Supporting Information

Sila Morita-Baylis-Hillman Reaction of Cyclopropenes

Stepan Chuprakov, Denis Malyshev, Alexander Trofimov, and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago,
845 West Taylor Street, Chicago, Illinois 60607-7061

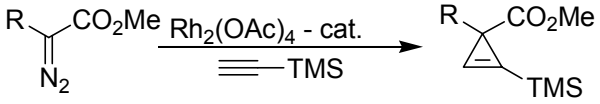
Content

General Information

NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz) or DPX-400 instruments. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P Flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Anhydrous solvents were purchased from Aldrich and distilled over sodium or calcium hydride prior to use, and stored over 4Å MS under inert atmosphere. Aldehydes and ketones were purchased from Aldrich, Acros Organics or Alfa Aesar, distilled over anhydrous $MgSO_4$ prior to use, and stored over 4Å MS under inert atmosphere.

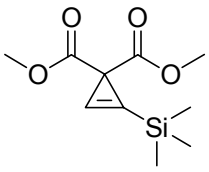
Starting Materials

Dimethyl 1-(trimethylsilyl)cyclopropene-3,3-dicarboxylate **1a**[1] and ethyl 1,3-bis(trimethylsilyl) cyclopropene-3-carboxylate **1d**[2] were known and prepared via literature procedures. Cyclopropenes **1b** and **1c** were prepared via Rh(II)-catalyzed cyclopropenation of corresponding diazocompounds with trimethylsilylacetylene.[1]



General preparative procedure. To a stirred mixture of trimethylsilylacetylene (15 mL) and Rh(II) acetate dimer (11 mg, 0.025 mmol) in a two-neck 25 mL flask, equipped with a condenser, a solution of the corresponding diazocompound (10.0 mmol) in 5 mL of trimethylsilylacetylene was added via a syringe pump over 16 hrs at 55°C under inert atmosphere. The reaction mixture was stirred for additional 2 hrs. The excess of trimethylsilylacetylene was distilled off at ambient pressure and the residue was purified via flash Silica chromatography or bulb-to-bulb distillation. The recovered trimethylsilylacetylene was used in syntheses without any additional purification.

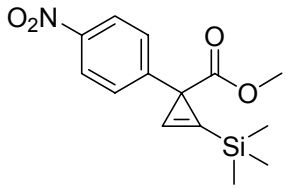
Dimethyl 1-(trimehylsilyl)cyclopropene-3,3-dicarboxylate **(1a)**



1a: ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.04 (s, 1H), 3.69 (s, 6H), 0.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 172.1, 113.7, 110.6 (+), 52.1 (+), 30.5, -1.9 (+); LR EI MS *m/z* 228.0 (M^+).

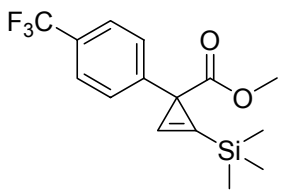
[1] Rubin, M.; Gevorgyan, V. *Synthesis* **2004**, 796.
[2] (a) Arrowood, T. L.; Kass, S. R. *Tetrahedron* **1999**, *55*, 6739; (b) Zrinski, I.; Novak-Coumbassa, N.; Eckert-Maksic, M. *Organometallics* **2004**, *23*, 2806.

Methyl 1-(trimethylsilyl)-3-(4-nitrophenyl)cyclopropene-3-carboxylate **(1b)**



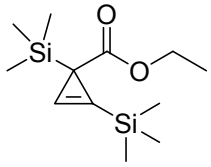
1b: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.06 - 8.21 (m, 2H), 7.42 - 7.52 (m, 2H), 7.37 (s, 1H), 3.69 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 174.6, 150.5, 146.0, 128.9 (+), 123.1 (+), 119.2, 113.9 (+), 52.1 (+), 31.2, -1.6 (+).

Methyl 1-(trimethylsilyl)-3-(4-trifluoromethylphenyl)cyclopropene-3-carboxylate **(1c)**



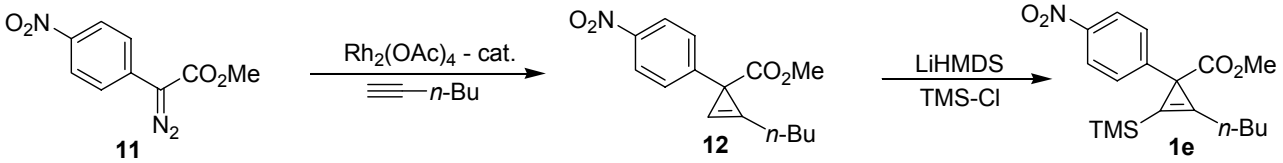
1c: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 - 7.59 (m, 2H), 7.35 - 7.45 (m, 3H), 3.69 (s, 3H), 0.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 175.3, 146.7, 128.5 (+), 128.1 (q, J^{2}_{FC} = 32.4 Hz), 124.8 (+, q, J^{3}_{FC} = 3.7 Hz), 124.3 (q, J^{1}_{FC} = 272.0 Hz), 119.5, 114.8 (+), 52.0 (+), 31.1, -1.5 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ ppm -63.9; LR EI MS *m/z* 314.0 (M^+).

Methyl 1,3-bis(trimethylsilyl)cyclopropene-3-carboxylate **(1d)**



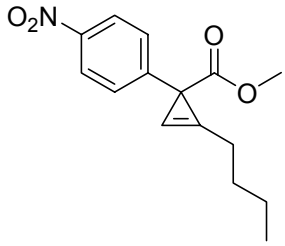
1d: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.15 (s, 1H), 4.00 - 4.12 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.20 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 178.3, 115.7 (+), 114.5, 59.9 (-), 17.4, 14.3 (+), -1.3 (+); LR EI MS *m/z* 256.1 (M^+).

Cyclopropene **1e** was prepared from compound **12** using procedure by Fox *et al*.[3] Compound **12** was obtained via standard Rh(II)-catalyzed cyclopropenation[4] of 1-hexyne with methyl (4-nitrophenyl)diazoacetate **11**:



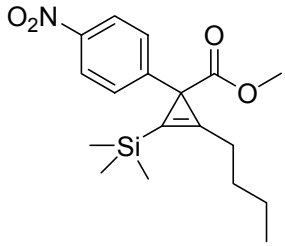
[3] Pallerla, M. K.; Fox, J. M. *Org. Lett.* **2005**, *7*, 3593.
[4] Davies, H. M. L.; Lee, G. H. *Org. Lett.* **2004**, 6, 1233.

Methyl 1-butyl-3-(4-nitrophenyl)cyclopropene-3-carboxylate **(12)**



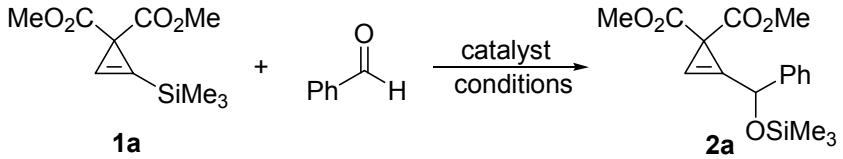
12: (78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.07-8.23 (m, 2H), 7.37-7.54 (m, 2H), 6.66 (t, *J* = 1.5 Hz, 1H), 3.70 (s, 3H), 2.55 (tt, *J* = 7.4, 1.7 Hz, 2H), 1.50 - 1.58 (m, 2H), 1.29 - 1.41 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 174.5, 149.6, 146.2, 129.0 (+), 123.2 (+), 120.1, 95.8 (+), 52.2 (+), 32.9, 28.7 (-), 24.0 (-), 22.2 (-), 13.6 (+); LR EI MS *m/z* 275.3 (M^+).

Methyl 1-(trimethylsilyl)-2-butyl-3-(4-nitrophenyl)cyclopropene-3-carboxylate **(1e)**



1e: (77%); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.02 - 8.21 (m, 2H), 7.38 - 7.57 (m, 2H), 3.67 (s, 3H), 2.48 - 2.69 (m, 2H), 1.49 - 1.71 (m, 2H), 1.31 - 1.47 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 174.8, 151.2, 145.6, 128.4 (+), 127.9, 123.0 (+), 107.4 (+), 51.7 (+), 34.4, 29.2 (-), 25.2 (-), 22.3 (-), 13.7 (+), -1.2 (+); LR EI MS *m/z* 346.9.0 (M^+).

Optimization of the Reaction Conditions



General procedure for optimization of the reaction conditions. To an oven-dried 1 mL Wheaton mini-inert vial catalyst, solvent, and benzaldehyde (20 μL, 0.2 mmol) were added under nitrogen atmosphere, followed by 22.8 mg (0.1 mmol) of 1-(trimethylsilyl)cyclopropene-3,3-dicarboxylate **1a**. The reaction mixture was stirred at temperature and for time listed in Table 1. Dibenzyl ether (5 μL) was added to the reaction mixture as an internal standard and the yield of dimethyl 1-[trimethylsiloxy(phenyl)methyl]cyclopropene-3,3-dicarboxylate **2a** was determined by GC analysis using quantitatively calibrated mass selective detector. The results are summarized in Table 1.

Table 1. Optimization of the Reaction Conditions

#	Catalyst[a]	mol %	solvent	Concentration, mol/L	T, °C	Time, h	Yield, %
1	Quinuclidine	25	DMF	1	rt	21 h	0
2	DBU	25	DMF	1	rt	3 h	0
3	Urotropine	25	DMF	1	rt	21 h	37
4	DMAP	25	DMF	1	rt	21 h	47
5	Boratrane	25	DMF	1	rt	21 h	0
6	(−)-*N*-Methylephedrine	25	DMF	1	rt	21 h	31
7	Imidazole	25	DMF	1	rt	21 h	0
8	DABCO	25	DMF	1	rt	21 h	59
9	DABCO	25	THF	1	rt	14 h	27
10	DABCO	25	THF/water[b]	1	rt	1 h	0
11	DABCO	25	MeOH	1	rt	1 h	0[f]
12	DABCO	25	DCM	1	rt	21 h	6
13	DABCO	25	Toluene	1	rt	21 h	43
14	DABCO	25	DMF	0.5	rt	21 h	56
15	DABCO	25	DMF	2	rt	5 h	66
16	DABCO	10	DMF	1	rt	21 h	58
17	DABCO	5	DMF	1	rt	21 h	58
18	**13**	25	DMF	1	rt	21 h	22
19	PBu_3	25	DMF	1	rt	21 h	10
20	P(*t*-Bu)$_3$	25	DMF	1	rt	21 h	49
21	$PHPr_2$	25	DMF	1	rt	21 h	38
22	PCy_3	25	DMF	1	rt	21 h	47
23	PPh_3	25	DMF	1	rt	21 h	54
24	(±)-BINAP	25	DMF	1	rt	21 h	15
25	TTMPP	25	DMF	1	rt	3 h	57
26	TTMPP	25	DMF	1	0ºC	26 h	58
27	TTMPP	25	DMF	1	50ºC	0.3 h	53
28	TTMPP	5	DMF	1	rt	6 h	62
29	TTMPP	25	Toluene	1	rt	3 h	50
30	P(*o*Tol)$_3$	5	DMF	1	rt	48 h	21
31	P(furyl)$_3$	5	DMF	1	rt	48 h	14
32	P(O*i*Pr)$_3$	5	DMF	1	rt	48 h	35
33	$AsPh_3$	5	DMF	1	rt	48 h	14
34	TTMPP	5	DMA	1	rt	6 h	61
35	TTMPP	5	DMSO	1	rt	6 h	63
36	TTMPP	5	BuCN	1	rt	6 h	62
37	TTMPP	5	THF	1	rt	6 h	64
38	TTMPP	5	NMP	1	rt	6 h	50
39	TTMPP	5	Pyridine	1	rt	6 h	61
40	TTMPP	5	Dioxane	2	rt	6 h	73
41	TTMPP	1	Dioxane[c]	2	rt	6 h	79

[a] DMAP = 4-(dimethylamino)pyridine; Boratrane = 4,6,11-trioxa-1-aza-5-borabicyclo[3.3.3]undecane; (−)-*N*-Methylephedrine = (-)-(1*R*,2*S*)-2-Dimethylamino-1-phenylpropanol; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DABCO = 1,4-diazabicyclo[2.2.2]octane; (±)-BINAP = (±)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene; TTMPP = tris(2,4,6-trimethoxyphenyl)phosphine; **13** = 2-Diphenylphosphino-2'-(N,N-dimethylamino)biphenyl. [b] 2 eqv. (0.2 mmol) of water were added to the reaction [c]0.5 mmol scale.

Decomposition of cyclopropene 1a in the presence of TTMPP

The following experiment was performed to evaluate stability of 1-silylcyclopropene in the presence of phosphine catalyst. To an oven-dried 1 mL Wheaton mini-inert vial TTMPP and dry 1,4-dioxane (0.10 mL) were added under nitrogen atmosphere, followed by 22.8 mg (0.1 mmol) of 1-(trimethylsilyl)cyclopropene-3,3-dicarboxylate **1a**. Dibenzyl ether (5 μL) was added to the same vial as an internal standard, and the reaction mixture was stirred at room temperature for 8h. The reaction was monitored by GC/MS and an amount of the consumed starting material was determined by GC analysis using quantitatively calibrated mass selective detector. This experiment was run with 1 and 5 mol % of catalyst. Representative results are listed in Table 2.

Table 2

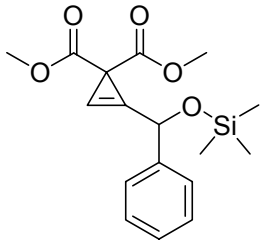
Time, hrs	2	4.5	8
% of **1a** decomposed (**1 mol %** of TTMPP)	1	13	17
% of **1a** decomposed (**5 mol %** of TTMPP)	10	24	45

Thus, it is apparent that, under prolonged time, TTMPP causes significant decomposition of **1a**. Consequently, the employment of lower catalyst loading allowed for higher material balance, and hence higher efficiency of the *sila*-MBH reaction.

TTMPP-Catalyzed coupling of 1-silylcyclopropenes with aldehydes and ketones

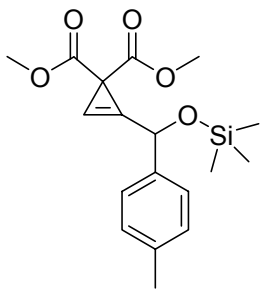
General preparative procedure. To an oven-dried 3 mL Wheaton microreactor tris(2,4,6-(trimethoxyphenyl)phosphine (2.66 mg, 0.005 mmol), carbonyl compound (0.6 mmol), anhydrous dioxane (250 μL) and cyclopropene **1** (0.5 mmol) were added at nitrogen atmosphere. The reaction mixture was stirred at room temperature until judged complete by GC/MS analysis. A flash Silica chromatography was directly applied to the reaction mixture to afford cyclopropene **2** as colorless oil.

***Dimethyl 1-[trimethylsilyloxy(phenyl)methyl]cyclopropene-3,3-dicarboxylate* (2a)**



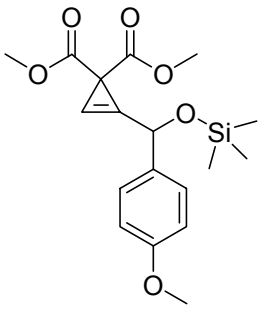
2a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.35 - 7.41 (m, 2H), 7.30 - 7.35 (m, 2H), 7.24 - 7.30 (m, 1H), 6.56 (d, J = 1.7 Hz, 1H), 5.76 (d, J = 1.1 Hz, 1H), 3.68 (s, 3H), 3.41 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.3, 170.6, 139.3, 128.6 (+), 128.3 (+), 126.6 (+), 116.2, 95.2 (+), 69.6 (+), 52.4 (+), 52.1 (+), 34.4, 0.1 (+); FT IR (neat): 3139, 2953, 2902, 1743, 1454, 1436, 1285, 1246, 1194, 1095, 1064, 881, 847, 753 cm^{-1}; HR EI MS *m/z* 334.1235, Calcd for $C_{17}H_{22}O_5Si$ 334.1237.

***Dimethyl 1-[trimethylsilyloxy(4-methylphenyl)methyl]cyclopropene-3,3-dicarboxylate* (2b)**



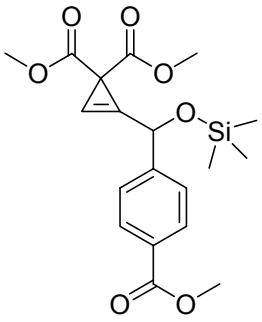
2b: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.24 (s, 2H), 7.10 - 7.16 (m, 2H), 6.53 (d, J = 1.5 Hz, 1H), 5.72 (s, 1H), 3.67 (s, 3H), 3.42 (s, 3H), 2.31 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1, 170.5, 137.8, 136.2, 129.0 (+), 126.4 (+), 116.1, 94.8 (+), 69.2 (+), 52.1 (+), 51.9 (+), 34.2, 21.1 (+), -0.1 (+);FT IR (neat): 3140, 2953, 2901, 1734, 1435, 1285, 1253, 1089, 1068, 883, 843, 757 cm^{-1}; HR EI MS *m/z* 348.1390, Calcd for $C_{18}H_{24}O_5Si$ 348.1393.

Dimethyl 1-[trimethylsilyloxy(4-methoxyphenyl)methyl]cyclopropene-3,3-dicarboxylate **(2c)**



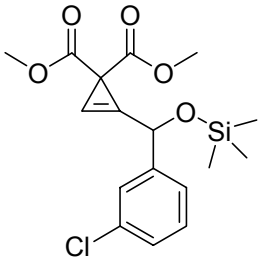
2c: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.27 - 7.30 (m, 2H), 6.85 (s, 2H), 6.54 (d, *J* = 1.5 Hz, 1H), 5.70 (d, *J* = 1.1 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.45 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1, 170.5, 159.4, 131.3, 127.8 (s), 116.1, 113.7 (+), 94.7 (+), 69.0 (+), 55.3 (+), 52.2 (+), 51.9 (+), 34.2, -0.1 (+); FT IR (neat): 3139, 2953, 1734, 1612, 1513, 1436, 1284, 1247, 1174, 1070, 885, 844, 758 cm^{-1}; HR EI MS *m/z* 364.1343, Calcd for $C_{18}H_{24}O_6Si$ (M^+) 364.1342.

Dimethyl 1-[trimethylsilyloxy-(4-methoxycarbonylphenyl)methyl]cyclopropene-3,3-dicarboxylate **(2d)**



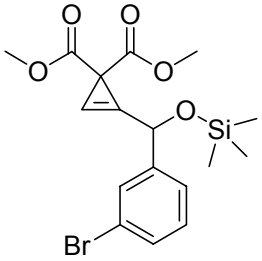
2d: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.01 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 1.5 Hz, 1H), 5.82 (br. s., 1H), 3.91 (s, 3H), 3.68 (s, 3H), 3.43 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 170.8, 170.3, 166.7, 144.1, 129.9, 129.7 (+), 126.2 (+), 115.5, 95.8 (+), 68.9 (+), 52.2 (+), 52.1 (+), 52.0 (+), 34.2, -0.2 (+); HR EI MS *m/z* 392.1294, Calcd for $C_{19}H_{24}O_7Si$ 392.1291.

Dimethyl 1-[trimethylsilyloxy(3-chlorophenyl)methyl]cyclopropene-3,3-dicarboxylate **(2e)**



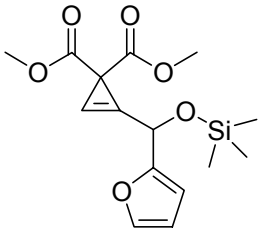
2e: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38 (s, 1H), 7.20 - 7.32 (m, 3H), 6.59 (d, *J* = 1.5 Hz, 1H), 5.74 (d, *J* = 1.3 Hz, 1H), 3.69 (s, 3H), 3.47 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 170.9, 170.3, 141.2, 134.3, 129.7 (+), 128.3 (+), 126.5 (+), 124.5 (+), 115.5, 95.7 (+), 52.2 (+), 52.0 (+), 34.2, -0.2 (+); HR EI MS *m/z* 368.0846, Calcd for $C_{17}H_{21}O_5SiCl$ 368.0847.

Dimethyl 1-[trimethylsilyloxy(3-bromophenyl)methyl]cyclopropene-3,3-dicarboxylate **(2f)**



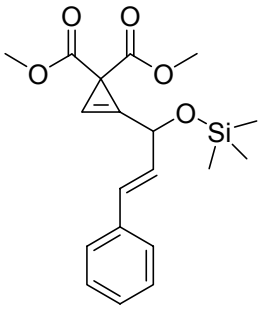
2f: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.54 (t, *J* = 1. 6 Hz, 1H), 7.41 (dt, *J* = 7.9, 0.8 Hz, 1H), 7.28 - 7.33 (m, 1H), 7.17 - 7.23 (m, 1H), 6.59 (d, *J* = 1.5 Hz, 1H), 5.73 (s, 1H), 3.69 (s, 3H), 3.48 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 170.9, 170.3, 141.4, 131.2 (+), 130.0 (+), 129.4 (+), 125.0 (+), 122.4, 115.6, 95.8 (+), 68.6 (+), 52.2 (+), 52.1 (+), 34.2, -0.2 (+); HR EI MS *m/z* 412.0343, Calcd for $C_{17}H_{21}O_5BrSi$ 412.0342.

***Dimethyl 1-[trimethylsilyloxy(2-furyl)methyl]cyclopropene-3,3-dicarboxylate* (2g)**



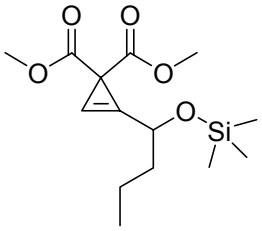
2g: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.31 - 7.46 (m, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 6.21 - 6.43 (m, 2H), 5.80 (d, *J* = 1.1 Hz, 1H), 3.69 (s, 3H), 3.60 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 170.8, 170.5, 151.2, 142.7 (+), 113.7, 110.4 (+), 108.0 (+), 96.8 (+), 63.1 (+), 52.3 (+), 52.2 (+), 34.1, -0.3 (+); FT IR (neat): 3141, 2954, 2923, 1731, 1436, 1284, 1252, 1149, 1069, 877, 848, 753 cm^{-1}; HR EI MS *m/z* 324.1029, Calcd for $C_{15}H_{20}O_6Si$ 324.1029.

***Diemthyl 1-[(2E)-1-trimethylsilyloxy-3-phenylprop-2-ene]cyclopropene-3,3-dicarboxylate* (2h)**



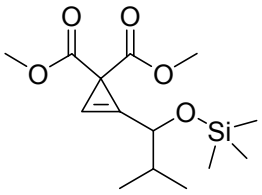
2h: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.34 - 7.39 (m, 2H), 7.29 - 7.34 (m, 2H), 7.22 - 7.27 (m, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.60 (d, *J* = 1.3 Hz, 1H), 6.21 (dd, *J* = 15.9, 6.5 Hz, 1H), 5.39 (dt, *J* = 6.6, 1.2 Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1, 170.9, 136.1, 131.7 (+), 128.6 (+), 128.0 (+), 126.7 (+), 126.6 (+), 114.9, 95.2 (+), 68.2 (+), 52.3 (+), 33.8, -0.0 (+); HR EI MS *m/z* 360.1392, Calcd for $C_{19}H_{24}O_5Si$ 360.1393.

***Dimethyl 1-(1-trimethylsilyloxybutyl)cyclopropene-3,3-dicarboxylate* (2i)**



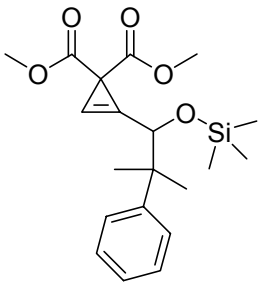
2i: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.49 (d, *J* = 1.5 Hz, 1H), 4.68 (ddd, *J* = 7.2, 5.6, 1.4 Hz, 1H), 3.70 (d, *J* = 2.9 Hz, 6H), 1.56 - 1.71 (m, 2H), 1.27 - 1.52 (m, 2H), 0.90 (t, *J* = 7.3, 3H), 0.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.2, 171.2, 116.1, 94.9 (+), 67.0 (+), 52.2 (+), 37.6 (-), 33.8, 18.4 (-), 13.7 (+), -0.2 (+); FT IR (neat): 3137, 2958, 2875, 1736, 1436, 1279, 1265, 1118, 1069, 903, 847, 757 cm^{-1}; HR EI MS *m/z* 300.1394, Calcd for $C_{14}H_{24}O_5Si$ 300.1393.

***Dimethyl 1-(trimethylsilyloxy-2-methylpropyl)cyclopropene-3,3-diarboxylate* (2j)**



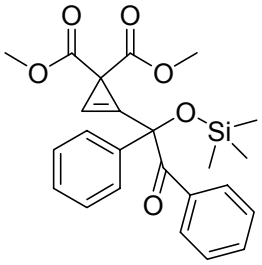
2j: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.52 (d, *J* = 1.1 Hz, 1H), 4.48 (dd, *J* = 4.6, 1.1 Hz, 1H), 3.69 (s, 6H), 1.81 - 1.97 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.2, 115.5, 96.0 (+), 72.2 (+), 52.1 (+), 33.8, 32.9 (+), 18.5 (+), 16.9 (+), -0.2 (+); FT IR (neat): 3139, 2957, 2902, 1736, 1436, 1283, 1253, 1064, 878, 845, 758 cm^{-1}; HR EI MS *m/z* 299.1315, Calcd for $C_{14}H_{23}O_5Si$ 299.1317.

