

## Supplementary Materials

# SILP materials as effective catalysts in selective monofunctionalization of 1,1,3,3-tetramethyldisiloxane

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<sup>1</sup>H NMR data for obtained ionic liquids:

[P<sub>888</sub>][NTf<sub>2</sub>]:

<sup>1</sup>H NMR (300 MHz, DMSO): 2.17 (6H,m, P-CH<sub>2</sub>-), 2.17 (8H,t, P-CH<sub>2</sub>), 1.27-1.47 (48H,m,-(CH<sub>2</sub>)<sub>6</sub>-), 0.87 (12H, t, -CH<sub>3</sub>)

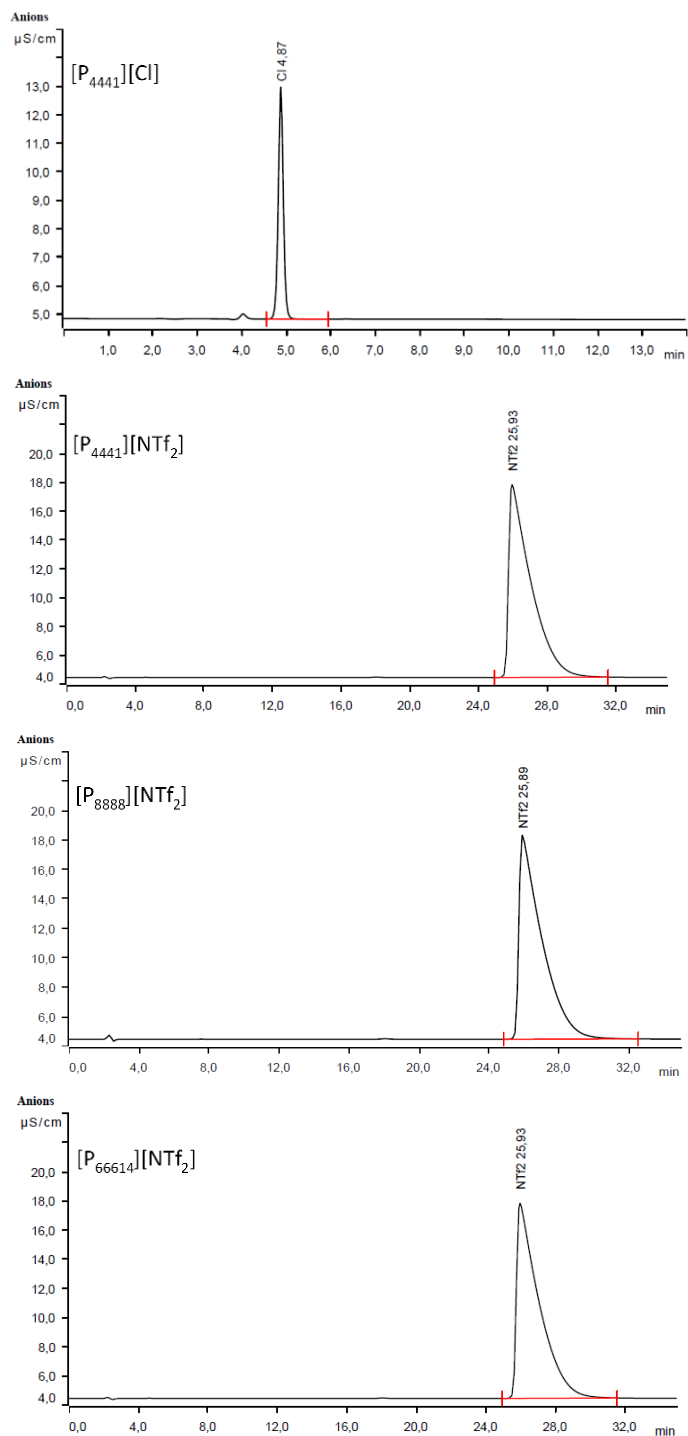
[P<sub>66614</sub>][NTf<sub>2</sub>]:

<sup>1</sup>H NMR (300 MHz, DMSO): 2.18 (8H, t, P-CH<sub>2</sub>-), 1.25-1.50 (48H, m, -(CH<sub>2</sub>)<sub>n</sub>-), 0.86-0.92 (12H, t, -CH<sub>3</sub>)

[P<sub>4441</sub>][NTf<sub>2</sub>]:

