Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

Controlling Stereochemistry in Polyketide Synthesis: 1,3- vs. 1,2-Asymmetric Induction in Methyl Ketone Aldol Additions to β-Super Siloxy Aldehydes

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Synthetic Efficiency

The development of new, more efficient synthetic methods is an ongoing challenge in contemporary organic chemistry.[1] The evaluation of synthetic efficiency has been discussed at great length in the literature, and numerous metrics have been defined. In our studies, we have evaluated the synthetic efficiency of the super silyl cascade aldol approach to polyketides in comparison to alternative methods. We have chosen four metrics to evaluate synthetic efficiency: 1) chemical yield (the most elementary metric) 2) stereoselectivity 3) atom economy 4) step economy (the most important metric).

To evaluate atom economy[2,3] of the super silyl aldol approach to polyketides, selected examples were compared to literature preparation of similar compounds using

[1] See refs. 1−3, 11,12,15 in main text.
[2] Trost, B. M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259–281

different strategies. To calculate atom economy for a single synthetic transformation, equation (S-1) was used, according to Eissen and coworkers.[4]

$$\text{atom economy } (\boldsymbol{AE}) = \frac{b_{\text{product}} \times \text{MW}_{\text{product}}}{a_{substrate\ 1} \times \text{MW}_{substrate\ 1} + \cdots + a_{substrate\ m} \times \text{MW}_{substrate\ m}} \quad \text{(eq. S-1)}$$

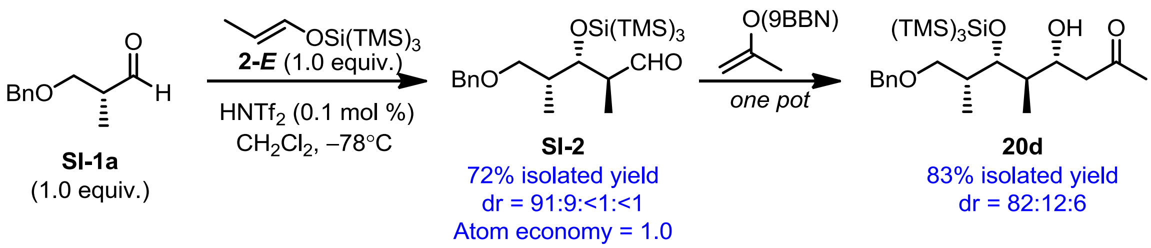
Where MW is molecular weight, and *a* and *b* are coefficients relating to the stoichiometry and ratios of reagents used. To evaluate atom-economy for a multistep synthesis with *n* steps, equation (S-2) was used.

$$\boldsymbol{AE}(\mathbf{1}, \ldots \boldsymbol{n}) = \frac{b_{\text{product}} \times \text{MW}_{\text{product}}}{\frac{a_{substrate\ 1} \times \text{MW}_{substrate\ 1}}{AE(1,\ldots n-1)} + \sum_{j=2}^{m} a_{substrate\ j} \times \text{MW}_{substrate\ j}} \quad \text{(eq. S-2)}$$

Where substrate$_1$ is the substrate in the final step of the reaction, and *n-1* is synthetic step proceeding the final step in the multistep sequence. Our calculations for this discussion include reagents involved in each reaction, adjusting for the reagent stoichiometry *a* or *b* in equations 1, 2. However, solvents, reagents used for workup and purification are not included.

Scheme S-1 shows the aldol reaction of Roche aldehyde **S-1a** with propanal-derived enolsilane ***E*-23.** Product **S-2** can be isolated in good yield and high selectivity. Unlike many aldol reactions, this variation results in perfect atom economy, due extremely low catalyst loading, transfer of the silyl group to the product and absence of exogenous Lewis acids, bases, or additives. The atom economic impact of the silyl group is only realized upon deprotection (see below). As shown in Scheme 5, of the main text, **3** can be used in a one-pot acetone addition, generating product **20d**.

Scheme S-1



Scheme S-2 Shows published methods for the synthesis of crotyl product **S-3** with equivalent stereochemistry.[5,6,7] As can be seen, the atom economy of this reaction is rather poor, due to the requirement of high molecular weight chiral crotyl donors required

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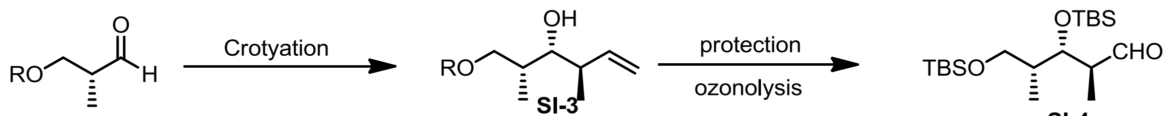
[3] Trost, B. M. *Science* **1991**, *254*, 1471–1477.
[4] Eissen, M.; Mazur, R.; Quebbemann, H.-G.; Pennemann, K.-H. *Helv. Chim. Acta* **2004**, *87*, 524–535.
[5] Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1989**, *54*, 1570–1576.
[6] Kim, H.; Ho, S.; Leighton, J. L. *J. Am. Chem. Soc.* **2011**, *133*, 6517–6520.
[7] Roush, W. R.; Ando, K.; Powers, D. B.; Halterman, R. L.; Palkowitz, A. D. *Tetrahedron Lett.* **1988**, *29*, 5579–5582.

for high selectivity. Furthermore, as evidenced in synthetic studies on Rutamycin B,[8] protection and oxidation steps are required to convert crotyl product **S-3** to aldehyde **S-4** (functional equivalent of **S-2**). The overall yield is 45% over three steps, and the calculated atom economy is 0.22.[9] When comparing the synthesis of **S-2** and **S-4**, the super silyl aldol route is more efficient in terms of four metrics: chemical yield, selectivity, step economy, and atom economy.

Scheme S-2.



SI-3

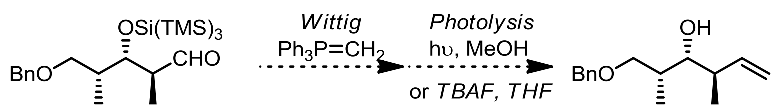
SI-4

entry	crotylation method	year published	dr	yield	atom economy (1 step)
1	Chiral crotyl borane	1989 [Ref. 5]	98:2	60%	0.23
2	Chiral crotyl boronate	1988 [Ref. 7]	97:3	80%	0.40
3	Chiral crotyl silane	2011 [Ref. 6]	97:3	86%	0.33

dr (crotylation) = 88:12
45% overall yield (3 steps)
atom economy = 0.22
[Ref. 8,12]

If the less functionalized crotyl product **SI-3** is desired instead, **SI-2** could be converted to **S-3a** by a two step olefination/deprotection sequence **(Scheme S-3)**. If photolysis is used to cleave the super silyl group, the atom economy for the 3-step sequence is expected to be 0.26. If TBAF is used for desilylation, the atom economy will be 0.20, both of which are comparable to crotylation methods in **S-2**. If **S-3** is desired, the super silyl approach would still be advantageous in that no expensive chiral reagent is required.

Scheme S-3. Conversion of **SI-2** to **SI-3a**



SI-2

SI-3a

The 2,3,4-*syn-syn* configured dipropionate stereotriad is also found in natural products. This stereochemical configuration can be accessed by aldol addition of ***Z*-23** and aldehyde **SI-1**, affording benzyl protected product **SI-5a** in good dr or TBS-protected **SI-5b** in excellent dr. The synthesis of functionally equivalent compounds has been reported in the total synthesis of Tedanolide[10] and Discodermolide.[11] The use of crotylboration or Evans' aldol reaction requires a greater number of steps, is lower yielding and has poor atom economy.

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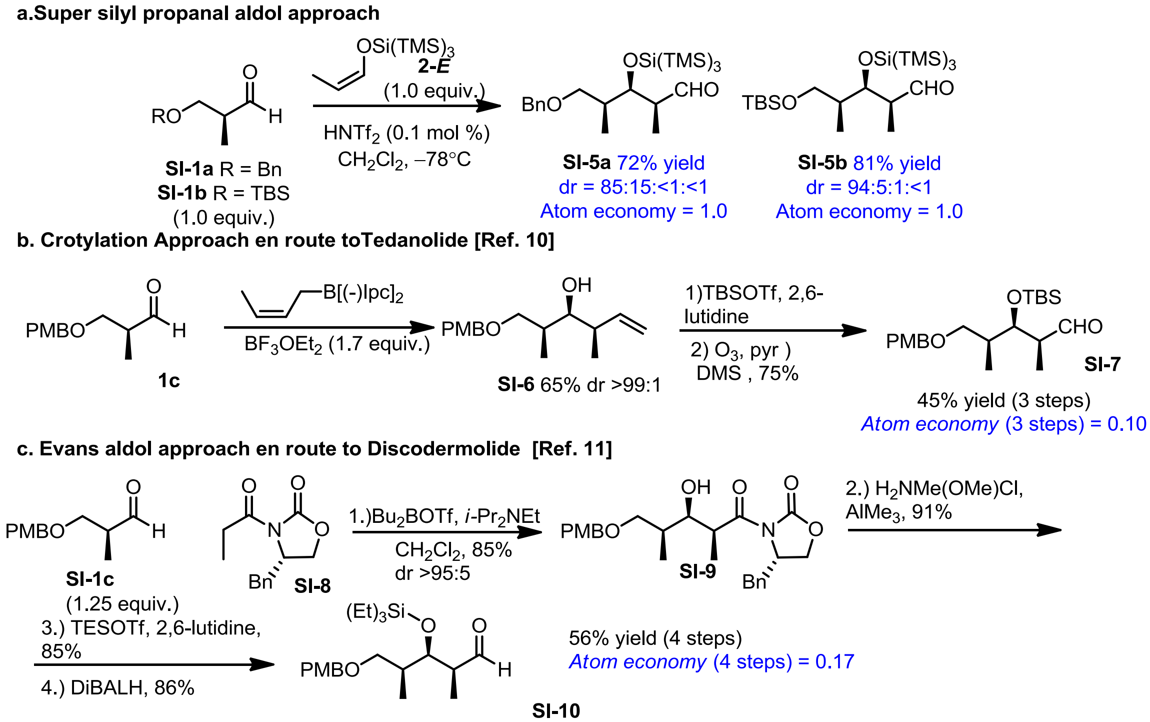
[8] White, J. D.; Hanselmann, R.; Jackson, R. W.; Porter, W. J.; Ohba, Y.; Tiller, T.; Wang, S. *J. Org. Chem.* **2001**, *66*, 5217–5231.

[9] Due to lack of experimental data the following assumptions were made for the 3 step sequence: step 1) S-S-**1a** (1equiv.) crotylboronate (1.2 equiv.); step 2: TBSOTf (1.3 equiv.), Et_3N (1.5 equiv.); step 3:O_3 (1 equiv. counted), DMS (10 equiv.)

[10] De Lemos, E. *et al. Chem. Eur. J.* **2008**, *14*, 11092–11112.

[11] Hassfeld, J.; Eggert, U.; Kalesse, M. *Synthesis* **2005**, 1183–1199.

Scheme S-4: Synthesis of *syn-syn* configured dipropionates:



In summary, quantitative analysis the synthetic efficiency of the super silyl aldol approach to polyketides demonstrates that it is highly efficient when compared to the state of the art in stereoselective synthesis. Although at first glance this strategy may appear to be atom-inefficient due to the use of larger than usual silyl groups, qualitative anslysis demonstrates that it is actually more atom-economical than alternative methods. It is also more efficient in terms of chemical yield (the simplest efficiency metric), step economy, and is comparable in terms of stereoselectivity. **Scheme S-3** demonstrates the fact that a longer sequence of steps, even a series of high yielding steps, is detrimental to synthetic efficiency because of the number of reagents used. As a result, improved step economy will more than likely improve efficiency as evaluated by other metrics such as yield, atom economy capital cost and *E*-factor.[12]

Furthermore, this study only analyzes single aldol reactions, whereas the main text describes our goal of stereoselective double, triple, and even tetra-aldol reactions. While direct comparisons to polyaldol reactions are difficult, this analysis suggests that the step- and atom-economy benefits will increase with each successive aldol cascade.

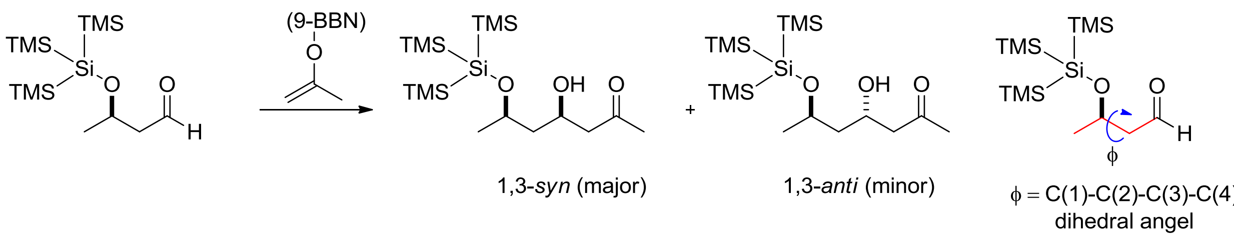
Computational Methods

Molecular geometries of the transition state structures of the reaction pathways were optimized using Density Functional Theory with Becke's three-parameter hybrid

[12] Constable, D. J. C.; Curzons, A. D.; Cunningham, V. L. *Green Chem.* **2002**, *4*, 521–527.

functional[13] and Lee, Yang, and Parr's (LYP)[14] correlation functional. The 6-31+G(d) basis sets were used in this study. All geometries were optimized without any symmetry restrictions and characterized as first-order saddle points (one imaginary frequency) by calculations of harmonic vibrational frequencies. Gibbs free energies of activation ($\Delta G^{\ddagger}$) were calculated as the difference of free energies of transition states. All calculations have been carried out using the Gaussian 03 and Gaussian 09 program package.[15] [16]

Computational data for enolborinate addition to β-super siloxy butanal
Computational experiments were performed as described above to reveal the transition state structures of acetone 9-BBN enolborinate addition to β-Super Siloxy Butanal (**Scheme S-5**). Relative energies for transition state structures are shown in **Table S-1**. Structures and Newman projections are shown in **Figure S-1**, with full data following.



Scheme S-5: Enolborinate aldol addition to β-super siloxy butanal

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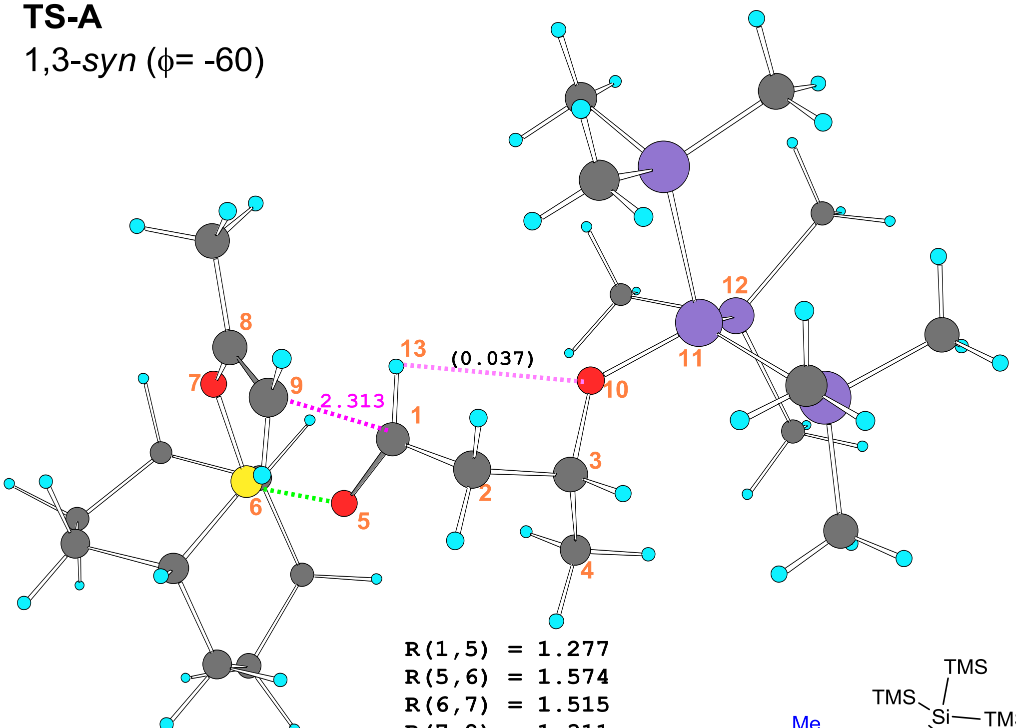
[13] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[14] Lee, C.; Yang, W.; Parr, R. G. *Phys. ReV. B* **1988**, *37*, 785–789.
[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapp,rich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision E.01*; Gaussian Inc., Wallingford, CT, 2004.
[16] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E. ; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, A˜.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; *Gaussian 09, Revision C.01*; Gaussian Inc.: Wallingford, CT, 2009.

Table S-1. Relative energies of the optimized transition state structures of the reaction using β-super siloxy butanal in kcal mol^{-1}. Relative to **A** (TS-H-syn(-60)).

TS	(ϕ)	1,3-*syn/anti*	Relative Electron Energy	Relative Free Energy
A	-60	*syn*	0.00	0.00
B	60	*syn*	1.18	1.50
C	180	*syn*	4.53	5.90
D	-60	*anti*	1.32	1.46
E	60	*anti*	0.88	1.02
ϕ = non-optimized C(1)-C(2)-C(3)-C(4) dihedral angle. Optimized dihedral angels shown in figure S1.				

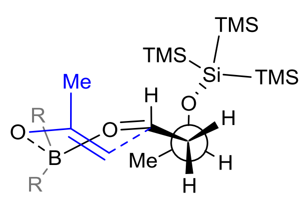
TS-A

1,3-*syn* (ϕ= -60)



R(1,5) = 1.277
R(5,6) = 1.574
R(6,7) = 1.515
R(7,8) = 1.311
R(8,9) = 1.383
D(2,3,10,11) = 146.9
D(3,10,11,12) = 107.7
R(4,12) = 4.374
R(10,13) = 2.727

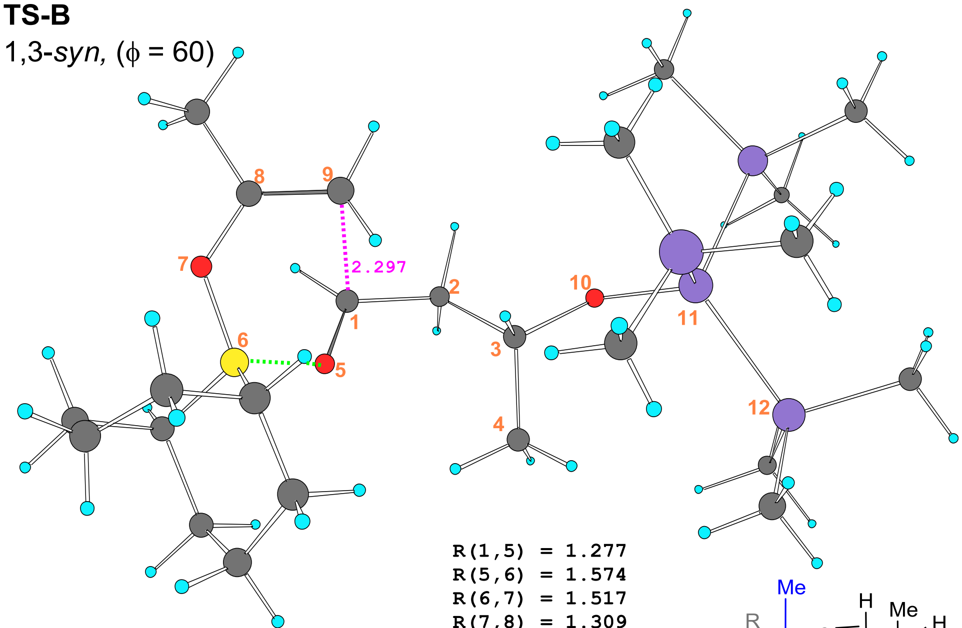
D(1,2,3,4) = -63.9
R(1,9) = 2.313



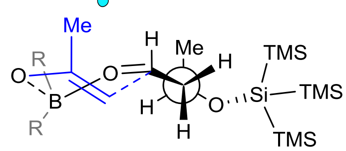
A

TS-B

1,3-*syn,* (ϕ = 60)



R(1,5) = 1.277
R(5,6) = 1.574
R(6,7) = 1.517
R(7,8) = 1.309
R(8,9) = 1.385
D(2,3,10,11) = 157.9
D(3,10,11,12) = 88.3
R(4,12) = 4.091

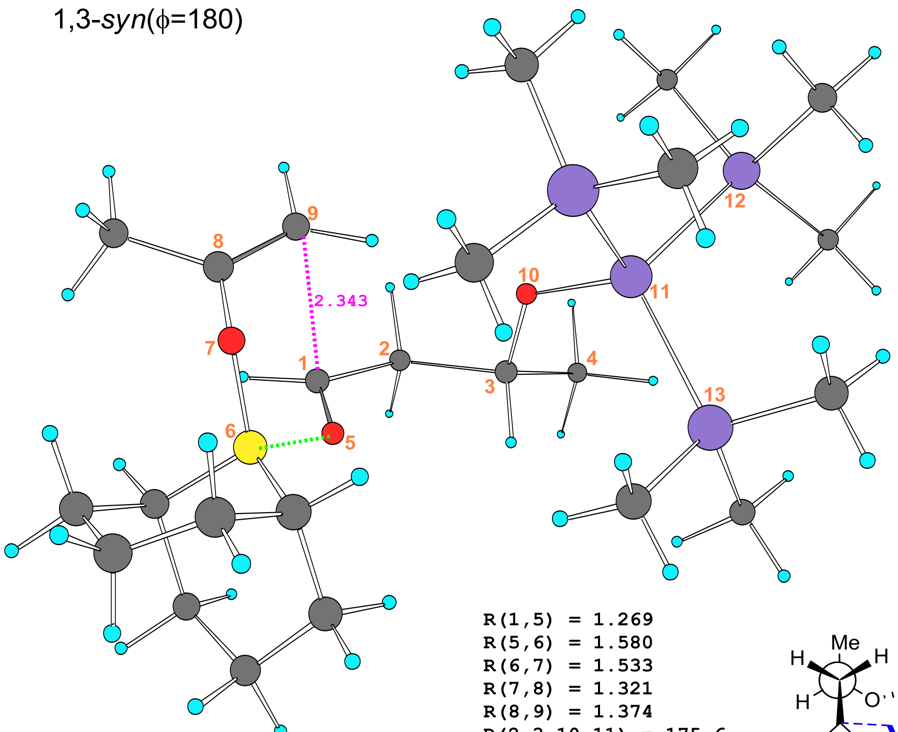


B

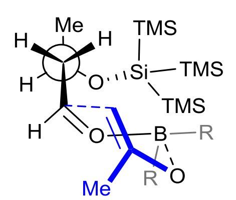
D(1,2,3,4) = 78.2
R(1,9) = 2.297

TS C

1,3-*syn*(ϕ=180)



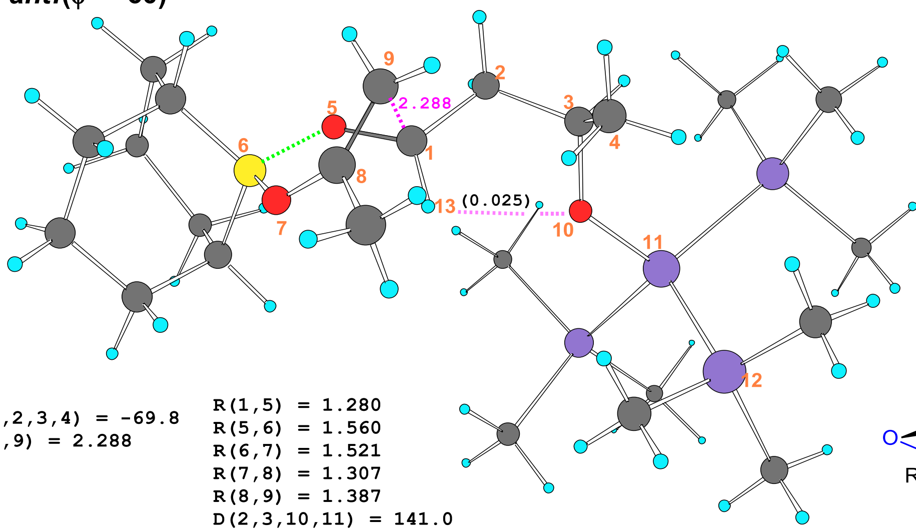
R(1,5) = 1.269
R(5,6) = 1.580
R(6,7) = 1.533
R(7,8) = 1.321
R(8,9) = 1.374
D(2,3,10,11) = 175.6
D(3,10,11,12) = 93.3
D(3,10,11,13) = -31.3
R(4,12) = 3.969
R(4,13) = 4.180

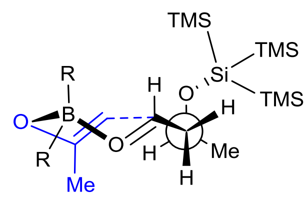


C

D(1,2,3,4) = 166.4
R(1,9) = 2.343

TS D
1,3-*anti*(ϕ = -60)



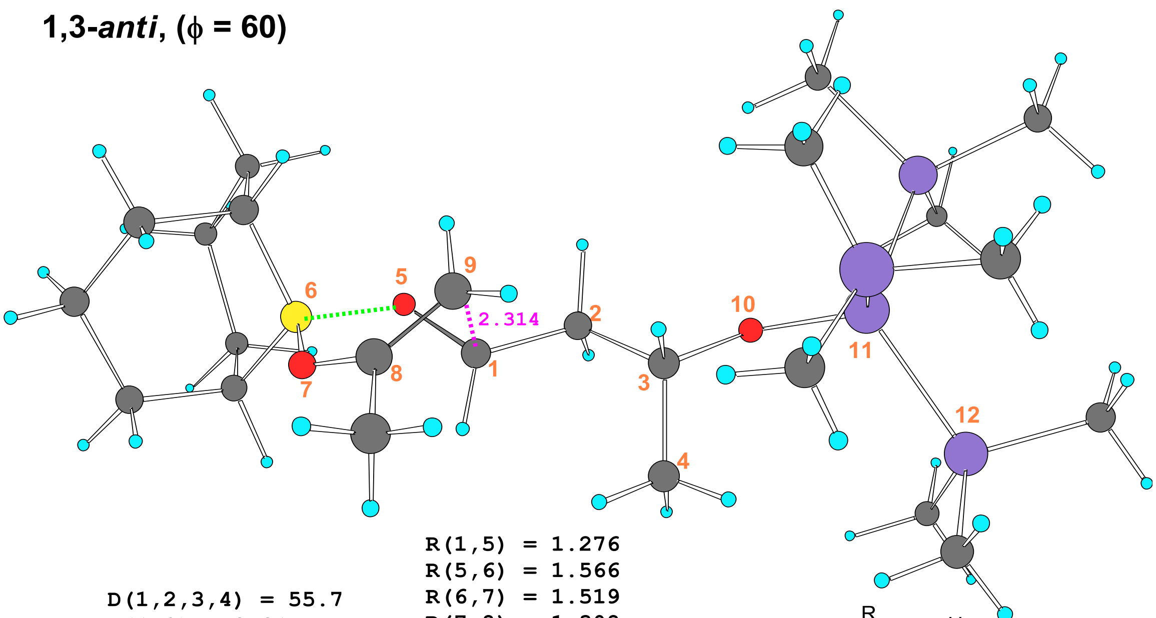


D

D(1,2,3,4) = -69.8
R(1,9) = 2.288

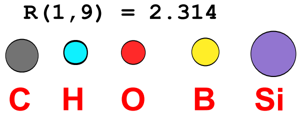
R(1,5) = 1.280
R(5,6) = 1.560
R(6,7) = 1.521
R(7,8) = 1.307
R(8,9) = 1.387
D(2,3,10,11) = 141.0
D(3,10,11,12) = 107.8
R(4,12) = 4.405
R(10,13) = 2.590

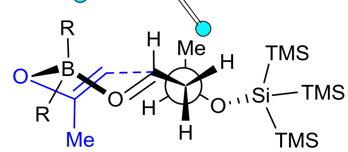
TS-E
1,3-*anti*, (ϕ = 60)



R(1,5) = 1.276
R(5,6) = 1.566
R(6,7) = 1.519
R(7,8) = 1.308
R(8,9) = 1.386
D(2,3,10,11) = 157.1
D(3,10,11,12) = 95.8
R(4,12) = 4.158

D(1,2,3,4) = 55.7
R(1,9) = 2.314



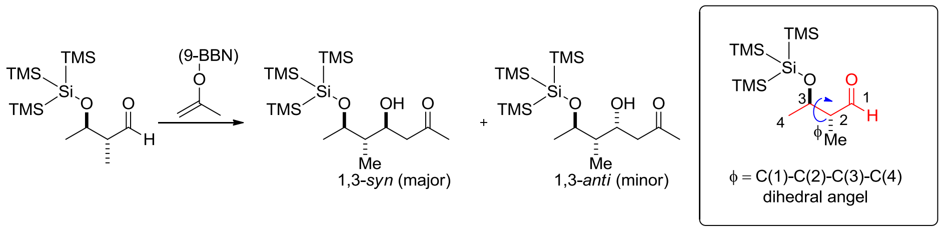


E

Figure S1. B3LYP optimized transition state structures and representative Newman projections of the enolborinate addition to β-super siloxy butanal. Mulliken electron population is in parenthesis.

Computational Data for Enolborinate Addition to α-Methyl β-Super Siloxy Butanal

Computational experiments were performed as described above to reveal the transition state structures of acetone 9-BBN enolborinate addition to α-Methyl β-Super Siloxy Butanal (**Scheme S-6**). Relative energies for transition state structures are shown in Table S-2. Structures and Newman projections are shown in **Figure S-2**, with full data following.



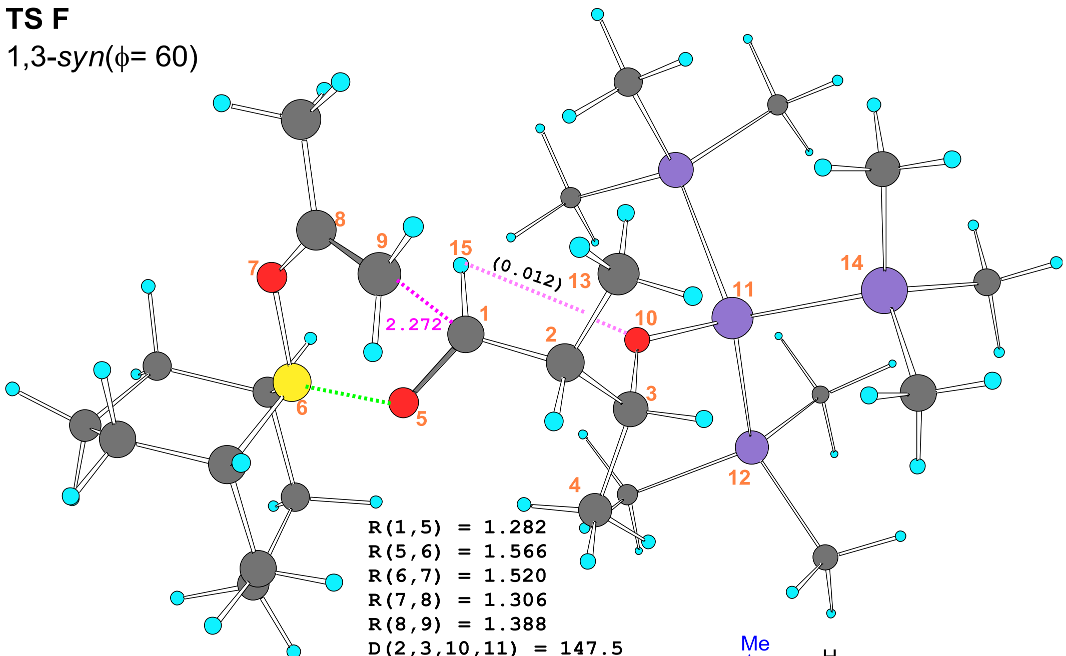
Scheme S-2: Enolborinate Addition to α-Methyl β-Super Siloxy Butanal

Table S-2: Calculated Transitions State Energies for Enolborinate Addition to α-methyl β-super Siloxy Butanal

TS	(ϕ)	1,3-*syn/anti*	Relative Electron Energy	Relative Free Energy
F	60	*syn*	0.45	0.00
G	180	*syn*	5.07	7.78
H	-60	*syn*	0.00	0.19
I	60	*anti*	0.09	0.40
J	-60	*anti*	0.92	1.57
ϕ = non-optimized dihedral angel. Optimized dihedral angel given in figure S2.				

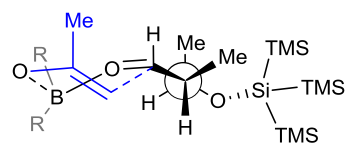
TS F

1,3-*syn*(ϕ= 60)



D(1,2,3,4) = -68.5
R(1,9) = 2.272
D(5,1,2,13) = -162.9

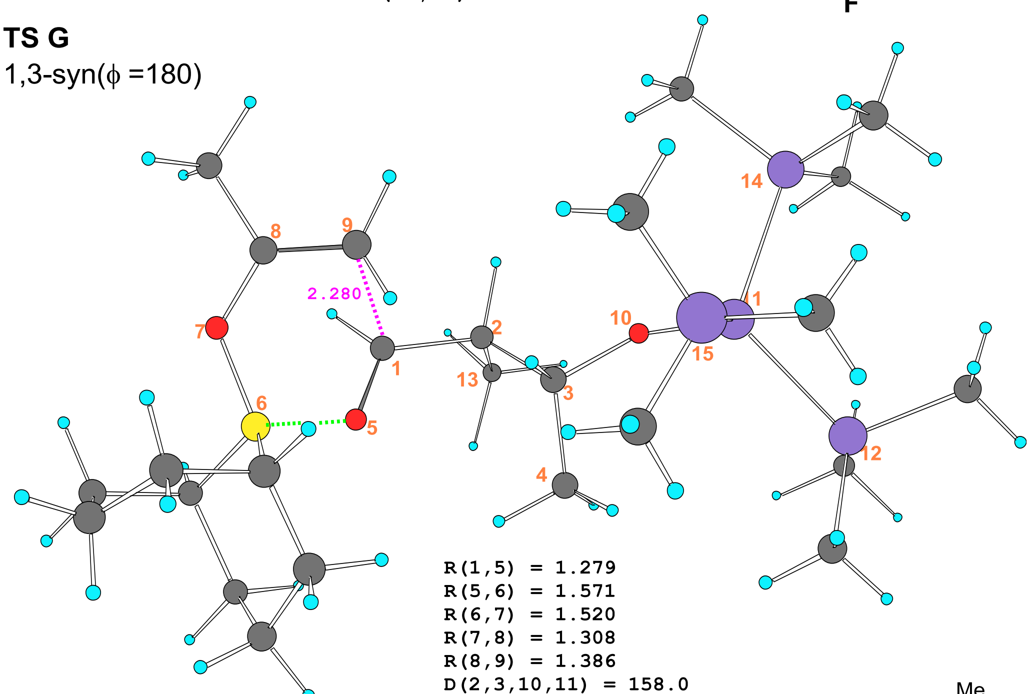
R(1,5) = 1.282
R(5,6) = 1.566
R(6,7) = 1.520
R(7,8) = 1.306
R(8,9) = 1.388
D(2,3,10,11) = 147.5
D(3,10,11,12) = 73.0
R(4,12) = 4.025
D(3,10,11,14) = -52.2
R(13,14) = 4.566
R(10,15) = 2.818



F

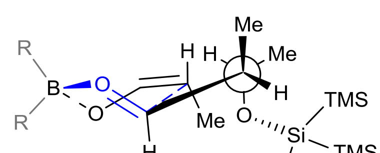
TS G

1,3-syn(ϕ =180)



D(1,2,3,4) = 78.7
R(1,9) = 2.280
D(5,1,2,13) = 97.3

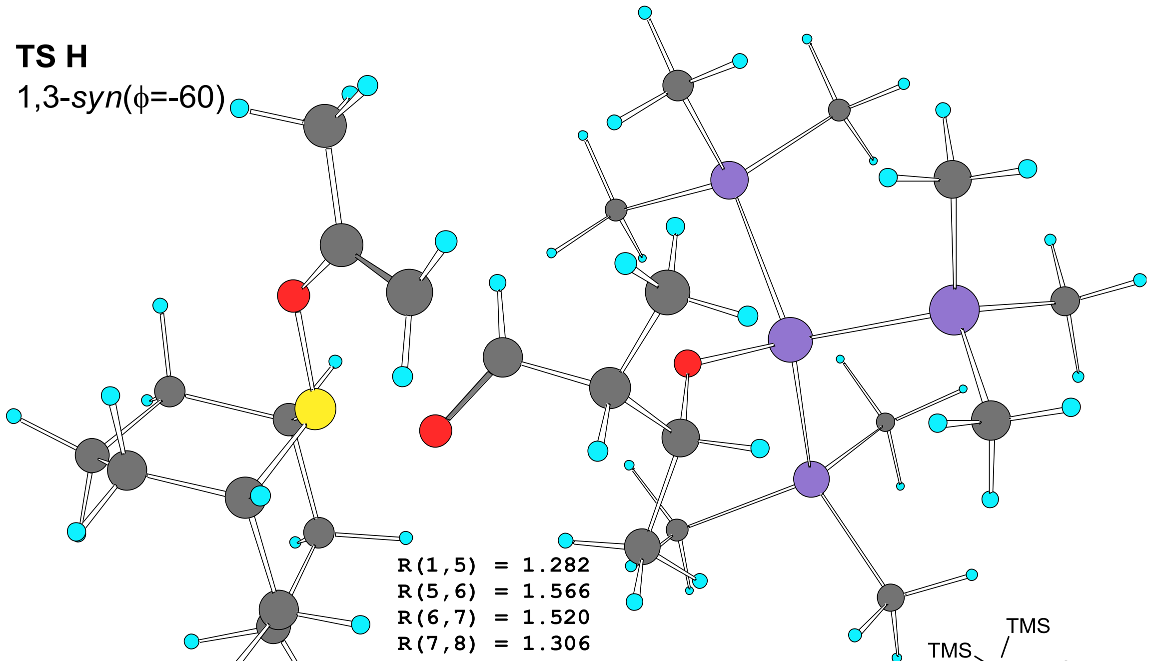
R(1,5) = 1.279
R(5,6) = 1.571
R(6,7) = 1.520
R(7,8) = 1.308
R(8,9) = 1.386
D(2,3,10,11) = 158.0
D(3,10,11,12) = 96.3
R(4,12) = 4.163
R(4,15) = 4.425
D(3,10,11,14) = -146.8
R(13,14) = 5.690
R(13,12) = 5.856



G

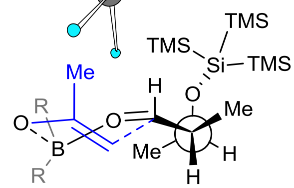
TS H

1,3-*syn*(ϕ=-60)



R(1,5) = 1.282
R(5,6) = 1.566
R(6,7) = 1.520
R(7,8) = 1.306
R(8,9) = 1.388
D(2,3,10,11) = 147.5
D(3,10,11,12) = 73.0
R(4,12) = 4.025
D(3,10,11,14) = -52.2
R(13,14) = 4.566
R(10,15) = 2.818

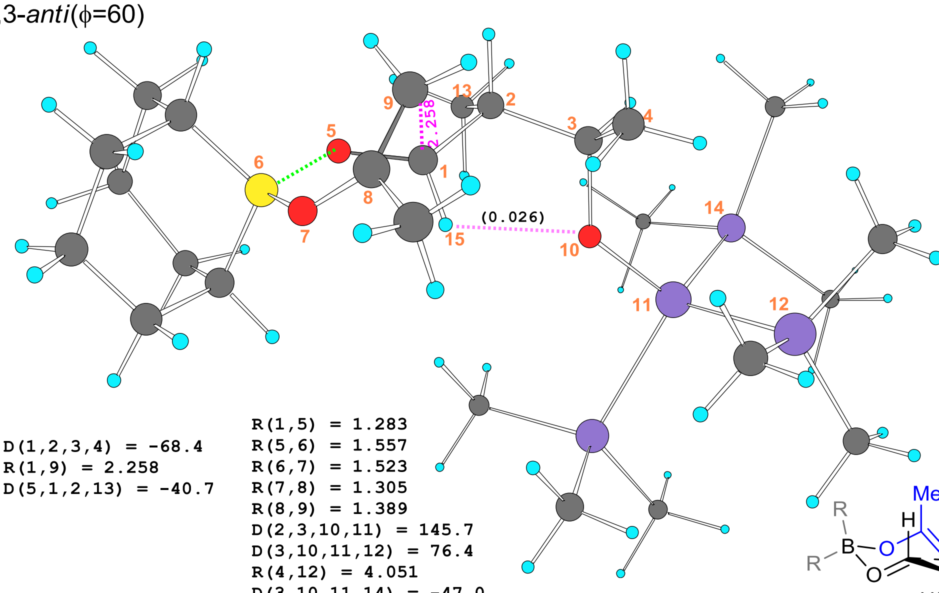
D(1,2,3,4) = -68.5
R(1,9) = 2.272
D(5,1,2,13) = -162.9



H

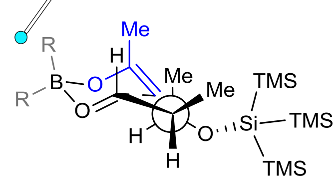
TS I

1,3-*anti*(ϕ=60)



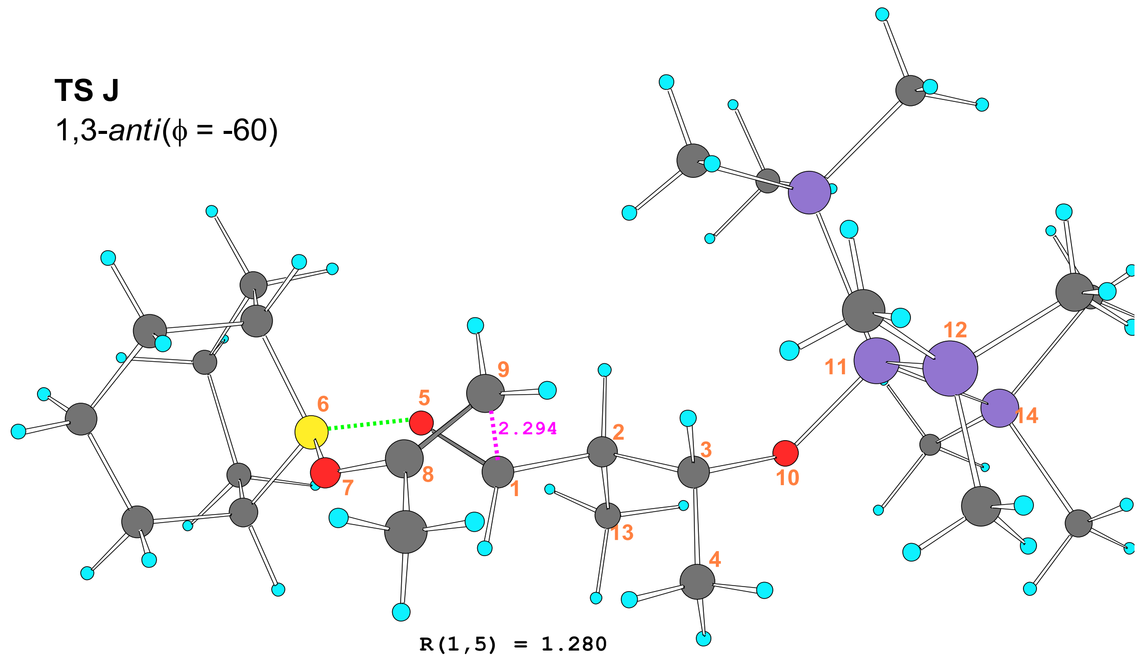
D(1,2,3,4) = -68.4
R(1,9) = 2.258
D(5,1,2,13) = -40.7

R(1,5) = 1.283
R(5,6) = 1.557
R(6,7) = 1.523
R(7,8) = 1.305
R(8,9) = 1.389
D(2,3,10,11) = 145.7
D(3,10,11,12) = 76.4
R(4,12) = 4.051
D(3,10,11,14) = -47.0
R(13,14) = 4.570
R(10,15) = 2.560



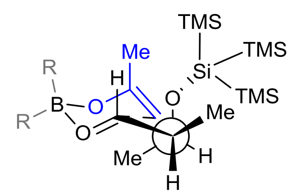
I

TS J
1,3-*anti*(ϕ = -60)



D(1,2,3,4) = 56.6
R(1,9) = 2.294
D(5,1,2,13) = -79.0

R(1,5) = 1.280
R(5,6) = 1.560
R(6,7) = 1.522
R(7,8) = 1.306
R(8,9) = 1.389
D(2,3,10,11) = 114.5
D(3,10,11,12) = 58.2
R(4,12) = 4.459
D(3,10,11,14) = 176.2
R(13,14) = 5.306



J

Figure S-2 Calculated Transition State Structures and Representative Newman Projections for Enolborinate Addition to *anti*-α-methyl β-super Siloxy Butanal

TS A
1,3-*syn*(ϕ=-60)
Method: B3LYP/6-31+G(d)
SCF Done: E(RB+HF-LYP) = -2355.18566238 A.U. after 9 cycles
Imaginary frequencies: 1(-214)
Zero-point correction= 0.736204 (Hartree/Particle)
Thermal correction to Energy= 0.782167
Thermal correction to Enthalpy= 0.783111
Thermal correction to Gibbs Free Energy= 0.655294
Sum of electronic and zero-point Energies= -2354.449458
Sum of electronic and thermal Energies= -2354.403495
Sum of electronic and thermal Enthalpies= -2354.402551
Sum of electronic and thermal Free Energies= -2354.530369

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.852159	2.530246	-1.554204

2	6	0	3.295613	2.581218	-0.244930
3	8	0	3.874131	1.589201	0.386450
4	6	0	3.011501	3.763121	0.646137
5	5	0	3.993316	0.156743	-0.093043
6	6	0	4.080495	-0.833226	1.176435
7	6	0	5.288097	-0.115676	-1.024051
8	6	0	5.253293	-1.585566	-1.513860
9	6	0	6.549885	0.257787	-0.202096
10	6	0	4.063829	-2.303308	0.685646
11	6	0	5.341138	-0.447544	1.993097
12	6	0	5.108027	-2.649797	-0.402054
13	6	0	6.661254	-0.414580	1.186697
14	8	0	2.710215	-0.121490	-0.961031
15	6	0	1.680057	0.632877	-0.942760
16	6	0	0.639235	0.470133	-2.012857
17	6	0	-0.493337	-0.509489	-1.604625
18	6	0	-0.012516	-1.944578	-1.389611
19	8	0	-1.109188	0.014798	-0.434029
20	14	0	-2.745322	-0.074432	0.073762
21	14	0	-3.167988	2.166068	0.780271
22	14	0	-2.860653	-1.597454	1.912293
23	14	0	-4.238076	-0.710856	-1.690043
24	6	0	-2.557955	3.365051	-0.566163
25	6	0	-5.018056	2.489123	1.091820
26	6	0	-2.213894	2.556887	2.380504
27	6	0	-3.751448	-2.342169	-2.545549
28	6	0	-5.966386	-0.958801	-0.928642
29	6	0	-4.372725	0.628278	-3.038179
30	6	0	-1.310878	-1.384252	2.990949
31	6	0	-4.405304	-1.238694	2.968845
32	6	0	-2.952338	-3.419934	1.364916
33	1	0	2.339488	3.399264	-1.956295
34	1	0	3.278538	1.845231	-2.274531
35	1	0	2.403667	3.456245	1.506544
36	1	0	2.502144	4.567623	0.109587
37	1	0	3.957140	4.148891	1.045881
38	1	0	3.211535	-0.702040	1.844212
39	1	0	5.296233	0.521349	-1.923869
40	1	0	6.156822	-1.810699	-2.103142
41	1	0	4.406951	-1.687041	-2.208296
42	1	0	7.460165	0.030877	-0.780123
43	1	0	6.544845	1.348228	-0.061427
44	1	0	4.196349	-2.990918	1.536437
45	1	0	3.061456	-2.512650	0.283659
46	1	0	5.464913	-1.130791	2.848697
47	1	0	5.167673	0.549056	2.422150
48	1	0	4.835507	-3.610562	-0.862869
49	1	0	6.081438	-2.821596	0.068503
50	1	0	7.423325	0.115560	1.776262
51	1	0	7.044550	-1.433734	1.070226
52	1	0	1.364269	1.077789	0.001855
53	1	0	0.175709	1.441583	-2.209389
54	1	0	1.118637	0.115136	-2.931446
55	1	0	-1.213463	-0.500923	-2.437473

56	1	0	-0.864651	-2.603528	-1.192171
57	1	0	0.677955	-2.006970	-0.542959
58	1	0	0.505778	-2.319164	-2.280547
59	1	0	-1.485419	3.234395	-0.753795
60	1	0	-2.717075	4.405820	-0.252670
61	1	0	-3.083205	3.220409	-1.517823
62	1	0	-5.160094	3.506322	1.481430
63	1	0	-5.441377	1.793913	1.826711
64	1	0	-5.610706	2.404902	0.172609
65	1	0	-2.582959	1.975287	3.233947
66	1	0	-1.143087	2.345667	2.272908
67	1	0	-2.320217	3.620261	2.635501
68	1	0	-2.809656	-2.259563	-3.100790
69	1	0	-4.532026	-2.624539	-3.265460
70	1	0	-3.645629	-3.168107	-1.832697
71	1	0	-6.692704	-1.173087	-1.724491
72	1	0	-6.320172	-0.071936	-0.389875
73	1	0	-5.987813	-1.804352	-0.230268
74	1	0	-4.754785	1.574706	-2.637230
75	1	0	-3.406503	0.836384	-3.514314
76	1	0	-5.064431	0.300094	-3.826109
77	1	0	-0.396925	-1.594550	2.423168
78	1	0	-1.341400	-2.075161	3.844315
79	1	0	-1.225841	-0.365869	3.387710
80	1	0	-4.463563	-1.957531	3.797519
81	1	0	-5.334012	-1.328234	2.392049
82	1	0	-4.382048	-0.234514	3.409211
83	1	0	-3.857673	-3.633900	0.783457
84	1	0	-2.086674	-3.714404	0.759495
85	1	0	-2.968741	-4.071619	2.249355

TS-B

1,3-*syn*(ϕ=60)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2355.18377975 A.U. after 8 cycles

Imaginary frequencies: 1(-245)

Zero-point correction= 0.736074 (Hartree/Particle)
Thermal correction to Energy= 0.781948
Thermal correction to Enthalpy= 0.782892
Thermal correction to Gibbs Free Energy= 0.655800
Sum of electronic and zero-point Energies= -2354.447706
Sum of electronic and thermal Energies= -2354.401832
Sum of electronic and thermal Enthalpies= -2354.400888
Sum of electronic and thermal Free Energies= -2354.527980

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.191355	2.307505	0.439954
2	6	0	-3.501775	2.585054	0.089092
3	8	0	-4.418161	1.677141	-0.132888
4	6	0	-3.962917	3.984360	-0.227463
5	5	0	-4.204195	0.180645	-0.263572
6	6	0	-5.316525	-0.437490	-1.252448
7	6	0	-4.287595	-0.615304	1.140738
8	6	0	-3.982986	-2.114106	0.890040
9	6	0	-5.686563	-0.343970	1.756284
10	6	0	-5.010210	-1.938126	-1.493558
11	6	0	-6.711192	-0.161744	-0.630921
12	6	0	-4.831866	-2.787390	-0.213351
13	6	0	-6.887584	-0.643054	0.828388
14	8	0	-2.756047	-0.006183	-0.850334
15	6	0	-2.109916	0.944242	-1.407285
16	6	0	-0.654366	0.789304	-1.745595
17	6	0	0.178444	-0.158097	-0.863701
18	6	0	-0.044068	-1.630304	-1.208983
19	8	0	1.540021	0.218979	-1.062041
20	14	0	2.901348	-0.047376	-0.056939
21	14	0	4.297445	1.748780	-0.775913
22	14	0	3.956119	-2.149267	-0.524752
23	14	0	2.358007	0.136220	2.270838
24	6	0	3.277357	3.353776	-0.816453
25	6	0	5.794713	2.008291	0.371719
26	6	0	4.940249	1.424964	-2.537765
27	6	0	1.049259	-1.125419	2.839875
28	6	0	3.935804	-0.187342	3.287720
29	6	0	1.717764	1.877947	2.698718
30	6	0	3.818697	-2.557949	-2.377458
31	6	0	5.802173	-2.037616	-0.061126
32	6	0	3.229046	-3.608761	0.461696
33	1	0	-1.502374	3.140062	0.548902
34	1	0	-1.928226	1.393492	0.954859
35	1	0	-4.309805	4.047127	-1.266682

36	1	0	-3.174663	4.722994	-0.061635
37	1	0	-4.820399	4.233581	0.409155
38	1	0	-5.297242	0.062026	-2.236694
39	1	0	-3.543764	-0.253405	1.870034
40	1	0	-4.099527	-2.685666	1.824808
41	1	0	-2.921544	-2.201137	0.616793
42	1	0	-5.807069	-0.917882	2.688943
43	1	0	-5.724306	0.715875	2.046214
44	1	0	-5.798375	-2.393514	-2.114207
45	1	0	-4.085838	-2.002434	-2.086604
46	1	0	-7.500859	-0.614582	-1.251704
47	1	0	-6.882234	0.923130	-0.665305
48	1	0	-4.365826	-3.746059	-0.484094
49	1	0	-5.814686	-3.049001	0.191485
50	1	0	-7.786480	-0.170829	1.250566
51	1	0	-7.096527	-1.717719	0.836076
52	1	0	-2.663664	1.668259	-2.011750
53	1	0	-0.609240	0.444289	-2.792963
54	1	0	-0.193173	1.781890	-1.740092
55	1	0	-0.098499	0.011884	0.186785
56	1	0	0.543941	-2.276427	-0.548963
57	1	0	0.265408	-1.823162	-2.243259
58	1	0	-1.098550	-1.899856	-1.099058
59	1	0	2.400655	3.242562	-1.465548
60	1	0	3.882789	4.182449	-1.208312
61	1	0	2.921307	3.642549	0.179661
62	1	0	6.432948	2.810206	-0.023771
63	1	0	6.414475	1.107892	0.459365
64	1	0	5.489398	2.302417	1.383417
65	1	0	5.604171	0.553241	-2.579613
66	1	0	4.115510	1.250996	-3.239497
67	1	0	5.509602	2.291926	-2.900076
68	1	0	0.080919	-0.982221	2.346387
69	1	0	0.883451	-1.021329	3.921137
70	1	0	1.365912	-2.158350	2.653576
71	1	0	3.716917	-0.070075	4.357856
72	1	0	4.746230	0.507657	3.039018
73	1	0	4.313778	-1.206580	3.141352
74	1	0	2.475569	2.647017	2.506910
75	1	0	0.824234	2.141843	2.119887
76	1	0	1.450479	1.933775	3.762826
77	1	0	2.772945	-2.663649	-2.688823
78	1	0	4.330536	-3.505102	-2.595860
79	1	0	4.272663	-1.779946	-3.002571
80	1	0	6.283391	-3.013258	-0.213963
81	1	0	5.947442	-1.761809	0.990546
82	1	0	6.341752	-1.306379	-0.674867
83	1	0	3.340942	-3.466690	1.543549
84	1	0	2.164327	-3.769505	0.255650
85	1	0	3.757244	-4.534914	0.196129

TS-C

1,3-*syn*(ϕ=180)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2355.17844557 A.U. after 9 cycles

Imaginary frequencies: 1(-192)

Zero-point correction= 0.736117 (Hartree/Particle)
Thermal correction to Energy= 0.781821
Thermal correction to Enthalpy= 0.782766
Thermal correction to Gibbs Free Energy= 0.657490
Sum of electronic and zero-point Energies= -2354.442329
Sum of electronic and thermal Energies= -2354.396624
Sum of electronic and thermal Enthalpies= -2354.395680
Sum of electronic and thermal Free Energies= -2354.520955

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.363738	-2.615229	-0.671728
2	6	0	2.641866	-2.548994	-0.173006
3	8	0	3.041932	-1.516464	0.547542
4	6	0	3.680117	-3.604262	-0.460046
5	5	0	3.371945	-0.145667	-0.053762
6	6	0	4.770155	-0.087671	-0.866453
7	6	0	3.396415	0.992732	1.070994
8	6	0	3.525287	2.376438	0.383706
9	6	0	4.538264	0.662639	2.067153
10	6	0	4.903094	1.302764	-1.544610
11	6	0	5.913060	-0.411870	0.134443
12	6	0	4.704850	2.516325	-0.606374
13	6	0	5.927454	0.443285	1.423545
14	8	0	2.128611	0.094609	-0.998655
15	6	0	1.853098	-0.708376	-1.942194
16	6	0	0.590769	-0.530531	-2.741802
17	6	0	-0.545660	0.288164	-2.110367
18	6	0	-1.577575	0.634223	-3.188389
19	8	0	-1.118302	-0.461139	-1.041657
20	14	0	-2.349702	0.035249	0.057586
21	14	0	-1.862733	-1.207235	2.047503
22	14	0	-4.476515	-0.664726	-0.809296
23	14	0	-2.329502	2.388527	0.530562
24	6	0	-0.107371	-0.859927	2.677920
25	6	0	-3.064872	-0.744069	3.451879
26	6	0	-2.039510	-3.073883	1.715109
27	6	0	-2.436369	3.497562	-1.016673
28	6	0	-3.863936	2.771715	1.595182
29	6	0	-0.782937	2.912652	1.502217
30	6	0	-4.255450	-2.297542	-1.762477
31	6	0	-5.708798	-0.973766	0.611237
32	6	0	-5.302673	0.593367	-1.979955

33	1	0	1.066749	-3.469380	-1.274953
34	1	0	0.573386	-1.971289	-0.307976
35	1	0	4.538900	-3.168954	-0.984798
36	1	0	3.275354	-4.432510	-1.049025
37	1	0	4.058417	-3.999844	0.490632
38	1	0	4.843325	-0.838636	-1.674297
39	1	0	2.457554	1.000640	1.646676
40	1	0	3.600098	3.175885	1.138218
41	1	0	2.589220	2.567161	-0.162769
42	1	0	4.622719	1.451732	2.831675
43	1	0	4.253278	-0.252646	2.604541
44	1	0	5.882145	1.393648	-2.042009
45	1	0	4.154596	1.362864	-2.350259
46	1	0	6.891808	-0.320804	-0.363679
47	1	0	5.816263	-1.467692	0.423338
48	1	0	4.551956	3.416835	-1.219137
49	1	0	5.629587	2.700515	-0.050569
50	1	0	6.587089	-0.041019	2.158187
51	1	0	6.393392	1.411819	1.214048
52	1	0	2.669180	-1.236664	-2.441898
53	1	0	0.914650	-0.013563	-3.661016
54	1	0	0.218407	-1.509701	-3.063830
55	1	0	-0.117805	1.217407	-1.708144
56	1	0	-2.395436	1.224919	-2.768865
57	1	0	-1.999572	-0.277344	-3.628278
58	1	0	-1.120890	1.227315	-3.990314
59	1	0	0.670200	-1.066853	1.936111
60	1	0	0.097525	-1.488990	3.555597
61	1	0	0.007215	0.184895	2.989178
62	1	0	-2.852655	-1.372022	4.328204
63	1	0	-4.117361	-0.893854	3.186892
64	1	0	-2.942540	0.299948	3.764807
65	1	0	-3.067606	-3.348489	1.448810
66	1	0	-1.381604	-3.408412	0.904538
67	1	0	-1.768870	-3.640905	2.616382
68	1	0	-1.547896	3.414573	-1.653731
69	1	0	-2.512805	4.546901	-0.699466
70	1	0	-3.315656	3.276318	-1.633271
71	1	0	-3.856852	3.832679	1.880444
72	1	0	-3.891226	2.183842	2.519916
73	1	0	-4.799853	2.584843	1.054480
74	1	0	-0.746259	2.444438	2.492753
75	1	0	0.145267	2.650872	0.981207
76	1	0	-0.785648	4.001206	1.651309
77	1	0	-3.579083	-2.181587	-2.617509
78	1	0	-5.222785	-2.648787	-2.146909
79	1	0	-3.842963	-3.086479	-1.122355
80	1	0	-6.688233	-1.248155	0.196213
81	1	0	-5.854988	-0.085813	1.238306
82	1	0	-5.387085	-1.794000	1.263587
83	1	0	-5.505694	1.548193	-1.479651
84	1	0	-4.698121	0.803432	-2.869562
85	1	0	-6.266220	0.193914	-2.325630

TS D

1,3-*anti*(ϕ=-60)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2355.18355023 A.U. after 8 cycles

Imaginary frequencies: 1(-255)

Zero-point correction= 0.736194 (Hartree/Particle)
Thermal correction to Energy= 0.782089
Thermal correction to Enthalpy= 0.783034
Thermal correction to Gibbs Free Energy= 0.655510
Sum of electronic and zero-point Energies= -2354.447356
Sum of electronic and thermal Energies= -2354.401461
Sum of electronic and thermal Enthalpies= -2354.400517
Sum of electronic and thermal Free Energies= -2354.528040

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.740914	2.735081	-1.179013
2	6	0	-3.199035	2.591690	0.122208
3	8	0	-3.809993	1.531330	0.580443
4	6	0	-2.884614	3.605642	1.192333
5	5	0	-3.950582	0.187293	-0.117870
6	6	0	-5.297424	0.058102	-1.002299
7	6	0	-3.966175	-0.992705	0.982998
8	6	0	-3.971016	-2.362350	0.255817
9	6	0	-5.178604	-0.762933	1.920732
10	6	0	-5.284427	-1.310647	-1.729681
11	6	0	-6.512564	0.272925	-0.060124
12	6	0	-5.072167	-2.540309	-0.815872
13	6	0	-6.541084	-0.619086	1.203145
14	8	0	-2.716242	0.048585	-1.061198
15	6	0	-1.650416	0.741368	-0.915181
16	6	0	-0.611225	0.644712	-2.004424
17	6	0	0.786759	1.153178	-1.614760
18	6	0	0.873852	2.669902	-1.428311
19	8	0	1.169300	0.475616	-0.421551
20	14	0	2.692301	-0.148333	0.064376
21	14	0	2.107593	-2.299620	0.921374
22	14	0	3.535671	1.272168	1.791042
23	14	0	4.246671	-0.327402	-1.751333
24	6	0	0.962416	-3.166672	-0.323752
25	6	0	3.640456	-3.392060	1.212162
26	6	0	1.168912	-2.134893	2.567615
27	6	0	4.544984	1.326204	-2.650488
28	6	0	5.915879	-0.893563	-1.030041
29	6	0	3.691948	-1.602790	-3.051868
30	6	0	2.076436	1.889167	2.843319
31	6	0	4.744248	0.315405	2.909553
32	6	0	4.459690	2.798777	1.122048
33	1	0	-3.200251	2.202958	-2.001323
34	1	0	-2.209577	3.647368	-1.433371
35	1	0	-2.278007	3.148931	1.984644

36	1	0	-3.819212	3.938916	1.659283
37	1	0	-2.361718	4.477352	0.790762
38	1	0	-5.357000	0.836671	-1.781025
39	1	0	-3.059573	-0.961342	1.612197
40	1	0	-4.053568	-3.181915	0.987961
41	1	0	-2.991768	-2.489000	-0.228603
42	1	0	-5.250300	-1.578370	2.658472
43	1	0	-4.987035	0.153123	2.496746
44	1	0	-6.218665	-1.448171	-2.297560
45	1	0	-4.477560	-1.286123	-2.475982
46	1	0	-7.453003	0.129489	-0.616203
47	1	0	-6.506469	1.326024	0.256249
48	1	0	-4.820162	-3.408681	-1.441967
49	1	0	-6.017473	-2.800590	-0.328795
50	1	0	-7.273380	-0.205411	1.911722
51	1	0	-6.922303	-1.611307	0.940741
52	1	0	-1.316748	0.991290	0.092697
53	1	0	-0.534482	-0.424256	-2.247796
54	1	0	-0.967217	1.141907	-2.914328
55	1	0	1.460881	0.870331	-2.437234
56	1	0	1.910148	2.969656	-1.238892
57	1	0	0.262833	2.997546	-0.581529
58	1	0	0.529130	3.194538	-2.327974
59	1	0	0.044259	-2.589871	-0.485255
60	1	0	0.668607	-4.156094	0.052059
61	1	0	1.443742	-3.310992	-1.298261
62	1	0	3.335606	-4.348406	1.658447
63	1	0	4.359814	-2.925616	1.896217
64	1	0	4.167791	-3.621630	0.278111
65	1	0	1.798336	-1.721053	3.364824
66	1	0	0.287961	-1.489855	2.465921
67	1	0	0.818323	-3.120758	2.902102
68	1	0	3.647758	1.693960	-3.162494
69	1	0	5.325821	1.195125	-3.412339
70	1	0	4.882045	2.111424	-1.963853
71	1	0	6.643190	-1.030826	-1.841750
72	1	0	5.837508	-1.845950	-0.493101
73	1	0	6.334803	-0.153737	-0.337018
74	1	0	3.580680	-2.605456	-2.622229
75	1	0	2.733664	-1.332898	-3.512938
76	1	0	4.437267	-1.668343	-3.856382
77	1	0	1.362789	2.457106	2.234400
78	1	0	2.432514	2.549150	3.646038
79	1	0	1.527862	1.062117	3.309166
80	1	0	5.121622	0.973551	3.703975
81	1	0	5.612903	-0.060387	2.354940
82	1	0	4.262585	-0.542060	3.394358
83	1	0	5.363630	2.522325	0.565608
84	1	0	3.831628	3.405609	0.458477
85	1	0	4.771367	3.441688	1.956773

TS-E

1,3-*anti*(ϕ=60)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2355.18425994 A.U. after 13 cycles

Imaginary frequencies: 1(-220)

Zero-point correction= 0.735999 (Hartree/Particle)
Thermal correction to Energy= 0.781976
Thermal correction to Enthalpy= 0.782920
Thermal correction to Gibbs Free Energy= 0.655514
Sum of electronic and zero-point Energies= -2354.448261
Sum of electronic and thermal Energies= -2354.402284
Sum of electronic and thermal Enthalpies= -2354.401340
Sum of electronic and thermal Free Energies= -2354.528746

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.332153	-1.598124	-1.154350
2	6	0	3.375085	-2.183629	-0.453463
3	8	0	4.408704	-1.540163	0.023684
4	6	0	3.337811	-3.632593	-0.038107
5	5	0	4.604278	-0.035217	0.095229
6	6	0	5.323495	0.588672	-1.210466
7	6	0	5.505014	0.330776	1.381883
8	6	0	5.578559	1.872681	1.529188
9	6	0	6.881727	-0.362484	1.215702
10	6	0	5.382244	2.129872	-1.054335
11	6	0	6.707410	-0.095492	-1.366593
12	6	0	6.020284	2.638566	0.259553
13	6	0	7.612142	-0.056774	-0.112795
14	8	0	3.171582	0.586075	0.213352
15	6	0	2.158344	-0.090983	0.592706
16	6	0	0.806229	0.550196	0.485513
17	6	0	-0.422436	-0.370982	0.566013
18	6	0	-0.453558	-1.223556	1.836347
19	8	0	-1.548685	0.496966	0.501427
20	14	0	-3.164168	0.179475	0.023117
21	14	0	-3.749980	2.272788	-0.957911
22	14	0	-4.500027	-0.274437	1.957209
23	14	0	-3.327103	-1.610211	-1.561310
24	6	0	-2.379527	2.781959	-2.173447
25	6	0	-5.406187	2.191838	-1.893828
26	6	0	-3.873899	3.620793	0.379078
27	6	0	-2.576905	-3.242285	-0.922171
28	6	0	-5.173276	-1.926460	-1.907427
29	6	0	-2.473431	-1.184026	-3.209394
30	6	0	-3.861629	0.760260	3.419481
31	6	0	-6.314932	0.198776	1.618983
32	6	0	-4.491903	-2.107599	2.480237
33	1	0	2.465362	-0.679970	-1.710721
34	1	0	1.513877	-2.238400	-1.470468

35	1	0	3.360415	-3.717858	1.055672
36	1	0	4.235390	-4.137941	-0.414354
37	1	0	2.455431	-4.148456	-0.425162
38	1	0	4.758845	0.379837	-2.134252
39	1	0	5.054623	-0.064086	2.309563
40	1	0	6.251008	2.144214	2.358712
41	1	0	4.580468	2.230845	1.821549
42	1	0	7.545114	-0.098975	2.055092
43	1	0	6.719613	-1.447235	1.284432
44	1	0	5.920881	2.576851	-1.905291
45	1	0	4.353299	2.512057	-1.114148
46	1	0	7.255378	0.347223	-2.213750
47	1	0	6.530965	-1.146667	-1.636773
48	1	0	5.774158	3.703101	0.384087
49	1	0	7.111042	2.603147	0.173353
50	1	0	8.428497	-0.781976	-0.243145
51	1	0	8.102267	0.919950	-0.045106
52	1	0	2.309896	-0.876487	1.336374
53	1	0	0.738627	1.264315	1.323661
54	1	0	0.764833	1.147367	-0.430626
55	1	0	-0.418201	-1.035448	-0.309827
56	1	0	-1.370279	-1.820540	1.873713
57	1	0	-0.421625	-0.587016	2.728703
58	1	0	0.390975	-1.921899	1.874031
59	1	0	-1.407511	2.831904	-1.668779
60	1	0	-2.589704	3.774905	-2.593655
61	1	0	-2.285492	2.079904	-3.010217
62	1	0	-5.663088	3.186055	-2.283970
63	1	0	-6.233161	1.867861	-1.250470
64	1	0	-5.360590	1.507101	-2.749779
65	1	0	-4.703918	3.442078	1.073357
66	1	0	-2.951230	3.683837	0.968469
67	1	0	-4.038423	4.601845	-0.087231
68	1	0	-1.495362	-3.167830	-0.758203
69	1	0	-2.742900	-4.038917	-1.660472
70	1	0	-3.034791	-3.564919	0.020327
71	1	0	-5.280968	-2.707312	-2.672543
72	1	0	-5.687255	-1.030940	-2.276078
73	1	0	-5.705180	-2.270340	-1.011861
74	1	0	-2.949840	-0.329883	-3.705538
75	1	0	-1.413536	-0.936398	-3.073403
76	1	0	-2.528790	-2.038518	-3.897673
77	1	0	-2.818120	0.519693	3.654621
78	1	0	-4.462051	0.565972	4.318583
79	1	0	-3.911680	1.835092	3.208836
80	1	0	-6.933273	-0.049587	2.492321
81	1	0	-6.731640	-0.339661	0.758790
82	1	0	-6.432153	1.272458	1.429199
83	1	0	-4.886516	-2.761118	1.692731
84	1	0	-3.489568	-2.467666	2.741584
85	1	0	-5.127333	-2.241520	3.366576

TS-F

1,3-*syn*(ϕ = -60)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2394.49743653 A.U. after 7 cycles

Imaginary frequencies: 1(-242)

Zero-point correction= 0.764680 (Hartree/Particle)
Thermal correction to Energy= 0.811936
Thermal correction to Enthalpy= 0.812880
Thermal correction to Gibbs Free Energy= 0.683448
Sum of electronic and zero-point Energies= -2393.732757
Sum of electronic and thermal Energies= -2393.685500
Sum of electronic and thermal Enthalpies= -2393.684556
Sum of electronic and thermal Free Energies= -2393.813988

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.188097	-2.882003	-0.953782
2	6	0	-3.635895	-2.589510	0.326578
3	8	0	-3.997588	-1.401023	0.728239
4	6	0	-3.596006	-3.608199	1.436448
5	5	0	-3.817855	-0.097751	-0.032586
6	6	0	-3.682740	1.114043	1.023503
7	6	0	-5.047886	0.248289	-1.025436
8	6	0	-4.716629	1.557140	-1.786793
9	6	0	-6.346709	0.307488	-0.179404
10	6	0	-3.381469	2.432442	0.268016
11	6	0	-4.981571	1.151859	1.870671
12	6	0	-4.345070	2.765064	-0.896153
13	6	0	-6.293956	1.237664	1.055612
14	8	0	-2.527194	-0.276161	-0.901877
15	6	0	-1.669576	-1.209617	-0.713516
16	6	0	-0.613221	-1.455679	-1.766938
17	6	0	0.469573	-0.325616	-1.733798
18	6	0	0.051764	-2.830735	-1.607876
19	6	0	-0.045260	1.038172	-2.191182
20	8	0	1.012436	-0.267973	-0.416570
21	14	0	2.599744	0.137473	0.088888
22	14	0	2.487841	-0.494988	2.386751
23	14	0	3.080251	2.480299	-0.104653
24	14	0	4.262220	-1.148694	-1.069501
25	6	0	1.651627	-2.198208	2.525432
26	6	0	4.214758	-0.606653	3.181154
27	6	0	1.450721	0.752901	3.378459
28	6	0	4.122122	-1.040628	-2.968207
29	6	0	5.984632	-0.490600	-0.588543
30	6	0	4.188066	-2.991185	-0.594169
31	6	0	1.582544	3.537256	0.400535
32	6	0	4.522910	2.902819	1.068010
33	6	0	3.617072	2.994611	-1.859850
34	1	0	-2.886569	-3.904663	-1.158040
35	1	0	-3.496424	-2.294133	-1.807970

36	1	0	-2.942230	-3.263813	2.247408
37	1	0	-3.255206	-4.585127	1.084552
38	1	0	-4.601052	-3.716808	1.861859
39	1	0	-2.846528	0.941517	1.722772
40	1	0	-5.201053	-0.533850	-1.787360
41	1	0	-5.560201	1.842453	-2.435858
42	1	0	-3.874154	1.346748	-2.460984
43	1	0	-7.198678	0.605389	-0.811647
44	1	0	-6.567923	-0.713717	0.163022
45	1	0	-3.369014	3.280563	0.971299
46	1	0	-2.360328	2.363971	-0.133573
47	1	0	-4.948930	1.994850	2.579542
48	1	0	-5.007816	0.240161	2.483384
49	1	0	-3.887606	3.542856	-1.525047
50	1	0	-5.257973	3.218114	-0.496396
51	1	0	-7.138780	0.996141	1.716861
52	1	0	-6.461061	2.273006	0.740698
53	1	0	-1.418903	-1.492076	0.311636
54	1	0	-1.098709	-1.389258	-2.748686
55	1	0	1.248572	-0.650653	-2.440285
56	1	0	0.864329	-2.942618	-2.334687
57	1	0	-0.660369	-3.642779	-1.774404
58	1	0	0.479738	-2.947966	-0.606747
59	1	0	0.783173	1.751127	-2.248849
60	1	0	-0.797173	1.431835	-1.504047
61	1	0	-0.495034	0.965663	-3.188808
62	1	0	0.650928	-2.182824	2.077915
63	1	0	1.542196	-2.484639	3.580293
64	1	0	2.229974	-2.983888	2.024823
65	1	0	4.117644	-0.863159	4.244937
66	1	0	4.764495	0.340351	3.122507
67	1	0	4.834305	-1.381920	2.713839
68	1	0	1.927212	1.739715	3.421993
69	1	0	0.452234	0.883213	2.944487
70	1	0	1.322135	0.402774	4.411788
71	1	0	3.223489	-1.542617	-3.346522
72	1	0	4.989277	-1.533713	-3.429321
73	1	0	4.102413	-0.004848	-3.327370
74	1	0	6.761085	-1.124292	-1.038731
75	1	0	6.145415	-0.494456	0.496035
76	1	0	6.149748	0.532863	-0.946658
77	1	0	4.397055	-3.145302	0.471247
78	1	0	3.207572	-3.433521	-0.807045
79	1	0	4.938398	-3.557177	-1.163143
80	1	0	0.720066	3.376381	-0.255775
81	1	0	1.843759	4.603346	0.351099
82	1	0	1.259685	3.320856	1.425535
83	1	0	4.796680	3.960193	0.950272
84	1	0	5.419268	2.306136	0.861258
85	1	0	4.255353	2.749837	2.120458
86	1	0	4.540529	2.489885	-2.169170
87	1	0	2.852453	2.779937	-2.615698
88	1	0	3.809574	4.075990	-1.887533

TS G

1,3-*syn*(ϕ = 60)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2394.49672589 A.U. after 9 cycles

Imaginary frequencies: 1(-246)

Zero-point correction= 0.764422 (Hartree/Particle)
Thermal correction to Energy= 0.811772
Thermal correction to Enthalpy= 0.812716
Thermal correction to Gibbs Free Energy= 0.682435
Sum of electronic and zero-point Energies= -2393.732304
Sum of electronic and thermal Energies= -2393.684954
Sum of electronic and thermal Enthalpies= -2393.684010
Sum of electronic and thermal Free Energies= -2393.814291

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.137059	2.249457	0.619387
2	6	0	-3.451207	2.555894	0.303577
3	8	0	-4.378584	1.667047	0.057721
4	6	0	-3.901479	3.971902	0.052651
5	5	0	-4.177190	0.173744	-0.140831
6	6	0	-5.303738	-0.390577	-1.145933
7	6	0	-4.264157	-0.674450	1.232232
8	6	0	-3.979510	-2.166217	0.922990
9	6	0	-5.656510	-0.410049	1.865580
10	6	0	-5.017668	-1.884691	-1.445829
11	6	0	-6.691450	-0.121134	-0.506924
12	6	0	-4.843153	-2.785124	-0.200517
13	6	0	-6.866586	-0.656474	0.933703
14	8	0	-2.738280	0.000774	-0.746455
15	6	0	-2.095531	0.974779	-1.270599
16	6	0	-0.647656	0.828952	-1.669887
17	6	0	0.178197	-0.148036	-0.797848
18	6	0	-0.587947	0.515655	-3.184768
19	6	0	-0.030343	-1.628839	-1.116231
20	8	0	1.543681	0.226621	-0.986385
21	14	0	2.905893	-0.062495	0.007405
22	14	0	4.176865	1.914591	-0.406414
23	14	0	4.098027	-2.002144	-0.735664
24	14	0	2.372486	-0.253608	2.336034
25	6	0	3.003475	3.411238	-0.348042
26	6	0	5.556499	2.177408	0.879807
27	6	0	4.971942	1.869845	-2.135891
28	6	0	1.079087	-1.600200	2.707978
29	6	0	3.969989	-0.726738	3.261377
30	6	0	1.738588	1.389163	3.061522
31	6	0	3.992819	-2.137157	-2.630064
32	6	0	5.929193	-1.838889	-0.233189
33	6	0	3.451916	-3.634846	0.004357
34	1	0	-1.437530	3.070164	0.749693
35	1	0	-1.878501	1.316074	1.100885

36	1	0	-4.260232	4.082239	-0.978567
37	1	0	-3.103598	4.694964	0.239684
38	1	0	-4.748494	4.202149	0.710066
39	1	0	-5.282831	0.145656	-2.110646
40	1	0	-3.512155	-0.349342	1.970606
41	1	0	-4.098531	-2.772024	1.835634
42	1	0	-2.920810	-2.255802	0.640269
43	1	0	-5.779802	-1.019109	2.775317
44	1	0	-5.678971	0.637770	2.197518
45	1	0	-5.814853	-2.306021	-2.078963
46	1	0	-4.097329	-1.937437	-2.046241
47	1	0	-7.490269	-0.539129	-1.140374
48	1	0	-6.848445	0.966347	-0.498069
49	1	0	-4.391542	-3.738581	-0.511288
50	1	0	-5.827215	-3.049306	0.199493
51	1	0	-7.756587	-0.188867	1.379246
52	1	0	-7.090204	-1.727720	0.901132
53	1	0	-2.660392	1.721115	-1.837860
54	1	0	-0.189220	1.815153	-1.531786
55	1	0	-0.102115	0.029446	0.250595
56	1	0	0.458543	0.426600	-3.492684
57	1	0	-1.045035	1.323325	-3.768107
58	1	0	-1.107055	-0.415887	-3.432042
59	1	0	0.521993	-2.247296	-0.400767
60	1	0	0.337127	-1.864777	-2.120317
61	1	0	-1.088389	-1.898845	-1.051499
62	1	0	2.207749	3.312736	-1.096001
63	1	0	3.552553	4.338542	-0.561074
64	1	0	2.527366	3.523061	0.633432
65	1	0	6.137584	3.074713	0.626671
66	1	0	6.256502	1.334193	0.920430
67	1	0	5.151557	2.324200	1.888672
68	1	0	5.736420	1.087892	-2.219982
69	1	0	4.223197	1.690829	-2.917116
70	1	0	5.457557	2.830769	-2.354830
71	1	0	0.095848	-1.368035	2.282848
72	1	0	0.950617	-1.698558	3.794795
73	1	0	1.384297	-2.580030	2.322173
74	1	0	3.775813	-0.752573	4.342380
75	1	0	4.782464	-0.010994	3.089718
76	1	0	4.333204	-1.720302	2.971643
77	1	0	2.487979	2.185721	2.979252
78	1	0	0.826977	1.737957	2.561244
79	1	0	1.503053	1.265309	4.127393
80	1	0	2.956114	-2.265727	-2.963055
81	1	0	4.567668	-3.003760	-2.984119
82	1	0	4.391761	-1.244983	-3.126851
83	1	0	6.481819	-2.740899	-0.529352
84	1	0	6.050433	-1.720805	0.850594
85	1	0	6.413477	-0.983036	-0.718610
86	1	0	3.522185	-3.650090	1.098868
87	1	0	2.407463	-3.830042	-0.266477
88	1	0	4.050138	-4.475248	-0.374151

TS H

1,3-*syn* (ϕ = 180)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2394.48935655 A.U. after 8 cycles

Imaginary frequencies: 1(-202)

Zero-point correction= 0.764742 (Hartree/Particle)
Thermal correction to Energy= 0.810884
Thermal correction to Enthalpy= 0.811829
Thermal correction to Gibbs Free Energy= 0.687466
Sum of electronic and zero-point Energies= -2393.724615
Sum of electronic and thermal Energies= -2393.678472
Sum of electronic and thermal Enthalpies= -2393.677528
Sum of electronic and thermal Free Energies= -2393.801890

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.268734	2.375413	1.130420
2	6	0	2.537020	2.474760	0.609992
3	8	0	2.964109	1.644777	-0.323133
4	6	0	3.541455	3.484329	1.105999
5	5	0	3.300709	0.168691	-0.068962
6	6	0	4.712047	-0.055707	0.692555
7	6	0	3.331252	-0.665472	-1.434972
8	6	0	3.490404	-2.171091	-1.100642
9	6	0	4.455569	-0.084626	-2.331663
10	6	0	4.879476	-1.565322	1.014515
11	6	0	5.835447	0.523526	-0.209406
12	6	0	4.686306	-2.521834	-0.185400
13	6	0	5.849249	0.002837	-1.666287
14	8	0	2.079705	-0.307446	0.805047
15	6	0	1.815437	0.254432	1.913766
16	6	0	0.604701	-0.164283	2.721440
17	6	0	-0.529492	-0.818477	1.896551
18	6	0	1.151002	-1.101531	3.831699
19	6	0	-1.609198	-1.407258	2.810295
20	8	0	-1.072455	0.169003	1.019843
21	14	0	-2.336949	-0.006627	-0.137123
22	14	0	-1.886977	1.681173	-1.778981
23	14	0	-4.438066	0.492781	0.920139
24	14	0	-2.383648	-2.160608	-1.198077
25	6	0	-0.152752	1.516061	-2.530832
26	6	0	-3.133963	1.542564	-3.212895
27	6	0	-2.054539	3.418305	-1.016702
28	6	0	-2.420480	-3.629660	0.016944
29	6	0	-3.977147	-2.264032	-2.238776
30	6	0	-0.899615	-2.417439	-2.358176
31	6	0	-4.162174	1.820838	2.256105
32	6	0	-5.688835	1.184805	-0.340801
33	6	0	-5.289765	-1.002286	1.742684
34	1	0	0.955977	3.062352	1.912776

35	1	0	0.493019	1.800235	0.643039
36	1	0	4.423411	2.978764	1.517924
37	1	0	3.118143	4.152244	1.861856
38	1	0	3.890573	4.087117	0.258604
39	1	0	4.779505	0.481323	1.656600
40	1	0	2.386353	-0.553489	-1.989865
41	1	0	3.566444	-2.765075	-2.025633
42	1	0	2.564693	-2.503545	-0.606673
43	1	0	4.543690	-0.667229	-3.262835
44	1	0	4.147978	0.926372	-2.633081
45	1	0	5.868420	-1.752835	1.463176
46	1	0	4.146270	-1.831934	1.791613
47	1	0	6.822172	0.337018	0.244651
48	1	0	5.714464	1.615381	-0.235982
49	1	0	4.557222	-3.545860	0.194985
50	1	0	5.605279	-2.549679	-0.779409
51	1	0	6.490463	0.662390	-2.268894
52	1	0	6.334481	-0.978212	-1.698852
53	1	0	2.638509	0.680404	2.492604
54	1	0	0.198943	0.731969	3.207339
55	1	0	-0.088183	-1.625344	1.293184
56	1	0	0.399170	-1.266905	4.607734
57	1	0	2.029559	-0.662626	4.318060
58	1	0	1.447384	-2.073268	3.419912
59	1	0	-2.439696	-1.794239	2.215701
60	1	0	-2.002831	-0.644326	3.493113
61	1	0	-1.224834	-2.242964	3.403618
62	1	0	0.649437	1.577238	-1.788865
63	1	0	0.006020	2.325569	-3.257354
64	1	0	-0.032254	0.567103	-3.066097
65	1	0	-2.966790	2.370177	-3.915895
66	1	0	-4.176946	1.595162	-2.882941
67	1	0	-3.006068	0.609671	-3.775054
68	1	0	-3.061544	3.604997	-0.624267
69	1	0	-1.340577	3.572370	-0.199047
70	1	0	-1.850603	4.181053	-1.780785
71	1	0	-1.508328	-3.698843	0.621248
72	1	0	-2.504545	-4.564154	-0.555134
73	1	0	-3.276167	-3.585867	0.701043
74	1	0	-3.998336	-3.219115	-2.781394
75	1	0	-4.045620	-1.462284	-2.983045
76	1	0	-4.880199	-2.220726	-1.617682
77	1	0	-0.913192	-1.711420	-3.196837
78	1	0	0.059957	-2.296771	-1.841916
79	1	0	-0.926056	-3.431590	-2.780100
80	1	0	-3.475351	1.475061	3.037400
81	1	0	-5.114849	2.079664	2.738112
82	1	0	-3.740719	2.739771	1.831335
83	1	0	-6.645940	1.373898	0.164459
84	1	0	-5.885900	0.486890	-1.163653
85	1	0	-5.356716	2.133258	-0.778617
86	1	0	-5.479784	-1.811684	1.027364
87	1	0	-4.709756	-1.419641	2.573550
88	1	0	-6.262033	-0.689146	2.147780

TS I

1,3-*anti*(ϕ =-60)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2394.49597828 A.U. after 8 cycles

Imaginary frequencies: 1(-263)

Zero-point correction= 0.764812 (Hartree/Particle)
Thermal correction to Energy= 0.811995
Thermal correction to Enthalpy= 0.812939
Thermal correction to Gibbs Free Energy= 0.684192
Sum of electronic and zero-point Energies= -2393.731166
Sum of electronic and thermal Energies= -2393.683983
Sum of electronic and thermal Enthalpies= -2393.683039
Sum of electronic and thermal Free Energies= -2393.811786

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.685681	2.484877	-1.463728
2	6	0	-3.128991	2.558096	-0.149689
3	8	0	-3.778742	1.605169	0.460808
4	6	0	-2.745536	3.697611	0.758934
5	5	0	-3.990554	0.186900	-0.052646
6	6	0	-5.342656	0.015498	-0.924653
7	6	0	-4.081952	-0.825131	1.201190
8	6	0	-4.169005	-2.280543	0.675036
9	6	0	-5.280968	-0.390680	2.082957
10	6	0	-5.414425	-1.441637	-1.448282
11	6	0	-6.543554	0.438227	-0.038631
12	6	0	-5.281376	-2.539529	-0.367795
13	6	0	-6.631477	-0.260377	1.339011
14	8	0	-2.770927	-0.138471	-0.963686
15	6	0	-1.677418	0.531742	-0.946921
16	6	0	-0.658068	0.247429	-2.039312
17	6	0	0.739357	0.826010	-1.709495
18	6	0	-0.582959	-1.272697	-2.301770
19	6	0	0.802246	2.355261	-1.718928
20	8	0	1.146876	0.310389	-0.442085
21	14	0	2.714172	-0.105975	0.115073
22	14	0	2.182705	-1.346039	2.085069
23	14	0	4.022096	1.825833	0.681788
24	14	0	3.904785	-1.467190	-1.462494
25	6	0	0.775321	-2.564816	1.708341
26	6	0	3.691132	-2.326185	2.708180
27	6	0	1.605226	-0.187206	3.480277
28	6	0	4.045333	-0.677825	-3.192738
29	6	0	5.678567	-1.720059	-0.814070
30	6	0	3.104751	-3.181025	-1.675204
31	6	0	2.942915	3.157168	1.509318
32	6	0	5.380276	1.315570	1.917370
33	6	0	4.894985	2.610067	-0.820594

34	1	0	-3.197337	1.872963	-2.194381
35	1	0	-2.118433	3.323982	-1.854638
36	1	0	-2.132690	3.330760	1.592170
37	1	0	-3.652784	4.130065	1.197447
38	1	0	-2.202637	4.482724	0.226638
39	1	0	-5.352090	0.674545	-1.808901
40	1	0	-3.177736	-0.760938	1.831114
41	1	0	-4.299504	-2.982242	1.514547
42	1	0	-3.199835	-2.531998	0.220113
43	1	0	-5.406945	-1.089089	2.925949
44	1	0	-5.031734	0.582340	2.528662
45	1	0	-6.354355	-1.600431	-2.001083
46	1	0	-4.606538	-1.573636	-2.182434
47	1	0	-7.489877	0.275502	-0.579304
48	1	0	-6.471624	1.523226	0.124777
49	1	0	-5.087684	-3.502657	-0.862385
50	1	0	-6.240702	-2.666375	0.144359
51	1	0	-7.333487	0.298572	1.974767
52	1	0	-7.079659	-1.252069	1.218126
53	1	0	-1.303672	0.895858	0.011693
54	1	0	-1.005971	0.721955	-2.966221
55	1	0	1.416860	0.455797	-2.493215
56	1	0	0.104331	-1.468203	-3.133409
57	1	0	-1.566168	-1.669938	-2.564460
58	1	0	-0.219875	-1.806877	-1.418961
59	1	0	1.835962	2.692209	-1.593998
60	1	0	0.205881	2.782027	-0.907329
61	1	0	0.432027	2.754532	-2.671038
62	1	0	-0.115332	-2.043794	1.338873
63	1	0	0.488678	-3.107303	2.619503
64	1	0	1.062940	-3.309321	0.956278
65	1	0	3.434868	-2.851556	3.638175
66	1	0	4.551467	-1.680618	2.921804
67	1	0	4.012521	-3.083525	1.982818
68	1	0	2.399650	0.494747	3.807082
69	1	0	0.746039	0.420881	3.172502
70	1	0	1.296020	-0.777034	4.353982
71	1	0	3.082296	-0.649259	-3.716541
72	1	0	4.734152	-1.270239	-3.810998
73	1	0	4.435150	0.346012	-3.152712
74	1	0	6.219835	-2.405205	-1.480796
75	1	0	5.699442	-2.155201	0.191830
76	1	0	6.243142	-0.780354	-0.783151
77	1	0	3.093424	-3.747289	-0.736153
78	1	0	2.070656	-3.110512	-2.032195
79	1	0	3.670110	-3.770842	-2.409772
80	1	0	2.177265	3.545680	0.828307
81	1	0	3.565360	4.004264	1.828561
82	1	0	2.429820	2.767017	2.396096
83	1	0	6.017854	2.180547	2.145696
84	1	0	6.028370	0.524251	1.522027
85	1	0	4.959416	0.959329	2.865118
86	1	0	5.600328	1.912521	-1.288647
87	1	0	4.191612	2.938716	-1.595352

88	1	0	5.467437	3.492409	-0.502941

TS J

1,3-*anti*(ϕ = 60)

Method: B3LYP/6-31+G(d)

SCF Done: E(RB+HF-LYP) = -2394.49729675 A.U. after 8 cycles

Imaginary frequencies: 1(-226)

Zero-point correction= 0.764861 (Hartree/Particle)

Thermal correction to Energy= 0.812047

Thermal correction to Enthalpy= 0.812991

Thermal correction to Gibbs Free Energy= 0.683643

Sum of electronic and zero-point Energies= -2393.732435

Sum of electronic and thermal Energies= -2393.685249

Sum of electronic and thermal Enthalpies= -2393.684305

Sum of electronic and thermal Free Energies= -2393.813653

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.077507	1.889881	0.771210
2	6	0	3.223769	2.370796	0.152380
3	8	0	4.263255	1.643376	-0.157812
4	6	0	3.311727	3.783229	-0.367339
5	5	0	4.371122	0.126195	-0.092529
6	6	0	4.932856	-0.412342	1.323278
7	6	0	5.364295	-0.396618	-1.251404
8	6	0	5.361396	-1.947256	-1.258294
9	6	0	6.757509	0.239405	-1.018494
10	6	0	4.914827	-1.962362	1.305588
11	6	0	6.335285	0.212717	1.550350
12	6	0	5.641525	-2.616898	0.107653
13	6	0	7.346755	0.021417	0.395408
14	8	0	2.927649	-0.424008	-0.309323
15	6	0	2.004341	0.274262	-0.855266
16	6	0	0.622105	-0.321552	-0.927117
17	6	0	-0.533119	0.713417	-1.003898
18	6	0	0.623162	-1.299873	-2.129041
19	6	0	-0.426104	1.693215	-2.174373
20	8	0	-1.759532	-0.005047	-1.123458
21	14	0	-3.069733	-0.100606	-0.024553
22	14	0	-4.613948	-1.415312	-1.282954
23	14	0	-3.993666	2.053378	0.475496
24	14	0	-2.428301	-1.239743	1.984717
25	6	0	-3.671299	-2.821797	-2.146276
26	6	0	-5.954971	-2.170401	-0.162525
27	6	0	-5.473228	-0.370940	-2.621066
28	6	0	-0.964309	-0.397487	2.866381
29	6	0	-3.886683	-1.267943	3.209560
30	6	0	-1.918835	-3.036117	1.610833
31	6	0	-4.199956	3.122247	-1.086407

32	6	0	-5.719927	1.811021	1.246174
33	6	0	-2.941699	3.050082	1.713916
34	1	0	2.104789	1.023335	1.418072
35	1	0	1.271285	2.595134	0.950215
36	1	0	3.480360	3.781994	-1.451527
37	1	0	4.176680	4.280729	0.087922
38	1	0	2.413324	4.361981	-0.138426
39	1	0	4.300386	-0.092145	2.168063
40	1	0	5.021116	-0.066796	-2.247910
41	1	0	6.088195	-2.326105	-1.994755
42	1	0	4.374191	-2.279543	-1.611824
43	1	0	7.477158	-0.133968	-1.764754
44	1	0	6.666524	1.319860	-1.197476
45	1	0	5.344511	-2.357977	2.239855
46	1	0	3.863816	-2.284629	1.296137
47	1	0	6.779356	-0.180673	2.478879
48	1	0	6.195705	1.290772	1.715598
49	1	0	5.348669	-3.675394	0.050000
50	1	0	6.720117	-2.626651	0.295027
51	1	0	8.185242	0.717762	0.541331
52	1	0	7.788547	-0.978558	0.458203
53	1	0	2.289263	0.984498	-1.636000
54	1	0	0.475098	-0.912268	-0.015781
55	1	0	-0.525011	1.284779	-0.065520
56	1	0	-0.376079	-1.727461	-2.246012
57	1	0	1.340934	-2.107531	-1.958133
58	1	0	0.894775	-0.798756	-3.065342
59	1	0	-1.280901	2.376097	-2.163420
60	1	0	-0.435645	1.164430	-3.132999
61	1	0	0.486598	2.297356	-2.113751
62	1	0	-2.911175	-2.423579	-2.828451
63	1	0	-4.362195	-3.439508	-2.736074
64	1	0	-3.164928	-3.477865	-1.428579
65	1	0	-6.677326	-2.732397	-0.770033
66	1	0	-6.515490	-1.406355	0.389761
67	1	0	-5.530850	-2.868190	0.569759
68	1	0	-6.118928	0.402429	-2.187673
69	1	0	-4.744824	0.125466	-3.273394
70	1	0	-6.103826	-1.011065	-3.253069
71	1	0	-0.057618	-0.386847	2.250574
72	1	0	-0.723233	-0.942194	3.789613
73	1	0	-1.190141	0.638723	3.144621
74	1	0	-3.620280	-1.871044	4.088236
75	1	0	-4.794476	-1.702010	2.774739
76	1	0	-4.135928	-0.261919	3.568532
77	1	0	-2.750591	-3.625112	1.205833
78	1	0	-1.094292	-3.086949	0.889066
79	1	0	-1.581150	-3.531434	2.531446
80	1	0	-3.234742	3.419146	-1.512853
81	1	0	-4.743489	4.043545	-0.835392
82	1	0	-4.764107	2.606159	-1.871480
83	1	0	-6.135416	2.785435	1.537354
84	1	0	-5.694277	1.182649	2.144288
85	1	0	-6.423301	1.353158	0.539874

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86	1	0	-2.859147	2.546108	2.684447
87	1	0	-1.924081	3.227408	1.344117
88	1	0	-3.402268	4.031772	1.891204

General Procedures

All non-aqueous reactions were carried out under an atmosphere of nitrogen in flame-dried glassware and were stirred using a magnetic stir plate. All reactions were carried out using anhydrous solvent unless otherwise noted. Anhydrous CH_2Cl_2, THF, Et_2O, and toluene were dried using an M BRAUN solvent system (A2 alumina). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogenous materials unless noted otherwise. (*S*)-2-methyl butanal,[17] (*S*)-2-phenyl propanal,[18] *N*-benzyl, *N*-tosyl (*S*)-2-aminopropanal[19] 3-*t*-Butyldimethylsiloxy propanal[20] (*R*)-3-benzyloxy-2-methyl propanal[21] were prepared according to literature procedures. All other aldehydes were obtained from Sigma Aldrich and distilled prior to use.

Triflimide ($HNTf_2$) was obtained from Sigma Aldrich and manipulated in a N_2 atmosphere glovebox. Dimethyl aluminum triflimide (Me_2AlNTf_2) was prepared from Me_3Al and $HNTf_2$ according to the literature procedure.[22] Pentafluorophenylbis(trifyl)methide $C_6F_5CH(Tf)_2$[23] was prepared according to the literature procedure. BF_3OEt_2, LiHMDS (1.0 M toluene), 9-BBNOTf (0.5 M hexanes), Bu_2BOTf (1.0 M CH_2Cl_2), (*c*-Hex)$_2$BCl, (+)DIPCl, (−) DIPCl were obtained from Sigma Aldrich. Acetone TMS enol ether (isopropenyloxy trimethylsilane) was obtained from Sigma Aldrich. L-PTZ (L-proline tetrazole, (*S*)-(–)-5-(2-Pyrrolidinyl)-1*H*-tetrazole) was obtained from Chiro Technology (Japan). The *R*-enantiomer (D-PTZ) was synthesized from D-proline according to published procedures.[24] All other reagents were obtained from commercial sources.

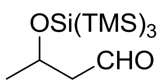
All reactions were monitored by thin layer chromatography (TLC) on Whatman Partisil ® K6F TLC plates (silica gel 60 Å, 0.25 mm thickness) and visualized using a UV lamp (366 or 254 nm) or by use of one of the following visualization reagents: PMA: 10 g phosphomolybdic acid/ 100 mL ethanol; $KMnO_4$: 0.75 g potassium permanganate, 5 g K_2CO_3, / 100mL water; ANIS: 10% v/v concentrated H_2SO_4 and 6% v/v *p*-anisaldehyde in ethanol. Products were isolated by flash chromatography (Zeochem® Zeoprep 60 Eco® silica gel 43-60 µm) or by automated flash chromatography using a Biotage® Isolera One® system (UV detector), using SNAP® cartridges.

Middle infrared spectra were recorded as thin films on polished sodium chloride plates using a Nicolet 6700 FTIR spectrometer unless otherwise noted. ^{13}C, and ^{1}H NMR

[17] Anelli, P.; Montanari, F.; Quici, S. *Org. Synth.* **1990**, *69*, 212 ,*Org. Synth.* **1993**, *Coll. Vol. 8*, 367
[18] Vogt, M; Ceylan, S.; Kirschning, A. *Tetrahedron,* **2010**, *66*, 6450-6456
[19] Preparation of alanine methyl ester hydrochloride: *Eur. J. Org. Chem.*, **2010,** *22,* 4276. Conversion to *N*-tosyl 2-aminopropanal: *Tetrahedron,* **1998**, *54*, 6051. Product was recrystallized from boiling hexanes/ethyl acetate.
[20] W. H. Pearson, J. E. Kropf, A. L. Choy, Ill, Y. Lee, J.W. Kampf *J. Org. Chem*. **2007**, *72,* 4135.
[21] Kawabata, T.; Kimura, Y.; Ito, Y.; Terashima, S. *Tetrahedron* **1988, *44*,** 2149
[22] Marx, A.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2000,** *39,* 178.
[23] A. Hasegawa, K. Ishihara, H. Yamamoto, *Angew. Chem.* **2003**, *115,* 5909–5911;
[24] *Org. Syn* **2008**, *85*, 72.

spectra were recorded on a Bruker Avance Model DRX 500 or DRX 400. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak $CDCl_3$ δ = 7.26 ppm, for ^{1}H, δ = 77.16 for ^{13}C; C_6D_6 δ = 7.16 ppm for ^{1}H, δ = 128.0 ppm for ^{13}C, or calibrated to tetramethyl silane (δ = 0.00). Diastereomeric ratios were determined by ^{1}H NMR integration of the unpurified reaction mixture. When noted, the diastereomeric ratio could not be determined by ^{1}H NMR analysis of the crude mixture and instead given after silica gel flash chromatography. Integral values were determined using standard, uncalibrated NMR experiments and should be viewed accordingly. All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad; app, apparent.

Synthetic Procedures and Data for compounds 1 (Tables 1,2, 3).



1a

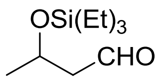
General procedure 1 (GP 1)

To a stirring solution of CH_2Cl_2 (3 mL) at 0°C was added triflic acid (0.28 mL, 3.15 mmol, 1.05 equiv.). Tris(trimethylsilyl)silane was added dropwise over 2 min and gas evolution was observed. The reaction mixture was warmed to ambient temperature and stirred for one hour before being re-cooled to 0°C. CH_2Cl_2 (5 mL) was added, followed by *i*-Pr_2NEt (0.78 mL, 4.5 -mL, 1.5 equiv.). (*R*) – ethyl 3-hydroxy-butarate was added in one portion (0.39 mL, 3 mmol, 1.0 equiv.) The reaction was stirred for one hour at ambient temperature and quenched by addition of 5 mL saturated aqueous $NaHCO_3$. The mixture was diluted with hexanes (40 mL) and the layers were separated. The organic layer was washed consecutively with saturated aqueous NH_4Cl (20 mL), H_2O (20mL) and brine (20 mL), and was dried over anhydrous $MgSO_4$. The organic layer was filtered and concentrated under reduced pressure. The material was sufficiently pure and was used without further purification.

A stirring solution of the methyl ester (3 mmol) in CH_2Cl_2 (30 mL) was cooled to −85°C. Diisobutylaluminum hydride (3.75 mL, 1.0 M hexanes, 1.25 equiv.) was added slowly over 10 min. The temperature was maintained at −78°C for 1 hour then cooled to −90°C. The reaction was quenched by slow addition of a mixture of Et_2O (2 mL) and MeOH (1 mL). The mixture was stirred vigorously and allowed to warm to ambient temperature, whereupon saturated aqueous NaK(tartarte) was added (30mL). The biphasic mixture was stirred for 2 hr, then diluted with 60 mL hexanes. The layers were separated and the organic layer was washed consecutively with saturated aqueous $NaHCO_3$ (20mL) and brine (20 mL), followed by drying over $MgSO_4$ followed by filtration and concentration under reduced pressure. The crude material was purified by flash chromatography on silica gel (25g, 1-5% Et_2O/hexanes) to yield the product as a waxy solid (0.91 g, 90% yield for 2 steps).

Data for 1a: TLC: R_f = 0.27 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 295K), δ = 202.26, 68.93, 53.00, 23.91, 0.5; ^{1}H NMR (500 MHz, $CDCl_3$, 295K), δ =

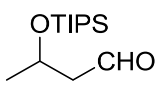
9.77 (t, *J*=2.4 Hz, 1 H), 4.03 (sxt, *J*=6.0 Hz, 1 H), 2.44 - 2.48 (m, 2 H), 1.21 (d, *J*=6.1 Hz, 3 H), 0.19 (s, 27 H);LRMS (API-ES +): $C_{13}H_{35}O_2Si_4^+$ $[M+H]^+$ m/z = 335.2 (100%); FTIR (thin film):2944, 2868, 2722, 1728, 1464, 1117, 1032, 883, 680; colorless oil.



1b

Prepared according to GP using commercial TESOTf

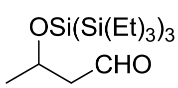
Data for 1b: TLC: R_f = 0.38 (10:90 EtOAc/Hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 295K) δ = 202.31, 64.45, 53.21, 24.40, 6.92, 4.98; ^{1}H NMR (500 MHz, $CDCl_3$, 295K) δ 9.80 (t, *J*=2.4 Hz, 1 H), 4.36 (sxt, *J*=6.1 Hz, 1 H), 2.57 (ddd, *J*=15.9, 6.7, 3.1 Hz, 1 H), 2.47 (ddd, *J*=15.6, 5.2, 1.8 Hz, 1 H), 1.25 (d, *J*=6.1 Hz, 3 H), 0.95 (t, *J*=7.9 Hz, 6 H), 0.60 (q, *J*=7.7 Hz, 6 H); LRMS (API-ES +): $C_{11}H_{30}NO_3Si^+$ $[M + NH_4+MeOH]^+$ m/z = 252.1 (85%); FTIR (thin film):2957, 2978, 2827, 2723, 1730, 1457, 1376, 1135, 1016, 744; colorless oil



Prepared according to GP using commercial TESOTf

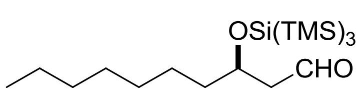
1c[25]

Data for 1c TLC: R_f = 0.39 (10:90 EtOAc/Hexanes);^{13}C NMR (500 MHz, $CDCl_3$, 295K), δ = 202.48, 64.93, 53.36, 24.45, 18.18, 12.50; ^{1}H NMR (500 MHz, $CDCl_3$, 295K), δ = 9.86 (t, *J*=2.4 Hz, 1 H), 4.46 (sxt, *J*=5.9 Hz, 1 H), 2.56 (app dd, *J*=5.8, 2.4 Hz, 2 H), 1.29 (d, *J*=6.1 Hz, 3 H), 1.02 - 1.08 (m, 21 H); LRMS (API-ES +): $C_{13}H_{29}O_2Si^+$ $[M+H]^+$ m/z = 245.2 (100%); FTIR (thin film):2950, 2894, 2823, 2719, 1729, 1374, 1245, 1111, 1011, 834, 687; colorless oil



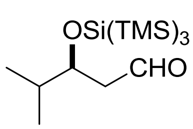
1d

Synthesized and used *in situ*



1e

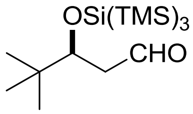
Previously described compound



1f

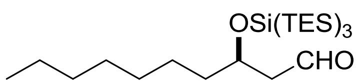
Generated and used *in situ*

[25] Silylation of ethyl 3-hydroxybutarate: *J. Org. Chem*., **1989**, *54*, 3792. Reduction of ester to aldehyde: *J. Am. Chem. Soc.*, **2000**, *122*, 3792.

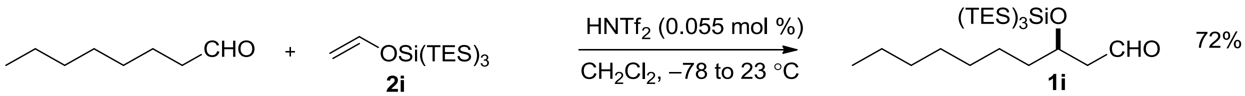


1g
Generated and used *in situ*

1h
^{13}C NMR (500 MHz, $CDCl_3$): δ = 201.62, 138.32, 128.57, 127.83, 77.07, 70.37, 50.64, 19.94; ^{1}H NMR (500 MHz, $CDCl_3$): δ =9.79 (t, *J*=2.1 Hz, 1 H), 4.61 (d, *J*=11.6 Hz, 1 H), 4.48 (d, *J*=11.6 Hz, 1 H), 4.05 - 4.13 (m, 1 H), 2.71 (ddd, *J*=16.2, 7.3, 2.4 Hz, 1 H), 2.52 (ddd, *J*=16.5, 4.9, 1.8 Hz, 1 H), 1.30 (d, *J*=6.1 Hz, 3 H); LRMS (API-ES +): m/z = 193.2 (100%); FTIR (thin film): 3064, 2973, 2727, 1725, 1377, 1098, 1060, 738, 698; colorless oil

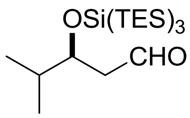


1i
Prepared according to **Scheme S-7.**
Scheme S-7:

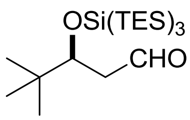


General Procedure 2 (GP 2)
A dry 25mL round bottomed flask with magnetic stir bar was charged with **2i** (1.14, 2.72 mmol), fitted with a septum and purged with N_2. CH_2Cl_2 (7.0 mL) and octanal (430μL) were added sequentially, stirred and cooled to −78 °C in a dry ice/acetone bath. $HNTf_2$ (150μL, 0.010 M CH_2Cl_2, 1.5 x 10^{-3} mmol) was added dropwise. After stirring for 1 h at the same temperature, TLC analysis indicated formation of product, and the reaction vessel was allowed to warm to ambient temperature, and the reaction was quenched by the addition of sat. aq. $NaHCO_3$ (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (5mL). The combined organic layers were dried (Na_2SO_4), filtered through cotton and concentrated. Flash column chromatography (75mL silica gel, 12→20% CH_2Cl_2/hexanes eluent) afforded 1.06 g of **1i** a colorless oil (72%).
Data for 1i TLC: R_f = 0.2 (80:20 hexanes/CH_2Cl_2); FTIR: (thin film): 2953, 2934, 2875, 2727, 1726, 1461, 1416, 1235, 1004, 723; LRMS (APCI +) $C_{28}H_{65}O_2Si^+$ $[M+H]^+$ m/z = 545.5 (25%); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 202.6, 73.3, 49.4, 37.2, 31.7, 29.7, 29.2, 24.9, 22.6, 14.0, 9.8, 8.6, 5.3, 4.7; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.70 (dd, *J*= 3.5, 2.0 Hz, 1H), 3.75 (dddd, *J* = 4.5, 6.0, 4.5, 6.0 Hz, 1H), 2.53, (ddd, *J*= 15.5, 6.0, 2.0 Hz, 1H), 2.39 (ddd, *J* = 15.5, 4.5, 3.5 Hz, 1H), 1.51-1.61 (m, 1H), 1.40-1.48 (m, 1H), 1.2-1.3 (m,

10 H), 1.1-1.18 (m, 1 H), 1.04, (t, J = 8Hz, 27H), 0.88 (t, J = 7.0Hz, 3H), 0.76 (q, J = 8.0Hz, 18H).

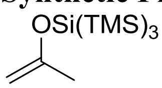


1j
Generated according to **GP 2** and used *in situ*

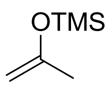


1k
Generated according to **GP 2** and used *in situ*

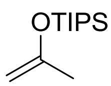
Synthetic Procedures and Data for enolsilanes 2 and 23



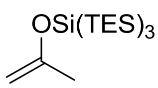
2a Previously described compound[26]



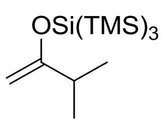
2b Obtained from Sigma Aldrich and reused without further purification.



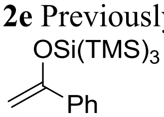
2c Previously described compound[27]



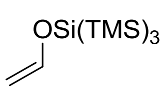
2d Previously described compound.[28]



2e Previously described compound[9]

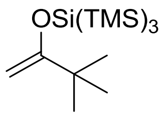


2f Previously described compound[9]

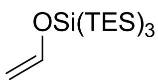


[26] Boxer, M. B.; Akakura, M.; Yamamoto, H. *J. Am. Chem. Soc.* **2008**, *130*, 1580–1582.
[27] Simchen, G.; Jonas, S. *Journal für Praktische Chemie/Chemiker-Zeitung* **1998**, *340*, 506–512.
[28] Yamaoka, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **2010**, *132*, 5354–5356.

