SUPPORTING INFORMATION FOR

Unprecedented Organocatalytic Reduction of Lignin Model Compounds to Phenols and Primary Alcohols Using Hydrosilanes

*Elias Feghali, Thibault Cantat**

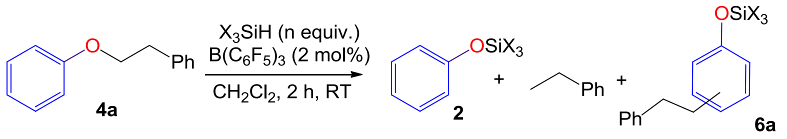
CEA, IRAMIS, SIS2M, F-91191 Gif-sur-Yvette France.

CNRS, UMR SIS2M n° 3299 CEA – CNRS, F-91191 Gif-sur-Yvette France.

E-mail: thibault.cantat@cea.fr

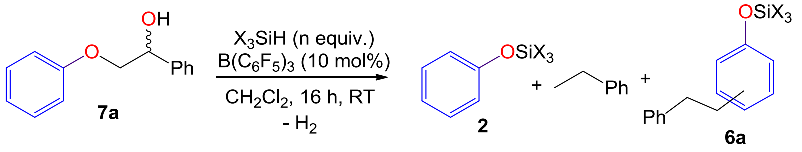
Table of Contents

Supplementary equations



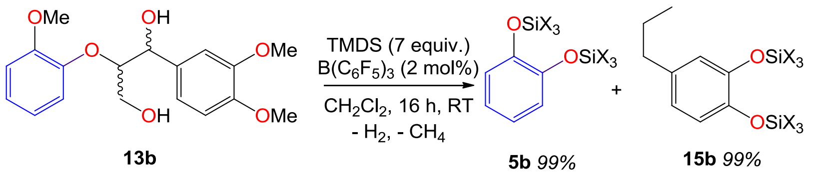
(S1)

	2		6a
X_3SiH=PMHS (1 equiv.)	*94%*	*94%*	*6%*
X_3SiH=TMDS (0.5 equiv.)	*96%*	*96%*	*4%*



(S2)

	2		6a
X_3SiH=PMHS (4 equiv.)	*84%*	*84%*	*16%*
X_3SiH=TMDS (2 equiv.)	*92%*	*92%*	*8%*



(S3)

$SiX_3=SiMe_2OSiMe_2H$

Experimental details

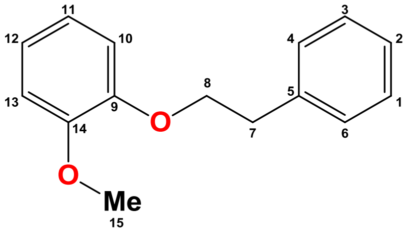
General considerations

All reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 60 ºC before use. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to solvent impurities. Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Dichloromethane (and d_2-CH_2Cl_2) was dried over CaH_2 and distilled before use. The synthesis of compounds **7a**,**7b** was perused according to the method of Ellman *et al.*[1] Compound **4a** was synthesized according to the procedure described by Lercher *et al.*[2] Compound **13b** was synthesized according to the method of Bolm *et al.*[3] Et_3SiD was obtained using procedures described in references 4 and 5.

Synthesis of β-O-4 models

Synthesis of 1-methoxy-2-phenethoxybenzene (4b)

A mixture of NaOH (2.5 g, 53.7 mmol) and guaiacol (6.7 g, 53.7 mmol) in toluene (11 ml) was heated at 100 °C for 30 min to generate the phenolate anion. 1-bromo-phenylethane (5 g, 27 mmol) was then slowly added (over 5 min) and the resulting mixture was stirred at 100 °C overnight. The reaction mixture was cooled down to RT and filtrated over a coarse porosity frit. The solution was then washed with (2 x 10 ml) NaOH solution (3 M) and distilled water (2 x 10 ml), and dried over $MgSO_4$. Finally, the product was purified by distillation under reduced pressure to yield **4b** as a yellow oil. Without further optimization, this procedure yielded **4b** in a low 10% yield.



^{1}**H NMR** ($CDCl_3$, 298 K) *δ* (ppm) = *δ* (ppm) = 7.60-7.08 (m, 5H, 1-2-3-4-6), 7.04-6.69 (m, 4H, 10-11-12-13), 4.22 (t, *J* = 7.7 Hz, 2H, 8), 3.88 (s, 3H, 15), 3.18 (t, *J* = 7.7 Hz, 2H, 7).

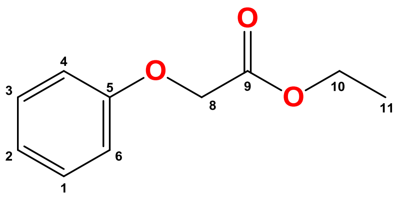
^{13}**C NMR** ($CDCl_3$, 298 K) *δ* (ppm) = 149.5 (9), 148.3 (14), 138.1 (5), 129.2 (1-3), 128.6 (4-6), 126.6 (2), 121.3 (11), 121.0 (12), 113.3 (10), 112.0 (13), 69.8 (8), 56.1 (15), 35.9 (7).

Synthesis of 2-phenoxy-1-phenylpropane-1,3-diol (13a)

Compound **13a** was synthetized using a similar procedure described by Bolm *et al.*[3] for the synthesis of compound **13b**.

Synthesis of ethyl-2-phenoxyacetate

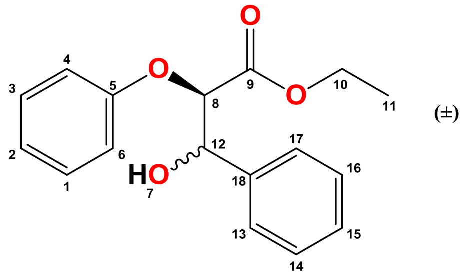
A mixture of K_2CO_3 (8.29 g, 0.060 mol, 1.2 equiv.), 2-methoxyphenol (4.70 g, 0.050 mol, 1 equiv.) and acetone (250 mL) was heated to reflux for 30 minutes. Ethylbromoacetate (8.35 g, 0.050 mol, 1 equiv.) was then added dropwise with a syringe, over 5 min, and the reaction mixture was kept under reflux for 16 h. After cooling the solution down to RT, the crude mixture was filtered over celite and the filtrate was evaporated under reduced pressure. The resulting yellow oil was then dissolved in diethyl ether (100 mL) and washed with an aqueous NaOH solution (10% w/w, 3 x 25 mL), water (25 mL) and brine (25 mL). After drying over $MgSO_4$, the organic phase was filtered and evaporated under reduced pressure, to yield ethyl 2-phenoxyacetate (6.0 g; 33.3 mmol; 67 %) as slightly yellow oil.



