

Supporting Information

for

Organoaluminum Cation for Carbonyl Activation

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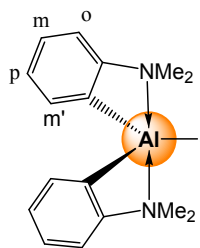
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GENERAL METHODS AND SYNTHETIC PROCEDURES AND CHARACTERIZATION

General Methods: All manipulations were performed under argon atmosphere using standard Schlenk and glove-box techniques.^[1] The solvents used for syntheses and for NMR experiments were dried, distilled and degassed prior to use by standard methods.^[2] $[(\text{NMe}_2)\text{C}_6\text{H}_4\text{Li}]$ ^[3] and $[(\text{CH}_3\text{CN})_2\text{Ag}][\text{B}(\text{C}_6\text{H}_3\text{Cl}_2)_4]$ were prepared according to the literature procedure.^[4] Commercially available anhydrous AlCl_3 and MesMgBr (1M THF solution) were used without any further purification. Aldehydes and ketones were dried with appropriate drying agents before use. Et_3SiH , PhSiH_3 , HBpin and tributyltinhydride were used without any further purification. NMR measurements were performed on Bruker 500 MHz spectrometer. The chemical shifts (δ ppm) in ^1H and ^{13}C NMR spectra were referenced to the residual signals of the deuterated solvents. ^{19}F & ^{31}P NMR spectra were referenced to CFCl_3 and H_3PO_4 (85%) respectively. The chemical shifts (δ ppm) in ^{11}B NMR spectra were referenced to NaBH_4 in D_2O . Analytically pure compounds for elemental analysis were obtained by repeated crystallisation of the products. Elemental analyses were performed on Elemental Vario Micro Cube.



Compound 1: A diethyl ether solution of $[(\text{NMe}_2)_6\text{C}_6\text{H}_4\text{Li}]$ (0.6g, 4.72mmol) was added dropwise to a diethyl ether solution of aluminum chloride (0.31g, 2.36mmol) -70°C . The reaction mixture was gradually warmed up to ambient temperature and stirred for two hours. It was filtered and concentrated to 10 ml. Colorless crystals precipitated from this solution at 0°C . Yield: 0.5 g (70%); **Elemental analysis** for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Cl}_1\text{Al}_1$: C, 63.46; H, 6.65; N, 9.25. Found: C, 63.2; H, 6.63; N, 9.24; **$^1\text{H NMR}$** (CD_2Cl_2 , 500 MHz): δ 2.97 (s, 6H, NMe_2), 7.26 (m, 2H, *o,m*- C_6H_4), 7.36 (t, 1H, *p*- C_6H_4) ($^3J_{\text{HH}} = 6.3$ Hz), 7.61 (d, 1H, *m'*- C_6H_4) ($^3J_{\text{HH}} = 5$ Hz); **$^{13}\text{C NMR}$** (CD_2Cl_2 , 126 MHz): 48.2 (s, NMe_2), 117.2(s, *o*- C_6H_4), 127.8 (s, *m*- C_6H_4), 129 (s, $\text{C}_6\text{H}_4\text{-N}$), 129.9(s, *p*- C_6H_4), 137(s, *m'*- C_6H_4), 159.8(s, $\text{C}_6\text{H}_4\text{-Al}$).

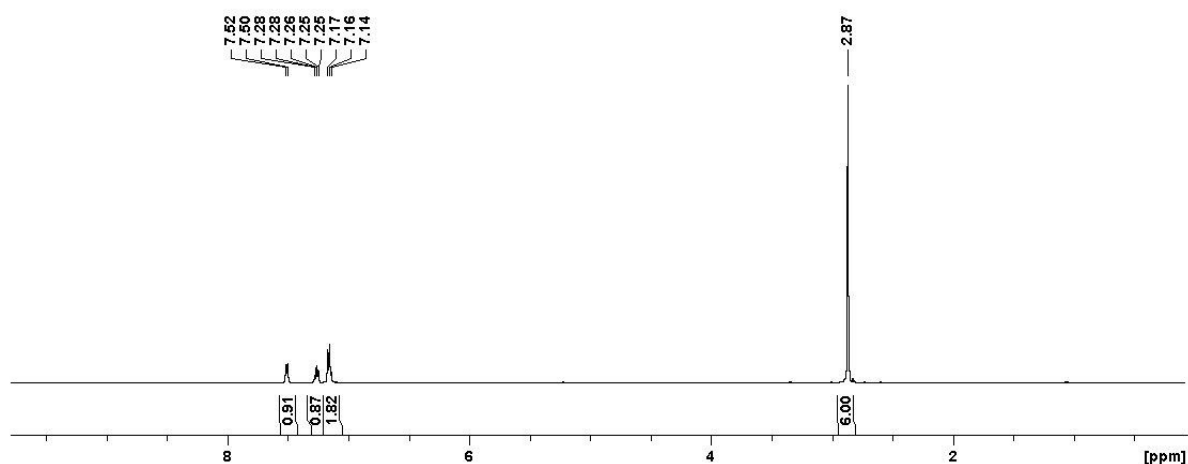


Figure S1: $^1\text{H NMR}$ spectrum ($[\text{CD}_2\text{Cl}_2]$, 500 MHz) of compound 1.

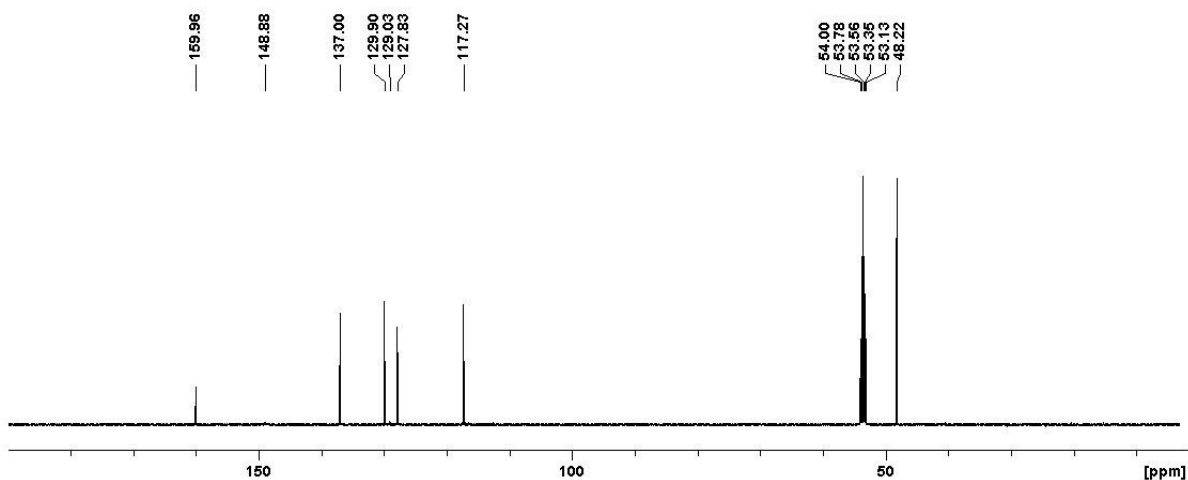
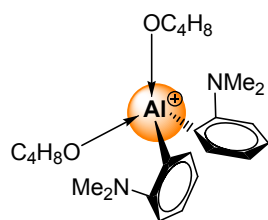


Figure S2: $^{13}\text{C NMR}$ spectrum ($[\text{CD}_2\text{Cl}_2]$, 126 MHz) of compound 1.



Compound 2: A solution of **1** (0.08 g, 0.26 mmol) in tetrahydrofuran was added dropwise to a solution of $[(\text{CH}_3\text{CN})_2\text{Ag}][\text{B}(\text{C}_6\text{H}_3\text{Cl}_2)_4]$ (0.23 g, 0.26 mmol) in tetrahydrofuran at -78°C . The reaction temperature was gradually allowed to attain ambient temperature and stirred for few minutes. The reaction mixture was filtered and the filtrate was concentrated layered with 15 mL n-hexane to obtain colorless crystals at 0°C . Yield 0.23g (81%); Elemental analysis for $\text{C}_{52}\text{H}_{56}\text{N}_2\text{O}_3\text{Cl}_8\text{B}_1\text{Al}_1$: C, 57.91; H, 5.23; N, 2.59. Found: C, 57.64; H, 5.21; N, 2.58; $^1\text{H NMR}$ (CD_2Cl_2 , 500 MHz): δ 1.93 (t, 12H, *o*-THF), 2.91 (s, 12H, NMe_2), 3.85 (t, 12H, *m*-THF), 6.99 (s, *p*- BAr^{Cl}), 7.04 (s, *o*- BAr^{Cl}), 7.34 (d, 2H, *o*- C_6H_4) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.4 (t, 2H, *m*- C_6H_4) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.52 (t, 2H, *p*- C_6H_4) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.63 (d, 2H, *m'*- C_6H_4) ($^3J_{\text{HH}} = 5\text{Hz}$); $^{13}\text{C NMR}$ (CD_2Cl_2 , 126 MHz): δ 25.5 (s, *m*-THF), 47.6 (s, NMe_2), 70.8 (s, *o*-THF), 117.3 (s, *o*- C_6H_4), 123 (s, *p*- BAr_4^{Cl}), 129.5 (s, *m*- C_6H_4), 132.2 (s, *p*- C_6H_4), 132.9 (q, *i*- $\text{C}_6\text{H}_4\text{-N}$), 133.1 (s, *o*- BAr_4^{Cl}), 137.2 (s, *m'*- C_6H_4), 159.2 (s, $\text{Al-C}_6\text{H}_4$), 164.6 (q, *i*- BAr_4^{Cl}); $^{11}\text{B NMR}$ (CD_2Cl_2 , 160.5 MHz): δ -6.93 (s, BAr_4^{Cl}).

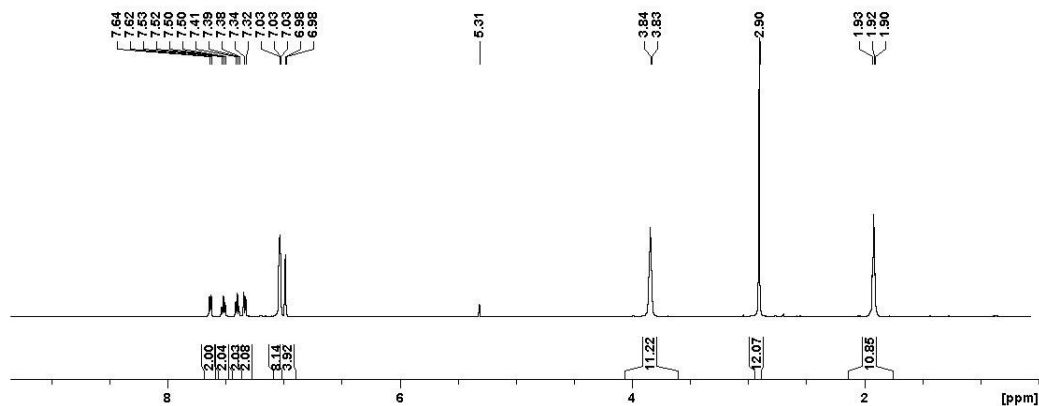


Figure S3: $^1\text{H NMR}$ spectrum ($[\text{CD}_2\text{Cl}_2]$, 500 MHz) of compound **2**.

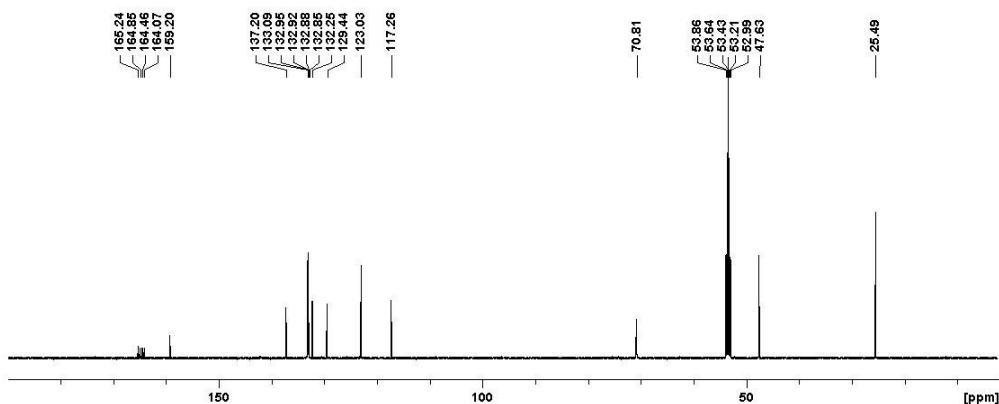


Figure S4: $^{13}\text{C NMR}$ spectrum ($[\text{CD}_2\text{Cl}_2]$, 126 MHz) of compound **2**.

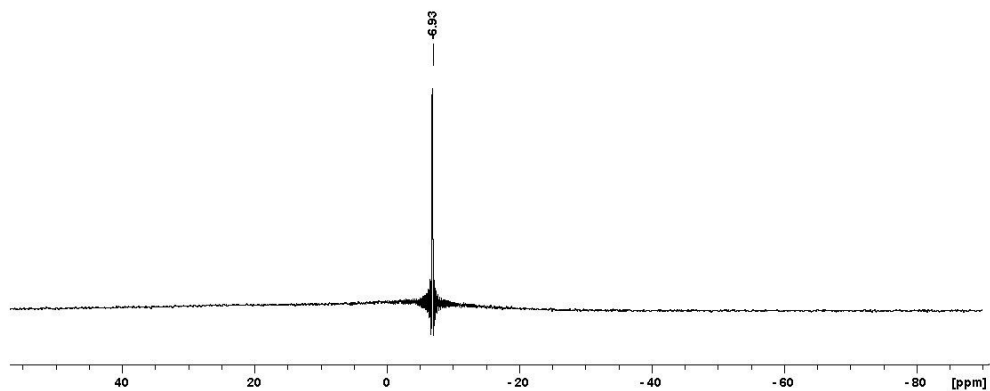
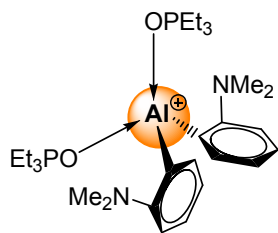


Figure S5: ^{11}B NMR spectrum ($[\text{CD}_2\text{Cl}_2]$, 160.5 MHz) of compound **2**.



Compound 3: A solution of **2** (0.02 g, 0.018 mmol) in CD_2Cl_2 was reacted with OPEt_3 (0.005 g, 0.036 mmol) in an NMR tube fitted with a *J*-Young joint. The resulting solution was layered with *n*-hexane and allowed to stand overnight at 0°C to afford colorless crystals. Yield: 0.0172 g (82%); Elemental analysis for $\text{C}_{52}\text{H}_{62}\text{P}_2\text{O}_2\text{N}_2\text{Cl}_6\text{B}_1\text{Al}_1$: C, 55.25; H, 5.52; N, 2.47. Found: C, 54.92; H, 5.49; N, 2.45; **^1H NMR** (CD_2Cl_2 , 500 MHz): δ 0.98 (m, 18H, OPCH_2CH_3), 1.73 (m, 12H, OPCH_2CH_3), 1.73 (m, 8H, Free *m*-THF), 2.51 (s, 12H, NMe_2), 3.59 (t, 8H, Free *m*-THF), 6.88 (m, 4H, *o,m*- C_6H_4), 6.91 (s, *p*- BAR^{Cl}), 6.95 (s, *o*- BAR^{Cl}), 7.17 (t, 2H, *p*- C_6H_4) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.42 (t, 2H, *m'*- C_6H_4) ($^3J_{\text{HH}} = 10\text{Hz}$); **^{13}C NMR** (CD_2Cl_2 , 126 MHz): δ 5 (s, OPCH_2CH_3), 17.4, 18 (s, OPCH_2CH_3), 25.6 (s, *m*-THF), 46.2 (s, NMe_2), 67.7 (s, *o*-THF), 116.7 (s, *o*- C_6H_4), 122.2 (s, *m*- C_6H_4), 123 (s, *p*- BAR_4^{Cl}), 129.2 (s, *p*- C_6H_4), 132.8 (q, *i*- C_6H_4 -Al), 133.1 (s, *o*- BAR_4^{Cl}), 128.4 (s, *m*- C_6H_4), 137.9 (s, *m'*- C_6H_4), 161.4 (s, *i*- $\text{C}_6\text{H}_4\text{NMe}_2$), 164.8 (q, *i*- BAR_4^{Cl}); **^{11}B NMR** (CD_2Cl_2 , 160.5 MHz): δ -6.93 (s, BAR_4^{Cl}); **^{31}P NMR** (CD_2Cl_2 , 202.5 MHz): δ 75.45 (s, OPCH_2CH_3).

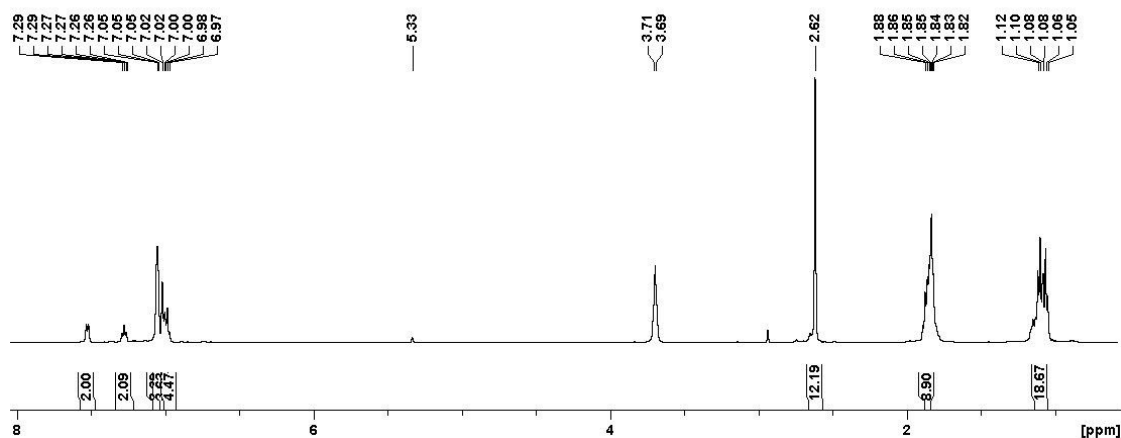


Figure S6: ^1H NMR spectrum ($[\text{CD}_2\text{Cl}_2]$, 500 MHz) of compound **3**.

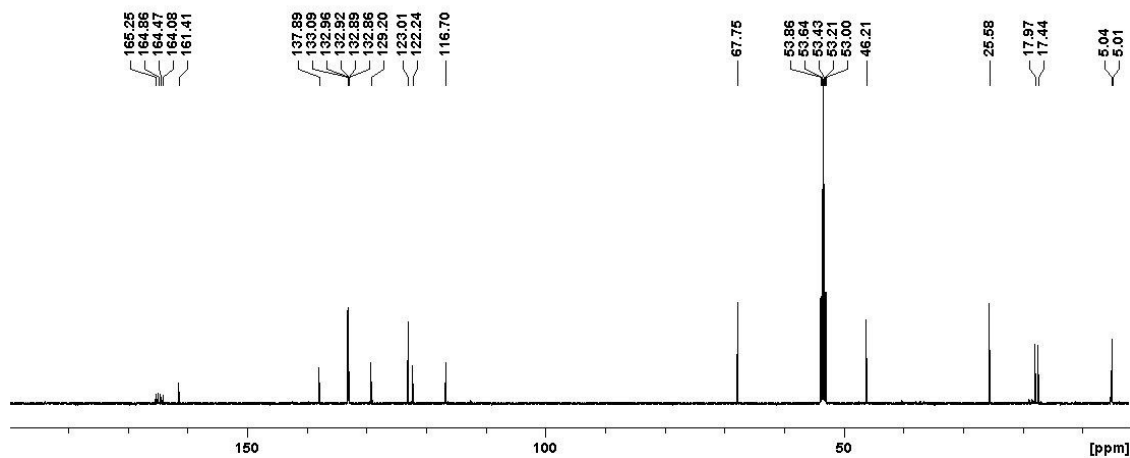


Figure S7: ^{13}C NMR spectrum ($[\text{CD}_2\text{Cl}_2]$, 126 MHz) of compound **3**.

