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Poly(imidazolium) Carbosilane Dendrimers: Synthesis, Catalytic Activity in Redox Esterification of α,β -Unsaturated Aldehydes and Recycling via Organic Solvent Nanofiltration

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Abstract: Three series of poly(ionic) carbosilane dendrimers peripherally functionalized with imidazolium groups substituted on N-3 with methyl, isopropyl and 2,6-diisopropylphenyl (Dipp) were prepared up to the 3rd generation together with model monovalent imidazolium iodides and used as N-heterocyclic carbene (NHC) precursors. Catalytic activity of model and dendritic NHCs generated in situ by deprotonation with DBU was tested in redox esterification of α,β -unsaturated aldehydes and the influence of substitution, dendrimer generation, temperature and substrate structure on the reaction outcome was evaluated. Dipp substituted NHCs showed high activity and selectivity in the reaction with primary alcohols. Effectiveness of organic solvent nanofiltration for the recycling of dendritic NHCs was demonstrated on the 1st generation Dipp substituted catalyst in model redox esterification of cinnamaldehyde with benzyl alcohol. A marked increase in both activity and selectivity in the first four reaction runs was observed and this improved performance was preserved in the following catalytic cycles.

Keywords: immobilization; organocatalysis; N-heterocyclic carbenes; umpolung; poly(cationic) dendrimers; nanofiltration

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1. Introduction

Azolium salts can act as effective organocatalysts [1,2], providing catalytically active species with different mechanisms of substrate activation [3–5]. Besides simple activation of substrates' nucleophilic center by hydrogen bonding or ion-pair interaction, enabling e.g., cycloaddition of carbon dioxide to epoxides [6,7], they can serve as precursors of N-heterocyclic carbenes (NHCs). These subtle species generated by deprotonation of azolium salts offer an entirely unique active site through the carbene atom and its tunable surroundings, able to promote a broad range of chemical transformations [8–11]. Over the last two decades, the practical application of so called *umpolung* principle provided access to a wide library of compounds [12,13]. Nevertheless, while many aspects of NHC-catalyzed *umpolung* reactions, such as activity and selectivity of the catalysts, were studied and optimized, only few studies dealing with the problem of catalyst separation and reuse have been reported so far, moreover, they were limited to benzoin condensation [14–16] and Stetter reaction [17].

Increasing the sustainability of homogeneous catalytic processes and overcoming the major drawback of organocatalysis, i.e., high catalyst loading, by means of catalyst recycling is still a challenge. Recently we developed a branched fluororous tag designed for easy fluorophilization of various substrates [18,19]. Highly fluorophilic imidazolium salts bearing this tag were used as NHC precursors and applied in redox esterification carried

out in fluorous biphasic system, which allowed for their effective recycling [20]. Such solution allows the reaction to proceed in fully homogeneous mode, but it is unsuitable for continuous processes. Accordingly, immobilization or incorporation of a homogeneous catalyst in a solid (inorganic or polymeric) support still remains a predominant approach for the separation of catalysts from reaction mixtures [21], although the homogeneity of the active site is lost to some extent. Many types of immobilized ionic liquids (ILs) on different supports, such as silica [22], MOFs [23], zeolites, various nanoparticles and other materials, have been described [24]. Somewhat surprisingly, soluble macromolecules, such as dendrimers, are much less utilized, in spite of their potential advantages.

Dendrimers, as highly branched macromolecules with regular, tunable structure and low polydispersity due to a well-controlled synthesis [25], can be considered as chemical individuals, despite of their size. They seem to be ideally suited for the attachment of functional moieties at defined positions, yielding their multivalent analogs as optimal systems to study multivalency and the effect of immobilization. Several methods have been proposed for the recovery of dendrimers from reaction mixtures [26,27], nevertheless most of them makes use of different solubility of components and phase separation [26,28–30]. There are also some reports on magnetically recoverable dendrimers and catalysts with dendritic ligands utilizing their interaction with magnetic nanoparticles [31,32]. Recovery methods based on molecular enlargement of the active group, employing membrane processes for the separation of the homogeneous catalyst and other reaction components, are reported much less than it would correspond to the high suitability of this approach for dendritic catalysts. Dialysis in commercially available membrane bags, a slow, diffusion-driven process, is mostly used [33,34]. Despite low efficiency of early attempts [35], a substantial effort was made to develop the method [36,37].

We have previously tested carbosilane dendritic supports for immobilization of both metal-based [38] and metal-free catalysts, which recycling by means of organic solvent nanofiltration (OSN) [39] was also accomplished [40]. OSN proved to be a very effective method, enabling separation of homogeneous reaction components under mild conditions with low energy and material input. This study expands our previous research to another type of catalysts and aims to the preparation of multivalent NHCs. We describe the influence of the attachment of imidazolium salts to dendritic supports on their catalytic performance in redox esterification, their activity towards a wide variety of substrates and their recycling by OSN. We also report the positive effect of OSN on the activity of multivalent NHC catalyst, leading to increase of reaction rate in subsequent reactions.

2. Results and Discussion

2.1. Synthesis and Characterization

For this study, three novel series of monovalent models and multivalent dendritic catalysts were prepared using the synthetic protocol that we have recently developed for the preparation of related cationic carbosilane compounds; a thorough description of synthesis and characterization data can be found in the Experimental Section and in the published papers [40,41]. The final synthetic step involving quaternization of imidazoles with either model 3-iodopropylbutyldimethylsilane or 3-iodopropyl-terminated dendrimers is depicted in Scheme 1.

Scheme 1. Synthesis of model and dendritic imidazolium precatalysts.

Whereas the quaternization step with methyl- and isopropylimidazole is nearly quantitative according to both NMR and ESI MS spectra (Supplementary Material), giving almost monodisperse products, the reaction with hindered diisopropylphenylimidazole (DippIm) is less effective, which leads to defects in the structure at higher generations and lower loading of imidazolium units. HRMS showed the presence of iodopropyl and/or hydroxypropyl-terminated branches, the same types of defects we have reported previously for poly(phosphonium) carbosilane dendrimers [42]. The sum of quaternization-related defects typically did not exceed 5% as estimated from 1H NMR and HRMS (with the exception of $G_2(DippImI)_8$, in which nearly 20% of defective branches were present according to 1H NMR). However, as the quantification is rather inaccurate due to peak overlap and the progress of catalysis is quite insensitive to such small differences in catalyst concentration, the calculation of catalyst loading was based on the nominal number of active groups in the molecule without defects.

2.2. Screening of Catalysts

All model imidazolium salts were tested as precatalysts of redox esterification of cinnamaldehyde and benzyl alcohol (Table 1). This reaction is often used as a benchmark allowing facile evaluation of the catalytic performance of newly prepared compounds [43,44]. Preliminary experiments were performed at 100 °C in toluene, with 10 mol% catalyst loading and 10 mol% of the base (DBU); dioctyl phthalate was added as an inert standard to enable accurate quantification of GC-FID data. As evident from entries 1 and 5, the catalysts generated from methyl- and *iso*-propyl-substituted model imidazolium salts G_0MeImI and $G_0iPrImI$ by deprotonation showed similar performance to previously described fluorinated analogs, for which also a superior activity of the methyl-substituted compound was observed [20]. To our delight, the third model $G_0DippImI$ bearing a sterically demanding 2,6-diisopropylphenyl (Dipp) group manifested by far the highest activity, reaching the full conversion of the starting aldehyde in less than 20 min (entry 8) and confirming the previously observed positive influence of bulky aryl substituents on azolium on the catalyst performance [45]. All three models showed high selectivity for the formation of saturated ester and only small quantities of byproducts **4** and **5a** reported previously to accompany this reaction [20] were detected by GC (Table 1).

Table 1. Screening of catalysts and reaction conditions in redox esterification of cinnamaldehyde with benzyl alcohol.

$\text{1a} + \text{2a} \xrightarrow[\text{toluene, 100}^\circ\text{C, 5h}]{\text{precatalyst, DBU}} \text{3a} + \text{4} + \text{5a}$

Entry	Precatalyst	Loading [mol%]	Base [mol%]	Conversion [%] ^a	Yield 3a/4/5a [%] ^a		
1	G ₀ MeImI	10	10	96	87	7	2
2	G ₁ (MeImI) ₄	10	10	25	20	3	1
3	G ₂ (MeImI) ₈	10	10	20	15	1	1
4	G ₃ (MeImI) ₁₆	10	10	21	16	4	1
5	G ₀ iPrImI	10	10	38	31	6	1
6	G ₁ (iPrImI) ₄	10	10	10	2	7	1
7	G ₂ (iPrImI) ₈	10	10	9	2	5	-
8 ^b	G ₀ DippImI	10	10	100	94	5	1
9 ^c	G ₀ DippImI	1	10	100	94	6	-
10	G ₀ DippImI	1	2	73	72	-	1
11 ^d	G ₀ DippImI	10	10	100	93	3	3
12 ^e	G ₀ DippImI	10	10	100	65	9	8
13 ^f	G ₀ DippImI	10	10	52	15	8	12
14	G ₁ (DippImI) ₄	1	10	72	69	1	2
15	G ₁ (DippImI) ₄	1	2	51	47	-	1
16	G ₂ (DippImI) ₈	1	10	63	61	0.5	-
17	G ₂ (DippImI) ₈	1	2	21	20	-	0.4
18	G ₃ (DippImI) ₁₆	1	10	26	22	0.4	2
19	G ₃ (DippImI) ₁₆	1	2	7	4	-	-

^a As determined by GC according to internal standard; ^b reaction time 20 min; ^c reaction time 90 min; ^d reaction temperature 80 °C, reaction time 3 h; ^e reaction temperature 60 °C; ^f reaction temperature 40 °C.