^{1}**H NMR** (CDCl$_3$, 298 K) δ (ppm) = 1.30 (t, J = 7.1 Hz, 3H, 11), 4.27 (q, J = 7.1 Hz, 2H, 10), 4.62 (s, 2H, 8), 6.90 (d, J = 7.9 Hz, 2H, 4-6), 6.99 (t, J = 7.0 Hz, 1H, 2), 7.30 (t, J = 7.7 Hz, 2H, 1-3).
^{13}**C NMR** (CDCl$_3$, 298 K) δ (ppm) =169.08 (9), 157.86 (5), 129.64 (1-3), 121.80 (2), 114.71 (4-6), 65.45 (8), 61.45 (10), 14.25 (11).

Synthesis of ethyl-3-hydroxy-2-phenoxy-3-phenylpropanoate

A solution of *n*-BuLi in hexanes (7.3 mL, 1.6 M, 11.5 mmol) was added dropwise over 20 min to a solution of diisopropylamine (1,11 g, 11 mmol) in THF (25 mL), at 0 °C. After 20 min at 0 °C the solution turned pale yellow. The resulting mixture was cooled down to –78 °C, and a solution of ethyl-2-phenoxyacetate (1.80 g, 10 mmol) in THF (30 mL) was then added over a period of 1 h. Benzaldehyde (1.02 g, 95.7 mmol) in THF (30 mL) was added over 30 min at –78 °C and the solution was stirred for 90 min at –78 °C, prior to the addition of distilled water (60 mL). The aqueous phase was then extracted with ethyl acetate (3 x 80 mL). The combined organic phases were washed with a 1 N aqueous HCl solution (80 mL), water (80 mL) and brine (80 mL), then dried over MgSO$_4$. The yellowish crude solid (2.4 g), obtained after removal of the volatiles under reduced pressure, was purified by column chromatography, with cyclohexane:ethyl acetate (7:3) as an eluent. After solvent evaporation ethyl-2-benzyl-3-hydroxy-3-phenylpropanoate was obtained as a yellowish oil (2.36 g, 83 %, erythro:threo 65:35). The isomers were identified by comparison of the $^{3}J_{8\text{-}12}$ coupling constants obtained for the analogue compound ethyl-3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate, described in reference 6.



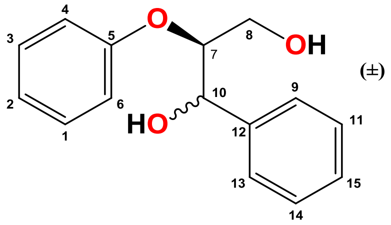
^{1}**H NMR** (CDCl$_3$, 298 K) Erythro isomer δ (ppm) = 7.54 - 7.13 (m, 7H, 1-3-13-14-15-16-17), 7.06 - 6.78 (m, 3H, 2-4-6), 5.21 (d, J = 5.3 Hz, 1H, 12), 4.76 (d, *J* = 5.3 Hz, 1H, 8), 4.11 (q, *J* = 7.2 Hz, 2H, 10), 2.93 (br.s, 1H, 7), 1.10 (t, *J* = 7.2 Hz, 3H, 11).
^{13}**C NMR** (CDCl$_3$, 298 K) Erythro isomer δ (ppm) = 169.6, 157.5, 139.1, 129.7, 128.7, 128.5, 126.8, 122.2, 115.5, 80.8, 74.35, 61.6, 14.1.

^{1}**H NMR** (CDCl$_3$, 298 K) Threo isomer δ (ppm) = 7.61 – 7.14 (m, 7H, 1-3-13-14-15-16-17), 7.10 - 6.90 (m, 3H, 2-4-6), 5.15 (t, *J* = 7.0 Hz, 1H, 12), 4.71 (d, *J* = 7.0 Hz, 1H, 8), 4.06 (q, *J* = 7.2 Hz, 2H, 10), 3.07 (br. s, 1H, 7), 1.05 (t, *J* = 7.2 Hz, 3H, 11).

^{13}**C NMR** ($CDCl_3$, 298 K) Threo isomer δ (ppm) = 169.5, 157.6, 138.5, 129.8, 128.7, 128.6, 126.9, 122.4, 114.8, 81.8, 75.0, 61.5, 14.0.

Synthesis of 13a

A suspension of $LiAlH_4$ (331.6 mg, 8.7 mmol, 2.5 equiv.) in THF (9 mL) was stirred at 0 °C under argon, and a THF (12 mL) solution of ethyl-3-hydroxy-2-phenoxy-3-phenylpropanoate (1 g, 3.5 mmol, 1 equiv.) was added dropwise over 20 min. When gas evolution ended, the mixture was warmed to 60 °C for 3 h. After cooling to 0 °C, the mixture was quenched by adding distilled water (0.35 mL), aqueous NaOH solution (15% w/w, 0.35 mL) and additional water (0.91 mL), in this order. The mixture was then stirred for 30 min at ambient temperature. The suspension was filtered through celite, dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by flash chromatography (using a 97:3 CH_2Cl_2/MeOH mixture as the eluent). After solvent removal under reduced pressure 2-phenoxy-1-phenylpropane-1,3-diol (**13a**) was obtained as a white solid (769 mg, 90 %).

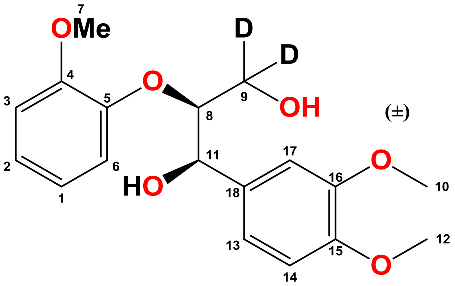


^{1}**H NMR** ($CDCl_3$, 298 K) Erythro isomer δ (ppm) = 7.54 - 7.15 (m, 7H, 1-3-9-11-13-14-15), 7.06 - 6.78 (m, 3H, 2-4-6), 5.09 (d, J = 5.0 Hz, 1H, 10), 4.41 (d, J = 5.0 Hz, 1H, 7), 3.88 (q, J = 11.5 Hz, 2H, 8), 3.05 (br.s, 1H, OH), 2.42 (br. s, 1H, OH).
^{13}**C NMR** ($CDCl_3$, 298 K) Erythro isomer δ (ppm) = 157.6, 140.4, 129.7, 128.6, 128.0, 126.4, 122.0, 116.7, 81.8, 74.1, 61.3.

