DOI: 10.1002/adsc.201400641

Catalytic Synergism in a $\mathrm{C_{60}IL_{10}TEMPO_2}$ Hybrid in the Efficient Oxidation of Alcohols

Hazi Ahmad Beejapur,[a] Vincenzo Campisciano,[a] Francesco Giacalone,[a,*] and Michelangelo Gruttadauria[a,*]

[a] Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF) Sezione di Chimica, Università di Palermo, Viale delle Scienze s/n, Ed. 17, I-90128 Palermo, Italy
Fax: (+39)-091-596-825; phone: (+39)-091-238-97530; e-mail: francesco.giacalone@unipa.it or michelangelo.gruttadauria@unipa.it

Received: July 2, 2014; Revised: September 2, 2014; Published online: ■■ ■■, 0000

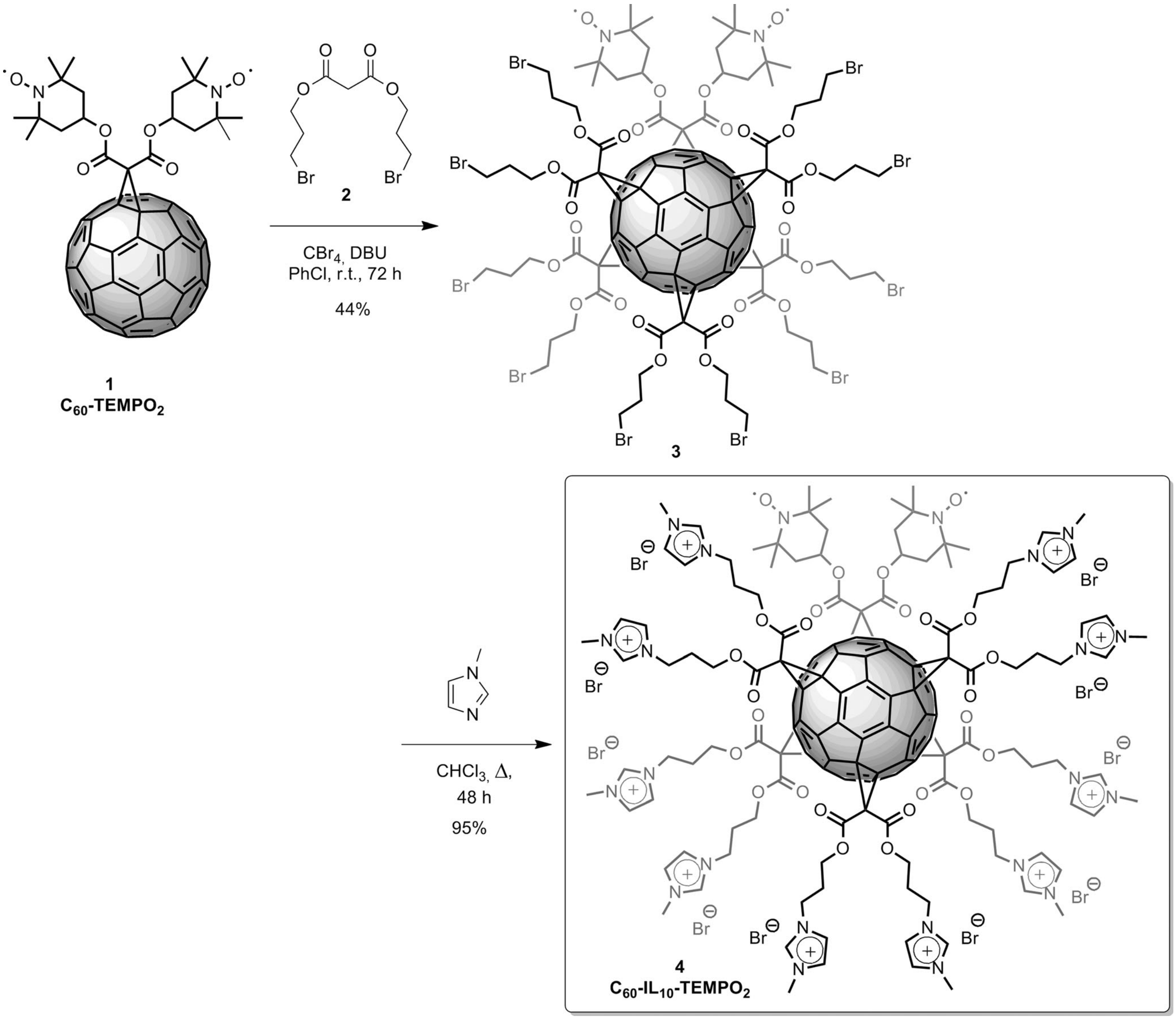
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400641.

Abstract: A novel fullerene [5:1]hexakisadduct bearing two 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) radicals and ten 1-propyl-3-methylimidazolium bromide moieties has been synthesized and characterized. Such an $\mathrm{C_{60}IL_{10}TEMPO_2}$ hybrid has been successfully employed as a catalyst in the selective oxidation of a wide series of alcohols and is highly active at just 0.1 mol% loading. Moreover, it can be easily recovered by adsorption onto a multilayered covalently-linked SILP phase (mlc-SILP) through a "release and catch" approach and reused for up to 12 cycles without loss in efficiency. Interestingly, a catalytic synergistic effect of TEMPO and imidazolium bromide moieties combined in the same hybrid has been clearly shown.