2g Previously described compound[29]



2h ^{13}C NMR (500MHz, $CDCl_3$, 295K) δ = 170.39, 82.85, 36.93, 28.34, 0.56; ^{1}H NMR (500MHz, $CDCl_3$, 295K) δ = 3.98 (d, *J*=1.8 Hz, 1 H), 3.79 (d, *J*=1.8 Hz, 1 H), 1.03 (s, 9 H), 0.21 (s, 27 H);



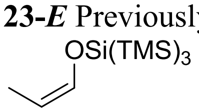
2i

Synthetic procedure for 2i

A flame-dried 100 mL round-bottomed flask fitted with a rubber septum containing a magnetic stir bar was charged with *tris*(triethylsilyl)silane (5.63 g, 15 mmol). CH_2Cl_2 (22 mL) was added and the stirring flask was cooled to 0 °C. Triflic acid was added dropwise by syringe over 4 min. Gas evolution was observed. The reaction vessel was allowed to warm to ambient temperature and the reaction was stirred for 1 h. To a dry 25 mL secondary pear-shaped flask fitted with a rubber septum was added acetaldehyde (0.74 g, 17 mmol) under N_2. The flask was immediately cooled to 0 °C and CH_2Cl_2 (mL) and Et_3N (3.2 mL, 23 mmol) were added. The contents of the flask were mixed and transferred by syringe to the reaction flask at 0°C in a dropwise manner. The reaction was stirred for 25 min then quenched by the addition of $NaHCO_3$ (sat. aq., 25mL) hexanes. The mixture was stirred vigorously then diluted with 50mL hexanes. The organic layer was washed with H_2O (2 x 25mL), $NaHCO_3$ (25mL), and brine (25mL), dried over Na_2SO_4, filtered through cotton and concentrated. Purification by flash chromatography (200 mL silica gel, hexanes eluent) afforded **20** as a colorless oil (3.64 g, 58%).

Data for 20: TLC: R_f = 0.59 (hexanes); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 150.8, 92.6, 8.7, 5.3 ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.20 (dd, *J*=13.1, 5.5 Hz, 1 H), 4.23 (dd, *J*=13.4, 0.6 Hz, 1 H), 3.95 (dd, *J*=5.5, 0.6 Hz, 1 H), 1.03 (t, *J*=7.9 Hz, 27 H), 0.79 (q, *J*=7.9 Hz, 18 H); FTIR (thin film): 2953, 2909, 2876, 1622, 1460, 1416, 1310, 1171, 1001, 828, 724. GCMS (EI) $C_{18}H_{43}OSi_4^+$ $[M – CH_3CH_2]^+$ m/z = 387.2 (20%)

23-*E* Previously described compound[30]



23-*Z* Previously described compound[13]

Synthetic procedure and data for compounds 3

[29] Boxer, M. B.; Yamamoto, H. *Org. Lett.* **2005**, *7*, 3127–3129.,Boxer, M. B.; Yamamoto, H. *Nature Protocols* **2006**, *1*, 2434–2438.

[30] Brady, P. B.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 1942–1946.

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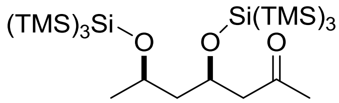
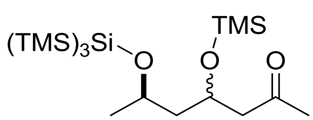
Compounds **3a-3l** (Table 1, entries 1 – 12), were prepared according to **GP3.**



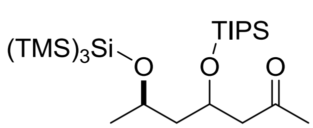
General procedure 3 (GP3)

A dry 10mL round bottomed flask with magnetic stir bar was charged with aldehyde **1a** (83mg, 0.2 mmol), enolsilane **2a** (73 mg, 0.24 mmol) , then fitted with a septum and purged with N_2. CH_2Cl_2 (2.0 mL) was added, and the vessel was cooled to −45 °C in a dry ice/acetonitrile bath. $HNTf_2$ (20μL, 0.010 M CH_2Cl_2,) was added dropwise. After stirring for 1 h at the same temperature, TLC analysis indicated formation of product and consumption of starting materials, and the reaction vessel was allowed to warm to ambient temperature, then was quenched by the addition of sat. aq. $NaHCO_3$ (10 mL). The mixture was poured over 20 mL hexanes. The layers were then separated, and the organic layer was washed with H_2O, dried (Na_2SO_4), filtered through cotton and concentrated. Flash column chromatography (16mL silica gel, 12→35% CH_2Cl_2/hexanes eluent) afforded **3a** (76%). **Data for 3a:** TLC: R_f = 0.60 (10:90 EtOAc/Hexanes); ^{13}C NMR (500MHz, $CDCl_3$, 295K) δ = 207.86, 70.76, 69.53, 50.05, 46.28, 31.12, 23.96, 0.7; ^1H NMR (500MHz, $CDCl_3$, 295K) δ = 3.95 - 4.06 (m, 1 H), 3.66 (dqdd, *J*=8.2, 6.1, 6.1, 6.1, 4.0, 1.8 Hz, 1 H), 2.63 (dd, *J*=14.3, 4.9 Hz, 1 H), 2.45 (dd, *J*=14.3, 6.4 Hz, 1 H), 2.14 (s, 3 H), 1.71 (ddd, *J*=13.6, 8.4, 5.5 Hz, 1 H), 1.34 (ddd, *J*=13.4, 8.9, 4.3 Hz, 1 H), 1.13 (d, *J*=6.1 Hz, 3 H), 0.18 (s, 27 H), 0.18 (s, 27 H); LRMS (API-ES): $C_{16}H_{39}O_2Si_4^+$ [M – $TMS_3SiO]^+$ m/z = 375.2 (100%); FTIR (thin film):2949, 2893, 1719, 1244, 1035, 835, 687, 623; white solid



3b

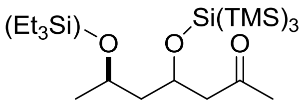
Data for 3bTLC: R_f = 0.22 (10:90 EtOAc/Hexanes); ^{13}C NMR (500MHz, $CDCl_3$, 295K, mixture of diastereomers) δ = 207.71, 207.67, 70.13, 69.78, 67.58, 66.49, 51.80, 51.74, 48.41, 47. 58, 31.77, 31.68, 24.01, 23.20, 0.61, 0.48; ^1H NMR (500MHz, $CDCl_3$, 295K, 1:1 mixture of diastereomers) δ = 4.22 (quin, *J*=6.1 Hz, 1 H), 4.16 - 4.21 (m, 1 H), 3.60 (sxt, *J*=6.1 Hz, 1 H), 3.51 (sxt, *J*=6.1 Hz, 1 H), 2.60 (dd, *J*=15.0, 8.2 Hz, 2 H), 2.57 (d, *J*=5.8 Hz, 2 H), 2.44 (dd, *J*=15.0, 4.3 Hz, 1 H), 2.15 (s, 3 H), 2.14 (s, 3 H), 1.64 (s, 3 H), 1.54 (s, 0 H), 1.14 (s, 2 H), 1.12 (d, *J*=4.3 Hz, 3 H), 0.18 (s, 27 H), 0.09 (s, 8 H), 0.08 (s, 9 H)



3c

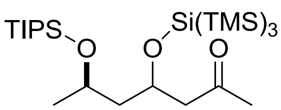
Data for 3c: TLC: R_f = 0.33 (10:90 EtOAc/Hexanes); ^{13}C NMR (500MHz, $CDCl_3$, 295K, mixture of diastereomers) δ = 208.05, 207.60, 70.43, 69.55, 67.71, 67.08, 51.72, 50.72, 48.33, 46.99, 32.05, 31.74, 23.91, 23.67, 18.33, 18.31, 12.81, 12.75, 0.62; ^1H NMR (500MHz, $CDCl_3$, 295K, mixture of diastereomers) δ = 4.39 - 4.52 (m, 1 H), 4.29

(ddt, *J*=8.9, 7.2, 4.4, 4.4 Hz, 1 H), 3.61 - 3.73 (m, 1 H), 3.46 (dquin, *J*=7.5, 5.9, 5.9, 5.9, 5.9 Hz, 1 H), 2.74 (dd, *J*=14.8, 4.7 Hz, 1 H), 2.57 - 2.63 (m, 1 H), 2.49 - 2.55 (m, 2 H), 2.17 (s, 3 H), 2.15 - 2.16 (m, 3 H), 1.60 - 1.77 (m, 4 H), 1.53 (ddd, *J*=13.1, 9.1, 4.4 Hz, 1 H), 1.13 (d, *J*=6.1 Hz, 3 H), 1.12 (d, *J*=6.4 Hz, 3 H), 1.02 - 1.06 (m, 52 H), 0.18 (s, 54 H);LRMS (API-ES +): $C_{25}H_{61}O_3Si_5^+$ $[M+H]^+$ m/z = 549.3 (100%); LRMS (API-ES –): $C_{22}H_{51}O_3Si_4^-$ $[M – TMS]^-$ m/z = 475.2 (35%). FTIR (thin film): 2949, 2894, 1715, 1372, 1245, 1093, 835, 687; colorless oil.



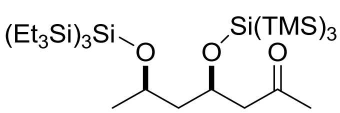
3d

Data for 3d: TLC: R_f = 0.69 (10:90 EtOAc/Hexanes);^{13}C NMR (500MHz, $CDCl_3$, 295K, mixture of diastereomers) δ =207.79, 207.45, 71.74, 70.95, 66.53, 65.55, 51.32, 50.16, 47.43, 46.58, 31.89, 31.73, 24.58, 24.40, 7.06, 5.24, 0.64. ^{1}H NMR (500MHz, $CDCl_3$, 295K, mixture of diastereomers) δ =3.96 - 4.02 (m, 1 H), 3.90 - 3.95 (m, 1 H), 3.85 - 3.90 (m, 1 H), 3.78 - 3.84 (m, 1 H), 2.55 - 2.71 (m, 2 H), 2.42 - 2.54 (m, 3 H), 2.13 (s, 3 H), 2.13 (s, 2 H), 1.51 - 1.77 (m, 2 H), 1.34 - 1.45 (m, 1 H), 1.14 (d, *J*=6.1 Hz, 6 H), 0.93 (t, *J*=8.2 Hz, 18 H), 0.67 - 0.68 (m, 12 H), 0.57 (q, *J*=7.7 Hz, 15 H), 0.16 - 0.22 (m, 54 H); LRMS (API-ES +) $C_{16}H_{39}O_2Si_4^+$ $[M – TESO]^+$ m/z = 375.2 (100%); FTIR (thin film): 2953, 2878, 1718, 1373, 1245, 1058, 837, 745; colorless oil.



3e

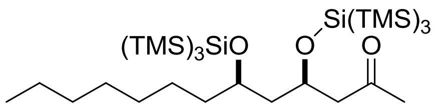
Data for 3e: TLC: R_f = 0.66 (10:90 EtOAc/Hexanes); ^{13}C NMR (500MHz, $CDCl_3$, 295K, mixture of diastereomers) δ = 207.46, 71.42, 70.69, 66.52, 65.95, 70.78, 50.81, 50.78, 47.77, 47.06, 31.86, 31.70, 24.18, 24.07, 138.39, 18.35, 18.30, 18.28, 12.7, 12.63, 0.66; ^{1}H NMR (500MHz, $CDCl_3$, 295K, mixture of diastereomers) δ =4.05 - 4.19 (m, 1 H), 3.96 - 4.04 (m, 1 H), 3.82 - 3.93 (m, 1 H), 2.65 (dd, *J*=15.3, 6.1 Hz, 1 H), 2.52 - 2.59 (m, 1 H), 2.45 - 2.51 (m, 1 H), 2.13 (s, 3 H), 1.62 - 1.82 (m, 3 H), 1.44 (dt, *J*=13.4, 6.4 Hz, 1 H), 1.20 (d, *J*=6.1 Hz, 3 H), 1.17 (d, *J*=6.1 Hz, 2 H), 1.02 - 1.08 (m, 21 H), 0.15 - 0.22 (m, 27 H) LRMS (API-ES +) $C_{16}H_{39}O_2Si_4^+$ [M-TIPSO]$^+$ m/z = 375.2 (100%), $C_{25}H_{61}O_3Si_5^+$ $[M+H]^+$ m/z = 549.2 (92%). FTIR (thin film): 2946, 2867, 1720, 1464, 1376, 1245, 1104, 1015, 882, 836, 684; colorless oil.



3f

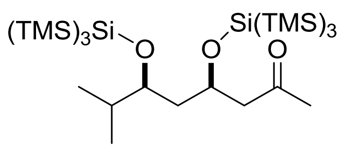
Data for 3f: TLC: R_f = 0.22 (25:75 CH_2Cl_2/hexanes); ^{13}C NMR (500MHz, $CDCl_3$, 295K,) δ = 207.11, 70.35, 70.10, 51.36, 46.18, 31.58, 22.87, 9.04, 5.57, 0.66; ^{1}H NMR (500MHz, $CDCl_3$, 295K,) δ = 3.89 - 4.00 (m, 1 H), 3.58 - 3.70 (m, 1 H), 2.53 - 2.67 (m, 2 H), 2.12 (s, 2 H), 1.65 - 1.77 (m, 1 H), 1.37 (dt, *J*=13.4, 6.6 Hz, 1 H), 1.10 (d, *J*=6.1 Hz, 3 H), 0.99 - 1.07 (m, 27 H), 0.71 - 0.82 (m, 18 H), 0.14 - 0.23 (m, 27 H); LRMS (API-ES +) $C_{16}H_{39}O_2Si_4^+$ $[M – TES_3SiO]^+$ m/z = 375.2 (100%); LRMS (API-ES –) $C_{31}H_{75}O_3Si_7^-$

[M – TMS]$^-$ m/z = 691.3, (40%); FTIR (thin film):2953, 2876, 1719, 1458, 1418, 1376, 1245, 1091, 1005, 838, 724; colorless oil



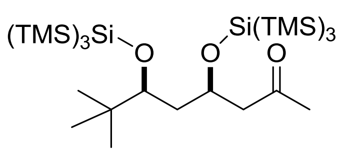
3g

Data for 3g: TLC: R_f = 0.11 (CH_2Cl_2:hexanes 25:75); ^{1}H NMR (500 MHz, $CDCl_3$): 4.01 (dq, *J*=8.1, 5.8 Hz, 1 H), 3.47 (tt, *J*=8.2, 4.3 Hz, 1 H), 2.59 (dd, *J*=14.2, 5.3 Hz, 1 H), 2.48 (dd, *J*=18.3, 6.1 Hz, 1 H), 2.14 (s, 3 H), 1.63 (ddd, *J*=13.4, 7.6, 4.9 Hz, 1 H), 1.37 - 1.46 (m, 2 H), 1.28 (br. s., 10 H), 0.88 (t, *J*=6.9 Hz, 3 H), 0.19 (s, 27 H), 0.18 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 207.8, 73.6, 70.8, 50.0, 43.5, 37.8, 32.1, 31.9, 30.1, 29.5, 25.3, 22.8, 14.3, 0.8, 0.7; FTIR (thin film): 2955, 2896, 2857, 1720, 1373, 1245, 1052, 836, 755, 688, 624.



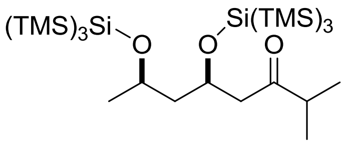
3h

Data for 3h:TLC: R_f = 0.30 (CH_2Cl_2:hexanes 25:75); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.97 (quin, *J*=6.3 Hz, 1 H), 3.45 (ddd, *J*=8.4, 5.0, 3.1 Hz, 1 H), 2.55 - 2.65 (m, 2 H), 2.46 - 2.54 (m, 1 H), 2.15 (s, 3 H), 1.73 - 1.87 (m, 1 H), 1.54 - 1.69 (m, 1 H), 1.26 (ddd, *J*=13.1, 7.8, 5.0 Hz, 1 H), 0.87 (d, *J*=6.7 Hz, 3 H), 0.84 (d, *J*=7.0 Hz, 3 H), 0.82 (d, *J*=6.7 Hz, 3 H), 0.18 (s, 54 H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 207.57, 77.28, 70.86, 50.12, 38.62, 32.17, 17.73, 17.51, 17.36, 0.97, 0.70; LRMS (API-ES +) $C_{27}H_{71}O_3Si_8^+$ [M+H]$^+$ m/z = 667.2 (100%); FTIR (thin film): 2958, 2895, 1720, 1386, 1246, 1032, 831, 755, 687.4, 624; colorless oil.



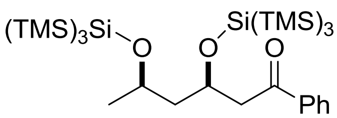
3i

Data for 3i:TLC: R_f = 0.30 (CH_2Cl_2:hexanes 25:75); ^{13}C NMR (500 MHz, $CDCl_3$): δ =206.82, 79.86, 70.44, 52.28, 42.74, 36.65, 31.48, 27.2, 26.27, 1.16, 0.88; ^{1}H NMR (500 MHz, $CDCl_3$): δ =4.16 (sxt, *J*=5.5 Hz, 1 H), 3.36 (dd, *J*=8.4, 3.8 Hz, 1 H), 2.73 (dd, *J*=16.5, 4.6 Hz, 1 H), 2.54 (dd, *J*=16.3, 8.1 Hz, 1 H), 2.13 (s, 3 H), 1.60 - 1.70 (m, 1 H), 1.53 - 1.60 (m, 1 H), 0.90 (s, 9 H), 0.18 - 0.20 (m, 54 H); ^{1}H NMR (500 MHz, $CDCl_3$): δ = LRMS (API-ES +) $C_{19}H_{45}O_2Si_4^+$ [M – TMS_3SiO]$^+$ m/z = 417.1 (100%); LRMS (APCI -) $C_{25}H_{63}O_3Si_7^-$ [M – TMS]$^-$ m/z = 607.2 (100%). FTIR (thin film):2950, 2894, 1720, 1394, 1244, 1090, 1021, 835, 687; white solid.



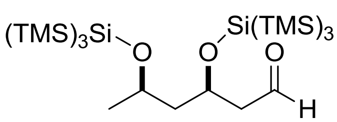
3j

Data for 3j:[13]C NMR (500 MHz, $CDCl_3$): δ = 213.01, 70.61, 69.75, 47.01, 46.25, 42.15, 23.66, 18.26, 17.75, 0.70; [1]H NMR (500 MHz, $CDCl_3$): δ =4.01 (quin, *J*=5.5 Hz, 1 H), 3.68 (sxt, *J*=5.8 Hz, 1 H), 2.66 (dd, *J*=15.3, 5.5 Hz, 1 H), 2.55 - 2.63 (m, 1 H), 2.49 (dd, *J*=16.0, 6.6 Hz, 1 H), 1.65 - 1.74 (m, 1 H), 1.29 - 1.38 (m, 1 H), 1.13 (d, *J*=5.8 Hz, 3 H), 1.07 (d, *J*=7.0 Hz, 3 H), 1.05 (d, *J*=7.0 Hz, 3 H), 0.18 - 0.20 (m, 27 H), 0.17 (d, *J*=1.8 Hz, 27 H); LRMS (API-ES +) $C_{27}H_{71}O_3Si_8^+$ $[M+H]^+$ m/z = 667.3 (100%); FTIR (thin film): 2949, 2894, 1717, 1257, 1244, 1049, 835, 687, 624; waxy solid



3k

Data for 3k:[13]C NMR (500 MHz, $CDCl_3$) δ = 199.07, 138.14, 132.88, 128.55, 128.51, 71.22, 69.82, 46.69, 45.34, 23.63, 0.68; [13]C NMR (500 MHz, $CDCl_3$) δ = 7.94 (d, *J*=7.9 Hz, 2 H), 7.50 - 7.56 (m, 1 H), 7.41 - 7.49 (m, 2 H), 4.20 (sxt, *J*=5.5 Hz, 1 H), 3.75 (sxt, *J*=6.0 Hz, 1 H), 3.11 (dd, *J*=15.3, 5.5 Hz, 1 H), 3.04 (dd, *J*=15.3, 6.4 Hz, 1 H), 1.79 (dt, *J*=13.4, 6.6 Hz, 1 H), 1.44 - 1.54 (m, 1 H), 1.18 (d, *J*=6.1 Hz, 3 H), 0.17 (s, 27 H), 0.14 (s, 27 H); LRMS (API-ES +) $C_{30}H_{69}O_3Si_8^+$ $[M +H]^+$ m/z = 701.3 (100%); FTIR (thin film): 2949, 2894, 1687, 1244, 1055, 835, 623; white solid.



3l

Data for 3l:[13]C NMR (500 MHz, $CDCl_3$, 295K) δ = 202.6, 70.01, 69.36, 49.72, 46.58, 24.05, 0.72, 0.62; [1]H NMR (500 MHz, $CDCl_3$, 295K) δ = 9.77 (dq, *J*=2.1, 0.6 Hz, 1 H), 4.10 (sxt, *J*=5.2 Hz, 2 H), 3.57 - 3.68 (m, 2 H), 2.60 (dd, *J*=15.0, 4.0 Hz, 1 H), 2.38 (ddd, *J*=15.3, 6.7, 3.7 Hz, 1 H), 1.82 (ddd, *J*=13.7, 8.8, 5.0 Hz, 1 H), 1.42 (ddd, *J*=12.8, 8.9, 3.7 Hz, 2 H), 1.15 (d, *J*=6.1 Hz, 3 H), 0.18 (d, *J*=1.5 Hz, 54 H); LRMS (API-ES −) $C_{21}H_{55}O_3Si_7$ $[M – TMS]^+$ m/z = 551.2 (40%); LRMS (APCI +) $C_9H_{27}OSi_4^+$ $[TMS_3SiO]^+$ m/z = 263.0 (100%); waxy semi-solid.

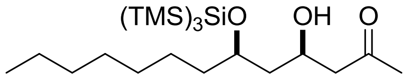
Stereochemical assignment for compounds 3

Compounds 3 were assigned 1,3 *syn* based on prior studies.[31]

Synthetic procedures and data for compounds 5

Compounds **5** (Table 3) were prepared according to **GP4**

[31] Boxer, M. B.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 48–49.



5a

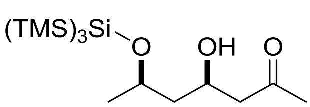
General Procedure 4: To a dry 1 dram vial containing a magnetic stir bar and fitted with a septum was added CH_2Cl_2 (0.5 mL) and acetone (30μL, 0.41 mmol) under an N_2 atmosphere. The solution was stirred, and cooled to −78 °C. Chlorodicyclohexylborane (0.4 mL, 1.0 M hexanes) and triethylamine (60 μL, 0.43 mmol) were sequentially added dropwise, resulting in the immediate formation of a white precipitate (Et_3NHCl. The vial was stirred for 5 min at this temperature then warmed to 0°C. A separate 10mL round-bottomed flask containing a magnetic stir bar and fitted with a septum was charged with **1e** (105 mg, 0.21 mmol). CH_2Cl_2 (1.8 mL) was added and the flask was cooled to −78 °C. The enolborinate solution was added dropwise to the reaction flask (0.2 mL CH_2Cl_2 rinse), leaving some of the white precipitate behind. The reaction was stirred 30 min, and TLC analysis indicated >90% conversion of the starting material. The reaction was quenched by the addition of MeOH (1 mL) and pH 7.0 Buffer (0.2 M, 4 mL). The mixture was allowed to warm to ambient temperature and stirred vigorously. H_2O_2 was then added (30% aq., 0.1 mL), and the reaction was stirred for 30min. The mixture was poured onto H_2O, the layers separated, and the aqueous layer extracted with CH_2Cl_2 (5 mL) and hexanes (5 mL) the combined organic layers were dried (Na_2SO_4), filtered through cotton and concentrated. Flash column chromatography (16mL silica gel, 5→20% Et_2O/hexanes eluent) afforded 102 mg of **5a** a colorless oil (72%).

Data for **5a**: TLC: R_f = 0.11 (5:95 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ = 4.12 - 4.21 (m, 1 H), 3.66 (d, *J*=1.8 Hz, 1 H), 3.61 (spt, *J*=4.1 Hz, 1 H), 2.57 (dd, *J*=9.2, 7.8 Hz, 1 H), 2.16 (s, 3 H), 1.55 - 1.64 (m, 2 H), 1.43 - 1.54 (m, 2 H), 1.26 (br. s., 10 H), 0.87 (t, *J*=6.9 Hz, 3 H), 0.20 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 208.9, 76.9, 66.9, 51.1, 42.3, 37.6, 31.9, 30.0, 29.5, 22.8, 14.2, 0.7; FTIR (thin film): 3479 (br, OH), 2948, 2857, 1714 (C=O), 1245, 1074, 837; LRMS (APCI+) $C_{22}H_{53}O_3Si_4^+$ $[M + H]^+$ 477.2 (100%).

5c (See **6c**)

5d (See **6d**)

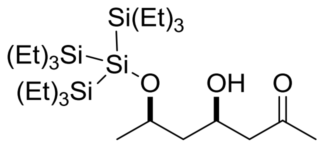
5f (See **6f**)



5i

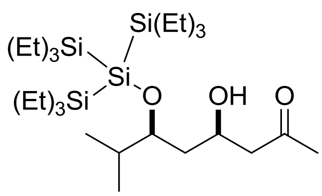
Data for 5i: TLC: R_f = 0.37 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 208.65, 72.72, 68.86, 50.86, 45.43, 30.86, 23.78, 0.56; ^1H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.09 - 4.20 (m, 1 H), 3.72 - 3.81 (m, 1 H), 3.64 (s, 1 H), 2.57 (dd, *J*=16.8, 7.3 Hz, 1 H), 2.50 (dd, *J*=16.8, 5.2 Hz, 1 H), 2.13 (s, 3 H), 1.50 (d, *J*=6.4 Hz, 1 H), 1.12 (d, *J*=6.1 Hz, 3 H), 0.15 - 0.19 (m, 27 H); LRMS (API-ES +): $C_{16}H_{41}O_3Si_4^+$ $[M +H]^+$ m/z = 393.2 (100%); FTIR (thin film): 3482 (br), 2947, 2868, 1721, 1464, 1773, 1245, 1103, 836, 684.

colorless oil



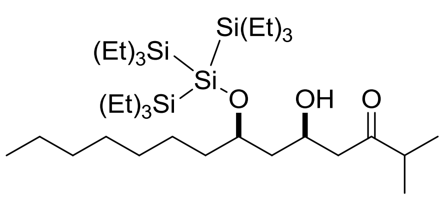
5l

Data for 5l: TLC: R_f = 0. (EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 209.50, 71.57, 65.75, 50.94, 45.60, 30.75, 32.25, 8.94, 5.48; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.05 - 4.21 (m, 1 H), 3.71 (sxt, *J*=6.1 Hz, 1 H), 3.23 (d, *J*=2.7 Hz, 1 H), 2.50 - 2.61 (m, 2 H), 2.14 (s, 3 H), 1.62 (ddd, *J*=14.3, 9.5, 6.7 Hz, 1 H), 1.39 (ddd, *J*=13.7, 6.1, 3.4 Hz, 1 H), 1.12 (d, *J*=6.1 Hz, 3 H), 1.03 (t, *J*=7.9 Hz, 27 H), 0.76 (q, *J*=7.7 Hz, 18 H); LRMS (API-ES): $C_{25}H_{59}O_3Si_4^+$ $[M + H]^+$ m/z = 519.3 (100%); FTIR (Thin film): 3483, 2951, 2875, 2729, 1713, 1458, 1417, 1376, 1095, 1004, 723, 579; colorless oil



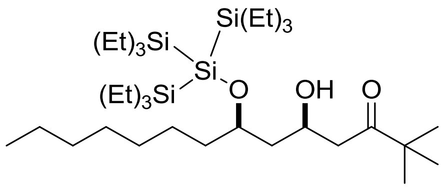
5n

Data for 5n: TLC: R_f = 0.20 (10:90 Et_2O/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 209.11, 79.41, 66.18, 50.96, 38.27, 32.01, 30.77, 17.50, 17.16, 9.03, 5.60; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.06 - 4.16 (m, 1 H), 3.46 (ddd, *J*=7.7, 5.9, 2.9 Hz, 1 H), 3.26 (br. s., 1 H), 2.51 - 2.58 (m, 2 H), 2.15 (s, 3 H), 1.46 - 1.56 (m, 1 H), 1.36 - 1.43 (m, 1 H), 1.03 (t, *J*=7.9 Hz, 27 H), 0.85 (d, *J*=6.7 Hz, 3 H), 0.74 - 0.81 (m, 18 H); LRMS (API-ES): $C_{27}H_{61}O_2Si_4^+$ $[M – OH]^+$ m/z = 529.4 (100%); FTIR (thin film): 3495, 2953, 2728, 1716, 1877, 1458, 1418, 1367, 1005, 722; colorless oil



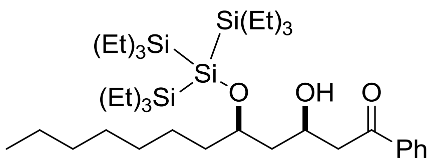
5o

Data for **5o:** TLC: R_f = 0.13 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 215.68, 75.52, 65.65, 47.69, 41.82, 41.47, 36.34, 31.93, 30.06, 29.46, 24.80, 22.78, 18.14, 18.10, 8.98, 5.53; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ =4.07 - 4.17 (m, 1 H), 3.51 - 3.60 (m, 1 H), 3.35 (d, *J*=2.7 Hz, 1 H), 2.64 (dd, *J*=17.4, 4.0 Hz, 1 H), 2.58 (s, 2 H), 1.48 - 1.63 (m, 3 H), 1.36 - 1.46 (m, 1 H), 1.19 - 1.33 (m, 10H), 1.09 (d, *J*=7.0 Hz, 3 H), 1.09 (d, *J*=7.0 Hz, 3 H), 1.03 (t, *J*=7.8 Hz, 27 H), 0.85 - 0.91 (m, 0 H), 0.77 (q, *J*=7.6 Hz, 18 H); LRMS (API-ES): $C_{32}H_{72}O_3Si_4^+$ $[M+H]^+$ m/z = 631.5 (100%); FTIR (thin film): 3509 (br), 2952, 2874, 1704, 1463, 1416, 1378, 1236, 1005, 723; colorless oil



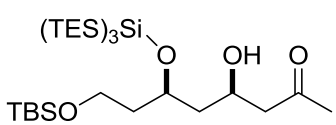
5p

Data for 5p: TLC: R_f = 0.19 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 217.20, 75.44, 65.67, 44.00, 41.86, 36.27, 31.95, 30.08, 29.47, 26.38, 24.71, 22.79, 14.22, 8.99, 5.53; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.09 (spt, *J*=4.1 Hz, 1 H), 3.49 - 3.60 (m, 1 H), 3.40 (d, *J*=2.7 Hz, 1 H), 2.65 (dd, *J*=17.7, 4.3 Hz, 1 H), 2.58 (dd, *J*=17.7, 7.3 Hz, 1 H), 1.48 - 1.61 (m, 3 H), 1.38 - 1.47 (m, 1 H), 1.26 (br. s., 10 H), 1.12 (s, 9 H), 1.03 (t, *J*=7.9 Hz, 27 H), 0.87 (t, *J*=6.7 Hz, 3 H), 0.76 (q, *J*=7.6 Hz, 18 H); LRMS (API-ES): $C_{34}H_{77}O_3Si_4^+$ $[M+H]^+$ m/z = 645.5 (100%); FTIR (thin film):3524 (br), 2952, 1696, 1458, 1418, 1394, 1236, 1063, 1004, 722; colorless oil



5q

Data for 5q: TLC: R_f = 0.13 (25:75 CH_2Cl_2/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ =200.53, 137.04, 133.46, 128.72, 128.18, 75.58, 65.85, 46.02, 41.93, 36.44, 31.92, 30.07, 29.47, 24.77, 22.78, 14.21, 8.99, 5.54; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 7.95 (dd, *J*=8.4, 1.4 Hz, 2 H), 7.57 (tt, *J*=7.6, 1.2 Hz, 1 H), 7.46 (t, *J*=7.9 Hz, 2 H), 4.28 - 4.37 (m, 1 H), 3.56 - 3.66 (m, 1 H), 3.48 (d, *J*=2.7 Hz, 1 H), 3.16 (dd, *J*=17.4, 4.0 Hz, 1 H), 3.09 (dd, *J*=17.4, 7.6 Hz, 1 H), 1.63 - 1.73 (m, 2 H), 1.51 - 1.61 (m, 1 H), 1.40 - 1.50 (m, 1 H), 1.27 (br. s., 9 H), 1.16 (d, *J*=6.4 Hz, 1 H), 1.00 - 1.08 (m, 27 H), 0.88 (t, *J*=7.0 Hz, 3 H), 0.78 (q, *J*=8.0 Hz, 18 H); LRMS (API-ES): $C_{36}H_{73}O_3Si_4^+$ $[M+H]^+$ m/z = 665.5 (100%); FTIR (thin film):3545 (br), 2952, 2874, 1679, 1623,1598,1581, 1460,1415, 1376, 1209, 1004, 732; colorless oil



5r

R_f = 0.28 (1:4 Et_2O/hexanes); IR (neat): 3487 (br, OH), 2952, 2875, 1712 (C=O), 1462, 1416, 1255, 1091, 1005, 836 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ 4.23−4.17 (m, 1H), 3.72−3.58 (m, 3H), 3.29 (d, 1H, *J* = 2.5 Hz), 2.58 (dd, *J* = 17.1, 3.5 Hz), 2.51 (dd, 1H, *J* = 17.1, 8.3 Hz), 2.15 (s, 3H), 1.88−1.80 (m, 1H), 1.60−1.48 (m, 3H), 1.03 (t, 27H, *J* = 7.8 Hz), 0.87 (s, 9H), 0.77 (q, 18H, 7.8 Hz), 0.02 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, 293K) δ 209.3, 72.9, 65.1, 59.7, 51.0, 41.9, 38.3, 30.6, 25.9, 18.3, 8.9, 5.4, −5.46, −5.54; LRMS (API-ES+) $C_{32}H_{74}NaO_4Si_5$ $[M + Na]^+$ 685.4 (100%).

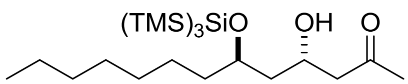
Stereochemical assignments for compounds 5

Electronic Supplementary Material (ESI) for Chemical Science

Compound **5a** was determined to be 1,3-*syn* by comparison to its corresponding1,3-*anti* diastereomer **6a**, which was determined to be 1,3-*anti* by conversion to acetonide and evaluation of ^{13}C NMR resonances.

Synthetic Procedures and Data for compounds 6 (Table 3)

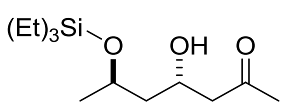
Compounds **6a-6j** (Table 2) were prepared according to **GP 5**.



6a

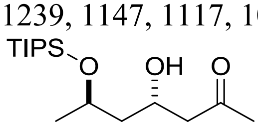
General Procedure 5 A dry 10mL round bottomed flask with magnetic stir bar was charged with aldehyde **1e** (118mg, 0.387 mmol), and enolsilane **2a** (105 mg), then fitted with a septum and purged with N_2. CH_2Cl_2 (2.5 mL) was added, and the vessel was cooled to −78 °C. BF_3**.**OEt_2 (1.0 M CH_2Cl_2) was added dropwise. After stirring for 20 min at the same temperature, TLC analysis indicated formation of product and consumption of starting materials and formation of product. The reaction was quenched by addition sat. aq. $NaHCO_3$ (10 mL). The mixture was stirred vigourously, and warmed to 0°C. The layers were then separated, and the aqueous layer was extracted with CH_2Cl_2 (2x 3 mL) and hexanes (3mL). The combined organic layers were dried (Na_2SO_4), filtered through cotton and concentrated. Flash column chromatography (12mL silica gel, 2→10% v/v EtOAc/hexanes eluent) afforded **6a** a colorless oil (90mg, 75%).

Data for 6a: R_f = 0.26 (1:4 Et_2O/hexanes); IR (neat): 3479 (br, OH), 2948, 2857, 1714 (C=O), 1245, 1074, 837 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ 4.38–4.32 (m, 1H), 3.84 (br s, 1H), 3.68–3.62 (m, 1H), 2.63 (dd, 1H, *J* = 16.5, 7.5 Hz), 2.47 (dd, 1H, *J* = 16.5, 5.0 Hz), 2.17 (s, 3H), 1.66–1.48 (m, 4H), 1.31–1.11 (m, 10H), 0.88 (t, 3H, *J* = 6.8 Hz), 0.20 (s, 27H); ^{13}C NMR (126 MHz, $CDCl_3$, 293K) δ 208.4, 76.4, 64.7, 51.2, 40.1, 35.9, 31.8, 30.9, 29.8, 29.3, 25.6, 22.6, 14.1, 0.5; LRMS (APCI+) $C_{22}H_{53}O_3Si_4$ $[M + H]^+$ 477.2 (100%), $C_{22}H_{51}O_2Si_4$ $[M - OH]^+$ 459.2 (38%); colorless oil.



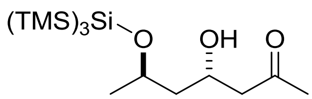
6c

Data for 6c: TLC: R_f = 0.14 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 209.27, 66.46, 64.74, 50.93, 44.68, 30.92, 23.63, 6.94, 4.94; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.30 - 4.40 (m, 1 H), 4.13 - 4.20 (m, 1 H), 3.64 (d, *J*=2.1 Hz, 1 H), 2.59 (dd, *J*=16.8, 8.2 Hz, 1 H), 2.52 (dd, *J*=16.5, 3.7 Hz, 1 H), 1.60 (ddd, *J*=14.0, 10.1, 3.4 Hz, 1 H), 1.44 (ddd, *J*=14.3, 7.0, 2.4 Hz, 1 H), 1.21 (d, *J*=6.4 Hz, 3 H), 0.95 (t, *J*=7.9 Hz, 9 H), 0.60 (q, *J*=8.0 Hz, 6 H);LRMS (API-ES): $C_{13}H_{29}O_3Si^+$ $[M+H]^+$ m/z = 261.2 (100%); FTIR (thin film):3481 (br), 2957, 2912, 2877, 1713, 1458, 1417, 1374, 1239, 1147, 1117, 1007, 746, colorless oil;



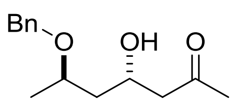
6d

Data for 6d: TLC: R_f = 0.15 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 208.83, 67.6, 64.81, 44.32, 31.00, 23.16, 18.23, 12.49; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.45 (tdd, *J*=8.0, 8.0, 4.2, 2.1 Hz, 1 H), 4.31 (dd, *J*=5.3, 3.8 Hz, 1 H), 3.81 (d, *J*=1.8 Hz, 1 H), 2.62 (dd, *J*=16.8, 8.2 Hz, 1 H), 2.49 (dd, *J*=16.5, 4.3 Hz, 1 H), 2.17 (s, 3 H), 1.67 - 1.75 (m, 2 H), 1.48 (ddd, *J*=14.0, 5.2, 2.1 Hz, 2 H), 1.28 (d, *J*=6.4 Hz, 3 H), 1.06 (s, 21 H); LRMS (API-ES): $C_{16}H_{35}O_3Si^+$ $[M+H]^+$ m/z = 303.3 (100%); FTIR (thin film):3489, 2943, 2887, 1715, 1464, 1419, 1373, 1256, 1098, 1057, 1014, 833, 877; colorless oil



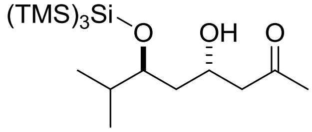
6e

Data for 6e: TLC: R_f = 0.20 (10:75 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 208.70, 71.90, 64.79, 51.18, 43.87, 30.99, 22.57, 0.52, 0.51; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.34 - 4.41 (m, 1 H), 3.83 - 3.93 (m, 1 H), 3.75 (s, 1 H), 2.60 (dd, *J*=16.5, 8.2 Hz, 1 H), 2.46 (dd, *J*=16.5, 4.9 Hz, 1 H), 2.16 (s, 3 H), 1.63 (ddd, *J*=14.0, 10.2, 3.5 Hz, 1 H), 1.42 (ddd, *J*=14.3, 5.5, 2.1 Hz, 1 H), 1.20 (d, *J*=6.4 Hz, 3 H), 0.18 (s, 27 H); LRMS (API-ES): $C_{16}H_{39}O_2Si_4^+$ $[M – OH]^+$ m/z = 375.2 (100%); HRMS (ESI/APCI +): $C_{16}H_{39}O_2Si_4^+$ $[M+H–H_2O]^+$ m/z = 375.2025 (calc: 375.2027; 0.91 ppm) $C_{16}H_{41}O_3Si_4^+$ $[M+H]^+$ m/z = 393.2131 (calc: 393.2133, 0.94 ppm);



6f

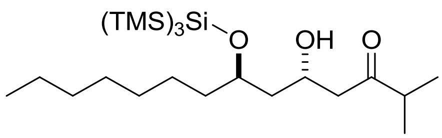
Data for 6f: TLC: R_f = 0.15 (25:75 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 209.53, 138.61, 128.53, 127.94, 127.76, 72.23, 70.92, 64.85, 50.50, 43.20, 30.86, 19.66; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 7.35 - 7.41 (m, 18 H), 7.32 (dd, *J*=4.7, 3.8 Hz, 1 H), 4.66 (d, *J*=11.3 Hz, 1 H), 4.48 (d, *J*=11.3 Hz, 5 H), 4.38 (d, *J*=5.2 Hz, 1 H), 3.85 - 3.94 (m, 1 H), 3.36 (br. s., 1 H), 2.60 (m, *J*=6.4 Hz, 2 H), 2.18 (s, 3 H), 1.65 - 1.73 (m, 1 H), 1.58 - 1.65 (m, 1 H), 1.28 (d, *J*=6.1 Hz, 3 H); (LMRS (API-ES) $C_7H_{13}O_2^+$ [M – benzyl- $OH+H]^+$ m/z = 129.1 (100%); HRMS (ESI-TOF +) $C_{14}H_{21}O_3^+$ $[M+H]^+$ m/z = 237.140909 (calc: 237.14907, 10 ppm); FTIR (thin film): 3466, 2968, 2931, 1711, 1454, 1419, 1376, 1165, 1095, 1064, 740, 699; colorless oil



6g

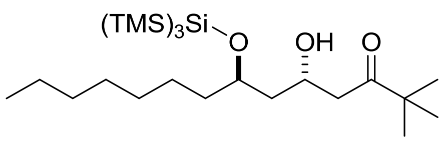
Data for 6g: TLC: R_f = 0.11 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 203.39, 78.99, 64.88, 51.20, 37.37, 32.89, 30.86, 19.27, 16.38, 0.80; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.25 (dqd, *J*=9.9, 4.0, 4.0, 4.0, 2.7 Hz, 1 H), 3.49 (ddd, *J*=7.8, 5.0, 2.7 Hz, 1 H), 2.59 (dd, *J*=17.7, 8.2 Hz, 1 H), 2.53 (dd, *J*=17.1, 4.3 Hz, 1 H), 2.16 (s, 3 H), 1.82 - 1.92 (m, 1 H), 1.42 - 1.49 (m, 2 H), 1.37 (ddd, *J*=14.0, 7.9, 2.7 Hz, 2

H), 0.87 (d, *J*=7.0 Hz, 3 H), 0.81 (d, *J*=7.0 Hz, 3 H), 0.19 (s, 27 H); LRMS (API-ES): $C_{18}H_{43}O_2Si_4^+$ $[M - OH]^+$ m/z = 403.3 (100%), $C_{18}H_{45}O_3Si_4^+$ $[M+H]^+$ m/z = 421.2 (50%); FTIR (thin film):3480 (br) 2958, 2895, 1716, 1680, 1367, 1245, 1040, 835, 687; colorless oil.



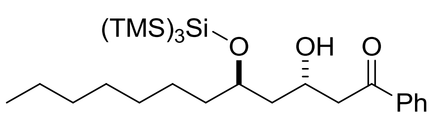
6h

Data for 6h: TLC: R_f = 0.44 (10:90 EtOAc/hexanes);^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 214.53, 76.34, 64.80, 47.92, 41.57, 40.67, 36.20, 31.91, 29.97, 29.41, 25.61, 22.77, 18.17, 18.10, 14.22, 0.61; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.28 - 4.39 (m, 1 H), 3.79 (s, 1 H), 3.65 (m, *J*=7.6, 5.2, 5.2, 3.1 Hz, 1 H), 2.66 (dd, *J*=16.9, 7.2 Hz, 1 H), 2.58 (dquin, *J*=13.9, 7.0, 7.0, 7.0, 7.0 Hz, 1 H), 2.49 (dd, *J*=17.1, 5.2 Hz, 1 H), 1.47 - 1.64 (m, 4 H), 1.27 (br. s., 10 H), 1.16 (d, *J*=7.9 Hz, 1 H), 1.08 (d, *J*=7.0 Hz, 3 H), 0.87 (t, *J*=6.7 Hz, 3 H), 0.19 (s, 27 H); LRMS(API-ES): $C_{24}H_{57}O_3Si_4^+$ $[M+H]^+$ m/z = 505.4 (100%); FTIR (thin film):3081, 2958, 2995, 1716, 1879, 1387, 1367, 1245, 1040, 835, 687, 624; colorless oil



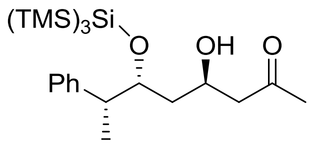
6i

Data for 6i: TLC: R_f = 0. (EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 216.01, 76.20, 64.82, 44.32, 40.90, 36.34, 31.93, 29.99, 29.41, 26.38, 25.52, 27.79, 14.24, 0.62; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 4.23 - 4.45 (m, 1 H), 3.82 (s, 1 H), 3.66 (br. s, 1 H), 2.70 (dd, *J*=17.5, 6.9 Hz, 1 H), 2.53 (dd, *J*=17.4, 5.2 Hz, 1 H), 1.49 - 1.63 (m, 4 H), 1.28 (br. s., 10 H), 1.19 (br. s., 1 H), 1.12 (s, 9 H), 0.19 (s, 27 H); LRMS (API-ES): $C_{25}H_{59}O_3Si_4^+$ $[M+H]^+$ m/z = 519.3 (100%); FTIR (thin film):3489, 2956, 2858, 1697, 1465, 1394, 1367, 1245, 1066, 838, 687, 624



6j

Data for 6j:TLC: R_f = 0.44 (EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$, 293K) δ = 199.56, 137.18, 133.34, 128.72, 128.27, 76.52, 65.05, 46.45, 40.61, 36.16, 31.92, 29.98, 29.42, 25.63, 22.79, 14.25, 0.63; ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ = 7.96 (d, *J*=7.9 Hz, 2 H), 7.56 (t, *J*=7.3 Hz, 1 H), 7.45 (t, *J*=7.3 Hz, 2 H), 4.51 - 4.59 (m, 1 H), 3.96 (s, 1 H), 3.67 - 3.74 (m, 1 H), 3.23 (dd, *J*=17.1, 6.7 Hz, 1 H), 3.02 (dd, *J*=16.9, 5.6 Hz, 1 H), 1.55 - 1.76 (m, 5 H), 1.28 (br. s., 10 H), 1.19 (m, *J*=8.5 Hz, 1 H), 0.88 (t, *J*=6.7 Hz, 3 H), 0.20 (s, 27 H); HRMS (CI +) $C_{27}H_{54}O_3Si_4$ $[M]^+$ m/z = 538.3153 (calc.: 538.3150, 5.6 ppm), $C_{19}H_{47}O_2Si_4$ [M-acetophenone]$^+$ m/z = 419.2686 (calc: 419.2653, 8 ppm).



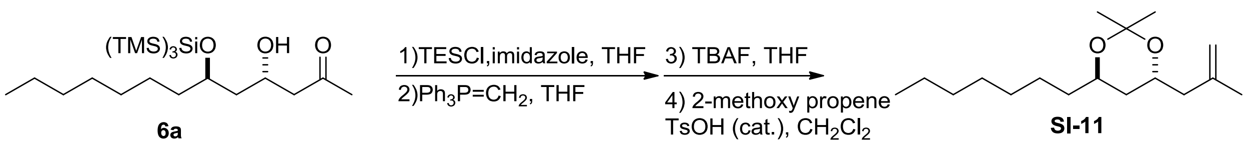
6k

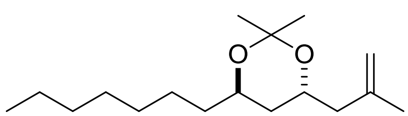
Data for 6k: TLC: R_f = 0.21 (20:80 Et_2O/hexanes);FTIR (thin film) 3527, 2951, 2874, 1711, 1458, 1416, 1236, 1080, 1004, 700; LRMS (API-ES +) $C_{32}H_{74}O_4NaSi_5^+$ $[M+Na]^+$ m/z = 685.4 (100%). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 209.1, 144.0, 128.3, 128.0, 126.3, 78.9, 65.4, 50.8, 43.0, 40.0, 30.6, 15.1, 0.7; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.17-7.28 (m, 5H), 4.09, (m, 1H), 3.82 (m, 1H),3.01-3.02 (m, 2H), 2.47-2.52 (m, 2H), 2.14 (s, 3H), 1.43-1.45 (m, 2H), 1.24 (d, *J* = 3H), 0.19 (s, 27 H).

Stereochemical assignment for compounds 6

Compound **6a** was determined to be 1,3-*anti* configured by conversion to SI-1by the synthetic sequence shown in **Scheme S-8.** 1,3-diol ^{13}C resonances at δ = 100.2, 29.5, 29.2 indicated a 1,3-*anti* configuration as established by Rychnovsky.[32,33,34]

Scheme S-8: Preparation of **SI-11**





SI-11

General Procedure 6: (1) To a dry 25 mL round bottomed flask was added **3-*A*** (141 mg, 0.3 mmol) under a N_2 atmosphere. Imidazole (37 mg, 0.54 mmol) was added followed by THF. The stirring reaction flask was cooled to 0 °C. TESCl was then added (75μL, 0.45 mmol) dropwise. The cooling bath was removed and the reaction stirred for an addition 2 h. The reaction was then diluted with H_2O (10 mL) and hexanes (5 mL). The layers were separated and the organic layer was extracted with EtOAc/Hexanes (1:4, 5 mL). The combined organic layers were washed with H_2O, $NaHCO_3$ (sat. aq.) and brine (10 mL each), dried over Na_2SO_4, filtered through cotton, and concentrated under reduced pressure. The silyl ether was purified by column chromatography (20 mL silica, 2→5% EtOAc/hexanes eluent) affording a colorless oil (163 mg, 93%).

(2) To a stirring suspension of methyltriphenylphosphium bromide (220mg, 0.53 mmol) in anhydrous THF (1.5 mL) at 0°C was added *n*-Butyllithium (0.210mL, 0.62mmol, 2.5 M hexanes), dropwise. The yellow solution was stirred at this temperature

[32] Rychnovsky, S. D.; Skalitzky, D. J. *Tetrahedron Lett.* **1990**, *31*, 945–948.
[33] Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, *58*, 3511–3515.
[34] Evans, D. A.; Rieger, D. L.; Gage, J. R. *Tetrahedron Lett.* **1990**, *31*, 7099–7100.

for 45 min then cooled to −78°C. In a separate flask, the intermediate was described above was dissolved in anhydrous THF(0.3 mL) and added to the ylide solution by syringe, dropwise. The flask was rinsed with 2x 0.2 mL THF and added to the reaction vessel to quantitate the transfer. The reaction was slowly warmed to 0°C over 3 hr and quenched by the addition of 5 mL MeOH/H_2O (3:2 v/v) and 3 mL of saturated aqueous NH_4Cl. 20mL hexanes was then added. The layers were separated and the organic layer was washed with 5 mL of H_2O and 5 mL of brine. The organic layer was dried over Na_2SO_4, filtered through cotton and evaporated. The crude mixture was purified by flash chromatography (16 mL SiO_2 with hexanes as an eluent.

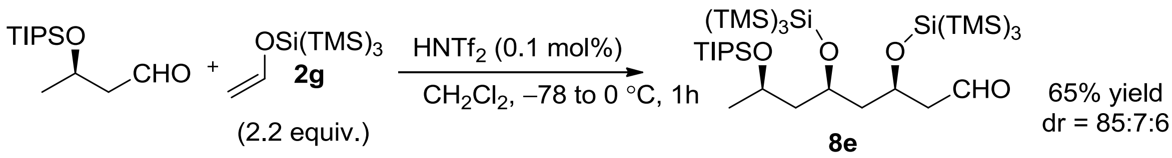
(3)The resulting olefin (145 mg, 92% yield) was dissolved in THF and cooled to 0°C and tetrabutylammonium fluoride (0.50 mL, 0.05 mmol, 1.0M THF) was added dropwise. Gas evolution was observed. The stirring solution was warmed to 23°C and stirred for an additional 30 min. 0.05 mL glacial acetic acid and the reaction was stirred overnight. The solvent was evaporated. The mixture was redissolved in 25 mL ethyl acetate and washed with water (2x 7mL) and brine (10mL) the organic layer was dried over Na_2SO_4, filtered through cotton and evaporated. The crude reaction mixture was purified by flash chromatography (16 mL SiO_2) with *i*-PrOH/Hexanes as the eluent (2%→20% v/v), giving the intermediate diol (55 mg, >95 yield).

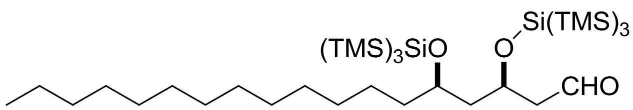
(4)The intermediate diol (24 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and cooled to 0°C. 2-methoxypropene (11μL, 0.11 mmol) was added, followed by *p*-toluenesulfonic acid monohydrate (0.2 mg) was added. The reaction was stirred for 1h and slowly warmed to 23°C. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ (2mL). The layers were separated and aqueous layer was extracted with CH_2Cl_2 (2x 5mL CH_2Cl_2). The organic layer was dried over Na_2SO_4, filtered through cotton and evaporated. The crude reaction mixture was purified by flash chromatography (5mL SiO_2) with EtOAc/hexanes as an eluent (1%→5% v/v) to give acetonide **SI-11** (22 mg, 78% yield).

Data for SI-11: TLC: R_f = 0.44 (5:95 EtOAc/hexanes); FTIR (thin film) 2931, 2856, 1651, 1458, 1378, 1224, 1168, 1028, 889; LRMS (API-ES +): $C_{17}H_{31}O^+$ $[M – H_2O+ H]^+$ m/z = 251.2 (20%). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 142.4, 112.1, 100.2, 66.6, 65.1, 44.1, 38.5, 35.9, 31.8, 29.6, 29.5, 29.2, 25.4, 25.0, 24.8, 22.8, 22.6, 14.1; (500 MHz, $CDCl_3$) δ = 4.78 (s, 1H), 4. 74 (s, 1H), 3.97 (app quint. *J* = 6.5Hz, 1H), 3.75 (m, 1H), 2.27 (dd, *J* = 7 Hz, 9.5 Hz, 1H), 2.11 (dd, *J* = 6 Hz, 9.5 Hz, 1H), 1.73 (s, 3H), 1.48-1.161 (m, 3H), 1.40-1.44 (m, 2H), 1.36 (s, 3H), 1.34 (s, 3H), 1.25-1.31 (m, 10H), 0.86 (t, *J* = 7 Hz, 1H)

Synthetic procedures and data for compounds 8
Compounds **8** were prepared according to **GP 7**, according to Scheme **S-5**[8]

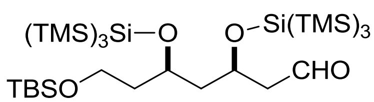
Scheme S-9: synthesis of **8d**



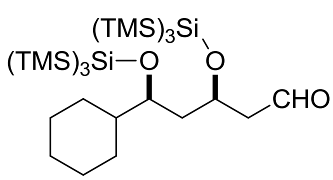


8a Known compound[8]

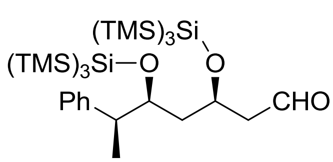
Data for **8a:** TLC: R_f = 0.49 (20:80 CH_2Cl_2/hexanes)FTIR (thin film) 2926, 2896, 2854, 1727, 1466, 1394, 1257, 1084, 836, 687, 624; ^{13}C NMR (500 MHz, $CDCl_3$) δ = 202.4, 73.4, 69.6, 49.5, 43.6, 37.9, 31.9, 29.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 25.3, 22.7, 14.1, 0.8, 0.6; ^{1}H NMR 500 MHz, $CDCl_3$) δ = 9.77 (dd, 1H, J = 4.0, 1.1 Hz), 4.14−4.08 (m, 1H), 3.39 (app tt, 1H, J = 8.5, 4.3 Hz), 2.57 (ddd, 1H, *J* = 15.2, 4.7, 1.1 Hz), 2.36 (ddd, 1H, *J* = 15.2, 6.8, 4.0Hz), 1.74 (ddd, 1H, *J* = 14.0, 9.0, 5.5 Hz), 1.64−1.56 (m, 1H), 1.47 (ddd, 1H, *J* = 13.2, 9.3, 4.0 Hz), 1.33−1.23 (m, 23H), 0.88 (t, 3H, *J* = 6.8 Hz), 0.19 (s, 27H), 0.18 (s, 27H)



Data for 8b: TLC: R_f = 0.07 (25:75 CH_2Cl_2/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 202.36, 70.86, 69.9, 59.70, 49.71, 43.69, 40.21, 26.08, 18.39, 0.83, 0.67, -5.27, -5.32; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.76 (dd, *J*=3.4, 1.5 Hz, 1 H), 4.07 - 4.22 (m, 1 H), 3.57 - 3.69 (m, 3 H), 2.56 (ddd, *J*=15.3, 4.5, 1.2 Hz, 1 H), 2.35 (ddd, *J*=15.3, 6.8, 3.8 Hz, 1 H), 1.95 (dtd, *J*=12.9, 7.8, 7.8, 4.7 Hz, 1 H), 1.76 (ddd, *J*=13.7, 8.7, 5.6 Hz, 1 H), 1.47 - 1.55 (m, 2 H), 0.87 (s, 9 H), 0.18 (d, *J*=1.8 Hz, 54 H), 0.03 (s, 6 H); LRMS (API-ES): $C_{31}H_{80}O_4NaSi_9^+$ $[M+Na]^+$ m/z = 791.3 (15%)



8c Known compound[35]



8d PB-5135 Known compound[18]

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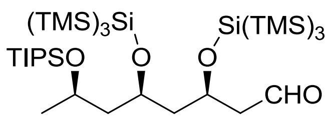
[35] Boxer, M. B.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 48–49.

General Procedure GP 7

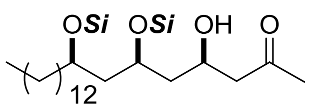
To a flame-dried 50 mL round bottomed-flask was added enolsilane **2g** (960mg, 3.3 mmol, 2.2 equiv.), CH_2Cl_2 (12 mL), and (*S*) 2-phenyl propanal (199µL, 1.5 mmol). The stirring flask was cooled to –78°C in a dry ice/acetone cooling bath. $HNTf_2$ (0.010M CH_2Cl_2, 100µL) was added dropwise over 2 min. The reaction was stirred at this temperature for 15 min then slowly warmed to 0°C over the course of 1.5h. The reaction was judged to be complete by consumption of **2g**, (*S*) 2-phenyl propanal, and formation of product. The reaction was quenched by addition of 5mL pH 7.0 phosphate buffer and stirred vigorously. The layers were separated and the aqueous phases was extracted with hexanes (3x 5mL). The combined organic layers were dried (Na_2SO_4), filtered (cotton plug) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography with CH_2Cl_2/hexanes as an eluent (5→20% gradient) to give **8d** as a colorless oil (760 mg, 71%). Previously described compound.



8e Known compound[18]

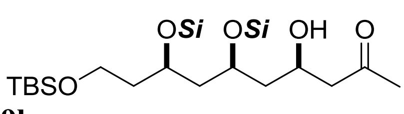
Synthetic procedures and Data for Compounds 9-12.

Compounds 9 and 10 were synthesized according to **GP 4** and **GP 5**, respectively.



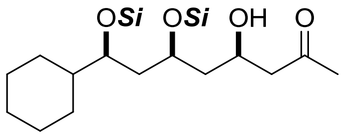
9a

TLC: R_f = 0.1 (5:95 Et_2O/hexanes); FTIR (thin film): 3148 (br), 2926, 2854, 1713, 1395, 1366, 1244, 1047, 837, 687; LRMS (APCI −) $C_{39}H_{94}O_4Si_8^-$ $[M+^{35}Cl]^-$ m/z = 885.5 (10%), $C_{33}H_{76}O_4Si_6^-$ $[M\text{-}TMS_2]^-$ m/z = 703 (100%); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 208.1, 73.8, 73.4, 66.9, 66.9, 51.2, 44.1, 41.8, 38.2, 31.9, 30.5, 29.85, 29.66, 29.64, 29.59, 29.55, 29.45, 29.35, 25.35, 22.7, 14.1, 0.7, 0.6; ^1H NMR 500 MHz, $CDCl_3$) δ = 4.35 (br, app tt, *J* = 6.4, 4.3, 1H), 4.10 (s, 1H), 3.99 (app dq, *J* = 9.8, 4.2, 1H), 3.34-3.40 (m, 1H), 2.65 (dd, *J* = 16.4, 6.7 Hz, 1H), 2.45 (dd, *J* = 16.4, 5.5 Hz), 2.15 (s, 3H), 1.78-1.5 (m, 7H), 1.24-1.34 (m, 24H), 0.88 (t, *J* =6.9 Hz, 3H), 0.205 (s, 27H), 0.17 (s, 27H).



9b

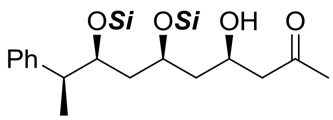
TLC: R_f = 0.27 (10:90 EtOAc/hexanes); ^{13}C NMR 500 MHz, $CDCl_3$) δ = 208.34, 73.95, 70.79, 67.00, 59.76, 51.42, 43.99, 42.05, 40.48, 30.67, 26.07, 18.39, 0.82, 0.79, -5.32; ^1H NMR 500 MHz, $CDCl_3$) δ = 4.17 - 4.29 (m, 1 H), 3.91 (tt, *J*=8.8, 4.6 Hz, 1 H), 3.77 (s, 1 H), 3.53 - 3.68 (m, 3 H), 2.54 (m, *J*=15.6, 8.2 Hz, 1 H), 2.49 (dd, *J*=16.2, 4.3 Hz, 1 H), 2.18 (s, 3 H), 1.98 (dtd, *J*=12.7, 8.0, 8.0, 4.6 Hz, 1 H), 1.71 (ddd, *J*=13.0, 9.6, 5.5 Hz, 1 H), 1.63 (ddd, *J*=14.0, 4.3, 2.7 Hz, 1 H), 1.33 - 1.53 (m, 3 H), 0.87 (s, 9 H), 0.20 - 0.22 (m, 27 H), 0.18 (s, 27 H); LRMS (API-ES) $C_{34}H_{87}O^5Si_9^+$ $[M+H]^+$ m/z = 827.2 (100%)



9c

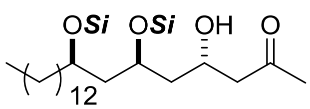
TLC: R_f = 0.29 (10:90 EtOAc/hexanes); ^{13}C NMR 500 MHz, $CDCl_3$) δ = 208.73, 77.54, 73.22, 66.22, 51.33, 43.02, 42.51, 39.80, 30.70, 28.77, 27.53, 27.03, 26.70, 26.43, 0.99, 0.78; ^{1}H NMR 500 MHz, $CDCl_3$) δ =4.15 - 4.24 (m, 1 H), 3.84 (ddd, *J*=12.8, 8.0, 6.4 Hz, 1 H), 3.57 (d, *J*=1.5 Hz, 1 H), 3.33 (dt, *J*=8.8, 3.4 Hz, 1 H), 2.50 - 2.56 (m, 2 H), 2.17 (s, 3 H), 1.75 (d, *J*=11.0 Hz, 2 H), 1.64 - 1.71 (m, 3 H), 1.52 - 1.58 (m, 2 H), 1.44 - 1.52 (m, 2 H), 1.29 (ddd, *J*=13.0, 8.4, 4.0 Hz, 1 H), 1.21 (tt, *J*=12.5, 3.1 Hz, 1 H), 1.03 - 1.16 (m, 1 H), 0.97 (qd, *J*=12.8, 3.1 Hz, 1 H), 0.20 (s, 27 H), 0.18 (s, 27 H);

LRMS (API-ES):



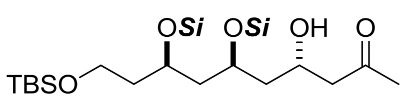
9d

R_f = 0.33 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 209.15, 144.66, 128.52, 128.09, 126.07, 77.13, 71.75, 65.61, 51.08, 43.53, 42.37, 40.84, 30.76, 14.87, 1.05, 0.84; 7.26 - 7.35 (m, 6 H), 7.16 - 7.25 (m, 2 H), 4.20 (dqd, *J*=9.8, 4.8, 4.8, 4.8, 2.4 Hz, 1 H), 3.89 - 3.96 (m, 1 H), 3.85 (td, *J*=6.5, 3.2 Hz, 1 H), 3.33 (d, *J*=2.1 Hz, 1 H), 3.03 (qd, *J*=7.0, 3.4 Hz, 1 H), 2.23 (s, 3 H), 1.83 (ddd, *J*=13.7, 10.1, 5.8 Hz, 1 H), 1.60 (td, *J*=6.4, 4.0 Hz, 3 H), 1.51 (ddd, *J*=13.4, 7.6, 2.3 Hz, 1 H), 1.37 (dd, *J*=7.2, 2.6 Hz, 1 H), 1.27 (d, *J*=7.3 Hz, 1 H), 0.20 (s, 27 H), 0.19 (s, 27 H); LRMS (API-ES): $C_{34}H_{75}O_3Si_8^+$ [M – OH]$^+$ m/z = 755.3 (10%).



10a

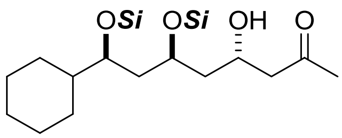
R_f = 0.2 (5:95 Et_2O/hexanes); FTIR (thin film) 3469 (br), 2948, 2926, 2895, 1717, 1437, 1373, 1244, 1050, 836; LRMS (APCI +) $C_{39}H_{93}O_3Si_8^+$ [M-OH]$^+$ m/z = 833.5 (10%), $C_{30}H_{68}O_3Si_4^+$ [M-TMS$_3$SiOH]$^+$ m/z = 587.5 (100%). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 207.3, 74.0, 73.5, 64.8, 51.4, 41.4, 38.9, 38.7, 31.92, 30.94, 29.96, 29.69, 29.65, 29.63, 29.53, 29.35, 25.45, 22.7, 14.1, 0.6, 0.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.20-4.24 (m, 1H), 3.91, (app tt, *J* = 9.0, 4.5 Hz, 1H), 3.82 (s, 1H), 3.37 (br, app. tt, *J* = 9.4, 4.8, 1H), 2.46-2.56 (m, 2H), 2.19 (s, 3H) 1.70 (ddd, *J* = 12.5, 10.0, 5.2 Hz, 1H), 1.61-1.67 (m, 2H), 1.37-1.53 (m, 2H) 1.24-1.34 (m, 25 H), 0.88 (t, *J* = 3H), 0.21 (s, 27H), 0.17 (s, 27H).



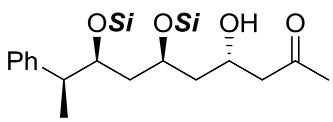
10b

TLC: R_f = 0.40 (10:90 EtOAc/hexanes) ^{13}C NMR (500 MHz, $CDCl_3$, 295K) δ = 207.63, 73.18, 71.18, 64.97, 59.78, 51.44, 41.97, 41.14, 39.42, 31.09, 26.09, 18.37, 0.82, 0.65, -

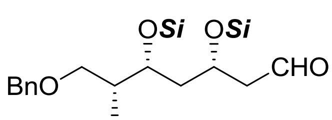
5.31; ^{1}H NMR (500 MHz, $CDCl_3$, 295K) δ = 4.34 (br. s., 1 H), 3.93 - 4.05 (m, 2 H), 3.60 - 3.72 (m, 2 H), 3.53 - 3.60 (m, 1 H), 2.61 (dd, *J*=16.2, 7.0 Hz, 1 H), 2.46 (dd, *J*=16.5, 4.9 Hz, 1 H), 2.17 - 2.19 (m, 1 H), 2.14 - 2.16 (m, 3 H), 1.95 - 2.05 (m, 1 H), 1.64 - 1.76 (m, 4 H), 1.48 - 1.61 (m, 3 H), 0.88 (s, 9 H), 0.20 (s, 27 H), 0.18 (d, *J*=1.8 Hz, 25 H), 0.04 (s, 6 H); LRMS (API-ES+) $C_{34}H_{87}O_5Si_9^+$ $[M+H]^+$ m/z = 827.2 (100%); colorless oil



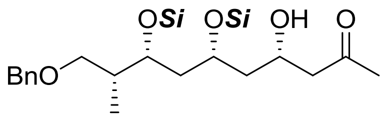
10c
^{13}C NMR (500 MHz, $CDCl_3$, 295K) δ = 207.40, 77.75, 74.46, 64.70, 51.59, 44.09, 39.07, 36.68, 31.03, 30.15, 29.85, 27.03, 26.79, 26.40, 26.22, 0.98, 0.62; ^{1}H NMR (500 MHz, $CDCl_3$, 295K) δ = 4.27 - 4.35 (m, 1 H), 4.14 (s, 1 H), 3.90 - 4.00 (m, 1 H), 3.28 (d, *J*=8.5 Hz, 1 H), 2.65 (dd, *J*=16.5, 6.4 Hz, 1 H), 2.46 (m, *J*=5.8 Hz, 1 H), 2.15 (s, 3 H), 1.68 - 1.83 (m, 5 H), 1.58 - 1.68 (m, 3 H), 1.48 - 1.58 (m, 2 H), 1.11 - 1.36 (m, 3 H), 0.93 - 1.10 (m, 2 H), 0.17 - 0.22 (m, 54 H)
LRMS (API-ES +) $C_{32}H_{79}O_4Si_8^+$ $[M+H]^+$ m/z = 751.3 (90%), $C_{23}H_{51}O_3Si_4^+$ $[M – TMS_3SiO]^+$ m/z = 487.4 (100%)



10d
R_f = 0.36 (10:90 EtOAc/hexanes) ^{13}C NMR (500 MHz, $CDCl_3$, 295K) δ = 208.08, 142.60, 128.63, 128.11, 126.37, 78.60, 73.26, 64.64, 51.36, 43.54, 40.84, 38.67, 30.99, 29.86, 17.41, 1.33, 0.54; ^{1}H NMR (500 MHz, $CDCl_3$, 295K) δ = 7.26 - 7.33 (m, 6 H), 7.22 (td, *J*=5.7, 2.9 Hz, 1 H), 4.27 - 4.44 (m, 1 H), 3.90 (s, 1 H), 3.86 (sxt, *J*=4.3 Hz, 1 H), 3.68 (dt, *J*=8.9, 3.4 Hz, 1 H), 3.11 (qd, *J*=7.0, 4.1 Hz, 1 H), 2.69 (dd, *J*=16.9, 7.2 Hz, 1 H), 2.54 (dd, *J*=16.8, 5.2 Hz, 1 H), 2.21 (s, 3 H), 1.77 (ddd, *J*=14.3, 10.2, 4.1 Hz, 2 H), 1.53 - 1.68 (m, 3 H), 1.36 (d, *J*=7.3 Hz, 3 H), 0.27 (s, 27 H), 0.10 (s, 27 H); LRMS (API-ES+) $C_{25}H_{49}O_3Si_4^+$ $[M – TMS_3SiO]^+$ m/z = 509.3 (100%), $C_{34}H_{77}O_4Si_8^+$ $[M+H]^+$ m/z = 773.2 (15%).

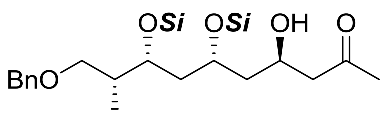


12 Prepared according to **GP 6**
Data for 12: R_f = 0.32 (5:95 EtOAc/hexanes);^{13}C NMR (500 MHz, $CDCl_3$, 295K) δ = 201.49, 138.76, 128.36, 127.83, 127.50, 75.05, 73.44, 72.71, 69.77, 50.10, 40.01, 38.23, 13.02, 0.9, 0.69; ^{13}C NMR (500 MHz, $CDCl_3$, 295K) δ = 9.80 - 9.86 (m, 1 H), 4.58 (d, *J*=12.2 Hz, 1 H), 4.47 (d, *J*=11.6 Hz, 1 H), 4.08 (quin, *J*=6.0 Hz, 1 H), 3.55 - 3.65 (m, 2 H), 3.27 (t, *J*=8.9 Hz, 1 H), 2.63 (ddd, *J*=15.6, 6.4, 1.8 Hz, 1 H), 2.51 (ddd, *J*=15.6, 5.5, 3.1 Hz, 1 H), 2.03 - 2.13 (m, 1 H), 1.64 - 1.76 (m, 1 H), 1.48 (br. s., 1 H), 0.97 (d, *J*=7.0 Hz, 3 H), 0.24 (s, 54 H); LRMS (API-ES +) $C_{33}H_{75}O_4Si_8^+$ $[M+H]^+$ m/z = 759.3 (20%);



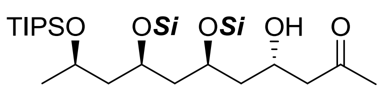
13

R_f = 0.27 (10:90 EtOAc/hexanes);
^{13}C NMR (500 MHz, $CDCl_3$, 295K) δ =208.88, 138.82, 128.33, 127.82, 127.46, 75.32, 73.38, 72.93, 72, 39, 65.75, 51.12, 42.47, 39.48, 38.25, 30.69, 13.06, 0.86, 0.77; ^{1}H NMR (500 MHz, $CDCl_3$, 295K) δ = 7.36 (d, *J*=4.6 Hz, 4 H), 7.30 (q, *J*=3.9 Hz, 1 H), 4.57 (d, *J*=11.9 Hz, 1 H), 4.45 (d, *J*=11.9 Hz, 1 H), 4.16 - 4.25 (m, 1 H), 3.86 (quin, *J*=6.6 Hz, 1 H), 3.55 - 3.62 (m, 2 H), 3.48 (s, 1 H), 3.23 (t, *J*=9.0 Hz, 1 H), 2.53 - 2.62 (m, 2 H), 2.19 - 2.24 (m, 3 H), 2.03 - 2.12 (m, 1 H), 1.62 - 1.70 (m, 1 H), 1.55 - 1.62 (m, 1 H), 1.45 - 1.54 (m, 2 H), 0.96 (d, *J*=6.7 Hz, 3 H), 0.22 - 0.24 (m, 32 H), 0.21 (s, 27 H); LRMS (API-ES) $C_{36}H_{81}O_5Si_8^+$ $[M+H]^+$ m/z = 817.3 (100%)



14

^{13}C NMR (500 MHz, $CDCl_3$, 320 K) δ = 207.45, 138.69, 128.39, 127.87, 127.55, 76.52, 74.13, 73.61, 71.67, 64.62, 51.40, 39.39, 36.58, 30.99, 15.09, 0.89, 0.61; ^{1}H NMR (500 MHz, $CDCl_3$, 320 K) δ =7.34 - 7.43 (m, 4 H), 7.28 - 7.34 (m, 1 H), 4.54 - 4.60 (m, 1 H), 4.44 - 4.52 (m, 1 H), 4.35 (s, 1 H), 4.07 (s, 1 H), 3.94 (s, 1 H), 3.63 - 3.70 (m, 1 H), 3.43 - 3.49 (m, 1 H), 3.21 (t, *J*=9.0 Hz, 1 H), 2.69 (dd, *J*=16.8, 6.4 Hz, 1 H), 2.52 (dd, *J*=17.1, 6.1 Hz, 1 H), 2.19 (br. s, 3 H), 2.12 (dtt, *J*=9.7, 6.5, 6.5, 3.3, 3.3 Hz, 1 H), 1.62 - 1.76 (m, 3 H), 1.52 - 1.61 (m, 1 H), 1.07 (d, *J*=7.0 Hz, 3 H), 0.86 - 1.00 (m, 1 H), 0.22 (s, 54 H); LRMS (API-ES) $C_{36}H_{81}O_5Si_8^+$ $[M+H]^+$ m/z = 817.3 (100%);



10e

TLC: R_f = 0.42 (10:90 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$, 320 K) δ = 4.27 - 4.36 (m, 1 H), 4.04 - 4.14 (m, 1 H), 3.97 (sxt, *J*=4.9 Hz, 1 H), 3.70 (tt, *J*=9.2, 4.8 Hz, 1 H), 3.63 (d, *J*=2.4 Hz, 1 H), 2.55 (dd, *J*=15.6, 8.2 Hz, 1 H), 2.47 (dd, *J*=16.2, 4.0 Hz, 1 H), 2.17 (s, 3 H), 2.01 (ddd, *J*=13.3, 8.4, 5.2 Hz, 1 H), 1.66 - 1.80 (m, 3 H), 1.50 (ddd, *J*=14.3, 5.5, 2.4 Hz, 1 H), 1.27 - 1.34 (m, 3 H), 1.24 (d, *J*=6.1 Hz, 3 H), 1.06 (s 18 H), 0.20 (s, 27 H), 0.19 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$, 320 K) δ = 208.1, 72.9, 70.0, 66.1, 65.1, 51.2, 48.6, 42.9, 40.3, 30.9, 24.8, 18.44, 18.36, 12.9, 0.9, 0.6; LRMS (API-ES+) $C_{38}H_{94}O_5NaSi_9^+$ $[M+Na]^+$ m/z = 905.2 (100%).

Stereochemical assignments for compounds 9,10 13, 14: Compounds **9a** was determined to be *syn-syn* by conversion to compound **SI-12** according to **GP 7** and evaluation of its ^{13}C NMR shifts according to the method described by Kishi.[36,37]

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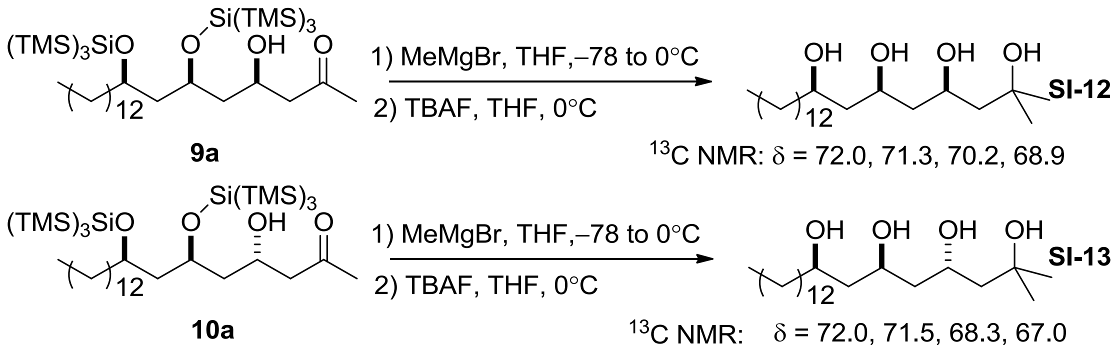
[36] Kobayashi, Y.; Tan, C.-H.; Kishi, Y. *Journal of the American Chemical Society* **2001**, *123*, 2076–2078.
[37] Kobayashi, Y.; Tan, C.-H.; Kishi, Y. *Helvetica Chimica Acta* **2000**, *83*, 2562–2571.

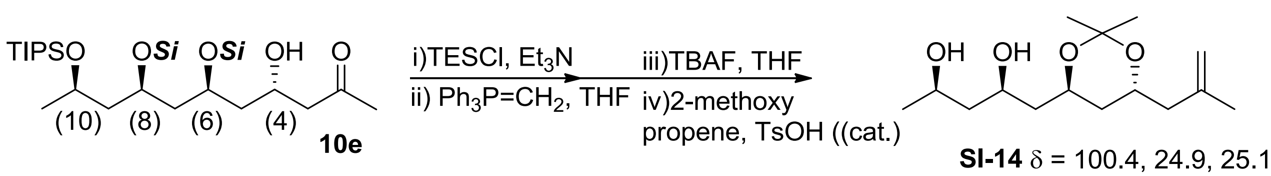
Resonances at 72.0, 71.3, 70.2 and 68.9 indicated a *syn-syn* configuration. In a similar manner, **10a** was converted to **SI-13** and determined to be *anti-syn* by resonances at 72.0, 71.5, 68.3 and 67.0 (**Scheme S-10**). Compounds **9b, 9c, 9d, 10a, 10b, 10c, 10d** were assigned by analogy.

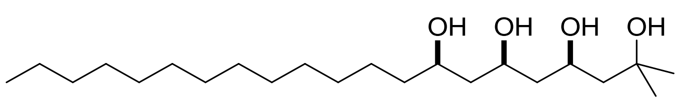
Scheme S-10



Stereochemical determination: The C(6)-C(8)-C(10) stereochemistry of **10e** was assigned *syn-syn*, by previous determination of stereochemistry of **8e**.[18] The C(4) stereochemistry was determined to be (*S*) (1,3-*anti* aldol) by conversion to **SI-14** following procedure **GP6** (**Scheme S-11**). Analysis of the ^{13}C NMR spectrum indicated C(4)-C(6)-*anti*- stereochemistry (δ = 100.4, 24.9, 25.1).

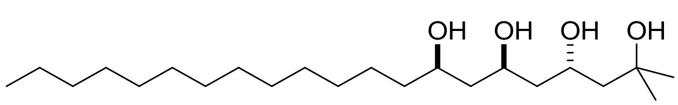
Scheme S-11





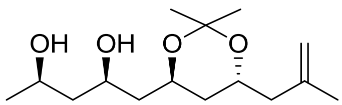
SI-12

Data for **SI-2:**TLC: R_f = 0.11 (10:90 *i*-PrOH/hexanes);FTIR (thin film) 3370, 2919, 2850, 1467, 1378, 1324, 1132, 847; LRMS (APCI –) $C_{22}H_{46}{}^{35}ClO_4^-$ $[M+{}^{35}Cl]^-$ m/z = 409.2 (100%), $C_{22}H_{46}{}^{37}ClO_4^-$ $[M+{}^{37}Cl]^-$ m/z = 411.2 (36%); ^{13}C NMR (500 MHz, CD_3OD) δ = 71.9, 71.5, 70.4, 46.1, 44.8, 38.6, 32.9, 30.63, 30.57, 30.55, 30. 26, 28.7, 26.3, 23.5, 14.4; ^{1}H NMR (500 MHz, CD_3OD) δ = 4.15 (dddd, *J* = 7.6, 7.5, 5.2, 5.0 Hz, 1H), 3.97 (app tt, *J* = 8.3, 4.4, 1H), 3.71-3.77 (m, 1H), 1.50-1.64 m (5H), 1.38-1.48 (m, 3H), 1.24-1.34 (m, 25H), 1.23 (s, 3H), 0.88 (t, *J* = 6.9 Hz, 3H).



SI-13

Data for SI-13: TLC: R_f = 0.26 (15:85 *i*-PrOH/hexanes); FTIR (thin film) 3349 (br), 2919, 2850, 2496, 1468, 1378, 1137, 1081, 740.1, LRMS(APCI –) $C_{22}H_{46}{}^{35}ClO_4^-$ $[M+{}^{35}Cl]^-$ m/z = 409.2 (100%), $C_{22}H_{46}{}^{37}ClO_4^-$ $[M+{}^{37}Cl]^-$ m/z = 411.2 (37%); ^{13}C NMR (500 MHz, CD_3OD) δ = 72.0, 71.5, 68.3, 67.0, 46.6, 45.3, 38.6, 32.9, 30.72, 30.66, 30.35, 28.7, 26.4, 23.6, 14.4; ^1H NMR (500 MHz, CD_3OD) δ = 4.21 (br, app. t *J* = 4.3 Hz, 1H), 3.98-4.04 (m, 1H), 3.72-3.78 (m, 1H)1.55-1.65 (m, 6H), 1.34-1.38 (m, 6 H), 1.25-1.31 (m, 35H), 1.23 (s, 3H), 0.88 (t*, J* = 7 Hz, 1H).

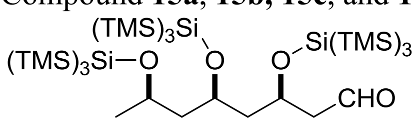


SI-14

Data for SI-4: ^1H NMR (500 MHz, $CDCl_3$) δ = 4.78 (s, 3 H), 4.74 (s, 1 H), 3.93 - 4.03 (m, 4 H), 2.28 (dd, *J*=14.3, 7.6 Hz, 1 H), 2.13 (dd, *J*=14.3, 5.8 Hz, 1 H), 1.83 (dt, *J*=14.0, 7.2 Hz, 1 H), 1.74 (s, 3 H), 1.55 - 1.65 (m, 3 H), 1.45 - 1.53 (m, 2 H), 1.36 (s, 3 H), 1.34 (s, 3 H), 1.17 (d, *J*=6.1 Hz, 3 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 142.4, 112.3, 100.4, 65.7, 65.2, 65.1, 63.0, 44.2, 42.4, 38.6, 38.3, 25.1, 24.9, 23.0, 22.4; LRMS (API-ES+) $C_{12}H_{21}O_2^+$ $[M – acetone – OH]^+$ m/z = 197.0 (95%).

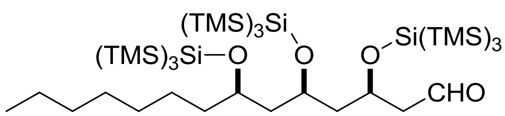
Synthetic Procedures, Stereochemical determination, and data for 15, 16, 17, 18

Compound **15a**, **15b, 15c**, and **17** were prepared according to published procedure[38].



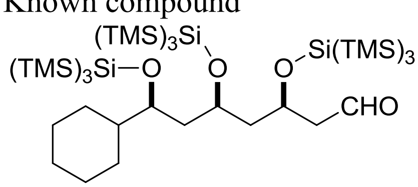
15a

^{13}C NMR (500 MHz, $CDCl_3$, 290 K) δ = 202.24, 69.80, 69.76, 69.12, 49.95, 48.58, 44.36, 24.51, 0.96, 0.75; ^1H NMR (500 MHz, $CDCl_3$, 290 K) δ = 9.75 (t, *J*=2.1 Hz, 1 H), 4.18 - 4.31 (m, 1 H), 3.65 (qd, *J*=8.9, 4.6 Hz, 2 H), 2.50 (ddd, *J*=15.4, 3.7, 1.8 Hz, 1 H), 2.33 (ddd, *J*=15.3, 8.9, 3.7 Hz, 1 H), 1.95 (ddd, *J*=12.8, 9.8, 4.9 Hz, 1 H), 1.75 (ddd, *J*=12.8, 9.8, 5.5 Hz, 1 H), 1.48 (ddd, *J*=12.8, 9.2, 3.7 Hz, 1 H), 1.16 - 1.22 (m, 1 H), 1.17 (br. s., 3 H), 0.18 (s, 81 H); LRMS (API-ES +) $C_{26}H_{67}O_3Si_8^+$ $[M – TMS_3SiO]^+$ m/z = 651.2 (80%)



15b

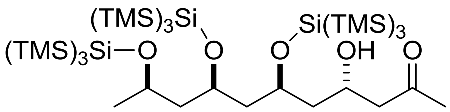
Known compound[21]



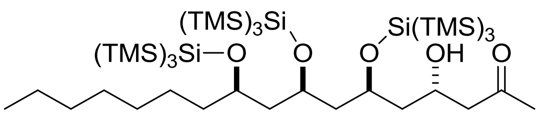
15c

[38] Albert, B. J.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2010**, *49*, 2747–2749.

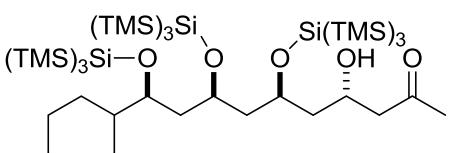
Known compound[21]



16a Prepared according to **GP 4**
^{13}C NMR (500 MHz, $CDCl_3$, 290 K) δ = 208.73, 72.14, 69.71, 69.36, 65.05, 51.23, 48.84, 43.90, 41.49, 30.97, 24.47, 1.03, 0.81; ^{1}H NMR (500 MHz, $CDCl_3$, 290 K) δ =4.22 - 4.38 (m, 1 H), 3.88 - 4.04 (m, 1 H), 3.66 (m, *J*=3.4 Hz, 2 H), 3.30 (d, *J*=3.1 Hz, 1 H), 2.48 - 2.59 (m, 2 H), 2.17 (s, 3 H), 1.95 (ddd, *J*=13.1, 9.5, 4.9 Hz, 1 H), 1.65 - 1.75 (m, 2 H), 1.56 (ddd, *J*=13.0, 9.5, 3.5 Hz, 1 H), 1.44 (ddd, *J*=14.0, 7.0, 2.7 Hz, 1 H), 1.17 (d, *J*=6.1 Hz, 3 H), 0.16 - 0.22 (m, 81 H); LRMS (API-ES+) $C_{44}H_{113}O_5Si_{12}^+$ $[M+H]^+$ m/z = 973.5 (100%);



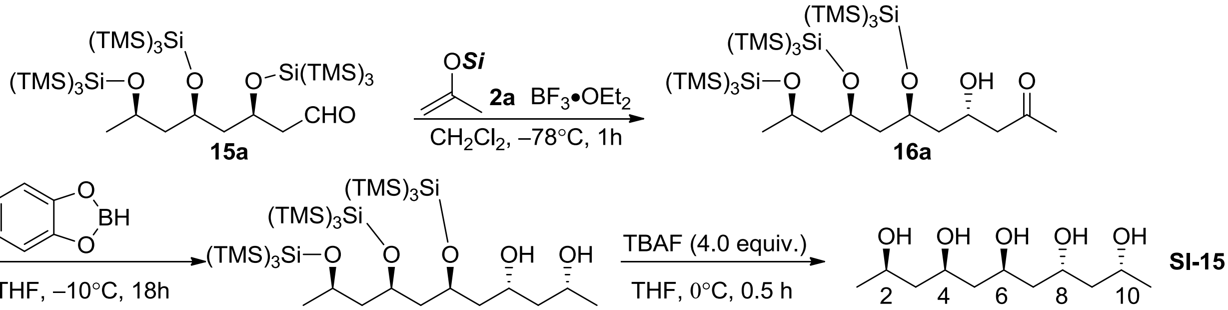
16b Prepared according to **GP 4**
^{13}C NMR (500 MHz, $CDCl_3$, 290 K) δ = 208.97, 77.68, 72.03, 69.90, 64.93, 51.30, 41.57, 30.95, 27.12, 26.83, 26.27, 1.15, 1.10, 0.84; ^{1}H NMR (500 MHz, $CDCl_3$, 290 K) δ = 4.27 - 4.37 (m, 1 H), 3.94 (br. s., 1 H), 3.69 (tt, *J*=9.3, 4.6 Hz, 1 H), 3.34 (d, *J*=9.8 Hz, 1 H), 3.17 (d, *J*=3.1 Hz, 1 H), 2.52 (d, *J*=5.8 Hz, 2 H), 2.18 (s, 3 H), 1.67 - 1.85 (m, 5 H), 1.50 - 1.66 (m, 4 H), 1.48 (br. s., 0 H), 1.01 - 1.33 (m, 5 H), 0.20 (d, *J*=2.1 Hz, 81 H); $C_{44}H_{112}O_5Si_{12}^+$ $[M+H]^+$ m/z = 1057.5 (100%);

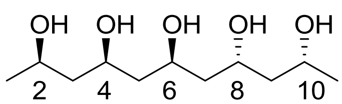


16c Prepared according to **GP 4** ^{13}C NMR (500 MHz, $CDCl_3$, 290 K) δ = 208.86, 73.68, 71.88, 69.59, 65.03, 51.23, 46.05, 43.95, 41.68, 38.65, 31.80, 30.95, 29.91, 29.38, 26.20, 22.76, 14.28, 1.00, 0.87, 0.83; ^{13}C NMR (500 MHz, $CDCl_3$, 290 K) δ = 4.26 - 4.40 (m, 1 H), 3.88 - 4.10 (m, 1 H), 3.71 (d, *J*=4.0 Hz, 1 H), 3.40 (br. s., 1 H), 3.21 (d, *J*=3.7 Hz, 1 H), 2.52 (d, *J*=5.8 Hz, 2 H), 2.18 (s, 3 H), 1.80 (t, *J*=8.9 Hz, 1 H), 1.62 - 1.74 (m, 3 H), 1.47 - 1.57 (m, 1 H), 1.36 - 1.45 (m, 2 H), 1.15 - 1.34 (m, 12 H), 0.84 - 0.94 (m, 3 H), 0.14 - 0.27 (m, 81 H); LMRS (API-ES) $C_{43}H_{108}O_5Si_{12}^+$ $[M+H]^+$ m/z = 1041.5 (100%)

Stereochemical determination of 16a: There stereochemistry of **16a** was confirmed by derivatization to **SI-5**, by a 1,3-*syn*- selective chelation controlled reduction followed by desilylation (**Scheme S-12).** The stereochemistry of resultant penta-ol **SI-15** was determined as follows: C(2),C(4), C(6) was assigned to be *syn-syn* based on the stereochemical outcome of the tri-aldol cascade to form **15a.**[21]The C(8)-C(10) *syn* stereochemistry was assigned to the literature precedent of 1,3-chelation controlled-*syn* reduction.[39] Finally, ^{13}C NMR analysis revealed PB-5149 to possess C_1-symmetry, indicating C(6)-C(8) *anti*-relationship resulting from a 1,3-*anti* aldol addition to **15**a. **16b** and **16c** were assigned by analogy.

Scheme S-12

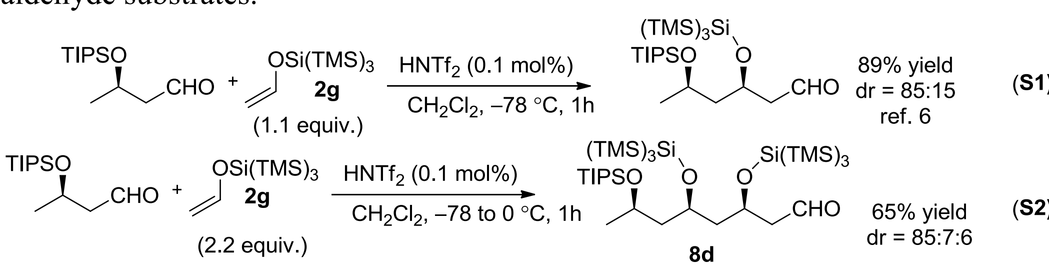




Data for SI-15 ^1H NMR (500MHz, CD_3OD, 294K) δ = 3.98 - 4.06 (m, 2 H), 3.91 - 3.98 (m, 3 H), 1.65 - 1.69 (m, 1 H), 1.61 - 1.65 (m, 1 H), 1.57 - 1.61 (m, 2 H), 1.52 - 1.57 (m, 2 H), 1.49 (ddd, *J*=14.0, 5.2, 4.3 Hz, 1 H), 1.18 (d, *J*=6.1 Hz, 6 H); ^{13}C NMR (500MHz, CD_3OD, 294K) δ = 70.16, 68.08, 67.90, 67.34, 67.32, 47.50, 46.88, 46.07, 45.97, 23.68, 23.66; LRMS (API-ES +) $C_{11}H_{24}NaO_5^+$ $[M+Na]^+$ m/z = 259.2 (100%), $C_{11}H_{25}O_5^+$ $[M+H]^+$ m/z 237.2 (40%); LRMS (API-ES –) $C_{11}H_{24}{}^{35}ClO_5^-$ $[M+{}^{35}Cl]^-$ m/z = 271.0 (100%), $C_{11}H_{24}{}^{37}ClO_5^-$ $[M+{}^{37}Cl]^-$ m/z = 273.1 (30%); HRMS-TOF (ESI/CI multimode +): $C_{11}H_{25}O_5^+$ $[M+H]^+$ m/z = 237.1703 (calc: 237.17023, 0.2 ppm); HRMS-TOF (ESI/CI multimode –): $C_{11}H_{24}{}^{35}ClO_5^-$ m/z = 271.1310 (calc: 271.13125, 0.9 ppm)

Additional data for eq. 3,4,5

In order to determine diastereoselection for the overall tetra-aldol process of eq. 5 compound **18**, the individual aldol steps were evaluated using diastereomerically pure aldehyde substrates.



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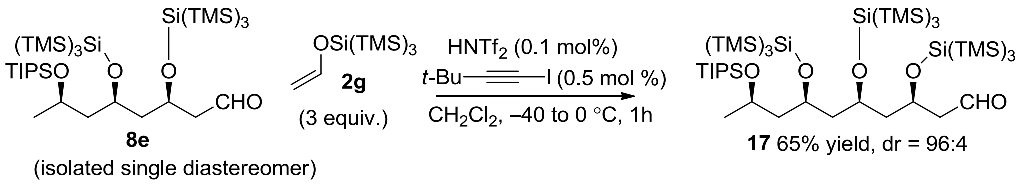
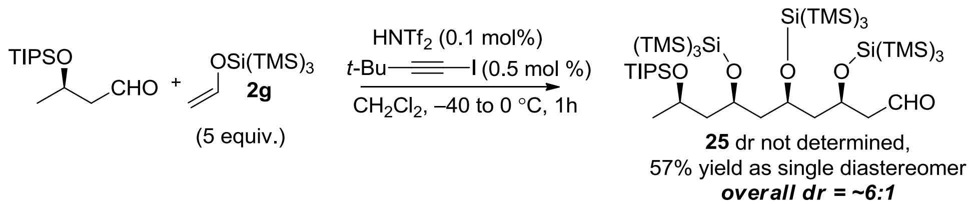
[39] Evans et. al. *J. Org. Chem.* **1990**, *55*, 5190.

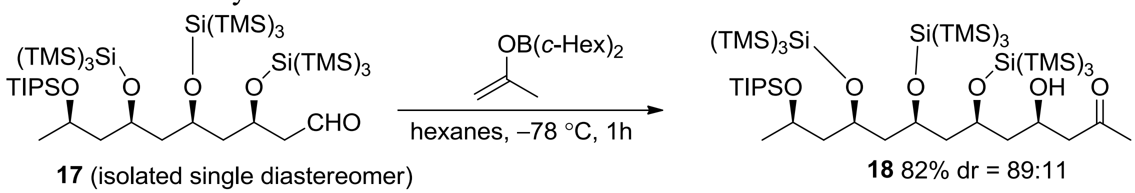


(S4)



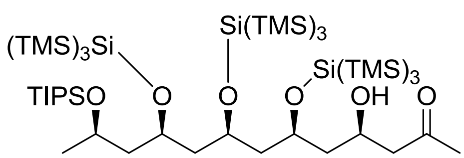
(S5)

Aldol reaction of **23** and **17** yields **25** with excellent diastereoselectivity. Because the dr of the triple aldol reaction of **17** and *R*)-3-(TIPSOxy)butanal (eq. **S5**) cannot be directly determined by ^{1}H NMR, the dr can be inferred by comparing eq. **S4** and eq. **S**2. Thus the diastereoselectivity of **S5** can be estimated at ~5:1.



(S6)

Reaction of **17** with acetone enolborinate by **GP 4** gives product **18** in good selectivity dr = 89:11. The overall diastereoselectivity (ds) of the tetraaldol sequence in eq. 5, therefore is approximately 75%

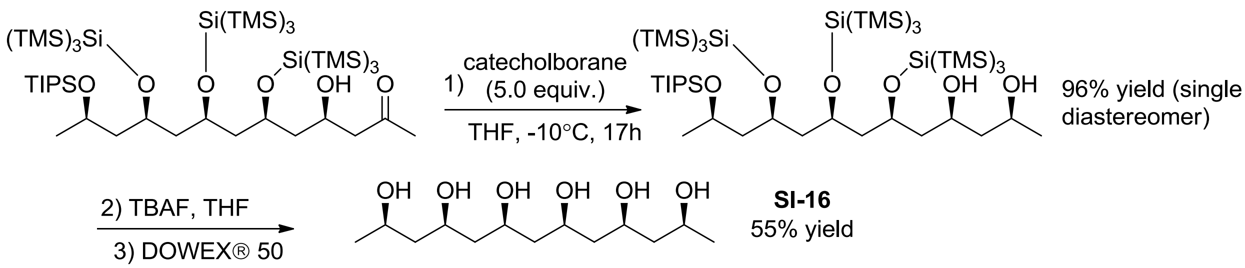


18

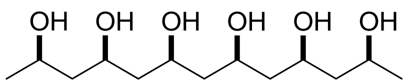
Data for 26: TLC: R_f = 0.58 (10:90 EtOAc/hexanes); ^{1}H NMR (500 MHz, C_6D_6, 333K) δ = 4.55 - 4.64 (m, 1 H), 4.37 - 4.45 (m, 1 H), 4.24 (tt, *J*=9.0, 4.4 Hz, 1 H), 4.14 - 4.21 (m, 1 H), 4.10 (tt, *J*=9.0, 4.4 Hz, 1 H), 2.40 - 2.57 (m, 2 H), 2.21 - 2.30 (m, 1 H), 2.13 - 2.20 (m, 2 H), 2.09 (ddd, *J*=12.9, 9.7, 5.3 Hz, 1 H), 1.92 - 2.01 (m, 1 H), 1.88 (ddd, *J*=12.5, 8.9, 3.5 Hz, 1 H), 1.81 (s, 3 H), 1.61 (d, *J*=6.0 Hz, 3 H), 1.33 - 1.39 (m, 21 H), 0.53 (s, 27 H), 0.47 - 0.50 (m, 54 H); ^{13}C NMR (500 MHz, C_6D_6, 333K) δ = 207.3, 73.5, 71.3, 70.4, 66.9, 65.7, 50.9, 48.1, 46.5, 46.2, 45.1, 30.0, 24.4, 18.8, 18.7, 13.2, 1.5, 1.32, 1.27; LRMS (API-ES+) $C_{49}H_{123}O_5Si_{13}^+$ [M-OH]$^+$ m/z = 1155.5 (22%), $C_9H_{27}Si_4^+$ [TMS$_3$Si]$^+$ m/z = 247.3 (95%). FTIR (thin film): 3521 (br), 2947, 2894, 2867, 1715, 1376, 1244, 1034, 835, 686, 624.

Stereochemical assignment: 18 was determined to be C(4)-C(6)-C(8)-C(10)-(C12)-*syn-syn-syn-syn*-configured by previous determination of the stereochemistry of intermediate **17**. The C(4) stereochemistry was determined to be *(R)* by conversion to C_2-symmetric *meso*- hexa-ol **SI-16** by a *syn*-selective[22] reduction and desilylation sequences shown in

Scheme S-13. C_2- symmetry was inferred from the simplicity of ^{13}C NMR spectrum: resonances at δ = 70.1, 70.0, 67.3, 46.8, 45.4, 45.3, 23.7 ppm.



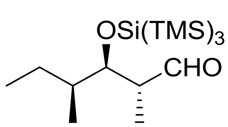
Scheme S-13: Synthesis of hexa-ol **SI-16**



SI-16

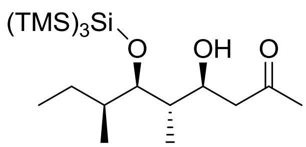
(1) A 25 mL flame-dried round-bottomed flask with magnetic stir bar was charged with ketone **26** (171mg, 0.15 mmol), fitted with a rubber septum, and purged with N_2. THF (1 mL) was added and the reaction was stirred and cooled to -10°C. Catecholborane (0.75 mL,1.0 M THF, obtained from Sigma-Aldrich) was added dropwise. The reaction was stirred overnight, then quenched by addition of methanol (1mL) and NaK tatrate solution (sat. aq., 2mL). The biphasic mixture was stirred at r.t. for 2 hrs, then extracted with CH_2Cl_2 (3x 5 mL). The combined organic layers were dried (Na_2SO_4), filtered through cotton, and concentrated. Flash chromatography (35mL SiO_2, 0.5 →5% v/v EtOAc/hexanes eluent) yield the intermediate diol (166mg, 94% yield). (2) The intermediate diol (166 mg, 0.141 mmol) was added to a dry 25 mL round-bottomed flask containing a magnetic stir bar and fitted with a septum. THF (1.0 mL) was added, the reaction cooled to 0°C and TBAF (0.8 mL, 1.0 THF) was added dropwise (gas evolution observed). The reaction was stirred for 1 h, and the volatiles were then removed by evacuation. 15 mL H_2O was added, the aqueous layer was extracted with CH_2Cl_2, Et_2O, and EtOAc (5 mL each). The aqueous layer was concentrated, revealing the product contaminated with a large excess of $Bu_4N^+X^-$. (3) The mixture was purified by passing through a column of DOWEX®-50WX8-200 ion exchange resin (30g, pretreated by elution of MeOH (100mL), 1N HCl (100mL) and H_2O (100mL) eluting with 1 N NH_4OH. Evaporation of the volatiles gave **SI-16** (20 mg, 54% yield).
Data for SI-16: ^{1}H NMR (500 MHz, CD_3OD) δ = 3.88 - 4.06 (m, 6 H), 1.50 - 1.74 (m, 10 H), 1.18 (d, *J*=6.1 Hz, 6 H); ^{13}C NMR (500 MHz, CD_3OD) δ = 70.1, 70.0, 67.3, 46.8, 45.4, 45.3, 23.7; LRMS (API-ES −) $C_{13}H_{27}O_6^-$ $[M–H]^-$ m/z = 279.1 (100%);

Synthetic Procedures, Stereochemical Assignments, and Data for Compounds 20, 21, and 22



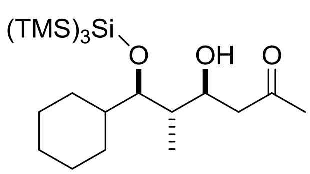
19a

Known compound.[13] Prepared by Me_2AlNTf_2-catalyzed aldol reaction of ***E*-23** and (*S*)-2-methyl propanal. Stereochemistry previously determined.
Data for 19a: TLC: (CH_2Cl_2:hexanes, 25:75)R_f = 0.38; ^{1}H NMR (500 MHz, C_6D_6, dr = 88:8:4) δ 9.73 (d, *J*=1.8 Hz, 1 H), 3.53 (t, *J*=3.9 Hz, 1 H), 2.36 (ddd, *J*=7.1, 3.4, 2.0 Hz, 1 H), 1.43 - 1.55 (m, 2 H), 1.00 (d, *J*=7.1 Hz, 3 H), 0.84 - 0.95 (m, 1 H), 0.82 (t, *J*=7.1 Hz, 3 H), 0.77 (d, *J*=7.0 Hz, 3 H), 0.25 (s, 27 H); FTIR (thin film): 2961, 2893, 1724, 1459, 1425, 1245, 1023, 834, 756, 687, 624; ^{13}C NMR (500 MHz, C_6D_6, dr = 88:8:4) δ= 202.5, 83.6, 49.7, 40.5, 26.8, 15.6, 12.3, 12.1, 0.9; LRMS (APCI +) $C_9H_{28}OSi_4Na^+$ $[TMS_3SiOHNa]^+$ m/z = 288.1 (100%), $C_{17}H_{43}O_2Si_4^+$ $[M+H]^+$ m/z = 391.2 (30%). $[a]_D^{24}$ =−12.020° (*c* 1.00, CH_2Cl_2).



22a Prepared according to **GP: 4** with the following modifications: Acetone 9-BBN enolborinate must be generated at −78 °C, rather than 0°C as it is unstable at higher temperatures. A solution of the aldehyde is therefore added to a stirring solution of enolborinate at −78°C.
Data for 22a: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.97 (tt, *J*=9.2, 2.6 Hz, 1 H), 3.64 (dd, *J*=2.4, 0.9 Hz, 1 H), 3.49 (dd, *J*=4.9, 3.1 Hz, 1 H), 2.63 (dd, *J*=15.9, 2.6 Hz, 1 H), 2.44 (dd, *J*=15.9, 9.5 Hz, 1 H), 2.20 (s, 3 H), 1.83 - 1.92 (m, 1 H), 1.67 - 1.77 (m, 0 H), 1.48 - 1.58 (m, 2 H), 1.08 - 1.19 (m, 1 H), 0.87 - 0.93 (m, 3 H), 0.85 (d, *J*=6.9 Hz, 3 H), 0.82 (d, *J*=7.0 Hz, 3 H), 0.22 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 209.5, 84.5, 70.5, 48.7, 41.4, 39.7, 30.9, 25.0, 15.7, 15.4, 12.2, 0.9; FTIR (thin film) 3497 (br), 2961, 2894, 1711, 1380, 1244, 1041, 836, 687; LRMS (APCI +): $C_{20}H_{49}O_3Si_4^+$ $[M+H]^+$ m/z = 449.2 (100%),: $C_{20}H_{47}O_2Si_4^+$ $[M - OH]^+$ m/z = 431.2 (65%).

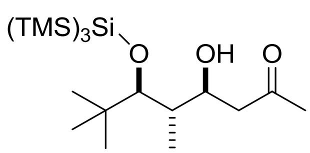
Procedure for one-pot *anti*-propionaldehyde, *anti*-acetone addition: GP 7



22b
General procedure GP 7: An oven-dried 10 mL pear-shaped flask (primary reaction flask) was equipped with a magnetic stir bar and septum, then charged with ***E*-23** (96 mg, 0.315 mmol), CH_2Cl_2 (2 mL) and cyclohexane carboxyaldehyde (36.5 µL, 0.3 mmol). The stirring reaction was cooled to –78 °C, and $HNTf_2$ was added dropwise (30 mL, 0.01M CH_2Cl_2 3 x 10^{-4} mmol). The reaction was stirred at this temperature for 1.5 h, then warmed to –45 °C, stirred for 30min, then re-cooled to –78 °C, at which point <3µL Et_3N was added to quench the Lewis acid catalyst. Simultaneously, an oven-dried secondary reaction flask (25 mL round-bottomed) was charged with toluene (1.5 mL), acetone (26

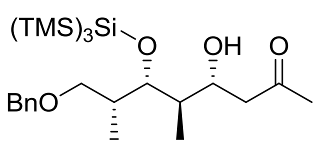
μL, 0.36 mmol), and Et_3N (56 μL, 0.39 mmol). The stirring flask was cooled to –78 °C, at which point 9-BBN OTf (0.5 M hexanes, 0.720 mL) was added dropwise, with immediate formation of a white precipitate. After stirring for 15min, the contents of the primary reaction flask were slowly cannulated to the secondary reaction flask over 3 min, down the side of the flask to minimize local heating. The primary flask was rinsed (2 x 0.3 mL). The reaction was stirred for 45 min at –78 °C then warmed to –45°C. The reaction was quenched by addition of MeOH (0.2 mL) and pH 7.0 buffer (0.2 M, 4 mL), warmed to 0 °C, and stirred vigorously. Et_2O was then added (2 mL), followed by 1 mL 3:1 $MeOH/H_2O_2$ (30% aq.). The biphasic mixture was stirred vigorously for 0.5 h. H_2O was added (5mL), and the layers were separated. The aqueous layer was extracted (3x 3mL Et_2O, and the combined organic layers were washed with $NaHCO_3$, dried (Na_2SO_4), filtered (cotton plug) and concentrated. The mixture was purified by flash chromatography (16 mL SiO_2, EtOAc/Hex 0.5→3% v/v). 135 mg, 95% yield colorless oil.

TLC: R_f = 0.27 (10:90 EtOAc/Hexanes); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 209.2, 85.6, 70.5, 48.7, 43.7, 40.7, 30.8, 29.6, 27.4, 26.6, 26.2, 16.4, 0.8; ^1H NMR (500 MHz, $CDCl_3$) δ =3.99 (tt, *J*=9.2, 2.2 Hz, 1 H), 3.67 (t, *J*=0.9 Hz, 1 H), 3.34 (t, *J*=4.1 Hz, 1 H), 2.60 (dd, *J*=15.4, 2.9 Hz, 1 H), 2.42 (dd, *J*=15.6, 9.5 Hz, 1 H), 2.18 (s, 3 H), 1.70 - 1.78 (m, 3 H), 1.61 - 1.68 (m, 2 H), 1.50 - 1.57 (m, 2 H), 1.09 - 1.25 (m, 3 H), 0.97 - 1.08 (m, 1 H), 0.80 (d, *J*=7.0 Hz, 3 H), 0.19 - 0.23 (m, 27 H); LRMS (API-ES): $C_{22}H_{51}O_3Si_4^+$ $[M+H]^+$ m/z = 475.2 (20%);



22c

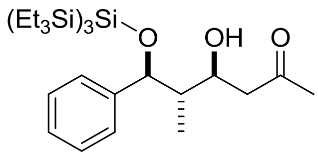
^{13}C NMR (500 MHz, $CDCl_3$) δ =209.1, 89.6, 70.6, 49.1, 42.0, 37.5, 31.4, 27.1, 17.8, 1.5; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.01 (tt, *J*=8.9, 2.7 Hz, 1 H), 3.54 (s, 1 H), 3.30 (d, *J*=4.0 Hz, 1 H), 2.61 (dd, *J*=15.1, 2.3 Hz, 1 H), 2.42 (dd, *J*=15.3, 8.9 Hz, 1 H), 2.19 (s, 3 H), 1.76 (dqd, *J*=10.3, 6.9, 6.9, 6.9, 3.7 Hz, 1 H), 0.90 (s, 9 H), 0.88 (d, *J*=7.0 Hz, 3 H), 0.23 (s, 27 H); $C_{20}H_{49}O_3Si_4^+$ $[M + H]^+$ m/z = 449.3; $C_{20}H_{47}O_2Si_4^+$ $[M – OH]^+$ m/z = 431.3 (85%)



22d

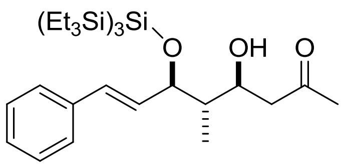
TLC: R_f = 0.17 (10:90 EtOAc/hexanes), ^{13}C NMR (500 MHz, $CDCl_3$) δ = 209.09, 137.86, 128.55, 128.00, 127.88, 76.56, 75.10, 73.5, 70.38, 48.87, 44.93, 35.04, 31.04, 13.16, 11.58, 0.83; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.28 - 7.41 (m, 5 H), 4.58 (d, *J*=11.3 Hz, 1 H), 4.49 (d, *J*=11.6 Hz, 1 H), 3.88 - 3.97 (m, 2 H), 3.61 (dd, *J*=3.1, 1.2 Hz, 1 H), 3.41 (t, *J*=8.2 Hz, 1 H), 3.36 (dd, *J*=8.9, 5.5 Hz, 1 H), 2.60 (dt, *J*=15.6, 0.9 Hz, 1 H), 2.52 (dd, *J*=15.9, 9.5 Hz, 1 H), 2.21 (s, 3 H), 2.05 (m, *J*=7.0 Hz, 1 H), 1.72 - 1.81 (m, 1 H), 0.90 (d, *J*=6.7 Hz, 3 H), 0.83 (d, *J*=6.7 Hz, 3 H), 0.24 (s, 27 H); FTIR (thin film):3485 (br), 2948, 2893, 1713, 1380, 1244, 1105, 1030, 837, 744, 687, 511; HMRS-TOF:

$C_{26}H_{51}O_3Si_4^+$ [M-OH]$^+$ m/z = 523.2900 (calc.: 523.2915, 3ppm), $C_{26}H_{53}O_4Si_4^+$ [M+H]$^+$ m/z = 541.3003 (calc.: 541.3020, 3ppm) colorless oil.



