Electronic Supplementary Information for:

Synthesis of 1,3-Diaryl-3-trifluoromethylcyclopropenes by Transition-Metal-Free Reaction of 2,2,2-Trifluoroacetophenone Tosylhydrazones with Alkynes: The Effect of the Trifluoromethyl Group

Raquel Barroso,[a] Azucena Jiménez,[a] M. Carmen Pérez-Aguilar,[a] María-Paz Cabal,[a,*] Carlos Valdés[a,*]

Departamento de Química Orgánica e Inorgánica and Instituto Universitario de Química Organometálica "Enrique Moles". Universidad de Oviedo. c/ Julián Clavería 8. Oviedo, 33006. Spain

Contents

1. Experimental……2

1.1 General Considerations……2

2. Synthesis……3

2.1. Synthesis of trisubstituted cyclopropenes……3

2.2. Synthesis of tetrasubstituted cyclopropenes……9

4. Computational Modeling……22

5. NMR Spectra……41

6. HMQC (C-F) NMR Spectra……76

7. References……84

1. Experimental

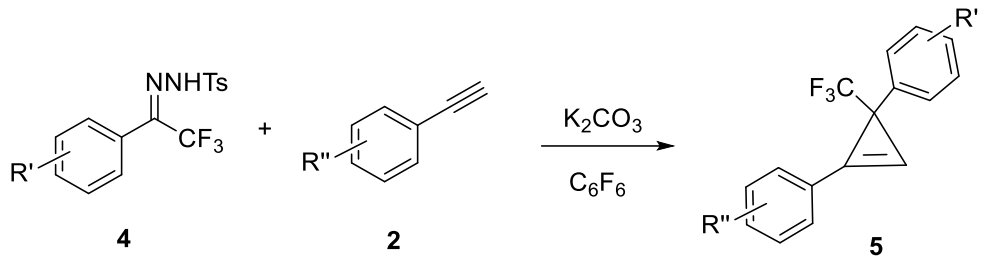
1.1 General considerations:

Reactions performed by conventional heating were carried out in a RR98030 12 place Carousel Reaction Station™ from Radleys Discovery Technologies, equipped with gas tight threaded caps with a valve, cooling reflux head system, and digital temperature controller. K_2CO_3 was purchased from Fluka, stored in a flask purged with nitrogen and weighted in the air. Hexafluorobenzene (99 %) is commercially available form Alfa Aesar co. All the alkynes are commercially available from Aldrich Chemical co. *N*-tosylhydrazones were prepared from the corresponding carbonyl compounds and *p*-toluenesulfonyl hydrazide through previously described methodologies[1].

NMR spectra were recorded in $CDCl_3$ at 600, 400 or 300 MHz for ^1H, 151, 101 or 75 MHz for ^{13}C and 282 MHz for ^{19}F with tetramethylsilane as internal standard for ^1H and the residual solvent signals as standard for ^{13}C. The data is being reported as s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, td = triple doublet, q = quatriplet, qt = quintuplet and m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. HRMS were measured in EI mode, and the mass analyser of the HRMS was TOF.

2. Synthesis

2.1 Synthesis of trisubstituted cyclopropenes



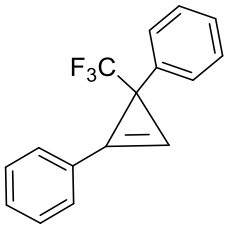
4 **2** **5**

General procedure:

In a carousel tube reactor under nitrogen atmosphere the corresponding *N*-tosylhydrazone (**4**) (1 equiv, 0.1 mmol), the terminal alkyne (**2**) (2 equiv) and K_2CO_3 (2 equiv) were dissolved in 3 ml of C_6F_6 and the mixture was stirred at 85 ^oC for 21 h. Then, the solution was washed with $NaHCO_3$ (2 x 5 mL), NaCl (sat) (2 x 5 mL) and extracted with dichloromethane. The organic phase was dried over Na_2SO_4, filtered and the solvents were removed under slight vacuum. All the crudes were purified by flash chromatography (silica gel, eluent). Note: cyclopropenes **5** can be volatile compounds, therefore careful solvent removal is recommended.

(1-(Trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (5a)[2]

Following the general procedure, from methyl-*N'* -(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.058 mmol, 20 mg), phenylacetylene (0.117 mmol, 13 µL) and K_2CO_3 (0.117 mmol, 16 mg), were obtained 7.8 mg of **5a** (52 % isolated yield) as a red oil. R_f 0.59 (15:1 Hexane/AcOEt).



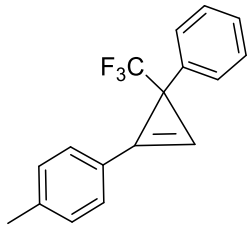
5a

1-Methyl-4-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (5b)

Following the general procedure, from methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.058 mmol, 20 mg), *p*-methylphenylacetylene (0.117 mmol, 15 µL) and K_2CO_3 (0.117 mmol, 16 mg), were obtained 4.8 mg of **5b** (30 % isolated yield) as a red oil. R_f 0.36 (Hexane). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.41 (s, 3H, CH_3), 7.10 (bs, 1H), 7.24-7.39 (m, 5H), 7.45 (m, 2H), 7.57 (d, J = 7.9 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 21.6 (CH_3), 32.9 (q, J_{CF} = 35.7 Hz, C), 97.7 (q, J_{CF} = 2.6 Hz, CH), 117.1 (C), 122.3

(C), 126.7 (q, J_{CF} = 272.9 Hz, CF_3).127.1 (CH), 127.6 (2CH), 128.3 (2CH), 129.7 (2CH), 130.0 (2CH), 138.3 (C), 140.8 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -63.98 (CF_3).

EI HRMS: calcd. for $C_{17}H_{13}F_3$: 274.0969, found: 274.0973.

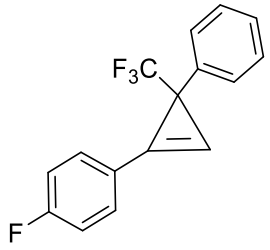


5b

1-Fluoro-4-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (5c)

Following the general procedure, from methyl-*N*′ -(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.117 mmol, 40 mg), *p*-fluorophenylacetylene (0.23 mmol, 26 µL) and K_2CO_3 (0.23 mmol, 32 mg), were obtained 10 mg of **5c** (31 % isolated yield) as an orange oil. R_f 0.33 (20:1 Hexane/AcOEt). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.16 (t, *J* = 8.9 Hz, 3H), 7.32 (m, 3H), 7.43 (m, 2H), 7.66 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 31.8 (q, J_{CF} = 35.1 Hz, C), 98.4 (CH), 116.1 (C), 116.3 (d, J_{CF} = 22.1 Hz, 2CH), 121.4 (d, J_{CF} = 2.8 Hz, C), 126.2 (CF_3), 127.3 (CH), 127.6 (2CH), 128.4 (2CH), 132.0 (d, J_{CF} = 8.8 Hz, 2CH), 137.9 (C), 163.8 (d, J_{CF} = 277.1 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.02 (CF_3), -108.50 (F).

EI HRMS: calcd. for $C_{16}H_{10}F_4$: 278.0719, found: 278.0718.

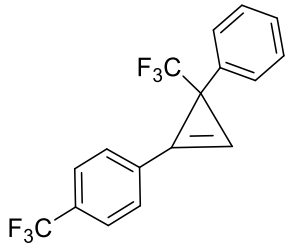


5c

1-(3-Phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)-4-(trifluoromethyl)benzene (5d)

Following the general procedure, from methyl-*N*′ -(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.058 mmol, 20 mg), *p*-trifluoromethylphenylacetylene (0.117 mmol, 16 µL) and K_2CO_3 (0.117 mmol, 16 mg), were obtained 9.8 mg of **5d** (51 % isolated yield) as an orange oil. R_f 0.35 (20:1 Hexane/AcOEt). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.37 (m, 7H), 7.76 (q, *J* = 8.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 32.3 (q, J_{CF} = 37.6 Hz, C), 96.0 (q, J_{CF} = 2.9 Hz, CH), 114.5 (2CH), 117.6 (C), 123.7 (q, J_{CF} = 276.9 Hz, C), 126.5 (q, J_{CF} = 280.7 Hz, C), 127.0 (CH), 127.5 (2CH), 128.3 (2CH), 128.5 (C), 130.7 (2CH), 138.4 (q, J_{CF} = 33.8 Hz, C), 161.2 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.97 (CF_3), -64.12 (CF_3).

EI HRMS: calcd. for $C_{17}H_{10}F_6$: 328.0687, found: 328.0690.

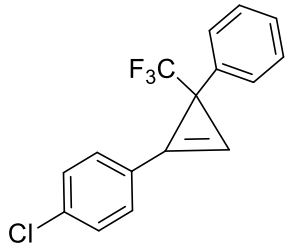


5d

1-Chloro-4-(3-phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (5e)

Following the general procedure, from methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.058 mmol, 20 mg), *p*-chlorophenylacetylene (0.117 mmol, 16 mg) and K_2CO_3 (0.117 mmol, 16 mg), were obtained 7 mg of **5e** (40 % isolated yield) as a colorless oil. R_f 0.39 (20:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.22 (m, 1H), 7.32 (m, 3H), 7.43 (m, 4H), 7.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 32.7 (q, J_{CF} = 33.8 Hz, C), 99.6 (q, J_{CF} = 2.8 Hz, CH), 116.5 (C), 123.6 (C), 126.4 (q, J_{CF} = 278.4, CF_3), 127.3 (CH), 127.6 (2CH), 128.5 (2CH), 129.4 (2CH), 131.2 (2CH), 136.5 (C), 137.8 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.05 (CF_3).

EI HRMS: calcd. for $C_{16}H_{10}ClF_3$: 294.0423, found: 294.0431.

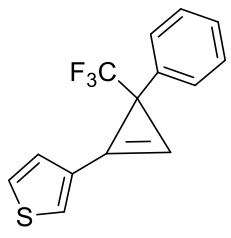


5e

3-(3-Phenyl-3-(trifluoromethyl)cycloprop-1-en-1-yl)thiophene (5f)

Following the general procedure, from methyl-*N'* -(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.058 mmol, 20 mg), 3-ethynylthiophene (0.117 mmol, 12 µl) and K_2CO_3 (0.117 mmol, 16 mg), were obtained 4.6 mg of **5f** (30 % isolated yield) as a yellow oil. R_f 0.42 (15:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.03 (q, *J* = 1.3 Hz, 1H), 7.32 (m, 2H), 7.35 (m, 2H), 7.42 (m, 3H), 7.69 (dd, *J* = 3.1, 1.3 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 32.1 (q, J_{CF} = 34.9 Hz, C), 96.3 (q, J_{CF} = 2.8 Hz, CH), 112.1 (C), 126.0 (q, J_{CF} = 277.1 Hz, CF_3), 126.4 (C), 127.0 (CH), 127.2 (CH), 127.7 (2CH), 128.1 (CH), 128.4 (2CH), 129.0 (CH), 138.1 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.31 (CF_3).

EI HRMS: calcd. for $C_{14}H_9F_3S$: 266.0377, found: 266.0378.

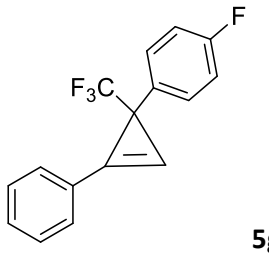


5f

1-Fluoro-4-(2-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (5g)

Following the general procedure, from *N'*-(-4-fluorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (0.056 mmol, 20 mg), phenylacetylene (0.11 mmol, 12 µL) and K_2CO_3 (0.11 mmol, 15 mg), were obtained 15 mg of **5g** (96% isolated yield) as an orange oil. R_f 0.47 (20:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.01 (t, *J* = 8.7 Hz, 2H). 7.19 (q, *J* = 1.6 Hz, 1H), 7.41 (m, 2H), 7.48 (m, 3H), 7.66 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 31.7 (q, J_{CF} = 33.7 Hz, C), 98.9 (q, J_{CF} = 2.8 Hz, CH), 115.3 (d, J_{CF} = 21.2 Hz, 2CH), 117.7 (q, J_{CF} = 2.4 Hz, C), 124.9 (C), 126.6 (q, J_{CF} = 278.2 Hz, CF_3), 129.1 (2CH), 129.5 (d, J_{CF} = 8.3 Hz, 2CH), 130.0 (2CH), 130.6 (CH), 134.0 (q, J_{CF} = 3.3 Hz, C), 162.0 (d, J_{CF} = 249.1 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.35 (CF_3), -115.20 (F).

EI HRMS: calcd. for $C_{16}H_{10}F_4$: 278.0703, found: 278.0705.

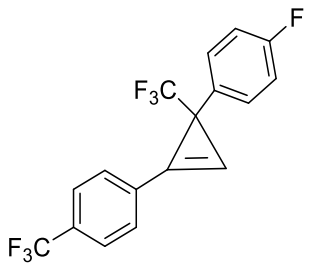


5g

1-Fluoro-4-(1-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)cycloprop-2-en-1-yl)benzene (5h)

Following the general procedure, from N'-(4-fluorophenyl)-2,2,2-trofluoroethylidene)-4-methylbenzenesulfonohydrazide (0.110 mmol, 40 mg), trifluorometilphenylacetylene (0.220, 37.5 mg) and K_2CO_3 (0.220 mmol, 30.4 mg), were obtained 18 mg of **5h** (56% isolated yield) as a yellowish oil. R_f 0.31 (30:1 Hexane/AcOEt).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.03 (t, *J* = 8.7 Hz, 2H), 7.38 (s, 1H), 7.40 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 31.9 (q, *J* = 37.1 Hz, C), 102.1 (q, J_{CF} = 2.7 Hz, CH), 115.5 (d, J_{CF} = 21.6 Hz, 2CH), 116.9 (C), 123.6 (q, J_{CF} = 273.7 Hz, CF_3), 126.1 (q, J_{CF} = 3.6 Hz, 2CH), 126.5 (q, J_{CF} = 273.7 Hz, CF_3), 128.3 (C), 129.4 (d, J_{CF} = 7.6 Hz, 2CH), 130.1 (2CH), 131.7 (q, J_{CF} = 34.1 Hz, C), 133.3 (d, *J* = 3.2 Hz, C), 162.0 (d, *J* = 246 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$) δ= -62.97 (CF_3), -64.45 (CF_3), -114.58(CF).

EI HRMS: calcd. For $C_{17}H_9F_7$: 346.0589, found: 346.0595.

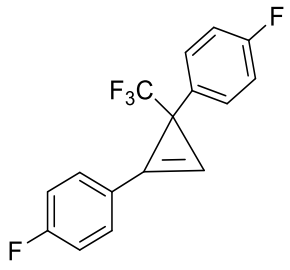


5h

4, 4'-(1-(Trifluoromethyl)cycloprop-2-ene-1,2-diyl)bis(fluorobenzene) (5i)

Following the general procedure, from *N'*-(4-fluorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (0.11 mmol, 40 mg), *p*-fluorophenylacetylene (0.22 mmol, 25 µL) and K_2CO_3 (0.22 mmol, 30 mg), were obtained 21 mg of **5i** (63 % isolated yield) as a red oil. R_f 0.28 (50:1 Hexane/AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.00 (t, *J* = 8.7 Hz, 2H), 7.15 (m, 3H), 7.39 (m, 2H), 7.65 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 31.7 (q, J_{CF} = 35.8 Hz, C), 98.4 (CH), 115.3 (d, J_{CF} = 21.6 Hz, 2CH), 116.4 (d, J_{CF} = 22.4 Hz, 2CH), 116.7 (d, J_{CF}= 2.2 Hz, C), 121.2 (d, J_{CF}= 3.3 Hz, C), 126.5 (q, J_{CF} = 278.9 Hz, CF_3), 129.4 (d, J_{CF} = 8.2 Hz, 2CH), 132.0 (d, J_{CF} = 8.9 Hz, 2CH), 133.7 (d, J_{CF} = 3.0 Hz, C), 162.0 (d, J_{CF} = 246.4 Hz, C), 163.9 (d, J_{CF} = 252.5 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.34 (CF_3), -108.19 (F), -115.01 (F).

EI HRMS: calcd. for $C_{16}H_9F_5$: 296.0624, found: 296.0617.

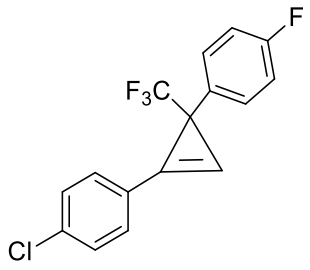


5i

1-Chloro-4-(3-(4-fluorophenyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (5j)

Following the general procedure, from *N'*-(-4-fluorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (0.147 mmol, 53 mg), *p*-chlorophenylacetylene (0.29 mmol, 46 mg) and K_2CO_3 (0.29 mmol, 40 mg), were obtained 22 mg of **5j** (47 % isolated yield) as a yellow oil. R_f 0.34 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.02 (t, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 1.6 Hz, 1H), 7.39 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 31.8 (q, J_{CF} = 35.7 Hz, C), 99.7 (q, J_{CF} = 2.9 Hz, CH), 115.4 (d, J_{CF} = 21.4 Hz, 2CH), 116.8 (q, J_{CF} = 2.1, C), 126.4 (q, J_{CF}= 277.6 Hz, CF_3), 123.4 (C), 129.3 (d, J_{CF} = 8.1 Hz, 2CH), 129.4 (2CH), 131.1 (2CH), 133.6 (d, J_{CF} = 3.3 Hz, C), 136.7 (C), 162.1 (d, J_{CF} = 246.6 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.38 (CF_3), -114.88 (F).

EI HRMS: calcd. for $C_{16}H_9ClF_4$: 312.0329, found: 312.0319.



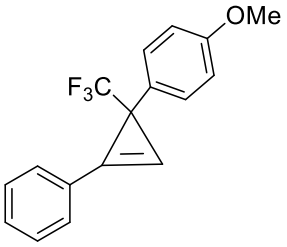
5j

1-Methoxy-4-(2-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (5k)

Following the general procedure, from *N'*-(-4-methoxyphenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (0.11 mmol, 42 mg), phenylacetylene (0.22 mmol, 24 µl) and

K_2CO_3 (0.22 mmol, 30 mg), were obtained 19 mg of **5k** (61% isolated yield) as a yellow oil. R_f 0.24 (20:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.80 (s, 3H, OCH_3), 6.87 (d, *J* = 8.7 Hz, 2H), 7.20 (q, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.47 (m, 3H), 7.68 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 31.6 (q, J_{CF} = 35.3 Hz, C), 55.2 (OCH_3), 99.4 (q, J_{CF} = 2.9 Hz, CH), 113.8 (2CH), 118.1 (q, J_{CF} = 2.4 Hz, C), 125.2 (C), 126.8 (q, J_{CF} = 277.4 Hz, CF_3), 129.0 (4CH), 129.9 (2CH), 130.3 (CH), 130.3 (C), 158.8 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.40 (CF_3).

EI HRMS: calcd. for $C_{17}H_{13}F_3O$: 290.0902, found: 290.0911.

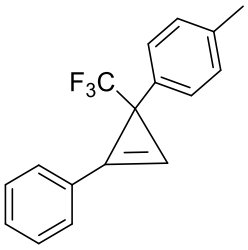


5k

1-Methyl-4-(2-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (5l)

Following the general procedure, from *N'*-(-4-methylphenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (0.056 mmol, 20 mg), phenylacetylene (0.112 mmol, 12 µl) and K_2CO_3 (0.112 mmol, 15 mg), were obtained 7.2 mg of **5l** (47 % isolated yield) as a yellow oil. R_f 0.26 (15:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.33 (s, 3H, CH_3), 7.15 (m, 3H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.46 (m, 3H), 7.67 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 21.0 (CH_3), 32.0 (q, J_{CF} = 35.3 Hz, C), 99.0 (q, J_{CF} = 2.9 Hz, C), 117.7 (C), 125.2 (C), 126.6 (CF_3), 127.6 (2CH), 128.9 (2CH), 129.1 (2CH), 130.0 (2CH), 130.3 (CH), 135.1 (C), 136.9 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.17 (CF_3).

EI HRMS: calcd. for $C_{17}H_{13}F_3$: 274.1017, found: 274.1018.

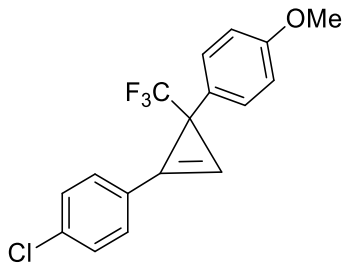


5l

1-Chloro-4-(3-(4-methoxyphenyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (5m)

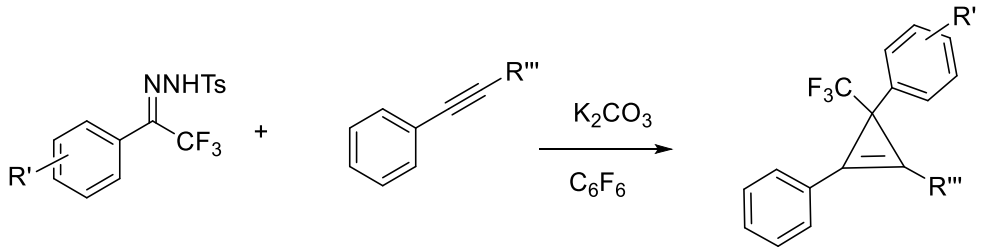
Following the general procedure, from 4-methoxy-*N'* -(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfonohydrazide (0.107 mmol, 40 mg), *p*-chlorophenylacetylene (0.21 mmol, 33 mg) and K_2CO_3 (0.21 mmol, 29 mg), were obtained 7.2 mg of **5m** (47 % isolated yield) as a yellow oil. R_f 0.17 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.80 (s, 3H, OCH_3), 6.86 (d, *J* = 8.7 Hz, 2H), 7.20 (bs, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 31.7 (q, J_{CF} = 33.7 Hz, C), 55.3 (OCH_3), 100.1 (q, J_{CF} = 3.1 Hz, C), 113.9 (2CH), 117.1 (q, J_{CF} = 2.2 Hz, C), 126.6 (q, J_{CF} = 277.6 Hz, CF_3), 123.7 (C), 128.9 (2CH), 129.4 (2CH), 131.1 (2CH), 132.7 (q, J_{CF} = 2.1 Hz, C), 136.4 (C), 158.8 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -64.46 (CF_3).

EI HRMS: calcd. for $C_{17}H_{12}ClF_3O$: 324.0512, found: 324.0522.



5m

2.2 Synthesis of tetrasubstituted cyclopropenes



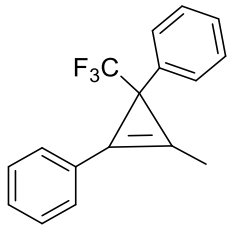
4 **6** **7**

General procedure:

In a carousel tube reactor under nitrogen atmosphere the corresponding *N*-tosylhydrazone (**4**) (1 equiv, 0.1 mmol), the internal alkyne (**6**) (2 equiv) and K_2CO_3 (2 equiv) were dissolved in 3 ml of C_6F_6 and the mixture was stirred at 110 ^oC for 24h. Then, the solution was washed with $NaHCO_3$ (2 x 5 mL), NaCl (sat) (2 x 5 mL) and extracted with dichloromethane. Then, the organic phase was dried over Na_2SO_4 and filtered to remove the solvent under slight vacuum. All the crudes were purified by flash chromatography (silica gel, eluent). Note: cyclopropenes **7** can be volatile compounds therefore careful solvent removal is recommended.

(3-Methyl-1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (7a)[3]

Following the general procedure, from methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.117 mmol, 40 mg), 1-phenyl-1-propyne (0.23 mmol, 29 µl) and K_2CO_3 (0.23 mmol, 32 mg), were obtained 30.8 mg of **7a** (96 % isolated yield) as a colorless oil. R_f 0.33 (Hexane).

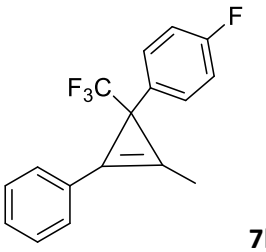


7a

1-Fluoro-4-(2-methyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7b)

Reaction performed at 1 mmol scale. Following the general procedure, from *N'*-(-4-fluorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (1 mmol, 0.36 g), 1-phenyl-1-propyne (2 mmol, 0.25 ml) and K_2CO_3 (2 mmol, 0.27 g), were obtained 0.21 g of **7b** (71 % isolated yield) as a colorless oil. R_f 0.29 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.40 (s, 3H, CH_3), 7.00 (t, *J* = 8.7 Hz, 2H), 7.42 (m, 5H), 7.58 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.2 (CH_3), 33.6 (q, J_{CF} = 33.8 Hz, C), 108.8 (C), 109.6 (C), 115.2 (d, J_{CF} = 21.3 Hz, 2CH), 126.0 (C), 127.0 (q, J_{CF} = 277.8 Hz, CF_3), 128.9 (2CH), 129.3 (2CH), 129.4 (d, J_{CF} = 7.2 Hz, 2CH), 130.0 (CH), 134.1 (d, J_{CF} = 2.8 Hz, C), 161.8 (d, J_{CF} = 249.5 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -63.32 (CF_3), -115.57 (F).

EI HRMS: calcd. for $C_{17}H_{12}F_4$: 292.0875, found: 292.0882.

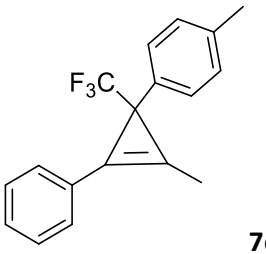


7b

1-Methyl-4-(2-methyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7c)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfonohydrazide (0.11 mmol, 41 mg), diphenylacetylene (0.22 mmol, 39 mg) and K_2CO_3 (0.22 mmol, 30 mg), were obtained 25 mg of **7c** (77 % isolated yield) as a white solid. R_f 0.16 (Hexane). ^{1}H NMR (300 MHz, 298K, $CDCl_3$) δ (ppm) = 2.33 (s, 3H), 2.40 (s, 3H), 7.12 (d, *J* =7.8 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.44 (m, 3H), 7.60 (dd, *J* = 7.8, 1.5 Hz, 2H). ^{13}C NMR (75 MHz, 298K, $CDCl_3$) δ= 9.3 (CH_3), 21.0 (CH_3), 33.2 (q, J_{CF} = 34.5 Hz, C), 108.8 (q, J_{CF} = 2.4 Hz, C), 109.7 (q, J_{CF} = 2.4 Hz, C), 126.3 (C), 127.1 (q, J_{CF} = 278 Hz, C), 127.6 (2CH), 128.3 (CH), 128.9 (2CH), 129.1 (2CH), 129.3 (2CH), 135.3 (C), 136.6 (C). ^{19}F NMR (282 MHz, 298K, $CDCl_3$): δ -63.20.

EI HRMS: calcd. For $C_{18}H_{15}F_3$: 288.1126, found: 288.1114.



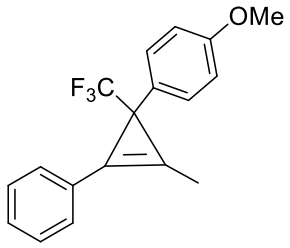
7c

1-Methoxy-4-(2-methyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7d)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (0.080 mmol, 31 mg), 1-phenylpropyne

(0.16 mmol, 20 µl) and K_2CO_3 (0.16 mmol, 22 mg), were obtained 21 mg of **7d** (86 % isolated yield) as a colorless oil. R_f 0.31 (20:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.40 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.85 (d, *J* = 8.8 Hz, 2H), 7.33 (m, 2H), 7.42 (m, 3H), 7.60 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 9.4 (CH_3), 32.7 (q, J_{CF} = 34.5 Hz, C), 55.2 (OCH_3), 109.2 (q, J_{CF} = 2.5 Hz, C), 110.0 (q, J_{CF} = 2.5 Hz, C), 113.8 (2CH), 127.1 (d, J_{CF} = 278.3 Hz, CF_3), 126.4 (C), 128.9 (2CH), 129.0 (2CH), 129.1 (CH), 129.3 (2CH), 130.4 (C), 158.6 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -63.47 (CF_3).

EI HRMS: calcd. for $C_{18}H_{15}F_3O$: 304.1058, found: 304.1061.

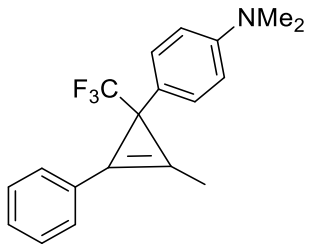


7d

***N*, *N*-dimethyl-4-(2-methyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)aniline (7e)**

Following the general procedure, from 4-methyl-*N*′ -(2,2,2-trifluoro-1-(4-dimethylaminophenyl)ethylidene)benzenesulfonohydrazide (0.20 mmol, 78 mg), 1-phenyl-1-propyne (0.40 mmol, 50 µl) and K_2CO_3 (0.40 mmol, 55 mg), were obtained 19 mg of **7e** (30 % isolated yield) as a yellow oil. R_f 0.32 (10:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.40 (s, 3H, CH_3), 2.93 (s, 6H, $2CH_3$), 6.69 (d, *J* = 8.4 Hz, 2H), 7.31 (s, 1H), 7.43 (m, 4H), 7.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 9.4 (CH_3), 33.1 (q, J_{CF} = 33.4 Hz, C), 40.9 ($2CH_3$), 109.3 (C), 110.3 (C), 113.0 (CH), 127.4 (q, J_{CF} = 278.1 Hz, CF_3), 122.3 (C), 126.6 (C), 128.7 (2CH), 128.8 (2CH), 128.9 (2CH), 129.3 (2CH), 162.2 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -63.55 (CF_3).

EI HRMS: calcd. for [M+1]: [$C_{19}H_{19}F_3N$]: 318.1464, found: 318.1462.



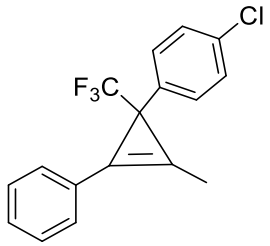
7e

1-Chloro-4-(2-methyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7f)

Following the general procedure, from 4-methyl-*N*′ -(2,2,2-trifluoro-1-(4-chlorophenyl)ethylidene)benzenesulfonohydrazide (0.40 mmol, 0.15 g), 1-phenyl-1-propyne (0.80 mmol, 100 µl) and K_2CO_3 (0.80 mmol, 0.11 g), were obtained 54 mg of **7f** (44 % isolated yield) as a colorless oil. R_f 0.33 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.39 (s, 3H, CH_3), 7.27 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.43 (m, 3H), 7.57 (dd, *J* = 8.1, 1.6 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 9.2 (CH_3), 33.0 (q, J_{CF} = 35.0 Hz, C), 108.4 (q, J_{CF} = 2.5 Hz, C), 109.2 (q, J_{CF} = 2.5 Hz, C), 125.8 (C), 126.8 (q, J_{CF} = 278.1 Hz, CF_3), 127.5 (CH), 128.2 (CH), 128.5 (2CH), 128.9

(2CH), 129.3 (2CH), 131.5 (CH), 132.8 (C), 136.8 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -63.12 (CF_3).

EI HRMS: calcd. for $C_{17}H_{12}ClF_3$: 308.0599, found: 308.0579.

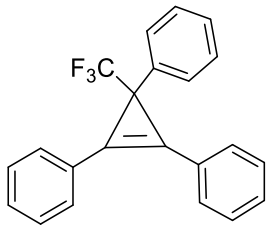


7f

(3-(Trifluoromethyl)cycloprop-1-ene-1,2,3-triyl)tribenzene (7g)

Following the general procedure, from methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.116 mmol, 40 mg), diphenylacetylene (0.232 mmol, 42 mg) and K_2CO_3 (0.232 mmol, 32 mg), were obtained 28 mg of **7g** (72 % isolated yield) as a yellow oil. R_f 0.29 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.29-7.40 (m, 3H), 7.50 (m, 8H), 7.80 (m, 4H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 33.5 (d, J_{CF} = 34.5 Hz, C), 109.9 (2C), 127.0 (q, J_{CF} = 278.2 Hz, CF_3), 126.2 (C), 127.0 (CH), 127.6 (CH), 128.1 (CH), 128.4 (CH), 128.7 (CH), 129.1 (4CH), 129.8 (2CH), 130.0 (4CH), 131.2 (C), 137.4 (C).^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.02 (CF_3).

EI HRMS: calcd. for $C_{22}H_{15}F_3$: 336.1126, found: 336.1122.

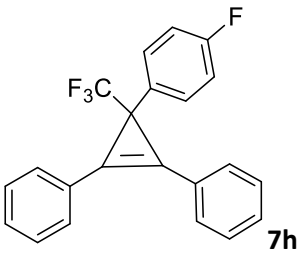


7g

(3-(4-Fluorophenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene (7h)

Following the general procedure, from *N'*-(-4-fluorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (0.12 mmol, 42 mg), diphenylacetylene (0.232, 42 mg) and K_2CO_3 (0.23 mmol, 32 mg), were obtained 27 mg of **7h** (62 % isolated yield) as a yellowish solid. R_f 0.27 (Hexane).^{1}H NMR (400 MHz, 298K, $CDCl_3$) δ (ppm) = 6.99 (t, *J* = 8.6 Hz, 2H), 7.51 (m, 8H), 7.78 (m, 4H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ (ppm) = 33.4 (q, J_{CF} = 34.6 Hz, C), 110.0 (2C), 115.3 (d, J_{CF} = 21.2 Hz, 2CH), 126.0 (2C), 126.9 (q, J_{CF} = 277.7 Hz, CF_3), 129.2 (2CH), 129.3 (d, J_{CF} = 8.1 Hz, 2CH), 130.0 (8CH), 133.2 (d, J_{CF} = 2.4 Hz, C), 161.9 (d, J_{CF} = 245.5 Hz, C). ^{19}F NMR (282 MHz, 298K, $CDCl_3$) δ (ppm) = -62.33 (F), -115.33 (CF_3).

EI HRMS: calcd. For $C_{22}H_{14}F_4$: 354.1032, found: 354.1029.

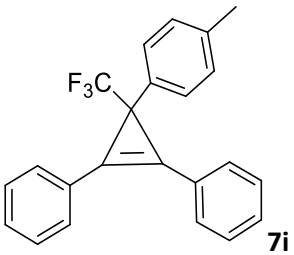


7h

(3-(*p*-Tolyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene (7i)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfono hydrazide (0.116 mmol, 41.3 mg), diphenylacetylene (0.232, 41.3 mg) and K_2CO_3 (0.23 mmol, 32 mg), were obtained 33 mg of **7i** (82 % isolated yield) as a yellow oil. R_f 0.32 (30:1 Hexane/AcOEt). ^{1}H NMR (400 MHz, 298K, $CDCl_3$) δ (ppm) = 2.3 (s, 3H), 7.13 (d, *J* = 8 Hz, 2H), 7.45 (m, 4H), 7.51 (m, 4H), 7.79 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 21.0 (CH_3), 33.4 (q, J_{CF} = 34.3 Hz, C), 110.3 (2C), 126.1 (q, J_{CF} = 277.9 Hz, CF_3), 126.3 (2C), 127.5 (2CH), 129.0 (4CH), 129.1 (2CH), 129.7 (2CH), 130.0 (4CH), 134.3 (C), 136.7 (C). ^{19}F NMR (256.25 MHz, 298K, $CDCl_3$) δ (ppm) = -62.17 (CF_3).

EI HRMS: calcd. For $C_{23}H_{17}F_3$: 350.1282, found: 350.1273.

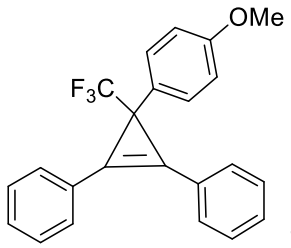


7i

(3-(4-Methoxyphenyl)-3-(trifluoromethyl)cycloprop-1-ene-1,2-diyl)dibenzene (7j)

Following the general procedure, from 4-Methyl-*N'* -(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (0.11 mmol, 41 mg), diphenylacetylene (0.22 mmol, 39 mg) and K_2CO_3 (0.22 mmol, 30 mg), were obtained 25 mg of **7j** (62 % isolated yield) as a colorless oil. R_f 0.13 (20:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.78 (s, 3H, CH_3O), 6.84 (d, *J* = 8.9 Hz, 2H), 7.47 (m, 8H), 7.79 (dd, *J* = 8.3, 1.5 Hz, 4H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 33.5 (q, J_{CF} = 33.8 Hz, C), 55.6 (CH_3O), 110.8 (2C), 114.2 (2CH), 126.7 (2C), 127.0 (q, J_{CF} = 281.2 Hz, CF_3), 129.3 (2CH), 129.5 (4CH), 129.9 (C), 130.1 (2CH), 130.4 (4CH), 159.0 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.43 (CF_3).

EI HRMS: calcd. for $C_{23}H_{17}F_3O$: 366.1215, found: 366.1217.

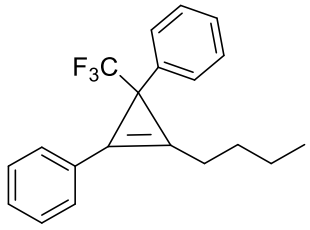


7j

(3-Butyl-1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (7k)

Following the general procedure, from methyl-*N*′-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.058 mmol, 20 mg), 1-phenyl-1-hexyne (0.117 mmol, 21 µl) and K_2CO_3 (0.117 mmol, 16 mg), were obtained 7.3 mg of **7k** (40 % isolated yield) as a colorless oil. R_f 0.40 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.97 (t, *J* = 7.3 Hz, 3H, CH_3). 1.46 (q, *J* = 7.4 Hz, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.73 (td, *J* = 7.4, 3.0 Hz, 2H, CH_2), 7.30 (m, 4H), 7.41 (m, 4H), 7.58 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 13.7 (CH_3), 22.5 (CH_2), 24.2 (CH_2), 29.6 (CH_2), 33.5 (q, J_{CF} = 34.6 Hz, C), 107.8 (q, J_{CF} = 2.4 Hz, C), 113.7 (C), 127.1 (q, J_{CF} = 277.8 Hz, CF_3), 126.2 (C), 126.7 (CH), 127.5 (2CH), 128.3 (2CH), 128.9 (2CH), 129.1 (CH), 129.4 (2CH), 138.5 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.67 (CF_3).

EI HRMS: calcd. for $C_{20}H_{19}F_3$: 316.1439, found: 316.1440.

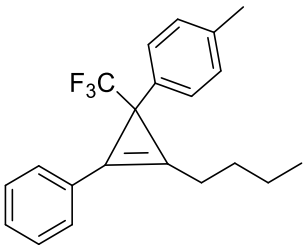


7k

1-(2-Butyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-4-methylbenzene (7l)

Following the general procedure, from 4-methyl-*N*′ -(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfonohydrazide (0.1 mmol, 36 mg), 1-phenylhexyne (0.2 mmol, 34 µl) and K_2CO_3 (0.2 mmol, 28 mg), were obtained 22.1 mg of **7l** (67 % isolated yield) as a yellow oil. R_f 0.35 (30:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.97 (t, *J* = 7.3 Hz, 3H, CH_3), 1.46 (q, *J* = 7.4 Hz, 2H, CH_2), 1.76 (qd, *J* = 7.4, 2.0 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.73 (td, *J* = 7.4, 3.4 Hz, 2H, CH_2), 7.11 (d, *J* = 7.9 Hz, 2H), 7.31 (s, 2H), 7.43 (m, 3H), 7.60 (dd, *J* = 8.3, 1.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 13.7 (CH_3), 21.0 (CH_3), 22.5 (CH_2), 24.2 (CH_2), 29.6 (CH_2), 33.7 (q, J_{CF} = 34.2 Hz, C), 108.0 (q, J_{CF} = 2.8 Hz, C), 113.9 (C), 127.1 (d, J_{CF} = 277.0 Hz, CF_3), 126.3 (C), 127.5 (2CH), 128.9 (2CH), , 129.0 (3CH), 129.4 (2CH), 135.4 (C), 136.4 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.84 (CF_3).

EI HRMS: calcd. for $C_{21}H_{21}F_3$: 330.1590, found: 330.1580.

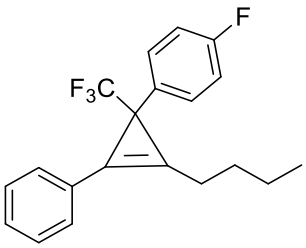


7l

1-(2-Butyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)-4-fluorobenzene (7m)

Following the general procedure, from *N'*-(4-fluorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (0.11 mmol, 40 mg), 1-phenyl-1-hexyne (0.22 mmol, 39 µl) and K_2CO_3 (0.22 mmol, 30 mg), were obtained 21 mg of **7m** (56 % isolated yield) as a colorless oil. R_f 0.42 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.97 (t, *J* = 7.3 Hz, 3H, CH_3), 1.46 (q, *J* = 7.4 Hz, 2H CH_2), 1.77 (m, 2H, CH_2), 2.73 (td, *J* = 7.4, 1.7 Hz, 2H, CH_2), 6.99 (t, *J* = 8.7 Hz, 2H), 7.42 (m, 5H), 7.59 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 13.7 (CH_3), 22.5 (CH_2), 24.2 (CH_2), 29.5 (CH_2), 33.0 (q, J_{CF} = 34.4 Hz, C), 107.9 (q, J_{CF} = 2.3 Hz, C), 114.0 (C), 115.2 (d, J_{CF} = 21.2 Hz, 2CH), 127.0 (q, J_{CF} = 278.2 Hz, CF_3), 126.0 (C), 129.0 (2CH), 129.2 (2CH), 129.4 (2CH), 131.5 (CH), 134.3 (d, J_{CF} = 2.5 Hz, C), 161.8 (d, J_{CF} = 245.4 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -63.00 (CF_3), -115.83 (F).

EI HRMS: calcd. for $C_{20}H_{19}F_4$ [M+1]: 335.1402, found: 335.1417.

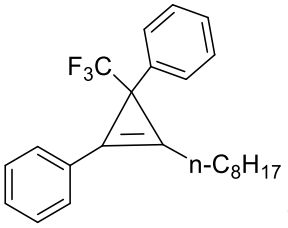


7m

(3-Octyl-1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (7n)

Following the general procedure, from methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.18 mmol, 62 mg), 1-phenyl-1-decyne (0.37 mmol, 79 mg) and K_2CO_3 (0.37 mmol, 51 mg), were obtained 20 mg of **7n** (79 % isolated yield) as a colorless oil. R_f 0.44 (Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.90 (m, 3H, CH_3), 1.33 (m, 10H, CH_2), 1.79 (qt, *J* = 7.6 Hz, 2H, CH_2), 2.73 (td, *J* = 7.4, 2.5 Hz, 2H, CH_2), 7.30 (m, 3H, CH), 7.42 (m, 5H, CH), 7.58 (m, 2H, CH).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 14.1 (CH_3), 22.6 (CH_2), 24.5 (CH_2), 27.5 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 33.5 (q, J_{CF} = 34.4 Hz, C), 107.8 (C), 113.8 (C), 127.1 (q, J_{CF} = 278.2 Hz, CF_3), 126.2 (C), 126.7 (CH), 127.5 (2CH), 128.3 (2CH), 128.9 (2CH), 129.1 (CH), 129.4 (2CH), 138.5 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.64 (CF_3).

EI HRMS: calcd. for $C_{24}H_{27}F_3$: 373.2135, found: 373.2141.

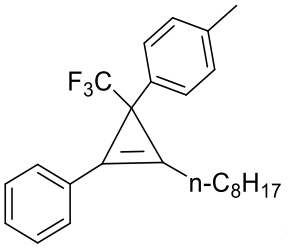


7n

1-Methyl-4-(2-octyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7o)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfonohydrazide (0.26 mmol, 85 mg), 1-phenyl-1-decyne (0.51 mmol, 0.11g) and K_2CO_3 (0.51 mmol, 70 mg), were obtained 56.2 mg of **7o** (56 % isolated yield) as a yellow oil. R_f 0.42 (Hexane). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 0.92 (t, *J* = 7.0 Hz, 3H, CH_3), 1.30 (m, 8H, CH_2), 1.48 (m, 2H, CH_2), 1.80 (qt, *J* = 7.4, 1.9 Hz, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.73 (td, *J* = 7.5, 2.7 Hz, 2H, CH_2), 7.13 (d, *J* = 8.0 Hz, 2H), 7.31 (m, 2H), 7.40 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.60 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 14.1 (CH_3), 21.0 (CH_3), 22.7 (CH_2), 24.6 (CH_2), 27.5 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 33.3 (q, J_{CF} = 34.7 Hz, C), 108.0 (q, J_{CF} = 2.4 Hz, C), 114.0 (C), 127.2 (q, J_{CF} = 278.1 Hz, CF_3), 126.3 (C), 127.5 (2CH), 128.9 (2CH), 129.0 (CH), 129.1 (2CH), 129.4 (2CH), 135.5 (C), 136.4 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.79 (CF_3).

EI HRMS: calcd. for $C_{25}H_{29}F_3$: 386.2216, found: 386.2208.

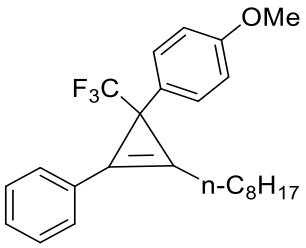


7o

1-Methoxy-4-(2-octyl-3-phenyl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7p)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (0.203 mmol, 76 mg), 1-phenyl-1-decyne (0.406 mmol, 87mg) and K_2CO_3 (0.406 mmol, 56 mg), were obtained 32.6 mg of **7p** (40 % isolated yield) as a yellow oil. R_f 0.42 (20:1 Hexane/AcOEt). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 0.92 (t, *J* = 6.9 Hz, 3H, CH_3), 1.32 (m, 10H, CH_2), 1.80 (qd, *J* = 7.3, 2.1 Hz, 2H, CH_2), 2.75 (td, *J* = 7.6, 2.5 Hz, 2H, CH_2), 3.81 (s, 3H, OCH_3), 6.86 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.61 (dd, *J* = 8.3, 1.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 14.1 (CH_3), 22.7 (CH_2), 24.6 (CH_2), 27.6 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 32.9 (q, J_{CF} = 35.1 Hz, C), 55.3 (OCH_3), 108.3 (q, J_{CF} = 2.4 Hz, C), 113.8 (2CH), 114.4 (q, J_{CF} = 2.0 Hz, C), 126.4 (C), 127.2 (q, J_{CF} = 278.3 Hz, CF_3), 128.9 (4CH), 129.0 (CH), 129.4 (2CH), 130.6 (C), 158.5 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -63.06 (CF_3).

EI HRMS: calcd. for $C_{25}H_{29}F_3O$: 402.2154, found: 402.2162.

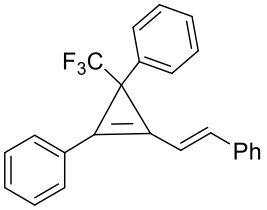


7p

(*E*)-[3-styryl-1-(trifluoromethyl)cycloprop-2-ene-1, 2-diyl]benzene (7q)

Following the general procedure, from methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.11 mmol, 39 mg), (*E*)-but-1-en-3-yne-1,4-diyldibenzene[4] (0.23 mmol, 46 mg) and K_2CO_3 (0.22 mmol, 30 mg), were obtained 20 mg of **7q** (51 % isolated yield) as a yellow oil. R_f 0.26 (50:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.10 (d, *J* = 15.8 Hz, 1H, CH), 7.22 (d, *J* = 15.6 Hz, 1H, CH), 7.42 (m, 10H), 7.55 (m, 3H), 7.68 (dd, *J* = 7.0, 1.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 33.5 (q, J_{CF} = 34.8 Hz, C), 108.6 (q, J_{CF} = 2.4 Hz, C), 110.6 (q, J_{CF} = 2.0 Hz, C), 112.0 (CH), 126.8 (q, J_{CF} = 280.0 Hz, CF_3), 126.6 (C), 127.0 (CH), 127.3 (2CH), 127.7 (2CH), 128.4 (2CH), 128.8 (2CH), 129.0 (2CH), 129.2 (CH), 129.6 (CH), 129.7 (2CH), 135.9 (C), 137.3 (C), 140.2 (CH). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.05 (CF_3).