^{1}**H NMR** ($CDCl_3$, 298 K) Threo isomer δ (ppm) = 7.54 - 7.15 (m, 7H, 1-3-9-11-13-14-15), 7.06 - 6.78 (m, 3H, 2-4-6), 5.04 (m, 1H, 10), 4.42- 4.25 (m, 1H, 7), 4.15 – 4.01 (m, 2H, 8), 3.05 (br.S, 1H, OH), 2.06 (br. S, 1H, OH).
^{13}**C NMR** ($CDCl_3$, 298 K) Threo isomer δ (ppm) = 158.1, 139.8, 129.8, 128.3, 128.2, 127.0, 122.1, 116.6, 82.9, 73.9, 61.1.

Synthesis of 3-d_2-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (13b-D_2)

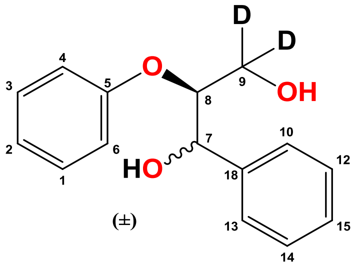
13b-D_2 was prepared using the same procedure described for compound **13b**[3] starting from ethyl-3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (250 mg, 0.66 mmol, 1 eq) and $LiAlD_4$ (69.3 mg, 1.65 mmol, 2.5 equiv). After solvent removal under reduced pressure a white solid of erythro-3d_2-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-l,3-propanediol (**13b-D_2**) was obtained (200 mg, 0.59 mmol, 89 %).



^{1}H NMR ($CDCl_3$, 298 K) δ (ppm) = 7.19 - 6.67 (m,7H, 1-2-3-6-13-14-17), 4.98 (d, *J* = 4.6 Hz, 1H, 11), 4.15 (d, J = 4.6 Hz, 1H, 8), 3.93-3.78 (m, 9H, 7-10-12), 3.60 (br.s, 1H, OH), 2.76 (br.s, 1H, OH).
^{13}C NMR ($CDCl_3$, 298 K): δ (ppm) = 151.7, 149.1, 148.5, 146.9, 132.5, 124.4, 121.8, 121.1, 118.5, 112.2, 111.0, 109.2, 87.5, 72.7, 56.0.

Synthesis of 3-d$_2$-2-phenoxy-1-phenylpropane-1,3-diol (13a-D2)

Compound **13a-D$_2$** was prepared using the same procedure described for compound **13a** with ethyl 3-hydroxy-2-phenoxy-3-phenylpropanoate (250 mg, 0.87 mmol, 1 eq) and $LiAlD_4$ (42.0 mg, 91.7 mmol, 2.5 equiv). After solvent removal under reduced pressure (166 mg, 0.67 mmol, 77 %) of 3-d$_2$-2-phenoxy-1-phenylpropane-1,3-diol (**13a-D$_2$**) was obtained as a white solid.



^{1}H NMR ($CDCl_3$, 298 K) Erythro isomer δ (ppm) = 7.60 – 7.16 (m, 7H, 1-3-10-12-13-14-15), 7.14 - 6.80 (m, 3H, 2-4-6), 5.11 (d, *J* = 5.0 Hz, 1H, 7), 4.42 (d, *J* = 5.0 Hz, 1H, 8), 3.12 (br.s, 1H, OH), 2.40 (br.s, 1H, OH).

^{13}C NMR ($CDCl_3$, 298 K) Erythro isomer δ (ppm) = 157.5, 140.3, 129.6, 128.5, 127.9, 126.4, 121.9, 116.6, 81.7, 74.0, 58.2 - 62.5 (m).

^{1}H NMR ($CDCl_3$, 298 K) Threo isomer δ (ppm) 7.60 – 7.16 (m, 7H, 1-3-10-12-13-14-15), 7.14 - 6.80 (m, 3H, 2-4-6), 5.02 - 5.09 (m, 1H, 7), 4.52 – 4.44 (m, 1H, 8), 3.12 (br.s, 1H, OH), 2.40 (br.s, 1H, OH).

^{13}C NMR ($CDCl_3$, 298 K) Threo isomer δ (ppm) =158.0, 139.7, 129.7, 128.6, 128.2, 127.0, 122.0, 116.5, 82.8, 73.8, 58.2 - 62.5 (m).

Typical procedure for the catalytic hydrosilylation of lignin model compounds

The procedure is detailed for the conversion of 2-phenoxy-1-phenylethanol (**7a**) to **8** using Et_3SiH as the reductant:

A flask equipped with a J. Young valve was charged with **7a** (100 mg, 0.47 mmol, 1 eq) and CH_2Cl_2 (1.4 mL) and the mixture was stirred until total dissolution of the starting materials. A mixture of Et_3SiH (131.2 mg, 1.1 mmol) and $B(C_6F_5)_3$ (4.8 mg, 0.01 mmol) in CH_2Cl_2 (1.4 mL) was added slowly, at RT, and stirring was continued for 2 h at RT. The reaction was monitored by ^1H RMN, after the addition of toluene as an internal standard.

Typical procedure for hydrolysis of the silylated alcohols

The procedure is detailed for the hydrolysis of the crude products resulted from the reduction of **7a** to **2** and **8**.

After completion of the hydrosilylation reaction, NEt_3 (0.5 mL) was added and the suspension was filtered through celite. The volatiles were then removed under reduced pressure and 0.5 mL of HCl 1M in MeOH was added to the crude mixture. The suspension was stirred for 16 h at RT and the products were then purified by column chromatography onto silica gel using a mixture of hexane/Et_2O (5:1) as eluent. The yield of the hydrolysis step was 66% according to GC-MS analysis (commercial samples of 2-phenylethanol and phenol were used as external standards). Other hydrolysis methods, including the use of trifluloroacetic acid in Et_2O, HCl in THF, TBAF in THF or $FeCl_3$ in MeOH, led to significantly lower yields.

Characterization of intermediate products observed in the hydrosilylation reactions

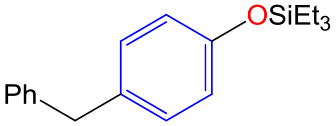
Characterization of 2

^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.07 - 7.34 (m, 2H, Ar-H), 7.04 - 6.73 (m, 3H, Ar-H), 1.12 - 0.85 (m, 9H, CH_3), 0.85 - 0.45 (m, 6H, CH_2).
^{13}C NMR (CD_2Cl_2, 298 K) δ(ppm) = 155.7, 129.5, 121.4, 120.1, 6.6, 5.1.

Characterization of 3

The para-isomer is observed as the major by-product upon reduction of **1** (92.1 mg, 0.5 mmol) with 1 equiv. Et_3SiH (54.7 mg, 0.5 mmol), following the detailed procedure described hereinabove.

