Supplemental Information

for

Leaving Group Effects on the Selectivity of the Silylation of Alcohols — the Reactivity-Selectivity Principle Revisited

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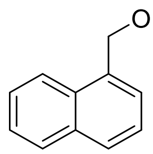
1) Synthesis and Reagents

1.1 Naphthalene-1-ylmethanol (**4a**)

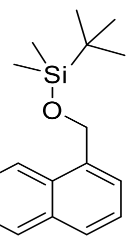


4a

15 mmol (0.567 g, 0.5 equivalents) of $NaBH_4$ are solved in 100 mL THF and cooled down to -10°C. 30 mmol (4.68 g, 4.07 mL, 1.0 equivalents) of 1-naphthaldehyde were dissolved in 50 mL THF and added dropwise to the solution. The reaction was allowed to stir 30 min at rt. The reaction process was monitored by TLC. The reaction was quenched by adding 2M HCl until no further H_2 evolved. The reaction mixture was extracted three times with DCM (20 mL) and washed with brine (20 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. A column chromatography on silica (*iso*-hexane:ethylacetate, 4:1) led to a white solid product **4a** in 95 % yield (4.50 g).

***R*$_f$** = 0.20 (*i*hexane/EtOAc, 4:1).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (bs, 1H, OH), 5.05 (s, 2H, CH_2), 7.40 – 7.61 (m, 4H), 7.81 – 7.87 (m, 1H), 7.88 – 7.96 (m, 1H), 8.03 – 8.14 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.37, 123.69, 125.27, 125.88, 126.32, 128.48, 128.69, 131. 25,133.80, 136.33.
MS (EI) m/z (%) = 158.1 ($[M+H]^+$, 83), 141.1 ($[M-OH]^+$, 20), 129.2 ($[M-CH_2OH]^+$, 100).
HRMS (EI) $C_{11}H_{10}O$ requires 158.0732 g/mol, found 158.0726 g/mol.

1.2 *tert*-Butyldimethyl(naphthalen-1-ylmethoxy)silane (**5a**)



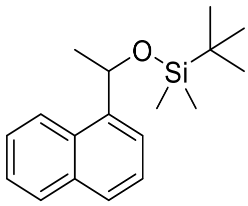
5a

0.32 g (2 mmol) **4a** and 0.36 g (2.4 mmol) TBSCl were dissolved in 15 mL DCM and 0.33 mL (0.24 g, 2.4 mmol) TEA was added. 0.010 g (0.08 mmol) DMAP (**6**) was added and the reaction stirred for 12 h at rt. The reaction mixture was quenched by adding NH_4Cl-solution and was extracted three times with 10 mL DCM. The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. Column chromatography on silica (*iso*-hexane:DCM, 4:1) led to **5a** as a colorless oil in 82 % yield (0.44 g).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 6H, $Si(CH_2)_2$), 0.97 (s, 9H, Si*t*Bu), 5.22 (s, 2H, CH_2), 7.59 – 7.47 (m, 3H), 7.59 – 7.61 (m, 1H), 7.79 (d, J = 8.1, 1H), 7.93 – 7.86 (m, 1H), 8.01 – 8.02 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = -5.22, 18.45, 25.95, 63.38, 123.27, 123.76, 125.44, 125.51, 125.78, 127.53, 128.58, 130.78, 133.49.

^{29}Si NMR (80 MHz, $CDCl_3$): δ = 20.58.
MS (**EI**) m/z (%) = 272.17 (0.6, [M]), 215.09 (72, [M-*t*Bu]$^+$), 141.07 (100), [M-OTBDMS]$^+$) 115.05 (13, [TBDMS]).
HRMS (EI) $C_{17}H_{24}OSi$ requires 272.1596 g/mol, found 271.1590 g/mol.

1.3 *tert*-Butyldimethyl(1-(naphthalen-1-yl)ethoxy)silane (**5b**)



5b

0.35 g (2 mmol) **4b** and 0.36 g (2.4 mmol) TBSCl were dissolved in 15 mL DCM and 0.33 mL (0.24 g 2.4 mmol) TEA was added. 0.010 g (0.08 mmol) DMAP (**6**) was added and the reaction stirred for 48 h at rt. The reaction mixture was quenched by adding NH_4Cl-solution and was extracted three times with 10 mL DCM. The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. Column chromatography on silica (*iso*-hexan:DCM, 4:1) led to **5b** as a yellowish oil in 76 % yield (0.46 g).

^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.10 (s, 3H, $SiCH_3$-*t*Bu), 0.10 (s, 3H, $SiCH_3$-*t*Bu), 0.95 (s, 9H, $(CH_3)_2Si$-tBu), 1.60 (d, J = 6.4, 3H, CH_3CH-OR), 5.61 (q, *J* = 6.6, 1H, CH), 7.44 – 7.55 (m, 3H), 7.67 – 7.78 (m, 2H), 7.85 – 7.91 (m, 1H), 8.11 (d, J = 7.3, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.92, −4.83, 18.30, 25.89, 26.62, 68.48, 122.67, 123.34, 125.15, 125.53, 125.57, 127.17, 128.82, 129.88.
^{29}Si NMR (80 MHz, $CDCl_3$): δ = 18.42.
HRMS (EI) $C_{18}H_{26}OSi$: requires 286.1753 g/mol, found: 286.1744 g/mol.
MS (EI) m/z (%) = 215.16 (6), 155.17 (23, [M - $C_6H_{15}OSi$]), 141.15 (33), 115.14 (13, [$C_6H_{15}Si$]), 76.09 (27, [C_6H_4]), 75.09 (100, [C_6H_3]).

2) Competition experiments

2.1 Preparing the samples

In order to achieve the needed accuracy three stock solutions have been prepared. This is necessary to guarantee the experimental reproducibility, however one should always try to minimize the number of stock solutions. The alcohols **4a** and **4b** were mixed in separate stock solutions (Stock A, B), while the silyl reagent was in a third stock solution (Stock C). Since no catalyst is needed for this reaction in DMF, no further stock solution was prepared. In Table S1 one can see the stock solutions for the silylation of **4a** and **4b**.

Table S1. Overview of stock solutions for competition experiment.

	substance	n [mmol]	M [g/mol]	m [mg]	c [M]
stock A (10 mL)	**4a**	6.6	158.20	1,044.10	0.66
stock B (10 mL)	**4b**	6.6	172.23	1,136.69	0.66
stock C (5 mL)	TBS-X	11.0			2.2

Dry DMF is stored in a glovebox over molecular sieves as well as freshly distilled Et_3N. All stock solutions have been prepared in a glovebox atmosphere in order to avoid water or other impurities in the reaction mixture for the reactions in DMF. Moreover, both alcohols have been dried by washing with dry toluene and removing the solvent afterwards for several times. For the reaction in $CDCl_3$ the stock solutions have been prepared under normal laboratory conditions.
3 mL of stock A and stock B were mixed in a 25 mL flask with a magnetic stir bar and sealed with a septum. Freshly distilled Et_3N was added in equimolar amounts as compared to the silyl reagent. Under steady mixing with a magnetic stirrer and temperature control with a water bath various amounts of stock C were added using a syringe pump within 15 min.
In contrast to the prior method for the reaction in chloroform DMAP (**6**) was added as catalyst in various amounts based on the amount of silyl reagent. A sample of 0.05 mL was taken and diluted with 1 mL methylene chloride and analyzed by GC, 55(0)-5-150(0)-20-280(20).

Table S2. Retention times of products, reactants, and side-products.

Substance	Retention time	Substance	Retention time
4a	15.914	TBSCl	5.015
4b	15.940	TBSOTf	
5a	16.921	TBSCN	7.481
5b	16.538	MTBSTFA	7.940
$(TBS)_2O$	9.340	TBS-Imi	
DMAP	13.218		

The determination of the selectivity was performed by GC and ^1H NMR, if possible. The respective area factors were taken into account by measuring a calibration curve of **5a** and **5b** in different concentrations. These area factors will be used to calculate the exact ratio between both products (Figure S1, Equation **S1**).

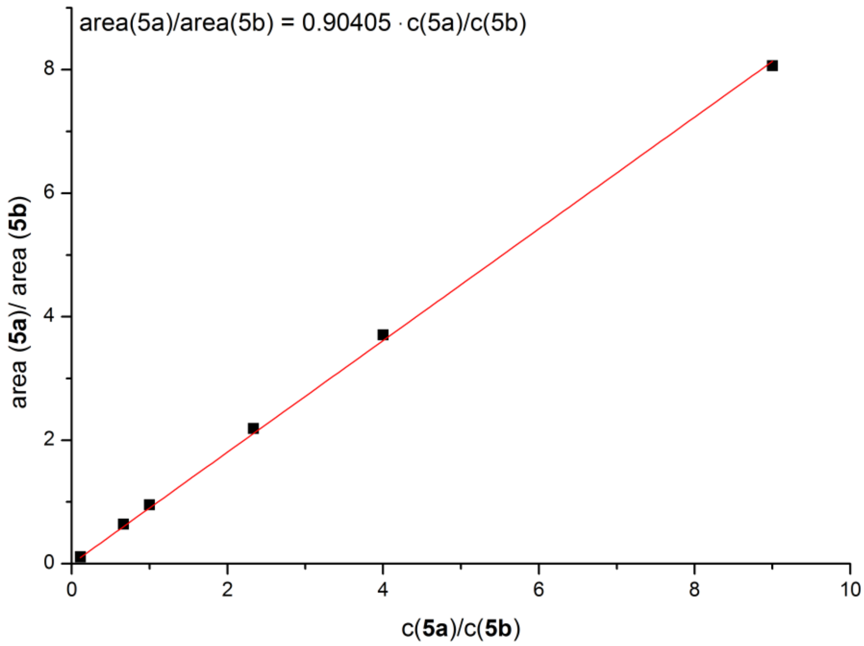


Figure S1. Calibration curve for GC analysis **5a** and **5b.**

The calibration curve provides equation S1, which can be easily transformed in equation S2. Using this equation one can derive the product ratio from the GC areas between **5a** and **5b.**

$$\frac{\text{area}\,(\mathbf{5a})}{\text{area}\,(\mathbf{5b})} = 0.90405 \cdot \frac{c\,(\mathbf{5a})}{c\,(\mathbf{5b})} \qquad (\mathbf{S1})$$

$$\frac{\dfrac{\text{area}\,(\mathbf{5a})}{\text{area}\,(\mathbf{5b})}}{0.90405} = \frac{c\,(\mathbf{5a})}{c\,(\mathbf{5b})} \qquad (\mathbf{S2})$$

The selectivity will be calculated using equation S3 by GC peak areas. For NMR measurements the concentration can be directly obtained by the integrals divided by the number of protons (S4).

$$S = \frac{[\text{Product-1}] - [\text{Product-2}]}{[\text{Product-1}] + [\text{Product-2}]} \qquad (\mathbf{S3})$$

$$S = \frac{\text{Int}_{5a}/2 - \text{Int}_{5b}/3}{\text{Int}_{5a}/2 + \text{Int}_{5b}/3} \qquad (\mathbf{S4})$$

Conversion can't be measured directly by GC measurements since **4a** and **4b** appear at almost the same retention time (Table S2). Therefore, the most accurate conversion can be obtained by NMR measurements using the signals of **4a, 4b, 5a,** and **5b** with equation S5.

$$\text{Conversion} = \frac{\text{Int}_{5a}/2 + \text{Int}_{5b}/3}{\text{Int}_{5a}/2 + \text{Int}_{5b}/3 + \text{Int}_{4a}/2 + \text{Int}_{4b}/3} \cdot 100\% \qquad (\mathbf{S5})$$

Since the conversion defined by experimental design is inaccurate, we obtained more accurate values by NMR measurements of the reaction mixtures. Figure S2 displays the importance of this step and the influence on the analysis of the data. We measured the relative rate of TBSCl (**1a**) with DMAP in ref. 7 separately (S=120), we take this as a value for the quality of the fit. Since it is known that the accuracy of NMR measurements when it comes to ratios of 1:100 lacks behind GC accuracy, the combination of NMR conversions and GC selectivites provides the best values for the purpose. All results for TBSCl, TBSCN, TBSOTf are listed in Table S3.

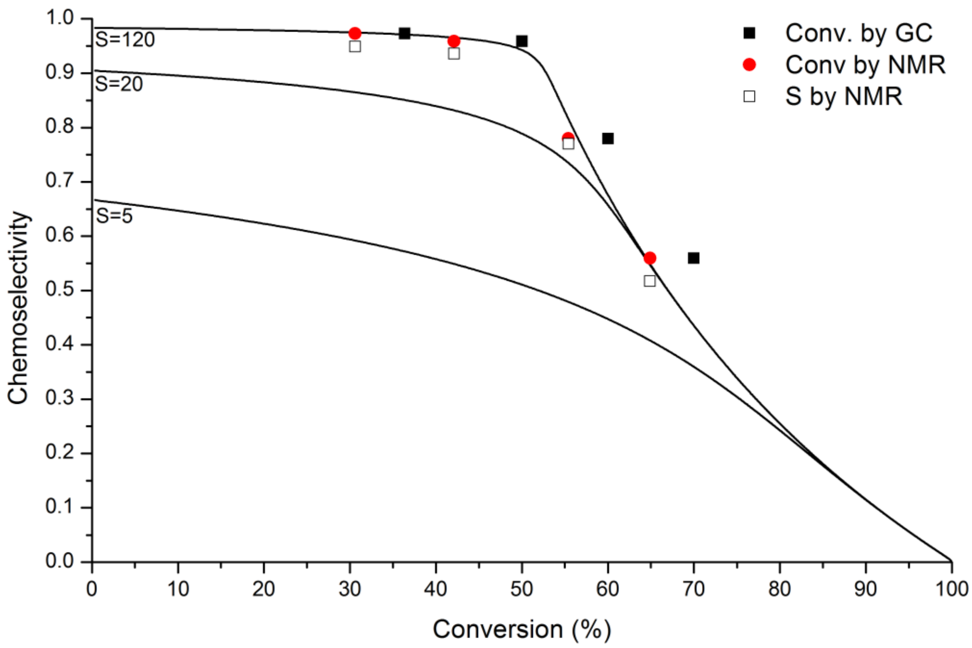
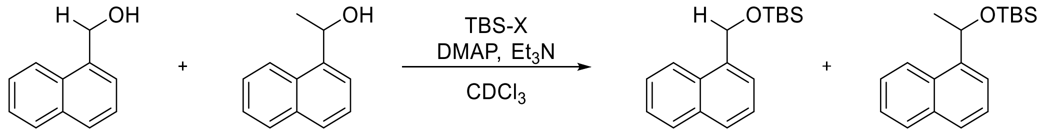


Figure S2. Selectivity vs conversion using various methods for data processing.

General procedure (I) for competition experiments reactions with **4a** and **4b** in various solvents: 3.0 mL of a 10 mL stock solution I (**4a**, 6.6 mmol, 1.04 g and 3, 0.165 mmol, 16.69 mg) was mixed with 3.0 mL of a 10 mL stock solution II (**4b**, 6.6 mmol, 1.14 g and **3b**, 0.165 mmol, 16.69 mg) in a dried flask and stirred at rt. Using a syringe pump 0.6 mL of a 5 mL stock solution III (**1a**–**1c**, 0.825 mmol) were added over 15 min and stirred for 20 min at rt.



4a **4b** **5a** **5b**

Table S3. Competition experiment data obtained by GC and NMR.

Reagent	Area (GC) (**5a**)	Area(GC) (**5b**)	Area Factor **(5a/5b)**	[**5a**]$_{rel}$	[**5b**]$_{rel}$	Conv. (Exp.)	Chemos. C(GC)	Conv. (NMR)	Chemos. C (NMR)
TBSCl (1a)	3271130	49755	0.90405	72.72	1	36.4	0.9729	30.6	0.9486
	3013782	46077		72.35	1		0.9727	30.5	0.9440
	3110997	46078		74.68	1		0.9736	31.0	0.9491
							0.9731	**30.7**	**0.9472**
	3262945	73489	0.90405	49.11	1	50.0	0.9601	42.1	0.9356
	5935767	141972		46.25	1		0.9577	41.9	0.9410
	3127003	73155		47.28	1		0.9586	43.1	0.9351
							0.9588	**42.3**	**0.9372**
	10909491	1494539	0.90405	8.07	1	60.1	0.7796	55.4	0.7699
	10372739	1429864		8.02	1		0.7784	55.5	0.7616
	9319756	1266785		8.14	1		0.7811	55.6	0.7684
							0.7797	**55.5**	**0.7666**
	5639899	1623987	0.90405	3.84	1	70.0	0.5869	64.1	0.5167
	11982143	3910565		3.39	1		0.5443	64.9	0.5267
	8550272	2770864		3.41	1		0.5468	63.9	0.5186
							0.5594	**64.3**	**0.5207**
TBSCN (1c)	2420909	19909	0.90405	134.50	1	40.0	0.9852	30.9	0.9530
	3955832	38963		112.30	1		0.9823	31.1	0.9541
	3513931	34585		112.39	1		0.9824	32.0	0.9642
							0.9833	**31.4**	**0.9570**
	2723427	25828	0.90405	116.64	1	50.0	0.9830	39.6	0.9535
	2682127	35539		83.48	1		0.9763	39.9	0.9526
	4299545	57642		82.51	1		0.9760	39.9	0.9550
							0.9785	**39.8**	**0.9537**
	6864167	193285	0.90405	39.28	1	60.1	0.9504	44.3	0.9305
	32129521	1081725		32.85	1		0.9409	47.0	0.9023
	14415068	349263		45.65	1		0.9571	45.8	0.9150
							0.9495	**45.7**	**0.9159**
	4989709	266864	0.90405	20.68	1	70.0	0.9078	54.8	0.7562
	10167793	737146		15.26	1		0.8770	54.4	0.7689
	11312752	818258		15.29	1		0.8772	54.8	0.7564
							0.8873	**54.7**	0.7605

Reagent	Area (GC) (**5a**)	Area(GC) (**5b**)	Area Factor **(5a/5b)**	[**5a**]$_{rel}$	[**5b**]$_{rel}$	Conv. (Exp.)	Chemos. C(GC)	Conv. (NMR)	Chemos. C (NMR)
TBSOTf (1b, CDCl$_3$)	3064483	1016373	0.90405	3.34	1	40	0.5387	31.2	0.5008
	2205348	846208		2.88	1		0.4849	31.0	0.5311
	2136966	699012		3.38	1		0.5435	31.5	0.5114
							0.5224	**31.2**	**0.5144**
	2928638	1052831	0.90405	3.08	1	50	0.5094	38.9	0.5263
	5721449	2096360		3.02	1		0.5024	42.6	0.3070
	3877309	1310266		3.27	1		0.5320	38.0	0.2076
							0.5146	**39.8**	**0.3470**
	4516043	2111322	0.90405	2.37	1	60	0.4058	47.3	0.8499
	3334781	1433377		2.57	1		0.4403	50.4	0.1426
	3040793	1277113		2.63	1		0.4496	50.3	0.2095
							0.4319	**49.3**	**0.4006**
	3369721	1720945	0.90405	2.17	1	70	0.3683	63.3	0.3045
	4009721	1920945		2.31	1		0.3956	63.6	0.3305
	3379721	1760945		2.12	1		0.3596	63.4	0.3311
							0.3745	**63.4**	**0.3221**
TBSCl (1a, DMF)	1725017	131078	0.90405	14.56	1	30	0.8714	n.d.	n.d.
	1342632	97404		15.25	1		0.8769		
	1835639	159008		12.77	1		0.8548		
	1849493	157898		12.96	1		0.8567		
							0.8649		
	3337973	346086	0.90405	10.67	1	40	0.8286	n.d.	n.d.
	3514745	355260		10.94	1		0.8325		
	3106008	288116		11.92	1		0.8453		
							0.8355		
	3951097	498093	0.90405	8.77	1	50	0.7954	n.d.	n.d.
	3641637	444840		9.06	1		0.8011		
	4802772	639736		8.30	1		0.7850		
							0.7938		
	7864588	1410043	0.90405	6.17	1	60	0.7210	n.d.	n.d.
	4634963	815327		6.29	1		0.7256		
	5487605	1085751		5.59	1		0.6965		
							0.7144		
TBSOTf (1b, CD$_2$Cl$_2$, 20 °C)	3877309	1310266	0.90405	3.27	1	40	0.5320	33.7	0.5610
	2109572	610874		3.82	1		0.5851	33.7	0.5353
	5721449	2096360		3.02	1		0.5024	34.0	0.5263
							0.5398	**33.8**	**0.5409**
	2821575	968452	0.90405	3.22	1	50	0.5264	42.1	0.3741
	2146966	835012		2.84	1		0.4797	42.8	0.3699
	2172964	781920		3.07			0.5091	44.1	0.3789

Reagent	Area (GC) (**5a**)	Area(GC) (**5b**)	Area Factor **(5a/5b)**	[**5a**]$_{rel}$	[**5b**]$_{rel}$	Conv. (Exp.)	Chemos. C(GC)	Conv. (NMR)	Chemos. C (NMR)
					1		**0.5051**	**43.0**	**0.3743**
	2226409	1042608	0.90405	2.36	1	60	0.4051	54.7	0.2934
	4503490	2014975		2.47	1		0.4240	53.7	0.2857
	3294765	1423378		2.56	1		0.4383	53.2	0.2914
							0.4225	**53.9**	**0.2902**
	3398191	1589807	0.90405	2.36	1	70	0.4055	61.2	0.3123
	2145548	1050455		2.26	1		0.3864	60.1	0.3003
	2300275	1005665		2.53	1		0.4334	60.3	0.3070
							0.4084	**60.6**	**0.3066**
TBSOTf (1b, CD_2Cl_2, 0 °C)	1968637	529002	0.90405	4.12	1	40	0.6091	33.71	0.246
	3414660	776490		4.86	1		0.6590	35.52	0.686
	1971526	473710		4.60	1		0.6431	29.29	0.221
							0.6370	**32.84**	**0.384**
	1571940	434591	0.90405	4.00	1	50	0.6001	43.20	0.486
	1489603	454630		3.62	1		0.5675	44.90	0.588
	1591084	536331		3.28	1		0.5329	43.78	0.454
							0.5668	**43.96**	**0.509**
	2618088	823791	0.90405	3.52	1	60	0.5571	52.90	0.392
	2530339	886079		3.16	1		0.5191	53.68	0.374
	2721691	833146		3.61	1		0.5665	53.69	0.385
							0.5475	**53.43**	**0.384**
	3040109	1101499	0.90405	3.05	1	70	0.5065	61.70	0.378
	3257844	1469260		2.45	1		0.4207	62.69	0.284
	3531648	1486161		2.63	1		0.4488	61.79	0.368
							0.4587	**62.06**	**0.343**
TBSOTf (1b, CD_2Cl_2, -78 °C)	1727894	194665	0.90405	9.82	1	40	0.8151	35.7	0.6681
	2598820	341024		8.43	1		0.7879	35.5	0.6858
	1180213	119161		10.96	1		0.8327	35.4	0.6551
							0.8119	**35.5**	**0.6696**
	3849275	566426	0.90405	7.52	1	50	0.7652	45.4	0.5809
	3750990	557297		7.45	1		0.7632	44.9	0.5876
	3172248	518087		6.77	1		0.7427	45.1	0.5715
							0.7570	**45.1**	**0.5800**
	2671220	469236	0.90405	6.30	1	60	0.7259	56.8	0.3523
	2930228	533476		6.08	1		0.7173	56.2	0.3698
	1897181	449518		4.67	1		0.6472	56.8	0.3487
							0.6968	**56.6**	**0.3569**
	4818607	1442983	0.90405	3.69	1	70	0.5739	62.8	0.2675
	4868159	1376218		3.91	1		0.5929	62.7	0.2845

Reagent	Area (GC) (**5a**)	Area(GC) (**5b**)	Area Factor **(5a/5b)**	[**5a**]$_{rel}$	[**5b**]$_{rel}$	Conv. (Exp.)	Chemos. C(GC)	Conv. (NMR)	Chemos. C (NMR)
	4778726	1467228		3.60	1		0.5655	63.1	0.2697
							0.5774	**62.9**	**0.2739**

2.2 Simulation of Chemoselectivities

With the help of CoPaSi[4] the S-values for the competition experiments have been simulated. Shown in Figure S3 are the used reactions, in which the k-values have been modified in order to achieve the S-values. The values k_1, k_{-1}, and k_3 were used as constants, while k_{prim} and k_{sec} have been changed.

$$[\mathrm{CAT}] + [\mathrm{TBSCl}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{CAT\text{-}TBS}] + [\mathrm{Cl}^-]$$

$$[\mathrm{CAT\text{-}TBS}] + [\mathrm{ROH}] \xrightarrow{k_{Prim}} [\mathrm{Product\text{-}1}] + [\mathrm{CAT\text{-}H}^+]$$

$$[\mathrm{CAT\text{-}TBS}] + [\mathrm{ROH}] \xrightarrow{k_{Sec}} [\mathrm{Product\text{-}2}] + [\mathrm{CAT\text{-}H}^+]$$

$$[\mathrm{CAT\text{-}H}^+] + [\mathrm{Base}] \xrightarrow{k_3} [\mathrm{CAT}] + [\mathrm{BaseH}^+]$$

Figure S3 Reaction equations for the simulation with CoPaSi.

The conversion was calculated based on the used silyl reagent and the selectivity following equation (S31). Shown in Figure S4 are the selectivity curves for this generalized reaction scheme.

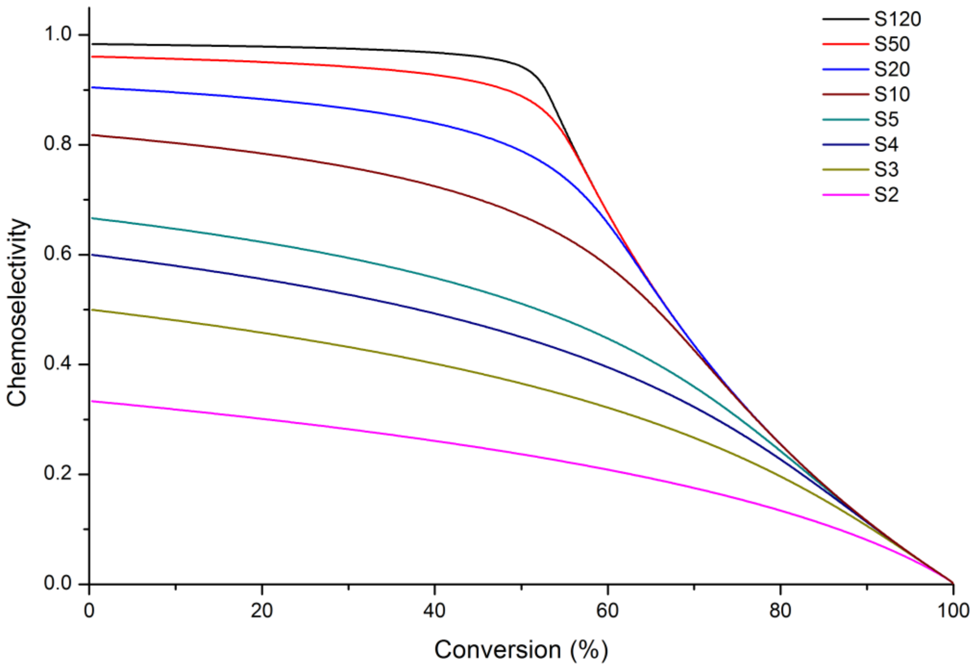


Figure S4 Selectivity curves a competition reaction.

3) Direct Rate Measurements

3.1 Sample preparation

Stock solutions of the relevant compounds have been prepared as shown in Table S4. For the NMR experiments three stock solutions have been prepared with freshly distilled $CDCl_3$. For the measurements in DMF-d_7 the stock solutions were prepared under glovebox conditions.

Table S4. Overview of stock solutions for kinetic measurements. The concentration of the catalyst can be changed if necessary.

	substance	n [mmol]	m[g]	Volume[mL]	c[M]	equiv.
stock A	TBS-X Dioxane	3.6 1.0	0.542 0.088	 0.086	0.72 0.2	1.2 0.33
stock B	Et_3N **4a**	3.6 3.0	0.364 0.475	0.498	0.72 0.6	1.2 1.0
stock C	Cat	0.12	0.015		0.024	

$CDCl_3$ and Et_3N were freshly distilled under N_2 from CaH_2 before preparing the stock solutions. NMR tubes have been dried under vacuum using a special apparatus and flushed with N_2 three times to eliminate water. 200 µL of each stock solution are then transferred using a Hamilton syringe or a 200 µL Eppendorf pipette to the NMR tube, which is closed with a cap and sealed with parafilm. In case of long reaction times ($t_{1/2}$ > 400 min) the tube is flame-sealed

3.2 Measuring and processing

The samples were sealed and have been measured at the same machine (200 MHz NMR) using 32 cycles at 23°C. For longer reaction times the samples have been constantly shaken mechanically. At least ten data points should be determined for an accurate time-conversion curve and were processed with the program MestReNova 9.1. First of all one compares the integrals of the reactant and the product in all measured NMR spectra. Furthermore, the reaction time at the point of measuring this specific NMR is recorded. For a better understanding a typical NMR spectrum for the silylation of **4a** with **1a** is depicted in Figure S5.

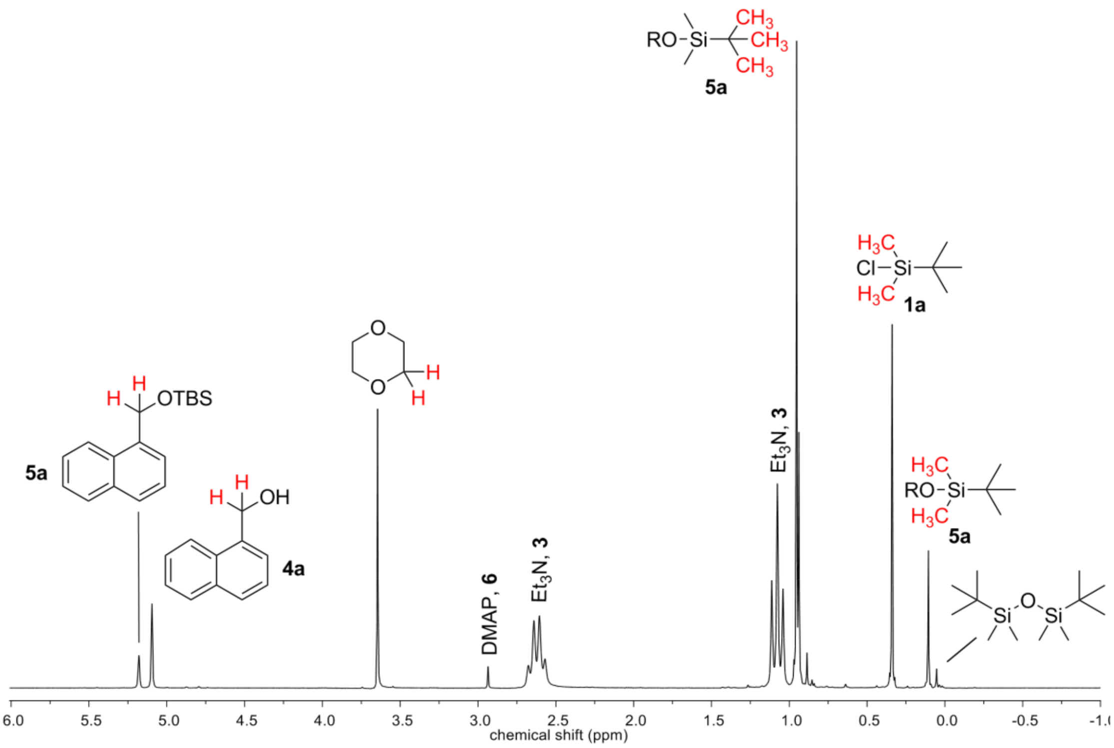


Figure S5 [1]H NMR spectrum of the benchmark reaction in $CDCl_3$ using the primary alcohol **4a**, **3b** as the auxiliary base, and DMAP as the catalyst.

All spectra were imported in MestReNova and the subsequent steps have been carried out: Apodization, exponential 0.1; Baseline Correction, Bernstein polynominal fit; Phase correction, Auto (Global Method). In order to calculate the conversion from the integrals, equation S1 was used. One has to multiply either with 100 % in case of the alcohol **5a** signals or with 120 % in case of the TBDMS signals. This set of data is based on TBDMS signals and is therefore multiplied with 120%.

$$\text{conversion} = \frac{I_{TBDMSOR}}{\Sigma\, I_{TBDMSOR} + I_{TBDMSCl}} \cdot 120\ \% \qquad (\mathbf{S6})$$

The plots have been prepared with OriginPro 8. For the plot of conversion y versus reaction time one can easily fit different integrated rate laws. Before fitting the data one has to choose, which kinetic rate law is most suitable for this type of reaction. On the following pages several rate laws will be shown and the best one will be used for fitting.

The plots of conversion versus time were fitted with equation (**S7**), where y_0 is the conversion at infinite time of reaction, t_0 is the starting point of the reaction, and k_{eff} the rate of the reaction.

$$\text{conversion} = y_0 \cdot \left[1 - \frac{0.2}{1.2\, e^{k_{eff}(0.2)(t-t_0)} - 1}\right] \qquad (\mathbf{S7})$$

A half-life can be calculated with equation (**S8**):

$$t_{1/2} = \frac{\ln(1.166)}{0.2 \cdot k_{eff}} \quad \textbf{(S8)}$$

Previous equations are based on a modified second order rate law. The silylation of alcohol **5a** requires a silylating reagent (TBDMSCl, **1a**) as a reaction partner. By assuming that during the reaction the concentration of the catalyst is constant and that triethylamine (**2**) does not participate at all in the rate determining step, the following equation for the second-order reaction can be written:

$$\mathrm{ROH + TBDMSCl \xrightarrow{k_2} TBDMSOR} \quad \textbf{(S9)}$$

The rate law for a second-order reaction is shown in equation **S9.**

$$-\frac{d\,[\mathrm{ROH}]}{d\,t} = k_2 \cdot [\mathrm{ROH}] \cdot [\mathrm{TBDMSCl}] \quad \textbf{(S10)}$$

Since there is no one to one ratio in this reaction one has to take the actual ratio of reactants into account. The ratio at the beginning of the reaction between both reactants is important for the further proceeding and is expressed in equation **S11.**

$$\frac{[\mathrm{TBDMSCl}]_0}{[\mathrm{ROH}]_0} = n \qquad (n > 1) \quad \textbf{(S11)}$$

Furthermore, the concentrations of the alcohol can be expressed from the conversion and the initial concentration $[\mathrm{ROH}]_0$. If the ratio of the initial concentrations of alcohol and TBDMSCl is assumed to be n (eq. **S11**), than the concentration of TBDMSCl can be expressed by equation **S13.**

$$[\mathrm{ROH}] = [\mathrm{ROH}]_0 \cdot (1-y) \quad \textbf{(S12)}$$

$$[\mathrm{TBDMSCl}] = [\mathrm{ROH}]_0 \cdot (n-y) \quad \textbf{(S13)}$$

By taking equation **S12** and **S13** into account, the effective rate law can be written as:

$$-[\mathrm{ROH}]_0 \frac{d\,(1-y)}{d\,t} = k_2 \cdot [\mathrm{ROH}]_0^2 \cdot (1-y)(n-y) \quad \textbf{(S14)}$$

Rearranging the variables under the condition that $k_{eff} = k_2[\mathrm{ROH}]_0$ leads to equation **S15.**

$$\frac{d\,(1-y)}{(1-y)(n-y)} = -k_{eff} \cdot dt \quad \textbf{(S15)}$$

Integration and several transformations of equation **S15** leads to equation **S21.**

$$\int_0^y \frac{d\,(1-y)}{(1-y)(n-y)} = -\int_{t_0}^{t} k_{eff} \cdot dt \qquad (S16)$$

$$\frac{1}{(1-y)(n-y)} = \left(\frac{1}{1-y} - \frac{1}{n-y}\right) / (n-1) \qquad (S17)$$

$$\ln\left(\frac{1}{1-y}\right) - \ln\left(\frac{n}{n-y}\right) = -(n-1) \cdot k_{eff} \cdot (t-t_0) \qquad (S18)$$

$$\ln\left(\frac{n-y}{n \cdot (1-y)}\right) = -(n-1) \cdot k_{eff} \cdot (t-t_0) \qquad (S19)$$

$$\frac{n-y}{n \cdot (1-y)} = e^{k_{eff} \cdot (n-1) \cdot (t-t_0)} \qquad (S20)$$

$$y = 1 - \frac{n-1}{n \cdot e^{k_{eff} \cdot (n-1) \cdot (t-t_0)} - 1} \qquad (S21)$$

Equation **S21** expresses the conversion for the ideal second-order reaction, but only works for n > 1. For kinetic measurements it is necessary to take errors of preparing and mixing the samples into account. This can be achieved by adding another variable y_0, which acts as conversion axis rescaling parameter. The final equation is given below by equation **S22**:

$$y = y_0 \cdot \left(1 - \frac{n-1}{n \cdot e^{k_{eff} \cdot (n-1) \cdot (t-t_0)} - 1}\right) \qquad (S22)$$

For the silylation of an alcohol the silylation reagent (**1a**, TBSCl) is used in 1.2 equivalents which leads to equation **S7.**
In order to get a half-life time from this results the general equation **S22** is used.

$$t_{1/2} = \frac{\ln \frac{2n-1}{n}}{(n-1) \cdot k_{eff}} \qquad (S22)$$

Since the ratio (n) between ROH and TBDMSCl is known to be 1.2, one can change this equation to equation **S8**.

On the following pages all plots which are used for this publication are shown in the order of their appearance.

2.3.1 Alternative options for calculating the conversion

As shown before the conversion can be calculated by using the signals of TBDMSCl (**1a**) and the product. In addition the signal of the alcohol can be used in a similar way (**S19**).

$$\text{conversion} = \frac{I_{TBDMSOR}}{\Sigma\, I_{TBDMSOR} + I_{ROH}} \cdot 100\,\% \qquad (S24)$$

Another way is to use the specific ratios of TBDMSCl (**1a**) and alcohol to calculate the conversion. Moreover, the external standard dioxane can be used. The ratios are: TBDMSCl/ROH = 1.2, TBDMSCl/dioxane = 3.6, and

TBDMSOR/Dioxane =3.0. By using these ratios and the concentrations and not only the integrals one can easily build up the following equations.

$$\text{conversion} = \frac{[\text{ROH}]_0 - [\text{ROH}]}{[\text{ROH}]_0} \cdot 100\ \% \qquad (\textbf{S25})$$

$$\text{conversion} = \frac{[\text{TBDMSCl}]_0 - [\text{TBDMSOR}]}{[\text{ROH}]_0} \cdot 100\ \% \qquad (\textbf{S26})$$

$$\text{conversion} = \frac{[\text{TBDMSCl}]_0 - [\text{TBDMSOR}]}{1/1.2\ [\text{TBDMSCl}]_0} \cdot 100\ \% \qquad (\textbf{S27})$$

$$\text{conversion} = \left[1.2 - 1.2 \cdot \frac{[\text{TBDMSOR}] / [\text{dioxane}]_0}{[\text{TBDMSCl}]_0 / [\text{dioxane}]_0}\right] \cdot 100\ \% \qquad (\textbf{S28})$$

By using the integrals and the amount of protons each signal has the equations **S29** and **S30** can be built for the decrease of the TBDMSCl or alcohol signal.

$$\text{conversion} = \left[1.2 - 1.2 \cdot \frac{I_{\text{TBDMSCl}} / 6}{I_{\text{dioxane}} / 8} / 3.6\right] \cdot 100\ \% \qquad (\textbf{S29})$$

$$\text{conversion} = \left[1.2 - 1.2 \cdot \frac{I_{\text{HOR}} / 2}{I_{\text{dioxane}} / 8} / 3.0\right] \cdot 100\ \% \qquad (\textbf{S30})$$

The second alternative is to use the increasing signals of the product either the TBDMS- (**S31**) or the alcohol-based (**S32**) signals.

$$\text{conversion} = \left[\frac{I_{\text{TBDMSOR}} / 6}{I_{\text{dioxane}} / 8} / 3.0\right] \cdot 100\ \% \qquad (\textbf{S31})$$

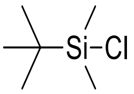
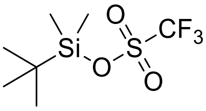
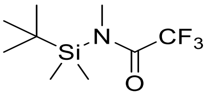
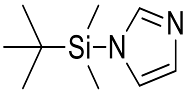
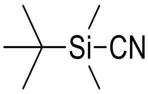
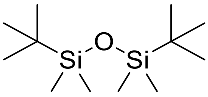
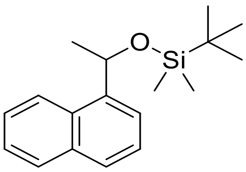
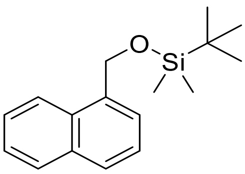
$$\text{conversion} = \left[\frac{I_{\text{ROTBDMS}} / 2}{I_{\text{dioxane}} / 8} / 3.0\right] \cdot 100\ \% \qquad (\textbf{S32})$$

A very carefully comparison of all options came to the conclusion that using the integral ratios of TBDMS as defined in eq. (**S6**) is the best choice. The alcohol signals tend to overlap in some of the kinetics runs. The reproducibility of the results using the external standard is lower as compared to that for eq. (**S6**).

3.4 NMR shifts for reactants and products

For a better overview we here provide all spectroscopic data of reactants and products in Table S5.

Table S5. ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts of silicon-containing reactants and products [ppm, in $CDCl_3$].

Structures	^{29}Si	^{1}H	^{13}C
	36.12	0.98 (s, 9H, *t*Bu), 0.37[1] (s, 6H, Si$(CH_3)_2$)	25.60, 19.06, -1.54
	43.84	1.00 (s, 9H, *t*Bu), 0.45[1] (s, 6H, Si$(CH_3)_2$)	118.57 (q, *J*=317.4), 24.80, 18.20, -4.23
	26.69	3.07 (s, 3H, CH_3), 0.99 (s, 9H, Bu), 0.26[1] (s, 6H,Si$(CH_3)_2$)	117.18 (q, J=277.9), 144.48 (q, J=37.6), 34.39, 27.04, 25.58, 18.71, -3.95
	17.26	7.54, 7.15, 6.92, 0.88 (s, 9H, *t*Bu), 0.43[1] (s, 6H, Si$(CH_3)_2$)	140.86, 130.48, 120.93, 25.66, 17.83, -5.38
	-1.52	1.01 (s, 9H, *t*Bu), 0.29[1] (s, 6H, Si$(CH_3)_2$)	126.11, 25.65, 16.31, -5.92,
	9.91	0.85 (s, 18H, *t*Bu), 0.00(s, 12H, Si$(CH_3)_2$)	
	18.42	– 0.01 (s, 3H,Si(CH_3)), 0.10[1] (s, 3H, Si(CH_3))), 0.95 (s, 9H,*t*Bu), 1.60 (d, *J*=6.4, 3H, MeCH-OR), 5.61 (q, *J* = 6.6, 1H, CH), 7.44-7.55 (m, 3H), 7.67-7.78 (m, 2H), 7.85-7.91 (m, 1H), 8.11 (d, *J* = 7.3, 1H).	129.88, 128.82, 127.17, 125.57, 125.53 , 125.15, 123.34, 122.67, 68.48, 26.62, 25.89, , 18.30, -4.83, -4.92
	20.58	0.14[1] (s, 6H, Si$(CH_3)_2$), 0.97 (s, 9H, *t*Bu), 5.22 (s, 2H, CH_2), 7.47 -7.59 (m, 3H), 7.59 - 7.61 (m, 1H), 7.79 (d, *J* = 8.1, 1H), 7.86 - 7.93 (m, 1H), 8.00 - 8.05 (m, 1H).	128.57, 127.54,. 125.79, 125.51, 125.45, 123.77, 123.27, 63.39, 29.17, 25.98, 18.46, -5.22

[1]Used for integration in NMR kinetic measurements.