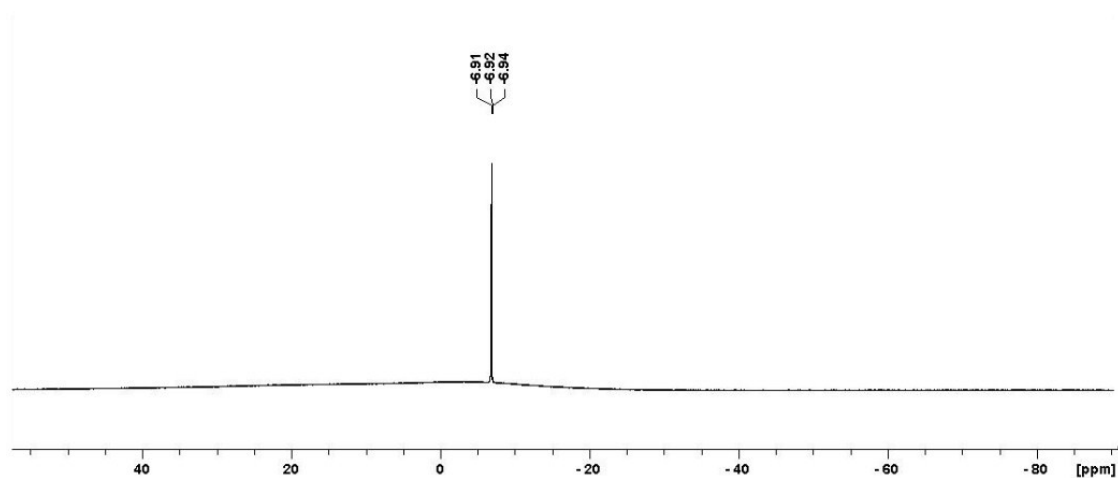


Figure S8: ^{11}B NMR ($[\text{CD}_2\text{Cl}_2]$, 160.5 MHz) of compound **3**.

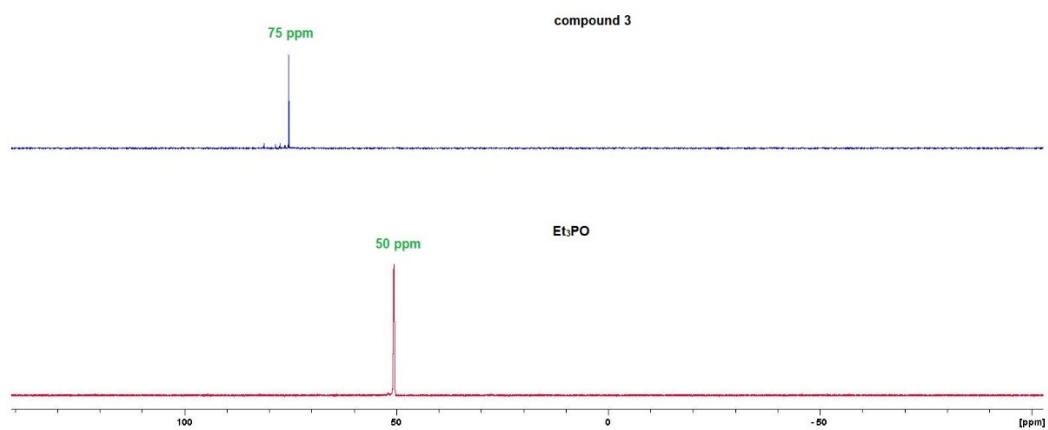
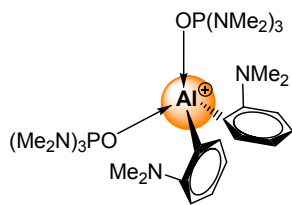


Figure S9: Stacked ^{31}P NMR ($[\text{CD}_2\text{Cl}_2]$, 202 MHz) of compound Et₃PO (below) and compound **3** (above).



Compound 4: A solution of **2** (0.04 g, 0.037 mmol) in tetrahydrofuran was treated with $\text{OP}(\text{NMe}_2)_3$ (25.8 μL , 0.148 mmol). The reaction mixture was stirred for an hour and the resulting solution was layered with n-hexane to afford colorless crystals after 5 days. Yield: 0.036 g. (79.6 %); Elemental analysis for $\text{C}_{52}\text{H}_{68}\text{P}_2\text{O}_2\text{N}_8\text{Cl}_8\text{B}_1\text{Al}_1$: C, 51.17; H, 5.61; N, 9.18. Found: C, 50.78; H, 5.57; N, 9.16; $^1\text{H NMR}$ (CD_2Cl_2 , 500 MHz): δ 2.54 (s, 29H, NMe_2 , OPNMe_2), 2.56 (s, 19H, NMe_2 , OPNMe_2), 1.81 (m, 8H, Free *m*-THF), 3.67 (t, 8H, Free *m*-THF), 6.88 (t, 2H, *m*- C_6H_4) ($^3J_{\text{HH}} = 5\text{Hz}$), 6.99 (s, *p*- BAR_4^{Cl}), 7.03 (m, *o*- BAR_4^{Cl}), 7.03 (m, 2H, *o*- C_6H_4), 7.23 (t, 2H, *p*- C_6H_4) ($^3J_{\text{HH}} = 5\text{Hz}$), 7.54 (t, 2H, *m'*- C_6H_4) ($^3J_{\text{HH}} = 5\text{Hz}$); $^{13}\text{C NMR}$ (CD_2Cl_2 , 126 MHz): δ 25.6 (s, *m*-THF), 36.4 (s, OPNMe_2), 46.1 (s, NMe_2), 67.7 (s, *o*-THF), 112.4 (s, *m*- BAR_4^{Cl}), 117.1 (s, *o*- C_6H_4), 122.2 (s, *m*- C_6H_4), 123 (s, *p*- BAR_4^{Cl}), 128.8 (s, *p*- C_6H_4), 132.8 (q, *i*- $\text{C}_6\text{H}_4\text{-Al}$), 133 (s, *o*- BAR_4^{Cl}), 137.7 (s, *m'*- C_6H_4), 162.2 (s, *i*- $\text{C}_6\text{H}_4\text{NMe}_2$), 164.6 (q, *i*- BAR_4^{Cl}); $^{11}\text{B NMR}$ (CD_2Cl_2 , 160.5 MHz): δ -6.93 (s, BAR_4^{Cl}). $^{31}\text{P NMR}$ (CD_2Cl_2 , 202.5 MHz): δ 24.1 (t, OPNMe_2).

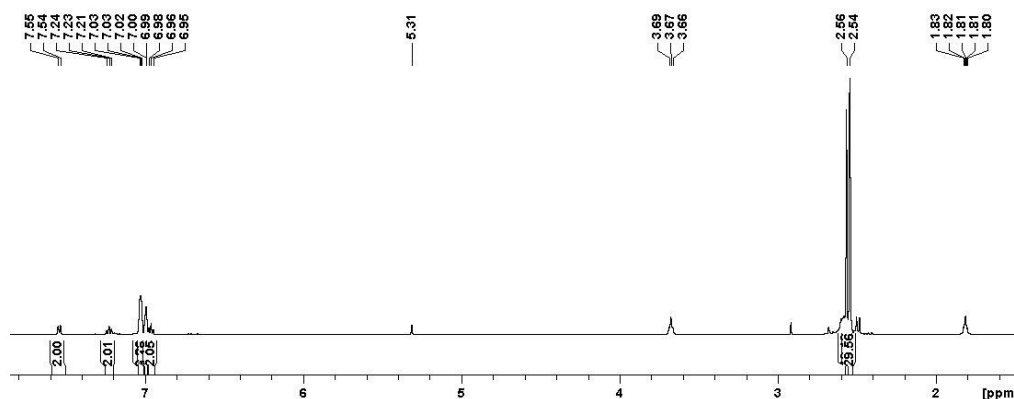


Figure S10: $^1\text{H NMR}$ ($[\text{CD}_2\text{Cl}_2]$, 500 MHz) of compound **4**.

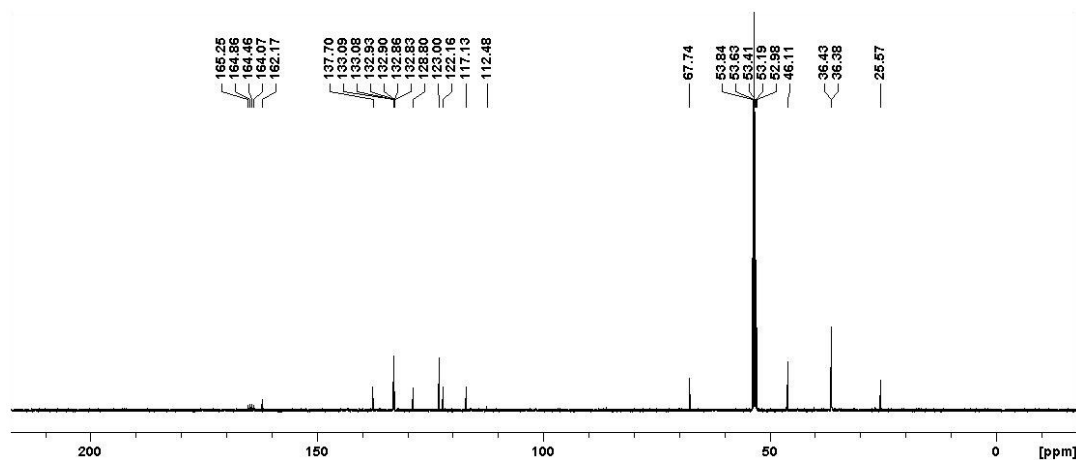


Figure S11: $^{13}\text{C NMR}$ ($[\text{CD}_2\text{Cl}_2]$, 126 MHz) of compound **4**.

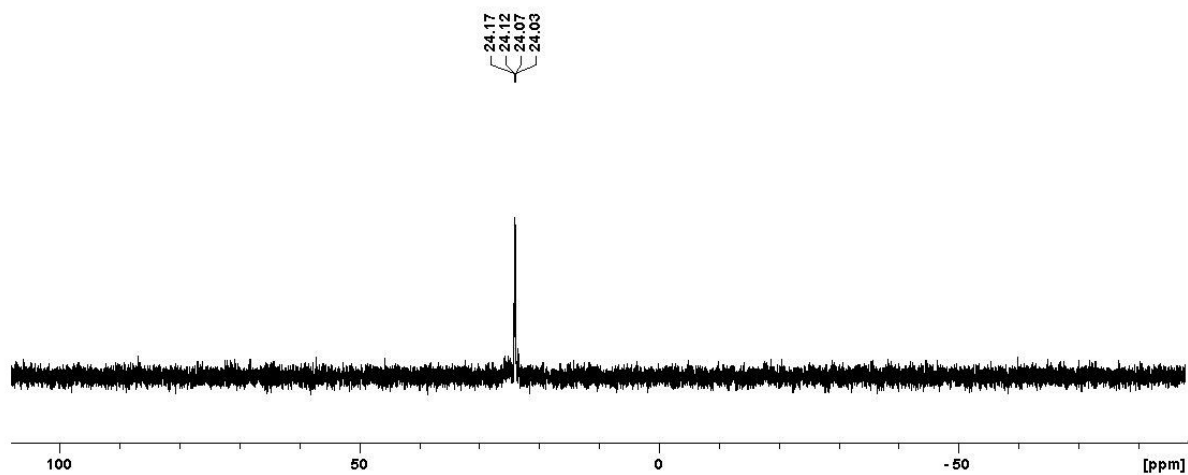


Figure S12: ³¹P NMR ([CD₂Cl₂], 202 MHz) of compound 4.

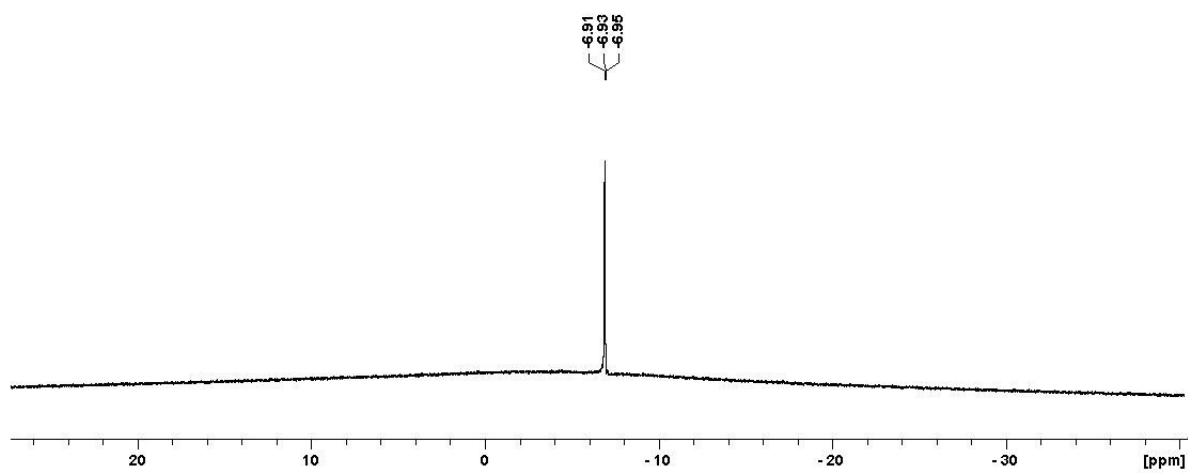
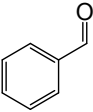
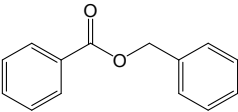
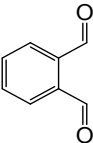
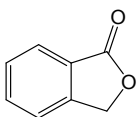
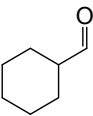
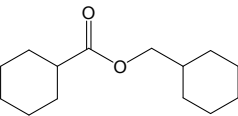
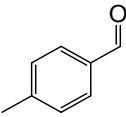
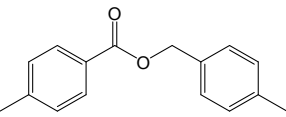
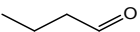
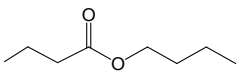
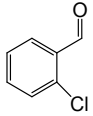
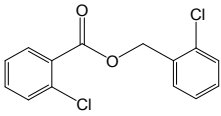


Figure S13: ¹¹B NMR ([CD₂Cl₂], 160.5 MHz) of compound 4.

CATALYTIC ALDEHYDE DIMERIZATION (TISCHENKO REACTION)

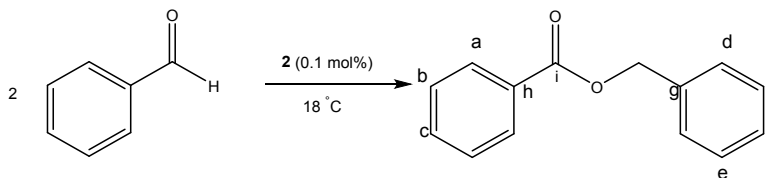
Typical reaction procedure: Catalytic amount of **2** was introduced into a known volume of aldehyde and stirred 18 °C. The progress of the reaction was monitored by taking an aliquot of the reaction mixture and measuring ¹H NMR in C₆D₆ at regular time intervals. Mesitylene was used as an internal standard to calculate the yield of the product.

Table S1: Summary of catalytic aldehyde dimerization. a) Solvent free neat reactions, b) reaction performed in 0.1 mL C₆D₆, c) Reaction performed in 0.4 mL C₆D₆.

Substrate	Catalyst (mol %)	Product	TON	TOF	Yield (%)
	0.1		1000	2000	99 ^a
	0.5		800	1600	98 ^c
	0.5		200	6000	98 ^a
	0.5		200	600	99 ^a
	2		50	200	98 ^b
	5		19.2	38.4	96 ^c

Benzaldehyde dimerization:

2 (0.005 g, 0.004 mmol), benzaldehyde (471.2 μ l, 4.63 mmol), mesitylene (215 μ l, 1.54 mmol).



Scheme S1: Catalytic dimerization of benzaldehyde.

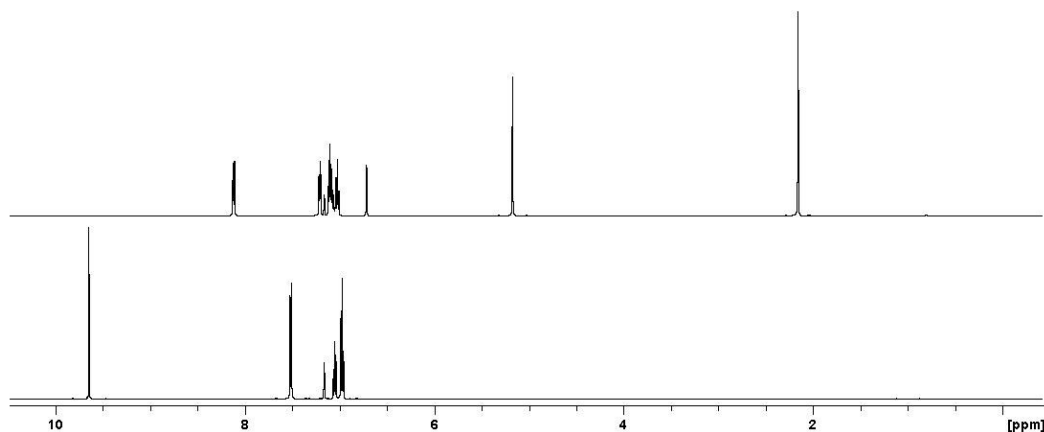


Figure S14: Stacking of ^1H NMR spectra of benzaldehyde (bottom) and after (top) the product formation recorded in C_6D_6 with internal reference (mesitylene).

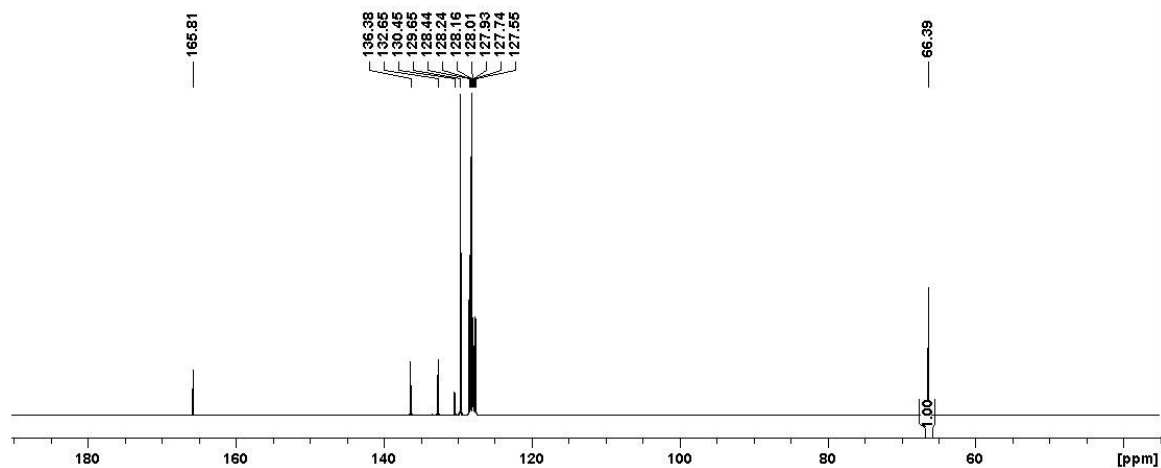


Figure S15: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of benzyl benzoate.

^1H NMR (C_6D_6 , 500 MHz): δ 5.17 (s, 2H, OCH_2), 7.03 (t, 2H, *c,f*-CH) ($^3J_{\text{HH}} = 5\text{Hz}$), 7.11 (m, 4H, *b,e*-CH), 7.21 (d, 2H, *d*-CH) ($^3J_{\text{HH}} = 5\text{Hz}$), 8.1 (d, 2H, *a*-CH) ($^3J_{\text{HH}} = 5\text{Hz}$). (**NMR Yield: 99 %**); ^{13}C NMR (C_6D_6 , 126 MHz): δ 66.3 (s, OCH_2), 128.2 (s, *c,f*- C_6H_5), 128.1 (s, *d*- C_6H_5), 128.4 (s, *b*- C_6H_5), 129.6 (s, *a*- C_6H_5), 130.4 (s, *h*- C_6H_5), 132.6 (s, *e*- C_6H_5), 136.4 (s, *g*- C_6H_5), 165.8 (s, *i*-C=O).