***Dimethyl 1-[1-trimethylsilyloxy-2-methyl-2-phenylpropyl]cyclopropene-3,3-dicarboxylate* (2k)**



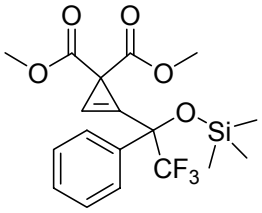
2k: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.34 - 7.39 (m, 2H), 7.27 - 7.32 (m, 2H), 7.15 - 7.24 (m, 1H), 6.36 (d, J = 1.7 Hz, 1H), 4.83 (d, J = 1.8 Hz, 1H), 3.67 (s, 3H), 3.62 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H), -0.06 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.2, 171.0, 146.3, 128.0 (+), 126.5 (+), 126.2 (+), 115.0, 97.4 (+), 75.7 (+), 52.1 (+), 52.0 (+), 43.1 (+), 36.6, 34.3, 24.5 (+), 23.3 (+), -0.4 (+); FT IR (neat): 2953, 1734, 1436, 1279, 1252, 1093, 1068, 880, 845, 759 cm^{-1} HR EI MS *m/z* 376.1708, Calcd for $C_{20}H_{28}O_5Si$ 376.1706.

***Dimethyl 1-[1-trimethylsilyloxy-2-oxo-1,2-diphenylethyl]cyclopropene-3,3-dicarboxylate* (2p)**



2p: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.76 - 7.86 (m, 2H), 7.49 - 7.62 (m, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.22 - 7.30 (m, 3H), 6.78 (s, 1H), 3.77 (s, 3H), 3.26 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 195.8, 170.3, 170.0, 138.8, 133.5, 132.9 (+), 130.9 (+), 128.7 (+), 128.4 (+), 127.9 (+), 125.3 (+), 116.3, 98.0 (+), 84.3, 52.3 (+), 51.7 (+), 35.9, 1.6 (+); FT IR (neat): 2952, 2360, 1737, 1686, 1448, 1435, 1286, 1253, 1071, 880, 850 cm^{-1} ; HR EI MS *m/z* 438.1496, Calcd for $C_{24}H_{26}O_6Si$ 438.1499.

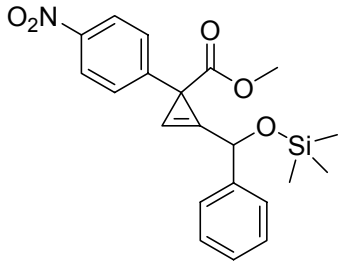
***Methyl 1-(1-trimethylsilyloxy-1-phenyl-2,2,2-trifluoroethyl)cyclopropene-3,3-dicarboxylate* (2q)**



2q: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.59 - 7.65 (m, 2H), 7.34 - 7.41 (m, 3H), 7.02 (s, 1H), 3.70 (s, 3H), 3.61 (s, 3H), 0.17 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 169.8, 169.6, 135.4, 129.3 (+), 128.2 (+), 127.1 (+), 119.9 - 127.0 (q, J^1_{FC} = 287.6 Hz), 113.0, 102.7 (+), 77.6 (q, J^2_{CF} = 32.4 Hz) 52.3 (+), 35.2, 1.5 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ ppm -167.3; FT IR (neat): 2955, 2360, 2339, 1734, 1437, 1289, 1257, 1181, 1069, 878, 740 cm^{-1} ; HR EI MS *m/z* 402.11086, Calcd for $C_{18}H_{21}O_5SiF_3$ 402.11104.

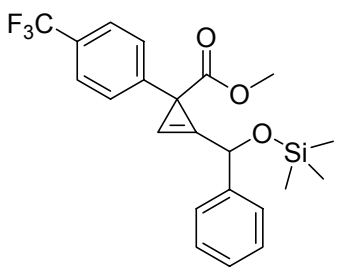
Note: Compounds **2l-o** were obtained as approximately 1:1 mixtures of diastereomers, which could not be separated by flash Silica chromatography. The following analytical data are reported for mixtures.

Methyl 1-[trimethylsilyloxyphenylmethyl]-3-(4-nitrophenyl)cyclopropene-3-carboxylate **(2l)**



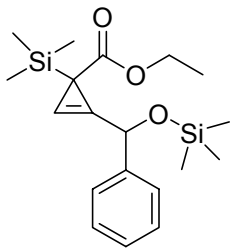
2l: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.06 - 8.18 (m, 2H), 7.94 - 8.03 (m, 2H), 7.46 - 7.59 (m, 12H), 6.90 (d, J = 1.1 Hz, 1H), 6.86 (d, J = 1.7 Hz, 1H), 5.81 (s, 1H), 5.74 (d, J = 1.3 Hz, 1H), 3.55 (s, 3H), 3.54 (s, 3H), 0.10 (s, 9H), 0.10 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.6, 173.4, 148.8, 148.2, 146.4, 146.2, 139.9, 139.2, 129.4 (+), 129.3 (+), 128.5 (+), 128.4 (+), 128.2 (+), 128.1 (+), 126.4 (+), 126.1 (+), 123.1 (+), 122.8 (+), 121.4, 121.1, 99.7 (+), 98.1 (+), 69.6 (+), 69.3 (+), 52.1 (+), 52.1 (+), 35.3, 34.9, -0.1 (+), -0.1 (+); FT IR (neat): 3139, 2953, 1719, 1599, 1518, 1348, 1253, 1219, 1109, 1069, 879, 853 cm^{-1}; HR EI MS *m/z* 397.1342, Calcd for $C_{21}H_{23}O_5NSi$ 397.1345.

Methyl 1-(trimethylsilyloxyphenylmethyl)-3-(4-trifluoromethylphenyl)cyclopropene-3-carboxylate **(2m)**



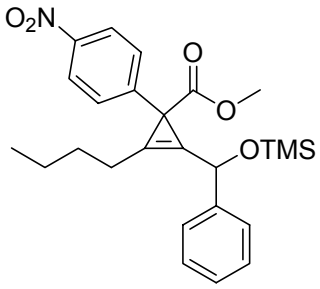
2m: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.51 (s, 4H), 7.16 - 7.43 (m, 14H), 6.91 (d, J = 1.3 Hz, 1H), 6.87 (d, J = 1.7 Hz, 1H), 5.80 (s, 1H), 5.75 (d, J = 1.3 Hz, 1H), 3.55 (s, 3H), 3.51 (s, 3H), 0.11 (s, 9H), 0.10 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 174.1, 173.8, 145.2, 144.5, 140.0, 139.4, 128.9 (+), 128.8 (+), 128.4 (+), 128.3 (+), 128.1 (+), 128.0 (+), 126.5 (+), 126.2 (+), 124.9 (+, q, J^3_{FC} = 2.8 Hz), 124.5 (+, q, J^3_{FC} = 2.8 Hz), 124.3 (q, J^1_{FC} = 271.9 Hz), 124.3 (q, J^1_{FC} = 271.9 Hz), 121.9, 121.5, 100.1 (+), 98.7 (+), 69.6 (+), 69.5 (+), 51.9 (+), 51.9 (+), 35.4, 35.0, -0.1 (+), -0.1 (+); ^{19}F NMR (470.59 MHz, $CDCl_3$) δ ppm -63.9; HR EI MS *m/z* 420.1367, Calcd for $C_{22}H_{23}O_3SiF_3$ 420.1369.

Ethyl 1-(trimethylsilyloxyphenylmethyl)-3-trimethylsilylcyclopropene-3-carboxylate **(2n)**

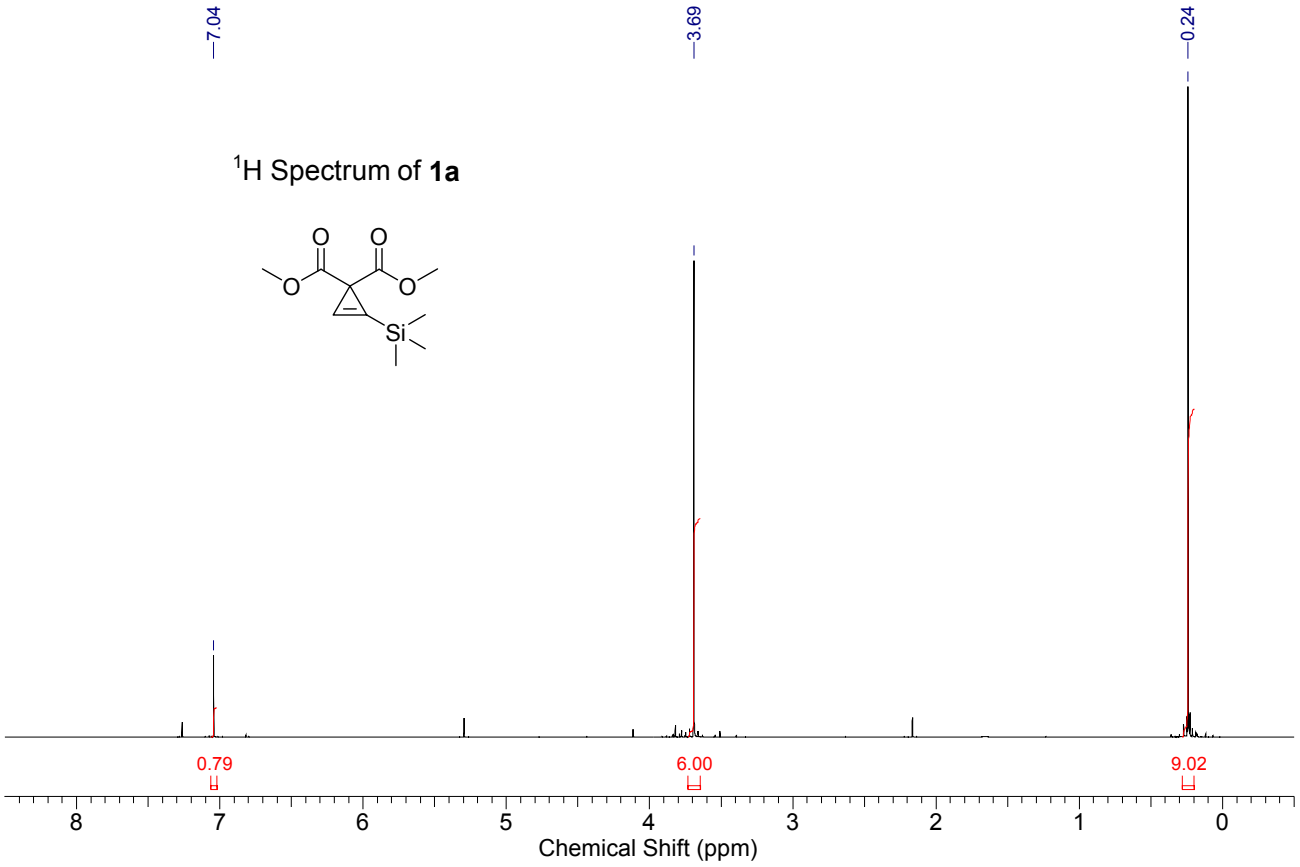


2n: The reaction was carried at 50^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.17 - 7.47 (m, 10H), 6.52 (d, J = 1.1 Hz, 1H), 6.47 (d, J = 1.8 Hz, 1H), 5.72 (s, 1H), 5.64 (d, J = 1.8 Hz, 1H), 3.92 - 4.02 (m, 4H), 1.15 (t, J = 7.15 Hz, 6H), 0.13 (s, 9H), 0.11 (s, 9H), 0.04 (s, 9H), -0.14 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.0, 140.9, 140.2, 128.3 (+), 128.2 (+), 127.9 (+), 127.7 (+), 126.5 (+), 126.2 (+), 119.1, 118.3, 97.7 (s), 96.8 (s), 70.0 (+), 69.9 (+), 60.0 (+), 22.7, 22.0, 14.2 (+), 0.0 (+), -0.1 (+), -1.3 (+), -1.7 (+); HR EI MS *m/z* 362.1733, Calcd for $C_{19}H_{30}O_3Si_2$ 362.1734.

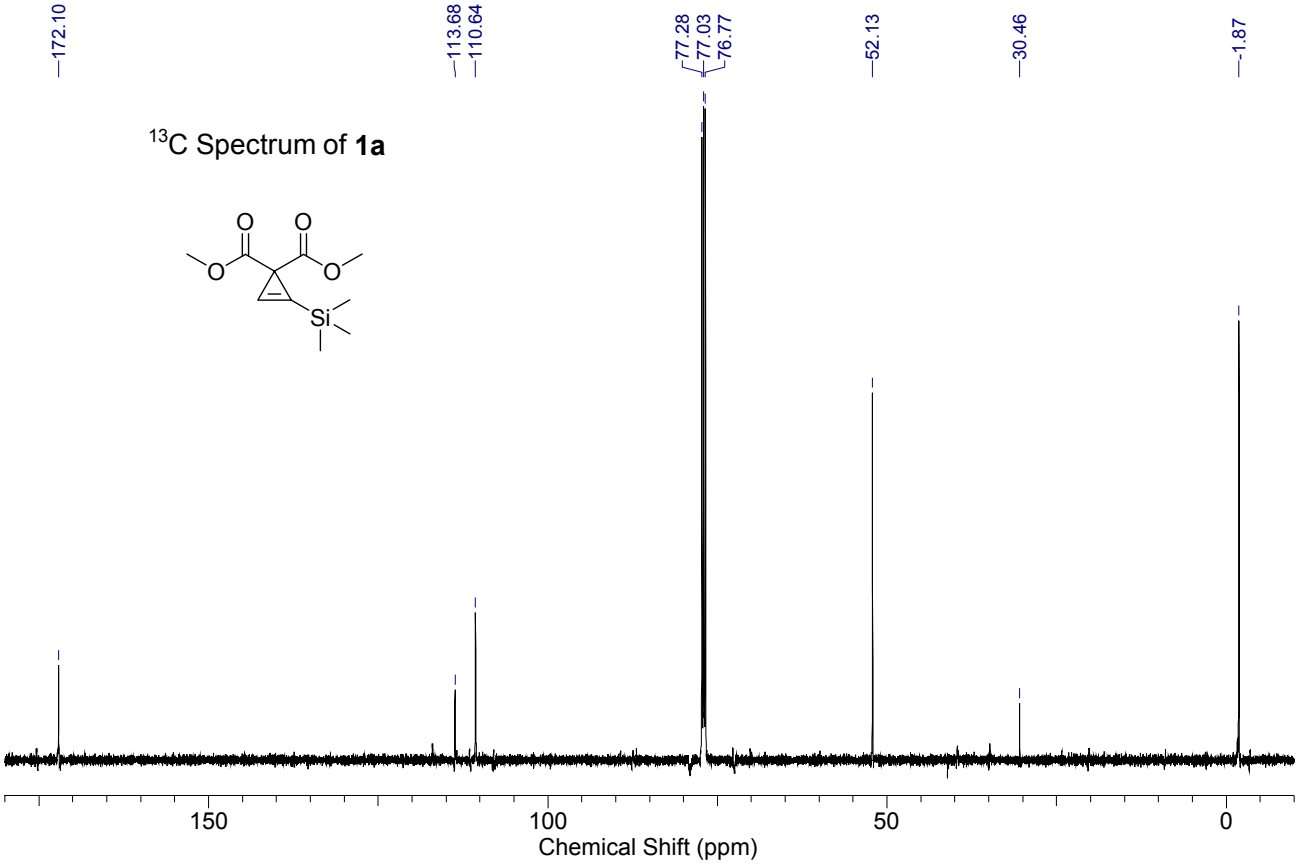
***Methyl 1-(trimethylsilyloxyphenylmethyl)-2-butyl-3-(4-nitrophenyl)cyclopropene-3-carboxylate* (2o)**



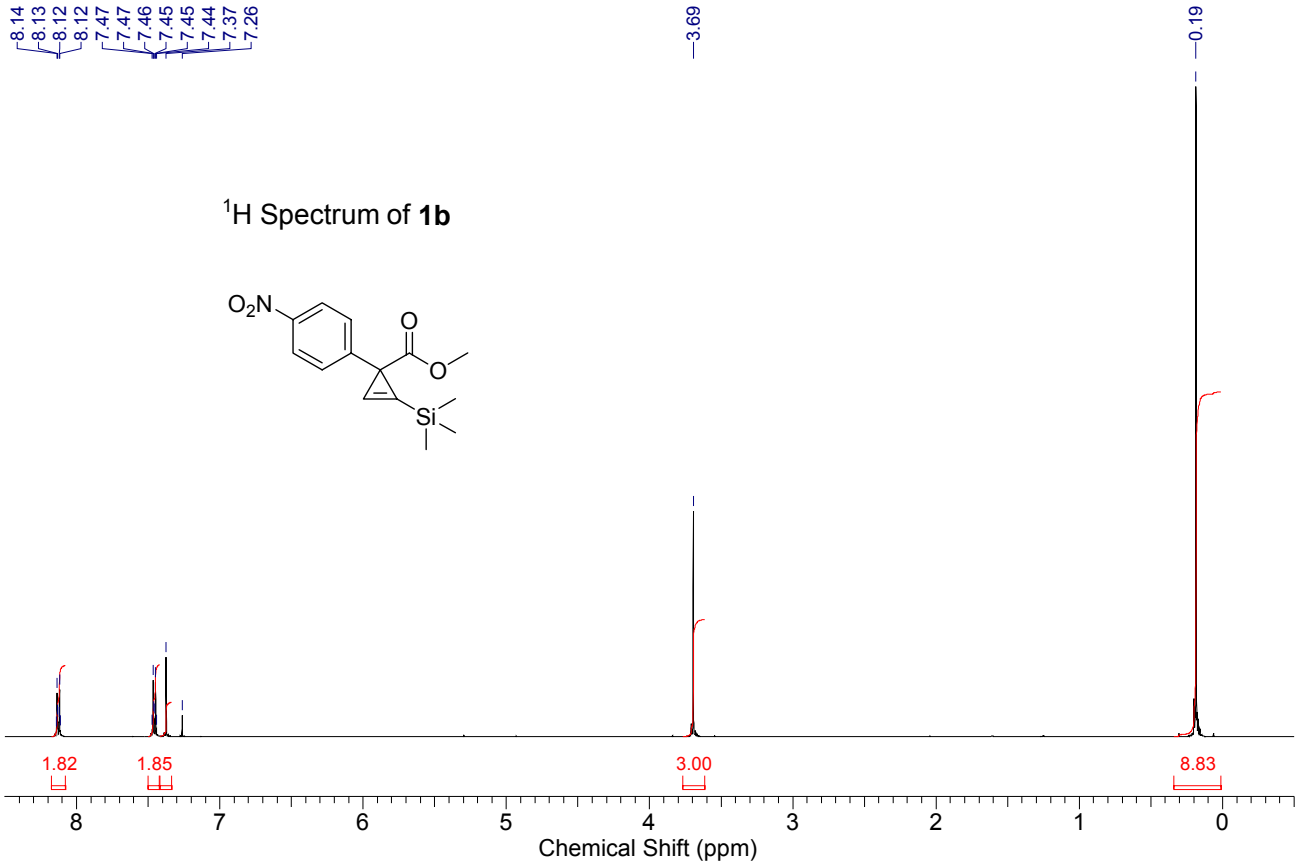
2o: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.08 - 8.16 (m, 2H), 7.98 - 8.07 (m, 2H), 7.55 - 7.65 (m, 2H), 7.20 - 7.45 (m, 12H), 5.76 (s, 1H), 5.69 (s, 1H), 3.58 (s, 3H), 3.48 (s, 3H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.37 (td, *J* = 7.3, 1.7 Hz, 2H), 1.44 - 1.56 (m, 2H), 1.11 - 1.40 (m, 6H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.76 (t, *J* = 7.3 Hz, 3H), 0.09 (s, 9H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.8, 149.6, 149.5, 146.0, 145.9, 141.0, 140.2, 129.4 (+), 129.3 (+), 128.4 (+), 128.3 (+), 128.0 (+), 127.9 (+), 126.3 (+), 126.1 (+), 123.0 (+), 122.9 (+), 113.9, 112.2, 110.7, 110.5, 69.1 (+), 69.0 (+), 51.8 (+), 51.7 (+), 37.3, 36.6, 29.0 (-), 28.8 (-), 23.6 (-), 23.4 (-), 22.3 (-), 22.2 (-), 13.6 (+), 13.5 (+), -0.1 (+), -0.2 (+); HR EI MS *m/z* 453.1973, Calcd for $C_{25}H_{31}O_5NSi$ 453.1971.