EI HRMS: calcd. for $C_{24}H_{17}F_3$: 362.1277, found: 362.1263.

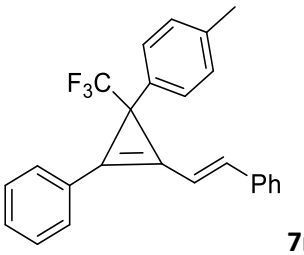


7q

(*E*)-1-methyl-4-(2-phenyl-3-styryl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7r)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfonohydrazide (0.127 mmol, 45 mg), (*E*)-but-1-en-3-yne-1,4-diyldibenzene[4] (0.25 mmol, 52 mg) and K_2CO_3 (0.25 mmol, 34 mg), were obtained 39.2 mg of **7r** (82 % isolated yield) as a yellow oil. R_f 0.29 (50:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.34 (s, 3H, CH_3), 7.17 (m, 4H), 7.40 (m, 8H), 7.58 (m, 2H), 7.68 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 21.0 (CH_3), 33.2 (q, J_{CF} = 34.5 Hz, C), 108.7 (C), 110.8 (C), 112.1 (CH), 126.6 (C), 127.3 (2CH), 127.6 (2CH), 126.8 (d, J_{CF} = 275.4 Hz, CF_3), 128.8 (2CH), 129.0 (2CH), 129.1 (2CH), 129.3 (CH), 129.5 (CH), 129.7 (2CH), 134.3 (C), 135.9 (C), 136.8 (C), 140.1 (CH). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.20 (CF_3).

EI HRMS: calcd. for $C_{25}H_{19}F_3$: 376.1458, found: 376.1432.

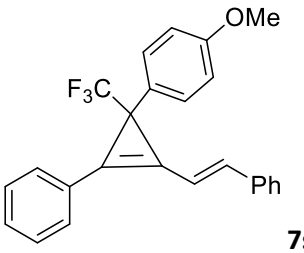


7r

(*E*)-1-methoxy-4-(2-phenyl-3-styryl-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7s)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (0.061 mmol, 23 mg), (*E*)-but-1-en-3-yne-1,4-diyldibenzene (0.12 mmol, 25 mg) and K_2CO_3 (0.12 mmol, 17 mg), were obtained 7.2 mg of **7s** (30 % isolated yield) as a colorless oil. R_f 0.31 (20:1 Hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.79 (s, 3H, OCH_3), 6.86 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 15.5 Hz, 1H, CH), 7.20 (d, *J* = 15.5 Hz, 1H, CH), 7.45 (m, 8H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 32.9 (q, J_{CF} = 33.8 Hz, C), 55.2 (CH_3), 109.0 (C), 111.2 (C), 112.2 (CH), 113.8 (2CH), 126.7 (d, J_{CF} = 278.5 Hz, CF_3), 127.3 (2CH), 128.8 (2CH), 129.0 (4CH), 129.1 (CH), 129.4 (C), 129.5 (CH), 129.7 (2CH), 135.9 (C), 140.0 (CH), 158.7 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.48 (CF_3).

EI HRMS: calcd. for $C_{25}H_{19}F_3O$: 392.1371, found: 392.1395.

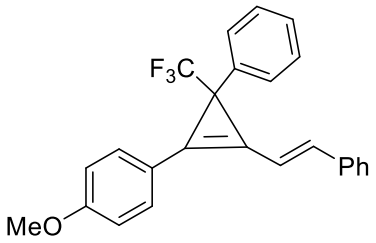


7s

(*E*)-1-methoxy-4-(3-phenyl-2-styryl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (7t)

Following the general procedure, from methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (0.085 mmol, 29 mg), (*E*)-1-methoxy-4-(4-phenylbut-3-en-1-yn-1-yl)benzene[5] (0.17 mmol, 40 mg) and K_2CO_3 (0.17 mmol, 24 mg), were obtained 12 mg of **7t** (36 % isolated yield) as a yellow oil. R_f 0.23 (10:1 Hexane/AcOEt).^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.87 (s, 3H, OCH_3), 7.00 (m, 3H), 7.19 (m, 1H, CH), 7.32 (m, 6H), 7.53 (d, *J* = 6.9 Hz, 4H), 7.61 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 33.3 (q, J_{CF} = 33.5 Hz, C), 55.4 (CH_3), 105.9 (C), 110.2 (C), 112.3 (CH), 114.6 (2CH), 119.2 (C), 126.9 (q, J_{CF} = 274.8 Hz, CF_3), 126.9 (CH), 127.2 (2CH), 127.6 (CH), 128.4 (2CH), 128.8 (2CH), 128.9 (2CH), 131.3 (2CH), 136.1 (C), 137.5 (C), 138.9 (CH), 160.7 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -61.99 (CF_3).

EI HRMS: calcd. for [M+1]: [$C_{25}H_{20}F_3O$]: 393.1449, found: 393.1458.

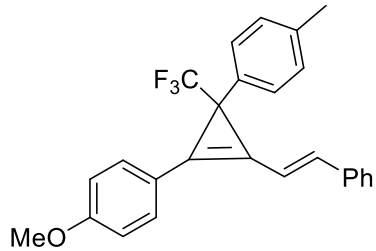


7t

(*E*)-1-methoxy-4-(2-styryl-3-(*p*-tolyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzene (7u)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfonohydrazide (0.067 mmol, 24 mg), (*E*)-1-methoxy-4-(4-phenylbut-3-en-1-yn-1-yl)benzene (0.13 mmol, 31.4 mg) and K_2CO_3 (0.13 mmol, 19 mg), were obtained 10.6 mg of **7u** (39 % isolated yield) as a yellow oil. R_f 0.13 (50:1 Hexane/AcOEt).^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.33 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.99 (d, *J* = 8.7 Hz, 2H), 7.14 (m, 4H), 7.38 (m, 5H), 7.53 (d, *J* = 6.9 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 21.0 (CH_3), 33.0 (q, J_{CF} = 37.7 Hz, C), 55.4 (OCH_3), 106.1 (C), 110.4 (C), 112.3 (CH), 114.6 (2CH), 119.3 (C), 127.1 (2CH), 127.6 (CH), 127.9 (q, J_{CF} = 277.9 Hz, CF_3), 128.8 (2CH), 128.8 (2CH), 129.1 (2CH), 131.3 (2CH), 134.5 (C), 136.1 (C), 136.6 (C), 138.8 (CH), 160.7 (C).^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.15 (CF_3).

EI HRMS: calcd. for [M+1]: [$C_{26}H_{22}F_3O$]: 407.1606, found: 407.1616.

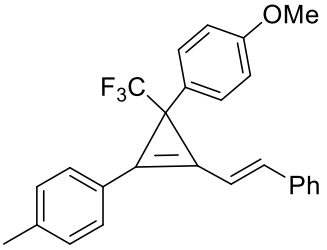


7u

(*E*)-1-methoxy-4-(2-styryl-3-(*p*-tolyl)-1-(trifluoromethyl)cycloprop-2-en-1-yl)benzene (7v)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (0.16 mmol, 60 mg), (*E*)-1-methyl-4-(4-phenylbut-3-en-1-yn-1-yl)benzene (0.32 mmol, 0.11 g) and K_2CO_3 (0.32 mmol, 44 mg), were obtained 30.6 mg of **7v** (42 % isolated yield) as a yellow oil. R_f 0.15 (50:1 Hexane/AcOEt).^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.43 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.86 (d, *J* = 8.7 Hz, 2H, CH), 7.07 (d, *J* = 15.7 Hz, 1H), 7.21 (d, *J* = 15.7 Hz, 1H), 7.29 (m, 2H), 7.33-7.50 (m, 5H), 7.56 (t, *J* = 7.5 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 21.6 (CH_3), 32.8 (q, J_{CF} = 32.9 Hz, C), 55.2 (OCH_3), 107.9 (C), 111.1 (C), 112.4 (CH), 113.8 (2CH), 123.9 (C), 127.2 (2CH), 127.3 (q, J_{CF} = 273.1 Hz, CF_3), 128.8 (2CH), 129.0 (3CH), 129.3 (CH), 129.6 (C), 129.7 (2CH), 129.8 (2CH), 136.0 (C), 139.4 (CH), 140.0 (C), 158.6 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.44 (CF_3).

EI HRMS: calcd. for [M+1]: [$C_{26}H_{22}F_3O$]: 407.1629, found: 407.1615.

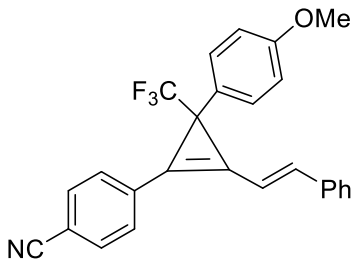


7v

(*E*)-4-(3-(4-methoxyphenyl)-2-styryl-3-(trifluoromethyl)cycloprop-1-en-1-yl)benzonitrile (7w)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (0.059 mmol, 21 mg), (*E*)-4-(4-phenylbut-3-en-1-yn-1-yl)benzonitrile[5] (0.118 mmol, 27 mg) and K_2CO_3 (0.118 mmol, 16.3 mg), were obtained 7.9 mg of **7w** (32 % isolated yield) as a yellow oil. R_f 0.25 (6:1 Hexane/AcOEt).^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.80 (s, 3H, OCH_3), 6.87 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 3.5 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 5H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.74 (s, 4H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 33.2 (d, J_{CF} = 33.9 Hz, C), 55.3 (OCH_3), 109.2 (C), 111.5 (CH), 112.4 (C), 113.4 (C), 114.0 (2CH), 118.5 (C), 126.8 (q, J_{CF} = 276.1 Hz, CF_3), 127.6 (2CH), 128.4 (C), 128.8 (2CH), 129.0 (2CH), 129.8 (2CH), 129.9 (CH), 131.1 (C), 132.7 (2CH), 135.4 (C), 142.5 (CH), 157.9 (C), 158.9 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.62 (CF_3).

EI HRMS: calcd. for [M+1]: [$C_{26}H_{19}F_3NO$]: 418.1413, found: 418.1408.

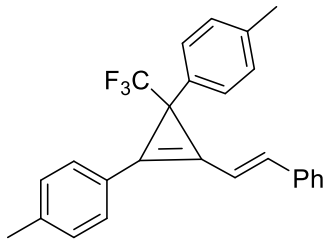


7w

(*E*)-4,4'-(3-styryl-1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)bis(methylbenzene) (7x)

Following the general procedure, from 4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methylphenyl)ethylidene)benzenesulfonohydrazide (0.093 mmol, 33 mg), (*E*)-1-methyl-4-(4-phenylbut-3-en-1-yn-1-yl)benzene[5] (0.19 mmol, 41 mg) and K_2CO_3 (0.19 mmol, 26 mg), were obtained 13.8 mg of **7x** (38 % isolated yield) as a yellow oil. R_f 0.31 (30:1 Hexane/AcOEt).^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.33 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 7.12 (dd, *J* = 17.9, 11.2 Hz, 4H), 7.24 (d, *J* = 11.2 Hz, 1H), 7.39 (m, 6H), 7.54 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 21.0 (CH_3), 21.6 (CH_3), 33.1 (q, J_{CF} = 33.3 Hz, C), 107.6 (C), 110.7 (C), 112.3 (CH), 123.8 (C), 126.3 (q, J_{CF} = 278.1 Hz, CF_3), 127.2 (2CH), 127.6 (2CH), 128.8 (2CH), 129.0 (CH), 129.1 (2CH), 129.7 (2CH), 129.8 (2CH), 134.4 (C), 136.0 (C), 136.6 (C), 139.4 (CH), 139.9 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.17 (CF_3).

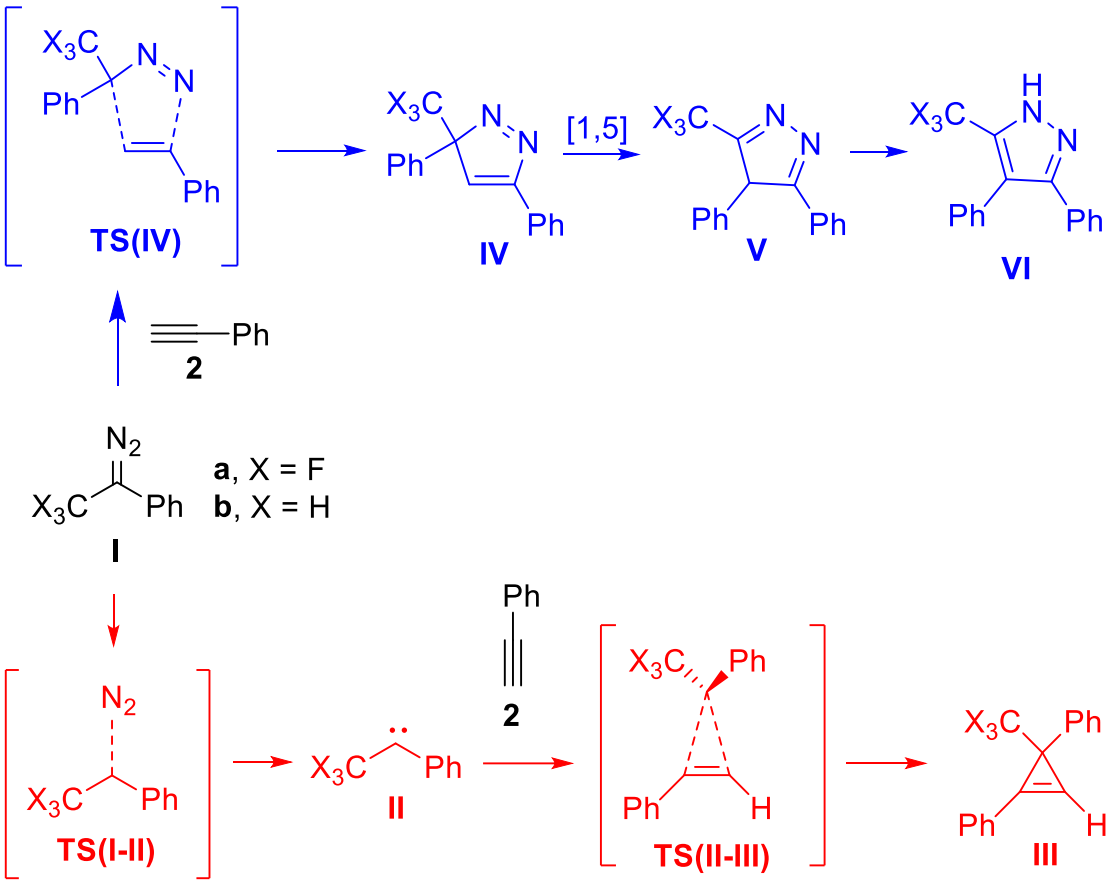
EI HRMS: calcd. for [M+1]: [$C_{26}H_{22}F_3$]: 391.1668, found: 391.1663.



7x

4. Computational Modeling

Methods: All calculations were performed with the Gaussian09 package of programs.[6] Full geometry optimizations were carried out employing the M06-2X hybrid functional with the 6-311++G** basis set, denoted as M06-2X/6-311++G**.[7] Harmonic force constants were computed at the optimized geometries employing the same level of theory to characterize the stationary points as minima or saddle points. Zero-point vibrational corrections were determined from the harmonic vibrational frequencies to convert the total energies E_{el} to Gibbs free energies G. Solvation free energies were calculated at the same level considering benzene as the solvent and employing the IEF-PCM model with the United Atom Topological Model (UAHF) to define the cavity. Frontier Orbital Energies for diazo compounds **Ia**, **Ib** and phenylacetylene were obtained from a single point HF/6-311G** calculation on the geometries optimized at the M06-2X/6-311++G** level. Computational data, three-dimensional models and cartesian coordinates for all the stationary points found are included below. The three-dimensional models have been rendered with CYLview.[8]



Scheme S1. Reaction pathways calculated

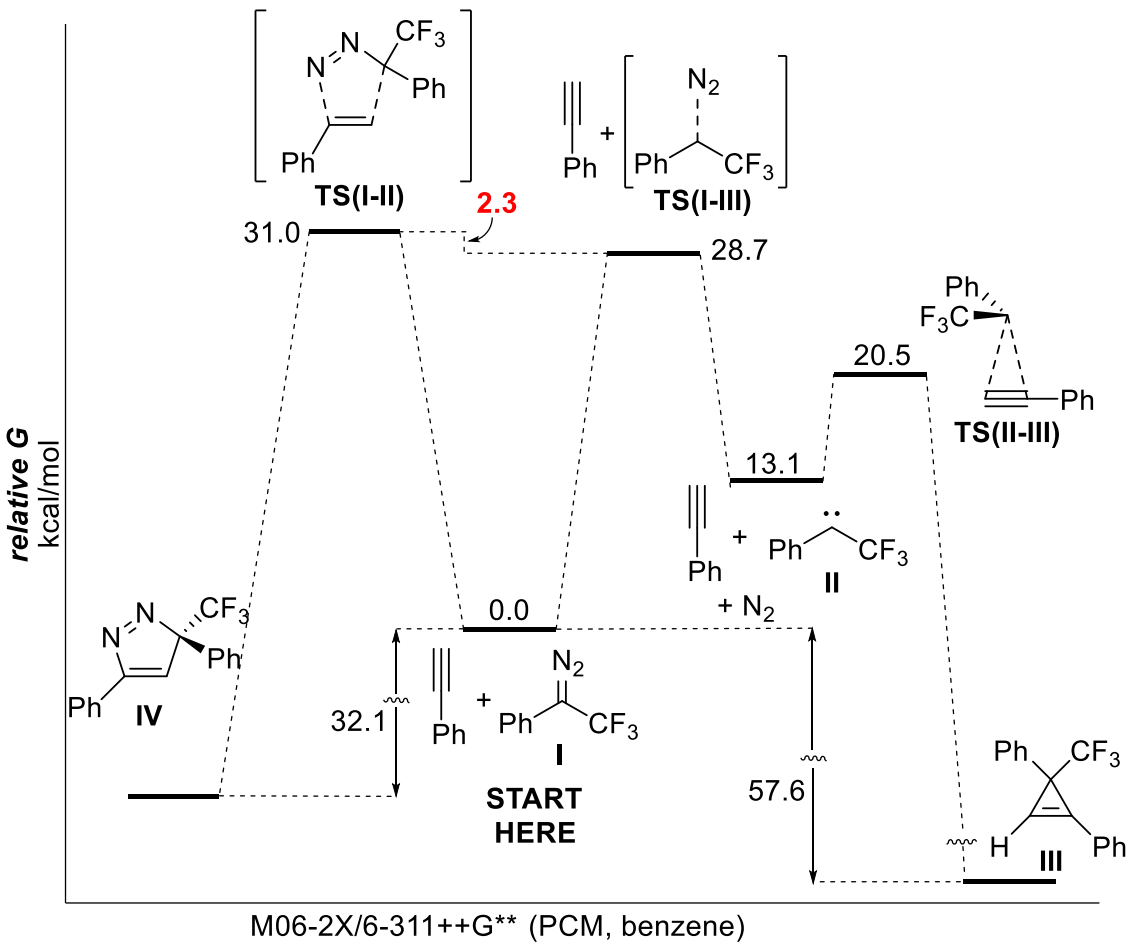
Table S1: Relative Energy data obtained for the stationary points at the M06-2X/6-311++G** level. Relative energy values are given in kcal·mol^{-1} E_{el}: electronic energy; G: Gibbs free energy in vacuum; G_{solv}: Gibbs free energy taking into account solvation effects in benzene.

Model a: X = CF3

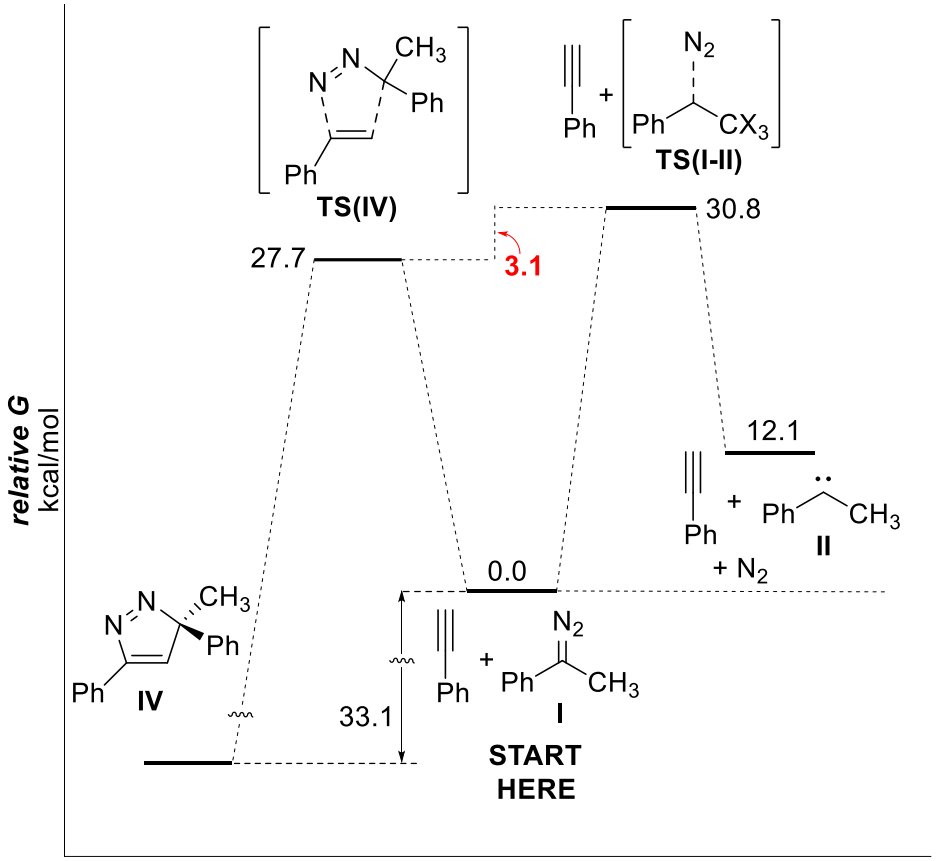
Relative E	I+2	TS(I-II)+2	II + 2+N2	TS(II-III)+N2	III+N2	TS(IV)	IV
E_{el}	0	32.2	27.8	21.3	-61.6	16.4	-50.9
G	0	29.5	14.5	20.0	-58.3	29.8	-32.3
G_{solv}	0	28.7	13.8	20.4		31.0	-32.1
ΔG_{act}		**28.7**		6.6		**31.0**	
$\Delta\Delta G_{act}$						**2.3**	

Model B: X = CH3

Relative E	I+2	TS(I-II)+2	II + 2+N2			TS(IV)	IV
Eel	0	34.6	27.5			15.0	-56.2
G	0	31.4	13.3			27.0	-33.1
Gsolv	0	30.8	12.1			27.7	-33.1
ΔG_{act}		**30.8**				**27.7**	
$\Delta\Delta G_{act}$						**-3.1**	



Scheme S2: Gibbs free energy representation of the reactions pathways calculated for the reaction between phenylacetylene and (1-diazo-2,2,2-trifluoroethyl)benzene **Ia** at the M06-2X/6-311++G**/PCM(benzene) level.



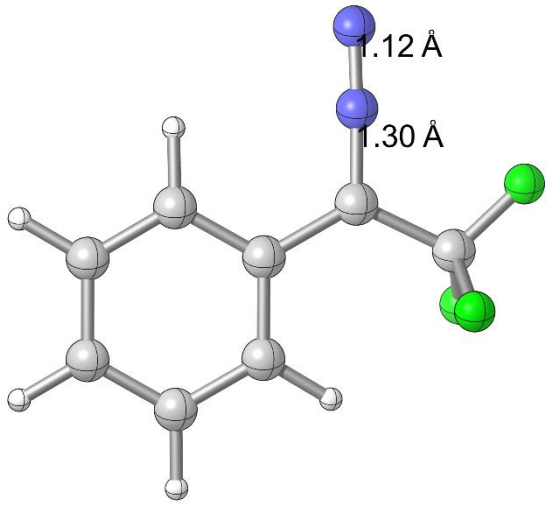
Scheme S3: Gibbs free energy representation of the reactions pathways calculated for the reaction between phenylacetylene and (1-diazoethyl)benzene **Ib** at the M06-2X/6-311++G**/PCM(benzene) level.

Ia

Gas phase:
E(RM062X) = -716.783194476

Zero-point correction=	0.121062 (Hartree/Particle)
Thermal correction to Energy=	0.131720
Thermal correction to Enthalpy=	0.132665
Thermal correction to Gibbs Free Energy=	0.083205
Sum of electronic and zero-point Energies=	-716.662132
Sum of electronic and thermal Energies=	-716.651474
Sum of electronic and thermal Enthalpies=	-716.650530
Sum of electronic and thermal Free Energies=	-716.699989

PCM:
E(RM062X) = -716.788215800



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.583107	-1.389489	0.000231
2	6	0	1.217263	-1.138057	0.000258
3	6	0	0.745679	0.179956	-0.000022
4	6	0	1.670637	1.230973	-0.000336
5	6	0	3.033172	0.967723	-0.000349
6	6	0	3.498354	-0.343133	-0.000067
7	1	0	2.931082	-2.415556	0.000451
8	1	0	0.523907	-1.969045	0.000513
9	1	0	1.330053	2.260653	-0.000580
10	1	0	3.733343	1.794447	-0.000594
11	1	0	4.562077	-0.545757	-0.000081
12	6	0	-0.696254	0.444994	0.000008
13	6	0	-1.747989	-0.611190	0.000028
14	7	0	-1.135542	1.673040	0.000043
15	7	0	-1.471133	2.746523	0.000062
16	9	0	-1.661696	-1.415369	1.072543
17	9	0	-1.661553	-1.415521	-1.072349
18	9	0	-2.972035	-0.070482	-0.000077

N2

Gas phase:
E(RM062X) = -109.522095878

Zero-point correction= 0.005731 (Hartree/Particle)

Thermal correction to Energy= 0.008092
Thermal correction to Enthalpy= 0.009036
Thermal correction to Gibbs Free Energy= -0.012692
Sum of electronic and zero-point Energies= -109.516364
um of electronic and thermal Energies= -109.514004
Sum of electronic and thermal Enthalpies= -109.513060
Sum of electronic and thermal Free Energies= -109.534788

PCM:
E(RM062X) = -109.522477771

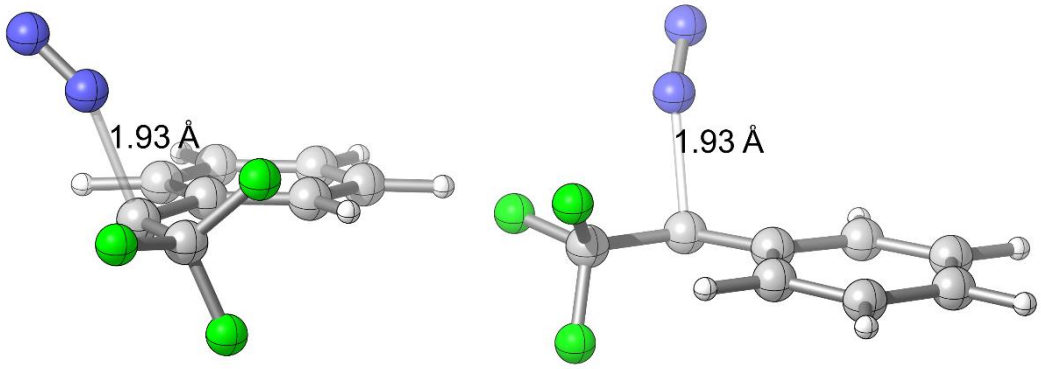
TS(I-II)a

Gas phase:
E(RM062X) = -716.731875519

Zero-point correction= 0.117317 (Hartree/Particle)
Thermal correction to Energy= 0.128452
Thermal correction to Enthalpy= 0.129396
Thermal correction to Gibbs Free Energy= 0.078831
Sum of electronic and zero-point Energies= -716.614558
Sum of electronic and thermal Energies= -716.603424
Sum of electronic and thermal Enthalpies= -716.602479
Sum of electronic and thermal Free Energies= -716.653044

PCM:
E(RM062X) = -716.738151695

1 imaginary frequency= -322.60



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.666303	0.347426	-0.678108
2	7	0	-1.245608	1.773859	0.490351
3	7	0	-1.440812	2.834069	0.676079
4	6	0	-1.697881	-0.635198	-0.192451
5	9	0	-1.526852	-1.758207	-0.909045

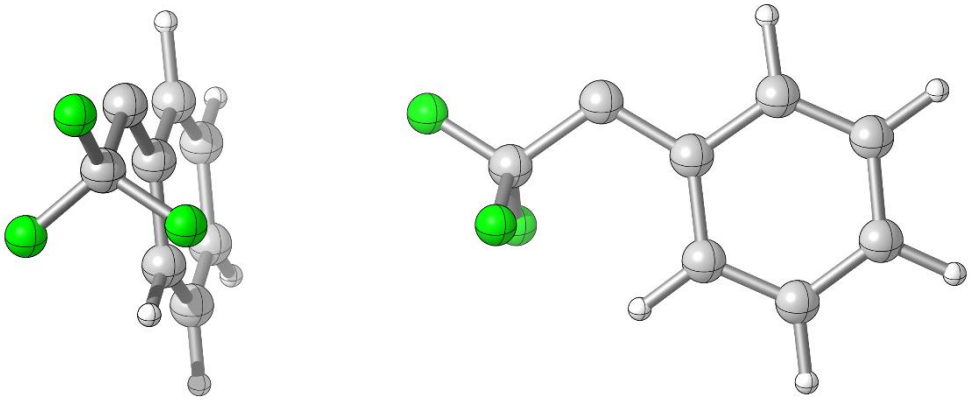
6	9	0	-2.945367	-0.196391	-0.405034
7	9	0	-1.668312	-0.995480	1.115270
8	6	0	0.718396	0.097398	-0.281684
9	6	0	1.170188	-1.002472	0.472571
10	6	0	1.671506	0.997354	-0.792266
11	6	0	2.526775	-1.187586	0.696907
12	1	0	0.464147	-1.719377	0.870396
13	6	0	3.022321	0.833701	-0.531606
14	1	0	1.319027	1.821199	-1.402741
15	6	0	3.450087	-0.265862	0.209173
16	1	0	2.865646	-2.046610	1.263326
17	1	0	3.743057	1.541869	-0.922047
18	1	0	4.507312	-0.410452	0.400107

IIa

Gas phase:
E(RM062X) = -607.216747763

Zero-point correction=	0.109586 (Hartree/Particle)
Thermal correction to Energy=	0.118493
Thermal correction to Enthalpy=	0.119437
Thermal correction to Gibbs Free Energy=	0.074669
Sum of electronic and zero-point Energies=	-607.107162
Sum of electronic and thermal Energies=	-607.098255
Sum of electronic and thermal Enthalpies=	-607.097311
Sum of electronic and thermal Free Energies=	-607.142078

PCM:
E(RM062X) = -607.223656742



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.773196	1.069727	-0.000025
2	6	0	-1.919551	0.090942	-0.000053
3	9	0	-1.901169	-0.706512	-1.091789
4	9	0	-3.110683	0.694655	-0.000295
5	9	0	-1.901326	-0.706037	1.092039
6	6	0	0.514778	0.460421	-0.000013
7	6	0	0.813292	-0.931520	0.000187
8	6	0	1.596419	1.375210	-0.000167

9	6	0	2.123705	-1.363614	0.000237
10	1	0	0.010519	-1.657573	0.000336
11	6	0	2.909838	0.937747	-0.000176
12	1	0	1.349565	2.430231	-0.000284
13	6	0	3.166202	-0.430893	0.000040
14	1	0	2.348705	-2.423007	0.000418
15	1	0	3.728663	1.645997	-0.000318
16	1	0	4.192235	-0.782723	0.000065

Phenylacetylene

Gas phase:
E(RM062X) = -308.337578957

Zero-point correction=	0.110408 (Hartree/Particle)
Thermal correction to Energy=	0.116751
Thermal correction to Enthalpy=	0.117695
Thermal correction to Gibbs Free Energy=	0.080048
Sum of electronic and zero-point Energies=	-308.227171
Sum of electronic and thermal Energies=	-308.220828
Sum of electronic and thermal Enthalpies=	-308.219884
Sum of electronic and thermal Free Energies=	-308.257531

PCM:

E(RM062X) = -308.341977005

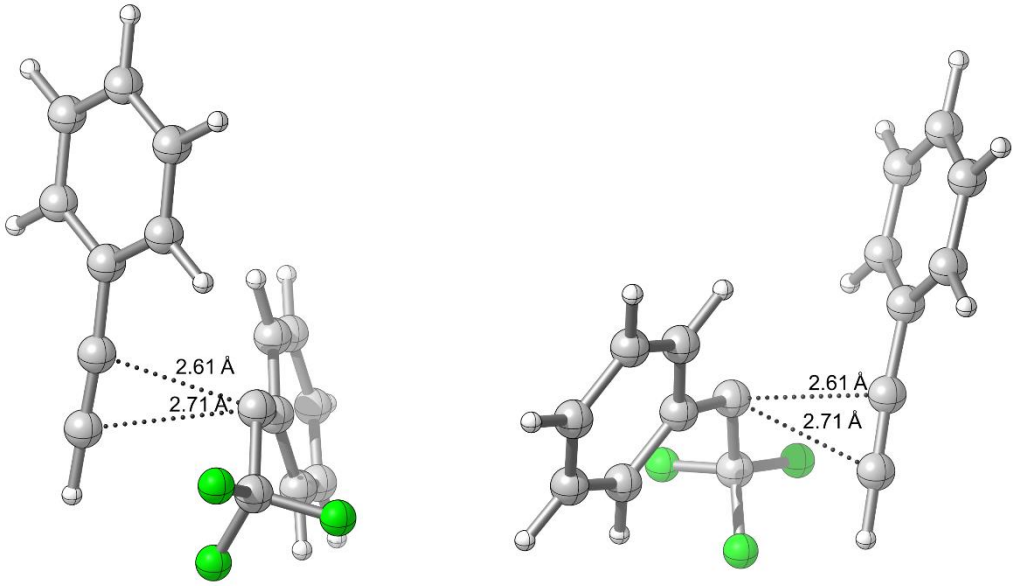
TS(II-III)a

Gas Phase:
E(RM062X) = -915.564660439

Zero-point correction=	0.220600 (Hartree/Particle)
Thermal correction to Energy=	0.236873
Thermal correction to Enthalpy=	0.237818
Thermal correction to Gibbs Free Energy=	0.173856
Sum of electronic and zero-point Energies=	-915.344060
Sum of electronic and thermal Energies=	-915.327787
Sum of electronic and thermal Enthalpies=	-915.326843
Sum of electronic and thermal Free Energies=	-915.390804

PCM:
E(RM062X) = -915.573024900

1 imaginary frequency= -69.34



Standard orientation:

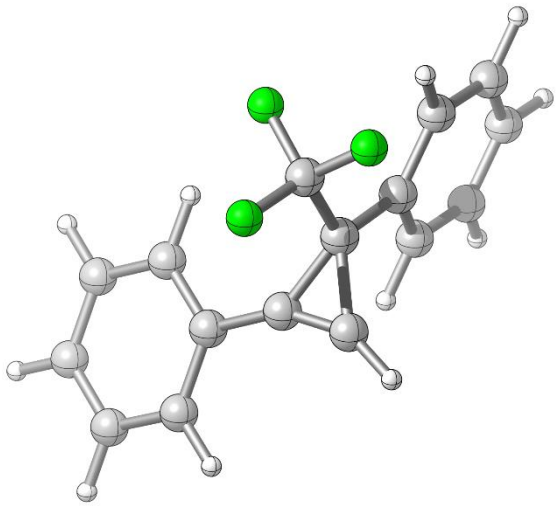
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.073501	-0.581292	1.336041
2	6	0	0.130591	-0.873503	2.030380
3	6	0	-0.764951	-0.619007	-0.516975
4	1	0	-0.703857	-1.148101	2.632194
5	6	0	-1.473711	0.618310	-0.310847
6	6	0	-2.846020	0.761411	-0.000173
7	6	0	-0.708271	1.786710	-0.515426
8	6	0	-3.415230	2.020601	0.090649
9	1	0	-3.465189	-0.114221	0.144978
10	6	0	-1.269656	3.044522	-0.375225
11	1	0	0.337750	1.662058	-0.774209
12	6	0	-2.626738	3.158310	-0.079813
13	1	0	-4.471918	2.122947	0.306043
14	1	0	-0.666755	3.933219	-0.515576
15	1	0	-3.077301	4.140465	0.011548
16	6	0	-1.528215	-1.883031	-0.233063
17	9	0	-0.728945	-2.951894	-0.141358
18	9	0	-2.319366	-1.937305	0.873403
19	9	0	-2.342077	-2.075765	-1.292285
20	6	0	2.246309	-0.203073	0.600517
21	6	0	3.116722	0.753587	1.134791
22	6	0	2.526931	-0.787592	-0.638943
23	6	0	4.258928	1.119326	0.433480
24	1	0	2.891012	1.199754	2.095897
25	6	0	3.672958	-0.418404	-1.329316
26	1	0	1.826937	-1.503518	-1.049037
27	6	0	4.538859	0.533962	-0.797378
28	1	0	4.931354	1.859930	0.849670
29	1	0	3.888610	-0.872502	-2.289024
30	1	0	5.430814	0.819625	-1.342510

IIIa

Gas phase:
E(RM062X) = -915.696881982

Zero-point correction=	0.225631 (Hartree/Particle)
Thermal correction to Energy=	0.240930
Thermal correction to Enthalpy=	0.241874
Thermal correction to Gibbs Free Energy=	0.181170
Sum of electronic and zero-point Energies=	-915.471251
Sum of electronic and thermal Energies=	-915.455952
Sum of electronic and thermal Enthalpies=	-915.455008
Sum of electronic and thermal Free Energies=	-915.515712

PCM:
E(RM062X) = -915.704680369



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.789126	0.440141	0.917212
2	6	0	-0.033302	0.834426	1.889923
3	6	0	0.644377	0.700933	0.556375
4	1	0	0.152297	1.047978	2.927470
5	6	0	1.575074	-0.454204	0.277164
6	6	0	2.801051	-0.303240	-0.376234
7	6	0	1.199257	-1.734117	0.697055
8	6	0	3.624339	-1.402644	-0.597664
9	1	0	3.128706	0.670018	-0.716840
10	6	0	2.021546	-2.830642	0.473136
11	1	0	0.250078	-1.876160	1.201851
12	6	0	3.241338	-2.669799	-0.175491
13	1	0	4.572537	-1.262281	-1.103289
14	1	0	1.705714	-3.812833	0.804649
15	1	0	3.885427	-3.522978	-0.351420
16	6	0	0.923358	1.979913	-0.202416
17	9	0	-0.032510	2.894709	-0.006399
18	9	0	2.086633	2.554558	0.161873
19	9	0	0.997371	1.771816	-1.531226
20	6	0	-2.012844	-0.061630	0.332187
21	6	0	-3.164650	-0.223758	1.108665

22	6	0	-2.033122	-0.393885	-1.024569
23	6	0	-4.325044	-0.714209	0.528301
24	1	0	-3.140135	0.039100	2.160115
25	6	0	-3.197549	-0.886875	-1.599787
26	1	0	-1.131494	-0.264130	-1.613581
27	6	0	-4.342170	-1.046440	-0.825281
28	1	0	-5.218931	-0.837435	1.127846
29	1	0	-3.212287	-1.144899	-2.651815
30	1	0	-5.250548	-1.429941	-1.274668

TS(IV)a

Gas phase:

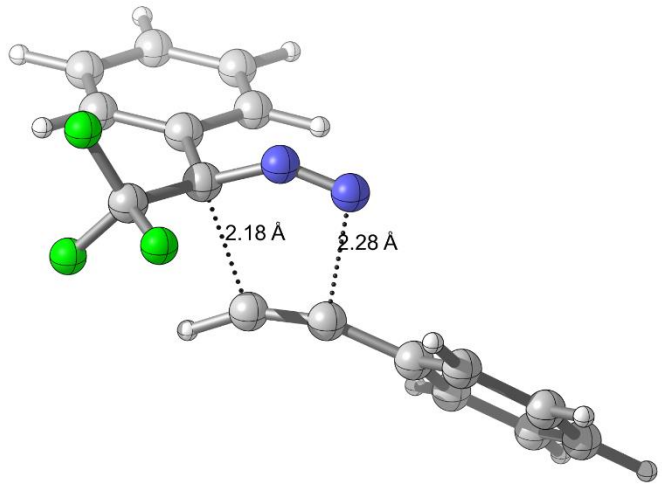
E(RM062X) = -1025.09469398

Zero-point correction= 0.232465 (Hartree/Particle)
Thermal correction to Energy= 0.249985
Thermal correction to Enthalpy= 0.250929
Thermal correction to Gibbs Free Energy= 0.184792
Sum of electronic and zero-point Energies= -1024.862229
Sum of electronic and thermal Energies= -1024.844709
Sum of electronic and thermal Enthalpies= -1024.843765
Sum of electronic and thermal Free Energies= -1024.909902

PCM:

E(RM062X) = -1025.10234082

1 imaginary frequency= -496.6



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.385007	-0.199386	1.171089
2	6	0	-1.453604	-0.108121	0.560702
3	1	0	0.244395	-0.188871	2.036347

4	6	0	1.217174	-0.598927	-0.252751
5	7	0	0.351769	-0.692680	-1.283761
6	7	0	-0.752527	-0.590941	-1.551642
7	6	0	1.742079	-1.950488	0.162473
8	6	0	2.100812	0.590679	-0.218610
9	6	0	1.606174	1.812908	-0.689699
10	6	0	3.381557	0.540958	0.335880
11	6	0	2.384975	2.957074	-0.620736
12	1	0	0.604052	1.866701	-1.100938
13	6	0	4.151861	1.697066	0.413895
14	1	0	3.788859	-0.390559	0.706823
15	6	0	3.661957	2.904321	-0.066610
16	1	0	1.991976	3.894990	-0.994482
17	1	0	5.144029	1.644877	0.845687
18	1	0	4.268416	3.800228	-0.011302
19	6	0	-2.854296	0.146086	0.328409
20	6	0	-3.642755	-0.740113	-0.413073
21	6	0	-3.444215	1.295249	0.869412
22	6	0	-4.996552	-0.489459	-0.592594
23	1	0	-3.186109	-1.622656	-0.843939
24	6	0	-4.795370	1.548499	0.672277
25	1	0	-2.832804	1.979677	1.445201
26	6	0	-5.576678	0.655929	-0.055154
27	1	0	-5.599434	-1.186848	-1.162041
28	1	0	-5.239935	2.442609	1.093191
29	1	0	-6.631586	0.852463	-0.204531
30	9	0	2.836588	-2.335652	-0.516482
31	9	0	2.081562	-1.928560	1.459013
32	9	0	0.822381	-2.900334	-0.008271

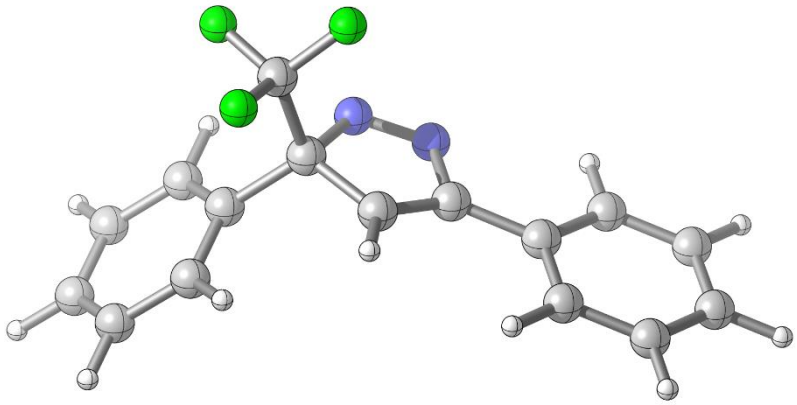
IVa

Gas phase

E(RM062X) = -1025.20182903

Zero-point correction=	0.237445 (Hartree/Particle)
Thermal correction to Energy=	0.252978
Thermal correction to Enthalpy=	0.253923
Thermal correction to Gibbs Free Energy=	0.192793
Sum of electronic and zero-point Energies=	-1024.964384
Sum of electronic and thermal Energies=	-1024.948851
Sum of electronic and thermal Enthalpies=	-1024.947907
Sum of electronic and thermal Free Energies=	-1025.009036

PCM:
E(RM062X) = -1025.21090129



Standard orientation:

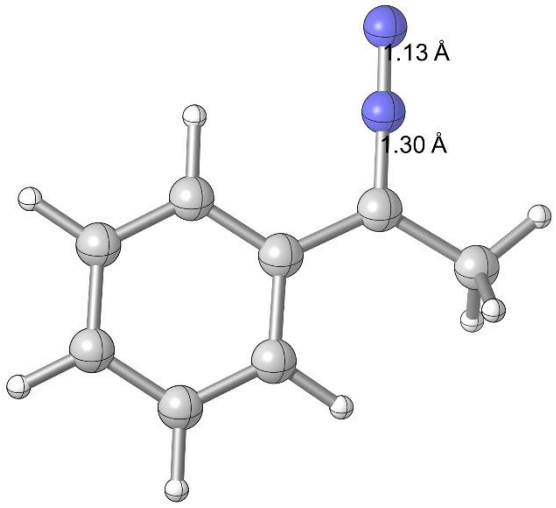
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.332056	0.071957	-0.677990
2	6	0	-1.336100	0.069049	0.205768
3	1	0	-0.368069	-0.153897	-1.731600
4	6	0	0.894817	0.483503	0.071317
5	7	0	0.385741	0.712148	1.450166
6	7	0	-0.827428	0.474581	1.499345
7	6	0	-2.760436	-0.251082	0.075737
8	6	0	-3.620885	-0.072191	1.162044
9	6	0	-3.275001	-0.732053	-1.133005
10	6	0	-4.973904	-0.366409	1.035662
11	1	0	-3.222839	0.297920	2.098201
12	6	0	-4.624934	-1.023288	-1.254662
13	1	0	-2.614866	-0.881991	-1.979678
14	6	0	-5.479314	-0.840330	-0.169227
15	1	0	-5.634536	-0.223748	1.882335
16	1	0	-5.013096	-1.395186	-2.195395
17	1	0	-6.534126	-1.068570	-0.264832
18	6	0	1.419386	1.836779	-0.429060
19	9	0	0.478246	2.782710	-0.370696
20	9	0	1.806536	1.733045	-1.708864
21	9	0	2.463698	2.258481	0.280100
22	6	0	2.024940	-0.537311	0.095245
23	6	0	2.823890	-0.665158	1.231291
24	6	0	2.293250	-1.316403	-1.029380
25	6	0	3.872022	-1.578226	1.242056
26	1	0	2.620014	-0.051465	2.098998
27	6	0	3.346383	-2.223330	-1.015118
28	1	0	1.689631	-1.213701	-1.922957
29	6	0	4.135099	-2.358673	0.121861
30	1	0	4.485753	-1.675464	2.129501
31	1	0	3.550068	-2.822863	-1.894202
32	1	0	4.954618	-3.067275	0.132975

Ib

Gas phase:
E(RM062X) = -419.042113954

Zero-point correction=	0.144065 (Hartree/Particle)
Thermal correction to Energy=	0.152807
Thermal correction to Enthalpy=	0.153752
Thermal correction to Gibbs Free Energy=	0.110036
Sum of electronic and zero-point Energies=	-418.898049
Sum of electronic and thermal Energies=	-418.889306
Sum of electronic and thermal Enthalpies=	-418.888362
Sum of electronic and thermal Free Energies=	-418.932078

