00
1.05
0.99
2.08
3.20
2.17
1.96
1.97
f1 (ppm)


xj140113-2
158.874
157.868
142.170
133.790
132.493
129.538
128.890
127.550
126.435
123.716
118.059
109.107
105.671
77.352
77.053
76.717
71.140
55.380
29.737
27.568
23.106
23.082
23.056
23.031
f1 (ppm)



3-(2-(trifluoromethyl)-3,4-dihydronaphthalen-1-yl)oxazolidin-2-one (**3x**)



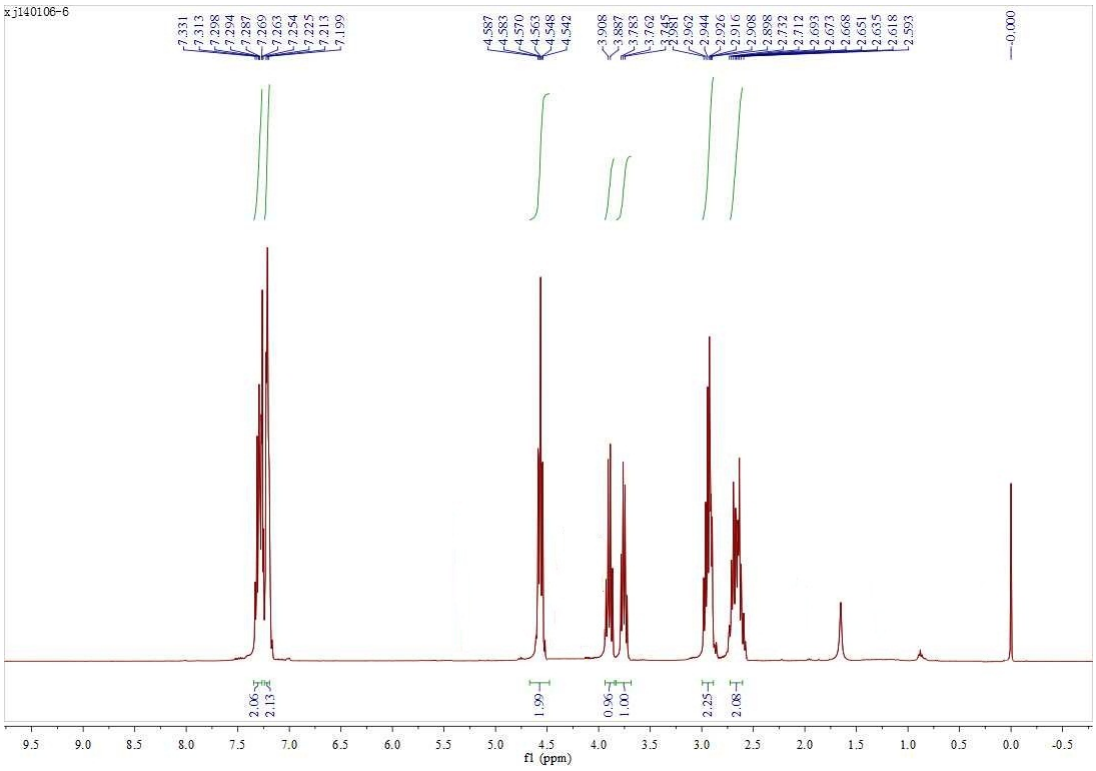
Prepared according to General Procedure **E.**

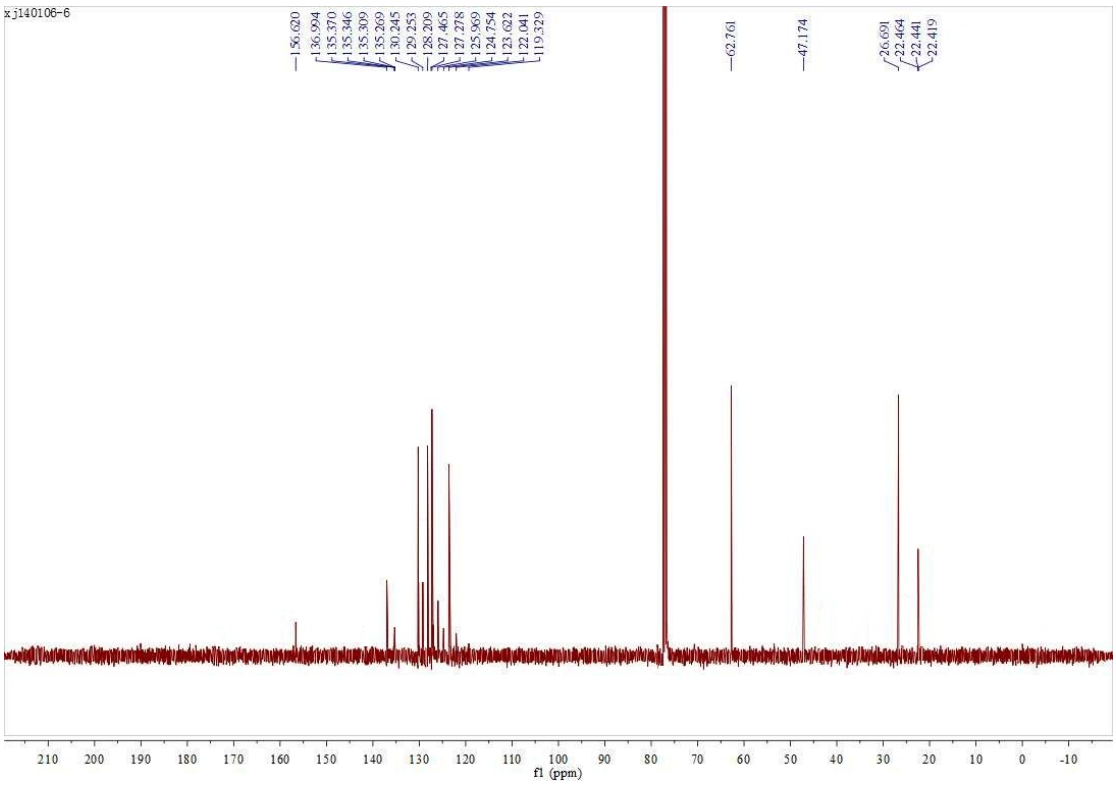
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.21 (m, 2H), 4.67 – 4.48 (m, 2H), 3.90 (dd, *J* = 16.7, 8.5 Hz, 1H), 3.75 (dd, *J* = 15.3, 8.4 Hz, 1H), 2.99 – 2.89 (m, 2H), 2.73 – 2.59 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.62, 136.99, 135.32 (q, *J* = 3.7 Hz), 130.25, 129.25, 128.21, 127.28, 125.97, 123.62, 123.39 (q, *J* = 271 Hz), 62.76, 47.17, 26.69, 22.45 (q, *J* = 2.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.87.

HRMS calcd for $C_{14}H_{12}F_3NO_2$ ($[M]^+$): 283.0820; found: 283.0824.


xj140106-6
7.331
7.313
7.298
7.294
7.287
7.269
7.263
7.254
7.225
7.213
7.199
4.587
4.583
4.570
4.563
4.548
4.542
3.908
3.887
3.783
3.762
3.345
3.261
2.962
2.944
2.926
2.916
2.908
2.898
2.732
2.712
2.693
2.673
2.668
2.651
2.635
2.618
2.593
0.000
2.06
2.13
1.99
0.96
1.00
2.25
2.08
f1 (ppm)


xj140106-6
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136.994
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135.346
135.309
135.269
130.245
129.253
128.209
127.465
127.278
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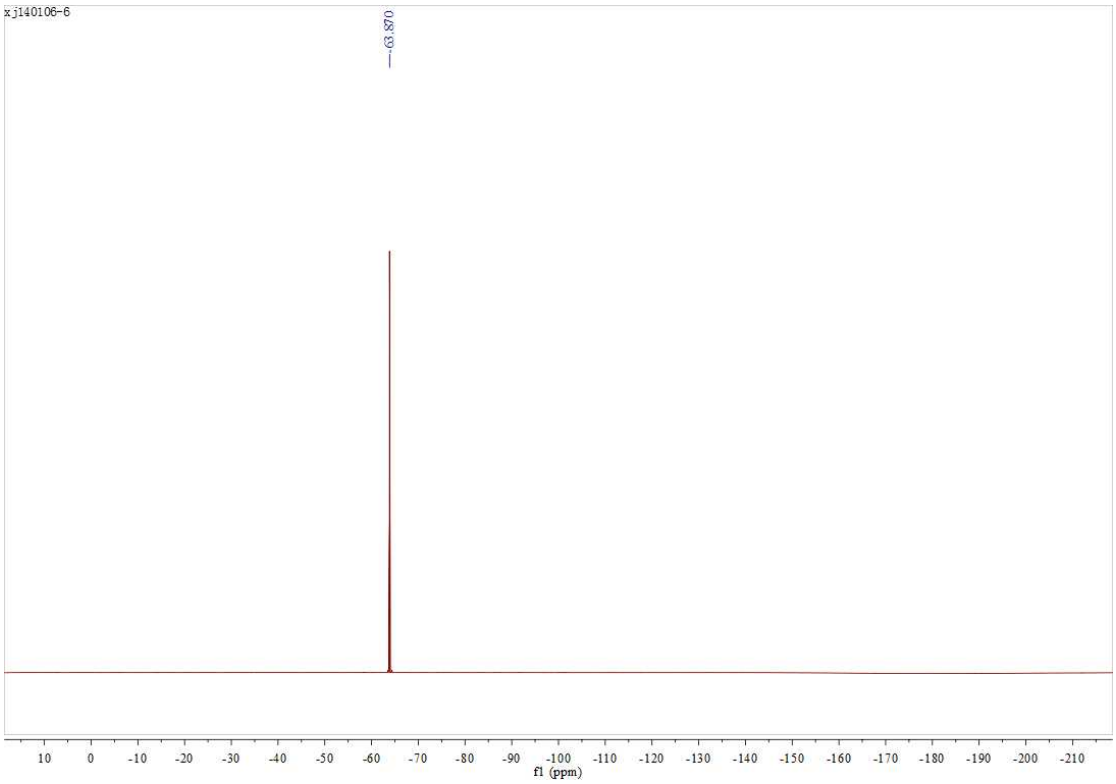
123.622
122.041
119.329
62.761
47.174
26.691
22.464
22.441
22.419
f1 (ppm)

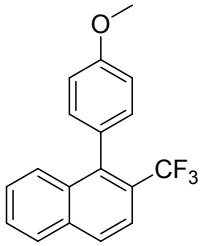


IV. Synthetic Application

1. Representative Procedure for Aromatization[2]

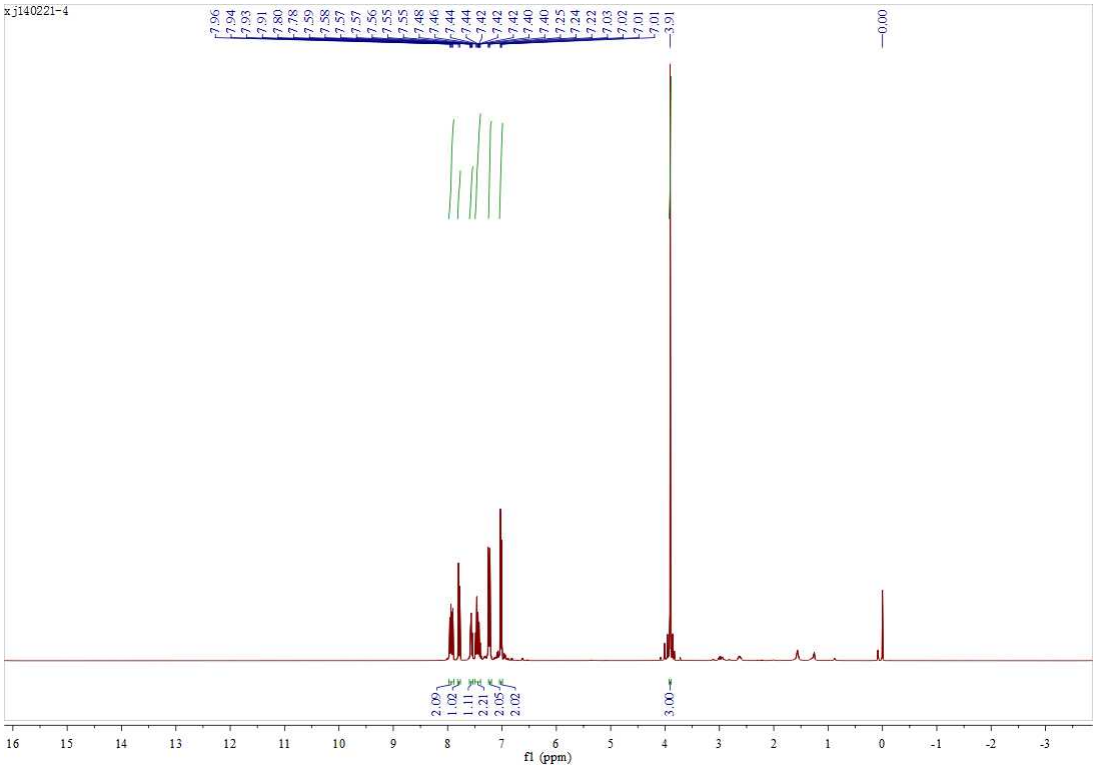
To a solution of 4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2-dihydronaphthalene (**3a**, 0.2 mmol) in toluene (2 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2 equiv) and the mixture heated to reflux for 16 h. The reaction mixture was cooled to room temperature and quenched by addition of $NaHCO_3$. The aqueous layer was separated and extracted with dichloromethane. The combined organics were washed with brine, dried ($MgSO_4$) and the solvent removed in vacuo. Purification by flash chromatography gave **4a**.