Kinetic experiments on benzaldehyde dimerization :

0.05 mol% of **2** was introduced into a known volume of aldehyde and stirred 18 °C. The progress of the reaction was monitored for one hour by taking an aliquot of the reaction mixture and measuring ^1H NMR in C_6D_6 at regular time intervals. Mesitylene was used as an internal standard to calculate the yield of the product.

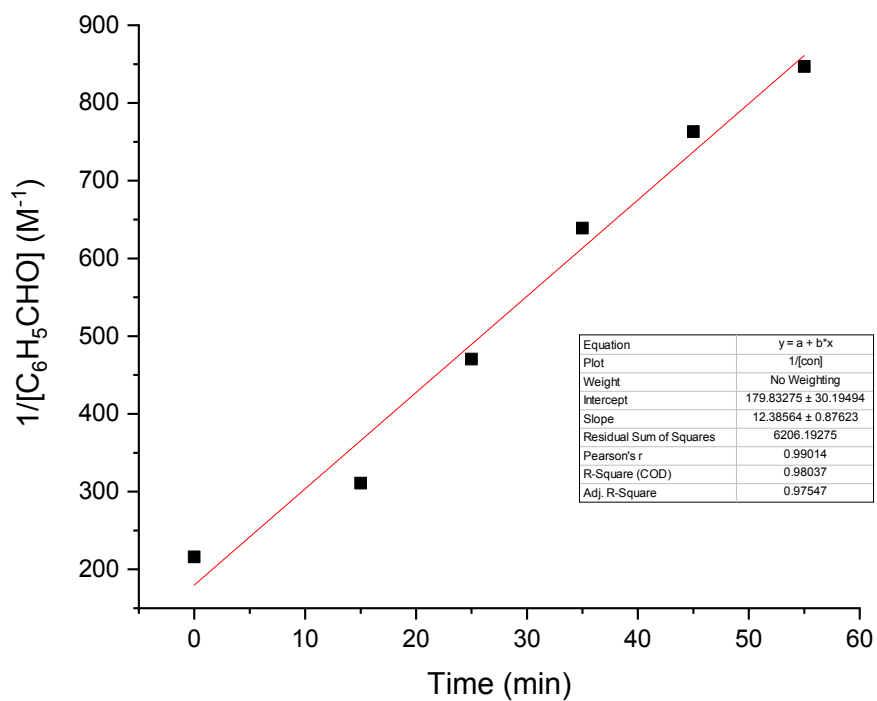


Figure S16: A plot of $1/[\text{C}_6\text{H}_5\text{CHO}]$ vs the reaction time for the benzaldehyde dimerization.

Control reaction:

A reaction between benzaldehyde and 0.25 eq. of **2** in CD_2Cl_2 .

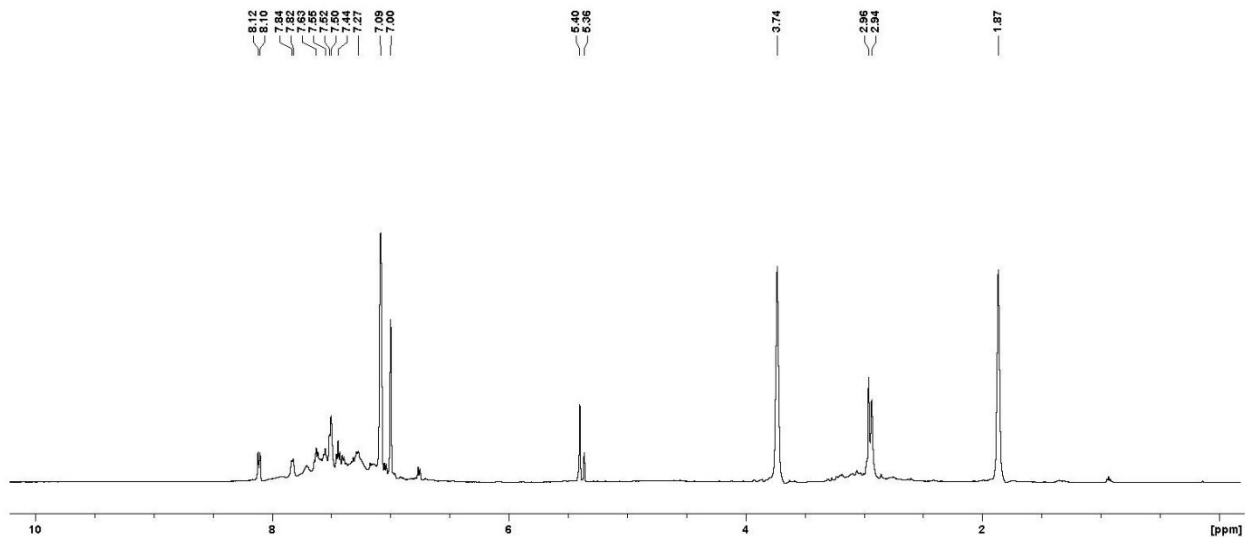


Figure S17: ^1H NMR spectrum ($[\text{CD}_2\text{Cl}_2]$, 500 MHz) of **2** and benzaldehyde (1 : 4).

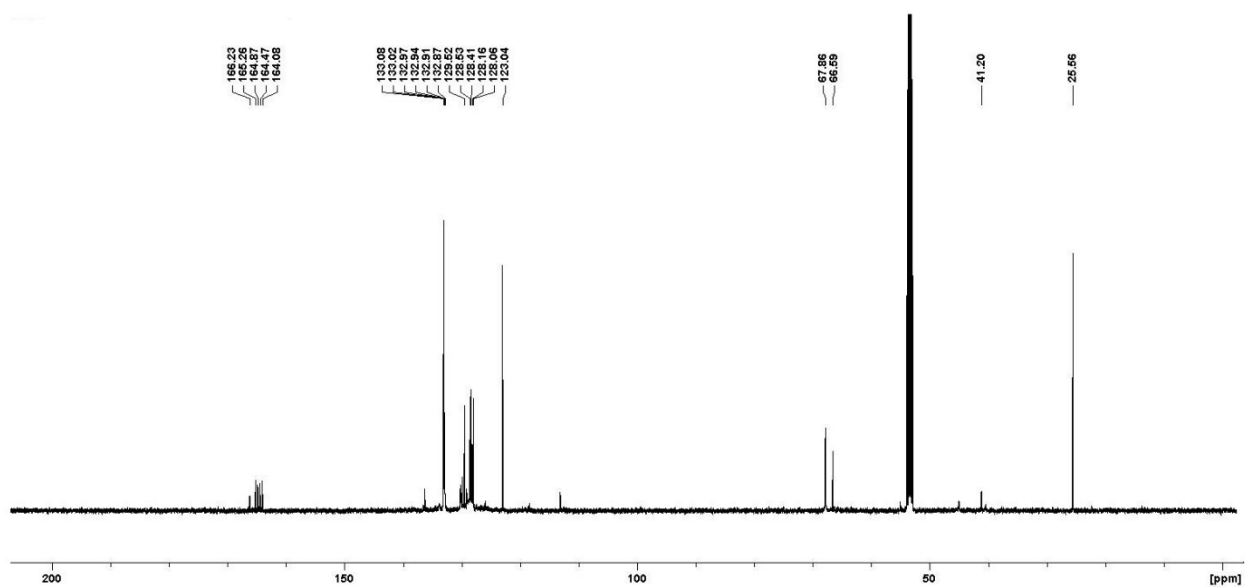
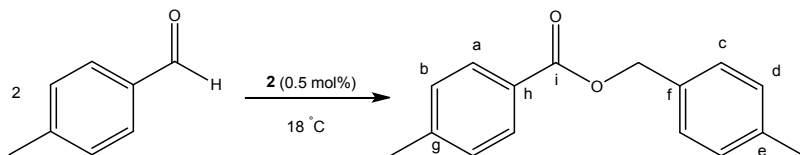


Figure S18: ^{13}C NMR spectrum ($[\text{CD}_2\text{Cl}_2]$, 126 MHz) of **2** and benzaldehyde (1 : 4)

Dimerization of p-tolualdehyde:

0.5 mol% **2** (0.005 g, 0.004 mmol), p-tolualdehyde (109.3 μ l, 0.92 mmol) and mesitylene (43 μ l, 0.31 mmol).



Scheme S2: Catalytic dimerization of p-tolualdehyde.

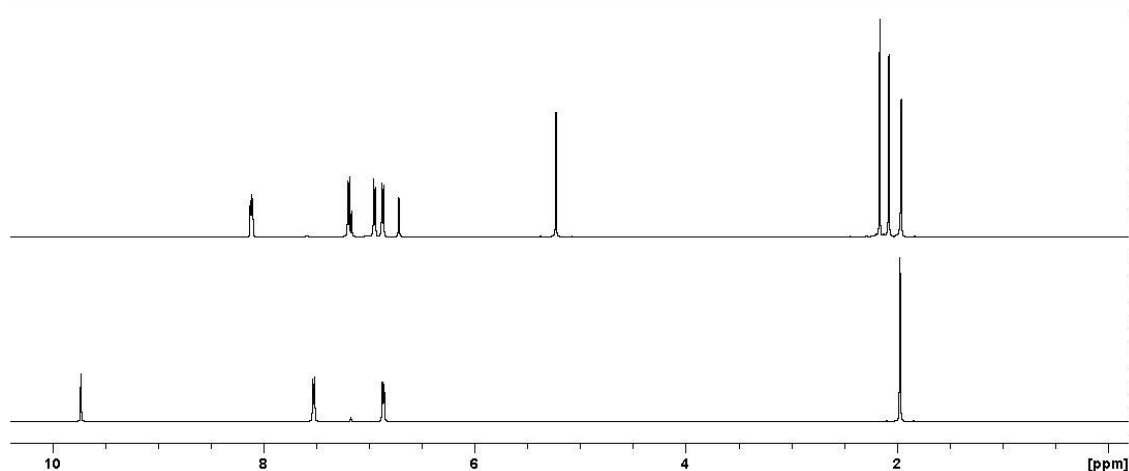


Figure S19: Stacking of ^1H NMR spectra of p-tolualdehyde (bottom) and after (top) the product formation recorded in C_6D_6 with internal reference (mesitylene).

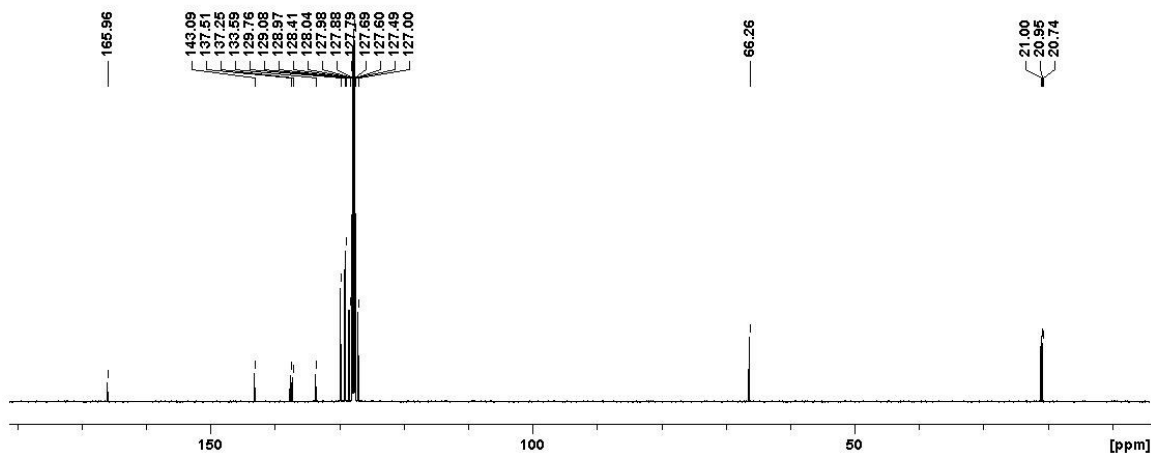
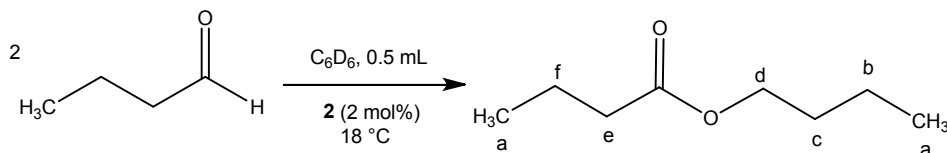


Figure S20: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of 4-methylbenzyl 4-methylbenzoate

^1H NMR (C_6D_6 , 500 MHz): δ 2.07 (s, 3H, CH_3), 5.23 (s, 2H, OCH_2), 6.87 (d, 2H, $c\text{-CH}$) ($^3J_{\text{HH}} = 10\text{Hz}$), 6.94 (d, 2H, $d\text{-CH}$) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.18 (d, 2H, $b\text{-CH}$) ($^3J_{\text{HH}} = 5\text{Hz}$), 8.12 (d, 2H, $a\text{-CH}$) ($^3J_{\text{HH}} = 5\text{Hz}$). (**NMR Yield: 99 %**); ^{13}C NMR (C_6D_6 , 126 MHz): δ 21 (s, CH_3), 66.2 (s, OCH_2), 128.4 (s, $b\text{-C}_6\text{H}_5$), 128.9 (s, $c\text{-C}_6\text{H}_5$), 129 (s, $d\text{-C}_6\text{H}_5$), 129.7 (s, $a\text{-C}_6\text{H}_5$), 133.6 (s, $e\text{-C}_6\text{H}_5$), 137.2 (s, $f\text{-C}_6\text{H}_5$), 137.5 (s, $g\text{-C}_6\text{H}_5$), 143.1 (s, $h\text{-C}_6\text{H}_5$), 166 (s, $i\text{-C=O}$).

Dimerization of butanal:

2 (0.005 g, 0.004 mmol), butanal (20.85 μ l, 0.23 mmol) and mesitylene (10.75 μ l, 0.07 mmol).



Scheme S3: Catalytic dimerization of butanal.

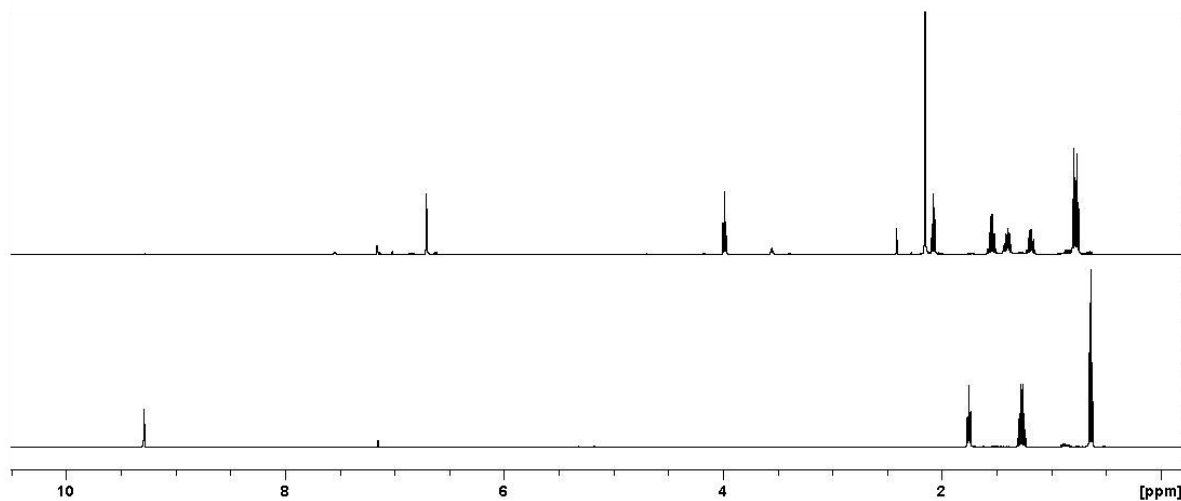


Figure S21: Stacking of 1H NMR spectra of butanal (bottom) and after (top) the product formation recorded in C_6D_6 with internal reference (mesitylene).

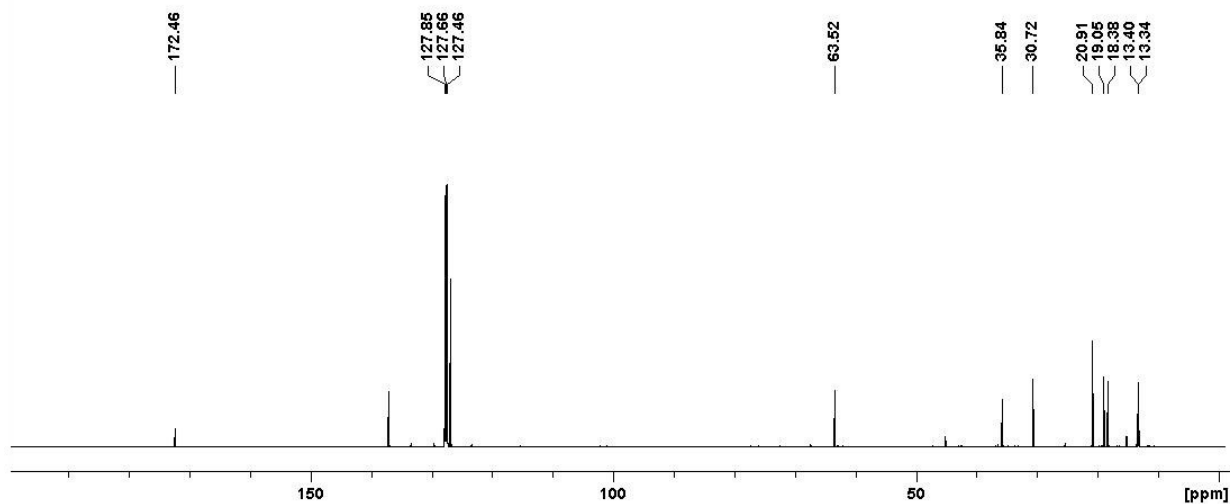
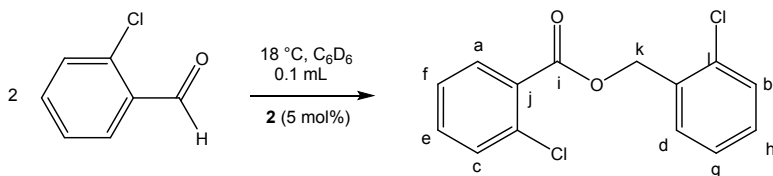


Figure S22: ^{13}C NMR spectrum ($[C_6D_6]$, 126 MHz) of butyl butyrate.

1H NMR (C_6D_6 , 500 MHz): δ 0.77 (t, 3H, CH_3) ($^3J_{HH} = 5$ Hz), 1.19 (sextet, 2H, $b-CH_2$) ($^3J_{HH} = 5$ Hz), 1.4 (quintet, 2H, $c-CH_2$) ($^3J_{HH} = 5$ Hz), 1.55 (sextet, 2H, $f-CH_2$) ($^3J_{HH} = 5$ Hz), 2.07 (t, 2H, $e-CH_2$) ($^3J_{HH} = 5$ Hz), 3.98 (t, 2H, $d-OCH_2$) ($^3J_{HH} = 5$ Hz). (**NMR Yield: 98 %**); ^{13}C NMR (C_6D_6 , 126 MHz): δ 13.3, 13.4 (s, $a-CH_3$), 18.4 (s, $b-CH_2$), 19 (s, $f-CH_2$), 30.72 (s, $c-CH_2$), 35.8 (s, $e-CH_2$), 63.5 (s, $d-OCH_2$), 172.4 (s, $i-C=O$).

Dimerization of 2-chloro benzaldehyde:

2 (0.005 g, 0.004 mmol), 2-chloro benzaldehyde (104.2 μ l, 0.09 mmol) and mesitylene (4.3 μ l, 0.03 mmol).



Scheme S4: Catalytic dimerization of 2-chloro benzaldehyde.