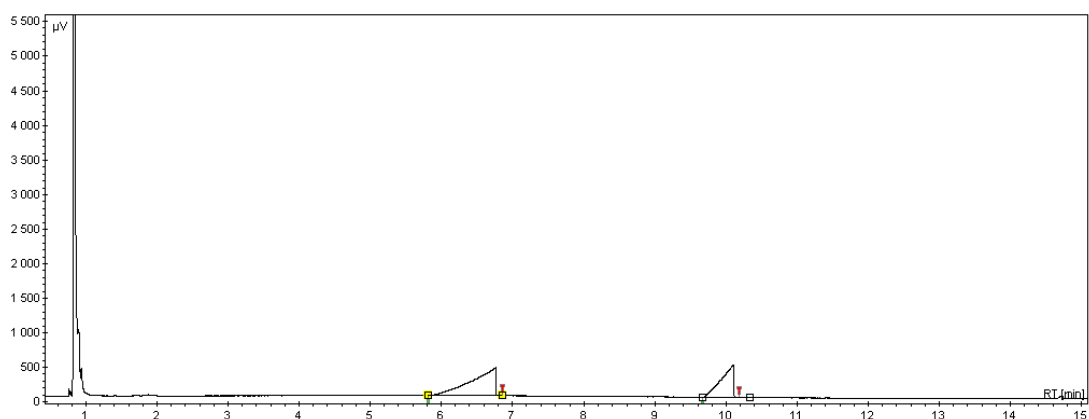
<sup>1</sup>H NMR: (300 MHz, DMSO): 2.17 (6H, m, P-CH<sub>2</sub>-), 1.80 (3H, s, P-CH<sub>3</sub>), 1.43 (12H, m, -CH<sub>2</sub>-CH<sub>2</sub>-), 0.92 (9H, t, -CH<sub>3</sub>)

## IC analysis of Ionic Liquids

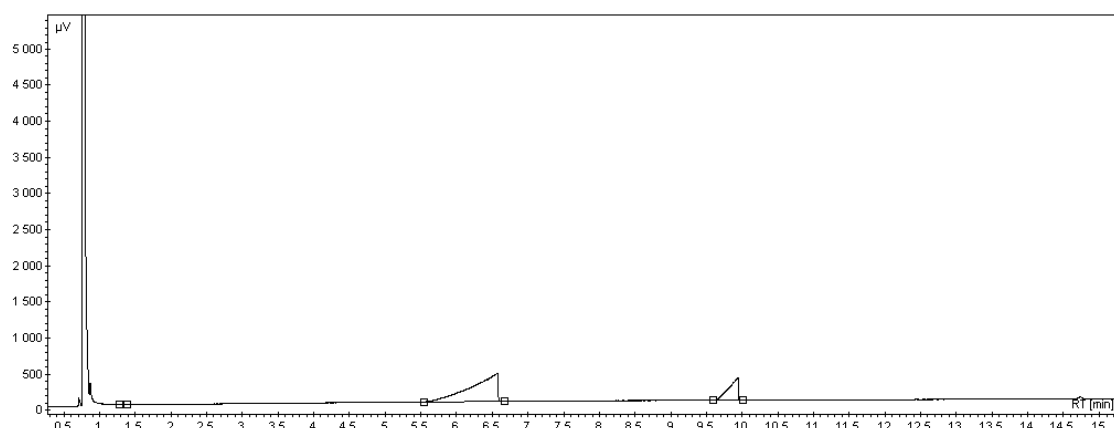


**Figure S1.** IC chromatograms of synthesized ILs with [NTf<sub>2</sub>] anion from their chloride precursors. No peak observance at ~4.9 min means that [Cl]<sup>-</sup> content in ionic liquid is below limit of detection.