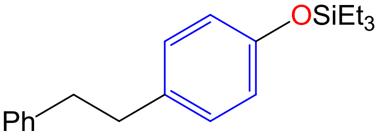
^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.08 – 6.71 (m, 9H, Ar-H), 3.97 (s, 2H, CH_2), 1.10 - 0.84 (m, 9H, CH_3), 0.84 - 0.44 (m, 6H, Si-CH_2).



Characterization of 6a

6a para-isomer is obtained as the major Friedel-Crafts coupling product upon reduction of **4a** (99.1 mg, 0.5 mmol, 1 equiv.) with 2 equiv. Et_3SiH (109.3 mg, 1 mmol), following the detailed procedure described hereinabove.

^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.10 – 6.73 (m, 9H, Ar-H), 2.87 (s, 4H, CH_2), 1.11 - 0.84 (m, 9H, CH_3), 0.85 - 0.44 (m, 6H, Si-CH_2).

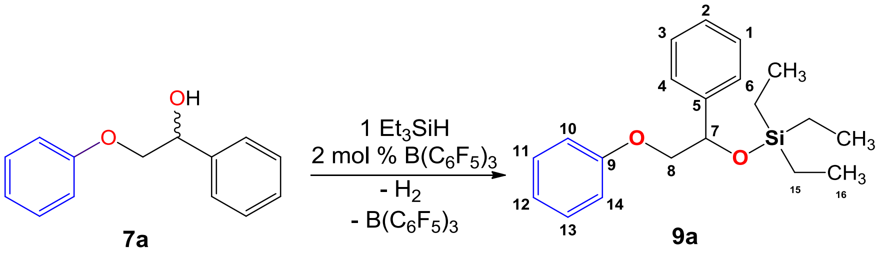


Characterization of 8

^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.31 - 7.19 (m, 5H, Ar-H), 3.81 (t, *J* = 6.8 Hz, 2H, CH_2), 2.82 (t, *J* = 6.7 Hz, 2H, Ar-CH_2), 1.12 - 0.86 (m, 9H, CH_3), 0.68 - 0.50 (m, 6H, Si-CH_2).
^{13}C NMR (CD_2Cl_2, 298 K) δ(ppm) = 139.8, 129.4, 128.6, 126.4, 64.0, 39.7, 7.0, 5.2.

Characterization of 9a

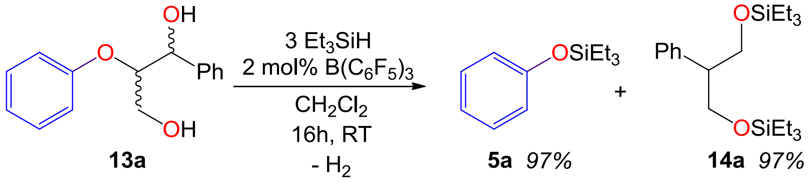
9a is observed as the unique product upon reduction of **7a** with 1 equiv. Et_3SiH (54.7 mg, 0.5 mmol, 1 equiv.), in the procedure detailed thereabove.



^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.58-7.16 (m, 7H, 1-2-3-4-6-11-13), 7.06-6.80 (m, 3H, 10-12-14), 5.08 (d, 1H, J = 5.8 Hz, 7), 4.05-3.91 (m, 2H, 8), 1.01-0.81 (m, 9H, 16), 0.7-0.53 (m, 6H, 15).
^{13}C NMR (CD_2Cl_2, 298 K) δ(ppm) = 159.2, 142.4, 129.8, 128.6, 128.0, 126.7, 121.0, 114.7, 74.3, 73.8, 6.9, 5.1.

Characterization of 14a

14a is observed as the unique product upon reduction of **13a** (122.1 mg, 0.5 mmol, 1 eq) with 3 equiv. Et_3SiH (164.0 mg, 1.5 mmol, 3 eq), following the detailed procedure given thereabove.



^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.44-7.10 (m, 5H, Ar-H), 4.09-3.76 (m, 4H, CH_2), 3.03-2.92 (quin, 1H, *J*= 6.2 Hz, Ph-CH), 1.11-0.87 (m, 18H, CH_3), 0.67-0.48 (m, 12H, Si-CH_2).
^{13}C NMR (CD_2Cl_2, 298 K) δ(ppm) =142.0, 129.0, 128.4, 126.8, 64.1, 51.4, 7.0, 4.7.

Characterization of 15a

^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.34 - 7.10 (m, 5H, Ar-H), 2.59 (t, *J*= 7.4 Hz, 2H, Ph-CH_2), 1.64 (sex, *J*= 7.4 Hz, 2H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3).
^{13}C NMR (CD_2Cl_2, 298 K) δ(ppm) = 142.7, 128.5, 128.3, 125.7, 38.1, 24.9, 13.7.

Characterization of deuterium labeled products

Characterization of 8-D$_1$

^{1}H NMR (CD_2Cl_2, 298 K) δ (ppm) = 7.31 - 7.19 (m, 5H, Ar-H), 3.83 (br.t, *J* = 6.6 Hz, 1H, CHD), 2.84 (d, *J* = 6.6 Hz, 2H, Ar-CH_2), 1.11 - 0.89 (m, 9H, CH_3), 0.70 - 0.51 (m, 6H, Si-CH_2).
^{13}C NMR (CD_2Cl_2, 298 K) δ (ppm) = 139.8, 129.5, 128.6, 126.5, 64.1 (t, *J* = 22.2 Hz), 39.9, 6.9, 5.3.

Characterization of [2-D$_2$]-ethylbenzene

^{1}H NMR (CD_2Cl_2, 298 K) δ (ppm) = 7.41 - 7.10 (m, 5H, Ar-H), 2.65 (br.t, *J* = 6.3 Hz, 1H, CH_2), 1.11 - 1.31 (m, 1H, CHD_2).
^{13}C NMR (CD_2Cl_2, 298 K) δ (ppm) = 144.25, 128.3, 127.9, 125.4, 29.0, 15.6 (m).

Characterization of 14a-D_1

^{1}H NMR (CD_2Cl_2, 298 K) δ (ppm) = 7.49 - 7.07 (m, 5H, Ar-H), 4.07 - 3.72 (m, 3H, CH_2 + CHD), 3.03 - 2.78 (m, 1H, Ph-CH), 1.21 - 0.84 (m, 18H, CH_3), 0.69 - 0.43 (m, 12H, Si-CH_2).
^{13}C NMR (CD_2Cl_2, 298 K) δ (ppm) =142.0, 128.9, 128.4, 126.8, 64.1,63.7 (t, *J* = 21.5 Hz), 51.3, 7.0, 4.2.