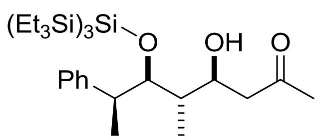
22f

^{13}C NMR (500 MHz, $CDCl_3$) δ = 210.6, 140.9, 128.0, 127.3, 126.9, 78.3, 69.3, 47.7, 45.3, 30.9, 9.4, 9.0, 5.4; ^{1}H NMR (500 MHz, $CDCl_3$) δ =7.30 (dd, *J*=8.2, 0.9 Hz, 2 H), 7.24 (td, *J*=7.6, 0.6 Hz, 2 H), 7.18 (tt, *J*=7.0, 1.2 Hz, 1 H), 4.91 (d, *J*=4.0 Hz, 1 H), 3.30 - 3.39 (m, 2 H), 2.56 (dd, *J*=17.4, 2.1 Hz, 1 H), 2.42 (dd, *J*=17.9, 8.7 Hz, 1 H), 2.11 (s, 3 H), 1.97 (dqd, *J*=10.5, 6.7, 6.7, 6.7, 3.1 Hz, 1 H), 0.99 (t, *J*=7.9 Hz, 27 H), 0.70 (q, *J*=7.9 Hz, 18 H), 0.61 (d, *J*=6.7 Hz, 3 H);

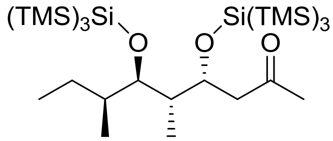


22h

^{13}C NMR (500 MHz, $CDCl_3$) δ = 210.5, 137.2, 131.3, 129.8, 128.6, 127.4, 126.4, 77.8, 69.7, 47.9, 45.2, 30.9, 9.4, 8.9, 5.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ =7.36 (dd, *J*=8.5, 1.2 Hz, 2 H), 7.31 (t, *J*=7.6 Hz, 2 H), 7.22 (m, *J*=7.3, 7.3, 7.3, 1.2, 1.2 Hz, 1 H), 6.52 (d, *J*=16.2 Hz, 1 H), 6.07 (dd, *J*=16.2, 7.0 Hz, 1 H), 4.44 (ddd, *J*=7.0, 4.3, 0.9 Hz, 1 H), 3.69 (tdd, *J*=9.5, 9.5, 3.7, 2.4 Hz, 1 H), 3.20 (d, *J*=4.0 Hz, 1 H), 2.70 (dd, *J*=17.7, 2.1 Hz, 1 H), 2.48 (dd, *J*=17.7, 9.5 Hz, 1 H), 2.16 (s, 3 H), 1.80 - 1.93 (m, 1 H), 1.03 (t, *J*=7.9 Hz, 27 H), 0.78 (m, *J*=7.6, 7.6, 7.6 Hz, 18 H); LRMS (API-ES+) $C_{33}H_{64}NaO_3Si_4^+$ [M+Na]$^+$ m/z = 643.2 (20%)

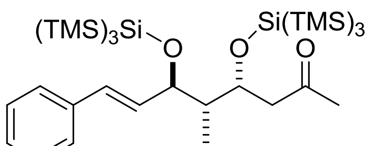


22i Me_2AlNTf_2 (0.5 mol%) used as a catalyst for the first aldol, rather than $HNTf_2$.
^{13}C NMR (500 MHz, $CDCl_3$) δ = 209.56, 145.60, 128.42, 128.16, 126.55, 79.25, 69.06, 49.04, 45.05, 42.76, 30.56, 21.05, 11.20, 9.19, 5.81; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.18 - 7.38 (m, 7 H), 4.06 (dd, *J*=8.2, 2.7 Hz, 1 H), 2.76 - 2.87 (m, 2 H), 2.47 (dd, *J*=16.8, 1.8 Hz, 1 H), 2.17 - 2.27 (m, 2 H), 2.03 (s, 3 H), 1.74 (quint, *J*=7.0, 7.0, 7.0, 7.0, 2.7, 2.7 Hz, 1 H), 1.32 (d, *J*=7.0 Hz, 3 H), 1.08 - 1.17 (m, 27 H), 0.85 (q, *J*=7.9 Hz, 21 H); LRMS (API-ES): $C_{33}H_{66}NaO_3Si_4^+$ [M+Na]$^+$ m/z = 645.3 (100%); $C_{33}H_{65}O_2Si_4^+$ [M – OH]$^+$ m/z = 605.5 (95%)



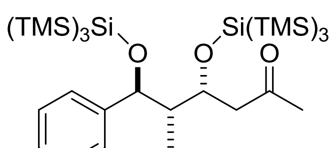
20a

[1]H NMR (500 MHz, $CDCl_3$) δ = 3.84 (dt, *J*=8.8, 3.5 Hz, 1 H), 3.32 (m, *J*=4.9, 1.2 Hz, 1 H), 2.74 (dd, *J*=17.1, 8.5 Hz, 1 H), 2.61 (dd, *J*=17.1, 3.1 Hz, 1 H), 2.13 (s, 3 H), 1.59 - 1.66 (m, 1 H), 1.51 - 1.59 (m, 1 H), 1.25 - 1.34 (m, 1 H), 1.16 - 1.25 (m, 1 H), 0.90 (d, *J*=7.0 Hz, 3 H), 0.87 (t, *J*=7.0 Hz, 3 H), 0.80 (d, *J*=6.7 Hz, 3 H), 0.19 (s, 27 H), 0.17 - 0.19 (m, 27 H); [13]C NMR (500 MHz, $CDCl_3$) δ = 205.9, 81.5, 72.7, 50.29, 46.03, 37.3, 31.2, 30.1, 14.5, 12.4, 9.5, 0.94, 0.91; FTIR (thin film): 2949, 2893, 1718, 1243, 1018.4, 835; LRMS (APCI+) $C_{20}H_{45}O_2Si_4$ $[M\text{-}OSiTMS_3]^+$ m/z = 431 (35%).



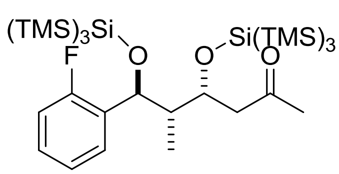
20b

[13]C NMR (500 MHz, $CDCl_3$) δ =206.7, 140.0, 131.2, 130.5, 128.6, 127.4, 126.8, 78.1, 74.4, 50.2, 47.0, 31.3, 10.9, 0.9, 0.7; [1]H NMR (500 MHz, $CDCl_3$) δ =7.36 (dd, *J*=7.9, 1.2 Hz, 2 H), 7.30 (t, *J*=7.3 Hz, 2 H), 7.22 (tt, *J*=7.0, 1.2 Hz, 1 H), 6.49 (d, *J*=15.9 Hz, 1 H), 6.18 (dd, *J*=15.9, 6.4 Hz, 1 H), 4.02 (ddd, *J*=6.1, 4.6, 1.2 Hz, 1 H), 3.83 (td, *J*=6.5, 4.1 Hz, 1 H), 2.78 (dd, *J*=16.5, 6.7 Hz, 1 H), 2.70 (dd, *J*=16.5, 4.0 Hz, 1 H), 2.16 (s, 3 H), 1.79 - 1.88 (m, 0 H), 0.86 (d, *J*=6.7 Hz, 3 H), 0.18 (s, 27 H), 0.17 (s, 27 H); LRMS (API-ES -) $C_{30}H_{63}O_3Si_7^-$ $[M – TMS]^-$ m/z = 667.2 (100%). FTIR (thin film): 3032, 2950, 2895, 1297, 1868, 1718, 1653, 1496, 1396, 1360, 1245, 1048, 836, 689. Waxy solid.



20c

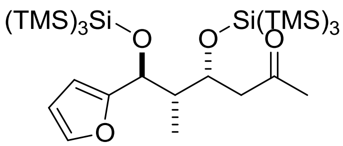
Compound previously described, and stereochemical determination previously established.[13]



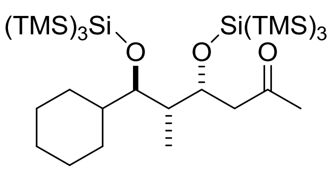
20d

[13]C NMR (500 MHz, $CDCl_3$) δ =159.89 (d, *J*=242.3 Hz), 130.18 (d, *J*=4.5 Hz), 129.39 (d, *J*=13.5 Hz), 128.98 (d, *J*=8.5 Hz), 124.17 (d, *J*=3.0 Hz), 115.16 (d, *J*=23.4 Hz), 73.29, 71.93, 49.52, 47.02, 31.53, 10.40, 0.87, 0.49; [1]H NMR (500 MHz, $CDCl_3$) δ =7.36 (td, *J*=7.5, 1.5 Hz, 1 H), 7.20 (tdd, *J*=7.3, 7.3, 5.5, 1.8 Hz, 1 H), 7.12 (t, *J*=7.3 Hz, 1 H), 6.95 (dd, *J*=9.9, 8.7 Hz, 1 H), 4.79 (d, *J*=4.9 Hz, 1 H), 3.45 (quind, *J*=4.9, 4.9, 4.9, 4.9, 0.9 Hz,

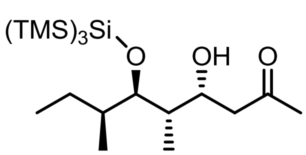
1 H), 2.79 (dd, *J*=16.2, 5.5 Hz, 1 H), 2.74 (dd, *J*=15.9, 4.3 Hz, 1 H), 2.16 (s, 3 H), 2.01 - 2.11 (m, 1 H), 0.79 (d, *J*=7.0 Hz, 3 H), 0.08 (s, 54H); ^{19}F NMR (500MHz, $CDCl_3$, 295K, $C_6H_5CF_3$ external std., δ =-63.72) δ = -119.41; LRMS (API-ES +):$C_{31}H_{70}FO_3Si_8^+$ $[M+H]^+$ m/z = 733.3 (18%), $C_{22}H_{42}FO_2Si_4$ $[M – TMS_3SiO]^+$ m/z = 469.2 (100%); LRMS (API-ES -) $C_{28}H_{60}FO_3Si_7^-$ $[M – TMS]^-$ m/z = 659.3 (100%); FTIR (thin film): 2949, 2894, 2071, 1925, 1863, 1727, 1704, 1615, 1585, 1458, 1367, 1244, 1046, 834, 687, 624; white solid.



20e
^{13}C NMR (500 MHz, $CDCl_3$) δ = 207.21, 155.37, 141.25, 110.51, 108.51, 74.67, 72.33, 48.96, 46.13, 31.65, 10.84, 0.91, 0.43; ^{1}H NMR (500 MHz, $CDCl_3$) δ =7.30 (t, *J*=0.9 Hz, 1 H), 6.32 (dd, *J*=3.1, 1.8 Hz, 1 H), 6.17 (d, *J*=2.7 Hz, 1 H), 4.53 (d, *J*=4.9 Hz, 1 H), 3.38 (tdd, *J*=5.2, 5.2, 4.3, 3.7 Hz, 1 H), 2.65 (dd, *J*=15.3, 3.7 Hz, 2 H), 2.57 (dd, *J*=15.6, 5.2 Hz, 2 H), 2.15 (s, 3 H), 1.97 - 2.06 (m, 1 H), 0.84 (d, *J*=6.7 Hz, 3 H), 0.14 (s, 27 H), 0.11 (s, 27 H); LRMS (API-ES +):$C_{29}H_{68}NaO_4Si_8^+$ $[M+Na]^+$ m/z = 727.3 (5%); LRMS (API-ES –): $C_{26}H_{59}O_4Si_7^-$$[M – TMS]^-$ m/z = 631.2 (100%); FTIR (thin film): 2949, 2894, 1720, 1705, 1245, 1051, 835, 687, 624; white solid.



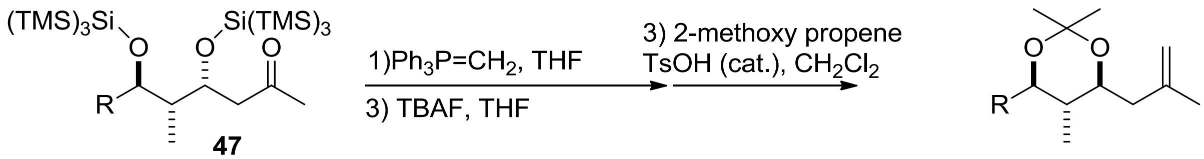
20f
^{13}C NMR (500 MHz, $CDCl_3$) δ =205.8, 82.0, 73.8, 51.1, 47.0, 40.6, 33.1, 31.1, 28.2, 26.8, 26.5, 26.4, 11.8, 1.00, 0.98; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.82 (td, *J*=7.0, 3.4 Hz, 1 H), 3.11 (dd, *J*=4.3, 1.8 Hz, 1 H), 2.75 (dd, *J*=17.2, 7.2 Hz, 1 H), 2.59 (dd, *J*=17.4, 3.4 Hz, 1 H), 2.13 (s, 3 H), 1.56 - 1.73 (m, 6 H), 1.34 - 1.51 (m, 2 H), 1.15 - 1.32 (m, 5 H), 1.01 - 1.12 (m, 1 H), 0.94 (d, *J*=7.0 Hz, 3 H), 0.20 (s, 27 H), 0.19 (s, 27 H); LRMS (APCI+), $C_{31}H_{76}O_3Si_8^+$ $[M+H]^+$ m/z = 721.3 (15%), $C_{22}H_{49}O_2Si_4^+$ $[M – TMS_3SiO]^+$ m/z = 457.2 (100%); LRMS (API-ES –) $C_{28}H_{67}O_3Si_7^-$ $[M – TMS]^-$ m/z = 647.2 (100%); FTIR (thin film): 2949, 2895, 1721, 1450, 1361, 1244, 1050, 835, 687; waxy solid



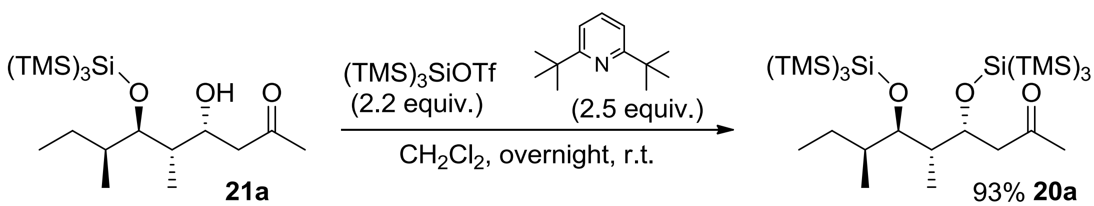
(21a) TLC: R_f = 0.16 (10:90 EtOAc/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 208.56, 87.68, 67.87, 48.84, 40.73, 37.67, 30.97, 24.10, 15.90, 13.28, 12.47, 1.00, 0.99; ^{1}HNMR (500 MHz, $CDCl_3$) δ = 4.46 (tt, *J*=6.4, 1.8 Hz, 1 H), 3.42 (s, 1 H), 3.35 (dd, *J*=4.3, 2.7 Hz, 1 H), 2.66 (dd, *J*=16.5, 7.9 Hz, 1 H), 2.40 (dd, *J*=16.5, 5.2 Hz, 1 H), 2.16 (s, 3 H), 1.69 - 1.76 (m, 1 H), 1.61 - 1.69 (m, 3 H), 1.13 - 1.23 (m, 1 H), 0.99 (d, *J*=7.3 Hz, 3 H), 0.91 (m, *J*=7.3, 7.3 Hz, 2 H), 0.88 (d, *J*=7.0 Hz, 3 H), 0.21 (s, 27 H); LRMS (APCI +): $C_{20}H_{49}O_3Si_4^+$ $[M+H]^+$ m/z = 449.2 (100%),: $C_{20}H_{47}O_2Si_4^+$ $[M - OH]^+$ m/z = 431.2 (65%).

Stereochemical assignment for compounds 20, 21, 22
The stereochemistry of 20a was determined to be 3,5-*anti* by conversion to **SI-7** (**Scheme S-10**). Compounds **20b**, **20c**, **20d, 20e**, and **20f** were assigned by analogy. The stereochemistry of compound **21a** was determined by conversion to **20a** (**Scheme S-11**). The stereochemistry of **22a** was assigned 3,4-*anti* by contrast to **21a.** The stereochemistry of **22f** was determined by conversion to **SI-8** (**Scheme S-8**). 3,5-*syn* stereochemistry was established by ^{13}C NMR resonances of δ = 23.3, 19.5, 98.7 ppm.

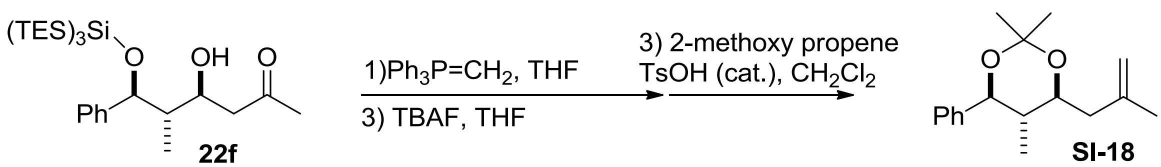
Scheme S-14

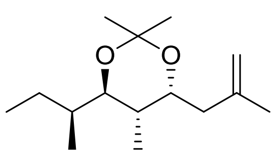


Scheme S-15

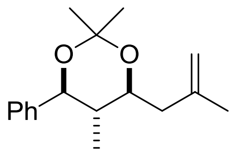


Scheme S-16

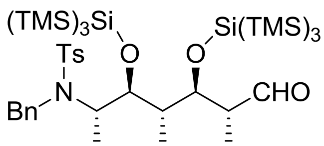




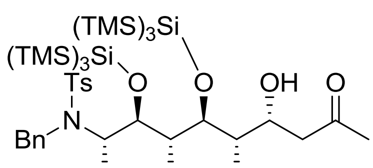
SI-17 Data for **SI-7:** TLC: R_f = 0.34 (5:95 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ = 4.73 - 4.82 (m, 2 H), 3.97 (dt, *J*=8.5, 4.9 Hz, 1 H), 3.18 (dd, *J*=7.3, 3.4 Hz, 1 H), 2.17 (dd, *J*=14.6, 8.9 Hz, 1 H), 2.06 (dd, *J*=14.6, 4.9 Hz, 1 H), 1.74 - 1.79 (m, 1 H), 1.76 (s, 1 H), 1.37 - 1.52 (m, 2 H), 1.31 - 1.32 (m, 3 H), 1.31 (s, 3 H), 1.18 - 1.28 (m, 1 H), 0.90 (d, *J*=6.7 Hz, 3 H), 0.90 (t, *J*=7.3 Hz, 3 H), 0.84 (d, *J*=6.7 Hz, 3 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 143.2, 111.8, 100.3, 77.3, 67.9, 39.1, 38.2, 36.8, 26.3, 25.6, 23.8, 23.2, 14.0, 12.5, 12.2; LRMS (APCI +) $C_{15}H_{29}O_2$ $[M+H]^+$ m/z = 241.2 (45%); FTIR (thin film) = 2964, 2935, 2877, 1653, 1437, 1379, 1227, 1172, 1021, 888.



SI-18
^{13}C NMR (500 MHz, $CDCl_3$) δ = 143.2, 140.9, 128.4, 128.1, 127.9, 112.2, 98.7, 78.7, 73.7, 41.5, 40.4, 30.4, 23.3, 19.5, 12.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 - 7.41 (m, 4 H), 7.25 - 7.31 (m, 1 H), 4.79 (d, *J*=18.6 Hz, 1 H), 4.43 (d, *J*=10.1 Hz, 1 H), 3.83 (ddd, *J*=11.3, 8.5, 2.7 Hz, 1 H), 2.39 (d, *J*=15.0 Hz, 1 H), 2.17 (dd, *J*=14.6, 8.5 Hz, 1 H), 1.81 (d, *J*=0.6 Hz, 3 H), 1.59 - 1.68 (m, 1 H), 1.56 (s, 3 H), 1.47 (s, 3 H), 0.66 (d, *J*=6.4 Hz, 3 H);



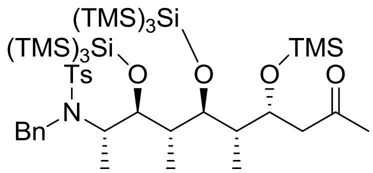
25 Known compound[13] Stereochemistry previously determined.
Data for 25:TLC: (EtOAc:hexanes, 10:90), R_f = 0.63; ^{1}H NMR (500MHz, $CDCl_3$) δ = 9.99 (s, 1 H), 7.08 - 7.16 (m, 5 H), 7.02 - 7.07 (m, 2 H), 6.90 - 6.97 (m, 2 H), 5.07 (dd, *J*=10.3, 2.4 Hz, 1 H), 4.79 (d, *J*=15.4 Hz, 1 H), 4.48 (qd, *J*=7.1, 1.5 Hz, 1 H), 4.43 (d, *J*=15.4 Hz, 1 H), 3.94 (dd, *J*=4.6, 1.7 Hz, 1 H), 2.85 (qd, *J*=6.7, 2.4 Hz, 1 H), 2.30 (s, 3 H), 2.06 (m, *J*=10.4, 7.4, 4.6 Hz, 1 H), 1.36 (d, *J*=7.0 Hz, 3 H), 1.16 (d, *J*=6.8 Hz, 3 H), 1.00 (d, *J*=7.6 Hz, 3 H), 0.30 (s, 27 H), 0.18 (s, 27 H); ^{13}C NMR (500MHz, $CDCl_3$) δ = 202.7, 142.1, 139.8, 136.5, 130.2, 129.1, 128.9, 128.0, 127.1, 127.0, 81.1, 75.3, 53.9, 53.3, 51.0, 42.7, 21.4, 20.2, 10.2, 7.6, 1.5, 1.3; LRMS (APCI +) $C_{41}H_{85}NO_5SSi_8^+$ $[M+H]^+$ m/z = 926.7 (8%), $C_{29}H_{50}NO_3SSi_4^+$ $[M – TMS_3SiOH – CH_3CH_2CHO]^+$ m/z = 604 (100%). FTIR (thin film): 2949, 2893, 1724, 1684, 1653, 1339, 1244, 1166, 1091, 1022, 836, 688. $[\alpha]_D^{25}$ = +7.72° (*c*, 1.00, CH_2Cl_2).



26a :
Data for 26a: TLC: R_f = 0.33 (10:90 acetone/hexanes); ^{1}H NMR (500MHz, $CDCl_3$) δ = 7.12 (s, 7 H), 6.97 (d, *J*=8.2 Hz, 2 H), 4.73 (d, *J*=15.3 Hz, 1 H), 4.41 (d, *J*=15.3 Hz, 1 H), 4.39 (q, *J*=7.3 Hz, 1 H), 4.31 (dd, *J*=10.1, 1.2 Hz, 1 H), 4.12 (t, *J*=9.9 Hz, 1 H), 3.91 (dd, *J*=4.6, 0.9 Hz, 1 H), 3.66 (d, *J*=18.0 Hz, 1 H), 3.39 (d, *J*=2.4 Hz, 1 H), 2.50 (dd, *J*=18.2, 10.5 Hz, 1 H), 2.32 (s, 3 H), 2.17 (s, 3 H), 2.06 (s, 1 H), 1.95 - 2.02 (m, 1 H), 1.60 - 1.76 (m, 1 H), 1.44 - 1.58 (m, 2 H), 1.31 (d, *J*=7.0 Hz, 3 H), 1.14 (d, *J*=6.7 Hz, 3 H), 1.14 (d, *J*=7.3 Hz, 3 H), 0.31 (s, 27 H), 0.16 (s, 27 H); ^{13}C NMR (500MHz, $CDCl_3$) δ = 211.5, 142.1, 138.8, 136.1, 129.8, 128.8, 127.9, 126.9, 126.8, 81.1, 75.7, 70.5, 52.9, 50.9, 48.2, 46.3, 41.9, 34.8, 30.8, 27.4, 22.7, 21.4, 20.0, 12.0, 10.0, 1.7, 1.2; FTIR (thin film): 3545,

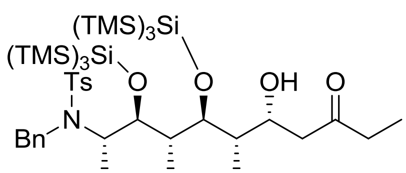
2948, 2894, 1711, 1652, 1599, 1332, 1245, 1165, 1026, 835, 690; LRMS (APCI+) $C_{44}H_{89}NNaO_6SSi_8^+$ $[M+Na]^+$ m/z = 1006.3 (35%).

Stereochemical Assignment: Stereochemistry confirmed by conversion to **SI-9** (TMSCl, Et_3N, CH_2Cl_2, DMAP (cat))**,** which was analyzed by single crystal X-ray diffraction analysis. Crytallographic information file can be obtained at CCDC # 936272 See below for details.



SI-19

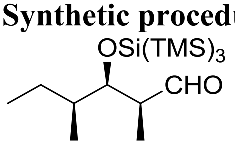
Data for SI-19 TLC: R_f=0.36 (10:90 EtOAc/hexanes); recrystallized by slow evaporation from Et_2O, mp = 217–219 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ = 7.02 - 7.17 (m, 7 H), 6.95 (d, *J*=8.2 Hz, 2 H), 4.68 (d, *J*=15.3 Hz, 1 H), 4.40 (d, *J*=15.3 Hz, 1 H), 4.35 (q, *J*=7.0 Hz, 1 H), 4.26 - 4.32 (m, 2 H), 3.88 (d, *J*=4.6 Hz, 1 H), 3.42 (d, *J*=17.1 Hz, 1 H), 2.62 (dd, *J*=17.2, 9.6 Hz, 1 H), 2.30 (s, 3 H), 2.11 (s, 3 H), 1.95 - 2.06 (m, 2 H), 1.27 (d, *J*=6.7 Hz, 3 H), 1.09 (d, *J*=7.3 Hz, 3 H), 1.05 (d, *J*=6.7 Hz, 3 H), 0.30 (s, 27 H), 0.16 (s, 27 H), 0.10 (s, 9 H); ^{13}C NMR (500MHz, $CDCl_3$) δ =207.7, 142.1, 138.8, 136.4, 129.8, 128.9, 127.9, 127.0, 126.9, 81.3, 76.3, 72.2, 52.8, 50.9, 49.8, 47.7, 41.8, 31.1, 21.5, 20.0, 13.3, 10.0, 1.8, 1.3, 0.8; FTIR: 2950, 2895, 1722, 1457, 1334, 1246, 11163, 1111, 1027, 835, 689. LRMS (APCI+) $C_{38}H_{69}NO_5SSi_5^+$ $[M-(TMS_3SiOH)_2]^+$ m/z = 790.3 (100%).



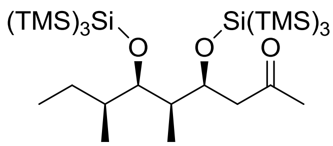
26b

Prepared according to TLC: R_f = 0.38 (10:90 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.71 (d, *J*=15.3 Hz, 1 H), 4.41 (d, *J*=15.1 Hz, 1 H), 4.37 (q, *J*=6.6 Hz, 1 H), 4.30 (d, *J*=10.2 Hz, 1 H), 4.12 (t, *J*=9.9 Hz, 1 H), 3.91 (d, *J*=4.4 Hz, 1 H), 3.62 (d, *J*=17.9 Hz, 1 H), 3.55 (s, 1 H), 2.39 - 2.58 (m, 3 H), 2.32 (s, 3 H), 2.03 - 2.11 (m, 1 H), 1.95 - 2.02 (m, 1 H), 1.29 (d, *J*=7.0 Hz, 3 H), 1.14 (t, *J*=6.0 Hz, 6 H), 1.00 (td, *J*=7.3, 1.0 Hz, 3 H), 0.30 (s, 27 H), 0.16 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 214.3, 142.1, 138.9, 136.3, 129.8, 128.9, 127.9, 127.0, 126.9, 81.2, 75.8, 70.7, 52.9, 51.0, 47.0, 46.6, 42.0, 36.8, 21.4, 20.2, 12.2, 10.1, 7.6, 1.8, 1.3; LRMS (API-ES +): $C_{36}H_{63}NO_5SSi_4^+$ $[M-Si(TMS)_3]^+$ m/z = 734.3 (36%), $C_{45}H_{91}NO_6NaSSi_4^+$ $[M+Na]^+$ m/z = 1020.5 (5%); FTIR (thin film): 3545, 2950, 2895, 1702, 1675, 1624, 1457, 1335, 1245, 1154, 1031, 835, 690, 654, 547.

Synthetic procedures and Data for 27a, 28, 31, 32, 33, 34



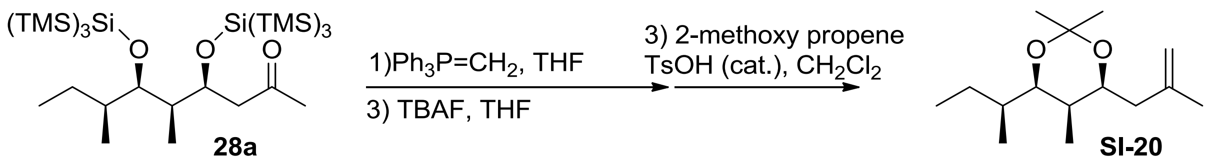
27a
Known compound.[7] Stereochemistry previously determined.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.82 (s, 1 H), 3.65 - 3.73 (m, 1 H), 2.46 - 2.54 (m, 1 H), 1.45 - 1.58 (m, 2 H), 1.06 - 1.19 (m, 2 H), 1.04 (d, *J*=7.0 Hz, 3 H), 0.88 (t, *J*=7.2 Hz, 6 H), 0.78 (d, *J*=6.7 Hz, 3 H), 0.19 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.1, 80.9, 50.4, 39.5, 26.1, 14.6, 12.5, 10.2, 0.8; LRMS (APCI +) $C_9H_{28}OSi_4Na^+$ $[TMS_3SiOHNa]^+$ m/z = 288.1 (100%), $C_{17}H_{43}O_2Si_4^+$ $[M+H]^+$ m/z = 391.2 (30%); 2961, 2893, 1724, 1459, 1425, 1245, 1023, 834, 756, 687, 624; $[a]_D^{21}$ =+33.97° (*c* 0.37, CH_2Cl_2).

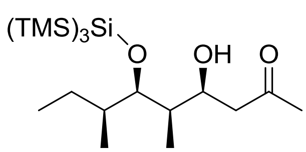


28a Prepared according to **GP2**, using Me_2AlNTf_2 as a catalyst instead of $HNTf_2$ (Table 3, entry 1). **28a**: TLC: R_f = 0.39 (25:75 CH_2Cl_2/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.01 (dt, *J*=9.4, 3.0 Hz, 1 H), 3.28 (dd, *J*=6.8, 1.7 Hz, 1 H), 2.77 (dd, *J*=16.4, 9.6 Hz, 1 H), 2.55 (dd, *J*=16.4, 3.5 Hz, 1 H), 2.13 (s, 3 H), 1.47 - 1.53 (m, 1 H), 1.37 - 1.46 (m, 1 H), 1.20 - 1.32 (m, 2 H), 0.90 (t, *J*=7.3 Hz, 3 H), 0.86 (d, *J*=6.7 Hz, 3 H), 0.82 (d, *J*=6.8 Hz, 3 H), 0.19 (s, 27 H), 0.17 - 0.18 (m, 27 H)^{13}C NMR (500 MHz, $CDCl_3$) δ = 206.6, 82.9, 72.3, 48.6, 41.4, 38.3, 31.3, 27.1, 12.2, 12.0, 11.9, 1.3, 0.7; FTIR (thin film): 2949, 2894, 1718, 1244, 1015, 835, 744; LRMS (APCI+) $C_{20}H_{45}O_2Si_4$ $[M\text{-}OSiTMS_3]^+$ m/z = 431 (35%).

Stereochemical Assignment: Stereochemistry at position C(3) of **28a** was determined to be (*S*) by conversion to 1,3-diol acetonide **SI-20** (**Scheme S-13**) following **GP 6** (steps 2-4). 3,5-*syn* stereochemistry was indicated by ^{13}C NMR analysis (δ = 99.0, 19.7, 30.2 ppm).

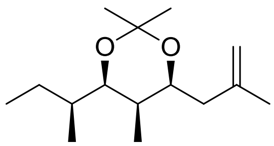
Scheme S-17



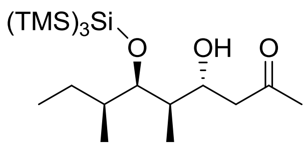


29a TLC: R_f = 0.17 (10:90 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.06 (dq, *J*=7.5, 3.8 Hz, 1 H), 3.36 (t, *J*=3.2 Hz, 1 H), 2.77 (d, *J*=3.1 Hz, 1 H), 2.58 (m, *J*=2.4 Hz, 2 H), 2.17 (s, 3 H), 1.52 - 1.63 (m, 4 H), 0.99 - 1.11 (m, 1 H), 0.88 (m, *J*=7.5, 7.5 Hz, 4 H), 0.88 (d, *J*=7.0 Hz, 3 H), 0.84 (d, *J*=7.0 Hz, 3 H), 0.20 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 210.0, 82.6, 69.6, 48.7, 40.3, 39.9, 31.0, 25.1, 15.2, 12.4, 10.7, 1.0; LRMS (APCI +) $C_{20}H_{48}NaO_3Si_4^+$ $[M + Na]^+$ m/z = 417.2 (100%).

Stereochemical Assignment: 29a was determined to be 3,4-*syn* by conversion to **SI-20**.



Data for SI-20: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.79 (s, 2 H), 4.76 (s, 1 H), 4.01 (ddd, *J*=7.6, 5.8, 2.1 Hz, 1 H), 3.41 (dd, *J*=9.8, 1.8 Hz, 1 H), 2.23 (dd, *J*=14.3, 7.3 Hz, 1 H), 2.10 (dd, *J*=14.5, 6.0 Hz, 1 H), 1.75 (s, 3 H), 1.45 - 1.55 (m, 2 H), 1.41 (s, 3 H), 1.40 (s, 3 H), 0.92 (d, *J*=6.4 Hz, 7 H), 0.88 (t, *J*=6.4 Hz, 3 H), 0.84 (d, *J*=6.7 Hz, 3 H); TLC: R_f = 0.31 (5:95 EtOAc/hexanes);^{13}C NMR (500 MHz, $CDCl_3$) δ = 142.7, 112.1, 99.0, 78.3, 72.1, 41.2, 35.5, 32.7, 30.2, 23.6, 23.1, 19.7, 15.6, 11.0, 4.9; FTIR (thin film): 2967, 2937, 1653, 1278, 1200, 1011, 836. LRMS (APCI +) $C_{15}H_{32}NO_2^+$ $[M + NH_4]^+$ m/z = 258 (40%), $C_{15}H_{27}O^+$ $[M-OH]^+$ m/z = 223 (35%);

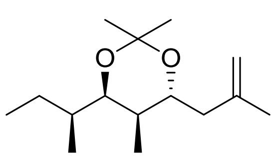


30a:

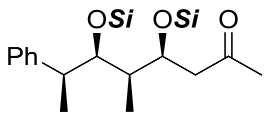
General Procedure GP9 An oven-dried 1dram vial was charged with a magnetic stir bar, **27a** (40mg, 0.1 mmol), acetone 0.4 mL, DMF (0.8 mL) and L-PTZ (2.6 mg, weighed on a microbalance, 0.02 mmol). The vial was sealed and stirred under air for 5 days. The reaction mixture was poured onto cold water (10 mL) and $NaHCO_3$ (sat. aq., 1 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 6 mL). The combined organic layers were washed with H_2O and brine (5 mL each), dried over Na_2SO_4, filtered through cotton and concentrated. Purification by flash chromatography (10 mL silica, 1-7% EtOAc/hexanes) afforded **30a** as a white semi-solid (32 mg, 71%).

Data for 30a:TLC: Rf = 0.23 (10:90 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.98 (tt, *J*=9.2, 2.4 Hz, 1 H), 3.89 - 3.94 (m, 1 H), 3.53 (d, *J*=5.5 Hz, 1 H), 2.57 (dd, *J*=15.9, 3.1 Hz, 1 H), 2.47 (dd, *J*=15.6, 8.9 Hz, 1 H), 2.20 (s, 3 H), 1.74 (dqd, *J*=9.4, 7.0, 7.0, 7.0, 2.1 Hz, 1 H), 1.45 - 1.57 (m, 2 H), 1.07 - 1.18 (m, 1 H), 0.92 (d, *J*=6.7 Hz, 3 H), 0.88 (t, *J*=7.5 Hz, 3 H), 0.76 (d, *J*=7.0 Hz, 3 H), 0.21 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 209.7, 83.6, 71.0, 49.0, 41.8, 38.4, 31.5, 27.2, 15.7, 13.3, 12.4, 0.9; FTIR (thin film): 3534 (br), 2949, 2894, 1712, 1381, 1244, 1016, 836, 686, 624; LRMS (APCI +) $C_{20}H_{48}NaO_3Si_4^+$ $[M + Na]^+$ m/z = 417.2 (100%).

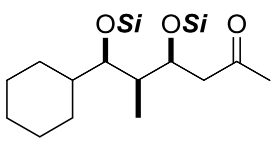
Stereochemical Assignment: The stereochemistry of **30a** determined by conversion to acetonide **SI-21** following **GP 6.** 3,5-*anti* stereochemistry was indicated by ^{13}C NMR analysis (δ = 100.8, 24.7,24.9 ppm).



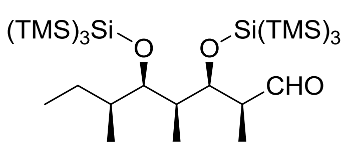
Data for SI-21: TLC: R_f = 0.37 (5:95 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.74 - 4.81 (m, 2 H), 3.37 - 3.42 (m, 1 H), 3.42 (dd, *J*=9.2, 4.3 Hz, 1 H), 2.24 (dd, *J*=15.0, 8.5 Hz, 1 H), 2.19 (dd, *J*=14.6, 4.3 Hz, 1 H), 1.75 (s, 3 H), 1.71 (quind, *J*=6.9, 6.9, 6.9, 6.9, 4.6 Hz, 1 H), 1.36 - 1.51 (m, 2 H), 1.34 (s, 3 H), 1.31 (s, 3 H), 0.93 - 0.98 (m, 0 H), 0.92 (d, *J*=6.4 Hz, 3 H), 0.90 (t, *J*=6.7 Hz, 3 H), 0.85 (d, *J*=6.7 Hz, 3 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 143.3, 112.0, 100.8, 73.8, 73.3, 43.1, 38.7, 34.3, 24.9, 24.7, 23.8, 23.0, 15.7, 12.1, 12.2; LRMS (APCI +) $C_{15}H_{29}O_2$ $[M+H]^+$ m/z = 241.2 (45%). FTIR (thin film) 2985, 2968, 2934, 2876, 1653, 1378, 1227, 1107, 996, 888.



28b dr = 90:8:2
^{1}H NMR (500MHz, $CDCl_3$, 294K) δ = 7.27 - 7.33 (m, 4 H), 7.19 - 7.25 (m, 1 H), 4.04 (dt, *J*=7.4, 4.7 Hz, 1 H), 3.70 (dd, *J*=7.0, 2.4 Hz, 1 H), 3.47 (dd, *J*=18.5, 4.7 Hz, 1 H), 2.80 (quin, *J*=7.0 Hz, 1 H), 2.53 (dd, *J*=18.6, 4.3 Hz, 1 H), 2.09 (s, 3 H), 1.74 (dqd, *J*=7.0, 6.8, 6.8, 6.8, 2.0 Hz, 1 H), 1.28 (d, *J*=7.0 Hz, 3 H), 0.34 (d, *J*=7.3 Hz, 3 H), 0.30 (s, 27 H), 0.20 (s, 27 H); ^{13}C NMR (500MHz, $CDCl_3$, 294K) δ = 206.74, 144.21, 128.37, 128.36, 126.34, 83.29, 73.04, 51.02, 44.87, 43.11, 30.69, 20.25, 15.72, 1.28, 0.85; LRMS (APCI +): $C_{24}H_{47}O_2Si_4^+$ $[M – TMS_3SiO]^+$ m/z = 479.2 (100%); FTIR (thin film):2949, 2894, 1926, 1868, 1720, 1680, 1453, 1365, 1245, 1067, 1031, 835, 687; waxy solid.

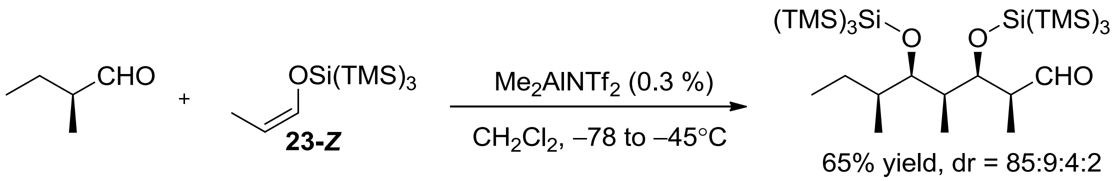


29c ^{1}H NMR (500MHz, $CDCl_3$, 294K) δ = 4.01 (dt, *J*=8.6, 3.3 Hz, 1 H), 3.27 (dd, *J*=5.5, 0.9 Hz, 1 H), 2.81 (dd, *J*=16.8, 8.9 Hz, 1 H), 2.54 (dd, *J*=16.9, 3.5 Hz, 1 H), 2.13 (s, 3 H), 1.72 - 1.81 (m, 2 H), 1.63 - 1.69 (m, 1 H), 1.49 - 1.62 (m, 4 H), 1.19 - 1.31 (m, 4 H), 1.07 - 1.18 (m, 2 H), 0.83 (d, *J*=6.7 Hz, 3 H), 0.20 (s, 27 H), 0.19 (s, 27 H); ^{13}C NMR (500MHz, $CDCl_3$, 294K) δ = 206.56, 81.59, 72.71, 48.71, 42.03, 41.08, 31.22, 29.58, 27.17, 26.67, 26.4, 12.07, 1.40, 0.81; LRMS (APCI +): $C_{22}H_{49}O_2Si_4^+$ $[M – TMS_3SiO]^+$ m/z = 457.4 (100%); LRMS (APCI -): $C_{28}H_{67}O_3Si_7^-$ $[M – TMS]^-$ m/z = 642.7 (55%), FTIR (thin film): 2948m 2854, 1719, 1445, 1359, 1244, 1014, 834m 745, 687, 624; waxy solid.



31 Synthesized by double propionaldehyde addition of **23-*Z*** and (*S*)-2-methylbutanal.[7] As shown in **Scheme S-17**

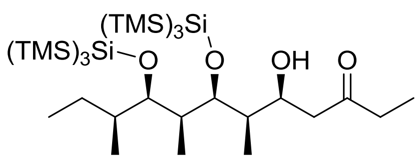
Scheme S-17



31

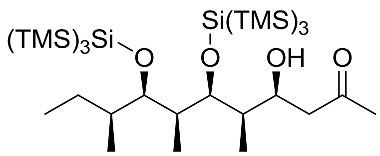
A 200 mL round bottomed flask with magnetic stir bar and septum was charged with **23-*Z*** (3.5g, 11.5 mmol), CH_2Cl_2 (60 mL), and (*S*)-2-methyl butanal (0.525 mL, 5.0 mmol). The reaction was cooled to −78 °C and freshly prepared Me_2AlNTf_2 (0.05 M CH_2Cl_2, 0.7 mL) was added dropwise. The reaction was stirred at −78 °C then warmed to −45 °C and stirred at this temperature overnight. The reaction was then quenched with 10mL of NaK tartrate (sat. aq.). The mixture was vigorously stirred at r.t. for 10 min, then poured on hexanes 100 mL. The layers were separated and the organic layer was washed with brined, dried ($MgSO_4$), filtered and concentrated. Flash chromatography (300 mL silica gel, 5→15% v/v CH_2Cl_2/hexanes yield **31** with good separation of diastereomers (3.15 g, 65% yield)

Data for 31:TLC: R_f = 0.36 (25:75 CH_2Cl_2/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.89 (s, 1 H), 3.83 (t, *J*=4.1 Hz, 1 H), 3.23 (dd, *J*=6.1, 2.4 Hz, 1 H), 2.65 (qd, *J*=7.0, 4.7 Hz, 1 H), 1.63 (quind, *J*=6.6, 6.6, 6.6, 6.6, 3.8 Hz, 1 H), 1.51 - 1.59 (m, 2 H), 1.46 (dqdd, *J*=8.0, 7.0, 7.0, 7.0, 6.7, 3.1 Hz, 1 H), 1.20 - 1.30 (m, 1 H), 1.04 (d, *J*=7.0 Hz, 3 H), 0.91 (t, *J*=7.3 Hz, 5 H), 0.89 (d, *J*=7.0 Hz, 3 H), 0.77 (d, *J*=6.7 Hz, 3 H), 0.20 (s, 27 H), 0.18 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 204.9, 82.8, 78.4, 51.0, 40.6, 38.3, 27.3, 14.1, 12.6, 12.0, 9.9, 1.3, 1.1; FTIR (thin film): 2940, 2894, 1723, 1457, 1244, 1018, 835, 686, 624; LRMS (APCI+) $C_{20}H_{47}O_2Si_4^+$ $[M–TMS_3SiO]^+$ m/z = 431.2 (100%). HRMS (FIA-APIC +) $C_{17}H_{43}O_2Si_4^+$ [M – **23*Z*** (retro-aldol)]$^+$ m/z (found: 391.2781 calc: 391.2340) (100%).



32 Synthesized according to **GP 4**. Enoloborination was conducted with 2-butanone rather than acetone, with (*c*-Hex)$_2$BCl and Et_3N at room 0°C.

Data for 32:TLC: R_f = 0.51 (10:90 EtOAc/hexanes); 4.16 (td, *J*=6.3, 3.2 Hz, 1 H), 3.42 (dd, *J*=5.0, 3.2 Hz, 1 H), 3.24 (dd, *J*=7.0, 1.8 Hz, 1 H), 3.00 (d, *J*=2.7 Hz, 1 H), 2.59 (dd, *J*=17.7, 9.8 Hz, 1 H), 2.52 (m, *J*=2.1 Hz, 1 H), 2.44 (q, *J*=7.3 Hz, 2 H), 1.80 (quind, *J*=6.9, 6.9, 6.9, 6.9, 3.5 Hz, 1 H), 1.59 - 1.67 (m, 1 H), 1.52 - 1.58 (m, 1 H), 1.42 (dqd, *J*=11.6, 7.6, 7.6, 7.6, 4.0 Hz, 1 H), 1.20 - 1.30 (m, 2 H), 1.06 (t, *J*=7.3 Hz, 3 H), 1.01 (d, *J*=7.0 Hz, 3 H), 0.95 (d, *J*=7.0 Hz, 3 H), 0.89 (t, *J*=7.3 Hz, 4 H), 0.78 (d, *J*=7.0 Hz, 3 H), 0.19 (br. s, 54 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 214.8, 83.0, 80.1, 67.3, 47.9, 42.2, 41.5, 38.9, 36.8, 27.4, 16.1, 12.9, 12.3, 11.1, 7.8, 1.4, 1.3; LRMS (APCI +) $C_{36}H_{55}O_3Si_4^+$ $[M – TMS_3SiO]^+$ m/z = 503.2 (55%), m/z = 387.2 (100%); LRMS (APCI -): $C_{29}H_{74}O_3Si_8^-$ [M-butanone]$^-$ m/z = 693.3 (15%).

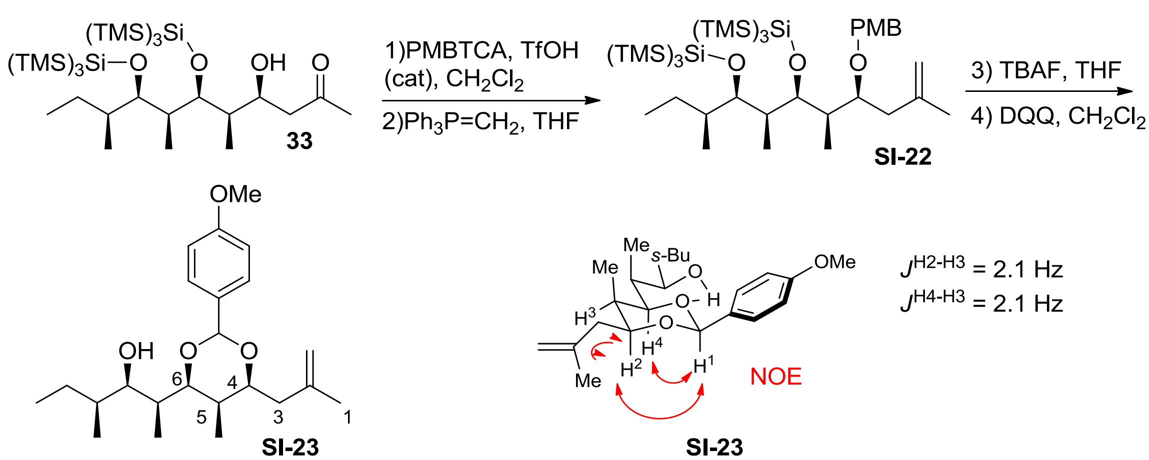


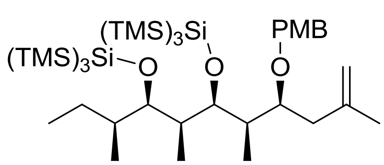
33 Synthesized according to **GP 4** using 9-BBNOTf for enolborination (Table 4, eq. 3).

Data for 33 TLC: $R_f = 0.38$ (10:90 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ =4.16 (dq, J=10.1, 2.4 Hz, 1 H), 3.42 (dd, J=5.0, 3.2 Hz, 1 H), 2.92 (d, J=2.7 Hz, 1 H), 2.62 (dd, J=17.7, 9.8 Hz, 1 H), 2.54 (dd, J=17.7, 2.1 Hz, 1 H), 2.16 (s, 3 H), 1.87 (qt, J=6.1, 3.4 Hz, 1 H), 1.80 (quind, J=6.9, 6.9, 6.9, 6.9, 3.4 Hz, 1 H), 1.58 - 1.66 (m, 1 H), 1.50 - 1.58 (m, 1 H), 1.34 - 1.48 (m, 1 H), 1.01 (d, J=7.0 Hz, 3 H), 0.94 (d, J=6.7 Hz, 3 H), 0.89 (t, J=7.5 Hz, 3 H), 0.78 (d, J=6.7 Hz, 3 H), 0.18 - 0.21 (m, 54 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 210.0, 83.0, 80.2, 67.2, 49.2, 42.1, 41.5, 38.9, 30.8, 27.4, 16.1, 12.9, 12.2, 11.0, 1.4, 1.3; LRMS (APCI –): $C_{32}H_{79}O_4Si_8$ $[M-H]^-$ m/z = 751.4 (90%); FTIR (thin film): 3543 (br), 2949, 2894, 1713, 1379, 1244, 1019, 835, 686, 624.

Stereochemical Assignment: 33 was determined to (*S*) at C(4) by conversion to *p*-methoxy benzylidene acetal **SI-23** as shown in **Scheme S-19.** The 2,3- *syn*-stereochemistry of **SI-23** was determined by vicinal couplings $J^{H2\text{-}H3}$ = 2.1 Hz $J^{H4\text{-}H3}$ = 2.1 Hz. A NOESY experiment revealed NOE between the benzylidine H and H^2/H^4, indicating C(4)-C(6)-*syn* stereochemistry. NOE interactions between H^2 and H^4 also support this structure. A COSY experiment validated assignment of ^{1}H NMR resonances.

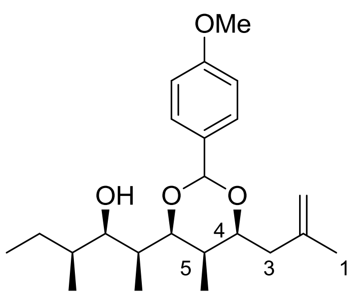
Scheme S-19: Synthesis of **SI-23** and selected ^{1}H NMR J values and NOE interactions.





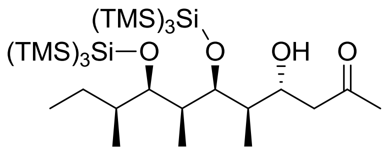
SI-22

(1) To a dry 10 mL round-bottomed flask with stir bar was added **33** (0.2 mmol). CH_2Cl_2 (0.5mL) and hexanes (1.5mL) were added and flask cooled to 0°C. *p*-methoxybenzyltrichloroacetimidate was added (90 mg, 0.35 mmol), followed by TfOH (0.03 mL, 1.0 M CH_2Cl_2). The reaction was allowed to warm to r.t., and stirred overnight. The reaction was then quenched by addition of $NaHCO_3$. Normal aqueous workup, followed by column chromatography (30 mL silica gel, 1→10% v/v Et_2O/hexanes) afford the PMB-protected alcohol in 71% yield.
(2) Wittig reaction performed according to **GP 6** (step 2), 63% yield)
Data for SI-22: TLC: R_f = 0.59 (20:80 Et_2O/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.20 (d, *J*=8.7 Hz, 2 H), 6.84 (d, *J*=8.7 Hz, 2 H), 4.37 (s, 2 H), 4.10 (qd, *J*=5.2, 1.1 Hz, 1 H), 3.48 (dd, *J*=6.5, 2.1 Hz, 1 H), 3.26 (dd, *J*=7.6, 1.1 Hz, 1 H), 2.78 (dd, *J*=16.9, 6.6 Hz, 1 H), 2.63 (dd, *J*=16.8, 5.2 Hz, 1 H), 2.12 (s, 3 H), 1.73 - 1.81 (m, 1 H), 1.56 - 1.70 (m, 2 H), 1.37 - 1.44 (m, 1 H), 1.26 - 1.35 (m, 1 H), 1.07 (d, *J*=6.9 Hz, 3 H), 1.04 (d, *J*=6.9 Hz, 3 H), 0.84 - 0.91 (m, 3 H), 0.73 (d, *J*=6.7 Hz, 3 H), 0.21 (s, 27 H), 0.19 (s, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 206.9, 159.1, 131.1, 129.2, 113.7, 84.0, 79.6, 75.4, 71.7, 55.4, 47.7, 42.7, 42.1, 38.1, 31.1, 27.9, 15.5, 13.2, 12.1, 12.1, 1.4, 1.3; LRMS (APCI –): $C_{37}H_{79}O_5Si_7$ $[M – TMS]^-$ m/z = 799.3 (60%);



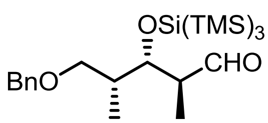
SI-23

Preparation of **3** TBAF desilylation carried out by analogy to **GP 6** (3). The resultant triol (28 mg, 0.073 mmol) was loaded into a 25mL round-bottomed flask. CH_2Cl_2 was added, and stirring mixture cooled to 0°C. Powdered molecular sieves (4Å, 150mg) were added and the reaction stirred for 1 h. DDQ (25 mg, 0.11 mmol) was then added. A blue color appeared immediately. After 2 h, the reaction was warmed to r.t. filtered through celite (Et_2O eluent). The resulting organic layer was washed with $NaHCO_3$ and brine (10 mL) each, dried (Na_2SO_4), filtered and concentrated. Flash chromatography (8 mL silica gel, 2→25% EtOAc/hexanes eluent) afforded **SI13** (16 mg, 58% yield), along with the fully oxidized *p*-methoxy benzoyl ester (7 mg, 24% yield).
Data for SI-23: TLC: R_f = 0.38 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43 (d, *J*=8.8 Hz, 2 H), 6.88 (d, *J*=8.5 Hz, 5 H), 5.51 (s, H^1), 4.81 (app d, *J*=7.3 Hz, 2 H), 4.02 (ddd, *J*=7.7, 5.7, 2.1 Hz, H^2), 3.80 (s, 1 H), 3.78 (dd, *J*=11.4, 2.1 Hz, H^4), 3.28 - 3.35 (m, 1 H), 2.41 (dd, *J*=14.0, 7.6 Hz, 1 H), 2.21 (dd, *J*=14.2, 6.0 Hz, 1 H), 2.02 (qdd, *J*=9.2, 9.2, 9.2, 6.9, 2.1 Hz, 6 H), 1.79 (s, 3 H), 1.74 (qt, *J*=6.8, 2.1 Hz, H^3), 1.53 (td, *J*=6.1, 3.1 Hz, 1 H), 1.42 - 1.50 (m, 1 H), 1.19 - 1.30 (m, 1 H), 1.00 (d, *J*=6.7 Hz, 1 H), 1.01 (d, *J*=5.5 Hz, 1 H), 0.97 (d, *J*=6.7 Hz, 3 H), 0.90 (t, *J*=7.3 Hz, 1 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 159.8, 142.5, 131.9, 127.4, 113.7, 112.7, 101.6, 84.1, 79.7, 74.6, 55.4, 41.1, 38.1, 35.8, 32.3, 24.9, 23.2, 15.7, 11.1, 8.8, 6.4; LRMS (API-ES +), $C_{23}H_{35}O_3$ $[M – OH]^+$ m/z = 359.1 (100%), $C_{23}H_{35}O_3^+$ $[M+H]^+$ m/z = 377.2 (35%).



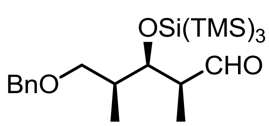
34 Synthesized according to **GP 9. Data for 34*:*** TLC: R_f = 0.60 (10:90 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.95 (tt, *J*=9.5, 2.5 Hz, 1 H), 3.75 (dd, *J*=5.8, 1.5 Hz, 1 H), 3.48 (d, *J*=2.7 Hz, 1 H), 3.21 (dd, *J*=4.9, 3.7 Hz, 1 H), 2.63 (dd, *J*=16.3, 2.6 Hz, 1 H), 2.44 (dd, *J*=16.5, 9.5 Hz, 1 H), 2.19 (s, 3 H), 1.83 (dqd, *J*=9.8, 7.0, 7.0, 7.0, 1.5 Hz, 1 H), 1.67 - 1.74 (m, 1 H), 1.64 (qt, *J*=7.0, 3.4 Hz, 1 H), 1.50 (dqd, *J*=13.2, 7.6, 7.6, 7.6, 3.4 Hz, 1 H), 1.13 - 1.23 (m, 1 H), 1.03 (d, *J*=7.0 Hz, 3 H), 0.88 (t, *J*=7.3 Hz, 3 H), 0.79 (d, *J*=6.7 Hz, 3 H), 0.72 (d, *J*=7.0 Hz, 3 H), 0.20 - 0.22 (m, 27 H), 0.19 - 0.20 (m, 27 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 210.0, 83.0, 79.7, 69.8, 48.6, 42.4, 41.0, 38.8, 31.3, 27.1, 16.4, 13.9, 12.2, 12.1, 1.4, 1.3; LRMS (APCI –): $C_{32}H_{79}O_4Si_8$ $[M – H]^-$ m/z = 751.4 (85%).

Stereochemical Assignment: 34 was assigned (*R*) at C(4) by contrast to **33.**

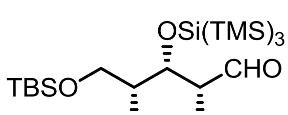


SI-3

TLC: R_f = 0.47 (25:75 CH_2Cl_2/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 203.83, 138.41, 128.41, 127.62, 127.57, 79.68, 72.92, 71.79, 50.75, 38.53, 15.01, 10.98, 0.82; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.61 - 9.68 (m, 1 H), 7.26 - 7.40 (m, 4 H), 4.42 (d, *J*=11.9 Hz, 1 H), 4.38 (d, *J*=11.9 Hz, 1 H), 3.84 (ddd, *J*=5.5, 3.8, 1.7 Hz, 1 H), 3.37 (dd, *J*=9.8, 5.2 Hz, 1 H), 3.30 (dd, *J*=8.5, 4.0 Hz, 1 H), 2.60 (s, 1 H), 1.95 (spt, *J*=5.8 Hz, 1 H), 1.15 (d, *J*=7.0 Hz, 3 H), 1.04 (d, *J*=7.0 Hz, 3 H), 0.23 (s, 27 H); LRMS (APCI +) $C_{23}H_{47}O_3Si_4^+$ $[M + H]^+$ m/z = 483.4 (100%)



SI-5a TLC: R_f = 0.42 (25:75 CH_2Cl_2/hexanes)^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.03, 138.56, 128.42, 127. 72, 127.60, 50.76, 37.29, 12.77, 0.89, 0.80; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.92 (s, 1 H), 7.22 - 7.44 (m, 5 H), 4.56 (d, *J*=11.0 Hz, 9 H), 4.48 (d, *J*=12.2 Hz, 5 H), 3.92 (dd, *J*=4.7, 2.9 Hz, 5 H), 3.66 - 3.75 (m, 1 H), 3.52 (dd, *J*=8.7, 6.0 Hz, 5 H), 3.30 (dd, *J*=8.7, 7.2 Hz, 5 H), 2.58 - 2.65 (m, 1 H), 2.04 (dqd, *J*=13.3, 6.6, 6.6, 6.6, 2.9 Hz, 5 H), 1.06 (d, *J*=6.7 Hz, 3 H), 0.90 (d, *J*=7.0 Hz, 3 H), 0.24 (s, 27 H); LRMS (APCI +) $C_{23}H_{47}O_3Si_4^+$ $[M + H]^+$ m/z = 483.4 (100%)

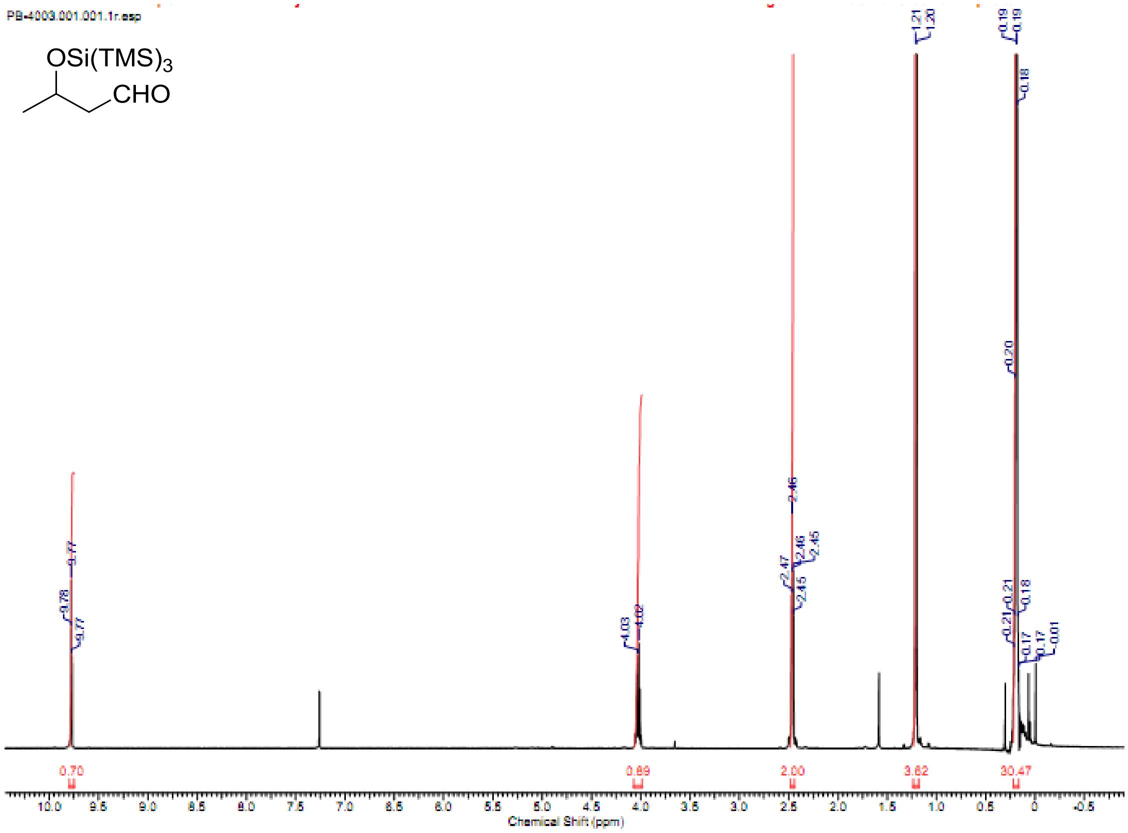


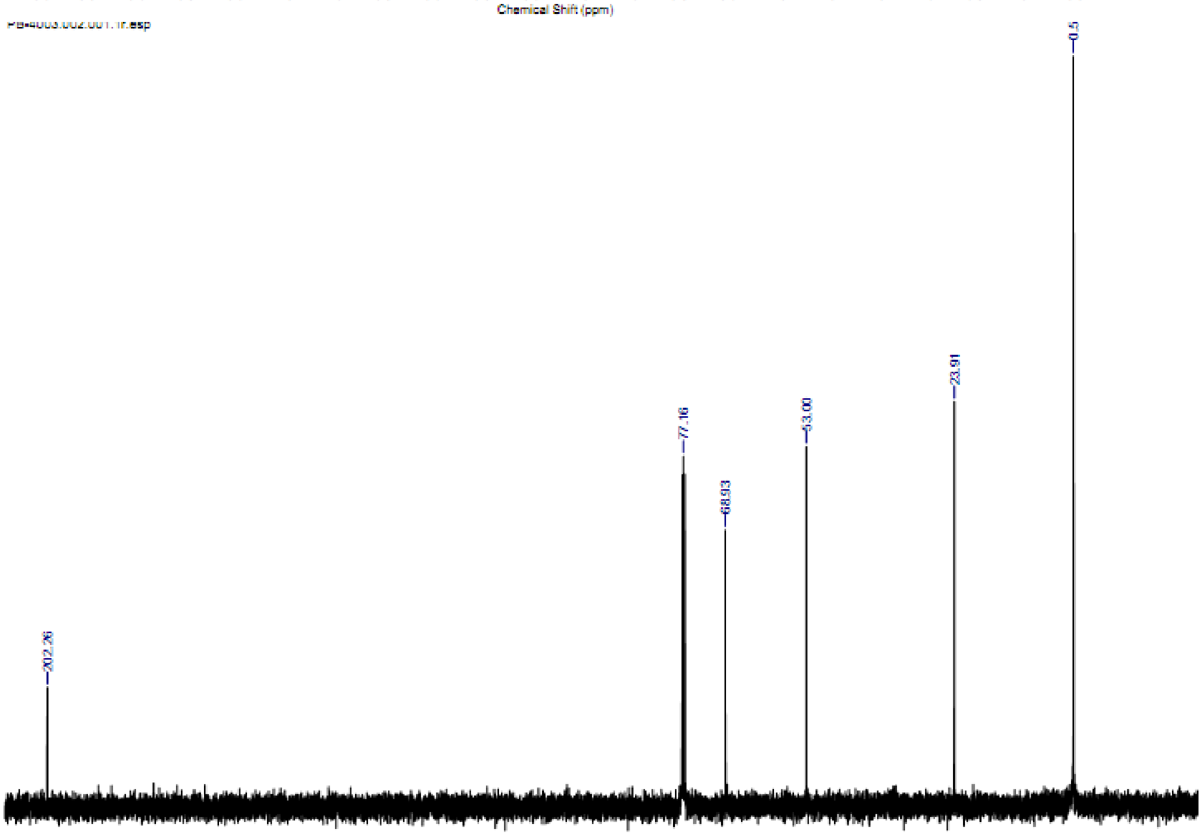
SI-5b

TLC: R_f = 0.36 (25:75 CH_2Cl_2/hexanes); ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.18, 78.12, 65.46, 51.17, 39.38, 26.05, 18.38, 12.21, 9.97, 0.83, -5.14, -.517; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.89 (s, 2 H), 3.87 (dd, *J*=4.9, 3.1 Hz, 1 H), 3.53 (dd, *J*=9.8, 6.4 Hz, 2 H), 3.39 (dd, *J*=9.8, 6.4 Hz, 2 H), 2.56 - 2.66 (m, 2 H), 1.72 - 1.81 (m, 1 H), 1.00 (d, *J*=7.0 Hz, 3 H), 0.87 (s, 5 H), 0.78 (d, *J*=7.0 Hz, 3 H), 0.21 (s, 27 H), 0.01 - 0.05 (m, 6 H); LRMS (APCI +) $C_{22}H_{55}O_3Si_5^+$ [M+H] m/z = 507.5 (32%).

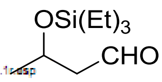
NMR spectra

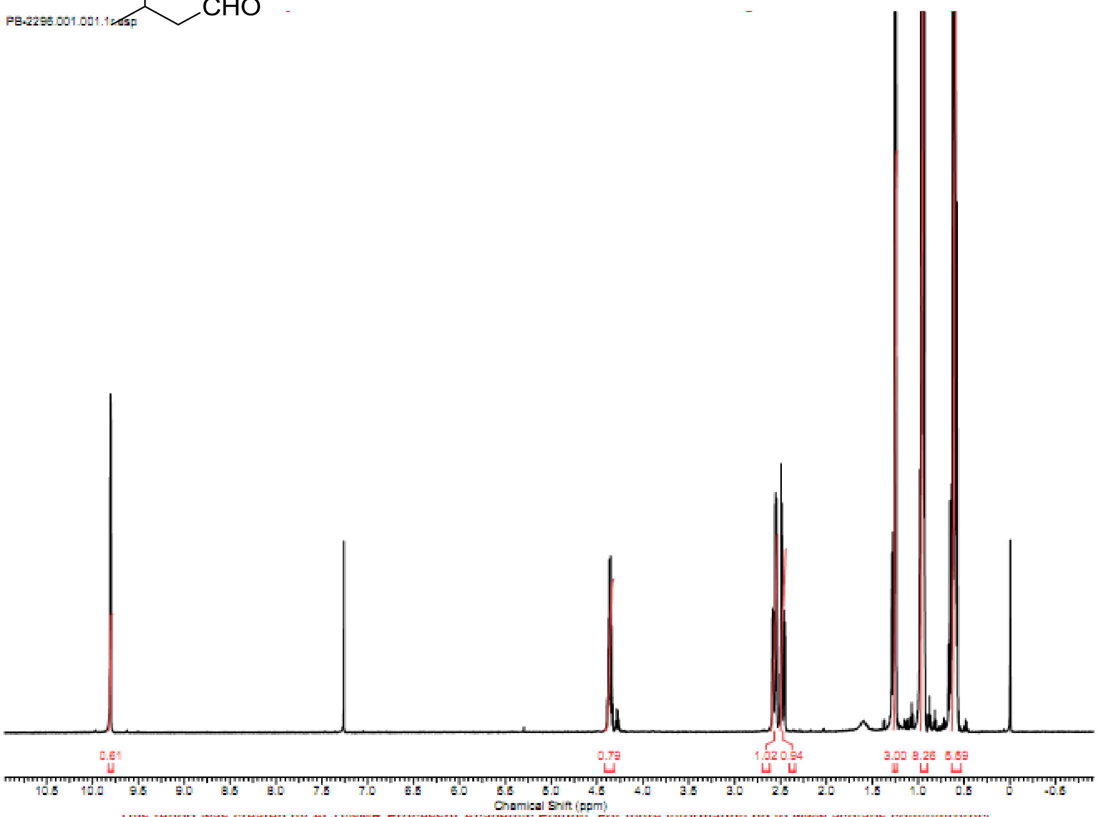
1a

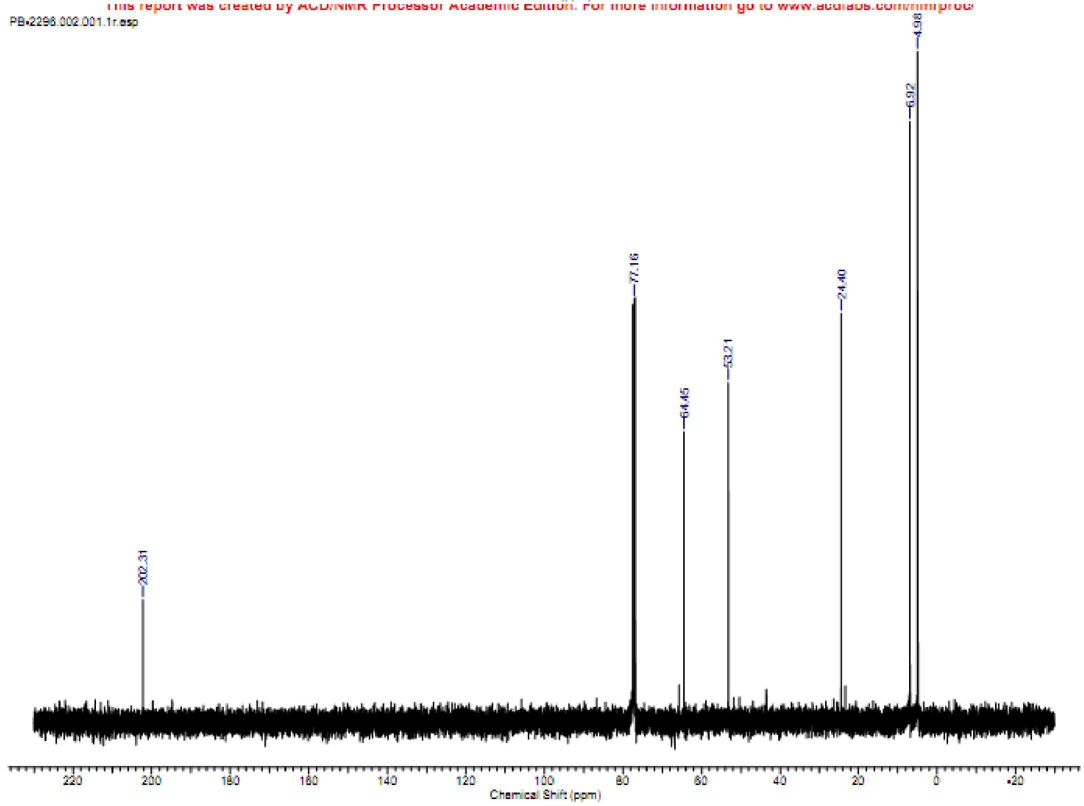

PB-4003.001.001.1r.esp
OSi(TMS)3
CHO
9.78
9.77
9.77
4.03
4.02
2.47
2.46
2.46
2.45
2.45
1.21
1.20
0.21
0.21
0.20
0.19
0.19
0.18
0.18
0.17
0.17
0.01
0.70
0.89
2.00
3.62
30.47
Chemical Shift (ppm)


202.26
77.16
68.93
53.00
23.91
0.5

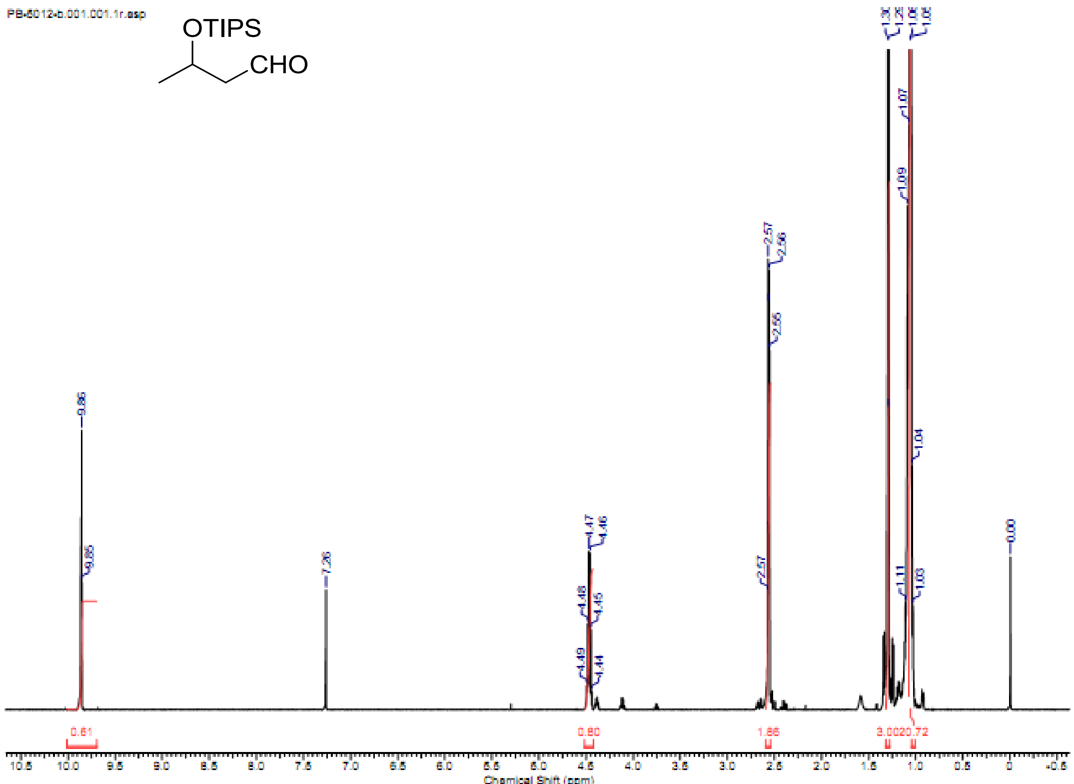
1b

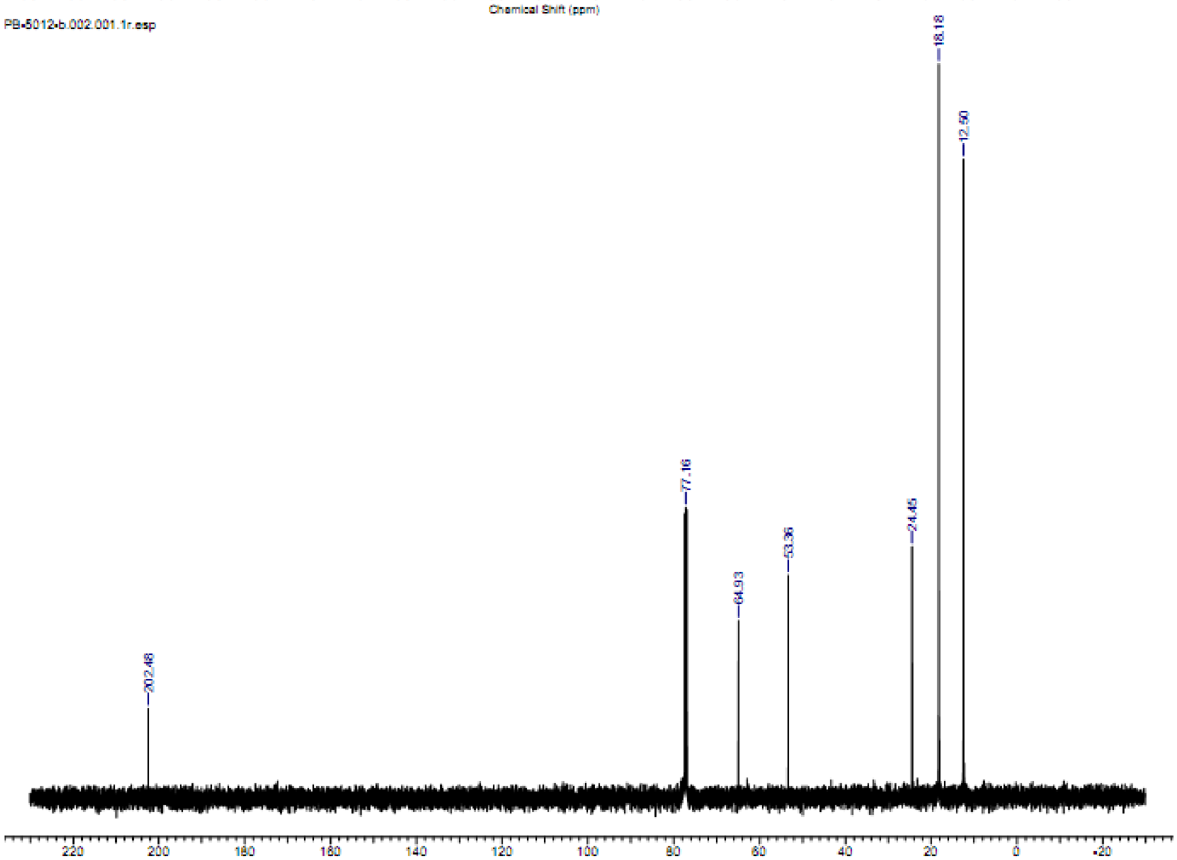

OSi(Et)3
CHO


PB-2296.001.001.1r.esp
0.61
0.79
1.02
0.94
3.00
9.26
6.69
Chemical Shift (ppm)

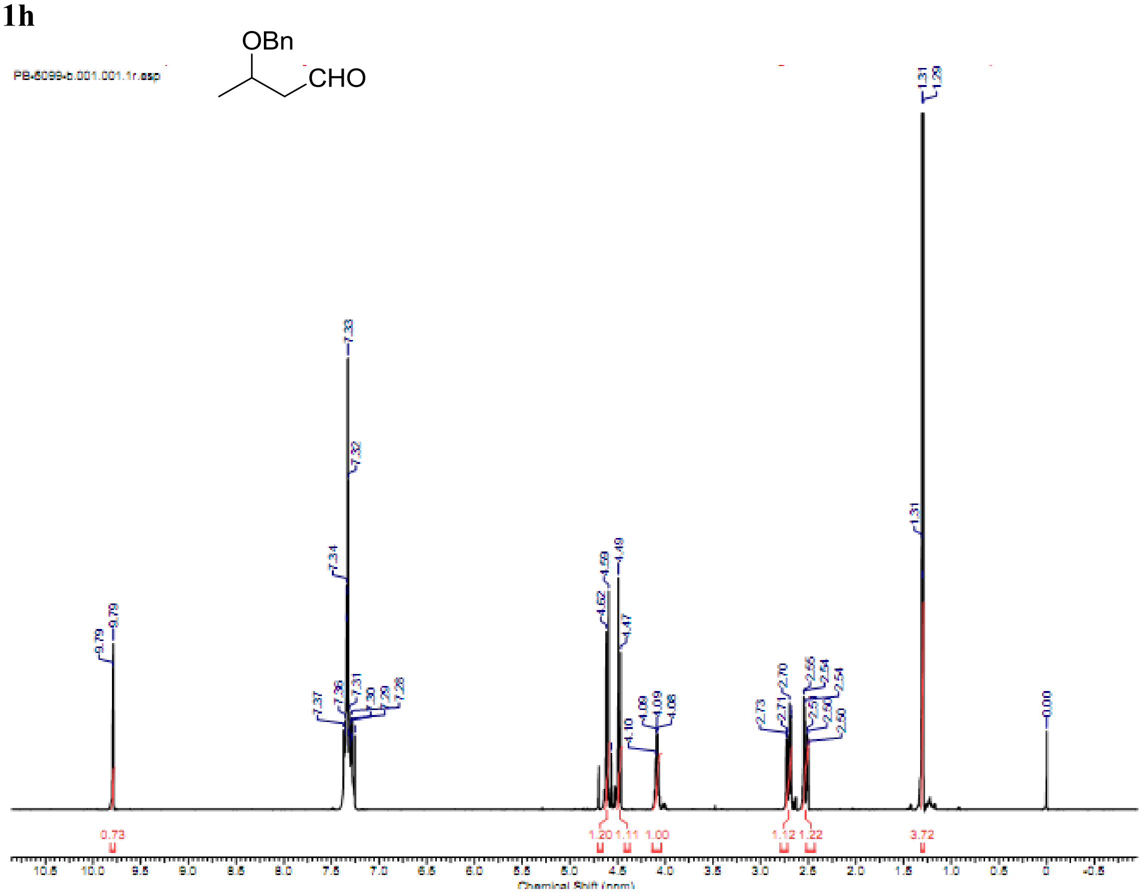

PB-2296.002.001.1r.esp
202.31
77.16
64.45
53.21
24.40
6.92
4.98
Chemical Shift (ppm)

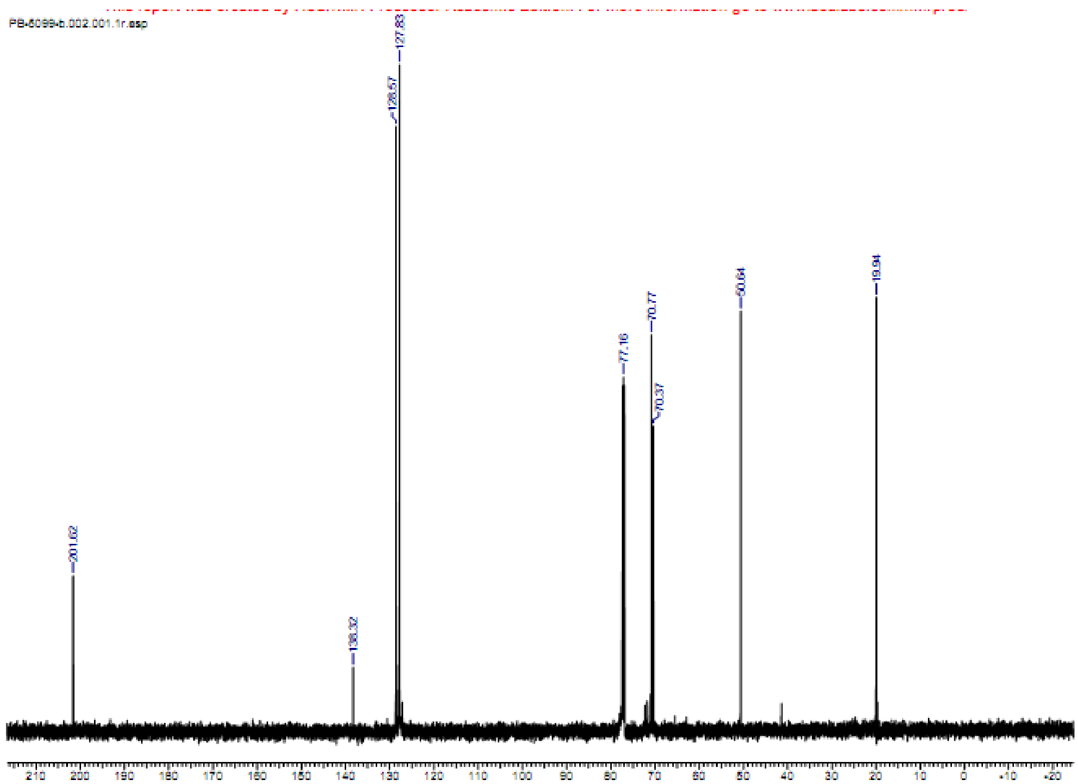
1c


PB-5012-b.001.001.1r.esp
OTIPS
CHO
Chemical Shift (ppm)

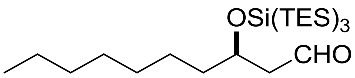

PB-5012-b.002.001.1r.esp
202.48
77.16
64.93
53.36
24.45
18.18
12.50

1h

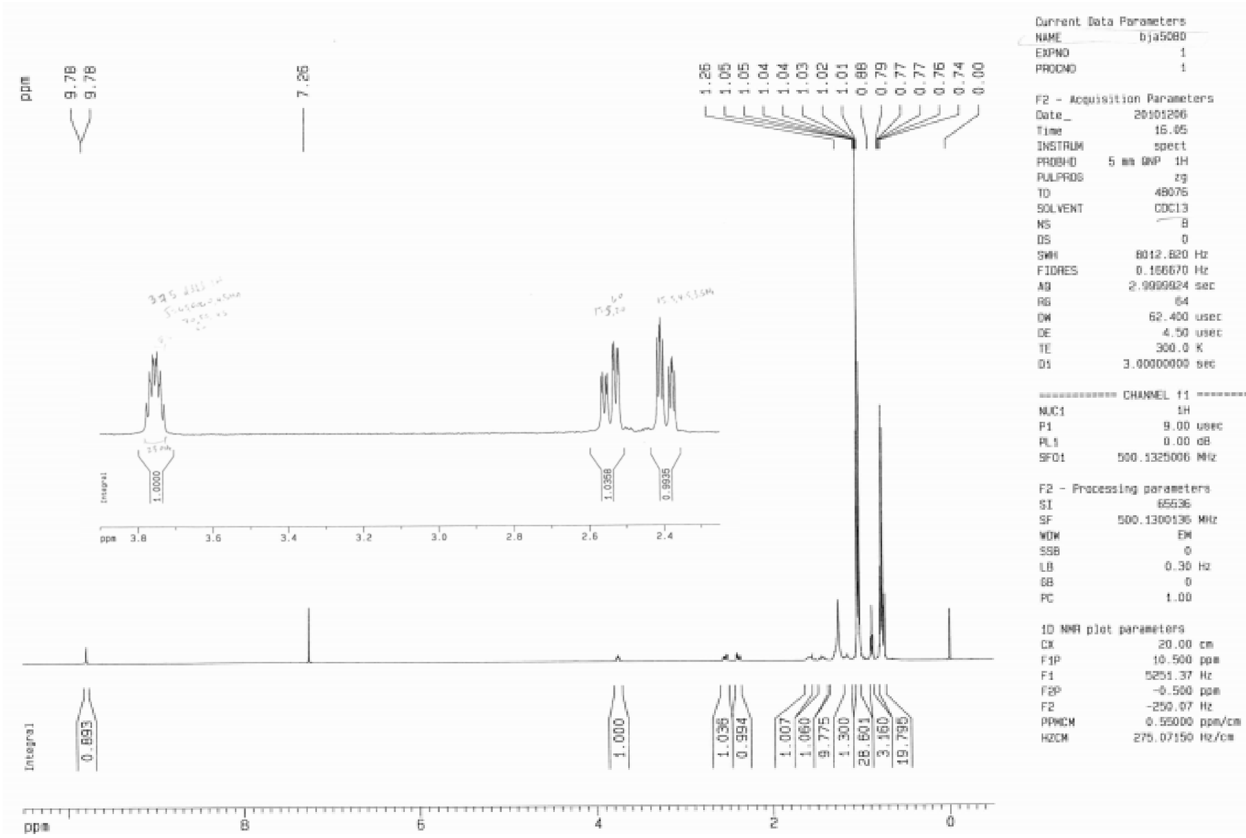

OBn
CHO
PB-5099-b.001.001.1r.esp
9.79
9.79
7.37
7.36
7.34
7.33
7.32
7.31
7.30
7.29
7.28
4.62
4.59
4.49
4.47
4.10
4.09
4.09
4.08
2.73
2.71
2.70
2.56
2.54
2.54
2.51
2.50
2.50
1.31
1.31
1.29
0.00
0.73
1.20
1.11
1.00
1.12
1.22
3.72
Chemical Shift (ppm)

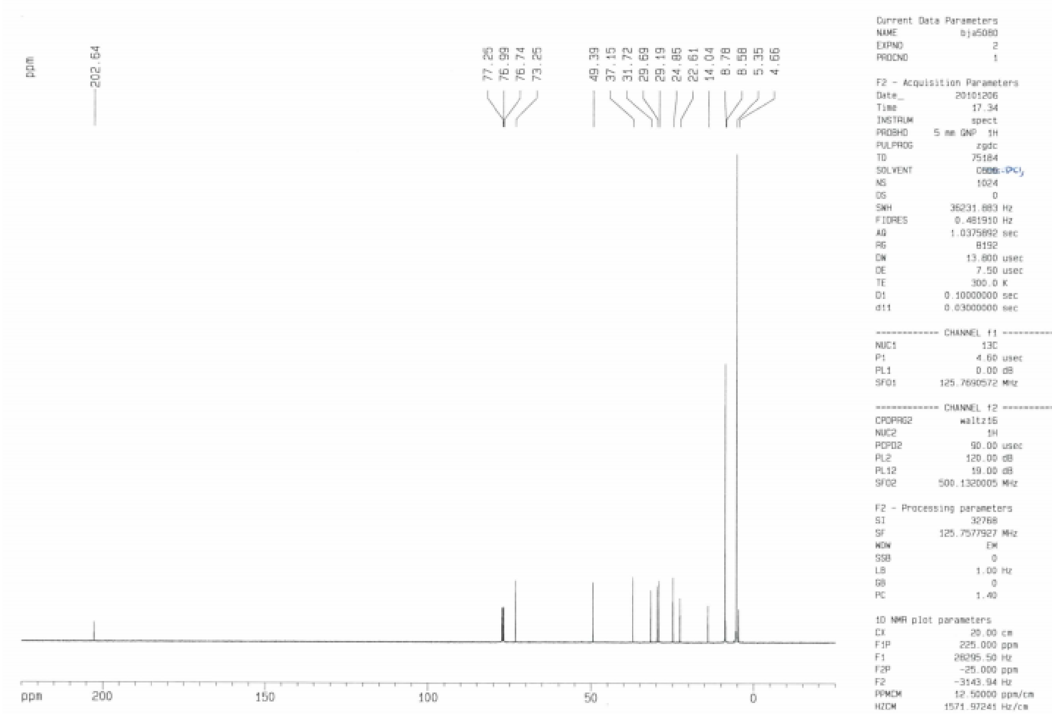

PB-5099-b.002.001.1r.esp
201.62
138.32
128.57
127.83
77.16
70.77
70.37
50.64
19.94

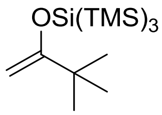
Electronic Supplementary Material (ESI) for Chemical Science



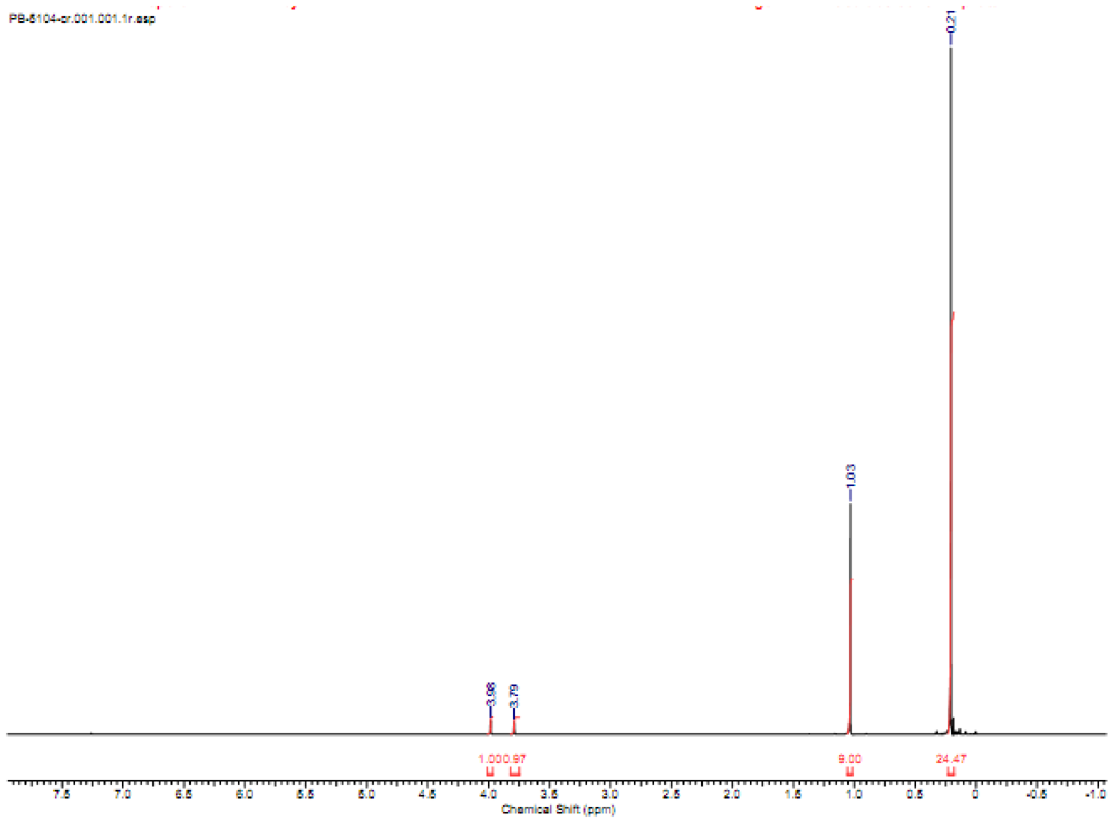
1i

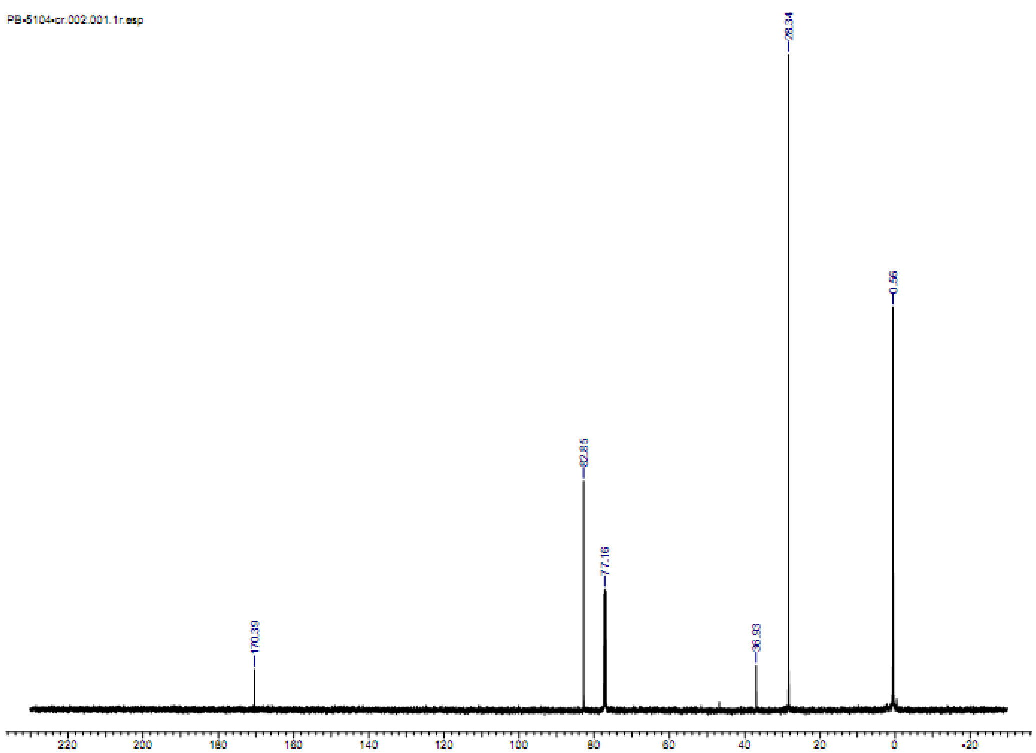




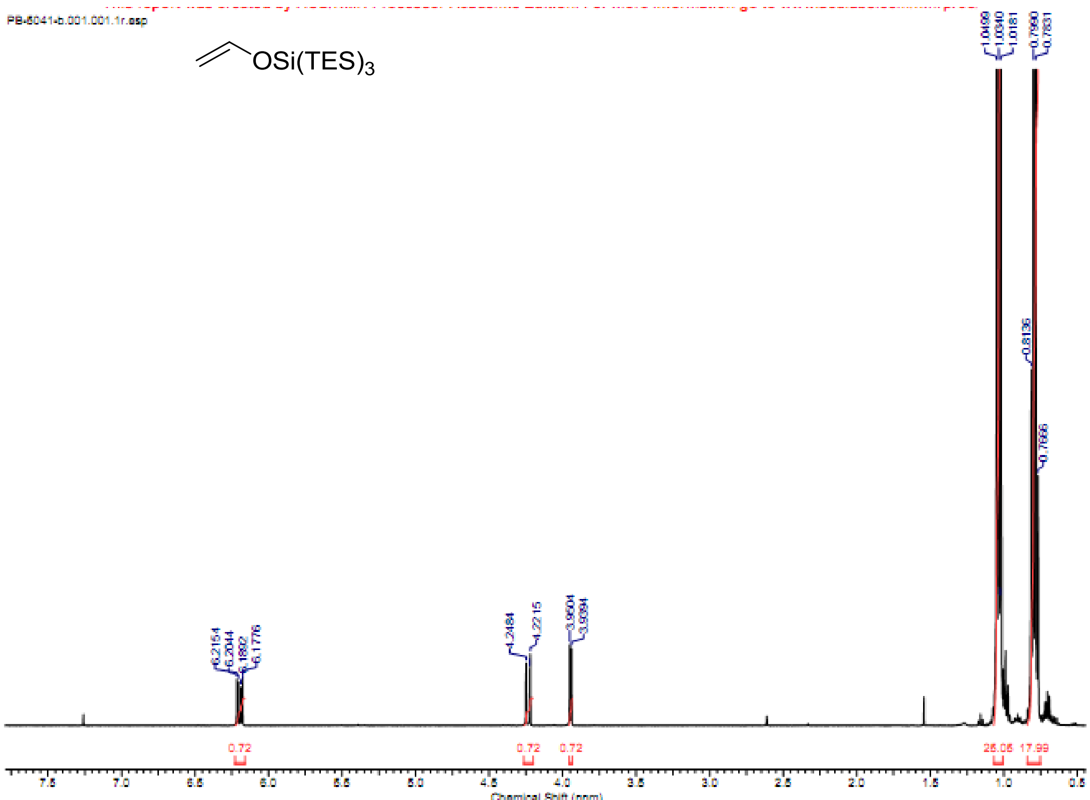

OSi(TMS)3

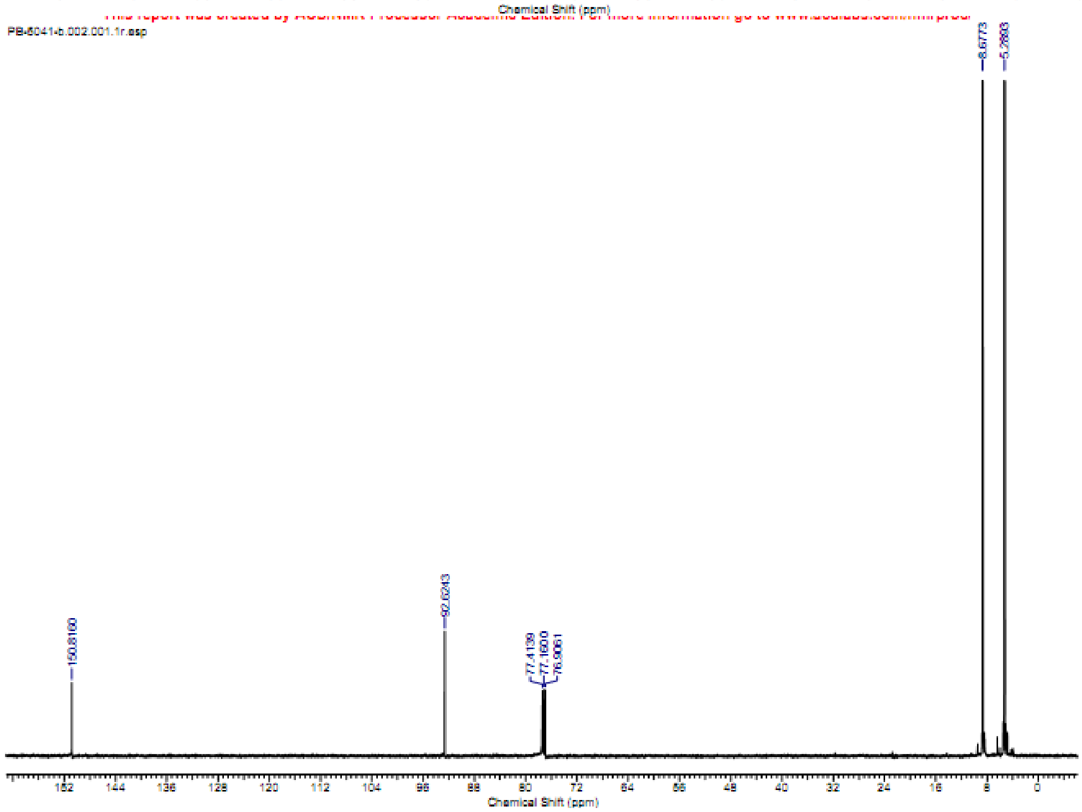
2h


PB-5104-cr.001.001.1r.esp
0.21
1.03
3.98
3.79
1.00
0.97
9.00
24.47
Chemical Shift (ppm)

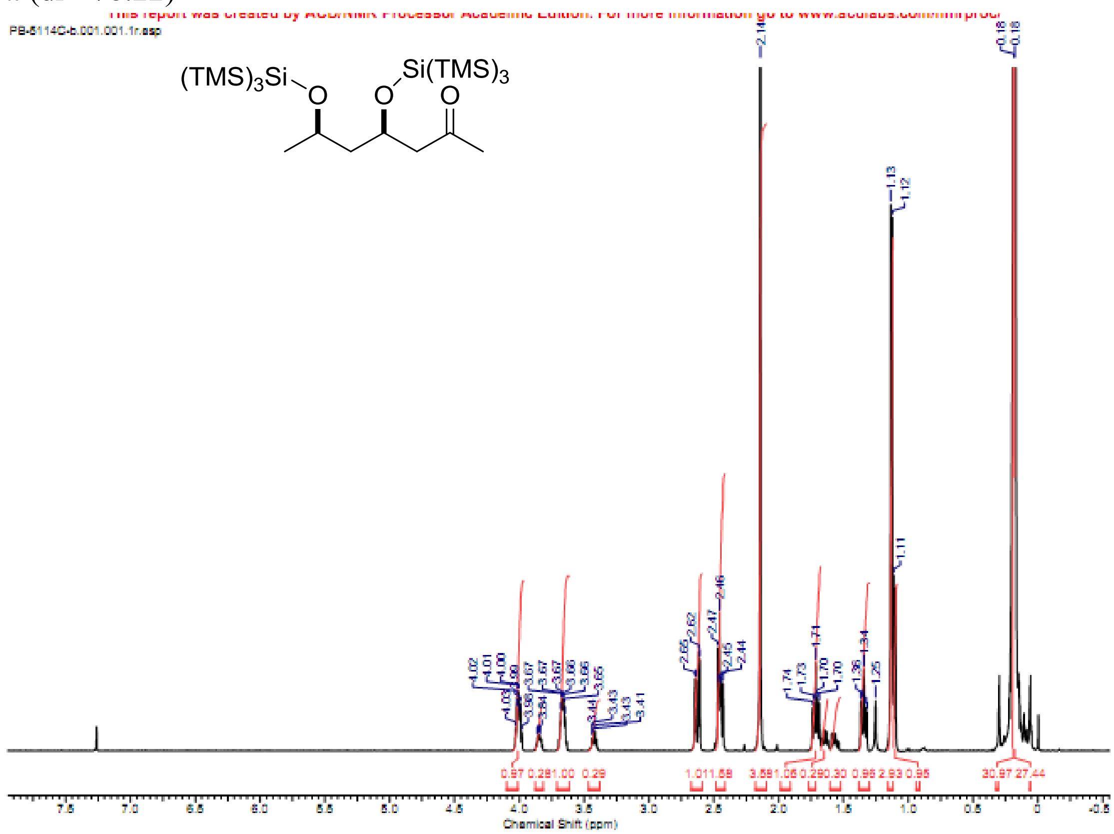

PB-5104-cr.002.001.1r.esp
28.34
0.56
82.85
77.16
170.39
36.93
Chemical Shift (ppm)

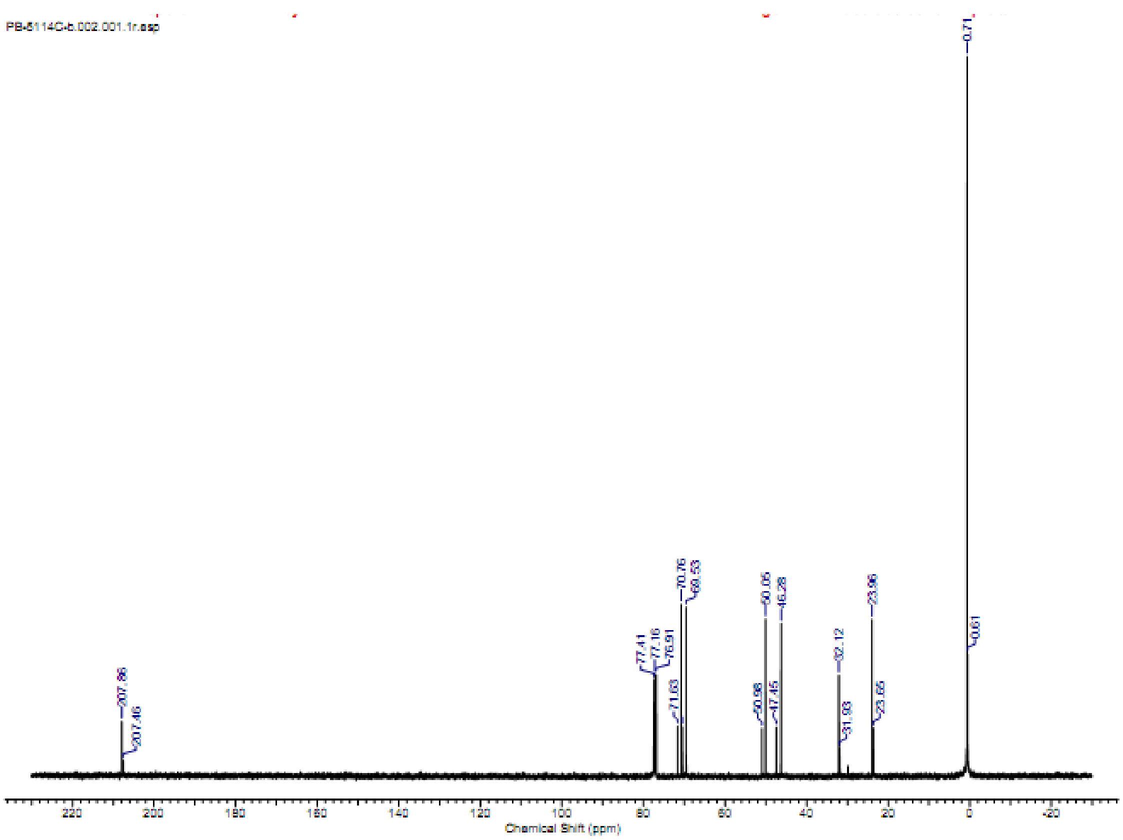
2i


PB-6041-b.001.001.1r.esp
OSi(TES)3
Chemical Shift (ppm)

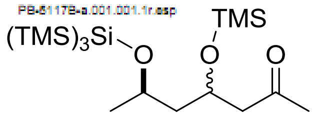

PB-6041-b.002.001.1r.esp
Chemical Shift (ppm)

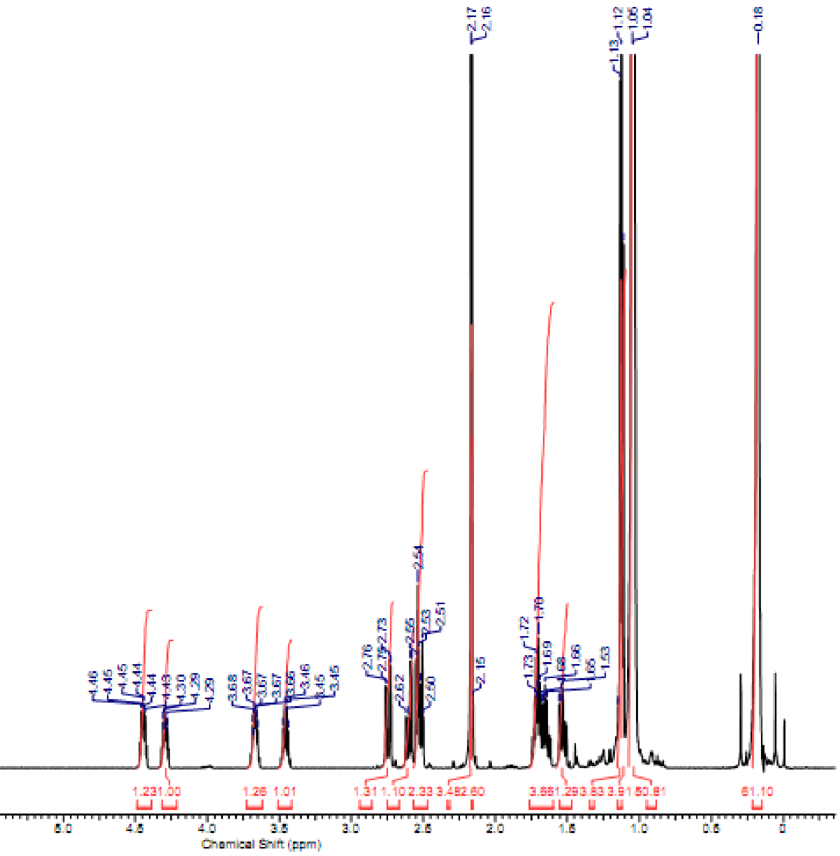
3a (dr =78:22)