PCM:
E(RM062X) = -419.046999628



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.312847	1.015420	0.000213
2	6	0	-0.937707	1.217169	0.000228
3	6	0	-0.056357	0.127517	0.000030
4	6	0	-0.597722	-1.167641	-0.000179
5	6	0	-1.970826	-1.359376	-0.000190
6	6	0	-2.839681	-0.270633	0.000004
7	1	0	-2.975062	1.873433	0.000364
8	1	0	-0.549384	2.228364	0.000393
9	1	0	0.058770	-2.030995	-0.000331
10	1	0	-2.365723	-2.368596	-0.000355
11	1	0	-3.911451	-0.425239	-0.000006
12	6	0	1.384423	0.372151	0.000044
13	6	0	2.008743	1.739845	0.000252
14	7	0	2.175398	-0.658106	-0.000153
15	7	0	2.847926	-1.570269	-0.000331
16	1	0	1.707889	2.306252	-0.885523
17	1	0	1.707914	2.305974	0.886213
18	1	0	3.095630	1.662720	0.000223

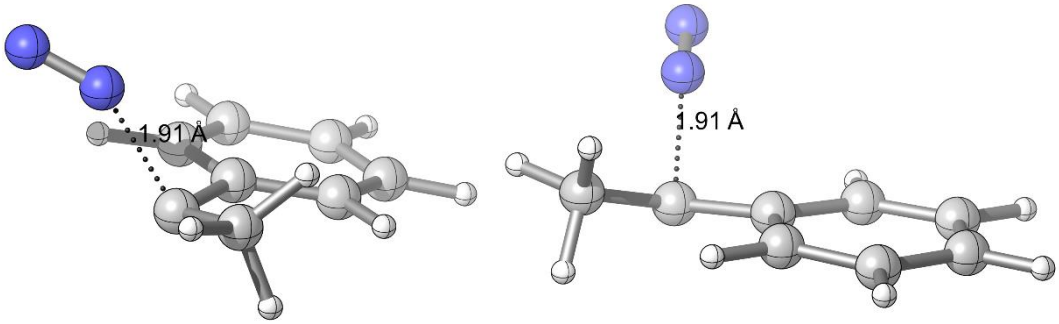
TS(I-II)b

Gas phase:
E(RM062X) = -727.355718284

Zero-point correction=	0.255172 (Hartree/Particle)
Thermal correction to Energy=	0.270818
Thermal correction to Enthalpy=	0.271762
Thermal correction to Gibbs Free Energy=	0.209134
Sum of electronic and zero-point Energies=	-727.100547
Sum of electronic and thermal Energies=	-727.084900
Sum of electronic and thermal Enthalpies=	-727.083956
Sum of electronic and thermal Free Energies=	-727.146584

PCM:
E(RM062X) = -727.363862164

1 imaginary frequency= -365.8



Standard orientation:

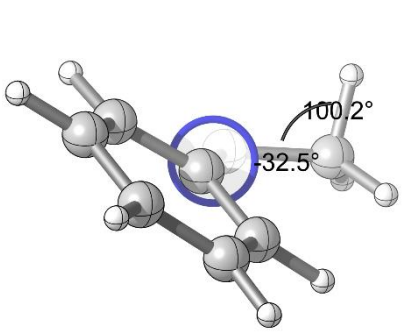
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.298246	0.532184	0.634047
2	7	0	-2.311875	-0.719270	-0.388258
3	7	0	-2.977098	-1.591724	-0.420144
4	6	0	-1.845552	1.828952	0.126544
5	6	0	0.088129	0.213389	0.250707
6	6	0	0.995847	1.200980	-0.159785
7	6	0	0.575611	-1.090795	0.446522
8	6	0	2.340128	0.896579	-0.356708
9	1	0	0.658730	2.219919	-0.307926
10	6	0	1.900262	-1.405073	0.199034
11	1	0	-0.109910	-1.852772	0.802070
12	6	0	2.792331	-0.406321	-0.195249
13	1	0	3.030210	1.678200	-0.652533
14	1	0	2.251391	-2.420773	0.337638
15	1	0	3.835552	-0.644902	-0.365639
16	1	0	-2.932655	1.861506	0.205168
17	1	0	-1.534442	2.148515	-0.875758
18	1	0	-1.467123	2.567891	0.845124

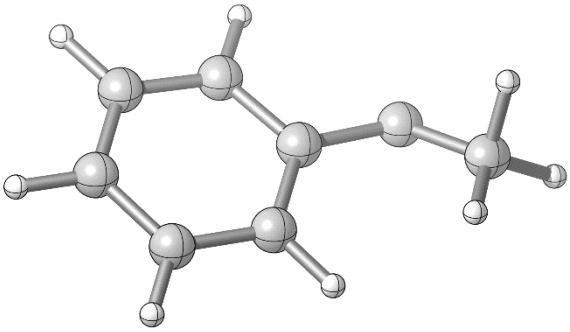
IIb

Gas phase:
E(RM062X) = -309.476157176

Zero-point correction=	0.131015 (Hartree/Particle)
Thermal correction to Energy=	0.138168
Thermal correction to Enthalpy=	0.139112
Thermal correction to Gibbs Free Energy=	0.099627
Sum of electronic and zero-point Energies=	-309.345142
Sum of electronic and thermal Energies=	-309.337989
Sum of electronic and thermal Enthalpies=	-309.337045
Sum of electronic and thermal Free Energies=	-309.376530

PCM:
E(RM062X) = -309.482093118





Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.887631	-0.678375	-0.317022
2	6	0	-2.884590	0.251972	0.238858
3	6	0	-0.503190	-0.276585	-0.153953
4	6	0	-0.048041	1.058619	-0.147324
5	6	0	0.452549	-1.306126	-0.053065
6	6	0	1.304712	1.344016	-0.043505
7	1	0	-0.754761	1.871295	-0.264520
8	6	0	1.797129	-1.017432	0.127305
9	1	0	0.098425	-2.328819	-0.109561
10	6	0	2.224169	0.308392	0.117214
11	1	0	1.648091	2.371498	-0.072058
12	1	0	2.517956	-1.818685	0.237783
13	1	0	3.279106	0.536131	0.219776
14	1	0	-3.097178	-0.242291	1.204683
15	1	0	-2.589196	1.284183	0.472828
16	1	0	-3.833085	0.219801	-0.299976

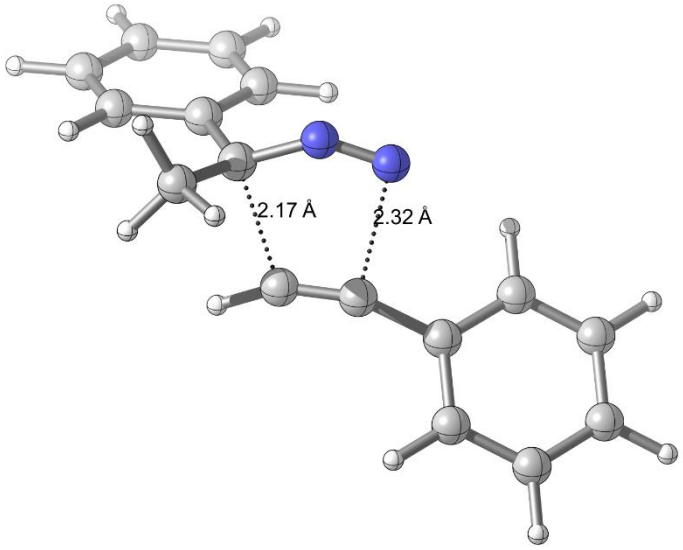
TS(IV)b

Gas phase:
E(RM062X) = -727.355718284

Zero-point correction=	0.255172 (Hartree/Particle)
Thermal correction to Energy=	0.270818
Thermal correction to Enthalpy=	0.271762
Thermal correction to Gibbs Free Energy=	0.209134
Sum of electronic and zero-point Energies=	-727.100547
Sum of electronic and thermal Energies=	-727.084900
Sum of electronic and thermal Enthalpies=	-727.083956
Sum of electronic and thermal Free Energies=	-727.146584

PCM:
E(RM062X) = -727.363862164

1 imaginary frequency= -498.8



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.111491	0.785315	-0.989186
2	6	0	-1.165115	0.406647	-0.470357
3	1	0	0.524025	1.019236	-1.818916
4	6	0	1.409459	1.118266	0.518121
5	7	0	0.582481	0.717448	1.503480
6	7	0	-0.469139	0.336653	1.738486
7	6	0	1.649340	2.607244	0.473481
8	6	0	2.493696	0.170634	0.171708
9	6	0	2.339703	-1.206459	0.381408
10	6	0	3.656931	0.630318	-0.449746
11	6	0	3.329315	-2.092862	-0.010960
12	1	0	1.435612	-1.581459	0.848206
13	6	0	4.644531	-0.265333	-0.851240
14	1	0	3.803112	1.690111	-0.619013
15	6	0	4.487904	-1.626893	-0.631075
16	1	0	3.195823	-3.154191	0.161947

17	1	0	5.541263	0.108635	-1.331017
18	1	0	5.258816	-2.322312	-0.939961
19	6	0	-2.545372	0.016943	-0.334337
20	6	0	-3.541767	0.753844	-0.988329
21	6	0	-2.918479	-1.094049	0.431312
22	6	0	-4.876003	0.385078	-0.878249
23	1	0	-3.255227	1.614692	-1.580584
24	6	0	-4.251897	-1.469049	0.523058
25	1	0	-2.153102	-1.652950	0.955648
26	6	0	-5.236180	-0.729670	-0.126757
27	1	0	-5.636953	0.966666	-1.385486
28	1	0	-4.525471	-2.335903	1.113302
29	1	0	-6.277229	-1.018480	-0.045356
30	1	0	0.753474	3.137561	0.795905
31	1	0	2.495940	2.910440	1.095907
32	1	0	1.859074	2.899424	-0.557467

IVb

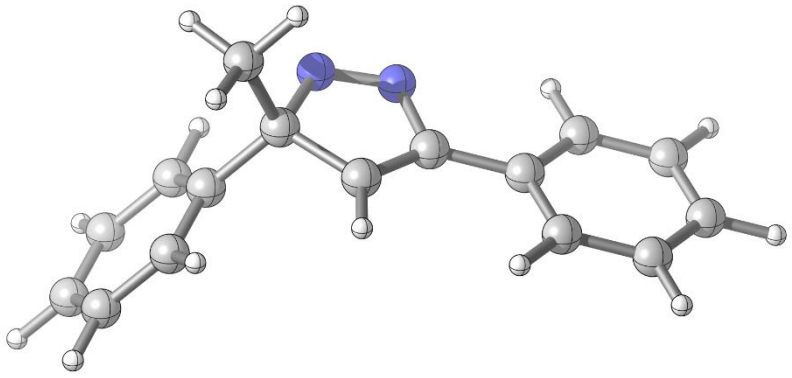
Gas phase:

E(RM062X) = -727.460152023

Zero-point correction=	0.261179 (Hartree/Particle)
Thermal correction to Energy=	0.275485
Thermal correction to Enthalpy=	0.276430
Thermal correction to Gibbs Free Energy=	0.217737
Sum of electronic and zero-point Energies=	-727.198973
Sum of electronic and thermal Energies=	-727.184667
Sum of electronic and thermal Enthalpies=	-727.183722
Sum of electronic and thermal Free Energies=	-727.242415

PCM:

E(RM062X) = -727.469358173



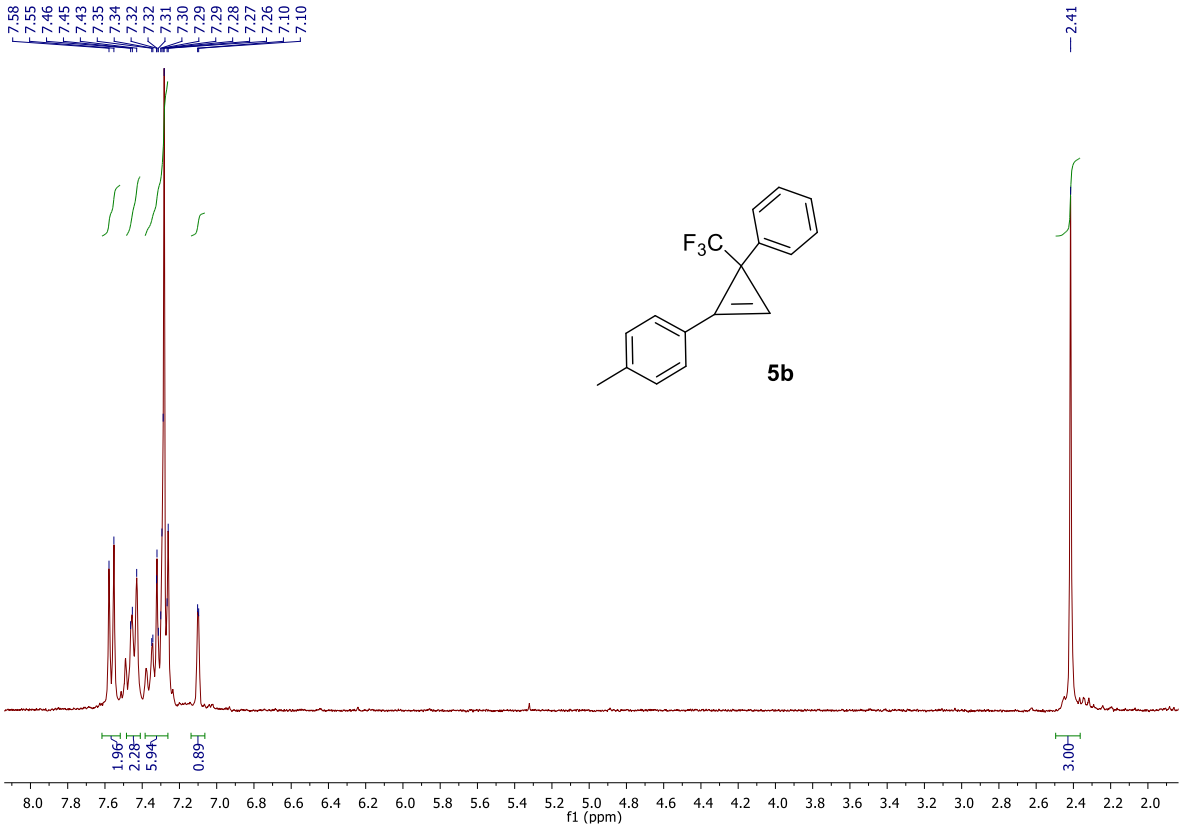
Standard orientation:

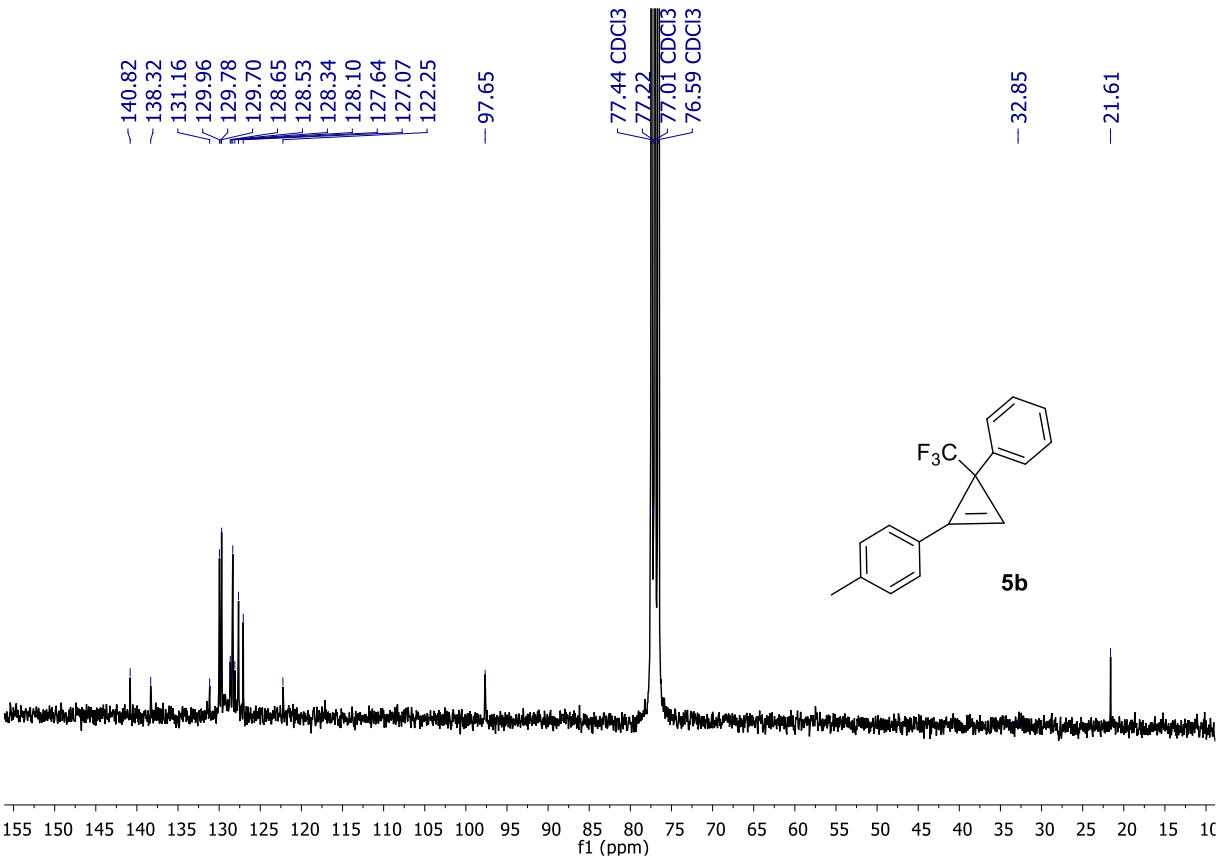
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.055613	0.215035	0.886608
2	6	0	-1.064822	-0.371307	0.232766
3	1	0	-0.054143	1.164011	1.400847

4	6	0	1.122712	-0.702761	0.789520
5	7	0	0.592884	-1.819165	-0.025110
6	7	0	-0.600445	-1.631901	-0.305502
7	6	0	1.517281	-1.308247	2.149936
8	1	0	2.299488	-2.052575	1.997816
9	1	0	1.896638	-0.524682	2.807200
10	1	0	0.651467	-1.781529	2.616638
11	6	0	2.329088	-0.066109	0.111460
12	6	0	2.922828	-0.633759	-1.014487
13	6	0	2.872106	1.102417	0.650098
14	6	0	4.039099	-0.034963	-1.592920
15	1	0	2.515052	-1.545176	-1.431959
16	6	0	3.986769	1.696385	0.072655
17	1	0	2.422383	1.553427	1.528980
18	6	0	4.574351	1.127945	-1.053912
19	1	0	4.491232	-0.485086	-2.468849
20	1	0	4.395994	2.603756	0.501064
21	1	0	5.443223	1.590319	-1.506660
22	6	0	-2.455510	0.030370	-0.008300
23	6	0	-3.287395	-0.766437	-0.800076
24	6	0	-2.967693	1.209464	0.543413
25	6	0	-4.603941	-0.386289	-1.035310
26	1	0	-2.893273	-1.680773	-1.224675
27	6	0	-4.281384	1.585475	0.306292
28	1	0	-2.334570	1.834471	1.163310
29	6	0	-5.105157	0.787705	-0.485391
30	1	0	-5.239307	-1.011443	-1.651693
31	1	0	-4.666049	2.501632	0.738566
32	1	0	-6.131526	1.081567	-0.670412

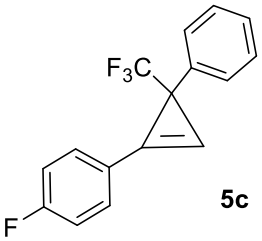
5. NMR Spectra

Trisubstituted cyclopropenes

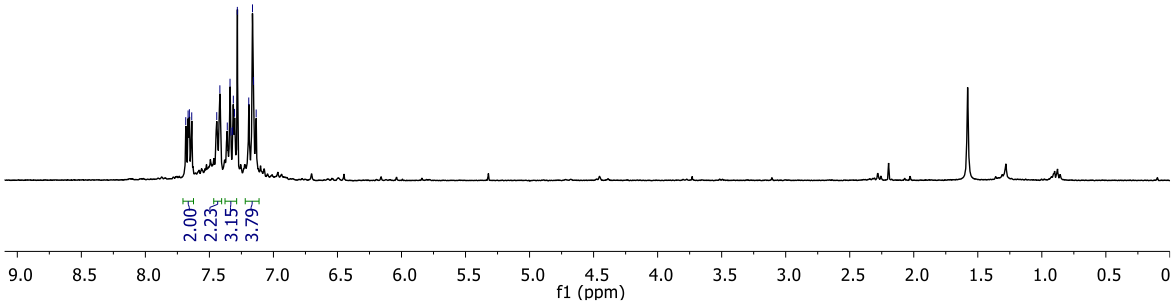


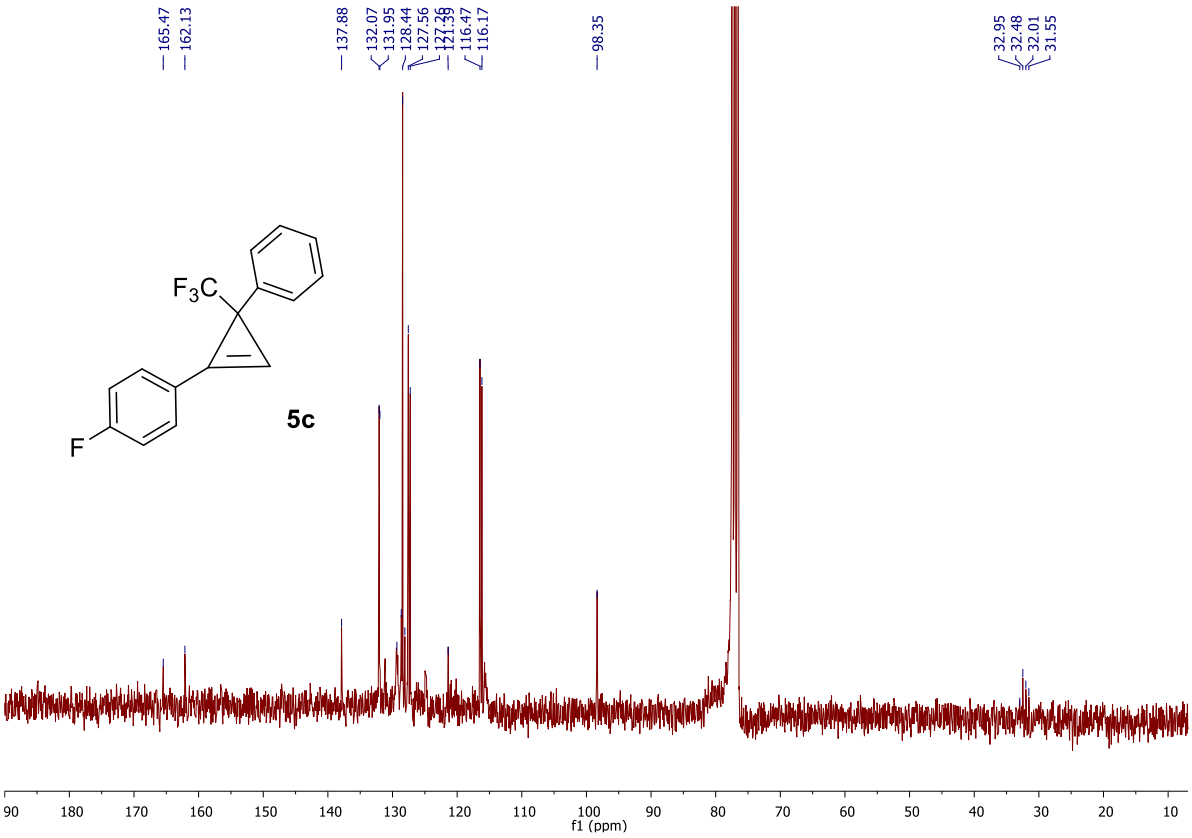


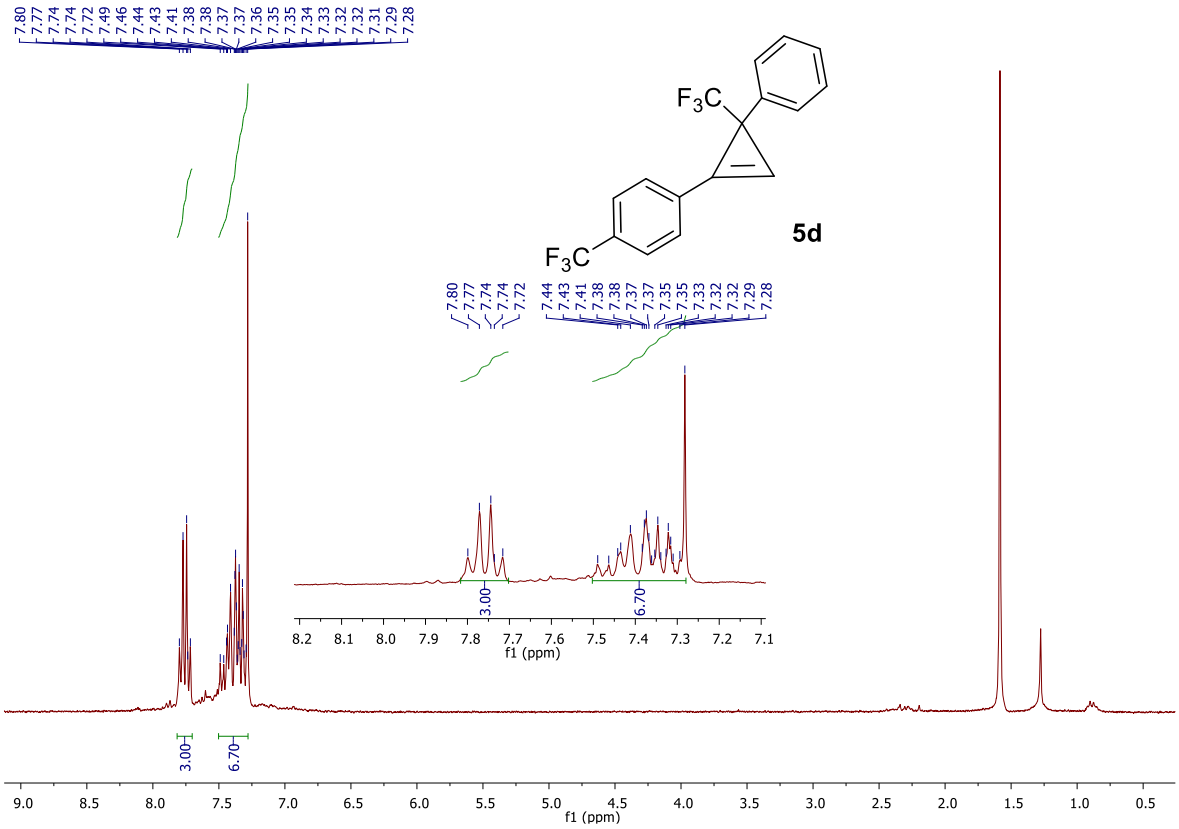

7.68
7.67
7.66
7.64
7.44
7.42
7.36
7.34
7.33
7.32
7.31
7.30
7.28
7.19
7.16
7.16
7.13

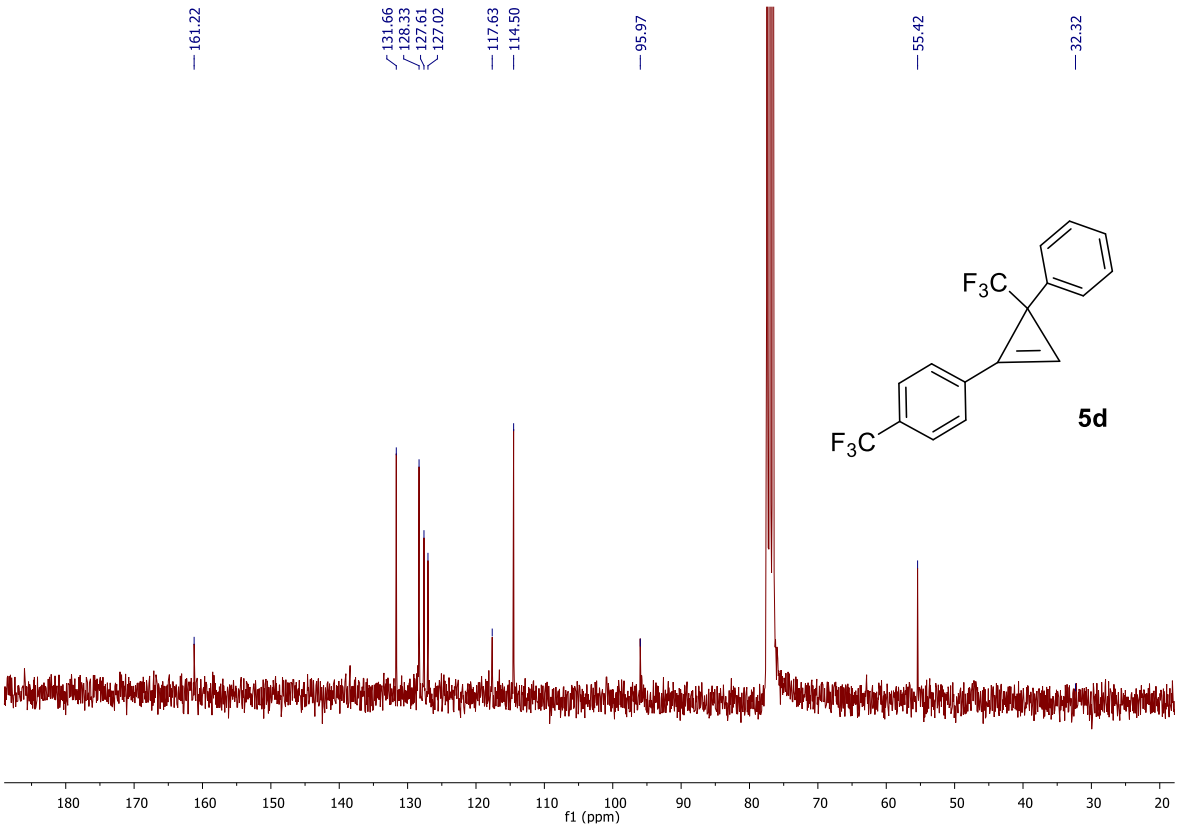

F3C
F

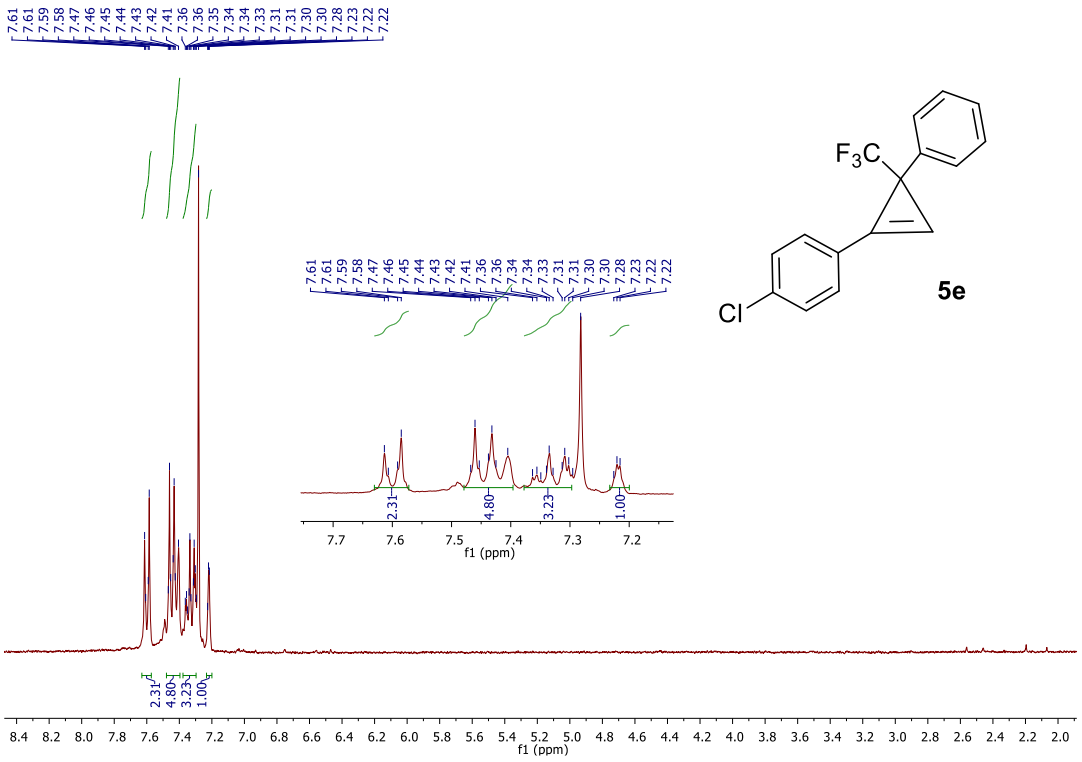
5c

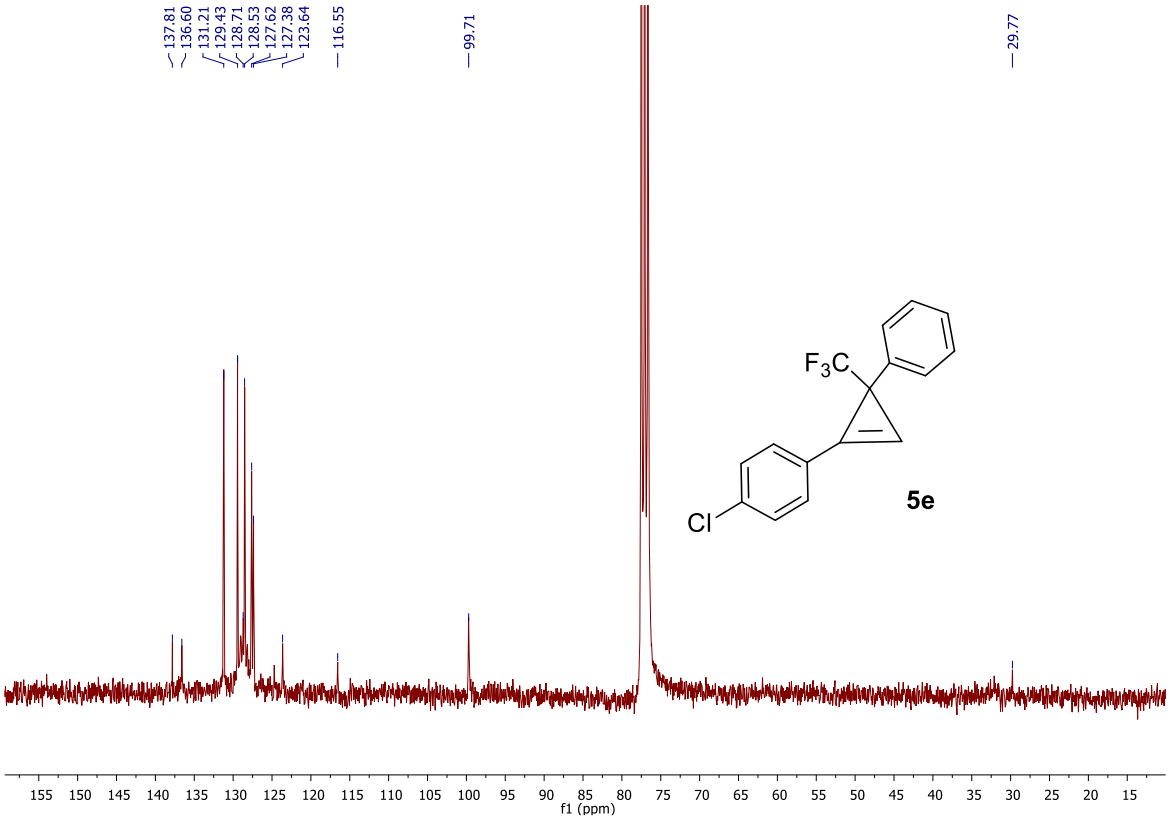

2.00
2.23
3.15
3.79
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

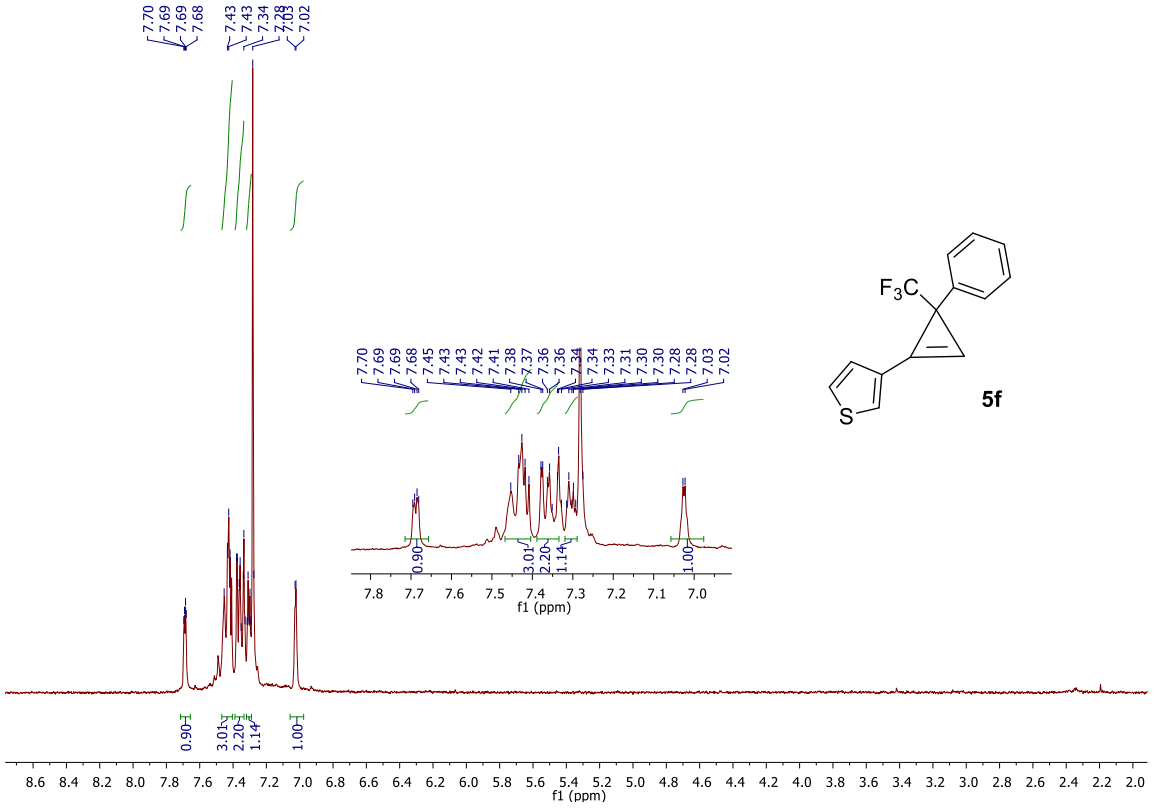

165.47
162.13
137.88
132.07
131.95
128.44
127.56
121.39
116.47
116.17
98.35
32.95
32.48
32.01
31.55
F3C
F
5c
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

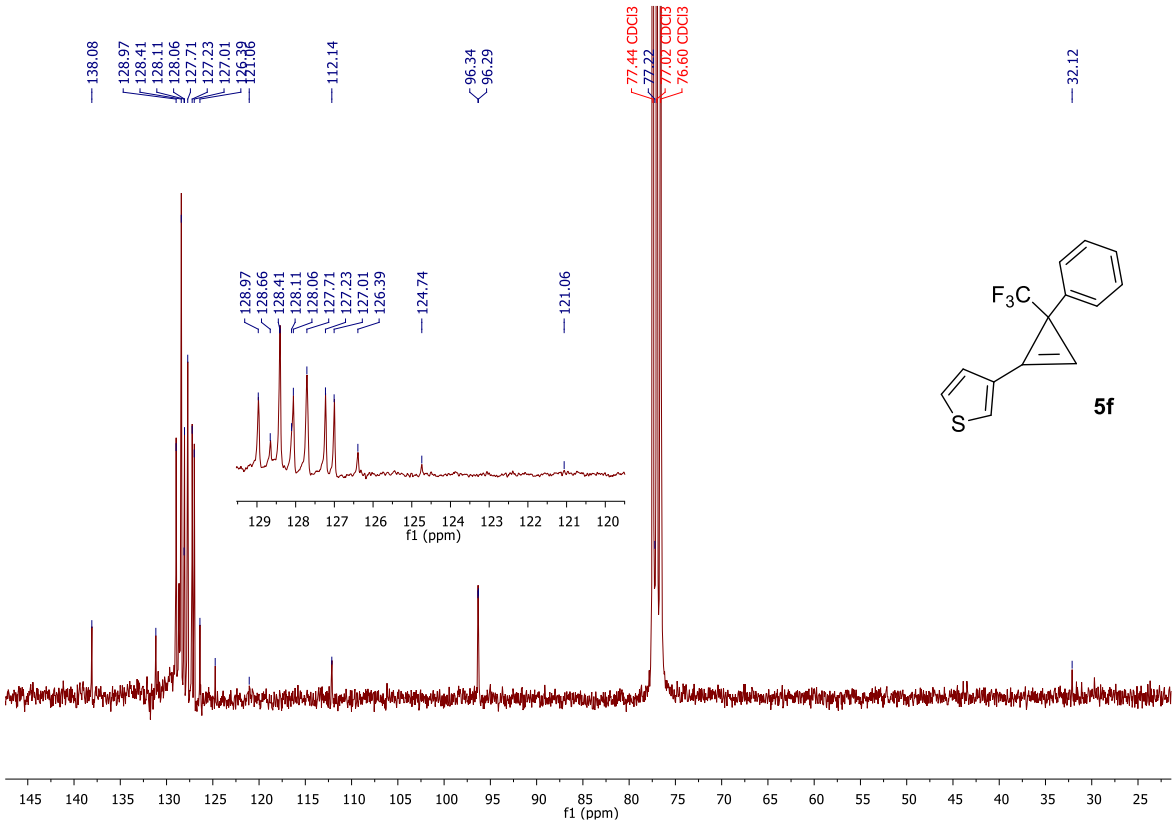

7.80
7.77
7.74
7.74
7.72
7.49
7.46
7.44
7.43
7.41
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.29
7.28
F3C
F3C
5d
3.00
6.70
f1 (ppm)

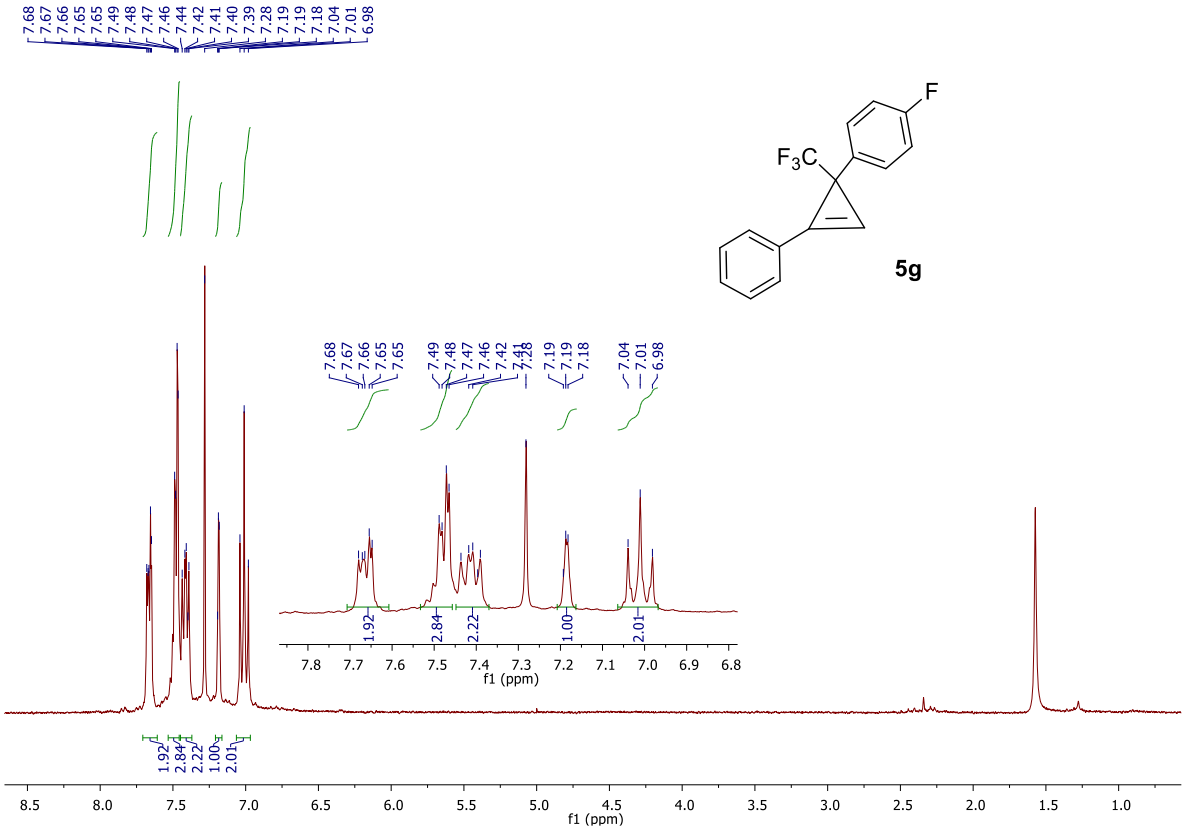

161.22
131.66
128.33
127.61
127.02
117.63
114.50
95.97
55.42
32.32
F3C
F3C
5d
f1 (ppm)

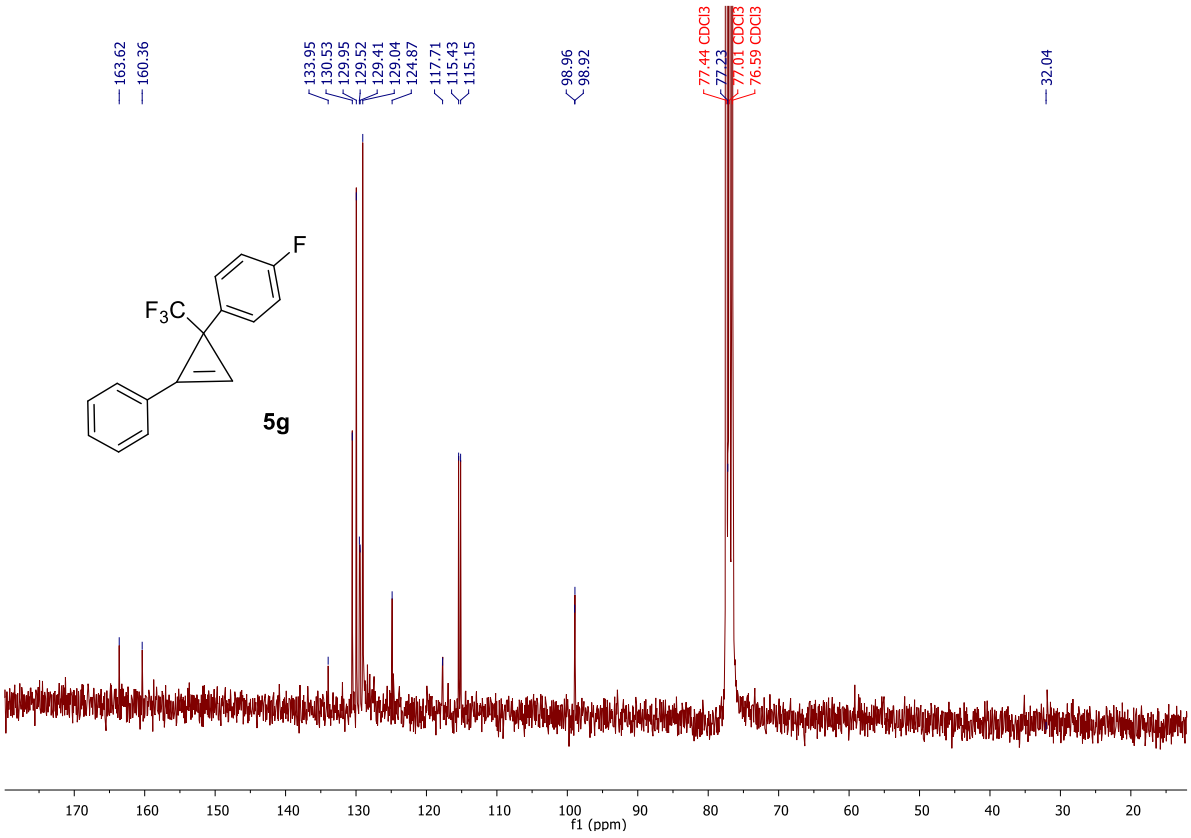

7.61
7.61
7.59
7.58
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.36
7.36
7.35
7.34
7.34
7.33
7.31
7.31
7.30
7.30
7.28
7.23
7.22
7.22
2.31
4.80
3.23
1.00
f1 (ppm)
F3C
Cl
5e

