Radical Acylalkylation of 1,3-Enynes to Access Allenic Ketones via *N*-Heterocyclic Carbene Organocatalysis

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[‡] *Antibiotics Research and Re-evaluation Key Laboratory of Sichuan Province, Sichuan Industrial Institute of Antibiotics, School of Pharmacy, Chengdu University, Chengdu 610106, China.*

[#] *These authors contributed equally to this work.*

Supplementary Information

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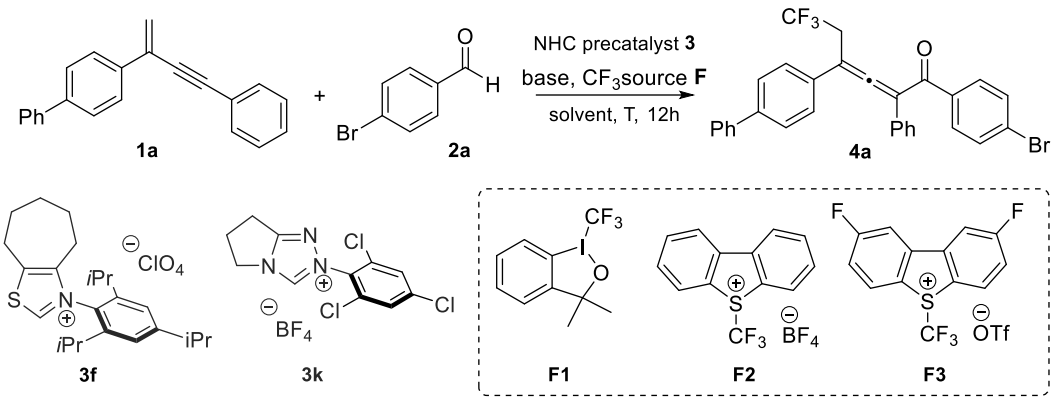
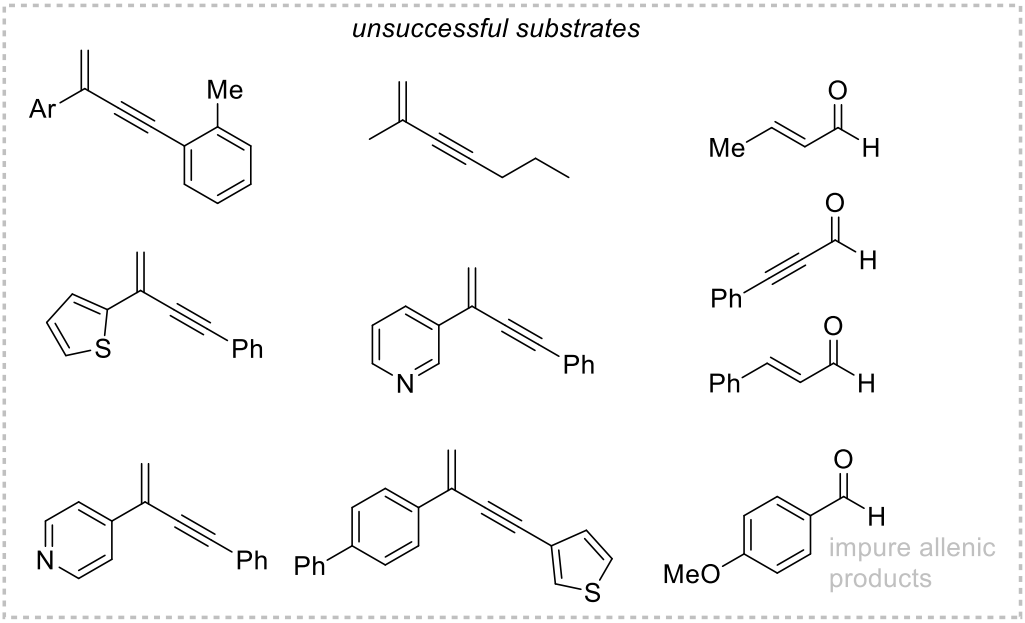
1. Further Optimization Studies

Table S1. Optimization of the 1,4-difunctionalization of 1,3-enynes **1a**[a]



entry	cat **3**	base	solvent	CF_3 source	Temp. (°C)	Yield (%)[b]
1	**3f**	Cs_2CO_3	Actone	**F1**	60	84
2	**3f**	Cs_2CO_3	iPr_2O	**F1**	60	71
3	**3f**	DABCO	CF_3Ph	**F1**	60	38
4	**3k**	Cs_2CO_3	CF_3Ph	**F1**	60	55
5	**3f**	Cs_2CO_3	CF_3Ph	**F2**	60	49
6	**3f**	Cs_2CO_3	CF_3Ph	**F3**	60	21
7	**3f**	Cs_2CO_3	CF_3Ph	**F1**	20	77
8	**3f**	Cs_2CO_3	CF_3Ph	**F1**	80	91

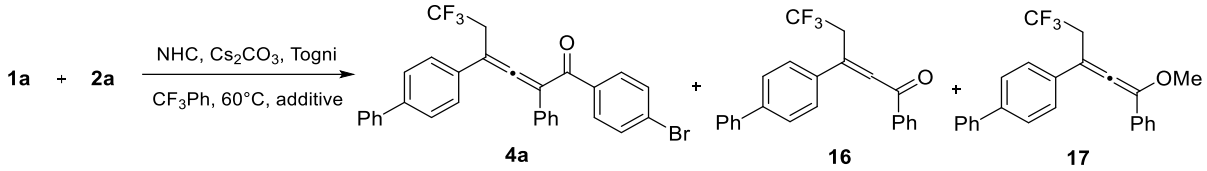
[a] The reactions were carried out with **1a** (0.15 mmol), aldehyde **2a** (0.10 mmol), NHC **3** (0.02 mmol), base (0.04 mmol) and CF_3 source **F** (0.15 mmol) in solvent (1.0 mL) for 12h.[b] Isolated yield of **4a**.



Schemem S1. unsuccessful substrates

2. Mechanism Studies

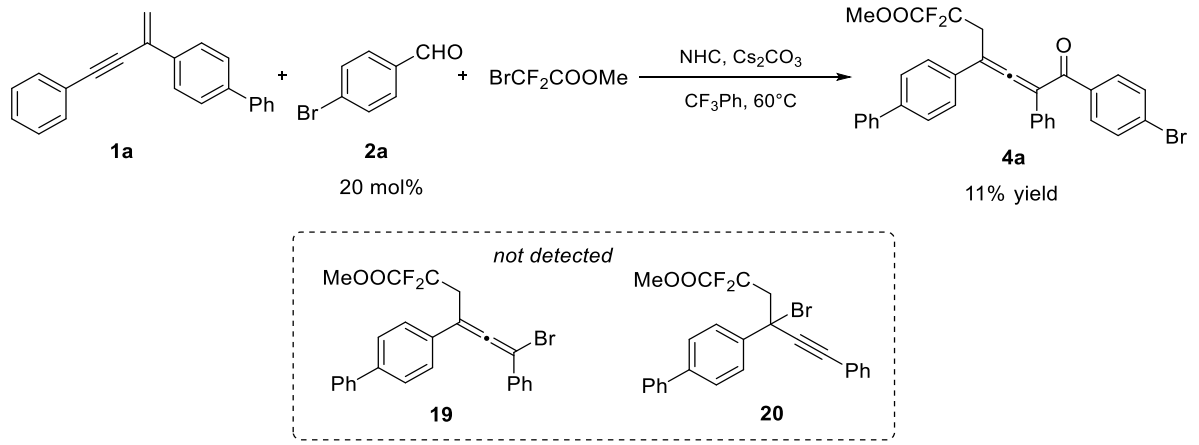
2.1 Intermolecular Cation-Traping Experiments



entry	additive	equiv	**4a**	**16**	**17**
1	none	0	99%	/	/
2	H_2O	5.0	75%	0	/
3	H_2O	1.0	73%	0	/
4	H_2O	0.5	84%	0	/
5	MeOH	5.0	54%	/	0
6	MeOH	1.0	56%	/	0
7	MeOH	0.5	75%	/	0

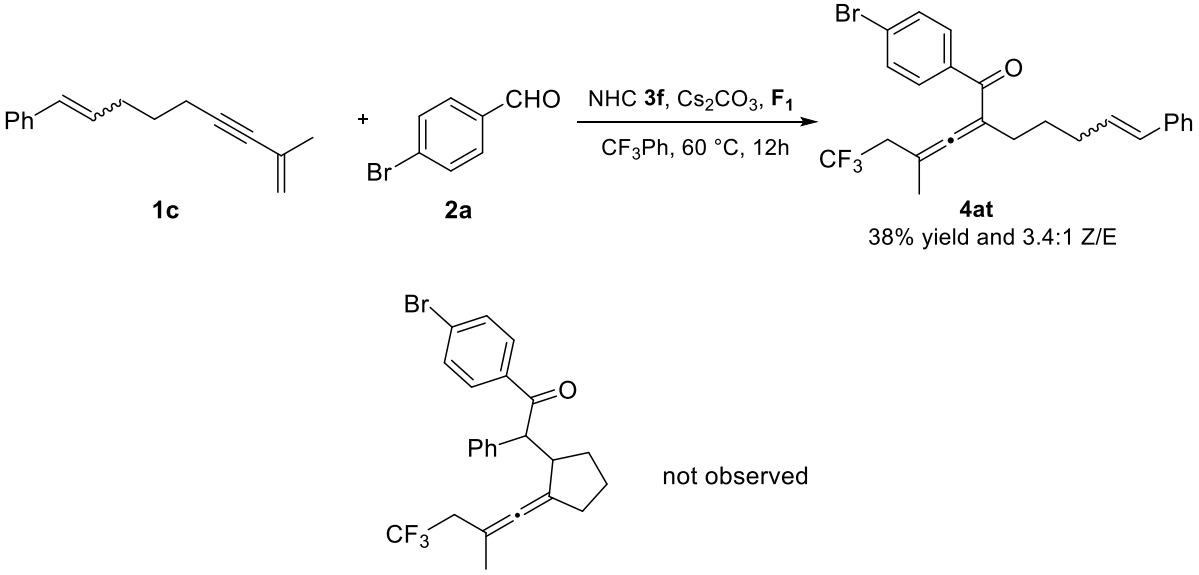
To a flame-dried Schlenk tube were added NHC **3f** (0.02 mmol), 1,3-enynes **1a** (0.15 mmol), Togni I reagent **F1** (0.15 mmol) and Cs_2CO_3 (0.04 mmol), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, a solution of the corresponding aldehydes **2a** (0.10 mmol) and the additive in anhydrous CF_3Ph (1.0 mL) was added via syringe. The resulting suspension was heated to 60 by oil bath °C for 12 h, after which the reaction mixture was concentrated under reduced pressure and the resulting crude material was purified by column chromatography on silica gel to afford the corresponding products **4a**. No cation-traping products **16** or **17** was observed by HRMS analysis.

2.2 Probe for Putative Intermediates



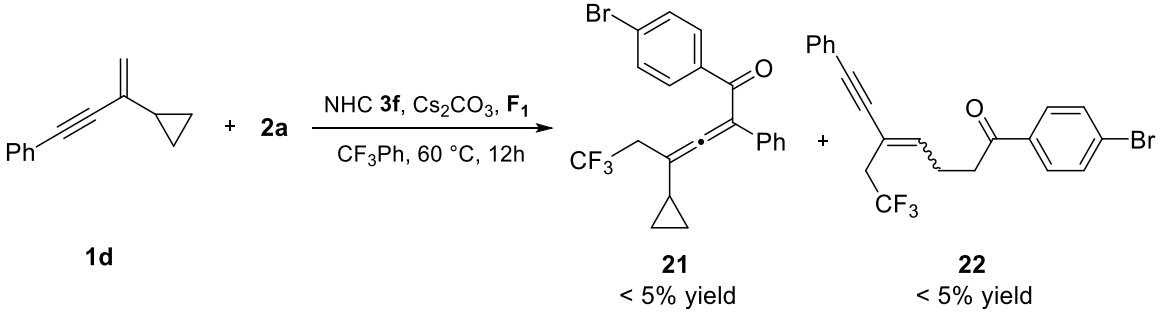
To a flame-dried Schlenk tube were added NHC **3f** (0.02 mmol), 1,3-enynes **1a** (0.15 mmol) and Cs_2CO_3 (0.04 mmol), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, a solution of the corresponding aldehydes **2a** (0.02 mmol) and $BrCF_2COOMe$ (0.15 mmol) in anhydrous CF_3Ph (1.0 mL) was added via syringe. The resulting suspension was heated to 60 °C by oil bath for 12 h, after the reaction mixture was concentrated under reduced pressure and the resulting crude material was purified by column chromatography on silica gel to afford the corresponding products **4a** with 11% yield. No product **19** or **20** was observed by HRMS analysis.

2.2 Ring-closing Experiment



To a flame-dried Schlenk tube were added NHC **3f** (0.02 mmol), 1,3-enynes **1c** (0.15 mmol), Togni **I** reagent **F1** (0.15 mmol) and Cs_2CO_3 (0.04 mmol), and the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, a solution of the corresponding aldehydes **2a** (0.10 mmol) in anhydrous CF_3Ph (1.0 mL) was added via syringe. The resulting suspension was heated to 60 °C by oil bath for 12 h, after the reaction mixture was concentrated under reduced pressure and the resulting crude material was purified by column chromatography to afford the corresponding products **4at** in 38% yield as a mixture of cis and trans isomers. In this reaction, the radical addition product was not observed.

7.6 Ring-opening Experiment

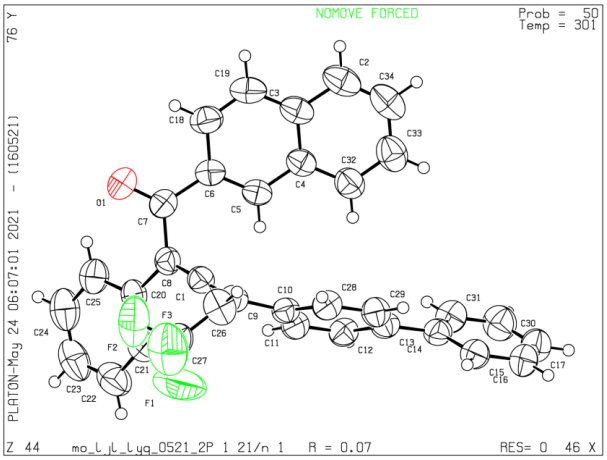


To a flame-dried Schlenk tube were added NHC **3f** (0.02 mmol), 1,3-enynes **1d** (0.15 mmol), Togni I reagent **F1** (0.15 mmol) and Cs_2CO_3 (0.04 mmol), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, a solution of the corresponding aldehydes **2a** (0.10 mmol) in anhydrous CF_3Ph (1.0 mL) was added via syringe. The resulting suspension was heated to 60 °C by oil bath for 12 h, and no product **21** or **22** was observed.

3. Crystal Data and Structure Refinement for 4s

To a tube containing **4s** (20 mg) was added a 40:1 mixture of petroleum ether and ethyl acetate (about 4 mL). The tube was kept aside for 6 days at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the structure of **4s**. The data were collected by a Bruker APEX-II CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 301.0 K. CCDC 2108115 (**4s**) contains the supplementary crystallographic data for this paper.

Crystal Data (at 50% probability level)



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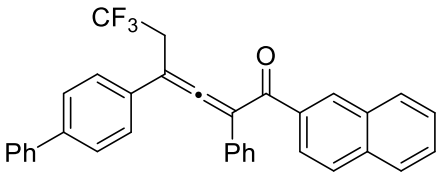
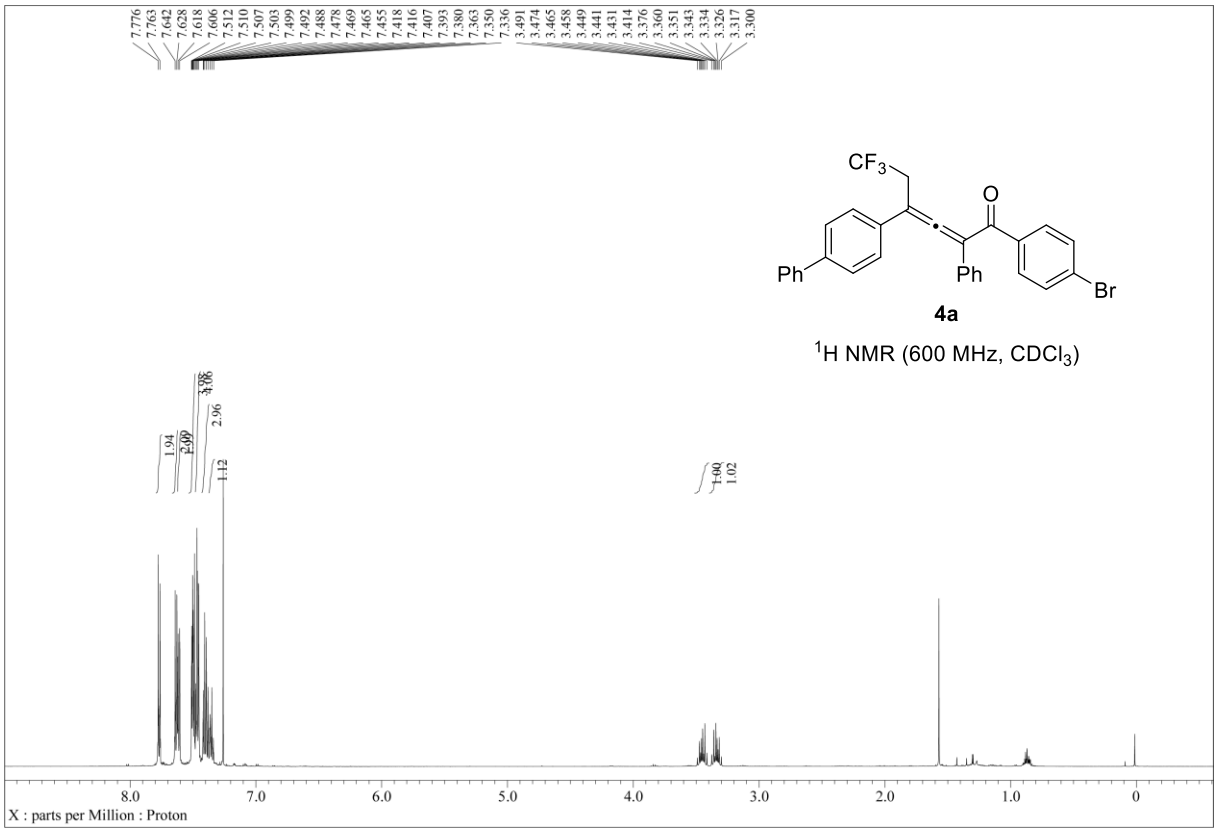


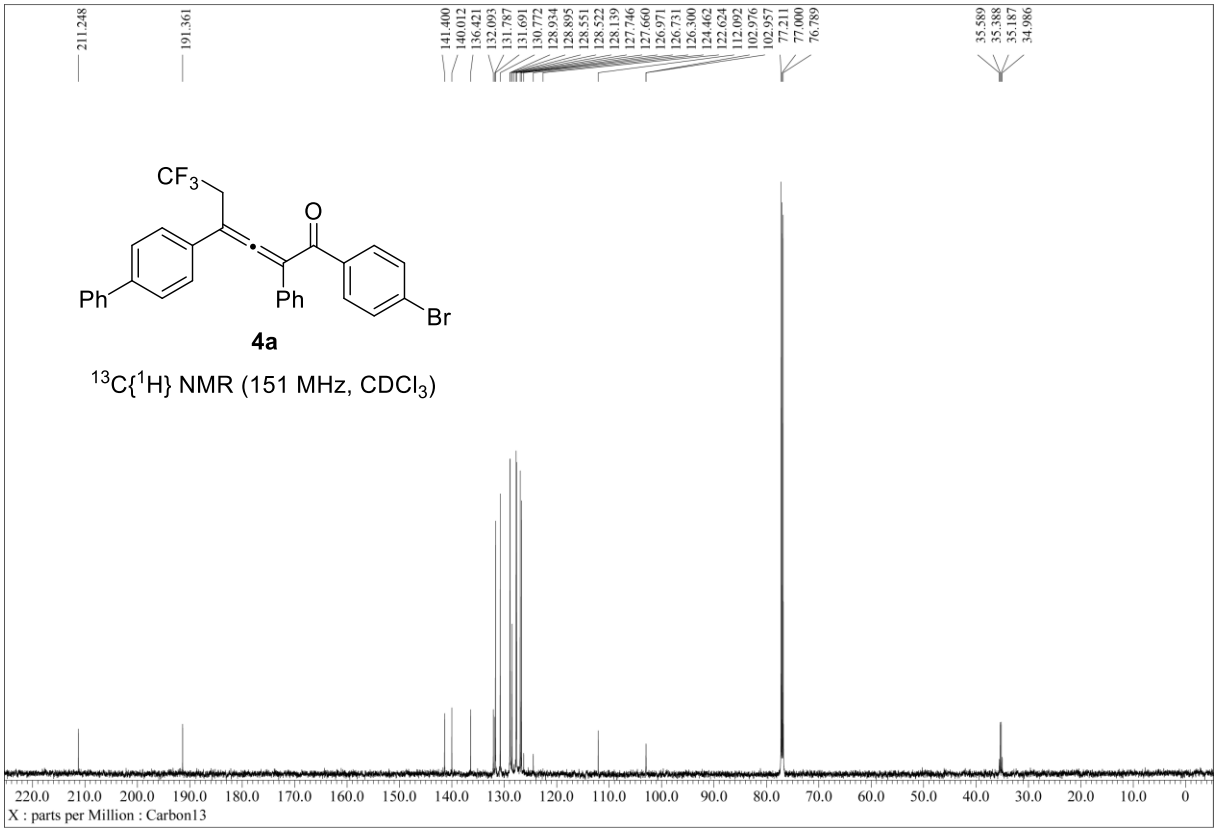
4s

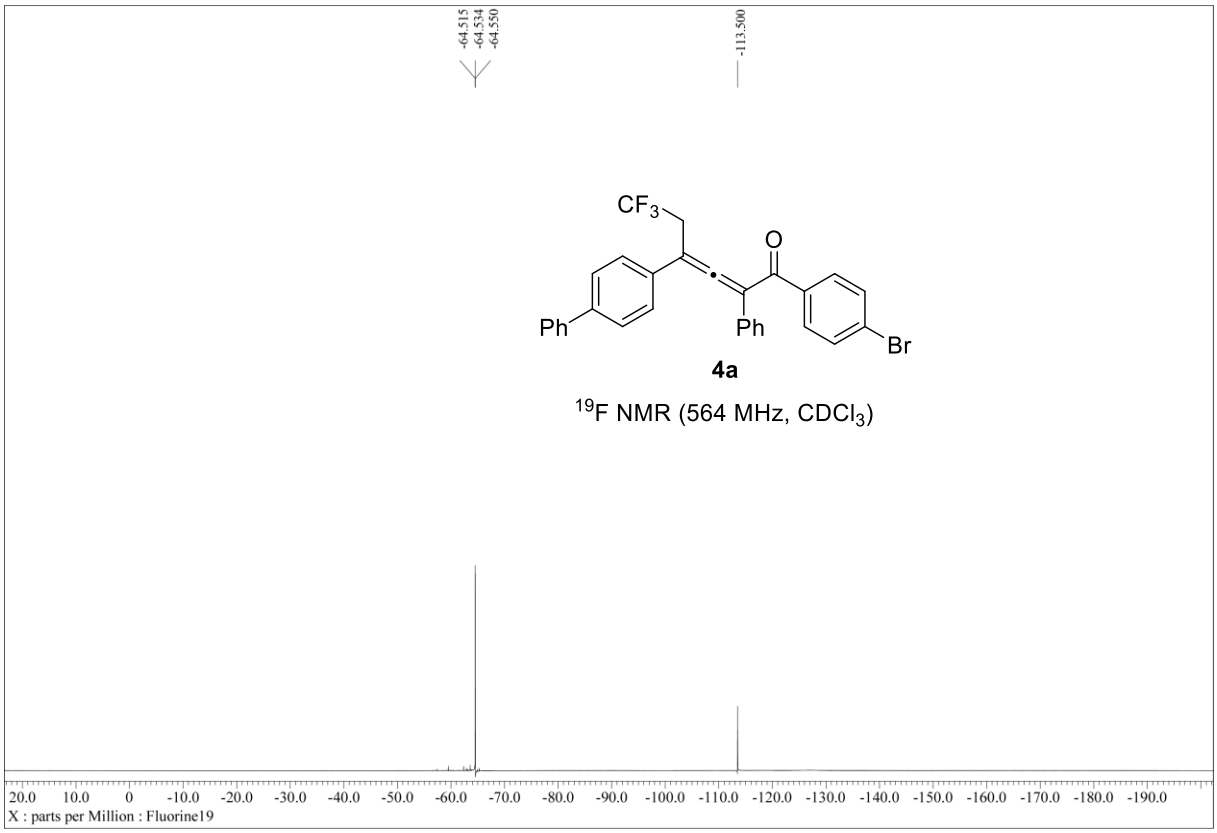
Identification code	**4s**
Empirical formula	$C_{34}H_{22}F_3O$
Formula weight	503.51
Temperature/K	301.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.963(4)
b/Å	27.249(10)
c/Å	10.129(4)
α /°	90
β /°	109.647(12)
γ /°	90
Volume/Å^3	2589.6(17)
Z	4
ρ_{calc}g/cm3	1.291
μ /mm^{-1}	0.091
F(000)	1044.0
Crystal size/mm^3	0.35 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.524 to 55.124
Index ranges	$-12 \leqslant h \leqslant 12, -35 \leqslant k \leqslant 35, -13 \leqslant l \leqslant 13$
Reflections collected	32152
Independent reflections	5909 [$R_{int} = 0.0867$, $R_{sigma} = 0.0575$]
Data/restraints/parameters	5909/7/344
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	$R_1 = 0.0662$, $wR_2 = 0.1573$
Final R indexes [all data]	$R_1 = 0.1373$, $wR_2 = 0.2000$
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.30

4. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

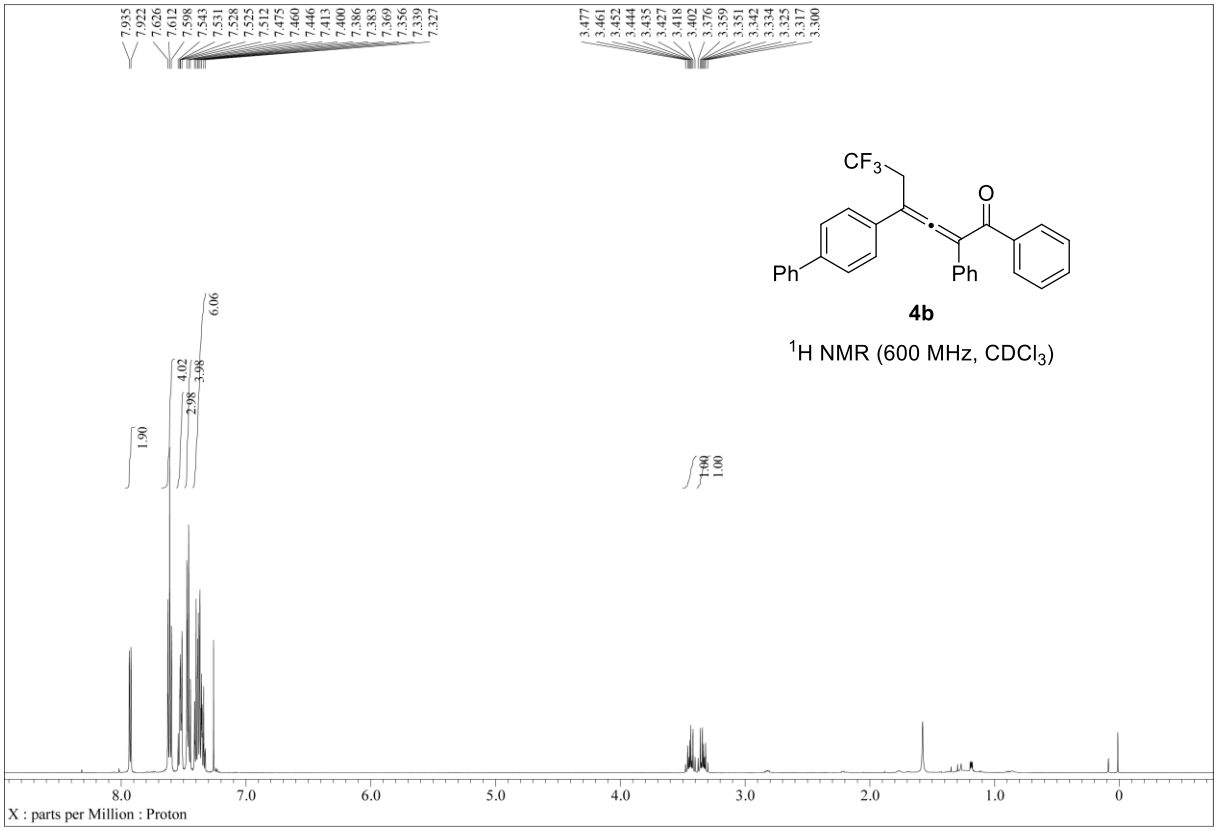






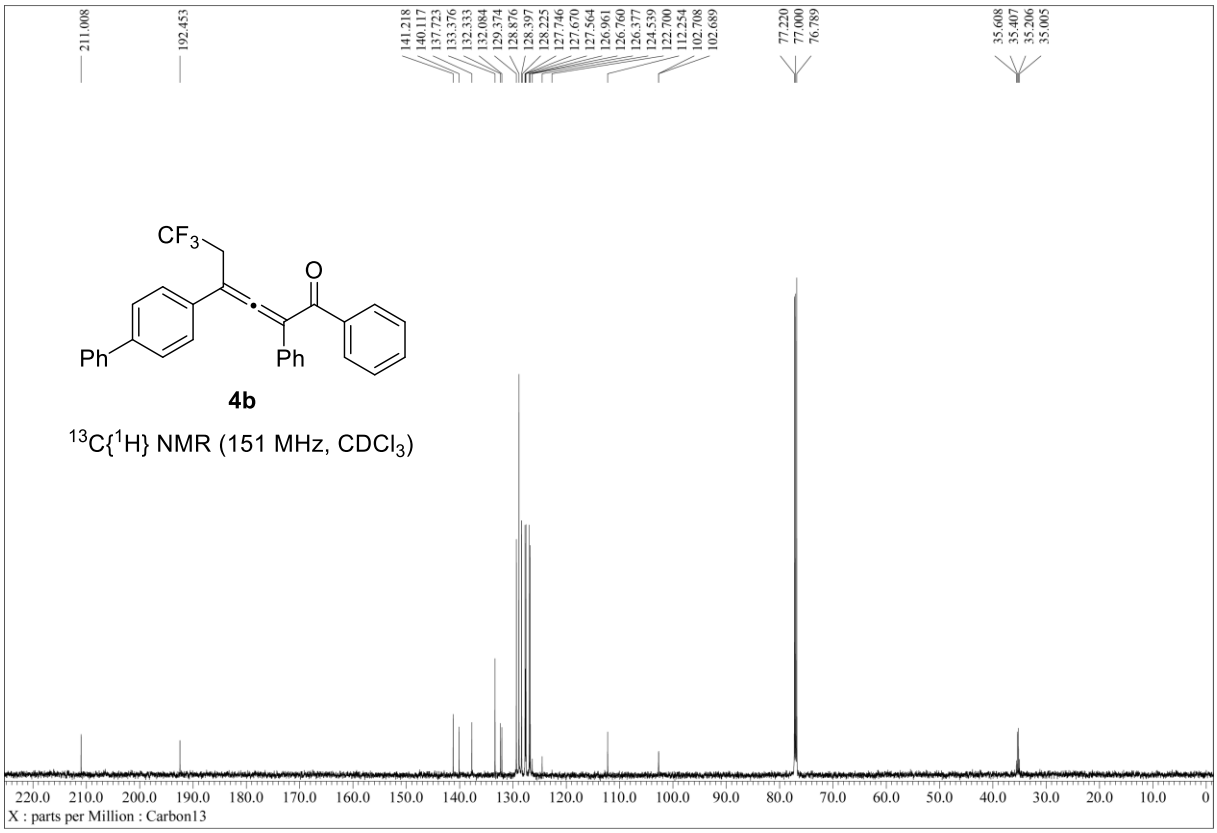
4a

^{19}F NMR (564 MHz, $CDCl_3$)



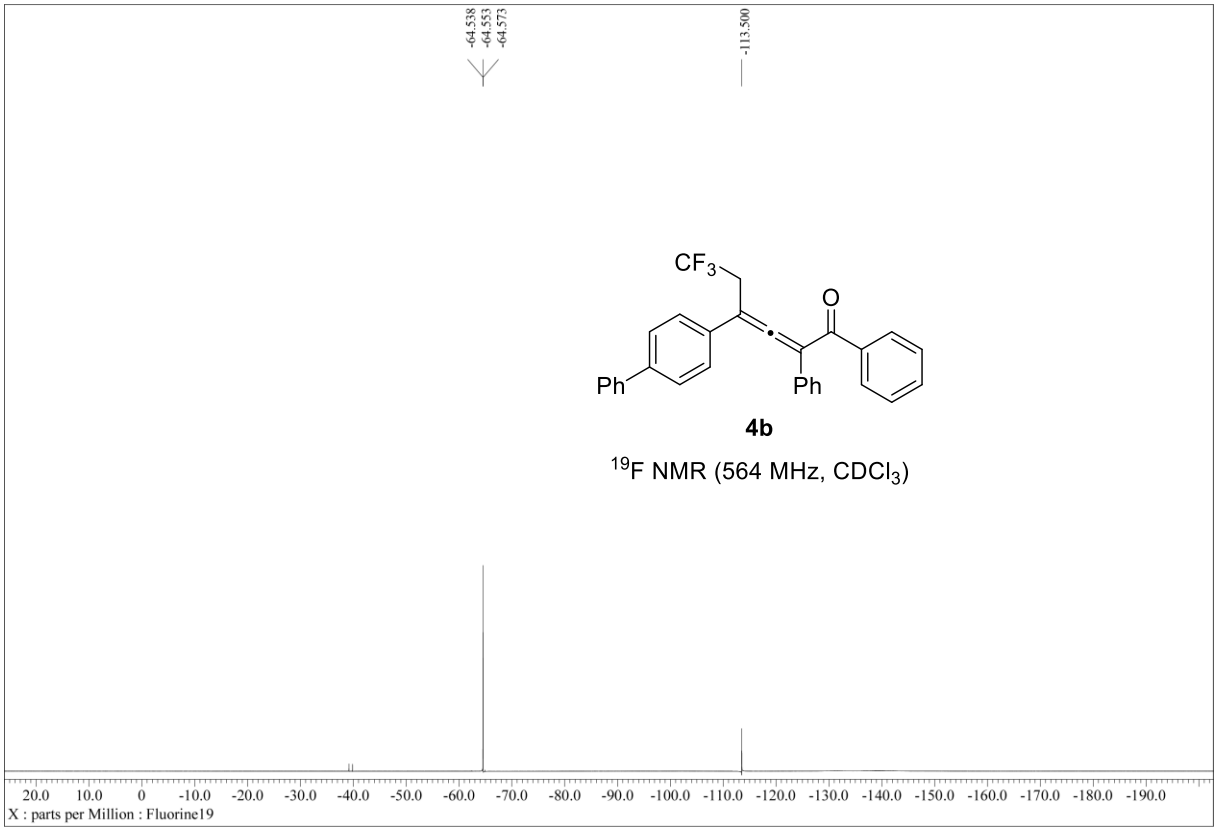
4b

^{1}H NMR (600 MHz, $CDCl_3$)



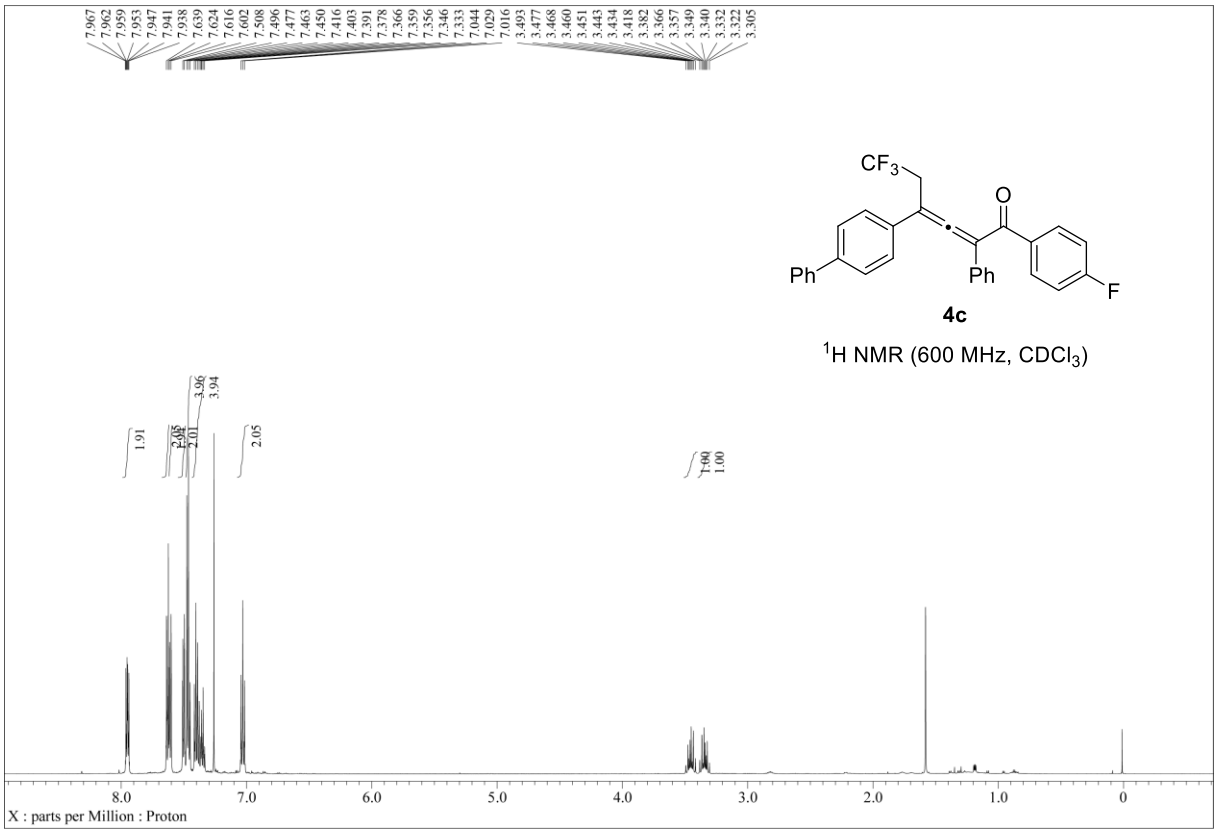
4b

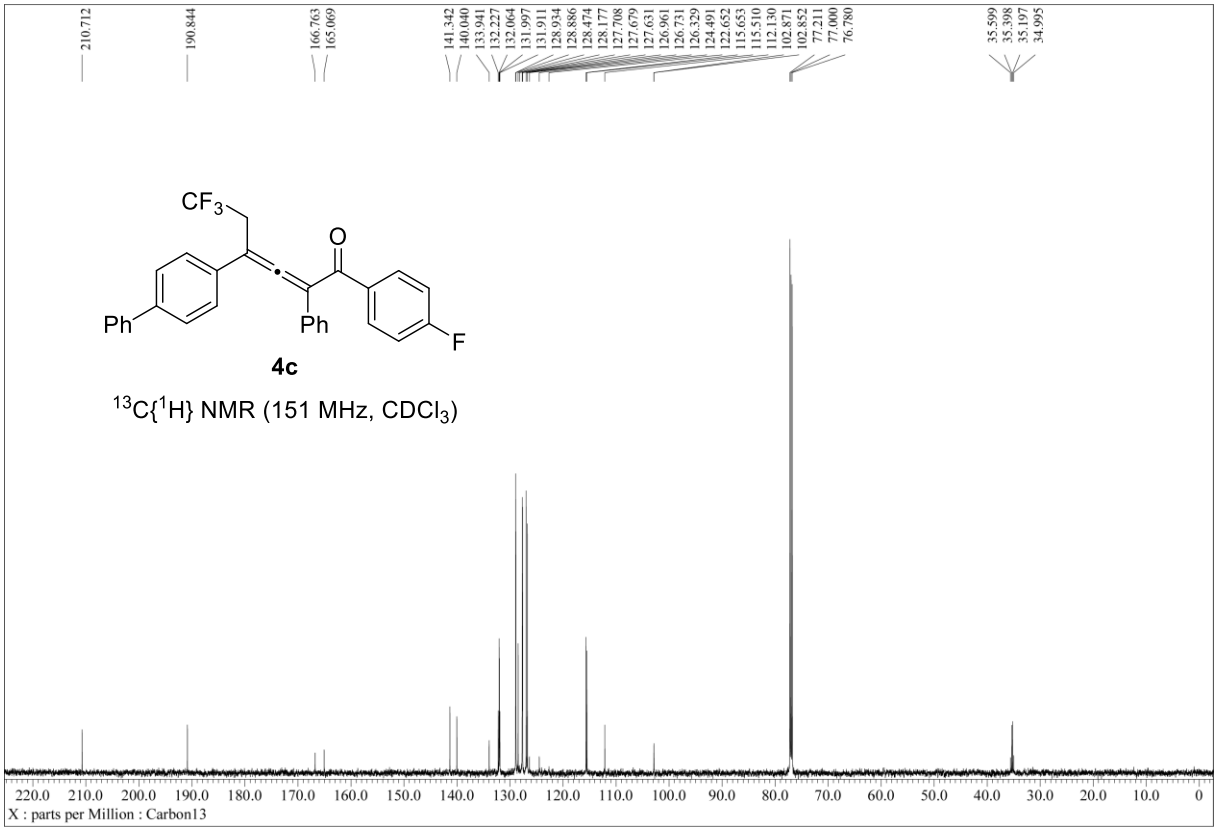
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

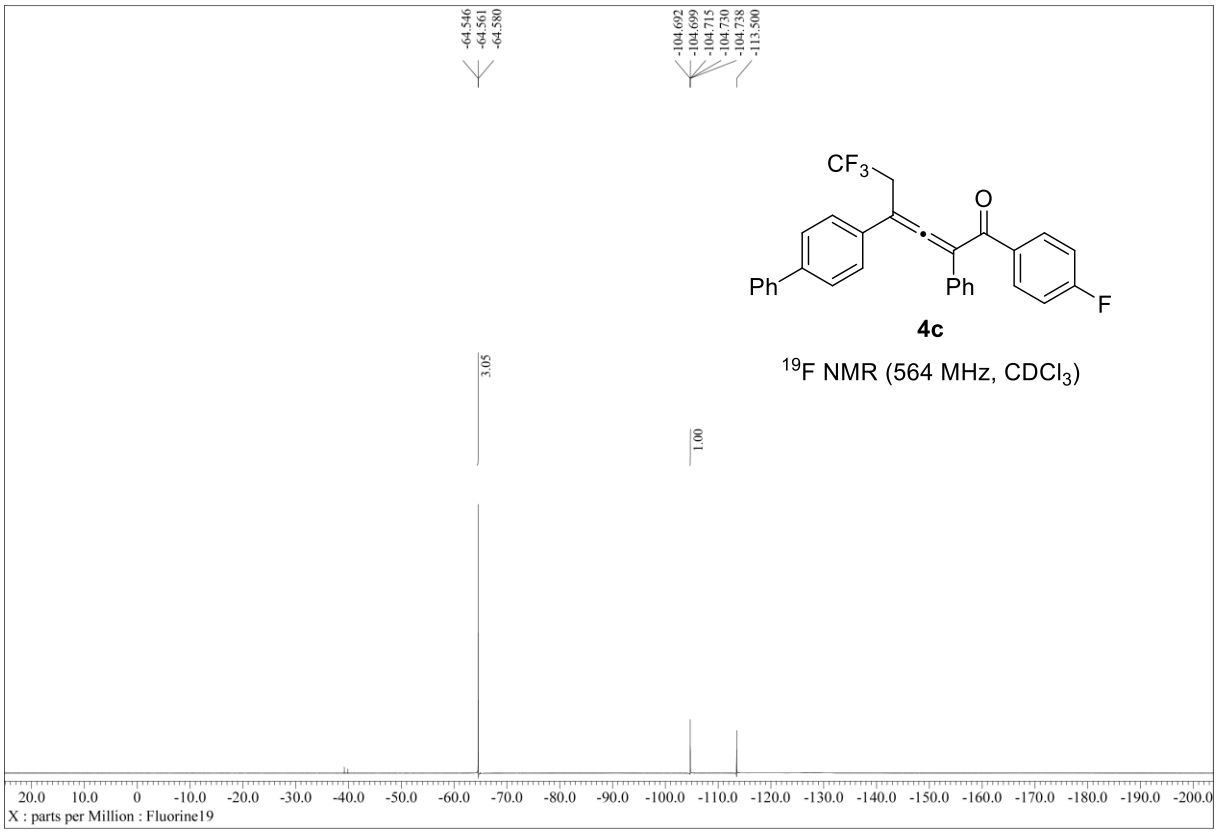


4b

^{19}F NMR (564 MHz, $CDCl_3$)

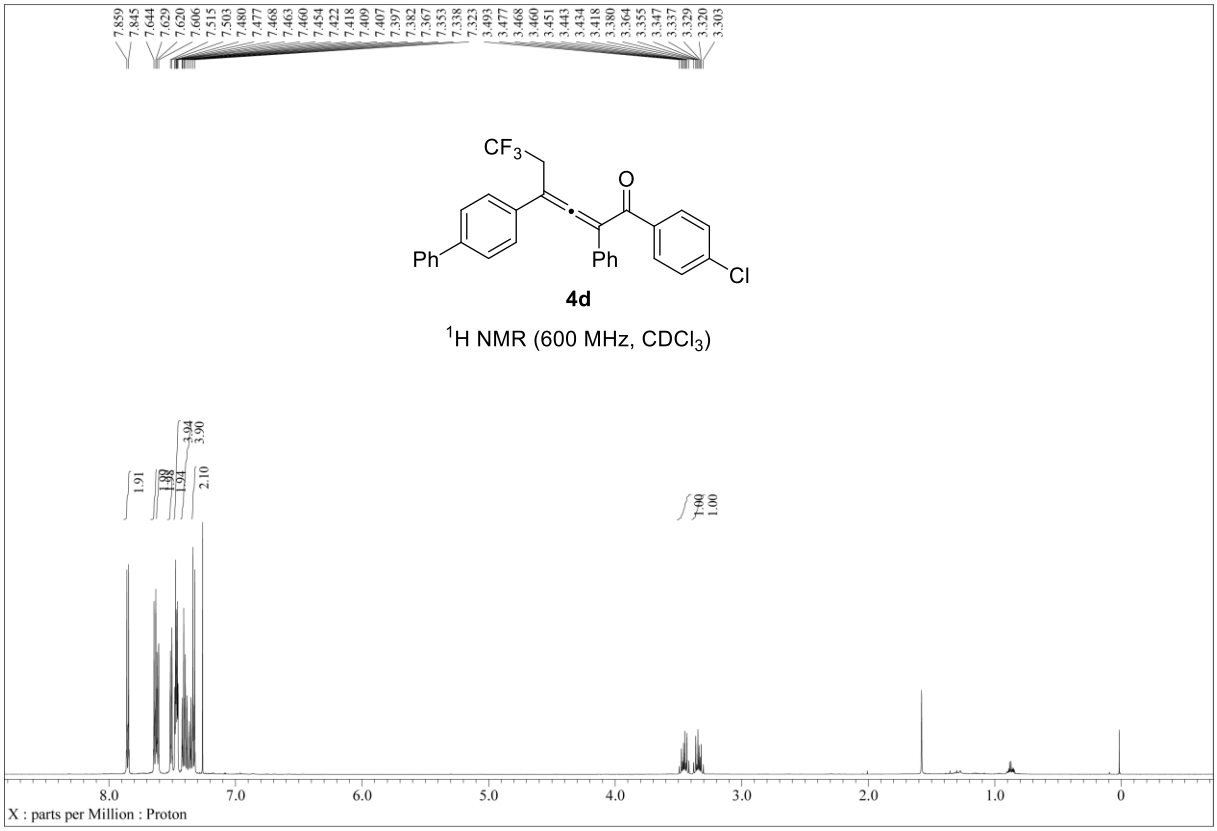

7.967 7.962 7.959 7.953 7.947 7.941 7.938 7.639 7.624 7.616 7.602 7.508 7.496 7.477 7.463 7.450 7.416 7.403 7.391 7.378 7.366 7.359 7.356 7.346 7.333 7.044 7.029 7.016 3.493 3.477 3.468 3.460 3.451 3.443 3.434 3.418 3.382 3.366 3.357 3.349 3.340 3.332 3.322 3.305
CF3
O
Ph
Ph
F
4c
1H NMR (600 MHz, CDCl3)
1.91 2.05 2.01 3.96 3.94 2.05 1.00 1.00
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


210.712 190.844 166.763 165.069 141.342 140.040 133.941 132.227 132.064 131.997 131.911 128.934 128.886 128.474 128.177 127.708 127.679 127.631 126.961 126.731 126.329 124.491 122.652 115.653 115.510 112.130 102.871 102.852 77.211 77.000 76.780 35.599 35.398 35.197 34.995
CF3
O
Ph
Ph
F
4c
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13



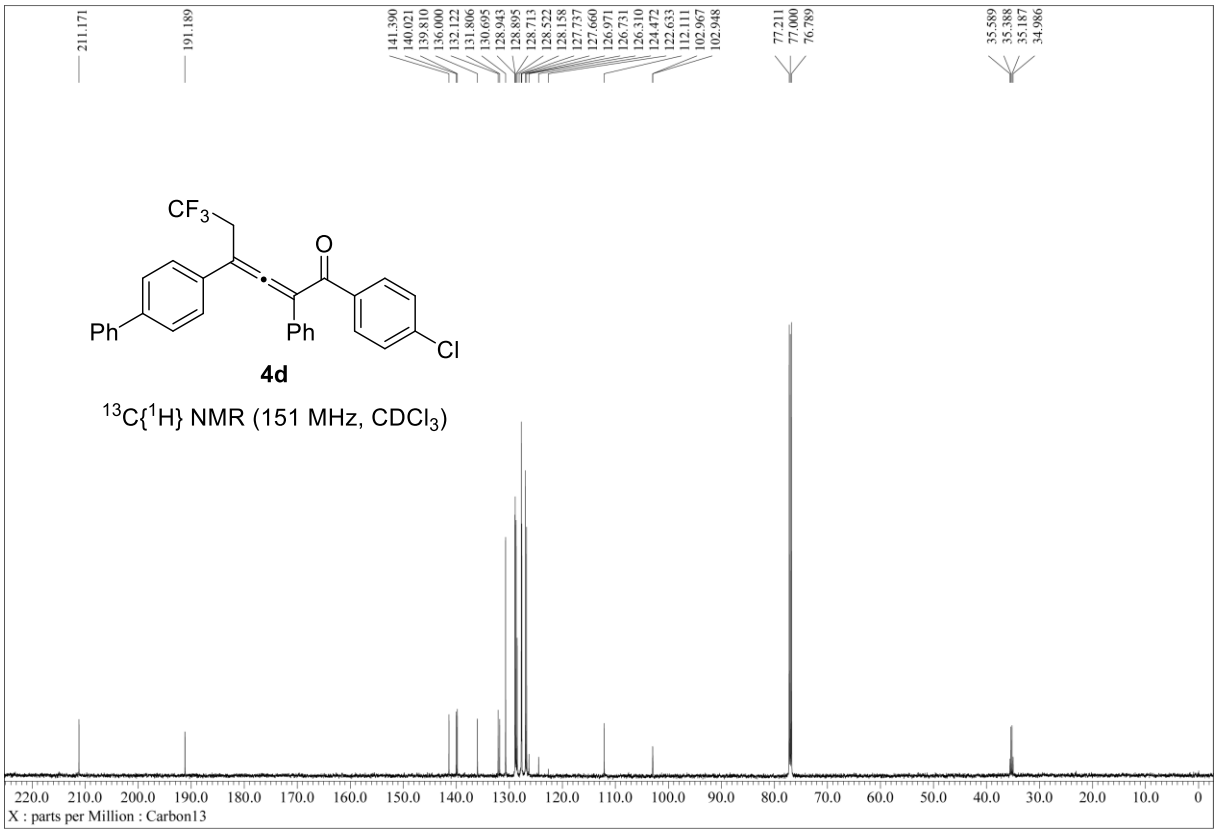
4c

^{19}F NMR (564 MHz, $CDCl_3$)



4d

^{1}H NMR (600 MHz, $CDCl_3$)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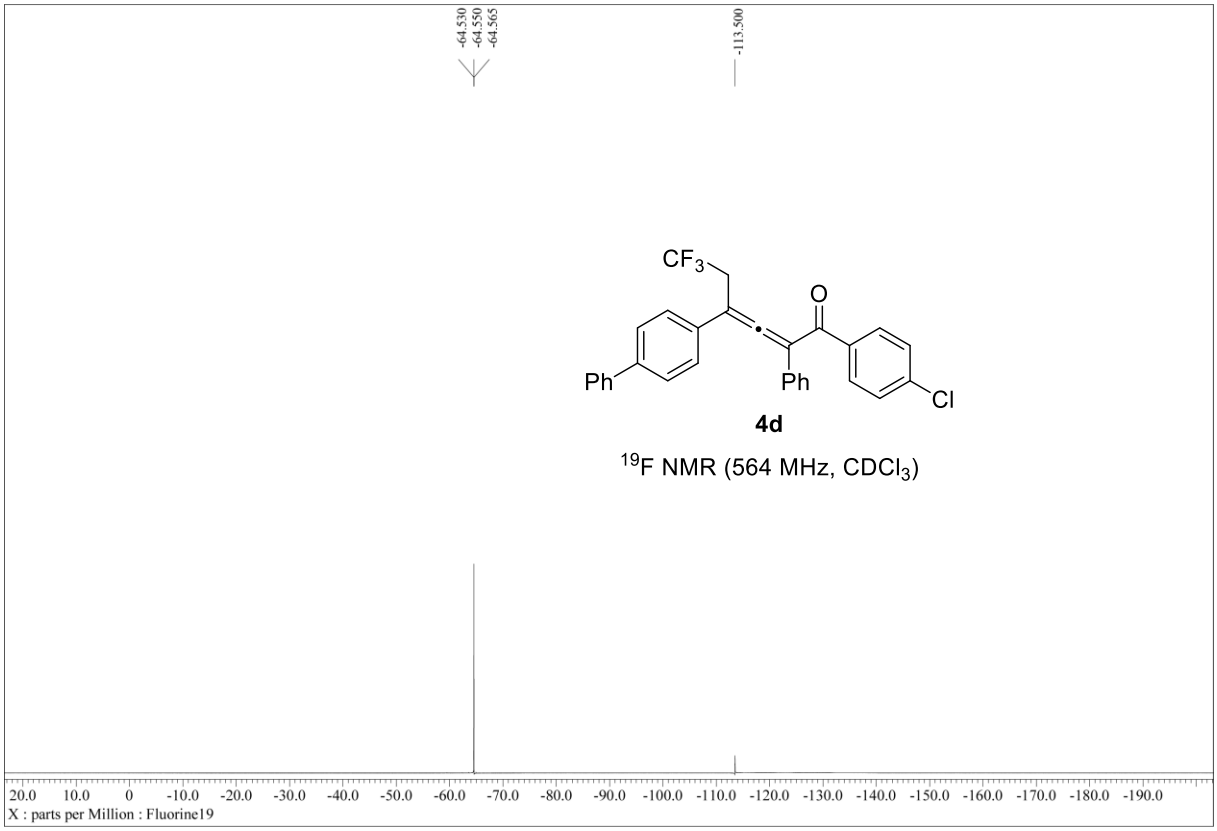
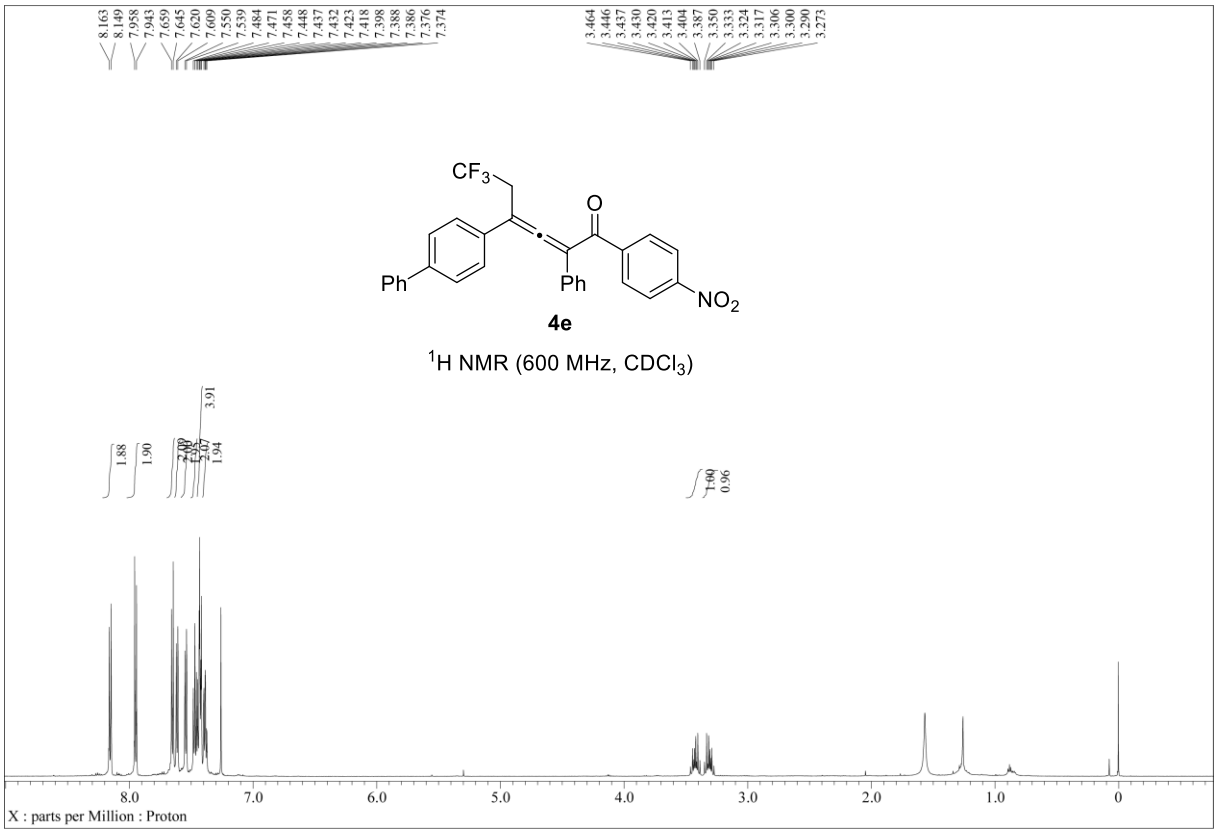
141.390
140.021
139.810
136.000
132.122
131.806
130.695
128.943
128.895
128.713
128.522
128.158
127.737
127.660
126.971
126.731
126.310
124.472
122.633
112.111
102.967
102.948
77.211
77.000
76.789
35.589
35.388
35.187
34.986
CF3
O
Ph
Ph
Cl
4d
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.530
-64.550
-64.565
-113.500
CF3
O
Ph
Ph
Cl
4d
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19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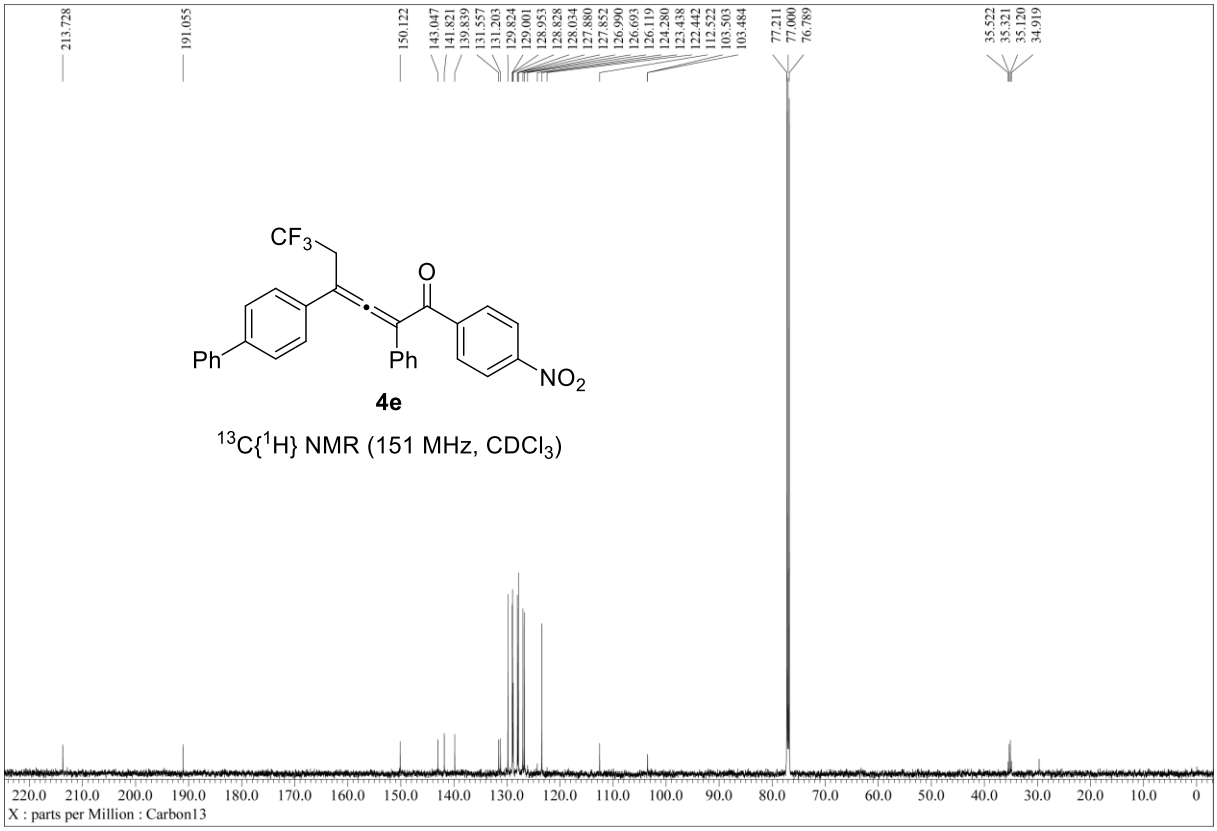
7.958
7.943
7.659
7.645
7.620
7.609
7.550
7.539
7.484
7.471
7.458
7.448
7.437
7.432
7.423
7.418
7.398
7.388
7.386
7.376
7.374
3.464
3.446
3.437
3.430
3.420
3.413
3.404
3.387
3.350
3.333
3.324
3.317
3.306
3.300
3.290
3.273
CF3
O
Ph
Ph
NO2
4e
1H NMR (600 MHz, CDCl3)
3.91
1.88
1.90
1.94
1.00
0.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


