Silene Equivalents Through the Rhodium Catalysed Reactions of α-Hypersilyl Diazoesters - A Computational and Experimental Study

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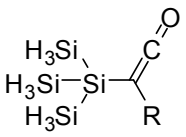
Computational Details

Calculations were carried out using Gaussian03 software package.[1] The geometries were optimised with density functional theory using Becke's three parameter hybrid functional (B3LYP),[2,3] with the 6-311+G(d,p) valence triple zeta basis set of Pople and co-workers, augmented with diffuse functions on non-hydrogen atoms, for the model compounds and 6-311G(d,p) for the full compounds.[4] Frequencies were calculated at B3LYP/6-311+G(d,p) for the model compounds and at B3LYP/6-311G(d,p) for the full compounds in order to identify them as minima. The NMR chemical shifts were evaluated by using the gauge-including atomic orbitals method (GIAO)[5] with the B3LYP functional. For these calculations we used 6-311+G(2d,p) basis set. In order to compare isotropic shieldings with experimental chemical shifts the NMR parameters for tetramethylsilane were calculated and used as the reference molecule.

Cartesian coordinates of optimized molecules at B3LYP/6-311+G(d,p)level



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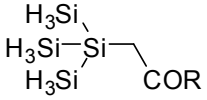

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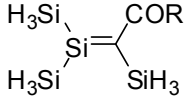

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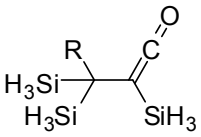

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R = OMe (**a**)
R = NH_2 (**b**)
R = SMe (**c**)
R = Me (**d**)

Silylketene 5a

E_{abs}=-1430.08595 a.u.

```
0 1
 Si                -0.57624400   -0.05506400   -0.00330300
 C                  1.27607100    0.22152800    0.23718000
 Si                -1.42922400   -0.98780600    1.99643500
 H                 -1.15014700   -0.08657700    3.14493400
 H                 -2.90297600   -1.15159100    1.86522100
 H                 -0.83130300   -2.32095300    2.26452000
 Si                -1.66004000    2.00530800   -0.43275100
 H                 -1.13379900    2.64303200   -1.66826300
 H                 -3.10955400    1.73221200   -0.61712100
 H                 -1.48782100    2.94627400    0.70461100
 Si                -0.98533900   -1.51230900   -1.82268800
 H                 -0.30783000   -2.82081000   -1.61687900
 H                 -2.44692800   -1.75834600   -1.95483100
 H                 -0.48527200   -0.91895600   -3.09182400
 C                  1.79507700    1.43323600    0.12188900
 O                  2.20693900    2.51562400    0.00251600
 O                  2.08702200   -0.81829100    0.72041100
 C                  2.84300800   -1.50169800   -0.28543500
 H                  2.19016200   -1.93158100   -1.05196200
 H                  3.56552500   -0.83000800   -0.76130800
 H                  3.37518100   -2.30155800    0.23000100
```

Silylketene 5b

E_{abs} = -1370.91197 a.u.

```
0 1
 Si                -0.02566900    0.36518500    0.00000000
 C                  0.72086900   -1.37438100    0.00000000
 Si                 0.72086900    1.50237400    1.93684000
 H                  2.19704800    1.37009400    2.08191400
 H                  0.39079400    2.94995500    1.84901200
 H                  0.08119300    0.93708500    3.15470700
 Si                -2.39259900    0.32160800    0.00000000
 H                 -2.91152800   -0.36806700    1.20997300
 H                 -2.88583600    1.72433500    0.00000000
 H                 -2.91152800   -0.36806700   -1.20997300
 Si                 0.72086900    1.50237400   -1.93684000
 H                  0.39079400    2.94995500   -1.84901200
 H                  2.19704800    1.37009400   -2.08191400
 H                  0.08119300    0.93708500   -3.15470700
 C                 -0.09734200   -2.41206200    0.00000000
 O                 -0.86167600   -3.28708000    0.00000000
 N                  2.14163000   -1.65694300    0.00000000
 H                  2.60153800   -1.28506100    0.82353600
```

H	2.60153800	-1.28506100	-0.82353600

Silylketene 5c

E_{abs} = -1753.09246 a.u.

0 1

C	-1.15294900	1.91122300	-0.04433700
C	-0.93226900	0.62056100	-0.18459400
S	-2.37409100	-0.30599100	-0.74189300
Si	0.78441200	-0.14235700	0.00805600
O	-1.33672500	3.05106900	0.07782500
C	-3.11214900	-0.90368500	0.82732300
H	-3.98865400	-1.48696600	0.53742100
H	-3.42854900	-0.06775900	1.45058700
H	-2.41907000	-1.54501800	1.37048900
Si	1.17517200	-1.56756600	-1.83828000
Si	0.92979200	-1.37133700	2.02447600
Si	2.43585500	1.55478600	0.04957100
H	2.47898700	2.28648100	-1.24388900
H	3.76065200	0.92435300	0.28981500
H	2.16798000	2.52961800	1.14019700
H	0.86431100	-0.86256800	-3.10898900
H	0.36495700	-2.80926700	-1.75391800
H	2.61419300	-1.94853700	-1.84080800
H	-0.10385800	-2.44088300	2.06941100
H	0.73065200	-0.47884400	3.19802200
H	2.26862300	-2.01128300	2.13547200

Silylketene 5d

E_{abs} = -1354.87902 a.u.

0 1

Si	-0.07064100	2.40416900	-0.00516700
Si	0.35365300	0.07629200	0.00009200
Si	1.60287300	-0.45448000	1.93860500
Si	1.60799900	-0.46179100	-1.93308200
C	-1.24978300	-0.92363300	-0.00010200
C	-2.37024400	-0.24647800	-0.00008100
C	-1.25142600	-2.45096900	-0.00058600
O	-3.35223600	0.38343300	-0.00012000
H	-0.74299800	-2.84379200	-0.88545500
H	-2.26782000	-2.84925900	0.00217500
H	-0.73803400	-2.84422800	0.88118900
H	2.92018300	0.23584600	1.89620800
H	1.84768300	-1.91929800	2.03204300
H	0.87571100	-0.02051200	3.16127300
H	0.87652100	-0.04722900	-3.15989300
H	1.86773700	-1.92488700	-2.01213600
H	2.91823400	0.24222300	-1.89739200

H	-0.82684300	2.80940300	-1.21875500
H	1.23874100	3.10908000	-0.00081300
H	-0.83688600	2.81301700	1.20086600

Carbene 6a

E_{abs} = -1430.02845 a.u.

0 1

Si	-0.94302700	0.14274600	0.08588800
C	0.62175600	-0.37209200	0.83239700
Si	-0.97710800	1.97284600	-1.43015000
H	0.17367400	1.87063400	-2.36343200
H	-2.24422100	1.96715100	-2.20946900
H	-0.88907100	3.25394500	-0.68109800
Si	-1.03700300	-1.92085800	-1.15271400
H	-0.72075500	-3.08266200	-0.29549200
H	-2.44849800	-2.01539000	-1.61871800
H	-0.12848200	-1.82319800	-2.31555300
Si	-2.66703700	0.10050000	1.69885500
H	-2.41598100	1.12409600	2.74557600
H	-3.95966400	0.41030500	1.03121600
H	-2.74305700	-1.24377400	2.32330800
C	1.94428700	-0.34215000	0.35674400
O	2.28994800	-1.21819500	-0.43779900
O	2.75790900	0.60389500	0.86153700
C	4.14598200	0.51449800	0.47585100
H	4.56887500	-0.44079400	0.78911100
H	4.25386700	0.62308600	-0.60390700
H	4.63675700	1.33619500	0.99230700

Carbene 6b

E_{abs} = =-1370.84672 a.u.

0 1

Si	0.54151700	-0.04216300	0.00213200
C	-1.00382100	0.21566400	-0.94566200
Si	2.25285700	-0.78737200	-1.44627300
H	2.34489100	0.10645800	-2.62806900
H	3.55020000	-0.76748800	-0.71716300
H	1.97994000	-2.17830500	-1.88940300
Si	0.42611300	-1.25297300	2.04154200
H	0.14424600	-2.68876800	1.78789600
H	1.72560300	-1.14401300	2.75970300
H	-0.64300300	-0.69077500	2.90893000
Si	0.90724200	2.27823800	0.41463300
H	1.93591300	2.40139400	1.48150600
H	1.38296100	2.96815200	-0.80956000
H	-0.34053500	2.93325600	0.89012200
C	-2.31221500	-0.11491000	-0.61257300

O	-2.40001600	-1.32566500	-0.94025400
N	-3.32561000	0.63328000	-0.11491400
H	-3.23517100	1.63671800	-0.08949600
H	-4.25763000	0.25098300	-0.18713000

Carbene 6c

E_{abs} = =-1752.99635 a.u.

0 1

Si	-1.20049800	2.38114600	0.00367800
Si	-1.07392800	0.00697600	0.02885600
Si	-2.71597900	-0.76694100	-1.49083100
Si	-1.33136200	-0.84219000	2.23043100
C	0.55936300	-0.24472600	-0.76411300
H	-2.58900300	-2.23369600	-1.67447300
C	1.72560500	-0.89859800	-0.44414900
O	1.45932100	-2.11593300	-0.60700700
S	3.33430300	-0.28854500	-0.04959700
C	3.00114000	1.51075900	-0.07060100
H	2.40252700	1.81530000	0.78666900
H	2.51323900	1.79540900	-1.00339100
H	3.97484800	1.99655700	-0.01599400
H	-2.50037700	2.75857900	0.61794100
H	-1.13993700	2.89682200	-1.38597700
H	-0.10440100	2.98680400	0.80326300
H	-2.65599100	-0.43125700	2.77051700
H	-0.26597500	-0.28808800	3.10719700
H	-1.25035900	-2.32423500	2.23384100
H	-2.55889900	-0.07573500	-2.79482200
H	-4.06099900	-0.46276800	-0.93184600

Carbene 6d

E_{abs} = =-1354.78509 a.u.

0 1

Si	-1.08211400	2.31652000	0.07130900
Si	-0.58476200	-0.00560800	0.00702000
Si	-1.83846200	-1.00698500	-1.73124200
Si	-0.96749800	-0.99365700	2.12815500
C	1.17251400	0.05762900	-0.44367700
H	-0.18814700	3.02135000	1.02604600
C	2.48112400	-0.16245000	-0.28550900
O	2.45092400	-1.44575700	-0.37792000
C	3.69711300	0.67718500	-0.12443200
H	4.37995800	0.49191800	-0.95811600
H	4.21116900	0.39089600	0.79741700
H	3.44697100	1.73850500	-0.08780000
H	-2.41205000	-0.88847700	2.47159200
H	-0.17515900	-0.27924900	3.16323800

H	-0.58281400	-2.42736700	2.11437200
H	-1.62085300	-0.27125400	-3.00309100
H	-3.28422400	-0.95349300	-1.38155200
H	-1.44011600	-2.42701900	-1.90165100
H	-2.48899500	2.46957900	0.52722600
H	-0.93792600	2.92269600	-1.27600000

Silene 7a

E_{abs} = -1430.11926 a.u.

0 1

Si	0.84324600	-0.85823900	0.00000000
C	0.00000000	0.67252400	0.00000000
Si	3.20463100	-0.91125100	0.00000000
H	3.74037500	-0.24573000	1.21370400
H	3.62462300	-2.33601000	0.00000000
H	3.74037500	-0.24573000	-1.21370400
Si	-0.43968900	-2.83671900	0.00000000
H	-1.26310500	-2.91408600	-1.22830000
H	0.51880500	-3.97893800	0.00000000
H	-1.26310500	-2.91408600	1.22830000
Si	0.83218200	2.34768400	0.00000000
H	0.49253900	3.14372200	1.20742200
H	2.30517700	2.12482300	0.00000000
H	0.49253900	3.14372200	-1.20742200
C	-1.46695300	0.59555700	0.00000000
O	-2.14567500	-0.42009700	0.00000000
O	-2.03559500	1.82977300	0.00000000
C	-3.47224200	1.87576400	0.00000000
H	-3.86986200	1.38398600	-0.88893800
H	-3.86986200	1.38398600	0.88893800
H	-3.72834900	2.93320400	0.00000000

Silene 7b

E_{abs} = =-1370.93105 a.u.

0 1

Si	-0.85311700	0.09290900	-0.01076900
C	0.83382300	-0.36948800	0.01009500
Si	-2.53110100	-1.57081600	-0.03880200
H	-2.39871400	-2.47556000	1.13123100
H	-3.85007300	-0.89056200	0.02149000
H	-2.45515200	-2.36976400	-1.28854900
Si	-1.39071100	2.38554600	-0.01658600
H	-0.74941600	3.06726300	-1.16330800
H	-2.87115600	2.47685300	-0.18993900
H	-1.04478100	3.00306800	1.28341700
Si	1.40167500	-2.14299000	0.07747600
H	0.26054000	-3.05403700	-0.19418300

H	2.45795100	-2.40845200	-0.94454400
H	1.98452200	-2.50161500	1.39855700
C	1.77776200	0.77879600	0.02042200
O	1.41670700	1.94302200	0.21335400
N	3.10825800	0.50277800	-0.17776100
H	3.40949700	-0.36972900	-0.58188100
H	3.72136800	1.29799500	-0.27637400

Silene 7c

E_{abs} = -1753.08549 a.u.

0 1

Si	3.57432900	0.29075000	0.00000000
Si	1.35613900	-0.52389700	0.00000000
C	-1.32217700	-0.05456600	0.00000000
Si	0.92982700	-2.84204600	0.00000000
C	0.00000000	0.59176400	0.00000000
Si	0.25272200	2.44972300	0.00000000
H	-0.32607300	3.09626900	1.20584200
H	-0.32607300	3.09626900	-1.20584200
H	1.71826400	2.70223900	0.00000000
H	3.83425700	1.10477100	-1.21356700
H	4.47995100	-0.88668100	0.00000000
H	3.83425700	1.10477100	1.21356700
H	0.19942700	-3.22892300	1.22885500
H	2.25256900	-3.53125200	0.00000000
H	0.19942700	-3.22892300	-1.22885500
O	-1.51442300	-1.26330000	0.00000000
S	-2.72973900	1.07524100	0.00000000
C	-4.10014500	-0.12538500	0.00000000
H	-4.05169800	-0.75002900	0.89014300
H	-4.05169800	-0.75002900	-0.89014300
H	-5.01969600	0.45977800	0.00000000

Silene 7d

E_{abs} = -1354.86225 a.u.

0 1

Si	2.54788200	-1.57599300	-0.00040700
Si	0.87224800	0.09094200	0.00009500
C	-1.77282100	0.78764700	0.00022500
Si	1.42376700	2.37984500	-0.00027100
C	-0.82520700	-0.35276200	0.00037000
Si	-1.39323800	-2.13227400	0.00061000
H	-2.21126200	-2.45989400	-1.19942700
H	-2.21444200	-2.45817200	1.19892600
H	-0.20447700	-3.02455000	0.00278500
H	2.43854900	-2.42684100	-1.21217900
H	2.44119400	-2.42486100	1.21299000

H	3.86741700	-0.89412900	-0.00239800
H	0.91692200	3.02799800	-1.23147800
H	2.91370800	2.47391000	-0.00240700
H	0.92057400	3.02752000	1.23268000
O	-1.39057000	1.95750600	0.00211300
C	-3.26185000	0.49485900	-0.00213500
H	-3.81819900	1.43109100	-0.00521100
H	-3.53922900	-0.09077700	0.88004800
H	-3.53614500	-0.09508400	-0.88236700

Ketene 8a

E_{abs} = -1430.16714 a.u.

0 1

Si	-0.60235600	-0.20780000	0.04313400
C	1.19344400	0.32024300	-0.19853500
Si	-1.17774300	-1.97102200	-1.41558300
H	-0.31060100	-3.15735700	-1.19550600
H	-2.59615700	-2.35944100	-1.19830200
H	-1.02092700	-1.51552600	-2.82328400
Si	-2.04272200	1.66193800	-0.23948300
H	-1.90561700	2.20519600	-1.61707300
H	-3.44838000	1.22073300	-0.03887600
H	-1.74213600	2.74948100	0.73042200
Si	2.64056900	-0.84006500	0.07940000
H	2.72836200	-1.22972800	1.50867100
H	2.46444900	-2.06753500	-0.73436400
H	3.89208000	-0.14836600	-0.31796400
C	1.46012900	1.54721700	-0.56136100
O	1.68834900	2.64011200	-0.88777800
O	-0.76449900	-0.89709900	1.55846200
C	-0.55322900	-0.25739300	2.81338000
H	-1.30766100	0.51612800	2.99623100
H	-0.63665700	-1.01793500	3.59089200
H	0.44189800	0.19713200	2.86822600

Ketene 8b

E_{abs} = -1370.97146 a.u.

0 1

Si	-0.63827300	-0.26063800	-0.29469200
C	1.15700000	0.19032900	0.13689000
Si	-1.78654600	1.69576800	-0.95147500
H	-1.31461300	2.12102700	-2.29863800
H	-3.25352500	1.46029800	-1.01707200
H	-1.51947100	2.79640700	0.01240600
Si	-1.61784600	-1.36429100	1.54869400
H	-1.40772700	-0.56821700	2.78719200
H	-3.07861100	-1.55887500	1.34611900

H	-0.98362300	-2.69952800	1.73147900
Si	2.56400300	-0.71856900	-0.69107000
H	2.44415500	-2.18104700	-0.46218500
H	2.56269100	-0.47472500	-2.15580400
H	3.84765200	-0.23782600	-0.11971500
C	1.45155300	1.11804800	1.00697600
O	1.70013900	1.94824700	1.78536100
N	-0.67081100	-1.36829500	-1.63048100
H	-0.57173700	-1.08005600	-2.59240200
H	-0.58068800	-2.36740800	-1.52447700

Ketene 8c

E_{abs} = -1753.13768 a.u.