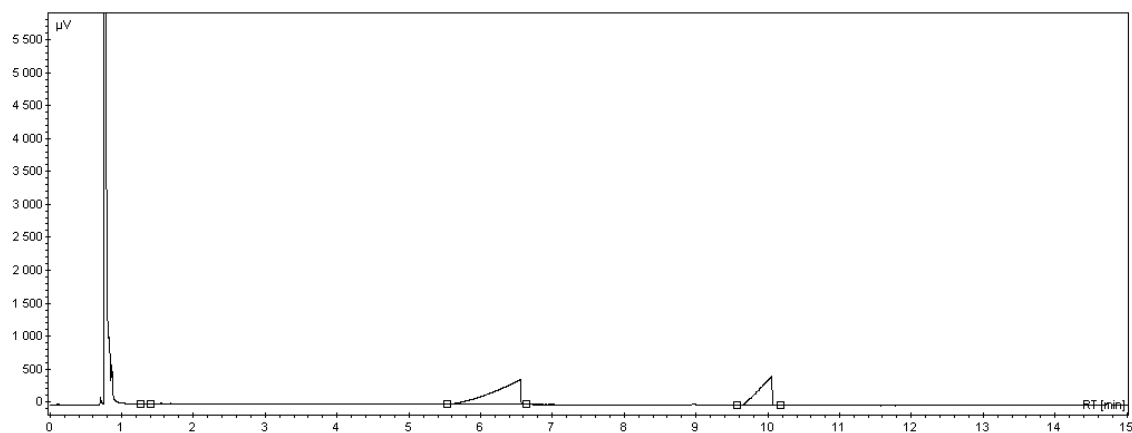
## GC-MS chromatograms



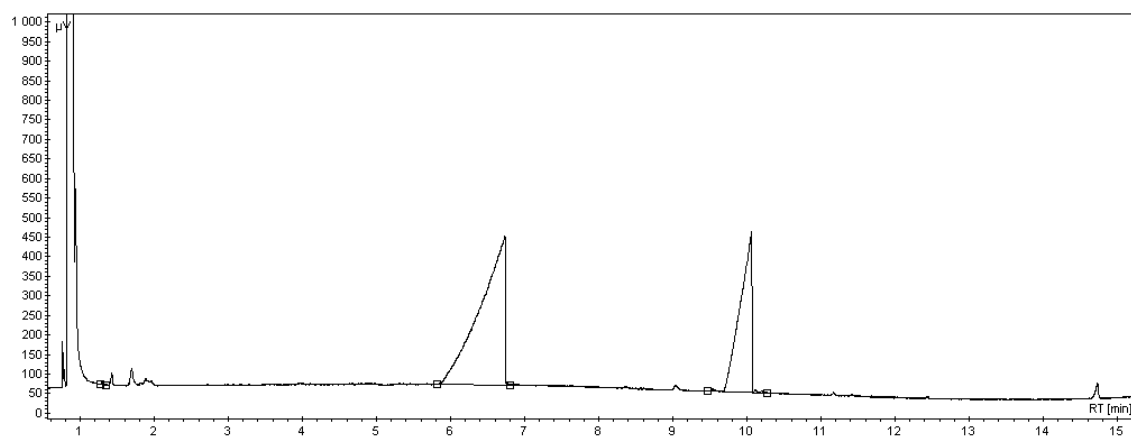
**Figure S2.** GC chromatogram of post reaction mixture obtained from reaction using SILP (A1) after 1<sup>st</sup> reaction cycle; retention times 0.9 min – acetone, 1.5-2.0 min – substrates (1-octene, TMDSO), 6.7 min – decane (internal standard), 10.1 min – product A (octylotetramethyldisiloxane)



**Figure S3.** GC chromatogram of post reaction mixture obtained from reaction using SILP (B1) after 1<sup>st</sup> reaction cycle; retention times 0.9 min – acetone, 1.5-2.0 min – substrates (1-octene, TMDSO), 6.7 min – decane (internal standard), 10.1 min – product A (octylotetramethyldisiloxane)

