Supporting Information

for

Selective dimerization of α-methylstyrene by tunable bis(catecholato)germane Lewis acid catalysts

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1. General Experimental

All reactions were conducted under a nitrogen atmosphere using an MBraun Labmaster 130 glovebox. Solvents and reagents were purified by standard methods. GeCl$_2$•diox (Gelest), tetrabromocatechol (Sigma-Aldrich), tetrachlorocatechol (Sigma-Aldrich), tetrachloroquinone (Fisher), and 3,5-di-*tert*-butylquinone (Fisher) were obtained from commercial sources. NMR data were obtained on a 600 MHz INOVA, 400 MHz INOVA or a 400 MHz Bruker Avance III NMR spectrometer. The standards used were as follows: residual CDCl$_3$ (7.26 ppm), CD$_2$Cl$_2$ (5.32 ppm), toluene-d_8 (tol-d_8: 2.09 ppm) for ^{1}H NMR spectra; CDCl$_3$ (77.16 ppm) for ^{13}C NMR spectra; J values are reported in Hertz. ESI mass spectra were recorded on a Bruker microTOF II mass spectrometer with an electrospray interface in negative ion mode while EI mass spectra were recorded on a Thermo Scientific DFS (Double Focusing Sector) mass spectrometer (reported in mass-to-charge units, *m/z*). Elemental analyses were performed by the University of Western Ontario – Analytical Services.

1.1 Synthesis of Bis(catecholato)germanes

Route A: Synthesis from GeCl$_2$•diox and Quinone

$$2 \ GeCl_2 \bullet diox \ + \ 2$$

X = 3,5-^{t}Bu, Cl
Donor = THF, Et$_2$O or ACN
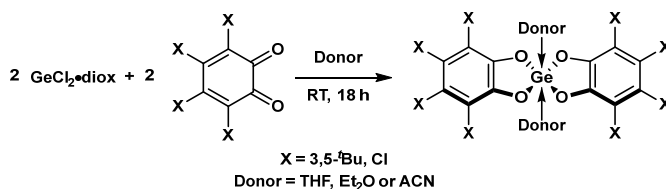
A solution of quinone (2.50 mmol) dissolved in THF, Et$_2$O or ACN (3 mL) was added dropwise to a clear solution of GeCl$_2$•diox (0.58g, 2.50 mmol) dissolved in the same solvent (3 mL). For the di-*tert*-butyl derivatives, the solution became pale yellow during the course of the addition. After 18 h of stirring, the crude reaction mixture was dried *in vacuo*. The resulting white solid was triturated in hexanes and then dried. For the chlorinated derivatives, the reaction mixture turned orange and a pale peach solid precipitated from solution. The reaction mixture was allowed to stir overnight. The precipitate was separated by centrifugation and then dried *in vacuo*. The mother liquor was placed in the freezer overnight which resulted in the precipitation of more solid which was subsequently isolated by centrifugation and dried *in vacuo*.

Ge(dtbc)$_2$(THF)$_2$[1]

Yield = 87%; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.88 (br, 2 H, aromatic-H), 6.75 (br, 2 H, aromatic-H), 3.91-3.84 (m, 8 H, O-CH$_2$), 1.96-1.89 (m, 8 H, O-CH$_2$-C$\underline{H}_2$), 1.44 (br s, 18 H, *t*Bu), 1.29 (s, 18 H,

*t*Bu); ^{13}C NMR (CDCl$_3$, 100.61 MHz): δ 142.9 (aromatic C), 141.9 (aromatic C), 141.2 (aromatic C), 135.5 (aromatic C), 115.6 (aromatic CH), 110.3 (aromatic CH), 68.3 (THF, OCH$_2$), 35.0 (*t*Bu *q*-C), 34.4 (*t*Bu *q*-C), 31.7 (*t*BuCH$_3$), 29.7 (*t*BuCH$_3$), 25.7 (THF, CH$_2$); EI-MS *m/z* 514.2123 (calcd for C$_{28}$H$_{40}$^{74}GeO$_4$, *m/z* 514.2139) (M-2THF).

Ge(dtbc)$_2$(ACN)$_2$

Yield = 74%; ^{1}H NMR (CDCl$_3$, 400 MHz): Product was too insoluble to obtain clean NMR data; EI-MS *m/z* 514.26 (calcd for C$_{28}$H$_{40}$^{74}GeO$_4$, *m/z* 514.2138) (M-2ACN).

Ge(cat^{Cl})$_2$(THF)$_2$

Yield = 48%; EI-MS: *m/z* 557.6651 (calcd for C$_{12}$^{35}Cl$_8$^{70}GeO$_4$, *m/z* 557.6548) (M-2THF).

Ge(cat^{Cl})$_2$(Et$_2$O)$_2$

Yield = 87%; EI-MS: *m/z* 557.6538 (calcd for C$_{12}$^{35}Cl$_8$^{70}GeO$_4$, *m/z* 557.6548) (M-2Et$_2$O).

Ge(cat^{Cl})$_2$(ACN)$_2$[2]

Yield = 88%. EA: calcd for C$_{16}$H$_6$Cl$_8$GeO$_4$N$_2$: 29.73% C, 0.94% H; found 29.70% C, %H was below the method reporting limit.

Route B: Synthesis from GeCl$_4$ and Catechol
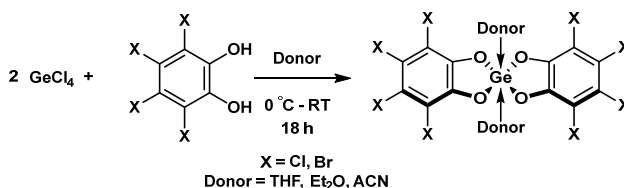
A clear solution of GeCl$_4$ (0.1 g, 0.47 mmol) in THF, Et$_2$O or ACN (3 mL) was added dropwise to a suspension of either tetrachlorocatechol or tetrabromocatechol (0.94 mmol) in THF, Et$_2$O or ACN (3 mL) cooled to 0 °C (For the ACN derivative, 2 mL of DCM was also added to improve solubility of the catechol). After 30 minutes, the formation of white precipitate was observed, and the reaction mixture was warmed to room temperature and allowed to stir overnight. The precipitate was separated by centrifugation, triturated with DCM, and then dried *in vacuo*.

Ge(cat^{Br})$_2$(THF)$_2$

Yield = 46%; EI-MS: *m/z* 919.25 (calcd for C$_{12}$^{79}Br$_3$^{81}Br$_5$^{74}GeO$_4$, *m/z* 919.2414) (M-2THF); EA: calcd for C$_{20}$H$_{16}$Br$_8$GeO$_6$: 22.57% C, 1.52% H; found 22.89 %C, %H was below the method reporting limit.

Ge(cat^{Br})$_2$(Et$_2$O)$_2$

Yield = 11%; EI-MS: m/z 919.26 (calcd for $C_{12}{}^{79}Br_3{}^{81}Br_5{}^{74}GeO_4$, m/z 919.2414) (M-2Et$_2$O).

Ge(cat^{Br})$_2$(ACN)$_2$

Yield = 15%; EI-MS: m/z 919.25 (calcd for $C_{12}{}^{79}Br_3{}^{81}Br_5{}^{74}GeO_4$, m/z 919.2414) (M-2ACN); EA: calcd for $C_{14}H_3Br_8GeO_4N$ (M-ACN): 17.50% C, 0.31% H; found 17.51% C, %H was below the method detection limit.

1.2 Reactions of Bis(catecholato)germanes with Tetrabutylammonium Chloride

To a solution/suspension of the bis(catecholato)germane derivative (0.032 mmol) in THF (2 mL) was added a solution NBu$_4$Cl (0.009 g; 0.032 mmol) in THF (2 mL) dropwise and the reaction mixture was allowed to stir overnight. The resulting clear solution was dried *in vacuo* to yield the resulting bis(catecholato)germanium chloride salt.

[NBu$_4$][Ge(dtbc)$_2$Cl]

Yield = 89%; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.77 (br, 2 H, aromatic-H), 6.63 (br, 2 H, aromatic-H), 2.92 (m, 8 H, N-CH$_2$), 1.43 (s, 18 H, tBu), [1.22-1.37 (br, N-CH$_2$-CH$_2$-CH$_2$), 1.25 (s, tBu), 34 H total] 0.87 (t, 12 H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100.61 MHz): δ 147.66, 144.28, 138.83, 132.43, 112.14, 106.98, 58.37, 34.80, 34.48, 32.07, 29.81, 23.88, 19.60, 13.75. ESI-MS (negative ion) 549.1537 m/z (calcd for $C_{28}H_{40}{}^{35}ClO_4{}^{70}Ge$, [Ge(dtbc)$_2Cl^-$] m/z 549.1806).

[NBu$_4$][Ge(cat^{Cl})$_2$Cl]

Yield = >100%[i]; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.22 (br, 8 H, N-CH$_2$), 1.66 (br, 8 H, N-CH$_2$-CH$_2$), 1.39 (br, 8 H, CH$_2$-CH$_3$) 0.95 (br t, 12 H, CH$_3$); ESI-MS (negative ion) 592.6246 m/z (calcd for $C_{12}O_4{}^{35}Cl_9{}^{70}Ge$, (Ge(cat^{Cl})$_2Cl^-$) m/z 592.6236).

[NBu$_4$][Ge(cat^{Br})$_2$Cl]

Yield = 73%[i]; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.26 (br, 8 H, N-CH$_2$), 1.66 (br, 8 H, N-CH$_2$-CH$_2$), 1.34 (br, 8 H, CH$_2$-CH$_3$) 0.92 (t, 12 H, CH$_3$); ESI-MS (negative ion) 954.2129 m/z (calcd for $C_{12}O_4Br_8{}^{35}Cl{}^{70}Ge$, (Ge(cat^{Br})$_2Cl^-$) m/z 954.2089).

1.3 Reaction of Ge(dtbc)$_2$(THF)$_2$ with Pyridine

Pyridine (2 equiv.) was added to a solution of Ge(dtbc)$_2$(THF)$_2$ dissolved in DCM. The reaction was allowed to stir overnight before the solution was dried *in vacuo*. The resulting solid was re-dissolved in

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[i] THF is still evident (0.5 – 1 equiv) in the ^{1}H NMR spectra even after drying *in vacuo*: [NBu$_4$][Ge(cat^{Cl})$_2$Cl]: 0.6 eq of THF still remain; [NBu$_4$][Ge(cat^{Br})$_2$Cl]: 0.5 eq of THF still remain;

CDCl$_3$ to record the ^{1}H NMR spectrum. The chemical shifts observed match those of the reported Ge(dtbc)$_2$(py)$_2$.[3]

2. Gutmann-Beckett Assessment of Lewis Acidity

To a suspension of bis(catecholato)germane in DCM (1 mg/mL) was added 1/3 equivalent of triethylphosphine oxide and the mixture was left to stir overnight. An aliquot of the reaction mixture was taken and a ^{31}P{^{1}H} NMR spectrum was recorded (**Table S.1**).

Table S.1: The ^{31}P{^{1}H} NMR data for the Gutmann-Beckett analysis using sub-stoichiometric amounts of triethylphosphine oxide

Compound	^{31}P Chemical Shift (ppm) {Acceptor Number}	
	Donor = THF	Donor = ACN
Ge(3,5-dtbc)$_2$(OPEt$_3$)	82.6 {92}	82.8 {92}
Ge(cat^{Cl})$_2$(OPEt$_3$)•donor	84.0 {95}	88.2 {104}
Ge(cat^{Br})$_2$(OPEt$_3$)•donor	85.7 {99}	88.4 {105}

One equivalent of bis(catecholato)germane•2(THF) (20 mg/mL) and 0.5, 1, 2, and 3 eq. of triethylphosphine oxide were placed in DCM-d_2 (0.5 mL) in an NMR tube. A ^{31}P{^{1}H} NMR spectrum of the mixture was immediately recorded. Signals assigned to the two equivalents of free THF, which originated from the starting bis(catecholato)germane, are omitted from the NMR assignments. Free triethylphosphine oxide was also observed upon addition of 2 or 3 equivalents (51 ppm).

Ge(3,5-dtbc)$_2$(OPEt$_3$)

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 162 MHz): δ 82.4; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.88 (d, *J* = 2.3 Hz, 2 H, Ar-H), 6.70 (d, *J* = 2.3 Hz, 2 H, Ar-H) 1.93 (dq, *J* = 12.1 Hz, 7.7 Hz, 6 H, P-CH$_2$), 1.43 (s, 18 H, *t*Bu-CH$_3$), 1.28 (s, 18 H, *t*Bu-CH$_3$), 1.04 (dt, *J* = 17.9 Hz, 7.7 Hz, 9 H, P-CH$_2$-C$\underline{H}$$_3$); ^{13}C NMR (CDCl$_3$, 100.61 MHz)[ii]: δ 147.7, 143.4, 141.2, 133.4, 113.0, 107.9, 35.1, 34.9, 32.1, 30.0, 18.2, 17.5, 5.4, 5.3; ESI-MS *m/z* 648.3 (cald for C$_{34}$H$_{55}$^{70}GeO$_5$P: 648.2999).

