Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Carbopalladation of bromoene-alkynylsilanes: Mechanistic insights and synthesis of fused-ring bicyclic silanes and phenols

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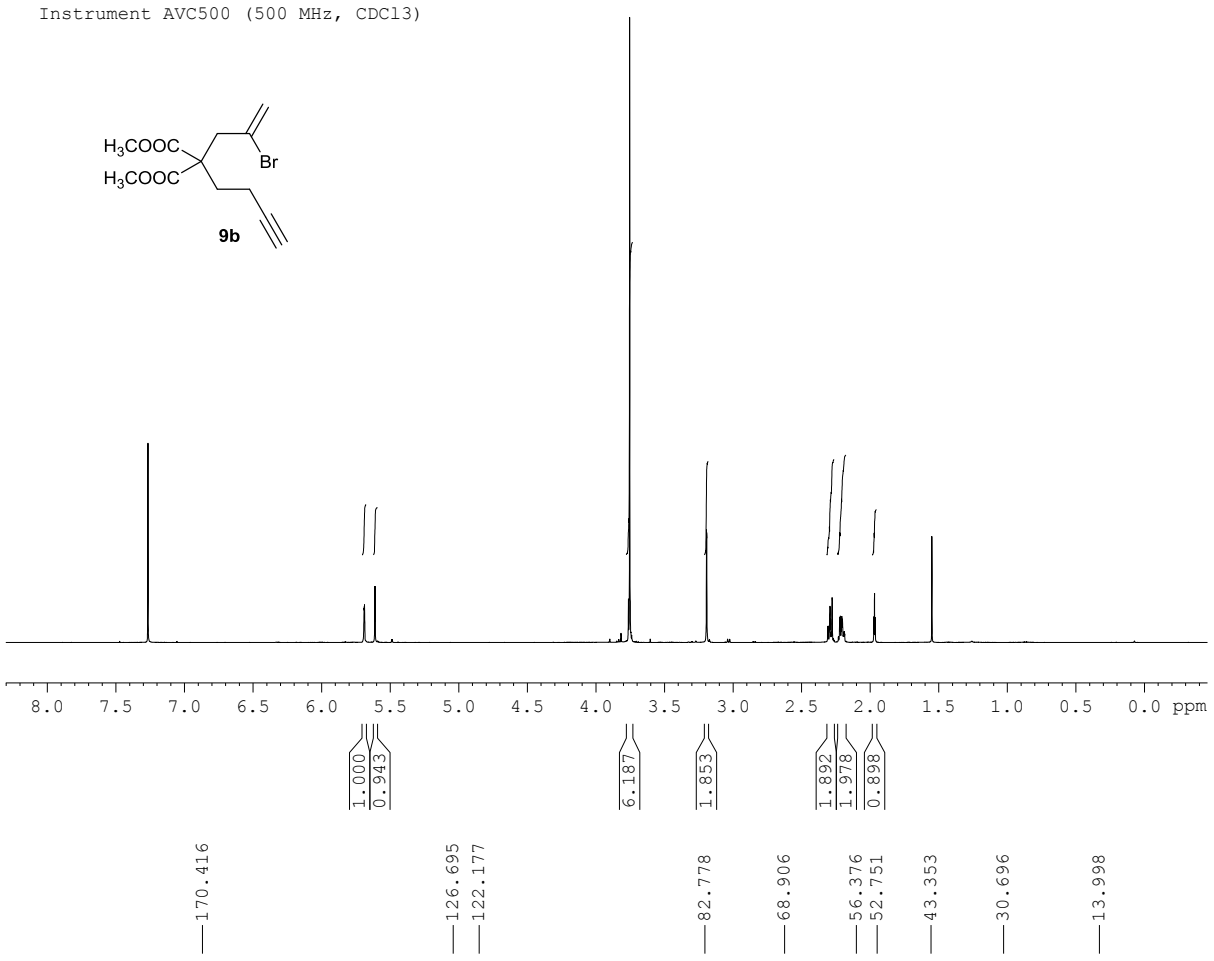
Supporting Information

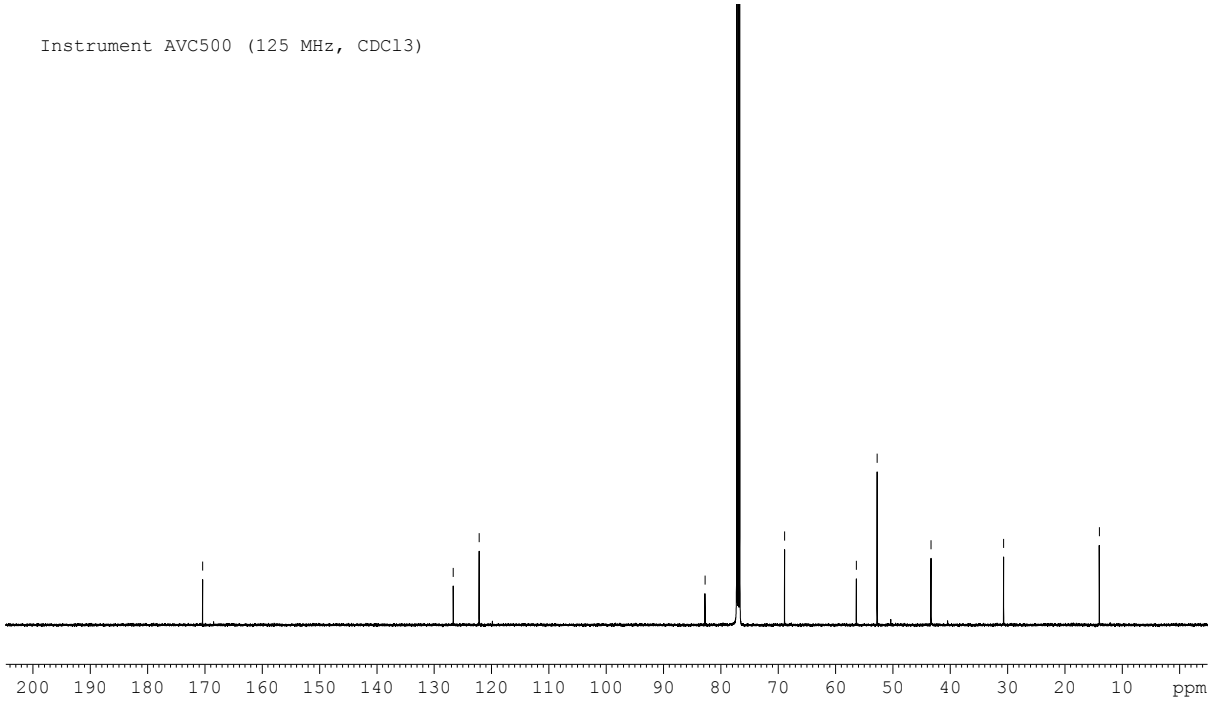
Procedure for VT NMR experiment: Conversion of 22 to 25/26 using stoichiometric $Pd(PPh_3)_4$ (Manuscript Figure 2)

To an NMR tube containing $Pd(PPh_3)_4$ (64 mg, 0.055 mmol) under an Ar atmosphere was added a degassed solution of bromoenyne **22** (20 mg, 0.055 mmol) in d_8-toluene (0.5 mL). An NMR spectrum of this mixture at RT was acquired for the spectrum t = 0 min. The NMR tube and its contents was then heated in a preheated oil bath (110 °C) for 1 min, before it was rapidly cooled to RT, and a second NMR spectrum at RT was acquired for t = 1 min. The NMR tube was then returned to the oil bath for a further 4 min, before it was again cooled to RT and a third spectrum was acquired for t = 5 min (total time at 110 °C). The process was continued to acquire spectra for t = 10 min and t = 20 min, after which time tributyl(vinyl)stannane (26.3 mg, 0.083 mmol) was added. The mixture was then heated to 110 °C for a further 10 min, before it was cooled to RT and a final spectrum was acquired.

Procedure for VT NMR experiment: Conversion of 1:0.32 mixture of 25 and 26 to 25 (Manuscript Figure 3)

A degassed solution of **25** and **26** (1:0.32 ratio, 8.8 mg, 0.029 mmol), and 1,4-dimethoxybenzene (2.0 mg) in d_8-toluene (0.6 mL) was added via syringe to a septum-capped vial containing $Pd(PPh_3)_4$ (3.3 mg, 0.003 mmol, 10 mol%) under an Ar atmosphere. The resulting solution was added via syringe to an NMR tube capped under an Ar atmosphere. A ^1H NMR spectrum of this mixture at RT was acquired for the spectrum t = 0 min. The NMR tube and its contents was then heated in a preheated oil bath (110 °C) for 21 h, with periodic cooling of the mixture to enable the recording of a ^1H NMR spectrum at room temperature.


Instrument AVC500 (500 MHz, CDCl3)
H3COOC
H3COOC
Br
9b
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 0.0 ppm
1.000
0.943
6.187
1.853
1.892
1.978
0.898


170.416
126.695
122.177
82.778
68.906
56.376
52.751
43.353
30.696
13.998
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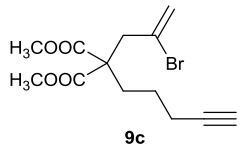
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Instrument AVC500 (500 MHz, CDCl3)



9c

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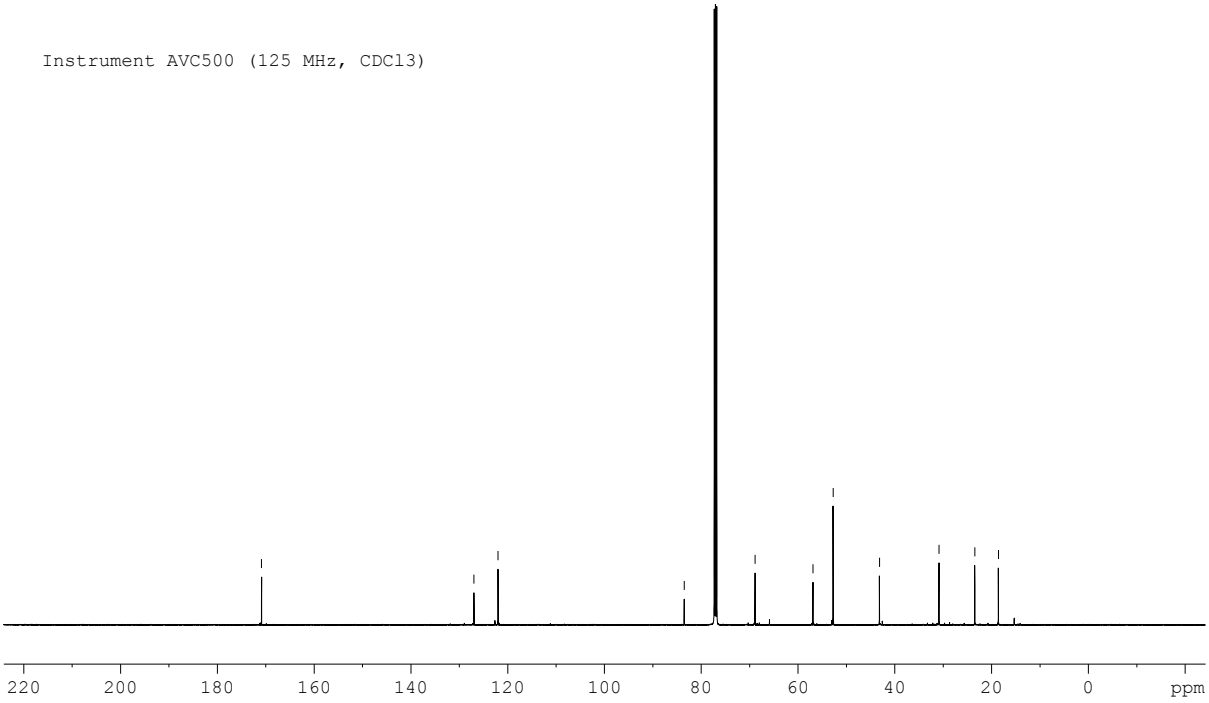

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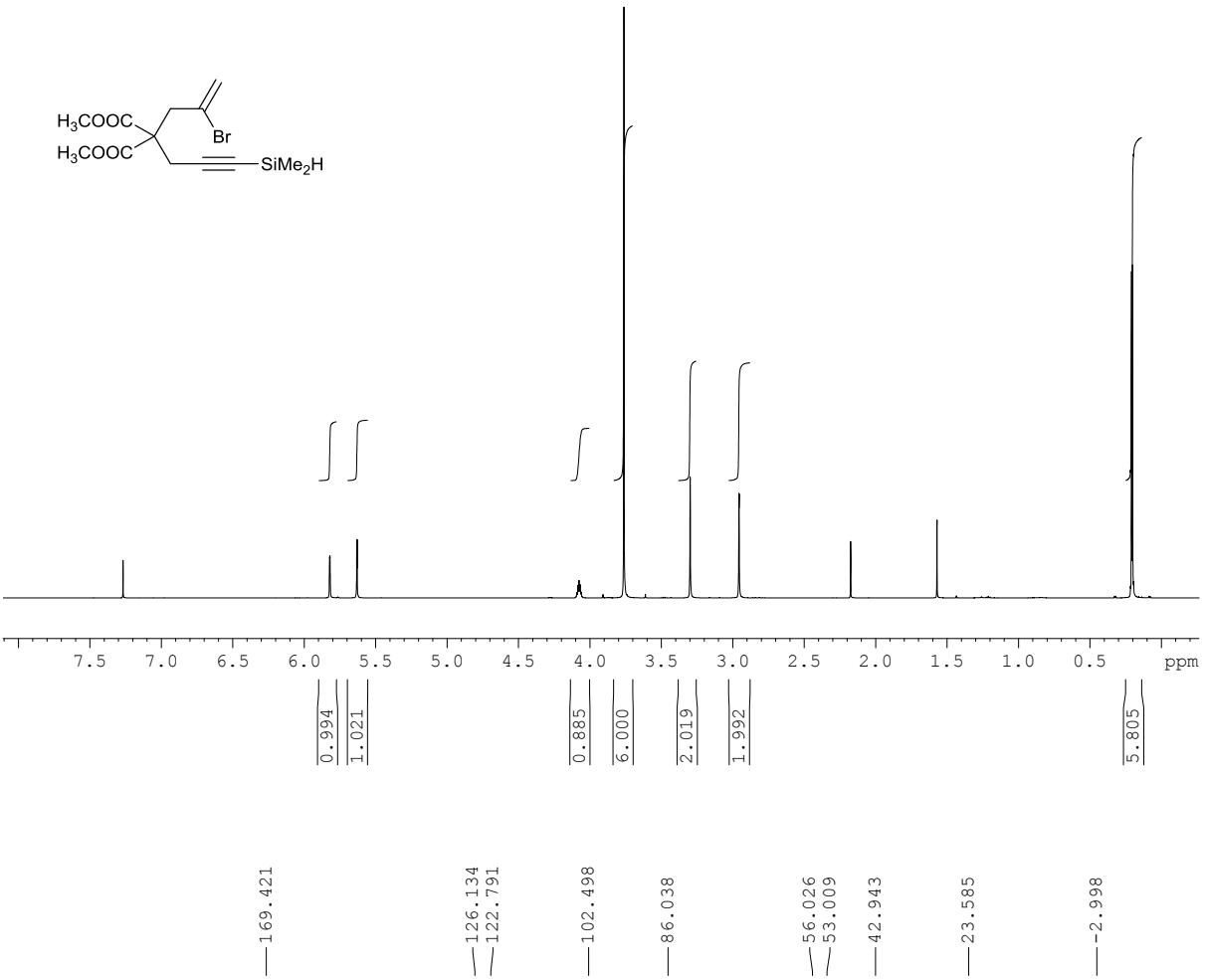

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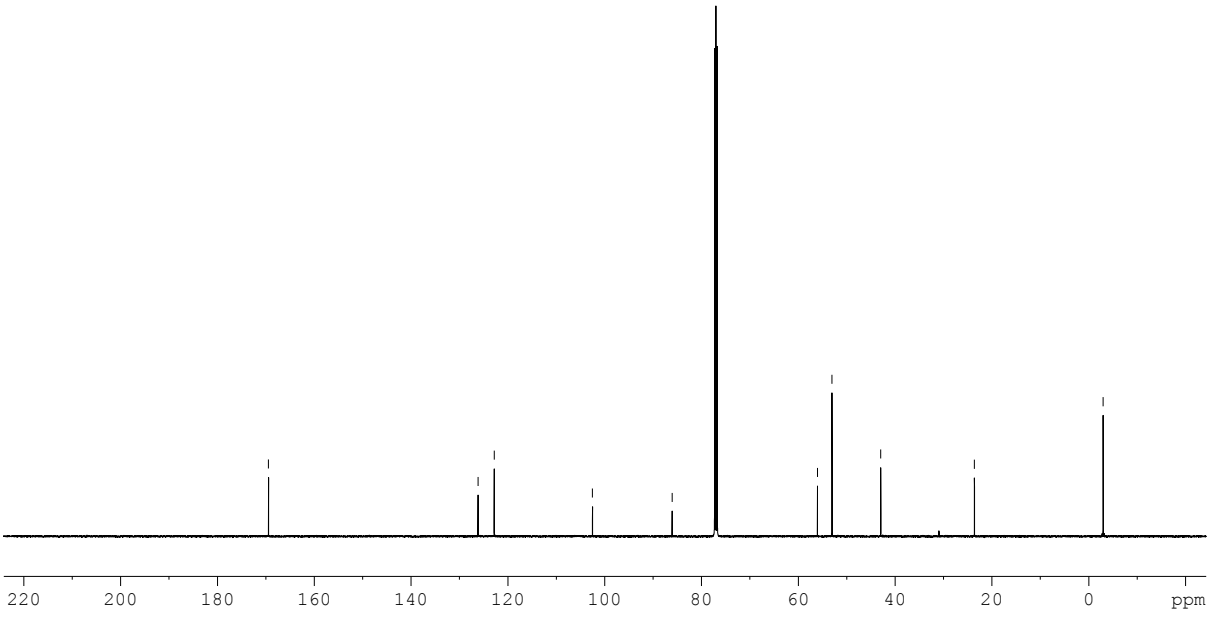