3.5 Experimental Details for Direct Rate Measurements

All air and water sensitive manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Calibrated flasks for kinetic measurements were dried in the oven at 120 °C for at least 12 hours prior to use and then assembled quickly while still hot, cooled under a nitrogen stream and sealed with a rubber septum. Hygroscopic substances such as TBSOTf (**1b**) and DMF-d_7 have been handled only in a glovebox. All commercial chemicals were of reagent grade and were used as received unless otherwise noted. $CDCl_3$ was refluxed for at least one hour over CaH_2 and subsequently distilled. ^{1}H and ^{13}C NMR spectra were recorded at room temperature. All 1H chemical shifts are reported in ppm (δ) relative to $CDCl_3$ (7.26); ^{13}C chemical shifts are reported in ppm (δ) relative to $CDCl_3$ (77.16). 1H NMR kinetic data were measured on a 200 MHz spectrometer at 23 °C. HRMS spectra (ESI-MS or EI-MS) were measured using a FT instrument. All kinetic measurements with reaction times longer than 24 h were mechanically shaken at room temperature. For each reaction the rotation speed was set at 480 turns per minute. Analytical TLCs were determined using aluminium sheets silica gel Si 60 F254. All other chemicals were purchased from commercial suppliers at the highest available grade, stored over orange gel in an exsiccator and used without any further purification.

General procedure (I) for benchmark reactions of **4a** with 2 mol% / 3 mol% / 4 mol% catalyst: 0.2 mL from 5.0 mL of stock solution I (TBS (3.6 mmol), dioxane (0.088 mg, 0.086 mL)), 0.2 mL from 5 mL of stock solution II **4a** (475 mg, 3.0 mmol), Et_3N (3, 364 mg, 0.50 mL)) and 0.2 mL of 5 mL stock solution III (0.06 / 0.09 / 0.12 mmol of catalyst) were mixed in a NMR tube and sealed.

General procedure (II) for benchmark reactions of **4b** with 10 mol% / 20 mol% / 30 mol% catalyst: 0.2 mL from 5.0 mL of stock solution I (TBS (3.6 mmol), dioxane (0.088 mg, 0.086 mL)), 0.2 mL from 5 mL of stock solution II **4b** (517 mg, 3.0 mmol), Et_3N (3, 364 mg, 0.50 mL)) and 0.2 mL of 5 mL stock solution III (0.12 / 0.24 / 0.36 mmol of DMAP) were mixed in a NMR tube and sealed.

General procedure (III) for benchmark reactions of **4b** in DMF-d_7 with 30 mol% catalyst and without: 0.2 mL from 1 mL of stock solution I (TBS-X, 0.72 mmol), 0.2 mL from 1 mL of stock solution II **4b** (517 mg, 3.0 mmol), Et_3N (3, 364 mg, 0.10 mL)) and 0.2 mL of 1 mL stock solution III DMAP (0.18 mmol, 21.99 mg) were mixed in a NMR tube and sealed.

Table S6. Overview of direct rate measurement data for all silyl reagents in various solvents.

System	Catalyst (mol%)	Alcohol	Solvent	k_{eff}	$t_{1/2}$ (min)
TBSCl (**1a**)	DMAP (4)	**4b**	$CDCl_3$	2.40E-04	3199.1
				2.45E-04	3132.8
Avg.				***2.43E-04***	***3165.6***
	DMAP (10)	**4b**	$CDCl_3$	5.03E-04	1525.3
				5.08E-04	1512.0
				4.94E-04	1553.8
Avg.				***5.02E-04***	***1530.2***
	DMAP (20)	**4b**	$CDCl_3$	1.04E-03	738.4
				1.06E-03	724.4
				1.07E-03	717.7
Avg.				***1.06E-03***	***726.7***
	DMAP (30)	**4b**	$CDCl_3$	1.60E-03	479.9
				1.66E-03	462.6
				1.69E-03	454.4
Avg.				***1.63E-03***	***471.1***

System	Catalyst (mol%)	Alcohol	Solvent	k_{eff}	$t_{1/2}$ (min)
	DMAP (0)	**4b**	DMF-d_7	1.15E-01	6.7
				9.97E-02	7.7
				9.59E-02	8.0
Avg.				***1.04E-01***	***7.4***
	DMAP (30)	**4b**	DMF-d_7	1.05E-01	7.3
				1.12E-01	6.9
Avg.				***1.09E-01***	***7.1***
	DMAP (0.5)	**4a**	$CDCl_3$	3.43E-03	223.9
				3.47E-03	221.3
Avg.				***3.45E-03***	***222.6***
	DMAP (1)	**4a**	$CDCl_3$	6.20E-03	123.9
				6.20E-03	123.9
Avg.				***6.20E-03***	***123.9***
	DMAP (2)	**4a**	$CDCl_3$	1.01E-02	76.4
				9.67E-03	79.4
				8.58E-03	89.5
Avg.				***9.43E-03***	***81.4***
	DMAP (3)	**4a**	$CDCl_3$	1.83E-02	42.0
				1.80E-02	42.6
				1.82E-02	42.2
Avg.				***1.82E-02***	***42.3***
	DMAP (4)	**4a**	$CDCl_3$	2.45E-02	31.3
				2.76E-02	27.9
				2.47E-02	31.1
				2.47E-02	31.0
Avg.				***2.54E-02***	***30.1***
TBSOTf (**1b**)	DMAP (0)	**4b**	$CDCl_3$	2.98E+00	0.258
				5.35E+00	0.144
				4.92E+00	0.156
Avg.				***4.42E+00***	***0.174***
	DMAP (10)	**4b**	$CDCl_3$	5.49E+00	0.140
				5.10E+00	0.151
Avg.				***5.30E+00***	***0.145***
	DMAP (20)	**4b**	$CDCl_3$	4.97E+00	0.154
				4.85E+00	0.158
				6.31E+00	0.122
Avg.				***5.38E+00***	***0.143***
	DMAP (30)	**4b**	$CDCl_3$	4.63E+00	0.166
				5.57E+00	0.138
Avg.				***5.10E+00***	***0.151***
	DMAP (0)	**4b**	DMF-d_7	5.08E+00	0.151
				4.68E+00	0.164
Avg.				***4.88E+00***	***0.157***
	DMAP (15)	**4b**	DMF-d_7	4.07E+00	0.189
				3.21E+00	0.239
Avg.				***3.64E+00***	***0.211***
	DMAP (30)	**4b**	DMF-d_7	6.10E+00	0.126
				2.17E+00	0.353
Avg.				***4.14E+00***	***0.186***
TBSCN (**1c**)	DMAP (10)	**4b**	$CDCl_3$	2.28E-05	33634.8
				2.34E-05	32810.4
				2.24E-05	34212.9
Avg.				***2.29E-05***	***33542.8***
	DMAP (20)	**4b**	$CDCl_3$	5.10E-05	15055.0
				5.45E-05	14098.8
Avg.				***5.27E-05***	***14561.2***

System	Catalyst (mol%)	Alcohol	Solvent	k_{eff}	$t_{1/2}$ (min)
	DMAP (30)	**4b**	$CDCl_3$	8.69E-05	8832.5
				8.65E-05	8878.4
Avg.				***8.67E-05***	***8855.4***
	DMAP (0)	**4b**	DMF-d_7	3.62E-02	21.2
				3.80E-02	20.2
Avg.				***3.71E-02***	***20.7***
	DMAP (30)	**4b**	DMF-d_7	3.38E-02	22.7
				4.52E-02	17.0
Avg.				***3.95E-02***	***19.4***
	DMAP (1)	**4a**	$CDCl_3$	1.10E-03	698.1
				1.10E-03	698.1
				1.12E-03	685.6
Avg.				***1.11E-03***	***693.9***
	DMAP (2)	**4a**	$CDCl_3$	1.56E-03	492.2
				1.57E-03	489.1
				1.58E-03	486.0
Avg.				***1.57E-03***	***489.1***
	DMAP (3)	**4a**	$CDCl_3$	1.28E-03	599.9
				1.20E-03	639.9
				1.20E-03	639.9
Avg.				***1.23E-03***	***626.0***
	DMAP (4)	**4a**	$CDCl_3$	1.86E-03	412.8
				1.92E-03	399.9
				1.99E-03	385.9
Avg.				***1.92E-03***	***399.3***
MTBSTFA (**1e**)	DMAP (30)	**4b**	$CDCl_3$	4.91E-05	15637.6
				4.88E-05	15727.2
Avg.				***4.90E-05***	***15682.3***
	DMAP (0)	**4b**	DMF-d_7	9.35E-03	82.1
				2.18E-02	35.3
Avg.				***1.06E-02***	***49.4***
	DMAP (30)	**4b**	DMF-d_7	7.81E-03	98.3
				1.33E-02	59.6
Avg.				***1.43E-02***	***72.6***

4) Direct Rate Measurements – Results

All results of the direct rate measurements will be shown on the following pages, sorted by the leaving group of the silyl compound. The data have been normalized with y_0 obtained from equation S7 and plotted in order to reach a conversion of 100%.

As mentioned in the manuscript a linear correlation between catalyst concentration and silyl reagent was obtained for primary alcohol (**4a**) for the transformation with TBSCl (**1a**) and TBSCN (**1c**) (Figure S6).

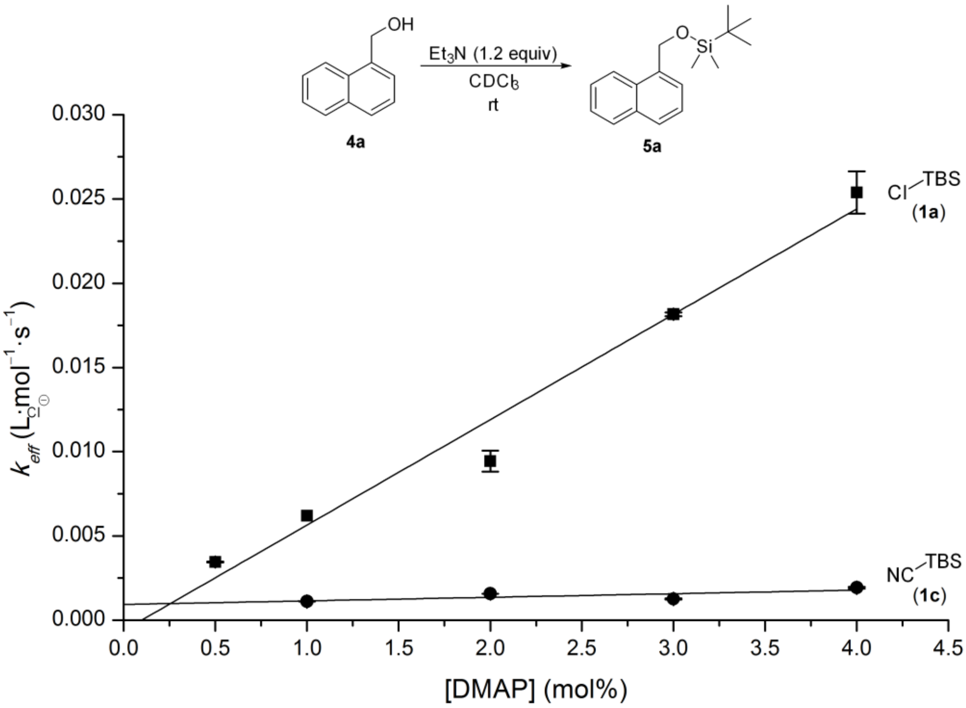


Figure S6. Influence of catalyst concentration on the silylation of primary alcohol **4a** with various silylation reagents in $CDCl_3$.

4.1 Time vs. conversion plots

*4.1.1 Measurements with TBSCl (**1a**)*

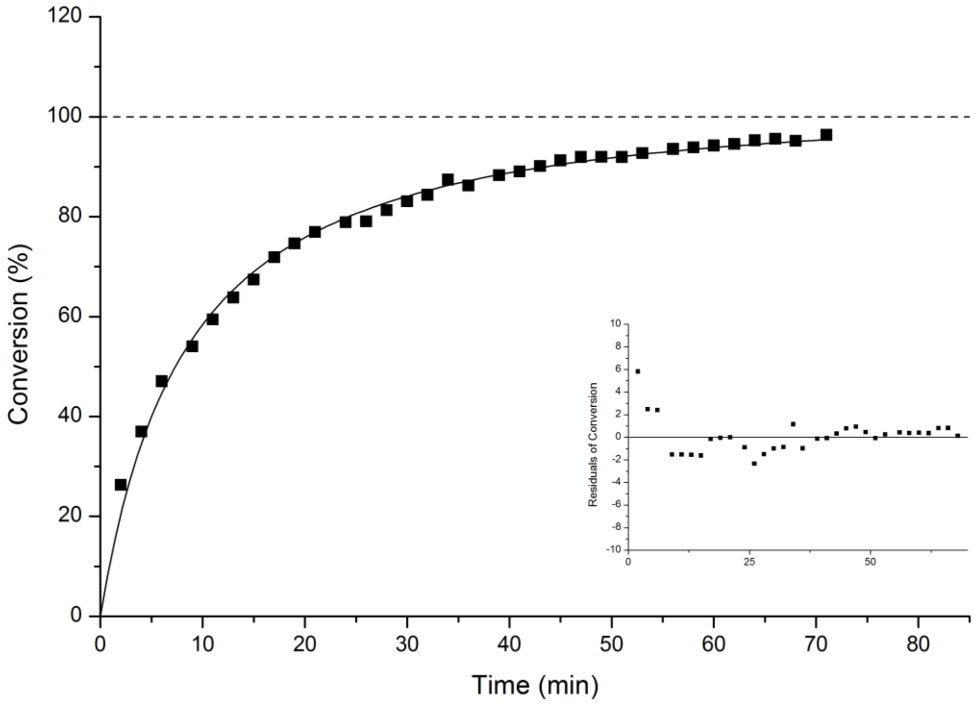


Figure S7 Conversion vs time plot of **4b** with 1.2 equiv of TEA (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP with 30 mol% catalyst loading in DMF-d_7.

R^2 = 0.9927 k_{eff} = 0.10517 $t_{1/2}$ = 7.3 min

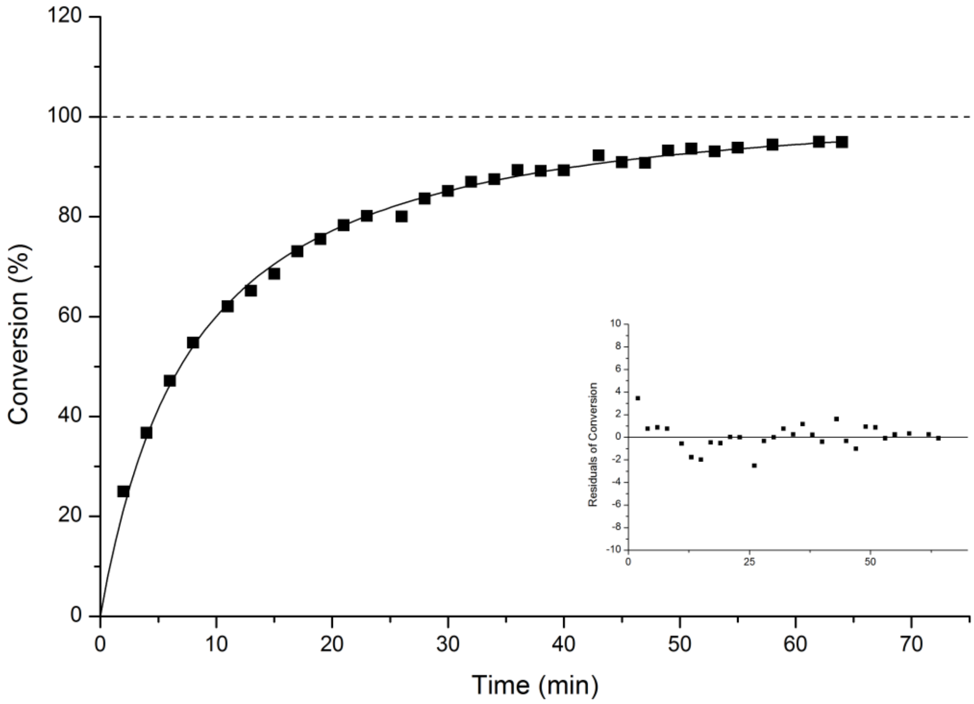


Figure S8 Second conversion vs time plot of **4b** with 1.2 equiv of TEA (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP with 30 mol% catalyst loading in DMF-d_7.

R^2 = 0.9961 k_{eff} = 0.11183 $t_{1/2}$ = 6.9 min

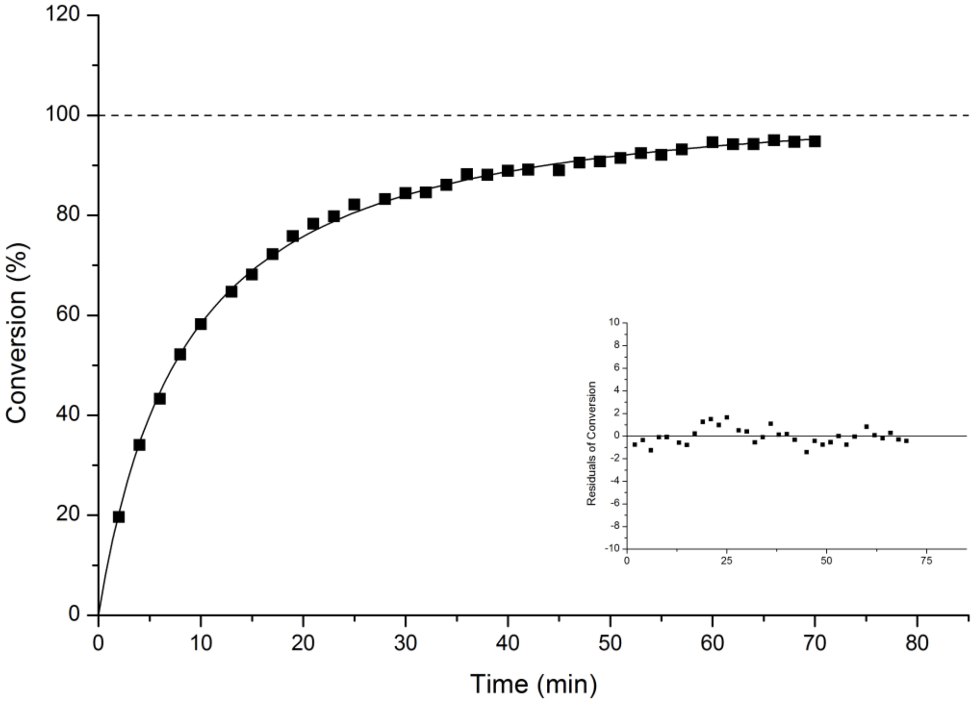


Figure S9 Conversion vs time plot of **4b** with 1.2 equiv of Imidazole (**3a**), 1.2 equiv TBSCl (**1a**), and no catalyst loading in DMF-d_7.

R^2 = 0.99841 k_{eff} = 0.1048 $t_{1/2}$ = 7.3 min

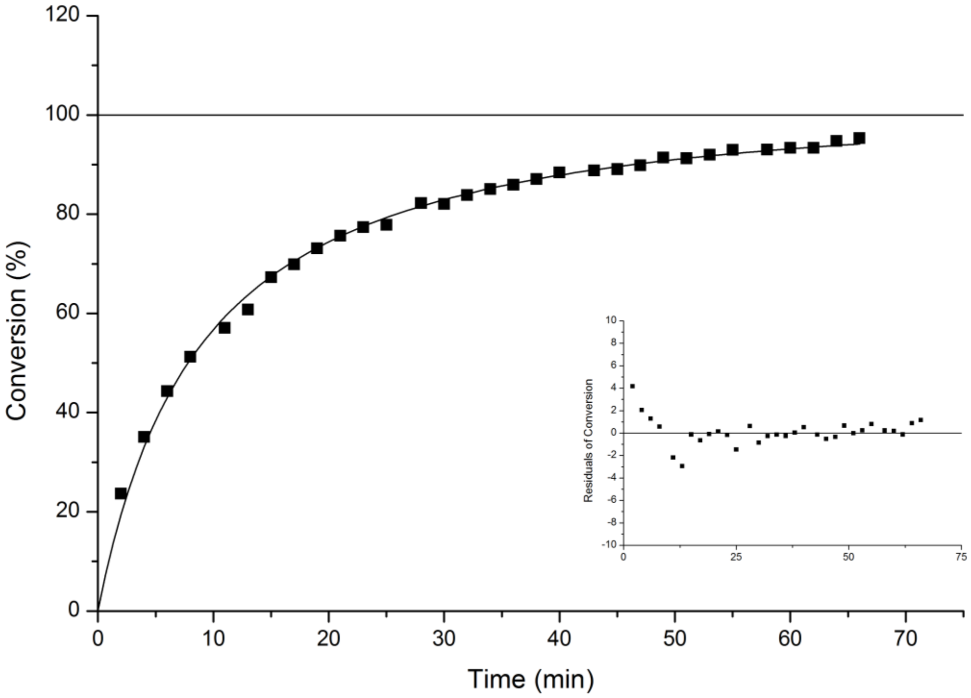


Figure S10 Second conversion vs time plot of **4b** with 1.2 equiv of Imidazole (**3a**), 1.2 equiv TBSCl (**1a**), and no catalyst loading in DMF-d_7.

R^2 = 0.99551 k_{eff} = 0.09875 $t_{1/2}$ = 7.8 min

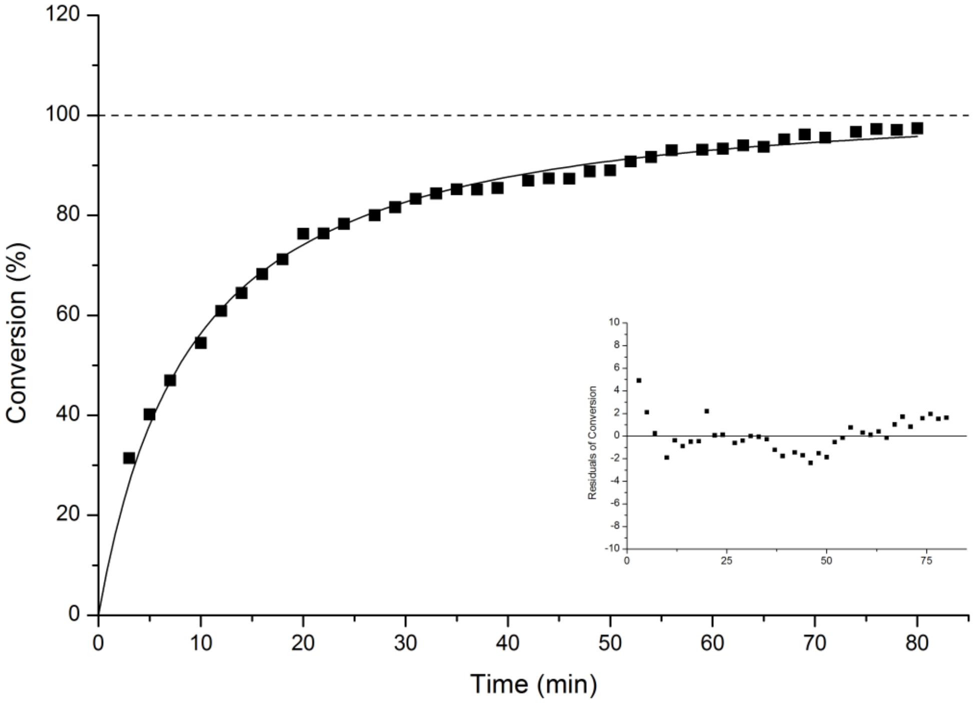


Figure S11 Conversion vs time plot of **4b** with 1.8 equiv of Imidazole (3a), 1.2 equiv TBSCl (**1a**), and no catalyst loading in DMF-d_7.

R^2 = 0.9920 k_{eff} = 0.09754 $t_{1/2}$ = 7.8 min

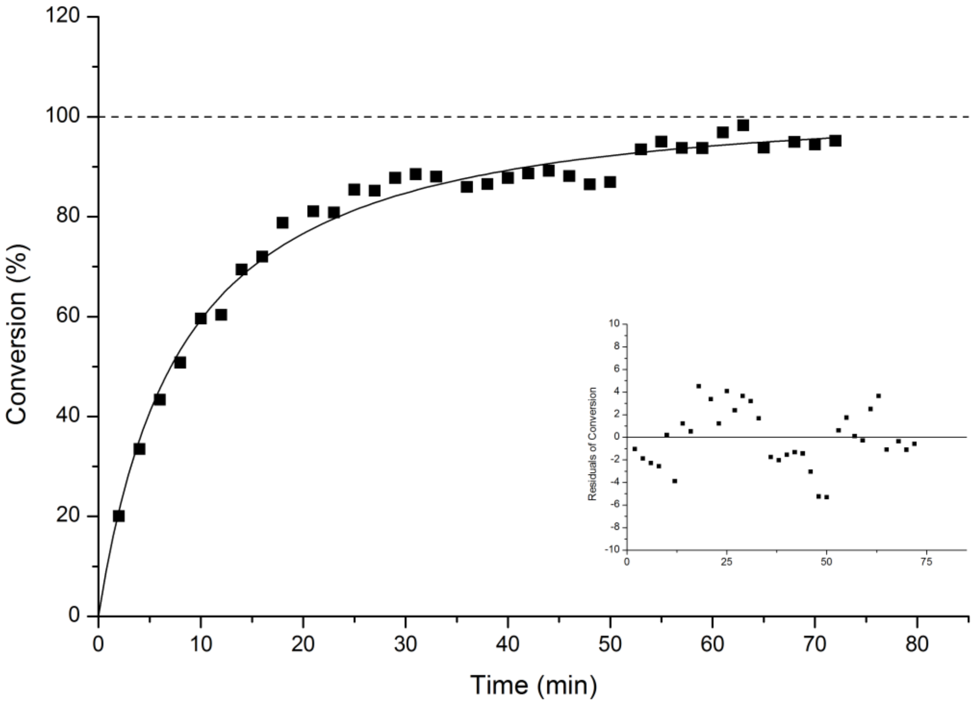


Figure S12 Second Conversion vs time plot of **4b** with 1.8 equiv of Imidazole (**3a**), 1.2 equiv TBSCl (**1a**), and no catalyst loading in DMF-d_7.

R^2 = 0.98095 k_{eff} = 0.10913 $t_{1/2}$ = 7.0 min

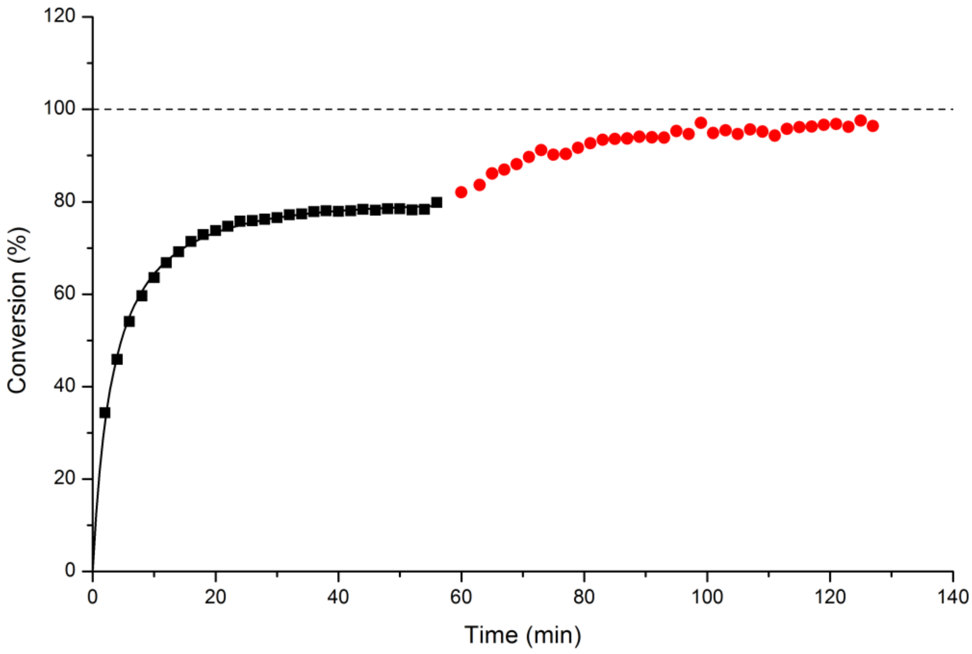


Figure S13 Conversion vs time plot of **4b** with 1.2 equiv TBSCl (**1a**) in DMF-d_7 (black) and addition of 1.2 equiv Et_3N (**3b**) (red).

R^2 = 0.9958 k_{eff} = 0.26426 $t_{1/2}$ = 2.9 min

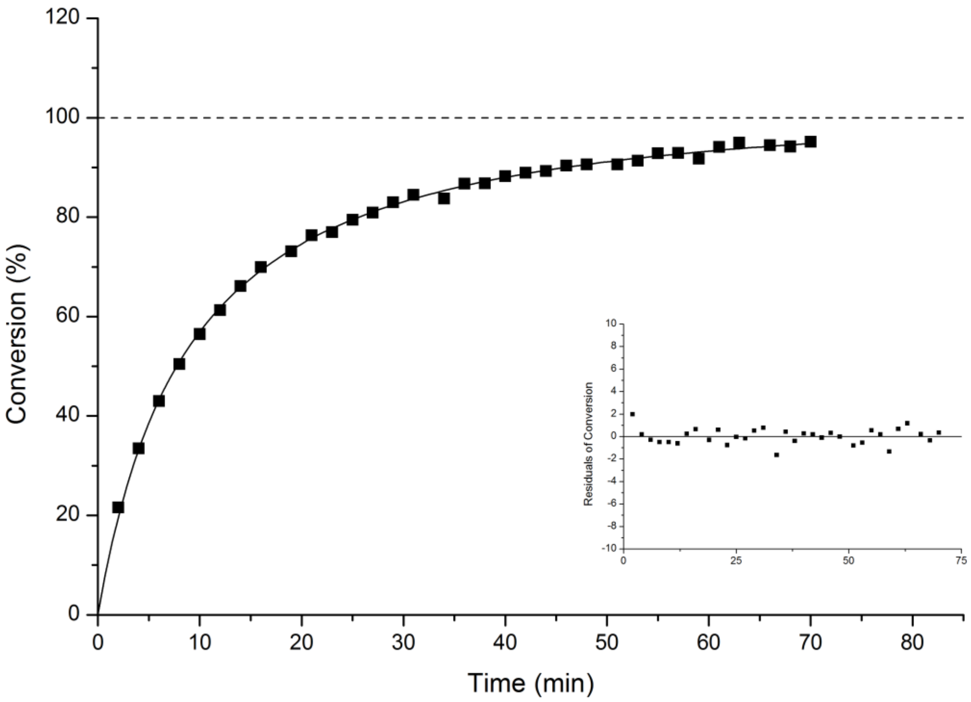


Figure S14 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**) and 1.2 equiv TBSCl (**1a**) in DMF-d_7.

R^2 = 0.99857 k_{eff} = 0.09868 $t_{1/2}$ = 7.7 min

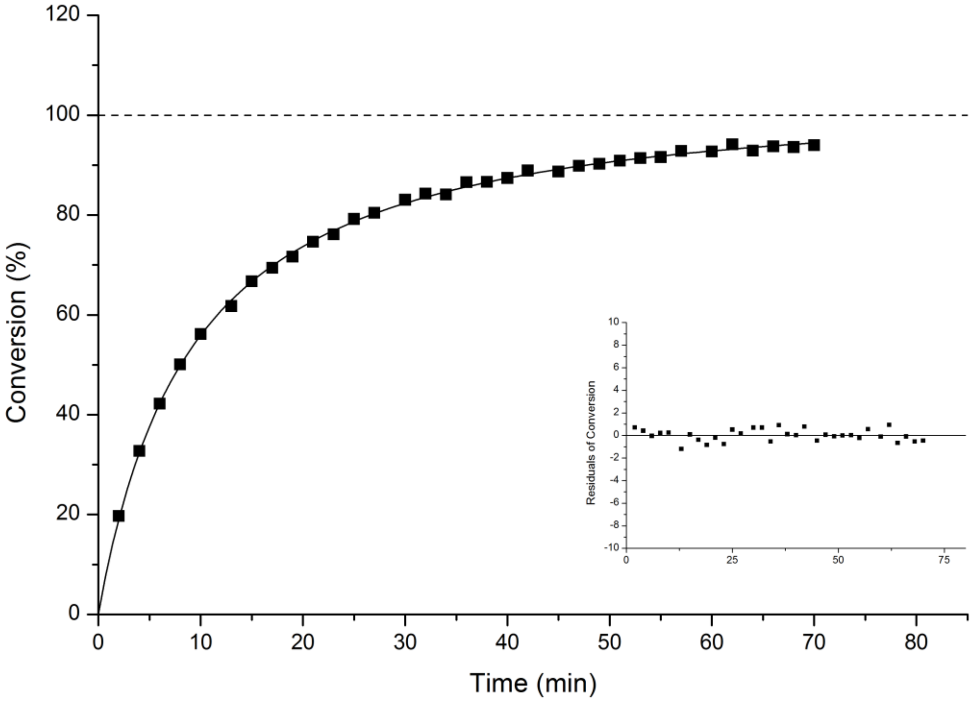


Figure S15 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), and 1.2 equiv TBSCl (**1a**) in DMF-d_7.

R^2 = 0.99919 k_{eff} = 0.09585 $t_{1/2}$ = 8.0 min

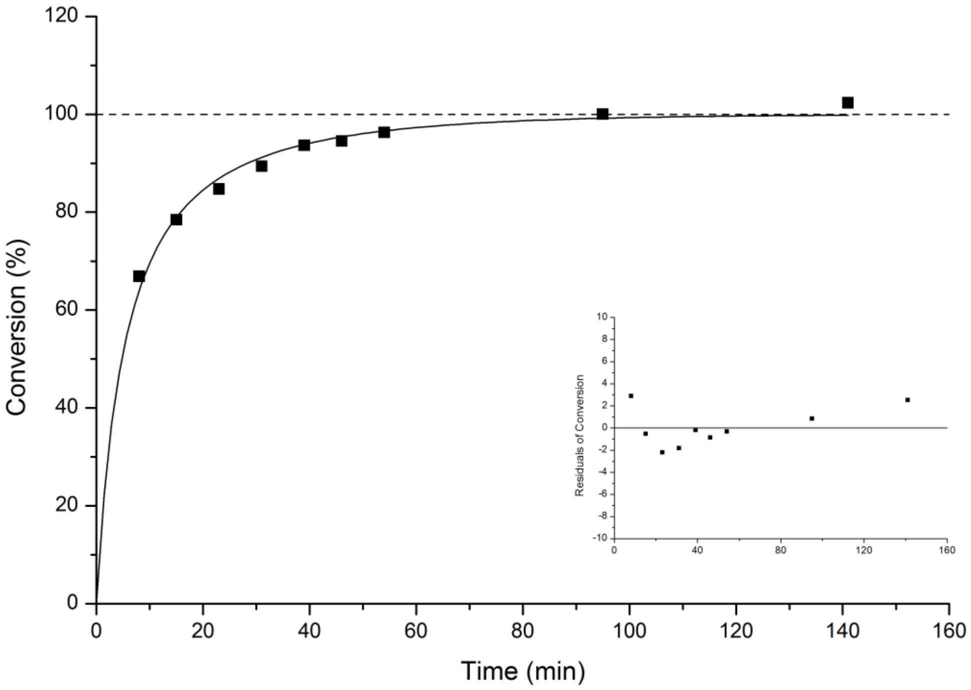


Figure S16 Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), and 1.2 equiv TBSCl (**1a**) in DMF-d_7.

R^2 = 0.97232 k_{eff} = 0.16206 $t_{1/2}$ = 6.7 min

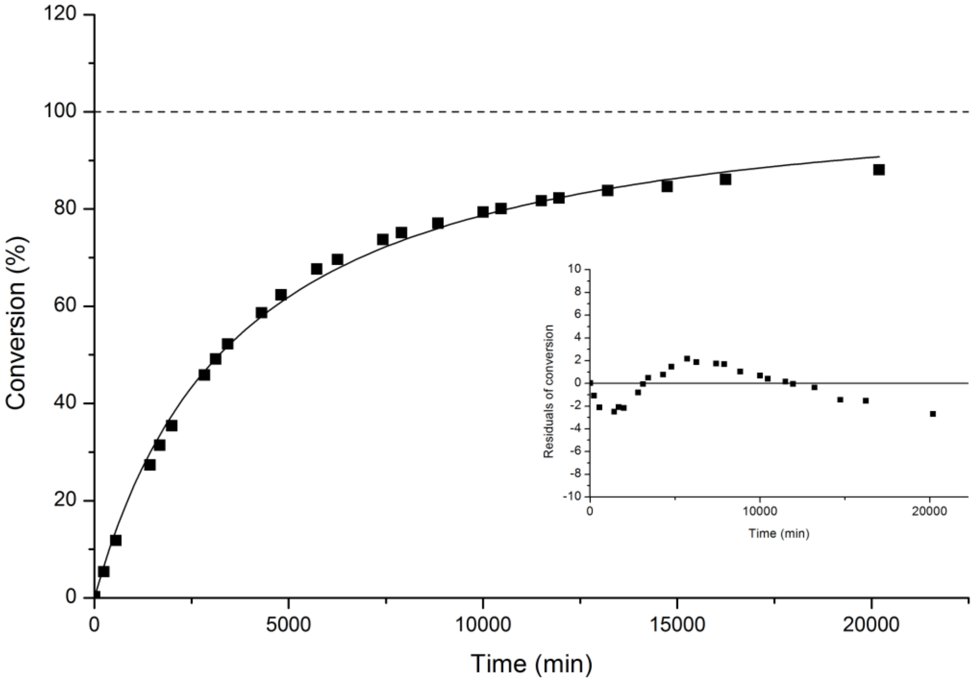


Figure S17 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 4.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99678 k_{eff} = 2.40×10^{-4} $t_{1/2}$ = 3199.1 min

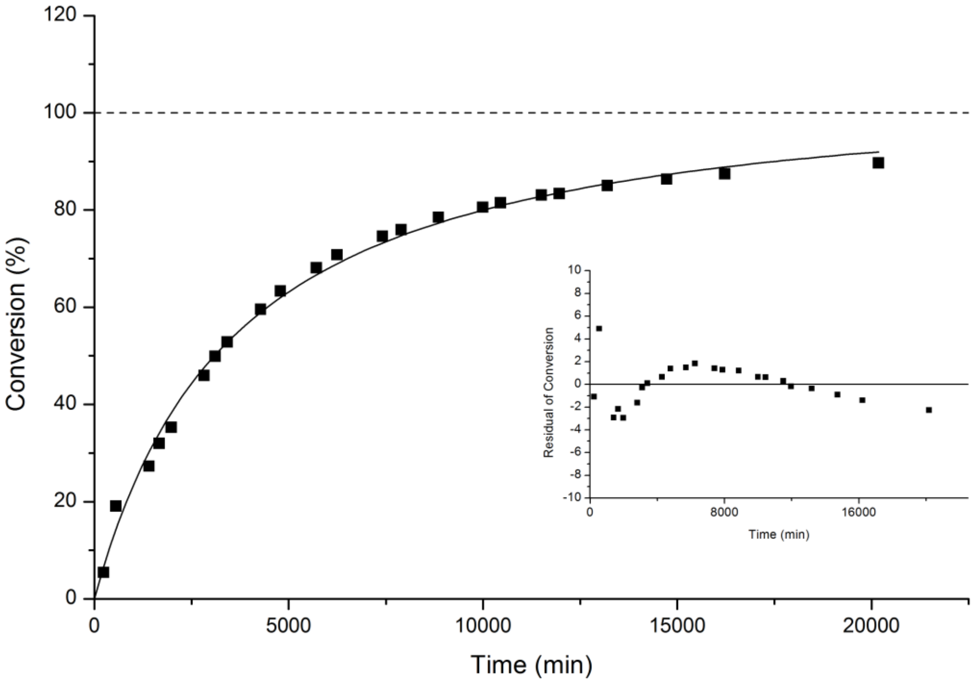


Figure S18. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 4.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.9943 k_{eff} = 2.451×10^{-4} $t_{1/2}$ = 3132.8 min

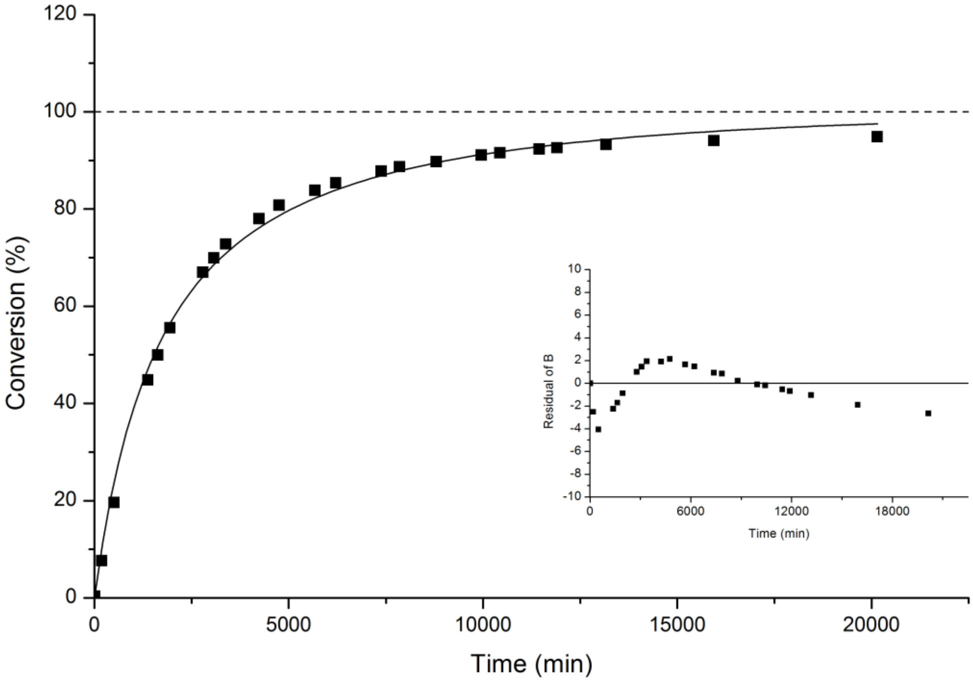


Figure S19. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 10.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99614 k_{eff} = 5.034×10^{-4} $t_{1/2}$ = 1525.3 min

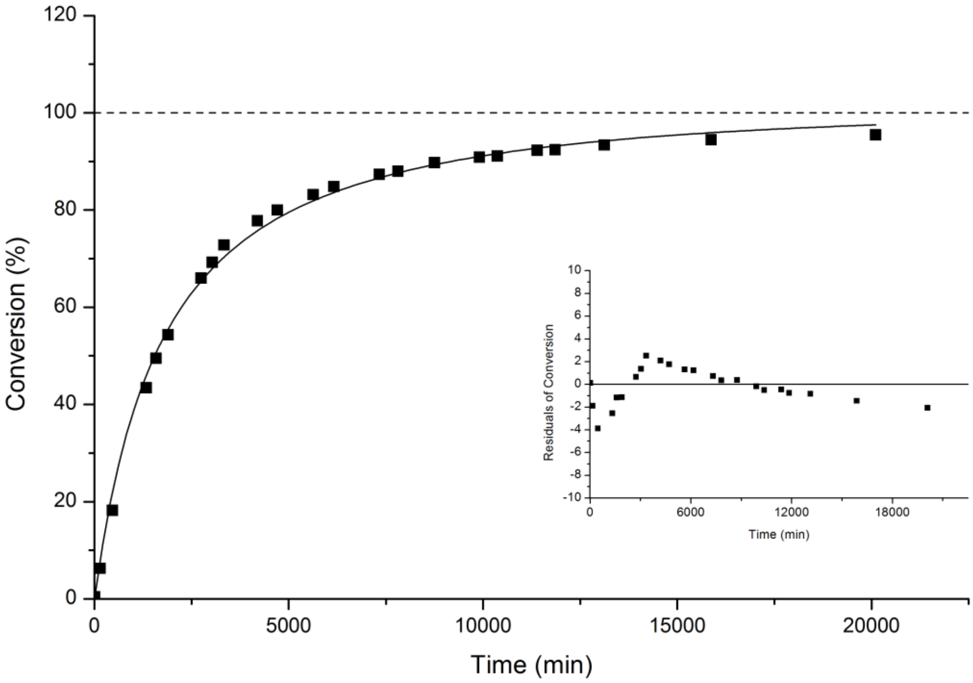


Figure S20. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 10.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99658 k_{eff} = 5.079×10^{-4} $t_{1/2}$ = 1512.0 min