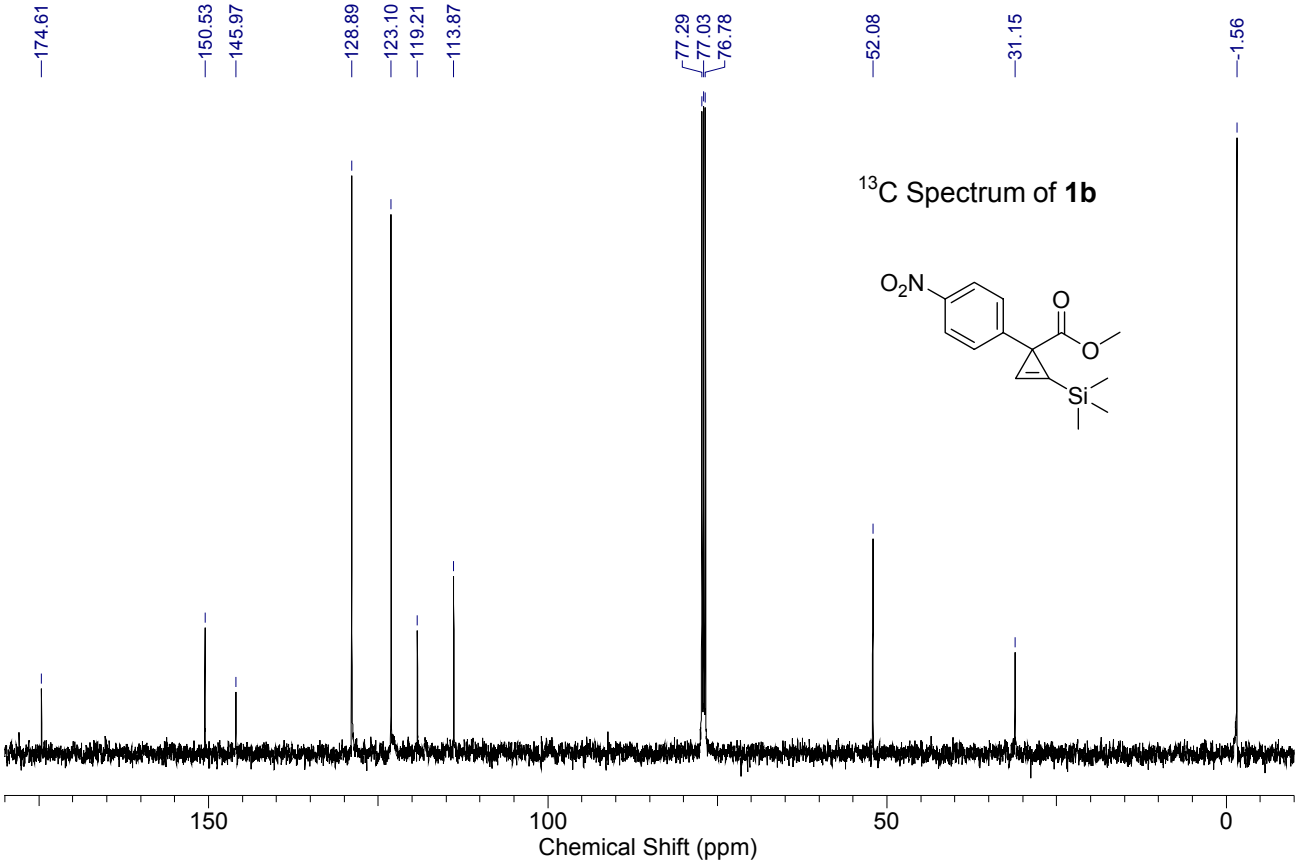


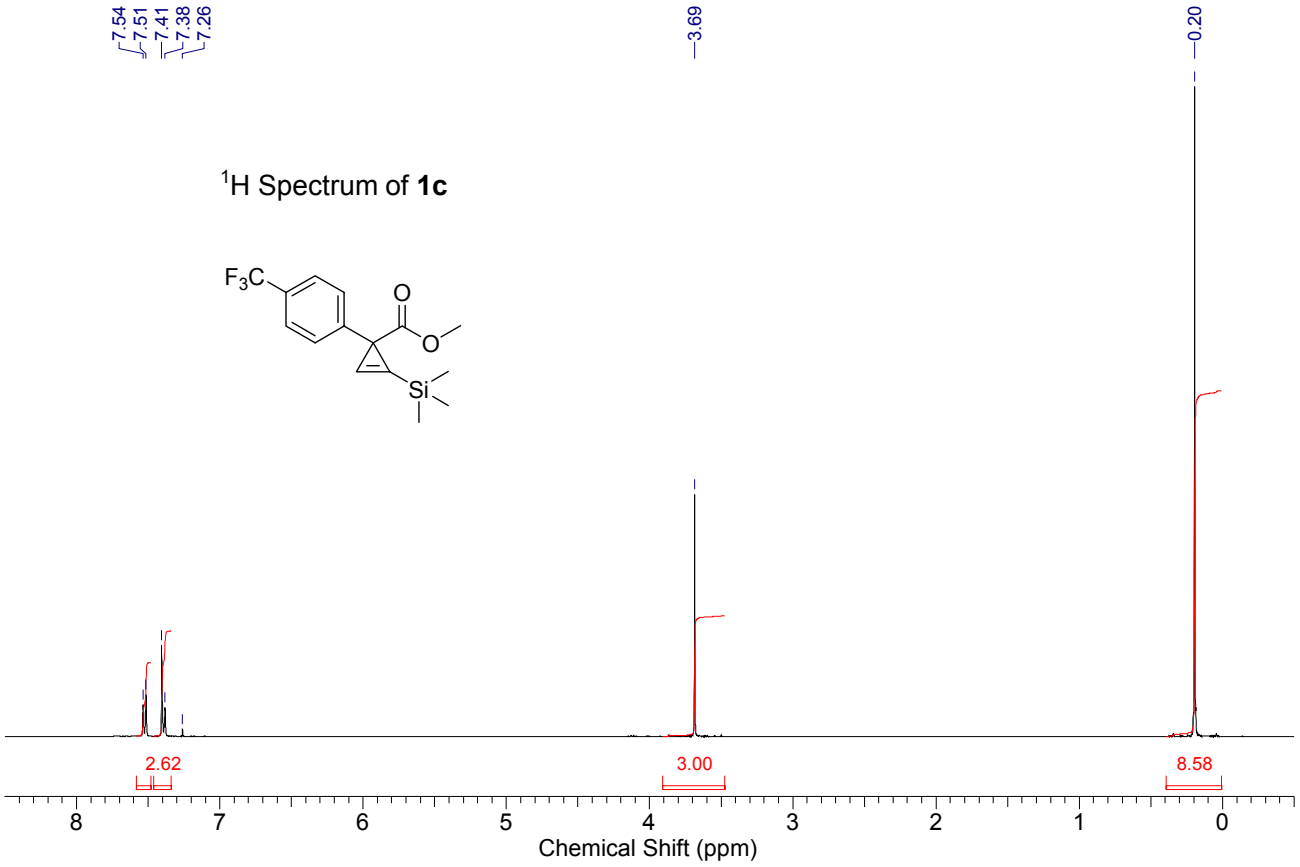
^{1}H Spectrum of **1a**

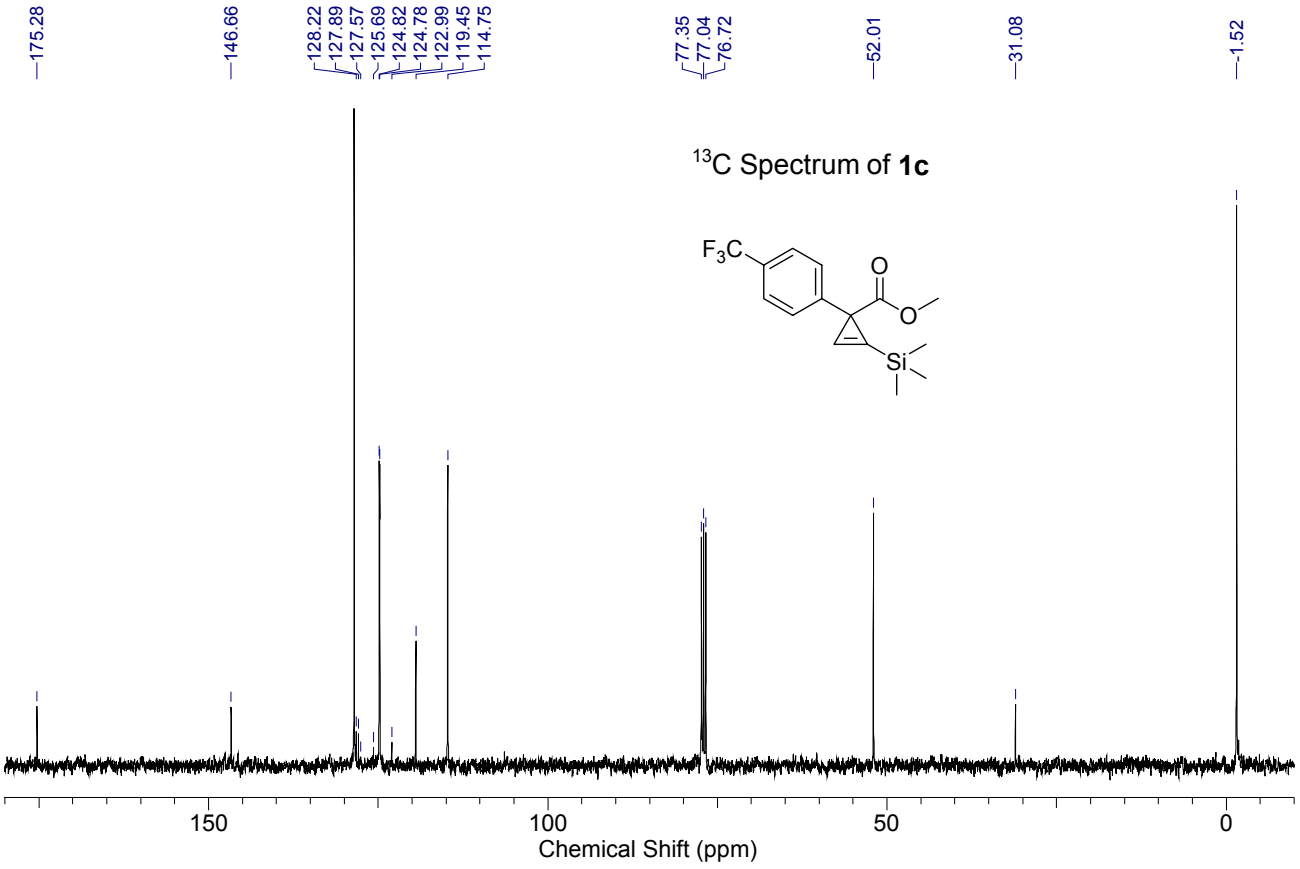


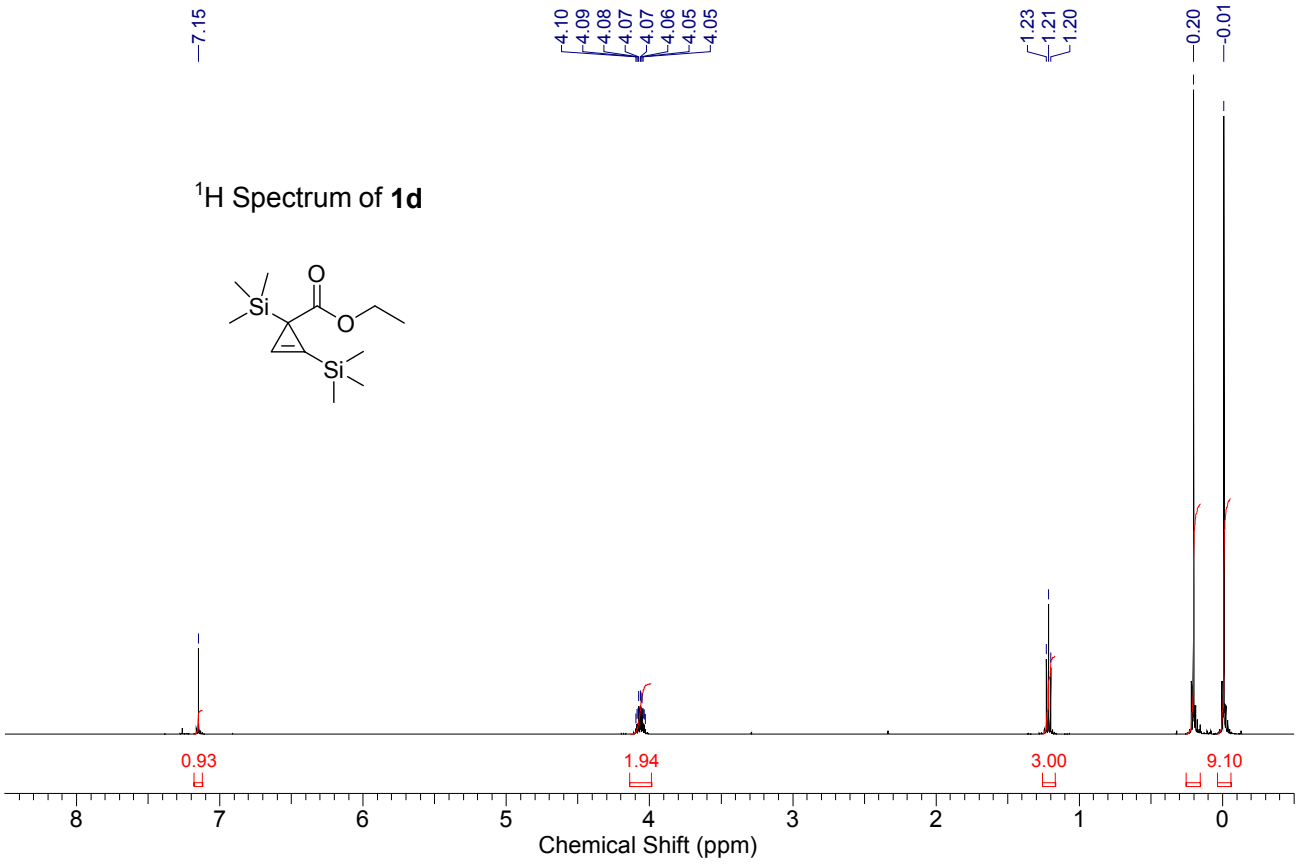
^{13}C Spectrum of **1a**


8.14
8.13
8.12
8.12
7.47
7.47
7.46
7.45
7.45
7.44
7.37
7.26
3.69
0.19
1H Spectrum of 1b
O2N
O
O
Si
1.82
1.85
3.00
8.83
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

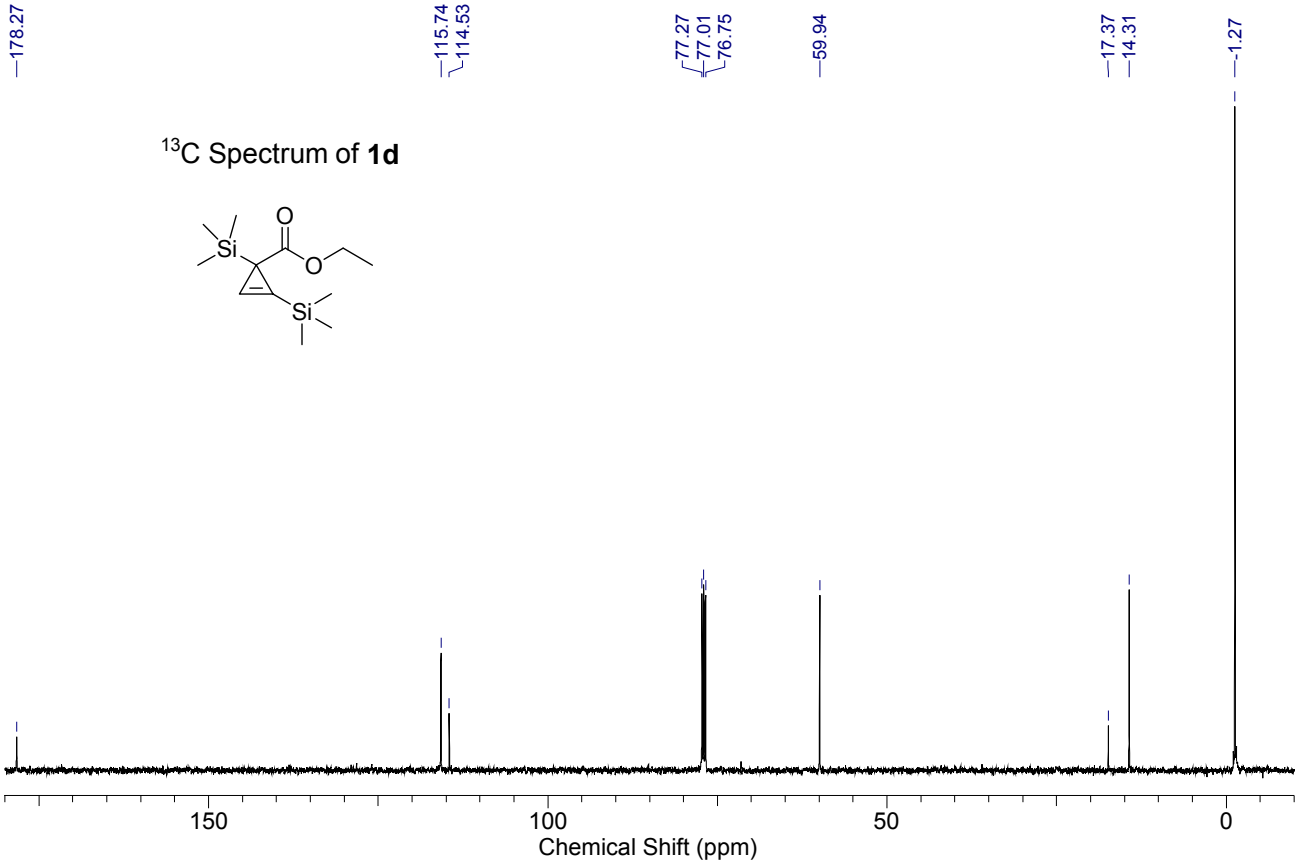

174.61
150.53
145.97
128.89
123.10
119.21
113.87
77.29
77.03
76.78
52.08
31.15
-1.56
13C Spectrum of 1b
O2N
O
O
Si
150
100
50
0
Chemical Shift (ppm)


7.54
7.51
7.41
7.38
7.26
3.69
0.20
^{1}H Spectrum of **1c**
F_3C
O
O
Si
2.62
3.00
8.58
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

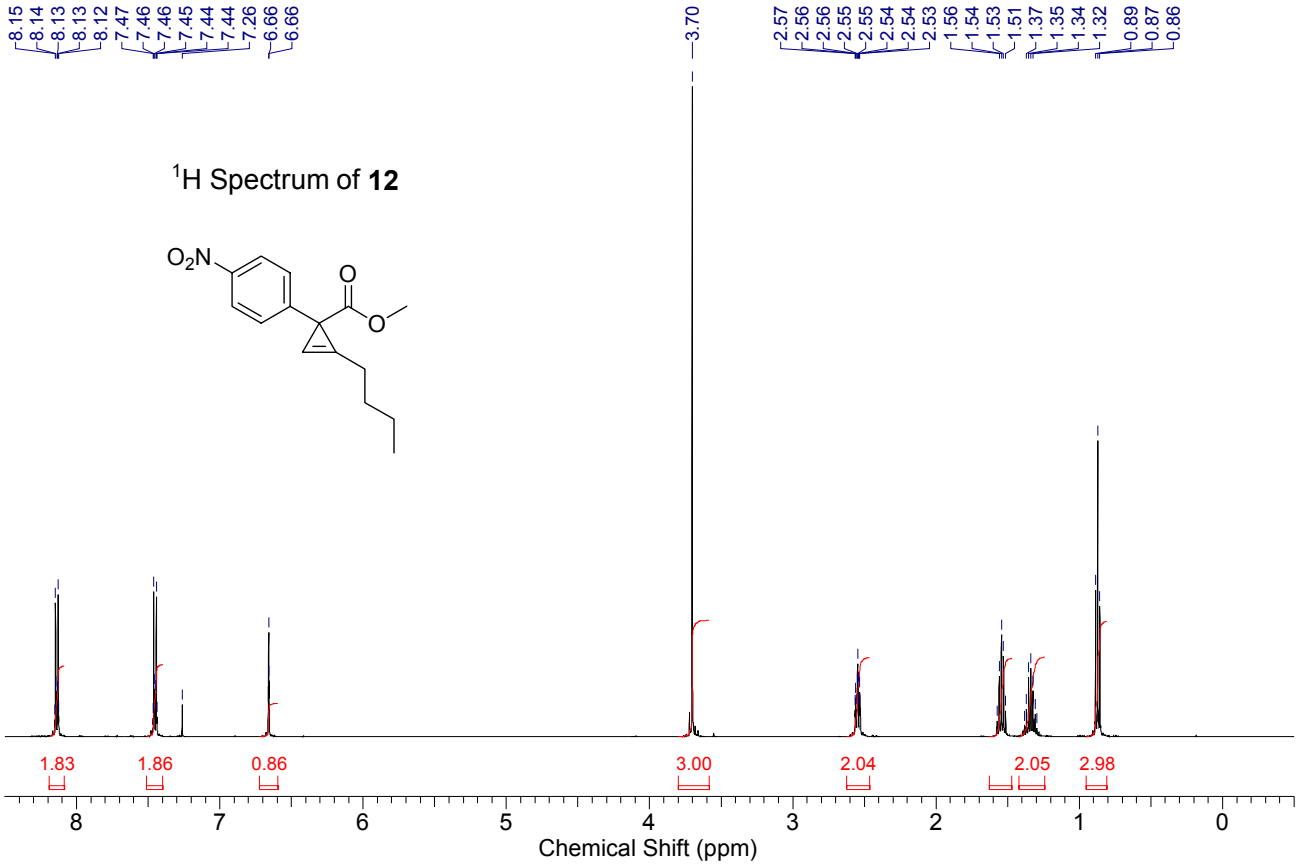

175.28
146.66
128.22
127.89
127.57
125.69
124.82
124.78
122.99
119.45
114.75
77.35
77.04
76.72
52.01
31.08
1.52
^{13}C Spectrum of **1c**
F_3C
O
O
Si
150
100
50
0
Chemical Shift (ppm)