Characterization of 14a-D_2

^{1}H NMR (CD_2Cl_2, 298 K) δ(ppm) = 7.46 - 7.05 (m, 5H, Ar-H), 4.00 - 3.74 (m, 2H, CH_2), 2.88 (t, *J* = 5.8 Hz, 1H, Ph-CH), 1.14 - 0.85 (m, 18H, CH_3), 0.67 - 0.44 (m, 12H, Si-CH_2).
^{13}C NMR (CD_2Cl_2, 298 K) δ(ppm) =142.0, 128.9, 128.4, 126.8, 64.0, 63.9-63.3 (m), 51.3, 7.0, 4.7.

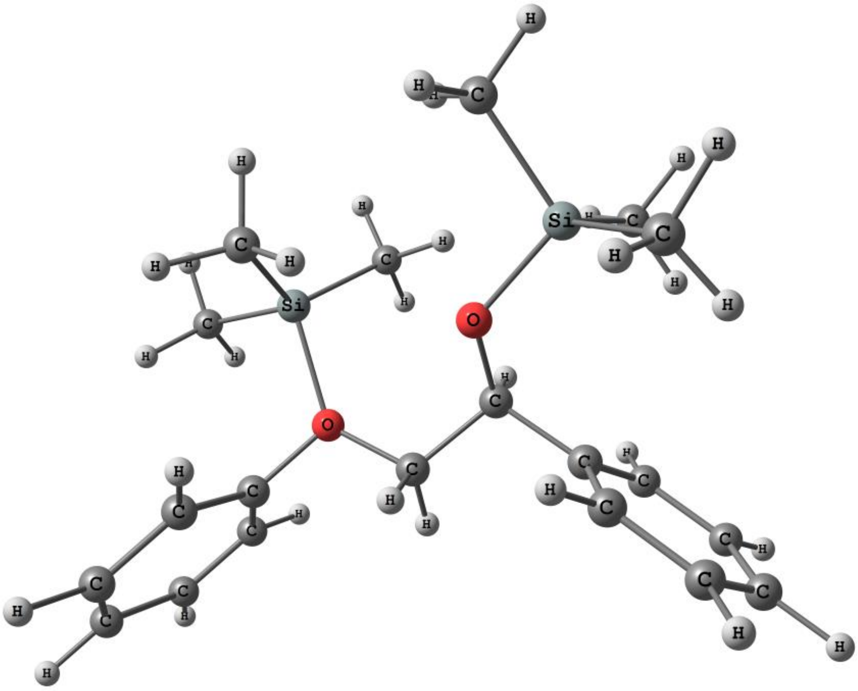
DFT Calculations

Computational Details

The M05-2X functional was employed to optimize the equilibrium molecular structure of the model compounds (obtained by replacing the $SiEt_3$ groups with $SiMe_3$).[7] This functional was specifically developed to describe organic systems with nonbonding interactions and proved to be efficient and reliable for investigating reaction mechanisms.[8] The 6-31+G* basis set was used for carbon, hydrogen, oxygen and silicon. All geometries were fully optimized without any symmetry constrains. Harmonic vibrational analyses were performed to characterize the structures as minima or transition states. Free energies were calculated within the harmonic approximation for vibrational frequencies. No solvent effects were used at this stage of the investigation since all the transformations described herein proceed both in polar (CH_2Cl_2) and non-polar (benzene) solvents. All calculations were carried out using the *Gaussian09* suite of codes.[9]

Optimized geometries and computed enthalpies and free energies

Compound 10a$^+$

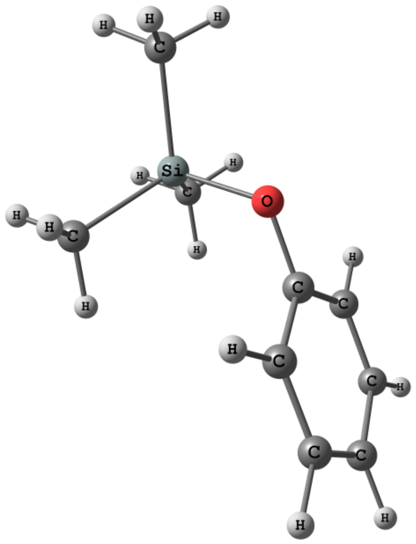


6	-6.262149000	-0.141497000	-1.900691000
6	-5.002330000	0.109395000	-1.365255000
6	-4.516955000	1.417528000	-1.297855000
6	-5.303252000	2.471304000	-1.765215000
6	-6.563991000	2.220262000	-2.301380000
6	-7.043836000	0.913928000	-2.368330000
1	-6.631371000	-1.157578000	-1.958194000
1	-4.383063000	-0.714328000	-1.027587000
1	-4.926224000	3.487921000	-1.722148000
1	-7.166290000	3.040484000	-2.670539000
1	-8.022433000	0.718153000	-2.787715000
6	-3.160741000	1.691101000	-0.672916000
1	-2.905432000	2.745666000	-0.830789000
6	-3.336573000	1.417377000	0.803857000
1	-3.525058000	0.359871000	0.975477000
8	-2.122674000	0.856251000	-1.140144000
14	-1.702965000	0.695734000	-2.801388000
6	0.121447000	0.272373000	-2.780366000
1	0.478142000	0.159049000	-3.807627000
1	0.725770000	1.048717000	-2.305451000
1	0.305374000	-0.672913000	-2.264601000
6	-2.030386000	2.323350000	-3.677329000
1	-1.682511000	2.236967000	-4.710920000
1	-3.098158000	2.550624000	-3.713872000
1	-1.508327000	3.173829000	-3.232126000
6	-2.663895000	-0.689078000	-3.613946000

1	-2.201462000	-0.922751000	-4.577547000
1	-2.644554000	-1.599378000	-3.009660000
1	-3.704755000	-0.418136000	-3.797517000
1	-4.125790000	2.028674000	1.235304000
8	-2.122227000	1.744363000	1.622966000
6	-2.359380000	1.424346000	3.002428000
6	-2.783859000	2.441024000	3.838923000
6	-2.161973000	0.119025000	3.419740000
6	-3.007228000	2.128679000	5.178482000
1	-2.923548000	3.444104000	3.455468000
6	-2.389129000	-0.174383000	4.763357000
1	-1.841234000	-0.643092000	2.719789000
6	-2.807306000	0.827477000	5.637687000
1	-3.334670000	2.902545000	5.860140000
1	-2.240432000	-1.184128000	5.122566000
1	-2.981540000	0.592935000	6.679509000
14	-0.330094000	1.919048000	1.156940000
6	0.394166000	2.620563000	2.725083000
1	-0.063598000	3.570362000	3.008671000
1	0.336516000	1.937068000	3.573143000
1	1.453892000	2.813863000	2.525918000
6	0.294613000	0.204857000	0.799794000
1	-0.423416000	-0.367748000	0.213995000
1	1.219386000	0.274176000	0.219844000
1	0.524289000	-0.322292000	1.728030000
6	-0.256943000	3.210919000	-0.178670000
1	-0.827147000	4.098029000	0.107611000
1	0.789678000	3.519169000	-0.270869000
1	-0.593066000	2.860813000	-1.150219000