Keywords: alcohols; fullerene; ionic liquids; oxidation; TEMPO; 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)

In the last decades TEMPO-like catalysts have emerged as powerful, metal-free and environmentally sustainable alternatives in the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds.[1] Nevertheless, their high price prompted scientists examine the development of supported TEMPO catalysts in order to obtain recyclable materials. Hence, TEMPO has been covalently immobilized onto various supports such as silica,[2] magnetic nanoparticles,[3] soluble[4] and insoluble[5] organic polymers, and carbon nanotubes.[6]

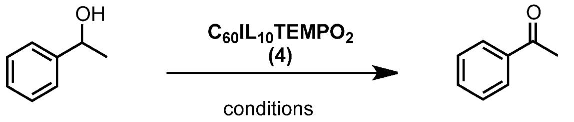
However, although several of these materials were catalytically active and easily recyclable, they often suffer from the inherent drawback of heterogeneous catalysis, namely the reduced mass transfer that makes reactions slower than in the case of their homogeneous counterparts.[7] In this regard, very recently a new approach called "release and catch" has been highlighted.[8] In this strategy, the catalytic system is non-covalently immobilized on the support, but the catalytic moiety is released in solution over the course of the reaction and it is recaptured at the end of the reaction. In such a manner, the benefits of homogeneous (high catalytic activity and reaction rates) and heterogeneous catalysis (easy separation and recycling) are combined. Interestingly, the "release and catch" approach has found application in organometallic-based catalysts,[9] organocatalysts[10] and metal-based catalysts.[11] In the past few years, we have been engaged in the use of silica-supported ionic liquid-like phase monolayers (SILLP) and multilayers (mlc-SILP) as reversible catalyst reservoirs. Both kinds of materials were excellently employed for organocatalyst recovery and recycling[10,12] as well as in the immobilization of Pd nanoparticles for C–C coupling processes in batch[13] and in flow.[14] On the other hand, we started exploring new recyclable TEMPO-based systems: 10 mol% of ionic liquid-tagged TEMPO derivatives were easily recovered with the help of mlc-SILP and recycled in up to 13 consecutive cycles with no loss in activity,[12d] whilst a series of fullerene-TEMPO derivatives with two, four and twelve TEMPO moieties can be quickly recovered through a short pad of silica and recycled for seven times.[15] With this background, we decided to explore the possibility to use the tridimensional [60]fullerene sphere as a molecular platform for combining the catalytic effect of two different components in the same molecule and if their close proximity would enhance the catalytic activity. Moreover, we planned to design a molecule in which the presence of ionic liquid tags would increase the compatibility between the final catalyst and our mlc-SILP materials.



Scheme 1. Synthesis of the $C_{60}IL_{10}TEMPO_2$ hybrid (**4**).

The choice of IL is strategic since the proper counter-anion may exert a catalytic role in the oxidation process. In this regard, we considered the bromide ions to be a good candidate given their widely recognized role in TEMPO-mediated Anelli oxidations,[16] as well as in combination with hypervalent iodine(III) reagents.[17] The presence of 30 equivalent double bonds in C_{60} makes this carbon allotrope a good candidate for multiple consecutive additions. Recently, some C_{60}-TEMPO systems have been prepared through Prato,[18] Bamford–Stevens,[19] or Bingel synthetic protocols.[20] In our case, we chose the Bingel–Hirsch protocol[21] in order to prepare the fullerene monoadduct **1**[22] which has been used as starting derivative in the synthesis of the $C_{60}IL_{10}TEMPO_2$ **4** hybrid (Scheme 1). Bingel reaction of **1** with 8 equivalents of bis(3-bromopropyl) malonate **2** afforded the [5:1]hexakis adduct **3** in 44% yield. Finally, the desired $C_{60}IL_{10}TEMPO_2$ **4** hybrid has been obtained in almost quantitative yield by treatment of **3** with *N*-methylimidazole. The presence of paramagnetic TEMPO moieties prevents the collection of valuable structural information by NMR spectroscopy. However, even though ^{1}H NMR spectra of **3** and **4** have very low resolution, some assignments can be made. The ^{1}H NMR spectrum of **4** shows the signals of the methylenic groups, as well as two signals of imidazolium moieties (the acid C-2 proton disappears after exchange with the deuterated solvent) and that of the methyl groups (Supporting Information, Figure S1). The octahedral substitution pattern of the C_{60} cage simplifies the ^{13}C NMR spectra of **3** and **4** (Suppporting Information, Figures S2 and S3), giving rise to two *sp*^{2} signals in the 147–139 ppm range along with an *sp*^{3} signal at

Table 1. Optimization of oxidation conditions and catalyst loading.



Entry	Conditions	Loading [%]	Time [h]	Yield [%]	TON
1[a]	NaClO	0.1	6.0	75	750
2[a]	NaClO	0.5	2.0	>95	200
3[b]	O_2/TBN	0.1	4.0	15	150
4[b]	O_2/TBN	0.5	4.0	50	100
5[b]	O_2/TBN	1.0	8.0	91	91
6[c]	BAIB/0.4[d]	0.1	0.7	>95	1000
7[c]	BAIB/1.6[d]	0.1	0.7	>95	1000
8[c]	BAIB/1.6[d]	0.05	2.0	>95	2000
9[c]	BAIB/1.6[d]	0.02	22.0	52	2600
10[c]	BAIB/1.6[d]	0.01	22.0	30	3000

[a] *Reaction conditions:* alcohol (0.8 mmol), 3 M NaClO (2.86 mL), 0.5 M KBr (0.16 mL), $NaHCO_3$ (1.28 mmol), CH_2Cl_2 (2 mL), 0–15 °C.

[b] *Reaction conditions:* alcohol (0.8 mmol), TBN (15 mol%), O_2 (balloon), water (0.5 mL), 50 °C.

[c] *Reaction conditions:* alcohol (0.8 mmol), BAIB (1.1 equiv.), CH_2Cl_2, room temperature.

[d] Substrate concentration in mol·L^{-1}.

ca. 70 ppm and the carbonyl at 162–164 ppm. However, in none of the spectra are the signals due to the paramagnetic TEMPO moieties discernable.