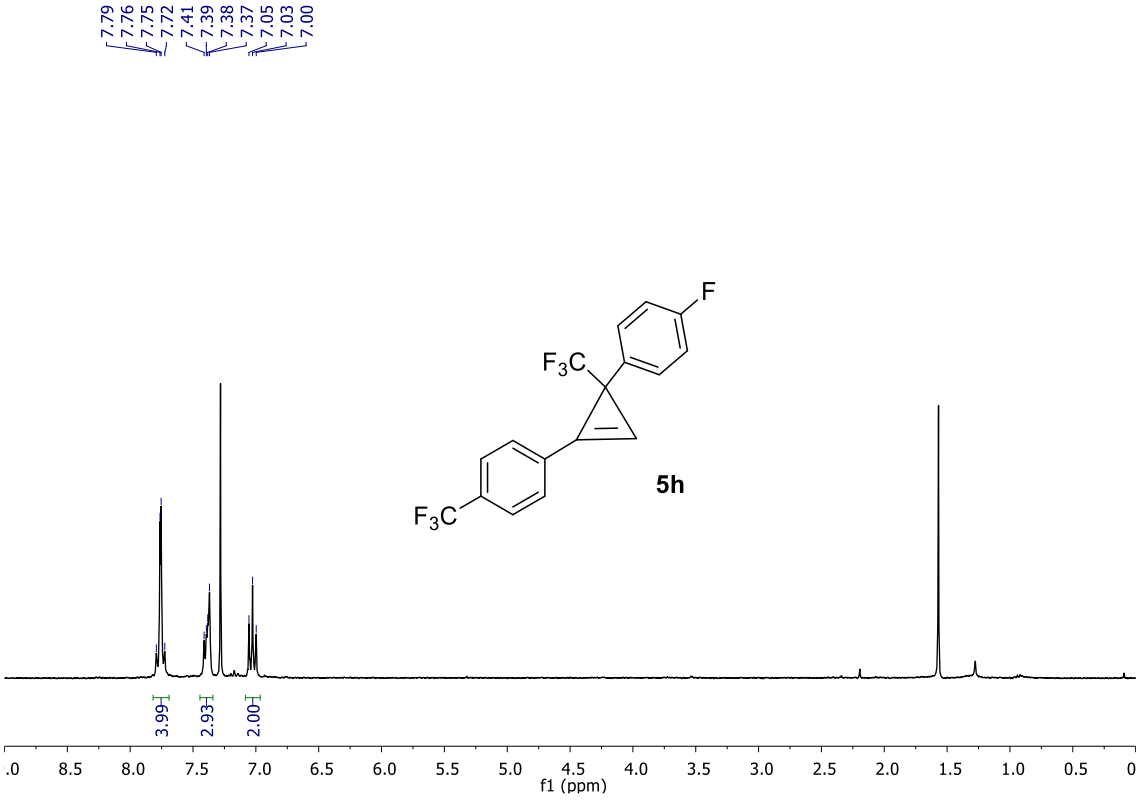

137.81
136.60
131.21
129.43
128.71
128.53
127.62
127.38
123.64
116.55
99.71
29.77
f1 (ppm)
F3C
Cl
5e

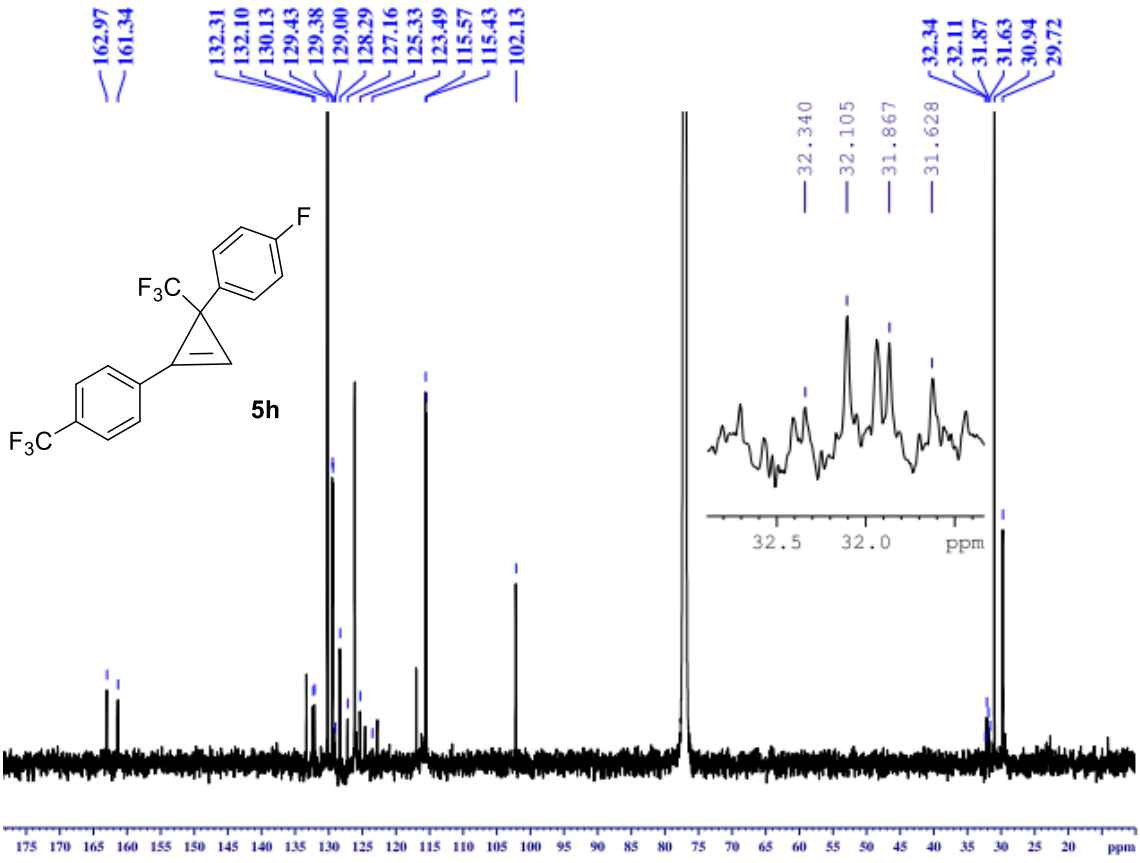

7.70
7.69
7.69
7.68
7.43
7.43
7.34
7.28
7.03
7.02
0.90
3.01
2.20
1.14
1.00
f1 (ppm)
F3C
S
5f

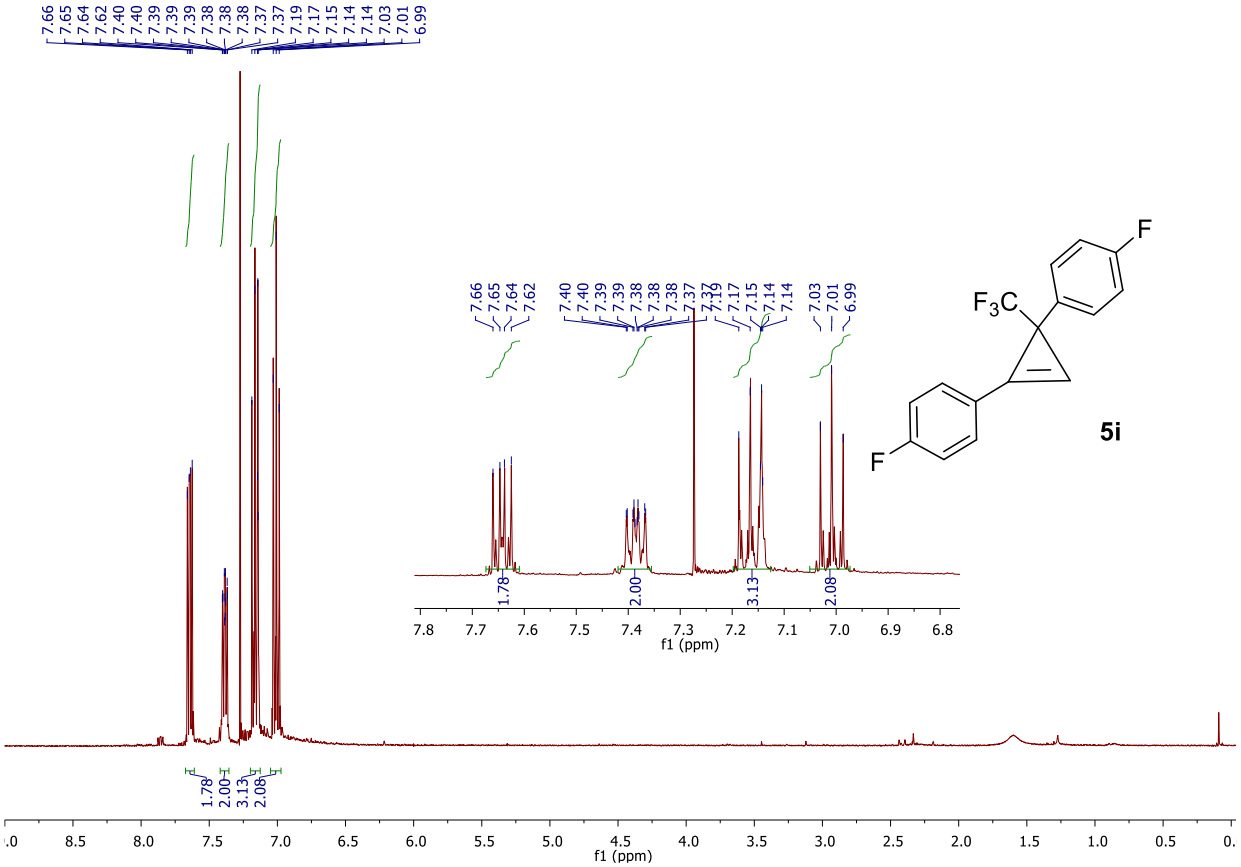

138.08
128.97
128.41
128.11
128.06
127.71
127.23
127.01
112.14
96.34
96.29
77.44 CDCl3
77.22
77.02 CDCl3
76.60 CDCl3
32.12
124.74
121.06
f1 (ppm)
F3C
S
5f

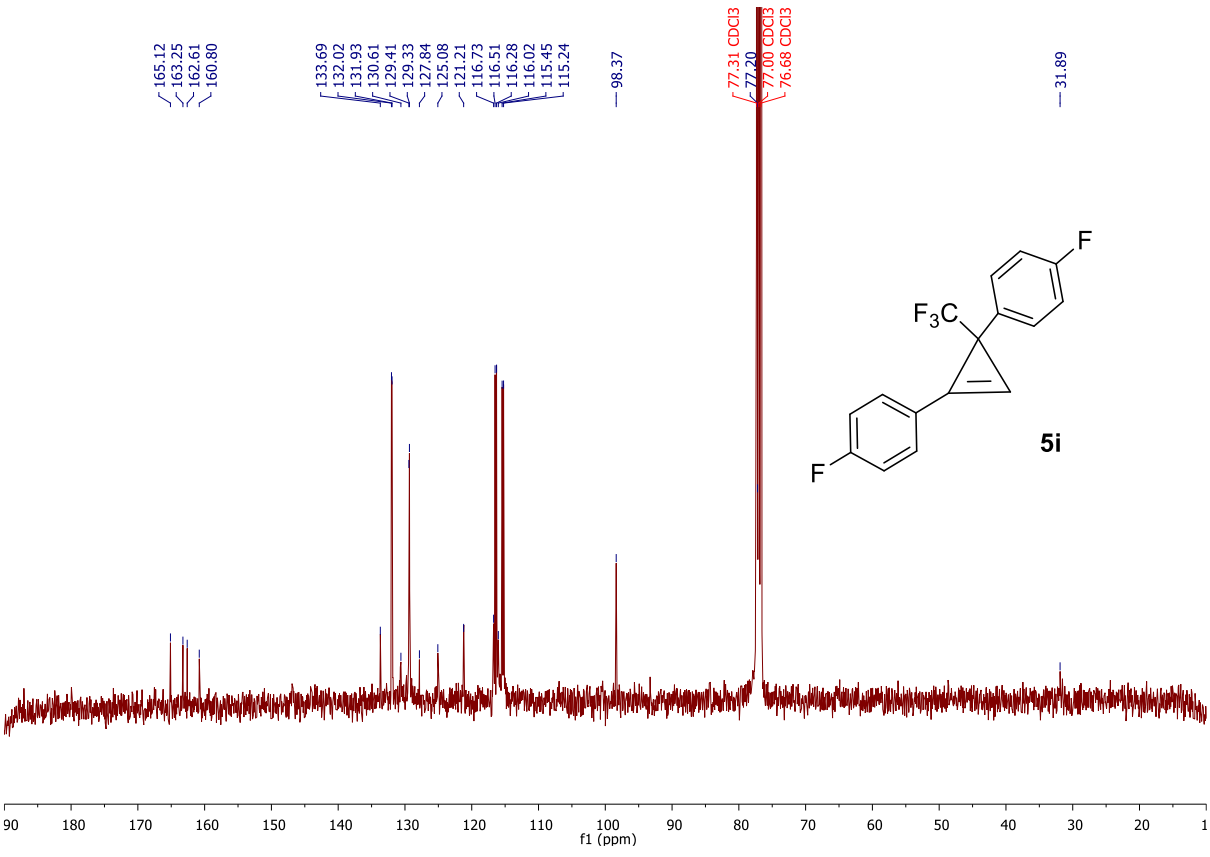

7.68
7.67
7.66
7.65
7.65
7.49
7.48
7.47
7.46
7.44
7.42
7.41
7.40
7.39
7.28
7.19
7.19
7.18
7.04
7.01
6.98
F
F3C
5g
1.92
2.84
2.22
1.00
2.01
f1 (ppm)

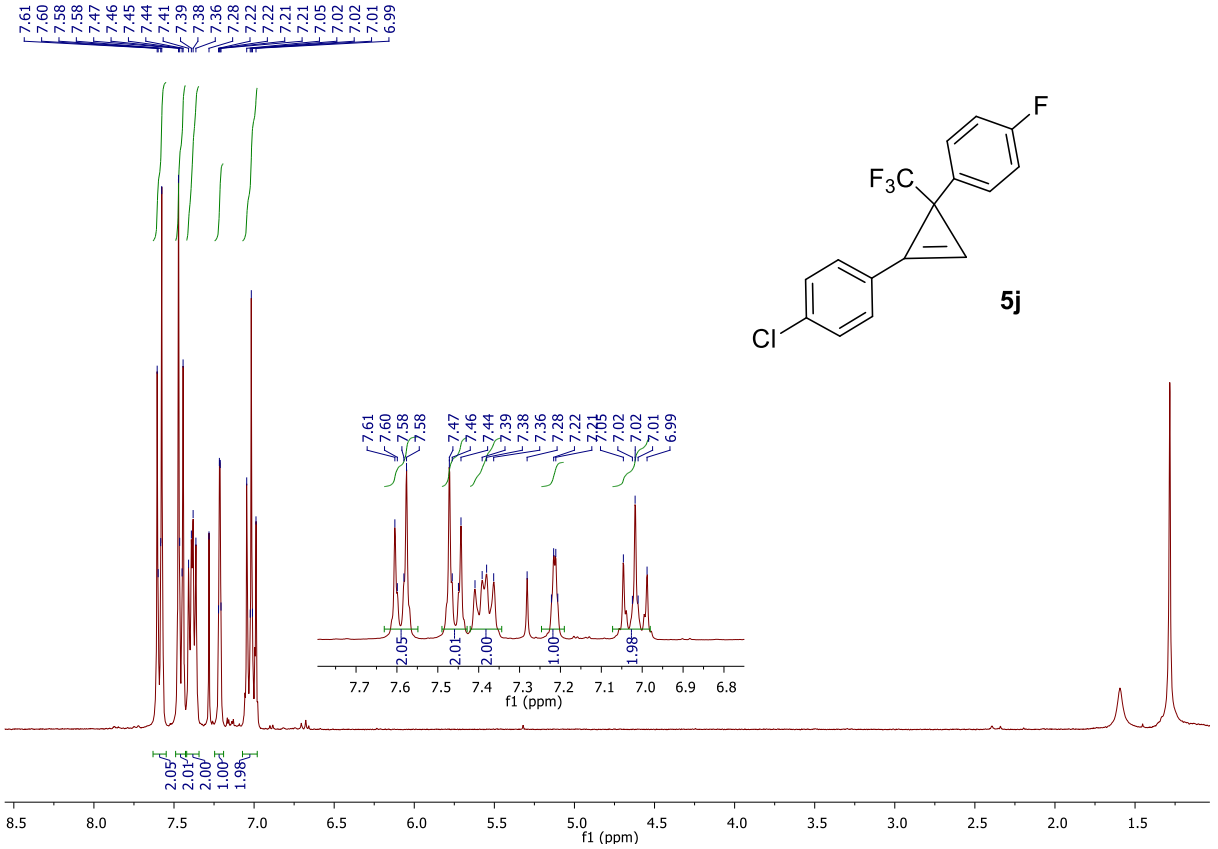

163.62
160.36
133.95
130.53
129.95
129.52
129.41
129.04
124.87
117.71
115.43
115.15
98.96
98.92
77.44 CDCl3
77.23
77.01 CDCl3
76.59 CDCl3
32.04
F
F3C
5g
f1 (ppm)

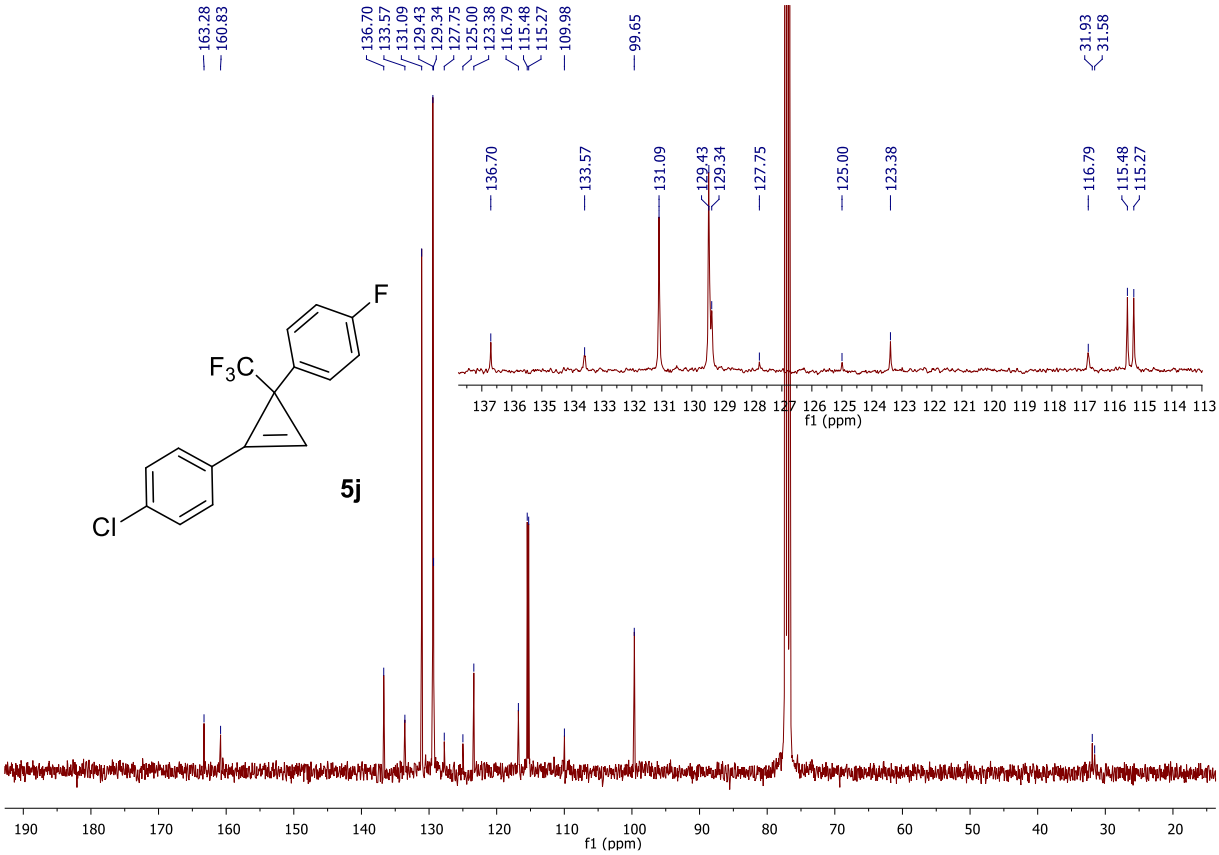

7.79
7.76
7.75
7.72
7.41
7.39
7.38
7.37
7.05
7.03
7.00
F
F3C
F3C
5h
3.99
2.93
2.00
f1 (ppm)

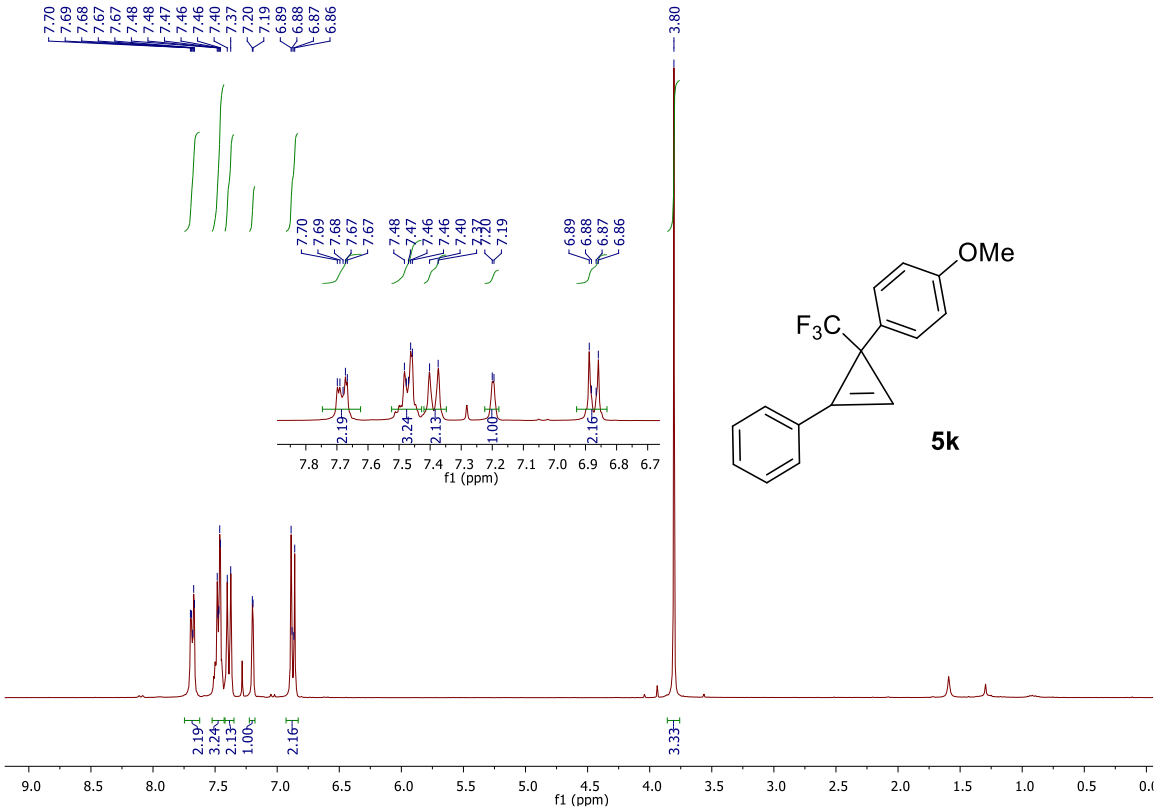

162.97
161.34
132.31
132.10
130.13
129.43
129.38
129.00
128.29
127.16
125.33
123.49
115.57
115.43
102.13
32.34
32.11
31.87
31.63
30.94
29.72
32.340
32.105
31.867
31.628
32.5
32.0
ppm
F
F3C
F3C
5h
ppm

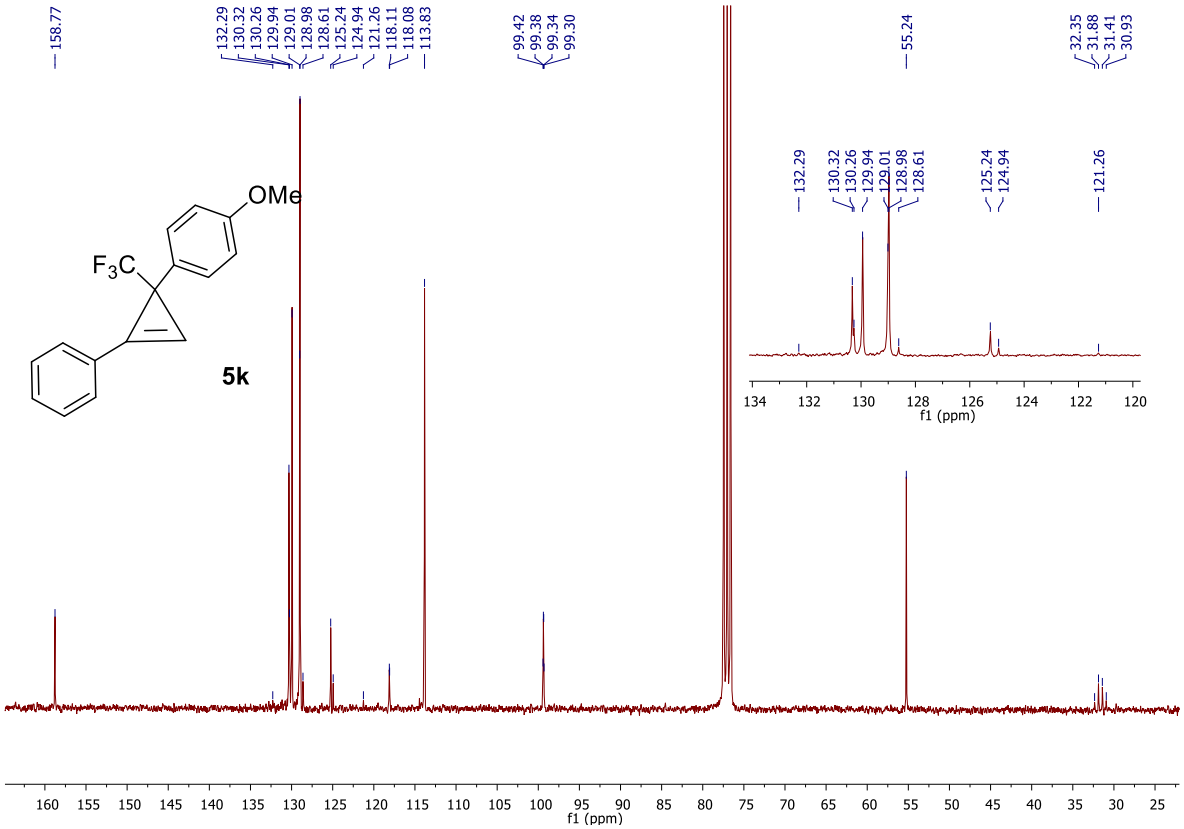

7.66
7.65
7.64
7.62
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.19
7.17
7.15
7.14
7.14
7.03
7.01
6.99
1.78
2.00
3.13
2.08
f1 (ppm)
F
F3C
F
5i

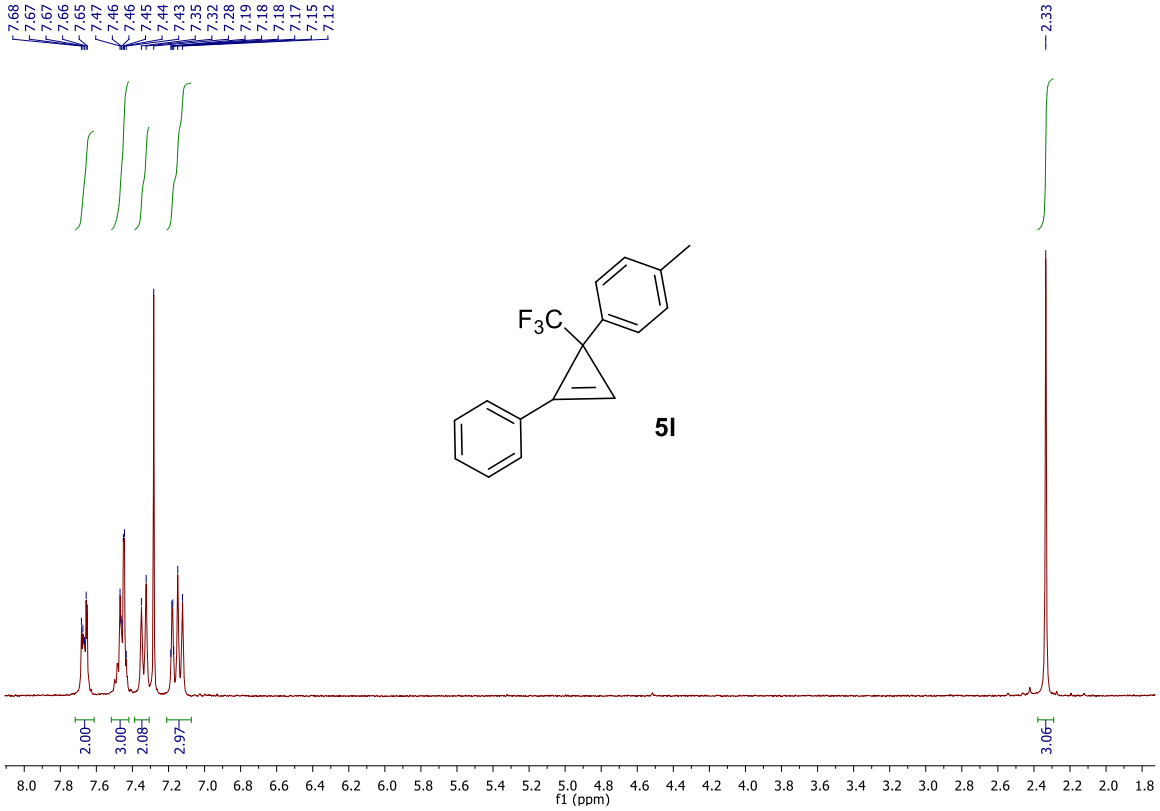

165.12
163.25
162.61
160.80
133.69
132.02
131.93
130.61
129.41
129.33
127.84
125.08
121.21
116.73
116.51
116.28
116.02
115.45
115.24
98.37
77.31 CDCl3
77.20
77.00 CDCl3
76.68 CDCl3
31.89
f1 (ppm)
F
F3C
F
5i

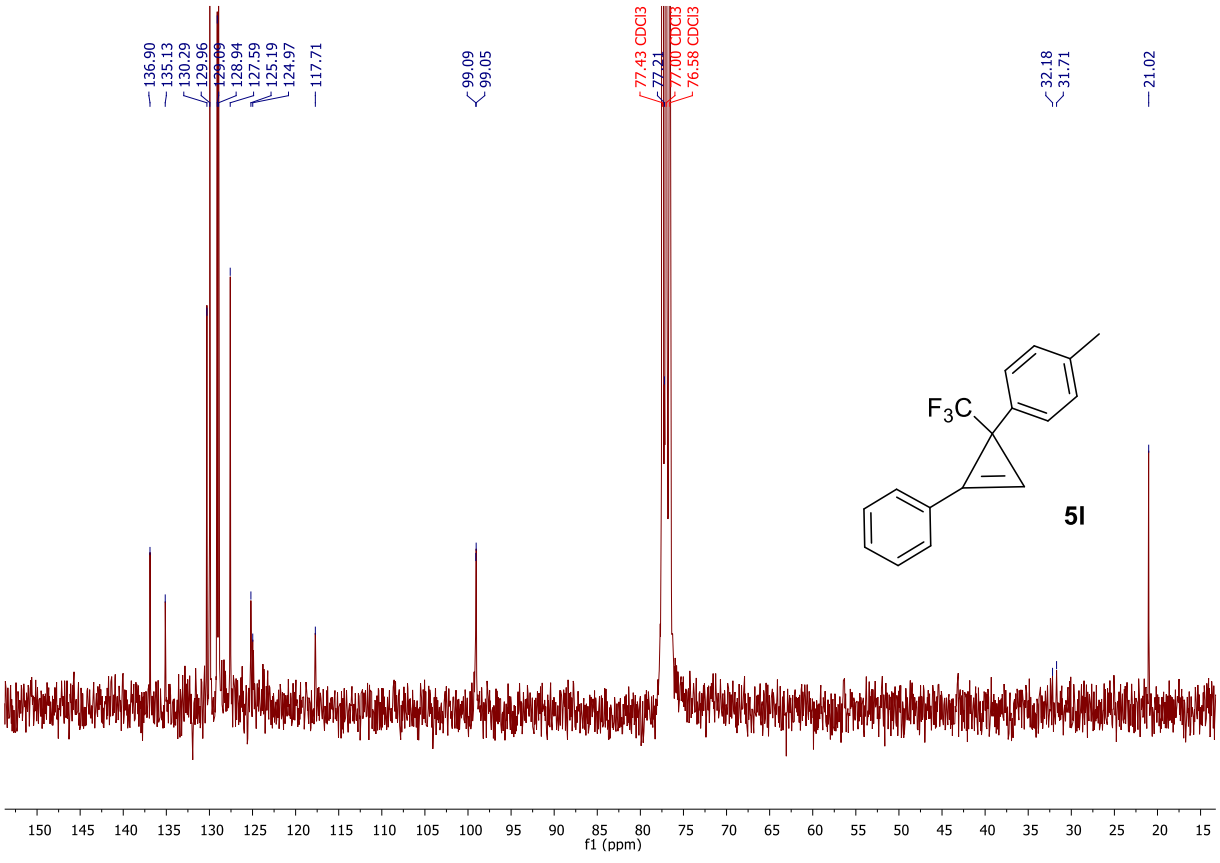

7.61
7.60
7.58
7.58
7.47
7.46
7.45
7.44
7.41
7.39
7.38
7.36
7.28
7.22
7.22
7.21
7.21
7.05
7.02
7.02
7.01
6.99
F
F3C
Cl
5j
2.05
2.01
2.00
1.00
1.98
f1 (ppm)

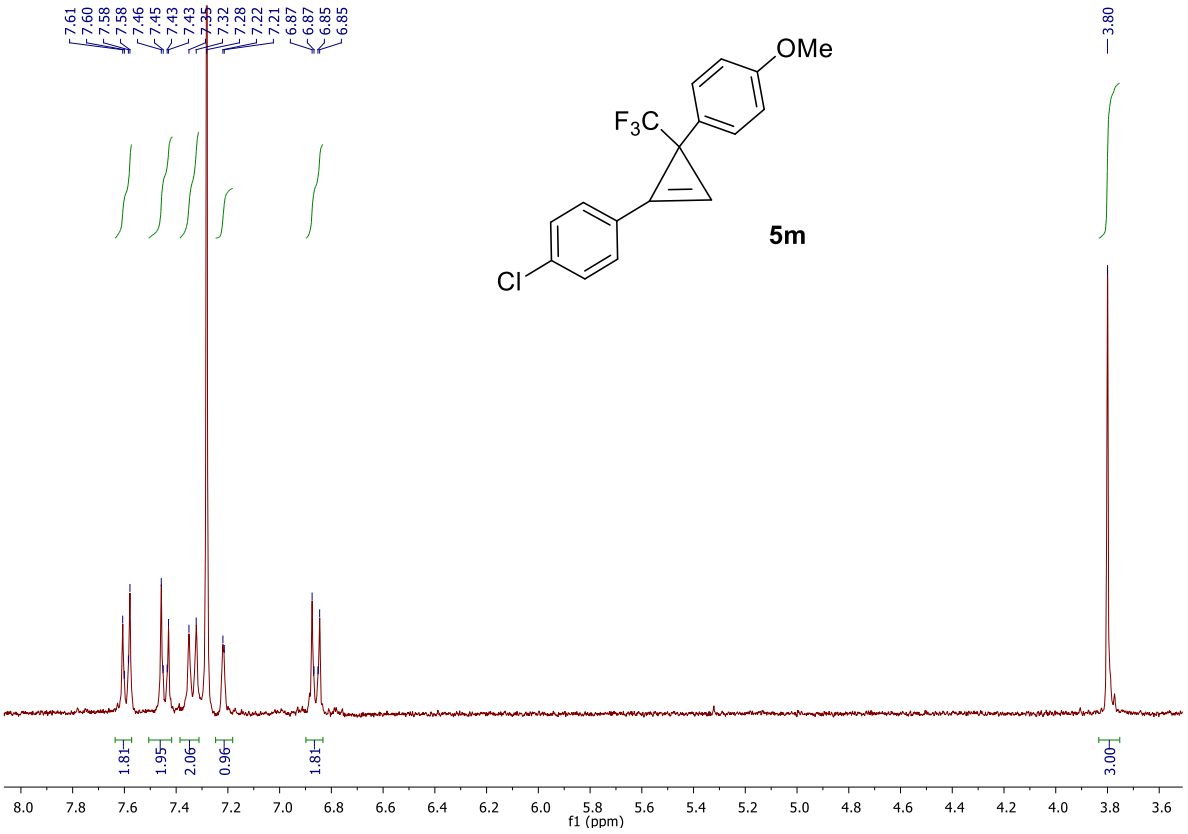

163.28
160.83
136.70
133.57
131.09
129.43
129.34
127.75
125.00
123.38
116.79
115.48
115.27
109.98
99.65
31.93
31.58
F
F3C
Cl
5j
f1 (ppm)

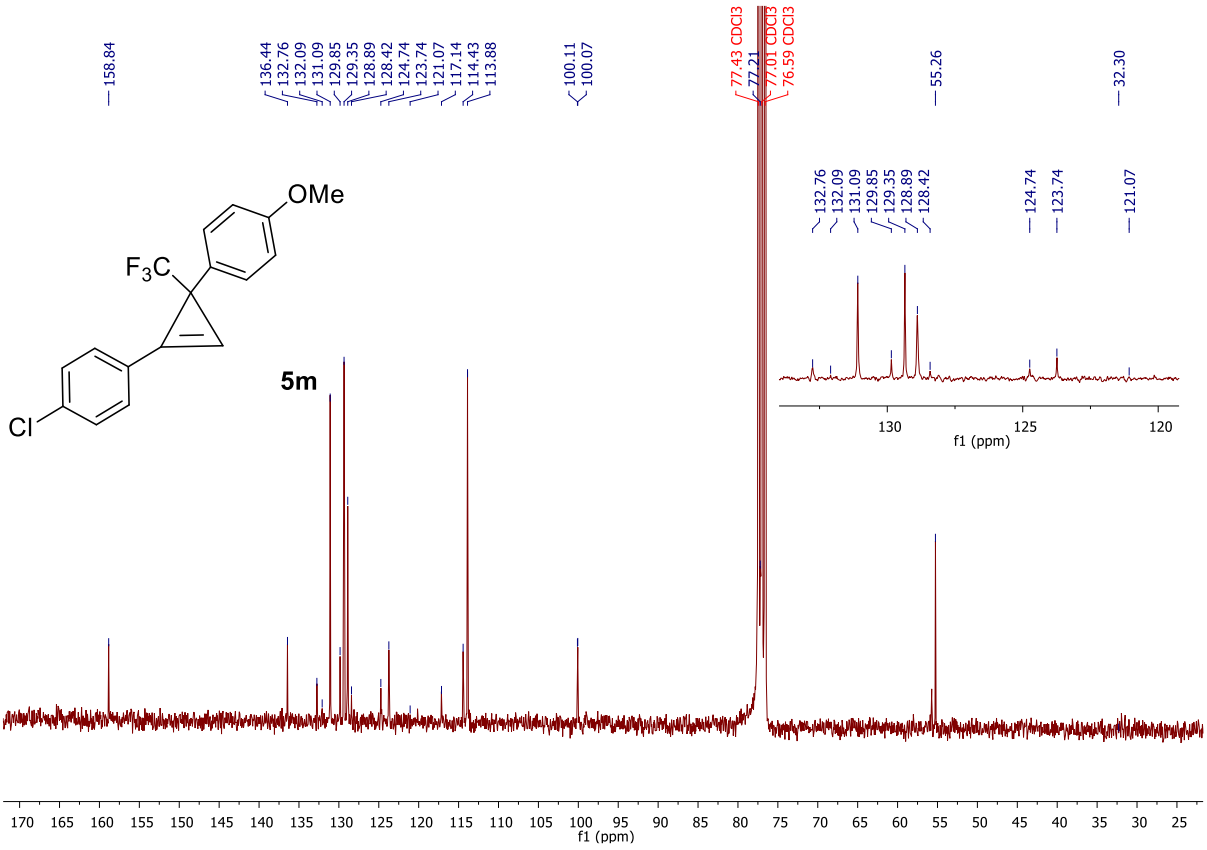

7.70
7.69
7.68
7.67
7.67
7.48
7.48
7.47
7.46
7.46
7.40
7.37
7.20
7.19
6.89
6.88
6.87
6.86
3.80
2.19
3.24
2.13
1.00
2.16
3.33
f1 (ppm)
OMe
F3C
5k


158.77
132.29
130.32
130.26
129.94
129.01
128.98
128.61
125.24
124.94
121.26
118.11
118.08
113.83
99.42
99.38
99.34
99.30
55.24
32.35
31.88
31.41
30.93
f1 (ppm)
OMe
F3C
5k

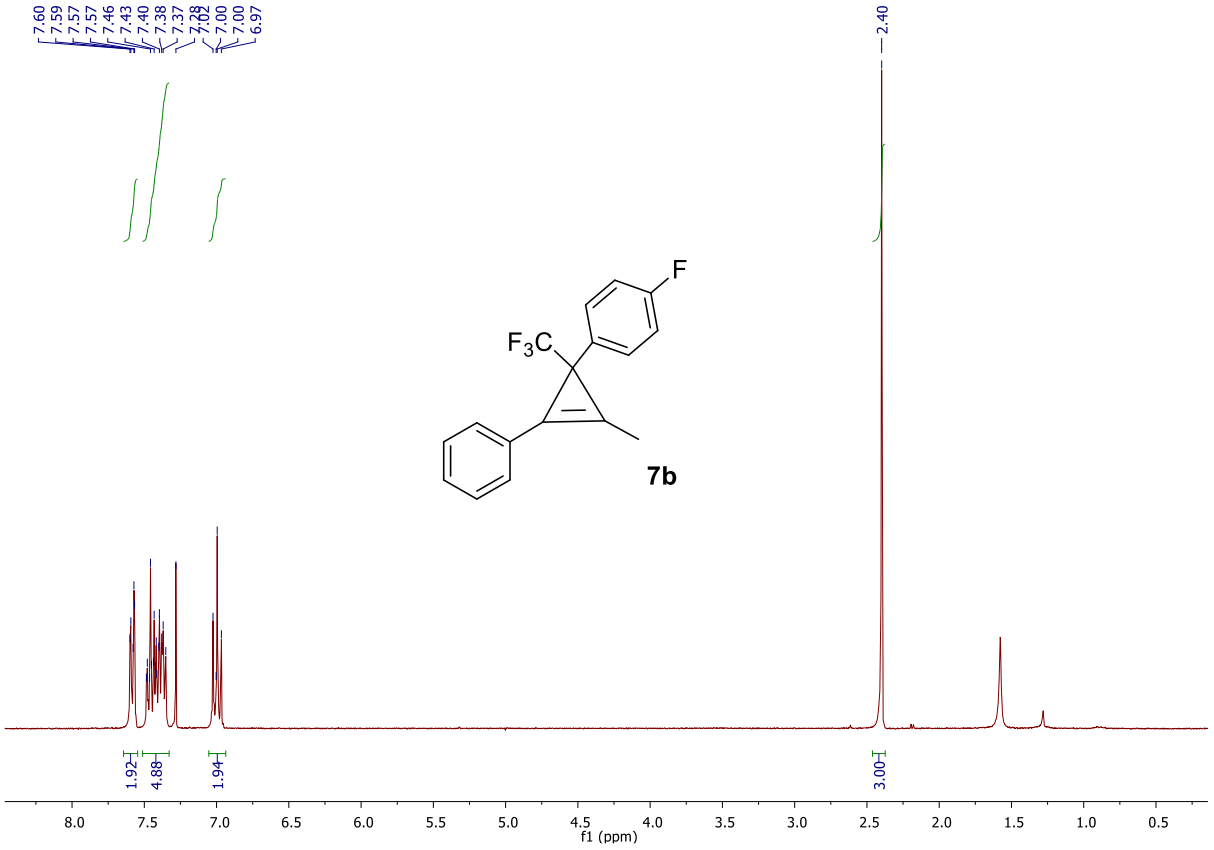

7.68
7.67
7.67
7.66
7.65
7.47
7.46
7.46
7.45
7.44
7.43
7.35
7.32
7.28
7.19
7.18
7.18
7.17
7.15
7.12
2.33
F3C
5l
2.00
3.00
2.08
2.97
3.06
f1 (ppm)

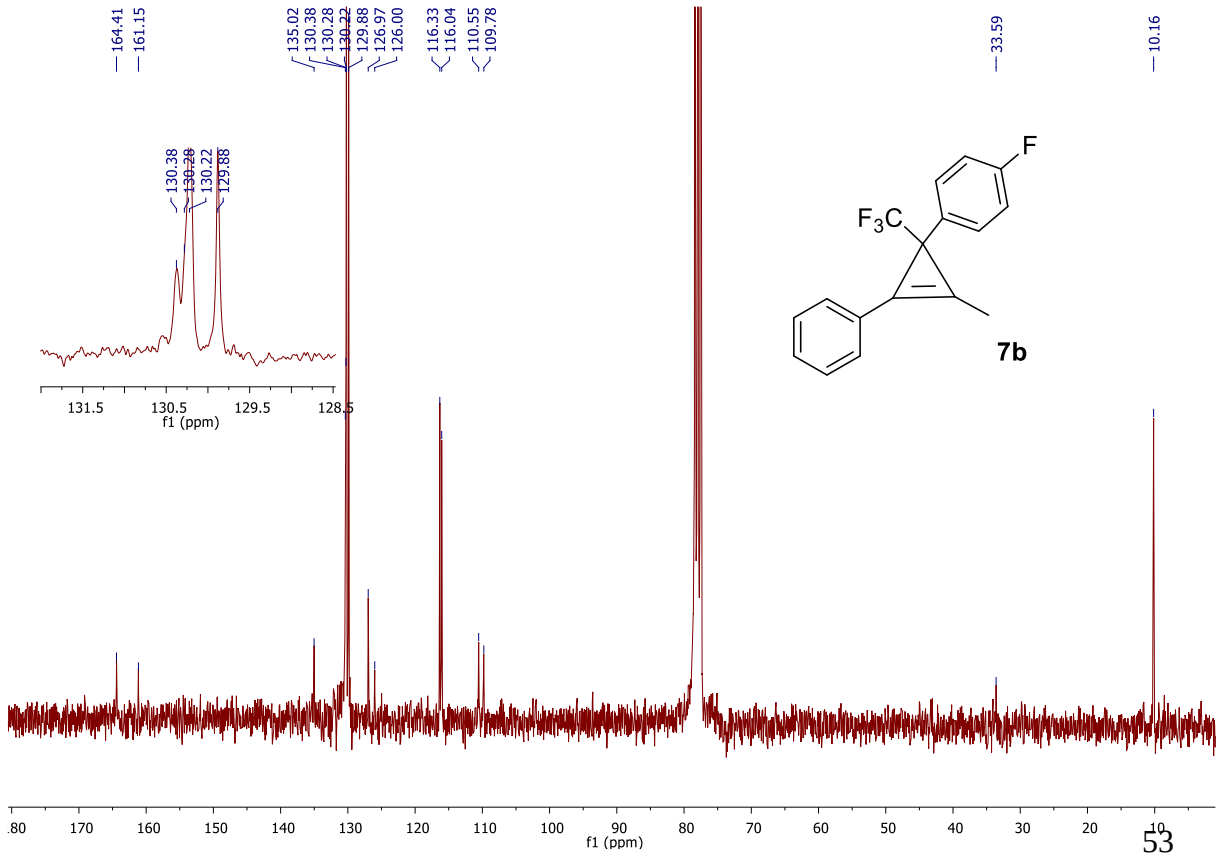

136.90
135.13
130.29
129.96
128.94
127.59
125.19
124.97
117.71
99.09
99.05
77.43 CDCl3
77.21
77.00 CDCl3
76.58 CDCl3
32.18
31.71
21.02
F3C
5l
f1 (ppm)