0 1

Si	1.12589200	-0.61902200	2.43262000
Si	0.54127400	0.02841000	0.23453200
S	1.10496600	-1.67586900	-0.98766500
Si	1.74661200	1.97366800	-0.37875100
C	-1.31887300	0.31478700	0.09740000
C	-1.76666700	1.51707700	-0.15291900
Si	-2.57639600	-1.06541700	0.28769200
O	-2.15896600	2.58986200	-0.37372000
H	-2.24724800	-1.86638500	1.49088500
H	-2.57011000	-1.95509300	-0.89929600
H	-3.92335300	-0.45944900	0.43567800
H	0.70311900	0.45583100	3.36940900
H	2.59871700	-0.79050000	2.53397600
H	0.46001000	-1.88847600	2.82117100
H	1.32872400	3.13338400	0.45276800
H	1.53305800	2.31557600	-1.81015300
H	3.19131600	1.71103900	-0.15427800
C	0.61999100	-1.13850800	-2.68405300
H	1.23472200	-0.30591700	-3.02382700
H	-0.43444300	-0.86575000	-2.71722300
H	0.78771700	-1.99633100	-3.33458800

Ketene 8d

E_{abs} = -1354.90369 a.u.

0 1

Si	-1.66296300	-0.47008800	-1.94057100
Si	-0.64583600	0.42486400	-0.00081900
Si	-1.66297300	-0.46235500	1.94247500
C	-0.83028500	2.31199000	-0.00455100
C	1.19550800	-0.02137500	0.00007000
C	2.05500300	0.96268400	-0.00152500
Si	1.88332100	-1.76164300	0.00293800

O	2.81323100	1.84643600	-0.00293700
H	1.41858400	-2.49732800	1.20573900
H	3.36537500	-1.69365200	0.00388700
H	1.42033000	-2.50069200	-1.19847200
H	-3.10984400	-0.11049800	1.95414700
H	-1.02974300	0.10157100	3.16547800
H	-1.54543700	-1.94407700	1.98748800
H	-1.03131300	0.09071500	-3.16582400
H	-3.11033600	-0.12031600	-1.95244800
H	-1.54335400	-1.95178900	-1.98082800
H	-0.36758400	2.75556700	-0.89057600
H	-0.36760700	2.75908400	0.87971800
H	-1.88796700	2.58925800	-0.00510900

Silaoxetene 12

E_{abs} = -1823.50178 a.u.

0 1

Si	-0.76190500	-0.05795600	-0.21599300
C	0.98659700	0.09280900	0.40571600
Si	-1.92023100	1.97546700	-0.61803000
Si	-1.98333300	-2.01035200	0.36015800
Si	2.05975000	0.46027000	1.86452700
C	1.31520000	-0.23986800	-0.87883300
O	0.22673300	-0.43663100	-1.67356300
O	2.52786900	-0.38439500	-1.42192900
C	2.61475900	-0.74696100	-2.82065300
H	2.10473700	-1.70061900	-2.97525700
H	2.10390600	0.01123300	-3.41864900
C	-2.90809000	-1.71733600	1.99080600
H	-3.64033100	-0.90945500	1.90157500
H	-3.44997100	-2.62125500	2.28810900
H	-2.22424400	-1.46008400	2.80479900
C	-0.77832700	-3.45516300	0.56351500
H	-0.23512700	-3.64982200	-0.36510700
H	-0.03992700	-3.25296900	1.34292900
H	-1.31677100	-4.36940000	0.83488600
C	-3.23928700	-2.43112200	-0.99700100
H	-3.78337700	-3.34581800	-0.73861400
H	-3.97555400	-1.63457200	-1.13469000
H	-2.74478700	-2.59860900	-1.95781800
C	-3.45477400	1.69649600	-1.69706500
H	-3.94745500	2.65086500	-1.91079200
H	-3.19543400	1.23626600	-2.65464100
H	-4.18692200	1.05129200	-1.20287400
C	-2.45984700	2.72479400	1.03817200
H	-3.14247800	2.06587500	1.58253900
H	-1.60196100	2.92481100	1.68591200
H	-2.97923500	3.67456300	0.87290200
C	-0.73910000	3.16197700	-1.50071000
H	-1.21659500	4.13404900	-1.66211100
H	0.16947800	3.32378600	-0.91517700
H	-0.44088300	2.76660600	-2.47529700
C	3.03682700	2.06324200	1.61143400
H	3.69065700	2.27413700	2.46417800

H	3.66417000	1.99618500	0.71765800
H	2.36835500	2.91991500	1.48228200
C	0.95633600	0.65371900	3.39161500
H	0.39719800	-0.26428000	3.59880400
H	1.55183600	0.88339000	4.28068000
H	0.23135300	1.46373700	3.26422900
C	3.29352900	-0.94226800	2.17358100
H	3.91911300	-1.10871300	1.29198000
H	3.95420900	-0.71547700	3.01675500
H	2.77740100	-1.88138900	2.39439300
C	4.08641900	-0.83673300	-3.16940000
H	4.58384400	0.12116900	-3.00347800
H	4.58453400	-1.59422200	-2.56056100
H	4.20206100	-1.10851400	-4.22192700

Silene 20

E_{abs} = -1823.47969 a.u.

0 1

Si	0.90972600	0.13023100	0.05377700
C	-0.81757000	-0.20787300	0.17275200
Si	1.66118200	2.40783900	0.23693300
Si	2.51589200	-1.59244900	-0.40567800
Si	-1.69516400	-1.86502200	0.44902000
C	-1.67372200	0.98729900	0.05878400
O	-1.36715300	2.14737700	0.28342900
O	-2.92712600	0.68113600	-0.38728700
C	-3.83499300	1.79050900	-0.56670300
H	-3.95687400	2.30697000	0.38854400
H	-3.39094100	2.50020900	-1.26891000
C	3.15858700	-2.41243600	1.17621700
H	2.37454000	-2.92844700	1.73245600
H	3.93217300	-3.14580500	0.92389800
H	3.61127900	-1.67271600	1.84274300
C	3.99851400	-0.79678400	-1.27922100
H	3.70482300	-0.23086400	-2.16765000
H	4.56221600	-0.13019300	-0.62497600
H	4.67648100	-1.59214900	-1.60798500
C	1.83166400	-2.87224200	-1.62538300
H	2.60857800	-3.61518600	-1.83758700
H	0.95053600	-3.40508600	-1.26782000
H	1.56871500	-2.39255800	-2.57257000
C	3.56213000	2.43908000	0.20309900
H	3.89475100	3.46058200	0.41931100
H	4.00791500	1.78804100	0.96068100
H	3.97304500	2.16069400	-0.76966100
C	1.06127200	3.48777500	-1.19369700
H	1.40611700	3.10446500	-2.15822100
H	-0.02658100	3.54798200	-1.20587200
H	1.46432100	4.49983700	-1.07631900
C	1.14768000	3.09347800	1.92186500
H	1.52110700	4.11831000	2.02672500
H	0.06298300	3.10331300	2.01906700
H	1.57100600	2.50347300	2.74004900
C	-3.14885800	-1.64057400	1.64291700

H	-3.54505800	-2.61985400	1.93187200
H	-2.82936800	-1.13247400	2.55811200
H	-3.95880700	-1.06090800	1.20043900
C	-2.31462500	-2.62379600	-1.16818400
H	-1.49157800	-2.82631100	-1.85919200
H	-2.84013900	-3.56673600	-0.98487500
H	-3.00657600	-1.93942100	-1.66457100
C	-0.56665300	-3.10676900	1.33053200
H	-0.20654200	-2.69949600	2.27996900
H	-1.15151600	-4.00336000	1.56210500
H	0.29756800	-3.43013400	0.75118400
C	-5.14736200	1.23538500	-1.08415800
H	-5.00417800	0.71656400	-2.03465300
H	-5.58821600	0.53445700	-0.37192700
H	-5.85684300	2.05201400	-1.24316200

Silene dimer 21

E_{abs} = -3647.02002 a.u.

0 1

Si	1.03101700	1.77146300	0.25569100
C	2.03276800	0.31395300	-0.42381600
Si	0.79713300	3.72945200	-1.14628100
Si	1.76414900	2.34032900	2.46191700
Si	3.59476900	0.60099800	-1.46540800
C	1.66014900	-0.94151400	-0.08432300
O	0.57858800	-1.26917100	0.65172500
O	2.40061400	-2.04224900	-0.44397900
C	2.97292600	-2.77830100	0.66193600
H	3.63094000	-2.10170600	1.22029400
H	2.17435700	-3.10039100	1.33402900
Si	-1.76414900	-2.34032900	2.46191700
Si	-1.03101700	-1.77146300	0.25569100
C	-2.03276800	-0.31395300	-0.42381600
Si	-0.79713300	-3.72945200	-1.14628100
Si	-3.59476900	-0.60099800	-1.46540800
C	-1.66014900	0.94151400	-0.08432300
O	-0.57858800	1.26917100	0.65172500
O	-2.40061400	2.04224900	-0.44397900
C	-2.97292600	2.77830100	0.66193600
H	-3.63094000	2.10170600	1.22029400
H	-2.17435700	3.10039100	1.33402900
C	3.74931600	-3.95952800	0.11363300
H	4.17332100	-4.53429800	0.94172700
H	3.10144900	-4.62133500	-0.46398400
H	4.56592600	-3.62997400	-0.52989800
C	-3.74931600	3.95952800	0.11363300
H	-4.17332100	4.53429800	0.94172700
H	-3.10144900	4.62133500	-0.46398400
H	-4.56592600	3.62997400	-0.52989800
C	4.80028800	-0.84541900	-1.63416000
H	5.66747400	-0.49244600	-2.20392500
H	5.16677900	-1.19889900	-0.66729500
H	4.36326500	-1.69135800	-2.16436900
C	-4.80028800	0.84541900	-1.63416000

H	-5.66747400	0.49244600	-2.20392500
H	-5.16677900	1.19889900	-0.66729500
H	-4.36326500	1.69135800	-2.16436900
C	4.63916400	1.98043500	-0.69053400
H	5.08753600	1.62261900	0.24188300
H	5.46011100	2.24818500	-1.36384100
H	4.09175600	2.89513500	-0.46692200
C	-4.63916400	-1.98043500	-0.69053400
H	-5.08753600	-1.62261900	0.24188300
H	-5.46011100	-2.24818500	-1.36384100
H	-4.09175600	-2.89513500	-0.46692200
C	3.07666300	1.04880000	-3.23101300
H	2.57569800	0.19312200	-3.69423000
H	2.38987600	1.89476300	-3.28170600
H	3.95229100	1.29152000	-3.84204600
C	-3.07666300	-1.04880000	-3.23101300
H	-2.57569800	-0.19312200	-3.69423000
H	-2.38987600	-1.89476300	-3.28170600
H	-3.95229100	-1.29152000	-3.84204600
C	-0.27001200	3.39945000	-2.67727300
H	-0.35907000	4.31832500	-3.26739900
H	0.16590600	2.63283700	-3.32315200
H	-1.27263500	3.07406900	-2.39564600
C	0.27001200	-3.39945000	-2.67727300
H	0.35907000	-4.31832500	-3.26739900
H	-0.16590600	-2.63283700	-3.32315200
H	1.27263500	-3.07406900	-2.39564600
C	2.40725400	4.54783500	-1.73787400
H	2.12944000	5.45839300	-2.28103100
H	3.05115400	4.84998400	-0.90823100
H	2.99598800	3.92922200	-2.41601900
C	-2.40725400	-4.54783500	-1.73787400
H	-2.12944000	-5.45839300	-2.28103100
H	-3.05115400	-4.84998400	-0.90823100
H	-2.99598800	-3.92922200	-2.41601900
C	-0.02945200	5.06416900	-0.07426600
H	0.64354200	5.39987500	0.71981700
H	-0.26410600	5.93735500	-0.69269400
H	-0.95578000	4.73033300	0.39290900
C	0.02945200	-5.06416900	-0.07426600
H	-0.64354200	-5.39987500	0.71981700
H	0.26410600	-5.93735500	-0.69269400
H	0.95578000	-4.73033300	0.39290900
C	-3.14164400	-3.64594400	2.47393500
H	-2.82794200	-4.58094400	2.00134600
H	-3.41345600	-3.87928100	3.50911800
H	-4.04503000	-3.30051900	1.96646100
C	3.14164400	3.64594400	2.47393500
H	2.82794200	4.58094400	2.00134600
H	3.41345600	3.87928100	3.50911800
H	4.04503000	3.30051900	1.96646100
C	-0.29870400	-3.04038500	3.44332300
H	-0.60832000	-3.26946900	4.46872900
H	0.08167100	-3.96413100	2.99890600
H	0.52716400	-2.32673700	3.49283800
C	0.29870400	3.04038500	3.44332300
H	0.60832000	3.26946900	4.46872900
H	-0.08167100	3.96413100	2.99890600
H	-0.52716400	2.32673700	3.49283800
C	-2.40725400	-0.79368400	3.34825500
H	-2.67914200	-1.03108300	4.38229500

H	-1.65372100	-0.00259300	3.36932700
H	-3.29506400	-0.39434700	2.85092400
C	2.40725400	0.79368400	3.34825500
H	2.67914200	1.03108300	4.38229500
H	1.65372100	0.00259300	3.36932700
H	3.29506400	0.39434700	2.85092400

Silaoxetene 22a

E_{abs} = -1430.12932 a.u.

0 1

Si	0.15839100	0.87869300	0.00000000
C	-0.87036100	-0.65699000	0.00000000
Si	0.34141800	2.12506900	1.99640400
H	0.44171000	1.20454400	3.15756500
H	1.53511200	3.01164200	1.96121200
H	-0.87052000	2.97493500	2.14484800
Si	0.34141800	2.12506900	-1.99640400
H	-0.87052000	2.97493500	-2.14484800
H	1.53511200	3.01164200	-1.96121200
H	0.44171000	1.20454400	-3.15756500
Si	-2.58913300	-1.31346500	0.00000000
H	-2.88221100	-2.14539900	1.19967400
H	-3.53182300	-0.16229600	0.00000000
H	-2.88221100	-2.14539900	-1.19967400
C	0.34141800	-1.29380200	0.00000000
O	1.38829300	-0.42024800	0.00000000
O	0.60130600	-2.59578600	0.00000000
C	1.98043200	-3.01663100	0.00000000
H	2.49256000	-2.65393700	-0.89179600
H	2.49256000	-2.65393700	0.89179600
H	1.94348900	-4.10359000	0.00000000

Silaoxetene 22b

E_{abs} = -1370.95146 a.u.

0 1

Si	-0.70607800	-0.00149500	0.07498800
C	1.11016400	0.00056400	-0.26643500
Si	-1.94654300	-1.97164500	-0.32536200
H	-1.16329200	-3.16369300	0.08845800
H	-3.23927200	-1.94955400	0.41054900
H	-2.24124100	-2.06276400	-1.78159300
Si	-1.92118600	2.00086700	-0.23240200
H	-2.20612500	2.17204200	-1.68317600
H	-3.21806500	1.95870100	0.49529500
H	-1.12615700	3.16073800	0.24693600
Si	2.39484300	0.03946000	-1.57180400
H	2.16950800	1.14576000	-2.54223100
H	3.73379500	0.24742800	-0.94237200
H	2.46917700	-1.22032500	-2.36333900
C	1.22591200	-0.04169700	1.10602300
O	-0.00455900	-0.04777700	1.70649200
N	2.28861900	-0.11323500	1.94917900
H	3.20549700	0.08697100	1.58280500
H	2.12136200	0.10573000	2.91906100

Carbene 23a

E_{abs} = -1430.03915 a.u.

0 3

Si	0.03591200	-0.98008400	0.00000000
C	0.50578900	0.78609300	0.00000000
Si	0.98196000	-1.96693100	1.93483500
H	0.43852200	-1.32483500	3.15943600
H	0.64093100	-3.41454600	1.95759800
H	2.46017000	-1.82021700	1.91936700
Si	-2.32940600	-1.18232500	0.00000000
H	-2.89808500	-0.55251900	-1.21699300
H	-2.67458700	-2.63088000	0.00000000
H	-2.89808500	-0.55251900	1.21699300
Si	0.98196000	-1.96693100	-1.93483500
H	2.46017000	-1.82021700	-1.91936700
H	0.64093100	-3.41454600	-1.95759800
H	0.43852200	-1.32483500	-3.15943600
C	0.00883700	2.13191600	0.00000000
O	-1.18442400	2.39944500	0.00000000
O	0.98196000	3.06842000	0.00000000
C	0.53602300	4.43759300	0.00000000
H	-0.06138500	4.64514100	-0.88918600
H	-0.06138500	4.64514100	0.88918600
H	1.44412100	5.03609800	0.00000000

Carbene 23b

E_{abs} = -1370.85624 a.u.