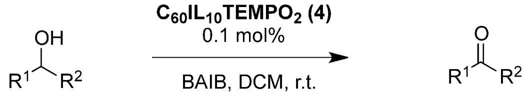
The FT-IR spectra of **3** and **4** systems clearly show the presence of the carbonyl stretching in 1742–1746 cm^{-1} range along with that of N–O$^{\bullet}$ radicals at 1463 cm^{-1} (Supporting Information, Figures S4 and S5). Finally, high resolution APCI-MS confirmed the proposed hexakis-adduct structure for **3** revealing the presence of relevant peaks at $m/z = 2850$ (M^+), at $m/z = 2678$ (M^+–TEMPO) and at $m/z = 2506$ (M^+–2 TEMPO) (Supporting Information, Figure S6). Unfortunately, due to its highly charged nature we were not able to obtain a good mass spectrum of **4**.

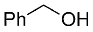
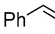
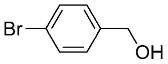
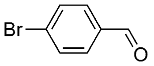
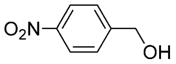
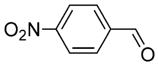
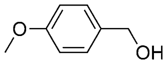
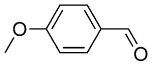
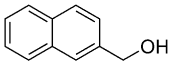
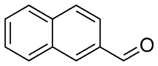
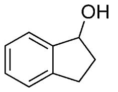
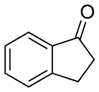
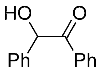
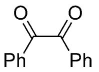
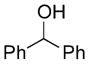
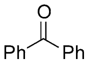
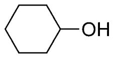
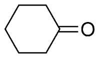
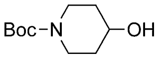
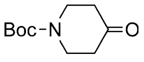
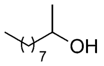
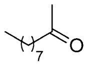
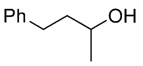
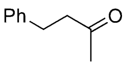
Hence, we tested catalyst **4** by applying three different conditions in which the co-oxidant has been varied for the oxidation of 1-phenylethanol to acetophenone: sodium hypochlorite solution (commercial bleach) in the presence of KBr and $NaHCO_3$ for adjusting the pH (Anelli's conditions),[16] oxygen in the presence of *tert*-butyl nitrite (TBN) as co-catalyst,[23] and hypervalent iodine(III) [bis(acetoxy)iodo]benzene (BAIB).[24] The results are collected in Table 1 and show that with NaClO as terminal oxidant 0.5 mol% of **4** are needed to fully convert 1-phenylethanol in 2 h (entry 2). When oxygen has been employed (entries 3–5) the catalyst loading had to be increased up to 1 mol% in order to get good conversion but with a rather long reaction time. On the other hand, complete conversions in very short reaction time (40 min) were obtained with just 0.1 mol% of $C_{60}IL_{10}TEMPO_2$ when BAIB in DCM was used (entries 6 and 7). These promising results prompted us to decrease the catalyst loading (entries 8–10).

Interestingly, 0.05 mol% of **4** are able to quantitatively oxidize 1-phenylethanol within 2 h with a turnover number (TON) of 2000 (entry 8). Higher TONs can be achieved by further decreasing the catalyst content down to 0.01 mol% albeit with incomplete conversions.

Hence, we checked the substrate scope of the reaction employing catalyst $C_{60}IL_{10}TEMPO_2$ at 0.1 mol% in the oxidation of a wide range of substrates (Table 2). Primary benzylic alcohols, such as benzyl,

Table 2. Catalytic oxidation of primary and secondary alcohols with $C_{60}IL_{10}TEMPO_2$ (**4**).[a]



Entry	Substrate	Product	Time [h]	Yield [%]
1			0.7	>95
2			1.0	>95
3			1.0	>95
4			1.0	>95
5			5.0	>95
6[b]			1.0	>95
7[b,c]			2.0	>95
8[c]			3.0	>95
9			1.0	>95
10[c]			3.0	>95
11[b,c]			4.0	>95
12[b,c]			8.0	>95
13	n-$C_6H_{12}OH$	n-$C_5H_{10}CHO$	1.5	>95
14[c]	n-$C_{10}H_{21}OH$	n-$C_9H_{19}CHO$	5.0	>95
15	$Ph(CH_2)_5OH$	$Ph(CH_2)_4CHO$	1.5	>95

[a] *Reaction conditions:* alcohol (0.8 mmol), BAIB (1.1 equiv.), CH_2Cl_2, room temperature.

[b] 0.5 mol% of catalyst **4**.

[c] 1.3 equiv. of BAIB.