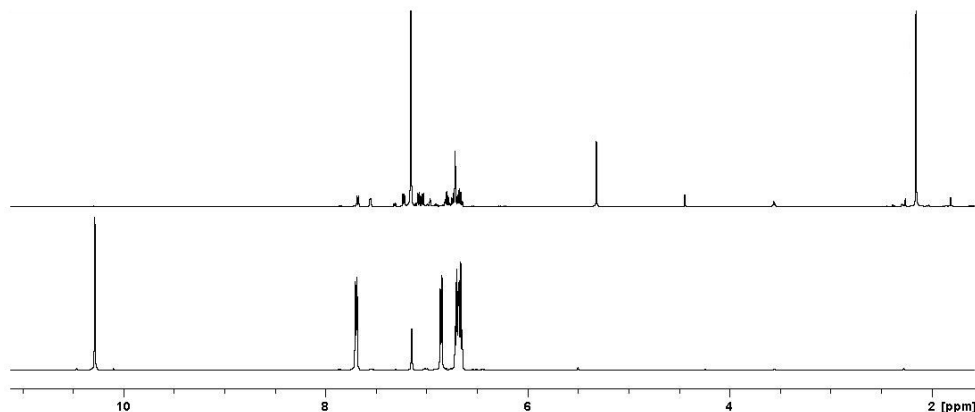


Figure S23: Stacking of ^1H NMR spectra of 2-chloro benzaldehyde (bottom) and after (top) the product formation recorded in C_6D_6 with internal reference (mesitylene).

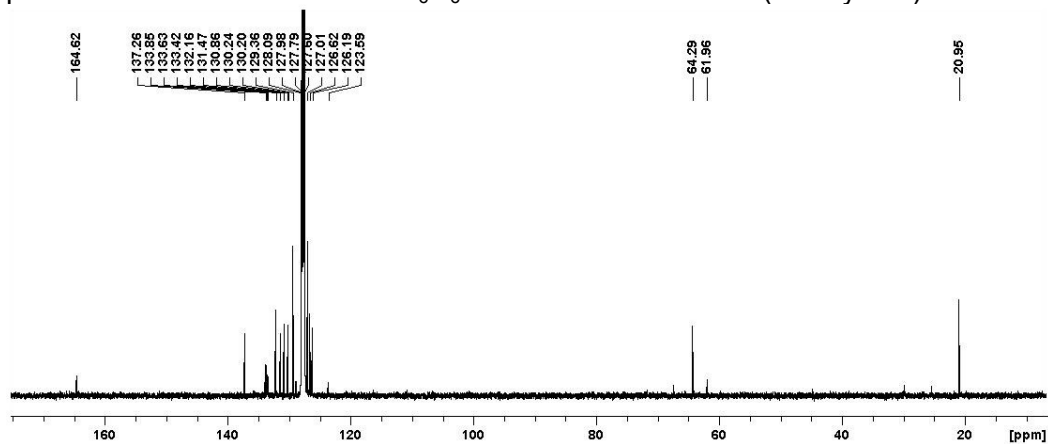
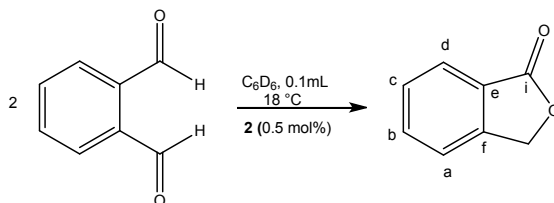


Figure S24: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of 2-chlorobenzyl 2-chlorobenzoate.

^1H NMR (C_6D_6 , 500 MHz) (Poor solubility): δ 5.32 (s, 2H, OCH_2), 6.66 (m, 2H, *g,h-CH*) ($^3J_{\text{HH}} = 5\text{Hz}$), 6.74 (t, 1H, *f-CH*) ($^3J_{\text{HH}} = 5\text{Hz}$), 6.8 (t, 1H, *e-CH*) ($^3J_{\text{HH}} = 5\text{Hz}$), 7.04 (d, 1H, *d-CH*) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.08 (d, 1H, *c-CH*) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.23 (d, 1H, *b-CH*) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.68 (d, 1H, *a-CH*) ($^3J_{\text{HH}} = 5\text{Hz}$). (**NMR Yield: 96 %**);
 ^{13}C NMR (C_6D_6 , 126 MHz): 64.3 (s, OCH_2), 126.2 (s, *e-C}_6\text{H}_4\text{Cl}), 126.6 (s, *g-C}_6\text{H}_4\text{Cl}), 127 (s, *h-C}_6\text{H}_4\text{Cl}), 128.1 (s, *c-C}_6\text{H}_4\text{Cl}), 129.3 (s, *f-C}_6\text{H}_4\text{Cl}), 130.2 (s, *l-C}_6\text{H}_4\text{Cl}), 130.2 (s, *b-C}_6\text{H}_4\text{Cl}), 130.8 (s, *d-C}_6\text{H}_4\text{Cl}), 131.5 (s, *a-C}_6\text{H}_4\text{Cl}), 137.2 (s, *j-C}_6\text{H}_4\text{Cl}), 164.6 9s, *i-C=O*).**********

Dimerization of o-phthalaldehyde:

2 (0.005 g, 0.004 mmol), o-phthalaldehyde (0.124 g, 0.92 mmol) and mesitylene (43 μ l, 0.31 mmol).



Scheme S5: Catalytic dimerization of o-phthalaldehyde.

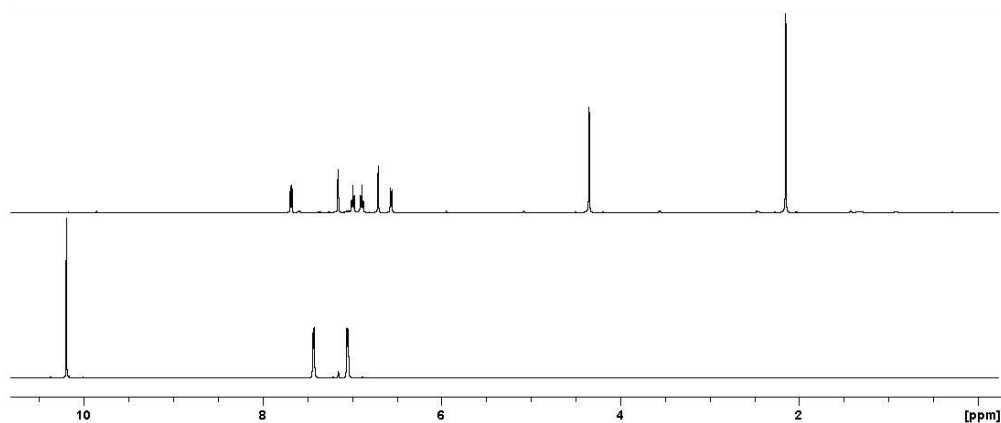


Figure S25: Stacking of 1H NMR spectra of o-phthalaldehyde (bottom) and after (top) the product formation recorded in C_6D_6 with internal reference (mesitylene).

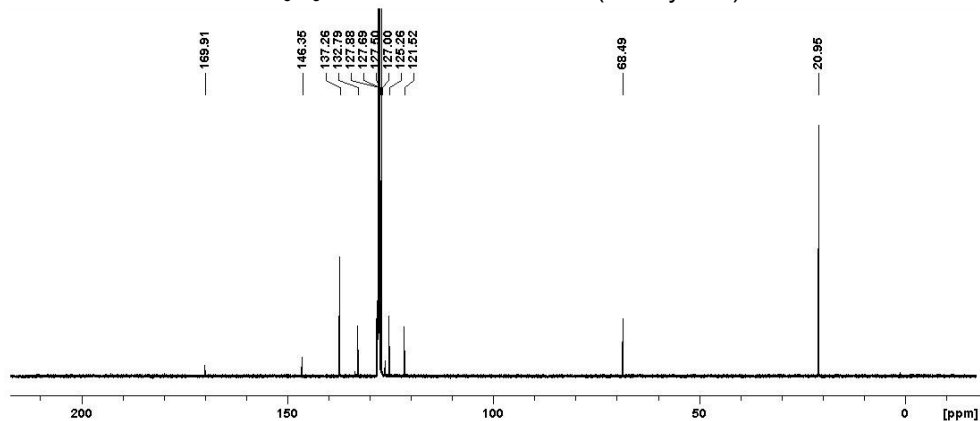
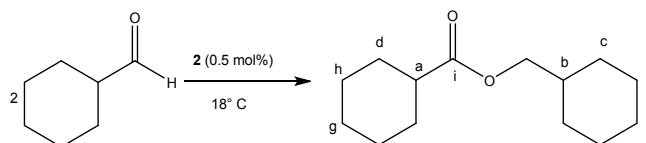


Figure S26: ^{13}C NMR spectrum ($[C_6D_6]$, 126 MHz) of 1-Isobenzofuranone.

1H NMR (C_6D_6 , 500 MHz)(Poor solubility): δ 4.35 (s, 2H, OCH_2), 6.56 (d, 1H, *a-CH*) ($^3J_{HH} = 5$ Hz), 6.99 (t, 1H, *b-CH*) ($^3J_{HH} = 5$ Hz), 6.89 (t, 1H, *c-CH*) ($^3J_{HH} = 5$ Hz), 7.68 (d, 1H, *d-CH*) ($^3J_{HH} = 10$ Hz). (**NMR Yield: 98 %**); ^{13}C NMR (C_6D_6 , 126 MHz): δ 68.5 (s, OCH_2), 121.5 (s, *d-C* $_6H_4$), 125.2 (s, *a-C* $_6H_4$), 128.5 (s, *b-C* $_6H_4$), 132.8 (s, *c-C* $_6H_4$), 137.2 (s, *e-C* $_6H_4$), 146.3 (s, *f-C* $_6H_4$), 169.9 (s, *i-C=O*).

Dimerization of cyclohexyl carboxaldehyde:

2 (0.005 g, 0.004 mmol), cyclohexyl carboxaldehyde (112.3 μ l, 0.92 mmol) and mesitylene (43 μ l, 0.31 mmol).



Scheme S6: Catalytic dimerization of cyclohexyl carboxaldehyde.

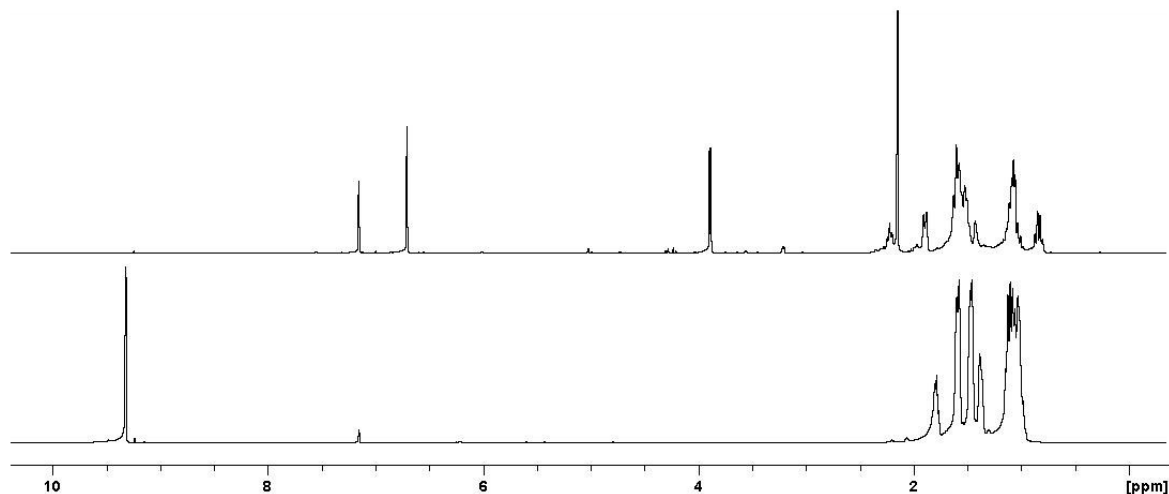


Figure S27: Stacking of ^1H NMR spectra of cyclohexyl carboxaldehyde (bottom) and after (top) the product formation recorded in C_6D_6 with internal reference (mesitylene).

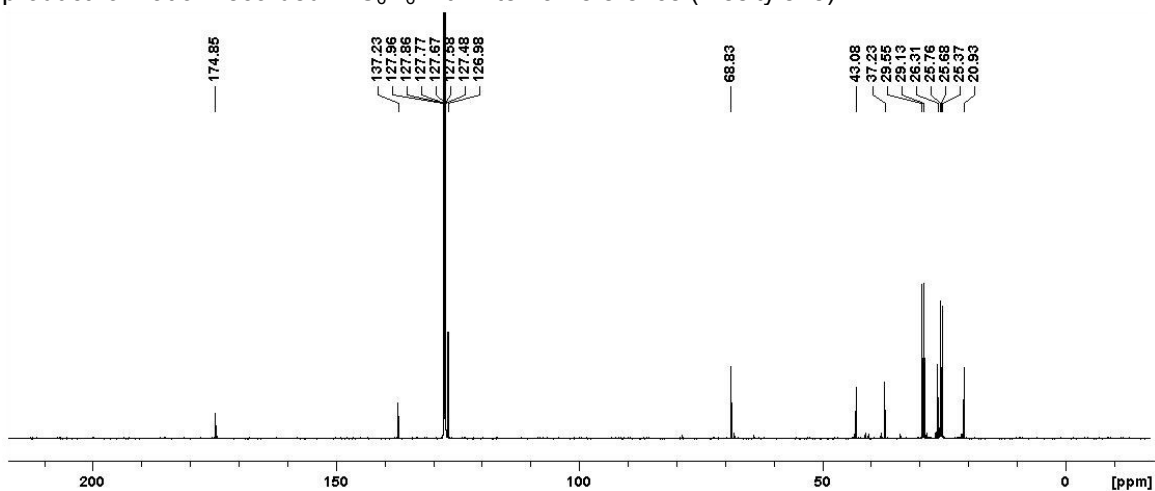
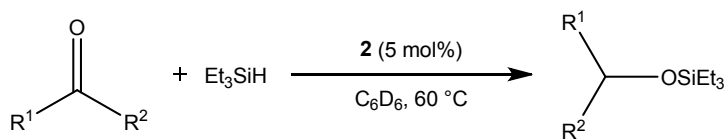


Figure S28: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of cyclohexylmethyl cyclohexanecarboxylate

^1H NMR (C_6D_6 , 500 MHz): δ 3.89 (s, 2H, OCH_2), 2.23 (m, 1H, CH), 1.9 (m, 1H, CH), 1.57 (m, 12H, CH_2), 1.08 (m, 6H, CH_2), 0.84 (m, 2H, CH_2). (NMR Yield: 98 %); ^{13}C NMR (C_6D_6 , 126 MHz): δ 25.3 (s, h - C_6H_{11}), 25.6 (s, g - C_6H_{11}), 25.7 (s, e - C_6H_{11}), 26.3 (s, f - C_6H_{11}), 29.1 (s, d - C_6H_{11}), 29.5 (s, c - C_6H_{11}), 37.2 (s, b - C_6H_{11}), 43.1 (s, a - C_6H_{11}), 68.8 (s, OCH_2), 174.8 (s, i - $\text{C}=\text{O}$).

CATALYTIC HYDROSILYLATION OF KETONES

Typical procedure: 5 mol % of **2** was loaded into an NMR tube fitted with a J Young joint containing C₆D₆ (0.5 mL). This was followed by the addition equimolar amounts of Et₃SiH and respective ketone. The solution was degassed by freeze-pump-thaw procedure and heated at 70 °C. The product formation was monitored by NMR spectroscopy. Mesitylene was used as an internal standard to calculate the yield of the product.



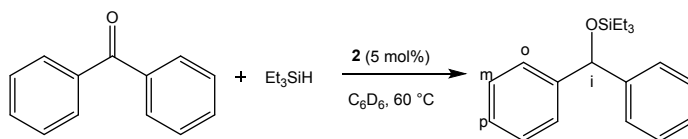
Scheme S7: General Hydrosilylation scheme

Table S2: Catalytic hydrosilylation promoted by **2**.

Substrate 1	Substrate 2	Temp (° C)	Product	Time (h)	Yield (%)
	Et ₃ SiH	60		32	95
	Et ₃ SiH	60		20	98
	Et ₃ SiH	60		34	98
	Et ₃ SiH	60		23	96
	Et ₃ SiH	60		15	98
	PhSiH ₃	25		108	99
	PhSiH ₃	25		53	99

Hydrosilylation of benzophenone:

2 (0.005 g, 0.004 mmol), benzophenone (0.0169 g, 0.09 mmol), triethylsilane (14.81 μ l, 0.09 mmol) and mesitylene (4.3 μ l, 0.03 mmol).



Scheme S8: Catalytic hydrosilylation of benzophenone.

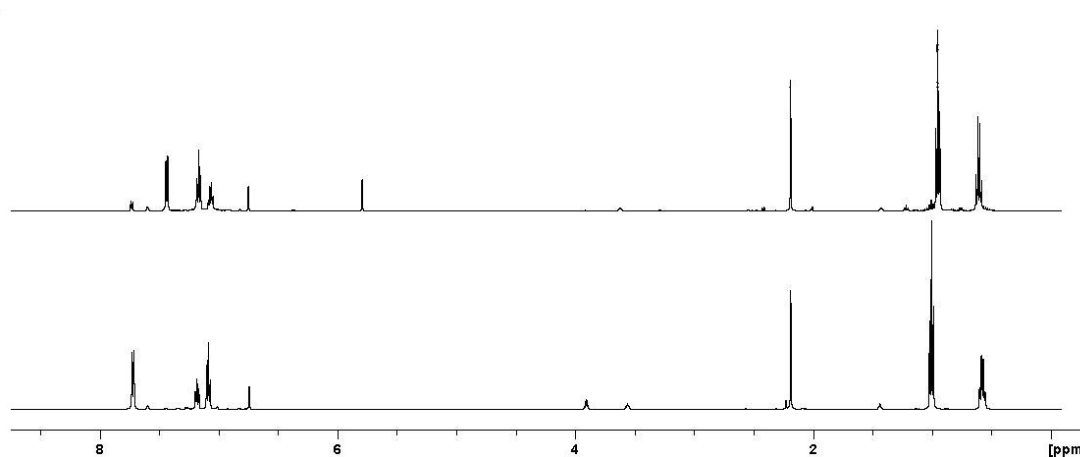


Figure S29: Stacking of ^1H NMR spectra of hydrosilylation mixture (Et_3SiH and benzophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C_6D_6 .

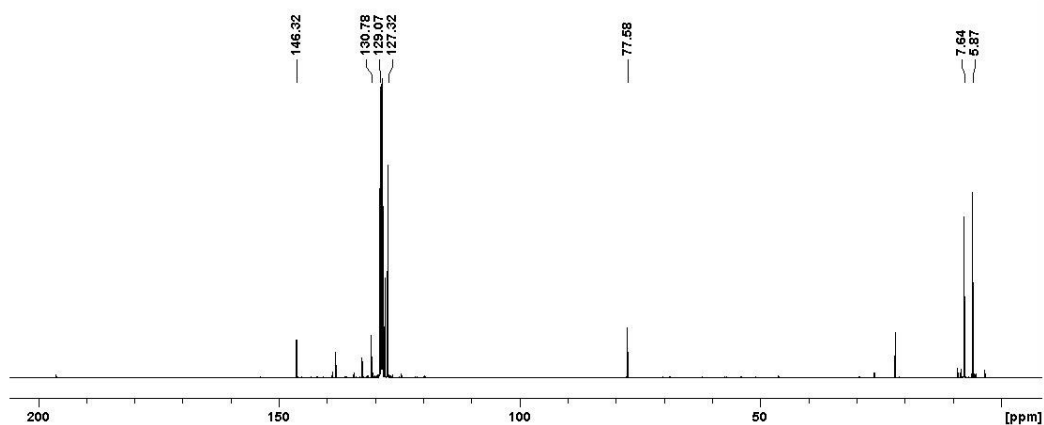
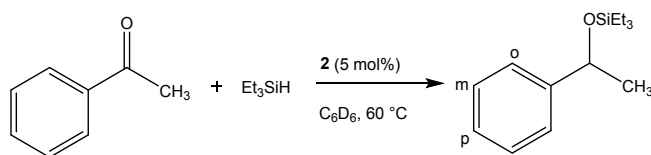


Figure S30: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of (benzhydroxy)triethylsilane

^1H NMR (C_6D_6 , 500 MHz): δ 0.59 (q, 6H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 5\text{Hz}$), 0.93 (t, 9H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 5\text{Hz}$), 2.16 (s, 3H, *Mes-CH*₃), 5.79 (s, 1H, *CH*), 6.71 (s, 1H, *Mes-CH*), 7.05 (t, 2H, *p-C*₆H₅) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.14 (t, 4H, *m-C*₆H₅) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.42 (t, 4H, *o-C*₆H₅) ($^3J_{\text{HH}} = 10\text{Hz}$). (**NMR Yield: 95.3 %**); ^{13}C NMR (C_6D_6 , 126 MHz): δ 5.8 (s, $\text{OSiCH}_2\text{CH}_3$), 7.6 (s, $\text{OSiCH}_2\text{CH}_3$), 77.5 (s, *CH-OSiEt*₃), 127.3 (s, *p-C*₆H₅), 129 (s, *o-C*₆H₅), 130.7 (s, *m-C*₆H₅), 146.3 (*i-C*₆H₅).