0 3

Si	0.58848900	-0.03100600	-0.00012000
C	-1.11431900	-0.70713100	-0.00095100
Si	1.68227200	-0.85536000	1.93200300
H	1.69914900	-2.34190200	1.92154800
H	3.08574500	-0.36287400	1.95586300
H	0.98856700	-0.38876300	3.16055400
Si	0.51022400	2.34048900	-0.00352900
H	-0.17369700	2.83511200	1.21567500
H	1.91184900	2.84650800	-0.00524100
H	-0.17533500	2.83144000	-1.22330700
Si	1.68621000	-0.86094100	-1.92757400
H	3.09035200	-0.37025500	-1.94887400
H	1.70118700	-2.34747200	-1.91382500
H	0.99632200	-0.39617400	-3.15896900
C	-2.49791600	-0.28488900	-0.00048300
O	-2.76906100	0.91932000	0.00063100
N	-3.45713400	-1.25639900	-0.00177800
H	-3.21081100	-2.23207400	0.00051900
H	-4.42821900	-0.98574200	0.00113700

Silene 24a

E_{abs} = -1430.06499 a.u.

0 3

Si	-0.93917200	-0.65258000	0.00040500
C	0.50858200	0.53200300	-0.00049900
Si	-2.20510500	-0.46962800	-1.98349800
H	-1.37524700	-0.89744500	-3.13942500
H	-3.38042400	-1.37212400	-1.86726100
H	-2.68563100	0.91704800	-2.23679200
Si	-2.20486900	-0.46685300	1.98419700
H	-2.68524900	0.92020700	2.23565200
H	-3.38026900	-1.36941200	1.86929500
H	-1.37492600	-0.89317300	3.14061300
Si	0.33128700	2.40954600	-0.00143100
H	0.95536900	2.98707700	-1.21813200
H	-1.11726900	2.73736800	-0.00174400
H	0.95503700	2.98815000	1.21493600
C	1.89573300	0.05605000	-0.00028100
O	2.87337500	0.78438100	-0.00029500
O	1.99672100	-1.29844500	0.00052200
C	3.33211900	-1.83267800	0.00109700
H	3.87393700	-1.50566700	-0.88775000
H	3.87354700	-1.50471100	0.88982900
H	3.21178500	-2.91384700	0.00165400

Silene 24b

E=-1370.87905226 a.u.

0 3

Si	-0.87796600	-0.03704800	-0.53999400
C	0.87837300	0.00276600	0.09295800
Si	-2.03932100	-1.99213400	0.08514600
H	-2.08766700	-2.17055700	1.56170600
H	-3.42732300	-1.89421000	-0.43724900
H	-1.37307400	-3.17575800	-0.51662500
Si	-2.02977400	1.99054800	-0.18777100
H	-1.34084900	3.08387100	-0.92021200
H	-3.40967900	1.83887300	-0.71850400
H	-2.10226900	2.35220300	1.25395400
Si	1.27639100	0.14796300	1.93444500
H	-0.01840200	0.17980700	2.66745500
H	2.05211000	-1.02585500	2.40337100
H	2.00417200	1.40890200	2.21865600
C	2.10023000	-0.06027400	-0.74349500
O	3.21534300	0.00411500	-0.22560300
N	1.95228900	-0.19178300	-2.09779200
H	1.04835300	-0.24054300	-2.53941300
H	2.78362700	-0.23273300	-2.66612200

TS1

E_{abs} = -1430.02250 a.u.

0 1

Si	0.82612000	0.08266900	0.03070000
C	-0.84826000	-0.14830100	-0.66418500
Si	1.04260900	-0.05425200	2.38933800
H	0.39902400	-1.29790500	2.88366600
H	2.48567200	-0.07175700	2.75126400
H	0.40528000	1.12393600	3.03118300
Si	1.72388700	-1.86991500	-1.01481600
H	1.77965600	-1.68850500	-2.48501300
H	3.10343200	-2.02731000	-0.48206600
H	0.92300100	-3.06836000	-0.66980400
Si	1.83756100	1.98347300	-0.94117200
H	1.12376500	3.21462900	-0.51350700
H	3.25082900	2.07247900	-0.48657400
H	1.80165100	1.87900700	-2.42164500
C	-2.03497000	-0.68462700	-0.21479300
O	-2.71675500	-1.67069700	-0.23493400
O	-2.44225400	0.59811900	0.33649700
C	-3.54681500	1.21953100	-0.35233300
H	-3.26690800	1.44747200	-1.38379800
H	-4.40919100	0.55109300	-0.33366900
H	-3.76634300	2.13857900	0.18863400

TS2

E_{abs} = -1430.02845 a.u.

0 1

Si	-0.94852700	0.14940000	0.10039300
C	0.61345700	-0.40202500	0.81003100
Si	-1.00970500	2.03950700	-1.33966000
H	0.16149600	2.00863800	-2.25199900
H	-2.26124800	2.02934100	-2.14346700
H	-0.97470100	3.28918800	-0.53533600
Si	-2.69515600	-0.02709700	1.67874100
H	-2.48442300	0.93947100	2.78683300
H	-3.98446600	0.29106300	1.00873700
H	-2.74733700	-1.40713900	2.22225300
Si	-0.95604600	-1.86488600	-1.23382200
H	-0.57493400	-3.05506100	-0.44621000
H	-2.37266500	-1.99519500	-1.67650900
H	-0.07870000	-1.66170700	-2.40660100
C	1.93791900	-0.34759800	0.33485100
O	2.30069900	-1.16680700	-0.50947200
O	2.74026300	0.57270500	0.90603100
C	4.13204400	0.51747600	0.52920400
H	4.56097700	-0.45057000	0.79112000
H	4.24896900	0.68845100	-0.54151900
H	4.61089500	1.31228000	1.09657300

TS3

E_{abs} = -1430.09327 a.u.

0 1

Si	-0.76630100	0.14358500	0.07359100
C	0.91503200	0.68540200	0.21977800
Si	-2.37865500	1.55803900	-0.95271100
H	-1.80436200	2.89563800	-1.23536500
H	-2.77993100	0.90790300	-2.22929400
H	-3.58700100	1.68506600	-0.09475500
Si	-1.73539500	-1.65524700	1.25734500
H	-0.68639600	-2.47044800	1.91775700
H	-2.65850700	-1.09913900	2.28217100
H	-2.52498700	-2.51210800	0.33147400
Si	1.66807100	2.32683100	0.61742300
H	2.61833300	2.77777000	-0.43333100
H	0.56372400	3.32101900	0.72187400
H	2.39112900	2.32124200	1.91773400
C	1.67706100	-0.44835400	-0.18269500
O	2.83455300	-0.77341000	-0.17410200
O	0.67973200	-1.35076300	-0.80328100
C	1.05618000	-2.71998500	-1.03536200
H	2.03750800	-2.73804100	-1.50886300
H	1.09212800	-3.27947100	-0.09751400
H	0.30636300	-3.14334900	-1.70222500

TS4

E_{abs} = -1430.09864 a.u.

0 1

Si	-1.00819300	-0.13643900	0.01317300
C	0.50378900	0.78080400	0.18862600
Si	-2.95258600	0.94342600	-0.82214200
H	-3.22831500	0.38047700	-2.17123600
H	-4.12429900	0.66155800	0.04945700
H	-2.73838500	2.40740400	-0.93216600
Si	-1.36255300	-2.29316400	0.89728200
H	-2.54151300	-2.24679200	1.80699500
H	-1.66472300	-3.24471500	-0.20232200
H	-0.17249700	-2.73419800	1.66225900
Si	0.92923700	2.48857900	0.74845900
H	1.77201900	3.21072200	-0.24238100
H	-0.34152400	3.24364400	0.92773100
H	1.65143700	2.50720000	2.05043400
C	1.38942600	-0.23574200	-0.27000200
O	0.90328400	-1.26151600	-0.82733100
O	2.71147100	-0.08967500	-0.11559800
C	3.55317900	-1.10677500	-0.69177600
H	3.42157100	-2.05262000	-0.16517900
H	3.31667300	-1.24508800	-1.74748600
H	4.57048200	-0.74140100	-0.56856200

TS5

E_{abs} = -1370.83682 a.u.

0 1

Si	-0.59244800	-0.09035600	-0.02593700
C	0.99267900	0.08777800	-0.88972600
Si	-0.50297700	2.21191400	0.66054300
H	-0.00199600	3.08744700	-0.42259500
H	-1.90719700	2.58342500	0.98449400
H	0.33940000	2.32518800	1.87294900
Si	-0.65890800	-1.48281900	1.89446900
H	0.53065800	-1.22414500	2.74400800
H	-1.89487300	-1.21145900	2.67651500
H	-0.66786600	-2.91044200	1.47967000
Si	-2.37406500	-0.37788500	-1.54715500
H	-3.66126400	-0.38408800	-0.80164300
H	-2.38411400	0.73195600	-2.53372000
H	-2.23364600	-1.67317800	-2.26186800
C	2.32917700	0.00978100	-0.50465400
O	3.03033700	0.73001700	0.19057500
N	2.73385200	-1.21559800	-1.13192500
H	2.94740800	-1.15075800	-2.11767100
H	3.42026900	-1.74219300	-0.60186200

TS6

E_{abs} = -1370.84600 a.u.

0 1

Si	-0.61169000	0.12727000	-0.05042900
C	0.91505300	-0.54363200	-0.68955500
Si	-2.50531400	-0.59792400	-1.26310900
H	-2.31842600	-2.00238900	-1.70034100
H	-3.71124200	-0.49652800	-0.39852400
H	-2.69554900	0.28337400	-2.44377600
Si	-0.76926000	2.25835300	0.99138600
H	-0.85433500	3.32408600	-0.03988900
H	-1.99194700	2.31338700	1.83738500
H	0.42423900	2.48653500	1.84545300
Si	-0.13866600	-1.72344500	1.44587000
H	-0.77832400	-1.36235900	2.74309800
H	-0.74759800	-2.96536800	0.91816700
H	1.30128900	-1.94789600	1.72828600
C	2.22728200	-0.00707900	-0.71353700
O	2.37076500	0.71709700	-1.71459800
N	3.22817400	-0.26959200	0.17689600
H	3.14354700	-1.06011500	0.79614500
H	4.16002500	-0.01763500	-0.12099600

TS7

E_{abs} = -1370.90409 a.u.

0 1

Si	0.69876800	0.06039200	0.02855400
C	-1.06557800	0.21802400	-0.05566500
Si	2.02411400	1.96106200	0.57266200
H	1.17983500	3.16363100	0.77676100
H	2.75366200	1.65505300	1.83374300
H	3.03292300	2.21563500	-0.49070900
Si	1.96455400	-1.71340900	-0.87024600
H	2.76178800	-1.22618200	-2.02838500
H	2.90608300	-2.22863400	0.16003500
H	1.06009500	-2.80527300	-1.30821200
Si	-2.15797900	1.58424500	-0.67595400
H	-1.31383700	2.79068500	-0.89925100
H	-2.81039000	1.24352100	-1.96838700
H	-3.22104100	1.92293300	0.30626300
C	-1.58331300	-1.02892000	0.43341000
O	-2.66358500	-1.57382600	0.31971700
N	-0.49082100	-1.67689800	1.22659800
H	-0.51349800	-1.33874200	2.18529800
H	-0.61025200	-2.69041800	1.25221600

TS8

E_{abs} = -1370.91679 a.u.

0 1

Si	-0.74130500	0.05845000	-0.02153200
C	1.01752900	0.26957000	0.06647500
Si	-2.09840900	1.95335400	-0.48225300
H	-2.70447300	1.76690000	-1.82818400
H	-3.20048500	2.07376700	0.50968500
H	-1.28563600	3.19627200	-0.48417300
Si	-1.90888400	-1.85281400	0.70775900
H	-0.98108200	-2.78745800	1.38775500
H	-2.96732600	-1.43398000	1.67031000
H	-2.57094400	-2.51273900	-0.44562800
Si	2.10801200	1.66416800	0.58397000
H	1.30970700	2.70644000	1.27949100
H	3.16709300	1.18421000	1.52357500
H	2.82097100	2.30440800	-0.55692300
C	1.40473200	-1.00946100	-0.47077200
O	0.49901600	-1.68678600	-1.05041900
N	2.66963400	-1.50447400	-0.39425500
H	3.33162100	-1.12936200	0.26557500
H	2.83562300	-2.42772100	-0.76379500

TS9

E_{abs} = -1430.01013 a.u.

0 3

Si	1.20767500	-0.01340800	0.01116700
C	-0.56911100	-0.23696700	-0.04893200
Si	2.45486900	-1.62225800	-1.17983500
H	2.42236900	-1.33486200	-2.63855400
H	3.86281000	-1.58322400	-0.70735900
H	1.88144700	-2.96763300	-0.92928600
Si	1.96011000	2.22443200	0.12302800
H	1.13888400	2.95893300	1.11507700
H	3.38320400	2.22121300	0.55278100
H	1.85353400	2.87360400	-1.20865300
Si	-0.02268800	-0.91553600	1.97423900
H	-0.51380400	-2.30233400	1.77849400
H	1.07628300	-1.02971500	2.99996000
H	-1.02377500	-0.03110700	2.62501000
C	-1.86559000	0.28912900	-0.39312800
O	-2.05473400	1.45220000	-0.70761100
O	-2.85593800	-0.62813900	-0.30133200
C	-4.17808000	-0.15992700	-0.62596600
H	-4.47935000	0.63815300	0.05425500
H	-4.21252400	0.21156300	-1.65134900
H	-4.82654400	-1.02571800	-0.51107100

TS10

E_{abs} = -1370.82631 a.u.

0 3

Si	-0.83484000	-0.00188000	0.04479200
C	0.90826500	-0.34117100	-0.22018900
Si	-2.32185200	-1.50588700	-0.99690000
H	-1.80945300	-2.89013300	-0.83540900
H	-3.65687400	-1.39432600	-0.35468600
H	-2.45350800	-1.20153700	-2.44702200
Si	-1.41693700	2.27758500	0.26377100
H	-1.38187200	2.94811400	-1.06077700
H	-2.79684200	2.35743400	0.81288800
H	-0.46941800	2.93137300	1.19698600
Si	0.56488800	-0.97423700	1.85122100
H	-0.42782400	-1.13856300	2.97445400
H	1.06200400	-2.35741500	1.61376700
H	1.61336900	-0.08597900	2.41544400
C	2.17409200	0.19955400	-0.69345200
O	2.28555800	1.40654100	-0.90450000
N	3.21507300	-0.67349800	-0.84286400
H	3.07649500	-1.66646300	-0.75329500
H	4.08217200	-0.32877500	-1.22483800

Transition state structures

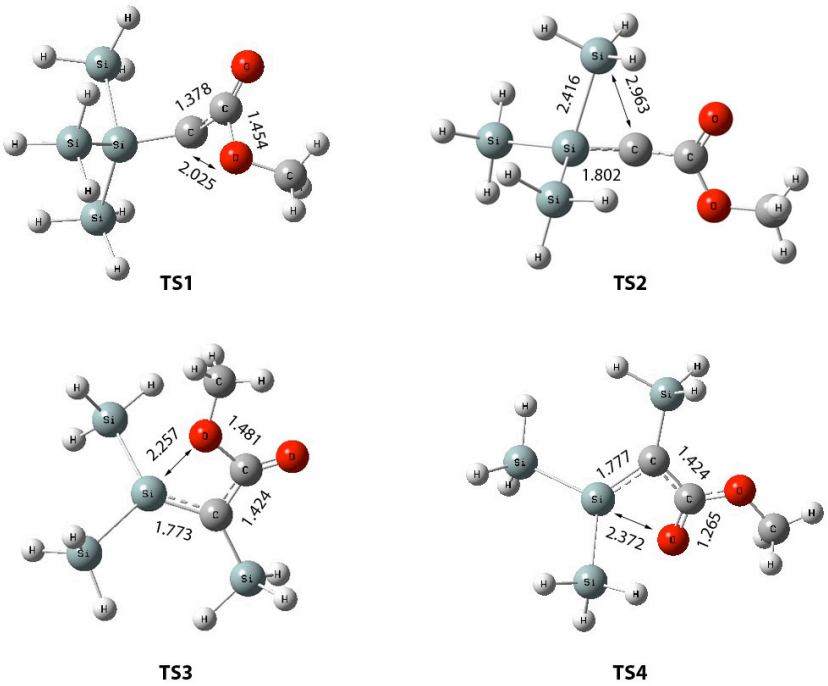


Figure. 1 Calculated transition state structures (B3LYP/ 6-311+G(d,p)) for the transformation of model carbene **6a** to silylketene **5a**, silaoxetene **19a** and silylketene **8a**.

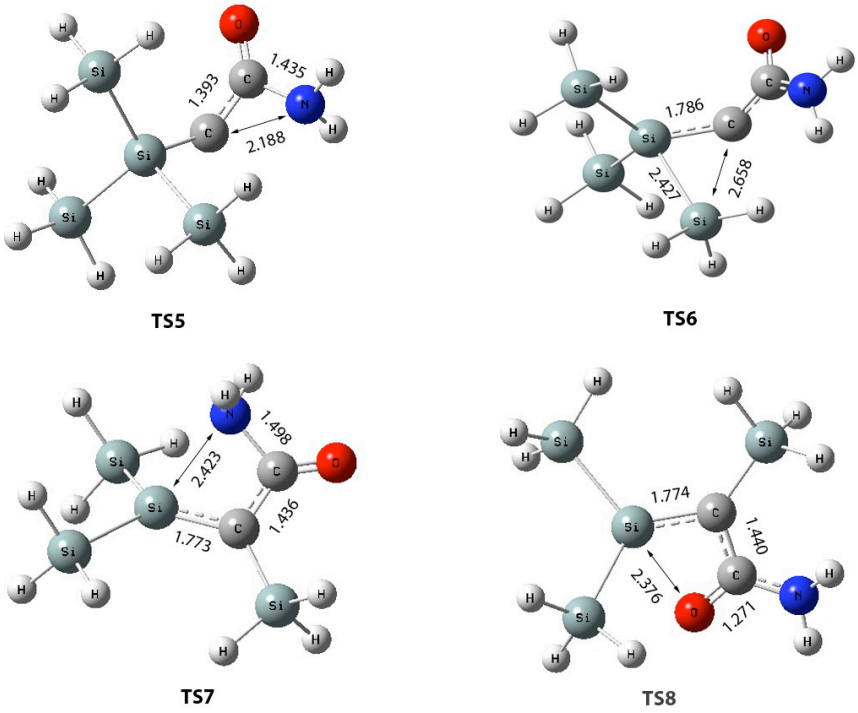


Figure. 2 Calculated transition state structures (B3LYP/ 6-311+G(d,p)) for the transformation of model carbene **6b** to silylketene **5b**, silaoxetene **19b** and silylketene **8b**.