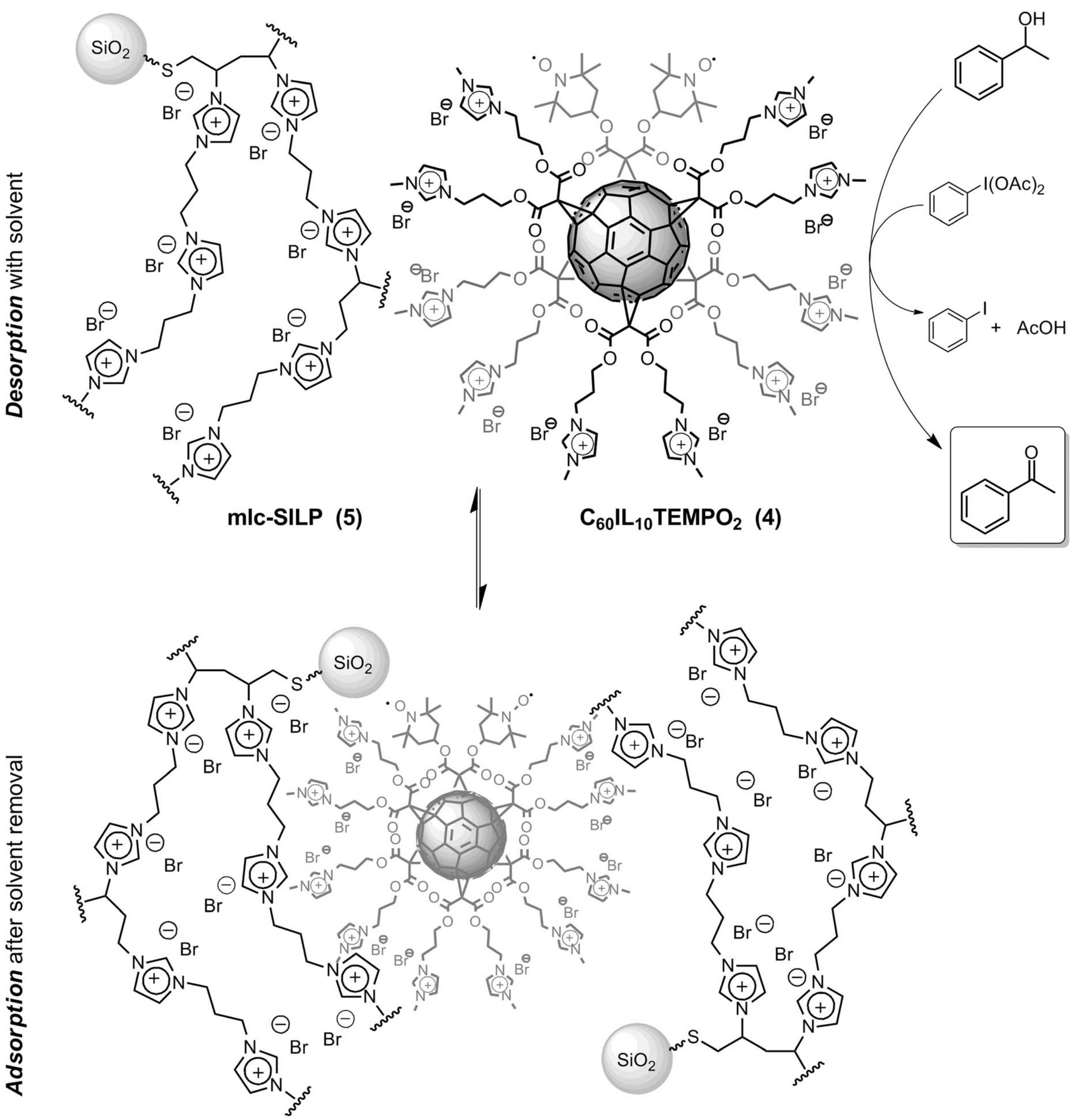


Figure 1. Catalyst recycling through "release and catch".

para-bromobenzyl, *para*-nitrobenzyl and *p*-methoxybenzyl alcohols were quantitatively converted in 40 min (entries 1–4) whereas 2-naphthalenemethanol required 5 h (entry 5). Secondary benzylic alcohols such as 1-indanol and benzoin were quantitatively converted but needed 0.5 mol% of **4** (entries 6 and 7) whilst diphenylmethanol gave benzophenone in >95% yield in 3 h (entry 8). Cyclohexanol was completely oxidized in 40 min (entry 9) whereas 1-Boc-4-hydroxypiperidine and acyclic secondary alcohols such as 2-decanol and 4-phenylbutan-2-ol (entries 10–12) required longer reaction times for quantitative conversions.

Finally, also primary aliphatic alcohols were transformed with excellent yields within 1.5–5 h (entries 13–15). Interestingly, in all cases, primary alcohols afforded the corresponding aldehydes selectively without undergoing the easy autoxidation to the respective carboxylic acid[25] probably due to the ability of TEMPO systems to act as free radical scavengers, and hence as an autoxidation inhibitor.[26]

Then we applied the "release and catch" approach for the recycling of $C_{60}IL_{10}TEMPO_2$ using mlc-SILP **5**. Once the first cycle was complete, support **5** was added and the solvent removed under reduced pressure causing the adsorption (catch) of the catalyst (Figure 1). Afterwards, the final product was extract-

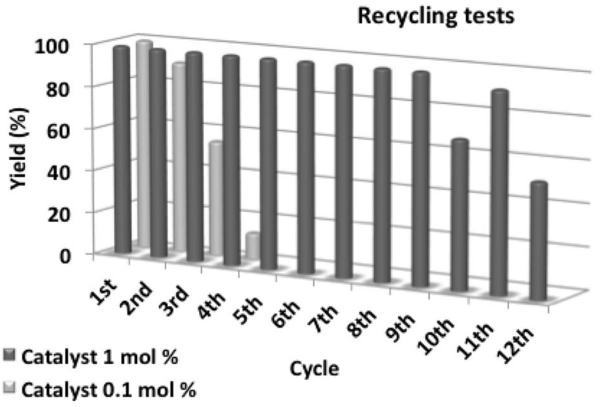
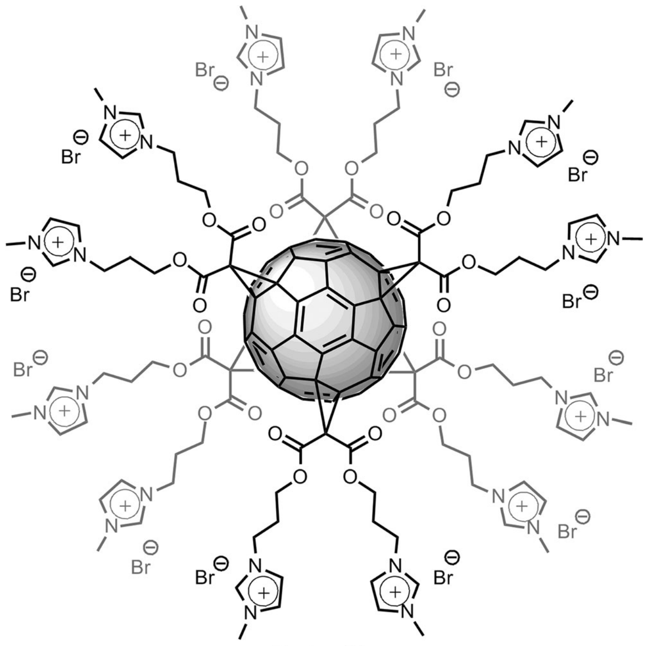


Figure 2. Recycling of $C_{60}IL_{10}TEMPO_2$ (**4**) (1.0 and 0.1 mol%) in the formation of acetophenone.