Exploiting the unprecedented high activity of **G₀DippImI**, we examined the influence of the reaction temperature (Figure 1a) and decrease in catalyst loading. It turned out that lowering the reaction temperature has a detrimental effect on selectivity and overall yield, benzyl cinnamate **5a** being the major side product at low temperature (entry 13). A similar change in selectivity was previously observed by Scheidt et al. for triazolium and imidazolium-based NHC catalysts in enantioselective redox esterification carried out at low temperature [46,47]. On the other hand, lowering the amount of the precatalyst to 1 mol% (with twofold excess of the base) had a positive effect on selectivity while the reaction rate was still fair (entry 10). The reaction rate could also be boosted by the use of larger excess of the base (10-fold to the catalyst) which, however, slightly lowered the selectivity (entry 9). It is clear that the base plays multiple role in the reaction and it serves not only to generate the active NHC moiety, but also facilitates other transformations in the catalytic cycle, as already suggested by Sohn and Bode [48].

Next, we examined the effect of the dendritic scaffold in the benchmark reaction. As apparent from Figure 1, a negative effect of immobilization was observed in all cases. Methylimidazolium derived dendritic catalysts showed a severe drop in activity compared to the model compound even in the first generation, while the differences between generations 1, 2 and 3 were negligible (Figure 1b). This behavior can be ascribed to a close proximity of active sites leading to preferential formation of intramolecular adducts between NHC and imidazolium moieties stabilizing the carbene and lowering its activity as an organocatalyst [11]. The dendrimers bearing isopropylimidazolium groups not only had a very low activity, but at the same time they exhibited poor selectivity (entries 6, 7), so they were excluded from further studies. On the other hand, in case of DippIm series the deactivation is not so severe and it is clearly generation dependent (Figure 1c). Again, the addition of excess base had a positive influence on the reaction rate (*cf.* Figure 1c,d), albeit less pronounced than in case of the corresponding model. Considering the amount of

defects in $G_2(\text{DippImI})_8$, the activity of one particular active site is very similar for G_1 and G_2 catalyst when large excess of base is used. Under the same conditions the activity of G_3 catalyst remained somewhat lower, although experiencing the largest increase (three times higher reaction rate). It seems clear that the bulky Dipp substituent effectively hinders the formation of adducts and it is responsible for the higher activity of this type of dendritic catalysts. The observed negative dendritic effect can be rationalized by a restricted mobility of active sites residing at the periphery of a dendrimer and their uneven distribution in solution (variable local concentration of catalyst), which implies lower probability of effective collisions with the base and substrates.

Figure 1. Time course of redox esterification of cinnamaldehyde with benzyl alcohol (4 equiv) in toluene; (a) effect of temperature on the reaction catalyzed by $G_0\text{DippImI}$ (10 mol%; DBU 10 mol%); (b) 100 °C, influence of the support, precatalyst from methylimidazolium series $G_n(\text{MeImI})_m$ ($n = 0-3$, 10/m mol%; DBU 10 mol%); (c,d) 100 °C, influence of the support and amount of the base, precatalyst from Dipp imidazolium series $G_n(\text{DippImI})_m$ ($n = 0-3$, 1/m mol%; DBU 2 mol% (c), 10 mol% (d)).

2.3. Screening of Substrates

Whereas the influence of the aldehyde structure on the course of redox esterification was extensively studied [43,48] and novel precatalysts were designed and synthesized to overcome the low reactivity of α -substituted enals [49], much less is known about the role of the other reaction component—the alcohol. Most studies use only simple primary alcohols (MeOH, EtOH, BnOH) and underestimate the possible influence of the alcohol structure, especially when sterically demanding mesityl and Dipp substituted NHCs are used. To evaluate the influence of the substrate structure on the reaction progress, the model **G₀DippImI** and dendritic precatalysts **G₁(DippImI)₄** and **G₂(DippImI)₈** were tested in the redox esterification of **1a** with selected alcoholic substrates representing various structural types (products depicted in Figure 2, data sorted according to alcohol type in Table 2). To allow a straightforward comparison between individual substrates and catalysts, the loading was set to 2 mol% of active sites (imidazolium groups) and 4 mol% of DBU in all cases, in spite of supposed lower activity of dendritic catalysts. In cases where the selectivity was fair but a large decrease in the reaction rate was observed when going from the model to dendritic catalysts, also the experiments with higher catalyst loading (10 mol% of active sites and 10% of DBU) were carried out. The reaction progress was monitored by CG-FID with sampling after 5, 24 and 100 h.

Figure 2. Structures of products obtained from the substrate screening and the highest GC yields achieved with model and dendritic (in parentheses) catalysts (**G₀DippImI** and **G₁(DippImI)₄**, respectively, unless otherwise noted).

Table 2. Yields and conversions ^a obtained in redox esterification of cinnamaldehyde with various alcohols catalyzed by imidazolium dendrimers of generations 0 to 2 ^b.

Loading ^c	Substrate (Product)	Benzyl alcohol 2a (3a)		1-Butanol 2b (3b)		Allyl alcohol 2c (3c)		Propargyl alcohol 2d (3d)	
	Time [h]	5	24	5	24	5	24	5	24
2	G ₀ DippImI	91 (93)	98 (100)	91 (100)	-	86 (89)	96 (100)	80 (83)	99 (100)
	G ₁ (DippImI) ₄	57 (58)	96 (97)	36 (45)	75 (86)	15 (20)	44 (52)	6 (6)	43 (48)
	G ₂ (DippImI) ₈	31 (31)	74 (76)	26 (32)	66 (76)	6 (7)	32 (35)	4 (5)	28 (36)
10	G ₁ (DippImI) ₄	-	-	-	-	72 (85)	83 (100)	73 (86)	84 (100)
	G ₂ (DippImI) ₈	-	-	-	-	69 (78)	83 (98)	57 (72)	78 (98)
Loading ^c	Substrate (Product)	Cyclopentanol 2e (3e)		Cyclohexanol 2f (3f)		Cycloheptanol 2g (3g)		Borneol 2h (3h)	
	Time [h]	5	100	5	100	5	100	5	100
2	G ₀ DippImI	31 (46)	82 (100)	20 (39)	74 (100)	8 (21)	50 (88)	3 (26)	13 (67)
	G ₁ (DippImI) ₄	11 (22)	50 (71)	11 (23)	45 (83)	4 (13)	10 (28)	1 (13)	4 (30)
	G ₂ (DippImI) ₈	6 (12)	38 (57)	2 (13)	20 (43)	3 (10)	11 (32)	1 (8)	3 (18)
10	G ₁ (DippImI) ₄	29 (57)	65 (98)	18 (53)	55 (100)	17 (58)	34 (92)	-	-
	G ₂ (DippImI) ₈	23 (48)	68 (99)	24 (58)	57 (100)	9 (45)	34 (92)	-	-
	G ₀ MeImI	66 (82)	81 (100) ^d	52 (73)	71 (93) ^d	53 (82)	66 (100) ^d	58 (83)	71 (100) ^d
	G ₁ (MeImI) ₄	13 (20)	69 (86)	10 (19)	64 (87)	9 (22)	48 (78)	9 (21)	42 (74)
	G ₂ (MeImI) ₈	30 (35)	81 (95)	12 (20)	68 (88)	19 (32)	64 (92)	26 (42)	63 (91)
Loading ^c	Substrate (Product)	2,2,3,3-Tetrafluoropropanol 2i (3i)		2,2-Dichloroethanol 2j (3j)		Isobutanol 2k (3k)		2-Butanol 2l (3l)	
	Time [h]	5	100	5	100	5	24	5	100
2	G ₀ DippImI	1 (3)	99 (100)	10 (13)	90 (90)	76 (85)	95 (100)	3 (20)	5 (30) ^d
	G ₁ (DippImI) ₄	0.4 (1)	8 (8)	2 (5)	20 (20)	15 (21)	32 (44)	2 (19)	3 (24) ^d
	G ₂ (DippImI) ₈	0.4 (1)	19 (20)	1 (2)	20 (21)	10 (11)	26 (34)	2 (14)	4 (23) ^d
10	G ₁ (DippImI) ₄	41 (54)	83 (100) ^d	48 (58)	80 (91)	67 (88)	77 (100)	-	-
	G ₂ (DippImI) ₈	35 (48)	94 (100) ^d	35 (48)	60 (83)	57 (72)	79 (100)	-	-
	G ₀ MeImI	-	-	17 (23)	59 (70)	-	-	41 (66)	65 (100)
	G ₁ (MeImI) ₄	-	-	1 (7)	4 (9)	-	-	4 (15)	8 (45)
	G ₂ (MeImI) ₈	-	-	5 (9)	15 (23)	-	-	8 (25)	14 (50)

^a Conversions given in parentheses; ^b conditions: 4 equiv of alcohol, 100 °C; yield of saturated ester and conversion of **1a** determined by GC according to internal standard; ^c loading in mol% referring to active groups, 4 and 10 mol% of DBU for 2 and 10 mol% of precatalyst, respectively; ^d after 24 h.

In our recent study utilizing fluorous imidazolium as a precatalyst we have observed that the use of secondary alcohols led to a slight decrease in the reaction rate, yield and selectivity [20]. Compared to those fluorinated NHCs, Dipp substituted organocatalysts demonstrated much higher sensitivity to the structure of alcohol, even if the trends were similar. Apart from benzyl alcohol, the best results were obtained for primary alcohols without substitution at α -carbon (**2b**, **2c**, **2d**). The reaction with α -substituted haloalcohols **2i** and **2j** was much slower, but the selectivity remained high. Generally, the difference between the activity of the model and dendritic catalysts was larger than observed for the benchmark reaction with benzyl alcohol. Secondary alcohols were poor substrates except for unsubstituted alicyclic alcohols (**2e**, **2f**, **2g**), which gave moderate yields. *Tert*-butyl alcohol and phenol gave only traces of products. The lack of G₀DippImI activity towards phenol contradicts our previous findings, as we have previously obtained fair yields of phenyl ester under the catalysis by fluorinated methylimidazolylidene [20]. A deeper insight into the complex reaction mechanism is needed to understand this unexpected behavior; a mechanistic study addressing the issue is currently underway. The typical side products (lactone **4** and unsaturated esters) were present in trace amounts (0–2%). However, especially for the combination of less reactive alcohols and dendritic catalysts, a marked difference was observed between the consumption of the aldehyde and the overall yield, pointing to the possible formation of higher molecular weight impurities.