Hydrosilylation of acetophenone:

2 (0.005 g, 0.004 mmol), acetophenone (10.81 μ l, 0.09 mmol), triethylsilane (14.81 μ l, 0.09 mmol) and mesitylene (4.3 μ l, 0.03 mmol).



Scheme S9: Catalytic hydrosilylation of acetophenone.

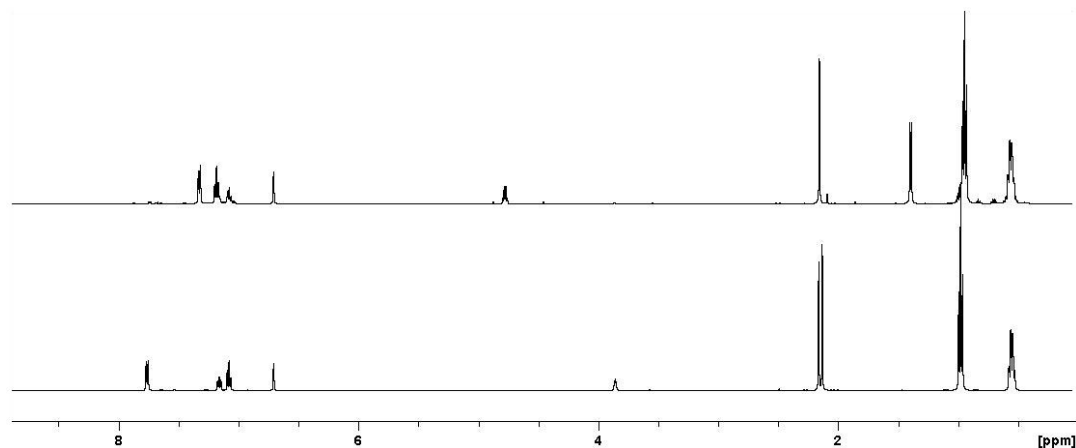


Figure S31: Stacking of ^1H NMR spectra of hydrosilylation mixture (Et_3SiH and acetophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C_6D_6 .

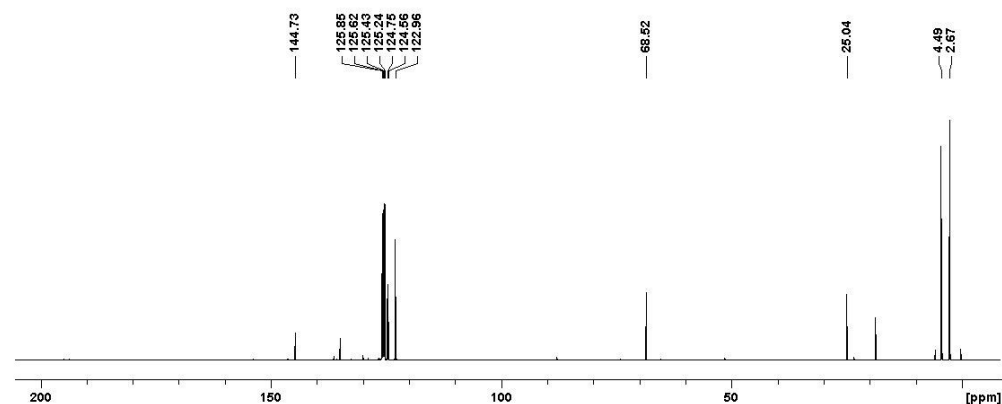
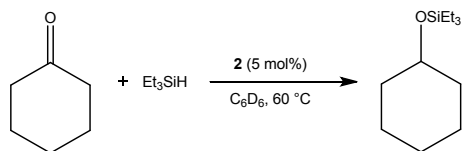


Figure S32: ^{13}C NMR ($[\text{C}_6\text{D}_6]$, 126 MHz) of triethyl(1-phenylethoxy)silane.

^1H NMR (C_6D_6 , 500 MHz): δ 0.57 (q, 6H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 10\text{Hz}$), 0.93 (t, 9H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 10\text{Hz}$), 1.39 (d, 3H, CH_3) ($^3J_{\text{HH}} = 10\text{Hz}$), 2.16 (s, 3H, Mes- CH_3), 4.77 (q, 1H, CH) ($^3J_{\text{HH}} = 10\text{Hz}$), 6.71 (s, 1H, Mes- CH), 7.08 (t, 2H, $p\text{-C}_6\text{H}_5$) ($^3J_{\text{HH}} = 5\text{Hz}$), 7.19 (t, 4H, $o\text{-C}_6\text{H}_5$) ($^3J_{\text{HH}} = 5\text{Hz}$), 7.33 (t, 4H, $m\text{-C}_6\text{H}_5$) ($^3J_{\text{HH}} = 5\text{Hz}$). (**NMR Yield: 98 %**); **^{13}C NMR (C_6D_6 , 126 MHz):** δ 2.6 (s, $\text{OSiCH}_2\text{CH}_3$), 4.5 (s, $\text{OSiCH}_2\text{CH}_3$), 25 (s, $\text{CH}_3\text{CHPhOSiEt}_3$), 68.5 (s, CH-OSiEt_3), 123 (s, $m\text{-C}_6\text{H}_5$), 124.5 (s, $p\text{-C}_6\text{H}_5$), 124.7 (s, $m\text{-C}_6\text{H}_5$), 144.7 ($i\text{-C}_6\text{H}_5$).

Hydrosilylation of cyclohexanone:

5 Mol% **2** (0.01 g, 0.009 mmol), cyclohexanone (19.2 μ l, 0.18 mmol), triethylsilane (29.62 μ l, 0.18 mmol) and mesitylene (8.6 μ l, 0.06 mmol).



Scheme S10: Catalytic hydrosilylation of cyclohexanone.

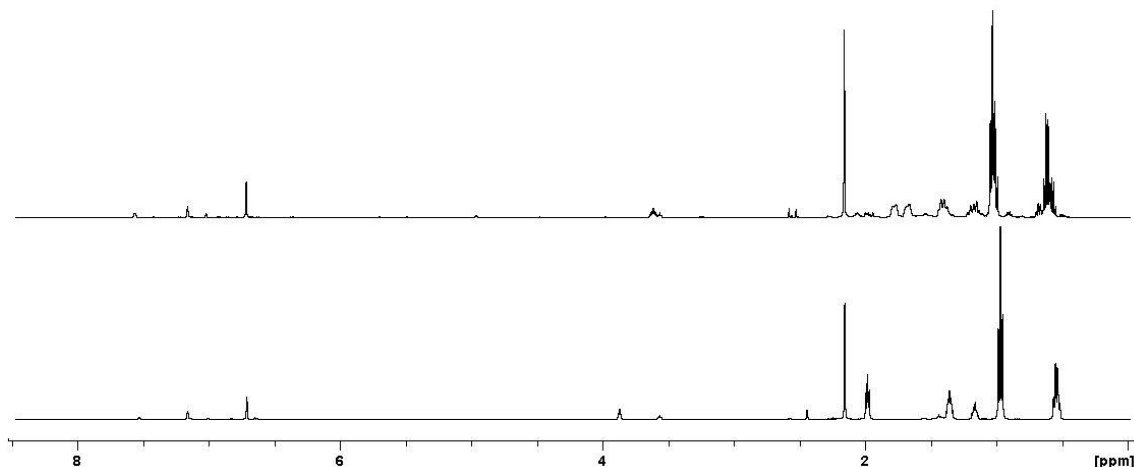


Figure S33: Stacking of ^1H NMR spectra of hydrosilylation mixture (Et_3SiH and cyclohexanone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C_6D_6 .

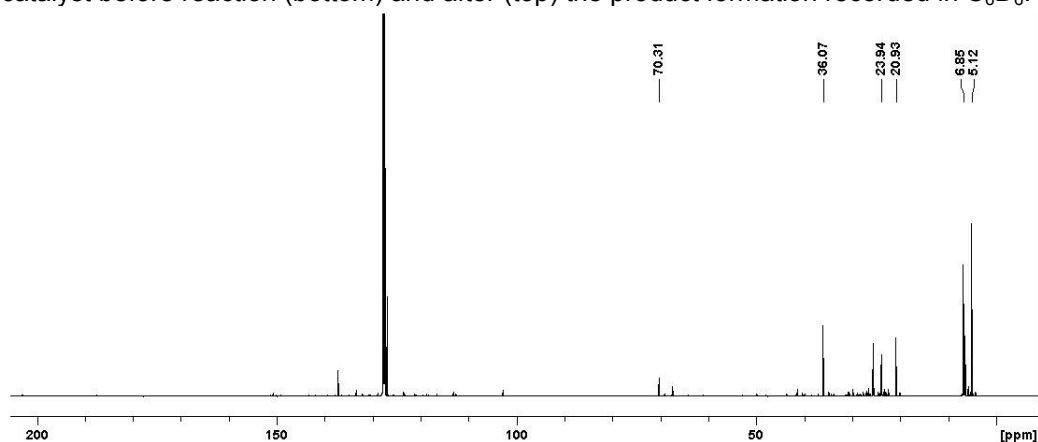
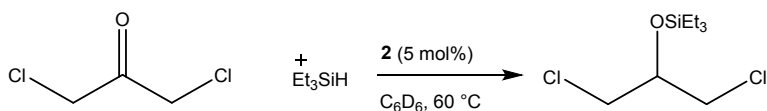


Figure S34: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of (cyclohexyloxy)triethylsilane

^1H NMR (C_6D_6 , 500 MHz): δ 0.57 (q, 6H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 10\text{Hz}$), 0.62 (t, 9H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 5\text{Hz}$), 1.03 (s, 3H, CH_3), 1.21 (m, 3H, C_6H_{10}), 1.43 (m, 3H, C_6H_{10}), 1.68 (m, 2H, C_6H_{10}), 1.77 (m, 2H, C_6H_{10}), 2.16 (s, 3H, *Mes-CH*), 3.61 (q, 1H, *CH*), 6.71 (s, 1H, *Mes-CH*). (NMR Yield: 96 %); ^{13}C NMR (C_6D_6 , 126 MHz): δ 5.1 (s, $\text{OSiCH}_2\text{CH}_3$), 6.8 (s, $\text{OSiCH}_2\text{CH}_3$), 21 (s, $\alpha\text{-C}_6\text{H}_{11}$), 24 (s, $\gamma\text{-C}_6\text{H}_{11}$), 36 (s, $\alpha, \beta\text{-C}_6\text{H}_{11}$), 70.3 (s, CHOSiEt_3).

Hydrosilylation of 1, 3-dichloroacetone:

2 (0.01 g, 0.009 mmol), 1, 3-dichloroacetone (0.02 g, 0.18 mmol), triethylsilane (29.62 μ l, 0.18 mmol) and mesitylene (8.6 μ l, 0.06 mmol).



Scheme S11: Catalytic hydrosilylation of 1, 3-dichloroacetone.

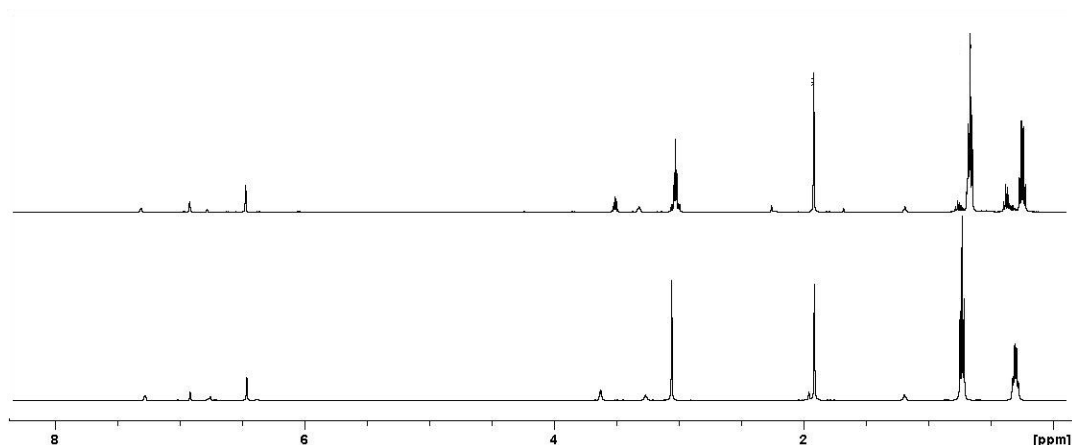


Figure S35: Stacking of ^1H NMR spectra of hydrosilylation mixture (Et_3SiH and 1, 3-dichloroacetone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C_6D_6 .

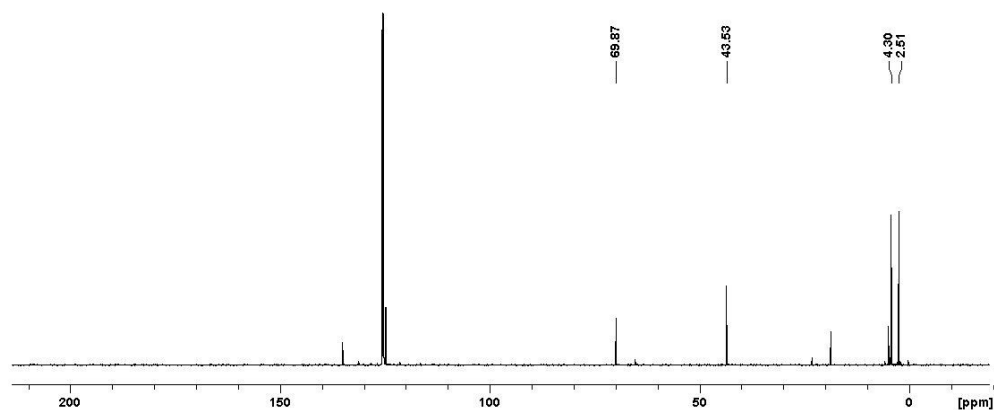
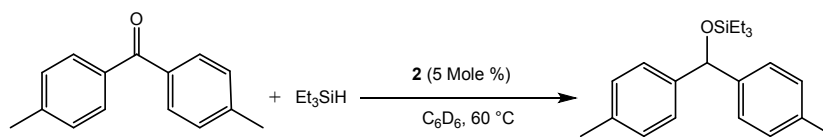


Figure S36: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of ((1,3-dichloropropan-2-yl)oxy)triethylsilane.

^1H NMR (C_6D_6 , 500 MHz): δ 0.48 (q, 6H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 5\text{Hz}$), 0.9 (t, 9H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 5\text{Hz}$), 2.16 (s, 3H, Mes- CH_3), 3.25 (t, 4H, CH_2) ($^3J_{\text{HH}} = 5\text{Hz}$), 3.74 (q, 1H, CH) ($^3J_{\text{HH}} = 5\text{Hz}$), 6.71 (s, 1H, Mes- CH). (NMR Yield: 98 %); ^{13}C NMR (C_6D_6 , 126 MHz): δ 2.5 (s, $\text{OSiCH}_2\text{CH}_3$), 4.3 (s, $\text{OSiCH}_2\text{CH}_3$), 43.5 (s, CH_2Cl), 69.8 (s, CHOSiEt_3).

Hydrosilylation of 4, 4'-dimethylbenzophenone:

2 (0.01 g, 0.009 mmol), 4, 4'-dimethylbenzophenone (0.03, 0.18 mmol), triethylsilane (29.62 μ l, 0.18 mmol) and mesitylene (8.6 μ l, 0.06 mmol).



Scheme S12: Catalytic hydrosilylation of 4, 4'-dimethylbenzophenone.

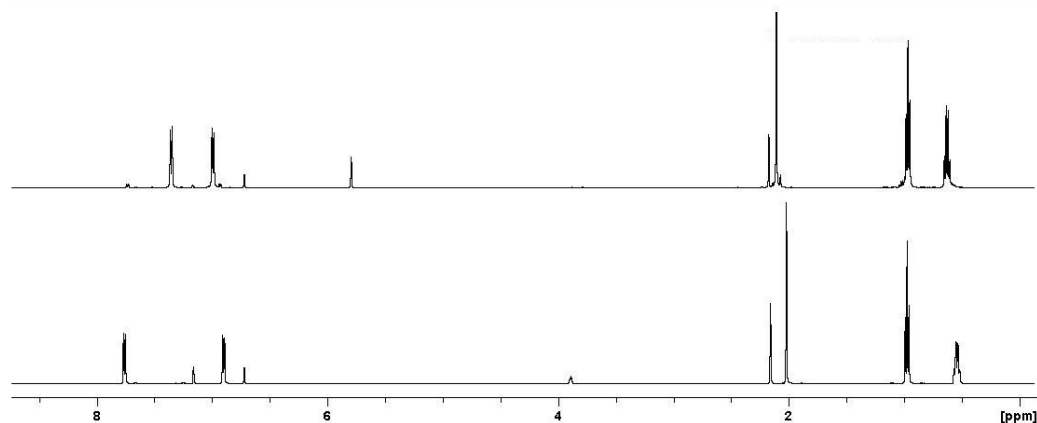


Figure S37: Stacking of ^1H NMR spectra of hydrosilylation mixture (Et_3SiH and 4, 4'-dimethylbenzophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C_6D_6 .

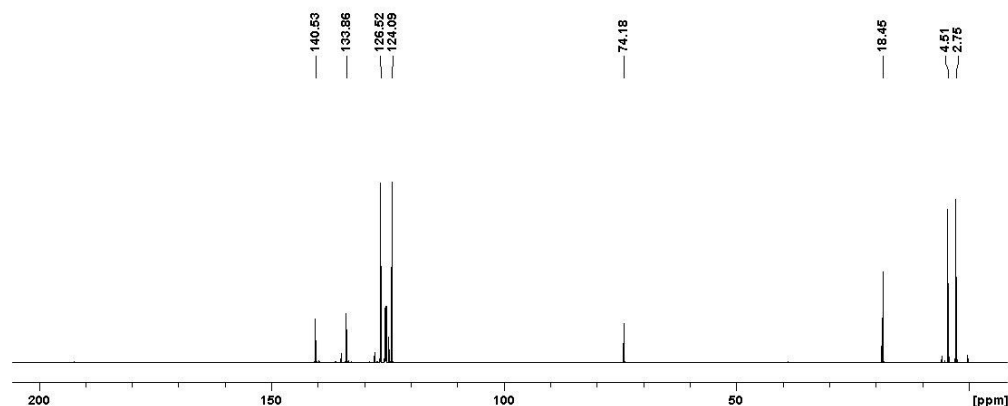


Figure S38: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of (di-p-tolylmethoxy)triethylsilane.

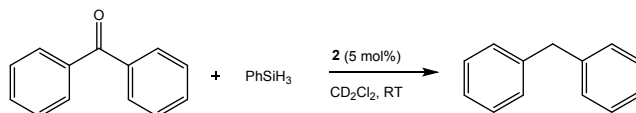
^1H NMR (C_6D_6 , 500 MHz): δ 0.62 (q, 6H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 5\text{Hz}$), 0.96 (t, 9H, $\text{OSiCH}_2\text{CH}_3$) ($^3J_{\text{HH}} = 5\text{Hz}$), 2.09 (s, CH_3), 2.16 (s, 3H, *Mes-CH*₃), 5.79 (s, 1H, *CH*), 6.72 (s, 1H, *Mes-CH*), 6.99 (d, 4H, C_6H_4) ($^3J_{\text{HH}} = 10\text{Hz}$), 7.37 (d, 4H, C_6H_4) ($^3J_{\text{HH}} = 10\text{Hz}$). (NMR Yield: 98 %); ^{13}C NMR (C_6D_6 , 126 MHz): δ 2.7 (s, $\text{OSiCH}_2\text{CH}_3$), 4.5 (s, $\text{OSiCH}_2\text{CH}_3$), 18.4 (s, CH_3), 74.2 (s, *CH-OSiEt*₃), 125 (s, $\alpha\text{-C}_6\text{H}_5$), 126.5 (s, $\beta\text{-C}_6\text{H}_5$), 133.8 (s, $\gamma\text{-C}_6\text{H}_5$), 140.5 (*i-C*₆H₅).

