Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Cleavage of C-O and C-H bonds in ethers by a genuine Si=O bond

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1. X-ray Crystallographic Analysis

Table S1. Crystallographic data of **10** (CCDC: 2036685).

formula	$C_{82}H_{120}O_6Si$
fw	1229.86
T(K)	100(2)
λ (Å)	1.54178
crystal system	Triclinic
space group	*P*-1
a (Å^3)	14.2558(14)
b (Å^3)	16.0358(16)
c (Å^3)	18.3169(19)
α(deg)	109.526(5)
β(deg)	101.604(4)
γ (deg)	98.201(4)
V (Å^3)	3764.6(7)
Z	2
D_{calc} (mg/cm^3)	1.085
μ (mm^{-1})	0.651
F (000)	1348
crystal size (mm)	0.10 x 0.10 x 0.05
θ range (deg)	2.656 to 68.000
reflns collected	61954
indep reflns/R_{int}	13316/0.0306
params	1045
GOF on F^2	1.056
*R*1, *wR*2 [$I>2\sigma(I)$]	0.0801, 0.2363
*R*1, *wR*2 (all data)	0.0851, 0.2439

Table S2. Crystallographic data of **11** (CCDC: 2036686).

formula	$C_{83}H_{118}N_2O_5Si$
fw	1251.88
T(K)	100(2)
λ (Å)	0.71073
crystal system	Monoclinic
space group	$P2_1/n$
a (Å^3)	17.7199(8)
b (Å^3)	18.1911(8)
c (Å^3)	26.3896(11)
α(deg)	90
β(deg)	99.4560(10)
γ (deg)	90
V (Å^3)	8391.0(6)
Z	4
D_{calc} (mg/cm^3)	0.991
μ (mm^{-1})	0.073
F (000)	2736
crystal size (mm)	0.20 x 0.20 x 0.1
θ range (deg)	1.292 to 24.999
reflns collected	50055
indep reflns/R_{int}	14785/0.0531
params	850
GOF on F^2	1.024
R1, wR2 [I>2σ (I)]	0.0883, 0.2174
R1, wR2 (all data)	0.1260, 0.2419

Table S3. Crystallographic data of **12** (CCDC: 2036687).

formula	$C_{148}\ H_{220}\ O_{12}\ Si_2$
fw	2247.41
T(K)	100(2)
λ (Å)	0.71073
crystal system	Triclinic
space group	*P*-1
a (Å^3)	13.867(3)
b (Å^3)	15.476(3)
c (Å^3)	16.803(3)
α(deg)	69.374(5)
β(deg)	83.503(5)
γ (deg)	80.551(5)
V (Å^3)	3323.1(11)
Z	1
D_{calc} (mg/cm^3)	1.123
μ (mm^{-1})	0.086
F (000)	1232
crystal size (mm)	0.10 x 0.10 x 0.05
θ range (deg)	1.297 to 25.800
reflns collected	41172
indep reflns/R_{int}	12657/0.1217
params	808
GOF on F^2	1.064
*R*1, *wR*2 [*I*>2σ (*I*)]	0.0928, 0.1873
*R*1, *wR*2 (all data)	0.1528, 0.2138

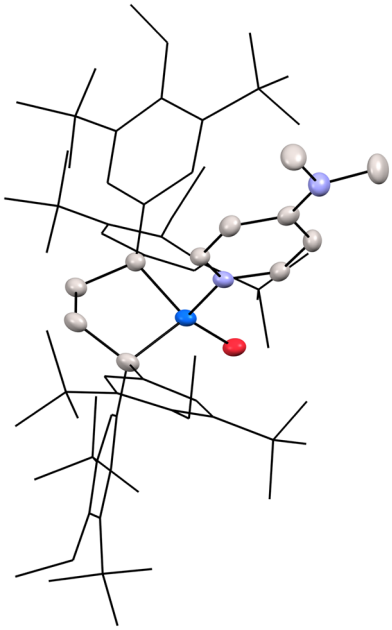


Figure S1. ORTEP of **11**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, disordered atoms and solvent molecules in the single crystal were omitted for clarity. Single crystals of **11** suitable for X-ray diffraction study were obtained by crystallization from benzene in an inert atmosphere.

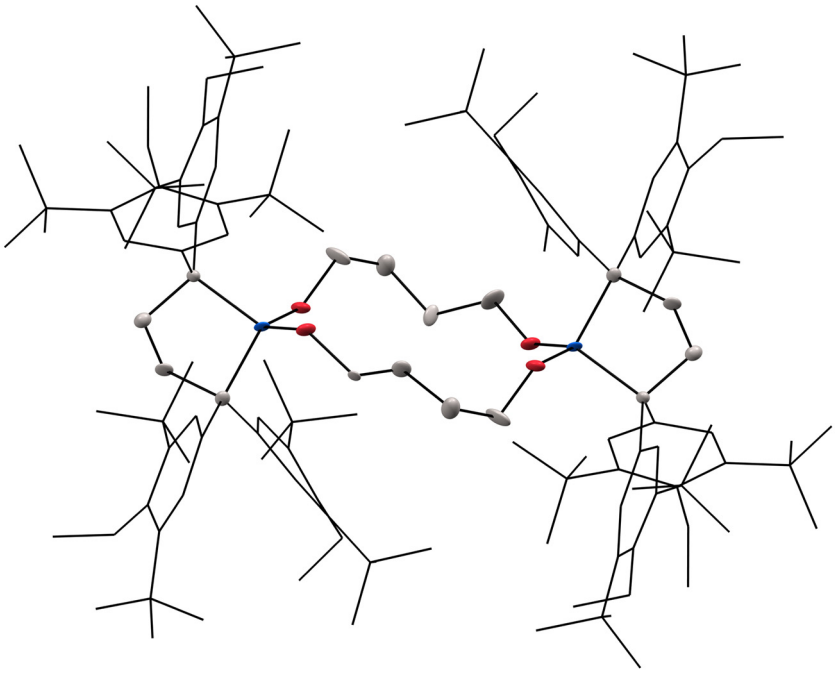


Figure S2. ORTEP of **12**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, disordered atoms and solvent molecules in the single crystal were omitted for clarity. Single crystals of **12** suitable for X-ray diffraction study were obtained by crystallization from benzene in an inert atmosphere.

2. Theoretical Calculations

All theoretical calculations were performed using the Gaussian 09[S1] and GRRM programs.[S2] Geometry optimization and frequency analysis for $Me_2Si=O$, EtOMe, *i*PrOMe, ethylene, propene, **15**, **15'**, **16**, **16'**, and **17** were carried out at the B3LYP-D3/6-311G(d) level of theory. Transition states **TS1, TS1', TS2, TS2'** were searched using the quadratic synchronous transit (QST2) method at the same level.[S3, S4] The initial guess for transition states **TS3, TS3'**, **TS4, TS4', TS5**, **TS6, TS6'** for the intermolecular reaction of **15 and 15'** were obtained using the optimized structure of **15** and **15'** and the multi-component artificial force-induced reaction (MC-AFIR) method.[S5] All transition states were confirmed by IRC calculations. The optimized equilibrium and transition structures are summarized in Tables S4-S36.

The intramolecular reactions of $Me_2Si=O$ and EtOMe calculated at the various calculation levels in the gas phase are summarized in Figures S3(a). Among the examined functionals (B3LYP-D3/6-311G(d), ωB97XD/6-311G(d). M06-2X/6-311G(d), and B97-D3/6-311G(d) level of theory), the B3LYP-D3/6-311G(d) level of theory provided the averaged relative energies for the equilibrium and transition structures [Figure S3(a)]. The reactions of $Me_2Si=O$ and EtOMe calculated at the B3LYP-D3/6-311G(d) level of theory in benzene and diethyl ether are compared with that in the gas phase [Figure S3(b)]. Although the relative energies of the equilibrium and transition structures depends on the solvent, the differences in the activation barrier are small. The atomic coordinates for these calculations are summarized in .xyz files (ESI2_functional.xyz and ESI3_solvent.xyz).

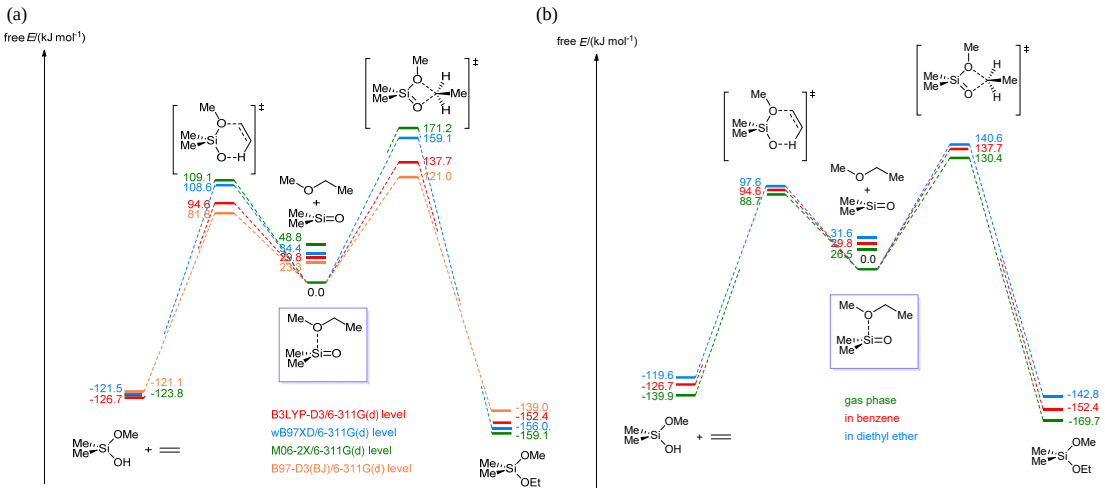


Figure S3. Reactions of dimethylsilanone and ethyl methyl ether calculated (a) at various levels of theory in the gas phase and (b) at the B3LYP-D3/6-311G(d) level of theory in some solvents.

The energy profiles for the reaction of $Me_2Si=O$ with EtOMe (Figure S4) is essentially the same as that of the reaction with ^{i}PrOMe (Figure S5) except for the intermolecular reaction of $Me_2Si=O$ with EtOMe providing disiloxane **18**, which was shown in sky blue lines (Figure S4). The formation of a disiloxane such as **18** is not found in the reaction with ^{i}PrOMe, suggesting that the steric demand of the ether suppress such a reaction route.

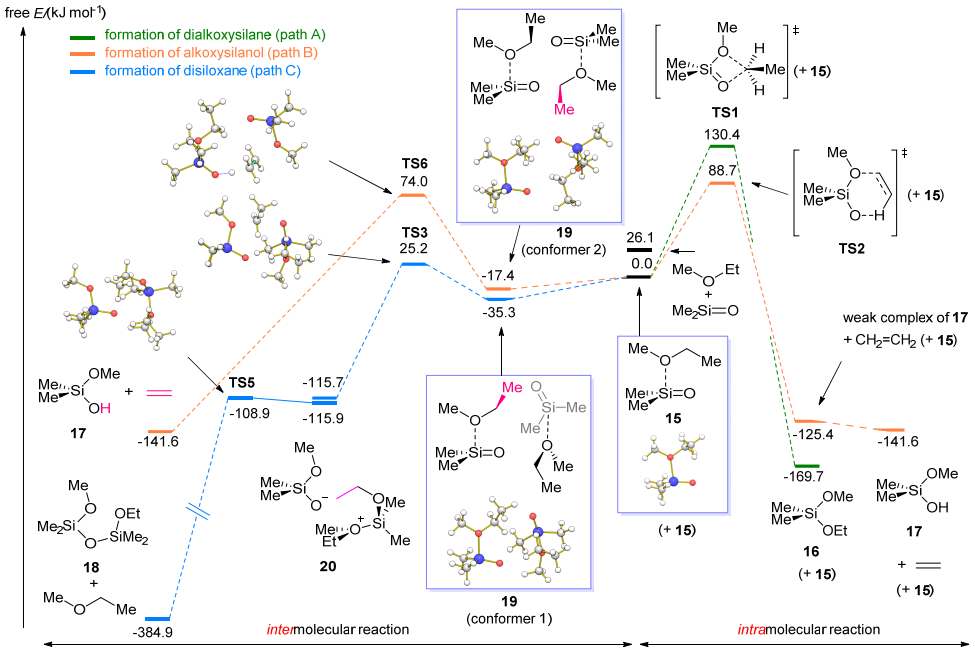


Figure S4. Reaction pathways and free energies for the reaction of dimethylsilanone and ethyl methyl ether in the gas phase calculated at the B3LYP-D3/6-311G(d) level of theory.

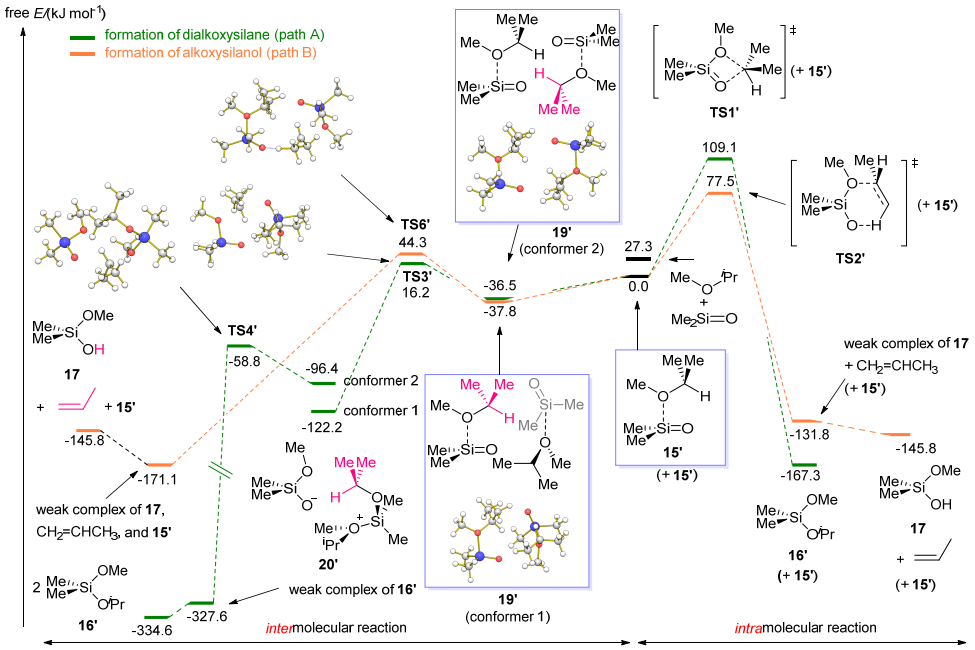


Figure S5. Reaction pathways and free energies for the reaction of dimethylsilanone and isopropyl methyl ether in the gas phase calculated at the B3LYP-D3/6-311G(d) level of theory.

Table S4. Atomic coordinates of **$Me_2Si=O$** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
O	-0.00006600	1.73369000	-0.00003100
C	-1.54366200	-0.85163400	-0.00001400
H	-2.44123900	-0.23217400	0.00058900
H	-1.56988300	-1.50345800	-0.87947900
H	-1.56931800	-1.50445100	0.87872700
C	1.54372100	-0.85153900	-0.00001800
H	1.56998900	-1.50340000	0.87941900
H	1.56937800	-1.50432200	-0.87878600
H	2.44127400	-0.23204600	-0.00062500
Si	-0.00000200	0.20209800	0.00004300

E = -444.635710714 a.u.
E + ZPVE = -444.559077 a.u.
Free energy (298.15 K) = -444.589745 a.u.

Table S5. Atomic coordinates of **EtOMe** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.81335500	0.02953200	0.00001700
H	-2.50125300	-0.81675700	-0.00010300
H	-2.00652500	0.64499800	-0.89168200
H	-2.00655100	0.64477500	0.89186500
O	-0.50391000	-0.49475200	-0.00002700
C	0.49560500	0.50974500	-0.00001500
H	0.38427500	1.15565600	0.88654000
H	0.38430600	1.15563600	-0.88658800
C	1.85132700	-0.17059200	0.00001600
H	1.95880800	-0.80300500	-0.88425300
H	2.65796200	0.56757000	0.00000300
H	1.95879200	-0.80295900	0.88432000

E(RB3LYP) = -194.397133462 a.u.
E + ZPVE = -194.288854 a.u.
Free energy (298.15 K) = -194.316574 a.u.

Table S6. Atomic coordinates of ***i*PrOMe** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.96010400	-0.11112700	0.08578400
H	-2.71345100	-0.71422700	-0.42254400
H	-2.13590800	0.94416200	-0.16161500
H	-2.08023900	-0.23783500	1.17225700
O	-0.70078300	-0.57293800	-0.35479800
C	0.42263100	-0.00466900	0.31994300
H	0.23569300	-0.03846400	1.40659900
C	1.60684600	-0.90191300	-0.01116800
H	1.78754000	-0.90063000	-1.08954800
H	2.51418200	-0.55903800	0.49293100
H	1.40091300	-1.92913400	0.29623900
C	0.66480800	1.44675200	-0.09938400
H	0.80830100	1.50168600	-1.18211400
H	-0.17342600	2.09506900	0.16637000
H	1.55757500	1.84766100	0.38876100

E(RB3LYP) = -233.725157841 a.u.
E + ZPVE = -233.588945 a.u.
Free energy (298.15 K) = -233.618862 a.u.

Table S7. Atomic coordinates of **15** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.15506300	-0.07748700	1.84326300
H	-0.31635400	-0.54102900	2.36943900
H	-1.17088300	0.98905400	2.08932200
H	-2.06983400	-0.51458500	2.25618500
C	-2.22016100	0.72523000	-0.93326600
H	-3.24501400	0.34501500	-0.87522200
H	-2.23559200	1.74748800	-0.54202600
H	-1.95043600	0.76356000	-1.99152000
Si	-1.06560800	-0.42849600	-0.00336000
O	-0.69660100	-1.83017700	-0.53944300
O	0.62415600	0.58483700	-0.38030200
C	0.90975000	1.88505600	0.15418100
H	-0.03213200	2.42644700	0.20142400
H	1.34249100	1.81117000	1.15334100
H	1.59411400	2.40846900	-0.51672800
C	1.78215800	-0.21605200	-0.79022600
H	1.33594800	-1.05091700	-1.32516800
H	2.36182800	0.40919000	-1.47520200
C	2.59408100	-0.70146400	0.39416600
H	1.97565600	-1.32647000	1.03999600
H	3.42406000	-1.31356700	0.03095600
H	3.01962200	0.11614500	0.98149600

E = -639.066164869 a.u.
E + ZPVE = -638.877754 a.u.
Free energy (298.15 K) = -638.916276 a.u.

Table S8. Atomic coordinates of **15'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-2.14223000	1.38415300	0.72089500
H	-1.60524500	2.33254600	0.63988900
H	-3.17332500	1.57002200	0.40380500
H	-2.17936200	1.09646300	1.77641600
C	-1.91463600	-1.63070500	0.11932900
H	-1.92346000	-1.78728000	1.20258300
H	-2.93313800	-1.81112400	-0.23888700
H	-1.27909800	-2.39535600	-0.33561700
Si	-1.36186800	0.09211300	-0.39870900
O	0.43048500	0.07360100	0.46885200
O	-0.99362100	0.40627000	-1.86798600
C	0.63972000	-0.42980900	1.79661500
H	0.76096300	-1.51404300	1.78424400
H	1.51483800	0.04334900	2.24116700
H	-0.23905600	-0.16520800	2.37975900
C	1.60396600	0.14331300	-0.44390400
H	1.11333200	0.39809700	-1.38393100
C	2.27109400	-1.21629500	-0.55654400
H	1.54108900	-1.98215100	-0.82573200
H	3.02256500	-1.17998000	-1.34880600
H	2.77896400	-1.51458800	0.36520200
C	2.52254000	1.26750100	0.00091900
H	1.96028700	2.19512900	0.12069200
H	3.04502200	1.04563200	0.93606400
H	3.28414000	1.43099700	-0.76570800

E = -678.395245147 a.u.
E + ZPVE = -678.178902 a.u.
Free energy (298.15 K) = -678.218996 a.u.

Table S9. Atomic coordinates of **16** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	0.32860800	0.31279600	1.87346500
H	-0.17571100	-0.60304700	2.19663900
H	1.31592000	0.32528900	2.34629000
H	-0.23523300	1.15867000	2.27713500
C	1.36685400	1.9388050	-0.54794800
H	0.87285300	2.84921400	-0.19677400
H	2.39114700	1.95018300	-0.16199400
H	1.41853900	1.98680500	-1.63858700
Si	0.44304500	0.41458900	0.00230000
O	-1.04652900	0.48648900	-0.70787000
O	1.15146600	-0.98175600	-0.56814900
C	2.32192500	-1.59105900	-0.05660800
H	3.20548200	-0.95489900	-0.19592800
H	2.22815200	-1.82518000	1.01139800
H	2.48584700	-2.52408600	-0.59929800
C	-2.02606900	-0.55245500	-0.71580200
H	-2.49452900	-0.53786100	-1.70425900
H	-1.54563100	-1.53120400	-0.59982900
C	-3.07294500	-0.32898800	0.36680800
H	-3.53421300	0.65463900	0.25016800
H	-3.85900700	-1.08847600	0.30823100
H	-2.62599300	-0.37674900	1.36327200

E = -639.128659869 a.u.
E + ZPVE = -638.940777 a.u.
Free energy (298.15 K) = -638.980910 a.u.

Table S10. Atomic coordinates of **16'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.27393900	1.04000600	1.60847100
H	-0.65882500	0.60105300	2.39845100
H	-1.18407300	2.12750100	1.68627500
H	-2.31742400	0.78556600	1.82140400
C	-1.86674600	1.11917500	-1.41968600
H	-2.90969000	0.82891000	-1.25673800
H	-1.83195800	2.21196100	-1.44924300
H	-1.56521300	0.75106900	-2.40382600
Si	-0.74272500	0.44357200	-0.08928000
O	-0.73371600	-1.22810500	-0.10073200
O	0.78641400	0.92735400	-0.46726200
C	-1.83036800	-2.04889000	0.25816400
H	-2.68808800	-1.89634400	-0.40939700
H	-1.51725700	-3.09157900	0.17703500
H	-2.15643700	-1.86669500	1.29007900
C	2.07257200	0.37864400	-0.14838400
H	2.77744300	1.19562400	-0.33838000
C	2.38990100	-0.78026800	-1.09004400
H	2.30495700	-0.45357100	-2.12891100
H	3.40757100	-1.14761000	-0.92551300
H	1.68685700	-1.60006700	-0.92930200
C	2.17658400	-0.02158400	1.32220900
H	1.91841000	0.81861700	1.97128600
H	1.50561000	-0.85573800	1.54480400
H	3.19666000	-0.33518800	1.56145700

E = -678.458210029 a.u.
E + ZPVE = -678.242126 a.u.
Free energy (298.15 K) = -678.282711 a.u.

Table S11. Atomic coordinates of **17** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-0.45074300	-1.58534300	-0.96950700
H	-0.15175700	-2.45693000	-0.37908600
H	-1.45879500	-1.77546600	-1.34943500
H	0.21744400	-1.53171700	-1.83528200
C	-0.91443400	1.46865100	-0.95965800
H	-0.27326000	1.60077100	-1.83690400
H	-1.94258200	1.36477600	-1.31811000
H	-0.86082900	2.38259300	-0.36271100
Si	-0.40461800	-0.01354100	0.05157200
O	1.11643400	0.16789700	0.70796500
O	-1.43836100	-0.08838200	1.34422600
C	2.33783600	0.13854900	-0.00776100
H	3.15504300	0.24310000	0.70841200
H	2.47225100	-0.80684300	-0.54852900
H	2.40607100	0.96405300	-0.72772700
H	-1.15946900	-0.56202000	2.13139500

E = -560.487323447 a.u.
E + ZPVE = -560.356783 a.u.
Free energy (298.15 K) = -560.391726 a.u.

Table S12. Atomic coordinates of **18** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.70490900	-0.42508600	1.91339800
H	-1.01800200	0.34758100	2.27096300
H	-2.72490800	-0.09412300	2.13231600
H	-1.52212800	-1.32727500	2.50462700
C	-2.53945800	-2.09886500	-0.56816300
H	-2.37767300	-3.04010800	-0.03478300
H	-3.59879600	-1.84221100	-0.46647900
H	-2.33973500	-2.27888800	-1.62792800
Si	-1.42938700	-0.74881300	0.08965500
O	0.13347000	-1.17293900	-0.18812200
O	-1.65997500	0.66670100	-0.76738400
C	-2.79816900	1.50355600	-0.67958000
H	-3.70629700	0.99426700	-1.02617300
H	-2.96624300	1.85708000	0.34539000
H	-2.63082600	2.37387700	-1.31703100
C	1.22668200	2.11188000	-0.31490500
H	0.55927100	1.80061500	-1.12495000
H	2.10563000	2.59400800	-0.75947000
C	0.49465200	3.07444200	0.60276000
H	-0.40354600	2.60018900	1.00402800
H	1.13342200	3.36804000	1.43919300
H	0.19489000	3.97630100	0.05980500
C	2.59845100	-1.55910600	1.22941300
H	2.14154200	-1.40426000	2.21073400
H	2.57573400	-2.63166300	1.01627900
H	3.64550300	-1.25168400	1.29861600
C	2.45298700	-0.73226100	-1.77885100
H	3.49044800	-0.38505700	-1.78257700
H	2.44521100	-1.76789100	-2.13077300
H	1.89887000	-0.13627000	-2.50991400
Si	1.68703400	-0.59416300	-0.07879400
O	1.66514900	0.98146000	0.44571200

E = -1083.88040659 a.u.
E + ZPVE = -1083.612541 a.u.
Free energy (298.15 K) = -1083.662586 a.u.

Table S13. Atomic coordinates of **ethylene** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	0.00000000	0.66365700	0.00000000
H	0.92267800	1.23666700	0.00000000
H	-0.92263800	1.23671400	0.00000000
C	0.00000000	-0.66365700	0.00000000
H	-0.92267800	-1.23666700	0.00000000
H	0.92263800	-1.23671400	0.00000000

E = -78.6077992401 a.u.
E + ZPVE = -78.556962 a.u.
Free energy (298.15 K) = -78.578486 a.u.

Table S14. Atomic coordinates of **propylene** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.28072200	-0.22038300	-0.00002200
H	-2.24139900	0.28448700	-0.00000800
H	-1.30354400	-1.30736600	0.00014800
C	-0.13491600	0.45388000	-0.00002100
H	-0.16633200	1.54329800	0.00011600
C	1.23344100	-0.16202500	0.00001800
H	1.18672400	-1.25409000	0.00032600
H	1.80871400	0.15211400	-0.87831400
H	1.80902200	0.15272200	0.87788100

E = -117.937345436 a.u.
E + ZPVE = -117.857810 a.u.
Free energy (298.15 K) = -117.882820 a.u.

Table S15. Atomic coordinates of **17 and ethylene** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.19280700	-0.42591200	1.83440400
H	-0.26190300	-0.36073400	2.40625000
H	-1.83603400	0.39846400	2.15900100
H	-1.68863900	-1.35726200	2.12309600
C	-2.43970300	-0.50847400	-0.99797800
H	-2.94740500	-1.45924500	-0.81194300
H	-3.14192800	0.29253400	-0.74620000
H	-2.23023700	-0.44804100	-2.06909700
Si	-0.86089900	-0.38330500	-0.01126100
O	0.12439300	-1.61758600	-0.49241900
O	-0.02631300	1.02305900	-0.36753100
C	-0.44826000	2.33411600	-0.03945800
H	-1.37772800	2.60279200	-0.55715100
H	-0.60370700	2.45585200	1.04007700
H	0.33097100	3.03149400	-0.35310800
C	3.04402800	-0.06601900	-0.70081000
H	2.28649400	0.50443200	-1.22751800
H	3.81801800	-0.54141300	-1.29634300
C	3.01267600	-0.17434300	0.62472400
H	2.23614100	0.31675400	1.20326500
H	1.07197100	-1.53037300	-0.33761300
H	3.75633000	-0.73897700	1.17924200

E = -639.105184422 a.u.
E + ZPVE = -638.921643 a.u.
Free energy (298.15 K) = -638.964039 a.u.

Table S16. Atomic coordinates of **17 and propylene** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-0.82603700	-0.47823900	-1.84985500
H	0.18030200	-0.13585600	-2.11073300
H	-0.94894500	-1.48431900	-2.26108700
H	-1.53596800	0.17433100	-2.36822800
C	-2.78448700	-1.05447000	0.49330600
H	-3.57017500	-0.41724500	0.07541500
H	-2.96638900	-2.07382900	0.14161500
H	-2.89534100	-1.05290900	1.58082600

Si	-1.08107900	-0.46593900	0.00985300
O	-0.81637500	1.09201400	0.56143000
O	0.00204600	-1.43912900	0.78249000
C	-1.51659400	2.23824300	0.11571000
H	-1.12301900	3.10752300	0.64661800
H	-1.38643800	2.40555100	-0.96143900
H	-2.59086300	2.16698400	0.32841500
C	2.94755300	0.05754300	0.48414800
H	3.10168500	0.09987300	1.56192500
C	2.49924300	1.33321000	-0.16194800
H	1.52863100	1.64219200	0.23768200
H	3.20923600	2.14228900	0.04019600
H	2.40407400	1.22654100	-1.24589500
C	3.14943900	-1.10075600	-0.14483900
H	3.47357600	-1.99086900	0.38469600
H	0.94755800	-1.28499800	0.65958000
H	3.00711300	-1.19837400	-1.21802900

E = -678.436749540 a.u.
E + ZPVE = -678.224670 a.u.
Free energy (298.15 K) = -678.269137 a.u.