As the bulky Dipp substituent obviously hinders the reaction with sterically more demanding alcohols, we also tested the methylimidazolium-derived catalysts in the reac-

tion with such substrates. Although the activity of $G_n(\text{MeImI})_m$ in the benchmark reaction was an order of magnitude lower than that of $G_n(\text{DippImI})_m$, the reaction rate in the case of more hindered alcohols was comparable or even higher and the selectivity was much better (Table 2). Esters of alicyclic alcohols were formed in good yields, the performance of the 2nd generation catalyst was slightly better than that of the 1st one.

Subsequently we carried out a short screening of representative α,β -unsaturated aldehydes with model $G_0\text{DippImI}$ as a precatalyst (Table 3, products depicted in Figure 2). As expected, α -substituted aldehydes **1b** and **1f** did not react at all and only a trace of saturated ester was obtained with β -substituted substrate **1c**; the major product in this case was the unsaturated ester **5m**. Other tested aldehydes gave moderate to fair yields of the target products but the rate was low compared to the reaction with cinnamaldehyde. The reactions with **1d** and **1g** were selective and only traces of low M_W byproducts were detected by GC. In the case of 2,4-decadienal, the participation of the double bond in a larger conjugated system accelerates the reaction rate, but it also promotes the formation of the unsaturated product **5o**. The lowest yield and selectivity were observed for *o*-nitrocinnamaldehyde **1h**, possibly due to the thermal instability of the enal and/or target product (a thermally induced degradation of products was observed during their isolation). Aside from aldehyde oligomers, a substantial quantity of the unsaturated ester **5q** was also formed. When employing the dendritic catalysts $G_1\text{DippImI}_4$ and $G_2\text{DippImI}_8$, again the decrease in both the rate and selectivity was observed, especially for the less activated substrate **1d** (Supplementary Information, Table S1).

Table 3. Redox esterification of selected aldehydes with benzyl alcohol catalyzed by $G_0\text{DippImI}$ ^a.

Entry	Substrate	Conversion ^b	Product	Yield ^b
1	2-methyl-2-butenal 1b	7	-	-
2	3-methyl-2-butenal 1c	12	5m	3
3	trans-2-hexenal 1d	96	3n	76
4	trans,trans-2,4-decadienal 1e	100	3o + 5o	66 + 10
5	α -methylcinnamaldehyde 1f	2	-	-
6	3-(4-(dimethylamino)phenyl)-2-propenal 1g	82	3p + 5p	73 + 1
7	3-(2-nitrophenyl)-2-propenal 1h	93	3q + 5q	45 + 16

^a Conditions: precatalyst loading 10 mol%, 10 mol% DBU, 4 equiv of benzyl alcohol, 100 °C, 5 h; ^b determined by GC according to internal standard.

2.4. Recycling of Dendritic Catalysts

To verify the feasibility of separation and repeated reuse of the prepared dendritic catalysts, a suitable protocol for catalyst recycling by organic solvent nanofiltration (OSN) was developed. The benchmark reaction was carried out as usual, only with higher loading of the catalyst (2.5 mol% corresponding to 10 mol% of active groups) which enabled to shorten the reaction time and marginalized the influence of catalyst losses due to material transfers between the reaction vessel and nanofiltration cell. We also tried to lower the excess of benzyl alcohol to 2 equiv with respect to the aldehyde. However, this led to insufficient solubility of the catalyst in the reaction mixture and another 2 equiv had to be added to reach the homogeneity. In the next cycles, the additional 2 equiv of benzyl alcohol were substituted by the same amount of *tert*-butyl alcohol as a cheaper and easier-to-remove solvent. A separate experiment with fresh catalyst showed that this change of reaction conditions had a negligible effect on the reaction progress (Figure 3).

As summarized in Table 4, the catalyst recycling by means of OSN had a positive influence on the reaction outcome. From the first to the fourth cycle, both the activity and product purity increased, reaching a very satisfactory level (TOF = 10 h⁻¹, purity over 97%). The isolated catalyst was analyzed by HRMS after each cycle (Supplementary Information, Figure S1). The results suggest that a certain part of active groups stays in the form of NHC which is stable enough [49] to outlast the nanofiltration, and this fraction increases with

increasing number of reaction/nanofiltration cycles due to repeated washing of iodide salt of DBU ([DBUH]I) off from the dendrimer. This can explain the observed increase in activity (better solubility and shifted equilibrium $\text{Im}^+ + \text{DBU} \rightleftharpoons \text{NHC} + \text{DBUH}^+$) as well as the markedly lower dendrimer recovery in the first nanofiltration cycle (the most extensive loss of HI from dendrimer). The higher reactivity of recycled catalyst was confirmed by a direct comparison of reaction kinetics with a fresh catalyst; more importantly, we have demonstrated that the recycled catalyst exhibited significant catalytic activity even in the absence of base (Figure 3) while fresh $\text{G}_1(\text{DippImI})_4$ showed no activity under such conditions. Considering that these tests were performed one month after the last cycle and meantime the recycled catalyst was stored on air in ambient temperature, the carbene moiety exhibits remarkable stability.

Figure 3. Comparison of the activity of fresh and 6 times recycled $\text{G}_1(\text{DippImI})_4$ (2.5 mol%) in the redox esterification of cinnamaldehyde (4 equiv of benzyl alcohol, toluene, 100 °C; 10% DBU unless otherwise noted). ^a 2 equiv of benzyl alcohol were replaced by *tert*-butyl alcohol.

Table 4. Recycling of $\text{G}_1(\text{DippImI})_4$ in redox esterification of cinnamaldehyde with benzyl alcohol ^a.

Run	Reaction Time [h]	TOF [h ^{−1}] ^b	Isolated Yield [%]	GC Purity [%]	Catalyst Recovery [%] ^c
1 ^d	3	3.3	79	93	77
2	2	5.0	73	97	89
3	1.5	6.7	68	97	95
4	1	10	73	98	92
5	1	10	72	98	95
6	1	10	73	98	92

^a Conditions: precatalyst loading 2.5 mol% (10 mol% with respect to active groups), 15 mol% DBU, 2 equiv of benzyl alcohol + 2 equiv of *tert*-butyl alcohol, 100 °C; ^b average value calculated from time to full conversion; ^c based on the weight of the isolated catalyst after nanofiltration; ^d 4 equiv of benzyl alcohol, without *tert*-butyl alcohol.

3. Materials and Methods

3.1. General Remarks

All experiments were carried out in anhydrous conditions under an inert atmosphere of argon or nitrogen, using standard Schlenk techniques, unless otherwise stated. Solvents were dried by usual procedures, then distilled and kept under argon. CDCl_3 and $\text{DMSO}-d_6$ were dried over molecular sieves. Starting iodopropyl terminated dendrimers $\text{G}_m(\text{PriI})_n$ were prepared as described previously [41]. All other used chemicals were commercial products and were used without further purification.

NMR spectra were measured on Bruker Avance 400 (^1H at 400.1 MHz; ^{13}C at 100.6 MHz; ^{29}Si { ^1H } (inept technique) at 79.5 MHz) at 25 °C. ^1H and ^{13}C NMR signals of prepared compounds were assigned to corresponding atoms utilizing HSQC, COSY and HMBS 2D NMR correlation spectra. ^1H and ^{13}C chemical shifts (δ /ppm) are given relative to solvent signals ($\delta_{\text{H}}/\delta_{\text{C}}$: DMSO- d_6 2.50/39.52); ^{29}Si spectra were referenced to external standard hexamethyldisilane (−19.87 ppm).

HRMS spectra were measured with Bruker MicrOTOF-QIII instrument in ESI⁺/ESI[−] mode (80–3000/30–1000 m/z , calibrated by sodium formate).

GC/FID and GC/MS analyses were performed on Agilent 6890 gas chromatograph equipped with DB-5MS column (30 m_0.25 mm_0.25 mm). Injector and detector temperatures were set at 260 °C and 300 °C, respectively. Helium was used as a carrier gas at a flow rate 1.61 mL/min. Oven temperature was set at 50 °C for 3 min and then programmed to 290 °C at a rate 10 °C/min. Quantitative data were calculated using Agilent MSD Chemstation D.02 from the FID peak areas assuming a linear response for the analytes and the internal standard dioctyl phthalate and applying relative response factors calculated from the molecular formula according to previously published method [50]. In the case of cinnamaldehyde, benzyl 3-phenylpropanoate and benzyl cinnamate the results were corrected with respect to experimentally determined calibration curves relative to dioctyl phthalate.

3.2. Synthesis of Model Imidazolium Salts and Poly(imidazolium) Carbosilane Dendrimers

General procedure. To a solution of the starting iodopropyl derivative $\text{G}_m(\text{PrI})_n$ (1.0 mmol) in acetonitrile (15 mL) a solution of a given imidazole (1.3 eq. for each iodide) in acetonitrile was added at 0 °C. The reaction mixture was then stirred at 70 °C for 48 h. The solvent was removed on the rotary evaporator and toluene (6 mL) was added to the residue to wash out the unreacted imidazole. The mixture was stirred at 80 °C for 6 h, let to cool down and decanted at room temperature. The residue was dried under vacuum to afford the product.

1-Methyl-3-[3-(butyldimethylsilyl)]propylimidazolium iodide (G_0MeImI). The compound was prepared from 3-(butyldimethylsilyl)propyl iodide (1 g, 3.52 mmol) and 1-methylimidazole (0.35 g, 4.22 mmol). Yield: 1.2 g (3.31 mmol, 94%) of a yellow liquid. ^1H NMR (DMSO- d_6 , 400 MHz, H-H COSY): δ −0.04 (s, 6H, SiMe_2), 0.39–0.43 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 0.46–0.50 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.85 (t, J = 7.0 Hz, 3H, CH_3CH_2), 1.18–1.32 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.71–1.79 (m, 2H, $\text{CH}_2\text{CH}_2\text{N}$), 3.85 (s, 3H, NMe), 4.12 (t, J = 7.2 Hz, 2H, CH_2N), 7.70, 7.77, 9.11 (3 $\times$ t, J = 1.7 Hz, 3 $\times$ 1H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz, HSQC, HMBC): δ −3.5 (SiMe_2), 11.1 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 13.7 (CH_2CH_3), 14.2 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 25.5, 26.0 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 35.8 (NMe), 51.6 (CH_2N), 122.2, 123.6, 136.5 (3 $\times$ CH). $^{29}\text{Si}\{^1\text{H}\}$ NMR (DMSO- d_6 , 80 MHz): δ 2.87. HRMS (ESI⁺) [$\text{C}_{13}\text{H}_{27}\text{N}_2\text{Si}$]⁺ calc. 239.1938 [M-I]⁺, found 239.1943 (100%).