213.728
191.055
150.122
143.047
141.821
139.839
131.557
131.203
129.824
129.001
128.953
128.828
128.034
127.880
127.852
126.990
126.693
126.119
124.280
123.438
122.442
112.522
103.503
103.484
77.211
77.000
76.789
35.522
35.321
35.120
34.919
CF3
O
Ph
Ph
NO2
4e
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
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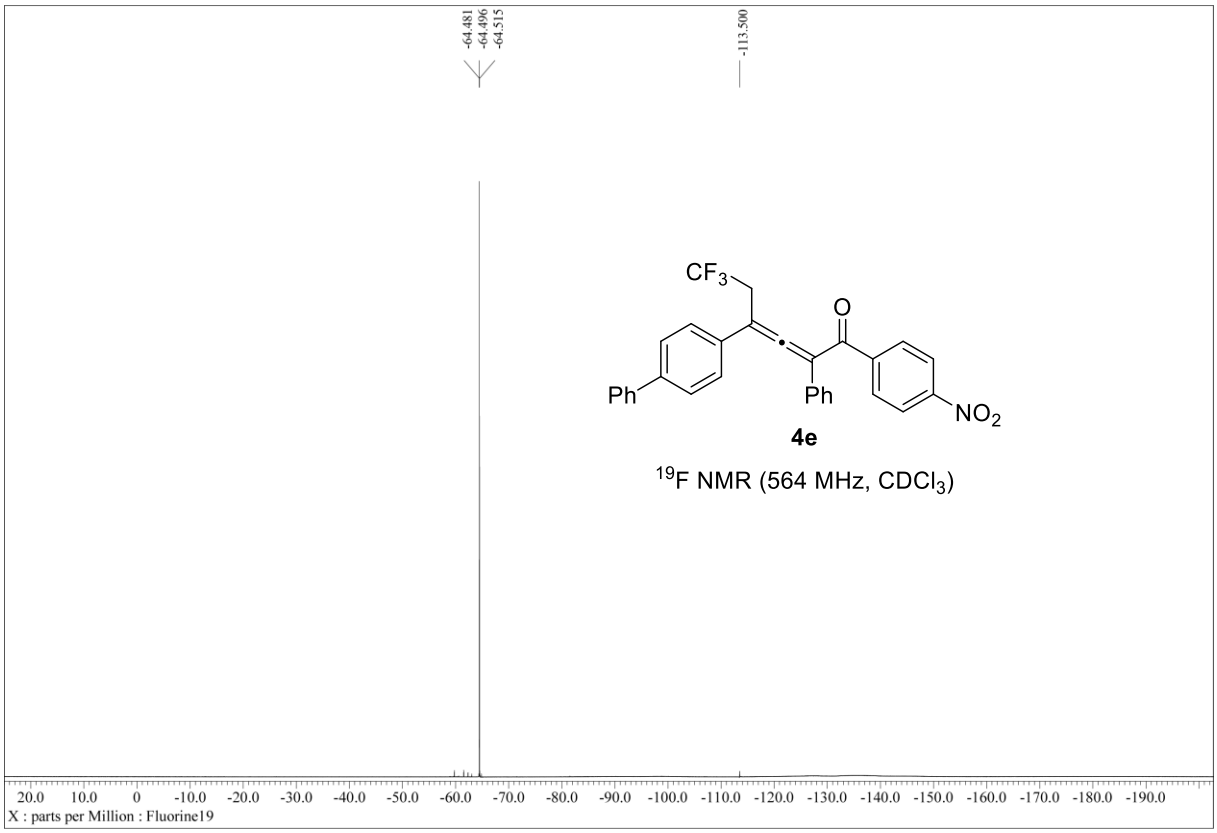
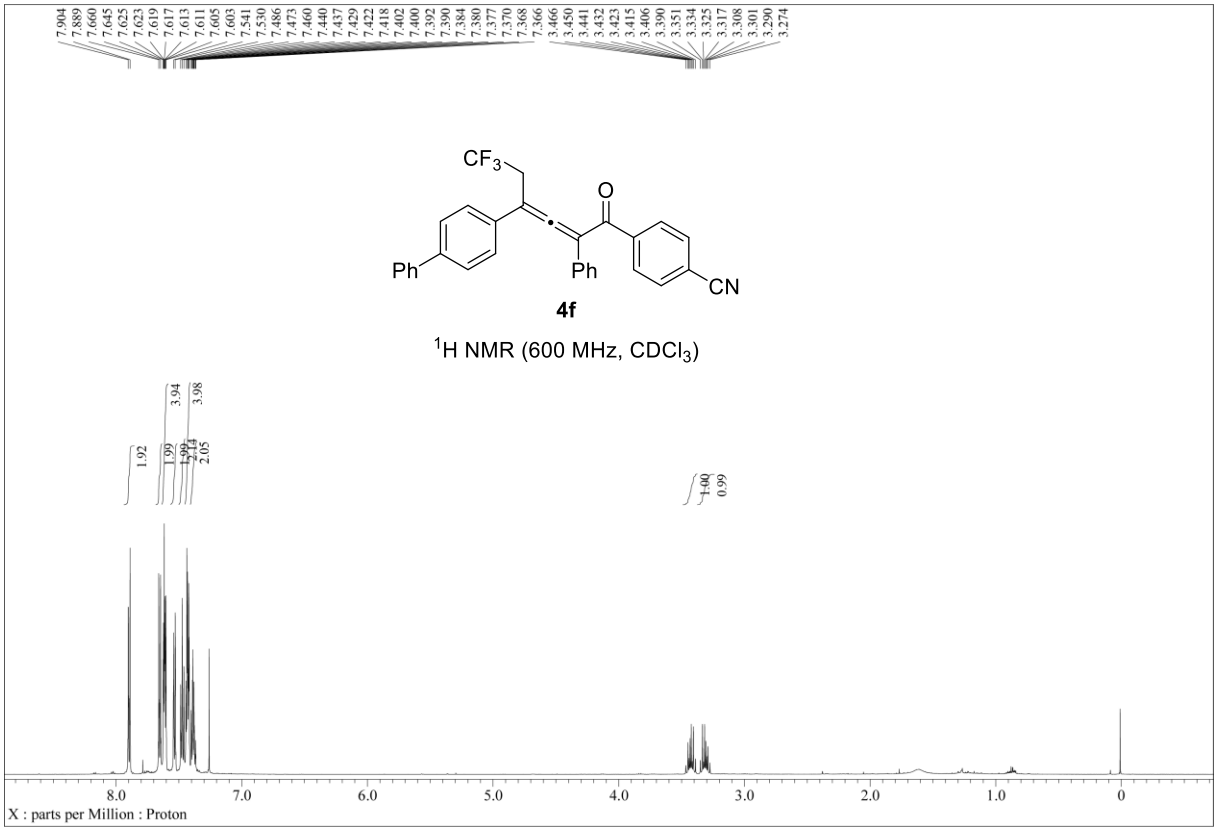
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



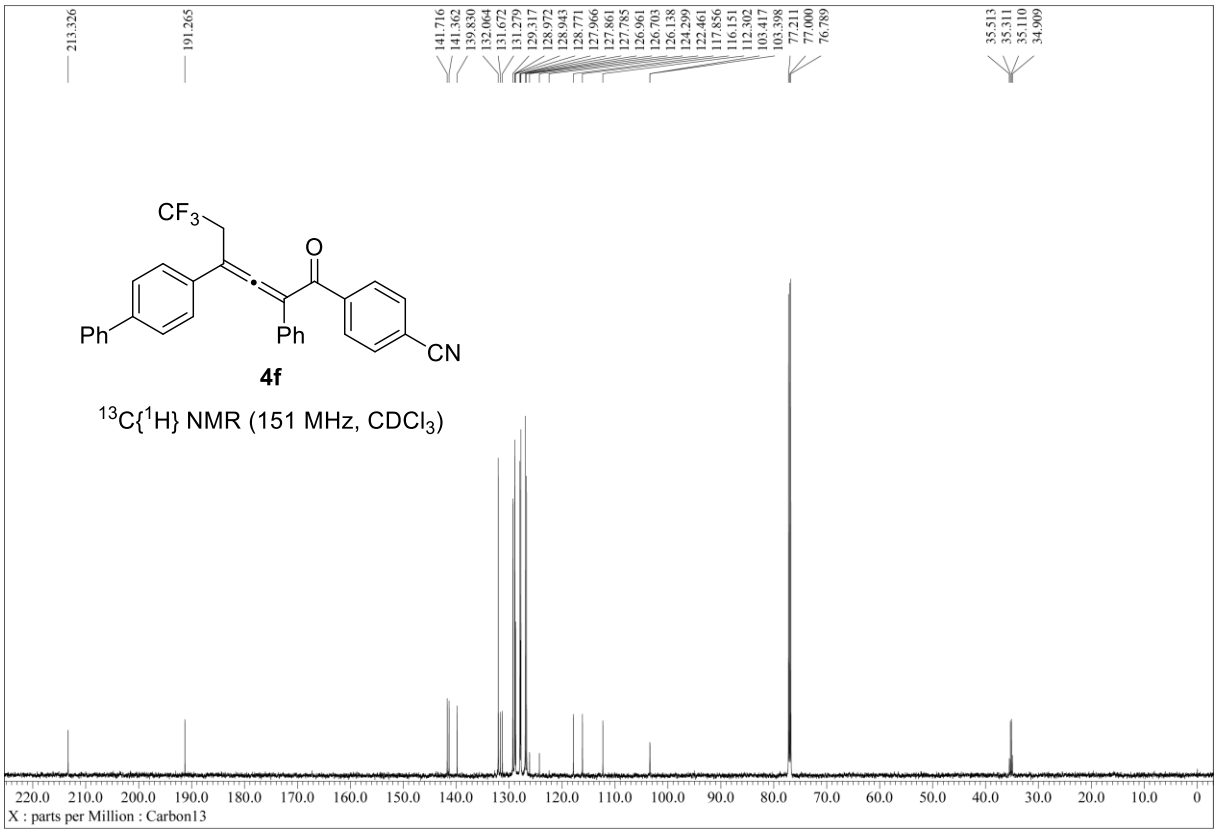
4e

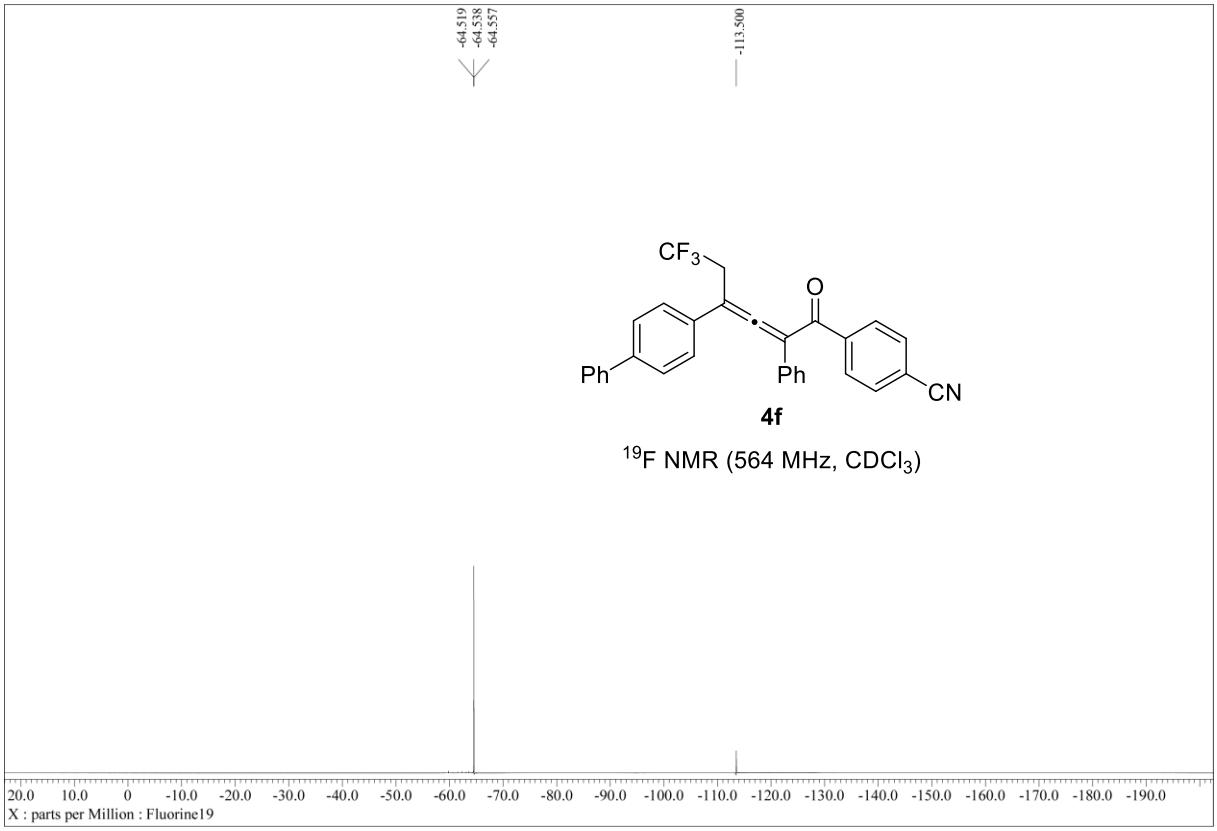
^{19}F NMR (564 MHz, $CDCl_3$)



4f

^{1}H NMR (600 MHz, $CDCl_3$)


213.326
191.265
141.716
141.362
139.830
132.064
131.672
131.279
129.317
128.972
128.943
128.771
127.966
127.861
127.785
126.961
126.703
126.138
124.299
122.461
117.856
116.151
112.302
103.417
103.398
77.211
77.000
76.789
35.513
35.311
35.110
34.909
CF3
O
Ph
Ph
CN
4f
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.519
-64.538
-64.557
-113.500
CF3
O
Ph
Ph
CN
4f
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
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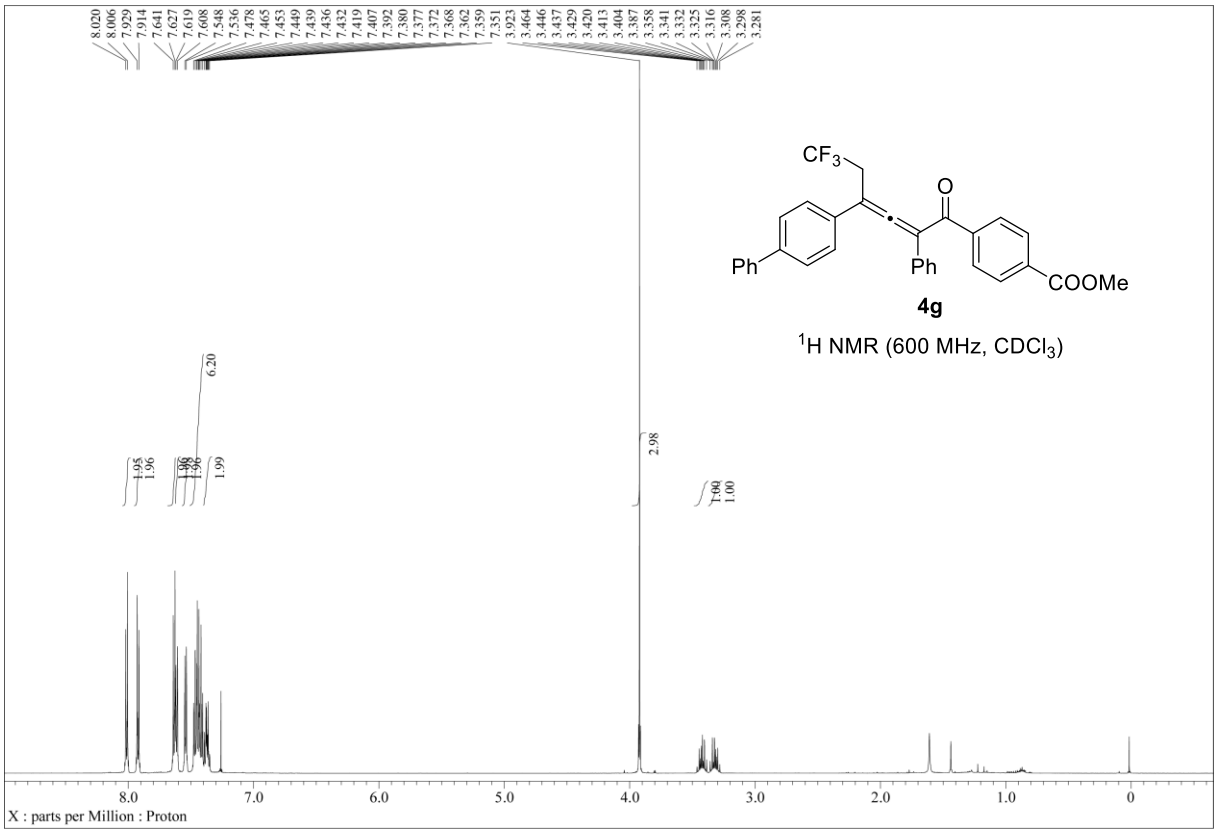
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7.641
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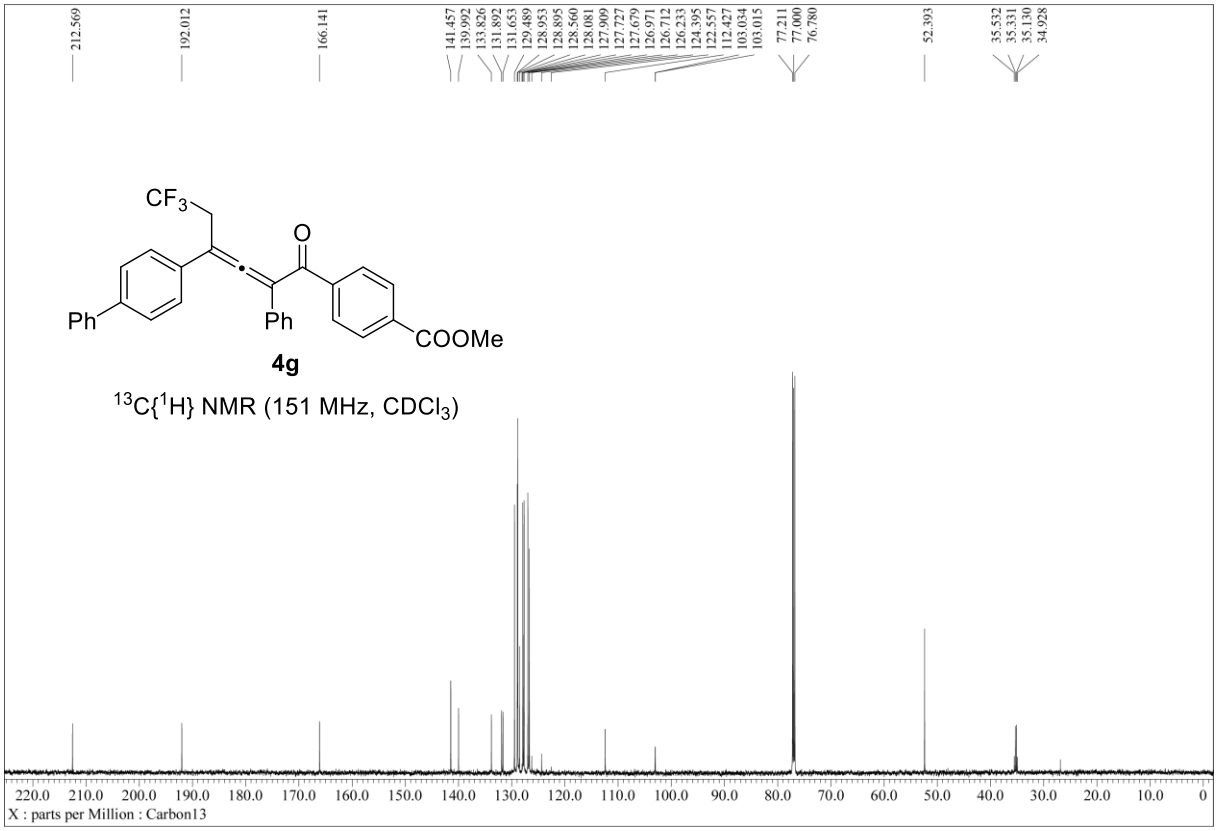
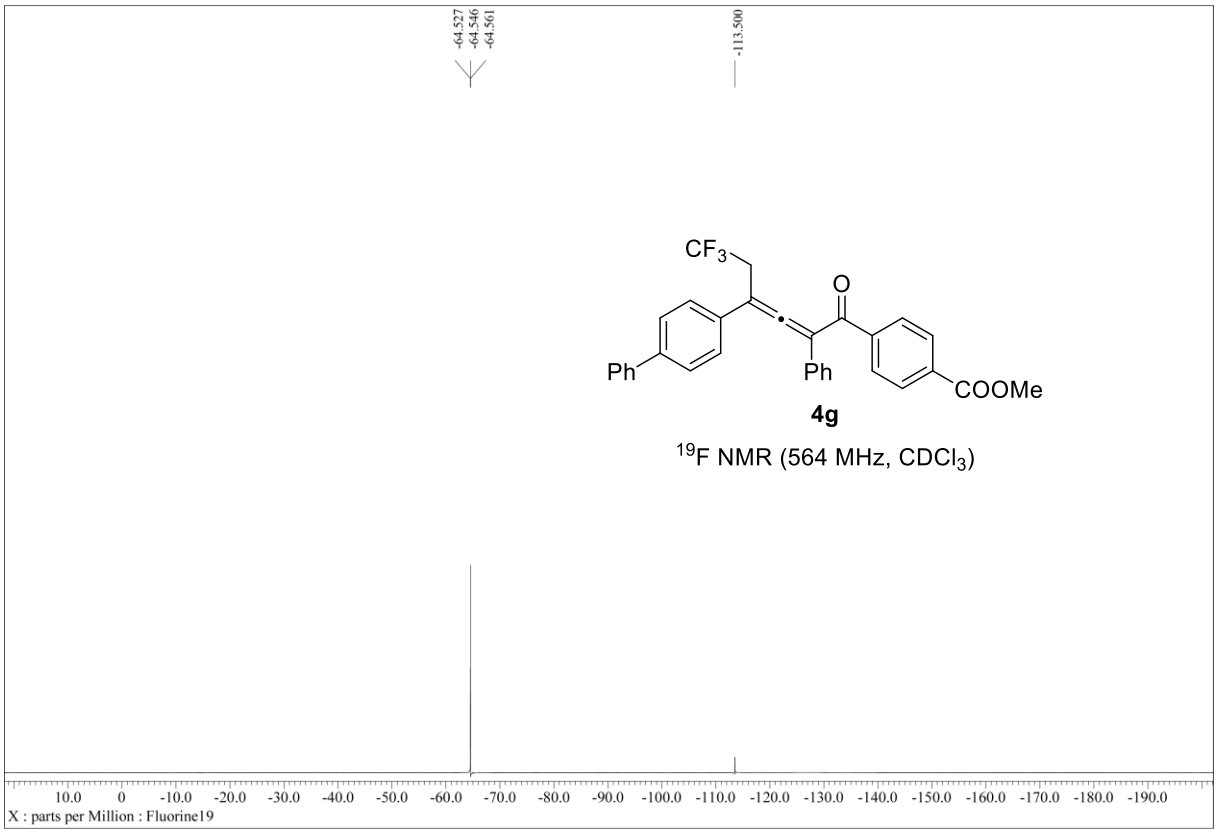
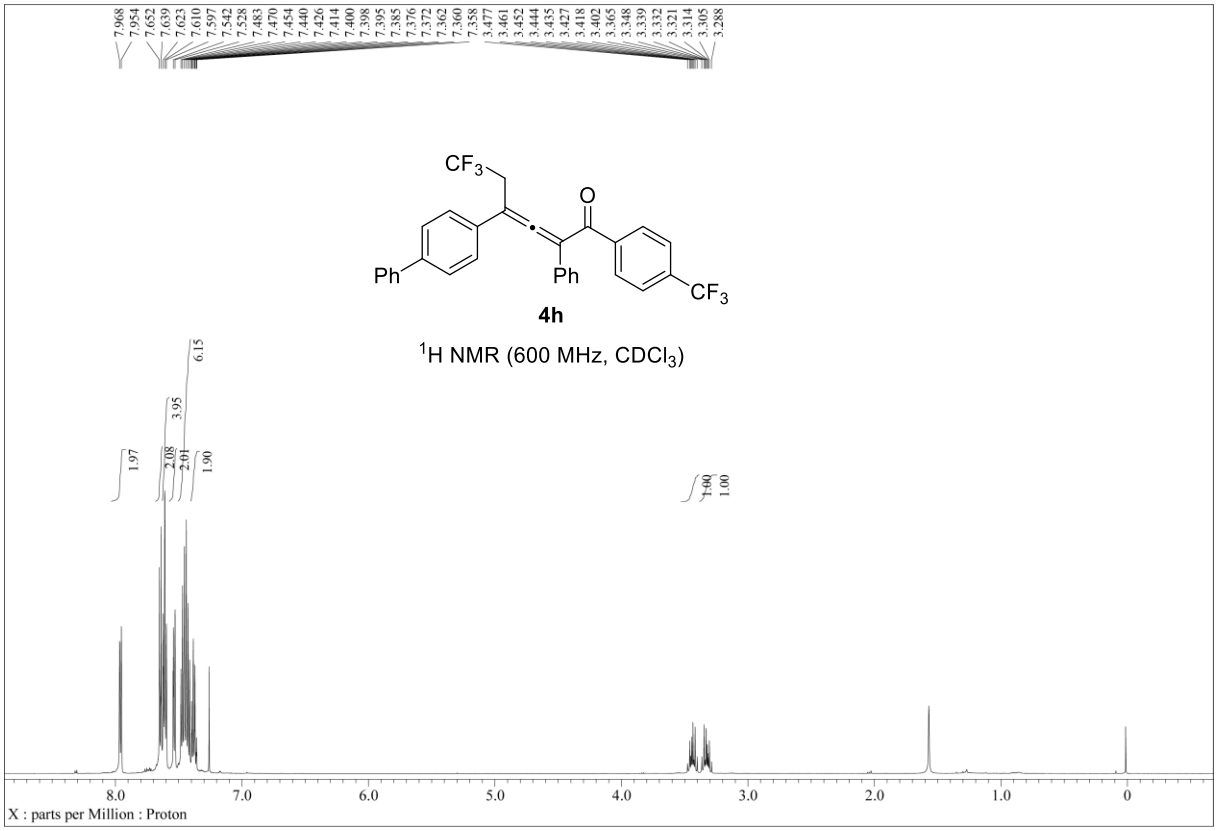
7.453
7.449
7.439
7.436
7.432
7.419
7.407
7.392
7.380
7.377
7.372
7.368
7.362
7.359
7.351
3.923
3.464
3.446
3.437
3.429
3.420
3.413
3.404
3.387
3.358
3.341
3.332
3.325
3.316
3.308
3.298
3.281
6.20
2.98
1.99
1.96
1.95
1.00
1.00
CF3
O
Ph
Ph
COOMe
4g
1H NMR (600 MHz, CDCl3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


212.569
192.012
166.141
141.457
139.992
133.826
131.892
131.653
129.489
128.953
128.895
128.560
128.081
127.909
127.727
127.679
126.971
126.712
126.233
124.395
122.557
112.427
103.034
103.015
77.211
77.000
76.780
52.393
35.532
35.331
35.130
34.928
CF3
O
Ph
Ph
COOMe
4g
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



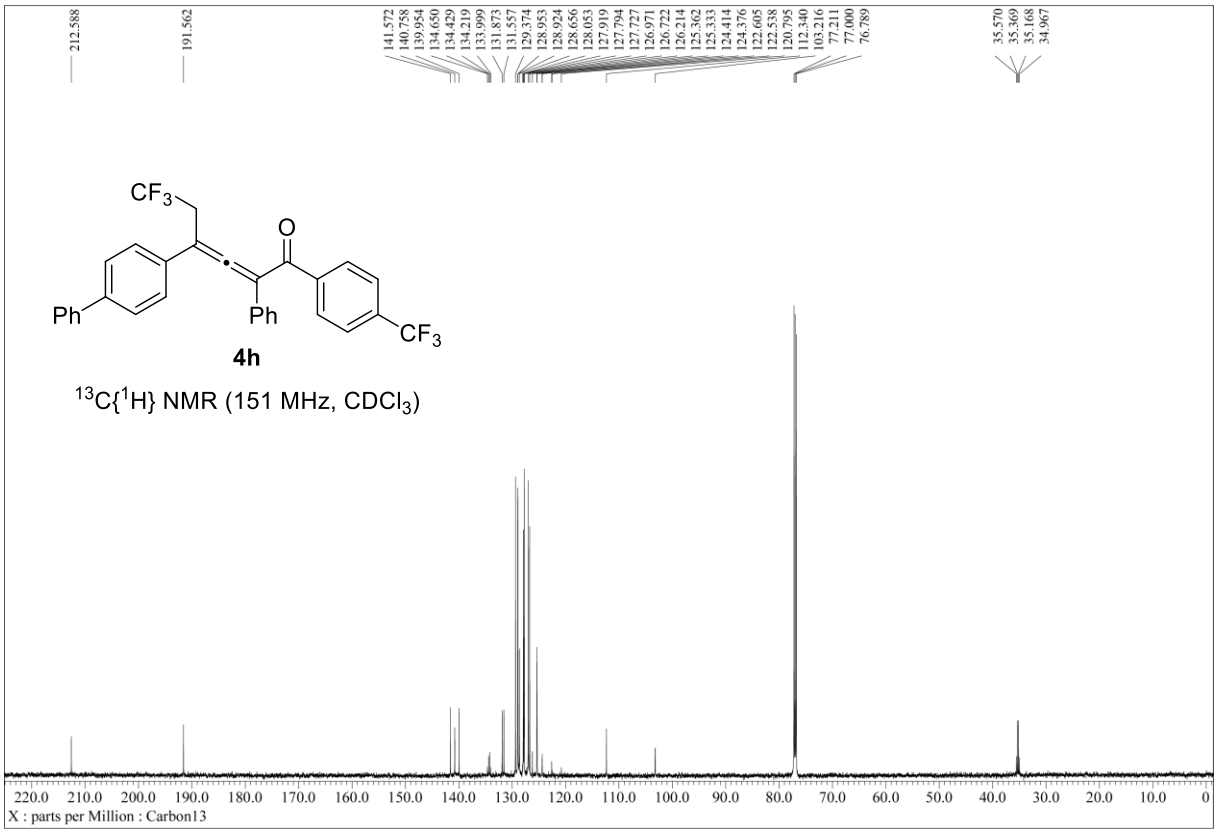
4g

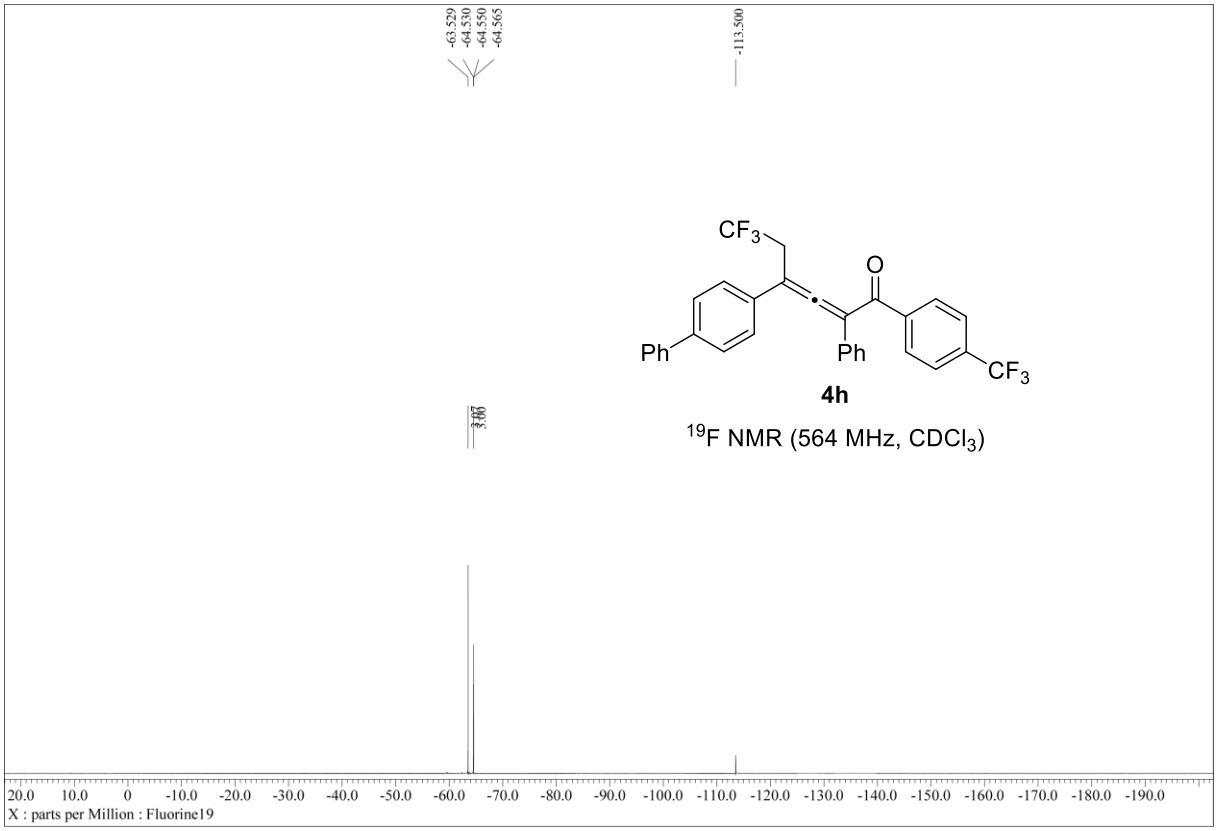
^{19}F NMR (564 MHz, $CDCl_3$)

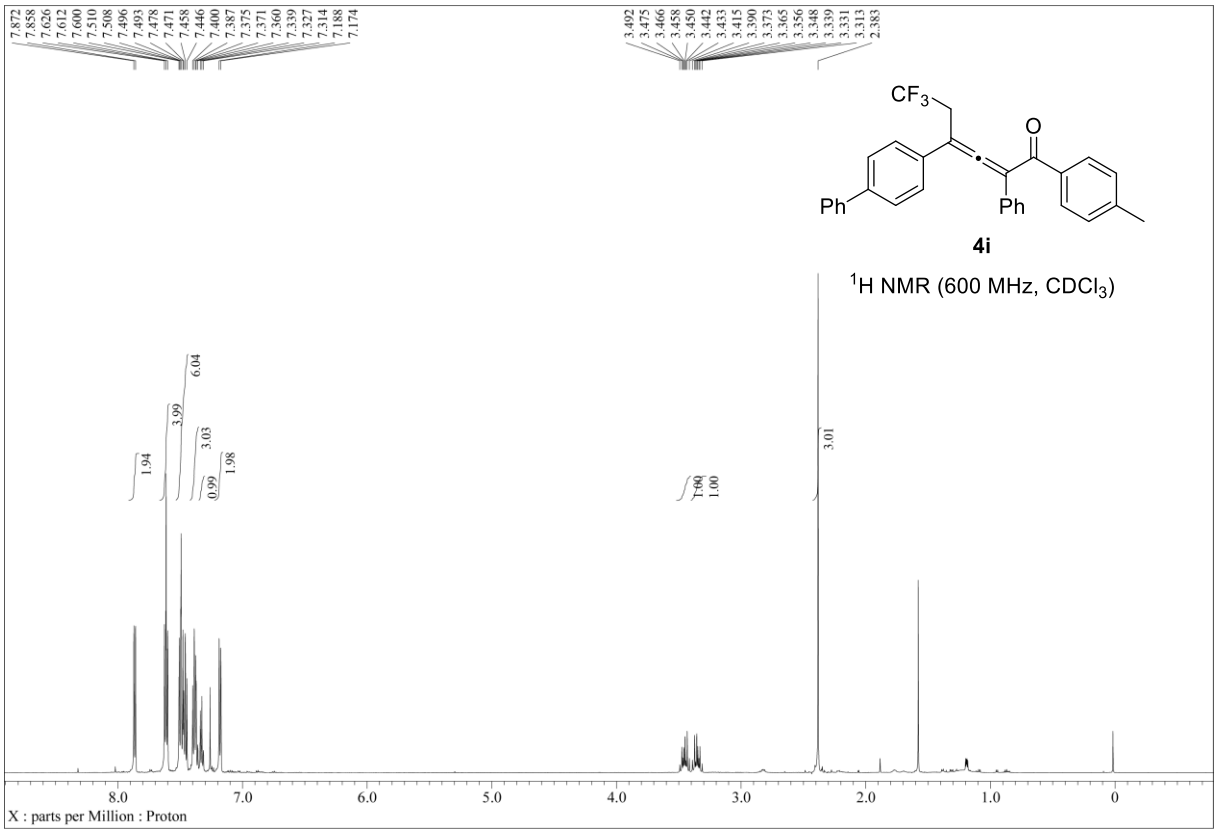


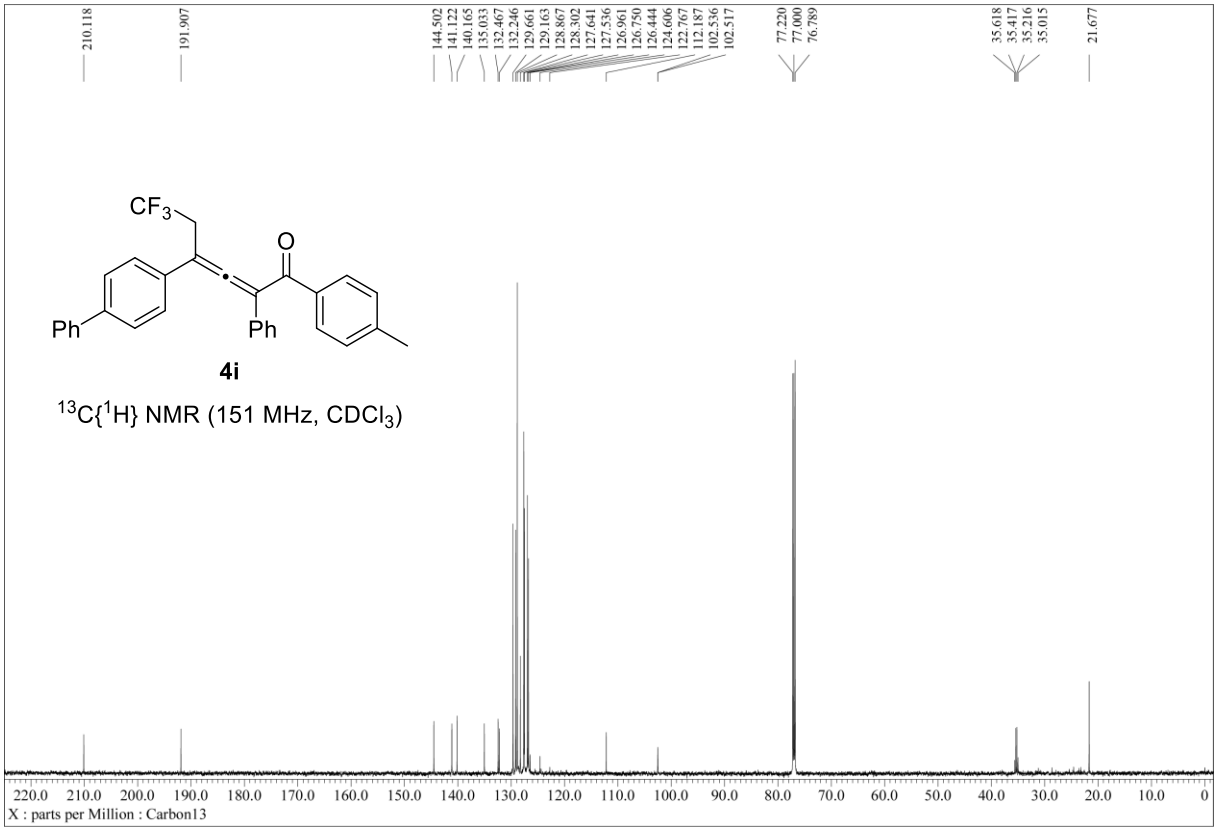
4h

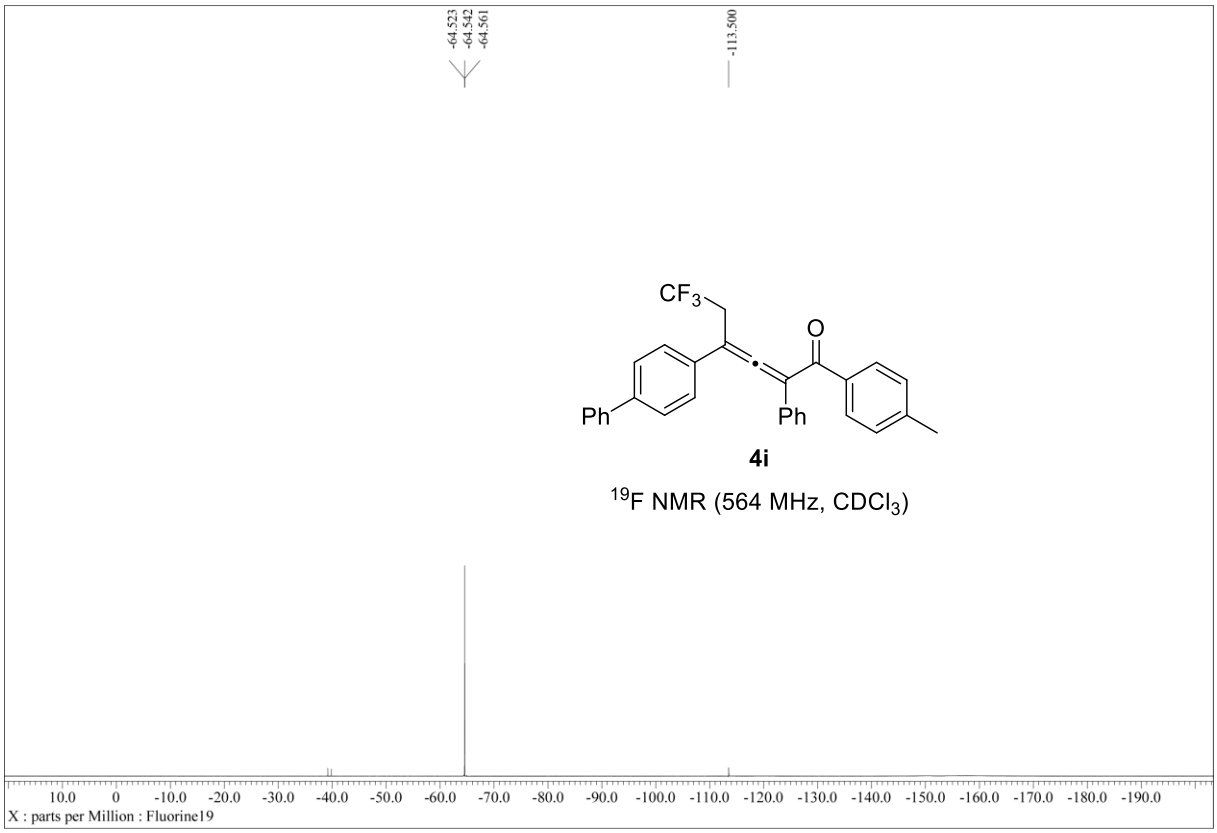
^{1}H NMR (600 MHz, $CDCl_3$)


212.588
191.562
141.572
140.758
139.954
134.650
134.429
134.219
133.999
131.873
131.557
129.374
128.953
128.924
128.656
128.053
127.919
127.794
127.727
126.971
126.722
126.214
125.362
125.333
124.414
124.376
122.605
122.538
120.795
112.340
103.216
77.211
77.000
76.789
35.570
35.369
35.168
34.967
CF3
O
Ph
Ph
CF3
4h
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-63.529
-64.530
-64.550
-64.565
-113.500
CF3
O
Ph
Ph
CF3
4h
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

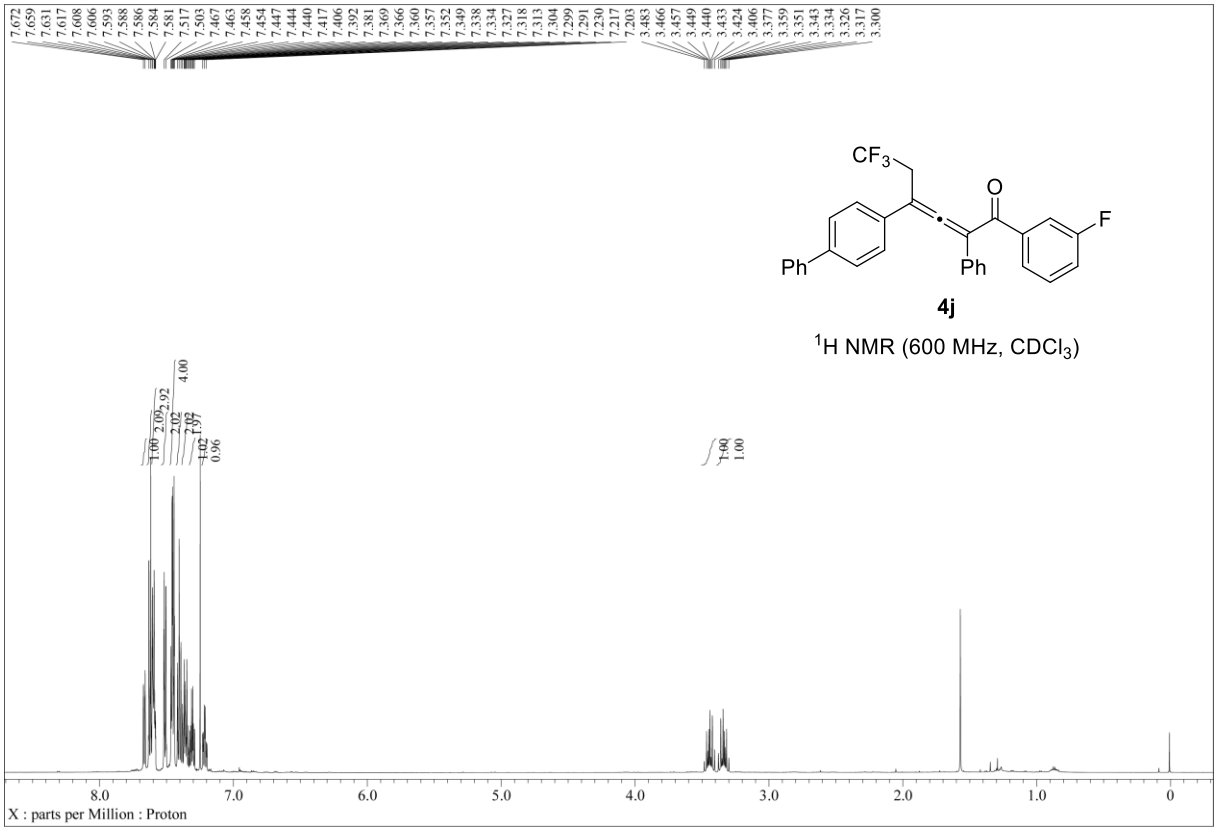

7.872
7.858
7.626
7.612
7.600
7.510
7.508
7.496
7.493
7.478
7.471
7.458
7.446
7.400
7.387
7.375
7.371
7.360
7.339
7.327
7.314
7.188
7.174
3.492
3.475
3.466
3.458
3.450
3.442
3.433
3.415
3.390
3.373
3.365
3.356
3.348
3.339
3.331
3.313
2.383
CF3
O
Ph
Ph
4i
1H NMR (600 MHz, CDCl3)
6.04
3.99
3.03
1.98
1.94
0.99
3.01
1.00
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


210.118
191.907
144.502
141.122
140.165
135.033
132.467
132.246
129.661
129.163
128.867
128.302
127.641
127.536
126.961
126.750
126.444
124.606
122.767
112.187
102.536
102.517
77.220
77.000
76.789
35.618
35.417
35.216
35.015
21.677
CF3
O
Ph
Ph
4i
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



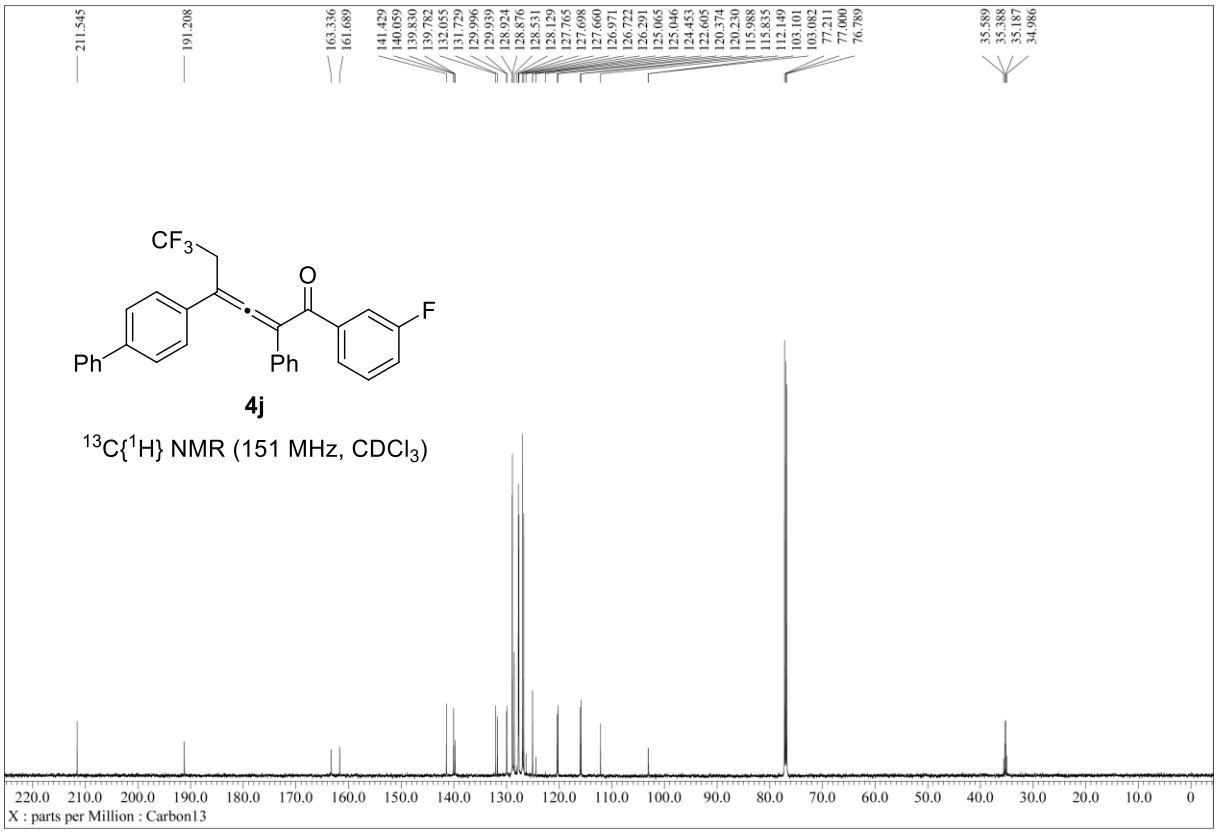
4i

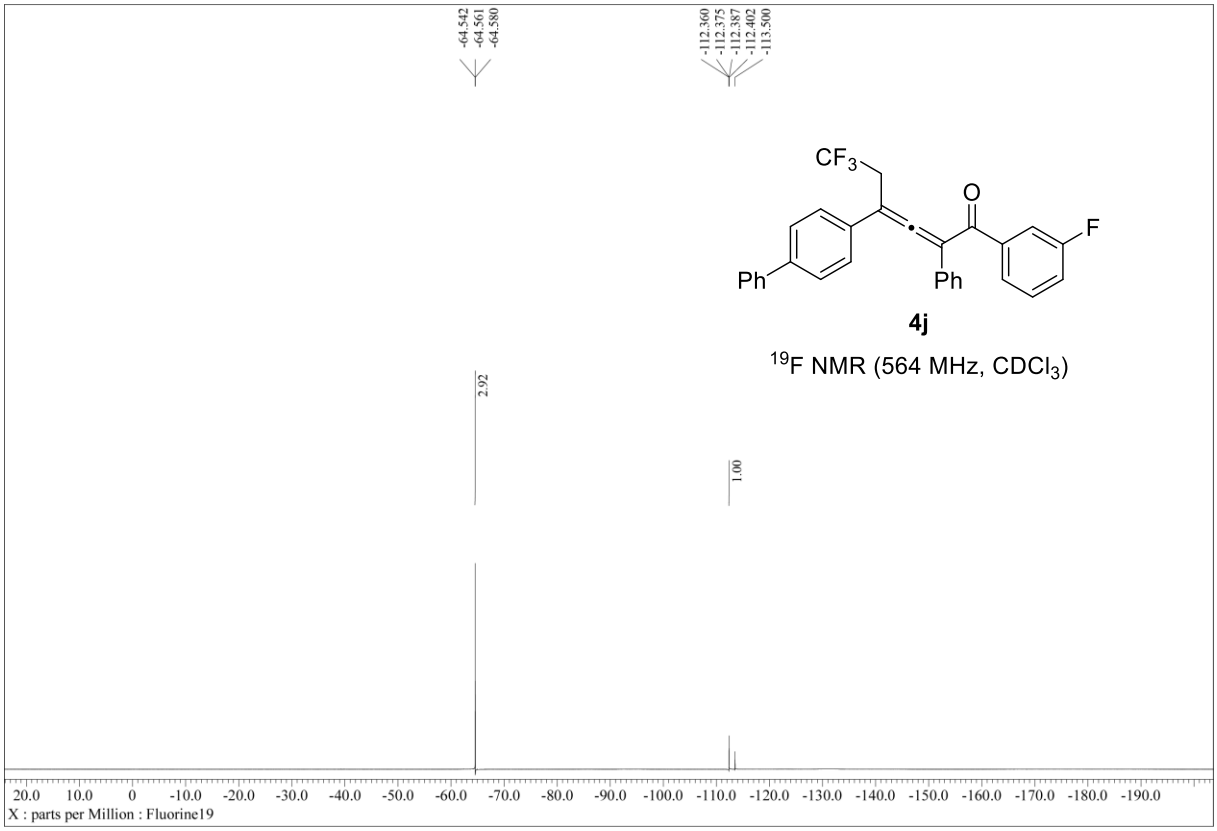
^{19}F NMR (564 MHz, $CDCl_3$)

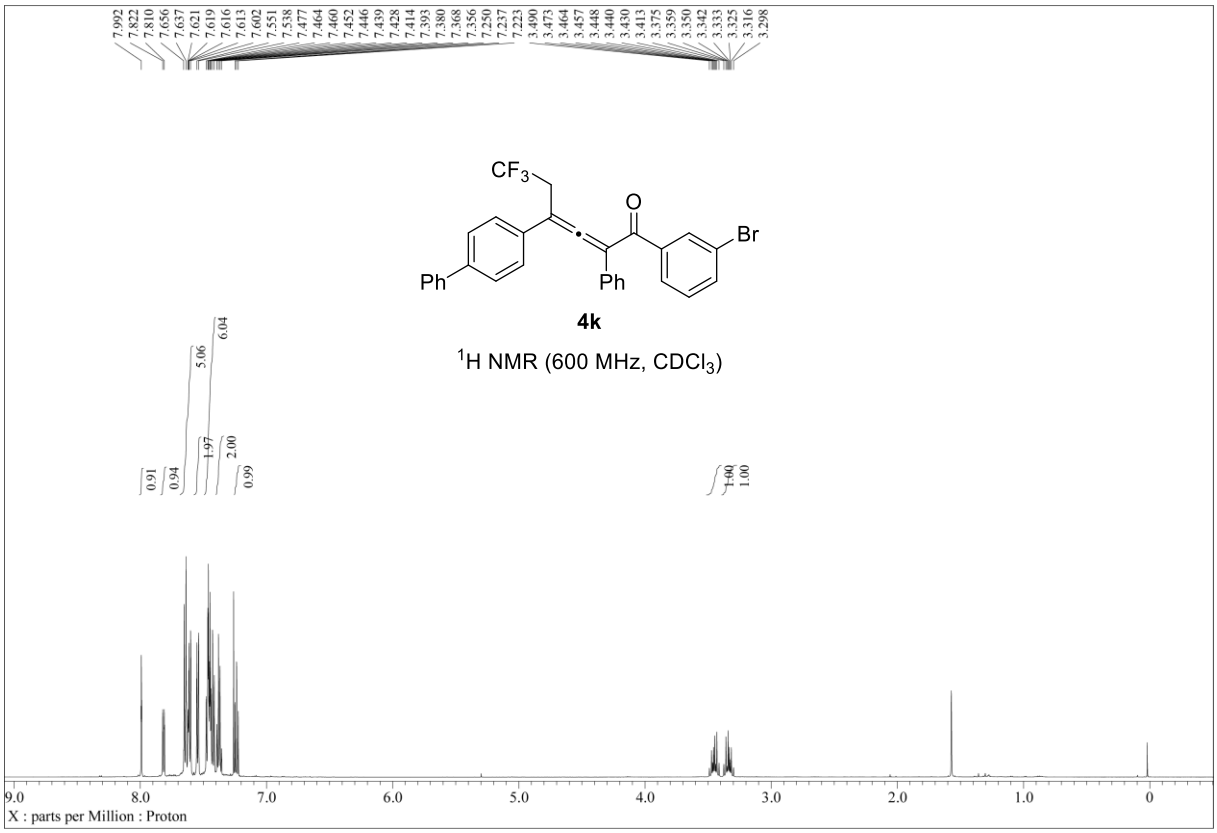


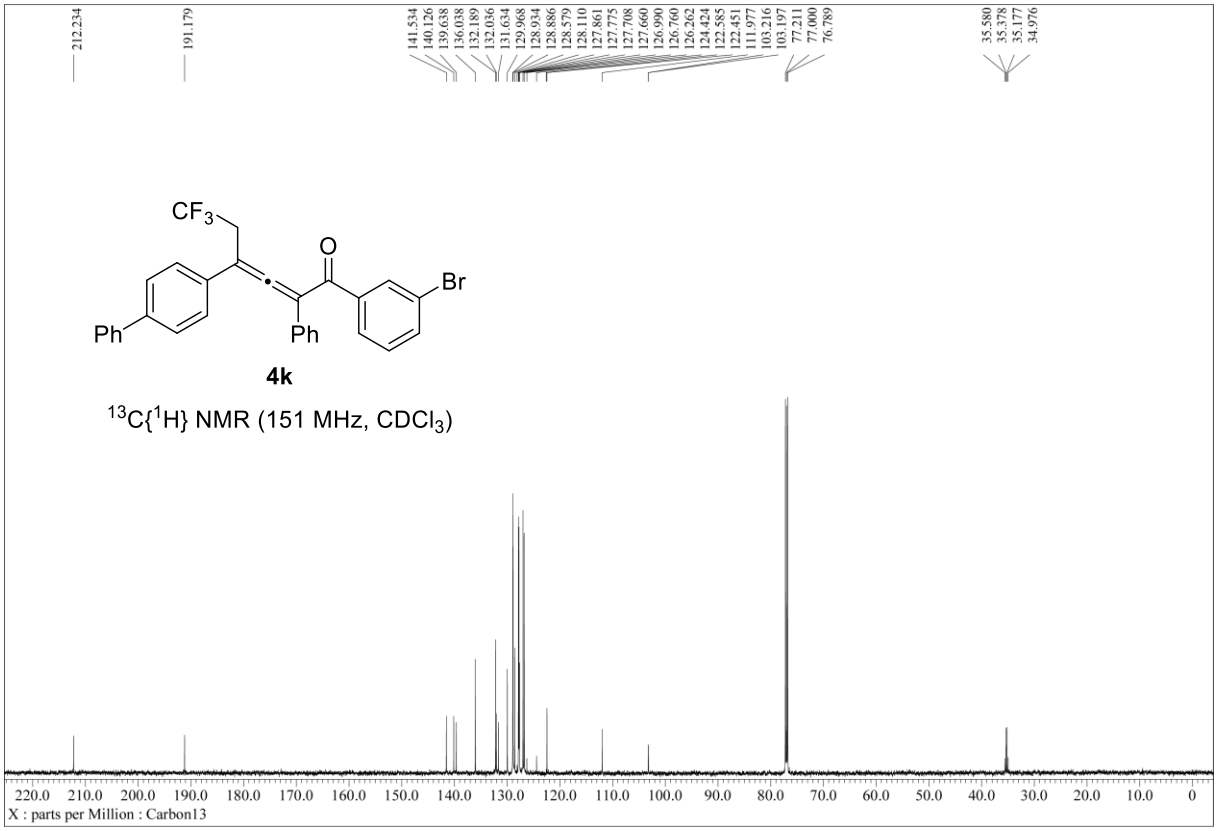
4j

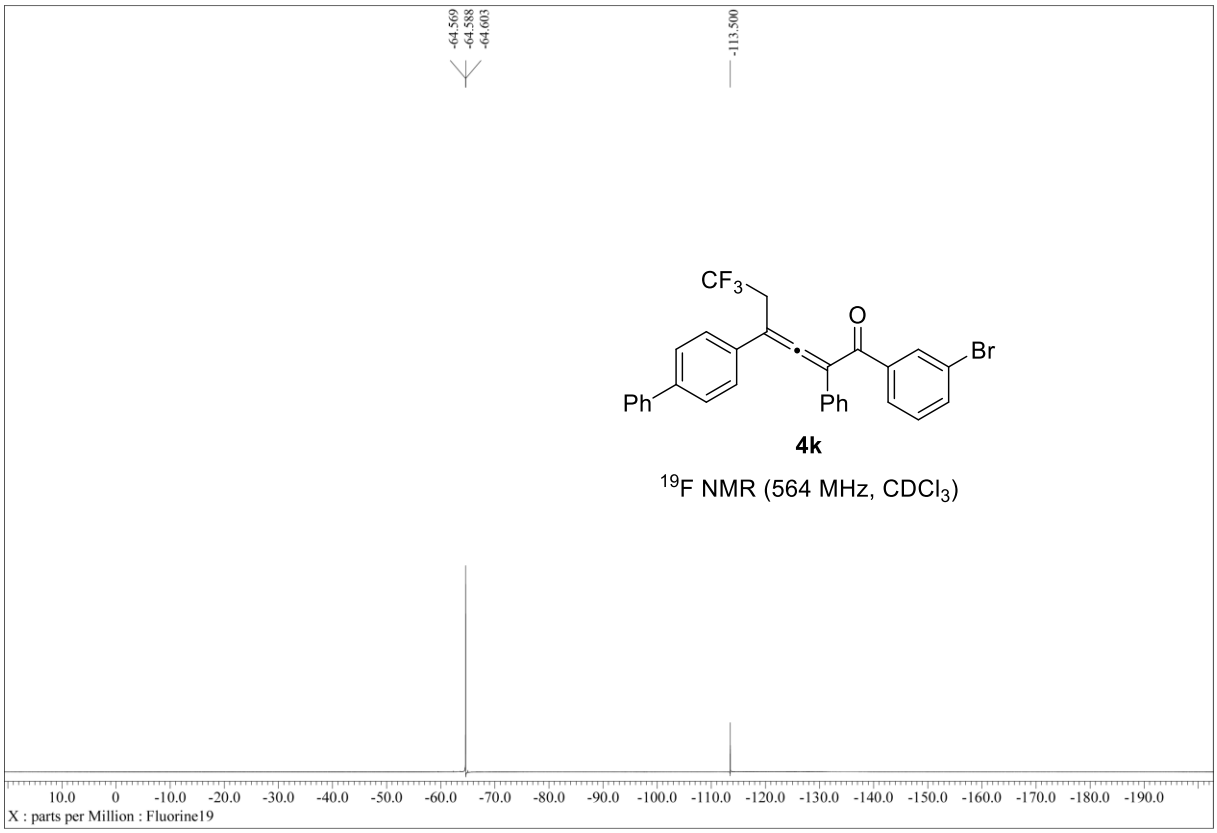
^{1}H NMR (600 MHz, $CDCl_3$)


211.545
191.208
163.336
161.689
141.429
140.059
139.830
139.782
132.055
131.729
129.996
129.939
128.924
128.876
128.531
128.129
127.765
127.698
127.660
126.971
126.722
126.291
125.065
125.046
124.453
122.605
120.374
120.230
115.988
115.835
112.149
103.101
103.082
77.211
77.000
76.789
35.589
35.388
35.187
34.986
CF3
O
F
Ph
Ph
4j
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.542
-64.561
-64.580
-112.360
-112.375
-112.387
-112.402
-113.500
CF3
O
F
Ph
Ph
4j
19F NMR (564 MHz, CDCl3)
2.92
1.00
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

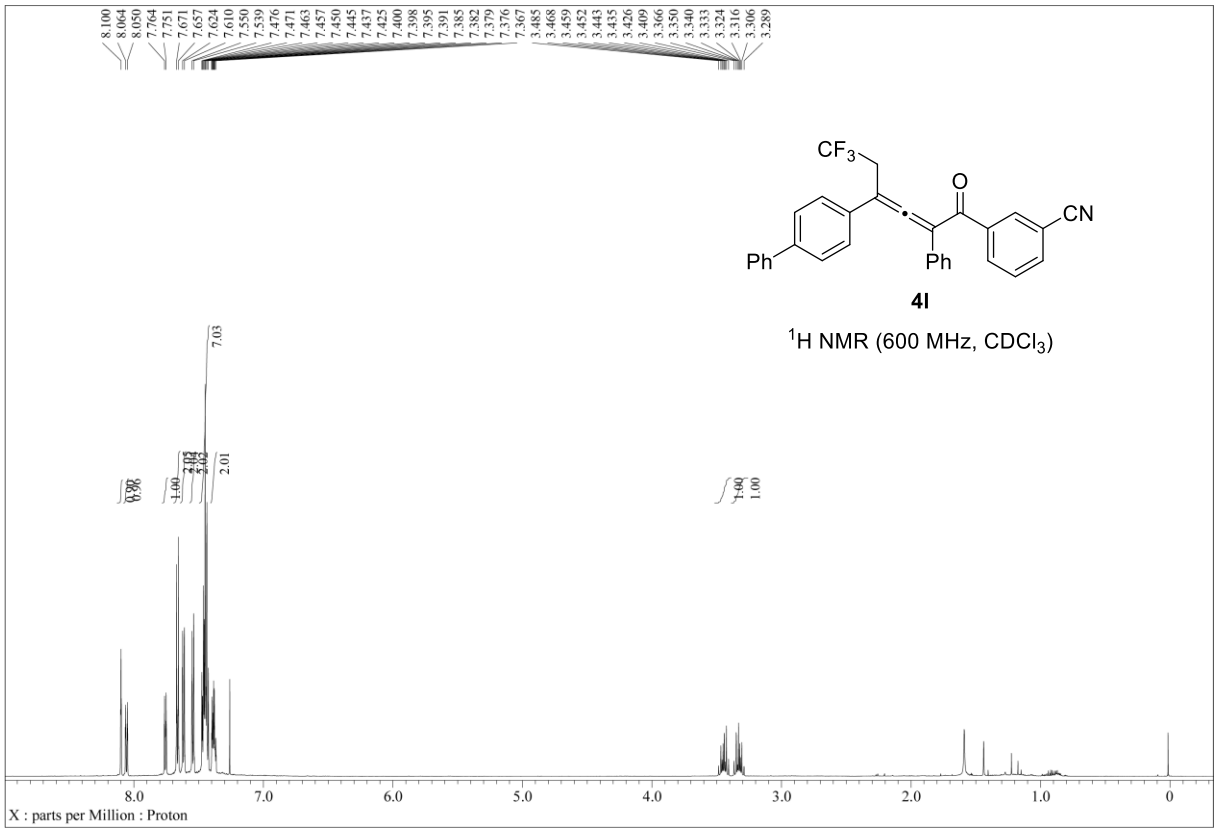

7.992
7.822
7.810
7.656
7.637
7.621
7.619
7.616
7.613
7.602
7.551
7.538
7.477
7.464
7.460
7.452
7.446
7.439
7.428
7.414
7.393
7.380
7.368
7.356
7.250
7.237
7.223
3.490
3.473
3.464
3.457
3.448
3.440
3.430
3.413
3.375
3.359
3.350
3.342
3.333
3.325
3.316
3.298
CF3
O
Br
Ph
Ph
4k
1H NMR (600 MHz, CDCl3)
6.04
5.06
1.97
2.00
0.91
0.94
0.99
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