Table S17. Atomic coordinates of **19** (conformer 1) optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	3.752894180295	1.702771705582	0.622612487314
H	3.504137521242	1.629275135789	1.684643974937
H	4.754833975845	1.289007874414	0.473955664899
H	3.808188130646	2.768329330048	0.378973127699
C	3.067410926742	0.410969336283	-2.117944729421
H	3.185736344677	1.298123126702	-2.747782393422
H	4.037187499961	-0.095725366344	-2.088896324121
H	2.352586117749	-0.245201990423	-2.622722518315
Si	2.415414353713	0.901202956164	-0.425342017920
O	0.938034702658	1.368848573426	-0.285878723574
O	2.436091679751	-0.854236045923	0.404106021911
C	3.602258578836	-1.694604328465	0.387876285262
H	3.586404699917	-2.337264298428	-0.495730344343
H	4.476492458495	-1.049015195086	0.363571690546
H	3.624315419343	-2.297723687273	1.294438791449
C	1.139670717147	-1.580695124192	0.492270950130
H	0.404926588956	-0.831129786678	0.236860001896
H	1.148758783130	-2.347141321598	-0.285400730832
C	0.892349120591	-2.138293847569	1.871807790661
H	0.983353909267	-1.350935569804	2.624479793517
H	-0.138226217936	-2.498293148098	1.865973777139
H	1.558981681979	-2.962836499722	2.137645076980
C	-4.249920418902	-0.710146201420	-1.020700142466
H	-4.817711589248	-0.732940540538	-0.086978630194
H	-4.519098140205	0.203267520321	-1.561152356790
H	-4.582293716986	-1.558629344552	-1.627354901114
C	-1.390864635541	-0.492286507285	-2.214508224408
H	-1.098043679297	-1.445385839413	-2.665950652243
H	-1.920482398499	0.082366138566	-2.980319571027
H	-0.479240383417	0.050165960480	-1.947887557367
Si	-2.408966966894	-0.829557337064	-0.667542161784
O	-1.859034571092	-1.826674466462	0.392215741851
O	-2.232612065583	0.905093893067	0.201708509776
C	-2.049390524419	2.116569662286	-0.575301297885
H	-2.607874476130	1.987913303950	-1.499717187549
H	-2.469390992524	2.955213415569	-0.019716208747
H	-0.984121122643	2.245958758439	-0.764117081497
C	-1.610070067642	0.946827894639	1.536679341336
H	-1.497542072515	-0.103324278283	1.797767085661
H	-0.625244134518	1.394598424535	1.402560607482
C	-2.506865627958	1.677924061755	2.514717964343
H	-3.490263794612	1.205391393775	2.566939812148
H	-2.057497633423	1.637540967324	3.511332347303
H	-2.639624362692	2.732243955834	2.259766190000

E = -1278.167350971273 a.u.

E + ZPVE = -1277.788194624736 a.u.
Free energy (298.15 K) = -1277.846029048642 a.u.

Table S18. Atomic coordinates of **19** (conformer 2) optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	3.043589003184	0.616617758593	1.995324303300
H	2.070215923686	0.396570875399	2.440617922292
H	3.741332169863	-0.172593165902	2.290470664489
H	3.394993641162	1.552037486655	2.442916319959
C	4.698991038944	0.979381360949	-0.543816640088
H	5.110591500002	1.932266034271	-0.195007458474
H	5.373925995698	0.192115410933	-0.192903560060
H	4.724263653849	1.006877847274	-1.635812930644
Si	2.949925627114	0.814094558874	0.128116620109
O	1.773100146191	1.583303202332	-0.532067180681
O	2.648127940681	-1.074522670876	-0.276359090085
C	3.083295045218	-1.574127777923	-1.558693361755
H	4.156064561325	-1.416714482361	-1.629117905365
H	2.867740613386	-2.640391361325	-1.610006093367
H	2.564650724364	-1.042008156427	-2.359193942347
C	1.267939094854	-1.521624334322	0.071809864567
H	0.862094046340	-0.759395013440	0.724662891554
H	0.673909407773	-1.505489208644	-0.837971861820
C	1.288637552364	-2.872377765565	0.742364591810
H	1.887958108897	-2.848329033545	1.655568472253
H	0.253722938807	-3.106748957167	0.995652037340
H	1.674529116983	-3.662779305822	0.092567646906
C	-3.913425559455	-0.227448071278	1.660076236281
H	-3.285476188820	0.338266328458	2.353402015143
H	-4.786266175671	0.384801121006	1.411822769331
H	-4.280167439235	-1.105052962352	2.201850669705
C	-4.071925534753	-1.408820267307	-1.189459501335
H	-4.310012948281	-2.458890259989	-0.992675567606
H	-5.024068530824	-0.874161612533	-1.262126679127
H	-3.578810328533	-1.368184944895	-2.164332263388
Si	-2.922563278807	-0.773729103648	0.157181594573
O	-1.514979933601	-1.402976076428	0.336440920823
O	-2.569904560924	0.979618916450	-0.609564650967
C	-3.609546062109	1.953488427518	-0.796836538650
H	-4.514939920839	1.419345269588	-1.075044066677
H	-3.778333008068	2.520456283861	0.119622410652
H	-3.320979784842	2.624535917000	-1.607377348791
C	-1.190031462163	1.531417408926	-0.527143236653
H	-0.547788103456	0.663030047915	-0.564821180532
H	-1.045647503973	2.116766004368	-1.435978758313
C	-0.962384080065	2.334953067797	0.730869692919
H	-1.136994388437	1.721755961742	1.618218388093
H	0.087415040057	2.629915537390	0.713272751140
H	-1.587173761726	3.230650049057	0.787426769854

E(el) = -1278.159596120966 a.u.
E + ZPVE =
Free energy (298.15 K) = -1277.839176559858 a.u.

Table S19. Atomic coordinates of **19'** (conformer 1) optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-3.653653305252	2.127857539684	0.008957392193
H	-3.277713607973	2.436414508240	-0.970465245624
H	-4.695550376391	1.813563265784	-0.104572485222
H	-3.656347187427	3.018088955020	0.645549299443
C	-3.439307122641	-0.195884986339	2.051049384457
H	-3.628362054458	0.399174200788	2.949949179734
H	-4.407168280766	-0.569308723277	1.701594564973
H	-2.831884302229	-1.052472473454	2.356049279663
Si	-2.524066881891	0.833421435795	0.772947998951
O	-1.020155738832	1.171547541366	0.993815232300
O	-2.510218323477	-0.429528231691	-0.679246097097
C	-3.717603429545	-1.046328988033	-1.157833324946

H	-3.969842578006	-1.915453707161	-0.549341241829
H	-4.510409672524	-0.304715441231	-1.096192088347
H	-3.583739958799	-1.339958115809	-2.197676638701
C	-1.210384312402	-1.146452738970	-0.978551501490
H	-0.514680962991	-0.576566934991	-0.375220405958
C	-0.861100354206	-0.983810131503	-2.440948014959
H	-0.904722867024	0.067245677697	-2.734950946242
H	0.165674514604	-1.338840135551	-2.546642033944
H	-1.505085817197	-1.568772174423	-3.104452748287
C	4.112544660265	-1.297416699624	1.018144222162
H	4.754069616996	-1.114628317144	0.151903936048
H	4.407624799054	-0.604733095596	1.813364280152
H	4.325967660118	-2.311218836953	1.372206073962
C	1.201472430275	-1.217347791644	2.073094919795
H	0.835141456125	-2.242763447484	2.186411852064
H	1.717522651371	-0.953908120824	3.001463103436
H	0.335437228165	-0.558365056463	1.960911273257
Si	2.299023893164	-1.129605203117	0.551110422385
O	1.782610498764	-1.705435956990	-0.801641201563
O	2.284472645359	0.780893922264	0.260584549858
C	2.049481536599	1.734097611204	1.329329852622
H	2.482094243333	1.304159927541	2.230090423686
H	2.569907659856	2.663052157525	1.097020755115
H	0.975582318658	1.876303723434	1.442739348343
C	2.208595539929	1.276352832974	-1.140081663293
H	2.024084359190	0.350778158125	-1.683877395072
C	3.563497488074	1.852785481251	-1.514240406086
H	4.352074102545	1.110384906266	-1.379543313691
H	3.555833214955	2.157764417302	-2.564280499607
H	3.808121644220	2.735089111582	-0.915584177100
C	-1.262309175584	-2.579266795067	-0.495830846407
H	-1.574573884446	-2.632566686058	0.549995021103
H	-1.923919866365	-3.206573813621	-1.100471219123
H	-0.243101552121	-2.960972307861	-0.572891674278
C	1.042126254997	2.232439171177	-1.321653003580
H	1.256274216273	3.228158947345	-0.923164325049
H	0.846583193052	2.341706349023	-2.392020675648
H	0.147060361892	1.854914376564	-0.825412980753

E(el) = -1356.829214696696 a.u.
E + ZPVE = -1356.393517260360 a.u.
Free energy (298.15 K) = -1356.451906189344 a.u.

Table S20. Atomic coordinates of **19'** (conformer 2) optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-4.277113060060	1.226937307295	1.385228027671
H	-3.822665638010	0.926198304102	2.332940985031
H	-4.509931798595	2.293690744730	1.463180898243
H	-5.229917949688	0.699068674519	1.278897209329
C	-3.980531093099	0.946667968405	-1.680887545027
H	-4.900755136441	0.354086373415	-1.678319201263
H	-4.257246711060	1.969495759091	-1.955444496783
H	-3.331884735571	0.566481131987	-2.475111387895
Si	-3.072201276947	0.954412397543	-0.032473181734
O	-2.821378161264	-0.944706438343	0.178194276886
O	-1.638959452961	1.551867761648	0.049644382582
C	-3.895018039123	-1.875458874400	-0.034778125910
H	-3.972918519024	-2.134028460425	-1.091504477835
H	-3.721431814039	-2.769793630416	0.561422164923
H	-4.813383137557	-1.398160080035	0.298950471694
C	-1.412937189543	-1.494588607809	0.102728539399
H	-0.833343264826	-0.581102157636	0.163159425295
C	-1.174252403104	-2.166775563877	-1.231444055487
H	-1.457542306819	-1.509490659198	-2.057497014275
H	-0.101256782600	-2.355533639570	-1.288887332651
H	-1.710146147390	-3.116010395549	-1.328341375800
C	-1.136805995202	-2.360658191225	1.311536483161
H	-1.413002352378	-1.840876376804	2.231765389607
H	-1.654183730929	-3.324469507657	1.274938108487

H	-0.060407804698	-2.540059760445	1.317187130427
C	4.266321314328	-1.226449218656	1.394503546789
H	3.802229230192	-0.931928123425	2.339498744811
H	4.504870725872	-2.292103889881	1.470494109429
H	5.216880193419	-0.692454626992	1.298536346999
C	3.993499689034	-0.948941180806	-1.673724418549
H	4.915470337379	-0.359224649343	-1.664032065212
H	4.269241605065	-1.972669122259	-1.945901880261
H	3.352197788564	-0.567027643982	-2.473028034503
Si	3.072305281825	-0.954549060917	-0.032614730985
O	2.821177265242	0.944816411400	0.174786786622
O	1.638060229726	-1.551024255485	0.038915556777
C	3.894669757376	1.875630833080	-0.038465192983
H	3.971530830934	2.134967403349	-1.095059093282
H	3.721838437381	2.769520478612	0.558580013839
H	4.813339255382	1.398024883064	0.293980385646
C	1.412649634514	1.494933767256	0.103205924707
H	0.833165983399	0.581599344625	0.166545015363
C	1.169988285164	2.165511165871	-1.231031788677
H	1.448788248135	1.506427139364	-2.057167220566
H	0.097127560698	2.356233162252	-1.284658879152
H	1.707240361018	3.113629499140	-1.331432936605
C	1.140343284721	2.362527150260	1.311828937840
H	1.420846062769	1.844409993471	2.231700740523
H	1.656338150004	3.326913170250	1.271722099050
H	0.063791244174	2.540747510837	1.321518285583

E(el) = -1356.825228002317 a.u.
E + ZPVE = -1356.390669279165 a.u.
Free energy (298.15 K) = -1356.452402176049 a.u.

Table S21. Atomic coordinates of **20** (conformer 1) optimised at the B3LYP-D3/6-311G(d) level of theory.

C	3.011508437405	1.503848384190	1.268977256428
H	2.600264251960	1.097470448520	2.199510885609
H	4.101481664548	1.404706516003	1.324203560770
H	2.788210478926	2.576282810952	1.255060986433
C	3.145587708684	1.285164287310	-1.781514111381
H	2.933613246780	2.348919840662	-1.935372511482
H	4.235103007390	1.179039404526	-1.730542295734
H	2.805963652840	0.753507238121	-2.677123344506
Si	2.257238502025	0.632458695514	-0.238813830221
O	0.670046122247	0.717195424022	-0.311636934581
O	2.702511384993	-1.009582966543	-0.097031961098
C	4.029965084862	-1.466852589566	-0.007773166391
H	4.620558472326	-1.207624909490	-0.898396902908
H	4.551807457446	-1.061606177785	0.871541705385
H	4.022389323644	-2.557953953437	0.081794972075
C	-0.137883878908	-2.102838698567	0.994826395241
H	0.546168911767	-1.828168215016	0.194897849070
H	-0.218184528322	-3.191977572878	1.053249313253
C	0.347671982699	-1.518174002944	2.303068902041
H	0.465745498878	-0.439600800549	2.202863022650
H	-0.344008805530	-1.741729236666	3.120630017906
H	1.327920440236	-1.935548621880	2.545556425857
C	-3.860285243340	-1.180220935517	-0.734958379141
H	-4.353895612117	-1.043157844509	0.230522503773
H	-4.347063366232	-0.520556752976	-1.459078793833
H	-4.035056027383	-2.211815349522	-1.053330350475
C	-1.064642339650	-0.998391395268	-2.169684393563
H	-0.801908250320	-2.050373881179	-2.318473211995
H	-1.613784935083	-0.665738742867	-3.054074741051
H	-0.143194909280	-0.425034212689	-2.048309269360
Si	-2.035087000706	-0.835964213339	-0.604037575986
O	-1.481667588200	-1.624874136871	0.702476100521
O	-2.127398774665	0.947824251773	-0.158336645658
C	-1.754486364345	1.920870445997	-1.200505848240
H	-2.195000599544	1.566275388762	-2.129427034030
H	-2.202829644292	2.873634667357	-0.932261409531
H	-0.663180047857	1.929473787553	-1.230466872779

C	-1.692737680667	1.356108453477	1.218596129736
H	-1.859203882470	0.465175067075	1.817082217580
H	-0.619301927795	1.523099890956	1.117945307510
C	-2.516605482715	2.522583732855	1.713068750795
H	-3.587777511373	2.318108103574	1.642249623683
H	-2.273552956168	2.683223942593	2.767109667833
H	-2.297514968700	3.454907374850	1.190167610867

E(el) = -1278.198090888370 a.u.
E + ZPVE = -1277.819467185114 a.u.
Free energy (298.15 K) = -1277.876680719629 a.u.

Table S22. Atomic coordinates of **20** (conformer 2) optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	3.015992883707	-1.503604897367	-1.268857376012
H	2.605028271356	-1.097162891099	-2.199471027304
H	4.105896071471	-1.403324760141	-1.323063071023
H	2.793724712879	-2.576253167398	-1.255639769996
C	3.147734195472	-1.283526189530	1.781947155024
H	2.939183673998	-2.347958461021	1.935768975471
H	4.236930554833	-1.173719691929	1.732092638467
H	2.805369062435	-0.752866720040	2.677107905760
Si	2.258873156963	-0.633795420230	0.238320529889
O	0.671811049074	-0.722180936186	0.309923982851
O	2.700177408043	1.009367059474	0.096362496019
C	4.026073465144	1.470884680334	0.006517897411
H	4.616472223764	1.218188255334	0.899161415484
H	4.550595771336	1.063369053528	-0.870146963626
H	4.014613804824	2.561511124402	-0.088409198367
C	-0.137807825565	2.101298048230	-0.996664851518
H	0.546413590953	1.827781799699	-0.196453941358
H	-0.217232626044	3.190357791437	-1.057437342441
C	0.346898544465	1.513242826088	-2.303716004234
H	0.466540187054	0.435149222954	-2.200215723935
H	-0.346026807811	1.733587765588	-3.121104986997
H	1.326277765660	1.931195119135	-2.548706577275
C	-3.859134198644	1.181861124173	0.738092456888
H	-4.354070997497	1.044430413650	-0.226661069716
H	-4.345134703766	0.522675815261	1.463168883149
H	-4.033197728134	2.213654084246	1.056183032850
C	-1.060395358254	0.998039930751	2.168155314630
H	-0.795944015691	2.049624488509	2.316588436198
H	-1.607723855953	0.665699589318	3.053778008501
H	-0.139957129568	0.423483875220	2.044326970618
Si	-2.034320591225	0.836778362274	0.604611140897
O	-1.481993866951	1.625323431531	-0.702586110810
O	-2.127680890062	-0.946891988890	0.159390416613
C	-1.754674212572	-1.919915105262	1.201696772459
H	-2.195015828345	-1.565183885484	2.130649802646
H	-2.203155719594	-2.872647111427	0.933567784345
H	-0.663310923445	-1.928806045221	1.231190681689
C	-1.695002242009	-1.356873812904	-1.217605300810
H	-1.856673543649	-0.464971165765	-1.815935418746
H	-0.622438683569	-1.529423794892	-1.117257533220
C	-2.525132789218	-2.518837928253	-1.712242749200
H	-3.595134000728	-2.307874940319	-1.642923395256
H	-2.281697781264	-2.681874438353	-2.765830567515
H	-2.312381524690	-3.452010536227	-1.188217931879

E(el) = -1278.198090497671 a.u.
E + ZPVE = -1277.819464770085 a.u.
Free energy (298.15 K) = -1277.876625962195 a.u.

Table S23. Atomic coordinates of **20'** (conformer 1) optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-3.263463300352	2.200805847719	-0.600889401214
H	-2.800358269031	2.261865091014	-1.591903018170
H	-4.345789092358	2.115181996334	-0.749588400790
H	-3.082068069667	3.156544779692	-0.097449794926

C	-3.474760672865	0.630292836614	2.025095363553
H	-3.296844470277	1.511335756420	2.650962293431
H	-4.558962118853	0.542516770358	1.892233305165
H	-3.141134711863	-0.244662871938	2.593451204309
Si	-2.525740685364	0.762203910572	0.390115328973
O	-0.943001113102	0.837901210132	0.559828443051
O	-2.900874347153	-0.654026262470	-0.490928201391
C	-4.208922434162	-1.048817941967	-0.825977332244
H	-4.836845826034	-1.208572716671	0.062495490589
H	-4.714871545162	-0.313104916371	-1.467909376994
H	-4.162734764170	-1.994875676412	-1.375671764974
C	0.052047900830	-1.791049845397	-0.830900133957
H	-0.499512127630	-0.939501798561	-0.436809715246
C	0.022796154395	-1.769059623827	-2.346743435577
H	0.417868965943	-0.825876362101	-2.732043681621
H	0.608958356591	-2.591261573417	-2.768832345004
H	-1.011155190956	-1.855897763813	-2.687322447402
C	3.822544065751	-1.186644442351	1.046376168800
H	4.343711591750	-1.135037351833	0.086922065212
H	4.316406837740	-0.500206289442	1.739769671304
H	3.949811743936	-2.201319679149	1.433478558798
C	0.981427323136	-0.751132094791	2.381169803725
H	0.765917996987	-1.776751984337	2.694507821151
H	1.462869029181	-0.243331895833	3.220731300585
H	0.040595322502	-0.247625990189	2.126035205840
Si	2.016382051899	-0.783317190977	0.853123834136
O	1.459790453222	-1.635794478212	-0.413989627044
O	2.107719502182	0.955674854176	0.290400388748
C	1.597041740608	2.052419672570	1.140834034693
H	2.006011654714	1.883850663623	2.134234859149
H	1.994826018821	2.982603818139	0.743743578361
H	0.504544028609	1.984326415234	1.112260175778
C	2.219852516303	1.246534520209	-1.191900085752
H	2.275242258839	0.244484602093	-1.612109386334
C	3.521874570815	1.988522331836	-1.421432091342
H	4.374469927983	1.427771013338	-1.033527303813
H	3.663619861528	2.129795969496	-2.496033982191
H	3.513097179819	2.978900440240	-0.960359389875
C	0.496571307834	-3.078320790002	-0.244209591814
H	-0.448844160378	-3.060831178973	0.847445563710
H	-1.547823268633	-3.176539414819	-0.521202464399
H	0.057761661937	-3.950305749390	-0.605438753718
C	0.965632178326	1.940825929652	-1.684387738133
H	0.981415958487	3.012604286667	-1.471681019637
H	0.902372184834	1.817991666556	-2.768719488322
H	0.081296602355	1.505746147297	-1.207958067690

E(el) = -1356.858969067837 a.u.

E + ZPVE = -1356.424533957957 a.u.

Free energy (298.15 K) = -1356.484542169125 a.u.

Table S24. Atomic coordinates of **20'** (conformer 2) optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	3.571180319399	-0.499198270454	1.295888342169
H	3.085560105279	-1.459223770803	1.498615290612
H	4.510094469651	-0.708084777153	0.771290475195
H	3.831989908404	-0.061515941283	2.264730137586
C	3.462963873102	2.120243851454	-0.283879617502
H	3.780632297341	2.751234711879	0.552647444543
H	4.368833733159	1.812897498096	-0.818557516522
H	2.882868611331	2.755451451941	-0.963354840637
Si	2.420348325367	0.659781967639	0.334391604783
O	1.061626007703	1.047073357445	1.040472321557
O	2.031430110493	-0.220528287362	-1.116557760866
C	3.016398068435	-0.790487052541	-1.949616794743
H	3.712195548548	-0.038009295099	-2.345651277101
H	3.607106987910	-1.555410718879	-1.428026306314
H	2.526358565017	-1.272089892624	-2.803569121713
C	-0.133374030987	-2.154373658990	0.799974162135

H	0.638505065062	-1.693361397778	0.180935288514
C	0.123269506463	-1.818689831475	2.257797205762
H	0.268890157833	-0.742325174983	2.359195457363
H	-0.711070388661	-2.160688149443	2.878418729821
H	1.033838736270	-2.314915611063	2.604344587111
C	-3.686055855085	-0.624625021496	-0.970738995152
H	-4.183089524718	-0.657998238078	-0.000644332402
H	-4.052589002698	0.248291040836	-1.517142841446
H	-3.994513424482	-1.515929343940	-1.525052684084
C	-0.928813395970	-1.000736302998	-2.380664468125
H	-1.215243429605	-2.011550649701	-2.687838151111
H	-1.174165100468	-0.324993575087	-3.203488185898
H	0.150581413304	-0.983039192584	-2.218076719469
Si	-1.832390833066	-0.610240023531	-0.807804533039
O	-1.425419749796	-1.571443222692	0.435150929815
O	-1.443180098586	1.117541263714	-0.450877738866
C	-0.475163820558	1.837562930029	-1.306140902335
H	0.226579805613	1.123834468417	-1.717933180838
H	-1.045116906678	2.364687517714	-2.070752660127
H	0.087206058064	2.502145899402	-0.662778040117
C	-1.674968562566	1.855767056805	0.890847683630
H	-0.640859785971	1.919618964547	1.245999355806
C	-2.506626446691	1.017244883655	1.834855583817
H	-2.070184987937	0.039221164841	2.015664893806
H	-2.521852265166	1.549599151148	2.789690430593
H	-3.542814292540	0.908827294328	1.505370947958
C	-0.213255936034	-3.646626970012	0.517215999523
H	-0.411675134406	-3.836664386308	-0.541308121210
H	0.731356009762	-4.132273595510	0.776765564884
H	-1.011995786016	-4.107287429338	1.105126017751
C	-2.337332125004	3.178443078383	0.559328442117
H	-3.315893379898	3.027680188176	0.094343689388
H	-2.488191073294	3.729804171356	1.490801172471
H	-1.731823742711	3.809425688587	-0.091385223973

E(el) = -1356.852824907174 a.u.
E + ZPVE = -1356.417214875530 a.u.
Free energy (298.15 K) = -1356.474710490415 a.u.

Table S25. Atomic coordinates of **weak complex of 16'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-3.745841257995	-1.366133542931	-1.099031697597
H	-3.024073550345	-1.865126502979	-1.750331803870
H	-4.279922757754	-2.135473339787	-0.532282815352
H	-4.477993039463	-0.865862005696	-1.739348754399
C	-4.106445118238	0.677073920122	1.186064635147
H	-4.852587122670	1.252470284979	0.630255658430
H	-4.648160470858	-0.058634151406	1.789746390759
H	-3.606878156329	1.365701401750	1.872440920642
Si	-2.887939382537	-0.139804643843	0.019014543503
O	-2.107524029897	0.946276875841	-0.941188367274
O	-1.693047742008	-0.894432351686	0.922038781312
C	-1.916040680812	-1.940933315775	1.847985682575
H	-2.588511335393	-1.634026040885	2.658550566218
H	-2.337236242904	-2.829491368640	1.361987714301
H	-0.955235763178	-2.217804446768	2.288379383790
C	1.166605717061	-1.748083174264	-0.683516986263
H	0.603270260842	-1.593771155250	0.243944339699
C	0.173987320365	-1.806264530773	-1.836283232756
H	-0.416941091752	-0.892352226742	-1.884461877283
H	0.707691094773	-1.924294505652	-2.783438047449
H	-0.510701248783	-2.650370775438	-1.713454757831
C	3.754925331815	1.586278199485	-0.883884703501
H	3.043870212081	2.171522671063	-1.472468867579
H	4.331298781631	2.279873852244	-0.266050234283
H	4.442094920286	1.100693036837	-1.581804528658
C	4.006292625536	-0.688275676005	1.238795670906
H	4.694608118999	-1.280296010091	0.629211801060
H	4.607824236596	-0.041796780160	1.885240521087

H	3.468981431399	-1.385319819937	1.888390979819
Si	2.857573630104	0.334190483535	0.159571242040
O	2.024599715978	-0.619702967955	-0.912846494691
O	1.836310238064	1.205547792356	1.144516735955
C	1.104626586922	0.738737728124	2.268043016891
H	0.189205771095	0.229081879784	1.953921161206
H	1.699450193103	0.058797443668	2.890450898144
H	0.830728466837	1.603152724679	2.876639837454
C	-0.880648835205	1.661086793707	-0.686222349721
H	-0.139834627747	0.949353725677	-0.322217311911
C	-0.406145409404	2.226553992067	-2.015277651300
H	-0.249462340607	1.424251183688	-2.738442014523
H	-1.147247094542	2.919993204186	-2.422748140555
H	0.539316884342	2.760011393802	-1.886218551631
C	1.993996076771	-3.027442810815	-0.580601446539
H	2.685970001510	-2.992704415716	0.263014785333
H	1.345508298222	-3.899103909357	-0.450707297871
H	2.579752402714	-3.167447075178	-1.493318843716
C	-1.083297482258	2.743285515630	0.367644104309
H	-0.144692946932	3.273393874056	0.543686666704
H	-1.844443356731	3.459110871160	0.044497318150
H	-1.398716794225	2.311218714073	1.320363860938

E(el) = -1356.935037763851 a.u.

E + ZPVE = -1356.501085030371 a.u.

Free energy (298.15 K) = -1356.562784217507 a.u.

Table S26. Atomic coordinates of **weak complex of 16', 17 and propene** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-3.456628913247	1.713644578483	-0.322289718797
H	-2.940222305223	2.273164493086	0.461686947763
H	-3.668855836419	2.418449464840	-1.132168161361
H	-4.419804945111	1.376243713020	0.072104592382
C	-3.285446079495	-0.858432440772	-2.070018256858
H	-4.281305692335	-1.131604646264	-1.709164844839
H	-3.413035156640	-0.404367944584	-3.057493765565
H	-2.706777083110	-1.774749452756	-2.215875548852
Si	-2.359232813315	0.335692710198	-0.958259072718
O	-2.272605017554	-0.729911804584	0.651257050851
O	-0.868175603717	0.664694854771	-1.275009242539
C	-3.417792060296	-1.483372058722	1.092126253142
H	-3.456104061780	-2.449803755994	0.589111183339
H	-3.370532001810	-1.615627032654	2.171266710925
H	-4.302814472418	-0.902068097001	0.844912878609
C	-0.919367395554	-1.175996348977	1.145572879005
H	-0.266660190219	-0.470702781714	0.648088514805
C	-0.611888451581	-2.578396352884	0.666512463365
H	-0.661135608622	-2.637451358925	-0.420479158383
H	0.417842413876	-2.801277105252	0.949535287703
H	-1.265455509150	-3.330135580788	1.118965806815
C	-0.835245128327	-0.983823199396	2.646258965565
H	-1.187773159587	0.007096959287	2.936568391249
H	-1.384557427190	-1.742503895711	3.210453862449
H	0.217107614139	-1.061338960641	2.924561836544
C	3.708103005130	-2.087958996960	-1.104219697797
H	3.234883019590	-3.048485119847	-0.881316921523
H	4.010212233688	-2.105304630898	-2.155322644585
H	4.619783658560	-2.016493179760	-0.502314972201
C	3.282311671112	0.986332970835	-1.170295786377
H	4.233416866375	1.147582480844	-0.651992282112
H	3.479475255017	1.068211266760	-2.243339239179
H	2.613665211163	1.807001366761	-0.895760100681
Si	2.524348755875	-0.678139332546	-0.762535972688
O	2.155331282718	-0.689567349336	0.892929353128
O	1.134257187597	-0.984919116233	-1.559466811173
C	3.091529456967	-0.332080111522	1.891959252220
H	3.426174657205	0.706976341634	1.785426166452
H	2.612626821019	-0.434001354031	2.869544011511
H	3.974211521820	-0.984740263336	1.878930828855

C	0.493744971963	3.156770978375	0.299608565014
H	0.106771261313	2.661540584131	-0.588136550054
C	1.030719496150	4.371540576328	0.216674302093
H	1.096779172629	4.900212512036	-0.729254712654
H	0.386210214598	-0.324474485973	-1.559307274215
H	1.429537547585	4.886546791101	1.088200505079
C	0.375550626169	2.354445620522	1.561165883032
H	0.887472598682	1.394070562523	1.453028983257
H	0.790413818684	2.877670400528	2.427679195547
H	-0.674626672355	2.122050244827	1.773962292205

E(el) = -1356.870564870869 a.u.
E + ZPVE = -1356.439542163560 a.u.
Free energy (298.15 K) = -1356.503155800356 a.u.