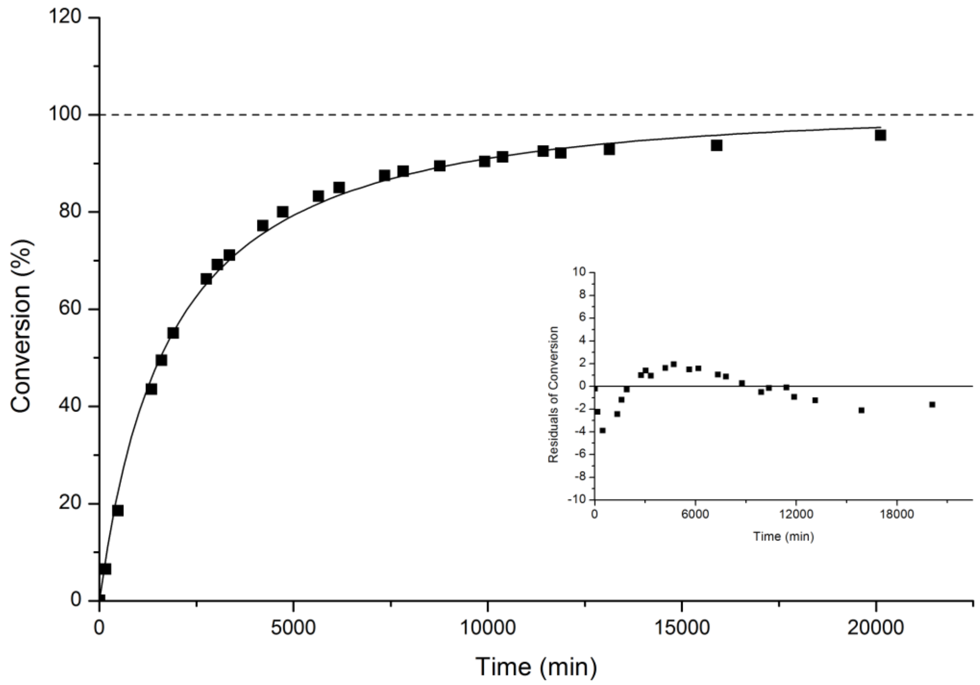


Figure S21. Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 10.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99678 k_{eff} = 4.94×10^{-4} $t_{1/2}$ = 1553.8 min

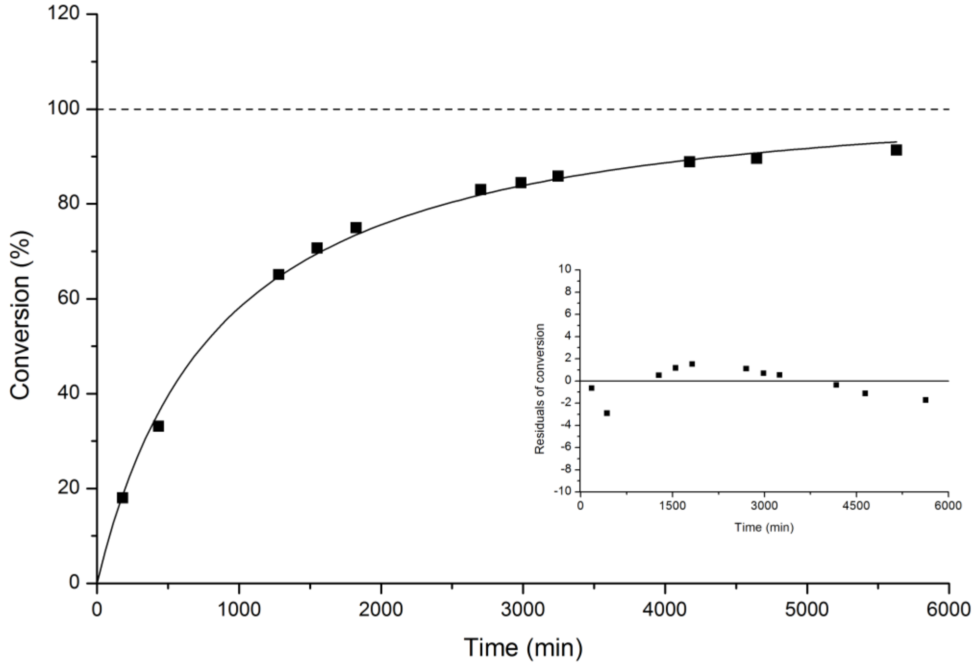


Figure S22. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 20.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99638 k_{eff} = 1.04×10^{-3} $t_{1/2}$ = 738.4 min

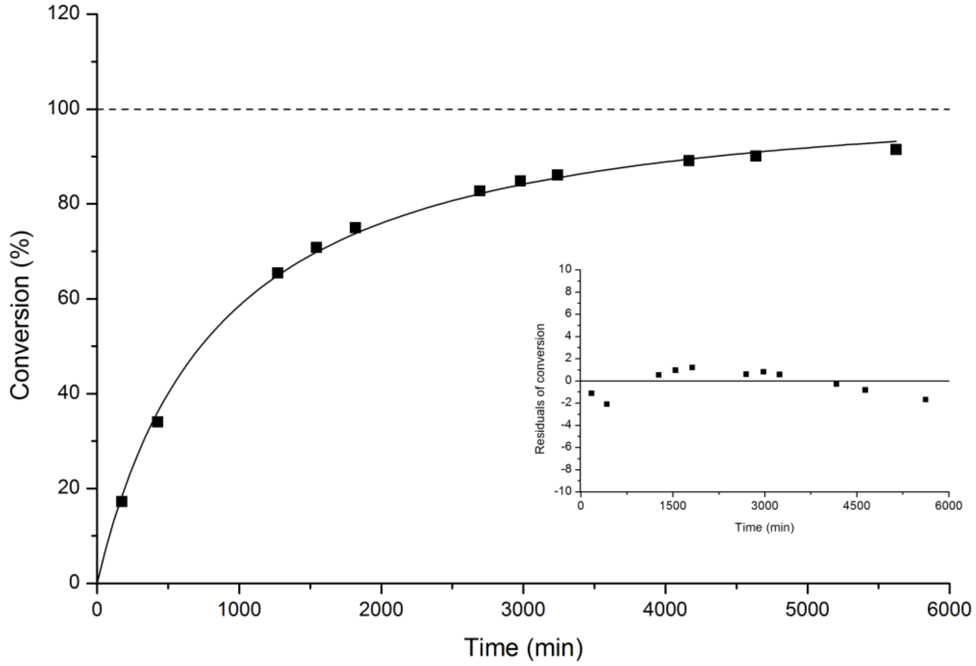


Figure S23. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 20.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.9975 k_{eff} = 1.06×10^{-3} $t_{1/2}$ = 724.5 min

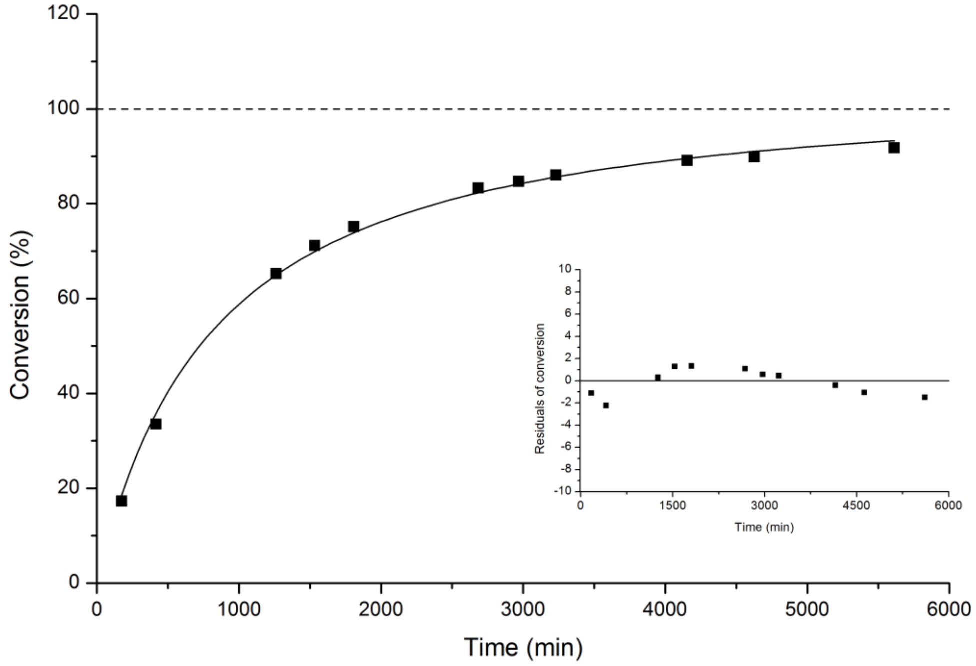


Figure S24. Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 20.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.9972 k_{eff} = 1.07×10^{-3} $t_{1/2}$ = 717.7 min

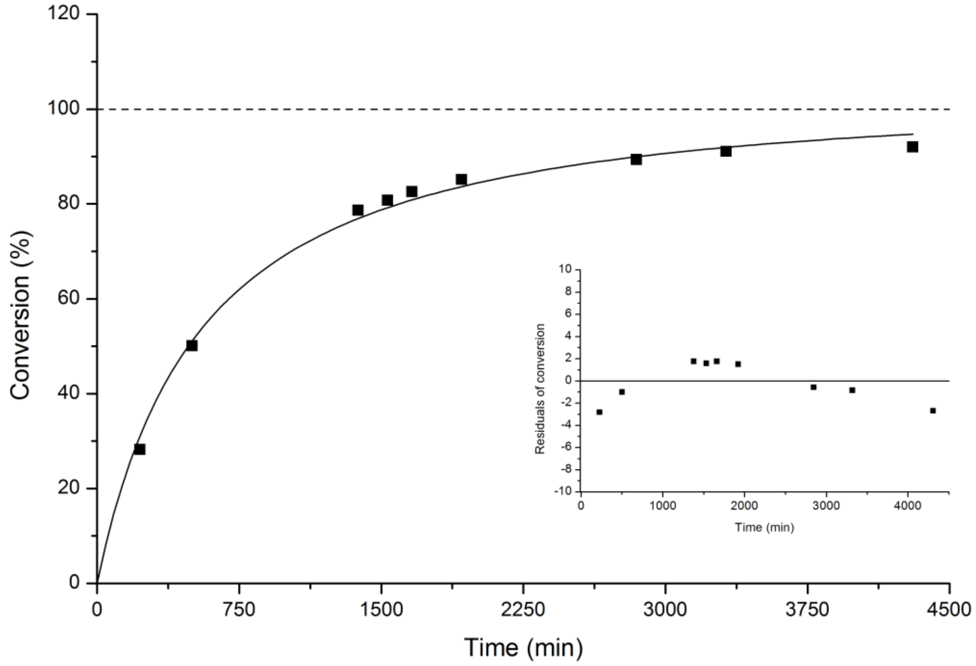


Figure S25. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 30.0 mol% catalyst loading.

R^2 = 0.9914 k_{eff} = 1.60×10^{-3} $t_{1/2}$ = 479.9 min

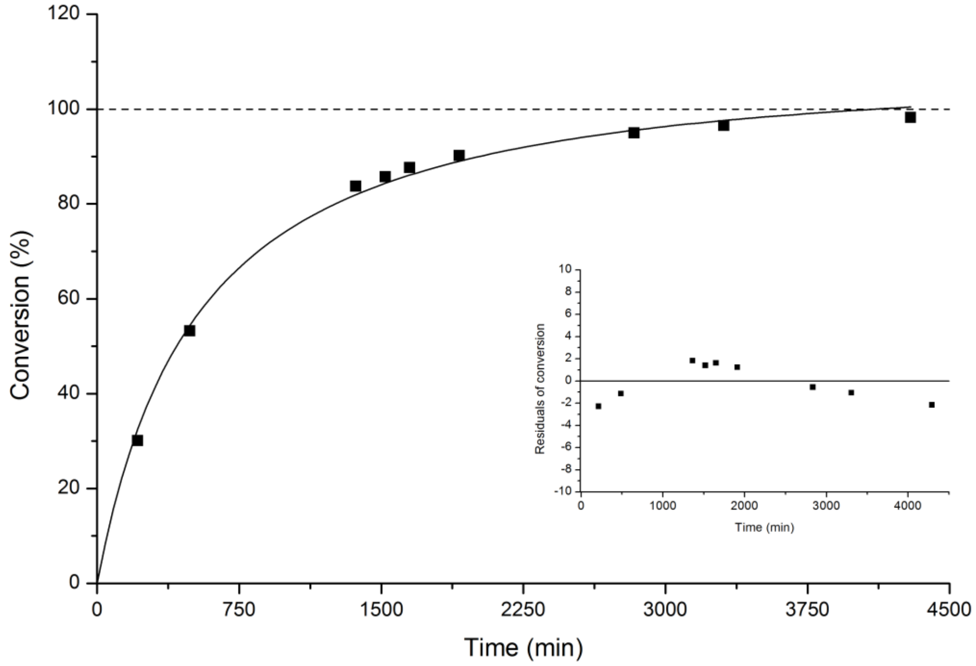


Figure S26. Second Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 30.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99404 k_{eff} = 1.66×10^{-3} $t_{1/2}$ = 462.6 min

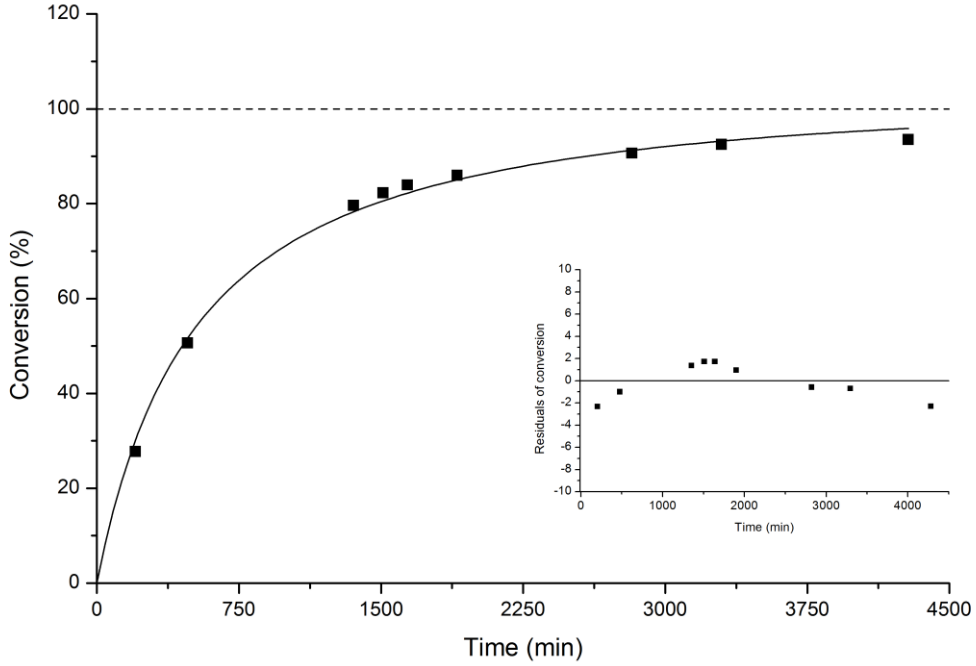


Figure S27. Third Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 30.0 mol% catalyst loading in $CDCl_3$.

$R^2 = 0.9938$ $k_{eff} = 1.69\times10^{-3}$ $t_{1/2} = 454.4$ min

*4.1.1.1 Primary Alcohol (**4a**)*

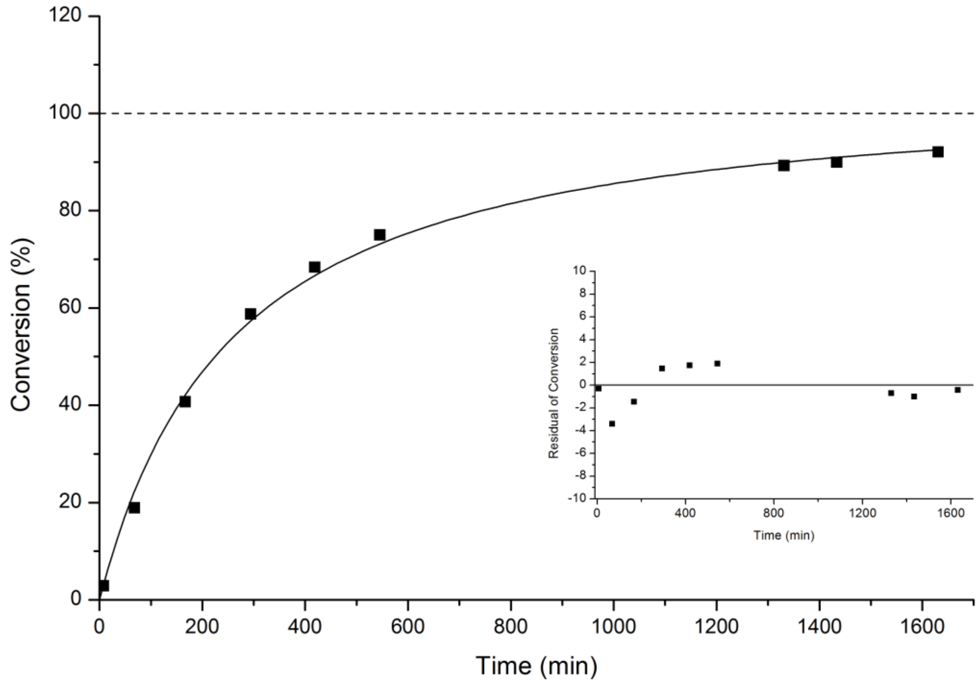


Figure S28. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 0.5 mol% catalyst loading in $CDCl_3$.

$R^2 = 0.99672$ $k_{eff} = 3.43\times10^{-3}$ $t_{1/2} = 223.8$ min

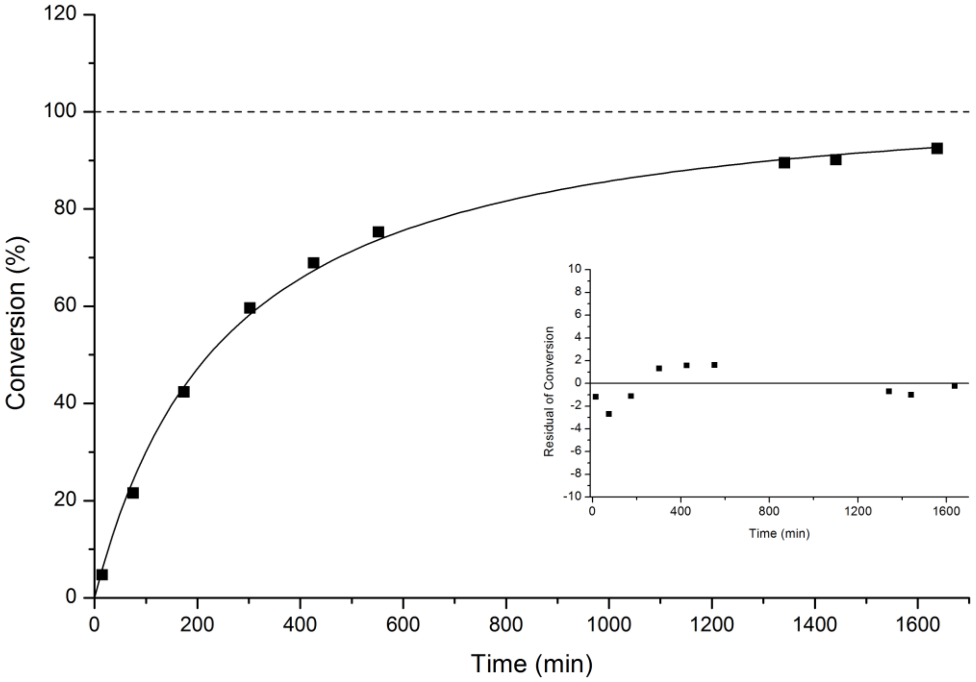


Figure S29. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 0.5 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99739 k_{eff} = 3.47×10^{-3} $t_{1/2}$ = 221.3 min

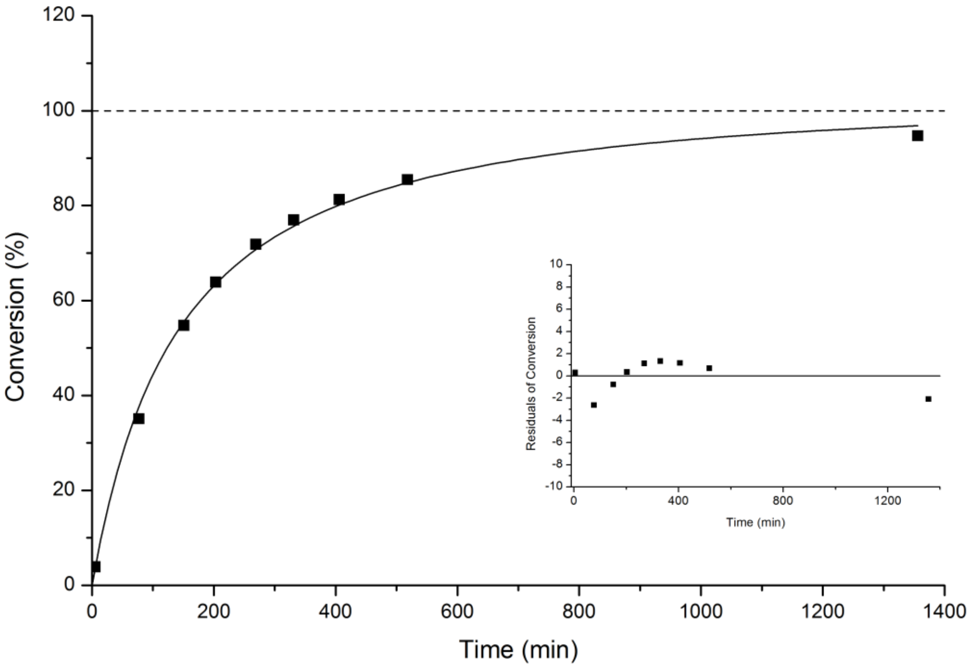


Figure S30. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 1.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99701 k_{eff} = 6.21×10^{-3} $t_{1/2}$ = 123.9 min

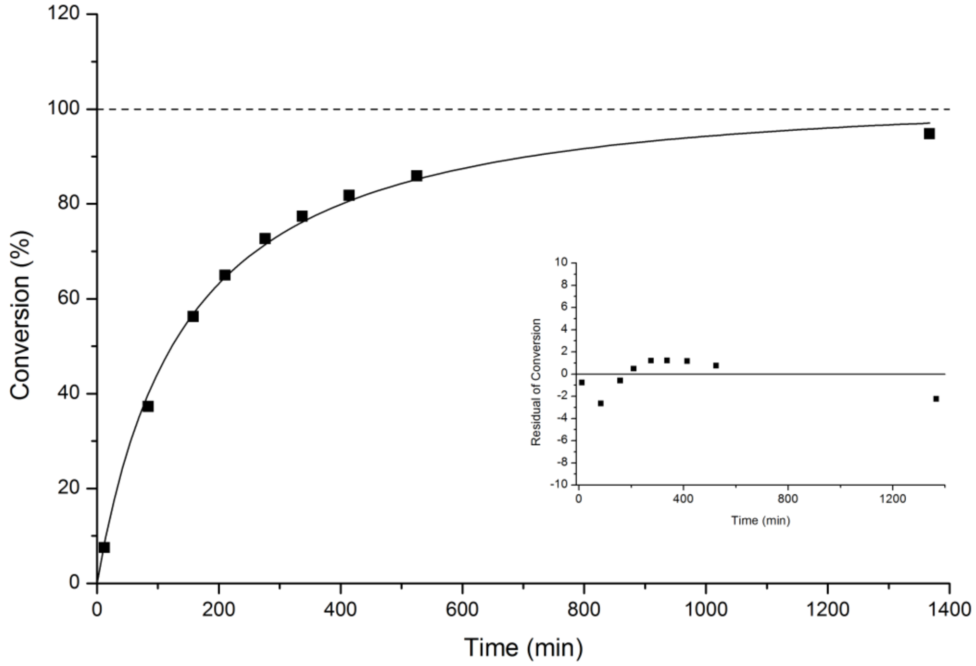


Figure S31. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 1.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99652 k_{eff} = 6.20×10^{-3} $t_{1/2}$ = 123.9 min

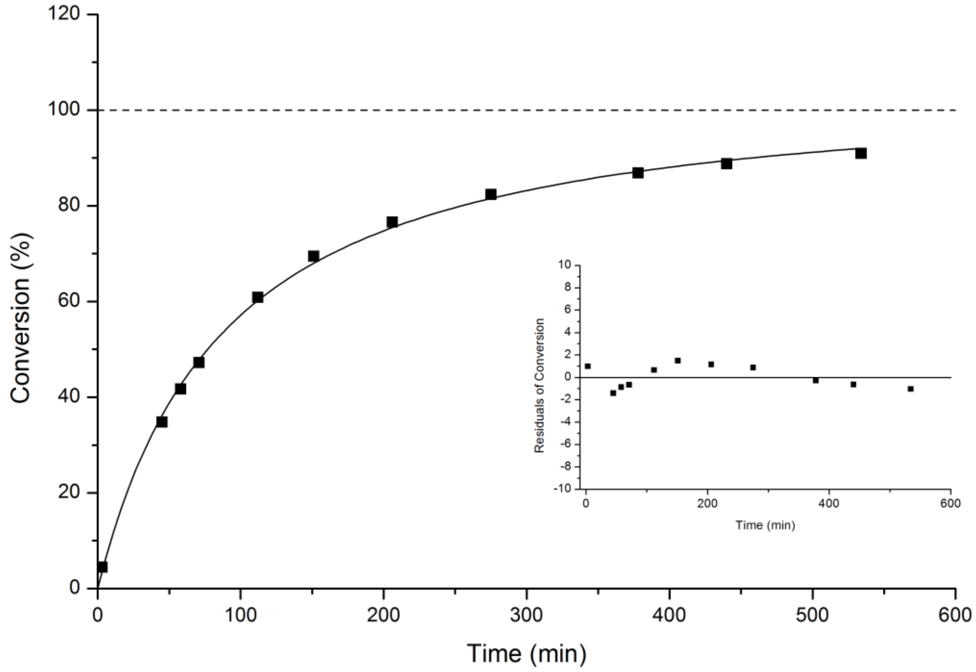


Figure S32. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 2.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99844 k_{eff} = 1.00×10^{-2} $t_{1/2}$ = 76.4 min

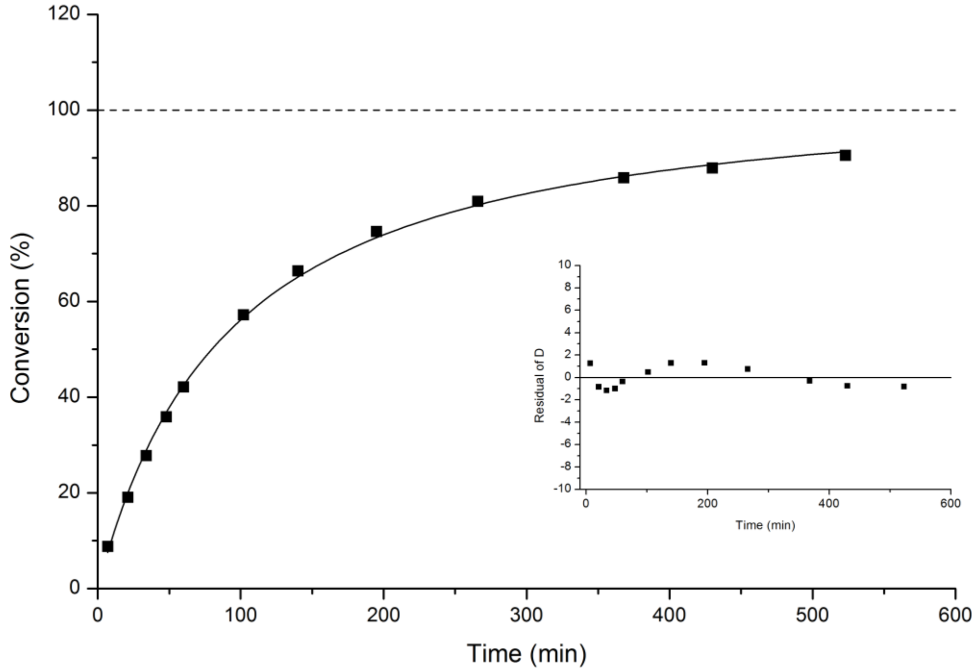


Figure S33. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 2.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99878 k_{eff} = 9.76×10^{-3} $t_{1/2}$ = 79.4 min

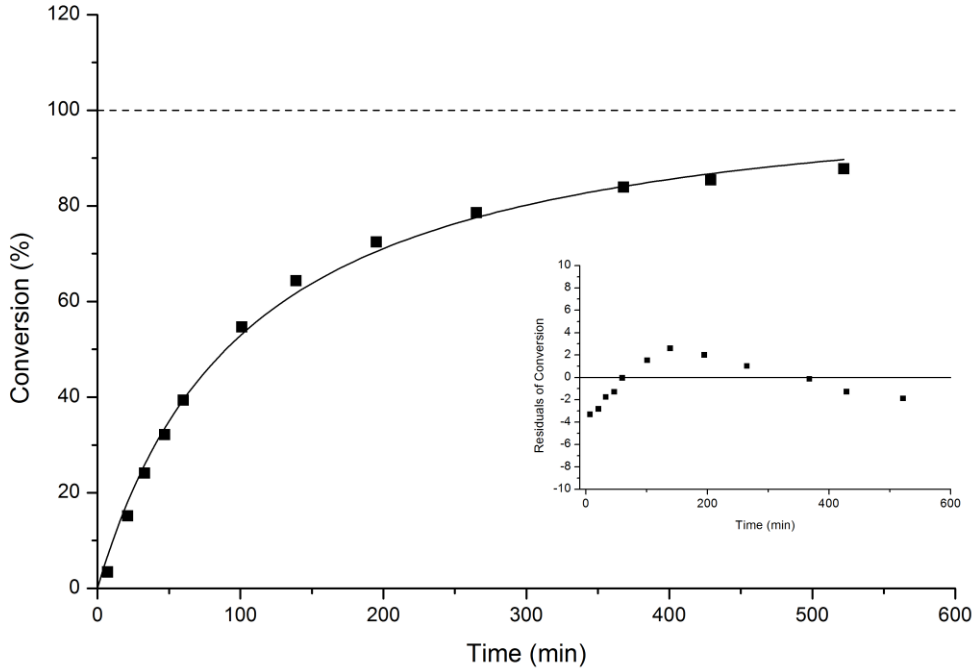


Figure S34. Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 2.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99511 k_{eff} = 8.58×10^{-3} $t_{1/2}$ = 89.5 min

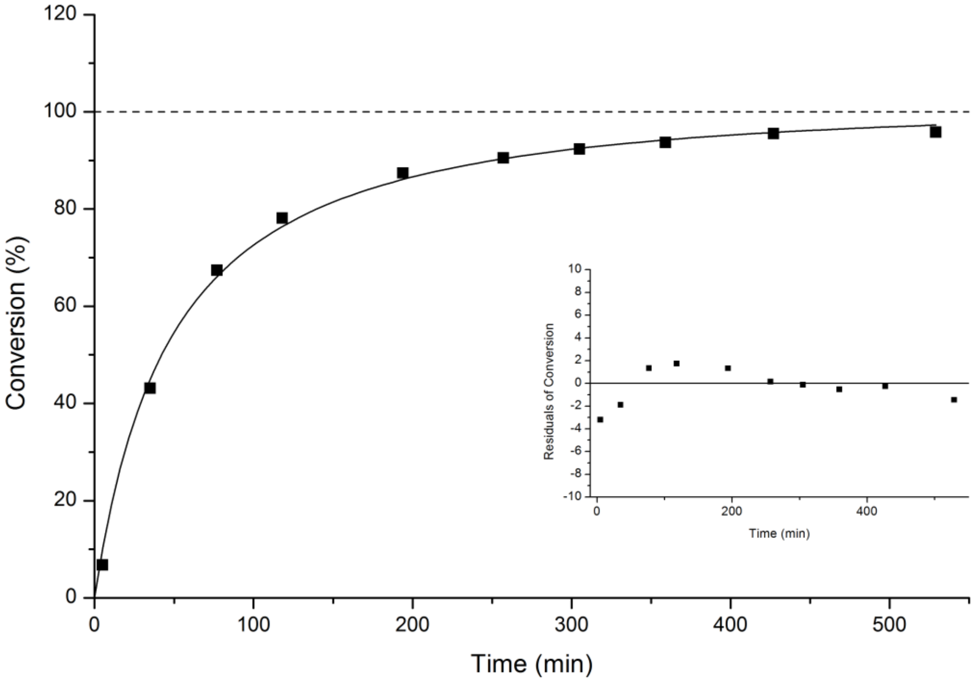


Figure S35. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 3.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99662 k_{eff} = 1.828×10^{-2} $t_{1/2}$ = 42.0 min

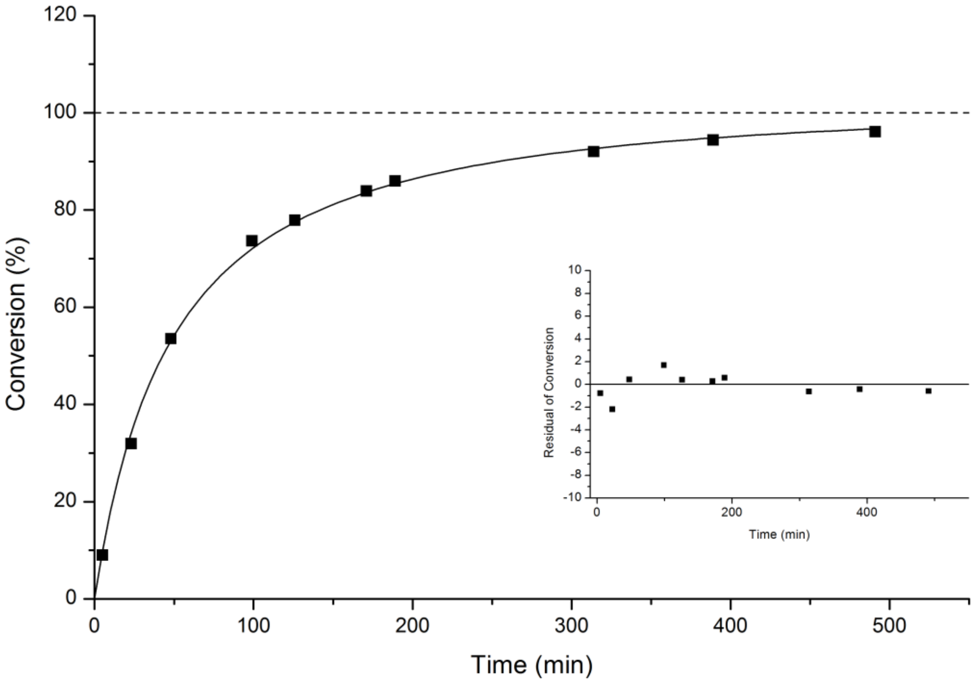


Figure S36. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 3.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99855 k_{eff} = 1.801×10^{-2} $t_{1/2}$ = 42.6 min

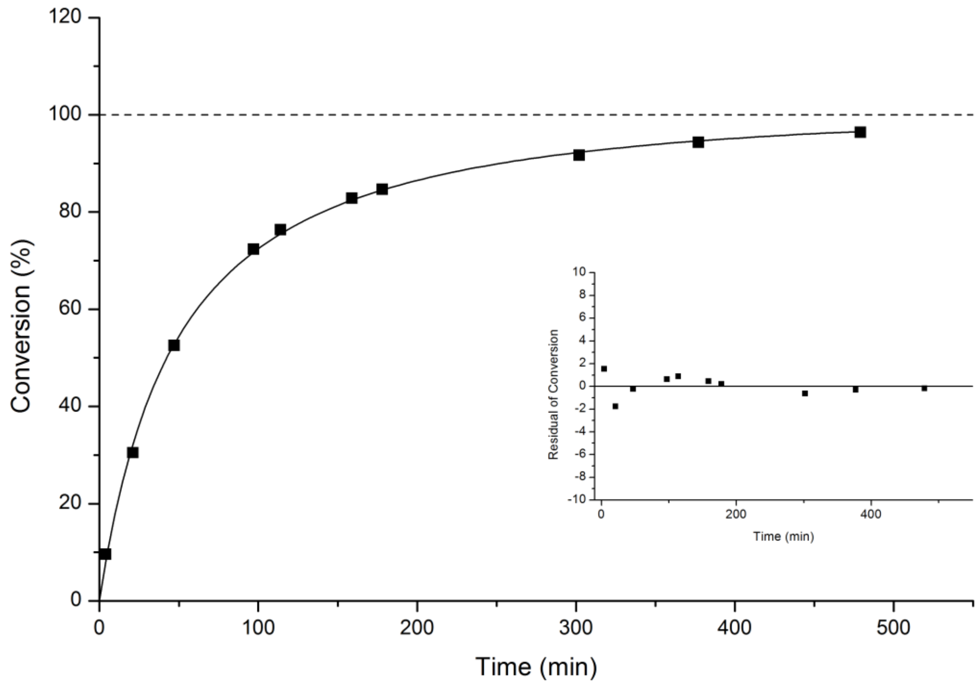


Figure S37. Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 3.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.9989 k_{eff} = 1.818×10^{-2} $t_{1/2}$ = 42.2 min

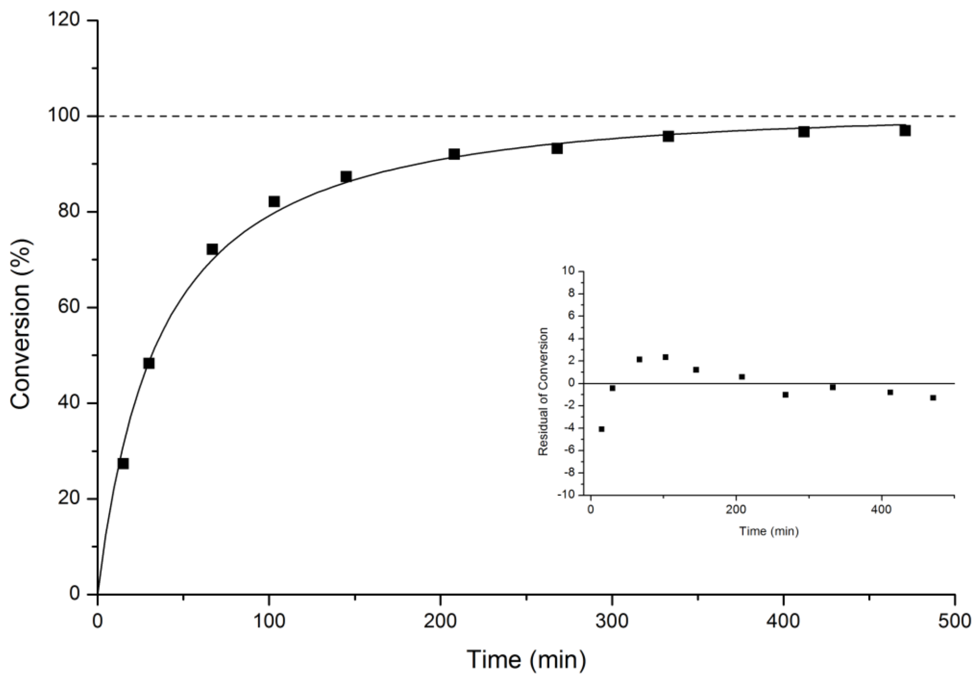


Figure S38. Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 4.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.9928 k_{eff} = 2.45×10^{-2} $t_{1/2}$ = 31.3 min

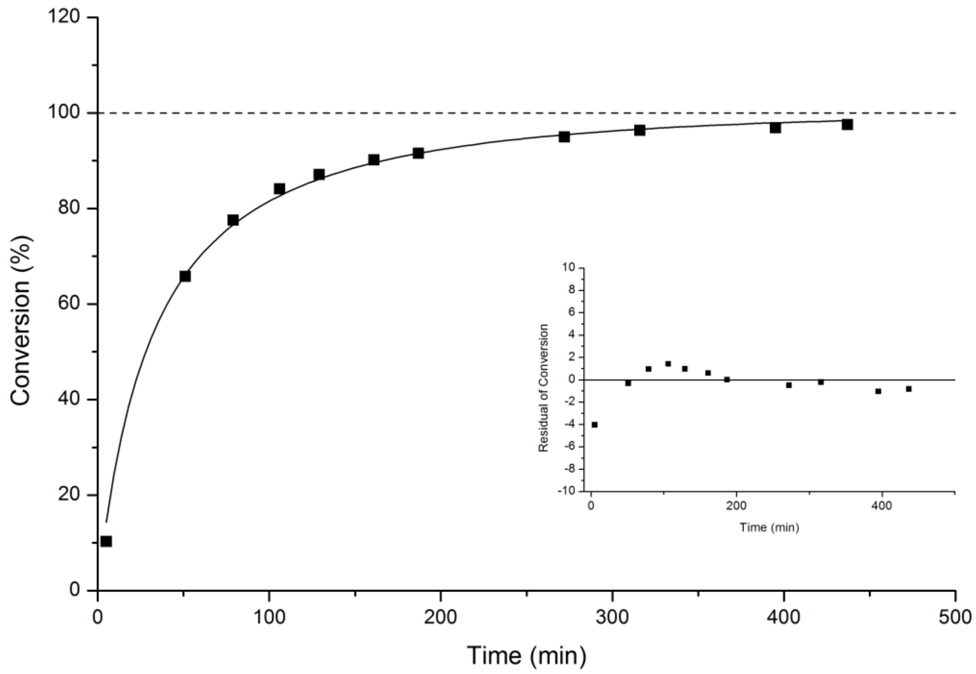


Figure S39. Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 4.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99609 k_{eff} = 2.75×10^{-2} $t_{1/2}$ = 27.9 min

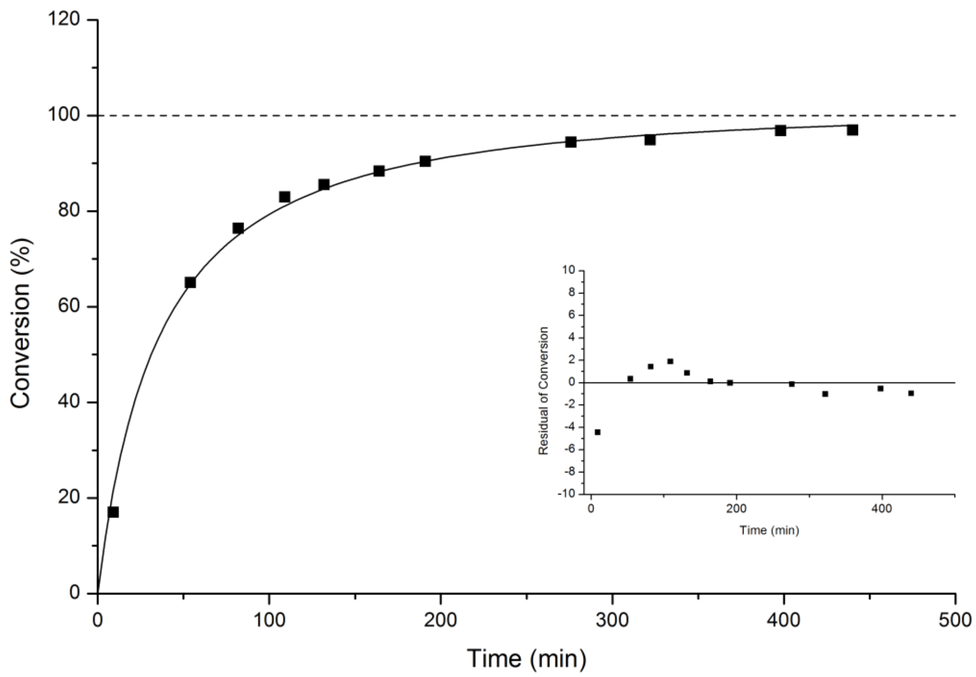


Figure S40. Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 4.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99416 k_{eff} = 2.473×10^{-2} $t_{1/2}$ = 31.1 min

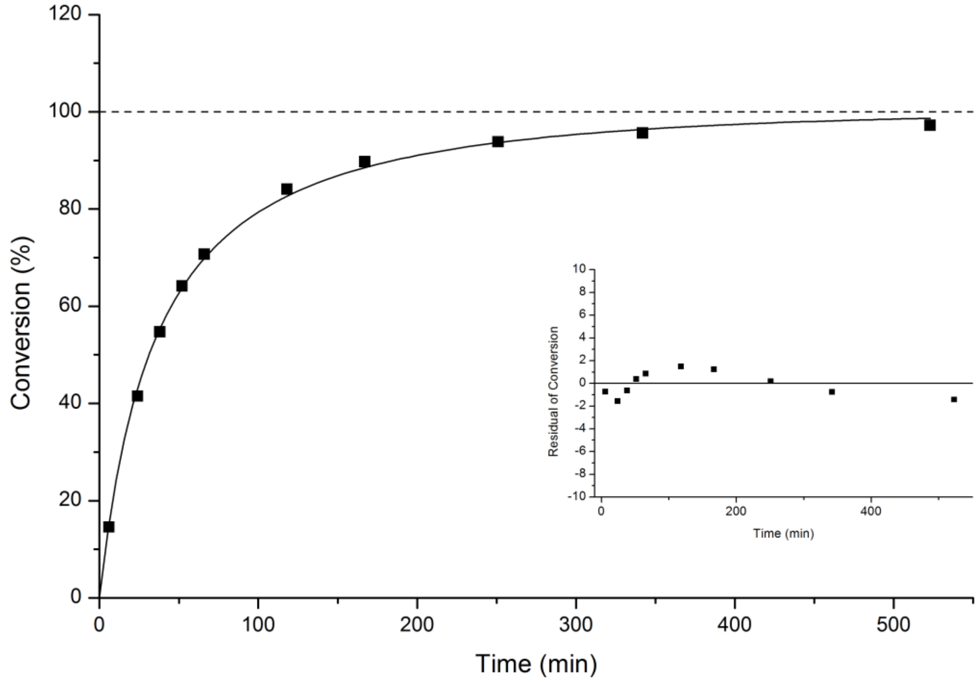


Figure S41. Forth conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCl (**1a**), and DMAP as catalyst with 4.0 mol% catalyst loading in $CDCl_3$.