212.234
191.179
141.534
140.126
139.638
136.038
132.189
132.036
131.634
129.968
128.934
128.886
128.579
128.110
127.861
127.775
127.708
127.660
126.990
126.760
126.262
124.424
122.585
122.451
111.977
103.216
103.197
77.211
77.000
76.789
35.580
35.378
35.177
34.976
CF3
O
Br
Ph
Ph
4k
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



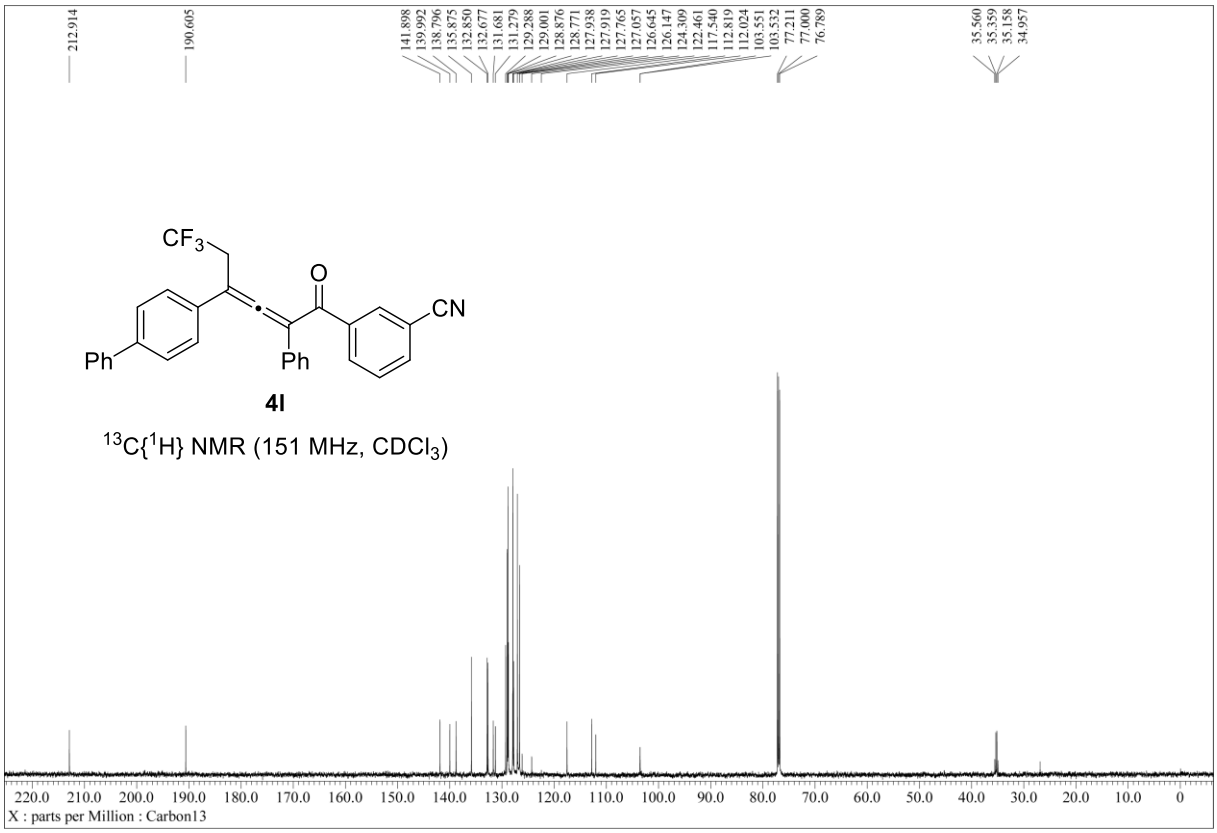
4k

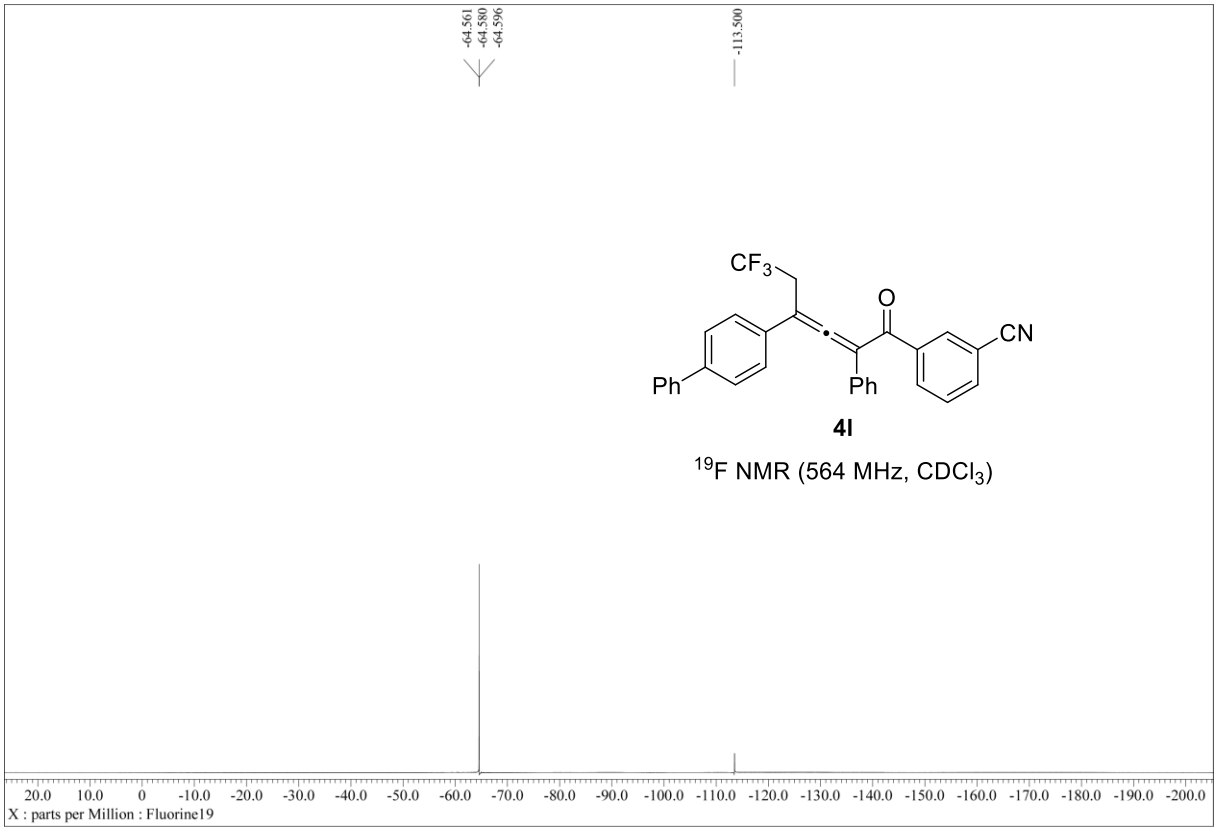
^{19}F NMR (564 MHz, $CDCl_3$)

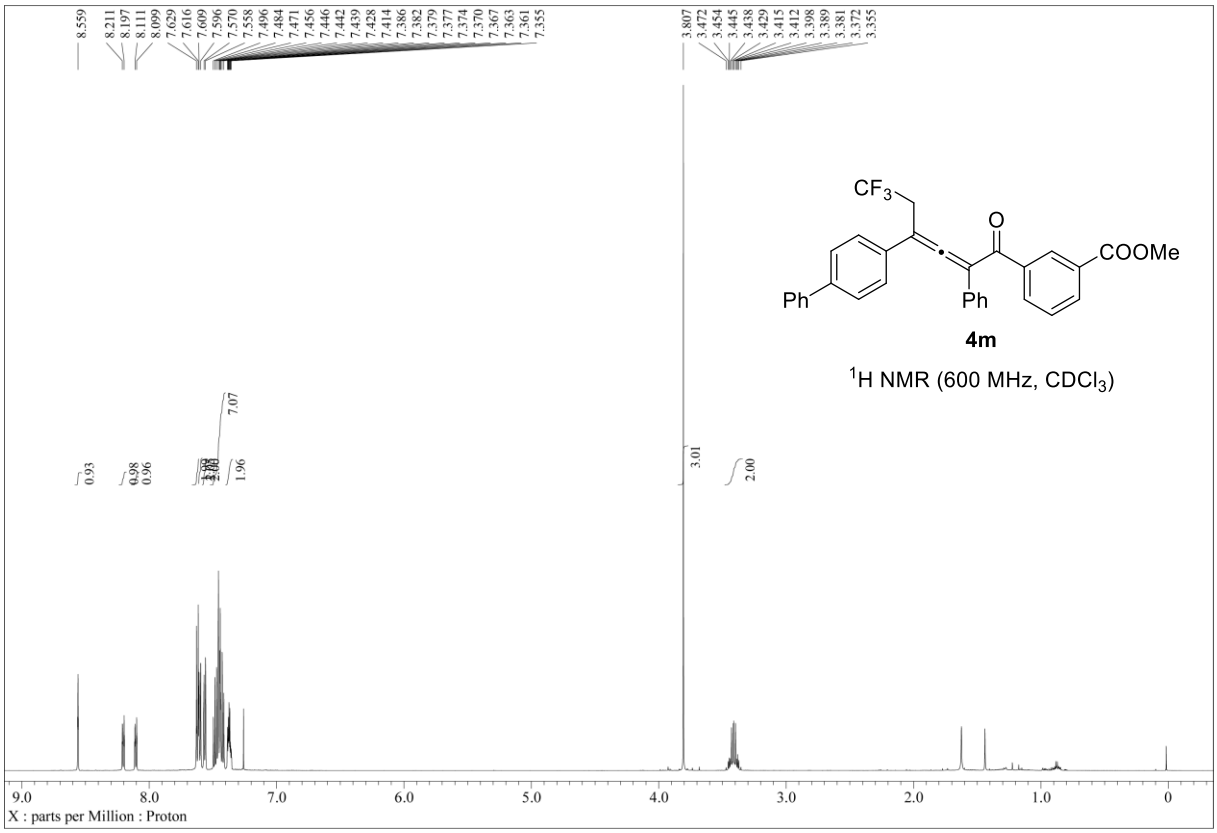


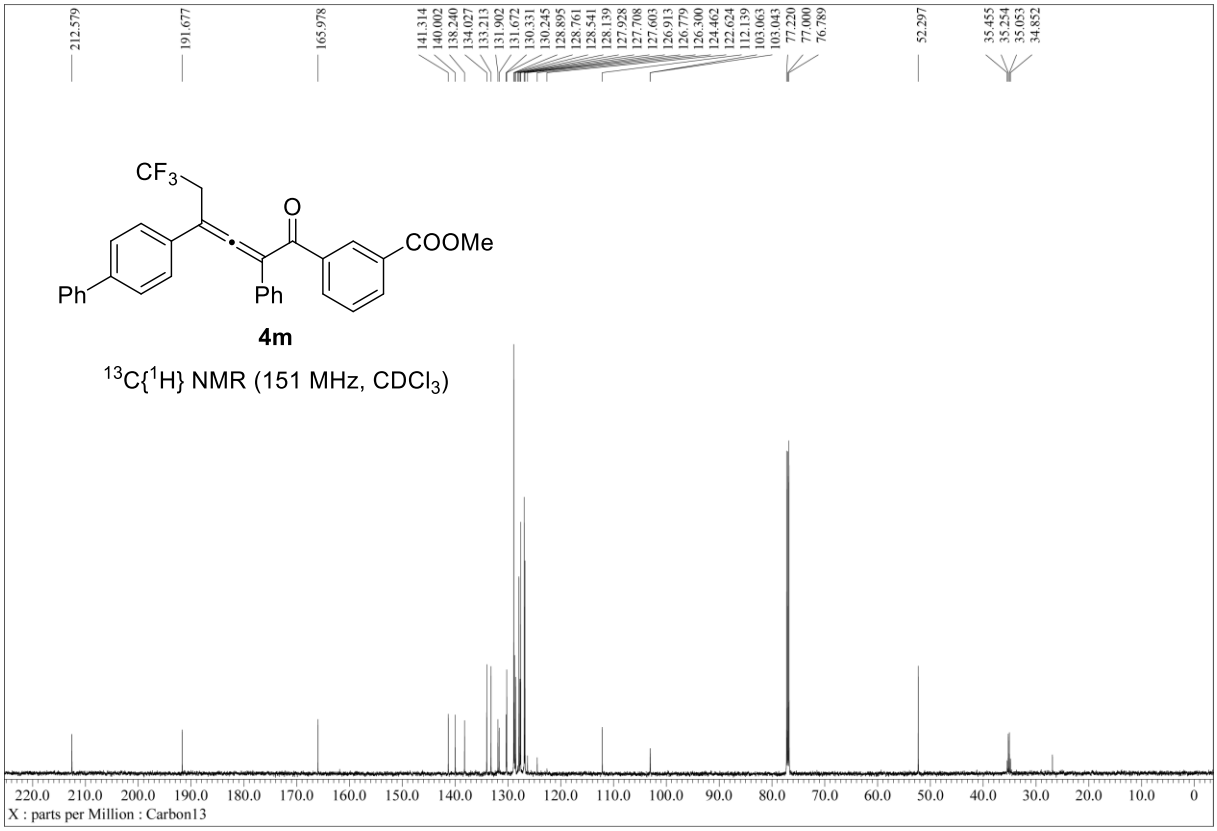
4l

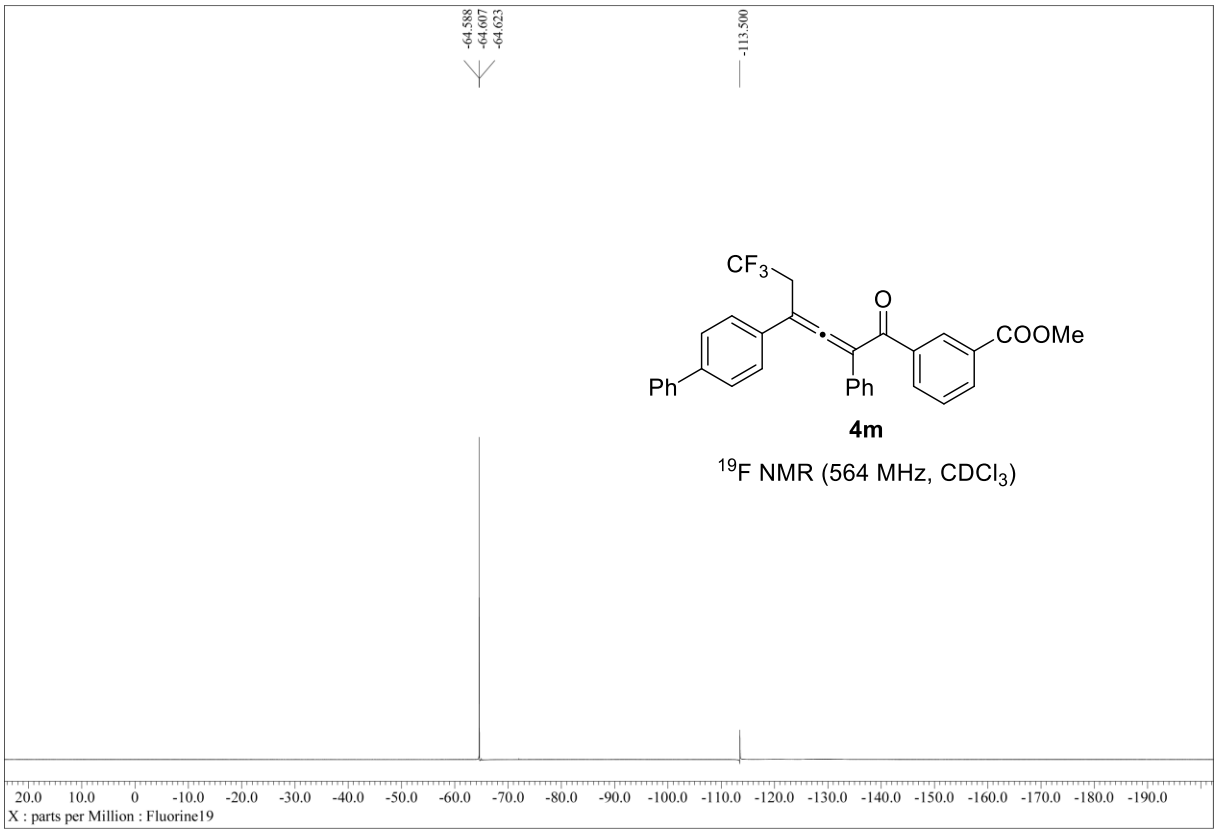
^{1}H NMR (600 MHz, $CDCl_3$)


212.914
190.605
141.898
139.992
138.796
135.875
132.850
132.677
131.681
131.279
129.288
129.001
128.876
128.771
127.938
127.919
127.765
127.057
126.645
126.147
124.309
122.461
117.540
112.819
112.024
103.551
103.532
77.211
77.000
76.789
35.560
35.359
35.158
34.957
CF3
O
CN
Ph
Ph
4l
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.561
-64.580
-64.596
-113.500
CF3
O
CN
Ph
Ph
4l
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
X : parts per Million : Fluorine19

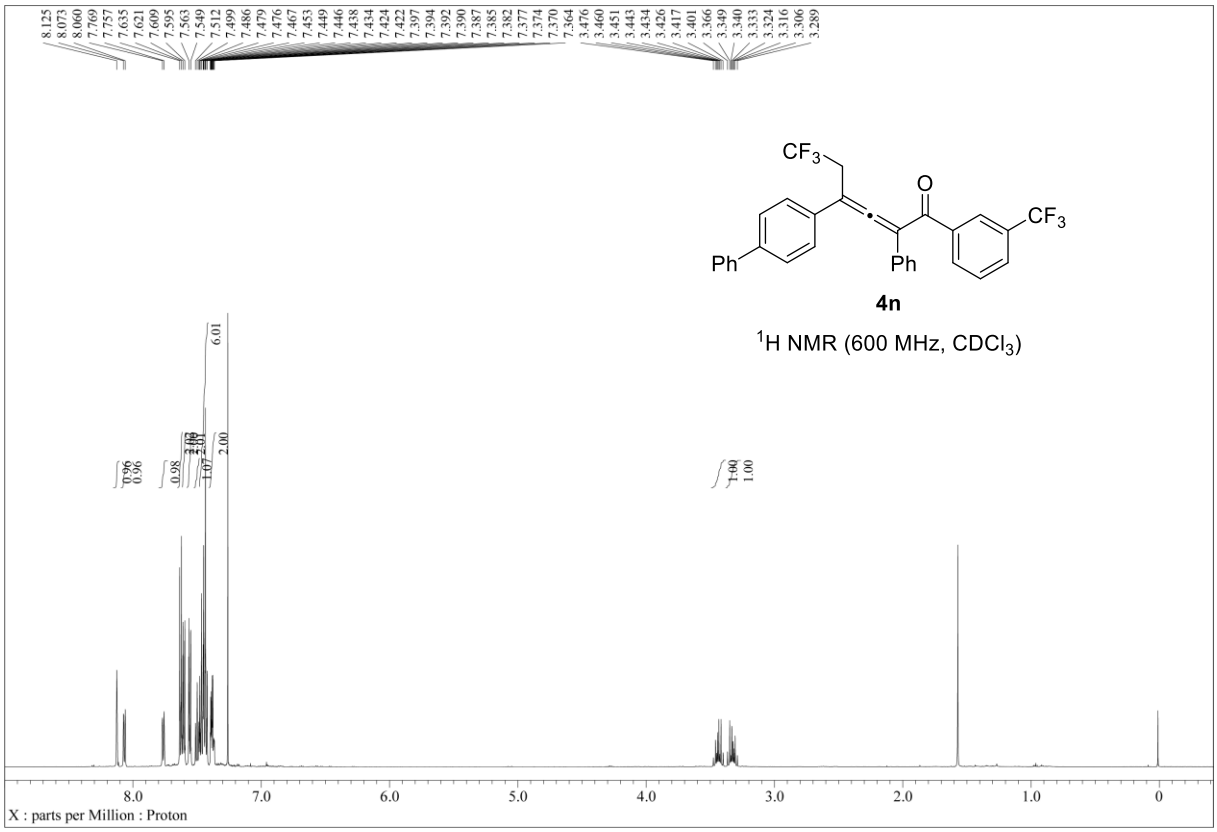

8.559
8.211
8.197
8.111
8.099
7.629
7.616
7.609
7.596
7.570
7.558
7.496
7.484
7.471
7.456
7.446
7.442
7.439
7.428
7.414
7.386
7.382
7.379
7.377
7.374
7.370
7.367
7.363
7.361
7.355
3.807
3.472
3.454
3.445
3.438
3.429
3.415
3.412
3.398
3.389
3.381
3.372
3.355
CF3
O
COOMe
Ph
Ph
4m
1H NMR (600 MHz, CDCl3)
0.93
0.98
0.96
7.07
1.96
3.01
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


212.579
191.677
165.978
141.314
140.002
138.240
134.027
133.213
131.902
131.672
130.331
130.245
128.895
128.761
128.541
128.139
127.928
127.708
127.603
126.913
126.779
126.300
124.462
122.624
112.139
103.063
103.043
77.220
77.000
76.789
52.297
35.455
35.254
35.053
34.852
CF3
O
COOMe
Ph
Ph
4m
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



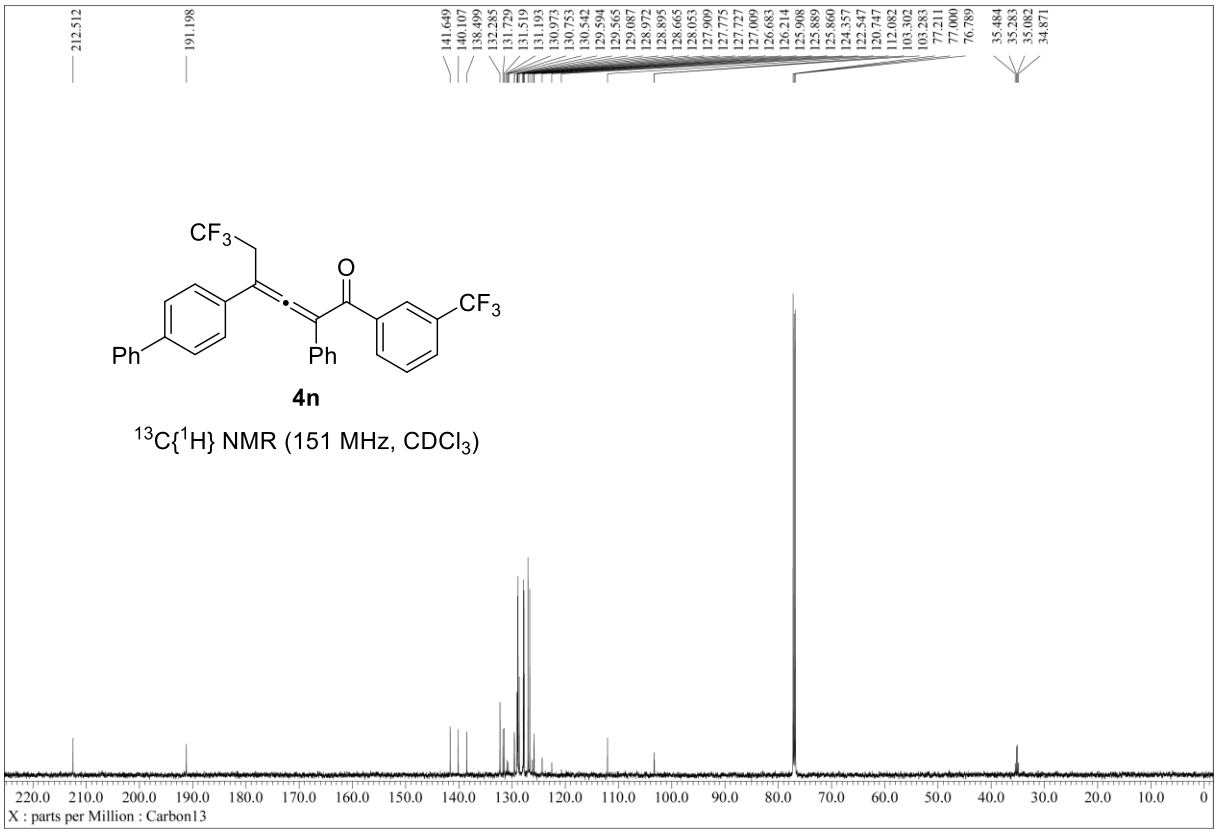
4m

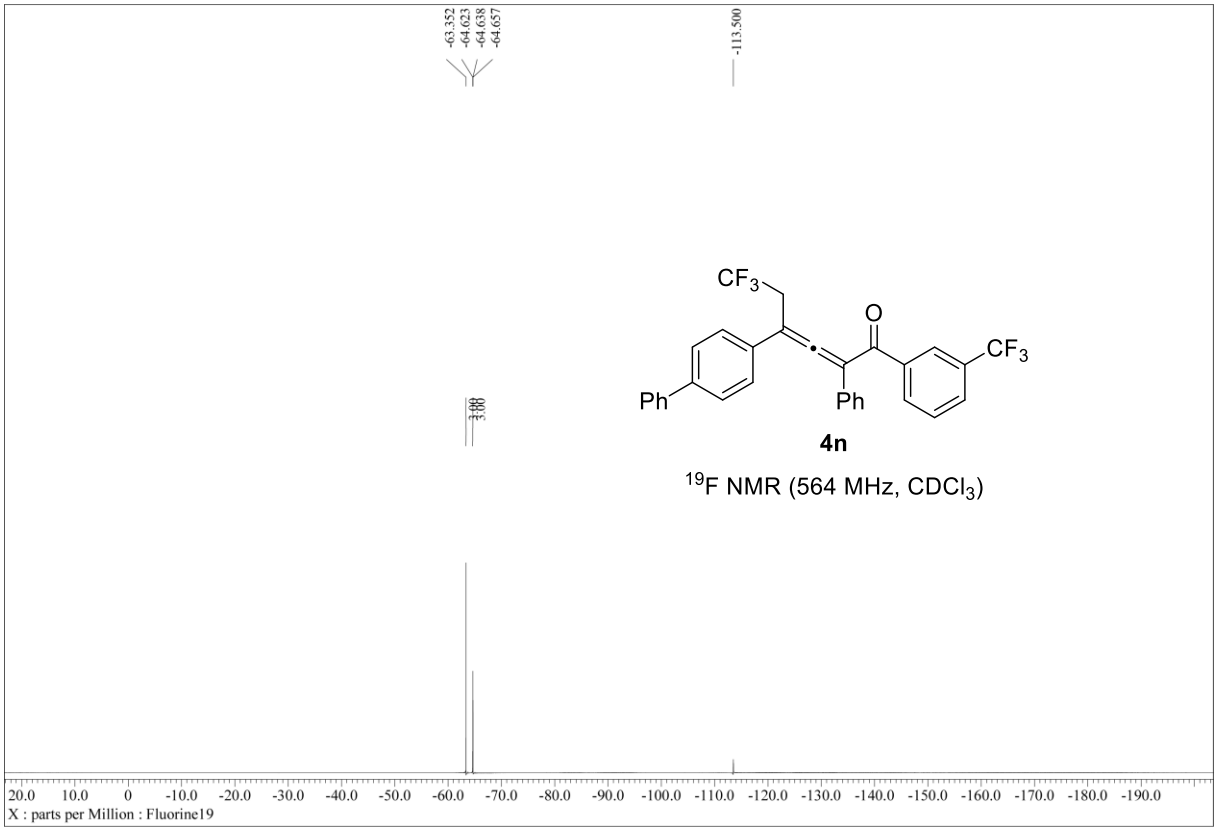
^{19}F NMR (564 MHz, $CDCl_3$)

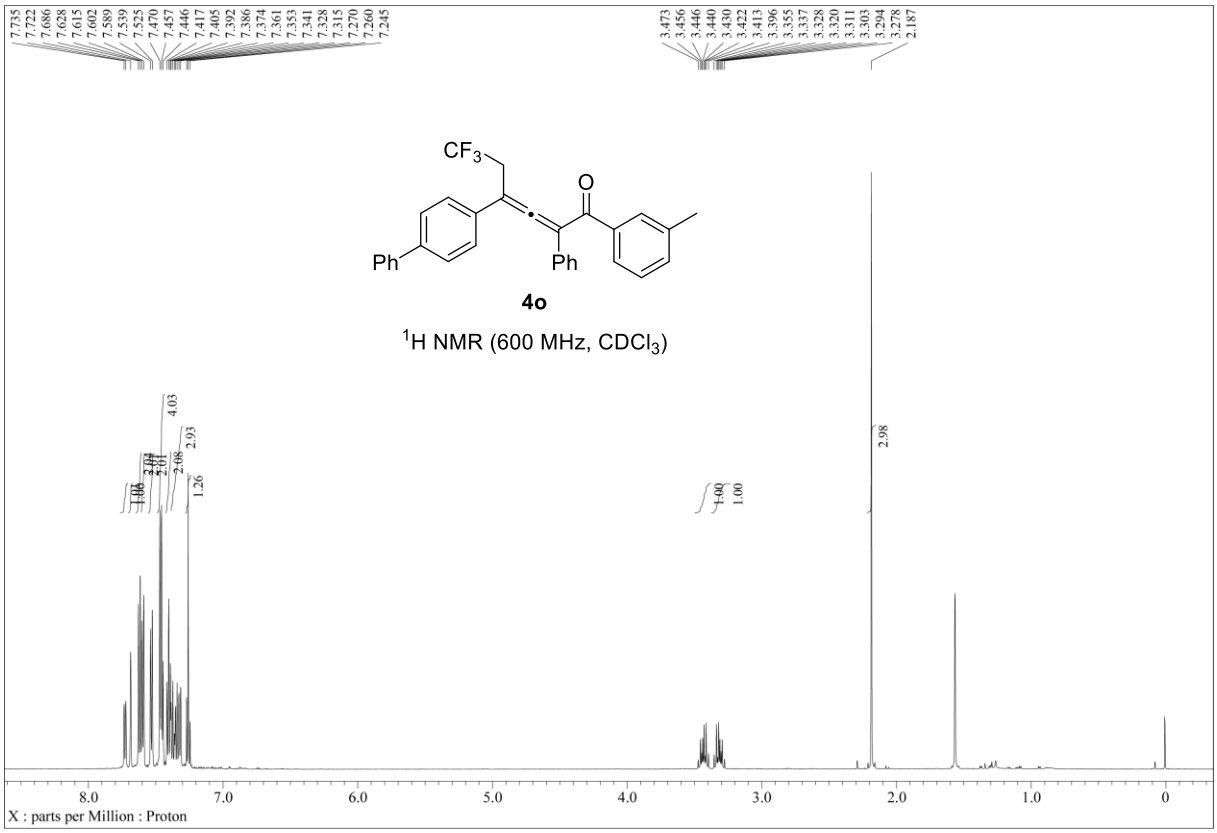


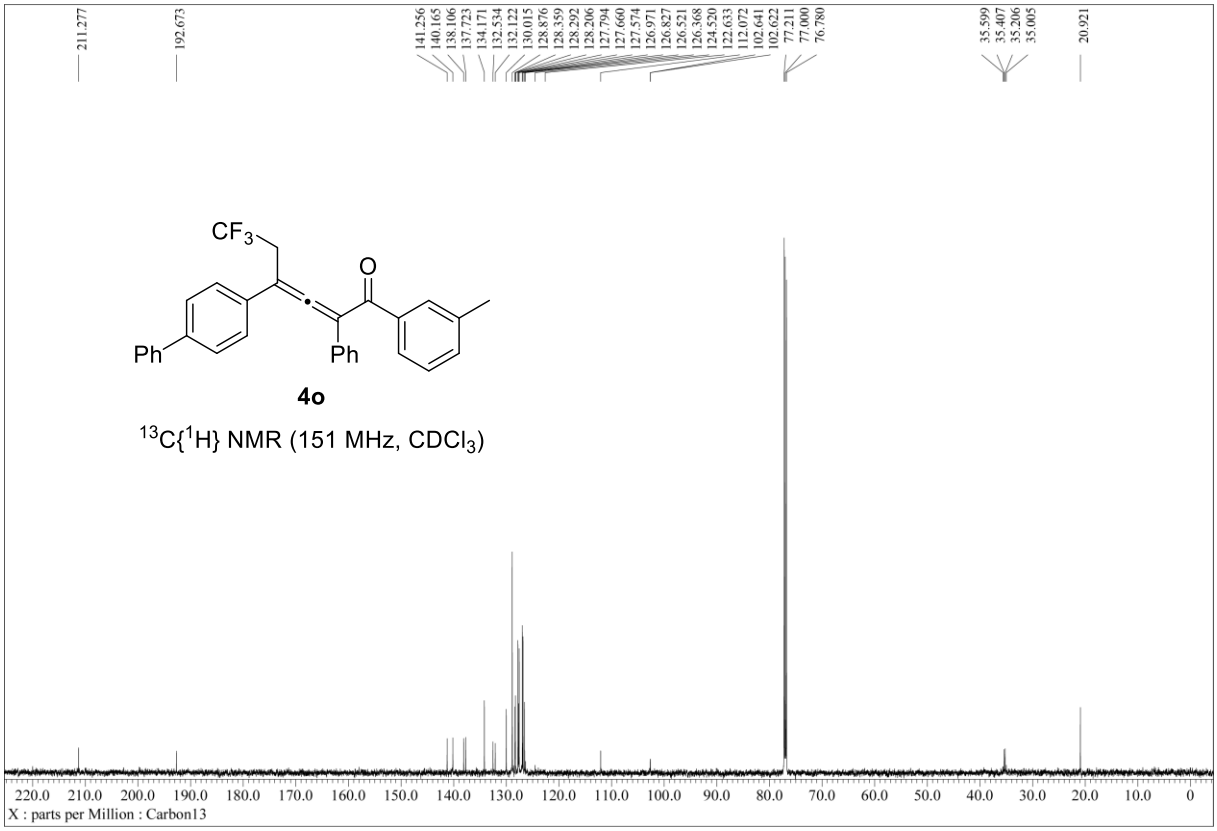
4n

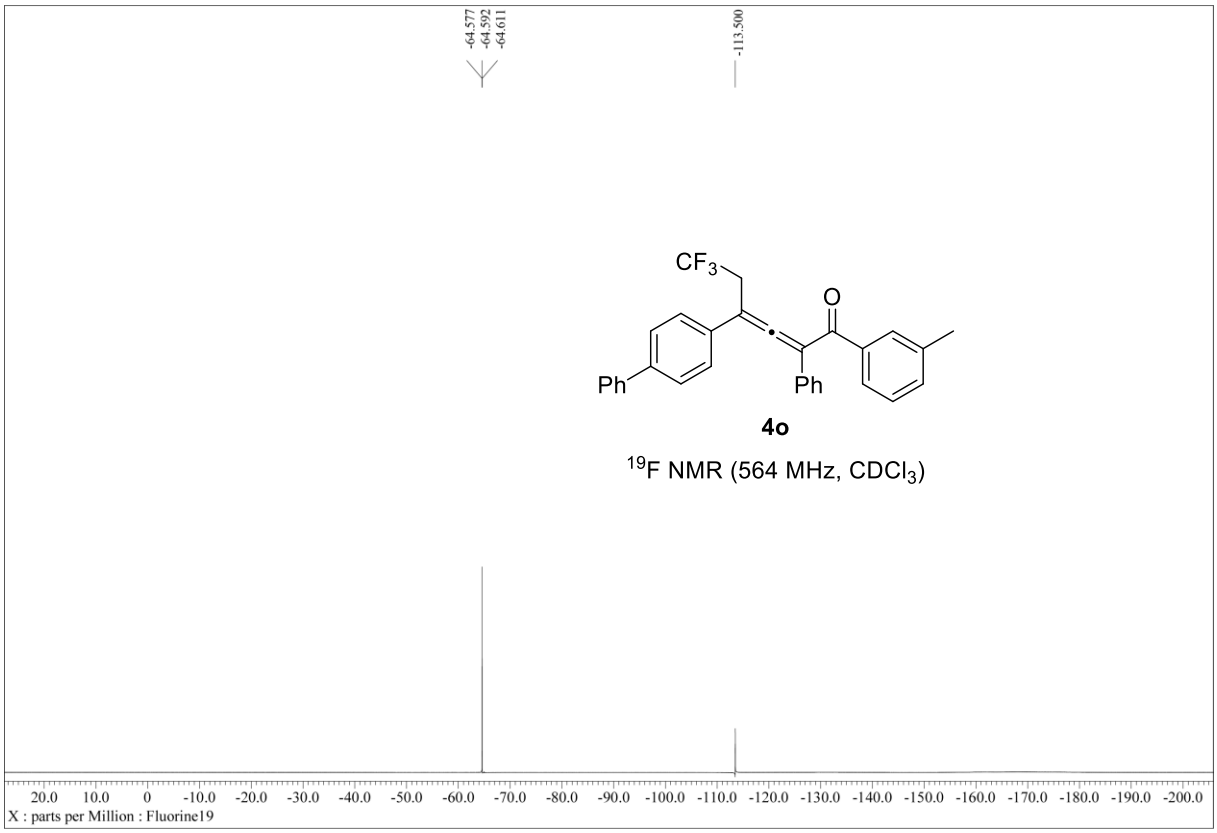
^{1}H NMR (600 MHz, $CDCl_3$)


212.512
191.198
141.649
140.107
138.499
132.285
131.729
131.519
131.193
130.973
130.753
130.542
129.594
129.565
129.087
128.972
128.895
128.665
128.053
127.909
127.775
127.727
127.009
126.683
126.214
125.908
125.889
125.860
124.357
122.547
120.747
112.082
103.302
103.283
77.211
77.000
76.789
35.484
35.283
35.082
34.871
CF3
O
CF3
Ph
Ph
4n
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-63.352
-64.623
-64.638
-64.657
-113.500
3.00
3.00
CF3
O
CF3
Ph
Ph
4n
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

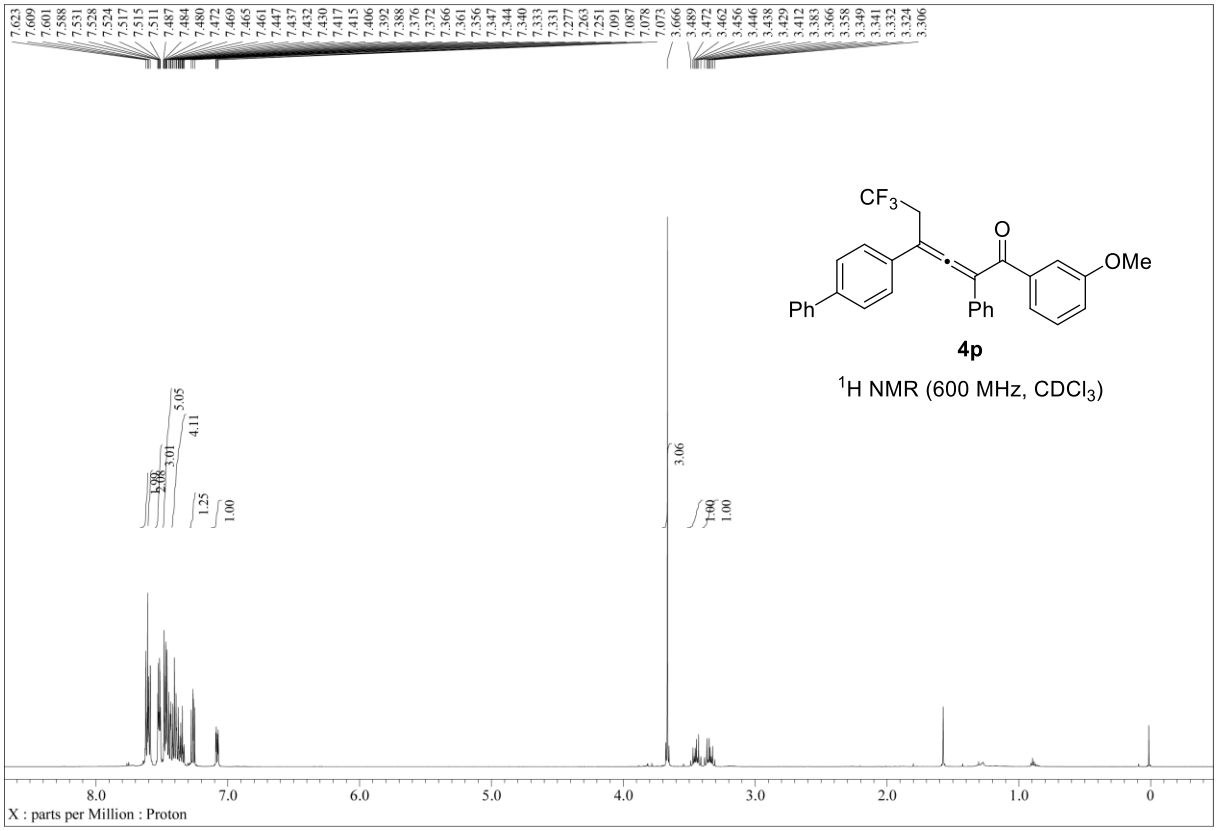

CF3
O
Ph
Ph
4o
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


CF3
O
Ph
Ph
4o
13C{1H} NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



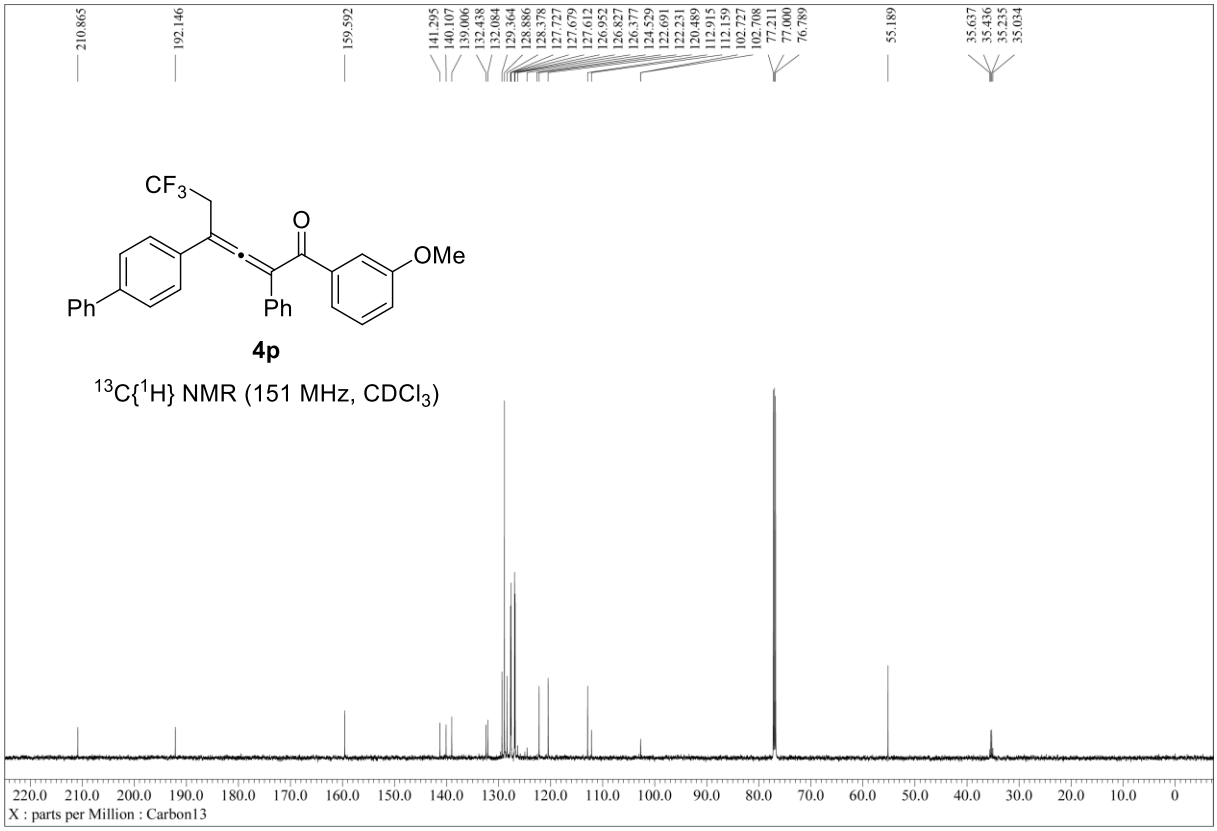
4o

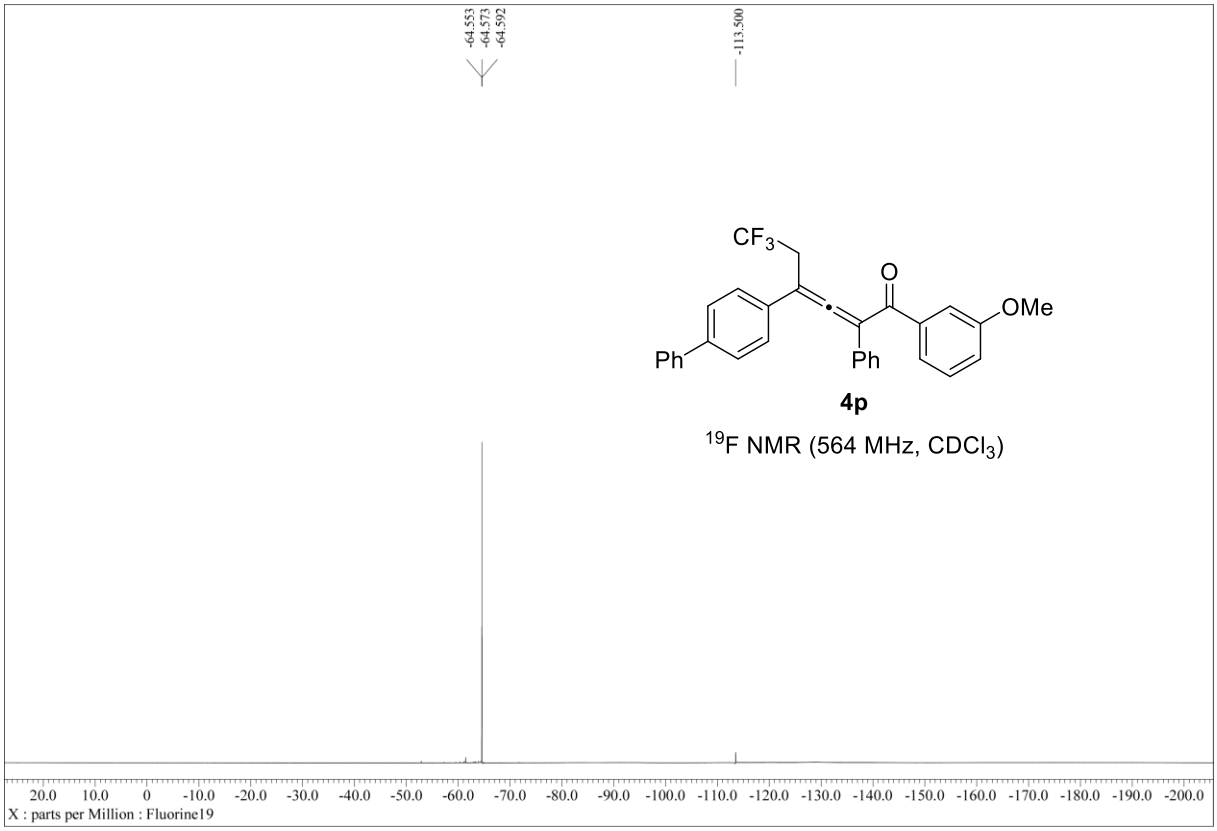
^{19}F NMR (564 MHz, $CDCl_3$)

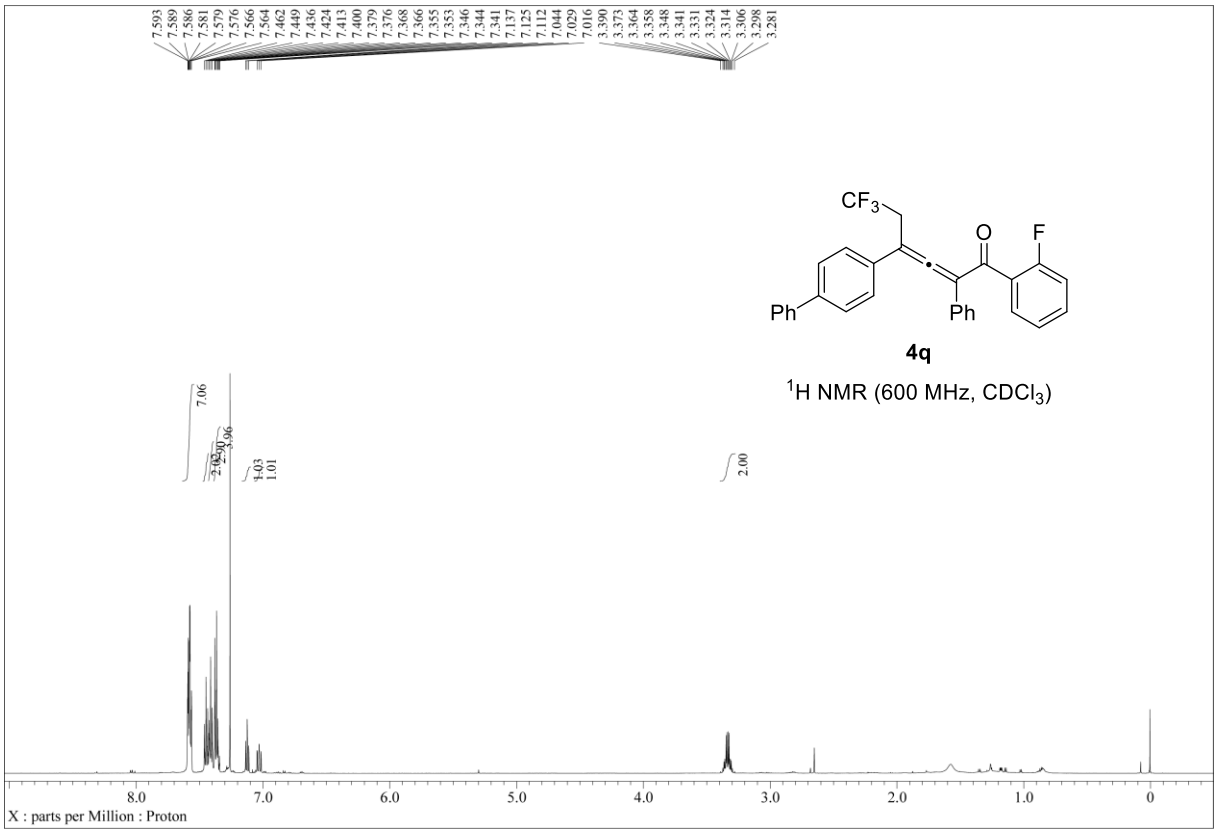


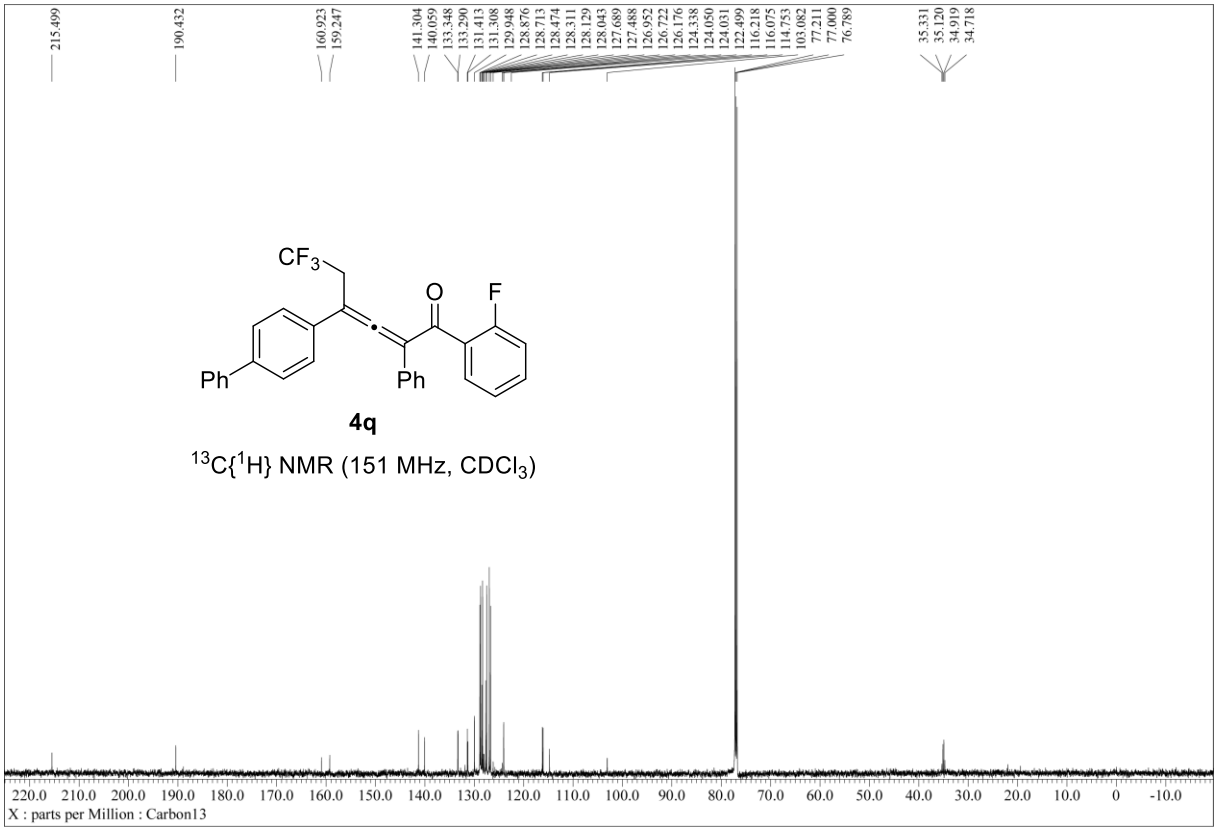
4p

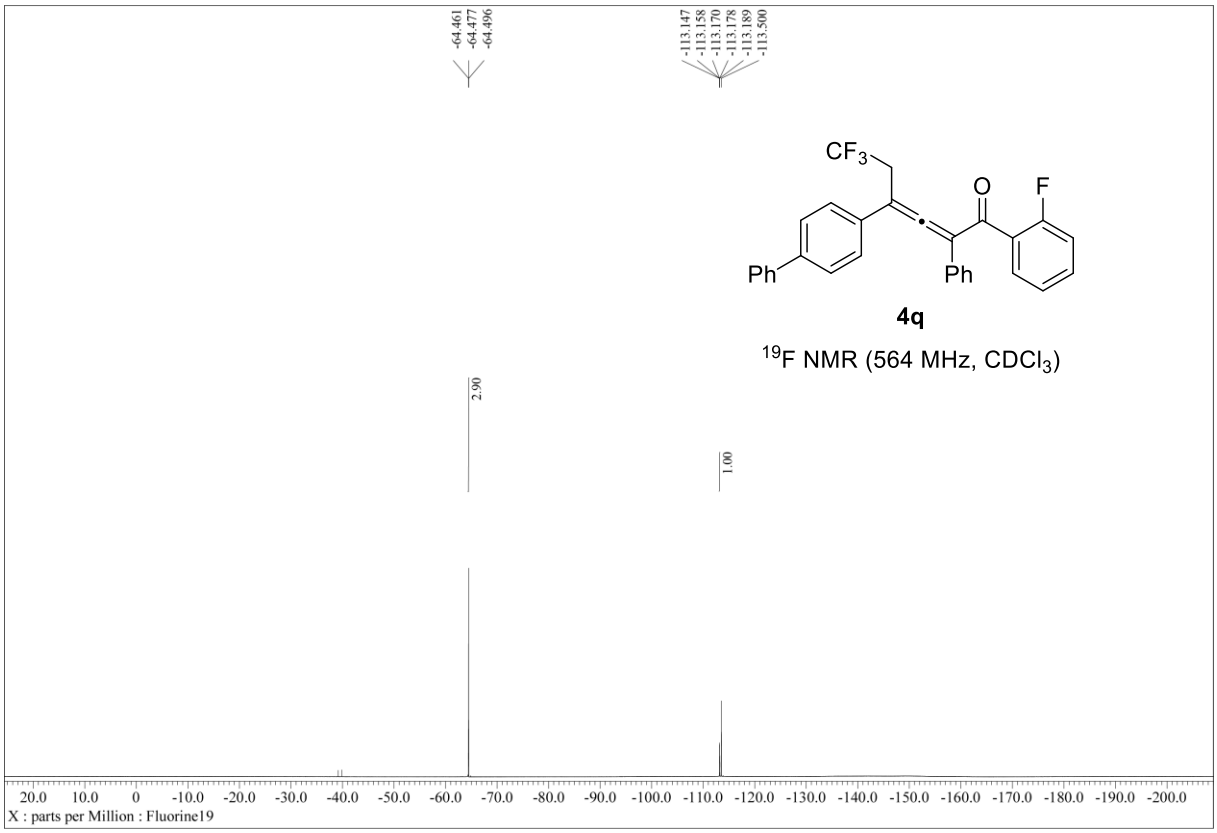
^{1}H NMR (600 MHz, $CDCl_3$)


210.865
192.146
159.592
141.295
140.107
139.006
132.438
132.084
129.364
128.886
128.378
127.727
127.679
127.612
126.952
126.827
126.377
124.529
122.691
122.231
120.489
112.915
112.159
102.727
102.708
77.211
77.000
76.789
55.189
35.637
35.436
35.235
35.034
CF3
O
OMe
Ph
Ph
4p
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.553
-64.573
-64.592
-113.500
CF3
O
OMe
Ph
Ph
4p
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
X : parts per Million : Fluorine19

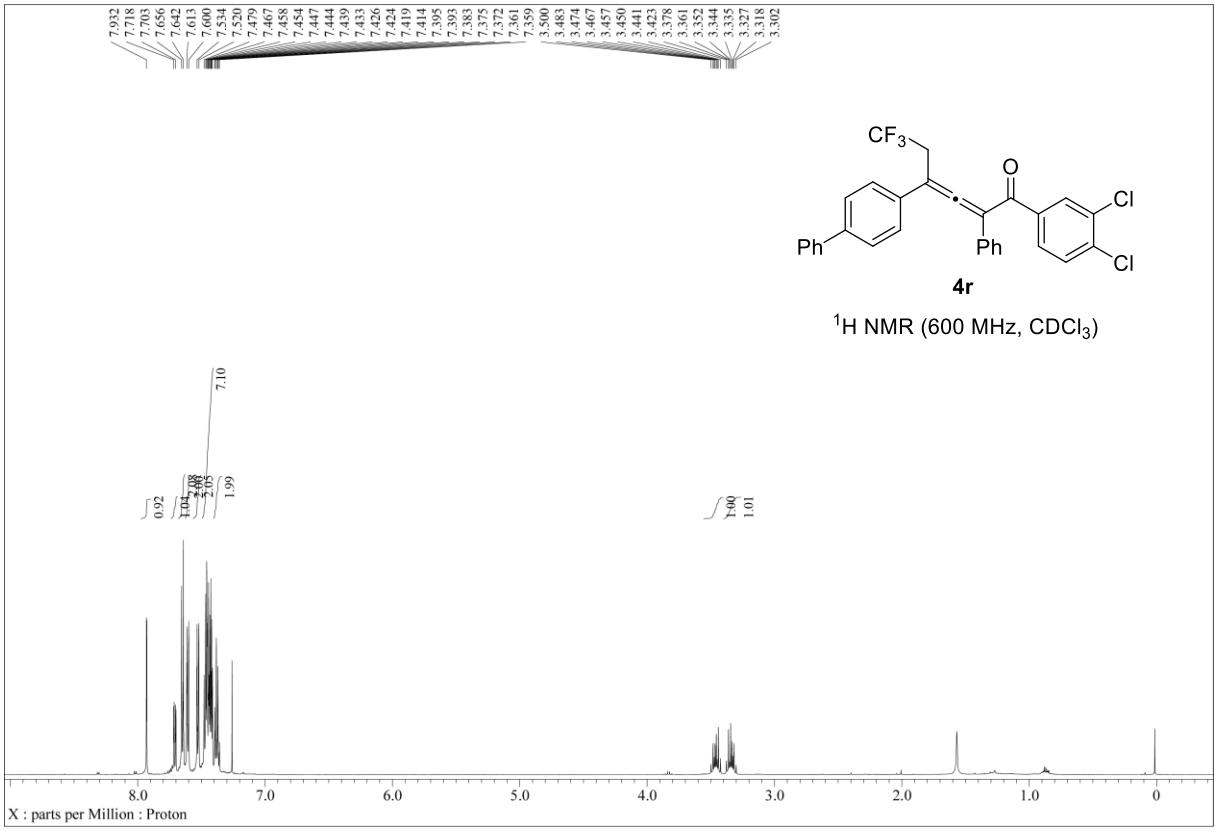

7.593 7.589 7.586 7.581 7.579 7.576 7.566 7.564 7.462 7.449 7.436 7.424 7.413 7.400 7.379 7.376 7.368 7.366 7.355 7.353 7.346 7.344 7.341 7.137 7.125 7.112 7.044 7.029 7.016 3.390 3.373 3.364 3.358 3.348 3.341 3.331 3.324 3.314 3.306 3.298 3.281
CF3
O
F
Ph
Ph
4q
1H NMR (600 MHz, CDCl3)
7.06
2.96
1.03
1.01
2.00
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


215.499
190.432
160.923
159.247
141.304
140.059
133.348
133.290
131.413
131.308
129.948
128.876
128.713
128.474
128.311
128.129
128.043
127.689
127.488
126.952
126.722
126.176
124.338
124.050
124.031
122.499
116.218
116.075
114.753
103.082
77.211
77.000
76.789
35.331
35.120
34.919
34.718
CF3
O
F
Ph
Ph
4q
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : Carbon13



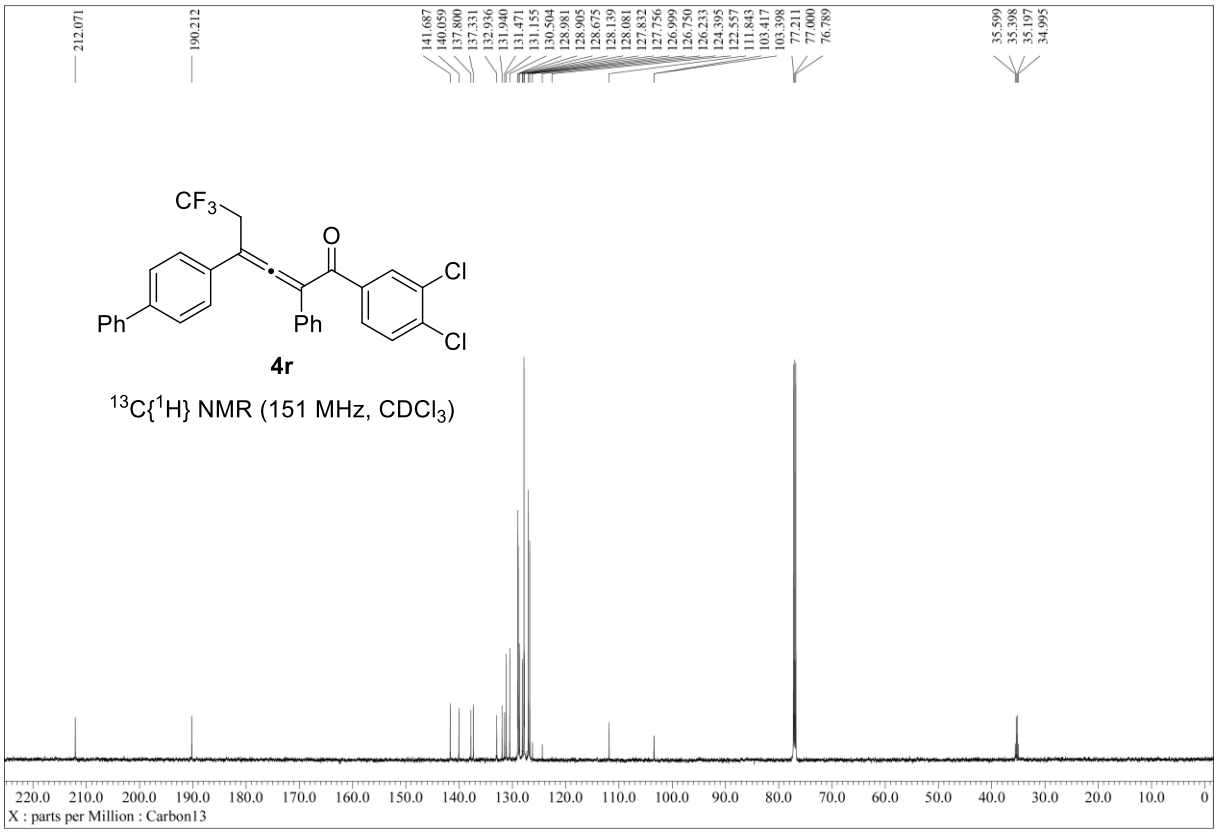
4q

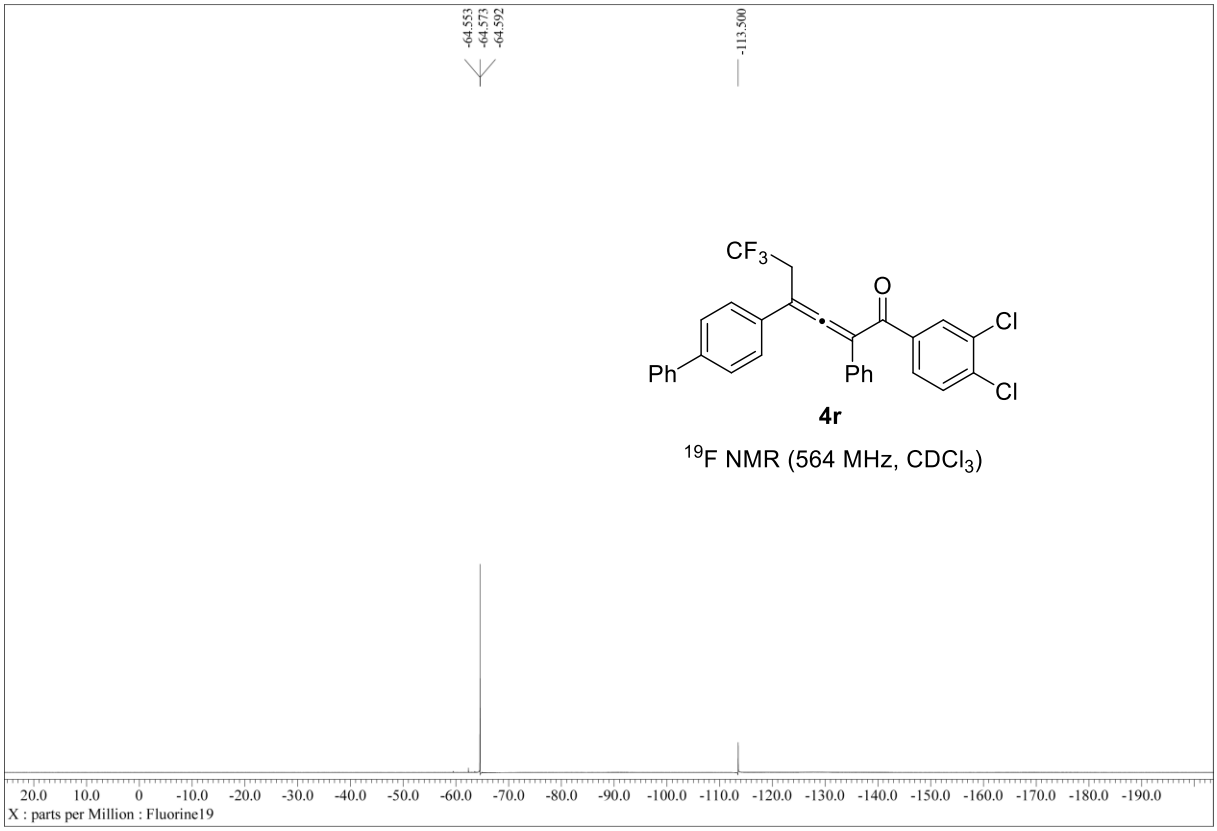
^{19}F NMR (564 MHz, $CDCl_3$)