Table S27. Atomic coordinates of **TS1** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.275007786057	0.162946411574	1.820590695792
H	-0.376994415577	0.216990851507	2.444061878434
H	-1.781277463467	1.133032347928	1.870320960409
H	-1.940882359827	-0.570662957607	2.285284796238
C	-2.370139731651	-0.187375911487	-1.030585030563
H	-3.138492078180	-0.917937367252	-0.759718736681
H	-2.822840206546	0.807115021890	-0.952311923827
H	-2.108995179897	-0.357908147077	-2.078487208107
Si	-0.849208125179	-0.356180602585	0.059010544555
O	0.095161227794	-1.618681949013	-0.130522886773
O	0.274987170570	0.858487774260	-0.527069679604
C	0.427931144862	2.203879047407	-0.123671388335
H	-0.414910834937	2.808158561146	-0.476643807996
H	0.504896464854	2.301782952502	0.964942118786
H	1.340388736693	2.602445806539	-0.580021811575
C	1.959738224472	-0.395645025368	-0.745083055535
H	1.790109324233	-1.327063316223	-1.256008332138
H	2.179010506710	0.445792787534	-1.389376249276
C	2.606306114019	-0.429458101049	0.583593372867
H	2.238435629249	-1.264382579172	1.173063450400
H	3.687615881640	-0.557678144720	0.410715122038
H	2.482916631784	0.506645371942	1.131437515135

E(el) = -639.012709405384 a.u.
E + ZPVE = -638.828341182897 a.u.
Free energy (298.15 K) = -638.866599611914 a.u.

Table S28. Atomic coordinates of **TS1'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-2.329745146769	0.485786890241	1.321389451697
H	-1.851465289259	0.976856779493	2.173639371673
H	-3.208050849895	1.079485584983	1.050368877776
H	-2.689703512469	-0.493881933608	1.655894768612
C	-1.919915418075	-0.673441935435	-1.490731456984
H	-2.350585869362	-1.614430743003	-1.130751745588
H	-2.728190024771	-0.111278363905	-1.968477832227
H	-1.194516912519	-0.915981457108	-2.274450319912
Si	-1.120679204932	0.343154027110	-0.114783817874
O	0.167039472067	-0.666556545028	0.500260028973
O	-0.308806833671	1.636194074500	-0.540943621043
C	0.130989616250	-2.062722342689	0.685572960016
H	0.022862179659	-2.603476128562	-0.263020376424
H	1.062112200511	-2.381813429480	1.166967778208
H	-0.696913184987	-2.350640061248	1.345465504189
C	1.922351252320	0.591819460508	-0.219303163612
H	1.553622719387	1.538827079956	-0.589800813721
C	2.296408560604	-0.417338529805	-1.227835915764
H	1.579024409451	-0.436353064240	-2.047750268925
H	3.255363271463	-0.082821889152	-1.657299736934
H	2.437148980259	-1.417895416947	-0.819021430493
C	2.448120961140	0.571760778456	1.156904436956
H	1.801402535578	1.141020176522	1.823155072862

H	2.609659959605	-0.431355346163	1.550873084183
H	3.416807637686	1.098517928913	1.125351853638

E(el) = -678.348232863690 a.u.
E + ZPVE = -678.136909331134 a.u.
Free energy (298.15 K) = -678.177447422389 a.u.

Table S29. Atomic coordinates of **TS2** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.523286858618	-0.030499832772	-1.704589817938
H	-0.745216162382	0.033850482199	-2.471491978773
H	-1.962023942251	-1.032928777537	-1.748010828196
H	-2.308136257245	0.678055128268	-1.987229315565
C	-2.082320350040	0.013478579154	1.325920014118
H	-2.866104815129	0.777880037323	1.335617513419
H	-2.578276529143	-0.954049979447	1.197978721571
H	-1.605378012684	0.027839304479	2.309763200508
Si	-0.829708185972	0.408567580505	-0.013509478950
O	-0.031954738157	1.771379375278	0.111983458941
O	0.445110387062	-0.834986159920	0.238198770990
C	0.207207579314	-2.221888401674	0.039960784596
H	-0.764016725731	-2.493572210654	0.458547309352
H	0.225225173051	-2.481357562291	-1.023910314307
H	0.976959547652	-2.795388848480	0.563445698387
C	2.269173102972	-0.431675556984	0.003616128931
H	2.334909769162	-0.973251226574	-0.934674101521
H	2.527751129259	-1.024947337232	0.873337256549
C	2.479132046206	0.975013641896	0.014872269710
H	2.859492324814	1.386620058398	-0.918627812782
H	1.328907918889	1.477267876436	0.073450210198
H	2.978188111409	1.359907520279	0.901989564549

E(el) = -639.026631125075 a.u.
E + ZPVE = -638.844825485231 a.u.
Free energy (298.15 K) = -638.882480319073 a.u.

Table S30. Atomic coordinates of **TS2'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-1.553525921375	-0.500511668885	1.763318795088
H	-0.706853165119	-0.483084057472	2.456266979266
H	-2.377663952634	0.028590521571	2.252010224540
H	-1.868948575016	-1.542193316868	1.639771590753
C	-2.479182912448	0.050341839256	-1.115917850227
H	-2.864483537309	-0.974445572037	-1.124015277814
H	-3.324404513191	0.710194280094	-0.895185682689
H	-2.134624722900	0.295667937378	-2.124708249464
Si	-1.109156813445	0.338216303193	0.138138280449
O	0.232765370251	-0.660970315367	-0.498074723703
O	-0.479980861848	1.787019882388	0.226092803860
C	0.120471383377	-2.061126590587	-0.687874988968
H	-0.755654386413	-2.287676202518	-1.300962037033
H	1.005763331822	-2.424994841129	-1.218807532174
H	0.038050668647	-2.594339914024	0.265198763280
C	2.091154052346	-0.020448653977	-0.384525856360
H	2.293195940018	-0.644575309537	-1.249137992471
C	2.465585178455	-0.592240745059	0.943148667655
H	2.209274666946	-1.647070123489	1.040393311885
H	3.552602625208	-0.499260874446	1.057872563412
H	1.997426850589	-0.026297962663	1.750420686371
C	2.037746372429	1.396306201352	-0.555909961420
H	2.219285098436	1.750623710144	-1.568433077796
H	0.897547752906	1.703517483264	-0.252808468593
H	2.595772913336	1.946520567857	0.203612664658

E(el) = -678.360722361185 a.u.
E + ZPVE = -678.150349207031 a.u.
Free energy (298.15 K) = -678.189461436519 a.u.

Table S31. Atomic coordinates of **TS3** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	3.761633042478	1.692953785575	0.571317660100
H	3.436088097899	1.875210632666	1.599620687757
H	4.719148698797	1.162285082656	0.612351108222
H	3.950899010961	2.667667474092	0.110321429136
C	3.108686218600	0.252100448718	-2.071383077126
H	3.178279318200	1.130838281284	-2.720283408237
H	4.103959879294	-0.203217518307	-2.036300281273
H	2.432841284891	-0.454995134304	-2.563672892245
Si	2.436608138102	0.749061232008	-0.377818620219
O	0.961116694068	1.304137902497	-0.345725953140
O	2.387041006277	-0.813200122708	0.511086523935
C	3.381442812862	-1.813903789447	0.377304388323
H	3.314111147412	-2.321628650381	-0.591495385243
H	4.378958746472	-1.375205109969	0.476692742223
H	3.256978522340	-2.551140049912	1.174659647934
C	0.539114533251	-1.406265431176	0.790968104695
H	0.300833643978	-0.417924756712	0.445356707337
H	0.620411650163	-2.193614922477	0.059324277048
C	0.612309290073	-1.730741745532	2.243862040454
H	0.737790264988	-0.825910166568	2.839503684425
H	-0.316285545231	-2.225594595864	2.527865407195
H	1.438230735244	-2.411011093151	2.461879784458
C	-4.071491733912	-1.033048606474	-0.877372120244
H	-4.611489965334	-0.949246350553	0.069143499515
H	-4.446470763785	-0.257908634776	-1.552977136147
H	-4.323454998301	-2.003493280957	-1.315478997182
C	-1.232539541280	-0.793819461608	-2.180737876648
H	-0.928198018142	-1.803759494365	-2.472808877462
H	-1.774178105425	-0.361415354857	-3.026187946702
H	-0.326904913035	-0.204483299270	-2.009033033645
Si	-2.228217792079	-0.892115653529	-0.597306224192
O	-1.596049201602	-1.702330065789	0.598910927652
O	-2.165092322240	0.929620710519	-0.026770741291
C	-1.887821097734	1.999055241652	-0.985452566306
H	-2.372137670019	1.720889572804	-1.918125246286
H	-2.339787118799	2.915029523904	-0.608370920604
H	-0.803747553952	2.076838653813	-1.085677912308
C	-1.689826574466	1.235121882648	1.342494165956
H	-1.621265472258	0.260781151128	1.819545531606
H	-0.687727308646	1.648939183010	1.222154611355
C	-2.672472951348	2.139577900060	2.055383362870
H	-3.668021446856	1.690864590471	2.085498445753
H	-2.334082781158	2.284417945173	3.085311108950
H	-2.747754776184	3.127900181362	1.597071783020

E(el) = -1278.145706681141 a.u.
E + ZPVE = -1277.768254833565 a.u.
Free energy (298.15 K) = -1277.822965497431 a.u.

Table S32. Atomic coordinates of **TS3'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-3.505900071278	2.228948774029	-0.047017519564
H	-3.033955719844	2.623164544945	-0.952262994985
H	-4.541241924191	1.970266640291	-0.293705993129
H	-3.543249434198	3.045072585959	0.681682708014
C	-3.487801849378	-0.056615325907	2.015944700897
H	-3.532300932950	0.588182027983	2.899321786809
H	-4.520104449073	-0.293617053311	1.736526872551
H	-3.001752608075	-0.988055394585	2.324037350004
Si	-2.507277354728	0.782494235261	0.638017168257
O	-0.972780318848	1.029874102366	0.907205092798
O	-2.566519058811	-0.402987884478	-0.692057414400
C	-3.759399623648	-1.022896956245	-1.129777375559
H	-4.139442467911	-1.740145137278	-0.393652039391
H	-4.532818528904	-0.272890835037	-1.324022717270
H	-3.566689287152	-1.551424991916	-2.068036342841
C	-0.746466337667	-1.302390567360	-0.954550256712
H	-0.455690647507	-0.510403528092	-0.287956644126

C	-0.647155503411	-1.096117500966	-2.425352311484
H	-0.572226244882	-0.037315625681	-2.670397450455
H	0.251184848437	-1.610050805253	-2.770199583965
H	-1.506281719644	-1.526328634156	-2.946282651695
C	3.999370913073	-1.408830424077	0.820557889814
H	4.550327946234	-1.240779157974	-0.108610045863
H	4.436934694395	-0.772739486355	1.596472106753
H	4.166726122686	-2.449758749361	1.114101906421
C	1.201915062390	-1.167458364949	2.180754339663
H	0.884263260697	-2.202977362059	2.340344342620
H	1.772896771753	-0.866211420866	3.063564919118
H	0.306288032787	-0.542344676702	2.106180031848
Si	2.169515183672	-1.077904791494	0.584108208545
O	1.496757110371	-1.636540179388	-0.726762720360
O	2.242587793705	0.801461553690	0.309904536494
C	1.939229056077	1.755589331862	1.373315184615
H	2.382441168023	1.357329721823	2.282868703863
H	2.419265915498	2.702559303003	1.131940060489
H	0.854698573213	1.836646103696	1.456279614278
C	2.208178702825	1.310786337187	-1.095631363331
H	2.046433368075	0.391802512333	-1.656518013436
C	3.570004634303	1.902357159220	-1.413732428835
H	4.363696707394	1.169752052431	-1.256271423993
H	3.595468169244	2.216726711779	-2.460597923069
H	3.780894693777	2.782473038199	-0.800007184938
C	-1.088142706254	-2.647652380797	-0.410995135545
H	-1.241851069738	-2.612281060019	0.667212926521
H	-1.982079420098	-3.053188942319	-0.891286458865
H	-0.255311755976	-3.317116946409	-0.628406510943
C	1.036820847694	2.254305019698	-1.306945615646
H	1.238403667548	3.256407028239	-0.919124749097
H	0.858055384787	2.348695230192	-2.381658916785
H	0.137634462682	1.872806679145	-0.817924984005

E(el) = -1356.808054991148 a.u.
E + ZPVE = -1356.374892137816 a.u.
Free energy (298.15 K) = -1356.431812339068 a.u.

Table S33. Atomic coordinates of **TS4'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z C -3.715748862695 1.667127957675 0.481558083247
H	-2.973849664384	2.429149599948	0.740730045652
H	-4.271620405082	2.025474425630	-0.392090366040
H	-4.422704343944	1.613010213491	1.315455253247
C	-4.186158319136	-1.170324375027	-0.564147424950
H	-4.989513409593	-1.388495468271	0.147057775611
H	-4.655075808196	-0.756131927721	-1.464156598359
H	-3.732932451327	-2.128940107244	-0.839466555822
Si	-2.894071841879	-0.017366075664	0.207417381602
O	-2.072543593777	-0.611737077439	1.422871599441
O	-1.756277870055	0.254586178933	-1.093886780038
C	-2.100357493989	0.955191922898	-2.266004632950
H	-2.963785457481	0.511049992231	-2.780830875566
H	-2.335523320075	2.009085256682	-2.064758378062
H	-1.252874155546	0.930205263537	-2.962843690943
C	0.833356612707	1.943164501245	0.443273699381
H	0.187870755901	1.486695252662	-0.314717109695
C	0.037958782017	2.098594038924	1.728724959641
H	-0.478916428623	1.173633351743	1.991729274151
H	0.702085331218	2.403328932109	2.542762043106
H	-0.727317157296	2.868739239093	1.602331923538
C	4.042097653903	-0.872618471284	0.791026170606
H	3.669959887470	-1.306421128243	1.720165449205
H	4.530635968057	-1.667396165825	0.220462108724
H	4.802999252192	-0.131999692274	1.052050634644
C	3.285673510518	0.603581505731	-1.830859413499
H	4.010280276740	1.394457740273	-1.614457044559
H	3.796356004498	-0.139228246059	-2.449666601369
H	2.487773131761	1.055243700617	-2.425115449791
Si	2.685752709290	-0.081972081527	-0.199548717392

O	1.941386148177	1.034659421856	0.726764373984
O	1.532885916707	-1.362527309820	-0.548949242271
C	0.989112611213	-1.544211454426	-1.887791297372
H	0.042519347112	-1.006847980617	-1.957743909980
H	1.700556951127	-1.175160150442	-2.621551671597
H	0.842832157280	-2.609638119097	-2.045674386757
C	0.173104304821	-1.594521966203	0.665866026455
H	-0.326768860037	-0.682432034389	0.402319675076
C	0.791023291011	-1.623257764046	2.020868525215
H	1.351645408890	-0.722450422921	2.254810230374
H	-0.080071548660	-1.631834717085	2.683914944185
H	1.388634819129	-2.520416435212	2.196447611777
C	1.403780354984	3.257898209842	-0.071217624378
H	1.979651595401	3.114401659557	-0.989248761910
H	0.596622335063	3.962799634424	-0.286806461724
H	2.061032389292	3.705476827421	0.679246833972
C	-0.498693424009	-2.855133355237	0.230163810833
H	0.195343985122	-3.699383224536	0.195929869225
H	-1.257554822873	-3.043216409198	0.991875788580
H	-1.031936281546	-2.748665669203	-0.711495420074

E(el) = -1356.835924936077 a.u.
E + ZPVE = -1356.402638184583 a.u.
Free energy (298.15 K) = -1356.460377073073 a.u.

Table S34. Atomic coordinates of **TS5** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-3.171716924850	1.258309831553	-1.416950516577
H	-2.792866101318	0.750420125640	-2.309874248268
H	-4.251983308798	1.079562596417	-1.371195481097
H	-3.030774491423	2.333650883085	-1.570286543491
C	-3.096036263082	1.478593785468	1.633897434663
H	-2.954060097893	2.564787160736	1.625511463738
H	-4.175890081182	1.296538675507	1.675037195766
H	-2.665651174066	1.102281525022	2.568739365110
Si	-2.255854430079	0.672500168376	0.135968756882
O	-0.677538952533	0.860149453132	0.091969679073
O	-2.576670192621	-1.002357364101	0.270542100817
C	-3.866795187854	-1.558196707401	0.353306354202
H	-4.409652884115	-1.216721455893	1.246495552658
H	-4.481620504875	-1.317824900605	-0.526317541834
H	-3.779177768830	-2.647952462352	0.411880687724
C	0.145333930228	-1.980696149159	-1.287460616824
H	-0.603063055563	-1.824266846563	-0.511154182316
H	0.228242537894	-3.049497061124	-1.503588832883
C	-0.224646565616	-1.194828844346	-2.527196284251
H	-0.356171871994	-0.145641895738	-2.264910794114
H	0.539050163939	-1.296461753850	-3.303989038786
H	-1.174095855368	-1.564287310624	-2.924870215782
C	3.684744451221	-1.362143405182	0.896014370585
H	4.286703991920	-1.183436213766	0.001390999881
H	4.118777786705	-0.781990439168	1.715458745786
H	3.776865534242	-2.421537555365	1.151494109589
C	0.765869367663	-1.138816398246	2.039775716273
H	0.429915413323	-2.179695821800	2.069240841209
H	1.241946366544	-0.915486208769	2.997930716063
H	-0.109992683030	-0.507743172728	1.890525594491
Si	1.902602082371	-0.912081536588	0.598672161873
O	1.461175871035	-1.578158015984	-0.814189046304
O	2.122723932847	0.888946248225	0.305927489154
C	1.679393353002	1.805670450465	1.371982214532
H	1.998099216529	1.365587671378	2.314130385167
H	2.195989083095	2.750180184082	1.224100464846
H	0.592975314875	1.869198253544	1.280589928820
C	1.880263250970	1.424954579092	-1.074943943583
H	2.030026588757	0.562912201578	-1.718461924354
H	0.821403984604	1.687400664421	-1.076357266375
C	2.857820799122	2.533758767788	-1.389398099105
H	3.891671257197	2.214621523474	-1.236387617540

H	2.739523528638	2.798952005343	-2.443757766513
H	2.677753361964	3.441132026482	-0.810485834864

E(el) = -1278.198019085485 a.u.
E + ZPVE = -1277.819469093420 a.u.
Free energy (298.15 K) = -1277.874023945949 a.u.

Table S35. Atomic coordinates of **TS6** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	2.634803421831	0.395756672381	2.108363353453
H	1.569835011069	0.288277953240	2.323992287965
H	3.149537856160	-0.487930609168	2.495088694843
H	2.990577769052	1.260263159369	2.677174684736
C	4.827036429486	0.732058453899	-0.043707336057
H	5.246401705326	1.586277300891	0.496593876044
H	5.358040200886	-0.160061298321	0.301163113299
H	5.047092999957	0.888830050005	-1.101864225259
Si	2.993189126030	0.664686598941	0.295781752814
O	2.117889464939	1.717545100138	-0.504232696102
O	2.549152691351	-1.022675568552	-0.370005436008
C	3.101794030587	-1.468791688072	-1.634663040730
H	4.182248722414	-1.367412748023	-1.582837978824
H	2.837684375834	-2.516082230237	-1.765223541688
H	2.693365465425	-0.864722814195	-2.446111242678
C	1.103807211973	-1.458433632859	-0.177354621182
H	0.628799608797	-0.684692049320	0.410272861772
H	0.643286522884	-1.448922549411	-1.159932235742
C	1.046848555024	-2.798706005312	0.500738712570
H	1.518493679845	-2.766359823002	1.485512609751
H	-0.016153558475	-3.017896195351	0.613242883104
H	1.514853262425	-3.590569177057	-0.090381418283
C	-3.344388472038	-0.139169488619	1.934186781120
H	-2.531976576358	0.461147201527	2.356895203875
H	-4.273084086929	0.429272083967	2.051947686561
H	-3.435936096902	-1.037359633097	2.553593104026
C	-4.520596259889	-1.363796610251	-0.621949560901
H	-4.762371474790	-2.327045427059	-0.160788308091
H	-5.399353088054	-0.719006916848	-0.509087955524
H	-4.370470354511	-1.539877718232	-1.691068408276
Si	-2.962995412983	-0.624294740257	0.143535448610
O	-1.591119538535	-1.351892139147	-0.104050458783
O	-2.871889985477	0.958217527653	-0.697810595507
C	-3.684763746350	2.063066281467	-0.350124520961
H	-4.717351995351	1.743189662322	-0.181377247207
H	-3.318257542066	2.558799847328	0.556479467638
H	-3.678046924123	2.782640526631	-1.174206894215
C	-0.989176610110	1.488181595092	-0.980866457231
H	-0.790730445641	0.434123857182	-1.114447738201
H	-1.216526321173	2.042413695917	-1.885791230969
C	-0.417689495940	2.157826874796	0.102521768666
H	-0.366183897938	1.605533395762	1.040442751676
H	0.925316437884	1.993610222009	-0.288342735678
H	-0.620084296336	3.219678870507	0.226912975388

E(el) = -1278.119491899211 a.u.
E + ZPVE = -1277.748477047945 a.u.
Free energy (298.15 K) = -1277.804378313285 a.u.

Table S36. Atomic coordinates of **TS6'** optimised at the B3LYP-D3/6-311G(d) level of theory.

atom	x	y	z
C	-4.792079263575	1.184397860371	-0.115665996335
H	-5.001343106171	1.219800326026	0.956665833079
H	-5.004852050547	2.182361133201	-0.510908093029
H	-5.493594193125	0.493411767914	-0.591183794665
C	-2.686561792010	0.317576925620	-2.236579157298
H	-3.368834676100	-0.468569576485	-2.574445269276
H	-2.819570008961	1.175942542394	-2.901641120336
H	-1.664507162143	-0.044396080131	-2.377026560780
Si	-2.993923149823	0.807388263929	-0.457407787020

O	-2.767983722958	-0.835977948195	0.385786312259
O	-1.951724686910	1.776851584878	0.227986218595
C	-3.823373884182	-1.795009975253	0.606314543940
H	-3.985843412867	-2.390353603344	-0.292795347117
H	-3.539820521964	-2.438425800743	1.435908632140
H	-4.722984975936	-1.246505897650	0.869404055297
C	-1.327162736704	-1.368654953385	0.488644816207
H	-0.749153379289	-0.571491588050	0.035518201433
C	-1.162603479496	-2.626155535365	-0.329802790981
H	-1.534320470712	-2.494243114391	-1.349015700539
H	-0.082733184003	-2.787485213716	-0.371536128900
H	-1.646164558754	-3.495997238730	0.122885242735
C	-0.962678313695	-1.489789454929	1.947249184565
H	-1.148629732427	-0.549823494913	2.470032939948
H	-1.502218356349	-2.297211293062	2.451079380570
H	0.107529111145	-1.705573142497	1.965865899550
C	4.503498504643	-1.683070481334	0.426011813415
H	4.463031635213	-1.702542026834	1.519219089409
H	4.578068065626	-2.719702340746	0.081188816129
H	5.430288082096	-1.175014309263	0.135905446847
C	3.174608904592	-0.692844399329	-2.151636081341
H	4.137979014801	-0.268947976203	-2.455416028355
H	3.095022938367	-1.679791937767	-2.619068211436
H	2.387190337877	-0.067784949154	-2.586572143225
Si	2.965519944253	-0.841026978515	-0.272846039924
O	3.131180772564	0.817240709029	0.308431073196
O	1.556162608758	-1.356130246013	0.218340097126
C	3.974273069918	1.775830704806	-0.289150196927
H	3.571933306267	2.128755355395	-1.247727415980
H	4.071111927173	2.633372805466	0.384543492364
H	4.977935195528	1.371391212967	-0.466346377260
C	1.120005104573	1.573686090588	0.701283763213
H	0.984111034661	0.516847362661	0.911810246955
C	0.578408200881	2.054275539298	-0.487957329452
H	0.544205434897	1.353410176240	-1.319655570674
H	-0.683790400795	1.975654715987	-0.090159908869
H	0.772259798867	3.087769792030	-0.770940823997
C	1.452609331254	2.456204699719	1.851123333169
H	2.231653645587	2.000591438715	2.461763561691
H	1.761104206151	3.456804220343	1.540107974989
H	0.554293969653	2.557053217503	2.473069095777

E(el) = -1356.787638540384 a.u.

E + ZPVE = -1356.361140974909 a.u.

Free energy (298.15 K) = -1356.421121904677 a.u.

3. Spectra of Products

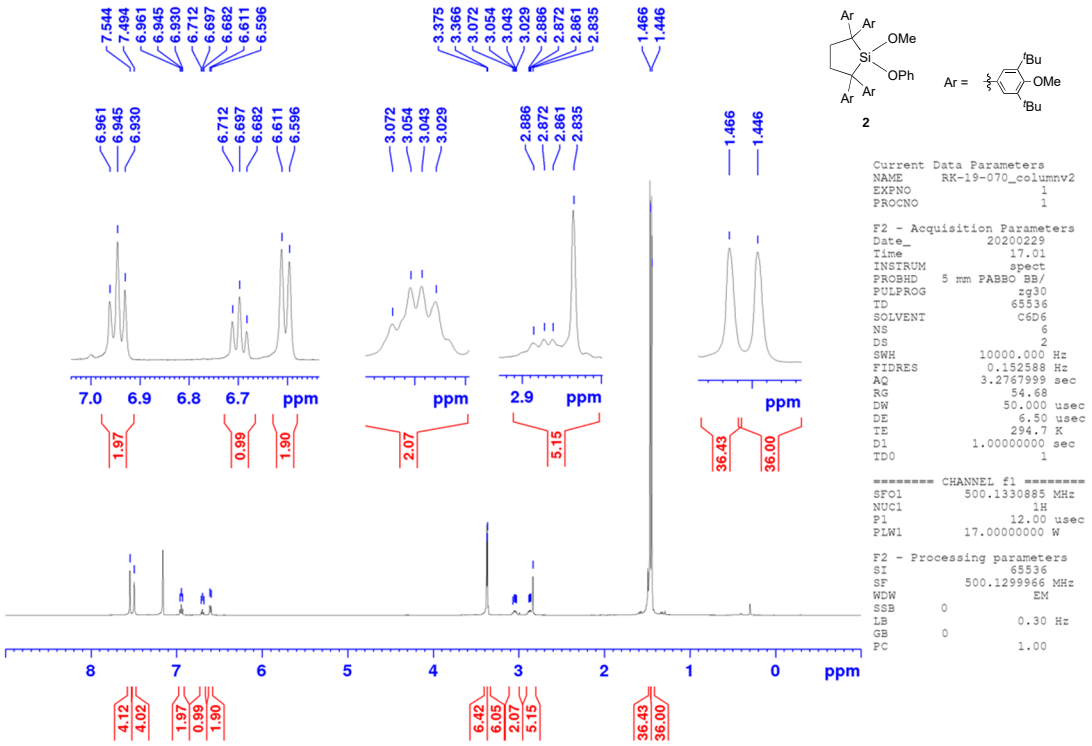


Figure S6. ^{1}H NMR spectrum of **2** (500 MHz, C_6D_6, r.t.).