Sum of electronic and thermal Energies= -1509.485714 Hartree/particle
Sum of electronic and thermal Free Energies= -1509.575237 Hartree/particle

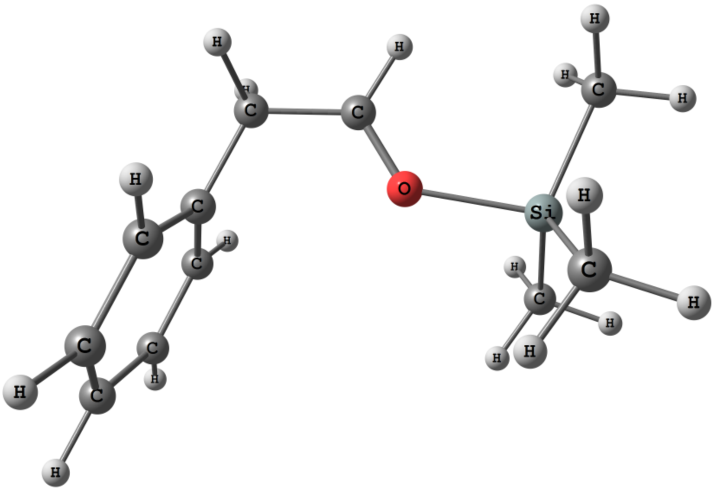
Compound 2



6	-2.110089000	-1.011212000	0.106736000
6	-0.730245000	-1.016142000	-0.082328000
6	-0.039429000	0.193008000	-0.165890000
6	-0.727050000	1.401798000	-0.055835000
6	-2.106859000	1.396530000	0.133213000
6	-2.804666000	0.192544000	0.213122000
1	-2.642173000	-1.952390000	0.174479000
1	-0.175049000	-1.943112000	-0.155865000
1	-0.168964000	2.328378000	-0.109512000
1	-2.636409000	2.337442000	0.221311000
1	-3.876926000	0.192352000	0.362550000
8	1.320970000	0.193765000	-0.322784000
14	2.058203000	0.186068000	-1.848505000
6	1.526901000	1.715501000	-2.798456000
1	0.443508000	1.733913000	-2.940831000
1	1.817018000	2.627069000	-2.270238000
1	1.996057000	1.733099000	-3.786172000
6	3.891104000	0.195659000	-1.483305000
1	4.170813000	-0.681727000	-0.896015000
1	4.473687000	0.188035000	-2.408019000
1	4.166047000	1.085877000	-0.913407000
6	1.542884000	-1.360316000	-2.779958000
1	1.835212000	-2.262636000	-2.237280000
1	0.460940000	-1.387943000	-2.931127000
1	2.020261000	-1.388083000	-3.763539000

Sum of electronic and thermal Energies= 715.890700 Hartree/particle
Sum of electronic and thermal Free Energies= -715.942313 Hartree/particle

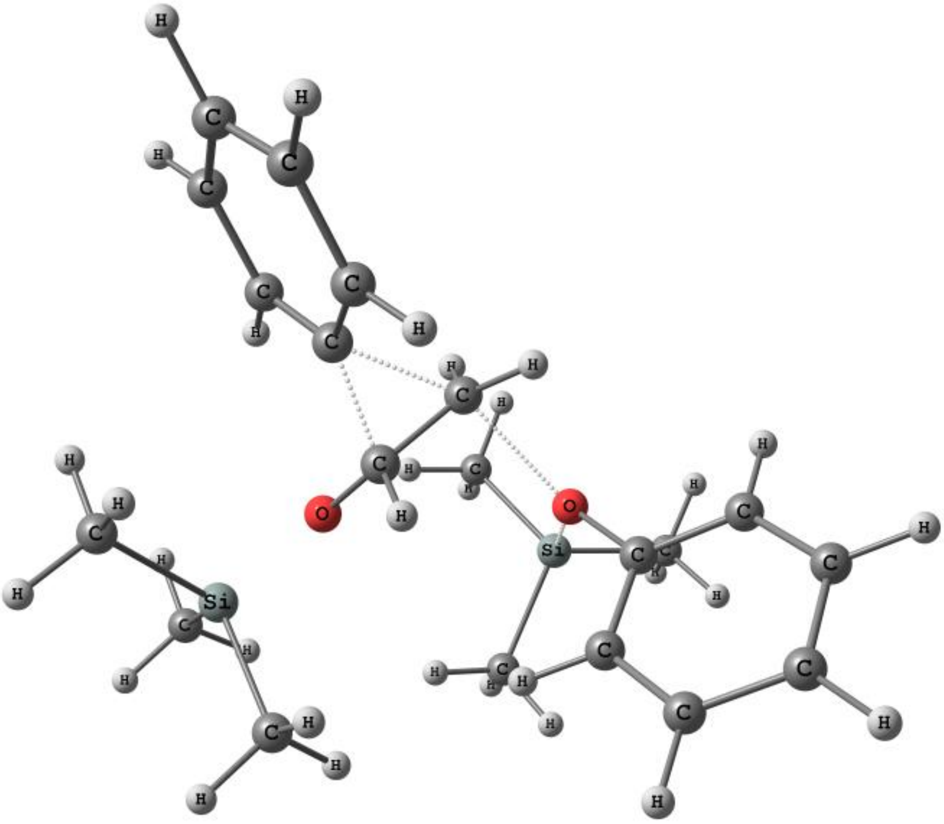
Compound 12a$^+$



6	-3.205175000	0.316870000	-1.738024000
6	-1.903220000	0.560802000	-1.308917000
6	-1.667161000	0.986642000	-0.001692000
6	-2.738035000	1.171247000	0.873124000
6	-4.039511000	0.926809000	0.443246000
6	-4.273115000	0.498219000	-0.861857000
1	-3.385310000	-0.003011000	-2.756291000
1	-1.075826000	0.433442000	-1.999073000
1	-2.561684000	1.520486000	1.885152000
1	-4.868644000	1.081989000	1.121536000
1	-5.285747000	0.317164000	-1.198579000
6	-0.257386000	1.225241000	0.470469000
1	0.409613000	1.565642000	-0.335700000
1	-0.190988000	2.025241000	1.223427000
6	0.405944000	0.052403000	1.073831000
1	1.434453000	0.149743000	1.434613000
8	-0.163106000	-1.045769000	1.188756000
14	0.421350000	-2.638987000	1.900124000
6	-0.803710000	-2.885953000	3.269081000
1	-1.825358000	-2.867727000	2.884436000
1	-0.641208000	-3.859524000	3.739193000
1	-0.708097000	-2.123084000	4.044220000
6	2.168991000	-2.299906000	2.444955000
1	2.571042000	-3.221519000	2.877274000
1	2.829974000	-2.029942000	1.617900000
1	2.233517000	-1.536652000	3.224150000
6	0.247674000	-3.765558000	0.439505000
1	0.484788000	-4.791501000	0.733807000
1	-0.776007000	-3.755444000	0.059956000
1	0.923647000	-3.488379000	-0.371748000