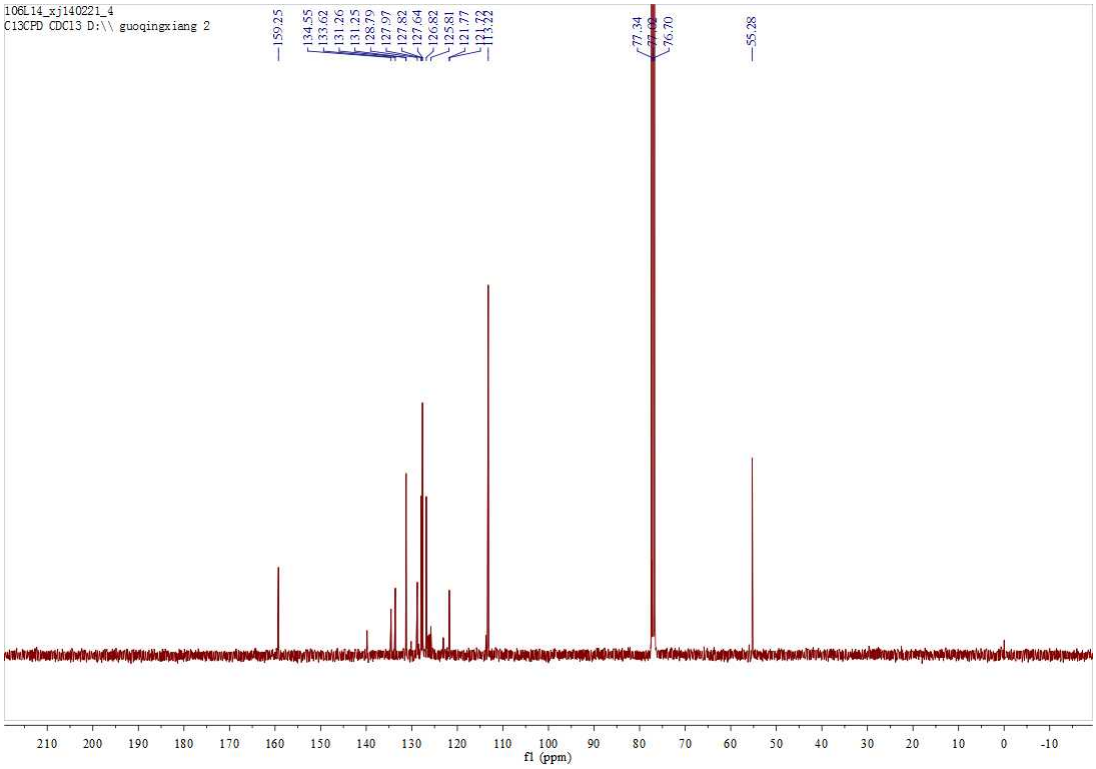
1-(4-methoxyphenyl)-2-(trifluoromethyl)naphthalene **(4a)**

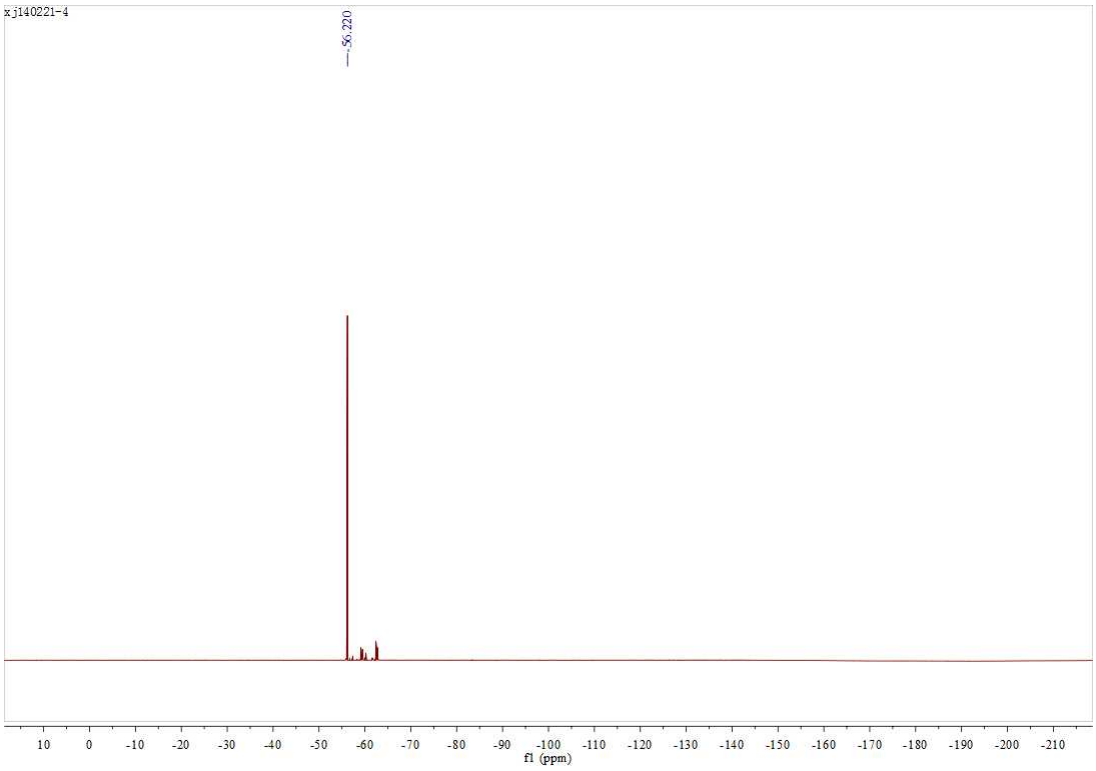


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 13.5, 8.5 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.57 (t, *J* = 6.6Hz, 1H), 7.50 – 7.39 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.25, 139.81, 134.55, 133.62, 131.25 (q, *J* = 1.3 Hz), 128.79, 127.97, 127.82, 127.66, 127.63, 126.82, 126.24 (q, *J* = 29 Hz), 124.45(q, *J* = 273 Hz), 121.74 (q, *J* = 5.0 Hz), 113.22, 55.28;
^{19}F NMR (376 MHz, $CDCl_3$) δ -56.22.

HRMS calcd for $C_{18}H_{13}F_3O$ ([M]$^+$): 302.0918; found: 302.0922.



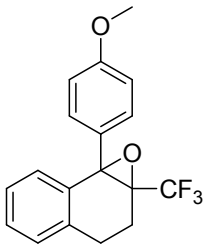




2. Representative Procedure for Epoxidation[3]

A solution of m-Chloroperbenzoic acid (70% w/w, 0.8 mmol, 4 equiv) in $CHCl_3$ (2 mL) was added dropwise to a solution of 4-(4-methoxyphenyl)-3-(trifluoromethyl)-1,2- dihydronaphthalene (**3a**, 0.2 mmol) in $CHCl_3$ (0.6 mL) at 0 °C, and the solution was warmed to room temperature. After the solution was stirred for 12 h, CH_2Cl_2 (10 mL) was added, and the reaction mixture was washed with 2.5 M NaOH three times. The organic phase was dried over sodium sulfate and concentrated under reduced pressure, and purified by column chromatography on silica gel with petroleum ether / ethyl acetate to afford **5a**.

7b-(4-methoxyphenyl)-1a-(trifluoromethyl)-1a,2,3,7b-tetrahydronaphtho[1,2-b]oxirene **(5a)**