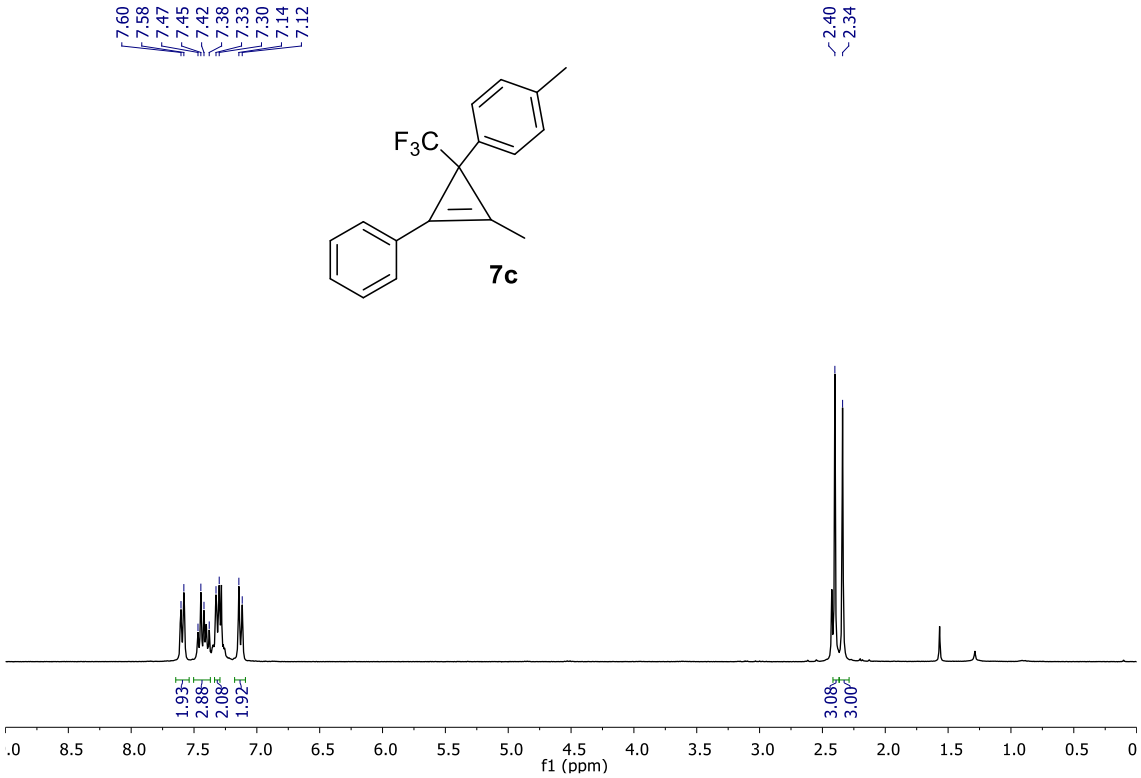

7.61
7.60
7.58
7.58
7.46
7.45
7.43
7.43
7.35
7.32
7.28
7.22
7.21
6.87
6.85
6.85
3.80
OMe
F3C
Cl
5m
1.81
1.95
2.06
0.96
1.81
3.00
f1 (ppm)

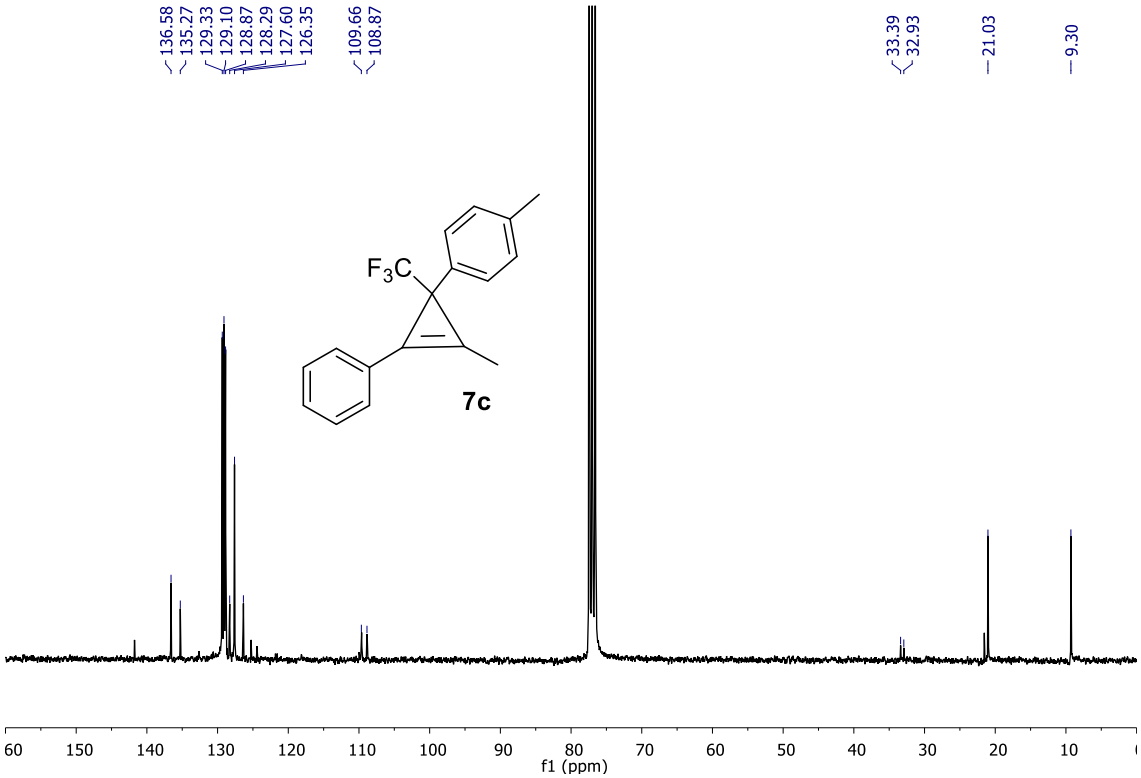

158.84
136.44
132.76
132.09
131.09
129.85
129.35
128.89
128.42
124.74
123.74
121.07
117.14
114.43
113.88
100.11
100.07
77.43 CDCl3
77.21
77.01 CDCl3
76.59 CDCl3
55.26
32.30
OMe
F3C
Cl
5m
132.76
132.09
131.09
129.85
129.35
128.89
128.42
124.74
123.74
121.07
130
125
120
f1 (ppm)
f1 (ppm)

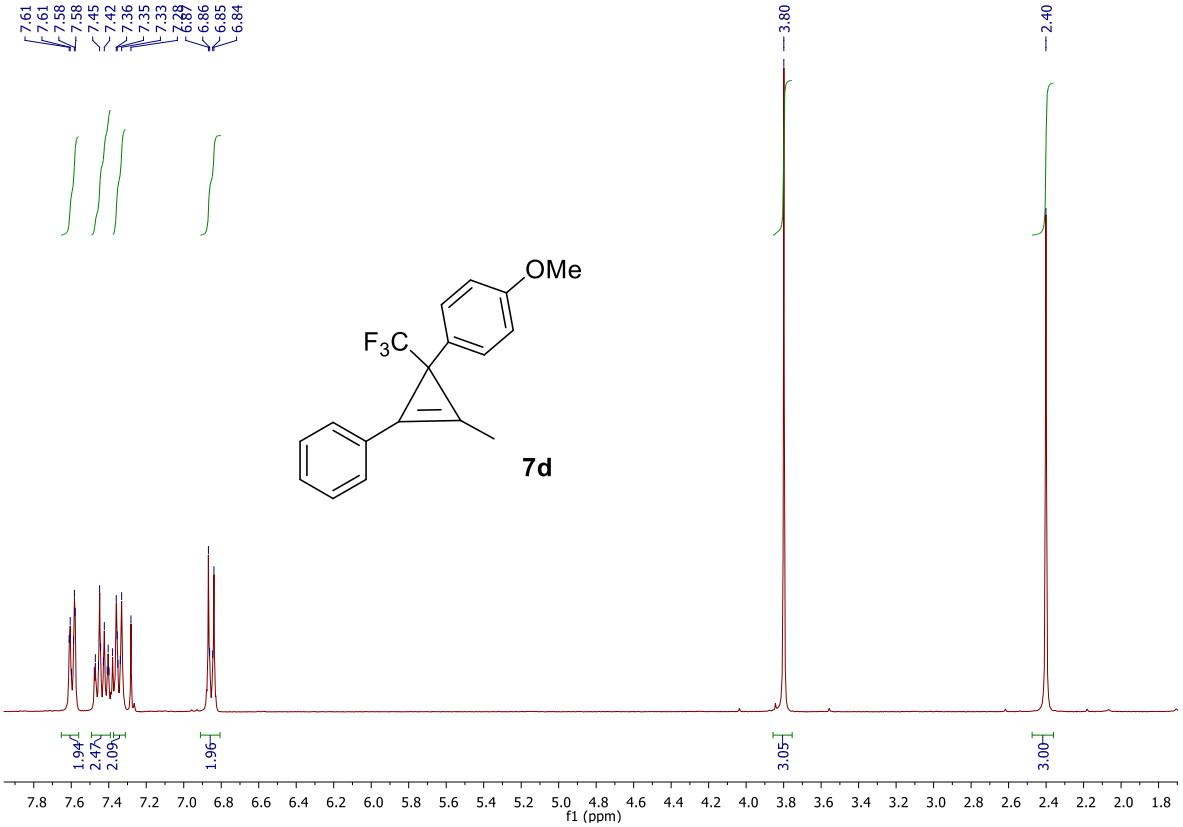
Tetrasubstituted cyclopropenes

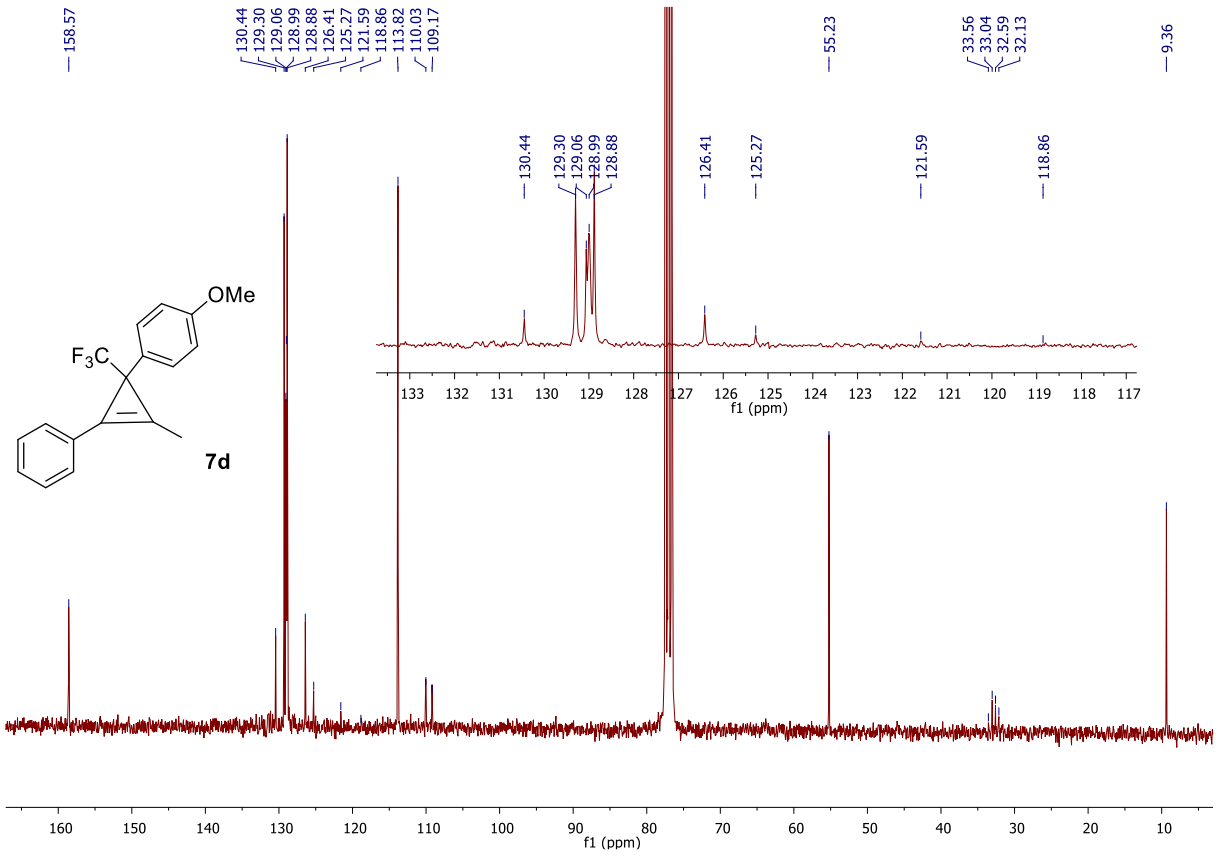


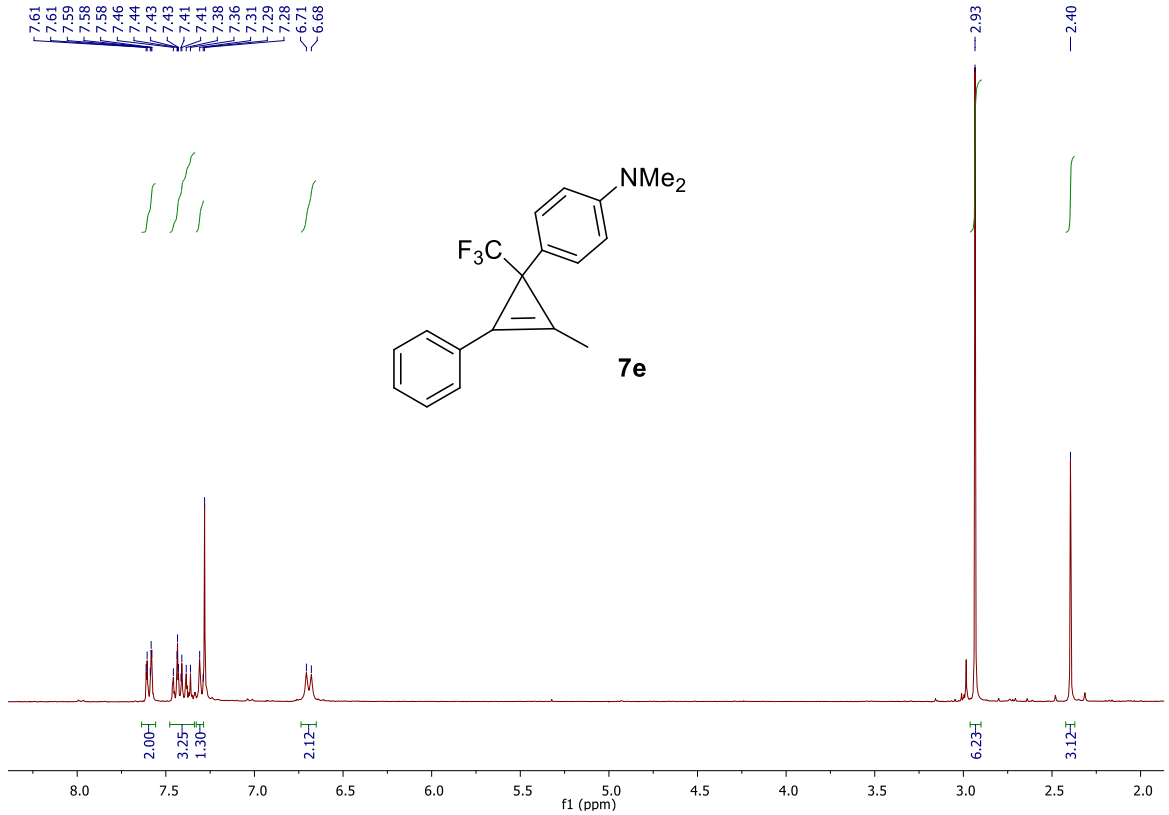


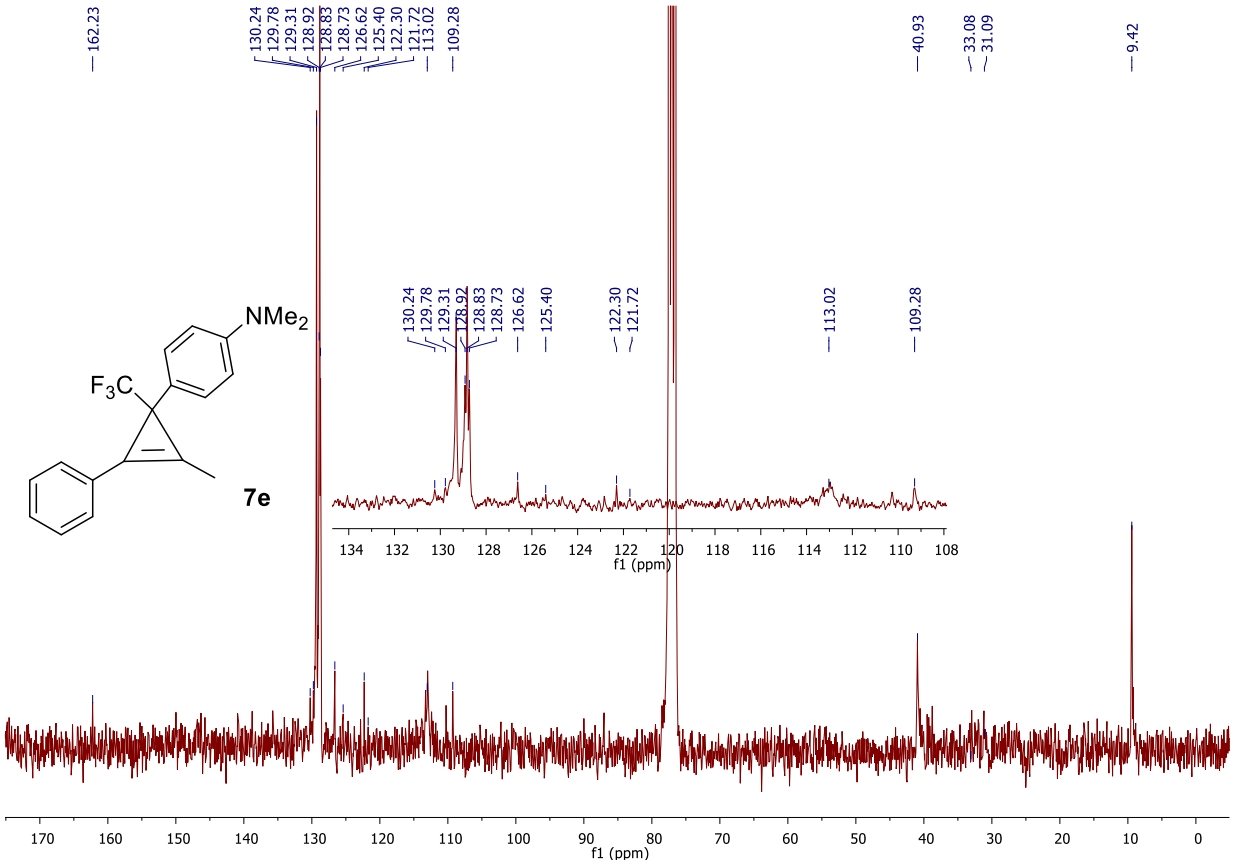

7.60
7.58
7.47
7.45
7.42
7.38
7.33
7.30
7.14
7.12
2.40
2.34
F3C
7c
1.93
2.88
2.08
1.92
3.08
3.00
f1 (ppm)

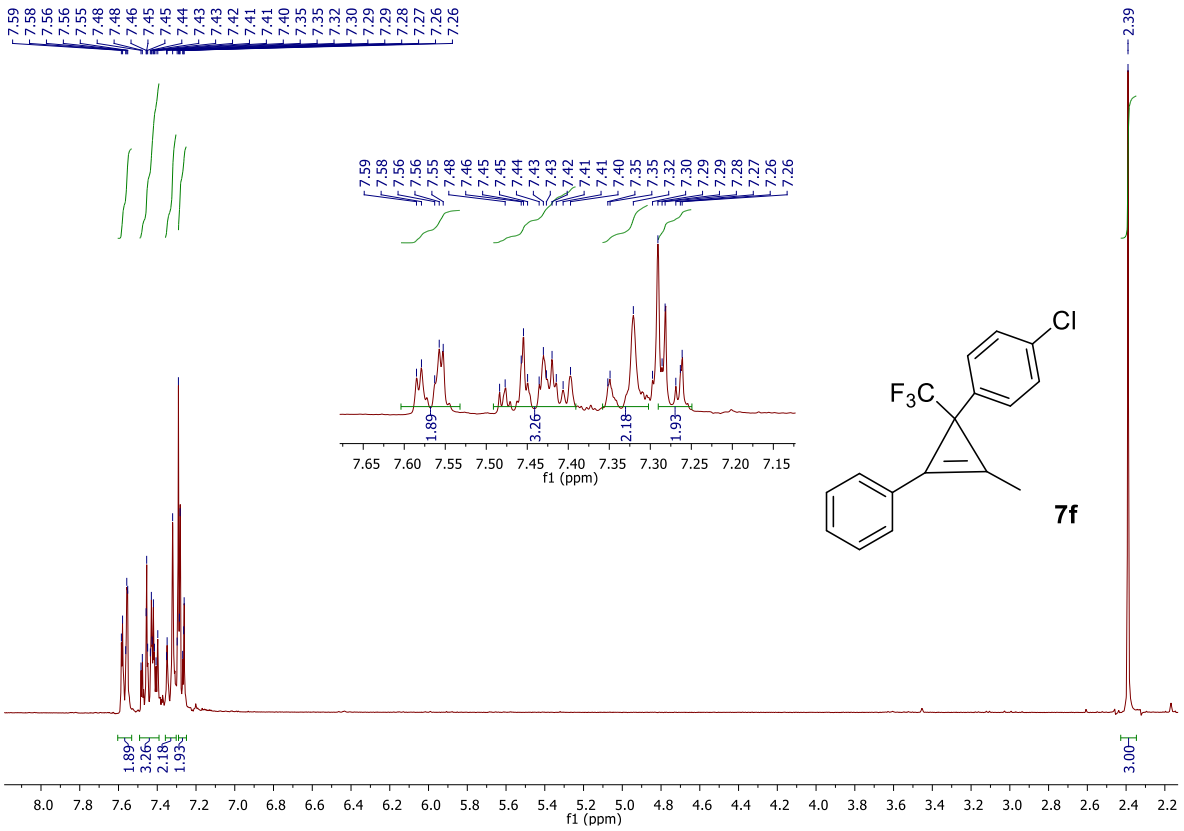

136.58
135.27
129.33
129.10
128.87
128.29
127.60
126.35
109.66
108.87
33.39
32.93
21.03
9.30
F3C
7c
f1 (ppm)

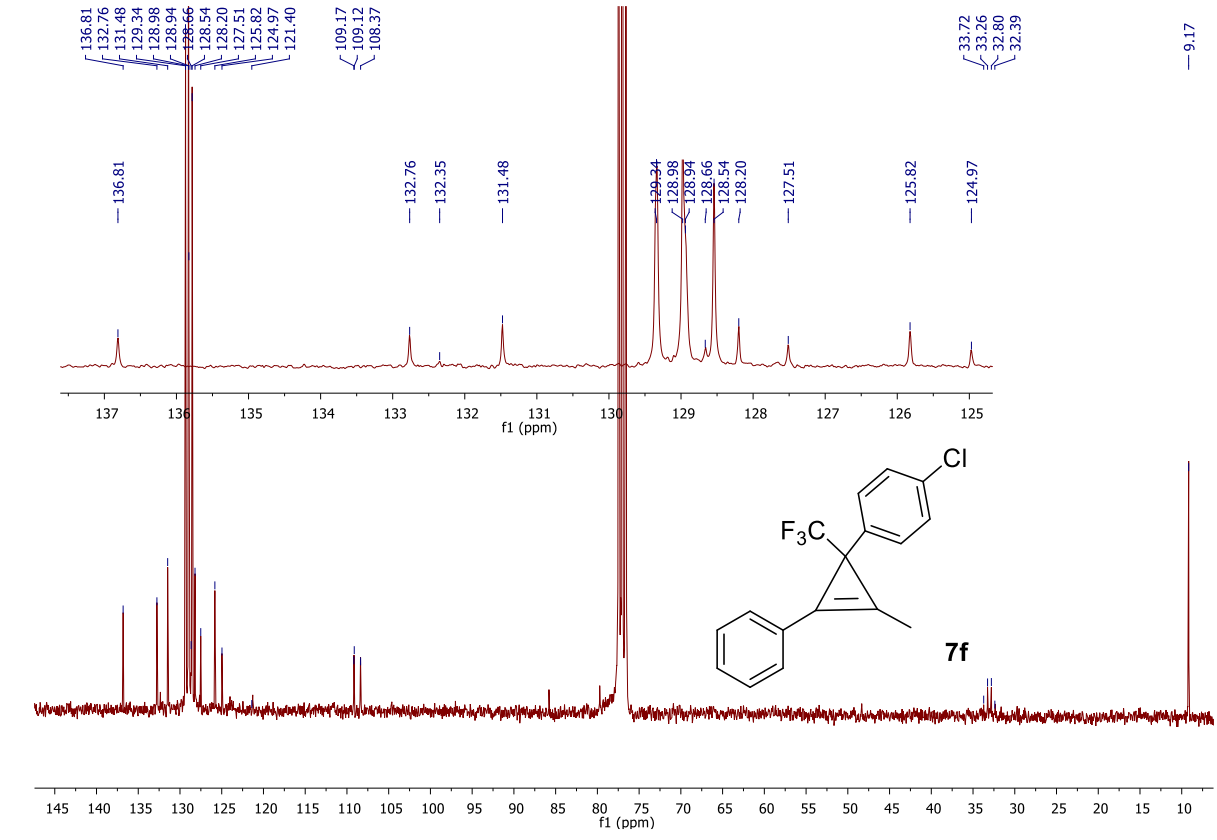

7.61
7.61
7.58
7.58
7.45
7.42
7.36
7.35
7.33
7.28
6.87
6.86
6.85
6.84
3.80
2.40
OMe
F3C
7d
1.94
2.47
2.09
1.96
3.05
3.00
f1 (ppm)

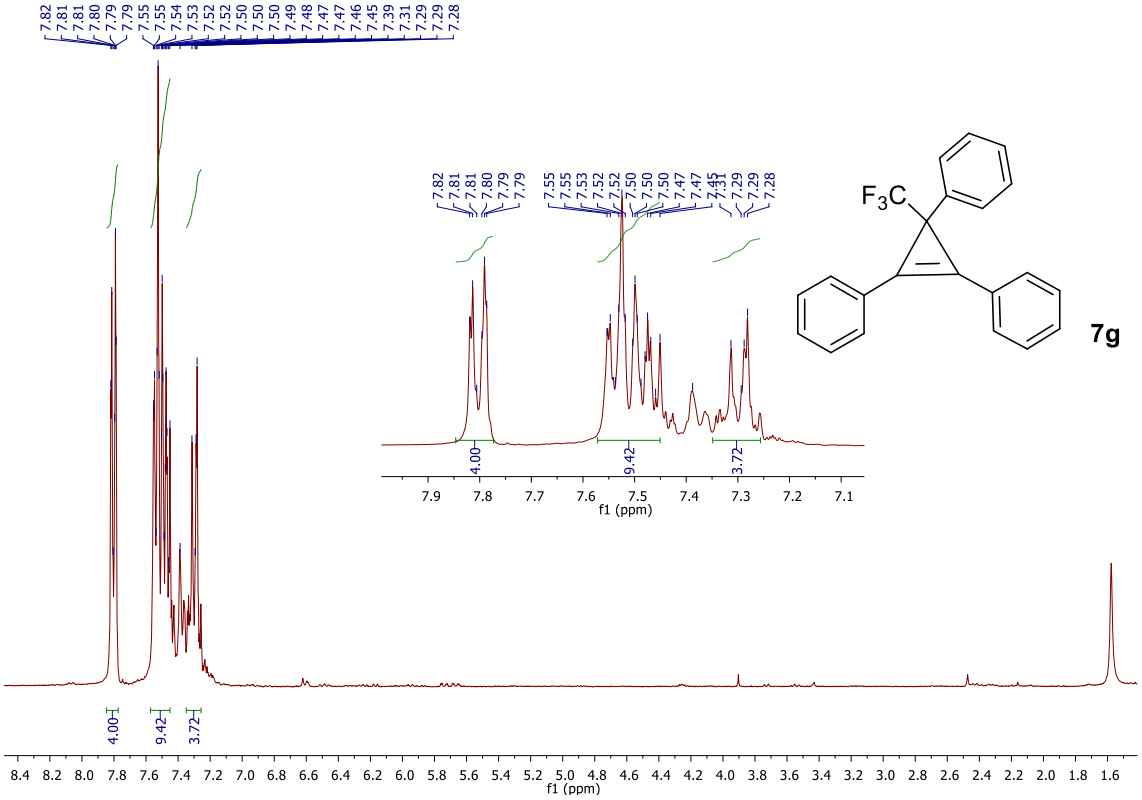

158.57
130.44
129.30
129.06
128.99
128.88
126.41
125.27
121.59
118.86
113.82
110.03
109.17
55.23
33.56
33.04
32.59
32.13
9.36
OMe
F3C
7d
f1 (ppm)

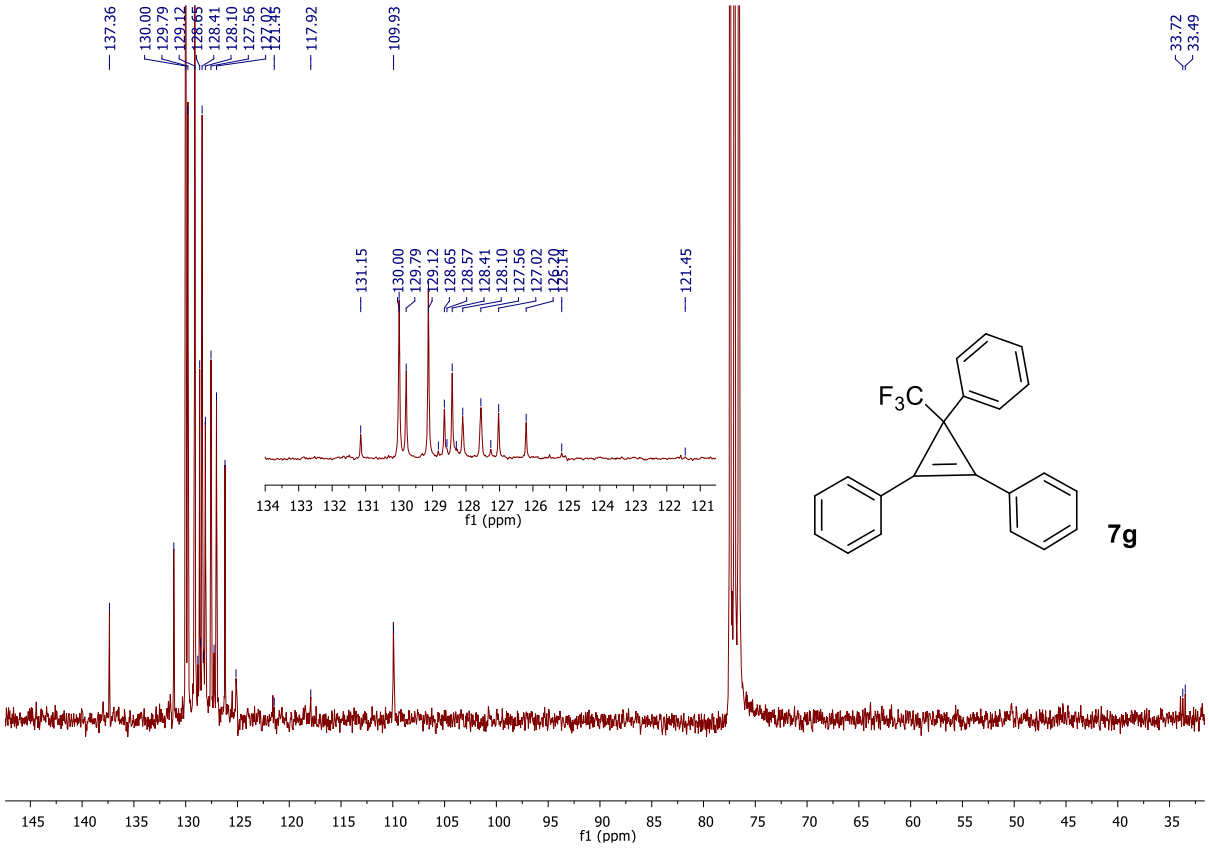

7.61
7.61
7.59
7.58
7.58
7.46
7.44
7.43
7.43
7.41
7.41
7.38
7.36
7.31
7.29
7.28
6.71
6.68
2.93
2.40
NMe2
F3C
7e
2.00
3.25
1.30
2.12
6.23
3.12
f1 (ppm)

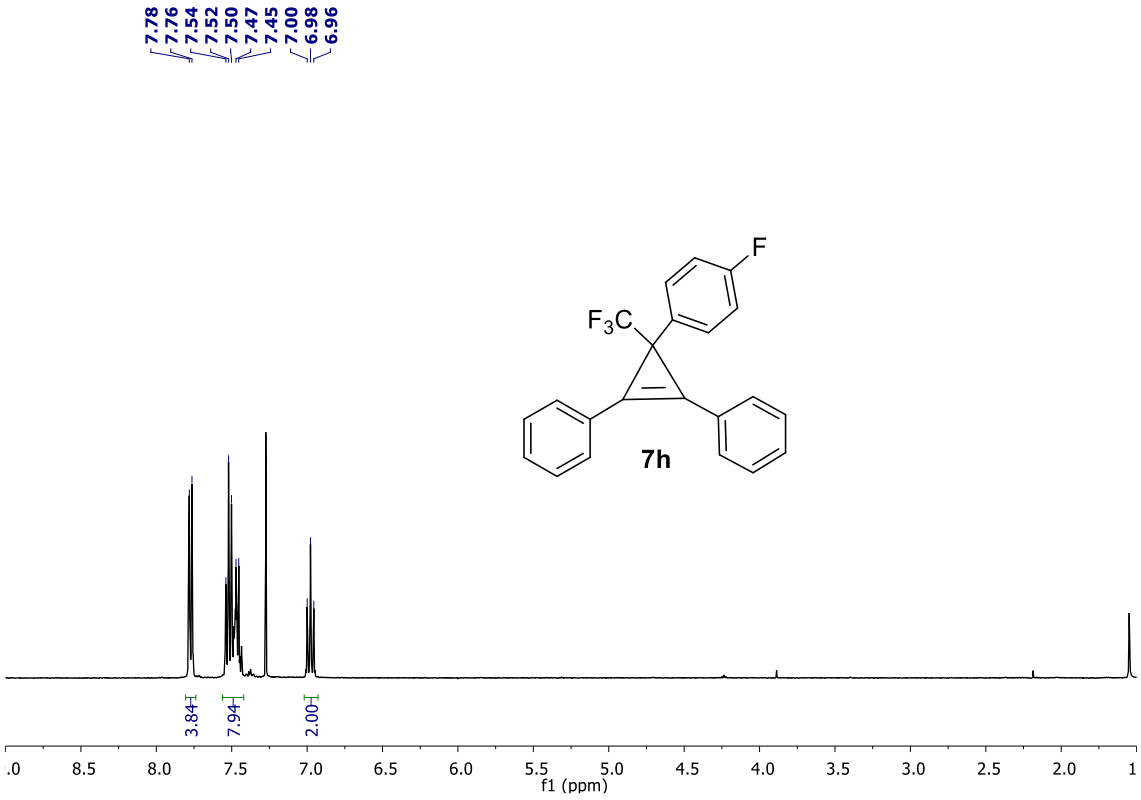

162.23
130.24
129.78
129.31
128.92
128.83
128.73
126.62
125.40
122.30
121.72
113.02
109.28
40.93
33.08
31.09
9.42
NMe2
F3C
7e
f1 (ppm)

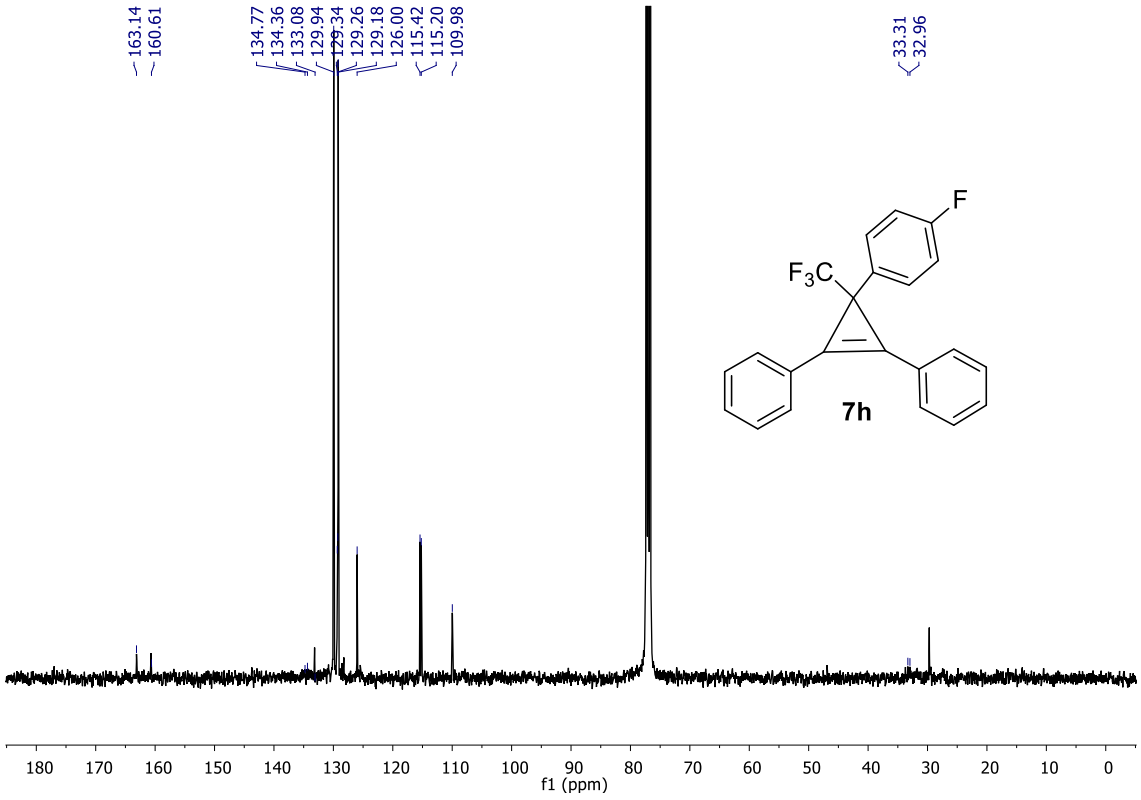

7.59 7.58 7.56 7.56 7.55 7.48 7.48 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.40 7.35 7.35 7.32 7.30 7.29 7.29 7.28 7.27 7.26 7.26
2.39
1.89
3.26
2.18
1.93
3.00
f1 (ppm)
Cl
F3C
7f

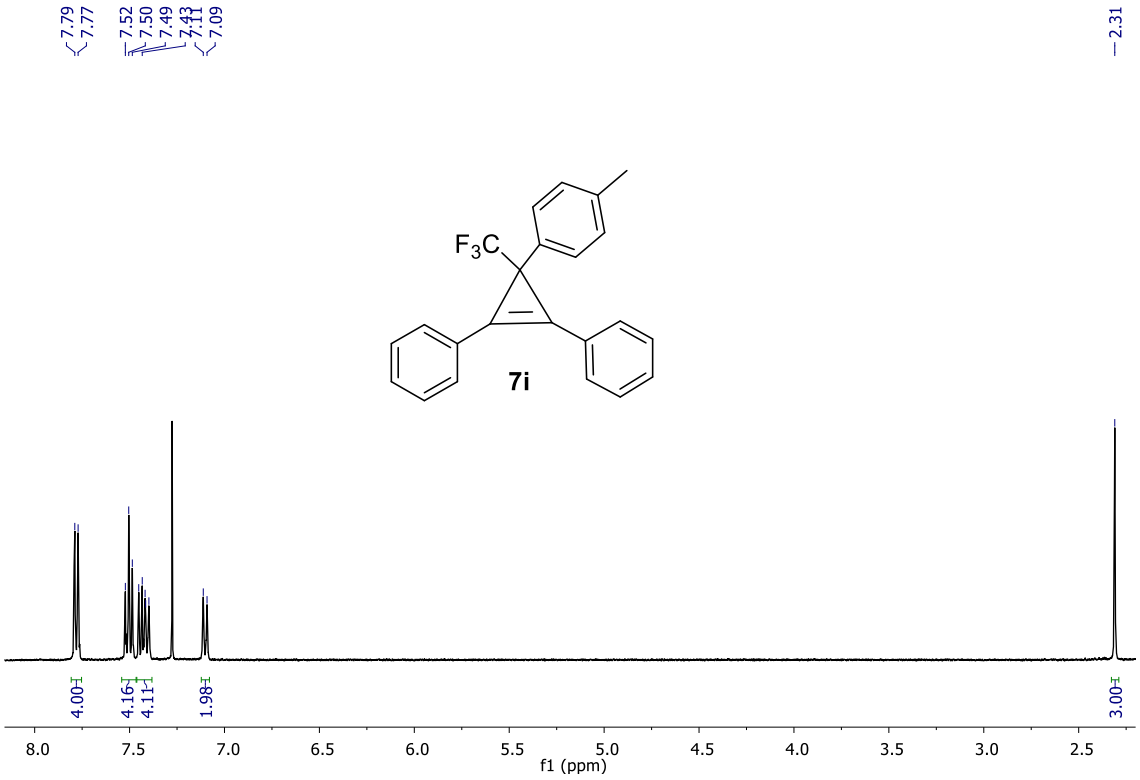

136.81 132.76 131.48 129.34 128.98 128.94 128.66 128.54 128.20 127.51 125.82 124.97 121.40
109.17 109.12 108.37
33.72 33.26 32.80 32.39
9.17
f1 (ppm)
Cl
F3C
7f

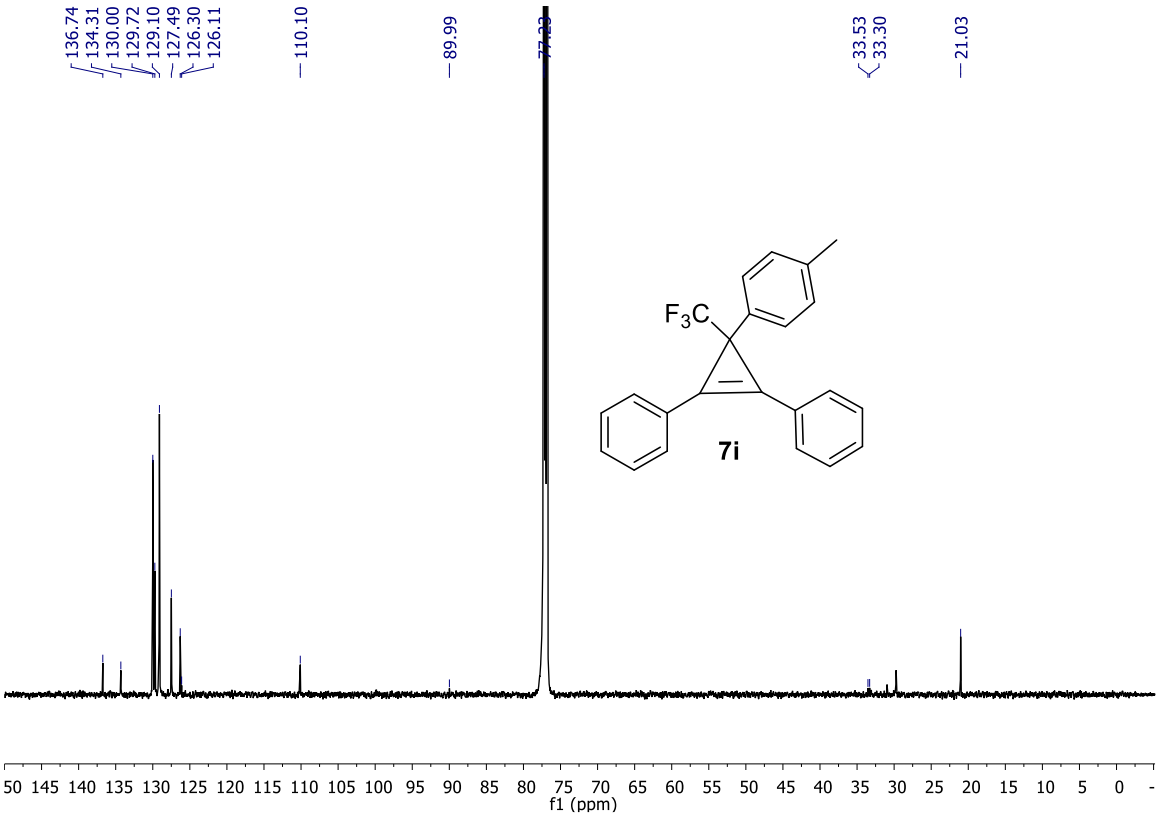

7.82 7.81 7.81 7.80 7.79 7.79 7.55 7.55 7.54 7.53 7.52 7.52 7.50 7.50 7.50 7.49 7.48 7.47 7.47 7.46 7.45 7.39 7.31 7.29 7.29 7.28
4.00
9.42
3.72
f1 (ppm)
F3C
7g