R^2 = 0.99823 k_{eff} = 2.474×10^{-2} $t_{1/2}$ = 31.0 min

*4.1.2 Measurements with TBSOTf (**1b**)*

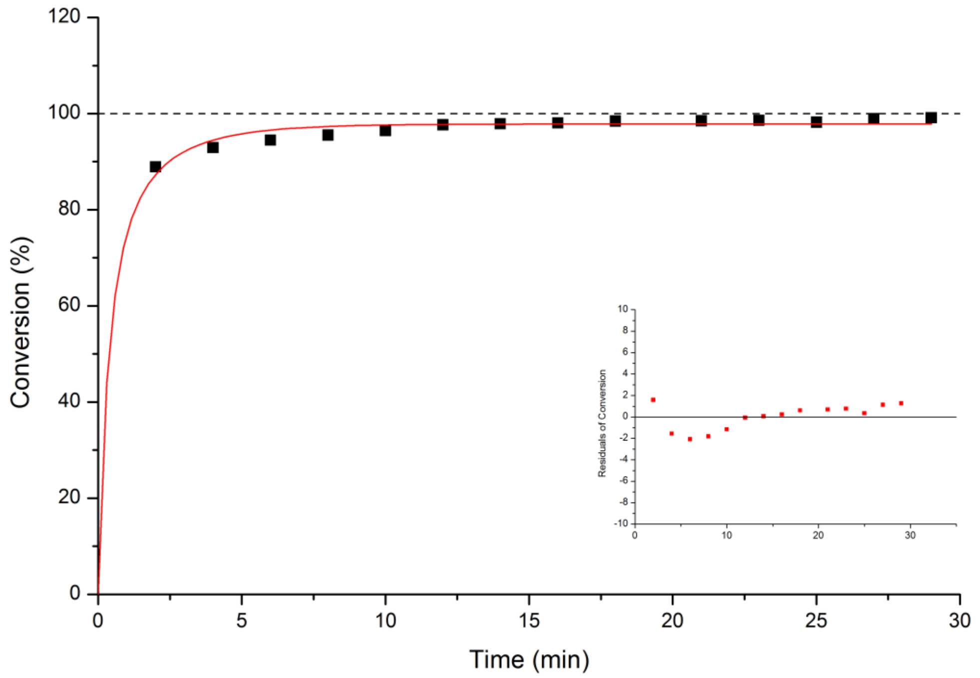


Figure S42 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 30 mol% DMAP as catalyst in DMF-d_7.

R^2 = 0.8343 k_{eff} = 2.137 $t_{1/2}$ = 0.353 min

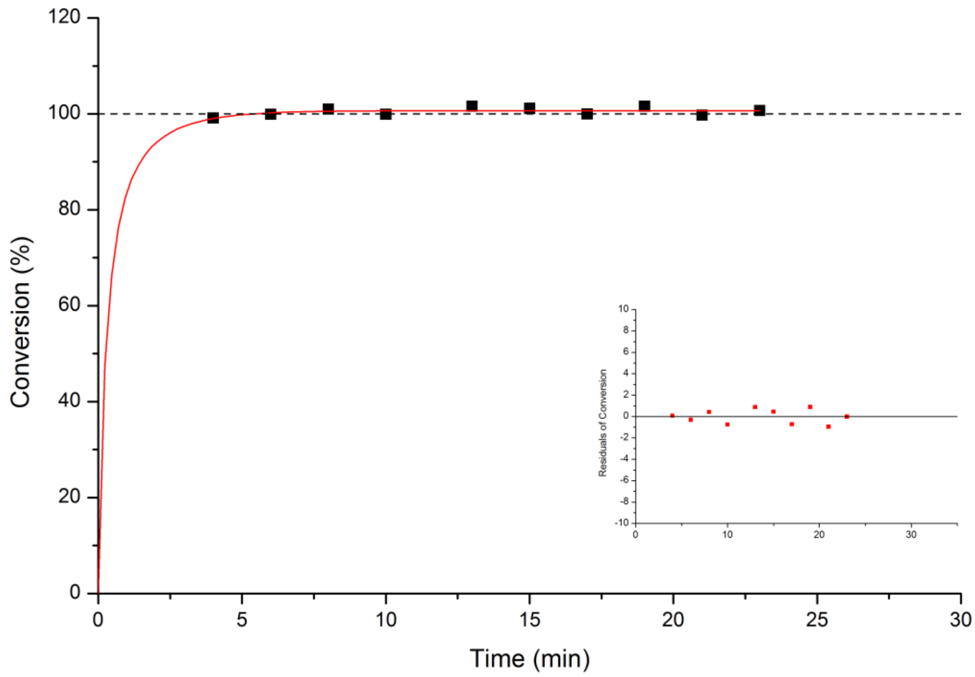


Figure S43 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 30 mol% DMAP as catalyst in DMF-d_7.

R^2 = 0.9215 k_{eff} = 2.9975 $t_{1/2}$ = 0.256 min

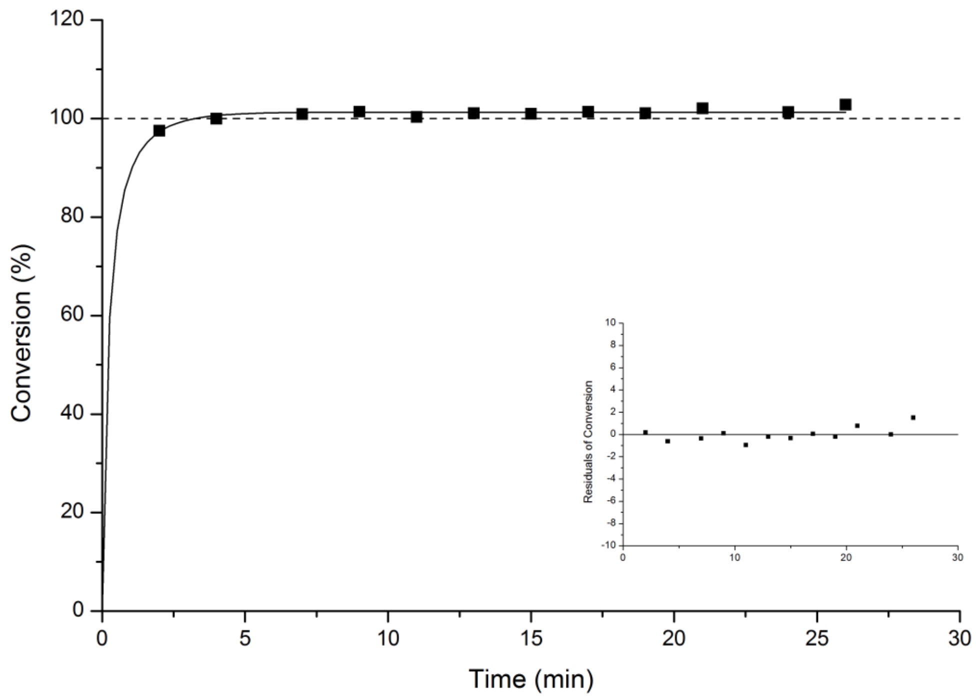


Figure S44 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 15 mol% DMAP as catalyst in DMF-d_7.

R^2 = 0.7241 k_{eff} = 4.065 $t_{1/2}$ = 0.189 min

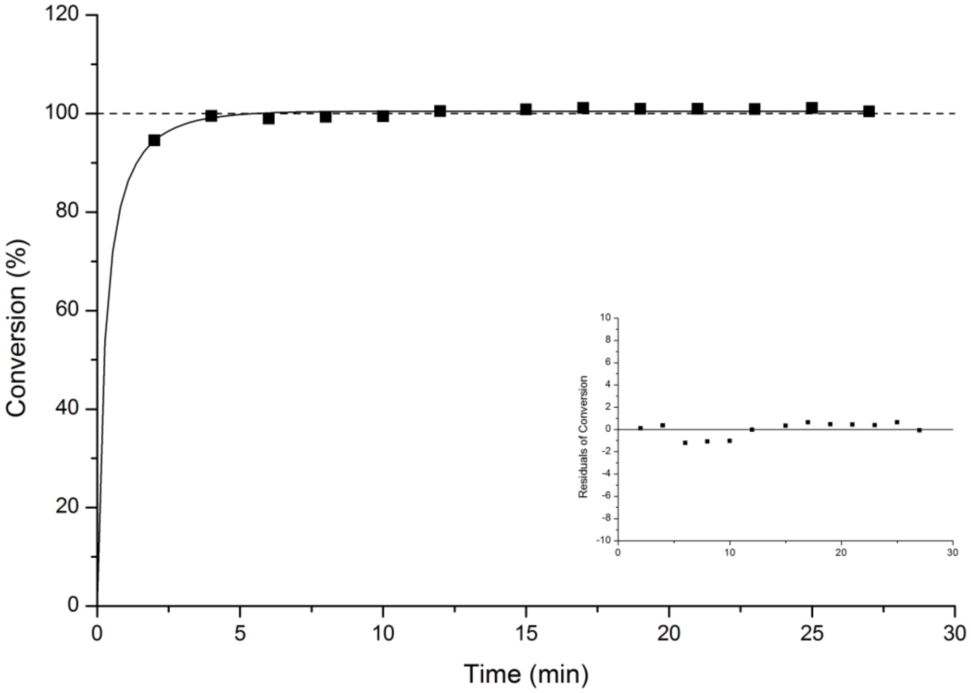


Figure S45 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 15 mol% DMAP as catalyst in DMF-d_7.

$R^2 = 0.8465$ $k_{eff} = 3.214$ $t_{1/2} = 0.239$ min

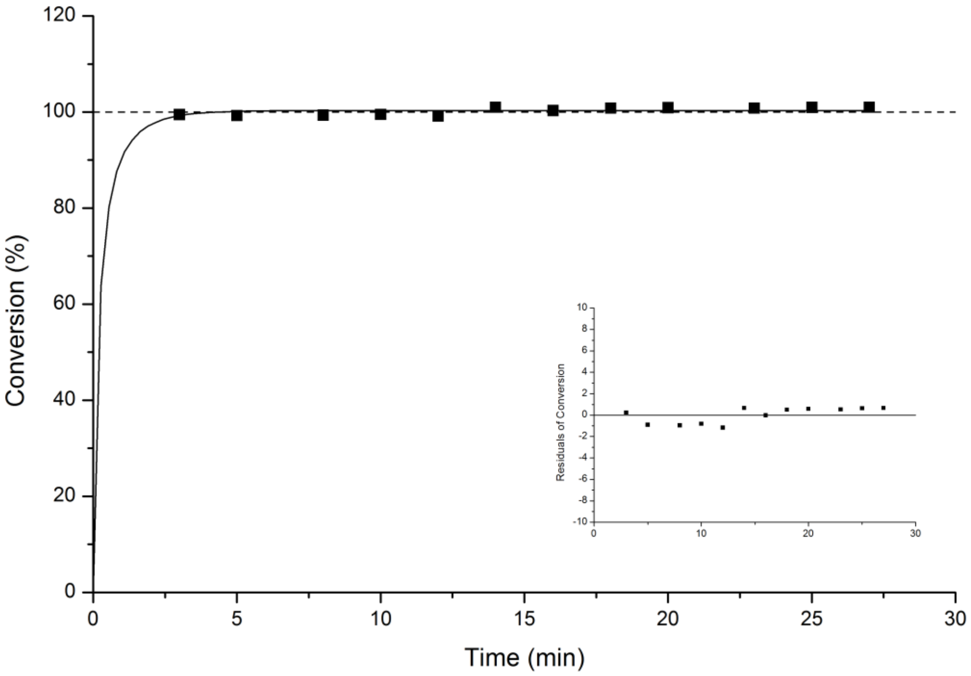


Figure S46 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and no catalyst in DMF-d_7.

$R^2 = 0.9944$ $k_{eff} = 4.681$ $t_{1/2} = 0.164$ min

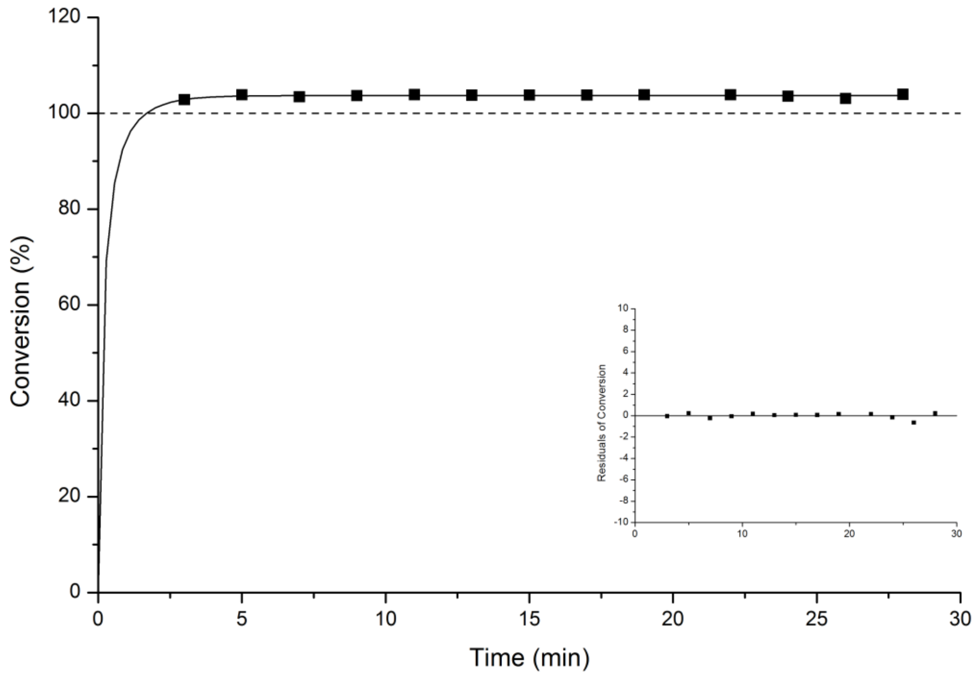


Figure 47 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and no catalyst in DMF-d_7.

R^2 = 0.9987 k_{eff} = 5.084 $t_{1/2}$ = 0.151 min

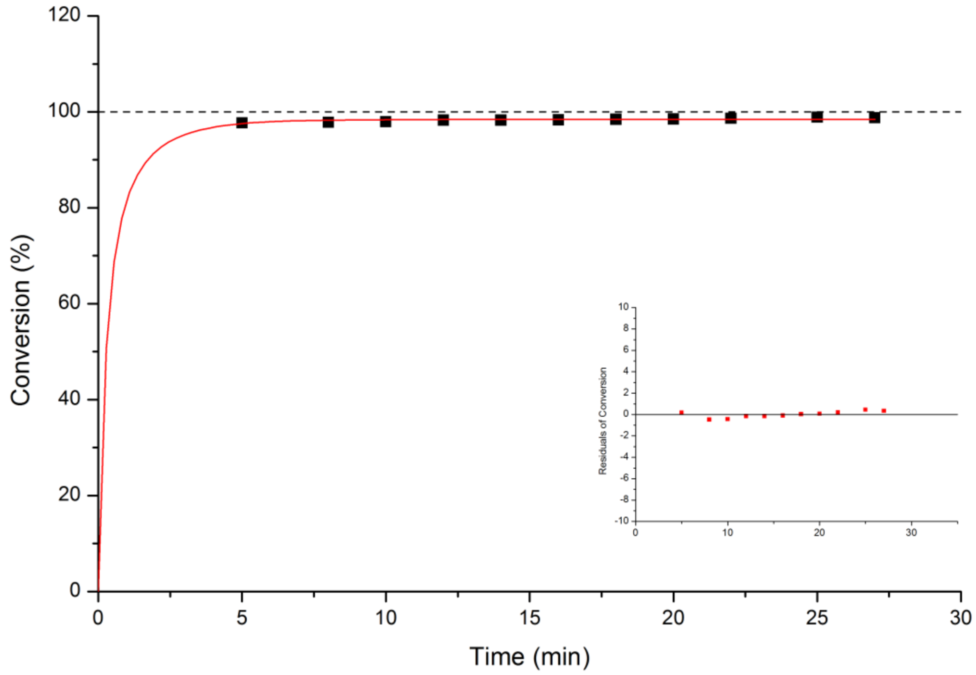


Figure S48 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and no catalyst in $CDCl_3$.

R^2 = 0.3241 k_{eff} = 2.979 $t_{1/2}$ = 0.258 min

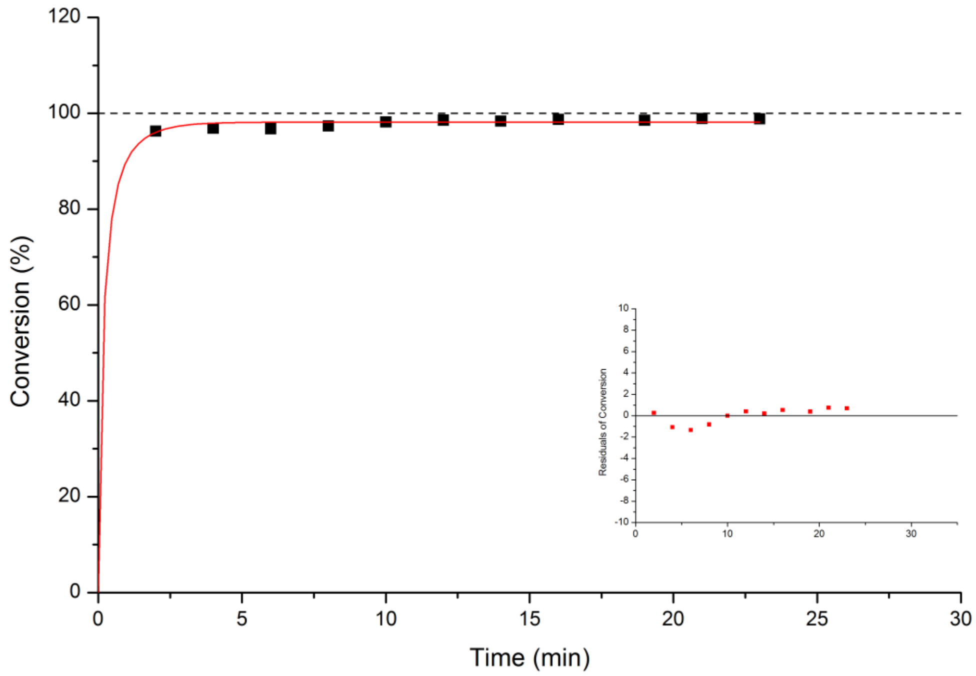


Figure S49 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and no catalyst in $CDCl_3$.

R^2 = 0.33046 k_{eff} = 5.3482 $t_{1/2}$ = 0.144 min

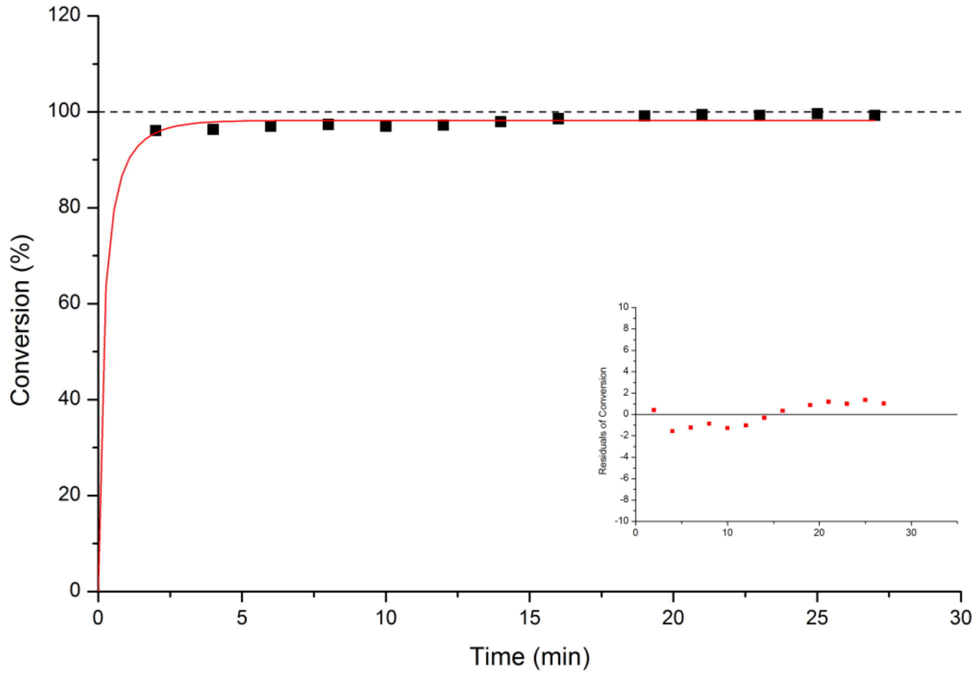


Figure S50 Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and no catalyst in $CDCl_3$.

R^2 = 0.2043 k_{eff} = 4.9206 $t_{1/2}$ = 0.156 min

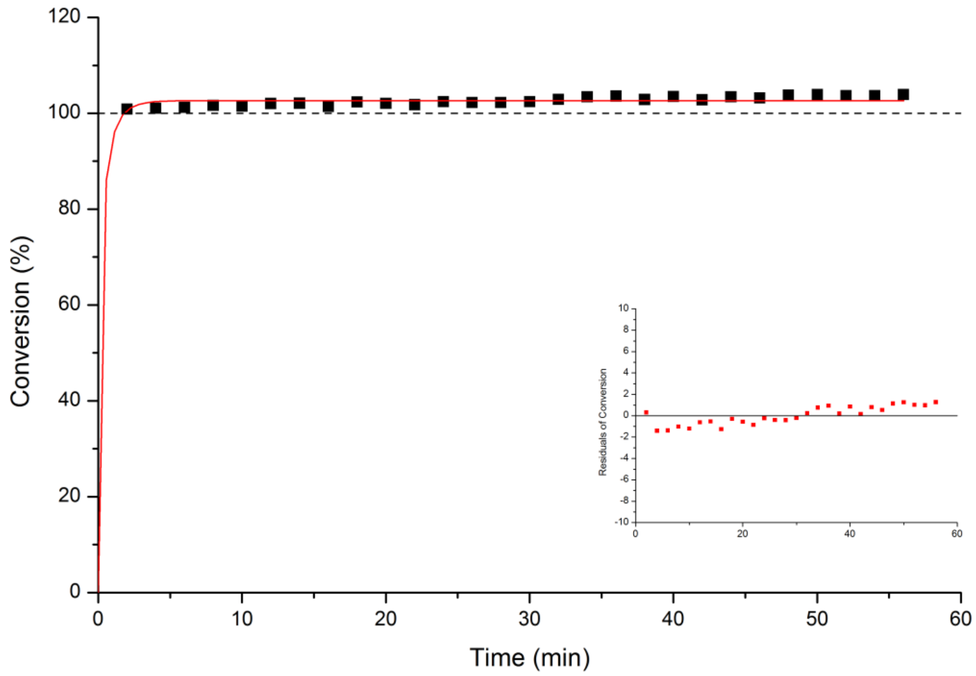


Figure S51 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 10 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.11972 k_{eff} = 5.4947 $t_{1/2}$ = 0.140 min

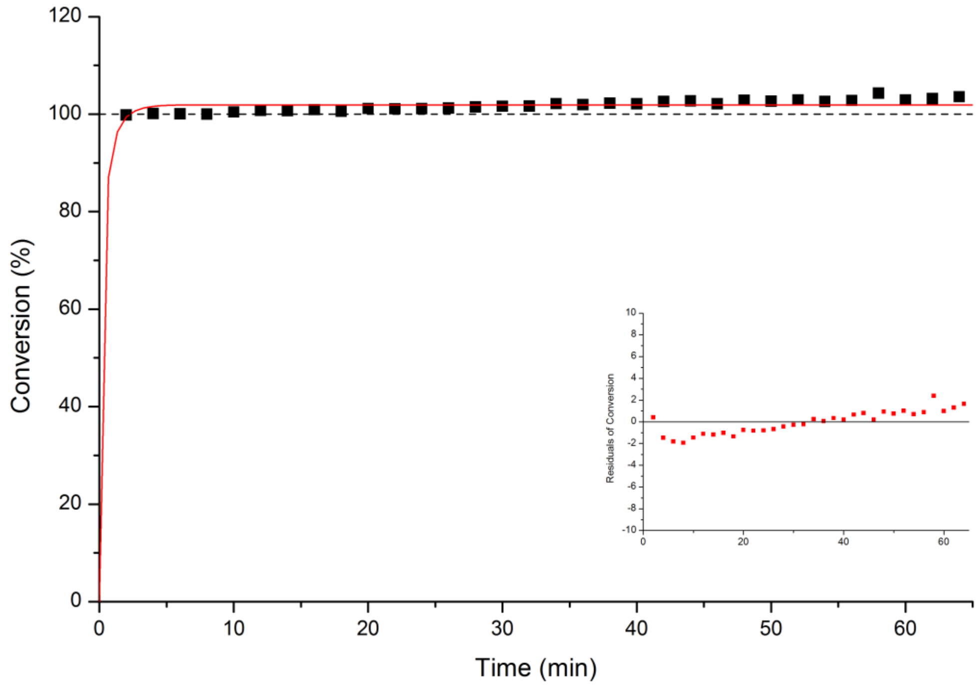


Figure S52 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 10 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.0862 k_{eff} = 5.0958 $t_{1/2}$ = 0.151 min

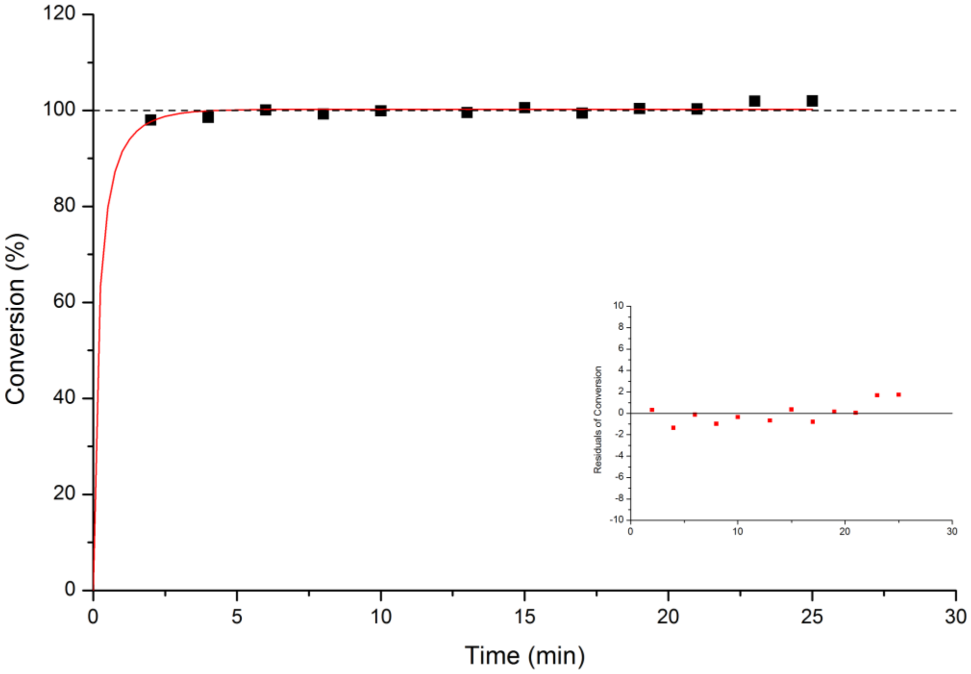


Figure S53 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 20 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.2780 k_{eff} = 4.974 $t_{1/2}$ = 0.154 min

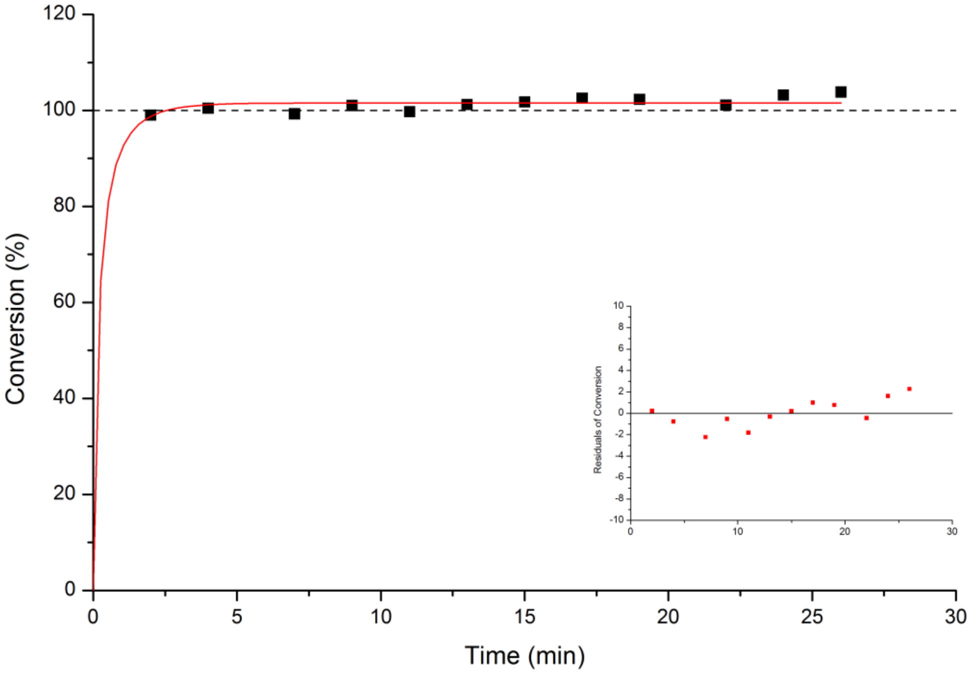


Figure S54 Second Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 20 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.1758 k_{eff} = 4.848 $t_{1/2}$ = 0.158 min

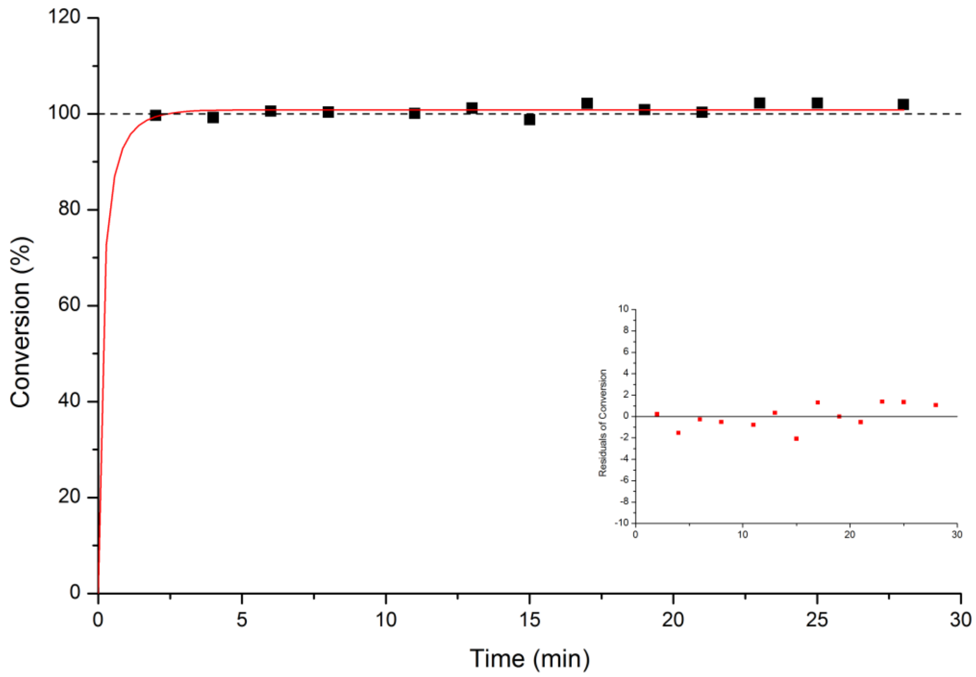


Figure S55 Third Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 20 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.0170 k_{eff} = 6.3133 $t_{1/2}$ = 0.122 min

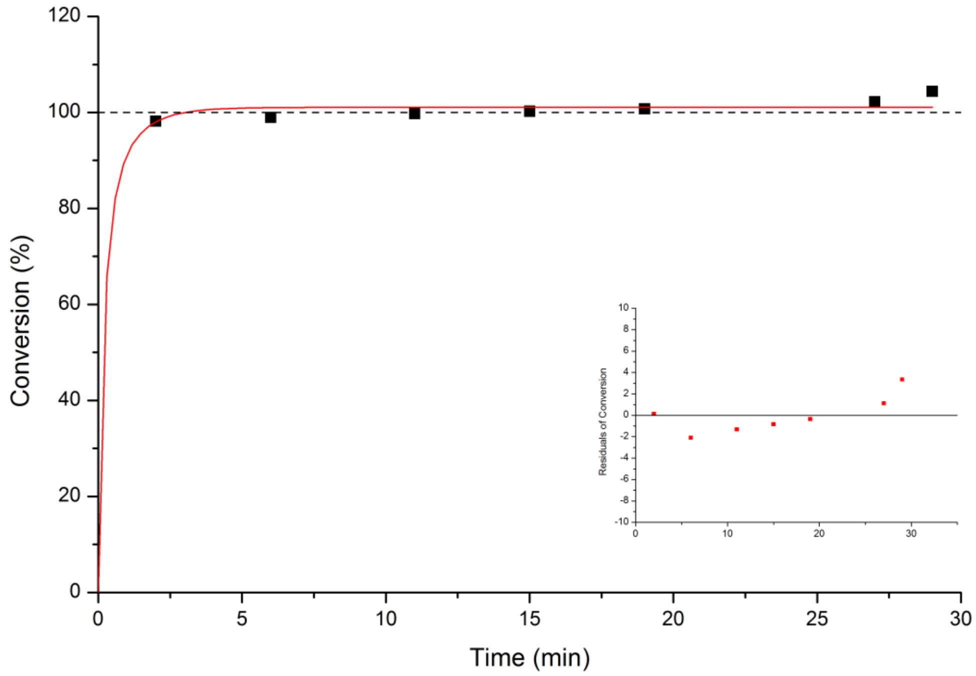


Figure S56 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 30 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.1333 k_{eff} = 4.629 $t_{1/2}$ = 0.166 min

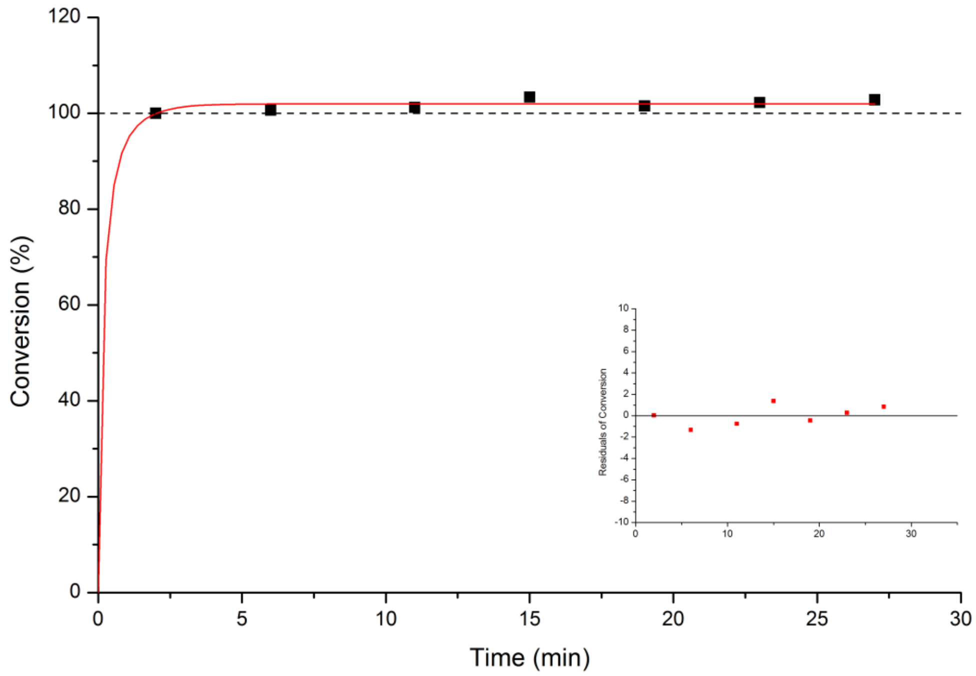


Figure S57 Second Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSOTf (**1b**), and 30 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.2728 k_{eff} = 5.566 $t_{1/2}$ = 0.138 min

*4.1.3 Measurements with TBSCN (**1c**)*

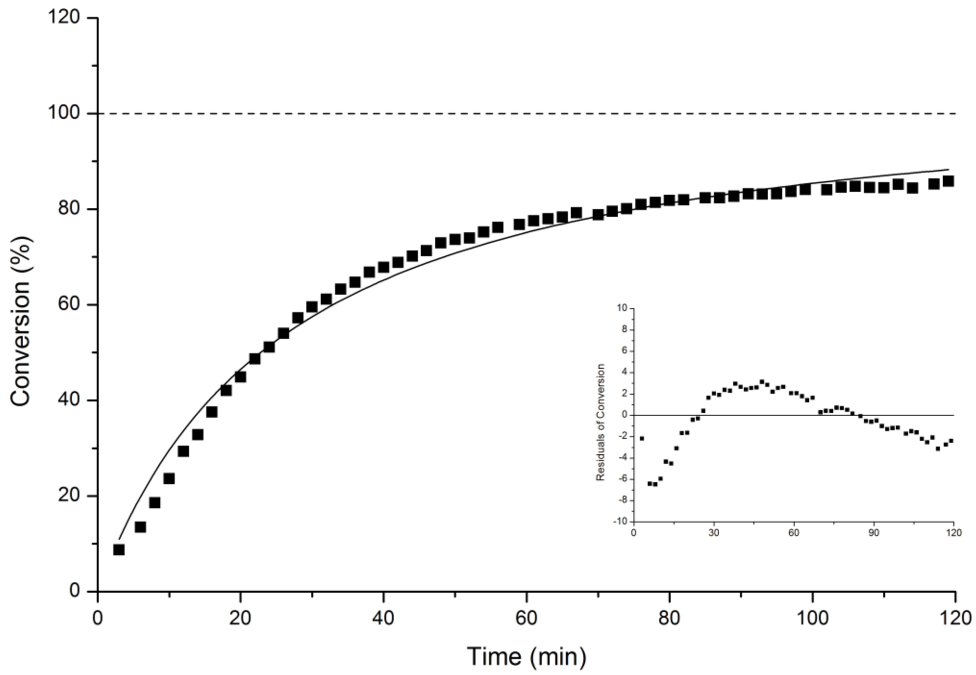


Figure S58 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 30 mol% DMAP as catalyst in DMF-d_7.

R^2 = 0.9960 k_{eff} = 0.0452 $t_{1/2}$ = 17.0 min

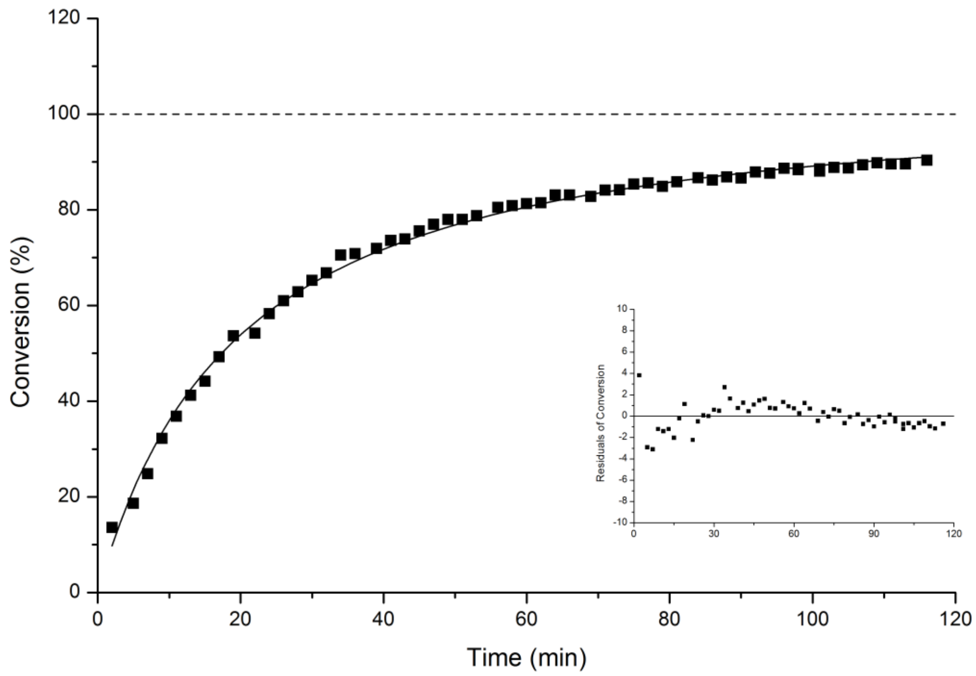


Figure S59 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 30 mol% DMAP as catalyst in DMF-d_7.