1-Isopropyl-3-[3-(butyldimethylsilyl)]propylimidazolium iodide (G_0iPrImI). The compound was prepared from 3-(butyldimethylsilyl)propyl iodide (0.21 g, 0.74 mmol) and 1-isopropylimidazole (0.11 g, 1.00 mmol). Yield: 0.25 g (0.64 mmol, 87%) of a brownish yellow viscous liquid. ^1H NMR (DMSO- d_6 , 400 MHz, H-H COSY): δ −0.05 (s, 6H, SiMe_2), 0.39–0.45 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 0.46–0.50 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.84 (t, J = 7.0 Hz, 3H, CH_3CH_2), 1.19–1.30 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.47 (d, J = 7.0 Hz, 6H, CHMe_2), 1.74–1.82 (m, 2H, $\text{CH}_2\text{CH}_2\text{N}$), 4.12 (t, J = 7.2 Hz, 2H, CH_2N), 4.65 (hept, J = 7.0 Hz, 1H, CHMe), 7.84, 7.93, 9.31 (3 $\times$ t, J = 1.7 Hz, 3 $\times$ 1H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz, HSQC, HMBC): δ −3.5 (SiMe_2), 11.1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 13.6 (CH_2CH_3), 14.1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 22.3 (CHMe_2), 24.3 ($\text{CH}_2\text{CH}_2\text{N}$), 25.5, 25.9 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 51.6 (CH_2N), 52.1 (CHMe_2), 120.5, 122.4, 134.7 (3 $\times$ CH). $^{29}\text{Si}\{^1\text{H}\}$ NMR (DMSO- d_6 , 80 MHz): δ 2.86. HRMS (ESI⁺) [$\text{C}_{15}\text{H}_{31}\text{N}_2\text{Si}$]⁺ calc. 267.2251 [M-I]⁺, found 267.2256 (100%); (ESI[−]) I[−] calc. 126.9039, found 126.9045 (100%).

1-(2,6-diisopropylphenyl)-3-[3-(butyldimethylsilyl)]propylimidazolium iodide ($\text{G}_0\text{DippImI}$). The compound was prepared from 3-(butyldimethylsilyl)propyl iodide (0.11 g, 0.38 mmol)

and 1-(2,6-diisopropylphenyl)imidazole (0.12 g, 0.52 mmol). Yield: 0.18 g (0.35 mmol, 93%) of a yellow solid. ^1H NMR (DMSO- d_6 , 400 MHz, H-H COSY): δ −0.03 (s, 6H, SiMe₂), 0.30–0.34 (m, 2H, CH₂CH₂CH₂N), 0.47–0.51 (m, 2H, CH₂CH₂CH₂CH₃), 0.85 (t, J = 7.1 Hz, 3H, CH₃CH₂), 1.14 (t, J = 6.6 Hz, 12H, Me₂CH), 1.20–1.32 (m, 4H, CH₂CH₂CH₃), 1.83–1.90 (m, 2H, CH₂CH₂N), 2.25 (hept, J = 6.6 Hz, 2H, Me₂CH), 4.28 (t, J = 6.4 Hz, 2H, CH₂N), 7.47 (d, J = 7.8 Hz, 2H, CH_{Ph}), 7.64 (t, J = 7.8 Hz, 1H, CH_{Ph}), 8.13, 8.15, 9.62 (3 × t, J = 1.5 Hz, 3 × 1H, CH_{Im}). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz, HSQC): δ −3.6 (SiMe₂), 10.7 (CH₂CH₂CH₂N), 13.7 (CH₂CH₃), 14.2 (CH₂CH₂CH₂CH₃), 23.7, 23.8 (CHMe₂), 24.0 (CH₂CH₂N), 25.5, 26.0 (CH₂CH₂CH₃), 28.1 (CHMe), 52.2 (CH₂N), 123.4 (CH_{Im}), 124.4 (2 CH_{Ph}), 125.3 (CH_{Im}), 130.5 (N-C_q), 131.5 (CH_{Ph}), 137.7 (CH_{Im}), 145.0 (2 iPr-C_q). $^{29}\text{Si}\{^1\text{H}\}$ NMR (DMSO- d_6 , 80 MHz): δ 2.86. HRMS (ESI+) [C₂₄H₄₁N₂Si]⁺ calc. 385.3033 [M-I]⁺, found 385.3039 (100%); (ESI−) I[−] calc. 126.9039, found 126.9022 (100%).

Dendrimer G₁(MeImI)₄. The compound was prepared from dendrimer G₁(PrI)₄ (1.20 g, 1.09 mmol) and 1-methylimidazole (0.43 g, 5.21 mmol). Yield: 1.51 g (1.05 mmol, 97%) of a yellow liquid. ^1H NMR (DMSO- d_6 , 400 MHz, H-H COSY): δ −0.05 (s, 24H, SiMe₂), 0.38–0.42 (m, 8H, CH₂CH₂CH₂N), 0.50–0.56 (m, 16H, Si⁰CH₂CH₂CH₂), 1.26–1.33 (m, 8H, Si⁰CH₂CH₂), 1.70–1.78 (m, 8H, CH₂CH₂N), 3.86 (s, 12H, NMe), 4.11 (t, J = 7.2 Hz, 8H, CH₂N), 7.80, 7.90, 9.13 (3 × t, J = 1.8 Hz, 3 × 4H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz, HSQC, HMBC): δ −3.5 (SiMe₂), 11.3 (CH₂CH₂CH₂N), 16.9 (Si⁰CH₂), 18.1 (Si⁰CH₂CH₂), 19.3 (Si⁰CH₂CH₂CH₂), 24.4 (CH₂CH₂N), 35.8 (NMe), 51.5 (CH₂N), 122.2, 123.5, 136.4 (3 × CH). $^{29}\text{Si}\{^1\text{H}\}$ NMR (DMSO- d_6 , 80 MHz): δ 0.73 (Si⁰), 2.25 (Si¹). HRMS (ESI+) [C₄₈H₉₆N₈Si₅I₃]⁺ calc. 1305.3733 [M-I]⁺, found 1305.3734 (100%); [C₄₈H₉₆N₈Si₅I₂]²⁺ calc. 589.2341 [M-2I]²⁺, found 589.2348 (100%); [C₄₈H₉₆N₈Si₅I]³⁺ calc. 350.5211 [M-3I]³⁺, found 350.5212 (100%); [C₄₈H₉₆N₈Si₅]⁴⁺ calc. 231.1645 [M-4I]⁴⁺, found 231.1645 (100%).

Dendrimer G₂(MeImI)₈. The compound was prepared from dendrimer G₂(PrI)₈ (1.00 g, 0.40 mmol) and 1-methylimidazole (0.36 g, 4.40 mmol). Yield: 1.17 g (0.37 mmol, 93%) of a pale yellow waxy solid. ^1H NMR (DMSO- d_6 , 400 MHz, H-H COSY): δ −0.11 (s, 12H, SiMe), −0.06 (s, 48H, SiMe₂), 0.38–0.42 (m, 16H, CH₂CH₂CH₂N), 0.49–0.55 (m, 48H, Si¹CH₂CH₂CH₂), 1.24–1.32 (m, 24H, Si¹CH₂CH₂), 1.70–1.78 (m, 16H, CH₂CH₂N), 3.86 (brs, 24H, NMe), 4.12 (t, J = 7.2 Hz, 16H, CH₂N), 7.72, 7.77, 9.15 (3 × m, 3 × 8H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz, HSQC, HMBC): δ −4.9 (SiMe), −3.5 (SiMe₂), 11.3 (CH₂CH₂CH₂N), 17.1 (Si⁰CH₂), 18.0 (Si¹CH₂CH₂CH₂Si²), overlapped (Si⁰CH₂CH₂), 18.2 (Si¹CH₂CH₂CH₂Si²), 18.5 (Si⁰CH₂CH₂CH₂), 19.3 (Si¹CH₂CH₂CH₂Si²), 24.4 (CH₂CH₂N), 35.8 (NMe), 51.5 (CH₂N), 122.2, 123.6, 136.5 (3 × CH). $^{29}\text{Si}\{^1\text{H}\}$ NMR (DMSO- d_6 , 80 MHz): δ 0.82 (Si⁰), 1.06 (Si¹), 2.22 (Si²). HRMS (ESI+) [C₁₁₂H₂₂₈N₁₆Si₁₃I₇]⁺ calc. 3051.8667 [M-I]⁺, found 3051.8731 (100%); [C₁₁₂H₂₂₈N₁₆Si₁₃I₆]²⁺ calc. 1462.4808 [M-2I]²⁺, found 1462.4803 (100%); [C₁₁₂H₂₂₈N₁₆Si₁₃I₅]³⁺ calc. 932.6855 [M-3I]³⁺, found 932.6856 (100%); [C₁₁₂H₂₂₈N₁₆Si₁₃I₄]⁴⁺ calc. 667.7879 [M-4I]⁴⁺, found 667.7897 (100%); [C₁₁₂H₂₂₈N₁₆Si₁₃I₃]⁵⁺ calc. 508.8493 [M-5I]⁵⁺, found 508.8498 (100%).