Ge(3,5-dtbc)$_2$(OPEt$_3$)$_2$

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 162 MHz): δ 66.6 (-80 °C) ; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.84 (d, *J* = 2.3

[ii] Signals for the quaternary carbons were not observed

Hz, 2 H, Ar-H), 6.66 (d, J = 2.3 Hz, 2 H, Ar-H), 1.75 (dq, J = 12.2 Hz, 7.7 Hz, 12 H, P-CH$_2$), 1.43 (s, 18 H, tBu-CH$_3$), 1.28 (s, 18 H, tBu-CH$_3$), 0.99 (dt, J = 17.5 Hz, 7.7 Hz, 18 H, P-CH$_2$-CH$_3$); ^{13}C NMR (CDCl$_3$, 100.61 MHz)[ii]: δ 148.1, 144.0, 140.5, 133.0, 112.5, 107.9, 35.1, 34.9, 32.1, 30.1, 19.0, 18.4, 5.7, 5.6; ESI-MS m/z 781.4 (cald for C$_{40}$H$_{70}$^{70}GeO$_6$P$_2$ 782.3859).

trans-Ge(cat^{Cl})$_2$(OPEt$_3$)$_2$

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 162 MHz): δ 70.5; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.65 (dq, J = 11.7 Hz, 7.7 Hz, 12 H, P-CH$_2$), 0.87 (dt, J = 17.8 Hz, 7.7 Hz, 18 H, P-CH$_2$-CH$_3$).

cis-Ge(cat^{Cl})$_2$(OPEt$_3$)$_2$

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 162 MHz): δ 75.0; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.96-2.10 and 2.10-2.24 (each m, 12 H total, diastereotopic P-CH$_2$), 1.13 (dt, J = 16.3 Hz, 7.7 Hz, 18 H, P-CH$_2$-CH$_3$).

trans-Ge(cat^{Br})$_2$(OPEt$_3$)$_2$

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 162 MHz): δ 75.1; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.65 (dq, J = 11.7 Hz, 7.8 Hz, 12 H, P-CH$_2$), 0.87 (dt, J = 17.9 Hz, 7.7 Hz, 18 H, P-CH$_2$-CH$_3$).

cis-Ge(cat^{Br})$_2$(OPEt$_3$)$_2$

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 162 MHz): δ 75.8; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.98-2.12 and 2.12-2.26 (each m, 12 H total, diastereotopic P-CH$_2$), 1.11 (dt, J = 15.7 Hz, 7.7 Hz, 18 H, P-CH$_2$-CH$_3$).

3. Catalytic Oligomerization of Alkenes

3.1 General Catalytic Procedures and Product Characterization

General Procedure for Oligomerization experiments: a mixture containing the alkene (0.2 mmol), catalyst (0.009 mmol) and mesitylene (0.02 mmol) as an internal standard in 0.5 mL deuterated solvent (CD$_2$Cl$_2$, tol-d_8) were allowed to react for 24 hours in sealed NMR tubes. The conversions and the product mixture compositions were determined by integration against the internal standard and are an average of 2-3 runs. Discrepancies in the mass balances are attributed to the averaging of the results.

General procedure for attempted hydrosilylation experiments: a mixture containing the alkene (0.2 mmol), triethylsilane (0.2 mmol), catalyst (0.009 mmol) and mesitylene (0.02 mmol) as an internal standard in 0.5 mL deuterated solvent (CD$_2$Cl$_2$, tol-d_8) were allowed to react for 24 hours in sealed NMR tubes.

Control experiments for the hydrosilylation and oligomerization reactions without catalyst were performed in parallel. Conversion of alkene to products was determined by integration against mesitylene (C_9H_{12}) as an internal standard.

No conversion of starting material was observed in any experiments (hydrosilylation or oligomerization) using cyclohexene, phenylacetylene, triethoxyvinylsilane, or 1-methylcyclohexene as substrates

Reactions with styrene produced polystyrene as the major product: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.20-7.00 (3H, bs), 6.65-6.45 (2H, bs), 1.84 (1H, bs), 1.47 (2H, bs).[4]

Reactions with α-methylstyrene produced the following compounds (**Chart 3**): 2,4-diphenyl-4-methyl-1-pentene (**III**), 2,4-diphenyl-4-methyl-2-pentene (**IV**), and 1,3,3-trimethyl-1-phenylindane (**V**). The structures of the products were confirmed using ^{1}H, ^{13}C, ^{1}H-^{1}H gCOSY, ^{1}H-^{13}C gHSQC, and ^{1}H-^{13}C gHMBC spectroscopy.

4-methyl-2,4-diphenyl-1-pentene (**III**): ^{1}H NMR (400 MHz, tol-d_8): δ 7.00-7.30 (m, 10 H), 5.10 (d, J = 1 Hz, 1 H), 4.74 (d, J = 1 Hz, 1 H), 2.71 (s, 2 H), 1.15 (s, 6 H).

(*E*)-4-methyl-2,4-diphenyl-2-pentene (**IV**): ^{1}H NMR (400 MHz, tol-d_8): δ 7.00-7.30 (m)[iii], 6.09 (s, 1 H), 1.53 (s, 3 H), 1.42 (s, 6 H).
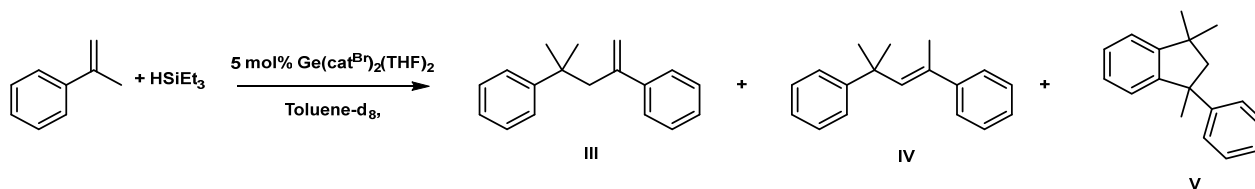
1,3,3-trimethyl-1-phenylindane (**V**): ^{1}H NMR (400 MHz, tol-d_8): δ 7.00-7.30 (m, 9 H), 2.33 (d, J = 13 Hz, 1 H), 2.05 (d, J = 13 Hz, 1 H), 1.58 (s, 3 H), 1.24 (s, 3H), 1.00 (s, 3 H).

[iii] Since dimer **IV** was never obtained cleanly and always formed as a mixture, clean integration of the ^{1}H signals in the aryl region was not possible.
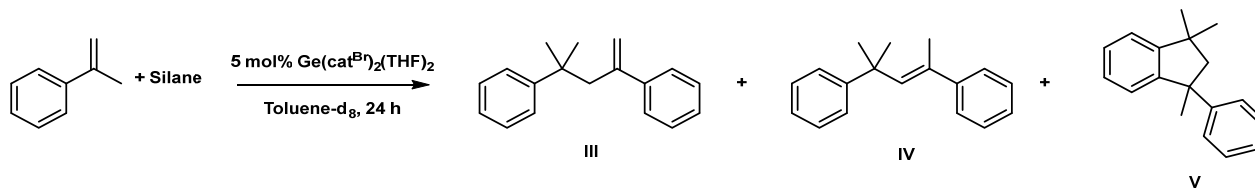
3.2 Reaction Optimization using α-methylstyrene

Table S.2: Reaction Optimization for the dimerization of α-methylstyrene.[a]

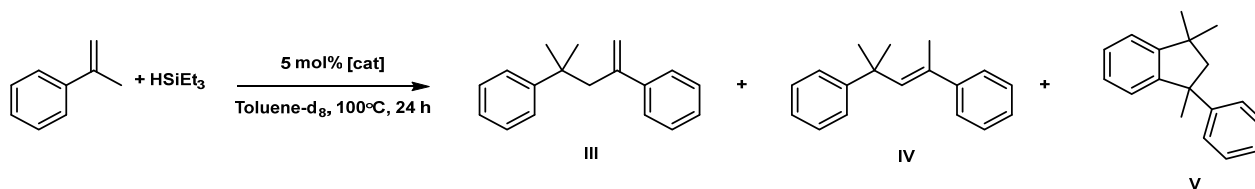| Entry	Catalyst Loading	Time (h)	Temp. (°C)	Silane Conc. (M)	Silane Equivalents	% Conv.	Product Mixture Composition (%)[b]		
							III	IV	V
1	5 mol %	24	25	0.4	1	5	1	0	0
				0.0	0	15	3	0	0
2	5 mol %	24	0	0.4	1	3	1	0	0
				0.0	0	18	4	0	0
3	5 mol %	24	80	1.9	5	0	0	0	0
				0.4	1	11	11	0	0
				0.0	0	91	45	26	8
4	5 mol %	24	100	1.9	5	9	2	0	0
				0.4	1	21	14	0	0
				0.0	0	93	34	38	20
5	5 mol %	3	100	0.4	1	6	1	0	0
				0.0	0	46	33	3	1
6	5 mol %	6	100	0.4	1	7	2	0	0
				0.0	0	75	53	19	2
7	5 mol %	72	100	1.9	5	8	5	0	0
				0.4	1	18	18	0	0
				0.0	0	95	18	35	21
8	10 mol %	24	100	1.9	5	46	14	2	0
				0.4	1	20	11	0	0
				0.0	0	95	29	31	30
9	10 mol %	24	80	1.9	5	8	3	0	0
				0.0	0	93	39	26	21

[a]Shaded regions indicate an altered variable relative to entry 1. [b]Determined by integration of ^{1}H signals against an internal standard.

Table S.3: Silane substrate scope for the investigation of dimerization of α-methylstyrene.[a]

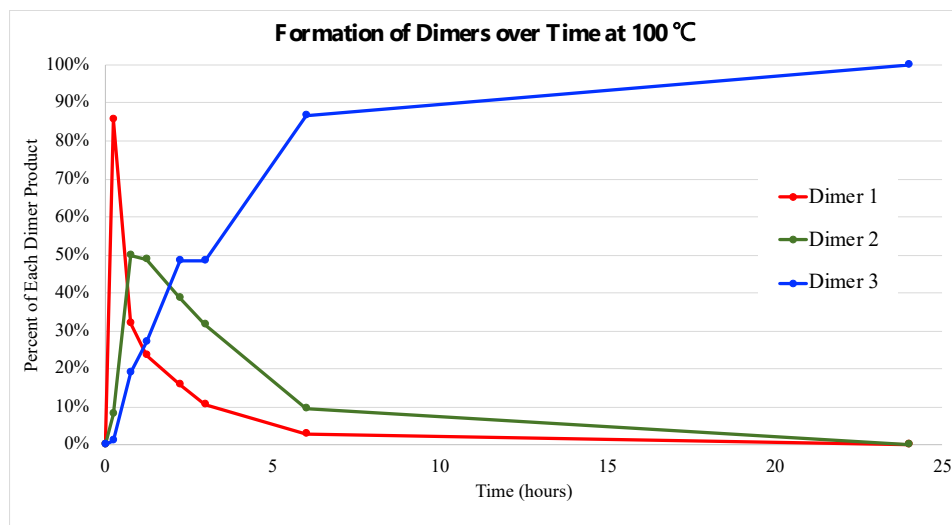| Entry	Catalyst Loading	Silane	Temp. (°C)	Silane Conc. (M)	Silane Equivalents	% Conv.	Product Mixture Composition (%)[b]		
							III	IV	V
1	5 mol %	Tetramethyl-disiloxane	25	0.4	1	6	0	0	0
				0.0	0	12	2	0	0
2	5 mol %	Dimethyl-phenylsilane	25	0.4	1	4	2	0	0
				0.0	0	12	3	0	0
3	5 mol %	Pentamethyl-disiloxane	25	0.4	1	6	2	0	0
				0.0	0	11	1	0	0
4	5 mol %	Pentamethyl-disiloxane	80	0.4	1	23	12	0	0
				0.0	0	87	38	13	2
5	5 mol %	(TMS)₃SiH	80	0.4	1	22	20	0	0
				0.0	0	94	27	50	10

[a]Shaded regions indicate an altered variable from entry 1, Table S2. [b]Determined by integration of ^{1}H signals against an internal standard.

Table S.4: The effect of catechol substitution and donor ligands on the dimerization of α-methylstyrene[a]

Entry	Catalyst	Silane Conc. (M)	Silane Equivalents	% Conv.	Product Mixture Composition (%)[b]		
					III	IV	V
1	Ge(cat^{Cl})₂ ·THF	0.4	1	4	4	0	0
		0.0	0	94	17	25	8
2	Ge(cat^{Cl})₂ · 2ACN	0.4	1	16	12	0	0
		0.0	0	>99	0	0	>99
3	Ge(cat$^{3,5-dtbc}$)₂ · 2THF	0.4	1	2	0	0	0
		0.0	0	18	3	1	0

[a]Shaded regions indicate an altered variable from entry 1, Table S2. [b]Determined by integration of ^{1}H signals against an internal standard.

Figure S.1: Dimer products **III** (red trace)**, IV** (green trace)**,** and **V** (blue trace) formed in reactions with α-methylstyrene and $Ge(cat^{Br})_2(ACN)_2$ over a period of 24 hours at 100 ℃.

4. Computational Details

All calculations (except G3/G4) have been performed with ORCA 4.1.2 and ORCA 4.2. Geometry optimizations were performed with PBEh-3c/def2-mSVP as implemented in ORCA, using grid5 settings. All calculated geometries have been confirmed as energetic minima on the potential energy surface by analytical calculation of harmonic frequencies at the PBEh-3c level. In case of negative frequencies >10 cm^{-1}, the geometries were reoptimized with grid6, TightOPT and VeryTightSCF settings. For the fluoride ion affinities, the optimized geometries were than used to calculate the single point energies at B3LYP D3(BJ)/def2-TZVPP level of theory using the RIJCOSX approximation and def2/J as the auxiliary basis set. For the reaction coordinate calculations, the optimized geometries were used to calculate the thermodynamic values at BP86 D3(BJ)/def2-SVP level of theory using the RIJCOSX approximation and def2/J as the auxiliary basis set.

Table S.5: The anchor point data used in the determination of FIA values

Species	kJ	Reaction 2
Me_3Si^+	-1071911.3	
Me_3SiF	-1334866.1	952.5
F^-	-262002.2	

Table S.6: Calculated data for the determination of the FIA values of the bis(catecholato)germane complexes.