$R^2 = 0.9848$ $k_{eff} = 0.03377$ $t_{1/2} = 22.7$ min

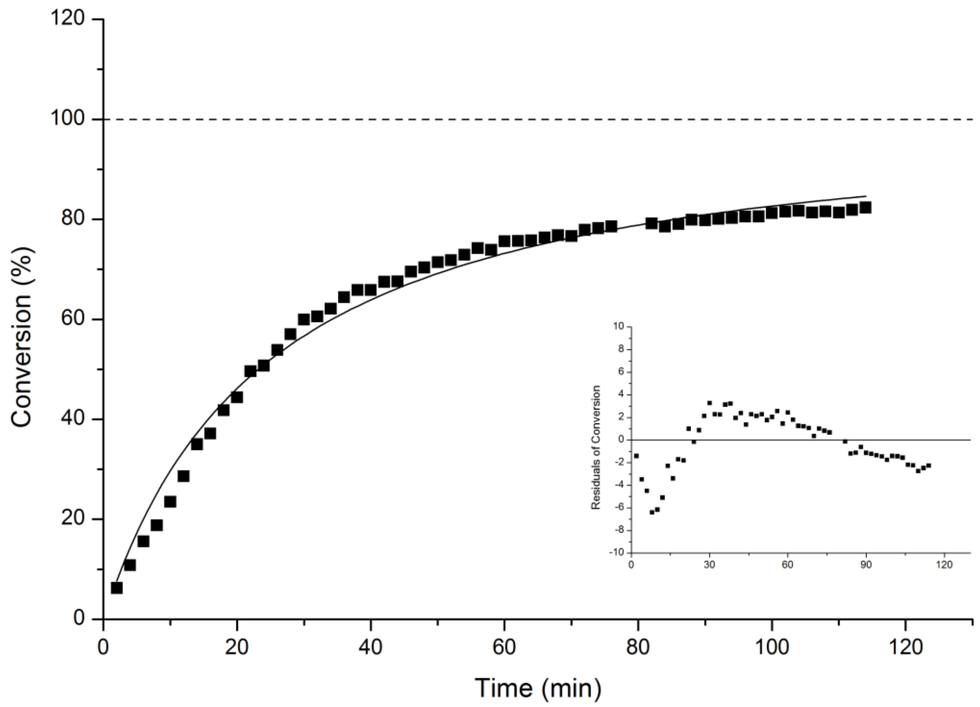


Figure S60 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and no catalyst in DMF-d_7.

$R^2 = 0.9861$ $k_{eff} = 3.619\times10^{-2}$ $t_{1/2} = 21.2$ min

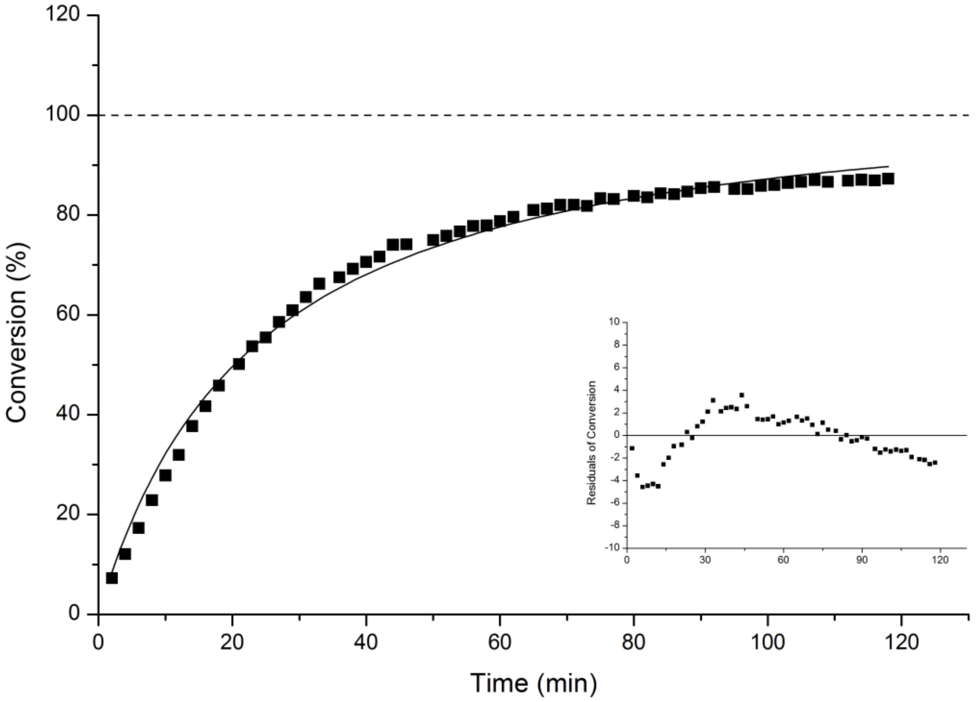


Figure S61 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and no catalyst in DMF-d_7.

R^2 = 0.99096 k_{eff} = 3.802×10^{-2} $t_{1/2}$ = 20.2 min

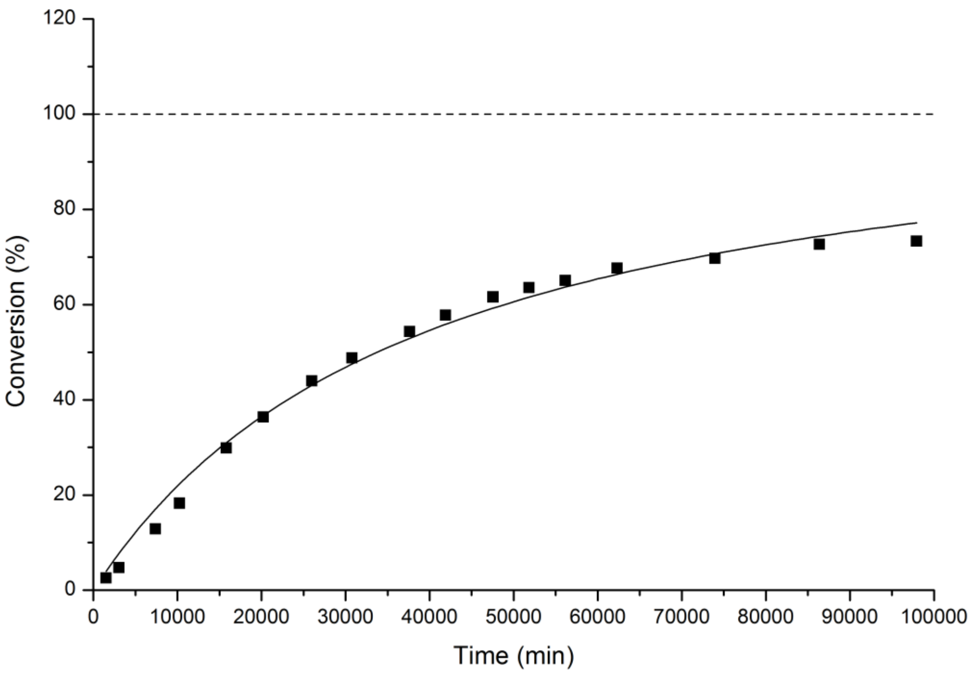


Figure S62 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 10 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.99029 k_{eff} = 2.283×10^{-5} $t_{1/2}$ = 33634.8 min

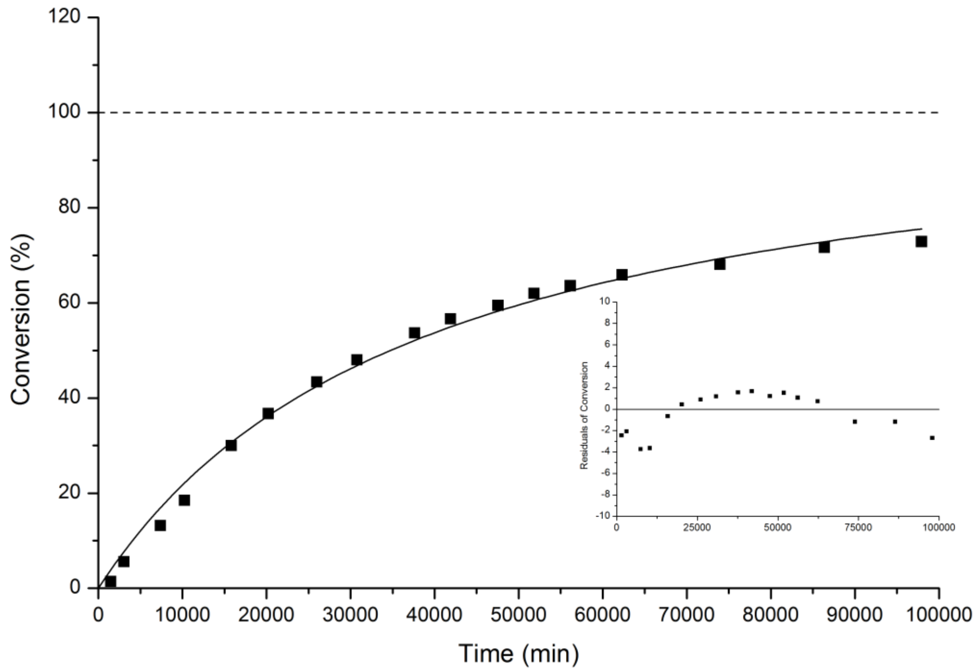


Figure S63 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 10 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.99274 k_{eff} = 2.340×10^{-5} $t_{1/2}$ = 32810.4 min

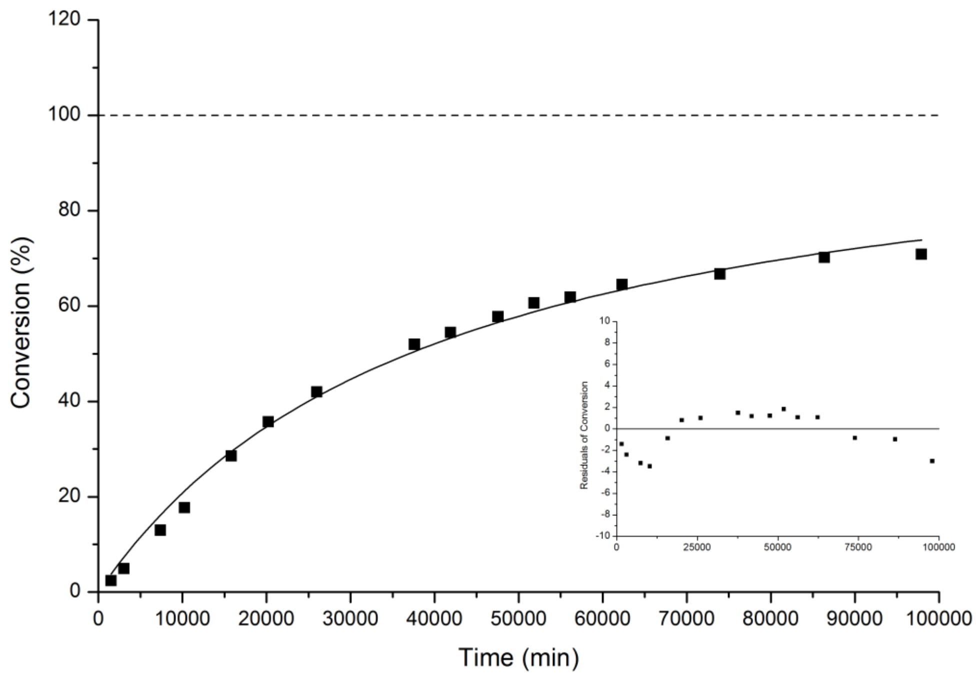


Figure S64 Third conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 10 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9932 k_{eff} = 2.244×10^{-5} $t_{1/2}$ = 34212.9.0 min

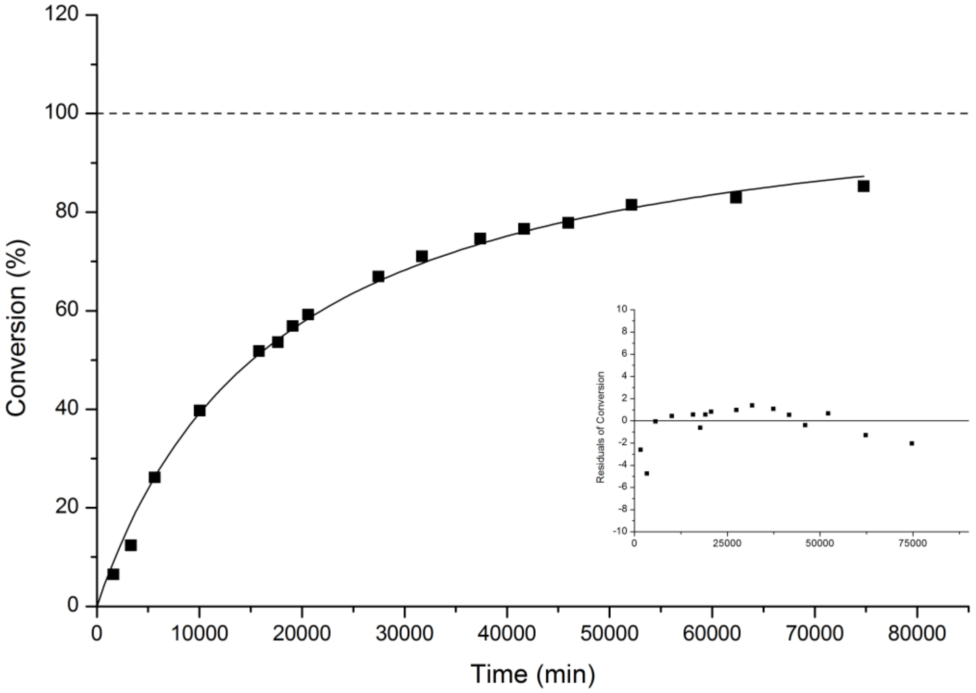


Figure S65 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 20 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.99517$ $k_{eff} = 5.100\times10^{-5}$ $t_{1/2} = 15055.0$ min

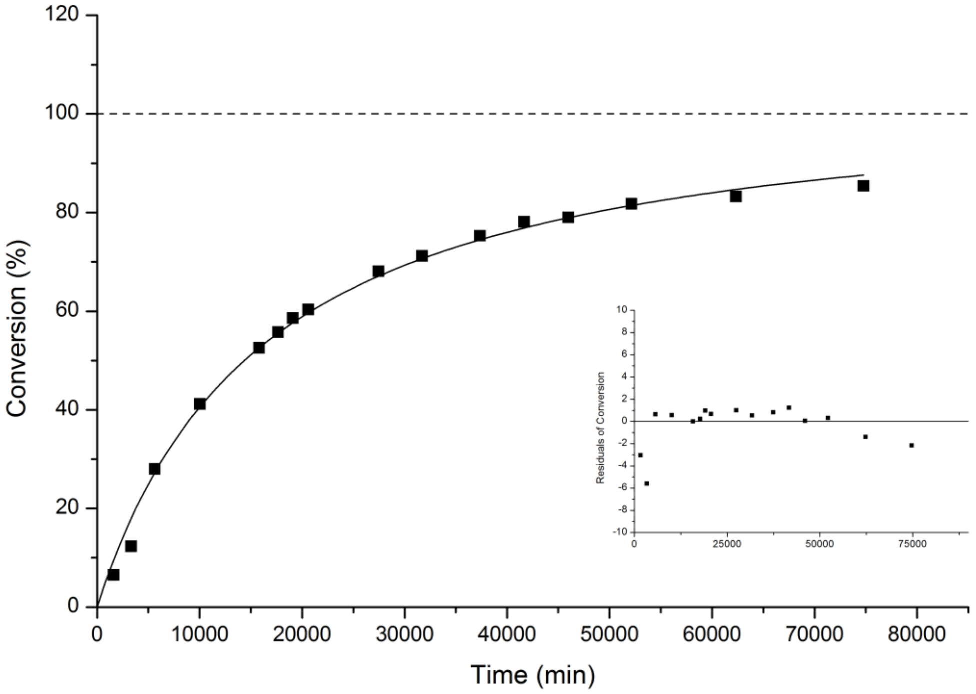


Figure S66 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 20 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.9938$ $k_{eff} = 5.446\times10^{-5}$ $t_{1/2} = 14098.8$ min

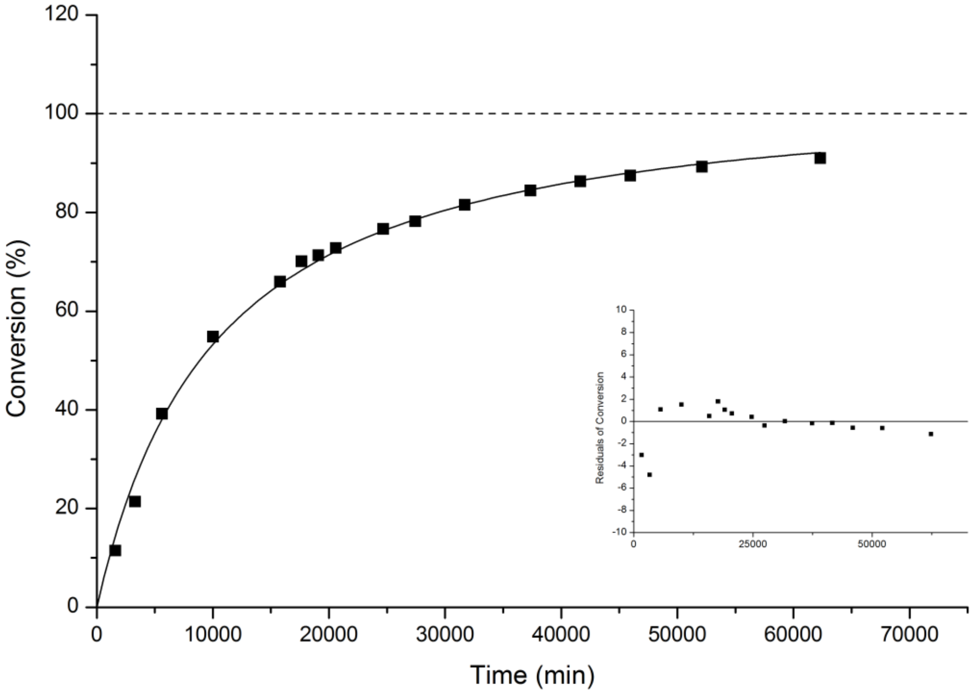


Figure S67 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 30 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.9947$ $k_{eff} = 8.6942\times10^{-5}$ $t_{1/2} = 8832.5$ min

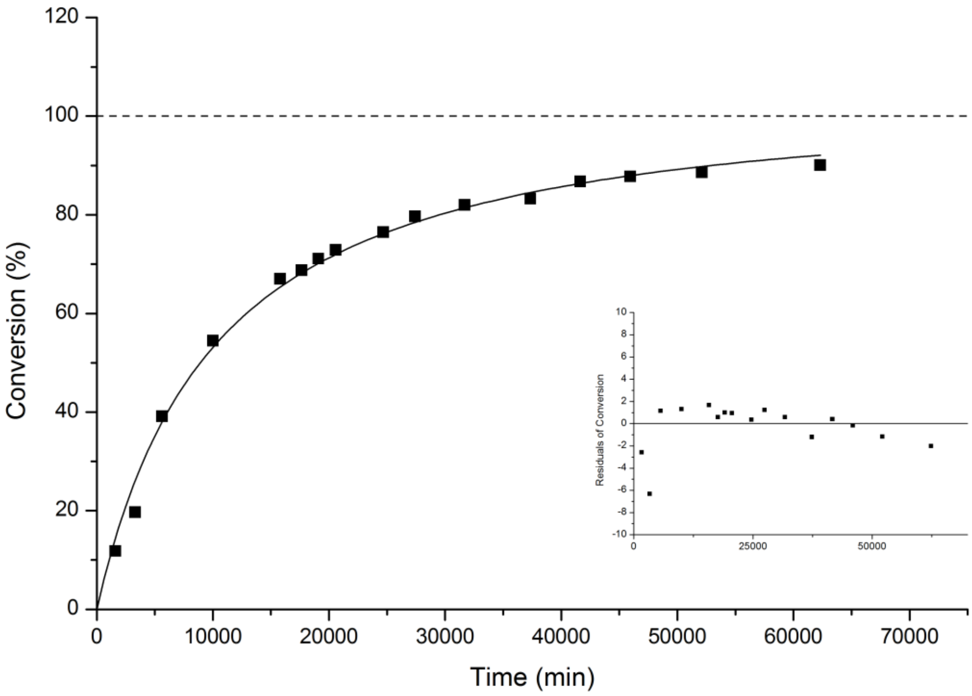


Figure S68 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 30 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.9922$ $k_{eff} = 8.649\times10^{-5}$ $t_{1/2} = 8878.4$ min

*4.1.3.1 Primary Alcohol (**4a**)*

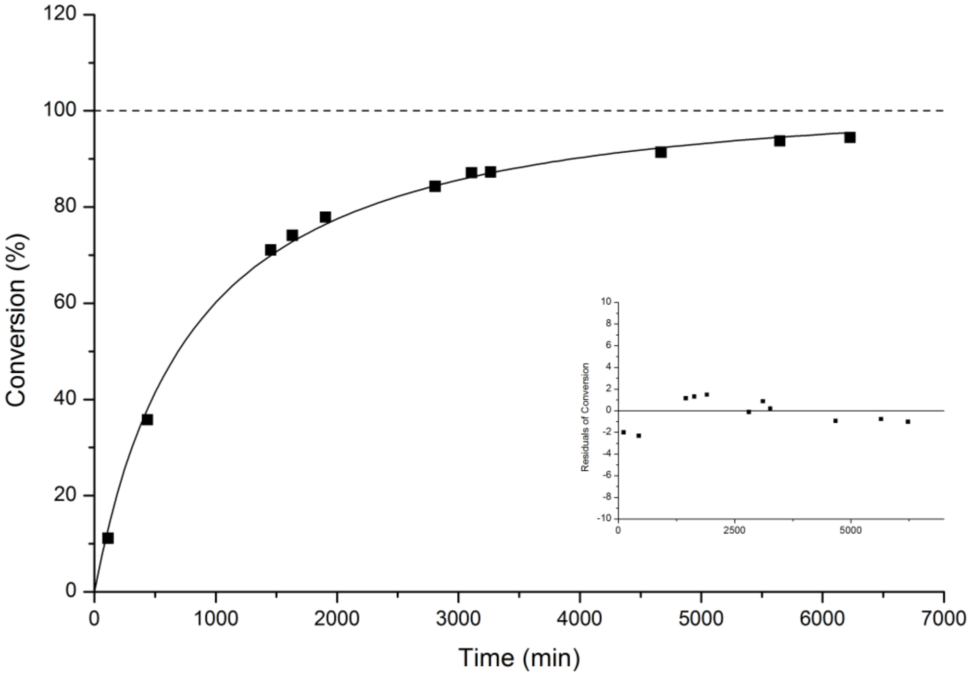


Figure S69 Conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 1 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9971 k_{eff} = 1.10×10^{-3} $t_{1/2}$ = 698.1 min

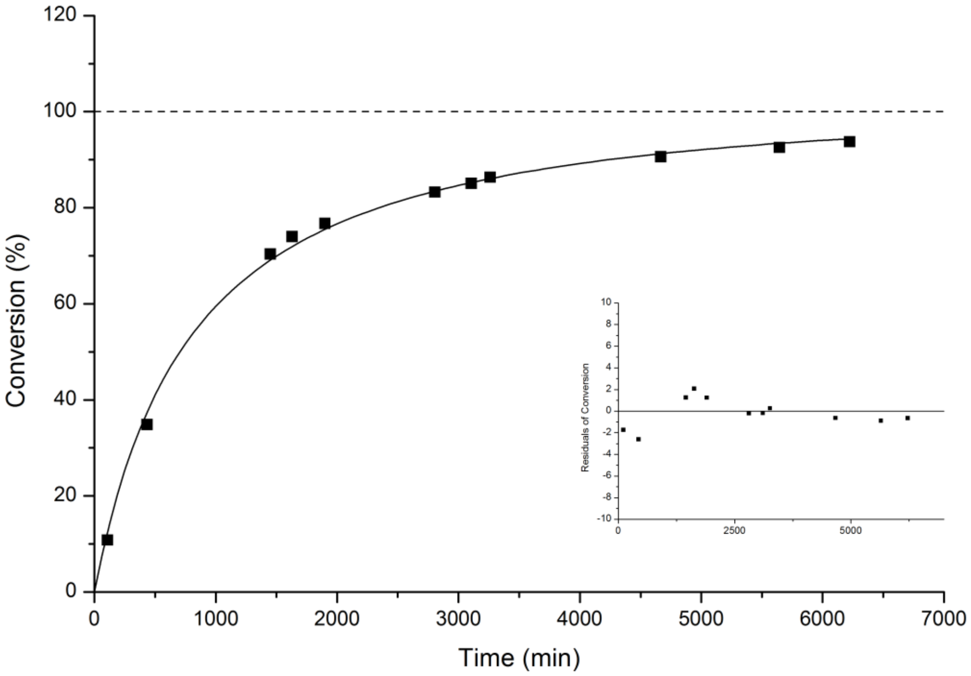


Figure S70 Second conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 1 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9969 k_{eff} = 1.10×10^{-3} $t_{1/2}$ = 698.1 min

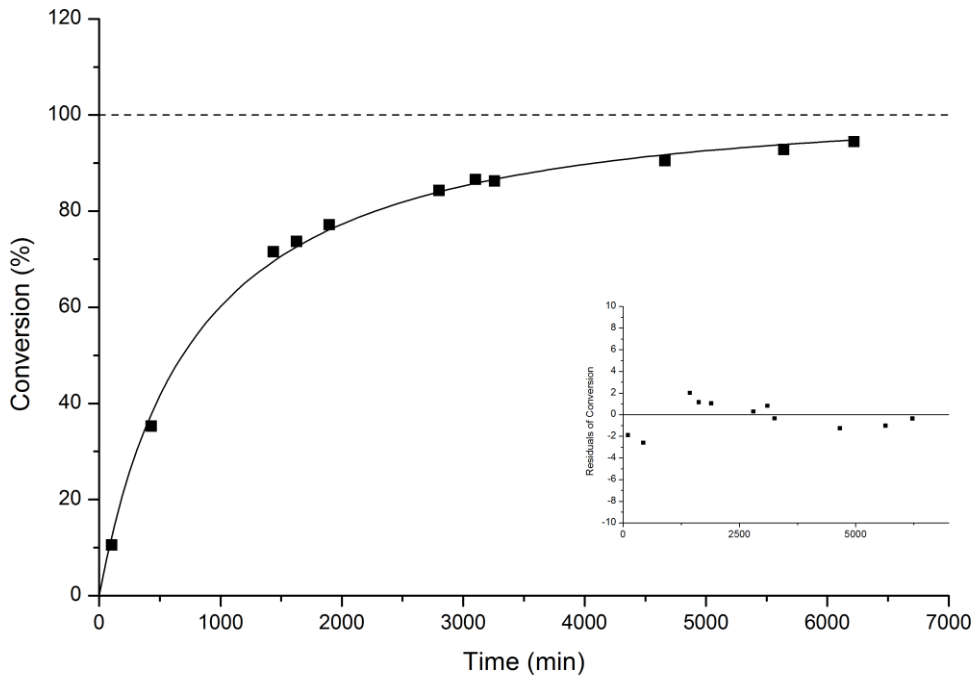


Figure S71 Third conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 1 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.9917$ $k_{eff} = 1.12\times10^{-3}$ $t_{1/2} = 685.6$ min

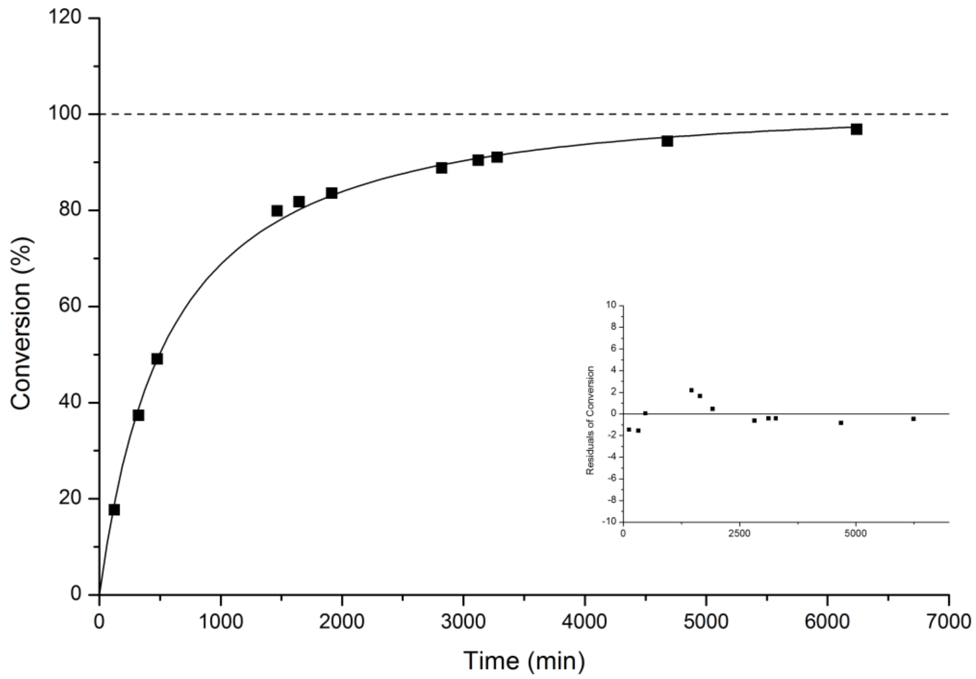


Figure S72 Conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 2 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.9978$ $k_{eff} = 1.56\times10^{-3}$ $t_{1/2} = 492.2$ min

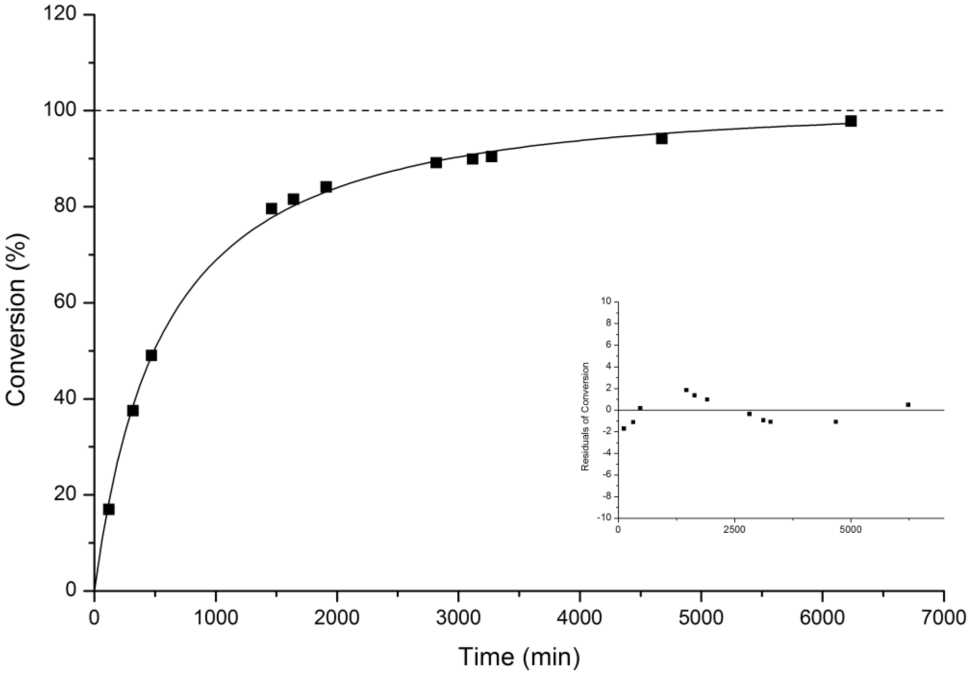


Figure S73 Second conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 2 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.9978$ $k_{eff} = 1.57\times10^{-3}$ $t_{1/2} = 489.1$ min

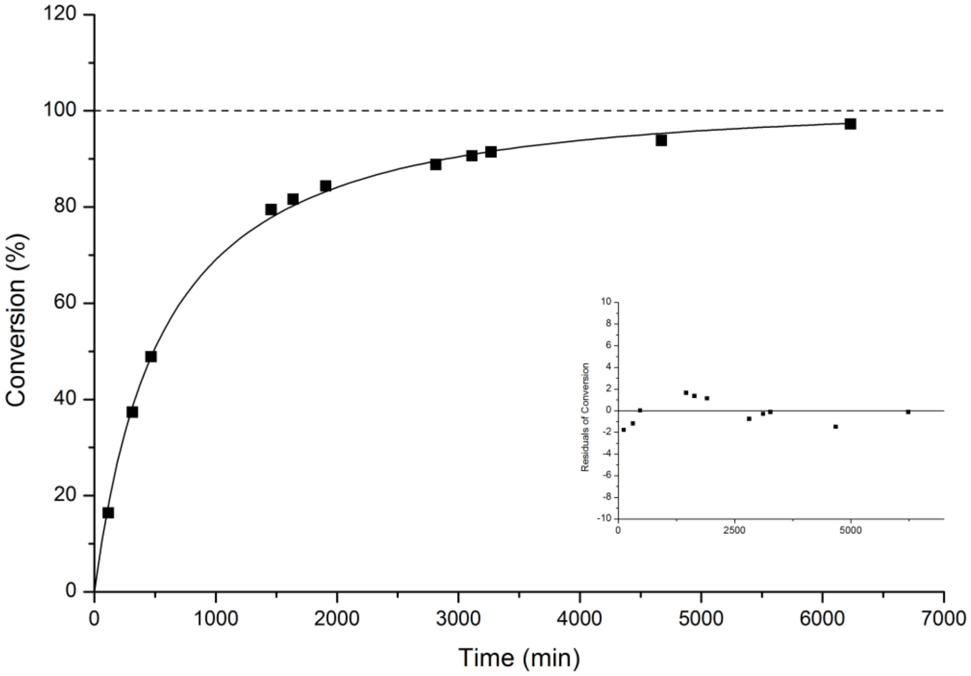


Figure S74 Third conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 2 mol% DMAP as catalyst in $CDCl_3$.

$R^2 = 0.9979$ $k_{eff} = 1.58\times10^{-3}$ $t_{1/2} = 486.0$

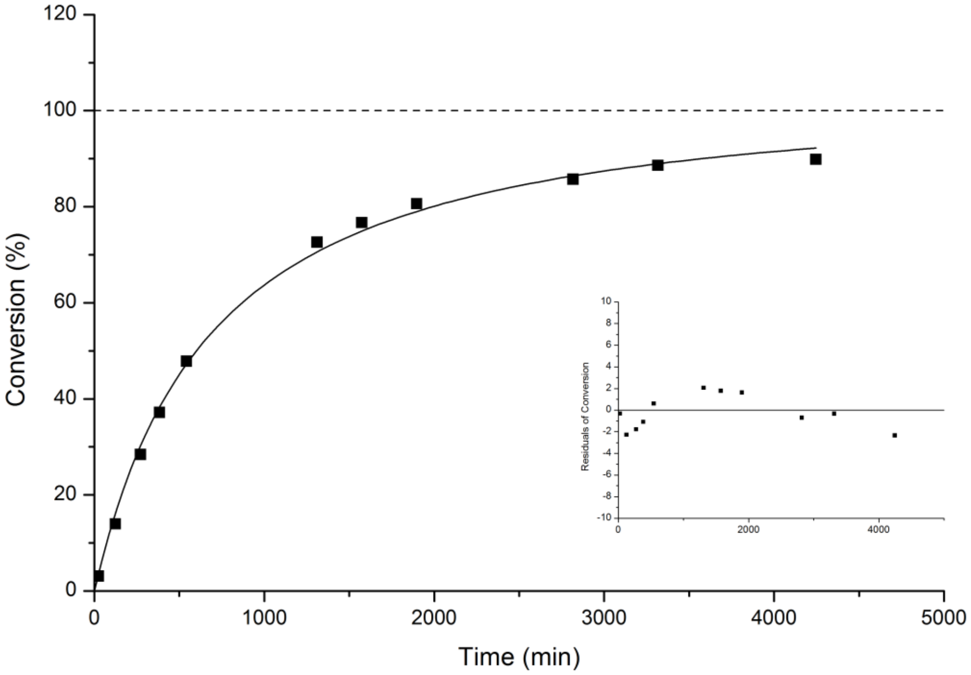


Figure S75 Conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 3 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9959 k_{eff} = 1.20×10^{-3} $t_{1/2}$ = 639.9

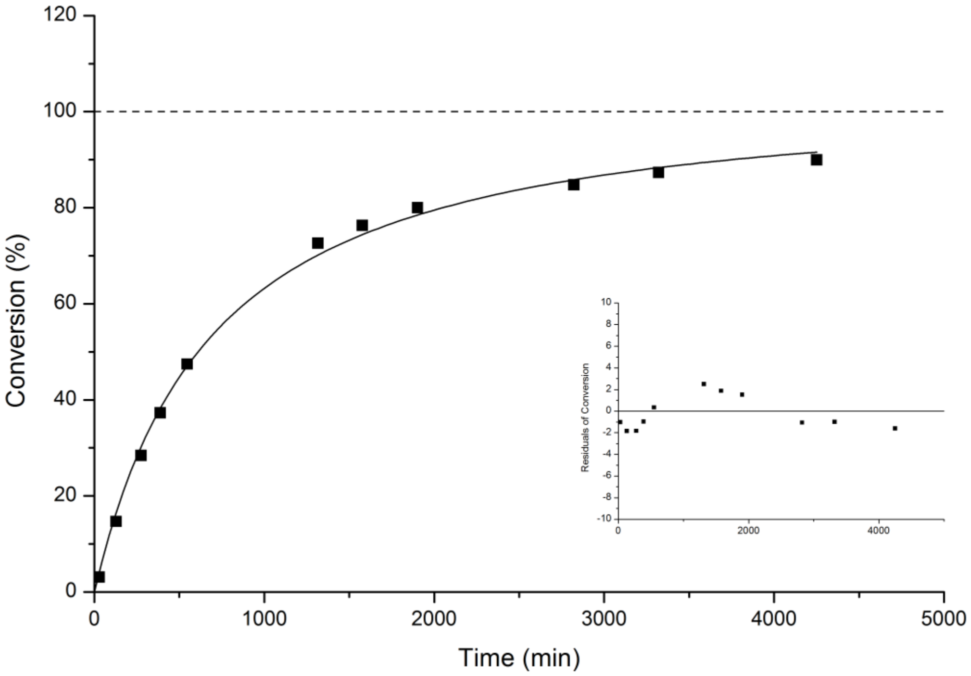


Figure S76 Second conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 3 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9971 k_{eff} = 1.28×10^{-3} $t_{1/2}$ = 599.9

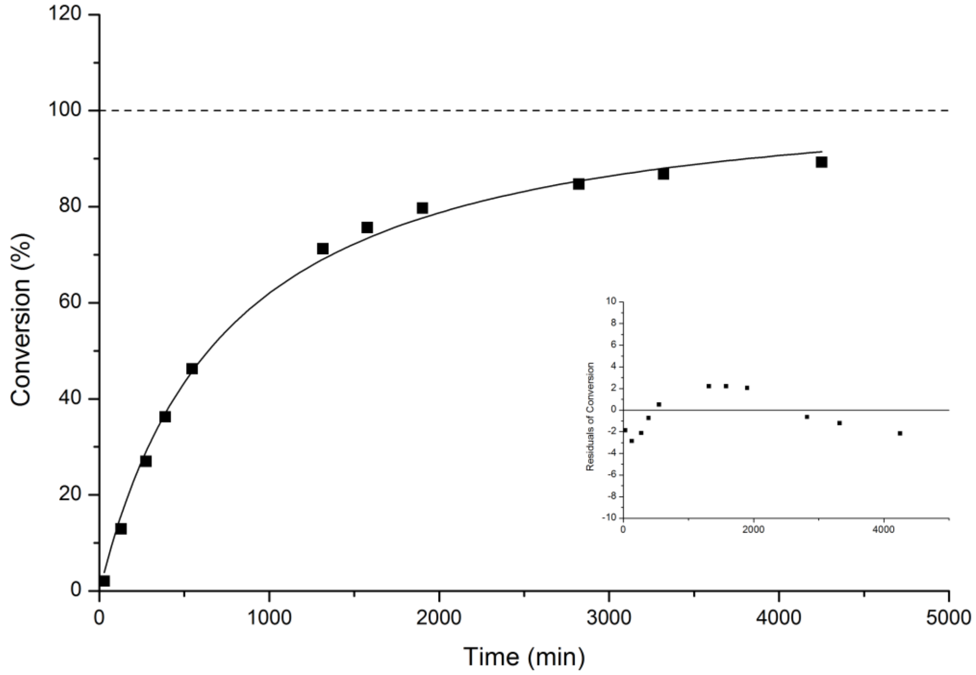


Figure S77 Third conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 3 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9975 k_{eff} = 1.20×10^{-3} $t_{1/2}$ = 639.9

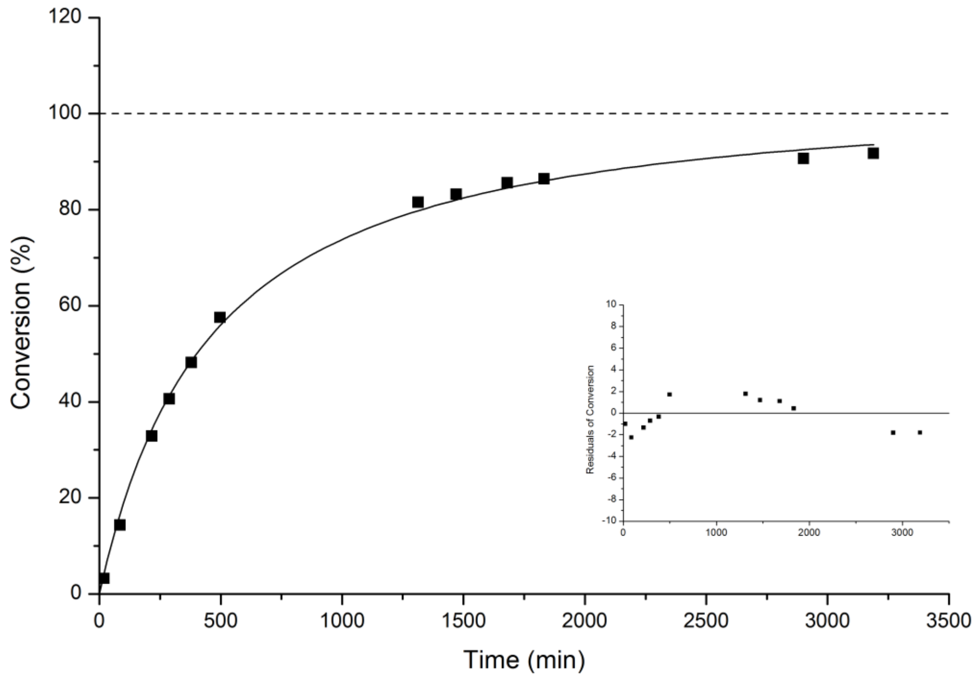


Figure S78 Conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 4 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9975 k_{eff} = 1.92×10^{-3} $t_{1/2}$ = 399.9 min

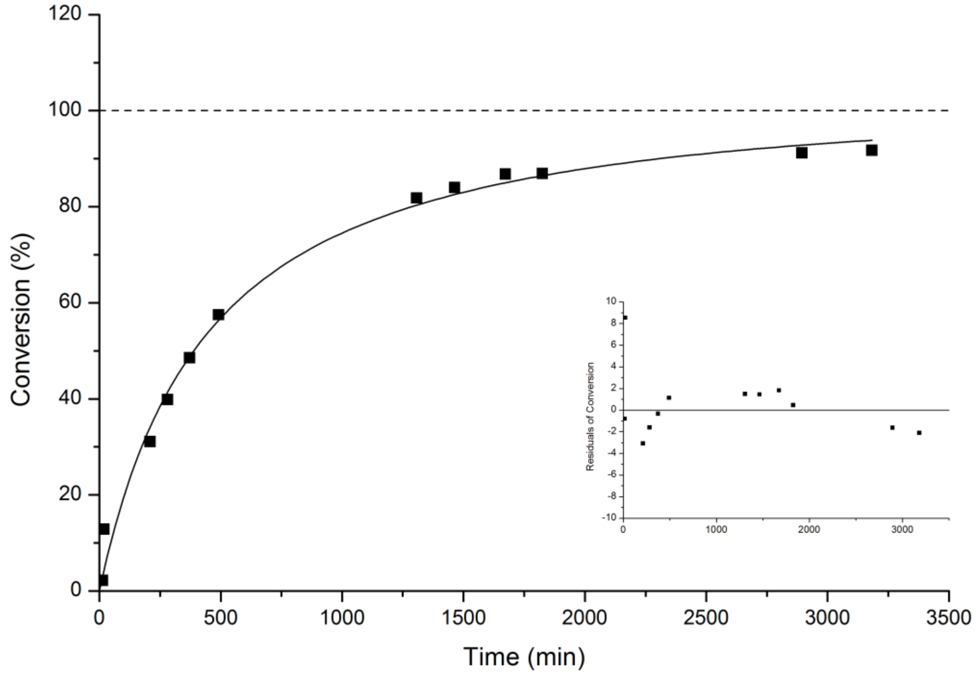


Figure S79 Second conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 4 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9901 k_{eff} = 1.99×10^{-3} $t_{1/2}$ = 385.9 min

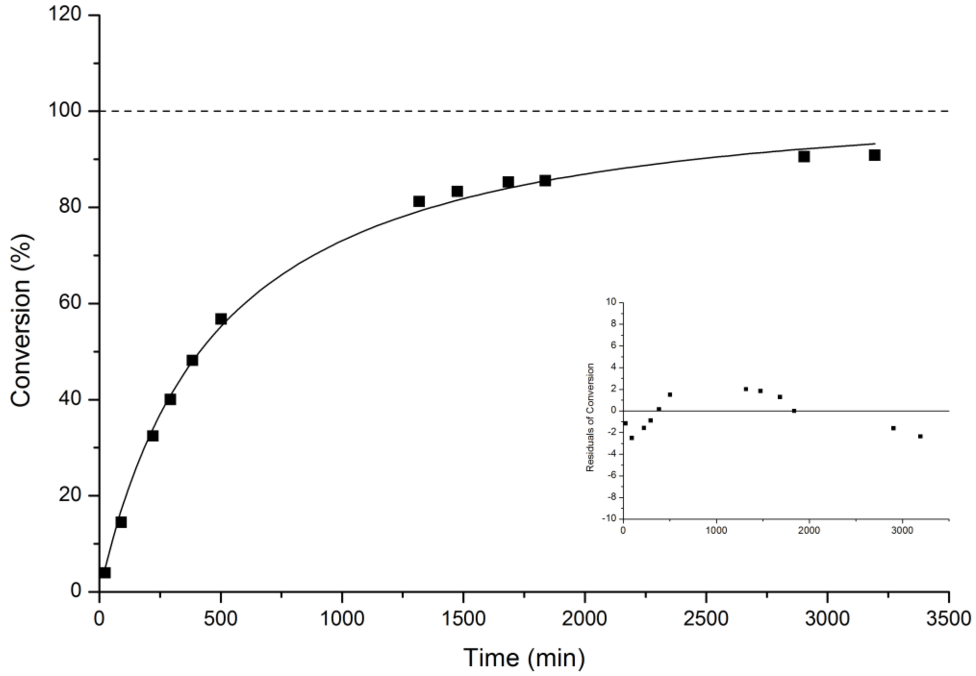


Figure S80 Third conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv TBSCN (**1c**), and 4 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9968 k_{eff} = 1.87×10^{-3} $t_{1/2}$ = 410.6 min

4.1.4 Measurements with MTBSTFA (**1e**)

Due to impurities in the reagent MTBSTFA (**1e**) in the region of the product in the NMR spectra at t=0, determined by a separate measurement in DMF-d_7, the measured conversion is obtained too high (5 % yield enhancement) based on this impurity. Therefore, this amount was removed from the determined yield in order to correct this values. The yields with this reagent where obtained in a rather low area compared to the other reagents. This effect was only observed in DMF-d_7 and was not found in $CDCl_3$.

