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Electronic Supplementary Information

On the reactivity of anodically generated trifluoromethyl radicals toward aryl alkynes in organic/aqueous media

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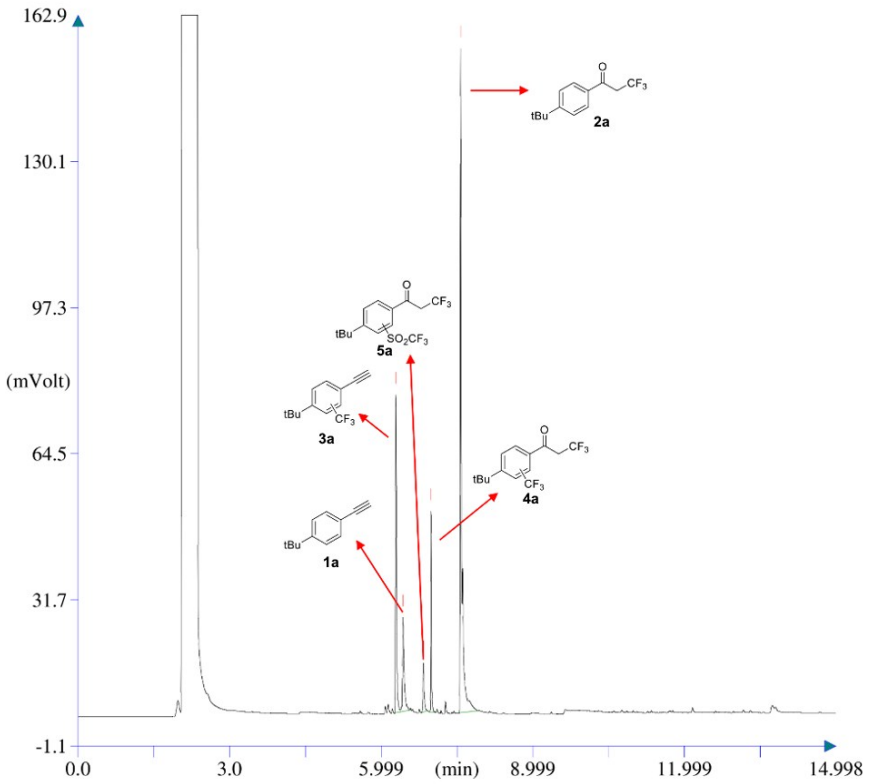


Fig. S1. GC-FID analysis of a crude reaction mixture for the electrochemical transformation of 4-*tert*-butylphenylacetylene (**1a**) (Table 1, entry 4)

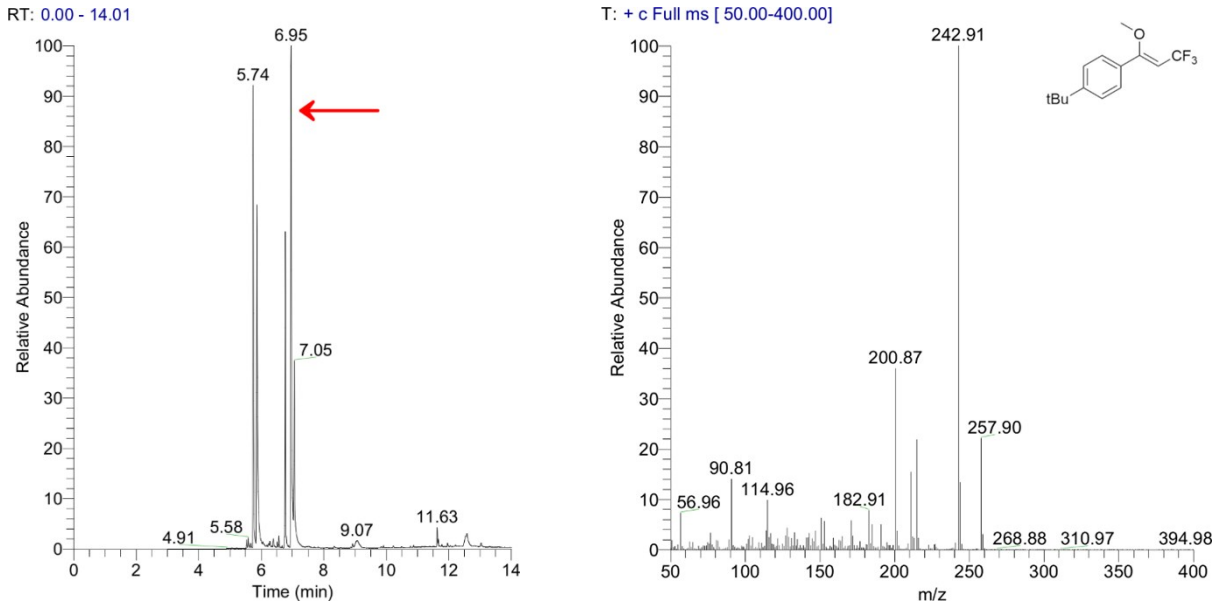
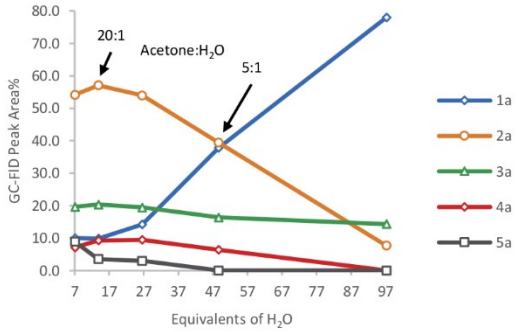
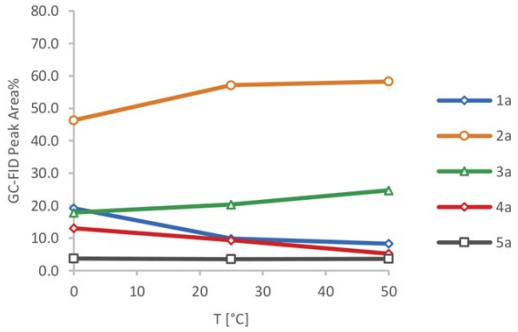


Fig. S2. GC-MS chromatogram and mass spectrum (peak at 6.95 min) of a crude reaction mixture of 0.5 mmol 4-*tert*-butylphenylacetylene, 0.6 mmol $NaSO_2CF_3$, 0.25 mmol Et_4NBF_4, 2.5 mL MeOH and 125 µL H_2O after electrolysis, indicating formation of (*E/Z*)-1-(*tert*-butyl)-4-(3,3,3-trifluoro-1-methoxyprop-1-en-1-yl)benzene.

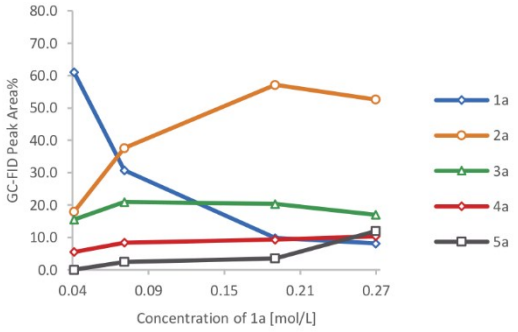
a) Influence of Equivalents of H_2O



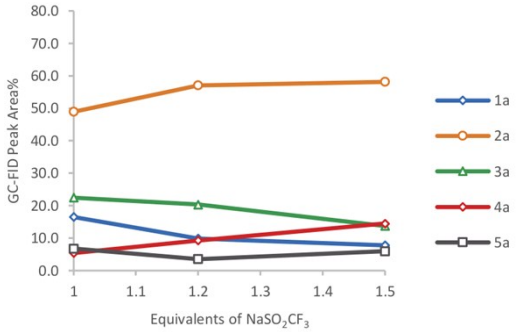
b) Influence of Temperature (°C)



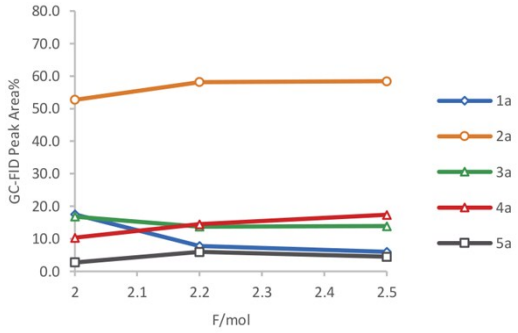
c) Influence of Concentration of **1a** (mol/L)



d) Influence of Equivalents of $NaSO_2CF_3$



e) Influence of Amount of Charge (F/mol)



f) Influence of current (I)

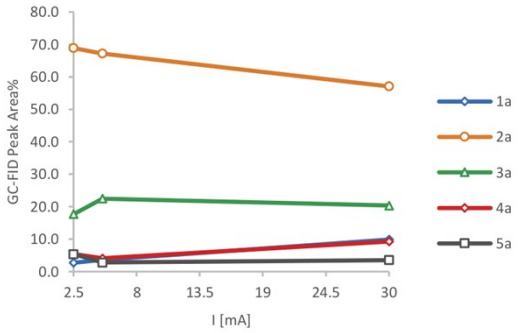
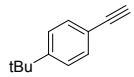
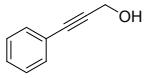
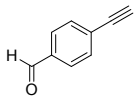


Fig. S3. Electrochemical transformation of **1a**. Starting conditions: 0.5 mmol substrate, 1.2 equiv. $NaSO_2CF_3$, Acetone:H_2O 20:1 (v/v), 0.1 M Et_4NBF_4, 2.2 F/mol, constant current (30 mA), anode: graphite, cathode: stainless steel, 2.625 mL reaction volume.

Table S1. Effect of various mediators on the electrochemical transformation of aromatic alkynes. General conditions: 0.2 M 4-*tert*-butylphenylacetylene, 0.24 M (1.2 equiv.) $NaSO_2CF_3$, 5 mol% mediator (unless stated otherwise), 0.1 M electrolyte (Et_4NBF_4, unless stated otherwise), 2.5 mL acetone, 125 µL H_2O, room temperature, constant current, anode: graphite (G), cathode: stainless steel (SS).

Substrate	Mediator	high current (30 mA)			low current (5 mA)		
		conv.	sel. ket.[1]	sel. ar.[2]	conv.	sel. ket.[1]	sel. ar[2]
	no mediator	90	63	37	96	69	31
	NPh_3	92	63	37	97	66	34
	TEMPO	86	59	41	96	63	37
	$Mn(OAc)_3*2H_2O$	94	64	36	99	69	31
	no mediator	82	66[3]	34	81	64[3]	36
	NPh_3	82	67[3]	33	78	78[3]	22
	TEMPO	76	69[3]	31	57	73[3]	27
	$Mn(OAc)_3*2H_2O$	75	75[3]	25	56	75[3]	25
	no mediator	79	30	70	92	40	60
	NPh_3	45	41	59	80	47	53
	TEMPO	56	30	70	84	39	61
	$Mn(OAc)_3*2H_2O$	71	30	70	29	55	45

[1] selectivity for formation of α-trifluoromethyl ketone [2] selectivity for radical addition products on aromatic ring [3] selectivity for formation of 1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (see Fig. S4)

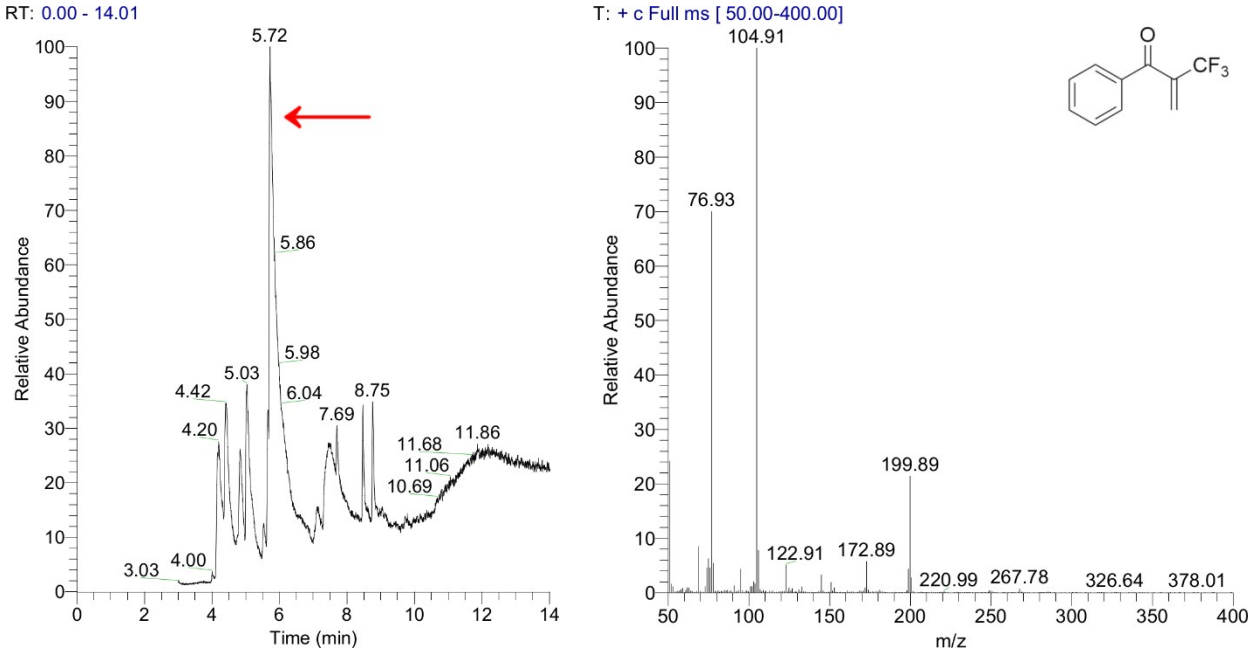


Fig. S4. GC-MS chromatogram and mass spectrum (peak at 5.72 min) of a crude reaction mixture of 0.5 mmol 3-phenyl-2-propyn-1-ol, 0.6 mmol $NaSO_2CF_3$, 0.25 mmol Et_4NBF_4, 2.5 mL acetone and 125 µL H_2O after electrolysis, indicating formation of 1-phenyl-2-(trifluoromethyl)prop-2-en-1-one.

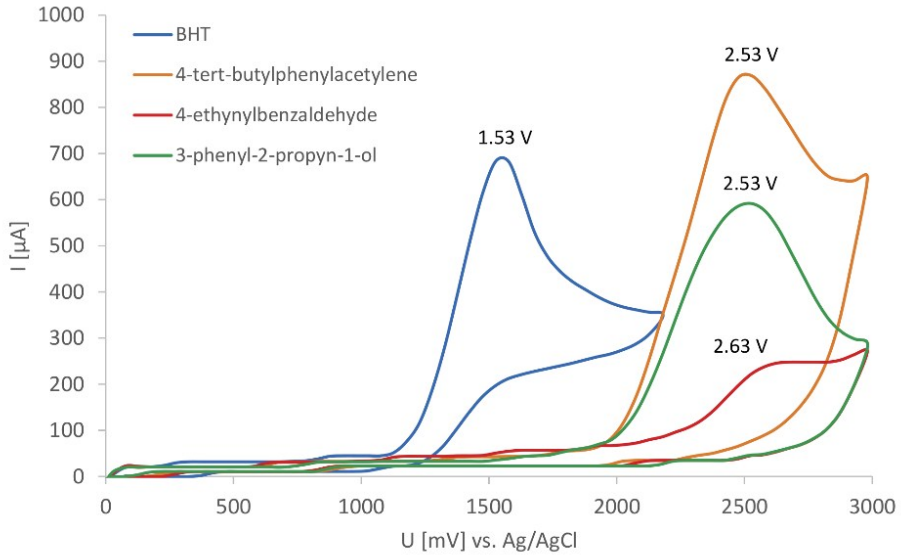


Fig. S5. Cyclic voltammograms of butylated hydroxytoluene (2,6-di-tert-butyl-4-methylphenol) (BHT), 4-*tert*-butylphenylacetylene, 4-ethynylbenzalhdehyde, 3-phenyl-2-propyn-1-ol. Conditions: 10 mM analyte, 100 mM Bu_4NBF_4 in acetonitrile. Working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgCl. Scan rate: 200 mV/s.

Reaction mechanism & radical trapping experiments

The proposed mechanism is initiated by the anodic oxidation of the triflinate anion, giving rise to the corresponding CF_3SO_2 radical, which decomposes into a CF_3 radical upon liberation of SO_2. The presence of trifluoromethylated and trifluoromethanesulfonylated species in most reactions implies the intermittent presence of both radicals. In Fig. S6, a GC-MS chromatogram of the crude reaction mixture of the model substrate **1a** after electrolysis under typical conditions is depicted, along with mass spectra at 5.74, 6.31 and 6.47 min, corresponding to trifluoromethylated and trifluoromethanesulfonylated compounds.

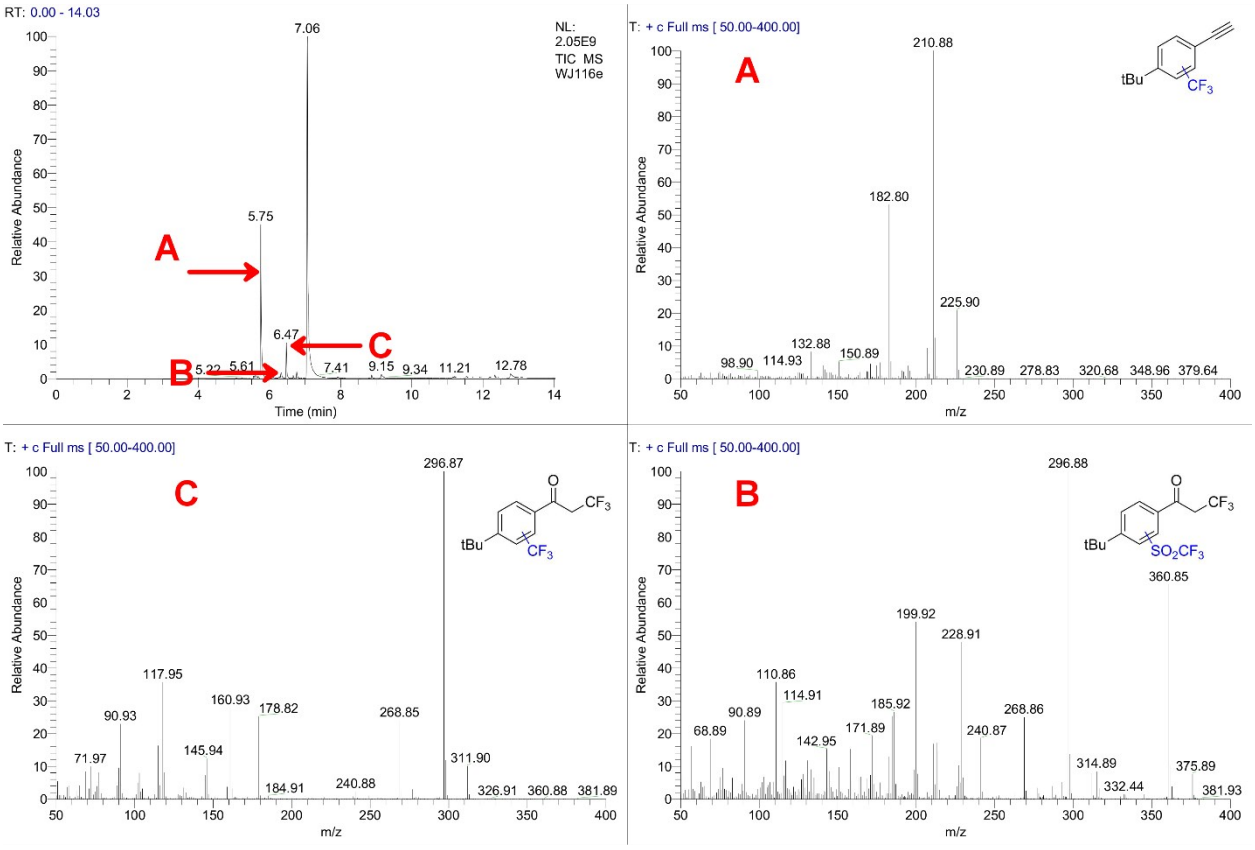


Fig. S6. GC-MS chromatogram of a typical reaction mixture of the model substrate (**1a**) and extracted mass spectra from the peaks at 5.74, 6.31 and 6.47 min. Most likely, these products result from the reaction of SO_2CF_3 and CF_3 radicals with the aromatic ring of the substrate or product.