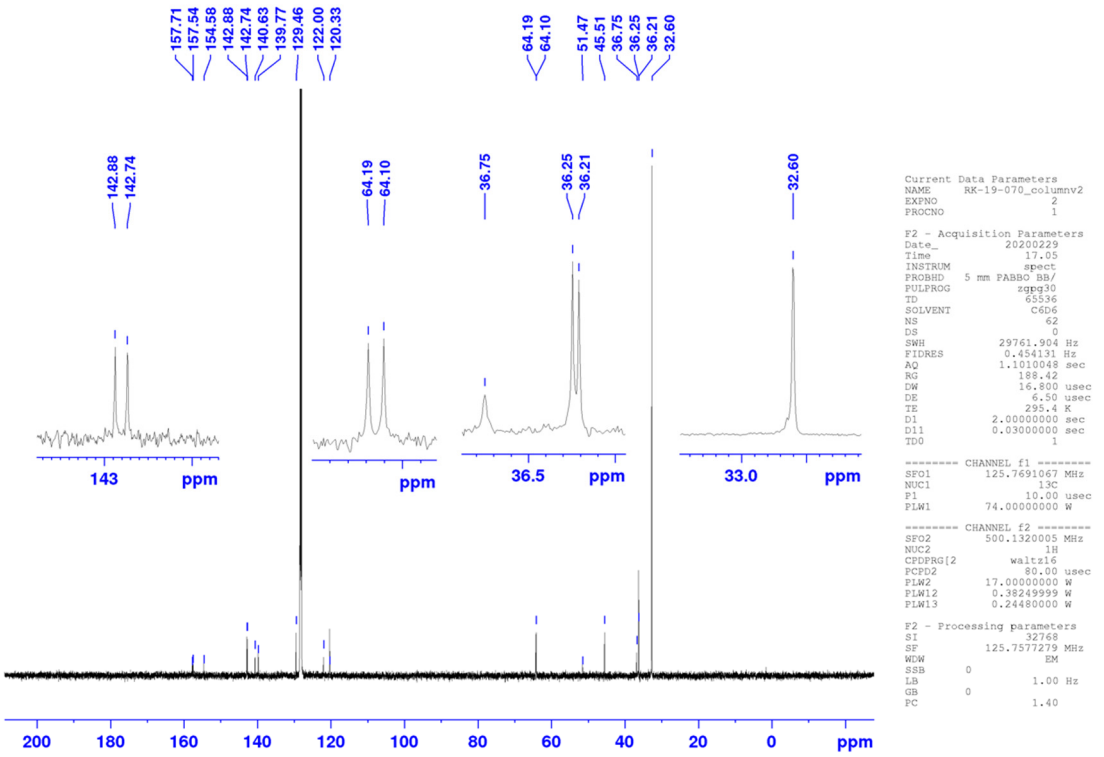


Figure S7. ^{13}C{H} NMR spectrum of **2** (125 MHz, C_6D_6, r.t.).

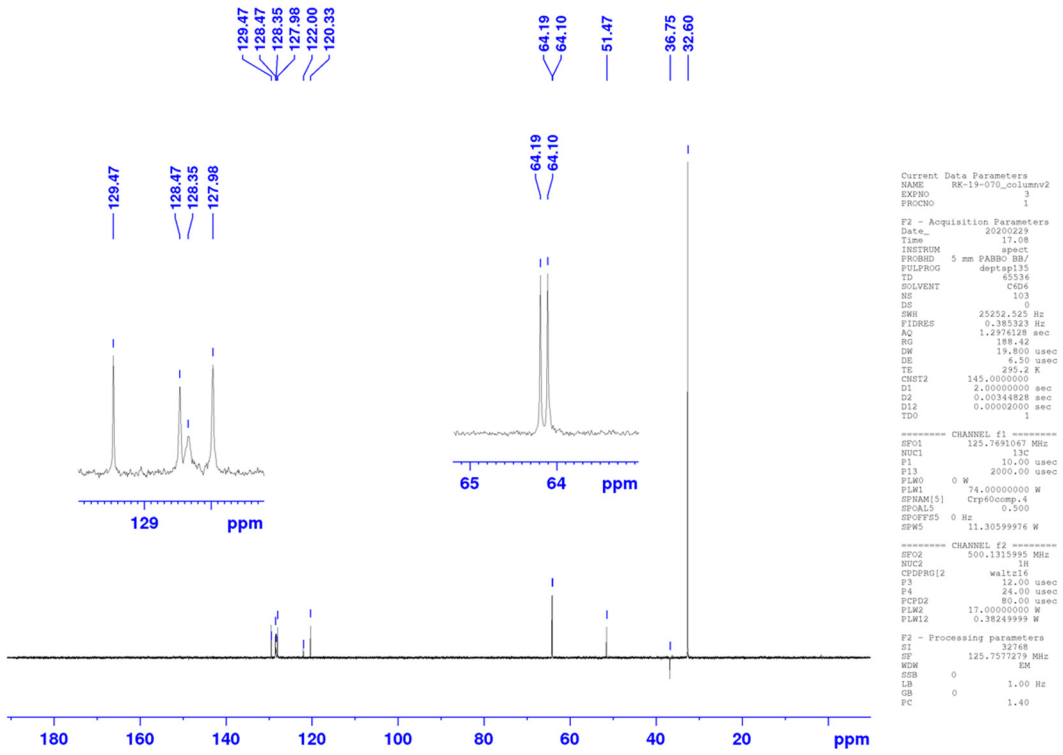


Figure S8. $^{13}C\{H\}$ (dept 135) NMR spectrum of **2** (125 MHz, C_6D_6, r.t.). The signal at 128.5 ppm is derived from solvent (C_6D_5H)

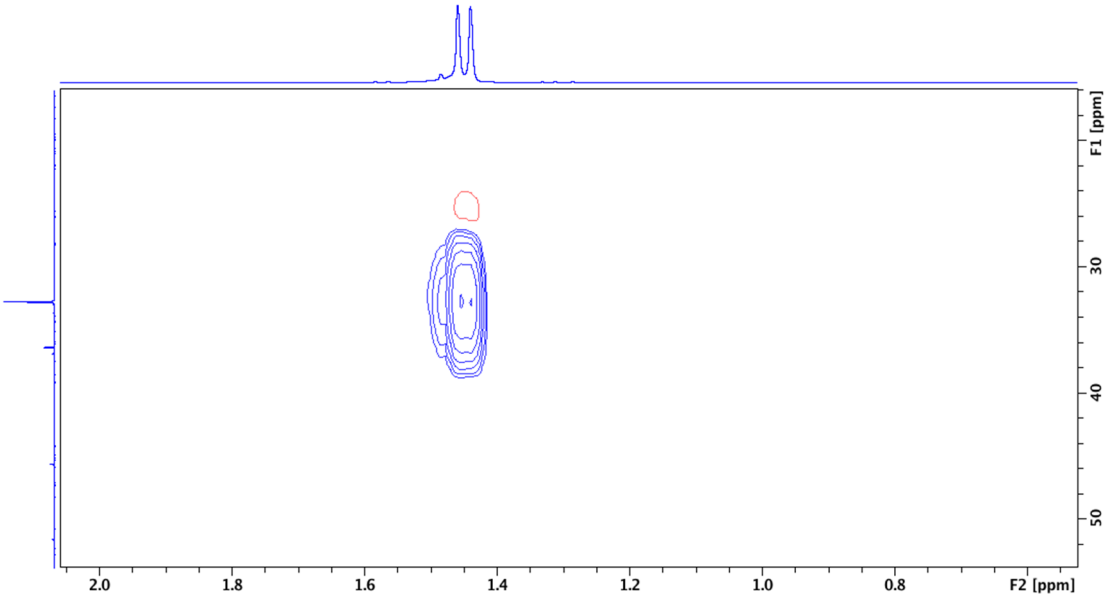


Figure S9. ^{1}H-^{13}C HSQC NMR spectrum of **2** (125 MHz, C_6D_6, r.t.).

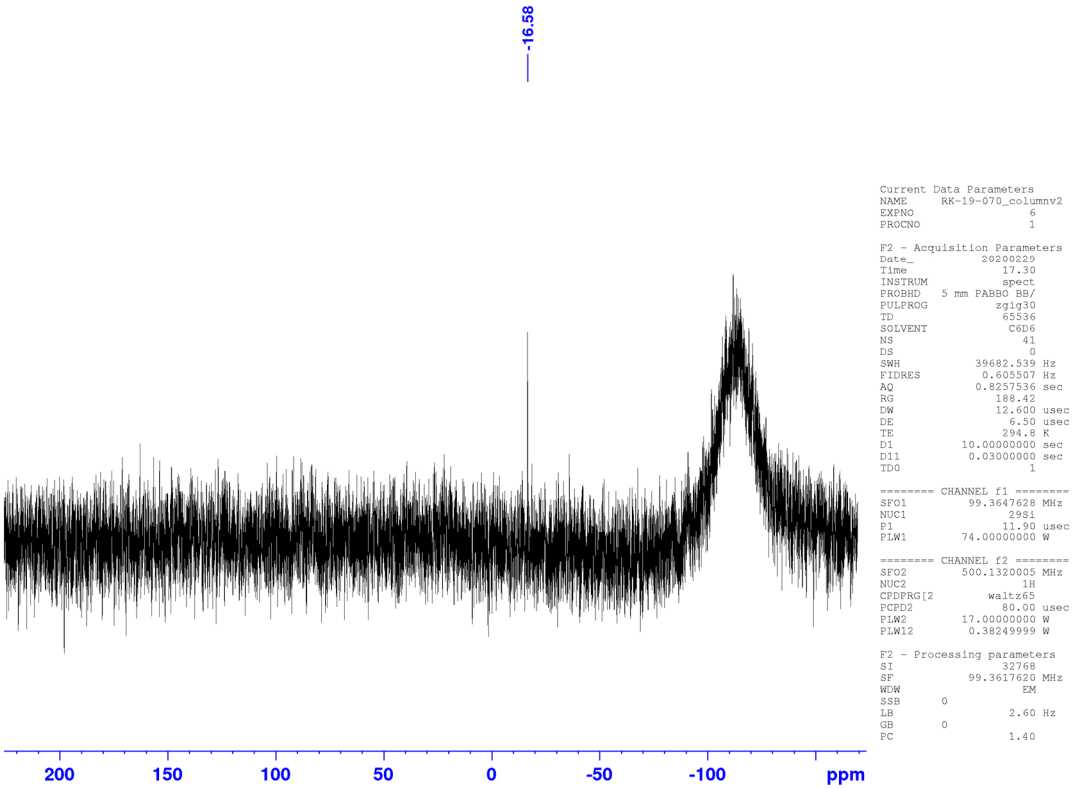


Figure S10. $^{29}Si\{H\}$ NMR spectrum of **2** (99 MHz, C_6D_6, r.t.).

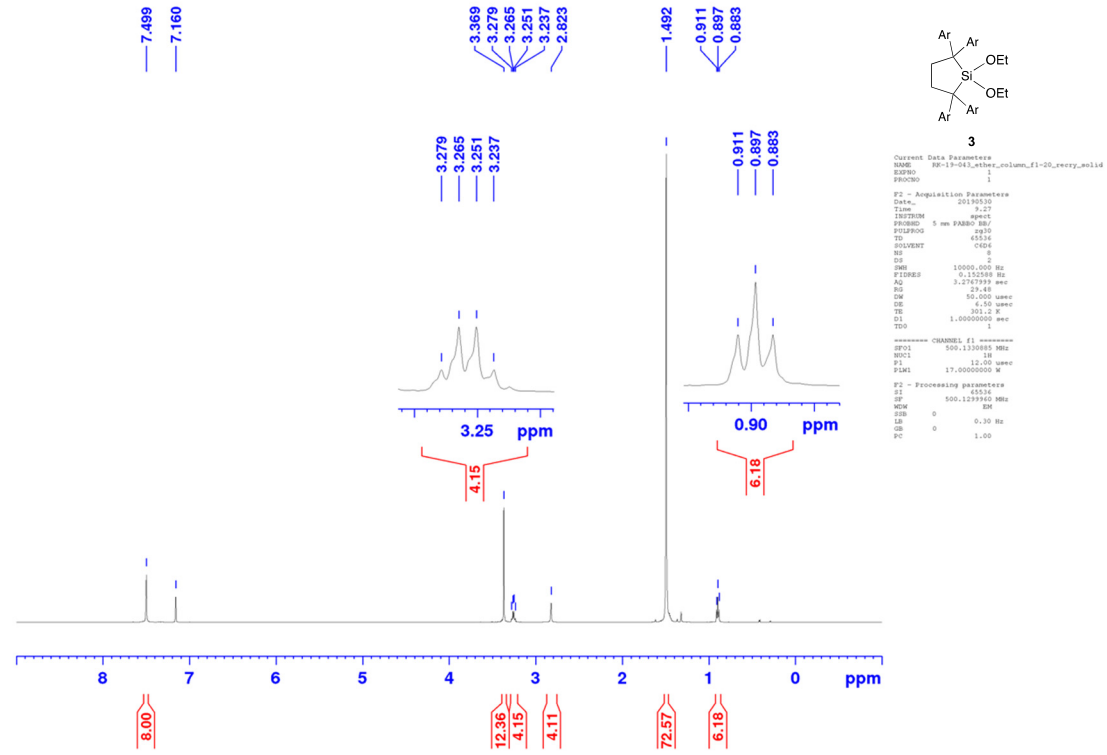


Figure S11. ^{1}H NMR spectrum of **3** (500 MHz, C_6D_6, r.t.).

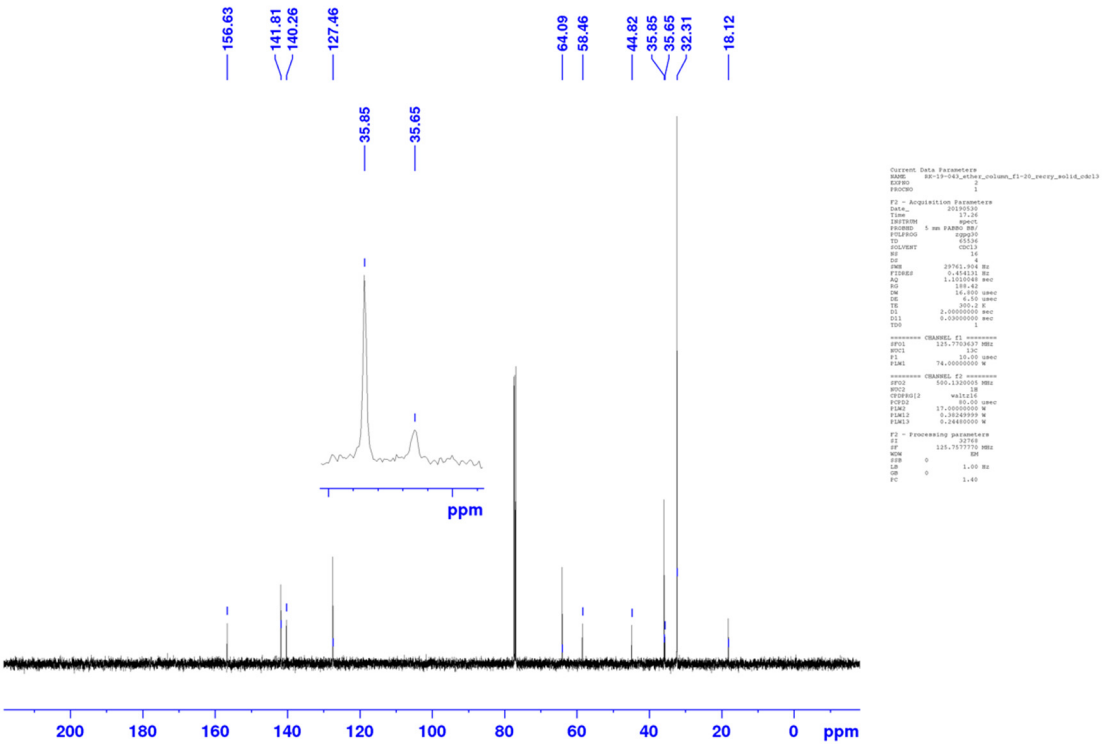


Figure S12. $^{13}C\{H\}$ NMR spectrum of **3** (125 MHz, $CDCl_3$, r.t.).

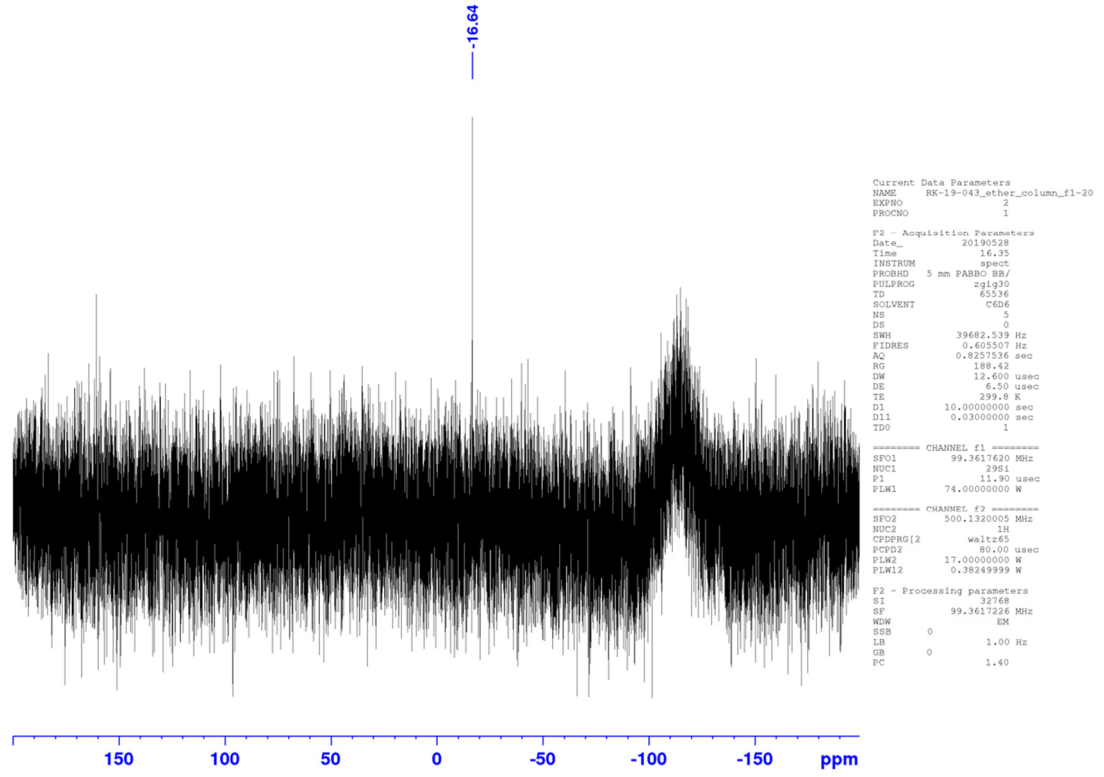


Figure S13. $^{29}Si\{H\}$ NMR spectrum of **3** (99 MHz, C_6D_6, r.t.).

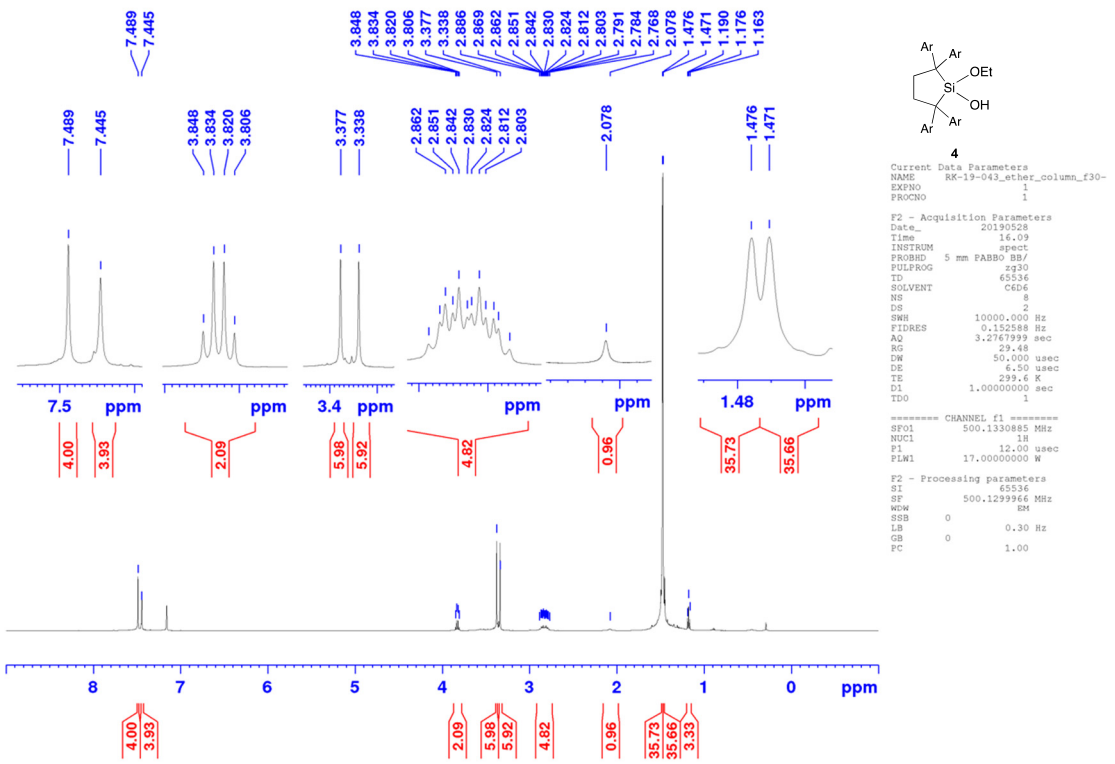


Figure S14. ^{1}H NMR spectrum of **4** (500 MHz, C_6D_6, r.t.)

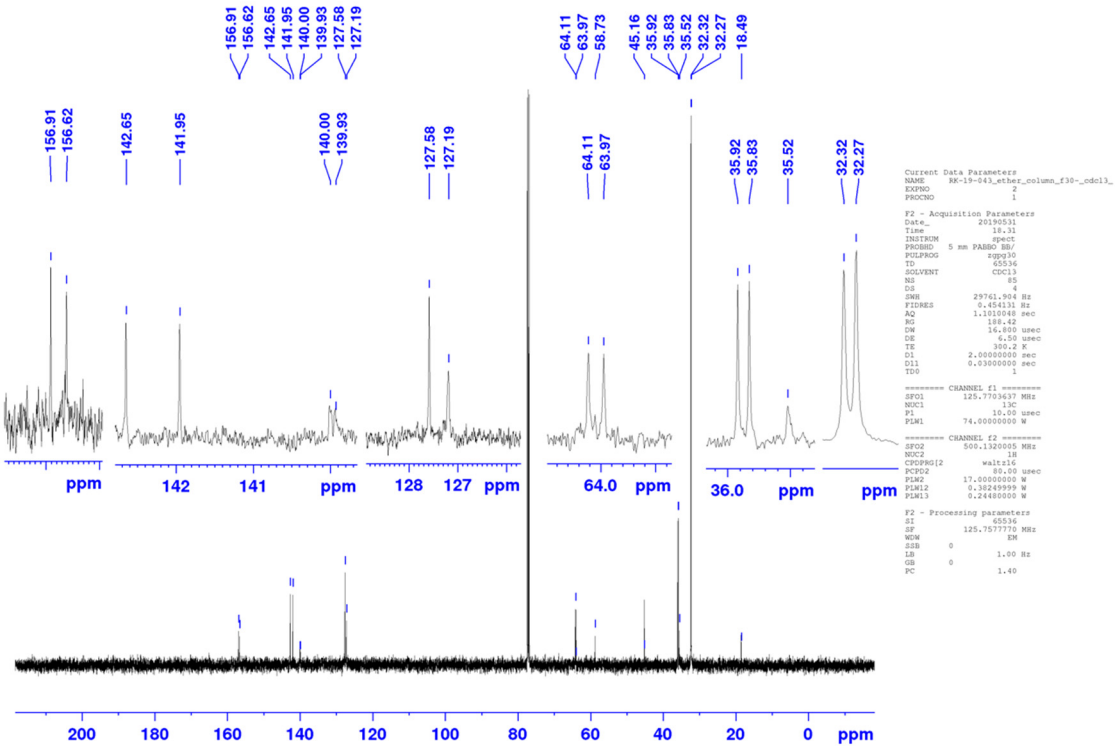


Figure S15. ^{13}C{H} NMR spectrum of **4** (125 MHz, $CDCl_3$, r.t.).

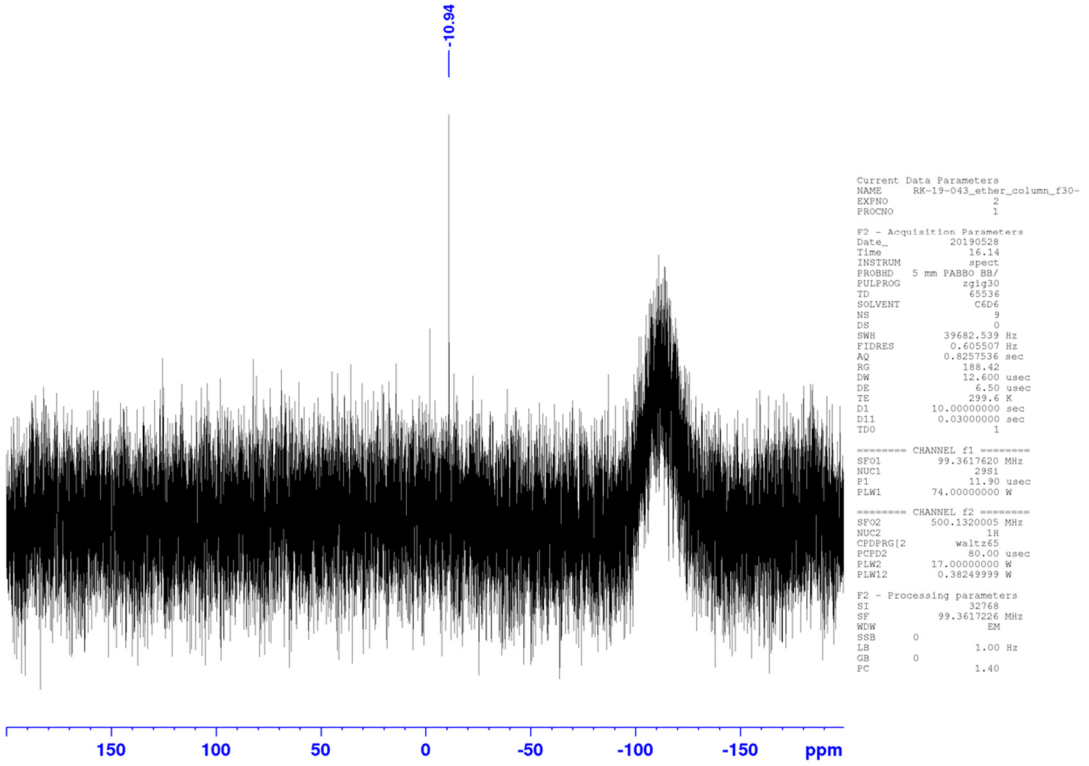


Figure S16. $^{29}Si\{H\}$ NMR spectrum of **4** (99 MHz, C_6D_6, r.t.).

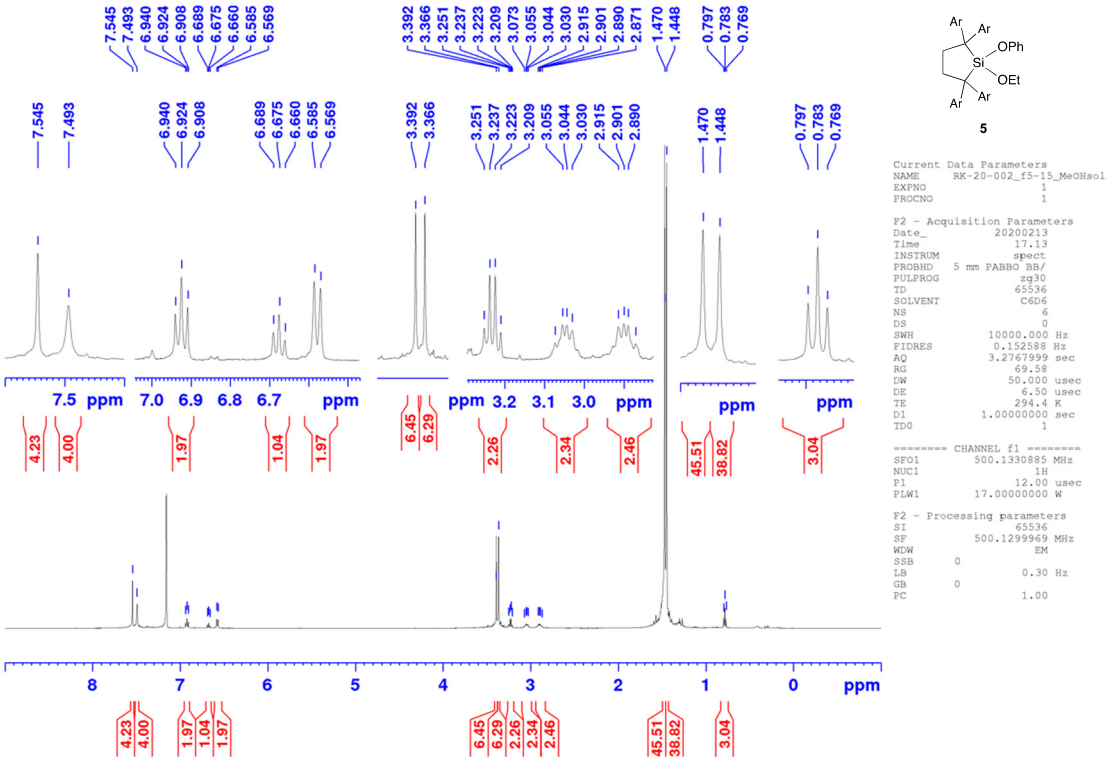


Figure S17. ^{1}H NMR spectrum of **5** (500 MHz, C_6D_6, r.t.).