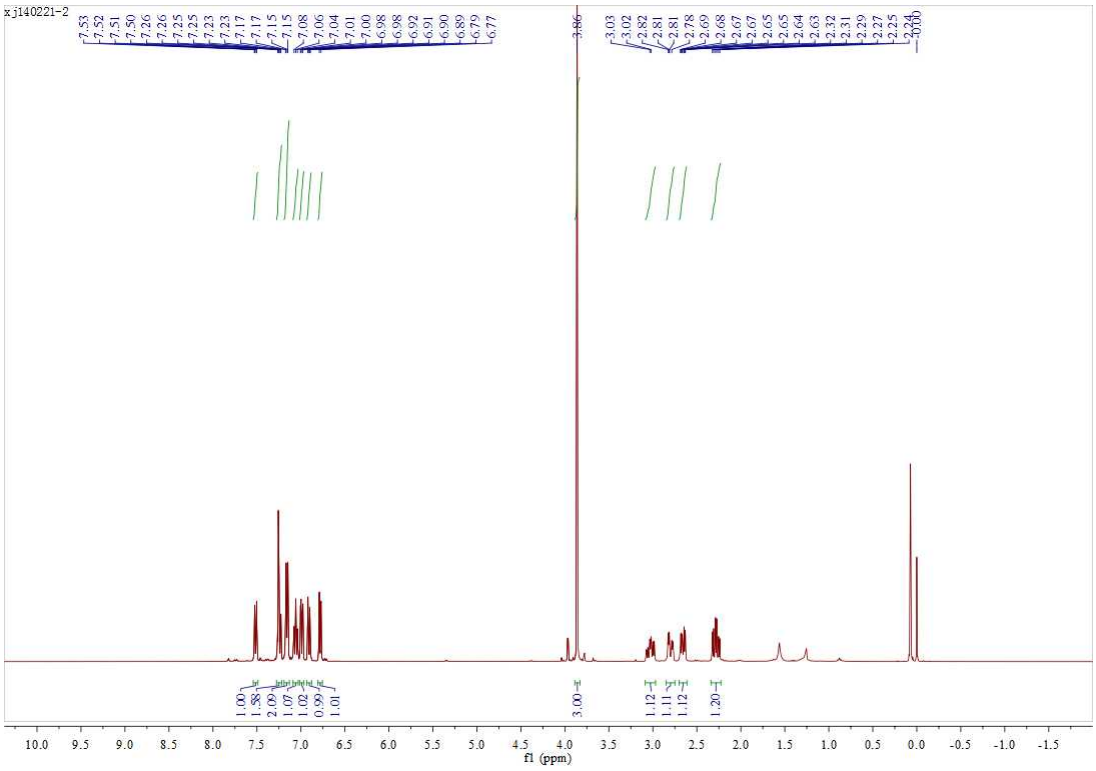


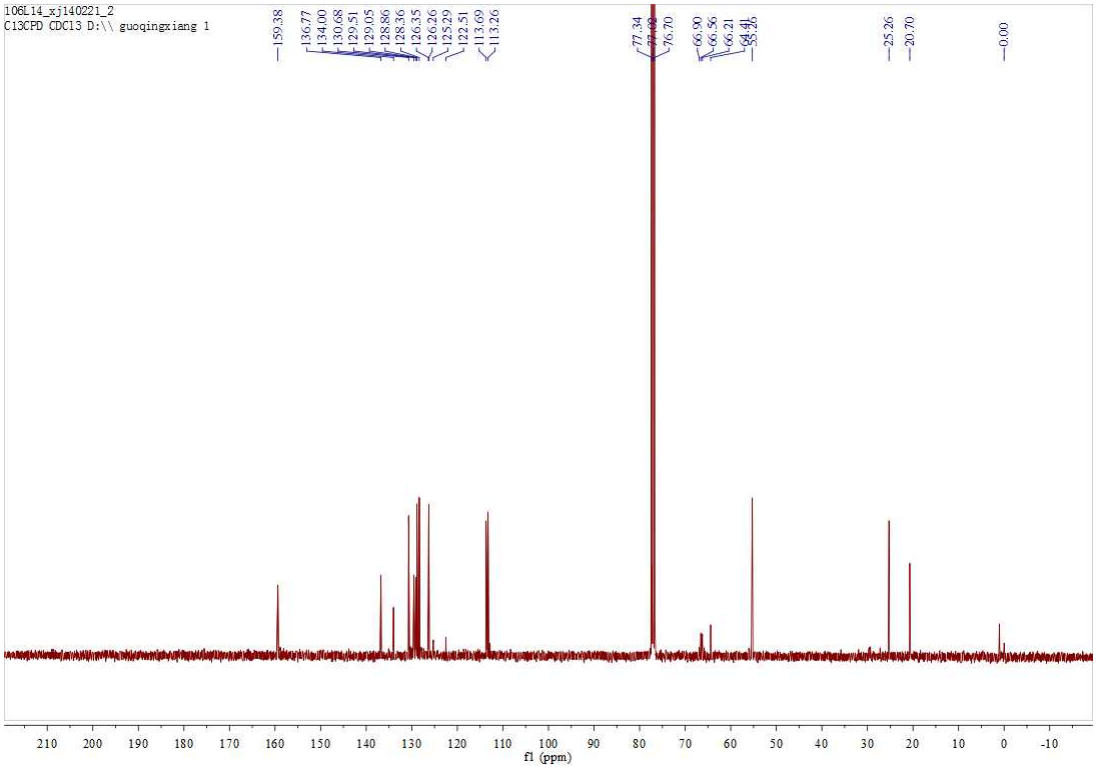
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.25 (t, *J* = 7.4Hz, 1H), 7.16 (d, *J* = 8.4, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.91 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 3.09 – 2.97 (m, 1H), 2.85 – 2.75 (m, 1H), 2.66 (m, 1H), 2.28 (m, 1H);

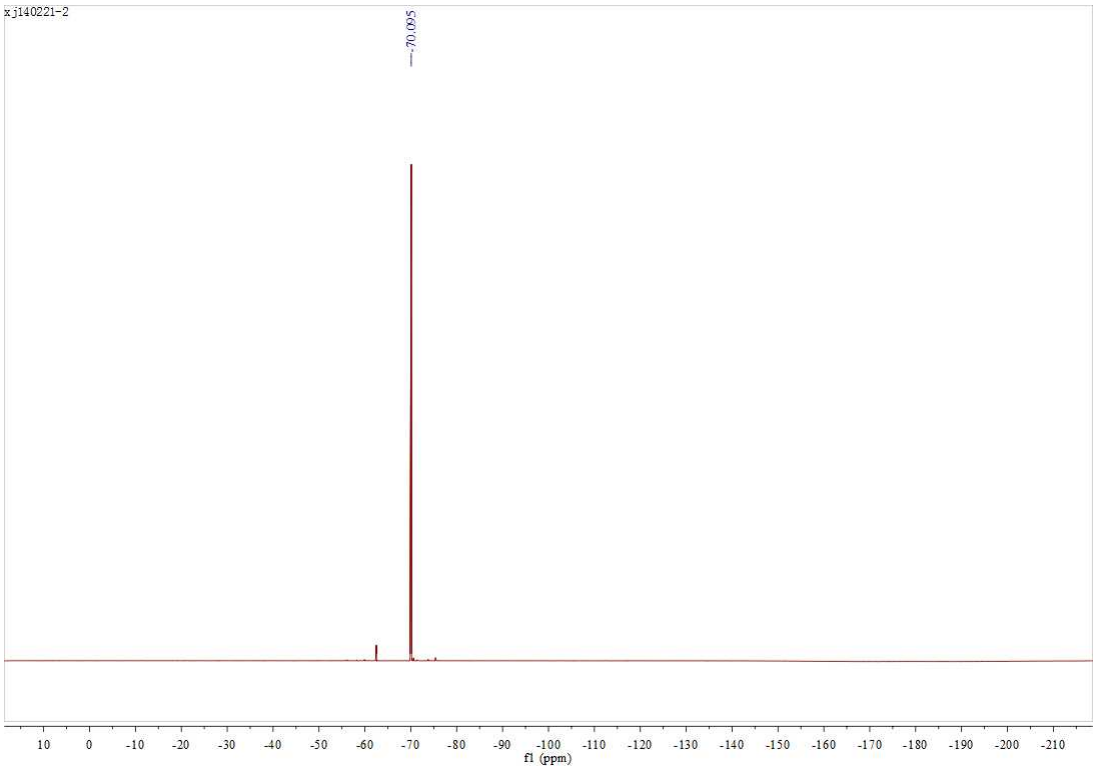
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.38, 136.77, 134.00, 130.68, 129.51, 129.05, 128.86, 128.36, 126.35, 126.26, 123.90 (q, *J* =278 Hz), 113.69, 113.26, 66.38 (q, *J* =35 Hz), 64.41, 55.26, 25.26, 20.70;

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.09.

HRMS calcd for $C_{18}H_{15}F_3O_2$ ([M]$^+$): 320.1024; found: 320.1029.



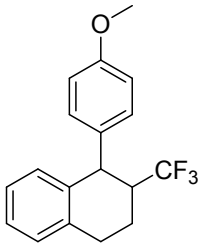




3. Representative Procedure for Hydrogenation[4]

An oven-dried reaction tube was charged with a magnetic stir-bar, **3a** (0.2 mmol), and 5% Pd on carbon (18 mg). The vessel was sealed before being evacuated and filled with argon, and then methanol (2 ml) and THF (0.2 ml) was added..The reaction was stirred at room temperature under H_2 atmosphere (345 kpa) for 12 h. At the conclusion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with brine for once and then dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **6a.**

1-(4-methoxyphenyl)-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene **(6a)**

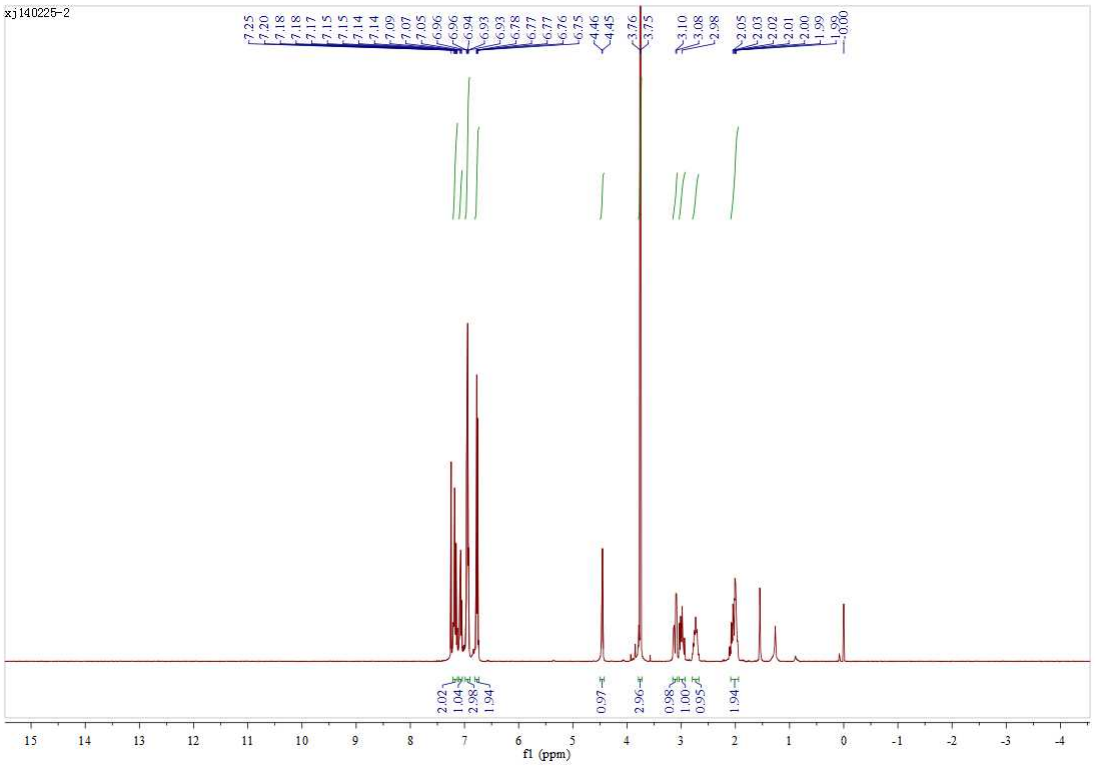


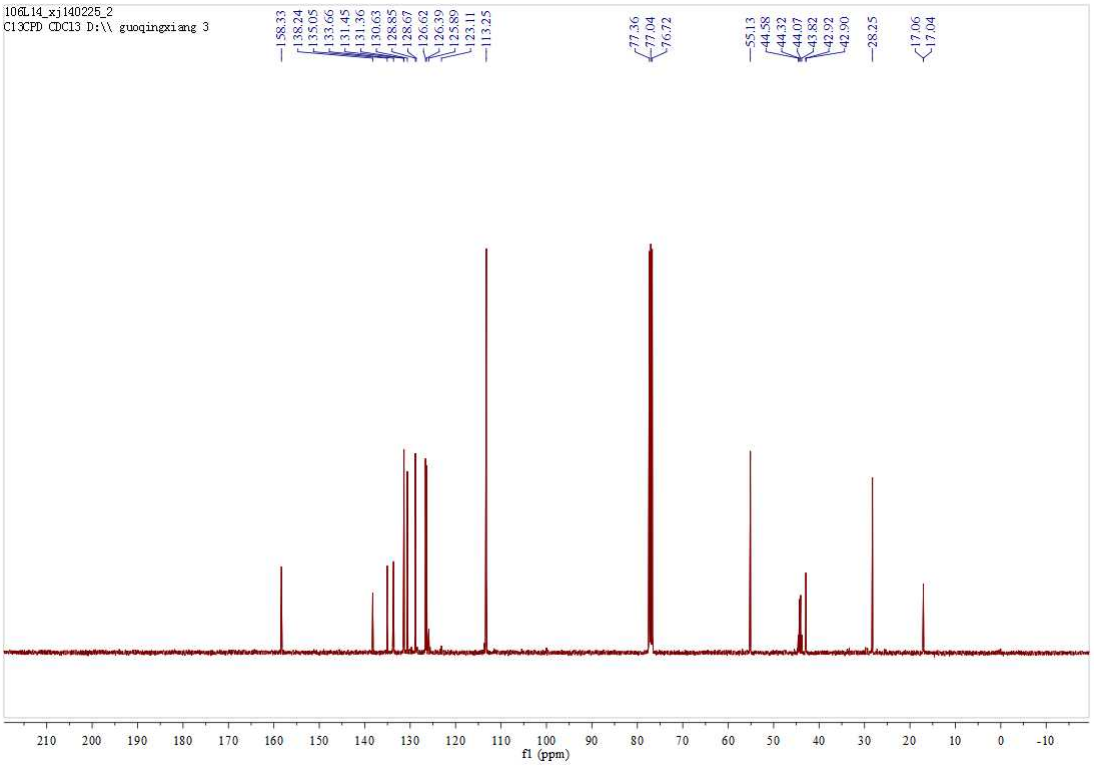
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.99 – 6.90 (m, 3H), 6.81 – 6.73 (m, 2H), 4.46 (d, *J* = 4.2 Hz, 1H), 3.75 (d, *J* = 1.5 Hz, 3H), 3.15 – 3.07 (m, 1H), 3.04 – 2.93 (m, 1H), 2.77 – 2.69 (m, 1H), 2.09 – 1.94 (m, 2H);