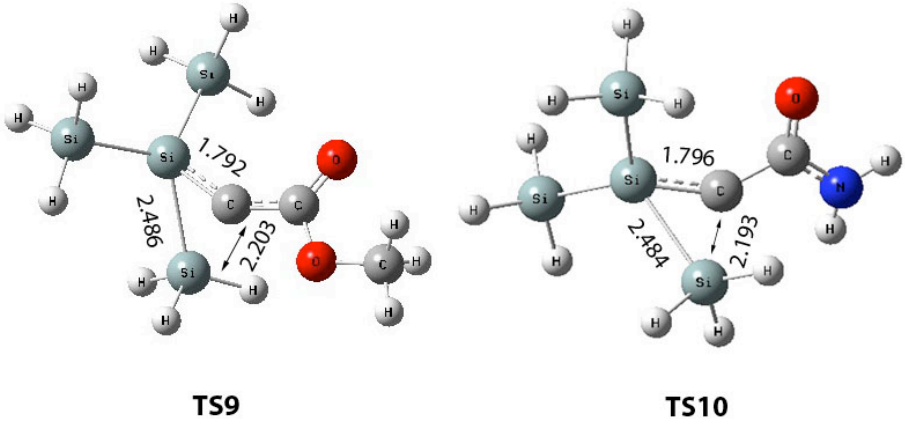


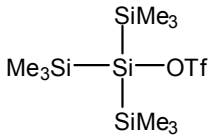
Figure. 3 Calculated transition state structures (B3LYP/ 6-311+G(d,p)) for the transformation of model triplet carbene **20a** to triplet silene **20b**.

Experimental Procedures

General Procedures

All reactions were carried out under an argon atmosphere unless otherwise stated. Commercially available solvents and reagents were used without further purification, apart from the following: 40-60 pet. ether was redistilled before use and refers to the fraction of light petroleum ether boiling in the range 40-60 ^{o}C. Analytical thin layer chromatography (TLC) was performed using commercially available aluminium backed plates coated with silica gel 60 F_{254} (UV_{254}) or aluminiumoxide N (UV_{254}), and visualised under ultra-violet light (at 254 nm), or through staining with ethanolic phosphomolybdic acid followed by heating. Flash column chromatography was carried out using 200-400 mesh silica gel 40-63 μm or neutral aluminiumoxide. Melting points were determined either using Thermo Scientific 9100 or Gallenkamp melting point apparatus and are uncorrected. Gas-Chromatography mass spectra (EI) were taken using a Thermo-Finnigan Trace with a 25 cm column connected to a VG Mass Lab Trio 1000. Electrospray mass spectra (ES) were obtained on a Micromass LCT Mass Spectrometer. High resolution mass spectra were obtained using a Thermo-Finnigan LTQFT mass spectrometer or Xevo QToF mass spectrometer (Waters UK, Ltd) by Durham University Mass Spectrometry service, or performed by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR were recorded in $CDCl_3$ (unless otherwise stated) on Varian Mercury-200 (^{1}H), Varian Mercury-400 (^{1}H, ^{13}C, ^{19}F), Bruker Avance-400 (^{1}H, ^{13}C, ^{29}Si), Varian Inova-500 (^{1}H, ^{13}C, ^{29}Si) or Varian VNMRS-700 (^{1}H, ^{13}C, ^{29}Si) and reported as follows: chemical shift δ (ppm) (number of protons, multiplicity, coupling constant *J* (Hz), assignment). All ^{13}C spectra were proton decoupled. The chemical shifts are reported using the residual signal of $CHCl_3$ as the internal reference (δ_H = 7.27 ppm; δ_C = 77.0 ppm). All chemical shifts are quoted in parts per million relative to tetramethylsilane (δ_H = 0.00 ppm) and coupling constants are given in Hertz to the nearest 0.5 Hz. Assignment of spectra was carried out using COSY, NOESY, HSQC, and HMBC experiments. Infrared spectra were recorded as a solution in $CHCl_3$ on a Perkin-Elmer FT-IR 1600 spectrometer or using a Diamond ATR (attenuated total reflection) accessory (Golden Gate).

Tris(trimethylsilyl)silyl trifluoromethanesulfonate 9a



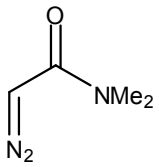
Method A[6]

Trifluoromethanesulfonic acid (1.38 ml, 15.6 mmol) was added dropwise (5 min) via syringe to a solution of phenyltris(trimethylsilyl)silane (5.05 g, 15.6 mmol) in dry dichloromethane (50.0 ml) at 0 °C. The reaction mixture was stirred for 20 min and then warmed to room temperature. The reaction mixture was stirred for a further 40 min after which time solvent was evaporated directly using a vacuum manifold to give the product as a colourless semi solid material (5.93 g, 99%). Product must be used immediately. IR (ATR) 2954, 2896, 1381, 1245, 1200, 1151, 951, 828, 691 cm^{-1}; δ_H (400MHz) 0.30 (27H, s, Si(C***H***$_3$)$_3$); δ_C (100MHz) 118.5 ((q, $^1J_{C\text{-}F}$ = 315.7Hz, ***C***F_3), -0.7 (Si(***C***H_3)$_3$); δ_F (376MHz) -76.9; δ_{Si} (139MHz) -11.7 (***Si***$(CH_3)_3$), -74.4 (***Si***-OTf).

Method B[7]

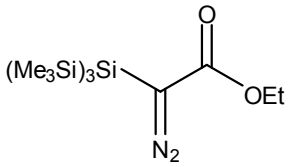
Trifluoromethanesulfonic acid (0.89 ml, 10.0 mmol) was added dropwise (4 min) via syringe to a solution of allyltris(trimethylsilyl)silane (4.14 g, 14.3 mmol) in dry dichloromethane (50.0 ml) at -78 °C. The reaction mixture was stirred for 40 min at room temperature after which time solvent was evaporated directly using a vacuum manifold. Distillation gave the title compound as a colourless semi solid material along with several inseparable components (2.38 g, 60%). B.p. 94-97 °C/0.6 mbar. Spectroscopic data for product **9** were consistent with data presented in *Method A*.

2-Diazo-N,N-dimethylacetamide[8] 10b



To a solution of 2-diazo-*N,N*-dimethyl-3-oxobutanamide (11.44 g, 73.8 mmol) in dry acetonitrile (80 ml) was added a solution of potassium hydroxide (8%, 80 ml) within 10 min. The mixture was stirred at room temperature for 16 h. After addition of water (80 ml) the mixture was extracted with ethyl acetate (3 x 80 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica (ethyl acetate) afforded the product as a yellow oil (6.26 g, 75%). R_f 0.2 (ethyl acetate); IR (ATR) 3069, 2931, 2092, 1604, 1487, 1450, 1393, 1261, 1175, 1127, 1060, 863, 723, 631 cm^{-1}; δ_H (700MHz) 4.96 (1H, s, 2-***H***), 2.91 (6H, s, $N(C\boldsymbol{H}_3)_2$); δ_C (175MHz) 165.8 (***C***O), 46.1($\boldsymbol{C}N_2$), 36.2 ($N(\boldsymbol{C}H_3)_2$); m/z (EI) 113 ($[M]^{+\cdot}$, 25%), 72 (38), 70 (21), 44 (20), 42 (100), 28 (20).

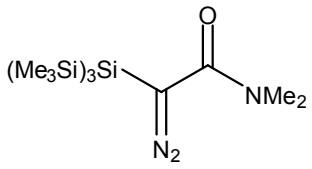
Ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate[9] 11a



Ethyldiisopropylamine (2.94 ml, 16.9 mmol) followed by tris(trimethylsilyl)silyl trifluoromethanesulfonate (5.83 g, 15.3 mmol) in diethyl ether (50 ml) were added at -78°C to a solution of ethyl 2-diazoacetate (1.61 g, 15.3 mmol) in diethyl ether (50 ml). The reaction mixture was allowed to warm up to room temperature, and stirred for 24 h. The reaction was then quenched by addition of a saturated $NaHCO_3$ solution (70 ml). The aqueous layer was separated and extracted with Et_2O (3 x 50 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a yellow oil (4.6 g, 84%). R_f 0.7 (pet.

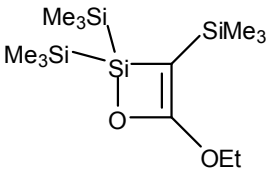
ether : diethyl ether 9:1); IR (ATR) 2949, 2893, 2071, 1682, 1395, 1365, 1241, 1197, 1096, 1063, 825, 739 cm^{-1}; δ_H (500MHz) 4.20 (2H, q, J = 7.0Hz, C***H***$_2$CH$_3$), 1.28 (3H, t, J = 7.0Hz, CH$_2$C***H***$_3$), 0.23 (27H, s, Si(C***H***$_3$)$_3$); δ_C (125MHz) 170.2 (***C***O), 60.9 (***C***H$_2$CH$_3$), 38.5 (***C***-2), 14.7 (CH$_2$***C***H$_3$), 1.0 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) -11.34, -80.2; m/z (EI) 332 ([M-N$_2$]$^{+\cdot}$, 0.1%), 215 (54), 117 (24), 73 (100), 45 ([EtO]$^{+\cdot}$, 34); HRMS (ASAP) found [M+H]$^{+\cdot}$ 361.1626, $C_{13}H_{33}O_2N_2Si_4$ requires [M+H]$^{+\cdot}$ 361.1619.

2-Diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*,*N*-dimethylacetamide[9] 11b



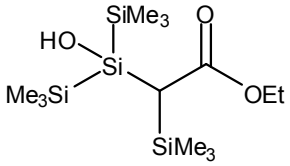
Ethyldiisopropylamine (2.99 ml, 17.1 mmol) followed by tris(trimethylsilyl)silyl trifluoromethanesulfonate (5.93 g, 15.6 mmol) in diethyl ether (50 ml) were added at -78^{o}C to a solution of 2-diazo-*N*,*N*-dimethylacetamide (1.76 g, 15.6 mmol) in diethyl ether (50 ml). The reaction mixture was allowed to warm up to room temperature, and stirred for 24 h. The reaction was then quenched by addition of a saturated $NaHCO_3$ solution (70 ml). The aqueous layer was separated and extracted with Et_2O (3 x 50 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in pet. ether, afforded the product as a yellow semi solid material (4.58 g, 82%). R_f 0.2 (pet. ether : diethyl ether 95:5); IR (ATR) 2949, 2893, 2040, 1617, 1369, 1243, 1167, 827, 745, 685 cm^{-1}; δ_H (700MHz) 2.99 (6H, s, N(C***H***$_3$)$_2$), 0.24 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175MHz) 168.9 (***C***O), 37.7 (N(***C***H$_3$)$_2$), 1.0 (Si(***C***H$_3$)$_3$); δ_{Si} (139MHz) -11.1, -75.7; m/z (EI) 217 (19%), 173 (37), 143 (12), 131 (21), 117 (23), 73 (100), 45 (14); HRMS (ASAP) found [M+H]$^{+\cdot}$ 360.1785, $C_{13}H_{34}ON_3Si_4$ requires [M+H]$^{+\cdot}$ 360.1779.

4-Ethoxy-2,2,3-tris(trimethylsilyl)-2H-1,2-oxasilete 12



To a solution of $Rh_2(pfb)_4$ (0.7 mg, 0.0007 mmol) in d_8-toluene (0.5 ml) was added dropwise (1 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.15 mg, 0.034 mmol) in d_8-toluene (0.5 ml). NMR spectroscopy indicated the formation of the intermediate product. δ_H (C_7D_8, -80 ^oC, 500MHz) 4.02 (2H, q, J = 7.2Hz, C***H***$_2$CH$_3$), 1.04 (1H, t, J = 7.2Hz, CH$_2$C***H***$_3$), 0.32 (9H, s, Si(C***H***$_3$)$_3$), 0.23 (18H, s, Si(C***H***$_3$)$_3$); δ_C (C_7D_8, -80 ^oC, 125MHz) 161.1 (***C***-4), 67.0 (***C***-3), 62.8 (***C***H$_2$CH$_3$), 15.0 (CH$_2$***C***H$_3$), 1.4 (Si(***C***H$_3$)$_3$), -2.1 (Si(***C***H$_3$)$_3$); δ_{Si} (C_7D_8, -80 ^oC, 99MHz) 35.6, -15.3, -17.1.

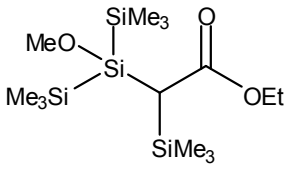
Ethyl 2-(2-hydroxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)acetate 13a



To a solution of $Rh_2(pfb)_4$ (23.3 mg, 0.022 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.16 g, 0.44 mmol) in toluene (10.0 ml). The solution was stirred for 1 h at room temperature after which time water (10 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 5 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 50% diethyl ether in hexane, afforded the silylalcohol as a white solid (89.6 mg, 58%). Mp: 57.1–58.5 ^oC; R_f 0.4 (pet. ether : diethyl ether 6:4); IR (ATR) 3340, 2953, 2895, 1655, 1365, 1243, 1182, 1039, 963, 831, 743 cm^{-1}; δ_H (700MHz) 4.08 (2H, q, J = 7.0Hz, C***H***$_2$CH$_3$), 2.06 (1H, s, 2-***H***), 1.26 (3H, t, J = 7.0Hz, CH$_2$C***H***$_3$), 0.19 (18H, s,

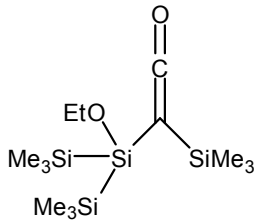
Si(C***H***$_3$)$_3$), 0.17 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175MHz) 174.5 (***C***O), 60.2 (***C***H$_2$CH$_3$), 31.0 (**C**-2), 14.5 (CH$_2$***C***H$_3$), 0.1 (Si(***C***H$_3$)$_3$), -1.0 (Si(***C***H$_3$)$_3$), -1.3 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 9.0, 3.8, -18.1, -18.2; m/z (ES+) 373 ([M+Na]$^{+\cdot}$, 100%), 360 (42), 338 (17), 301 (20), 219 (16); Anal. Calcd for $C_{13}H_{34}O_3Si_4$: C, 44.52; H, 9.77. Found: C, 44.43; H, 9.70.

Ethyl 2-(1-methoxy-1,2,2,2-tetramethyldisilyl)-2-(trimethylsilyl)acetate 13b



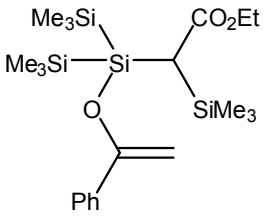
To a solution of $Rh_2(pfb)_4$ (23.3 mg, 0.022 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.16 g, 0.44 mmol) in toluene (10.0 ml). The reaction mixture was stirred for 1 h at room temperature. Dry methanol (0.5 ml) was added and the reaction mixture was stirred for 5 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the product as a colourless oil (0.07 g, 43%). R_f 0.4 (hexane : diethyl ether 95:5); IR (ATR) 2950, 2897, 1696, 1244, 1163, 1107, 1083, 1039, 827, 761, 721 cm^{-1}; δ_H (700MHz) 4.09 (1H, dq, *J* = 7.0Hz, *J* = 11.2Hz, C***H***$_2$CH$_3$), 4.02 (1H, dq, *J* = 7.0Hz, *J* = 11.2Hz, C***H***$_2$CH$_3$), 3.45 (3H, s, OC***H***$_3$), 2.23 (1H, s, 2-***H***), 1.24 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.21 (9H, s, Si(C***H***$_3$)$_3$), 0.19 (9H, s, Si(C***H***$_3$)$_3$), 0.17 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175MHz) 173.7 (***C***O), 60.0 (***C***H$_2$CH$_3$), 53.7 (O***C***H$_3$), 30.4 (***C***-2), 14.5 (CH$_2$***C***H$_3$), -0.08 (Si(***C***H$_3$)$_3$), -0.12 (Si(***C***H$_3$)$_3$), -0.7 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 13.3, 4.1, -18.0, -18.5; m/z (ES+) 365 ([M+H]$^{+\cdot}$, 10%), 333 (100), 319 (27), 263 (10), 219 (17); HRMS (ES+) found [M+H]$^{+\cdot}$ 365.1812, $C_{14}H_{37}O_3Si_4$ requires [M+ H]$^{+\cdot}$ 365.1814.