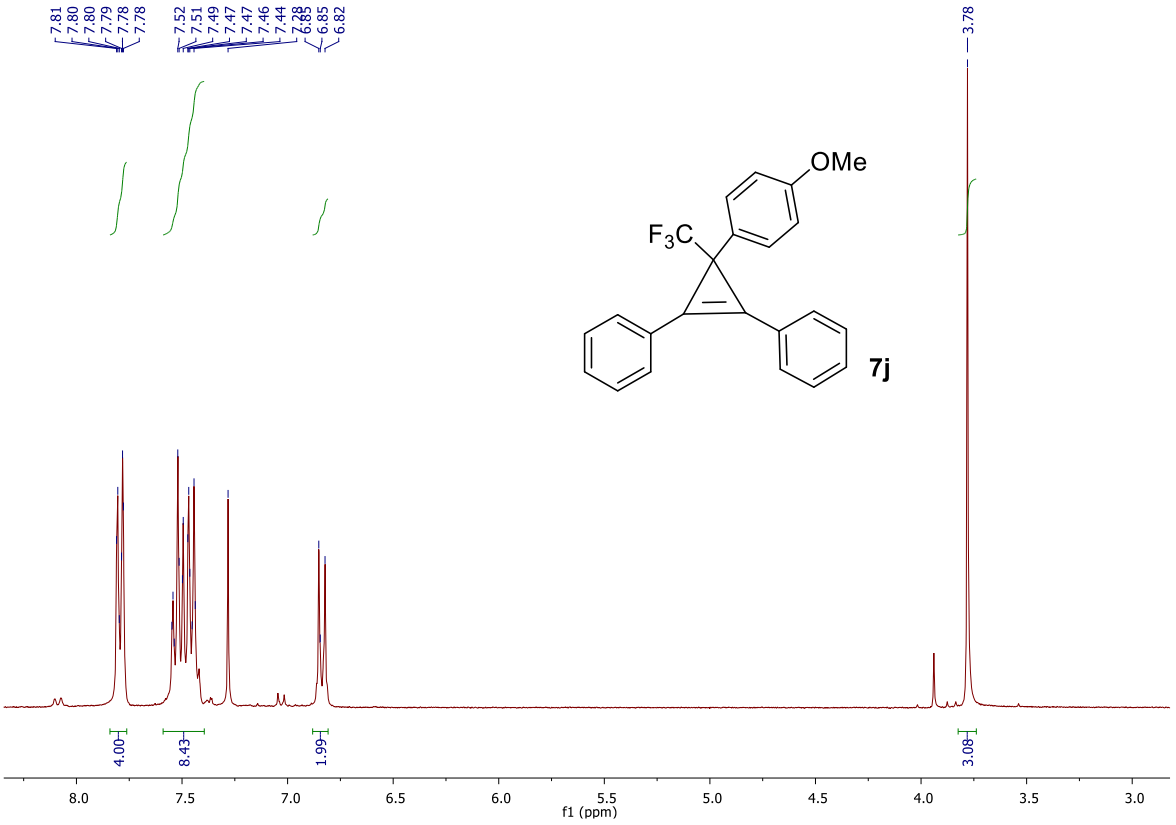

137.36 130.00 129.79 129.12 128.65 128.41 128.10 127.56 127.02 121.45 117.92 109.93 33.72 33.49
131.15 130.00 129.79 129.12 128.65 128.57 128.41 128.10 127.56 127.02 121.45
f1 (ppm)
F3C
7g

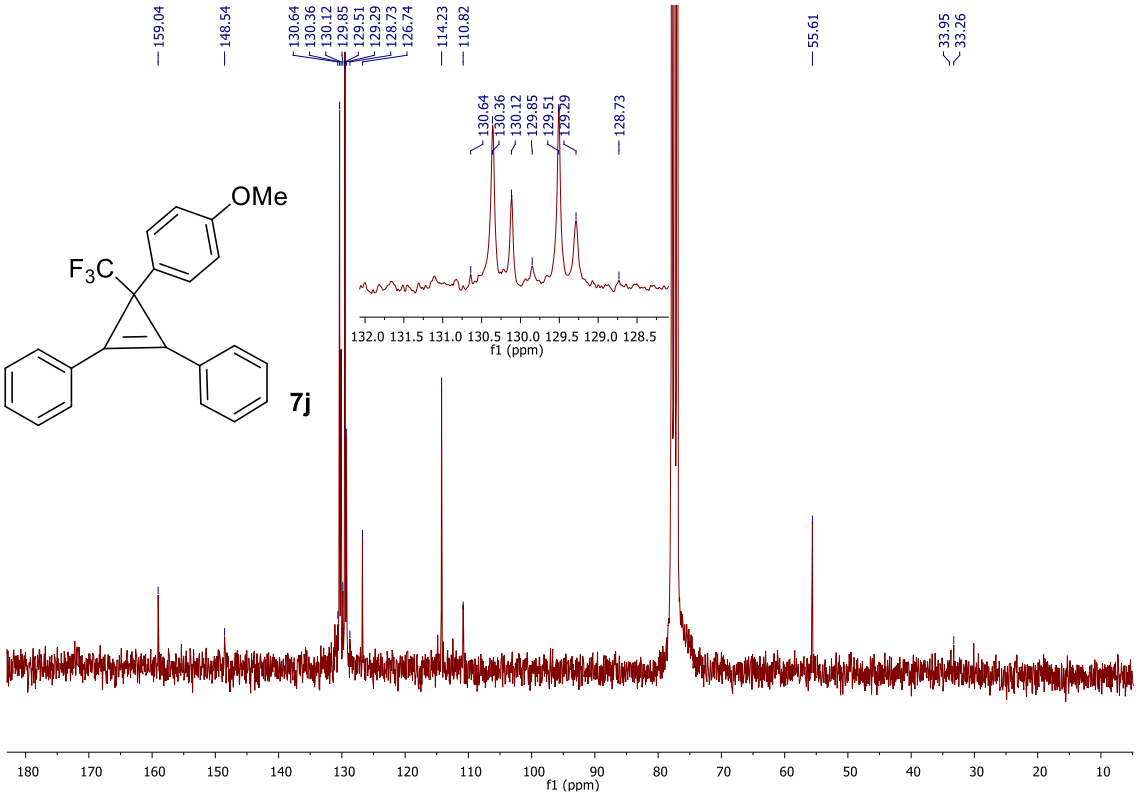

7.78
7.76
7.54
7.52
7.50
7.47
7.45
7.00
6.98
6.96
F
F3C
7h
3.84
7.94
2.00
f1 (ppm)

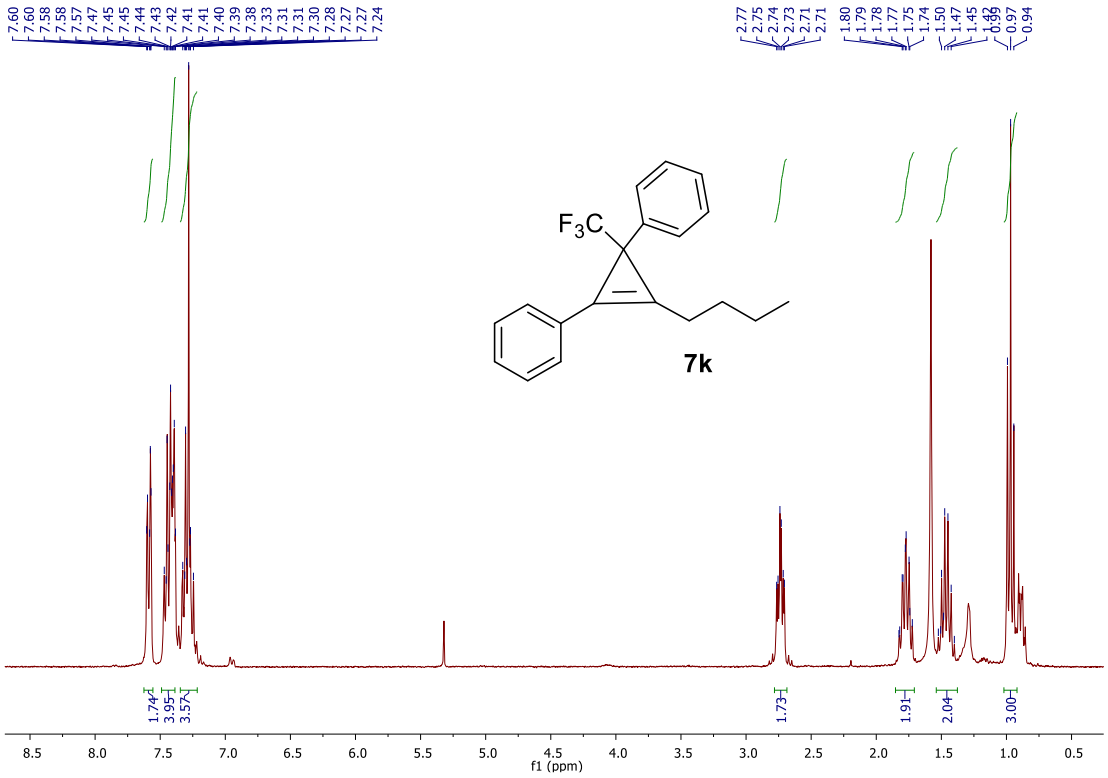

163.14
160.61
134.77
134.36
133.08
129.94
129.34
129.26
129.18
126.00
115.42
115.20
109.98
33.31
32.96
F
F3C
7h
f1 (ppm)

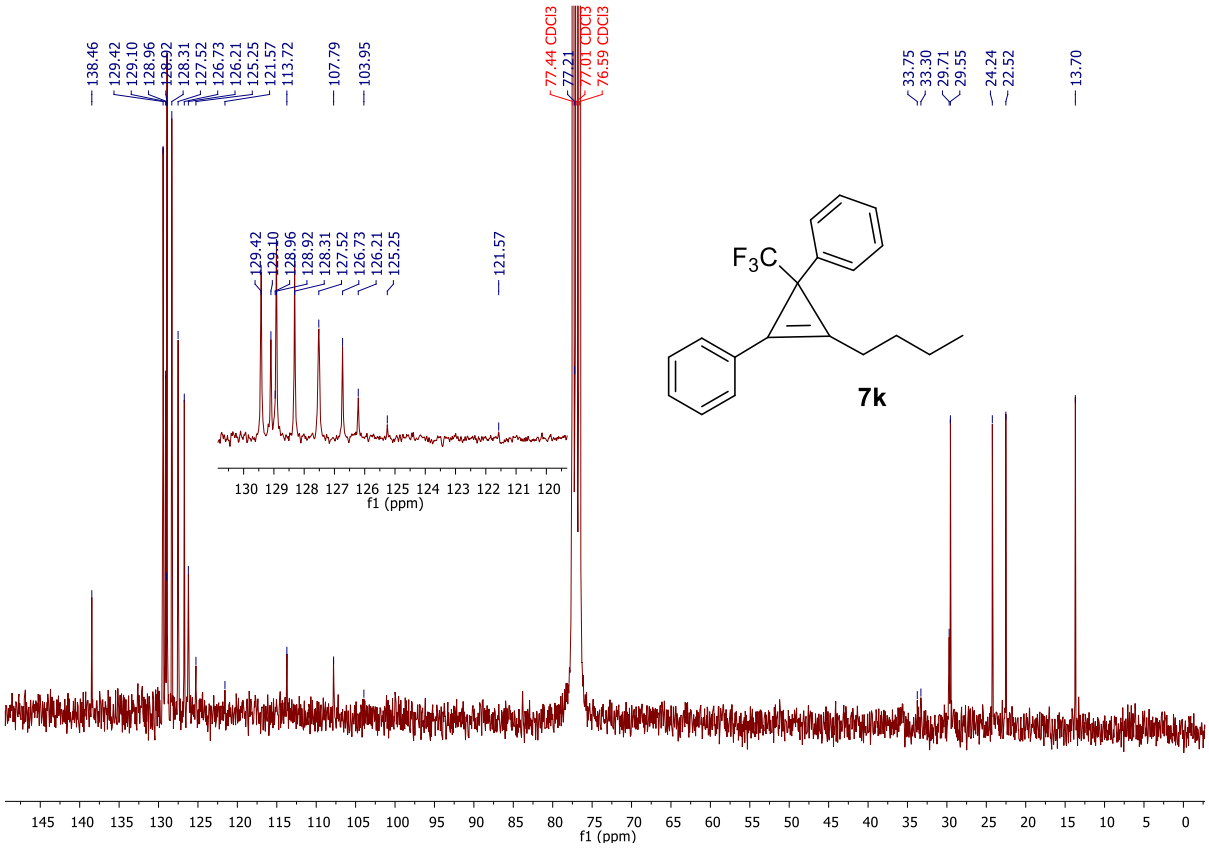

7.79
7.77
7.52
7.50
7.49
7.43
7.11
7.09
2.31
F3C
7i
4.00
4.16
4.11
1.98
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

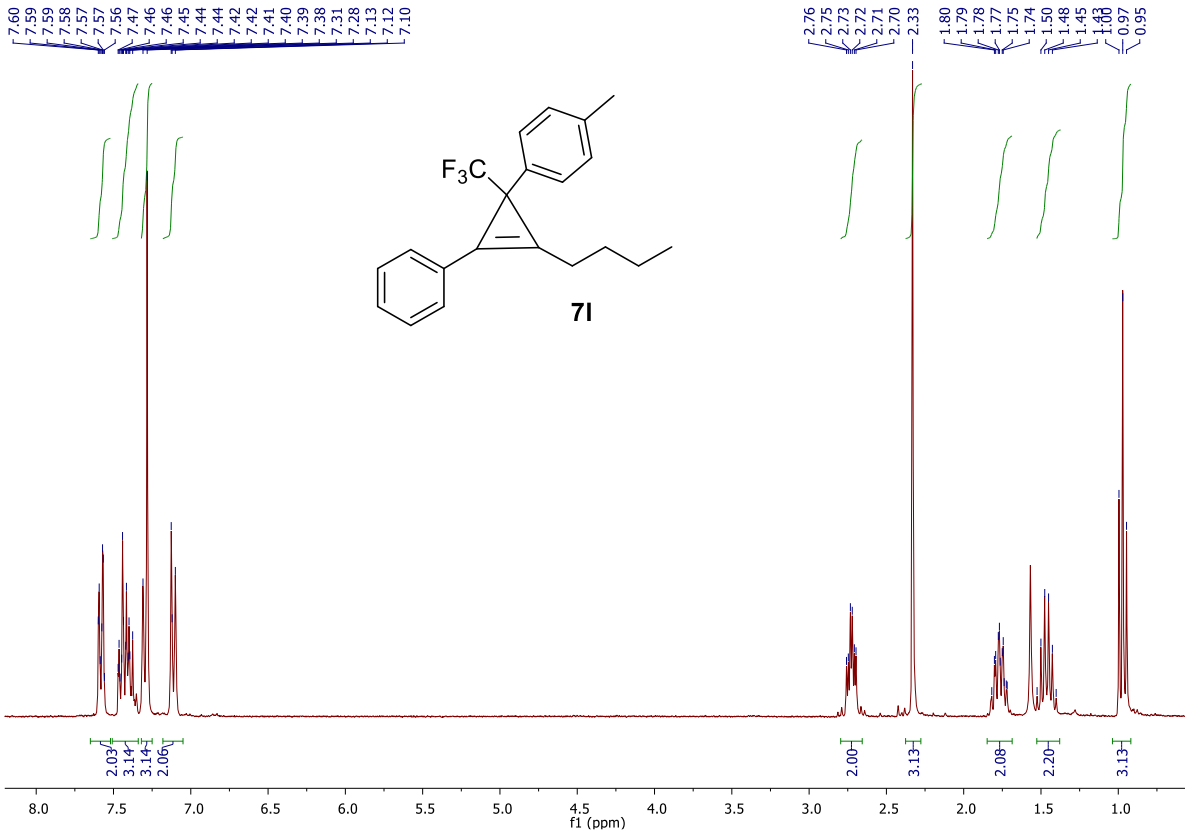

136.74
134.31
130.00
129.72
129.10
127.49
126.30
126.11
110.10
89.99
77.33
33.53
33.30
21.03
F3C
7i
50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -
f1 (ppm)

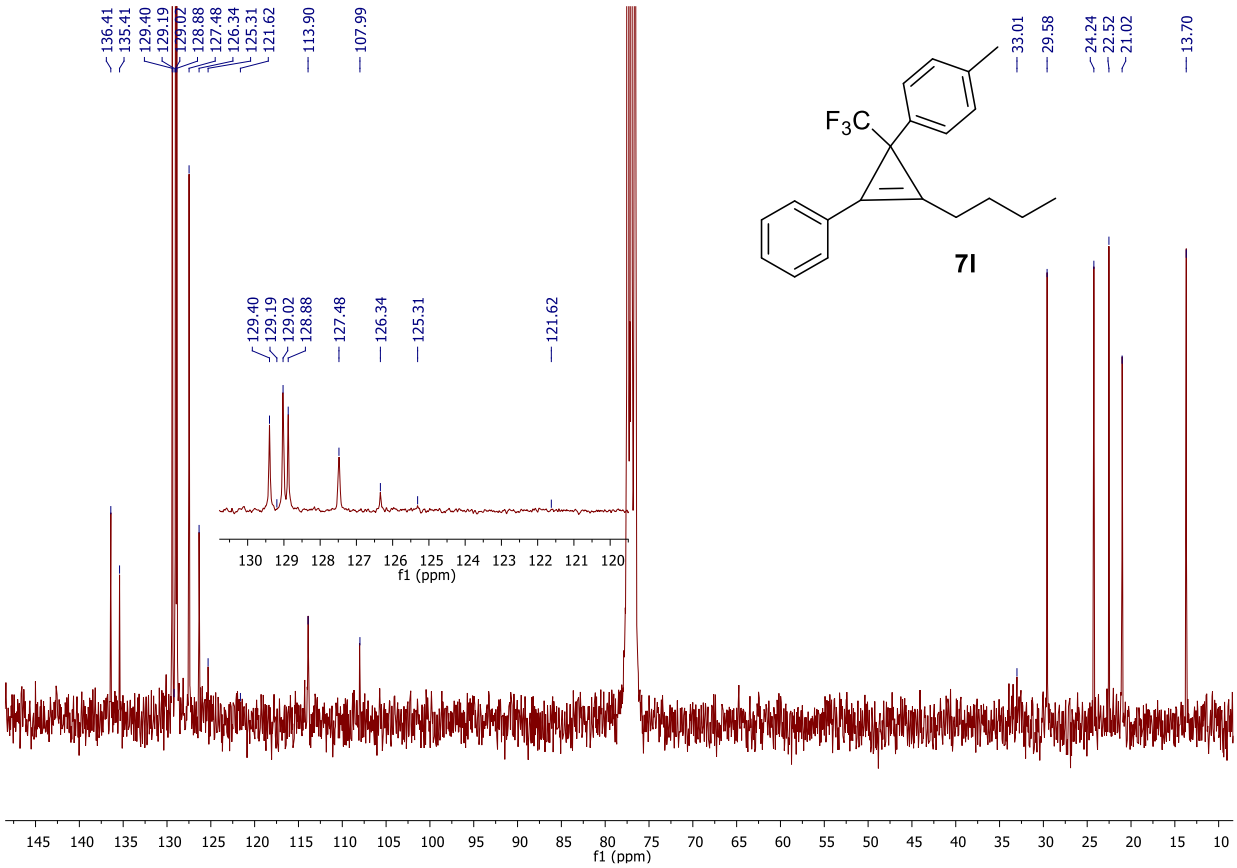

7.81
7.80
7.80
7.79
7.78
7.78
7.52
7.51
7.49
7.47
7.47
7.46
7.44
6.85
6.82
3.78
OMe
F3C
7j
4.00
8.43
1.99
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f1 (ppm)

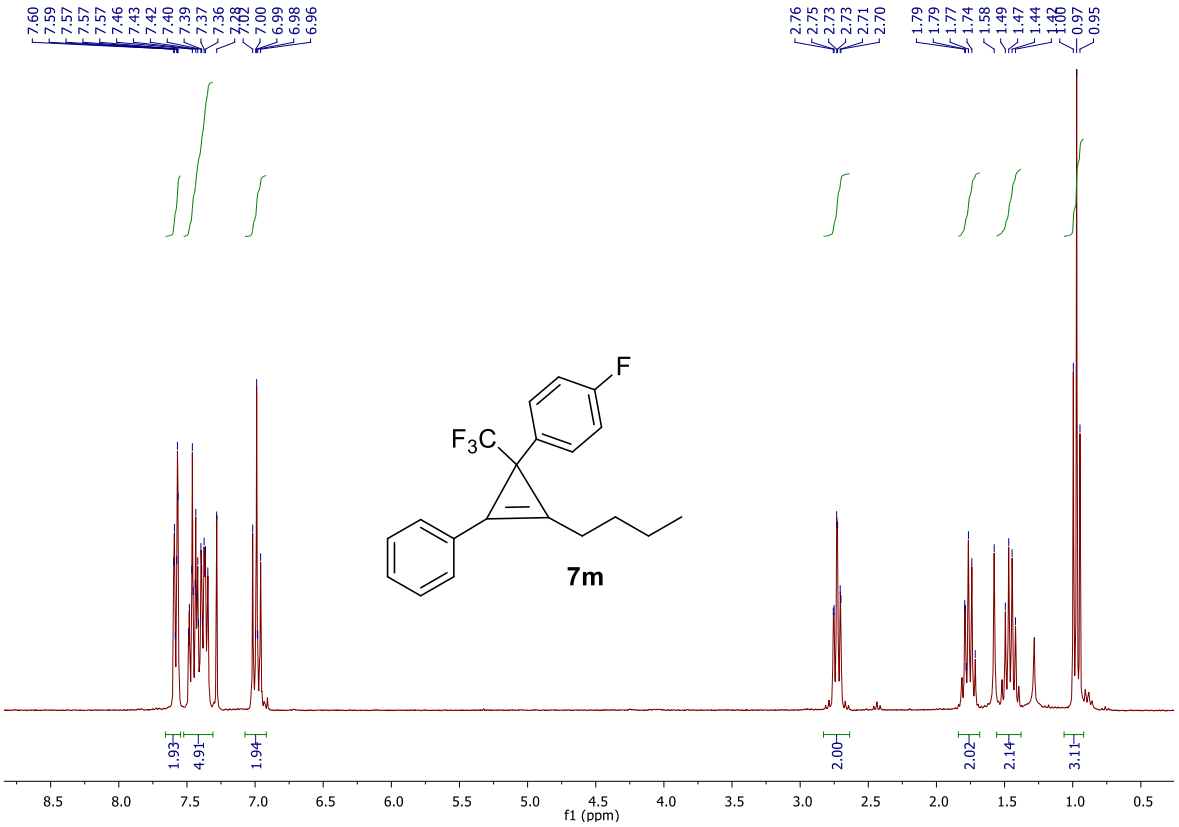

159.04
148.54
130.64
130.36
130.12
129.85
129.51
129.29
128.73
126.74
114.23
110.82
55.61
33.95
33.26
OMe
F3C
7j
132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

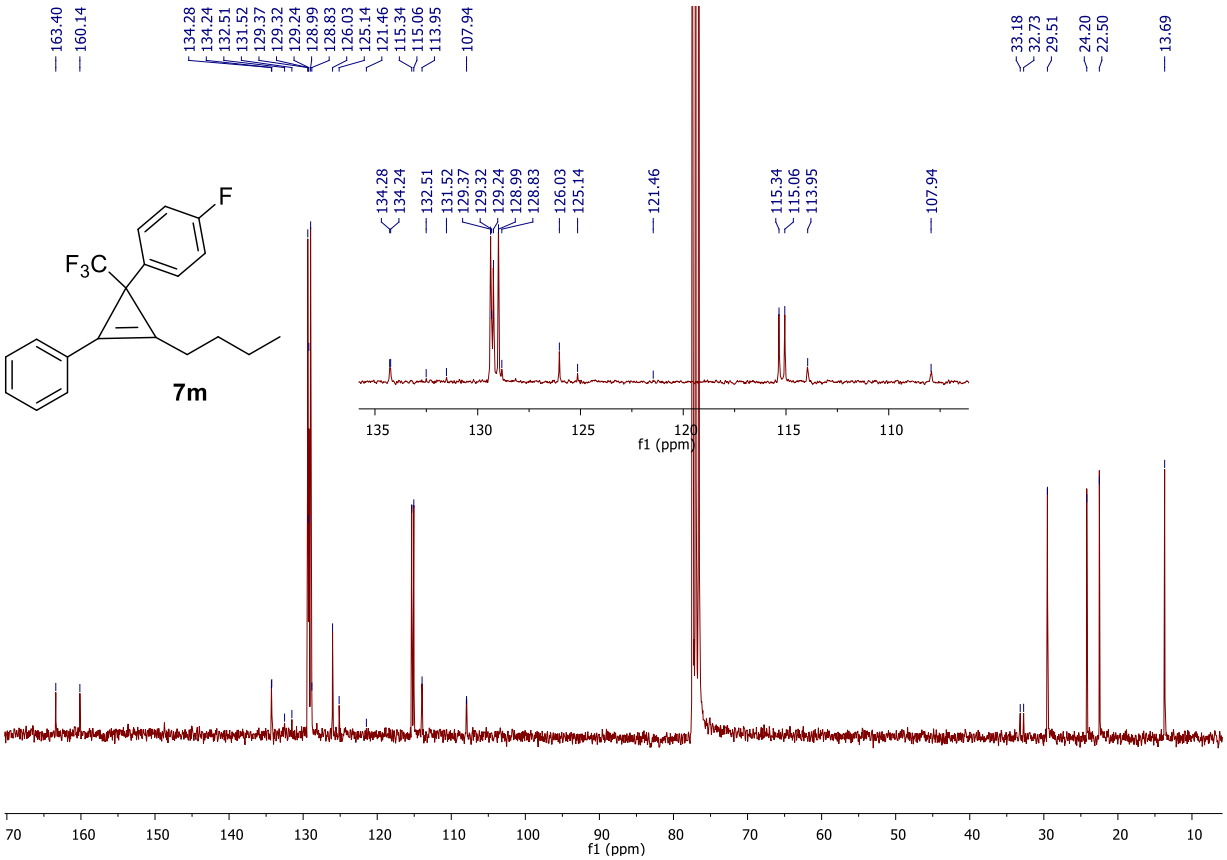

7.60
7.60
7.58
7.58
7.57
7.47
7.45
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.39
7.38
7.33
7.31
7.31
7.30
7.28
7.27
7.27
7.24
2.77
2.75
2.74
2.73
2.71
2.71
1.80
1.79
1.78
1.77
1.75
1.74
1.50
1.47
1.45
0.99
0.97
0.94
F3C
7k
1.74
3.95
3.57
1.73
1.91
2.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

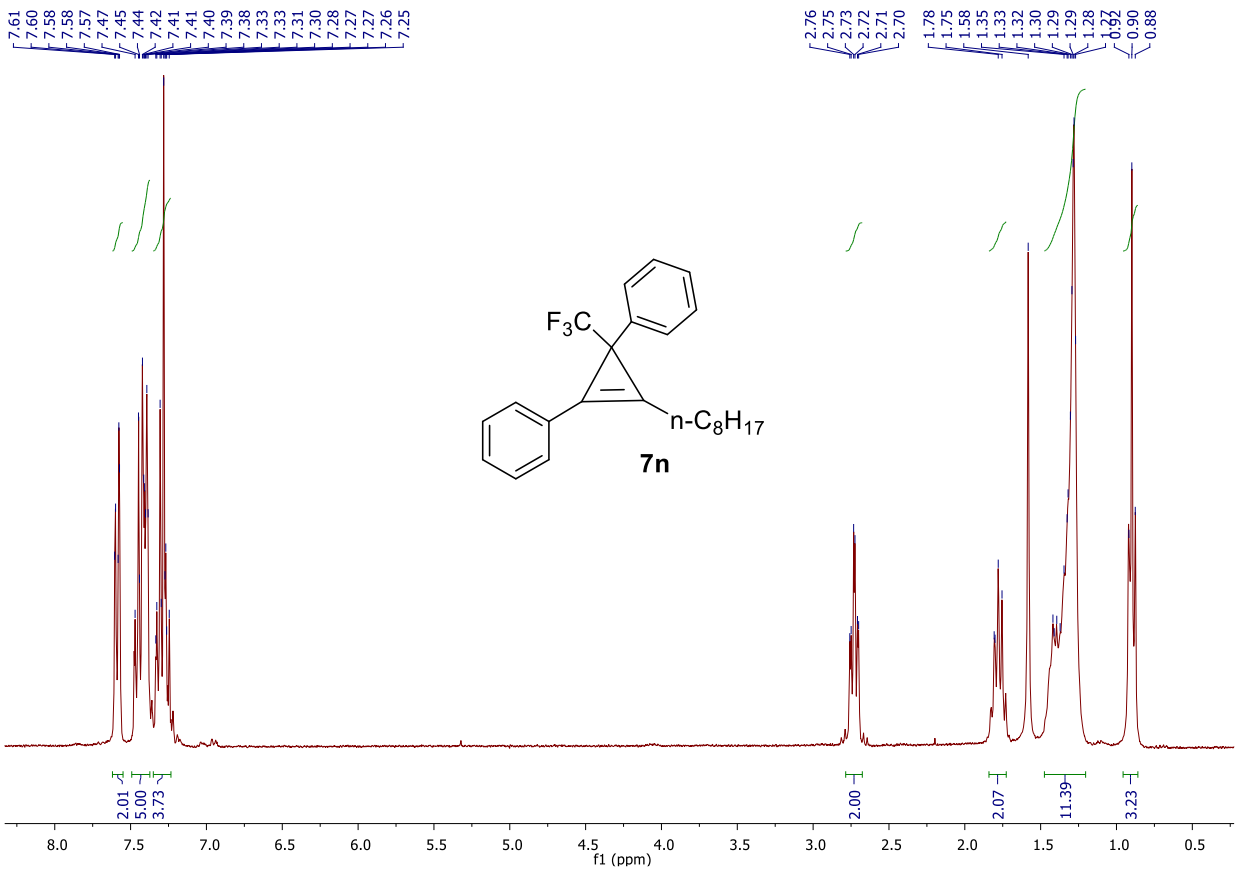

138.46
129.42
129.10
128.96
128.92
128.31
127.52
126.73
126.21
125.25
121.57
113.72
107.79
103.95
77.44 CDCl3
77.21
77.01 CDCl3
76.59 CDCl3
33.75
33.30
29.71
29.55
24.24
22.52
13.70
F3C
7k
130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

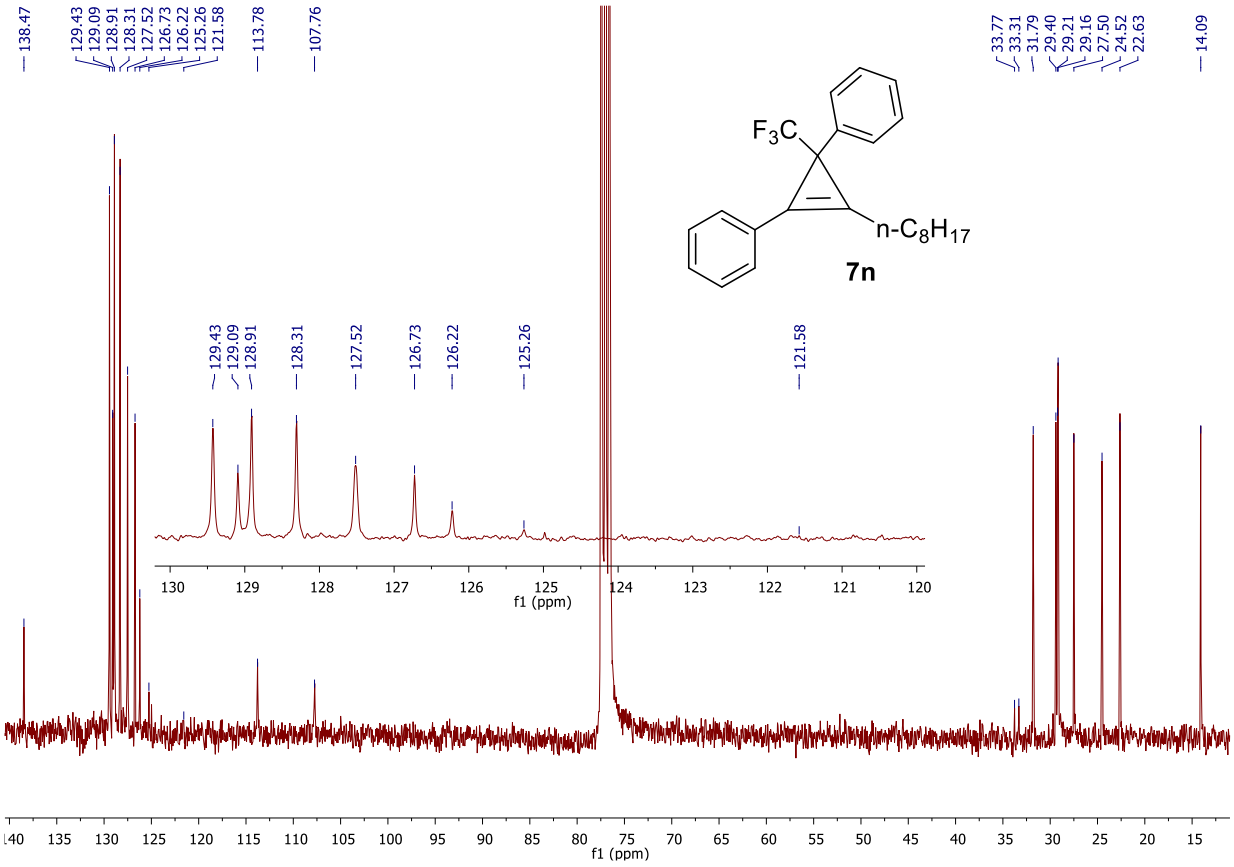

7.60 7.59 7.59 7.58 7.57 7.57 7.56 7.47 7.46 7.46 7.45 7.44 7.44 7.42 7.42 7.41 7.40 7.39 7.38 7.31 7.28 7.13 7.12 7.10
2.76 2.75 2.73 2.72 2.71 2.70 2.33
1.80 1.79 1.78 1.77 1.75 1.74 1.50 1.48 1.45 1.00 0.97 0.95
F3C
7l
2.03 3.14 3.14 2.06
2.00 3.13 2.08 2.20 3.13
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

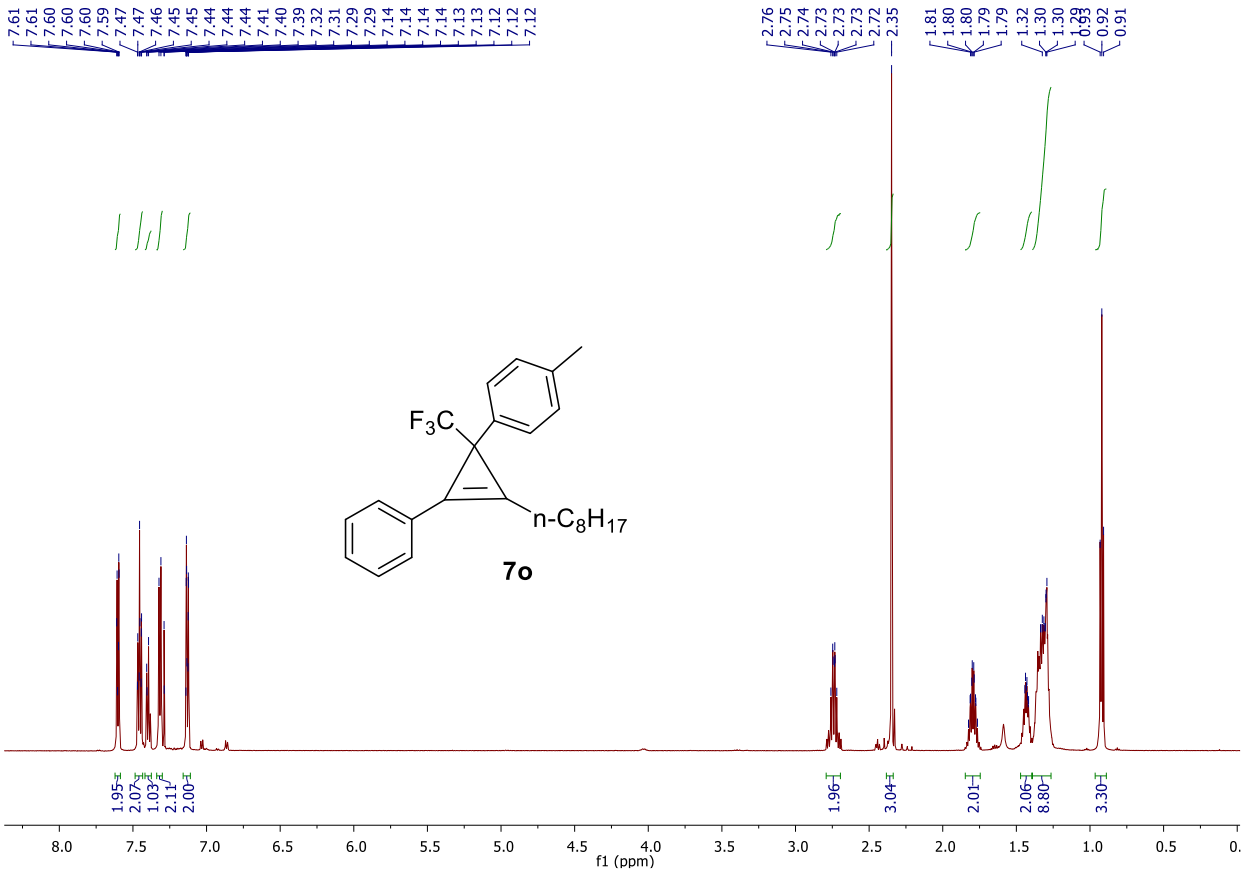

136.41 135.41 129.40 129.19 129.02 128.88 127.48 126.34 125.31 121.62 113.90 107.99
33.01 29.58 24.24 22.52 21.02 13.70
F3C
7l
129.40 129.19 129.02 128.88 127.48 126.34 125.31 121.62
130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

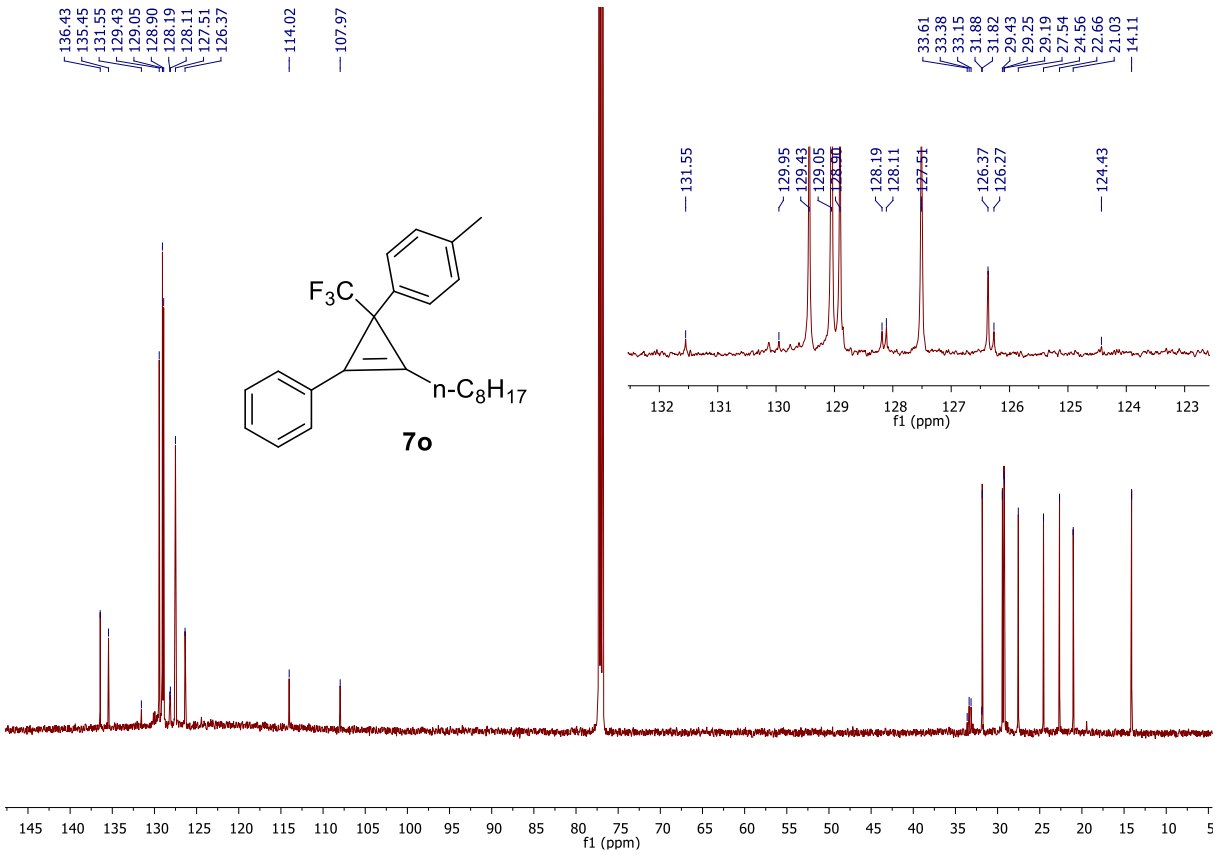

7.60
7.59
7.57
7.57
7.57
7.57
7.46
7.43
7.42
7.40
7.39
7.37
7.36
7.02
7.00
6.99
6.98
6.96
2.76
2.75
2.73
2.73
2.71
2.70
1.79
1.79
1.77
1.74
1.58
1.49
1.47
1.44
1.00
0.97
0.95
F
F3C
7m
1.93
4.91
1.94
2.00
2.02
2.14
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

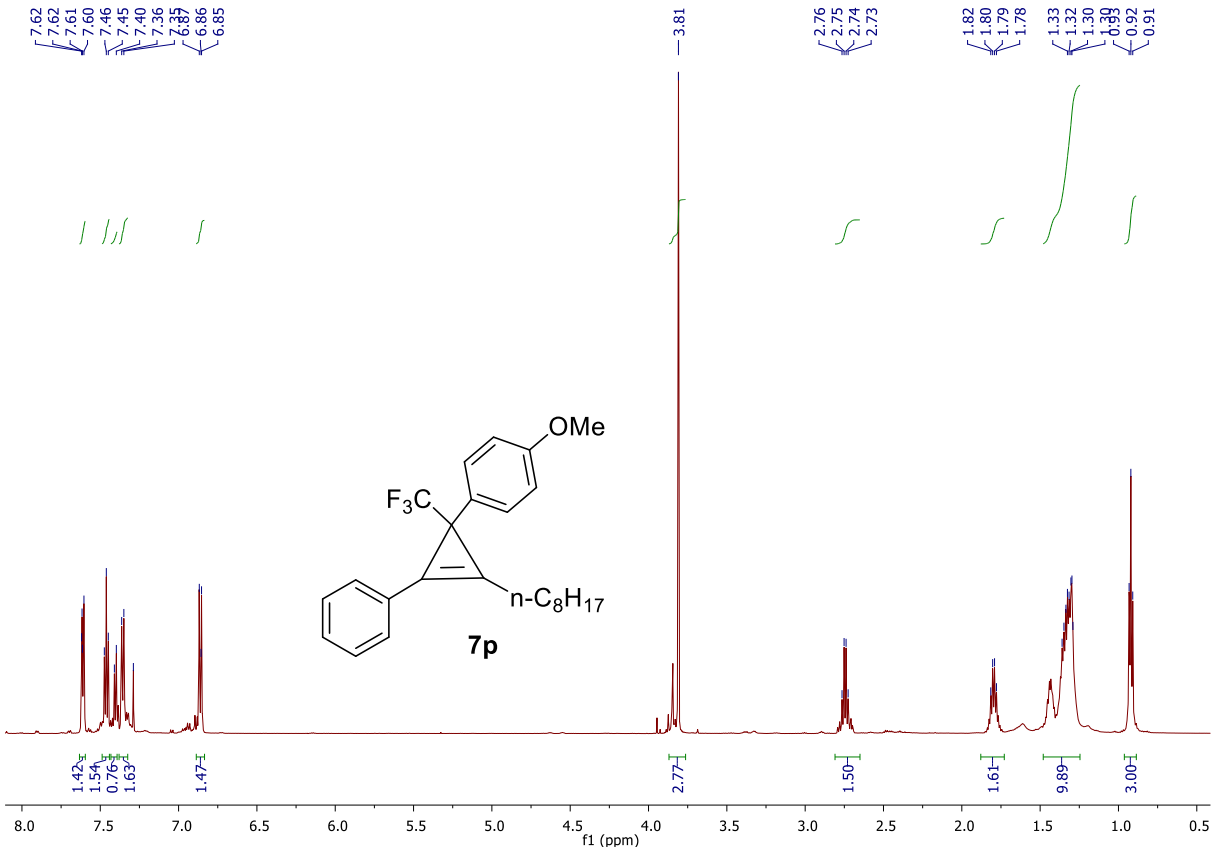

163.40
160.14
134.28
134.24
132.51
131.52
129.37
129.32
129.24
128.99
128.83
126.03
125.14
121.46
115.34
115.06
113.95
107.94
33.18
32.73
29.51
24.20
22.50
13.69
F
F3C
7m
135
130
125
120
115
110
f1 (ppm)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

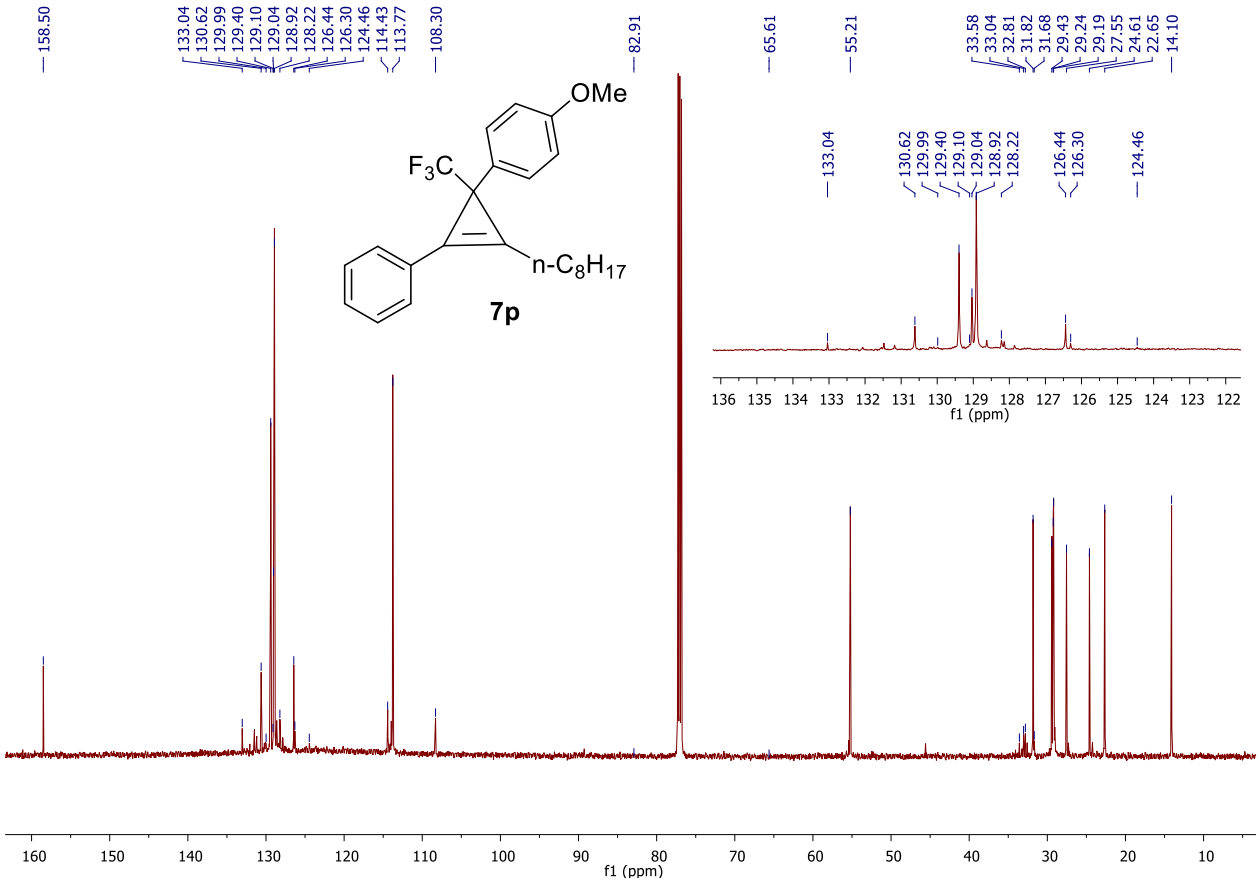

7.61
7.60
7.58
7.58
7.57
7.47
7.45
7.44
7.42
7.41
7.41
7.40
7.39
7.38
7.33
7.31
7.30
7.28
7.27
7.27
7.26
7.25
2.76
2.75
2.73
2.72
2.71
2.70
1.78
1.75
1.58
1.35
1.33
1.32
1.30
1.29
1.29
1.28
0.92
0.90
0.88
F3C
n-C8H17
7n
2.01
5.00
3.73
2.00
2.07
11.39
3.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