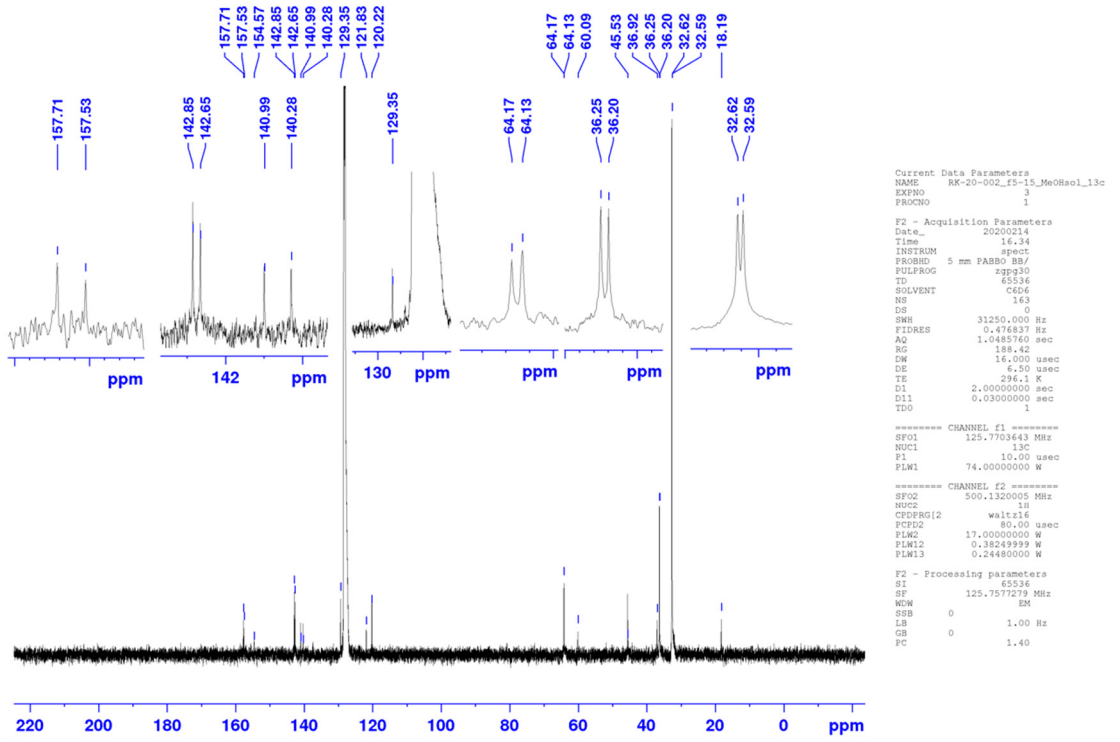


Figure S18. $^{13}C\{H\}$ NMR spectrum of **5** (125 MHz, C_6D_6, r.t.).

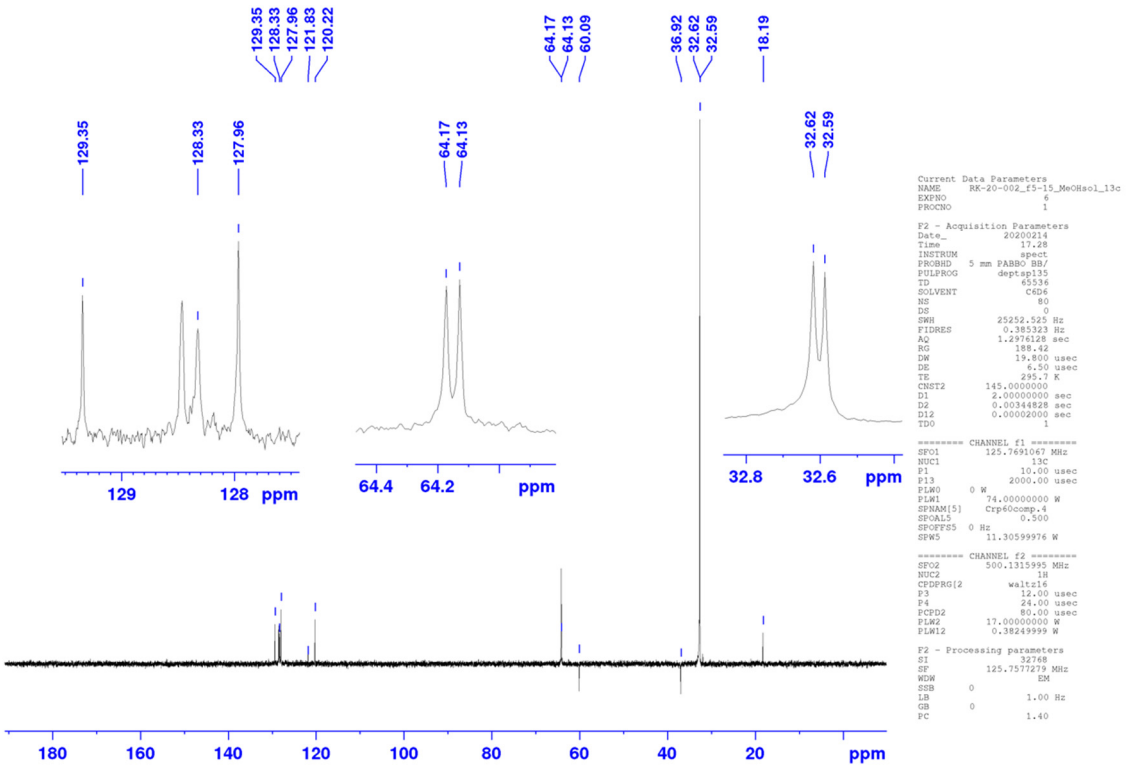


Figure S19. $^{13}C\{H\}$ (dept 135) NMR spectrum of **5** (125 MHz, C_6D_6, r.t.). The signal around 128.5 ppm is derived from solvent (C_6D_5H)

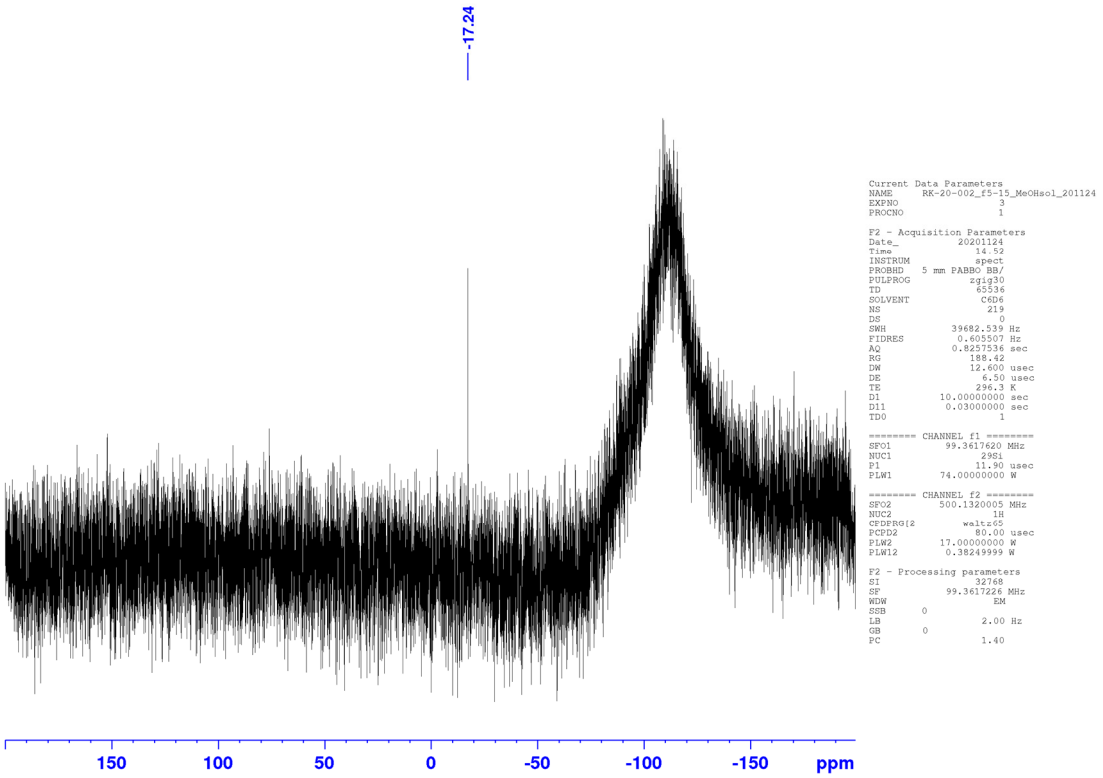


Figure S20. $^{29}Si\{H\}$ NMR spectrum of **5** (99 MHz, C_6D_6, r.t.).

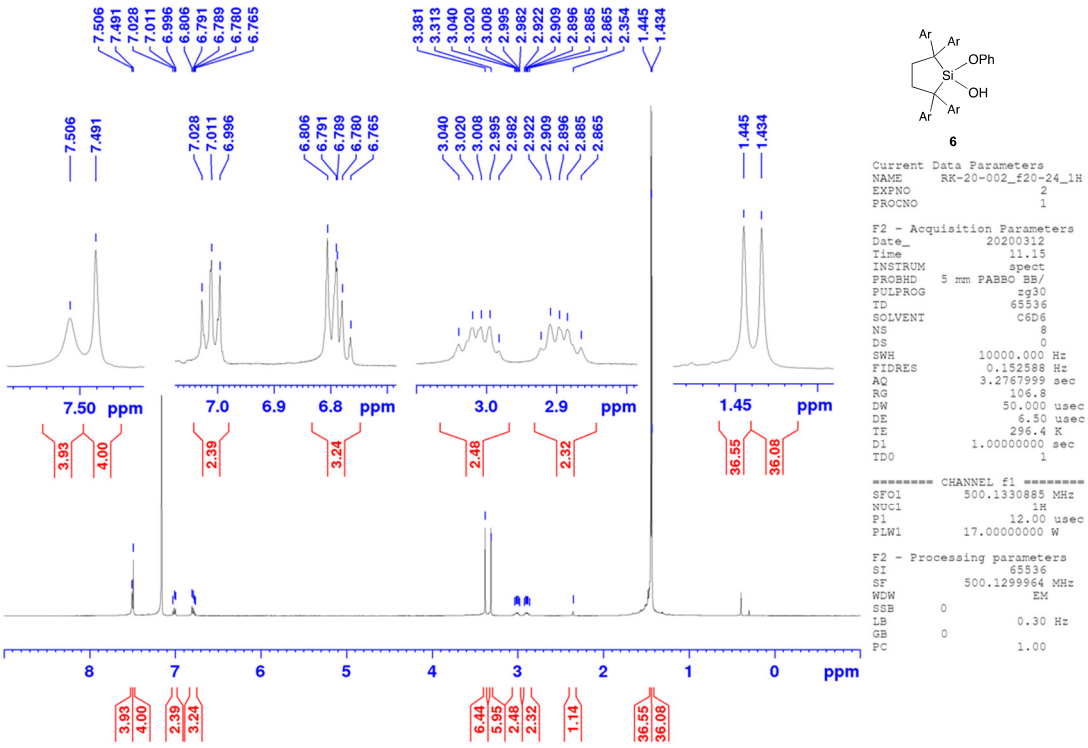


Figure S21. ^{1}H NMR spectrum of **6** (500 MHz, C_6D_6, r.t.).

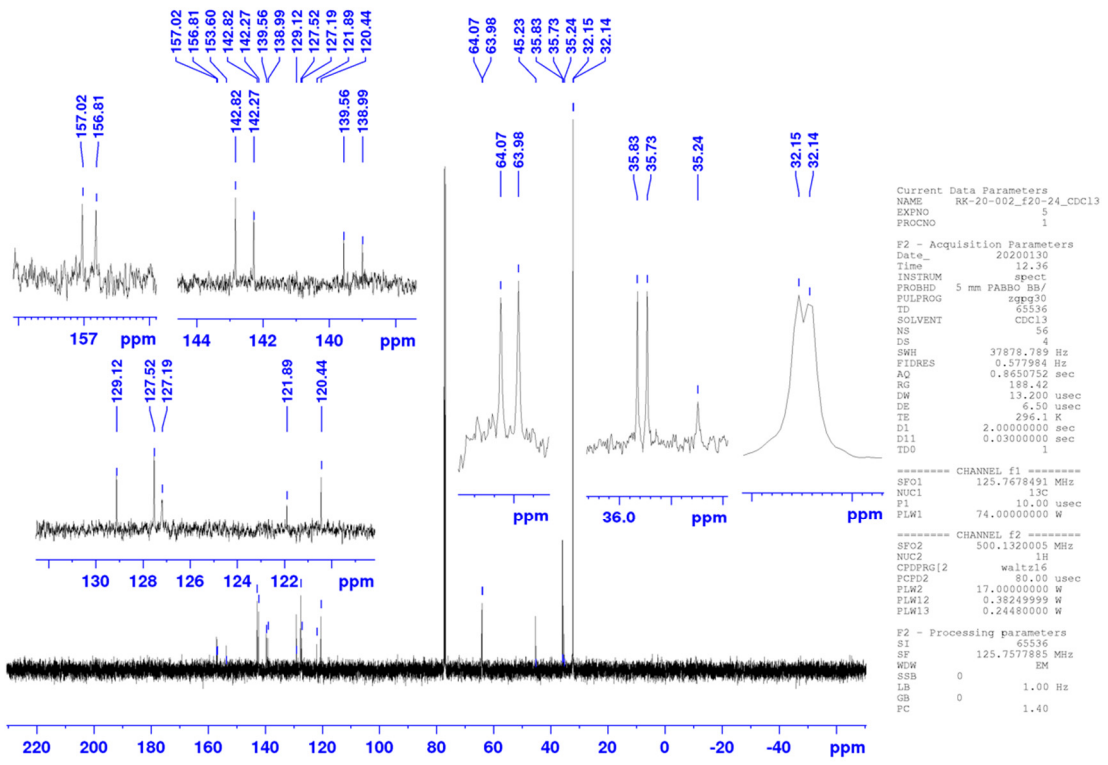


Figure S22. $^{13}C\{H\}$ NMR spectrum of **6** (125 MHz, $CDCl_3$, r.t.).

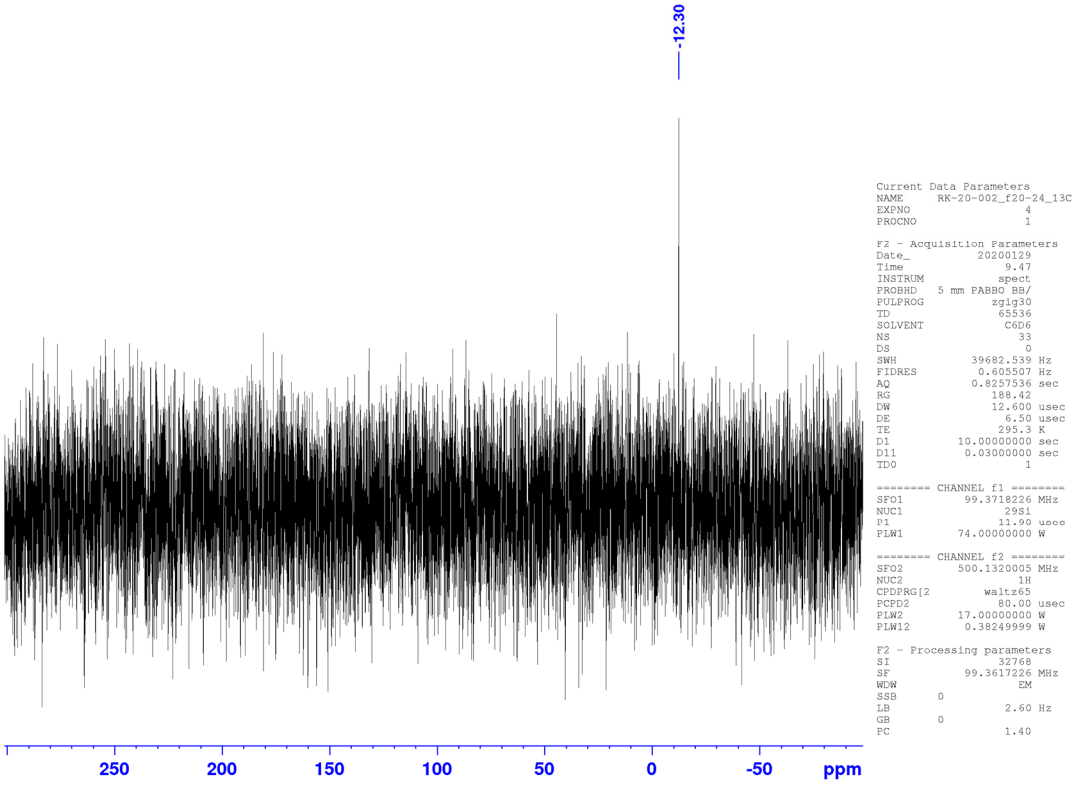


Figure S23. $^{29}Si\{H\}$ NMR spectrum of **6** (99 MHz, C_6D_6, r.t.).

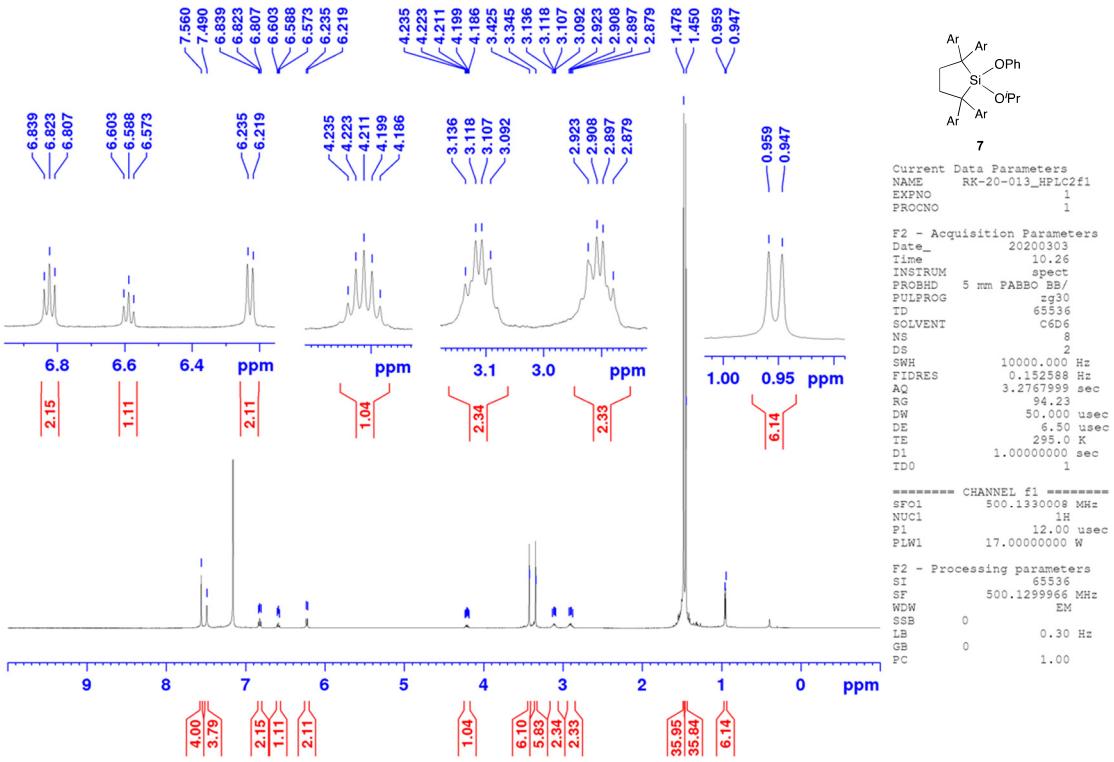


Figure S24. ^{1}H NMR spectrum of **7** (500 MHz, C_6D_6, r.t.).

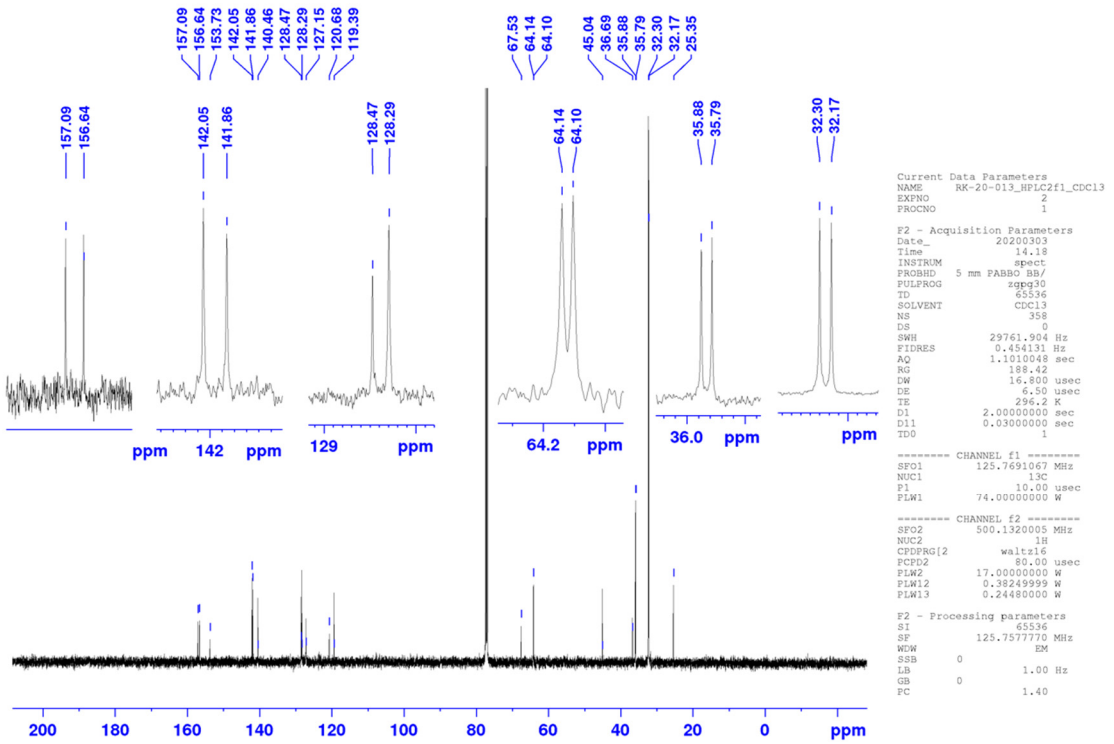


Figure S25. ^{13}C{H} NMR spectrum of **7** (125 MHz, $CDCl_3$, r.t.).

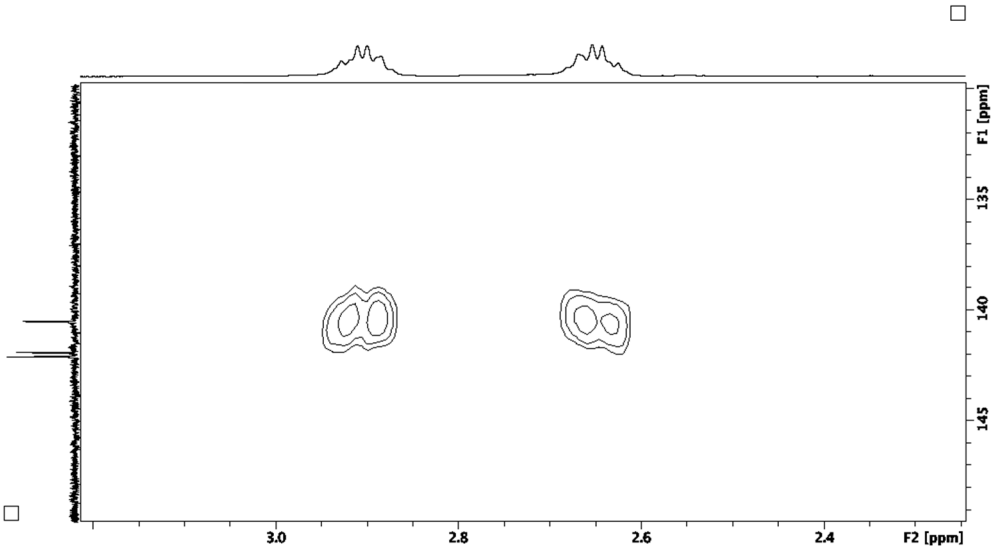


Figure S26. ^{1}H-^{13}C HMBC NMR spectrum of **7** (125 MHz, $CDCl_3$, r.t.).

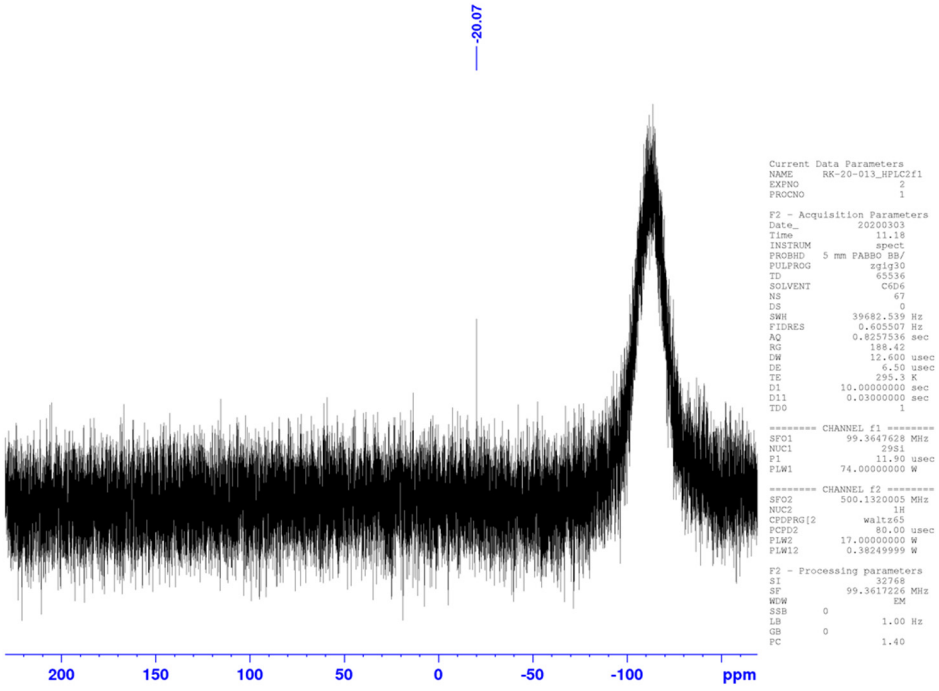


Figure S27. $^{29}Si\{H\}$ NMR spectrum of **7** (99 MHz, C_6D_6, r.t.).

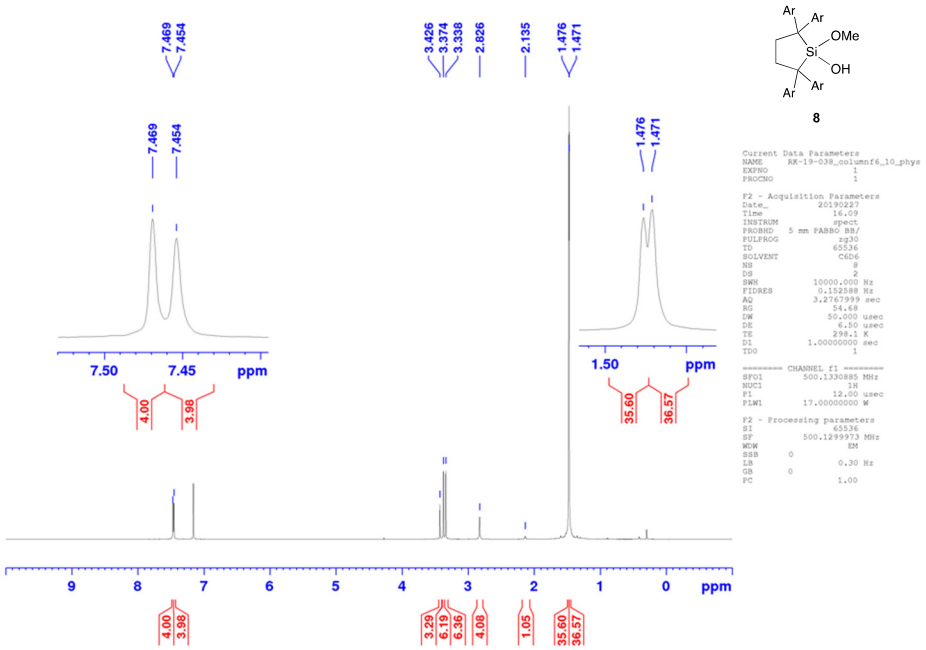


Figure S28. ^{1}H NMR spectrum of **8** (500 MHz, C_6D_6, r.t.).