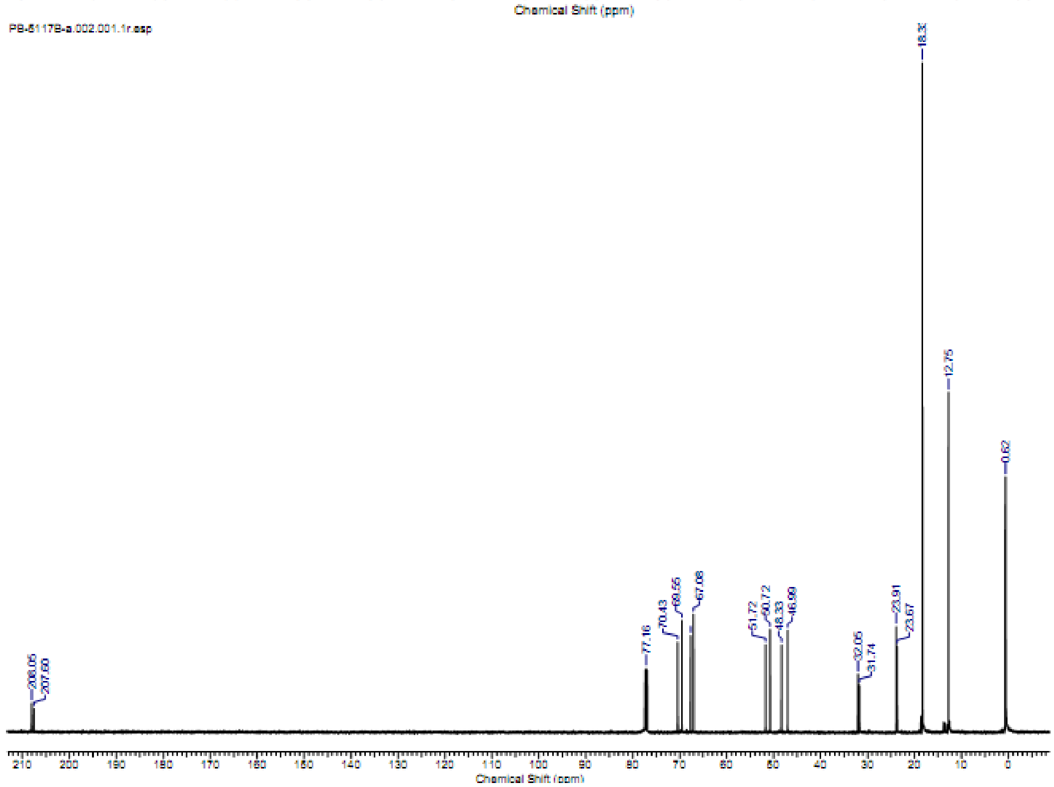

PB-5114C-b.001.001.1r.esp
(TMS)3Si
Si(TMS)3
O
O
O
Chemical Shift (ppm)


PB-5114C-b.002.001.1r.esp
Chemical Shift (ppm)

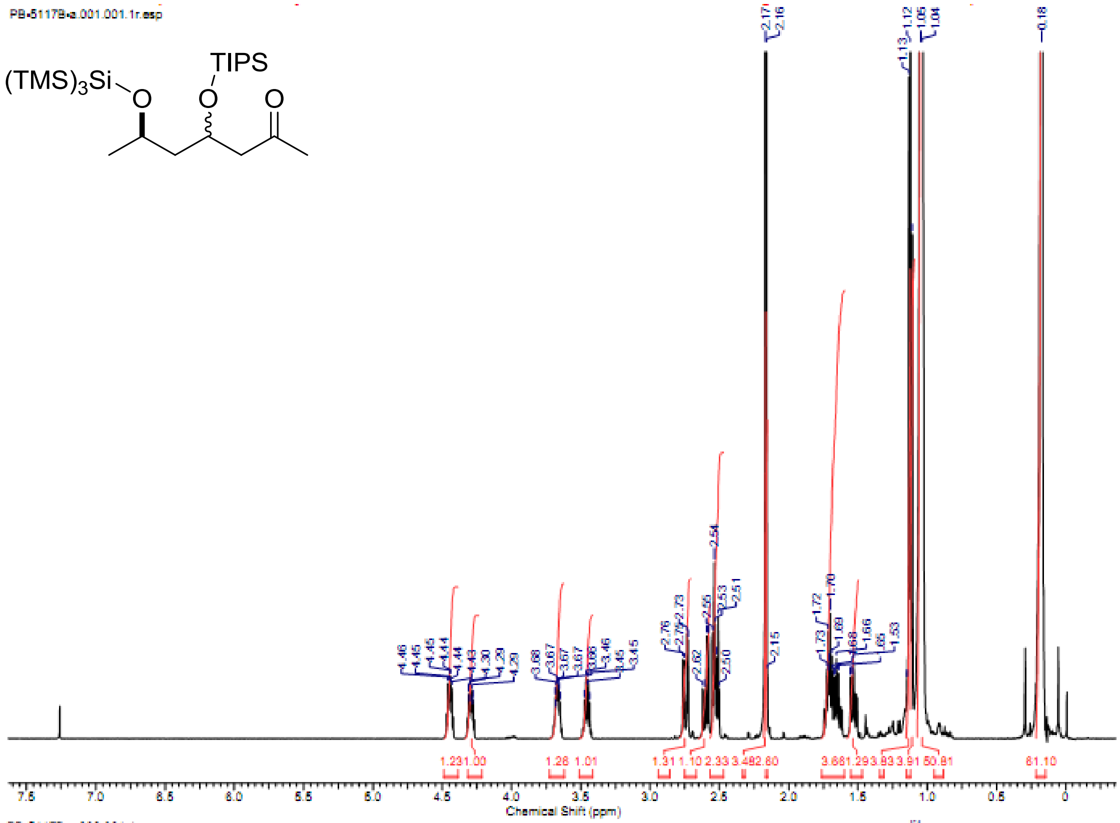
3b (dr ~1:1)

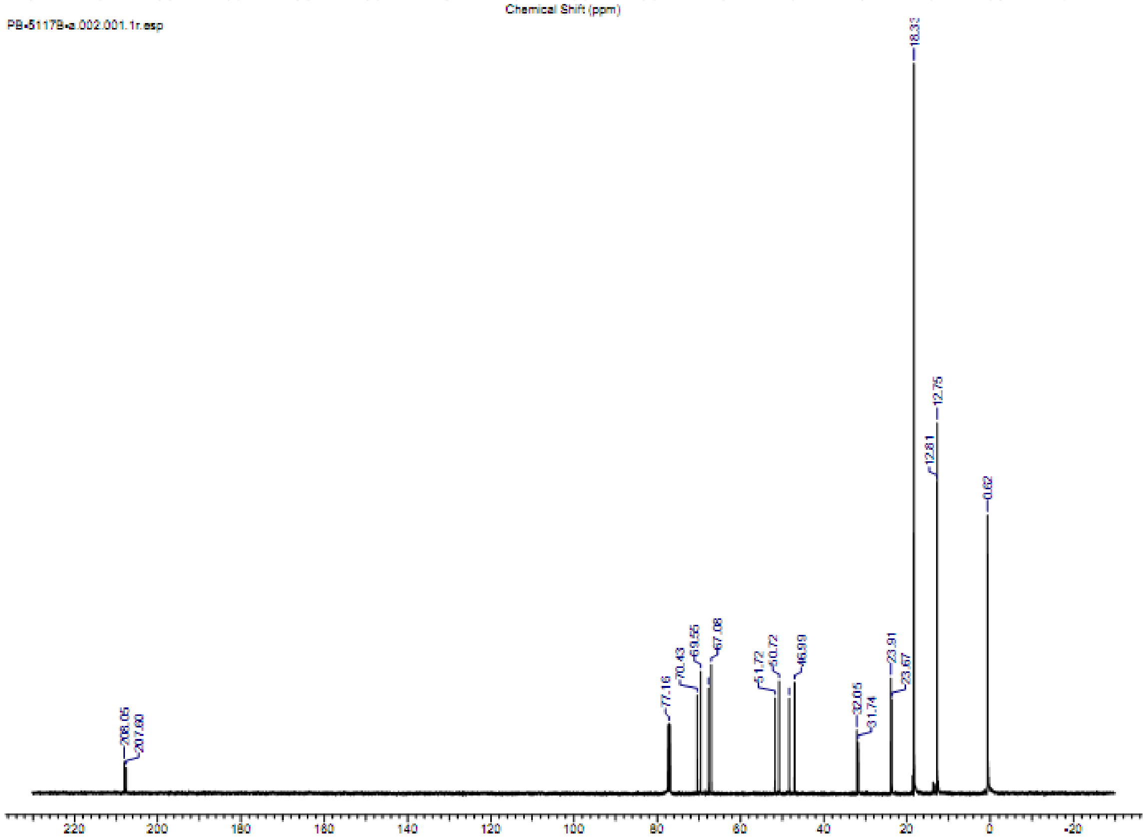

TMS
(TMS)3Si
O
O
O


PB-6117B-a.001.001.1r.esp
Chemical Shift (ppm)

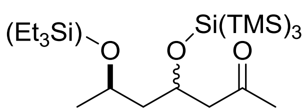

PB-6117B-a.002.001.1r.esp
Chemical Shift (ppm)

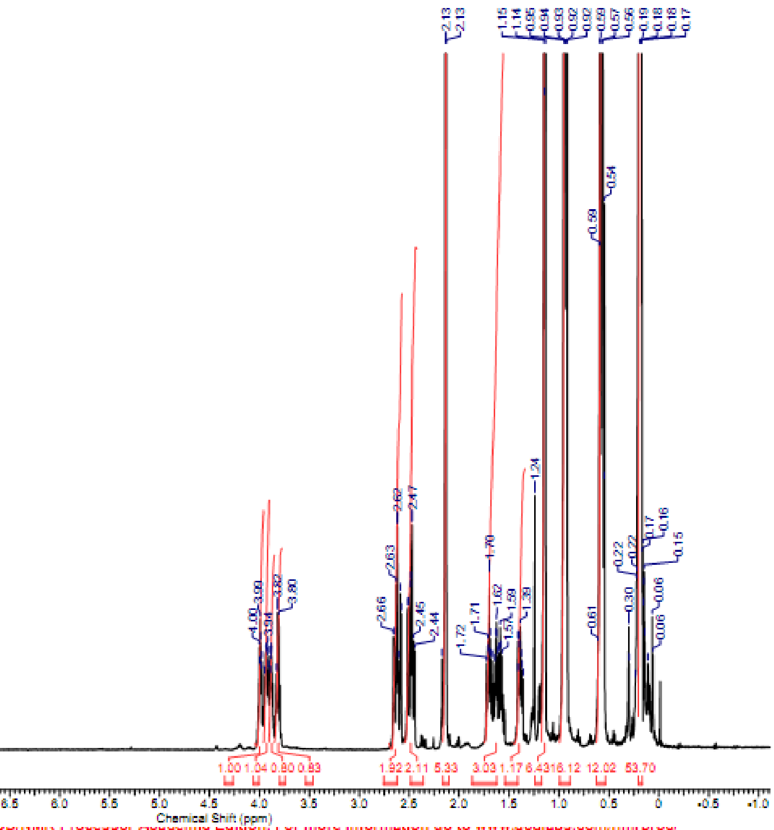
3c (dr ~1:1)

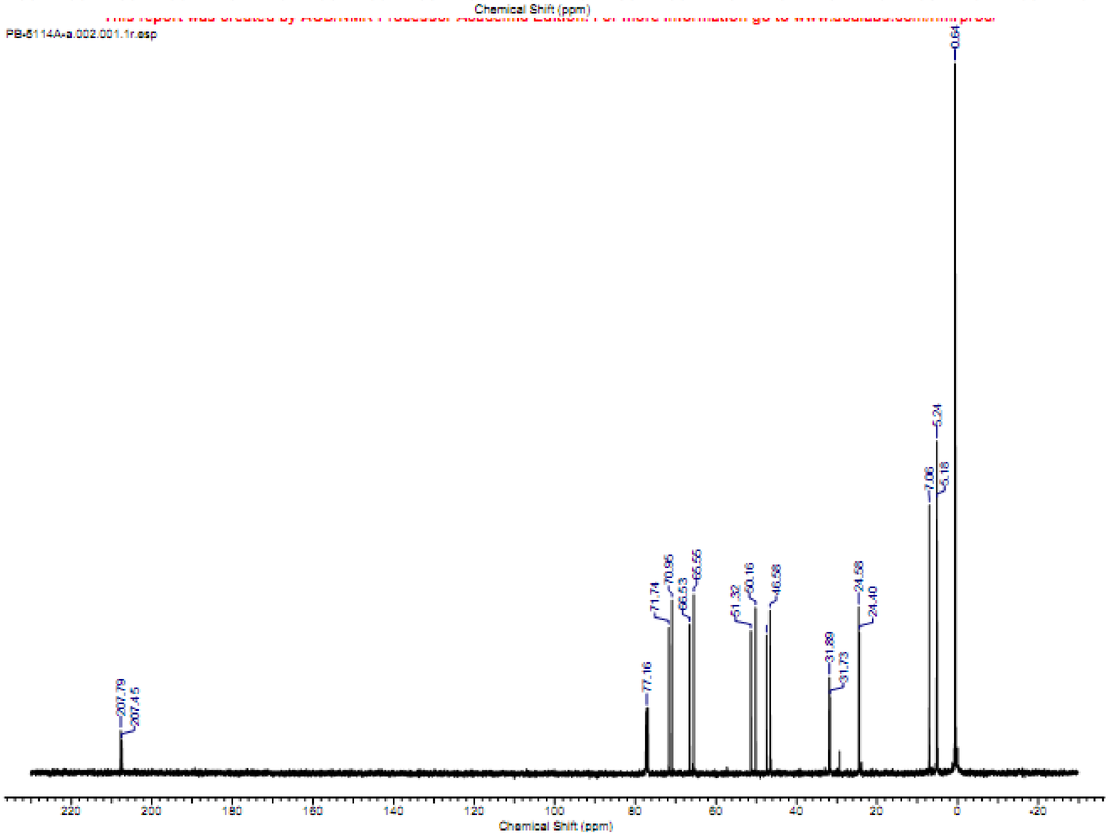

PB-5117B-a.001.001.1r.esp
TIPS
(TMS)$_3$Si
O
O
O
Chemical Shift (ppm)


PB-5117B-a.002.001.1r.esp
Chemical Shift (ppm)

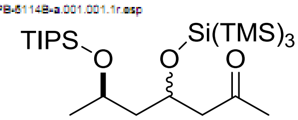
3d (dr ~1:1)

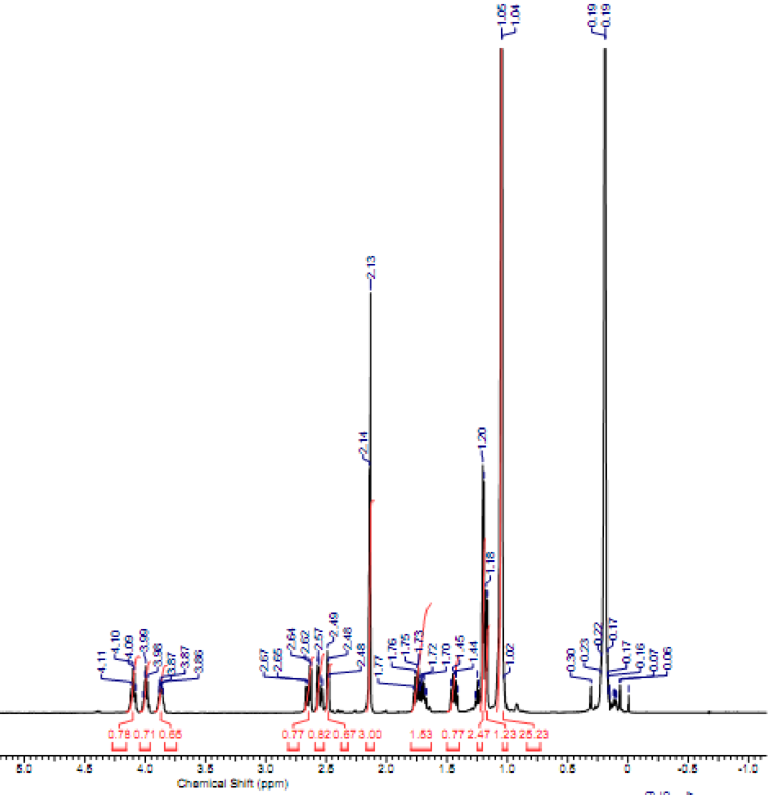

(Et3Si)
O
O
Si(TMS)3
O

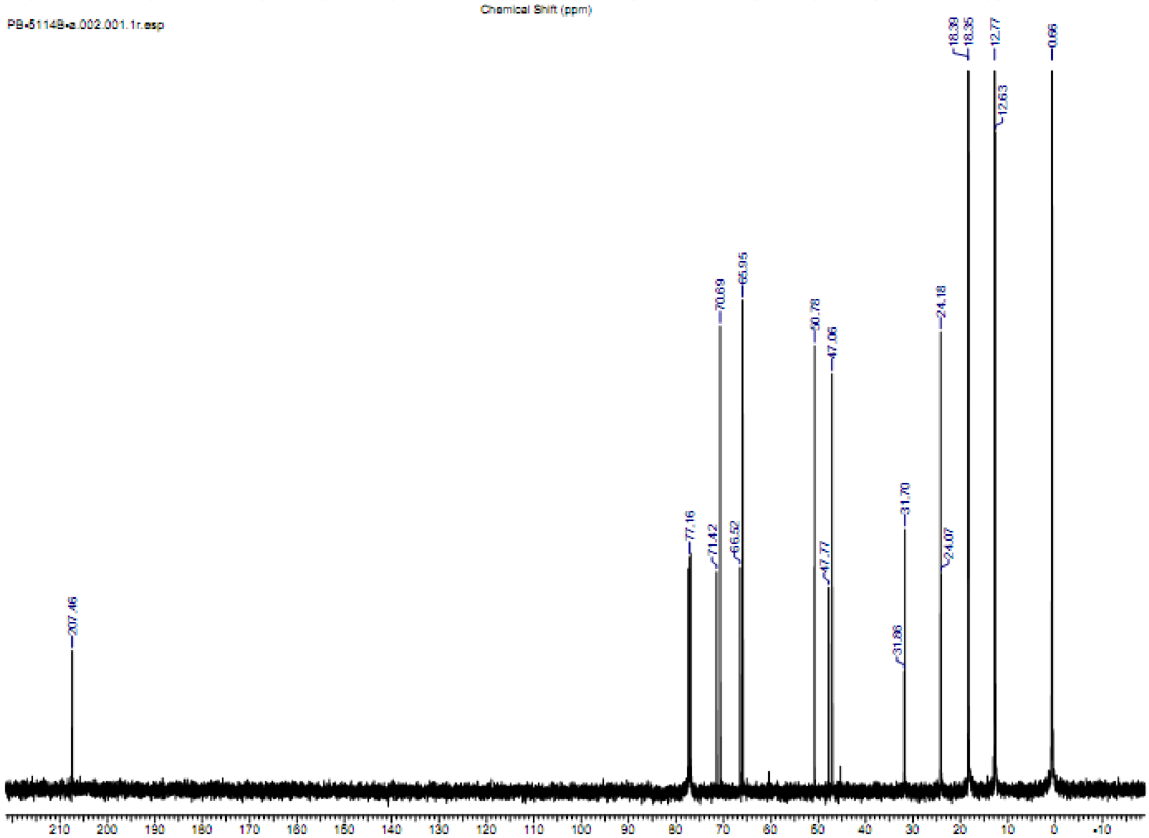

PB-5114A-a.001.001.1r.esp
Chemical Shift (ppm)


PB-5114A-a.002.001.1r.esp
Chemical Shift (ppm)

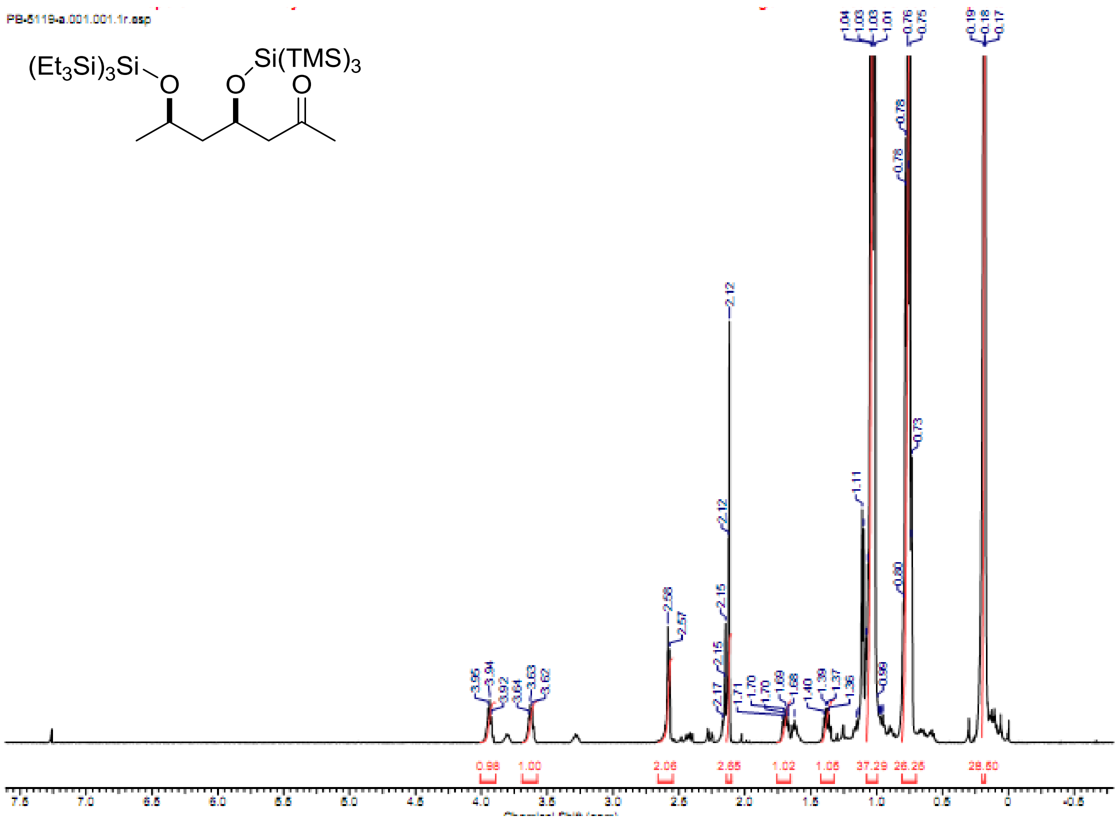
3e(dr ~1:1)

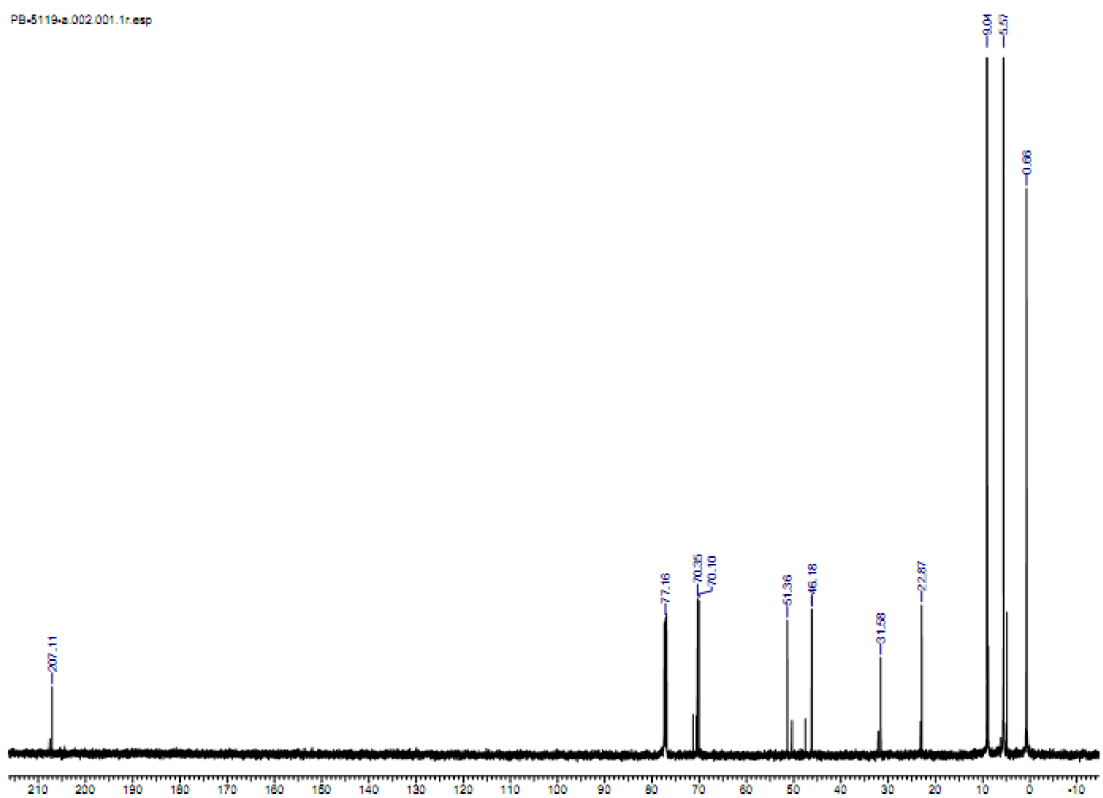

TIPS
O
O
Si(TMS)3
O


PB-5114B-a.001.001.1r.esp
Chemical Shift (ppm)

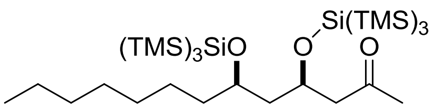

PB-5114B-a.002.001.1r.esp
Chemical Shift (ppm)

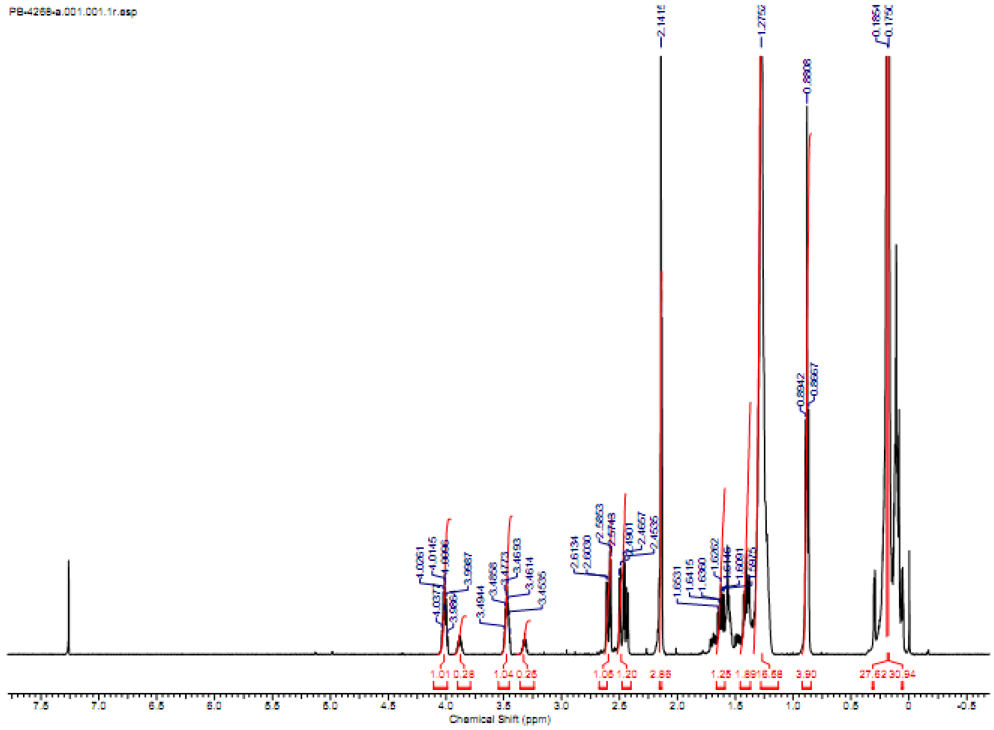
3f

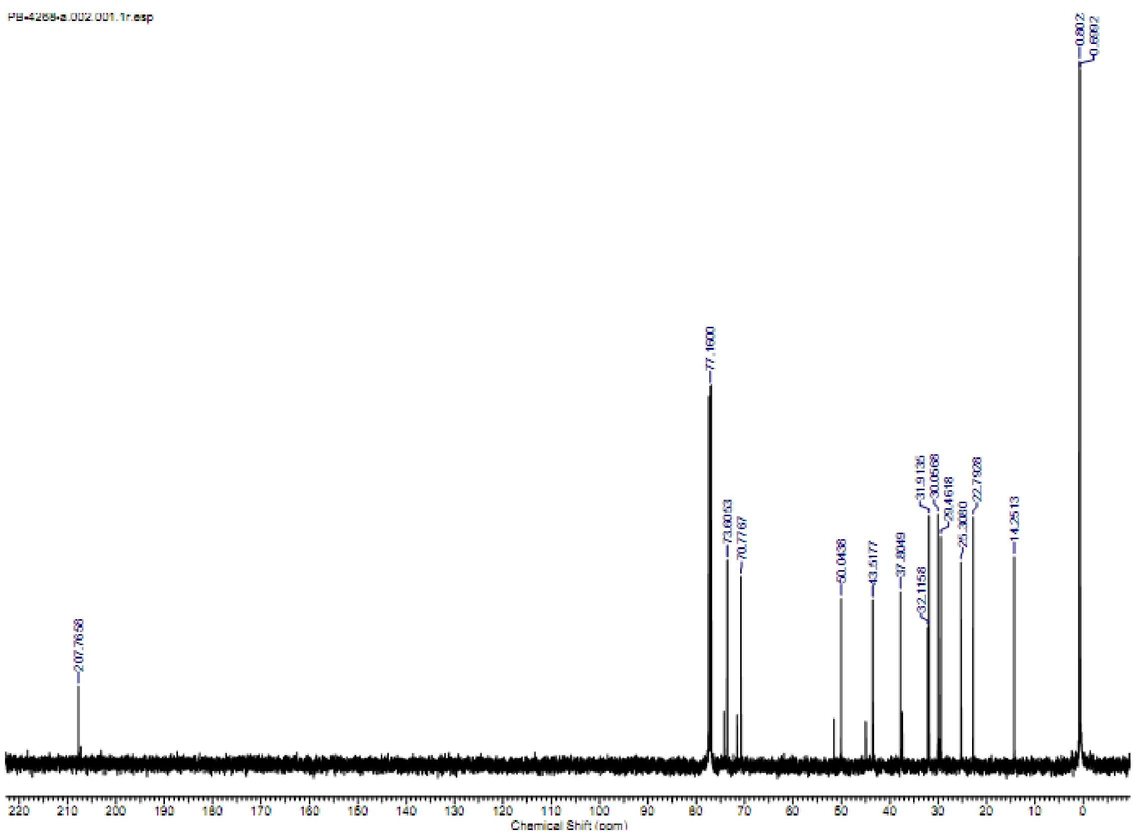




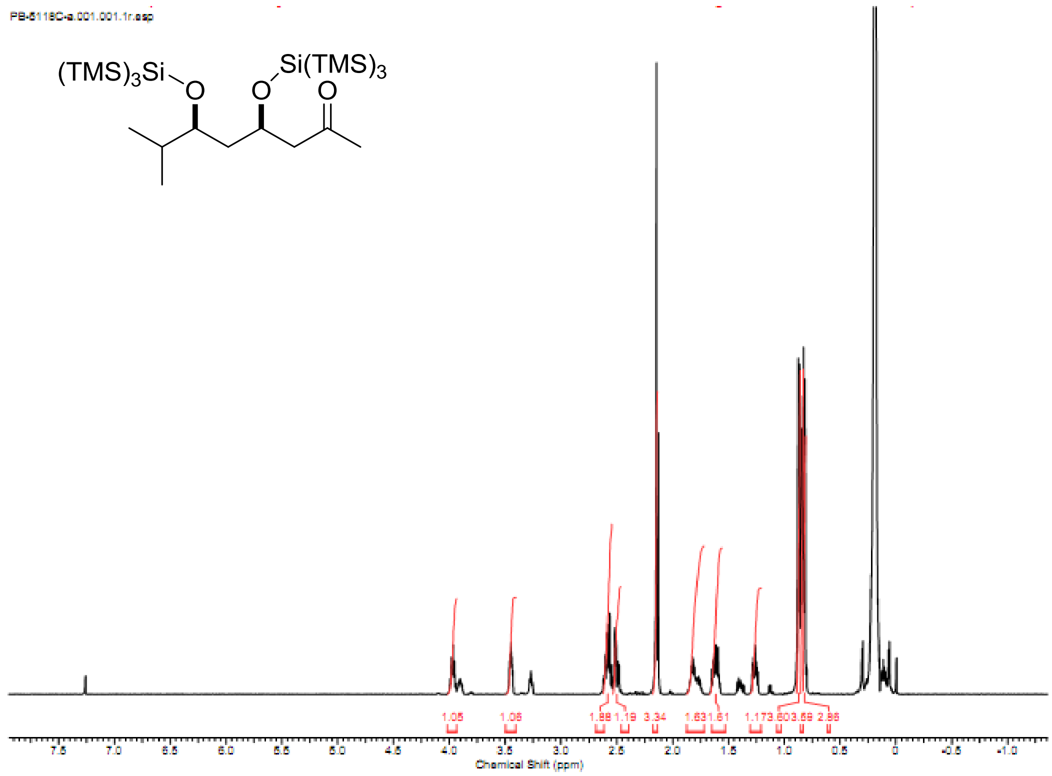
3g (dr = 81:19)

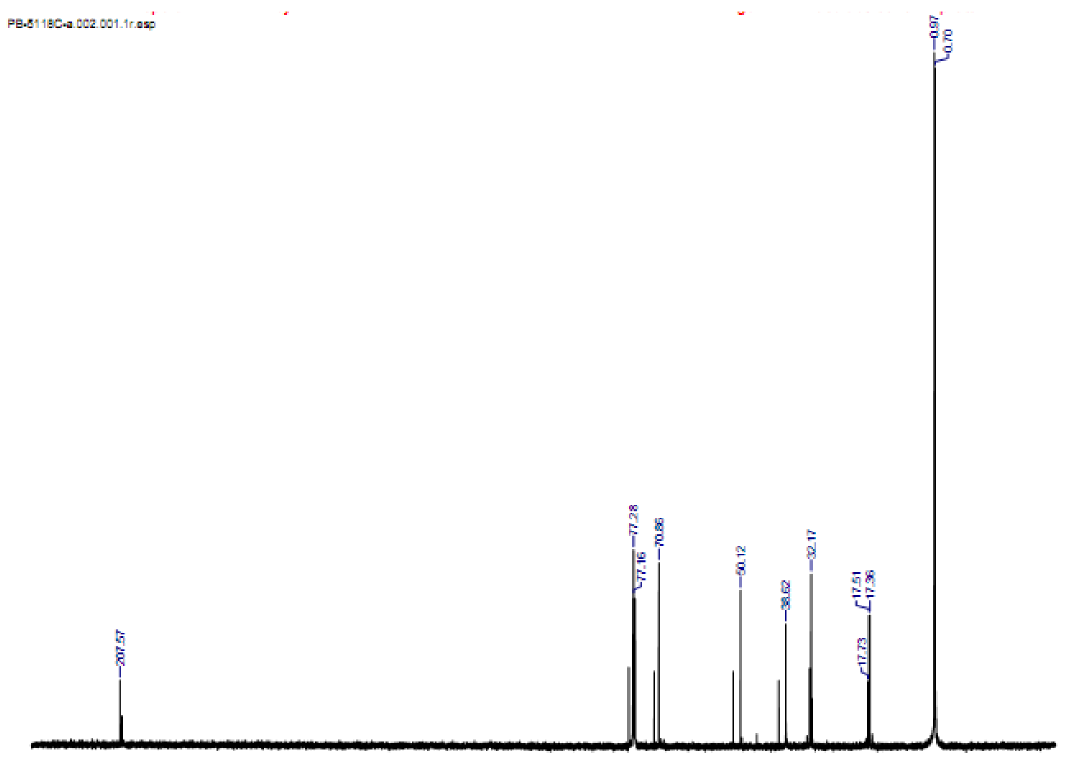

(TMS)$_3$SiO
Si(TMS)$_3$
O
O


PB-4268-a.001.001.1r.esp
Chemical Shift (ppm)

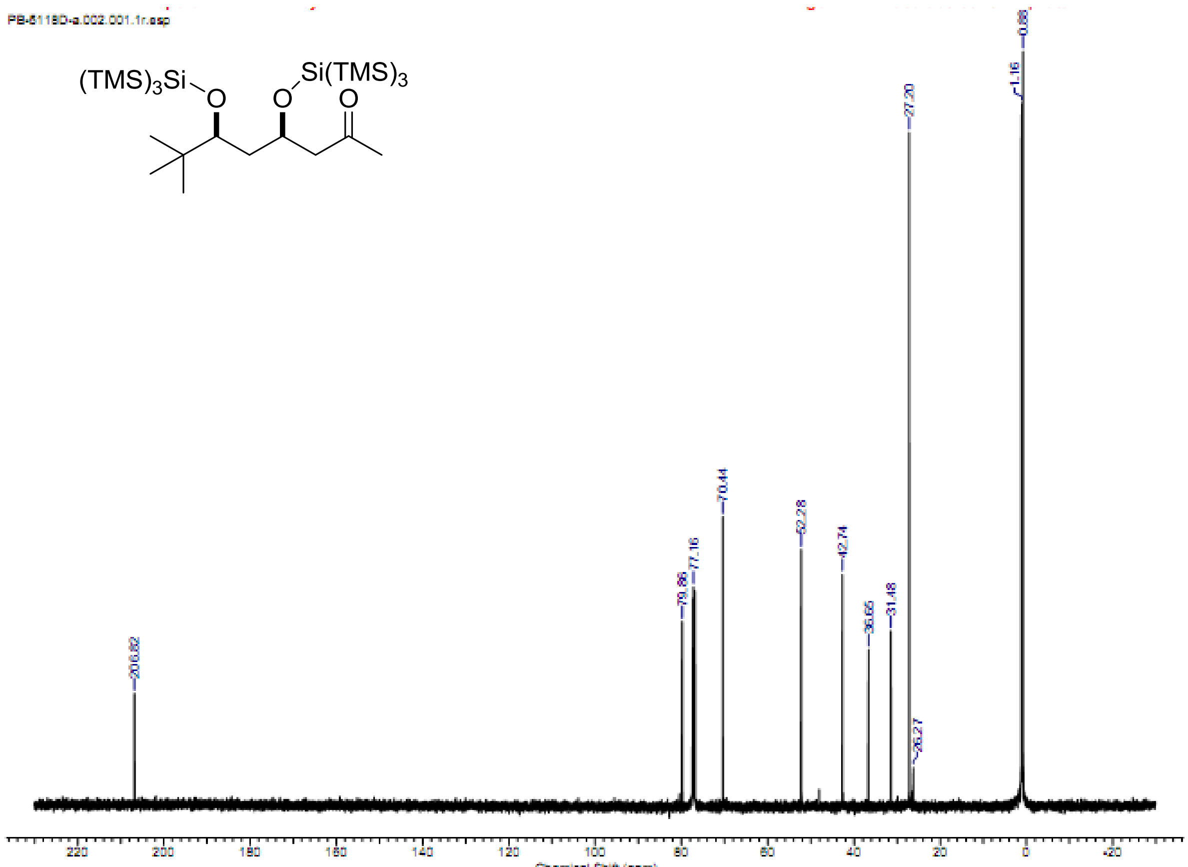

PB-4268-a.002.001.1r.esp
Chemical Shift (ppm)

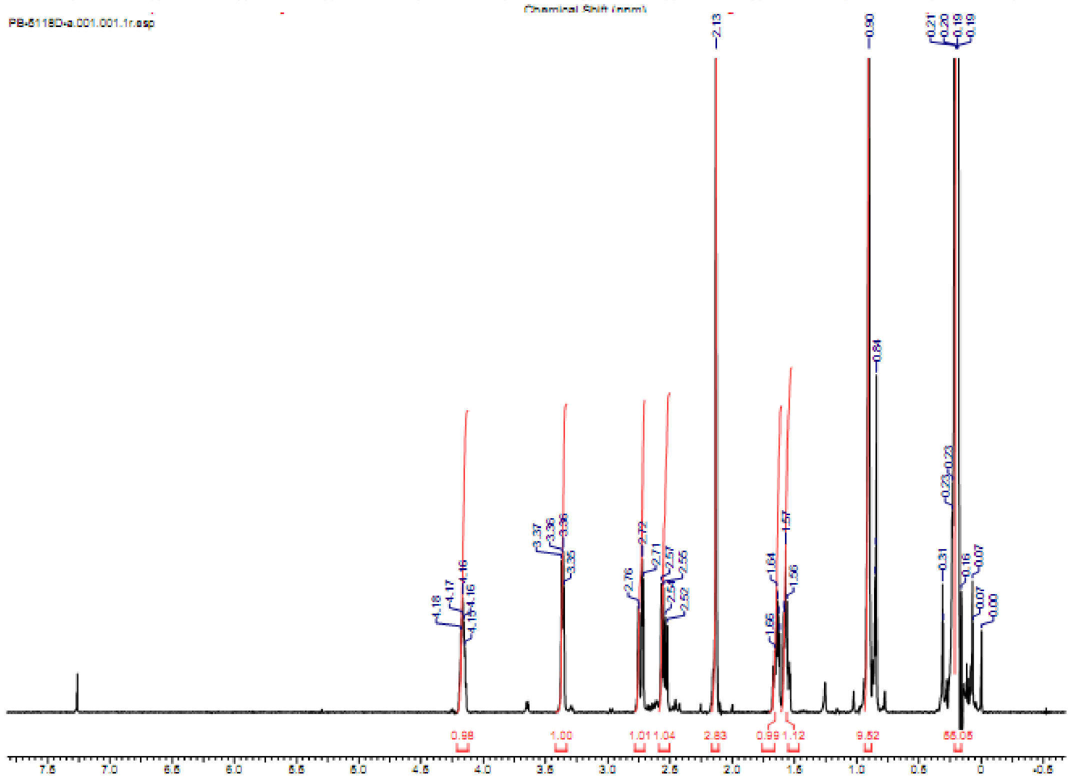
3h (mixture of diastereomers)



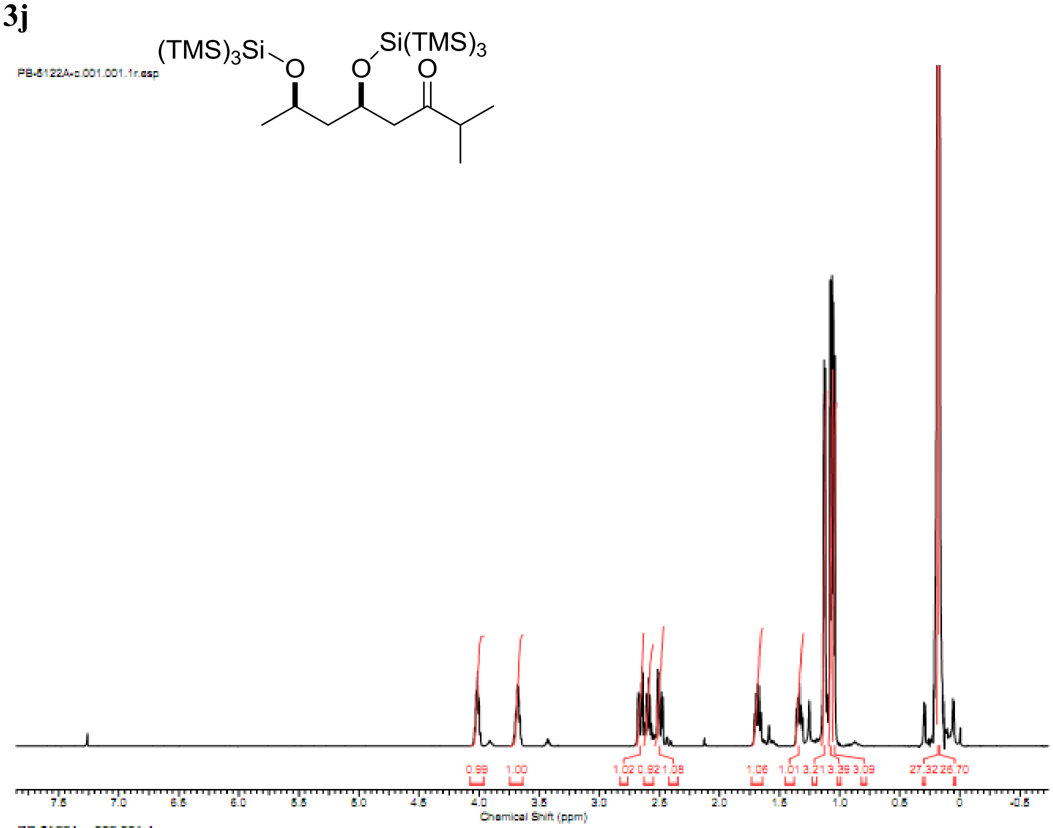


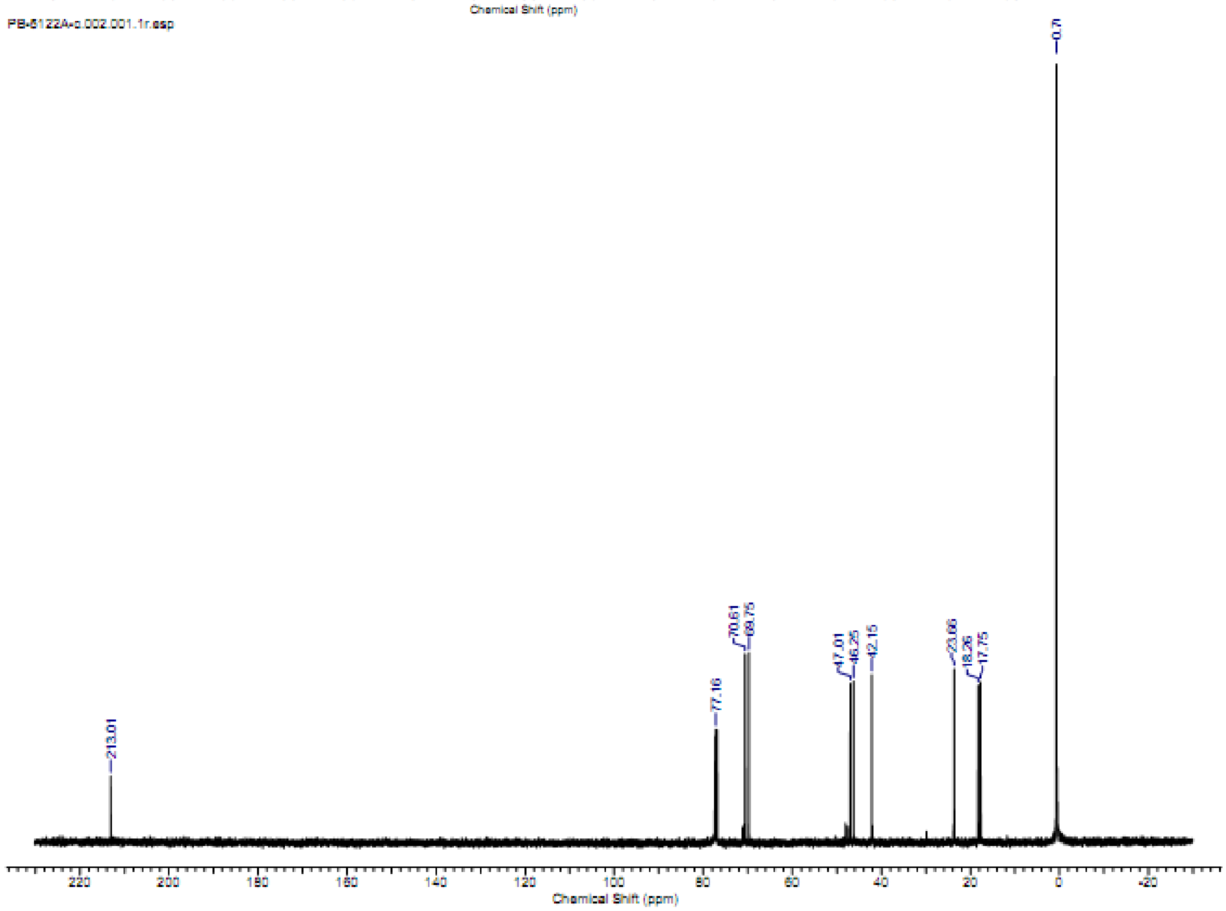
3i


PB-5118D-a.002.001.1r.esp
(TMS)3Si
Si(TMS)3
O
O
O
206.82
79.86
77.16
70.44
52.28
42.74
36.65
31.48
27.20
26.27
1.16
0.88
Chemical Shift (ppm)

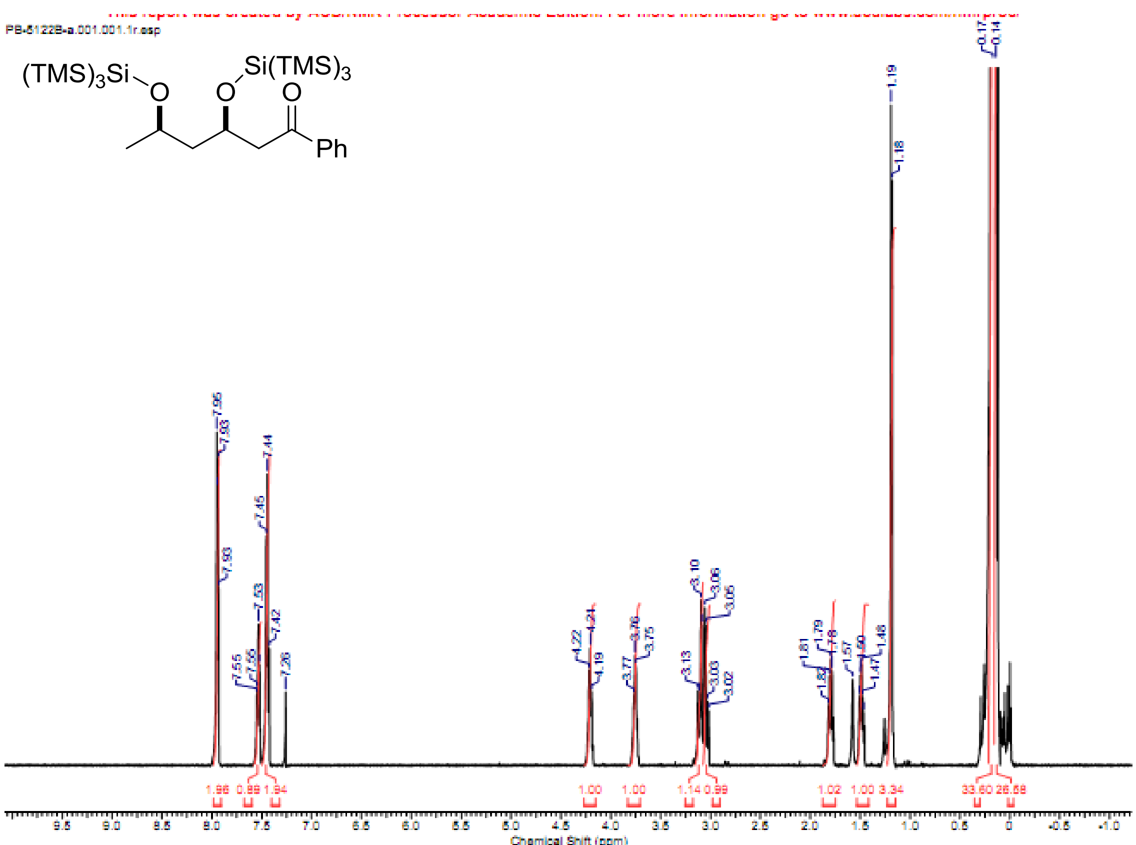

PB-5118D-a.001.001.1r.esp
2.13
0.90
0.84
0.21
0.20
0.19
0.19
4.18
4.17
4.16
4.15
4.16
3.37
3.36
3.36
3.35
2.76
2.72
2.71
2.57
2.55
2.54
2.52
1.66
1.64
1.57
1.56
0.31
0.23
0.23
0.16
0.07
0.07
0.00
0.98
1.00
1.01
1.04
2.83
0.99
1.12
9.52
55.05
Chemical Shift (ppm)

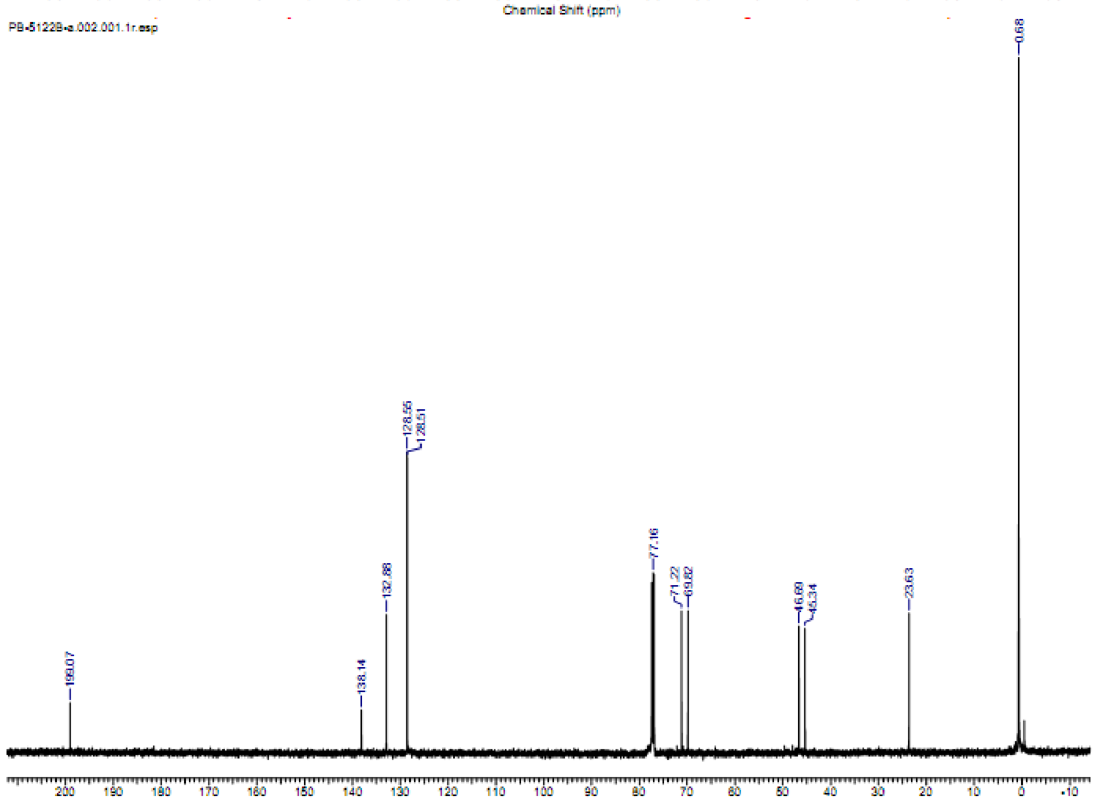
3j


(TMS)3Si
O
O
Si(TMS)3
O
PB-5122A-c.001.001.1r.esp
0.99
1.00
1.02
0.92
1.08
1.06
1.01
3.21
3.39
3.09
27.32
26.70
Chemical Shift (ppm)

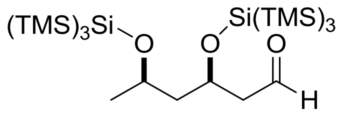

PB-5122A-c.002.001.1r.esp
213.01
77.16
70.61
69.75
47.01
46.25
42.15
23.66
18.26
17.75
Chemical Shift (ppm)

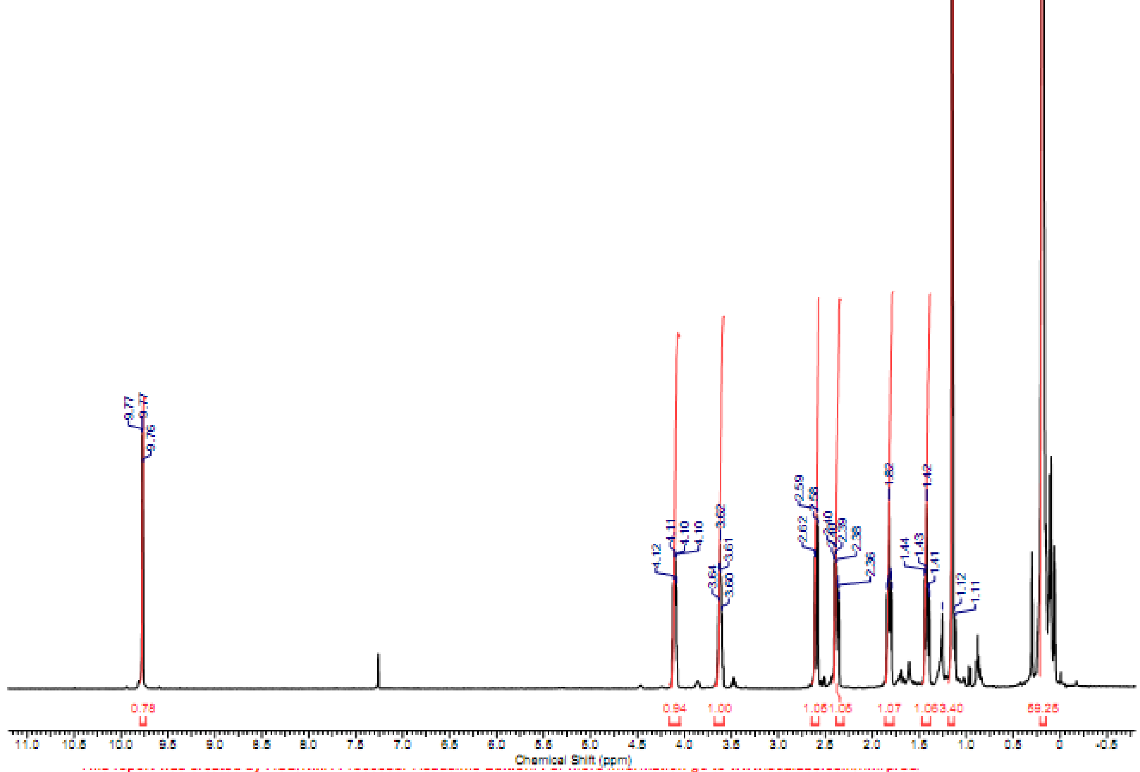
3k

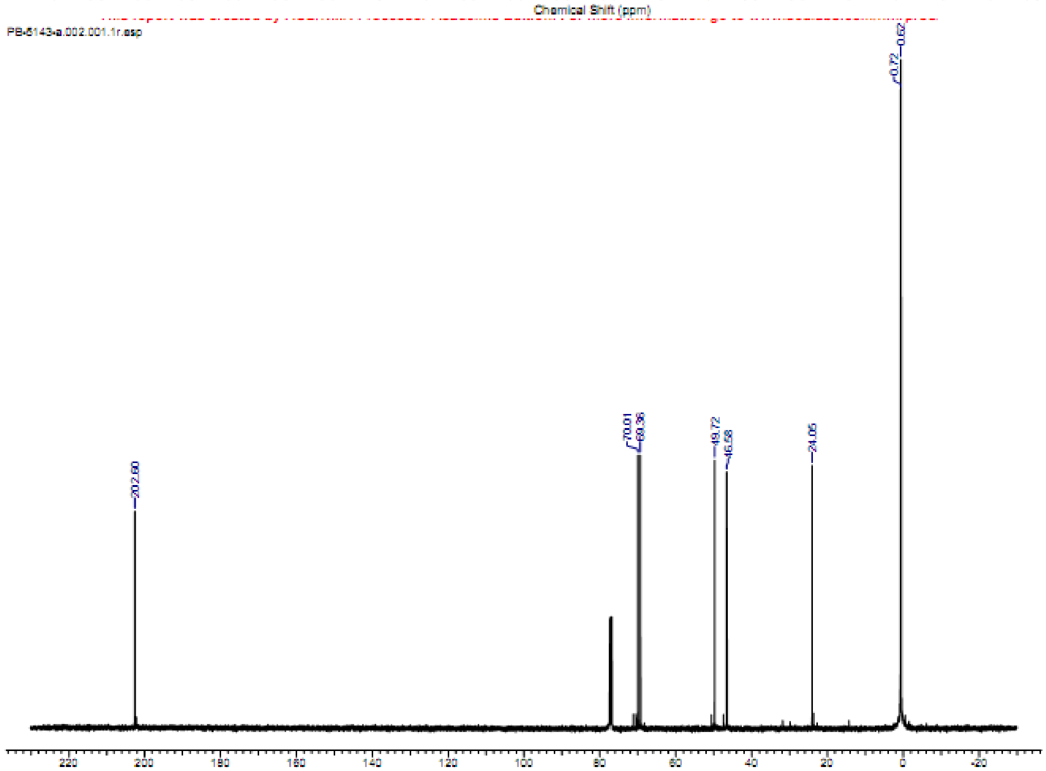

PB-5122B-a.001.001.1r.esp
(TMS)3Si
Si(TMS)3
O
Ph
Chemical Shift (ppm)


PB-5122B-a.002.001.1r.esp
199.07
138.14
132.88
128.55
128.51
77.16
71.22
69.82
46.69
45.34
23.63
0.68

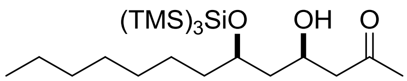
3l

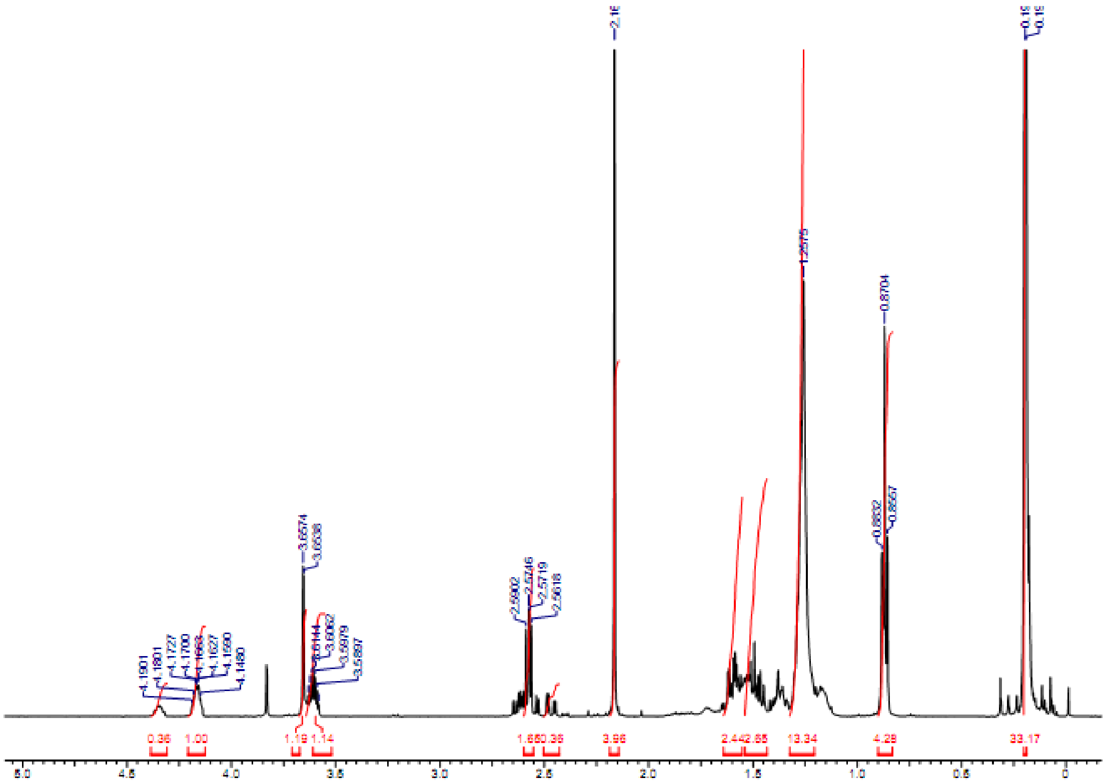

(TMS)3Si
Si(TMS)3
O
O
O
H

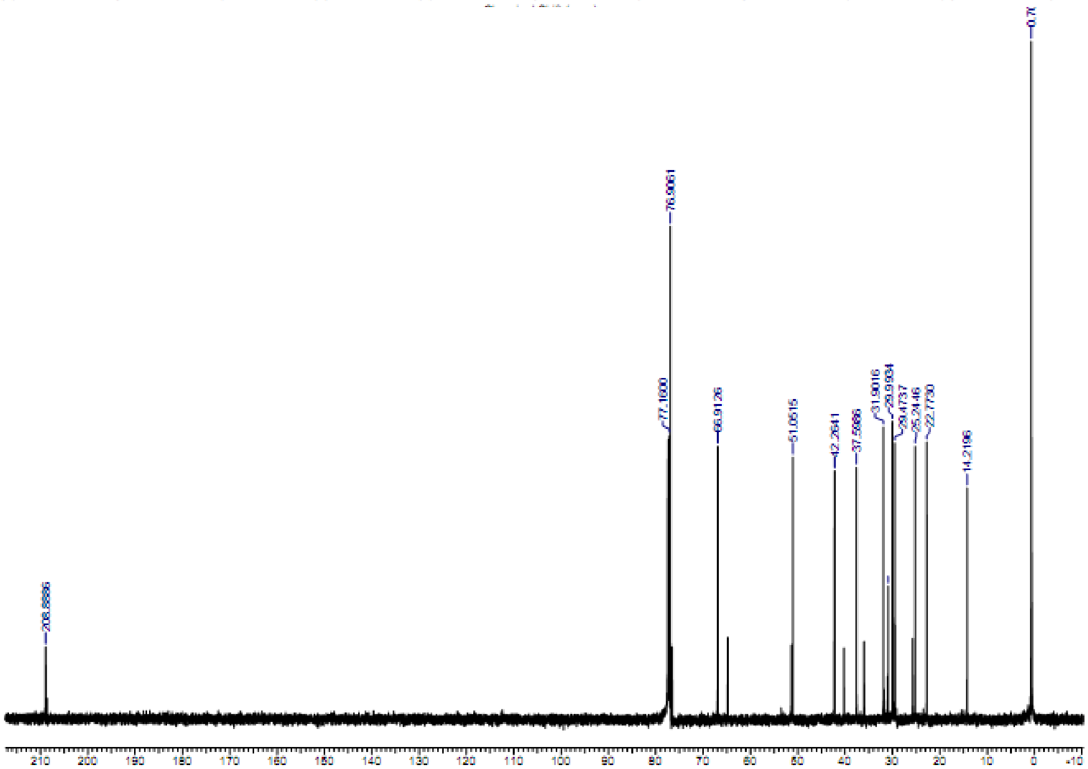

PB-5143-a.001.001.1r.esp
Chemical Shift (ppm)


PB-5143-a.002.001.1r.esp
202.60
70.01
69.36
49.72
46.58
24.05
-0.72
-0.62
Chemical Shift (ppm)

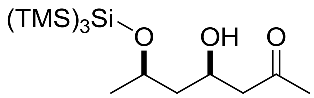
5a (dr = 74:26)

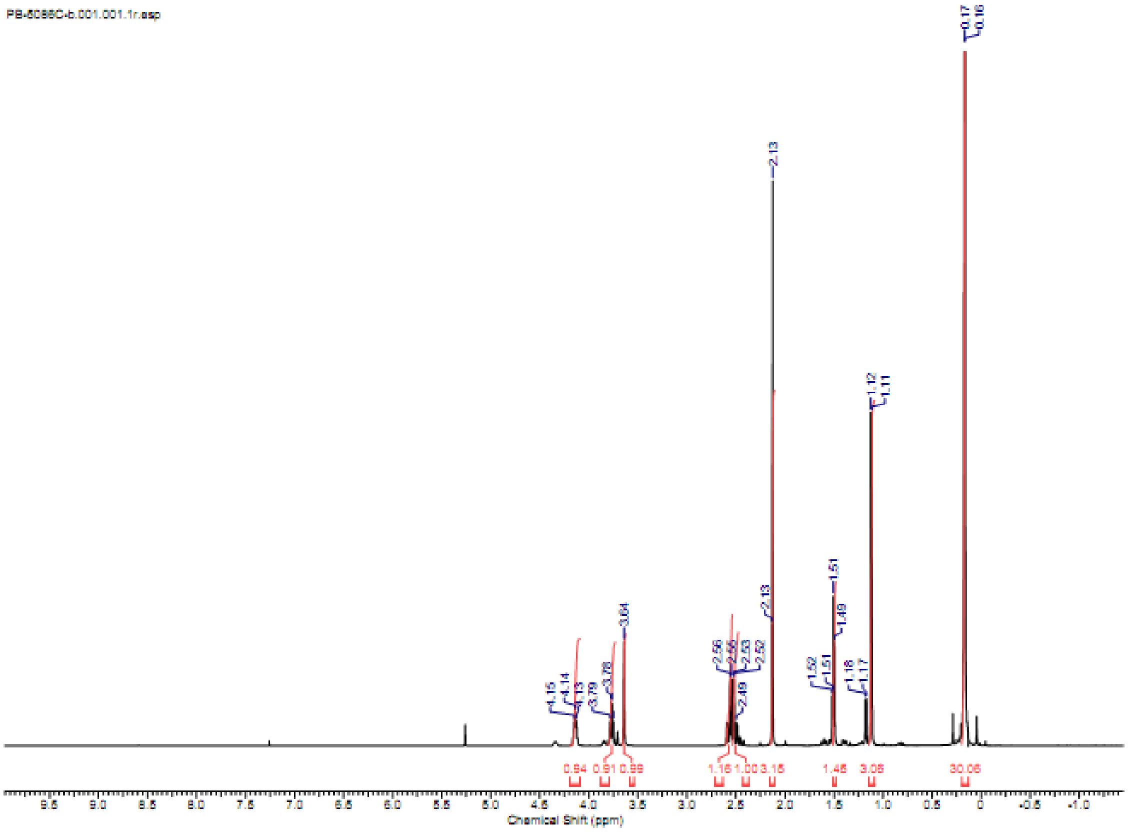


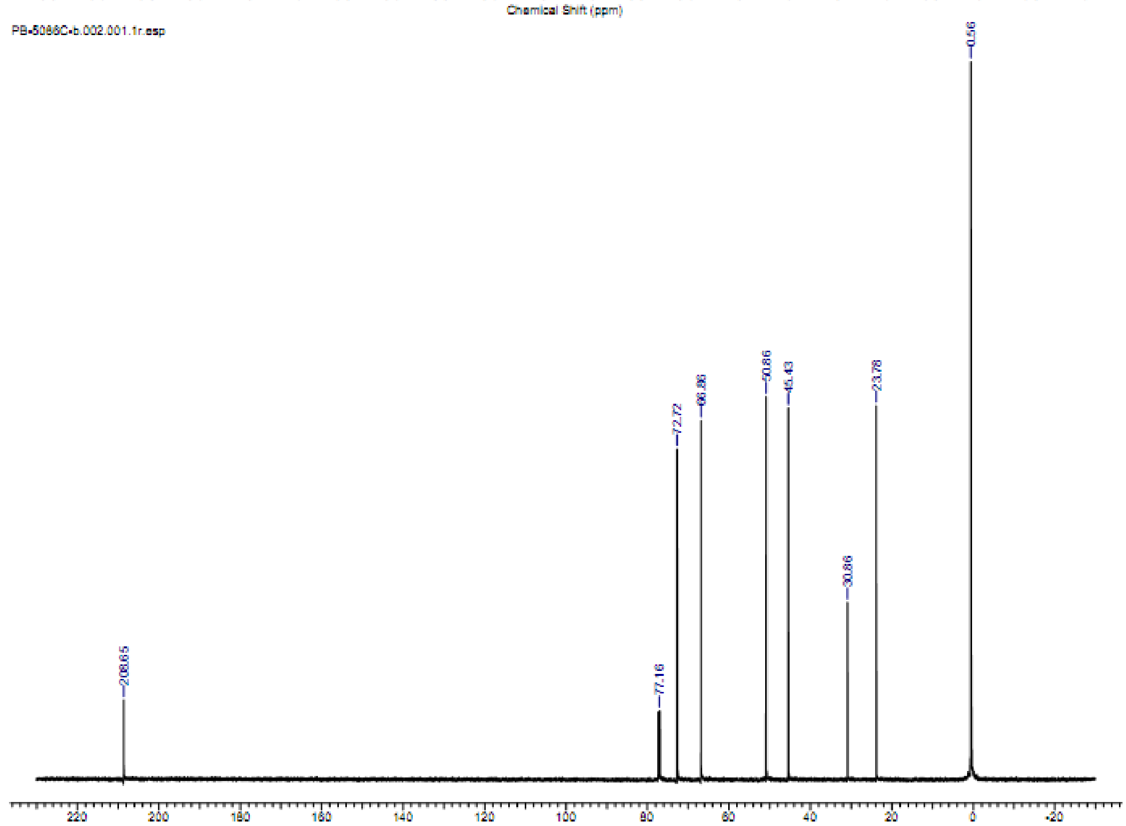




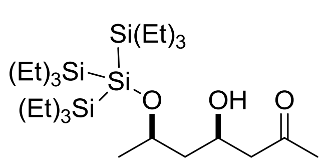
5i

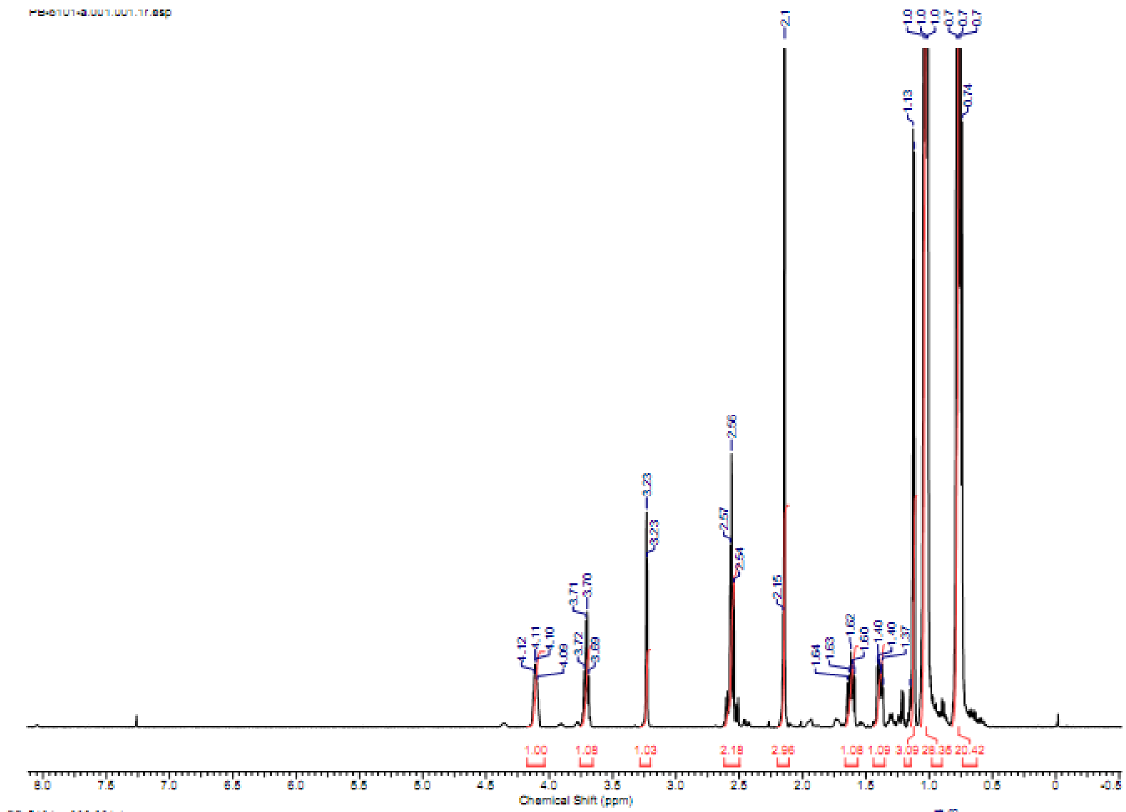


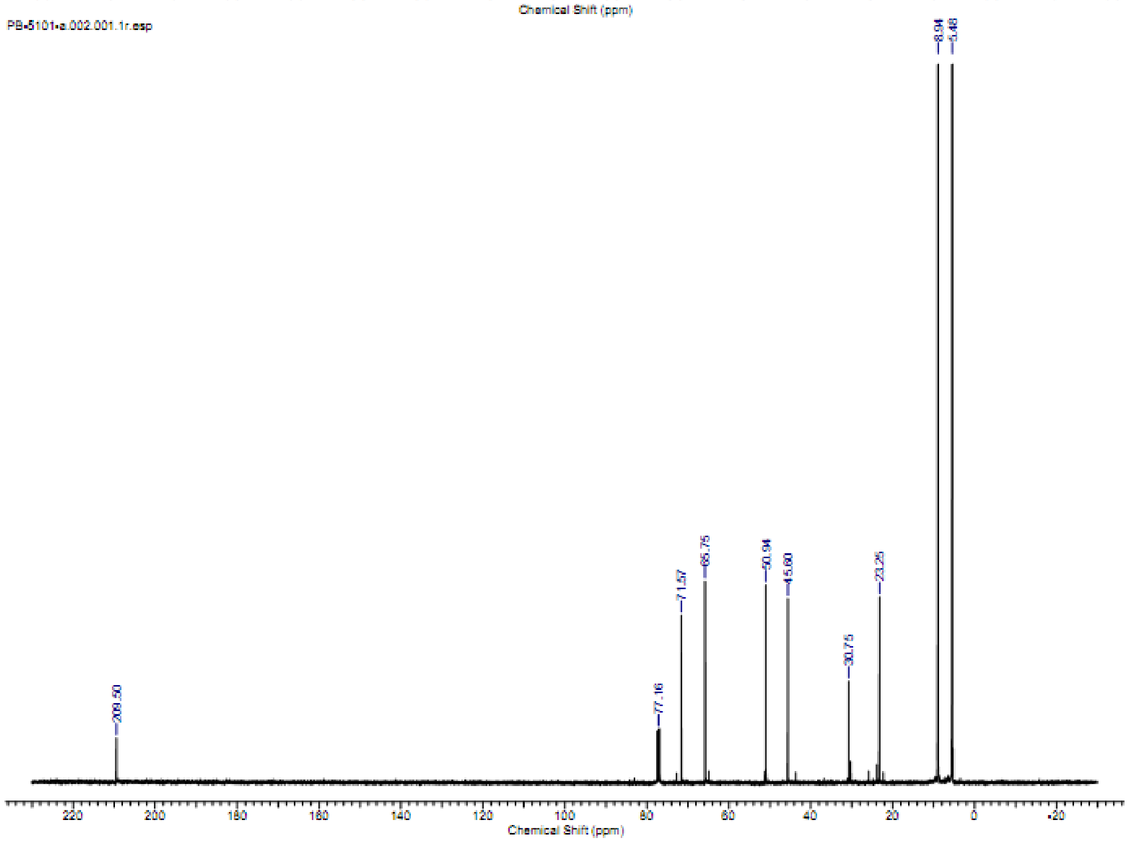

PB-5086C-b.001.001.1r.esp
0.17
0.16
2.13
1.12
1.11
1.51
1.49
3.64
2.13
2.56
2.55
2.53
2.52
2.49
4.15
4.14
4.13
3.79
3.78
1.52
1.51
1.18
1.17
0.94 0.91 0.99
1.16 1.00 3.16
1.46 3.05
30.06
Chemical Shift (ppm)


PB-5086C-b.002.001.1r.esp
0.56
72.72
66.86
50.86
45.43
23.78
30.86
208.65
77.16
Chemical Shift (ppm)

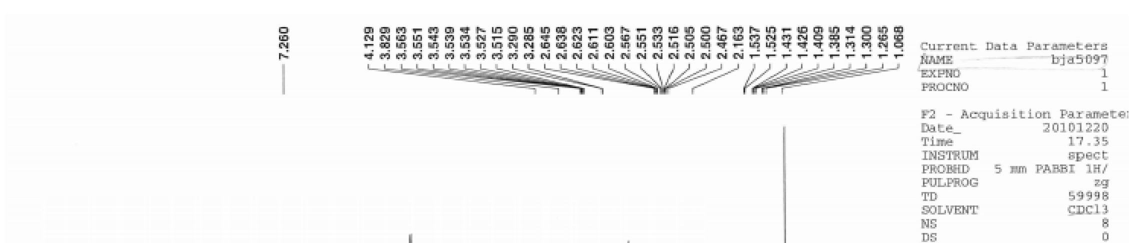
5l

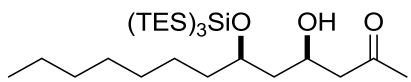

Si(Et)3
(Et)3Si
Si
(Et)3Si
O
OH
O

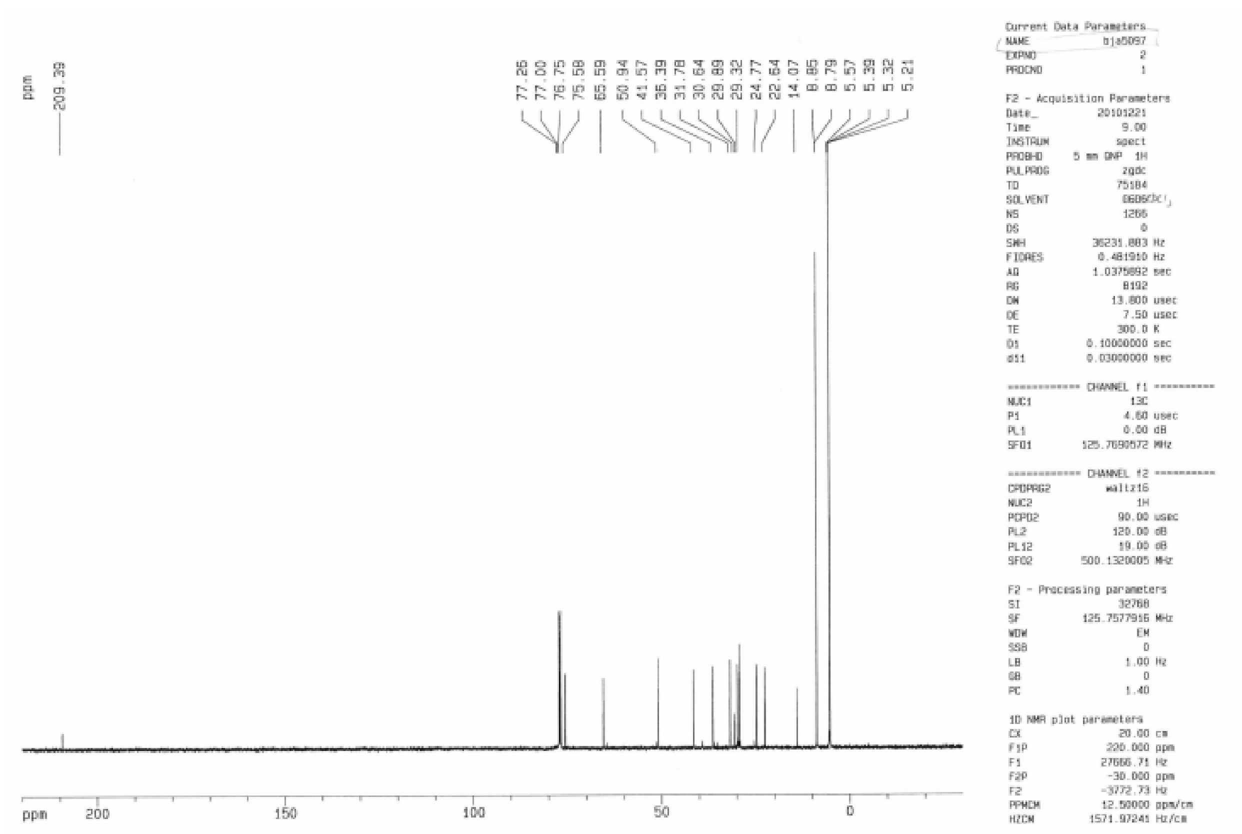

PB-5101-a.001.001.1r.esp
Chemical Shift (ppm)
4.12
4.11
4.10
4.09
3.72
3.71
3.70
3.69
3.23
3.23
2.57
2.56
2.54
2.15
2.1
1.64
1.63
1.62
1.60
1.40
1.40
1.37
1.13
1.0
1.0
1.0
0.7
0.7
0.7
0.74
1.00
1.08
1.03
2.18
2.96
1.08
1.09
3.09
28.38
20.42


PB-5101-a.002.001.1r.esp
Chemical Shift (ppm)
209.50
77.16
71.57
65.75
50.94
45.60
30.75
23.25
8.94
5.46

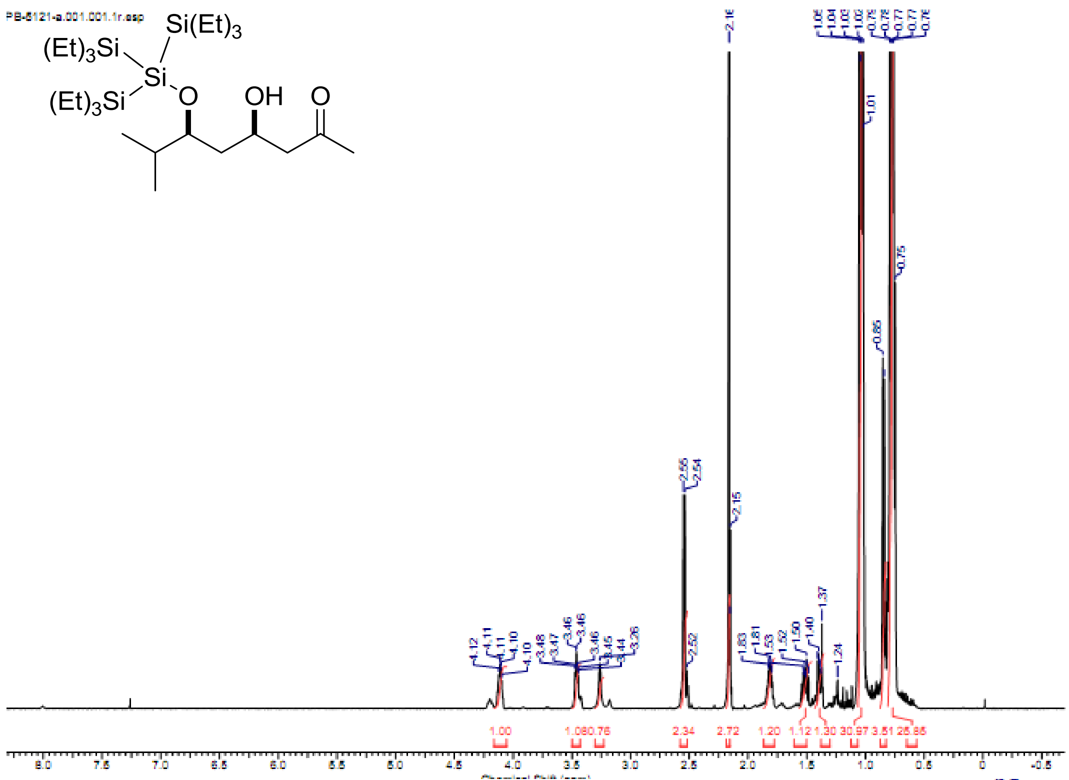
5m

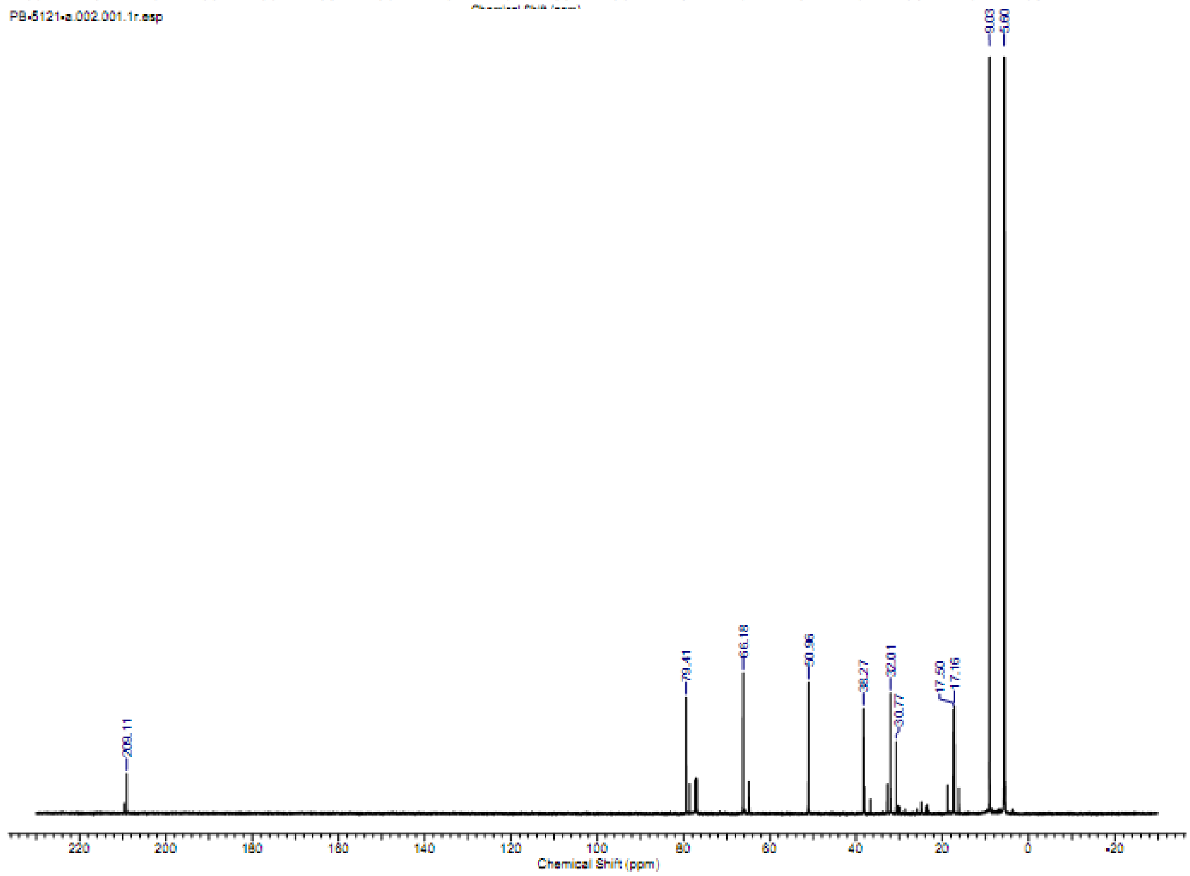

7.260
4.129
3.829
3.563
3.551
3.543
3.539
3.534
3.527
3.515
3.290
3.285
2.645
2.638
2.623
2.611
2.603
2.567
2.551
2.533
2.516
2.505
2.500
2.467
2.163
1.537
1.525
1.431
1.426
1.409
1.385
1.314
1.300
1.265
1.068
Current Data Parameters
NAME bja5097
EXPNO 1
PROCNO 1
F2 - Acquisition Paramete
Date_ 20101220
Time 17.35
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0



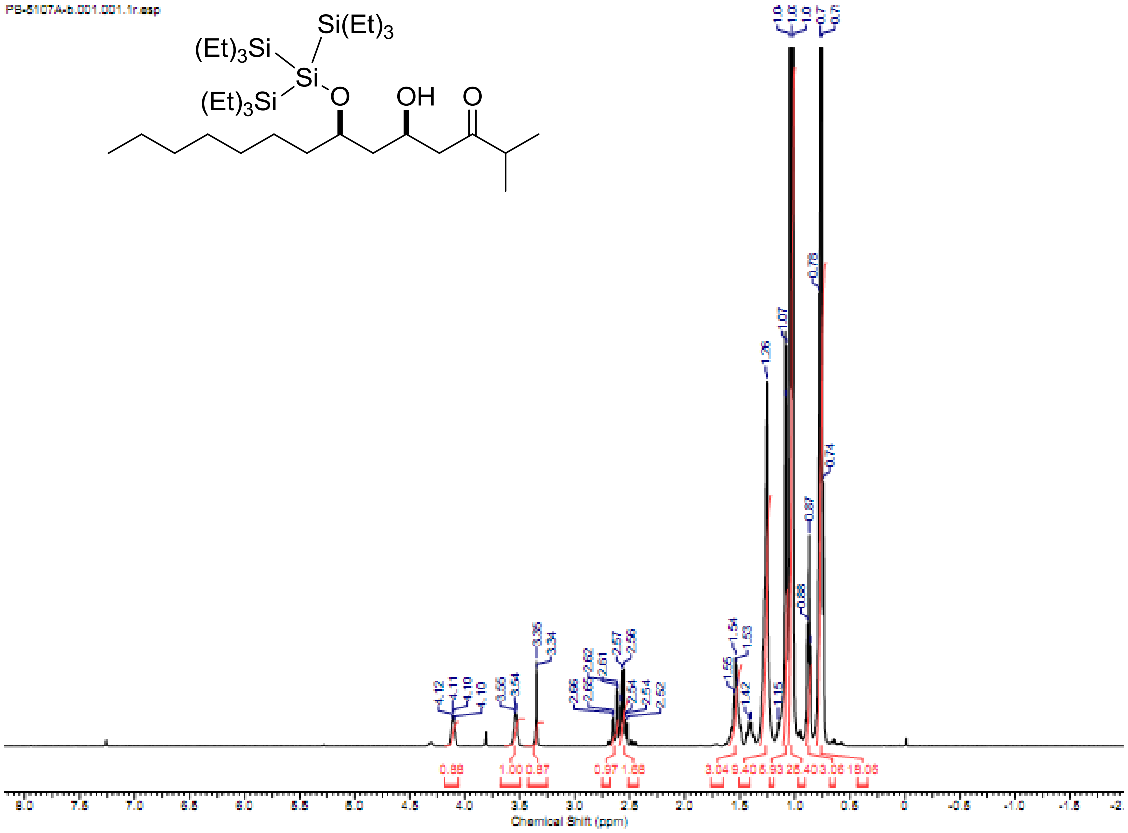


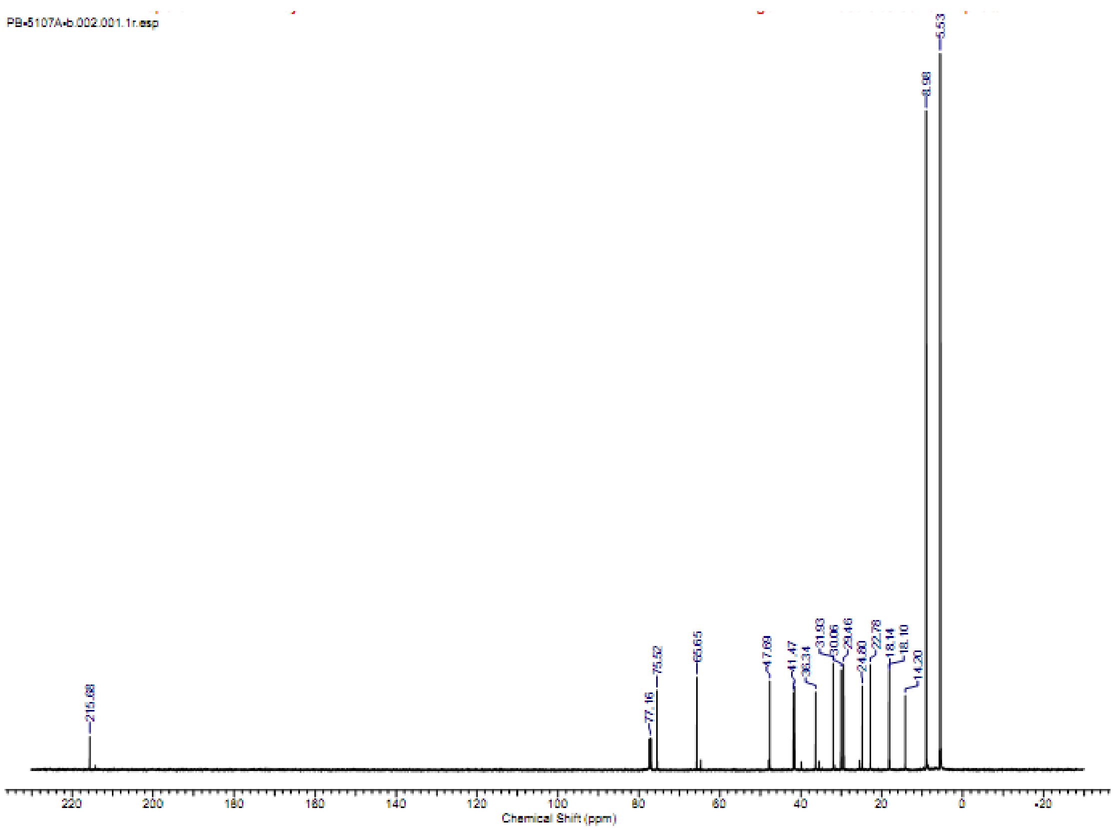
5n (mixture of diastereomers)


PB-5121-a.001.001.1r.esp
Si(Et)3
(Et)3Si
Si
(Et)3Si
O
OH
O

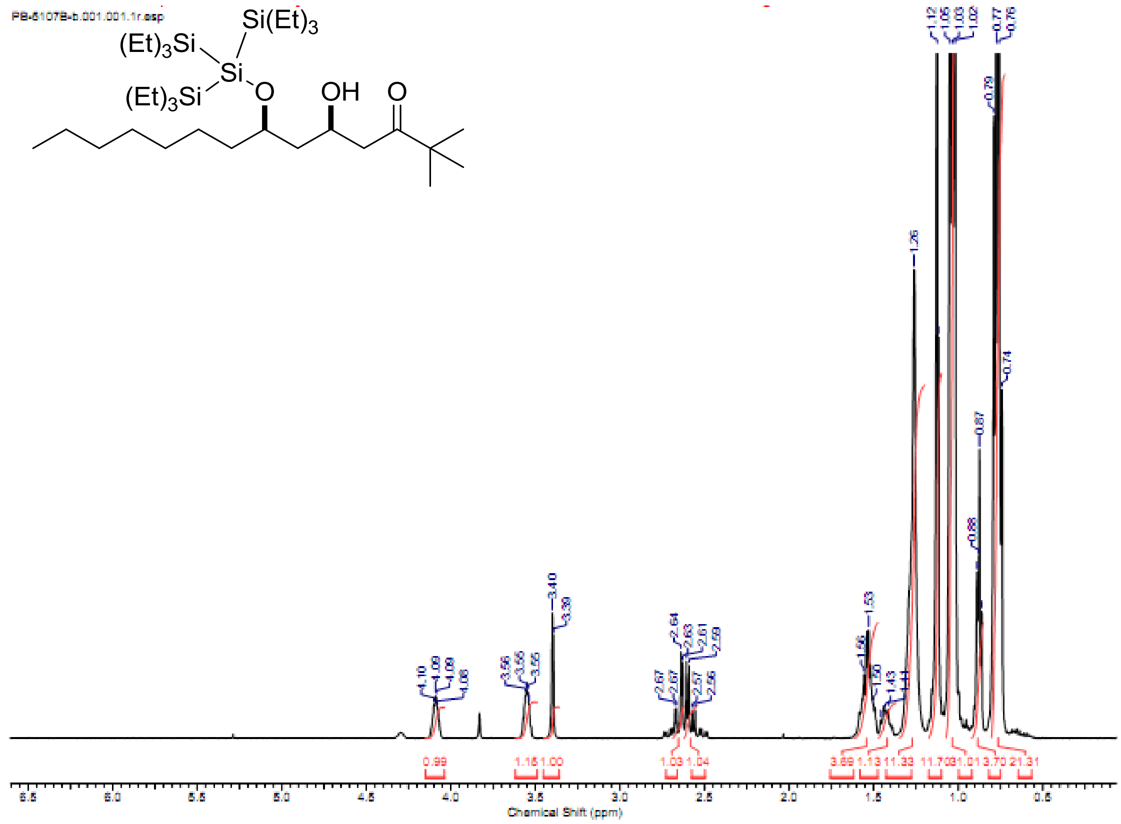

PB-5121-a.002.001.1r.esp
209.11
79.41
66.18
50.96
38.27
32.01
30.77
17.50
17.16
9.03
5.60
Chemical Shift (ppm)

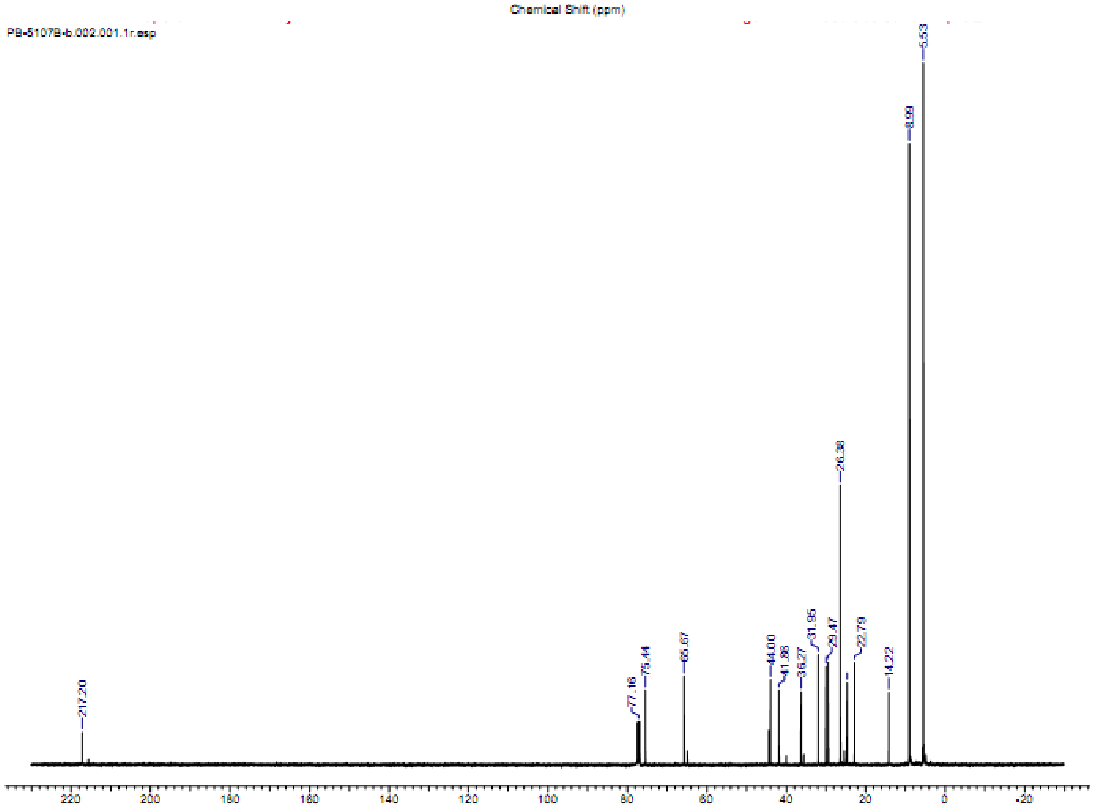
5o


PB-5107A-b.001.001.1r.esp
Si(Et)3
(Et)3Si
Si
(Et)3Si
O
OH
O
Chemical Shift (ppm)

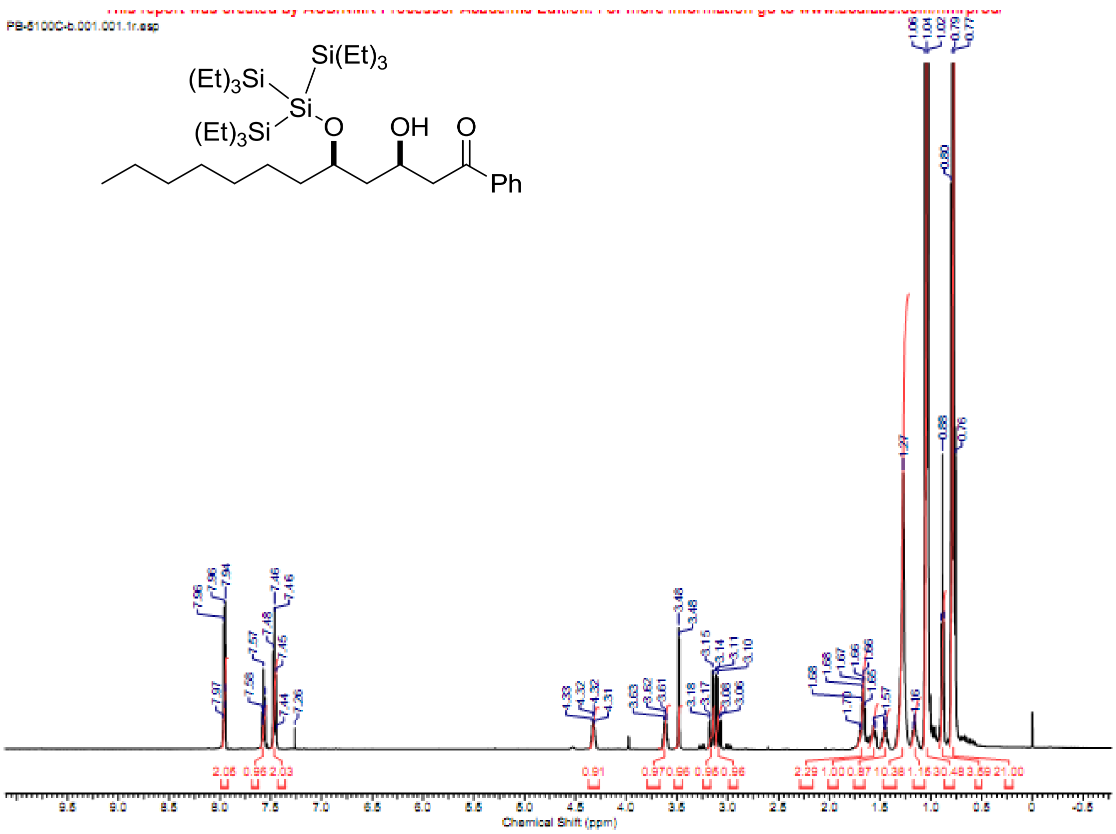

PB-5107A-b.002.001.1r.esp
215.68
77.16
75.52
65.65
47.69
41.47
36.34
31.93
30.06
29.46
24.80
22.78
18.14
18.10
14.20
8.98
5.53
Chemical Shift (ppm)

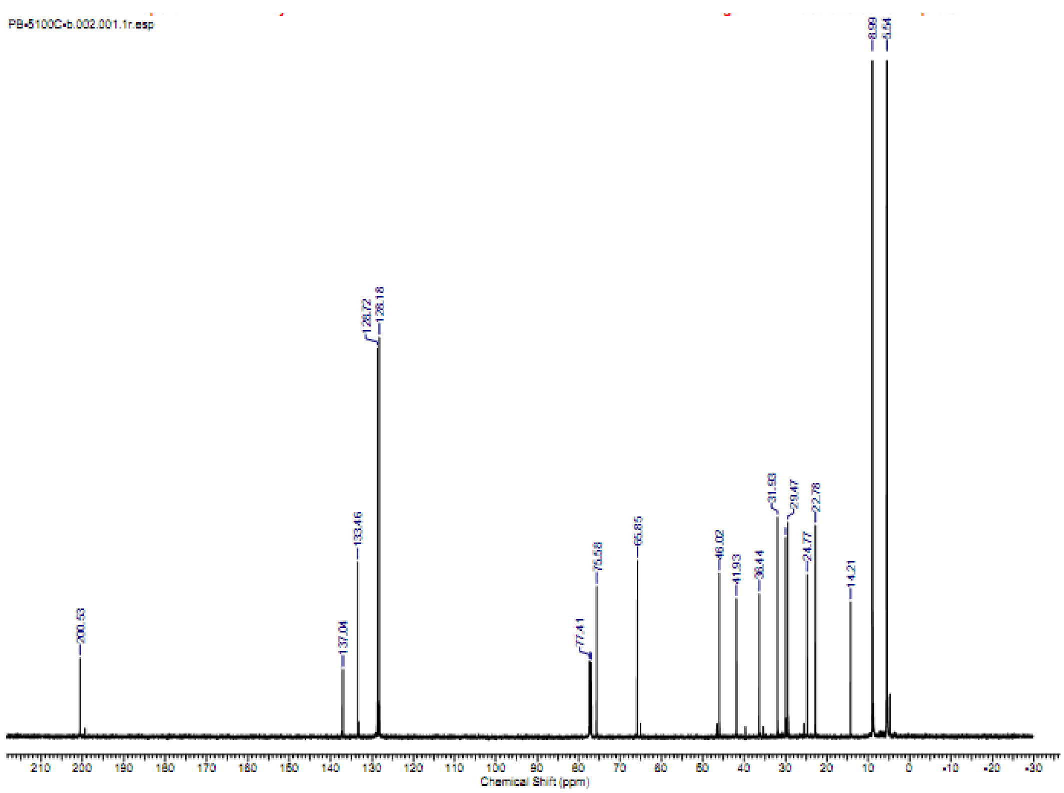
5p


PB-5107B-b.001.001.1r.esp
Si(Et)3
(Et)3Si
Si
(Et)3Si
O
OH
O
Chemical Shift (ppm)

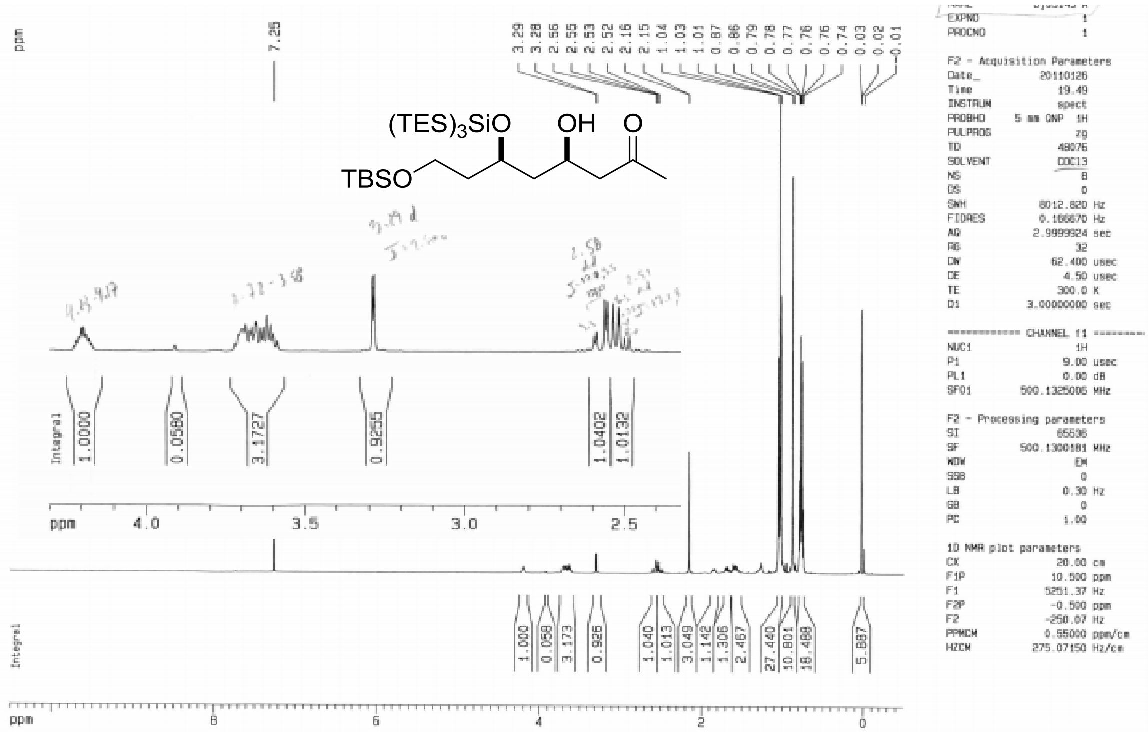

PB-5107B-b.002.001.1r.esp
217.20
77.16
75.44
65.67
44.00
41.86
36.27
31.95
29.47
26.38
22.79
14.22
8.99
5.53
Chemical Shift (ppm)