To provide further evidence for the presence of radical species in the reaction mechanism, **1a** was electrolyzed in the presence of BHT (2,6-di-tert-butyl-4-methylphenol) as trapping agent (1 equiv.). GC-MS analysis of the crude reaction mixture (Fig. S7) revealed the presence of α-trifluoromethyl ketone **2a** as well as CF_3 radical addition products to the aromatic ring of **1a** and BHT. Furthermore, a peak corresponding to the reaction of radical **9** (see Fig. 4) with BHT was observed. Addition of a SO_2CF_3 radical to BHT was not detected.

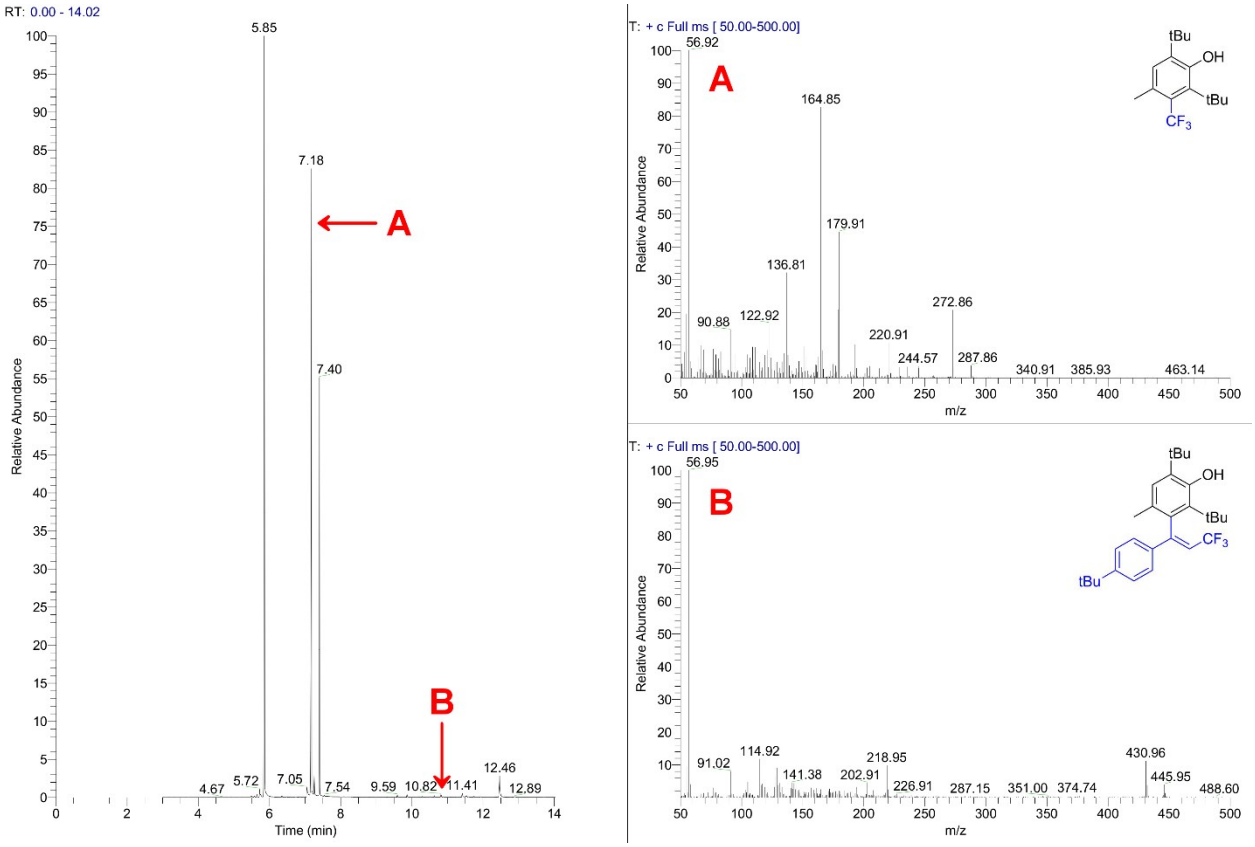


Fig. S7. GC-MS chromatogram of a typical reaction mixture of the model substrate (**1a**) with 1 equiv. BHT added. The mixture contains the peak corresponding to the trapping product of the CF_3 radical (A) and radical **9** (B).

HPLC monitoring of the reaction

To further elucidate the observed selectivity, an HPLC time study of the model reaction (0.2 M 4-*tert*-butylphenylacetylene, 0.4 M $NaSO_2CF_3$, 0.1 M Et_4NBF_4, 2.5 mL acetone, 125 µL H_2O, constant current: 30 mA) was conducted. Fig. S10 and S11a depict that the formation of α-trifluormethyl ketone **2a** is faster than the addition of the CF_3 radical to the aromatic ring of the substrate, affording **3a**. In addition, Fig. S10 highlights that increasing the amount of charge beyond 2.2 F/mol does not further enhance the product titer of **1a** and **2a**. Instead, along with additional conversion of **1a**, the concentration of other species and the speed of their formation increases, which implies further reaction of **2a** or **3a** to secondary products. Structures for two of these secondary products have been identified by GC-MS (Fig. S6).

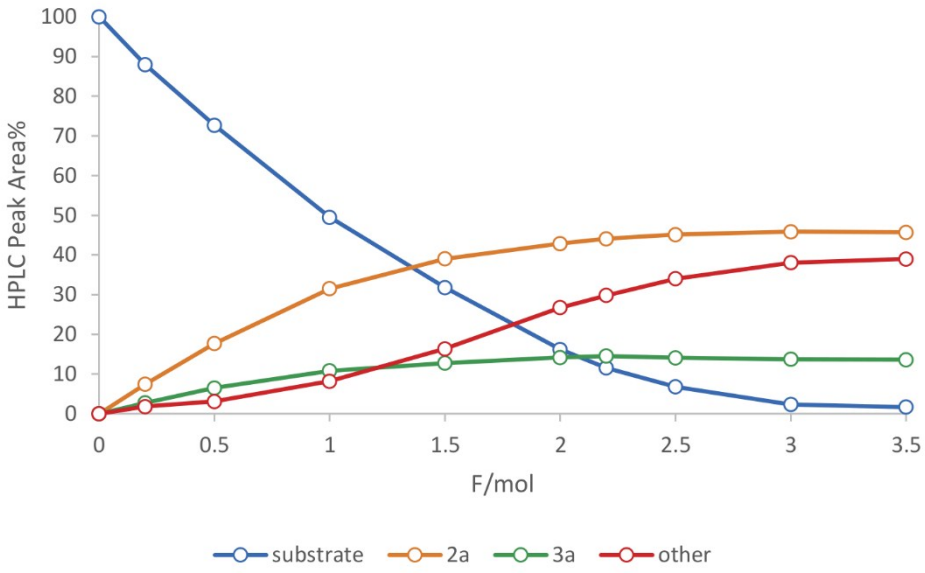
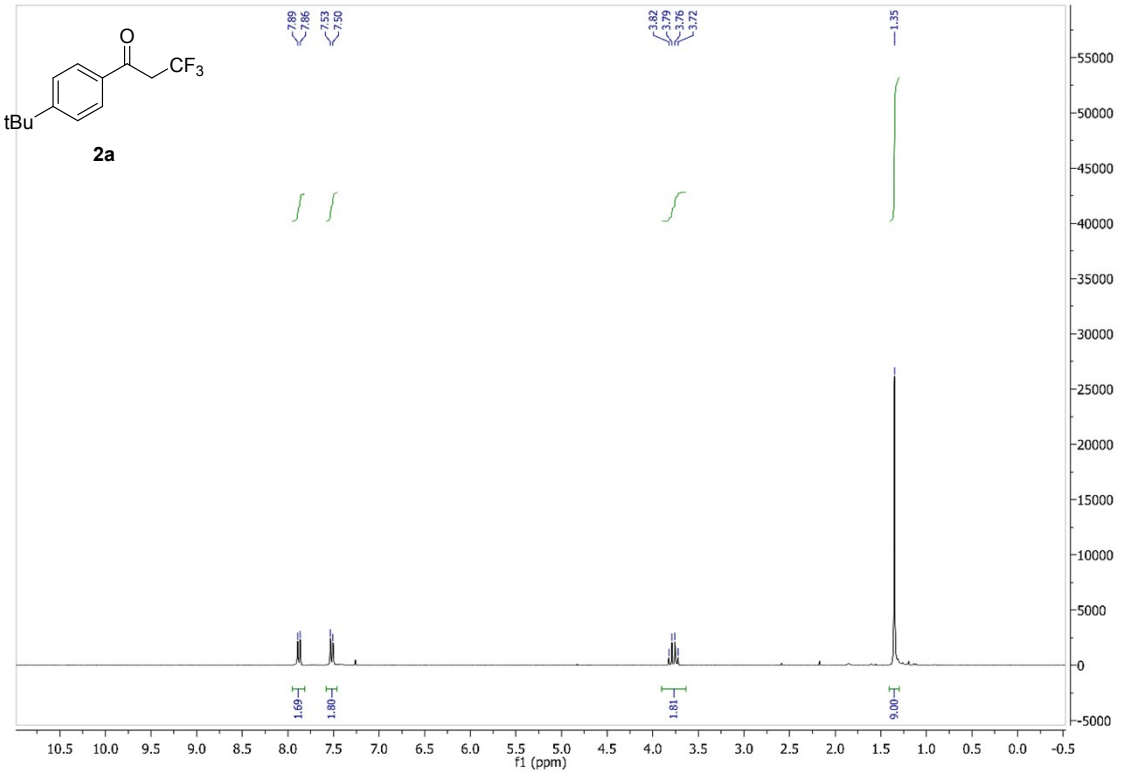
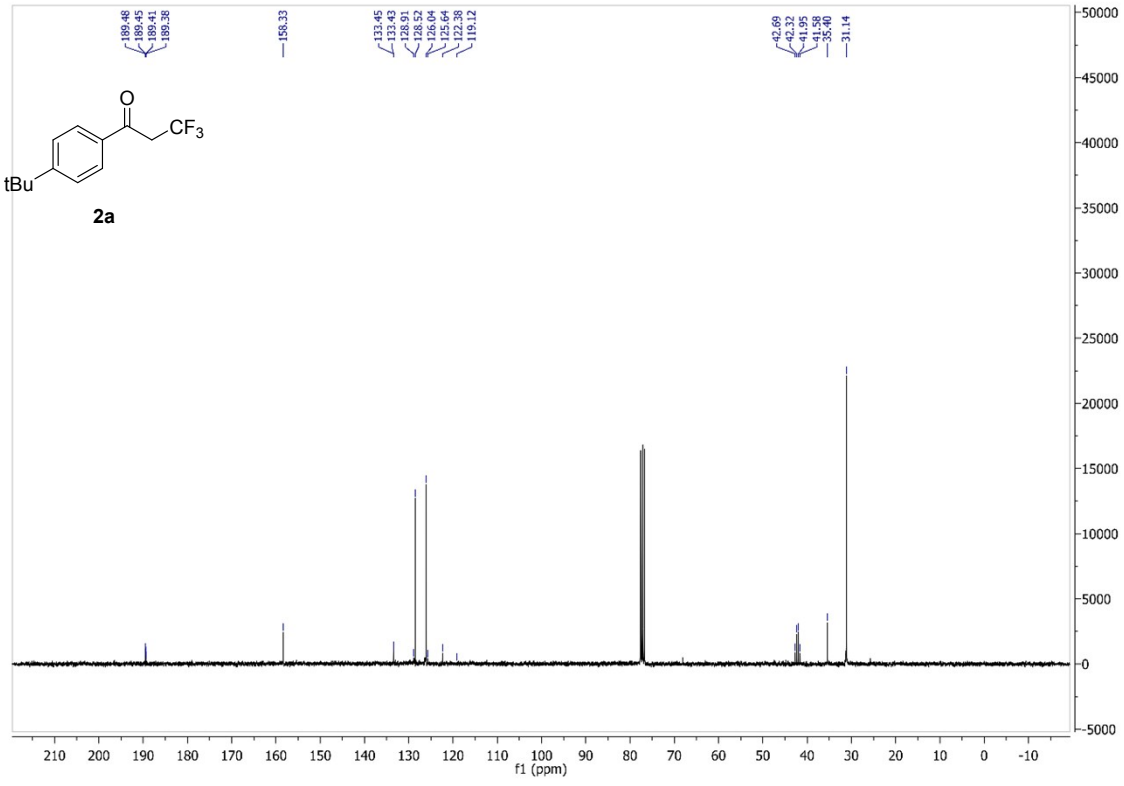
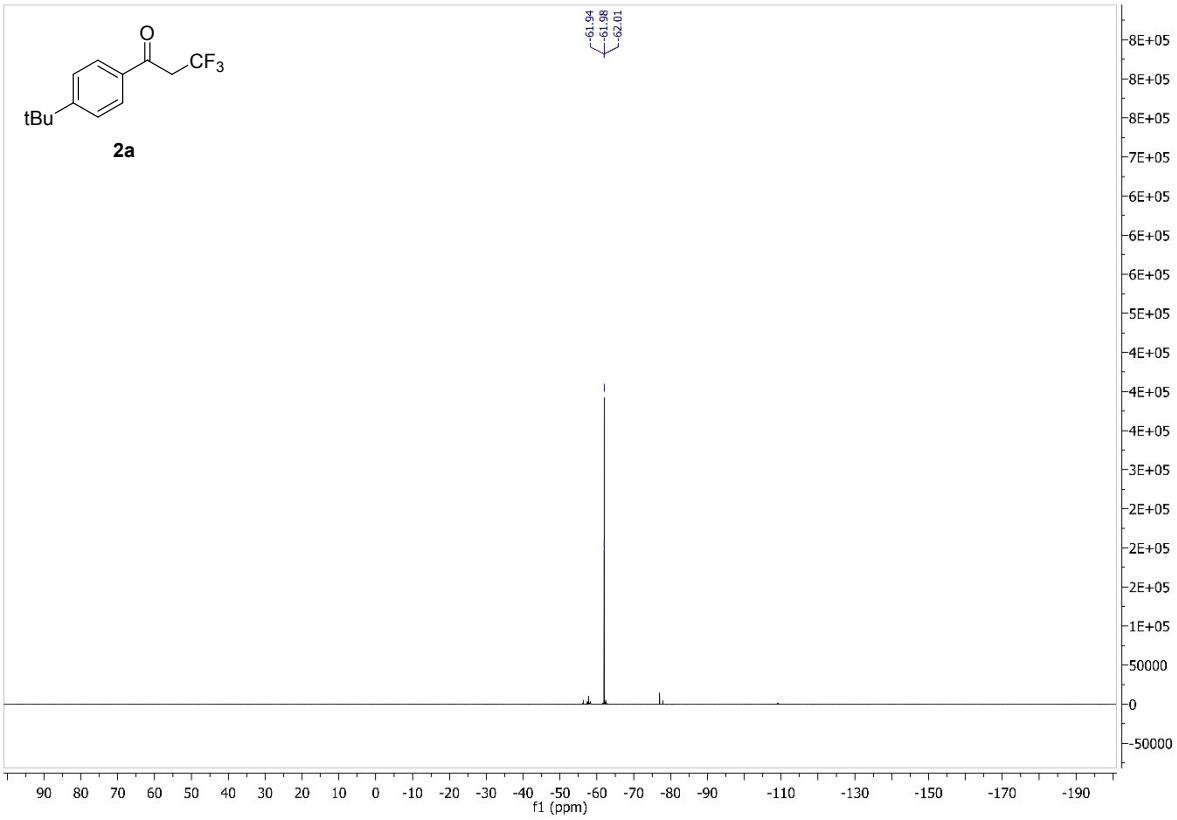


Fig. S8. Fate of different species in the electrochemical transformation of **1a** over time. Conditions: 0.2 M 4-*tert*-butylphenylacetylene, 0.4 M $NaSO_2CF_3$, 0.1 M Et_4NBF_4, 2.5 mL acetone, 125 µL H_2O, 30 mA (constant current).