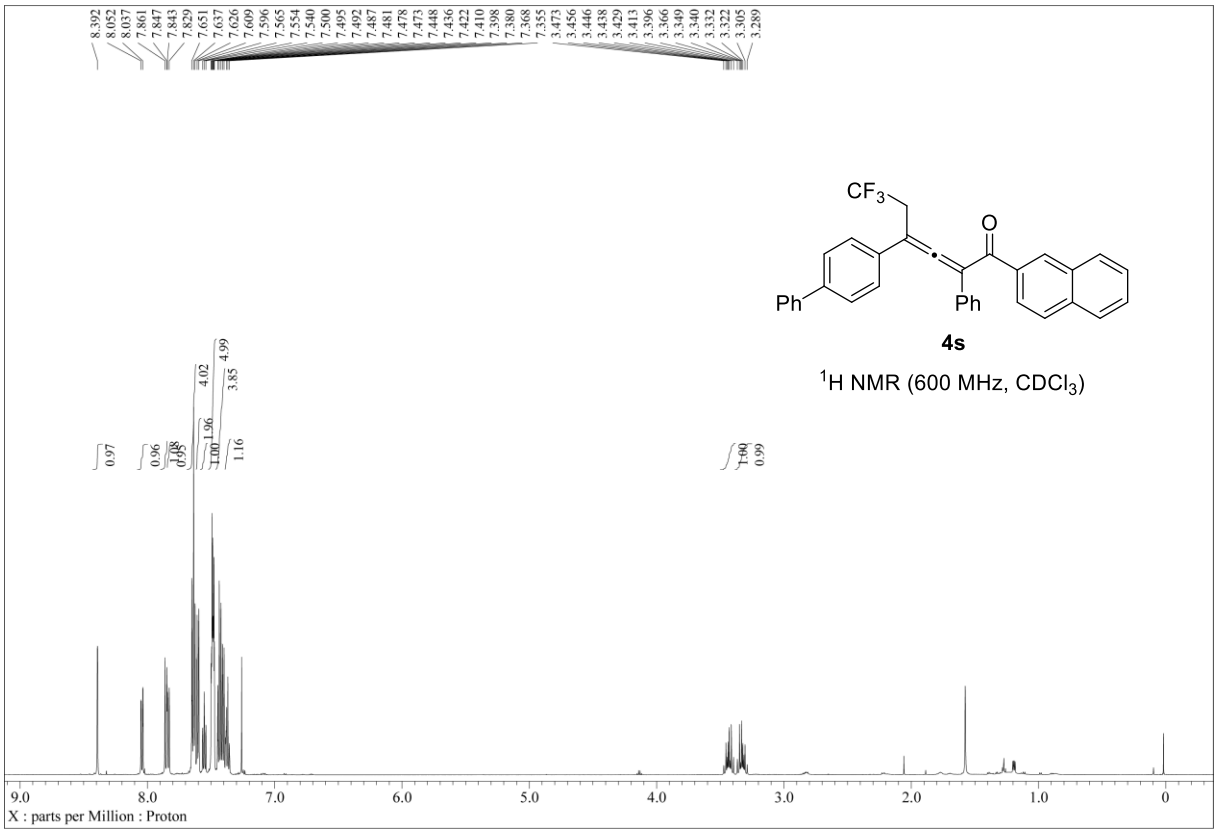


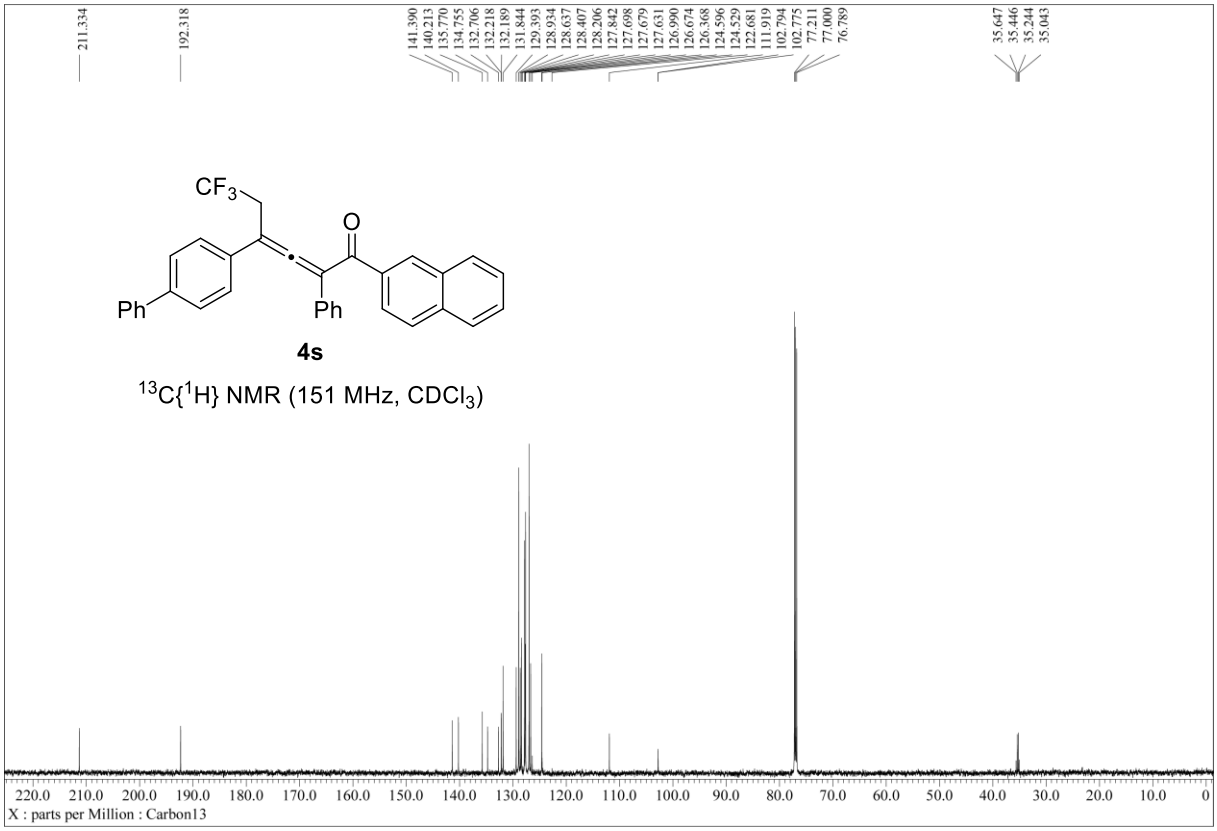
4r

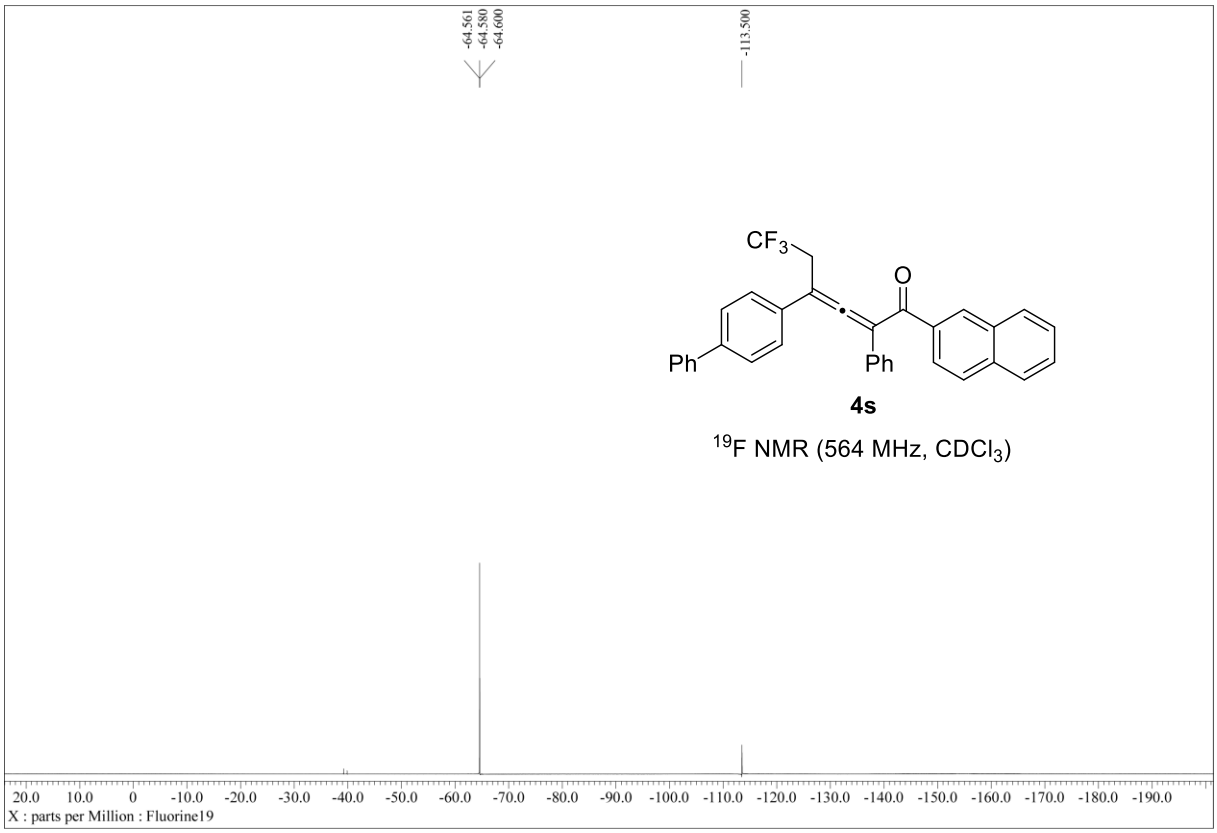
^{1}H NMR (600 MHz, $CDCl_3$)


212.071
190.212
141.687
140.059
137.800
137.331
132.936
131.940
131.471
131.155
130.504
128.981
128.905
128.675
128.139
128.081
127.832
127.756
126.999
126.750
126.233
124.395
122.557
111.843
103.417
103.398
77.211
77.000
76.789
35.599
35.398
35.197
34.995
CF3
O
Cl
Cl
Ph
Ph
4r
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.553
-64.573
-64.592
-113.500
CF3
O
Cl
Cl
Ph
Ph
4r
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

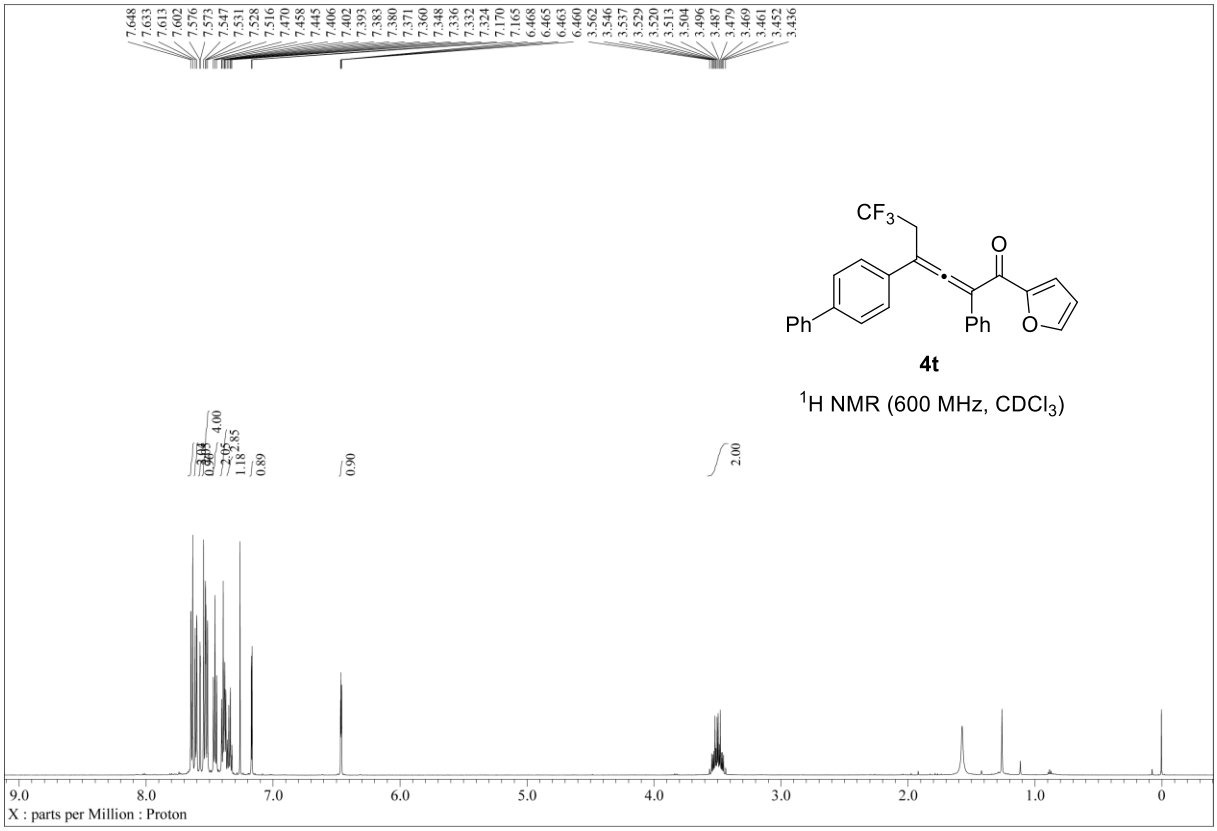

8.392
8.052
8.037
7.861
7.847
7.843
7.829
7.651
7.637
7.626
7.609
7.596
7.565
7.554
7.540
7.500
7.495
7.492
7.487
7.481
7.478
7.473
7.448
7.436
7.422
7.410
7.398
7.380
7.368
7.355
3.473
3.456
3.446
3.438
3.429
3.413
3.396
3.366
3.349
3.340
3.332
3.322
3.305
3.289
CF3
O
Ph
Ph
4s
1H NMR (600 MHz, CDCl3)
0.97
0.96
1.08
0.95
4.02
1.96
1.00
3.85
4.99
1.16
1.00
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


211.334
192.318
141.390
140.213
135.770
134.755
132.706
132.218
132.189
131.844
129.393
128.934
128.637
128.407
128.206
127.842
127.698
127.679
127.631
126.990
126.674
126.368
124.596
124.529
122.681
111.919
102.794
102.775
77.211
77.000
76.789
35.647
35.446
35.244
35.043
CF3
O
Ph
Ph
4s
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



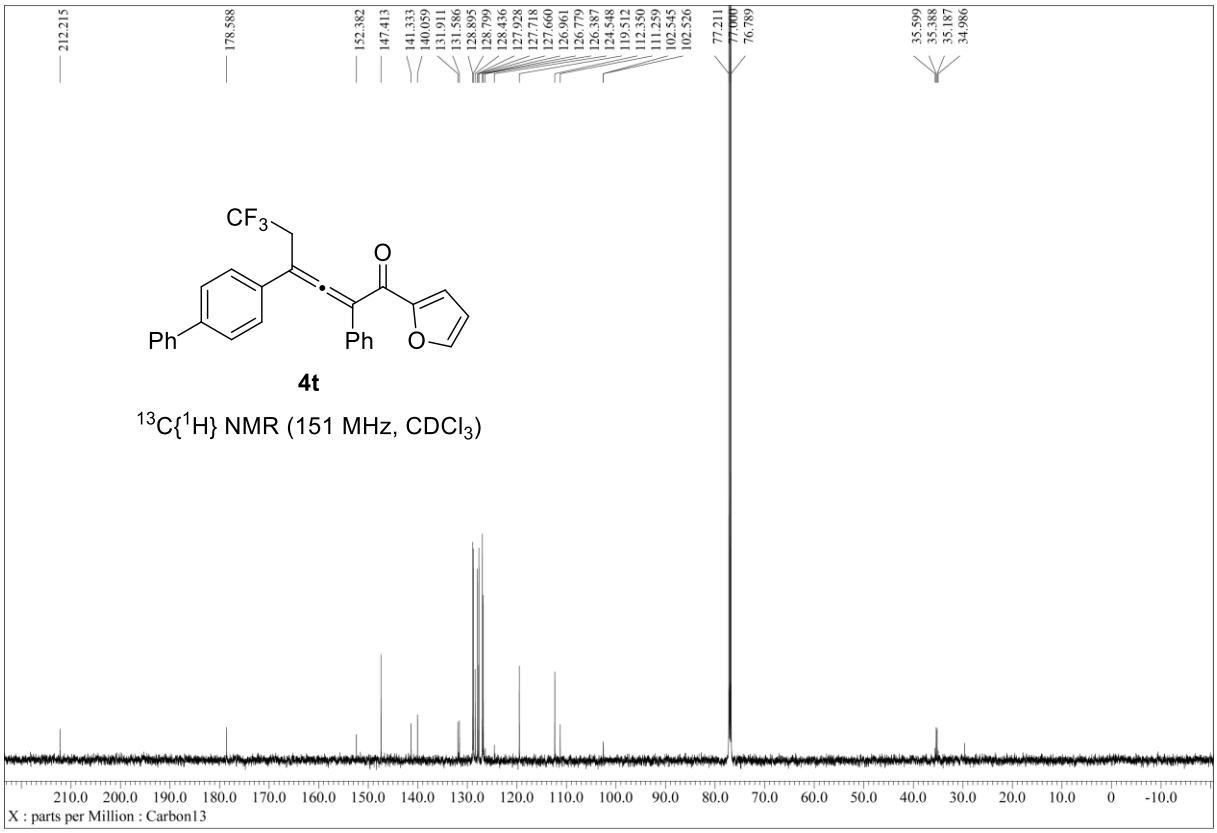
4s

^{19}F NMR (564 MHz, $CDCl_3$)



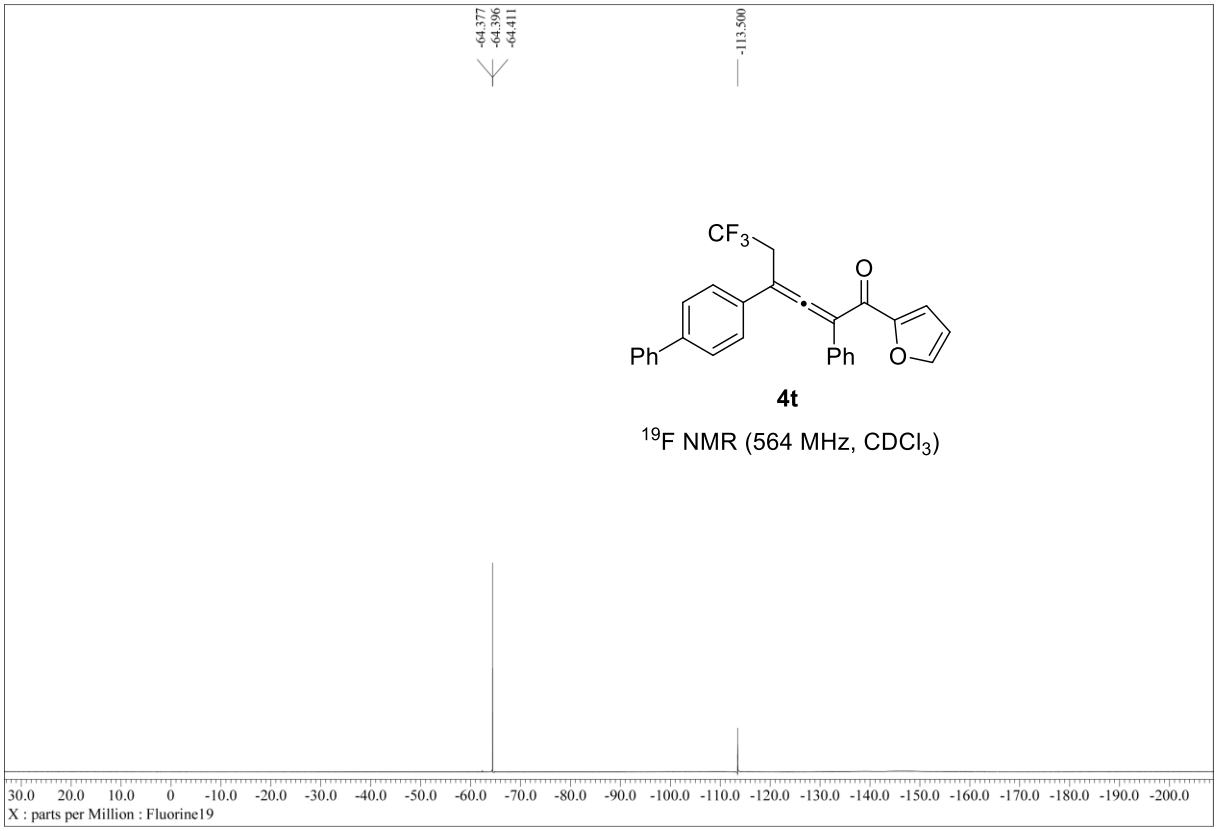
4t

^{1}H NMR (600 MHz, $CDCl_3$)



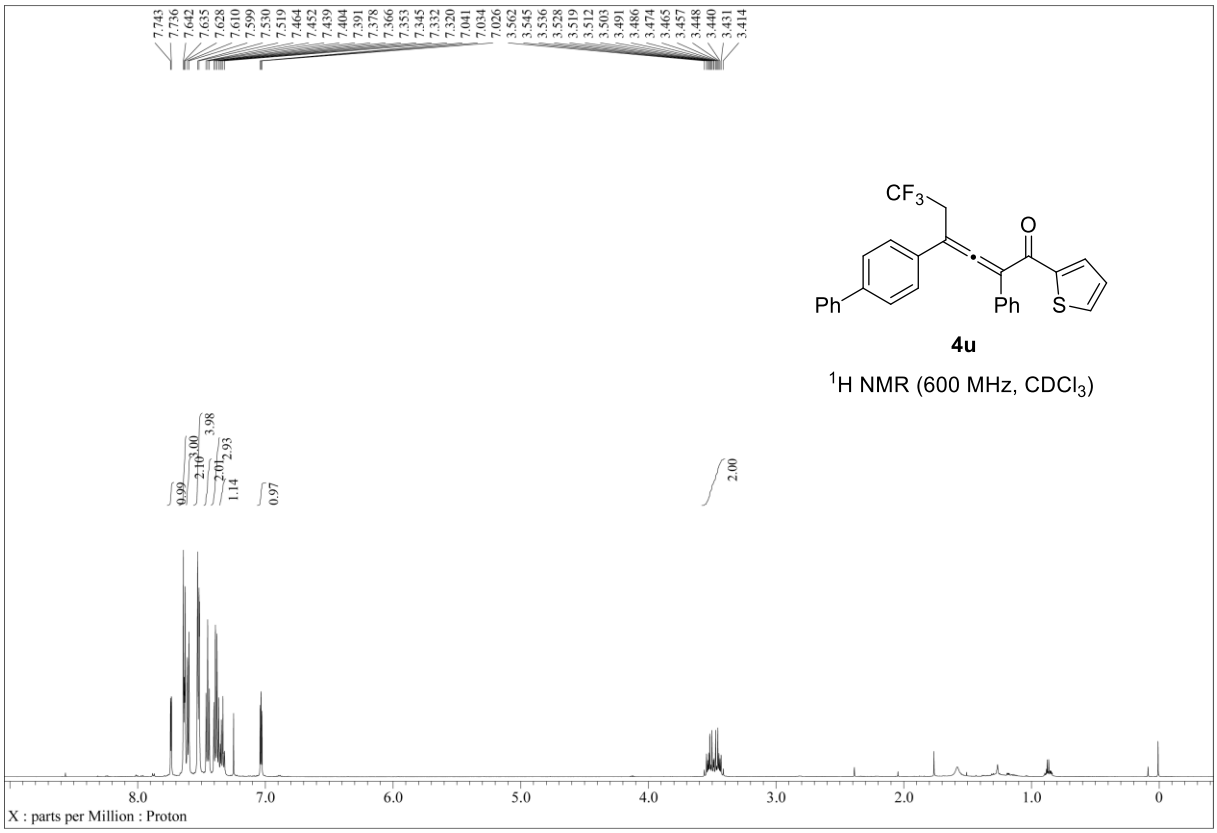
4t

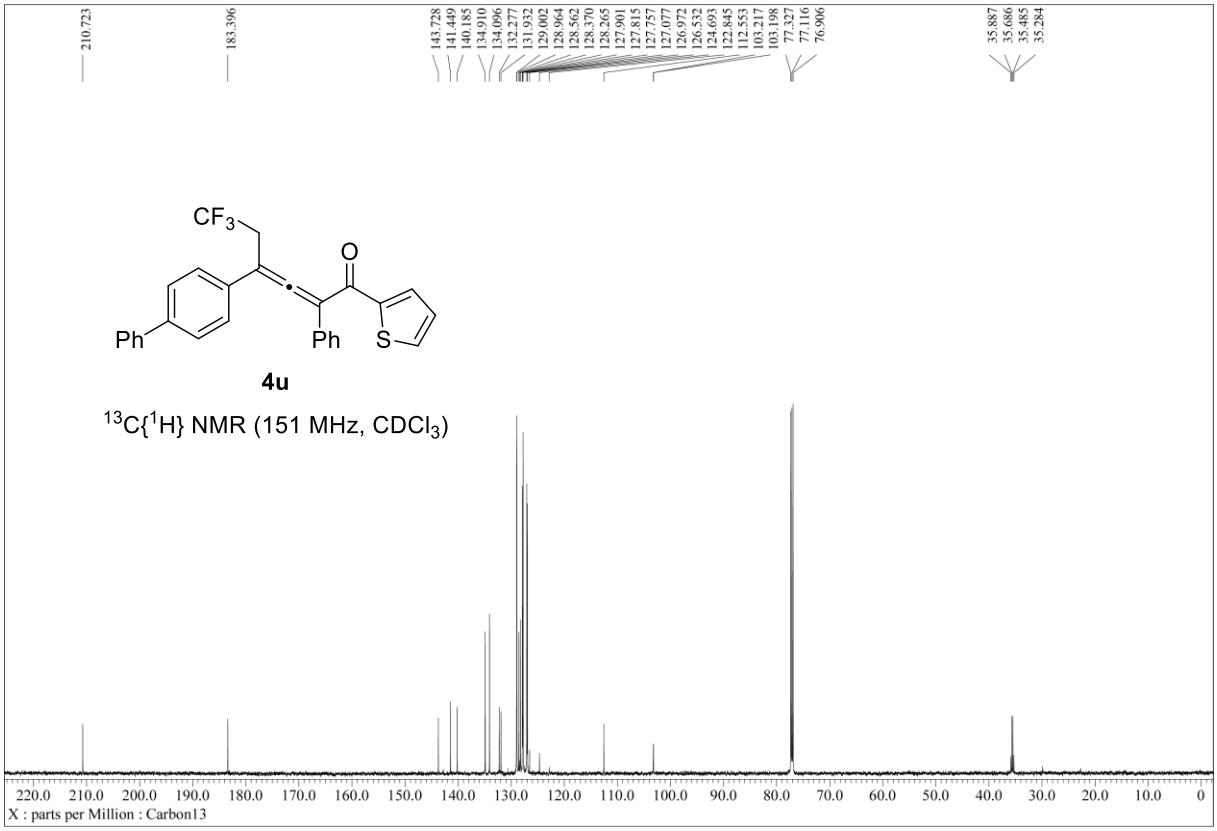
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

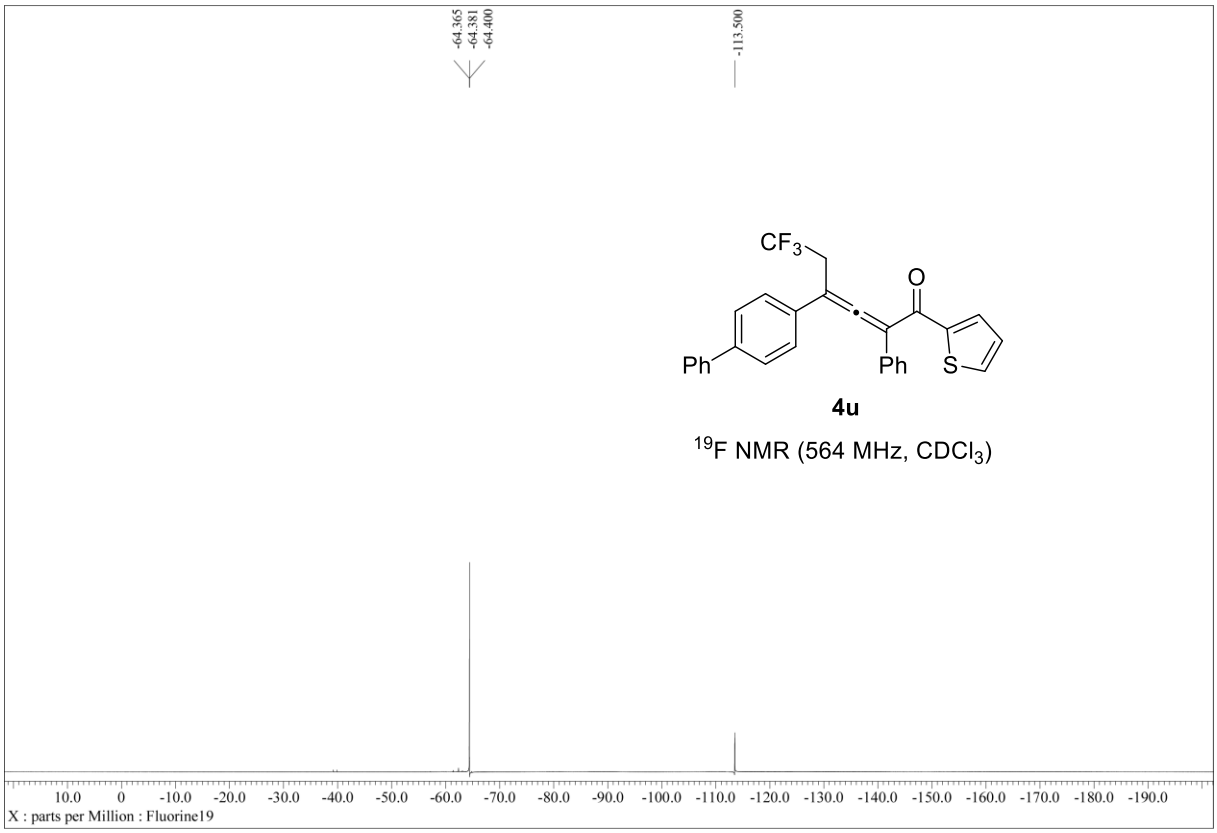


4t

^{19}F NMR (564 MHz, $CDCl_3$)

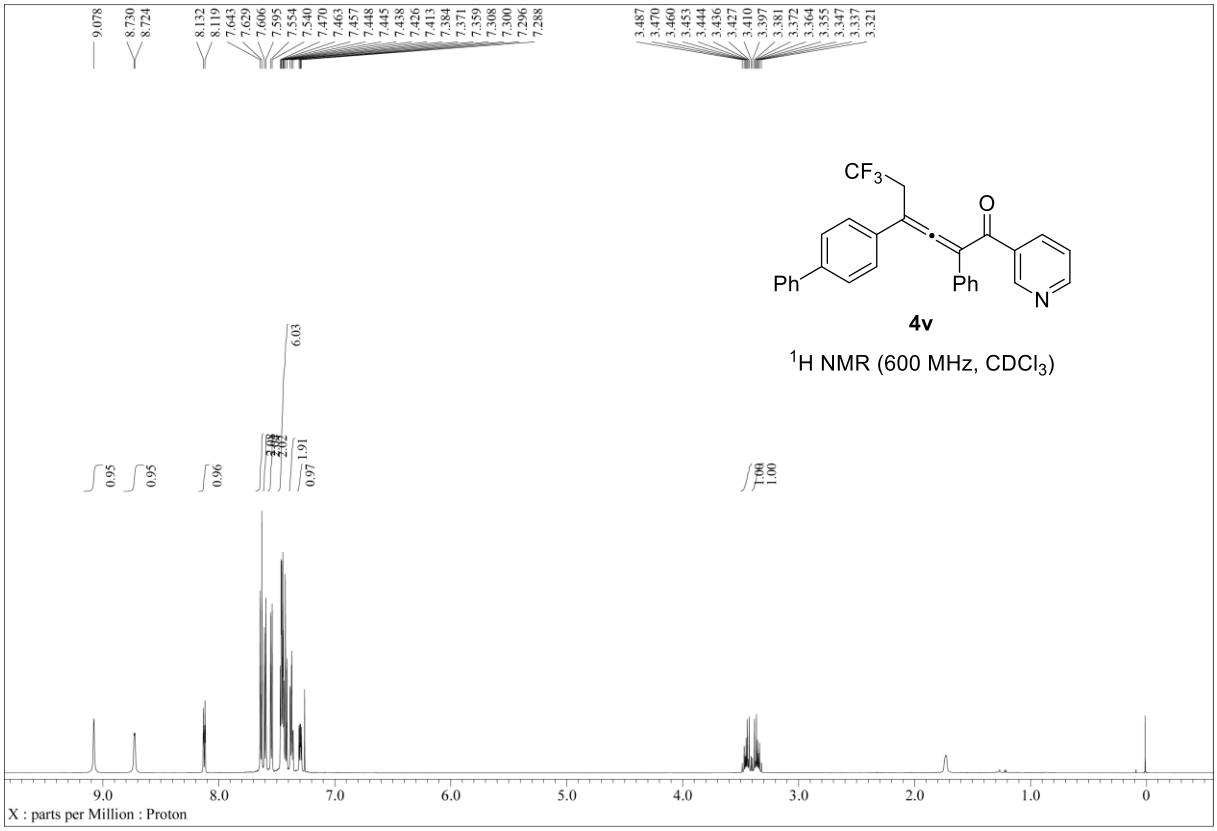

7.743
7.736
7.642
7.635
7.628
7.610
7.599
7.530
7.519
7.464
7.452
7.439
7.404
7.391
7.378
7.366
7.353
7.345
7.332
7.320
7.041
7.034
7.026
3.562
3.545
3.536
3.528
3.519
3.512
3.503
3.491
3.486
3.474
3.465
3.457
3.448
3.440
3.431
3.414
CF3
O
Ph
Ph
S
4u
1H NMR (600 MHz, CDCl3)
0.99
3.00
2.10
3.98
2.01
2.93
1.14
0.97
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


210.723
183.396
143.728
141.449
140.185
134.910
134.096
132.277
131.932
129.002
128.964
128.562
128.370
128.265
127.901
127.815
127.757
127.077
126.972
126.532
124.693
122.845
112.553
103.217
103.198
77.327
77.116
76.906
35.887
35.686
35.485
35.284
CF3
O
Ph
Ph
S
4u
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



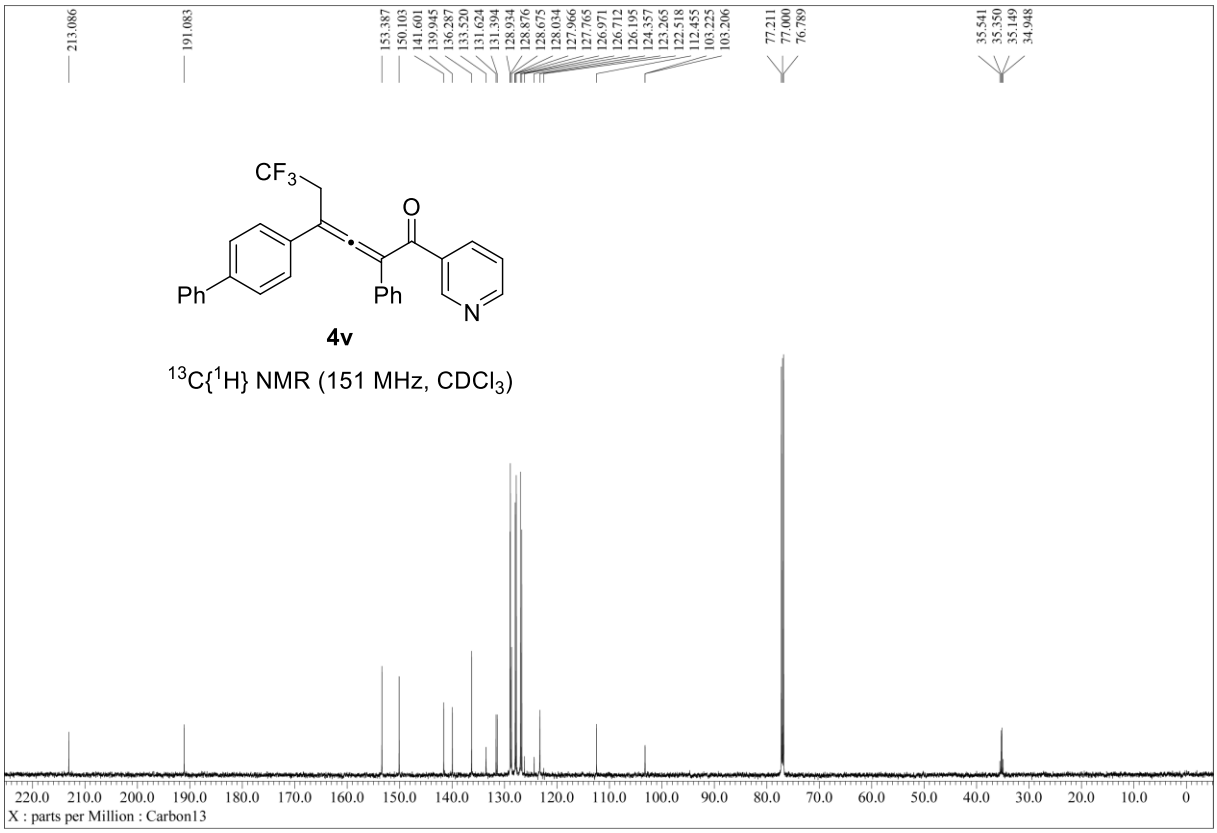
4u

^{19}F NMR (564 MHz, $CDCl_3$)

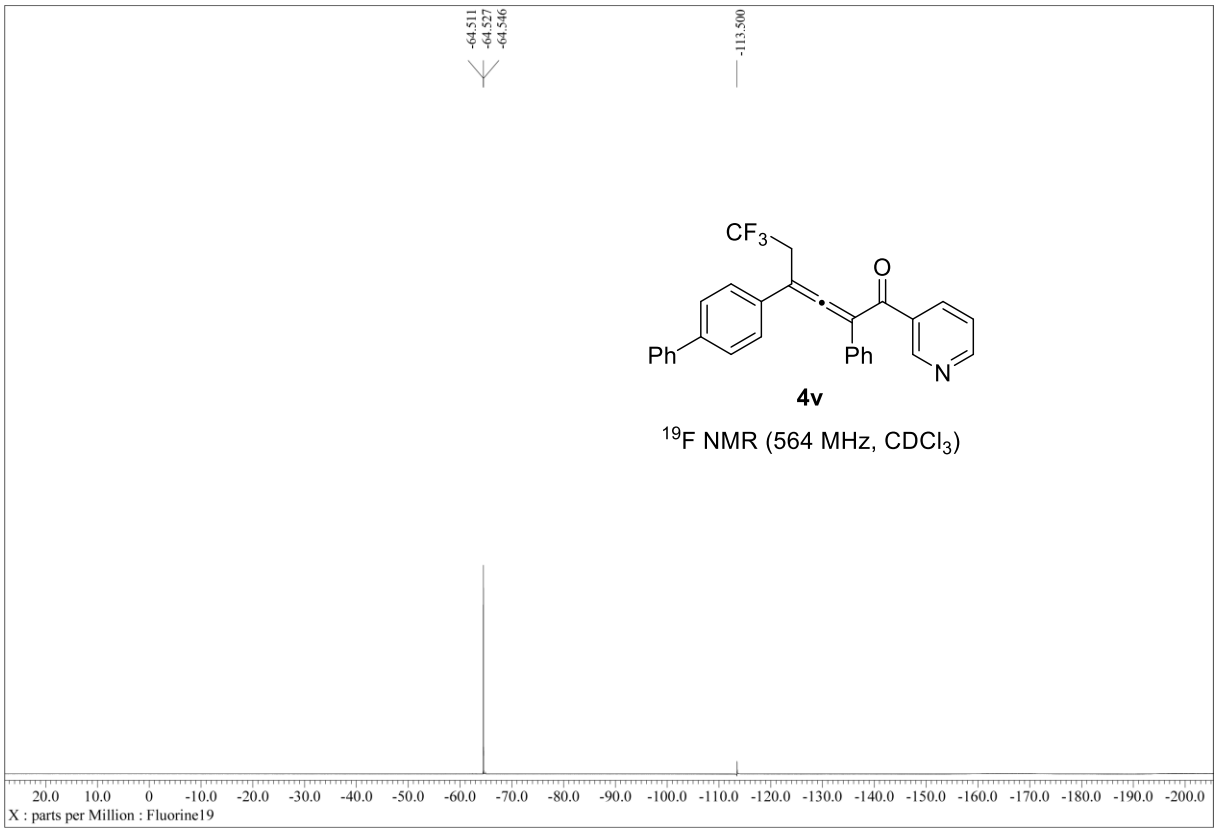


4v

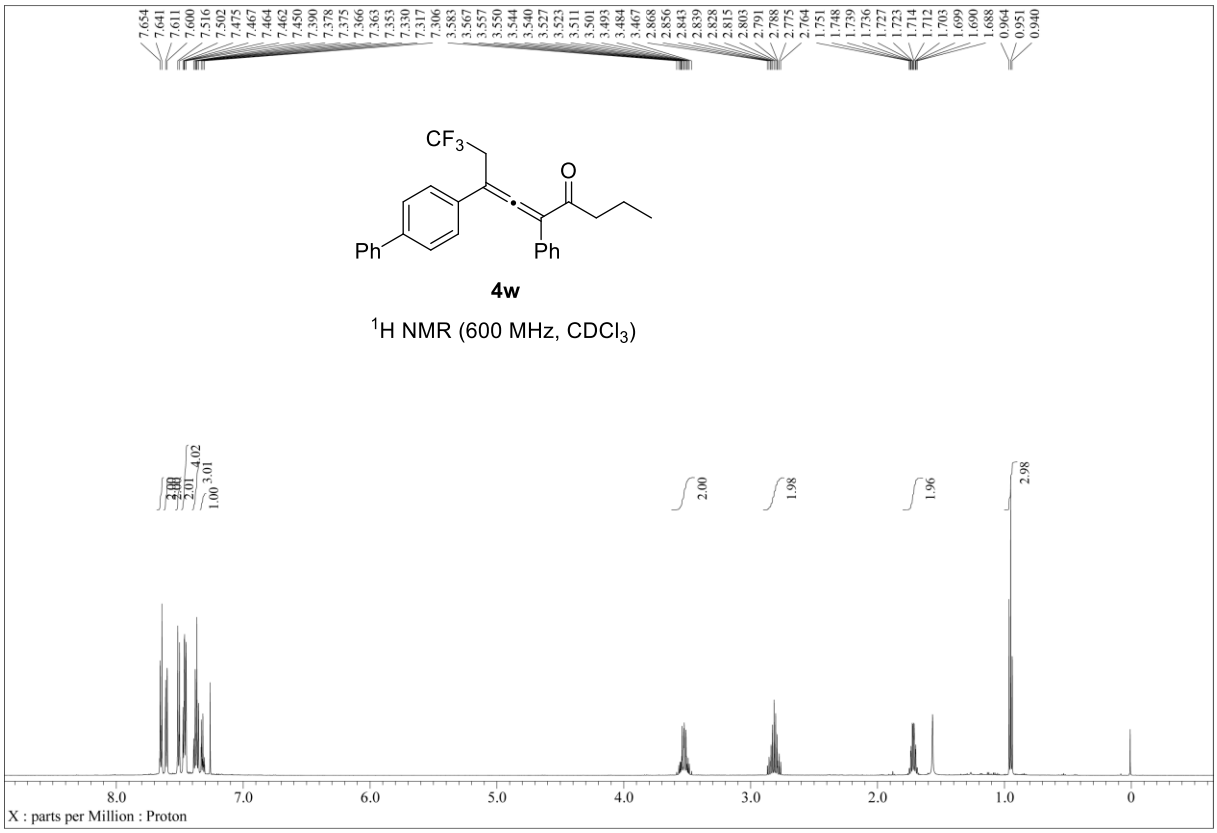
^{1}H NMR (600 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

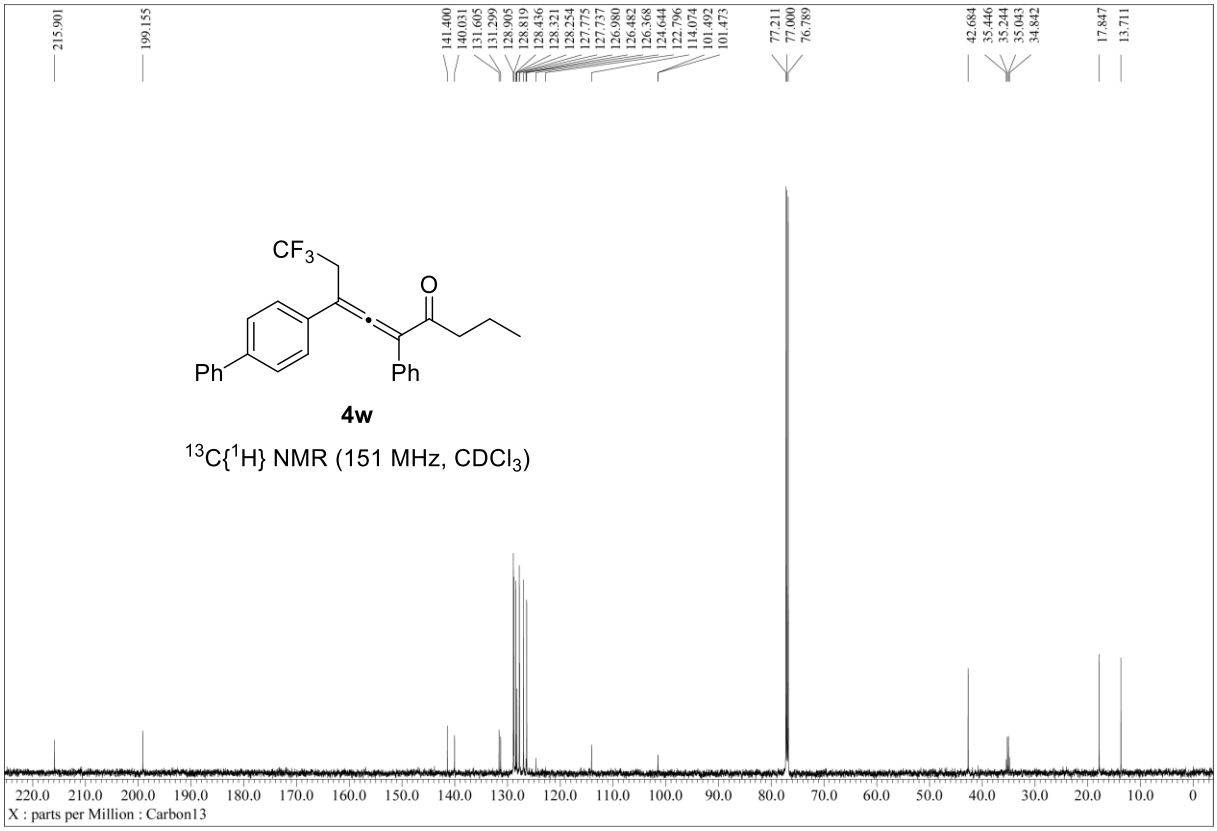


^{19}F NMR (564 MHz, $CDCl_3$)



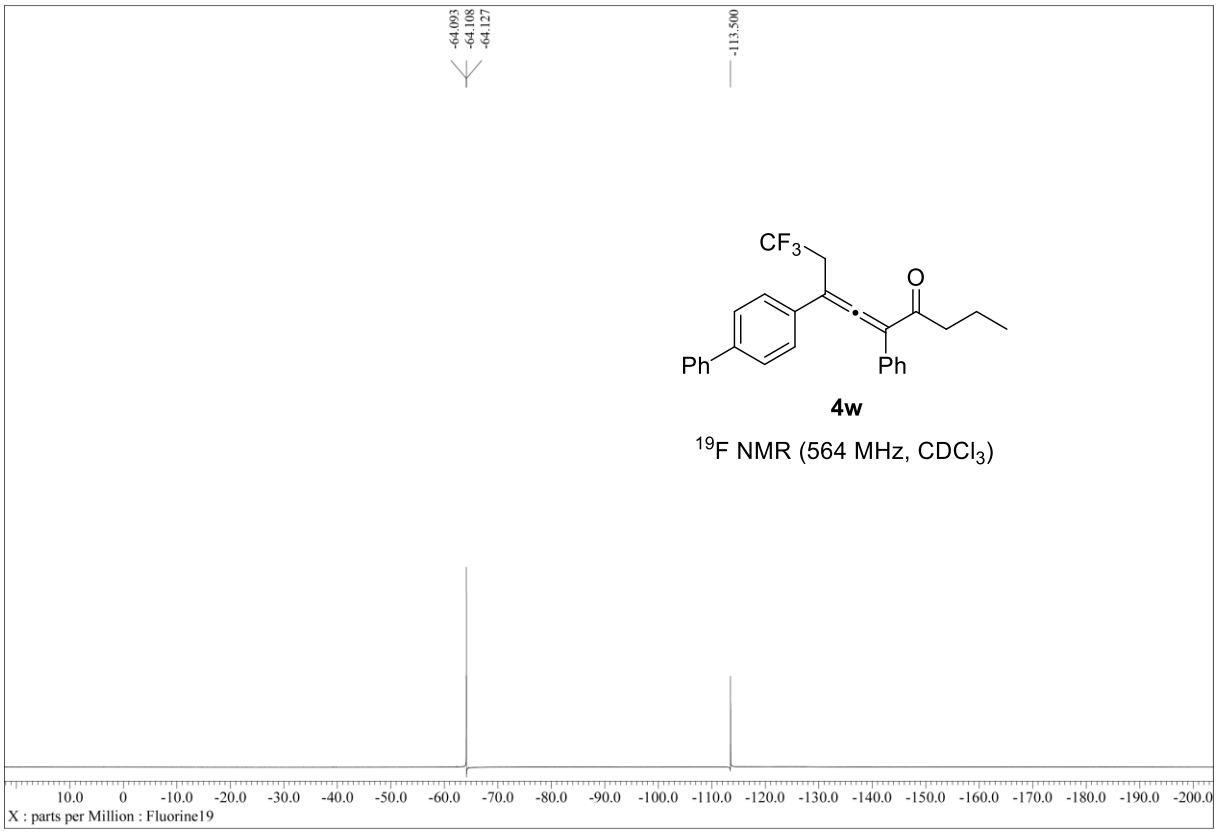
4w

^{1}H NMR (600 MHz, $CDCl_3$)



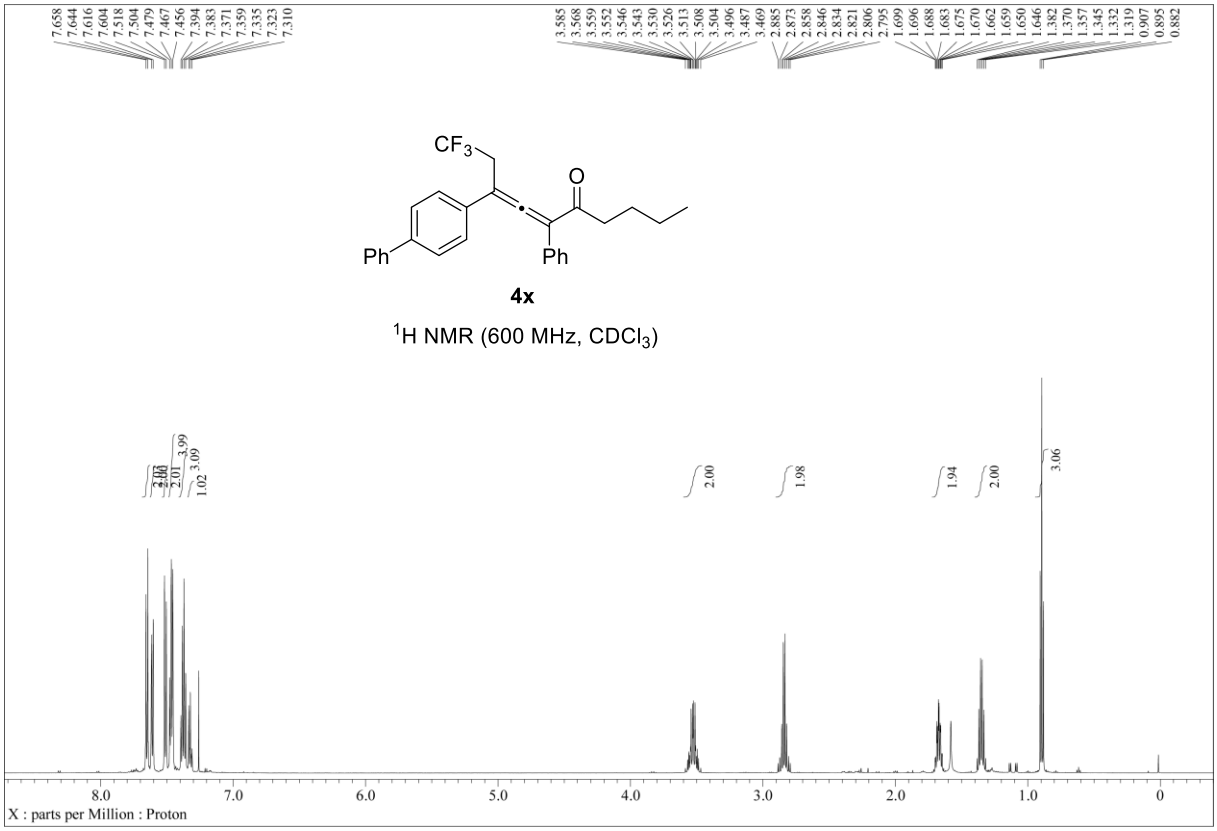
4w

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



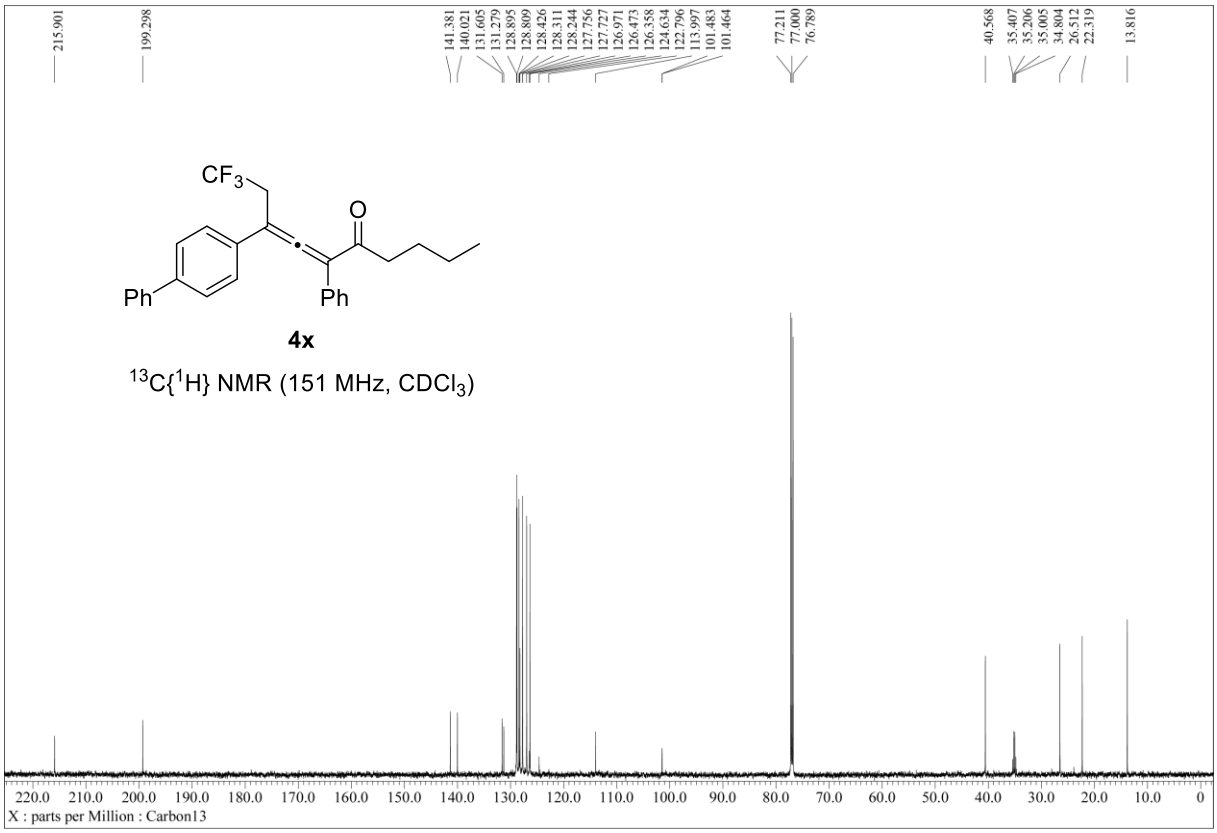
4w

^{19}F NMR (564 MHz, $CDCl_3$)



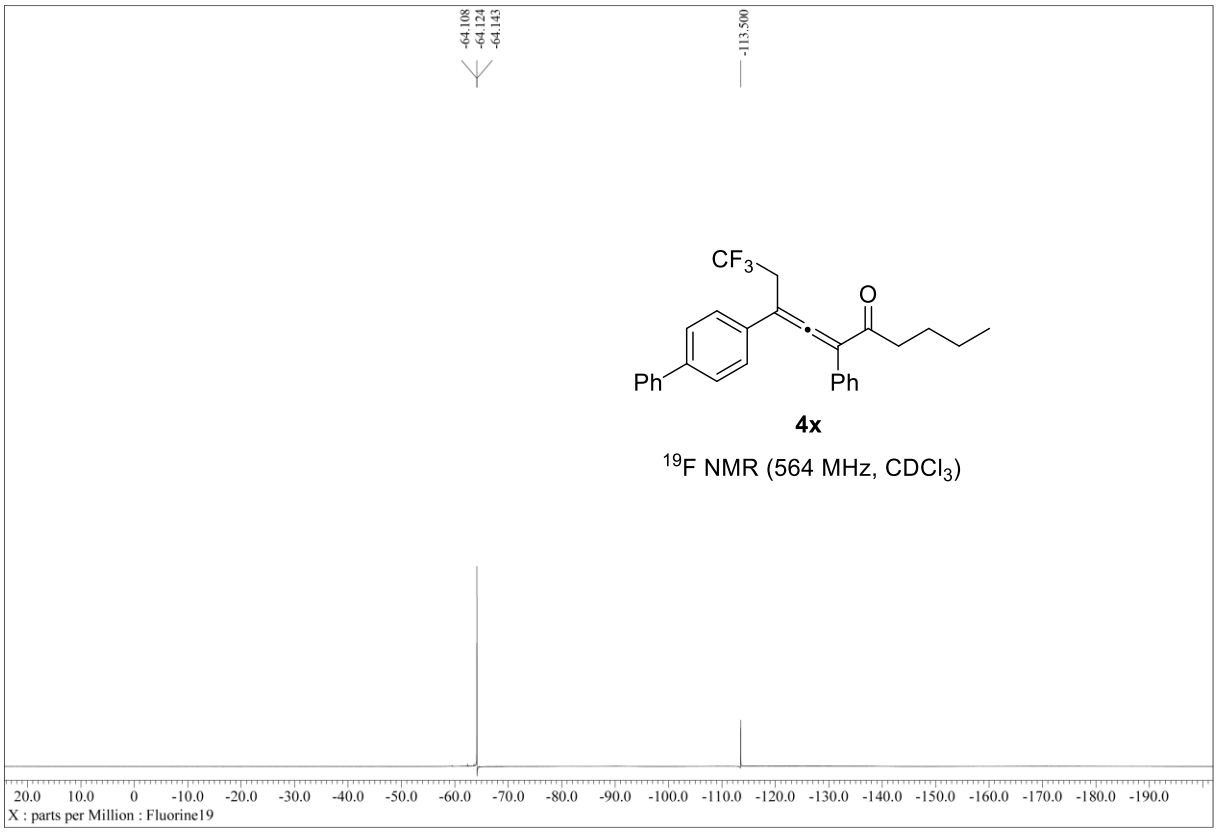
4x

^{1}H NMR (600 MHz, $CDCl_3$)