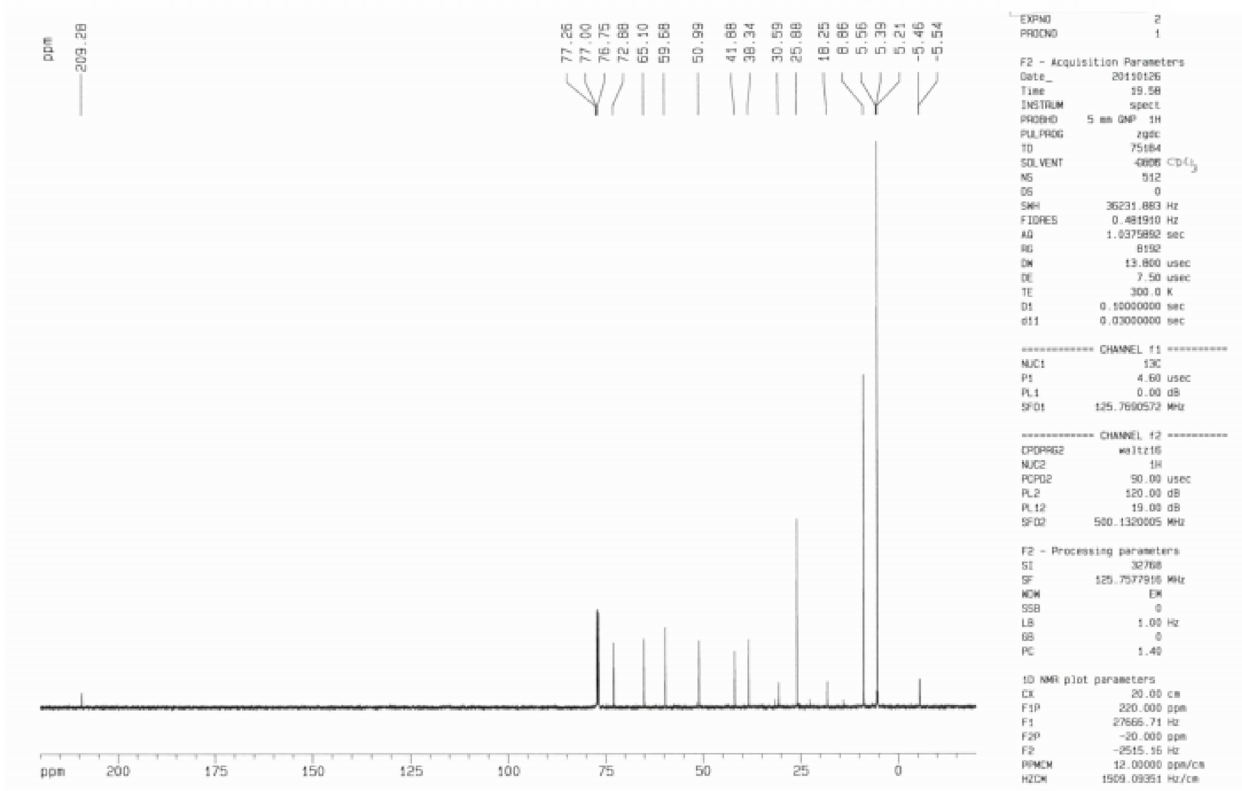
5q


PB-5100C-b.001.001.1r.esp
Si(Et)3
(Et)3Si
Si
(Et)3Si
O
OH
O
Ph
Chemical Shift (ppm)

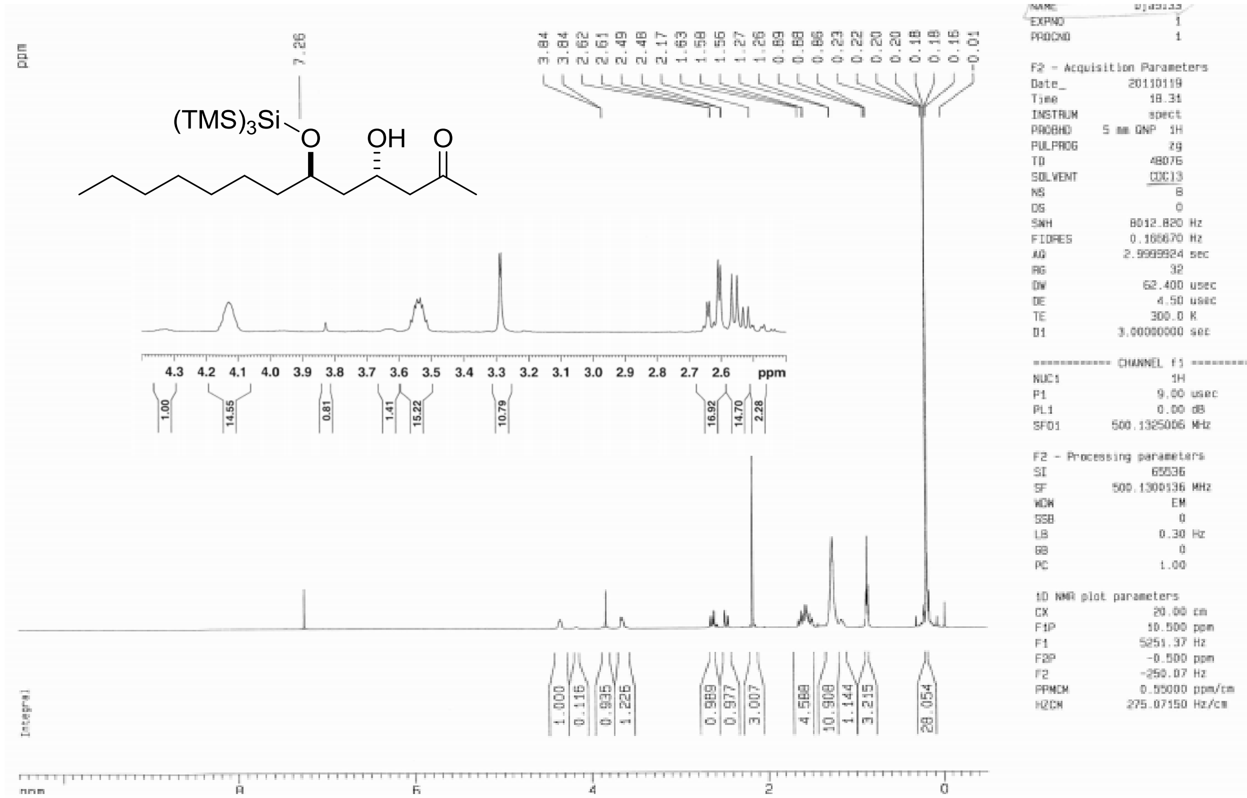

PB-5100C-b.002.001.1r.esp
Chemical Shift (ppm)

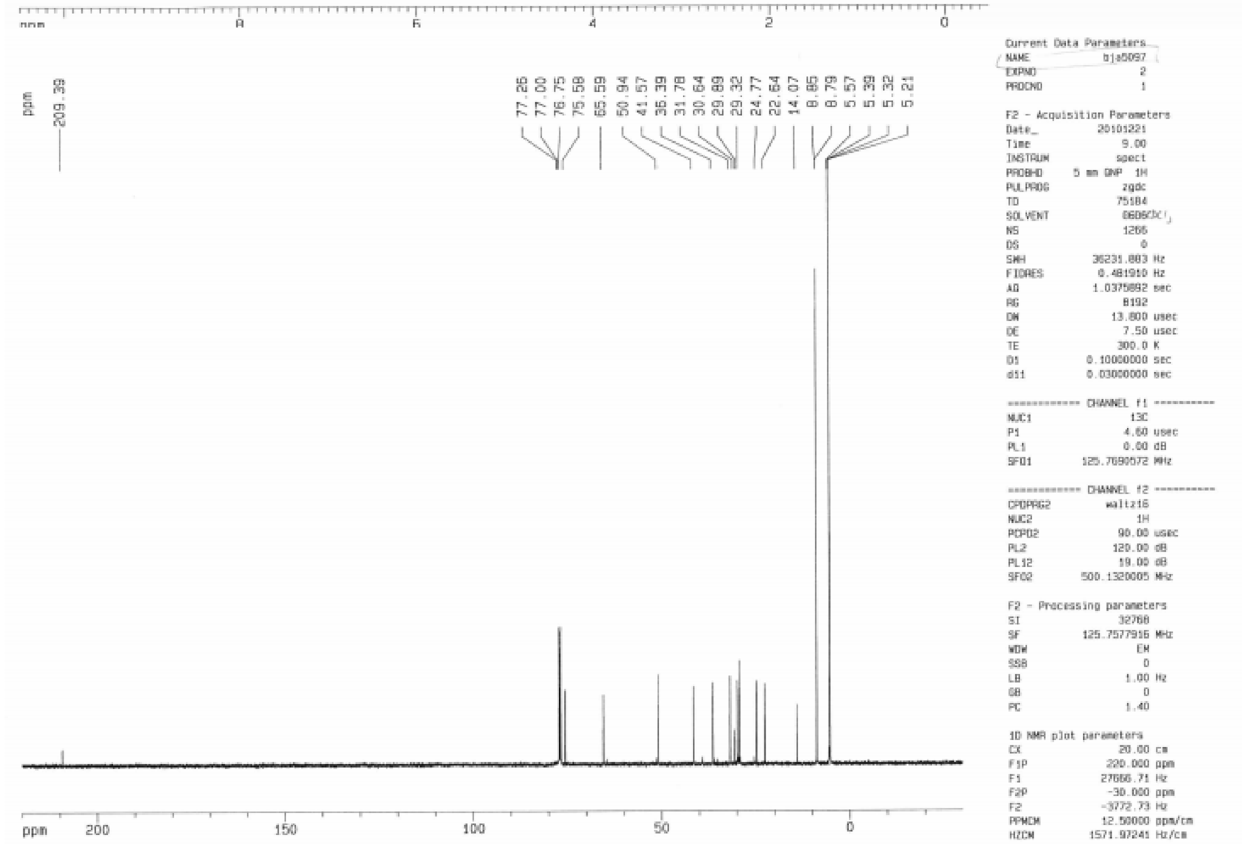
5r

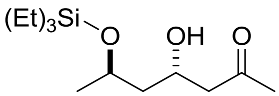




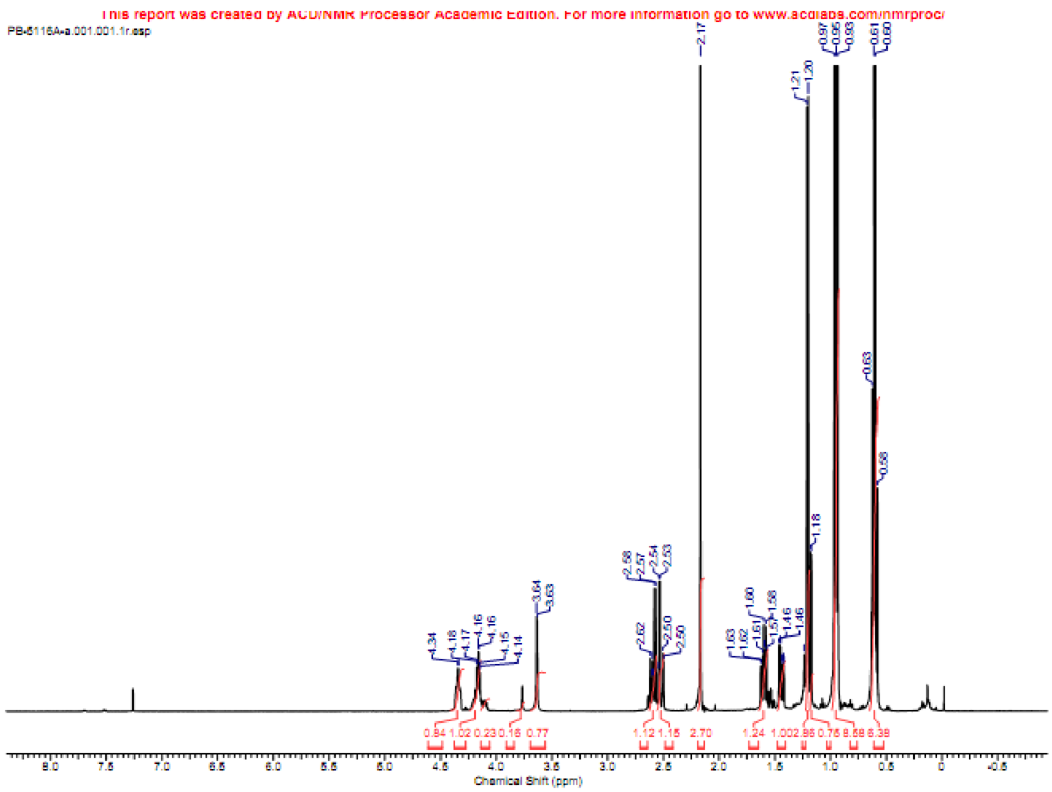
6a

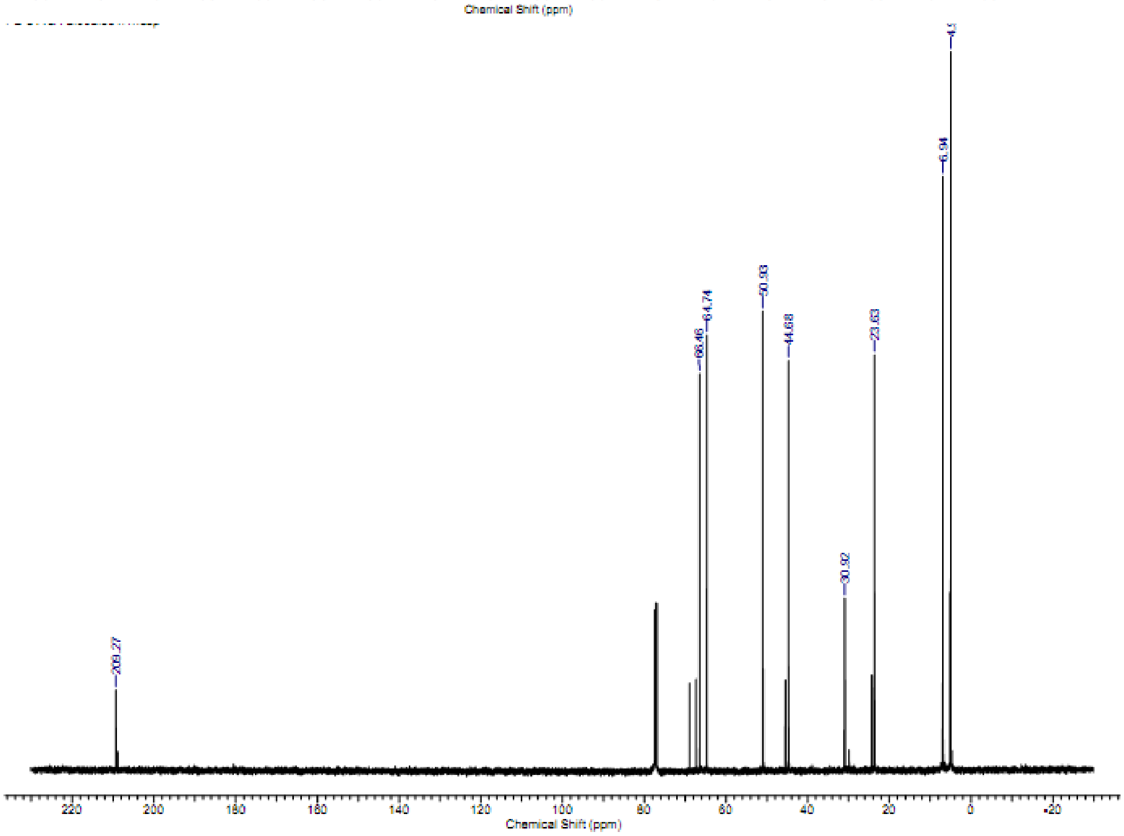

(TMS)3Si
O
OH
O
7.26
3.84
3.84
2.62
2.61
2.49
2.48
2.17
1.63
1.58
1.56
1.27
1.26
0.89
0.88
0.86
0.23
0.22
0.20
0.20
0.18
0.18
0.16
-0.01
ppm
Integral
1.000
0.116
0.935
1.226
0.989
0.977
3.007
4.588
10.908
1.144
3.215
28.054


209.39
77.25
77.00
76.75
75.58
65.59
50.94
41.57
35.39
31.78
30.64
29.89
29.32
24.77
22.64
14.07
8.85
8.79
5.57
5.39
5.32
5.21
ppm
200
150
100
50
0

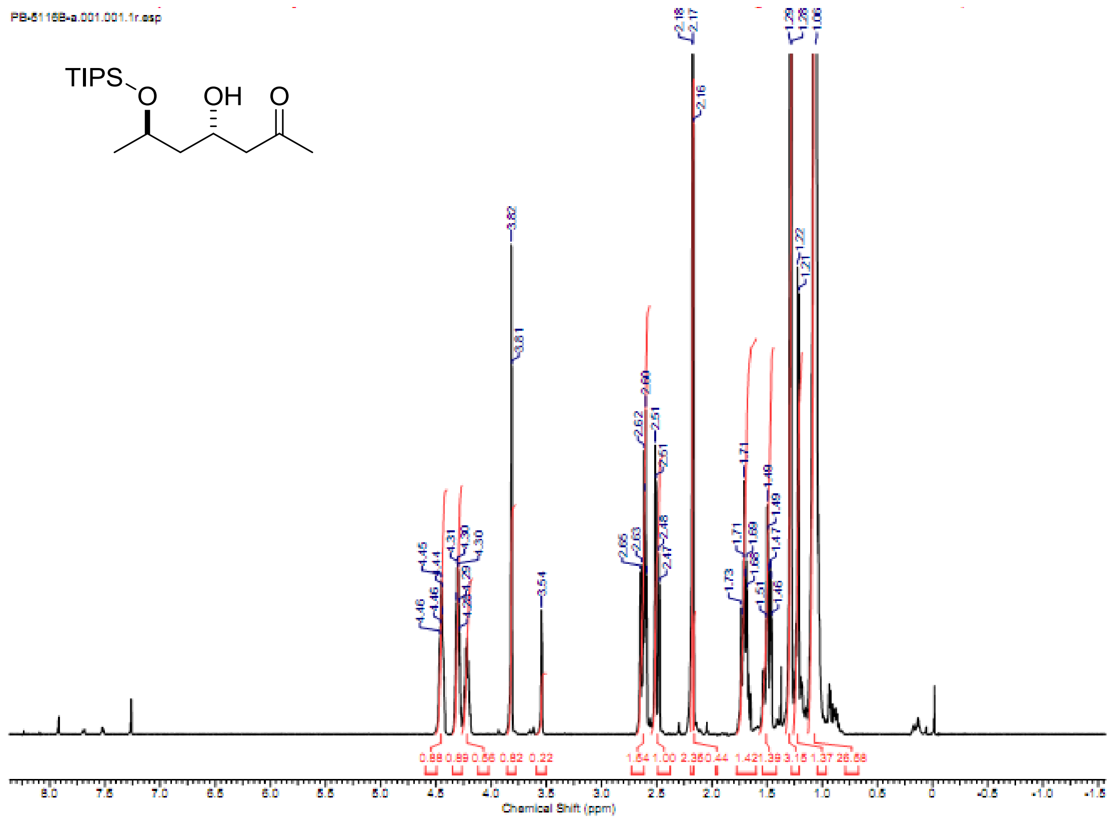


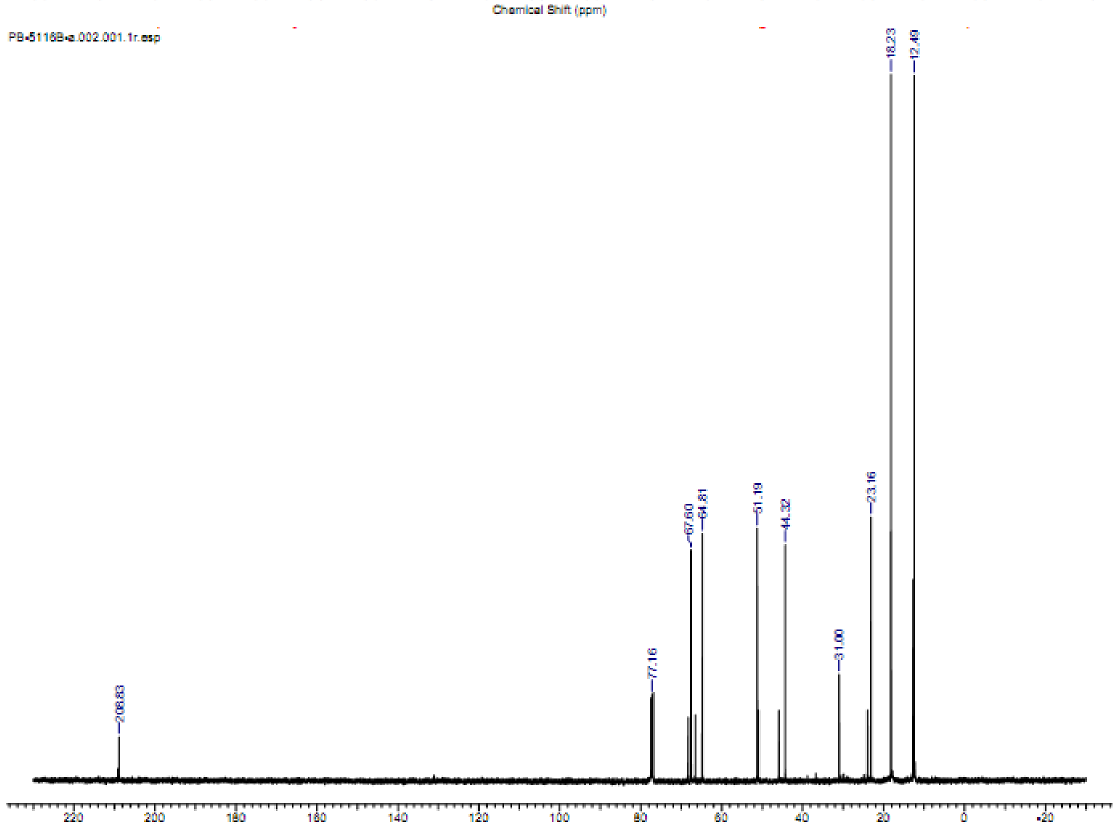
6c


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
Chemical Shift (ppm)

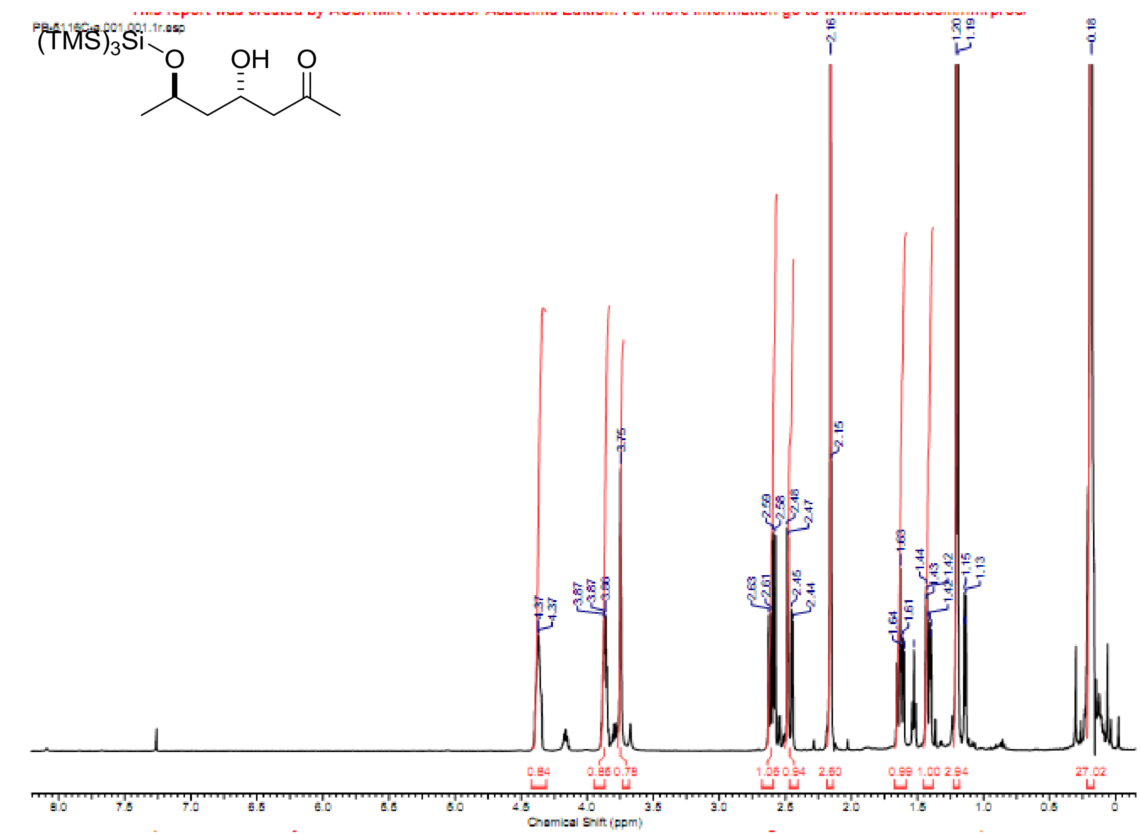

Chemical Shift (ppm)

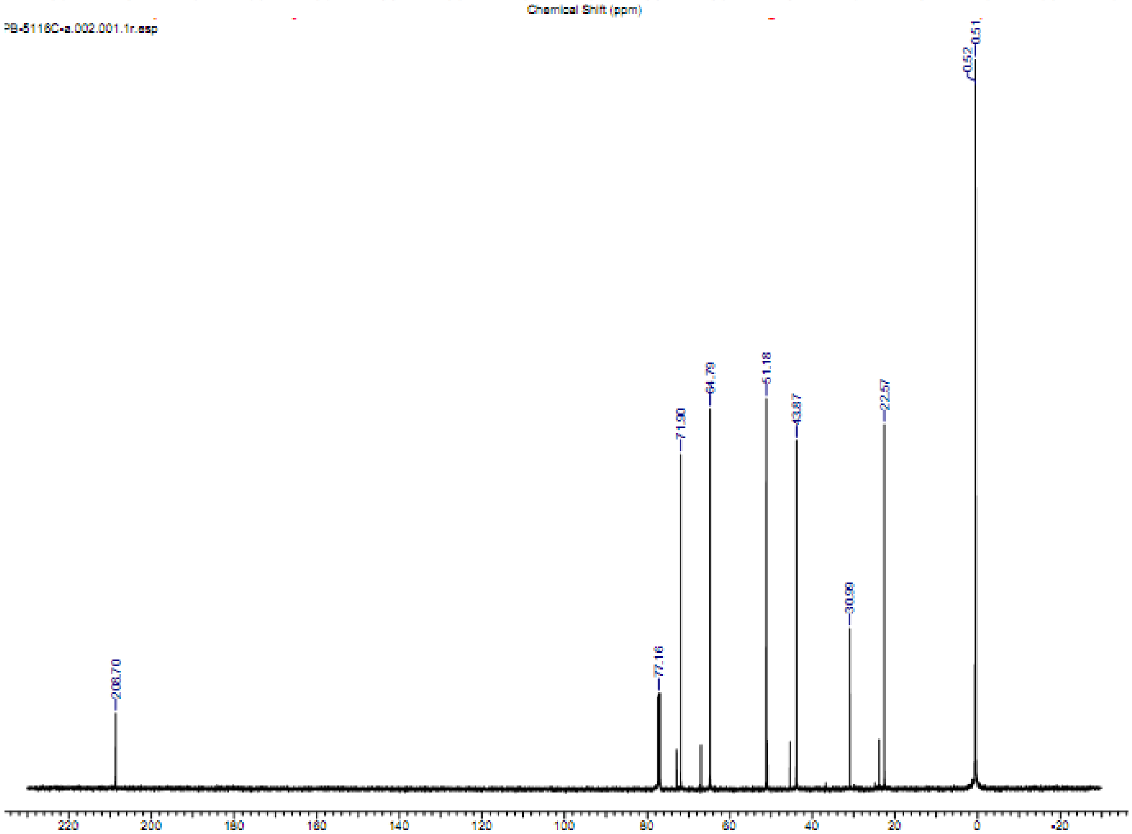
6d (mixture of diastereomers)



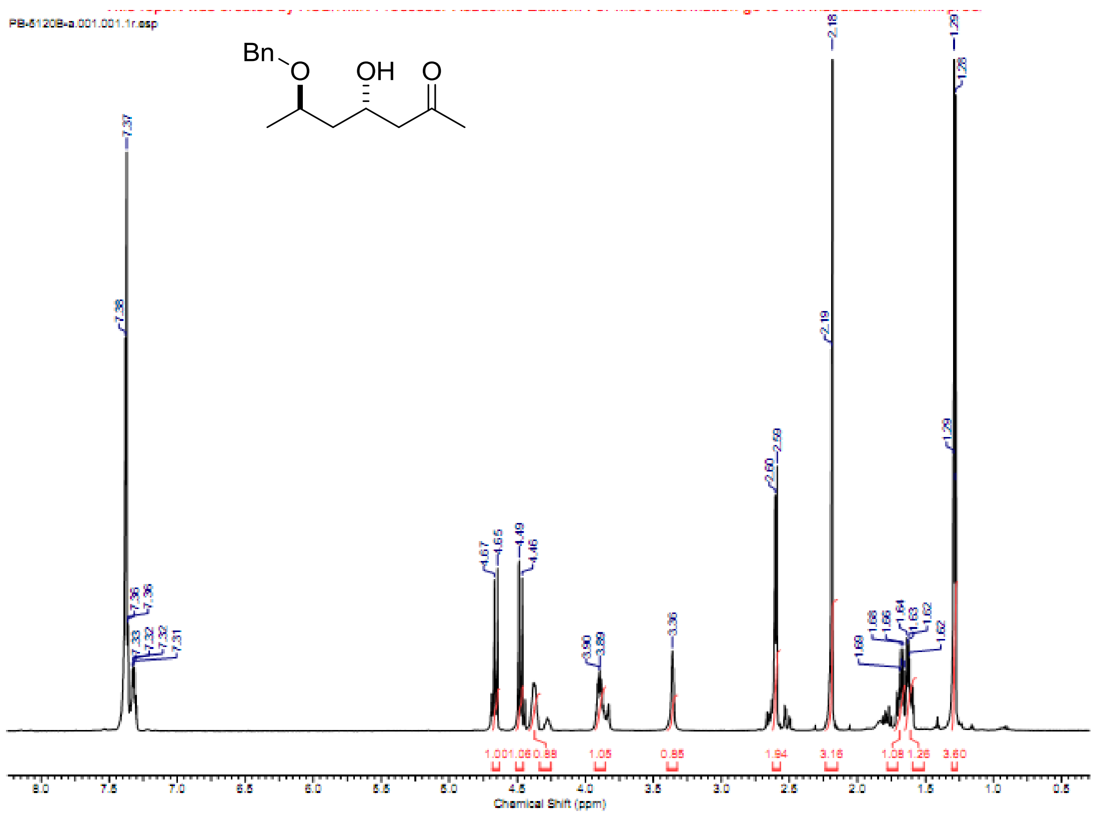


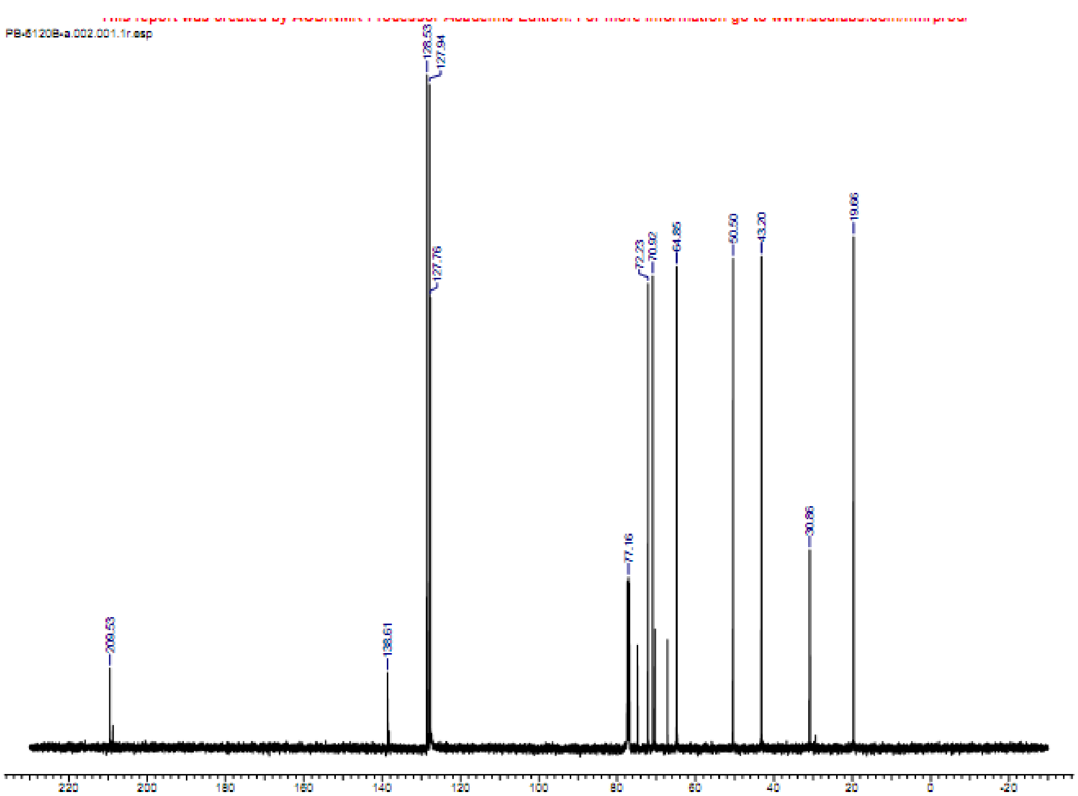
6e


PB-5116C-a.001.001.1r.esp
(TMS)3Si
O
OH
O
2.16
1.20
1.19
0.18
3.75
2.15
2.59
2.58
2.48
2.47
1.63
1.44
1.43
1.42
1.15
1.13
2.63
2.61
2.45
2.44
3.87
3.87
3.86
4.37
4.37
1.64
1.61
1.42
0.84
0.86
0.78
1.06
0.94
2.80
0.99
1.00
2.94
27.02
Chemical Shift (ppm)

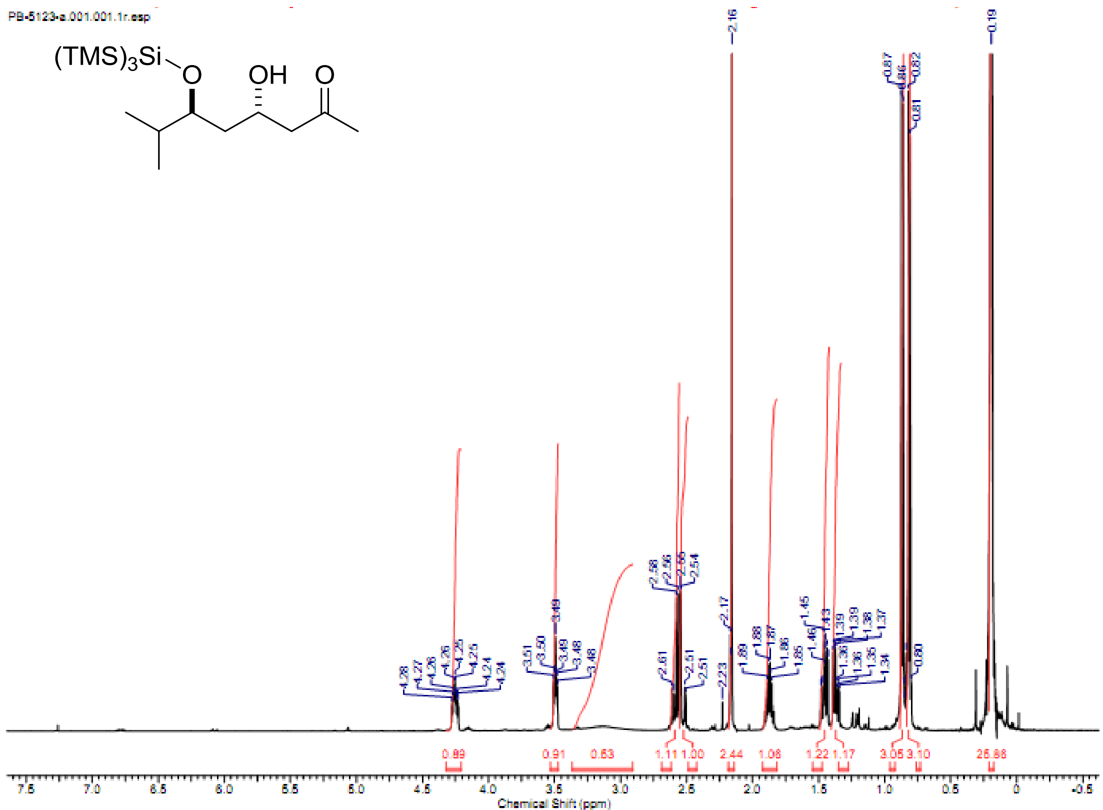

PB-5116C-a.002.001.1r.esp
0.52
0.51
64.79
51.18
71.90
43.87
22.57
30.99
77.16
208.70
Chemical Shift (ppm)

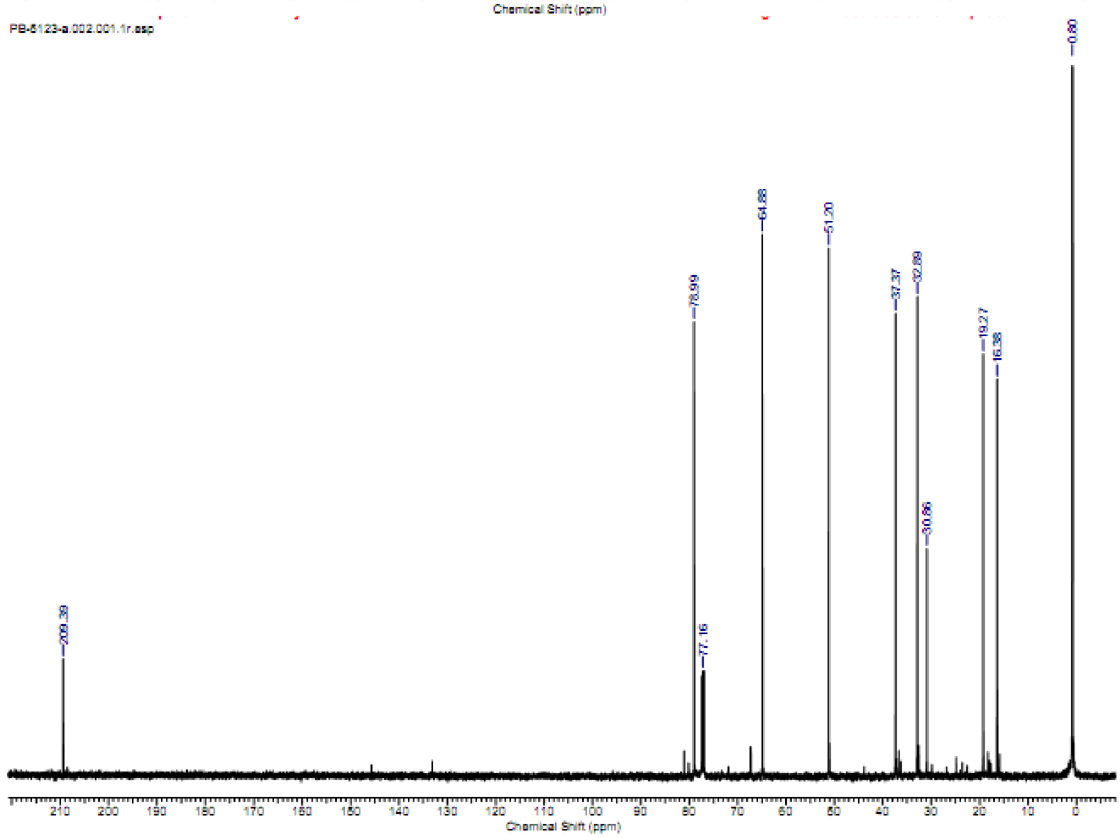
6f (mixture of diastereomers)



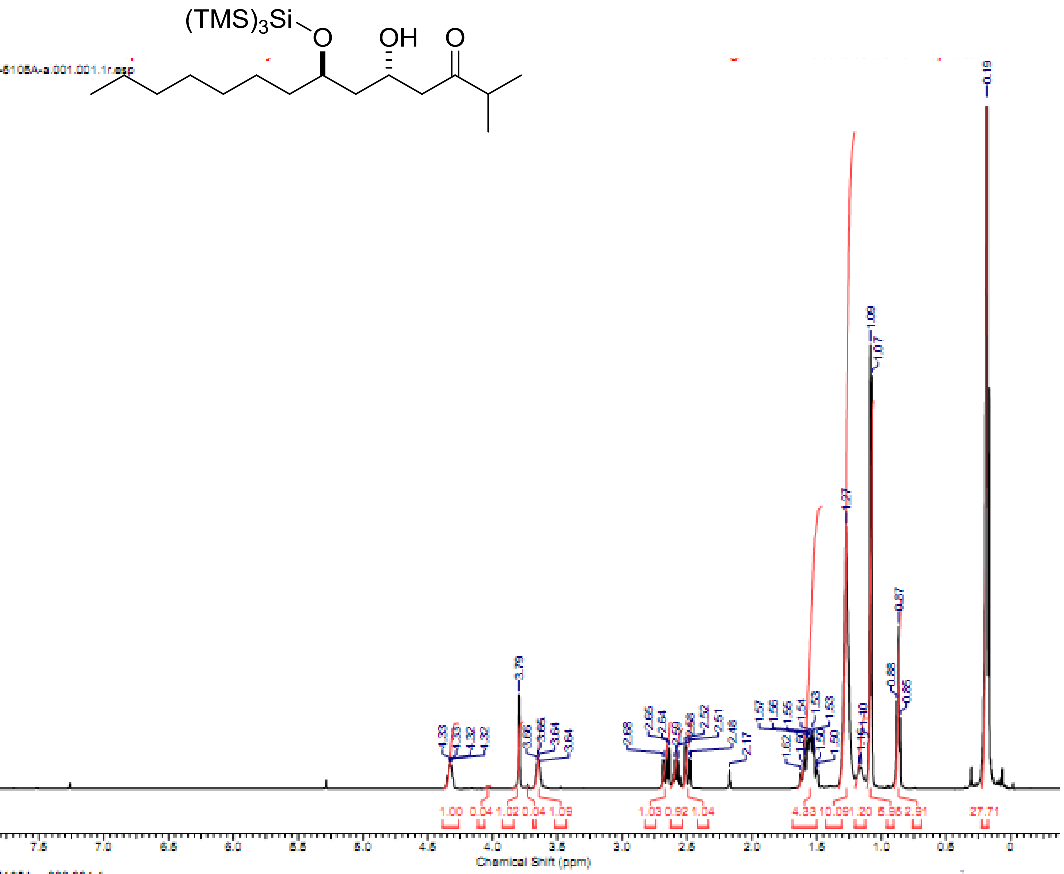


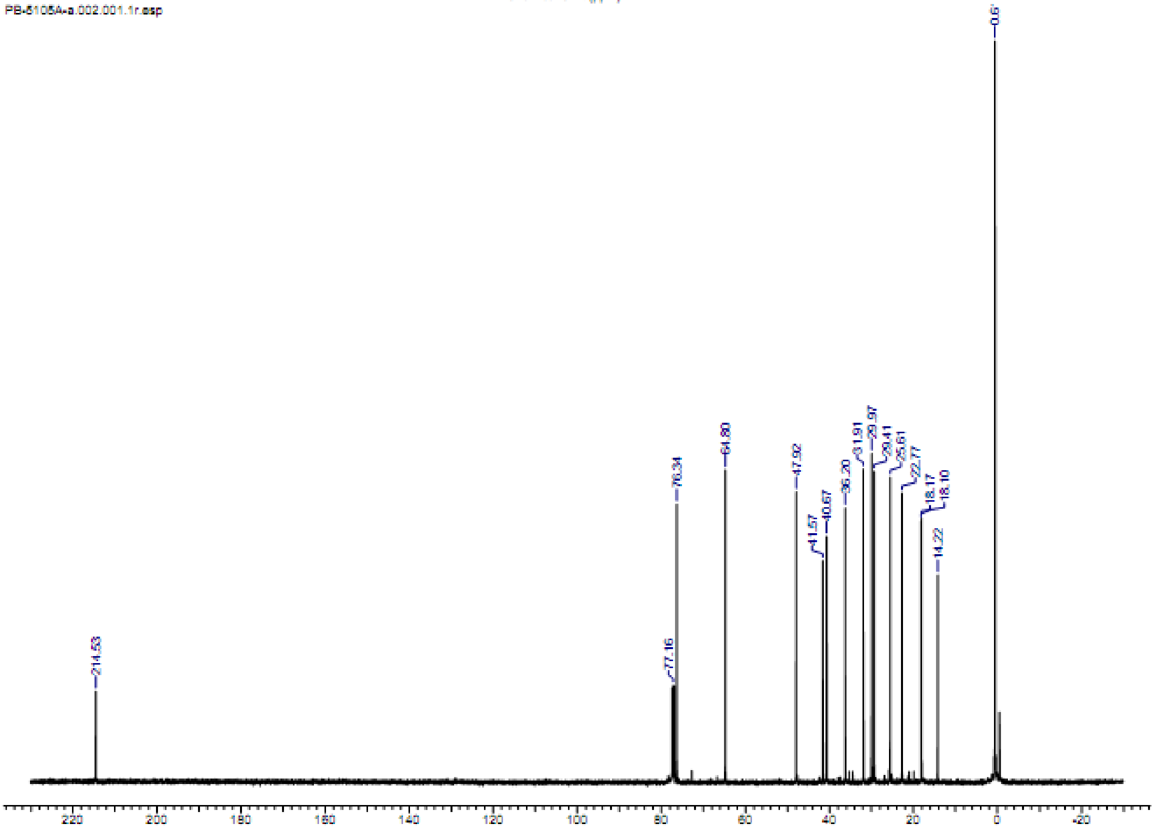
6g



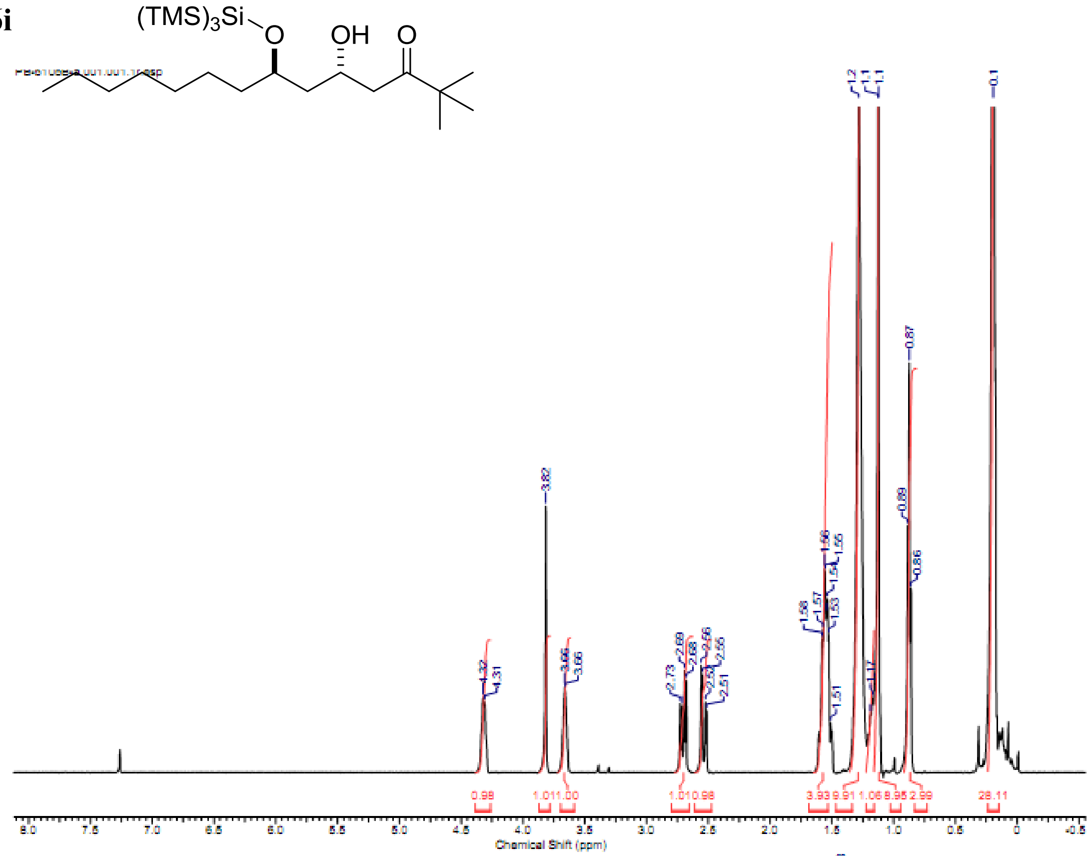


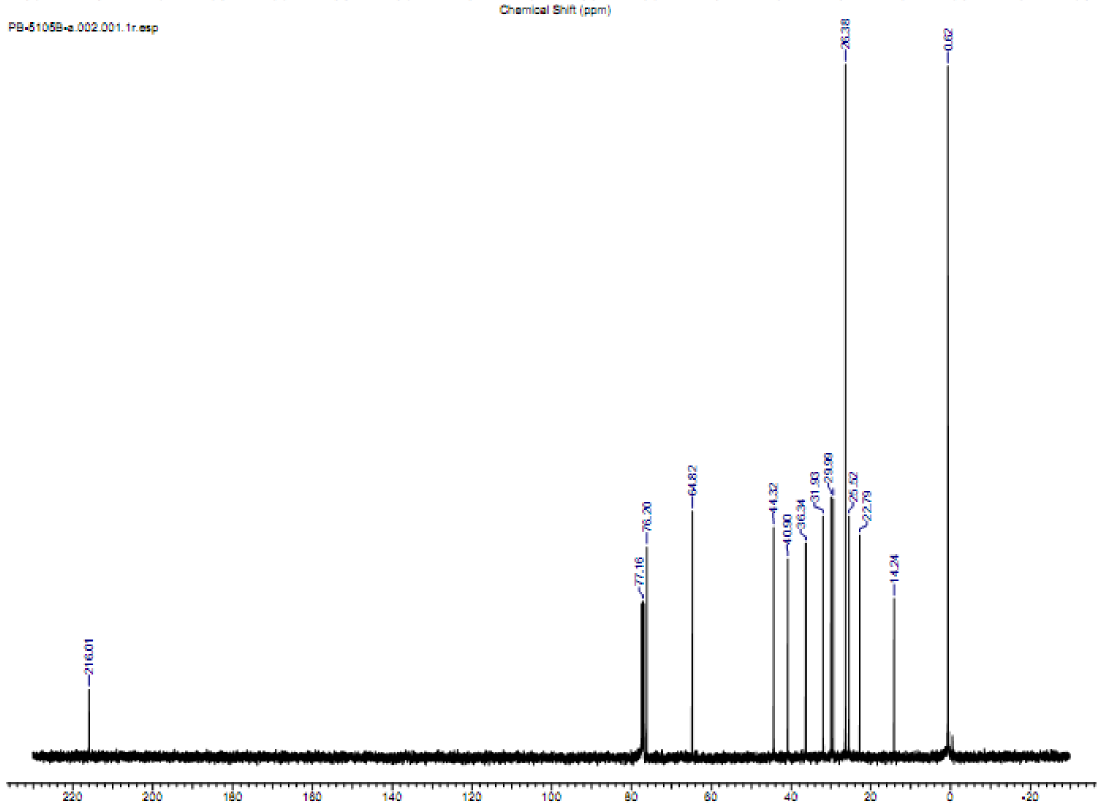
6h


(TMS)3Si
O
OH
O
PB-5105A-a.001.001.1r.esp
Chemical Shift (ppm)

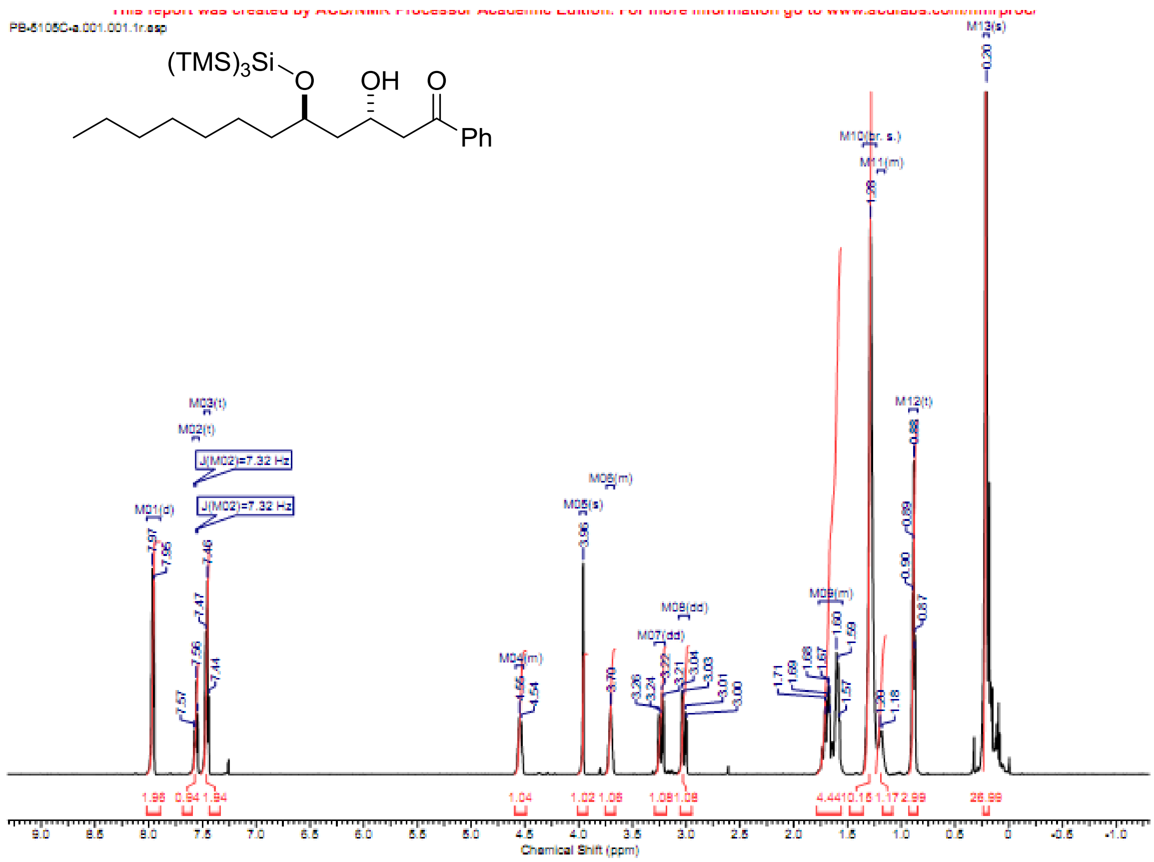

PB-5105A-a.002.001.1r.esp
Chemical Shift (ppm)

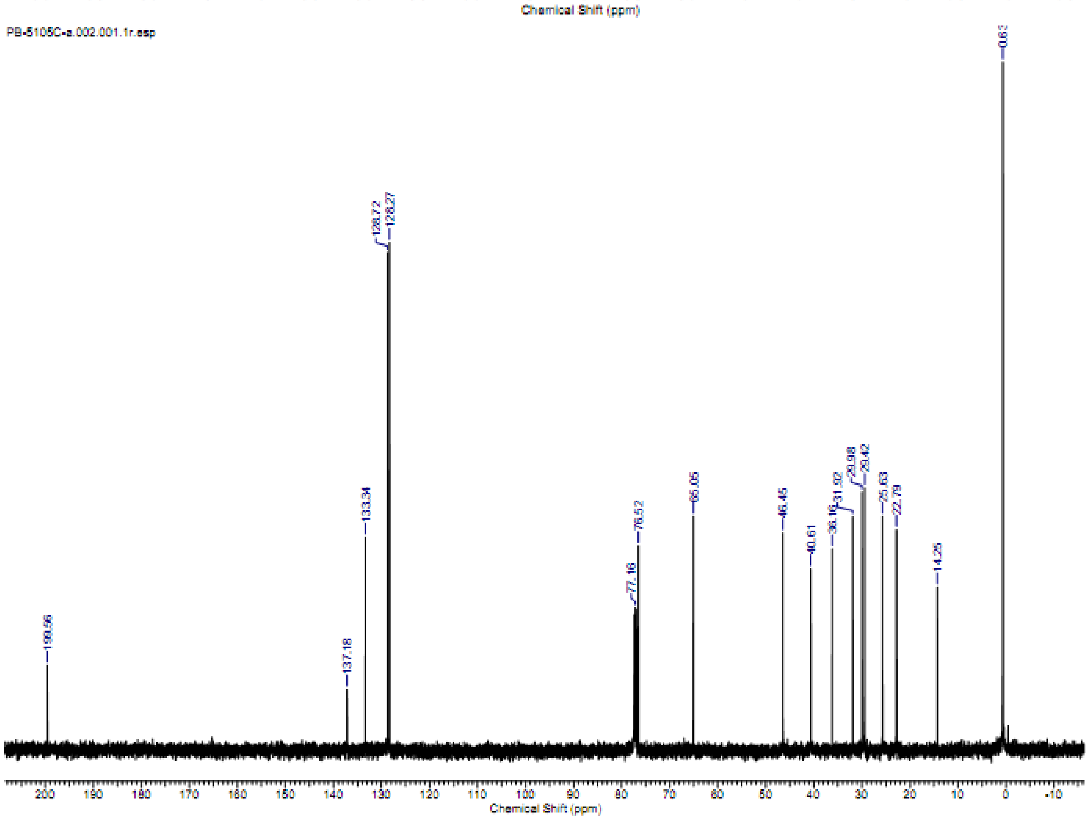
6i


(TMS)$_3$Si
O
OH
O
PB-5105B-a.001.001.1r.esp
Chemical Shift (ppm)
4.32
4.31
3.82
3.66
3.65
2.73
2.69
2.68
2.56
2.55
2.52
2.51
1.58
1.57
1.56
1.55
1.54
1.53
1.51
1.2
1.1
1.1
1.17
0.89
0.87
0.86
0.1
0.99
1.01
1.00
1.01
0.98
3.93
9.91
1.06
8.95
2.99
28.11

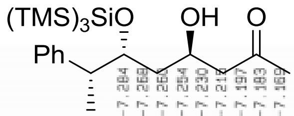

PB-5105B-a.002.001.1r.esp
Chemical Shift (ppm)
216.01
77.16
76.20
64.82
44.32
40.90
36.34
31.93
29.99
26.38
25.52
22.79
14.24
0.62

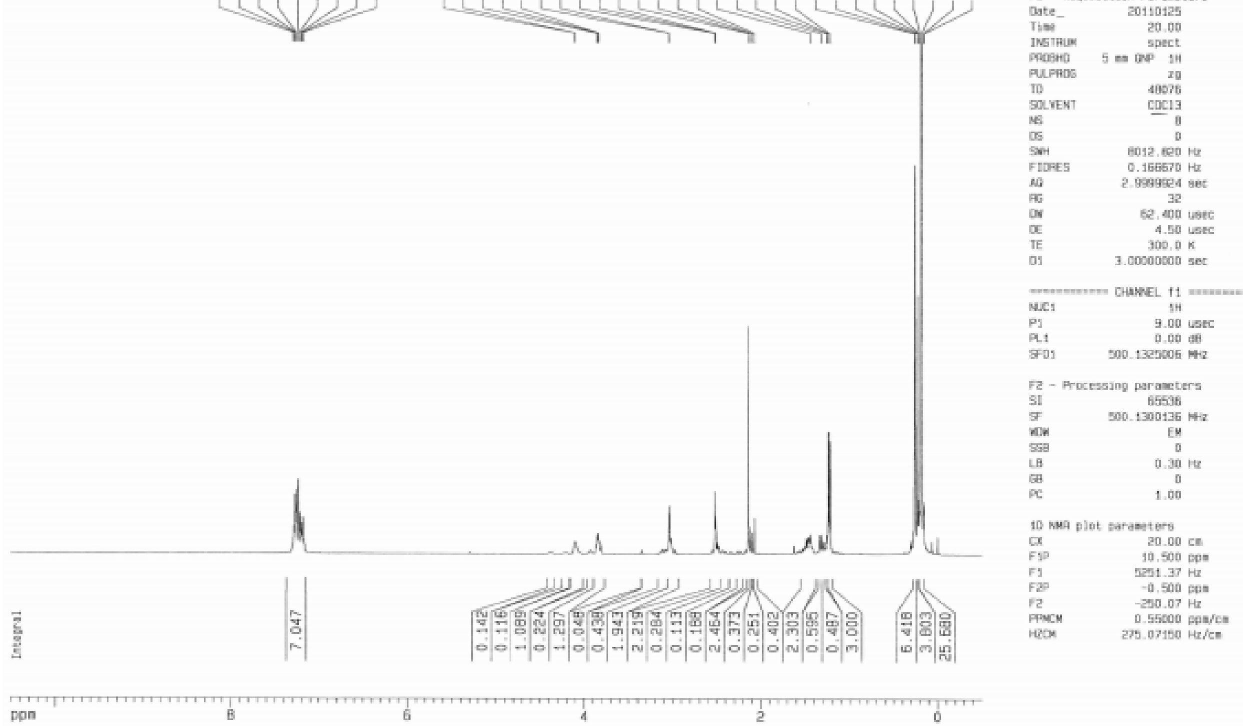
6j

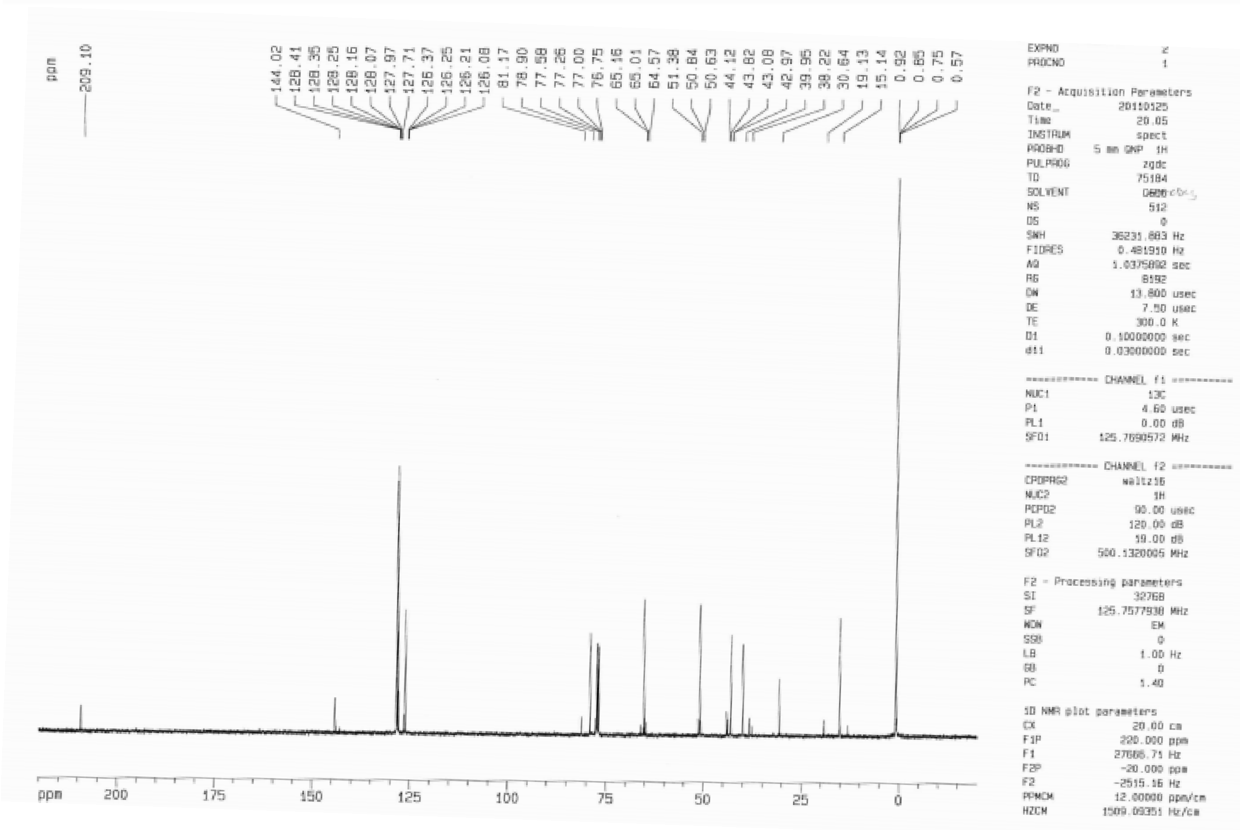

PB-5105C-a.001.001.1r.esp
(TMS)3Si
O
OH
O
Ph
Chemical Shift (ppm)


PB-5105C-a.002.001.1r.esp
Chemical Shift (ppm)

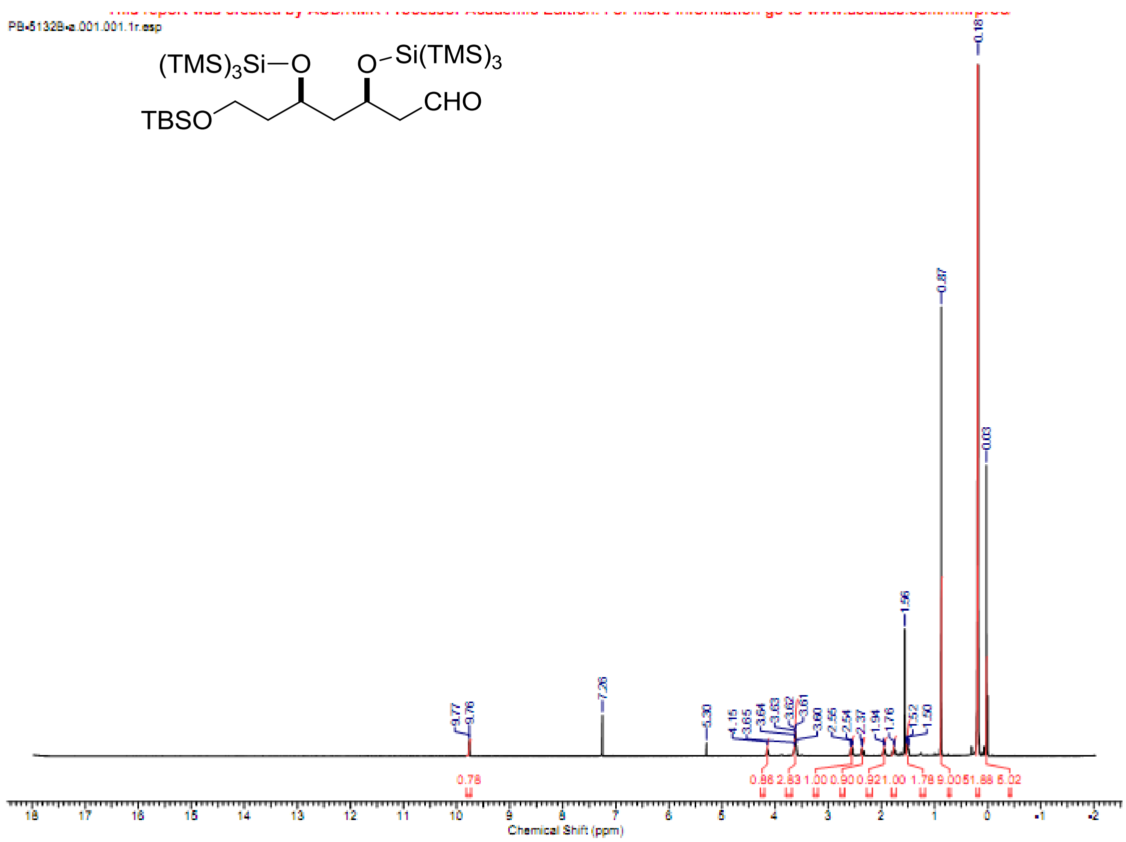
6k

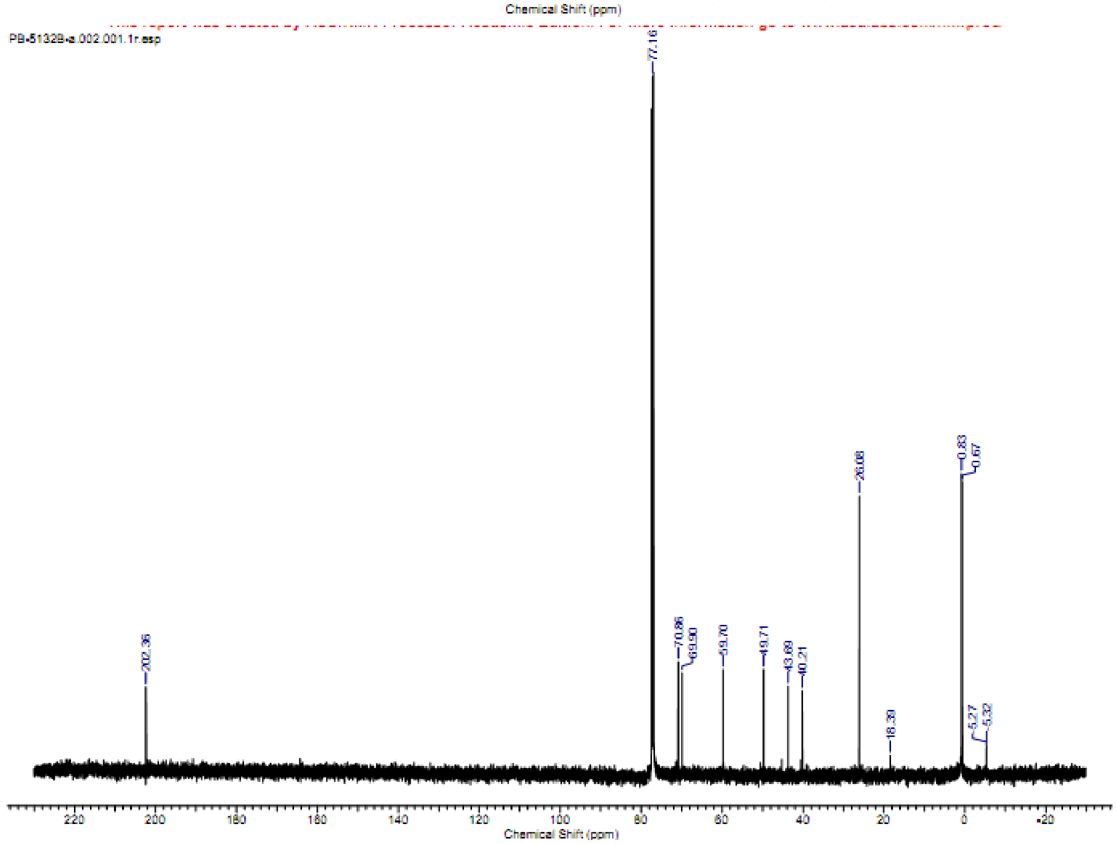


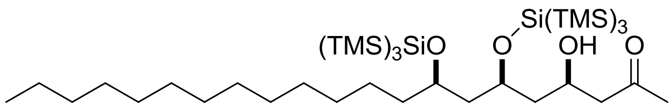




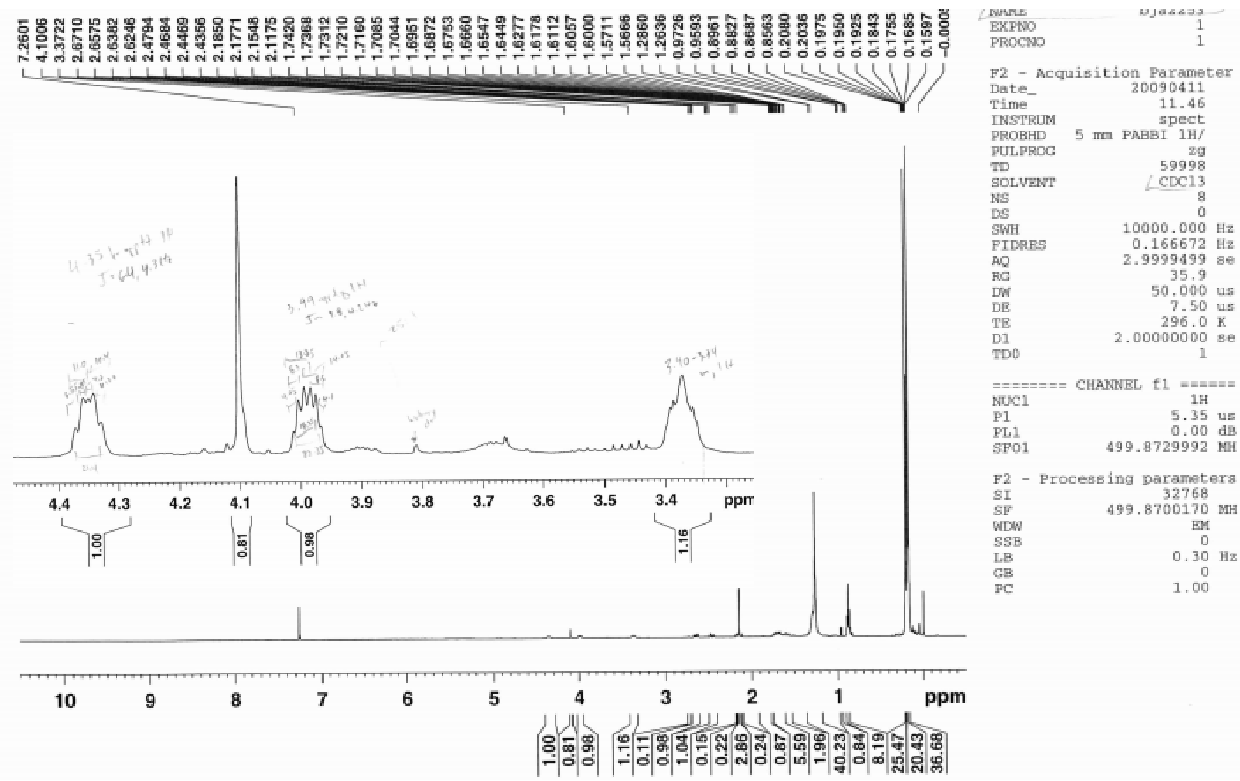
8b

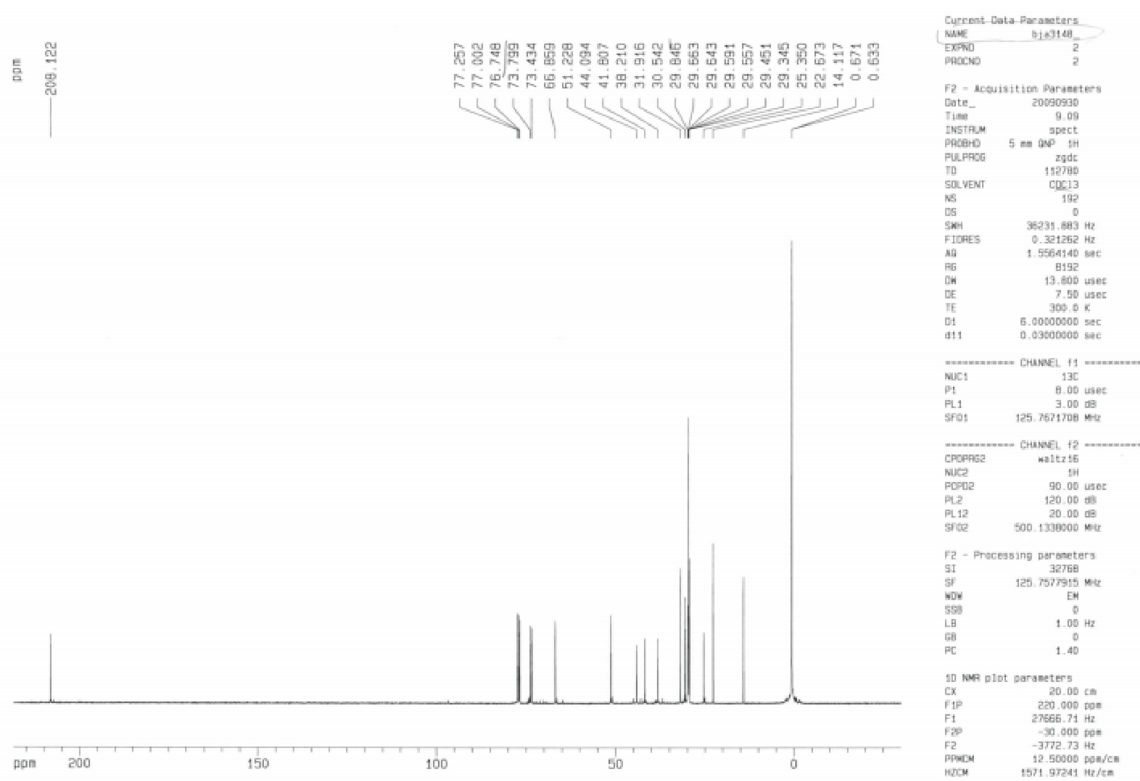

PB-5132B-a.001.001.1r.esp
(TMS)3Si—O
O-Si(TMS)3
TBSO
CHO
9.77
9.76
7.26
5.30
4.15
3.65
3.64
3.63
3.62
3.61
3.60
2.55
2.54
2.37
1.94
1.76
1.56
1.52
1.50
0.87
0.18
0.03
0.78
0.86
2.83
1.00
0.90
0.92
1.00
1.78
9.00
51.88
6.02
Chemical Shift (ppm)


PB-5132B-a.002.001.1r.esp
202.36
77.16
70.86
69.90
59.70
49.71
43.69
40.21
26.08
18.39
0.83
0.67
-5.27
-5.32
Chemical Shift (ppm)

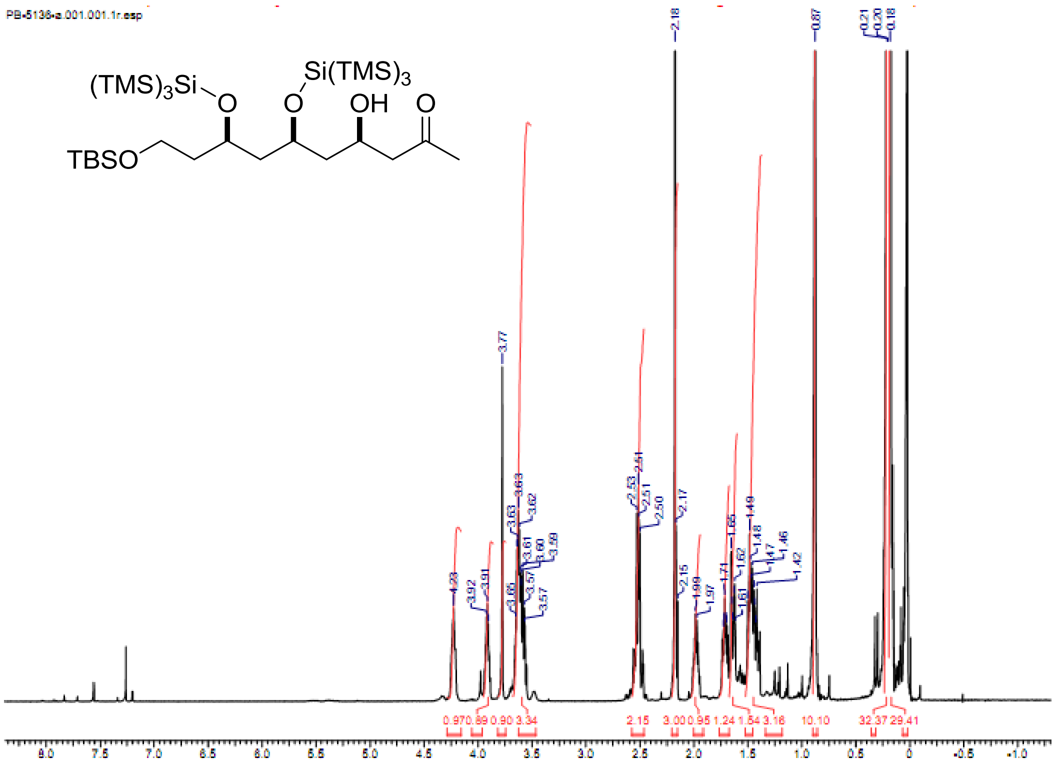

(TMS)3SiO
Si(TMS)3
O
OH
O

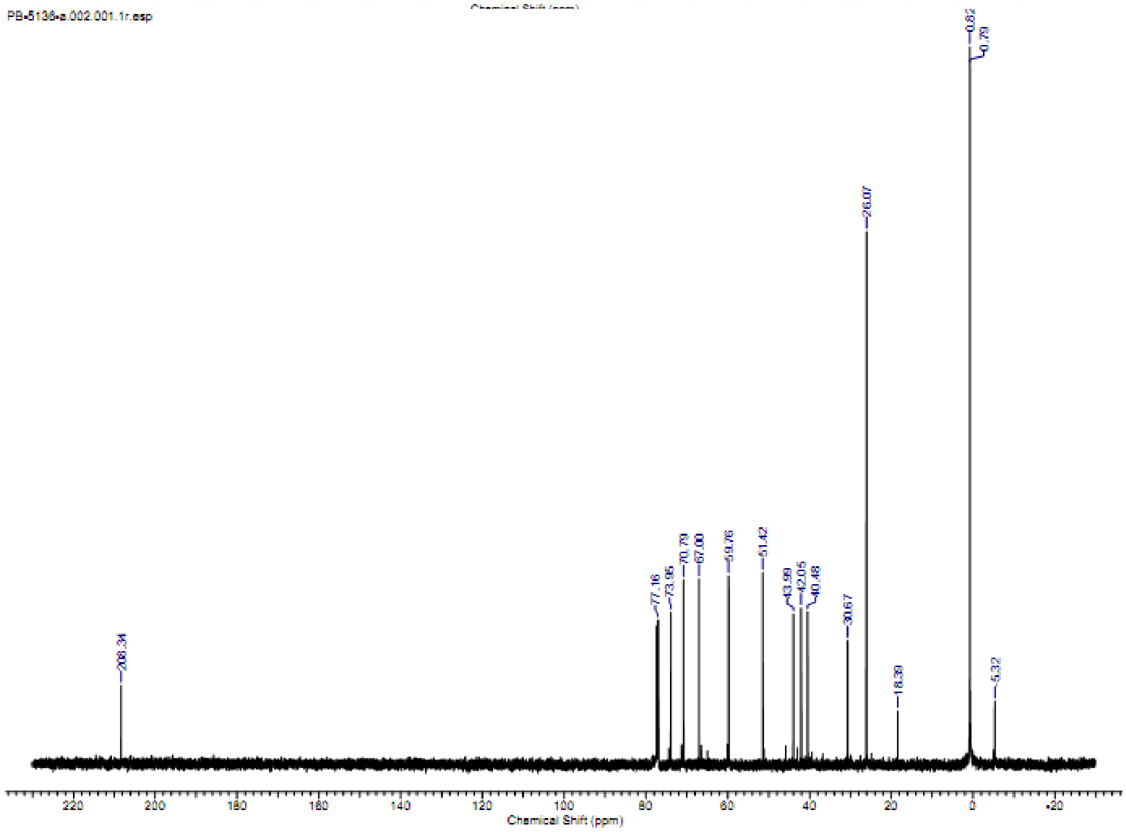
9a


NAME bja2233
EXPNO 1
PROCNO 1
F2 - Acquisition Parameter
Date_ 20090411
Time 11.46
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999499 se
RG 35.9
DW 50.000 us
DE 7.50 us
TE 296.0 K
D1 2.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 5.35 us
PL1 0.00 dB
SFO1 499.8729992 MH
F2 - Processing parameters
SI 32768
SF 499.8700170 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

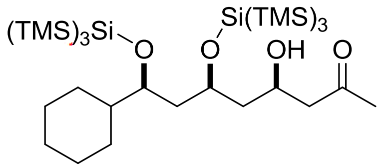

Current Data Parameters
NAME bja3148
EXPNO 2
PROCNO 2
F2 - Acquisition Parameters
Date_ 20090930
Time 9.09
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 152780
SOLVENT CDCl3
NS 192
DS 0
SWH 38231.883 Hz
FIDRES 0.321262 Hz
AQ 1.5564140 sec
RG 8192
DW 13.800 usec
DE 7.50 usec
TE 300.0 K
D1 6.00000000 sec
d11 0.03000000 sec
============ CHANNEL f1 ==========
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SFO1 125.7671708 MHz
============ CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 20.00 dB
SFO2 500.1338000 MHz
F2 - Processing parameters
SI 32768
SF 125.7577915 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P -30.000 ppm
F2 -3772.73 Hz
PPMCM 12.50000 ppm/cm
HZCM 1571.97241 Hz/cm
ppm

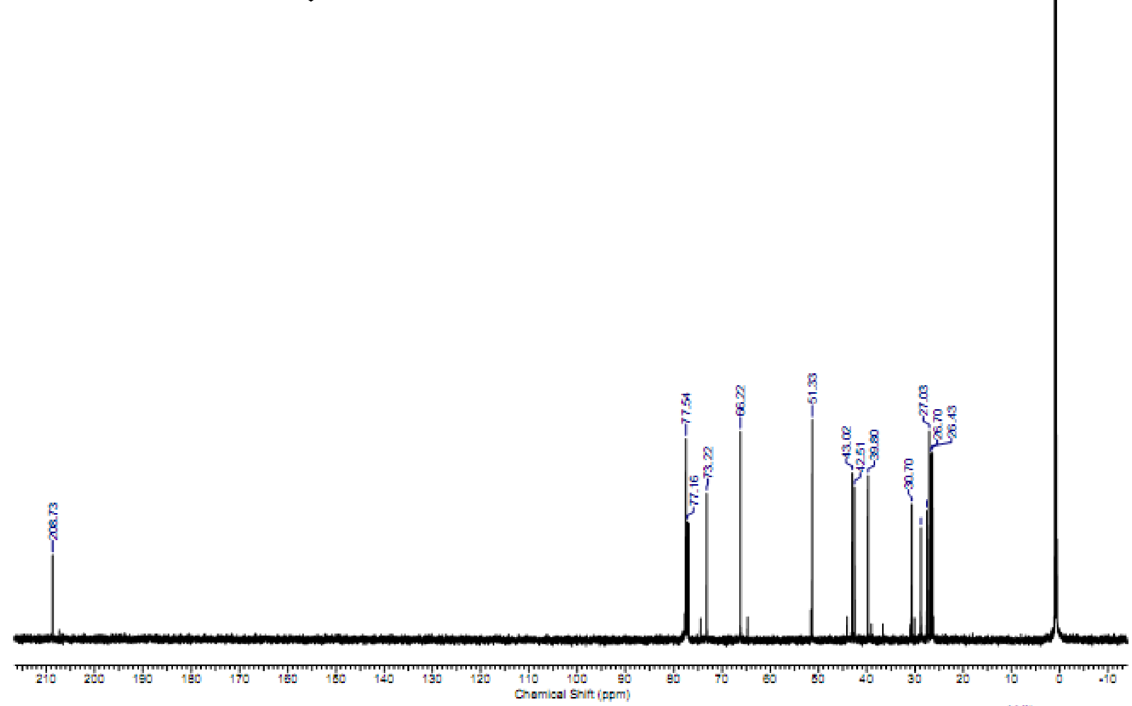
9b

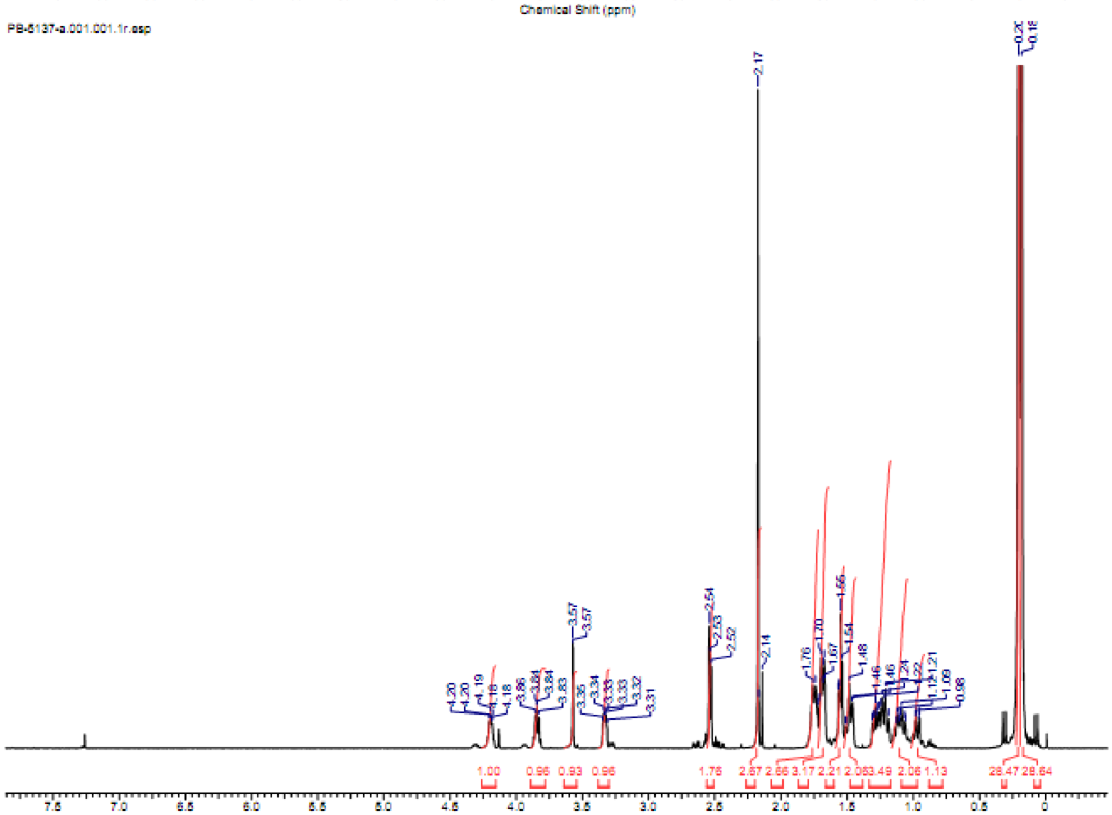

PB-5136-a.001.001.1r.esp
(TMS)3Si
Si(TMS)3
O
O
OH
O
TBSO
0.97
0.89
0.90
3.34
2.15
3.00
0.95
1.24
1.54
3.16
10.10
32.37
29.41


PB-5136-a.002.001.1r.esp
208.34
77.16
73.95
70.79
67.00
59.76
51.42
43.99
42.05
40.48
30.67
26.07
18.39
0.82
0.79
-5.32
Chemical Shift (ppm)

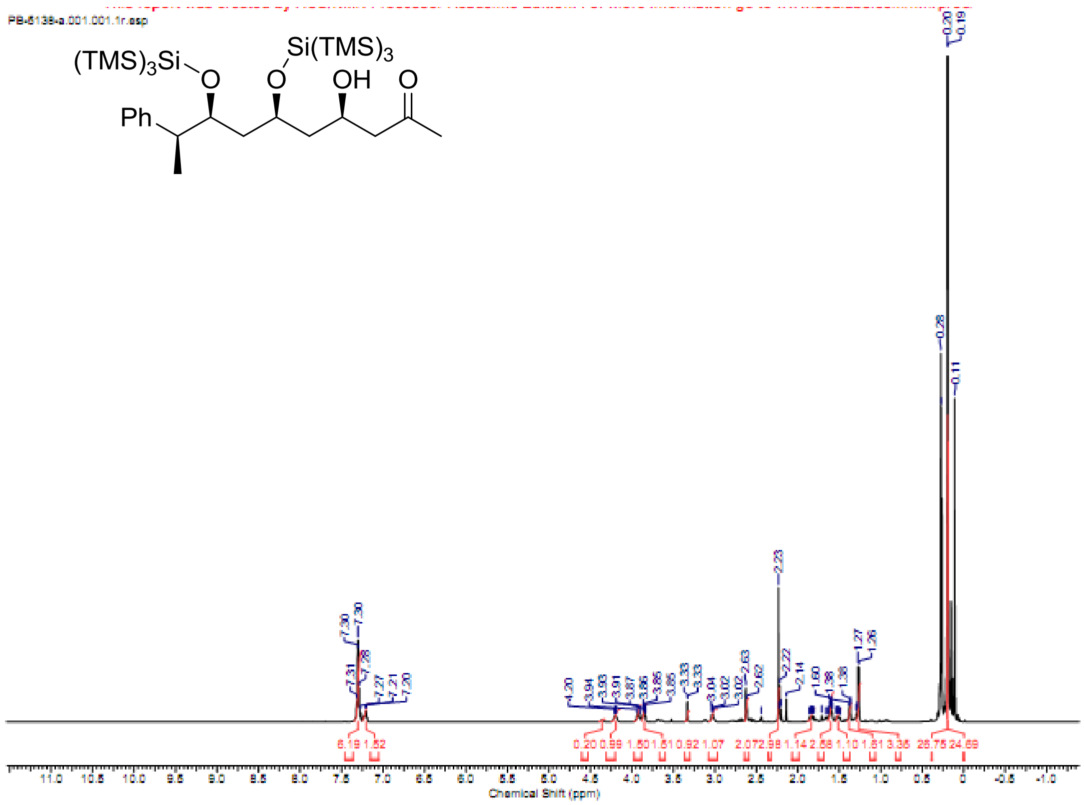
9c

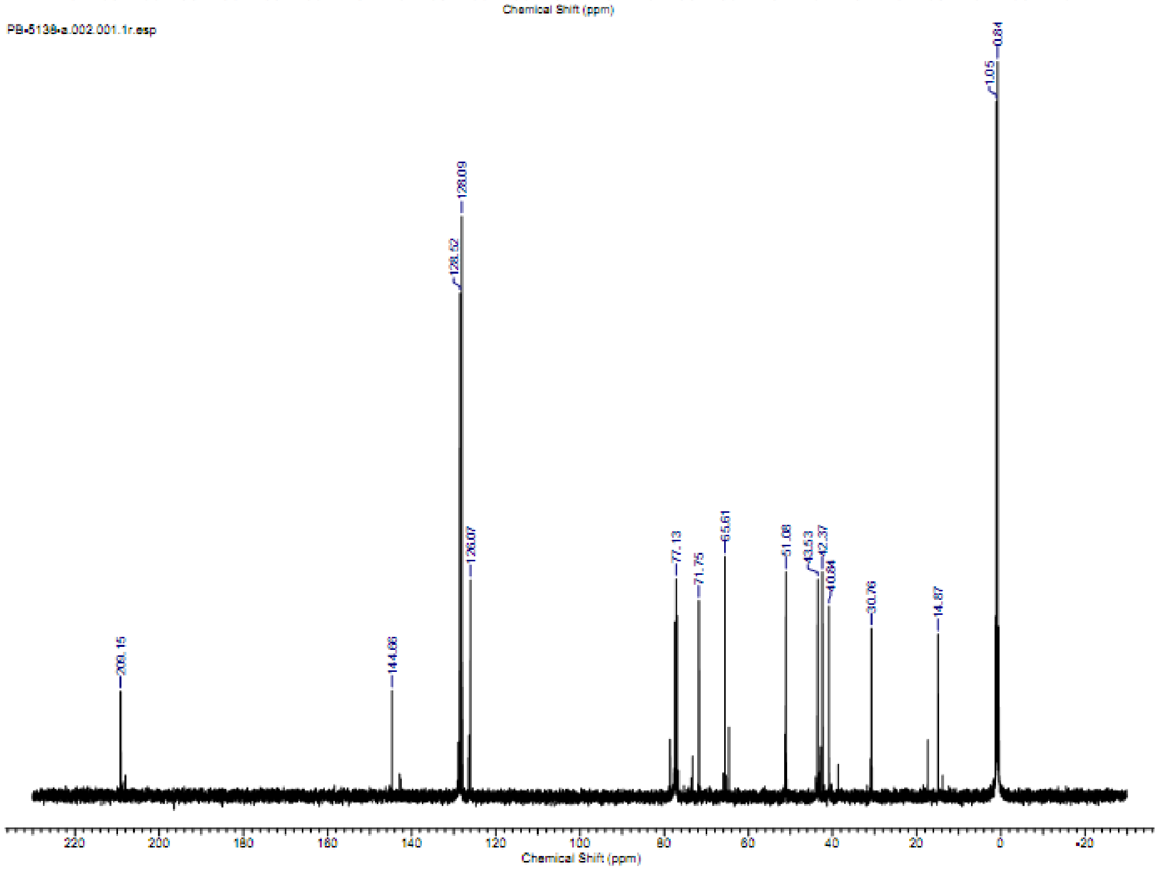

(TMS)3Si
Si(TMS)3
O
O
OH
O


PB-6137-a.002.001.1r.esp
208.73
77.54
77.16
73.22
66.22
51.33
43.02
42.51
39.80
30.70
27.03
26.70
26.43
0.99
0.78
Chemical Shift (ppm)

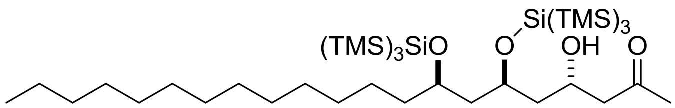

PB-6137-a.001.001.1r.esp
2.17
2.54
2.53
2.52
3.57
3.57
1.00
0.96
0.93
0.96
1.76
Chemical Shift (ppm)

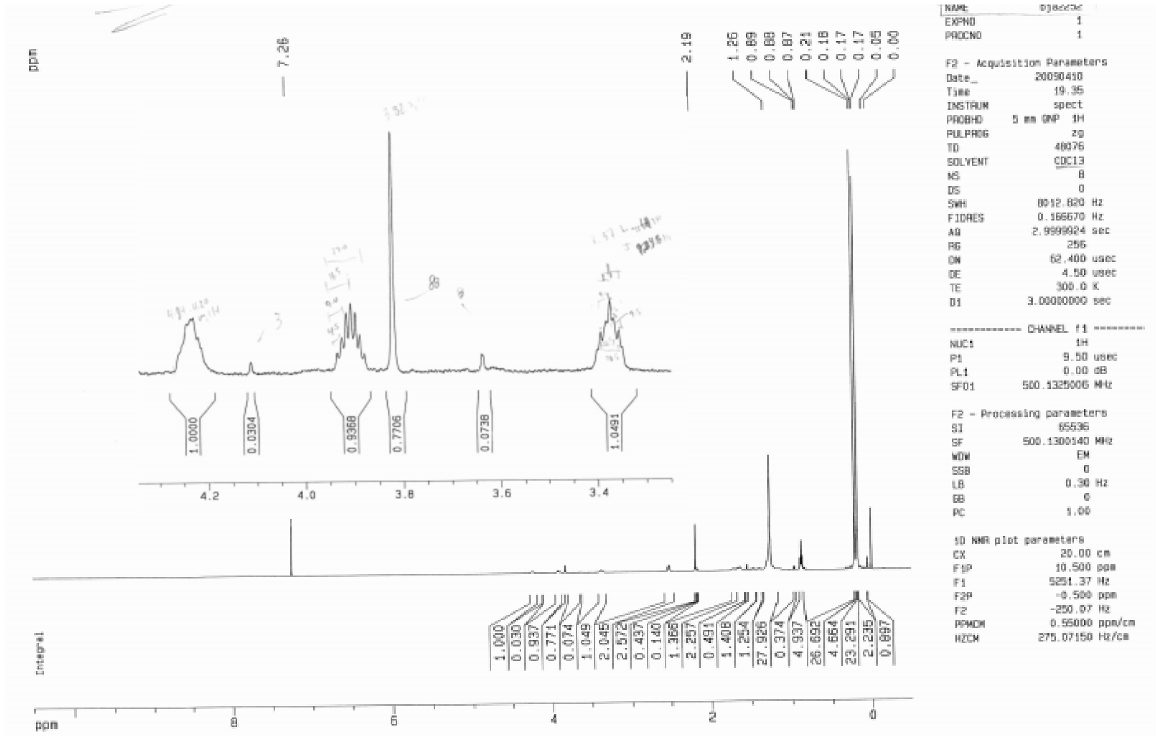
9d

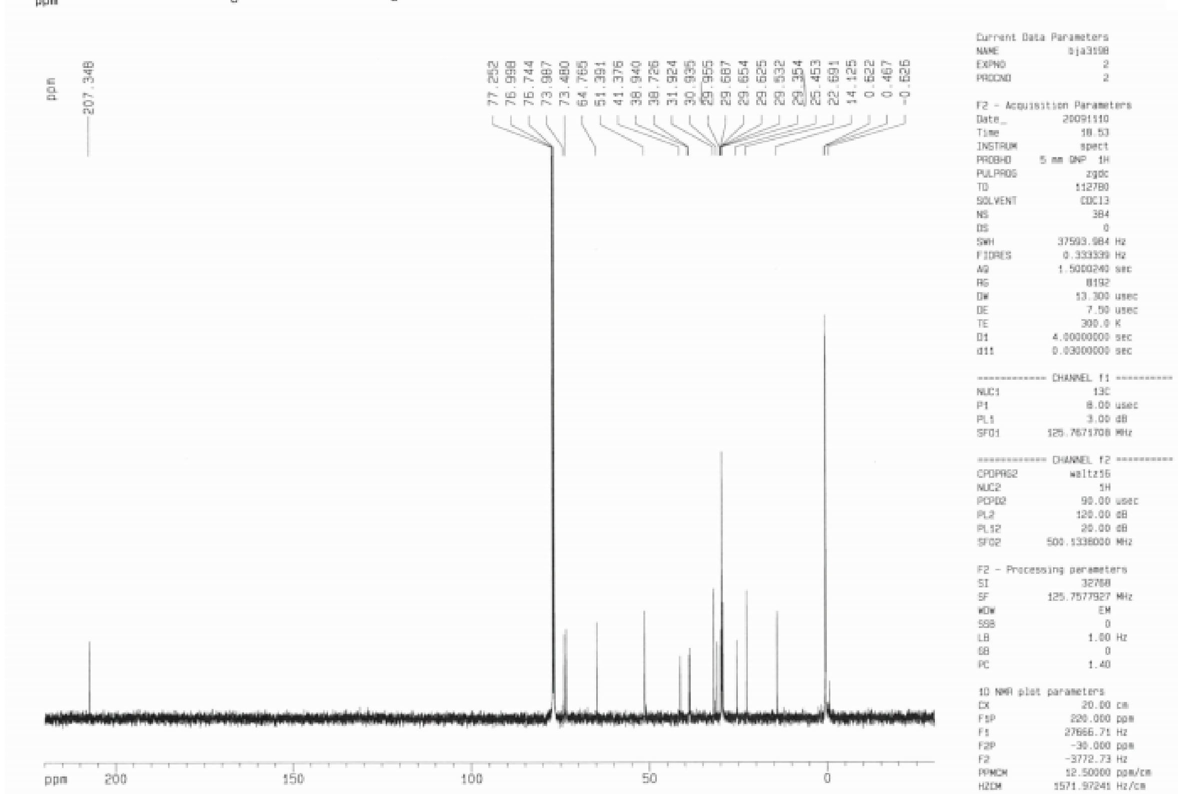

PB-5138-a.001.001.1r.esp
(TMS)3Si
Si(TMS)3
O
O
OH
O
Ph
Chemical Shift (ppm)


PB-5138-a.002.001.1r.esp
209.15
144.66
128.52
128.09
126.07
77.13
71.75
65.61
51.08
43.53
42.37
40.84
30.76
14.87
1.05
0.84
Chemical Shift (ppm)

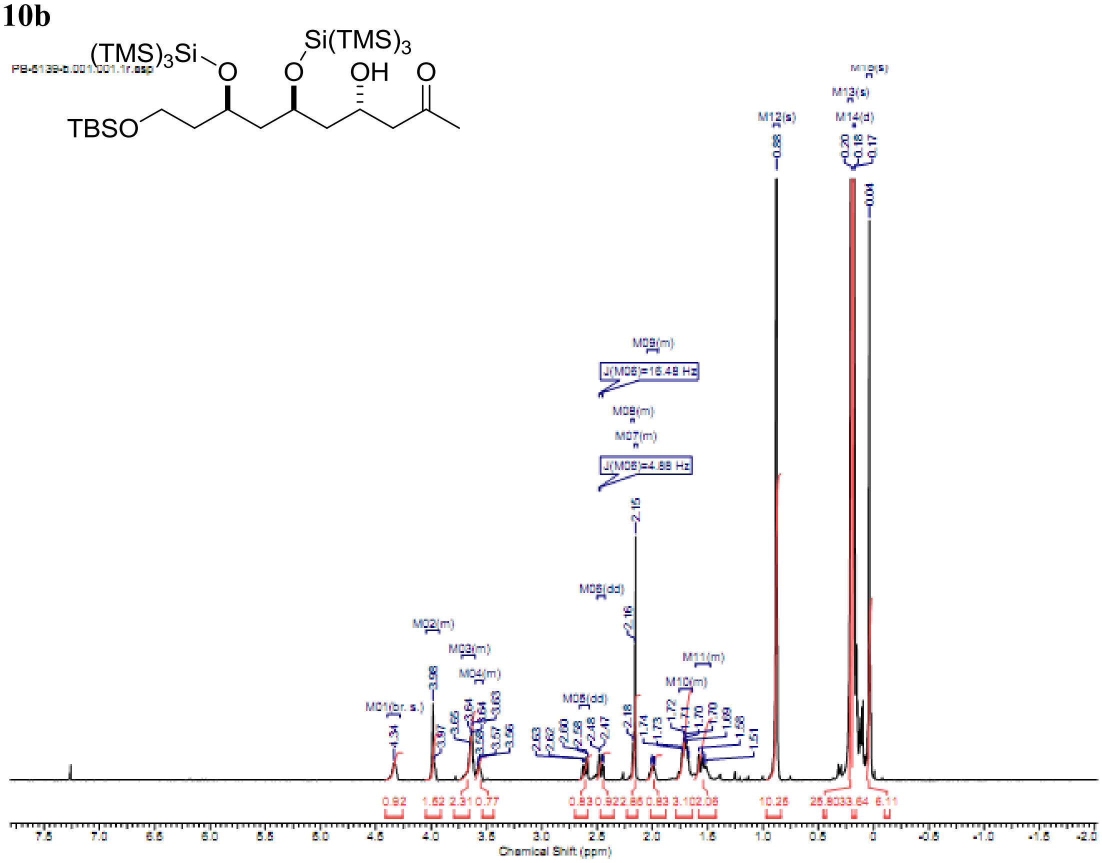
10a

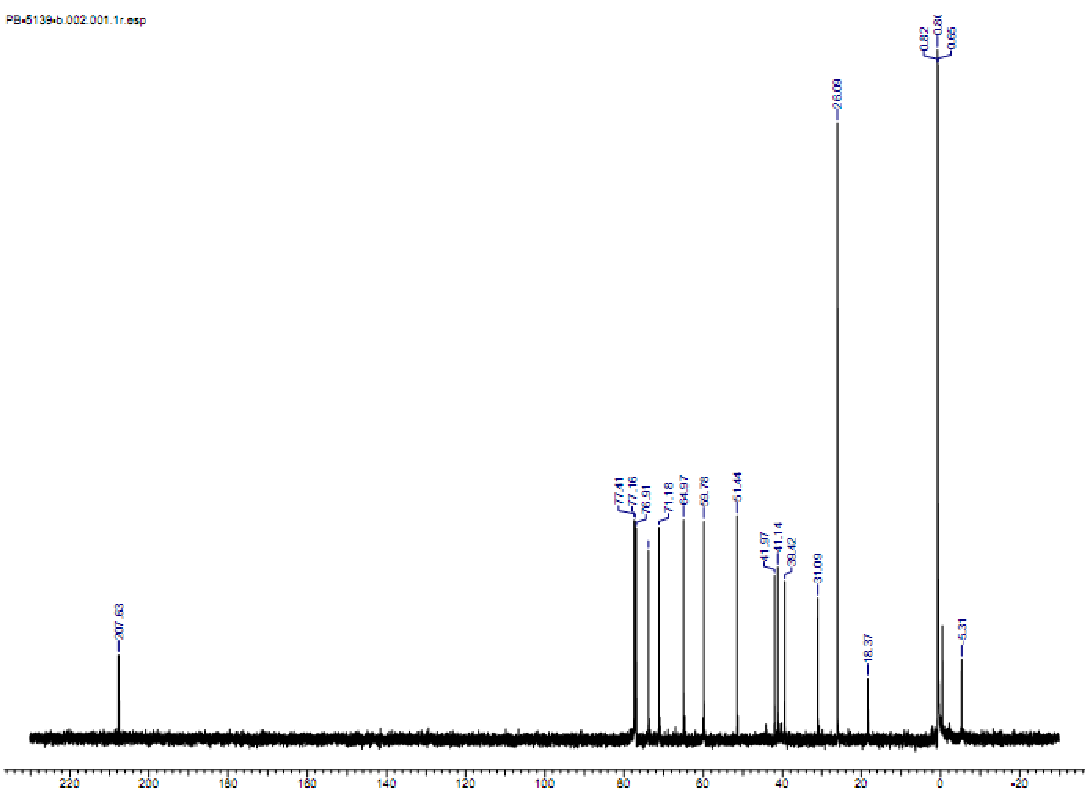




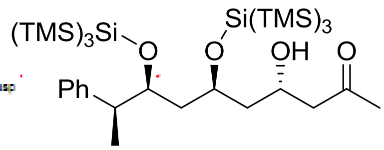


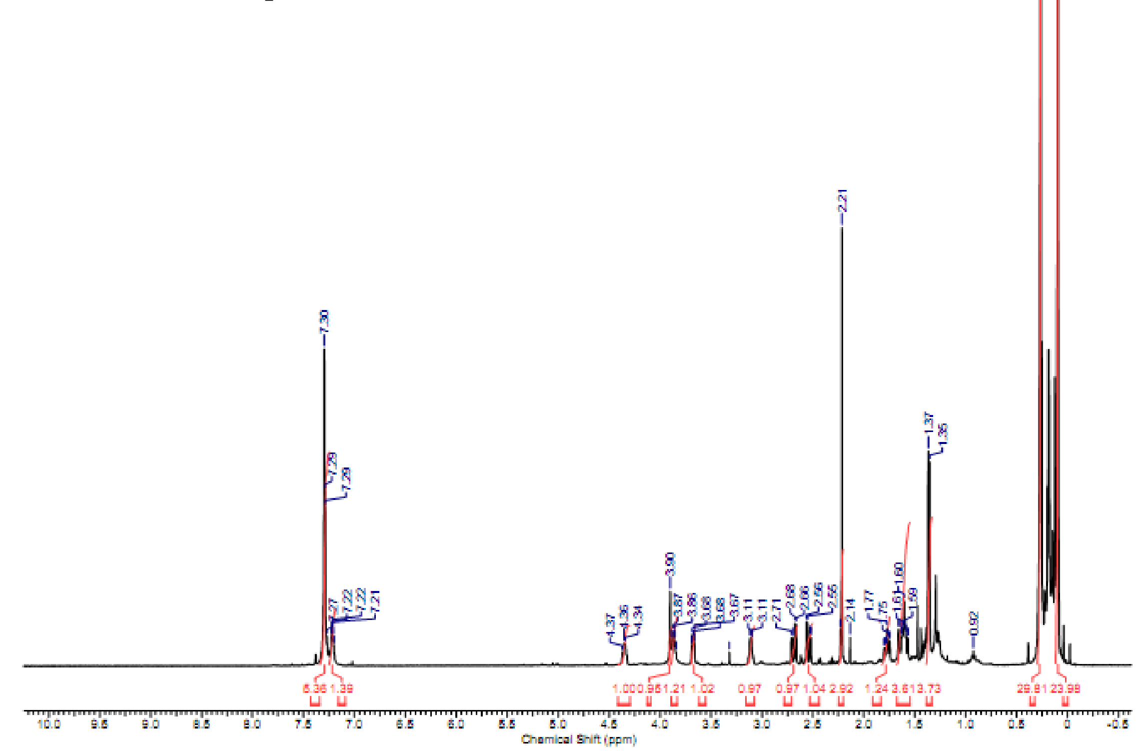
10b

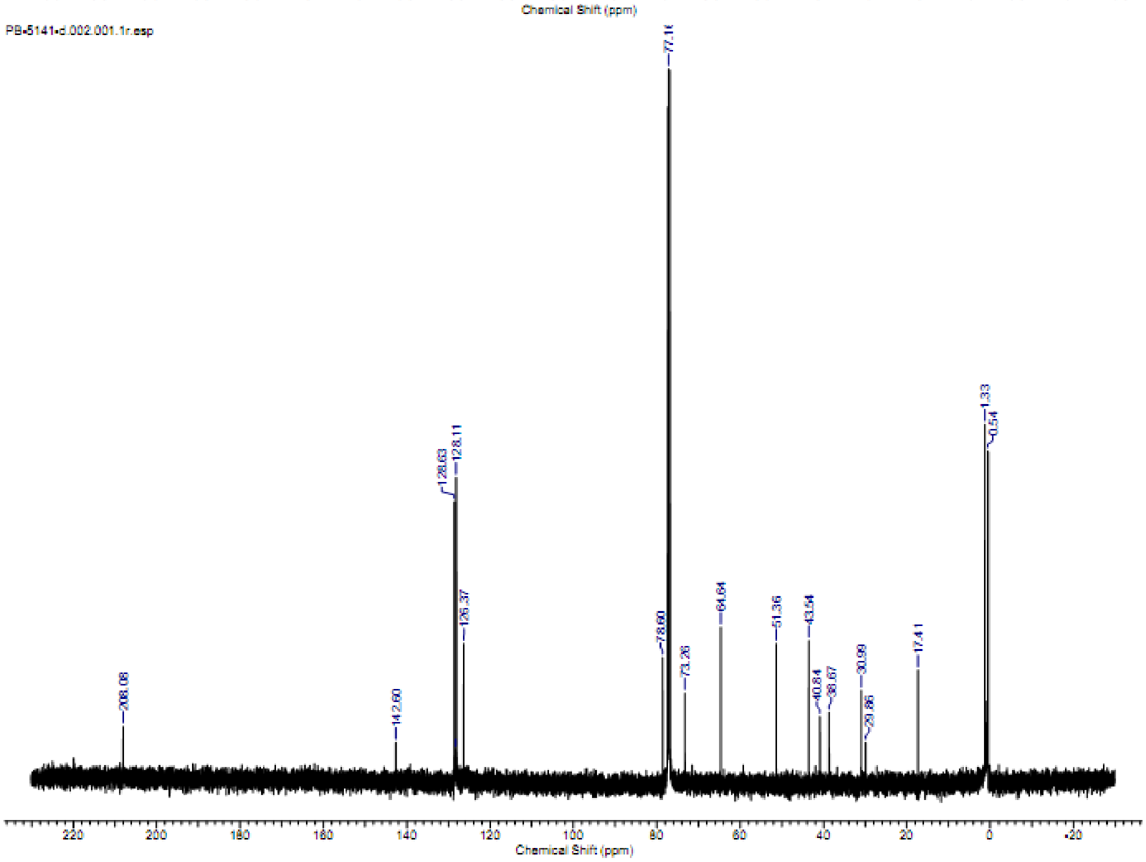

(TMS)3Si
Si(TMS)3
OH
O
TBSO
PB-5139-b.001.001.1r.esp
Chemical Shift (ppm)


