

Asymmetric Organocatalysis in Fullerenes Chemistry: Enantioselective Phosphine-catalyzed Cycloaddition of Allenates onto C₆₀**

Juan Marco-Martínez, Vanesa Marcos, Silvia Reboredo, Salvatore Filippone, and Nazario Martín*

Dedicated to Professor Juan Rojo on the occasion of his 70th birthday

The discovery of fullerenes as the first molecular allotropes of carbon in 1985,^[1] and their further preparation in macroscopic amounts by arc vaporization of graphite in 1990^[2] have profoundly influenced many aspects of contemporary chemistry. Since then, the family of carbon nanoforms has grown significantly first with the closely related carbon nanotubes (CNTs)^[3] and, more recently, with the advent of graphene in 2004.^[4] Nowadays, they are fully recognized as very useful carbon building blocks with potential applications in different scientific fields.^[5]

In particular, the huge number of papers, reviews and books written in the last two decades on fullerenes as molecular carbon allotropes give an idea of the unabated interest in these three-dimensional molecules.^[6] However, despite the high level of understanding of their chemical reactivity, the fine control of some fundamental aspects such as stereoselectivity and chirality are important issues that still remain to be properly addressed.^[7] A major breakthrough occurred, however, with the introduction of asymmetric metal catalysis to induce chirality onto the non-coordinating molecule of [60]fullerene, giving rise to chiral pyrrolidino-[3,4:1,2][60]fullerenes with complete control of the stereochemical outcome.^[8] Moreover, due to the growing interest of higher fullerenes, this methodology has also been successfully extended to higher fullerenes, namely C₇₀,^[9] as well as to metallofullerenes, namely La@C₇₂(C₆H₃Cl₂).^[10] The high degree of stereocontrol achieved demonstrates that this

methodology is able to face different levels of selectivity and stereocontrol, affording either the *cis* or *trans* adducts with excellent enantiomeric excesses.^[11] Nonetheless, a broader set of asymmetric methodologies is still urgently required to give access to a wider variety of chiral carbon building blocks and, hence, to new chiral carbon nanostructures. How chirality modifies the electronic properties of these carbon nanoforms is still an open question with important fundamental and technological interest.

Organocatalysis, on the other hand, has boosted the interest in organic synthesis as an efficient strategy for the construction of chiral molecules by the use of metal-free chiral catalysts.^[12] However, the use of this environmentally benign catalytic approach has not been previously addressed in fullerene chemistry, probably due to the lack of an activation method for the carbon cage when using an organocatalyst.

Application of organocatalysis in fullerenes chemistry would result in multiple benefits for both leading research fields. Firstly, the curved and highly reactive double bonds of fullerenes represent a novel and invaluable scenario for testing a variety of organic reactions with new organocatalysts. Secondly, fullerenes, especially the most abundant C₆₀ and C₇₀, have been regarded as a benchmark for testing new chemical reactions to be applied to related emerging carbon materials, namely endohedral fullerenes, CNTs and graphene.

In this communication, we report on the first organocatalytic cycloaddition onto fullerenes affording chiral five-member carbocyclic [60]fullerene derivatives in remarkably high enantiomeric excesses. In the process, easily available chiral phosphines have been employed as nucleophilic organocatalyst to promote a formal [3+2] stereoconvergent^[13] cycloaddition of racemic α -allenates onto C₆₀ affording chiral cyclopenteno[60]fullerenes bearing a versatile ester group. Furthermore, X-ray crystallographic analysis of a single crystal has allowed the unambiguous assignment of the configuration of the newly generated stereocenter and circular dichroism (CD) spectroscopy has allowed for a redefinition of a corrected *sector rule* for the assignment of the absolute configuration of [60]fullerene derivatives.^[14]

Among the different organocatalytic methods known so far, nucleophilic (or Lewis base) phosphine catalysis has emerged fuelled by very important factors, namely: i) the (commercial) availability of a wide array of chiral cyclic and acyclic phosphines, ii) the tunability of their nucleophilic strength by varying steric and electronic features of their

[*] Dr. J. Marco-Martínez,^[+] Dr. V. Marcos,^[+] Dr. S. Reboredo,^[+] Dr. S. Filippone, Prof. Dr. N. Martín
Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid
Ciudad Universitaria s/n, 28040 Madrid (Spain)
E-mail: nazmar@quim.ucm.es
Homepage: <http://www.ucm.es/info/fullerene/>
Prof. Dr. N. Martín
IMDEA-Nanociencia
Campus de la Universidad Autónoma de Madrid
28049 Madrid (Spain)

[+] These authors contributed equally to this work.