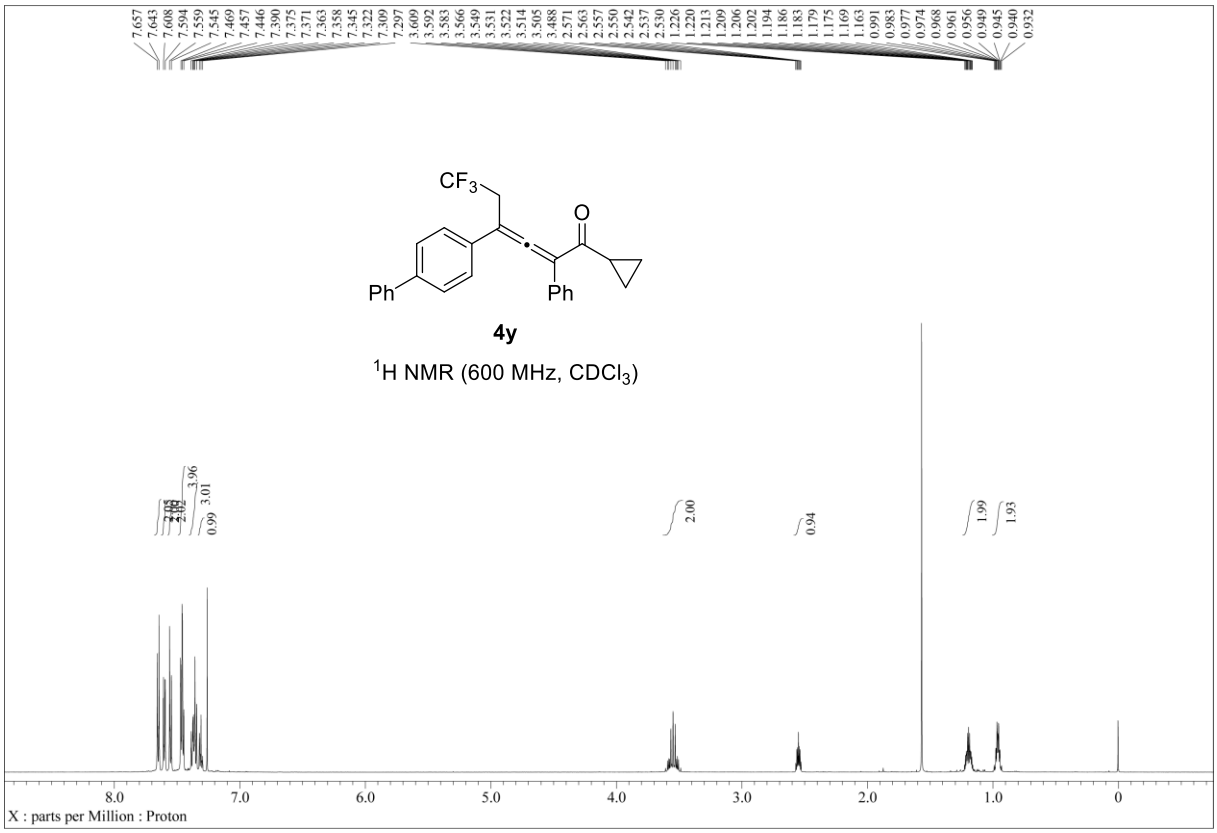
4x

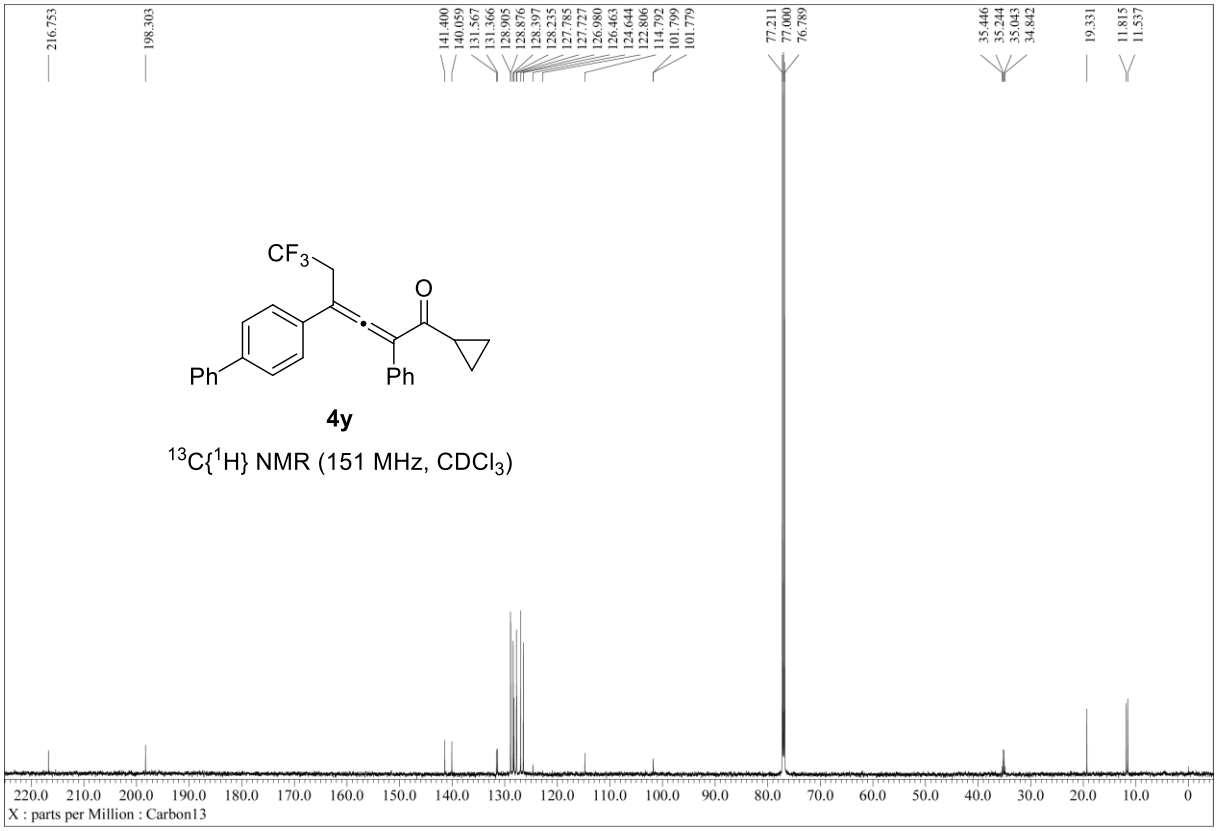
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

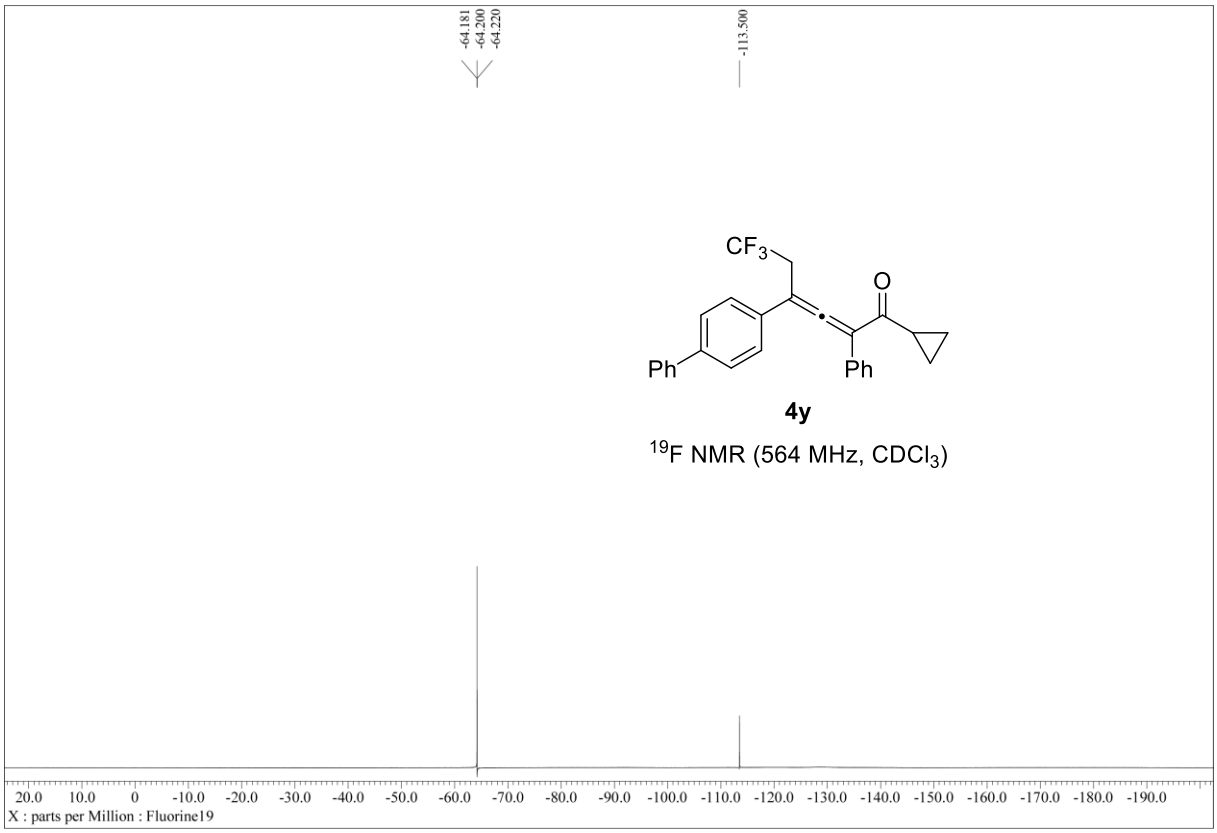


4x

^{19}F NMR (564 MHz, $CDCl_3$)

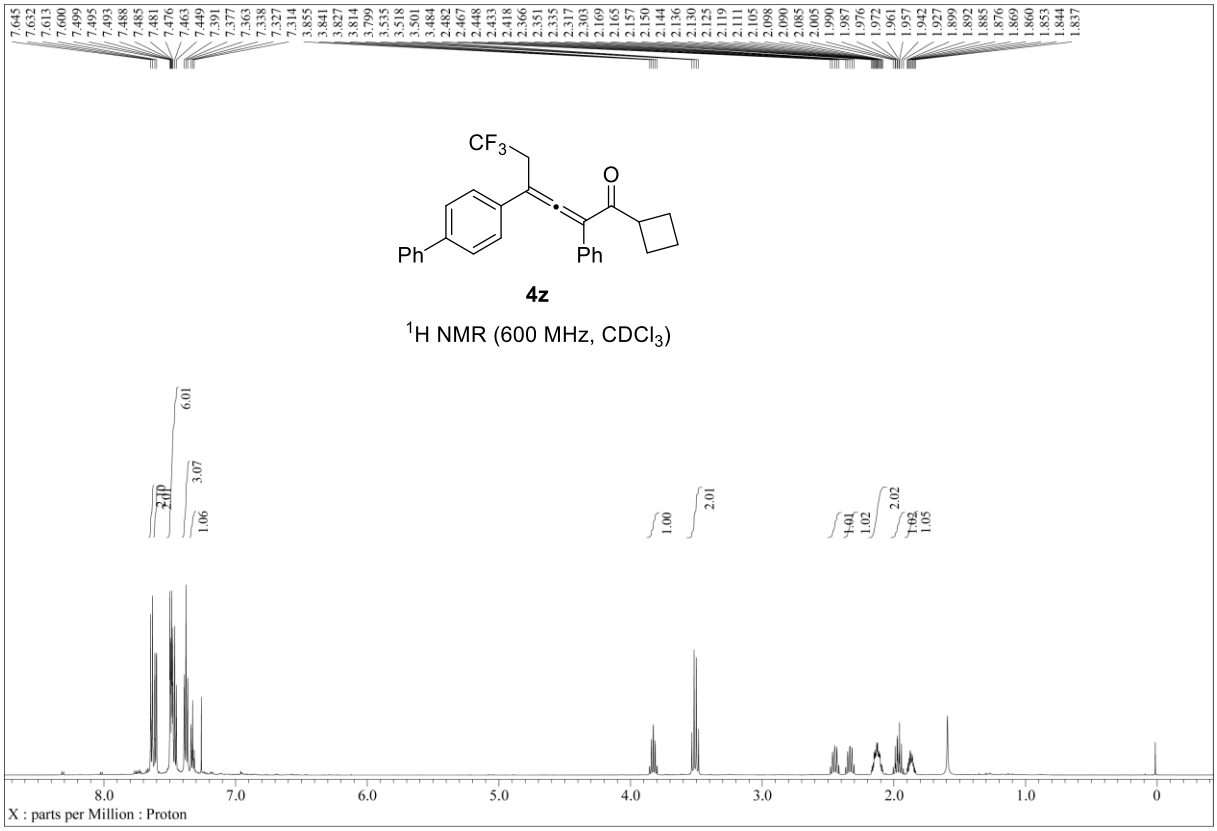

7.657
7.643
7.608
7.594
7.559
7.545
7.469
7.457
7.446
7.390
7.375
7.371
7.363
7.358
7.345
7.322
7.309
7.297
3.609
3.592
3.583
3.566
3.549
3.531
3.522
3.514
3.505
3.488
2.571
2.563
2.557
2.550
2.542
2.537
2.530
1.226
1.220
1.213
1.209
1.206
1.202
1.194
1.186
1.183
1.179
1.175
1.169
1.163
0.991
0.983
0.977
0.974
0.968
0.961
0.956
0.949
0.945
0.940
0.932
CF3
O
Ph
Ph
4y
1H NMR (600 MHz, CDCl3)
3.96
3.01
0.99
2.00
0.94
1.99
1.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


216.753
198.303
141.400
140.059
131.567
131.366
128.905
128.876
128.397
128.235
127.785
127.727
126.980
126.463
124.644
122.806
114.792
101.799
101.779
77.211
77.000
76.789
35.446
35.244
35.043
34.842
19.331
11.815
11.537
CF3
O
Ph
Ph
4y
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



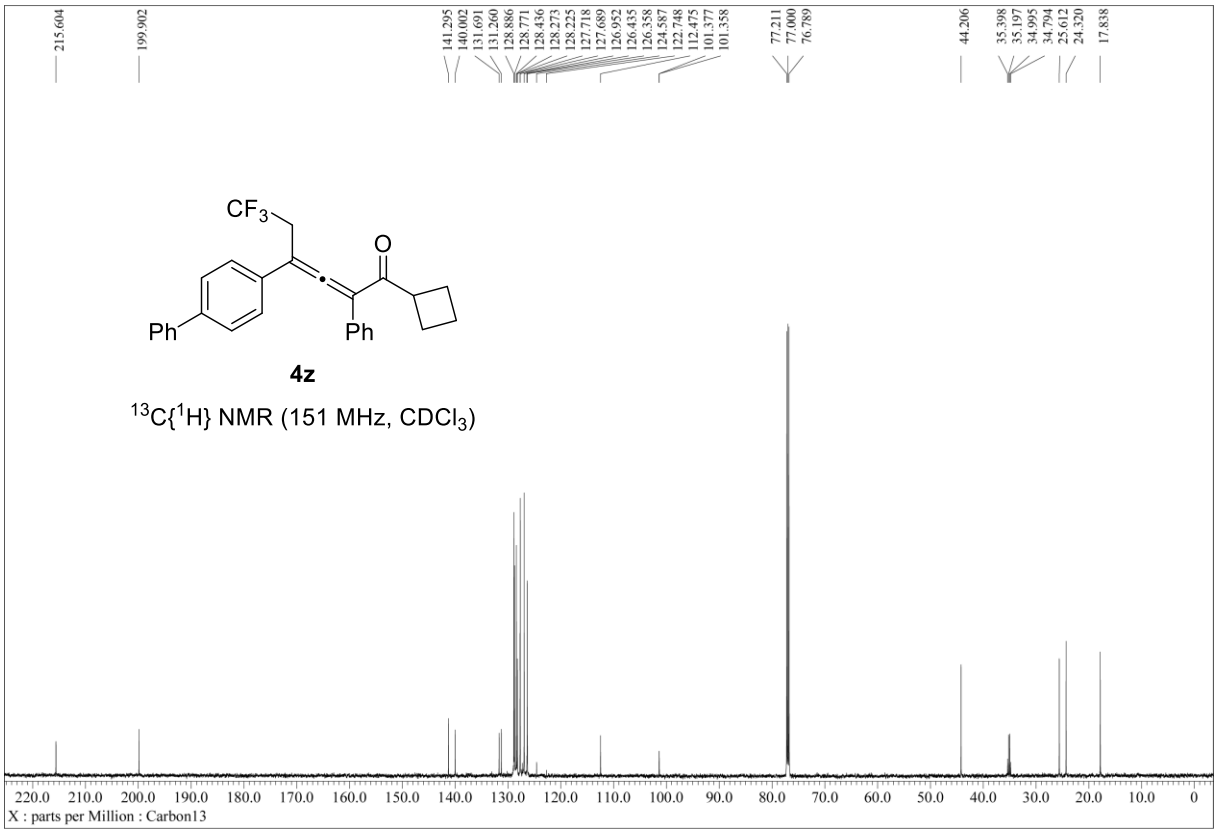
4y

^{19}F NMR (564 MHz, $CDCl_3$)



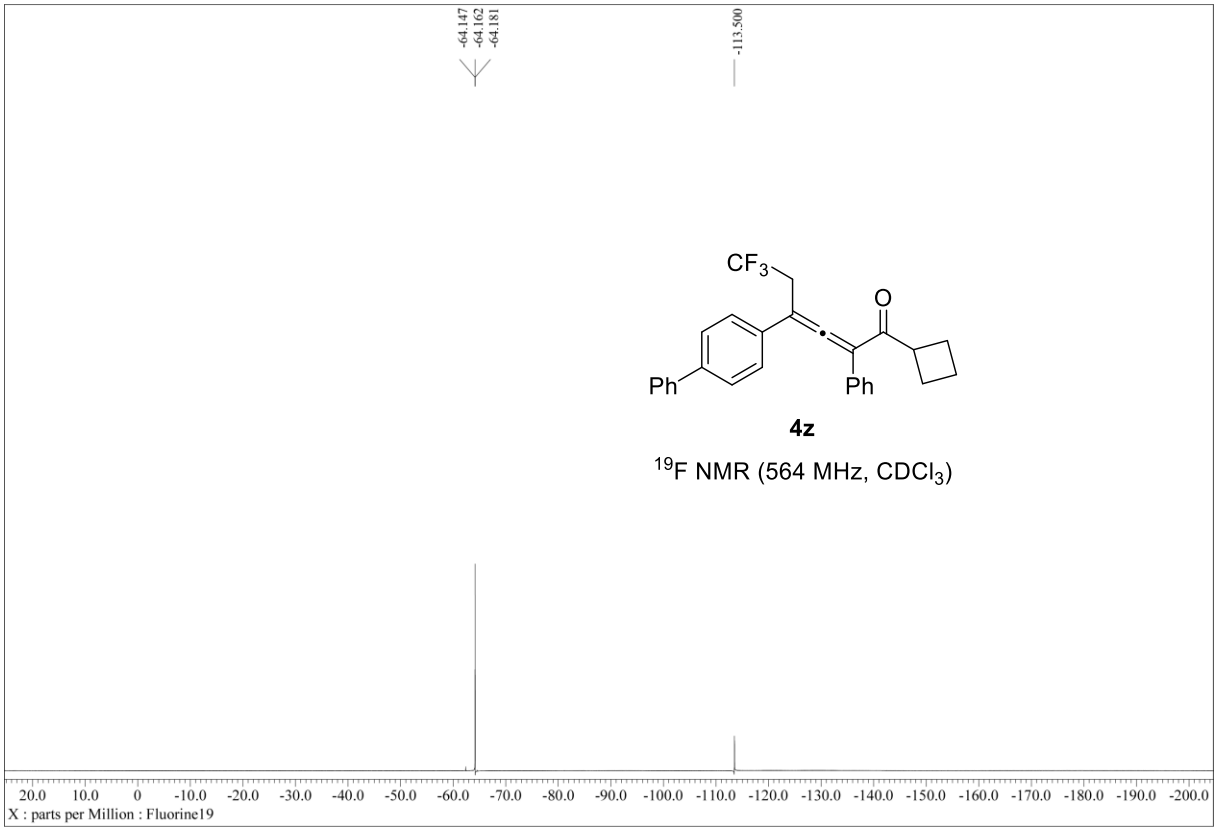
4z

^{1}H NMR (600 MHz, $CDCl_3$)



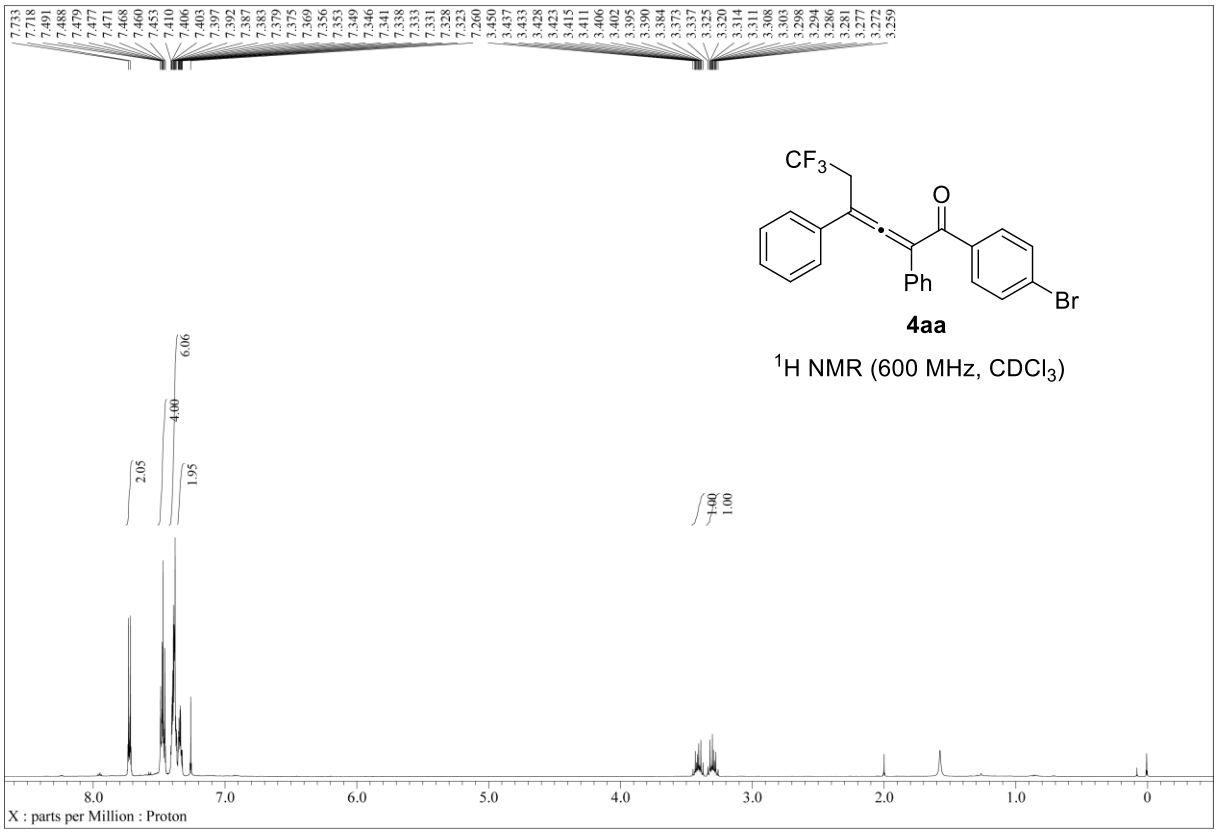
4z

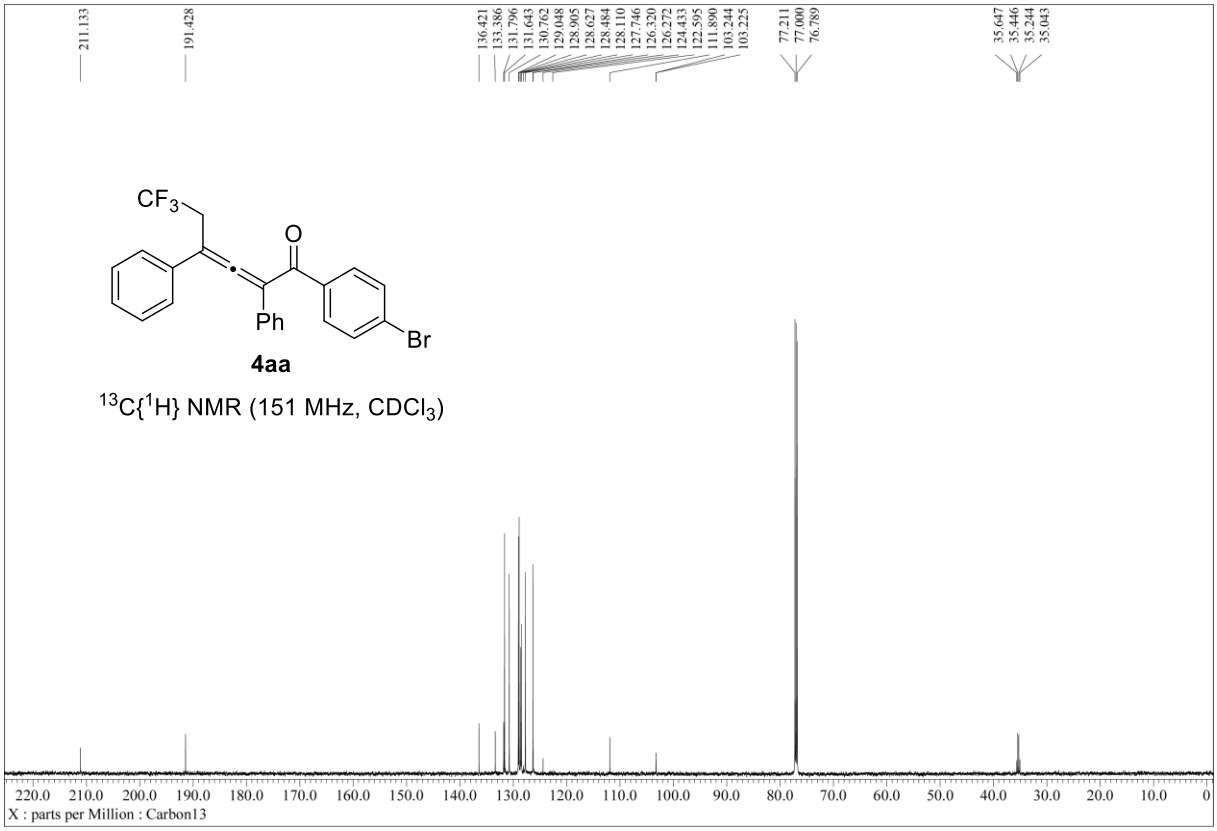
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

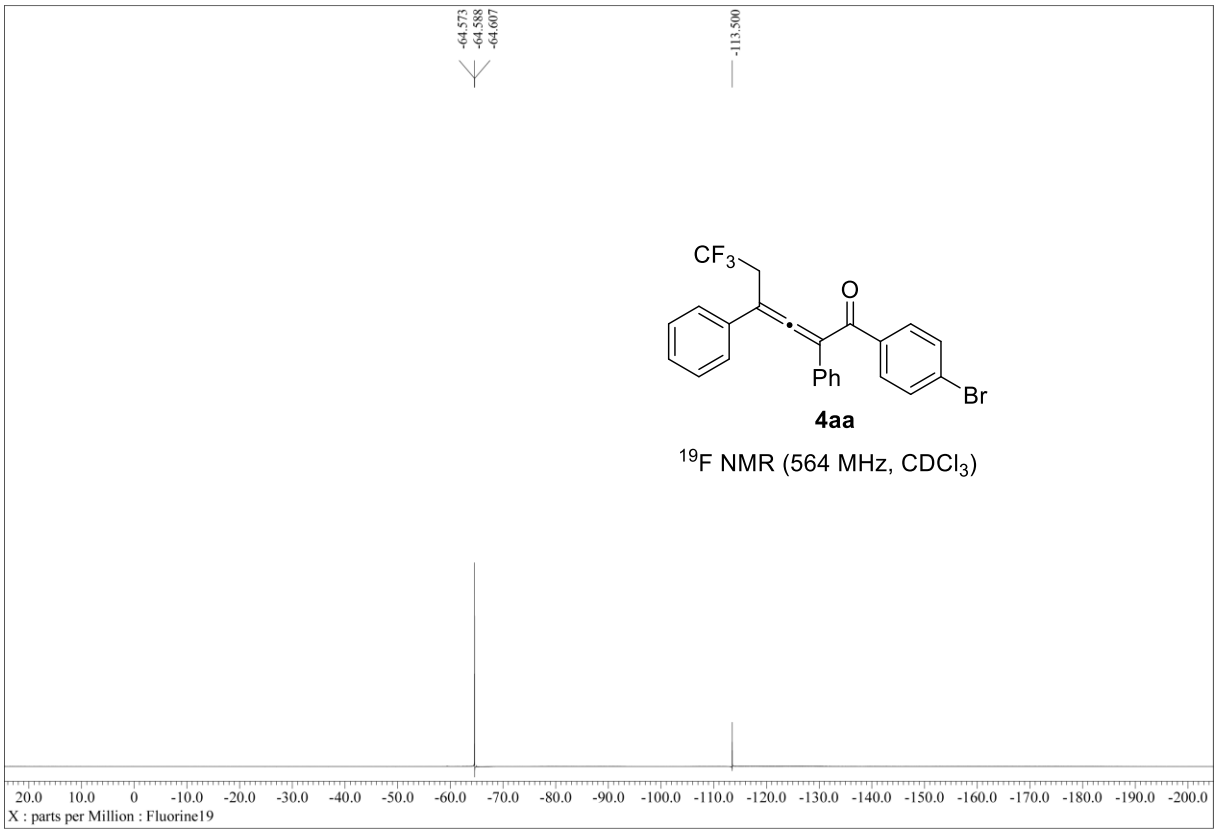


4z

^{19}F NMR (564 MHz, $CDCl_3$)

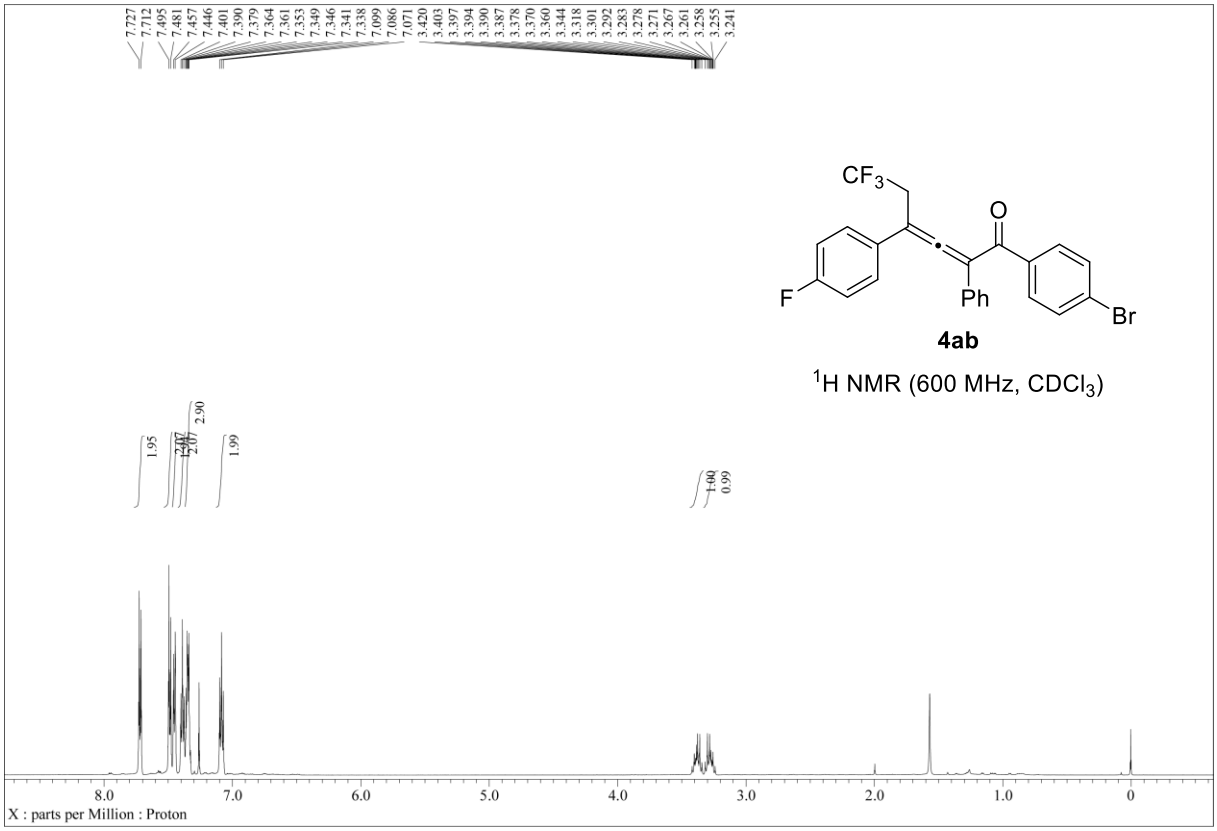

CF3
O
Ph
Br
4aa
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


CF3
O
Ph
Br
4aa
13C{1H} NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



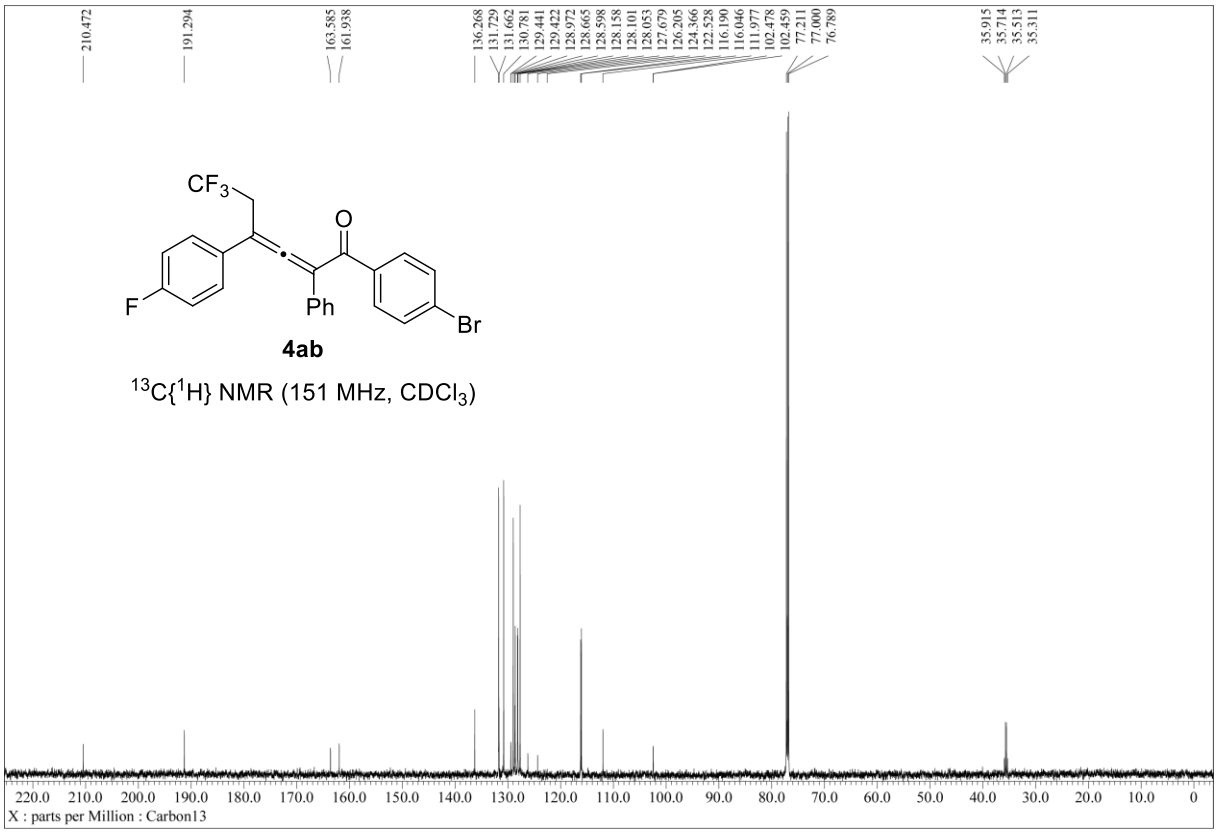
4aa

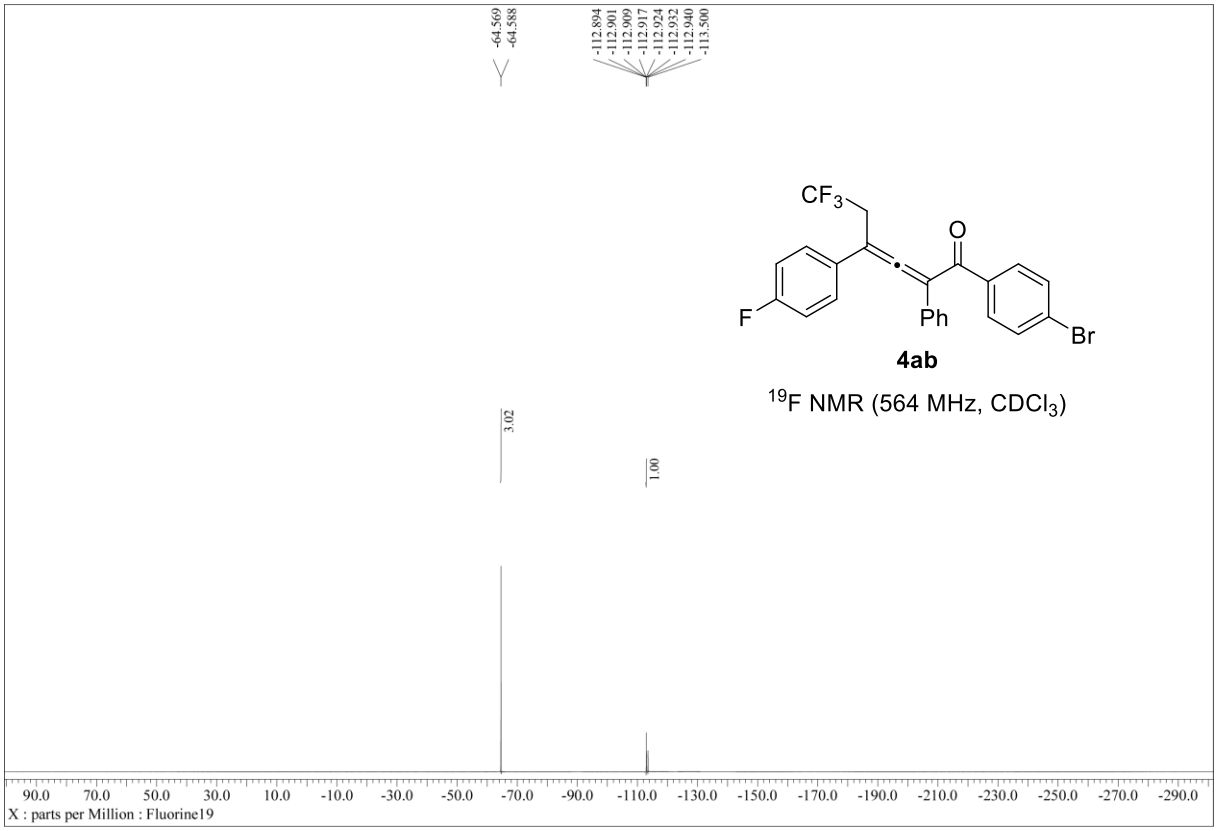
^{19}F NMR (564 MHz, $CDCl_3$)

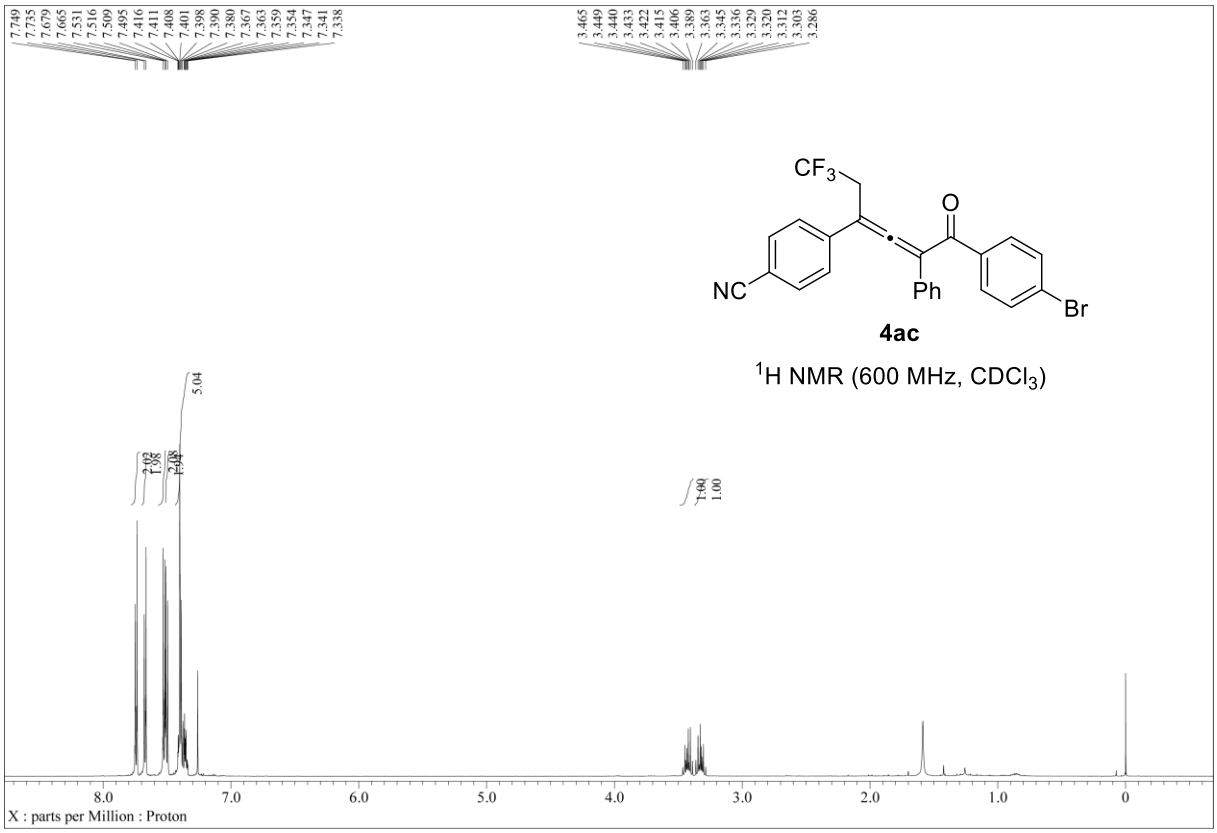


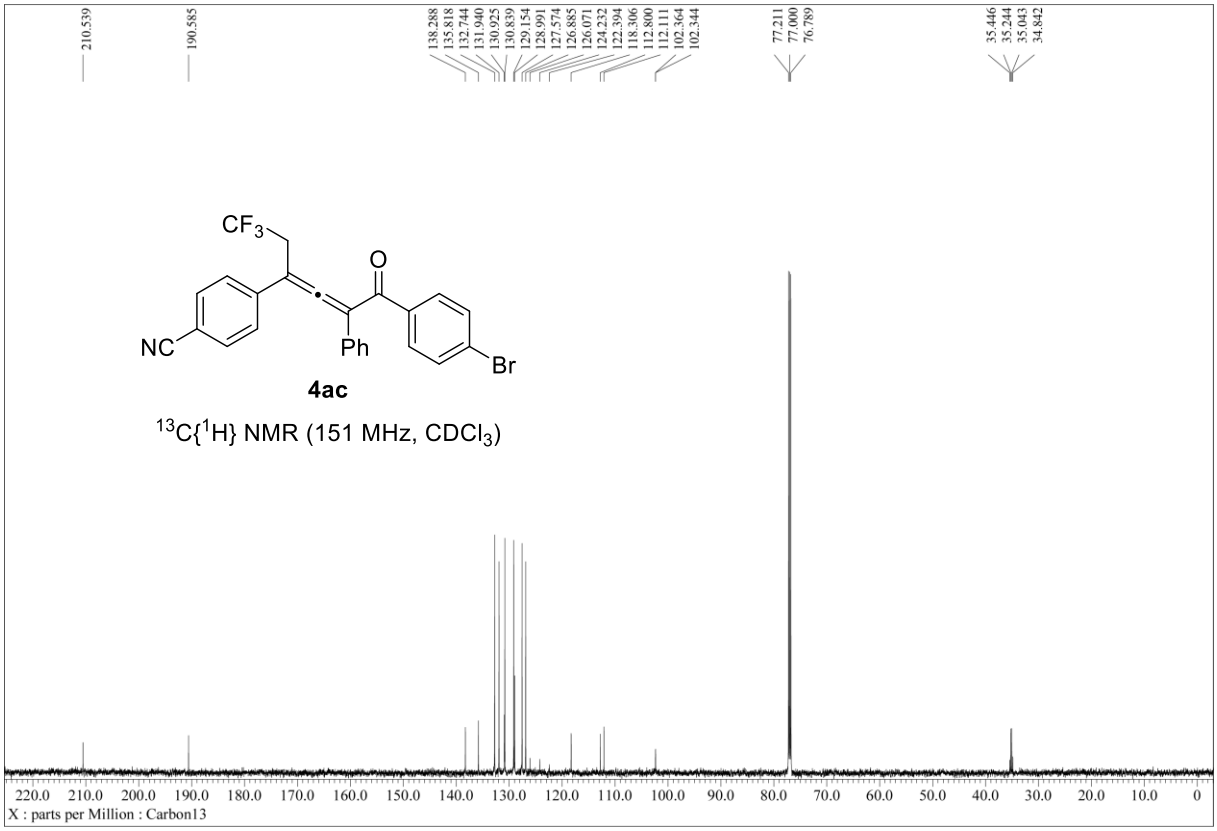
4ab

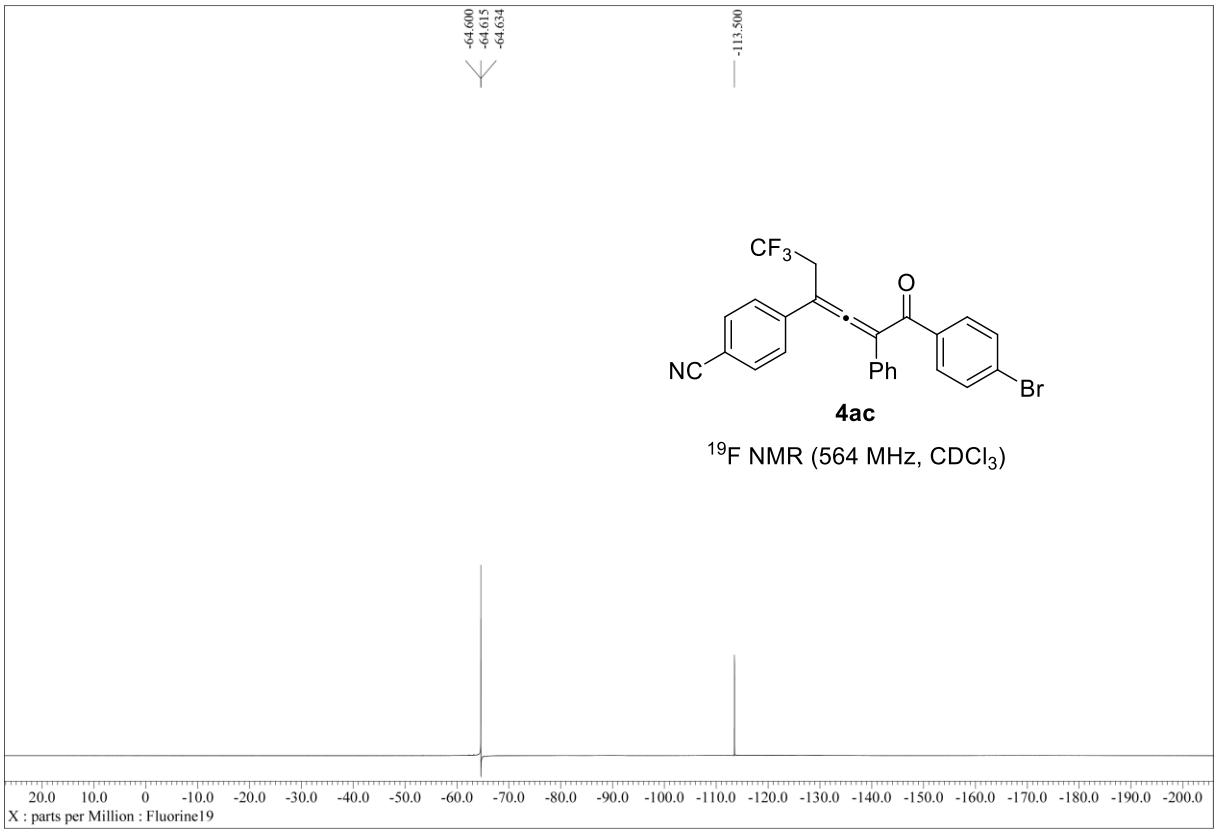
^{1}H NMR (600 MHz, $CDCl_3$)


210.472
191.294
163.585
161.938
136.268
131.729
131.662
130.781
129.441
129.422
128.972
128.665
128.598
128.158
128.101
128.053
127.679
126.205
124.366
122.528
116.190
116.046
111.977
102.478
102.459
77.211
77.000
76.789
35.915
35.714
35.513
35.311
CF3
O
F
Ph
Br
4ab
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.569
-64.588
-112.894
-112.901
-112.909
-112.917
-112.924
-112.932
-112.940
-113.500
CF3
O
F
Ph
Br
4ab
19F NMR (564 MHz, CDCl3)
3.02
1.00
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
X : parts per Million : Fluorine19

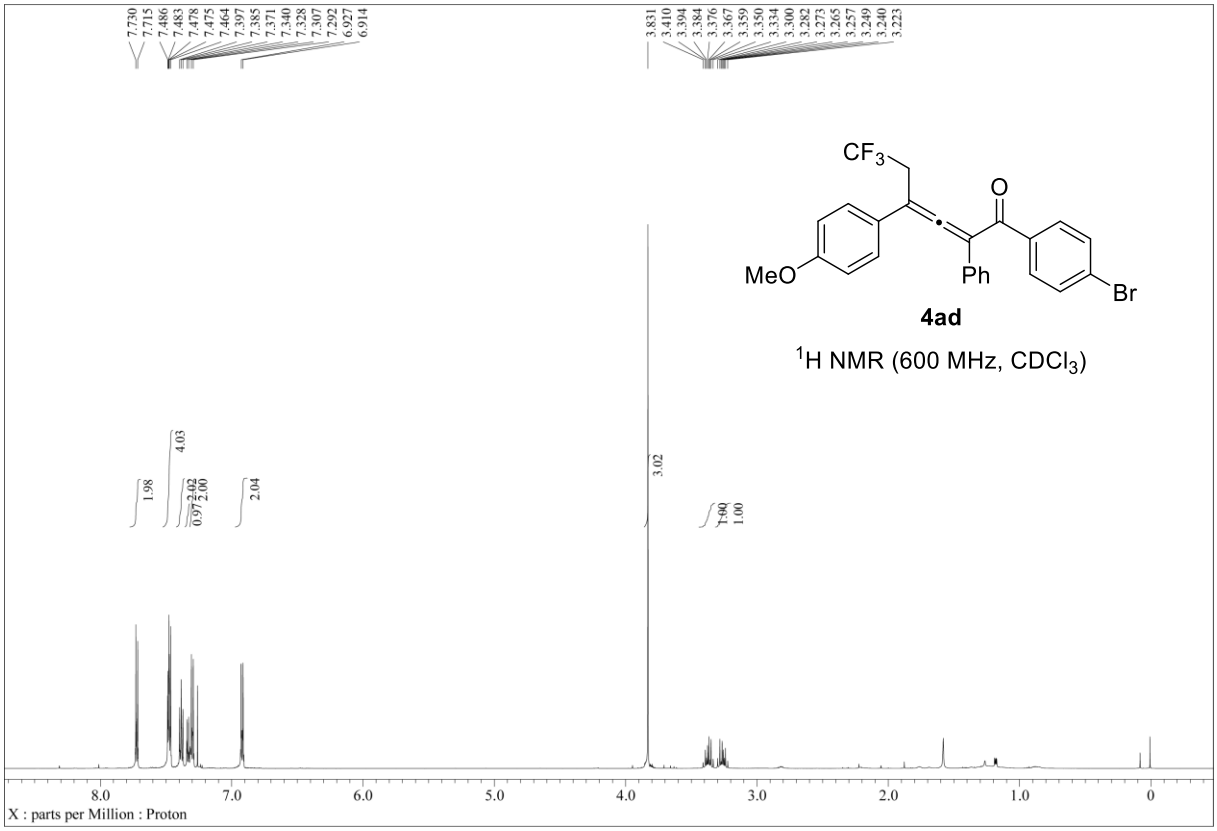

CF3
O
NC
Ph
Br
4ac
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


CF3
O
NC
Ph
Br
4ac
13C{1H} NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



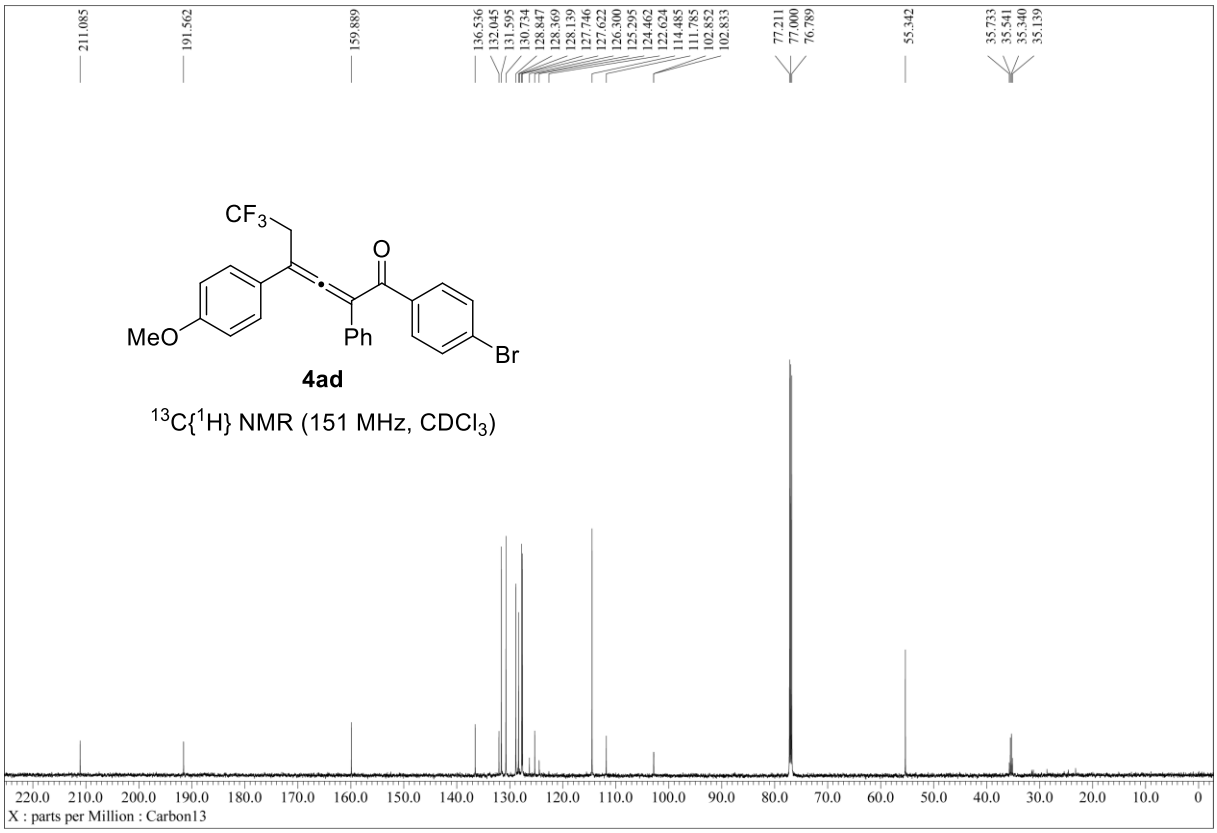
4ac

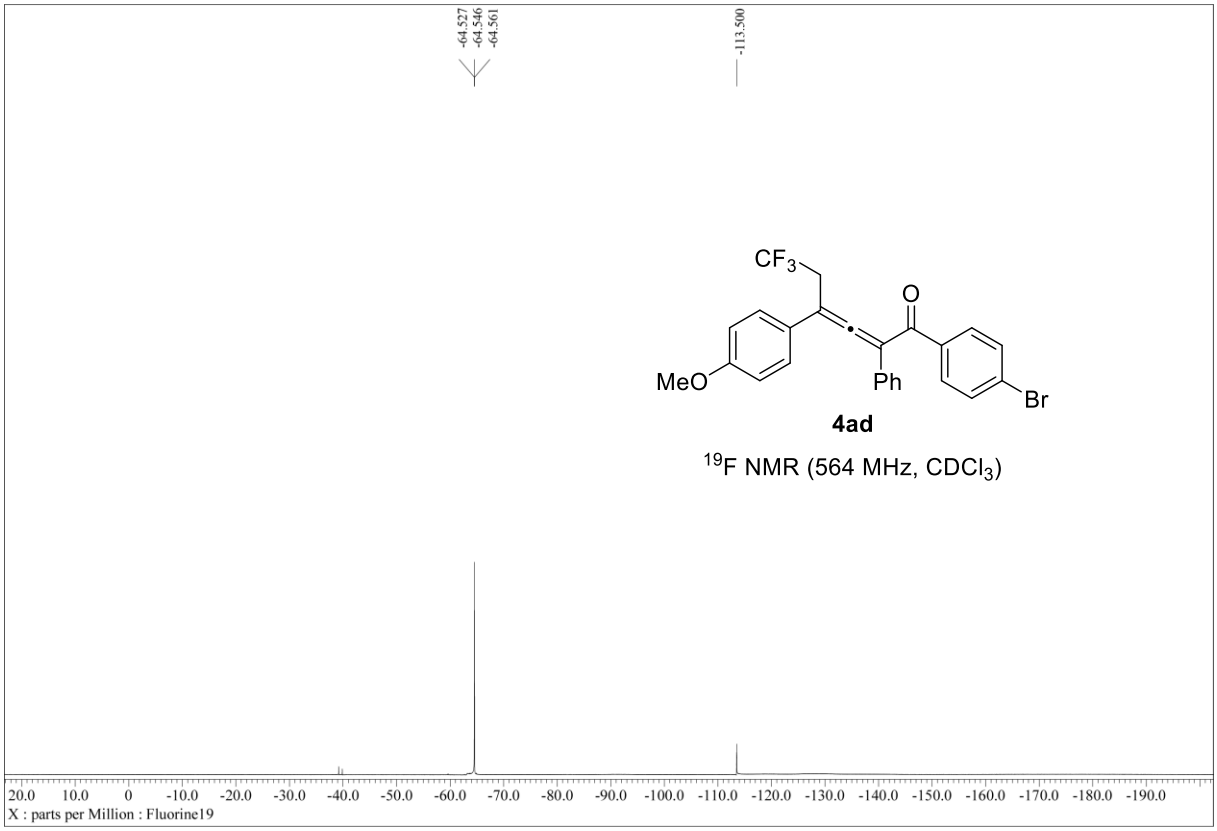
^{19}F NMR (564 MHz, $CDCl_3$)

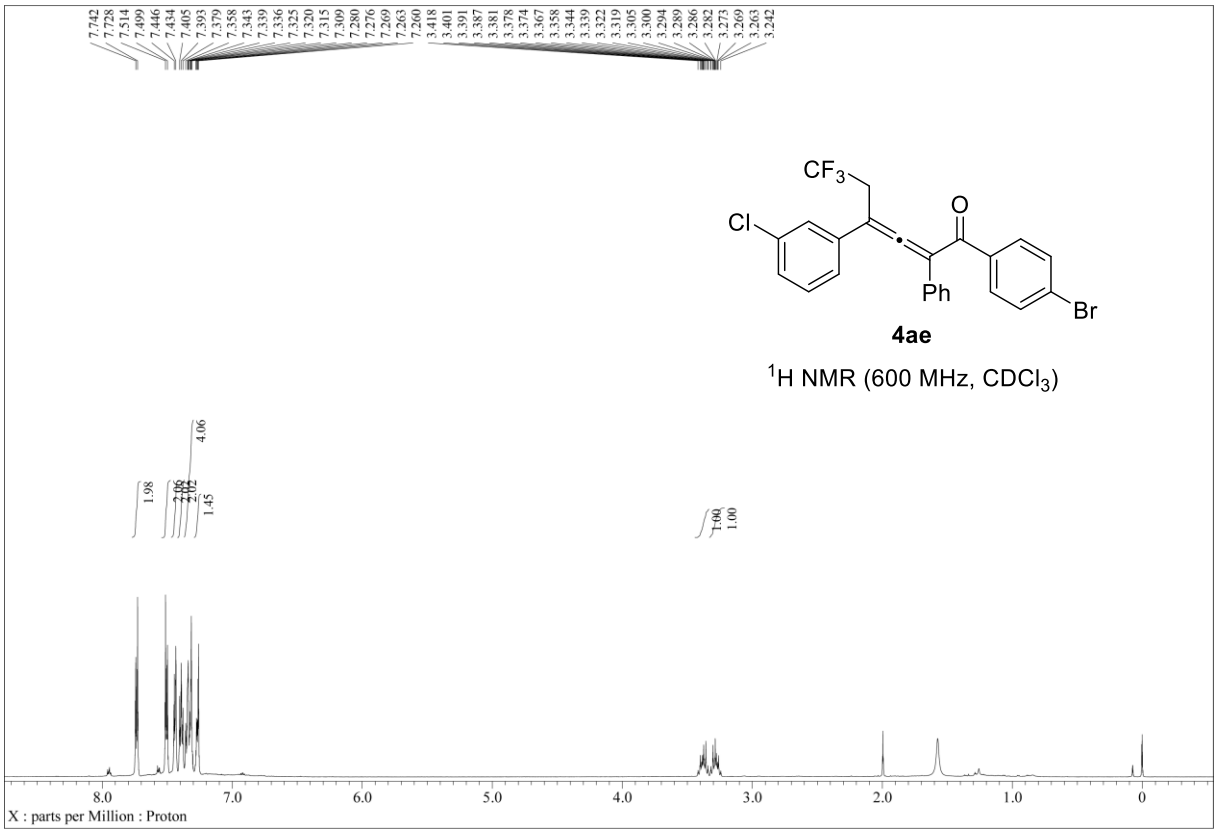


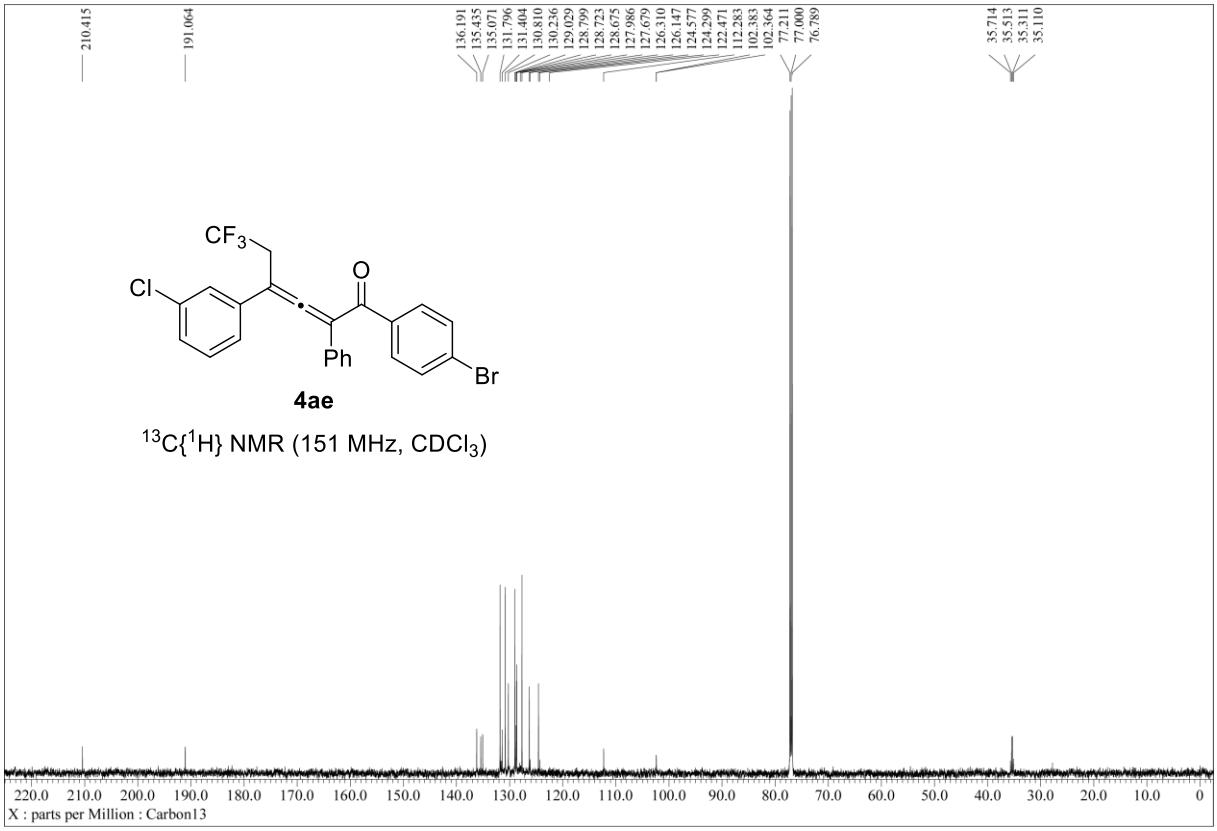
4ad

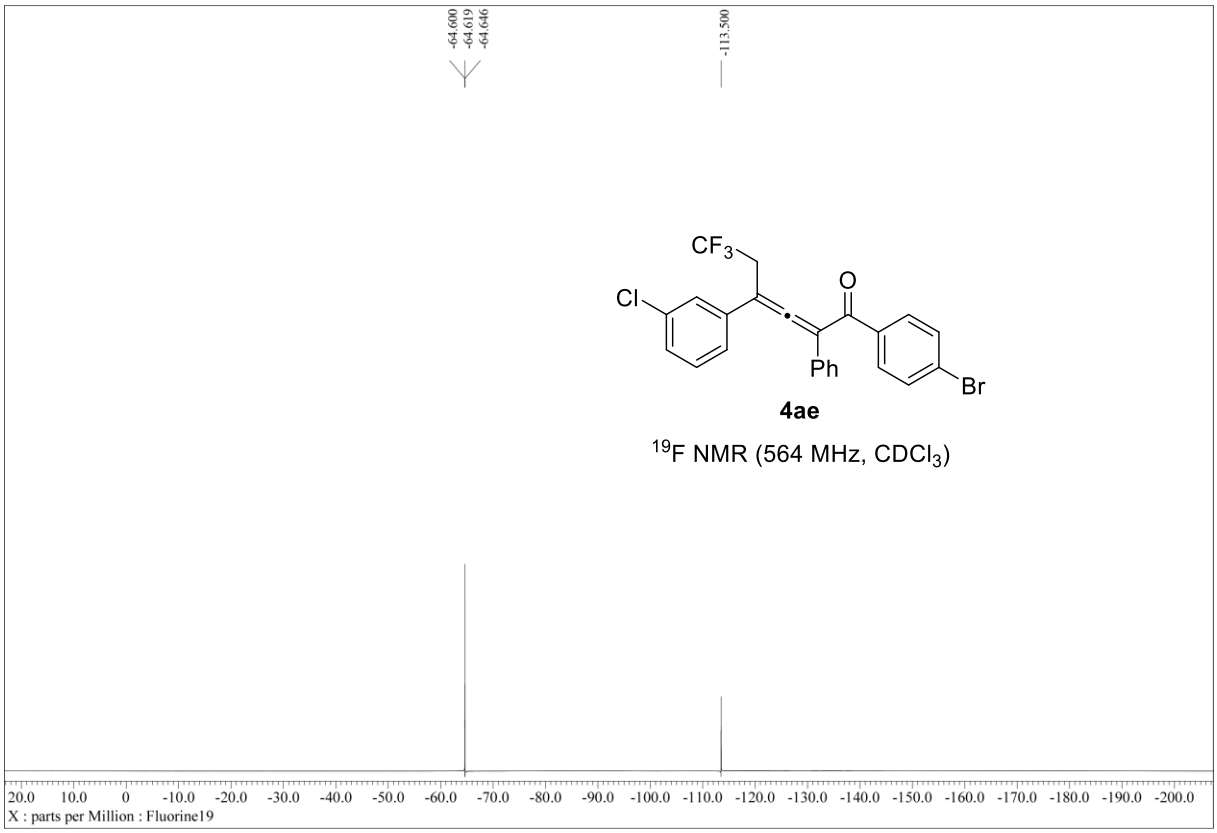
^{1}H NMR (600 MHz, $CDCl_3$)