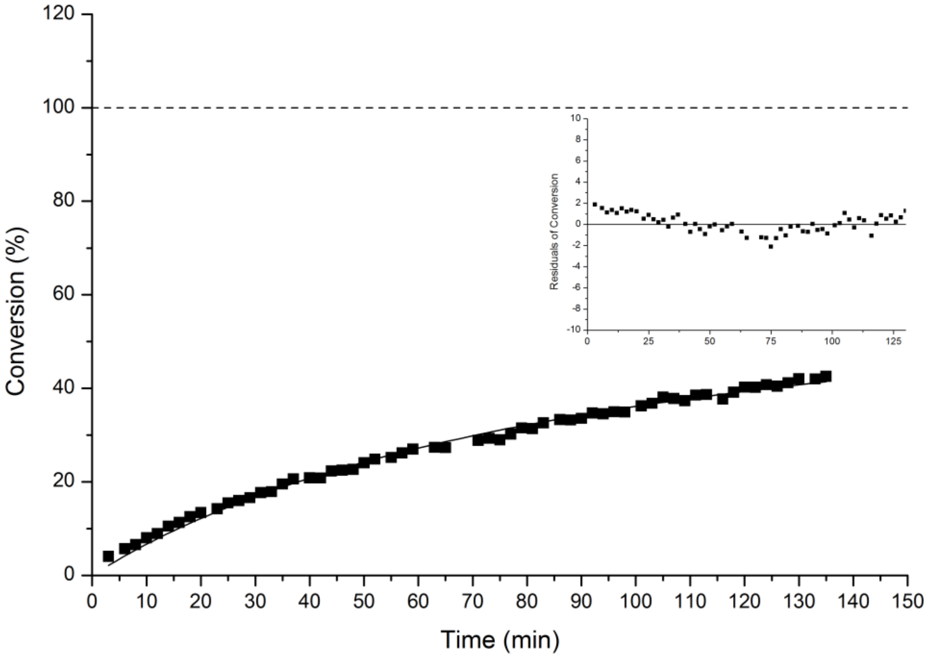


Figure S81 Conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv MTBSTFA (**1e**) and no catalyst in DMF-d_7.

R^2 = 0.9816 k_{eff} = 9.35×10^{-3} $t_{1/2}$ = 82.1 min

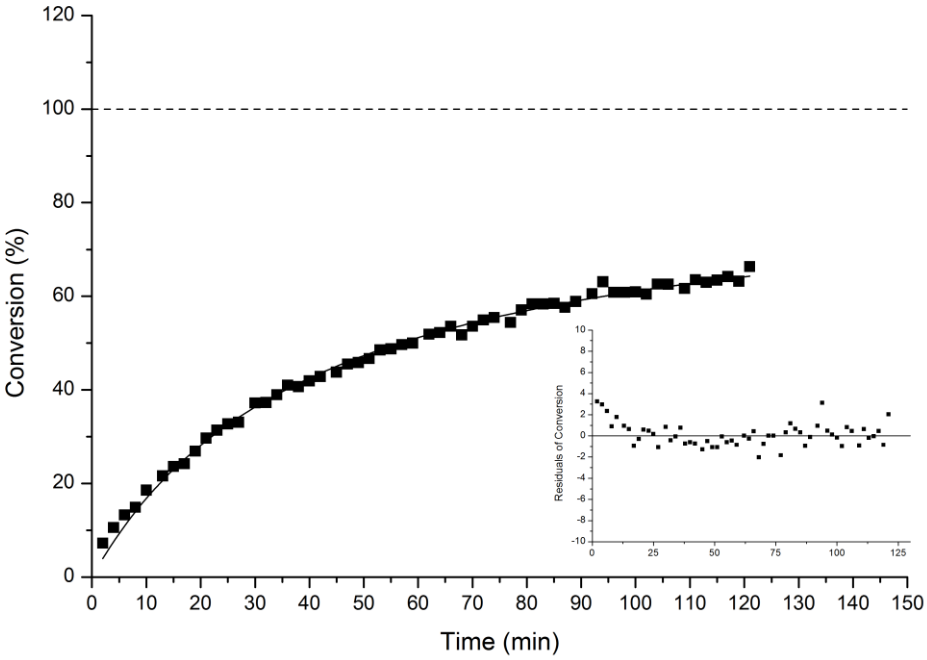


Figure S82 Second conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv MTBSTFA (**1e**), and no catalyst in DMF-d_7.

R^2 = 0.9778 k_{eff} = 2.177×10^{-3} $t_{1/2}$ = 35.3 min

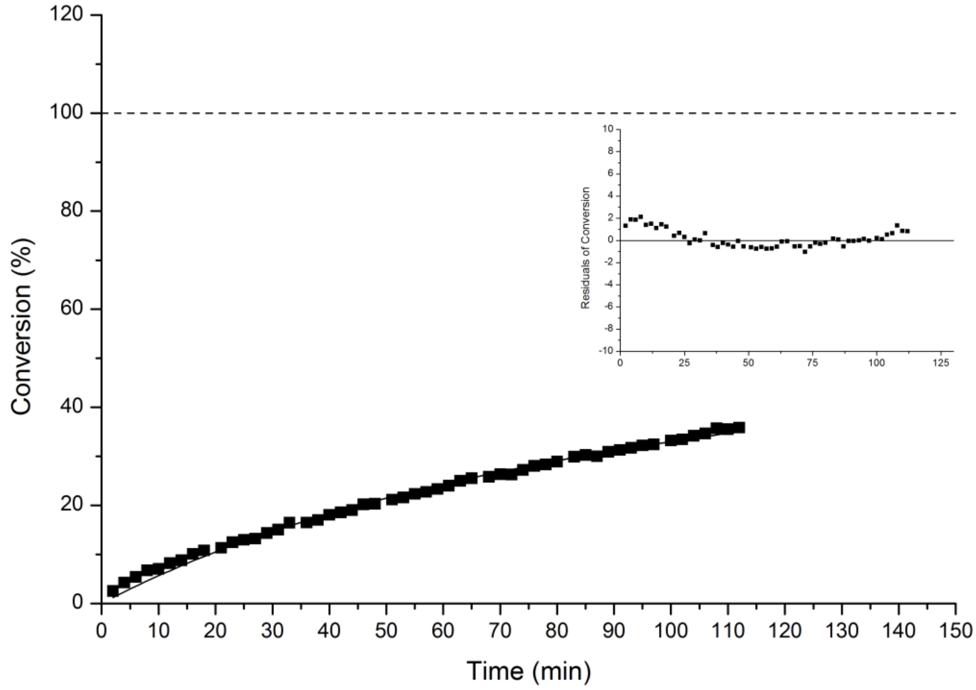


Figure S83 Conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv MTBSTFA (**1e**), and 30 mol% DMAP as catalyst in DMF-d_7.

R^2 = 0.9879 k_{eff} = 7.81×10^{-3} $t_{1/2}$ = 98.3 min

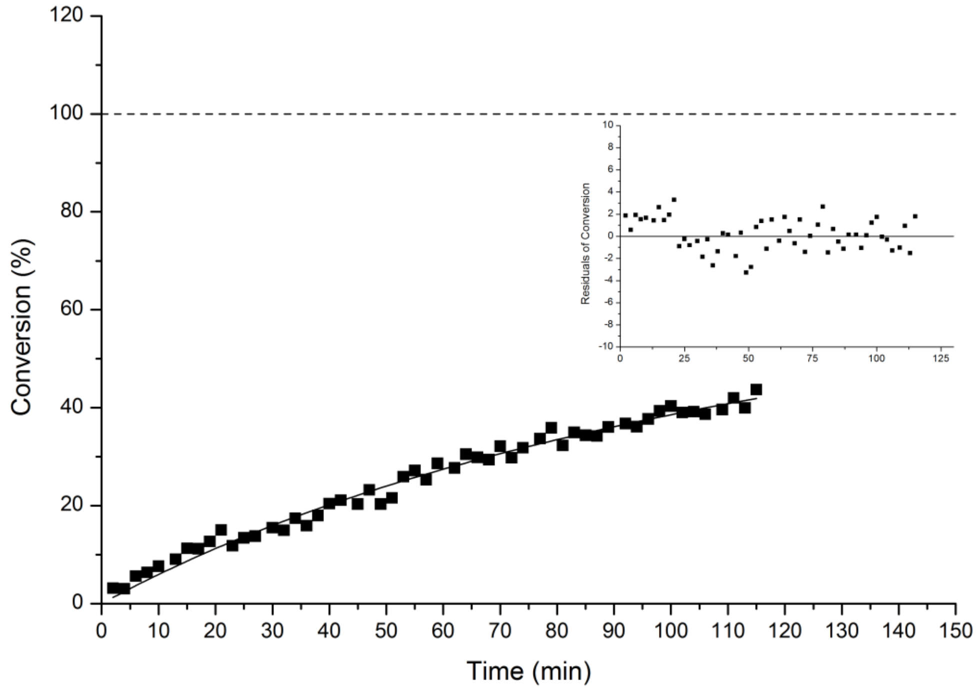


Figure S84 Second conversion vs time plot of **4a** with 1.2 equiv of Et_3N (**3**), 1.2 equiv MTBSTFA (**1e**), and 30 mol% DMAP as catalyst in DMF-d_7.

R^2 = 0.9804 k_{eff} = 1.337×10^{-2} $t_{1/2}$ = 57.4 min

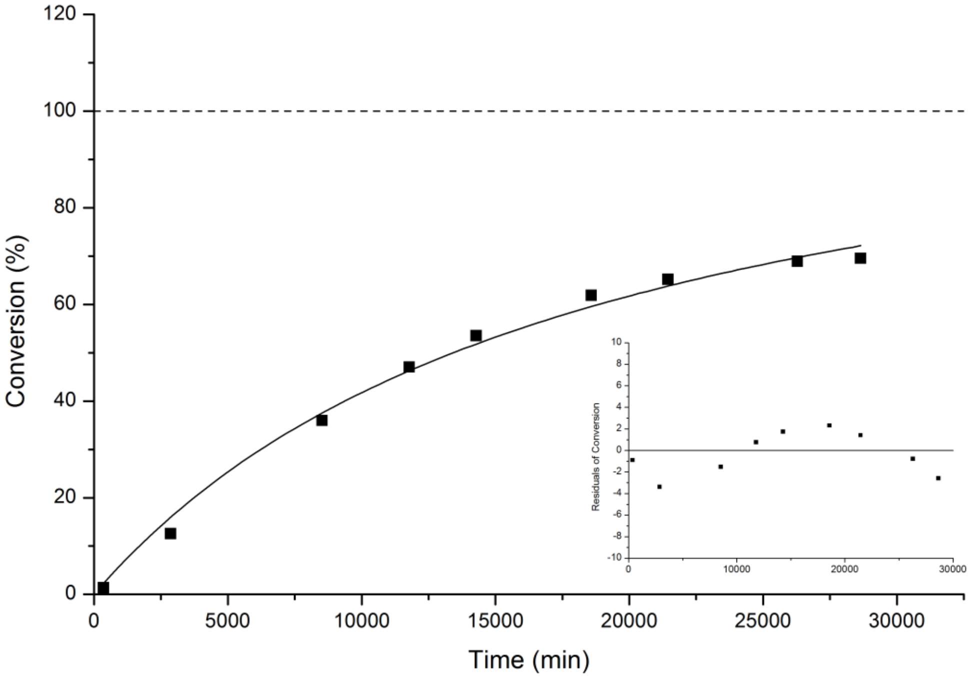


Figure S85 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv MTBSTFA (**1e**), and 30 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9924 k_{eff} = 4.911×10^{-5} $t_{1/2}$ = 15637.6 min

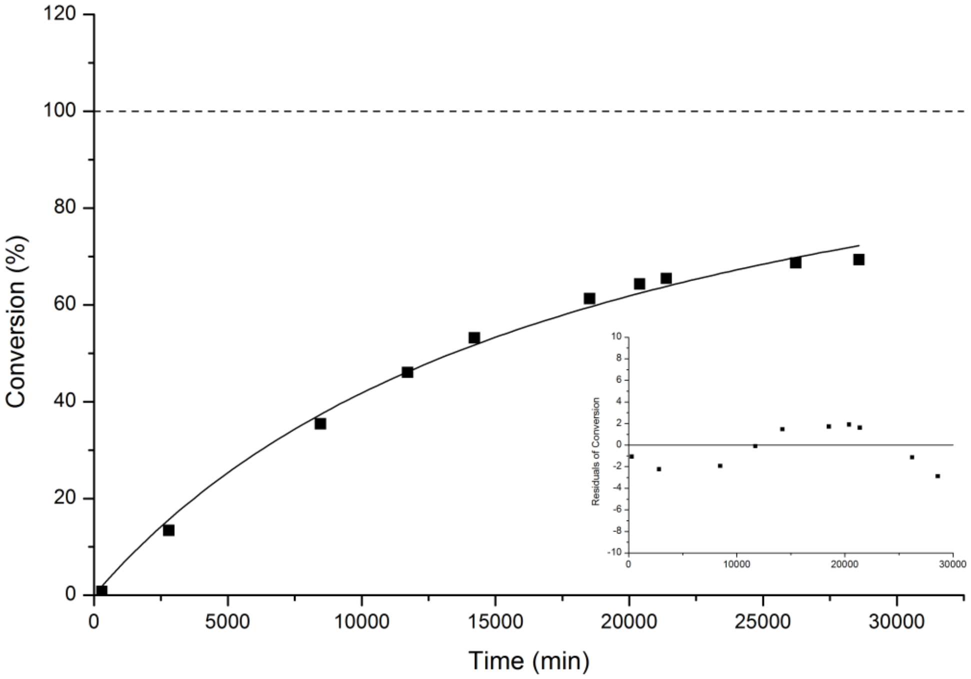


Figure S86 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3b**), 1.2 equiv MTBSTFA (**1e**), and 30 mol% DMAP as catalyst in $CDCl_3$.

R^2 = 0.9934 k_{eff} = 4.883×10^{-5} $t_{1/2}$ = 15727.2 min

*4.1.5 Measurements with TBSImi (**1d**)*

As already mentioned in the manuscript almost no conversion was observed with TBSImi (**1d**). Therefore the rates were estimated by comparing with the conversion for the slowest reagent (MTBSTFA, **1e**).

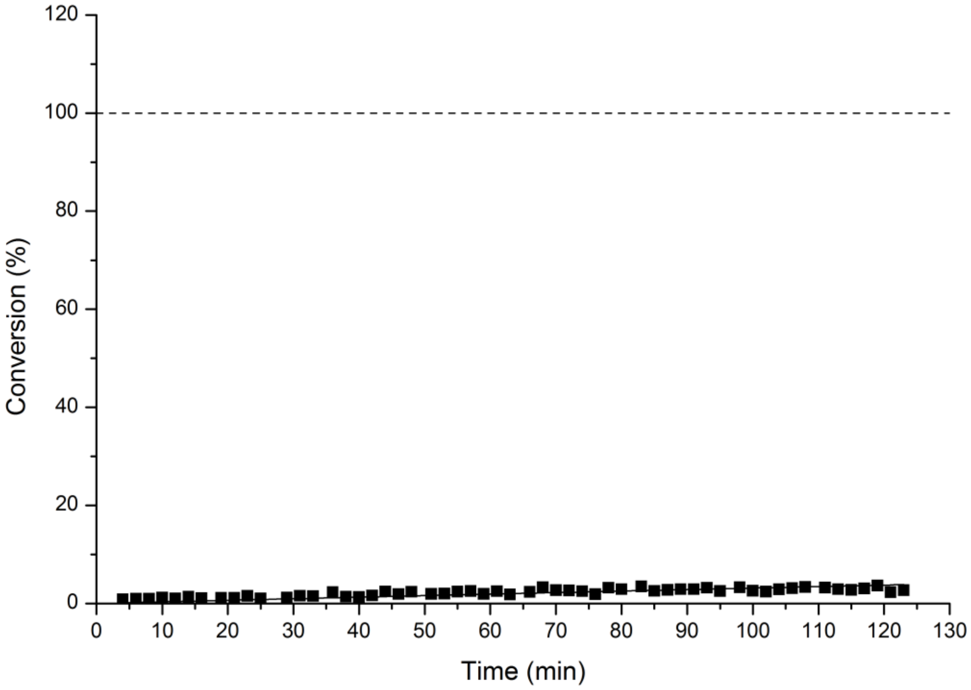


Figure S87 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3**), 1.2 equiv TBSImi (**1d**), and no catalyst in DMF-d_7.

Correlation with **1d** leads to a rate of k_{eff} = 7.54×10^{-4} and $t_{1/2}$ = 1018.4.

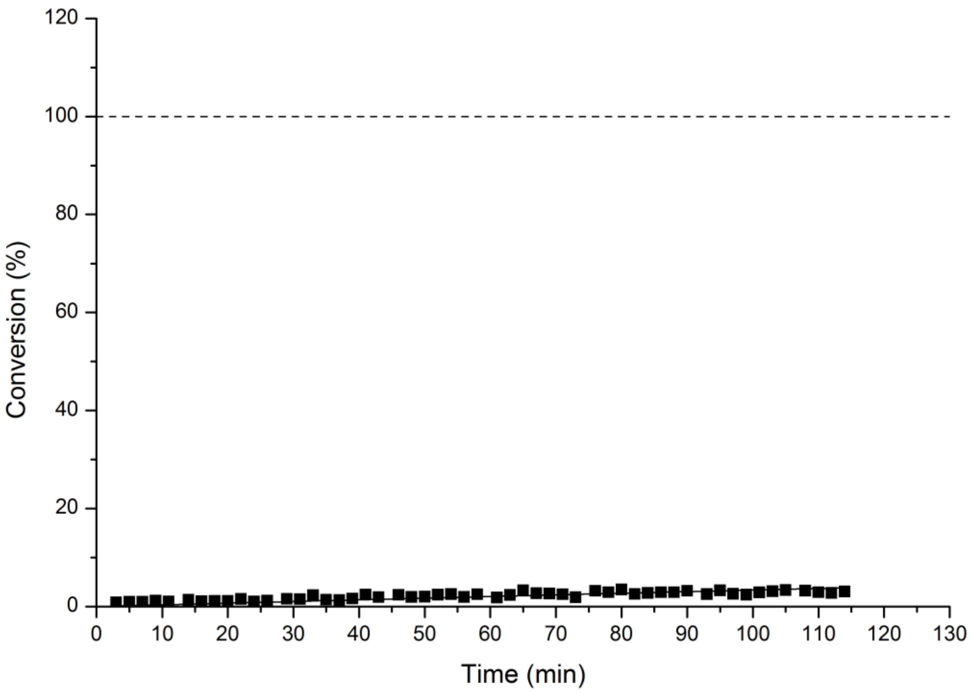


Figure S88 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3**), 1.2 equiv TBSImi (**1d**), and no catalyst in DMF-d_7.

Correlation with **1d** leads to a rate of k_{eff} = 7.79×10^{-4} and $t_{1/2}$ = 985.7.

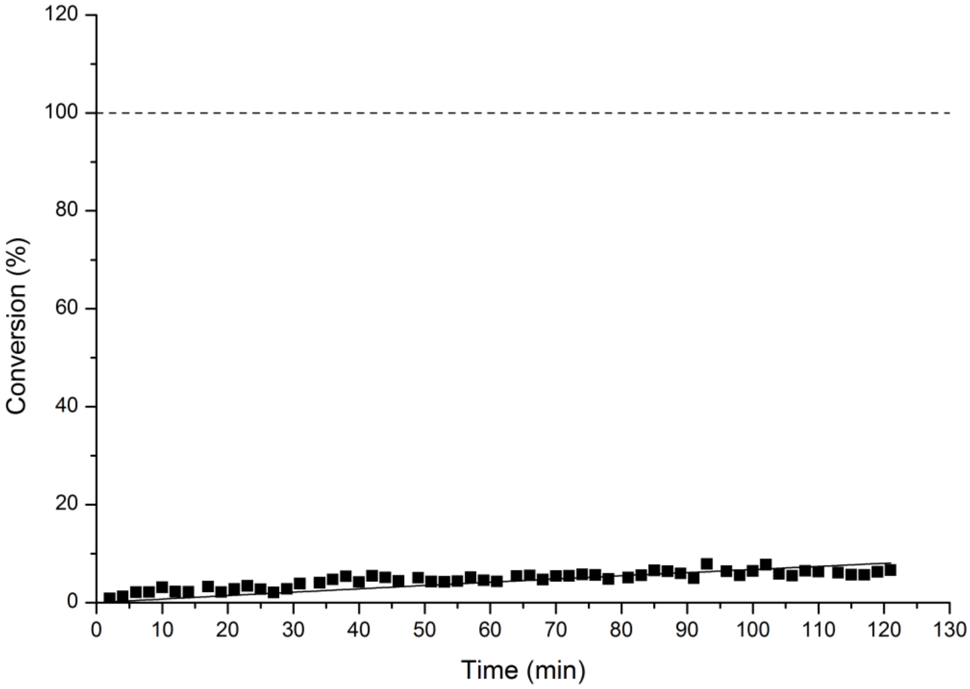


Figure S89 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3**), 1.2 equiv TBSImi (**1d**), and 30 mol% DMAP as catalyst in DMF-d_7.

Correlation with **1d** leads to a rate of $k_{eff} = 9.03 \times 10^{-4}$ and $t_{1/2} = 850.4$.

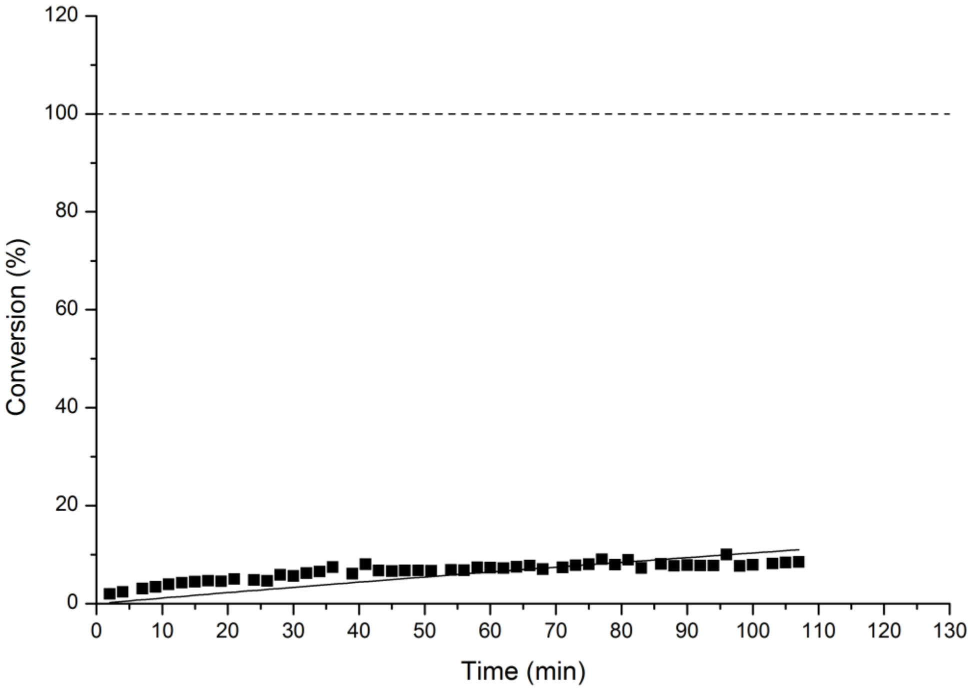


Figure S90 Second conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3**), 1.2 equiv TBSImi (**1d**), and 30 mol% DMAP as catalyst in DMF-d_7.

Correlation with **1d** leads to a rate of $k_{eff} = 1.19 \times 10^{-3}$ and $t_{1/2} = 645.4$.

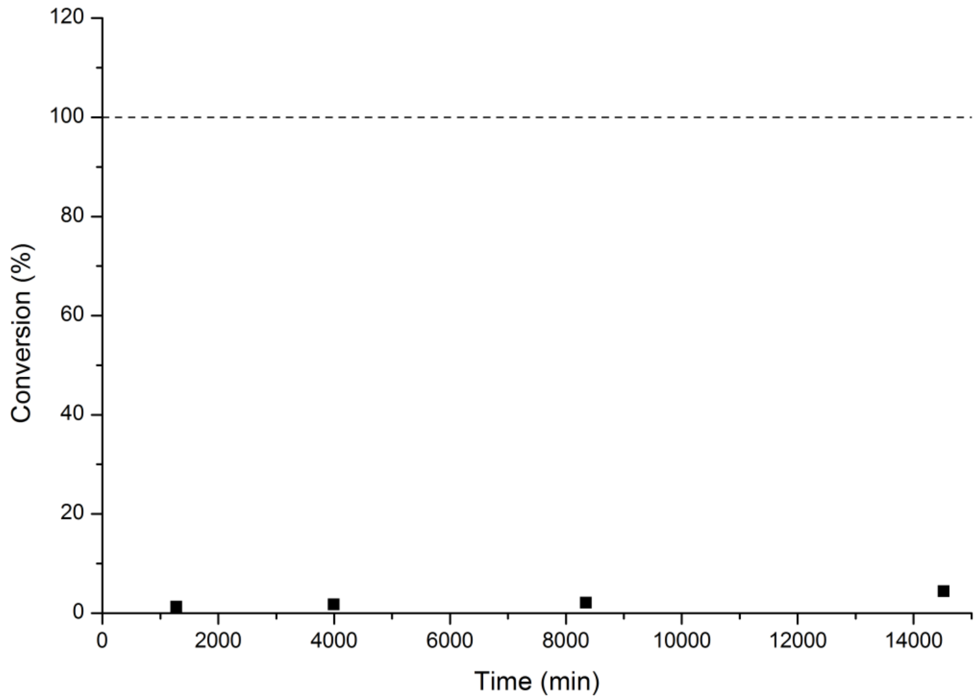


Figure S91 Conversion vs time plot of **4b** with 1.2 equiv of Et_3N (**3**), 1.2 equiv TBSImi (**1d**), and 30 mol% DMAP as catalyst in $CDCl_3$.

Correlation with **1d** leads to a rate of $k_{eff} = 4.1\times10^{-6}$ and $t_{1/2} = 1.84\cdot10^{+6}$.

4.2. Possible effects of autocatalysis

In order to understand the strong deviations of the plots for the measurement in DMF-d_7, an effort was made by using the tool CoPaSi to simulate the reaction rates. It became apparent that in polar solvents autocatalysis of the silyl reagent might be possible, which could explain the deviation of the fit for TBSCN, for instance. Using the reaction equations shown in Scheme **S1** for the example of TBSCN in DMF (Figure S59) leads to strong improvement of the fit.

$$[\text{CAT}] + [\text{TBS-X}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{CAT-TBS}] + [\text{X}^-]$$

$$[\text{CAT-TBS}] + [\text{ROH}] \xrightarrow{k_2} [\text{Product}] + [\text{CAT-H}^+]$$

$$[\text{TBS-X}] + [\text{ROH}] + [\text{X}^-] \xrightarrow{k'_2} [\text{Product}] + [\text{HX}] + [\text{X}^-]$$

$$[\text{CAT-H}^+] + [\text{Base}] \xrightarrow{k_3} [\text{CAT}] + [\text{BaseH}^+]$$

Scheme S1. Equations used to describe the reaction mechanism for the silylation reaction.

For all simulations k_3 was chosen as a fixed value (k_3 = 100) and the starting values were chosen randomly by the program for all remaining rates (k_1, k_{-1}, k_2 and k'_2). All settings and initial concentration for CoPaSi are displayed in Table **S7**.

Table S7 General starting parameters for CoPaSi simulations.

System	**Initial Value**
CAT (DMF)	12.9 M
ROH	0.20 M
TBS-X	0.24 M
Base	0.24 M
Volume	0.6 mL

The simulations for the obtained experimental data show a similar deviation as for the fitting function (**S7**). By adding the autocatalysis option with k'_2 the fit can be significantly improved as shown in Figure S91. Even though we know that an additional variable will improve any fit we still think that this is an option to describe the observed experimental data better.

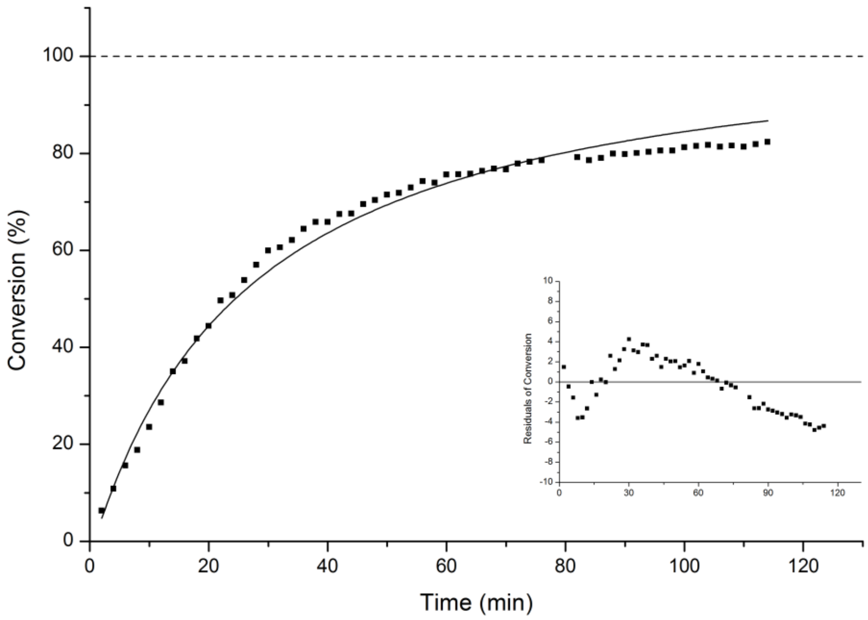


Figure S92 Simulation of TBSCN in DMF-d7 with CoPaSi.

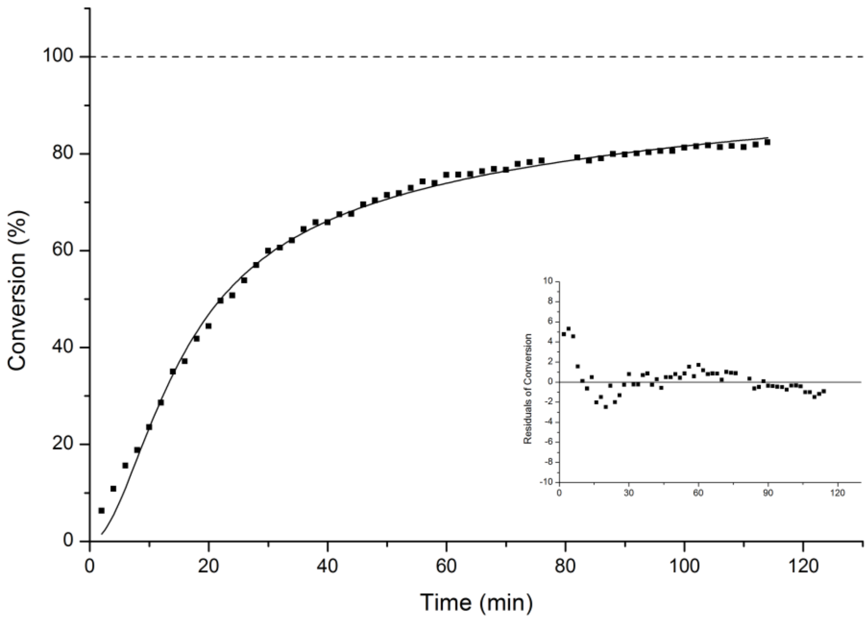


Figure S93 Simulation of TBSCN in DMF-d7 with CoPaSi and an autocatalysis option.

Furthermore, one can obtain the amount of autocatalysis based on the experimental data in this reaction. All other reagents were evaluated under the same conditions and lead to the results in Table S8. It seems that only cyanide has a quite large amount of autocatalysis present during the reaction.

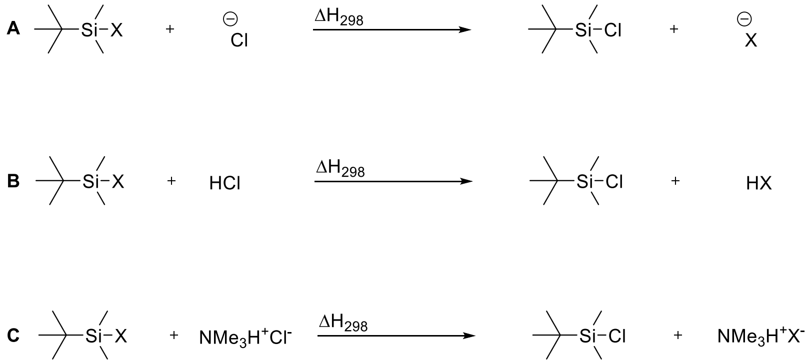
Table S8. Simulated k-values by CoPaSi for the reaction of alcohol **4b** with TBSCN (**1c**).

System	k_1	k_{-1}	k_2	k_2'
CN	9.962E-02	7.344E-02	1.649E-01	n.d.
CN-Auto	1.811E-03	2.266E-01	2.780E-06	5.994

5) Computational Methods

5.1 Methods and data sheets

The energies have been calculated as the reaction enthalpy at 298.15 K and 1 atm pressure for the exchange reaction for the counterion shown in Figure S91. We focused on the most common TBS group as the system of choice.

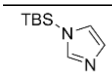
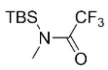
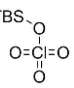
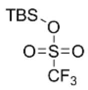


X = OTf, $OClO_3$, $MeNCOCF_3$, N_3, CN, Imi

Figure S94. Counterion transfer reaction show for A) Counterion only, B) Corresponding acid, and C) auxiliary base added.

All geometry optimizations and vibrational frequency calculations have been performed using the MPW1K hybrid functional in combination with the 6-31+G(d) basis set. Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The thermochemical corrections have been combined with single point energies calculated at the MP2(FC)/G3MP2large//MPW1K/6-31+G(d) level to yield enthalpies H_{298} at 298.15 K. In conformationally flexible systems enthalpies have been calculated as Boltzmann-averaged values over all available conformers. All quantum mechanical calculations have been performed with Gaussian 09.[1]

Table S6. Stabilization energies for silylation reagents in various reactions relative to TBSCl (gas phase data).

Reagent		A	B	C	ΔH_{Rxn}
	**1d**	+33.44	−30.83	−9.18	+74.20
TBS–CN	**1c**	+28.75	−51.73	−21.87	+54.35
TBS–N_3	**1f**	+5.47	−7.62	+10.90	+33.89
TBS–Cl	**1a**	0.00	0.00	0.00	0.00
	**1e**	−6.35	−60.61	−26.66	+37.86
	**1g**	−108.17	+20.62	−35.38	−65.32
	**1b**	−136.26	+29.93	−38.98	−54.33

In Table S7 the raw data for the silyl compounds (_sil) with various leavings groups will be shown, as well as, all counterions (_-) and protonated species (_H). The counterion in combination with the auxiliary base will be marked aux_f for frontside. If more than one conformer was obtained the energy was Boltzmann averaged.

Table S9 Data for various silyl compounds with different leaving groups and their anion and protonated adducts (gas phase data).

	MPW1K/6-31+G(d)		MP2(FC)/G3MP2large// MPW1K/6-31+G(d)		
System	**E_{tot}**	**H_{298}**	**E_{tot}**	**H_{298}**	**$\langle H_{298}\rangle$**
Cl					
sil_01	-987.420180	-987.202751	-985.934319	-985.716891	
_-	-460.276187	-460.273826	-459.770535	-459.768174	
_H	-460.802892	-460.792585	-460.302699	-460.292391	
_aux_f	-635.265133	-635.118645	-634.397798	-634.251311	
OTf					
sil_01	-1488.456837	-1488.203145	-1486.496515	-1486.242823	**-1486.242562**
sil_02	-1488.455451	-1488.201786	-1486.495424	-1486.241759	
_-	-961.381927	-961.346825	-960.380846	-960.345744	
_H	-961.840083	-961.790878	-960.855869	-960.806663	
_aux_f	-1136.321386	-1136.136398	-1134.976816	-1134.791828	
OClO3					
sil_01	-1287.805800	-1287.567884	-1286.119487	-1285.881572	**-1285.881346**
sil_02	-1287.803222	-1287.565218	-1286.117697	-1285.879693	
_-	-760.710805	-760.689910	-759.994724	-759.973830	
_H	-761.190301	-761.156741	-760.482554	-760.448993	
_aux_f	-935.673252	-935.503926	-934.598569	-934.429243	
MeNCOCF3					
sil_01	-1072.662903	-1072.367468	-1071.029448	-1070.734012	**-1070.733885**
sil_02	-1072.658548	-1072.362809	-1071.026837	-1070.731098	
_-_01	-545.522667	-545.446119	-544.864137	-544.787589	**-544.787589**
_-_02	-545.505921	-545.429693	-544.848974	-544.772746	
_H_01	-546.086672	-545.995938	-545.423208	-545.332474	
_H_02	-546.079856	-545.988150	-545.416836	-545.325129	**-545.3324712**
_aux_f	-720.527281	-720.302403	-719.503338	-719.278459	
N3					
sil_01	-691.314247	-691.082779	-690.133221	-689.901753	**-689.9018287**
sil_02	-691.314104	-691.082487	-690.133512	-689.901894	
_-	-164.160981	-164.145990	-163.966021	-163.951030	
_H	-164.712883	-164.686394	-164.506718	-164.480230	
_aux_f	-339.160846	-339.000931	-338.592011	-338.432096	
Imi					
sil_01	-752.743078	-752.460834	-751.379385	-751.097142	**-751.0971401**
sil_02	-752.743077	-752.460830	-751.379386	-751.097138	
_-	-225.582617	-225.518414	-225.199891	-225.135689	
_H	-226.153471	-226.074914	-225.762941	-225.684384	
_aux_f	-400.599879	-400.387971	-399.846963	-399.635055	
CN					
sil_01	-619.977791	-619.752387	-618.857927	-618.632524	
_-	-92.817228	-92.808869	-92.681217	-92.672858	
_H	-93.384897	-93.364434	-93.248191	-93.227728	
_aux_f	-267.830402	-267.677139	-267.328534	-267.175272	
4b					**-538.3516667**
_01	-539.599653	-539.372802	-538.579167	-538.352316	
_02	-539.598979	-539.372055	-538.578495	-538.351571	
_03	-539.598168	-539.371234	-538.577429	-538.350495	
_04	-539.597667	-539.370947	-538.577029	-538.350309	
_05	-539.596649	-539.369859	-538.575661	-538.348871	
_06	-539.595512	-539.368823	-538.576732	-538.350044	
_07	-539.595179	-539.368411	-538.575238	-538.348470	
5b					**-1063.779233**

	MPW1K/6-31+G(d)		MP2(FC)/G3MP2large// MPW1K/6-31+G(d)		
System	**E_{tot}**	**H_{298}**	**E_{tot}**	**H_{298}**	**$\langle H_{298}\rangle$**
_01	-1066.202182	-1065.771607	-1064.209301	-1063.778726	
_02	-1066.201693	-1065.770970	-1064.210703	-1063.779979	
_03	-1066.201319	-1065.770848	-1064.208978	-1063.778507	
_04	-1066.201216	-1065.770565	-1064.209273	-1063.778622	
_05	-1066.200263	-1065.769619	-1064.208587	-1063.777943	
_06	-1066.199730	-1065.769097	-1064.208500	-1063.777867	
_07	-1066.197458	-1065.766864	-1064.205506	-1063.774912	
Me_3N					
_01	-174.433383	-174.302577	-174.067320	-173.936515	

Table S10 Counterion transfer (in kJ/mol) for various groups relative to chloride (gas phase data).