2-(2-Ethoxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)ethenone 14



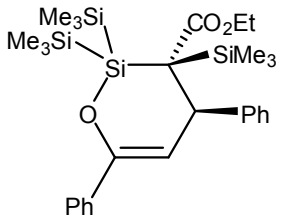
To a solution of $Rh_2(pfb)_4$ (23.0 mg, 0.022 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.16 g, 0.44 mmol) in toluene (10.0 ml). The reaction mixture was stirred for 48 h at room temperature. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a colourless oil (29.9 mg, 21%). R_f 0.7 (hexane : diethyl ether 95:5); IR (ATR) 2954, 2895, 2069, 1387, 1245, 1101, 1074, 939, 893, 830, 755, 731 cm^{-1}; δ_H (C_7D_8, 700MHz) 3.56 (2H, q, J = 7.0Hz, C***H***$_2$CH$_3$), 1.09 (3H, t, J = 7.0Hz, CH$_2$C***H***$_3$), 0.26 (9H, s, Si(C***H***$_3$)$_3$), 0.25 (18H, s, Si(C***H***$_3$)$_3$); δ_C (C_7D_8, 175MHz) 165.6 (***C***O), 61.4 (***C***H$_2$CH$_3$), 18.7 (CH$_2$***C***H$_3$), 1.6 (Si(***C***H$_3$)$_3$), 0.2 (***C***CO), -0.7 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 6.6, 5.7, -18.3; m/z (EI) 332 ($[M]^{+\cdot}$, 9%), 317 ($[M\text{-}CH_3]^{+\cdot}$, 49), 303 ($[M\text{-}CH_2CH_3]^{+\cdot}$, 49), 273 (30), 259 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 25), 215 (83), 199 (39), 191 (38), 155 (39), 147 (54), 131 (29), 117 (56), 99 (19), 97 (36), 83 (36), 73 (100), 59 (37), 45 (38); HRMS (EI) found $[M]^{+\cdot}$ 332.1478, $C_{13}H_{32}O_2Si_4$ requires $[M]^{+\cdot}$ 332.1474.

Ethyl 2-(1,1,1,3,3,3-hexamethyl-2-(1-phenylvinyloxy)trisilan-2-yl)-2-(trimethylsilyl)acetate 15



To a solution of $Rh_2(pfb)_4$ (58.7 mg, 0.056 mmol) in toluene (30.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.40 g, 1.11 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, acetophenone (0.16 ml, 1.33 mmol) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a colourless oil (0.12 g, 25%). R_f 0.6 (Al_2O_3 pH=7, hexane : diethyl ether 9:1); IR (ATR) 2953, 2896, 1694, 1314, 1300, 1285, 1244, 1158, 1105, 1075, 1027, 1003, 829, 771 cm^{-1}; δ_H (700MHz) 7.59-7.58 (2H, m, Ar-2,6-***H***), 7.34-7.32 (2H, m, Ar-3,5-***H***), 7.30-7.27 (1H, m, Ar-4-***H***), 4.88 (1H, d, J = 2.8Hz, CC***H***$_2$), 4.40 (1H, d, J = 2.8Hz, CC***H***$_2$), 4.13 (1H, dq, J = 11.2Hz, J = 7.0Hz, C***H***$_2$CH$_3$), 4.06 (1H, dq, J = 11.2Hz, J = 7.0Hz, C***H***$_2$CH$_3$), 2.50 (1H, s, 2-***H***), 1.26 (3H, t, J = 7.0Hz, CH$_2$C***H***$_3$), 0.27 (9H, s, Si(C***H***$_3$)$_3$), 0.192 (9H, s, Si(C***H***$_3$)$_3$), 0.190 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175MHz) 173.4 (***C***O), 157.8 (SiO***C***), 137.5 (Ar-***C***-1), 128.2 (Ar-***C***-4), 128.0 (Ar-***C***-3,5), 125.3 (Ar-***C***-2,6), 90.0 (C***C***H$_2$), 60.2 (***C***H$_2$CH$_3$), 29.6 (***C***-2), 14.5 (CH$_2$***C***H$_3$), 0.1 (Si(***C***H$_3$)$_3$), -0.1 (Si(***C***H$_3$)$_3$), -0.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 8.6, 4.3, -16.3, -16.7; m/z (ASAP) 451 ([M-H]$^{+\cdot}$, 7%); HRMS (ASAP) found [M+H]$^{+\cdot}$ 453.2153, $C_{21}H_{41}O_3Si_4$ requires [M+H]$^{+\cdot}$ 453.2133.

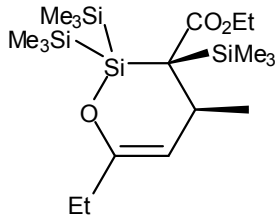
(3SR,4RS)-Ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 16



To a solution of $Rh_2(pfb)_4$ (25.3 mg, 0.024 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.17 g, 0.48 mmol) in toluene (10.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of *trans*-chalcone (0.12 ml, 0.57 mmol) in toluene (2.0 ml) was added and the reaction mixture was stirred for 1 h. Concentration,

followed by flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a white solid (0.13 g, 51%). Mp: 100.7–101.3 ^{o}C; R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2949, 2891, 1696, 1491, 1447, 1332, 1291, 1244, 1165, 1107, 1033, 832, 786, 753 cm^{-1}; δ_H (700MHz) 7.74-7.73 (2H, m, 4-Ar-2,6-***H***), 7.62-7.61 (2H, m, 6-Ar-2,6-***H***), 7.35-7.33 (2H, m, 6-Ar-3,5-***H***), 7.31-7.29 (3H, m, 4-Ar-3,5-***H***, 6-Ar-4-***H***,), 7.25-7.23 (1H, m, 4-Ar-4-***H***), 5.50 (1H, d, *J* = 2.8Hz, 4-***H***), 4.91 (1H, d, *J* = 2.8Hz, 5-***H***), 4.37 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.06 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.33 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.40 (9H, s, Si(C***H***$_3$)$_3$), 0.16 (9H, s, Si(C***H***$_3$)$_3$), -0.18 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (175MHz) 176.1 (***C***O), 152.1 (***C***-6), 145.0 (4-Ar-***C***-1), 137.4 (6-Ar-***C***-1), 131.2 (4-Ar-***C***-2,6), 128.1 (6-Ar-***C***-3,5), 127.8 (4-Ar-***C***-3,5), 127.7 (6-Ar-***C***-4), 126.8 (4-Ar-***C***-4), 124.5 (6-Ar-***C***-3,5), 106.3 (***C***-5), 61.0 (***C***H$_2$CH$_3$), 44.5 (***C***-4), 37.2 (***C***-3), 14.8 (CH$_2$***C***H$_3$), 0.8 (Si(***C***H$_3$)$_3$), 0.7 (CSi(***C***H$_3$)$_3$), 0.3 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 4.7, 3.1, -13.2, -14.3; m/z (ASAP) 541 ([M+H]$^{+\cdot}$, 11%); Anal. Calcd for $C_{28}H_{44}O_3Si_4$: C, 62.16; H, 8.20. Found: C, 62.04; H, 8.20.

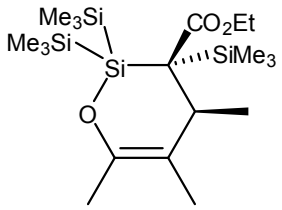
(3*SR*,4*SR*)-Ethyl 6-ethyl-4-methyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 22



To a solution of $Rh_2(pfb)_4$ (59.0 mg, 0.056 mmol) in toluene (30.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.41 g, 1.12 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of (*E*)-hex-4-en-3-one (0.15 ml, 1.35 mmol) in toluene (2.0 ml) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a white semisolid (0.24 g, 47%). R_f 0.6 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2958, 2896, 1707, 1660, 1458, 1369,

1329, 1243, 1161, 1041, 1000, 948, 906, 829, 745 cm^{-1}; δ_H (700MHz) 4.27 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, OC***H***$_2$CH$_3$), 4.12 (1H, s, 5-***H***), 3.98 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, OC***H***$_2$CH$_3$), 3.30 (1H, q, *J* = 7.0Hz, 4-***H***), 1.96 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.35 (3H, d, *J* = 7.0Hz, C***H***$_3$), 1.27 (3H, t, *J* = 7.0Hz, OCH$_2$C***H***$_3$), 0.99 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.29 (9H, s, Si(C***H***$_3$)$_3$), 0.21 (9H, s, CSi(C***H***$_3$)$_3$), -0.12 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175MHz) 175.5 (***C***O), 153.8 (***C***-6), 103.8 (***C***-5), 60.4 (O***C***H$_2$CH$_3$), 35.4 (***C***-3), 33.3 (***C***-4), 29.3 (***C***H$_2$CH$_3$), 23.5 (***C***H$_3$), 14.7 (OCH$_2$***C***H$_3$), 11.6 (CH$_2$***C***H$_3$), 2.1 (CSi(***C***H$_3$)$_3$), 0.4 (CSi(***C***H$_3$)$_3$), 0.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 4.6, 2.0, -14.89, -14.91; m/z (ASAP) 431 ($[M+H]^{+\cdot}$, 100%); HRMS (ASAP) found $[M+H]^{+\cdot}$ 431.2272, $C_{19}H_{43}O_3Si_4$ requires $[M+H]^{+\cdot}$ 431.2289.

(3*RS*,4*SR*)-Ethyl 4,5,6-trimethyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 23



To a solution of $Rh_2(pfb)_4$ (59.0 mg, 0.056 mmol) in toluene (30.0 ml) was added dropwise (10 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.40 g, 1.12 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of (*E*)-3-methylpent-3-en-2-one (0.15 ml, 1.34 mmol) in toluene (2.0 ml) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a white solid (0.27 g, 56%). Mp: 148.3–151.2 ^oC; R_f 0.6 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2958, 2902, 1697, 1440, 1384, 1230, 1175, 1040, 944, 829, 768, 744 cm^{-1}; δ_H (700MHz) 4.19 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.02 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 2.62 (1H, q, *J* = 7.0Hz, 4-***H***), 1.65 (3H, s, 6-C***H***$_3$), 1.61 (3H, s, 5-C***H***$_3$), 1.27 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 1.20 (3H, d, *J* = 7.0Hz, 4-C***H***$_3$), 0.26 (9H, s, Si(C***H***$_3$)$_3$), 0.17 (9H, s, Si(C***H***$_3$)$_3$), 0.12 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (175MHz) 174.9 (***C***O), 143.9 (***C***-6), 108.5 (***C***-5), 60.2

(***C***H_2CH_3), 38.0 (***C***-3), 37.4 (***C***-4), 20.1 (4-***C***H_3), 18.8 (6-***C***H_3), 18.7 (5-***C***H_3), 14.5 (CH_2***C***H_3), 1.1 (Si(***C***$H_3)_3$), 0.6 (Si(***C***$H_3)_3$), -0.3 (CSi(***C***$H_3)_3$); δ_{Si} (140MHz) 8.0, 1.0, -14.8, -17.8; m/z (ASAP) 431 ($[M+H]^{+\cdot}$, 100%); HRMS (ASAP) found $[M+H]^{+\cdot}$ 431.2274, $C_{19}H_{43}O_3Si_4$ requires $[M+H]^{+\cdot}$ 431.2289.

(3*SR*,4*RS*)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 24a and **(3RS,4RS)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 24b**

To a solution of $Rh_2(pfb)_4$ (59.8 mg, 0.057 mmol) in toluene (30.0 ml) was added dropwise (10 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.41 g, 1.13 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of (*E*)-4-phenylbut-3-en-2-one (0.20 g, 1.36 mmol) in toluene (5.0 ml) was added and the reaction mixture was stirred for 1 h to afford the title products as a 1:1 mixture of diastereoisomers. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product **24a** as a white solid (0.18 g, 34%) and product **24b** as a colourless oil (0.10 g, 18%).

Experimental data for compound **24a**:

Mp: 42.1–46.2 ^oC; R_f 0.7 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2986, 2949, 2890, 1694, 1493, 1376, 1325. 1288, 1248, 1174, 1159, 1092, 1041, 1005, 909, 829, 765 cm^{-1}; δ_H (500MHz) 7.68-7.67 (2H, m, Ar-2,6-***H***), 7.27-7.24 (2H, m, Ar-3,5-***H***), 7.22-7.18 (1H, m, Ar-4-***H***), 4.67 (1H, dd, *J* = 2.5Hz, *J* = 2.0Hz, 4-***H***), 4.52 (1H, d, *J* = 2.5Hz, 5-***H***), 4.34 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, C***H***$_2CH_3$), 4.01 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, C***H***$_2CH_3$), 1.82 (3H, d, *J* = 2.0Hz, C***H***$_3$), 1.29 (3H, t, *J* = 7.0Hz, CH_2C***H***$_3$), 0.31 (9H, s, Si(C***H***$_3)_3$), 0.20

(9H, s, Si(C***H***$_3$)$_3$), -0.20 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (125MHz) 176.1 (***C***O), 152.4 (***C***-6), 145.3 (Ar-***C***-1), 131.1 (Ar-***C***-2,6), 127.6 (Ar-***C***-3,5), 126.6 (Ar-***C***-4), 105.1 (***C***-5), 60.8 (***C***H$_2$CH$_3$), 44.1 (***C***-4), 36.8 (***C***-3), 22.8 (C***H***$_3$), 14.8 (CH$_2$***C***H$_3$), 0.72 (Si(***C***H$_3$)$_3$), 0.66 (CSi(***C***H$_3$)$_3$), 0.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 4.2, 1.7, -13.4, -14.9; m/z (ASAP) 479 ([M+H]$^{+\cdot}$, 18%); HRMS (ASAP) found [M+H]$^{+\cdot}$ 479.2284, $C_{23}H_{43}O_3Si_4$ requires [M+H]$^{+\cdot}$ 479.2289.

Experimental data for compound **24b**:

R_f 0.6 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2950, 2895, 1708, 1653, 1491, 1449, 1378, 1327, 1245, 1198, 1157, 1096, 1037, 1005, 979, 833, 743 cm^{-1}; δ_H (700MHz) 7.39-7.37 (2H, m, Ar-2,6-***H***), 7.24-7.22 (2H, m, Ar-3,5-***H***), 7.19-7.16 (1H, m, Ar-4-***H***), 4.50 (1H, d, *J* = 4.2Hz, 5-***H***), 4.21 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.01 (1H, d, *J* = 4.2Hz, 4-***H***), 3.97 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.78 (3H, s, C***H***$_3$), 1.25 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.32 (9H, s, Si(C***H***$_3$)$_3$), 0.07 (9H, s, Si(C***H***$_3$)$_3$), 0.06 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (175MHz) 174.3 (***C***O), 150.1 (***C***-6), 145.1 (Ar-***C***-1), 130.2 (Ar-***C***-2,6), 127.9 (Ar-***C***-3,5), 126.6 (Ar-***C***-4), 104.0 (***C***-5), 60.2 (***C***H$_2$CH$_3$), 43.5 (***C***-4), 38.3 (***C***-3), 22.2 (C***H***$_3$), 14.2 (CH$_2$***C***H$_3$), 0.9 (Si(***C***H$_3$)$_3$), 0.7 (CSi(***C***H$_3$)$_3$), 0.0 (Si(***C***H$_3$)$_3$); δ_{Si} (140MHz) 7.9, 3.7, -14.8, -15.7; m/z (ASAP) 479 ([M+H]$^{+\cdot}$, 8%); HRMS (ASAP) found [M+H]$^{+\cdot}$ 479.2297, $C_{23}H_{43}O_3Si_4$ requires [M+H]$^{+\cdot}$ 479.2289.

(2RS,3SR,4RS)-ethyl 2-methyl-4,6-diphenyl-2,3-bis(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 25

To a solution of $Rh_2(pfb)_4$ (17.5 mg, 0.0016 mmol) and *trans*-chalcone (82.6 mg, 0.397 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)acetate (0.10 g, 0.33 mmol) in toluene (10.0 ml). After addition, the reaction mixture was stirred for 30 min at room temperature. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a 2:1 mixture of diastereoisomers, albeit accompanied by significant amount of decomposition products. R_f 0.9 (pet. ether: diethyl ether 9:1); IR (ATR) 2962, 2900, 1702, 1498, 1450, 1328, 1249, 1173, 1107, 1040, 828, 780, 734 cm^{-1}. Further purification by preparative liquid chromatography enabled analytical samples of the major isomer to be obtained.