Sum of electronic and thermal Energies= -793.580444 Hartree/particle
Sum of electronic and thermal Free Energies= -793.639476 Hartree/particle

TS$_2$

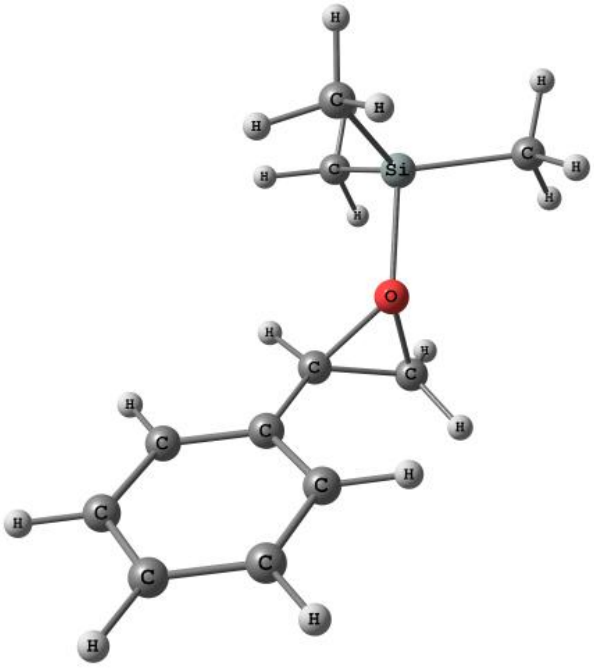


6	0.969792000	-0.743484000	1.389967000
6	1.345920000	-1.742600000	0.440781000
1	1.116892000	0.305916000	1.183753000
1	0.656807000	-1.047914000	2.377645000
1	1.418882000	-1.409183000	-0.595094000
6	2.727083000	-1.483606000	1.173454000
6	3.074744000	-2.284847000	2.272735000
6	3.643425000	-0.557554000	0.644702000
6	4.346479000	-2.180926000	2.817704000
1	2.355057000	-2.995185000	2.662255000
6	4.912302000	-0.463159000	1.192459000
1	3.359415000	0.065658000	-0.196817000
6	5.260539000	-1.275380000	2.276171000
1	4.628803000	-2.800773000	3.658274000
1	5.630230000	0.235047000	0.783242000
1	6.252919000	-1.198687000	2.702068000
6	-1.220619000	0.397997000	-0.234224000
6	-1.350633000	1.778150000	-0.099801000
6	-1.113661000	-0.192976000	-1.492024000
6	-1.380325000	2.573333000	-1.243240000
1	-1.439007000	2.208940000	0.890338000

6	-1.145991000	0.613093000	-2.629098000
1	-1.023137000	-1.269963000	-1.568786000
6	-1.278904000	1.994569000	-2.507705000
1	-1.489292000	3.646055000	-1.144764000
1	-1.073393000	0.158417000	-3.609241000
1	-1.307580000	2.616632000	-3.392738000
8	-1.147898000	-0.386457000	0.904233000
8	0.806361000	-2.982833000	0.640879000
14	1.138621000	-4.310126000	-0.412537000
14	-2.518178000	-1.276991000	1.485206000
6	-3.871875000	-0.038771000	1.828183000
1	-4.155817000	0.496273000	0.918784000
1	-4.763043000	-0.547242000	2.205682000
6	-3.026811000	-2.523694000	0.187651000
1	-3.400380000	-2.042522000	-0.718775000
1	-2.189943000	-3.173681000	-0.078749000
6	-1.863313000	-2.111757000	3.023213000
1	-2.663614000	-2.676738000	3.508145000
1	-1.065868000	-2.816955000	2.774054000
6	0.490663000	-3.864105000	-2.113703000
1	-0.590841000	-3.708135000	-2.103583000
1	0.696551000	-4.683345000	-2.808246000
6	0.209223000	-5.721554000	0.367845000
1	-0.854467000	-5.489355000	0.457847000
1	0.304449000	-6.627037000	-0.236291000
6	2.992506000	-4.572217000	-0.452539000
1	3.384085000	-4.819115000	0.536948000
1	3.525696000	-3.690312000	-0.818735000
1	-3.562970000	0.695834000	2.575454000
1	-1.491623000	-1.387175000	3.752538000
1	-3.828896000	-3.154529000	0.581404000
1	0.594959000	-5.942536000	1.365599000
1	0.966587000	-2.970167000	-2.526345000
1	3.235511000	-5.401621000	-1.122264000

Sum of electronic and thermal Energies= -1509.459903 Hartree/particle
Sum of electronic and thermal Free Energies= -1509.552665 Hartree/particle