Complex	Energy B3LYP D3(BJ)/def2-TZVPP		Thermal Correction PBEh-3c/def2-SVP		Electronic + Thermal	LA + Me$_3$SiY	Me$_3$Si+ + LA-F-	Rxn 1	FIA
	Hartree	kJ	Hartree	kJ	kJ	kJ	kJ	kJ	kJ
Ge(dtbc)$_2$	-3468.81	-9107359.86	0.68	1786.28	-9105573.59	-10442012.13	-10441492.90	519.23	433.27
Ge(dtbc)$_2$F$^-$	-3568.82	-9369935.50	0.68	1790.98	-9368144.52				
Ge(cat)$_2$	-2839.93	-7456226.40	0.20	512.82	-7455713.58	-8792152.12	-8791616.04	536.09	416.41
Ge(cat)$_2$F$^-$	-2939.93	-7718785.07	0.20	517.42	-7718267.65				
Ge(cat^F)$_2$	-3633.85	-9540669.19	0.14	358.27	-9540310.91	-10876749.46	-10876299.32	450.13	502.37
Ge(cat^F)$_2$F$^-$	-3733.89	-9803317.32	0.14	366.38	-9802950.94				
Ge(cat^{Cl})$_2$	-6516.41	-17108838.56	0.13	332.76	-17108505.81	-18444944.35	-18444499.64	444.71	507.79
Ge(cat^{Cl})$_2$F$^-$	-6616.45	-17371493.29	0.13	342.03	-17371151.25				
Ge(cat^{Br})$_2$	-23427.46	-61508778.69	0.12	323.92	-61508454.77	-62844893.31	-62844453.36	439.95	512.55
Ge(cat^{Br})$_2$F$^-$	-23527.50	-61771438.50	0.13	333.53	-61771104.97				
Ge(dtbc)$_2$ (ACN)	-3601.550124	-9455868.55	0.73	1921.77	-9453946.79	-10790385.33	-10789861.82	523.51	428.99
Ge(dtbc)$_2$ (ACN)F$^-$	-3701.560654	-9718446.16	0.74	1932.73	-9716513.44				
Ge(cat)$_2$ (ACN)	-2972.667157	-7804736.55	0.25	650.58	-7804085.97	-9140524.51	-9139991.90	532.61	419.89
Ge(cat)$_2$ (ACN)F$^-$	-3072.672461	-8067300.44	0.25	656.92	-8066643.52				
Ge(cat^F)$_2$ (ACN)	-3766.600672	-9889208.71	0.19	498.59	-9888710.11	-11225148.66	-11224680.20	468.45	484.05
Ge(cat^F)$_2$ (ACN)F$^-$	-3866.629872	-10151835.34	0.19	503.52	-10151331.82				
Ge(cat^{Cl})$_2$ (ACN)	-6649.164689	-17457379.49	0.18	471.04	-17456908.46	-18793347.00	-18792886.60	460.39	492.11
Ge(cat^{Cl})$_2$ (ACN)F$^-$	-6749.19924	-17720020.17	0.18	481.95	-17719538.22				
Ge(cat^{Br})$_2$ (ACN)	-23560.20926	-61857320.91	0.18	464.82	-61856856.09	-63193294.64	-63192841.94	452.70	499.80
Ge(cat^{Br})$_2$ (ACN)F$^-$	-23660.24586	-62119966.98	0.18	473.43	-62119493.55				
Ge(cat^{Br})$_2$ (THF)	-23659.9023	-62119064.95	0.25	662.72	-62118402.23	-63454840.77	-63454382.12	458.65	493.85
Ge(cat^{Br})$_2$ (THF)F$^-$	-23759.93649	-62381704.69	0.26	670.95	-62381033.74				
Ge(cat^{Br})$_2$ (Et$_2$O)	-23661.11041	-62122236.86	0.27	721.08	-62121515.77	-63457954.31	-63457500.02	454.29	498.21
Ge(cat^{Br})$_2$ (Et$_2$O)F$^-$	-23761.14629	-62384881.02	0.28	729.39	-62384151.64				

Table S.7: Calculated data for the determination of the GEI values of the bis(catecholato)germane complexes.

Complex	HOMO	LUMO	Chemical Potential (μ)	Chemical Hardness (η)	GEI Values (ω)
Ge(cat)$_2$	-6.369	-0.8745	-3.62175	5.4945	1.194
Ge(dtbc)$_2$	-6.0017	-0.6984	-3.35005	5.3033	1.058
Ge(cat^F)$_2$	-7.1595	-2.0776	-4.61855	5.0819	2.099
Ge(cat^{Cl})$_2$	-6.9335	-1.8747	-4.4041	5.0588	1.917
Ge(cat^{Br})$_2$	-6.8631	-1.9912	-4.42715	4.8719	2.012
Ge(cat)$_2$ACN	-5.4311	-1.4356	-3.43335	3.9955	1.475
Ge(dtbc)$_2$ACN	-5.1478	-1.4195	-3.28365	3.7283	1.446
Ge(cat^F)$_2$ACN	-6.1888	-2.154	-4.1714	4.0348	2.156
Ge(cat^{Cl})$_2$ACN	-6.1275	-2.1738	-4.15065	3.9537	2.179
Ge(cat^{Br})$_2$ACN	-6.1242	-2.1942	-4.1592	3.93	2.201
Ge(cat^{Br})$_2$Ether	-6.3495	-1.6325	-3.991	4.717	1.688
Ge(cat^{Br})$_2$THF	-6.4024	-1.6202	-4.0113	4.7822	1.682

Table S.8: Relative energies of Ge(cat^{Br})$_2$ derivatives. The raw data can be found in **Table S.9**.

Complex	Relative Enthalpy (kJ/mol)	Relative Gibbs Free Energy (kJ/mol)
Ge(cat^{Br})$_2$(ACN)$_2$ + Styrene +HSiEt$_3$	0	0
Ge(cat^{Br})$_2$(ACN) + ACN + Styrene +HSiEt$_3$	93.81	29.57
Ge(cat^{Br})$_2$ + 2ACN + Styrene +HSiEt$_3$	165.98	33.98
Ge(cat^{Br})$_2$(Styrene) + 2ACN +HSiEt$_3$	75.94	15.11
Cis-Ge(cat^{Br})$_2$(Styrene)(ACN) + ACN +HSiEt$_3$	2.03	6.59
Trans-Ge(cat^{Br})$_2$(Styrene)(ACN) + ACN +HSiEt$_3$	-26.01	-14.42
Ge(cat^{Br})$_2$H$^-$ + ACN--SiEt$_3^+$ + ACN + Styrene	288.64	223.77
Ge(cat^{Br})$_2$(ACN)H$^-$ + ACN--SiEt$_3^+$ + Styrene	243.15	237.85
Ge(cat^{Br})$_2$(H)(SiEt$_3$) + 2ACN + Styrene	99.17	44.08

Table S.9: Calculated data for determining the thermochemistry of key intermediates in the dimerization of styrene.

Complex	Enthalpy (hartree)	Enthalpy (kJ/mol)	Gibbs (hartree)	Gibbs (kJ/mol)
Ge(cat^{Br})$_2$(ACN)$_2$	-23692.90088	-62205711.27	-23692.99072	-62205947.13
Ge(cat^{Br})$_2$(ACN)	-23560.25869	-61857459.2	-23560.34328	-61857681.27
Ge(cat^{Br})$_2$(THF)$_2$	-23892.05995	-62728603.39	-23892.15298	-62728847.65
Ge(cat^{Br})$_2$(THF)	-23659.83407	-62118894.35	-23659.92072	-62119121.85
Ge(cat^{Br})$_2$	-23427.62475	-61509228.78	-23427.70542	-61509440.58
ACN	-132.6064582	-348158.2559	-132.6361785	-348236.2865
THF	-232.1676769	-609556.2356	-232.1991325	-609638.8223
Styrene	-309.302937	-812074.8612	-309.3421922	-812177.9256
Ge(cat^{Br})$_2$(Styrene)	-23736.96198	-62321393.68	-23737.0548	-62321637.37
Cis-Ge(cat^{Br})$_2$(Styrene)(ACN)	-23869.59659	-62669625.85	-23869.69422	-62669882.18
Trans-Ge(cat^{Br})$_2$(Styrene)(ACN)	-23869.60727	-62669653.89	-23869.70222	-62669903.19
HSiEt$_3$	-527.3560081	-1384573.199	-527.3986291	-1384685.101
SiEt$_3$$^+$	-526.494541	-1382311.417	-526.5342082	-1382415.564
ACN--SiEt$_3$$^+$	-659.1825821	-1730683.869	-659.2302814	-1730809.104
Ge(cat^{Br})$_2$H$^-$	-23428.35791	-61511153.7	-23428.43766	-61511363.07
Ge(cat^{Br})$_2$(ACN)H$^-$	-23560.9817	-61859357.45	-23561.06848	-61859585.28
Ge(cat^{Br})$_2$(H)(SiEt$_3$)	-23955.0062	-62893868.79	-23955.1002	-62894115.58

5. X-Ray Crystallography Details

5.1 General Considerations

The samples were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry-constrained fit of 9916 reflections with $5.46° < 2θ < 63.72°$. The data collection strategy was a number of $ω$ and $φ$ scans which collected data up to $67.682°$ ($2θ$). The frame integration was performed using SAINT.[5] The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[6]

The structures were solved by using a dual space methodology using the SHELXT program.[7] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at

idealized positions and were allowed to ride on the parent atom. The structural models were fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the SHELXL program from the SHELX suite of crystallographic software.[8] Graphic plots were produced using the Mercury program suite.[9]

Late in the refinement of the Ge(dtbc)$_2$(THF)$_2$ crystal, there was a large peak (2.68 e^-/ Å^3) approximately 1.54 Å from C6. It was possible to refine this peak as a partially occupied (20%) carbon. However, it is not clear that this is truly peak of chemical significance. The difference maps did not show additional peaks corresponding to a t-butyl group, and the NMR and MS data indicate that the structure of this compound is consistent with our proposed structure. In addition, the NMR data does not show evidence for the presence of a second compound.

Table S.10: Summary of Crystal Data for Ge(dtbc)$_2$(THF)$_2$, [NBu$_4$][Ge(cat^{Br})$_2$Cl], and Ge(dtbc)$_2$(OPEt$_3$)$_2$.

Formula	C$_{36}$H$_{56}$GeO$_6$	C$_{28}$H$_{36}$Br$_8$ClGeNO$_4$	C$_{40}$H$_{70}$GeO$_6$P$_2$
CCDC	2090115	2090116	2090117
Formula Weight (*g/mol*)	657.39	1197.90	781.49
Crystal Dimensions *mm*)	0.294 × 0.153 × 0.043	0.354 × 0.340 × 0.144	0.373 × 0.229 × 0.167
Crystal Colour and Habit	colourless plate	colourless prism	colourless prism
Crystal System	monoclinic	triclinic	triclinic
Space Group	P 2$_1$/c	P -1	P -1
Temperature, K	110	223	110
a, Å	7.091(2)	9.864(5)	8.012(3)
b, Å	18.355(5)	11.942(6)	9.945(4)
c, Å	12.889(5)	16.473(7)	14.528(6)
α,°	90	84.984(10)	109.138(11)
β,°	94.130(14)	88.202(8)	92.133(9)
γ,°	90	73.534(13)	95.396(13)
V, Å^3	1673.2(9)	1853.6(16)	1085.9(8)
Number of reflections to determine final unit cell	9916	9198	9440
Min and Max 2θ for cell determination, °	5.46, 63.72	4.76, 60.9	6.04, 74.58
Z	2	2	1
F(000)	704	1144	420
ρ (*g/cm*)	1.305	2.146	1.195

λ, Å, (MoKα)	0.71073	0.71073	0.71073
μ, (cm^{-1})	0.959	9.554	0.819
Diffractometer Type	Bruker Kappa Axis Apex2	Bruker Kappa Axis Apex2	Bruker Kappa Axis Apex2
Scan Type(s)	phi and omega scans	phi and omega scans	phi and omega scans
Max 2θ for data collection, °	67.682	61.112	84.336
Measured fraction of data	0.999	0.999	0.998
Number of reflections measured	56754	112781	125120
Unique reflections measured	6714	11316	15267
R$_{merge}$	0.0652	0.0456	0.0385
Number of reflections included in refinement	6714	11316	15267
Cut off Threshold Expression	I > 2sigma(I)	I > 2sigma(I)	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2	full matrix least-squares using F^2	full matrix least-squares using F^2
Weighting Scheme	w=1/[sigma^2(Fo^2)+(0.0458P)^2+1.9778P] where P=(Fo^2+2Fc^2)/3	w=1/[sigma^2(Fo^2)+(0.0219P)^2+1.5099P] where P=(Fo^2+2Fc^2)/3	w=1/[sigma^2(Fo^2)+(0.0399P)^2+0.0621P] where P=(Fo^2+2Fc^2)/3
Number of parameters in least-squares	202	392	232
R$_1$	0.0487	0.0275	0.0269
wR$_2$	0.1103	0.0518	0.0700
R$_1$ (all data)	0.0718	0.0462	0.0362
wR$_2$ (all data)	0.1195	0.0571	0.0733
GOF	1.045	1.033	1.045
Maximum shift/error	0.000	0.002	0.001
Min & Max peak heights on final ΔF Map (e^-/Å^3)	-0.678, 2.679	-0.928, 0.941	-0.323, 0.687

Where:

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$

$wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]^{\frac{1}{2}}$

$\qquad GOF = [\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{\frac{1}{2}}$