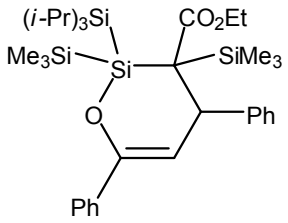
Experimental data for diastereoisomer A **25**

δ_H (700 MHz) 7.71-7.70 (2H, m, 4-Ar-2,6-*H*), 7.65-7.64 (2H, m, 6-Ar-2,6-*H*), 7.36-7.34 (2H, m, 6-Ar-3,5-*H*), 7.31-7.27 (3H, m, 4-Ar-3,5-*H*, 6-Ar-4-*H*,), 7.25-7.22 (1H, m, 4-Ar-4-*H*), 5.64 (1H, d, *J* = 3.2Hz, 5-*H*), 4.98 (1H, d, *J* = 3.2Hz, 4-*H*), 4.25 (1H, dq, *J* = 10.8Hz, *J* = 7.1Hz, C*H*$_2$CH$_3$), 4.15 (1H, dq, *J* = 10.8Hz, *J* = 7.1Hz, C*H*$_2$CH$_3$), 1.32 (3H, t, *J* = 7.1Hz, CH$_2$C*H*$_3$), 0.68 (3H, s, C*H*$_3$), 0.15 (9H, s, Si(C*H*$_3$)$_3$), -0.15 (9H, s, CSi(C*H*$_3$)$_3$); δ_C (175 MHz) 175.2 (*C*O), 150.7 (*C*-6), 144.9 (4-Ar-*C*-1), 137.2 (6-Ar-*C*-1), 130.7 (4-Ar-*C*-2,6), 128.1 (6-Ar-*C*-3,5), 127.9 (4-Ar-*C*-3,5), 127.8 (6-Ar-*C*-4), 126.8 (4-Ar-*C*-4), 124.7 (6-Ar-*C*-2,6), 106.9 (*C*-5), 60.7 (*C*H$_2$CH$_3$), 43.9 (*C*-4), 38.9 (*C*-3), 14.4 (CH$_2$*C*H$_3$), 1.6 (Si(*C*H$_3$)$_3$), 0.4 (*C*H$_3$), -1.0 (Si(*C*H$_3$)$_3$); δ_{Si} (140 MHz) -15.1, -17.5, -49.7; m/z (ES+) 483 ([M+H]$^{+\cdot}$, 100%);

Experimental data for diastereoisomer B

δ_H (700 MHz) 7.64-7.63 (2H, m, Ar-*H*), 7.51-7.50 (2H, m, Ar-*H*), 7.37-7.33 (2H, m, Ar-*H*), 7.31-7.27 (3H, m, Ar-*H*,), 7.18-7.16 (1H, m, Ar-*H*), 5.59 (1H, d, *J* = 7.1Hz, 5-*H*), 4.24 (1H, d, *J* = 7.1Hz, 4-*H*), 4.12 (1H, dq, *J* = 10.8Hz, *J* = 7.1Hz, C*H*$_2$CH$_3$), 3.96 (1H, dq, *J* = 10.8Hz, *J* = 7.1Hz, C*H*$_2$CH$_3$), 1.25 (3H, t, *J* = 7.1Hz, CH$_2$C*H*$_3$), 0.60 (3H, s, C*H*$_3$), 0.20 (9H, s, Si(C*H*$_3$)$_3$), -0.15 (9H, s, CSi(C*H*$_3$)$_3$); δ_C (175 MHz) 174.1 (*C*O), 152.4 (*C*-6), 144.8 (Ar-*C*), 137.5 (Ar-*C*), 130.9 (Ar-*C*), 128.1 (Ar-*C*), 127.8 (Ar-*C*), 127.7 (Ar-*C*), 126.7 (Ar-*C*), 124.8 (Ar-*C*), 105.8 (*C*-5), 60.3 (*C*H$_2$CH$_3$), 42.7 (*C*-4), 42.1 (*C*-3), 14.2 (CH$_2$*C*H$_3$), 0.3 (Si(*C*H$_3$)$_3$), -0.9 (*C*H$_3$), -1.2 (Si(*C*H$_3$)$_3$); m/z (ES+) 483 ([M+H]$^{+\cdot}$, 100%);

Ethyl 4,6-diphenyl-2-(triisopropylsilyl)-2,3-bis(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 26

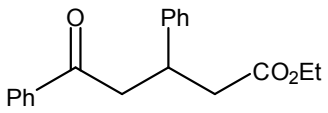


A solution of ethyl 2-diazo-2-(1,1,1-triisopropyl-3,3,3-trimethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.10 g, 0.227 mmol) and chalcone (0.094 g, 0.453 mmol) in toluene (3.0 ml) was stirred for 4 days at

110 °C. After that time, the solvent was evaporated in *vacuo* to yield the crude product which decomposed during purification.

^{1}H NMR (400 MHz) – characteristic peaks: 5.91 (1H, d, *J* = 9.2Hz, 4-***H***), 4.79 (1H, d, *J* = 9.2Hz, 5-***H***), 4.04 (1H, dq, *J* = 11.0Hz, *J* = 7.1Hz, C***H***$_2$CH$_3$), 3.88 (1H, dq, *J* = 11.0Hz, *J* = 7.1Hz, C***H***$_2$CH$_3$), 1.30 (3H, t, *J* = 7.1Hz, CH$_2$C***H***$_3$), 0.24 (18H, d, *J* = 8.4Hz, C***H***$_3$), 0.08 (9H, s, Si(C***H***$_3$)$_3$), -0.04 (9H, s, Si(C***H***$_3$)$_3$).

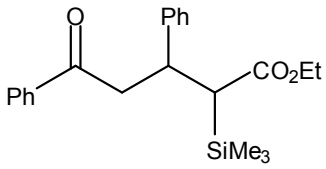
Ethyl 5-oxo-3,5-diphenylpentanoate[10] **27**



To a solution of methyl ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate (0.13 g, 0.24 mmol) in dry dichloromethane (4.0 ml) was added triethylamine trihydrofluoride complex (0.08 ml, 0.49 mmol). The mixture was stirred at room temperature for 3 days after which time saturated sodium bicarbonate solution (4.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 5 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 50% diethyl ether in hexane, afforded the product as a white solid (56.4 mg, 78%). Mp: 60.8-61.5 °C; R_f 0.4 (pet. ether : diethyl ether 1:1); IR (ATR) 3045, 2978, 1723, 1675, 1594, 1447, 1365, 1270, 1209, 1148, 1080, 1035, 984, 949, 852, 745 cm^{-1}; δ_H (700MHz) 7.92-7.91 (2H, m, 5-Ar-2,6-***H***), 7.55-7.53 (1H, m, 5-Ar-4-***H***), 7.44-7.42 (1H, m, 5-Ar-3,5-***H***), 7.29-7.26 (4H, m, 3-Ar-2,3,5,6-***H***), 7.20-7.18 (1H, m, 3-Ar-4-***H***), 4.04 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.02 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 3.88 (1H, dq, *J* = 7.7Hz, *J* = 7.0Hz, 3-***H***), 3.39 (1H, dd, *J* = 16.8Hz, *J* = 7.0Hz, 4-***H***), 3.34 (1H, dd, *J* = 16.8Hz, *J* = 7.0Hz, 4-***H***), 2.80 (1H, dd, *J* = 15.4Hz, *J* = 7.0Hz, 2-***H***), 2.68 (1H, dd, *J* = 15.4Hz, *J* = 7.7Hz, 2-***H***), 1.33 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$); δ_C (175MHz) 198.2 (***C***-5), 171.8 (***C***-1), 143.3 (3-Ar-***C***-1), 136.9 (5-Ar-***C***-1), 133.1 (5-Ar-***C***-4),

128.57 (5-Ar-***C***-3,5), 128.56 (3-Ar-***C***-3,5), 128.1 (5-Ar-***C***-2,6), 127.4 (3-Ar-***C***-2,6), 126.8 (3-Ar-***C***-4), 60.4 (***C***H_2CH_3), 44.6 (***C***-4), 40.8 (***C***-2), 37.6 (***C***-3), 14.1 (CH_2***C***H_3); m/z (EI) 296 ($[M]^{+\cdot}$, 14%), 251 ($[M\text{-}OEt]^{+\cdot}$, 14), 222 (35), 209 (53), 194 (16), 131 (47), 105 (100), 91 (16), 77 (58), 51 (20), 29 (22).

Ethyl 5-oxo-3,5-diphenyl-2-(trimethylsilyl)pentanoate[11] **28**

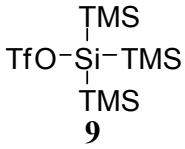


To a solution of methyl ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate (0.11 g, 0.21 mmol) in dry dichloromethane (4.0 ml) was added potassium hydrofluoride (0.02 g, 0.21 mmol) and trifluoroacetic acid (0.08 ml, 1.03 mmol). The mixture was stirred at room temperature for 17 h after which time saturated sodium bicarbonate solution (4.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 5 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 50% diethyl ether in hexane, afforded the product as a white solid (69.7 mg, ds 1:1, 92%). Mp: 36.7-72.3 ^oC; R_f 0.5 (pet. ether : diethyl ether 1:1); IR (ATR) 2955, 2901, 1707, 1686, 1597, 1449, 1362, 1325, 1250, 1179, 1138, 1027, 985, 913, 841, 744 cm^{-1}; δ_H (700MHz) 7.85-7.84 (2H, m, 5-Ar-2,6-***H***), 7.78-7.77 (2H, m, 5-Ar-2,6-***H***), 7.52-7.49 (2H, m, 5-Ar-4-***H***), 7.42-7.37 (2H, m, 5-Ar-3,5-***H***), 7.29-7.28 (2H, m, 3-Ar-2,6-***H***), 7.23-7.21 (2H, m, 3-Ar-2,3,5,6-***H***), 7.20-7.17 (2H, m, 3-Ar-3,5-***H***), 7.16-7.14 (1H, m, 3-Ar-4-***H***), 7.10-7.08 (1H, m, 3-Ar-4-***H***), 4.22 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2CH_3$), 4.15 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2CH_3$), 3.93-3.88 (2H, m, 3-***H***), 3.86 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2CH_3$), 3.80 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2CH_3$), 3.43 (1H, dd, *J* = 15.8Hz, *J* = 10.5Hz, 4-***H***), 3.41 (1H, dd, *J* = 15.8Hz, *J* = 10.5Hz, 4-***H***), 3.28 (1H, dd, *J* = 15.8Hz, *J* = 3.5Hz, 4-***H***), 3.26 (1H, dd, *J* = 15.8Hz, *J* = 3.5Hz, 4-***H***), 2.64 (1H, d, *J* = 10.5Hz, 2-***H***), 2.54 (1H, d, *J* = 11.2Hz, 2-***H***), 1.31 (3H, t, *J* = 7.0Hz, CH_2C***H***$_3$), 0.98 (3H, t, *J* = 7.0Hz, CH_2C***H***$_3$), 0.20 (9H, s, Si(C***H***$_3)_3$), -0.19 (9H, s, Si(C***H***$_3)_3$); δ_C (175MHz) 198.4 (***C***-5), 198.2 (***C***-5), 174.7 (***C***-1), 173.6 (***C***-1), 143.9 (3-Ar-***C***-

1), 142.2 (3-Ar-***C***-1), 137.2 (5-Ar-***C***-1), 137.0 (5-Ar-***C***-1), 132.9 (5-Ar-***C***-4), 132.8 (5-Ar-***C***-4), 128.47 (Ar), 128.45 (Ar), 128.43 (Ar), 128.40 (Ar), 128.1 (5-Ar-***C***-2,6), 128.03 (Ar), 128.02 (Ar), 127.9 (5-Ar-***C***-2,6), 127.0 (3-Ar-***C***-4), 126.4 (3-Ar-***C***-4), 60.1 (***C***H_2CH_3), 59.6 (***C***H_2CH_3), 46.5 (***C***-4), 44.8 (***C***-2), 44.6 (***C***-4), 44.4 (***C***-2), 40.9 (***C***-3), 40.5 (***C***-3), 14.4 (CH_2***C***H_3), 14.1 (CH_2***C***H_3), -1.2 (Si(***C***$H_3)_3$), -2.1 (Si(***C***$H_3)_3$); δ_{Si} (140MHz) 4.8, 3.9; m/z (EI) 368 ($[M]^{+\cdot}$, 11%), 340 ($[M\text{-}C_2H_4]^{+\cdot}$, 11), 322 ($[M\text{-EtOH}]^{+\cdot}$, 17), 307 (19), 281 (70), 263 (74), 131 (100), 105 (68), 77 ($[Ph]^{+\cdot}$, 36), 73 ($[EtOCO]^{+\cdot}$, 52), 45 ($[EtO]^{+\cdot}$, 11).

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

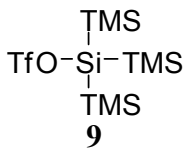
Tris(trimethylsilyl)silyl trifluoromethanesulfonate



9

^{13}C NMR (100 MHz, $CDCl_3$)

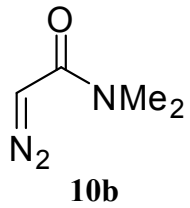
Tris(trimethylsilyl)silyl trifluoromethanesulfonate



9

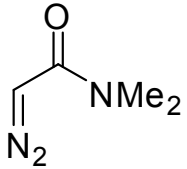
^{1}H NMR (700 MHz, $CDCl_3$)

2-Diazo-N,N-dimethylacetamide



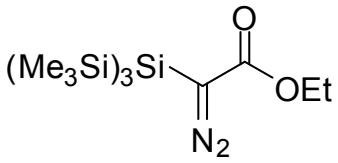
10b

^{13}C NMR (175 MHz, $CDCl_3$) **2-Diazo-N,N-dimethylacetamide**



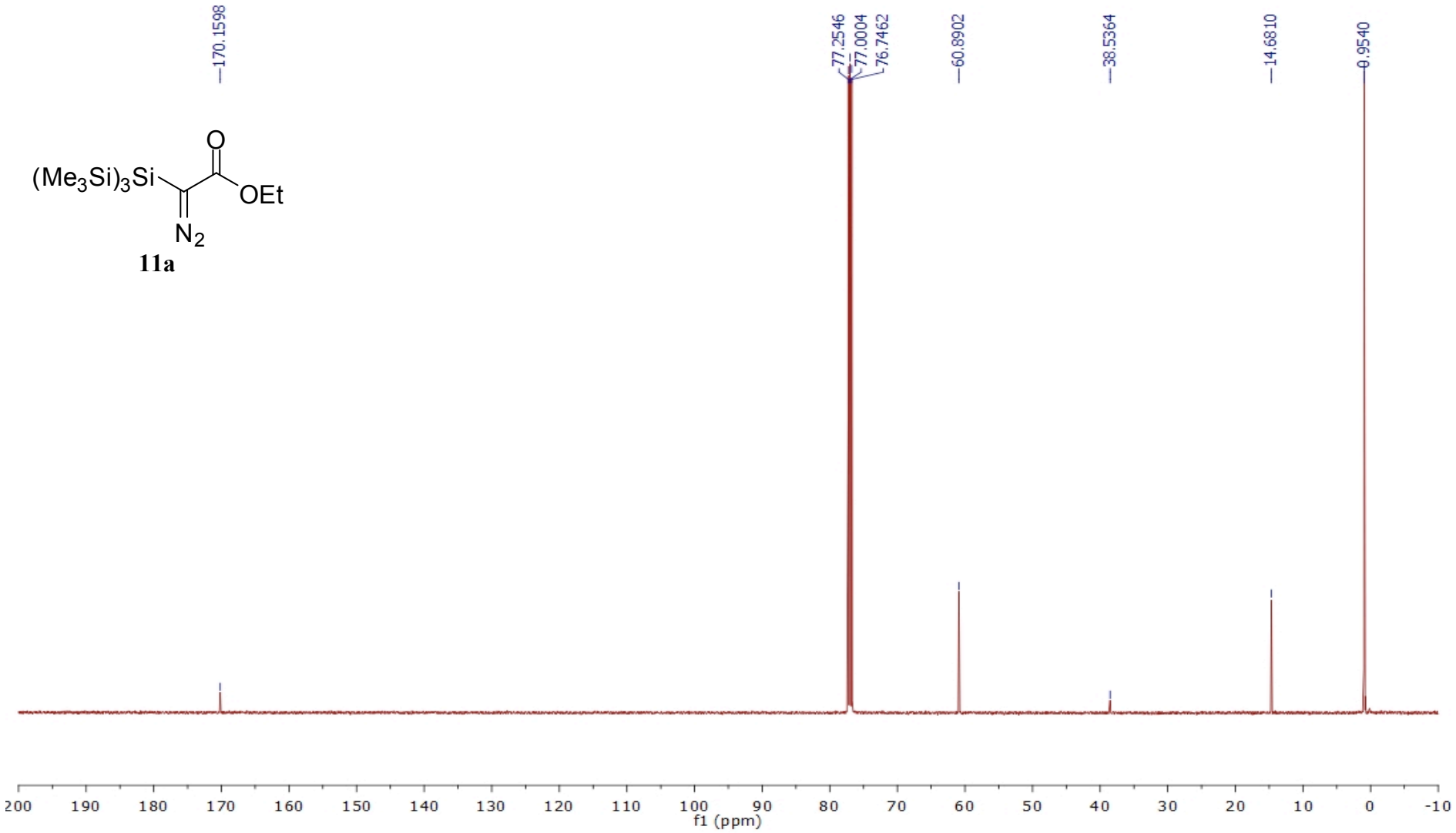
10b

^{1}H NMR (500 MHz, $CDCl_3$) **Ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate**



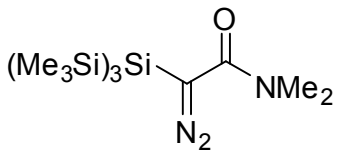
11a

^{13}C NMR (125 MHz, $CDCl_3$) **Ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate**



11a

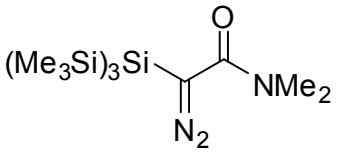
^{1}H NMR (700 MHz, $CDCl_3$) **2-Diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*,*N*-dimethylacetamide**



11b

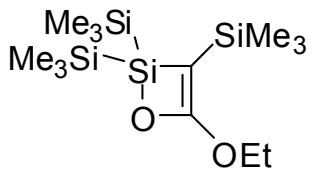
^{13}C NMR (175 MHz, $CDCl_3$)