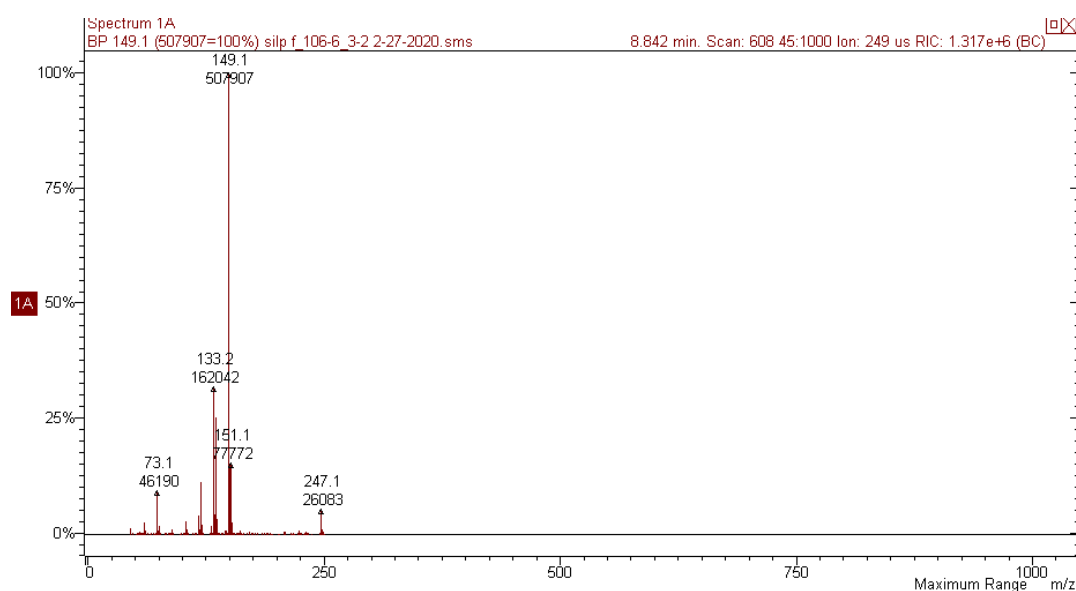


**Figure S4.** GC chromatogram of post reaction mixture obtained from reaction using SILP (C1) after 1<sup>st</sup> reaction cycle; retention times 0.9 min – acetone, 1.5-2.0 min – substrates (1-octene, TMDSO), 6.7 min – decane (internal standard), 10.1 min – product A (octylotetramethyldisiloxane)



**Figure S5.** Example of GC chromatogram of post reaction mixture obtained from reaction using SILP (C1) after 4<sup>th</sup> reaction cycle; retention times 0.9 min – acetone, 1.5-2.0 min – substrates (1-octene, TMDSO), 6.7 min – decane (internal standard), 10.1 min – product A (octylotetramethyldisiloxane), 14.7 min – product B (1,3-dioctyl-1,1,3,3-tetramethyldisiloxane)

### GC-MS mass spectrum



**Figure S6.** GC-MS mass spectrum of octylotetramethyldisiloxane obtained from reaction using SILP (A1) recorded at retention time 8.842 min.

**MS (ESI):**  $m/z$  (%) = 247 ( $[M+H]^+$ , 5); 149 ( $[\text{Si}(\text{CH}_3)_3\text{O}_2]^+$ , 100); 133 ( $[\text{Si}(\text{CH}_3)_3\text{O}]^+$ , 32); 73 ( $[\text{Si}(\text{CH}_3)_3]^+$ , 9)

## Conversion and selectivity of hydrosilylation reaction using SILP materials

**Table S1.** Conversion and selectivity of hydrosilylation reaction using SILP materials ([RhCl(PPh<sub>3</sub>)<sub>3</sub>]).

Cycle number	Catalyst (A1)				Catalyst (B1)				Catalyst (C1)									
	x <sup>a</sup> =10 <sup>-5</sup>		x <sup>a</sup> =10 <sup>-6</sup>		x <sup>a</sup> =10 <sup>-7</sup>		x <sup>a</sup> =10 <sup>-5</sup>		x <sup>a</sup> =10 <sup>-6</sup>		x <sup>a</sup> =10 <sup>-7</sup>		x <sup>a</sup> =10 <sup>-5</sup>		x <sup>a</sup> =10 <sup>-6</sup>		x <sup>a</sup> =10 <sup>-7</sup>	
	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>
1	>99	100	>99	100	>99	100	>99	98	>99	97	64	100	>99	99	>99	97	32	100
2	>99	100	>99	100	62	100	>99	98	>99	97	52	100	>99	99	>99	97	11	100
3	>99	100	>99	100	22	100	>99	98	>99	97	44	100	>99	99	>99	97	3	100
4	>99	100	>99	100	11	100	>99	98	61	100	9	100	>99	99	91	97		
5	>99	100	>99	100	3	100	86	98	84	100			>99	99	80	97		
6	>99	100	79	100			70	98	77	100			>99	97	64	96		
7	>99	100	53	100			68	97	46	100			>99	98	48	95		
8	>99	100	28	100			62	97	60	100			>99	98	46	95		
9	>99	100	15	100			54	97	24	100			>99	97	32	95		
10	>99	100					51	97					>99	98	58	95		
11	>99	100											>99	96				
12	>99	100											>99	97				
13	>99	100											>99	98				
14	>99	100											>99	97				
15	>99	100											98	97				
16	>99	100											98	94				
17	95	100											98	97				
18	82	100											96	97				
19	61	100											92	97				
20	39	100											90	97				
TOF [h <sup>-1</sup> × 10 <sup>3</sup> ]	3722		1340		394		1574		1496		536		3916		1432		92	

<sup>1</sup> conversion (C); <sup>2</sup> selectivity (S); <sup>a</sup> Molar ratio TMDSO:1-oct:[Rh] 2:1:2 × 10<sup>x</sup>

**Table S2.** Conversion and selectivity of hydrosilylation reaction using SILP materials ( $[\{\text{Rh}(\mu\text{-OSiMe}_3)(\text{cod})\}_2]$ ).