Copies of NMR spectra of all isolated compounds



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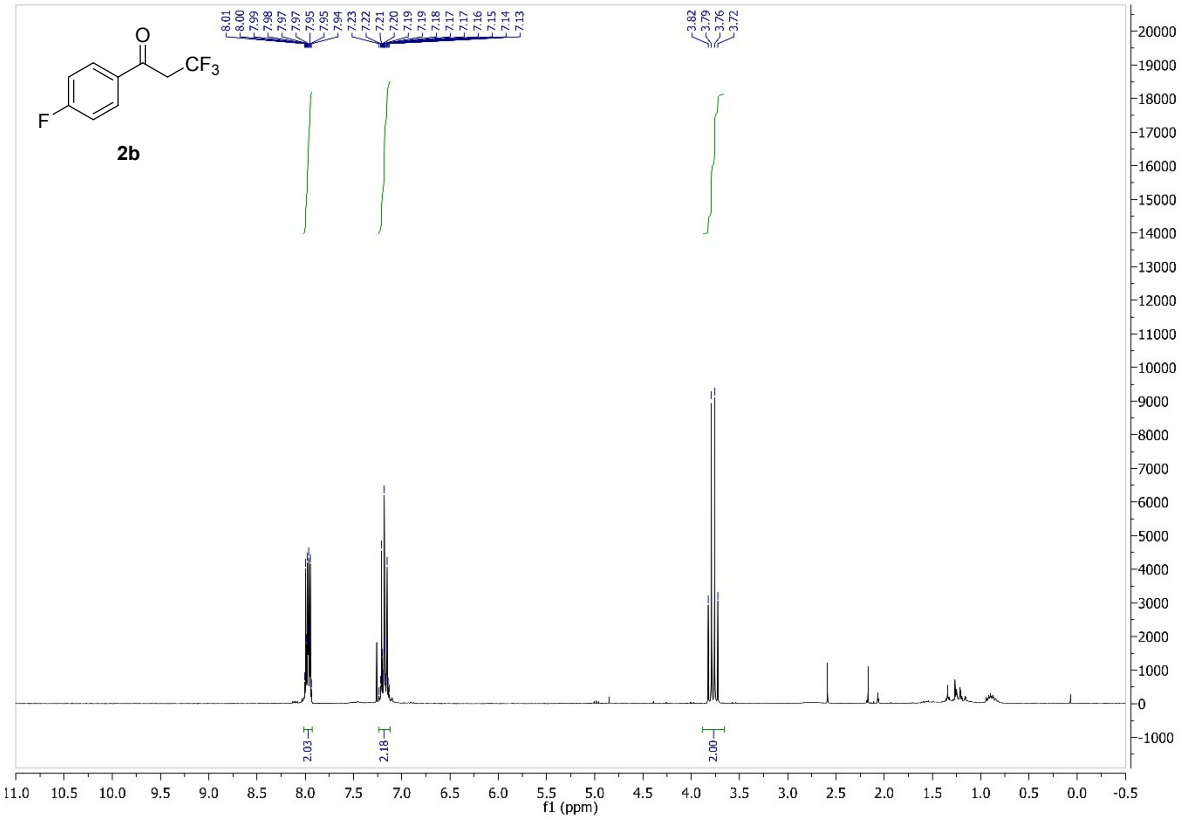
-62.01
f1 (ppm)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F
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8.00
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7.98
7.97
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7.95
7.95
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7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.17
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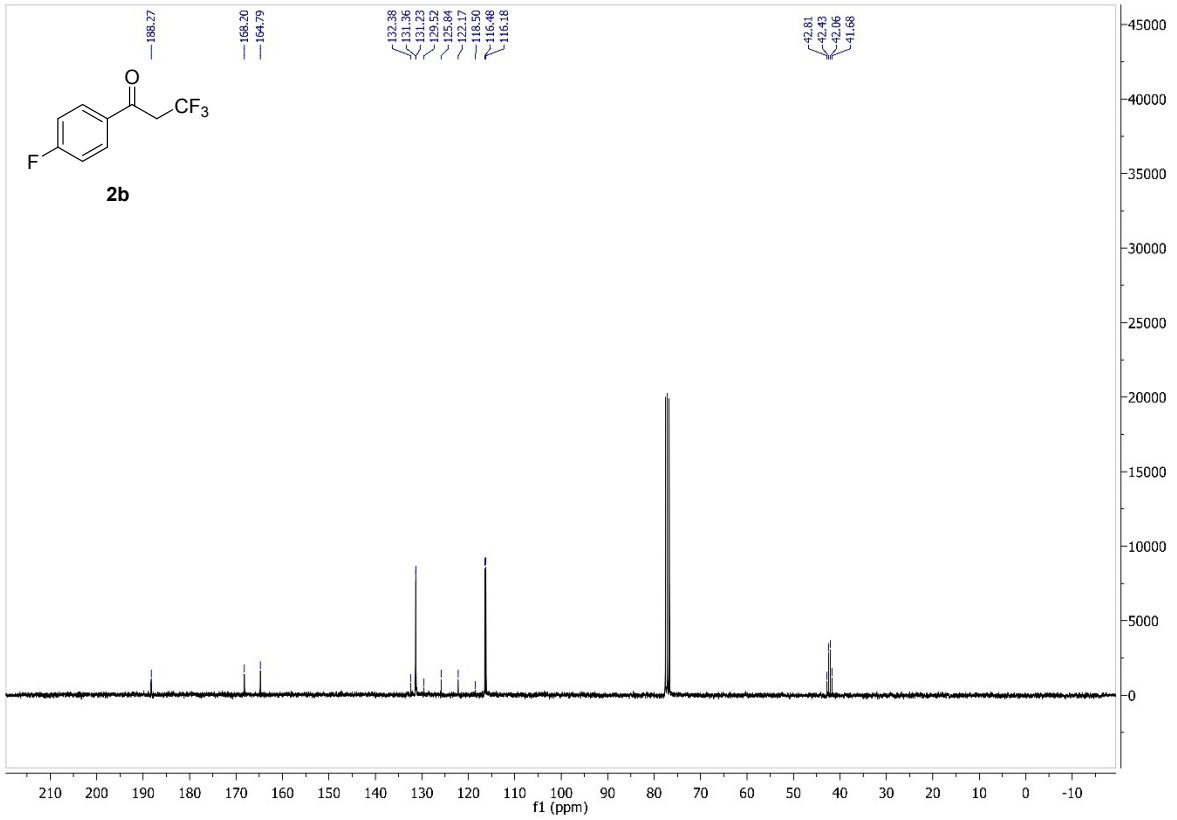
2.00
f1 (ppm)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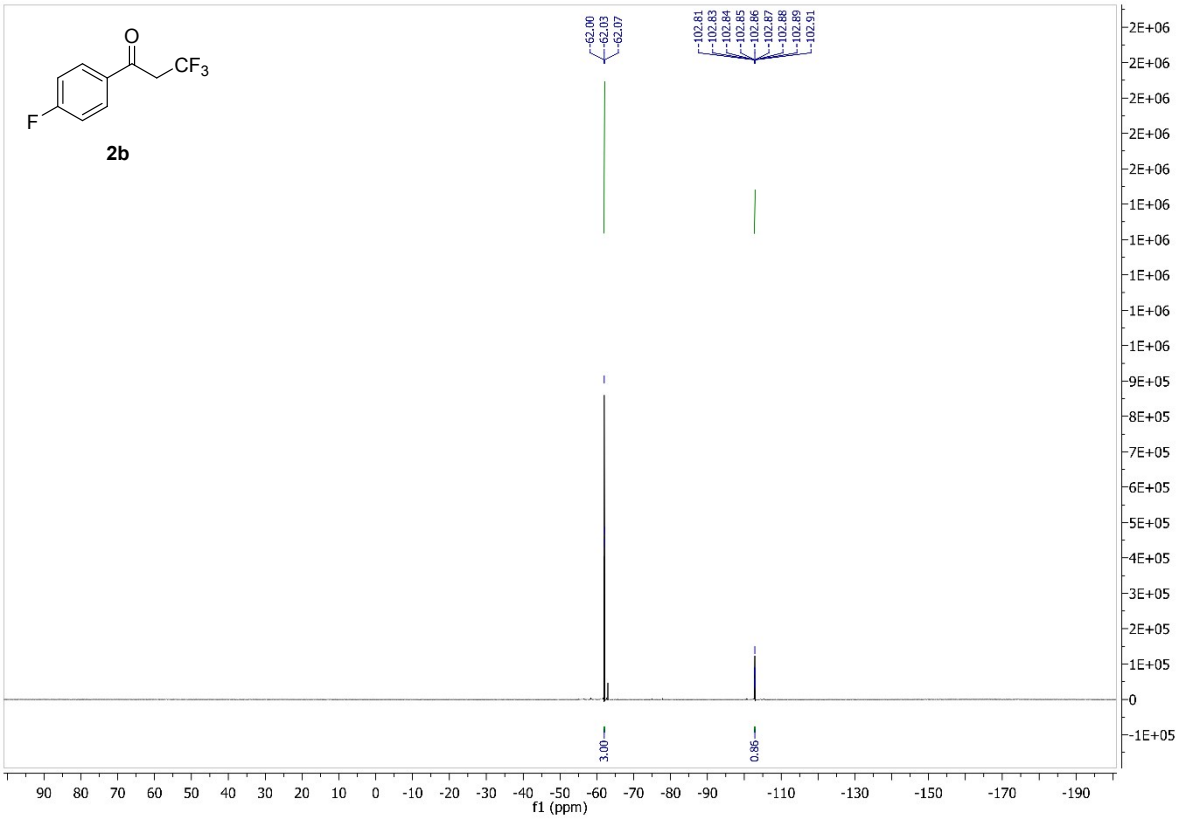
41.68
O
CF3
F
2b
f1 (ppm)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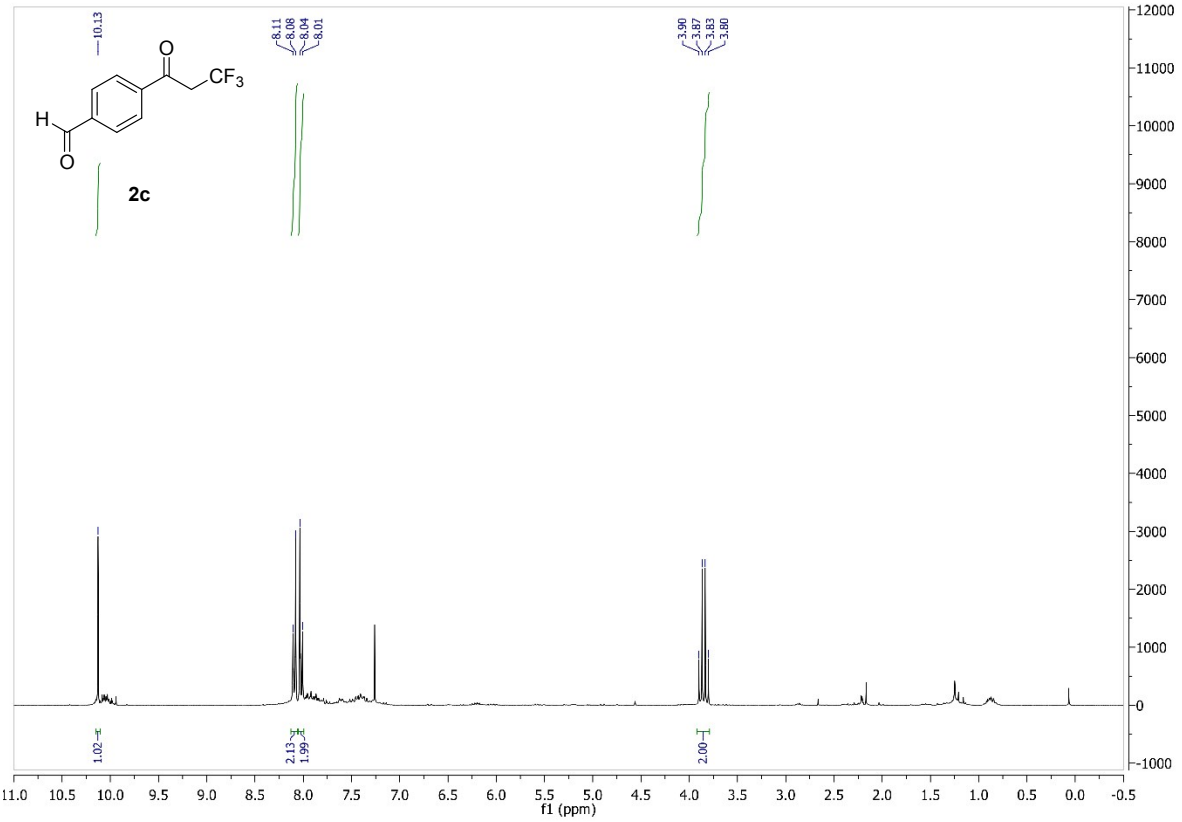