ed by using a proper solvent (diethyl ether) that does not dissolve the adsorbed catalyst. Hence, the solid catalytic material filtered off (support+catalyst) acts as a catalyst reservoir and can be employed in the next cycles with CH_2Cl_2, a solvent in which catalyst **4** is soluble and can be released in solution. In that way, 1 mol% of $C_{60}IL_{10}TEMPO_2$ **4** was recycled for 12 runs whilst 0.1 mol% were used in four consecutive reactions (Figure 2). In the first case, after 9 cycles with complete conversion, in the 10th run the yield dropped to 70%. Hence, the catalyst was separated from the support and used alone in the 11th cycle giving rise to 94% of conversion. Thus, in order to confirm a detrimental effect of the support (probably damaged after 10 cycles) a new cycle with the used mlc-SILP has been carried out yielding 54% of conversion. As a whole, the catalytic system operated with a TON >1100. Beside the damage experienced by the support after 10 cycles, the procedure still remains an easy approach to smoothly and quantitatively recover the catalyst with no need for its heterogeneization. In this regard, the catalyst cannot be easily recovered by simple filtration since it is employed in such a little amount and big percentages get lost during recovery. Less recyclable runs resulted with 0.1 mol% given that in the 4th cycle just 12% of acetophenone was isolated. In this case, due to the low amount of catalyst employed, even small losses for leaching during the recycling procedure have a big effect on the efficiency. However, given the small amounts used, the overall TON was >2500.

As stated before, bromide ions may have a role in the oxidation of alcohols[17b] and this may have a dominant part during the recycles due to the presence of additional Br^- present in the mlc-SILP **5**. In order to discern how the TEMPO moieties and bromide ions (distinguishing those present in catalyst **4** and those proceeding from support **5**) contribute to the oxidation process, a series of blank tests was conducted employing the fullerene monoadduct **1**, support **5**, and the symmetric hexakisadduct $C_{60}IL_{12}$ **6** (Figure 3).[27]

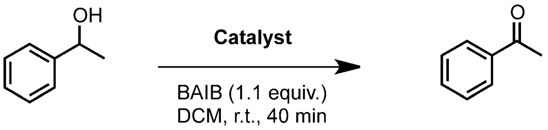


$C_{60}IL_{12}$ (6)

Figure 3. Chemical structure of $C_{60}IL_{12}$ (**6**).

The results are summarized in Table 3. First, a comparison between monoadduct **1** and catalyst **4** shows the important role of the imidazolium bromide moieties in the catalytic activity (Table 3 entry 1 *vs.* 1st cycle 1 mol% in Figure 2). It is noteworthy that when monoadduct **1** or $C_{60}IL_{12}$ **6** are employed separately in 1 and 5 mol%, respectively (the same amount present in 1 mol% of **4**), just 10 and 38% yields are obtained (entries 1 and 2), which summed give 48% *vs.* >95% obtained with **4** in the 1st cycle. However, a sensible

Table 3. Effect of each catalytic moiety on the oxidation of 1-phenylethanol.[a]



Entry	Catalyst	Loading [mol%]	Yield [%]
1	$C_{60}TEMPO_2$ (**1**)	1.0	10
2	$C_{60}IL_{12}$ (**6**)	5.0	38
3	**1+6**	1.0+5.0	93
4	mlc-SILP (**5**)	–[b]	34
5	$C_{60}TEMPO_2$ (**1**)	0.1	8
6	$C_{60}IL_{12}$ (**6**)	0.5	4
7	**1+6**	0.1+0.5	36

[a] *Reaction conditions:* alcohol (0.8 mmol), BAIB (1.1 equiv.), CH_2Cl_2 2 mL, room temperature, 40 min.

[b] 60 mg, i.e., the amount used in the recycling experiments.

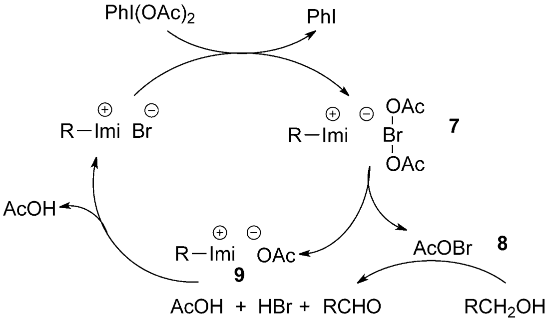
increase in conversion is achieved when the two catalysts are combined (entry 3) evidencing a kind of cooperation between them. As expected, also the support **5** displayed some catalytic activity affording 34% of acetophenone after 40 min (entry 4). Nevertheless, during the recycling, taking into account the sum of the three different contributions, we reach a value of 82%, lower than that obtained with the release and catch system (>95%). Such a synergistic effect is even more pronounced when the catalyst loading is reduced to 0.1 mol% for **1** and 0.5 mol% for **6** (entries 5 and 6). In this case the sum of the yields achieved with the two different catalysts reaches 12% whereas their combination 36% (entry 7), three times more but very far from the quantitative yield obtained with 0.1 mol% of $C_{60}IL_{10}TEMPO_2$ (Table 1, entry 6).

On the other hand, no beneficial effects have been observed when other terminal oxidants such as TBN or NaClO are employed. In the former case, after 8 h of reaction with 1 mol% of catalyst, **1** gave 86% yield *vs.* 91% obtained with **4**. Under Anelli's conditions, 0.1 mol% of **1** after 6 h gave acetophenone quantitatively,[15] whilst **4** afforded just 75% yield (Table 1, entry 1).