Dendrimer G₃(MeImI)₁₆. The compound was prepared from dendrimer G₃(PrI)₁₆ (0.65 g, 0.12 mmol) and 1-methylimidazole (0.24 g, 2.90 mmol). Yield: 0.74 g (0.11 mmol, 92%) of a yellow waxy solid. ^1H NMR (DMSO- d_6 , 400 MHz, H-H COSY): δ −0.13 (s, 12H, Si¹Me), −0.11 (s, 24H, Si²Me), −0.06 (s, 96H, SiMe₂), 0.39–0.43 (m, 32H, CH₂CH₂CH₂N), 0.49–0.55 (m, 112H, SiCH₂CH₂CH₂Si), 1.24–1.32 (m, 56H, SiCH₂CH₂CH₂Si), 1.71–1.79 (m, 32H, CH₂CH₂N), 3.87 (s, 48H, NMe), 4.13 (t, J = 7.3 Hz, 32H, CH₂N), 7.73, 7.80, 9.19 (3 × brs, 3 × 16H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz, HSQC, HMBC): δ −4.9 (Si^{1,2}Me), −3.5 (SiMe₂), 11.3 (CH₂CH₂CH₂N), 17.1 (Si⁰CH₂), 18.0 (Si²CH₂CH₂CH₂Si³), 18.1, 18.4 (Si¹CH₂CH₂CH₂Si²), overlapped (Si⁰CH₂CH₂), 18.2 (Si²CH₂CH₂CH₂Si³), 18.6 (Si⁰CH₂CH₂CH₂), 19.3 (Si²CH₂CH₂CH₂Si³), 24.4 (CH₂CH₂N), 35.9 (NMe), 51.5 (CH₂N), 122.2, 123.5, 136.4 (3 × CH). $^{29}\text{Si}\{^1\text{H}\}$ NMR (DMSO- d_6 , 80 MHz): δ 0.77 (Si⁰), 1.04 (Si^{1,2}), 2.20 (Si³). HRMS (ESI+) [C₂₄₀H₄₉₂N₃₂Si₂₉I₁₅]⁺ calc. 6543.8509 [M-I]⁺, [C₂₄₀H₄₉₂N₃₂Si₂₉I₁₄]²⁺ calc. 3208.4729 [M-2I]²⁺, both out of range; [C₂₄₀H₄₉₂N₃₂Si₂₉I₁₃]³⁺ calc. 2096.6803 [M-3I]³⁺, found 2096.7014 (100%); [C₂₄₀H₄₉₂N₃₂Si₂₉I₁₂]⁴⁺ calc. 1540.7840 [M-4I]⁴⁺, found 1540.7580 (100%); [C₂₄₀H₄₉₂N₃₂Si₂₉I₁₁]⁵⁺ calc. 1207.2461 [M-5I]⁵⁺, found 1207.2463 (100%);

$[C_{240}H_{492}N_{32}Si_{29}I_{10}]^{6+}$ calc. 984.8876 $[M-6I]^{6+}$, found 984.8814 (100%); $[C_{240}H_{492}N_{32}Si_{29}I_9]^{7+}$ calc. 826.0601 $[M-7I]^{7+}$, found 826.0625 (100%); $[C_{240}H_{492}N_{32}Si_{29}I_8]^{8+}$ calc. 706.9394 $[M-8I]^{8+}$, found 706.9372 (100%); $[C_{240}H_{492}N_{32}Si_{29}I_7]^{9+}$ calc. 614.2900 $[M-9I]^{9+}$, found 614.2889 (100%); $[C_{240}H_{492}N_{32}Si_{29}I_6]^{10+}$ calc. 540.1706 $[M-10I]^{10+}$, found 540.1754 (100%).

Dendrimer G₁(iPrImI)₄. The compound was prepared from dendrimer **G₁(PrI)₄** (0.35 g, 0.32 mmol) and 1-isopropylimidazole (0.19 g, 1.72 mmol). Yield: 0.36 g (0.23 mmol, 73%) of a brownish yellow viscous liquid. ¹H NMR (DMSO-*d*₆, 400 MHz, H-H COSY): δ −0.05 (s, 24H, SiMe₂), 0.38–0.42 (m, 8H, CH₂CH₂CH₂N), 0.50–0.56 (m, 16H, SiCH₂CH₂CH₂Si), 1.26–1.32 (m, 8H, Si⁰CH₂CH₂), 1.47 (d, *J* = 6.7 Hz, 24H, CHMe₂), 1.72–1.80 (m, 8H, CH₂CH₂N), 4.09 (t, *J* = 7.3 Hz, 8H, CH₂N), 4.62 (hept, *J* = 6.7 Hz, 4H, CHMe₂), 7.80, 7.90 (2 × t, *J* = 1.7 Hz, 2 × 4H, CH), 9.24 (brs, 4H, CH). ¹³C{¹H} NMR (DMSO-*d*₆, 101 MHz, HSQC): δ −3.5 (SiMe₂), 11.5 (CH₂CH₂CH₂N), 17.0 (Si⁰CH₂), 18.2 (Si⁰CH₂CH₂), 19.4 (Si⁰CH₂CH₂CH₂), 22.4 (CHMe₂), 24.4 (CH₂CH₂N), 51.7 (CH₂N), 52.3 (CHMe₂), 120.6, 122.5 (2 × CH), (from HSQC) 134.5 (CH). ²⁹Si{¹H} NMR (DMSO-*d*₆, 80 MHz): δ 0.72 (Si⁰), 2.25 (Si¹). HRMS (ESI+) $[C_{56}H_{112}N_8Si_5I_3]^+$ calc. 1417.4985 $[M-I]^+$, found 1417.4972 (100%); $[C_{56}H_{112}N_8Si_5I_2]^{2+}$ calc. 645.2967 $[M-2I]^{2+}$, found 645.2965 (100%); $[C_{56}H_{112}N_8Si_5I]^{3+}$ calc. 387.8961 $[M-3I]^{3+}$, found 387.8957 (100%); $[C_{56}H_{112}N_8Si_5]^{4+}$ calc. 259.1958 $[M-4I]^{4+}$, found 259.1963 (100%).

Dendrimer G₂(iPrImI)₈. The compound was prepared from dendrimer **G₂(PrI)₈** (0.42 g, 0.16 mmol) and 1-isopropylimidazole (0.19 g, 1.72 mmol). Yield: 0.39 g (0.37 mmol, 69%) of a brownish yellow viscous liquid. ¹H NMR (DMSO-*d*₆, 400 MHz, H-H COSY): δ −0.12 (s, 12H, SiMe), −0.06 (s, 48H, SiMe₂), 0.38–0.42 (m, 16H, CH₂CH₂CH₂N), 0.49–0.55 (m, 48H, Si¹CH₂CH₂CH₂), 1.24–1.32 (m, 24H, Si¹CH₂CH₂), 1.48 (d, *J* = 6.7 Hz, 48H, CHMe₂), 1.73–1.81 (m, 16H, CH₂CH₂N), 4.11 (t, *J* = 7.4 Hz, 16H, CH₂N), 4.64 (hept, *J* = 6.6 Hz, 8H, CHMe₂), 7.83, 7.93, 9.30 (3 × brs, 3 × 8H, CH). ¹³C{¹H} NMR (DMSO-*d*₆, 101 MHz, HSQC, HMBC): δ −4.9 (SiMe), −3.5 (SiMe₂), 11.3 (CH₂CH₂CH₂N), 17.1 (Si⁰CH₂), 18.0 (Si¹CH₂CH₂CH₂Si²), 18.1 (Si⁰CH₂CH₂), 18.2 (Si¹CH₂CH₂CH₂Si²), 18.5 (Si⁰CH₂CH₂CH₂), 19.3 (Si¹CH₂CH₂CH₂Si²), 22.4 (CHMe₂), 24.3 (CH₂CH₂N), 51.7 (CH₂N), 52.2 (CHMe₂), 120.6, 122.5, 134.7 (3 × CH). ²⁹Si{¹H} NMR (DMSO-*d*₆, 80 MHz): δ 0.79 (Si⁰), 1.04 (Si¹), 2.22 (Si²). HRMS (ESI+) $[C_{128}H_{260}N_{16}Si_{13}I_7]^+$ calc. 3276.1174 $[M-I]^+$, out of range; $[C_{128}H_{260}N_{16}Si_{13}I_6]^{2+}$ calc. 1574.6062 $[M-2I]^{2+}$, found 1574.6064 (100%); $[C_{128}H_{260}N_{16}Si_{13}I_5]^{3+}$ calc. 1007.4358 $[M-3I]^{3+}$, found 1007.4360 (100%); $[C_{128}H_{260}N_{16}Si_{13}I_4]^{4+}$ calc. 723.8506 $[M-4I]^{4+}$, found 723.8510 (100%); $[C_{128}H_{260}N_{16}Si_{13}I_3]^{5+}$ calc. 553.6995 $[M-5I]^{5+}$, found 553.6983 (100%); $[C_{128}H_{260}N_{16}Si_{13}I_2]^{6+}$ calc. 440.2654 $[M-6I]^{6+}$, found 440.2642 (100%).

Dendrimer G₁(DippImI)₄. The compound was prepared from dendrimer **G₁(PrI)₄** (0.25 g, 0.22 mmol) and 1-(2,6-diisopropylphenyl)imidazole (0.27 g, 1.18 mmol). Yield: 0.26 g (0.13 mmol, 59%) of a yellow solid. ¹H NMR (DMSO-*d*₆, 400 MHz, H-H COSY): δ −0.05 (s, 24H, SiMe₂), 0.29–0.34 (m, 8H, CH₂CH₂CH₂N), 0.51–0.56 (m, 16H, Si⁰CH₂CH₂CH₂), 1.14 (d, *J* = 6.8 Hz, 48H, Me₂CH), 1.28–1.33 (m, 8H, Si⁰CH₂CH₂), 1.82–1.89 (m, 8H, CH₂CH₂N), 2.25 (hept, *J* = 6.8 Hz, 8H, Me₂CH), 4.29 (t, *J* = 6.3 Hz, 8H, CH₂N), 7.47 (d, *J* = 7.8 Hz, 8H, CH_{Ph}), 7.64 (t, *J* = 7.8 Hz, 4H, CH_{Ph}), 8.13, 8.16, 9.64 (3 × t, *J* = 1.7 Hz, 3 × 4H, CH_{Im}). ¹³C{¹H} NMR (DMSO-*d*₆, 101 MHz, HSQC, HMBC): δ −3.6 (SiMe₂), 11.0 (CH₂CH₂CH₂N), 16.9 (Si⁰CH₂), 18.1 (Si⁰CH₂CH₂), 19.3 (Si⁰CH₂CH₂CH₂), 23.7, 23.8 (CHMe₂), 23.9 (CH₂CH₂N), 28.1 (CHMe₂), 52.1 (CH₂N), 123.4 (CH_{Im}), 124.4 (2 CH_{Ph}), 125.2 (CH_{Im}), 130.5 (N-C_q), 131.5 (CH_{Ph}), 137.6 (CH_{Im}), 145.0 (2 *i*Pr-C_q). ²⁹Si{¹H} NMR (DMSO-*d*₆, 80 MHz): δ 0.77 (Si⁰), 2.23 (Si¹). HRMS (ESI+) $[C_{92}H_{152}N_8Si_5I_3]^+$ calc. 1890.8410 $[M-I]^+$, found 1890.8392 (100%); $[C_{92}H_{152}N_8Si_5I_2]^{2+}$ calc. 881.9545 $[M-2I]^{2+}$, found 881.9556 (100%); $[C_{92}H_{152}N_8Si_5I]^{3+}$ calc. 545.6680 $[M-3I]^{3+}$, found 545.6674 (100%); $[C_{92}H_{152}N_8Si_5]^{4+}$ calc. 377.5247 $[M-4I]^{4+}$, found 377.5241 (100%).