PB-5139-b.002.001.1r.esp
Chemical Shift (ppm)

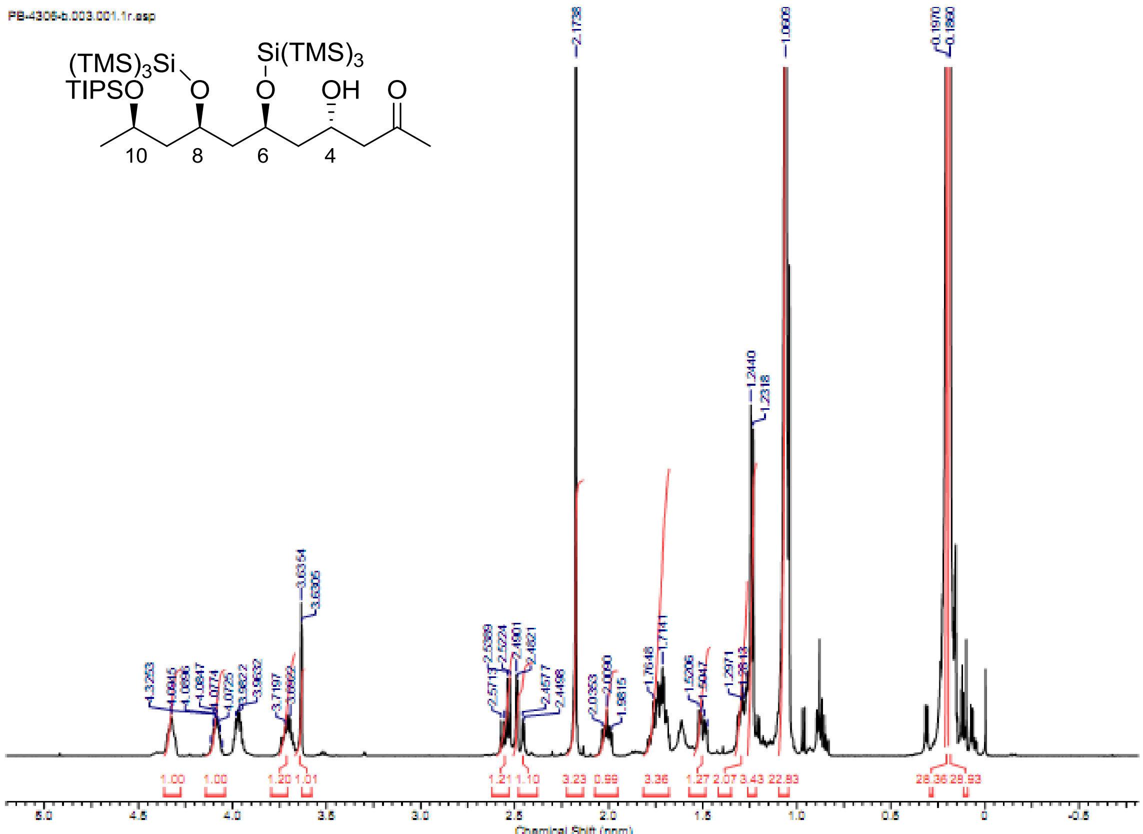
10d

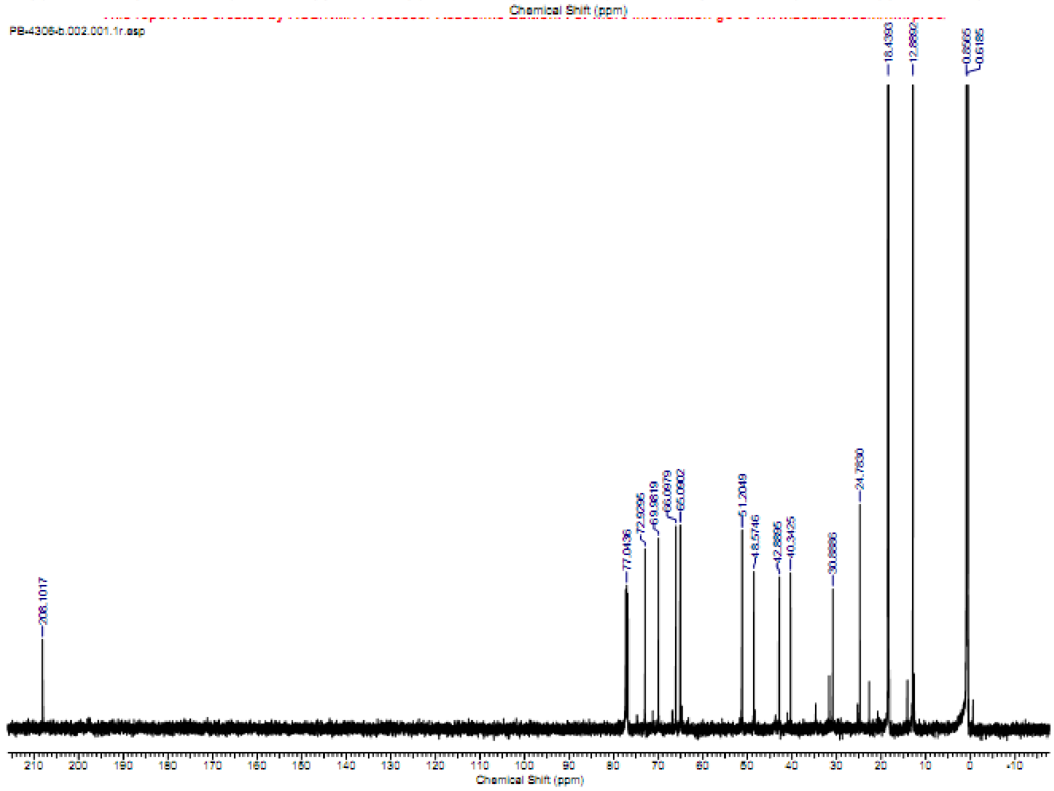

(TMS)3Si
Si(TMS)3
O
O
OH
O
Ph


PB-5141-d.001.001.1r.esp
7.30
7.29
7.29
7.27
7.22
7.22
7.21
4.37
4.36
4.34
3.90
3.87
3.86
3.68
3.68
3.67
3.11
3.11
2.71
2.68
2.66
2.56
2.55
2.21
2.14
1.77
1.75
1.61
1.60
1.59
1.37
1.35
0.92
0.27
0.10
6.36
1.39
1.00
0.96
1.21
1.02
0.97
0.97
1.04
2.92
1.24
3.61
3.73
29.81
23.98
Chemical Shift (ppm)

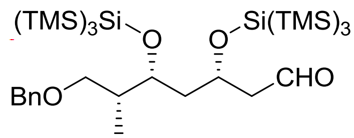

PB-5141-d.002.001.1r.esp
208.08
142.60
128.63
128.11
126.37
78.60
77.16
73.26
64.64
51.36
43.54
40.84
38.67
30.99
29.86
17.41
1.33
0.54
Chemical Shift (ppm)

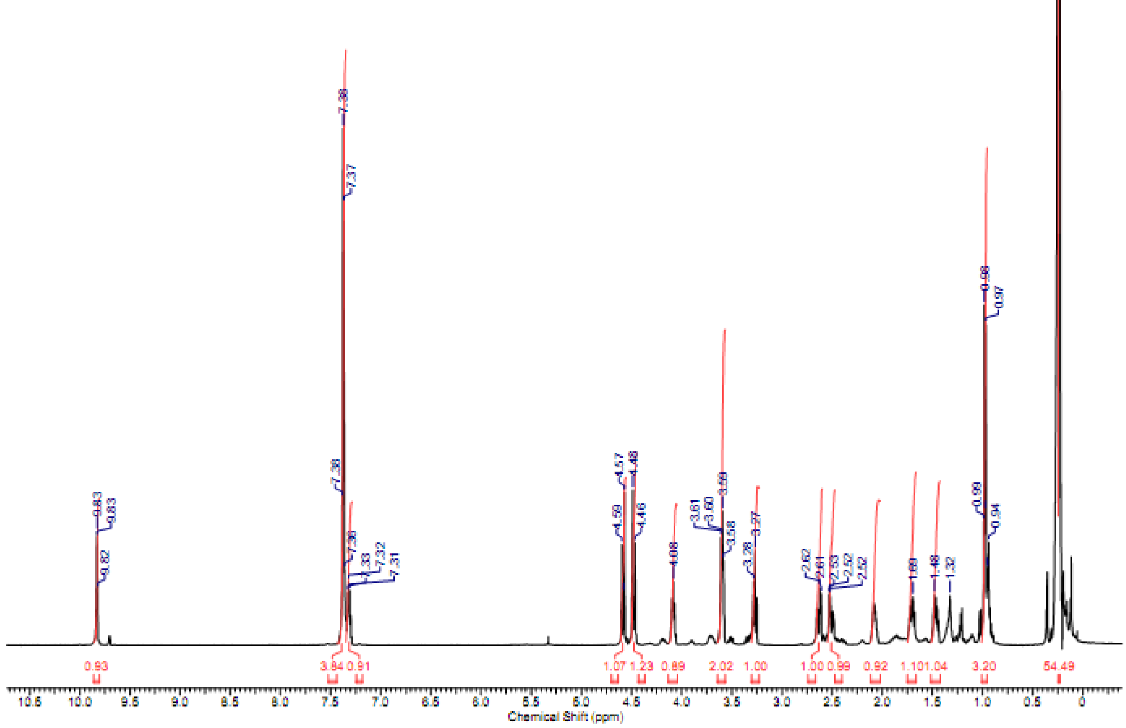
10e

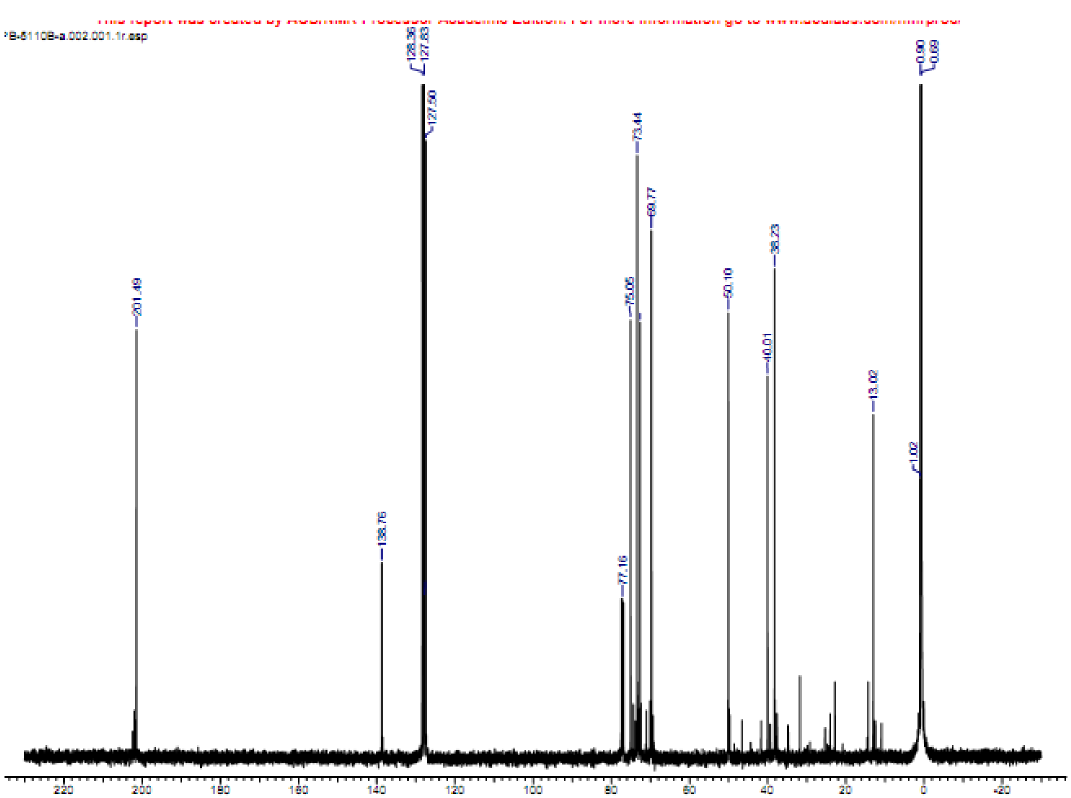

PB-4306-b.003.001.1r.esp
(TMS)3Si
TIPSO
O
Si(TMS)3
O
OH
O
10
8
6
4
Chemical Shift (ppm)


PB-4306-b.002.001.1r.esp
208.1017
77.0436
72.9295
69.9819
66.0979
65.0902
61.2049
58.5746
42.8895
40.3425
30.8886
24.7630
18.4393
12.8802
0.8565
0.6185
Chemical Shift (ppm)

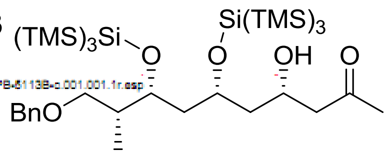
12

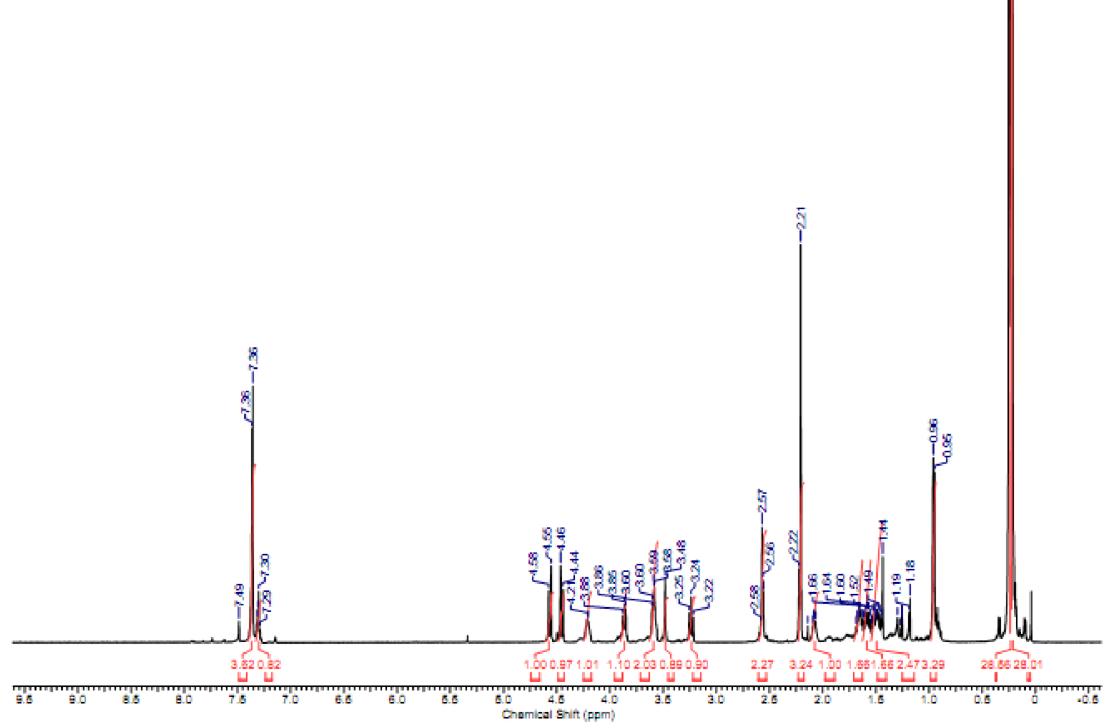

(TMS)3Si
Si(TMS)3
O
O
BnO
CHO

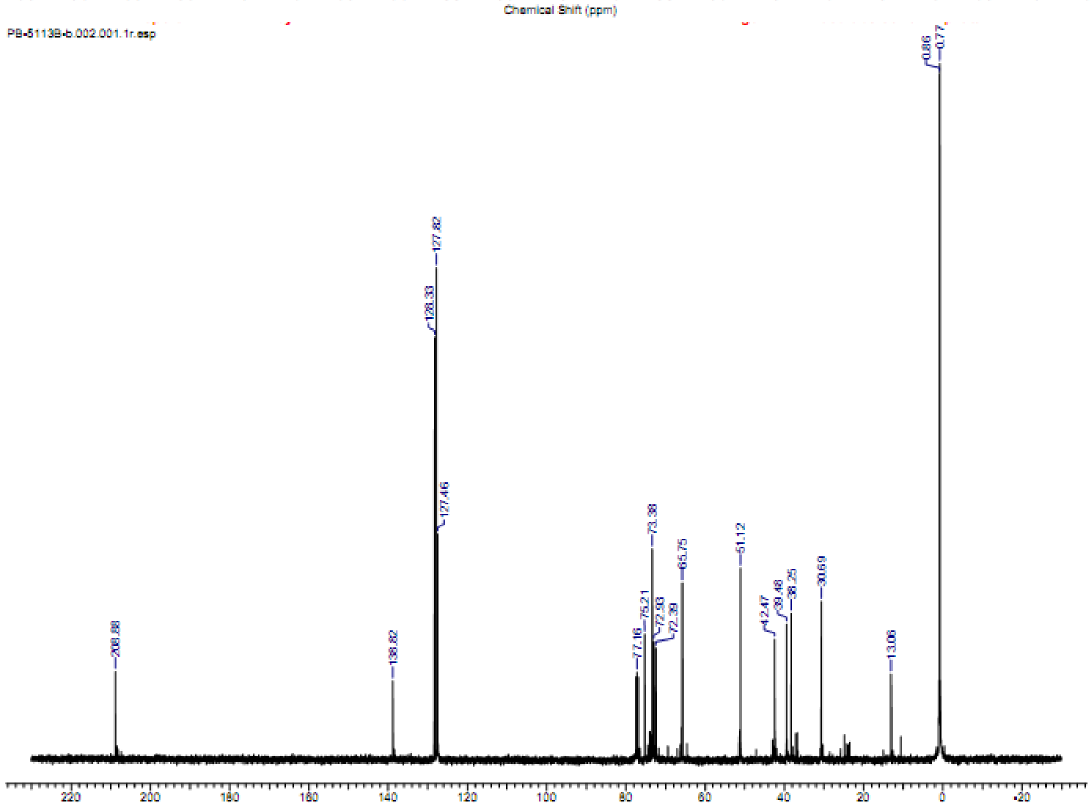

PB-5110B-a.001.001.1r.esp
Chemical Shift (ppm)


PB-5110B-a.002.001.1r.esp
Chemical Shift (ppm)

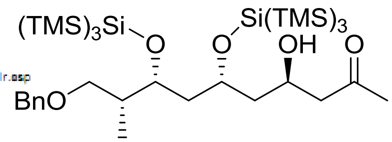
13

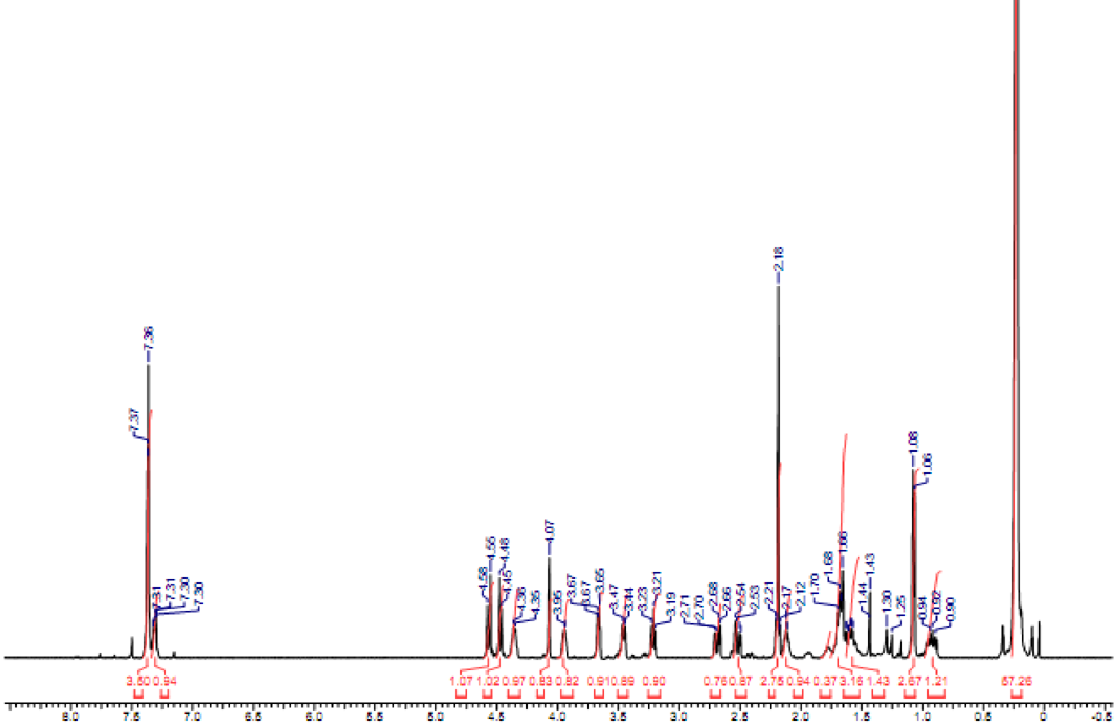

(TMS)$_3$Si
Si(TMS)$_3$
OH
O
BnO

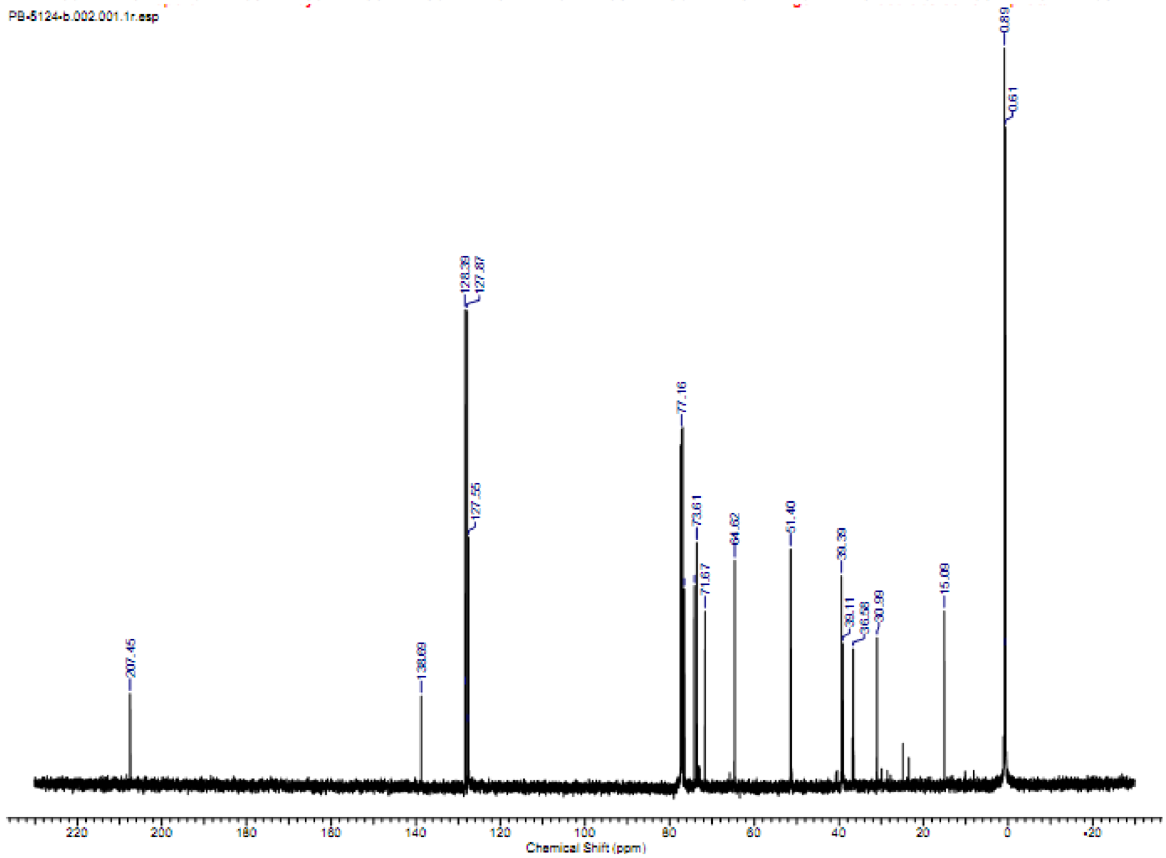

PB-5113B-c.001.001.1r.esp
Chemical Shift (ppm)


PB-5113B-b.002.001.1r.esp
Chemical Shift (ppm)

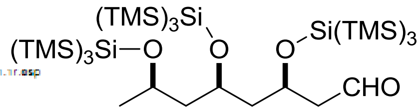
14

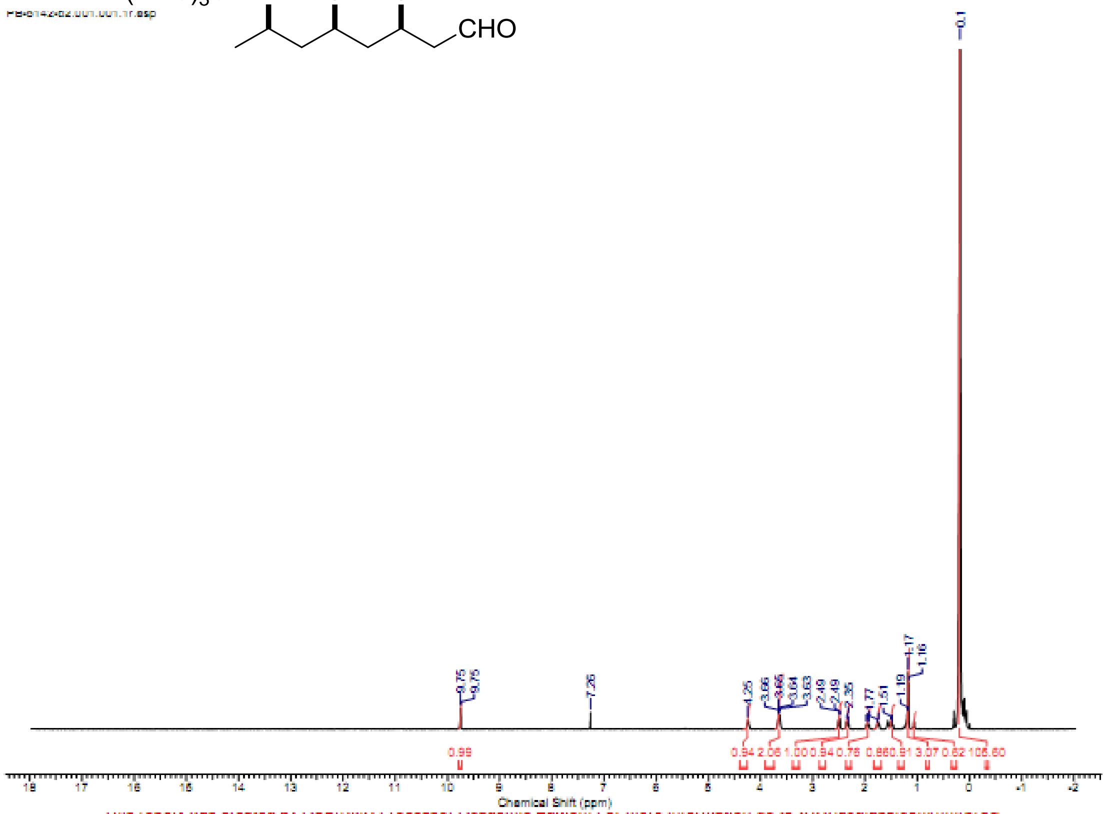

(TMS)3Si
O
O
Si(TMS)3
OH
O
BnO

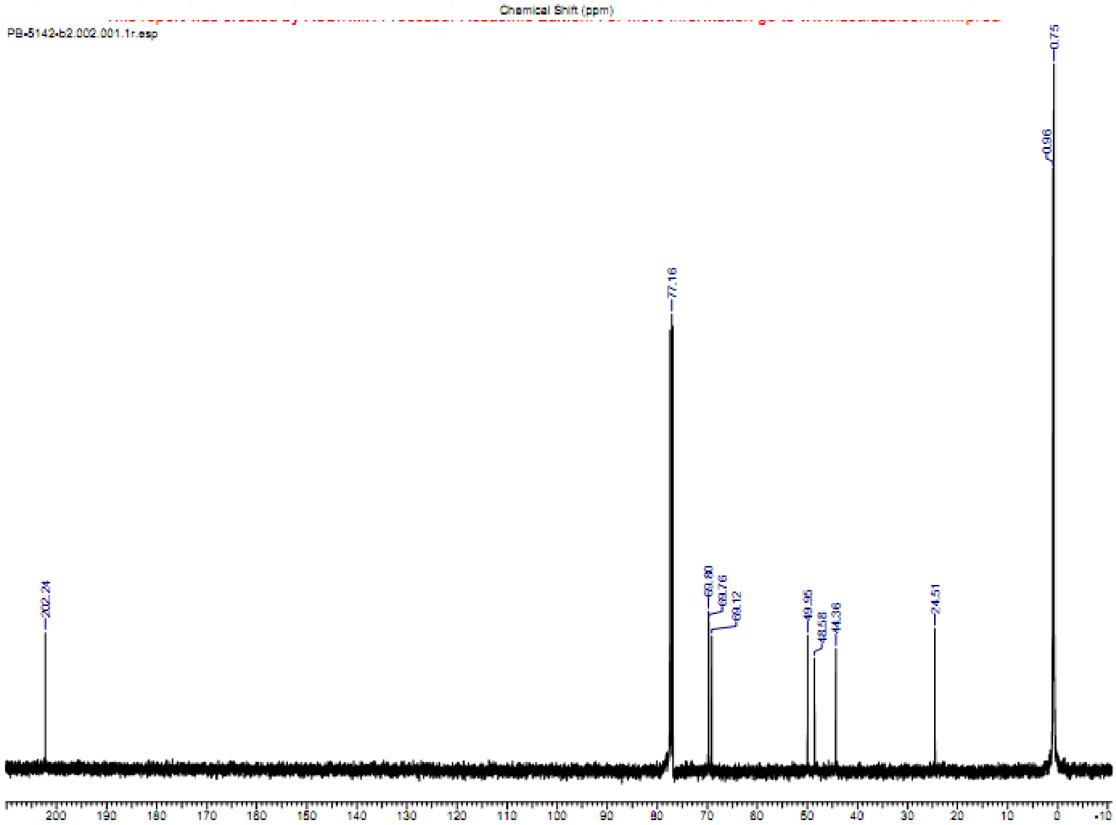

PB-5124-b.001.001.1r.esp


PB-5124-b.002.001.1r.esp
Chemical Shift (ppm)

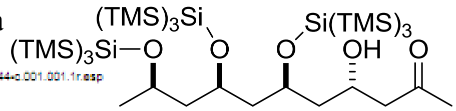
15a


(TMS)3Si
(TMS)3Si—O
O
O
Si(TMS)3
CHO

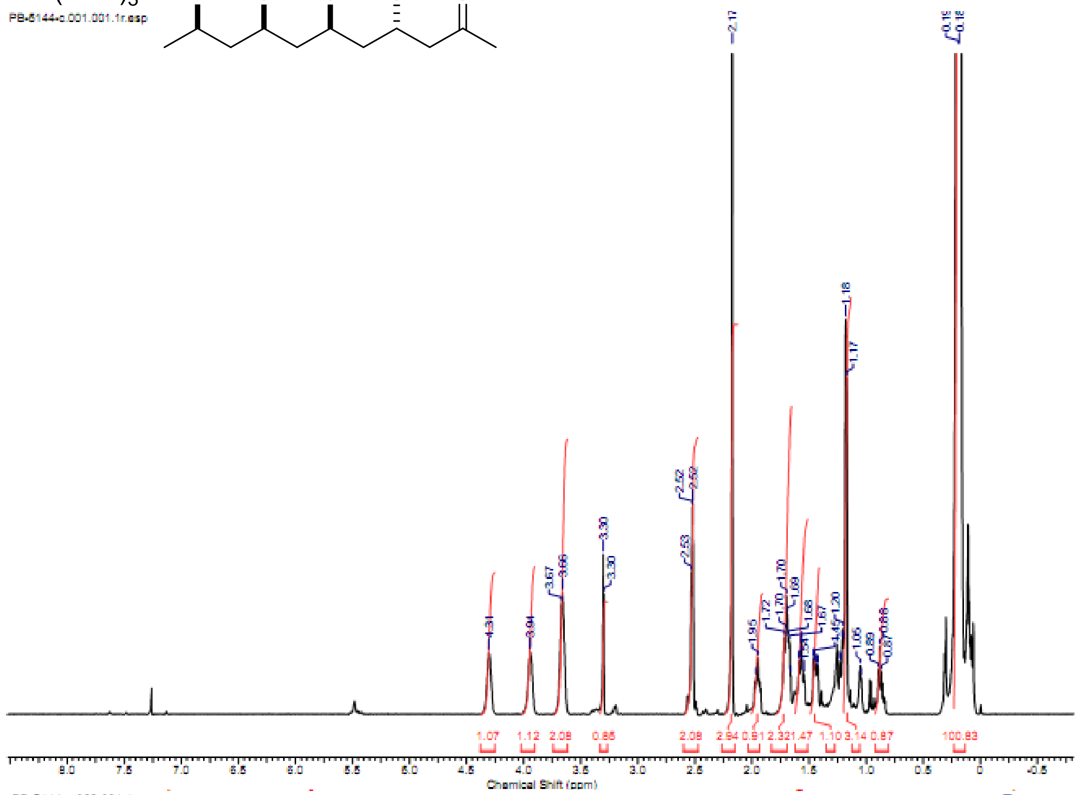

PB-5142-b2.001.001.1r.esp
Chemical Shift (ppm)


PB-5142-b2.002.001.1r.esp
Chemical Shift (ppm)

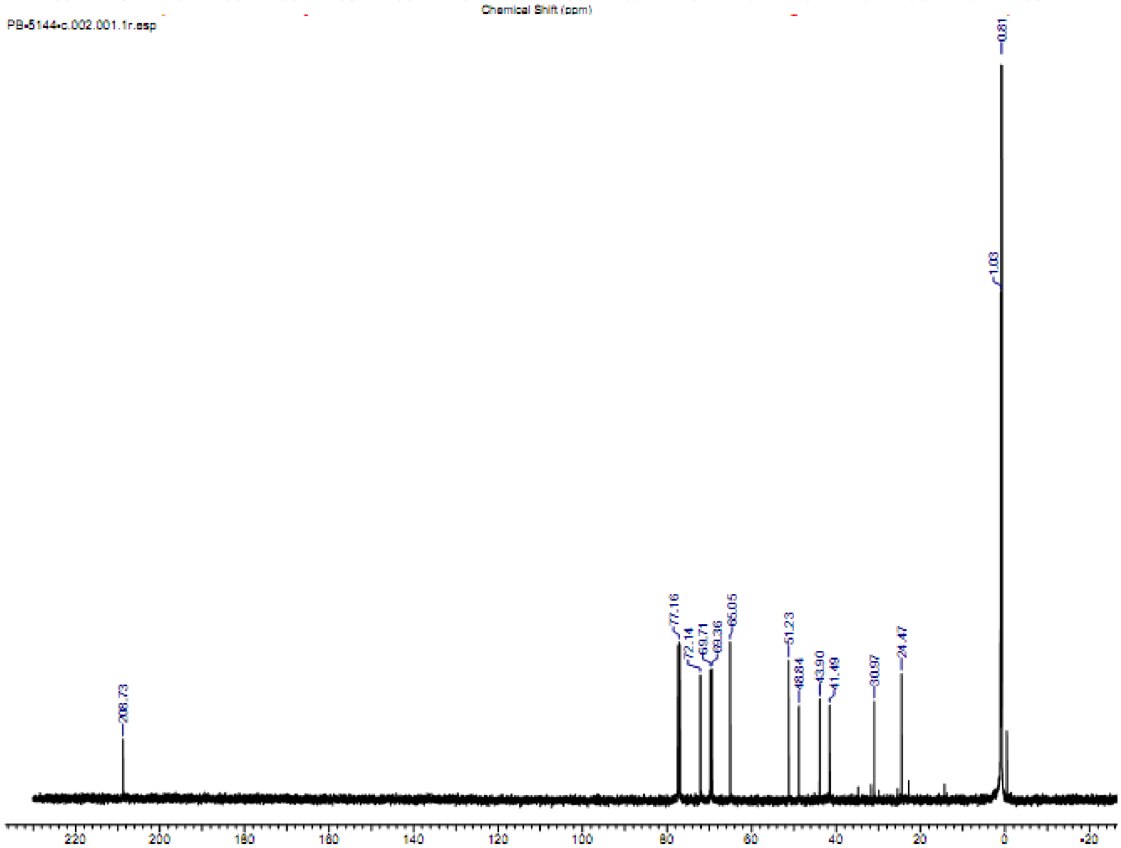
16a



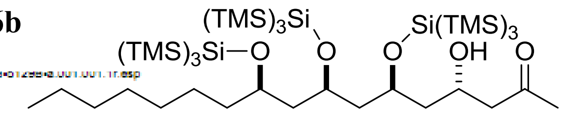
PB-5144-c.001.001.1r.esp

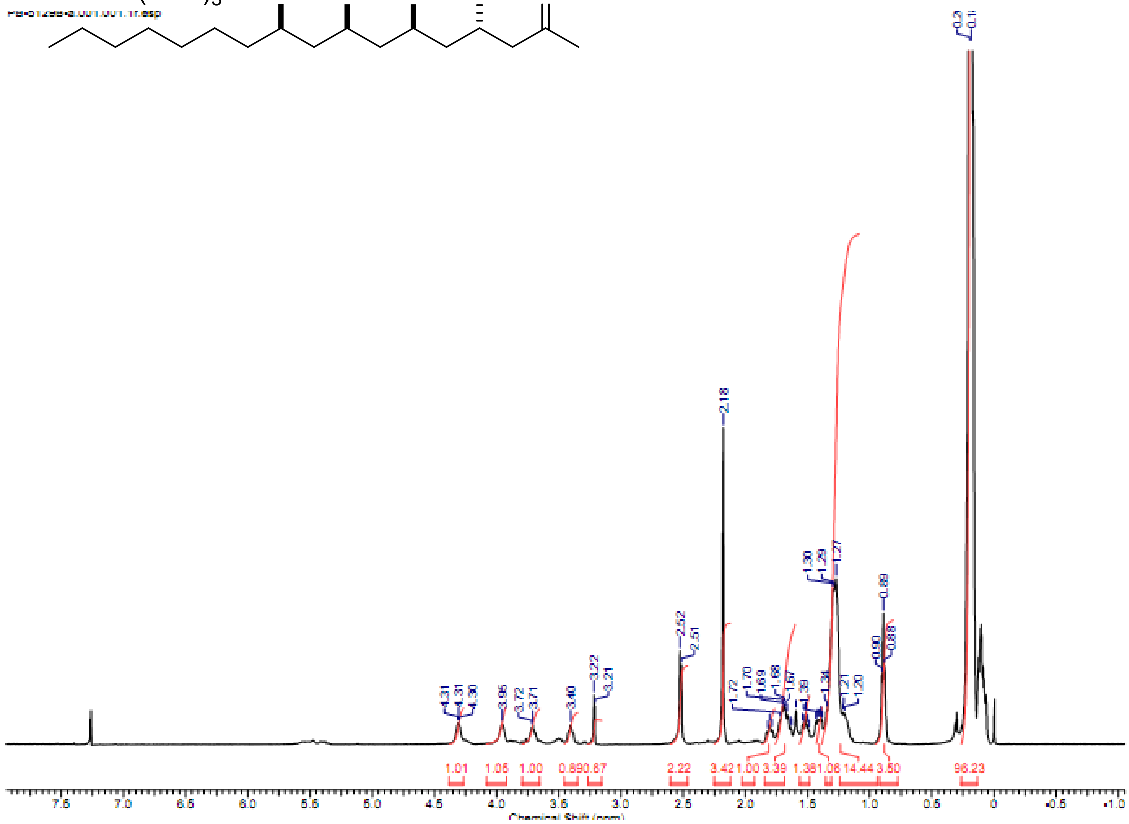


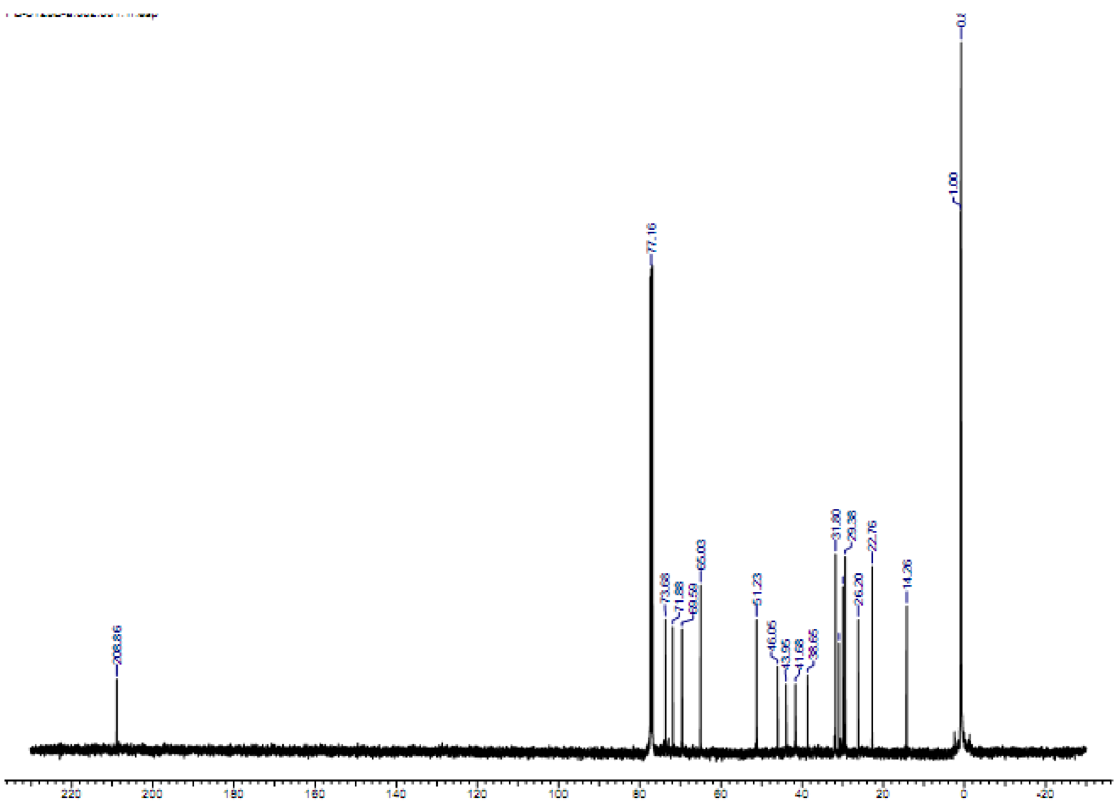
PB-5144-c.002.001.1r.esp



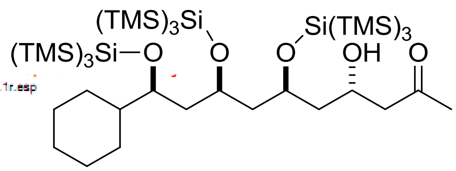
16b

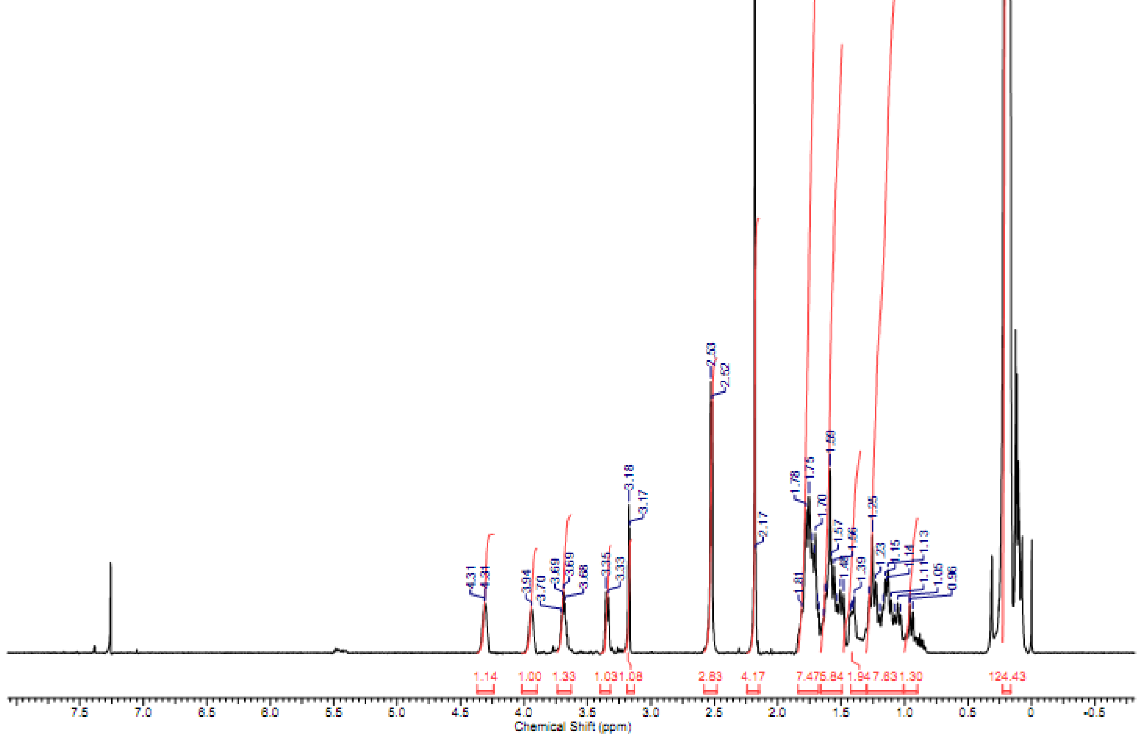


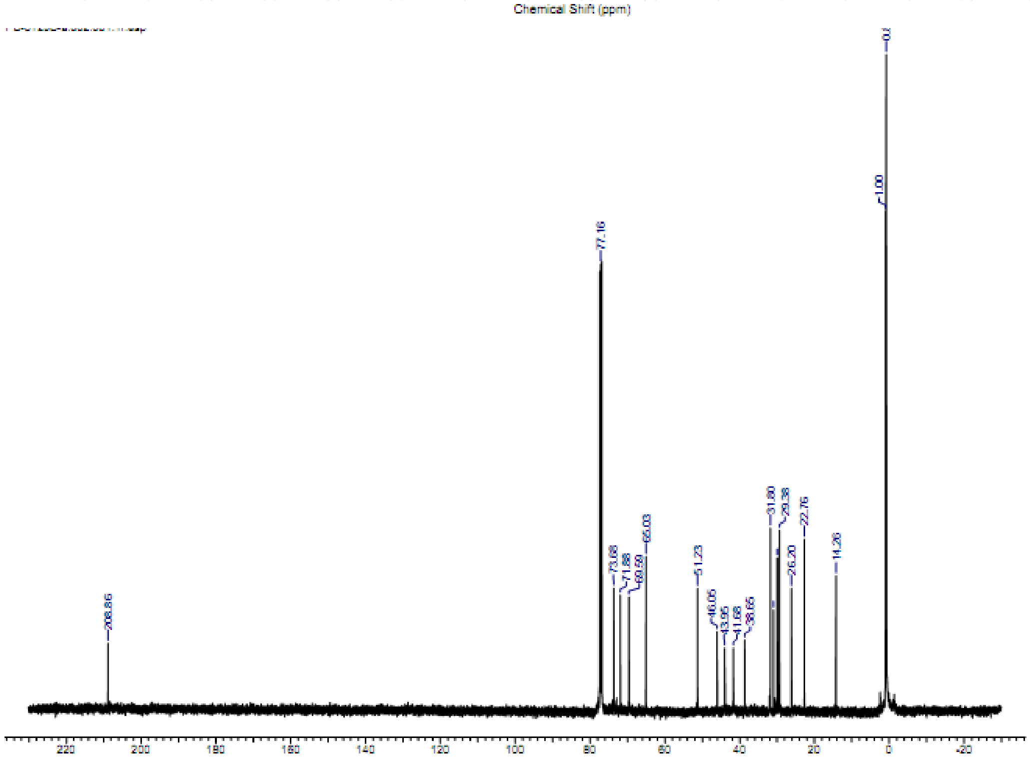




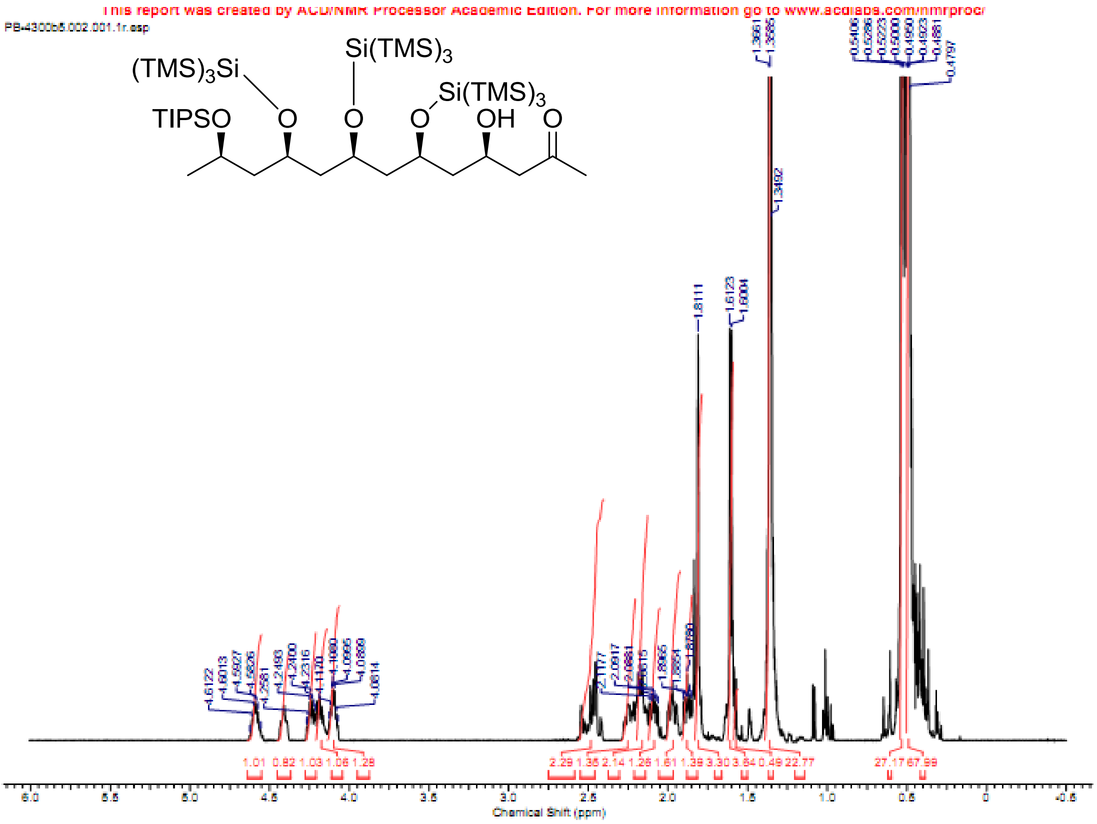
16c

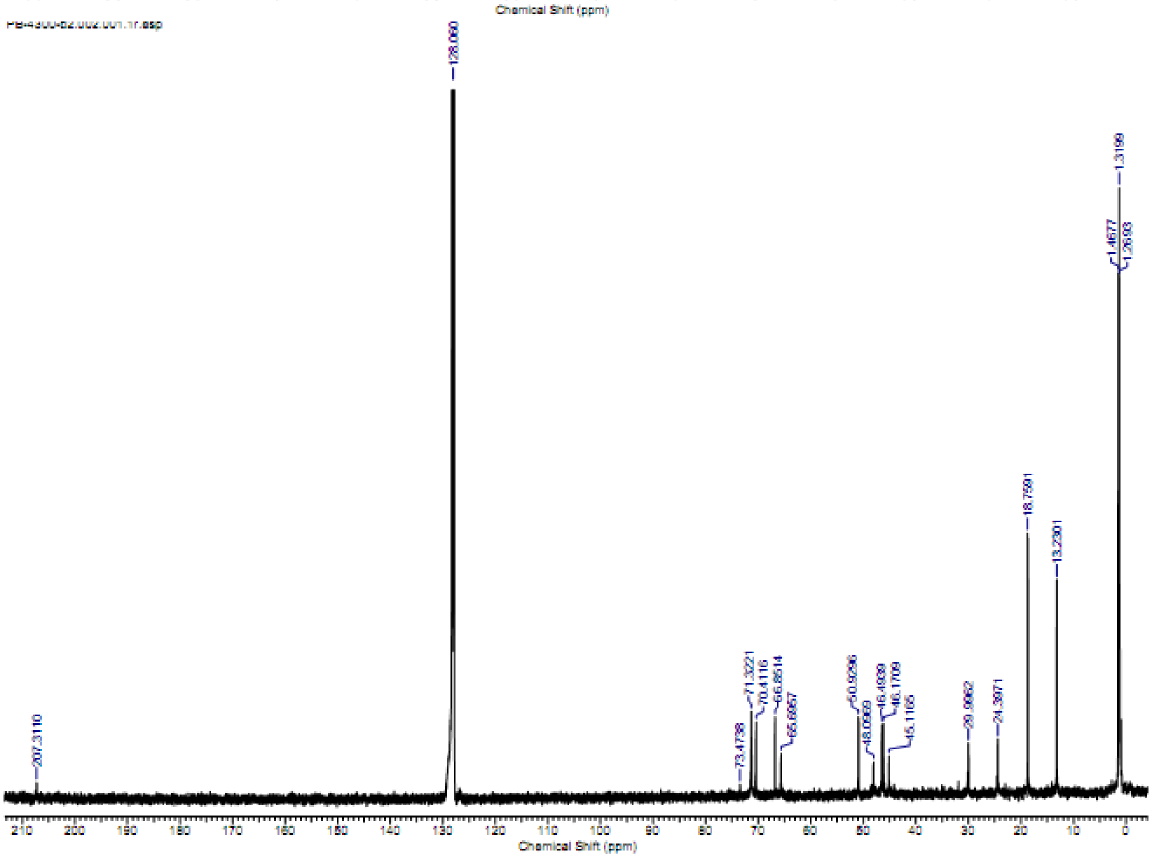

(TMS)3Si
(TMS)3Si—O
O
O
Si(TMS)3
OH
O


PB-5129A-a.001.001.1r.esp
Chemical Shift (ppm)

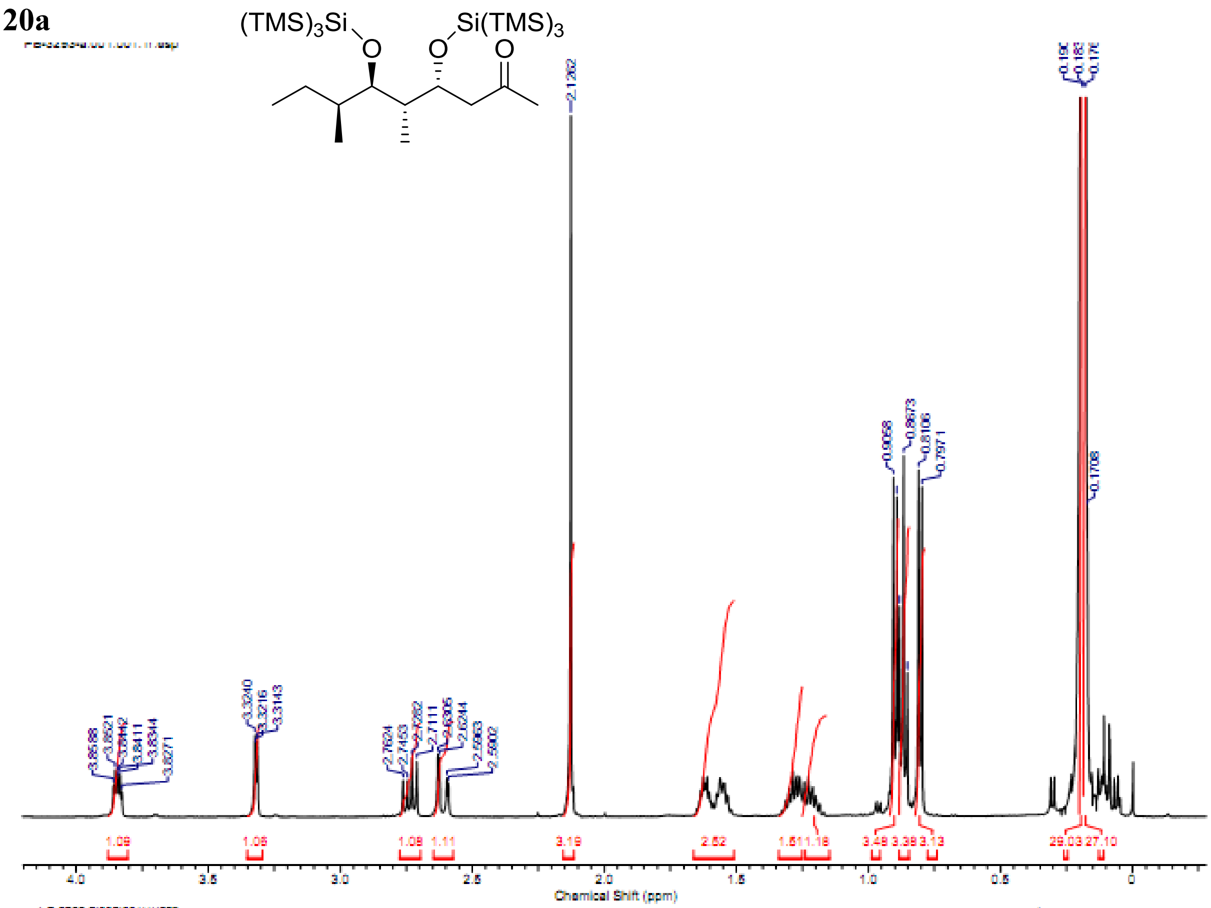

Chemical Shift (ppm)

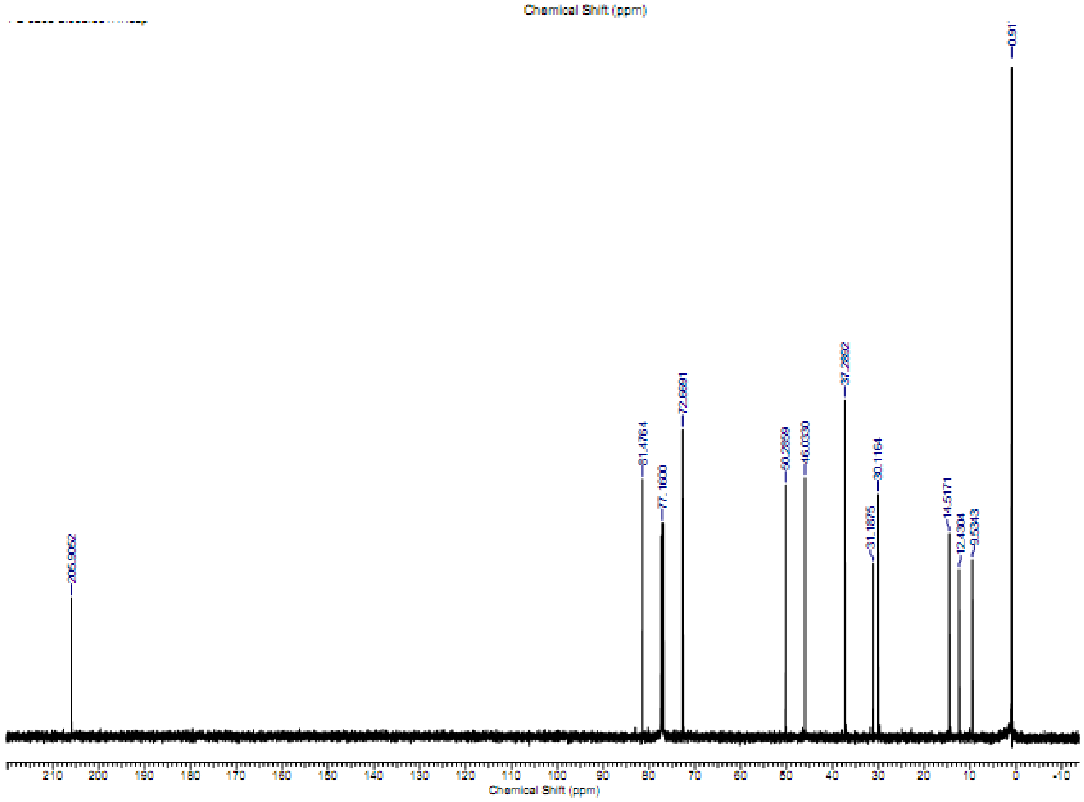
18


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
PB-4300b5.002.001.1r.esp
(TMS)3Si
Si(TMS)3
Si(TMS)3
TIPSO
O
O
O
OH
O
Chemical Shift (ppm)


PB-4300-b2.002.001.1r.esp
128.060
207.3110
73.4738
71.3221
70.4116
66.8514
65.6957
50.9296
48.0969
46.4939
46.1709
45.1105
29.9962
24.3971
18.7591
13.2301
1.4677
1.3199
1.2693
Chemical Shift (ppm)

20a


(TMS)3Si
Si(TMS)3
O
O
O
2.1262
0.9068
0.8673
0.8106
0.7971
0.1708
3.3240
3.3216
3.3143
1.09
1.06
1.09
1.11
3.19
2.52
1.51
1.18
3.49
3.39
3.13
29.03
27.10
Chemical Shift (ppm)


0.91
205.9062
81.4764
77.1600
72.6691
50.2959
46.0330
37.2892
31.1675
30.1164
14.5171
12.4304
9.5343
Chemical Shift (ppm)

Electronic Supplementary Material (ESI) for Chemical Science
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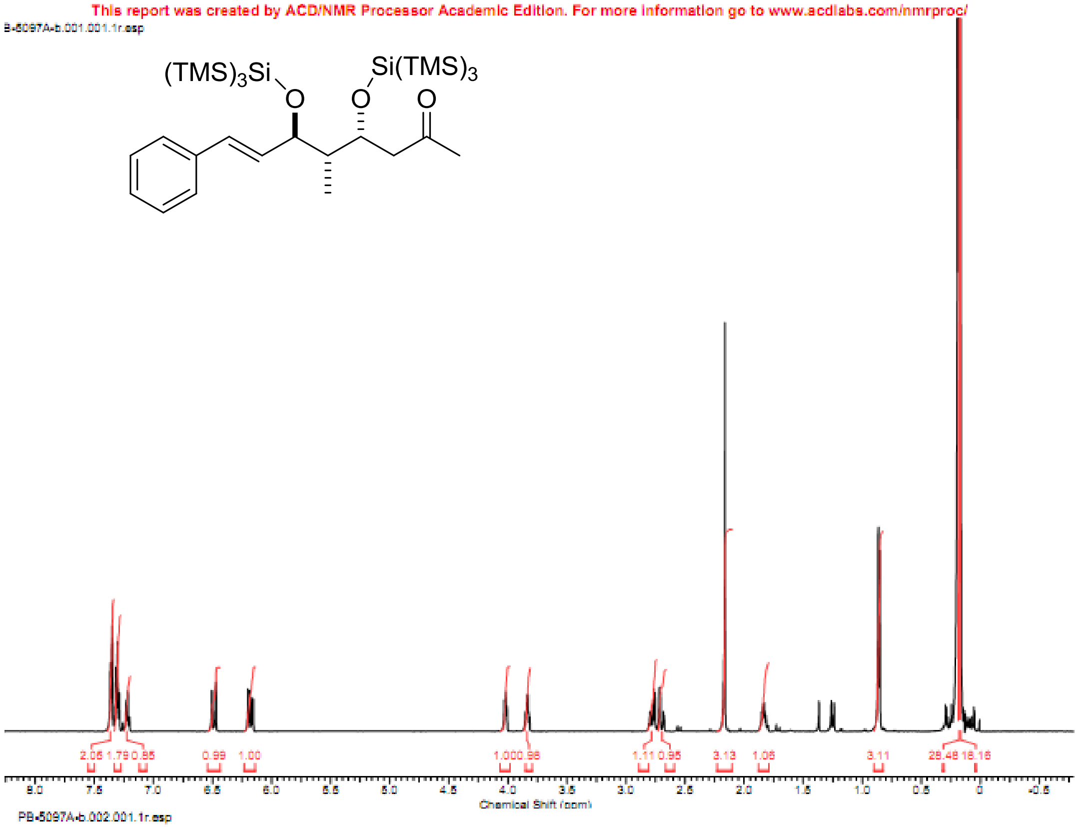
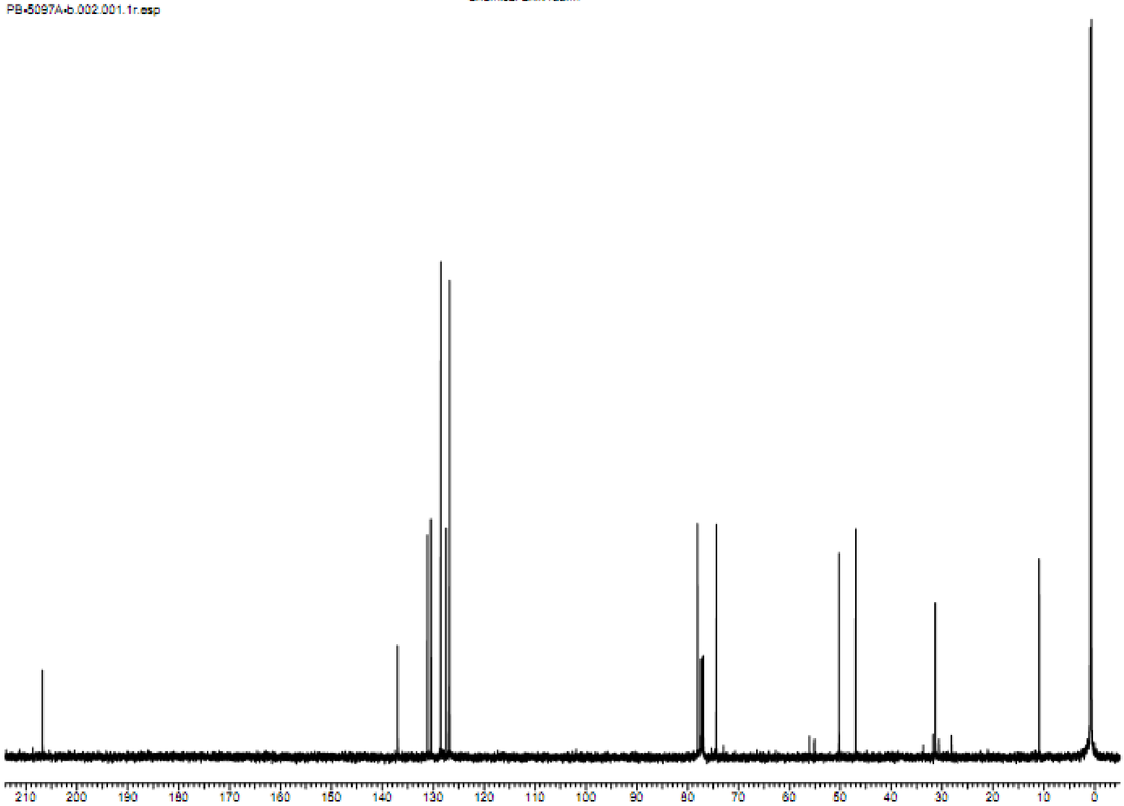
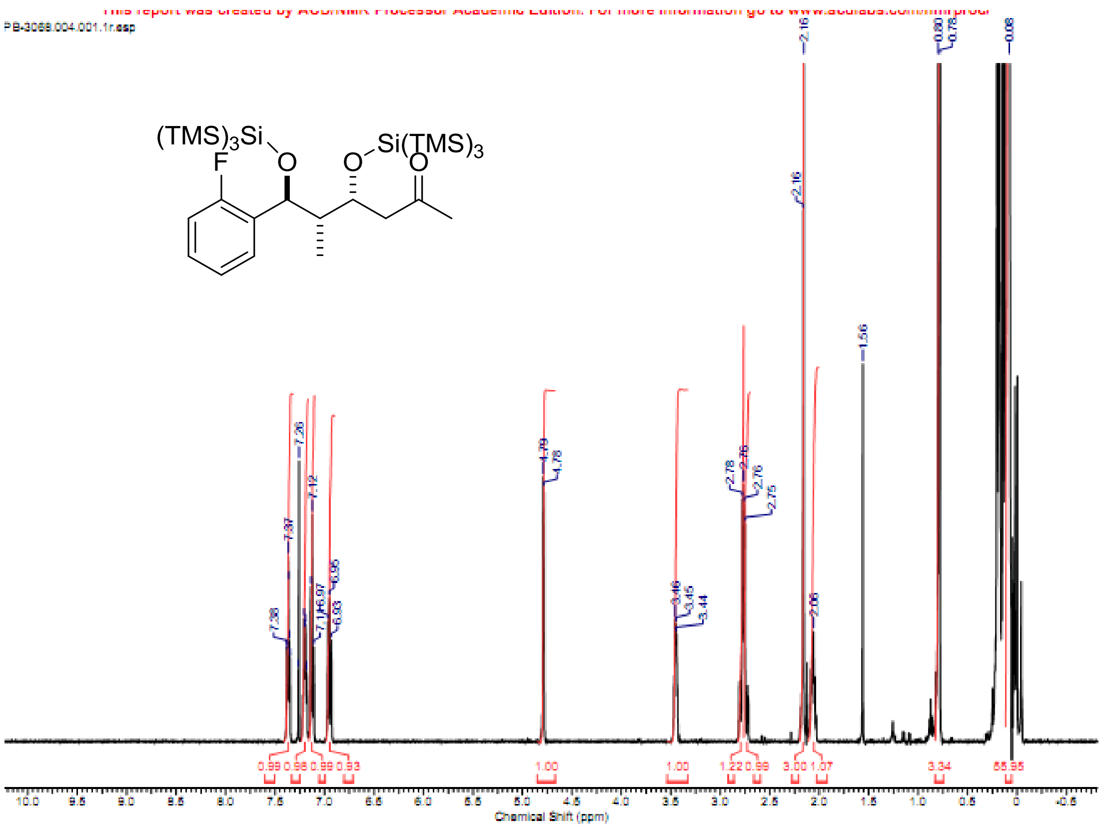
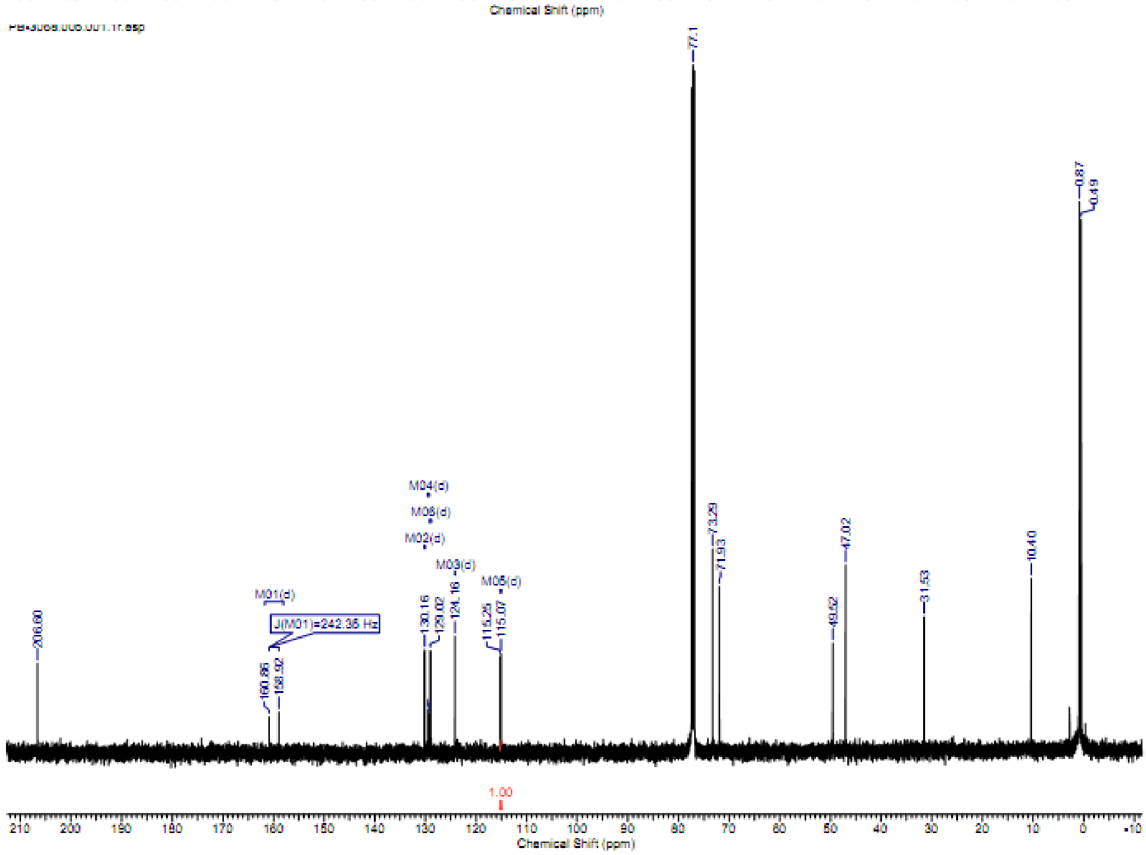
20b



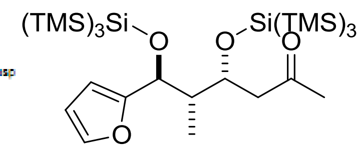


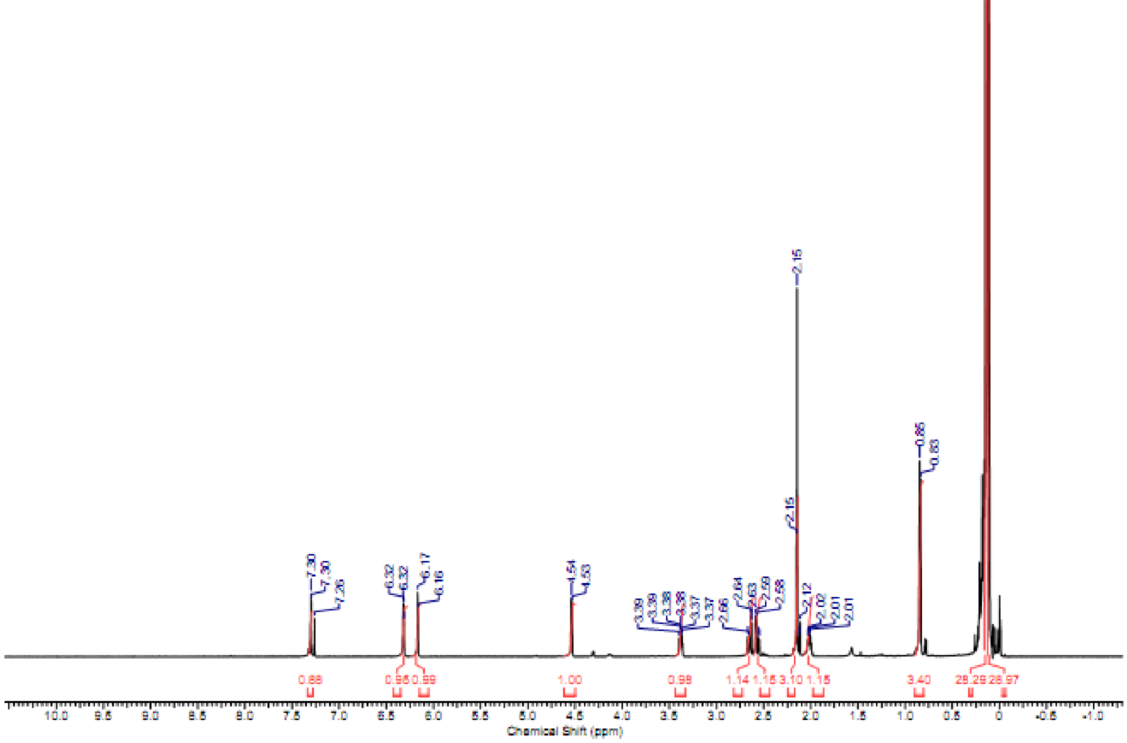
20d

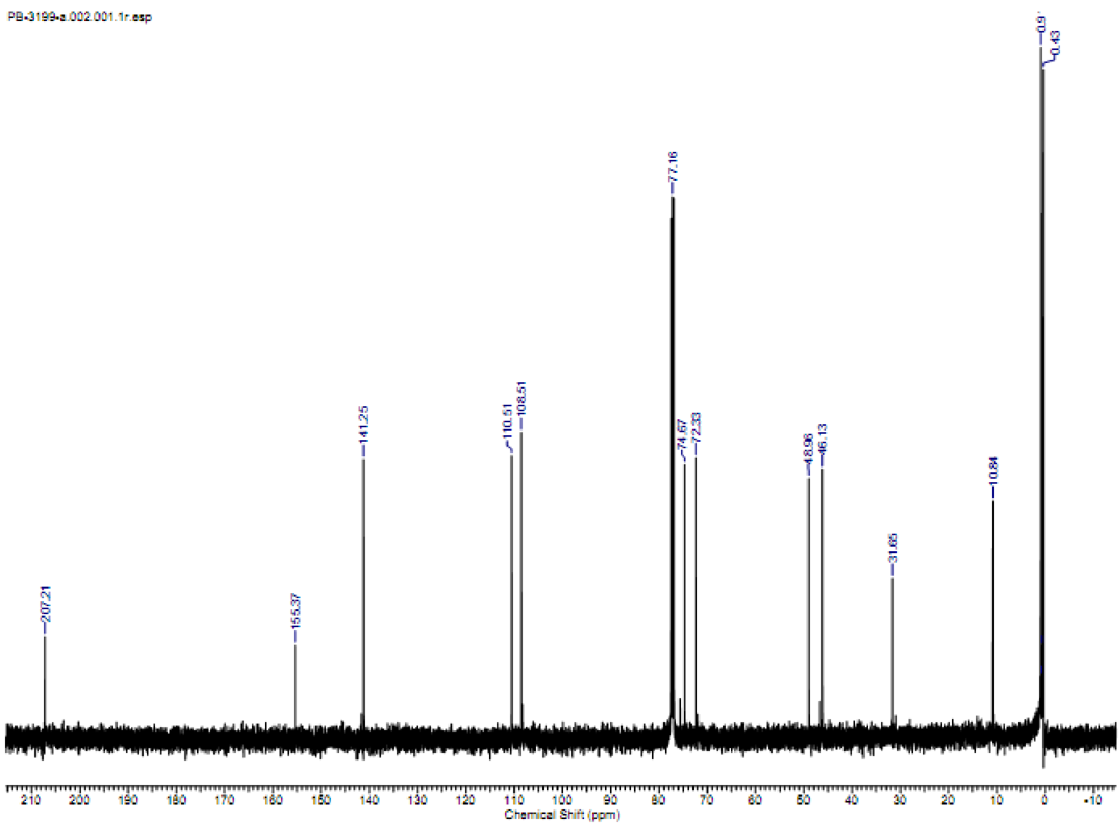




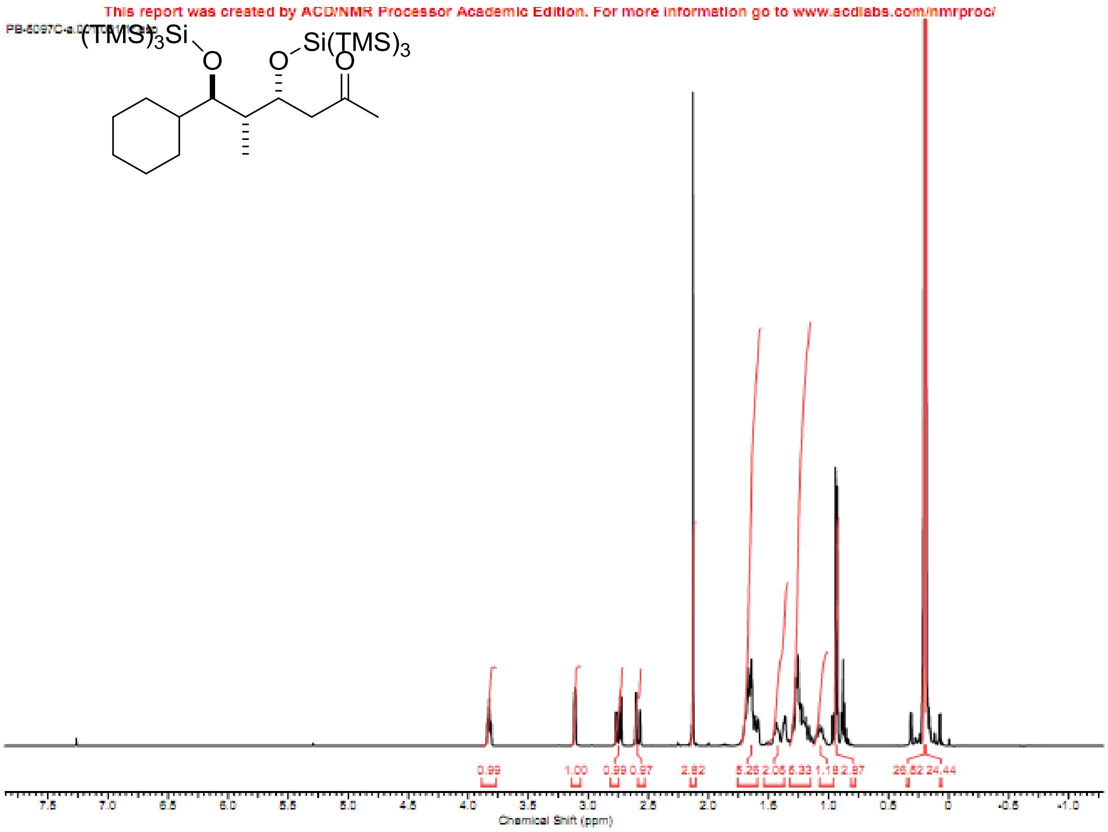
20e

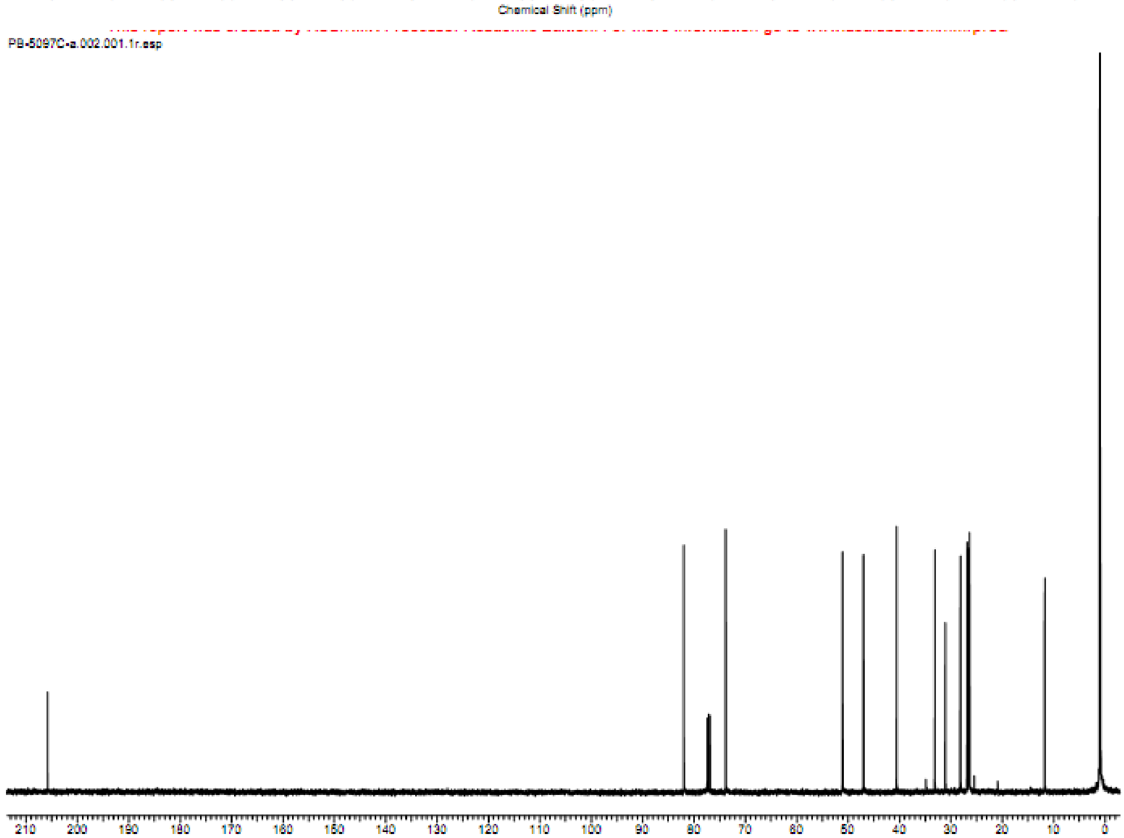

(TMS)3Si
Si(TMS)3
O
O
O
O


PB-3199-a.001.001.1r.esp
Chemical Shift (ppm)

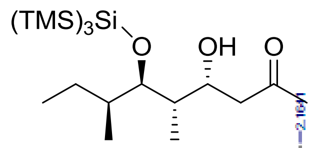

PB-3199-a.002.001.1r.esp
Chemical Shift (ppm)

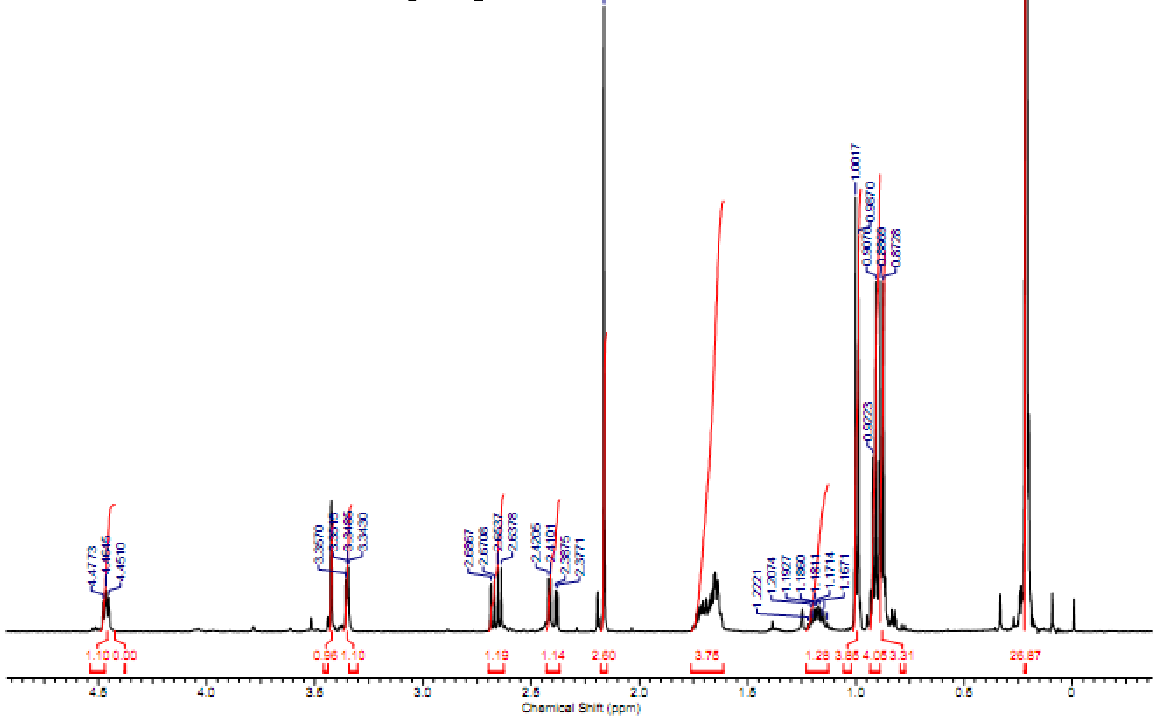
20f

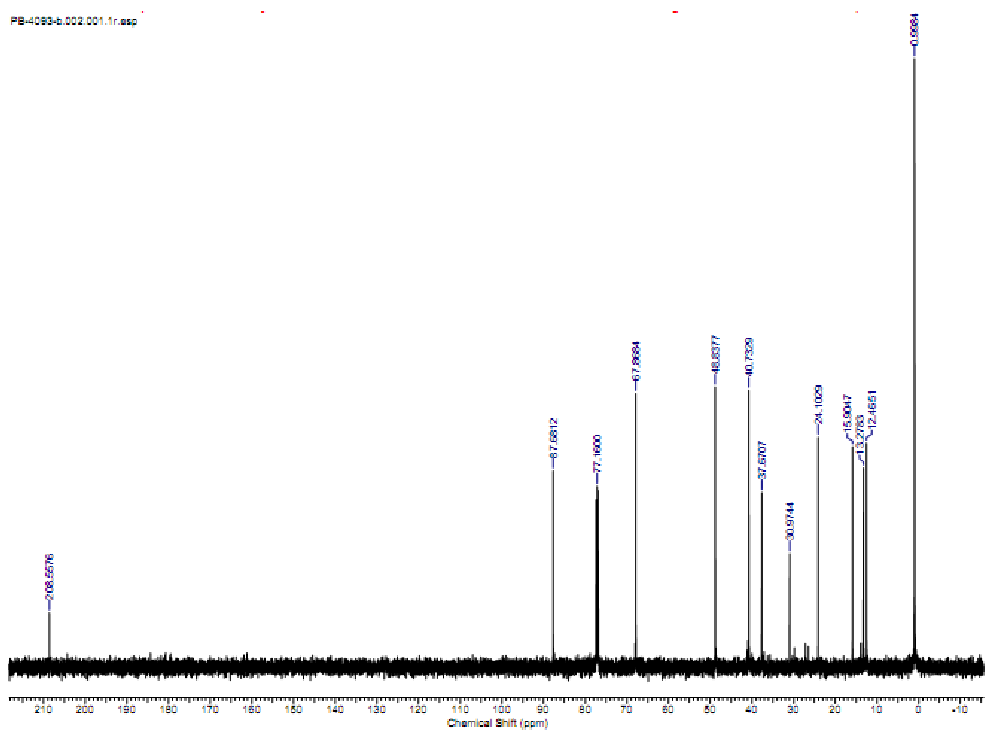

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
(TMS)3Si
Si(TMS)3
O
O
O
0.99
1.00
0.99
0.97
2.82
5.26
2.06
6.33
1.18
2.97
26.62
24.44
Chemical Shift (ppm)


PB-5097C-a.002.001.1r.esp

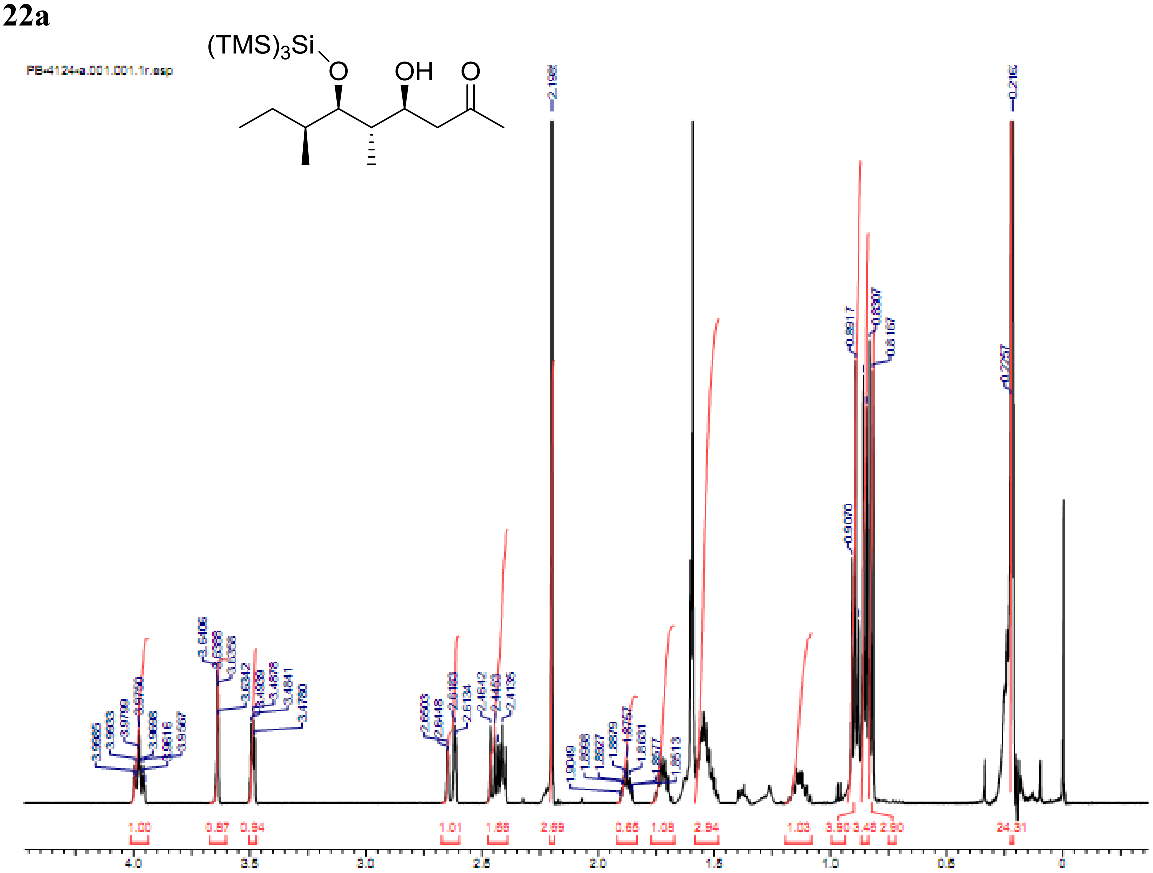
21a

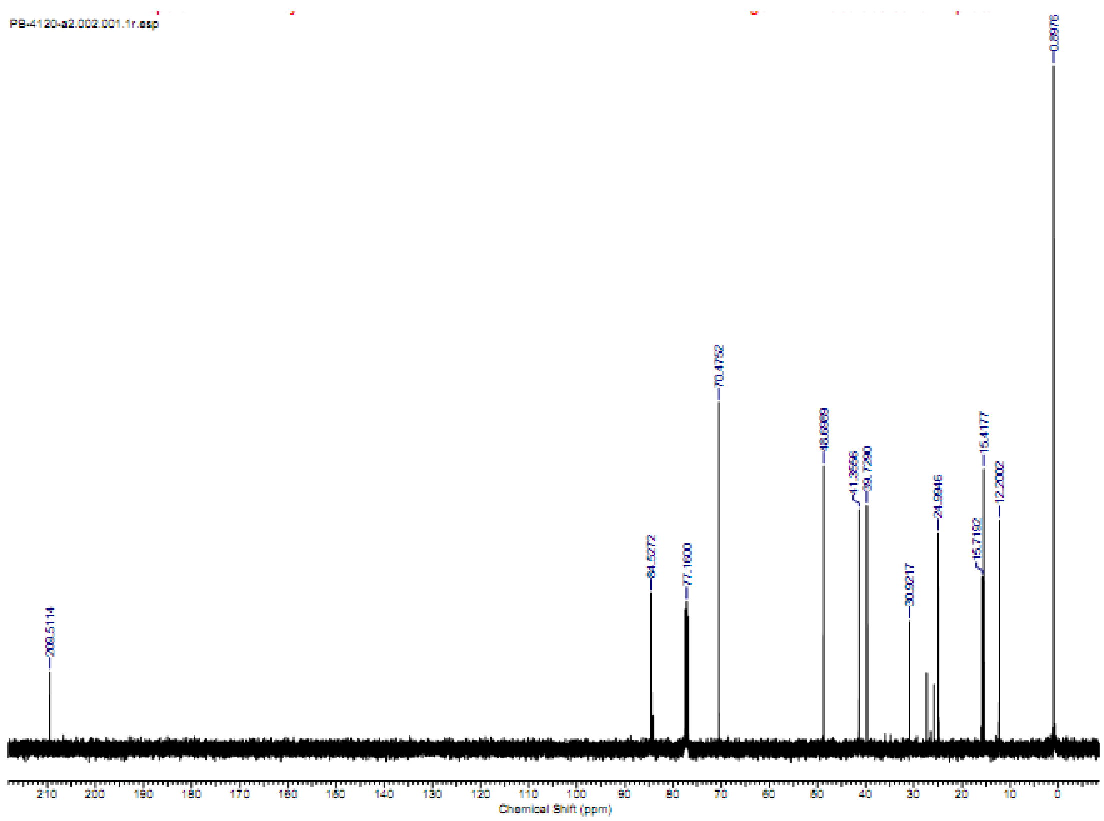

(TMS)3Si
O
OH
O


Chemical Shift (ppm)

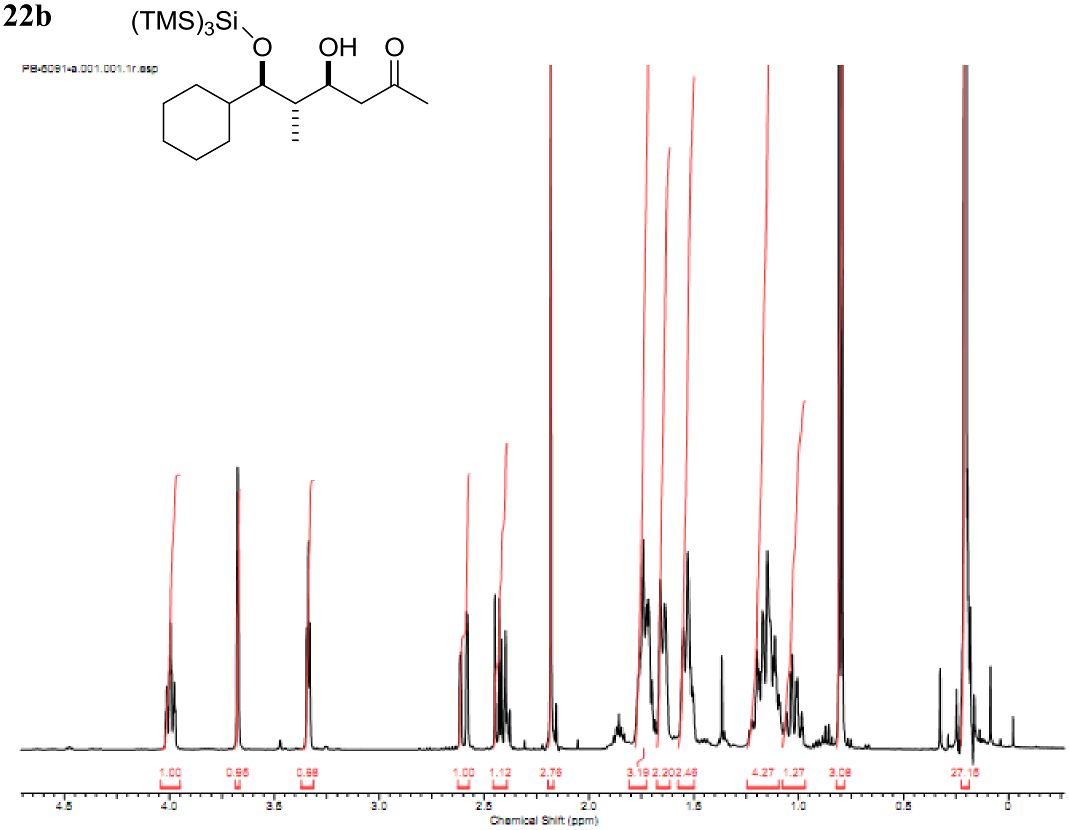

PB-4093-b.002.001.1r.esp
Chemical Shift (ppm)

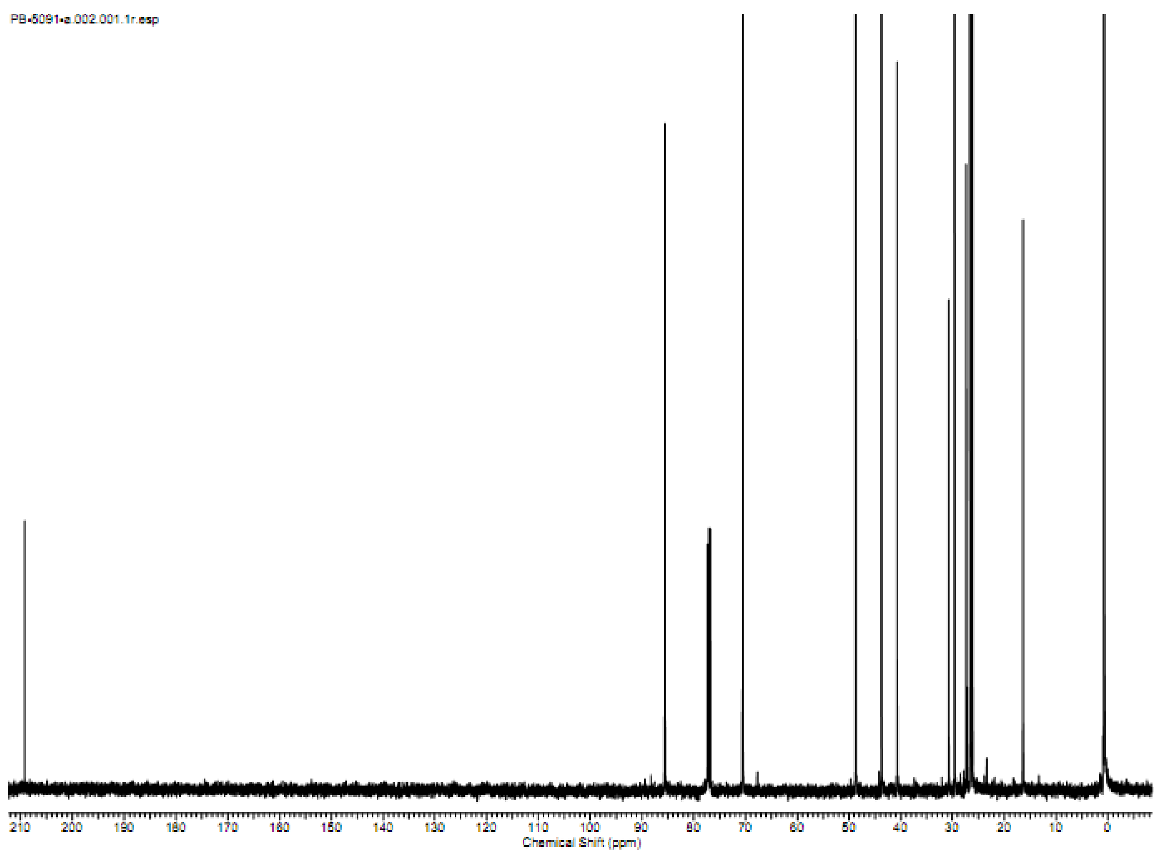
22a





22b


(TMS)3Si
O
OH
O
PB-5091-a.001.001.1r.esp
1.00
0.96
0.98
1.00
1.12
2.76
3.18
2.20
2.46
4.27
1.27
3.08
27.15
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


PB-5091-a.002.001.1r.esp
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

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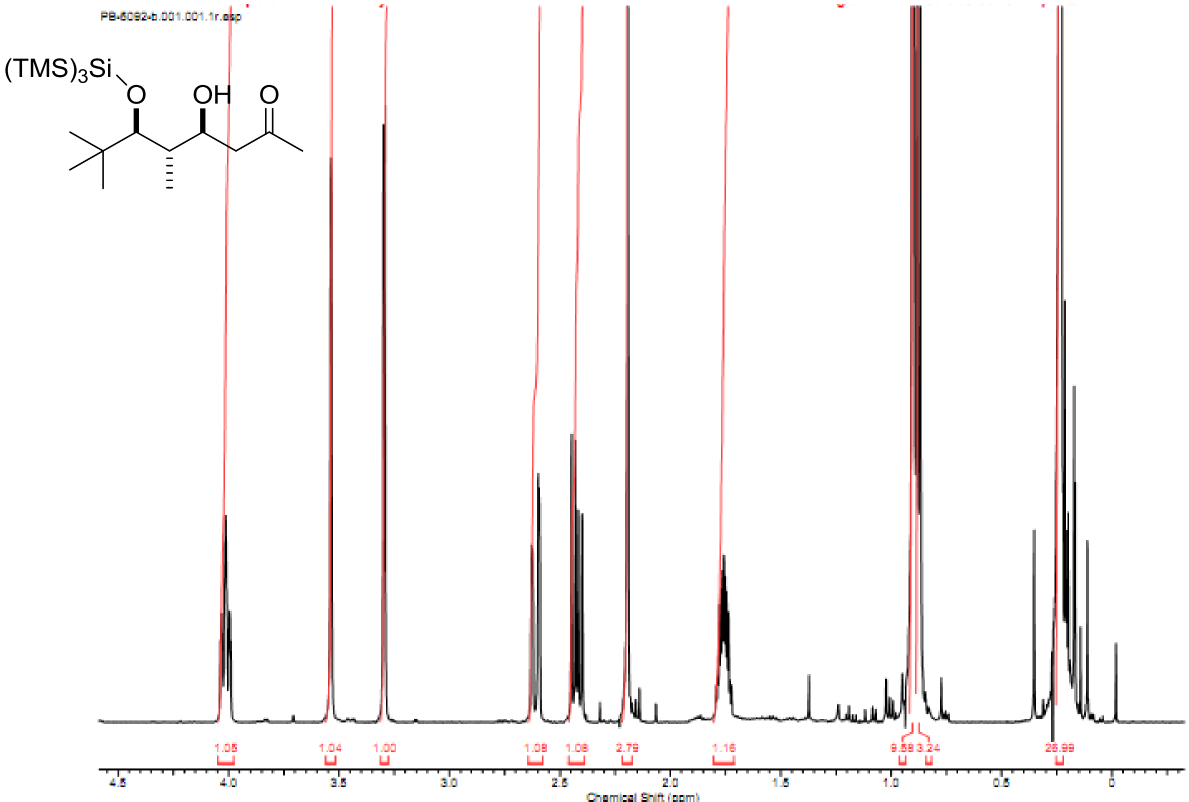
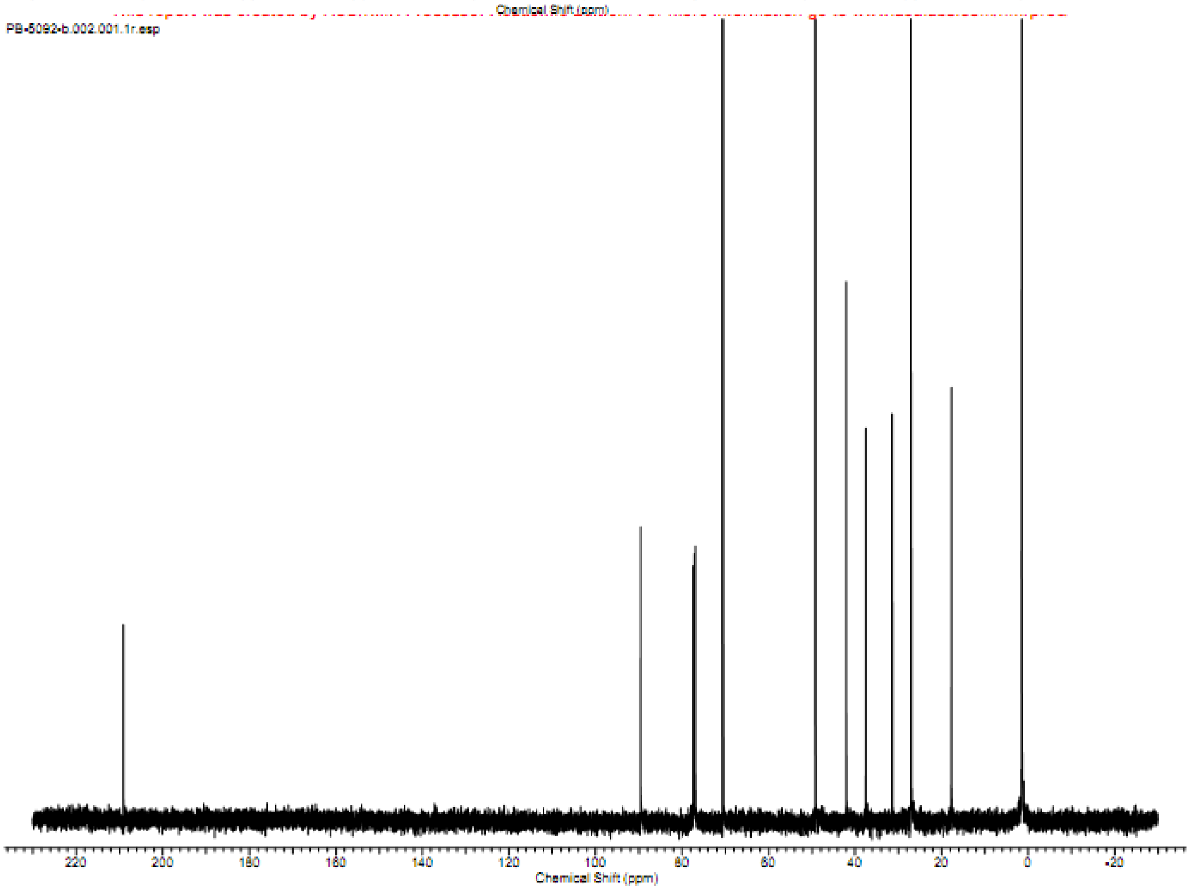
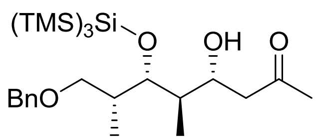
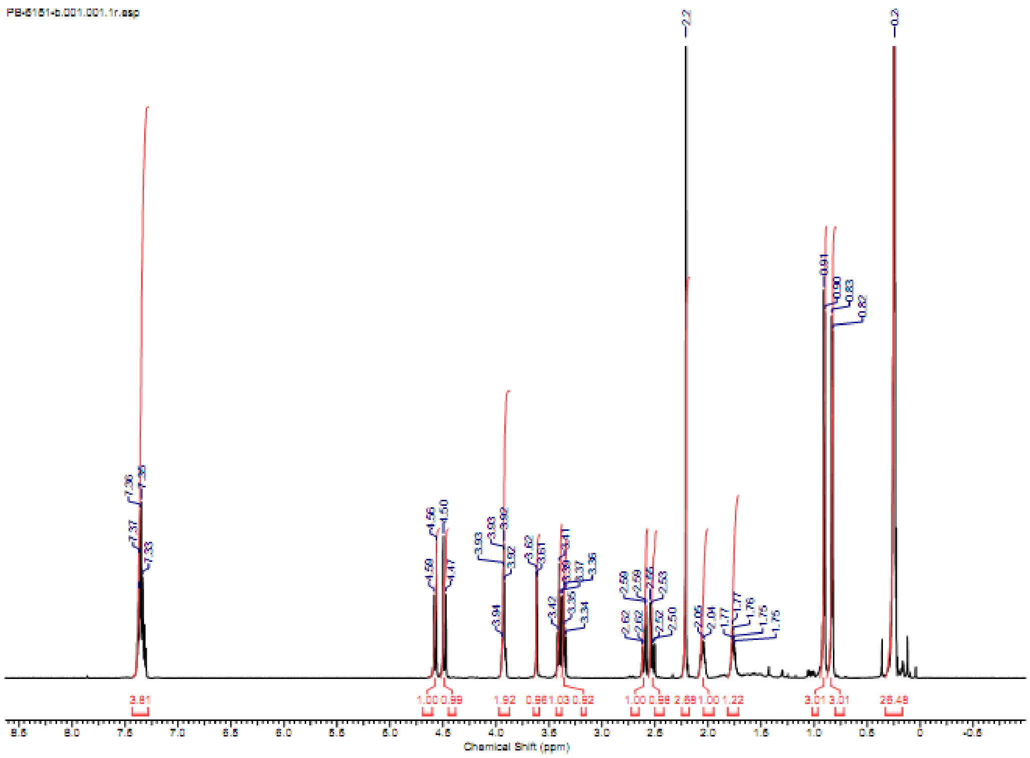
22c