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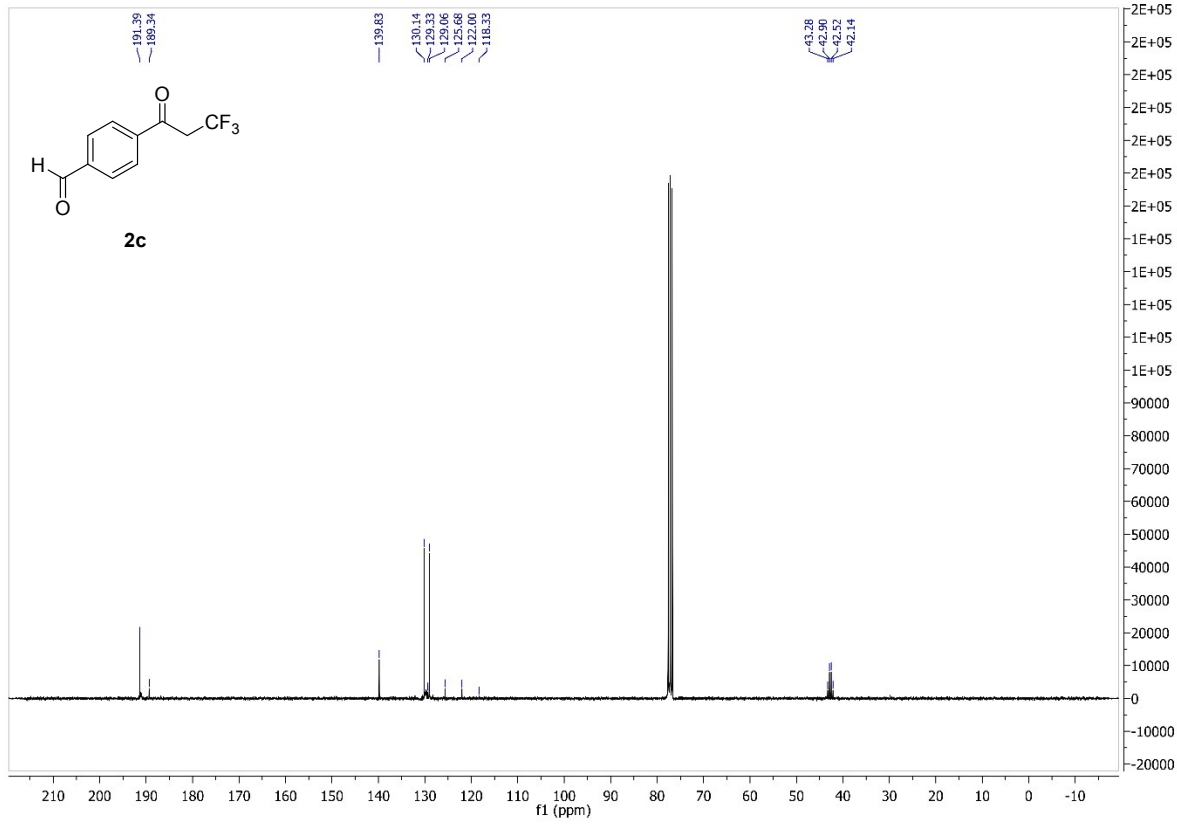
2.00
f1 (ppm)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CF3
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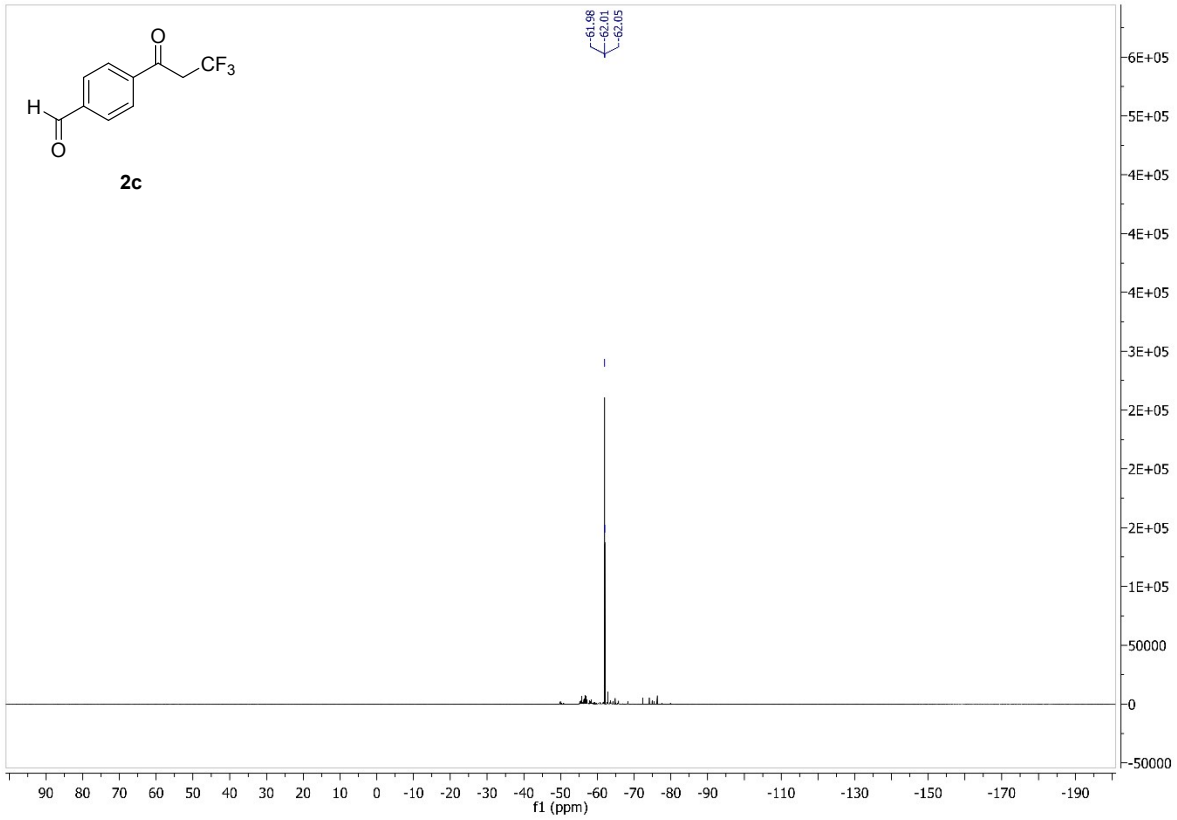
O
2c
f1 (ppm)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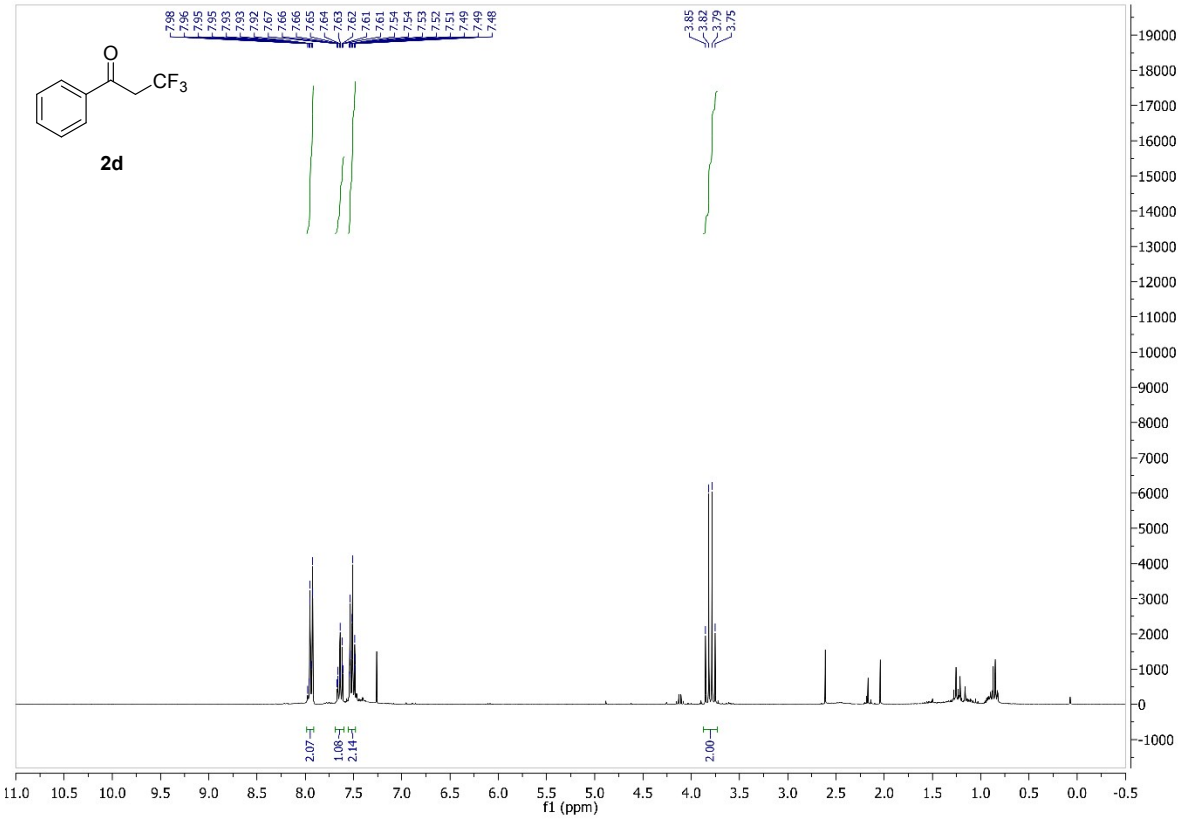
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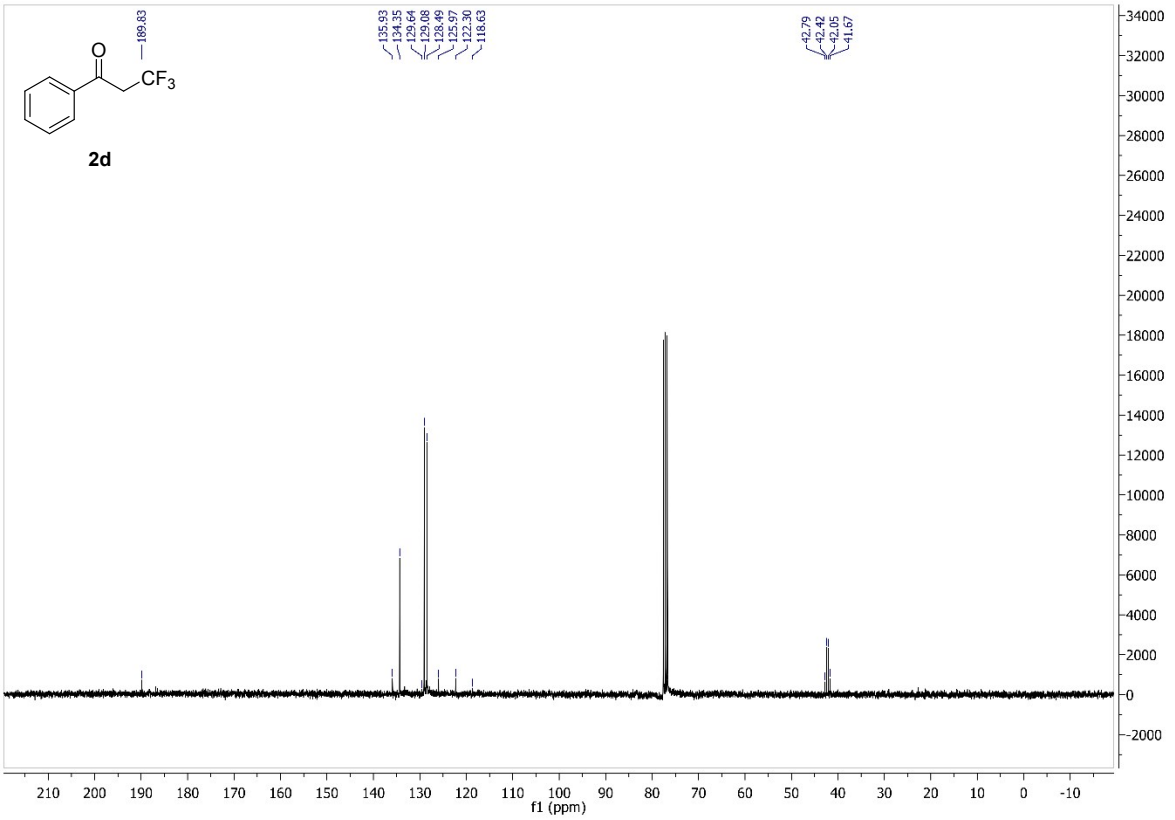
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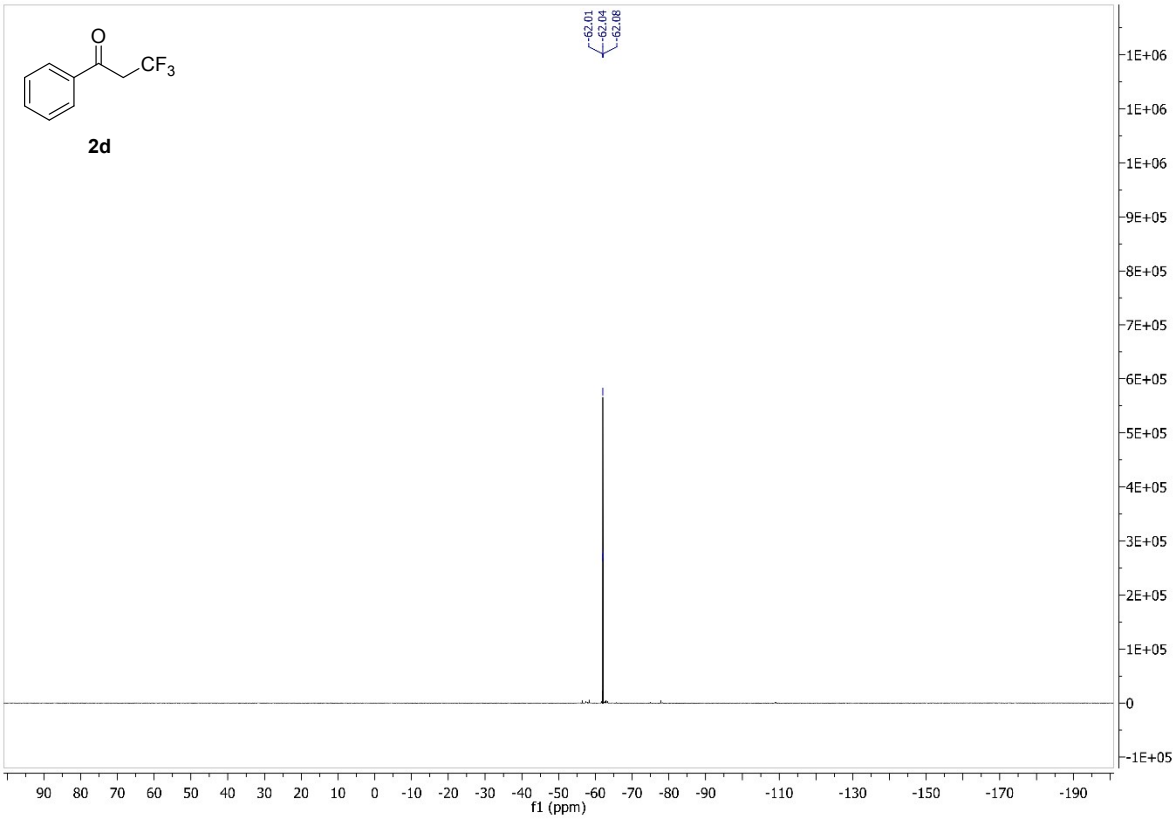
2d
f1 (ppm)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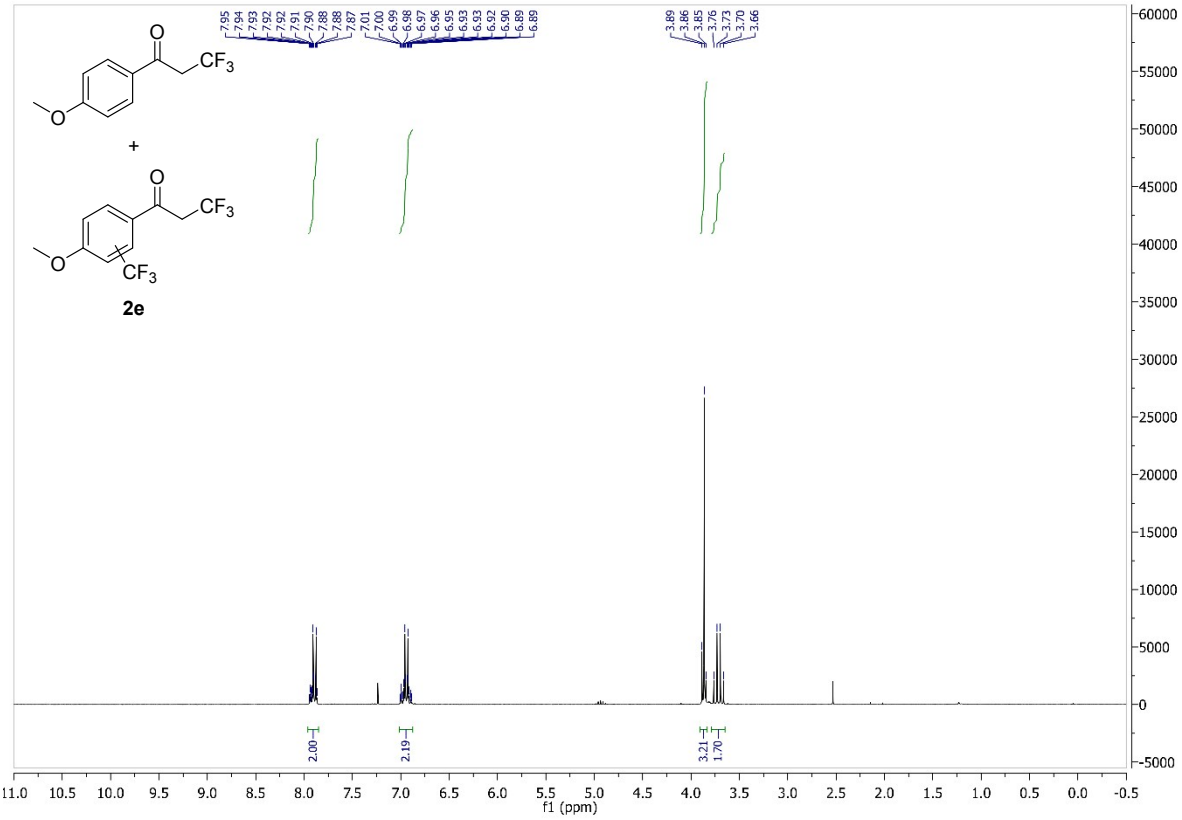
CF3
2d
f1 (ppm)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6.90
6.89
3.89
3.86
3.85