Dendrimer G₂(DippImI)₈. The compound was prepared from dendrimer **G₂(PrI)₈** (0.26 g, 0.10 mmol) and 1-(2,6-diisopropylphenyl)imidazole (0.25 g, 1.10 mmol). Yield: 0.24 g (55 μmol, 53%) of a yellow solid. ¹H NMR (DMSO-*d*₆, 400 MHz, H-H COSY): δ −0.11 (s, 12H, SiMe), −0.05 (s, 48H, SiMe₂), 0.29–0.33 (m, 16H, CH₂CH₂CH₂N), 0.51–0.58 (m,

48H, Si¹CH₂CH₂CH₂), 1.14 (d, *J* = 6.9 Hz, 96H, Me₂CH), 1.29–1.33 (m, 24H, Si¹CH₂CH₂), 1.81–1.88 (m, 16H, CH₂CH₂N), 2.24 (hept, *J* = 6.9 Hz, 16H, Me₂CH), 4.28 (brs, 16H, CH₂N), 7.46 (d, *J* = 7.8 Hz, 16H, CH_{Ph}), 7.64 (t, *J* = 7.8 Hz, 8H, CH_{Ph}), 8.13 (brs, 16H, CH_{Im}), 9.62 (brs, 8H, CH_{Im}). ¹³C{¹H} NMR (DMSO-*d*₆, 101 MHz, HSQC, HMBC): δ −4.9 (SiMe), −3.6 (SiMe₂), 10.9 (CH₂CH₂CH₂N), 17.1 (Si⁰CH₂), 18.0 (Si¹CH₂CH₂CH₂Si²), 18.1 (Si⁰CH₂CH₂), 18.3 (Si¹CH₂CH₂CH₂Si²), 18.5 (Si⁰CH₂CH₂CH₂), 19.3 (Si¹CH₂CH₂CH₂Si²), 23.7, 23.8 (Me₂CH), 23.9 (CH₂CH₂N), 28.1 (CHMe), 52.1 (CH₂N), 123.4 (CH_{Im}), 124.4 (2 CH_{Ph}), 125.2 (CH_{Im}), 130.5 (N-C_q), 131.5 (CH_{Ph}), 137.6 (CH_{Im}), 145.0 (2 *i*Pr-C_q). ²⁹Si{¹H} NMR (DMSO-*d*₆, 80 MHz): δ 0.81 (Si⁰), 1.06 (Si¹), 2.21 (Si²). HRMS (ESI+) [C₂₀₀H₃₄₀N₁₆Si₁₃I₇]⁺ calc. 4221.7459 [M-I]⁺, out of range; [C₂₀₀H₃₄₀N₁₆Si₁₃I₆]²⁺ calc. 2047.4204 [M-2I]²⁺, found 2047.4186 (100%); [C₂₀₀H₃₄₀N₁₆Si₁₃I₅]³⁺ calc. 1322.6453 [M-3I]³⁺, found 1322.6446 (100%); [C₂₀₀H₃₄₀N₁₆Si₁₃I₄]⁴⁺ calc. 960.2577 [M-4I]⁴⁺, found 960.2585 (100%); [C₂₀₀H₃₄₀N₁₆Si₁₃I₃]⁵⁺ calc. 742.8252 [M-5I]⁵⁺, found 742.8249 (100%); [C₂₀₀H₃₄₀N₁₆Si₁₃I₂]⁶⁺ calc. 597.8701 [M-6I]⁶⁺, found 597.8712 (100%); [C₂₀₀H₃₄₀N₁₆Si₁₃I]⁷⁺ calc. 494.3308 [M-7I]⁷⁺, found 494.3315 (100%).

Dendrimer G₃(DippImI)₁₆. The compound was prepared from dendrimer G₃(PrI)₁₆ (0.27 g, 51 μmol) and 1-(2,6-diisopropylphenyl)imidazole (0.24 g, 1.06 mmol). Yield: 0.26 g (29 μmol, 58%) of a brownish yellow viscous liquid. ¹H NMR (DMSO-*d*₆, 400 MHz, H-H COSY): δ −0.11 (brs, 36H, SiMe, Si²Me₂), −0.06 (s, 96H, Si³Me₂), 0.32 (m, 32H, CH₂CH₂CH₂N), 0.54 (m, 112H, SiCH₂CH₂CH₂Si), 1.13 (d, *J* = 6.8 Hz, 192H, Me₂CH), 1.29 (m, 56H, SiCH₂CH₂CH₂Si), 1.87 (m, 32H, CH₂CH₂N), 2.26 (hept, *J* = 6.9 Hz, 32H, Me₂CH), 4.33 (brs, 32H, CH₂N), 7.46 (d, *J* = 7.8 Hz, 32H, CH_{Ph}), 7.64 (t, *J* = 7.8 Hz, 16H, CH_{Ph}), 8.14, 8.22, 9.71 (3 × brs, 3 × 16H, CH_{Im}). ¹³C{¹H} NMR (DMSO-*d*₆, 101 MHz, HSQC, HMBC): δ −4.9 (Si^{1,2}Me), −3.6 (Si³Me₂), 10.9 (CH₂CH₂CH₂N), not detected (Si⁰CH₂CH₂CH₂), 18.0 (Si²CH₂CH₂CH₂Si³), 18.1, 18.4 (Si¹CH₂CH₂CH₂Si²), 18.2 (Si²CH₂CH₂CH₂Si³), 19.3 (Si²CH₂CH₂CH₂Si³), 23.7, 23.8 (Me₂CH), 24.0 (CH₂CH₂N), 28.1 (CHMe), 52.1 (CH₂N), 123.4 (CH_{Im}), 124.4 (2 CH_{Ph}), 125.2 (CH_{Im}), 130.4 (N-C_q), 131.5 (CH_{Ph}), 137.6 (CH_{Im}), 145.0 (2 *i*Pr-C_q). ²⁹Si{¹H} NMR (DMSO-*d*₆, 80 MHz): δ not detected (Si⁰), 1.04 (Si^{1,2}), 2.18 (Si³). HRMS (ESI+) [C₄₁₆H₇₁₆N₃₂Si₂₉I₁₅]⁺ calc. 8883.6098 [M-I]⁺, [C₄₁₆H₇₁₆N₃₂Si₂₉I₁₄]²⁺ calc. 4378.3524 [M-2I]²⁺, both out of range; [C₄₁₆H₇₁₆N₃₂Si₂₉I₁₃]³⁺ calc. 2836.5999 [M-3I]³⁺, found 2836.6001 (100%); [C₄₁₆H₇₁₆N₃₂Si₂₉I₁₂]⁴⁺ calc. 2125.7237 [M-4I]⁴⁺, found 2125.7254 (100%); [C₄₁₆H₇₁₆N₃₂Si₂₉I₁₁]⁵⁺ calc. 1675.1979 [M-5I]⁵⁺, found 1675.2001 (100%); [C₄₁₆H₇₁₆N₃₂Si₂₉I₁₀]⁶⁺ calc. 1374.8474 [M-6I]⁶⁺, found 1374.8471 (100%); [C₄₁₆H₇₁₆N₃₂Si₂₉I₉]⁷⁺ calc. 1160.3113 [M-7I]⁷⁺, found 1160.3122 (100%); [C₄₁₆H₇₁₆N₃₂Si₂₉I₈]⁸⁺ calc. 999.4093 [M-8I]⁸⁺, found 999.4080 (100%).

3.3. Redox Esterification of Cinnamaldehyde

In a typical experiment, 2.8 mg (5.0 μmol) of G₀DippImI was placed in a Schlenk flask which was then three times evacuated and refilled with argon. Cinnamaldehyde (66 mg, 0.50 mmol), alcohol (2.00 mmol), DBU (1.5 mg, 0.01 mmol) and internal standard for GC dioctyl phthalate (59 mg, 0.15 mmol) followed by 5 mL of toluene were added under the flow of argon. All components were thoroughly mixed, 30 μL sample was withdrawn for GC analysis and the reaction mixture was heated for a specified time in the oil bath of constant temperature (100 °C unless otherwise noted). Then the mixture was let to cool down and analyzed by GC. In case that samples were taken in the course of experiment for kinetic studies, for each point 30 μL of the reaction mixture was withdrawn via syringe under the flow of argon, dissolved in cold DCM and stored in refrigerator till analysis.

For the purpose of substrate screening of alcohols, a stock solution of cinnamaldehyde (0.1 mol.L^{−1}), DBU (4.0 mmol.L^{−1}) and dioctyl phthalate (0.03 mol.L^{−1}) in toluene and stock solutions of precatalysts in MeOH (20 mmol.L^{−1} with respect to active centers) were prepared and stored under argon at 4 °C. The composition of aldehyde stock solution was confirmed by GC-FID. In a typical experiment, 100 μL of a stock solution of a given precatalyst was placed in a Schlenk flask and the solvent was evaporated in vacuum. The flask was then three times evacuated and refilled with argon and 1.0 mL of substrate stock

solution was added under the flow of argon followed by 0.4 mmol of the corresponding alcohol. The reaction mixture was heated for a specified time to 100 °C in the oil bath and samples for GC were taken to follow the reaction progress. For the reactions with higher catalyst loading the amount of precatalyst stock solutions and the concentration of DBU in the stock solution were correspondingly increased.