[**] Financial support by the Ministerio de Economía y Competitividad (MINECO) of Spain (projects CTQ2011-24652; Consolider-Ingenio CSD2007-00010), the CAM (MADRISOLAR-2 project S2009/PPQ-1533), and the European Research Council ERC-2012-ADG_20120216 (Chirallcarbon) is acknowledged. The authors also thank the SGiker technical support for X-ray analysis.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201301292>.

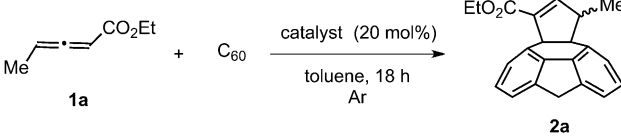
substituents and, iii) the ability to trigger the synthesis of cyclic and heterocyclic compounds.^[15] In particular, α -allenic esters (allenoates) activated by nucleophilic attack of phosphines to the central sp-hybridized carbon atom, have been widely used as three-carbon atoms building blocks in Lu's cycloaddition reaction^[16] onto electron-deficient double bonds for the preparation of five member unsaturated rings.^[17] Even though the first asymmetric variant was reported by Zhang^[18] shortly after Lu's pioneering work, only recently chiral phosphines have been deeply employed as catalyst in the cycloaddition reaction always onto electron poor double bonds such as α,β -unsaturated esters, ketones, amides, imines, etc.^[19]

Based on previous works,^[20] where the first racemic approaches for the phosphine catalyzed [3+2] cycloaddition reaction of ethyl 2-pentynoate and ethyl 2,3-pentadienoate onto [60]fullerene were reported, and encouraged by the aforementioned results, we decided to evaluate the enantioselective organocatalytic [3+2] cycloaddition reaction of ethyl 2,3-pentadienoate **1a** with [60]fullerene by using a series of chiral commercially available mono- and bi-dentate phosphines as organocatalysts (Figure 1 and Table 1, for more examples see Supporting Information).

As it is shown in Table 1, the most successful phosphines were those bearing at least two alkyl substituents (Figure 1), which resulted to be more nucleophilic than the respective aryl-substituted phosphines which afforded the final product in lower conversions (Table 1, entries 4 and 7).

Taking into account the importance of nucleophilicity and steric hindrance of the phosphorous atom in achieving good chemical reactivity and enantioselectivity, among the commercially available chiral phosphine ligands we turned our attention to aliphatic and structurally rigid phosphacycles where the phosphorous atom is part of a ring. Thus, phos-

Table 1: Chiral phosphine-catalyzed [3+2] cycloaddition of allenoate **1a** to [60]fullerene.^[a]



Entry	Phosphine	T [°C]	Conv. [%] ^[b]	ee [%] ^[c]
1	I	RT	40	60 (R)- 2a
2	II	RT	57	66 (R)- 2a
3	III	RT	48	82 (S)- 2a
4	IV	RT	10	76 (S)- 2a
5	V	RT	60	22 (R)- 2a
6	VI	RT	49	16 (S)- 2a
7	VII	RT	8	88 (R)- 2a
8	VIII	RT	43	56 (R)- 2a
9	IX	RT	67	16 (R)- 2a
10	III	-40	< 5	n.d.
11	III	0	27	50 (S)- 2a
12	III	40 (2.5 h)	80 ^[d]	84 (S)- 2a
13	III ^[e]	40 (2.5 h)	91 ^[d]	88 (S)- 2a
14	III ^[f]	RT (2 h)	49	88 (S)- 2a

[a] To a solution of [60]fullerene (0.017 mmol) and ligand (20 mol%) in dry toluene (5 mL), allenoate **1a** (0.016 mmol) was added at RT and the resulting mixture was stirred for 18 h under Ar. [b] Based on consumed [60]fullerene. [c] Determined by HPLC analysis. [d] The almost completed consumption of the fullerene was in a mixture of the desired product and bisadducts. [e] Reaction was carried out in 1 mL of toluene. [f] Reaction was carried out using 1 mL of toluene and 10% of catalyst. n.d.: not determined.