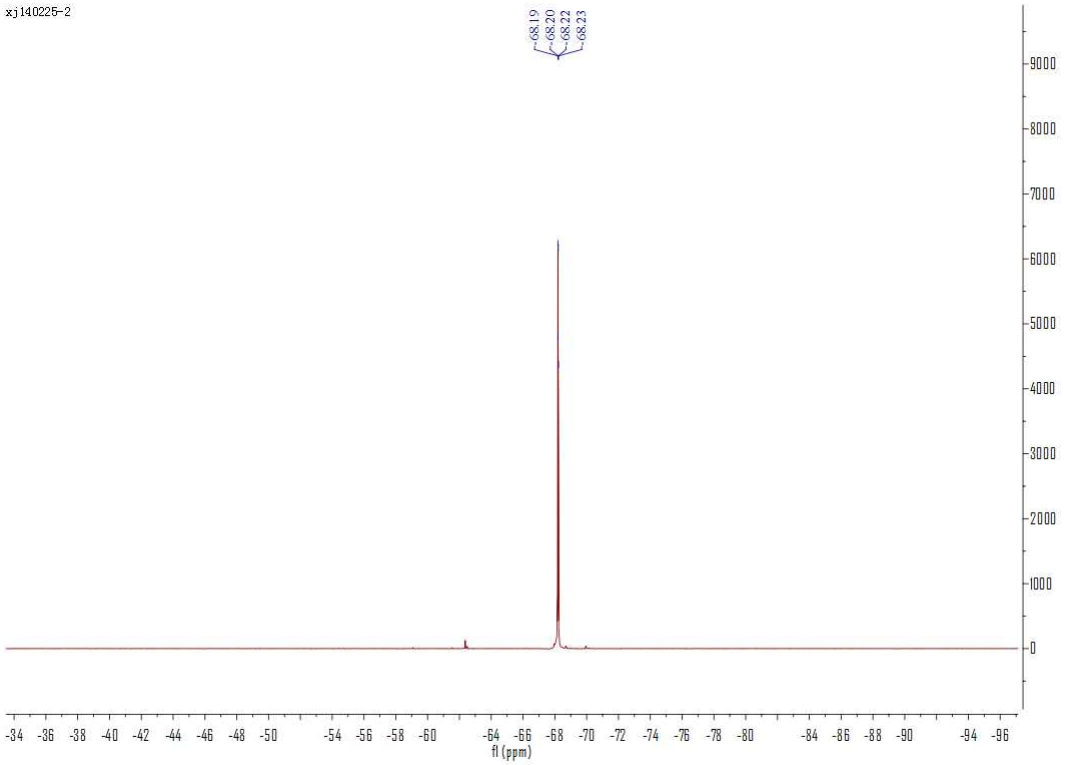
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.33, 138.24, 135.05, 133.66, 131.40 (q, *J* = 8.7 Hz), 130.63, 128.85, 127.28, 126.62, 126.39, 113.25, 55.13, 44.20 (q, *J* = 25 Hz), 42.91 (q, *J* = 1.8 Hz), 28.25, 17.05 (q, *J* = 2.3 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.20 (d, *J* = 11.3 Hz), -68.22 (d, *J* = 11.3 Hz).

HRMS calcd for $C_{18}H_{17}F_3O$ ([M]$^+$): 306.1231; found: 306.1235.

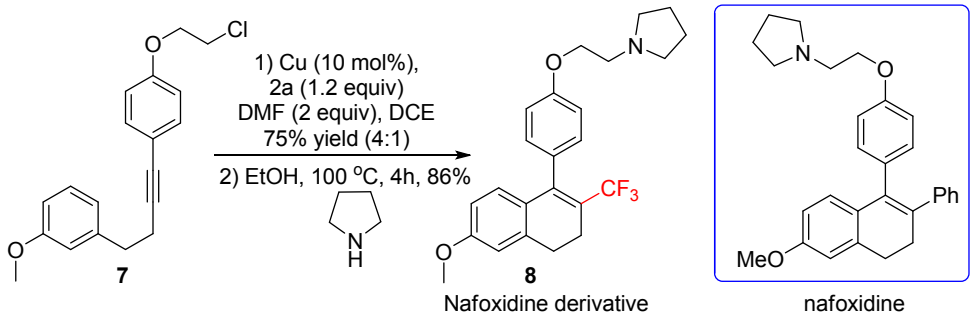




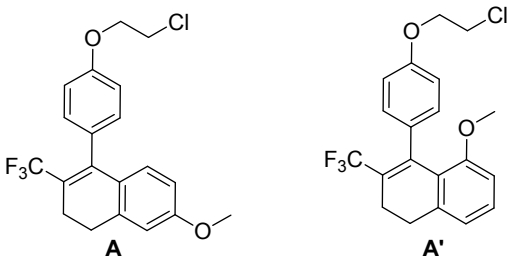


4. Synthesis of Nafoxidine derivative 8

1-(4-(4-(2-Chloroethoxy)phenyl)but-3-yn-1-yl)-3-methoxybenzene (**7**) was prepared according to the literature[1].



4-(4-(2-chloroethoxy)phenyl)-7-methoxy-3-(trifluoromethyl)-1,2-dihydronaphthalene (**A**)



Prepared according to General Procedure **D.** A reaction tube was charged with Cu (2.56 mg, 10 mmol%), **1A** (0.4 mmol) and **2a** (0.48 mmol, 163.2 mg), the vessel was sealed before being evacuated and filled with argon (three times). DMF (0.8 mmol, 61.6 μL), and DCE (2 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction

mixture was kept for 24 h at 80 °C. At the conclusion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with brine for once and then dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **A** as a white solid. The isomer **A'** was isolated as a mixture with **A** (1:4) to give an overall isolated yield of 75%.

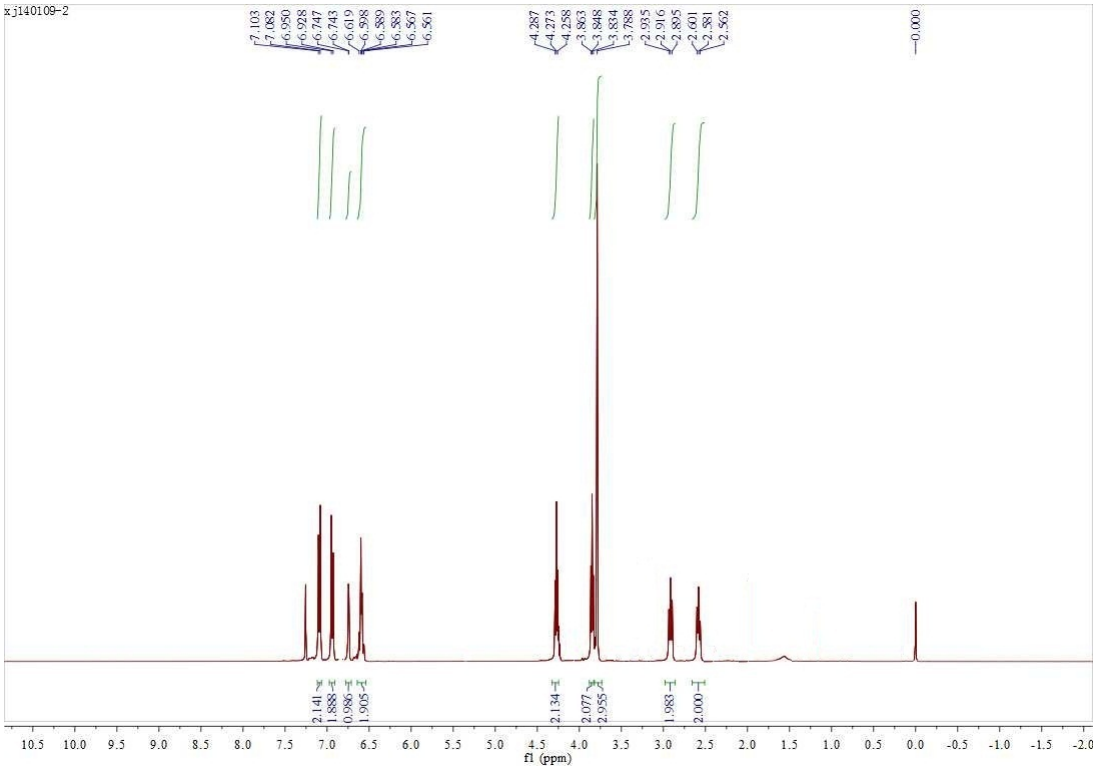
Characterisation data for major isomer (**A**):

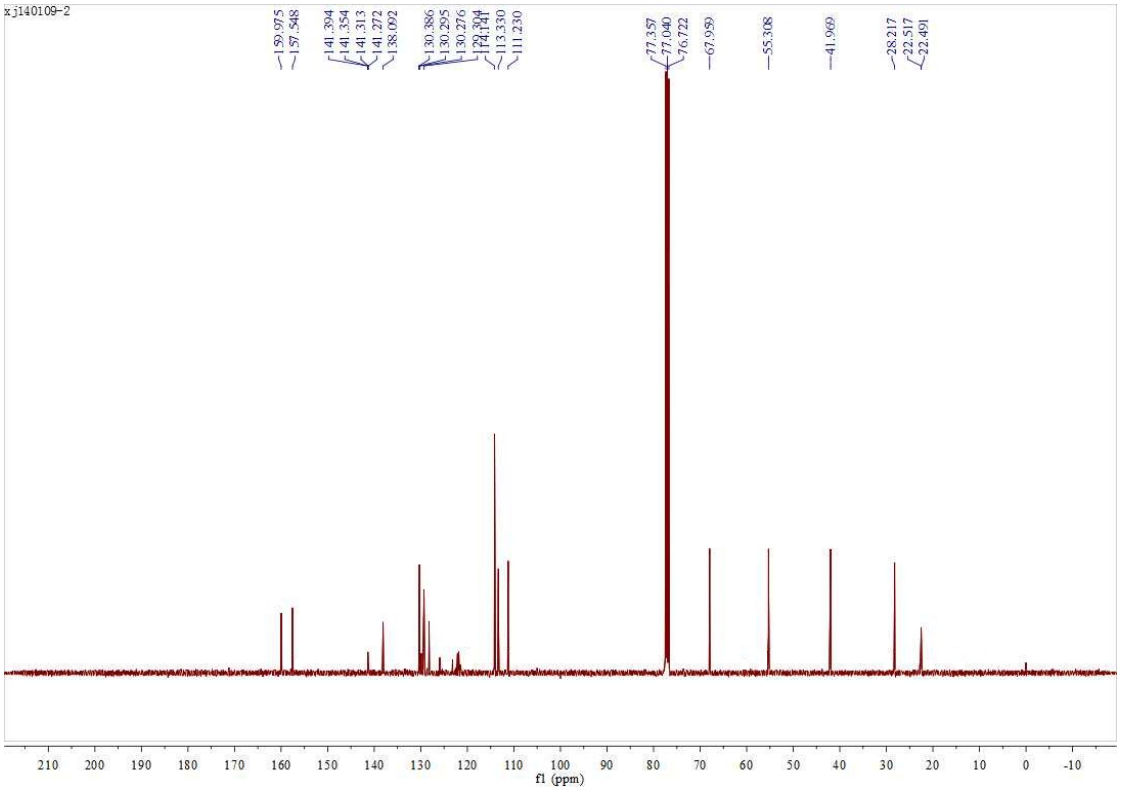
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.64 – 6.54 (m, 2H), 4.27 (t, *J* = 5.9 Hz, 2H), 3.85 (t, *J* = 5.9 Hz, 2H), 3.79 (s, 3H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.98, 157.55, 141.33 (q, *J* = 4.1 Hz), 138.09, 130.39, 130.28 (q, *J* = 1.8 Hz), 129.30, 128.21, 124.55 (q, *J* = 271 Hz), 121.97 (q, *J* = 28.4 Hz), 114.14, 113.33, 111.23, 67.96, 55.31, 41.97, 28.22, 22.50 (q, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.68.

HRMS calcd for $C_{20}H_{18}ClF_3O_2$ ([M]$^+$): 382.0947; found: 382.0949.