The procedure for substrate screening of aldehydes was analogous, using stock solution of benzyl alcohol (0.4 mol.L⁻¹), DBU (0.01 mol.L⁻¹) and dioctyl phthalate (0.03 mol.L⁻¹) in toluene to which the particular aldehyde (0.1 mmol) was added. Before the heating of the reaction mixture, a sample for GC was taken to confirm the ratio of the aldehyde to the internal standard.

Recycling experiments were performed on a larger scale without internal standard. The first cycle was set up with 1.00 mmol of cinnamaldehyde (132 mg), 4.00 mmol of benzyl alcohol (433 mg), 25.0 µmol of **G₁(DippImI)₄** (50.0 mg) and 0.15 mmol of DBU (23 mg) in 5 mL of toluene; the batch size in the following cycles was adapted to correspond with the amount of recycled precatalyst. The same concentration of all components at the start of all reaction runs was maintained, except benzyl alcohol, 50% of which was replaced by *tert*-butyl alcohol. After each cycle, **G₁(DippImI)₄** was separated from the reaction mixture by nanofiltration (*vide supra*), dried, weighted and checked by ESI MS. The product containing permeate was evaporated in vacuum, dissolved in dichloromethane, filtered through a short pad of silica gel and evaporated to dryness to afford the target ester.

3.4. Organic Solvent Nanofiltration

Nanofiltration was carried out using solvent resistant stirred cell (Millipore) equipped with 1 kDa MWCO regenerated cellulose ultrafiltration discs Ultracel® (Millipore) and PTFE encapsulated O-rings (ERIKS), with nitrogen as a driving gas. Reaction mixture was quantitatively transferred into the cell, diluted with methanol to a total volume of 25 mL and passed through the membrane until the residual volume 1 mL of retentate was reached. The retentate was diluted with 20 mL of methanol and filtered; this procedure was repeated 3 times and subsequently the retentate was withdrawn via cannula. The inner space of the cell was washed with 3 × 2 mL of methanol and the retentate and washings were combined and evaporated under vacuum to recover the dendritic catalyst. The cell was not disassembled and it was used directly for the next separation cycle. The product was obtained after the permeate workup.

4. Conclusions

We have demonstrated the feasibility of immobilization of imidazolium salts on the dendrimer periphery and their use as multivalent carbene precursors in NHC catalysed redox esterification of α,β -enals. Although the immobilization led to expected decrease of catalytic activity, the deactivation can be limited by appropriate substitution on imidazolium. From the studied types, Dipp substituted catalysts were least influenced and exhibited high activity and selectivity in the reactions with primary alcohols. On the other hand, the bulky Dipp substituent hinders the reaction with secondary alcohols, for which a clear relationship between the steric hindrance of the alcohol nucleophile and the yield and purity of the product was observed. This drop in both activity and selectivity is much less pronounced for methyl substituted dendritic NHCs, which makes them more competent catalysts in the case of alicyclic alcohols. The concept of dendritic catalyst recycling by nanofiltration, although not new, has been shown as especially suited for this class of active species. The separation from the reaction mixture was effective and the catalyst recovery was high even for the first generation Dipp imidazolium dendrimer. Moreover, OSN induced an increase of catalytic activity, partially compensating for the negative effect of immobilization. Such “activation” can be ascribed to a shift in the equilibrium between imidazolium iodide and the corresponding carbene induced by separation of DBU salt during nanofiltration. Dipp substituted NHCs proved to be particularly stable. At least a part of these carbene moieties was present in the recycled material even after several

weeks and it was capable to induce the redox esterification without added base which can, together with catalyst recycling, contribute to higher atom economy of the process.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111317/s1>, NMR spectra of all prepared precatalysts; synthesis and characterization of previously unpublished esters, EI-MS spectra of all identified products from redox esterification experiments; extended results of substrate screening of aldehydes; selected HRMS spectra of recycled **G₁(DippImI)₄**.

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References

- Xin, B.; Hao, J. Imidazolium-Based Ionic Liquids Grafted on Solid Surfaces. *Chem. Soc. Rev.* **2014**, *43*, 7171–7187. [CrossRef] [PubMed]
- Zhang, S.; Zhang, J.; Zhang, Y.; Deng, Y. Nanoconfined Ionic Liquids. *Chem. Rev.* **2017**, *117*, 6755–6833. [CrossRef] [PubMed]
- Fournier, A.H.; de Robillard, G.; Devillers, C.H.; Plasseraud, L.; Andrieu, J. Imidazolium and Potassium Hydrogen Carbonate Salts as Ecofriendly Organocatalysts for Oxazolidinone Synthesis. *Eur. J. Org. Chem.* **2016**, *2016*, 3514–3518. [CrossRef]
- Chakraborty Ghosal, N.; Santra, S.; Das, S.; Hajra, A.; Zyryanov, G.V.; Majee, A. Organocatalysis by an Aprotic Imidazolium Zwitterion: Regioselective Ring-Opening of Aziridines and Applicable to Gram Scale Synthesis. *Green Chem.* **2016**, *18*, 565–574. [CrossRef]
- Ghosh, D.; Lee, J.-Y.; Liu, C.-Y.; Chiang, Y.-H.; Lee, H.M. Direct C-H Arylations of Unactivated Arenes Catalyzed by Amido-Functionalized Imidazolium Salts. *Adv. Synth. Catal.* **2014**, *356*, 406–410. [CrossRef]
- Bobbink, F.D.; Dyson, P.J. Synthesis of Carbonates and Related Compounds Incorporating CO₂ using Ionic Liquid-Type Catalysts: State-of-the-Art and Beyond. *J. Catal.* **2016**, *343*, 52–61. [CrossRef]
- Büttner, H.; Longwitz, L.; Steinbauer, J.; Wulf, C.; Werner, T. Recent Developments in the Synthesis of Cyclic Carbonates from Epoxides and CO₂. *Top. Curr. Chem.* **2017**, *375*, 1–56. [CrossRef]
- Marion, N.; Díez-González, S.; Nolan, S.P. N-Heterocyclic Carbenes as Organocatalysts. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988–3000. [CrossRef]
- Ryan, S.J.; Candish, L.; Lupton, D.W. Acyl Anion Free N-Heterocyclic Carbene Organocatalysis. *Chem. Soc. Rev.* **2013**, *42*, 4906–4917. [CrossRef]
- Grossmann, A.; Enders, D. N-Heterocyclic Carbene Catalyzed Domino Reactions. *Angew. Chem. Int. Ed.* **2012**, *51*, 314–325. [CrossRef]
- Feroci, M.; Chiarotto, I.; Inesi, A. Advances in the Knowledge of N-Heterocyclic Carbenes Properties. The Backing of the Electrochemical Investigation. *Catalysts* **2016**, *6*, 178. [CrossRef]
- Menon, R.S.; Biju, A.T.; Nair, V. Recent Advances in Employing Homoenoates Generated by N-Heterocyclic Carbene (NHC) Catalysis in Carbon-Carbon Bond-Forming Reactions. *Chem. Soc. Rev.* **2015**, *44*, 5040–5052. [CrossRef]
- De Sarkar, S.; Biswas, A.; Samanta, R.C.; Studer, A. Catalysis with N-Heterocyclic Carbenes under Oxidative Conditions. *Chemistry* **2013**, *19*, 4664–4678. [CrossRef] [PubMed]
- Ma, S.; Toy, P. Self-Supported N-Heterocyclic Carbenes and Their Use as Organocatalysts. *Molecules* **2016**, *21*, 1100. [CrossRef] [PubMed]
- Cywar, R.M.; Wang, L.; Chen, E.Y.-X. Thermally Regulated Recyclable Carbene Catalysts for Upgrading of Biomass Furaldehydes. *ACS Sustain. Chem. Eng.* **2019**, *7*, 1980–1988. [CrossRef]
- Coupillaud, P.; Pinaud, J.; Guidolin, N.; Vignolle, J.; Fèvre, M.; Veaudecenne, E.; Mecerreyes, D.; Taton, D. Poly(Ionic Liquid)s Based on Imidazolium Hydrogen Carbonate Monomer Units as Recyclable Polymer-Supported N-Heterocyclic Carbenes: Use in Organocatalysis. *J. Polym. Sci. Part. A Polym. Chem.* **2013**, *51*, 4530–4540. [CrossRef]
- Barrett, A.G.M.; Love, A.C.; Tedeschi, L. ROMPgel-Supported Thiazolium Iodide: An Efficient Supported Organic Catalyst for Parallel Stetter Reactions. *Org. Lett.* **2004**, *6*, 3377–3380. [CrossRef]
- Strašák, T.; Št'astná, L.Č.; Bílková, V.; Skoupá, V.; Karban, J.; Cuřínová, P.; Čermák, J. Synthesis and Fluorophilicity of Compounds with Tris(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)Silyl Substituent. *J. Fluor. Chem.* **2015**, *178*, 23–29. [CrossRef]
- Strašák, T.; Čermák, J.; Červenková Št'astná, L.; Sýkora, J.; Fajgar, R. Cobalt(I) and Cobalt(III) Cyclopentadienyl Complexes with New Silicon-Branched Fluorous Tags. *J. Fluor. Chem.* **2014**, *159*, 15–20. [CrossRef]