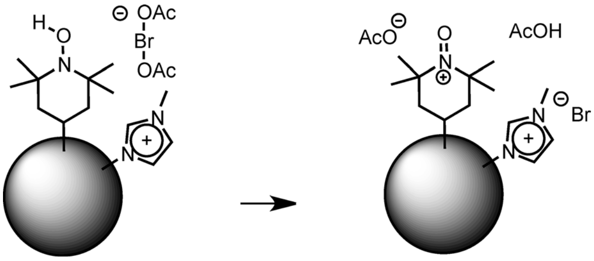
The mechanism of bromide ion promotion in the TEMPO/BAIB-mediated alcohol oxidation could be explained as follows. The formation of a certain amount of carbonyl compound in the absence of TEMPO (see Table 3) could be ascribed to the reaction of bromide ions of the imidazolium-based fullerene (or the imidazolium-based support) with [bis(acetoxy)iodo]benzene which may afford bis(acyloxy)bromate(I) anions **7** (Scheme 2). It has been assumed that the supported bis(acyloxy)bromate(I) anion is not an active oxidant but rather the acylated hypobromite **8**,[28] which can be released in solution.[29] Proton exchange between **9** and HBr will give the starting bromide-based material.

The intriguing high synergism probably has its origin from the close spatial proximity of TEMPO and Br^- that act as a concentrated phase in which the two catalysts are "confined", resulting in a better oxidation activity than the individual components. More precisely, what we suppose is that the spatial proximity of $[Br(OAc)_2]^-$ species to the reduced TEMPO species (TEMPOH) strongly favors the regeneration of the oxoammonium salt (Scheme 3). Then, the $[Br(OAc)_2]^-$ species may play a dual role: (i) regeneration of the oxammonium species, *via* the acylated hypobromite **8** and (ii) direct oxidation of the alcohol. Such a dual role in a confined space will increase the catalytic efficiency of the whole system.

Moreover, different oxidation mechanisms may operate simultaneously given that the activity of TEMPO/Br^-,[16] BAIB/Br^-,[17] and TEMPO/BAIB[24] pairs is well recognized. In this regard, more detailed mechanistic studies are currently in progress in our laboratory and will be reported in due course.



Scheme 2. Oxidation of alcohols catalyzed by bromide ions in the presence of BAIB.



Scheme 3. Synergic effect in the $C_{60}IL_{10}TEMPO_2$ catalyst.

In conclusion, a new $C_{60}IL_{10}TEMPO_2$ [5:1]hexakisadducts hybrid has been synthesized and used as catalyst in the oxidation of primary and secondary alcohols to carbonyl compounds. This molecule showed an outstanding catalytic activity even with low loadings and it was easily recovered through the "release and catch" approach employing an mlc-SILP as reversible support. In such a way up to 11 cycles have been carried out with almost no loss in catalytic activity. The analysis of the single parts of the catalyst evidenced a high synergistic effect in the $C_{60}IL_{10}TEMPO_2$ system, probably due to the close proximity of TEMPO and Br^- moieties that act as a highly concentrated phase.

Experimental Section

General Procedures for the Oxidations

Oxidation with oxygen: A mixture of alcohol (0.8 mmol), *tert*-butyl nitrite (15 mol%), and catalyst **4** in H_2O (0.5 mL) was prepared in a single-necked round-bottom flask. The flask was then filled with pure oxygen (balloon), and the resulting mixture was stirred at 50 °C, under an oxygen atmosphere. After the time indicated in Table 1, the reaction mixture was cooled down to room temperature, and Et_2O (3 × 5 mL) was added. The mixture was stirred for 5 min, the organic layers were separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude product which was purified by simple filtration with a pad of silica (AcOEt/petroleum ether). The conversion of the product was calculated by ^{1}H NMR after careful determination of its weight.

Oxidation with NaClO (Anelli): A mixture of alcohol (0.8 mmol), catalyst **4** and 0.16 mL of aqueous KBr (0.5 M) in 2 mL CH_2Cl_2 was prepared in a single-necked flask. The mixture was cooled to 0 °C, followed by the addition of 2.86 mL of NaOCl (0.35 M), and the solution was buffered to pH 8.6 with $NaHCO_3$ (108 mg). The biphasic reaction mixture was stirred vigorously, and the temperature of the solution was maintained between 0–15 °C until total consumption of the starting alcohol on TLC. Then, the solution was diluted with CH_2Cl_2 (3×10 mL), the organic layer was separated by extraction and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude compound, which contained the catalyst and the carbonyl compound. The crude compound was further purified by simple filtration with a pad of silica and the conversion of the product was calculated by ^{1}H NMR after careful determination of its weight.

Oxidation with BAIB: [Bis(acetoxy)iodo]benzene (0.88 mmol) was added to a solution of alcohol (0.8 mmol) and catalyst **4** in 2 mL CH_2Cl_2. The reaction mixture was stirred at room temperature and monitored by TLC. After the time indicated in Table 1, the solvent was removed under reduced pressure to afford the crude product which was purified by simple filtration with a pad of silica (AcOEt/petroleum ether) and the conversion of the product was calculated by ^{1}H NMR after careful determination of its weight.

Details for catalyst preparation and for the recycling experiments can be found in the Supporting Information.

Acknowledgements

Financial support from the University of Palermo and COST Action CM0905 ORCA are gratefully acknowledged. Mass spectra were provided by Centro Grandi Apparecchiature – UniNetLab – Università di Palermo funded by P.O.R. Sicilia 2000–2006, Misura 3.15 Quota Regionale.

References

[1] a) M. Zhao, J. Li, E. Mano, Z. Song, D. M. Tschaen, E. J. J. Grabowski, P. J. Reider, *J. Org. Chem.* **1999**, *64*, 2564–2566; b) R. A. Sheldon, I. W. C. E. Arends, G. J. T. Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774–781; c) P. Gamez, I. W. C. E. Arends, R. A. Sheldon, J. Reedijk, *Adv. Synth. Catal.* **2004**, *346*, 805–811; d) R. Liu, X. Liang, C. Dong, X. Hu, *J. Am. Chem. Soc.* **2004**, *126*, 4112–4113; e) R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051–1071; f) M. Shibuya, M. Tomizawa, I. Suzuki, Y. Iwabuchi, *J. Am. Chem. Soc.* **2006**, *128*, 8412–8413.