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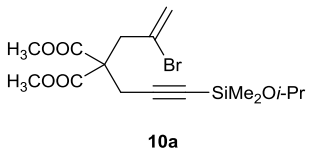
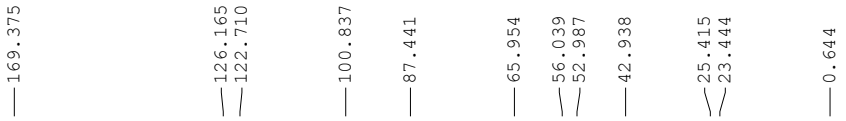
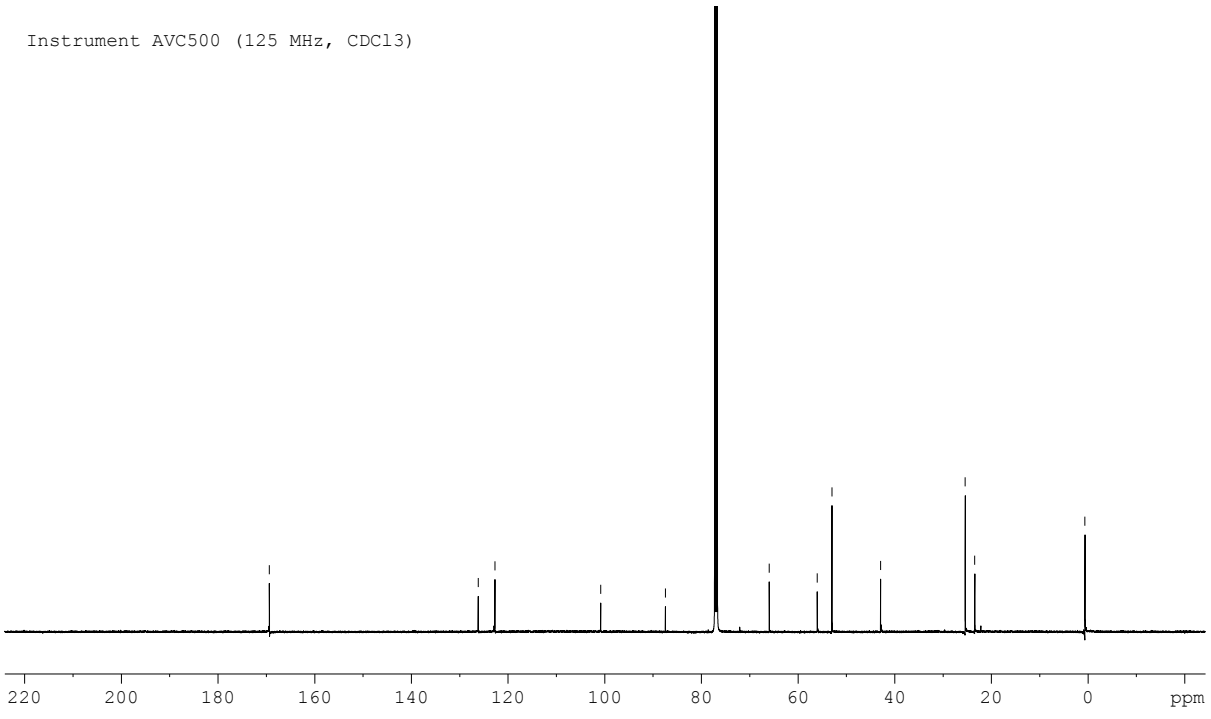


10a



Instrument AVC500 (125 MHz, CDCl3)



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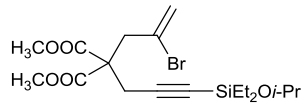
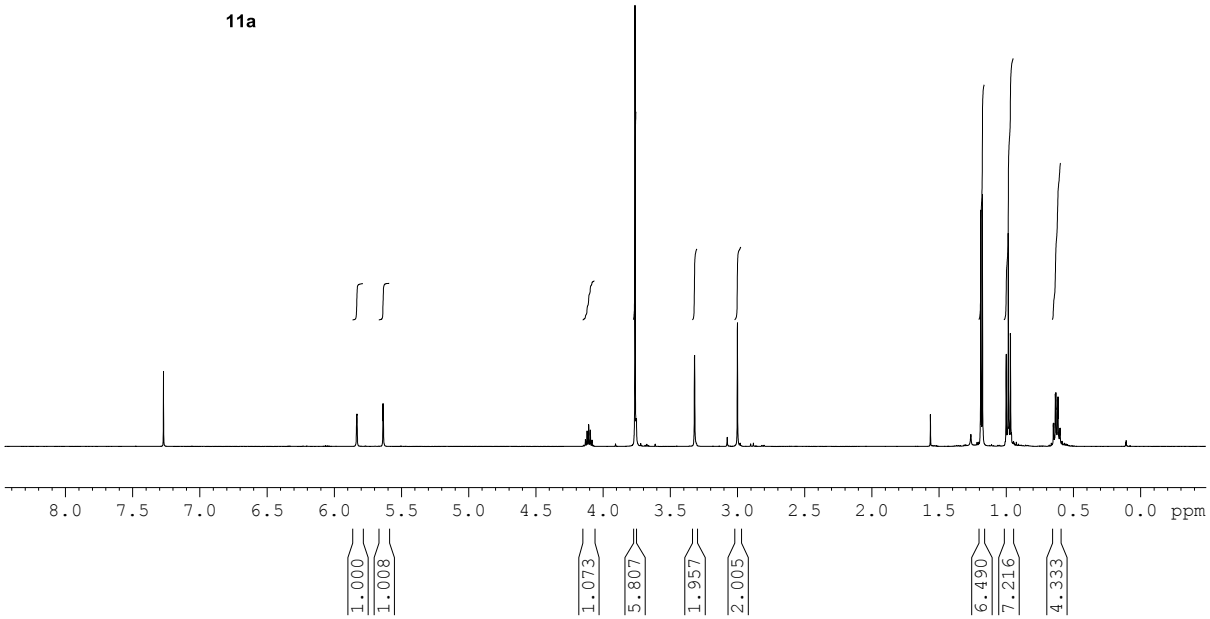


11a



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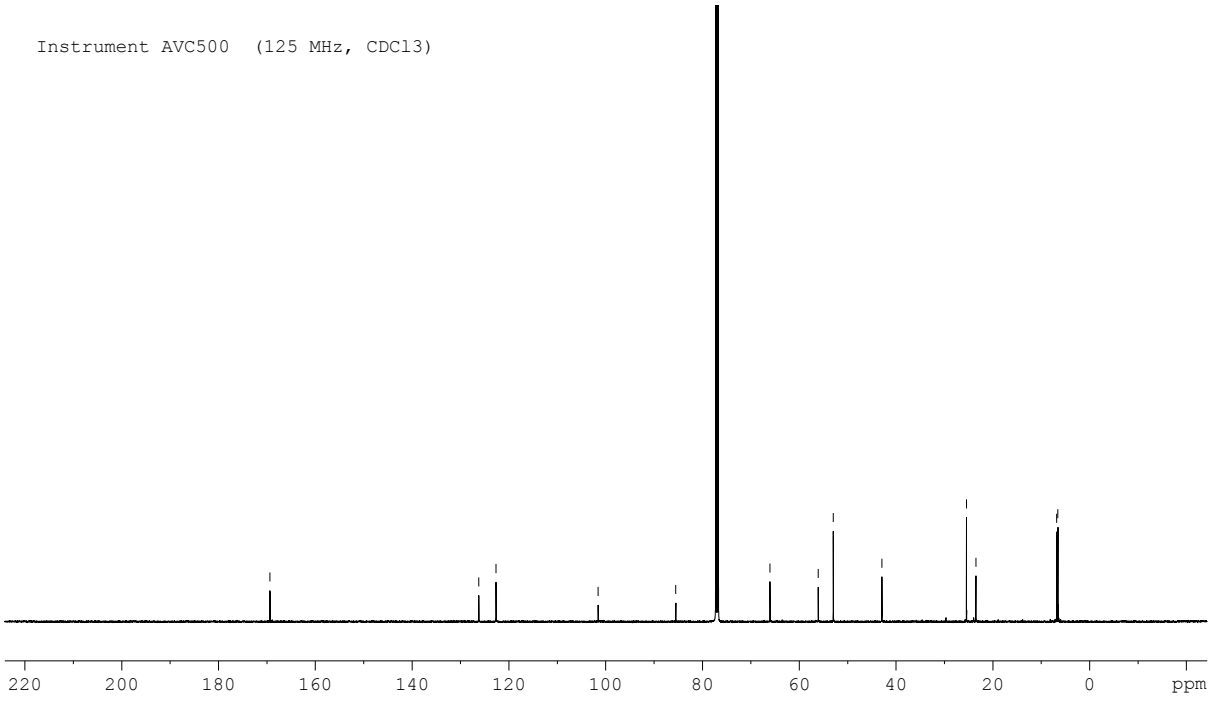

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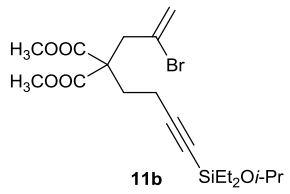
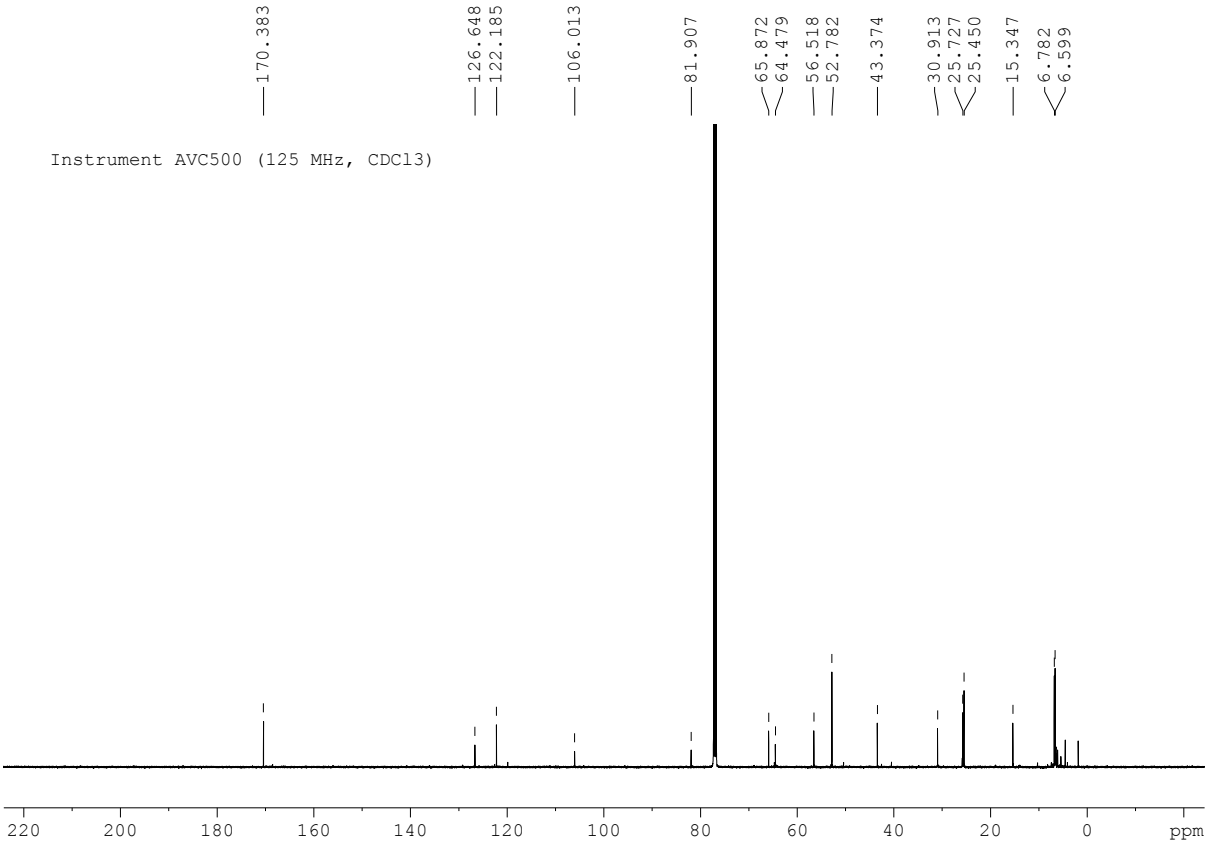
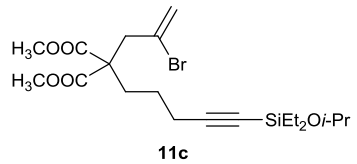


11b

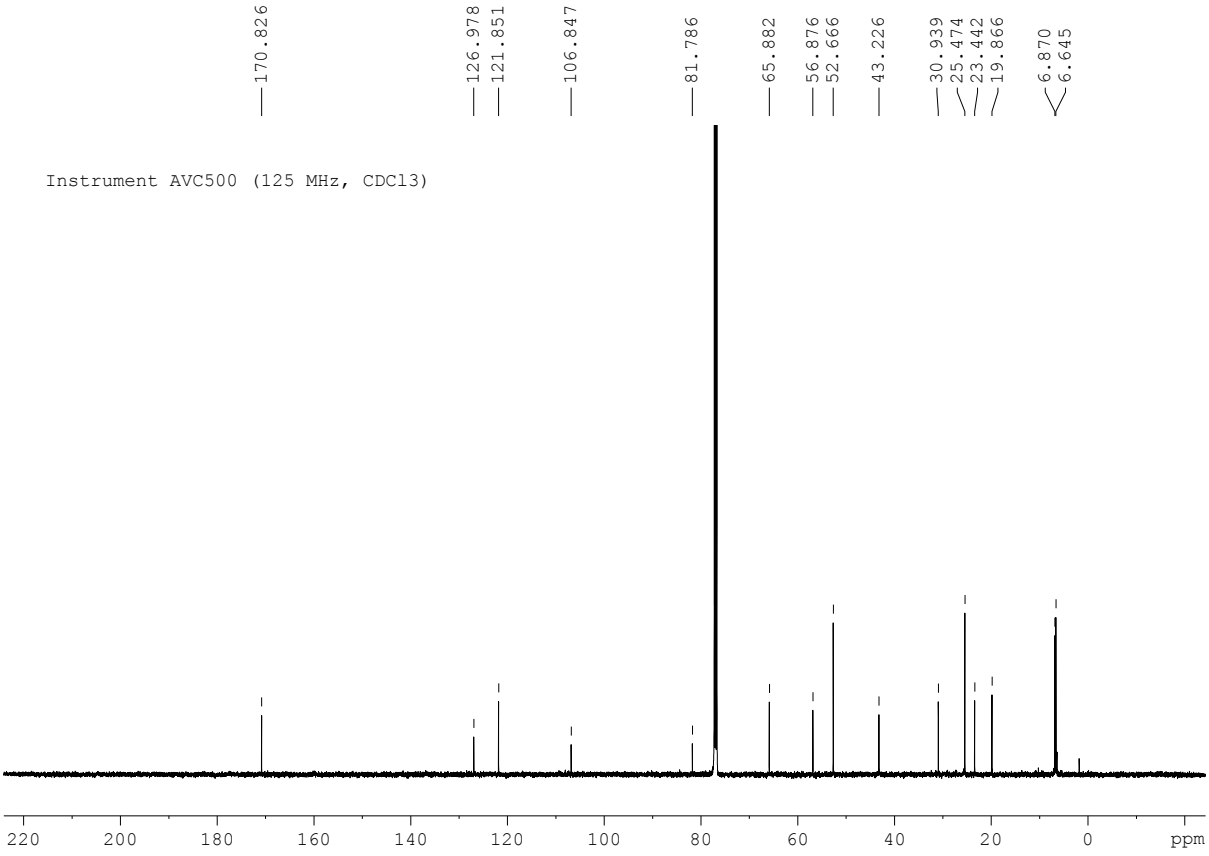
Instrument AVC500 (125 MHz, CDCl3)



Instrument AVC500 (500 MHz, CDCl3)

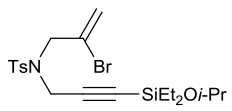


11c



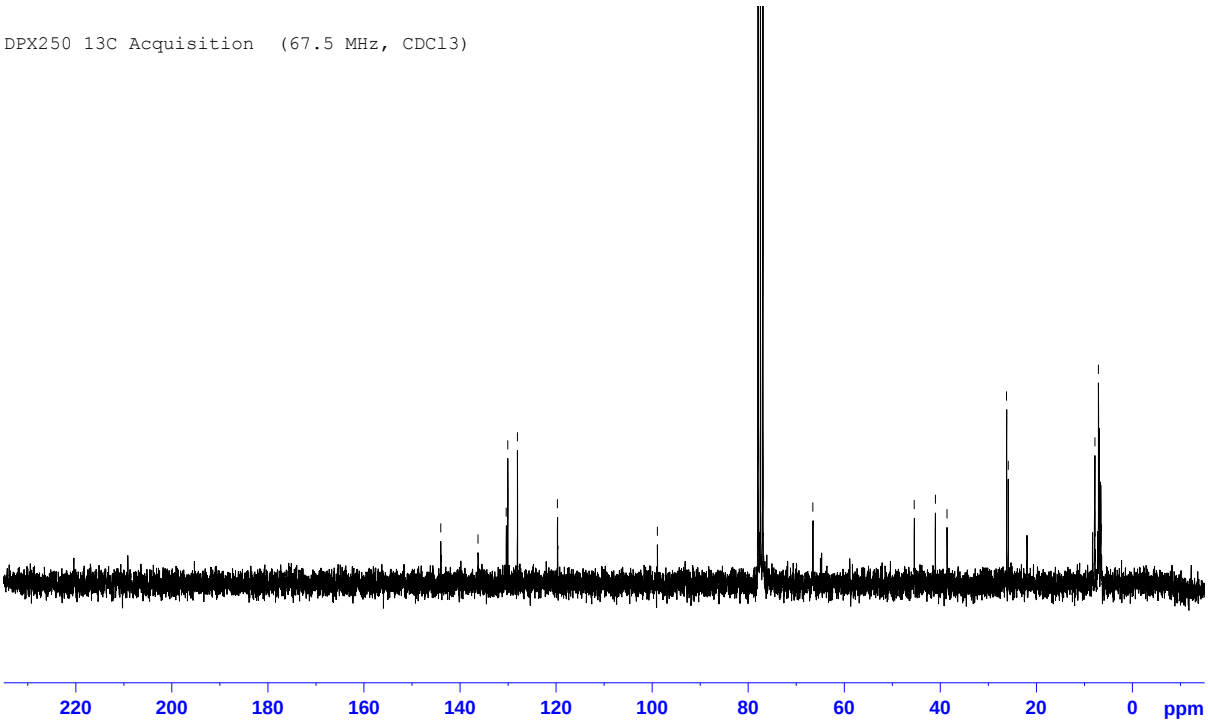
Instrument AVC500 (125 MHz, CDCl3)

DPX250 1H Acquisition (250 MHz, CDCl3)