20. Červenková Šťastná, L.; Bílková, V.; Cézová, T.; Cuřínová, P.; Karban, J.; Čermák, J.; Krupková, A.; Strašák, T. Imidazolium Based Fluorous N-Heterocyclic Carbenes as Effective and Recyclable Organocatalysts for Redox Esterification. *Eur. J. Org. Chem.* **2020**, *2020*, 3591–3598. [\[CrossRef\]](#)
21. Liu, Y.; Cheng, W.; Zhang, Y.; Sun, J.; Zhang, S. Controllable Preparation of Phosphonium-Based Polymeric Ionic Liquids as Highly Selective Nanocatalysts for the Chemical Conversion of CO₂ with Epoxides. *Green Chem.* **2017**, *19*, 2184–2193. [\[CrossRef\]](#)
22. Müllerová, M.; Šabata, S.; Matoušek, J.; Kormunda, M.; Holubová, J.; Bálková, R.; Petříčkovič, R.; Koštejn, M.; Kupčík, J.; Fajgar, R.; et al. Organoclays with Carbosilane Dendrimers Containing Ammonium or Phosphonium Groups. *New J. Chem.* **2018**, *42*, 1187–1196. [\[CrossRef\]](#)
23. Ding, M.; Jiang, H.L. Incorporation of Imidazolium-Based Poly(Ionic Liquid)s into a Metal-Organic Framework for CO₂ Capture and Conversion. *ACS Catal.* **2018**, *8*, 3194–3201. [\[CrossRef\]](#)
24. Poli, R. *Effects of Nanoconfinement on Catalysis*; Poli, R., Ed.; Springer International Publishing: Cham, The Netherlands, 2017. [\[CrossRef\]](#)
25. Tomalia, D.A. *Dendrimers and Other Dendritic Polymers*; Fréchet, J.M.J., Tomalia, D.A., Eds.; John Wiley & Sons, Ltd.: Chichester, UK, 2001; Volume 1. [\[CrossRef\]](#)
26. Perrier, A.; Keller, M.; Caminade, A.M.; Majoral, J.P.; Ouali, A. Efficient and Recyclable Rare Earth-Based Catalysts for Friedel-Crafts Acylations under Microwave Heating: Dendrimers Show the Way. *Green Chem.* **2013**, *15*, 2075–2080. [\[CrossRef\]](#)
27. Keller, M.; Perrier, A.; Linhardt, R.; Travers, L.; Wittmann, S.; Caminade, A.M.; Majoral, J.P.; Reiser, O.; Ouali, A. Dendrimers or Nanoparticles as Supports for the Design of Efficient and Recoverable Organocatalysts? *Adv. Synth. Catal.* **2013**, *355*, 1748–1754. [\[CrossRef\]](#)
28. Deng, G.-J.; Fan, Q.-H.; Chen, X.-M.; Liu, D.-S.; Chan, A.S.C. A Novel System Consisting of Easily Recyclable Dendritic Ru-BINAP Catalyst for Asymmetric Hydrogenation. *Chem. Commun.* **2002**, *15*, 1570–1571. [\[CrossRef\]](#)
29. Huang, Y.-Y.; He, Y.-M.; Zhou, H.-F.; Wu, L.; Li, B.-L.; Fan, Q.-H. Thermomorphic System with Non-Fluorous Phase-Tagged Ru(BINAP) Catalyst: Facile Liquid/Solid Catalyst Separation and Application in Asymmetric Hydrogenation. *J. Org. Chem.* **2006**, *71*, 2874–2877. [\[CrossRef\]](#)
30. Liu, J.; Ma, B.; Feng, Y.; He, Y.; Fan, Q.H. Dendritic [RuCl₂(BINAP)(DPEN)] Catalysts with “Sandwich” Multi-Layer Structure for Asymmetric Hydrogenation of Simple Aryl Ketones. *Inorg. Chim. Acta* **2014**, *409*, 106–111. [\[CrossRef\]](#)
31. Keller, M.; Collière, V.; Reiser, O.; Caminade, A.M.; Majoral, J.P.; Ouali, A. Pyrene-Tagged Dendritic Catalysts Noncovalently Grafted onto Magnetic Co/C Nanoparticles: An Efficient and Recyclable System for Drug Synthesis. *Angew. Chem. Int. Ed.* **2013**, *52*, 3626–3629. [\[CrossRef\]](#)
32. Bronstein, L.M. Magnetically Recoverable Catalysts with Dendritic Ligands for Enhanced Catalysis and Easy Separation. *ChemCatChem* **2015**, *7*, 1058–1060. [\[CrossRef\]](#)
33. Gaab, M.; Bellemin-Lapponnaz, S.; Gade, L.H. “Catalysis in a Tea Bag”: Synthesis, Catalytic Performance and Recycling of Dendrimer-Immobilised Bis- and Trisoxazoline Copper Catalysts. *Chemistry* **2009**, *15*, 5450–5462. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Nemanashi, M.; Meijboom, R. “Cat in a Bag” Recycling of Dendrimer Encapsulated Au Nanoparticles by Use of Dialysis Membrane Bag in the Reduction of 4-Nitrophenol: Proof of Heterogeneous Catalysis. *Catal. Commun.* **2016**, *83*, 53–57. [\[CrossRef\]](#)
35. Hovestad, N.J.; Eggeling, E.B.; Heidbüchel, H.J.; Jastrzebski, J.T.B.H.; Kragl, U.; Keim, W.; Vogt, D.; Van Koten, G. Selective Hydrovinylolation of Styrene in a Membrane Reactor: Use of Carbosilane Dendrimers with Hemilabile P,O Ligands. *Angew. Chem. Int. Ed.* **1999**, *38*, 1655–1658. [\[CrossRef\]](#)
36. Albrecht, M.; Hovestad, N.J.; Boersma, J.; Van Koten, G. Multiple Use of Soluble Metallodendritic Materials as Catalysts and Dyes. *Chemistry* **2001**, *7*, 1289–1294. [\[CrossRef\]](#)
37. Guerra, J.; Cantillo, D.; Kappe, C.O. Visible-Light Photoredox Catalysis Using a Macromolecular Ruthenium Complex: Reactivity and Recovery by Size-Exclusion Nanofiltration in Continuous Flow. *Catal. Sci. Technol.* **2016**, *6*, 4695–4699. [\[CrossRef\]](#)
38. Strašák, T.; Jaroschik, F.; Malý, M.; Čermák, J.; Sýkora, J.; Fajgar, R.; Karban, J.; Harakat, D. Titanocene Dichloride Complexes Bonded to Carbosilane Dendrimers via a Spacer of Variable Length—Molecular Dynamics Calculations and Catalysis of Allylic Coupling Reactions. *Inorg. Chim. Acta* **2014**, *409*, 137–146. [\[CrossRef\]](#)
39. Marchetti, P.; Jimenez Solomon, M.F.; Szekely, G.; Livingston, A.G. Molecular Separation with Organic Solvent Nanofiltration: A Critical Review. *Chem. Rev.* **2014**, *114*, 10735–10805. [\[CrossRef\]](#)
40. Červenková Šťastná, L.; Krupková, A.; Petrickovic, R.; Müllerová, M.; Matoušek, J.; Koštejn, M.; Cuřínová, P.; Jandová, V.; Šabata, S.; Strašák, T. Multivalent Bifunctional Carbosilane Dendrimer-Supported Ammonium and Phosphonium Organocatalysts for the Coupling of CO₂ and Epoxides. *ACS Sustain. Chem. Eng.* **2020**, *8*, 11692–11703. [\[CrossRef\]](#)
41. Strašák, T.; Malý, J.; Wróbel, D.; Malý, M.; Herma, R.; Čermák, J.; Müllerová, M.; Šťastná, L.Č.; Cuřínová, P. Phosphonium Carbosilane Dendrimers for Biomedical Applications-Synthesis, Characterization and Cytotoxicity Evaluation. *RSC Adv.* **2017**, *7*, 18724–18744. [\[CrossRef\]](#)
42. Cuřínová, P.; Krupková, A.; Červenková Šťastná, L.; Müllerová, M.; Čermák, J.; Strašák, T. ESI-TOF Mass Spectrometry of Cationic Carbosilane Dendrimers: A Potent Tool for Characterization of Structural Defects. *J. Mass Spectrom.* **2018**, *53*, 986–996. [\[CrossRef\]](#)
43. Chan, A.; Scheidt, K.A. Conversion of α,β -Unsaturated Aldehydes into Saturated Esters: An Umpolung Reaction Catalyzed by Nucleophilic Carbenes. *Org. Lett.* **2005**, *7*, 905–908. [\[CrossRef\]](#) [\[PubMed\]](#)

44. Wang, M.H.; Barsoum, D.; Schwamb, C.B.; Cohen, D.T.; Goess, B.C.; Riedrich, M.; Chan, A.; Maki, B.E.; Mishra, R.K.; Scheidt, K.A. Catalytic, Enantioselective β -Protonation through a Cooperative Activation Strategy. *J. Org. Chem.* **2017**, *82*, 4689–4702. [[CrossRef](#)] [[PubMed](#)]
45. Mahatthananchai, J.; Bode, J.W. The Effect of the N-Mesityl Group in NHC-Catalyzed Reactions. *Chem. Sci.* **2012**, *3*, 192–197. [[CrossRef](#)] [[PubMed](#)]
46. Maki, B.E.; Patterson, E.V.; Cramer, C.J.; Scheidt, K.A. Impact of Solvent Polarity on N-Heterocyclic Carbene-Catalyzed β -Protonations of Homoenolate Equivalents. *Org. Lett.* **2009**, *11*, 3942–3945. [[CrossRef](#)]
47. Maki, B.E.; Chan, A.; Scheidt, K.A. Protonation of Homoenolate Equivalents Generated by N-Heterocyclic Carbenes. *Synthesis* **2008**, *8*, 1306–1315. [[CrossRef](#)]
48. Sohn, S.S.; Bode, J.W. Catalytic Generation of Activated Carboxylates from Enals: A Product-Determining Role for the Base. *Org. Lett.* **2005**, *7*, 3873–3876. [[CrossRef](#)]
49. Yatham, V.R.; Harnying, W.; Kootz, D.; Neudörfl, J.M.; Schlörer, N.E.; Berkessel, A. 1,4-Bis-Dipp/Mes-1,2,4-Triazolylienes: Carbene Catalysts That Efficiently Overcome Steric Hindrance in the Redox Esterification of α - and β -Substituted α,β -Enals. *J. Am. Chem. Soc.* **2016**, *138*, 2670–2677. [[CrossRef](#)]
50. de Saint Laumer, J.-Y.; Cicchetti, E.; Merle, P.; Egger, J.; Chaintreau, A. Quantification in Gas Chromatography: Prediction of Flame Ionization Detector Response Factors from Combustion Enthalpies and Molecular Structures. *Anal. Chem.* **2010**, *82*, 6457–6462. [[CrossRef](#)]