[2] a) T. Dohi, K. I. Fukushima, T. Kamitanaka, K. Morimoto, N. Takenaga, Y. Kita, *Green Chem.* **2012**, *14*, 1493–1501; b) C. Bolm, F. Thomas, *Chem. Commun.* **1999**, 1795–1796; c) T. Fey, H. Fischer, S. Bachmann, K. Albert, C. Bolm, *J. Org. Chem.* **2001**, *66*, 8154–8159; d) B. Karimi, A. Biglari, J. H. Clark, V. Budarin, *Angew. Chem.* **2007**, *119*, 7348–7351; *Angew. Chem. Int. Ed.* **2007**, *46*, 7210–7213; e) B. Karimi, E. Badreh, *Org. Biomol. Chem.* **2011**, *9*, 4194–4198.

[3] a) A. Schätz, R. N. Grass, W. J. Stark, O. Reiser, *Chem. Eur. J.* **2008**, *14*, 8262–8266; b) A. K. Tucker-Schwartz, R. L. Garrell, *Chem. Eur. J.* **2010**, *16*, 12718–12726; c) B. Karimi, E. Farhangi, *Chem. Eur. J.* **2011**, *17*, 6056–6060; d) B. Karimi, E. Farhangi, *Adv. Synth. Catal.* **2013**, *355*, 508–516; e) Z. Zheng, J. Wang, M. Zhang, L. Xu, J. Ji, *ChemCatChem* **2013**, *5*, 307–312.

[4] a) M. Benaglia, A. Puglisi, O. Holczknecht, S. Quici, G. Pozzi, *Tetrahedron* **2005**, *61*, 12058–12064; b) C. X. Miao, L. N. He, J. Q. Wang, J. Gao, *Synlett* **2009**, 3291–3294.

[5] a) A. Dijksman, I. W. C. E. Arends, R. A. Sheldon, *Chem. Commun.* **2000**, 271–272; b) C. Tanyeli, A. Gümüş, *Tetrahedron Lett.* **2003**, *44*, 1639–1642; c) M. Gilhespy, M. Lok, X. Baucherel, *Catal. Today* **2006**, *117*, 114–119.

[6] a) J. P. Lindner, C. Roben, A. Studer, M. Stasiak, R. Ronge, A. Greiner, H. J. Wendorff, *Angew. Chem.* **2009**, *121*, 9035–9038; *Angew. Chem. Int. Ed.* **2009**, *48*, 8874–8877; b) Y. Wang, X. Song, S. Shao, H. Zhong, F. Lin, *RSC Adv.* **2012**, *2*, 7693–7698.

[7] a) G. Oehme, *Comprehensive Asymmetric Catalysis*, Springer, Heidelberg, Berling, **1999**, Vol. 3, pp 1377–1386; b) D. E. DeVos, B. F. Sels, P. A. Jacobs, *Adv. Catal.* **2001**, *46*, 1–87; c) J. A. Gladysz, *Pure Appl. Chem.* **2001**, *73*, 1319–1324.

[8] M. Gruttadauria, F. Giacalone, R. Noto, *Green Chem.* **2013**, *15*, 2608–2618.

[9] a) S. Wittmann, A. Schätz, R. N. Grass, W. J. Stark, O. Reiser, *Angew. Chem.* **2010**, *122*, 1911–1914; *Angew. Chem. Int. Ed.* **2010**, *49*, 1867–1870; b) C. Vriamont, M. Devillers, O. Riant, S. Hermans, *Chem. Eur. J.* **2013**, *19*, 12009–12017.

[10] E. Montroni, M. Lombardo, A. Quintavalla, C. Trombini, M. Gruttadauria, F. Giacalone, *ChemCatChem* **2012**, *4*, 1000–1006.

[11] a) M. I. Burguete, E. García-Verdugo, I. Garcia-Villar, F. Gelat, P. Licence, S. V. Luis, V. Sans, *J. Catal.* **2010**, *269*, 150–160; b) F. Zhao, B. M. Bhanage, M. Shirai, M. Arai, *Chem. Eur. J.* **2000**, *6*, 843–848; c) K. Köhler, W. Kleist, S. S. Pröckl, *Inorg. Chem.* **2007**, *46*, 1876–1883; d) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679; e) J. D. Webb, S. MacQuarrie, K. McEleney, C. M. Crudden, *J. Catal.* **2007**, *252*, 97–109; f) S. MacQuarrie, J. H. Horton, J. Barnes, K. McEleney, H.-P. Loock, C. M. Crudden, *Angew. Chem.* **2008**, *120*, 3324–3328; *Angew. Chem. Int. Ed.* **2008**, *47*, 3279–3282; g) J. M. Richardson, C. W. Jones, *J. Catal.* **2007**, *251*, 80–93.

[12] a) M. Gruttadauria, S. Riela, P. Lo Meo, F. D′Anna, R. Noto, *Tetrahedron Lett.* **2004**, *45*, 6113–6116; b) M. Gruttadauria, S. Riela, C. Aprile, P. Lo Meo, F. D′Anna, R. Noto, *Adv. Synth. Catal.* **2006**, *348*, 82–92; c) C. Aprile, F. Giacalone, M. Gruttadauria, A. M. Marculescu, R. Noto, J. D. Revell, H. Wennemers, *Green Chem.* **2007**, *9*, 1328–1334; d) H. A. Beejapur, F. Giacalone, R. Noto, P. Franchi, M. Lucarini, M. Gruttadauria, *ChemCatChem* **2013**, *5*, 2991–2999.

[13] a) M. Gruttadauria, L. F. Liotta, A. M. P. Salvo, F. Giacalone, V. La Parola, C. Aprile, R. Noto, *Adv. Synth. Catal.* **2011**, *353*, 2119–2130; b) R. Buscemi, F. Giacalone, S. Orecchio, M. Gruttadauria, *ChemPlusChem* **2014**, *79*, 421–426; c) C. Pavia, F. Giacalone, L. A. Bivona, A. M. P. Salvo, C. Petrucci, G. Strappaveccia, L. Vaccaro, C. Aprile, M. Gruttadauria, *J. Mol. Catal. A: Chem.* **2014**, *387*, 57–62.