Compound 11a$^+$

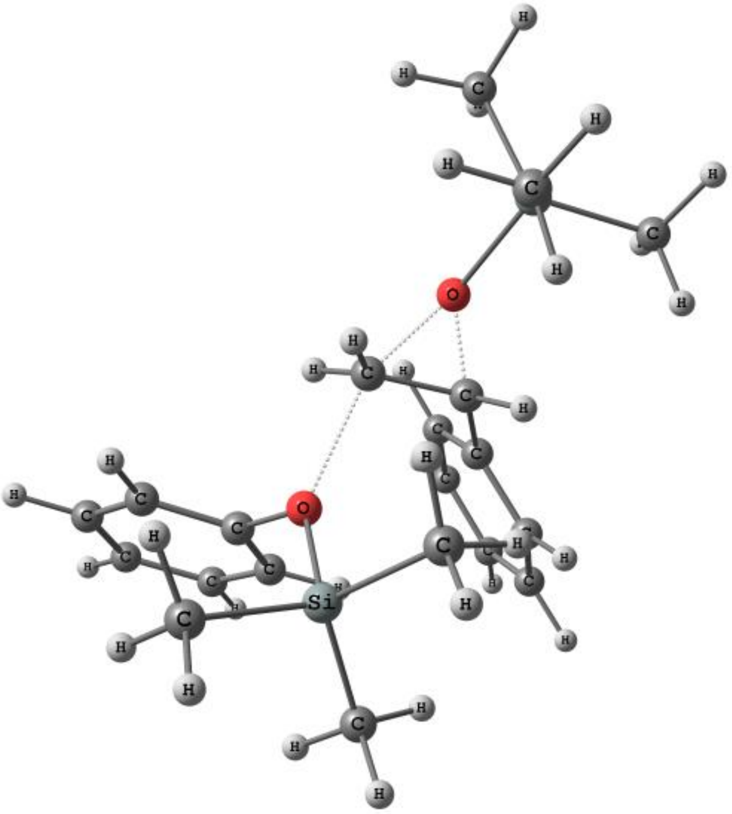


6	-4.680797000	-0.861742000	-1.025664000
6	-3.465983000	-1.518287000	-0.818204000
6	-2.364284000	-0.813128000	-0.353335000
6	-2.483053000	0.554785000	-0.084234000
6	-3.702833000	1.207454000	-0.276744000
6	-4.800142000	0.498770000	-0.756988000
1	-5.534667000	-1.415230000	-1.394660000
1	-3.380552000	-2.577638000	-1.021349000
1	-1.429346000	-1.333845000	-0.182507000
1	-3.794243000	2.266525000	-0.063069000
1	-5.742619000	1.005789000	-0.915485000
6	-1.343252000	1.357010000	0.389428000
1	-1.556036000	2.386625000	0.652882000
6	0.068561000	1.033306000	0.163995000
1	0.805892000	1.826934000	0.191662000
1	0.332943000	0.143442000	-0.391085000
8	-0.493673000	0.698252000	1.478969000
6	-0.013317000	3.250915000	2.852627000
1	0.422199000	3.711816000	3.744614000
1	-1.023561000	3.652771000	2.751302000
6	1.693017000	0.669613000	3.311276000
1	1.661483000	-0.420908000	3.268530000

1	2.396731000	1.030292000	2.557549000
6	-1.337300000	0.752824000	4.197495000
1	-2.321321000	1.105214000	3.880220000
1	-1.346664000	-0.338633000	4.205549000
14	0.001390000	1.402215000	3.093669000
1	2.092687000	0.950574000	4.289649000
1	-1.176503000	1.095433000	5.223182000
1	0.591259000	3.585153000	2.005740000

Sum of electronic and thermal Energies= -793.551777 Hartree/particle
Sum of electronic and thermal Free Energies= -793.612748 Hartree/particle

TS$_1$



6	-5.465587000	-1.285252000	0.902610000
6	-4.251315000	-0.601051000	0.926641000
6	-4.224322000	0.790288000	0.859059000
6	-5.428791000	1.480753000	0.771678000
6	-6.649825000	0.814448000	0.738252000
6	-6.662177000	-0.577507000	0.806874000
1	-5.479362000	-2.366046000	0.957014000
1	-3.320069000	-1.148558000	0.998117000
1	-3.289689000	1.337769000	0.868555000
1	-7.569763000	1.382437000	0.666774000

1	-7.606837000	-1.105606000	0.786620000
8	-5.413066000	2.875602000	0.668069000
6	-5.312255000	3.454483000	-1.298820000
1	-5.459898000	2.412182000	-1.536346000
1	-6.166113000	4.102964000	-1.182356000
6	-3.983644000	4.033640000	-1.486603000
1	-3.874054000	5.050160000	-1.112677000
6	-2.762970000	3.200014000	-1.295202000
6	-2.570437000	2.028713000	-2.028629000
6	-1.838259000	3.581032000	-0.323207000
6	-1.456540000	1.234395000	-1.776603000
1	-3.280727000	1.744972000	-2.796130000
6	-0.729084000	2.778623000	-0.065970000
1	-1.980764000	4.502520000	0.231831000
6	-0.540393000	1.604141000	-0.791712000
1	-1.301715000	0.328099000	-2.347903000
1	-0.010555000	3.075165000	0.687486000
1	0.325688000	0.983724000	-0.599051000
8	-4.555103000	3.994165000	-2.823167000
14	-4.805685000	5.461267000	-3.775867000
14	-5.517764000	3.827082000	2.124491000
6	-7.183069000	3.510118000	2.903536000
1	-7.296665000	4.134058000	3.794559000
1	-8.003231000	3.750191000	2.222717000
1	-7.286295000	2.468679000	3.215381000
6	-5.352798000	5.589303000	1.511999000
1	-5.510615000	6.275690000	2.348269000
1	-4.355730000	5.793530000	1.114605000
1	-6.098891000	5.836762000	0.751987000
6	-4.106007000	3.324273000	3.235957000
1	-4.210763000	2.288801000	3.566773000
1	-3.141540000	3.425577000	2.732454000
1	-4.090750000	3.958691000	4.126427000
6	-5.936058000	6.559230000	-2.765334000
1	-6.070373000	7.511705000	-3.285707000
1	-6.928916000	6.119484000	-2.642307000
1	-5.528787000	6.795507000	-1.778138000
6	-5.585262000	4.830337000	-5.338888000
1	-5.779887000	5.657589000	-6.026231000
1	-4.926170000	4.122001000	-5.844707000
1	-6.536056000	4.332721000	-5.137076000
6	-3.095360000	6.172943000	-3.982272000
1	-2.431783000	5.454186000	-4.467688000
1	-3.133521000	7.069580000	-4.606586000
1	-2.649065000	6.458096000	-3.026295000

Sum of electronic and thermal Energies= -1509.452677 Hartree/particle
Sum of electronic and thermal Free Energies= -1509.546297 Hartree/particle

References

1) J. M. Nichols, L. M. Bishop, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2010**, *132*, 12554–12555.
2) C. Zhao, J. A. Lercher, *Angew. Chem. Int. Ed.* **2012**, *51*, 5935–5940.
3) J. Buendia, J. Mottweiler, C. Bolm, *Chem. Eur. J.* **2011**, *17*, 13877–13882.
4) J.Stein, L. N. Lewis, Y. Gao, R. A. Scott, *J. Am. Chem. Soc.* **1999,** *121*, 3693-3703.
5) M. Brookhart and B. E. Grant, *J. Am. Chem. Soc.* **1993**, *115*, 2151-2156.
6) Mariano *et al.*, *J. Org. Chem.* **2010**, *75*, 6549–6562.
7) Zhao, Y., Schultz, N. E. & Truhlar, D. G. *J. Chem. Theory Comput.*, **2006**, *2*, 364-382; Zhao, Y. & Truhlar, D. G. *Accounts Chem. Res.*, **2008**, *41*, 157-167.
8) Simon, L. & Goodman, J. M. *Org. Biomol. Chem.*, **2011**, *9*, 689-700.
9) Gaussian 09, 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, Jr., J. A.; 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, N. J.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.