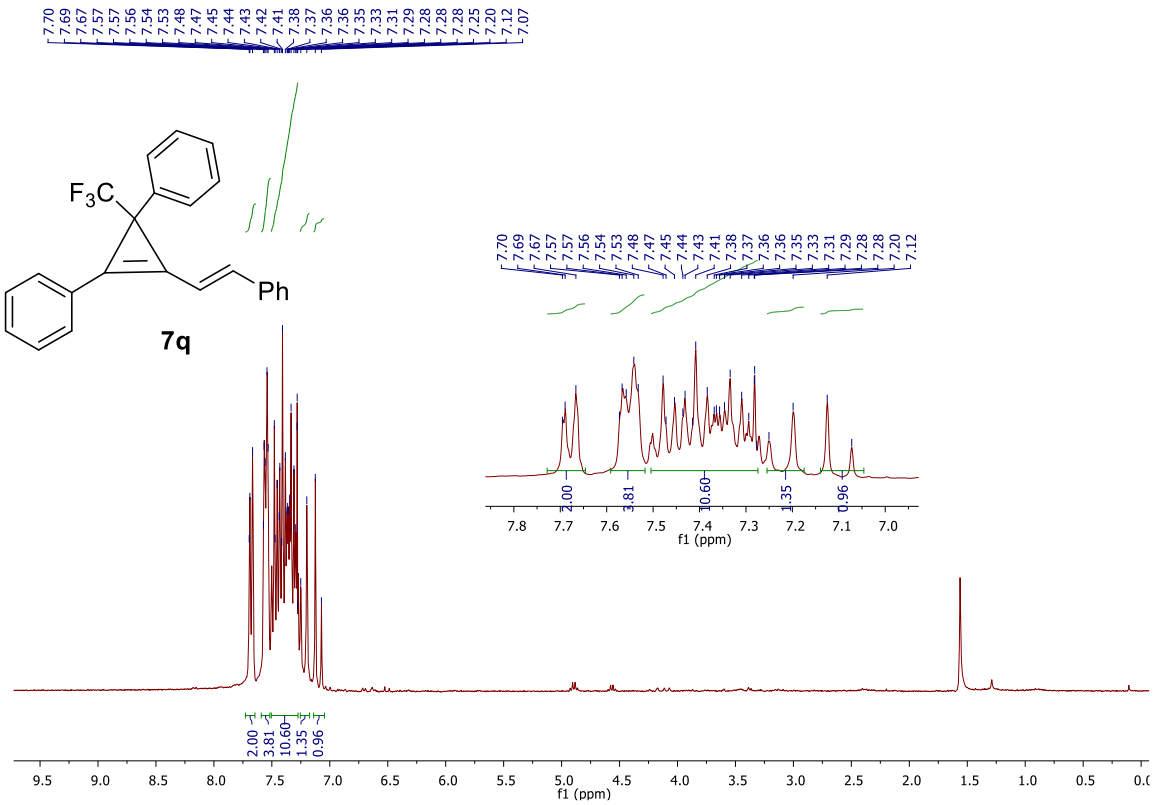

138.47
129.43
129.09
128.91
128.31
127.52
126.73
126.22
125.26
121.58
113.78
107.76
33.77
33.31
31.79
29.40
29.21
29.16
27.50
24.52
22.63
14.09
F3C
n-C8H17
7n
129.43
129.09
128.91
128.31
127.52
126.73
126.22
125.26
121.58
130
129
128
127
126
125
124
123
122
121
120
f1 (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

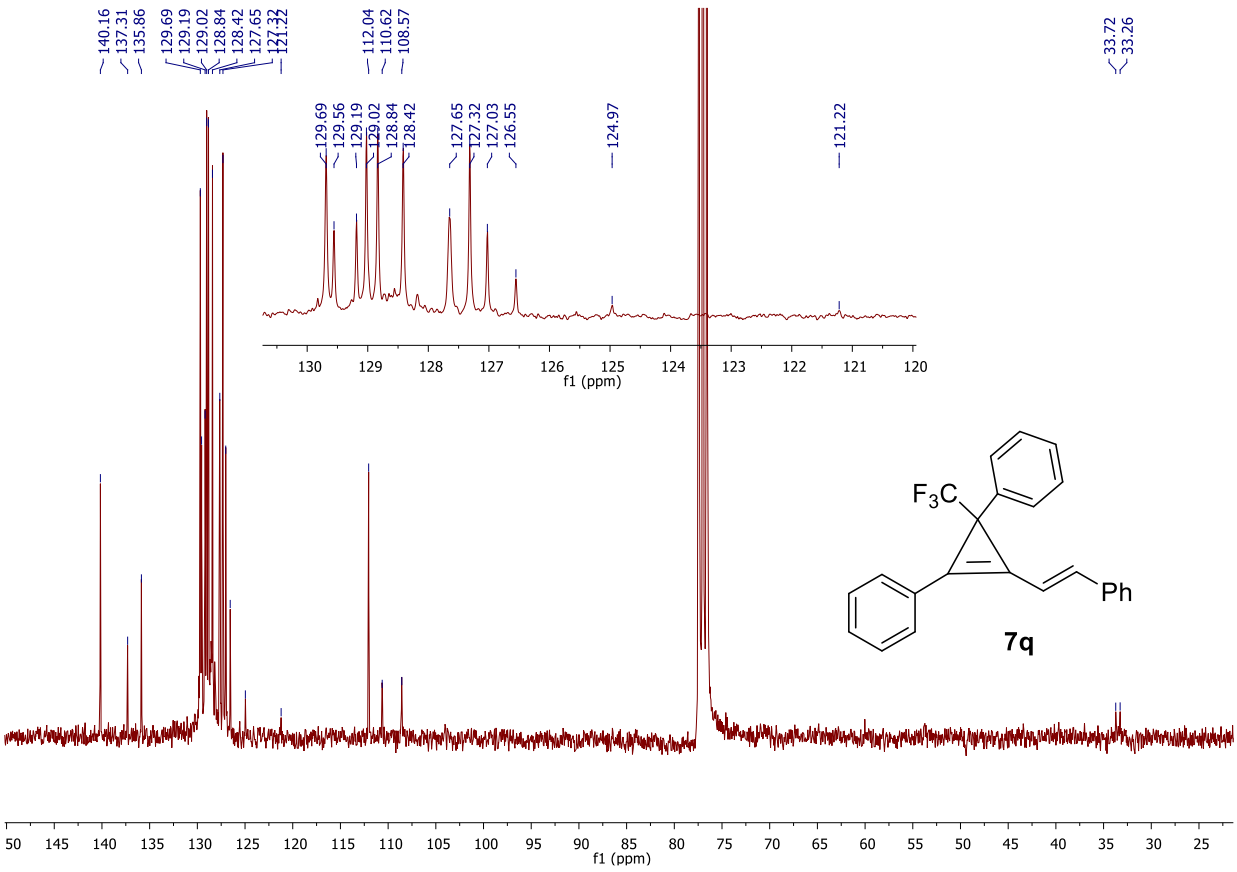

7.61 7.61 7.60 7.60 7.60 7.59 7.47 7.47 7.46 7.45 7.45 7.44 7.44 7.44 7.41 7.40 7.39 7.32 7.31 7.29 7.29 7.14 7.14 7.14 7.13 7.12 7.12 7.12
2.76 2.75 2.74 2.73 2.73 2.72 2.35
1.81 1.80 1.80 1.79 1.79 1.32 1.30 1.30 0.93 0.92 0.91
F3C
n-C8H17
7o
1.95 2.07 1.03 2.11 2.00 1.96 3.04 2.01 2.06 8.80 3.30
f1 (ppm)

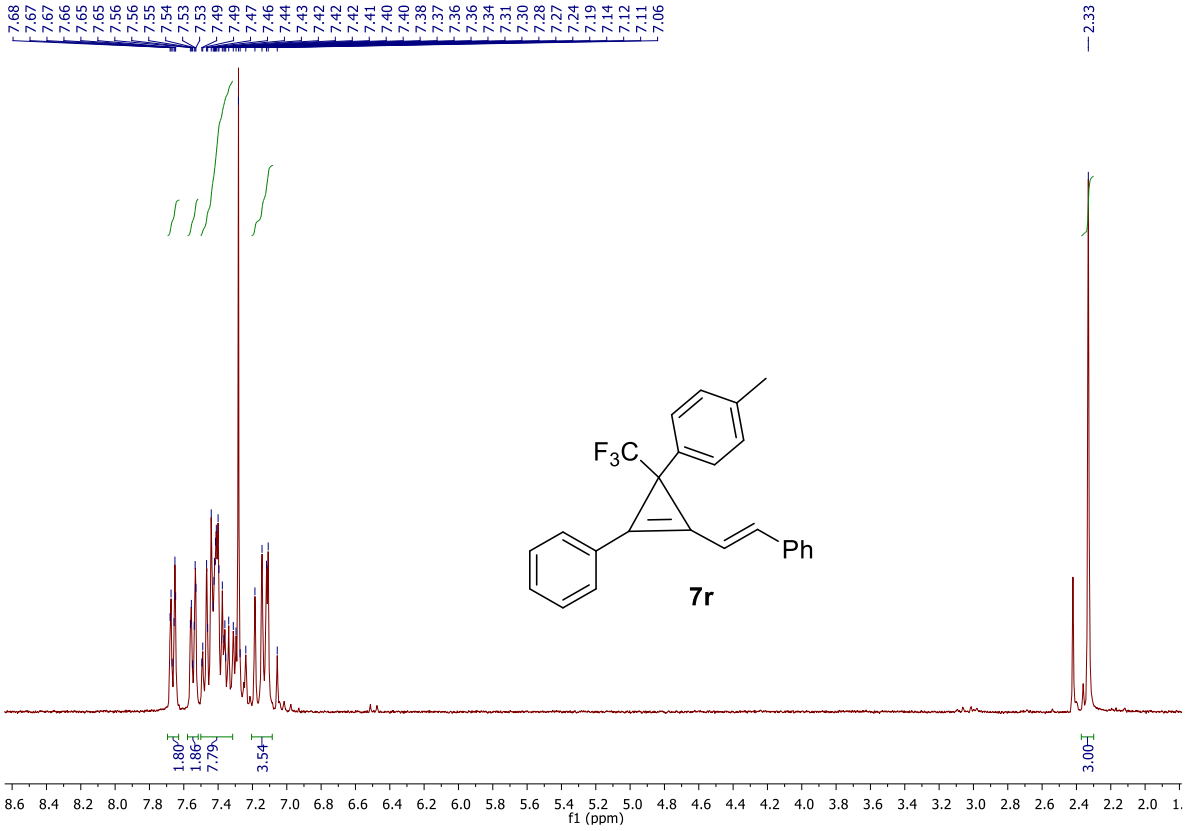

136.43 135.45 131.55 129.43 129.05 128.90 128.19 128.11 127.51 126.37 114.02 107.97
33.61 33.38 33.15 31.88 31.82 29.43 29.25 29.19 27.54 24.56 22.66 21.03 14.11
131.55 129.95 129.43 129.05 128.90 128.19 128.11 127.51 126.37 126.27 124.43
F3C
n-C8H17
7o
f1 (ppm)

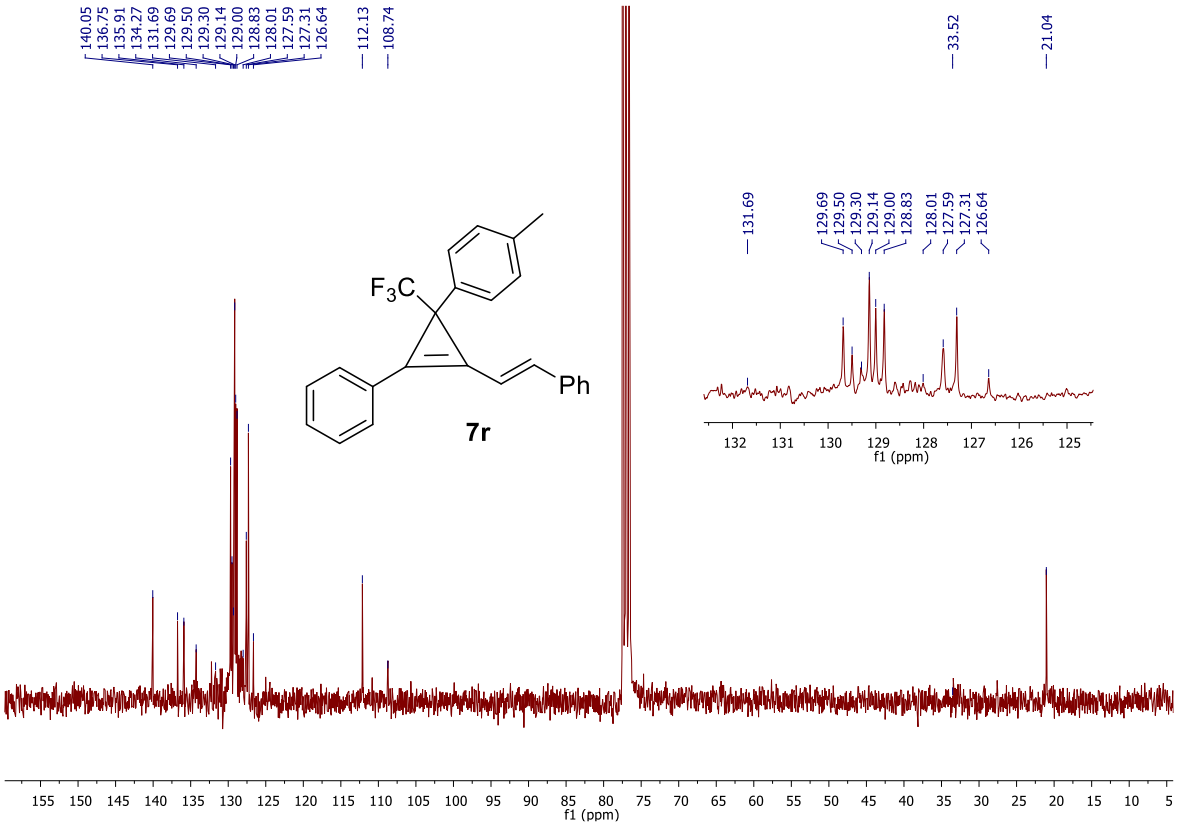

7.62
7.62
7.61
7.60
7.46
7.45
7.40
7.36
6.87
6.86
6.85
3.81
2.76
2.75
2.74
2.73
1.82
1.80
1.79
1.78
1.33
1.32
1.30
0.93
0.92
0.91
OMe
F3C
n-C8H17
7p
1.42
1.54
0.76
1.63
1.47
2.77
1.50
1.61
9.89
3.00
f1 (ppm)

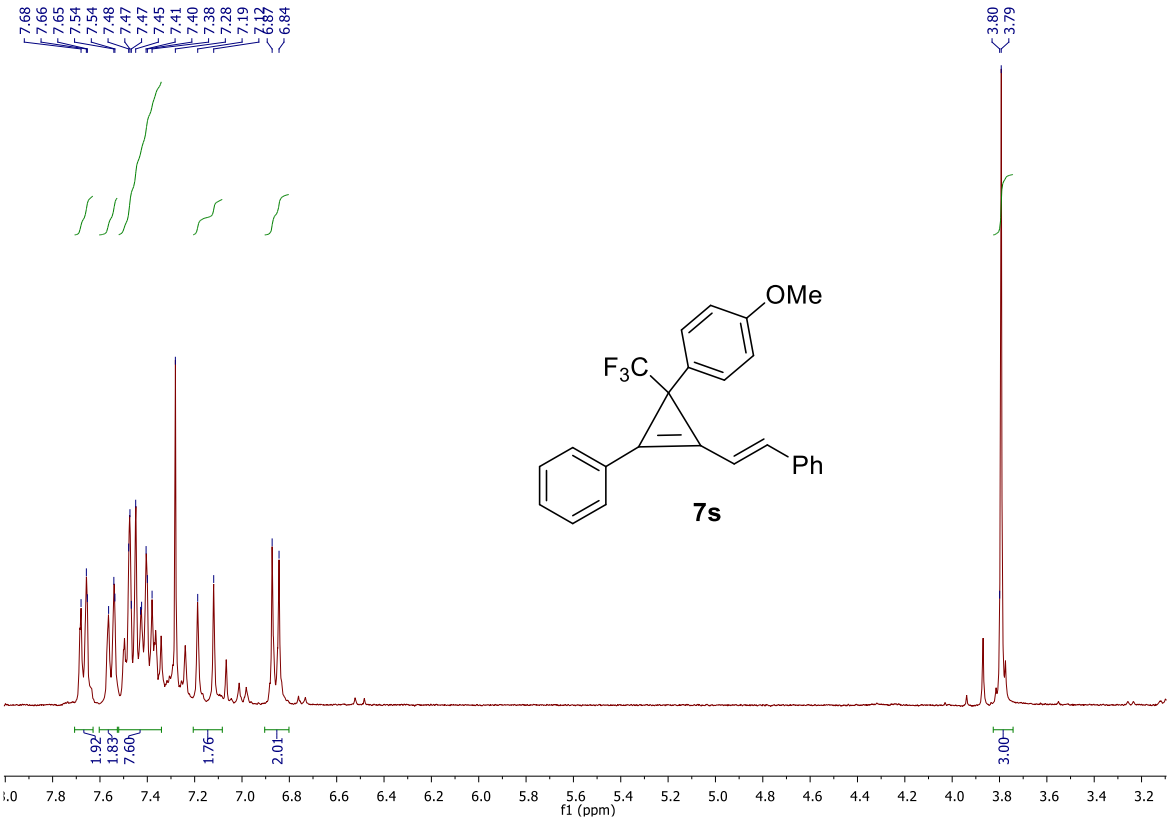

158.50
133.04
130.62
129.99
129.40
129.10
129.04
128.92
128.22
126.44
126.30
124.46
114.43
113.77
108.30
82.91
65.61
55.21
33.58
33.04
32.81
31.82
31.68
29.43
29.24
29.19
27.55
24.61
22.65
14.10
OMe
F3C
n-C8H17
7p
f1 (ppm)

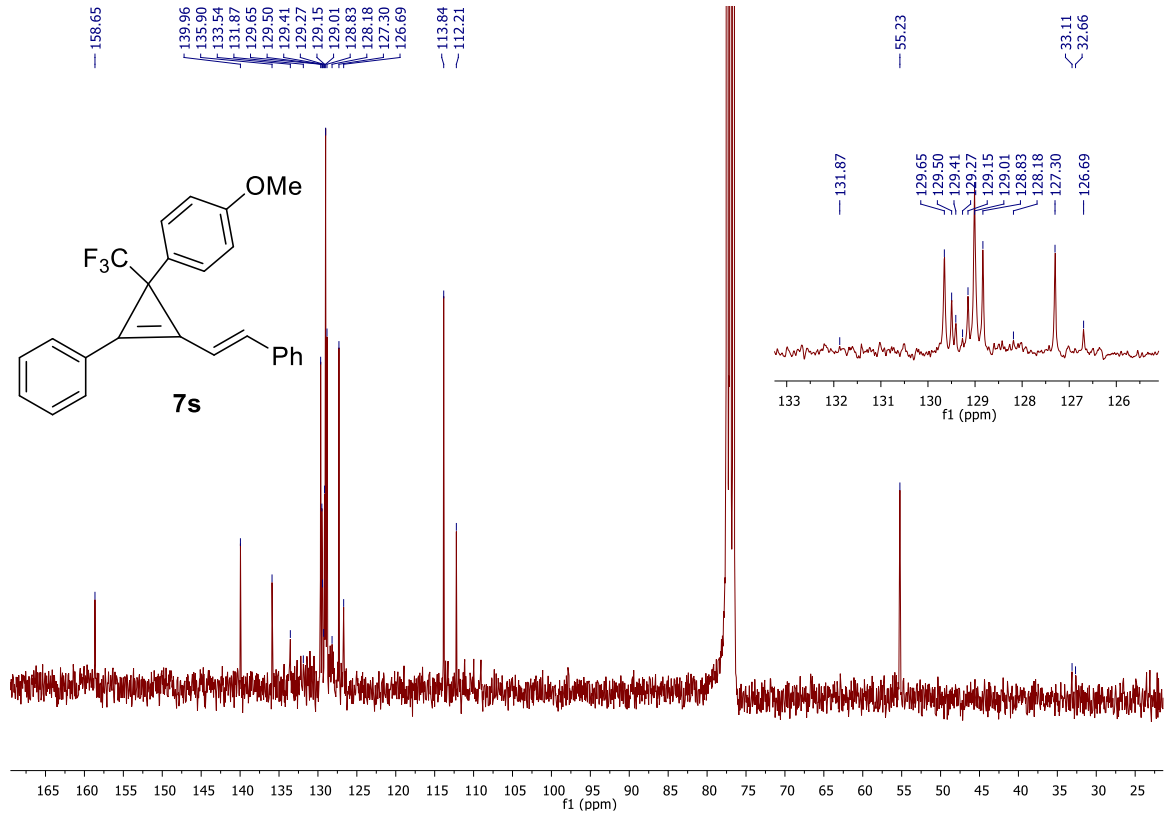

7.70
7.69
7.67
7.57
7.57
7.56
7.54
7.53
7.48
7.47
7.45
7.44
7.43
7.42
7.41
7.38
7.37
7.36
7.36
7.35
7.33
7.31
7.29
7.28
7.28
7.25
7.20
7.12
7.07
F3C
Ph
7q
2.00
3.81
10.60
1.35
0.96
f1 (ppm)

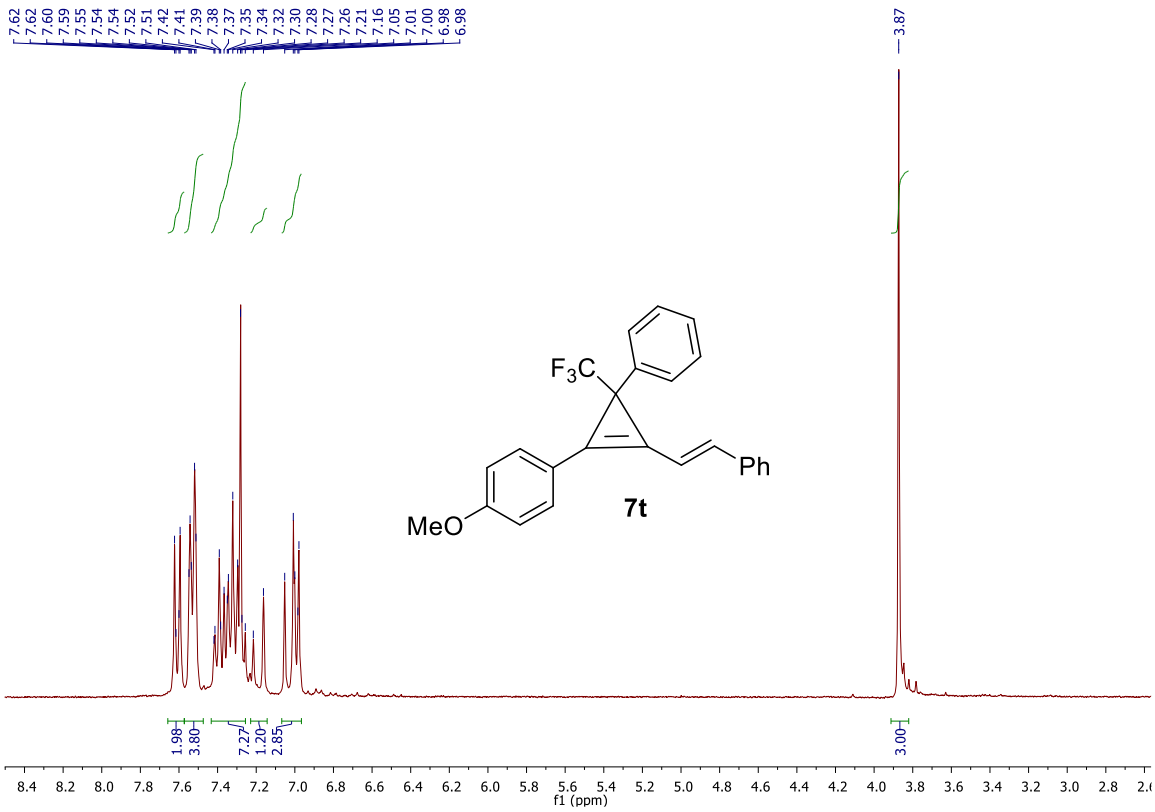

140.16
137.31
135.86
129.69
129.19
129.02
128.84
128.42
127.65
127.32
121.22
112.04
110.62
108.57
33.72
33.26
129.69
129.56
129.19
129.02
128.84
128.42
127.65
127.32
127.03
126.55
124.97
121.22
f1 (ppm)
F3C
Ph
7q
f1 (ppm)

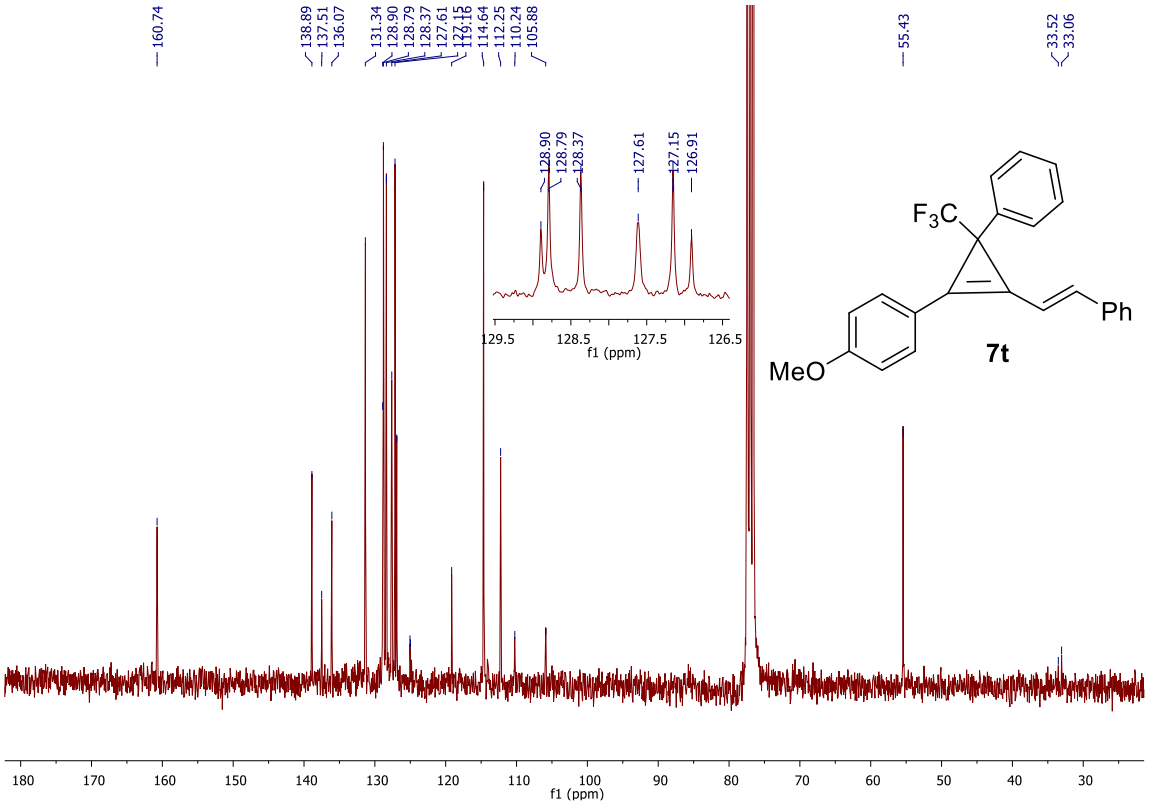

7.68 7.67 7.67 7.66 7.65 7.65 7.56 7.56 7.55 7.54 7.53 7.53 7.49 7.49 7.47 7.46 7.44 7.43 7.42 7.42 7.42 7.41 7.40 7.40 7.38 7.37 7.36 7.36 7.34 7.31 7.30 7.28 7.27 7.24 7.19 7.14 7.12 7.11 7.06
2.33
F3C
Ph
7r
1.80
1.86
7.79
3.54
3.00
f1 (ppm)

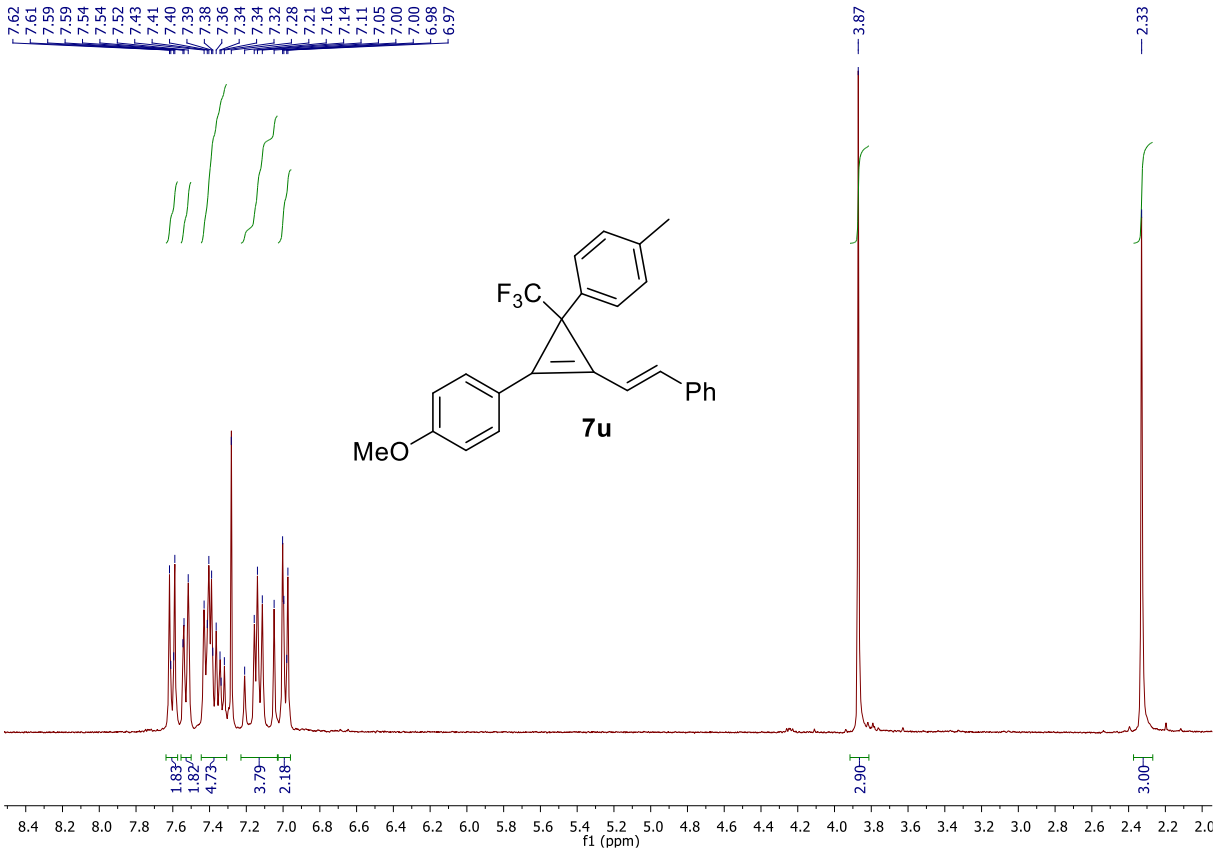

140.05 136.75 135.91 134.27 131.69 129.69 129.50 129.30 129.14 129.00 128.83 128.01 127.59 127.31 126.64
112.13
108.74
33.52
21.04
131.69
129.69 129.50 129.30 129.14 129.00 128.83 128.01 127.59 127.31 126.64
F3C
Ph
7r
f1 (ppm)

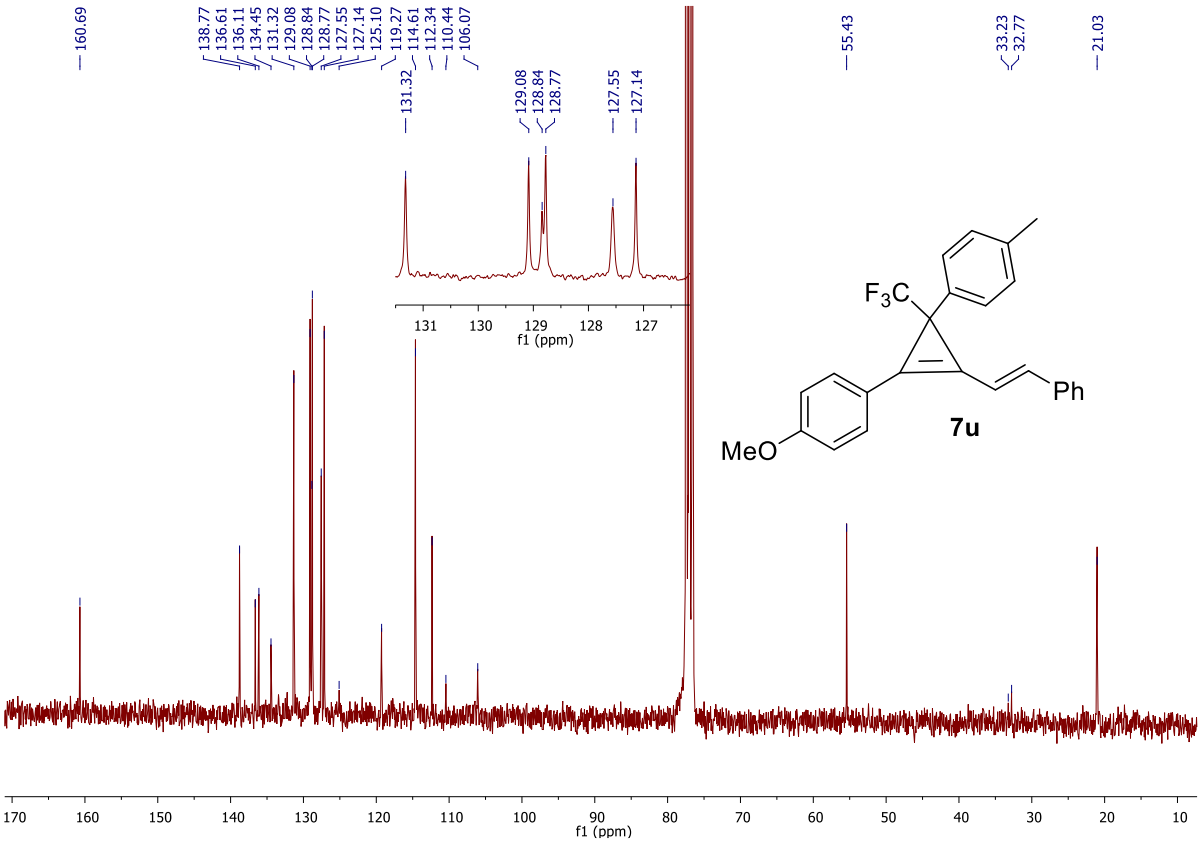

7.68
7.66
7.65
7.54
7.54
7.48
7.47
7.47
7.45
7.41
7.40
7.38
7.28
7.19
7.12
6.87
6.84
3.80
3.79
OMe
F3C
Ph
7s
1.92
1.83
7.60
1.76
2.01
3.00
f1 (ppm)

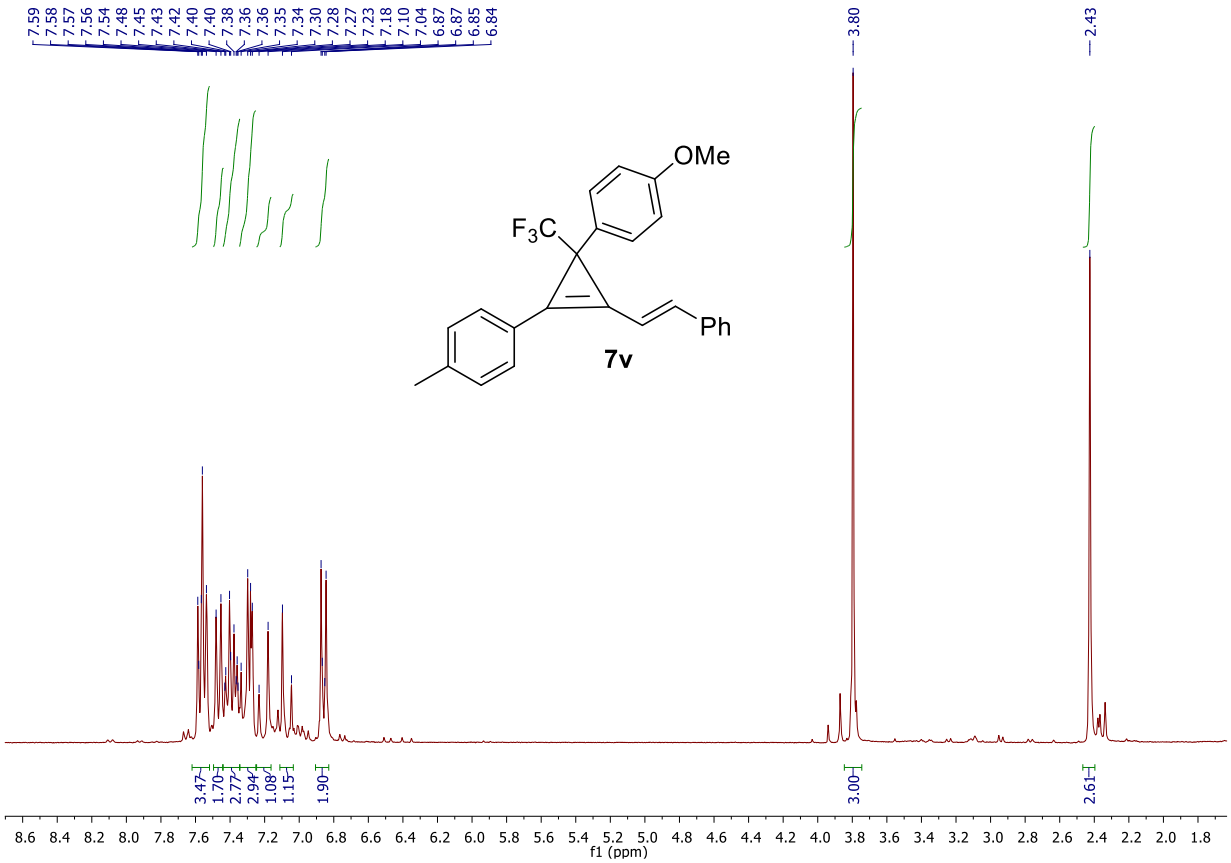

158.65
139.96
135.90
133.54
131.87
129.65
129.50
129.41
129.27
129.15
129.01
128.83
128.18
127.30
126.69
113.84
112.21
55.23
33.11
32.66
OMe
F3C
Ph
7s
131.87
129.65
129.50
129.41
129.27
129.15
129.01
128.83
128.18
127.30
126.69
f1 (ppm)
f1 (ppm)

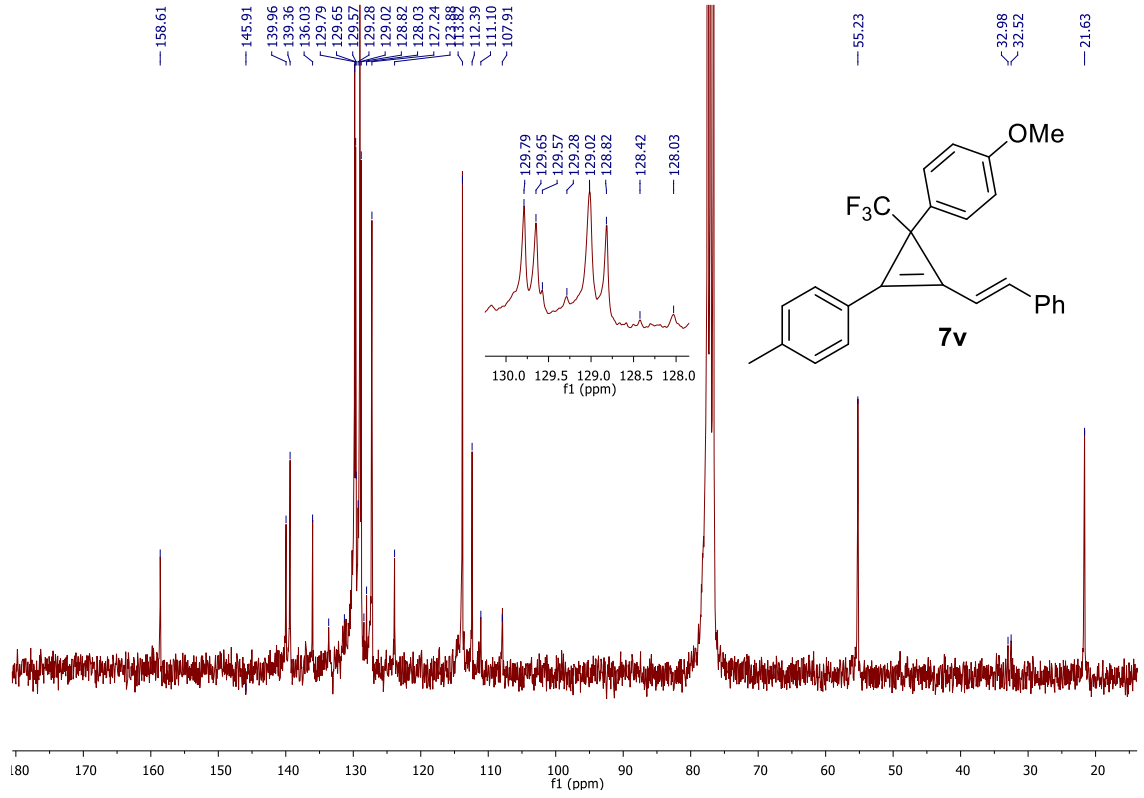

7.62
7.62
7.60
7.59
7.55
7.54
7.54
7.52
7.51
7.42
7.41
7.39
7.38
7.37
7.35
7.34
7.32
7.30
7.28
7.27
7.26
7.21
7.16
7.05
7.01
7.00
6.98
6.98
3.87
1.98
3.80
7.27
1.20
2.85
3.00
F3C
Ph
MeO
7t
f1 (ppm)

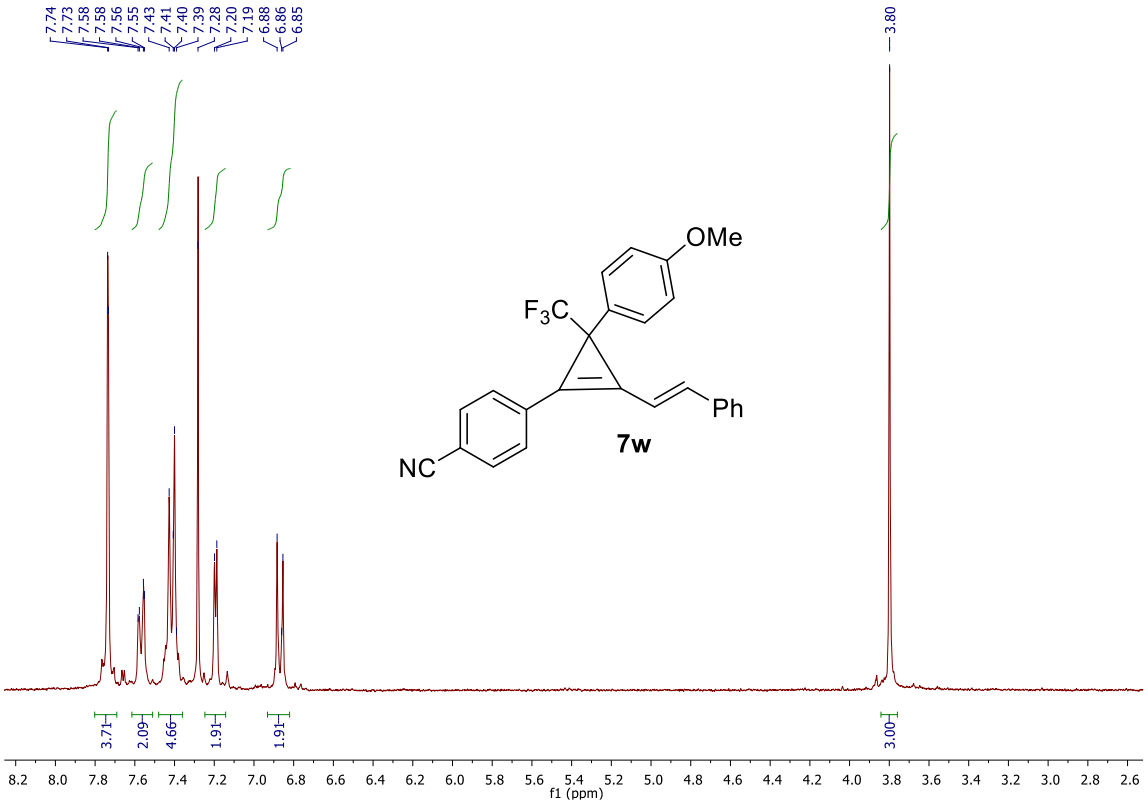

160.74
138.89
137.51
136.07
131.34
128.90
128.79
128.37
127.61
127.15
126.91
114.64
112.25
110.24
105.88
55.43
33.52
33.06
F3C
Ph
MeO
7t
f1 (ppm)