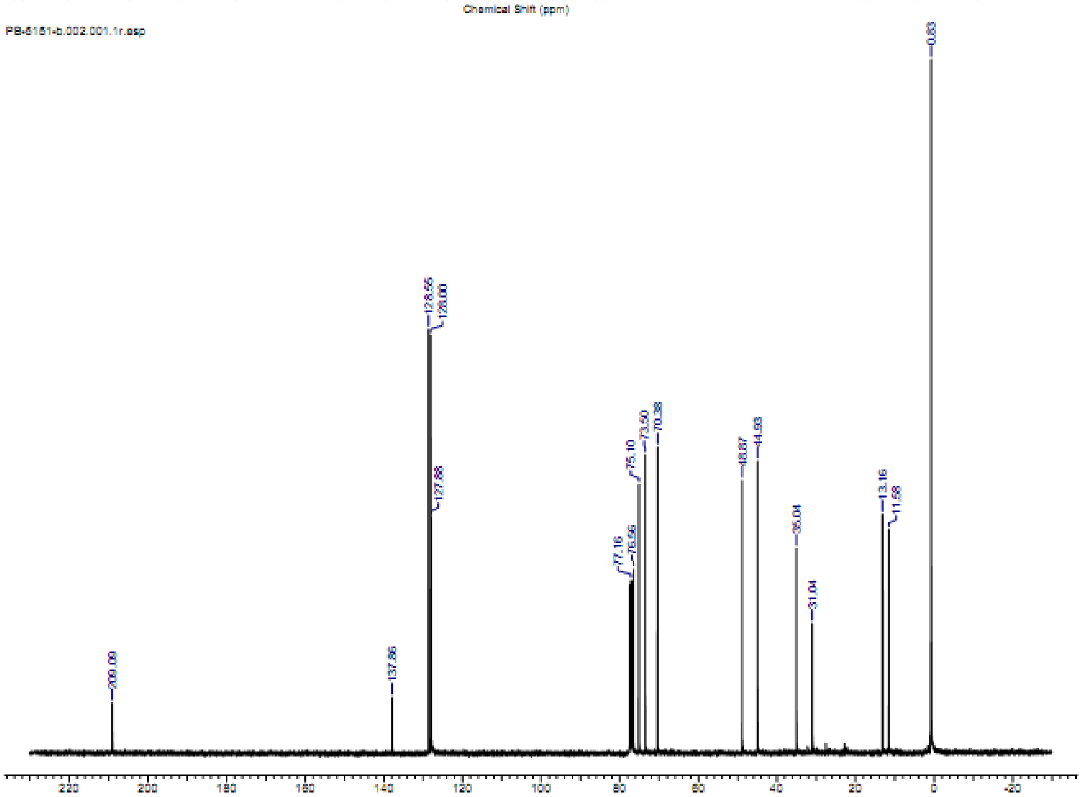




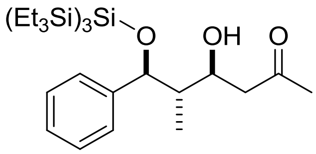
22d

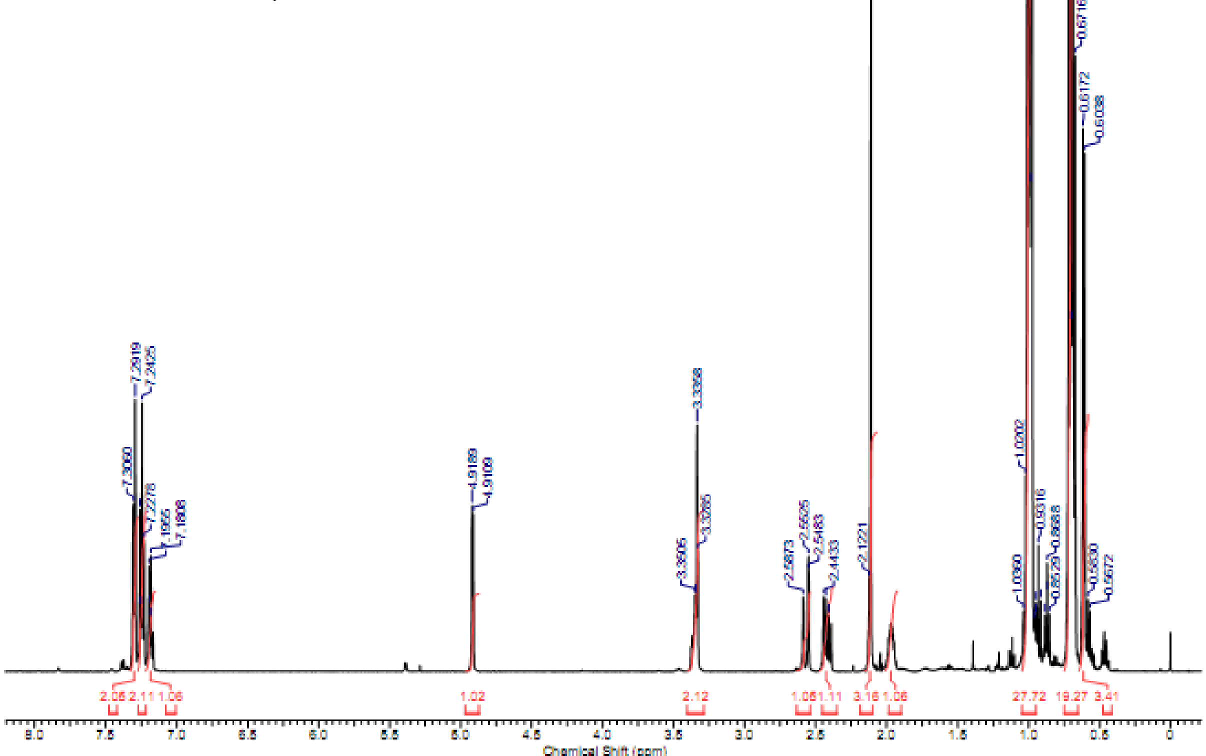


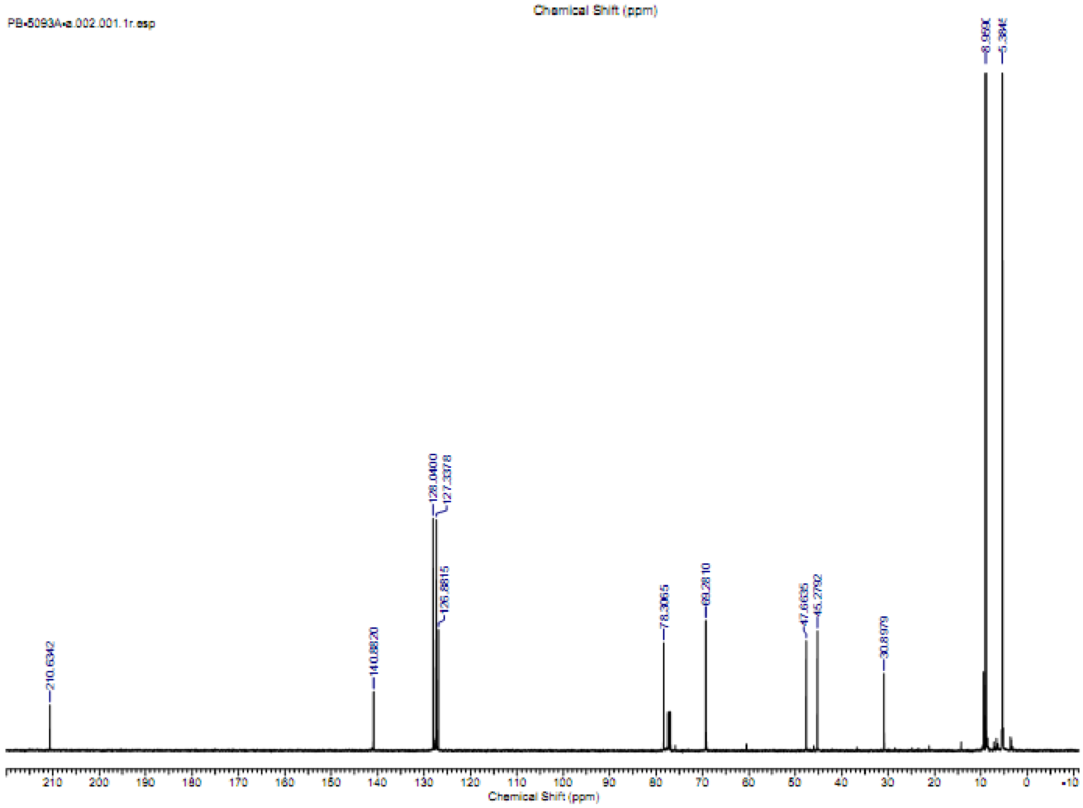

PB-5151-b.001.001.1r.esp
Chemical Shift (ppm)


PB-5151-b.002.001.1r.esp
Chemical Shift (ppm)

22f


(Et3Si)3Si
O
OH
O


PB-5093A-a.001.001.1r_2.esp
Chemical Shift (ppm)


PB-5093A-a.002.001.1r.esp
210.6342
140.8820
128.0400
127.3378
126.8815
78.3065
69.2810
47.6635
45.2792
30.8979
Chemical Shift (ppm)

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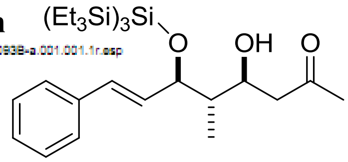
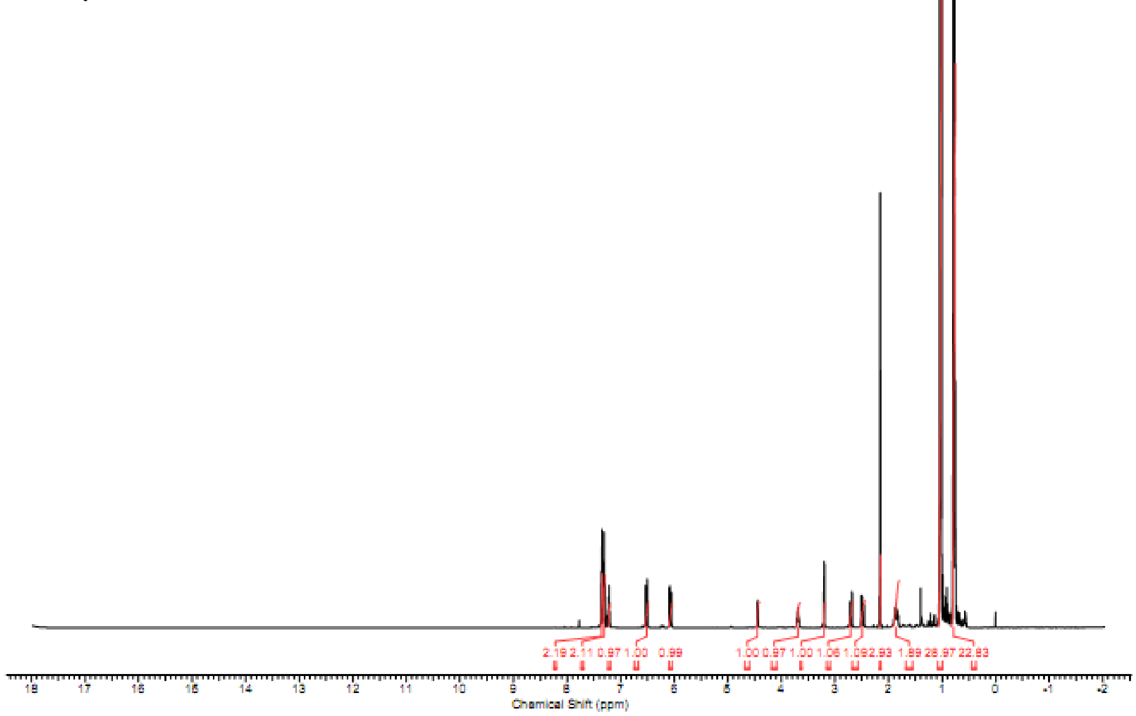
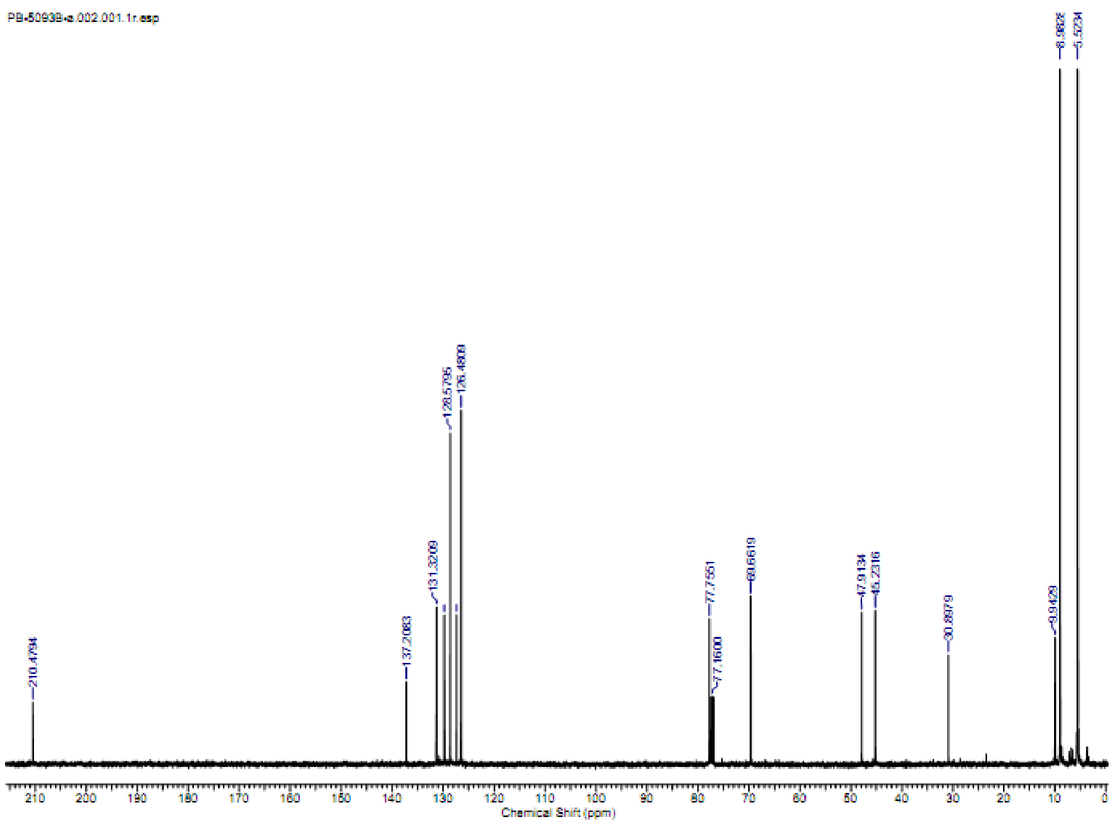
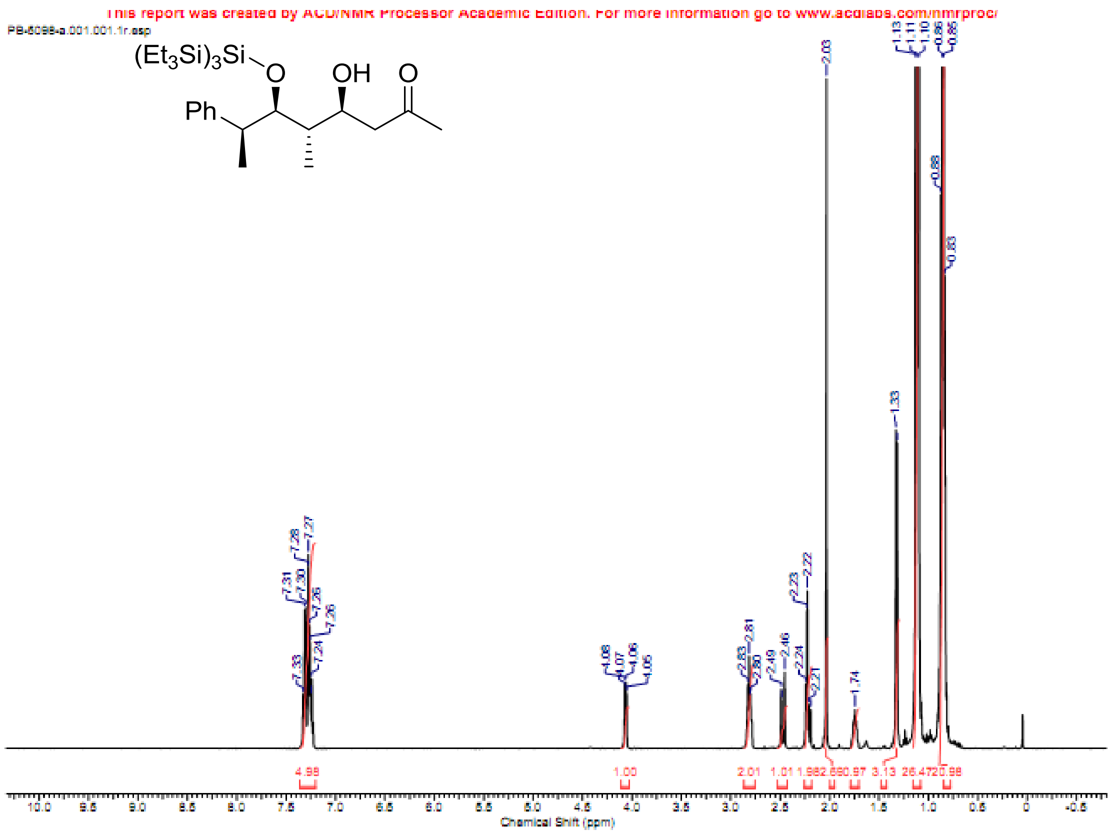
22h







22i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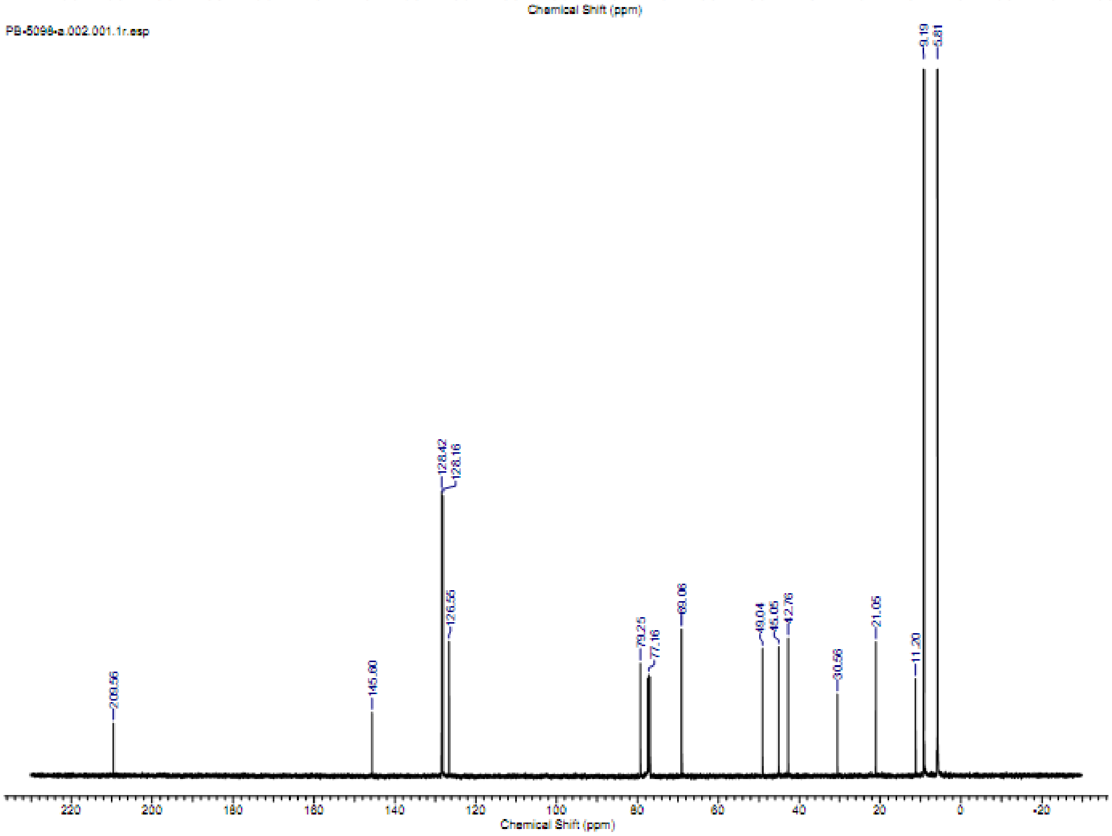
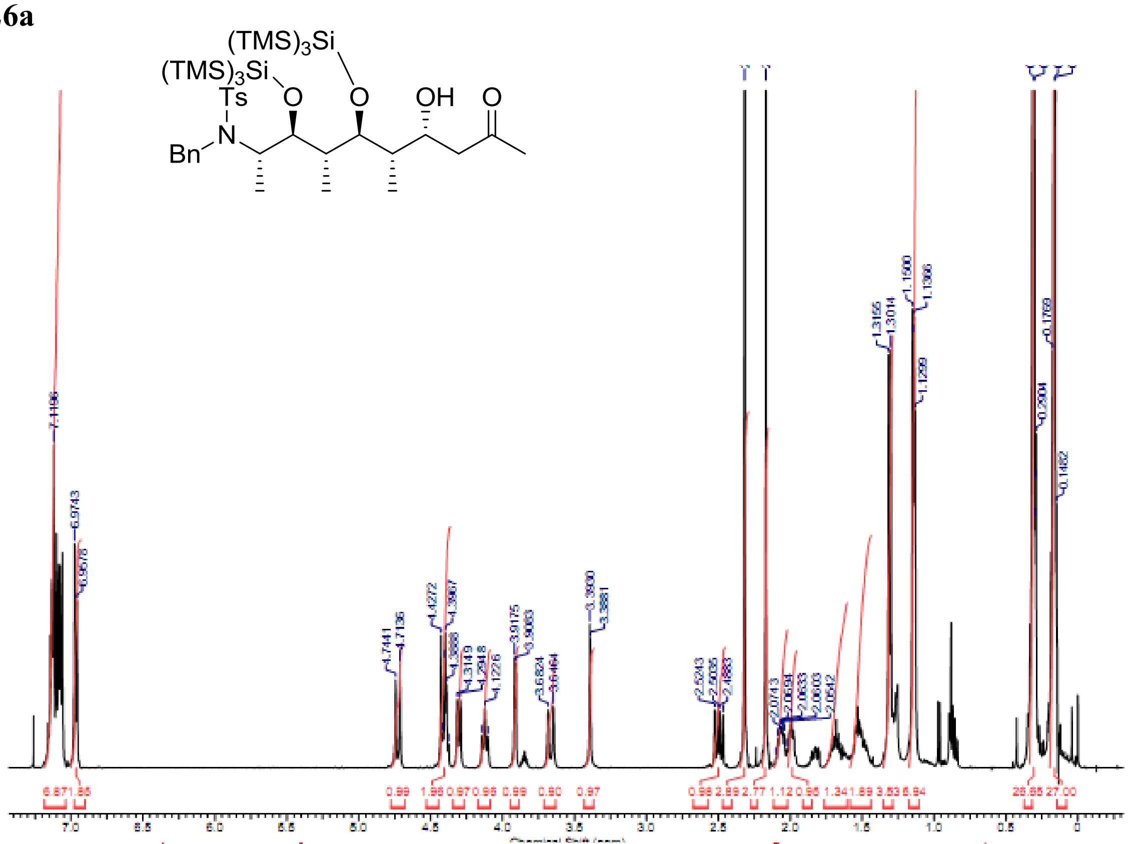
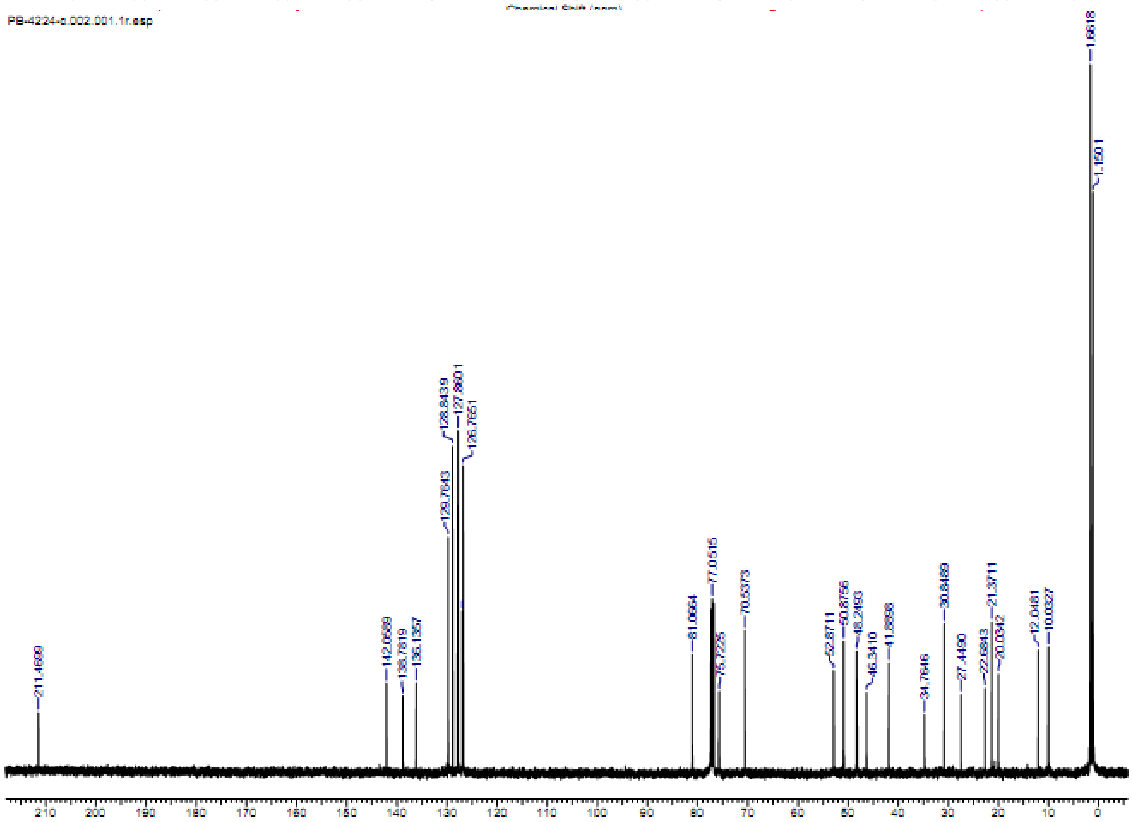
PB-5098-a.001.001.1r.esp
(Et3Si)3Si
O
OH
O
Ph
Chemical Shift (ppm)

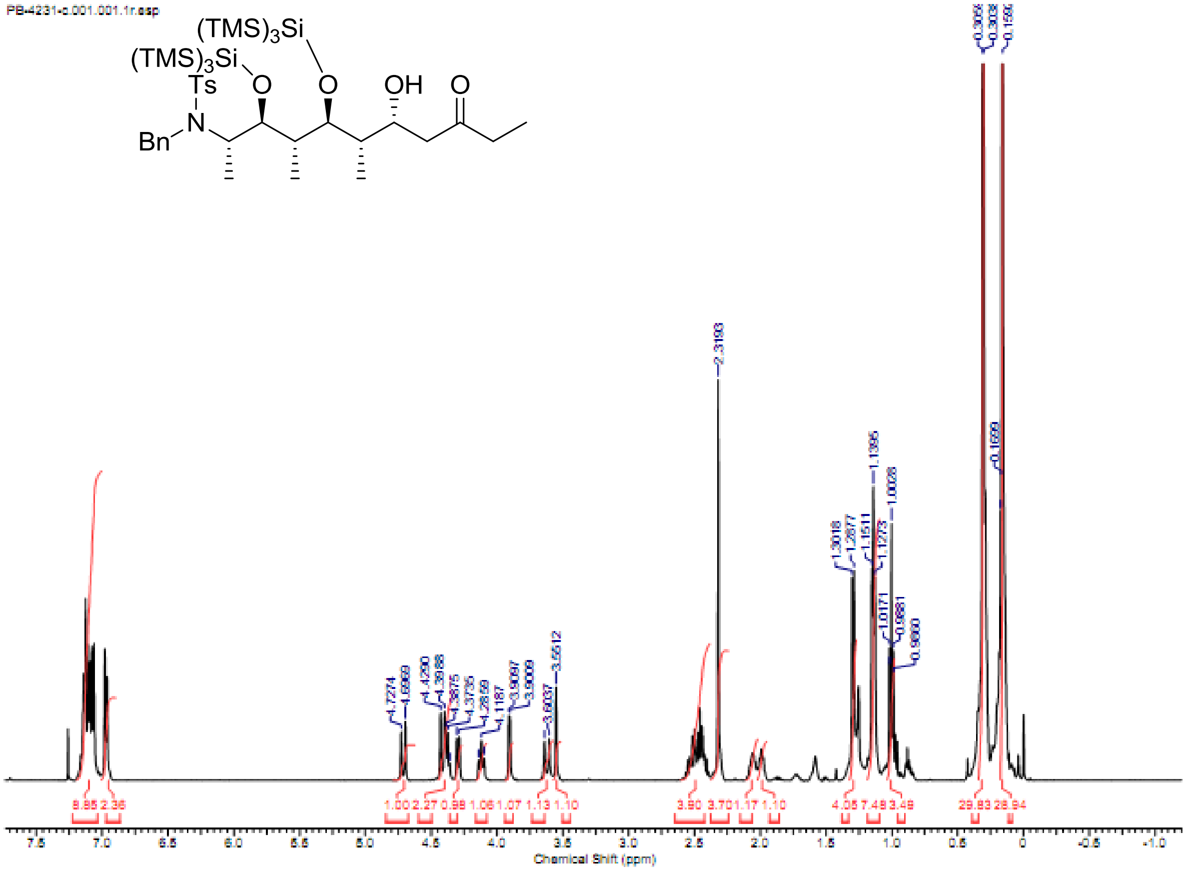

PB-5098-a.002.001.1r.esp
Chemical Shift (ppm)

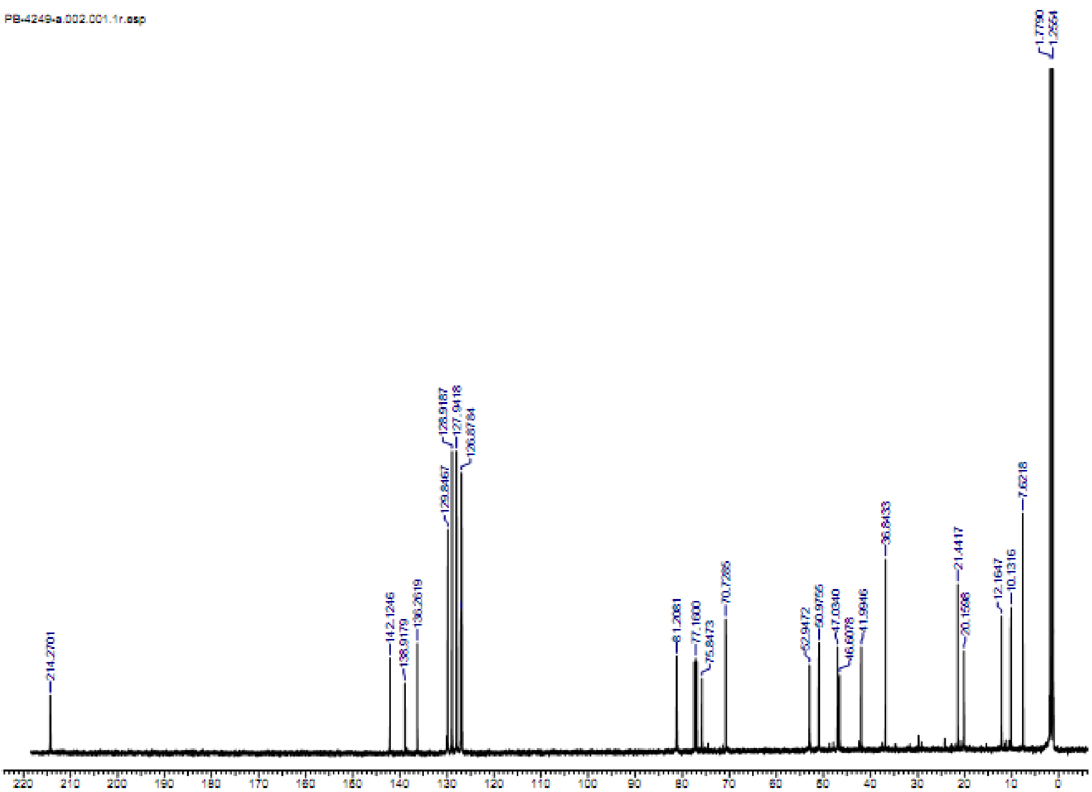
26a


(TMS)3Si
(TMS)3Si
Ts
O
O
OH
O
N
Bn
PB-4224-c.002.001.1r.esp

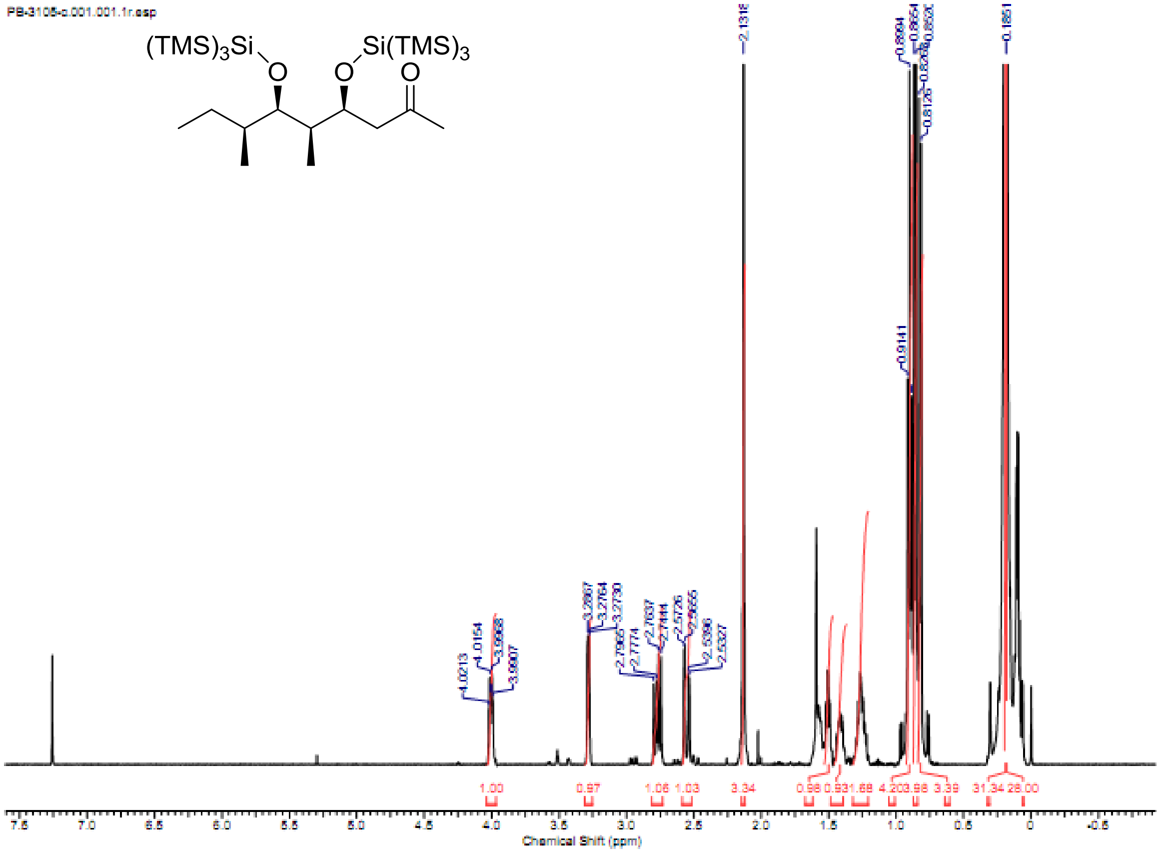

Chemical Shift (ppm)

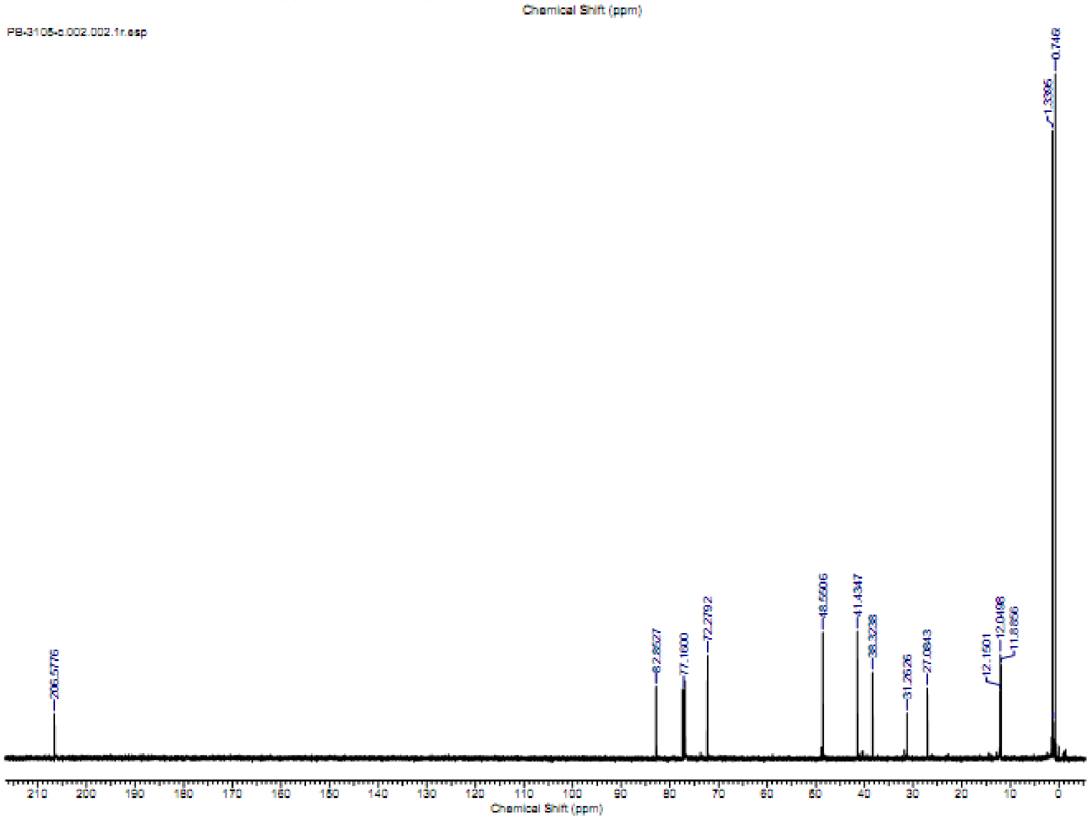
26b


PB-4231-c.001.001.1r.esp
(TMS)3Si
(TMS)3Si
Ts
N
Bn
O
O
OH
O
Chemical Shift (ppm)

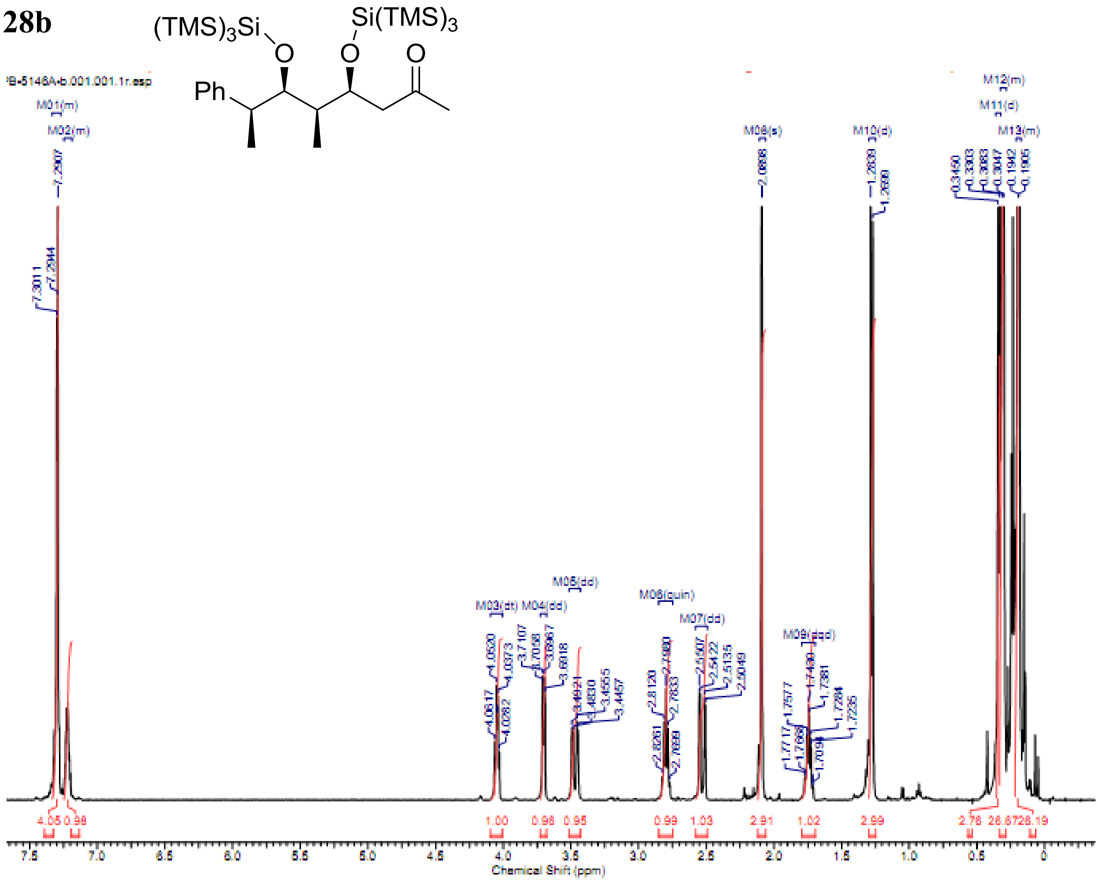

PB-4249-a.002.001.1r.esp
Chemical Shift (ppm)

28a


PB-3105-c.001.001.1r.esp
(TMS)3Si
Si(TMS)3
O
Chemical Shift (ppm)


PB-3105-c.002.002.1r.esp
Chemical Shift (ppm)

28b



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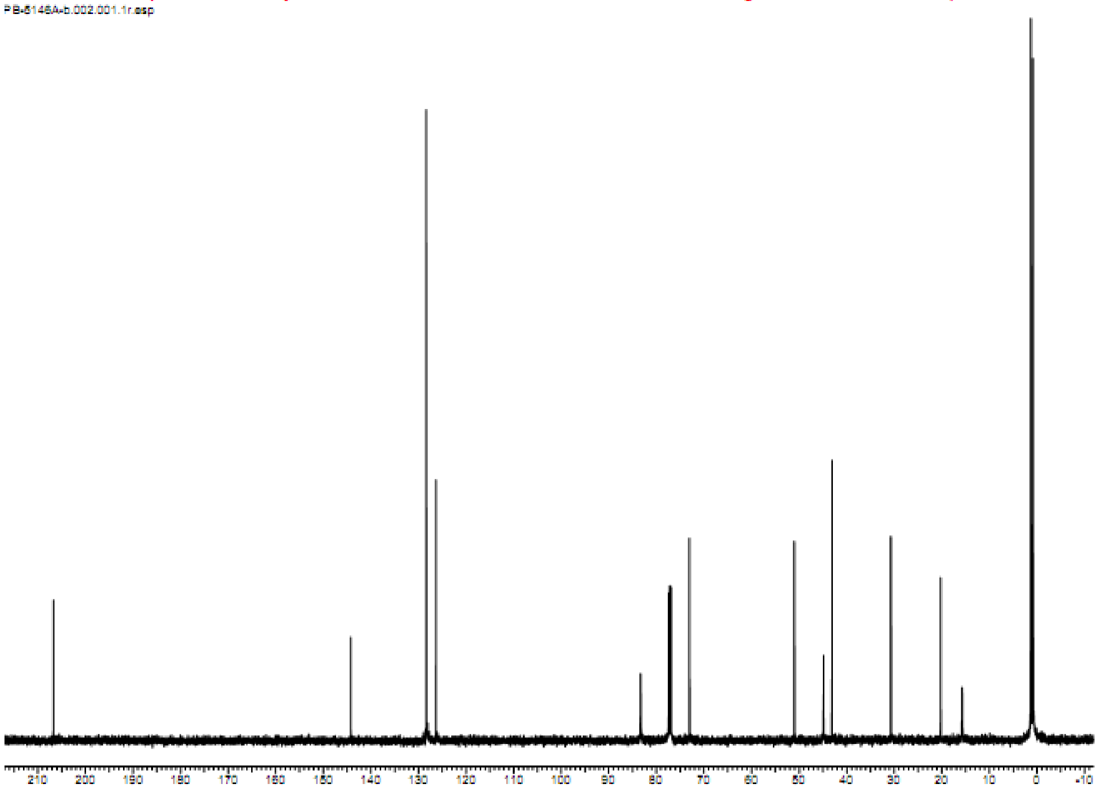
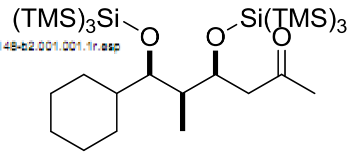
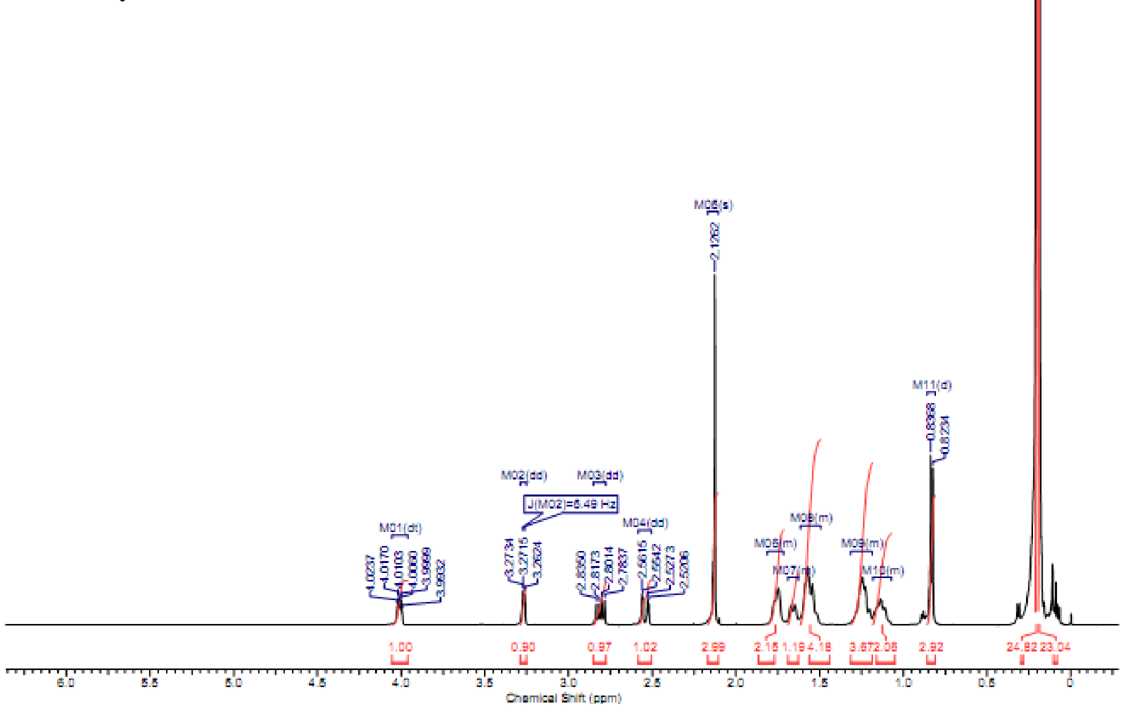
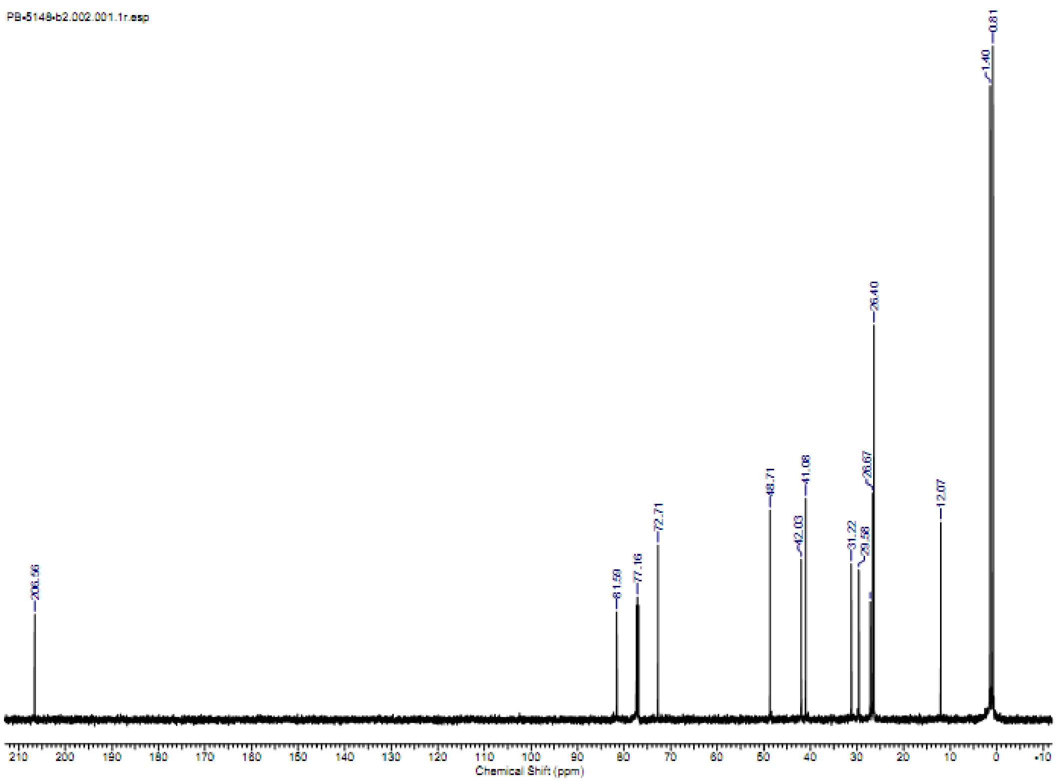


28c


(TMS)3Si
O
O
Si(TMS)3
O


PB-5148-b2.001.001.1r.esp
M01(dt)
M02(dd)
M03(dd)
J(M02)=6.49 Hz
M04(dd)
M05(s)
M06(m)
M07(m)
M08(m)
M09(m)
M10(m)
M11(d)
M12(s)
M13(s)
4.0237
4.0170
4.0103
4.0060
3.9999
3.9932
3.2734
3.2715
3.2624
2.8350
2.8173
2.8014
2.7837
2.5615
2.5542
2.5273
2.5206
2.1262
0.8368
0.8234
0.2092
0.1872
1.00
0.90
0.97
1.02
2.99
2.15
1.19
4.18
3.67
2.06
2.92
24.92
23.04
Chemical Shift (ppm)


PB-5148-b2.002.001.1r.esp
206.56
81.59
77.16
72.71
48.71
42.03
41.08
31.22
29.58
26.67
26.40
12.07
1.40
0.81
Chemical Shift (ppm)

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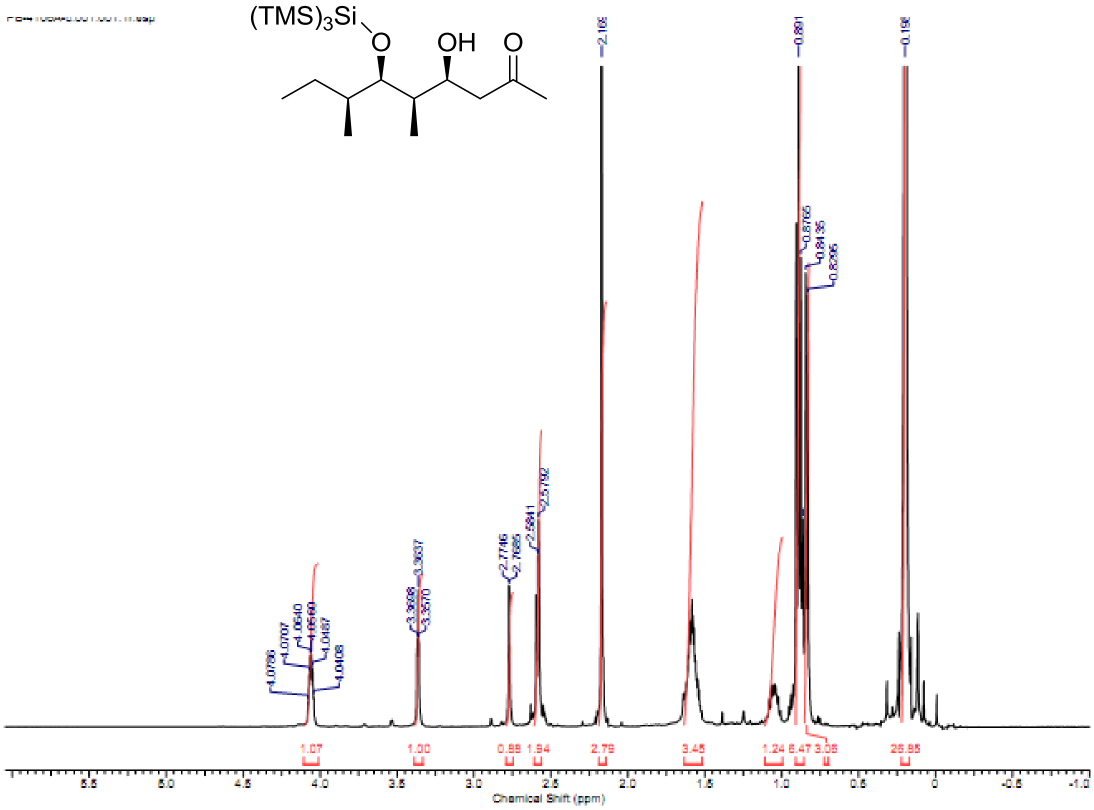
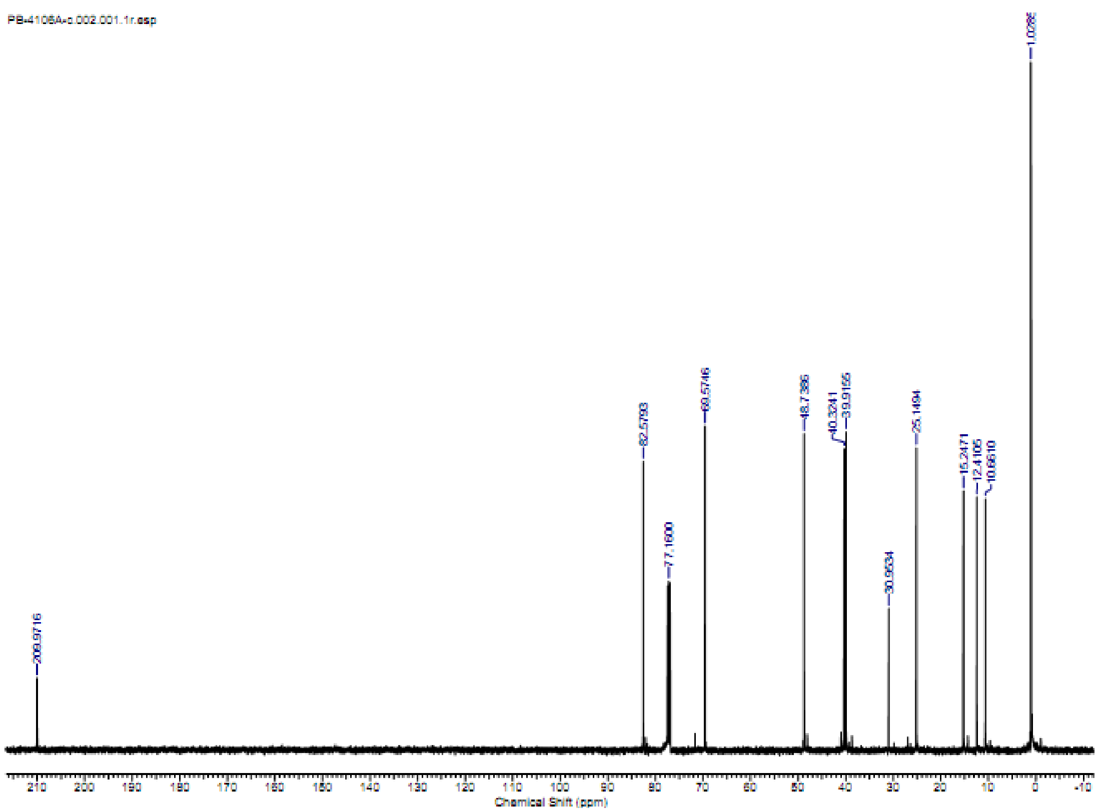
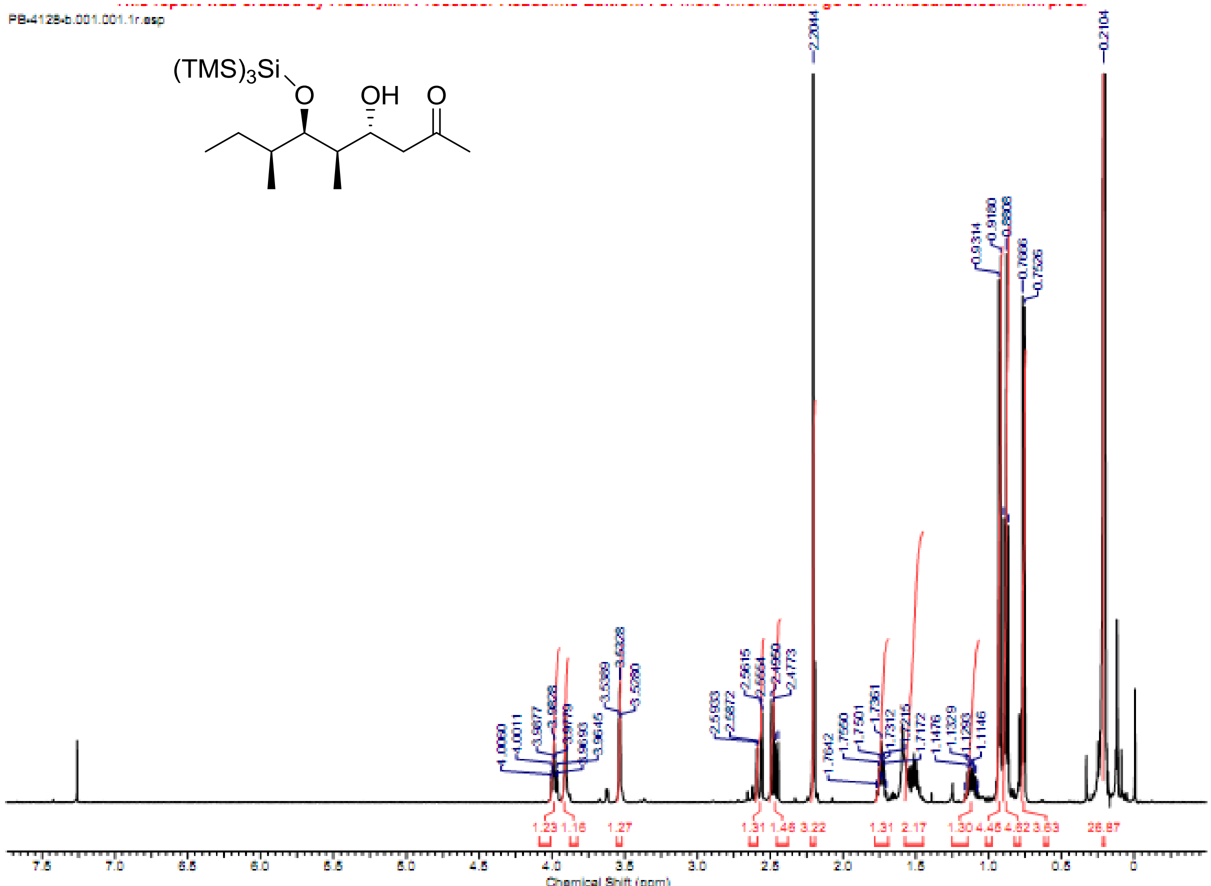
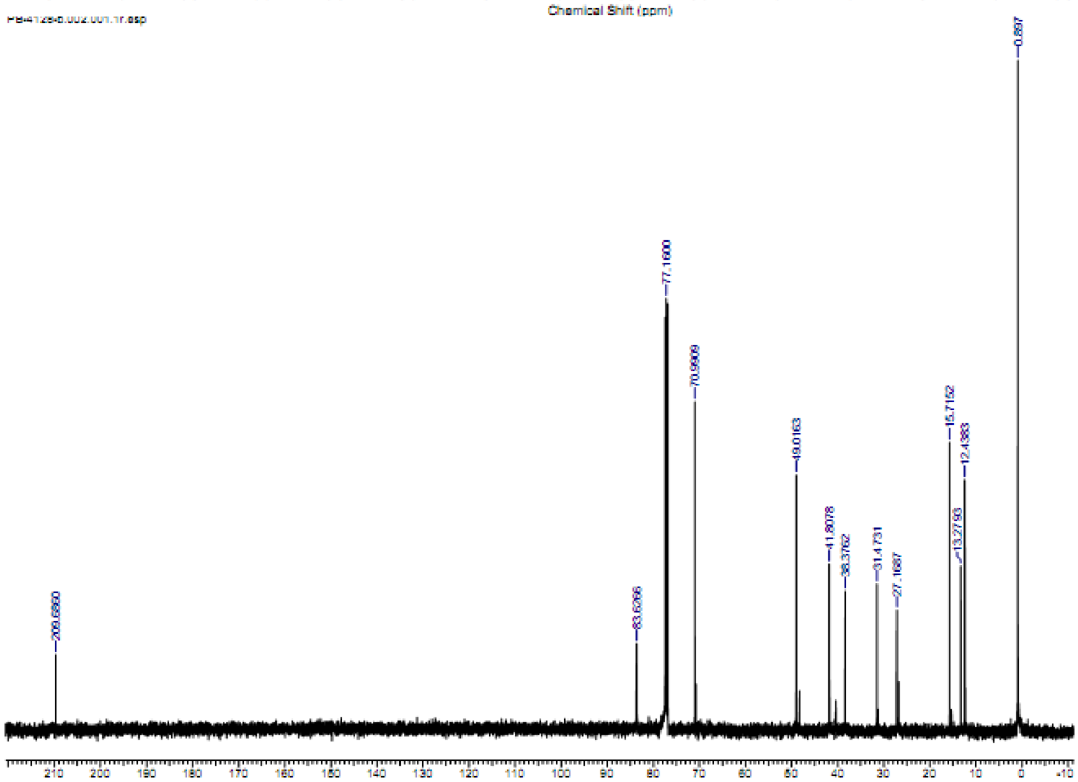
29a



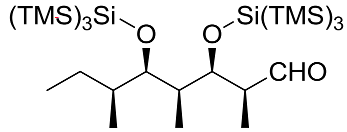


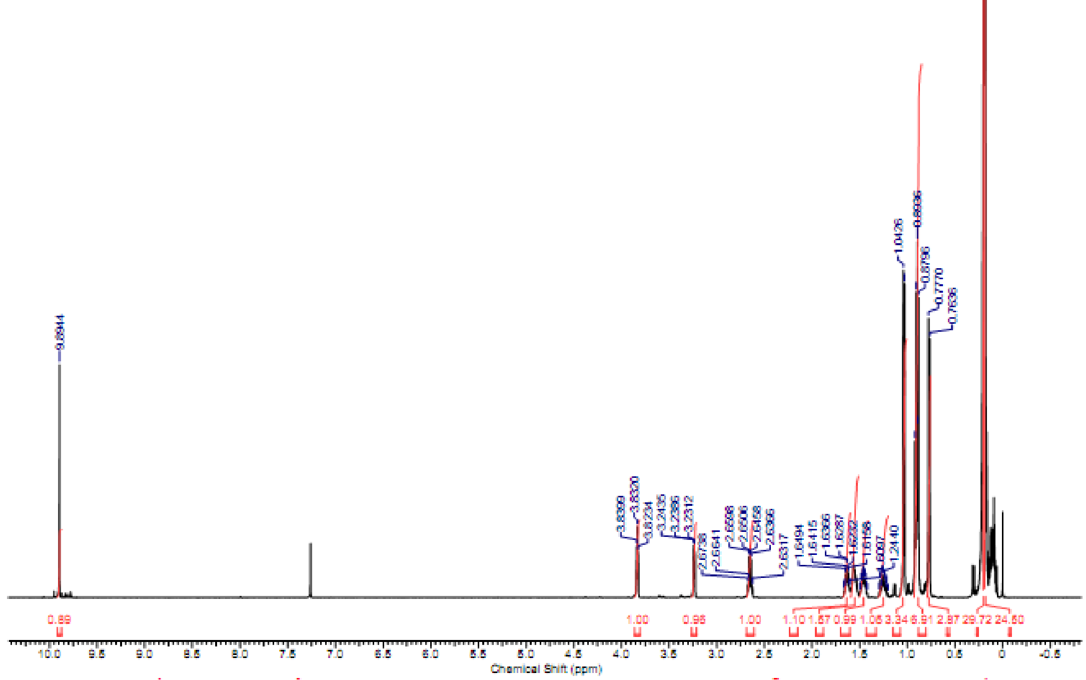
30a

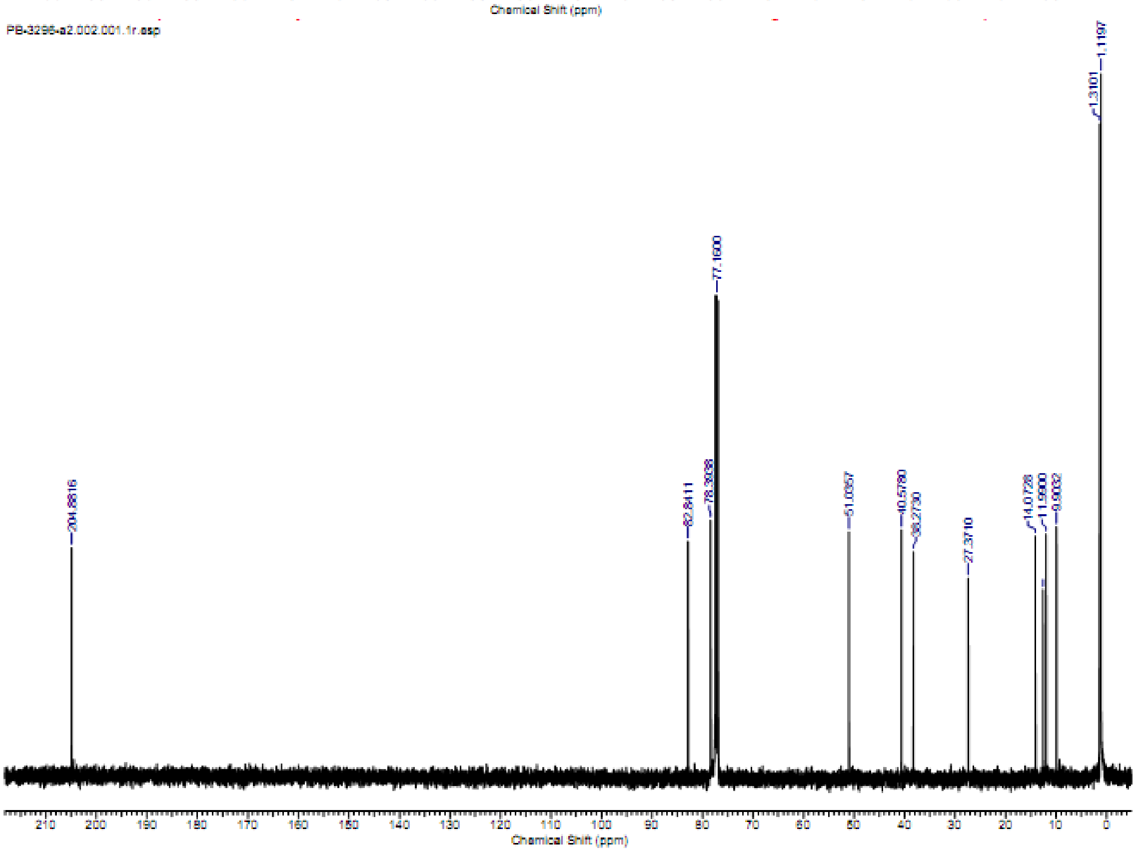

PB-4128-b.001.001.1r.esp
(TMS)3Si
O
OH
O
2.2044
0.2104
Chemical Shift (ppm)


209.6860
83.6266
77.1600
70.9909
49.0163
41.8078
38.3762
31.4731
27.1687
15.7152
13.2793
12.4383
Chemical Shift (ppm)

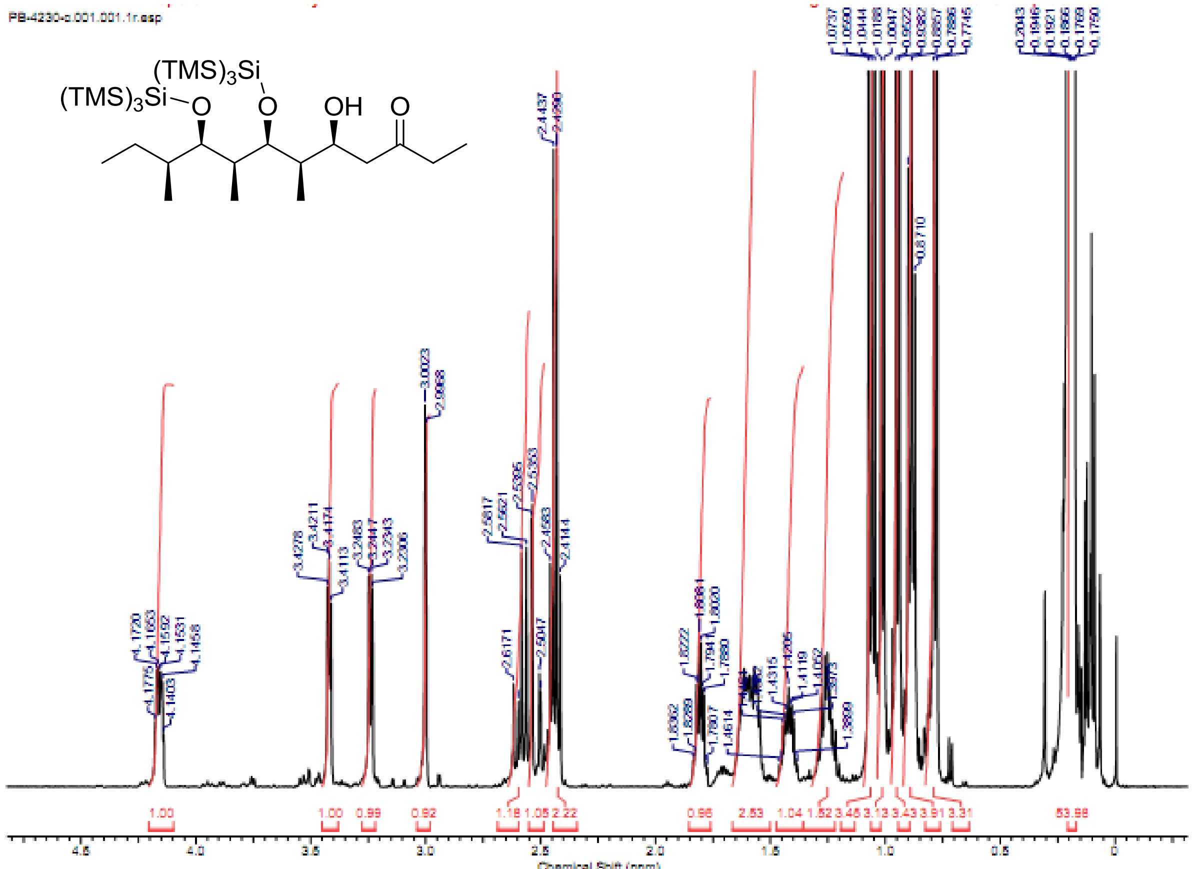
31

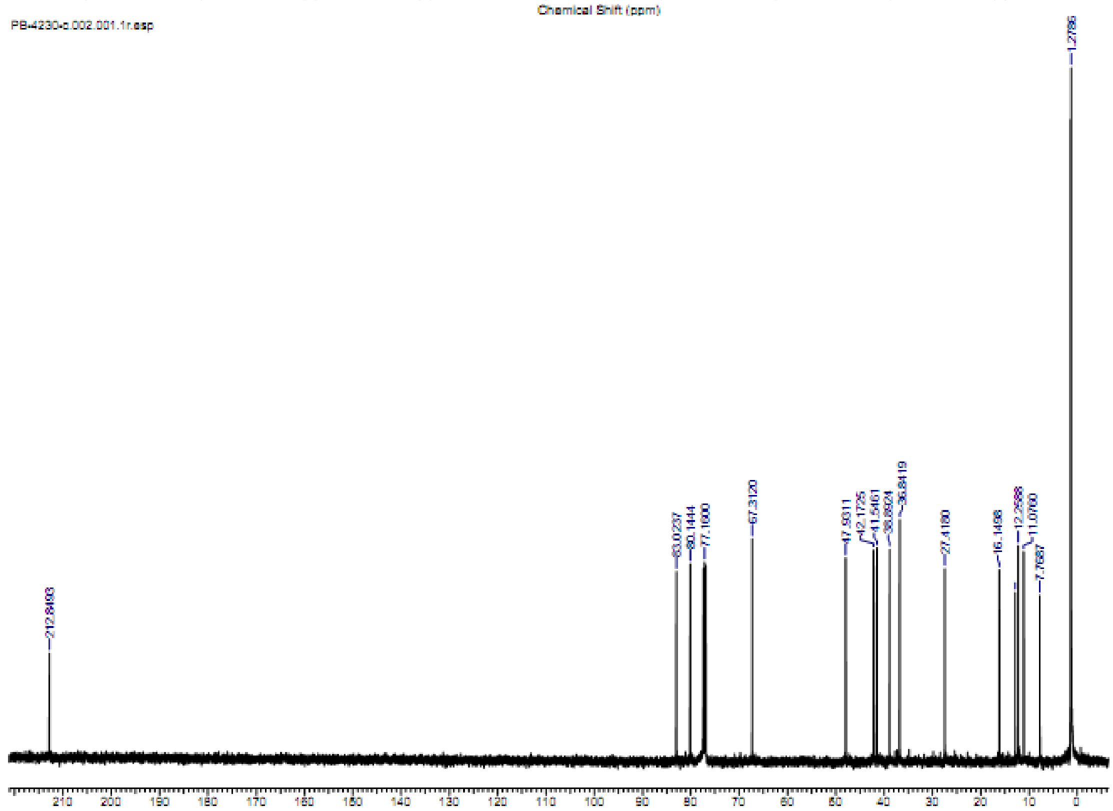

(TMS)$_3$Si
Si(TMS)$_3$
O
O
CHO


PB-3296-a2.001.001.1r.esp
Chemical Shift (ppm)

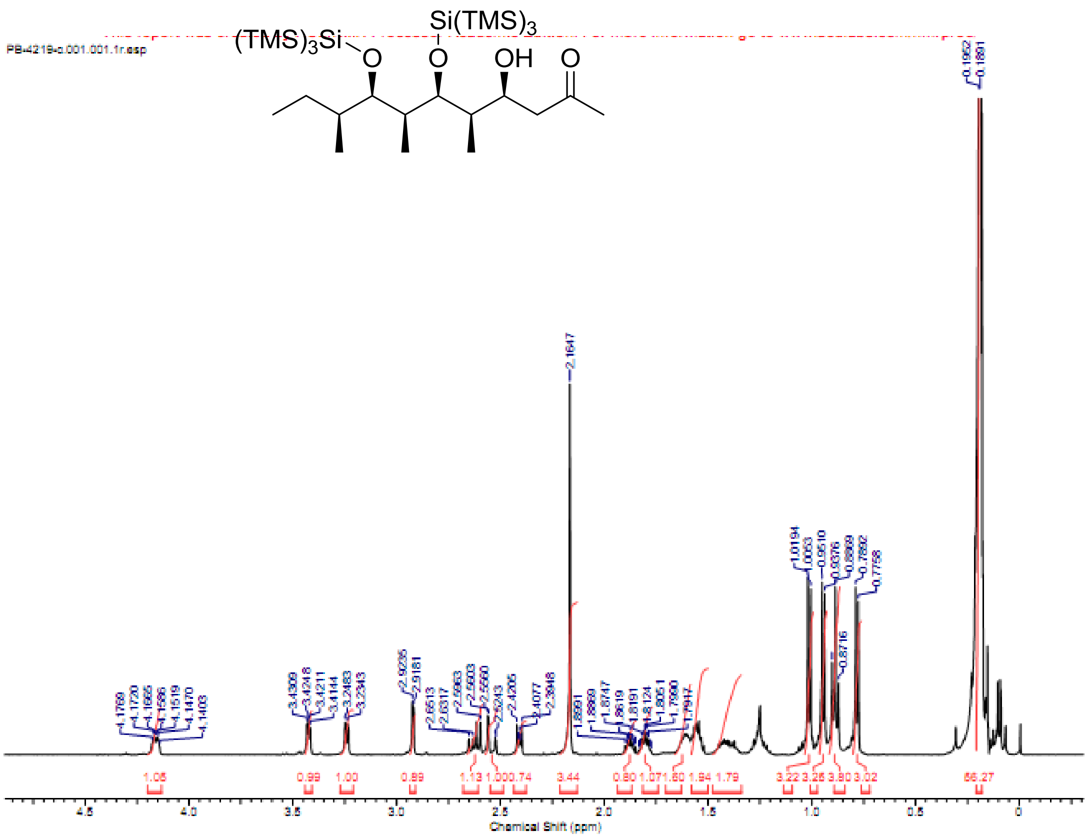

PB-3296-a2.002.001.1r.esp
Chemical Shift (ppm)

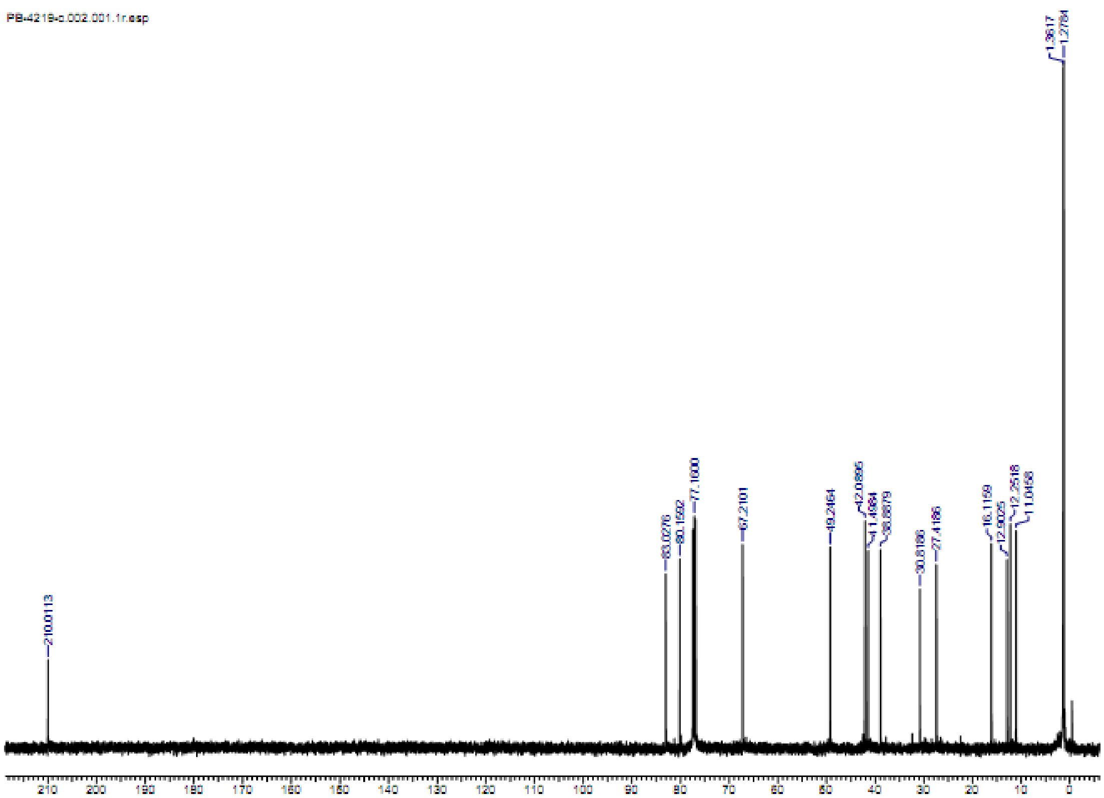
32


PB-4230-c.001.001.1r.esp
(TMS)3Si
(TMS)3Si
O
O
OH
O
Chemical Shift (ppm)

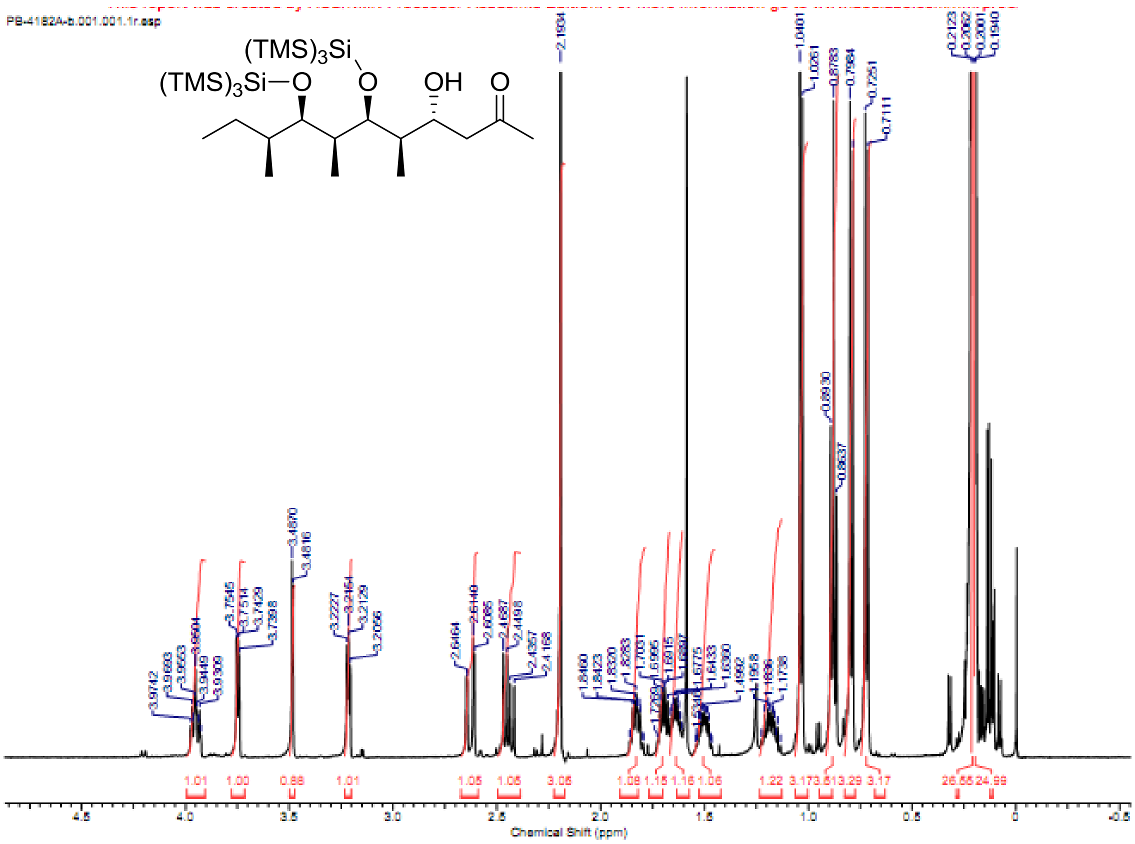

PB-4230-c.002.001.1r.esp
Chemical Shift (ppm)

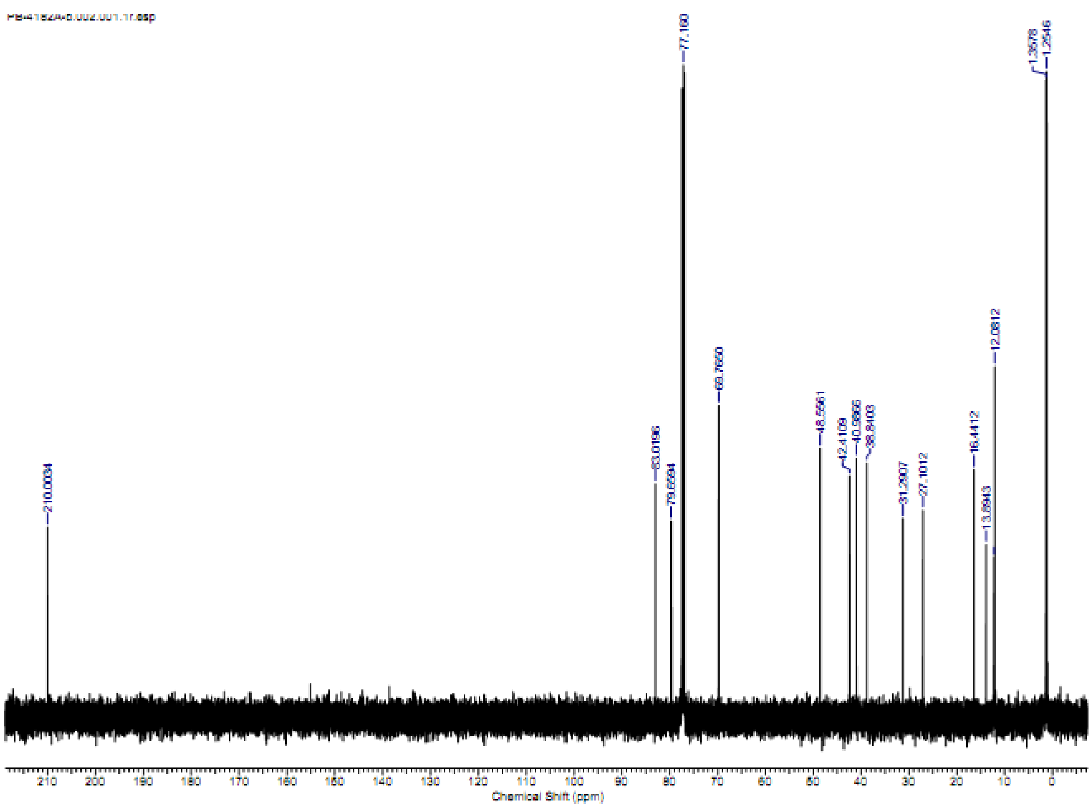
33


PB-4219-c.001.001.1r.esp
(TMS)3Si
Si(TMS)3
O
O
OH
O
2.1647
0.1952
0.1891
Chemical Shift (ppm)

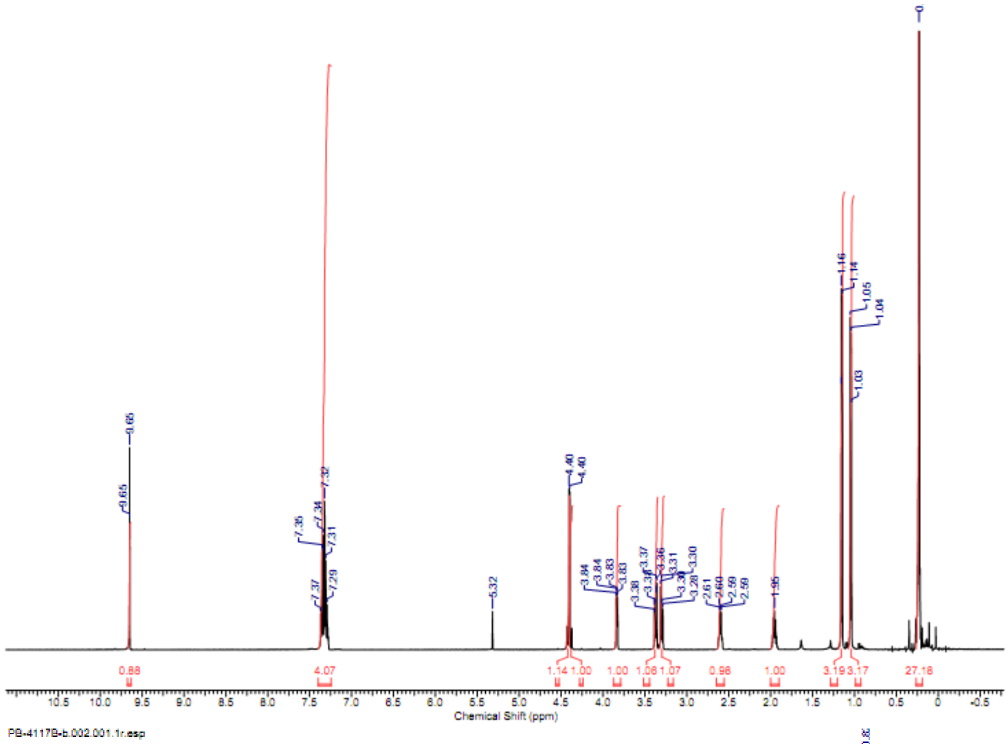

PB-4219-c.002.001.1r.esp
210.0113
77.1000
67.2101
49.2464
1.3617
1.2784
Chemical Shift (ppm)

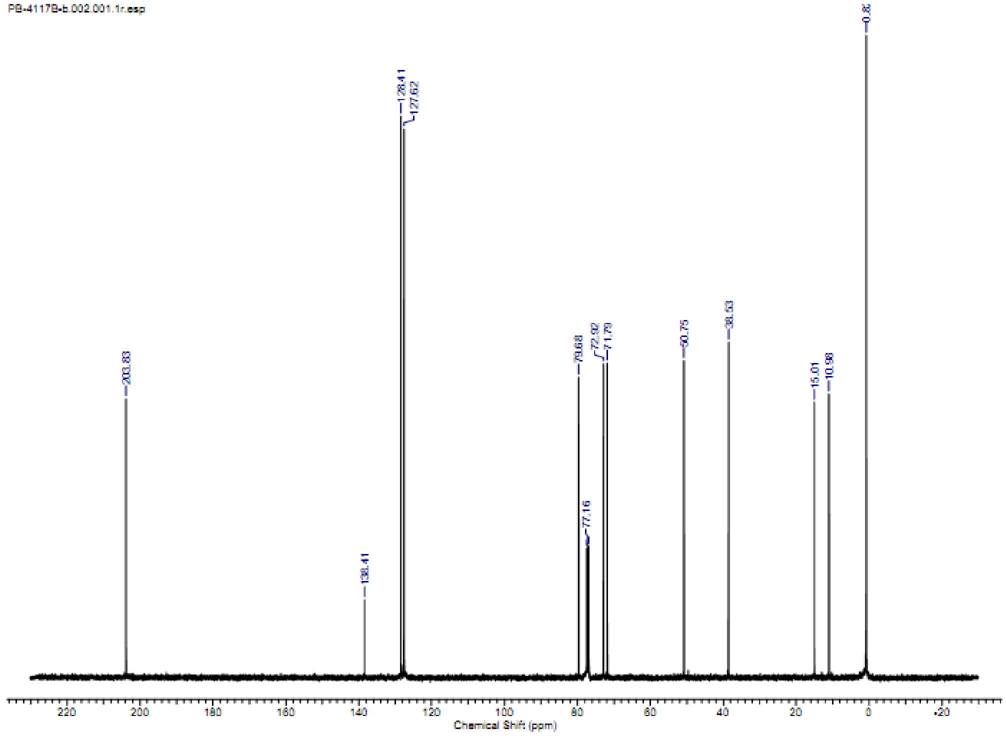
34


PB-4182A-b.001.001.1r.esp
(TMS)3Si
(TMS)3Si—O
O
OH
O
Chemical Shift (ppm)


PB-4182A-b.002.001.1r.esp
210.0034
83.0196
79.6594
77.160
69.7690
48.5561
42.4109
40.9866
38.8403
31.2907
27.1012
16.4412
13.6943
12.0812
1.3578
1.2546
Chemical Shift (ppm)

SI-3


9.65
9.65
7.37
7.35
7.34
7.32
7.31
7.29
5.32
4.40
4.40
3.84
3.84
3.83
3.83
3.38
3.37
3.36
3.30
3.28
2.61
2.60
2.59
2.59
1.95
1.16
1.14
1.05
1.04
1.03
0
0.88
4.07
1.14
1.00
1.00
1.06
1.07
0.96
1.00
3.19
3.17
27.18
Chemical Shift (ppm)
PB-4117B-b.002.001.1r.esp


203.83
138.41
128.41
127.62
79.68
77.16
72.92
71.79
50.75
38.53
15.01
10.98
0.82
Chemical Shift (ppm)

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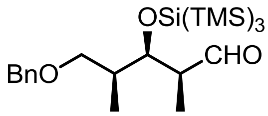
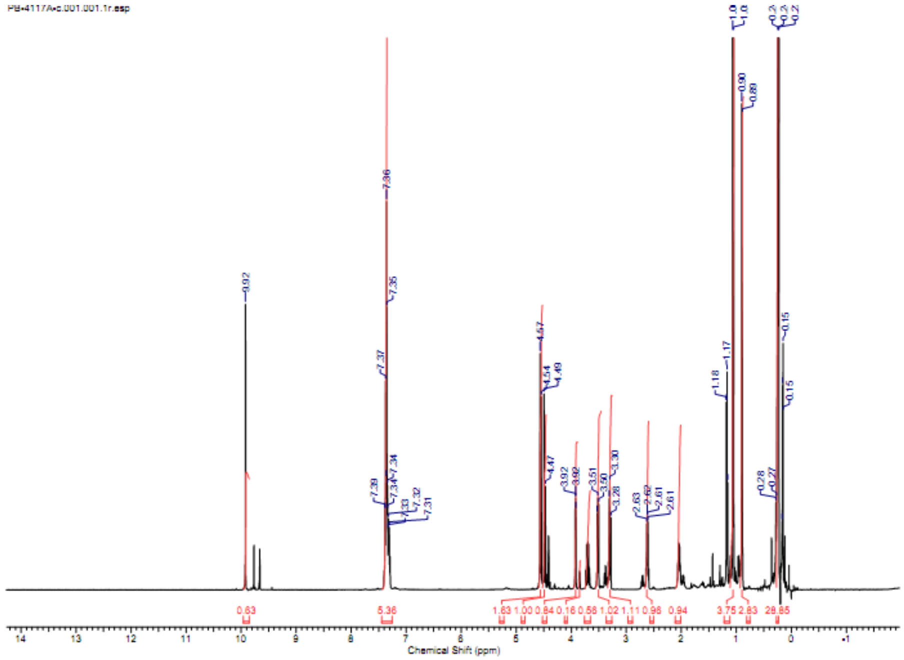
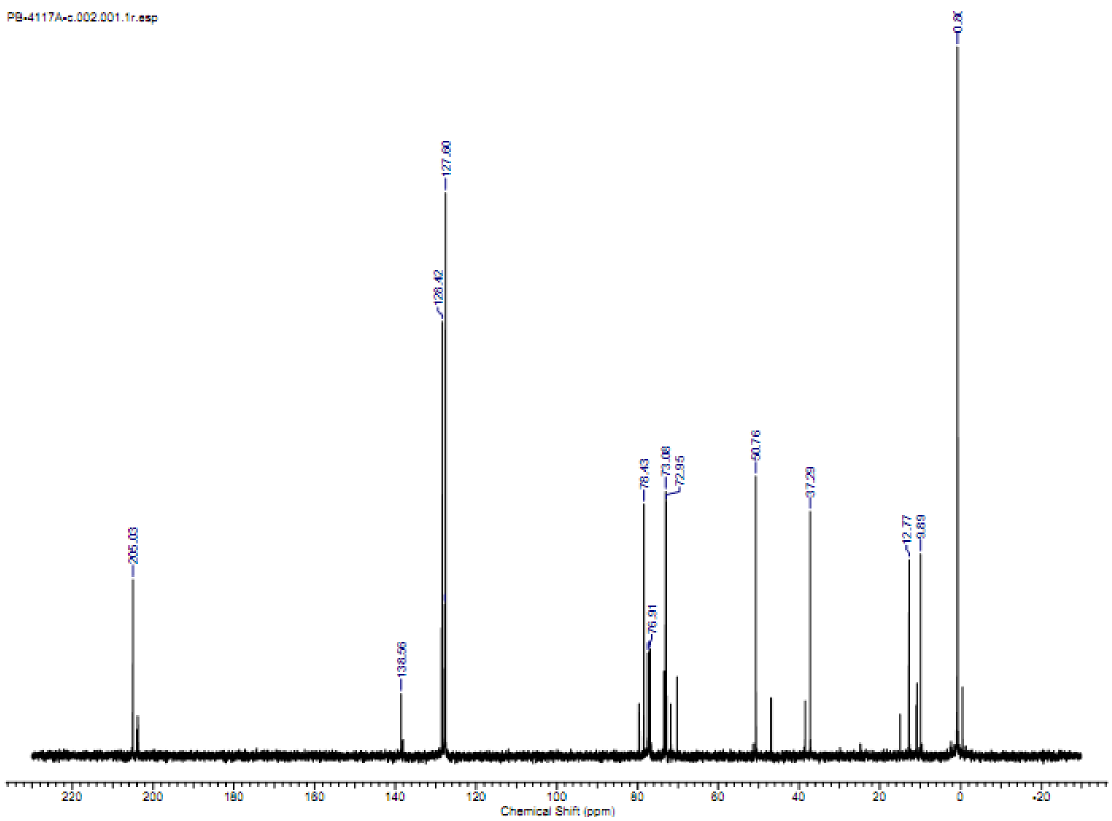
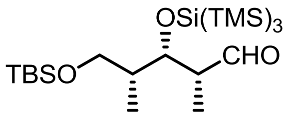


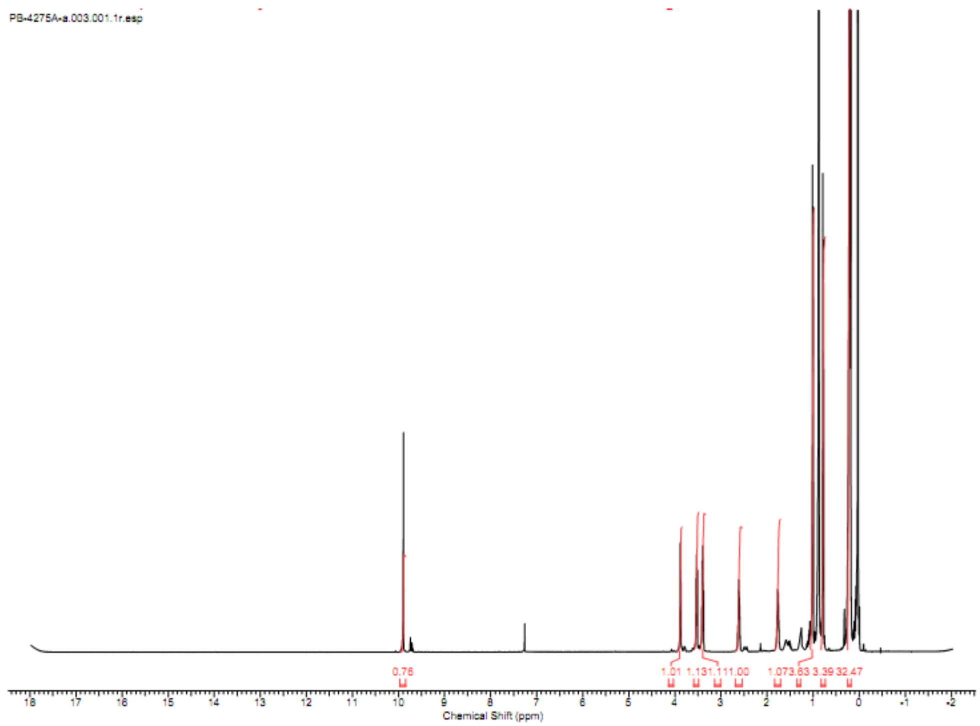
SI5a (dr = 86:14)






OSi(TMS)3
CHO
TBSO

SI5b


PB-4275A-a.003.001.1r.esp
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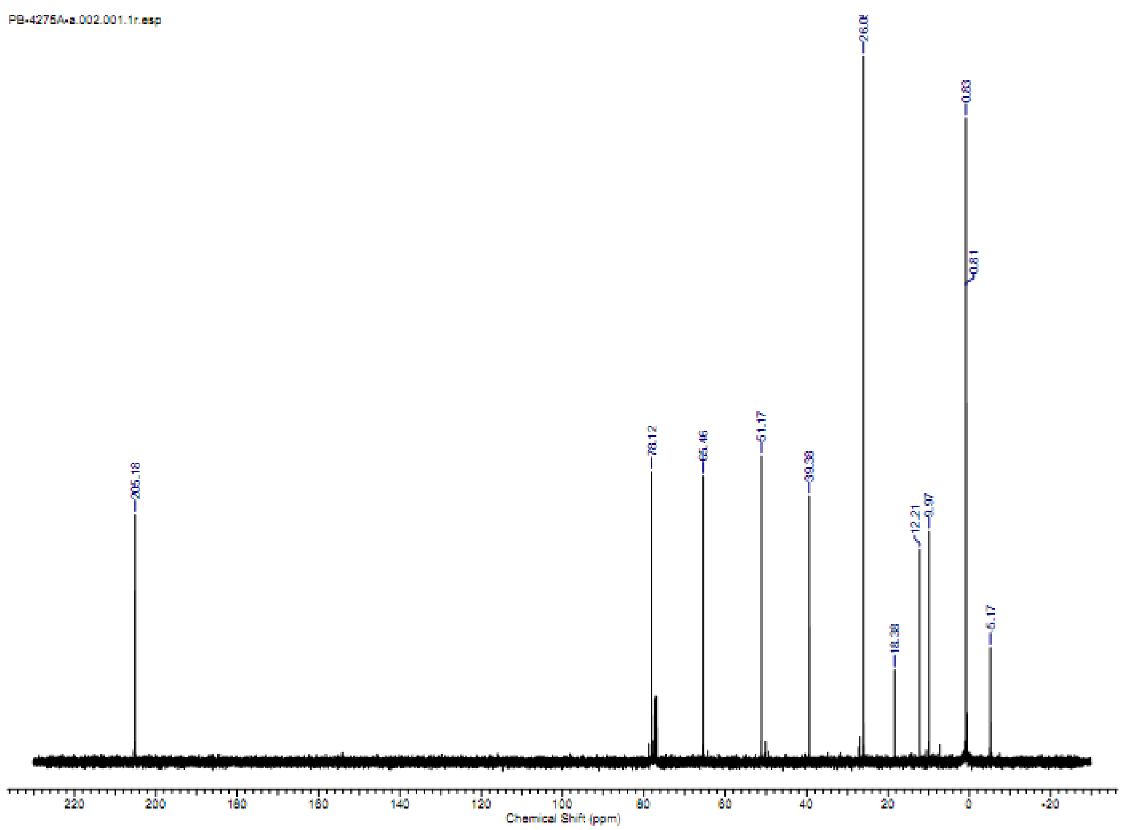
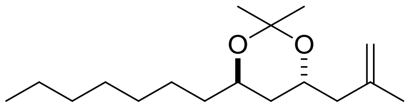
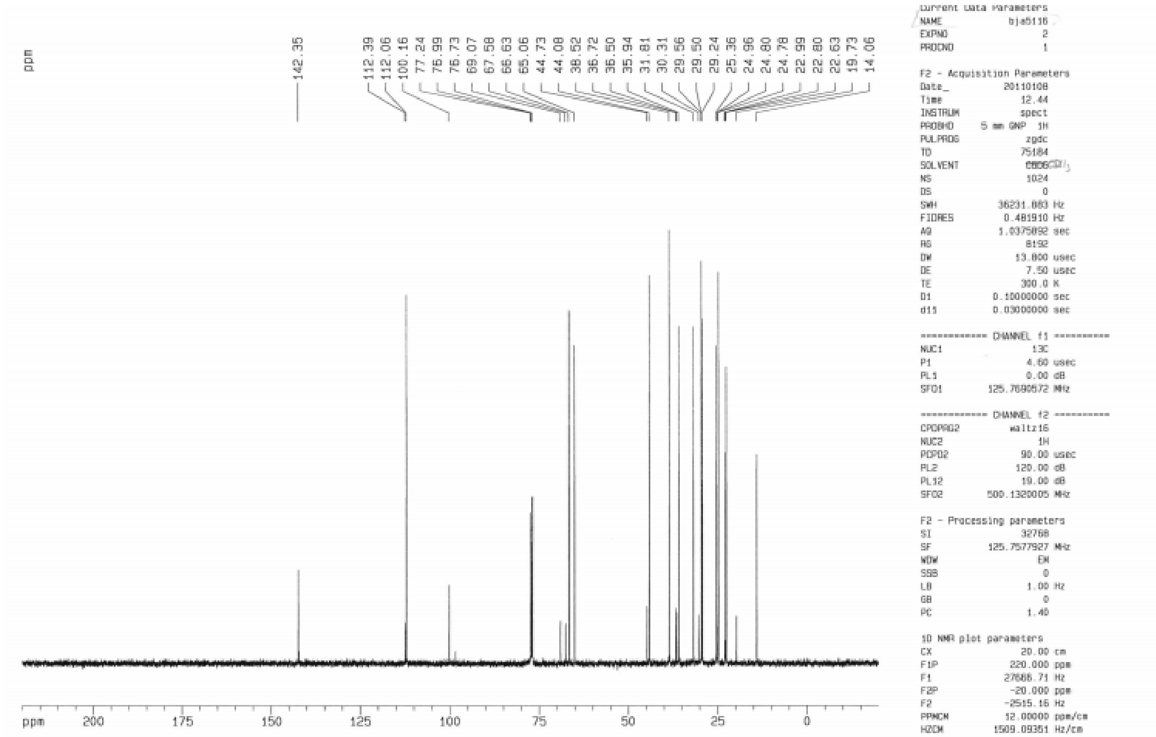
1.01 1.131.111.00
1.073.83 3.39 32.47
Chemical Shift (ppm)


PB-4275A-a.002.001.1r.esp
205.18
78.12
65.46
51.17
39.38
18.38
12.21
9.97
0.83
0.81
-5.17
Chemical Shift (ppm)

SI-11




142.35
112.39
112.06
100.16
77.24
76.99
76.73
69.07
67.58
66.63
65.06
44.73
44.08
38.52
36.72
36.50
35.94
31.81
30.31
29.56
29.50
29.24
25.36
24.96
24.80
24.78
22.99
22.80
22.63
19.73
14.06
ppm
200
175
150
125
100
75
50
25
0
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NAME bja5116
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
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Time 12.44
INSTRUM spect
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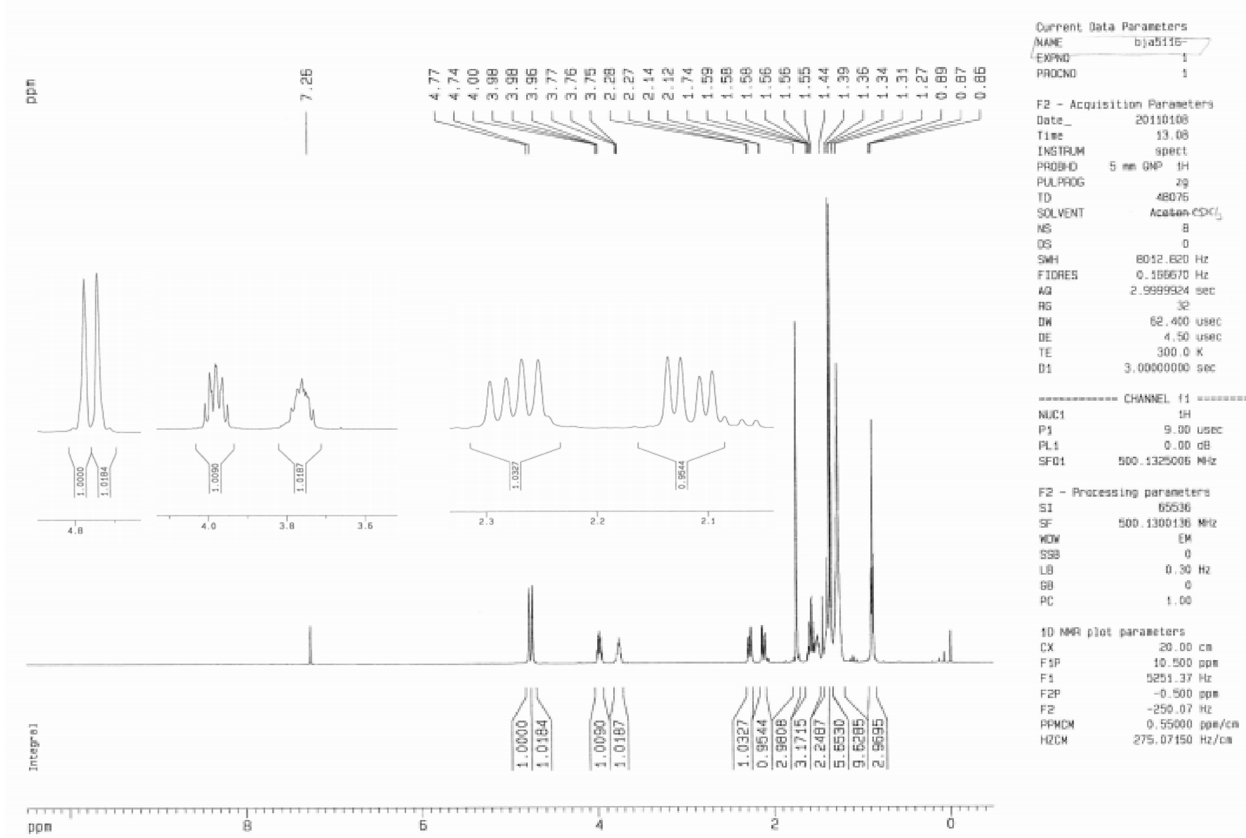
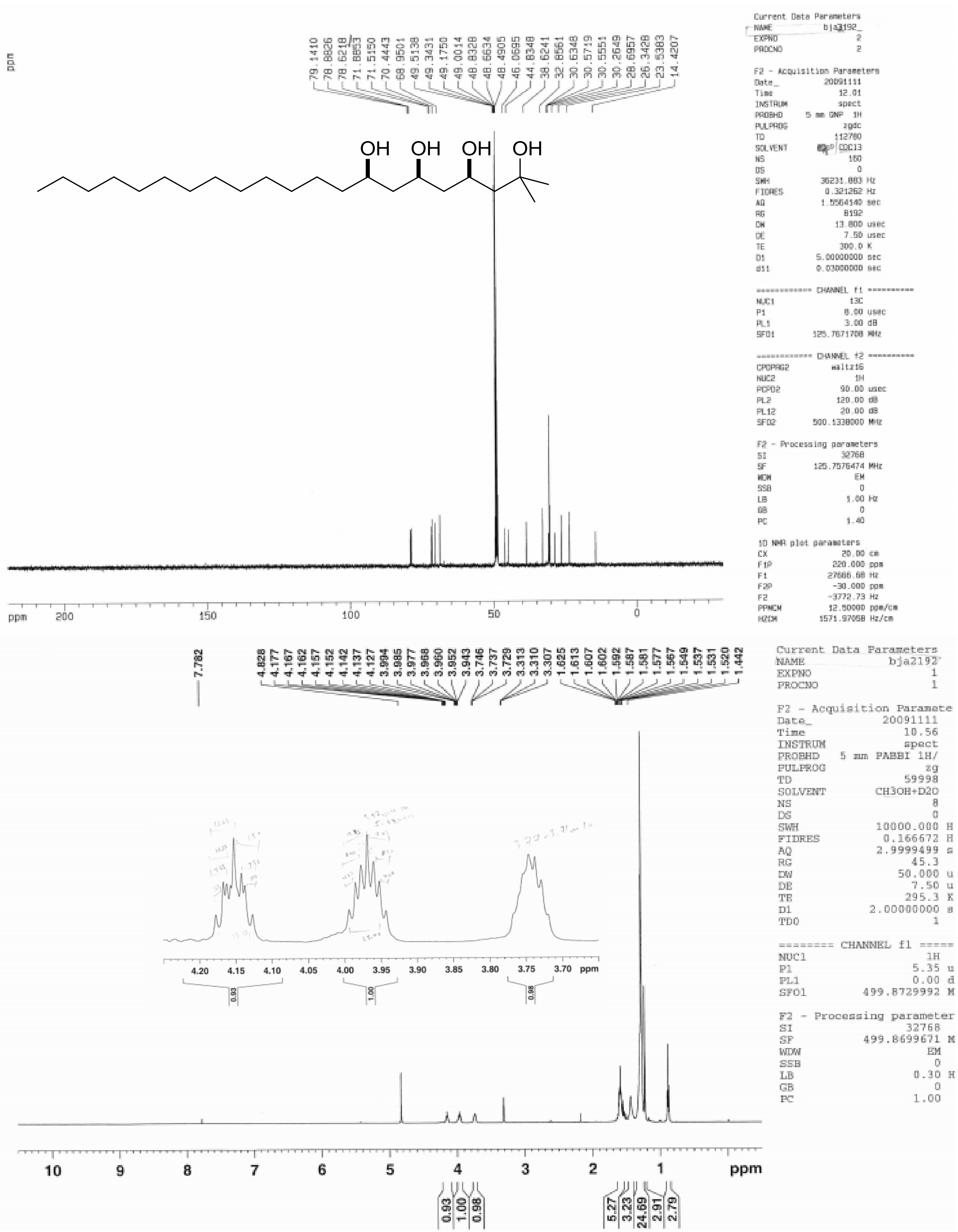
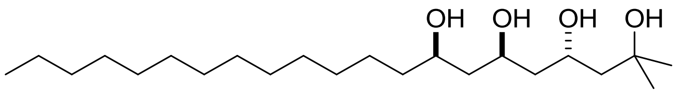
PULPROG zgdc
TD 75184
NS 1024
DS 0
SWH 36231.883 Hz
FIDRES 0.481910 Hz
AQ 1.0375892 sec
RG 8192
DW 13.800 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577927 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P -20.000 ppm
F2 -2515.16 Hz
PPMCM 12.00000 ppm/cm
HZCM 1509.09351 Hz/cm