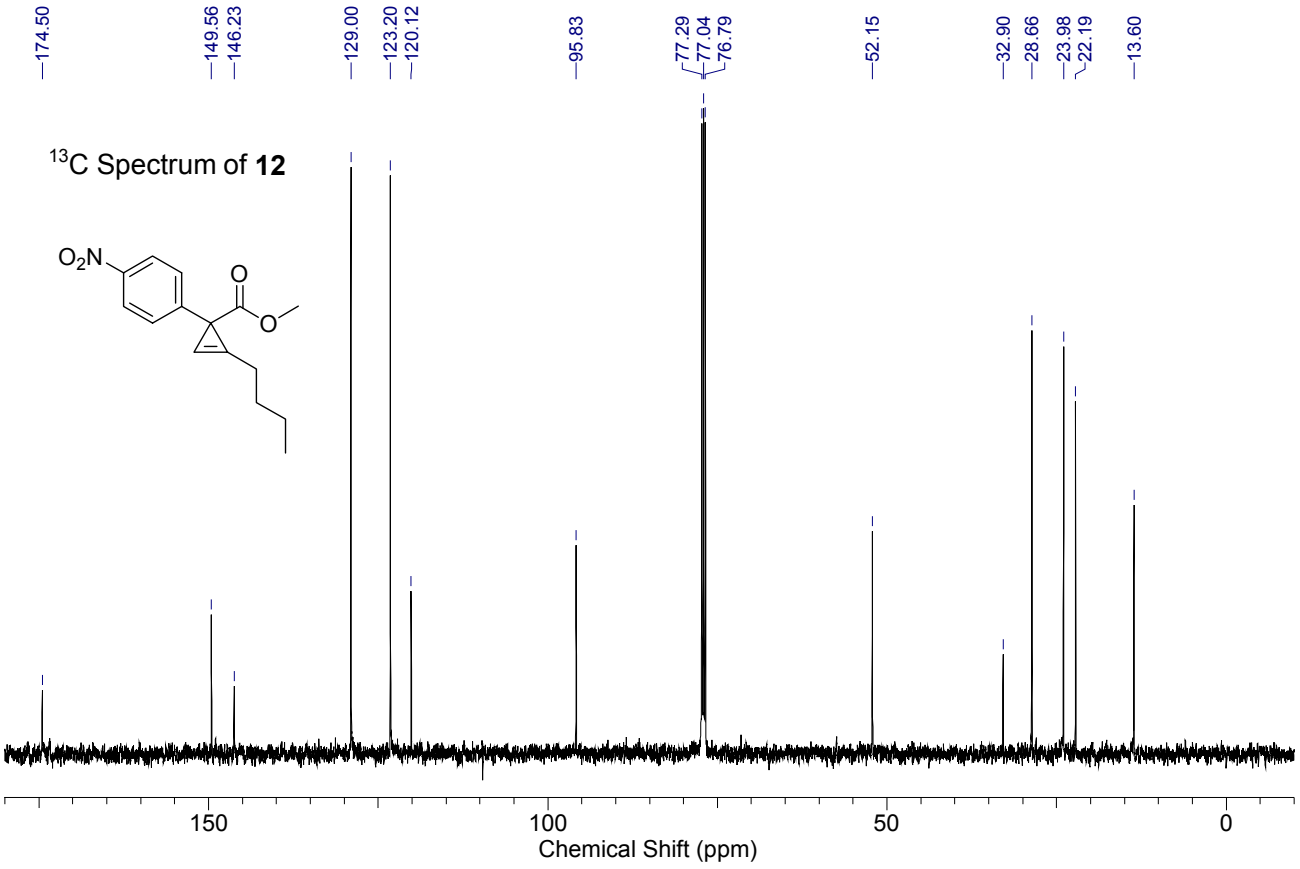


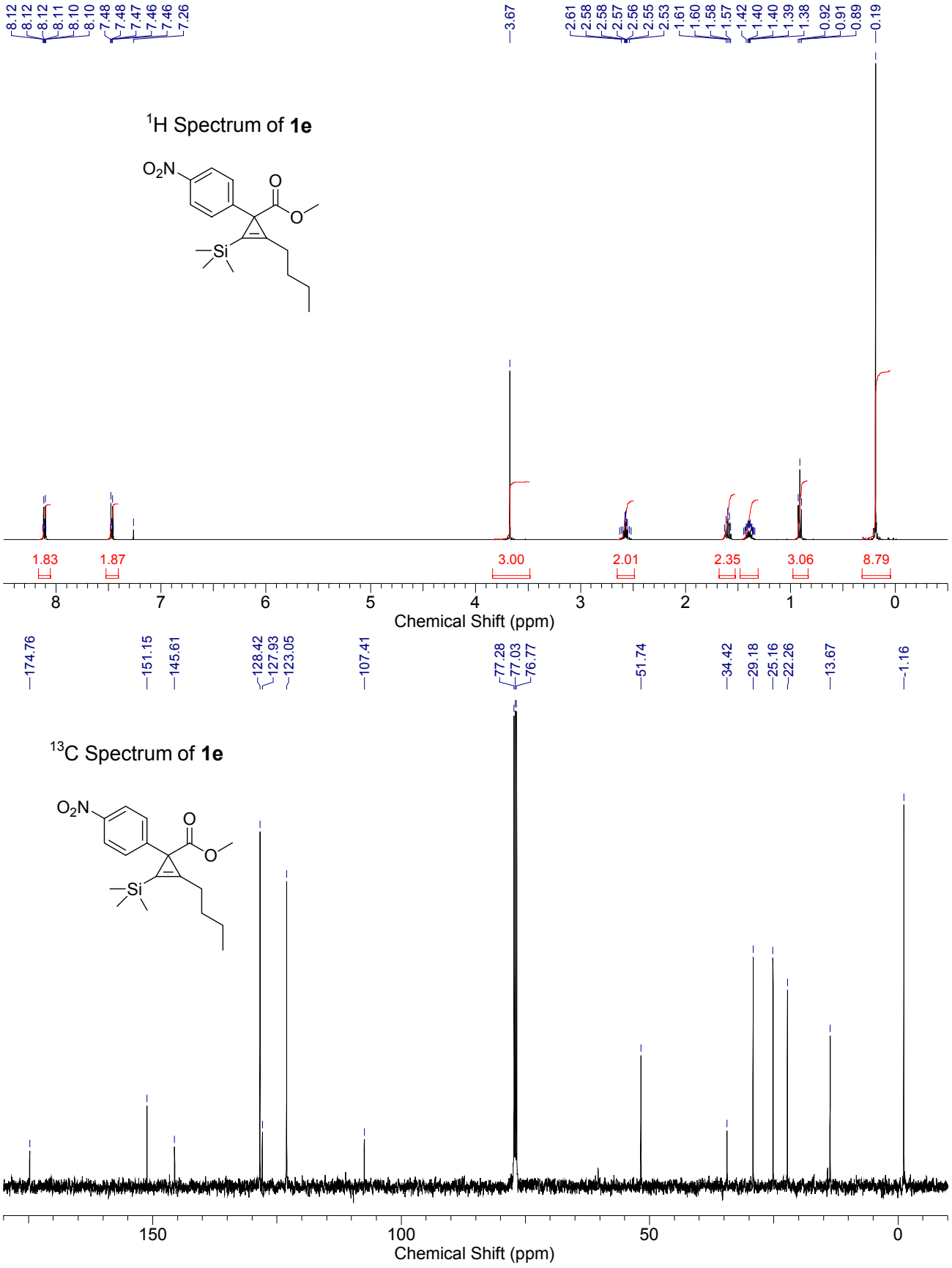
^{1}H Spectrum of **1d**

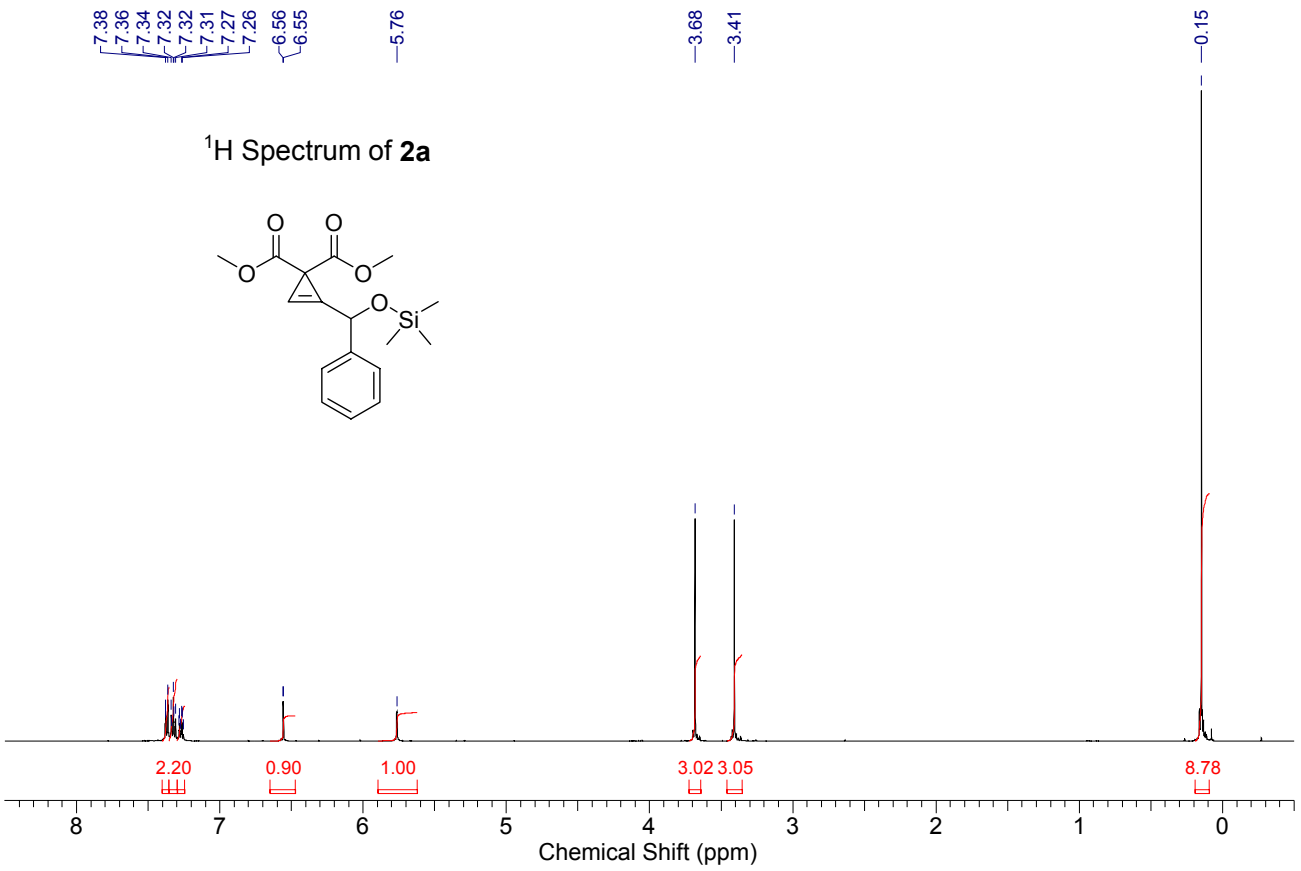


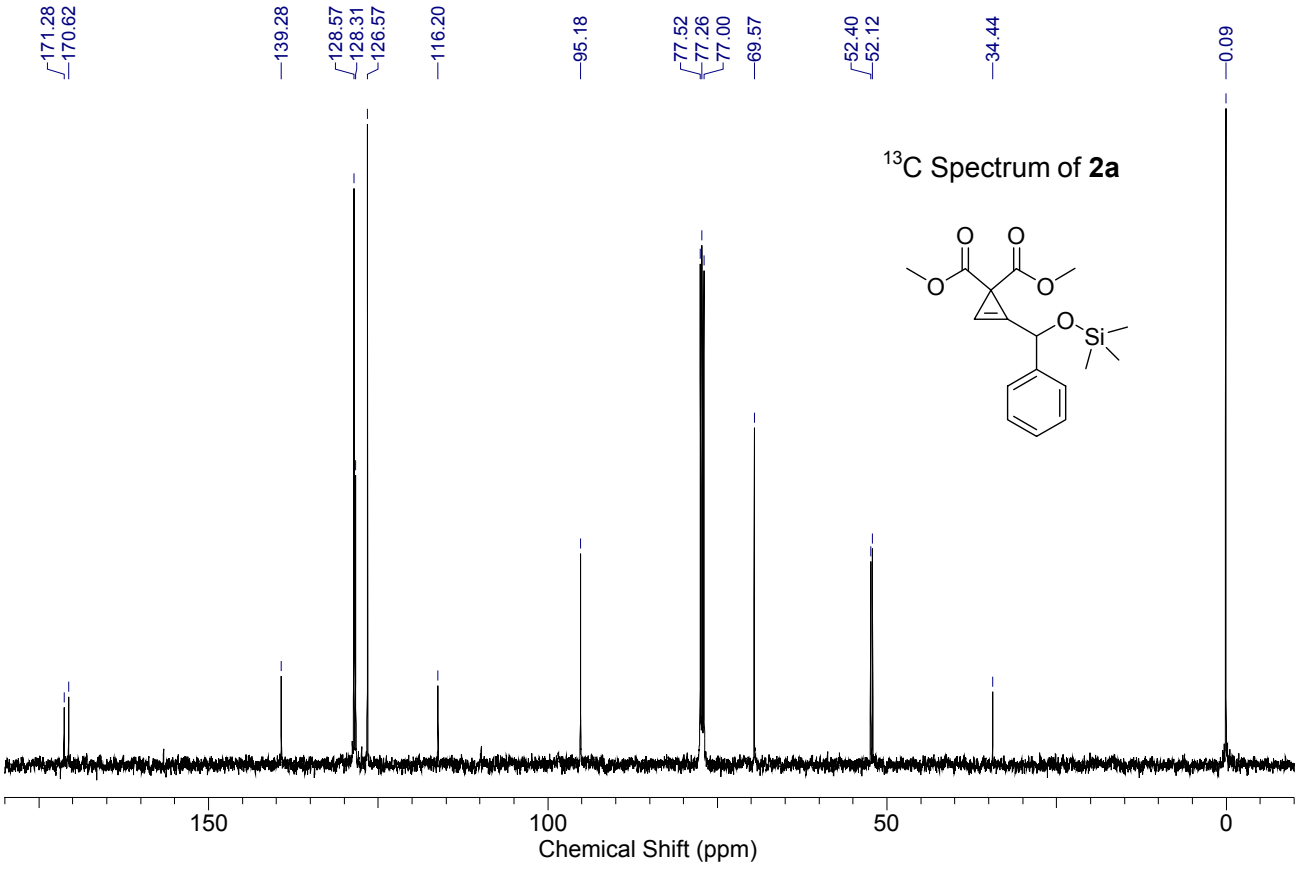
^{13}C Spectrum of **1d**

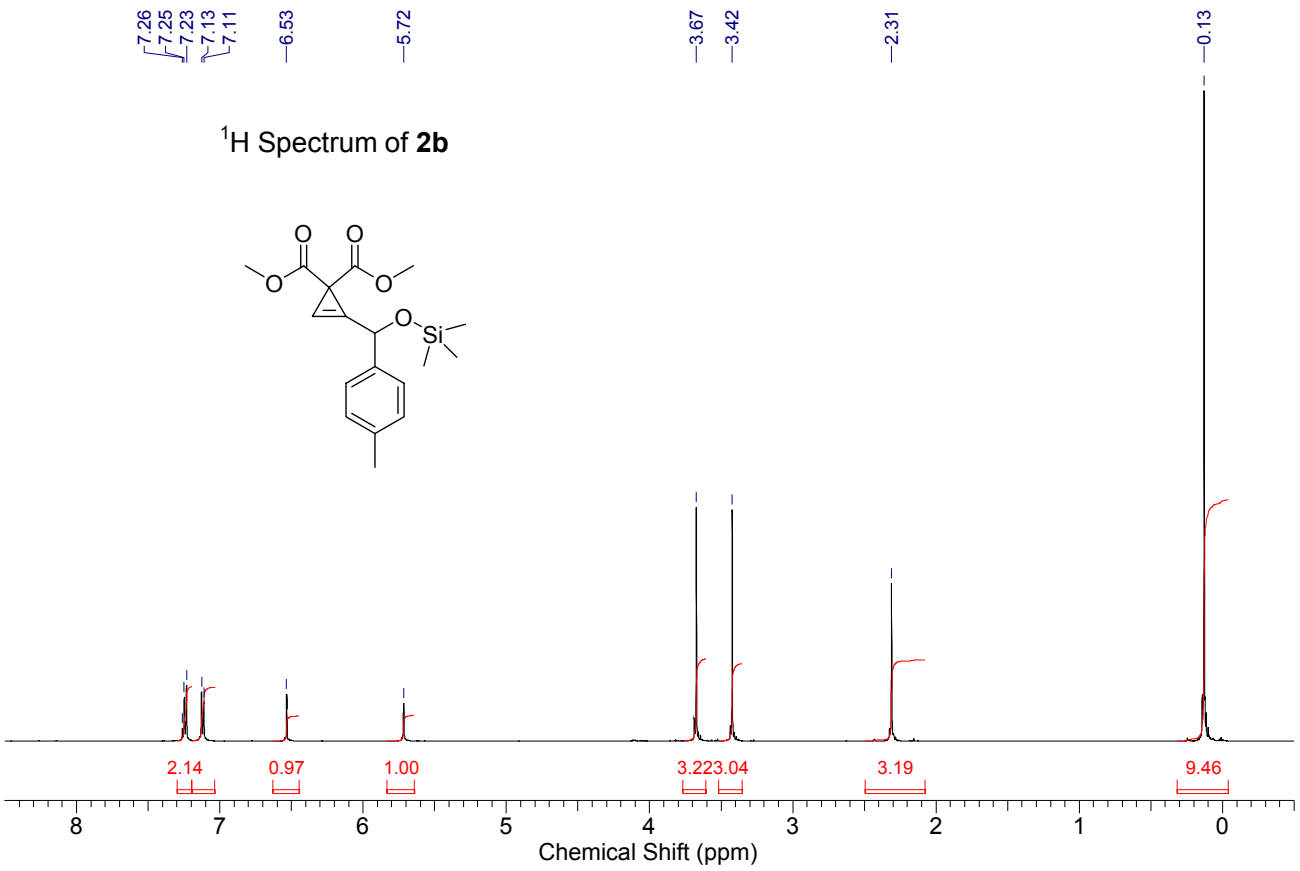

8.15
8.14
8.13
8.13
8.12
7.47
7.46
7.46
7.45
7.44
7.44
7.26
6.66
6.66
3.70
2.57
2.56
2.56
2.55
2.55
2.54
2.54
2.53
1.56
1.54
1.53
1.51
1.37
1.35
1.34
1.32
0.89
0.87
0.86
1H Spectrum of 12
O2N
O
O
1.83
1.86
0.86
3.00
2.04
2.05
2.98
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

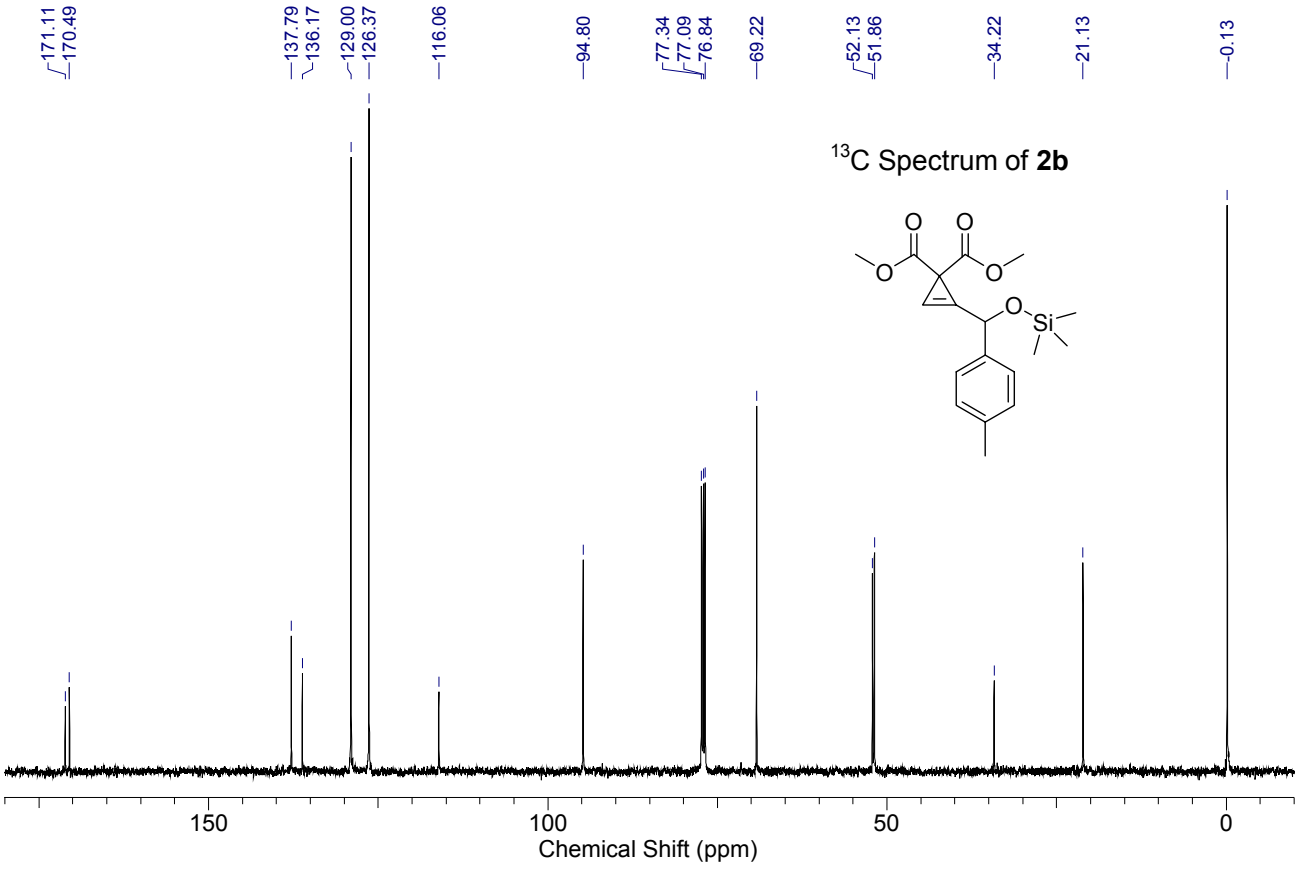

174.50
149.56
146.23
129.00
123.20
120.12
95.83
77.29
77.04
76.79
52.15
32.90
28.66
23.98
22.19
13.60
13C Spectrum of 12
O2N
O
O
150
100
50
0
Chemical Shift (ppm)

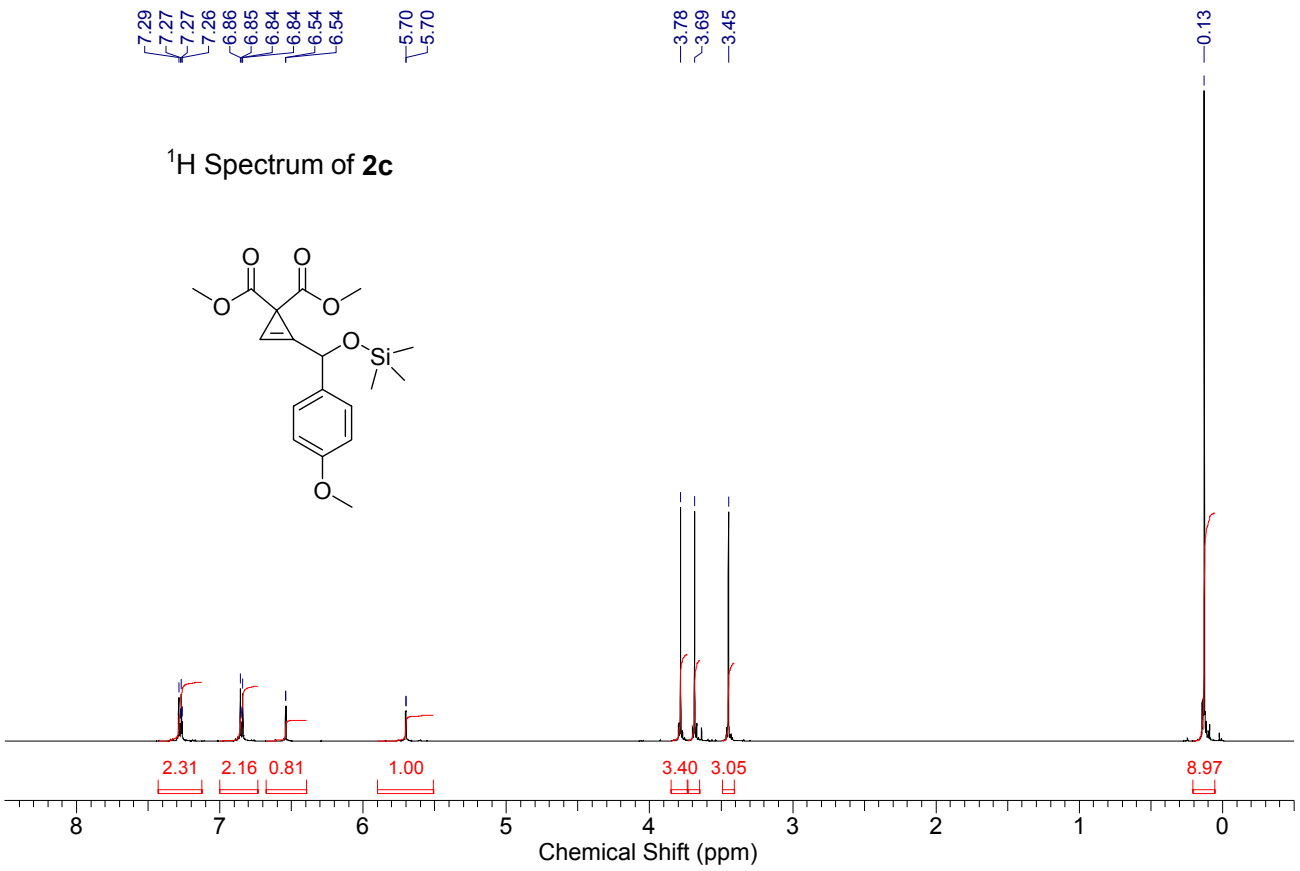

8.12
8.12
8.12
8.11
8.10
8.10
7.48
7.48
7.47
7.46
7.46
7.26
3.67
2.61
2.58
2.58
2.57
2.56
2.55
2.53
1.61
1.60
1.58
1.57
1.42
1.40
1.40
1.39
1.38
0.92
0.91
0.89
0.19
1H Spectrum of 1e
O2N
O
O
Si
1.83
1.87
3.00
2.01
2.35
3.06
8.79
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
174.76
151.15
145.61
128.42
127.93
123.05
107.41
77.28
77.03
76.77
51.74
34.42
29.18
25.16
22.26
13.67
1.16
13C Spectrum of 1e
O2N
O
O
Si
150
100
50
0
Chemical Shift (ppm)

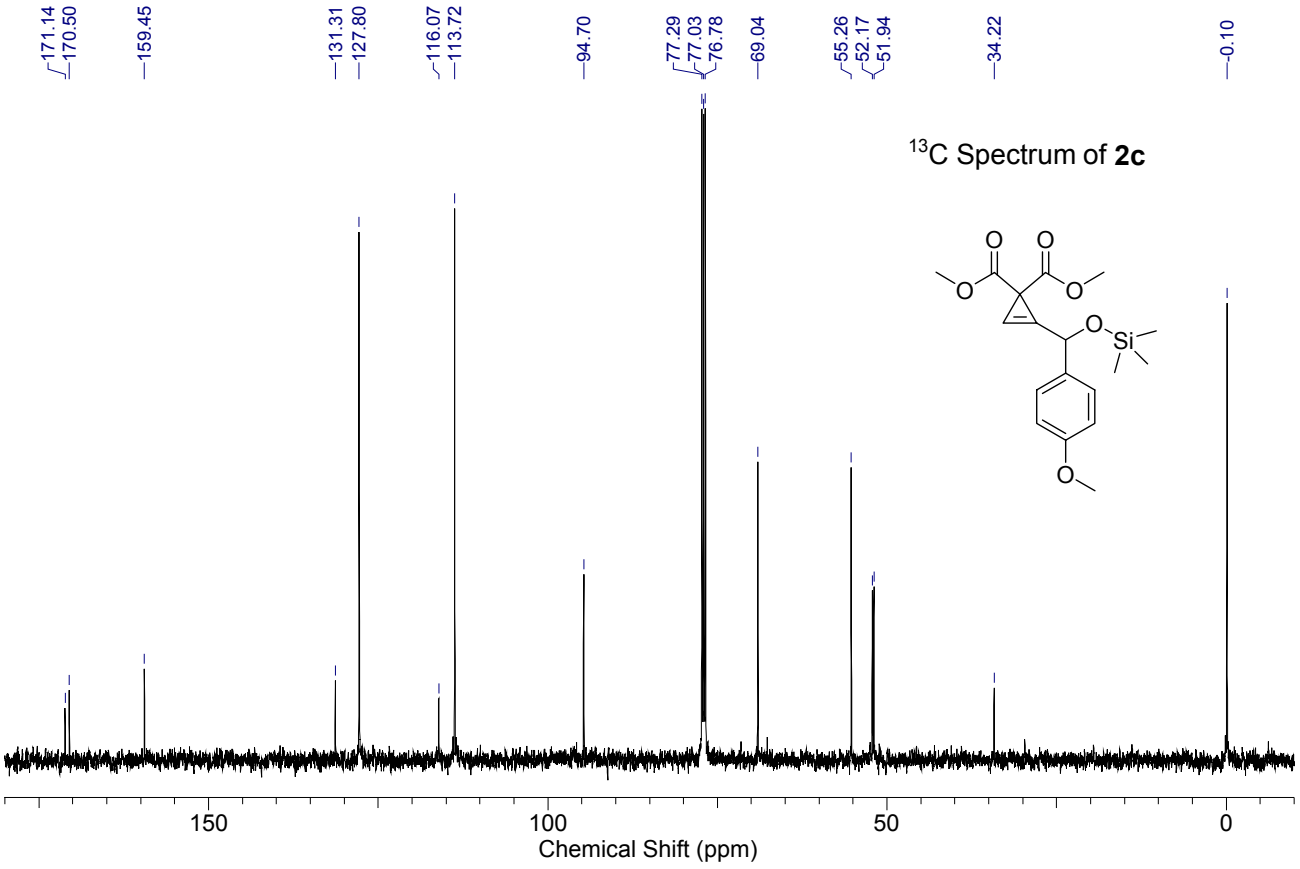

7.38
7.36
7.34
7.32
7.32
7.31
7.27
7.26
6.56
6.55
5.76
3.68
3.41
0.15
^{1}H Spectrum of **2a**
O
O
O
O
O
Si
2.20
0.90
1.00
3.02
3.05
8.78
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