6. NMR Spectra
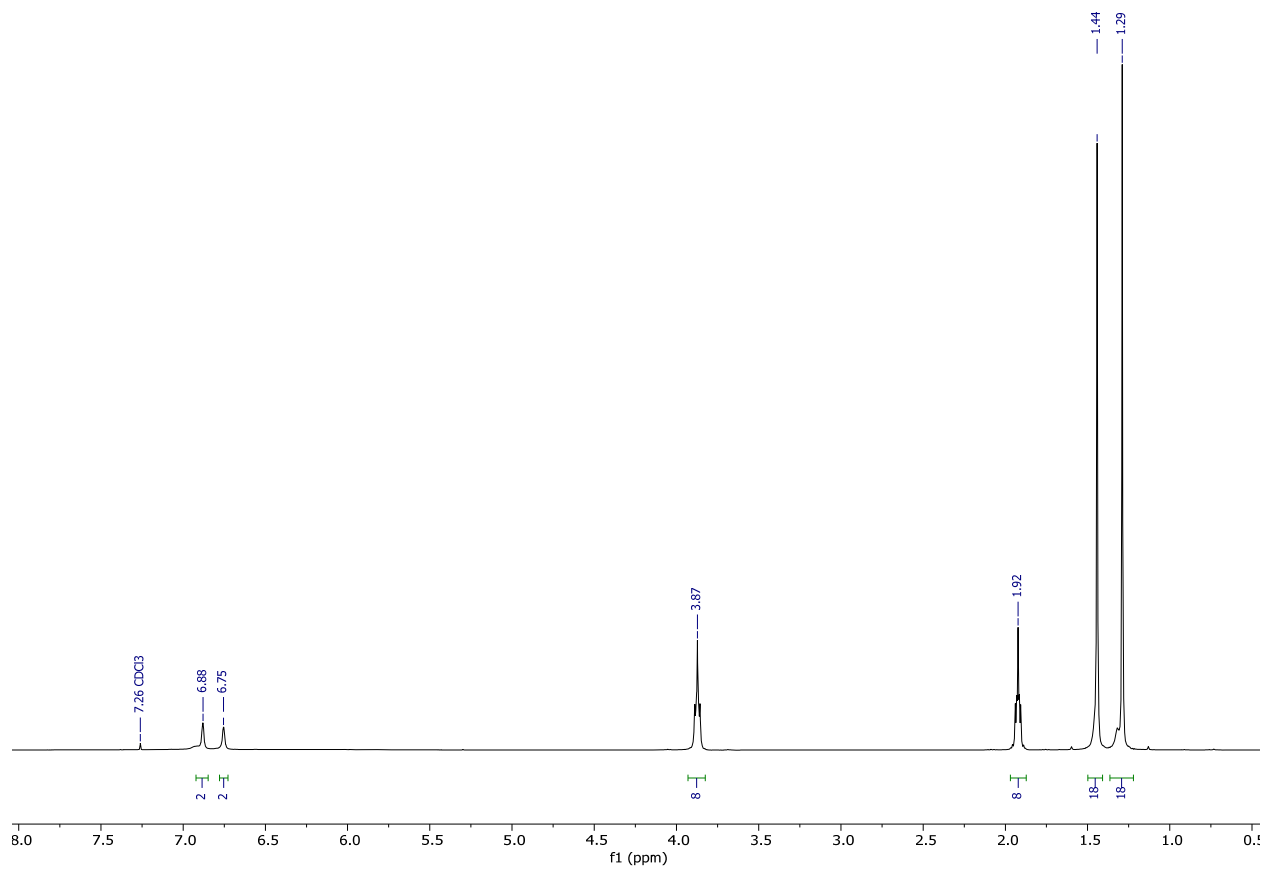
Figure S.2: ^1H NMR (CDCl$_3$, 400 MHz) spectrum of Ge(dtbc)$_2$(THF)$_2$.
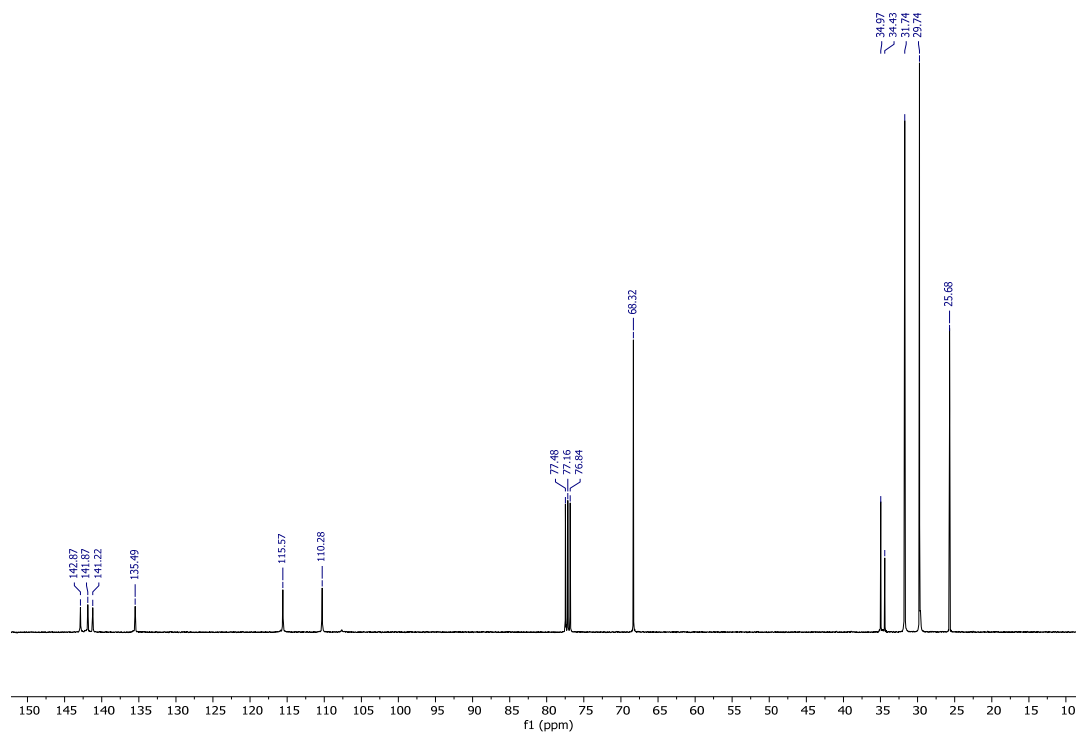
Figure S.3: $^{13}C\{^1H\}$ NMR (CDCl$_3$, 400 MHz) spectrum of Ge(dtbc)$_2$(THF)$_2$.
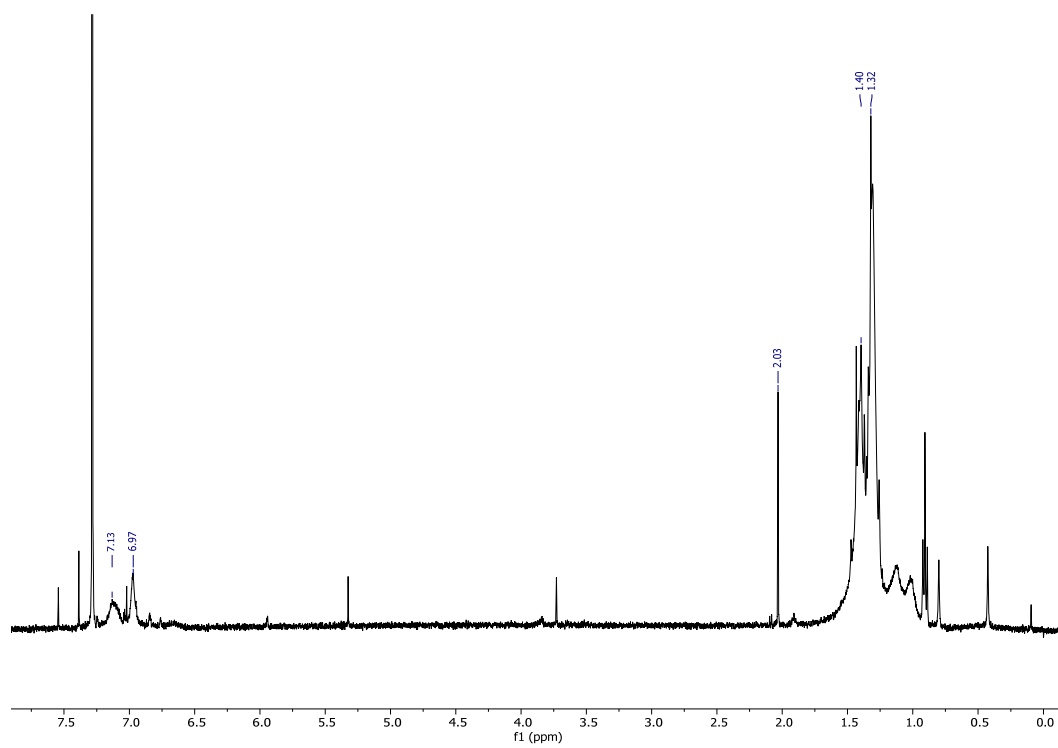
Figure S.4: ^1H NMR (CDCl$_3$, 400 MHz) spectrum of Ge(dtbc)$_2$(ACN)$_2$.
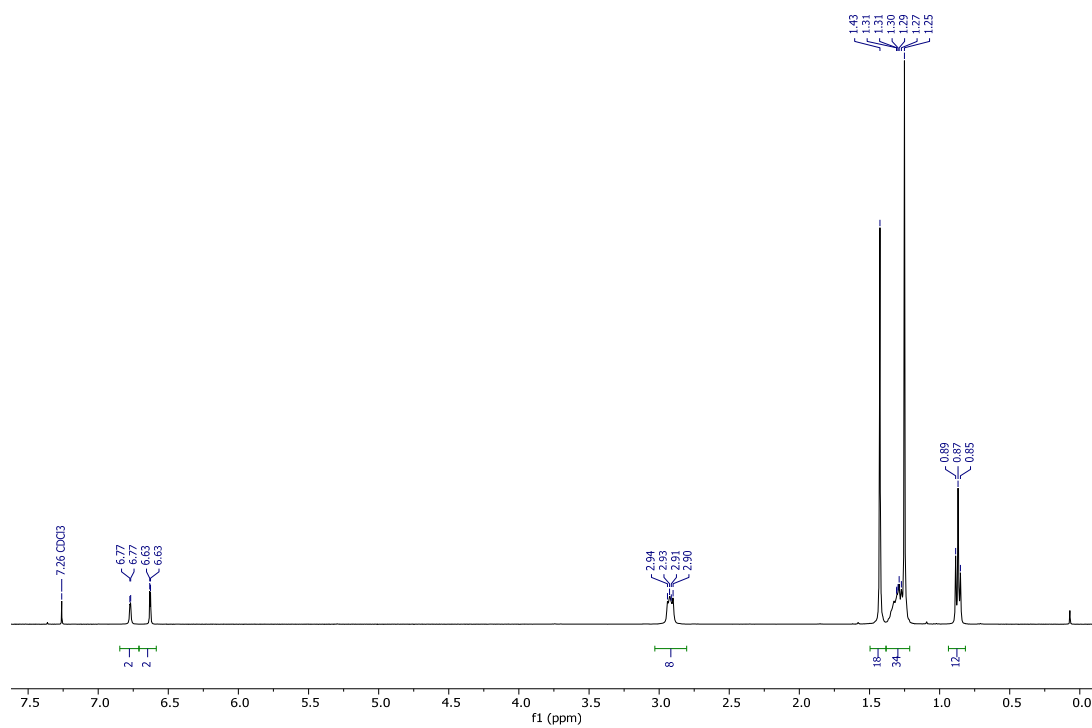
Figure S.5: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of [NBu$_4$][Ge(dtbc)$_2$Cl].
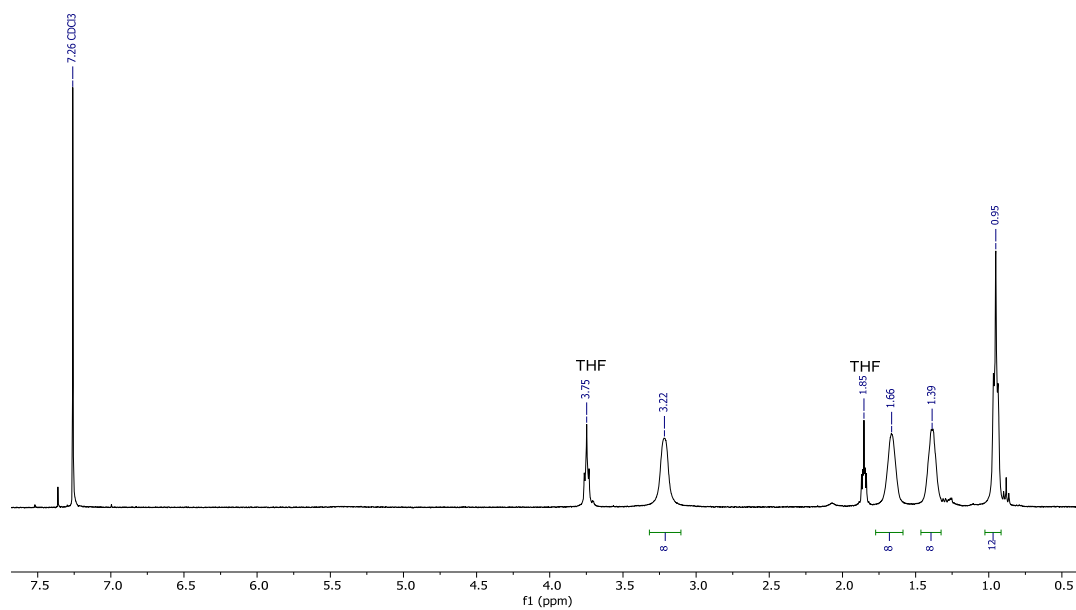
Figure S.6: ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of [NBu$_4$][Ge(cat^{Cl})$_2$Cl].
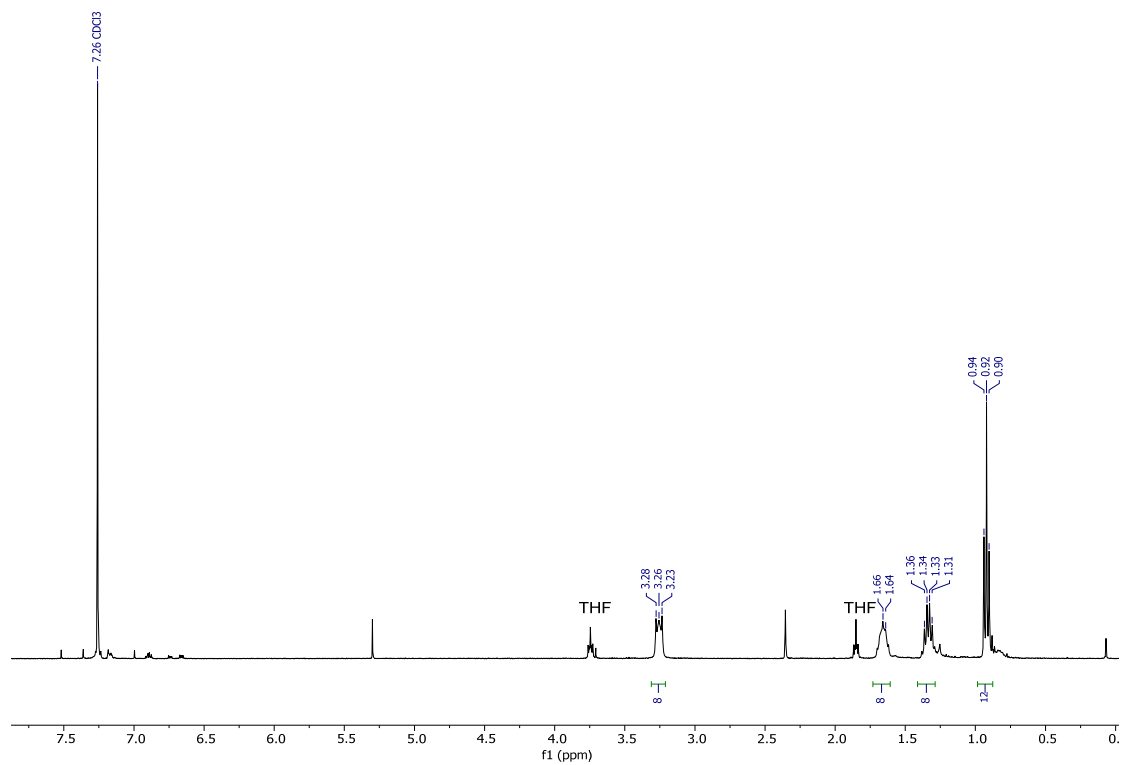
Figure S.7: ^1H NMR (CDCl$_3$, 400 MHz) spectrum of [NBu$_4$][Ge(cat^{Br})$_2$Cl].