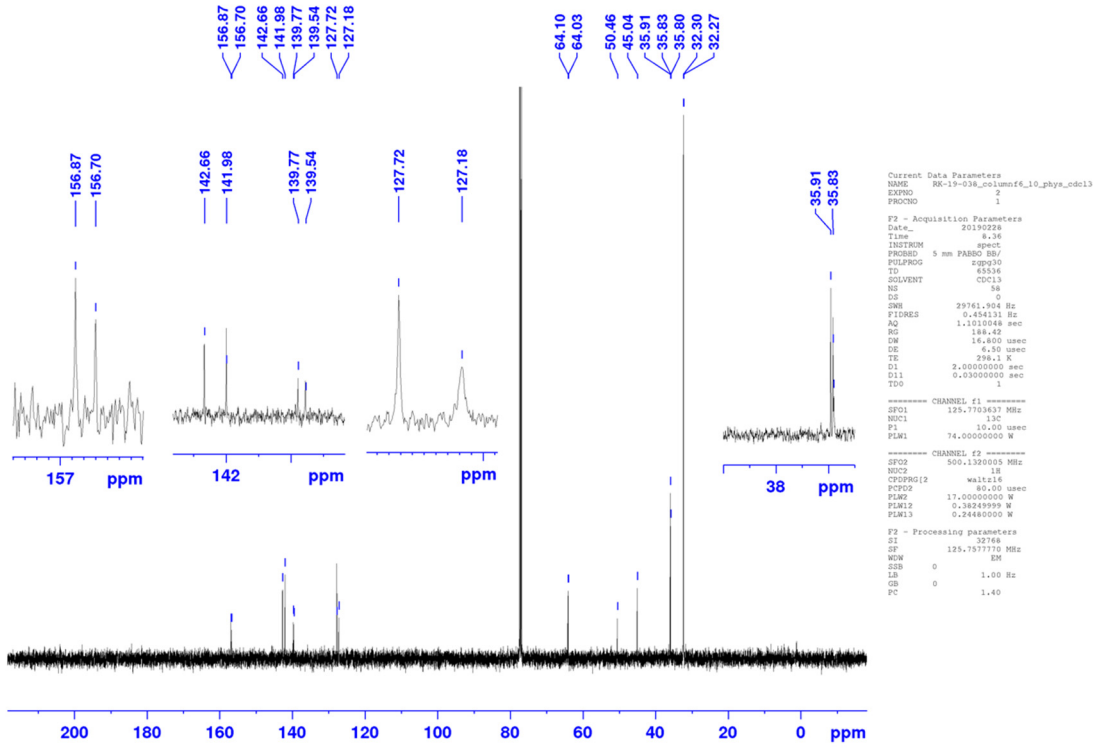


Figure S29. ^{13}C{H} NMR spectrum of **8** (125 MHz, C_6D_6, r.t.).

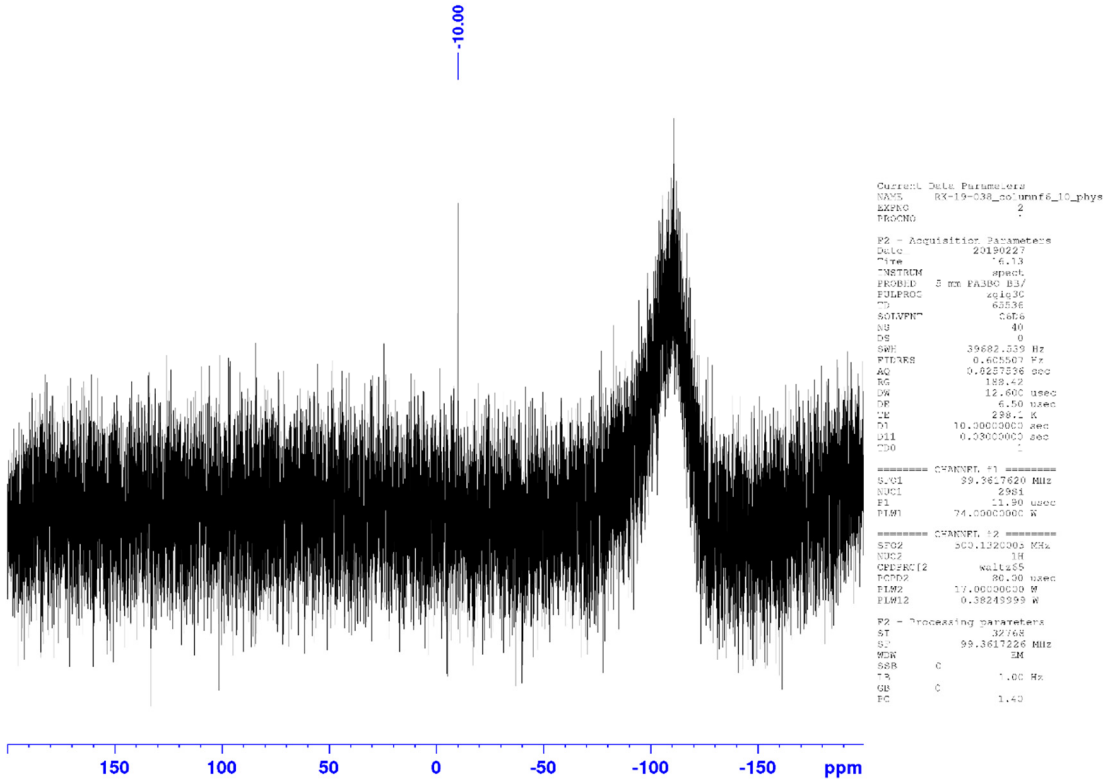
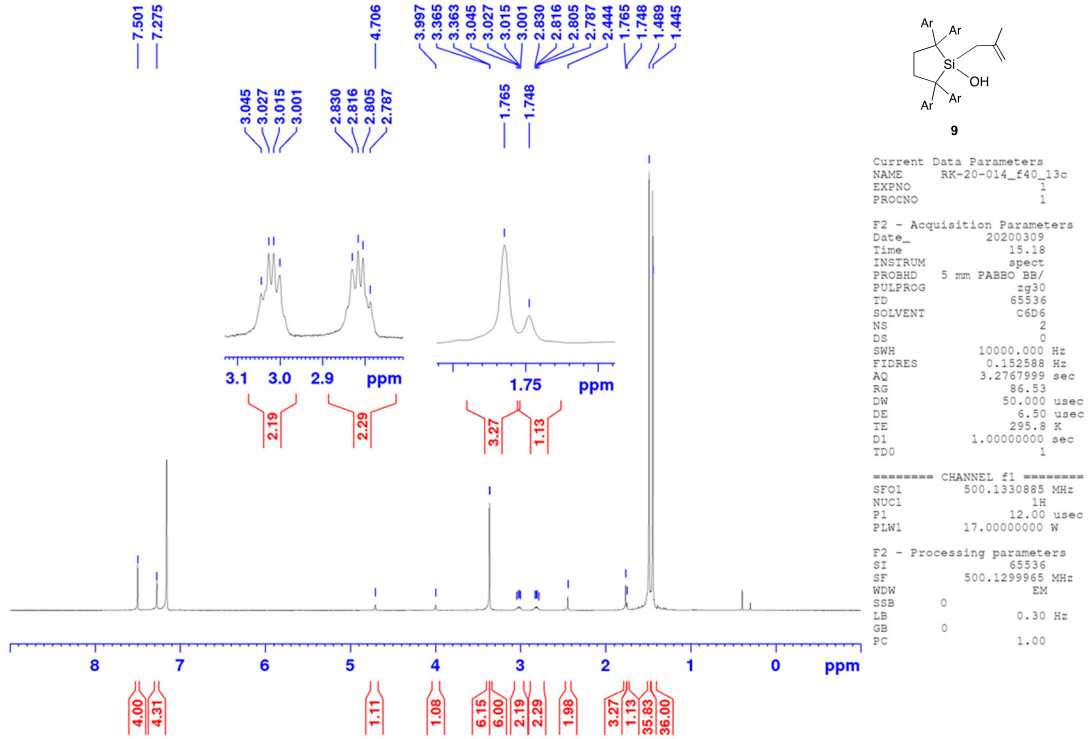


Figure S30. $^{29}Si\{H\}$ NMR spectrum of **8** (99 MHz, C_6D_6, r.t.).



9

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EXPNO 1
PROCNO 1

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Time 15.18
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT C6D6
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RG 86.53
DW 50.000 usec
DE 6.50 usec
TE 295.8 K
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NUC1 1H
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PLW1 17.00000000 W

F2 - Processing parameters
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SF 500.1299965 MHz
WDW EM
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GB 0
PC 1.00

Figure S31. ^{1}H NMR spectrum of **9** (500 MHz, C_6D_6, r.t.).

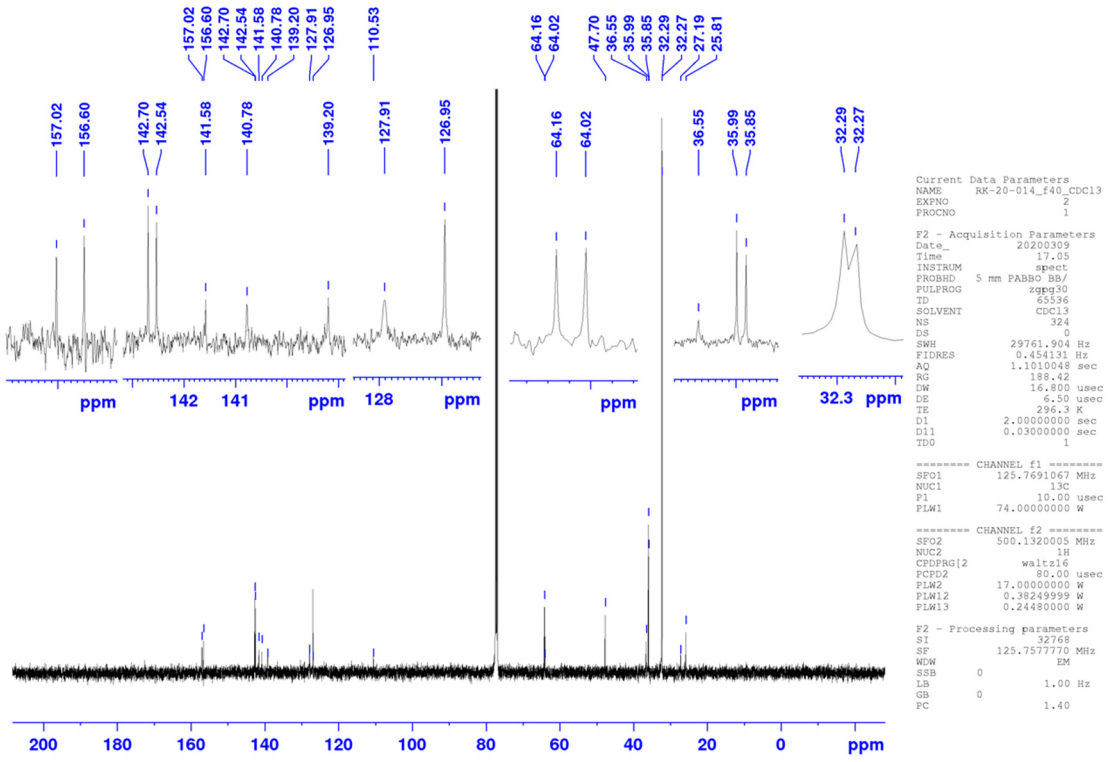

Figure S32. $^{13}C\{H\}$ NMR spectrum of **9** (125 MHz, $CDCl_3$, r.t.).

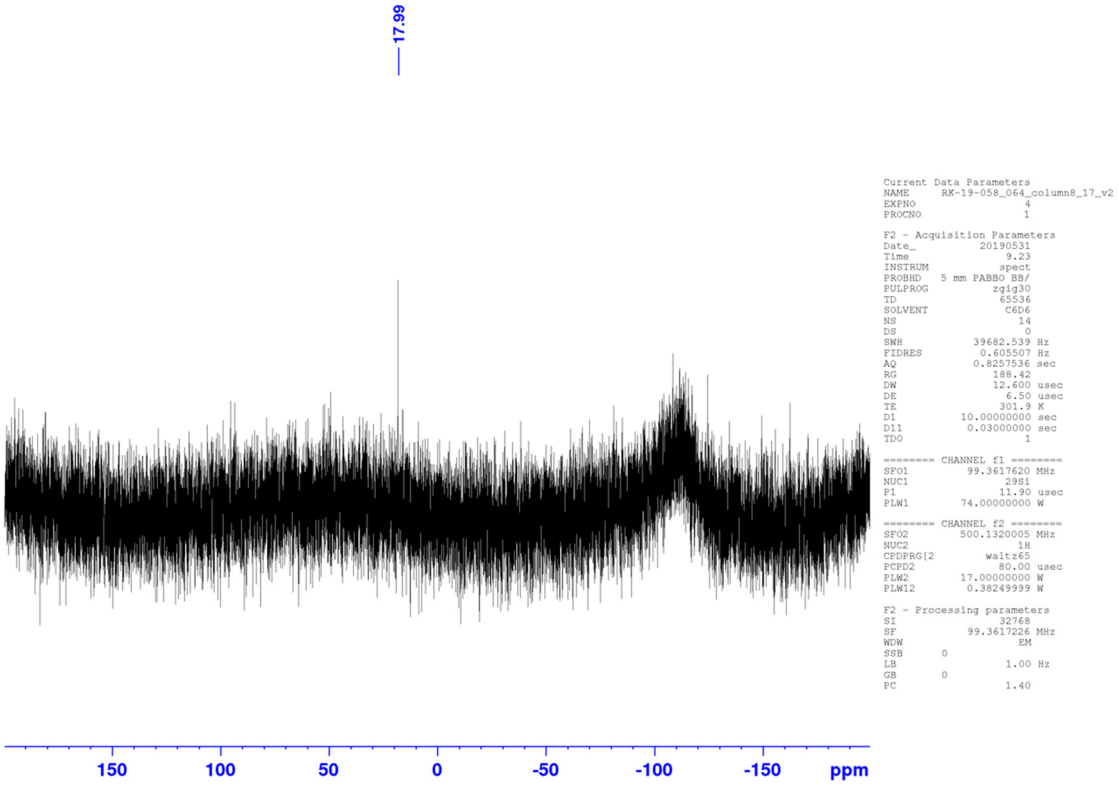

Figure S33. $^{29}Si\{H\}$ NMR spectrum of **9** (99 MHz, C_6D_6, r.t.).

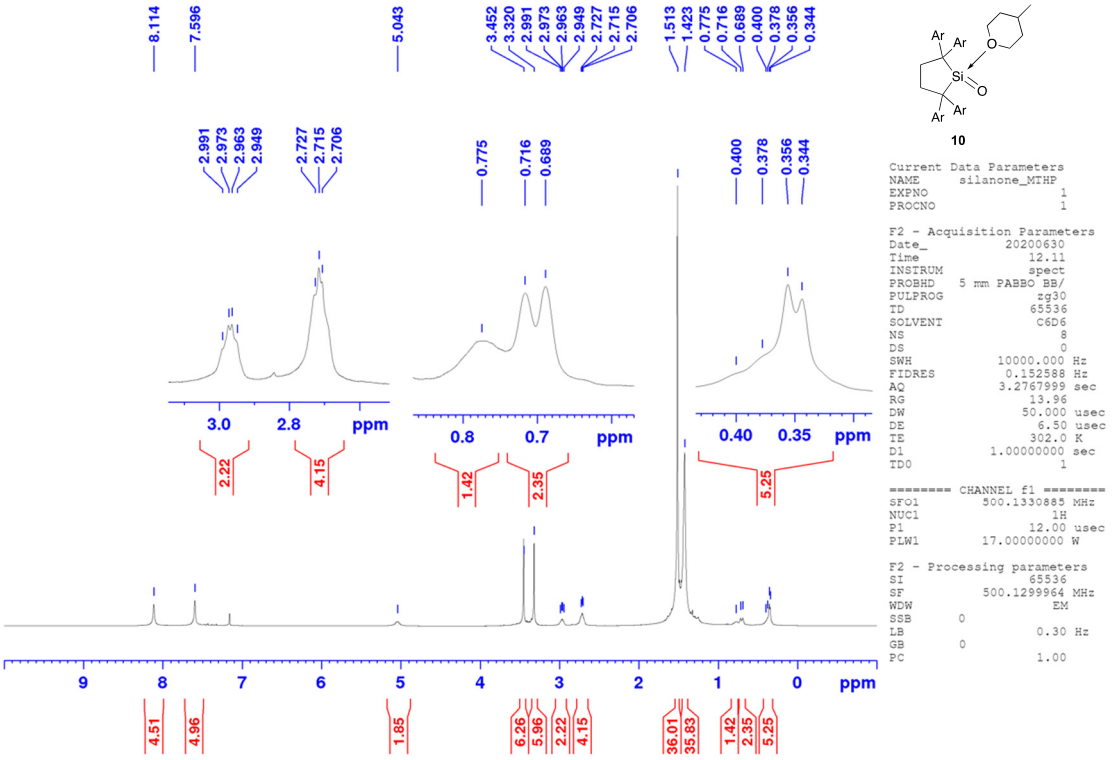

Figure S34. ^{1}H NMR spectrum of **10** (500 MHz, C_6D_6, r.t.).

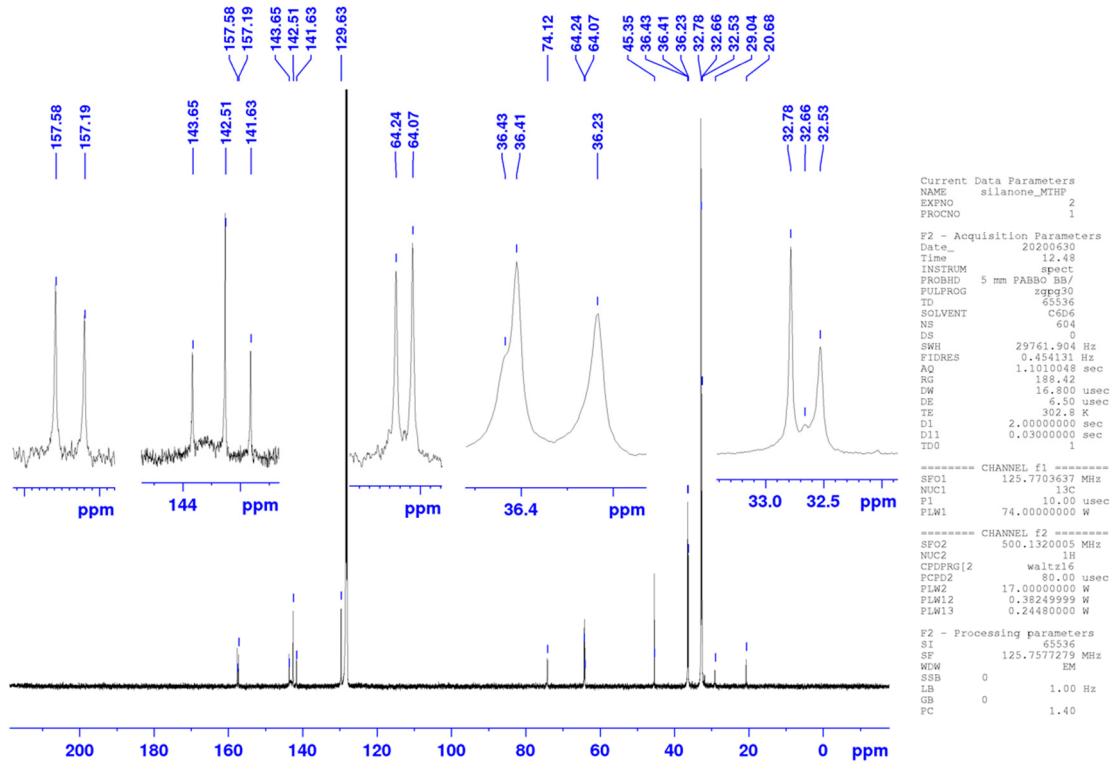

Figure S35. ^{13}C{H} NMR spectrum of **10** (125 MHz, C_6D_6, r.t.).

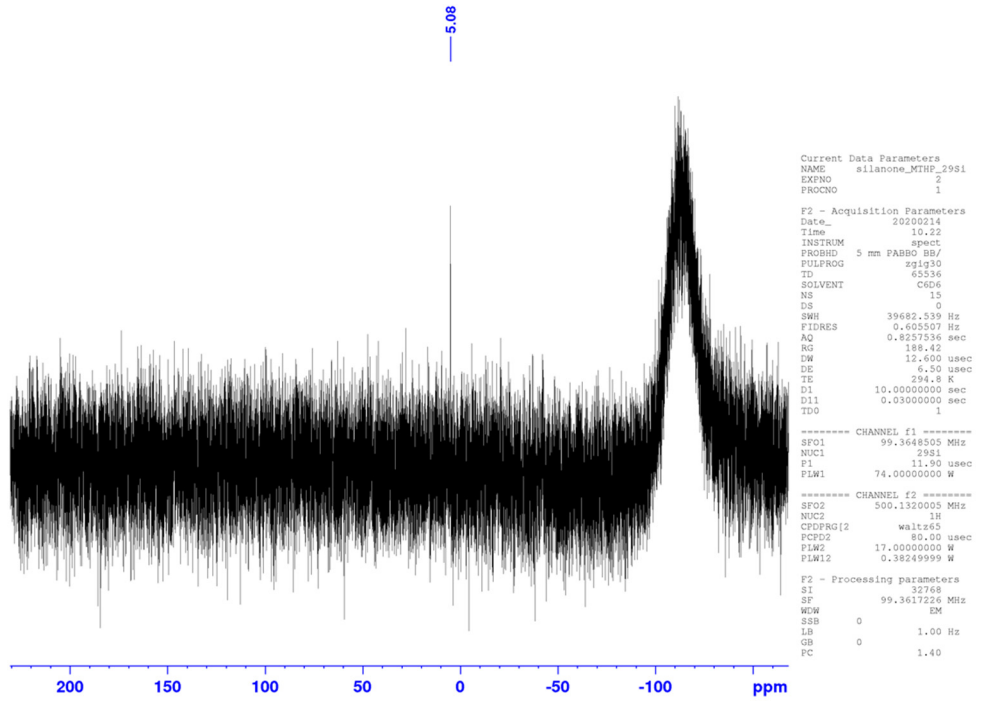

Figure S36. $^{29}Si\{H\}$ NMR spectrum of **10** (99 MHz, C_6D_6, r.t.).

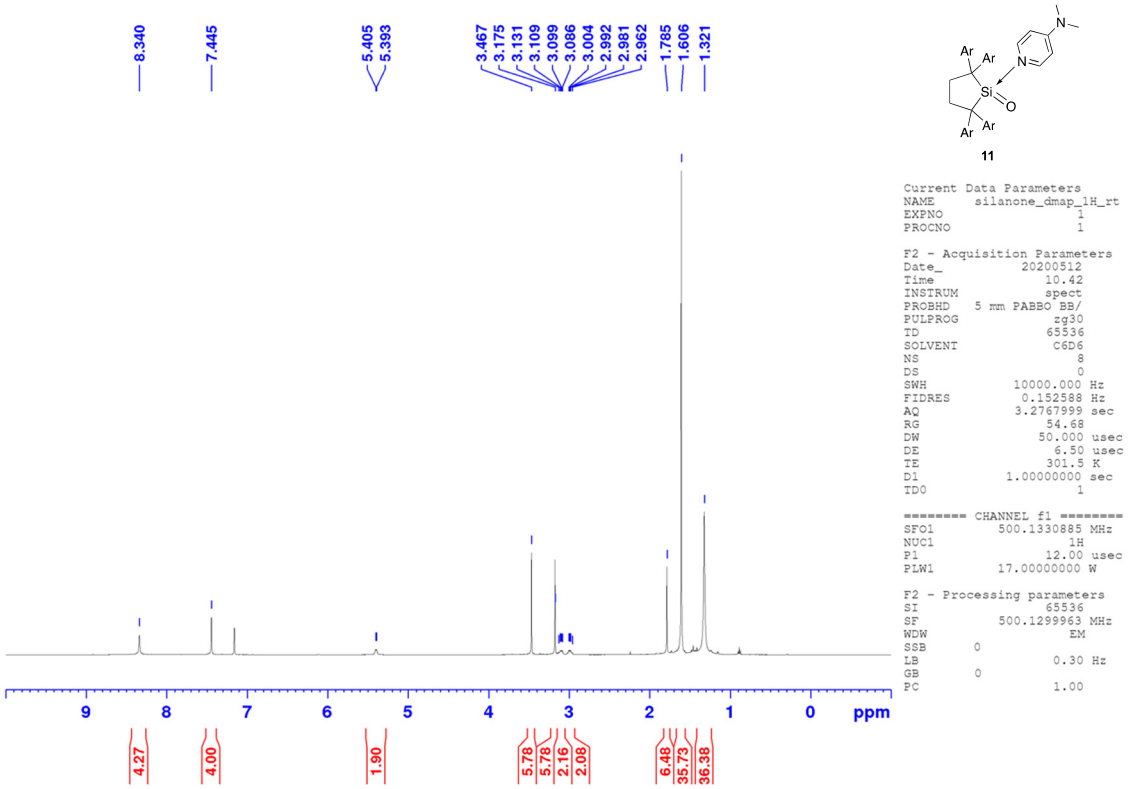

Figure S37. ^{1}H NMR spectrum of **11** (500 MHz, C_6D_6, r.t.).

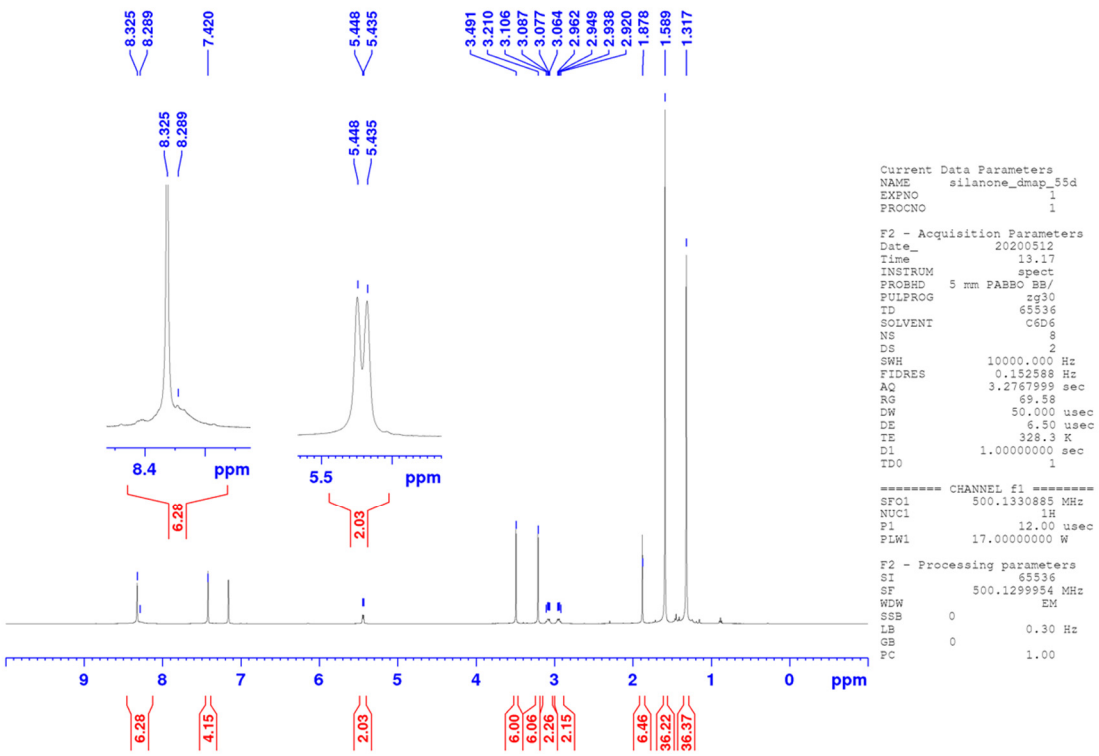

Figure S38. ^{1}H NMR spectrum of **11** (500 MHz, C_6D_6, 55 °C).

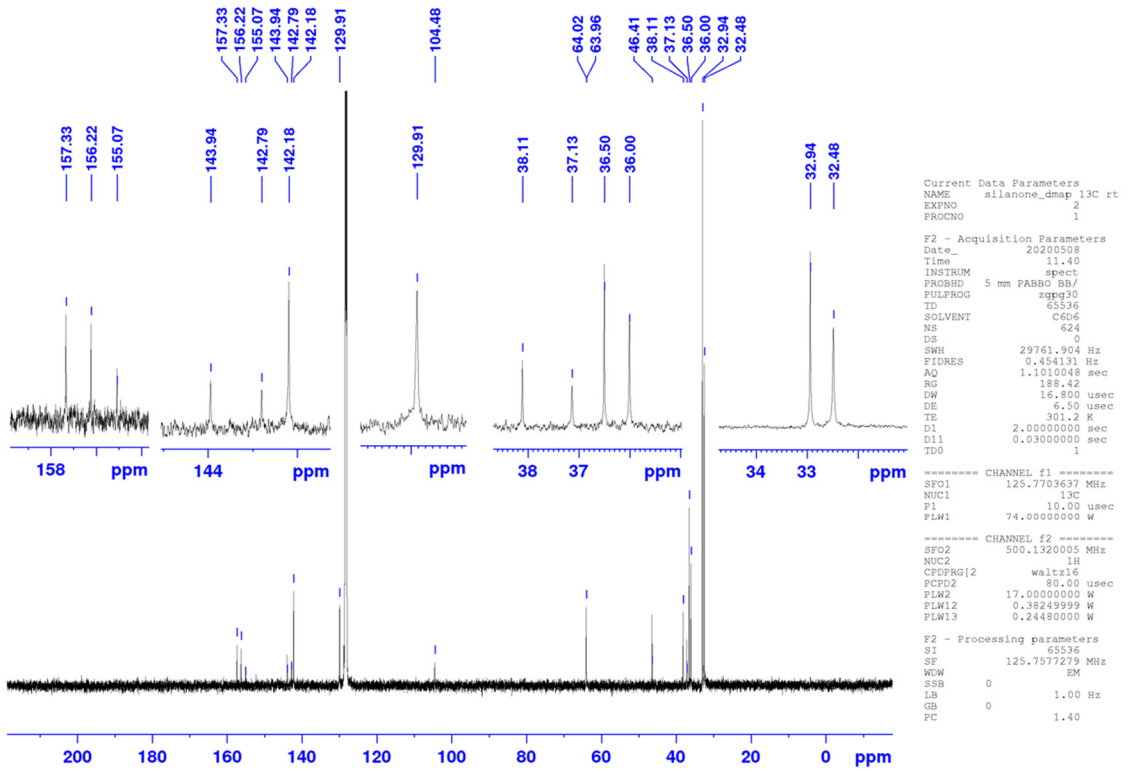

Figure S39. ^{13}C{H} NMR spectrum of **11** (125 MHz, C_6D_6, r.t.).