3.76
3.73
3.70
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CF3
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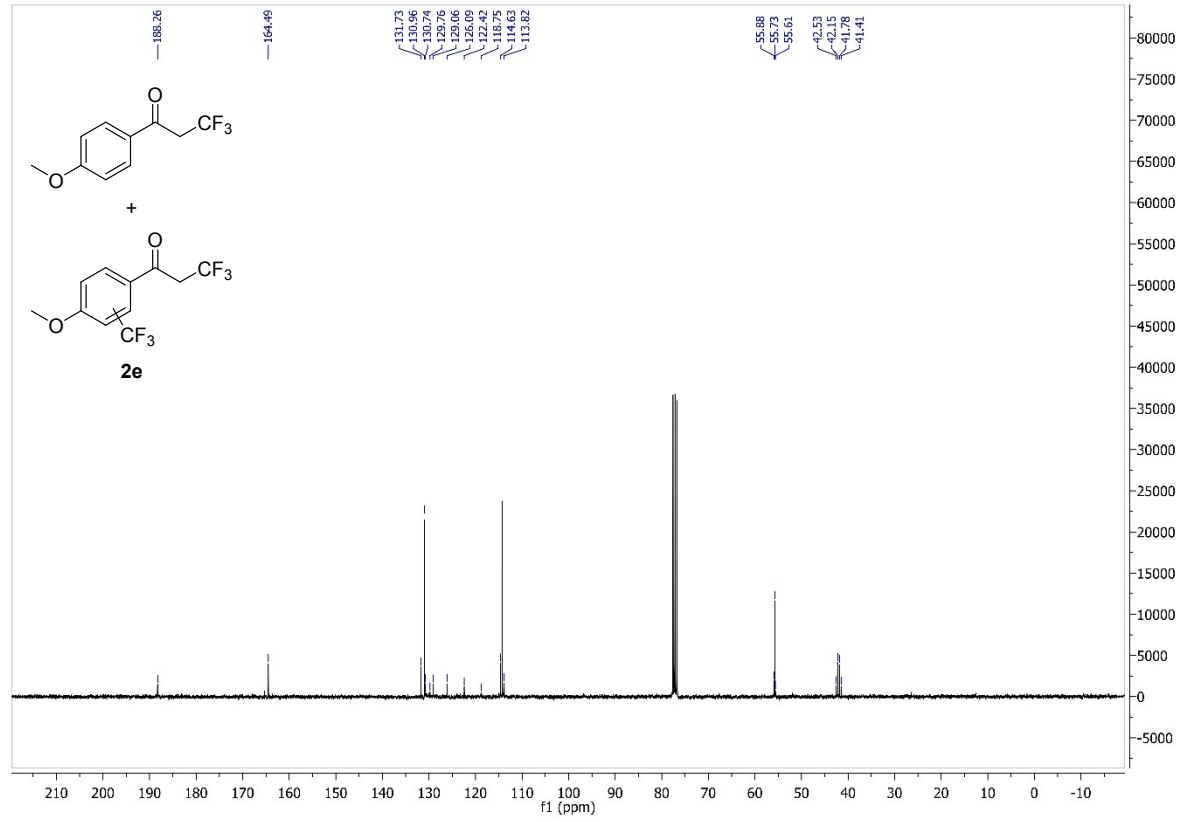
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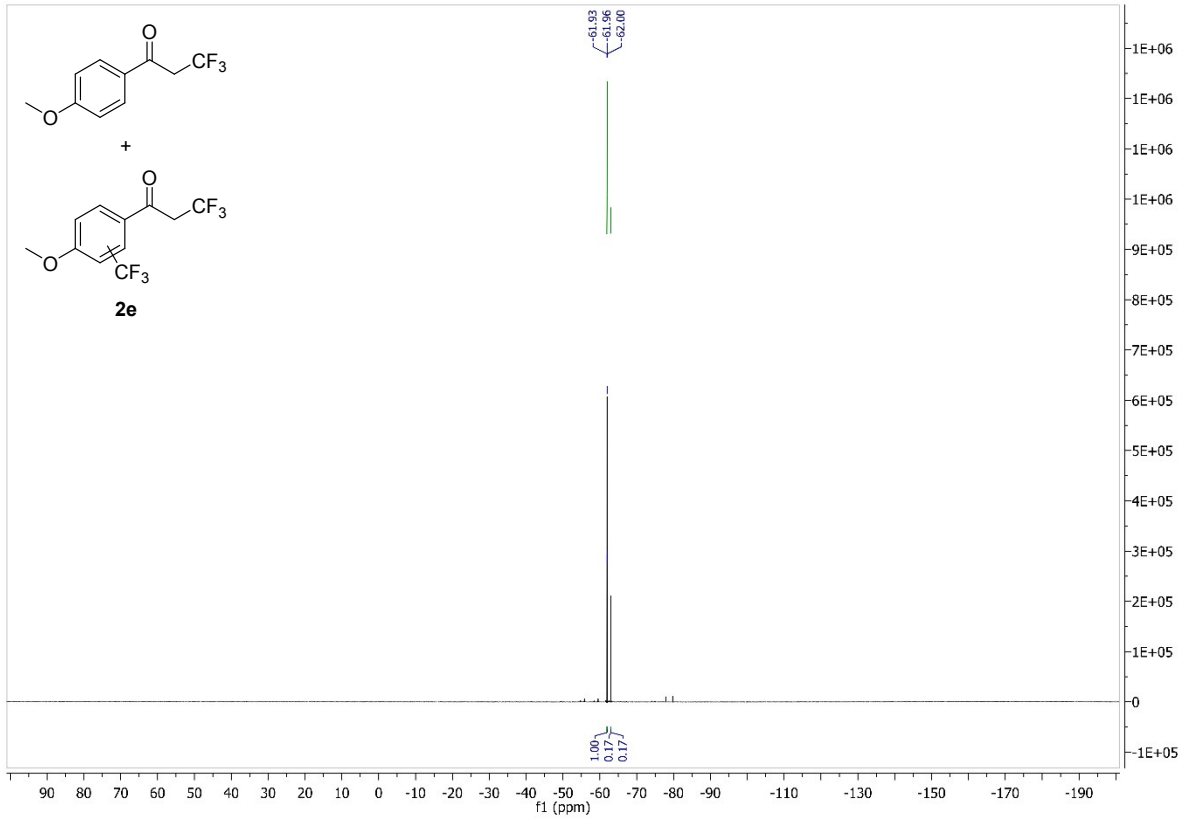
+
O
CF3
O
CF3
2e
f1 (ppm)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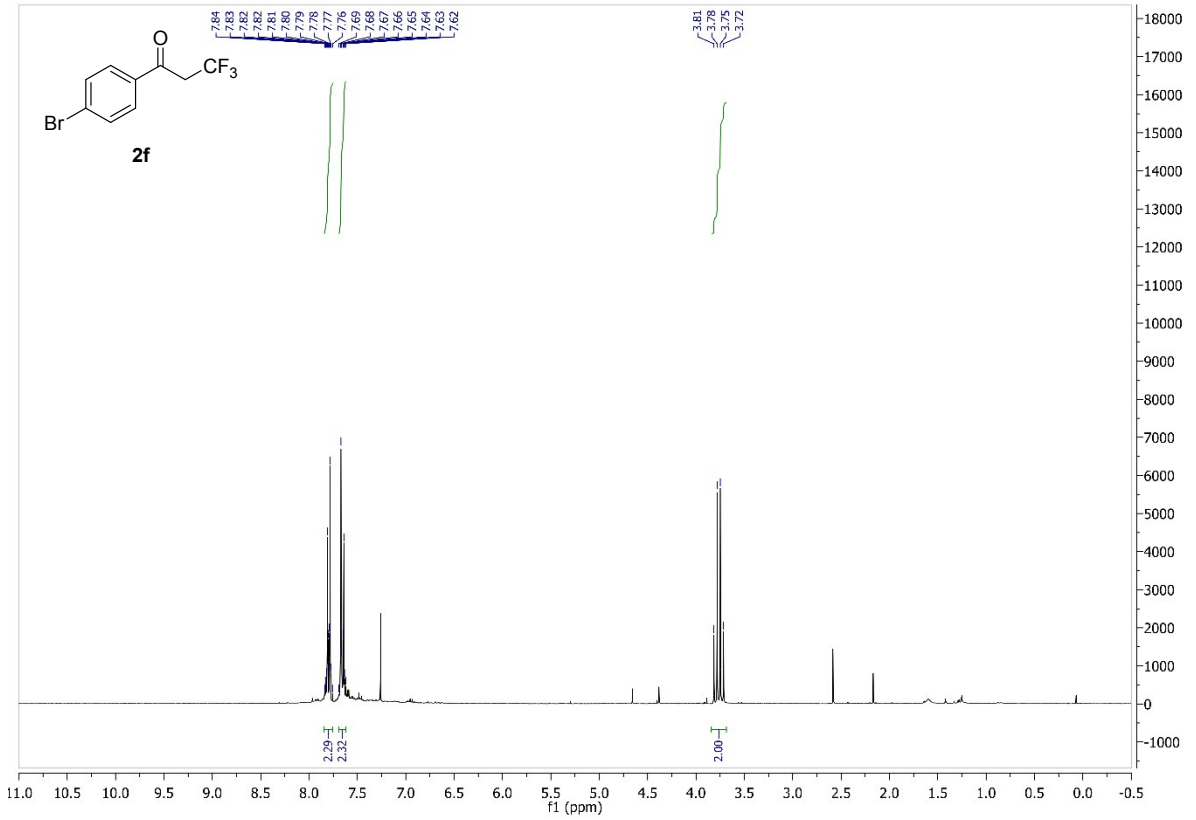
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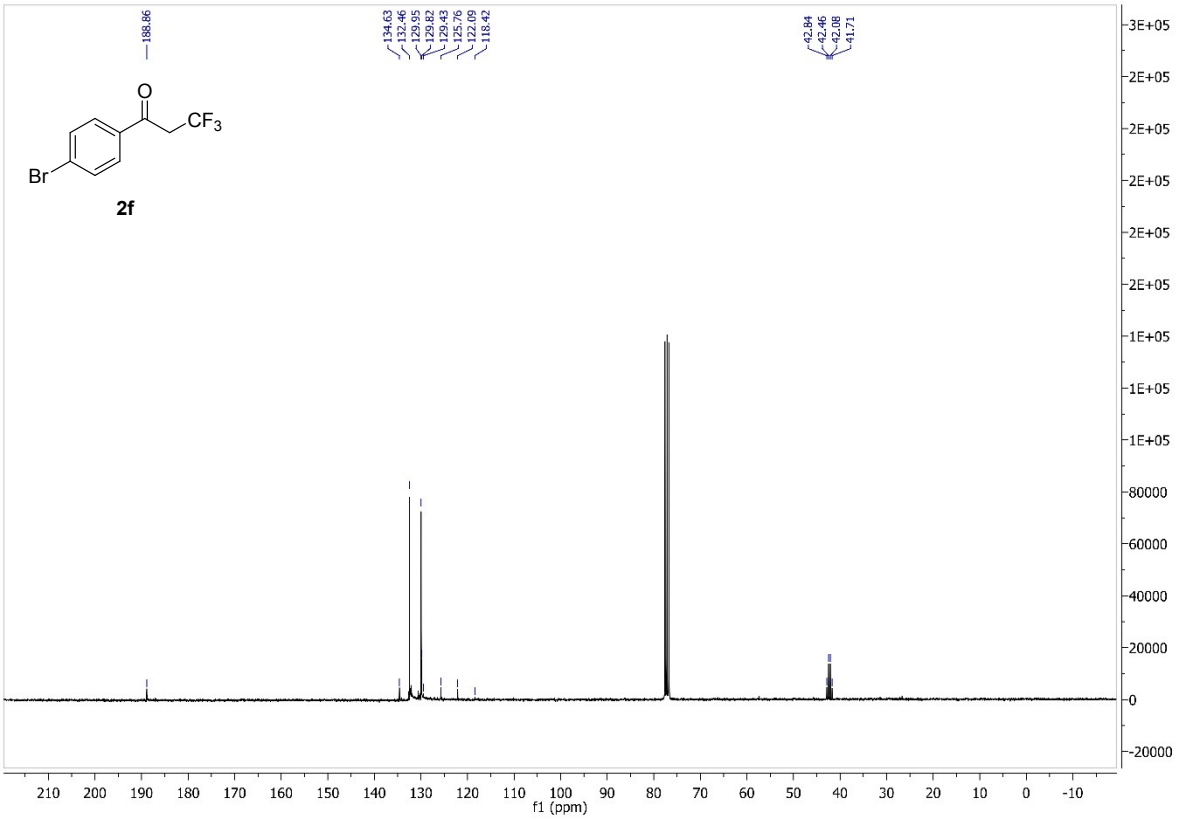
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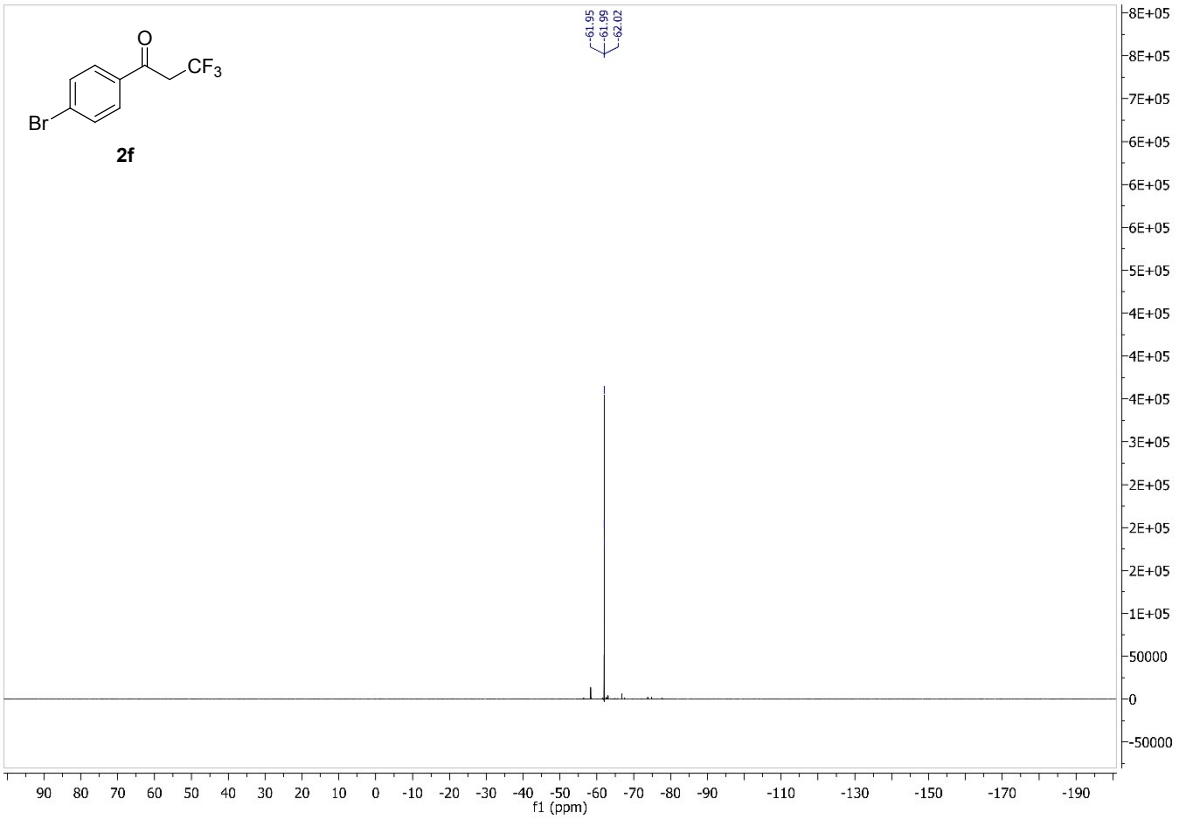
Br
2f
f1 (ppm)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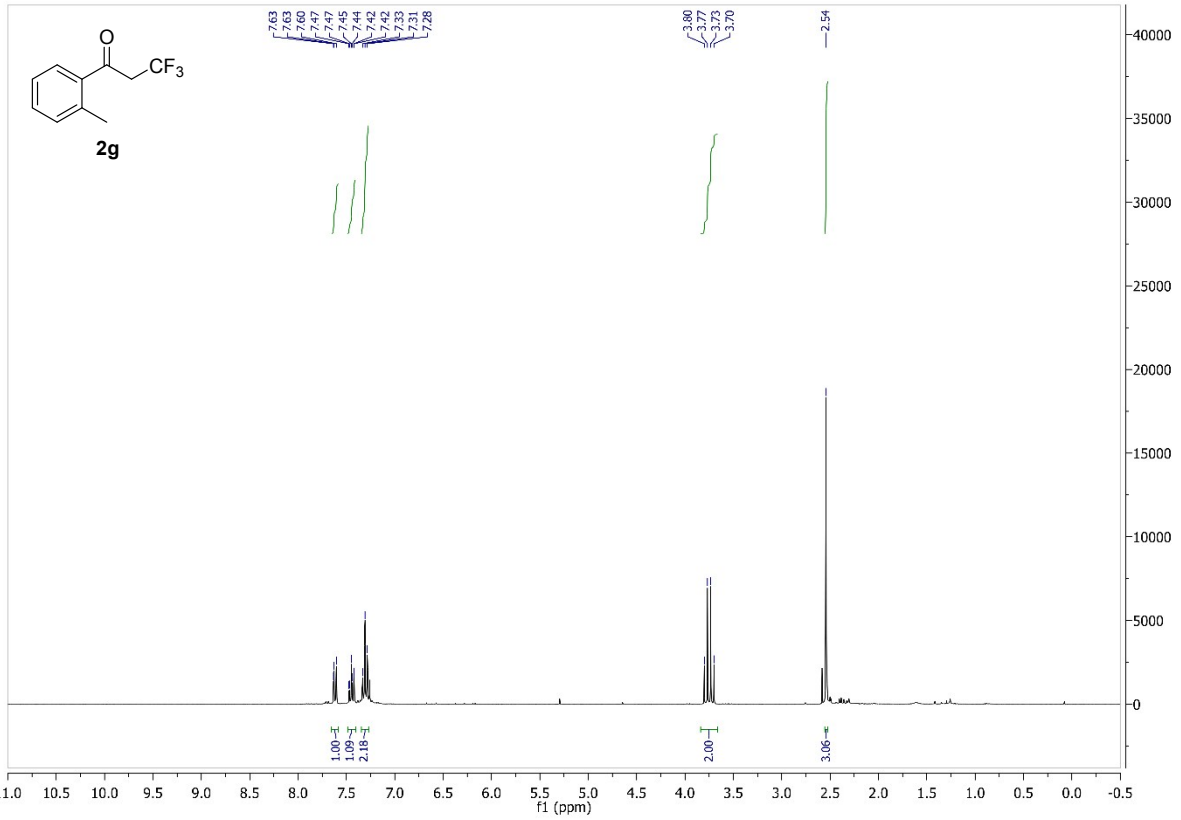
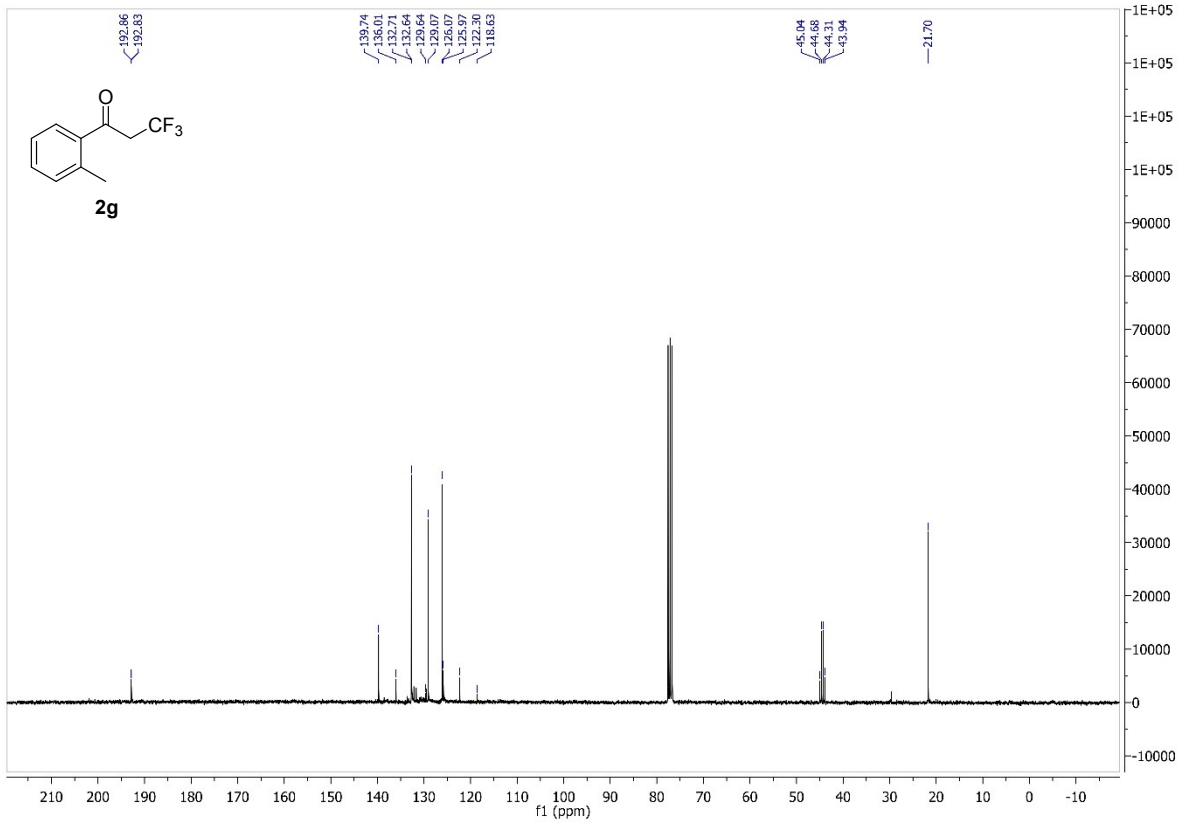
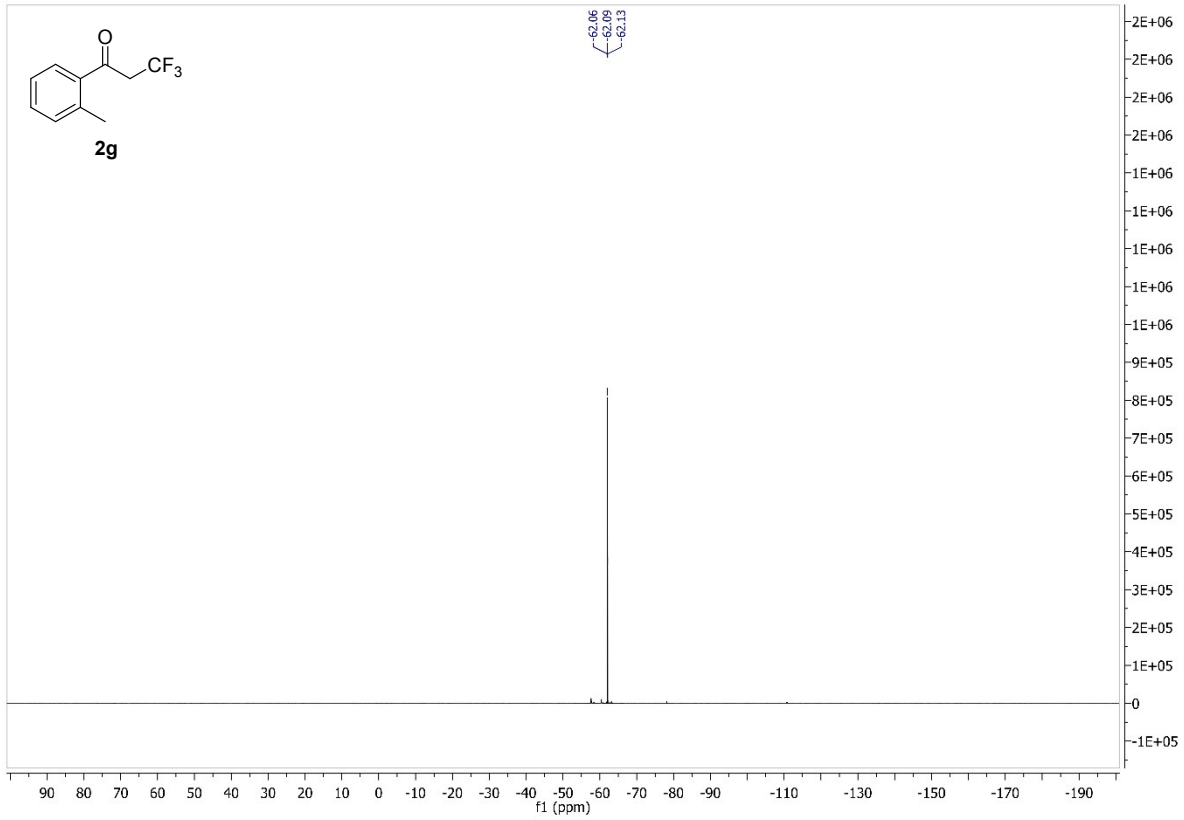
-61.99
-62.02
O
CF3
Br
2f
f1 (ppm)