211.085
191.562
159.889
136.536
132.045
131.595
130.734
128.847
128.369
128.139
127.746
127.622
126.300
125.295
124.462
122.624
114.485
111.785
102.852
102.833
77.211
77.000
76.789
55.342
35.733
35.541
35.340
35.139
CF3
O
MeO
Ph
Br
4ad
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.527
-64.546
-64.561
-113.500
CF3
O
MeO
Ph
Br
4ad
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

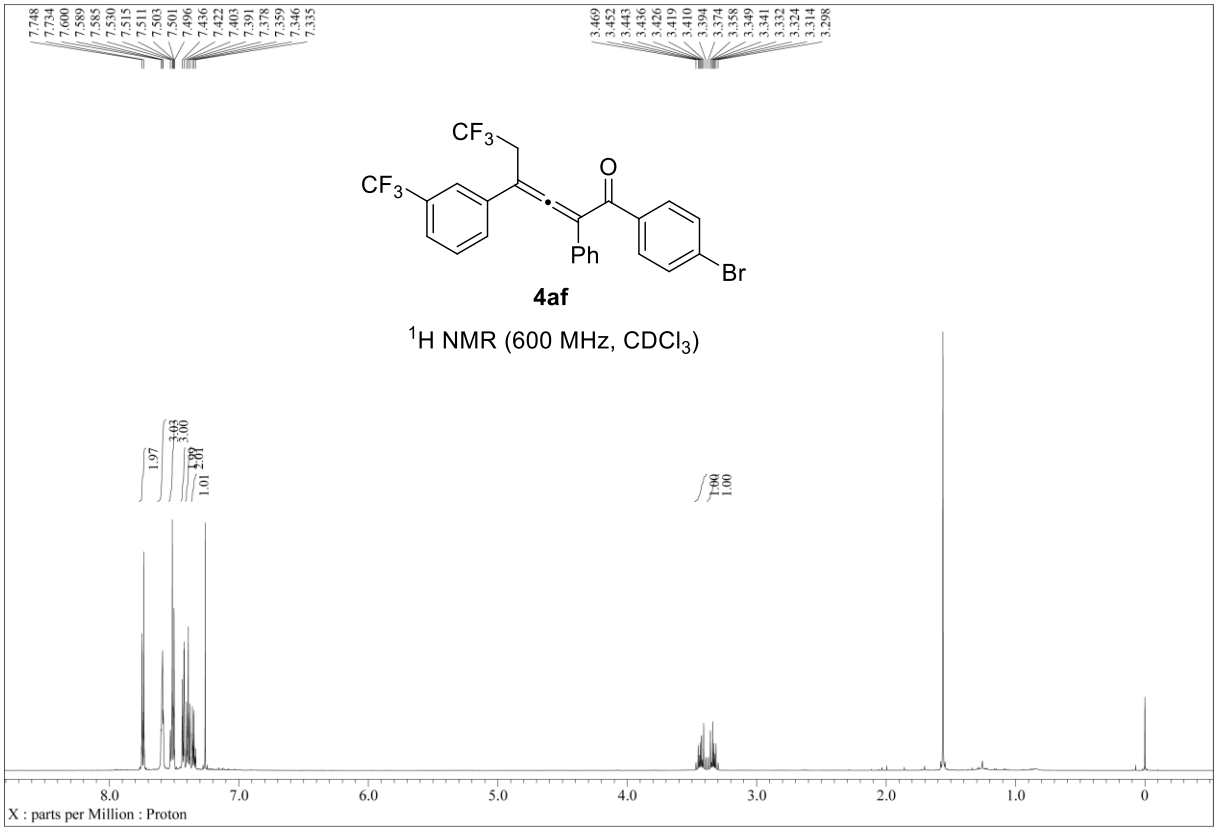

7.742
7.728
7.514
7.499
7.446
7.434
7.405
7.393
7.379
7.358
7.343
7.339
7.336
7.325
7.320
7.315
7.309
7.280
7.276
7.269
7.263
7.260
3.418
3.401
3.391
3.387
3.381
3.378
3.374
3.367
3.358
3.344
3.339
3.322
3.319
3.305
3.300
3.294
3.289
3.286
3.282
3.273
3.269
3.263
3.242
CF3
Cl
O
Ph
Br
4ae
1H NMR (600 MHz, CDCl3)
4.06
1.98
2.06
2.03
2.02
1.45
1.00
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


210.415
191.064
136.191
135.435
135.071
131.796
131.404
130.810
130.236
129.029
128.799
128.723
128.675
127.986
127.679
126.310
126.147
124.577
124.299
122.471
112.283
102.383
102.364
77.211
77.000
76.789
35.714
35.513
35.311
35.110
CF3
Cl
O
Ph
Br
4ae
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



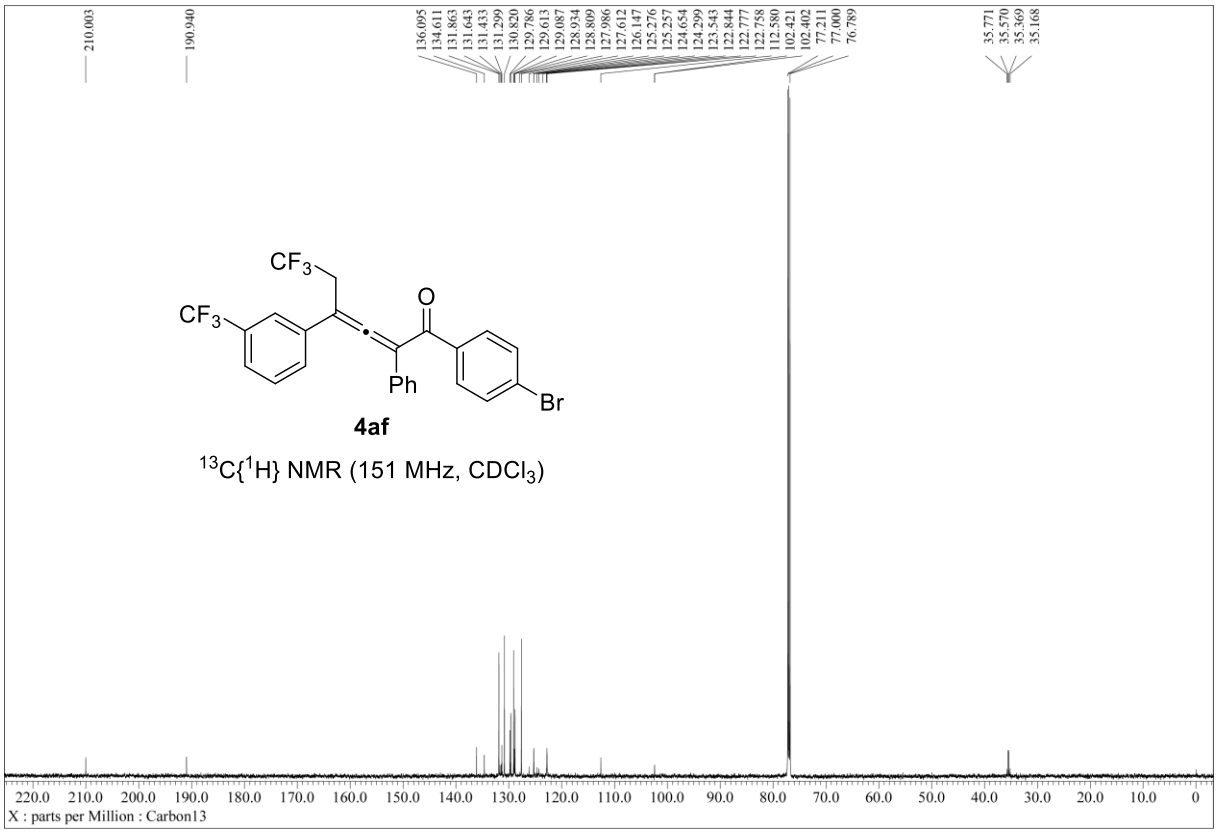
4ae

^{19}F NMR (564 MHz, $CDCl_3$)



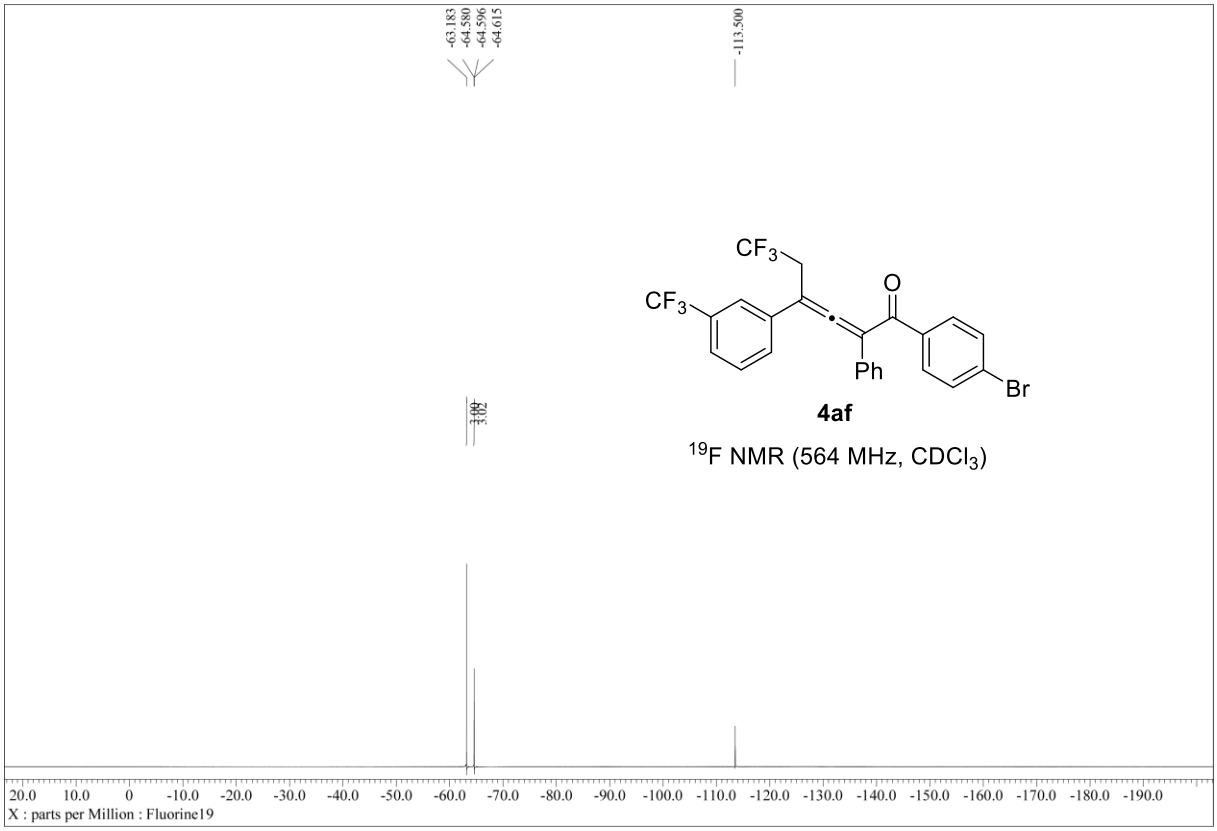
4af

^{1}H NMR (600 MHz, $CDCl_3$)



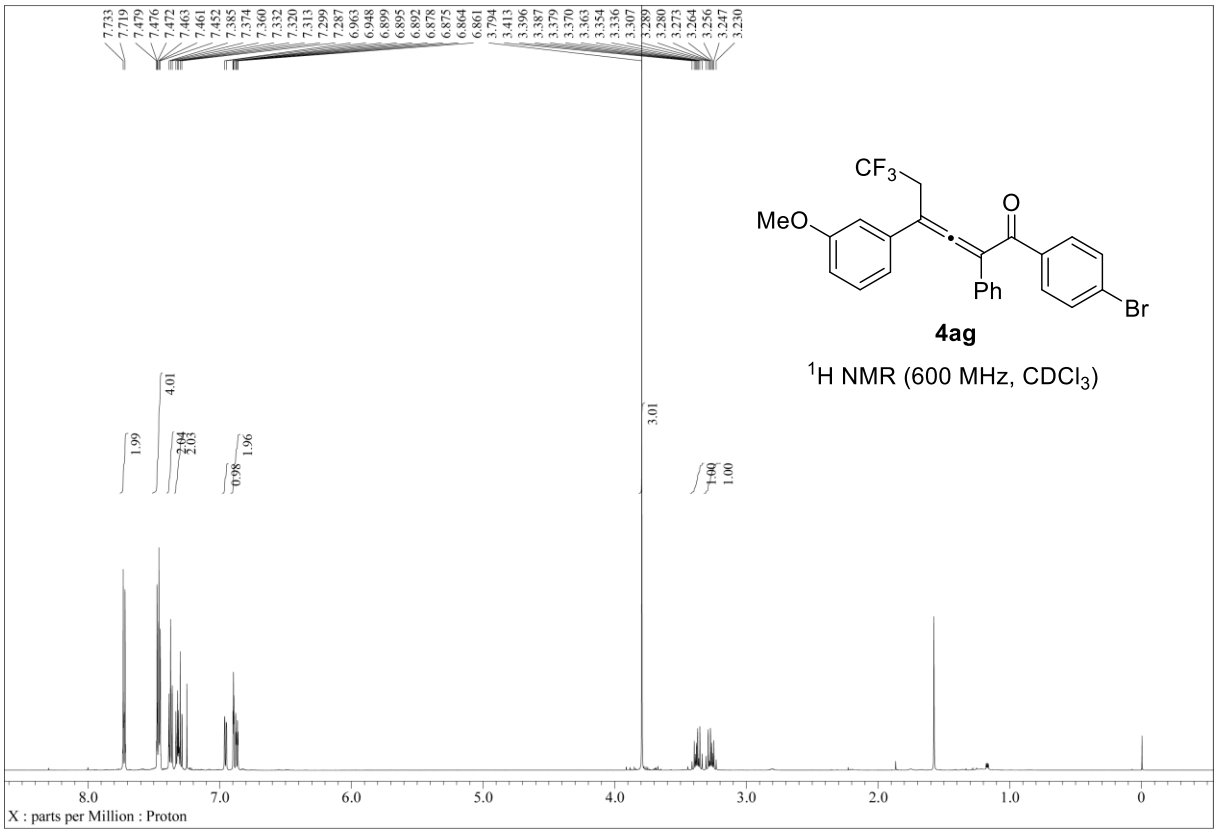
4af

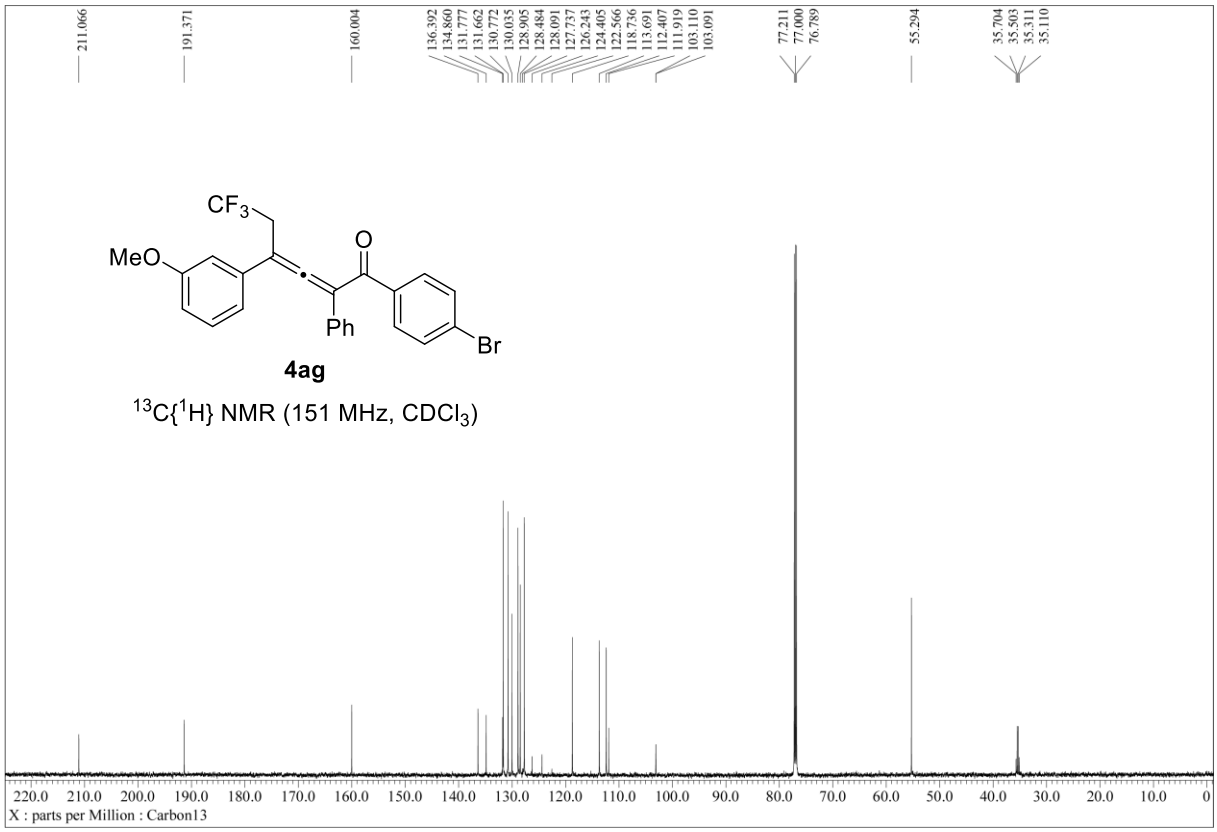
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

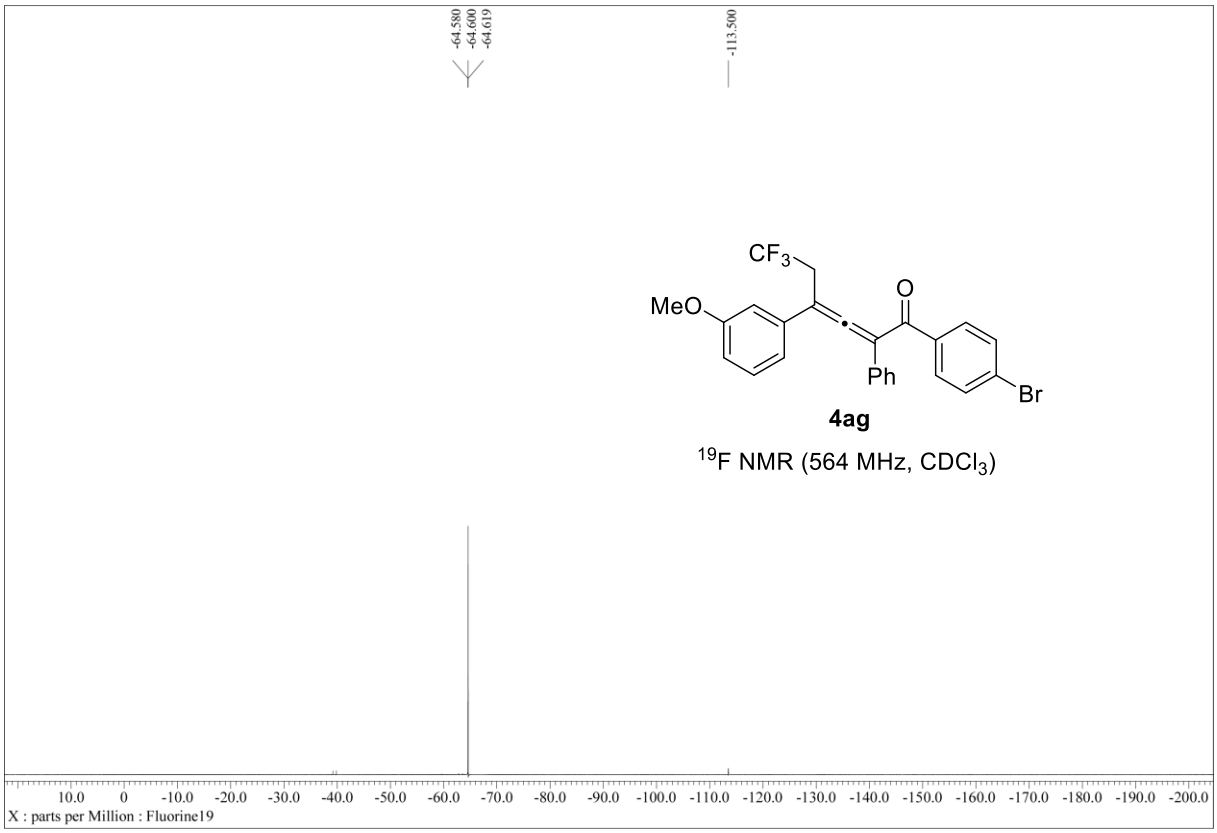


4af

^{19}F NMR (564 MHz, $CDCl_3$)

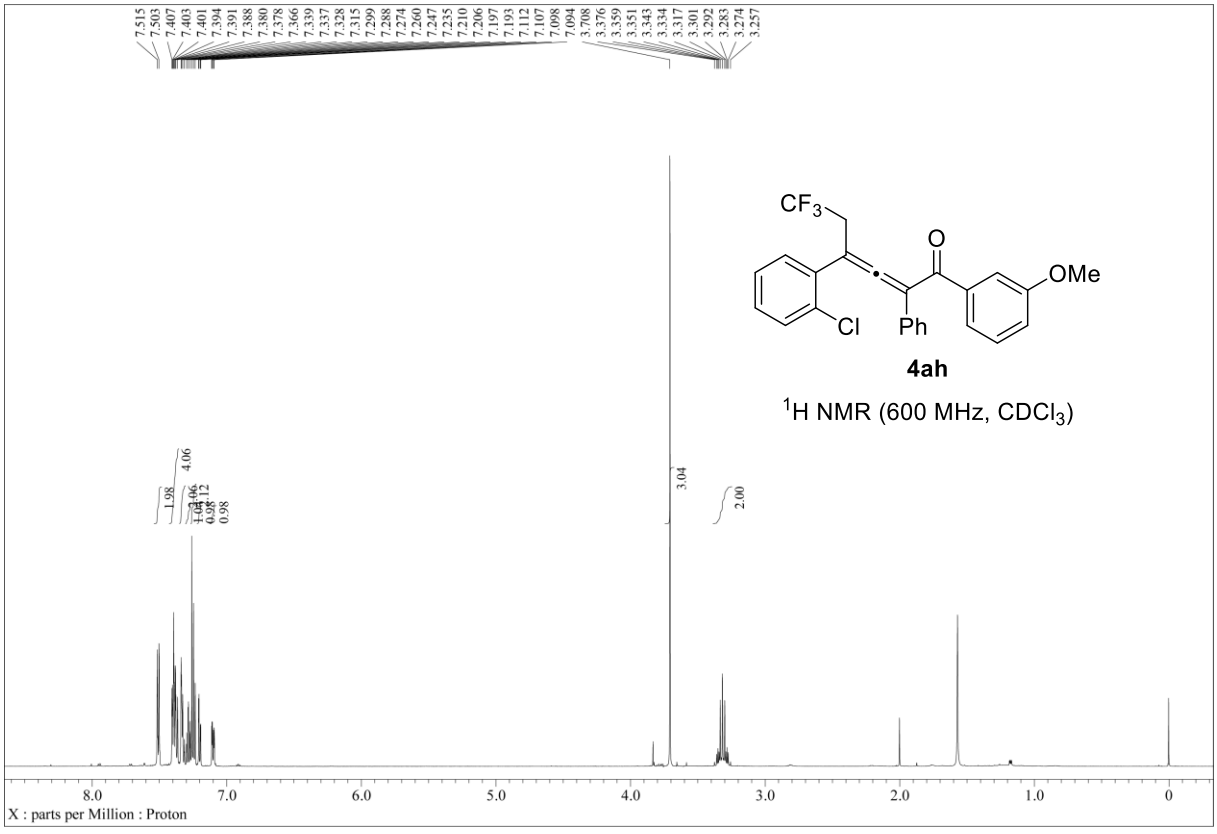

7.733
7.719
7.479
7.476
7.472
7.463
7.461
7.452
7.385
7.374
7.360
7.332
7.320
7.313
7.299
7.287
6.963
6.948
6.899
6.895
6.892
6.878
6.875
6.864
6.861
3.794
3.413
3.396
3.387
3.379
3.370
3.363
3.354
3.336
3.307
3.289
3.280
3.273
3.264
3.256
3.247
3.230
4.01
1.99
2.04
2.03
1.96
0.98
3.01
1.00
1.00
CF3
MeO
O
Ph
Br
4ag
1H NMR (600 MHz, CDCl3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


211.066
191.371
160.004
136.392
134.860
131.777
131.662
130.772
130.035
128.905
128.484
128.091
127.737
126.243
124.405
122.566
118.736
113.691
112.407
111.919
103.110
103.091
77.211
77.000
76.789
55.294
35.704
35.503
35.311
35.110
CF3
MeO
O
Ph
Br
4ag
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



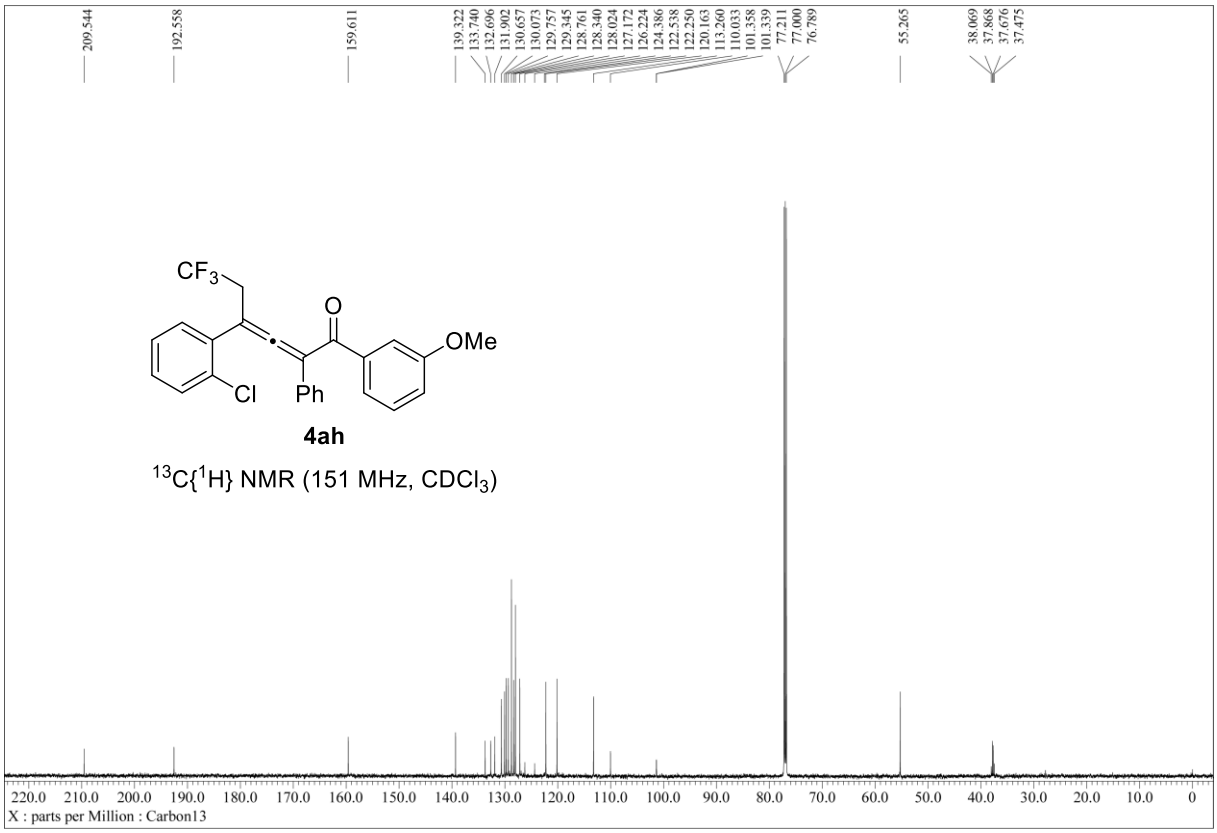
4ag

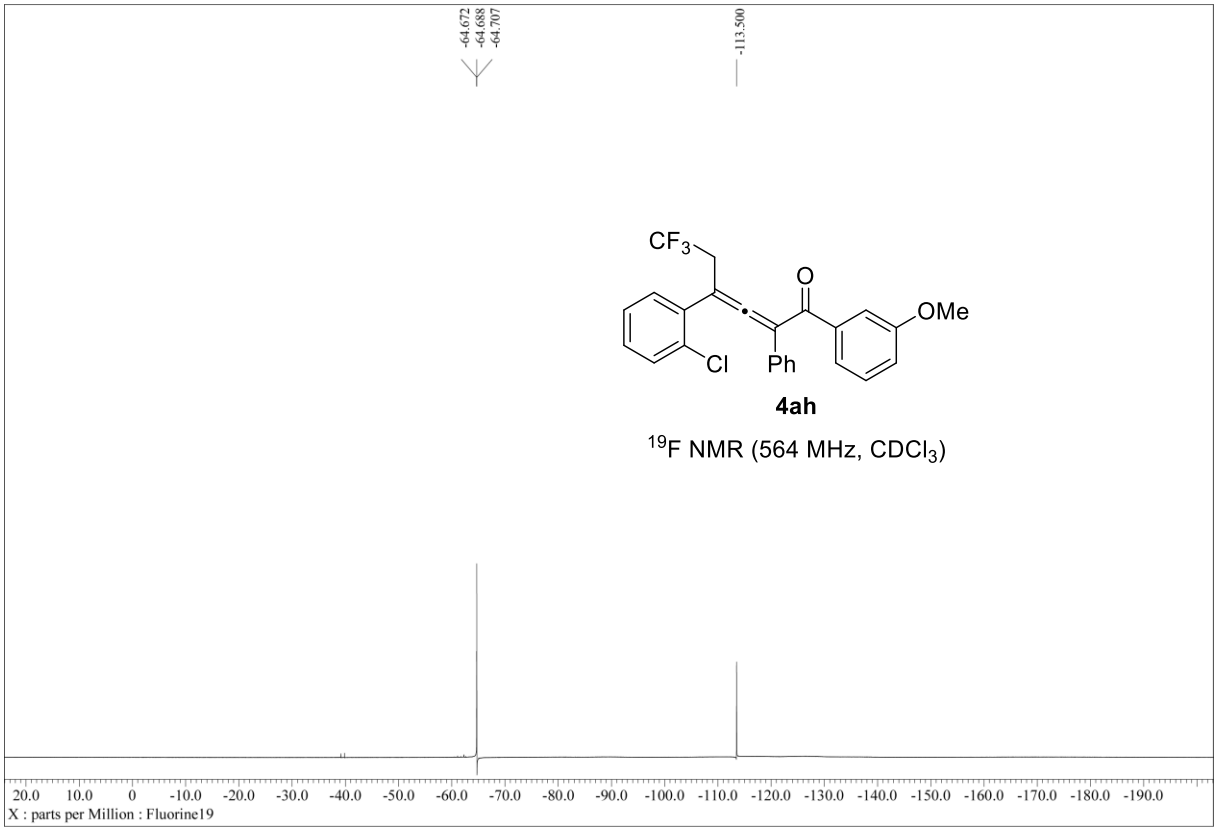
^{19}F NMR (564 MHz, $CDCl_3$)

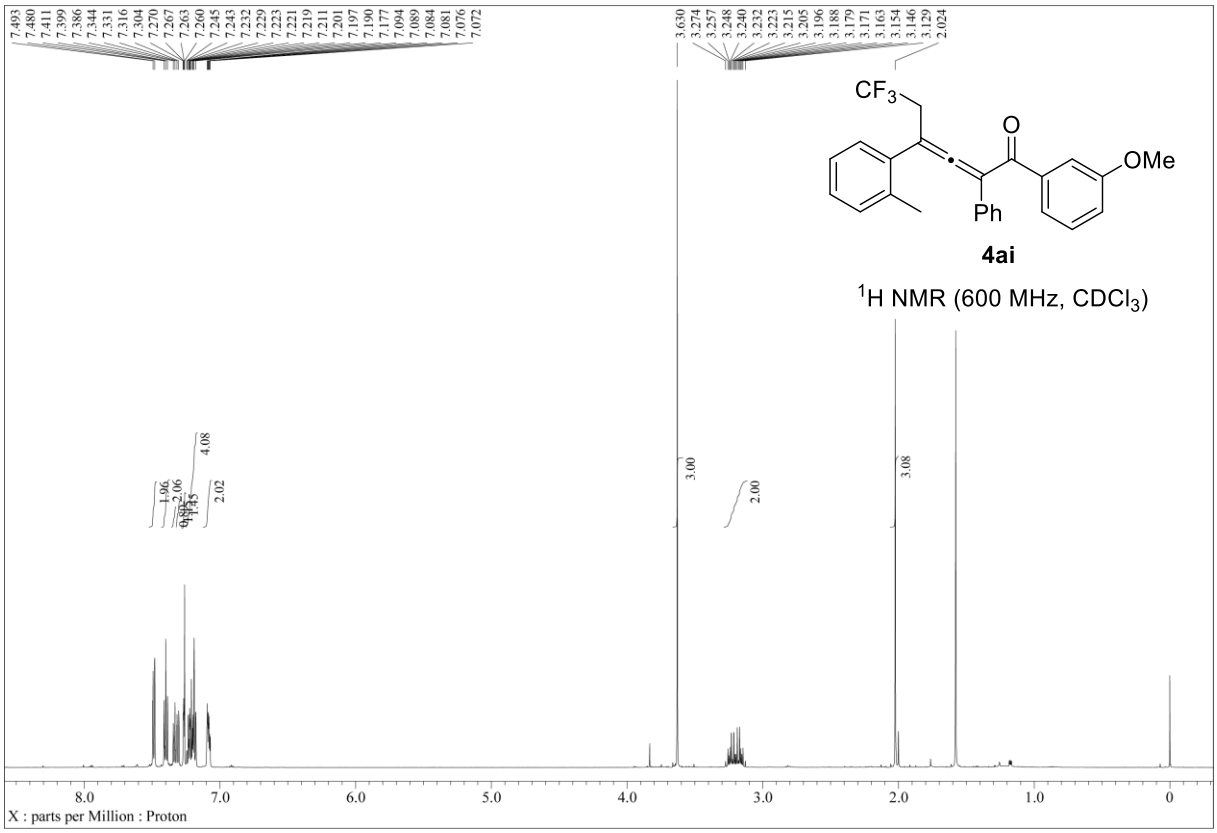


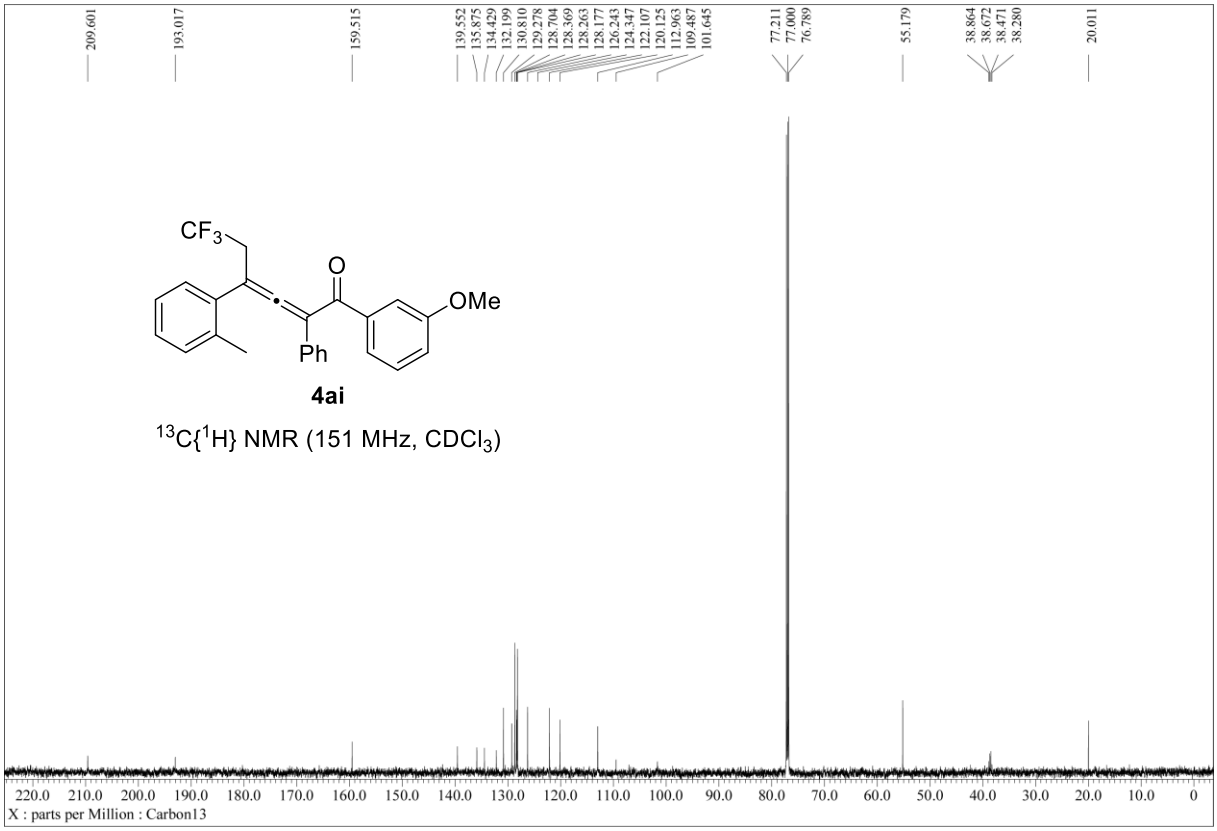
4ah

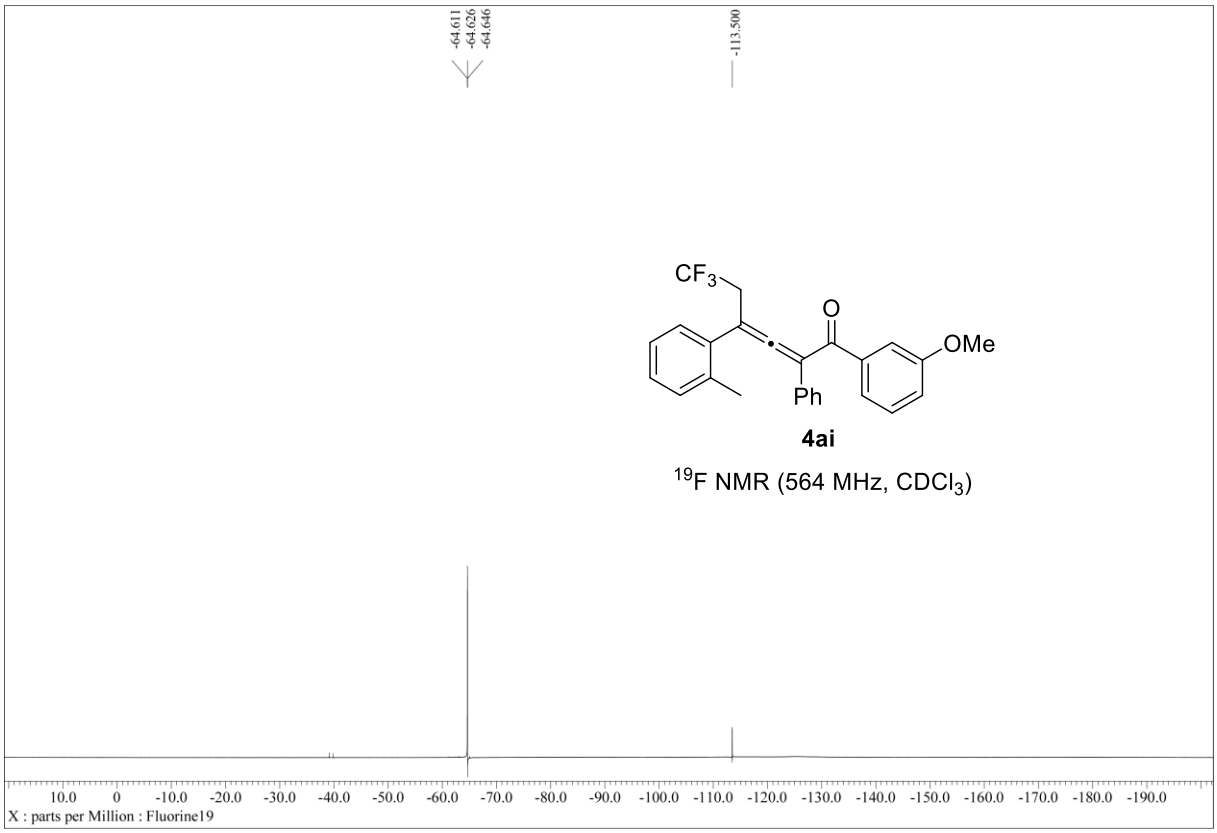
^{1}H NMR (600 MHz, $CDCl_3$)


209.544
192.558
159.611
139.322
133.740
132.696
131.902
130.657
130.073
129.757
129.345
128.761
128.340
128.024
127.172
126.224
124.386
122.538
122.250
120.163
113.260
110.033
101.358
101.339
77.211
77.000
76.789
55.265
38.069
37.868
37.676
37.475
CF3
O
OMe
Cl
Ph
4ah
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.672
-64.688
-64.707
-113.500
CF3
O
OMe
Cl
Ph
4ah
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

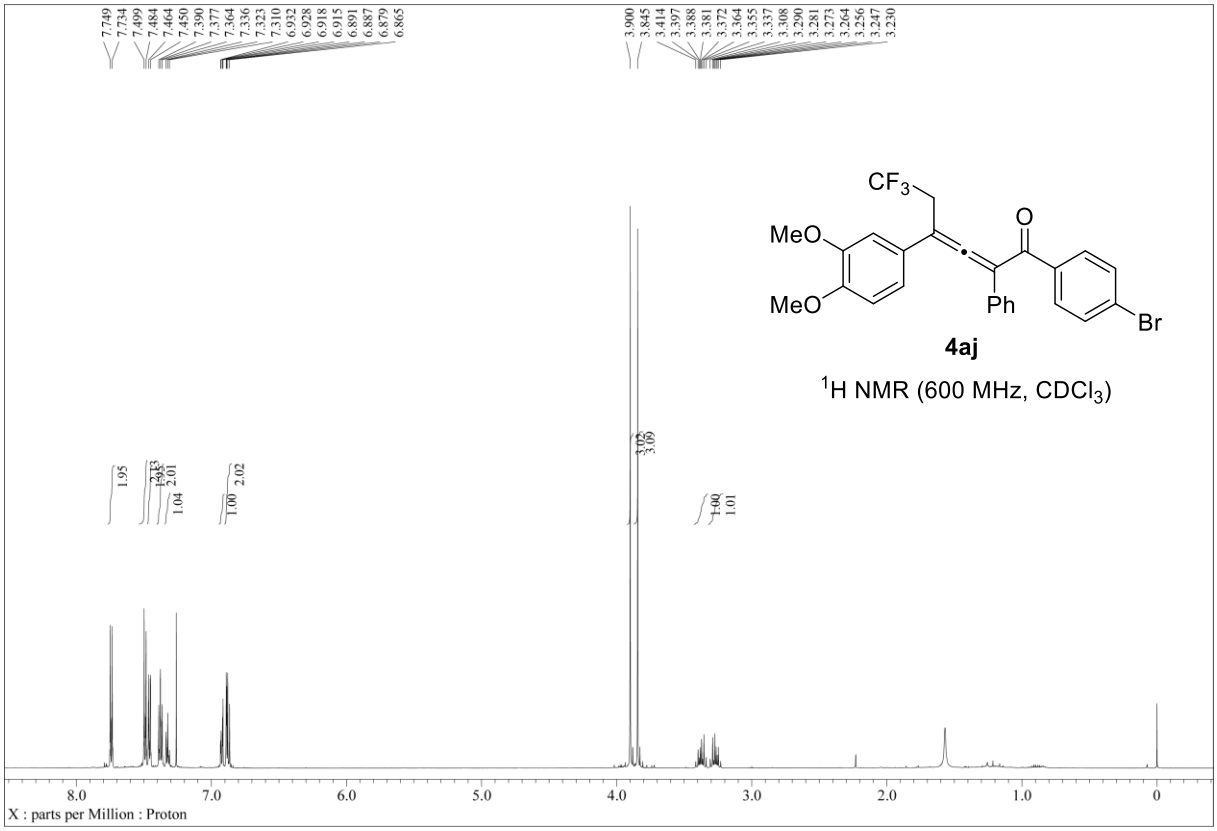

CF3
O
OMe
Ph
4ai
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


CF3
O
OMe
Ph
4ai
13C{1H} NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



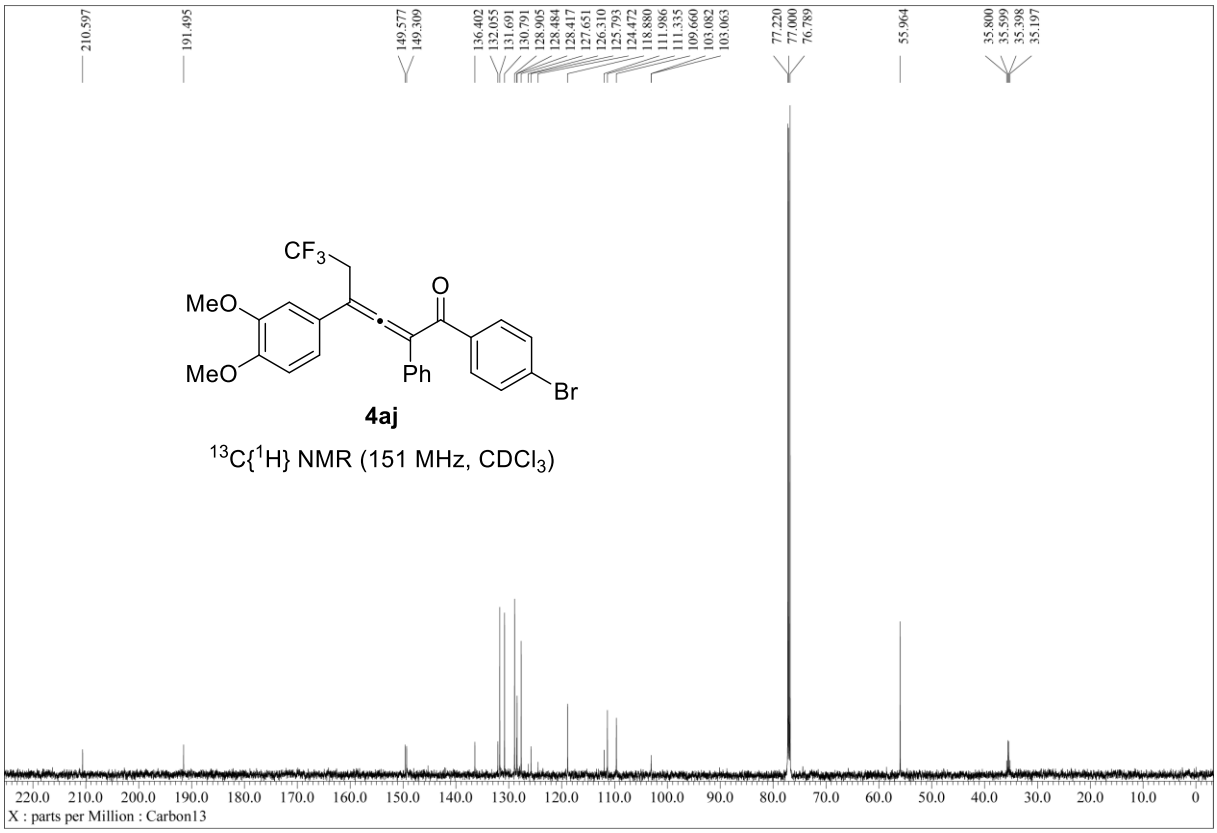
4ai

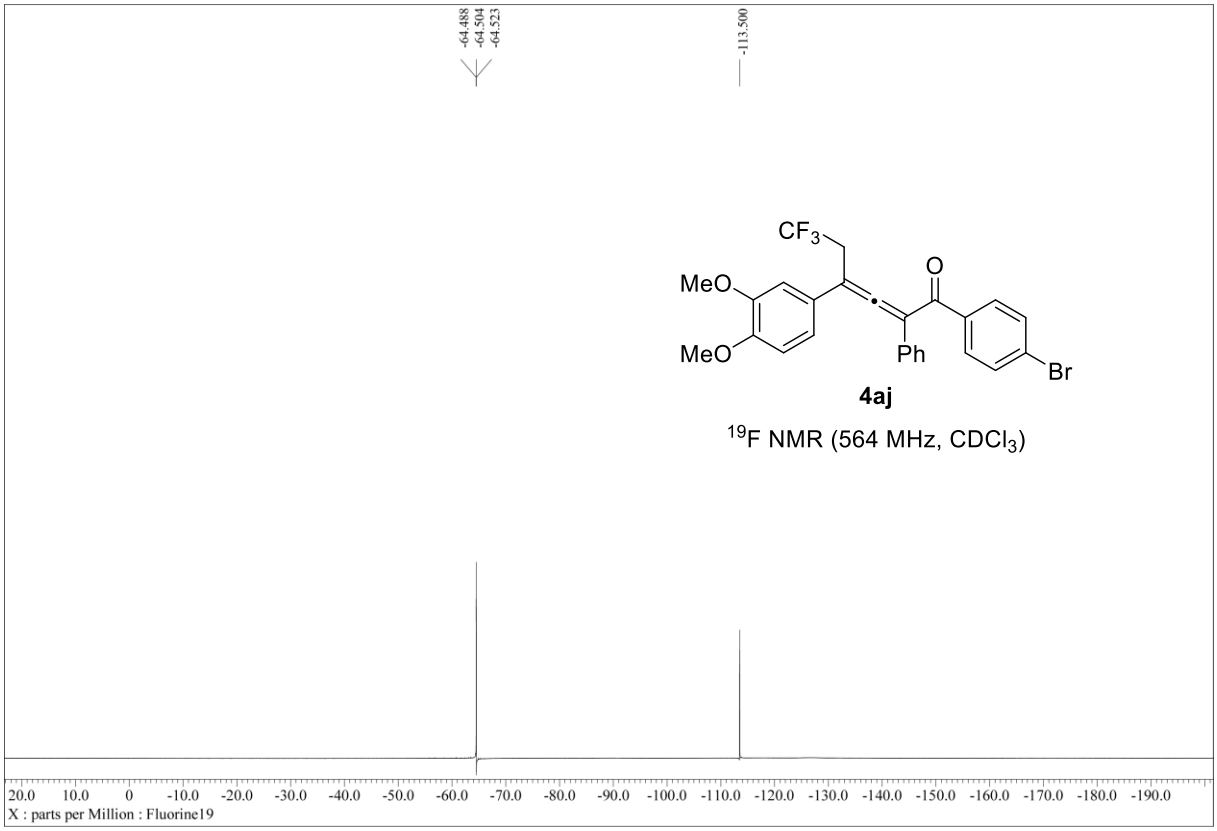
^{19}F NMR (564 MHz, $CDCl_3$)

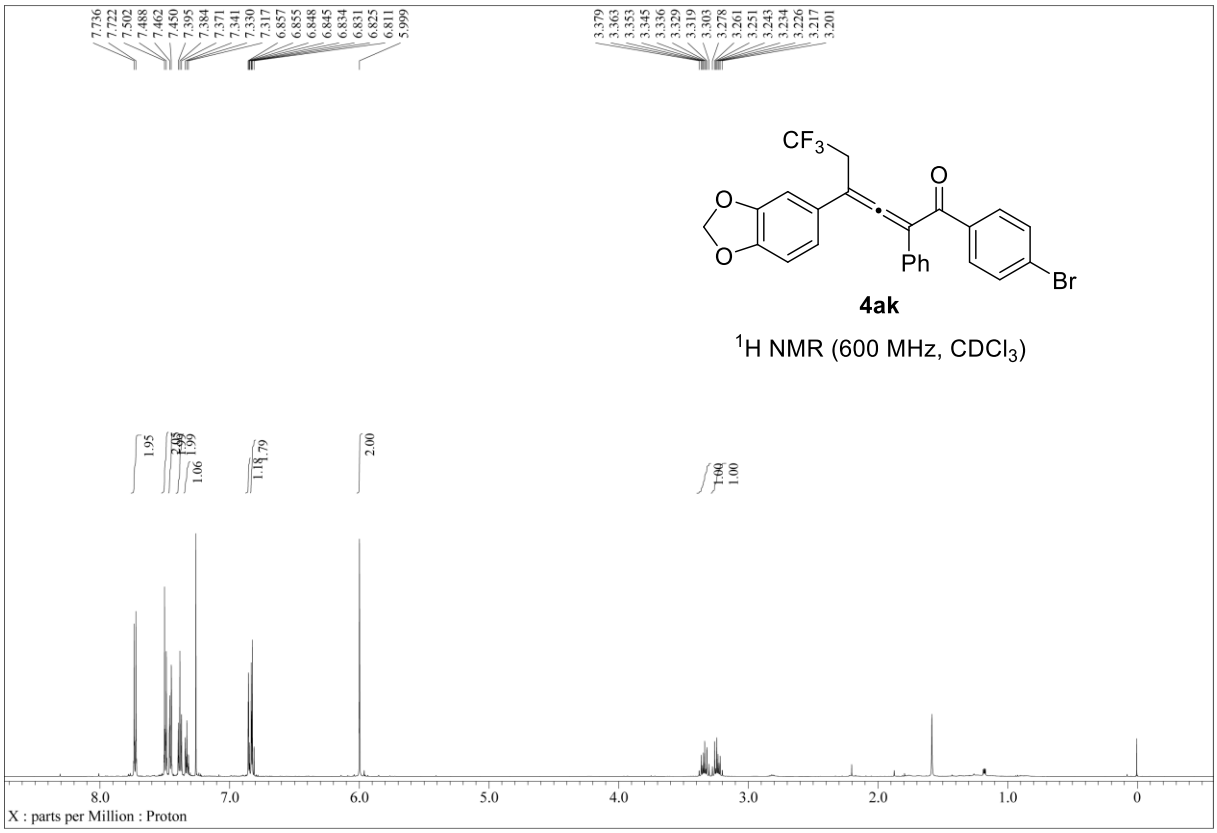


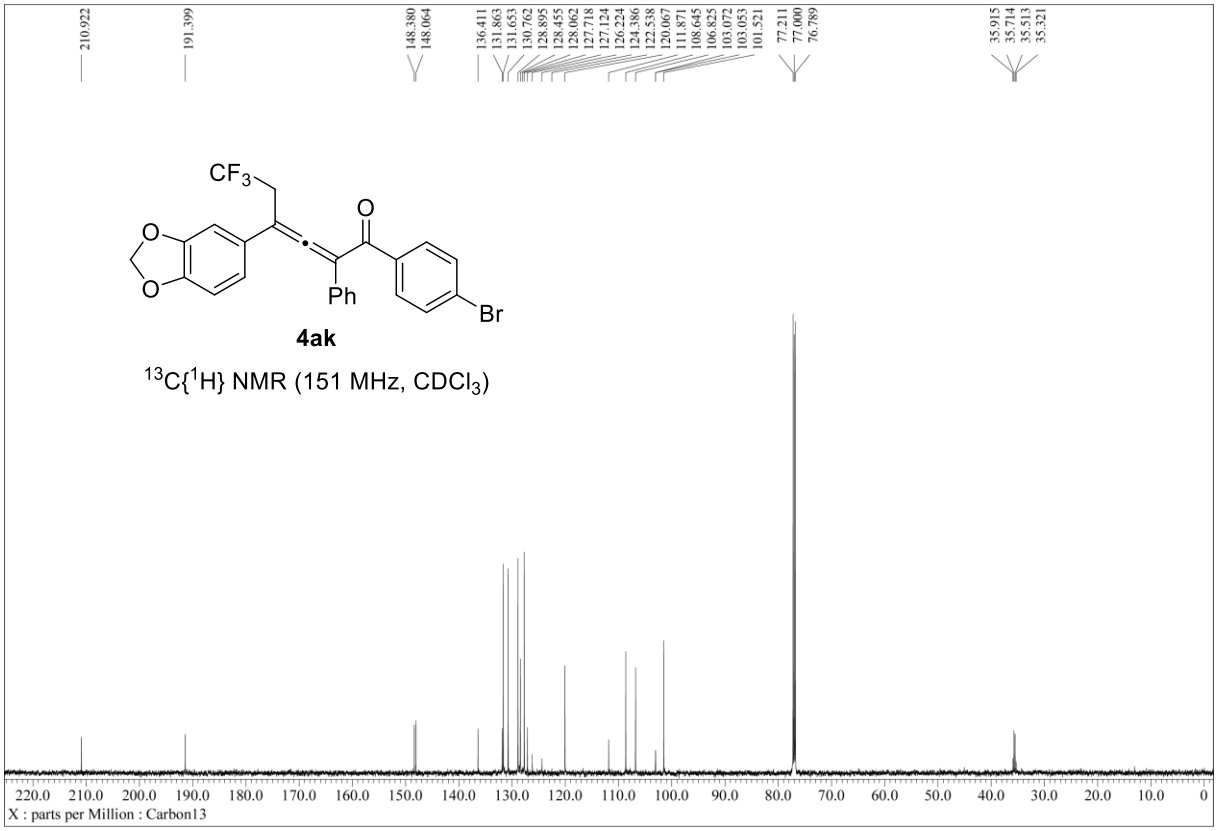
4aj

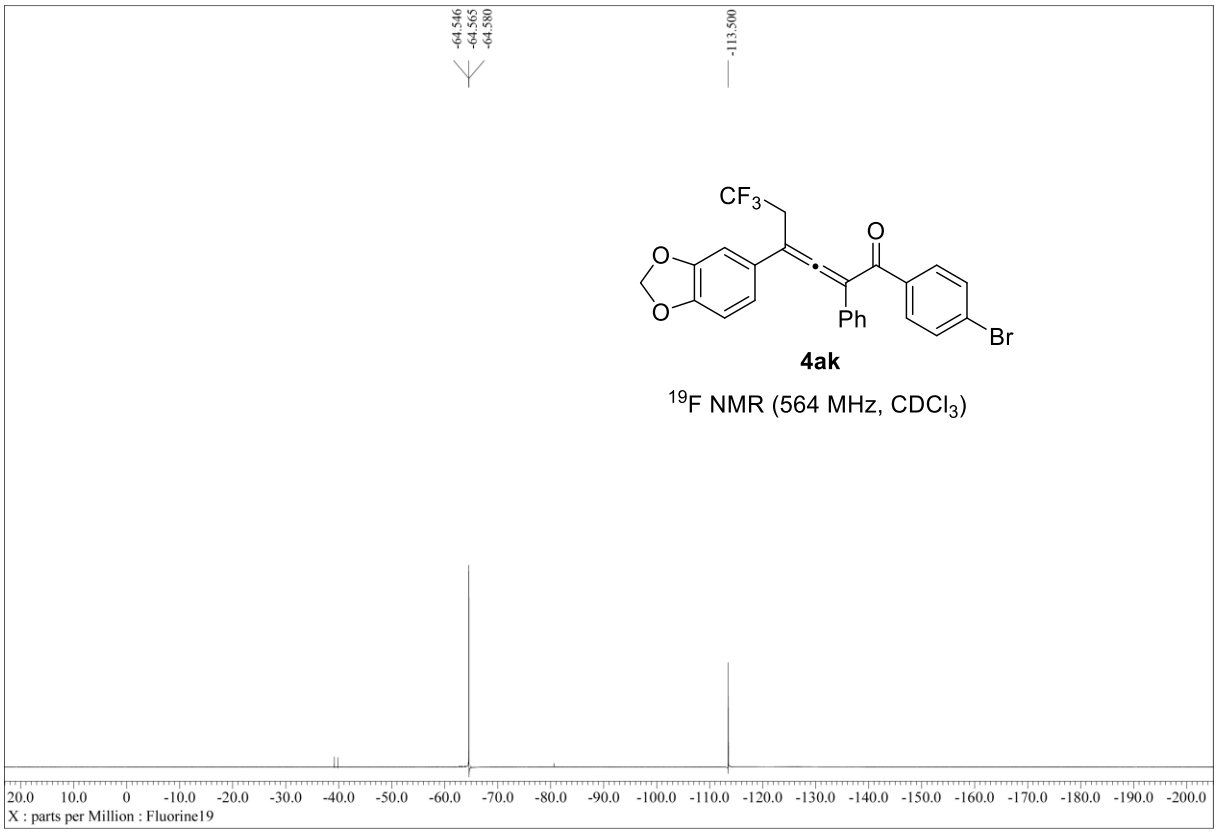
^{1}H NMR (600 MHz, $CDCl_3$)


210.597
191.495
149.577
149.309
136.402
132.055
131.691
130.791
128.905
128.484
128.417
127.651
126.310
125.793
124.472
118.880
111.986
111.335
109.660
103.082
103.063
77.220
77.000
76.789
55.964
35.800
35.599
35.398
35.197
CF3
MeO
MeO
O
Ph
Br
4aj
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.488
-64.504
-64.523
-113.500
CF3
MeO
MeO
O
Ph
Br
4aj
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

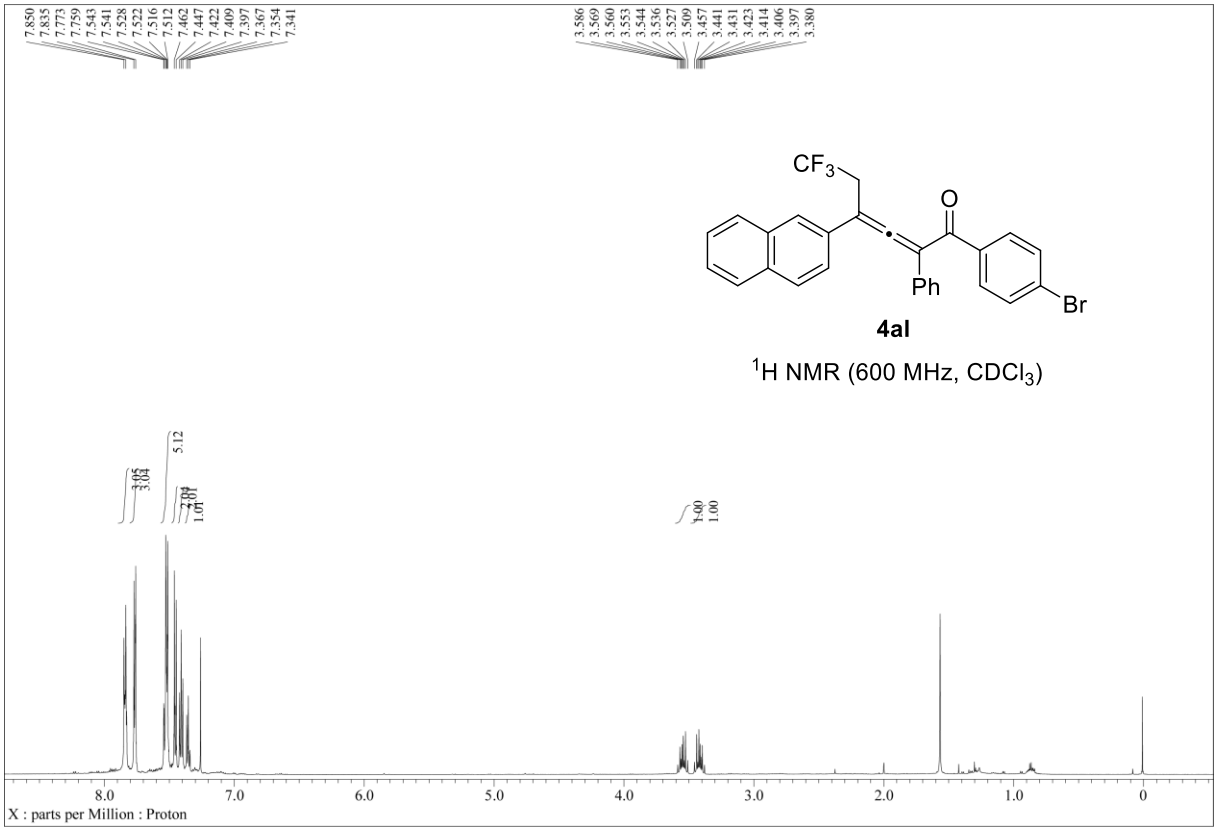

7.736
7.722
7.502
7.488
7.462
7.450
7.395
7.384
7.371
7.341
7.330
7.317
6.857
6.855
6.848
6.845
6.834
6.831
6.825
6.811
5.999
3.379
3.363
3.353
3.345
3.336
3.329
3.319
3.303
3.278
3.261
3.251
3.243
3.234
3.226
3.217
3.201
CF3
O
O
O
Ph
Br
4ak
1H NMR (600 MHz, CDCl3)
1.95
2.05
1.99
1.06
1.18
1.79
2.00
1.00
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