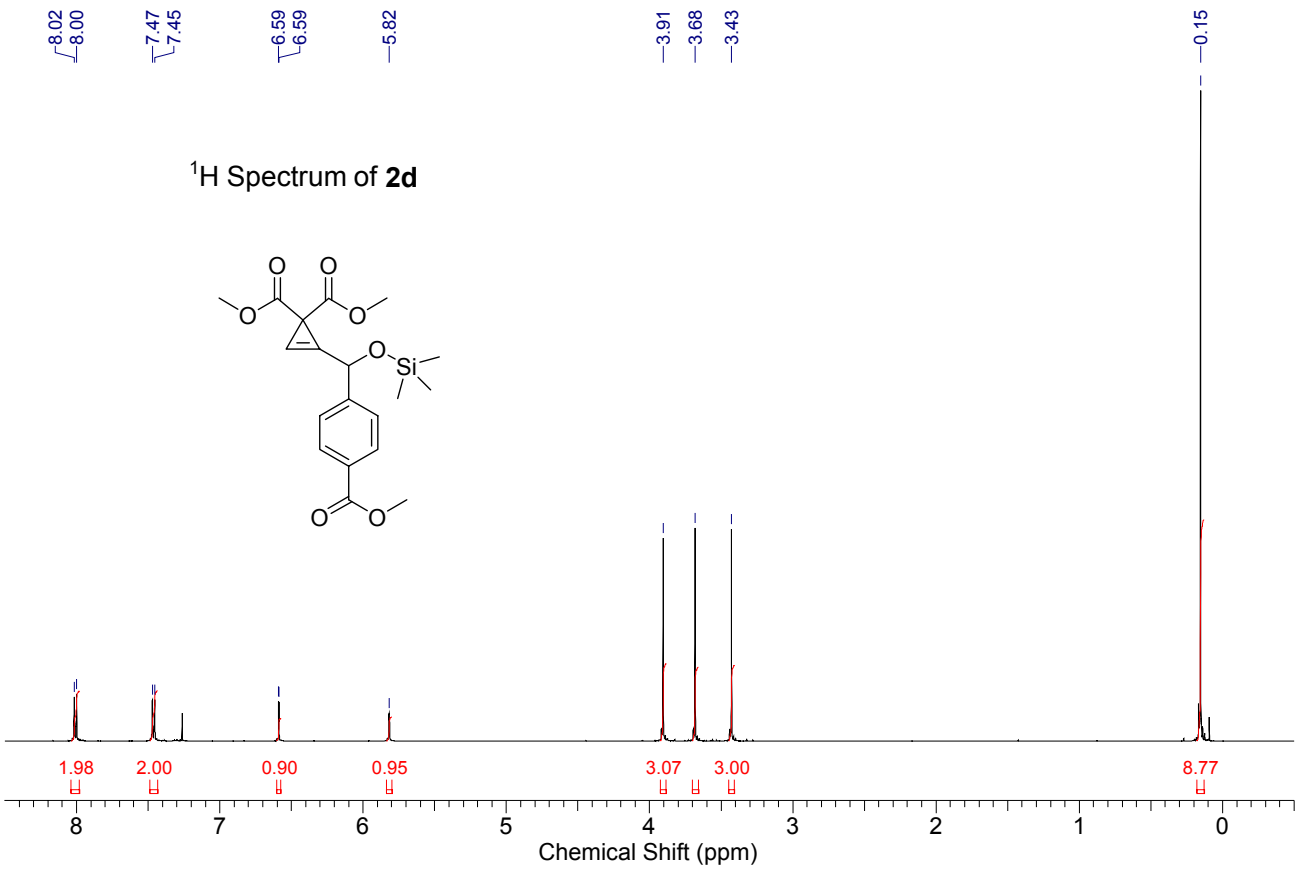

171.28
170.62
139.28
128.57
128.31
126.57
116.20
95.18
77.52
77.26
77.00
69.57
52.40
52.12
34.44
0.09
^{13}C Spectrum of **2a**
O
O
O
O
O
Si
150
100
50
0
Chemical Shift (ppm)


7.26
7.25
7.23
7.13
7.11
6.53
5.72
3.67
3.42
2.31
0.13
^{1}H Spectrum of **2b**
O
O
O
O
O
Si
2.14
0.97
1.00
3.22
3.04
3.19
9.46
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

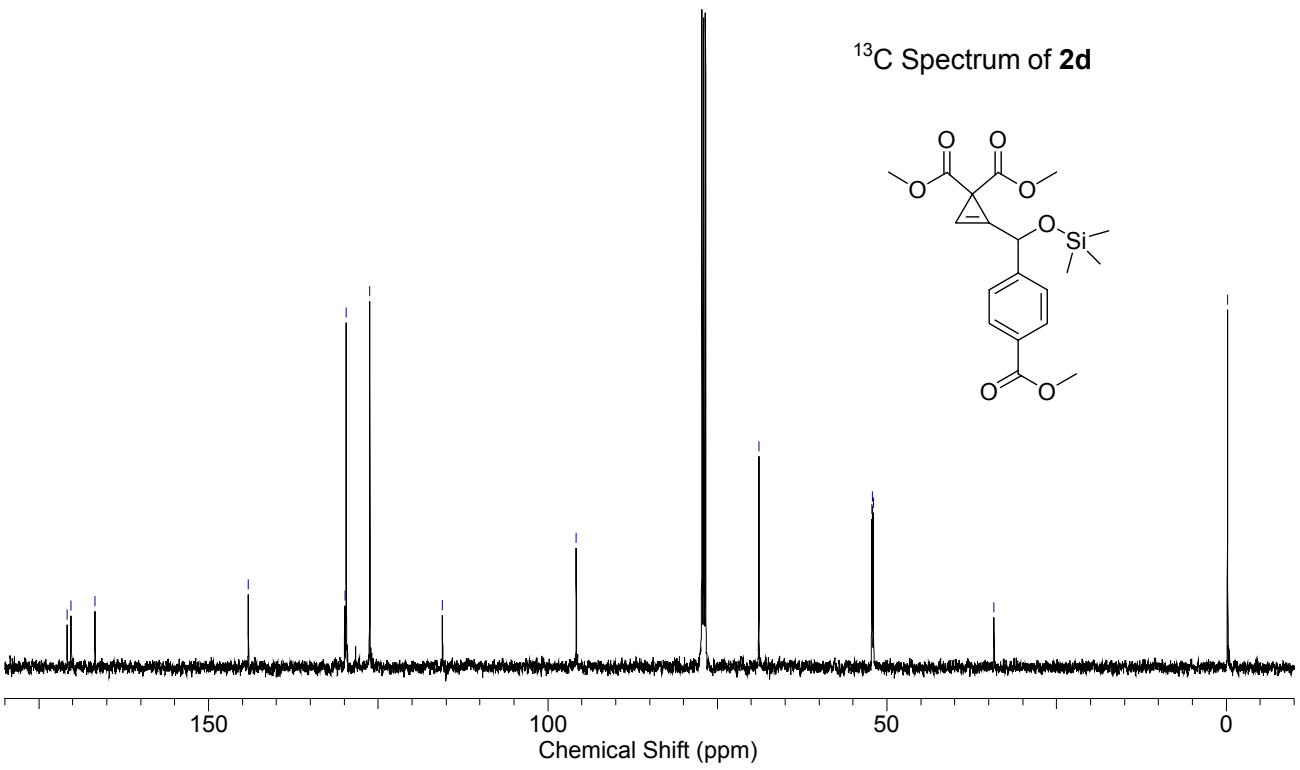

171.11
170.49
137.79
136.17
129.00
126.37
116.06
94.80
77.34
77.09
76.84
69.22
52.13
51.86
34.22
21.13
0.13
^{13}C Spectrum of **2b**
O
O
O
O
O
Si
150
100
50
0
Chemical Shift (ppm)


7.29
7.27
7.27
7.26
6.86
6.85
6.84
6.84
6.54
6.54
5.70
5.70
3.78
3.69
3.45
0.13
^{1}H Spectrum of **2c**
O
O
O
O
O
Si
O
2.31
2.16
0.81
1.00
3.40
3.05
8.97
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

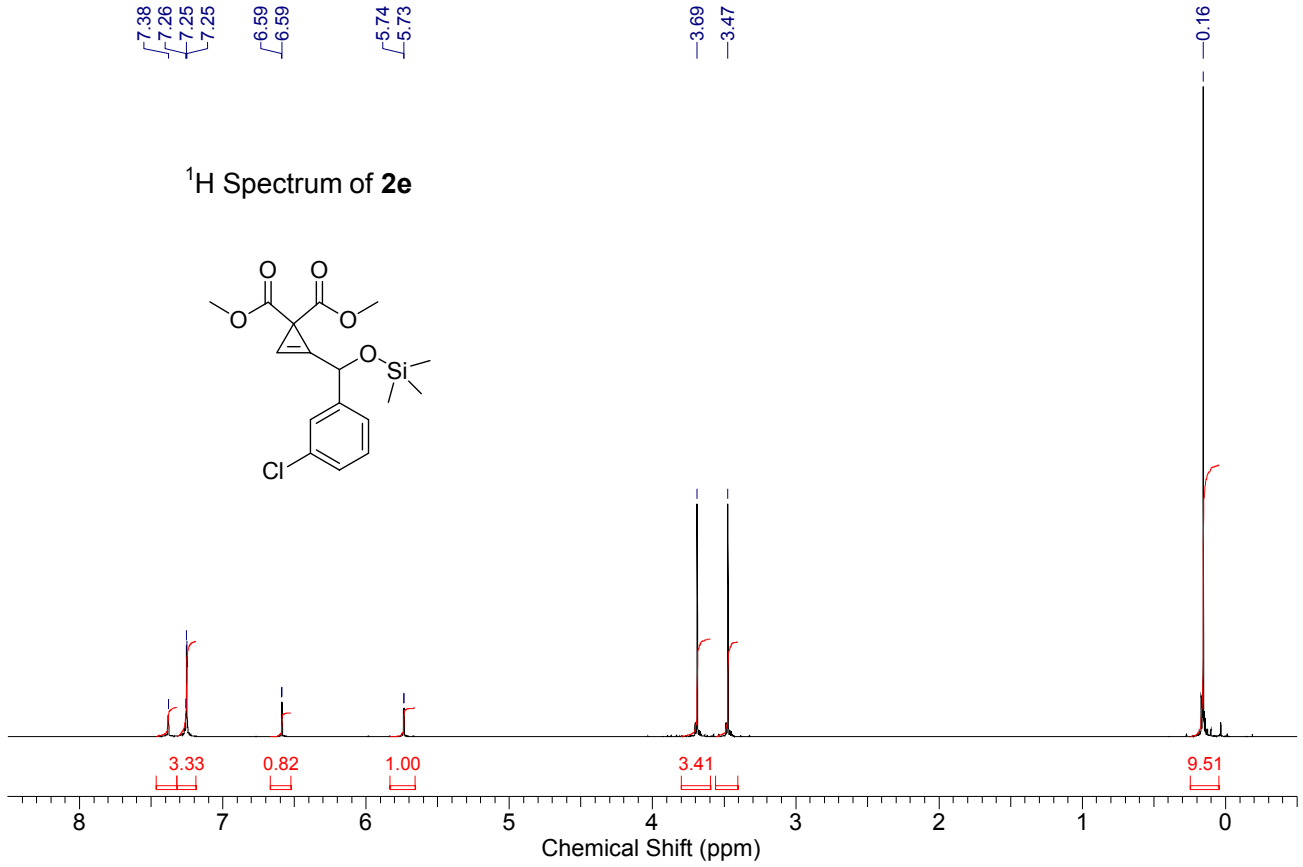

171.14
170.50
159.45
131.31
127.80
116.07
113.72
94.70
77.29
77.03
76.78
69.04
55.26
52.17
51.94
34.22
0.10
^{13}C Spectrum of **2c**
O
O
O
O
O
Si
O
150
100
50
0
Chemical Shift (ppm)