Deoxygenation of ketones.

Typical procedure: 5 mol % of **2** was loaded into an NMR tube fitted with a J Young joint containing CD₂Cl₂ (0.5 mL). This was followed by the addition equimolar amounts of PhSiH₃ and respective ketone. The solution was degassed by freeze-pump-thaw procedure and heated at 70 °C. The product formation was monitored by NMR spectroscopy. Mesitylene was used as an internal standard to calculate the yield of the product.

Deoxygenation of benzophenone

5 Mol% **2** (0.01 g, 0.009 mmol), benzophenone (0.03g, 0.18 mmol), phenylsilane (7.61 μl, 0.06 mmol) and mesitylene (8.6 μl, 0.06 mmol).



Scheme S13: Catalytic deoxygenation of benzophenone.

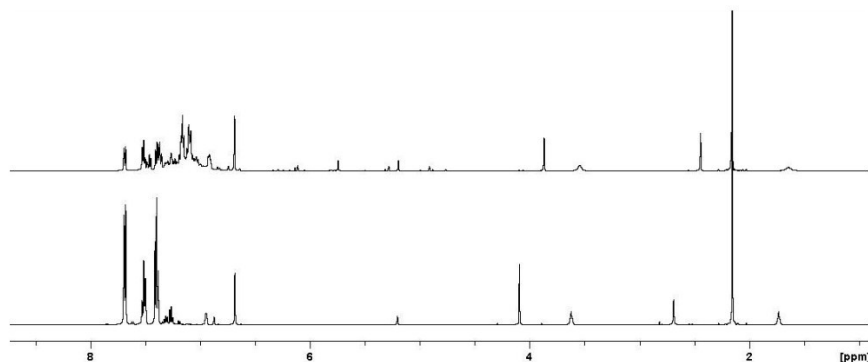


Figure S39: Stacking of ¹H NMR spectra of hydrosilylation mixture (PhSiH₃ and benzophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in CD₂Cl₂.

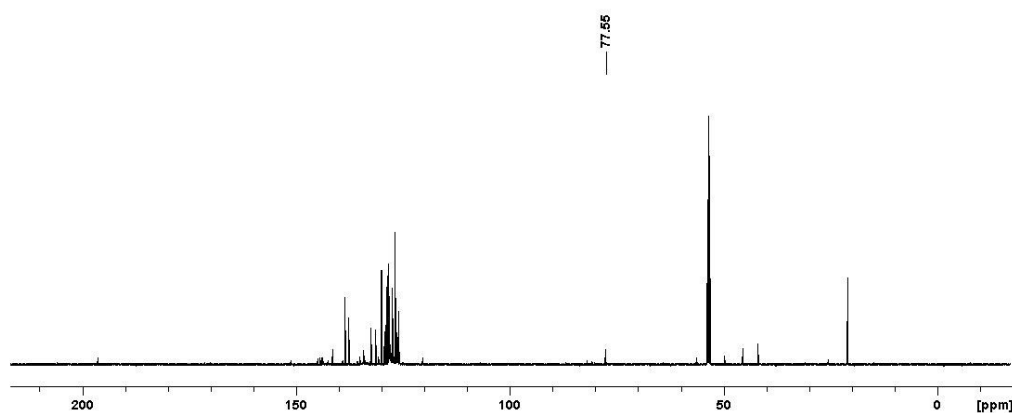
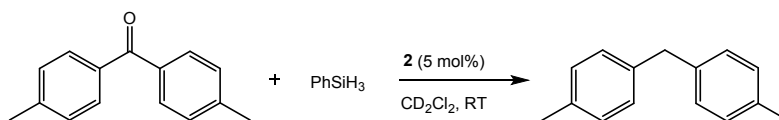


Figure S40: ¹³C NMR spectrum ([CD₂Cl₂], 126 MHz) of diphenylmethane.

¹H NMR (CD₂Cl₂, 500 MHz): δ 3.97 (s, Ph₂CH₂), 5.29 (s, PhSiH₂), 5.84 (s, Ph₂CHSiO) (NMR Yield: 99 % with respect to PhSiH₃); ¹³C NMR (CD₂Cl₂, 126 MHz): δ 77.5 (s, Ph₂CH₂).

Deoxygenation of 4,4'-dimethylbenzophenone

5 Mol% **2** (0.01 g, 0.009 mmol), 4, 4'-dimethylbenzophenone (0.03g, 0.18 mmol), phenylsilane (7.61 μ l, 0.06 mmol) and mesitylene (8.6 μ l, 0.06 mmol).



Scheme S14: Catalytic deoxygenation of 4, 4'-dimethylbenzophenone.

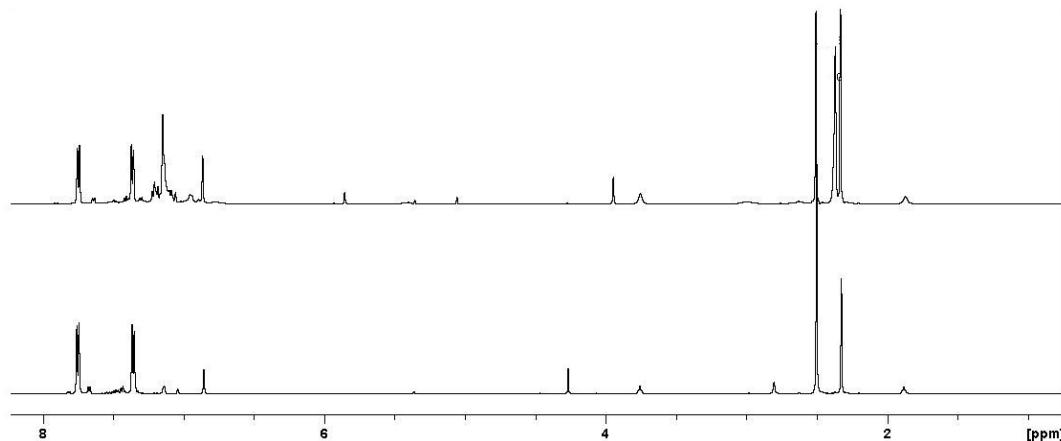


Figure S41: Stacking of ¹H NMR spectra of hydrosilylation mixture (PhSiH₃ and 4,4'-dimethylbenzophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in CD₂Cl₂.

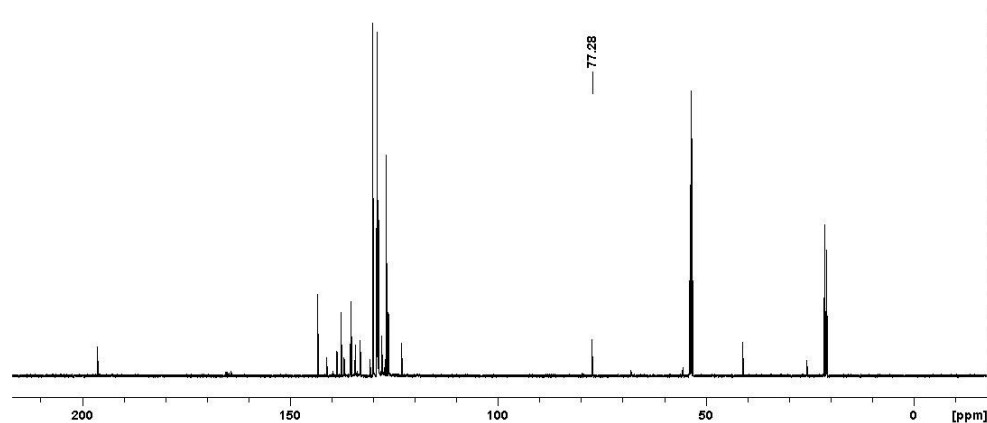


Figure S42: ¹³C NMR spectrum ([CD₂Cl₂], 126 MHz) of di-p-tolylmethane.

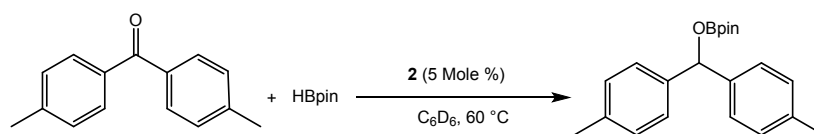
¹H NMR (CD₂Cl₂, 500 MHz): δ 4 (s, Ph₂CH₂), 5.33 (s, PhSiH₂), 5.88 (s, Ph₂CHSiO) (NMR Yield: 99 % with respect to PhSiH₃); ¹³C NMR (CD₂Cl₂, 126 MHz): δ 77.3 (s, Ph₂CH₂).

HYDROBORATION AND HYDROSTANNYLATION OF 4,4'-DIMETHYLBENZOPHENONE

Typical procedure: 5 mol % of **2** was loaded into an NMR tube fitted with a J Young joint containing CD₂Cl₂ (0.5 mL). This was followed by the addition equimolar amounts of HBpin/ (tBu)₃SnH and respective ketone. The solution was degassed by freeze-pump-thaw procedure and heated at 70 °C in the case of hydroboration while hydrostannylation was performed at ambient temperature. The product formation was monitored by NMR spectroscopy. Yield of the reactions at 20h was recorded. Mesitylene was used as an internal standard to calculate the yield of the product.

Hydroboration of 4,4'-dimethylbenzophenone:

2 (0.005 g, 0.004 mmol), 4,4'-dimethylbenzophenone (0.02g, 0.09 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (13.45 µl, 0.09 mmol) and mesitylene (4.3 µl, 0.03 mmol).



Scheme S15: Catalytic hydroboration of 4, 4'-dimethylbenzophenone.

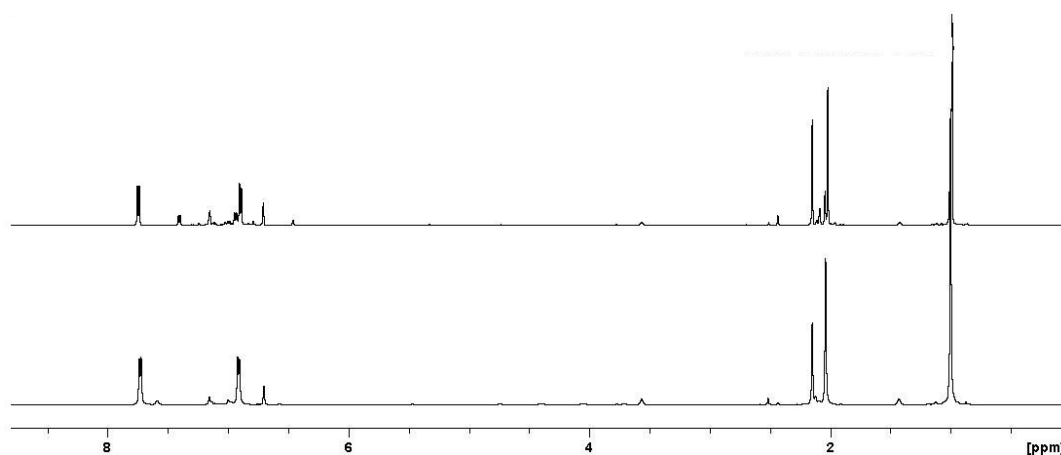


Figure S43: Stacking of ¹H NMR spectra of hydroboration mixture (HBpin and 4, 4'-dimethyl benzophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C₆D₆.

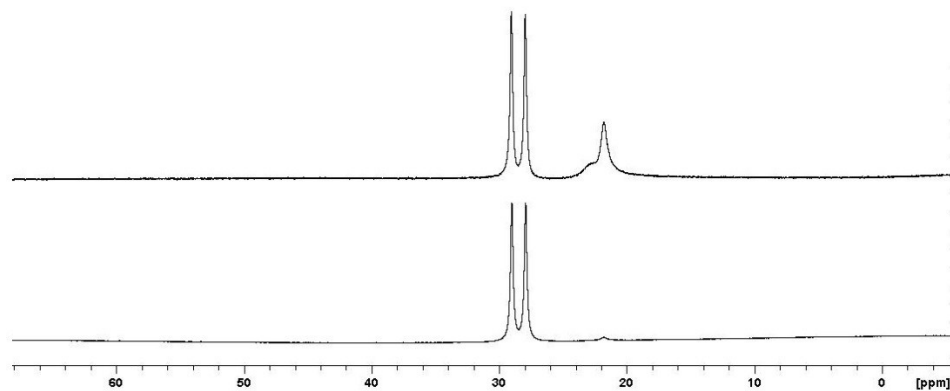


Figure S44: Stacking of ¹¹B NMR spectra of hydroboration mixture (PhSiH₃ and 4,4'-dimethyl benzophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C₆D₆.

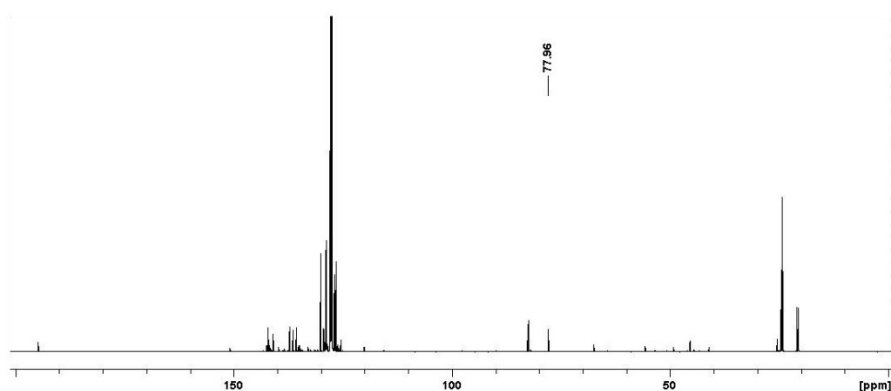


Figure S45: ¹³C NMR spectrum ([C₆D₆], 126 MHz) of 2-(di-p-tolylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

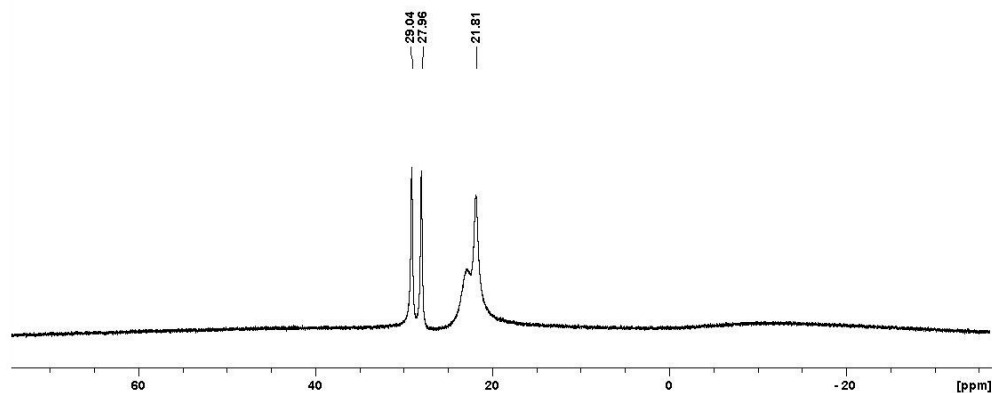
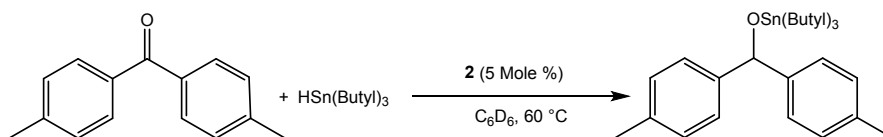


Figure S46: ¹¹B NMR spectrum ([C₆D₆], 160.5 MHz) of 2-(di-p-tolylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

¹H NMR (C₆D₆, 500 MHz): δ 6.47 (s, 1H, *CHOBpin*). (**NMR Yield at 20 h: 32 %** with respect to HBpin consumption from ¹¹B NMR); **¹³C NMR (C₆D₆, 126 MHz):** δ 78 (s, *CHOBpin*); **¹¹B NMR (C₆D₆, 160.5 MHz):** 21.8 (s, *CHOBpin*).

Hydrostannylation of 4,4'-dimethylbenzophenone

2 (0.005 g, 0.004 mmol), 4,4'-dimethylbenzophenone (0.019g, 0.09 mmol), tributyltinhydride (24.94 μ l, 0.09 mmol) and mesitylene (4.3 μ l, 0.03 mmol).



Scheme S16: Catalytic hydrostannylation of 4, 4'-dimethylbenzophenone.

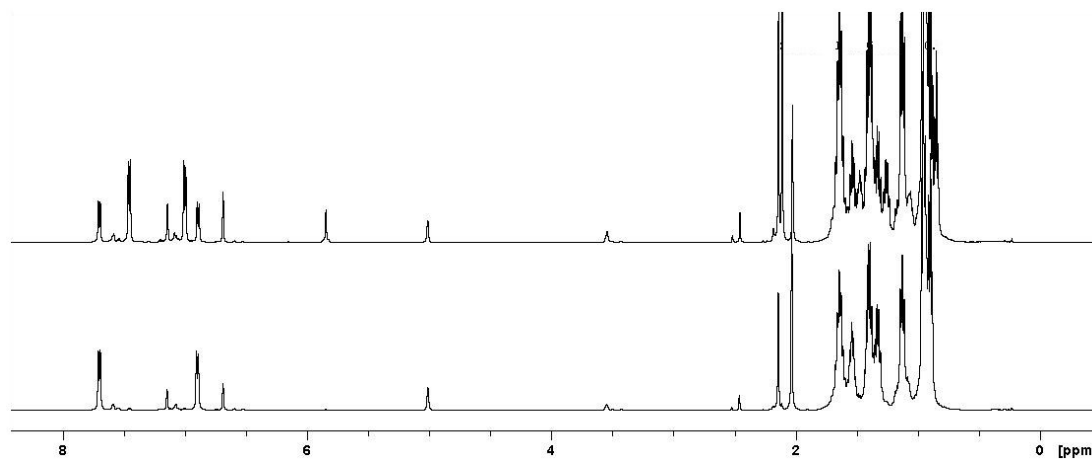


Figure S47: Stacking of ^1H NMR spectra of hydrostannylation mixture ($\text{HSn}(\text{Butyl})_3$ and 4,4'-dimethylbenzophenone) with catalyst before reaction (bottom) and after (top) the product formation recorded in C_6D_6 .

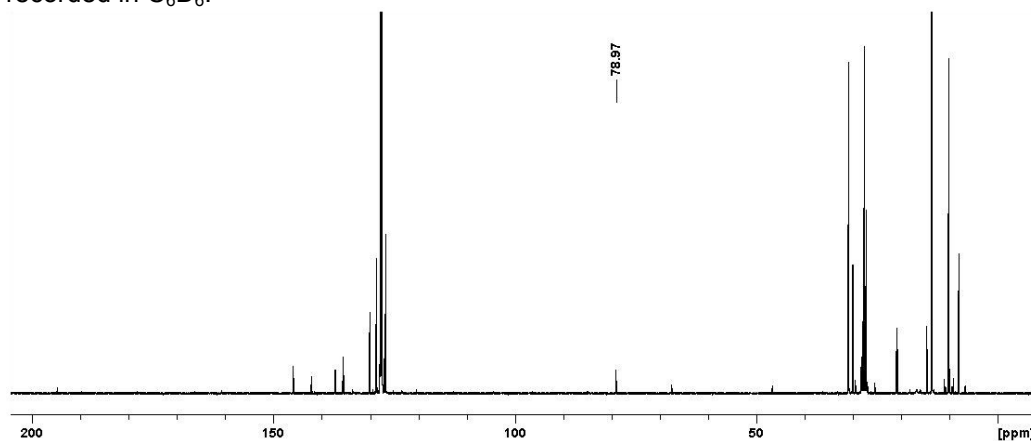


Figure S48: ^{13}C NMR spectrum ($[\text{C}_6\text{D}_6]$, 126 MHz) of tributyl(di-p-tolylmethoxy)stannane.