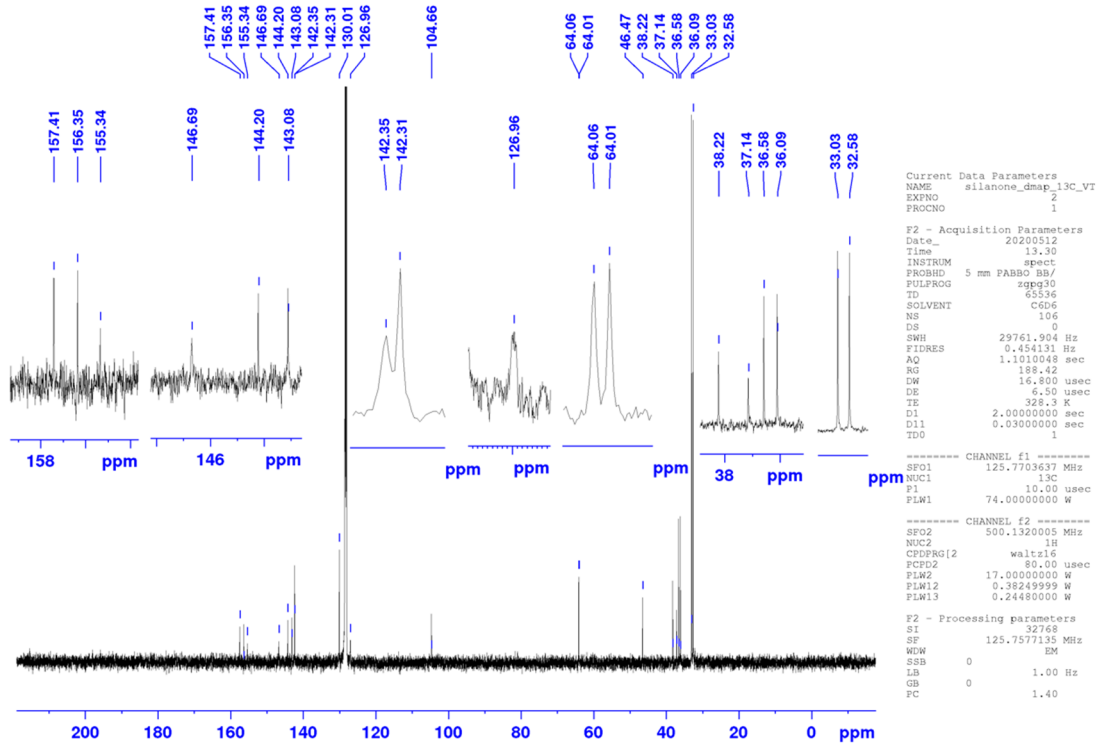

Figure S40. $^{13}C\{H\}$ NMR spectrum of **11** (125 MHz, C_6D_6, 55 °C).

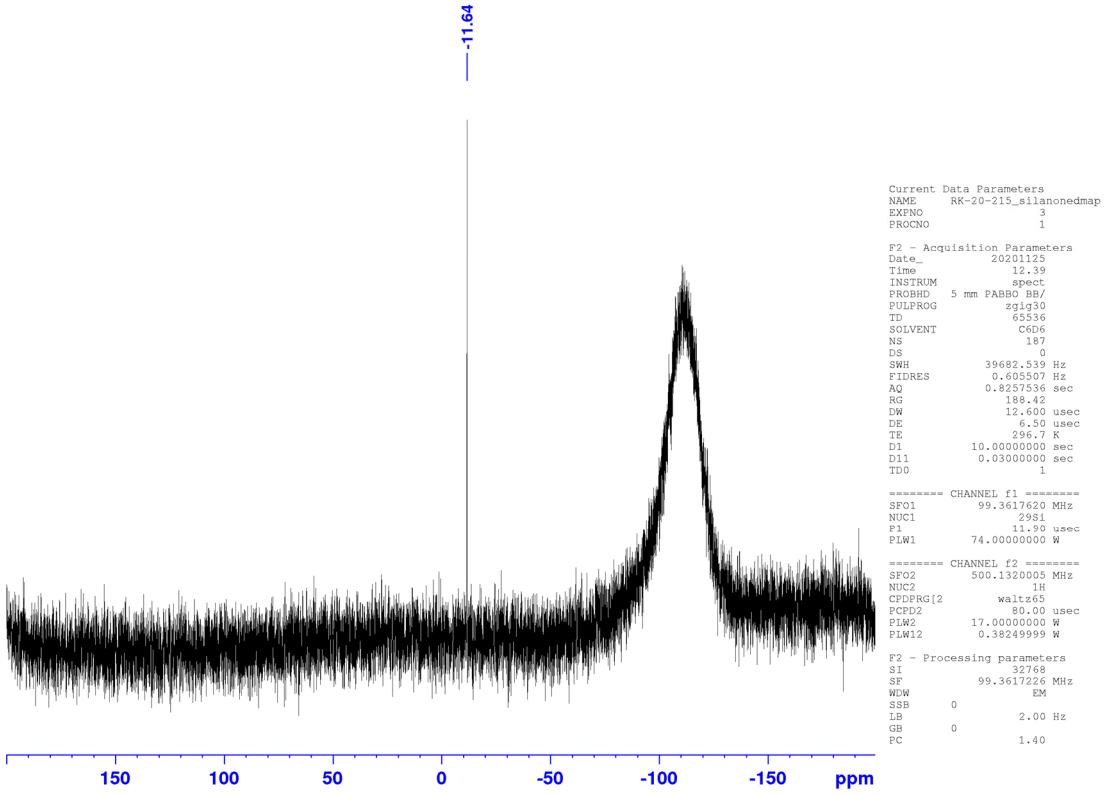

Figure S41. $^{29}Si\{H\}$ NMR spectrum of **11** (99 MHz, C_6D_6, r.t.).

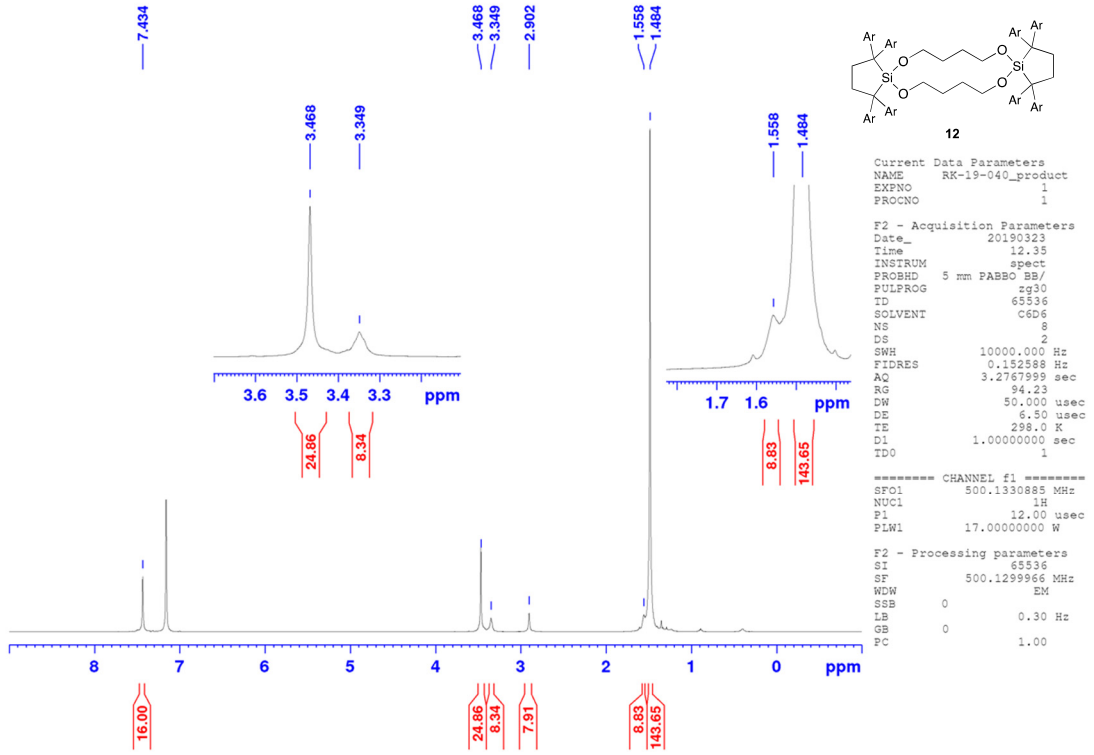

Figure S42. ^{1}H NMR spectrum of **12** (500 MHz, C_6D_6, r.t.).

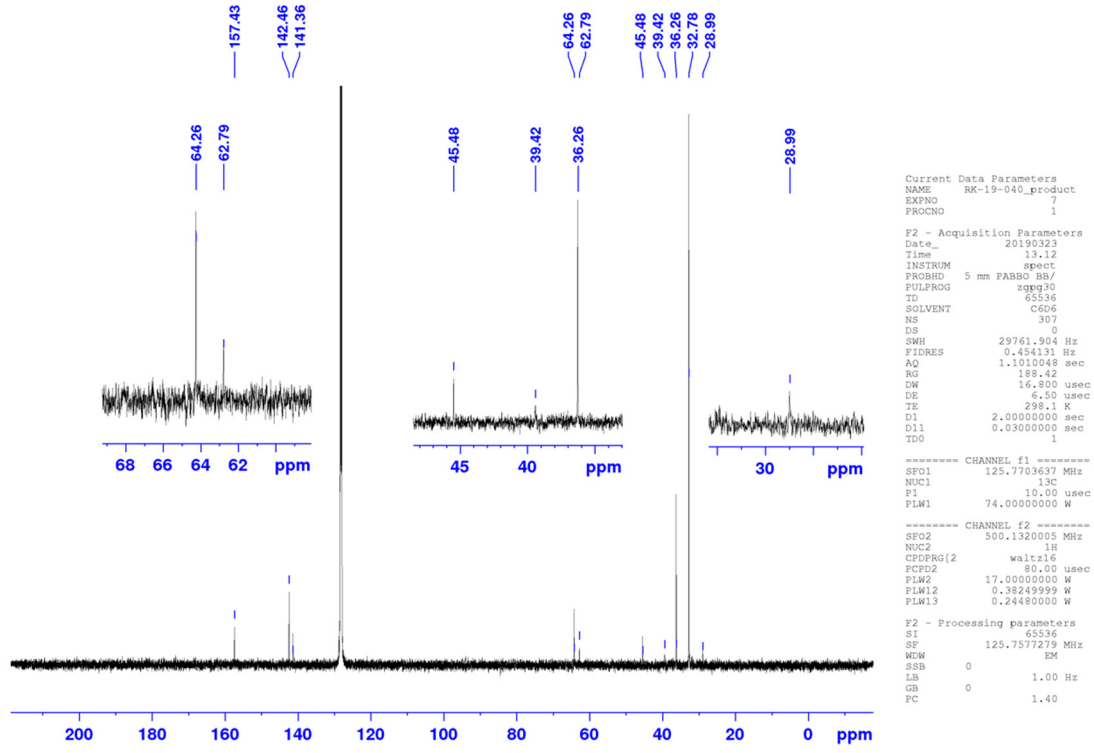

Figure S43. ^{13}C{H} NMR spectrum of **12** (125 MHz, C_6D_6, r.t.).

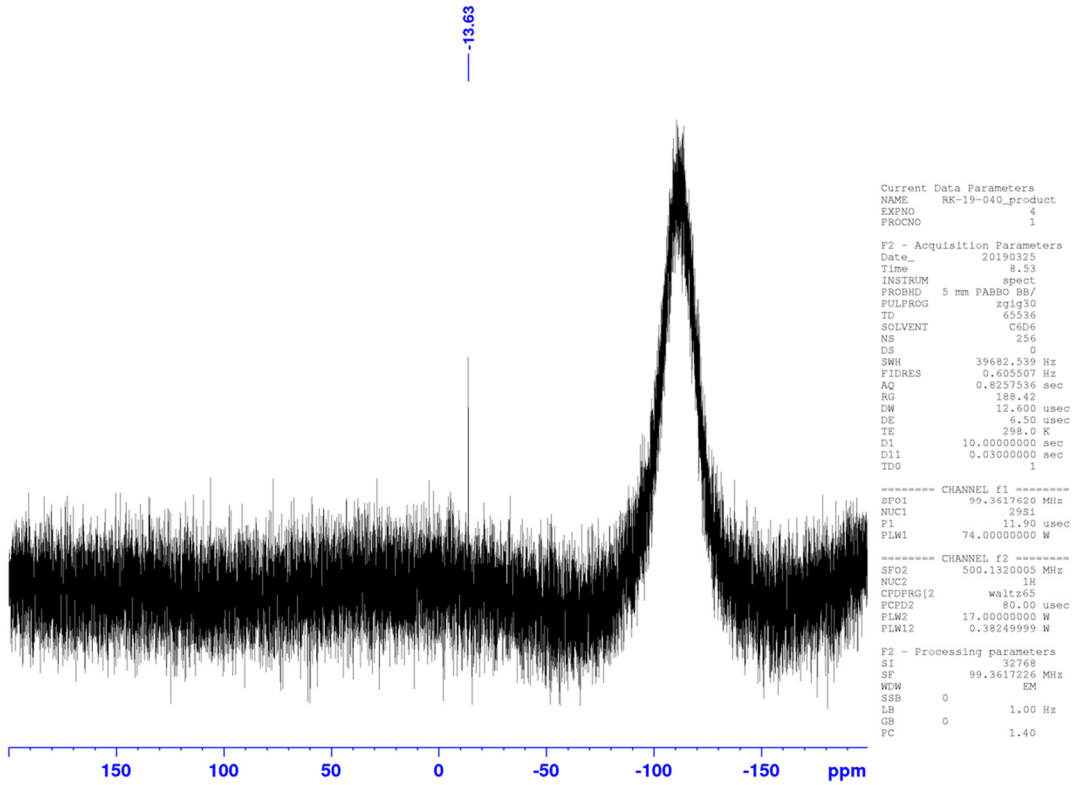

Figure S44. $^{29}Si\{H\}$ NMR spectrum of **12** (99 MHz, C_6D_6, r.t.).

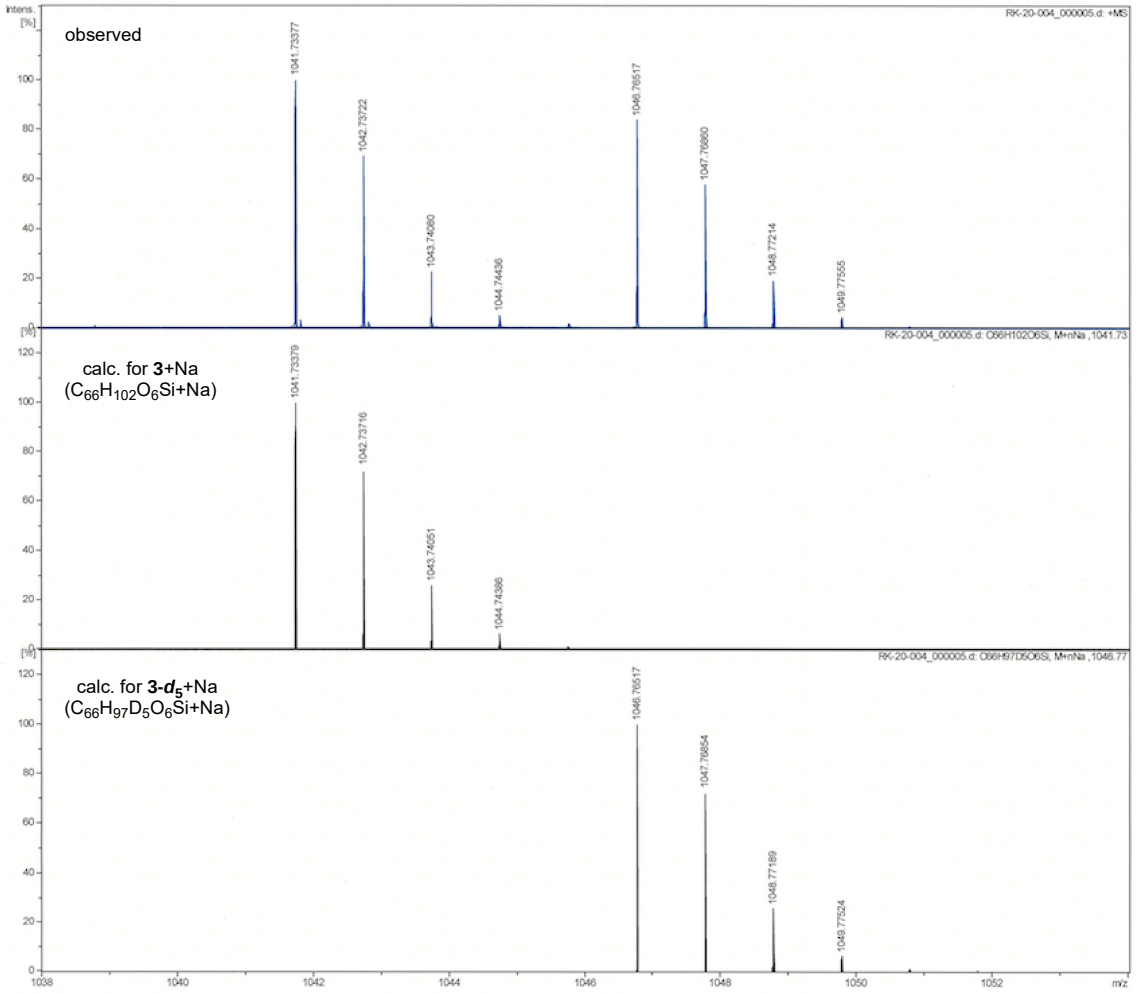

Figure S45. HRMS spectra of cross over experiment (ESI, ionization mode: positive)

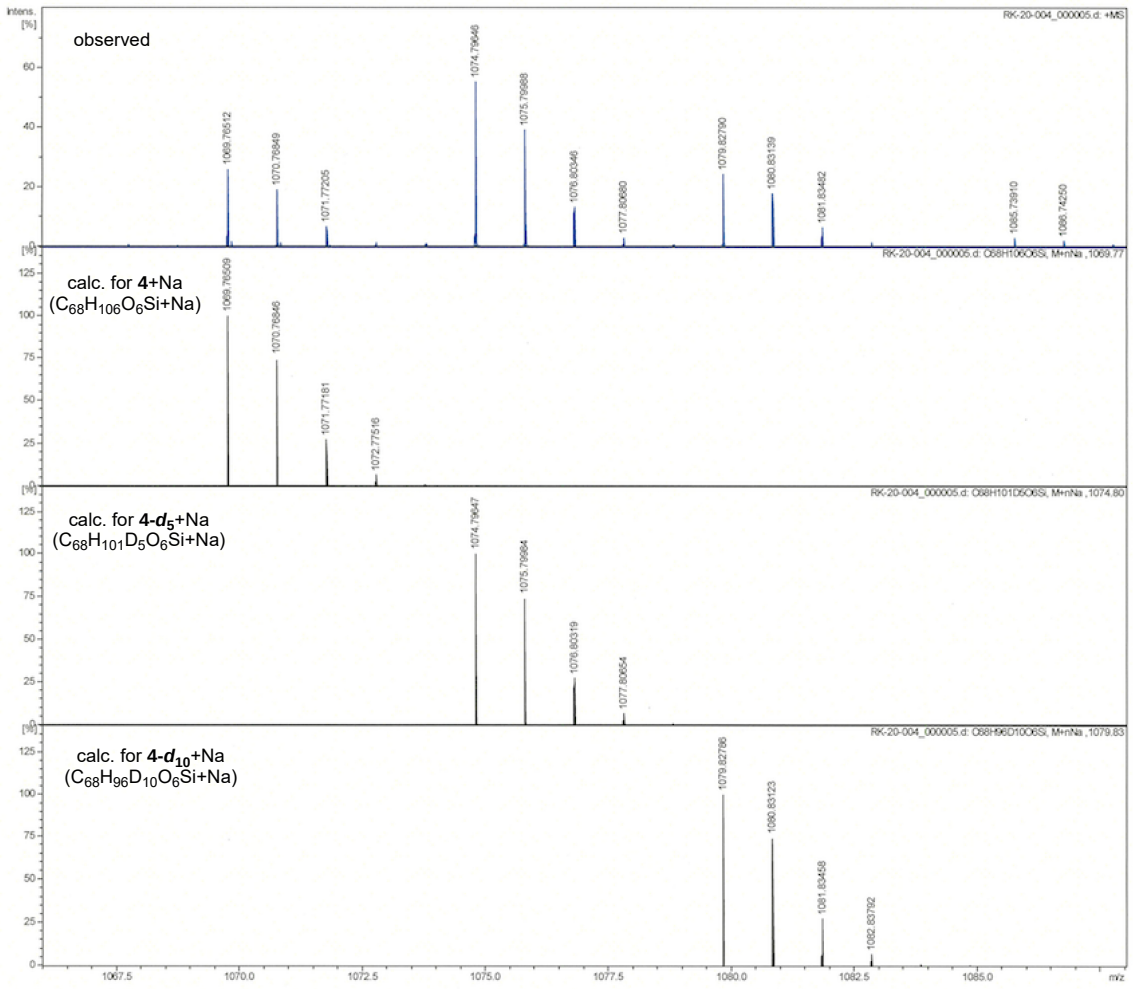

Figure S46. HRMS spectra of cross over experiment (ESI, ionization mode: positive)

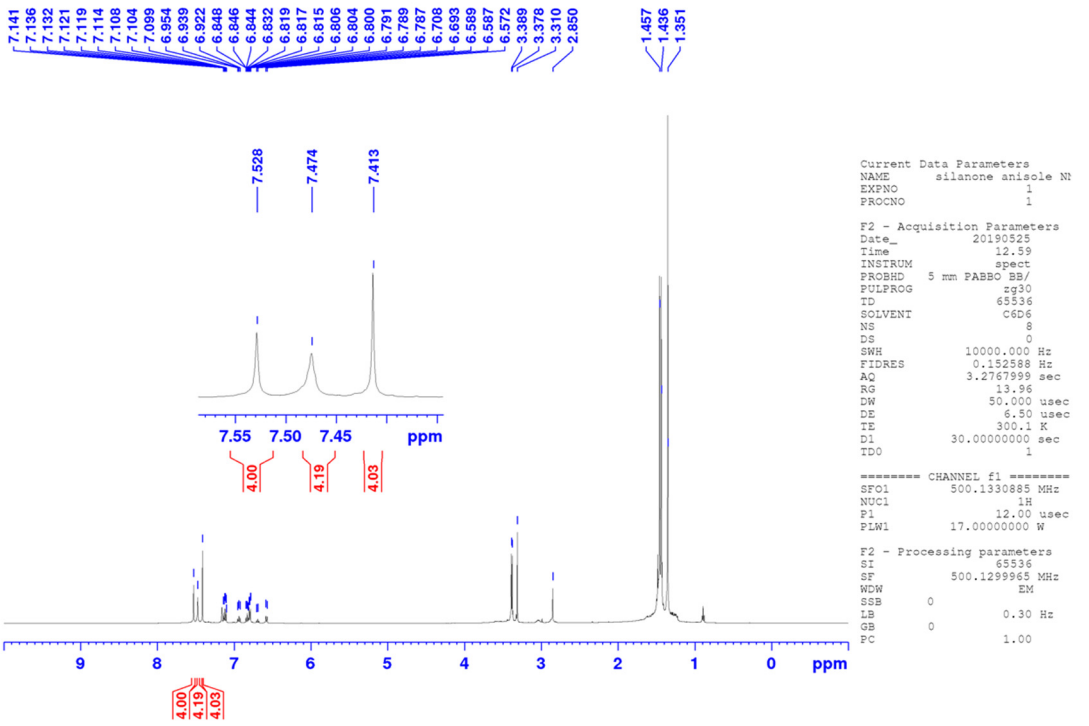

Figure S47. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with anisole containing **2** and 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

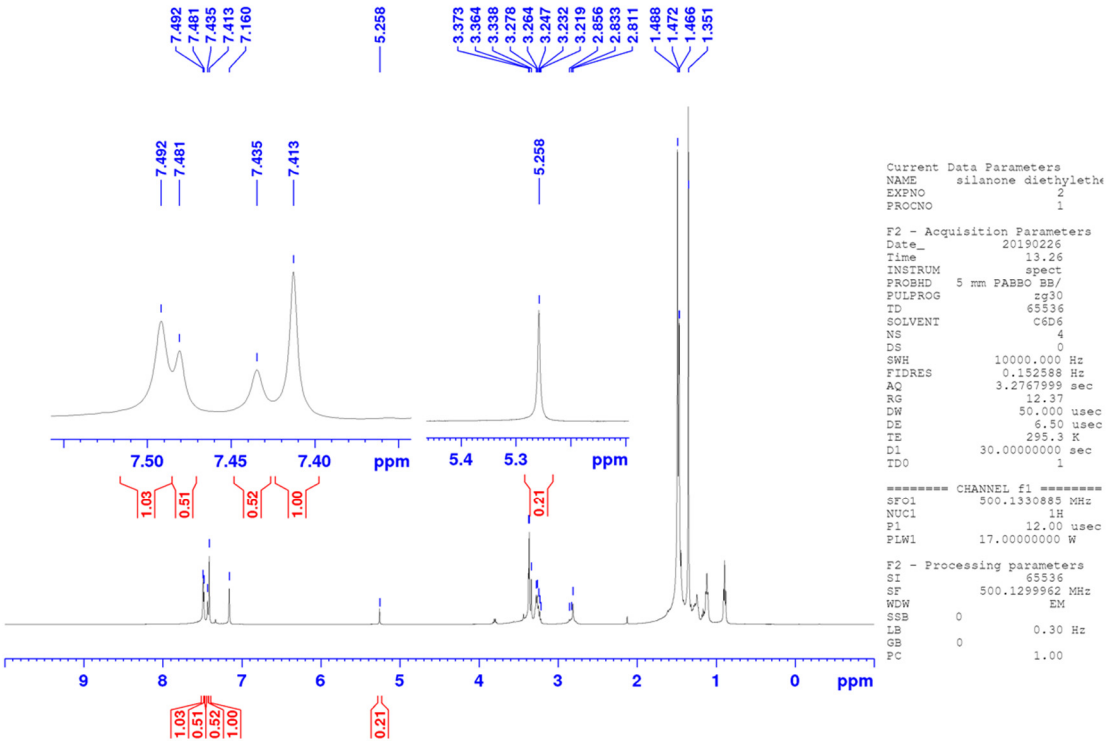

Figure S48. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with diethyl ether (0.1 M) containing **3**, **4**, ethylene and 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

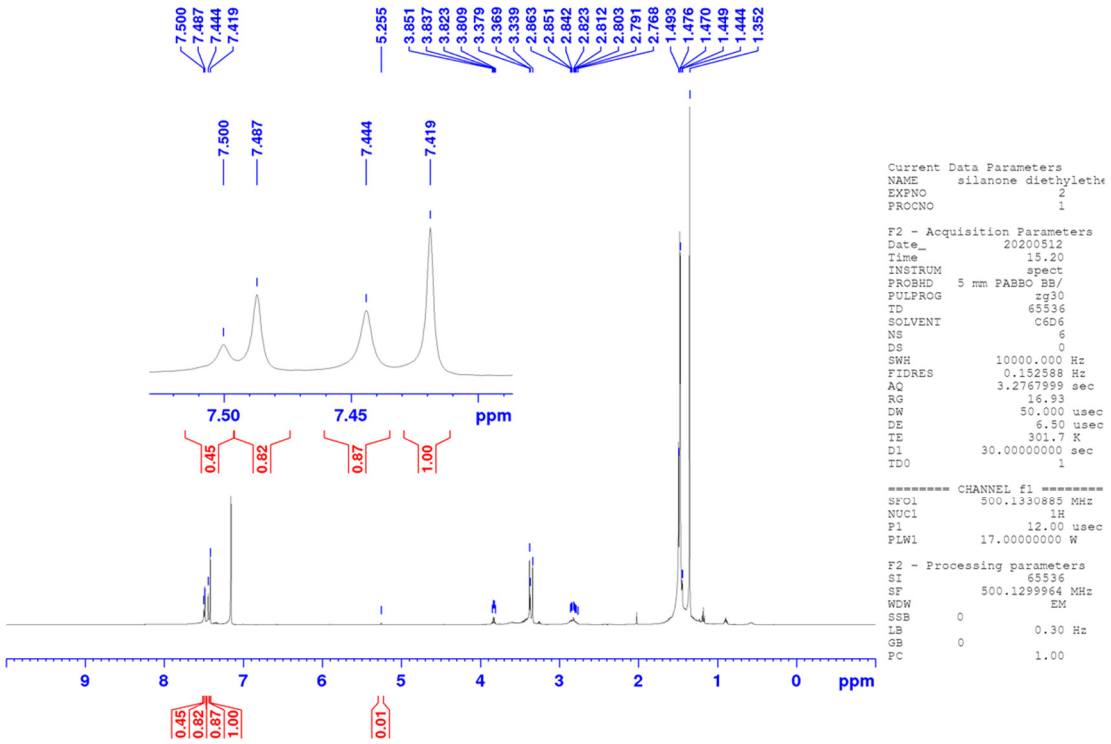

Figure S49. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with diethyl ether (0.01 M) containing **3**, **4**, ethylene and 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