Cycle number	Catalyst (A2)				Catalyst (B2)				Catalyst (C2)									
	$\chi^a=10^{-5}$		$\chi^a=10^{-6}$		$\chi^a=10^{-7}$		$\chi^a=10^{-5}$		$\chi^a=10^{-6}$		$\chi^a=10^{-7}$							
	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>						
1	>99	99	>99	100	26	100	>99	99	>99	97	100	100	>99	98	>99	100	>99	98
2	>99	100	>99	100	0		>99	99	>99	97	7	100	>99	98	>99	100	56	99
3	>99	100	>99	100			>99	99	>99	97			>99	98	>99	100		
4	>99	100	>99	100			>99	99	95	97			>99	98	>99	100		
5	>99	100	32	100			>99	99	81	98			>99	98	>99	100		
6	>99	100					>99	98	37				>99	98	>99	100		
7	>99	100					>99	99	28				>99	98	53	100		
8	>99	99					>99	99	19				>99	98	46	100		
9	90	99					>99	99	10				>99	98	32	100		
10	85	99					>99	98	9				>99	98	24	100		
11	77	100					>99	100					>99	98				
12	61	100					>99	100					>99	98				
13	52	100					>99	100					>99	98				
14	35	100					73	100					>99	98				
15	15	100					26	100					>99	98				
16													>99	98				
17													>99	98				
18													>99	98				
19													>99	98				
20													>99	97				
TOF [ $\text{h}^{-1} \times 10^3$ ]	2414		856		52		2772		1152		214		3960		1498		310	

<sup>1</sup> conversion (C); <sup>2</sup>selectivity (S); <sup>a</sup> Molar ratio TMDSO:1-oct:[Rh] 2:1:2x10<sup>x</sup>

**Table S3.** Conversion and selectivity of hydrosilylation reaction using SILP materials  $[\{\text{RhCl}(\text{cod})\}_2]$ .

Cycle number	Catalyst (A3)				Catalyst (B3)				Catalyst (C3)									
	$\chi^a=10^{-5}$		$\chi^a=10^{-6}$		$\chi^a=10^{-7}$		$\chi^a=10^{-5}$		$\chi^a=10^{-6}$		$\chi^a=10^{-7}$		$\chi^a=10^{-5}$		$\chi^a=10^{-6}$		$\chi^a=10^{-7}$	
	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>	C <sup>1</sup>	S <sup>2</sup>
1	>99	98	>99	98	10	100	>99	98	79	97	12	100	>99	99	>99	99	99	97
2	>99	98	>99	98	0	0	>99	98	73	97	0		>99	98	>99	100	63	100
3	>99	98	>99	98			>99	98	77	97			>99	97	>99	100	28	100
4	>99	98	>99	97			>99	98	71	97			>99	96	>99	100	5	100
5	>99	98	>99	97			>99	98	65	97			>99	94	>99	100		
6	>99	98	>99	97			>99	98	58	96			>99	97	>99	100		
7	>99	98	>99	97			>99	97	42	100			>99	98	>99	100		
8	>99	98	>99	97			>99	97	34	100			>99	98	>99	100		
9	>99	98	>99	97			>99	97	23	100			>99	98	99	100		
10	>99	98	>99	97			>99	97	18	100			>99	98	87	100		
11	>99	98	>99	97			>99	97					>99	98	55	97		
12	>99	98	>99	97			>99	97					>99	97	39	100		
13	>99	98	>99	97			>99	97					>99	97	38	100		
14	>99	98	>99	97			>99	97					>99	97	20	100		
15	>99	98	87	99			>99	97					>99	97	26	100		
16	>99	98	75	99			>99	99					>99	99				
17	>99	98	65	99			>99	99					>99	99				
18	>99	98	34	99			>99	99					>99	99				
19	>99	97					>99	99					>99	99				
20	>99	97					>99	99					>99	99				
TOF [ $\text{h}^{-1} \times 10^3$ ]	3960		3294		20		3960		1080		24		3960		2312		390	

<sup>1</sup> conversion (C); <sup>2</sup>selectivity (S); <sup>a</sup> Molar ratio TMDSO:1-oct:[Rh] 2:1:2x10<sup>x</sup>