[14] C. Pavia, E. Ballerini, L. A. Bivona, F. Giacalone, C. Aprile, L. Vaccaro, M. Gruttadauria, *Adv. Synth. Catal.* **2013**, *355*, 2007–2018.

[15] H. A. Beejapur, V. Campisciano, P. Franchi, M. Lucarini, F. Giacalone, M. Gruttadauria, *ChemCatChem* **2014**, *6*, 2419–2424.

[16] a) P. L. Anelli, S. Banfi, F. Montanari, S. Quici, *J. Org. Chem.* **1989**, *54*, 2970–2972; b) P. L. Anelli, C. Biffi, F. Montanari, S. Quici, *J. Org. Chem.* **1987**, *52*, 2559–2562.

[17] a) H. Tohma, S. Takizawa, T. Maegawa, Y. Kita, *Angew. Chem.* **2000**, *112*, 1362–1364; *Angew. Chem. Int. Ed.* **2000**, *39*, 1306–1308; b) W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem.* **2005**, *117*, 974–977; *Angew. Chem. Int. Ed.* **2005**, *44*, 952–955.

[18] a) Y. Li, Z. Mao, J. Xu, J. Yang, Z. Guo, D. Zhu, J. Li, B. Yin, *Chem. Phys. Lett.* **1997**, *265*, 361–364; b) A. Polimeno, M. Zerbetto, L. Franco, M. Maggini, C. Corvaja, *J. Am. Chem. Soc.* **2006**, *128*, 4734–4741; c) C. Corvaja, M. Maggini, M. Prato, G. Scorrano, M. Venzin, *J. Am. Chem. Soc.* **1995**, *117*, 8857–8858; d) F. Arena, F. Bullo, F. Conti, C. Corvaja, M. Maggini, M. Prato, G. Scorrano, *J. Am. Chem. Soc.* **1997**, *119*, 789–795; e) Y. Li, X. Lei, S. Jockusch, J. Y. C. Chen, M. Frunzi, J. A. Johnson, R. G. Lawler, Y. Murata, M. Murata, K. Komatsu, N. J. Turro, *J. Am. Chem. Soc.* **2010**, *132*, 4042–4043; f) S. Campestrini, C. Corvaja, M. De Nardi, C. Ducati, L. Franco, M. Maggini, M. Meneghetti, E. Menna, G. Ruaro, *Small* **2008**, *4*, 350–356.

[19] a) K. Matsuda, G. Ulrich, H. Iwamura, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1581–1588; b) T. Ishida, K. Shinozuka, M. Kubota, M. Ohashi, T. Nogami, *J. Chem. Soc. Chem. Commun.* **1995**, 1841–1842; c) T. Ishida, K. Shinozuka, T. Nogami, M. Kubota, M. Ohashi, *Tetrahedron* **1996**, *52*, 5103–5112; d) P. Ceroni, F. Conti, C. Corvaja, M. Maggini, F. Paolucci, S. Roffia, G. Scorrano, A. Toffoletti, *J. Phys. Chem. A* **2000**, *104*, 156–163.

[20] a) L. Franco, M. Mazzoni, C. Corvaja, V. P. Gubskaya, L. Berezhnaya, I. A. Nuretdinov, *Chem. Commun.* **2005**, 2128–2130; b) V. P. Gubskaya, L. S. Berezhnaya, V. V. Yanilkin, V. I. Morozov, N. V. Nastapova, Y. Y. Efremov, I. A. Nuretdinov, *Russ. Chem. Bull.* **2005**, *54*, 1642–1655.

[21] a) C. Bingel, *Chem. Ber.* **1993**, *126*, 1957–1959; b) I. Lamparth, A. Hirsch, *J. Chem. Soc. Chem. Commun.* **1994**, 1727–1728.

[22] V. P. Gubskaya, L. S. Berezhnaya, A. T. Gubaidullin, I. I. Faingold, R. A. Kotelnikova, N. P. Konovalova, V. I. Morozov, I. A. Litvinov, I. A. Nuretdinov, *Org. Biomol. Chem.* **2007**, *5*, 976–981.

[23] B. Karimi, E. Farhangi, *Chem. Eur. J.* **2011**, *17*, 6056–6060.

[24] a) A. De Mico, R. Margarita, L. Parlanti, A. Vescovi, G. Piancatelli, *J. Org. Chem.* **1997**, *62*, 6974–6977; b) O. Holczknecht, M. Cavazzini, S. Quici, I. Shepperson, G. Pozzi, *Adv. Synth. Catal.* **2005**, *347*, 677–688; c) J. S. Yadav, N. N. Yadav, T. S. Rao, B. V. S. Reddy, A. Al Khazim Al Ghamdi, *Eur. J. Org. Chem.* **2011**, *2011*, 4603–4608.

[25] R. A. Sheldon, J. K. Kochi, *Metal-catalyzed oxidations of organic compounds*, Academic Press, New York, **1981**.

[26] a) R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051–1071; b) R. A. Sheldon, I. W. C. E. Arends, *J. Mol. Catal. A: Chem.* **2006**, *251*, 200–214.

[27] See the Supporting Information for the synthesis and characterization of **6** as well as: V. Campisciano, V. La Parola, L. F. Liotta, F. Giacolone, M. Gruttadauria, *Chem. Eur. J.* **2015**, DOI: 10.1002/chem.201406067.

[28] R. Ben-Daniel, P. Alsters, R. Neumann, *J. Org. Chem.* **2001**, *66*, 8650–8653.

[29] M. Brünjes, G. Sourkouni-Argirusi, A. Kirschning, *Adv. Synth. Catal.* **2003**, *345*, 635–642.

Catalytic Synergism in a $C_{60}IL_{10}TEMPO_2$ Hybrid in the Efficient Oxidation of Alcohols

9

Adv. Synth. Catal. **2014**, *356*, 1 – 9

Hazi Ahmad Beejapur, Vincenzo Campisciano,
Francesco Giacalone,* Michelangelo Gruttadauria*