7.63
7.63
7.60
7.47
7.47
7.45
7.44
7.42
7.42
7.33
7.31
7.28
3.80
3.77
3.73
3.70
2.54
O
CF3
2g
1.00
1.09
2.18
2.00
3.06
f1 (ppm)


192.86
192.83
139.74
136.01
132.71
132.64
129.64
129.07
126.07
125.97
122.30
118.63
45.04
44.68
44.31
43.94
21.70
O
CF3
2g
f1 (ppm)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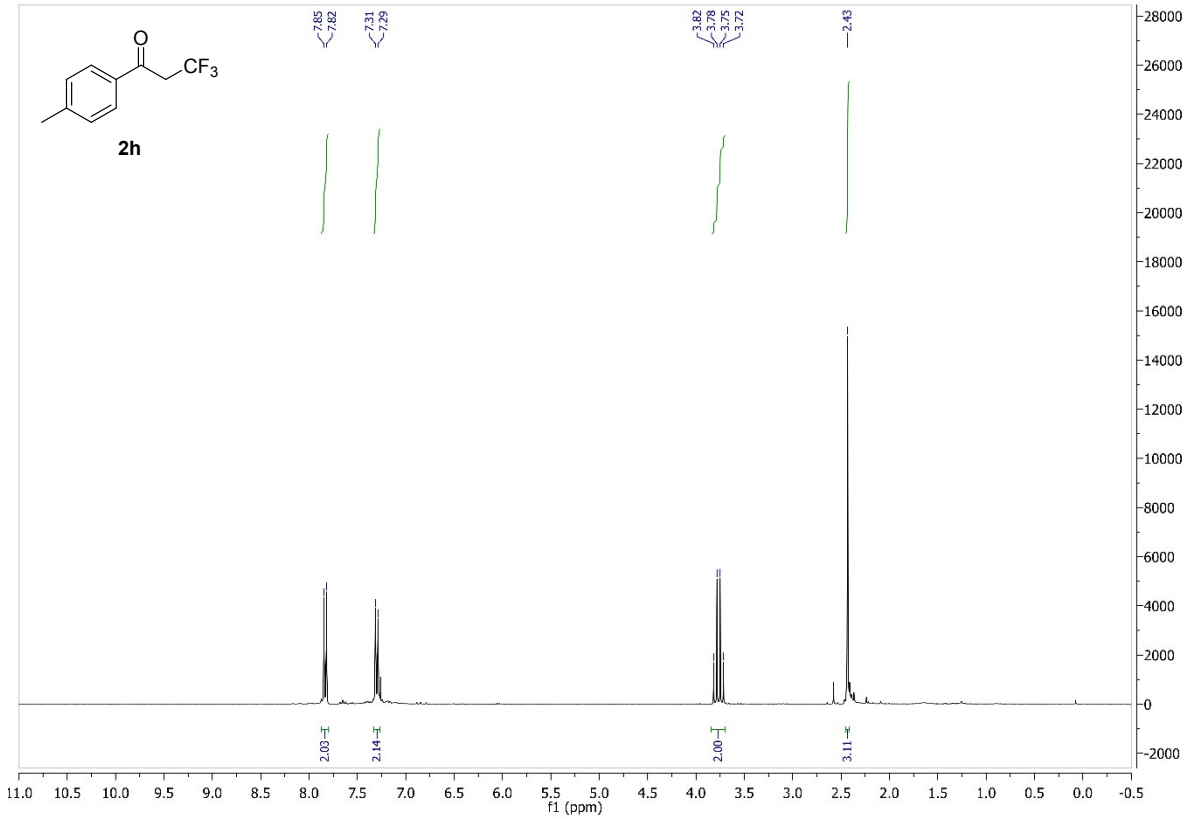
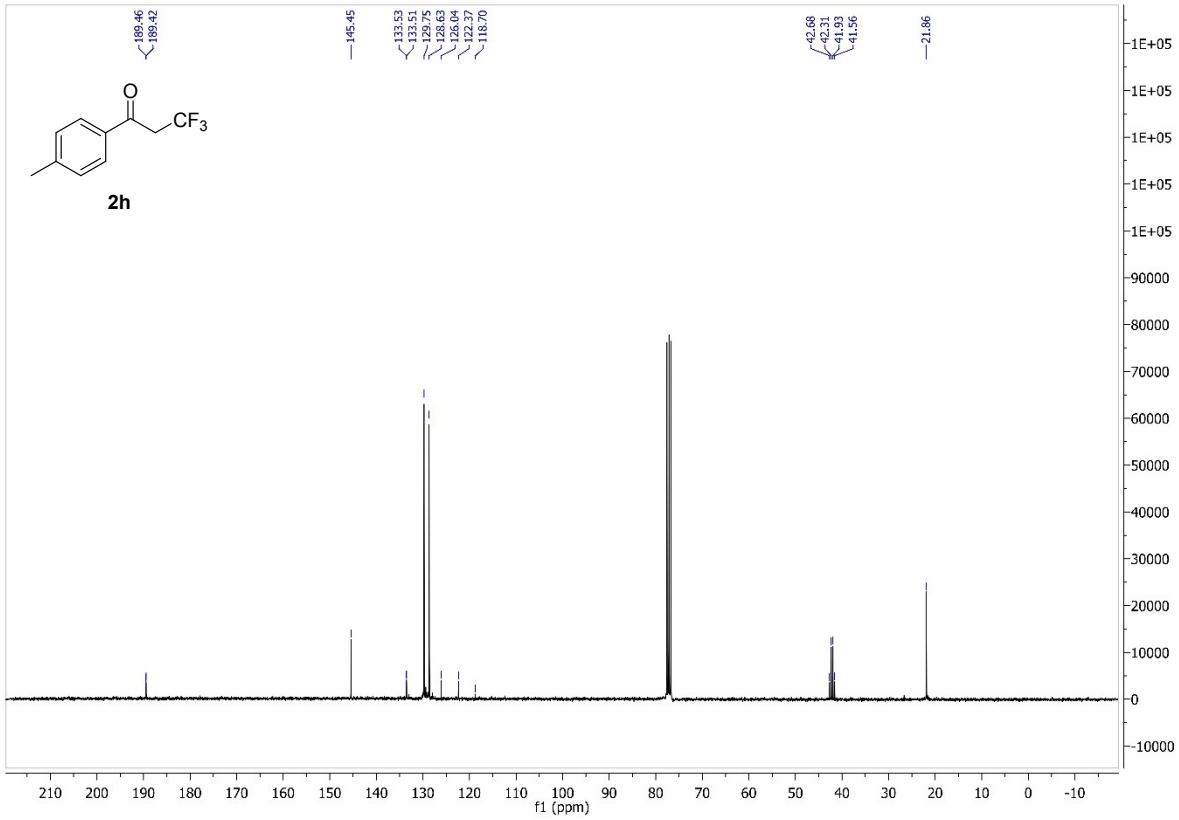
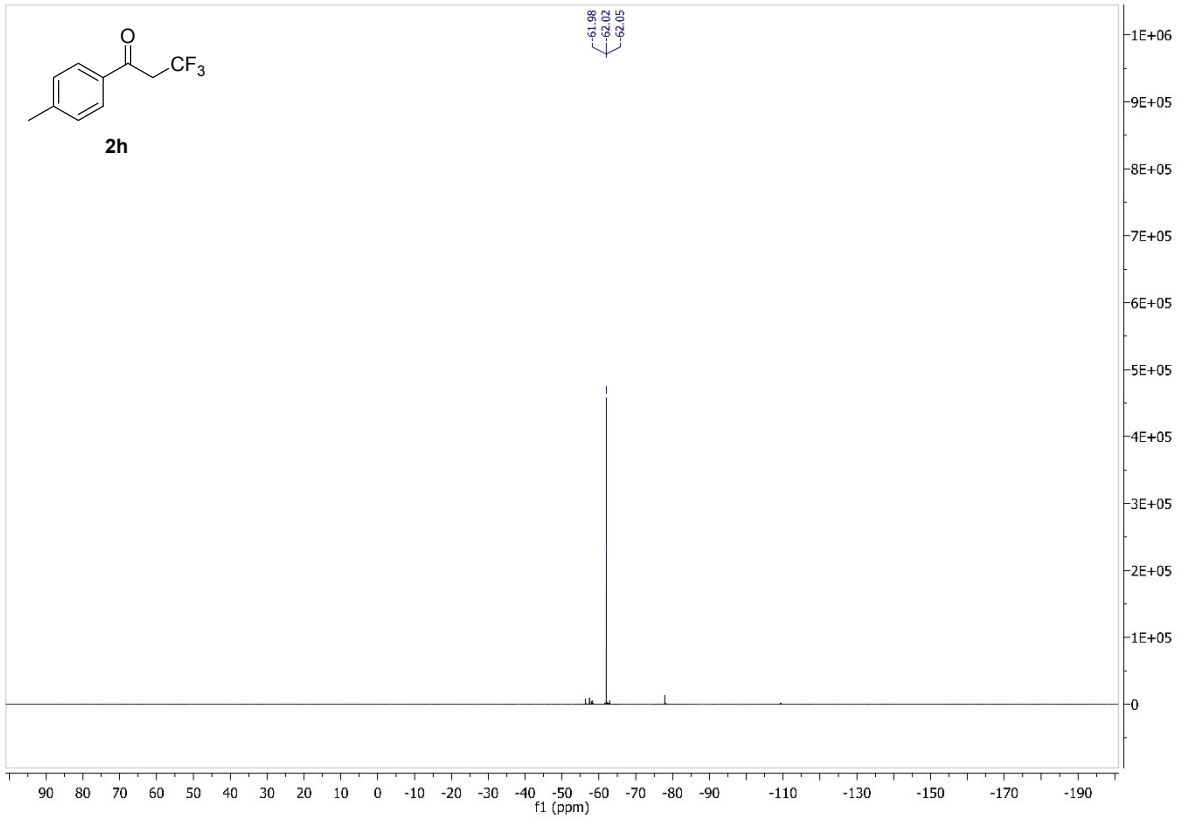
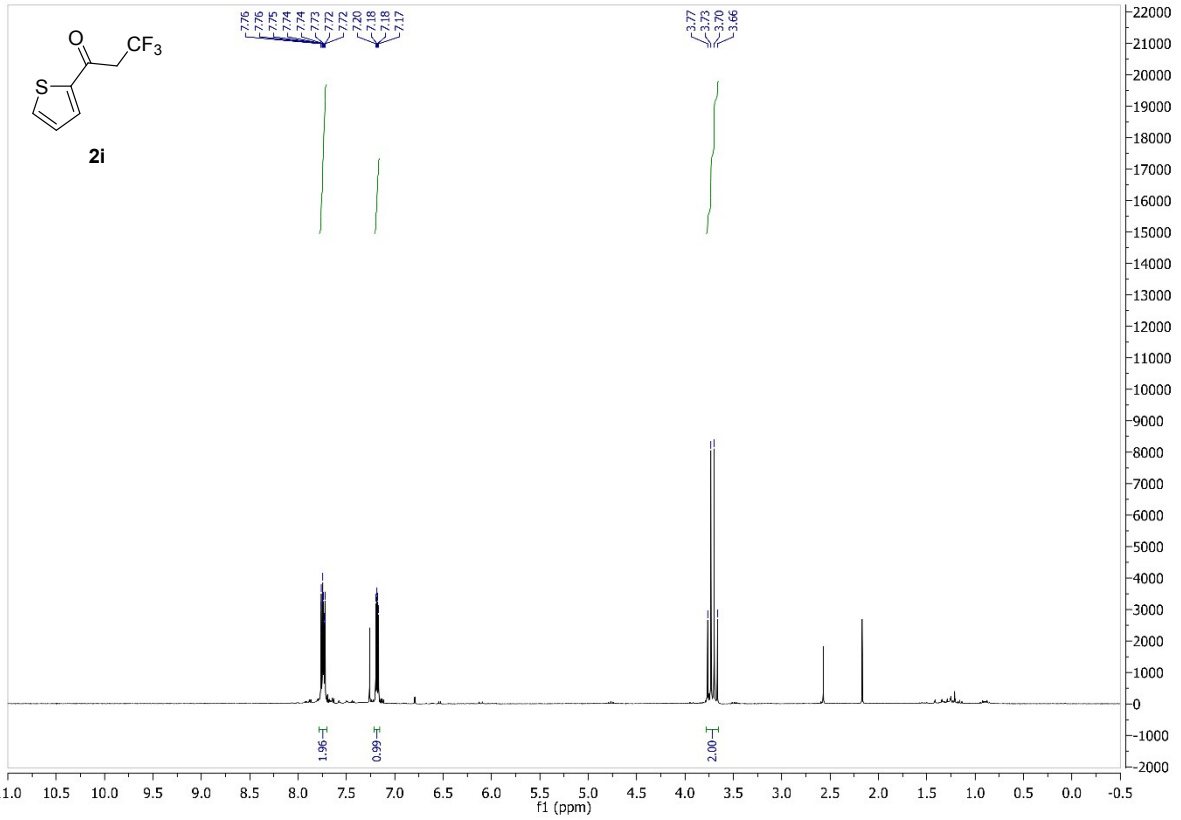
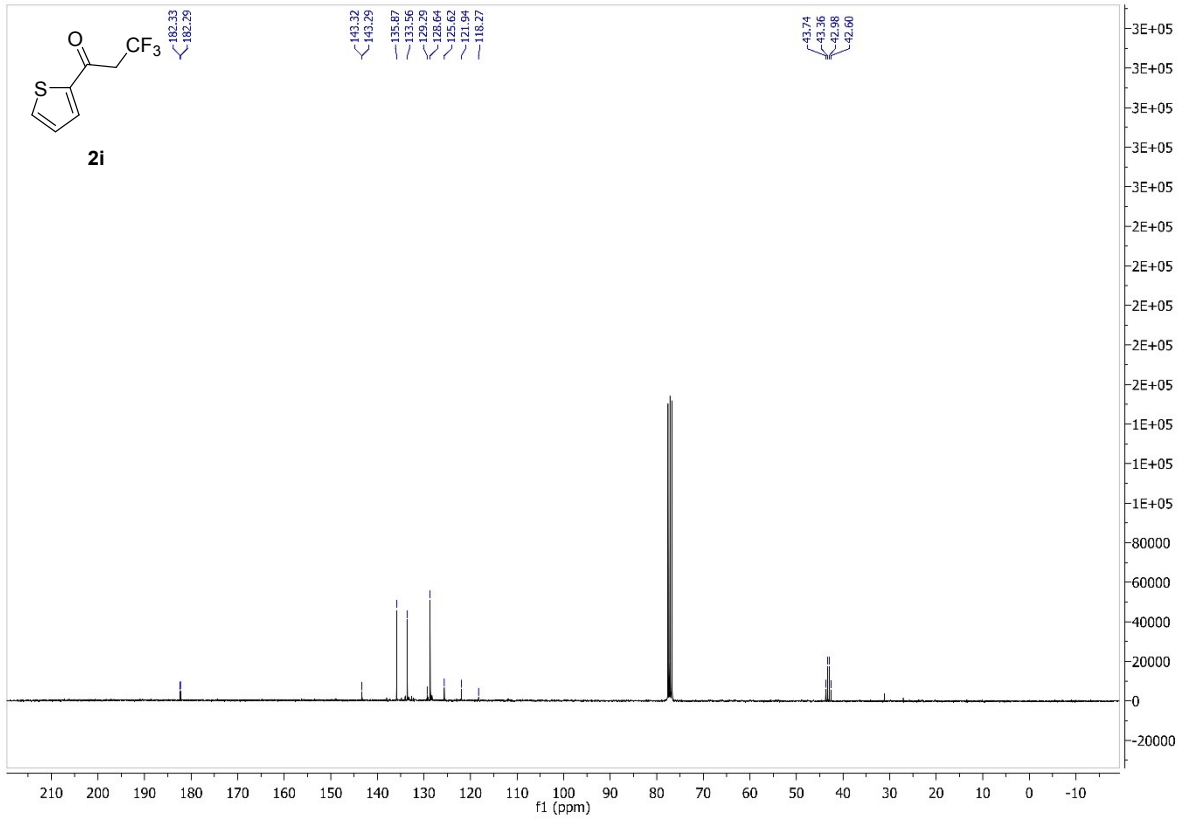
CF3
2g
-62.06
-62.09
-62.13
f1 (ppm)

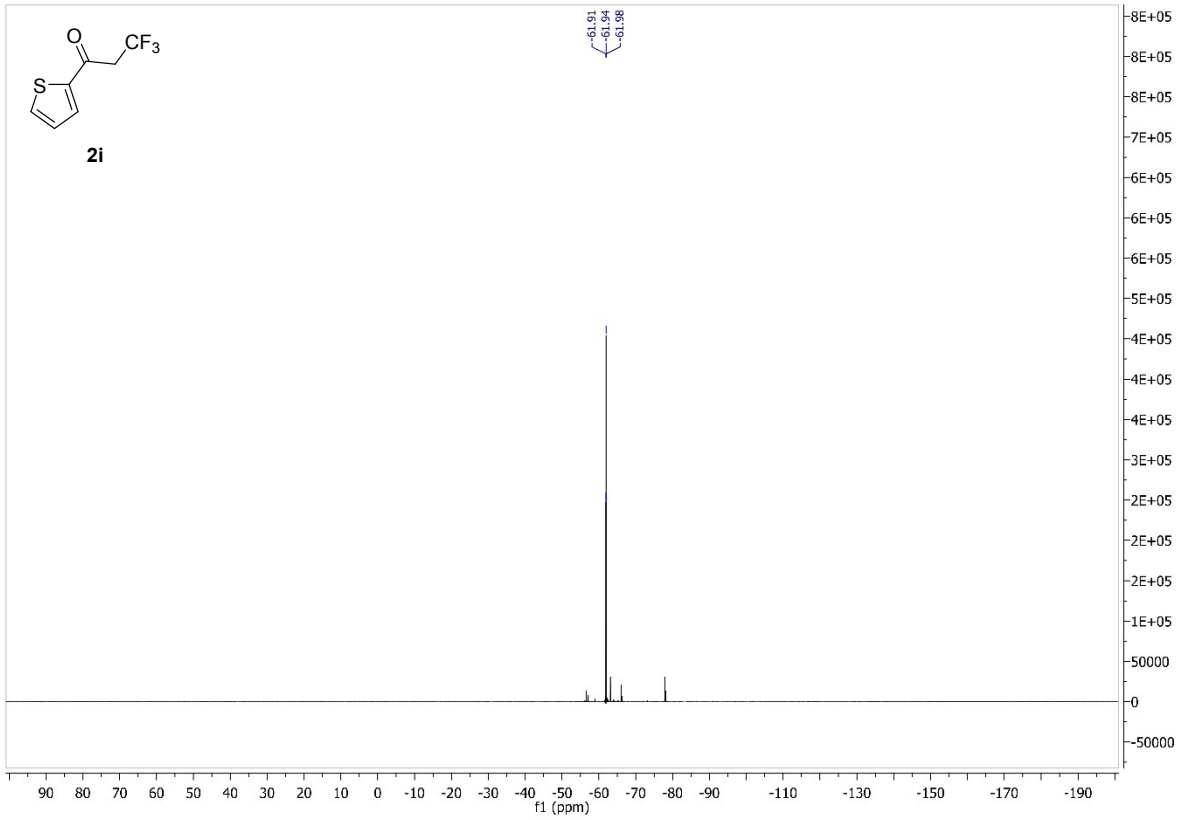

O
CF3
2h
7.85
7.82
7.31
7.29
3.82
3.78
3.75
3.72
2.43
2.03
2.14
2.00
3.11
f1 (ppm)


189.46
189.42
145.45
133.53
133.51
129.75
128.63
126.04
122.37
118.70
42.68
42.31
41.93
41.56
21.86
O
CF3
2h
f1 (ppm)


61.98
62.02
62.05
O
CF3
2h
f1 (ppm)

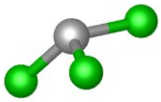

2i
7.76
7.76
7.75
7.74
7.74
7.73
7.72
7.72
7.20
7.18
7.18
7.17
3.77
3.73
3.70
3.66
1.96
0.99
2.00
f1 (ppm)


2i
182.33
182.29
143.32
143.29
135.87
133.56
129.29
128.64
125.62
121.94
118.27
43.74
43.36
42.98
42.60
f1 (ppm)


O
CF3
S
2i
-61.91
-61.94
-61.98
8E+05
8E+05
8E+05
7E+05
6E+05
6E+05
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
-50000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

Cartesian Coordinates, Energies and Imaginary Frequencies (for TSs) for all Calculated Structures

CF_3 radical

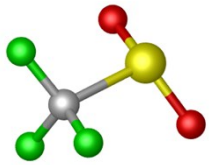


Sum of electronic and zero-point Energies= -337.543152
Sum of electronic and thermal Energies= -337.539728
Sum of electronic and thermal Enthalpies= -337.538784
Sum of electronic and thermal Free Energies= -337.568794