^1H NMR (C_6D_6 , 500 MHz): δ 5.85 (s, 2H, $\text{CHOSn}(\text{Butyl})_3$). (NMR Yield: 57.5 % with respect to the tributyltinhydride conversion); ^{13}C NMR (C_6D_6 , 126 MHz): δ 79 (s, $\text{CHOSn}(\text{Butyl})_3$).

OTHER NMR SPECTRA

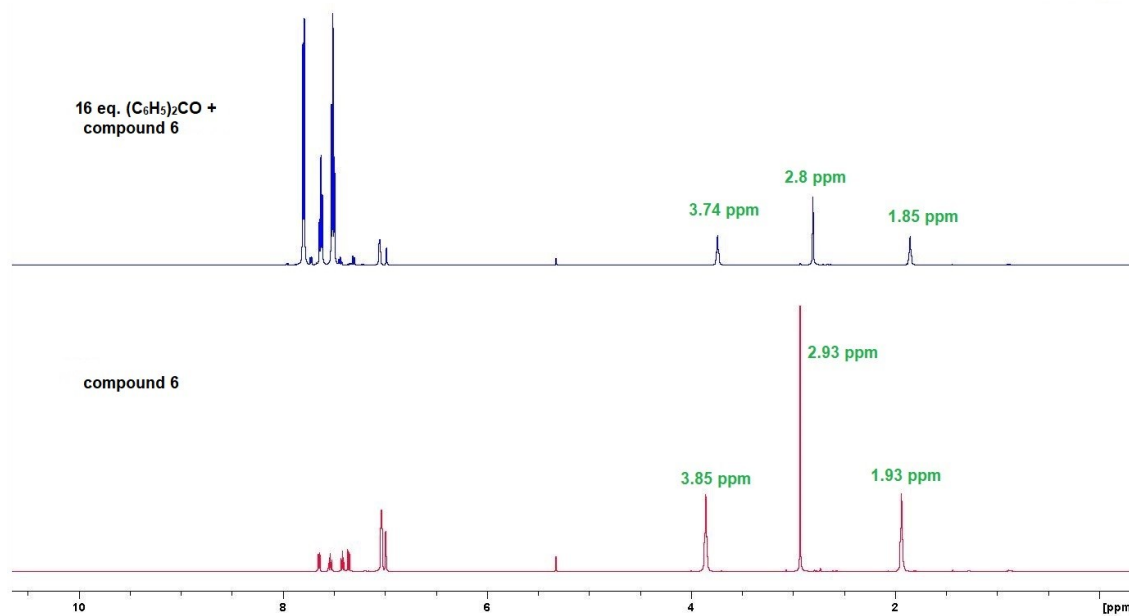


Figure S49: Stacking of ¹H NMR spectra of **2** (bottom) and **2**+16 eq. benzophenone (top) in CD₂D₂.

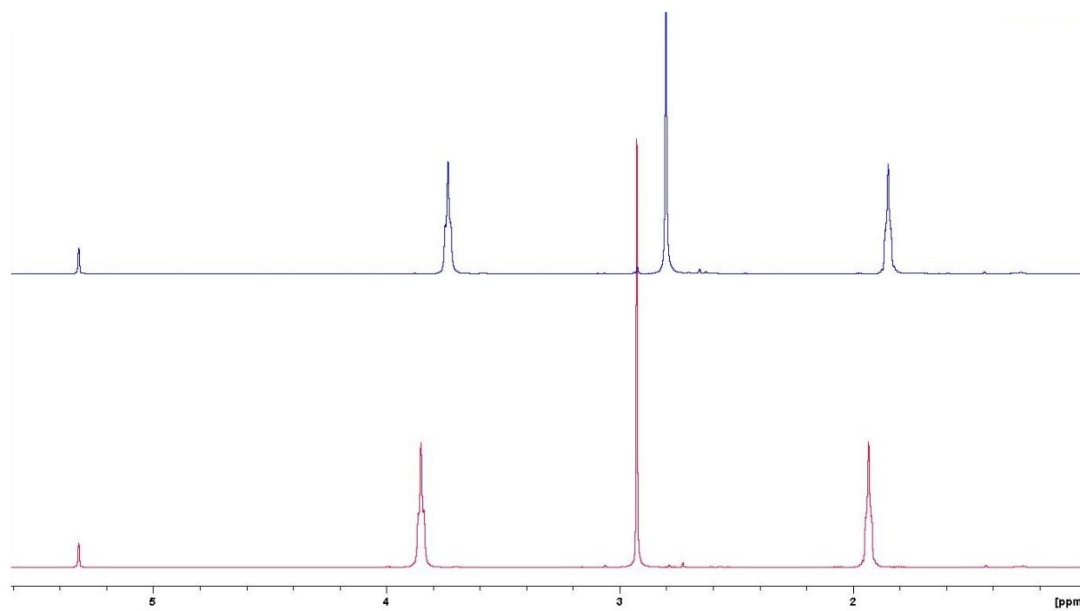


Figure S49a: Expanded form of stacked ¹H NMR spectra of **2** (bottom) and **2**+16 eq. benzophenone (top) in CD₂D₂.

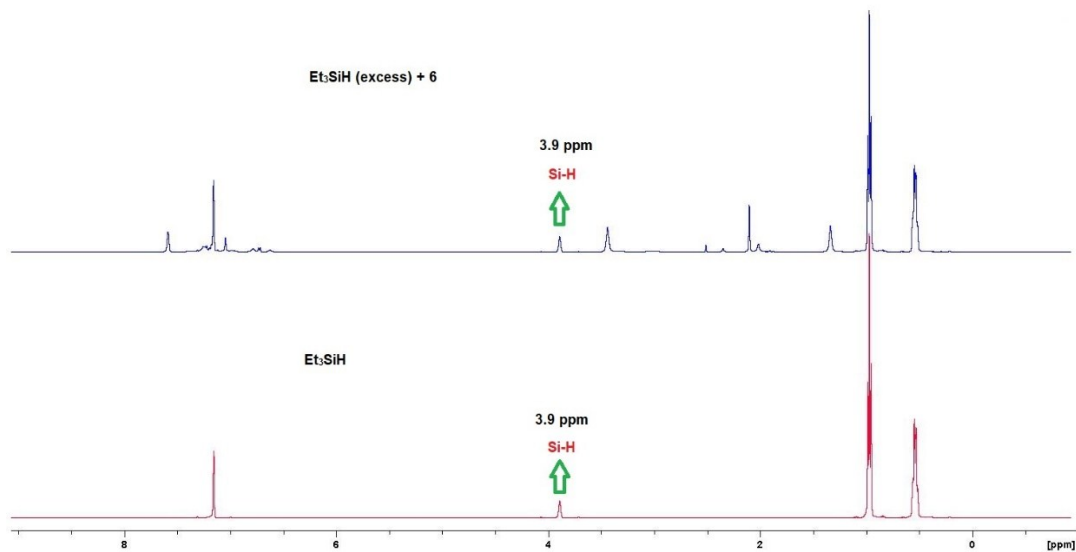


Figure S50: Stacking of ¹H NMR spectra of triethylsilane (bottom) and (top) triethylsilane + **2** in the ratio of 3:1 in C₆D₆.

Table S3: Reaction between Ph₂C=O and Et₃SiH in C₆D₆ at 60 °C catalyzed by **2** (5 mol%).

Et ₃ SiH:Ph ₂ C=O	Yield (6h)
1:1	45
1:2	58
1:4	63
1:6	67
1:8	72
1:10	76

Crystallographic Data

Table S4. Crystal data and structure refinement for **1**.

Identification code	compound_1
CCDC Code	1959215
Empirical formula	C ₁₆ H ₂₀ Al Cl N ₂
Formula weight	302.77
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P c c n
Unit cell dimensions	a = 17.9517(6) Å α = 90°. b = 22.8784(10) Å β = 90°. c = 7.7265(2) Å γ = 90°.
Volume	3173.32(19) Å ³
Z	8
Density (calculated)	1.267 Mg/m ³
Absorption coefficient	0.288 mm ⁻¹
F(000)	1280
Crystal size	0.120 x 0.100 x 0.080 mm ³
Theta range for data collection	2.902 to 24.998°.
Index ranges	-21 ≤ h ≤ 20, -27 ≤ k ≤ 17, -8 ≤ l ≤ 9
Reflections collected	12071
Independent reflections	2795 [R(int) = 0.0386]
Completeness to theta = 24.998°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.977 and 0.966
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2795 / 0 / 181
Goodness-of-fit on F ²	1.011
Final R indices [I > 2σ(I)]	R1 = 0.0354, wR2 = 0.0786
R indices (all data)	R1 = 0.0552, wR2 = 0.0890
Extinction coefficient	n/a
Largest diff. peak and hole	0.262 and -0.183 e.Å ⁻³

Table S5. Crystal data and structure refinement for **2**.

Identification code	compound_2	
CCDC Code	1959217	
Empirical formula	C ₅₀ H ₅₂ Al B Cl ₈ N ₂ O ₂	
Formula weight	1034.32	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 17.421(6) Å	α = 90°.
	b = 16.199(5) Å	β = 95.551(12)°.
	c = 17.674(6) Å	γ = 90°.
Volume	4964(3) Å ³	
Z	4	
Density (calculated)	1.384 Mg/m ³	
Absorption coefficient	0.513 mm ⁻¹	
F(000)	2144	
Crystal size	0.200 x 0.200 x 0.150 mm ³	
Theta range for data collection	1.174 to 24.994°.	
Index ranges	-20 ≤ h ≤ 20, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	
Reflections collected	60479	
Independent reflections	8730 [R(int) = 0.0813]	
Completeness to theta = 24.994°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.927 and 0.904	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8730 / 0 / 581	
Goodness-of-fit on F ²	1.014	
Final R indices [I > 2σ(I)]	R1 = 0.0448, wR2 = 0.1087	
R indices (all data)	R1 = 0.0698, wR2 = 0.1233	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.708 and -0.360 e.Å ⁻³	

Table S6. Crystal data and structure refinement for **3**.

Identification code	compound_3
CCDC Code	1959216
Empirical formula	C ₅₂ H ₆₂ Al B Cl ₈ N ₂ O ₂ P ₂
Formula weight	1130.36
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 14.079(5) Å α = 90° b = 17.811(6) Å β = 90° c = 22.443(7) Å γ = 90°
Volume	5628(3) Å ³
Z	4
Density (calculated)	1.334 Mg/m ³
Absorption coefficient	0.513 mm ⁻¹
F(000)	2352
Crystal size	0.120 x 0.080 x 0.075 mm ³
Theta range for data collection	1.815 to 25.998°
Index ranges	-17<=h<=16, -21<=k<=21, -27<=l<=27
Reflections collected	82574
Independent reflections	11056 [R(int) = 0.1664]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.963 and 0.941
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11056 / 253 / 551
Goodness-of-fit on F ²	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1282
R indices (all data)	R1 = 0.1434, wR2 = 0.1647
Absolute structure parameter	0.04(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.450 and -0.550 e.Å ⁻³

Table S7. Crystal data and structure refinement for **4**

Identification code	compound_4
CCDC Code	1959218
Empirical formula	C ₅₂ H ₆₈ Al B Cl ₈ N ₈ O ₂ P ₂
Formula weight	1220.47
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 13.7249(5) Å α = 90° b = 12.1252(4) Å β = 92.707(2)° c = 36.2951(12) Å γ = 90°
Volume	6033.4(4) Å ³
Z	4
Density (calculated)	1.344 Mg/m ³
Absorption coefficient	0.487 mm ⁻¹
F(000)	2544
Crystal size	0.240 x 0.185 x 0.120 mm ³
Theta range for data collection	1.771 to 25.998°
Index ranges	-16 ≤ h ≤ 16, -14 ≤ k ≤ 14, -44 ≤ l ≤ 44
Reflections collected	86993
Independent reflections	11842 [R(int) = 0.1179]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.944 and 0.892
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11842 / 430 / 863
Goodness-of-fit on F ²	1.001
Final R indices [I > 2σ(I)]	R1 = 0.0690, wR2 = 0.1763
R indices (all data)	R1 = 0.1256, wR2 = 0.2205
Extinction coefficient	n/a
Largest diff. peak and hole	0.848 and -0.512 e.Å ⁻³

Computational Details:

All DFT computations were performed using Gaussian 09^[5] quantum chemistry program package for molecular geometry optimization and energy calculations. Density functional theory (DFT) with the meta-hybrid functional M06-2X^[6] and the correlation-consistent polarized valence split basis set, cc-pVTZ^[7] for all atoms were used. Hessian matrix of force constants of stationary points were calculated to characterize intermediates and transition state on potential energy surface. Zero-point corrected energies are reported for all isomers. Natural bond orbital (NBO)^[8] analysis was carried out using NBO 6.0 as implemented in the Gaussian 09 program package to calculate charges on C and O atoms using the same level of theory (M06-2X/cc-pVTZ).

DFT Optimized coordinates of molecules

Cartesian coordinates and zero-point corrected total energies (a.u.) of DFT optimized structures using M06-2X functional and cc-pVTZ basis set for all atoms.

Compound 1

$E_{\text{TOTAL}} = -1433.595584$ a.u.

6	-0.553554000	1.669503000	-0.343643000
6	0.716066000	2.234303000	-0.324160000
6	1.028731000	3.478970000	-0.850225000
1	2.035182000	3.878054000	-0.809076000
6	0.000000000	4.205291000	-1.430866000
1	0.198770000	5.181948000	-1.851522000
6	-1.289195000	3.681252000	-1.472491000
1	-2.082749000	4.260075000	-1.927153000
6	-1.562815000	2.429291000	-0.937455000
1	-2.578975000	2.055745000	-0.987128000
6	2.310925000	1.954590000	1.502587000
1	2.982994000	2.766118000	1.208117000
1	2.876510000	1.191180000	2.034514000
1	1.539486000	2.337034000	2.164923000
6	2.703585000	0.859006000	-0.611694000
1	2.218146000	0.406146000	-1.474018000
1	3.310232000	0.107057000	-0.107757000
1	3.350306000	1.675119000	-0.947291000
6	0.553554000	-1.669503000	-0.343643000

6	-0.716066000	-2.234303000	-0.324160000
6	-1.028731000	-3.478970000	-0.850225000
1	-2.035182000	-3.878054000	-0.809076000
6	0.000000000	-4.205291000	-1.430866000
1	-0.198770000	-5.181948000	-1.851522000
6	1.289195000	-3.681252000	-1.472491000
1	2.082749000	-4.260075000	-1.927153000
6	1.562815000	-2.429291000	-0.937455000
1	2.578975000	-2.055745000	-0.987128000
6	-2.703585000	-0.859006000	-0.611694000
1	-2.218146000	-0.406146000	-1.474018000
1	-3.310232000	-0.107057000	-0.107757000
1	-3.350306000	-1.675119000	-0.947291000
6	-2.310925000	-1.954590000	1.502587000
1	-2.982994000	-2.766118000	1.208117000
1	-2.876510000	-1.191180000	2.034514000
1	-1.539486000	-2.337034000	2.164923000
7	1.681198000	1.345891000	0.322979000
7	-1.681198000	-1.345891000	0.322979000
13	0.000000000	0.000000000	0.584607000
17	0.000000000	0.000000000	2.758032000

Compound 2

$E_{\text{TOTAL}} = -1437.802646$ a.u.

6	-0.373098000	1.791246000	-0.720912000
6	-1.260140000	2.181608000	0.279761000
6	-2.056367000	3.315948000	0.212323000
1	-2.735282000	3.579885000	1.013945000
6	-1.961766000	4.110578000	-0.920337000
1	-2.568379000	5.001565000	-1.006718000
6	-1.087581000	3.762033000	-1.944656000
1	-1.023499000	4.387089000	-2.825360000
6	-0.307521000	2.616357000	-1.847751000
1	0.343722000	2.373430000	-2.679932000
6	-0.628528000	1.885707000	2.586482000
1	-0.511107000	1.140661000	3.373376000

1	0.343832000	2.292519000	2.318484000
1	-1.249440000	2.700607000	2.971283000
6	-2.571321000	0.744721000	1.796213000
1	-2.436478000	-0.021455000	2.558889000
1	-3.214313000	1.535187000	2.193190000
1	-3.060845000	0.281670000	0.944989000
6	-0.712602000	-1.699249000	0.700243000
6	-1.654394000	-1.912802000	-0.304430000
6	-2.667641000	-2.857651000	-0.229027000
1	-3.384275000	-2.985483000	-1.030901000
6	-2.743462000	-3.639267000	0.914762000
1	-3.522039000	-4.383682000	1.009565000
6	-1.819769000	-3.466299000	1.940276000
1	-1.887400000	-4.081010000	2.827938000
6	-0.821476000	-2.505467000	1.835894000
1	-0.137488000	-2.391191000	2.669155000
6	-0.916672000	-1.775526000	-2.593671000
1	-0.650116000	-1.078783000	-3.388453000
1	-0.039212000	-2.344177000	-2.294354000
1	-1.664195000	-2.473334000	-2.983345000
6	-2.629294000	-0.273602000	-1.874796000
1	-2.327323000	0.440618000	-2.640224000
1	-3.399561000	-0.932112000	-2.285771000
1	-3.046006000	0.287086000	-1.043571000
6	1.999375000	0.132089000	-2.343658000
1	2.123594000	1.164842000	-2.025587000
1	1.255146000	0.086565000	-3.137872000
6	3.299281000	-0.564661000	-2.718748000
1	3.506047000	-0.488122000	-3.782710000
1	4.137306000	-0.125120000	-2.176750000
6	3.061427000	-2.000017000	-2.249417000
1	3.979977000	-2.562801000	-2.106217000
1	2.430782000	-2.538071000	-2.957592000
6	2.317236000	-1.778587000	-0.948677000
1	1.666475000	-2.593180000	-0.636797000
1	2.999486000	-1.522632000	-0.133201000
6	1.909188000	-0.513070000	2.356431000

1	1.867390000	-1.548982000	2.027219000
1	1.166838000	-0.354180000	3.137270000
6	3.297147000	-0.042604000	2.765130000
1	4.063977000	-0.599342000	2.225308000
1	3.470110000	-0.172865000	3.830011000
6	3.298480000	1.420969000	2.324670000
1	2.743034000	2.036113000	3.033042000
1	4.296522000	1.836237000	2.213514000
6	2.558626000	1.344641000	1.004729000
1	2.050421000	2.256796000	0.699055000
1	3.211584000	1.001926000	0.196766000
7	-1.251524000	1.261366000	1.411695000
7	-1.444240000	-1.026758000	-1.444941000
8	1.480846000	-0.627249000	-1.217239000
8	1.546457000	0.333629000	1.231110000
13	0.052144000	-0.012472000	-0.008531000

Compound 3

$E_{\text{TOTAL}} = -2281.329491$ a.u.