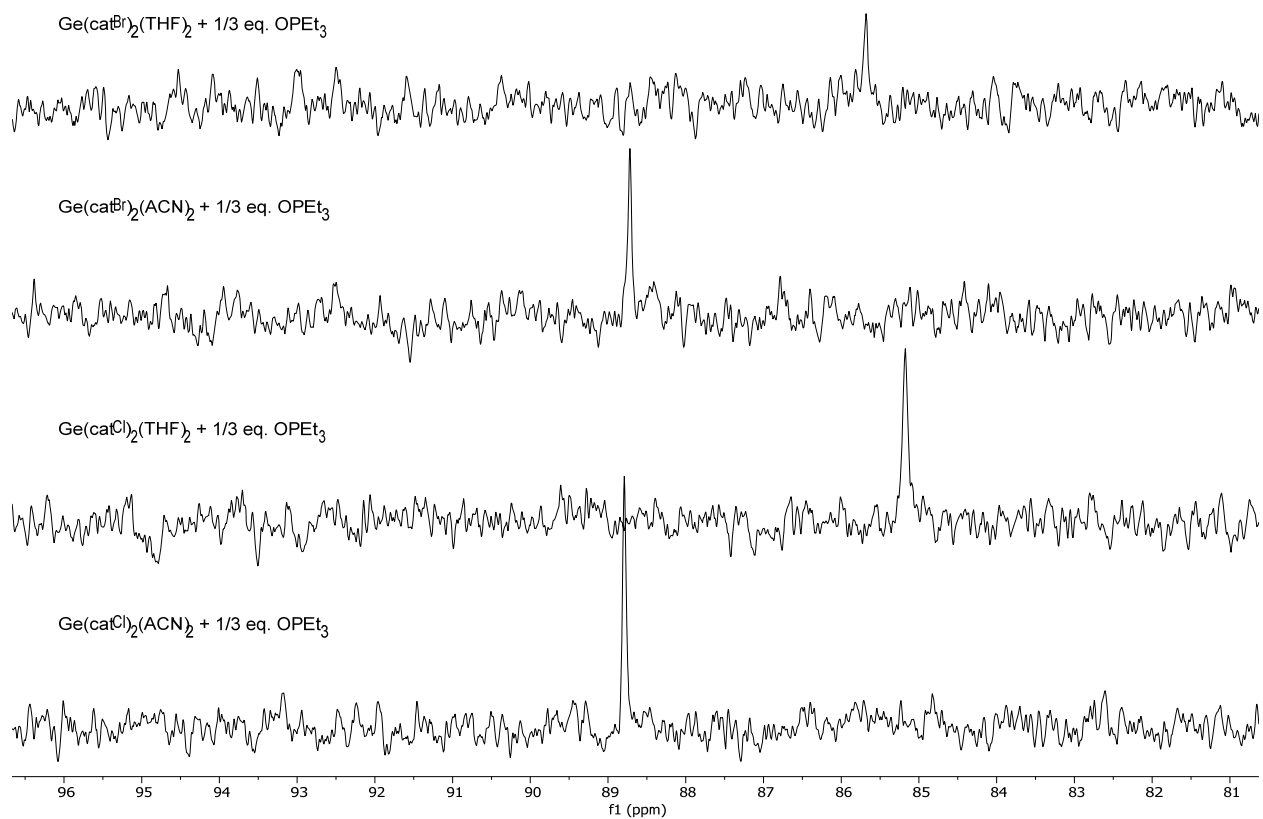
Figure S.8: $^{31}P\{^1H\}$ NMR (CH$_2$Cl$_2$, 162 MHz) stacked spectrum of the Gutmann-Beckett analysis performed with sub-stoichiometric amounts of triethylphosphine oxide on the halogenated bis(catecholato)germanes.
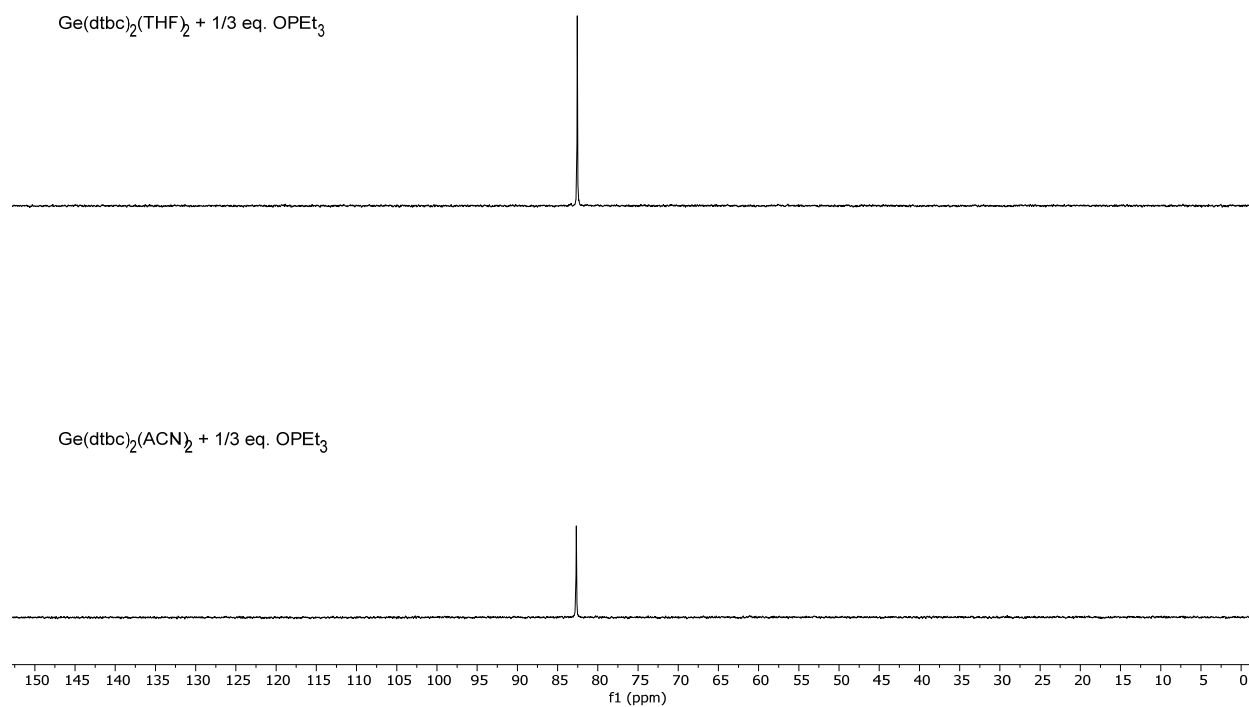
Figure S.9: $^{31}P\{^1H\}$ NMR (162 MHz, CD$_2$Cl$_2$) stacked spectrum of the Gutmann-Beckett analysis performed with sub-stoichiometric amounts of triethylphosphine oxide on the 3,5-di-*tert*-butyl bis(catecholato)germanes. In each case, the signal is assigned to Ge(3,5-dtbc)$_2$(OPEt$_3$).
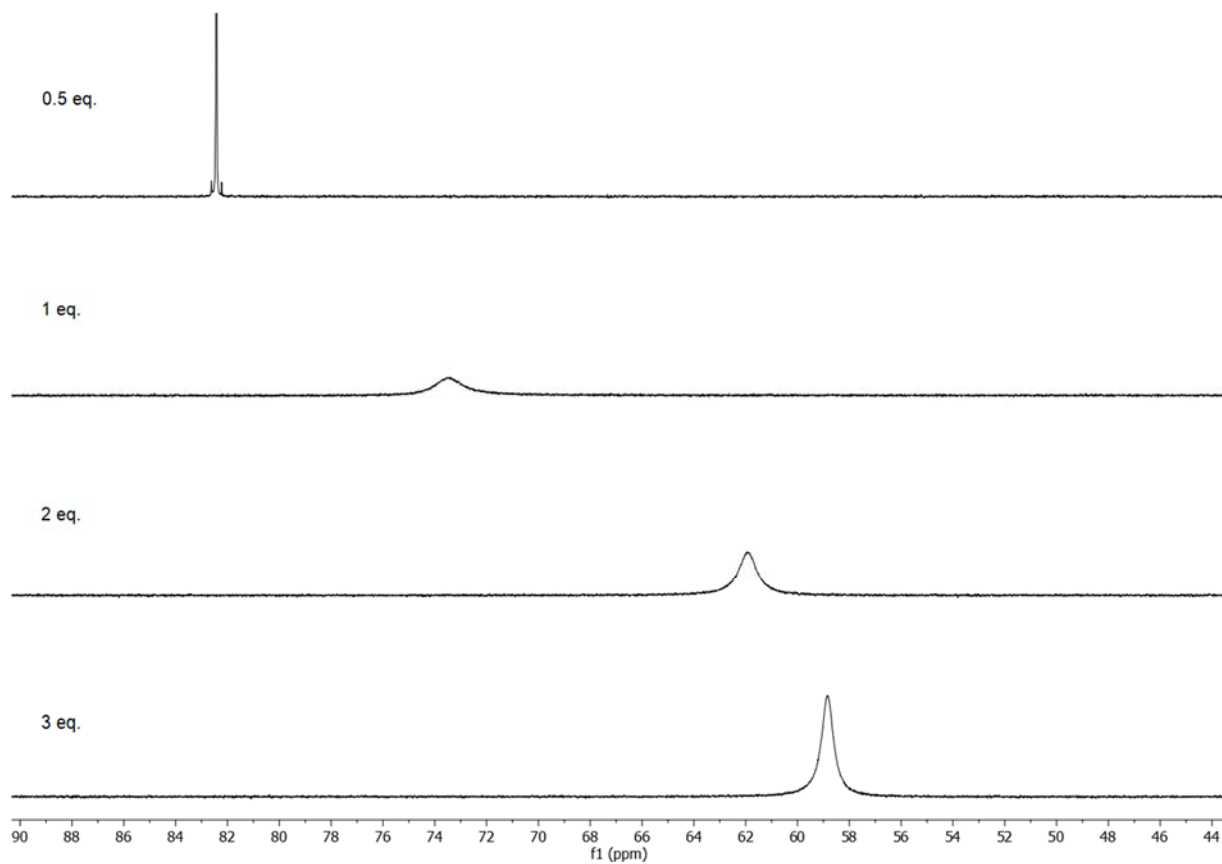
Figure S.10: $^{31}P\{^{1}H\}$ NMR (162 MHz in CD_2Cl_2) stacked spectra of Ge(3,5-dtbc)$_2$(THF)$_2$ and various equivalents of triethylphosphine oxide