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157.548
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141.354
141.313
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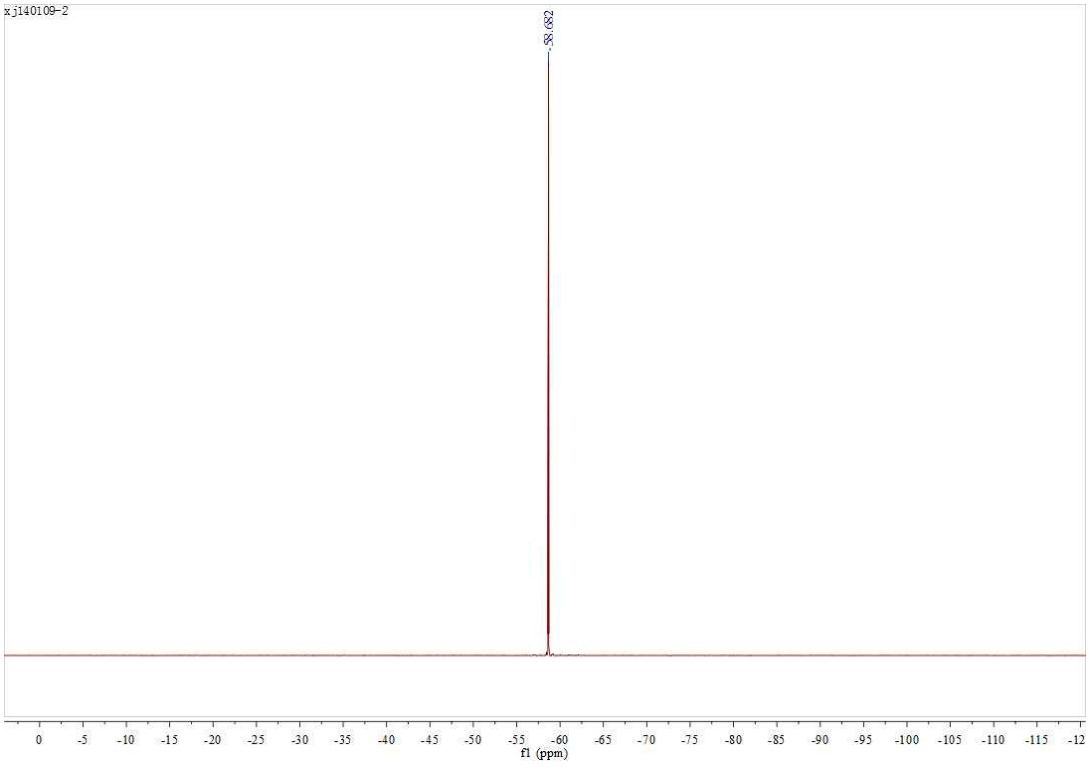
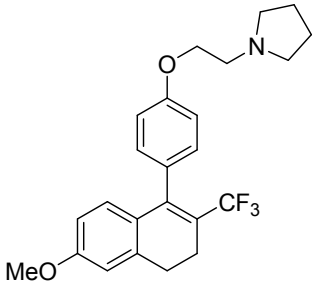
130.295
130.276
129.304
124.141
113.330
111.230
77.357
77.040
76.722
67.959
55.308
41.969
28.217
22.517
22.491
f1 (ppm)

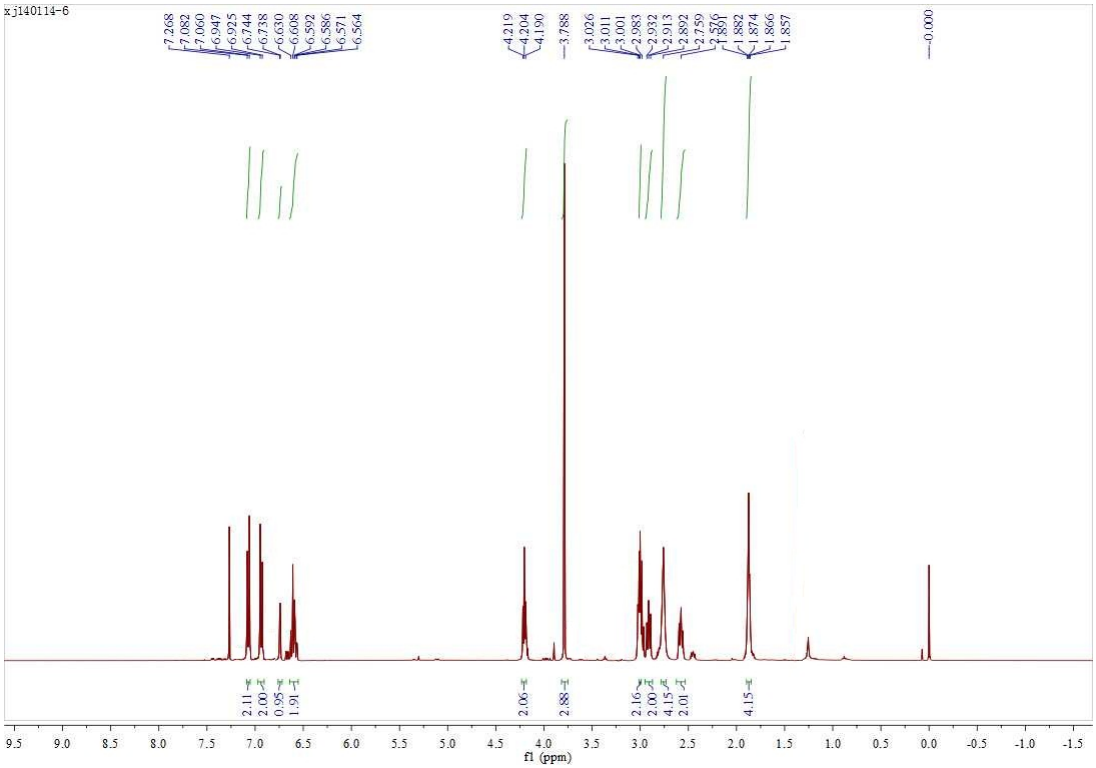

xj140109-2
-58.682
f1 (ppm)

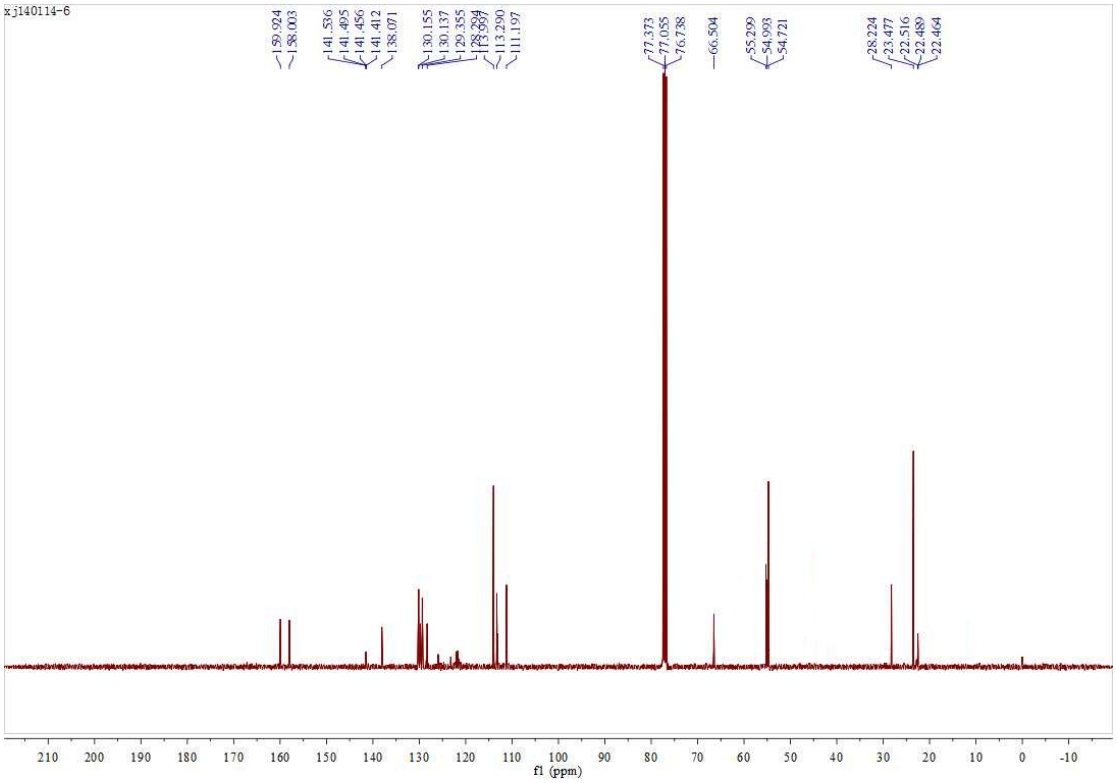
1-(2-(4-(6-methoxy-2-(trifluoromethyl)-3,4-dihydronaphthalen-1-yl)phenoxy)ethyl)pyrrolidine (**8**)



4-(4-(2-chloroethoxy)phenyl)-7-methoxy-3-(trifluoromethyl)-1,2-dihydronaphthalene (**A**) (76.4 mg, 0.2 mmol) was dissolved in ethanol (0.25 mL) and pyrrolidine (0.25 mL) and the mixture heated in a sealed tube for 4 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The residue was purified by flash chromatography on basic alumina to give compound **7** (71.7 mg, 86%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 2.3 Hz, 1H), 6.64 – 6.56 (m, 2H), 4.20 (t, *J* = 5.8 Hz, 2H), 3.79 (s, 3H), 3.01– 2.98 (m, 2H), 2.95 – 2.87 (m, 2H), 2.80 –2.72 (m, 4H), 2.58 (m, 2H), 1.91 – 1.84 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.92, 158.00, 141.47 (q, *J* = 4.2 Hz), 138.07, 130.15 (q, *J* = 1.8 Hz), 129.79, 129.36, 128.29, 124.57 (q, *J* = 272 Hz), 121.83 (q, *J* = 30.4 Hz), 114.00, 113.29, 111.20, 66.50, 55.30, 54.99, 54.72, 28.22, 23.48, 22.50 (q, *J* = 2.7 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -58.68.
HRMS calcd for $C_{11}H_9F_3O$ ([M]$^+$): 417.1916; found: 417.1921.




xj140114-6
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141.495
141.456
141.412
138.071
130.155
130.137
129.355
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113.290
111.197
77.373
77.055
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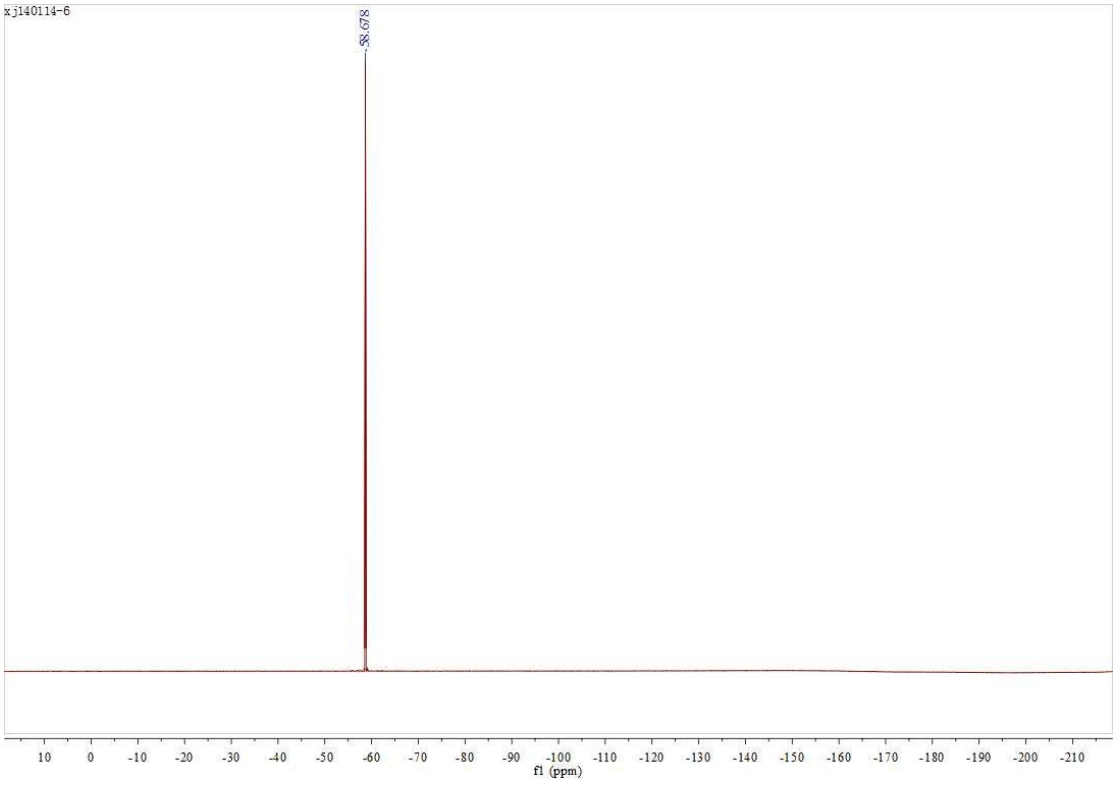
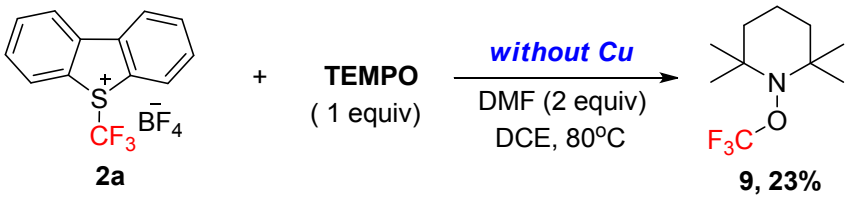
23.477
22.516
22.489
22.464
f1 (ppm)