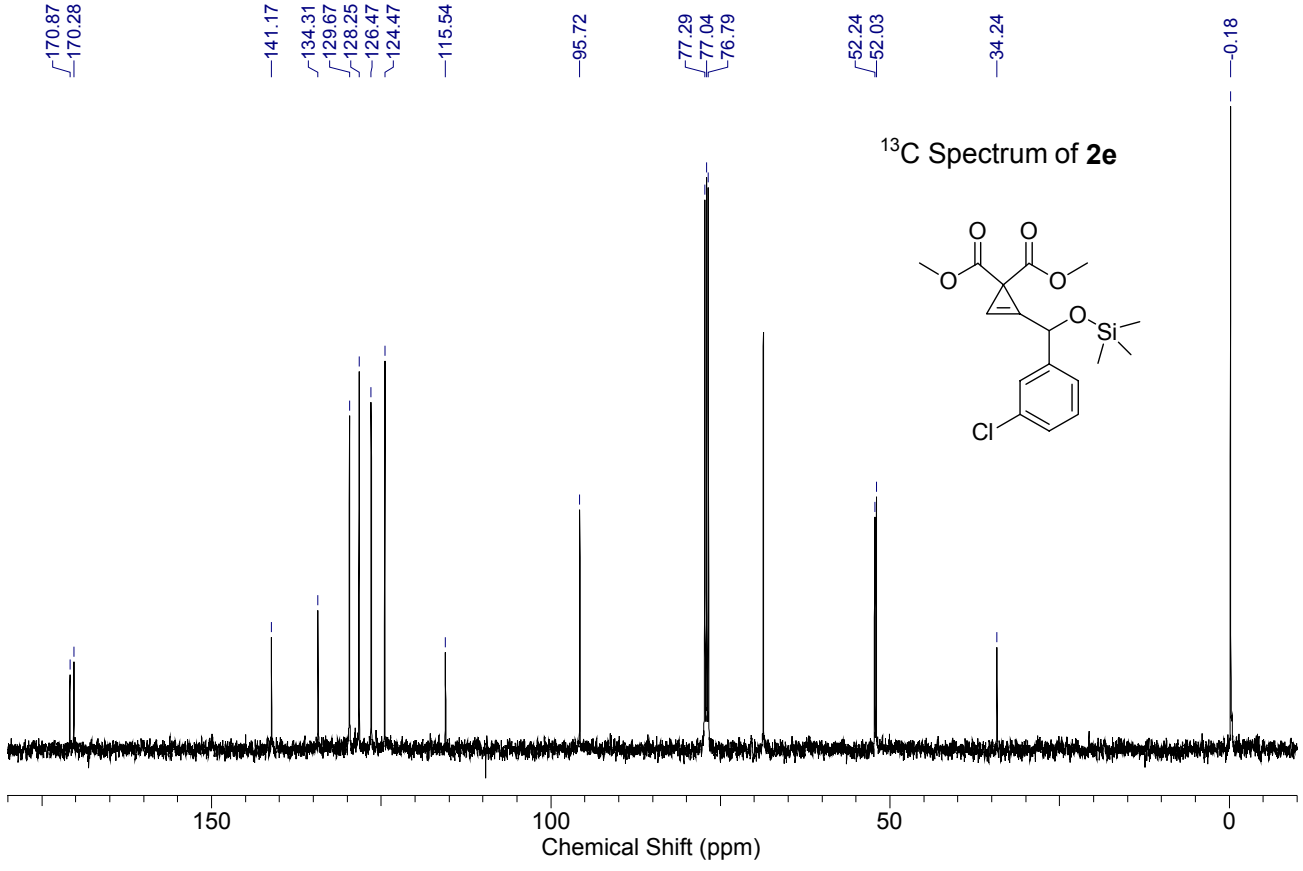
^{1}H Spectrum of **2d**



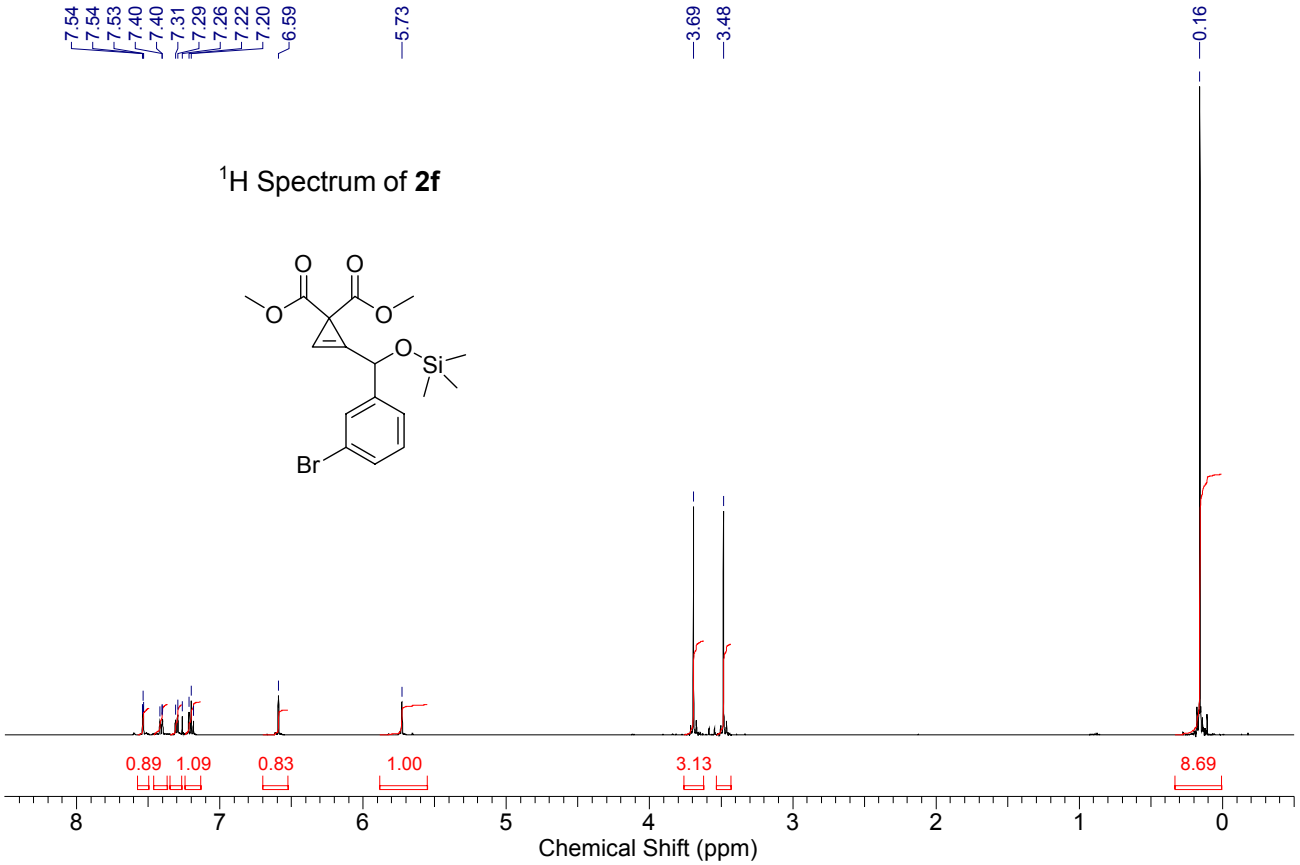
^{13}C Spectrum of **2d**



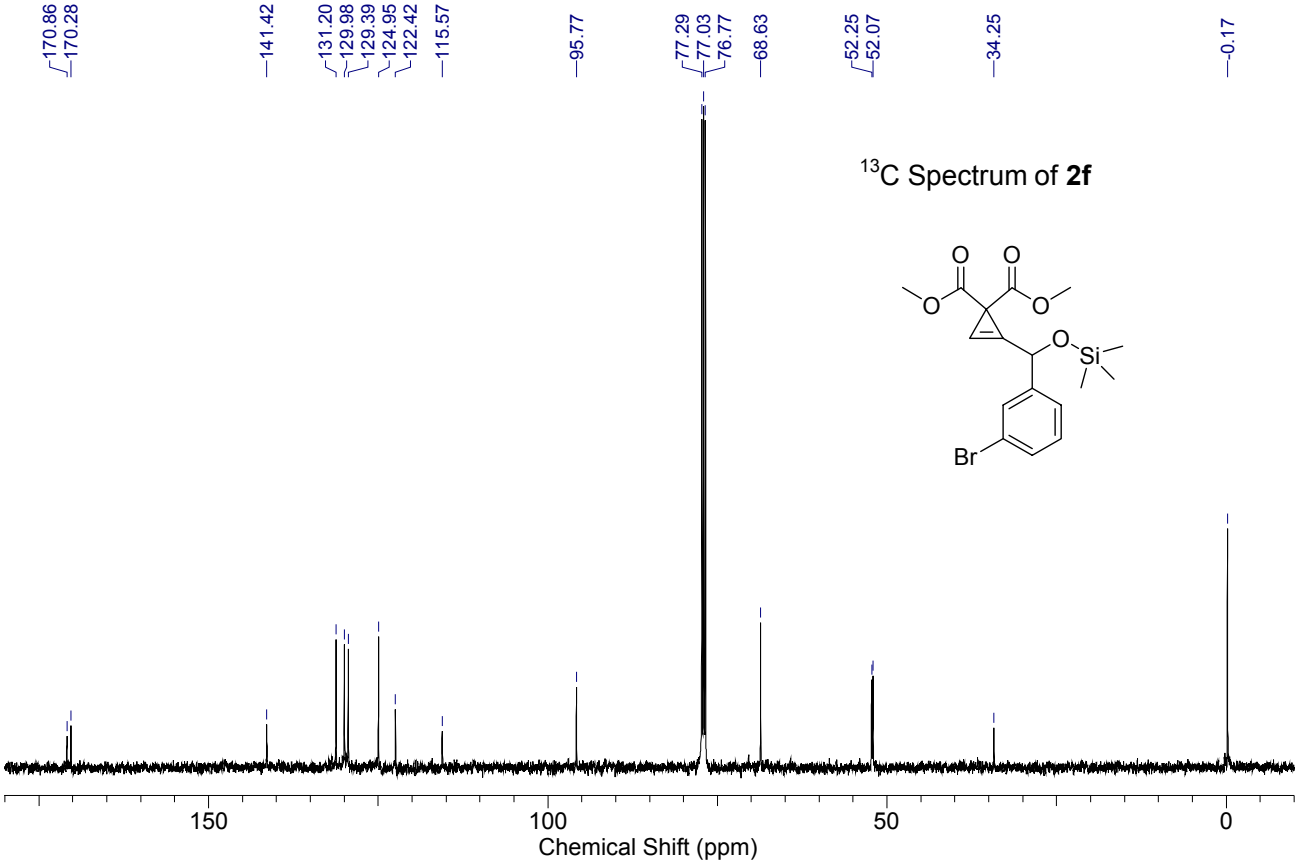
^{1}H Spectrum of **2e**



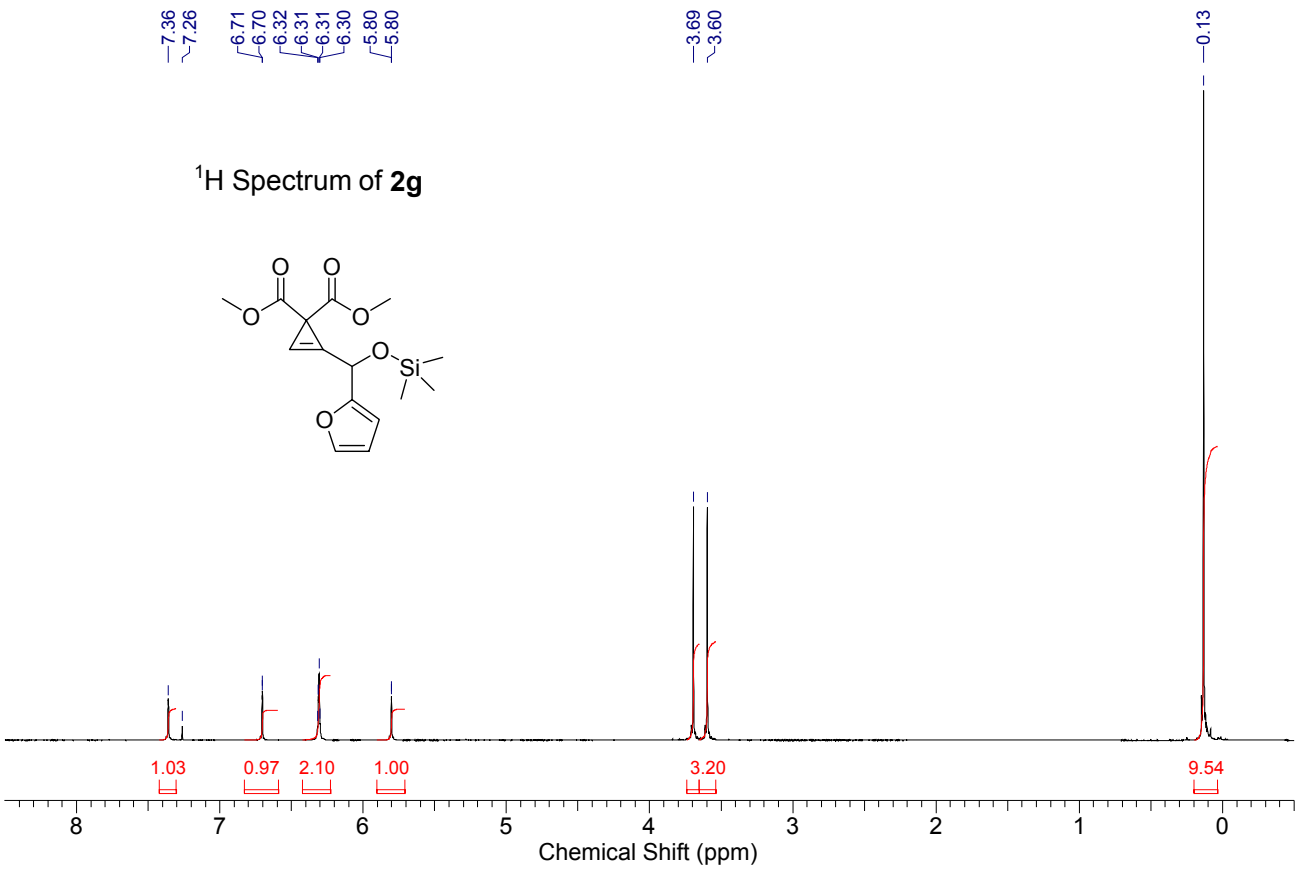
^{13}C Spectrum of **2e**

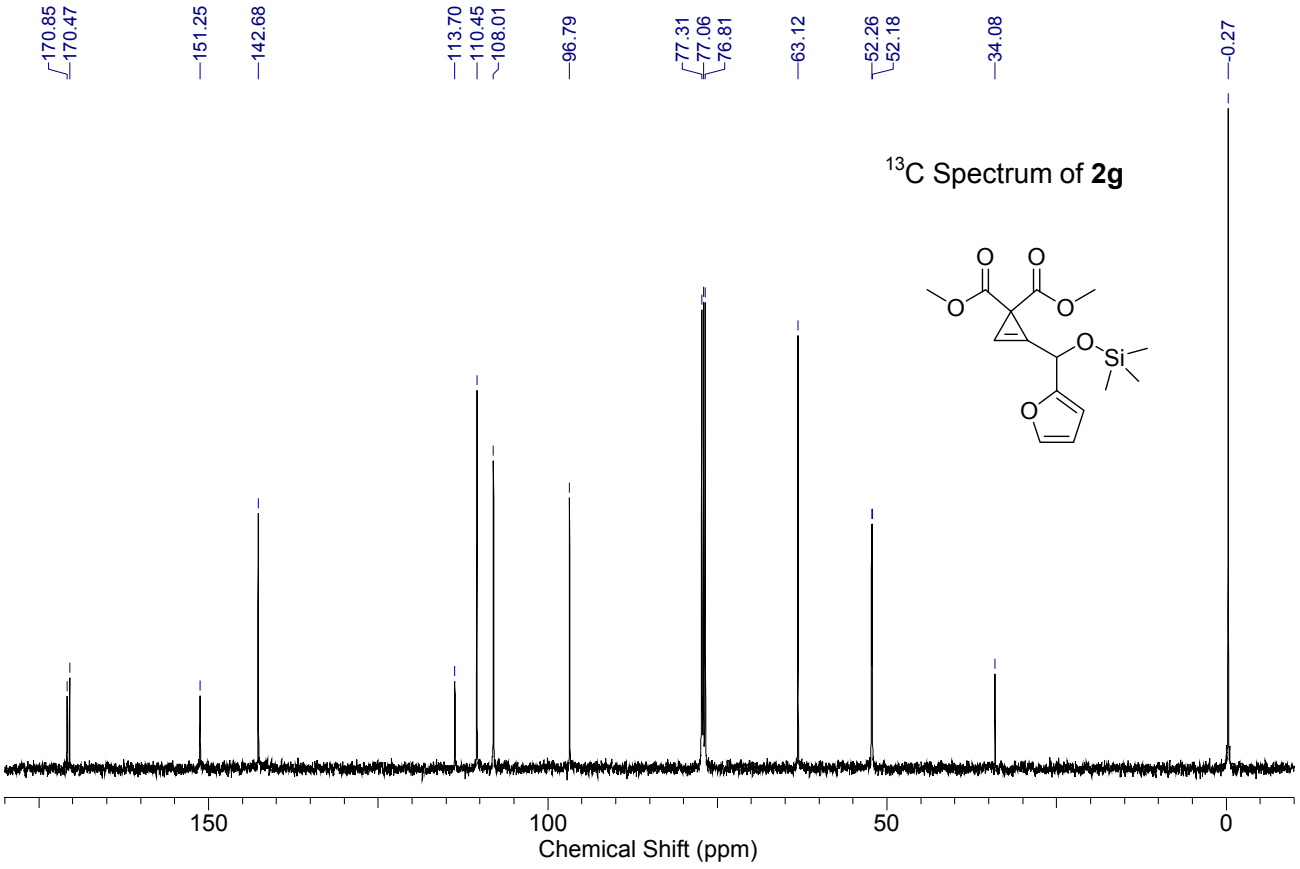


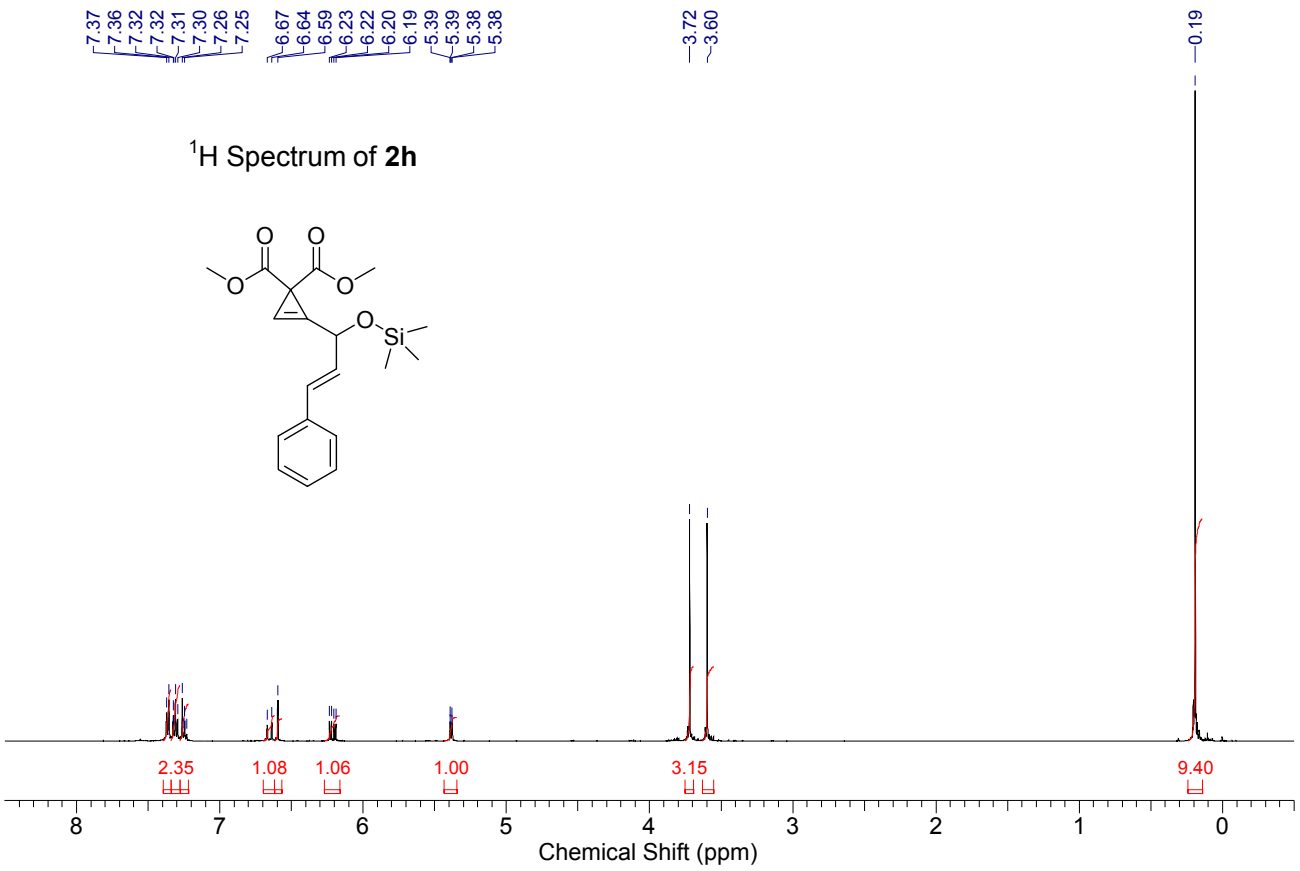
^{1}H Spectrum of **2f**



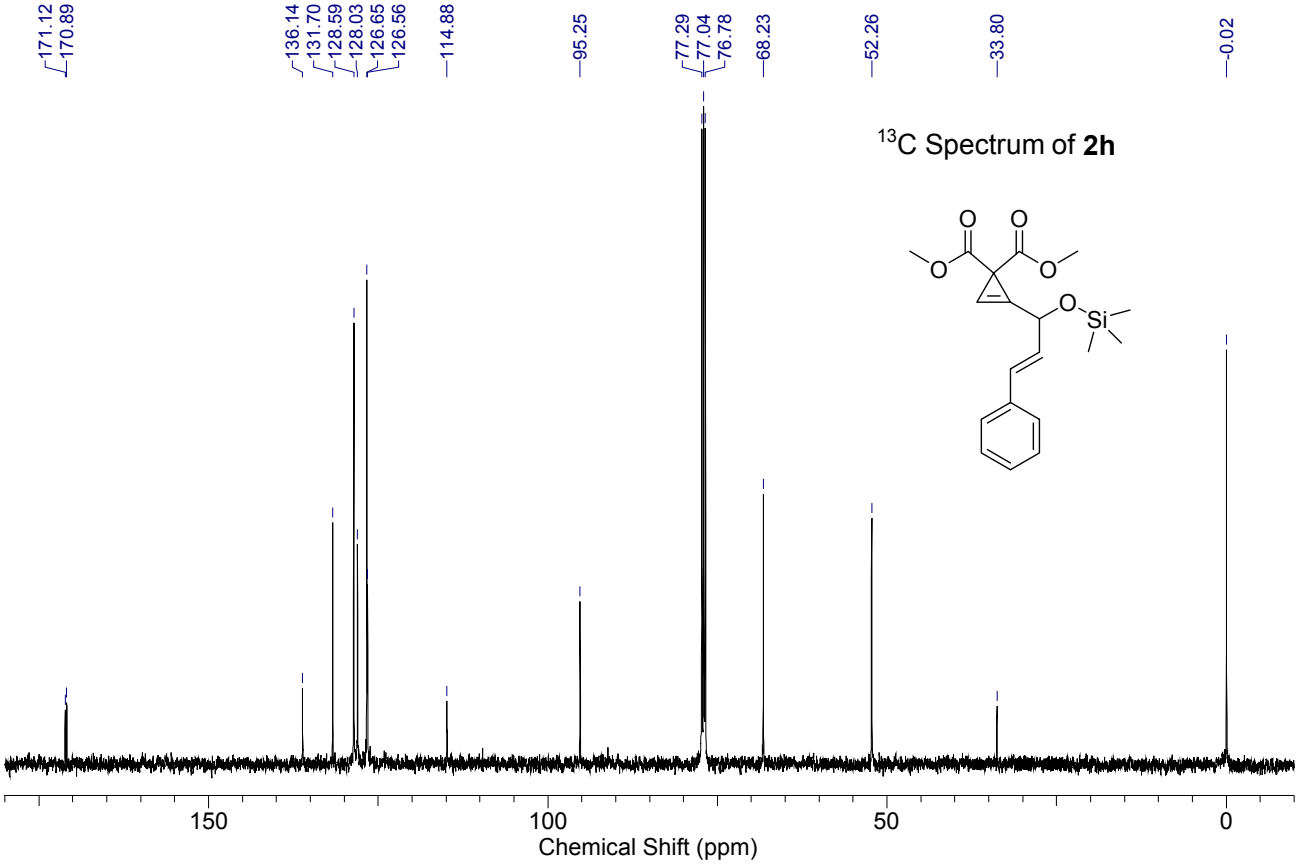
^{13}C Spectrum of **2f**


7.36
7.26
6.71
6.70
6.32
6.31
6.31
6.30
5.80
5.80
3.69
3.60
0.13
1H Spectrum of 2g
O
O
O
O
O
Si
O
1.03
0.97
2.10
1.00
3.20
9.54
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

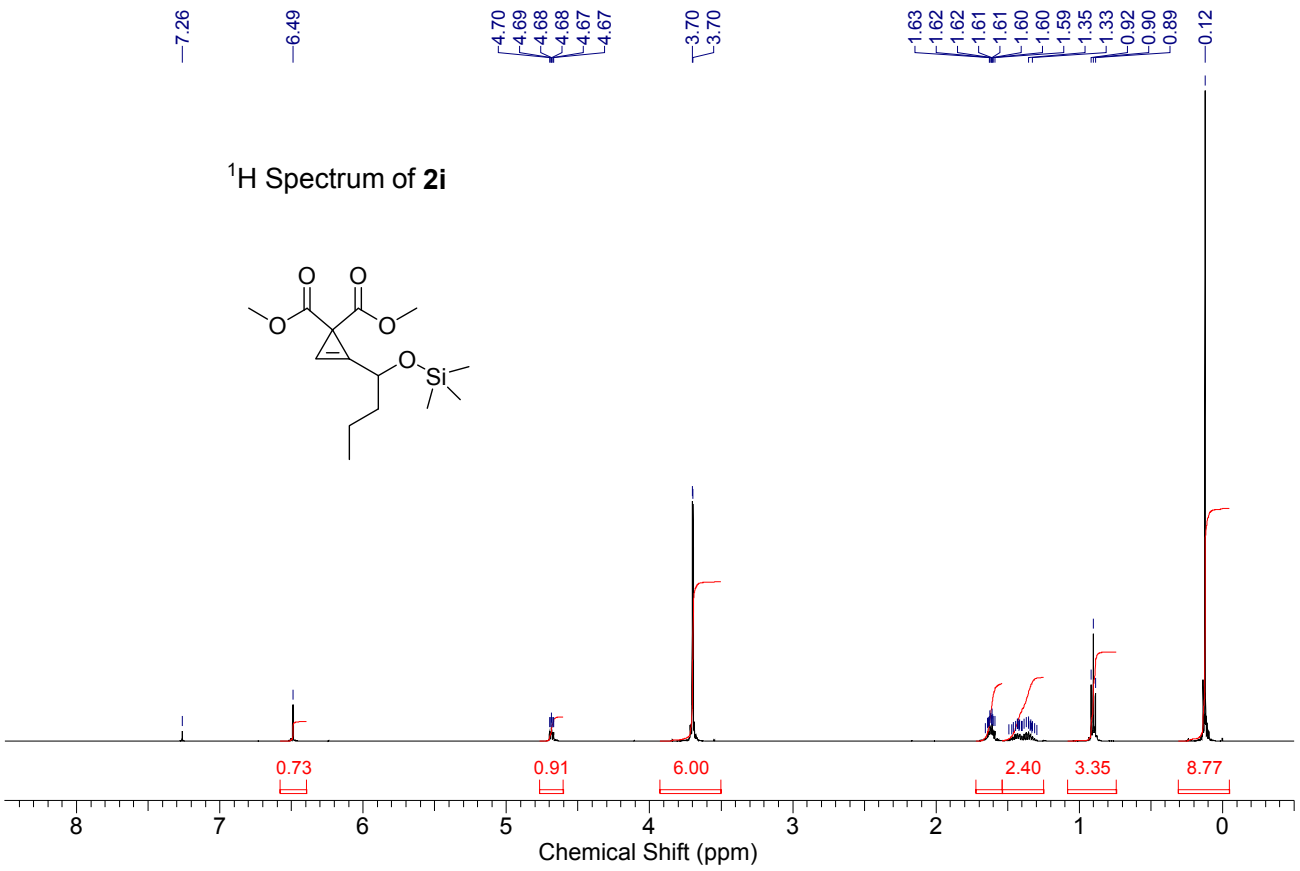

170.85
170.47
151.25
142.68
113.70
110.45
108.01
96.79
77.31
77.06
76.81
63.12
52.26
52.18
34.08
0.27
13C Spectrum of 2g
O
O
O
O
O
Si
O
150
100
50
0
Chemical Shift (ppm)