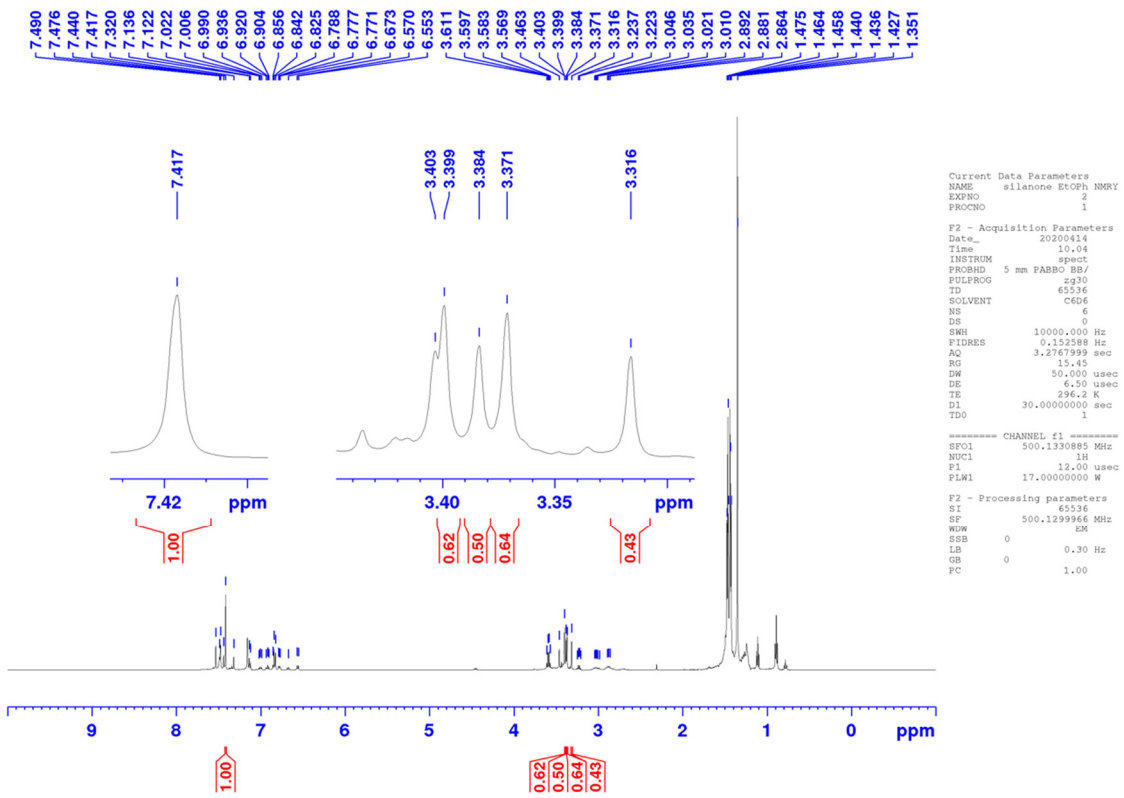

Figure S50. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with ethyl phenyl ether containing **5**, **6** and 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

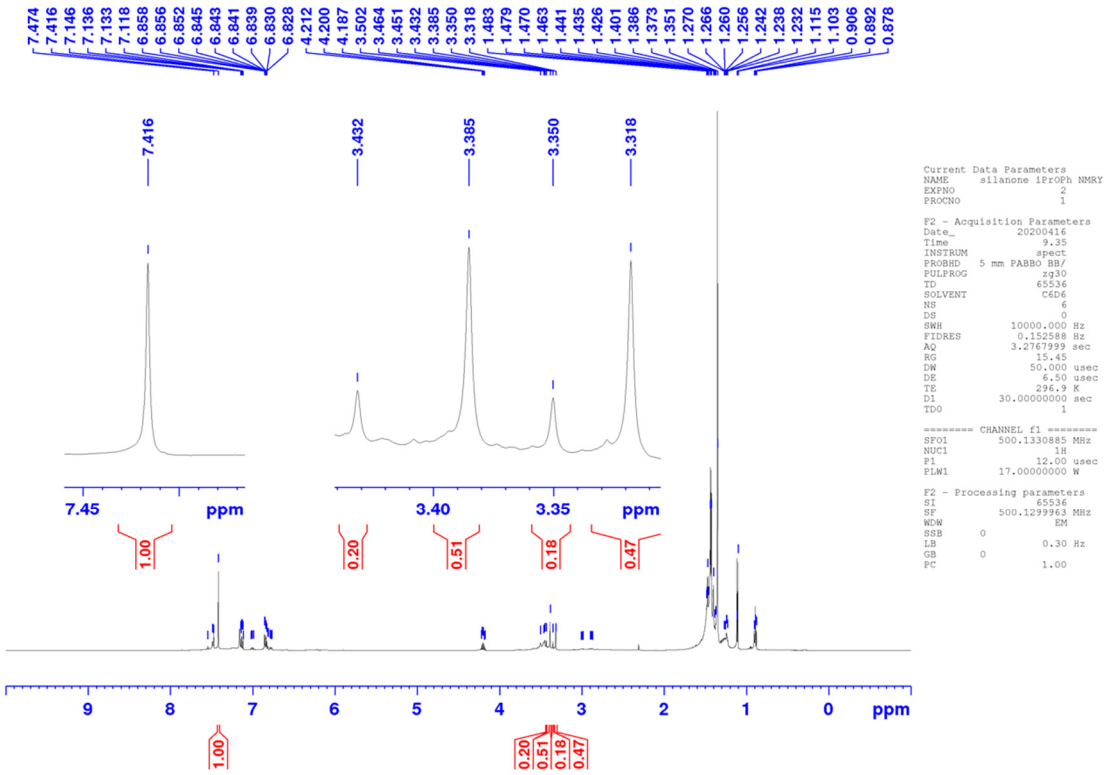

Figure S51. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with isopropyl phenyl ether containing **7**, **8** and 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

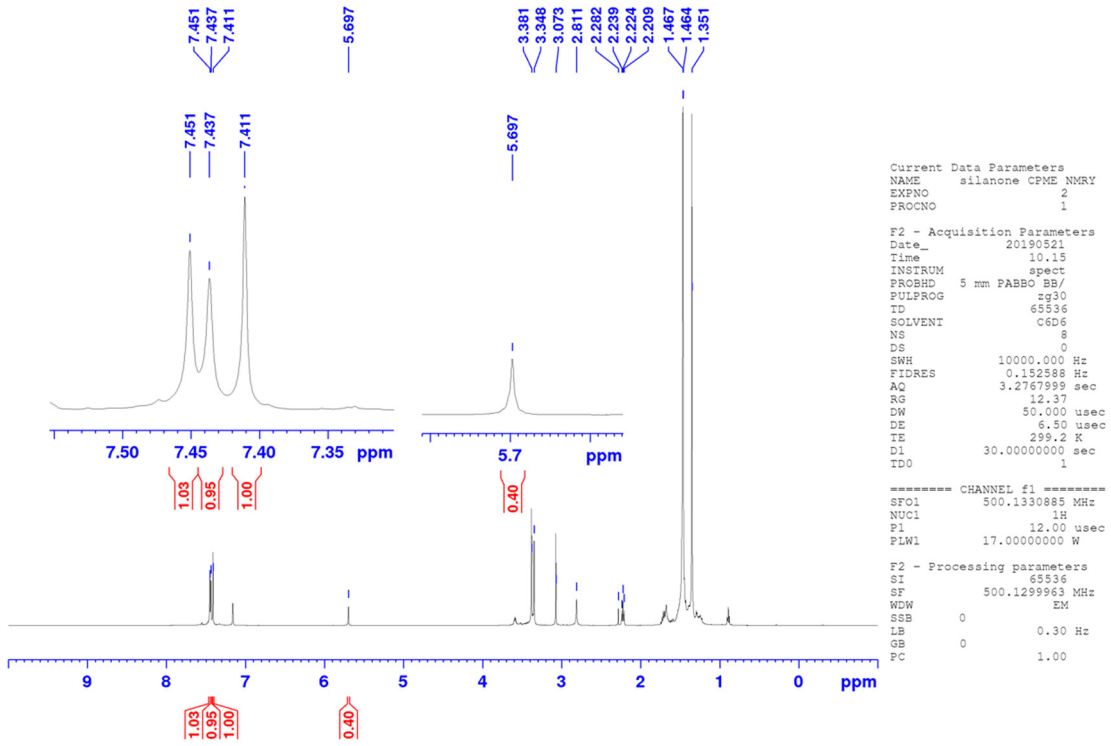

Figure S52. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with cyclopentyl methyl ether (CPME) containing **8**, cyclopentene and 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

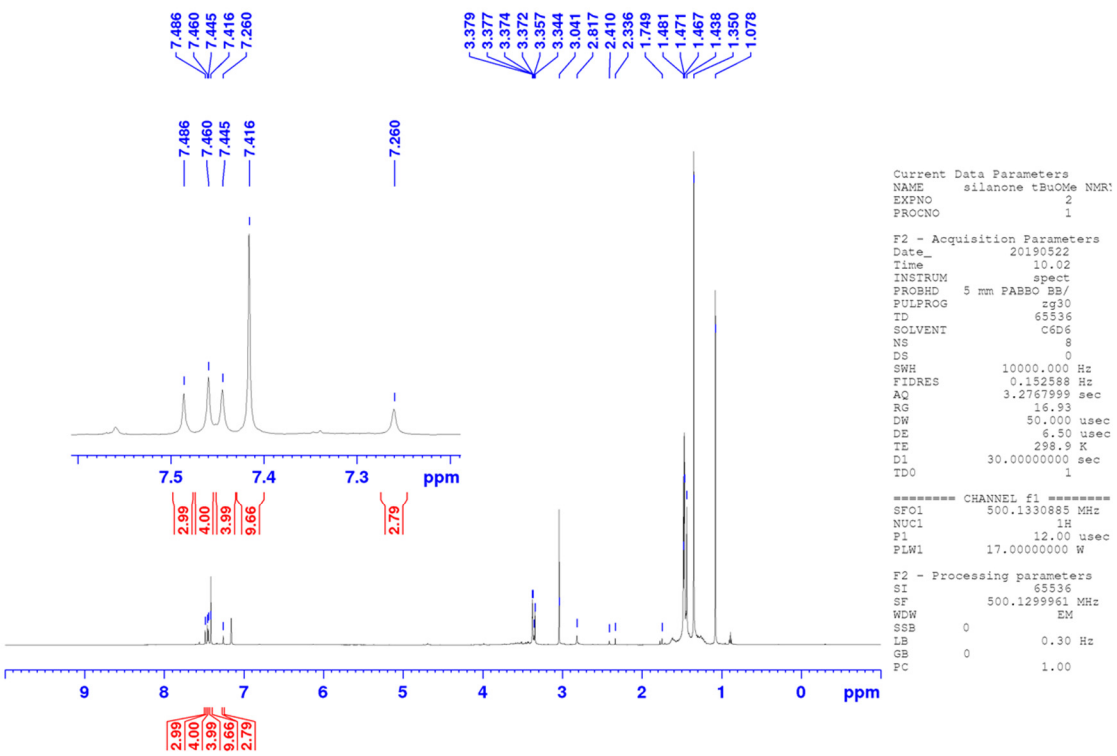

Figure S53. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with *t*butyl methyl ether containing **8**, **9** and 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

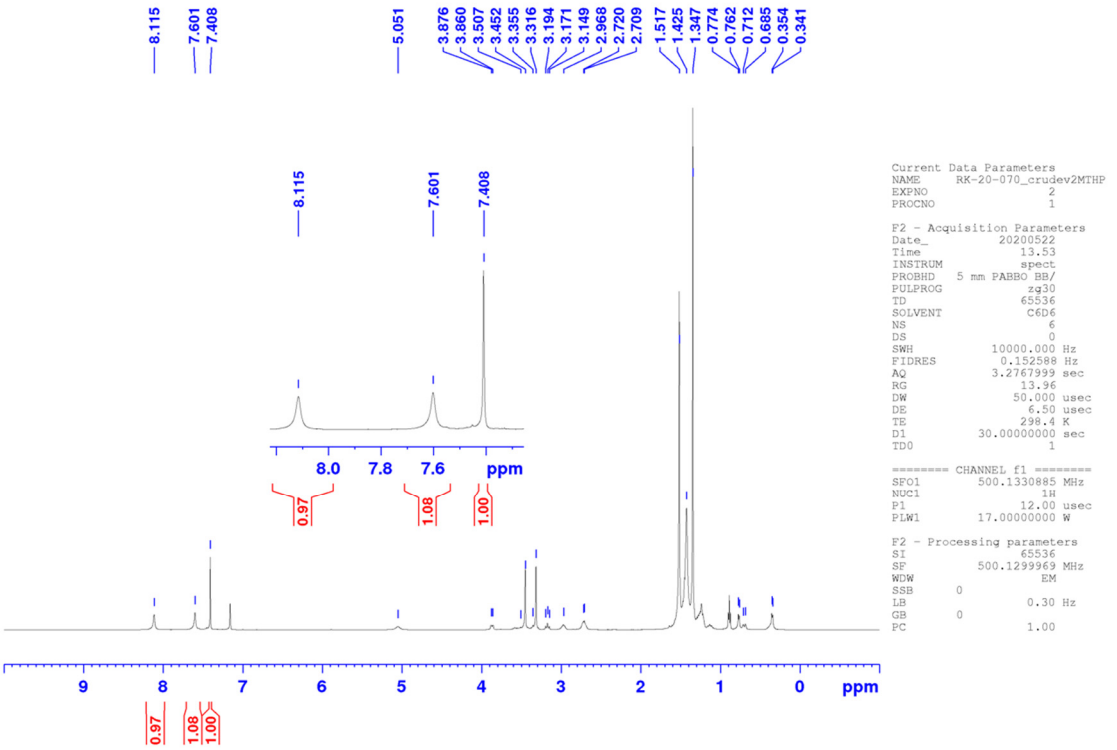

Figure S54. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **10** with diethyl ether containing 1,3,5-tri-*t*-butylbenzene after 2 h (500 MHz, C_6D_6, r.t.).

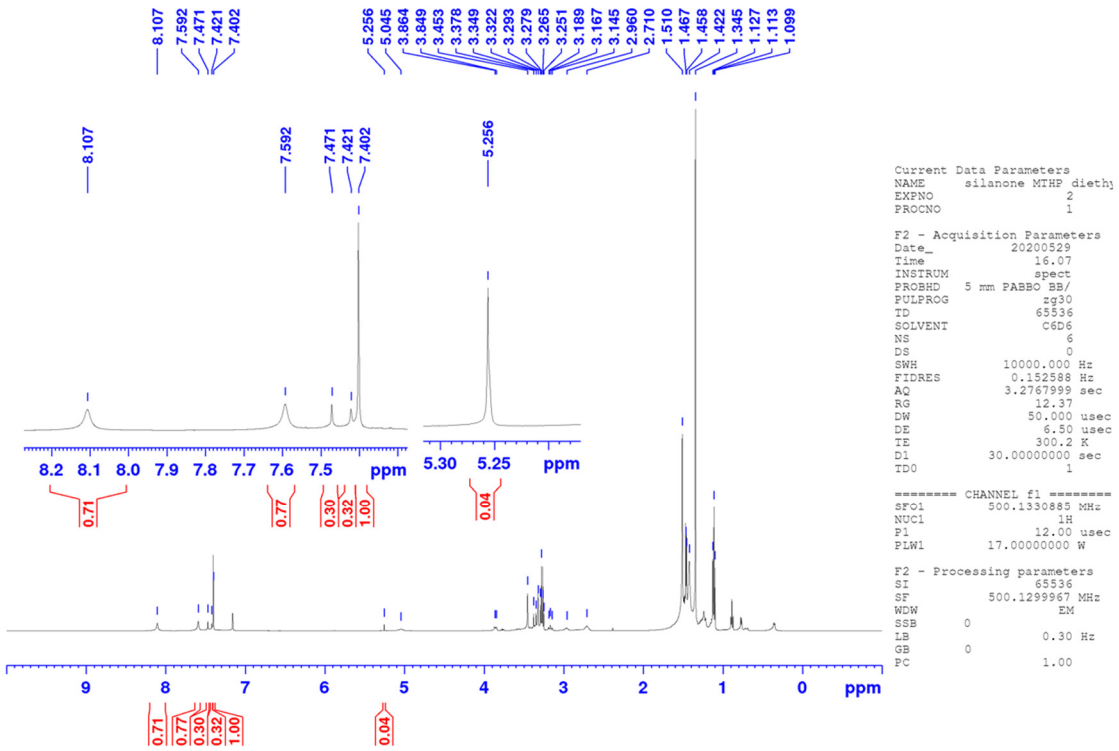

Figure S55. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **10** with diethyl ether containing 1,3,5-tri-*t*-butylbenzene after 1 week (500 MHz, C_6D_6, r.t.).

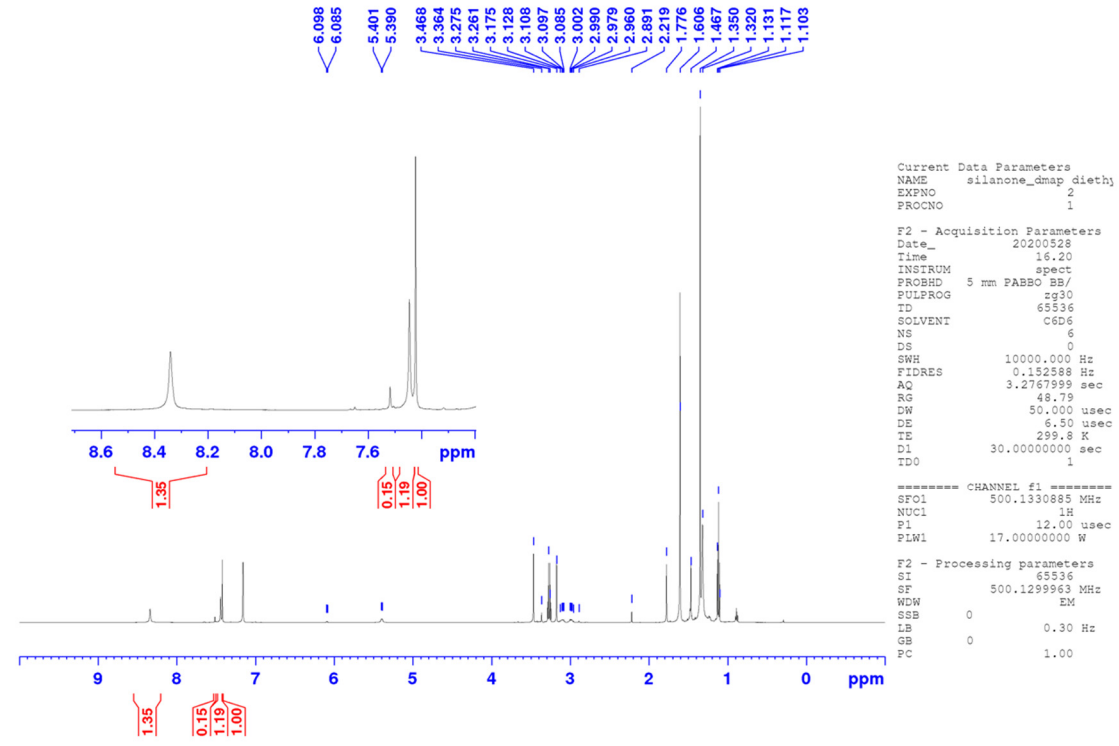

Figure S56. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **11** with diethyl ether containing 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

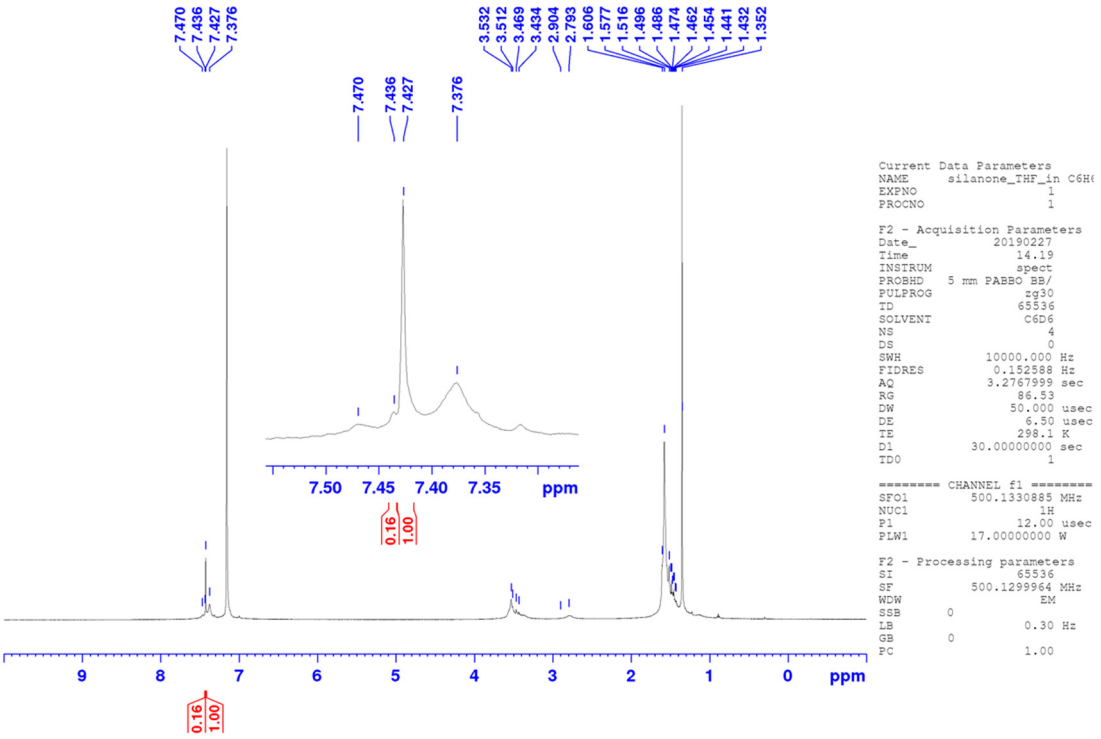

Figure S57. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with THF in C_6H_6 containing 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

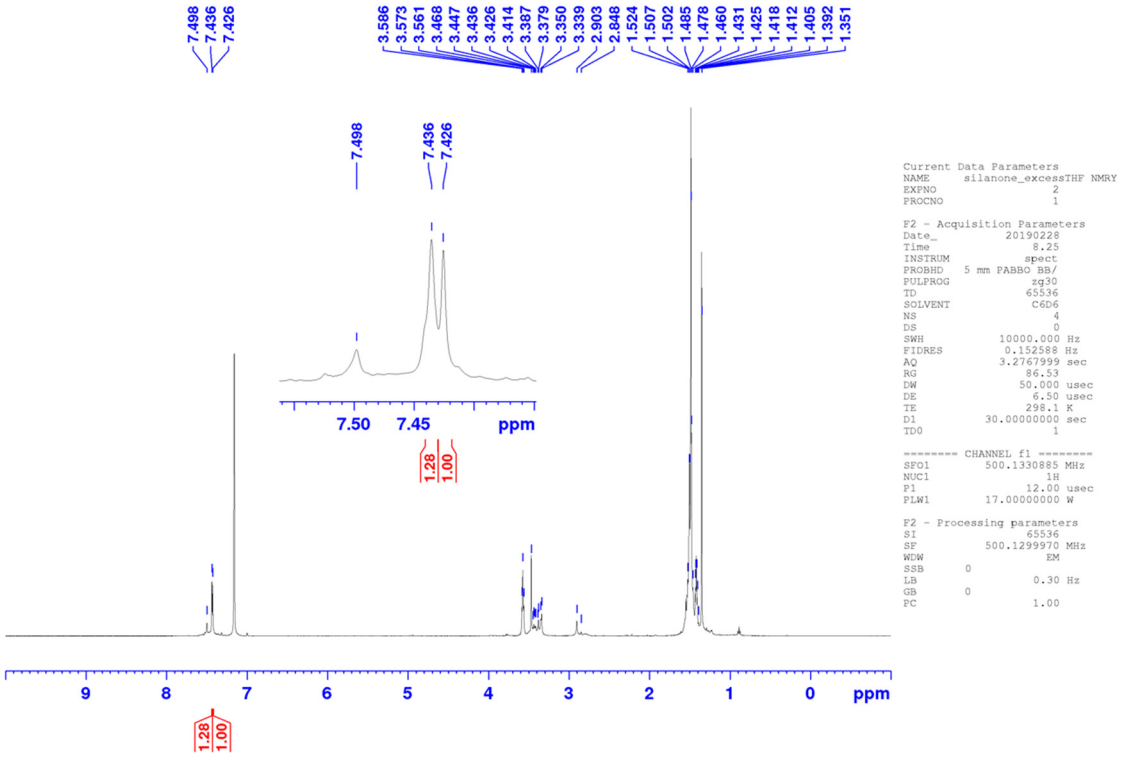

Figure S58. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with excess THF containing 1,3,5-tri-*t*-butylbenzene (500 MHz, C_6D_6, r.t.).

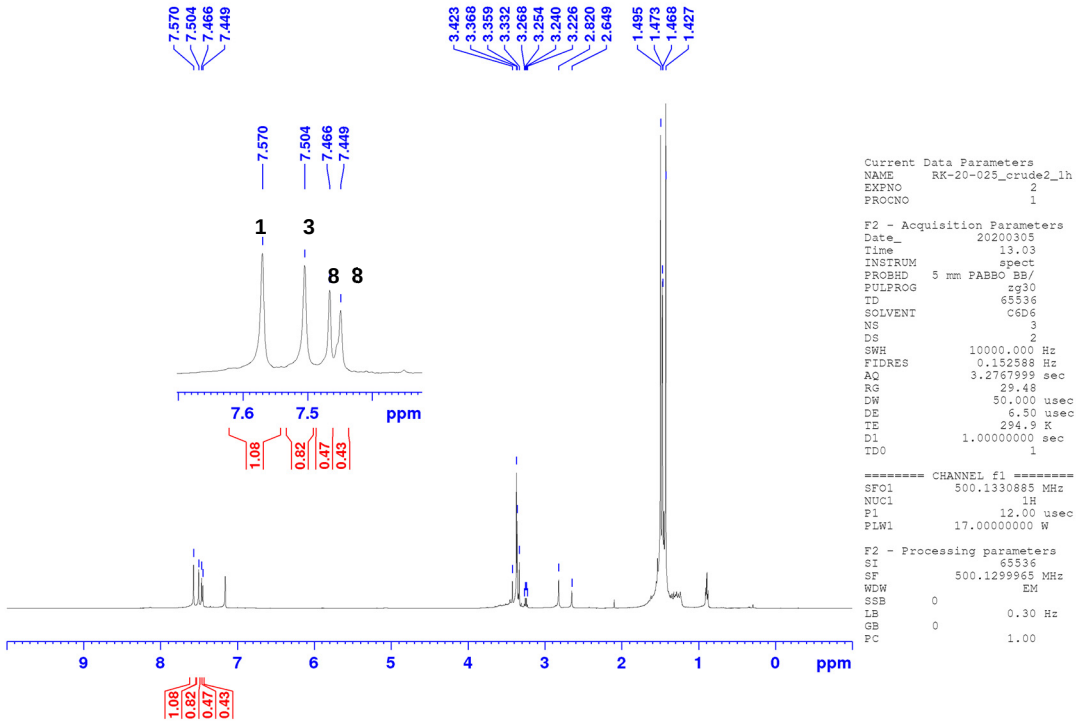

Figure S59. ^{1}H NMR spectrum of crude mixture obtained from the reaction of **1** with **3** and **8** (500 MHz, C_6D_6, r.t.).

4. Reference

S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2009.

S2 S. Maeda, Y. Harabuchi, Y. Osada, T. Taketsugu, K. Morokuma and K. Ohno, *GRRM 14*, see http://grrm.chem.tohoku.ac.jp/GRRM/; S. Maeda, K. Ohno and K. Morokuma, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3683–3701.

S3 C. Peng, H. B. Schlegel, *Israel J. Chem.*, 1993, **33**, 449–454.

S4 C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comp. Chem.,* 1996, **17**, 49–56.

S5 a) S. Maeda and K. Morokuma, *J. Chem. Phys.,* 2010, **132**, 241102; b) S. Maeda and K. Morokuma, *J. Chem. Theory Comput.,* 2011, **7**, 2335–2345.