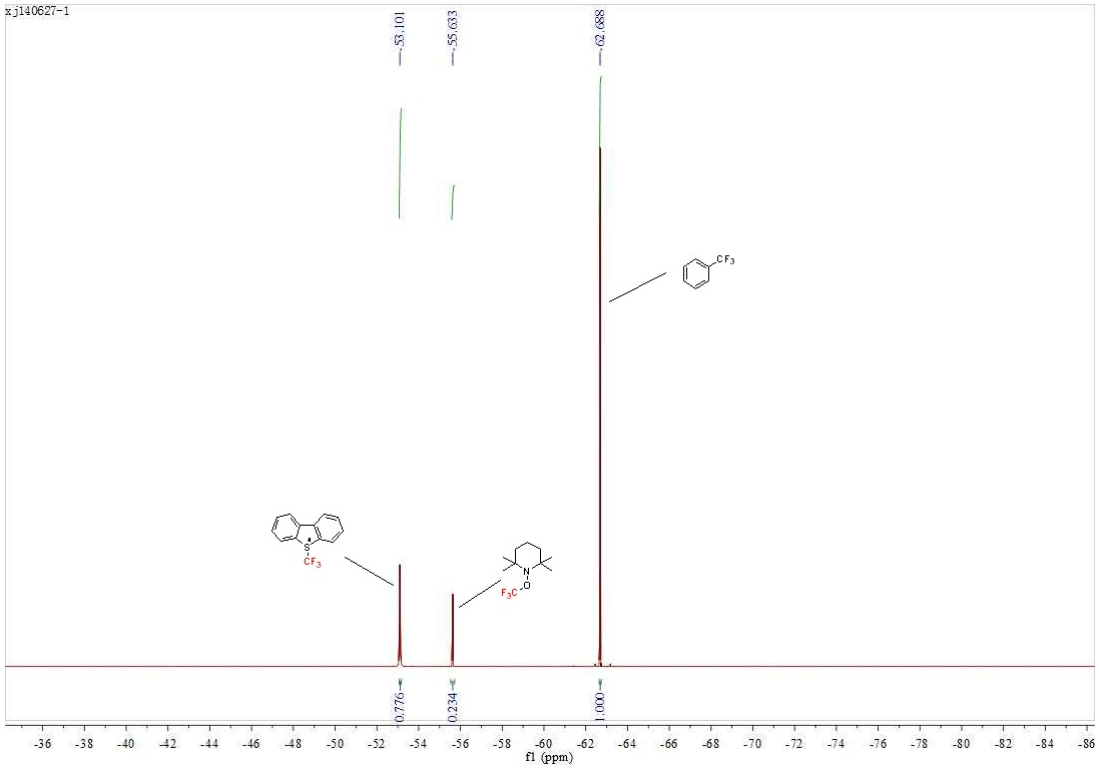

xj140114-6
58.678
f1 (ppm)

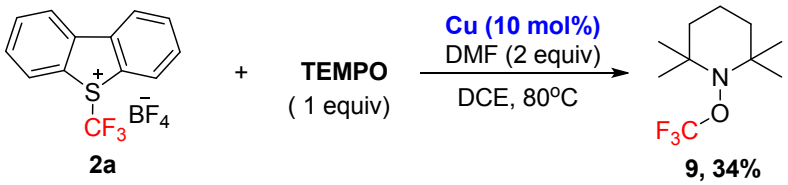
V. Mechanistic Study

1. capture of the CF_3 radical.



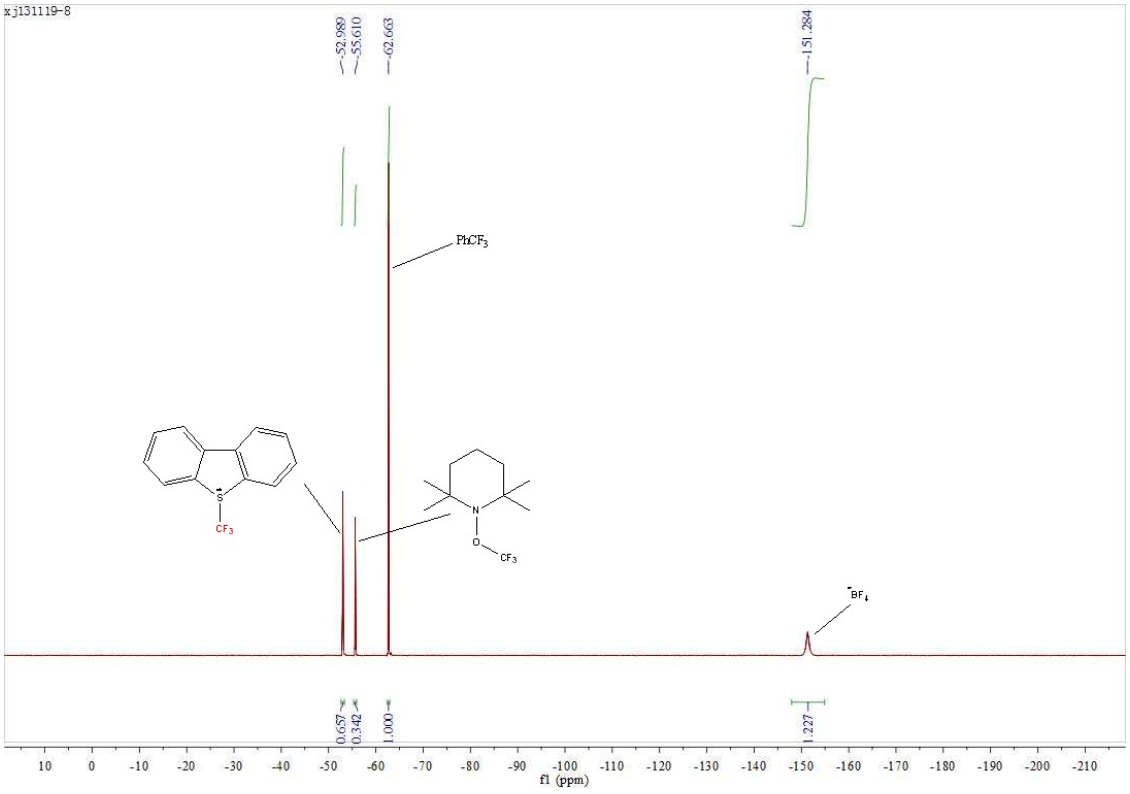
An oven-dried reaction tube was charged with a magnetic stir-bar, **2a** (0.1 mmol, 34 mg), TEMPO (0.1 mmol, 15.6 mg). The vessel was sealed before being evacuated and filled with argon (three times). DMF (0.4 mmol, 30.8 μL), and DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 1 h at the 80°C. Then, the stirring was stopped, and $PhCF_3$ (0.1 mmol, 12.5 μL) was added to the reaction mixture. ^{19}F NMR analysis of this reaction mixture showed that TEMPO-CF_3 was formed [^{19}FNMR (376 MHz, CDCl3) δ -55.61] in 23% ^{19}F NMR yield. ^{19}F NMR spectrum was matching with literature data.

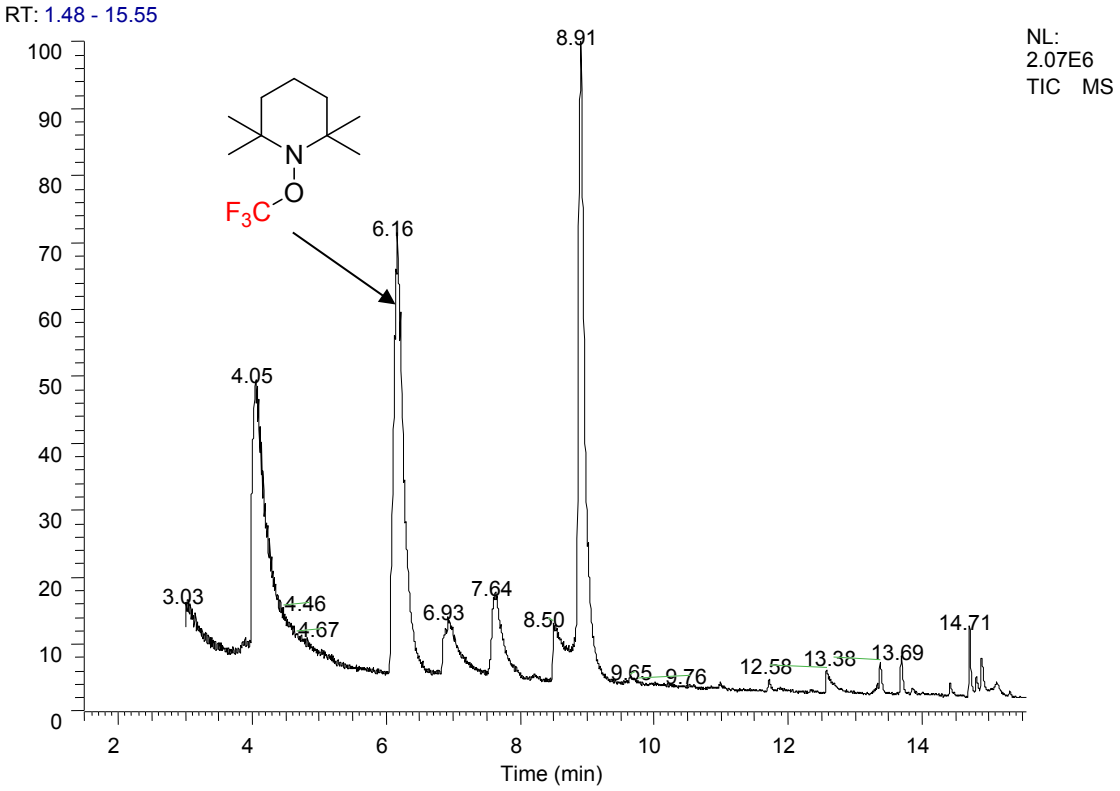


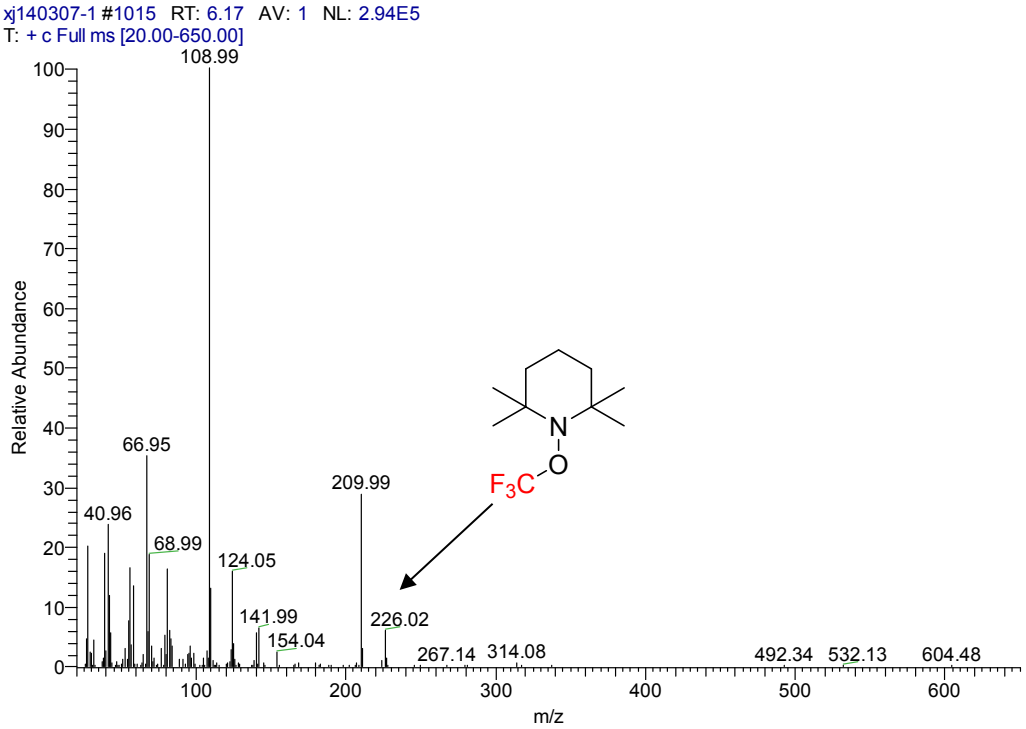


An oven-dried reaction tube was charged with a magnetic stir-bar, **2a** (0.1 mmol, 34 mg), TEMPO (0.1 mmol, 15.6 mg), and Cu powder (0.01 mmol, 0.64 mg). The vessel was sealed before being