pholane **VIII** and diphospholane ligands **V**, **VI**, and **IX** (Table 1, entries 8, 5, 6, and 9, respectively) led to good conversions although with unsatisfactory enantiomeric excesses. Interestingly, seven membered P-containing heterocycles proved to be better in terms of both reactivity and

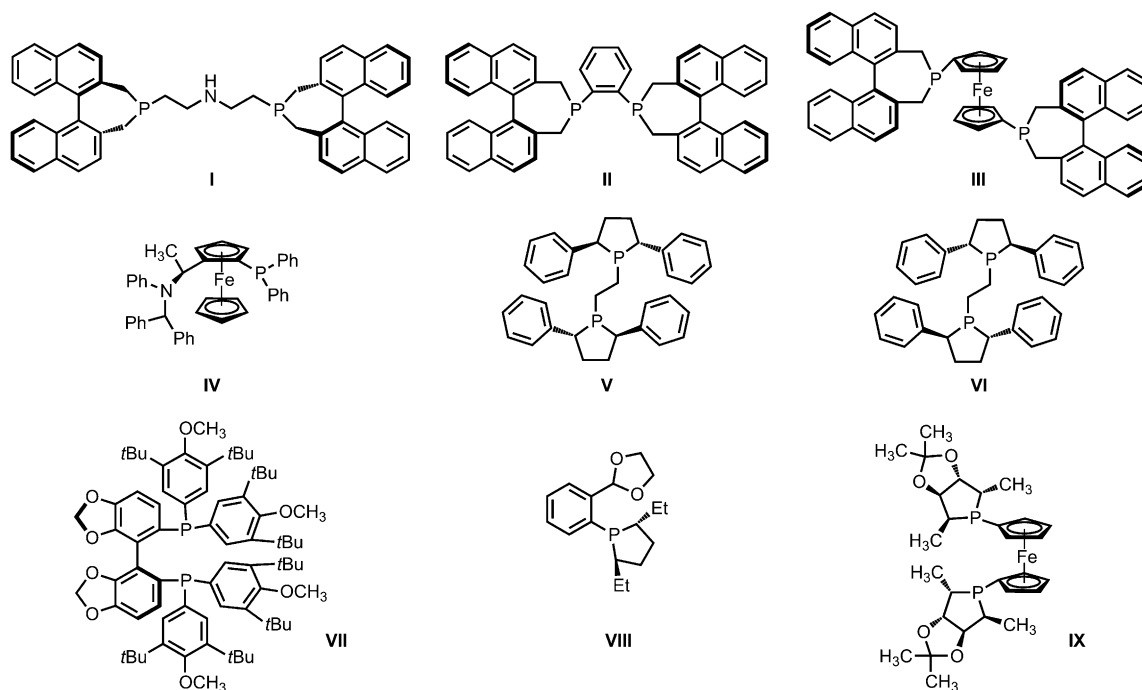


Figure 1. Commercially available chiral phosphines I–IX used in this study.

enantioselectivity. Indeed, dinaphthophosphine derivatives, **I**, **II** and **III**, gave rise to good conversions, taking into account the typical yields for fullerene functionalization. Considering the good conversion/enantioselectivity ratio provided by (*S,S*)-*f*-Binaphane **III** (Table 1, entry 3), this ferrocenyl-substituted phosphine was selected as the chiral organocatalyst of choice because of its higher nucleophilicity and its flexibility due to the low rotation barrier of the ferrocene backbone.^[21] Indeed, **III** gave the better result since it directs allenolate addition toward the 1-ethoxycarbonyl-3-methyl-1-cyclopenteno[4,5:1,2][60]fullerene **2a** with an enantiomeric ratio (*er*) of 91:9 in 48% conversion.