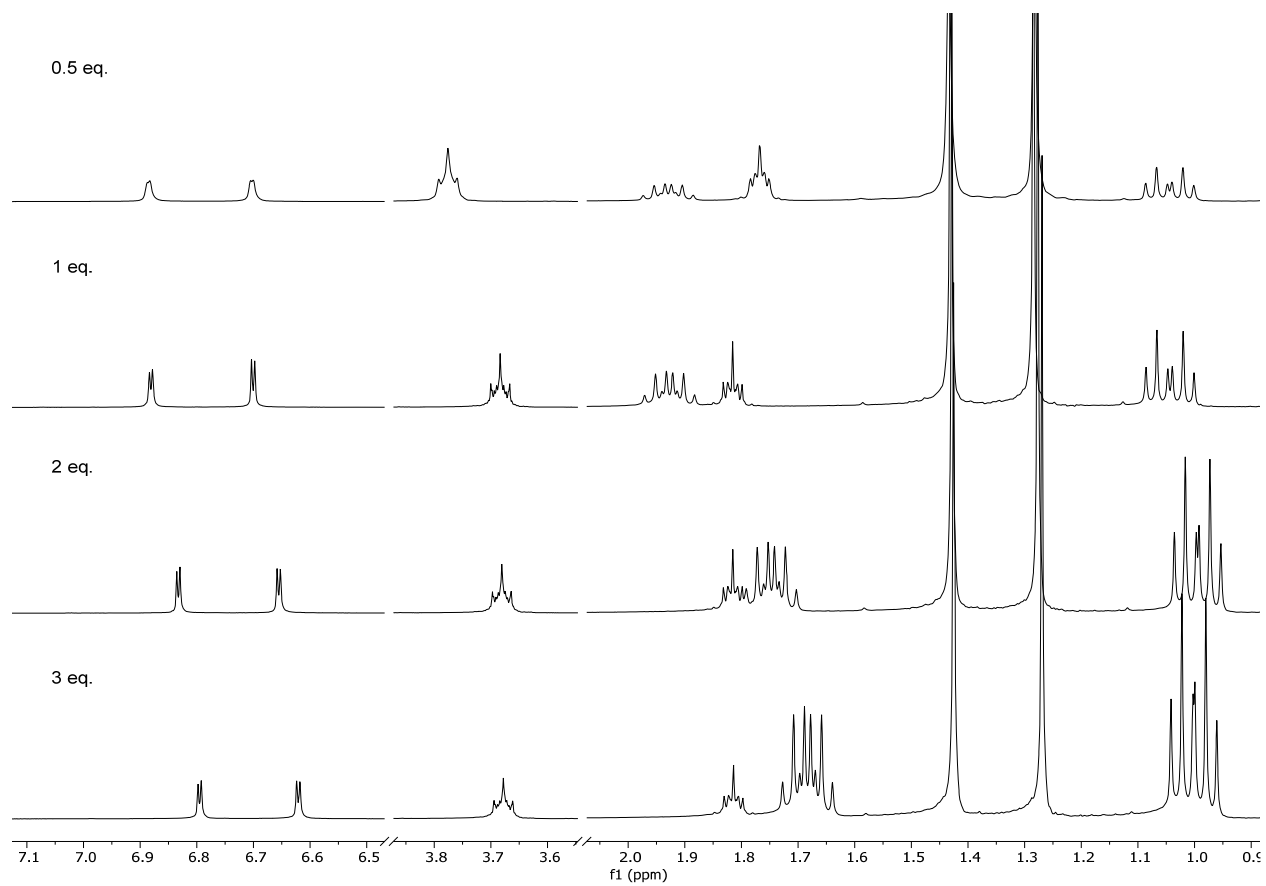
Figure S.11: ^{1}H NMR (400 MHz in CD_2Cl_2) stacked spectra of Ge(3,5-dtbc)$_2$(THF)$_2$ and various equivalents of triethylphosphine oxide
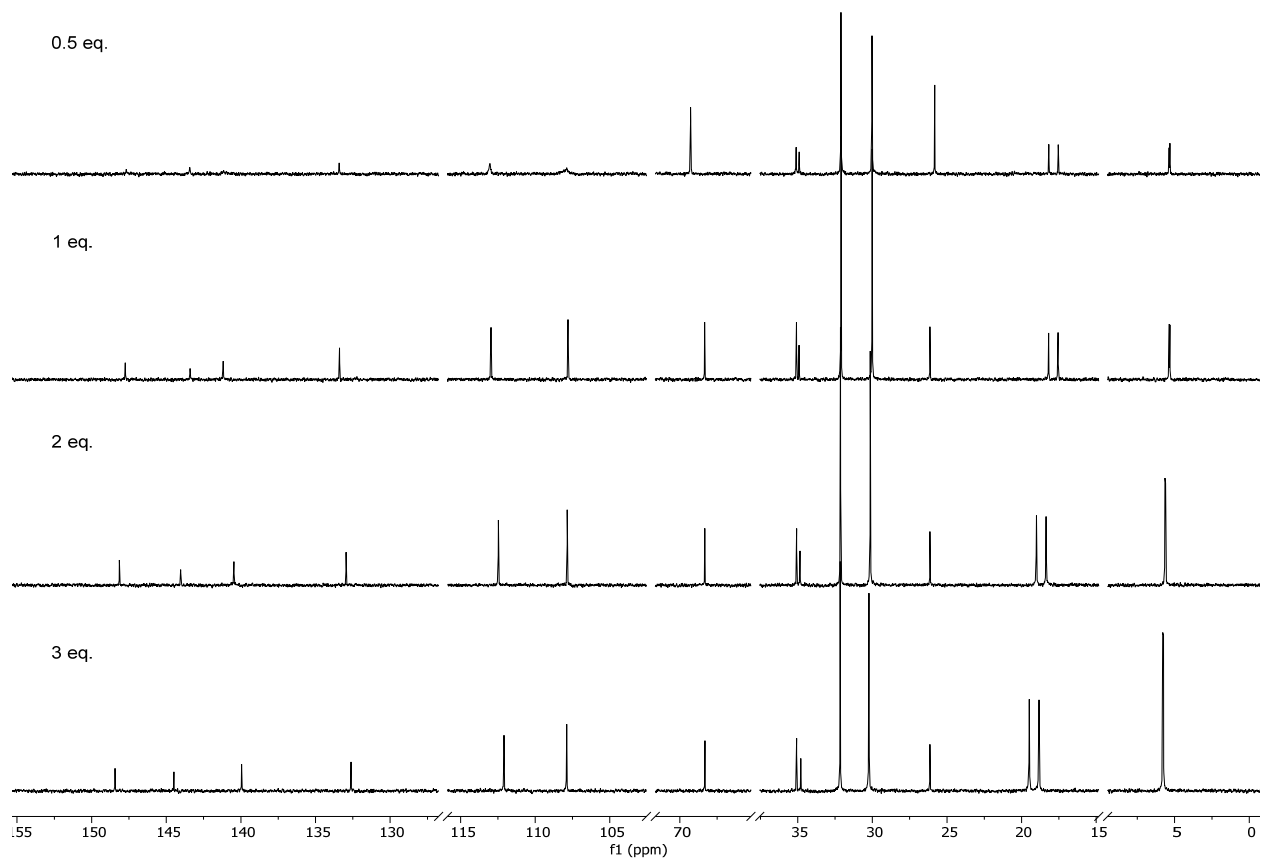
Figure S.12: $^{13}C\{^1H\}$ NMR (101 MHz in CD_2Cl_2) stacked spectra of Ge(3,5-dtbc)$_2$(THF)$_2$ and various equivalents of triethylphosphine oxide
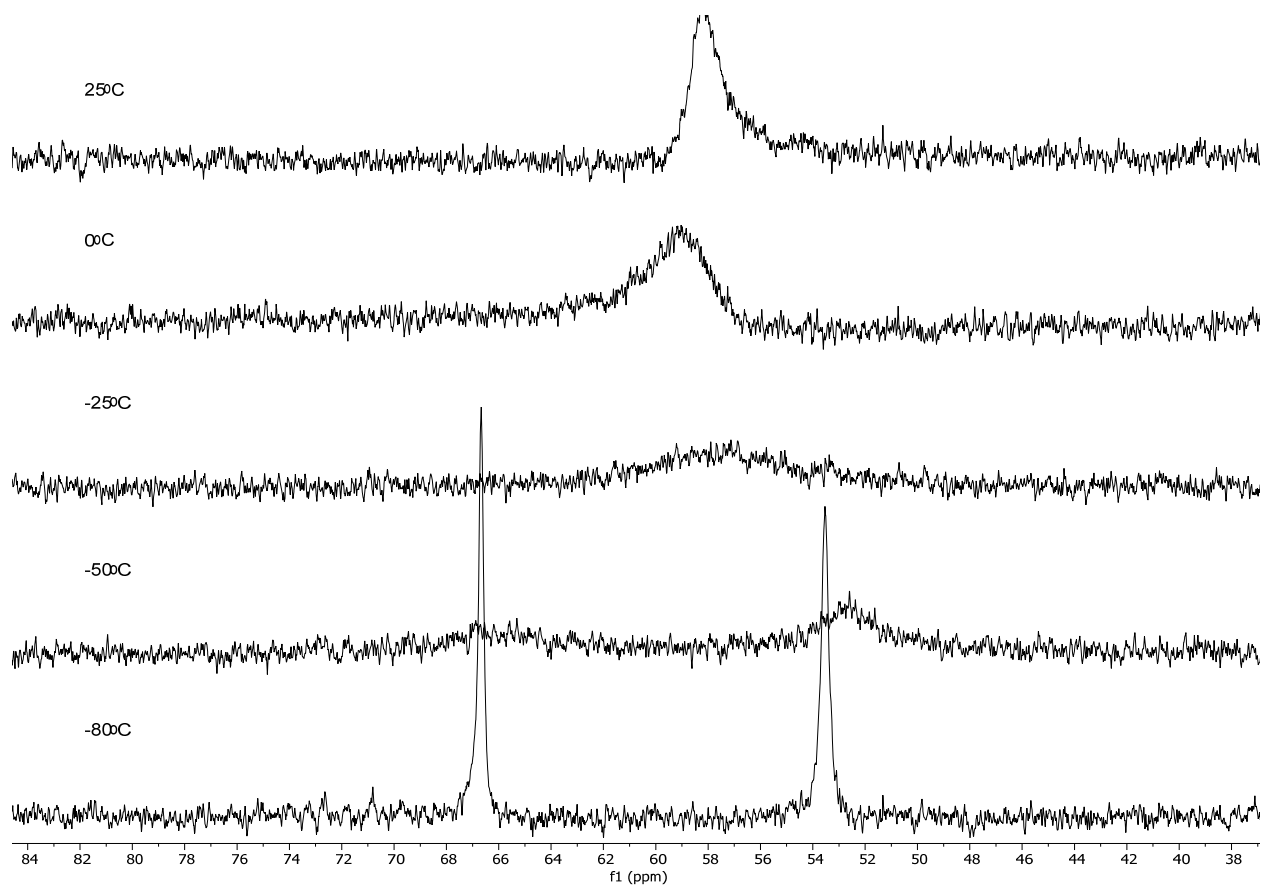
Figure S.13: $^{31}P\{^1H\}$ VT-NMR (162 MHz in CD_2Cl_2) stacked spectra of Ge(3,5-dtbc)$_2$(THF)$_2$ and 3 eq. of triethylphosphine oxide.
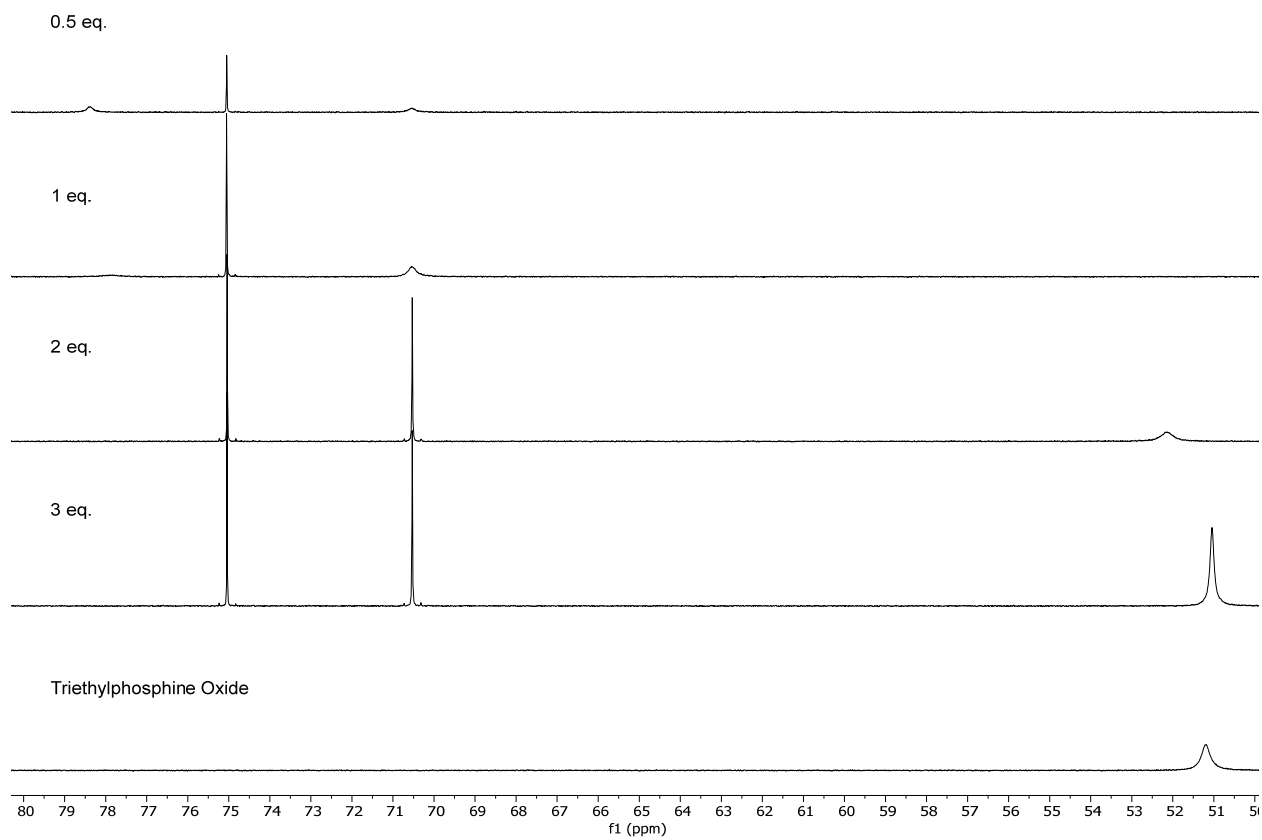
Figure S.14: $^{31}P\{^1H\}$ NMR (162 MHz in CD_2Cl_2) stacked spectra of $Ge(cat^{Cl})_2(THF)_2$ and various equivalents of triethylphosphine oxide
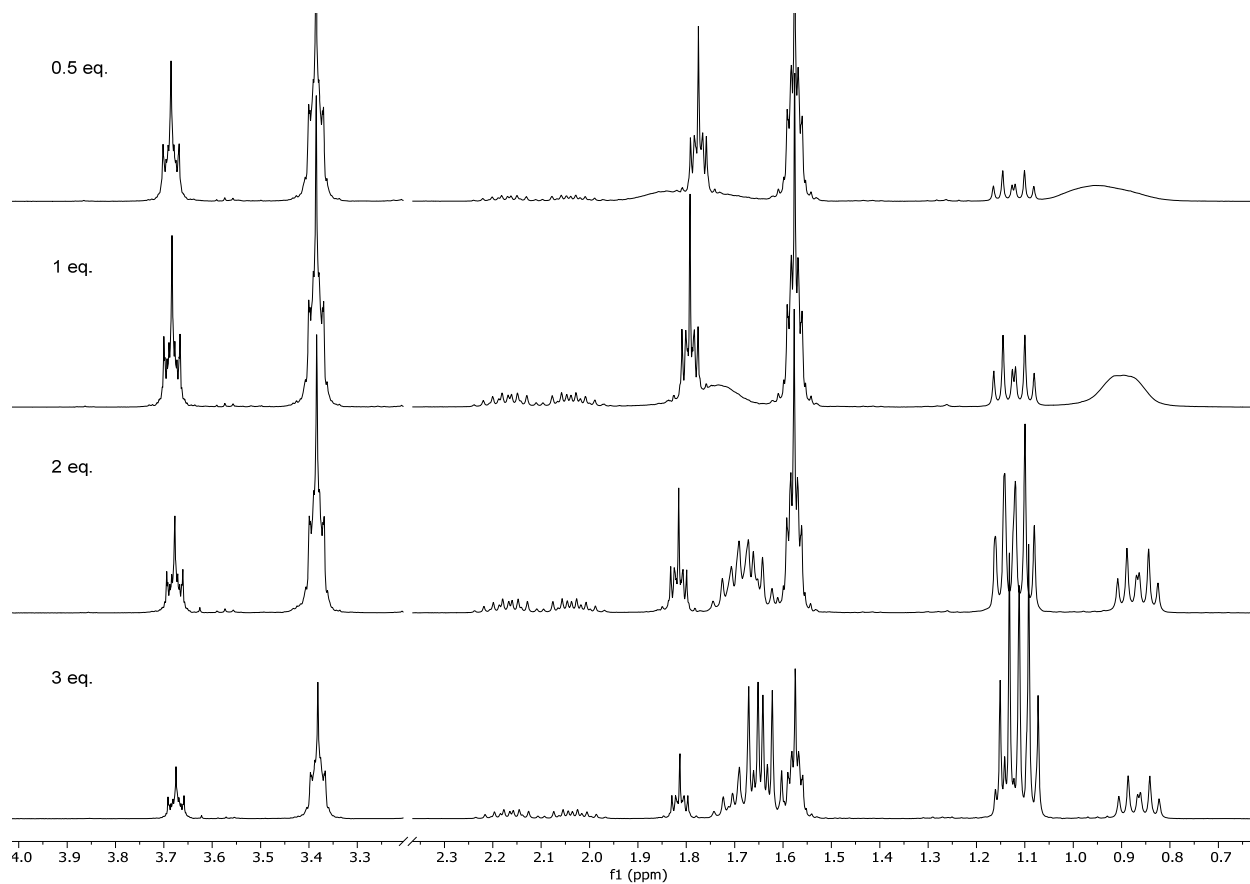