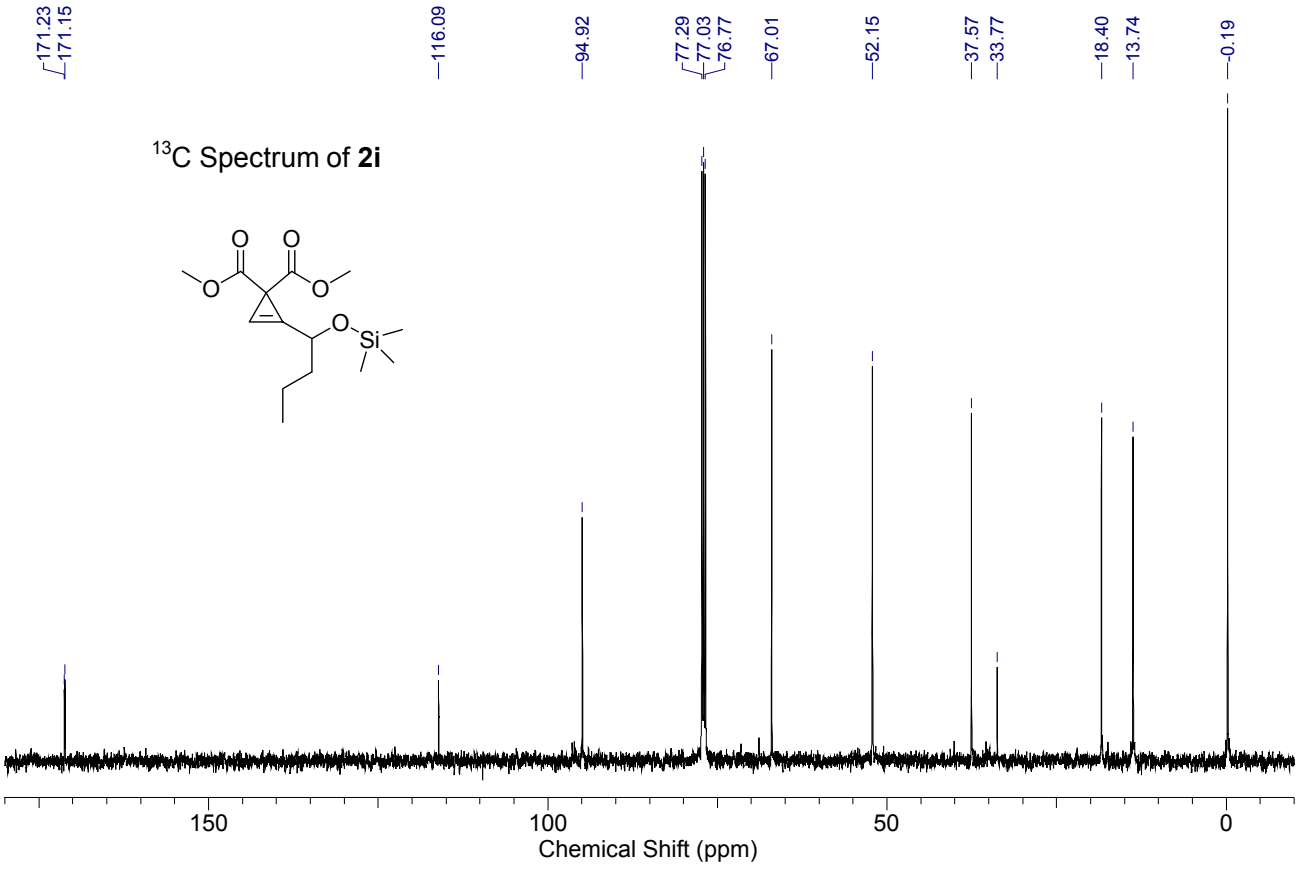
^{1}H Spectrum of **2h**



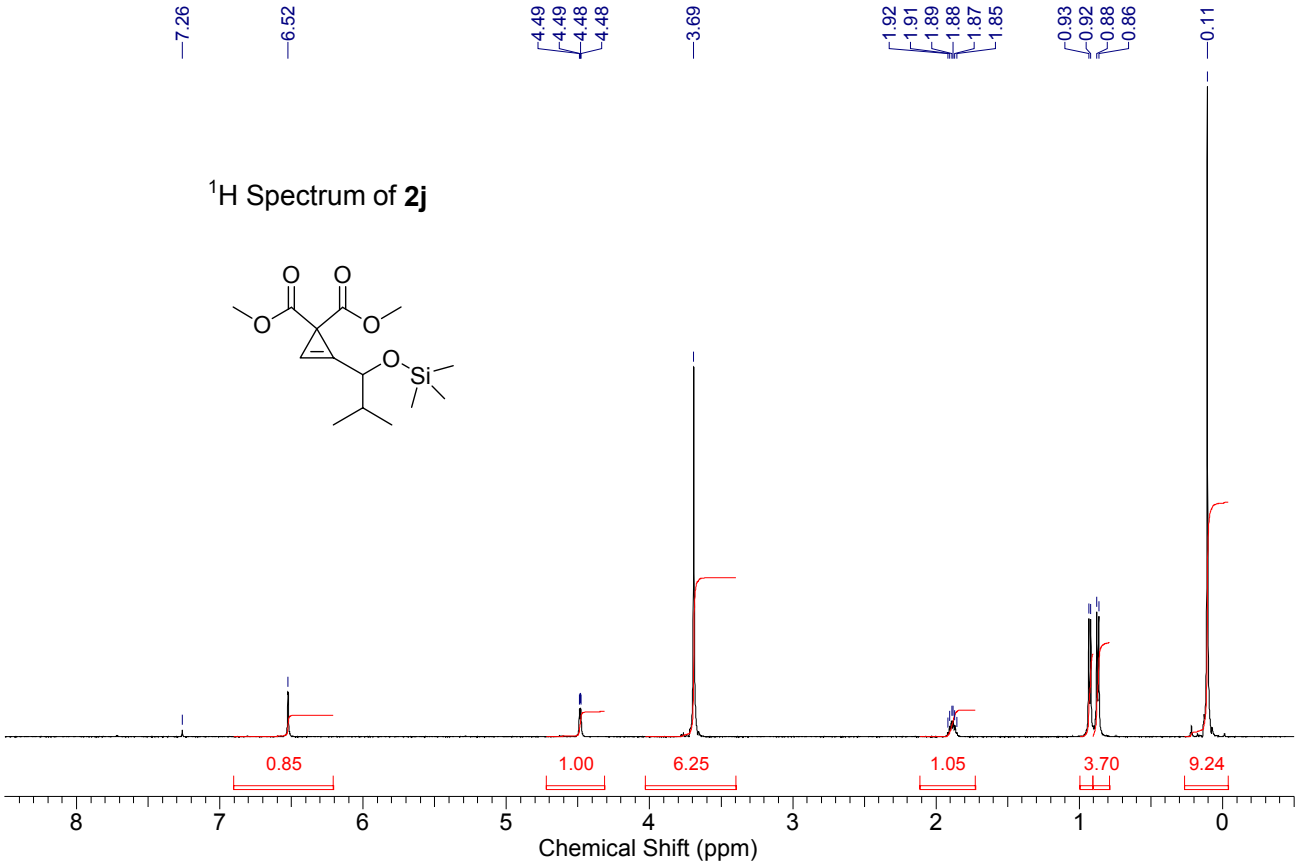
^{13}C Spectrum of **2h**



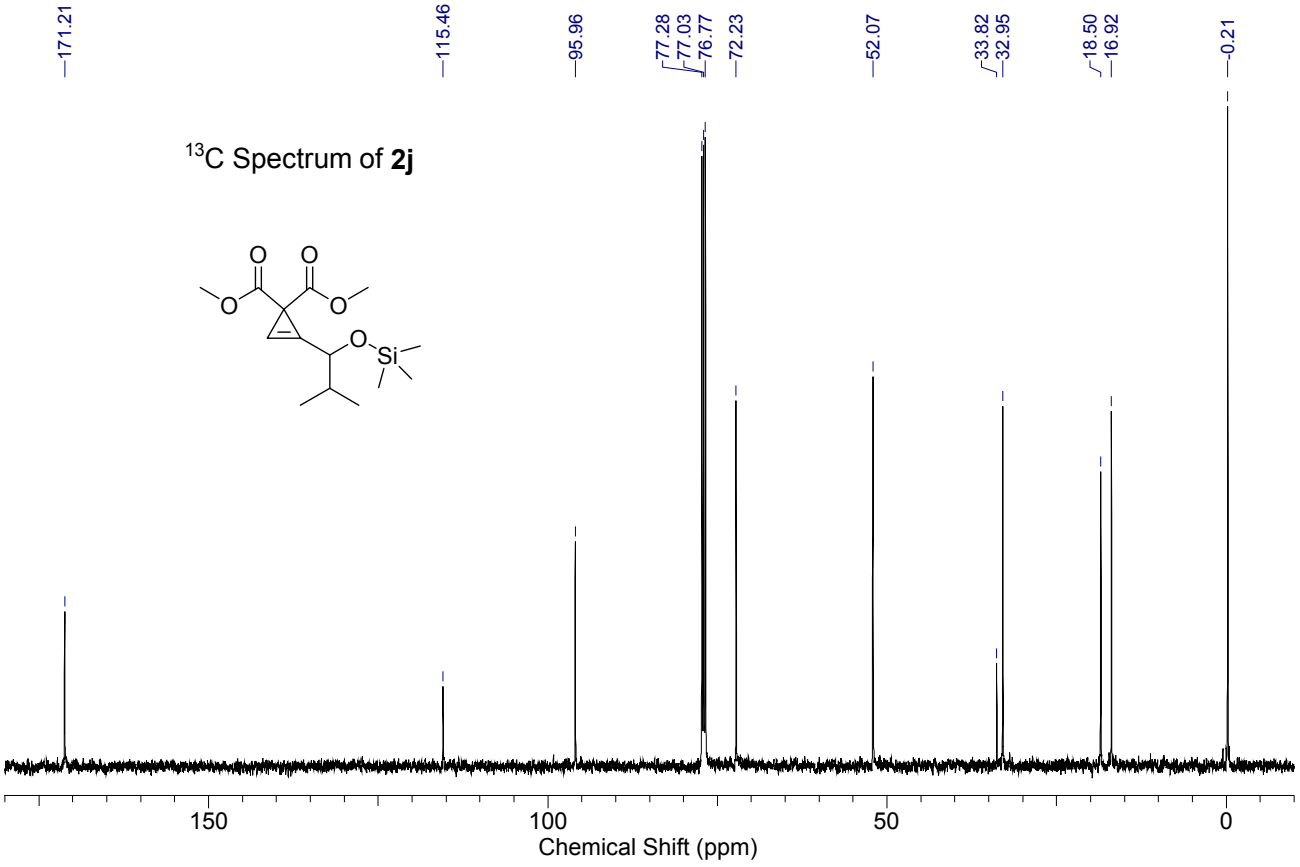
^{1}H Spectrum of **2i**



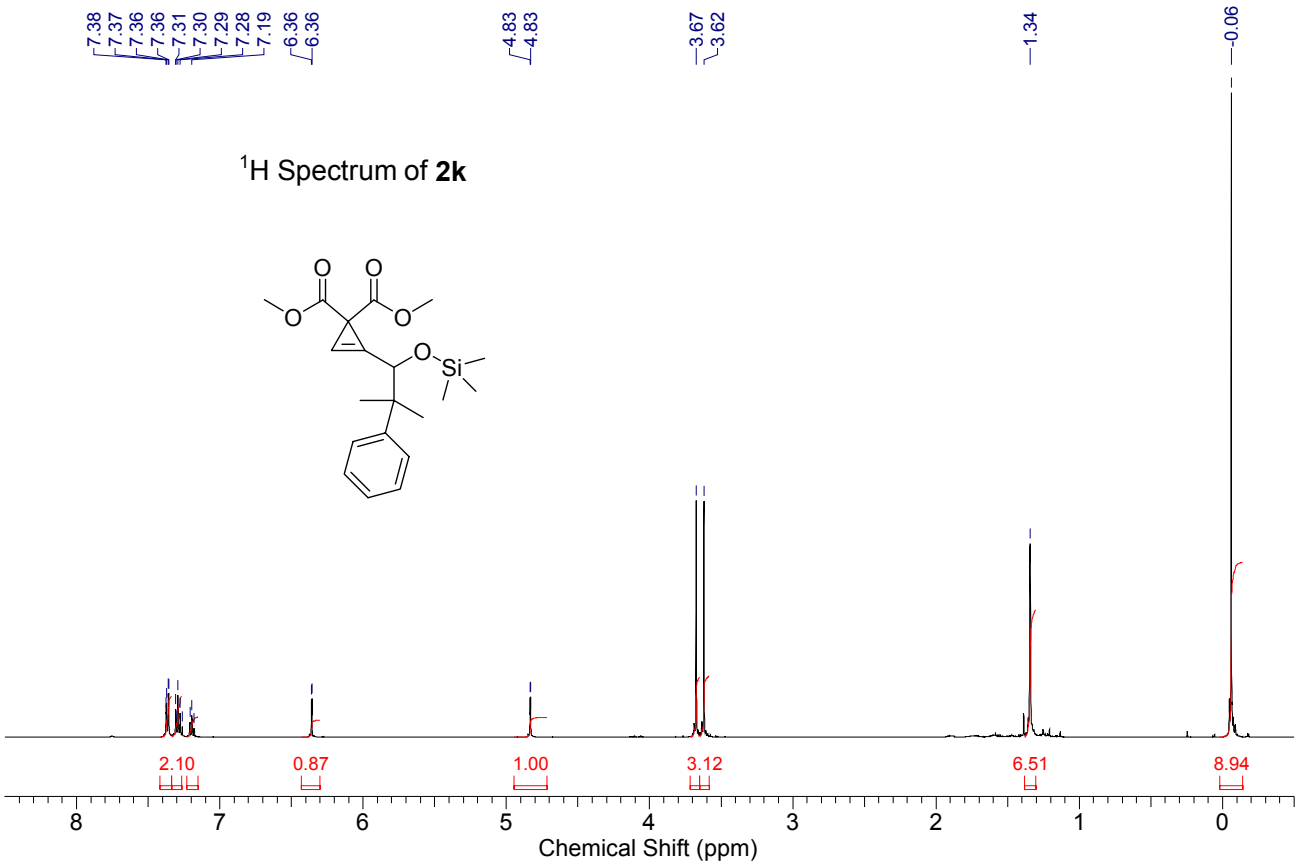
^{13}C Spectrum of **2i**



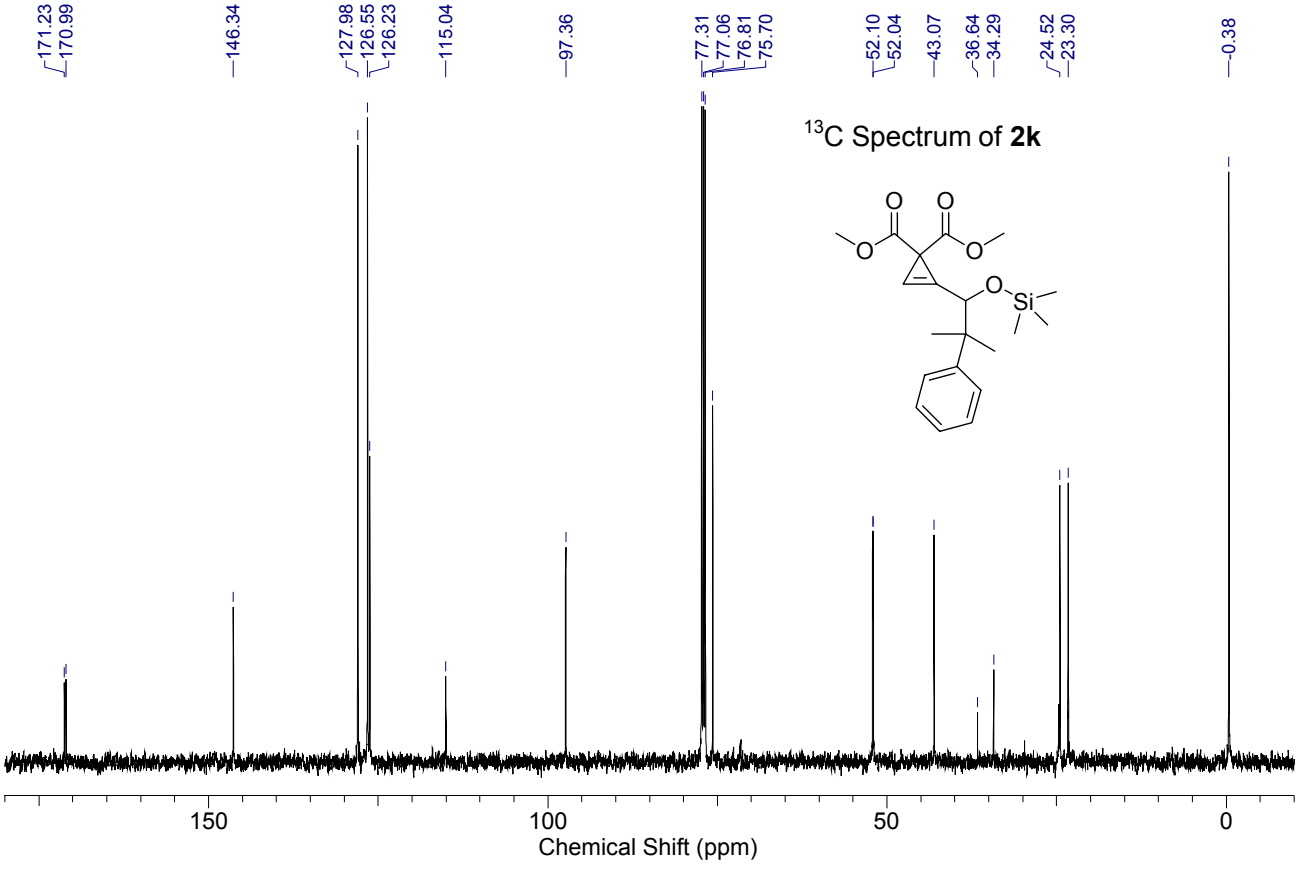
^{1}H Spectrum of **2j**



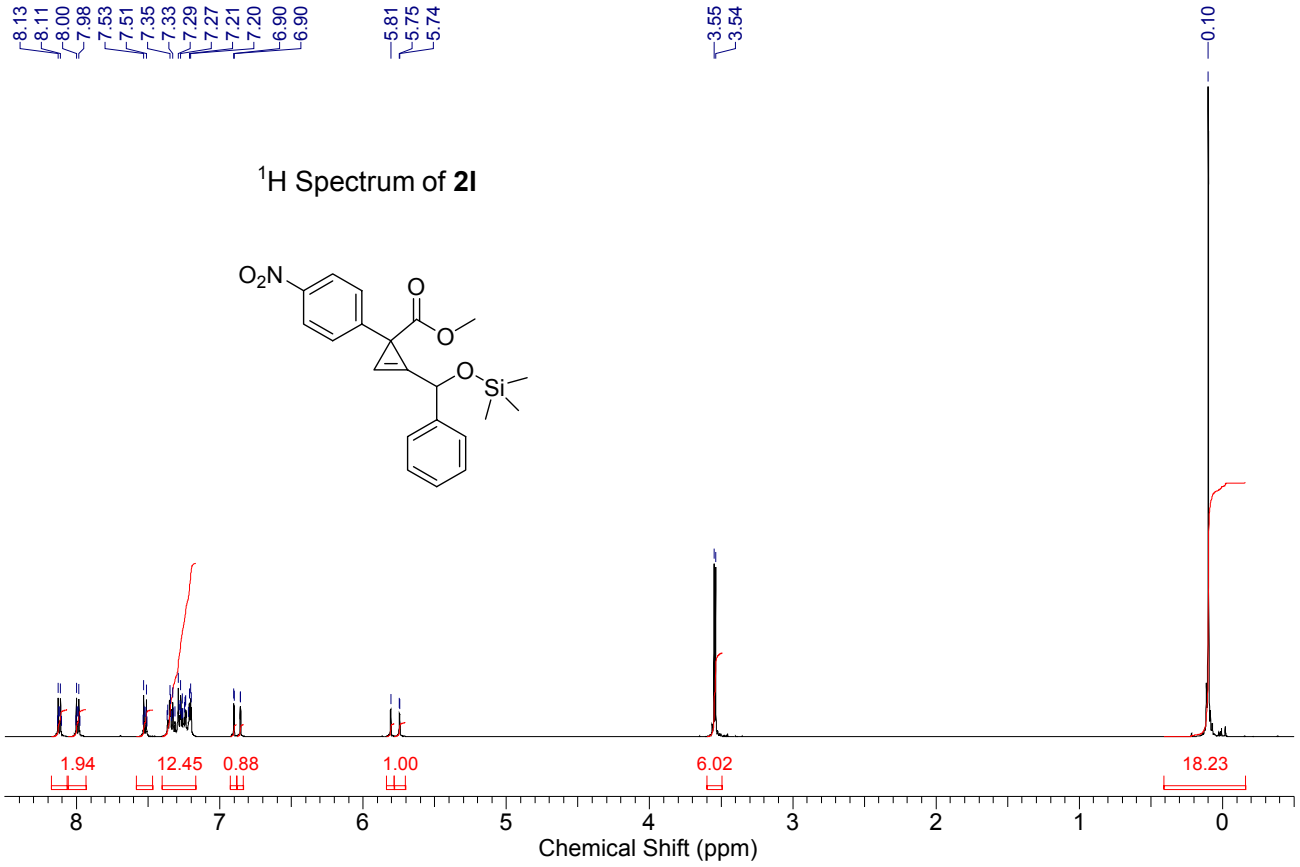
^{13}C Spectrum of **2j**

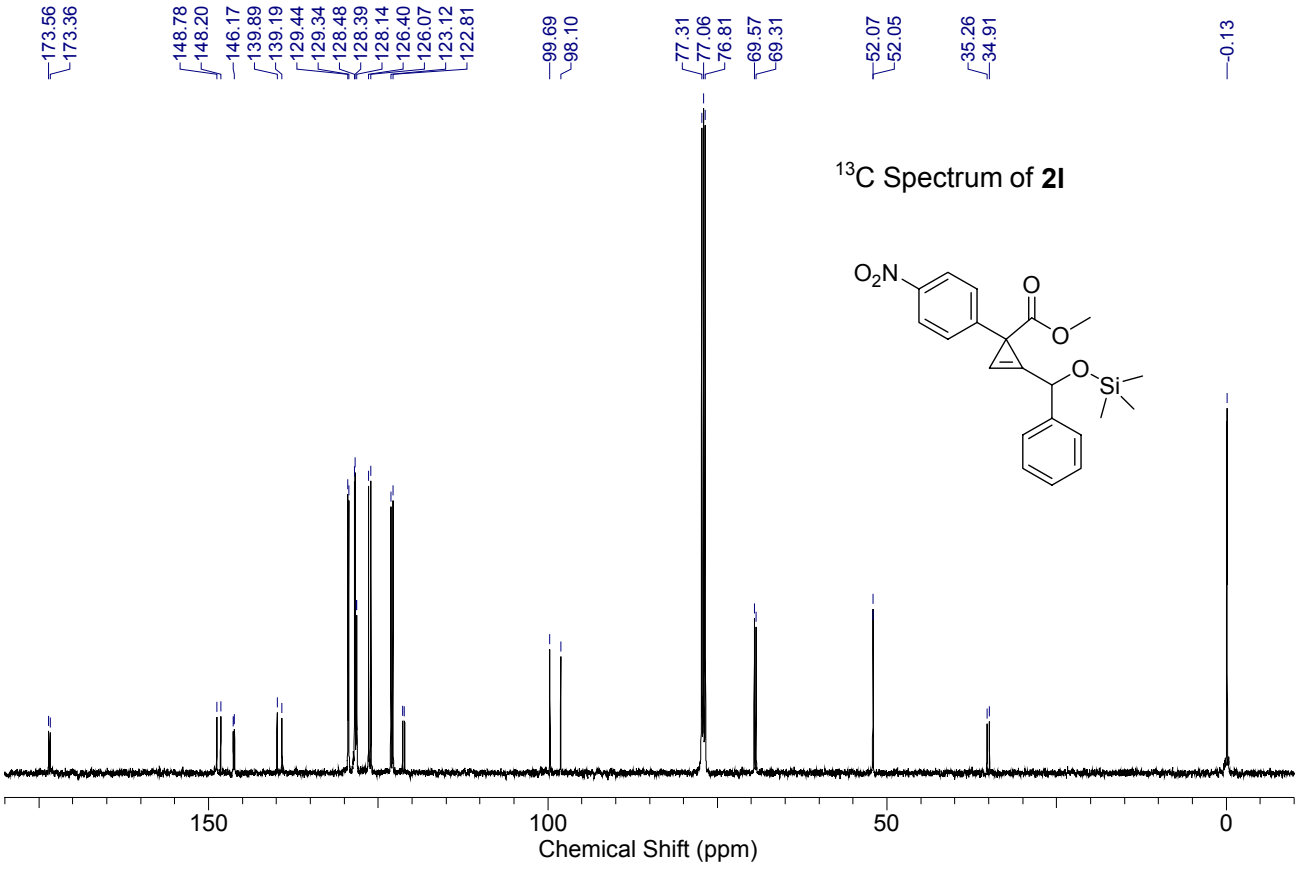


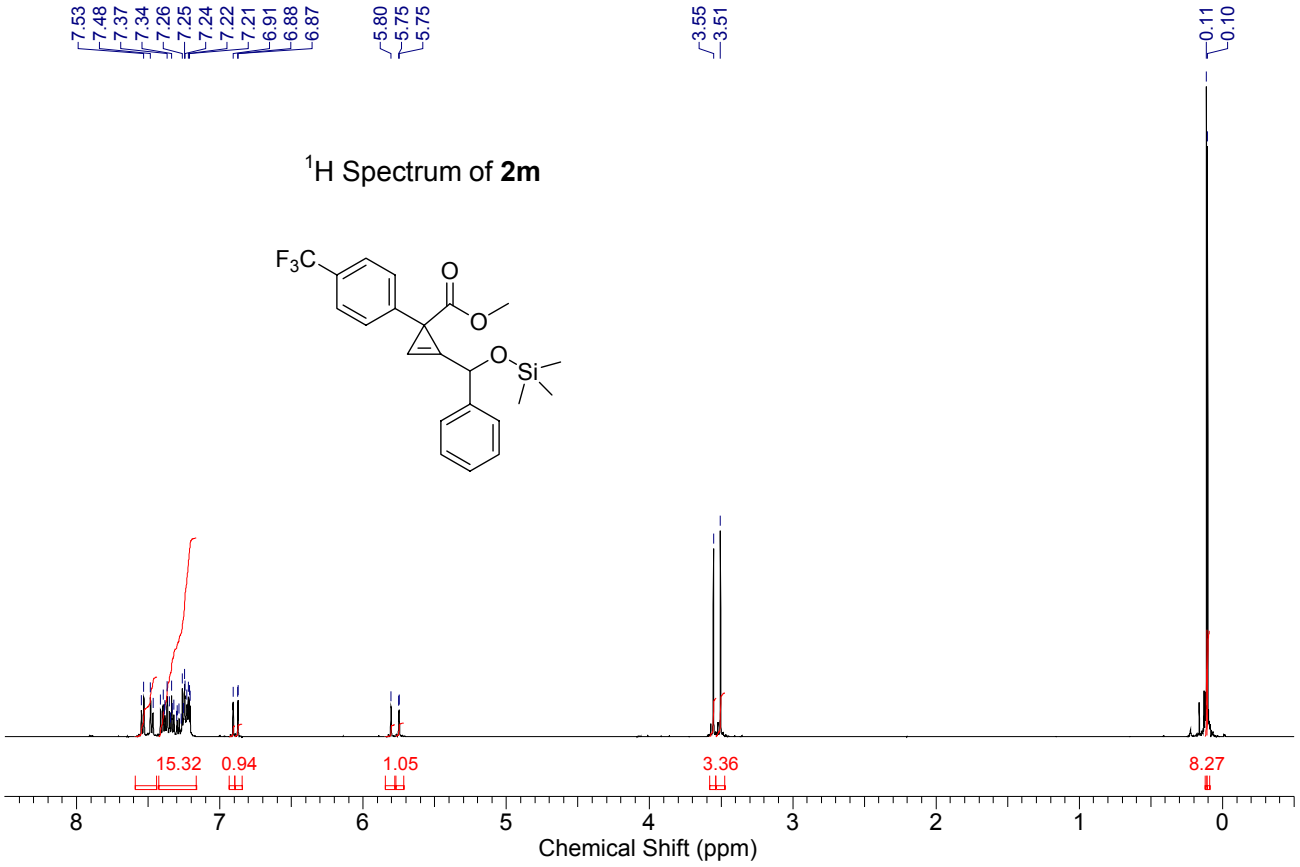
^{1}H Spectrum of **2k**



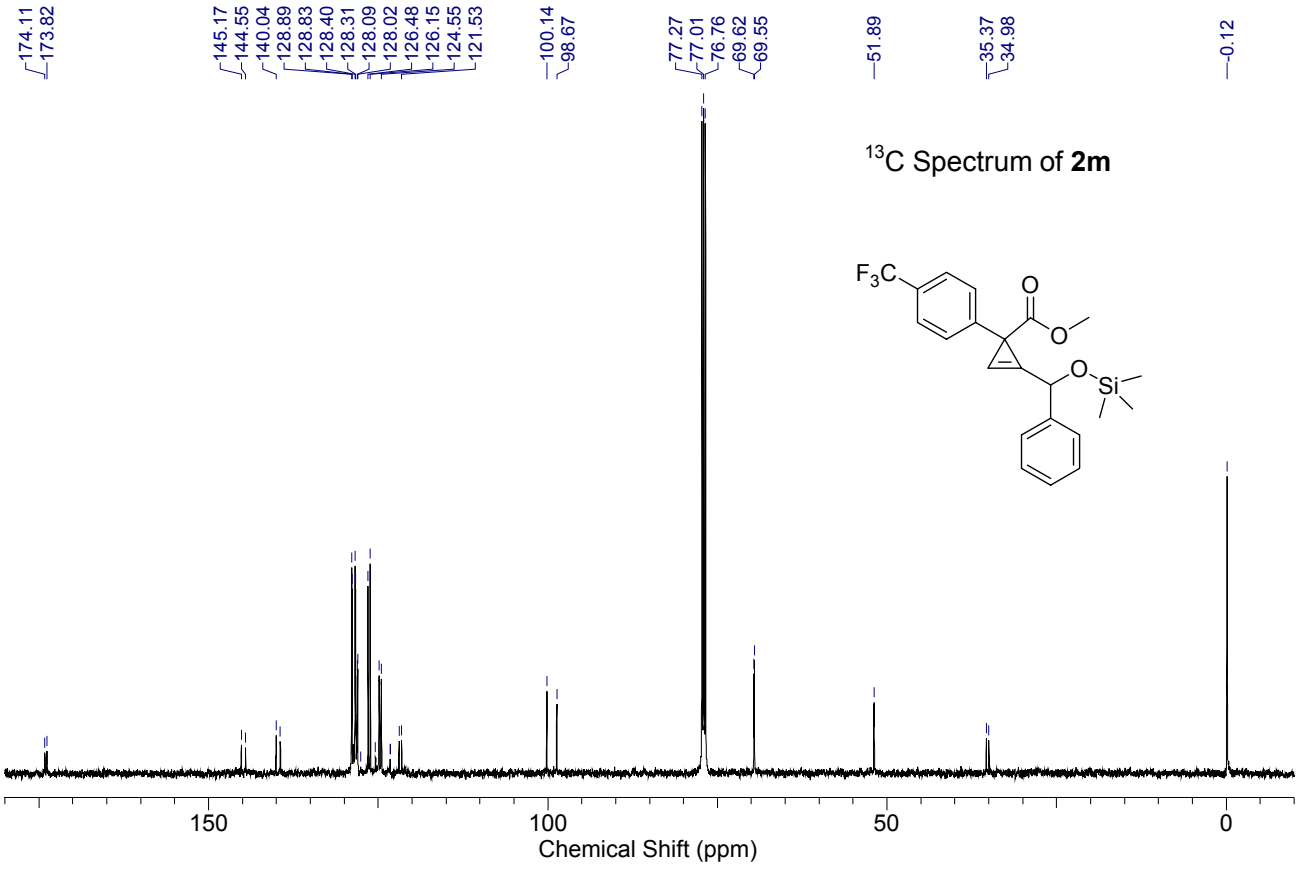
^{13}C Spectrum of **2k**


8.13
8.11
8.00
7.98
7.53
7.51
7.35
7.33
7.29
7.27
7.21
7.20
6.90
6.90
5.81
5.75
5.74
3.55
3.54
0.10
1H Spectrum of 2l
O2N
O
O
O
Si
1.94
12.45
0.88
1.00
6.02
18.23
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

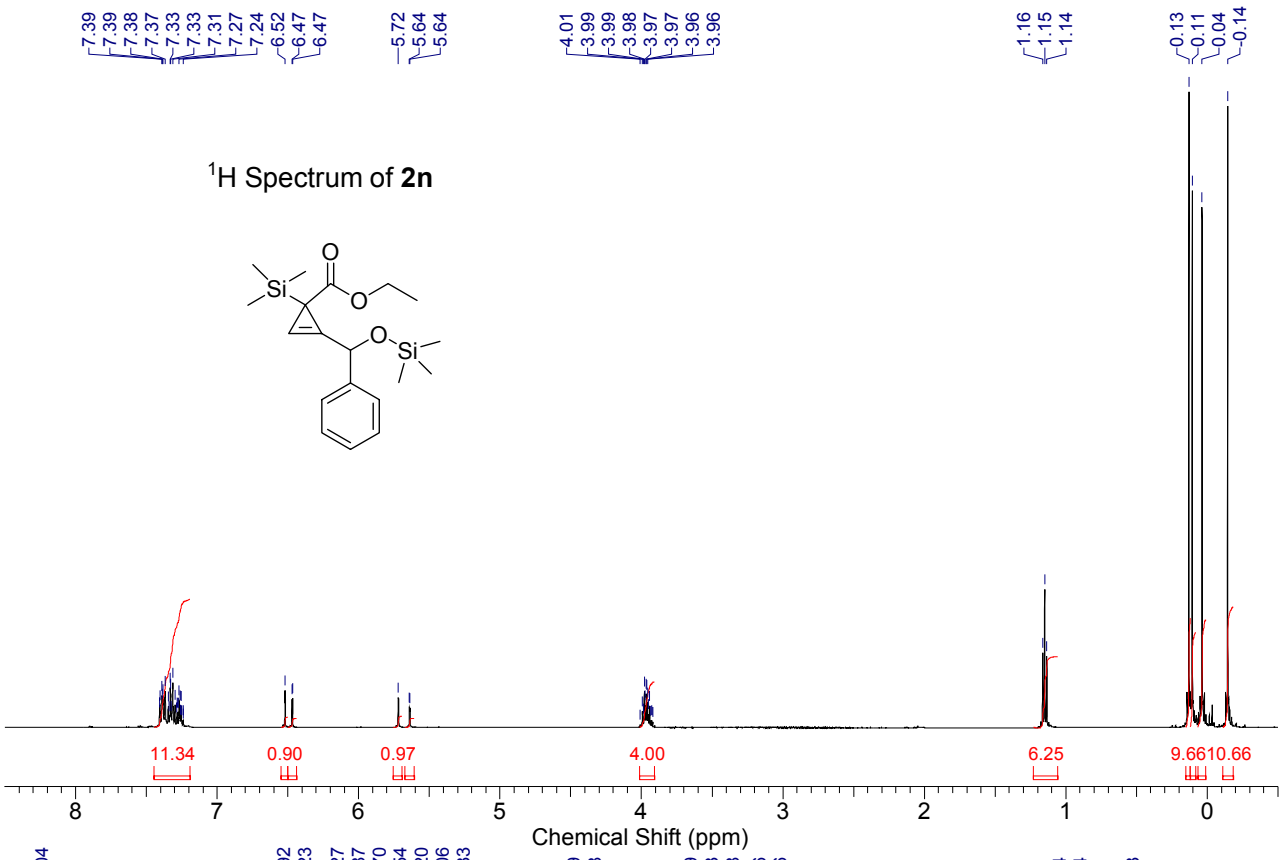

173.56
173.36
148.78
148.20
146.17
139.89
139.19
129.44
129.34
128.48
128.39
128.14
126.40
126.07
123.12
122.81
99.69
98.10
77.31
77.06
76.81
69.57
69.31
52.07
52.05
35.26
34.91
0.13
13C Spectrum of 2l
O2N
O
O
O
Si
150
100
50
0
Chemical Shift (ppm)