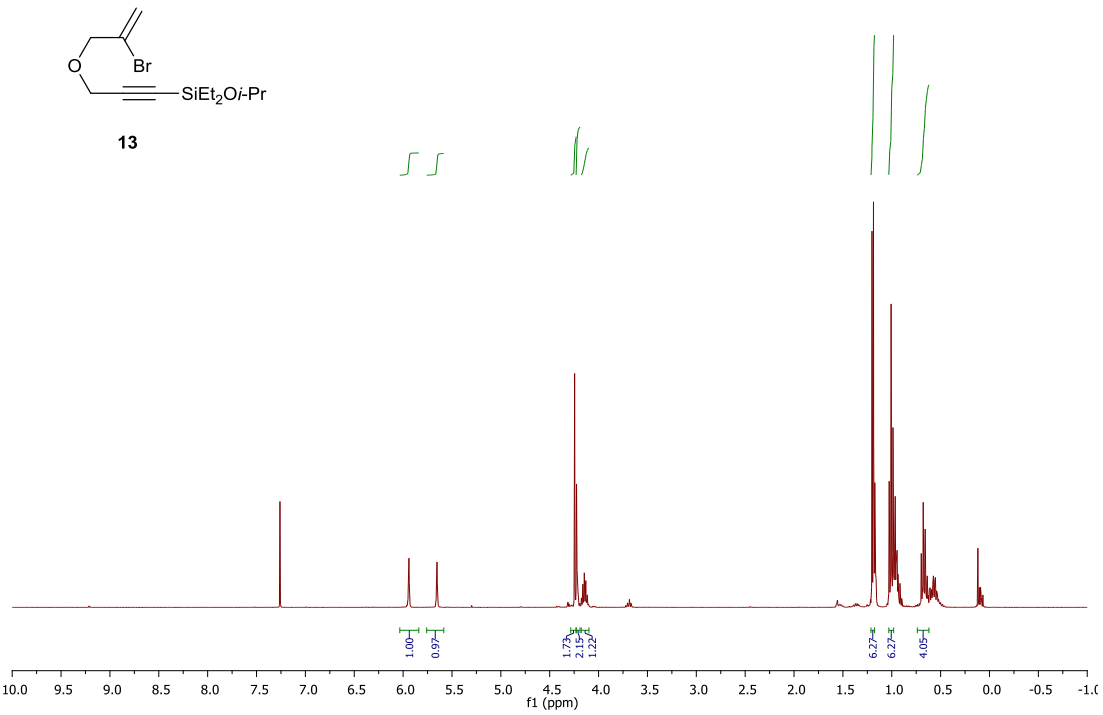
12

DPX250 13C Acquisition (67.5 MHz, CDCl3)

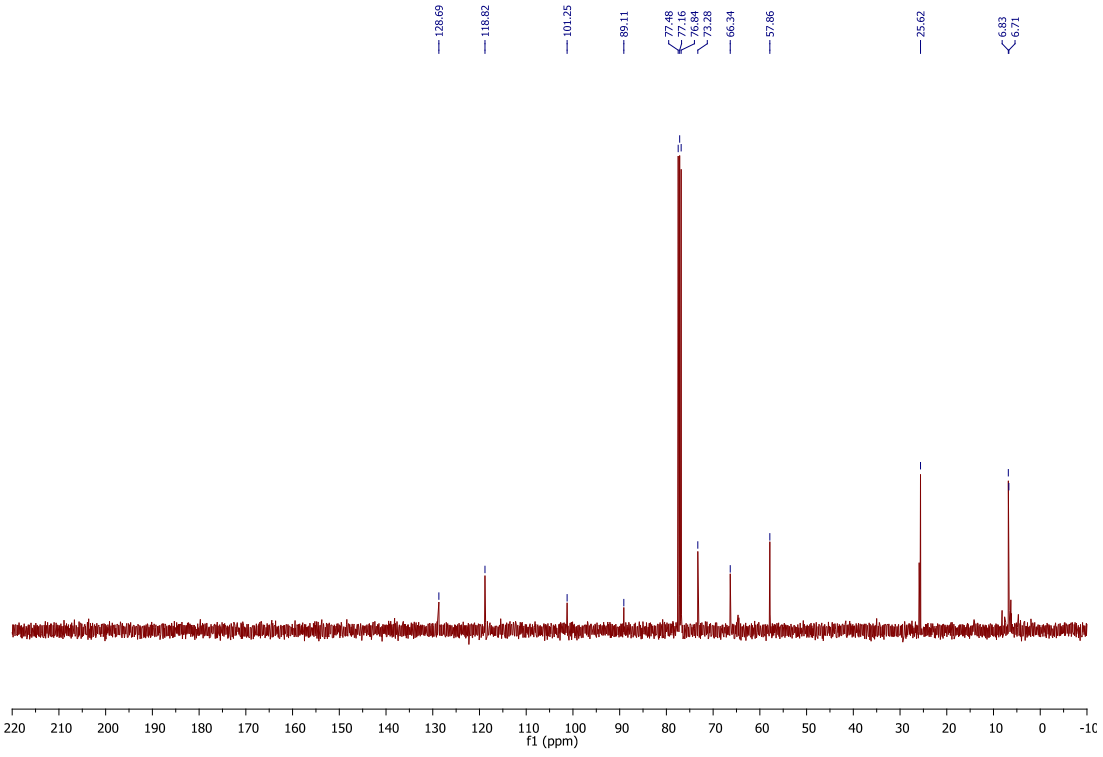


(3-(2-Bromoallyloxy)prop-1-ynyl)diethyl(isopropoxy)silane (13)

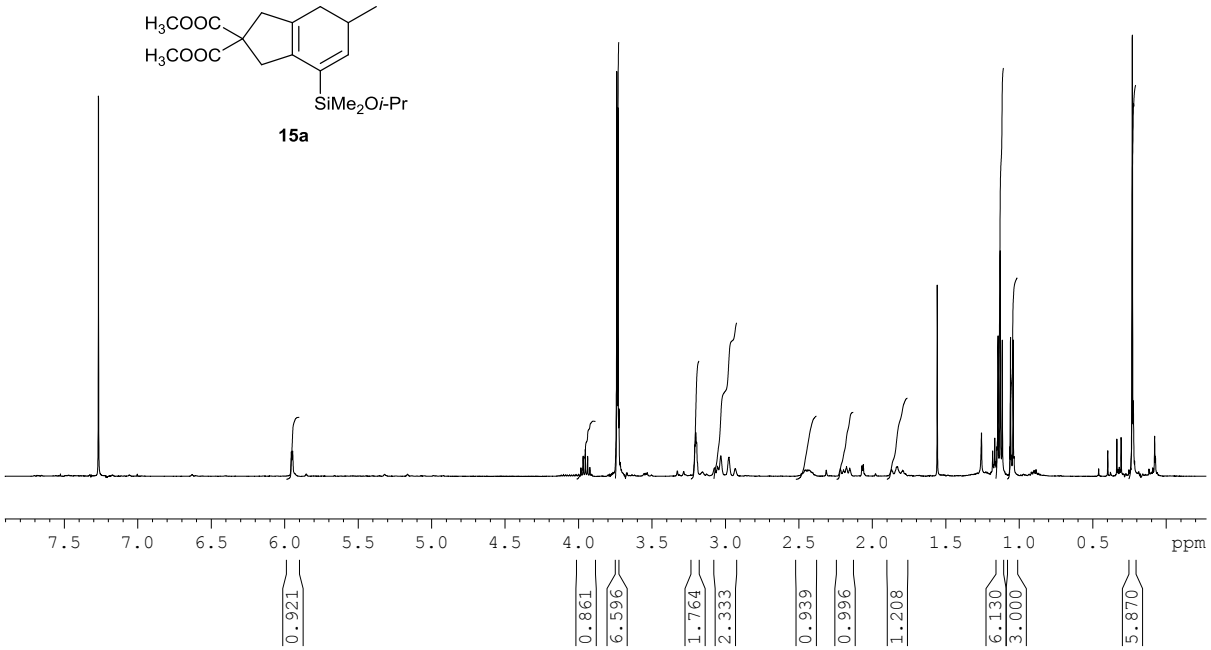
^{1}H NMR (400 MHz) in $CDCl_3$



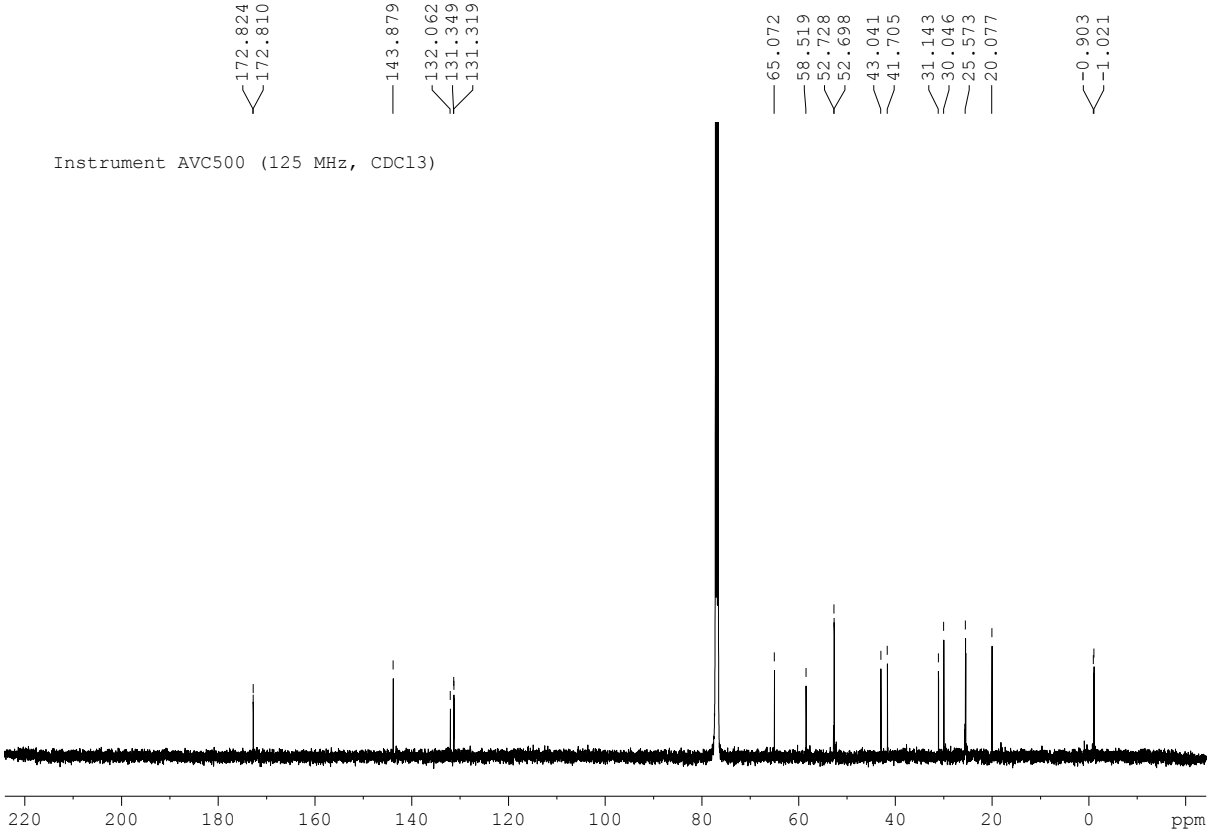
^{13}C NMR (101 MHz) in $CDCl_3$

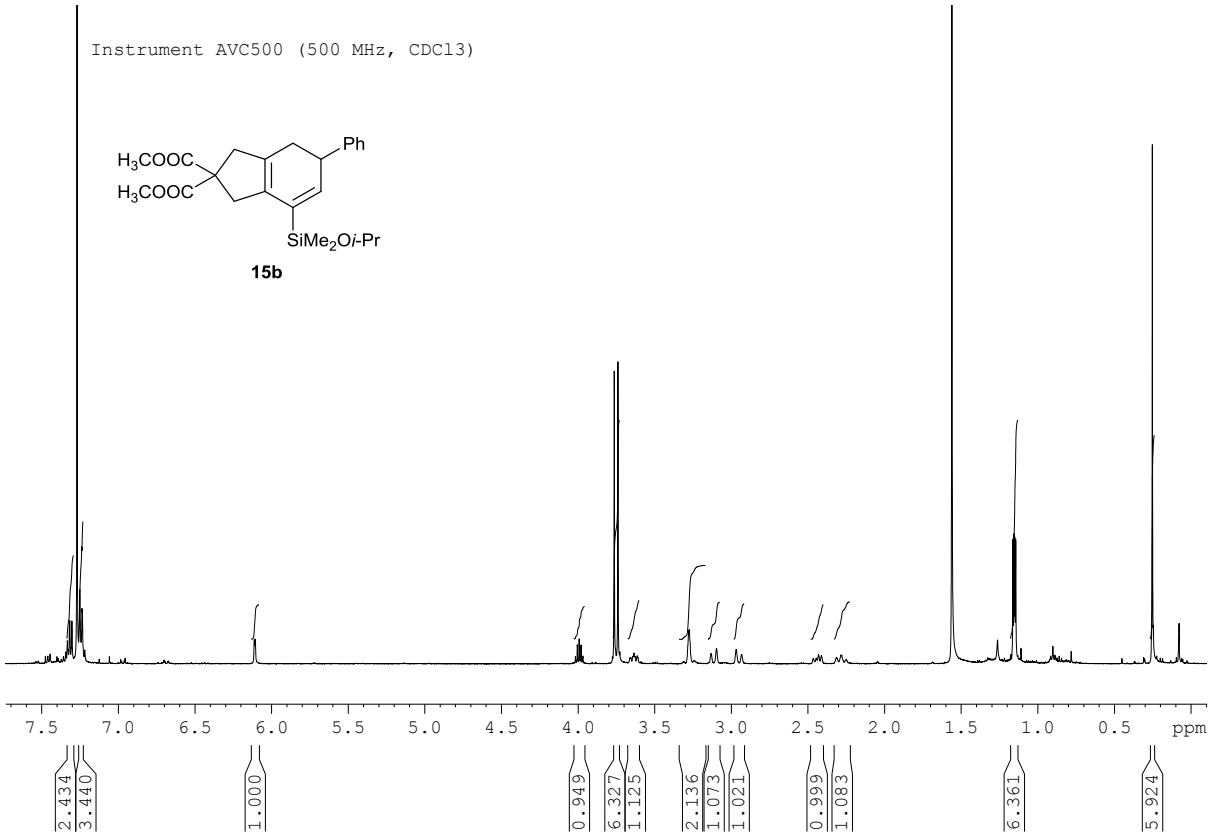


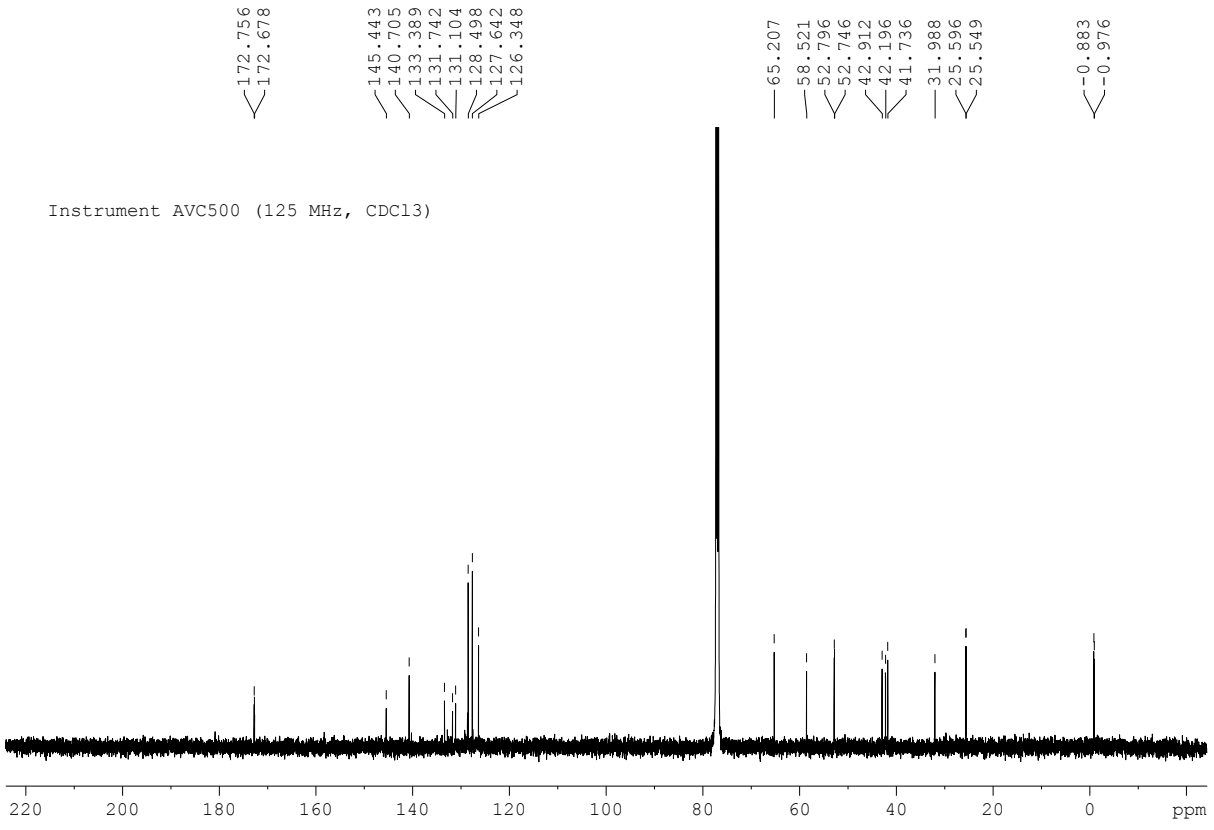
Instrument DPX400 (400 MHz, CDCl3)