210.922
191.399
148.380
148.064
136.411
131.863
131.653
130.762
128.895
128.455
128.062
127.718
127.124
126.224
124.386
122.538
120.067
111.871
108.645
106.825
103.072
103.053
101.521
77.211
77.000
76.789
35.915
35.714
35.513
35.321
CF3
O
O
O
Ph
Br
4ak
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



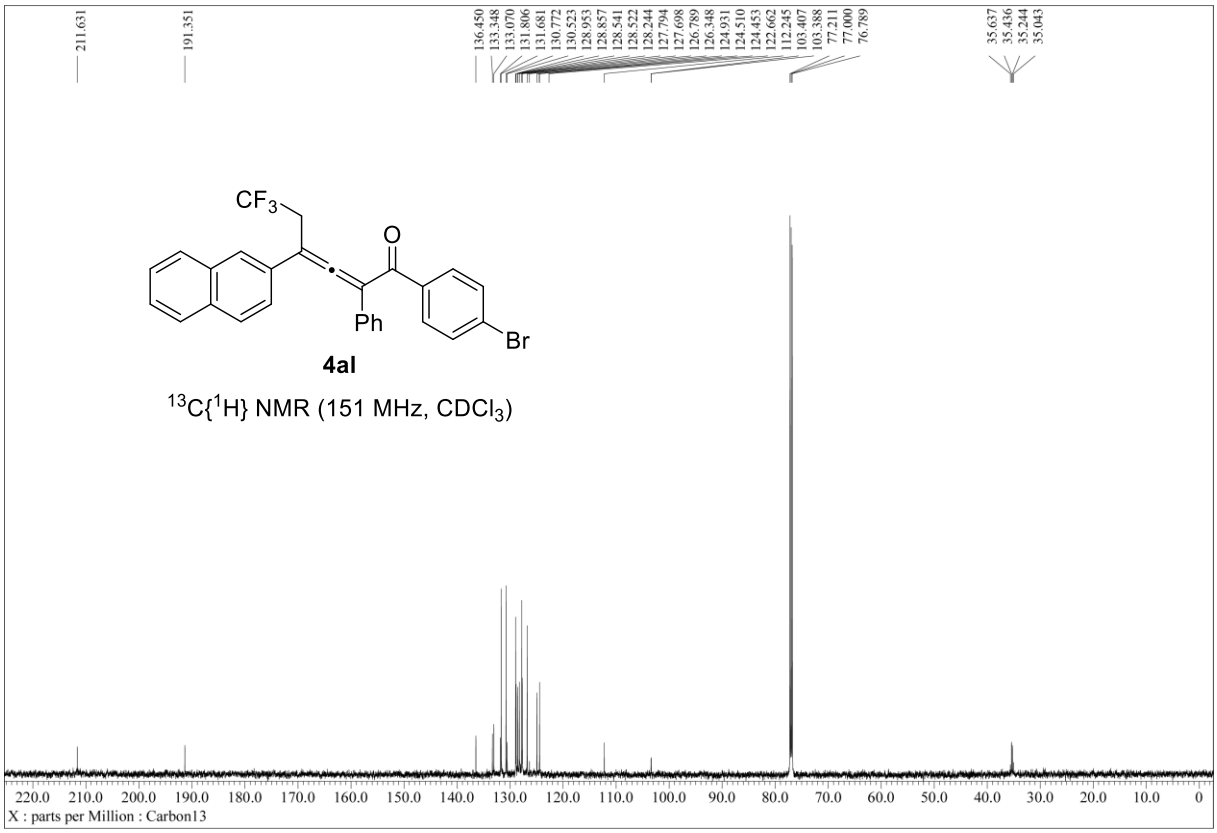
4ak

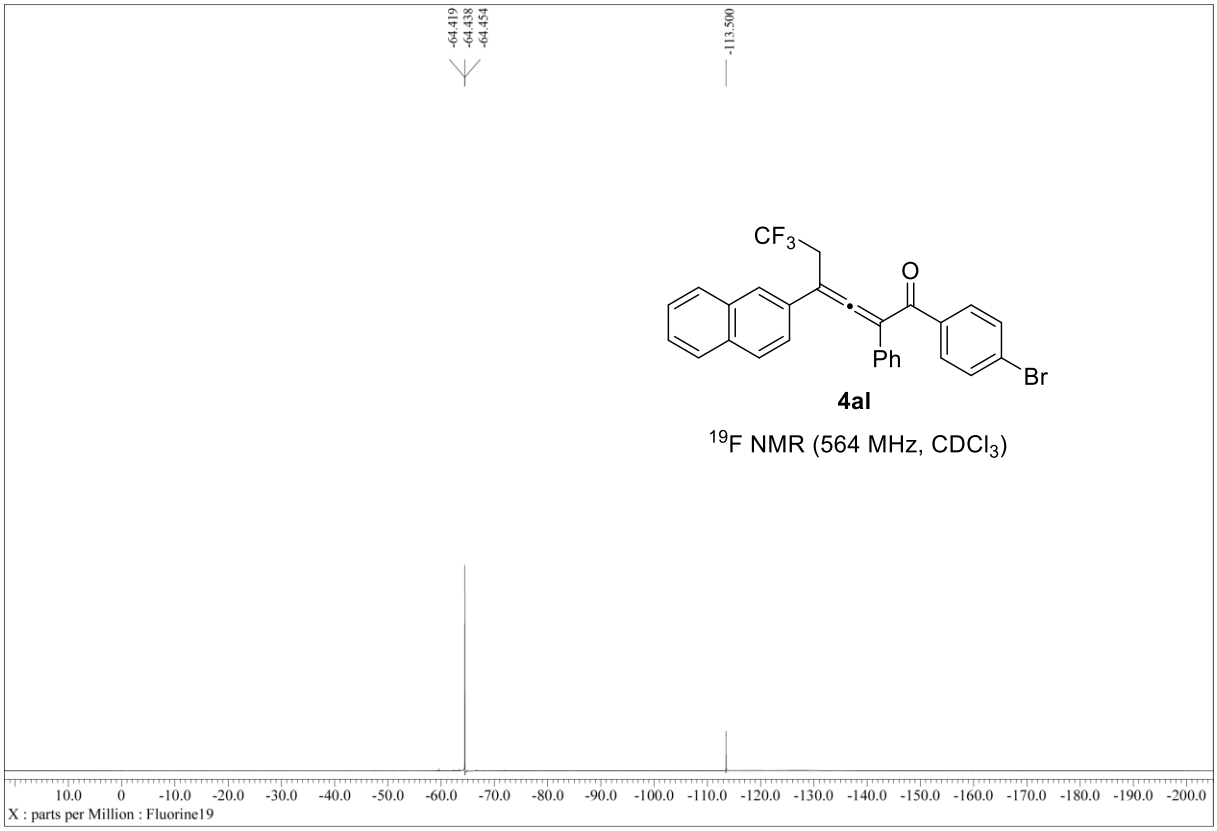
^{19}F NMR (564 MHz, $CDCl_3$)

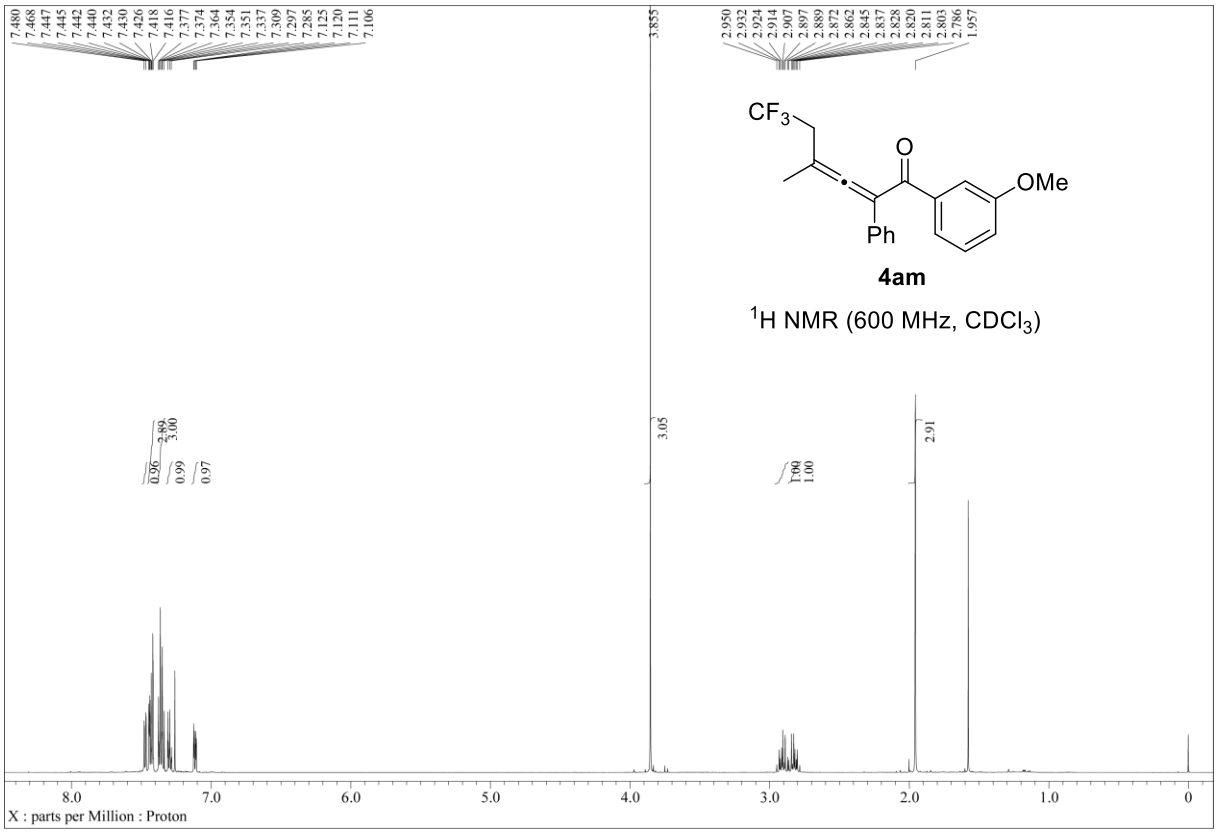


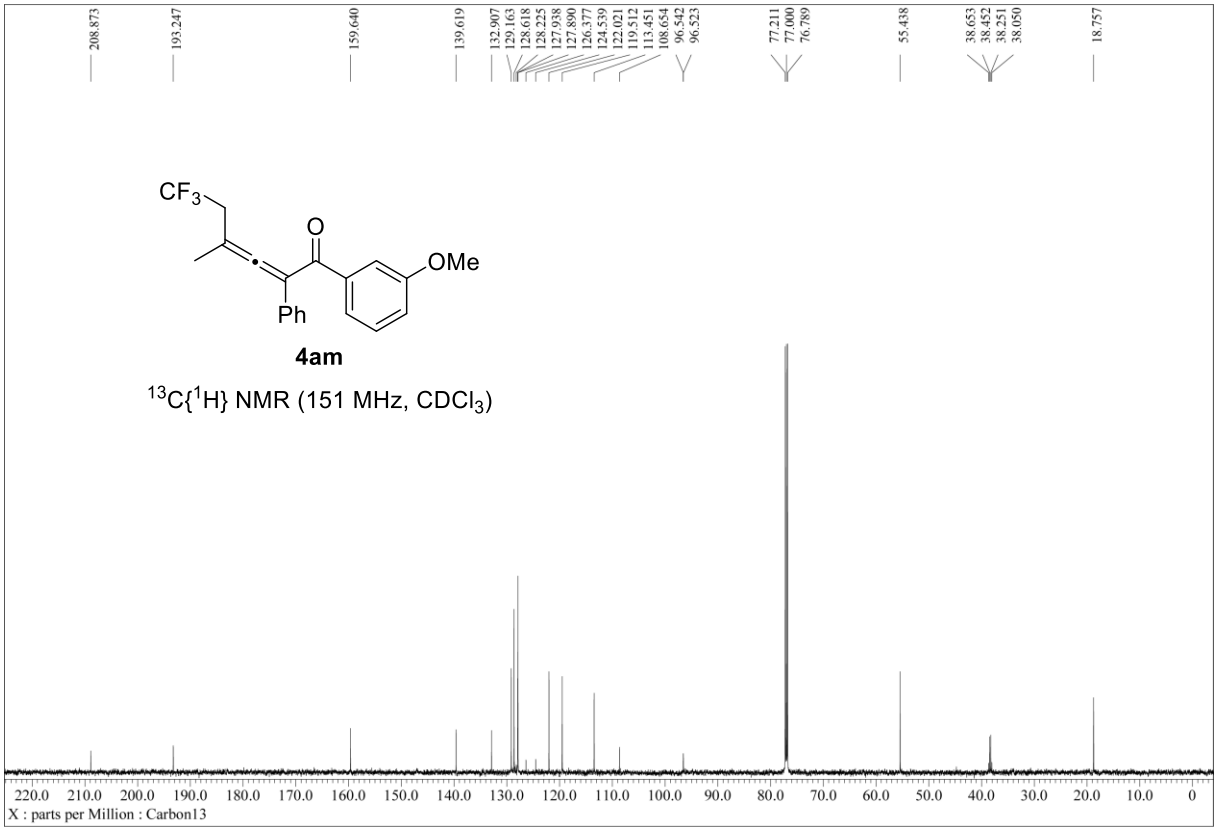
4al

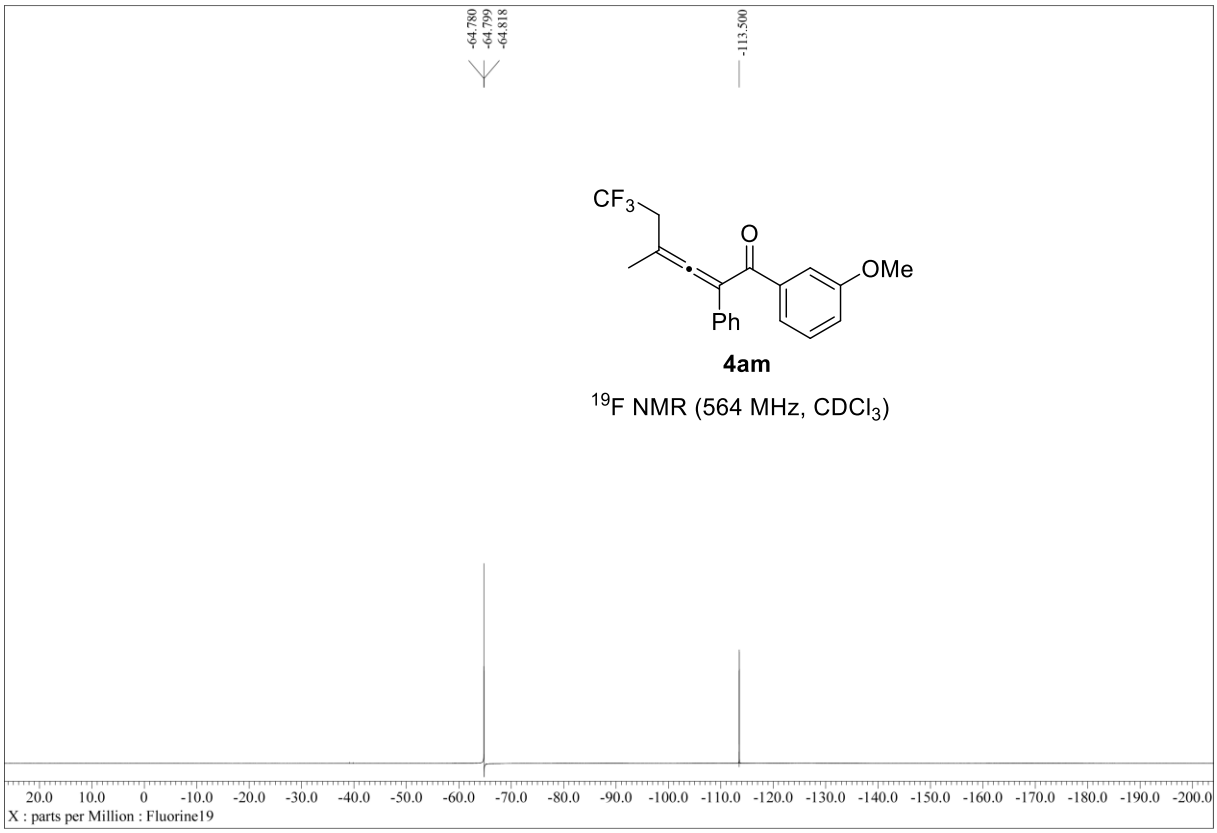
^{1}H NMR (600 MHz, $CDCl_3$)


211.631
191.351
136.450
133.348
133.070
131.806
131.681
130.772
130.523
128.953
128.857
128.541
128.522
128.244
127.794
127.698
126.789
126.348
124.931
124.510
124.453
122.662
112.245
103.407
103.388
77.211
77.000
76.789
35.637
35.436
35.244
35.043
CF3
O
Ph
Br
4al
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.419
-64.438
-64.454
-113.500
CF3
O
Ph
Br
4al
19F NMR (564 MHz, CDCl3)
10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
X : parts per Million : Fluorine19

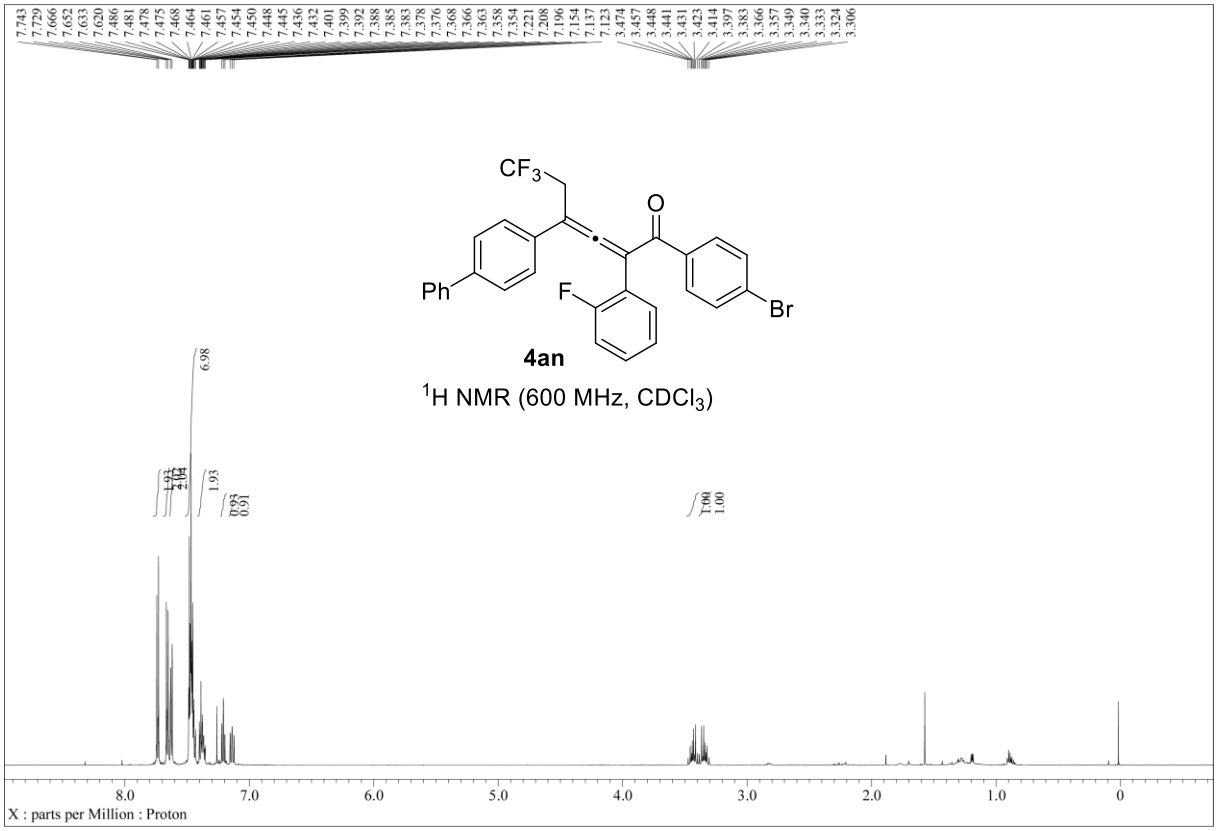

7.480
7.468
7.447
7.445
7.442
7.440
7.432
7.430
7.426
7.418
7.416
7.377
7.374
7.364
7.354
7.351
7.337
7.309
7.297
7.285
7.125
7.120
7.111
7.106
3.855
2.950
2.932
2.924
2.914
2.907
2.897
2.889
2.872
2.862
2.845
2.837
2.828
2.820
2.811
2.803
2.786
1.957
CF3
O
OMe
Ph
4am
1H NMR (600 MHz, CDCl3)
0.96
2.89
3.00
0.99
0.97
3.05
1.00
1.00
2.91
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


208.873
193.247
159.640
139.619
132.907
129.163
128.618
128.225
127.938
127.890
126.377
124.559
122.021
119.512
113.451
108.654
96.542
96.523
77.211
77.000
76.789
55.438
38.653
38.452
38.251
38.050
18.757
CF3
O
OMe
Ph
4am
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



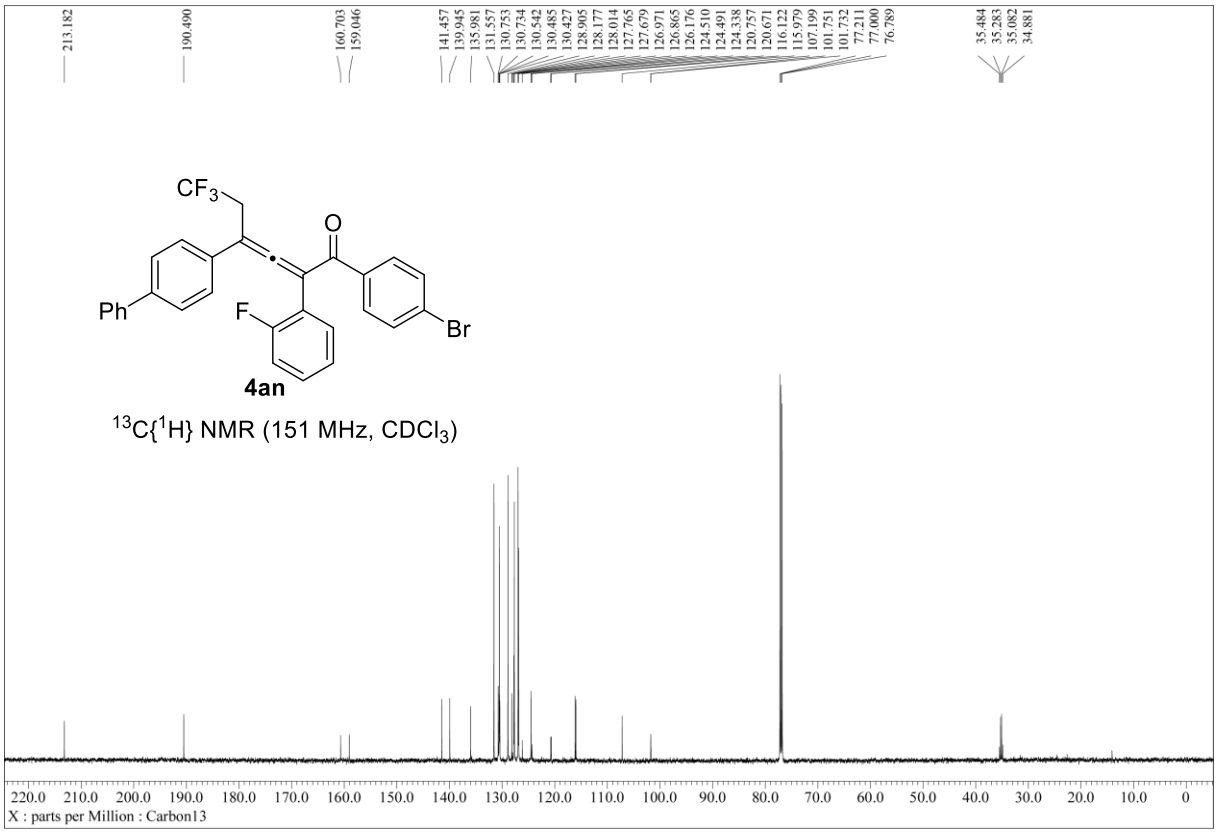
4am

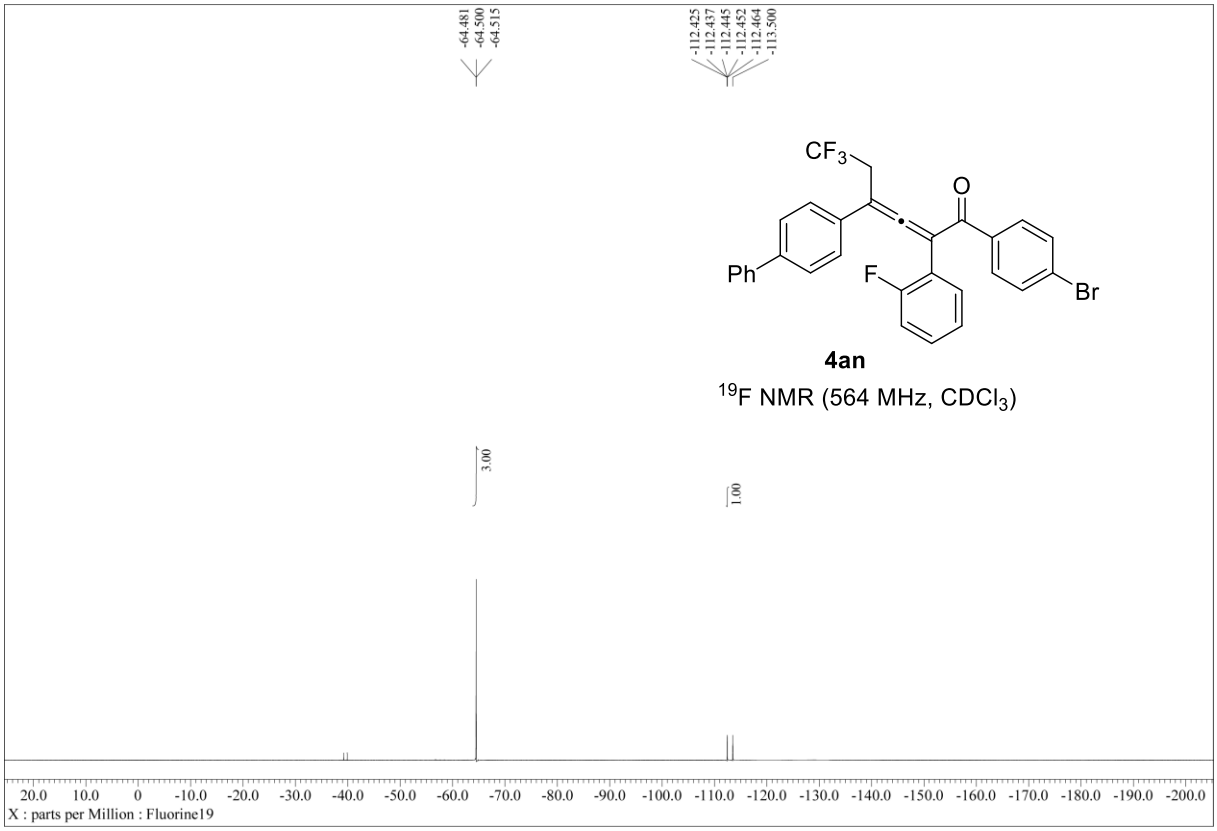
^{19}F NMR (564 MHz, $CDCl_3$)

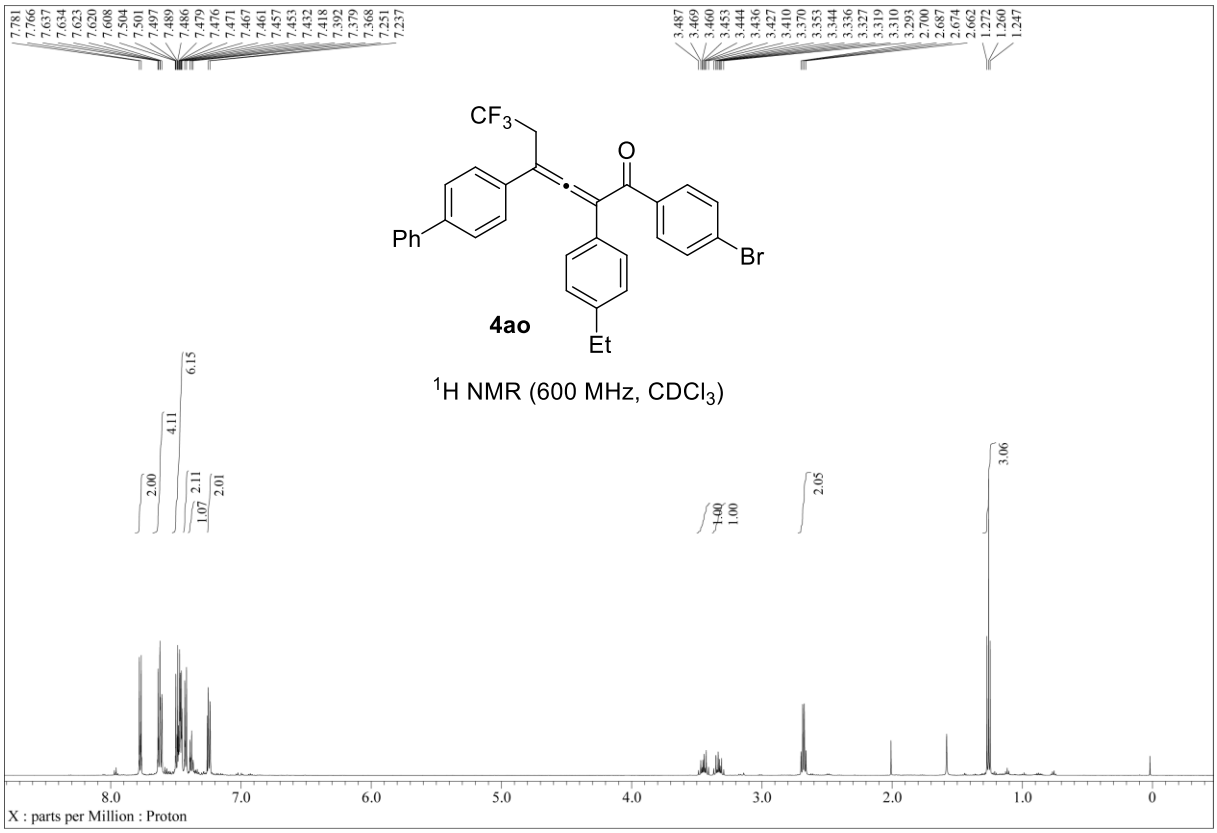


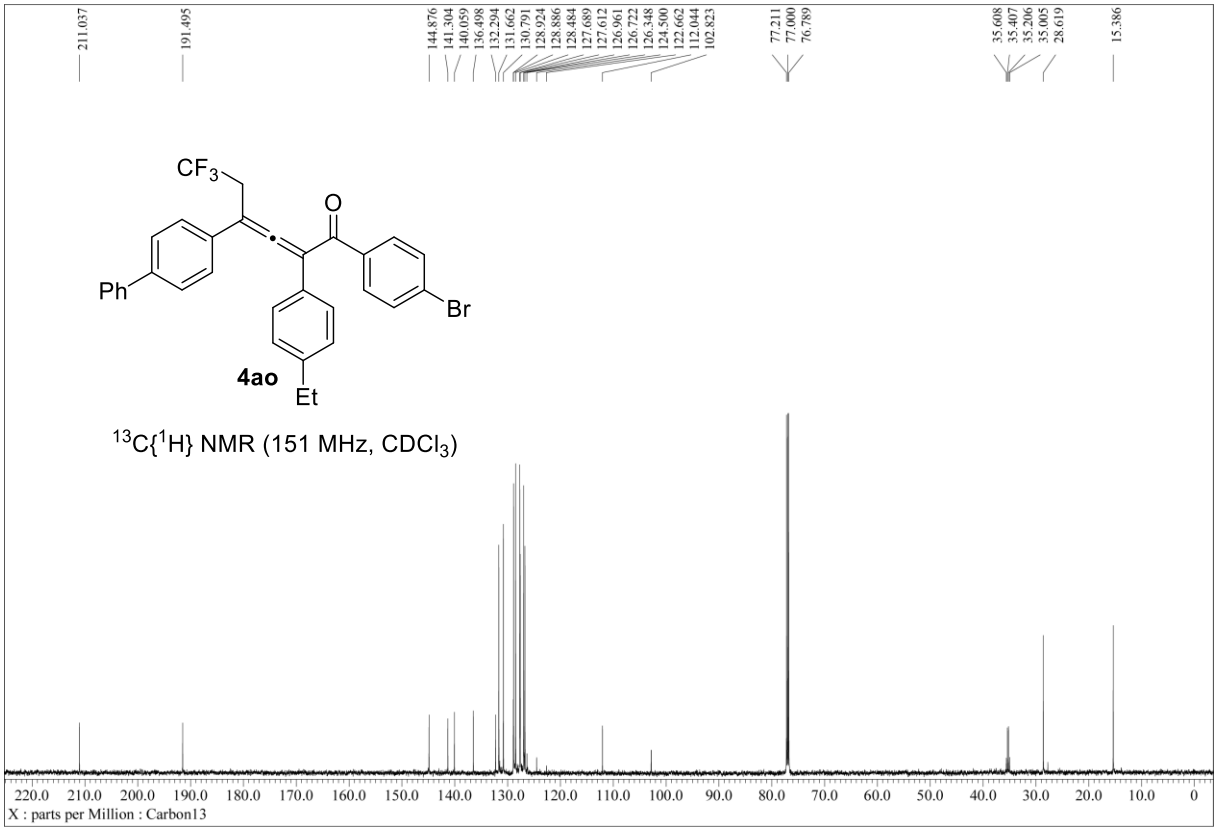
4an

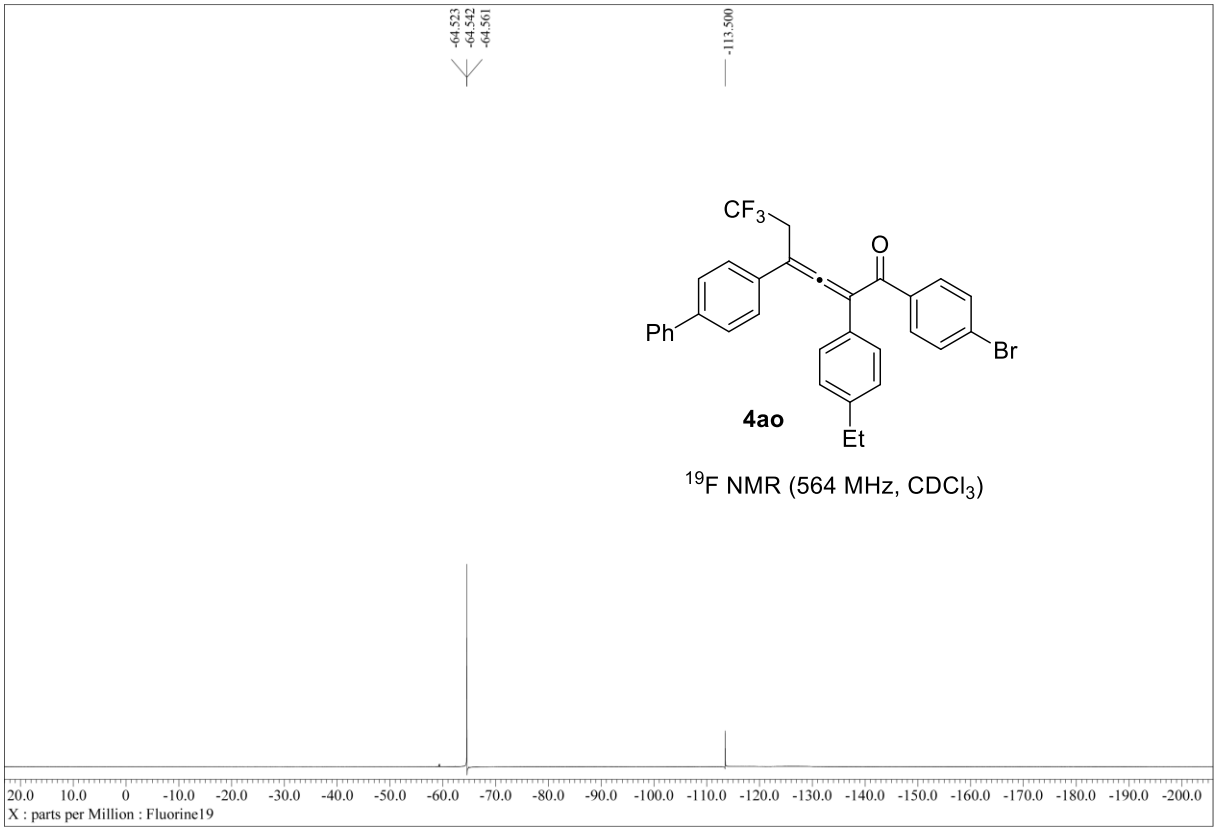
^{1}H NMR (600 MHz, $CDCl_3$)

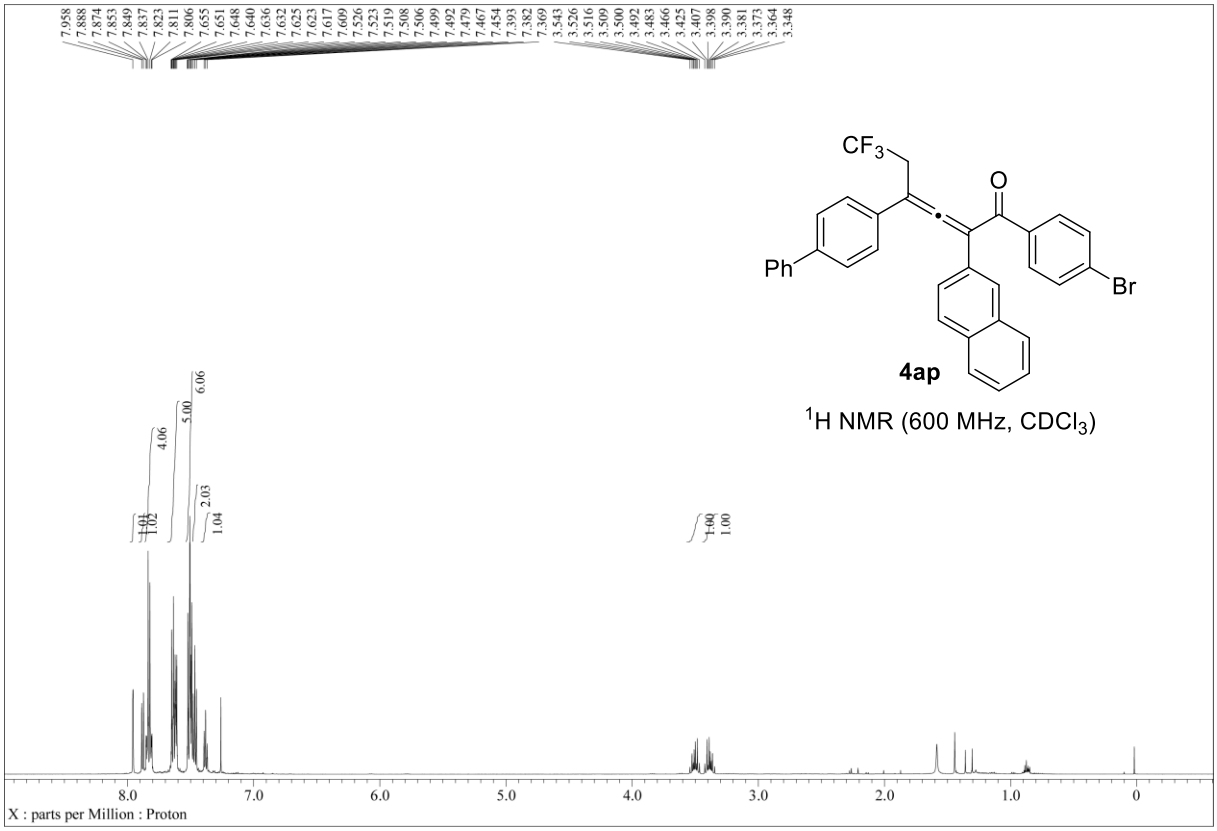

213.182
190.490
160.703
159.046
141.457
139.945
135.981
131.557
130.753
130.734
130.542
130.485
130.427
128.905
128.177
128.014
127.765
127.679
126.971
126.865
126.176
124.510
124.491
124.338
120.757
120.671
116.122
115.979
107.199
101.751
101.732
77.211
77.000
76.789
35.484
35.283
35.082
34.881
CF3
O
Ph
F
Br
4an
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13

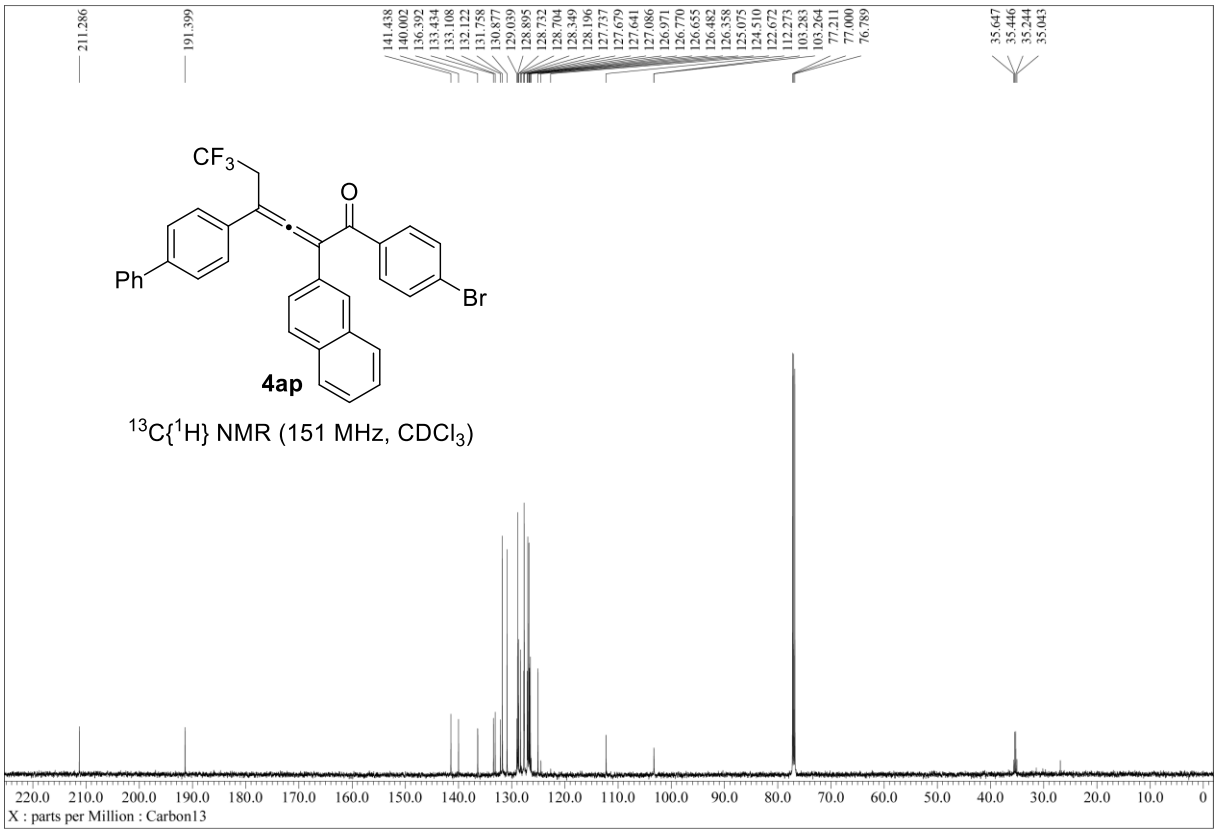

-64.481
-64.500
-64.515
-112.425
-112.437
-112.445
-112.452
-112.464
-113.500
CF3
O
Ph
F
Br
4an
19F NMR (564 MHz, CDCl3)
3.00
1.00
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
X : parts per Million : Fluorine19

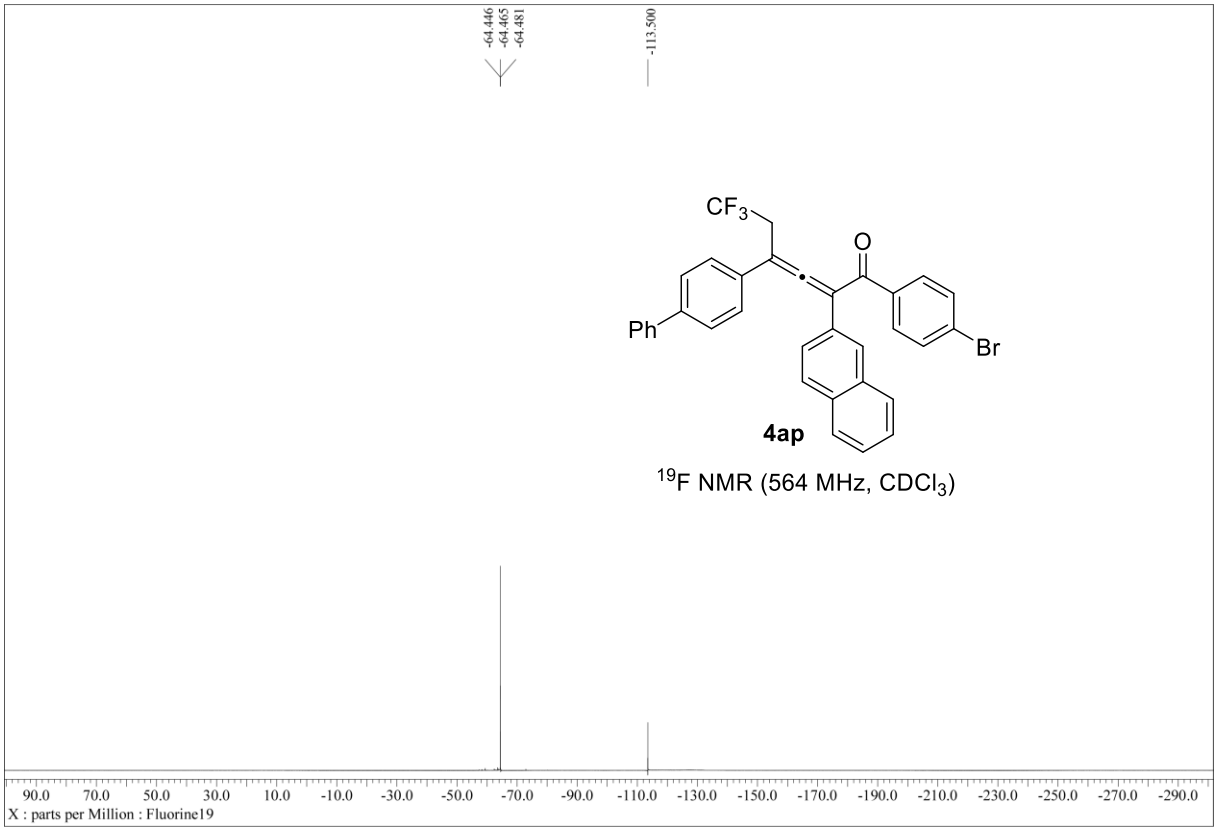

CF3
O
Ph
Br
Et
4ao
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

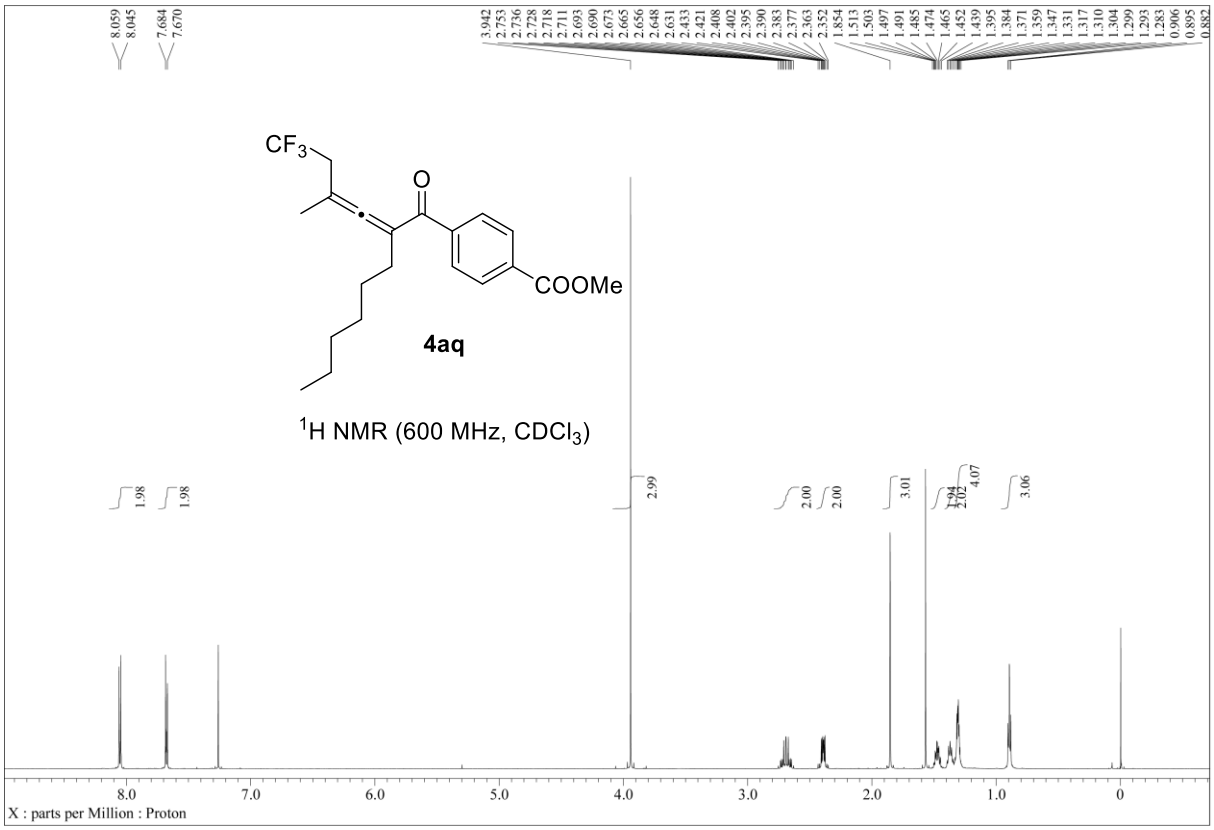

CF3
O
Ph
Br
Et
4ao
13C{1H} NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

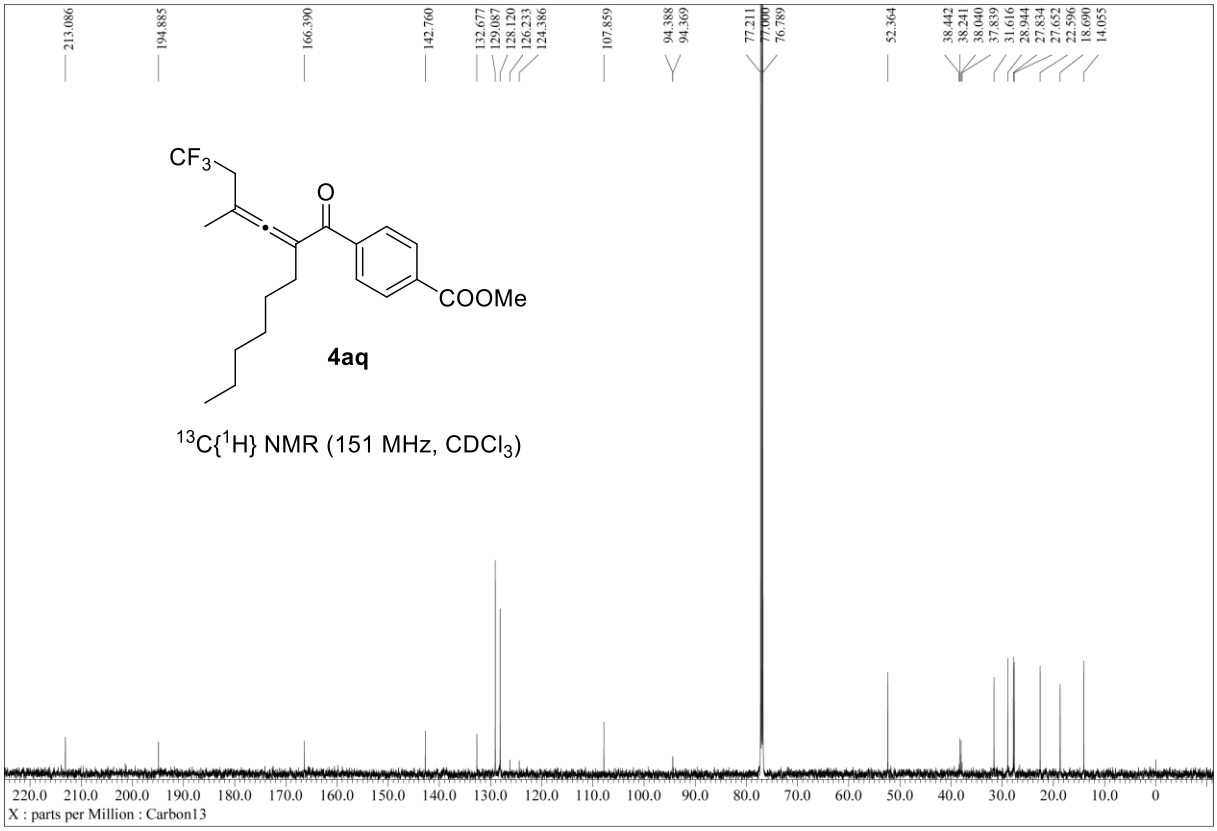

-64.523
-64.542
-64.561
-113.500
CF3
O
Ph
Br
4ao
Et
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
X : parts per Million : Fluorine19

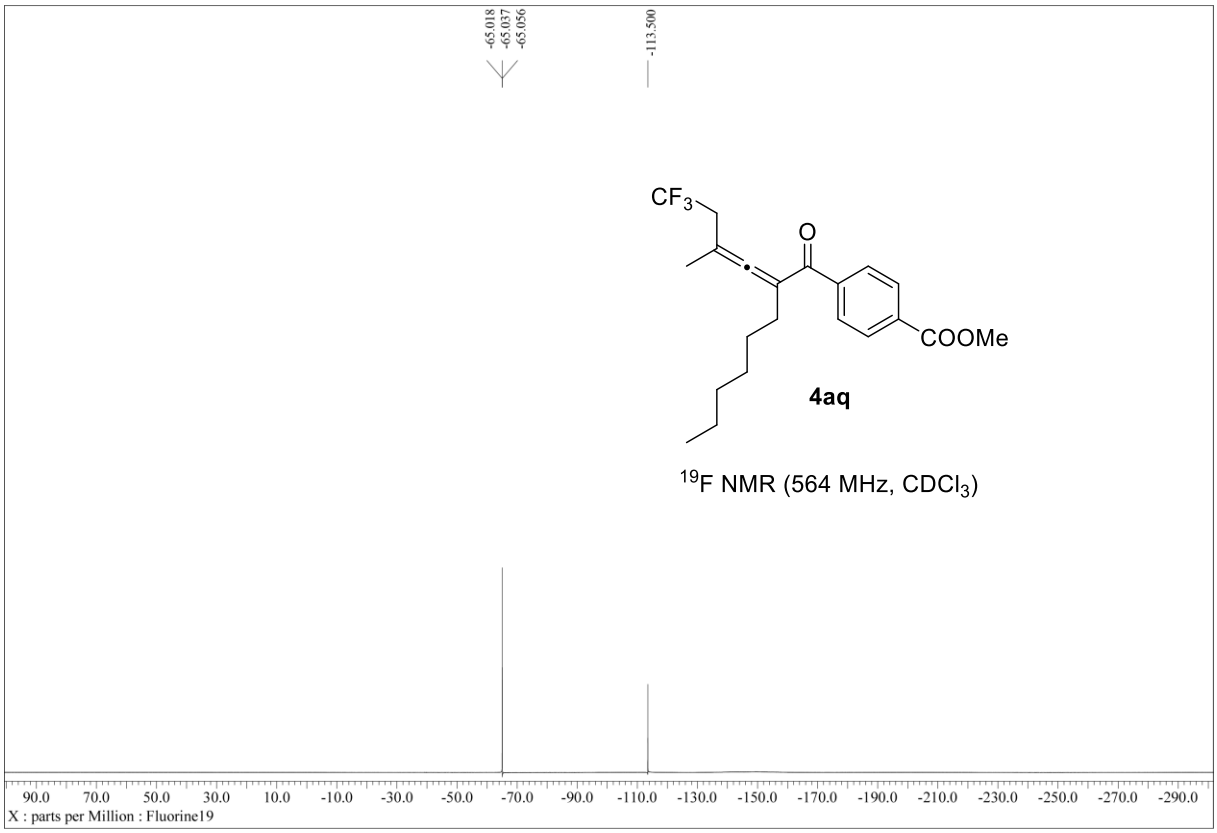

CF3
O
Ph
Br
4ap
1H NMR (600 MHz, CDCl3)
6.06
5.00
4.06
2.03
1.04
1.02
1.01
1.00
1.00
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


211.286
191.399
141.438
140.002
136.392
133.434
133.108
132.122
131.758
130.877
129.039
128.895
128.732
128.704
128.349
128.196
127.737
127.679
127.641
127.086
126.971
126.770
126.655
126.482
126.358
125.075
124.510
122.672
112.273
103.283
103.264
77.211
77.000
76.789
35.647
35.446
35.244
35.043
CF3
O
Ph
Br
4ap
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.446
-64.465
-64.481
-113.500
CF3
O
Ph
Br
4ap
19F NMR (564 MHz, CDCl3)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
X : parts per Million : Fluorine19

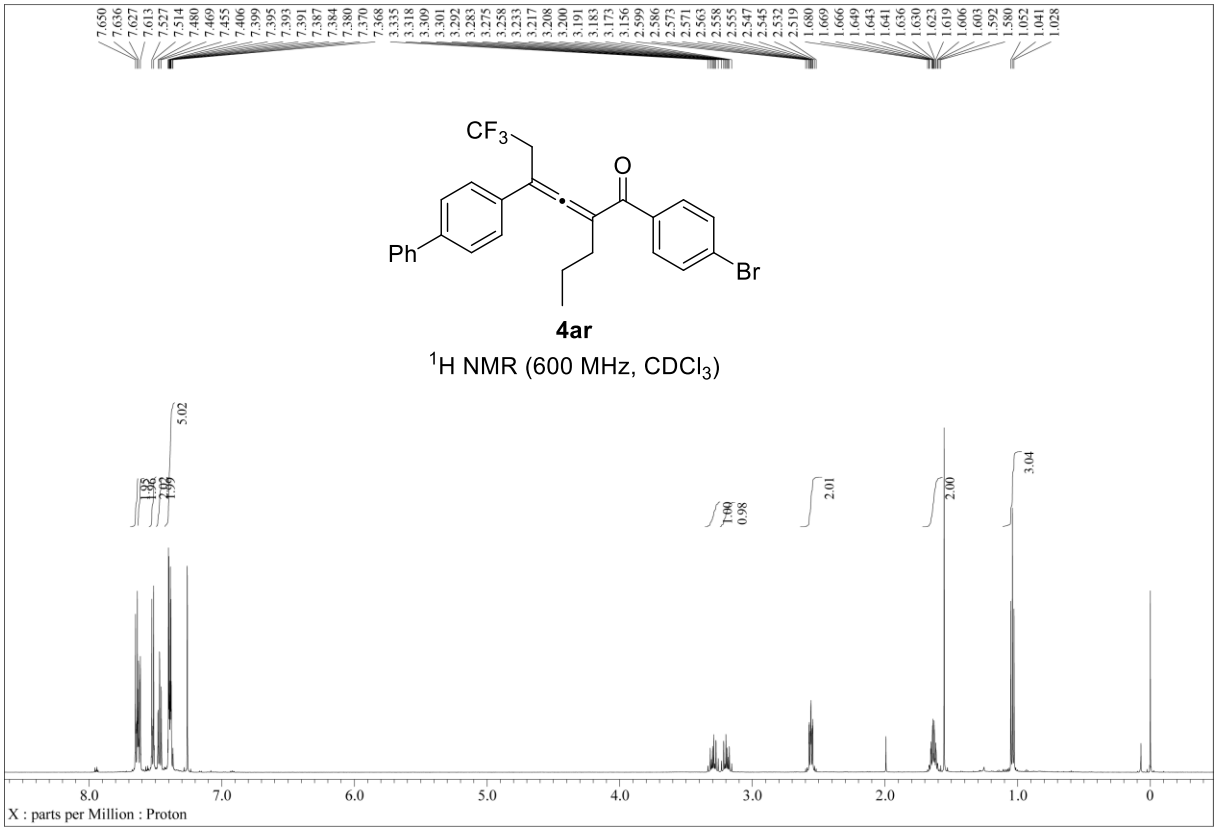

CF3
O
COOMe
4aq
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


CF3
O
COOMe
4aq
13C{1H} NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



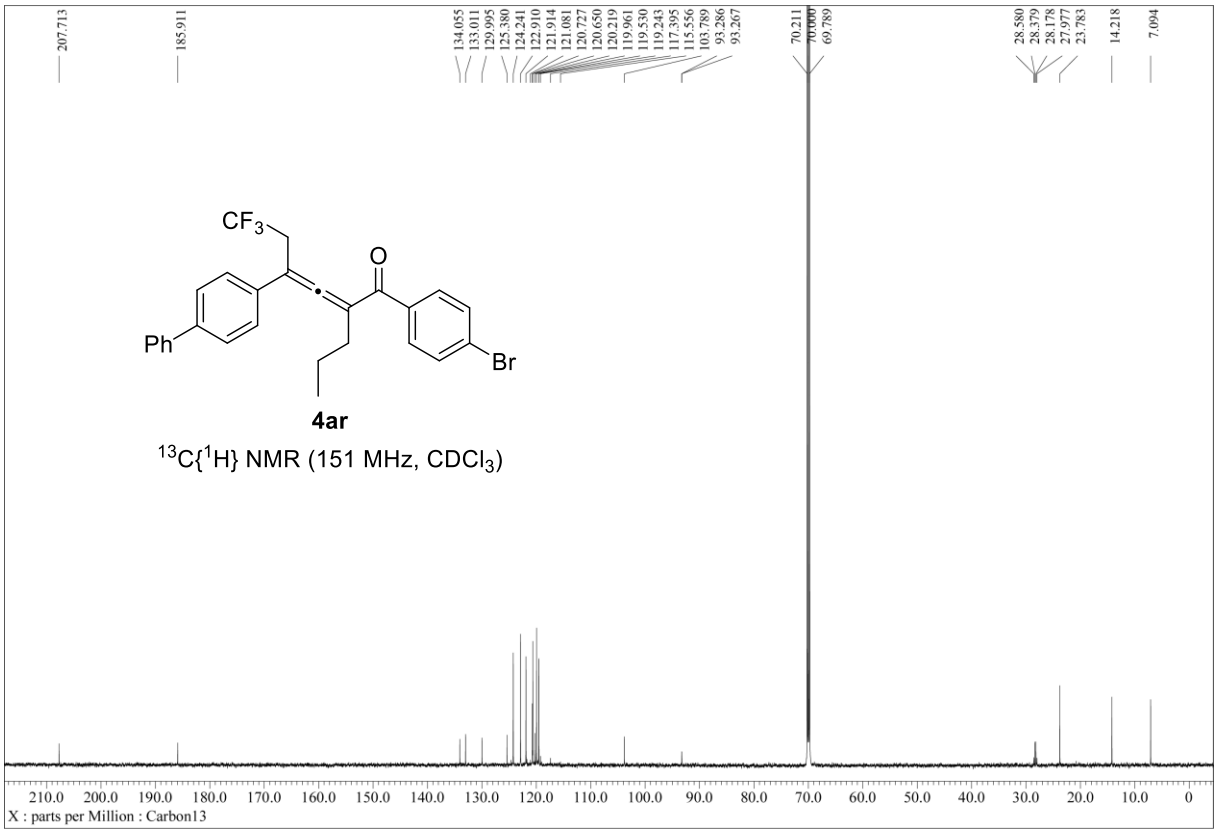
4aq

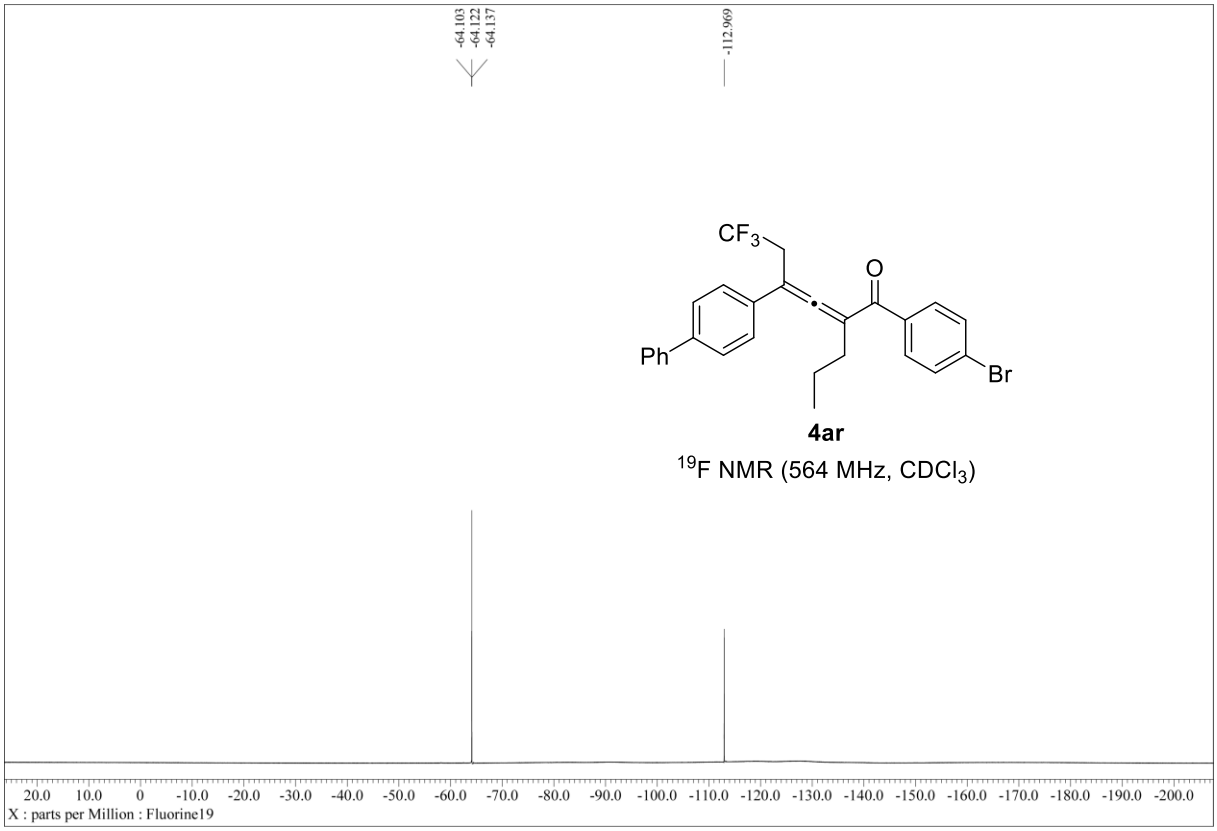
^{19}F NMR (564 MHz, $CDCl_3$)