Figure S.15: ^{1}H NMR (400 MHz in CD$_2$Cl$_2$) stacked spectra of Ge(cat^{Cl})$_2$(THF)$_2$ and various equivalents of triethylphosphine oxide
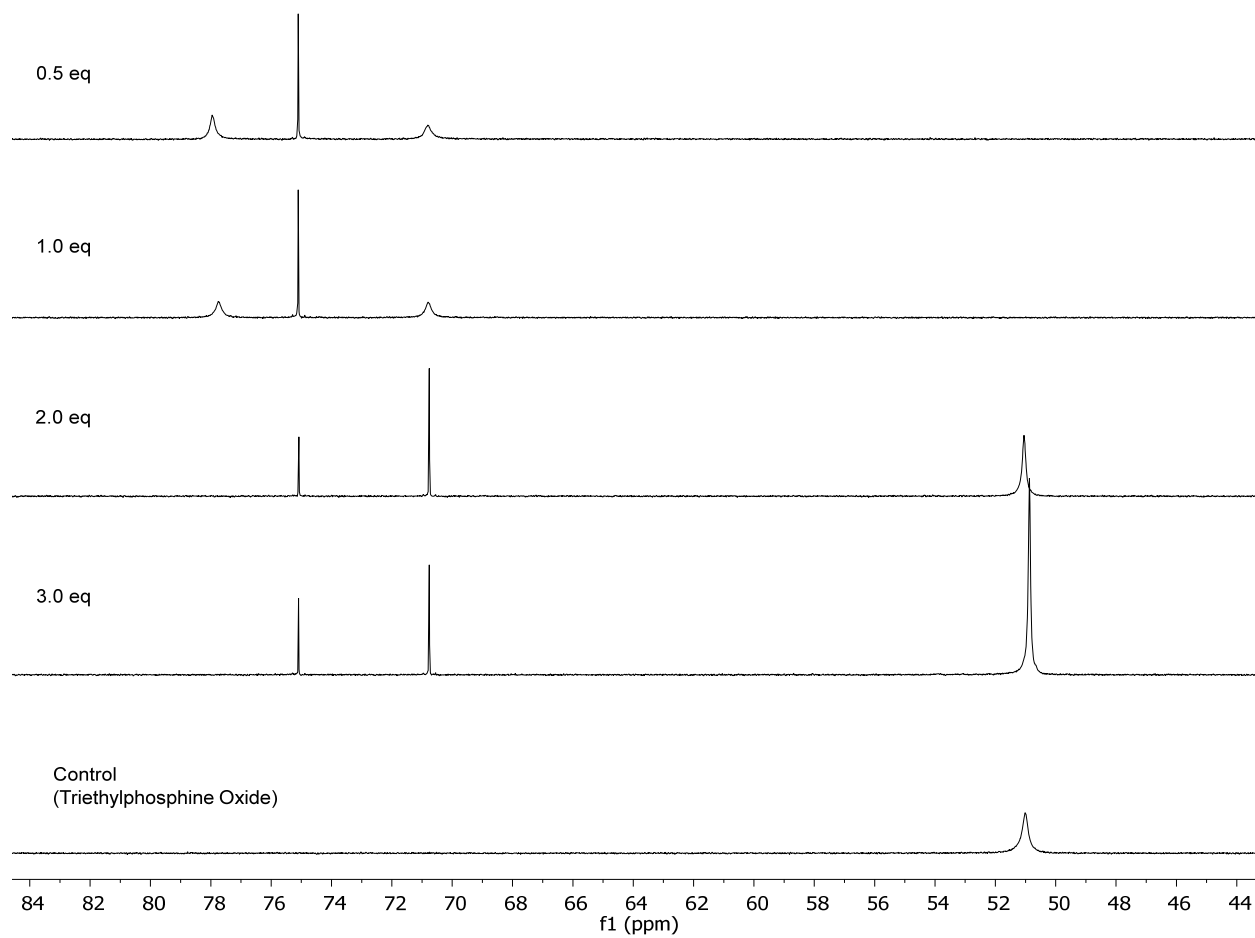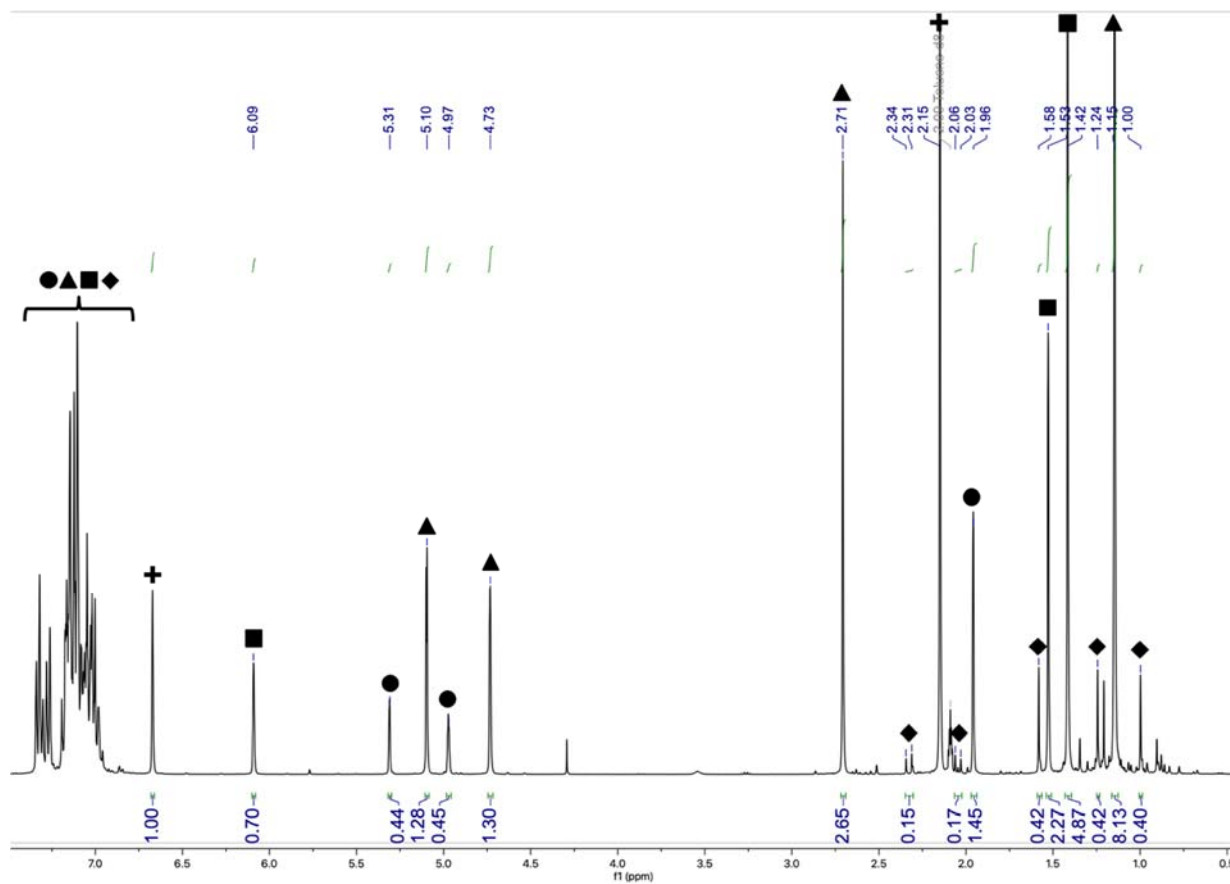
Figure S.16: $^{31}P\{^1H\}$ NMR (162 MHz in CD_2Cl_2) stacked spectra of $Ge(cat^{Br})_2(THF)_2$ and various equivalents of triethylphosphine oxide
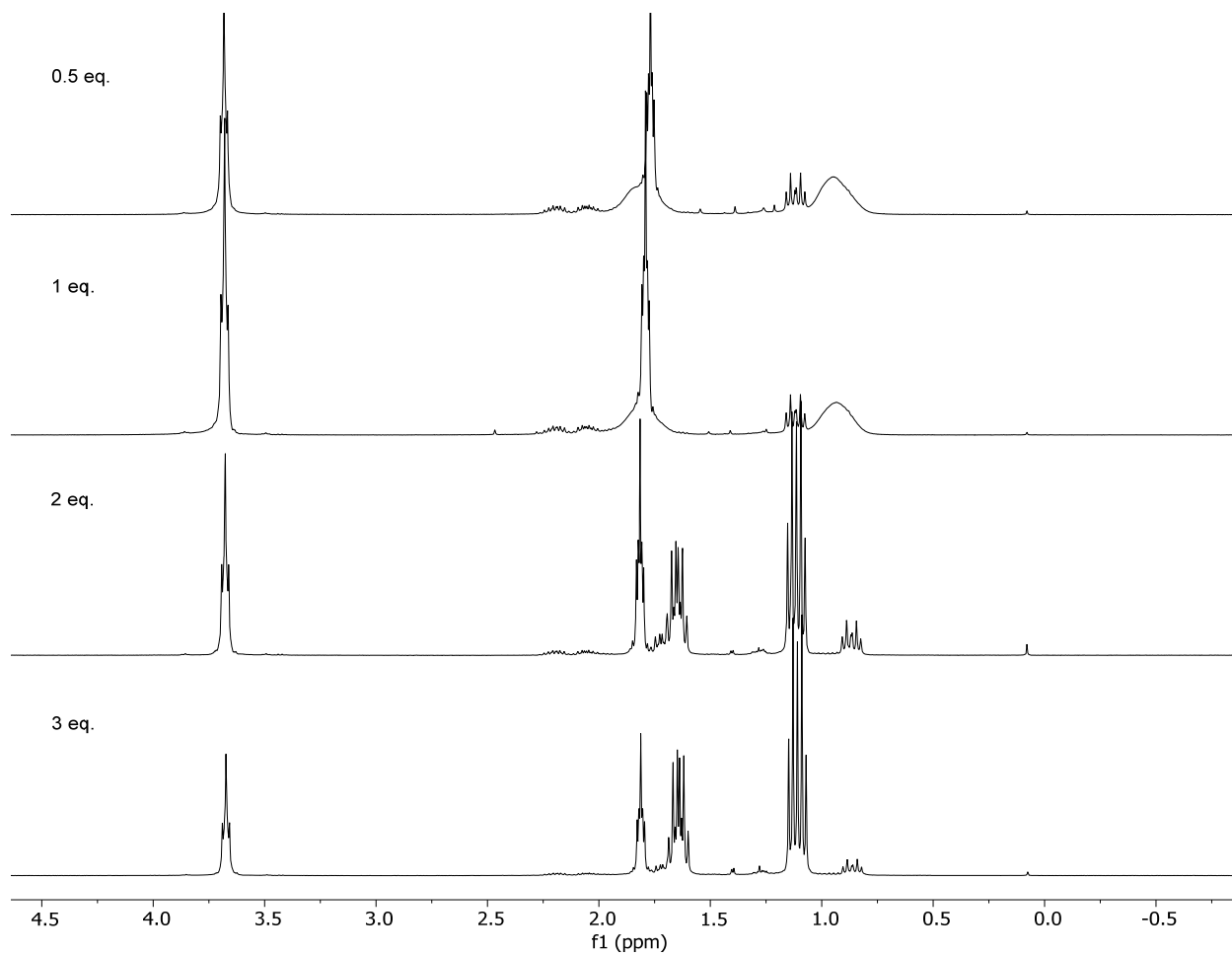
Figure S.17: ^{1}H NMR (400 MHz in CD$_2$Cl$_2$) stacked spectra of Ge(cat^{Br})$_2$(THF)$_2$ and various equivalents of triethylphosphine oxide
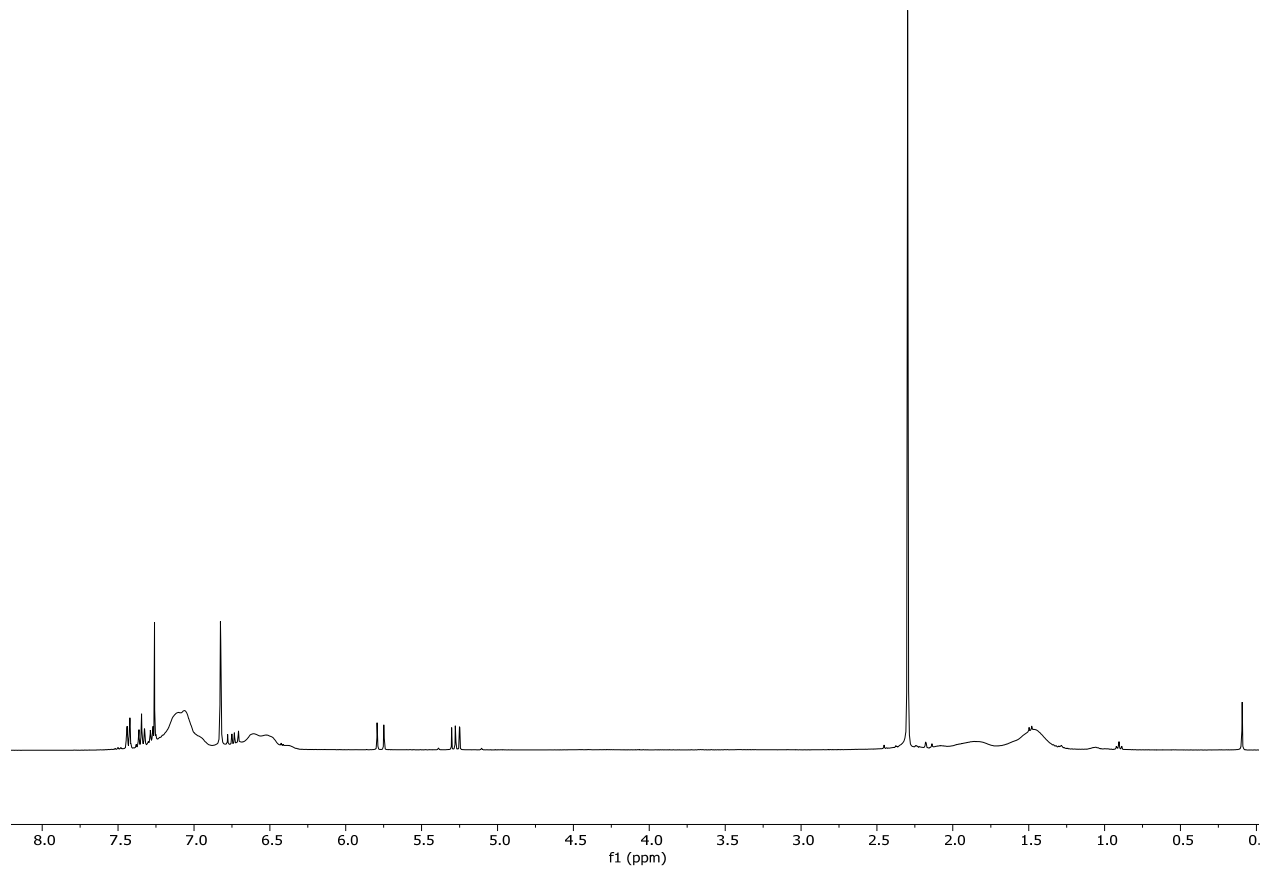
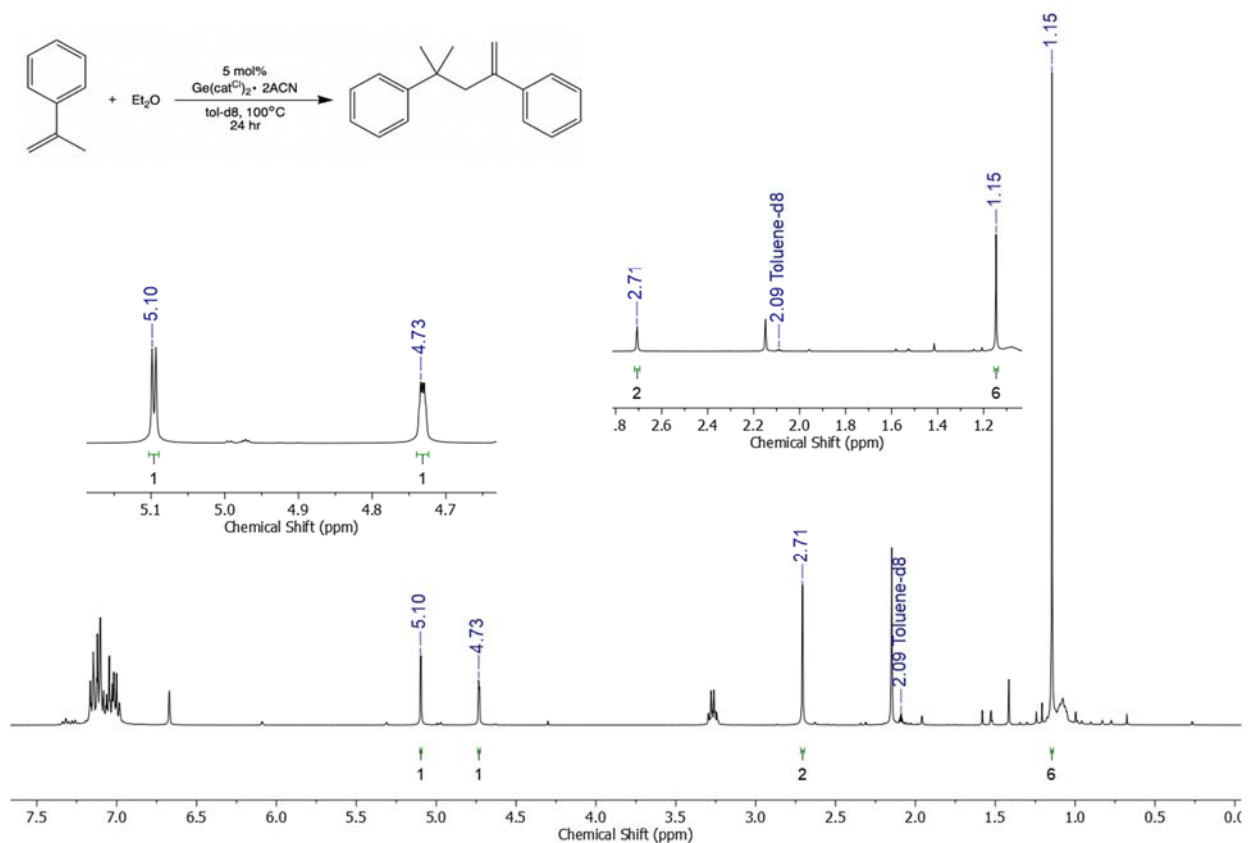**Figure S.18**: ^{1}H NMR (400 MHz in tol-d_8) spectrum of the polymerization of styrene with 5 mol% of Ge(cat^{Br})$_2$(THF)$_2$.