	(MPW1K/6-31+G(d))		(MP2(FC)/G3MP2large// MPW1K/6-31+G(d))	
System	**E_{tot}**	**H_{298}**	**E_{tot}**	**H_{298}**
OTf	-181.38	-190.62	-126.33	-136.26
OClO3	-128.64	-133.77	-102.45	-108.17
MeNCOCF3	-9.86	-19.89	+4.01	-6.35
Chloride	***0.00***	***0.00***	***0.00***	***0.00***
N3	+24.35	+20.65	+8.97	+5.47
CN	+43.50	+38.31	+33.94	+28.75
Imi	+43.24	+35.43	+41.25	+33.44

Table S11 Counterion transfer of protonated adducts (in kJ/mol) for various groups relative to chloride (gas phase data).

	(MPW1K/6-31+G(d))		(MP2(FC)/G3MP2large// MPW1K/6-31+G(d))	
System	**E_{tot}**	**H_{298}**	**E_{tot}**	**H_{298}**
MeNCOCF3	-107.79	-101.44	-66.64	-60.61
CN	-64.04	-58.32	-57.46	-51.73
Imi	-72.68	-63.66	-39.85	-30.83
N3	-41.80	-36.18	-13.44	-7.62
Chloride	***0.00***	***0.00***	***0.00***	***0.00***
OClO3	-4.70	+2.57	+13.95	+20.62
OTf	-1.40	+5.52	+23.70	+29.93

Table S12 Counterion transfer of protonated adducts with auxiliary base (frontside) for various groups relative to chloride (gas phase data).

	(MPW1K/6-31+G(d))		(MP2(FC)/G3MP2large// MPW1K/6-31+G(d))	
System	**E_{tot}**	**H_{298}**	**E_{tot}**	**H_{298}**
OTf	-51.45	-45.58	-44.17	-38.98
OClO3	-59.07	-52.90	-40.96	-35.38
MeNCOCF3	-51.00	-49.99	-27.34	-26.66
CN	-20.11	-23.26	-18.72	-21.87
Imi	-31.11	-29.52	-10.76	-9.18
Chloride	***0.00***	***0.00***	***0.00***	***0.00***
N3	-4.32	-5.93	+12.31	+10.90

Table S13 Data for *N*-heterocycles and their TBS adducts. Gas phase calculation with additional SMD values in $CHCl_3$

	MP2(FC)/G3MP2large //MPW1K/6-31+G(d)	ΔH_{298} (MP2(FC)/G3MP2large//MPW1K/6-31+G(d)) + ΔG_{solv} (SMD/MPW1K/6-31+G(d))		
System	**H_{298}**	**ΔG_{solv}**	**Δ H_{298} (Solv)**	**<H298> (Solv)**
Cl				
_sil_01	-985.716891	-0.008920	-985.725811	-985.725811
_-	-459.768174	-0.086198	-459.854372	
_H	-460.292391	-0.005357	-460.297748	
_aux_f	-634.251311	-0.029104	-634.280414	
OTf				
_sil_01	-1486.242823	-0.008960	-1486.251783	-1486.251526
_sil_02	-1486.241759	-0.009027	-1486.250786	
_-	-960.345744	-0.061979	-960.407723	
_H	-960.806663	-0.006630	-960.813293	
_aux_f	-1134.791828	-0.025090	-1134.816918	
OClO3				
_sil_01	-1285.881572	-0.008845	-1285.890417	-1285.890204
_sil_02	-1285.879693	-0.008707	-1285.888400	
_-	-759.973830	-0.067365	-760.041195	
_H	-760.448993	-0.006532	-760.455525	
_aux_f	-934.429243	-0.028361	-934.457603	
MeNCOCF3				
_sil_01	-1070.734012	-0.010640	-1070.744652	-1070.744429
_sil_02	-1070.731098	-0.011651	-1070.742749	
_-_01	-544.787589	-0.069708	-544.857297	-544.8572966
_-_02	-544.772746	-0.072107	-544.844852	
_H_01	-545.332474	-0.009110	-545.341584	-545.3415801
_H_02	-545.325129	-0.009329	-545.334459	
_aux_f	-719.278459	-0.010000	-719.288459	
N3				
_sil_01	-689.901753	-0.004158	-689.905911	-689.905873
_sil_02	-689.901894	-0.003938	-689.905832	
_-	-163.951030	-0.075854	-164.026884	
_H	-164.480230	-0.000498	-164.480728	
_aux_f	-338.432096	-0.004678	-338.436774	
Imi				
_sil_01	-751.097142	-0.018229	-751.115371	-751.1153694
_sil_02	-751.097138	-0.018229	-751.115368	
anion	-225.135689	-0.083254	-225.218943	
H	-225.684384	-0.016972	-225.701356	
_aux_f	-399.635055	-0.020082	-399.655137	
CN				
_sil_01	-618.632524	-0.008615	-618.641138	
_-	-92.672858	-0.084393	-92.757251	
_H	-93.227728	-0.004940	-93.232668	
_aux_f	-267.175272	-0.007549	-267.182821	
4b				-538.3704566
_01	-538.352316	-0.018952	-538.371267	
_02	-538.351571	-0.018269	-538.369840	
_03	-538.350495	-0.018890	-538.369385	
_04	-538.350309	-0.018851	-538.369160	
_05	-538.348871	-0.019947	-538.368818	
_06	-538.350044	-0.019521	-538.369565	
_07	-538.348470	-0.020320	-538.368790	

	MP2(FC)/G3MP2large //MPW1K/6-31+G(d)	ΔH_{298} (MP2(FC)/G3MP2large//MPW1K/6-31+G(d)) + ΔG_{solv} (SMD/MPW1K/6-31+G(d))		
System	**H_{298}**	**ΔG_{solv}**	**Δ H_{298} (Solv)**	**<H298> (Solv)**
5b				-1063.798615
_01	-1063.778726	-0.020040	-1063.798766	
_02	-1063.779979	-0.019165	-1063.799144	
_03	-1063.778507	-0.019898	-1063.798405	
_04	-1063.778622	-0.019782	-1063.798404	
_05	-1063.777943	-0.019520	-1063.797463	
_06	-1063.777867	-0.019199	-1063.797066	
_07	-1063.774912	-0.020758	-1063.795670	
Me_3N				
_01	-173.936515	-0.006626	-173.943141	

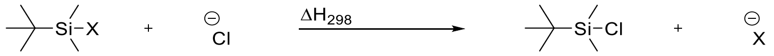


Table S14 Counterion transfer (in kJ/mol) for various groups relative to chloride (gas and solution phase data).

	MP2(FC)/G3MP2large// MPW1K/6-31+G(d)	ΔH_{298} (MP2(FC)/G3MP2large//MPW1K/6-31+G(d)) + ΔG_{solv} (SMD/MPW1K/6-31+G(d))
System	**ΔH_{298} (Gas)**	**ΔH_{298} (Sol)**
OTf	-136.26	-72.56
$OClO_3$	-108.17	-58.89
$MeNCOCF_3$	-6.35	+41.20
Chloride	***0.00***	***0.00***
N_3	+5.47	+19.83
CN	+28.75	+32.68
Imi	+33.44	+65.61

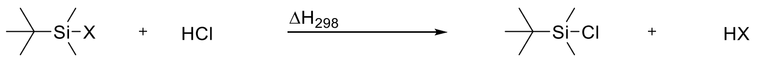


Table S15 Counterion transfer of protonated adducts (in kJ/mol) for various groups relative to chloride (gas and solution phase data).

	MP2(FC)/G3MP2large// MPW1K/6-31+G(d)	ΔH_{298} (MP2(FC)/G3MP2large//MPW1K/6-31+G(d)) + ΔG_{solv} (SMD/MPW1K/6-31+G(d))
System	**ΔH_{298} (Gas)**	**ΔH_{298} (Sol)**
MeNCOCF3	-60.61	-66.20
CN	-51.73	-51.44
Imi	-30.83	-36.89
N_3	-7.62	-7.66
Chloride	***0.00***	***0.00***
$OClO_3$	+20.62	+17.37
OTf	+29.93	+26.70

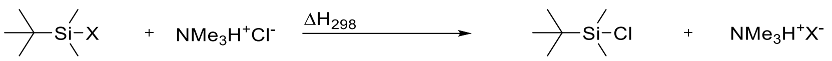


Table S16 Counterion transfer of protonated adducts with auxiliary base (frontside) for various groups relative to chloride (gas and solution phase data).

	MP2(FC)/G3MP2large// MPW1K/6-31+G(d)	ΔH_{298} (MP2(FC)/G3MP2large//MPW1K/6-31+G(d)) + ΔG_{solv} (SMD/MPW1K/6-31+G(d))
System	**ΔH_{298} (Gas)**	**ΔH_{298} (Sol)**
OTf	-38.98	-28.33
$OClO_3$	-35.38	-33.59
$MeNCOCF_3$	-26.66	+27.76
CN	-21.87	+33.92
Imi	-9.18	+38.95
Chloride	***0.00***	***0.00***
N_3	+10.90	+62.23

In addition we calculated the effect of the leaving group for the reaction enthalpy for alcohol **4b**. The data in Table S14 show that the reaction of TBSCl (**1a**) is slightly exothermic under these conditions. However, the addition of SMD solvation energies leads to an almost thermoneutral reaction for TBSCl (**1a**). This data shows that a reaction with any catalyst or auxiliary base is not possible for the chloride. In Table S15 trimethylamine was added as auxiliary base and changed the driving force of the reaction in the matter that for all reagents the reaction should be exothermic. For TBSCl (**1a**) this reaction yielded in -66.88 kJ mol^{-1} for the gas phase and -104.02 kJ mol^{-1} with SMD correction. The data is consistent for the other reagents in terms that faster reagents have a better stabilization than TBSCl (**1a**). For instance TBSOTf (**1b**) led to -132.35 kJ mol^{-1}, while TBSCN (**1c**) was found at -70.10 kJ mol^{-1} which in accordance to the experimental data. However, these calculation show a good number of -65.07 kJ mol^{-1} for TBS-Imi (**1d**), which was not reacting in the experiments at all. Even though one needs to admit that the number cannot directly be correlated to the experimental data, the general trend and the order of appearance is good.

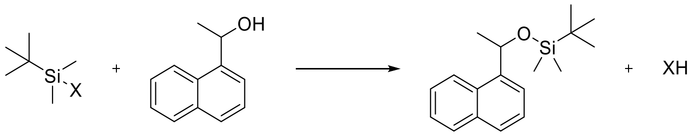


Table S17 Reaction enthalpies for the silylation of alcohol **4b** with various silyl reagents. (gas and solution phase data).

	(MPW1K/6-31+G(d))		(MP2(FC)/G3MP2large// MPW1K/6-31+G(d))		SMD
System	**E_{tot}**	**H_{298}**	**E_{tot}**	**H_{298} (Gas)**	**H_{298}(Sol)**
MeNCOCF3	-69.04	-71.61	-62.73	**-68.66**	-66.45
CN	-25.29	-28.49	-53.55	**-59.78**	-51.69
Imi	-33.93	-33.83	-35.94	**-38.88**	-37.14
N3	-3.05	-6.35	-9.53	**-15.67**	-7.91
Cl	+38.75	+29.83	+3.91	**-8.05**	-0.25
OClO3	+34.05	+32.39	+17.85	**+12.57**	+17.12
OTf	+37.35	+35.34	+27.60	**+21.88**	+26.45

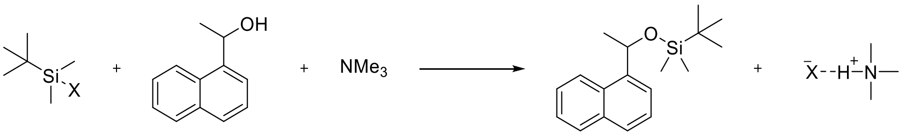


Table S18 Reaction enthalpies for the silylation of alcohol **4b** with various silyl reagents and auxiliary base trimethylamine (gas and solution phase data).

	(MPW1K/6-31+G(d))		(MP2(FC)/G3MP2large// MPW1K/6-31+G(d))		SMD
System	**E_{tot}**	**H_{298}**	**E_{tot}**	**H_{298} (Gas)**	**H_{298}(Sol)**
OTf	-88.47	-77.40	-113.20	**-105.85**	-132.35
$OClO_3$	-96.09	-84.72	-109.99	**-102.26**	-137.62
$MeNCOCF_3$	-88.02	-81.82	-96.36	**-93.54**	-76.26
CN	-57.12	-55.08	-87.74	**-88.74**	-70.10
Imi	-68.12	-61.34	-79.79	**-76.05**	-65.07
Cl	-37.02	-31.83	-69.03	**-66.88**	-104.02
N_3	-41.34	-37.75	-56.72	**-55.97**	-41.79

Table S19 Reaction enthalpies for the silylation of alcohol **4b** with various silyl reagents (Table S18, Table S19) and log(k_{eff}) (solution phase data).

	(MP2(FC)/G3MP2large// MPW1K/6-31+G(d)) + SMD		log (k_{eff})
System	No Me_3N	With Me_3N	
OTf	+26.45	-132.35	
$OClO_3$	+17.12	-137.62	n.d.
$MeNCOCF_3$	-66.45	-76.26	
CN	-51.69	-70.10	
Imi	-37.14	-65.07	
Cl	-0.25	-104.02	
N_3	-7.91	-41.79	n.d.

The influence of the auxiliary base in form of trimethylamine is depicted in the following two figures (S95, S96), where the negative driving forces through a free proton is compensated with Me_3N. This effect can be observed for silyl triflate (**1b**) very strongly.

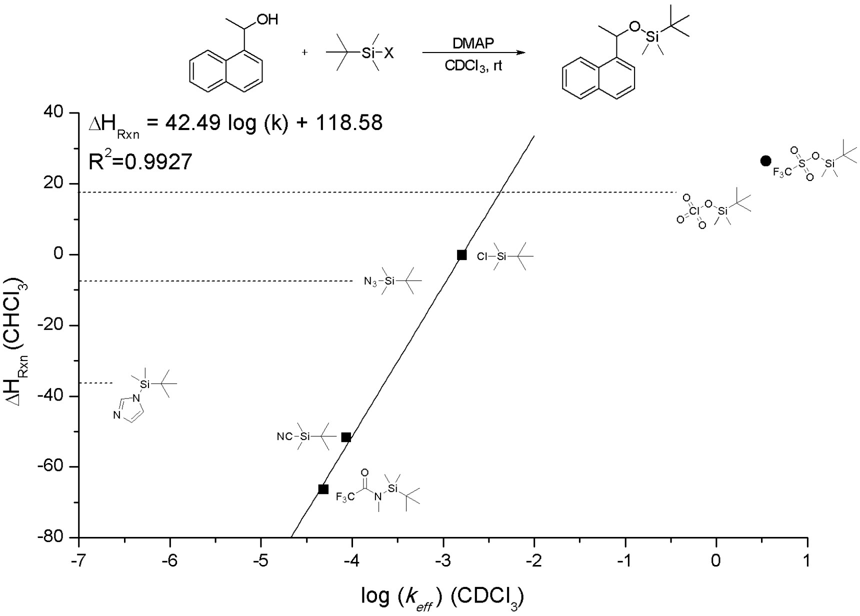


Figure S95. Correlation of silyl compounds with ΔH_{RXN} ($CDCl_3$) without any auxiliary base.

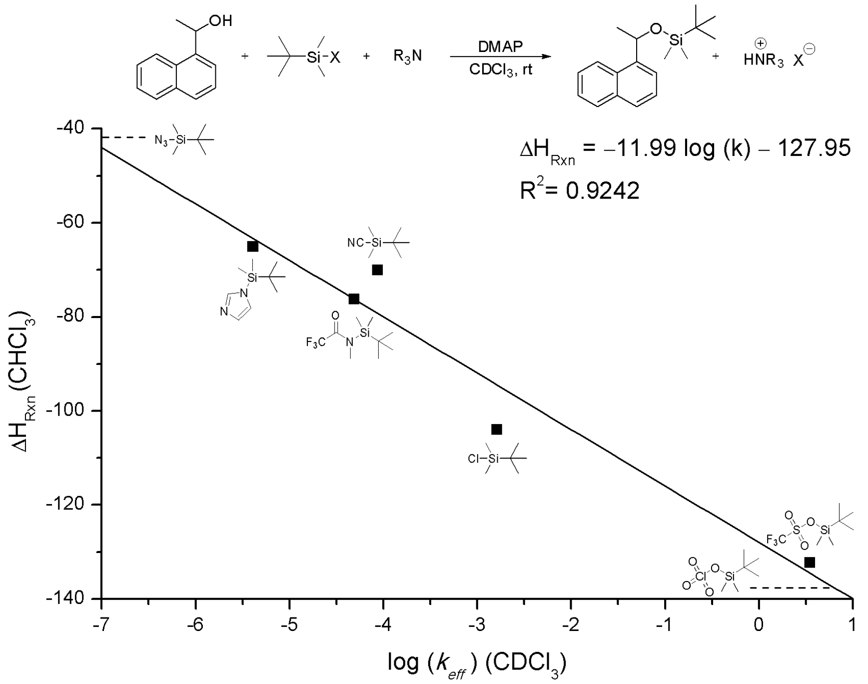


Figure S96. Correlation between reaction rate and ΔH_{RXN} with an auxiliary base.

Finally, we display the obtained NPA- and Mulliken-charges for the silyl groups, which do not help to find a better correlation between calculations and experiment (Table S20).

Table S20. Charge of silicon and TBS-groups (Best conformer).

	Si-X	NPA-Charges		Mulliken Charges	
TBS-X		**Si**	**TBS-Group**	**Si**	**TBS-Group**
Cl (**1a**)	2.0891	1.76864	0.41479	0.74936	0.17595
CN (**1c**)	1.8740	1.72526	0.47288	1.35259	0.68226
MTBSTFA (**1d**)	1.8099	2.00038	0.63221	0.89480	0.37368
IMI (**1e**)	1.7869	2.00954	0.65118	0.92245	0.43839
N_3 (**1f**)	1.7719	1.94482	0.58885	1.16686	0.41839
$OClO_3$ (**1g**)	1.7621	2.05146	0.69920	1.15282	0.47807
OTf (**1b**)	1.7502	2.06406	0.70114	1.04969	0.44573

5.2. Structures of all Systems

(Optimized at MPW1K/6-31+G(d) level)

Chloride (Cl)

_sil_01

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_-_01

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_H_01

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_aux_f

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_aux_b

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Trifalte (OTf)
_sil_01

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_-_01

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_H_01

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\RMSD=4.218e-09\PG=C01 [X(C1H1F3O3S1)]\\@

_aux_f

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53232\F,0,-2.577994,0.722329,1.161538\F,0,-1.269306,1.727735,-0.213399
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_aux_b

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.673411\H,0,3.666143,1.679925,0.154199\H,0,2.102916,1.188872,0.886909\
N,0,3.160967,-0.350218,-0.049455\O,0,0.134086,0.533431,1.049062\S,0,-0
.861246,0.867309,0.014178\O,0,-1.76357,1.9471,0.33633\O,0,-0.279442,0.
873117,-1.32942\C,0,-1.913724,-0.640435,0.000832\F,0,-2.84821,-0.56919
1,-0.931363\F,0,-1.164371,-1.71848,-0.252447\F,0,-2.502887,-0.827857,1
.171291\\Version=AM64L-G09RevC.01\State=1-A\HF=-1132.4087999\MP2=-1134
.9510373\RMSD=8.549e-09\PG=C01 [X(C4H10F3N1O3S1)]\\@

Perchlorate(OClO3)

_sil_01

1\1\GINC-STEAK\SP\RMP2-FC\GTMP2large\C6H15Cl1O4Si1\ROOT\21-Jun-2014\0\
\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,
1\C,0,-2.165183,-0.511479,-0.033192\C,0,-2.048909,-1.586758,1.046068\H
,0,-2.914252,-2.252535,1.000218\H,0,-1.156661,-2.19785,0.915857\H,0,-2
.022053,-1.160889,2.049244\C,0,-2.261812,-1.17655,-1.406159\H,0,-3.134
997,-1.832833,-1.437971\H,0,-2.376804,-0.447167,-2.208289\H,0,-1.38496
6,-1.784118,-1.626358\C,0,-3.42385,0.324458,0.213862\H,0,-4.305743,-0.
319839,0.18428\H,0,-3.414385,0.809249,1.191112\H,0,-3.564065,1.095287,
-0.544993\C,0,-0.330525,1.347225,1.72091\H,0,0.565061,1.966879,1.71295
6\H,0,-1.163148,1.979034,2.033284\H,0,-0.193208,0.571953,2.472008\C,0,
-0.658447,1.94182,-1.294804\H,0,-1.473875,2.651164,-1.149481\H,0,0.276
473,2.499259,-1.270919\H,0,-0.76352,1.50722,-2.287765\Si,0,-0.673757,0
.640672,0.034495\O,0,0.606814,-0.505511,-0.354627\Cl,0,2.152681,-0.275
966,-0.045235\O,0,2.409699,1.110125,-0.340987\O,0,2.81087,-1.187068,-0
.927267\O,0,2.322055,-0.591931,1.344479\\Version=AM64L-G09RevC.01\Stat
e=1-A\HF=-1283.7620504\MP2=-1286.1194875\RMSD=6.950e-09\PG=C01 [X(C6H1
5Cl1O4Si1)]\\@

_sil_02

1\1\GINC-ANGIE\SP\RMP2-FC\GTMP2large\C6H15Cl1O4Si1\PASCAL\21-Jun-2014\
0\\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\
0,1\C,0,1.749084,-0.781102,0.015227\C,0,1.40934,2.026247,-1.330643\H,0

,2.418549,2.372047,-1.10602\H,0,1.419576,1.565971,-2.317011\H,0,0.7617
51,2.900949,-1.378905\Si,0,0.803644,0.851682,-0.018521\O,0,-0.81698,0.
611348,-0.671434\Cl,0,-2.026361,-0.206701,-0.038983\O,0,-1.905425,-1.5
38356,-0.561114\O,0,-3.183785,0.488051,-0.507546\O,0,-1.848583,-0.1437
51,1.387926\C,0,0.660518,1.688323,1.637006\H,0,0.004799,2.555916,1.568
496\H,0,0.264643,1.032221,2.407881\H,0,1.641558,2.041956,1.957106\C,0,
3.213978,-0.429715,0.302327\H,0,3.808683,-1.345419,0.337906\H,0,3.6488
74,0.205544,-0.47007\H,0,3.340383,0.070061,1.264063\C,0,1.656073,-1.48
1229,-1.3405\H,0,2.041973,-0.862069,-2.150754\H,0,2.251179,-2.39758,-1
.323474\H,0,0.632659,-1.76024,-1.585983\C,0,1.246386,-1.721815,1.11041
7\H,0,1.29374,-1.266285,2.099378\H,0,0.222658,-2.047763,0.938792\H,0,1
.87202,-2.617544,1.134942\\Version=AM64L-G09RevC.01\State=1-A\HF=-1283
.7592625\MP2=-1286.1176966\RMSD=7.310e-09\PG=C01 [X(C6H15Cl1O4Si1)]\\@

_-_01

1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\Cl1O4(1-)\LOCAL\26-Jun-2014\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Titl
e Card Required\\-1,1\O,0,0.0874214694,1.1962381348,-0.372831854\Cl,0,
0.0973292627,2.4876501082,0.323994492\O,0,-0.2895610668,2.2902891354,1
.7255268298\O,0,-0.8535902271,3.3994373827,-0.3220120595\O,0,1.4450484
458,3.0648404648,0.2654054965\\Version=AM64L-G09RevC.01\HF=-758.805698
5\MP2=-759.9947243\RMSD=6.209e-09\PG=C03V [C3(Cl1O1),3SGV(O1)]\\@

_H_01

1\1\GINC-LIEBIG\SP\RMP2-FC\GTMP2large\Cl1H1O4\PASCAL\19-Jun-2014\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Titl
e Card Required\\0,1\Cl,0,0.1046197867,2.5762029366,0.3796302197\O,0,-
0.2732171309,2.2532844207,1.7229033237\O,0,-0.849367143,3.3389998594,-
0.3490546187\O,0,1.4592656336,3.0268866142,0.2645711556\O,0,0.06012332
43,1.1506170754,-0.4294623376\H,0,0.6937247634,0.5635212855,0.01181228
82\\Version=AM64L-G09RevC.01\State=1-A'\HF=-759.2888662\MP2=-760.48255
36\RMSD=6.511e-09\PG=CS [SG(Cl1H1O2),X(O2)]\\@

_aux_f

1\1\GINC-ANGIE\SP\RMP2-FC\GTMP2large\C3H10Cl1N1O4\PASCAL\11-Jul-2014\0
\\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0
,1\C,0,2.044524,1.255316,0.701895\H,0,1.300686,1.29239,1.489228\H,0,3.
050765,1.284565,1.112022\H,0,1.892171,2.091388,0.027256\C,0,1.983666,-
1.179631,0.825257\H,0,2.988262,-1.217861,1.238564\H,0,1.240935,-1.0991
14,1.610476\H,0,1.787276,-2.070706,0.238047\O,0,-0.552906,-0.010642,-1
.138734\Cl,0,-1.578063,0.000419,-0.038358\O,0,-0.812662,0.142398,1.212
972\O,0,-2.292026,-1.256984,-0.054513\O,0,-2.458404,1.129353,-0.23002\
C,0,2.754463,-0.08061,-1.213523\H,0,3.788566,-0.088605,-0.879556\H,0,2
.534548,-0.989292,-1.763992\H,0,2.577699,0.776784,-1.854415\N,0,1.8607
26,0.00073,-0.048502\H,0,0.873136,0.004756,-0.425442\\Version=AM64L-G0
9RevC.01\State=1-A\HF=-932.664148\MP2=-934.5985687\RMSD=3.808e-09\PG=C
01 [X(C3H10Cl1N1O4)]\\@

_aux_b

1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\C3H10Cl1N1O4\LOCAL\11-Jul-2014\0\
\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,
1\C,0,-1.976089,-0.645184,-1.265284\H,0,-2.288653,-1.68393,-1.249839\H
,0,-2.44176,-0.12238,-2.094646\H,0,-0.895045,-0.570415,-1.33667\C,0,-1
.976305,-0.773394,1.191401\H,0,-2.447175,-1.750633,1.155621\H,0,-0.895
844,-0.878513,1.158872\H,0,-2.283336,-0.238236,2.083689\O,0,0.981855,0
.83166,1.096723\Cl,0,1.508046,-0.000101,0.000003\O,0,0.976352,-1.36383
6,0.171494\O,0,2.951946,-0.003509,-0.001014\O,0,0.979478,0.534931,-1.2
67186\C,0,-1.973719,1.41881,0.073846\H,0,-2.440953,1.876528,0.939989\H
,0,-0.892923,1.441848,0.177038\H,0,-2.283399,1.924587,-0.834503\H,0,-3
.428944,0.002148,0.000073\N,0,-2.414158,0.000765,0.000056\\Version=AM6
4L-G09RevC.01\State=1-A\HF=-932.6467063\MP2=-934.5781965\RMSD=3.467e-0
9\PG=C01 [X(C3H10Cl1N1O4)]\\@

MeNCOCF3

_sil_01

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1\1\GINC-Q1\SP\RMP2-FC\GTMP2large\C9H18F3N1O1Si1\ROOT\21-Nov-2014\0\\#
 p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\
 N,0,-0.440511,0.603486,-0.146653\C,0,-0.841444,1.65309,-1.075396\H,0,0
 .009944,1.922836,-1.691359\H,0,-1.625483,1.318514,-1.744756\H,0,-1.183
 089,2.544557,-0.552279\C,0,2.285754,-0.70605,-0.484151\C,0,2.241315,-0
 .382485,-1.977227\H,0,2.840487,-1.106832,-2.535363\H,0,1.226306,-0.431
 751,-2.373408\H,0,2.646087,0.605683,-2.199631\C,0,1.780112,-2.131811,-
 0.271637\H,0,2.429664,-2.834326,-0.801497\H,0,1.774258,-2.415085,0.779
 832\H,0,0.767971,-2.268273,-0.647128\C,0,1.912333,2.296369,0.192984\H,
 0,1.238975,3.045841,0.610225\H,0,2.866737,2.405629,0.709232\H,0,2.0817
 05,2.545544,-0.853396\C,0,1.263437,0.26407,2.332318\H,0,1.050942,-0.76
 9302,2.590452\H,0,2.236007,0.53734,2.744484\H,0,0.514424,0.886457,2.82
 2639\C,0,-1.295291,-0.319492,0.328132\Si,0,1.258387,0.559598,0.488008\
 O,0,-0.977957,-1.231326,1.058662\C,0,-2.785918,-0.22678,-0.071041\F,0,
 -3.502941,-1.087398,0.6173\F,0,-3.284501,0.991552,0.154054\F,0,-2.9558
 4,-0.500702,-1.369037\C,0,3.733343,-0.615735,0.00516\H,0,4.356304,-1.3
 27323,-0.54306\H,0,4.163681,0.37454,-0.149874\H,0,3.822602,-0.860334,1
 .064351\\Version=AM64L-G09RevC.01\State=1-A\HF=-1068.1988012\MP2=-1071
 .0294477\RMSD=3.066e-09\PG=C01 [X(C9H18F3N1O1Si1)]\\@
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_sil_02

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1\1\GINC-TOFU\SP\RMP2-FC\GTMP2large\C9H18F3N1O1Si1\ROOT\21-Jun-2014\0\
 \#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,
 1\N,0,0.414653,1.072328,0.026584\C,0,0.084174,2.466279,0.335412\H,0,-0
 .98201,2.625633,0.233469\H,0,0.381662,2.704172,1.353124\H,0,0.611734,3
 .143429,-0.333545\C,0,-2.131861,-0.455286,0.672631\C,0,-2.572845,0.704
 615,1.564758\H,0,-3.29184,0.347598,2.306848\H,0,-1.737535,1.141644,2.1
 11195\H,0,-3.065041,1.498801,1.001757\C,0,-1.488224,-1.527017,1.549891
 \H,0,-2.20552,-1.870781,2.299966\H,0,-1.176503,-2.399243,0.976017\H,0,
 -0.616121,-1.149855,2.081934\C,0,-1.813204,1.334951,-1.850222\H,0,-1.0
 86487,1.898507,-2.436237\H,0,-2.426636,0.772469,-2.554928\H,0,-2.46742
 7,2.051151,-1.356067\C,0,-0.400226,-1.289879,-1.786985\H,0,0.048908,-2
 .130459,-1.26888\H,0,-1.292119,-1.653657,-2.300214\H,0,0.294148,-0.953
 544,-2.555027\C,0,1.718259,0.829673,0.289566\Si,0,-0.948055,0.126687,-
 0.697652\O,0,2.496181,1.663896,0.6922\C,0,2.286233,-0.582827,0.069465\
 F,0,3.439859,-0.714454,0.689539\F,0,1.472563,-1.53506,0.532681\F,0,2.4
 9235,-0.816245,-1.227616\C,0,-3.370831,-1.048239,-0.005474\H,0,-4.0811
 54,-1.386251,0.753404\H,0,-3.889519,-0.319949,-0.63003\H,0,-3.129585,-
 1.912532,-0.625039\\Version=AM64L-G09RevC.01\State=1-A\HF=-1068.193599
 2\MP2=-1071.0268371\RMSD=2.069e-09\PG=C01 [X(C9H18F3N1O1Si1)]\\@
```

_-_01

```
1\1\GINC-Q1\SP\RMP2-FC\GTMP2large\C3H3F3N1O1(1-)\ROOT\21-Nov-2014\0\\#
 p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\-1,1
 \N,0,-1.361959,-0.722481,0.000104\C,0,-2.741718,-0.325716,-0.000075\H,
 0,-3.376901,-1.214629,-0.000458\H,0,-3.005734,0.281764,0.875239\H,0,-3
 .005407,0.282361,-0.875073\C,0,-0.551169,0.28826,0.000078\O,0,-0.75212
 5,1.520925,0.000045\C,0,0.933952,-0.104778,0.000059\F,0,1.575173,0.396
 532,-1.07415\F,0,1.57532,0.396738,1.073906\F,0,1.193102,-1.416172,0.00
 0115\\Version=AM64L-G09RevC.01\State=1-A\HF=-543.1971966\MP2=-544.8641
 372\RMSD=7.057e-09\PG=C01 [X(C3H3F3N1O1)]\\@
```

_-_02

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1\1\GINC-Q1\SP\RMP2-FC\GTMP2large\C3H3F3N1O1(1-)\ROOT\21-Nov-2014\0\\#
 p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\-1,1
 \N,0,-1.619031,0.669351,0.007464\C,0,-2.139515,-0.665319,-0.003796\H,0
 ,-3.141263,-0.649616,0.435538\H,0,-2.259217,-1.063468,-1.02088\H,0,-1.
 568652,-1.413341,0.560091\C,0,-0.348217,0.926376,-0.006596\O,0,0.21139
 8,2.036265,-0.009232\C,0,0.676017,-0.257704,-0.002123\F,0,1.937536,0.1
 34042,-0.179221\F,0,0.669747,-0.946243,1.161987\F,0,0.446212,-1.173274
 ,-0.969217\\Version=AM64L-G09RevC.01\State=1-A\HF=-543.1791177\MP2=-54
 4.8489738\RMSD=6.641e-09\PG=C01 [X(C3H3F3N1O1)]\\@
```

_H_01

1\1\GINC-Q1\SP\RMP2-FC\GTMP2large\C3H4F3N1O1\ROOT\21-Nov-2014\0\\#p MP
2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Title C
ard Required\\0,1\C,0,-2.1189079766,-0.7353318049,0.1238053513\H,0,-2.
9522340662,-0.7566775402,0.8188722976\H,0,-2.4521914144,-1.0922884431,
-0.8496611934\H,0,-1.3342826,-1.3941454484,0.4819506433\C,0,-0.3462058
426,0.8473588942,-0.3356293478\O,0,0.4797320108,0.0153972639,-0.619123
3524\C,0,0.0471853998,2.3330296747,-0.3761198486\F,0,0.9779813436,2.58
6925664,0.5307691844\F,0,0.5226941492,2.6529557992,-1.5673564113\F,0,-
0.9932000605,3.1402325152,-0.1241359248\N,0,-1.6060895617,0.6094114474
,0.0430863979\H,0,-2.2192687815,1.385096518,0.2076779039\\Version=AM64
L-G09RevC.01\State=1-A\HF=-543.7715037\MP2=-545.4232078\RMSD=9.069e-09
\PG=C01 [X(C3H4F3N1O1)]\\@

_H_02

1\1\GINC-ANGIE\SP\RMP2-FC\GTMP2large\C3H4F3N1O1\PASCAL\18-Jun-2014\0\\
#p MP2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Ti
tle Card Required\\0,1\C,0,0.2335211141,-0.8918672972,-2.1844722588\H,
0,-0.280638806,-1.125664727,-3.1117061711\H,0,1.3025762102,-0.82772575
74,-2.3803067098\H,0,0.0493335946,-1.7045718313,-1.4912849534\C,0,-0.3
049743134,0.8325931703,-0.4246447188\O,0,-0.7090696151,1.9254992825,-0
.1139517299\C,0,0.2283678752,-0.1101646449,0.6722609085\F,0,0.25324116
32,0.496210368,1.8361511432\F,0,-0.5422383866,-1.1956020857,0.78378435
41\F,0,1.4671365396,-0.5247339632,0.3919129403\N,0,-0.2988868608,0.353
157989,-1.6782520114\H,0,-0.6324546049,1.024748487,-2.3479060428\\Vers
ion=AM64L-G09RevC.01\State=1-A\HF=-543.7645837\MP2=-545.4168355\RMSD=8
.251e-09\PG=C01 [X(C3H4F3N1O1)]\\@

_aux_f

1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\C6H13F3N2O1\LOCAL\26-Jun-2014\0\\
#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1
\N,0,0.094314,0.705627,-0.031601\C,0,0.50861,2.088331,0.006614\H,0,-0.
306549,2.688798,-0.386755\H,0,0.726765,2.422838,1.019926\H,0,1.380126,
2.265306,-0.615331\C,0,0.853417,-0.389941,-0.00227\O,0,0.431133,-1.526
456,0.007552\C,0,2.381536,-0.179441,0.001962\F,0,3.014897,-1.323216,0.
139274\F,0,2.791417,0.383585,-1.139691\F,0,2.760912,0.623417,1.001263\
H,0,-0.916803,0.510266,-0.016979\C,0,-2.833406,-0.86067,-1.183876\H,0,
-3.795935,-1.386689,-1.23944\H,0,-2.729315,-0.244397,-2.075385\H,0,-2.
032042,-1.595887,-1.177872\C,0,-3.741054,1.006366,-0.002779\H,0,-4.761
073,0.598243,0.010656\H,0,-3.619435,1.642787,0.872219\H,0,-3.635467,1.
623774,-0.893333\C,0,-2.816252,-0.838647,1.198817\H,0,-2.014052,-1.572
975,1.19531\H,0,-2.701054,-0.205678,2.077241\H,0,-3.777356,-1.3643,1.2
77343\N,0,-2.735602,-0.031411,-0.000746\\Version=AM64L-G09RevC.01\Stat
e=1-A\HF=-717.1009332\MP2=-719.5033379\RMSD=3.414e-09\PG=C01 [X(C6H13F
3N2O1)]\\@

_aux_b

1\1\GINC-ANGIE\SP\RMP2-FC\GTMP2large\C6H13F3N2O1\PASCAL\26-Jun-2014\0\
\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,
1\N,0,0.340993,1.218351,0.026299\C,0,1.305946,2.286806,0.003352\H,0,0.
830584,3.171304,-0.422488\H,0,1.634812,2.557429,1.010271\H,0,2.200268,
2.089857,-0.590657\C,0,0.67003,-0.028916,0.036399\O,0,-0.135596,-0.995
708,0.058481\C,0,2.156302,-0.462279,-0.000244\F,0,2.312852,-1.764338,0
.190074\F,0,2.721939,-0.173972,-1.184717\F,0,2.890853,0.153257,0.93854
\C,0,-2.802586,-0.805862,-1.227571\H,0,-3.272476,-1.784772,-1.239539\H
,0,-3.091611,-0.239252,-2.106942\H,0,-1.718932,-0.90439,-1.139033\C,0,
-2.769601,1.324357,-0.013536\H,0,-1.667083,1.31449,0.010251\H,0,-3.129
721,1.816378,-0.91242\C,0,-2.861396,-0.794201,1.216277\H,0,-1.774184,-
0.887015,1.183831\H,0,-3.198173,-0.222491,2.075145\H,0,-3.326086,-1.77
5647,1.21192\N,0,-3.266279,-0.075795,-0.019496\H,0,-3.16871,1.822556,0
.865262\H,0,-4.279884,-0.044629,-0.044203\\Version=AM64L-G09RevC.01\St
ate=1-A\HF=-717.0363719\MP2=-719.4470663\RMSD=2.958e-09\PG=C01 [X(C6H1
3F3N2O1)]\\@

Azide (N3)

_sil_01

1\1\GINC-LIEBIG\SP\RMP2-FC\GTMP2large\C6H15N3Si1\PASCAL\25-Jun-2014\0\
\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,
1\N,0,2.529316,-0.743796,-0.00194\N,0,3.655346,-0.720287,0.000263\N,0,
1.324941,-0.857628,-0.003601\C,0,0.458974,1.522729,-1.530322\H,0,0.351
736,0.938668,-2.443462\H,0,-0.240977,2.357512,-1.580802\H,0,1.464629,1
.945239,-1.525169\C,0,-1.515733,-0.374514,-0.000041\Si,0,0.166694,0.48
3277,0.000202\C,0,0.461661,1.516659,1.534309\H,0,-0.236976,2.352343,1.
588129\H,0,0.354024,0.929591,2.445474\H,0,1.467943,1.937691,1.530131\C
,0,-1.651623,-1.247448,-1.247015\H,0,-0.873514,-2.008929,-1.292099\H,0
,-2.617485,-1.759675,-1.241112\H,0,-1.603099,-0.661086,-2.165228\C,0,-
2.622902,0.680333,0.003281\H,0,-3.601989,0.19453,0.003058\H,0,-2.58155
9,1.318556,0.887115\H,0,-2.583188,1.322583,-0.877702\C,0,-1.649463,-1.
252889,1.243329\H,0,-1.599546,-0.670508,2.163996\H,0,-2.615265,-1.7652
12,1.236743\H,0,-0.87116,-2.014418,1.283812\\Version=AM64L-G09RevC.01\
State=1-A\HF=-688.3546652\MP2=-690.133221\RMSD=2.527e-09\PG=C01 [X(C6H
15N3Si1)]\\@

_sil_02

1\1\GINC-TOFU\SP\RMP2-FC\GTMP2large\C6H15N3Si1\ROOT\21-Jun-2014\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\N,
0,2.407316,-0.523925,-0.357136\N,0,3.310347,-1.081211,0.020795\N,0,1.4
76247,0.07393,-0.844692\C,0,-1.280078,-0.61495,0.003113\C,0,-0.770893,
-1.888254,0.677523\H,0,-1.549181,-2.655919,0.666521\H,0,0.09641,-2.303
333,0.163127\H,0,-0.497614,-1.723109,1.720434\C,0,-1.665058,-0.934595,
-1.440916\H,0,-2.42244,-1.722905,-1.461182\H,0,-2.086208,-0.069122,-1.
953297\H,0,-0.81038,-1.283534,-2.020585\C,0,-2.511167,-0.105755,0.7540
14\H,0,-3.303067,-0.858997,0.729737\H,0,-2.297423,0.101268,1.803442\H,
0,-2.919484,0.802812,0.309034\C,0,0.604213,1.147895,1.768729\H,0,1.393
685,1.899696,1.751217\H,0,-0.227101,1.561609,2.340377\H,0,0.982687,0.2
85336,2.316966\C,0,-0.411511,2.235023,-0.936956\H,0,-1.322955,2.688475
,-0.547221\H,0,0.380557,2.981806,-0.884847\H,0,-0.57315,2.002325,-1.98
8688\Si,0,0.071805,0.712561,0.026368\\Version=AM64L-G09RevC.01\State=1
-A\HF=-688.3544353\MP2=-690.1335115\RMSD=1.507e-09\PG=C01 [X(C6H15N3Si
1)]\\@

_-_01

1\1\GINC-SOLARIS\SP\RMP2-FC\GTMP2large\N3(1-)\PASCAL\25-Jun-2014\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Titl
e Card Required\\-1,1\N,0,0.6565192335,-0.125,0.\N,0,-0.51594447,-0.12
5,0.\N,0,-1.6884081735,-0.125,0.\\Version=AM64L-G09RevC.01\State=1-SGG
\HF=-163.3337122\MP2=-163.9660209\RMSD=5.935e-10\PG=D*H [O(N1),C*(N1.N
1)]\\@

_H_01

1\1\GINC-EDDY\SP\RMP2-FC\GTMP2large\H1N3\PASCAL\24-Nov-2013\0\\#p MP2(
FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Title Car
d Required\\0,1\N,0,-0.6102646995,0.0785865681,0.21734702\H,0,-1.34571
68493,0.5857284804,-0.2596134301\N,0,0.4767314527,0.6146521245,0.01171
80082\N,0,1.5277804869,0.9927952886,-0.0878141688\\Version=AM64L-G09Re
vC.01\State=1-A'\HF=-163.9015365\MP2=-164.5067185\RMSD=9.050e-09\PG=CS
[SG(H1N3)]\\@