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.329441
2	9	0	0.000000	1.251249	-0.073209
3	9	0	-1.083614	-0.625625	-0.073209
4	9	0	1.083614	-0.625625	-0.073209

CF_3SO_2 radical

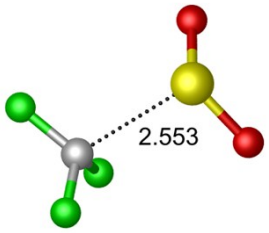


Sum of electronic and zero-point Energies= -886.122934
Sum of electronic and thermal Energies= -886.116185
Sum of electronic and thermal Enthalpies= -886.115240
Sum of electronic and thermal Free Energies= -886.155924

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.879743	0.000094	0.004821
2	9	0	1.054282	-0.001714	1.307621
3	9	0	1.396411	1.081981	-0.526790
4	9	0	1.396943	-1.080176	-0.529784
5	16	0	-1.015757	-0.000004	-0.342407
6	8	0	-1.478259	-1.276133	0.199392
7	8	0	-1.478625	1.275970	0.199378

TS CF_3SO_2 radical decomposition

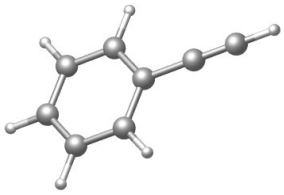


Imaginary Freq. (cm^{-1}): -111.1731
Sum of electronic and zero-point Energies= -886.111542
Sum of electronic and thermal Energies= -886.104228
Sum of electronic and thermal Enthalpies= -886.103284
Sum of electronic and thermal Free Energies= -886.146541

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.173058	0.004415	-0.001088
2	9	0	1.285560	-0.115370	1.292224
3	9	0	1.644382	1.135661	-0.441183
4	9	0	1.652514	-1.024288	-0.640125
5	16	0	-1.348793	0.001583	-0.400658
6	8	0	-1.655500	-1.237277	0.284211
7	8	0	-1.681971	1.235296	0.280639

1d



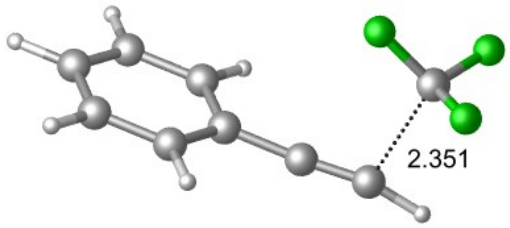
Sum of electronic and zero-point Energies= -308.238751
Sum of electronic and thermal Energies= -308.232424
Sum of electronic and thermal Enthalpies= -308.231479
Sum of electronic and thermal Free Energies= -308.269109

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000179	-2.204385	0.000000
2	6	0	1.206444	-1.507768	0.000000
3	6	0	1.211262	-0.118331	0.000000
4	6	0	0.000000	0.584778	0.000000
5	6	0	-1.211172	-0.118501	0.000000
6	6	0	-1.206184	-1.507938	0.000000
7	6	0	-0.000124	2.020475	0.000000
8	6	0	-0.000402	3.223868	0.000000
9	1	0	0.000266	-3.288368	0.000000
10	1	0	2.146320	-2.047540	0.000000
11	1	0	2.146479	0.429442	0.000000

12	1	0	-2.146457	0.429156	0.000000
13	1	0	-2.145996	-2.047820	0.000000
14	1	0	-0.000632	4.291947	0.000000

$TS_{1d\text{-}9d}$

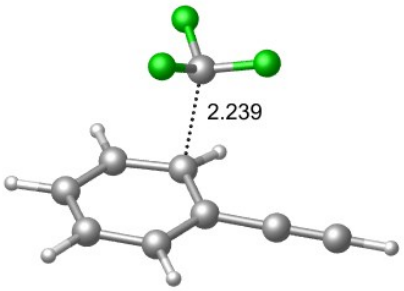


Imaginary Freq. (cm^{-1}): -398.6838
Sum of electronic and zero-point Energies= -645.783413
Sum of electronic and thermal Energies= -645.773263
Sum of electronic and thermal Enthalpies= -645.772318
Sum of electronic and thermal Free Energies= -645.822185

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.693985	0.104569	-0.618425
2	6	0	-3.105436	-1.144921	-0.431306
3	6	0	-1.858062	-1.246655	0.169671
4	6	0	-1.187955	-0.087716	0.589026
5	6	0	-1.783623	1.168675	0.399429
6	6	0	-3.031324	1.257841	-0.202687
7	6	0	0.093008	-0.186359	1.208551
8	6	0	1.225597	-0.258157	1.641822
9	1	0	-4.668357	0.180253	-1.087440
10	1	0	-3.620205	-2.042353	-0.754266
11	1	0	-1.393875	-2.214801	0.318274
12	1	0	-1.261949	2.060864	0.725694
13	1	0	-3.488778	2.229914	-0.347111
14	1	0	2.087312	-0.351791	2.270096
15	6	0	2.597812	0.023637	-0.246686
16	9	0	3.384940	1.070823	-0.047461
17	9	0	3.336221	-1.054777	-0.463431
18	9	0	1.813245	0.245335	-1.287064

$o\text{-}TS_{1d\text{-}12d}$

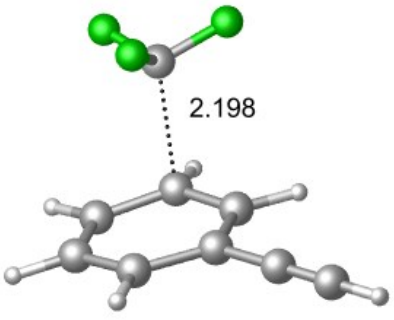


Imaginary Freq. (cm^{-1}): -355.4712
Sum of electronic and zero-point Energies= -645.781356
Sum of electronic and thermal Energies= -645.770570
Sum of electronic and thermal Enthalpies= -645.769626
Sum of electronic and thermal Free Energies= -645.820106

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.546511	-1.993151	-0.234602
2	6	0	0.624929	-1.461110	-1.119462
3	6	0	0.297766	-0.090350	-1.061035
4	6	0	1.041999	0.760927	-0.202957
5	6	0	1.963941	0.205725	0.686724
6	6	0	2.203705	-1.164411	0.681005
7	6	0	0.802466	2.170744	-0.223471
8	6	0	0.593508	3.356301	-0.244711
9	1	0	1.770474	-3.053395	-0.259171
10	1	0	0.117272	-2.096188	-1.836096
11	1	0	-0.311533	0.354461	-1.841539
12	1	0	2.502156	0.854071	1.368438
13	1	0	2.921859	-1.584800	1.375162
14	1	0	0.408946	4.408275	-0.261945
15	6	0	-1.573669	-0.255945	0.156094
16	9	0	-1.270178	-0.822423	1.315698
17	9	0	-2.101148	0.941474	0.375632
18	9	0	-2.452687	-1.014029	-0.488037

m-TS$_{1d\text{-}12d}$



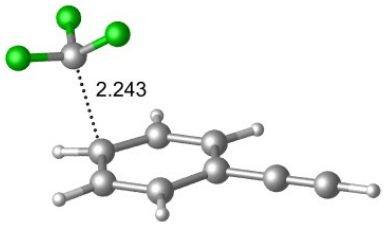
Imaginary Freq. (cm^{-1}): -364.9132
Sum of electronic and zero-point Energies= -645.779596
Sum of electronic and thermal Energies= -645.768833

Sum of electronic and thermal Enthalpies= -645.767889
Sum of electronic and thermal Free Energies= -645.818147

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.821757	-0.552371	-0.145793
2	9	0	-1.329814	-0.553071	-1.377744
3	9	0	-1.950230	-1.805449	0.275497
4	9	0	-3.014377	0.032445	-0.149971
5	6	0	-0.471635	1.804189	0.526340
6	6	0	-0.445332	0.545076	1.170047
7	6	0	0.696902	-0.273078	1.036094
8	6	0	1.704334	0.083709	0.143688
9	6	0	1.614934	1.290727	-0.570033
10	6	0	0.536199	2.148027	-0.359086
11	6	0	2.845401	-0.769498	-0.035500
12	6	0	3.802867	-1.481529	-0.187927
13	1	0	-1.304215	2.476020	0.699923
14	1	0	-1.142642	0.344277	1.977831
15	1	0	0.771431	-1.198028	1.595687
16	1	0	2.403606	1.559183	-1.262608
17	1	0	0.498020	3.096220	-0.882631
18	1	0	4.652112	-2.114508	-0.325223

p-TS$_{1d\text{-}12d}$



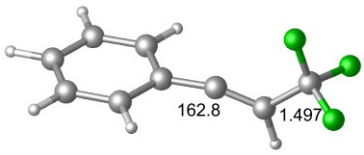
Imaginary Freq. (cm^{-1}): -360.9714
Sum of electronic and zero-point Energies= -645.781010
Sum of electronic and thermal Energies= -645.770230
Sum of electronic and thermal Enthalpies= -645.769286
Sum of electronic and thermal Free Energies= -645.819934

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.008954	-0.000353	-0.412042
2	9	0	1.261248	-0.001117	-1.506756
3	9	0	2.776649	1.082576	-0.403145
4	9	0	2.776080	-1.083663	-0.401251
5	6	0	0.645235	0.001292	1.369100
6	6	0	-0.024662	1.218826	1.117627
7	6	0	-1.258229	1.216198	0.496132
8	6	0	-1.881668	0.000175	0.166688
9	6	0	-1.258146	-1.215239	0.498219
10	6	0	-0.024585	-1.216719	1.119726
11	6	0	-3.156847	-0.000445	-0.483383

12	6	0	-4.227891	-0.001007	-1.033377
13	1	0	1.541755	0.001846	1.980809
14	1	0	0.450659	2.156970	1.379450
15	1	0	-1.762600	2.148977	0.272147
16	1	0	-1.762450	-2.148437	0.275832
17	1	0	0.450797	-2.154378	1.383166
18	1	0	-5.176914	-0.001510	-1.523176

9d

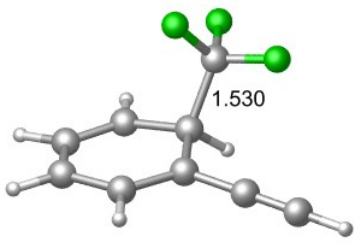


Sum of electronic and zero-point Energies= -645.848763
Sum of electronic and thermal Energies= -645.838462
Sum of electronic and thermal Enthalpies= -645.837518
Sum of electronic and thermal Free Energies= -645.887696

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.973533	0.003879	0.164975
2	6	0	-3.275809	1.211846	0.080069
3	6	0	-1.903389	1.222035	-0.085710
4	6	0	-1.190734	-0.003437	-0.178011
5	6	0	-1.909687	-1.225142	-0.085651
6	6	0	-3.282006	-1.207695	0.080546
7	6	0	0.186556	-0.005536	-0.316854
8	6	0	1.383117	-0.000911	-0.823707
9	1	0	-5.048768	0.006658	0.298319
10	1	0	-3.811674	2.151989	0.144625
11	1	0	-1.358198	2.156352	-0.149070
12	1	0	-1.369345	-2.162304	-0.148404
13	1	0	-3.822696	-2.145000	0.146023
14	1	0	1.589140	0.009505	-1.895579
15	6	0	2.609583	-0.000767	0.034497
16	9	0	3.417290	-1.038530	-0.256471
17	9	0	3.347630	1.110174	-0.155860
18	9	0	2.341407	-0.069736	1.343793

o-12d



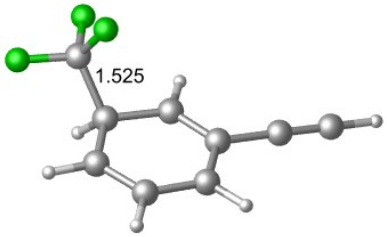
Sum of electronic and zero-point Energies= -645.823494

```
Sum of electronic and thermal Energies=             -645.813246
Sum of electronic and thermal Enthalpies=           -645.812302
Sum of electronic and thermal Free Energies=        -645.860507
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.369814	-0.933161	-0.260752
2	6	0	1.174954	-1.193732	-0.835149
3	6	0	0.014015	-0.243235	-0.722586
4	6	0	0.394565	1.101651	-0.140613
5	6	0	1.632157	1.289986	0.444237
6	6	0	2.608257	0.291569	0.432402
7	6	0	-0.539637	2.163949	-0.220427
8	6	0	-1.337252	3.066181	-0.306500
9	1	0	3.173028	-1.656803	-0.343690
10	1	0	1.003123	-2.117034	-1.375866
11	1	0	-0.463526	-0.108777	-1.702647
12	1	0	1.853897	2.253772	0.889086
13	1	0	3.567228	0.468678	0.902072
14	1	0	-2.041847	3.865726	-0.379779
15	6	0	-1.071729	-0.905881	0.127608
16	9	0	-0.674812	-1.104988	1.394576
17	9	0	-2.197297	-0.179458	0.184319
18	9	0	-1.412642	-2.107724	-0.367616

m-12d



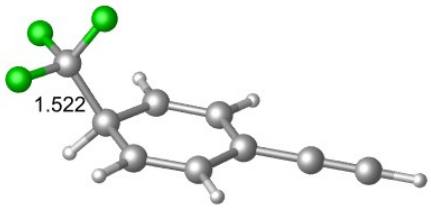

```
Sum of electronic and zero-point Energies=          -645.818963
Sum of electronic and thermal Energies=             -645.808609
Sum of electronic and thermal Enthalpies=           -645.807665
Sum of electronic and thermal Free Energies=        -645.856391
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.778329	-0.459208	0.076157
2	9	0	1.527534	-0.431658	1.394827
3	9	0	1.941145	-1.748884	-0.261263
4	9	0	2.964234	0.144020	-0.107044
5	6	0	0.567037	1.657396	-0.372132
6	6	0	0.675001	0.205604	-0.739840
7	6	0	-0.606484	-0.557481	-0.581902
8	6	0	-1.740217	0.034147	-0.105155
9	6	0	-1.758733	1.412905	0.260444
10	6	0	-0.590482	2.191206	0.098706
11	6	0	-2.950550	-0.732551	0.019322

12	6	0	-3.972306	-1.357422	0.127396
13	1	0	1.449152	2.273169	-0.503541
14	1	0	1.033869	0.107801	-1.777166
15	1	0	-0.613661	-1.602316	-0.869401
16	1	0	-2.670854	1.852484	0.641429
17	1	0	-0.625889	3.245257	0.350921
18	1	0	-4.878406	-1.915262	0.221092

p-12d

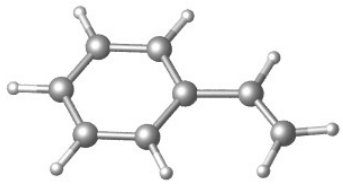


Sum of electronic and zero-point Energies= -645.826392
Sum of electronic and thermal Energies= -645.816069
Sum of electronic and thermal Enthalpies= -645.815125
Sum of electronic and thermal Free Energies= -645.864074

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.007917	-0.000024	0.174957
2	9	0	-1.637371	-0.000023	1.465281
3	9	0	-2.788347	1.078258	-0.004664
4	9	0	-2.788278	-1.078349	-0.004680
5	6	0	-0.817089	0.000021	-0.773385
6	6	0	-0.016065	1.257592	-0.593543
7	6	0	1.297601	1.234001	-0.281620
8	6	0	2.002673	0.000060	-0.101889
9	6	0	1.297640	-1.233905	-0.281673
10	6	0	-0.016024	-1.257532	-0.593598
11	6	0	3.374085	0.000074	0.227760
12	6	0	4.550376	-0.000113	0.508916
13	1	0	-1.284842	0.000032	-1.770836
14	1	0	-0.528987	2.202089	-0.734841
15	1	0	1.843730	2.163659	-0.167545
16	1	0	1.843806	-2.163545	-0.167634
17	1	0	-0.528917	-2.202039	-0.734935
18	1	0	5.589497	-0.000219	0.756806

1d´



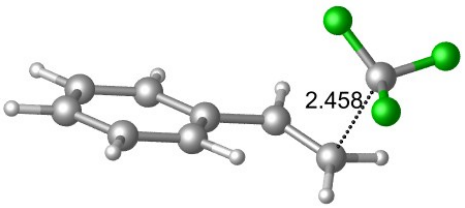
Sum of electronic and zero-point Energies= -309.459277

Sum of electronic and thermal Energies= -309.452588
Sum of electronic and thermal Enthalpies= -309.451644
Sum of electronic and thermal Free Energies= -309.490527

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.254756	0.267005	0.000003
2	6	0	-1.778743	-1.040034	-0.000001
3	6	0	-0.407668	-1.281735	-0.000003
4	6	0	0.510249	-0.225723	-0.000001
5	6	0	0.017588	1.086333	0.000002
6	6	0	-1.349863	1.328712	0.000004
7	1	0	-3.321427	0.460459	0.000004
8	1	0	-2.472825	-1.872938	-0.000002
9	1	0	-0.038690	-2.302547	-0.000005
10	1	0	0.704661	1.924993	0.000002
11	1	0	-1.713687	2.350131	0.000006
12	6	0	1.953210	-0.538326	-0.000003
13	6	0	2.955525	0.341229	0.000000
14	1	0	2.189473	-1.600324	-0.000008
15	1	0	3.984954	0.001147	-0.000002
16	1	0	2.794285	1.414319	0.000005

$TS_{1d'-9d'}$



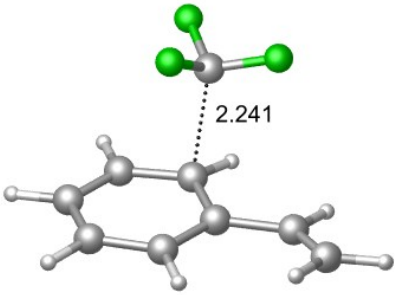
Imaginary Freq. (cm^{-1}): -323.3785
Sum of electronic and zero-point Energies= -647.007491
Sum of electronic and thermal Energies= -646.996412
Sum of electronic and thermal Enthalpies= -646.995467
Sum of electronic and thermal Free Energies= -647.047340

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.423914	-0.942915	0.145958
2	6	0	-3.440295	0.383086	0.570591
3	6	0	-2.311950	1.179738	0.409854
4	6	0	-1.153472	0.669848	-0.190558
5	6	0	-1.143968	-0.671753	-0.600278
6	6	0	-2.270028	-1.467797	-0.435292
7	6	0	0.013817	1.544066	-0.358925
8	6	0	1.056067	1.298710	-1.175746
9	1	0	-4.300827	-1.567304	0.274275
10	1	0	-4.331407	0.796510	1.029340
11	1	0	-2.323897	2.212486	0.743855
12	1	0	-0.246075	-1.098175	-1.035549
13	1	0	-2.246566	-2.504338	-0.752794