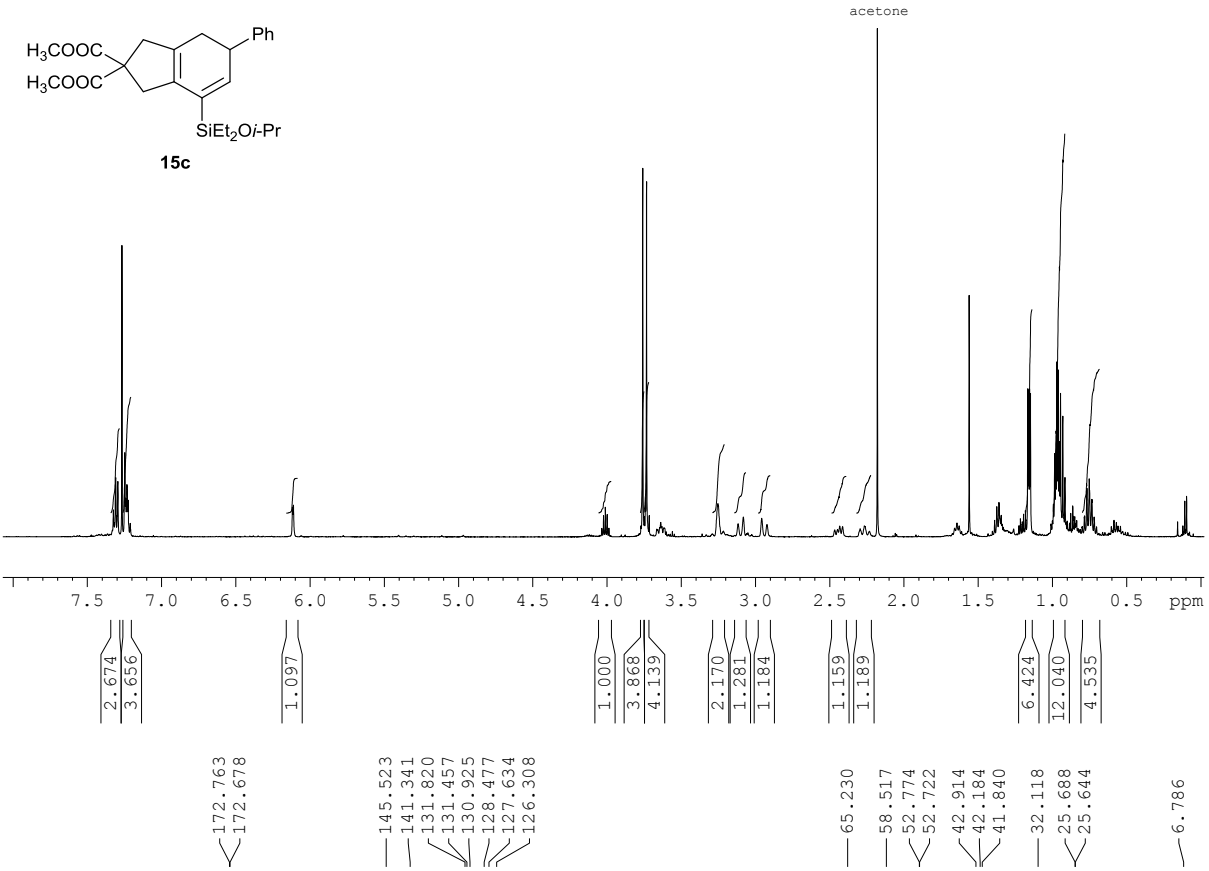
Instrument AVC500 (125 MHz, CDCl3)



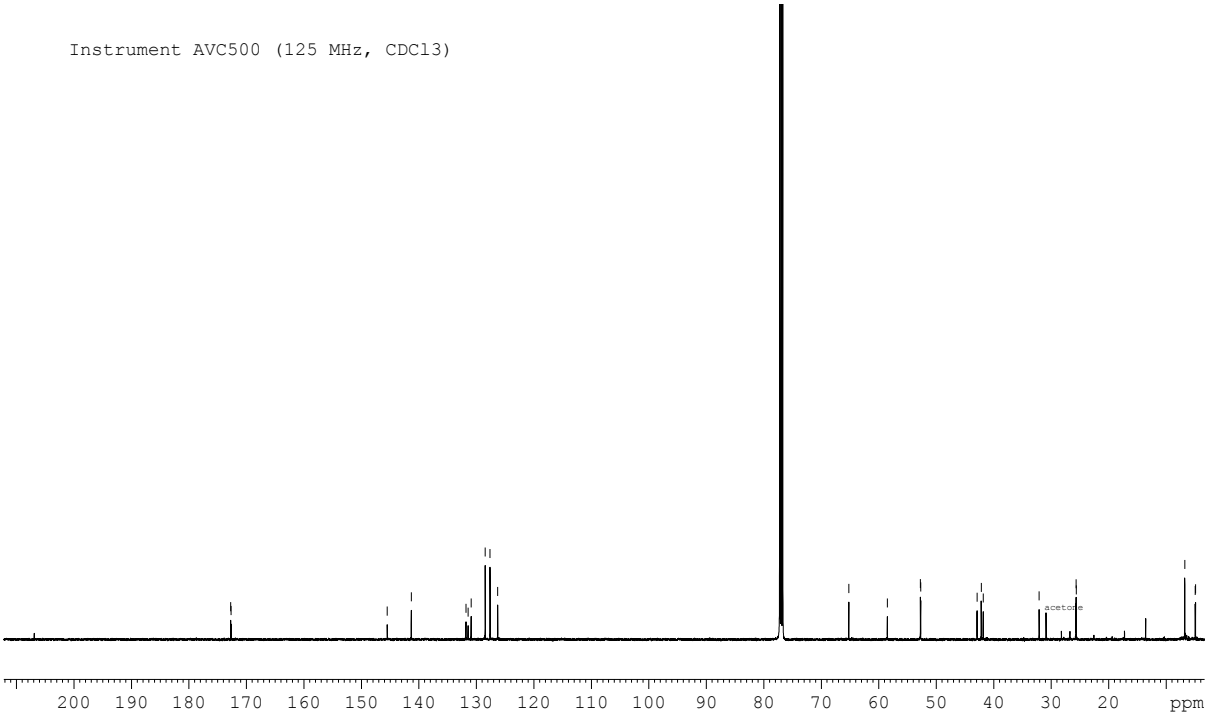

Instrument AVC500 (500 MHz, CDCl3)
H3COOC
H3COOC
Ph
SiMe2Oi-Pr
15b
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.434
3.440
1.000
0.949
6.327
1.125
2.136
1.073
1.021
0.999
1.083
6.361
5.924


172.756
172.678
145.443
140.705
133.389
131.742
131.104
128.498
127.642
126.348
65.207
58.521
52.796
52.746
42.912
42.196
41.736
31.988
25.596
25.549
-0.883
-0.976
Instrument AVC500 (125 MHz, CDCl3)
220 200 180 160 140 120 100 80 60 40 20 0 ppm

Instrument AVC500 (500 MHz, CDCl3)



Instrument AVC500 (125 MHz, CDCl3)



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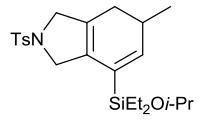
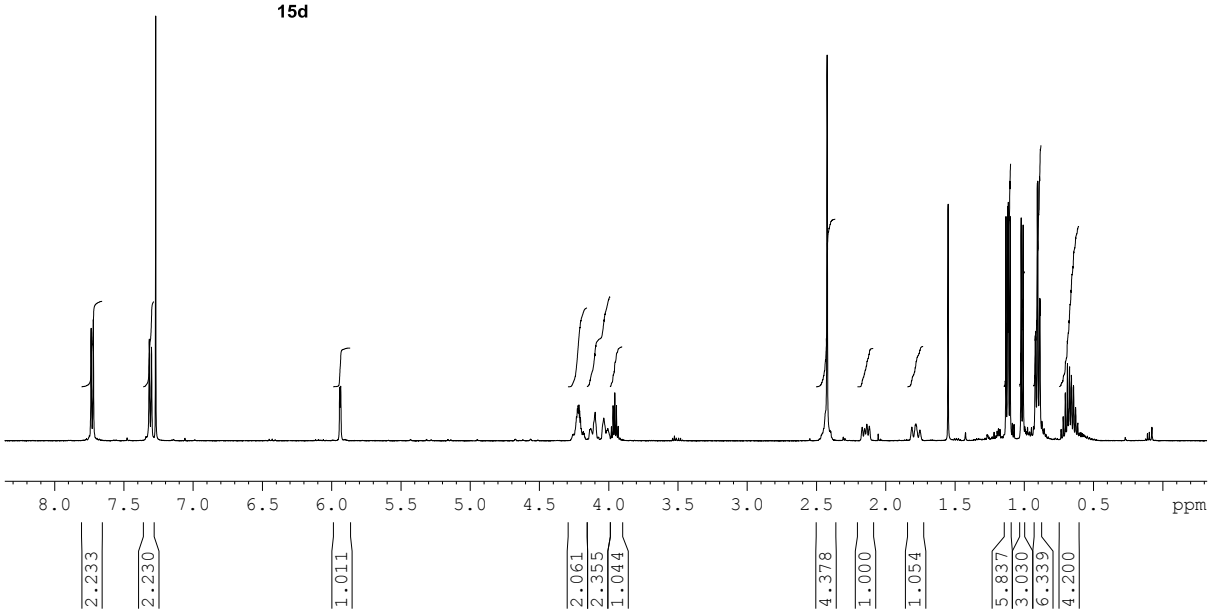
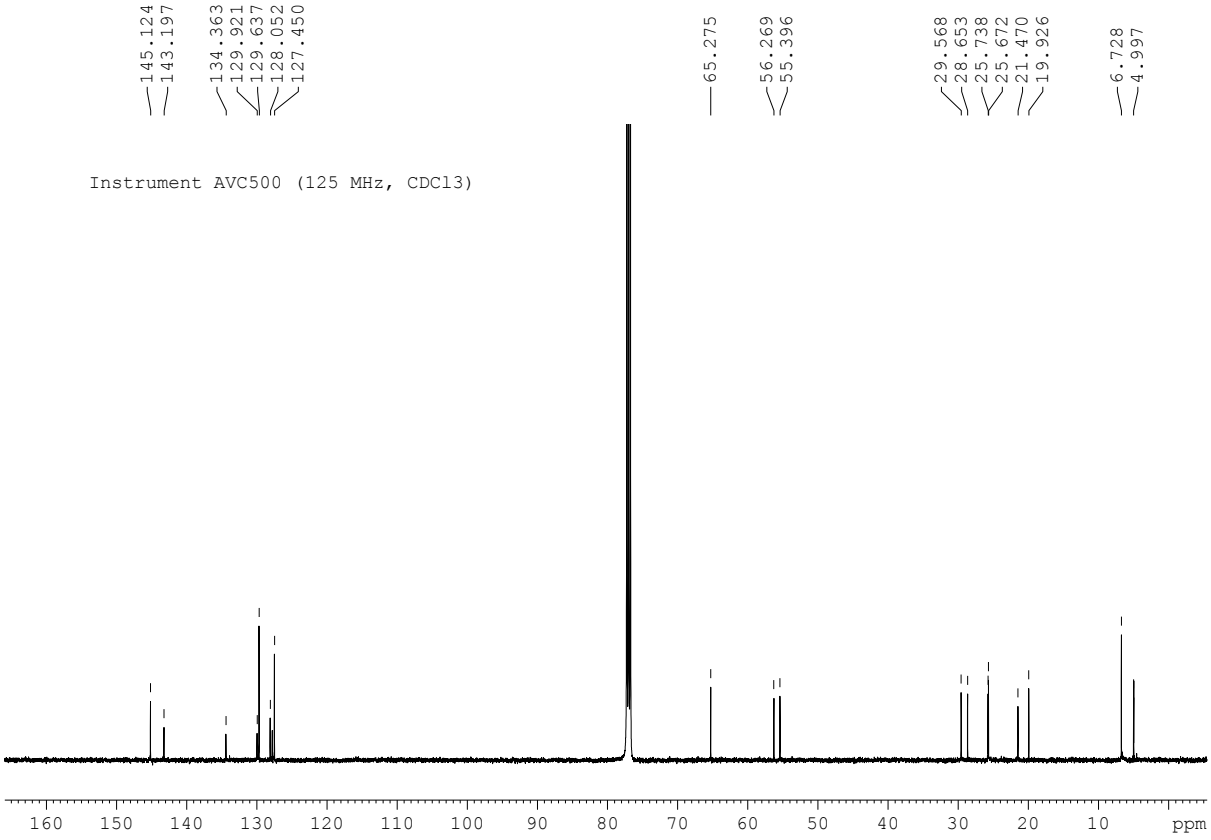


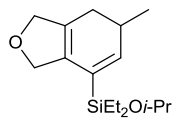
15d



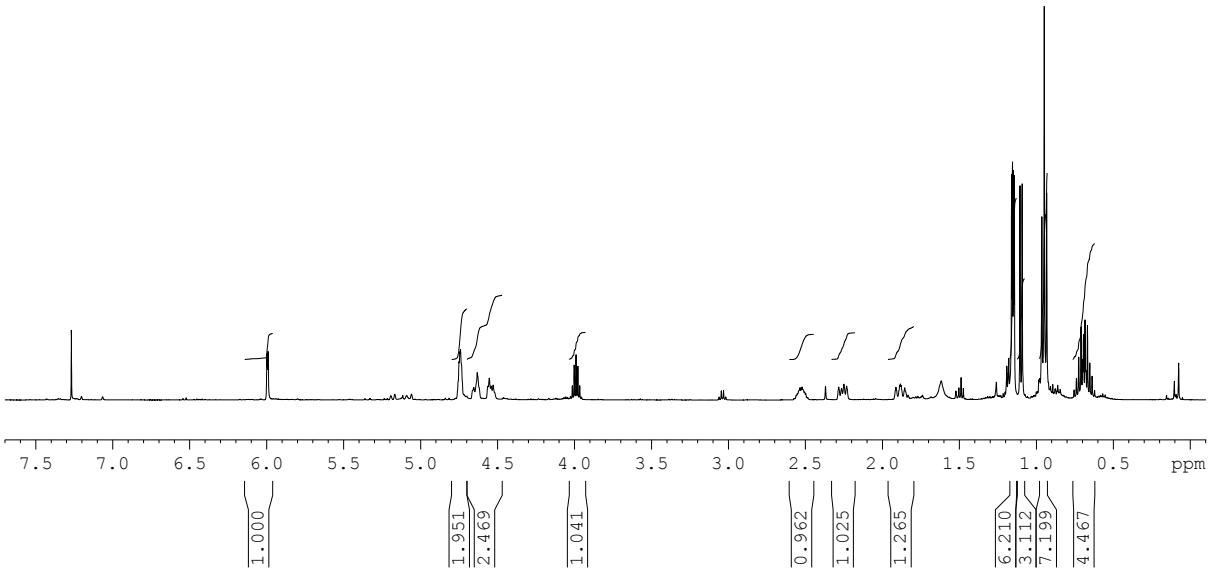


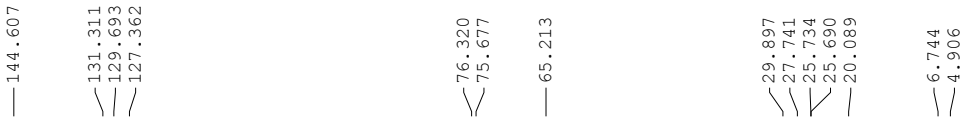
Instrument AVC500 (125 MHz, CDCl3)

Instrument AVC500 (500 MHz, CDCl3)