evacuated and filled with argon (three times). DMF (0.4 mmol, 30.8 μL), and DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 1 h at the 80°C. Then, the stirring was stopped, and $PhCF_3$ (0.1 mmol, 12.5 μL) was added to the reaction mixture. ^{19}F NMR analysis of this reaction mixture showed that TEMPO-CF_3 was formed [^{19}FNMR (376 MHz, CDCl3) δ -55.61] in 34% ^{19}F NMR yield. ^{19}F NMR spectrum was matching with literature data.




RT: 1.48 - 15.55
NL:
2.07E6
TIC MS
8.91
6.16
4.05
3.03
4.46
4.67
6.93
7.64
8.50
9.65
9.76
12.58
13.38
13.69
14.71
F3C
N
O
Time (min)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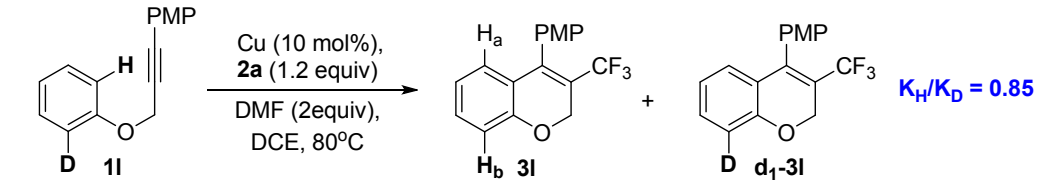
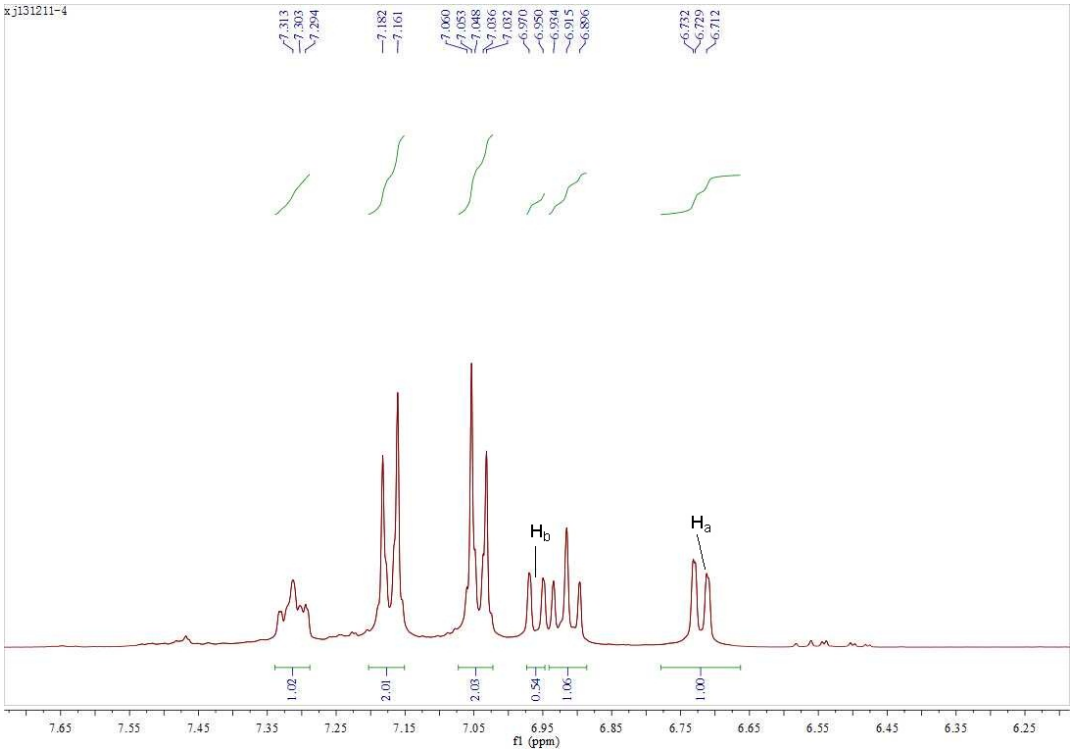
T: + c Full ms [20.00-650.00]
108.99
66.95
40.96
68.99
124.05
141.99
154.04
209.99
226.02
267.14
314.08
492.34
532.13
604.48
F3C
N
O
Relative Abundance
m/z

2. isotope labeling experiments

a. intramolecular isotope labeling experiments.

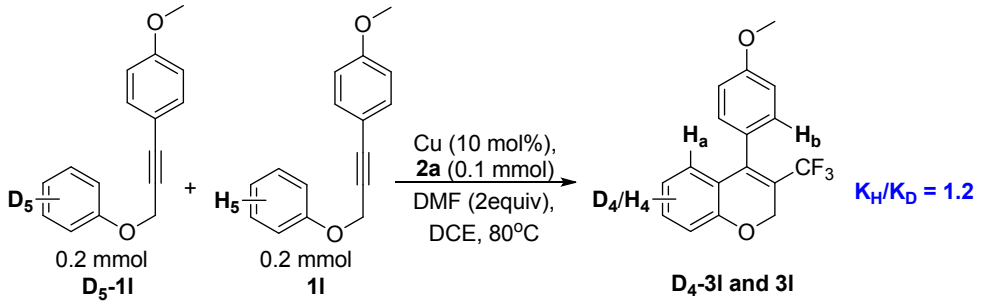
A reaction tube was charged with Cu (1.28 mg, 10 mmol%), ***d*$_1$-1l** (0.2 mmol, 47.8 mg) and **2a** (0.24 mmol, 81.7 mg), the vessel was sealed before being evacuated and filled with argon (three times). DMF (0.4 mmol, 30.8 μL), and DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 24 h at 80°C. At the conclusion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with brine for once and then dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **3l** and ***d*$_1$-3l**. The K_H/K_D was determined by the analysis followed by Yu et al. The ratio **3l** and ***d*$_1$-3l**. was analyzed by ^{1}H NMR. The yield of **3l, X,** was determined by integration of the H_b signal of **3l**, which appeared as a doublets approximately at 6.96 ppm. The total yield of **3l** and ***d*$_1$-3l**, Y was determined by integration of H_a of **3l** and ***d*$_1$-3l**, which appeared as d at 6.72 ppm. The yield of ***d*$_1$-3l**, Z, could then be determined from the following formula: Z = Y−X. Then K_H/K_D = Z/X = 0.46/0.54 = 0.85

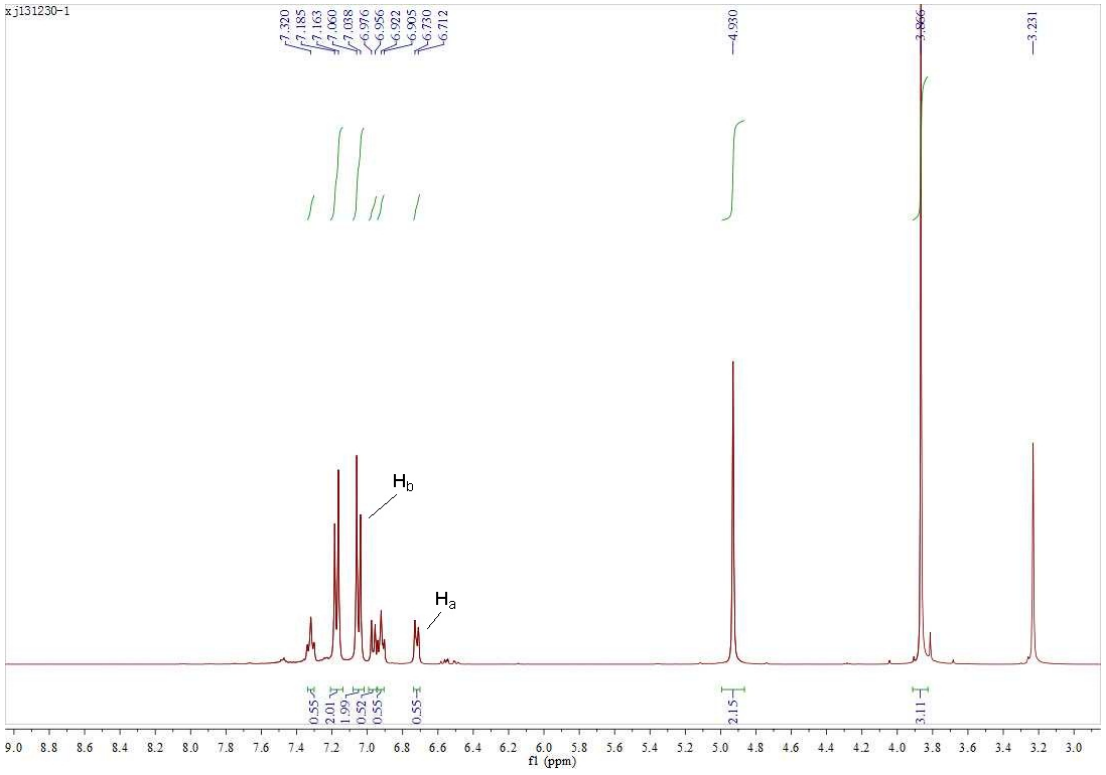




b. intermolecular isotope labeling experiments.

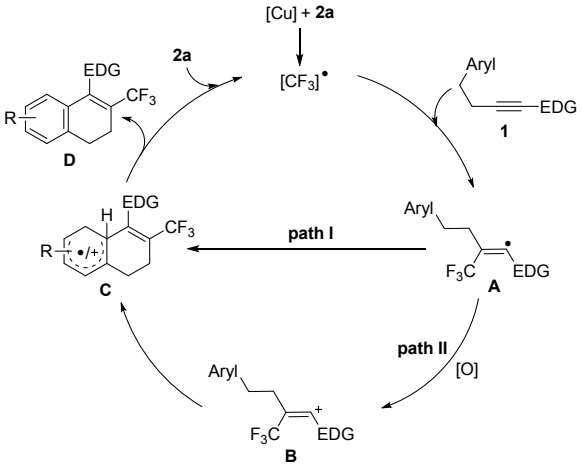
A reaction tube was charged with Cu (1.28 mg, 10 mmol%), ***d*$_5$-1l** (0.2 mmol, 47.8 mg) and **2a** (0.24 mmol, 81.7 mg), the vessel was sealed before being evacuated and filled with argon (three times). DMF (0.4 mmol, 30.8 μL), and DCE (1 mL) were added in turn by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was kept for 24 h at 80°C. At the conclusion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with brine for once and then dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **3l** and ***d*$_4$-3l**. The K_H/K_D was determined by the analysis followed by Yu et al.[5] The ratio **3l** and ***d*$_4$-3l**. was analyzed by ^{1}H NMR. The yield of **3l, X,** was determined by integration of the H_a signal of **3l**, which appeared as a doublets approximately at 6.72 ppm. The total yield of **3l** and ***d*$_4$-3l**, Y was determined by integration of H_b of **3l** and ***d*$_4$-3l**, which appeared as d at 7.04 ppm. The yield of ***d*$_4$-3l**, Z, could then be determined from the following formula: Z = Y−X. Then K_H/K_D = X/Z = 0.55/0.45 = 1.2.