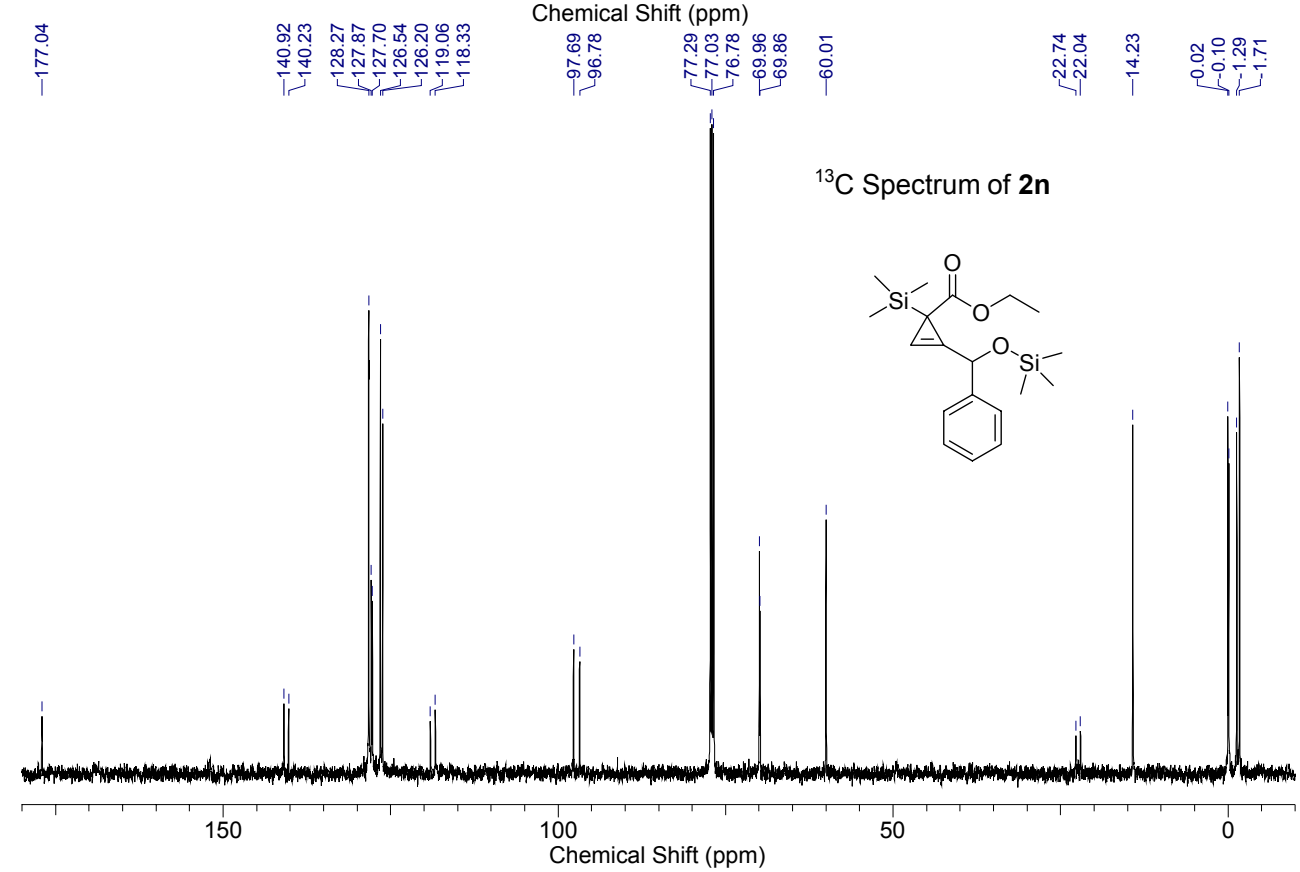


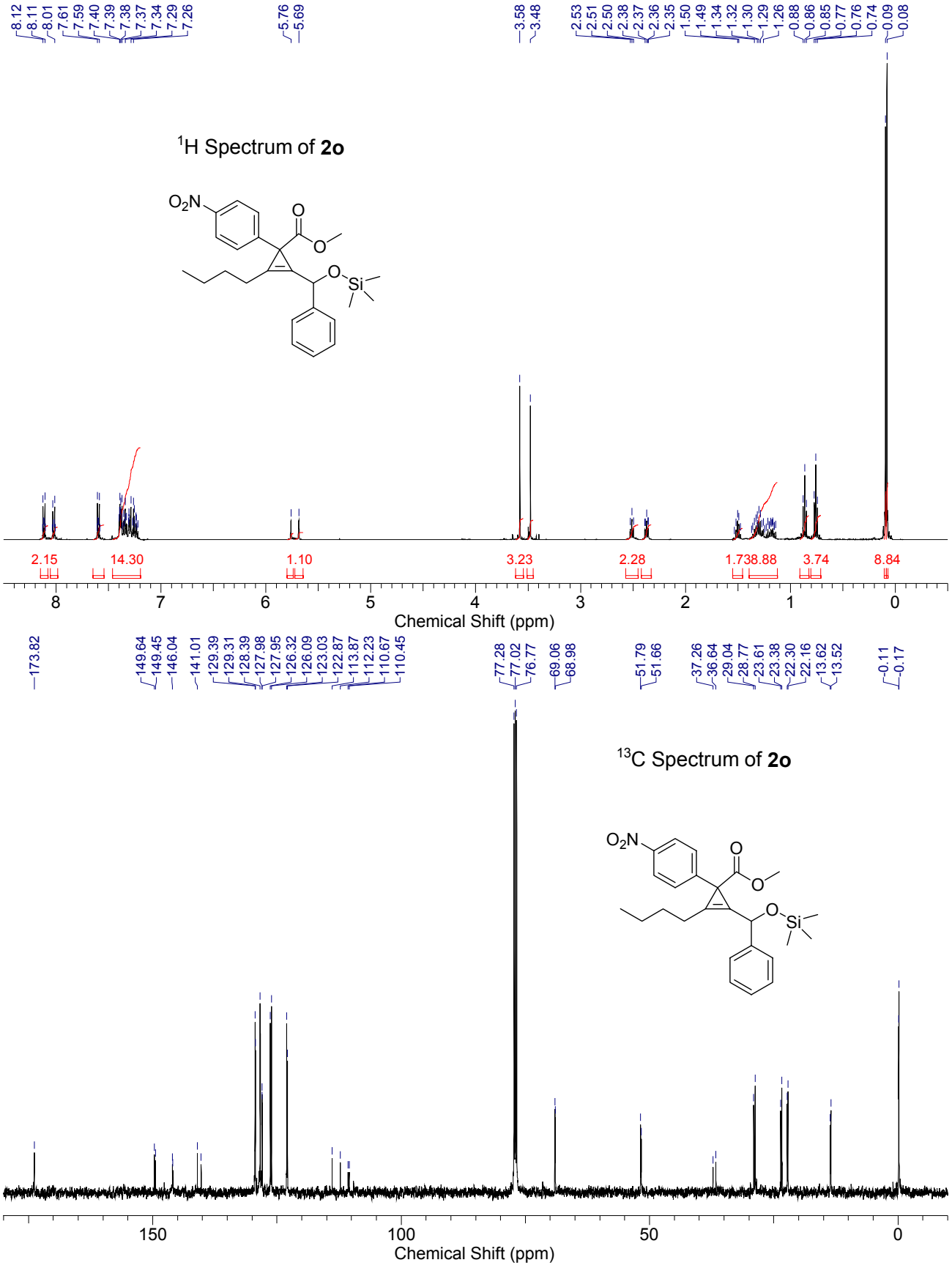
^{1}H Spectrum of **2m**

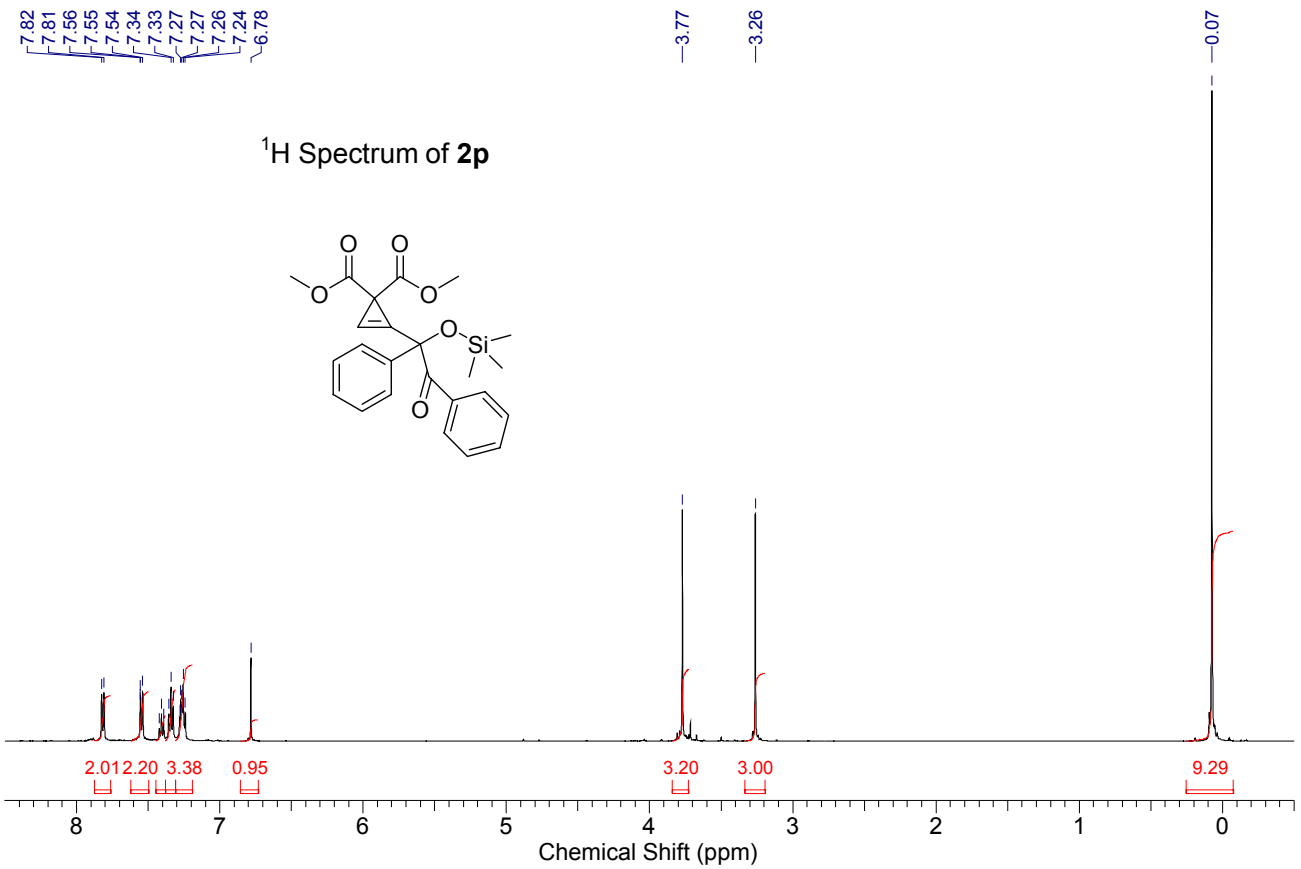


^{13}C Spectrum of **2m**

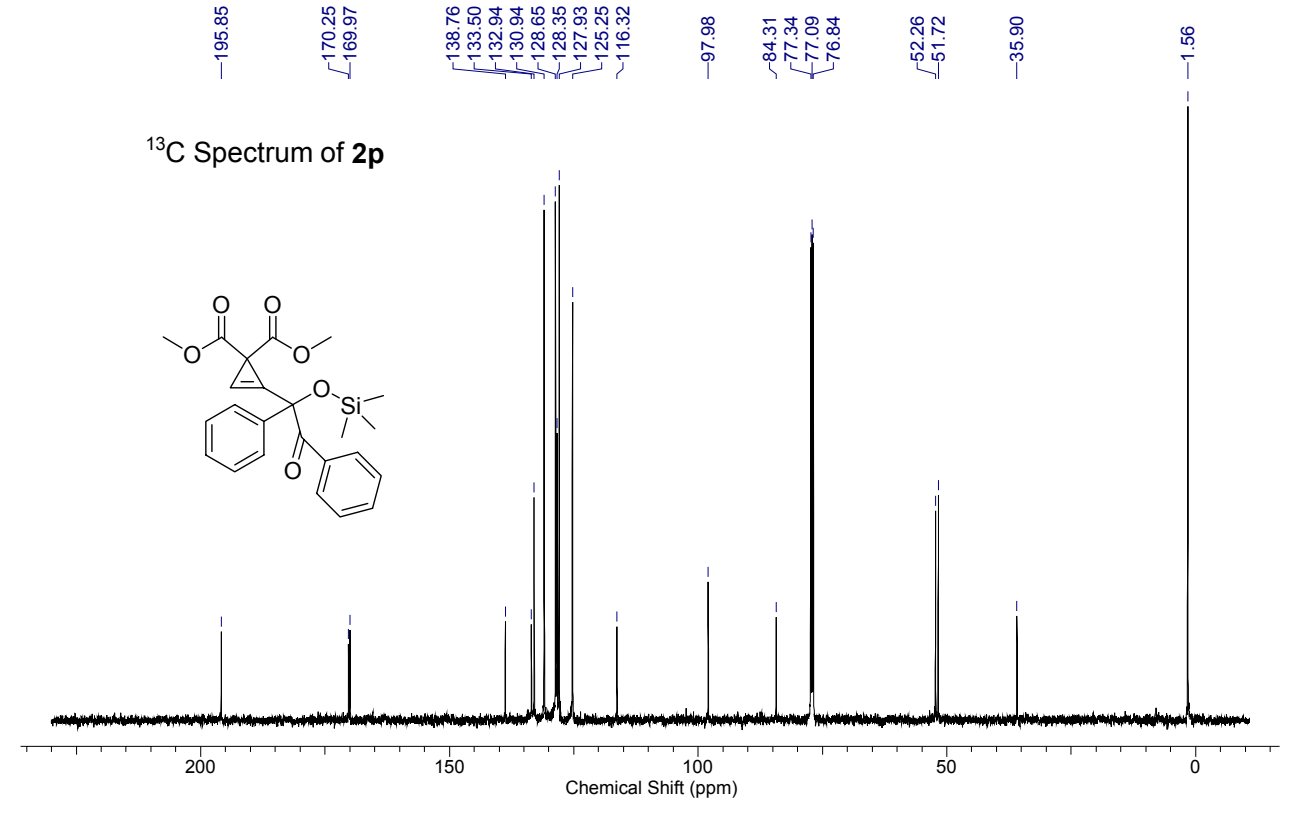

7.39
7.39
7.38
7.37
7.33
7.33
7.31
7.27
7.24
6.52
6.47
6.47
5.72
5.64
5.64
4.01
3.99
3.99
3.98
3.97
3.97
3.96
3.96
1.16
1.15
1.14
0.13
0.11
0.04
-0.14
^{1}H Spectrum of **2n**
O
Si
O
O
Si
11.34
0.90
0.97
4.00
6.25
9.66
10.66
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


177.04
140.92
140.23
128.27
127.87
127.70
126.54
126.20
119.06
118.33
97.69
96.78
77.29
77.03
76.78
69.96
69.86
60.01
22.74
22.04
14.23
0.02
-0.10
-1.29
-1.71
^{13}C Spectrum of **2n**
O
Si
O
O
Si
150
100
50
0
Chemical Shift (ppm)

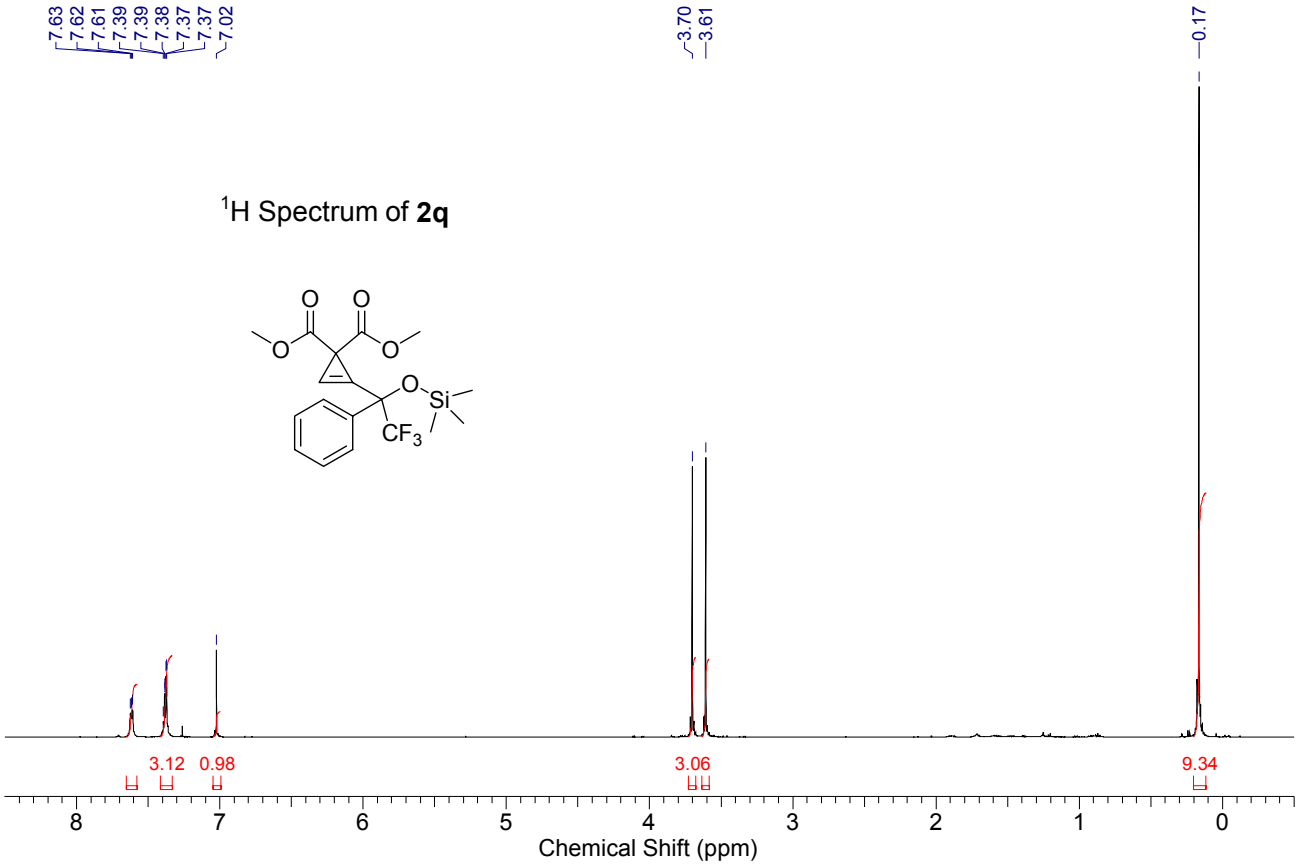

8.12
8.11
8.01
7.61
7.59
7.40
7.39
7.38
7.37
7.34
7.29
7.26
5.76
5.69
3.58
3.48
2.53
2.51
2.50
2.38
2.37
2.36
2.35
1.50
1.49
1.34
1.32
1.30
1.29
1.26
0.88
0.86
0.85
0.77
0.76
0.74
0.09
0.08
1H Spectrum of 2o
O2N
O
O
O
Si
2.15
14.30
1.10
3.23
2.28
1.73
8.88
3.74
8.84
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
173.82
149.64
149.45
146.04
141.01
129.39
129.31
128.39
127.98
127.95
126.32
126.09
123.03
122.87
113.87
112.23
110.67
110.45
77.28
77.02
76.77
69.06
68.98
51.79
51.66
37.26
36.64
29.04
28.77
23.61
23.38
22.30
22.16
13.62
13.52
-0.11
-0.17
13C Spectrum of 2o
O2N
O
O
O
Si
150
100
50
0
Chemical Shift (ppm)



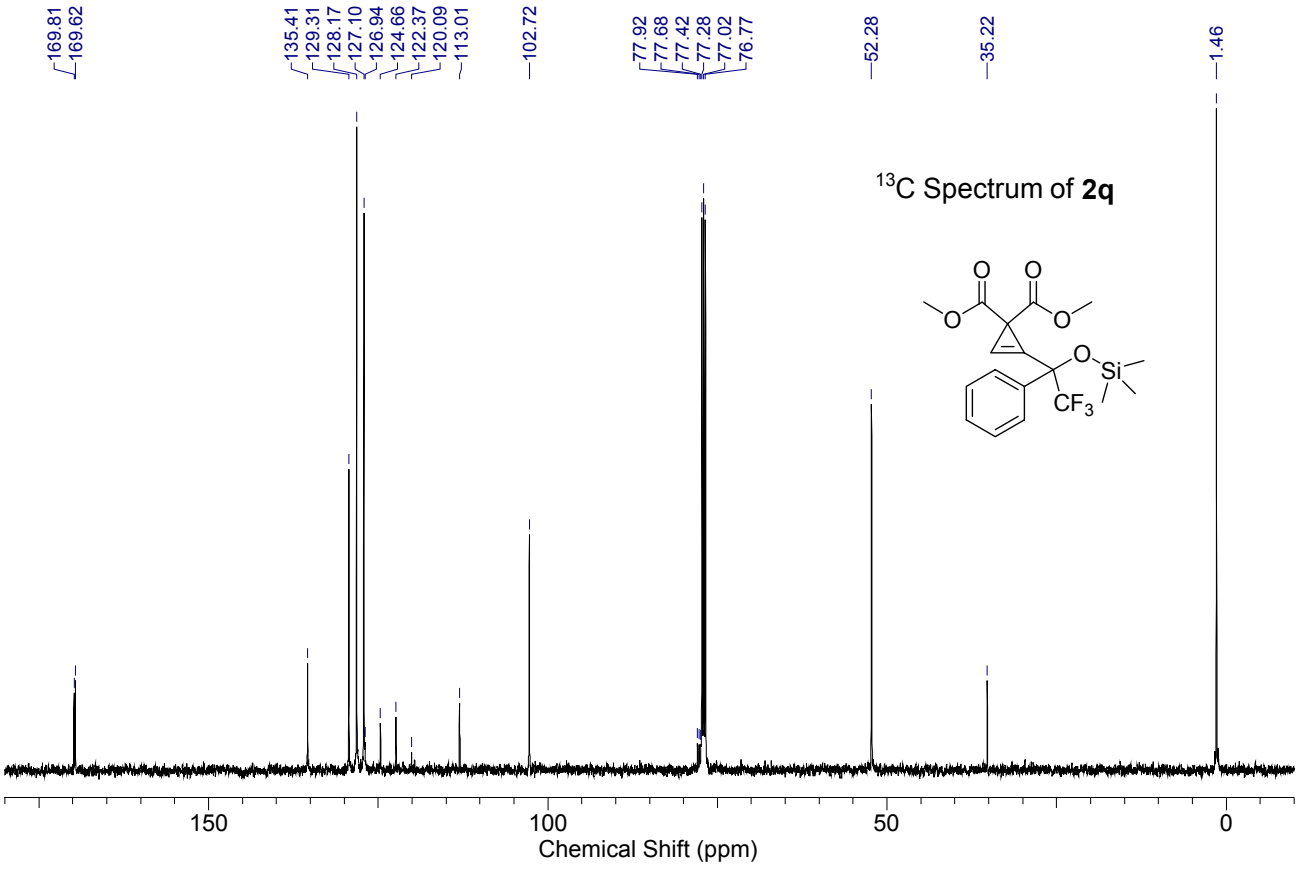
^{1}H Spectrum of **2p**



^{13}C Spectrum of **2p**



^{1}H Spectrum of **2q**



^{13}C Spectrum of **2q**