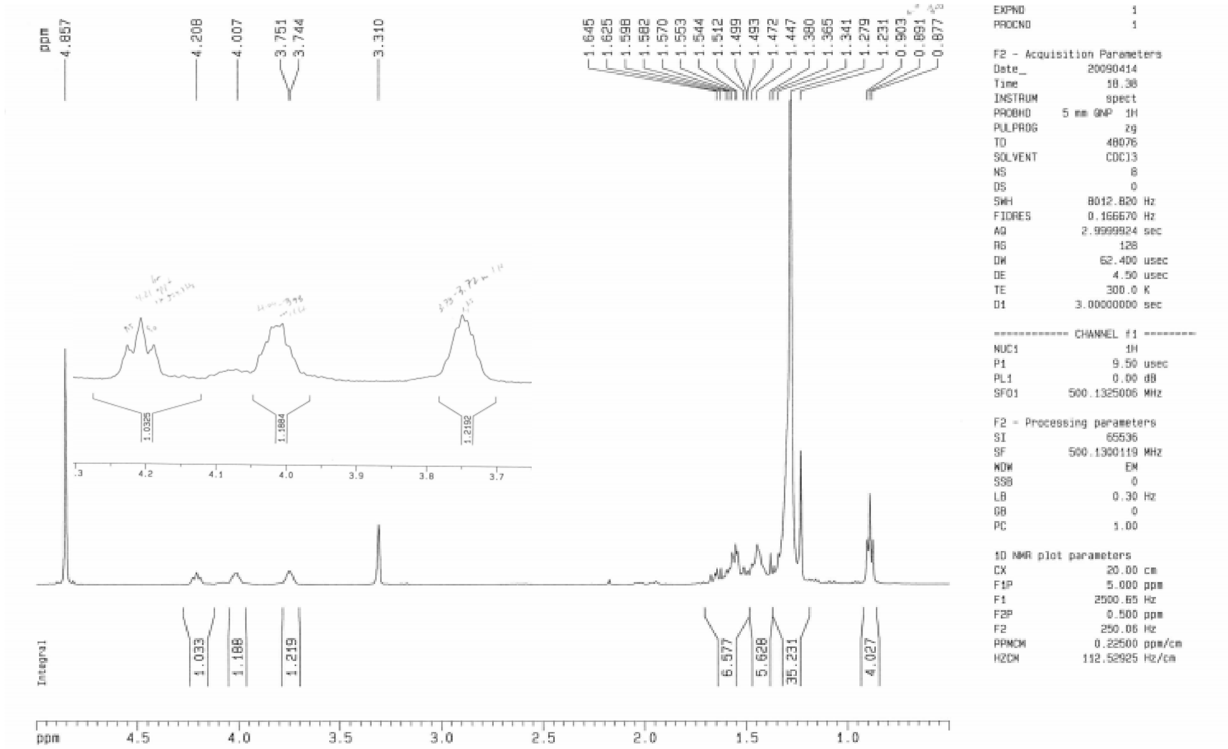

7.26
4.77
4.74
4.00
3.98
3.98
3.96
3.77
3.76
3.75
2.28
2.27
2.14
2.12
1.74
1.59
1.58
1.58
1.56
1.55
1.55
1.44
1.39
1.36
1.34
1.31
1.27
0.89
0.87
0.86
1.0000
1.0184
1.0090
1.0187
1.0327
0.9544
2.9808
3.1715
2.2487
5.5530
9.6285
2.9695
Integral
ppm
8
6
4
2
0
Current Data Parameters
NAME bja5116
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110108
Time 13.08
INSTRUM spect
PROBHD 5 mm GNP 1H
PULPROG zg
TD 48076
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 32
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300136 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.500 ppm
F1 5251.37 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.55000 ppm/cm
HZCM 275.07150 Hz/cm

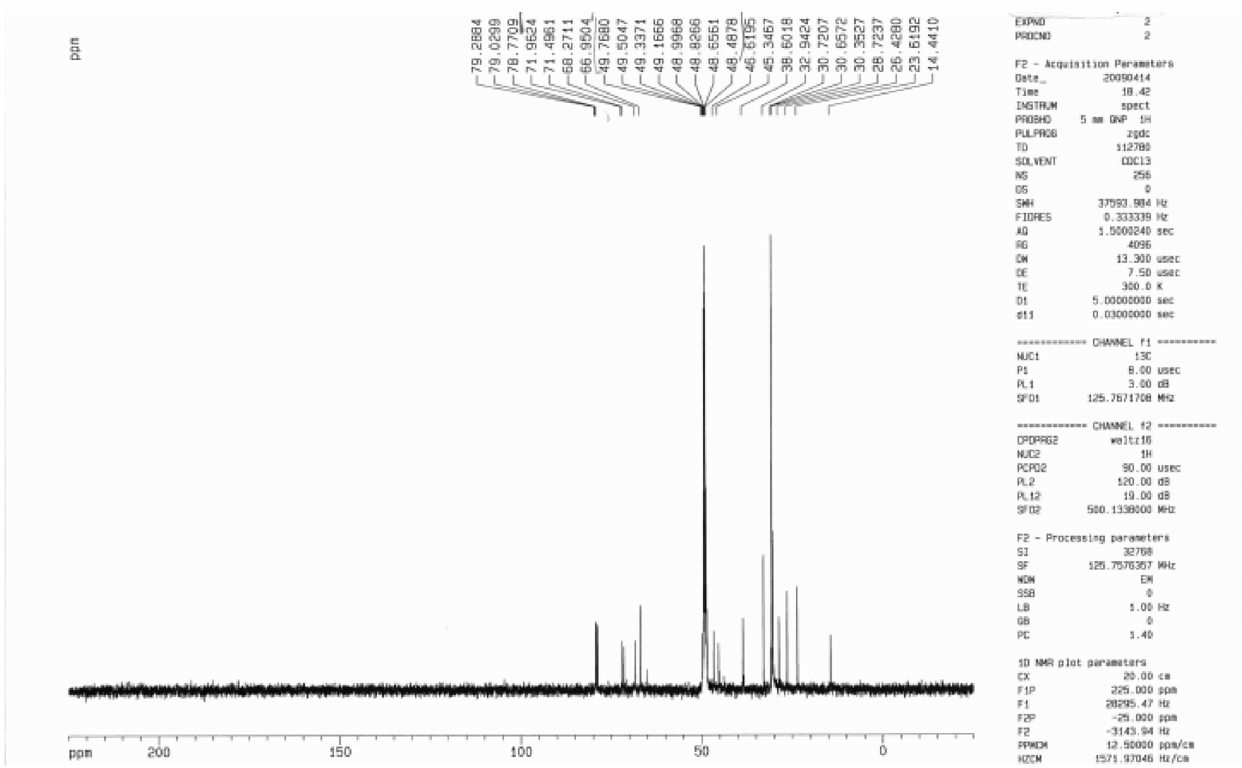
SI-12



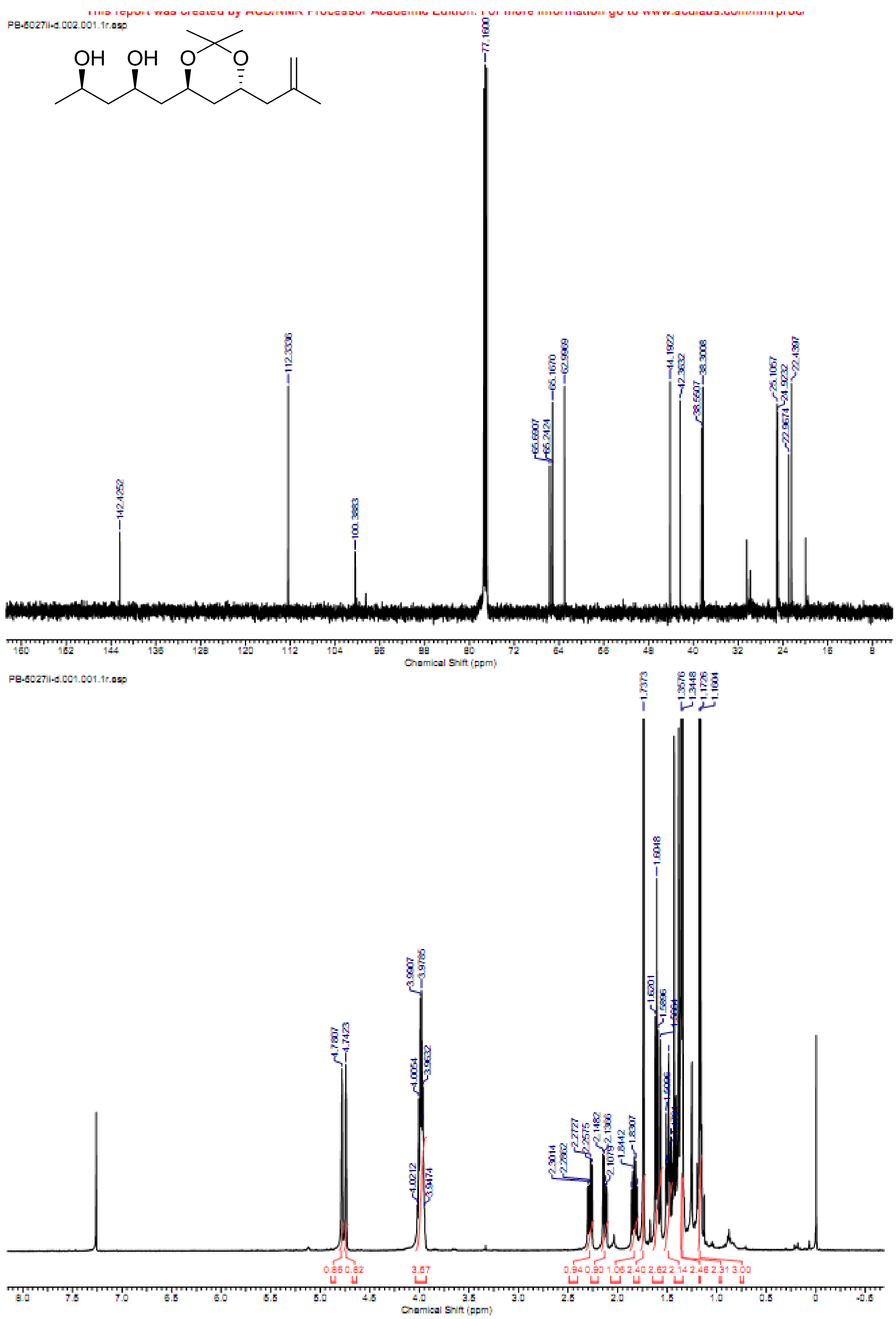

OH
OH
OH
OH

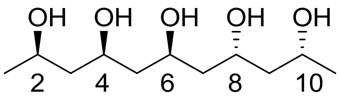
SI-13


ppm
4.857
4.208
4.007
3.751
3.744
3.310
1.645
1.625
1.598
1.582
1.570
1.553
1.544
1.512
1.499
1.493
1.472
1.447
1.380
1.365
1.341
1.279
1.231
0.903
0.891
0.877
Integral
1.033
1.188
1.219
6.577
5.628
35.231
4.027
1.0325
1.1884
1.2192
ppm 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090414
Time 18.38
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 5.000 ppm
F1 2500.65 Hz
F2P 0.500 ppm
F2 250.06 Hz
PPMCM 0.22500 ppm/cm
HZCM 112.52925 Hz/cm

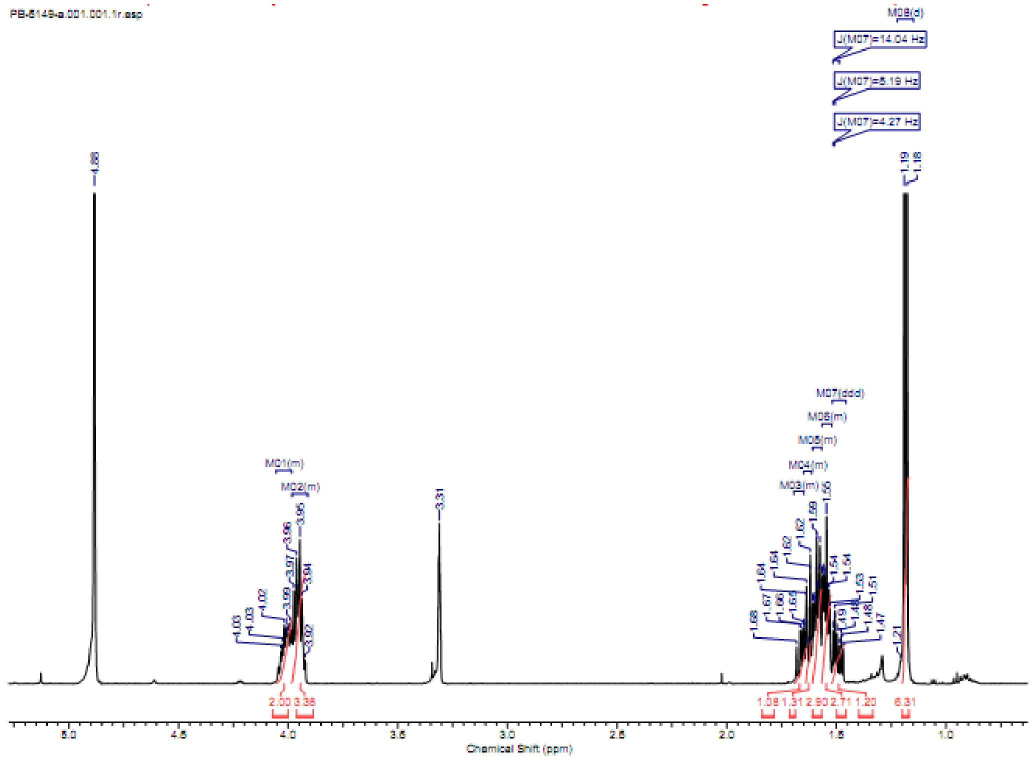

ppm
79.2884
79.0299
78.7709
71.9624
71.4961
68.2711
66.9504
49.7680
49.5047
49.3371
49.1666
48.9968
48.8266
48.6561
48.4878
46.6195
45.3467
38.6018
32.9424
30.7207
30.6572
30.3527
28.7237
26.4280
23.6192
14.4410
ppm 200 150 100 50 0
EXPNO 2
PROCNO 2
F2 - Acquisition Parameters
Date_ 20090414
Time 18.42
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 112780
SOLVENT CDCl3
NS 256
DS 0
SWH 37593.984 Hz
FIDRES 0.333339 Hz
AQ 1.5000240 sec
RG 4096
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 5.00000000 sec
d11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SFO1 125.7671708 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1338000 MHz
F2 - Processing parameters
SI 32768
SF 125.7576357 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 225.000 ppm
F1 28295.47 Hz
F2P -25.000 ppm
F2 -3143.94 Hz
PPMCM 12.50000 ppm/cm
HZCM 1571.97046 Hz/cm

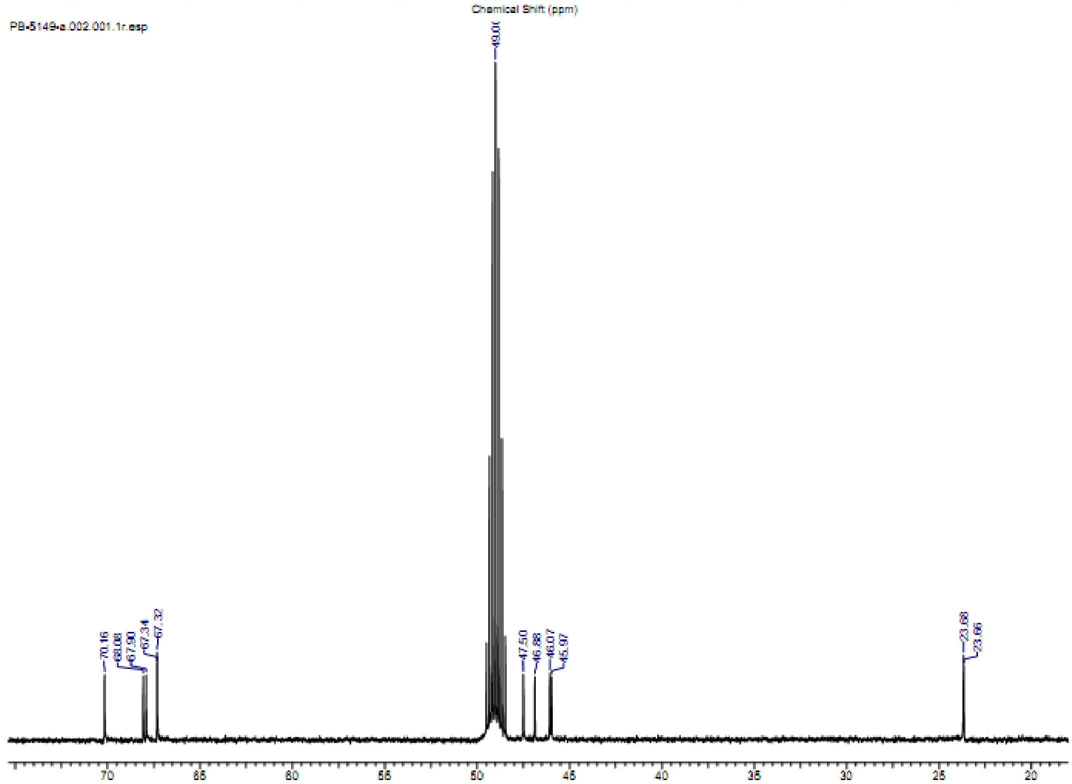
SI-14


OH
OH
O
O
142.4252
112.3336
100.3883
77.1600
Chemical Shift (ppm)
Chemical Shift (ppm)

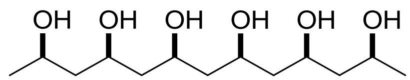

OH
OH
OH
OH
OH
2
4
6
8
10

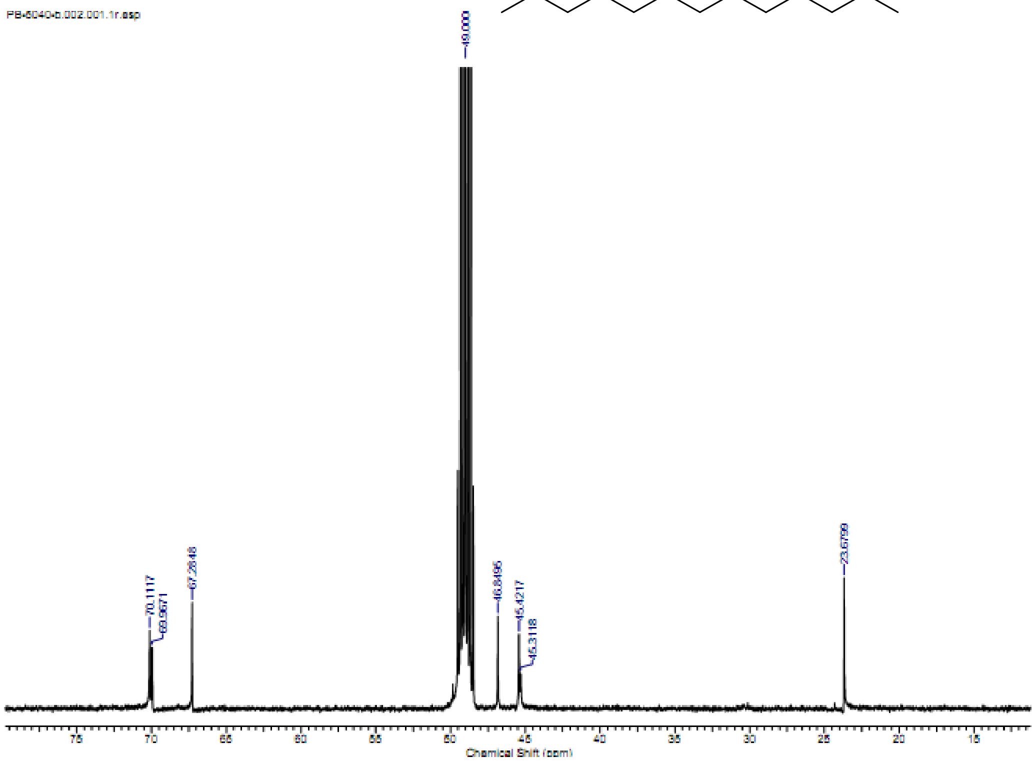
SI-15

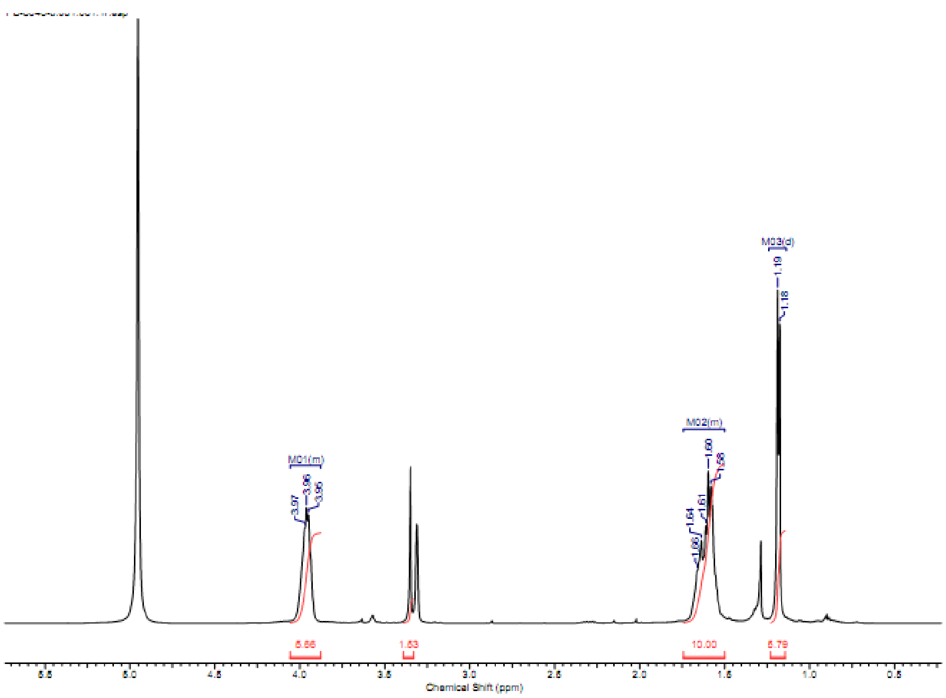

PB-5149-a.001.001.1r.esp
M08(d)
J(M07)=14.04 Hz
J(M07)=5.19 Hz
J(M07)=4.27 Hz
4.88
3.31
M01(m)
M02(m)
M03(m)
M04(m)
M05(m)
M06(m)
M07(ddd)
1.19
1.18
2.00
3.38
6.31
Chemical Shift (ppm)


PB-5149-a.002.001.1r.esp
70.16
67.32
47.50
46.88
46.07
45.97
Chemical Shift (ppm)

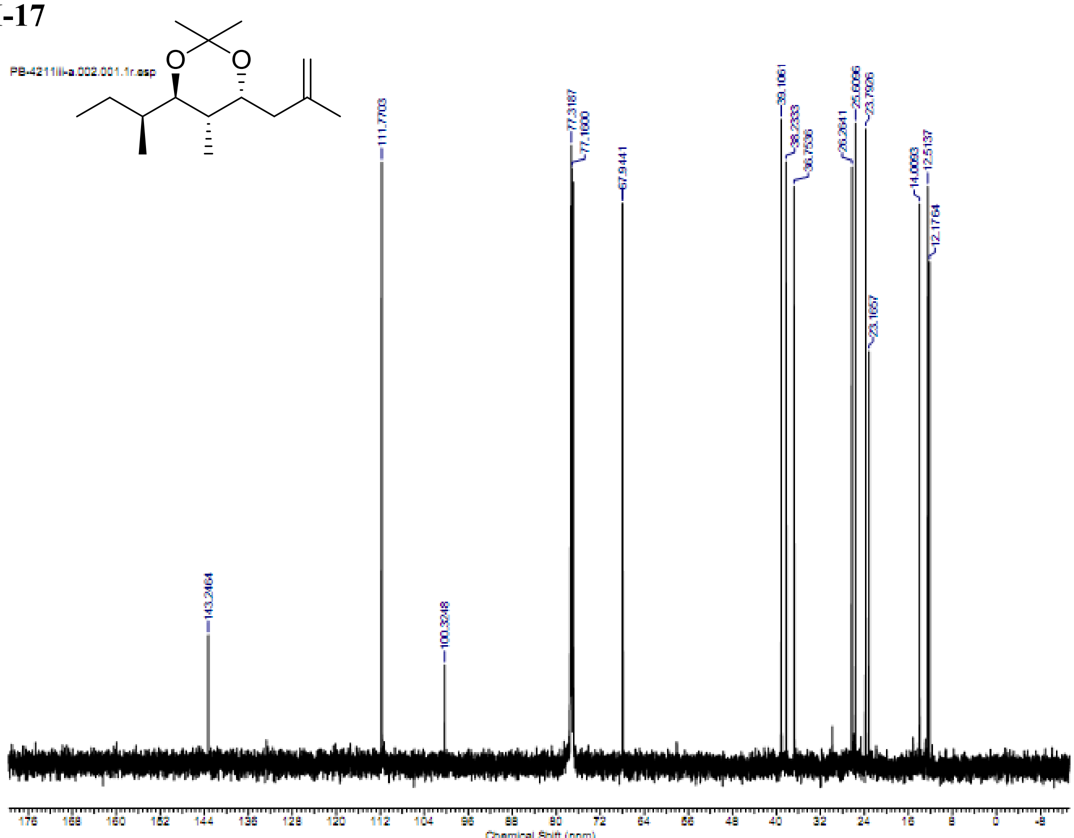
SI-16

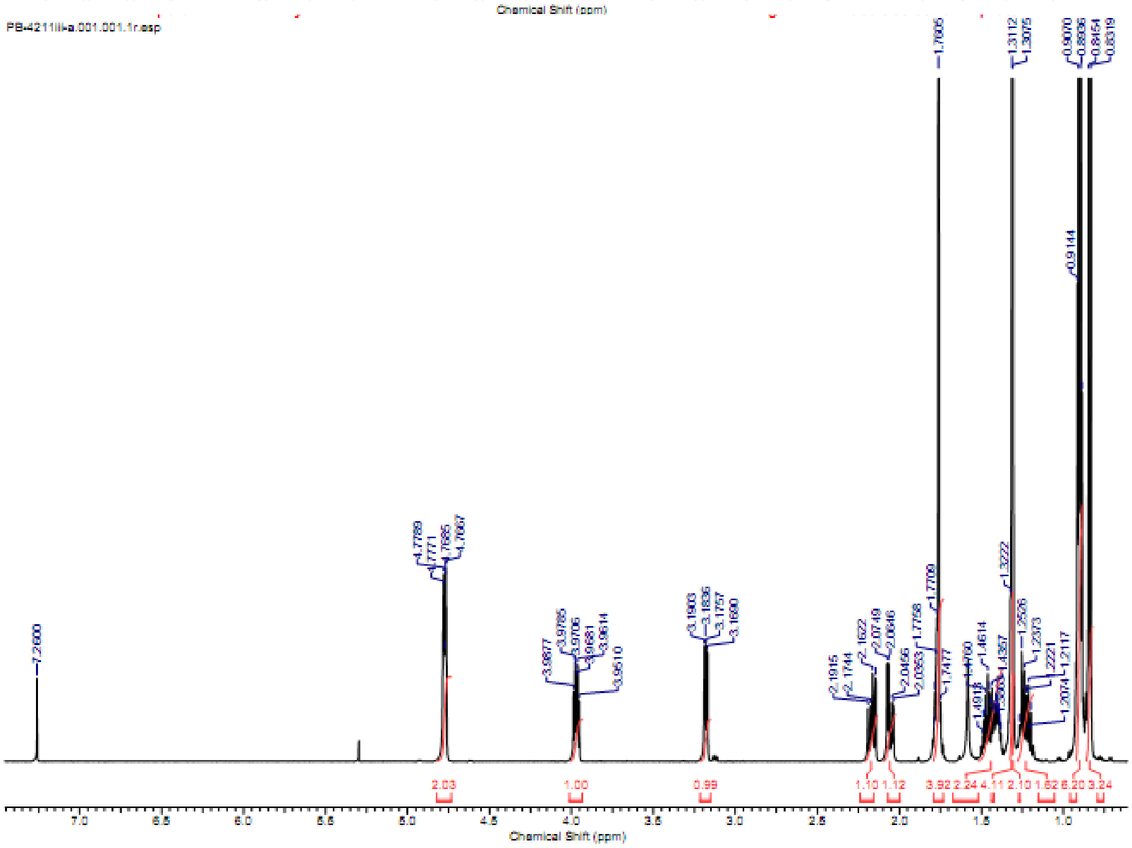

OH
OH
OH
OH
OH
OH


49.000
70.1117
69.9671
67.2848
46.8495
45.4217
45.3118
23.6799
Chemical Shift (ppm)

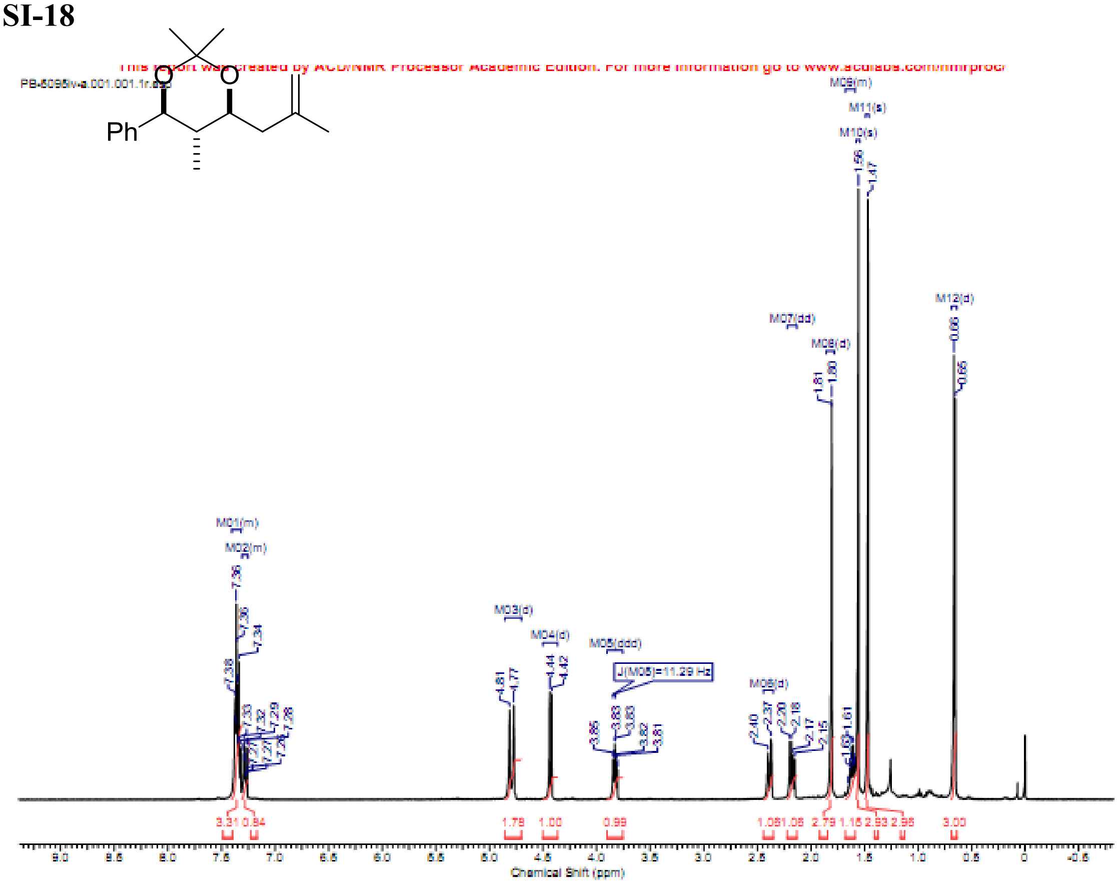

M03(d)
1.19
1.18
M02(m)
1.60
1.58
1.64
1.61
1.66
M01(m)
3.97
3.96
3.95
10.00
Chemical Shift (ppm)

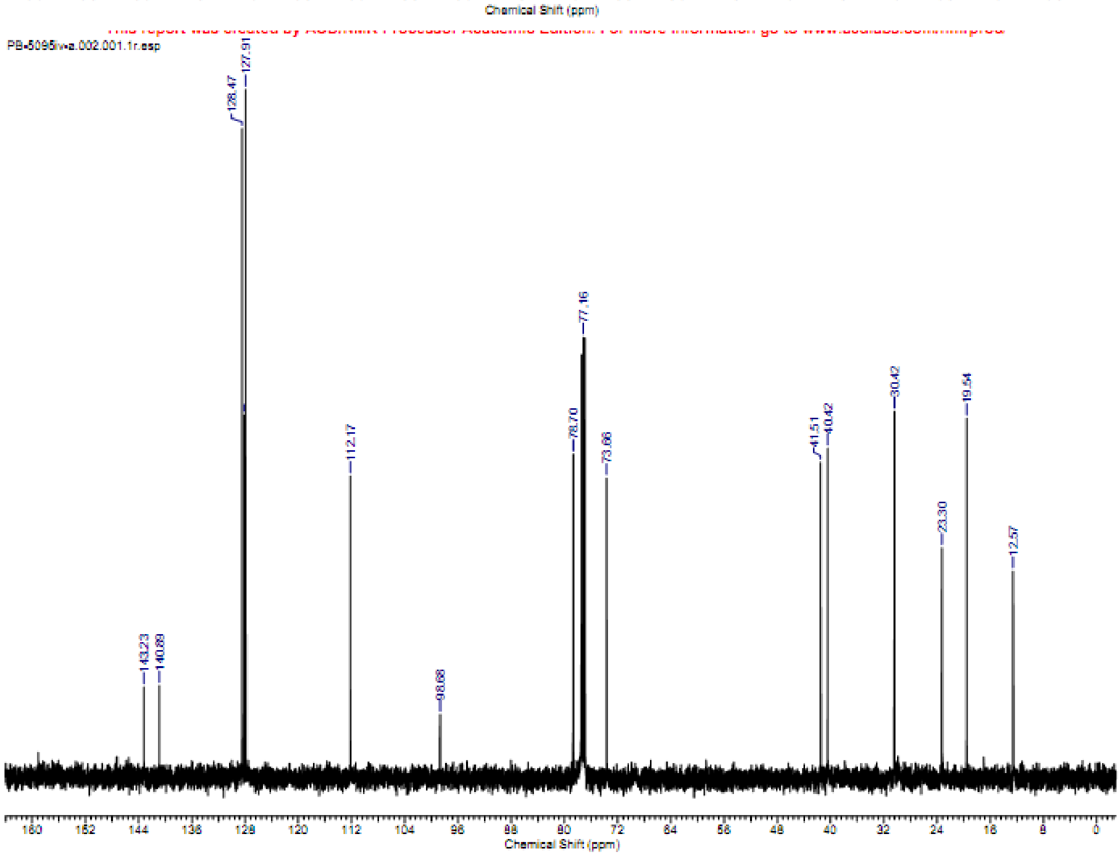
SI-17


O
O
PB-4211iii-a.002.001.1r.esp
143.2464
111.7703
100.3248
77.3187
77.1600
67.9441
39.1061
38.2333
36.7536
26.2641
25.6006
23.7926
23.1657
14.0693
12.5137
12.1764
Chemical Shift (ppm)

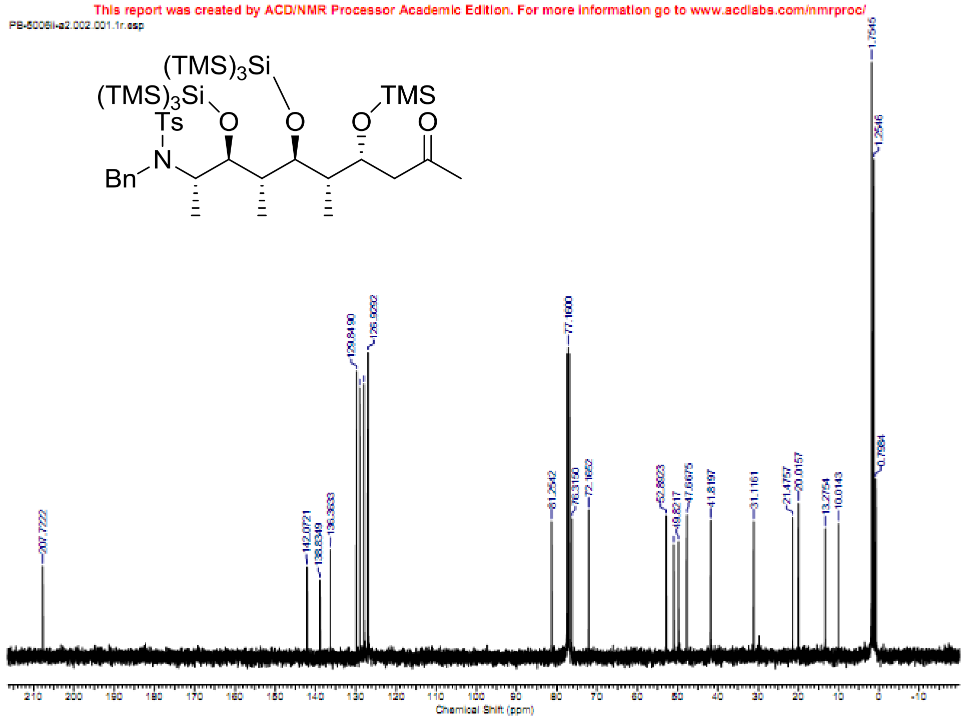

PB-4211iii-a.001.001.1r.esp
7.2600
2.03
1.00
0.99
1.10
1.12
3.92
2.24
4.11
2.10
1.82
6.20
3.24
Chemical Shift (ppm)

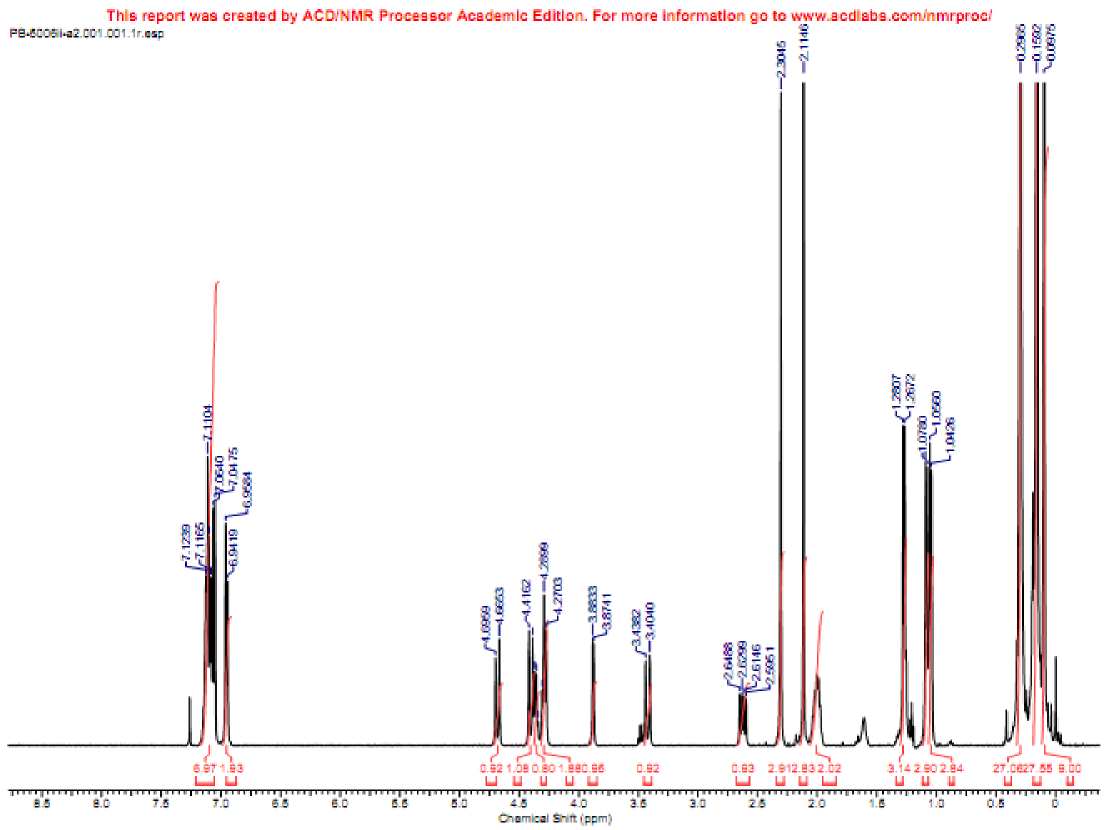
SI-18


Ph
O
O
PB-5095iv-a.001.001.1r.esp
M01(m)
M02(m)
M03(d)
M04(d)
M05(ddd)
J(M05)=11.29 Hz
M06(d)
M07(dd)
M08(d)
M09(m)
M10(s)
M11(s)
M12(d)
Chemical Shift (ppm)


PB-5095iv-a.002.001.1r.esp
143.23
140.89
128.47
127.91
112.17
98.68
78.70
77.16
73.66
41.51
40.42
30.42
23.30
19.54
12.57
Chemical Shift (ppm)

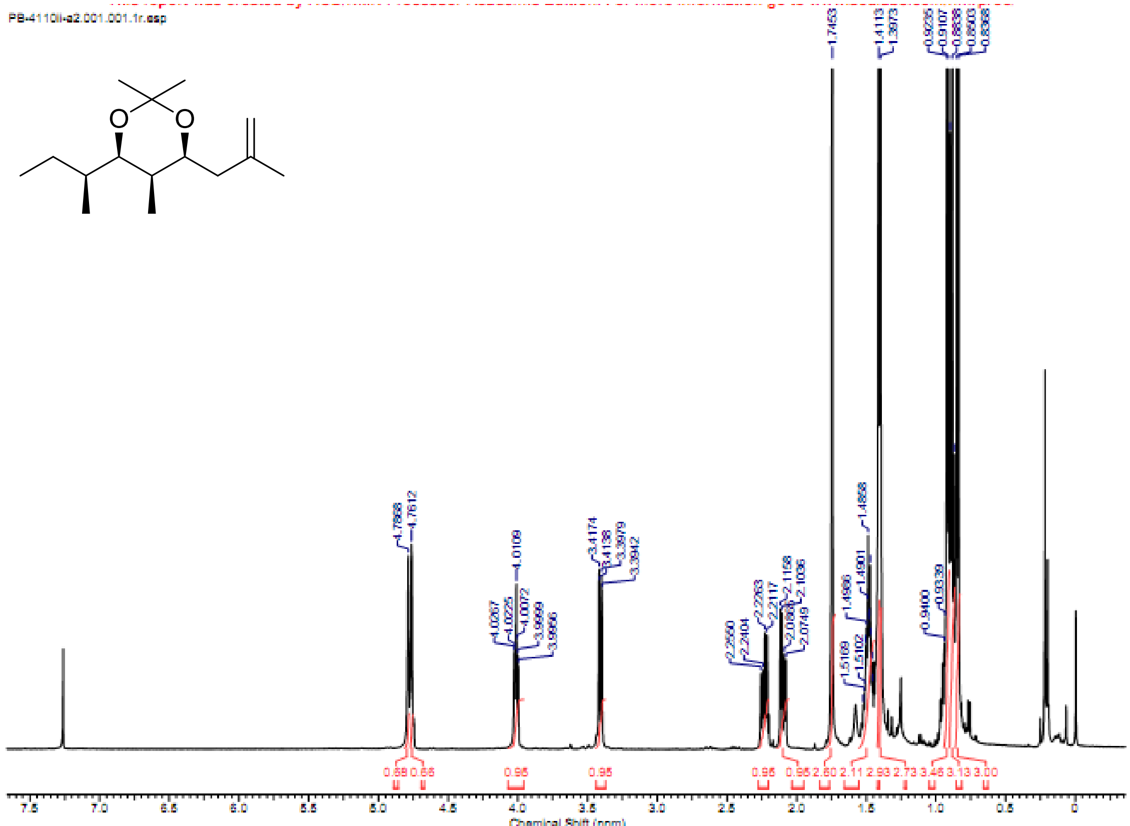
SI-19



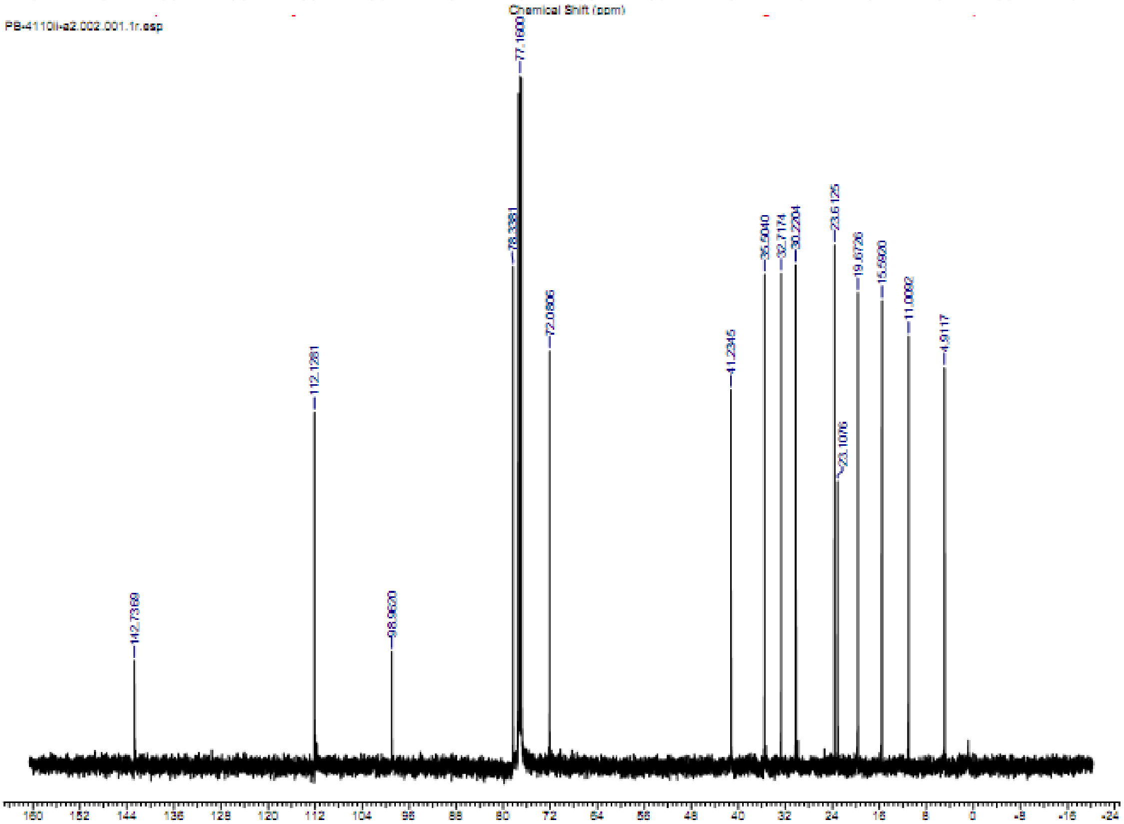


SI-20

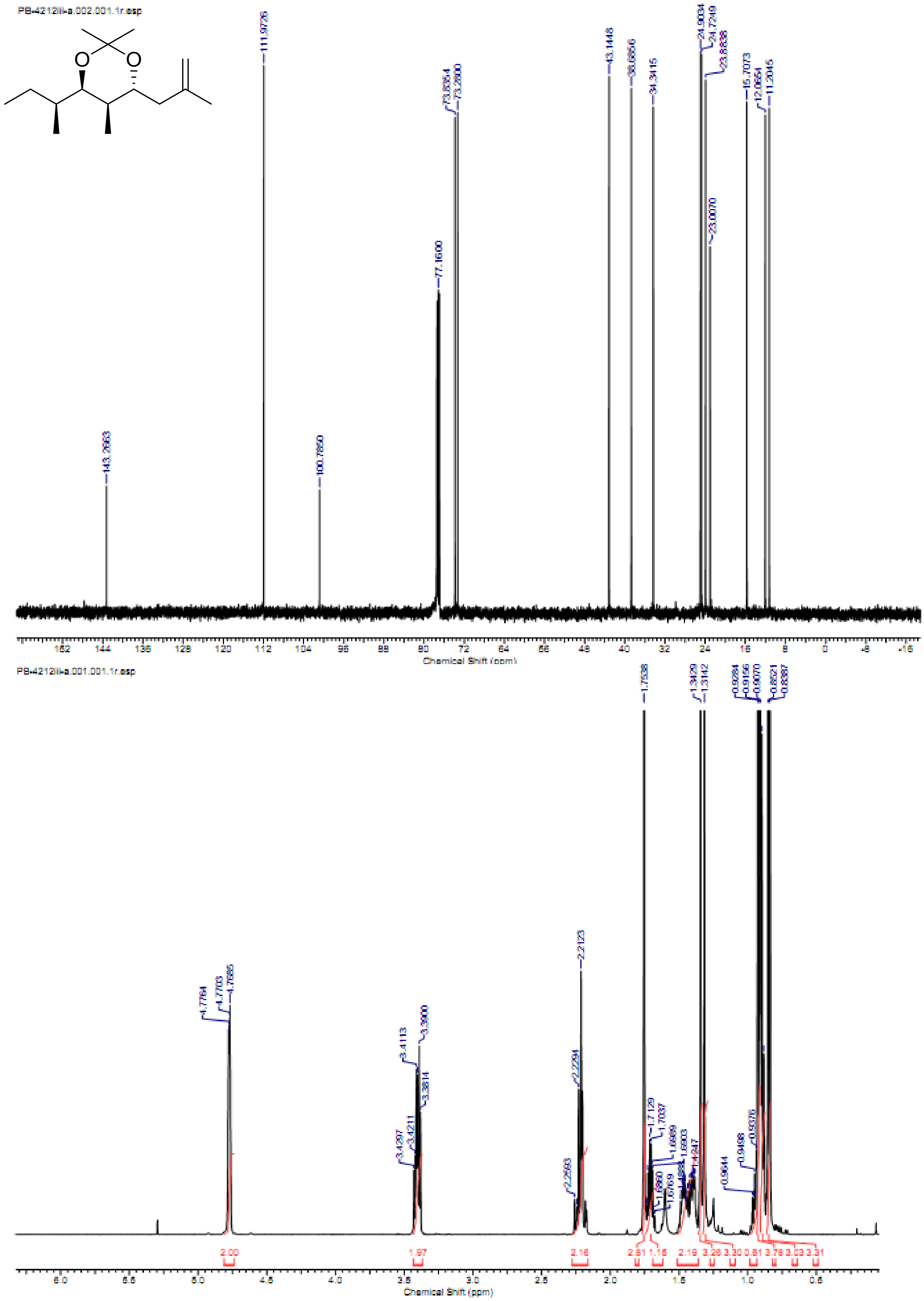
PB-4110ii-a2.001.001.1r.esp



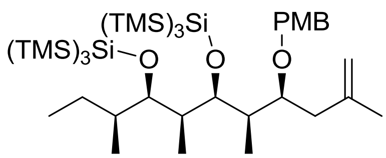
PB-4110ii-a2.002.001.1r.esp

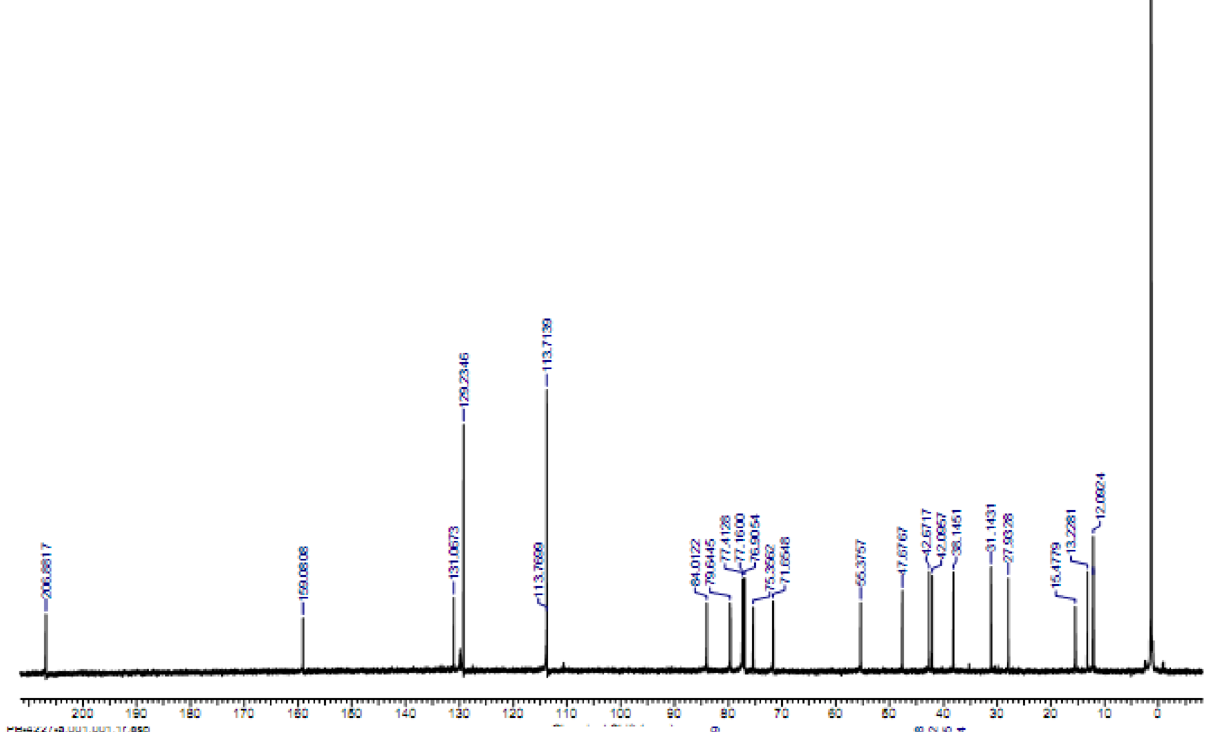


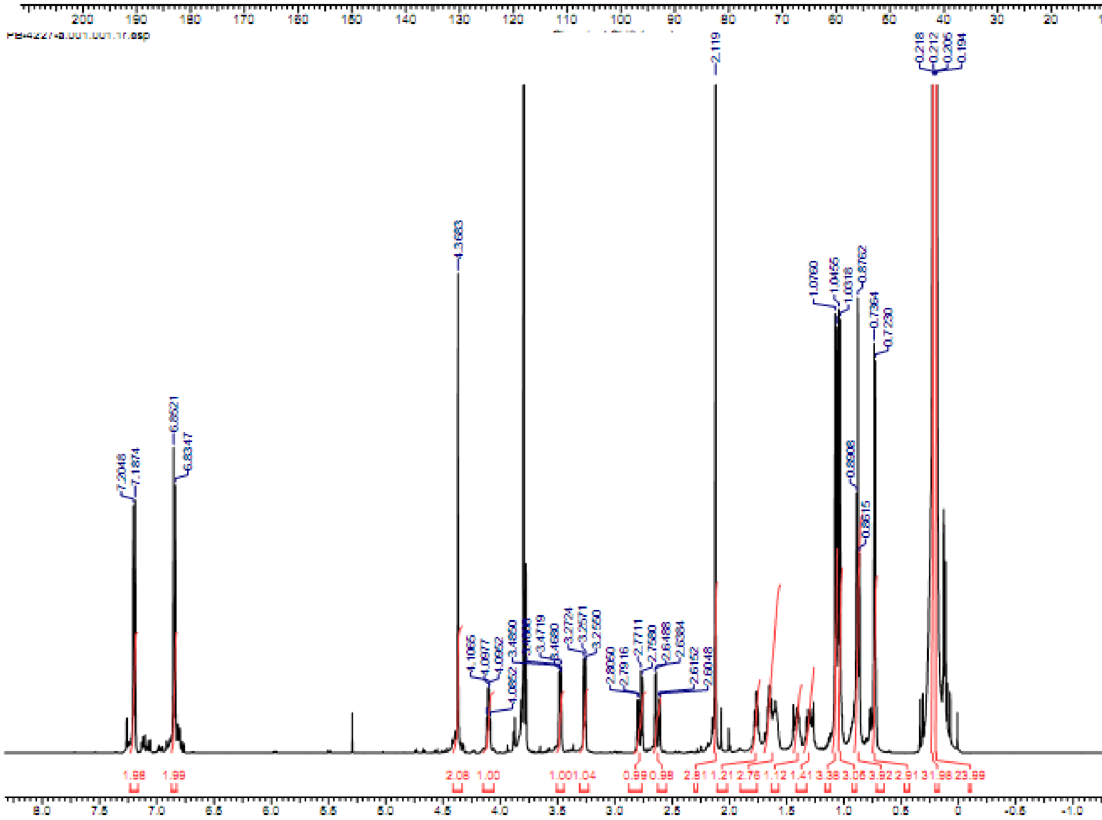
SI-21


PB-4212iii-a.002.001.1r.esp
Chemical Shift (ppm)
PB-4212iii-a.001.001.1r.esp
Chemical Shift (ppm)

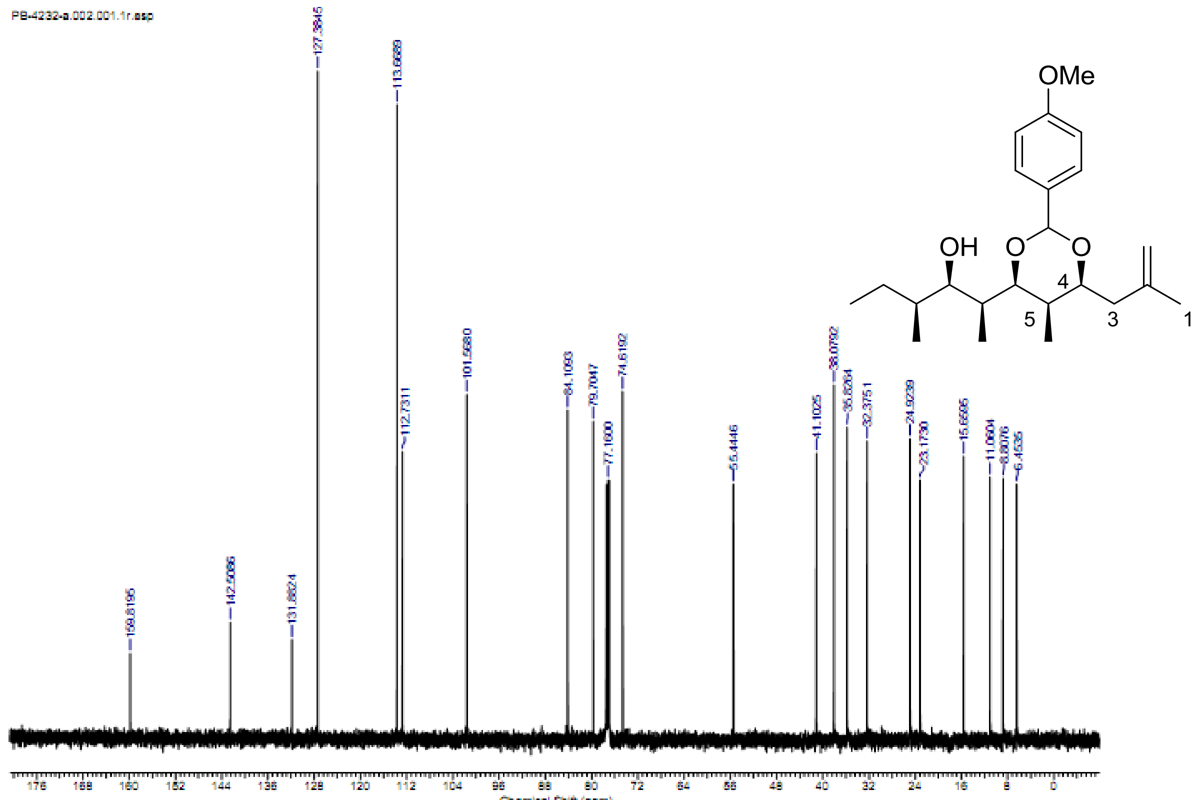
SI-22

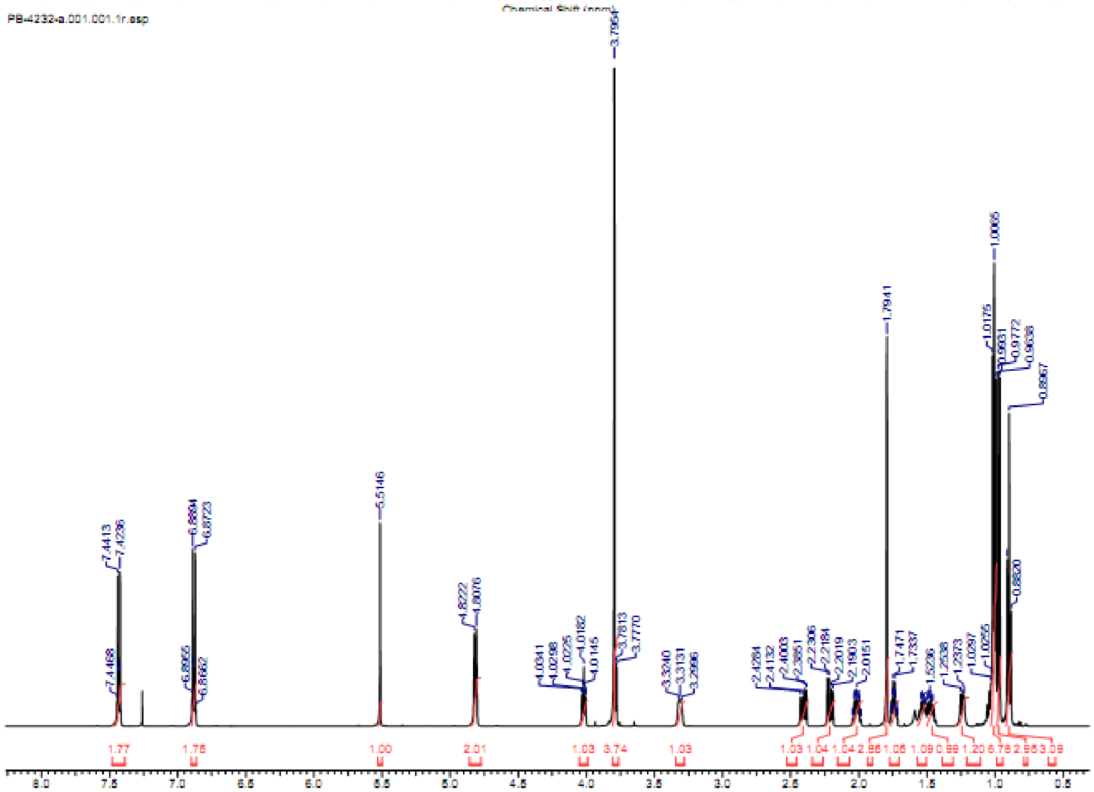




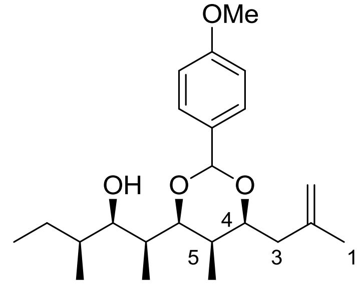


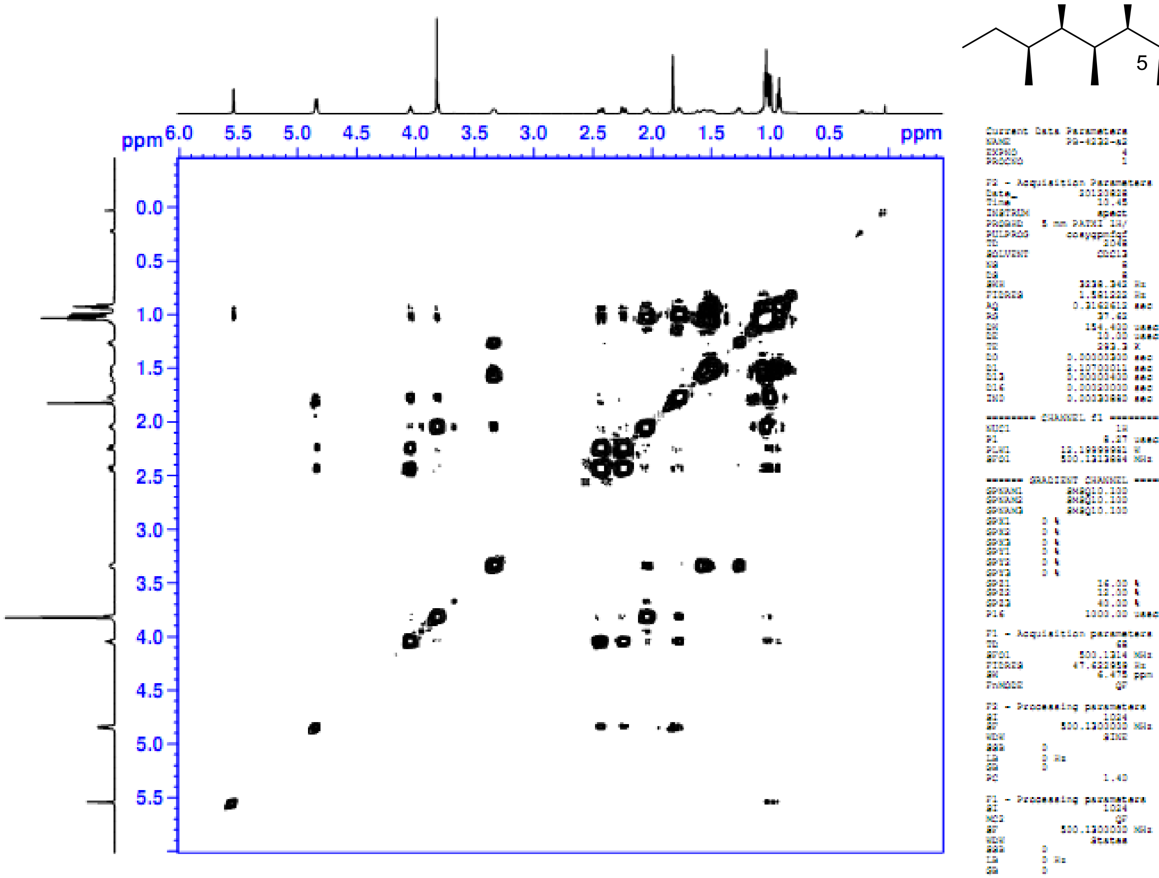
SI-23


PB-4232-a.002.001.1r.esp
OMe
OH
O
O
4
5
3
1
Chemical Shift (ppm)

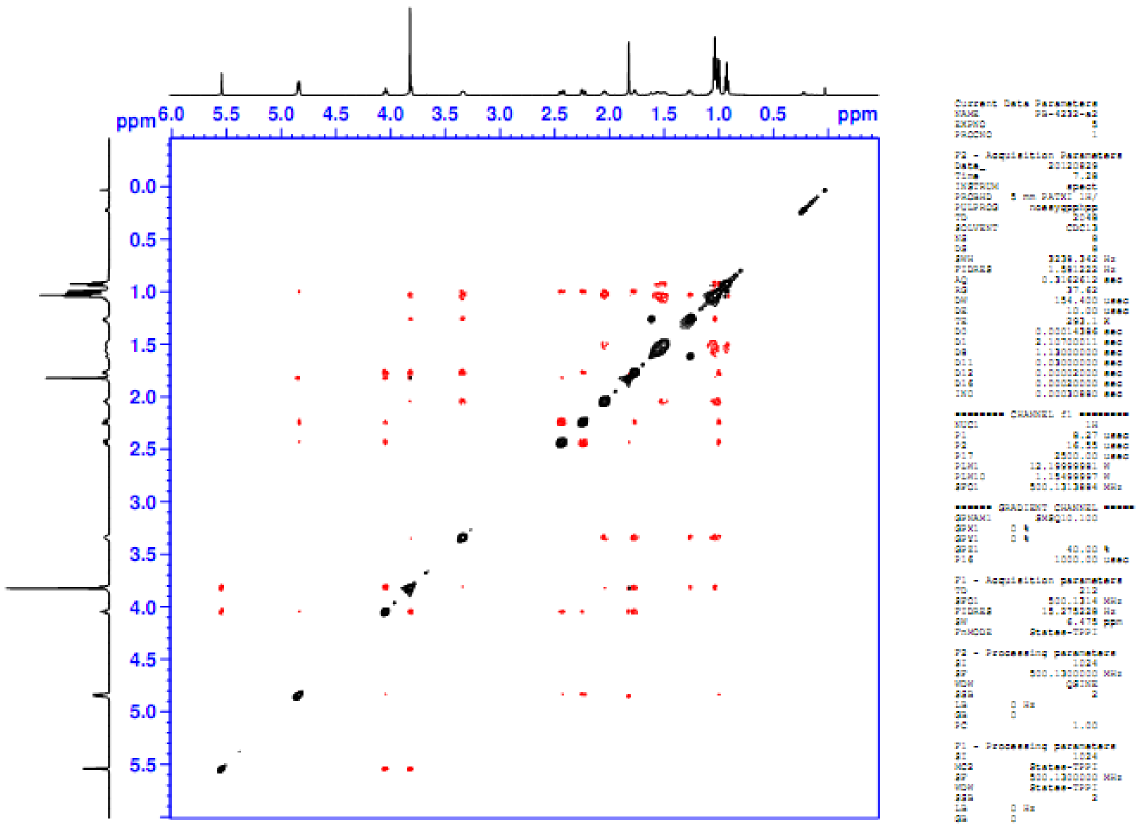

PB-4232-a.001.001.1r.esp
Chemical Shift (ppm)

COSY Spectrum of SI-23





NOESY SPECTRUM for SI-23



Crystal Structure Report for Compound SI19

$C_{47}H_{97}NO_6SSi_9$

Report Prepared for:

Patrick Brady and Mr. H. Yamamoto

October, 2012

Ian Steele (steele@geosci.uchicago.edu)

X-ray Laboratory, Searle B013, 773-834-5861

Department of Chemistry

The University of Chicago

5735 S. Ellis Ave.

Chicago, Il 60637

Crystallographic Experimental Section

Data Collection

An irregular broken fragment (0.40 x 0.24 x 0.12 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "full sphere" data set was obtained which samples approximately all of reciprocal space to a resolution of 0.75 Å using 0.3^{o} steps in ω using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Structure solution and refinement

The space group was determined as P1(bar) based on systematic absences and intensity statistics. Direct methods were used to locate most Si atoms and some C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C, N, O and S atoms. Following anisotropic refinement of all non-H atoms, ideal H-atom positions were calculated. Final refinement was anisotropic for all non-H atoms, and isotropic-riding for H atoms. No anomalous bond lengths or thermal parameters were noted. All ORTEP diagrams have been drawn with 50% probability ellipsoids.

Equations of interest:

$R_{int} = \Sigma | F_o^2 - \langle F_o^2 \rangle | / \Sigma | F_o^2|$

$R1 = \Sigma | | F_o| - | F_c|| / \Sigma| F_o|$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

where: $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$;

q, a, b, P as defined in [1]

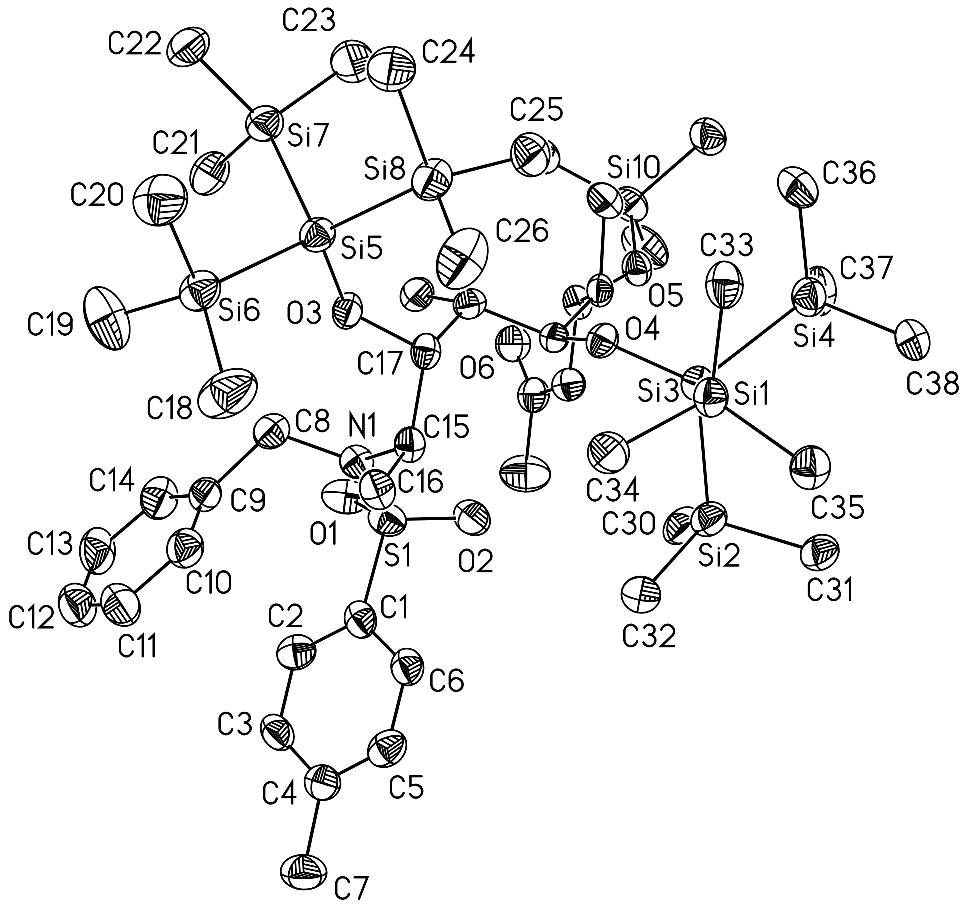
$GooF = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

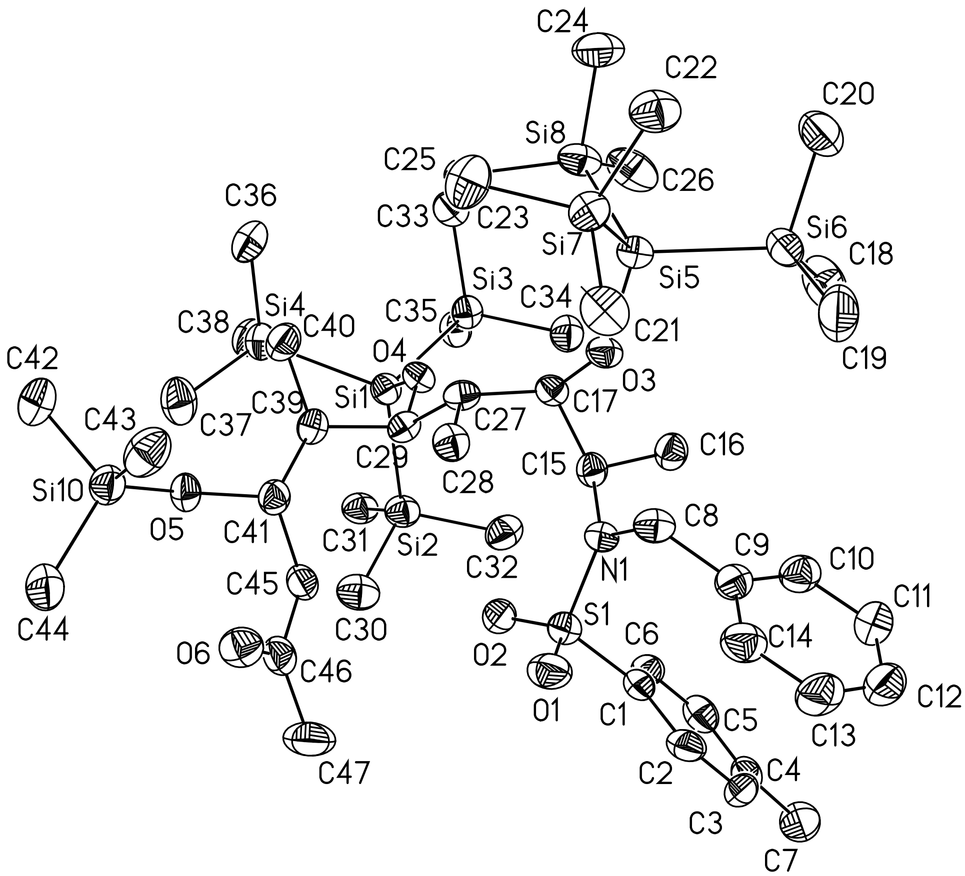
n = number of independent reflections;

p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).


C22
C23
C24
C25
Si7
C21
Si8
Si10
C36
C20
C26
Si5
C33
C37
O5
C19
Si6
O3
O4
Si4
C17
O6
Si3
Si1
C38
C18
C8
N1
C15
C14
C16
C34
C35
C9
O1
C30
C13
C10
S1
O2
Si2
C31
C12
C11
C1
C32
C2
C6
C3
C4
C5
C7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Si4
C38
C40
C21
C19
C42
O4
O3
Si1
C17
C39
C27
C37
C43
C16
C29
C15
Si10
C28
O5
C8
C41
C31
Si2
C9
C32
C10
N1
C45
C11
C44
C30
S1
C14
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O2
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C46
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O1
C1
C5
C13
C2
C4
C47
C3
C7

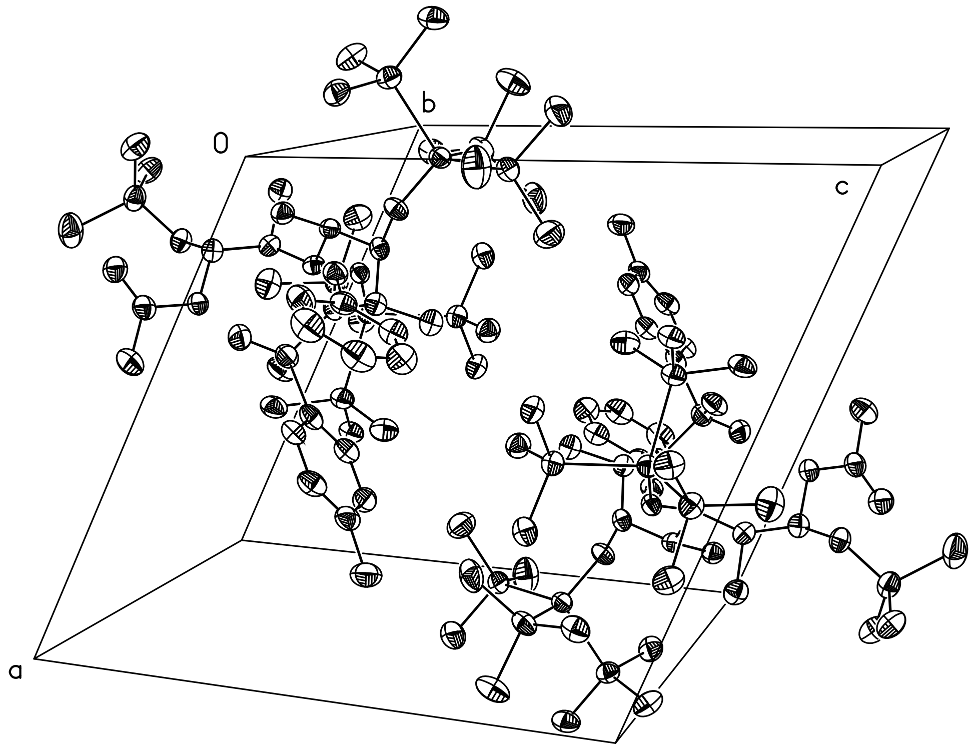
b
0
c
a

Table 1. Crystal and structure refinement for Brady11.

Identification Code	Brady11	
Empirical formula	$C_{47}H_{97}NO_6SSi_9$	
Formula weight	1057.13	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space Group	P1(bar)	
Unit cell dimensions	a = 13.583(4) Å	α = 110.618(7) °
	b = 15.995(5) Å	β = 111.892(6) °
	c = 16.961(5) Å	γ = 93.200(6) °
Volume	3125.1(17) $Å^3$	
Z	2	
Density (calculated)	1.123 Mg/m^3	
Absorption coefficient	0.265 mm^{-1}	
F(000)	1152	
Crystal size, color, habit	0.40 x 0.24 x 0.12 mm, transparent, irregular	
Theta range for data collection	1.65 – 28.73 °	
Index ranges	$-18 \le h \le 18$, $-20 \le k \le 21$, $-22 \le l \le 22$	
Reflections collected	37,882	
Independent reflections	15,162 (R_{int} = 0.0395)	
Reflections with $I > 4\sigma(F_o)$	6,006	
Absorption correction	SADABS based on redundant diffractions	
Max. and min. transmission	1.0, 0.773	
Refinement method	Full-matrix least squares on F^2	
Weighting scheme	$w = q [\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where:	
	$P = (F_o^2 + 2 F_c^2)/3$, a = 0.0316, b = 0.0, q =1	
Data / restraints / parameters	15162 / 0 / 603	
Goodness-of-fit on F^2	0.726	
Final R indices [I > 2 sigma(I)]	R1 = 0.0691, wR2 = 0.1018	
R indices (all data)	R1 = 0.1620, wR2 = 0.1210	
Largest diff. peak and hole	0.473, -0.376 $eÅ^{-3}$	

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for Brady11. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
C(1)	5089(3)	1144(3)	2777(3)	34(1)	
C(2)	5229(3)	315(3)	2816(3)	38(1)	
C(3)	6140(3)	266(3)	3518(3)	39(1)	
C(4)	6916(3)	1041(3)	4177(3)	37(1)	
C(5)	6744(3)	1866(3)	4134(3)	39(1)	
C(6)	5851(3)	1929(3)	3440(3)	35(1)	
C(7)	7916(3)	984(3)	4910(3)	51(1)	
C(8)	2274(3)	839(2)	2208(3)	35(1)	
C(9)	2746(3)	264(3)	2732(3)	34(1)	
C(10)	3294(3)	623(3)	3685(3)	41(1)	
C(11)	3683(3)	76(3)	4154(3)	48(1)	
C(12)	3516(4)	-849(3)	3665(3)	52(1)	
C(13)	2954(3)	-1218(3)	2719(3)	52(1)	
C(14)	2581(3)	-668(3)	2261(3)	46(1)	
C(15)	3077(3)	2535(2)	2675(2)	30(1)	
C(16)	3437(3)	2854(2)	3713(2)	36(1)	
C(17)	2020(3)	2823(2)	2237(2)	27(1)	
C(18)	1664(3)	3099(3)	5011(3)	70(2)	
C(19)	236(4)	1229(3)	3721(3)	68(2)	
C(20)	-729(3)	2869(3)	4305(3)	59(1)	
C(21)	-1199(3)	597(2)	952(3)	45(1)	
C(22)	-2587(3)	1727(3)	1743(3)	47(1)	
C(23)	-1843(3)	2165(3)	433(3)	51(1)	
C(24)	-1233(3)	4410(3)	2931(3)	58(1)	
C(25)	212(3)	4552(2)	1974(3)	45(1)	
C(26)	1173(3)	5053(3)	4076(3)	58(1)	
C(27)	1634(3)	2688(2)	1217(2)	28(1)	
C(28)	1244(3)	1683(2)	544(2)	34(1)	
C(29)	2453(3)	3220(2)	1048(2)	27(1)	
C(30)	5483(3)	3725(2)	1290(3)	44(1)	
C(31)	6309(3)	5760(2)	2414(3)	39(1)	
C(32)	5945(3)	4511(3)	3315(3)	44(1)	
C(33)	2566(3)	6623(2)	3244(3)	40(1)	
C(34)	3965(3)	5545(2)	4180(2)	41(1)	
C(35)	4999(3)	7094(2)	3933(2)	39(1)	
C(36)	1756(3)	5984(3)	681(3)	49(1)	
C(37)	3147(3)	5115(3)	-269(3)	54(1)	
C(38)	4111(3)	6871(2)	1391(3)	44(1)	
C(39)	2080(3)	3181(2)	65(2)	28(1)	
C(40)	972(3)	3435(2)	-260(2)	38(1)	
C(41)	2118(3)	2329(2)	-703(2)	31(1)	
C(42)	555(3)	2981(2)	-2884(3)	47(1)	
C(43)	-72(3)	1268(3)	-2649(3)	52(1)	
C(44)	1694(4)	1442(3)	-3325(3)	63(1)	
C(45)	3163(3)	2001(2)	-436(2)	33(1)	
C(46)	3150(3)	1065(3)	-1094(3)	36(1)	
C(47)	4193(3)	749(3)	-810(3)	60(1)	
N(1)	3060(2)	1551(2)	2241(2)	29(1)	

O(1)	3502(2)	312(2)	1165(2)	46(1)
O(2)	4358(2)	1922(2)	1661(2)	43(1)
O(3)	1175(2)	2373(2)	2353(2)	31(1)
O(4)	2704(2)	4159(2)	1699(2)	28(1)
O(5)	1968(2)	2556(2)	-1478(2)	33(1)
O(6)	2347(2)	603(2)	-1777(2)	42(1)
S(1)	3968(1)	1216(1)	1869(1)	36(1)
Si(1)	3655(1)	5036(1)	1939(1)	30(1)
Si(2)	5406(1)	4722(1)	2234(1)	36(1)
Si(3)	3799(1)	6116(1)	3370(1)	32(1)
Si(4)	3138(1)	5752(1)	881(1)	37(1)
Si(5)	183(1)	2723(1)	2645(1)	30(1)
Si(6)	372(1)	2471(1)	3973(1)	38(1)
Si(7)	-1440(1)	1770(1)	1396(1)	36(1)
Si(8)	116(1)	4258(1)	2920(1)	39(1)
Si(10)	1057(1)	2047(1)	-2554(1)	39(1)

Table 3. Bond lengths [Å] and angles [°] for Brady11.

C(1)-C(2)	1.372(5)	C(29)-C(39)	1.528(4)
C(1)-C(6)	1.380(5)	C(30)-Si(2)	1.861(4)
C(1)-S(1)	1.761(4)	C(31)-Si(2)	1.867(4)
C(2)-C(3)	1.390(5)	C(32)-Si(2)	1.865(4)
C(3)-C(4)	1.378(5)	C(33)-Si(3)	1.875(4)
C(4)-C(5)	1.374(5)	C(34)-Si(3)	1.857(3)
C(4)-C(7)	1.495(5)	C(35)-Si(3)	1.875(3)
C(5)-C(6)	1.378(5)	C(36)-Si(4)	1.861(4)
C(8)-N(1)	1.488(4)	C(37)-Si(4)	1.862(4)
C(8)-C(9)	1.505(5)	C(38)-Si(4)	1.869(4)
C(9)-C(10)	1.377(5)	C(39)-C(40)	1.530(4)
C(9)-C(14)	1.378(5)	C(39)-C(41)	1.539(4)
C(10)-C(11)	1.381(5)	C(41)-O(5)	1.430(4)
C(11)-C(12)	1.373(5)	C(41)-C(45)	1.505(4)
C(12)-C(13)	1.370(5)	C(42)-Si(10)	1.852(4)
C(13)-C(14)	1.369(5)	C(43)-Si(10)	1.842(4)
C(15)-N(1)	1.480(4)	C(44)-Si(10)	1.855(4)
C(15)-C(16)	1.514(4)	C(45)-C(46)	1.513(5)
C(15)-C(17)	1.531(4)	C(46)-O(6)	1.201(4)
C(17)-O(3)	1.431(4)	C(46)-C(47)	1.496(5)
C(17)-C(27)	1.536(4)	N(1)-S(1)	1.620(3)
C(18)-Si(6)	1.855(4)	O(1)-S(1)	1.426(3)
C(19)-Si(6)	1.860(4)	O(2)-S(1)	1.426(2)
C(20)-Si(6)	1.856(4)	O(3)-Si(5)	1.662(2)
C(21)-Si(7)	1.858(4)	O(4)-Si(1)	1.675(2)
C(22)-Si(7)	1.865(4)	O(5)-Si(10)	1.637(3)
C(23)-Si(7)	1.862(4)	Si(1)-Si(3)	2.3609(16)
C(24)-Si(8)	1.869(4)	Si(1)-Si(2)	2.3619(17)
C(25)-Si(8)	1.869(4)	Si(1)-Si(4)	2.3710(16)
C(26)-Si(8)	1.861(4)	Si(5)-Si(8)	2.3459(17)
C(27)-C(28)	1.527(4)	Si(5)-Si(6)	2.3498(17)
C(27)-C(29)	1.533(4)	Si(5)-Si(7)	2.3539(16)
C(29)-O(4)	1.445(4)		
C(2)-C(1)-C(6)	119.8(4)	O(3)-C(17)-C(15)	108.9(3)
C(2)-C(1)-S(1)	120.7(3)	O(3)-C(17)-C(27)	109.8(3)
C(6)-C(1)-S(1)	119.5(3)	C(15)-C(17)-C(27)	117.5(3)
C(1)-C(2)-C(3)	120.0(4)	C(28)-C(27)-C(29)	112.8(3)
C(4)-C(3)-C(2)	120.9(4)	C(28)-C(27)-C(17)	113.0(3)
C(5)-C(4)-C(3)	117.9(4)	C(29)-C(27)-C(17)	113.1(3)
C(5)-C(4)-C(7)	121.2(4)	O(4)-C(29)-C(39)	109.5(3)
C(3)-C(4)-C(7)	120.9(4)	O(4)-C(29)-C(27)	106.5(3)
C(4)-C(5)-C(6)	122.1(4)	C(39)-C(29)-C(27)	115.8(3)
C(5)-C(6)-C(1)	119.3(4)	C(29)-C(39)-C(40)	111.4(3)
N(1)-C(8)-C(9)	116.7(3)	C(29)-C(39)-C(41)	119.2(3)
C(10)-C(9)-C(14)	117.6(4)	C(40)-C(39)-C(41)	110.6(3)
C(10)-C(9)-C(8)	122.5(4)	O(5)-C(41)-C(45)	108.4(3)
C(14)-C(9)-C(8)	119.8(4)	O(5)-C(41)-C(39)	107.2(3)
C(9)-C(10)-C(11)	121.4(4)	C(45)-C(41)-C(39)	114.7(3)
C(12)-C(11)-C(10)	119.7(4)	C(41)-C(45)-C(46)	116.0(3)
C(13)-C(12)-C(11)	119.5(4)	O(6)-C(46)-C(47)	122.9(4)
C(14)-C(13)-C(12)	120.3(4)	O(6)-C(46)-C(45)	122.0(4)
C(13)-C(14)-C(9)	121.5(4)	C(47)-C(46)-C(45)	115.1(4)
N(1)-C(15)-C(16)	111.2(3)	C(15)-N(1)-C(8)	121.2(3)
N(1)-C(15)-C(17)	115.1(3)	C(15)-N(1)-S(1)	121.0(2)
C(16)-C(15)-C(17)	110.8(3)	C(8)-N(1)-S(1)	117.6(2)

C(17)-O(3)-Si(5)	133.0(2)	C(38)-Si(4)-Si(1)	109.11(13)
C(29)-O(4)-Si(1)	128.8(2)	O(3)-Si(5)-Si(8)	114.92(10)
C(41)-O(5)-Si(10)	129.3(2)	O(3)-Si(5)-Si(6)	108.17(10)
O(1)-S(1)-O(2)	120.00(17)	Si(8)-Si(5)-Si(6)	109.62(6)
O(1)-S(1)-N(1)	107.15(16)	O(3)-Si(5)-Si(7)	105.56(10)
O(2)-S(1)-N(1)	107.09(16)	Si(8)-Si(5)-Si(7)	109.49(6)
O(1)-S(1)-C(1)	107.17(18)	Si(6)-Si(5)-Si(7)	108.87(6)
O(2)-S(1)-C(1)	105.98(17)	C(18)-Si(6)-C(20)	106.06(19)
N(1)-S(1)-C(1)	109.14(16)	C(18)-Si(6)-C(19)	108.4(2)
O(4)-Si(1)-Si(3)	102.80(10)	C(20)-Si(6)-C(19)	108.5(2)
O(4)-Si(1)-Si(2)	114.58(10)	C(18)-Si(6)-Si(5)	115.05(15)
Si(3)-Si(1)-Si(2)	105.35(6)	C(20)-Si(6)-Si(5)	108.18(14)
O(4)-Si(1)-Si(4)	114.34(10)	C(19)-Si(6)-Si(5)	110.43(14)
Si(3)-Si(1)-Si(4)	106.34(6)	C(21)-Si(7)-C(23)	107.99(18)
Si(2)-Si(1)-Si(4)	112.16(6)	C(21)-Si(7)-C(22)	108.95(17)
C(30)-Si(2)-C(32)	107.55(18)	C(23)-Si(7)-C(22)	108.47(18)
C(30)-Si(2)-C(31)	108.15(17)	C(21)-Si(7)-Si(5)	108.21(13)
C(32)-Si(2)-C(31)	108.51(17)	C(23)-Si(7)-Si(5)	110.77(13)
C(30)-Si(2)-Si(1)	115.03(13)	C(22)-Si(7)-Si(5)	112.34(13)
C(32)-Si(2)-Si(1)	110.10(13)	C(26)-Si(8)-C(24)	107.04(19)
C(31)-Si(2)-Si(1)	107.33(12)	C(26)-Si(8)-C(25)	111.02(18)
C(34)-Si(3)-C(35)	107.55(17)	C(24)-Si(8)-C(25)	107.83(18)
C(34)-Si(3)-C(33)	108.29(17)	C(26)-Si(8)-Si(5)	111.95(14)
C(35)-Si(3)-C(33)	106.90(17)	C(24)-Si(8)-Si(5)	107.12(14)
C(34)-Si(3)-Si(1)	109.01(13)	C(25)-Si(8)-Si(5)	111.62(12)
C(35)-Si(3)-Si(1)	112.63(13)	O(5)-Si(10)-C(43)	111.07(16)
C(33)-Si(3)-Si(1)	112.28(12)	O(5)-Si(10)-C(42)	105.29(15)
C(36)-Si(4)-C(37)	108.09(19)	C(43)-Si(10)-C(42)	110.07(18)
C(36)-Si(4)-C(38)	108.08(18)	O(5)-Si(10)-C(44)	110.49(17)
C(37)-Si(4)-C(38)	105.35(18)	C(43)-Si(10)-C(44)	111.6(2)
C(36)-Si(4)-Si(1)	110.07(13)	C(42)-Si(10)-C(44)	108.08(18)
C(37)-Si(4)-Si(1)	115.82(14)		

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for Brady11. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	39(3)	40(3)	40(3)	22(2)	27(2)	17(2)
C(2)	34(3)	43(3)	41(3)	14(2)	22(2)	14(2)
C(3)	41(3)	46(3)	51(3)	33(3)	26(2)	22(2)
C(4)	35(3)	52(3)	37(3)	24(2)	21(2)	14(2)
C(5)	34(3)	47(3)	35(3)	12(2)	17(2)	4(2)
C(6)	37(3)	35(3)	43(3)	20(2)	23(2)	13(2)
C(7)	36(3)	71(3)	51(3)	30(3)	17(2)	18(2)
C(8)	32(2)	30(2)	41(3)	11(2)	17(2)	7(2)
C(9)	30(2)	33(3)	43(3)	18(2)	17(2)	7(2)
C(10)	39(3)	37(3)	52(3)	20(2)	22(2)	10(2)
C(11)	54(3)	51(3)	49(3)	29(3)	23(3)	17(3)
C(12)	55(3)	54(3)	69(4)	38(3)	33(3)	22(3)
C(13)	61(3)	32(3)	74(4)	26(3)	36(3)	14(2)
C(14)	49(3)	38(3)	58(3)	18(3)	30(3)	12(2)
C(15)	33(2)	29(2)	31(2)	14(2)	14(2)	5(2)
C(16)	42(3)	32(2)	33(2)	14(2)	15(2)	7(2)
C(17)	32(2)	18(2)	30(2)	7(2)	16(2)	5(2)
C(18)	44(3)	112(4)	44(3)	27(3)	15(3)	-1(3)
C(19)	109(4)	59(3)	58(3)	34(3)	46(3)	28(3)
C(20)	57(3)	80(4)	51(3)	27(3)	32(3)	20(3)
C(21)	42(3)	36(3)	43(3)	6(2)	15(2)	-5(2)
C(22)	32(3)	45(3)	60(3)	20(2)	19(2)	4(2)
C(23)	45(3)	50(3)	42(3)	17(2)	2(2)	-2(2)
C(24)	50(3)	54(3)	91(4)	38(3)	41(3)	27(2)
C(25)	47(3)	28(2)	62(3)	17(2)	26(2)	12(2)
C(26)	67(3)	35(3)	61(3)	-2(2)	39(3)	1(2)
C(27)	24(2)	23(2)	31(2)	8(2)	10(2)	5(2)
C(28)	31(2)	36(2)	34(2)	13(2)	13(2)	4(2)
C(29)	24(2)	23(2)	31(2)	12(2)	9(2)	4(2)
C(30)	32(3)	43(3)	57(3)	17(2)	22(2)	3(2)
C(31)	31(2)	43(3)	48(3)	19(2)	20(2)	9(2)
C(32)	36(3)	45(3)	52(3)	25(2)	16(2)	11(2)
C(33)	49(3)	28(2)	44(3)	13(2)	24(2)	7(2)
C(34)	41(3)	44(3)	37(3)	18(2)	16(2)	8(2)
C(35)	43(3)	36(3)	32(2)	10(2)	14(2)	3(2)
C(36)	51(3)	51(3)	50(3)	32(2)	15(2)	15(2)
C(37)	70(3)	48(3)	49(3)	24(2)	28(3)	4(2)
C(38)	46(3)	43(3)	49(3)	29(2)	18(2)	9(2)
C(39)	30(2)	23(2)	29(2)	12(2)	10(2)	1(2)
C(40)	42(3)	35(2)	36(2)	18(2)	13(2)	12(2)
C(41)	37(2)	28(2)	30(2)	14(2)	15(2)	7(2)
C(42)	48(3)	45(3)	39(3)	20(2)	7(2)	5(2)
C(43)	50(3)	42(3)	46(3)	16(2)	4(2)	7(2)
C(44)	90(4)	67(3)	42(3)	27(3)	31(3)	38(3)
C(45)	33(2)	40(3)	28(2)	14(2)	16(2)	8(2)
C(46)	39(3)	43(3)	35(3)	19(2)	21(2)	8(2)
C(47)	52(3)	65(3)	61(3)	17(3)	27(3)	32(3)
N(1)	32(2)	28(2)	30(2)	11(2)	16(2)	10(2)

O(1)	44(2)	52(2)	34(2)	9(2)	14(2)	21(2)
O(2)	40(2)	60(2)	52(2)	37(2)	29(2)	24(2)
O(3)	31(2)	27(2)	44(2)	17(1)	23(1)	8(1)
O(4)	29(2)	27(2)	30(2)	9(1)	16(1)	5(1)
O(5)	40(2)	33(2)	28(2)	15(1)	15(1)	6(1)
O(6)	44(2)	33(2)	43(2)	11(2)	16(2)	7(1)
S(1)	36(1)	45(1)	34(1)	19(1)	18(1)	18(1)
Si(1)	30(1)	29(1)	30(1)	12(1)	13(1)	5(1)
Si(2)	29(1)	38(1)	41(1)	16(1)	16(1)	7(1)
Si(3)	36(1)	28(1)	32(1)	11(1)	14(1)	4(1)
Si(4)	41(1)	38(1)	37(1)	18(1)	17(1)	6(1)
Si(5)	28(1)	29(1)	33(1)	11(1)	14(1)	7(1)
Si(6)	35(1)	45(1)	34(1)	14(1)	18(1)	7(1)
Si(7)	32(1)	34(1)	37(1)	13(1)	11(1)	4(1)
Si(8)	38(1)	31(1)	52(1)	13(1)	26(1)	10(1)
Si(10)	47(1)	37(1)	32(1)	14(1)	14(1)	12(1)

Table 5. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$Å^2$ x 10^3] for Brady11.

	x	y	z	U(eq)
H(2)	4704	-226	2363	45
H(3)	6228	-310	3543	47
H(5)	7257	2410	4597	47
H(6)	5761	2507	3419	42
H(7A)	7798	398	4959	77
H(7B)	8077	1486	5506	77
H(7C)	8529	1030	4743	77
H(8A)	1834	425	1550	42
H(8B)	1773	1146	2453	42
H(10)	3406	1262	4027	49
H(11)	4065	338	4811	58
H(12)	3788	-1230	3982	63
H(13)	2823	-1859	2379	62
H(14)	2199	-934	1604	55
H(15)	3646	2871	2590	36
H(16A)	2885	2566	3833	53
H(16B)	3533	3521	3994	53
H(16C)	4128	2683	3983	53
H(17)	2136	3492	2607	32
H(18A)	1772	3751	5132	105
H(18B)	2270	2859	4901	105
H(18C)	1633	3020	5550	105
H(19A)	293	1133	4275	102
H(19B)	814	1009	3547	102
H(19C)	-473	892	3209	102
H(20A)	-677	2753	4848	88
H(20B)	-1435	2538	3787	88
H(20C)	-656	3526	4456	88
H(21A)	-935	391	1460	67
H(21B)	-655	601	702	67
H(21C)	-1880	179	460	67
H(22A)	-2683	2349	2023	70
H(22B)	-2425	1448	2195	70
H(22C)	-3256	1361	1194	70
H(23A)	-2475	1724	-104	77
H(23B)	-1238	2213	258	77
H(23C)	-2027	2765	637	77
H(24A)	-1329	4212	3387	86
H(24B)	-1811	4043	2314	86
H(24C)	-1266	5057	3098	86
H(25A)	-332	4110	1372	67
H(25B)	940	4534	1992	67
H(25C)	79	5168	2064	67
H(26A)	1172	5686	4137	86
H(26B)	1888	4924	4135	86
H(26C)	1015	4970	4565	86
H(27)	979	2962	1077	33
H(28A)	756	1633	-74	51
H(28B)	853	1347	762	51

H(28C)	1870	1422	511	51
H(29)	3132	2977	1199	32
H(30A)	5127	3781	697	66
H(30B)	5115	3159	1255	66
H(30C)	6246	3708	1420	66
H(31A)	7066	5699	2649	59
H(31B)	6224	6303	2864	59
H(31C)	6109	5822	1822	59
H(32A)	5412	4041	3275	65
H(32B)	6080	5078	3851	65
H(32C)	6625	4302	3387	65
H(33A)	1916	6132	2941	59
H(33B)	2504	6978	2867	59
H(33C)	2632	7025	3859	59
H(34A)	3900	5957	4735	61
H(34B)	4682	5391	4359	61
H(34C)	3400	4984	3873	61
H(35A)	4980	7553	4489	58
H(35B)	4973	7371	3497	58
H(35C)	5670	6869	4109	58
H(36A)	1691	6215	1273	74
H(36B)	1210	5417	252	74
H(36C)	1641	6441	413	74
H(37A)	2985	5490	-632	80
H(37B)	2595	4544	-602	80
H(37C)	3864	4976	-180	80
H(38A)	3872	7190	976	65
H(38B)	4837	6762	1465	65
H(38C)	4134	7247	1998	65
H(39)	2599	3692	124	33
H(40A)	398	2908	-459	56
H(40B)	864	3608	-781	56
H(40C)	943	3950	253	56
H(41)	1503	1821	-893	37
H(42A)	115	3248	-2555	70
H(42B)	111	2736	-3555	70
H(42C)	1175	3454	-2717	70
H(43A)	209	797	-2437	78
H(43B)	-607	976	-3297	78
H(43C)	-417	1615	-2262	78
H(44A)	2285	1877	-3263	95
H(44B)	1148	1173	-3970	95
H(44C)	1987	956	-3148	95
H(45A)	3362	1994	185	39
H(45B)	3742	2451	-381	39
H(47A)	4131	166	-1299	89
H(47B)	4346	669	-232	89
H(47C)	4786	1207	-712	89

Table 6. Torsion angles [°] for Brady11.

C(6)-C(1)-C(2)-C(3)	-0.4(5)	C(6)-C(1)-S(1)-N(1)	-80.5(3)
S(1)-C(1)-C(2)-C(3)	177.5(3)	C(29)-O(4)-Si(1)-Si(3)	-162.9(2)
C(1)-C(2)-C(3)-C(4)	-0.6(6)	C(29)-O(4)-Si(1)-Si(2)	-49.1(3)
C(2)-C(3)-C(4)-C(5)	2.0(6)	C(29)-O(4)-Si(1)-Si(4)	82.3(3)
C(2)-C(3)-C(4)-C(7)	-177.6(3)	O(4)-Si(1)-Si(2)-C(30)	56.43(17)
C(3)-C(4)-C(5)-C(6)	-2.4(6)	Si(3)-Si(1)-Si(2)-C(30)	168.65(14)
C(7)-C(4)-C(5)-C(6)	177.1(3)	Si(4)-Si(1)-Si(2)-C(30)	-76.08(15)
C(4)-C(5)-C(6)-C(1)	1.5(6)	O(4)-Si(1)-Si(2)-C(32)	-65.26(17)
C(2)-C(1)-C(6)-C(5)	-0.1(5)	Si(3)-Si(1)-Si(2)-C(32)	46.96(15)
S(1)-C(1)-C(6)-C(5)	-178.0(3)	Si(4)-Si(1)-Si(2)-C(32)	162.23(14)
N(1)-C(8)-C(9)-C(10)	65.8(5)	O(4)-Si(1)-Si(2)-C(31)	176.81(16)
N(1)-C(8)-C(9)-C(14)	-118.0(4)	Si(3)-Si(1)-Si(2)-C(31)	-70.97(14)
C(14)-C(9)-C(10)-C(11)	1.2(6)	Si(4)-Si(1)-Si(2)-C(31)	44.30(14)
C(8)-C(9)-C(10)-C(11)	177.5(3)	O(4)-Si(1)-Si(3)-C(34)	49.75(16)
C(9)-C(10)-C(11)-C(12)	-0.6(6)	Si(2)-Si(1)-Si(3)-C(34)	-70.57(14)
C(10)-C(11)-C(12)-C(13)	-0.7(6)	Si(4)-Si(1)-Si(3)-C(34)	170.21(13)
C(11)-C(12)-C(13)-C(14)	1.3(7)	O(4)-Si(1)-Si(3)-C(35)	169.03(15)
C(12)-C(13)-C(14)-C(9)	-0.7(6)	Si(2)-Si(1)-Si(3)-C(35)	48.71(14)
C(10)-C(9)-C(14)-C(13)	-0.6(6)	Si(4)-Si(1)-Si(3)-C(35)	-70.51(14)
C(8)-C(9)-C(14)-C(13)	-176.9(4)	O(4)-Si(1)-Si(3)-C(33)	-70.24(16)
N(1)-C(15)-C(17)-O(3)	63.4(4)	Si(2)-Si(1)-Si(3)-C(33)	169.44(13)
C(16)-C(15)-C(17)-O(3)	-63.8(4)	Si(4)-Si(1)-Si(3)-C(33)	50.22(14)
N(1)-C(15)-C(17)-C(27)	-62.1(4)	O(4)-Si(1)-Si(4)-C(36)	47.55(18)
C(16)-C(15)-C(17)-C(27)	170.6(3)	Si(3)-Si(1)-Si(4)-C(36)	-65.15(15)
O(3)-C(17)-C(27)-C(28)	-55.4(4)	Si(2)-Si(1)-Si(4)-C(36)	-179.82(14)
C(15)-C(17)-C(27)-C(28)	69.8(4)	O(4)-Si(1)-Si(4)-C(37)	-75.40(18)
O(3)-C(17)-C(27)-C(29)	174.9(3)	Si(3)-Si(1)-Si(4)-C(37)	171.89(15)
C(15)-C(17)-C(27)-C(29)	-60.0(4)	Si(2)-Si(1)-Si(4)-C(37)	57.22(16)
C(28)-C(27)-C(29)-O(4)	177.2(3)	O(4)-Si(1)-Si(4)-C(38)	165.99(16)
C(17)-C(27)-C(29)-O(4)	-53.0(4)	Si(3)-Si(1)-Si(4)-C(38)	53.28(15)
C(28)-C(27)-C(29)-C(39)	55.2(4)	Si(2)-Si(1)-Si(4)-C(38)	-61.39(15)
C(17)-C(27)-C(29)-C(39)	-175.0(3)	C(17)-O(3)-Si(5)-Si(8)	0.5(3)
O(4)-C(29)-C(39)-C(40)	-68.9(4)	C(17)-O(3)-Si(5)-Si(6)	-122.4(3)
C(27)-C(29)-C(39)-C(40)	51.5(4)	C(17)-O(3)-Si(5)-Si(7)	121.2(3)
O(4)-C(29)-C(39)-C(41)	160.4(3)	O(3)-Si(5)-Si(6)-C(18)	61.2(2)
C(27)-C(29)-C(39)-C(41)	-79.2(4)	Si(8)-Si(5)-Si(6)-C(18)	-64.79(18)
C(29)-C(39)-C(41)-O(5)	-167.1(3)	Si(7)-Si(5)-Si(6)-C(18)	175.46(17)
C(40)-C(39)-C(41)-O(5)	61.9(4)	O(3)-Si(5)-Si(6)-C(20)	179.56(17)
C(29)-C(39)-C(41)-C(45)	-46.7(4)	Si(8)-Si(5)-Si(6)-C(20)	53.56(16)
C(40)-C(39)-C(41)-C(45)	-177.7(3)	Si(7)-Si(5)-Si(6)-C(20)	-66.19(16)
O(5)-C(41)-C(45)-C(46)	-72.2(4)	O(3)-Si(5)-Si(6)-C(19)	-61.80(19)
C(39)-C(41)-C(45)-C(46)	168.1(3)	Si(8)-Si(5)-Si(6)-C(19)	172.19(16)
C(41)-C(45)-C(46)-O(6)	-1.6(5)	Si(7)-Si(5)-Si(6)-C(19)	52.44(17)
C(41)-C(45)-C(46)-C(47)	-179.3(3)	O(3)-Si(5)-Si(7)-C(21)	37.67(16)
C(16)-C(15)-N(1)-C(8)	66.7(4)	Si(8)-Si(5)-Si(7)-C(21)	161.91(13)
C(17)-C(15)-N(1)-C(8)	-60.3(4)	Si(6)-Si(5)-Si(7)-C(21)	-78.26(14)
C(16)-C(15)-N(1)-S(1)	-107.6(3)	O(3)-Si(5)-Si(7)-C(23)	-80.53(17)
C(17)-C(15)-N(1)-S(1)	125.4(3)	Si(8)-Si(5)-Si(7)-C(23)	43.71(16)
C(9)-C(8)-N(1)-C(15)	-116.3(4)	Si(6)-Si(5)-Si(7)-C(23)	163.54(15)
C(9)-C(8)-N(1)-S(1)	58.2(4)	O(3)-Si(5)-Si(7)-C(22)	158.00(16)
C(15)-C(17)-O(3)-Si(5)	137.5(3)	Si(8)-Si(5)-Si(7)-C(22)	-77.77(14)
C(27)-C(17)-O(3)-Si(5)	-92.5(3)	Si(6)-Si(5)-Si(7)-C(22)	42.06(15)
C(39)-C(29)-O(4)-Si(1)	-62.3(4)	O(3)-Si(5)-Si(8)-C(26)	-77.22(18)
C(27)-C(29)-O(4)-Si(1)	171.7(2)	Si(6)-Si(5)-Si(8)-C(26)	44.83(15)
C(45)-C(41)-O(5)-Si(10)	111.6(3)	Si(7)-Si(5)-Si(8)-C(26)	164.20(14)
C(39)-C(41)-O(5)-Si(10)	-124.0(3)	O(3)-Si(5)-Si(8)-C(24)	165.73(18)
C(15)-N(1)-S(1)-O(1)	-155.4(2)	Si(6)-Si(5)-Si(8)-C(24)	-72.21(16)
C(8)-N(1)-S(1)-O(1)	30.1(3)	Si(7)-Si(5)-Si(8)-C(24)	47.16(16)
C(15)-N(1)-S(1)-O(2)	-25.4(3)	O(3)-Si(5)-Si(8)-C(25)	47.92(18)
C(8)-N(1)-S(1)-O(2)	160.1(2)	Si(6)-Si(5)-Si(8)-C(25)	169.97(14)
C(15)-N(1)-S(1)-C(1)	88.9(3)	Si(7)-Si(5)-Si(8)-C(25)	-70.66(15)
C(8)-N(1)-S(1)-C(1)	-85.6(3)	C(41)-O(5)-Si(10)-C(43)	15.7(3)
C(2)-C(1)-S(1)-O(1)	-14.1(3)	C(41)-O(5)-Si(10)-C(42)	134.8(3)
C(6)-C(1)-S(1)-O(1)	163.8(3)	C(41)-O(5)-Si(10)-C(44)	-108.7(3)
C(2)-C(1)-S(1)-O(2)	-143.4(3)		
C(6)-C(1)-S(1)-O(2)	34.5(3)		
C(2)-C(1)-S(1)-N(1)	101.6(3)		

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