_aux_f

1\1\GINC-ANGIE\SP\RMP2-FC\GTMP2large\C3H10N4\PASCAL\26-Jun-2014\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\H,
0,-0.587561,0.570382,0.006643\C,0,1.917927,1.180063,-0.131662\H,0,1.70
2017,1.846529,0.700766\H,0,2.997567,0.981886,-0.148288\H,0,1.64659,1.6
90554,-1.053365\C,0,1.352729,-0.915645,-1.127412\H,0,2.398478,-1.23933
8,-1.211498\H,0,0.728145,-1.801093,-1.026661\H,0,1.07621,-0.406062,-2.
048236\C,0,1.427875,-0.703928,1.25182\H,0,1.207867,-0.037776,2.083524\
H,0,0.801453,-1.588497,1.348732\H,0,2.478195,-1.015008,1.325075\N,0,1.
142983,-0.035133,0.001121\N,0,-1.541863,0.992507,0.005341\N,0,-2.40774

4,0.134352,0.002777\N,0,-3.284825,-0.572371,0.000307\\Version=AM64L-G09RevC.01\State=1-A\HF=-337.2358024\MP2=-338.5920111\RMSD=8.309e-09\PG=C01 [X(C3H10N4)]\\@

_aux_b

1\1\GINC-STEAK\SP\RMP2-FC\GTMP2large\C3H10N4\ROOT\26-Jun-2014\0\\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\H,0,-2.835354,-0.030655,0.006672\C,0,-1.352489,-0.894325,-1.099075\H,0,-1.74733,-0.514297,-2.036126\H,0,-0.260437,-0.858822,-1.081318\H,0,-1.720548,-1.899287,-0.91738\C,0,-1.349859,-0.513546,1.321221\H,0,-0.257787,-0.48462,1.291048\H,0,-1.74354,0.135585,2.09719\H,0,-1.717097,-1.525966,1.457479\C,0,-1.388388,1.391781,-0.218343\H,0,-1.783061,1.727994,-1.172091\H,0,-1.781582,2.004803,0.586681\H,0,-0.295887,1.385036,-0.218276\N,0,-1.820886,-0.013297,0.002878\N,0,1.274416,0.044241,-0.010248\N,0,3.611462,-0.02021,0.004755\N,0,2.461728,0.01166,-0.002628\\Version=AM64L-G09RevC.01\State=1-A\HF=-337.1824193\MP2=-338.5541368\RMSD=3.977e-09\PG=C01 [X(C3H10N4)]\\@

Imidazole (Imi)

_sil_01

1\1\GINC-ANGIE\SP\RMP2-FC\GTMP2large\C9H18N2Si1\PASCAL\25-Jun-2014\0\\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\C,0,-2.032652,0.043984,1.064159\C,0,-3.189005,-0.633561,-0.570612\C,0,-1.989676,-0.25012,-1.085922\N,0,-1.229563,0.194802,-0.026439\H,0,-1.707482,0.31739,2.053151\H,0,-4.041877,-1.029138,-1.093407\H,0,-1.620217,-0.245204,-2.094991\Si,0,0.466087,0.75731,-0.065487\N,0,-3.205515,-0.444267,0.781555\C,0,0.668606,1.91932,1.385404\H,0,0.545833,1.42332,2.347277\H,0,1.662485,2.367559,1.37574\H,0,-0.057229,2.730657,1.332925\C,0,0.679754,1.676834,-1.679914\H,0,1.666122,2.138813,-1.730797\H,0,0.577593,1.030863,-2.551168\H,0,-0.061023,2.471538,-1.766799\C,0,1.616595,-0.744038,0.061334\C,0,1.358549,-1.705868,-1.09784\H,0,2.025296,-2.569002,-1.023273\H,0,0.336047,-2.08359,-1.092967\H,0,1.543042,-1.240651,-2.06702\C,0,1.372972,-1.478365,1.379355\H,0,0.346269,-1.835241,1.464118\H,0,2.027275,-2.35141,1.447919\H,0,1.585064,-0.85015,2.245269\C,0,3.069983,-0.270181,0.0095\H,0,3.746002,-1.125502,0.088012\H,0,3.303882,0.239482,-0.926161\H,0,3.312487,0.40615,0.830394\\Version=AM64L-G09RevC.01\State=1-A\HF=-749.3351614\MP2=-751.3793855\RMSD=5.175e-09\PG=C01 [X(C9H18N2Si1)]\\@

_sil_02

1\1\GINC-STEAK\SP\RMP2-FC\GTMP2large\C9H18N2Si1\ROOT\25-Jun-2014\0\\#p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\C,0,2.032918,-0.045492,-1.063972\C,0,3.188872,0.634416,0.570096\C,0,1.989396,0.251768,1.085661\N,0,1.22954,-0.194661,0.02663\H,0,1.707983,-0.320366,-2.052637\H,0,4.041629,1.030703,1.09254\H,0,1.619665,0.248457,2.094637\Si,0,-0.466071,-0.757244,0.066138\N,0,3.205739,0.443095,-0.781776\C,0,-1.616592,0.743961,-0.061991\C,0,-0.679775,-1.675512,1.681262\H,0,-1.666409,-2.136847,1.732787\H,0,0.060555,-2.4706,1.768442\H,0,-0.576923,-1.029015,2.552042\C,0,-0.668589,-1.920515,-1.383749\H,0,0.057655,-2.731466,-1.330939\H,0,-1.662244,-2.369234,-1.373191\H,0,-0.54655,-1.425262,-2.3461\C,0,-1.359386,1.706298,1.096953\H,0,-0.336844,2.083925,1.092708\H,0,-2.025979,2.569471,1.021431\H,0,-1.544725,1.241582,2.066213\C,0,-1.372147,1.477782,-1.380148\H,0,-2.026465,2.350757,-1.449473\H,0,-0.345407,1.83468,-1.464384\H,0,-1.583643,0.849215,-2.245956\C,0,-3.069997,0.270089,-0.010925\H,0,-3.304485,-0.239362,0.924709\H,0,-3.745966,1.125396,-0.090036\H,0,-3.312002,-0.40642,-0.831819\\Version=AM64L-G09RevC.01\State=1-A\HF=-749.3351618\MP2=-751.3793856\RMSD=5.176e-09\PG=C01 [X(C9H18N2Si1)]\\@

_-_01

1\1\GINC-SOLARIS\SP\RMP2-FC\GTMP2large\C3H3N2(1-)\PASCAL\25-Jun-2014\0\\#p MP2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Title Card Required\\-1,1\N,0,3.429213749,5.6517956341,-0.1672935643\C,0,2.3002715966,5.7979883123,-0.8672915592\C,0,2.9991680018,5.77017077

03,1.1155177348\H,0,2.2917964862,5.7554112787,-1.9486360716\C,0,1.6323
633181,5.9814789872,1.1177586516\H,0,3.6812584947,5.6985066808,1.95126
70484\H,0,0.9633185987,6.1190538453,1.9557767592\N,0,1.182176975,5.999
3202113,-0.1635419688\\Version=AM64L-G09RevC.01\State=1-A\HF=-224.3111
979\MP2=-225.1998913\RMSD=9.890e-09\PG=C01 [X(C3H3N2)]\\@

_H_01
1\1\GINC-SOLARIS\SP\RMP2-FC\GTMP2large\C3H4N2\PASCAL\28-Oct-2013\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Titl
e Card Required\\0,1\C,0,2.2312692201,5.946956949,-0.8876522708\C,0,2.
9637430449,5.9688266741,1.1757726211\H,0,2.2554190241,5.9595501724,-1.
9629063688\C,0,1.6037798337,5.8872015703,1.1385142127\H,0,3.6661132208
,6.0012548499,1.9872765398\H,0,0.9215058054,5.8360638102,1.9679784427\
N,0,1.1590376846,5.8740115555,-0.1516427421\N,0,3.3524700897,6.0055168
163,-0.1343022881\H,0,4.2934607468,6.0672362923,-0.4727884765\\Version
=AM64L-G09RevC.01\State=1-A\HF=-224.8916444\MP2=-225.7629412\RMSD=5.82
0e-09\PG=C01 [X(C3H4N2)]\\@

_aux_f
1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\C6H13N3\LOCAL\26-Jun-2014\0\\#p M
P2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\H,0
,0.029277,-0.039406,0.004594\C,0,-2.360717,-0.935978,-1.00984\H,0,-2.0
15689,-1.941499,-0.776568\H,0,-3.456251,-0.957438,-1.08457\H,0,-1.9565
79,-0.654424,-1.980239\C,0,-2.300959,1.343027,-0.312313\H,0,-3.39297,1
.455851,-0.342903\H,0,-1.909613,2.028459,0.437245\H,0,-1.900871,1.6319
82,-1.282404\C,0,-2.361124,-0.399057,1.316219\H,0,-2.010716,-1.402538,
1.549695\H,0,-1.960958,0.282222,2.064435\H,0,-3.45677,-0.390295,1.3912
29\N,0,-1.898907,-0.010696,0.001617\C,0,1.843767,1.064547,0.001472\C,0
,3.149119,-0.603334,0.00047\C,0,1.882506,-1.112396,0.001886\N,0,1.0533
89,-0.028607,0.002345\H,0,1.445172,2.064175,0.001257\H,0,4.081003,-1.1
40485,-0.000481\H,0,1.510868,-2.12036,0.002167\N,0,3.113881,0.759718,0
.000207\\Version=AM64L-G09RevC.01\State=1-A\HF=-398.2282343\MP2=-399.8
469631\RMSD=9.232e-09\PG=C01 [X(C6H13N3)]\\@

_aux_b
1\1\GINC-SOLARIS\SP\RMP2-FC\GTMP2large\C6H13N3\PASCAL\25-Jun-2014\0\\#
p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\
H,0,-3.390472,-0.121874,0.009629\C,0,-1.869915,-0.697199,-1.22748\H,0,
-2.331891,-0.222198,-2.087478\H,0,-0.787878,-0.551905,-1.227697\H,0,-2
.131564,-1.749946,-1.194346\C,0,-1.857681,-0.703941,1.22796\H,0,-0.775
66,-0.560628,1.217732\H,0,-2.309648,-0.232717,2.095302\H,0,-2.120913,-
1.756206,1.192349\C,0,-2.028493,1.403161,0.006921\H,0,-2.447664,1.8664
03,-0.880597\H,0,-2.438607,1.861557,0.901155\H,0,-0.940385,1.442833,0.
001363\N,0,-2.379436,-0.039744,0.004699\C,0,1.553931,-0.9828,-0.007493
\C,0,3.031173,0.51094,0.007581\C,0,1.797319,1.120388,-0.006002\N,0,0.8
33585,0.154135,-0.015816\H,0,1.087012,-1.960004,-0.012871\H,0,4.010179
,0.962571,0.017715\H,0,1.554697,2.172943,-0.009584\N,0,2.869394,-0.836
408,0.006604\\Version=AM64L-G09RevC.01\State=1-A\HF=-398.1532042\MP2=-
399.7840402\RMSD=1.609e-09\PG=C01 [X(C6H13N3)]\\@

Cyanide (CN)
_sil_01
1\1\GINC-STEAK\SP\RMP2-FC\GTMP2large\C7H15N1Si1\ROOT\24-Jun-2014\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\S
i,0,-0.56223,0.464554,0.00001\C,0,-0.951348,1.445386,1.544163\H,0,-0.8
1625,0.851264,2.446633\H,0,-0.311788,2.325093,1.61966\H,0,-1.98517,1.7
89396,1.52669\C,0,1.18519,-0.268522,0.000004\C,0,-0.951291,1.445513,-1
.544079\H,0,-0.815782,0.851595,-2.446622\H,0,-1.985222,1.789202,-1.526
809\H,0,-0.311983,2.325431,-1.619256\C,0,2.202315,0.873539,-0.00009\H,
0,2.109842,1.507693,0.882614\H,0,3.217088,0.467957,0.000038\H,0,2.1099
8,1.507467,-0.882973\C,0,1.389948,-1.128924,1.246209\H,0,0.680546,-1.9
55428,1.293475\H,0,2.394143,-1.560343,1.239592\H,0,1.293926,-0.549931,
2.165116\C,0,1.389882,-1.129009,-1.246137\H,0,2.39406,-1.560471,-1.239
501\H,0,0.680432,-1.955473,-1.293299\H,0,1.293866,-0.550091,-2.165091\

C,0,-1.740025,-0.993095,-0.000046\N,0,-2.460644,-1.89378,-0.000077\\Ve
rsion=AM64L-G09RevC.01\State=1-A\HF=-617.3531308\MP2=-618.8579273\RMSD
=2.713e-09\PG=C01 [X(C7H15N1Si1)]\\@

_-_01

1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\C1N1(1-)\LOCAL\26-Jun-2014\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Title
Card Required\\-1,1\N,0,5.3783705355,-0.8570579323,-0.0006350031\C,0,
4.2054029445,-0.8568744477,-0.0003953969\\Version=AM64L-G09RevC.01\Sta
te=1-SG\HF=-92.3397725\MP2=-92.6812171\RMSD=1.869e-09\PG=C*V [C*(C1N1)
]\\@

_H_01

1\1\GINC-GOLEM\SP\RMP2-FC\GTMP2large\C1H1N1\ROOT\18-Jun-2014\0\\#p MP2
(FC)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Title Ca
rd Required\\0,1\N,0,5.3635037492,-0.8570556069,-0.000631966\C,0,4.217
206581,-0.8568762937,-0.0003978086\H,0,3.1516499399,-0.8567096105,-0.0
001801442\\Version=AM64L-G09RevC.01\State=1-SG\HF=-92.907093\MP2=-93.2
48191\RMSD=7.694e-09\PG=C*V [C*(H1C1N1)]\\@

_aux_f

1\1\GINC-PHOBOS\SP\RMP2-FC\GTMP2large\C4H10N2\ROOT\25-Jun-2014\0\\#p M
P2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\H,0
,1.186796,-0.000893,0.000617\C,0,-1.204079,0.746274,1.158514\H,0,-0.81
9312,1.76332,1.109642\H,0,-2.298715,0.795624,1.234272\H,0,-0.820013,0.
281103,2.064542\C,0,-1.205655,-1.376162,0.066712\H,0,-2.300363,-1.4653
39,0.071174\H,0,-0.821869,-1.928345,-0.789188\H,0,-0.821677,-1.843219,
0.971789\C,0,-1.203749,0.630651,-1.225433\H,0,-0.8187,1.647539,-1.2751
84\H,0,-0.819672,0.079563,-2.0819\H,0,-2.298339,0.672659,-1.305899\N,0
,-0.767386,-0.000146,0.000025\C,0,2.280454,-0.000666,0.000299\N,0,3.42
882,-0.000224,-0.000085\\Version=AM64L-G09RevC.01\State=1-A\HF=-266.24
37986\MP2=-267.3285344\RMSD=5.527e-09\PG=C01 [X(C4H10N2)]\\@

_aux_b

1\1\GINC-PHOBOS\SP\RMP2-FC\GTMP2large\C4H10N2\ROOT\25-Jun-2014\0\\#p M
P2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\H,0
,2.352078,0.01355,0.005882\C,0,0.877414,-0.684341,1.235939\H,0,1.24923
,-0.139332,2.097839\H,0,-0.212984,-0.678571,1.201456\H,0,1.267754,-1.6
97143,1.233059\C,0,0.886068,-0.725889,-1.210639\H,0,-0.204714,-0.71741
5,-1.18417\H,0,1.265118,-0.211054,-2.08776\H,0,1.275112,-1.7384,-1.169
927\C,0,0.865619,1.414602,-0.023336\H,0,1.238494,1.921082,0.861255\H,0
,1.246928,1.892009,-0.920463\H,0,-0.224495,1.37355,-0.027666\N,0,1.337
953,0.005387,0.002287\C,0,-2.017755,-0.020224,-0.009381\N,0,-3.183752,
0.00559,0.002713\\Version=AM64L-G09RevC.01\State=1-A\HF=-266.1852634\M
P2=-267.2683551\RMSD=3.939e-09\PG=C01 [X(C4H10N2)]\\@

NMe3

1\1\GINC-HP1\SP\RMP2-FC\GTMP2large\C3H9N1\ROOT\10-Apr-2015\0\\#p MP2(F
C)/GTMP2large scf=tight int=finegrid geom=check guess=read\\Title Card
Required\\0,1\N,0,-0.818472077,3.1018935436,0.0049609704\C,0,-0.39770
59929,3.7963036617,1.1934187091\H,0,-0.6704391456,4.8481017592,1.12381
08356\H,0,-0.8976073647,3.3757970311,2.0644988767\H,0,0.6897565888,3.7
354506258,1.3607884624\C,0,-0.5434901754,1.6917975348,0.0926850036\H,0
,-1.0434425711,1.2705543345,0.9633799184\H,0,-0.9242202408,1.184577632
6,-0.7923463261\H,0,0.5329159894,1.471336667,0.1765740211\C,0,-0.23669
26356,3.6801895296,-1.1777426021\H,0,-0.617315323,3.1736655575,-2.0632
185769\H,0,-0.5093694342,4.7319469875,-1.2481803736\H,0,0.8629813588,3
.6105302826,-1.1902040742\\Version=AM64L-G09RevC.01\State=1-A1\HF=-173
.3296747\MP2=-174.0673203\RMSD=5.785e-09\PG=C03V [C3(N1),3SGV(C1H1),X(
H6)]\\@

Compound **4b**

_1

1\1\GINC-AZAZEL\SP\RMP2-FC\GTMP2large\C12H12O1\ROOT\21-Nov-2012\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\C,
0,0.80634,-1.560078,-0.19746\C,0,2.124725,-1.923165,-0.176487\C,0,3.13
1724,-0.949556,-0.048149\C,0,2.79039,0.368565,0.056874\H,0,0.056899,-2
.330791,-0.292476\H,0,2.395448,-2.966022,-0.259117\H,0,4.170137,-1.247
426,-0.032667\H,0,3.556274,1.125571,0.156966\C,0,0.415336,-0.203347,-0
.091814\C,0,1.437507,0.77536,0.040319\C,0,1.087609,2.139226,0.155579\C
,0,-0.222185,2.518295,0.142132\C,0,-1.23681,1.552232,0.008485\C,0,-0.9
46159,0.218845,-0.111005\H,0,1.874781,2.873773,0.255963\H,0,-0.489871,
3.561164,0.23387\H,0,-2.271706,1.861985,0.004461\C,0,-2.076677,-0.7805
4,-0.229749\H,0,-1.772213,-1.583723,-0.905806\C,0,-2.44395,-1.38038,1.
112533\H,0,-2.801349,-0.596066,1.777215\H,0,-3.235289,-2.117205,0.9878
53\H,0,-1.583952,-1.858309,1.576858\O,0,-3.253359,-0.190284,-0.73223\H
,0,-3.079387,0.146579,-1.612822\\Version=AM64L-G09RevC.01\State=1-A\HF
=-536.443853\MP2=-538.579167\RMSD=4.591e-10\PG=C01 [X(C12H12O1)]\\@

_2

1\1\GINC-CALYPSO\SP\RMP2-FC\GTMP2large\C12H12O1\ROOT\19-Aug-2012\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\C
,0,-0.382144,-1.53886,-0.066506\C,0,-1.601674,-2.154202,-0.001534\C,0,
-2.784755,-1.397401,0.080324\C,0,-2.717591,-0.033777,0.087163\H,0,0.51
3557,-2.130097,-0.161613\H,0,-1.657545,-3.233286,-0.019585\H,0,-3.7417
85,-1.896465,0.131103\H,0,-3.620426,0.559185,0.14222\C,0,-0.27435,-0.1
26374,-0.048049\C,0,-1.473805,0.633885,0.022646\C,0,-1.41174,2.045572,
0.026328\C,0,-0.209841,2.685058,-0.041103\C,0,0.978709,1.934875,-0.105
776\C,0,0.974688,0.56382,-0.099435\H,0,-2.333918,2.60788,0.079387\H,0,
-0.16174,3.764416,-0.045385\H,0,1.92451,2.458602,-0.154466\C,0,2.31126
3,-0.145859,-0.096795\H,0,3.070694,0.611282,-0.314654\C,0,2.653556,-0.
763631,1.244352\H,0,2.688009,0.005719,2.013032\H,0,1.919192,-1.508673,
1.540112\H,0,3.62857,-1.244139,1.184827\O,0,2.405141,-1.174044,-1.0609
95\H,0,2.155855,-0.820705,-1.916703\\Version=AM64L-G09RevC.01\State=1-
A\HF=-536.4428908\MP2=-538.5784948\RMSD=5.031e-09\PG=C01 [X(C12H12O1)]
\\@

_3

1\1\GINC-CALYPSO\SP\RMP2-FC\GTMP2large\C12H12O1\ROOT\19-Aug-2012\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\C
,0,-0.768884,-1.541703,-0.170269\C,0,-2.083548,-1.919112,-0.168708\C,0
,-3.105585,-0.957843,-0.068349\C,0,-2.784819,0.365986,0.031023\H,0,0.0
01306,-2.294945,-0.21214\H,0,-2.339937,-2.96661,-0.238024\H,0,-4.14009
1,-1.269867,-0.066243\H,0,-3.561812,1.113899,0.112434\C,0,-0.401902,-0
.178023,-0.078926\C,0,-1.436718,0.788068,0.028198\C,0,-1.104055,2.1582
05,0.128466\C,0,0.199567,2.554028,0.114516\C,0,1.227389,1.597945,-0.00
5761\C,0,0.958837,0.257866,-0.101273\H,0,-1.90073,2.88456,0.213498\H,0
,0.454688,3.601351,0.188748\H,0,2.248676,1.946531,-0.031949\C,0,2.0652
19,-0.765913,-0.236455\H,0,1.829241,-1.403911,-1.088753\C,0,3.451679,-
0.197056,-0.460997\H,0,3.497785,0.411614,-1.363111\H,0,3.781505,0.4088
21,0.383213\H,0,4.151642,-1.022641,-0.566917\O,0,2.07513,-1.655542,0.8
65802\H,0,2.073604,-1.139144,1.674039\\Version=AM64L-G09RevC.01\State=
1-A\HF=-536.4419721\MP2=-538.5774288\RMSD=1.442e-09\PG=C01 [X(C12H12O1
)]\\@

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1\1\GINC-NAUTILUS\SP\RMP2-FC\GTMP2large\C12H12O1\ROOT\30-Aug-2012\0\\#
p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\
C,0,0.786481,-1.551795,-0.216187\C,0,2.100629,-1.929233,-0.189254\C,0,
3.116032,-0.967268,-0.047511\C,0,2.787173,0.353676,0.063413\H,0,0.0314
29,-2.315122,-0.324145\H,0,2.358471,-2.974333,-0.277776\H,0,4.15158,-1
.272748,-0.028067\H,0,3.561715,1.099673,0.171816\C,0,0.407069,-0.19265
7,-0.104049\C,0,1.439532,0.7767,0.040739\C,0,1.099643,2.141365,0.15924
3\C,0,-0.207725,2.530763,0.132853\C,0,-1.229986,1.577226,-0.014691\C,0
,-0.947403,0.241614,-0.131353\H,0,1.889163,2.87126,0.267374\H,0,-0.463
751,3.576445,0.219453\H,0,-2.258884,1.896463,-0.055183\C,0,-2.076252,-

0.753099,-0.241104\H,0,-1.807151,-1.508681,-0.982162\C,0,-2.35125,-1.4
35516,1.089466\H,0,-1.465694,-1.940341,1.470096\H,0,-2.662501,-0.69300
9,1.820754\H,0,-3.146907,-2.173616,0.98763\O,0,-3.235942,-0.075579,-0.
682574\H,0,-3.843596,-0.712008,-1.058582\\Version=AM64L-G09RevC.01\Sta
te=1-A\HF=-536.4413553\MP2=-538.5770295\RMSD=6.363e-09\PG=C01 [X(C12H1
2O1)]\\@

_5

1\1\GINC-NAUTILUS\SP\RMP2-FC\GTMP2large\C12H12O1\ROOT\30-Aug-2012\0\\#
p MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\
C,0,0.786045,-1.542898,-0.250198\C,0,2.099895,-1.920752,-0.212832\C,0,
3.112973,-0.963016,-0.027233\C,0,2.782301,0.355502,0.103522\H,0,0.0331
62,-2.300826,-0.403161\H,0,2.362299,-2.962302,-0.331068\H,0,4.147662,-
1.272325,0.004379\H,0,3.553366,1.102018,0.237068\C,0,0.404948,-0.18678
,-0.106531\C,0,1.434734,0.777761,0.061851\C,0,1.098765,2.145419,0.1740
48\C,0,-0.20401,2.540454,0.107215\C,0,-1.225972,1.586327,-0.056552\C,0
,-0.953009,0.248219,-0.1438\H,0,1.891125,2.869956,0.30205\H,0,-0.46151
2,3.587666,0.175462\H,0,-2.248167,1.923123,-0.138414\C,0,-2.082987,-0.
753432,-0.263886\H,0,-1.839626,-1.462433,-1.054431\C,0,-2.305265,-1.50
855,1.03798\H,0,-3.089782,-2.252927,0.909752\H,0,-1.40194,-2.006939,1.
381173\H,0,-2.60658,-0.813853,1.824405\O,0,-3.285615,-0.159535,-0.6900
89\H,0,-3.745595,0.195613,0.071986\\Version=AM64L-G09RevC.01\State=1-A
\HF=-536.4408621\MP2=-538.5767324\RMSD=4.595e-09\PG=C01 [X(C12H12O1)]\
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_6

1\1\GINC-GOLEM\SP\RMP2-FC\GTMP2large\C12H12O1\ROOT\11-Jun-2014\0\\#p M
P2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\C,0
,-0.383204,-1.54037,-0.087408\C,0,-1.59984,-2.159087,-0.007666\C,0,-2.
783677,-1.405341,0.090248\C,0,-2.719102,-0.041765,0.097297\H,0,0.51183
3,-2.127751,-0.204265\H,0,-1.653742,-3.238209,-0.031627\H,0,-3.739093,
-1.906511,0.150818\H,0,-3.622478,0.5495,0.161563\C,0,-0.277054,-0.1283
73,-0.064508\C,0,-1.47758,0.628854,0.019213\C,0,-1.41996,2.040428,0.02
1466\C,0,-0.220398,2.682407,-0.057798\C,0,0.969355,1.935389,-0.131263\
C,0,0.968623,0.565046,-0.1246\H,0,-2.343153,2.600228,0.083113\H,0,-0.1
74459,3.761848,-0.064897\H,0,1.912275,2.462517,-0.189827\C,0,2.30531,-
0.134233,-0.101568\H,0,3.057612,0.624431,-0.334712\C,0,2.631371,-0.710
901,1.26884\H,0,2.645678,0.078543,2.018548\H,0,1.898395,-1.455206,1.57
1013\H,0,3.616392,-1.181338,1.259982\O,0,2.339203,-1.129891,-1.104681\
H,0,3.214057,-1.521255,-1.115768\\Version=AM64L-G09RevC.01\State=1-A\H
F=-536.439961\MP2=-538.5756612\RMSD=4.360e-09\PG=C01 [X(C12H12O1)]\\@

_7

1\1\GINC-AZAZEL\SP\RMP2-FC\GTMP2large\C12H12O1\ROOT\21-Nov-2012\0\\#p
MP2(FC)/GTMP2large scf=tight int=finegrid\\Title Card Required\\0,1\C,
0,-0.76114,-1.544104,-0.161381\C,0,-2.072185,-1.932583,-0.166826\C,0,-
3.102135,-0.978949,-0.073351\C,0,-2.791227,0.34705,0.025728\H,0,0.0146
87,-2.291538,-0.19688\H,0,-2.320193,-2.982291,-0.234007\H,0,-4.134311,
-1.298599,-0.075713\H,0,-3.57404,1.089323,0.103049\C,0,-0.403336,-0.17
8324,-0.071498\C,0,-1.446318,0.779619,0.030087\C,0,-1.124915,2.151902,
0.129851\C,0,0.176063,2.556592,0.122916\C,0,1.211117,1.608208,0.010798
\C,0,0.952313,0.267789,-0.086845\H,0,-1.927234,2.872588,0.209865\H,0,0
.42356,3.605542,0.19965\H,0,2.229778,1.964069,-0.000635\C,0,2.0637,-0.
743549,-0.232673\H,0,1.817272,-1.373716,-1.095432\C,0,3.441236,-0.1595
37,-0.470881\H,0,3.465561,0.456773,-1.368185\H,0,3.770382,0.433785,0.3
80146\H,0,4.160939,-0.967055,-0.610768\O,0,2.058156,-1.543694,0.936625
\H,0,2.749311,-2.204012,0.860359\\Version=AM64L-G09RevC.01\State=1-A\H
F=-536.439598\MP2=-538.5752378\RMSD=3.133e-09\PG=C01 [X(C12H12O1)]\\@

Compound **5b**

_1

1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\C18H26O1Si1\LOCAL\25-Jul-2014\0\\
#p MP2(FC)/GTMP2large scf=tight int=finegrid maxdisk=200GB\\Title Card

Required\\0,1\C,0,2.92724,-1.489672,-0.027955\C,0,4.191645,-1.81773,-
0.432562\C,0,5.132829,-0.812472,-0.71945\C,0,4.780462,0.500681,-0.5924
28\H,0,2.229825,-2.284252,0.189162\H,0,4.470286,-2.856969,-0.53319\H,0
,6.129318,-1.08209,-1.038236\H,0,5.495763,1.282235,-0.810013\C,0,2.525
781,-0.13901,0.114649\C,0,3.482185,0.871901,-0.176123\C,0,3.122381,2.2
3132,-0.044423\C,0,1.864778,2.574958,0.356053\C,0,0.914229,1.577036,0.
63926\C,0,1.217114,0.246892,0.527262\H,0,3.859409,2.990881,-0.26634\H,
0,1.589452,3.615155,0.456684\H,0,-0.081963,1.856183,0.946343\C,0,0.173
535,-0.790006,0.883871\H,0,0.268956,-1.630682,0.189952\C,0,0.371907,-1
.307938,2.29836\H,0,0.226147,-0.492985,3.004926\H,0,-0.353933,-2.08965
2,2.5165\H,0,1.374842,-1.707321,2.438752\O,0,-1.123662,-0.257167,0.795
967\Si,0,-2.156304,-0.504015,-0.494069\C,0,-3.729472,0.443777,-0.03673
4\C,0,-4.362017,-0.170651,1.211583\H,0,-4.672439,-1.203104,1.046446\H,
0,-3.67613,-0.157249,2.058415\H,0,-5.254283,0.393252,1.498429\C,0,-4.7
26305,0.3762,-1.193523\H,0,-5.008779,-0.649669,-1.434993\H,0,-5.644362
,0.909014,-0.931047\H,0,-4.333257,0.837489,-2.100406\C,0,-3.389591,1.9
06139,0.248061\H,0,-4.297257,2.461531,0.501222\H,0,-2.700939,1.999804,
1.086975\H,0,-2.939241,2.398856,-0.614725\C,0,-2.484157,-2.34324,-0.68
2484\H,0,-2.844578,-2.787895,0.244738\H,0,-3.231727,-2.52988,-1.454654
\H,0,-1.582753,-2.881071,-0.97949\C,0,-1.380749,0.132099,-2.077367\H,0
,-2.015449,-0.077619,-2.939498\H,0,-1.201753,1.206176,-2.043514\H,0,-0
.418375,-0.348284,-2.259512\\Version=AM64L-G09RevC.01\State=1-A\HF=-10
60.9039287\MP2=-1064.2093005\RMSD=3.098e-09\PG=C01 [X(C18H26O1Si1)]\\@

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1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\C18H26O1Si1\LOCAL\25-Jul-2014\0\\
#p MP2(FC)/GTMP2large scf=tight int=finegrid maxdisk=200GB\\Title Card
Required\\0,1\C,0,1.567664,1.40361,0.758397\C,0,2.27126,2.560036,0.56
5\C,0,3.49419,2.547665,-0.130578\C,0,3.981688,1.371404,-0.623444\H,0,0
.617426,1.431605,1.265519\H,0,1.88107,3.49398,0.943898\H,0,4.040339,3.
468384,-0.277589\H,0,4.916769,1.350548,-1.166585\C,0,2.050564,0.163665
,0.274034\C,0,3.280225,0.158511,-0.438989\C,0,3.787187,-1.055409,-0.95
5401\C,0,3.104206,-2.22122,-0.775453\C,0,1.888293,-2.217928,-0.066522\
C,0,1.358682,-1.070015,0.463048\H,0,4.723311,-1.041781,-1.496634\H,0,3
.488024,-3.149253,-1.174159\H,0,1.361783,-3.153611,0.070333\C,0,0.0833
15,-1.183376,1.27231\H,0,-0.291247,-2.19952,1.118385\C,0,0.32563,-1.01
5484,2.762106\H,0,0.725555,-0.031681,2.99438\H,0,-0.612226,-1.1422,3.3
00415\H,0,1.035309,-1.762453,3.114378\O,0,-0.911594,-0.269732,0.877731
\Si,0,-1.8288,-0.344752,-0.51877\C,0,-3.389348,0.647434,-0.104795\C,0,
-4.141214,-0.030791,1.039276\H,0,-4.485493,-1.029364,0.766589\H,0,-3.5
19503,-0.120975,1.929788\H,0,-5.025624,0.553066,1.310461\C,0,-4.300739
,0.727893,-1.328831\H,0,-4.61997,-0.258135,-1.670005\H,0,-5.20541,1.29
342,-1.088856\H,0,-3.81854,1.232235,-2.166923\C,0,-3.000569,2.061717,0
.325364\H,0,-3.895662,2.639319,0.57406\H,0,-2.358546,2.050772,1.205643
\H,0,-2.477207,2.600804,-0.46531\C,0,-2.223748,-2.138109,-0.909393\H,0
,-2.672183,-2.659664,-0.063831\H,0,-2.921614,-2.203847,-1.74524\H,0,-1
.325811,-2.683577,-1.202568\C,0,-0.898695,0.399629,-1.963761\H,0,-1.50
0822,0.378277,-2.873343\H,0,-0.61063,1.433163,-1.774765\H,0,0.015317,-
0.160521,-2.161314\\Version=AM64L-G09RevC.01\State=1-A\HF=-1060.902550
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1\1\GINC-PHOENIX\SP\RMP2-FC\GTMP2large\C18H26O1Si1\PASCAL\28-Jul-2014\
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801,-0.435242\C,0,4.827775,-1.480886,-0.762954\C,0,4.76285,-0.121162,-
0.655583\H,0,1.70353,-2.293581,0.236829\H,0,3.755092,-3.336805,-0.5211
22\H,0,5.7367,-1.9594,-1.097892\H,0,5.620606,0.488636,-0.905056\C,0,2.
443545,-0.260812,0.114904\C,0,3.583117,0.521504,-0.217432\C,0,3.520787
,1.928055,-0.104888\C,0,2.375576,2.534768,0.320095\C,0,1.244952,1.7635
67,0.647112\C,0,1.257612,0.397921,0.552052\H,0,4.394501,2.511975,-0.35
9982\H,0,2.32862,3.610909,0.407776\H,0,0.340308,2.250221,0.979298\C,0,
0.027727,-0.389845,0.952774\H,0,-0.076415,-1.240287,0.273978\C,0,0.154
215,-0.911737,2.374077\H,0,1.051722,-1.515361,2.496734\H,0,0.209377,-0

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0.147777\C,0,-3.103565,-2.086679,-0.010657\H,0,-2.439279,-2.194462,0.8
47186\H,0,-3.935508,-2.781793,0.135337\H,0,-2.563503,-2.415152,-0.9000
04\C,0,-4.582424,-0.590699,-1.338446\H,0,-4.099396,-0.889966,-2.269515
\H,0,-5.428423,-1.265827,-1.181763\H,0,-4.993007,0.409937,-1.481167\C,
0,-4.382709,-0.282958,1.126531\H,0,-5.193068,-0.994608,1.309429\H,0,-3
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7,0.172331,-2.012808\H,0,-1.918711,0.411437,-2.866161\H,0,-0.379173,0.
776518,-2.097372\H,0,-0.989276,-0.872898,-2.109554\C,0,-2.758815,2.319
231,-0.379971\H,0,-3.560843,2.496781,-1.09693\H,0,-3.123871,2.599884,0
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26O1Si1)]\\@

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1\1\GINC-PHOBOS\SP\RMP2-FC\GTMP2large\C18H26O1Si1\ROOT\28-Jul-2014\0\\
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,1.30943\C,0,-4.751368,-0.697771,1.311932\C,0,-4.566757,0.482238,0.649
954\H,0,-1.793549,-2.197836,0.662338\H,0,-3.875664,-2.598308,1.835849\
H,0,-5.675489,-0.890227,1.837551\H,0,-5.343685,1.234709,0.646288\C,0,-
2.330686,-0.224275,-0.05208\C,0,-3.365108,0.750801,-0.043235\C,0,-3.17
7722,1.972798,-0.726204\C,0,-2.010839,2.220074,-1.387444\C,0,-0.982953
,1.2592,-1.394684\C,0,-1.120874,0.059272,-0.750201\H,0,-3.972724,2.705
755,-0.713847\H,0,-1.866982,3.155789,-1.908655\H,0,-0.058488,1.462997,
-1.91305\C,0,-0.005968,-0.960665,-0.822765\H,0,0.080913,-1.449297,0.15
1368\C,0,-0.298833,-2.017254,-1.8771\H,0,-0.322267,-1.548,-2.858829\H,
0,0.479462,-2.778939,-1.876079\H,0,-1.259656,-2.499259,-1.704888\O,0,1
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242,0.782001,1.162067\C,0,2.516294,2.217348,0.654238\H,0,3.355547,2.50
3922,0.01932\H,0,1.598063,2.36171,0.084804\H,0,2.493023,2.915716,1.495
72\C,0,3.955231,0.641667,1.940599\H,0,4.828786,0.849378,1.320744\H,0,3
.976438,1.350419,2.773238\H,0,4.074731,-0.356174,2.364315\C,0,1.475843
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,1.598416\H,0,1.517769,-0.535414,2.494916\C,0,3.942218,0.044362,-1.574
\H,0,3.724394,1.011006,-2.026924\H,0,4.941046,0.094147,-1.139872\H,0,3
.964891,-0.694538,-2.375207\C,0,2.927842,-2.182116,0.282418\H,0,3.9248
35,-2.289992,0.711079\H,0,2.213405,-2.499233,1.042167\H,0,2.857536,-2.
881352,-0.551369\\Version=AM64L-G09RevC.01\State=1-A\HF=-1060.9025244\
MP2=-1064.2092726\RMSD=2.036e-09\PG=C01 [X(C18H26O1Si1)]\\@

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1\1\GINC-IBLIS\SP\RMP2-FC\GTMP2large\C18H26O1Si1\LOCAL\28-Jul-2014\0\\
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24875\C,0,4.070632,2.141404,-0.089142\C,0,4.36302,0.882705,-0.529502\H
,0,0.956977,1.607994,1.133265\H,0,2.597057,3.394032,0.865208\H,0,4.785
151,2.942454,-0.213415\H,0,5.311113,0.675482,-1.007045\C,0,2.187698,0.
073154,0.252616\C,0,3.44004,-0.176214,-0.373394\C,0,3.751103,-1.476896
,-0.829252\C,0,2.857444,-2.494551,-0.674123\C,0,1.618012,-2.249301,-0.
055372\C,0,1.27102,-1.008684,0.412255\H,0,4.707816,-1.649196,-1.303063
\H,0,3.091333,-3.488853,-1.026587\H,0,0.920058,-3.068897,0.056023\C,0,
-0.05409,-0.870041,1.133607\H,0,-0.612644,-1.788848,0.932185\C,0,0.125
208,-0.766778,2.638503\H,0,0.655186,-1.639026,3.017693\H,0,0.69369,0.1
20321,2.907385\H,0,-0.848688,-0.710052,3.122431\O,0,-0.802927,0.238431
,0.699027\Si,0,-1.84308,0.336872,-0.604438\C,0,-3.615149,0.047726,0.01
75\C,0,-3.708774,-1.310856,0.710723\H,0,-4.727056,-1.483911,1.071133\H
,0,-3.462208,-2.134389,0.038749\H,0,-3.046785,-1.370287,1.575311\C,0,-
4.596417,0.079702,-1.15335\H,0,-5.619668,-0.061272,-0.793842\H,0,-4.57
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.139479,1.018686\H,0,-3.299893,1.171819,1.861246\H,0,-4.00231,2.127809
,0.557988\H,0,-4.992692,0.958141,1.419895\C,0,-1.384248,-0.922161,-1.9
16001\H,0,-1.514778,-1.952022,-1.583653\H,0,-2.00232,-0.785512,-2.8044

89\H,0,-0.343767,-0.804139,-2.217561\C,0,-1.631724,2.070941,-1.268999\
H,0,-2.330953,2.28742,-2.077172\H,0,-1.78082,2.816229,-0.488208\H,0,-0
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1\1\GINC-PHOBOS\SP\RMP2-FC\GTMP2large\C18H26O1Si1\ROOT\28-Jul-2014\0\\
#p MP2(FC)/GTMP2large scf=tight int=finegrid maxdisk=200GB\\Title Card
 Required\\0,1\C,0,1.814953,1.487916,0.525828\C,0,2.701851,2.444468,0.
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\H,0,0.92101,1.775351,1.053455\H,0,2.512595,3.483282,0.346487\H,0,4.54
5444,2.857939,-0.930807\H,0,4.96795,0.497817,-1.475683\C,0,2.031938,0.
117759,0.238837\C,0,3.194645,-0.232433,-0.50123\C,0,3.447524,-1.586968
,-0.813722\C,0,2.583325,-2.561101,-0.411272\C,0,1.432771,-2.216471,0.3
21724\C,0,1.144521,-0.918838,0.656183\H,0,4.336111,-1.835499,-1.377711
\H,0,2.772484,-3.597117,-0.65294\H,0,0.758527,-3.003838,0.633285\C,0,-
0.074595,-0.664101,1.517065\H,0,-0.656943,-1.589712,1.51101\C,0,0.3017
17,-0.372258,2.961061\H,0,0.897746,0.534217,3.035517\H,0,-0.599462,-0.
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,1.02426\Si,0,-2.417495,0.355607,0.425683\C,0,-2.427063,-0.118927,-1.4
1309\C,0,-2.004002,-1.576261,-1.59296\H,0,-2.008856,-1.841768,-2.65411
8\H,0,-0.994531,-1.756887,-1.223011\H,0,-2.681521,-2.264794,-1.085854\
C,0,-1.455074,0.779084,-2.177614\H,0,-1.737588,1.830984,-2.117493\H,0,
-0.436633,0.686365,-1.801938\H,0,-1.444086,0.507164,-3.23704\C,0,-3.83
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.731884\H,0,-2.444948,2.822419,0.122623\C,0,-3.450034,-0.849641,1.4307
43\H,0,-4.489417,-0.834067,1.100059\H,0,-3.103555,-1.880218,1.354549\H
,0,-3.442417,-0.574115,2.48598\\Version=AM64L-G09RevC.01\State=1-A\HF=
-1060.9011584\MP2=-1064.2084999\RMSD=3.865e-09\PG=C01 [X(C18H26O1Si1)]
\\@

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1\1\GINC-PHOENIX\SP\RMP2-FC\GTMP2large\C18H26O1Si1\PASCAL\28-Jul-2014\
0\\#p MP2(FC)/GTMP2large scf=tight int=finegrid maxdisk=200GB\\Title C
ard Required\\0,1\C,0,-1.563982,-1.162077,-0.983471\C,0,-2.20027,-2.36
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96,-1.068064,0.854966\C,0,2.667898,-0.55007,2.288348\H,0,2.882789,-1.3
54089,2.998122\H,0,3.373881,0.256685,2.49024\H,0,1.664872,-0.180553,2.
499519\C,0,4.211624,-1.564262,0.613289\H,0,4.454996,-2.363208,1.319034
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\H,0,3.524617,-0.469604,-2.393341\H,0,1.880519,-1.093434,-2.360322\H,0
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0.8989755\MP2=-1064.2055065\RMSD=8.219e-09\PG=C01 [X(C18H26O1Si1)]\\@

REFERENCES

[a] P. Patschinski and H. Zipse,
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Fax.: +49 89 2180 77738
e-mail: zipse@cup.uni-muenchen.de

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