Figure S.19: ^{1}H NMR (400 MHz in tol-d_8) spectrum of the dimerization of α-methylstyrene with 5 mol% of Ge(cat^{Br})$_2$(THF)$_2$ illustrating the mixture of dimers observed. ● = α-methylstyrene, ✚ = mesitylene, ▲ = dimer **III**, ■ = dimer **IV**, ◆ = dimer **V**. (Table 3, Entry 1)
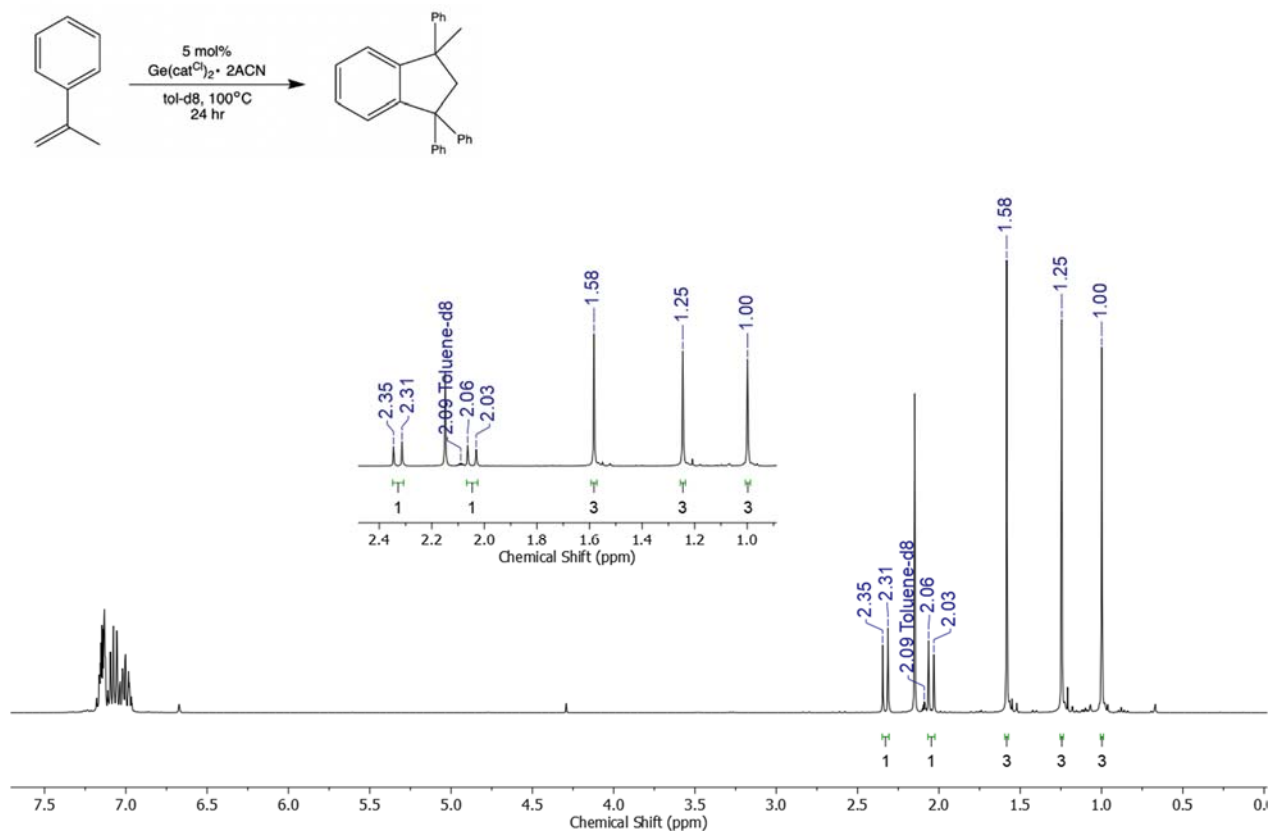
Figure S.20: ^{1}H NMR (400 MHz in tol-d_8) spectrum of the dimerization of α-methylstyrene with 5 mol% of Ge(cat^{Br})$_2$(ACN)$_2$, illustrating the selectivity towards dimer **V**. (Table 3, Entry 3)

Figure S.21: ^{1}H NMR (400 MHz in tol-d_8) spectrum of the dimerization of α-methylstyrene with 5 mol% of Ge(cat^{Cl})$_2$(ACN)$_2$ with 1 eq. of Et$_2$O added, illustrating the selectivity towards dimer **III**. (Table 3, Entry 7)

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