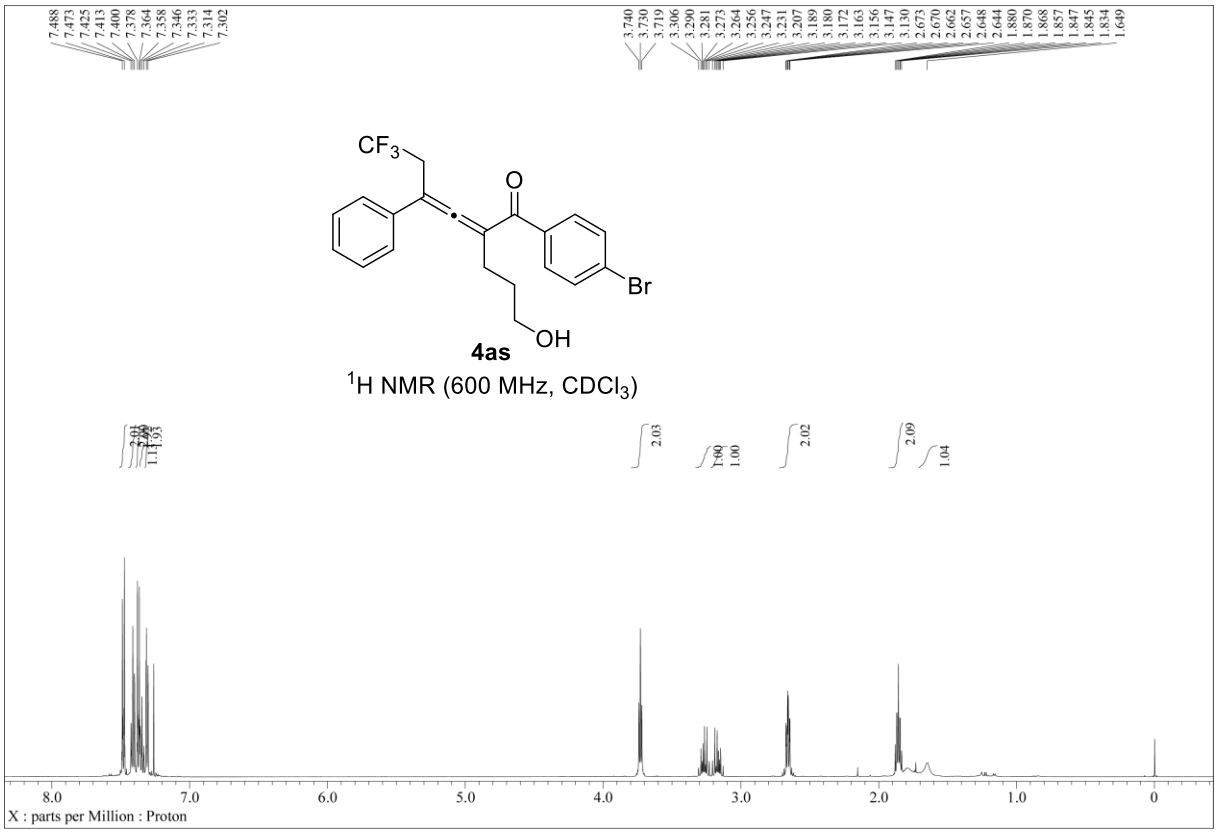


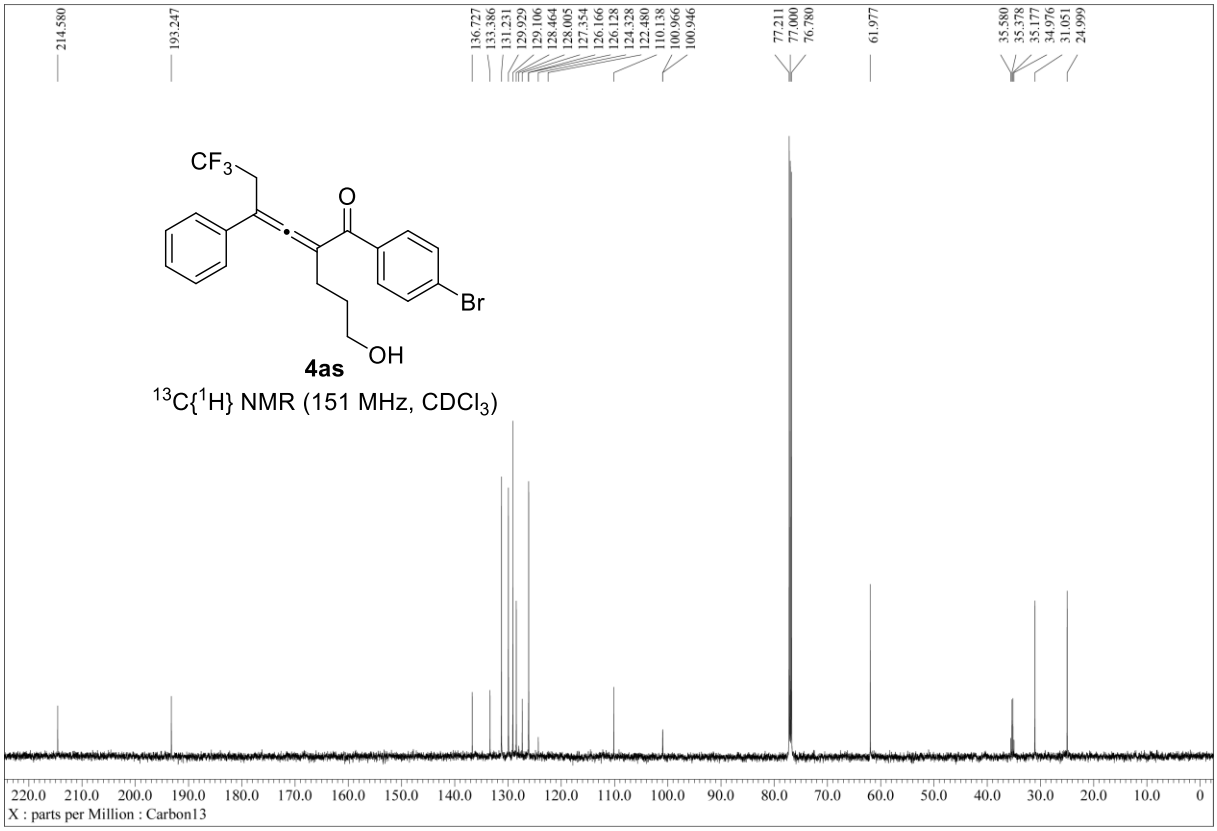
4ar

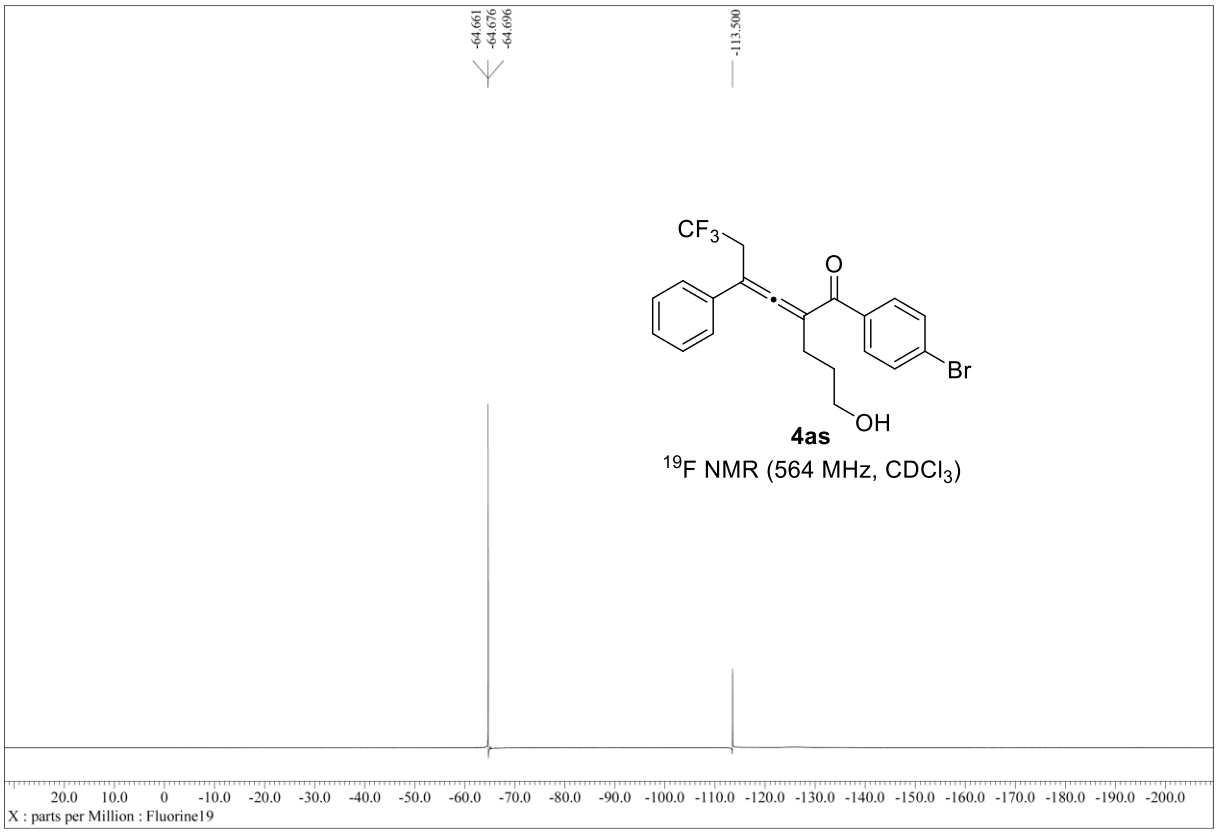
^{1}H NMR (600 MHz, $CDCl_3$)

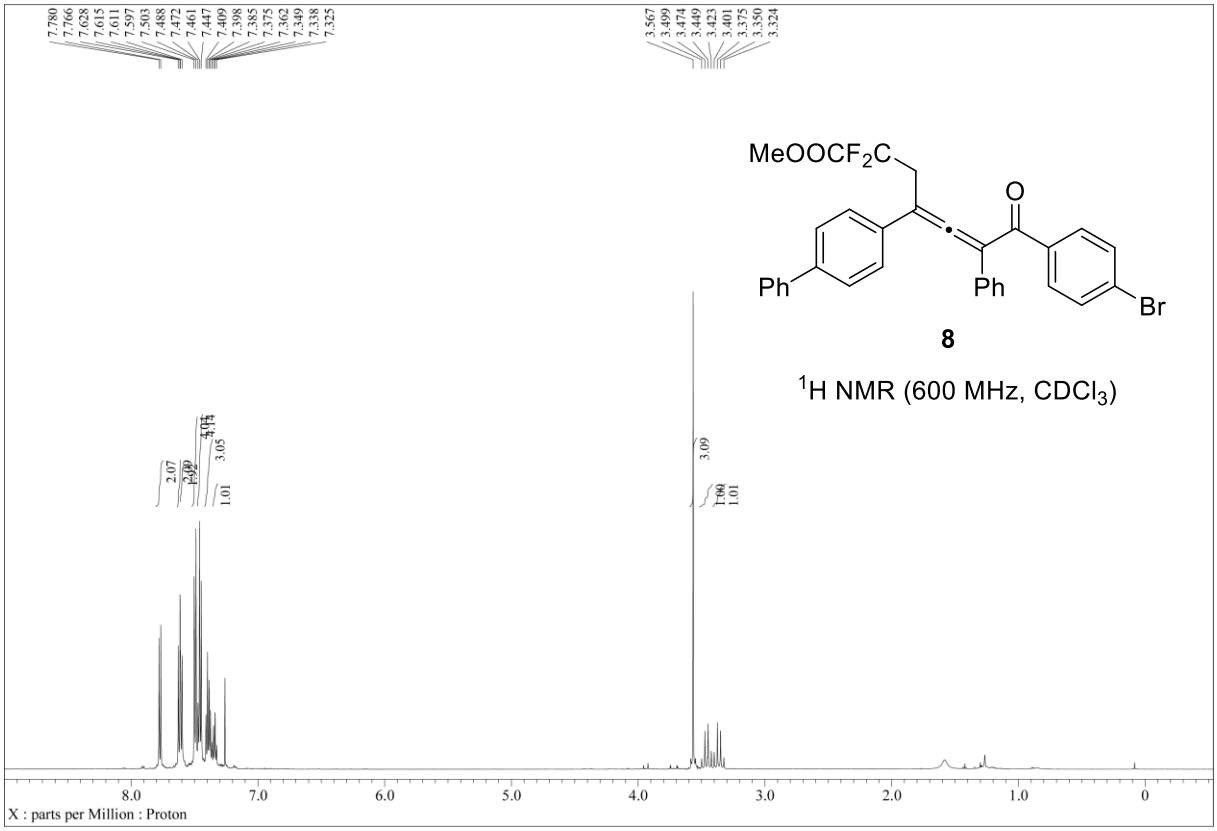

207.713
185.911
134.055
133.011
129.995
125.380
124.241
122.910
121.914
121.081
120.727
120.650
120.219
119.961
119.530
119.243
117.395
115.556
103.789
93.286
93.267
70.211
70.000
69.789
28.580
28.379
28.178
27.977
23.783
14.218
7.094
CF3
O
Ph
Br
4ar
13C{1H} NMR (151 MHz, CDCl3)
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13

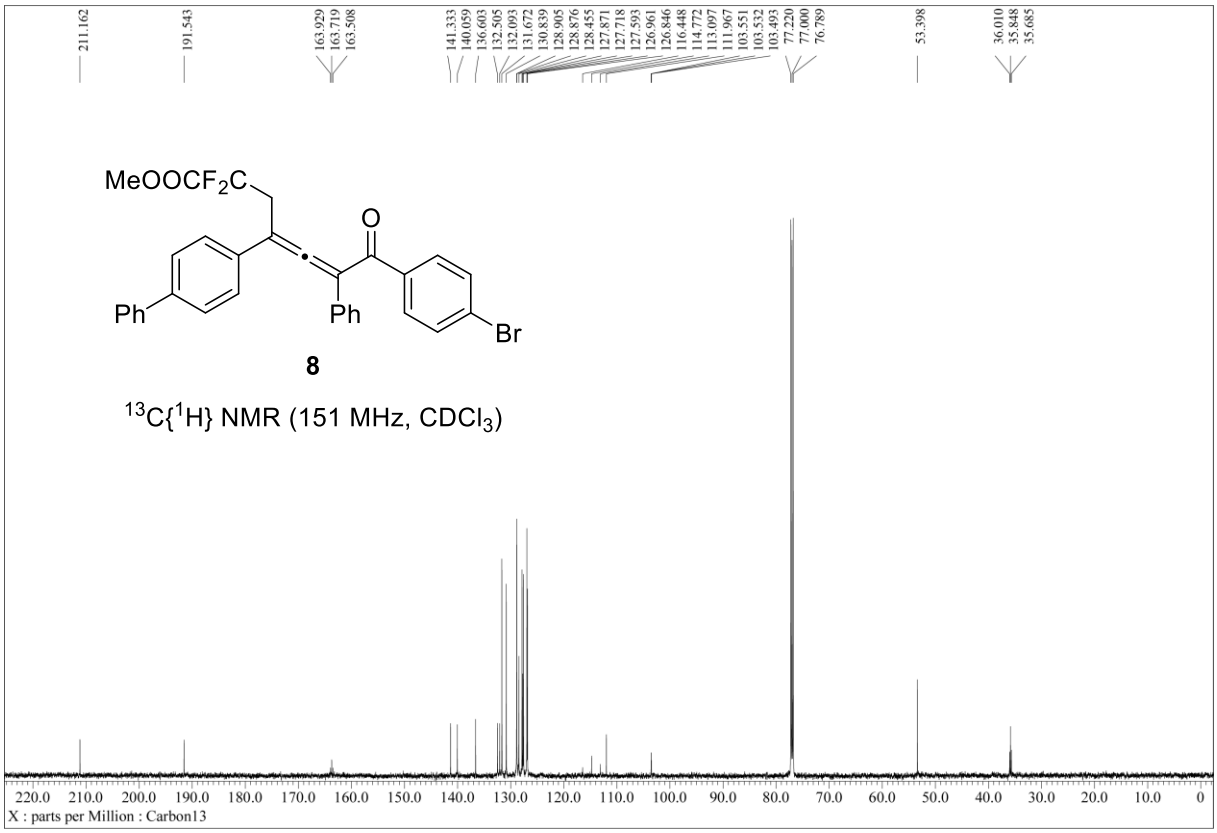

-64.103
-64.122
-64.137
-112.969
CF3
O
Ph
Br
4ar
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
X : parts per Million : Fluorine19

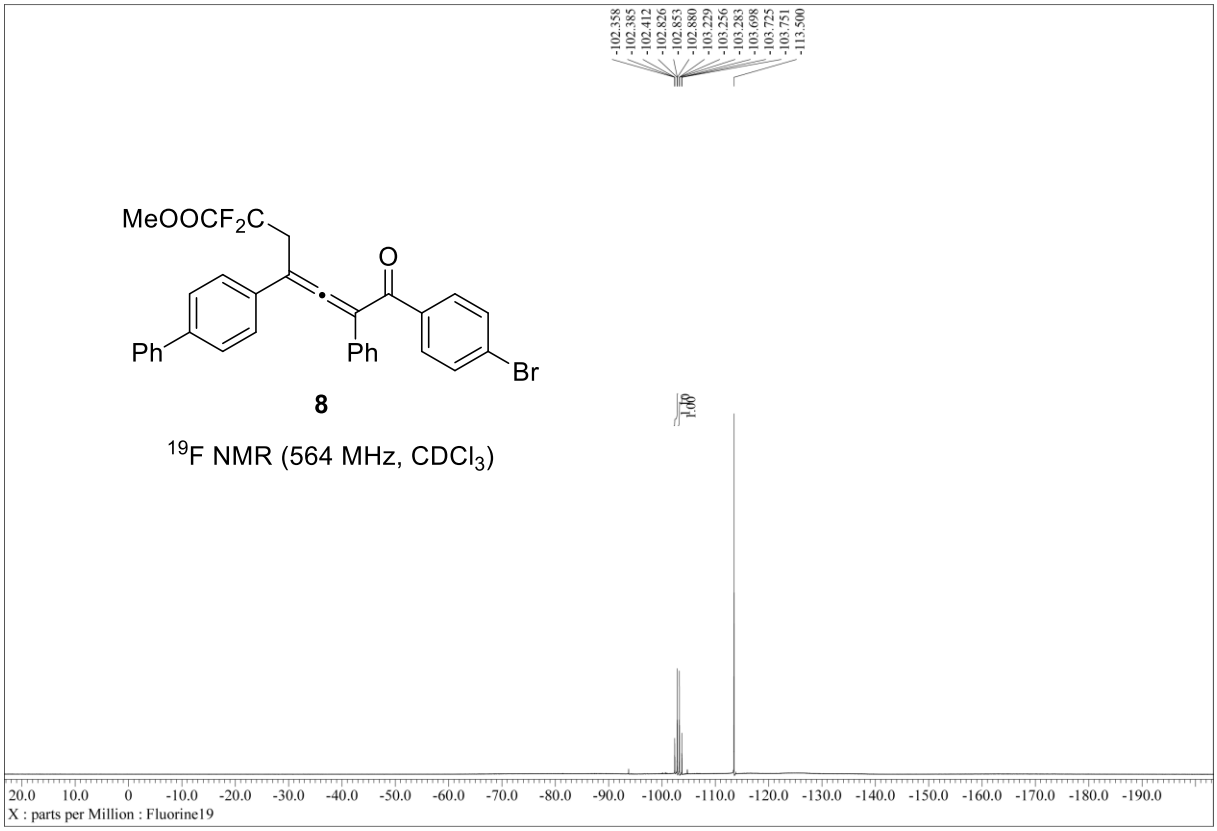

7.488
7.473
7.425
7.413
7.400
7.378
7.364
7.358
7.346
7.333
7.314
7.302
3.740
3.730
3.719
3.306
3.290
3.281
3.273
3.264
3.256
3.247
3.231
3.207
3.189
3.180
3.172
3.163
3.156
3.147
3.130
2.673
2.670
2.662
2.657
2.648
2.644
1.880
1.870
1.868
1.857
1.847
1.845
1.834
1.649
CF3
O
Br
OH
4as
1H NMR (600 MHz, CDCl3)
2.03
1.00
1.00
2.02
2.09
1.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

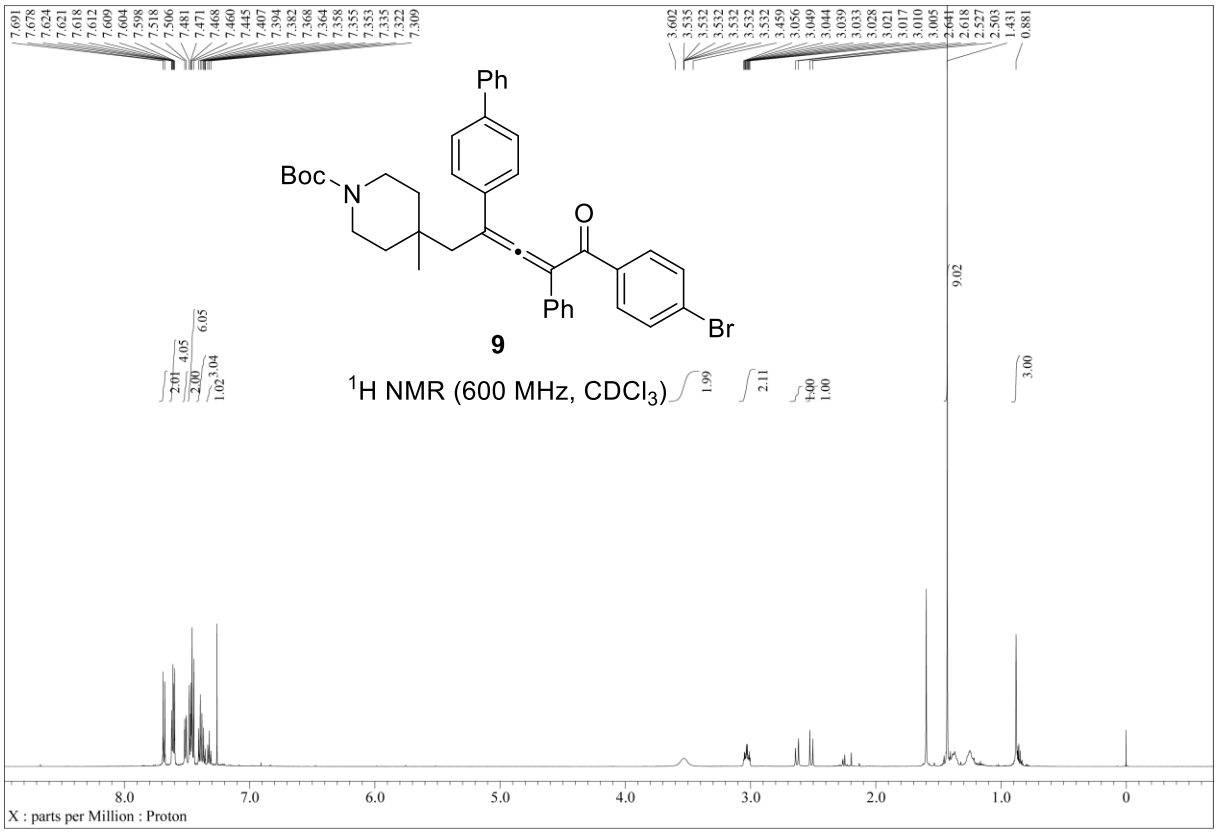

214.580
193.247
136.727
133.386
131.231
129.929
129.106
128.464
128.005
127.354
126.166
126.128
124.328
122.480
110.138
100.966
100.946
77.211
77.000
76.780
61.977
35.580
35.378
35.177
34.976
31.051
24.999
CF3
O
Br
OH
4as
13C{1H} NMR (151 MHz, CDCl3)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13

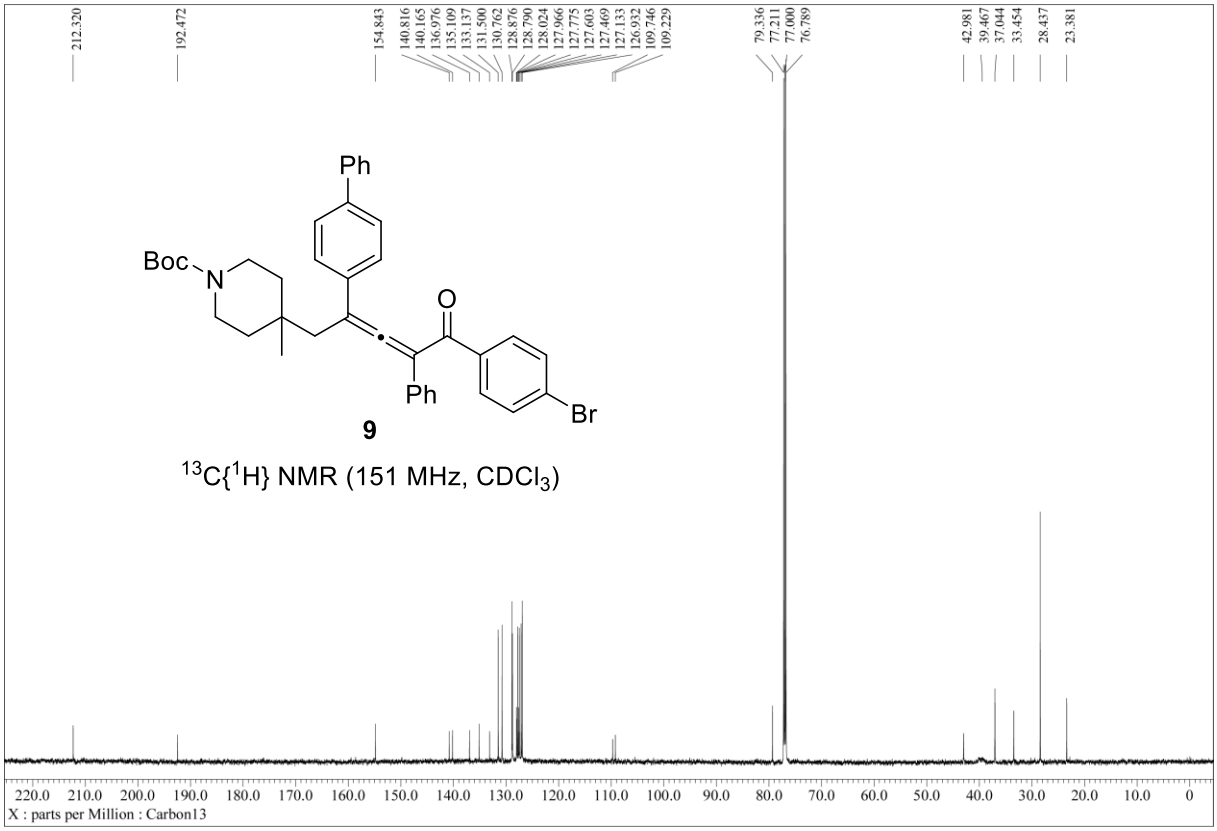

-64.661
-64.676
-64.696
-113.500
CF3
O
Br
OH
4as
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
X : parts per Million : Fluorine19

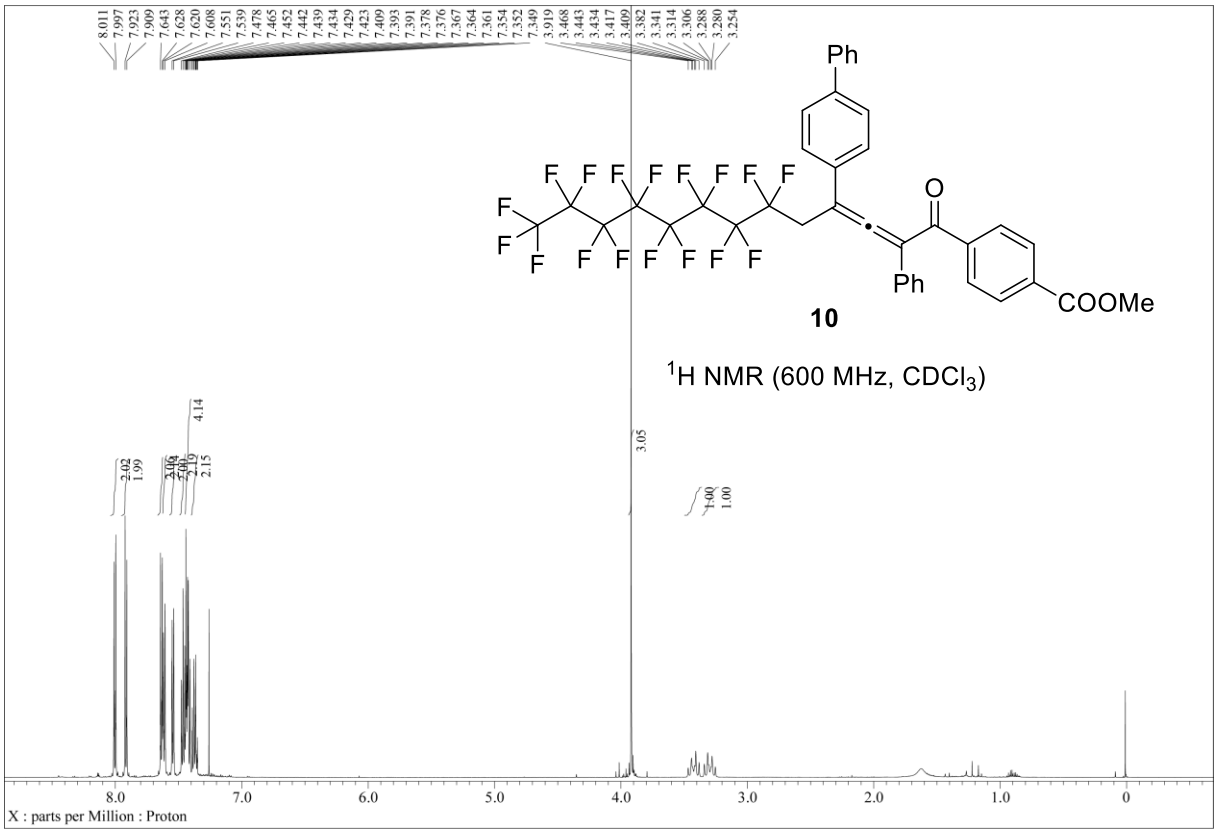

7.780
7.766
7.628
7.615
7.611
7.597
7.503
7.488
7.472
7.461
7.447
7.409
7.398
7.385
7.375
7.362
7.349
7.338
7.325
3.567
3.499
3.474
3.449
3.423
3.401
3.375
3.350
3.324
MeOOCF2C
O
Ph
Ph
Br
8
1H NMR (600 MHz, CDCl3)
2.07
3.05
1.01
3.09
1.00
1.01
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton

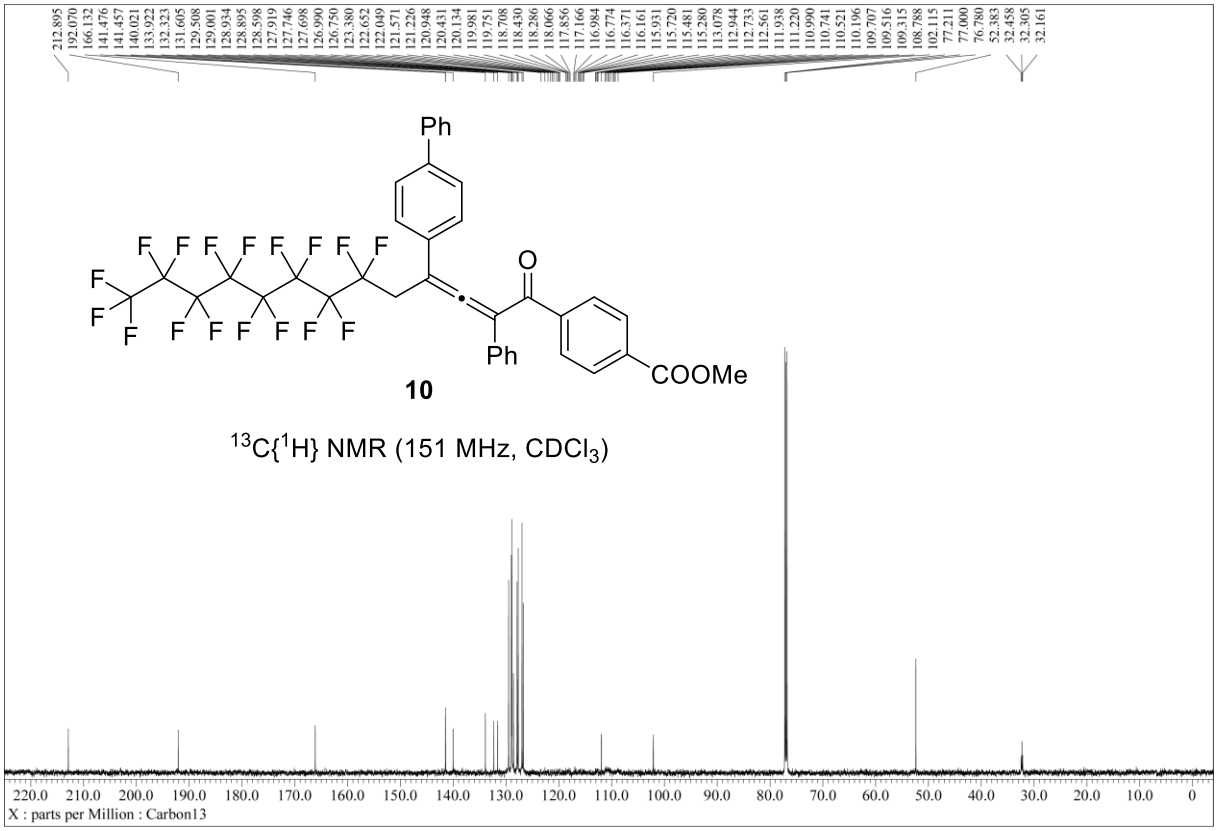

211.162
191.543
163.929
163.719
163.508
141.333
140.059
136.603
132.505
132.093
131.672
130.839
128.905
128.876
128.455
127.871
127.718
127.593
126.961
126.846
116.448
114.772
113.097
111.967
103.551
103.532
103.493
77.220
77.000
76.789
53.398
36.010
35.848
35.685
MeOOCF2C
O
Ph
Ph
Br
8
13C{1H} NMR (151 MHz, CDCl3)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13

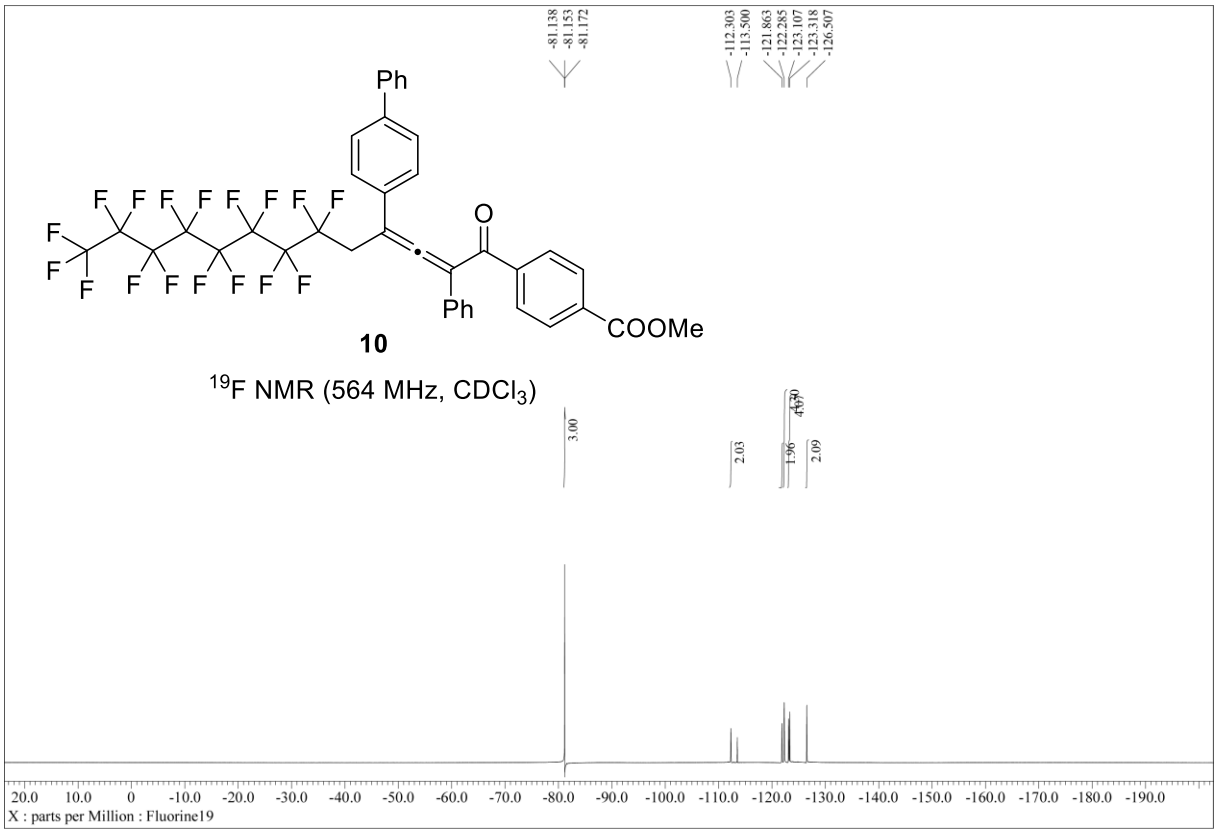

-102.358
-102.385
-102.412
-102.826
-102.853
-102.880
-103.229
-103.256
-103.283
-103.698
-103.725
-103.751
-113.500
1.00
MeOOCF2C
O
Ph
Ph
Br
8
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19

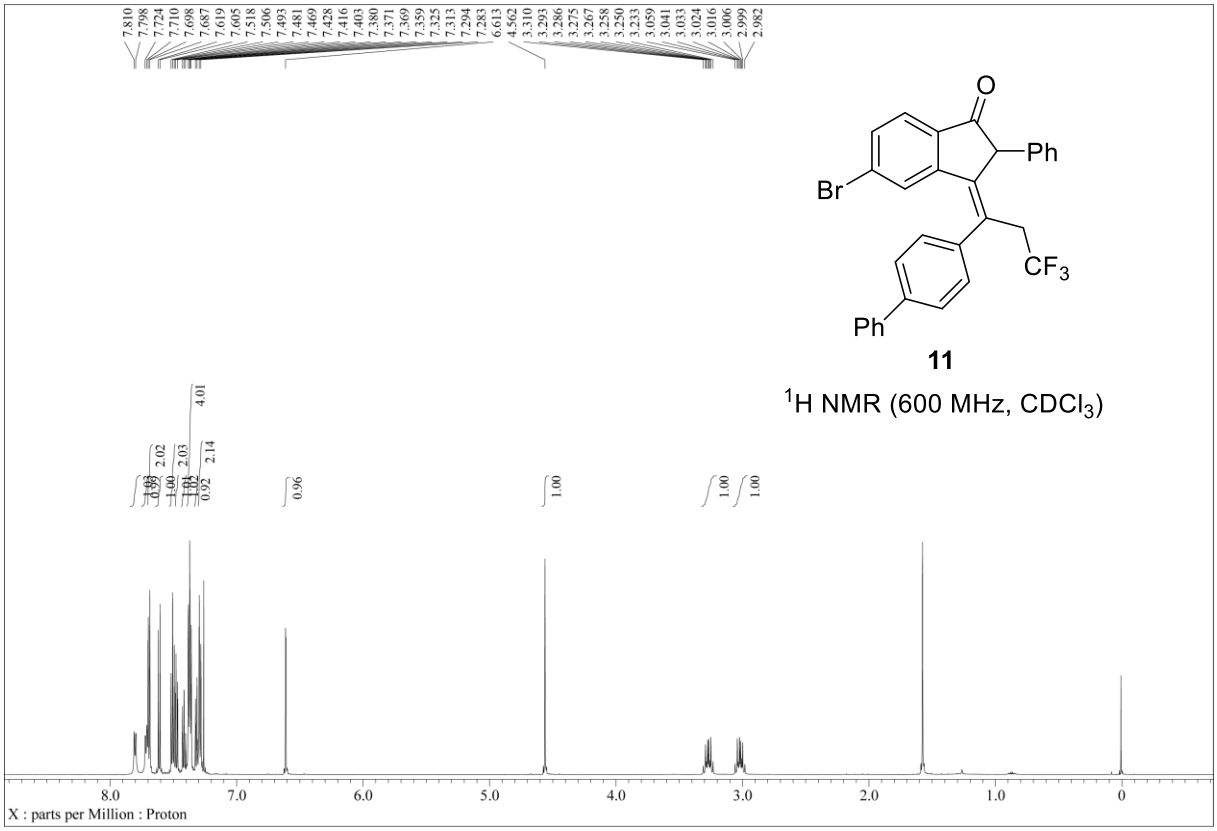

Boc
N
O
Ph
Ph
Br
9
^{1}H NMR (600 MHz, $CDCl_3$)
X : parts per Million : Proton

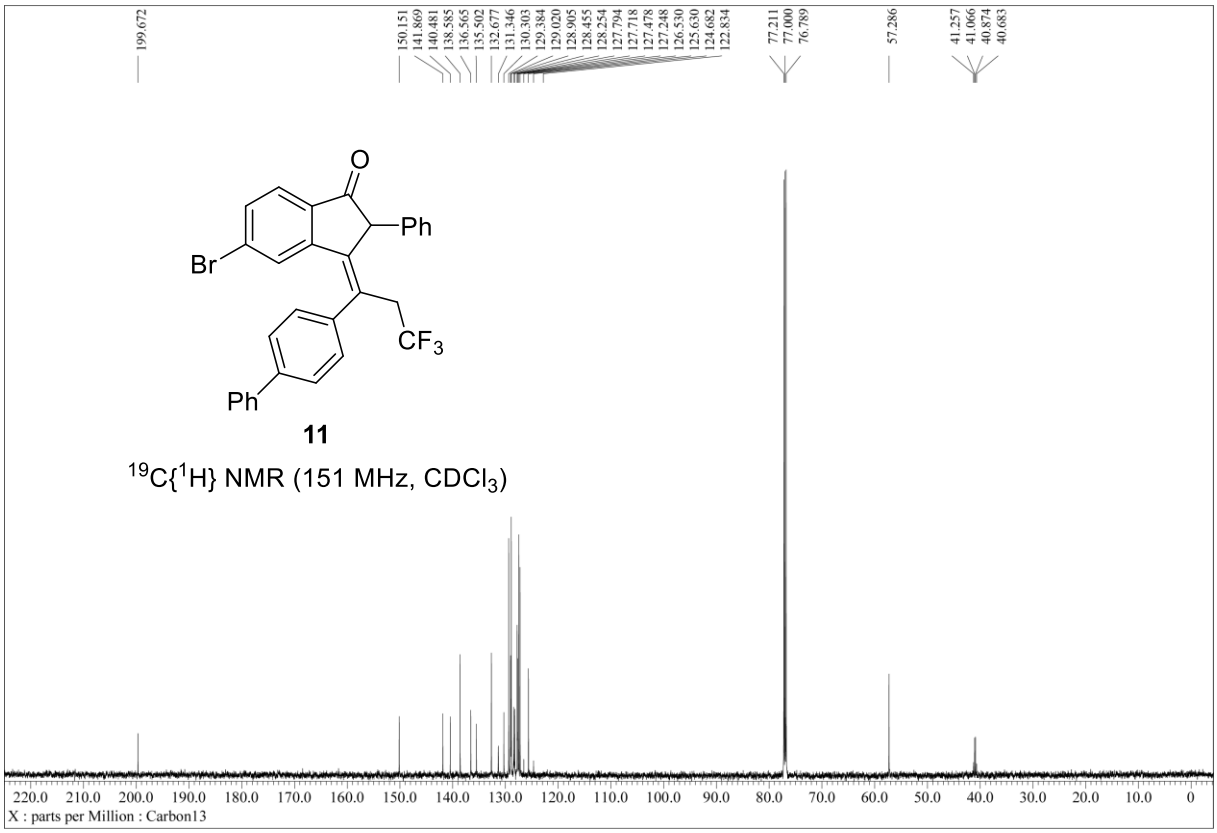

Boc
N
O
Ph
Ph
Br
9
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)
X : parts per Million : Carbon13


Ph
F F F F F F F F
F
F
F F F F F F F
O
Ph
COOMe
10
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


Ph
F F F F F F F F
F
F
F F F F F F F
O
Ph
COOMe
10
13C{1H} NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

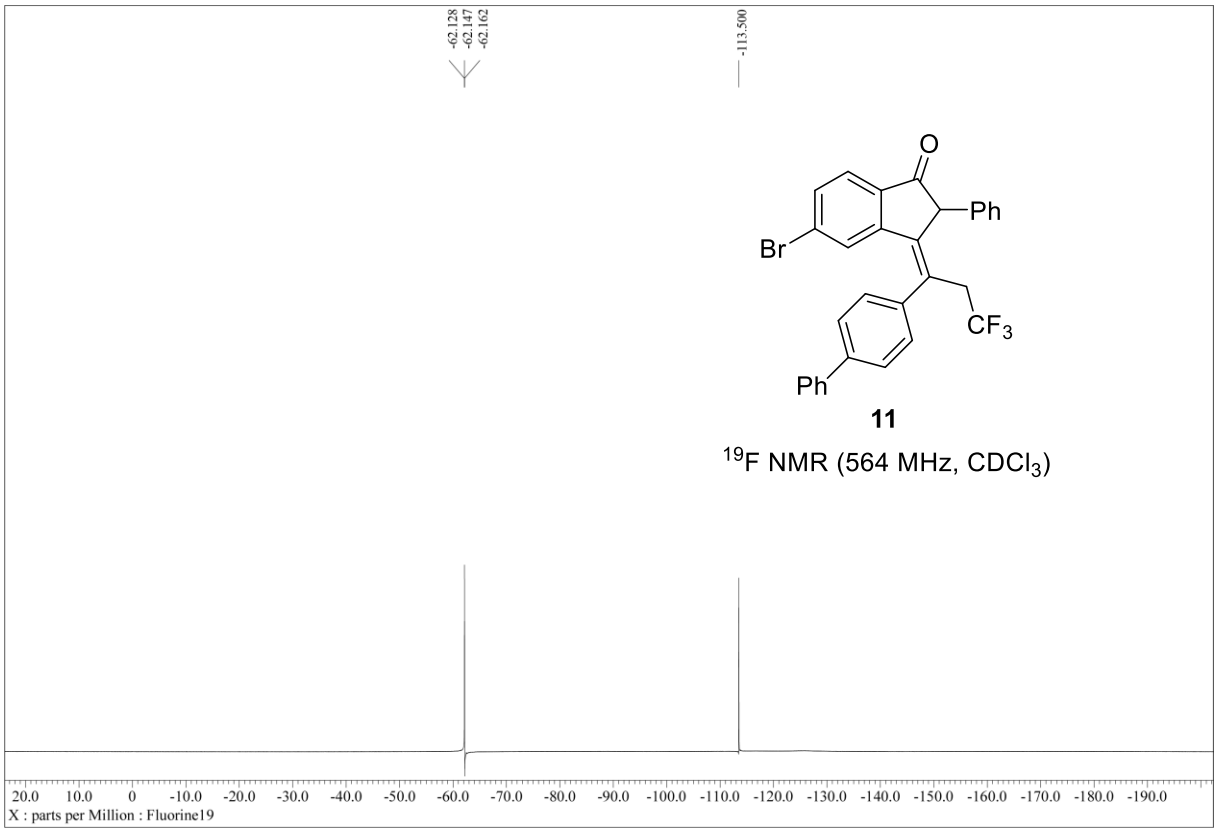

-81.138
-81.153
-81.172
-112.303
-113.500
-121.863
-122.285
-123.107
-123.318
-126.507
Ph
F F F F F F F F F
F
F
F F F F F F F
O
Ph
COOMe
10
19F NMR (564 MHz, CDCl3)
3.00
2.03
1.96
4.30
4.07
2.09
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19


7.810
7.798
7.724
7.710
7.698
7.687
7.619
7.605
7.518
7.506
7.493
7.481
7.469
7.428
7.416
7.403
7.380
7.371
7.369
7.359
7.325
7.313
7.294
7.283
6.613
4.562
3.310
3.293
3.286
3.275
3.267
3.258
3.250
3.233
3.059
3.041
3.033
3.024
3.016
3.006
2.999
2.982
O
Ph
Br
CF3
Ph
11
1H NMR (600 MHz, CDCl3)
4.01
2.02
2.03
2.14
0.96
1.00
1.00
1.00
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton



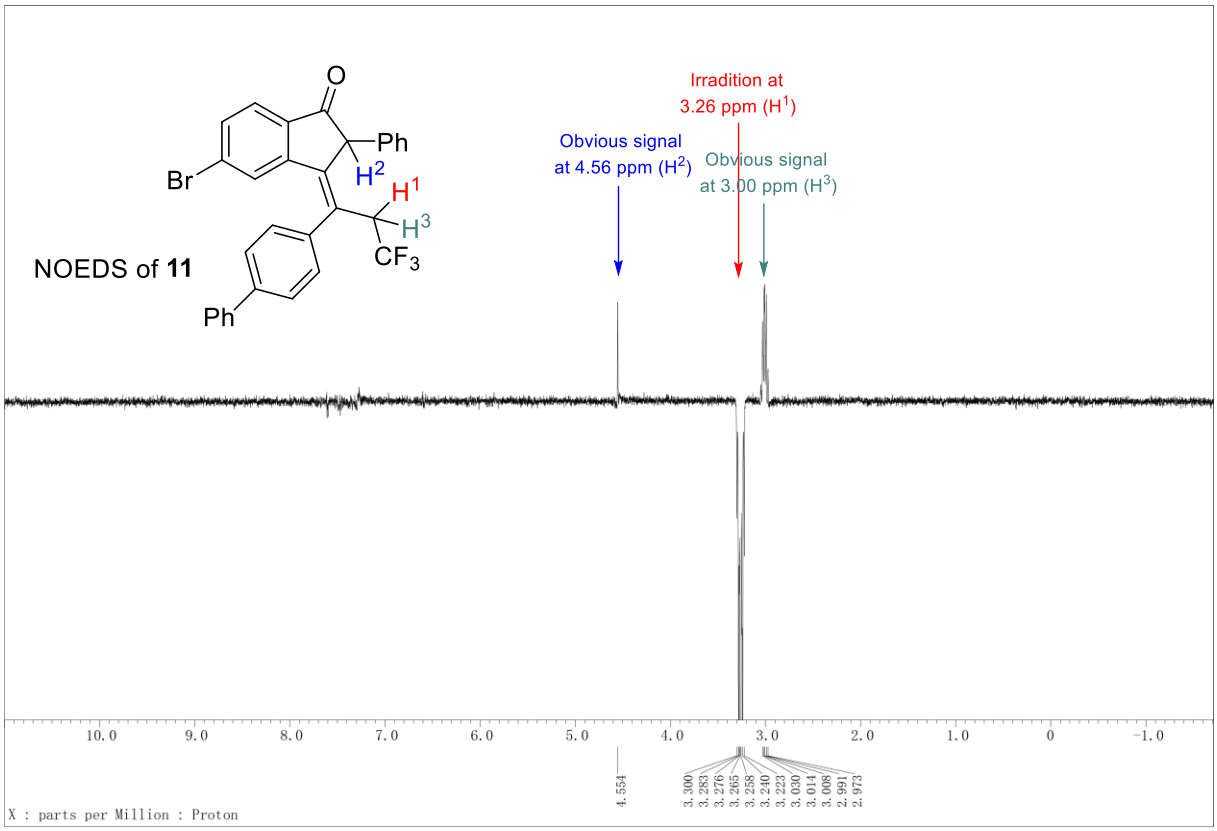
11

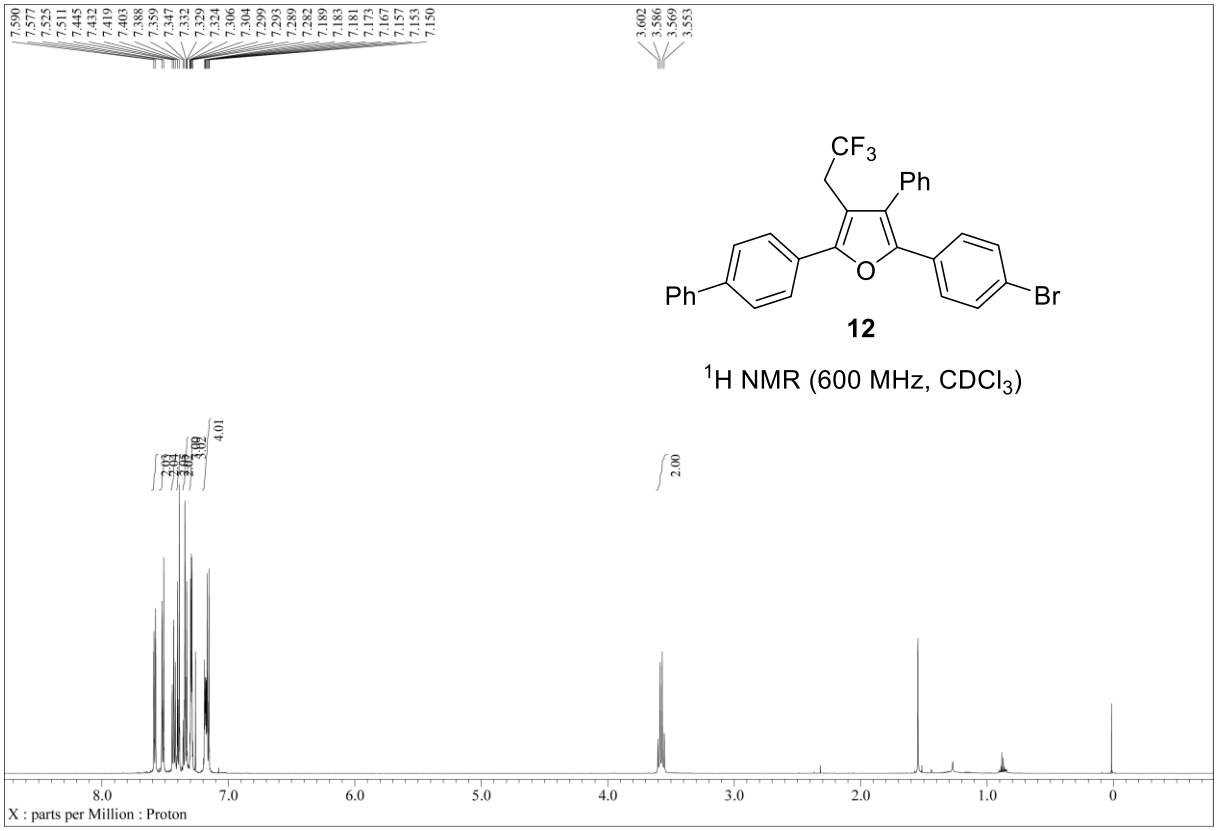
$^{19}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

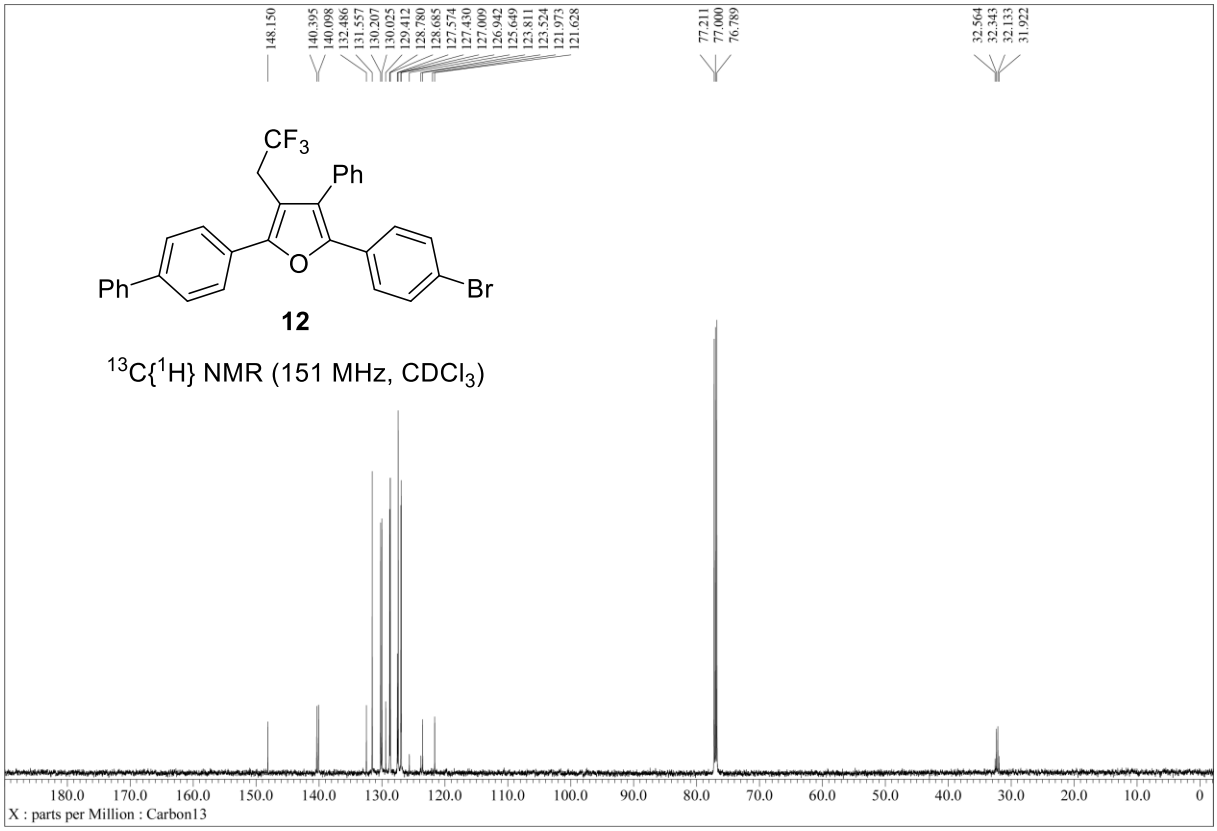


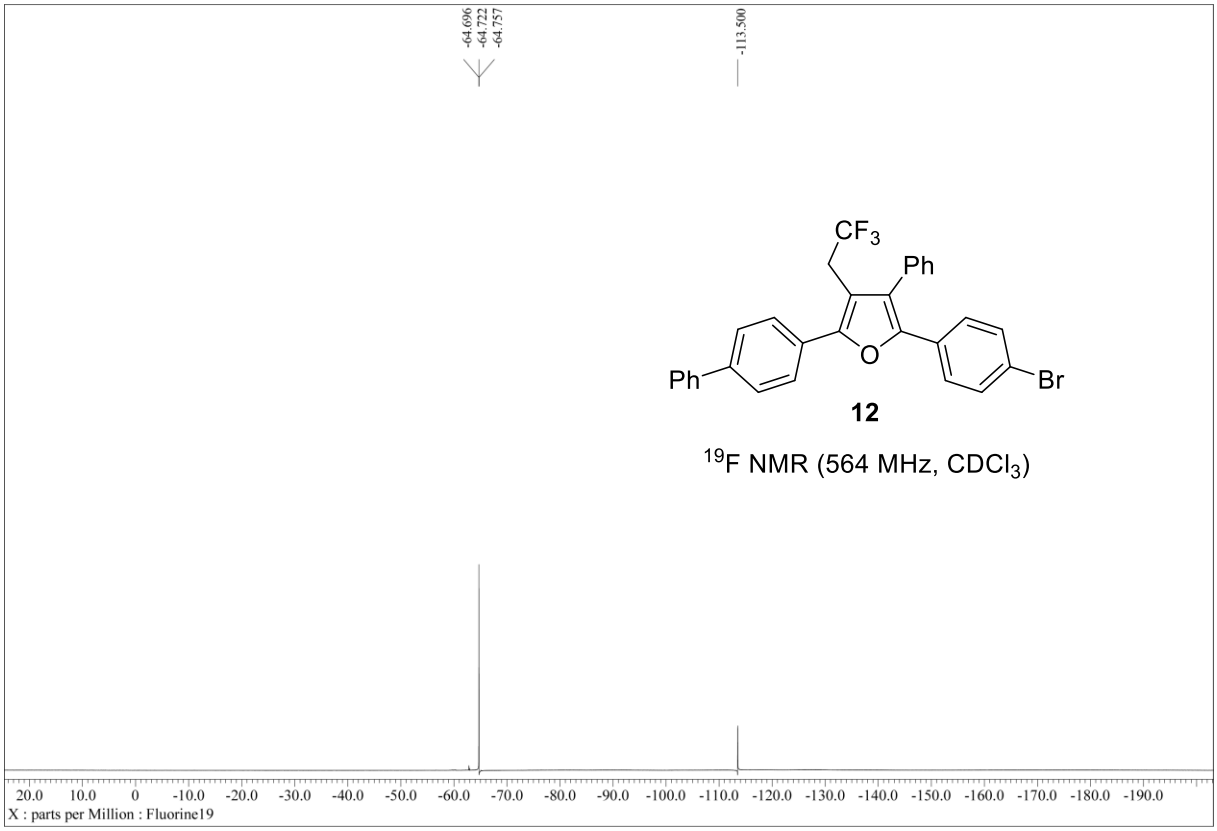
11

^{19}F NMR (564 MHz, $CDCl_3$)


NOEDS of 11
Irradition at
3.26 ppm (H1)
Obvious signal
at 4.56 ppm (H2)
Obvious signal
at 3.00 ppm (H3)
X : parts per Million : Proton


12
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


148.150
140.395
140.098
132.486
131.557
130.207
130.025
129.412
128.780
128.685
127.574
127.430
127.009
126.942
125.649
123.811
123.524
121.973
121.628
77.211
77.000
76.789
32.564
32.343
32.133
31.922
CF3
Ph
O
Ph
Br
12
13C{1H} NMR (151 MHz, CDCl3)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13


-64.696
-64.722
-64.757
-113.500
CF3
Ph
O
Ph
Br
12
19F NMR (564 MHz, CDCl3)
20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
X : parts per Million : Fluorine19