14	1	0	1.868989	2.011774	-1.257813
15	6	0	2.424429	-0.230181	0.178344
16	9	0	2.656999	-1.347568	-0.493161
17	9	0	3.570507	0.368680	0.462062
18	9	0	1.773317	-0.504857	1.295008
19	1	0	1.046787	0.480404	-1.889154
20	1	0	0.021482	2.445536	0.248979

o-TS$_{1d'-12d'}$

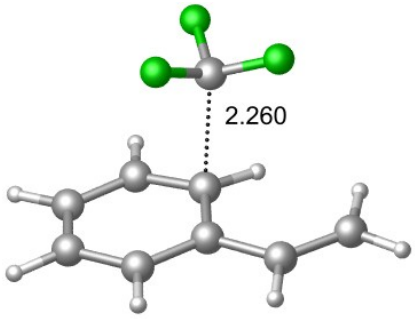


Imaginary Freq. (cm^{-1}): -339.2178
Sum of electronic and zero-point Energies= -647.003008
Sum of electronic and thermal Energies= -646.991882
Sum of electronic and thermal Enthalpies= -646.990938
Sum of electronic and thermal Free Energies= -647.042225

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.355857	2.530311	-0.077628
2	6	0	0.296053	1.725231	-0.991952
3	6	0	-0.053058	0.361081	-1.103051
4	6	0	-1.170082	-0.149455	-0.394157
5	6	0	-1.812603	0.688125	0.521630
6	6	0	-1.403691	2.005467	0.690731
7	1	0	-0.072687	3.570811	0.032540
8	1	0	1.099654	2.120319	-1.602841
9	1	0	0.357894	-0.227829	-1.918944
10	1	0	-2.658831	0.319404	1.090540
11	1	0	-1.919549	2.638985	1.403174
12	6	0	1.571984	-0.507310	0.172733
13	9	0	1.421365	-0.081014	1.421023
14	9	0	1.510708	-1.835208	0.155633
15	9	0	2.760390	-0.120276	-0.280379
16	6	0	-1.562777	-1.548358	-0.620833
17	6	0	-2.412227	-2.259405	0.124201
18	1	0	-1.085932	-2.026845	-1.473482
19	1	0	-2.634878	-3.290039	-0.128267
20	1	0	-2.904286	-1.850452	1.000734

o-TS$_{1d'-12d'}$ Isomer

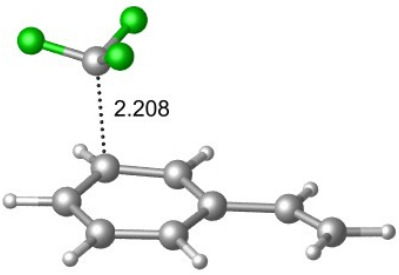


Imaginary Freq. (cm^{-1}): -339.8336
Sum of electronic and zero-point Energies= -647.003928
Sum of electronic and thermal Energies= -646.992914
Sum of electronic and thermal Enthalpies= -646.991970
Sum of electronic and thermal Free Energies= -647.042656

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.205329	-1.271044	0.391509
2	6	0	-1.114377	-1.023902	1.208427
3	6	0	-0.322128	0.124250	1.008586
4	6	0	-0.731664	1.110627	0.073675
5	6	0	-1.836002	0.836877	-0.735090
6	6	0	-2.559062	-0.344795	-0.593301
7	1	0	-2.792268	-2.172339	0.526573
8	1	0	-0.838388	-1.728711	1.984463
9	1	0	0.437882	0.365207	1.744748
10	1	0	-2.139519	1.569152	-1.476580
11	1	0	-3.412142	-0.534753	-1.234577
12	6	0	1.323383	-0.845692	-0.199668
13	9	0	0.828755	-1.156658	-1.391407
14	9	0	2.388587	-0.067809	-0.358029
15	9	0	1.689030	-1.961151	0.424271
16	6	0	-0.008810	2.377782	-0.099364
17	6	0	1.100857	2.749560	0.543803
18	1	0	-0.441444	3.054115	-0.833088
19	1	0	1.557738	3.711273	0.339246
20	1	0	1.589581	2.124635	1.284237

m-TS$_{1d'\text{-}12d'}$



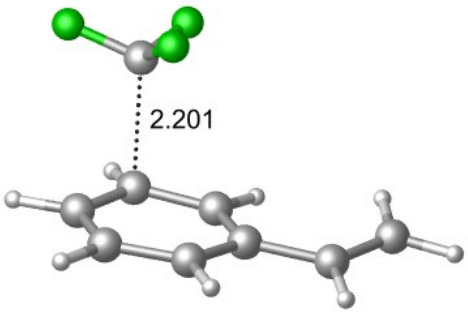
Imaginary Freq. (cm^{-1}): -355.2485
Sum of electronic and zero-point Energies= -647.000609

Sum of electronic and thermal Energies= -646.989571
Sum of electronic and thermal Enthalpies= -646.988627
Sum of electronic and thermal Free Energies= -647.039550

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.922110	-0.495874	-0.189436
2	9	0	-1.390658	-0.505494	-1.405596
3	9	0	-2.083643	-1.748883	0.224727
4	9	0	-3.108734	0.102124	-0.236679
5	6	0	-0.499888	1.820781	0.481016
6	6	0	-0.575427	0.595585	1.178167
7	6	0	0.532034	-0.281049	1.146163
8	6	0	1.617060	-0.033026	0.311961
9	6	0	1.626204	1.150002	-0.449488
10	6	0	0.583501	2.068180	-0.349148
11	1	0	-1.304654	2.541650	0.568085
12	1	0	-1.334493	0.461151	1.943149
13	1	0	0.516963	-1.181969	1.751040
14	1	0	2.465752	1.371816	-1.098246
15	1	0	0.630357	2.992969	-0.913136
16	6	0	2.723417	-1.010616	0.280620
17	6	0	3.778715	-0.984680	-0.532923
18	1	0	2.631854	-1.822014	0.999234
19	1	0	4.536599	-1.757729	-0.473445
20	1	0	3.923902	-0.211424	-1.280348

m-TS$_{1d'\text{-}12d'}$ Isomer



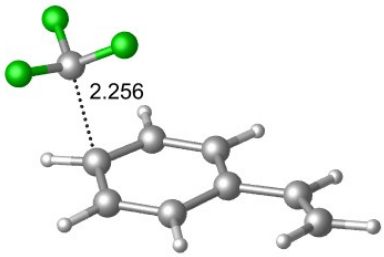
Imaginary Freq. (cm^{-1}): -355.2221
Sum of electronic and zero-point Energies= -647.000661
Sum of electronic and thermal Energies= -646.989583
Sum of electronic and thermal Enthalpies= -646.988639
Sum of electronic and thermal Free Energies= -647.039902

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.805337	-0.577028	-0.153208
2	9	0	-1.315583	-0.538188	-1.386456
3	9	0	-1.905888	-1.844516	0.235450
4	9	0	-3.014298	-0.023568	-0.147149
5	6	0	-0.586936	1.807596	0.633506

6	6	0	-0.444963	0.513228	1.190310
7	6	0	0.741622	-0.212194	0.959861
8	6	0	1.692215	0.253323	0.052575
9	6	0	1.486678	1.500365	-0.557789
10	6	0	0.363339	2.274144	-0.256321
11	1	0	-1.456082	2.406186	0.881010
12	1	0	-1.093930	0.213681	2.007902
13	1	0	0.889473	-1.154641	1.475322
14	1	0	2.226603	1.874047	-1.258137
15	1	0	0.247307	3.251167	-0.712034
16	6	0	2.917154	-0.504516	-0.273055
17	6	0	3.155337	-1.778798	0.036807
18	1	0	3.667726	0.052696	-0.828916
19	1	0	4.089610	-2.249816	-0.246989
20	1	0	2.436552	-2.393600	0.569117

p-TS$_{1d'\text{-}12d'}$

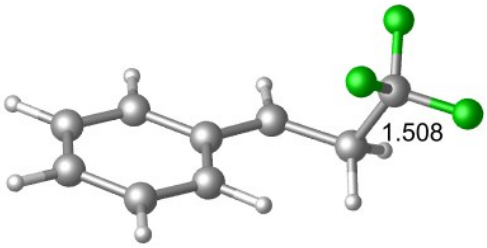


Imaginary Freq. (cm^{-1}): -345.5168
Sum of electronic and zero-point Energies= -647.002038
Sum of electronic and thermal Energies= -646.991003
Sum of electronic and thermal Enthalpies= -646.990059
Sum of electronic and thermal Free Energies= -647.041238

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.054741	-0.292609	-0.310566
2	9	0	1.296706	-0.741060	-1.303358
3	9	0	2.955168	0.555665	-0.797913
4	9	0	2.684114	-1.318404	0.254121
5	6	0	0.721022	0.746304	1.182924
6	6	0	0.150077	1.703102	0.319143
7	6	0	-1.086730	1.464946	-0.254212
8	6	0	-1.819558	0.306099	0.050123
9	6	0	-1.288590	-0.594917	0.992526
10	6	0	-0.056086	-0.369487	1.570816
11	1	0	1.622738	0.989748	1.735891
12	1	0	0.700726	2.604803	0.076149
13	1	0	-1.508630	2.186366	-0.946718
14	1	0	-1.860397	-1.467902	1.286855
15	1	0	0.337768	-1.066874	2.301640
16	6	0	-3.117719	0.094837	-0.607096
17	6	0	-3.867978	-1.007623	-0.539936
18	1	0	-3.465412	0.930213	-1.210862
19	1	0	-4.812778	-1.061904	-1.068705
20	1	0	-3.572991	-1.884174	0.027768

9d´

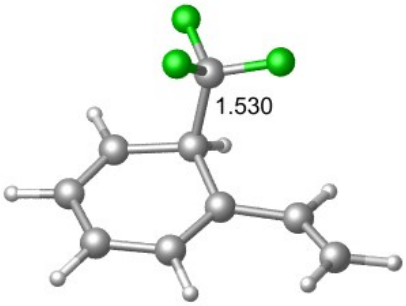


Sum of electronic and zero-point Energies= -647.080430
Sum of electronic and thermal Energies= -647.070255
Sum of electronic and thermal Enthalpies= -647.069311
Sum of electronic and thermal Free Energies= -647.117910

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.557052	-0.629970	-0.259541
2	6	0	3.359588	0.748917	-0.375838
3	6	0	2.123664	1.302717	-0.096376
4	6	0	1.031535	0.493156	0.312420
5	6	0	1.254228	-0.903073	0.423815
6	6	0	2.496812	-1.445945	0.140875
7	6	0	-0.216097	1.106373	0.590897
8	6	0	-1.441712	0.382162	1.047275
9	1	0	4.525835	-1.063548	-0.478720
10	1	0	4.178217	1.388661	-0.686237
11	1	0	1.971378	2.373373	-0.187431
12	1	0	0.446419	-1.559897	0.724463
13	1	0	2.645080	-2.516422	0.230397
14	1	0	-2.082347	1.041012	1.638011
15	6	0	-2.284626	-0.098763	-0.107075
16	9	0	-3.401864	-0.720927	0.312262
17	9	0	-2.684075	0.907942	-0.906676
18	9	0	-1.631895	-0.973238	-0.894675
19	1	0	-1.211119	-0.499010	1.651111
20	1	0	-0.295633	2.178389	0.451505

o-12d´



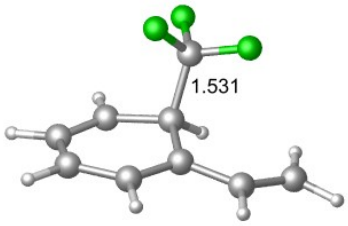
Sum of electronic and zero-point Energies= -647.044284
Sum of electronic and thermal Energies= -647.033729

Sum of electronic and thermal Enthalpies= -647.032785
Sum of electronic and thermal Free Energies= -647.081825

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.263706	2.531573	-0.163078
2	6	0	0.916124	1.519518	-0.770802
3	6	0	0.371859	0.115851	-0.757874
4	6	0	-1.065663	0.010342	-0.295015
5	6	0	-1.656469	1.098038	0.331277
6	6	0	-1.015060	2.326276	0.447891
7	1	0	0.693852	3.527070	-0.161953
8	1	0	1.871533	1.677482	-1.257599
9	1	0	0.484388	-0.345701	-1.748556
10	1	0	-2.675881	1.006130	0.690589
11	1	0	-1.514368	3.153742	0.936051
12	6	0	1.274591	-0.733863	0.138606
13	9	0	1.236954	-0.341281	1.422333
14	9	0	0.940600	-2.034335	0.124052
15	9	0	2.560172	-0.664353	-0.250063
16	6	0	-1.761405	-1.239559	-0.542531
17	6	0	-2.902055	-1.645263	0.040722
18	1	0	-1.294846	-1.899979	-1.269984
19	1	0	-3.350787	-2.592099	-0.235870
20	1	0	-3.407178	-1.064414	0.805258

o-12d´ Isomer



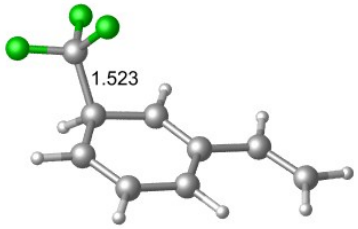
Sum of electronic and zero-point Energies= -647.046701
Sum of electronic and thermal Energies= -647.036395
Sum of electronic and thermal Enthalpies= -647.035450
Sum of electronic and thermal Free Energies= -647.083394

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.454410	-0.498294	-0.479452
2	6	0	1.283397	-0.844808	-1.053972
3	6	0	-0.002378	-0.140026	-0.700486
4	6	0	0.206703	1.190472	-0.009734
5	6	0	1.435280	1.452088	0.582236
6	6	0	2.536455	0.618434	0.412142
7	1	0	3.356289	-1.052064	-0.716335
8	1	0	1.219456	-1.675429	-1.747111
9	1	0	-0.623889	-0.021451	-1.596041
10	1	0	1.547398	2.373650	1.145426

11	1	0	3.479312	0.859579	0.886577
12	6	0	-0.807760	-1.086855	0.193318
13	9	0	-0.177312	-1.355224	1.349243
14	9	0	-2.016631	-0.606388	0.519601
15	9	0	-1.018576	-2.268673	-0.415064
16	6	0	-0.831478	2.193367	0.022247
17	6	0	-2.015574	2.151557	-0.615542
18	1	0	-0.586888	3.080639	0.602385
19	1	0	-2.705195	2.984423	-0.543222
20	1	0	-2.328150	1.307612	-1.220243

m-12d´

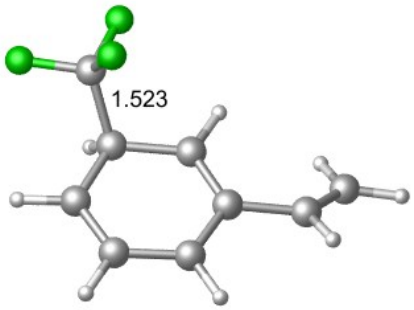


Sum of electronic and zero-point Energies= -647.041388
Sum of electronic and thermal Energies= -647.030753
Sum of electronic and thermal Enthalpies= -647.029809
Sum of electronic and thermal Free Energies= -647.079240

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.907181	-0.374470	0.098426
2	9	0	1.622648	-0.380251	1.410942
3	9	0	2.186327	-1.644173	-0.242567
4	9	0	3.046206	0.323912	-0.048079
5	6	0	0.558090	1.645959	-0.381873
6	6	0	0.776565	0.205527	-0.741658
7	6	0	-0.452988	-0.643458	-0.605291
8	6	0	-1.646227	-0.151966	-0.169219
9	6	0	-1.762430	1.229191	0.185009
10	6	0	-0.652299	2.090332	0.053007
11	1	0	1.396488	2.324519	-0.486116
12	1	0	1.164919	0.131036	-1.770476
13	1	0	-0.368735	-1.688747	-0.884777
14	1	0	-2.702419	1.623339	0.546905
15	1	0	-0.771741	3.139039	0.302914
16	6	0	-2.799850	-1.070721	-0.087180
17	6	0	-4.042040	-0.744846	0.269214
18	1	0	-2.579653	-2.102441	-0.351731
19	1	0	-4.819676	-1.500009	0.296422
20	1	0	-4.331837	0.264573	0.541588

m-12d´ Isomer

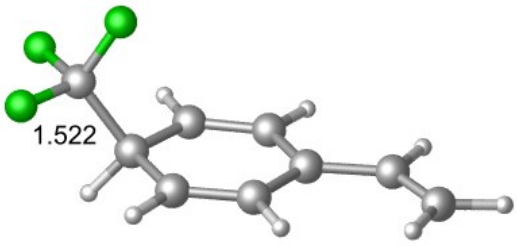


Sum of electronic and zero-point Energies= -647.040310
Sum of electronic and thermal Energies= -647.029576
Sum of electronic and thermal Enthalpies= -647.028632
Sum of electronic and thermal Free Energies= -647.078462

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.793265	-0.485676	0.078536
2	9	0	1.646814	-0.318410	1.403120
3	9	0	1.864224	-1.810492	-0.138301
4	9	0	2.994790	0.022502	-0.244837
5	6	0	0.668496	1.645998	-0.496552
6	6	0	0.669103	0.161349	-0.720450
7	6	0	-0.636682	-0.503946	-0.396621
8	6	0	-1.724240	0.193565	0.045444
9	6	0	-1.633047	1.598383	0.257054
10	6	0	-0.433598	2.290987	-0.034187
11	1	0	1.577346	2.190547	-0.725446
12	1	0	0.947521	-0.056821	-1.765348
13	1	0	-0.686961	-1.579455	-0.526663
14	1	0	-2.495798	2.136928	0.630308
15	1	0	-0.399104	3.365090	0.112373
16	6	0	-3.018310	-0.467851	0.328009
17	6	0	-3.446044	-1.599110	-0.229547
18	1	0	-3.657905	0.052090	1.037713
19	1	0	-4.409478	-2.018117	0.038420
20	1	0	-2.861728	-2.134851	-0.971311

p-12d´ Isomer



Sum of electronic and zero-point Energies= -647.049753
Sum of electronic and thermal Energies= -647.039156
Sum of electronic and thermal Enthalpies= -647.038212
Sum of electronic and thermal Free Energies= -647.087673

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.070379	-0.097246	0.167491
2	9	0	-1.692153	-0.179688	1.453664
3	9	0	-2.933505	0.929724	0.083479
4	9	0	-2.770918	-1.213166	-0.100476
5	6	0	-0.891443	0.073449	-0.779247
6	6	0	-0.191231	1.373895	-0.505453
7	6	0	1.121021	1.425360	-0.189948
8	6	0	1.940265	0.253644	-0.092674
9	6	0	1.320228	-1.014562	-0.371727
10	6	0	0.015302	-1.121392	-0.690329
11	1	0	-1.365142	0.106576	-1.772908
12	1	0	-0.776887	2.283176	-0.580290
13	1	0	1.587529	2.389134	-0.008176
14	1	0	1.922304	-1.915740	-0.335023
15	1	0	-0.420302	-2.091398	-0.903790
16	6	0	3.323428	0.387878	0.265052
17	6	0	4.223272	-0.609868	0.411067
18	1	0	3.659813	1.408517	0.434467
19	1	0	5.247179	-0.384552	0.685087
20	1	0	3.971908	-1.654472	0.265236