15e





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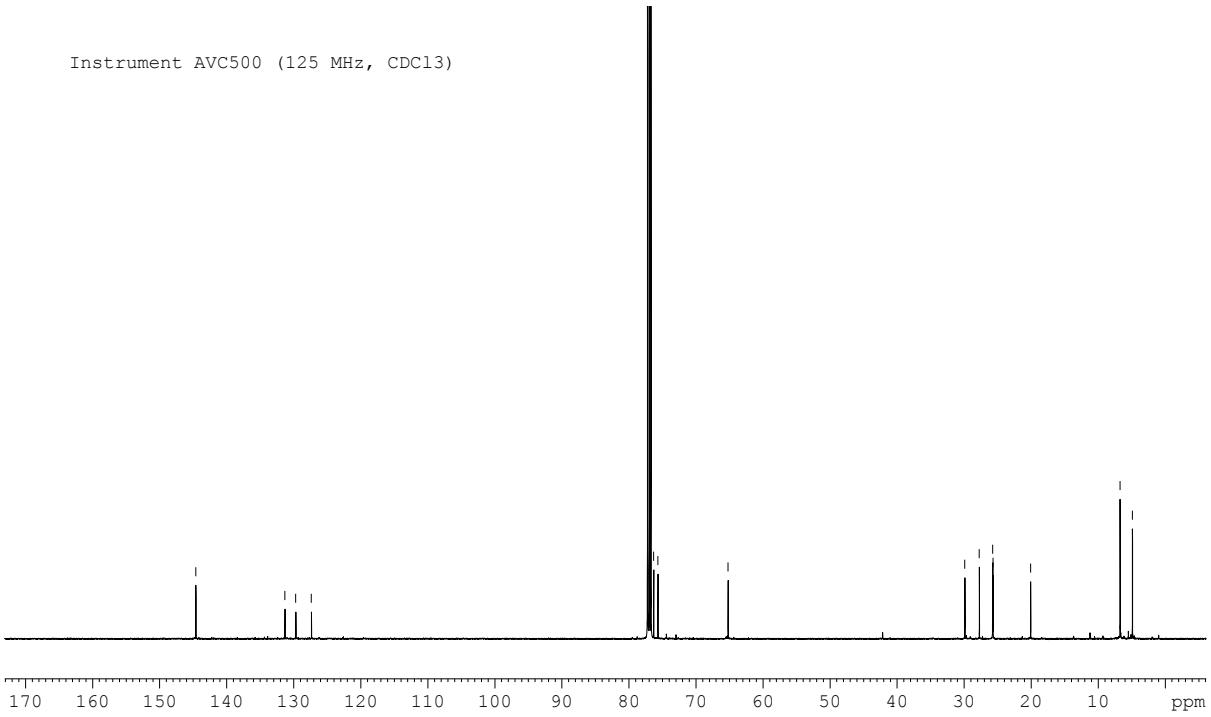
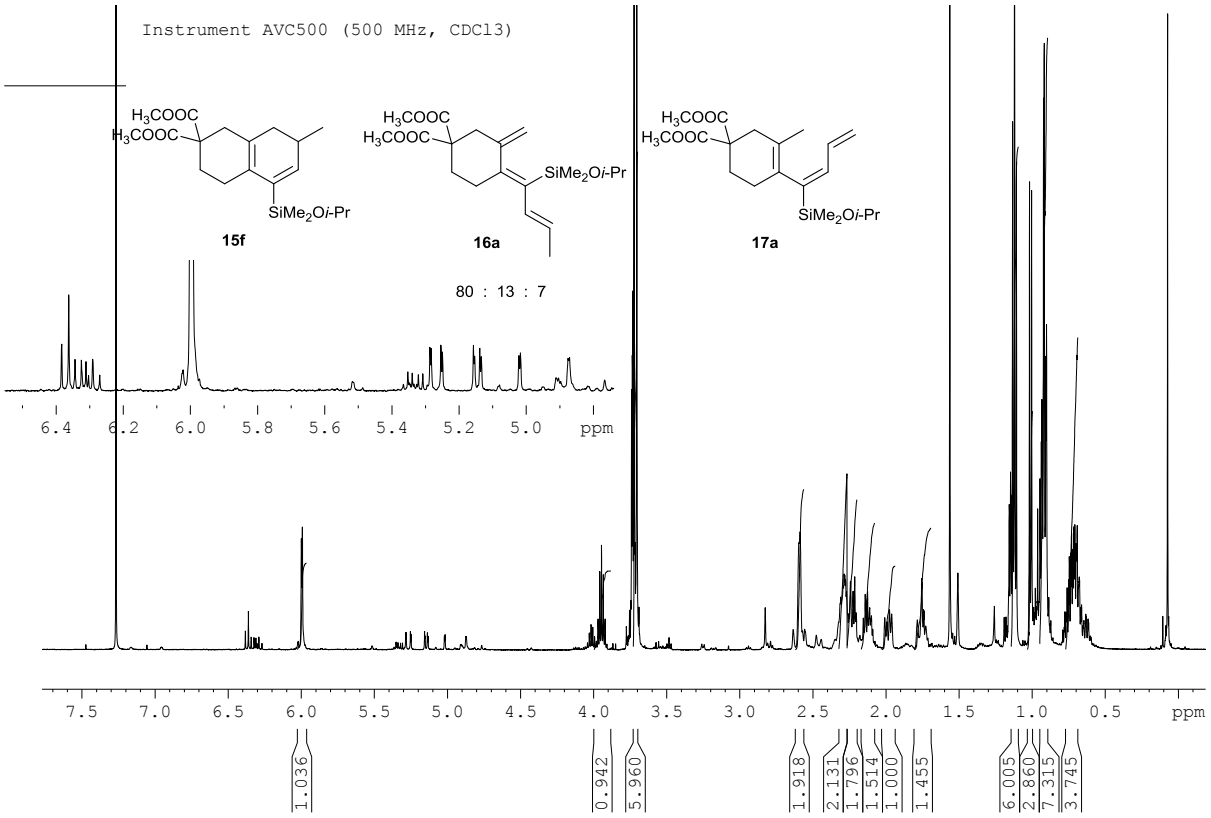
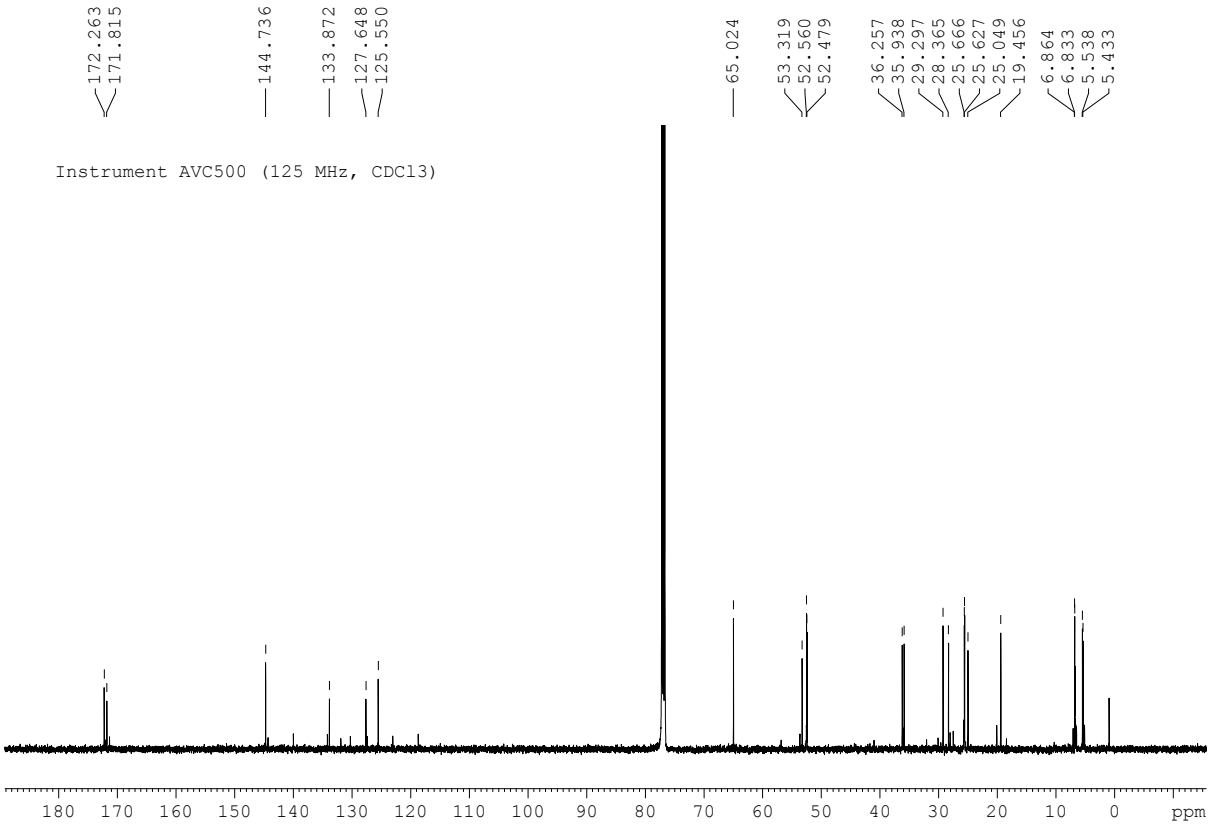
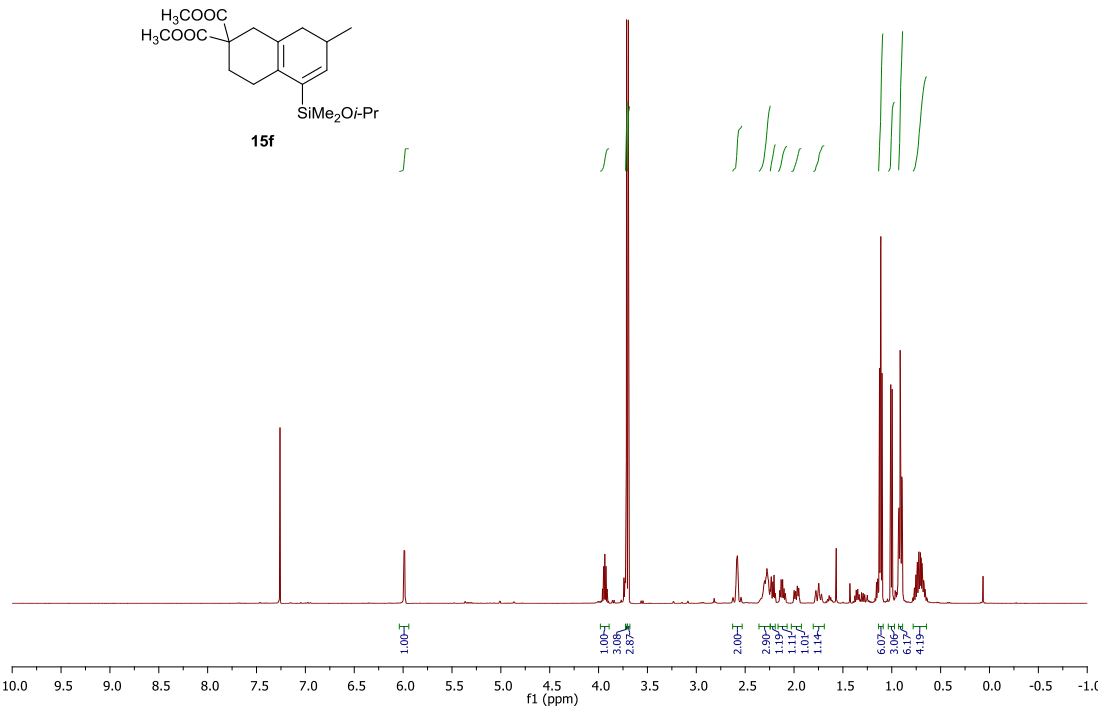


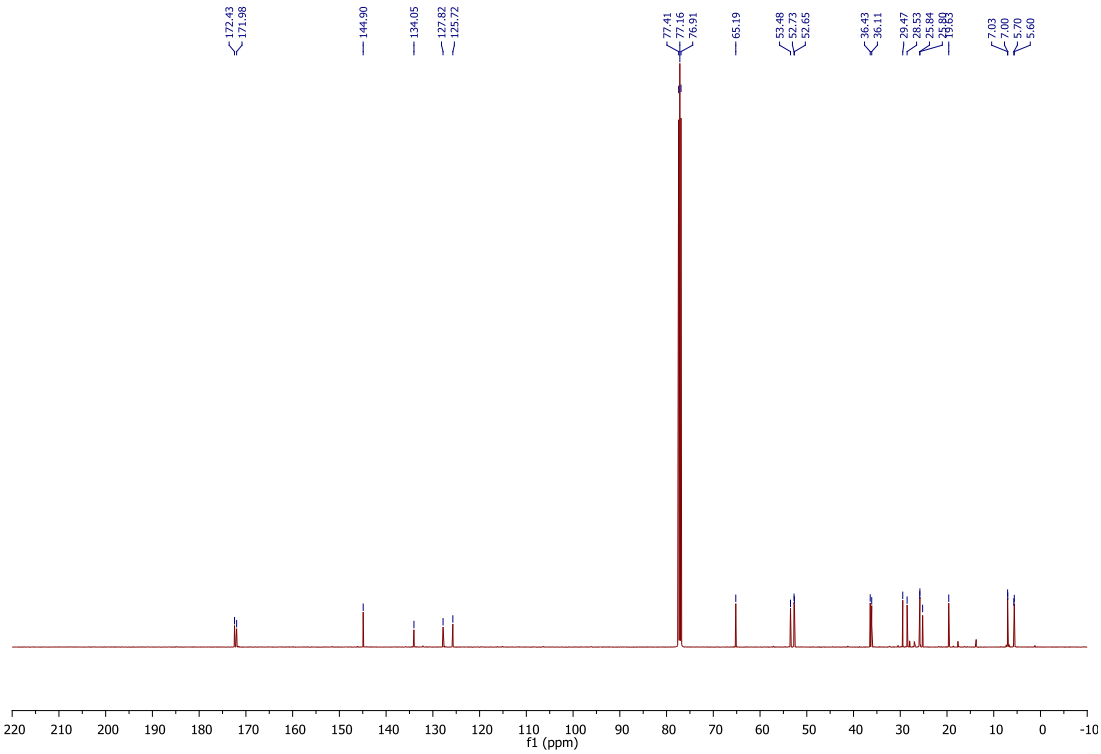

Instrument AVC500 (500 MHz, CDCl3)
H3COOC
H3COOC
SiMe2Oi-Pr
15f
16a
17a
80 : 13 : 7
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.036
0.942
5.960
1.918
2.131
1.796
1.514
1.000
1.455
6.005
2.860
7.315
3.745


172.263
171.815
144.736
133.872
127.648
125.550
65.024
53.319
52.560
52.479
36.257
35.938
29.297
28.365
25.666
25.627
25.049
19.456
6.864
6.833
5.538
5.433
Instrument AVC500 (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

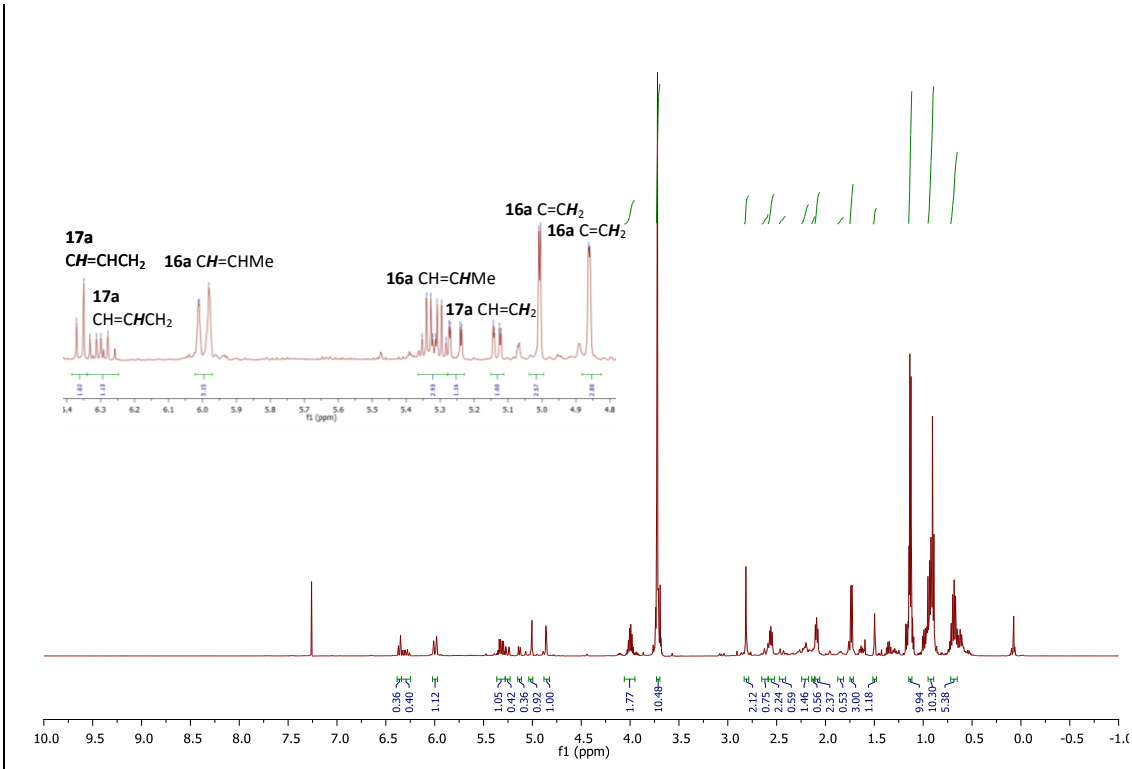
15f (purified) ^{1}H NMR (500 MHz) in $CDCl_3$



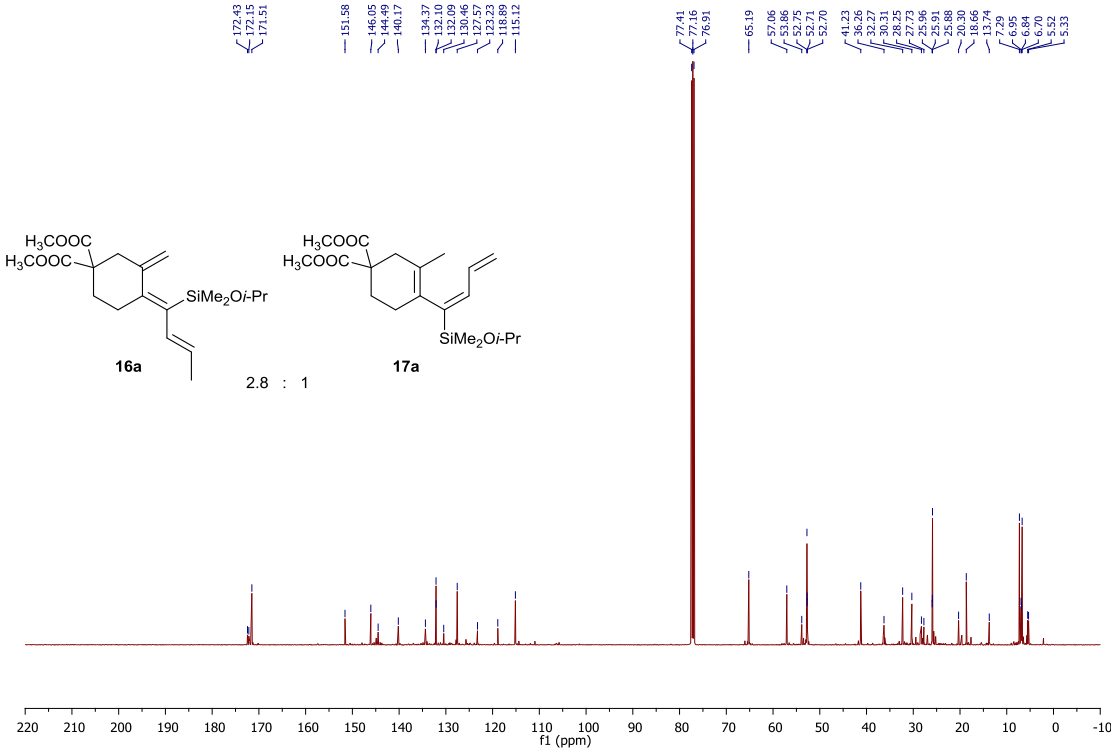
^{13}C NMR (126 MHz) in $CDCl_3$



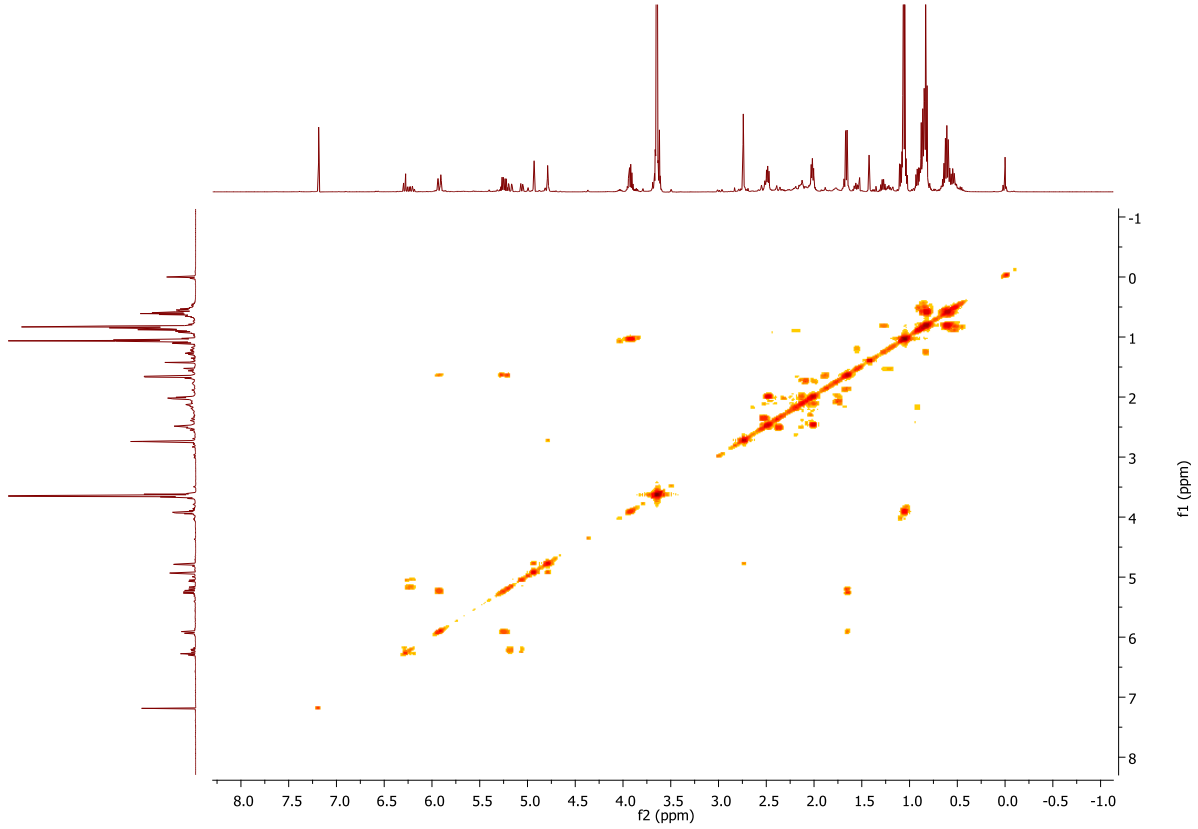
Purified mixture of **16a** / **17a** ^{1}H NMR (500 MHz) in $CDCl_3$