2-Diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*,*N*-dimethylacetamide



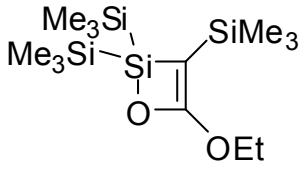
11b

^{1}H NMR (500 MHz, -80°C,C_7D_8) **4-Ethoxy-2,2,3-tris(trimethylsilyl)-2H-1,2-oxasilete**



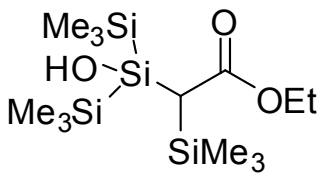
12

^{13}C NMR (125 MHz, -80°C, C_7D_8) **4-Ethoxy-2,2,3-tris(trimethylsilyl)-2H-1,2-oxasilete**



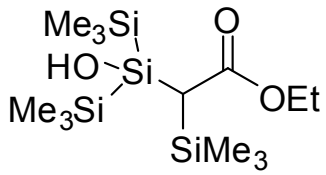
12

^{1}H NMR (700 MHz, $CDCl_3$) **Ethyl 2-(2-hydroxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)acetate**



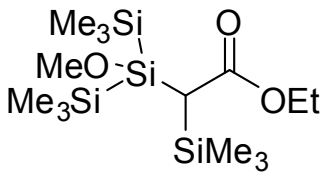
13a

^{13}C NMR (175 MHz, $CDCl_3$) **Ethyl 2-(2-hydroxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)acetate**



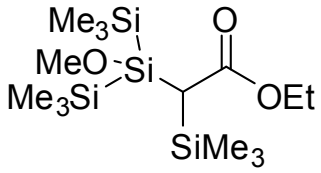
13a

^{1}H NMR (700 MHz, $CDCl_3$) **Ethyl 2-(1-methoxy-1,2,2,2-tetramethyldisilyl)-2-(trimethylsilyl)acetate**



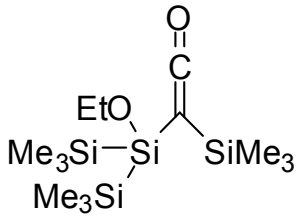
13b

^{13}C NMR (175 MHz, $CDCl_3$) **Ethyl 2-(1-methoxy-1,2,2,2-tetramethyldisilyl)-2-(trimethylsilyl)acetate**



13b

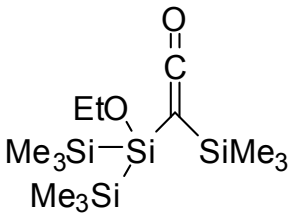
^{1}H NMR (700 MHz, C_7D_8) **2-(2-Ethoxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)ethenone**



14

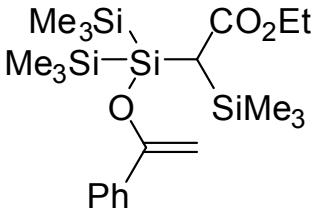
^{13}C NMR (175 MHz, C_7D_8)

2-(2-Ethoxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)ethenone



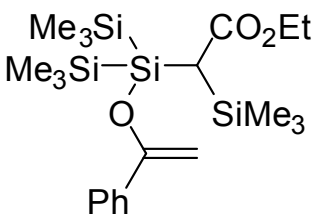
14

^{1}H NMR (700 MHz, $CDCl_3$) **Ethyl 2-(1,1,1,3,3,3-hexamethyl-2-(1-phenylvinyloxy)trisilan-2-yl)-2-(trimethylsilyl)acetate**



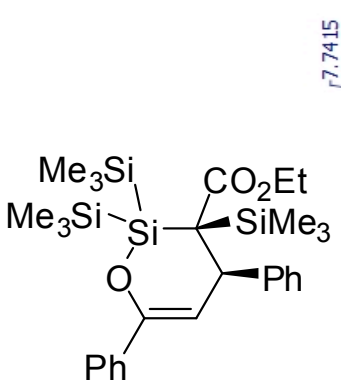
15

^{13}C NMR (175 MHz, $CDCl_3$) **Ethyl 2-(1,1,1,3,3,3-hexamethyl-2-(1-phenylvinyloxy)trisilan-2-yl)-2-(trimethylsilyl)acetate**



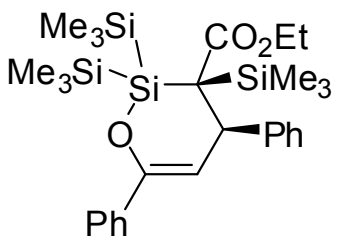
15

^{1}H NMR (700 MHz, $CDCl_3$) **(3*SR*,4*RS*)-Ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



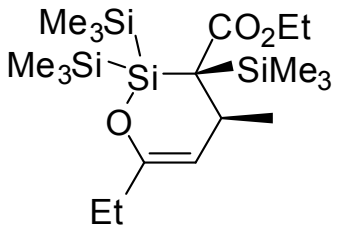
16

^{13}C NMR (175 MHz, $CDCl_3$) **(3*SR*,4*RS*)-Ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



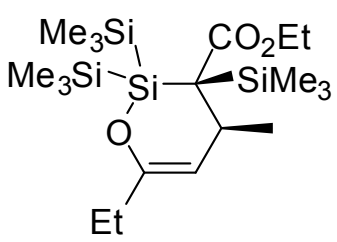
16

^{1}H NMR (700 MHz, $CDCl_3$) **(3*SR*,4*SR*)-Ethyl 6-ethyl-4-methyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



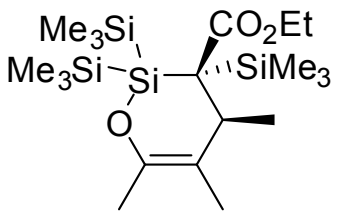
22

^{13}C NMR (175 MHz, $CDCl_3$) **(3*SR*,4*SR*)-Ethyl 6-ethyl-4-methyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



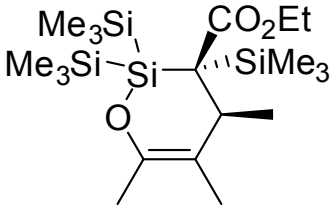
22

^{1}H NMR (700 MHz, $CDCl_3$) **(3*RS*,4*SR*)-Ethyl 4,5,6-trimethyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



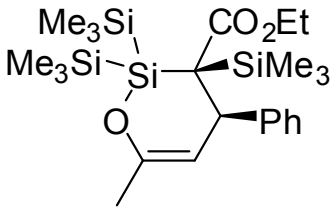
23

^{13}C NMR (175 MHz, $CDCl_3$) **(3*RS*,4*SR*)-Ethyl 4,5,6-trimethyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



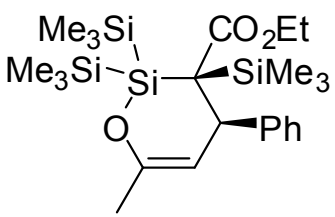
23

^{1}H NMR (500 MHz, $CDCl_3$) **(3*SR*,4*RS*)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



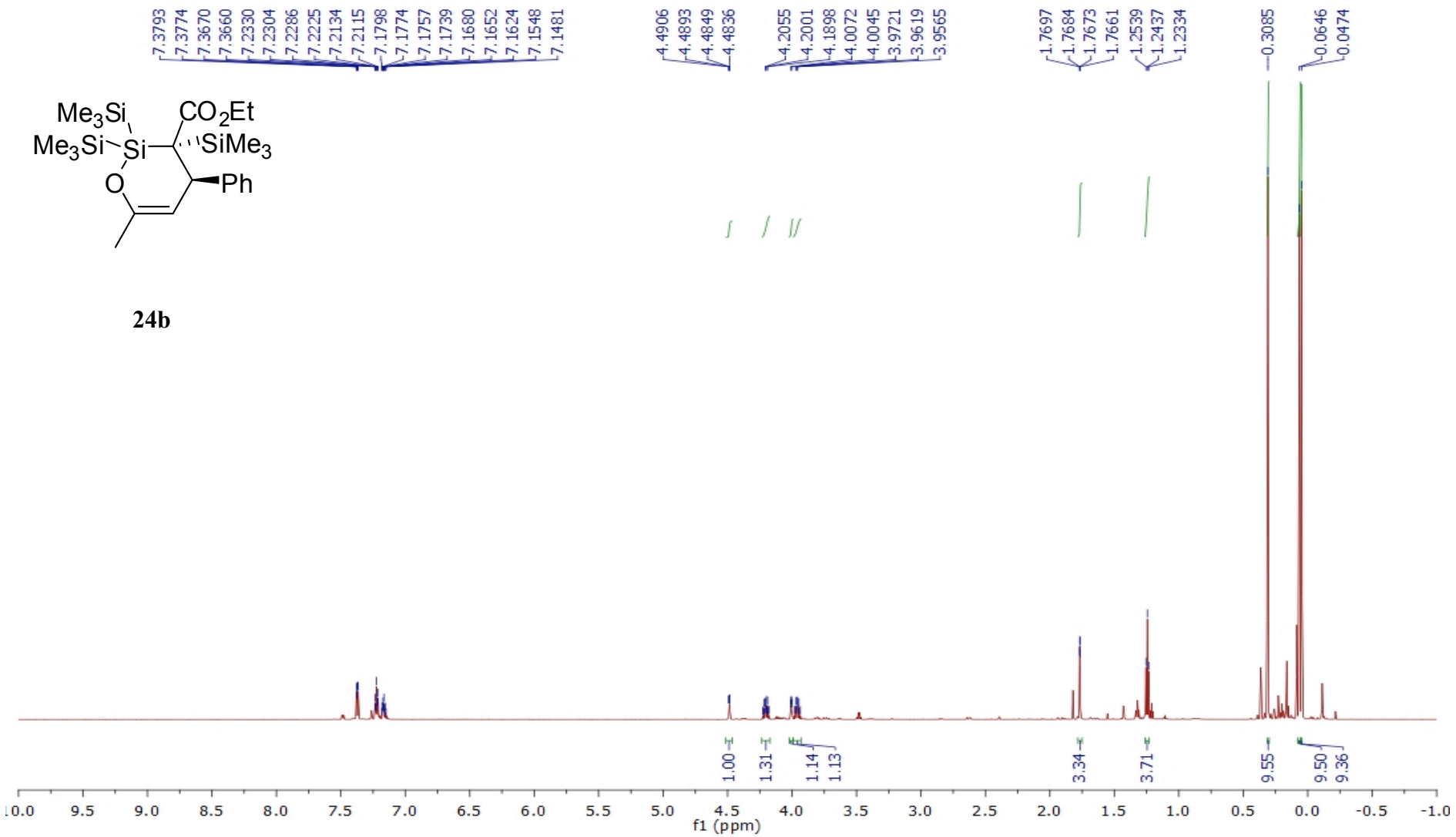
24a

^{13}C NMR (125 MHz, $CDCl_3$) **(3*SR*,4*RS*)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



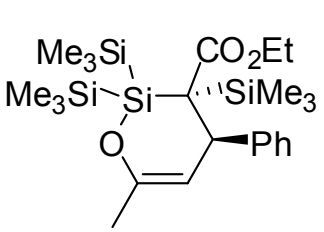
24a

^{1}H NMR (700 MHz, $CDCl_3$) **(3*RS*,4*RS*)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



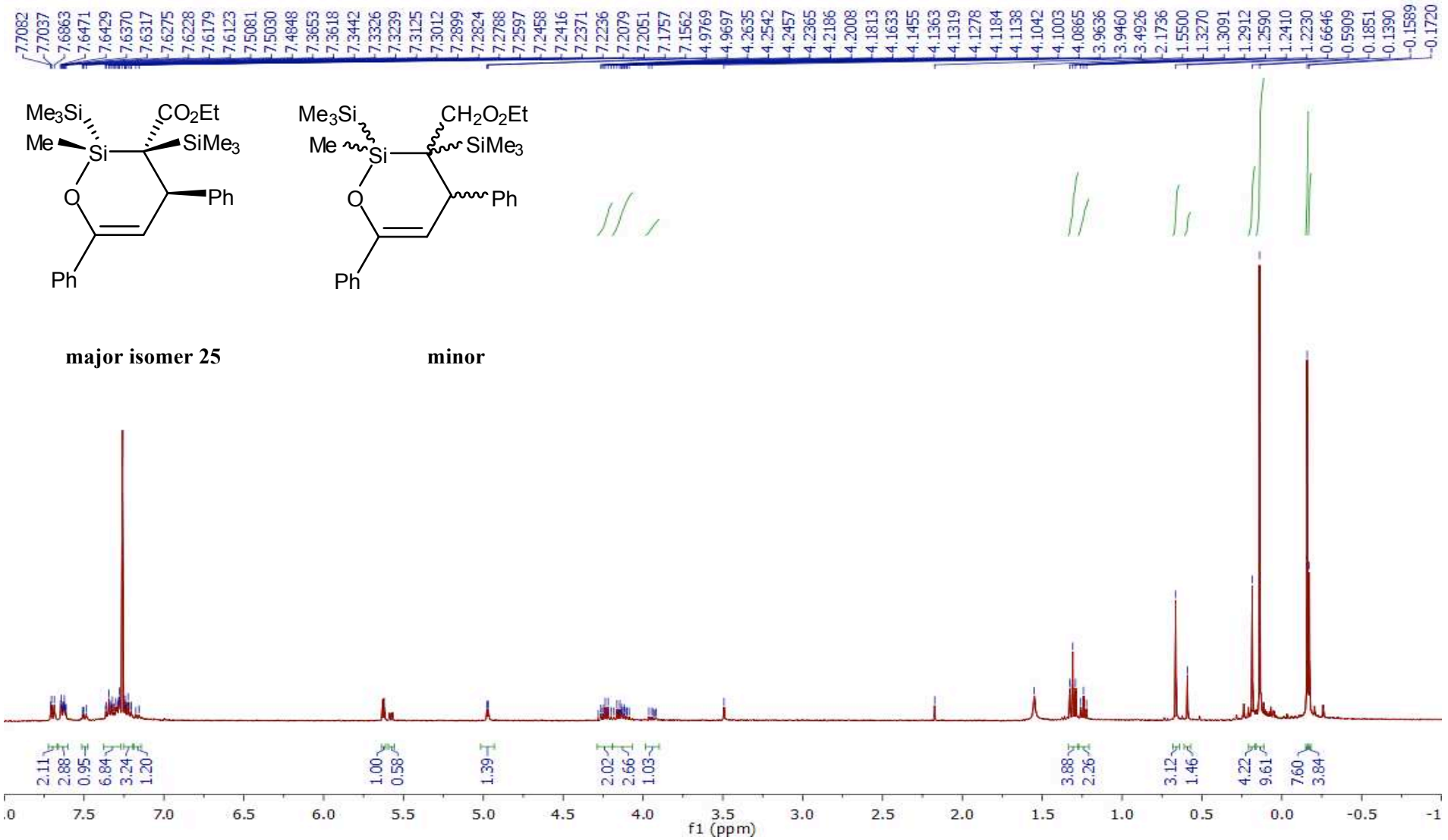
24b

^{13}C NMR (175 MHz, $CDCl_3$) **(3*RS*,4*RS*)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



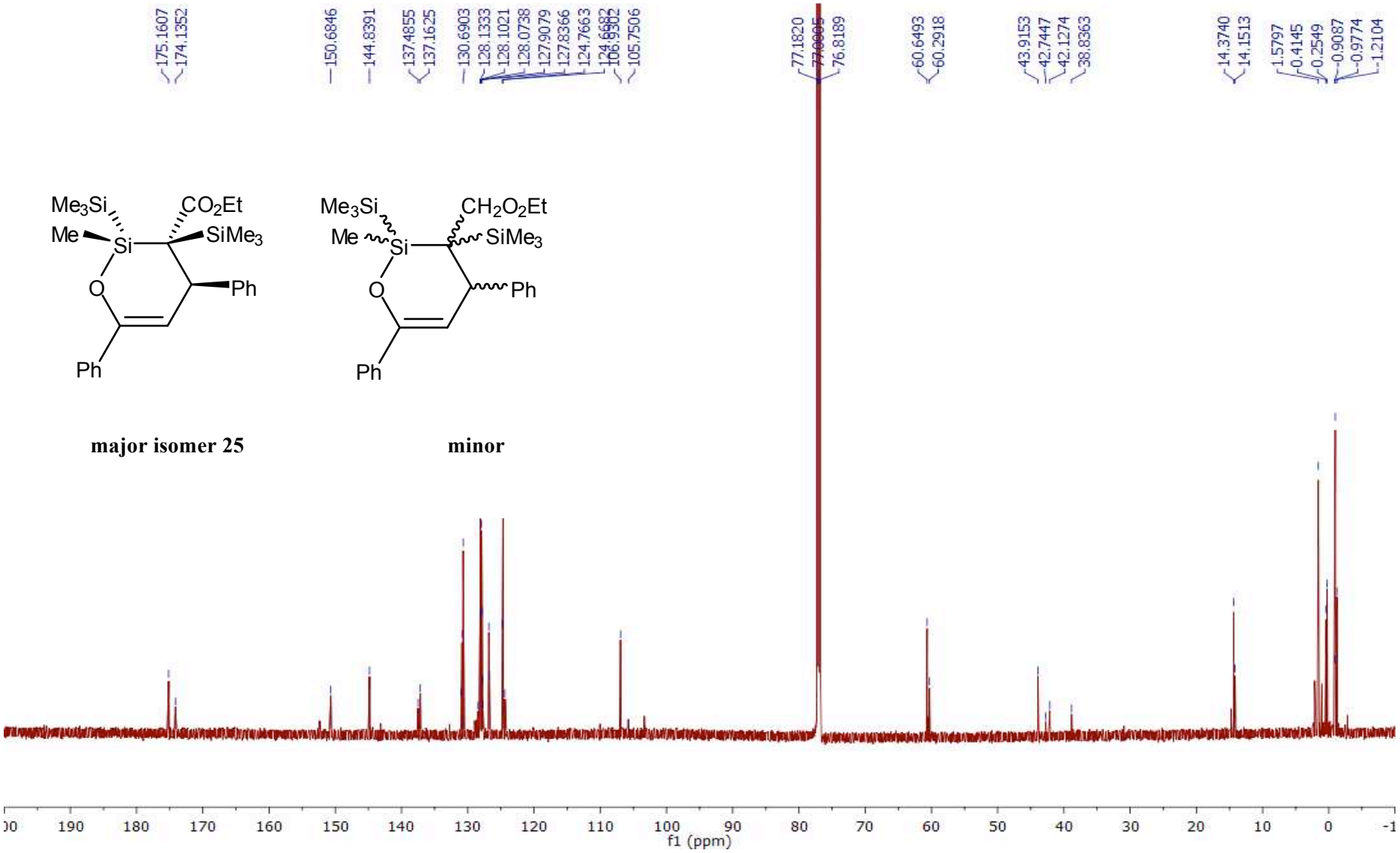
24b

^{1}H NMR (700 MHz, $CDCl_3$) **(2RS,3SR,4RS)-Ethyl 2-methyl-4,6-diphenyl-2,3-bis(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**