6	-0.462963000	1.986681000	-1.640513000
6	-0.008694000	3.233384000	-1.224652000
6	-0.162364000	4.395967000	-1.966936000
1	0.204356000	5.349656000	-1.607070000
6	-0.797038000	4.303704000	-3.196851000
1	-0.933786000	5.190289000	-3.801012000
6	-1.248280000	3.071521000	-3.660681000
1	-1.727070000	3.009781000	-4.629060000
6	-1.080606000	1.927674000	-2.891273000
1	-1.426202000	0.981691000	-3.295685000
6	2.074079000	3.568983000	-0.029365000
1	2.568602000	3.350927000	0.917817000
1	2.557873000	3.003802000	-0.822351000
1	2.176641000	4.638692000	-0.239160000
6	-0.014109000	3.961457000	1.095421000
1	0.470025000	3.790758000	2.055941000
1	0.015252000	5.030655000	0.862556000

1	-1.051575000	3.643627000	1.176221000
6	-0.439627000	0.835447000	1.805822000
6	-1.696316000	0.516940000	2.351556000
6	-1.858520000	0.367603000	3.730535000
1	-2.822537000	0.126392000	4.153136000
6	-0.786782000	0.547904000	4.595345000
1	-0.935723000	0.429997000	5.660279000
6	0.452270000	0.899378000	4.093196000
1	1.288532000	1.063276000	4.759643000
6	0.601096000	1.040046000	2.717295000
1	1.581845000	1.319161000	2.337933000
6	-3.986266000	-0.276989000	2.055539000
1	-4.703706000	-0.503621000	1.264276000
1	-3.720957000	-1.204706000	2.562055000
1	-4.494365000	0.378846000	2.774574000
6	-3.200315000	1.561218000	0.767553000
1	-3.966914000	1.329599000	0.026264000
1	-3.612166000	2.301397000	1.466098000
1	-2.357990000	2.004464000	0.244949000
7	0.666947000	3.170443000	0.064374000
7	-2.808036000	0.334677000	1.463394000
8	-0.251596000	-0.871845000	-0.642634000
8	1.931912000	0.583208000	-0.118993000
13	0.129169000	0.899246000	-0.099598000
15	-1.361027000	-1.914097000	-0.830025000
6	-0.717862000	-3.110116000	-2.037306000
1	0.344334000	-3.186300000	-1.790076000
1	-0.774037000	-2.626252000	-3.015460000
6	-1.685508000	-2.775652000	0.728921000
1	-0.865797000	-3.482704000	0.879770000
1	-1.591169000	-2.001987000	1.494937000
6	-2.888655000	-1.168747000	-1.456197000
1	-3.433083000	-0.832350000	-0.575304000
1	-2.564362000	-0.267099000	-1.980312000
6	-3.041024000	-3.476714000	0.813063000
1	-3.142170000	-4.269526000	0.073747000
1	-3.164215000	-3.923488000	1.798015000

1	-3.856468000	-2.769760000	0.667825000
6	-1.352176000	-4.499758000	-2.061850000
1	-0.857707000	-5.114421000	-2.811712000
1	-1.242484000	-5.001314000	-1.100947000
1	-2.410746000	-4.466067000	-2.309841000
6	-3.755139000	-2.050920000	-2.353914000
1	-4.625343000	-1.485890000	-2.682473000
1	-3.218573000	-2.375582000	-3.244717000
1	-4.115897000	-2.934891000	-1.829931000
15	2.858333000	-0.639486000	-0.084300000
6	2.278024000	-1.863667000	1.121749000
1	1.495704000	-2.439351000	0.624089000
1	1.779452000	-1.274428000	1.896766000
6	4.495029000	-0.030466000	0.389939000
1	4.556078000	0.952462000	-0.082347000
1	4.461906000	0.144529000	1.467969000
6	2.930069000	-1.387415000	-1.732627000
1	3.552311000	-0.734525000	-2.348522000
1	1.908204000	-1.291996000	-2.107020000
6	3.406384000	-2.837585000	-1.794292000
1	3.369932000	-3.193809000	-2.822194000
1	4.430311000	-2.950090000	-1.442629000
1	2.773161000	-3.491421000	-1.193921000
6	5.693461000	-0.892065000	-0.005289000
1	5.755896000	-1.008297000	-1.086647000
1	6.611933000	-0.411340000	0.325354000
1	5.658419000	-1.882549000	0.444399000
6	3.352145000	-2.768190000	1.723644000
1	3.850748000	-3.375212000	0.969395000
1	4.109754000	-2.188538000	2.249331000
1	2.898222000	-3.443428000	2.446338000

Compound 4

ETOTAL = -2613.374270 a.u.

6	0.841179000	1.950615000	-1.247765000
6	2.135288000	2.475811000	-1.090757000

6	2.771786000	3.120384000	-2.152453000
1	3.767661000	3.522865000	-2.038159000
6	2.133477000	3.267083000	-3.377448000
1	2.644870000	3.767699000	-4.188844000
6	0.846423000	2.790251000	-3.548503000
1	0.338770000	2.909954000	-4.496161000
6	0.222628000	2.145906000	-2.485485000
1	-0.781611000	1.761706000	-2.635741000
6	4.235089000	2.474241000	0.138009000
1	4.645909000	2.184746000	1.105441000
1	4.661305000	1.830320000	-0.631310000
1	4.557979000	3.507197000	-0.050756000
6	2.224206000	3.164878000	1.218981000
1	2.749503000	2.981591000	2.156505000
1	2.319152000	4.232215000	0.974902000
1	1.173961000	2.933173000	1.378808000
6	-0.895073000	1.193475000	1.792945000
6	-1.828893000	2.212074000	1.600205000
6	-2.643053000	2.681589000	2.625154000
1	-3.358069000	3.476238000	2.449468000
6	-2.527816000	2.112360000	3.886273000
1	-3.152442000	2.464446000	4.696217000
6	-1.608382000	1.092781000	4.111378000
1	-1.523585000	0.655804000	5.097797000
6	-0.801191000	0.643508000	3.072727000
1	-0.095593000	-0.159096000	3.267690000
6	-3.205843000	2.635288000	-0.358370000
1	-3.129462000	2.908556000	-1.412068000
1	-3.577609000	1.613916000	-0.290196000
1	-3.932855000	3.308045000	0.114050000
6	-1.362476000	4.084244000	0.125120000
1	-1.261471000	4.331103000	-0.931915000
1	-2.021484000	4.819244000	0.603907000
1	-0.378383000	4.148711000	0.582147000
7	2.792555000	2.318644000	0.172509000
7	-1.882944000	2.723071000	0.245551000
8	-1.451525000	-0.015220000	-0.949292000

8	0.909429000	-0.711227000	0.281928000
13	-0.130469000	0.803804000	0.019673000
15	2.171168000	-1.546832000	0.392116000
15	-2.425245000	-1.168342000	-0.757482000
7	3.328641000	-0.723705000	1.207254000
7	1.840283000	-2.945418000	1.203873000
7	2.700087000	-1.957424000	-1.107353000
7	-1.639542000	-2.533661000	-1.276066000
7	-2.906640000	-1.531025000	0.763844000
7	-3.799949000	-0.775846000	-1.572171000
6	2.980613000	0.036105000	2.401781000
1	2.991509000	-0.586152000	3.302621000
1	3.709773000	0.834430000	2.529003000
1	1.999601000	0.492774000	2.287444000
6	4.745288000	-1.014868000	1.043608000
1	5.303390000	-0.078893000	1.019631000
1	5.136199000	-1.626328000	1.862387000
1	4.920439000	-1.538248000	0.106185000
6	3.411039000	-3.192508000	-1.398573000
1	3.391963000	-3.864267000	-0.544140000
1	2.948161000	-3.696093000	-2.250113000
1	4.455154000	-2.989491000	-1.652890000
6	2.827466000	-0.937706000	-2.145499000
1	3.872652000	-0.640742000	-2.273264000
1	2.465125000	-1.340154000	-3.093496000
1	2.243118000	-0.054588000	-1.895626000
6	0.854647000	-3.872339000	0.665671000
1	0.146986000	-3.337944000	0.034829000
1	1.328899000	-4.673618000	0.088192000
1	0.302859000	-4.329091000	1.489311000
6	2.738554000	-3.539230000	2.183383000
1	3.338634000	-4.344179000	1.746373000
1	3.406232000	-2.791451000	2.599890000
1	2.149426000	-3.961136000	2.998626000
6	-1.988549000	-2.265689000	1.645405000
1	-0.966843000	-1.889303000	1.576601000
1	-2.327400000	-2.127060000	2.669453000

1	-1.995649000	-3.331778000	1.417457000
6	-3.918702000	-0.733007000	1.466043000
1	-4.553659000	-1.400119000	2.049706000
1	-3.444911000	-0.009473000	2.132905000
1	-4.542059000	-0.199619000	0.753974000
6	-4.981492000	-1.631018000	-1.524280000
1	-5.031584000	-2.288770000	-2.396060000
1	-4.980978000	-2.238481000	-0.622521000
1	-5.875435000	-1.005540000	-1.516310000
6	-3.759940000	0.101684000	-2.738919000
1	-3.772268000	-0.476810000	-3.666349000
1	-4.636128000	0.751845000	-2.725525000
1	-2.868230000	0.720024000	-2.712142000
6	-0.637568000	-2.427552000	-2.335946000
1	-1.092377000	-2.514507000	-3.327339000
1	-0.108568000	-1.481328000	-2.261927000
1	0.085326000	-3.238520000	-2.219892000
6	-2.350259000	-3.807888000	-1.287954000
1	-3.104119000	-3.834552000	-0.503739000
1	-2.836995000	-3.987266000	-2.251114000
1	-1.638885000	-4.617535000	-1.110734000

INT-1

E_{TOTAL} = -1664.053808 a.u.

6	-1.355707000	0.730729000	1.747455000
6	-2.195004000	-0.315193000	2.114913000
6	-3.044445000	-0.278665000	3.211134000
1	-3.684927000	-1.115319000	3.462354000
6	-3.053939000	0.873661000	3.983988000
1	-3.703203000	0.938106000	4.846341000
6	-2.234958000	1.948314000	3.650174000
1	-2.257970000	2.843574000	4.257207000
6	-1.400375000	1.879019000	2.541525000
1	-0.797160000	2.749098000	2.298087000
6	-1.438915000	-2.602062000	1.854550000

1	-1.187773000	-3.347838000	1.099003000
1	-0.532373000	-2.282379000	2.361534000
1	-2.114318000	-3.056265000	2.585931000
6	-3.339194000	-1.868467000	0.591996000
1	-3.132264000	-2.637041000	-0.151618000
1	-4.030542000	-2.269311000	1.338516000
1	-3.810203000	-1.030479000	0.084689000
6	-1.354661000	-0.736008000	-1.747016000
6	-2.197433000	0.307387000	-2.113698000
6	-3.047557000	0.268439000	-3.209300000
1	-3.690882000	1.103137000	-3.459754000
6	-3.054067000	-0.883724000	-3.982425000
1	-3.703822000	-0.950006000	-4.844270000
6	-2.231523000	-1.955887000	-3.649436000
1	-2.252260000	-2.851101000	-4.256619000
6	-1.396366000	-1.884259000	-2.541368000
1	-0.790371000	-2.752569000	-2.298539000
6	-1.448628000	2.596623000	-1.853522000
1	-1.199348000	3.343161000	-1.098104000
1	-0.541448000	2.279958000	-2.361249000
1	-2.125980000	3.048772000	-2.584389000
6	-3.345736000	1.856664000	-0.589923000
1	-3.140799000	2.624842000	0.154655000
1	-4.038368000	2.256532000	-1.335781000
1	-3.814375000	1.016723000	-0.083646000
7	-2.072355000	-1.446922000	1.202557000
7	-2.077916000	1.439362000	-1.201295000
13	-0.768786000	-0.002066000	0.000191000
6	3.022442000	-3.517643000	-1.047710000
6	3.995528000	-4.452881000	-0.742992000
6	4.308457000	-4.705096000	0.586445000
6	3.656936000	-4.029925000	1.617890000
6	2.686550000	-3.096168000	1.320567000
6	2.368288000	-2.838661000	-0.017555000
1	2.763401000	-3.308090000	-2.078458000
1	4.507827000	-4.983571000	-1.532469000
1	5.068584000	-5.436769000	0.825269000

1	3.912962000	-4.240523000	2.646525000
1	2.167164000	-2.557618000	2.101627000
6	1.350276000	-1.874761000	-0.366875000
1	1.137548000	-1.718524000	-1.432569000
8	0.710741000	-1.229211000	0.465334000
6	3.010549000	3.526747000	1.046261000
6	2.357483000	2.846400000	0.016327000
6	2.672090000	3.107315000	-1.322013000
6	3.637689000	4.045878000	-1.619768000
6	4.288145000	4.722397000	-0.588541000
6	3.978875000	4.466765000	0.741112000
1	2.754319000	3.314590000	2.077182000
1	2.153593000	2.567624000	-2.102872000
1	3.890827000	4.259147000	-2.648572000
1	5.044520000	5.457854000	-0.827662000
1	4.490313000	4.998540000	1.530416000
6	1.344231000	1.877608000	0.366027000
1	1.133796000	1.719179000	1.431851000
8	0.706191000	1.230347000	-0.465992000

TS

E_{TOTAL} = -2009.451524 a.u.

6	-1.652725000	-1.721773000	-0.998051000
6	-2.581460000	-2.157702000	-0.060172000
6	-3.774235000	-2.788614000	-0.385460000
1	-4.470784000	-3.120834000	0.374620000
6	-4.049785000	-2.987156000	-1.731623000
1	-4.966593000	-3.479991000	-2.026155000
6	-3.149334000	-2.560476000	-2.705529000
1	-3.380447000	-2.722802000	-3.749888000
6	-1.961948000	-1.935693000	-2.342636000
1	-1.286207000	-1.606078000	-3.123836000
6	-3.118741000	-1.105777000	2.080940000
1	-2.669576000	-0.814784000	3.029546000
1	-3.393415000	-0.208964000	1.531641000
1	-4.015894000	-1.697230000	2.284627000

6	-1.794143000	-3.119558000	2.012579000
1	-1.394742000	-2.878350000	2.995342000
1	-2.675563000	-3.756648000	2.125109000
1	-1.032168000	-3.658224000	1.452814000
6	1.006382000	-1.520687000	1.477716000
6	2.279430000	-1.953107000	1.061001000
6	3.346936000	-2.013796000	1.959188000
1	4.327825000	-2.331838000	1.640790000
6	3.158810000	-1.688914000	3.294717000
1	3.992260000	-1.757220000	3.980530000
6	1.908616000	-1.301117000	3.746152000
1	1.751629000	-1.063602000	4.789759000
6	0.864694000	-1.214972000	2.834036000
1	-0.101225000	-0.868248000	3.195050000
6	3.840381000	-2.576854000	-0.724958000
1	3.857830000	-2.731273000	-1.802765000
1	4.470378000	-1.720708000	-0.491872000
1	4.249356000	-3.472091000	-0.245330000
6	1.612944000	-3.435859000	-0.743623000
1	1.703709000	-3.560982000	-1.823213000
1	1.919819000	-4.368536000	-0.258719000
1	0.570815000	-3.245305000	-0.507778000
7	-2.137252000	-1.874483000	1.304195000
7	2.465659000	-2.322942000	-0.313926000
13	-0.436060000	-0.853885000	0.297657000
6	3.643768000	-0.224179000	-3.043325000
6	2.957193000	0.116546000	-1.880972000
6	3.501936000	1.029136000	-0.977612000
6	4.735775000	1.595044000	-1.244239000
6	5.418036000	1.260477000	-2.410148000
6	4.872960000	0.355401000	-3.312372000
1	3.210163000	-0.935986000	-3.735739000
1	2.957090000	1.267716000	-0.072546000
1	5.169229000	2.296374000	-0.544400000
1	6.381195000	1.707165000	-2.615902000
1	5.406794000	0.103024000	-4.217493000
6	1.672298000	-0.507614000	-1.585304000

1	1.327305000	-1.309001000	-2.246841000
8	0.876848000	0.018343000	-0.785791000
6	1.134714000	3.546055000	-0.004682000
6	2.354180000	4.106699000	0.347130000
6	2.998809000	3.701773000	1.507901000
6	2.425652000	2.731661000	2.321123000
6	1.202268000	2.174892000	1.982426000
6	0.565557000	2.579692000	0.814987000
1	0.649833000	3.833954000	-0.926469000
1	2.804722000	4.852142000	-0.293091000
1	3.948747000	4.141510000	1.779401000
1	2.929443000	2.405468000	3.220275000
1	0.754187000	1.413663000	2.604172000
6	-0.759583000	1.947862000	0.475912000
8	-1.069432000	0.756937000	0.885068000
8	-1.122522000	2.219398000	-0.923874000
6	-2.149861000	2.935473000	-0.439940000
1	-1.560125000	2.704430000	0.986734000
1	-1.985980000	4.010487000	-0.333756000
6	-3.489391000	2.426803000	-0.447955000
6	-4.529598000	3.247919000	0.012634000
6	-3.750499000	1.138567000	-0.930731000
6	-5.823682000	2.773656000	0.000325000
1	-4.311629000	4.245685000	0.372964000
6	-5.053800000	0.677039000	-0.946153000
1	-2.939227000	0.524898000	-1.296416000
6	-6.080940000	1.489563000	-0.478390000
1	-6.634927000	3.394221000	0.352184000
1	-5.263757000	-0.313624000	-1.324064000
1	-7.098975000	1.124202000	-0.493273000

INT-2

ETOTAL = -2009.545530 a.u.

6	-0.002287000	2.599209000	-0.258374000
6	1.142248000	3.209592000	0.241876000

6	1.493364000	4.529439000	-0.008224000
1	2.397143000	4.966221000	0.398199000
6	0.638723000	5.282852000	-0.797727000
1	0.876319000	6.315042000	-1.015144000
6	-0.530371000	4.718902000	-1.304536000
1	-1.192584000	5.324093000	-1.909084000
6	-0.846504000	3.393838000	-1.039088000
1	-1.758971000	2.984274000	-1.458861000
6	3.303761000	2.132441000	0.627912000
1	3.764978000	1.307393000	1.171141000
1	3.320396000	1.913816000	-0.438459000
1	3.890603000	3.037939000	0.801553000
6	1.903396000	2.738417000	2.490809000
1	2.432992000	2.012394000	3.103662000
1	2.382310000	3.715492000	2.591432000
1	0.875807000	2.802616000	2.841423000
6	-0.010416000	0.093989000	2.330627000
6	-1.291041000	-0.167912000	2.854987000
6	-1.446518000	-0.989247000	3.972613000
1	-2.427064000	-1.203024000	4.370891000
6	-0.338261000	-1.531239000	4.608146000
1	-0.477997000	-2.155695000	5.480039000
6	0.935592000	-1.257429000	4.140382000
1	1.803757000	-1.662976000	4.642242000
6	1.076408000	-0.458374000	3.012431000
1	2.081999000	-0.273080000	2.641042000
6	-3.723208000	-0.140552000	2.574573000
1	-4.482210000	0.284009000	1.918389000
1	-3.718163000	-1.221017000	2.438408000
1	-4.005654000	0.092309000	3.607865000
6	-2.475059000	1.878520000	2.308268000
1	-3.225954000	2.264213000	1.616157000
1	-2.742786000	2.199652000	3.322079000
1	-1.515674000	2.315622000	2.048133000
7	1.916800000	2.296095000	1.083632000
7	-2.429535000	0.418370000	2.213109000
13	0.340889000	0.825967000	0.539187000

6	-4.491191000	-0.605673000	-0.737921000
6	-3.195211000	-1.035292000	-0.463013000
6	-2.910124000	-2.394755000	-0.333702000
6	-3.927514000	-3.318682000	-0.482217000
6	-5.221703000	-2.888312000	-0.764877000
6	-5.506511000	-1.534834000	-0.894242000
1	-4.695880000	0.454260000	-0.834411000
1	-1.896085000	-2.701045000	-0.114793000
1	-3.721803000	-4.374689000	-0.378255000
1	-6.013601000	-3.615415000	-0.882143000
1	-6.513779000	-1.210232000	-1.112903000
6	-2.142909000	-0.045957000	-0.312144000
1	-2.432591000	1.010108000	-0.342766000
8	-0.944430000	-0.348733000	-0.259647000
6	4.427604000	-2.244293000	-1.358168000
6	5.207375000	-3.294346000	-0.908693000
6	4.908085000	-3.914244000	0.299084000
6	3.828808000	-3.488993000	1.064210000
6	3.048852000	-2.433044000	0.628698000
6	3.352231000	-1.809955000	-0.581974000
1	4.648260000	-1.756715000	-2.296505000
1	6.047155000	-3.632766000	-1.498332000
1	5.518650000	-4.737586000	0.643716000
1	3.594948000	-3.982516000	1.996711000
1	2.198252000	-2.098858000	1.207079000
6	2.506369000	-0.699395000	-1.026560000
8	1.666194000	-0.176378000	-0.288673000
8	2.703077000	-0.299479000	-2.252661000
6	1.812555000	0.678849000	-2.828409000
1	1.741520000	1.543485000	-2.165949000
1	2.315122000	0.975700000	-3.745734000
6	0.446108000	0.107434000	-3.103276000
6	0.198392000	-1.258697000	-3.106574000
6	-0.589482000	0.993384000	-3.377372000
6	-1.080007000	-1.734212000	-3.366073000
1	0.997916000	-1.962260000	-2.912714000
6	-1.865854000	0.517571000	-3.637496000

1	-0.395187000	2.058289000	-3.383970000
6	-2.114397000	-0.849445000	-3.627860000
1	-1.265911000	-2.799322000	-3.365335000
1	-2.664689000	1.213682000	-3.856721000
1	-3.110491000	-1.222865000	-3.823420000

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