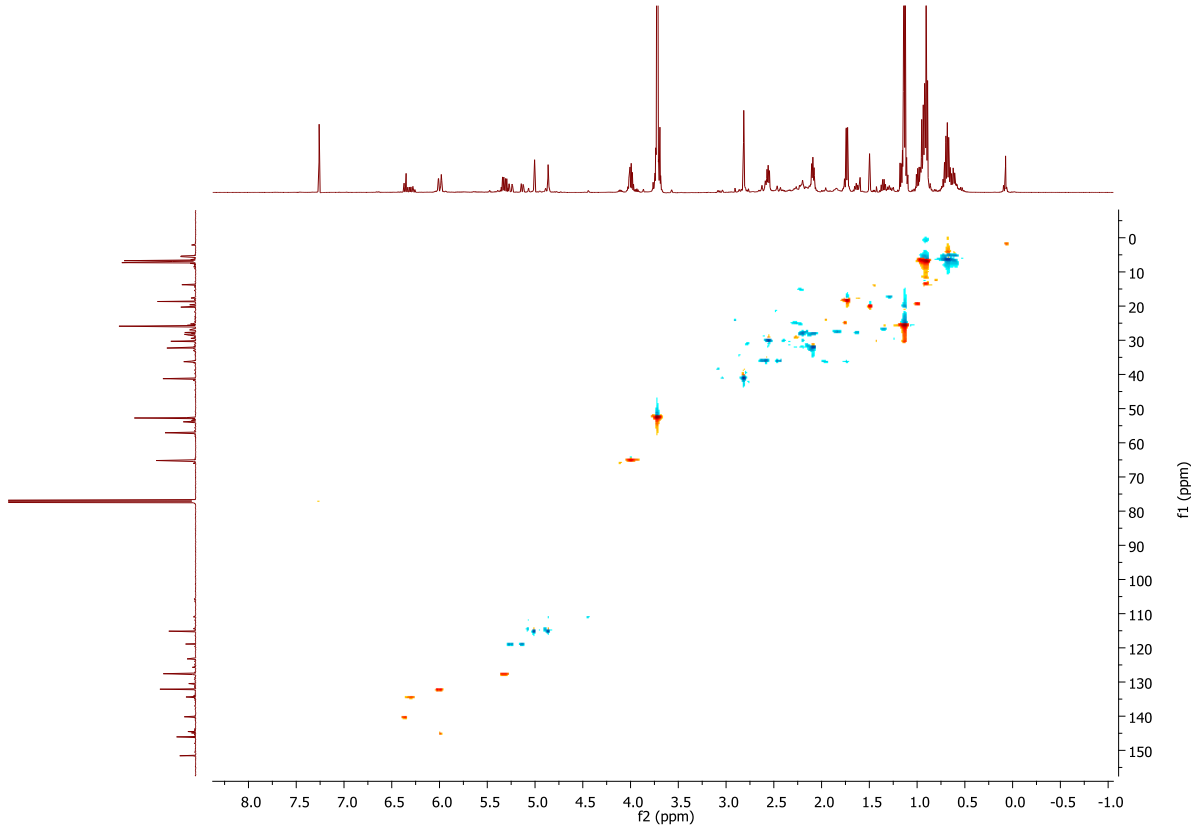
^{13}C NMR (126 MHz) in $CDCl_3$



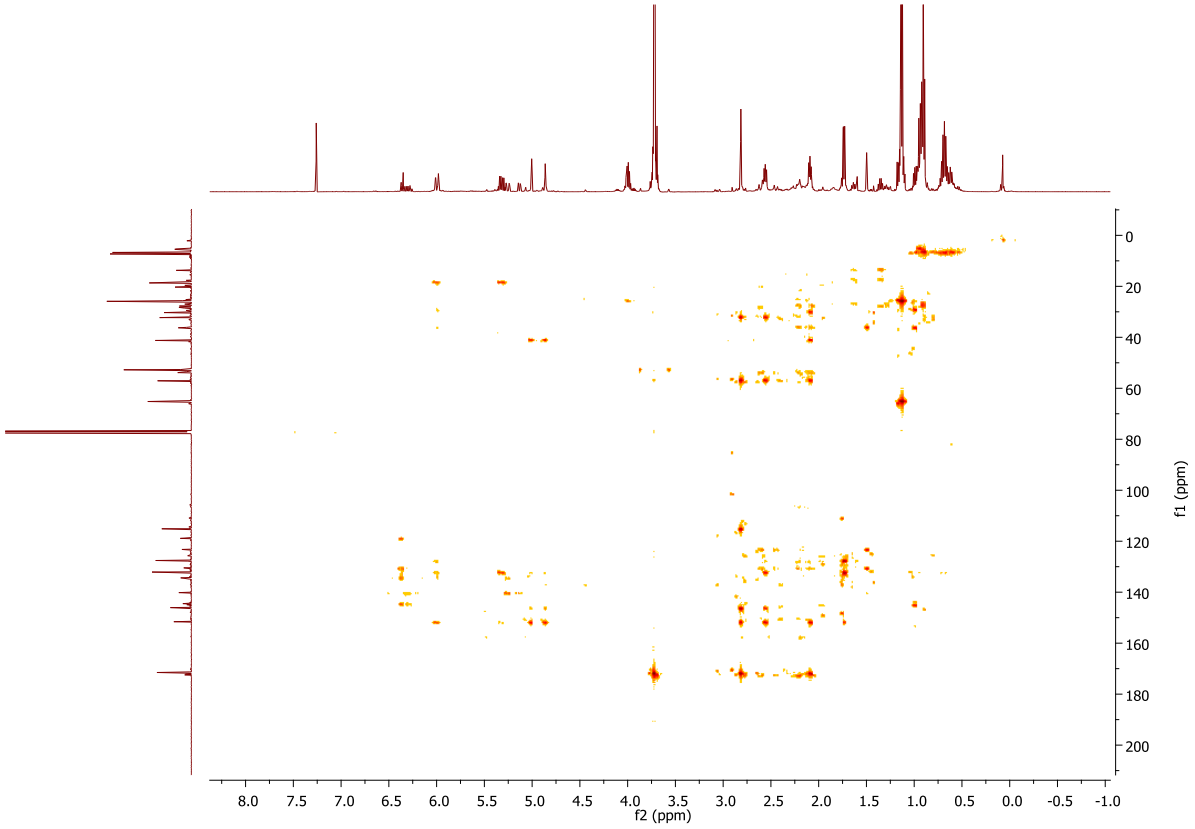
16a/17a COSY (in $CDCl_3$)



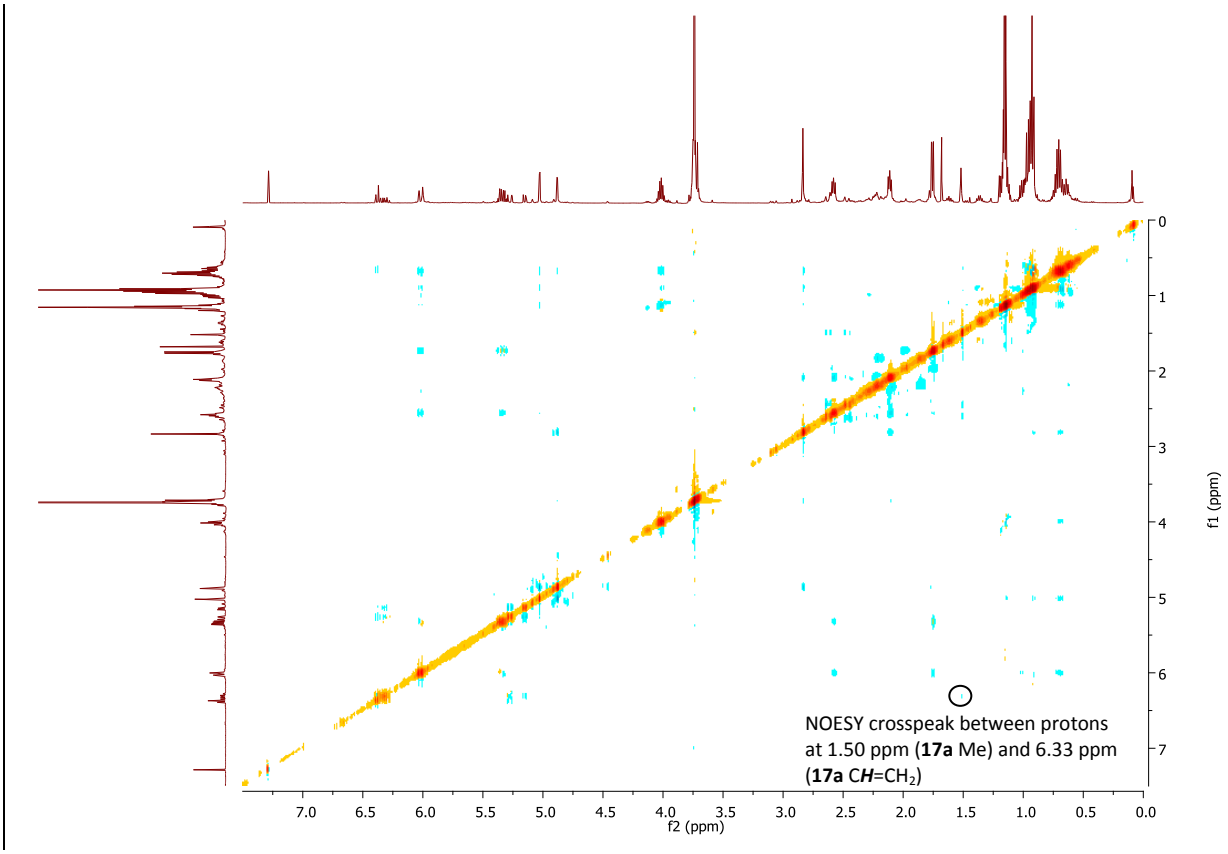
16a/17a HSQC (in $CDCl_3$)

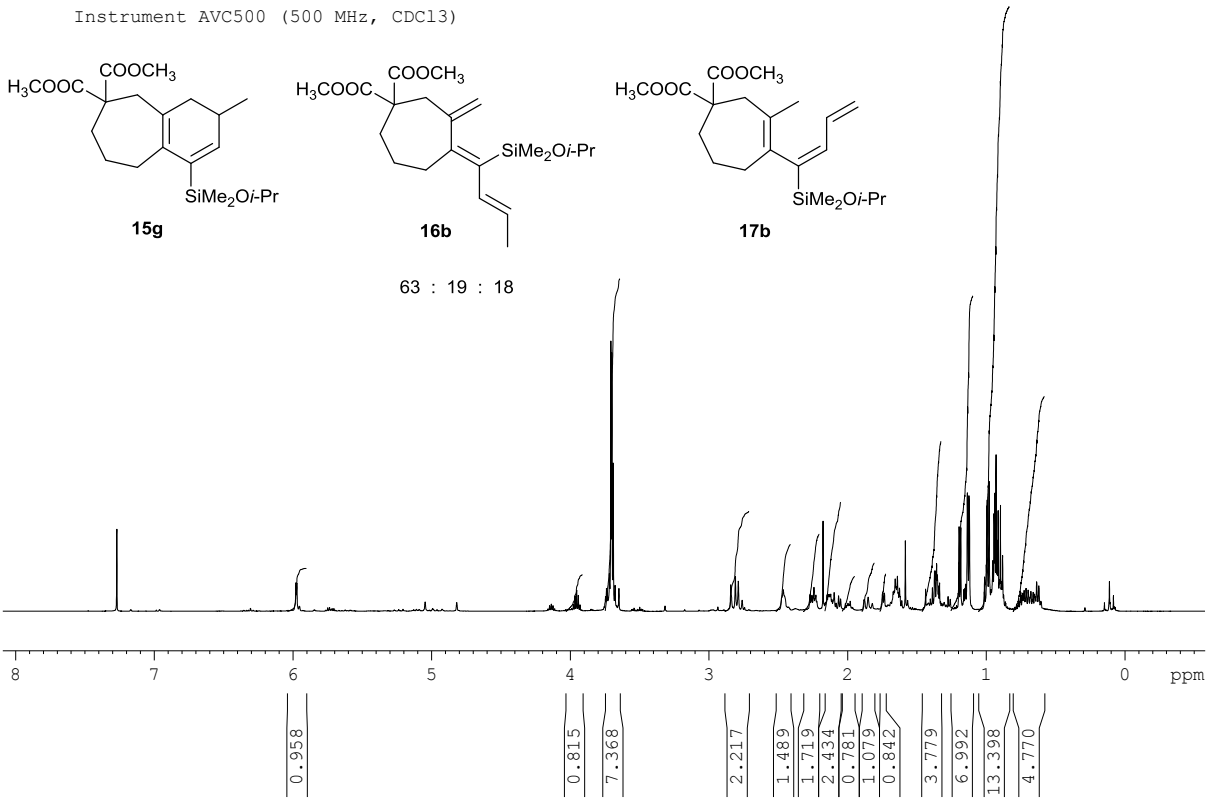


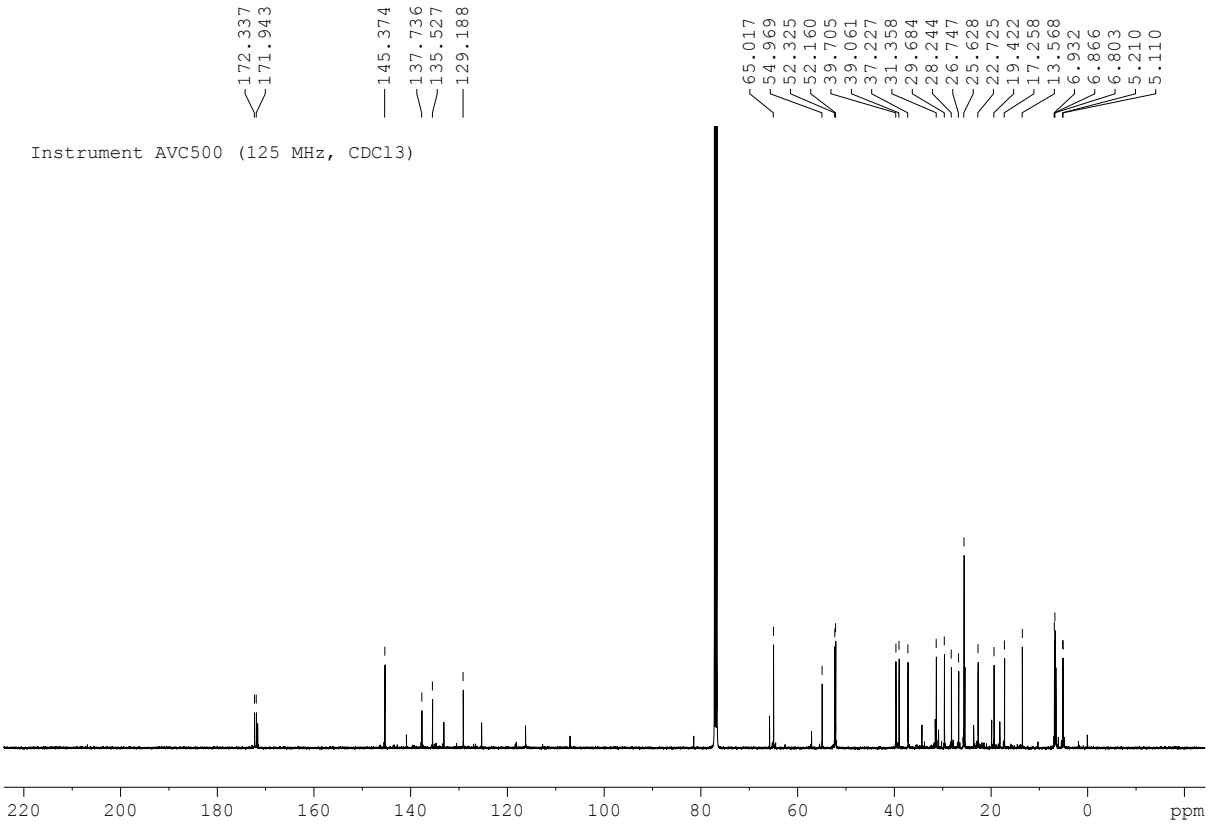
16a/17a HMBC (in $CDCl_3$)



16a/17a NOESY (in $CDCl_3$)

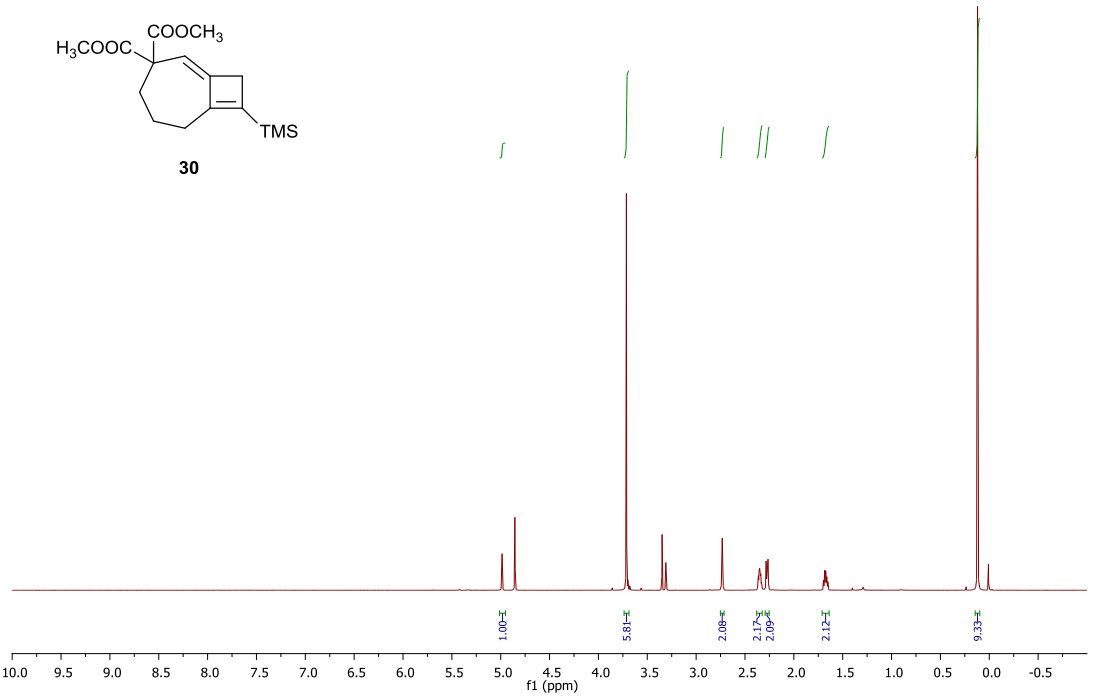



Instrument AVC500 (500 MHz, CDCl3)
15g
16b
17b
63 : 19 : 18
8 7 6 5 4 3 2 1 0 ppm
0.958 0.815 7.368 2.217 1.489 1.719 2.434 0.781 1.079 0.842 3.779 6.992 13.398 4.770