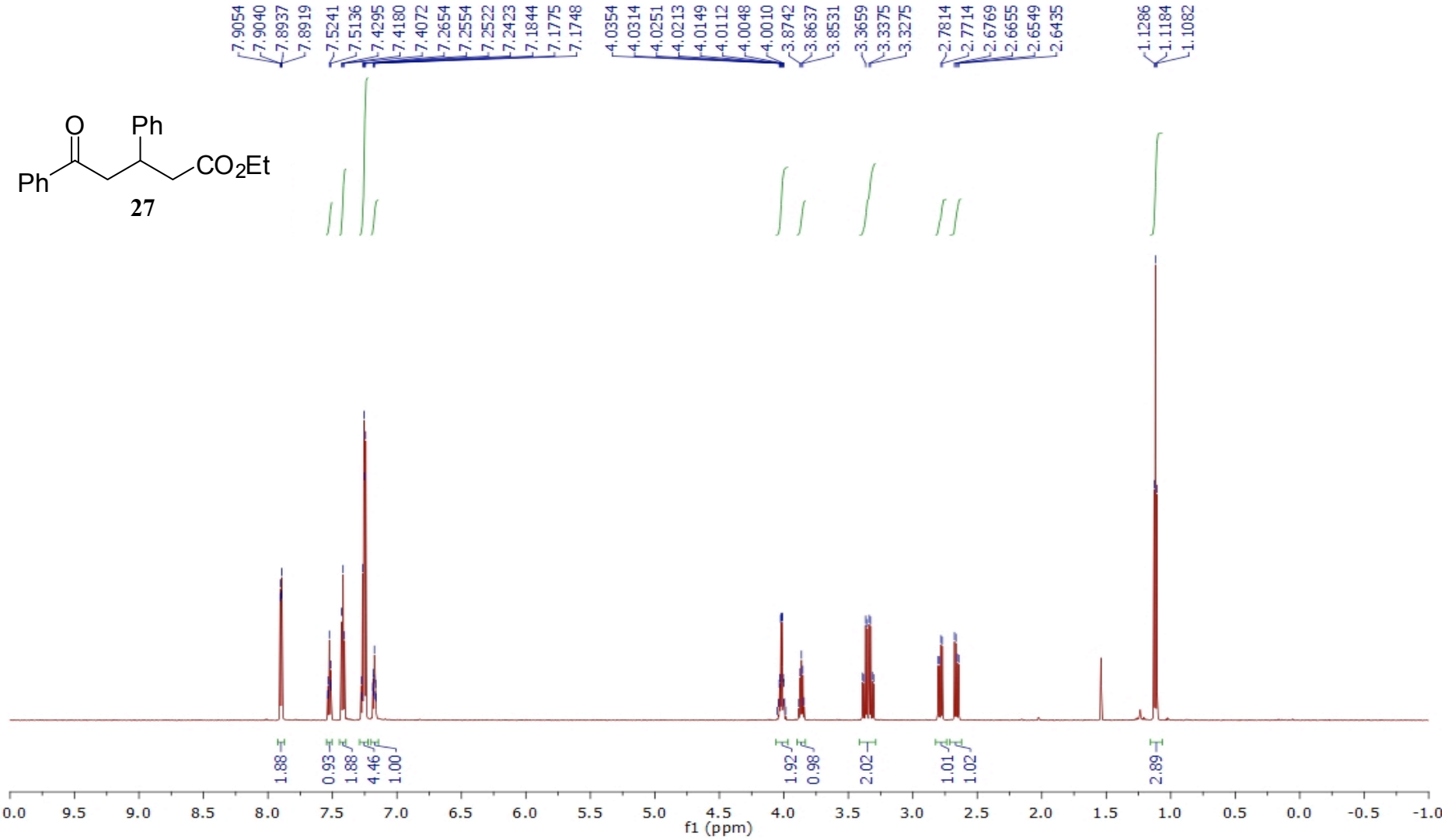
major isomer 25 **minor**

^{13}C NMR (175 MHz, $CDCl_3$) **(2RS,3SR,4RS)-Ethyl 2-methyl-4,6-diphenyl-2,3-bis(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate**

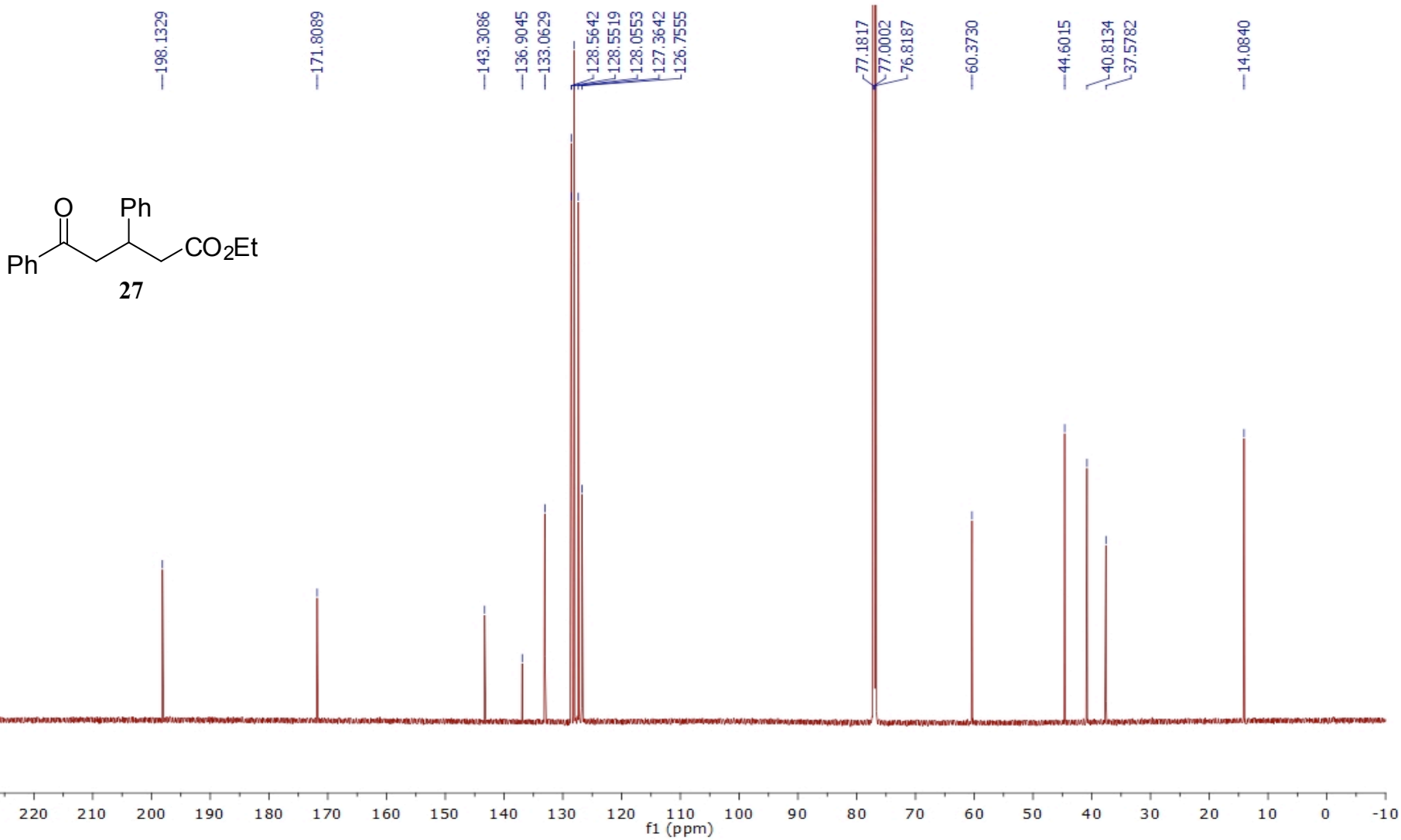


major isomer 25 **minor**

^{1}H NMR (700 MHz, $CDCl_3$) **Ethyl 5-oxo-3,5-diphenylpentanoate**

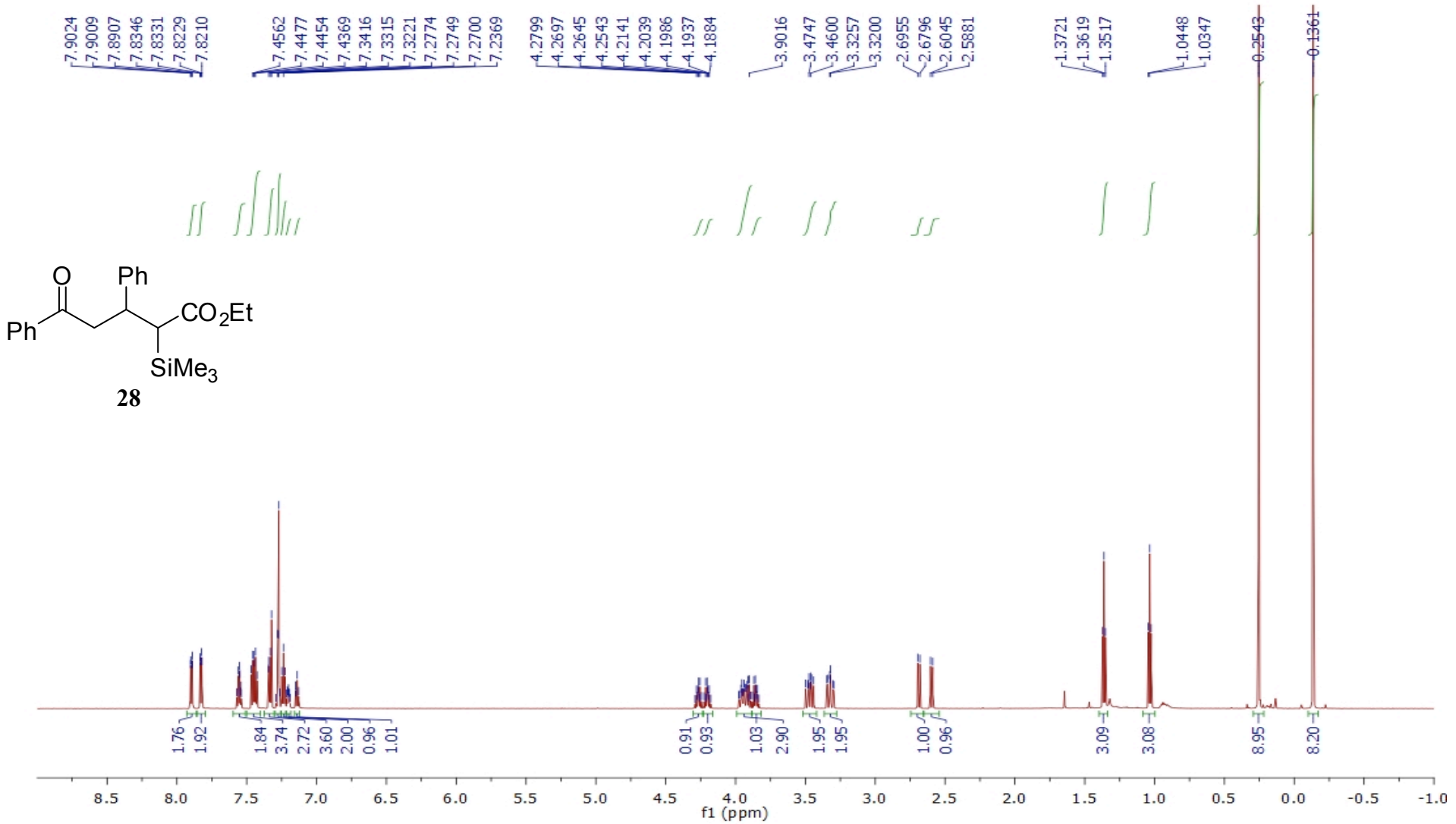


^{13}C NMR (175 MHz, $CDCl_3$) **Ethyl 5-oxo-3,5-diphenylpentanoate**



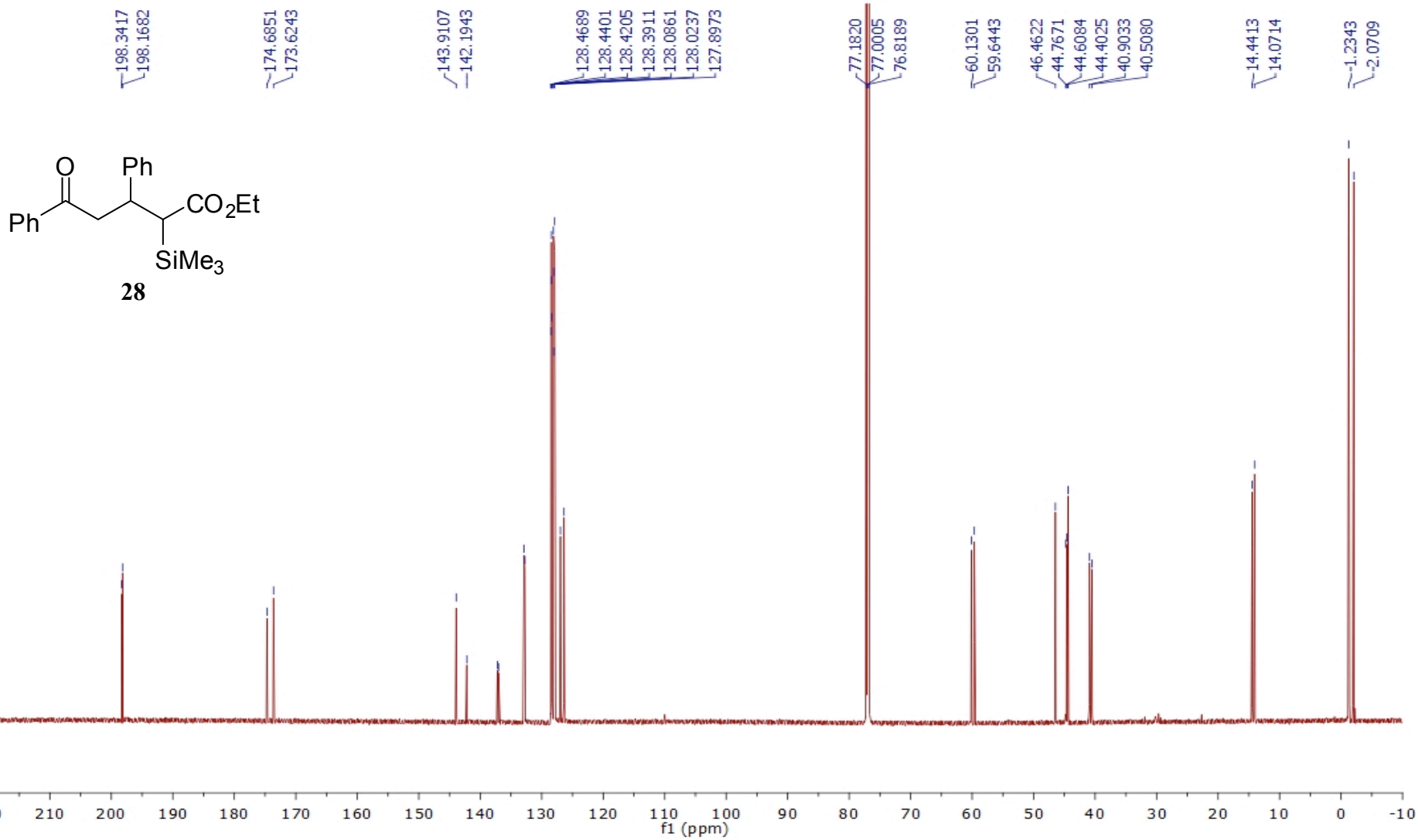
27

^{1}H NMR (700 MHz, $CDCl_3$) **Ethyl 5-oxo-3,5-diphenyl-2-(trimethylsilyl)pentanoate**



28

^{13}C NMR (175 MHz, $CDCl_3$) **Ethyl 5-oxo-3,5-diphenyl-2-(trimethylsilyl)pentanoate**



28

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