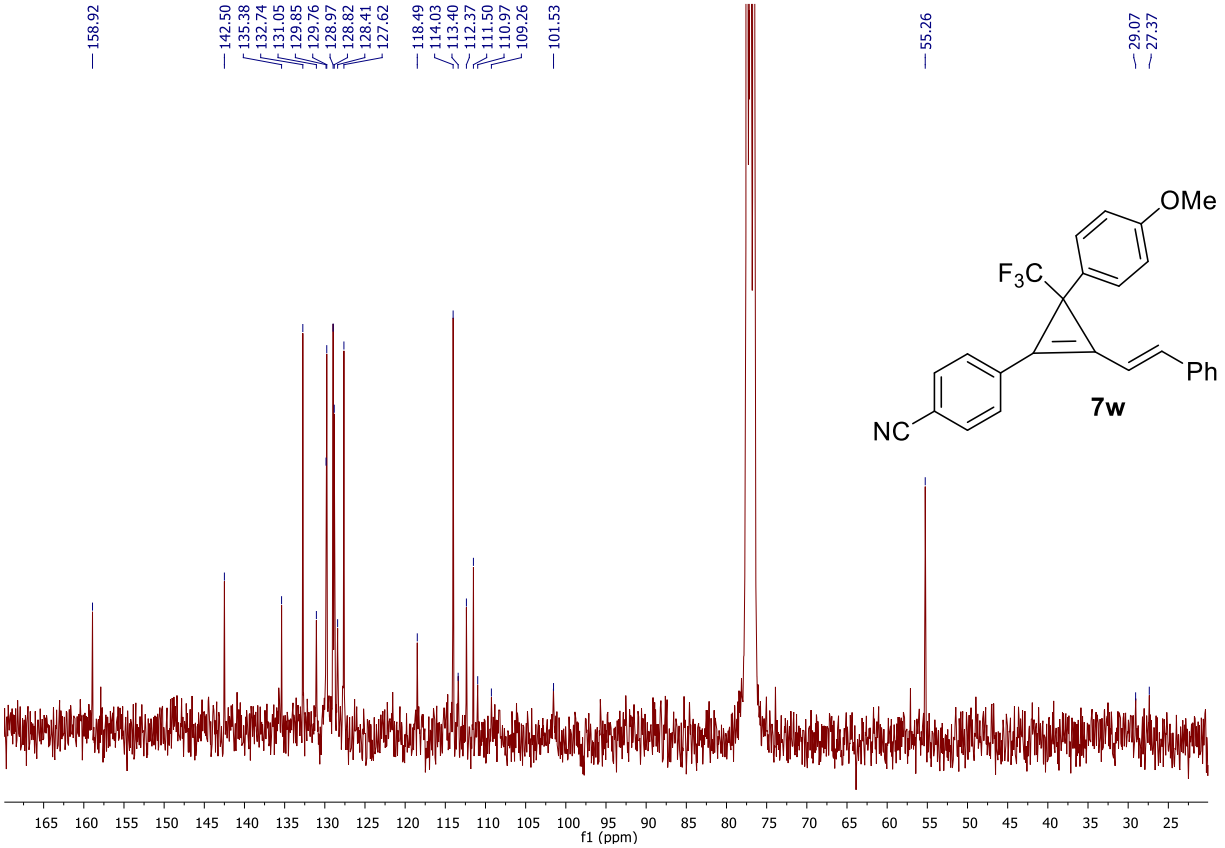

7.62
7.61
7.59
7.59
7.54
7.54
7.52
7.43
7.41
7.40
7.39
7.38
7.36
7.34
7.34
7.32
7.28
7.21
7.16
7.14
7.11
7.05
7.00
7.00
6.98
6.97
3.87
2.33
F3C
Ph
MeO
7u
1.83
1.82
4.73
3.79
2.18
2.90
3.00
f1 (ppm)

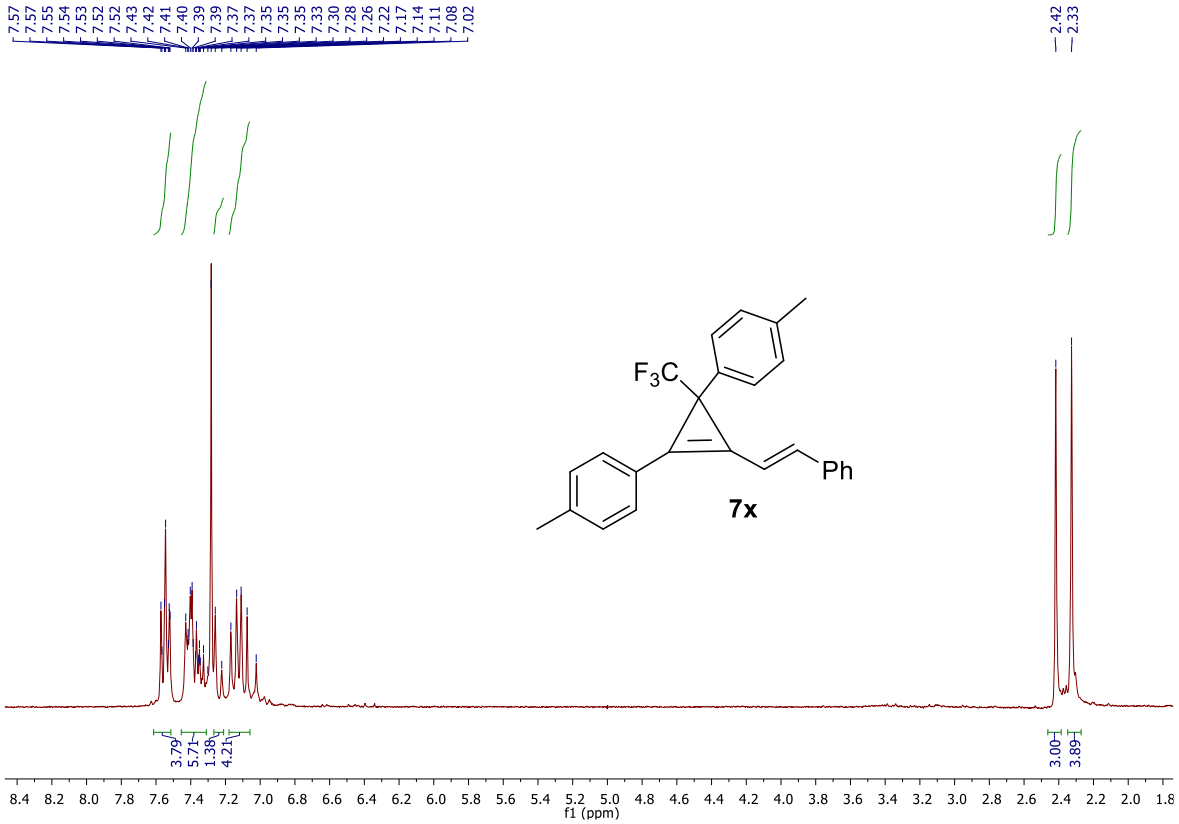

160.69
138.77
136.61
136.11
134.45
131.32
129.08
128.84
128.77
127.55
127.14
125.10
119.27
114.61
112.34
110.44
106.07
55.43
33.23
32.77
21.03
131.32
129.08
128.84
128.77
127.55
127.14
f1 (ppm)
F3C
Ph
MeO
7u
f1 (ppm)

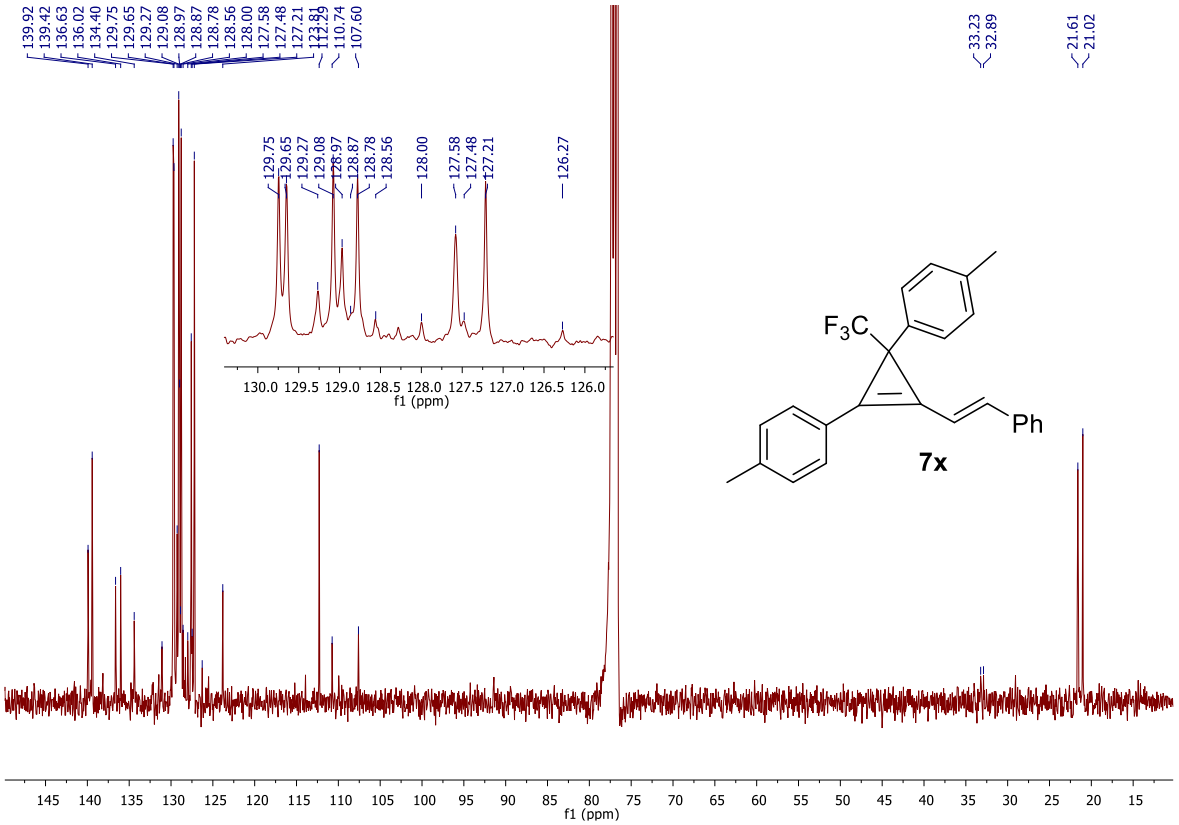

7.59
7.58
7.57
7.56
7.54
7.48
7.45
7.43
7.42
7.40
7.40
7.38
7.36
7.36
7.35
7.34
7.30
7.28
7.27
7.23
7.18
7.10
7.04
6.87
6.87
6.85
6.84
3.80
2.43
OMe
F3C
Ph
7v
3.47
1.70
2.77
2.94
1.08
1.15
1.90
3.00
2.61
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)


158.61
145.91
139.96
139.36
136.03
129.79
129.65
129.57
129.28
129.02
128.82
128.03
127.24
112.39
111.10
107.91
55.23
32.98
32.52
21.63
129.79
129.65
129.57
129.28
129.02
128.82
128.42
128.03
130.0 129.5 129.0 128.5 128.0
f1 (ppm)
OMe
F3C
Ph
7v
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


7.74
7.73
7.58
7.58
7.56
7.55
7.43
7.41
7.40
7.39
7.28
7.20
7.19
6.88
6.86
6.85
3.80
OMe
F3C
Ph
NC
7w
3.71
2.09
4.66
1.91
1.91
3.00
f1 (ppm)

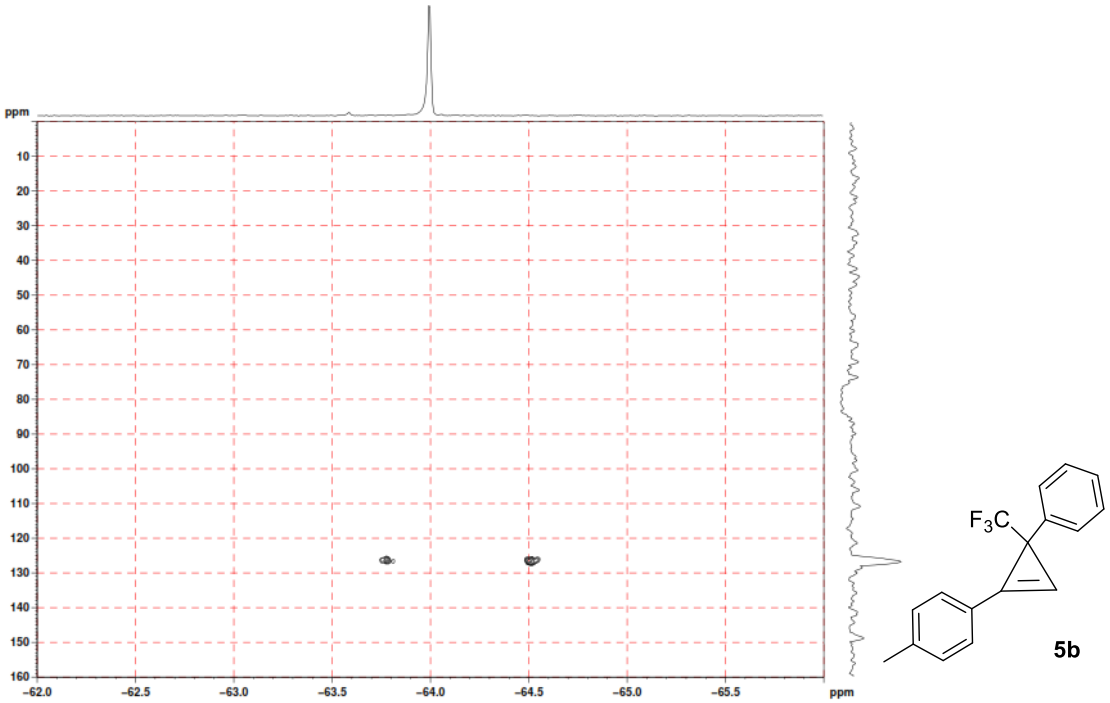

158.92
142.50
135.38
132.74
131.05
129.85
129.76
128.97
128.82
128.41
127.62
118.49
114.03
113.40
112.37
111.50
110.97
109.26
101.53
55.26
29.07
27.37
OMe
F3C
Ph
NC
7w
f1 (ppm)


7.57
7.57
7.55
7.54
7.53
7.52
7.52
7.43
7.42
7.41
7.40
7.39
7.39
7.37
7.37
7.35
7.35
7.33
7.30
7.28
7.26
7.22
7.17
7.14
7.11
7.08
7.02
2.42
2.33
F3C
Ph
7x
3.79
5.71
1.38
4.21
3.00
3.89
f1 (ppm)

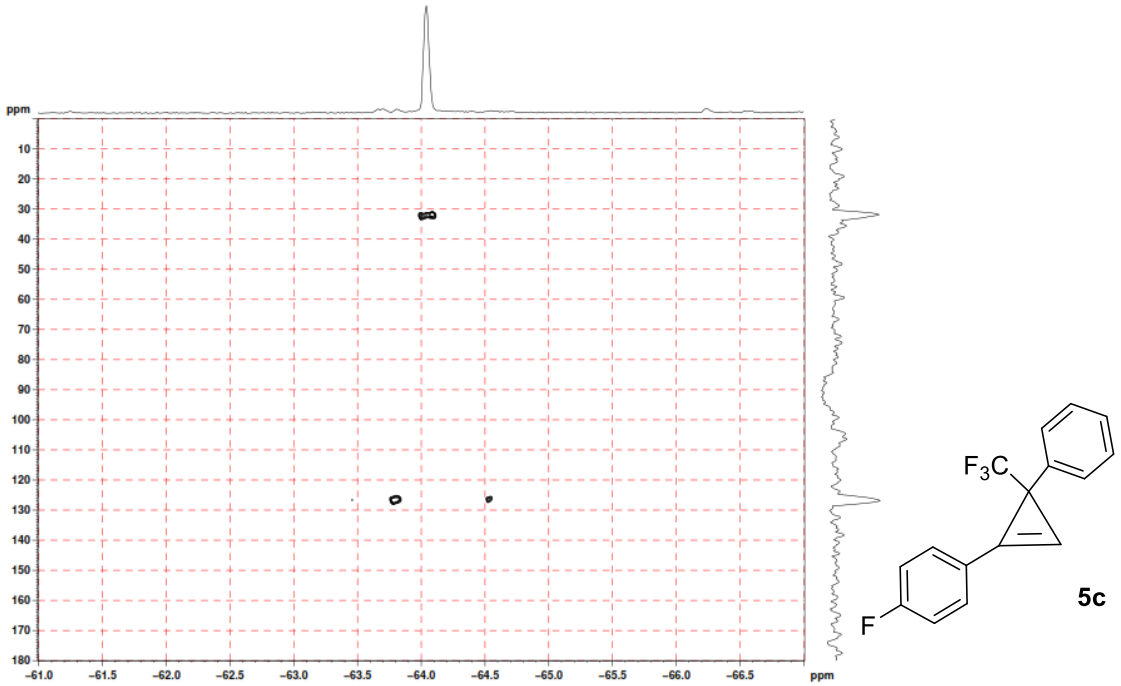

139.92
139.42
136.63
136.02
134.40
129.75
129.65
129.27
129.08
128.97
128.87
128.78
128.56
128.00
127.58
127.48
127.21
110.74
107.60
33.23
32.89
21.61
21.02
129.75
129.65
129.27
129.08
128.97
128.87
128.78
128.56
128.00
127.58
127.48
127.21
126.27
130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
f1 (ppm)
F3C
Ph
7x
f1 (ppm)

6. HMQC (C-F) NMR Spectra

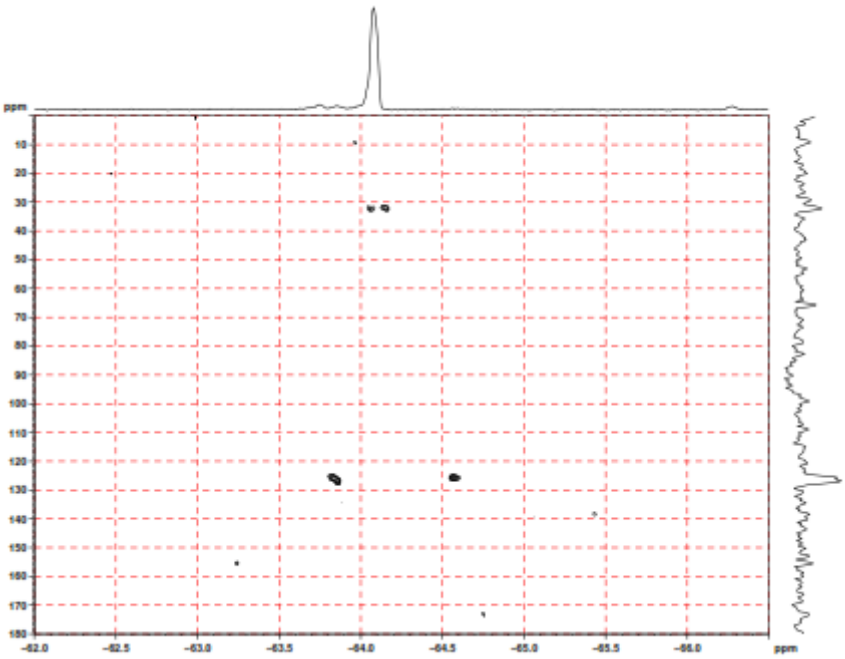
HMQC (C-F) experiments are provided to locate the chemical shift for *C*F_3 (~ 126 ppm) and *C*-CF_3 (~ 30 ppm) in ^{13}C NMR for those examples in which it could not be identified in the 1D ^{13}C NMR due to overlapping with aromatic signals and very slow relaxation respectively.

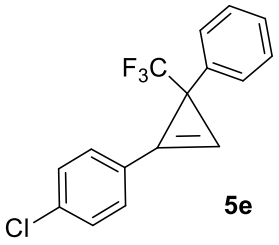


5b

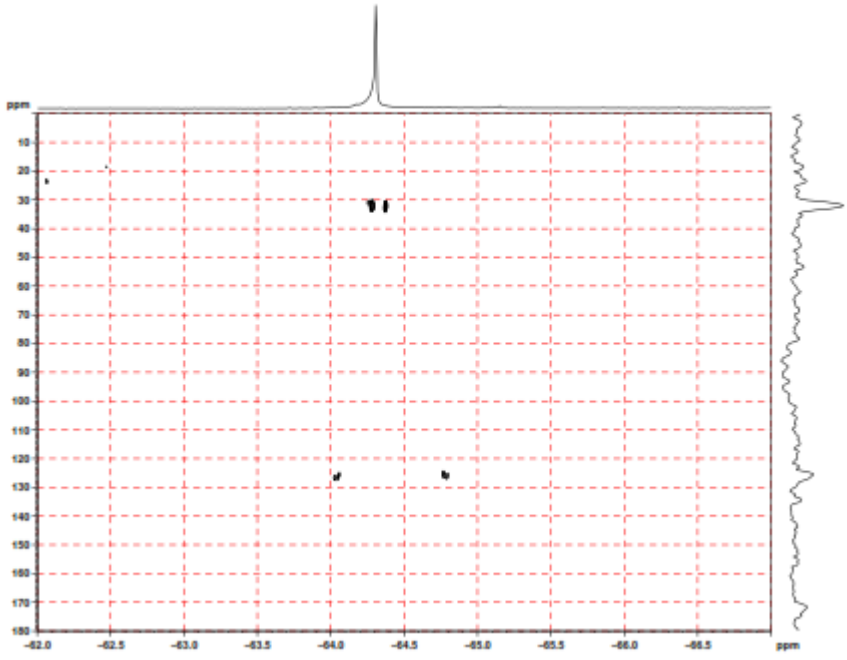


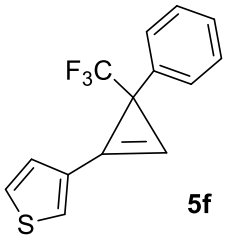
5c



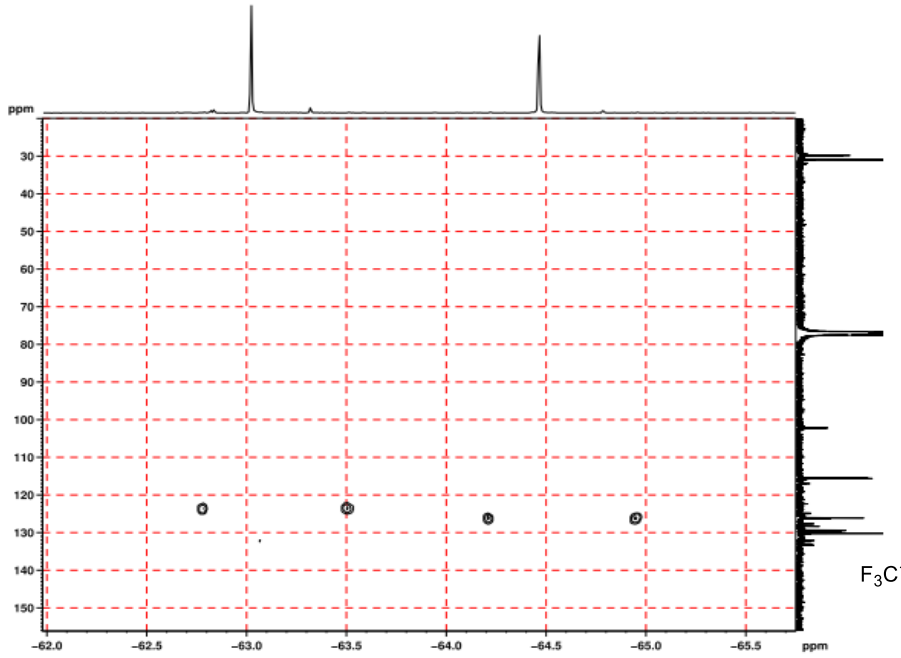


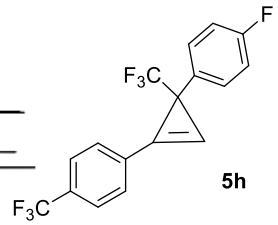
5e



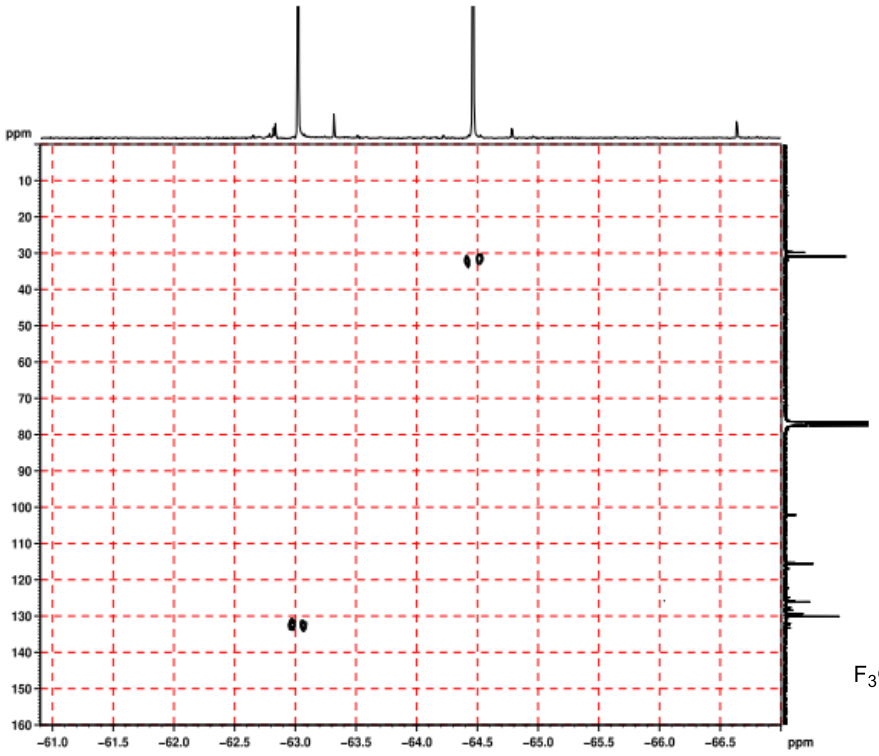


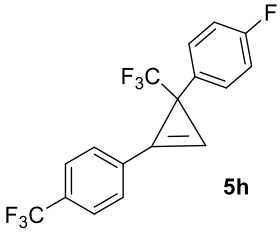
5f


ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
−62.0
−62.5
−63.0
−63.5
−64.0
−64.5
−65.0
−65.5
ppm

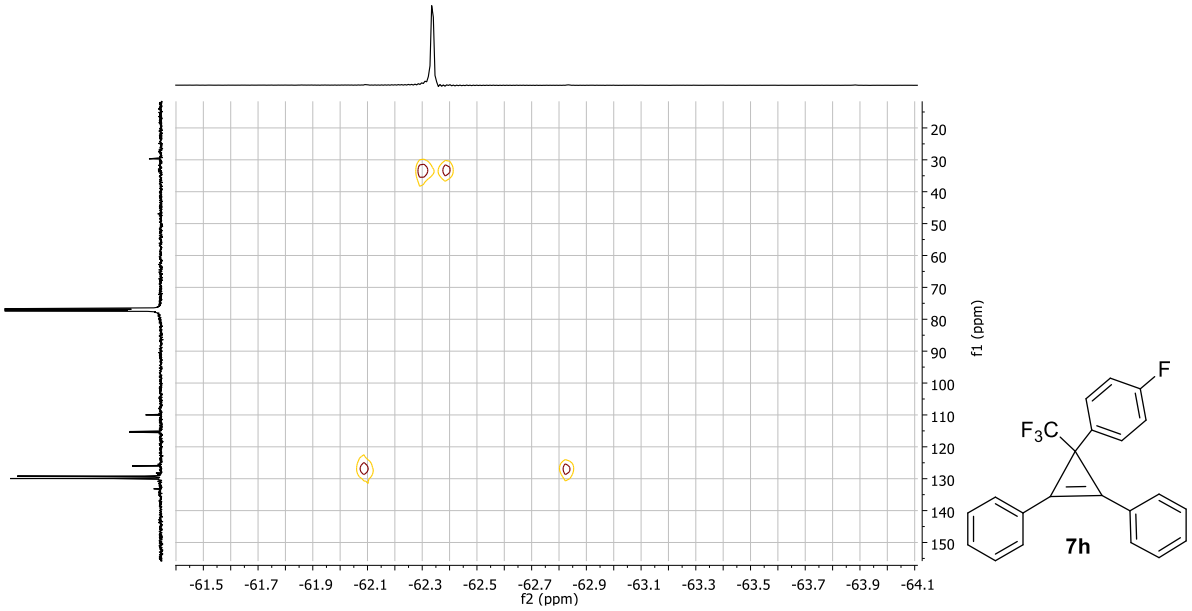

F
F3C
F3C

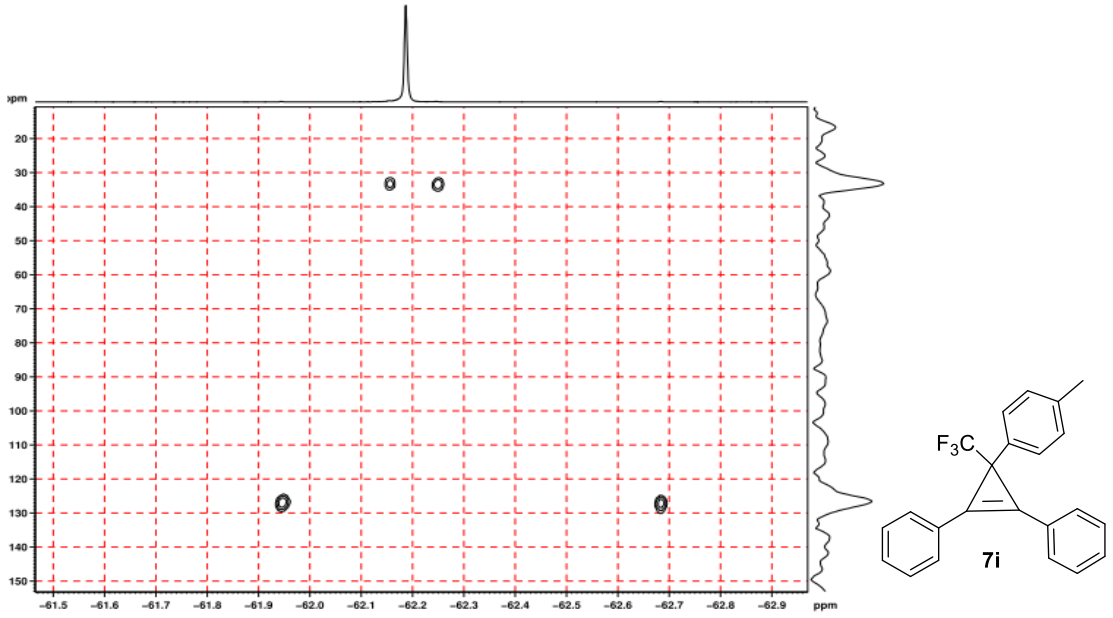
5h

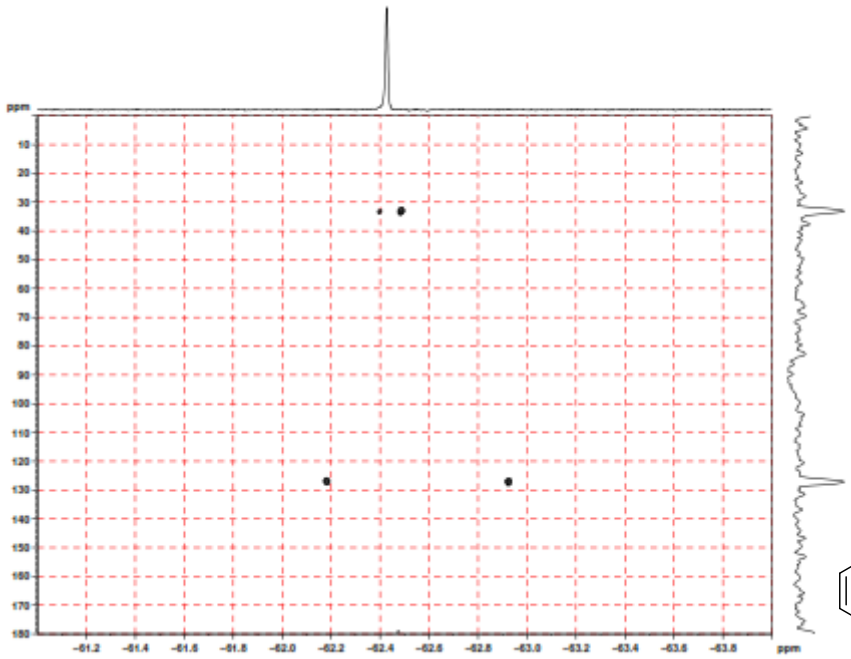

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
−61.0
−61.5
−62.0
−62.5
−63.0
−63.5
−64.0
−64.5
−65.0
−65.5
−66.0
−66.5
ppm

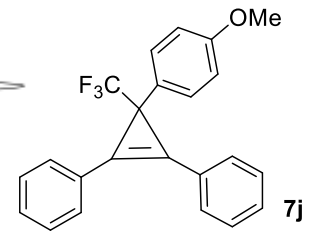

F
F3C
F3C

5h

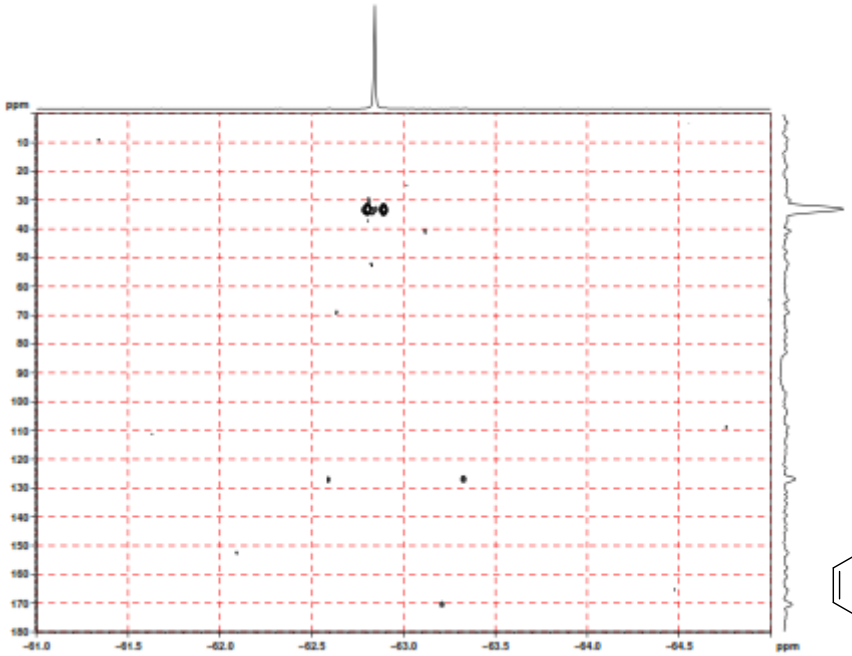

-61.5 -61.7 -61.9 -62.1 -62.3 -62.5 -62.7 -62.9 -63.1 -63.3 -63.5 -63.7 -63.9 -64.1
f2 (ppm)
20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
F
F3C
7h

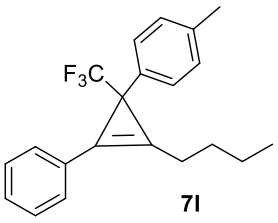

ppm
20 30 40 50 60 70 80 90 100 110 120 130 140 150
-61.5 -61.6 -61.7 -61.8 -61.9 -62.0 -62.1 -62.2 -62.3 -62.4 -62.5 -62.6 -62.7 -62.8 -62.9
ppm
F3C
7i


ppm
-61.2
-61.4
-61.6
-61.8
-62.0
-62.2
-62.4
-62.6
-62.8
-63.0
-63.2
-63.4
-63.6
-63.8
ppm

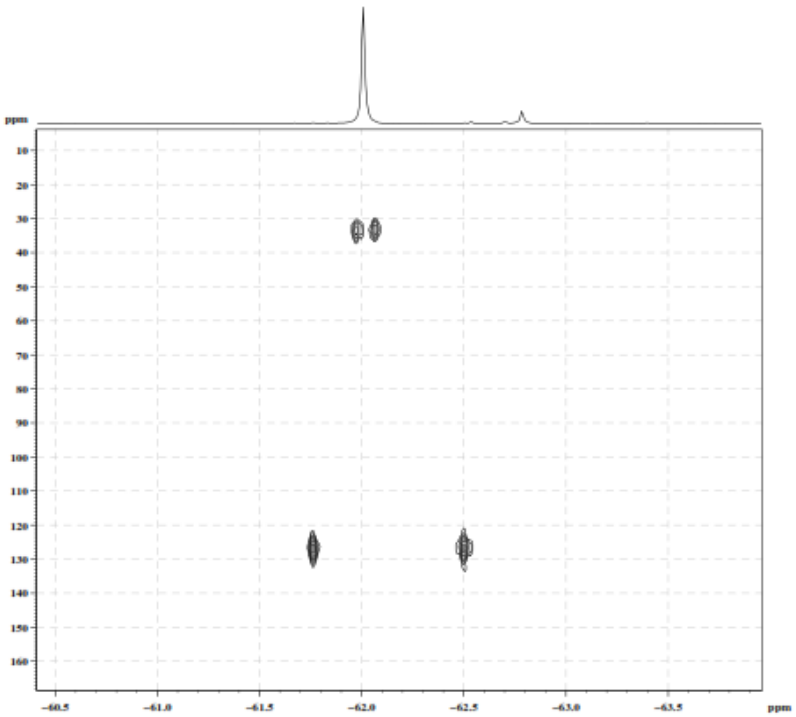

OMe
F3C

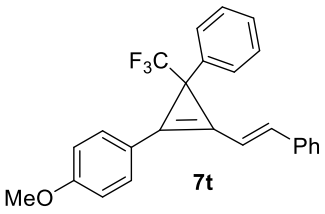
7j


ppm
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
ppm

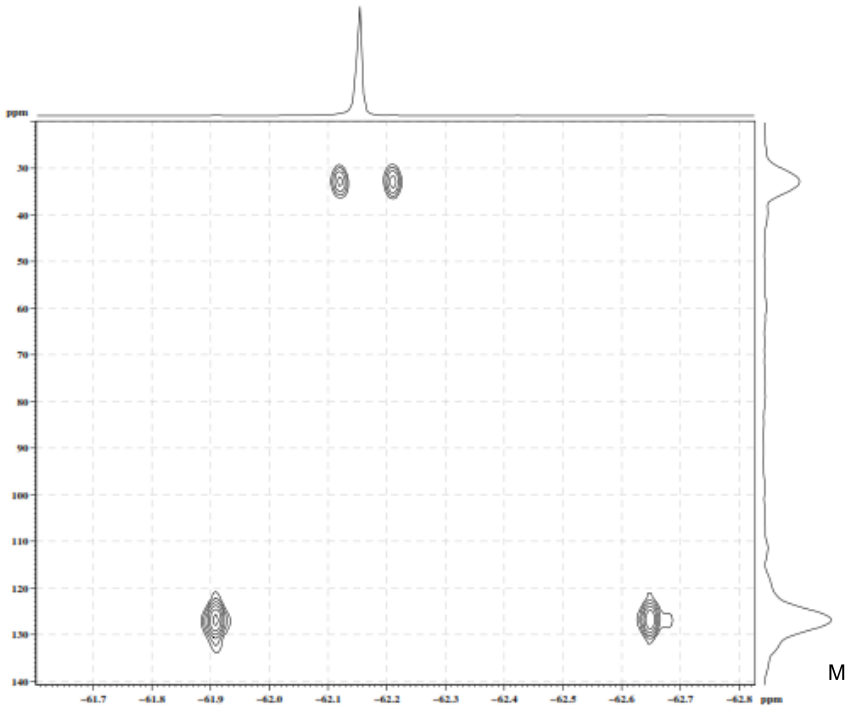

F3C

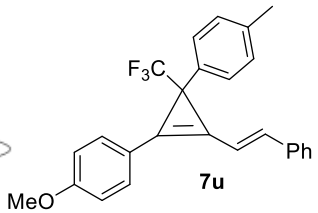
7l



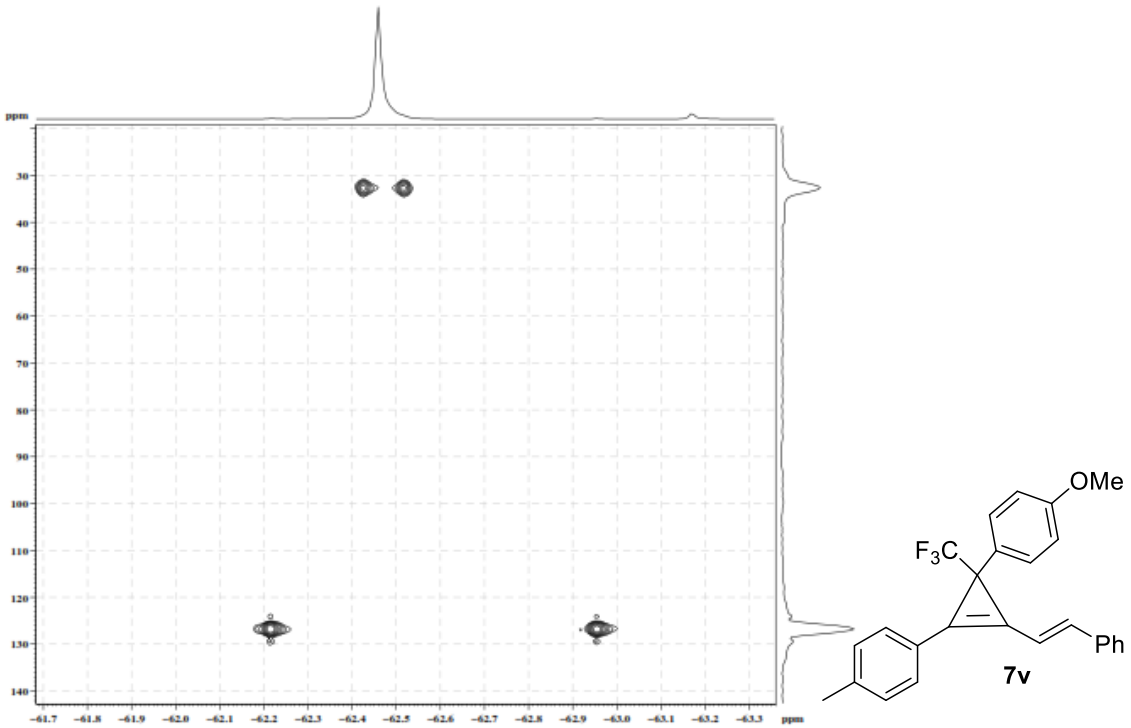


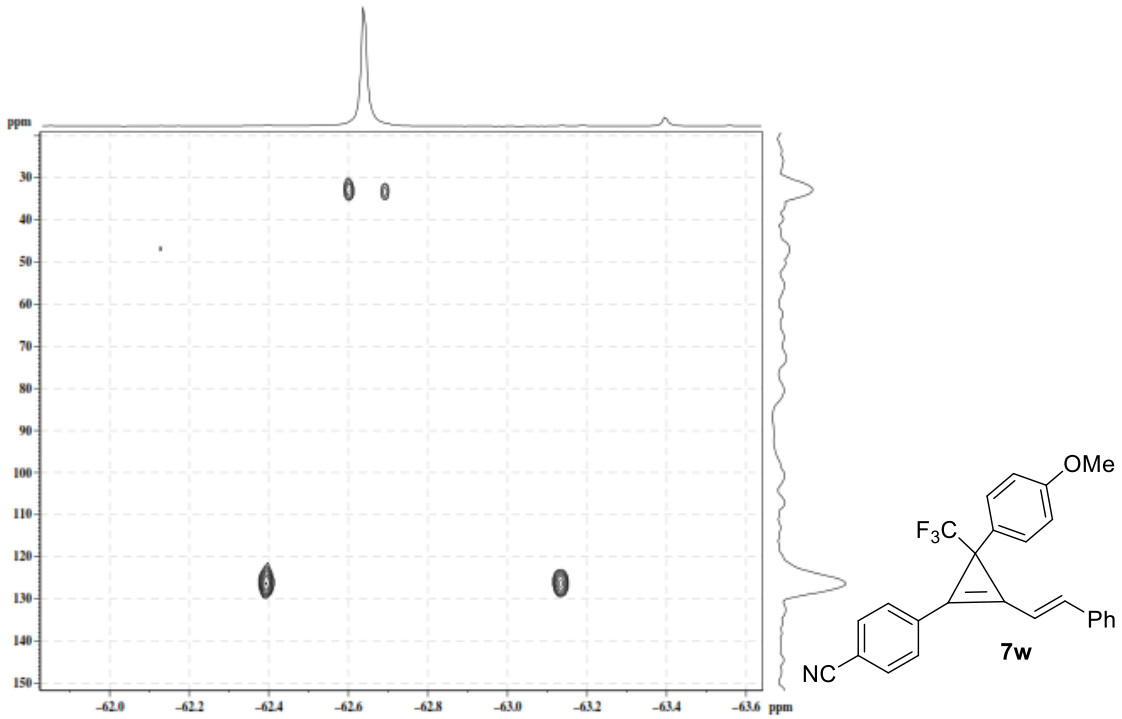
7t

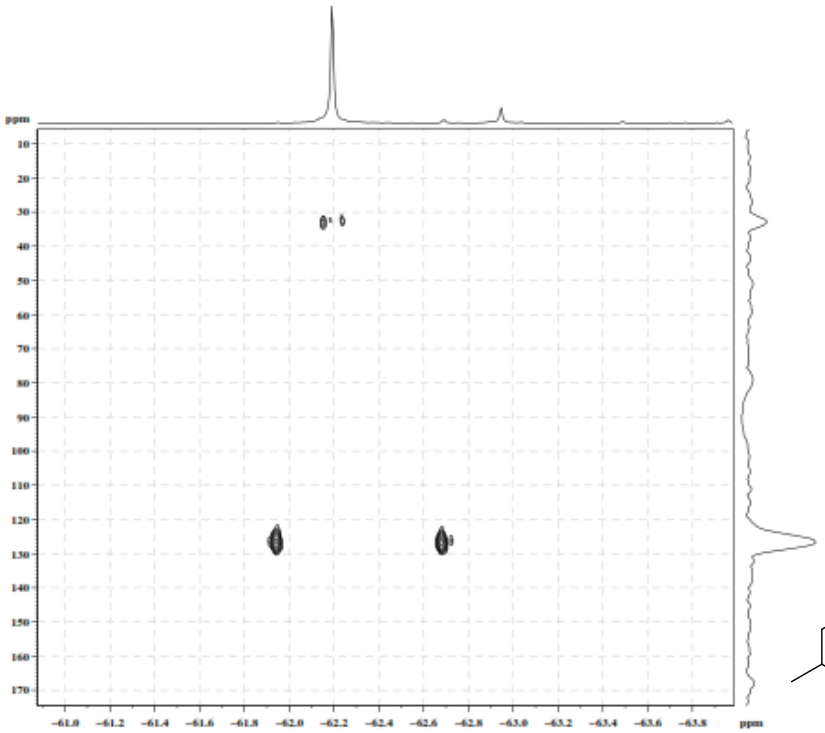


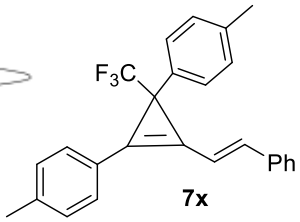


7u


ppm
30
40
50
60
70
80
90
100
110
120
130
140
−61.7 −61.8 −61.9 −62.0 −62.1 −62.2 −62.3 −62.4 −62.5 −62.6 −62.7 −62.8 −62.9 −63.0 −63.1 −63.2 −63.3 ppm
OMe
F3C
Ph
7v


ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
−62.0 −62.2 −62.4 −62.6 −62.8 −63.0 −63.2 −63.4 −63.6 ppm
OMe
F3C
Ph
NC
7w


ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
−61.0
−61.2
−61.4
−61.6
−61.8
−62.0
−62.2
−62.4
−62.6
−62.8
−63.0
−63.2
−63.4
−63.6
−63.8
ppm


F3C
Ph

7x

7. References

[1] V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley and J. -L. Vasse Winn, *J. Am. Chem. Soc.* 2003, **125**, 10926-10940.

[2] M. Uehara, H. Suematsu, Y. Yasutomi, T. Katsuki, *J. Am. Chem. Soc.*, 2011, **133**, 170-171.

[3] J. F. Briones and H. M. L. Davies, *Org. Lett.* 2011, **13**, 3984-3987.

[4] Y. Zhu, T. Li, X. Qu, P. Sun, H. Yang, J. Mao, *Org. Biomol. Chem.*, 2011, **9**, 7309-7312.

[5] P. Sun, H. Yan, L. Lu, D. Liu, G. Rong, J. Mao, *Tetr.*,2013, **69**, 6969-6974.

[6] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V.Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[7] The M06 family of global hybrid functionals have been reported to very give reliable reliable kinetic values for a large number of organic reactions: (a) Y. Zhao and D. Truhlar, *Theor. Chem. Account* 2008, **120**, 215-241. (b) X. Xu, I. M. Alecu and D. G. Truhlar, *J. Chem. Theory Comput.* 2011, **7**, 1667–1676.

[8] http://www.cylview.org/