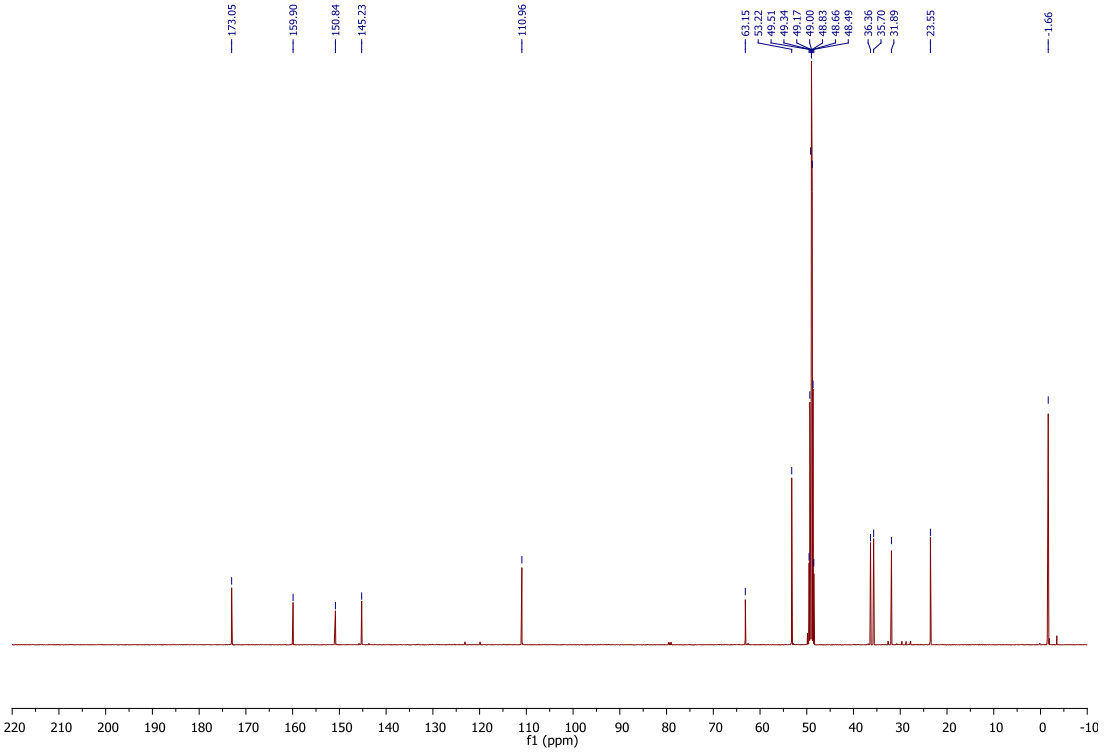

172.337 171.943 145.374 137.736 135.527 129.188
65.017 54.969 52.325 52.160 39.705 39.061 37.227 31.358 29.684 28.244 26.747 25.628 22.725 19.422 17.258 13.568 6.932 6.866 6.803 5.210 5.110
Instrument AVC500 (125 MHz, CDCl3)
220 200 180 160 140 120 100 80 60 40 20 0 ppm

Dimethyl 8-(trimethylsilyl)bicyclo[5.2.0]nona-1,7-diene-3,3-dicarboxylate (30)

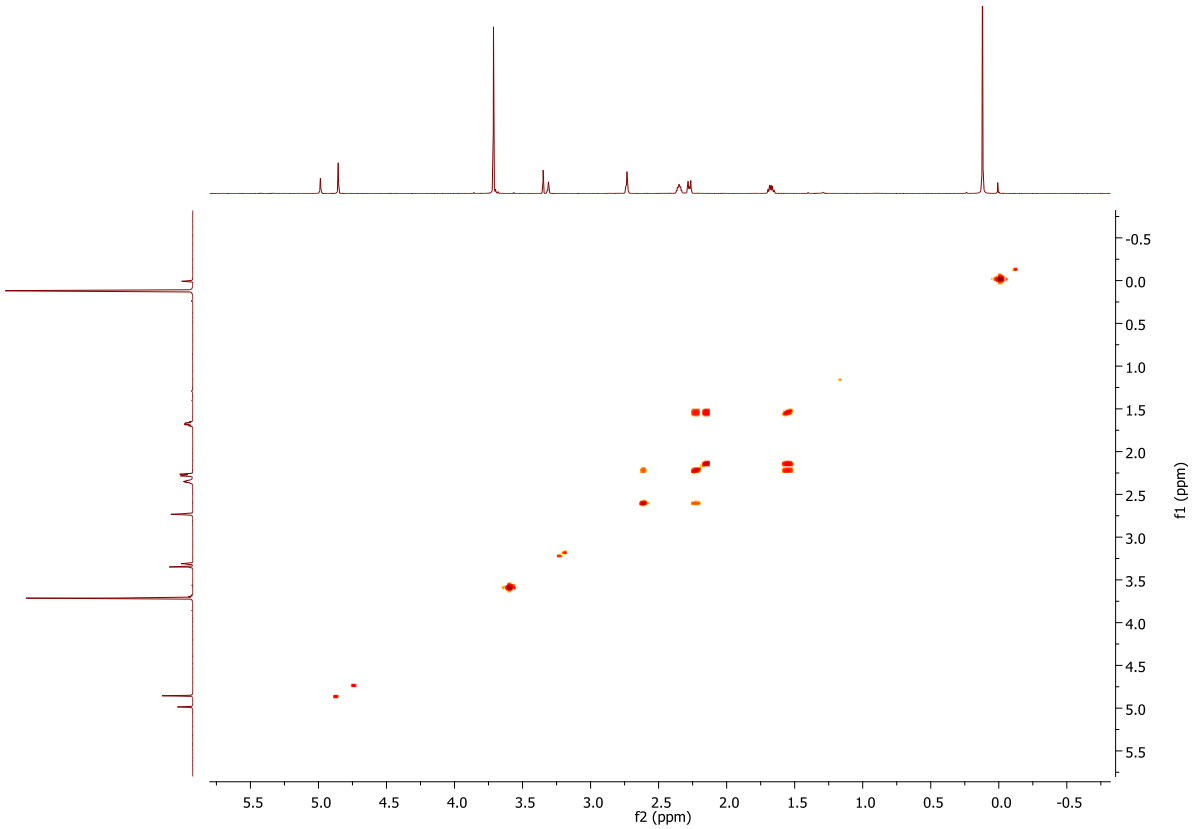
^{1}H NMR (500 MHz) in MeOD



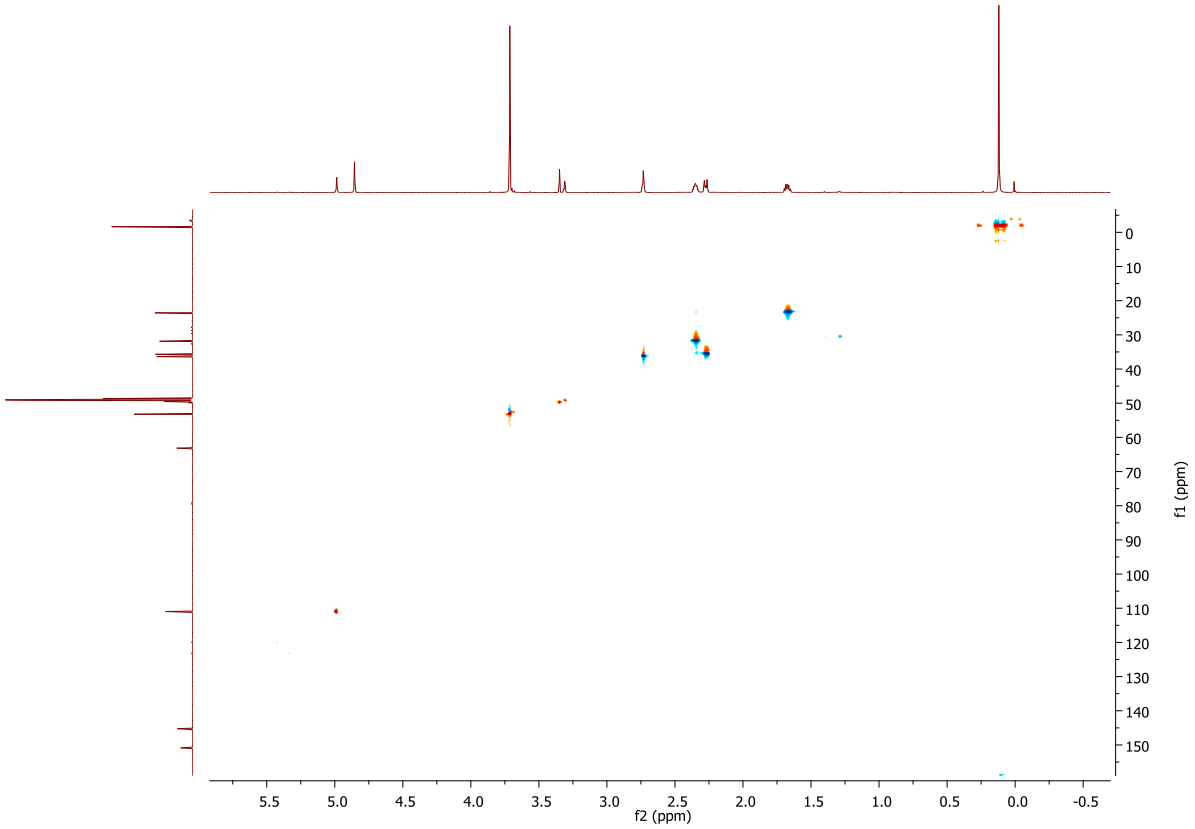
^{13}C NMR (126 MHz) in MeOD



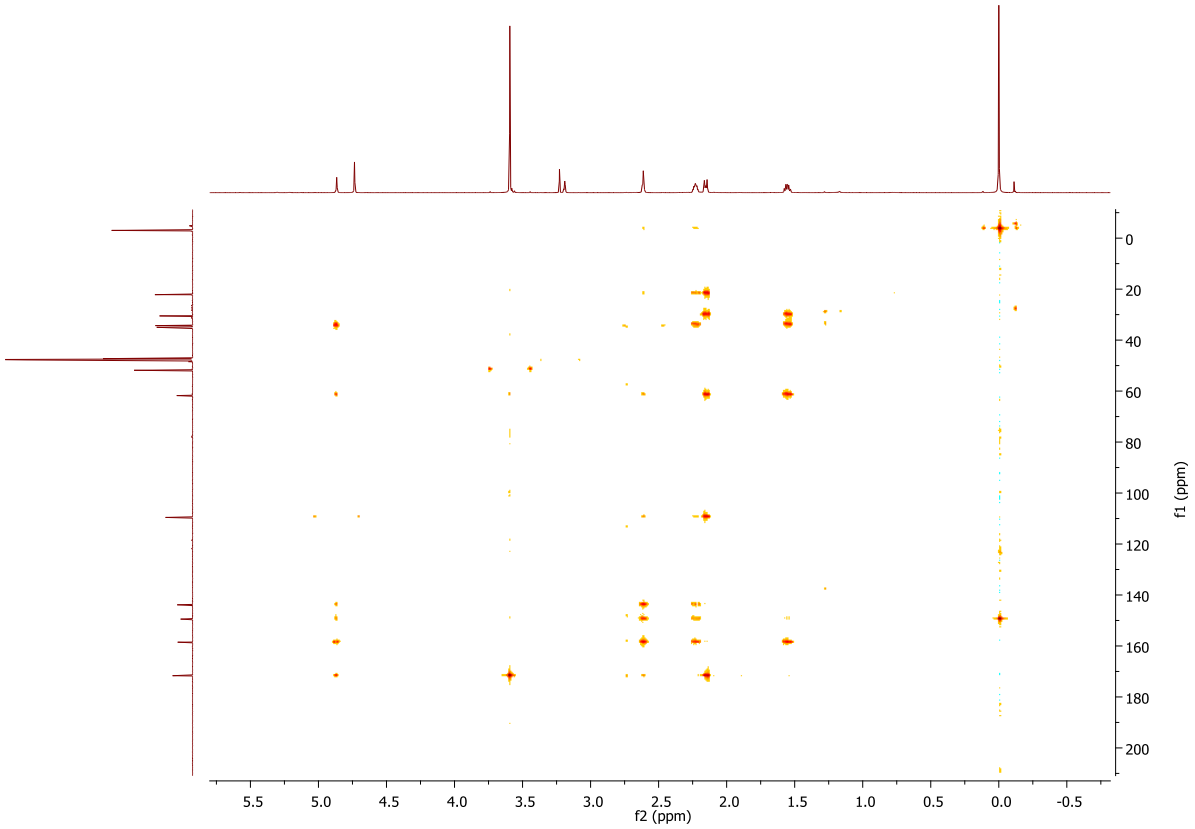
30 COSY (in MeOD)



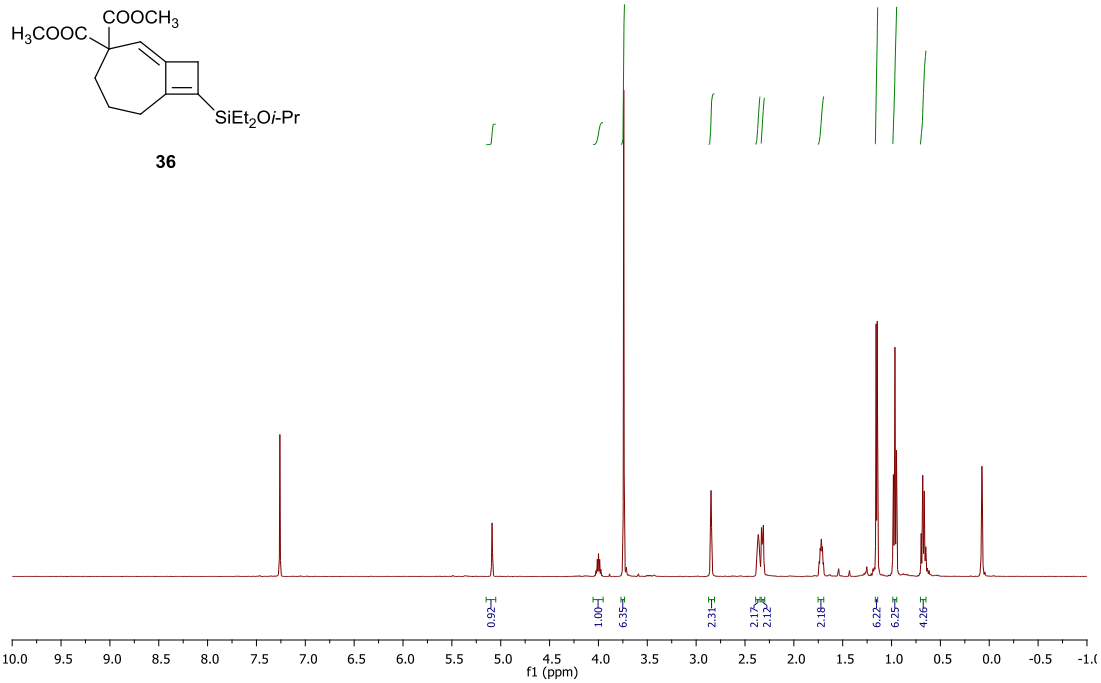
30 HSQC (in MeOD)



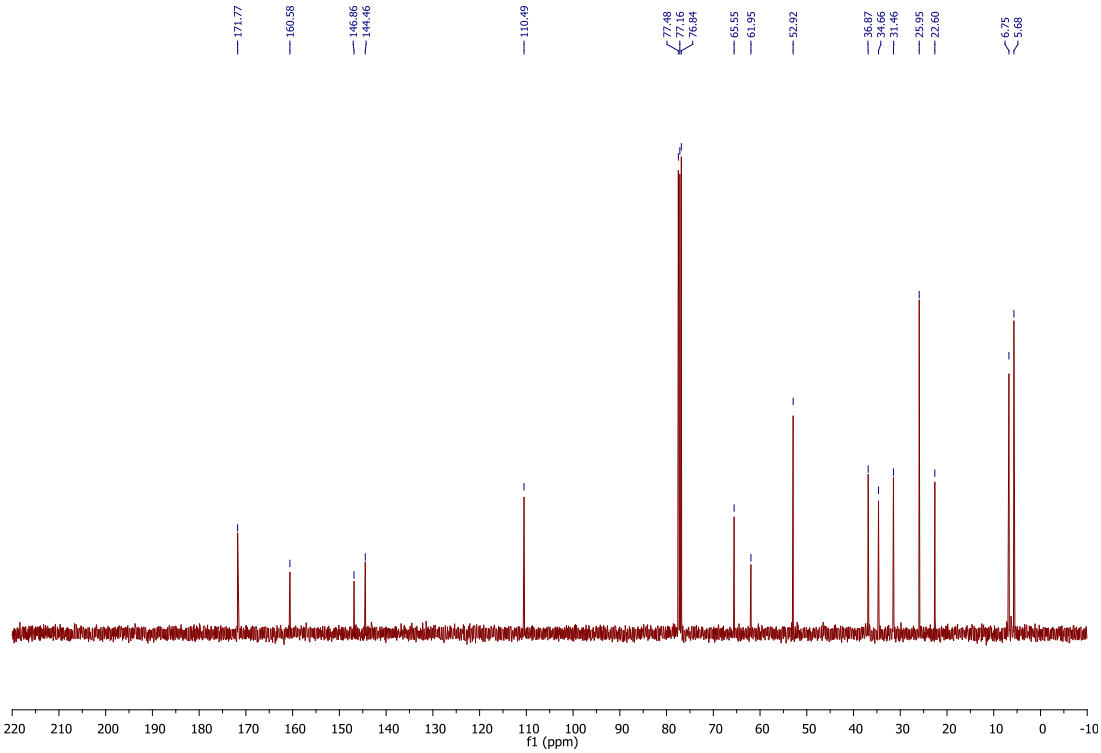
30 HMBC (in MeOD)



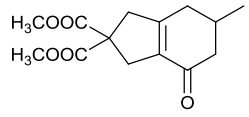
Dimethyl 8-(diethyl(isopropoxy)-λ^4-sulfanyl)bicyclo[5.2.0]nona-1,7-diene-3,3-dicarboxylate (36), ^{1}H NMR (500 MHz) in $CDCl_3$