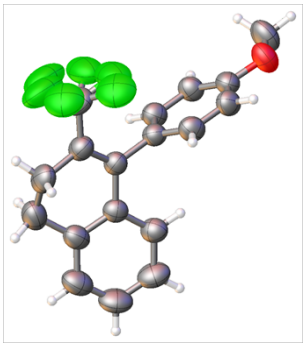
According to above mechanism investigations, a catalytic cycle for copper-catalyzed oxidative trifluoromethylation of alkylboronic acids was given in ***Scheme***

S1:



Scheme S1

VI. X-ray Crystal data for product 3a



ORTEP diagrams and tables of crystallographic data for Complex **3a**.

Table 1 Crystal data and structure refinement for 3a

Identification code	xj131024-1
Empirical formula	$C_{18}H_{15}F_3O$
Formula weight	304.30
Temperature/K	290(2)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	38.6451(16)
b/Å	18.5006(7)
c/Å	8.3788(3)
α/°	90.00
β/°	90.00

γ/°	90.00
Volume/Å^3	5990.5(4)
Z	16
ρ_{calc}mg/mm^3	1.350
m/mm^{-1}	0.915
F(000)	2528.0
Crystal size/mm^3	0.37 × 0.31 × 0.3
2Θ range for data collection	9.16 to 138.76°
Index ranges	-42 ≤ h ≤ 45, -18 ≤ k ≤ 22, -9 ≤ l ≤ 7
Reflections collected	3225
Independent reflections	1929[R(int) = 0.0146]
Data/restraints/parameters	1929/37/211
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0523, wR_2 = 0.1488
Final R indexes [all data]	R_1 = 0.0555, wR_2 = 0.1535
Largest diff. peak/hole / e Å^{-3}	0.27/-0.25
Flack parameter	?

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for xj131024-1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C16	9174.1(9)	920.9(18)	3007(6)	64.1(10)
C5	8358.5(8)	1593.3(17)	3570(5)	55.0(9)
C12	9135.7(8)	2190.0(18)	2531(5)	58.7(9)
O1	9865.0(7)	1408.5(15)	303(4)	78.9(9)
C15	9458.3(9)	881.0(18)	1994(5)	63.8(10)
C3	7735(1)	1699(2)	3722(7)	81.5(13)
C14	9581.0(8)	1502(2)	1260(5)	59.2(9)
C9	8717.9(10)	1678.5(19)	5956(5)	63.5(10)
C11	9010.4(8)	1574.2(17)	3297(4)	53.8(8)
C10	8700.8(8)	1619.8(18)	4350(4)	53.4(8)
C1	8001.0(11)	1347(2)	1274(6)	79.2(12)
C4	8059.1(9)	1758.4(19)	4450(6)	64.8(10)
C13	9419.0(8)	2152.6(18)	1526(5)	60.1(9)
C2	7710.8(11)	1500(3)	2152(7)	84.5(14)
C17	9048.4(13)	1706(3)	6851(6)	83.5(13)
C18	10001.4(12)	2043(2)	-463(7)	90.2(14)
C6	8325.6(10)	1388(2)	1974(5)	64.8(9)

C8	8397.1(11)	1695(3)	6979(5)	76.6(12)
C7	8096.4(11)	2037(3)	6105(6)	81.1(12)
F3	9033.9(14)	1305(4)	8185(7)	118.5(17)
F1	9333.7(13)	1534(5)	6154(8)	122.6(18)
F2	9094.4(18)	2362(4)	7480(11)	147(2)
F1'	9273(2)	2192(8)	6244(14)	122.6(18)
F3'	9247(3)	1093(7)	6546(14)	118.5(17)
F2'	9019(3)	1815(8)	8320(20)	147(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for xj131024-1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	62.5(19)	53.0(17)	77(3)	2.0(18)	2.3(19)	-4.5(14)
C5	54.7(18)	50.7(16)	60(2)	5.2(16)	0.1(16)	-4.2(12)
C12	57.4(17)	51.2(17)	67(2)	1.1(17)	-0.1(16)	-0.1(13)
O1	67.2(14)	79.6(17)	90(2)	2.2(16)	23.2(15)	6.3(12)
C15	60.8(19)	54.5(18)	76(3)	-5.7(18)	2.6(18)	3.8(14)
C3	57(2)	77(2)	110(4)	7(3)	-1(2)	6.1(17)
C14	48.1(15)	68(2)	62(2)	-6.6(18)	-0.5(16)	-0.5(14)
C9	67(2)	67(2)	57(3)	-4.0(18)	-1.1(17)	-8.5(16)
C11	51.1(16)	54.9(17)	55(2)	-0.6(15)	-1.3(15)	-3.9(13)
C10	54.5(18)	54.2(18)	51(2)	1.0(15)	3.8(15)	-5.2(13)
C1	81(3)	84(3)	72(3)	10(2)	-26(2)	-8(2)
C4	54.4(17)	57.0(18)	83(3)	0.1(19)	3.7(17)	-0.6(15)
C13	57.7(17)	56.8(17)	66(2)	5.1(17)	6.2(17)	-4.4(14)
C2	61(2)	93(3)	99(4)	14(3)	-22(2)	3(2)
C17	87(3)	109(4)	55(2)	-6(2)	-13(2)	-6(3)
C18	73(2)	98(3)	99(3)	7(3)	33(2)	1(2)
C6	61.2(19)	73(2)	60(2)	5.2(19)	-2.8(17)	-3.7(16)
C8	85(3)	90(3)	54(2)	-10(2)	12(2)	-11(2)
C7	76(2)	78(3)	88(3)	-13(2)	21(2)	-4(2)
F3	123(3)	139(4)	93(3)	27(3)	-35(3)	6(3)
F1	76(2)	190(5)	102(3)	-11(4)	-21(2)	-3(3)
F2	147(4)	125(4)	169(5)	-46(4)	-65(4)	-15(3)
F1'	76(2)	190(5)	102(3)	-11(4)	-21(2)	-3(3)
F3'	123(3)	139(4)	93(3)	27(3)	-35(3)	6(3)
F2'	147(4)	125(4)	169(5)	-46(4)	-65(4)	-15(3)

Table 4 Bond Lengths for xj131024-1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

C16	C15	1.390(5)	C9	C17	1.482(6)
C16	C11	1.386(5)	C9	C8	1.508(5)
C5	C10	1.476(5)	C11	C10	1.489(5)
C5	C4	1.406(5)	C1	C2	1.371(7)
C5	C6	1.396(6)	C1	C6	1.387(5)
C12	C11	1.395(5)	C4	C7	1.486(7)
C12	C13	1.383(5)	C17	F3	1.343(7)
O1	C14	1.370(4)	C17	F1	1.288(8)
O1	C18	1.438(5)	C17	F2	1.335(8)
C15	C14	1.387(5)	C17	F1'	1.351(13)
C3	C4	1.397(6)	C17	F3'	1.393(13)
C3	C2	1.369(7)	C17	F2'	1.252(16)
C14	C13	1.374(5)	C8	C7	1.512(7)
C9	C10	1.351(5)			

Table 5 Bond Angles for xj131024-1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	C16	C15	121.0(3)	C3	C2	C1	121.0(4)
C4	C5	C10	119.9(4)	F3	C17	C9	111.5(5)
C6	C5	C10	121.0(3)	F3	C17	F1'	135.1(6)
C6	C5	C4	119.1(3)	F3	C17	F3'	74.1(6)
C13	C12	C11	121.0(3)	F1	C17	C9	120.0(5)
C14	O1	C18	116.8(3)	F1	C17	F3	106.1(6)
C14	C15	C16	119.8(3)	F1	C17	F2	106.9(6)
C2	C3	C4	120.1(4)	F1	C17	F1'	56.1(6)
O1	C14	C15	115.4(3)	F1	C17	F3'	40.8(5)
O1	C14	C13	124.8(3)	F2	C17	C9	110.2(5)
C13	C14	C15	119.8(3)	F2	C17	F3	100.3(6)
C10	C9	C17	123.3(4)	F2	C17	F1'	57.1(6)
C10	C9	C8	121.8(4)	F2	C17	F3'	137.6(7)
C17	C9	C8	114.8(4)	F1'	C17	C9	112.8(6)
C16	C11	C12	118.2(3)	F1'	C17	F3'	96.7(8)
C16	C11	C10	121.4(3)	F3'	C17	C9	110.8(6)
C12	C11	C10	120.4(3)	F2'	C17	C9	115.2(8)
C5	C10	C11	117.1(3)	F2'	C17	F3	42.9(7)
C9	C10	C5	119.2(3)	F2'	C17	F1	124.3(8)
C9	C10	C11	123.7(3)	F2'	C17	F2	58.5(8)
C2	C1	C6	120.1(5)	F2'	C17	F1'	108.7(9)
C5	C4	C7	119.0(3)	F2'	C17	F3'	111.2(9)
C3	C4	C5	119.4(4)	C1	C6	C5	120.2(4)

C3	C4	C7	121.4(4)	C9	C8	C7	111.4(4)
C14	C13	C12	120.2(3)	C4	C7	C8	112.4(3)

Table 6 Torsion Angles for xj131024-1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C16	C15	C14	O1	179.1(4)	C4	C5	C10	C11	-169.0(3)
C16	C15	C14	C13	-0.6(6)	C4	C5	C6	C1	-0.1(5)
C16	C11	C10	C5	-94.9(4)	C4	C3	C2	C1	0.9(7)
C16	C11	C10	C9	84.7(5)	C13	C12	C11	C16	-0.9(5)
C5	C4	C7	C8	-35.9(5)	C13	C12	C11	C10	-178.7(3)
C12	C11	C10	C5	82.8(4)	C2	C3	C4	C5	-1.8(6)
C12	C11	C10	C9	-97.6(5)	C2	C3	C4	C7	174.4(4)
O1	C14	C13	C12	-179.2(4)	C2	C1	C6	C5	-0.8(6)
C15	C16	C11	C12	0.8(6)	C17	C9	C10	C5	179.7(4)
C15	C16	C11	C10	178.6(4)	C17	C9	C10	C11	0.1(6)
C15	C14	C13	C12	0.5(6)	C17	C9	C8	C7	151.1(4)
C3	C4	C7	C8	147.9(4)	C18	O1	C14	C15	-179.3(4)
C9	C8	C7	C4	46.0(5)	C18	O1	C14	C13	0.3(6)
C11	C16	C15	C14	0.0(6)	C6	C5	C10	C9	-166.9(4)
C11	C12	C13	C14	0.3(6)	C6	C5	C10	C11	12.7(5)
C10	C5	C4	C3	-177.0(3)	C6	C5	C4	C3	1.4(5)
C10	C5	C4	C7	6.8(5)	C6	C5	C4	C7	-174.9(4)
C10	C5	C6	C1	178.2(3)	C6	C1	C2	C3	0.4(7)
C10	C9	C17	F3	-138.3(5)	C8	C9	C10	C5	1.9(6)
C10	C9	C17	F1	-13.5(9)	C8	C9	C10	C11	-177.7(3)
C10	C9	C17	F2	111.1(6)	C8	C9	C17	F3	39.6(7)
C10	C9	C17	F1'	49.3(9)	C8	C9	C17	F1	164.4(6)
C10	C9	C17	F3'	-57.8(8)	C8	C9	C17	F2	-70.9(7)
C10	C9	C17	F2'	174.9(9)	C8	C9	C17	F1'	-132.7(8)
C10	C9	C8	C7	-30.9(6)	C8	C9	C17	F3'	120.1(7)
C4	C5	C10	C9	11.4(5)	C8	C9	C17	F2'	-7.2(11)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for xj131024-1.

Atom	*x*	*y*	*z*	U(eq)
H16	9093	503	3496	77
H12	9027	2632	2698	70
H15	9566	439	1810	77
H3	7535	1794	4305	98
H1	7980	1216	207	95
H13	9500	2569	1028	72

H2	7494	1469	1674	101
H18A	9838	2216	-1237	135
H18C	10215	1925	-986	135
H18B	10042	2411	322	135
H6	8522	1278	1378	78
H8B	8444	1967	7945	92
H8A	8336	1206	7285	92
H7A	7885	1942	6691	97
H7B	8130	2556	6070	97

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