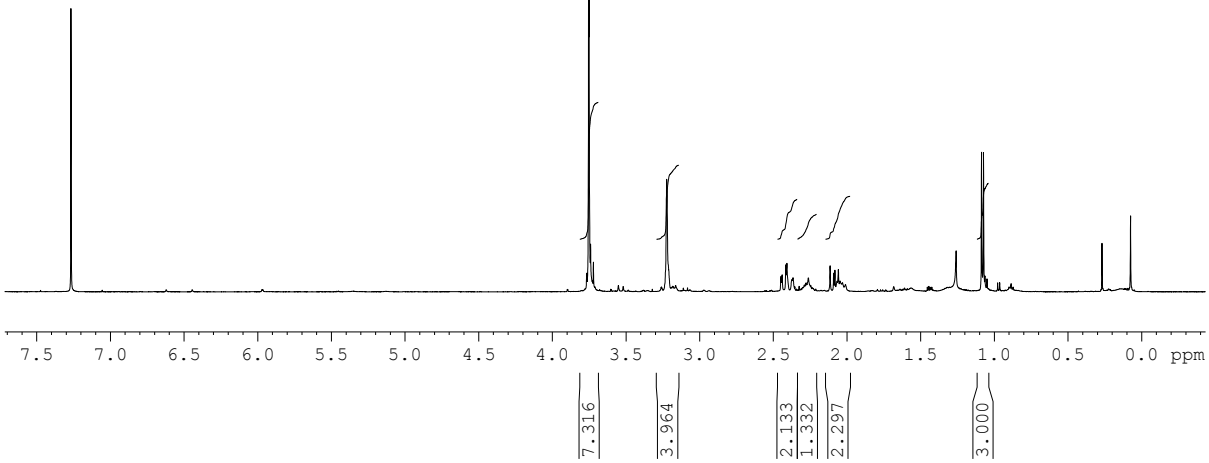
^{13}C NMR (101 MHz) in $CDCl_3$

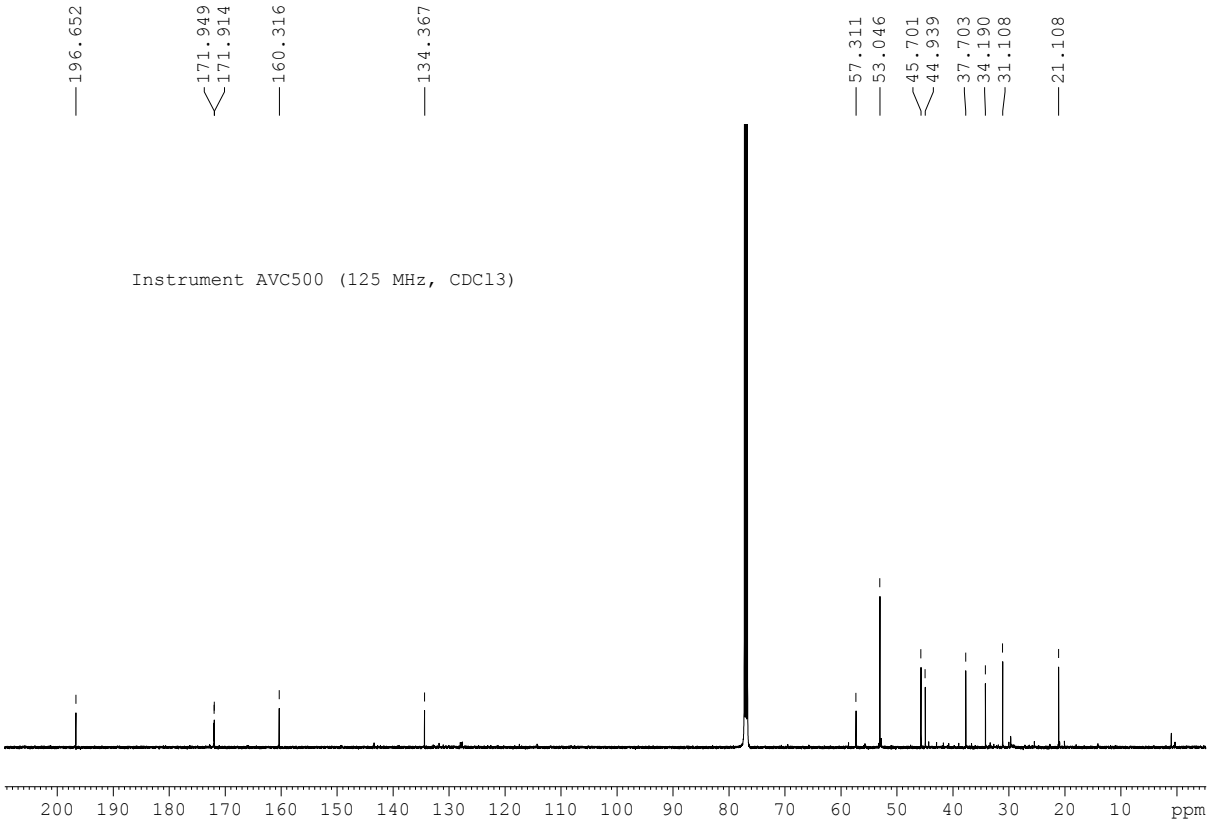


Instrument AVC500 (500 MHz, CDCl3)

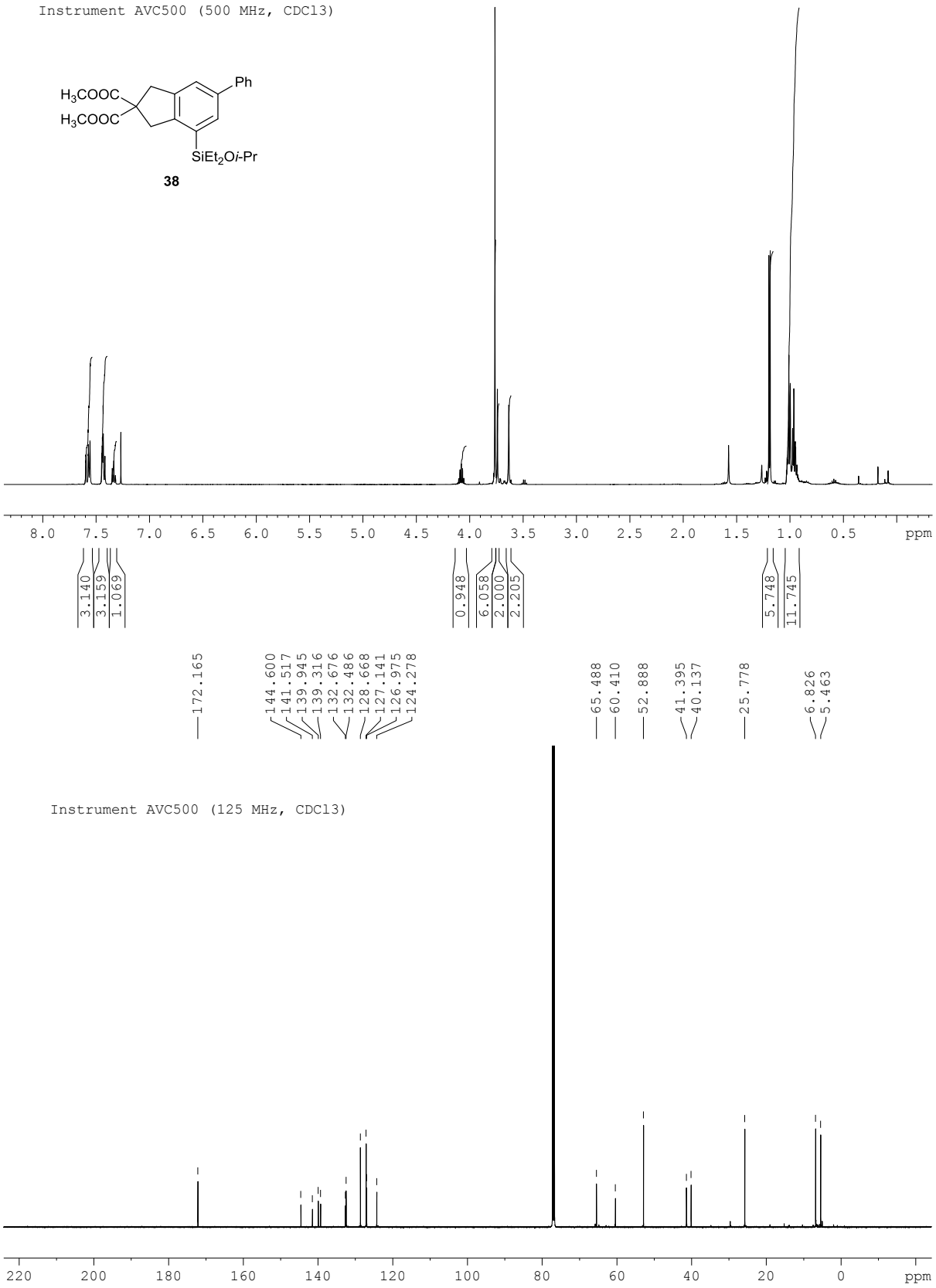


37

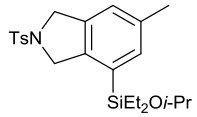




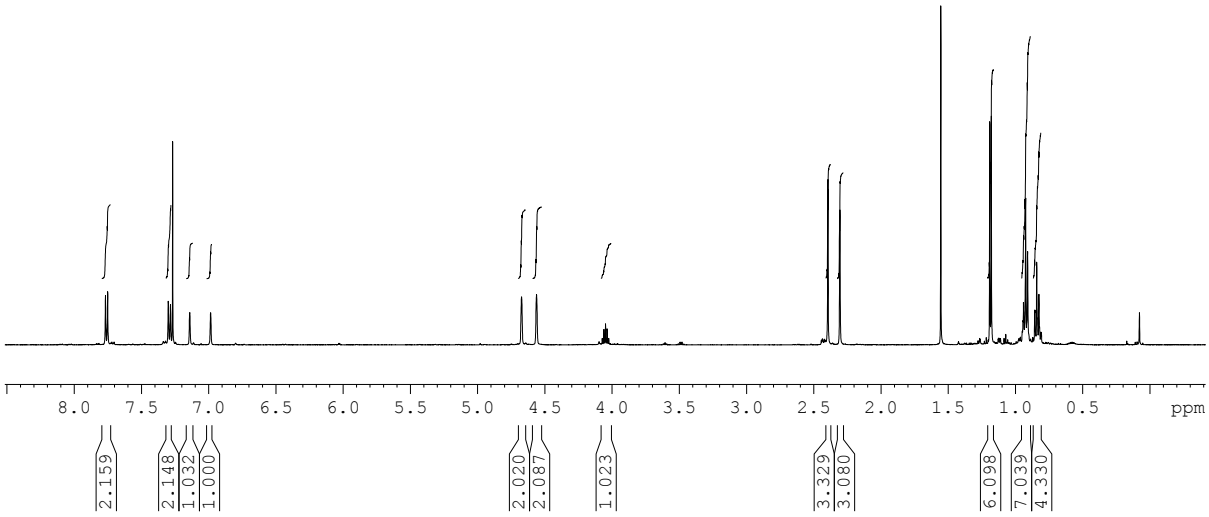
Instrument AVC500 (125 MHz, CDCl3)

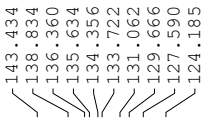

Instrument AVC500 (500 MHz, CDCl3)
H3COOC
H3COOC
Ph
SiEt2Oi-Pr
38
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.140
3.159
1.069
0.948
6.058
2.000
2.205
5.748
11.745
172.165
144.600
141.517
139.945
139.316
132.676
132.486
128.668
127.141
126.975
124.278
65.488
60.410
52.888
41.395
40.137
25.778
6.826
5.463
Instrument AVC500 (125 MHz, CDCl3)
220 200 180 160 140 120 100 80 60 40 20 0 ppm

Instrument AVC500 (500 MHz, CDCl3)

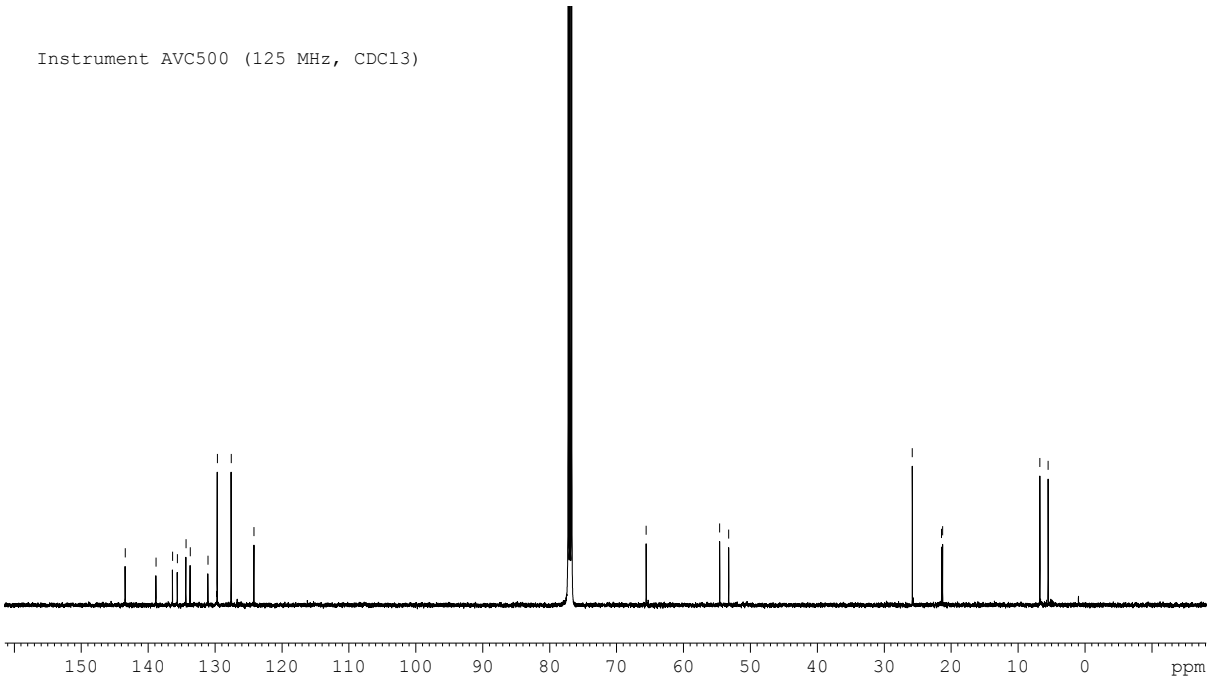


39

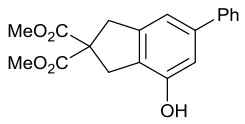




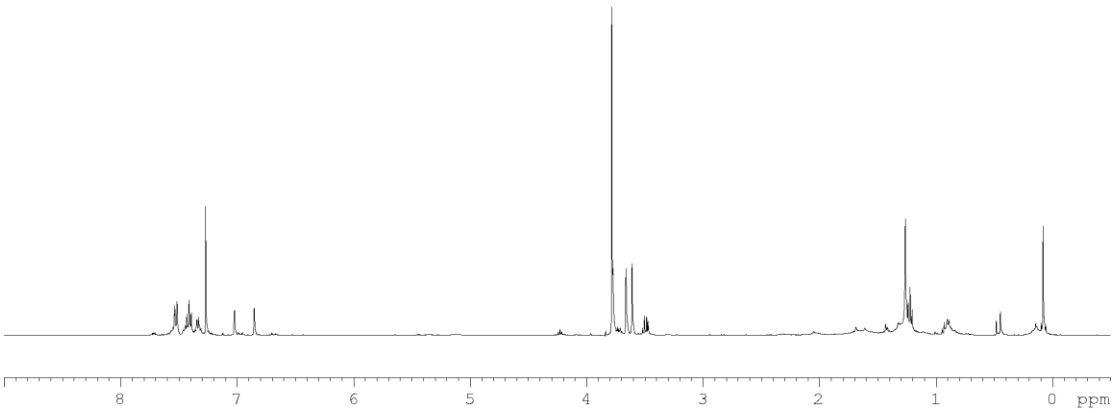
Instrument AVC500 (125 MHz, CDCl3)



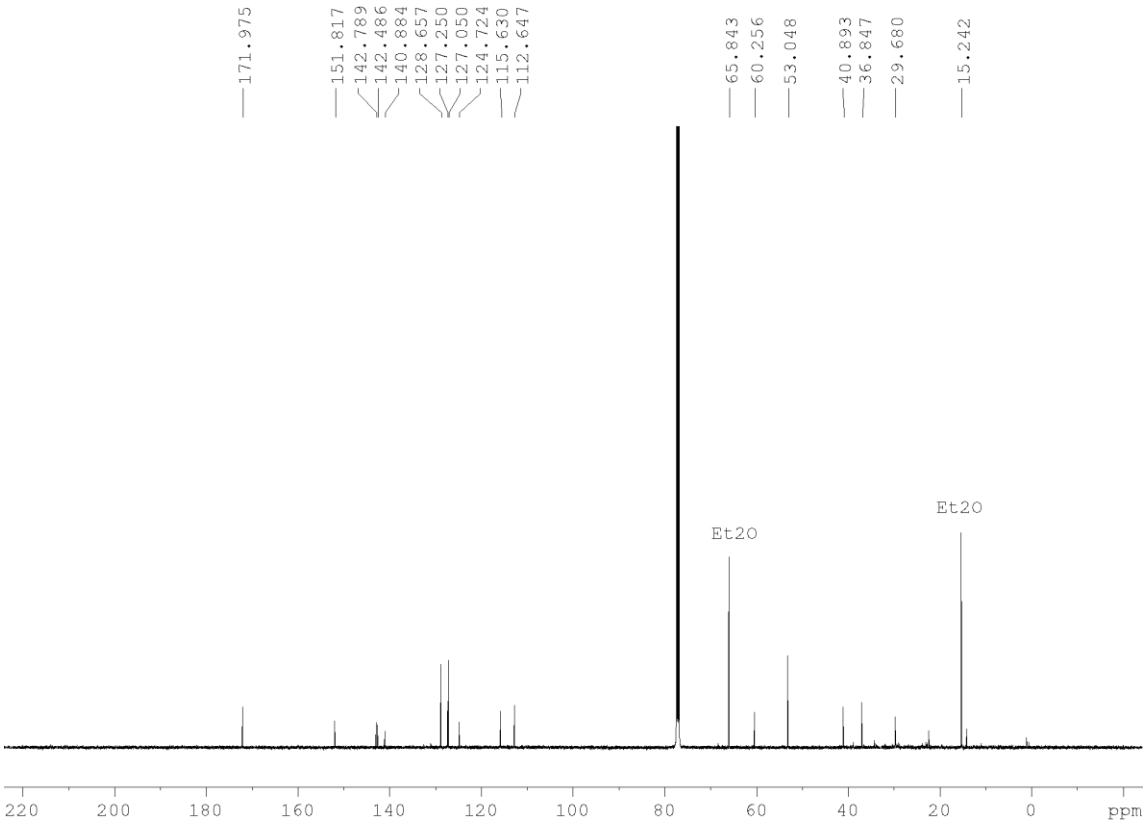
^{1}H NMR spectrum, 500 MHz, $CDCl_3$



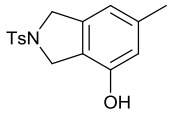
40



^{13}C NMR spectrum, 125 MHz, $CDCl_3$



Instrument AVC500 (500 MHz, CDCl3)



41