In order to optimize the synthetic process the reaction with **III** was examined under different reaction conditions (Table 1, and SI). The attempts to improve the *ee* by decreasing the temperature were unsuccessful, affording lower conversion and enantioselectivities (Table 1, entries 10 and 11). On the other hand, the reaction took place readily at 40 °C achieving, after 2.5 h, a remarkable 88% *ee* in 1 mL of toluene (Table 1, entry 13). However, long reaction times and high temperatures promoted the formation of undesired bis-adducts (Table 1, entries 12 and 13),^[22] retro-cycloaddition^[23] and racemization processes, resulting in a lower optical purity of the product. Finally, the use of 10% catalyst loading maintained high conversion values and, pleasingly, (*S*)-**2a** was obtained in a ratio of 94:6 (88% *ee*) versus the (*R*)-**2a** enantiomer (Table 1, entry 14).

Taking into account the aforementioned results, the optimal conditions were eventually established.^[24] Under these experimental conditions, a series of allenolates were reacted with C₆₀ in order to extend the scope of this new organocatalytic system (Table 2). Thus, different allenolates endowed with alkyl or aromatic groups such as Me, Et, *i*Pr, or Ph, as well as different alkoxy esters were tested. In general, aliphatic substituents afforded similar results. Thus, good conversions and excellent enantioselectivities were observed (Table 2, entries 1 and 2). However, the incorporation of

a branched aliphatic chain slightly decreased the conversion and the *ee* values (Table 2, entry 3). It is worth to note that when the reaction took place with the aromatic allenolate **1d**, a completely enantioselective process was observed (Table 2, entry 4). Finally, with a bulkier substituent in the ester group, a good conversion was achieved but with moderated *ee* value (Table 2, entry 5).

All new compounds (**2a–e**) were satisfactorily characterized by spectroscopic methods (¹H NMR, ¹³C NMR, UV-Vis, HRMS). As a typical feature, the ¹H NMR spectra of compounds **2a–e** showed the olefinic proton as a doublet at around 7.78–7.93 ppm. The ¹³C NMR (HSQC) spectra showed the olefinic C–H carbon of the organic addend at around 145–150 ppm.

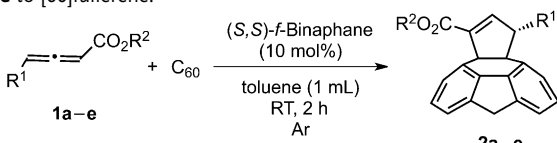
To ascertain the structural assignment of the novel compounds, as well as to show their electroactive character, we carried out cyclic voltammetry (CV) studies of **2a–e** in *o*-DCB/MeCN (4:1) containing Bu₄N⁺PF₆[–] (0.1 M) as supporting electrolyte at room temperature, along with pristine C₆₀ as a reference. Glassy carbon, platinum wire, and Ag/Ag⁺ electrodes were used as working, counter and reference electrodes respectively (see SI).

All the compounds studied (**2a–e**) showed three reversible reduction waves at similar values under these experimental conditions. A remarkable cathodic shift of the first half-wave reduction potential values (123–134 mV) relative to that for pristine C₆₀ (–1.006; –1.415; –1.878 V) was observed. These experimental findings have been accounted for by the saturation of one of the double bonds in the fullerene sphere, thus raising the energy of the LUMO.^[25] It is interesting to note, however, that for the characterization of fullerene adducts, cyclic voltammetry can be considered as a real spectroscopic technique. Actually, CV has been labeled as “electrochemical spectroscopy” since it can provide important structural information.^[26] In our case, since the reduction potential values of fullerenes are strongly influenced by the number of saturated double bonds in the fullerene sphere, we can easily discard the presence of bis-adducts by using this highly sensitive technique.^[27]

The mechanism of this reaction has not been rigorously investigated at this stage. However, based on Lu's^[16] initial proposal and some recent mechanistic studies,^[28] a plausible mechanism is presented in Figure 2. The catalytic cycle involves initial attack of the nucleophilic phosphine catalyst onto the electrophilic β-carbon of allenic ester **1a–e** to form zwitterionic intermediate **Ia** or **Ib**. Then, the zwitterionic intermediate **Ia** attacks the (6,6) double bond of the [60]fullerene to provide the intermediate **II**. The intramolecular conjugate addition of **II** accomplishes the [3+2] cyclization to form stabilized ylide intermediate **III**, which can subsequently undergo proton transfer to **IV** promoting catalyst elimination and giving rise to the cyclopenteno[4,5:1,2][60]fullerenes **2a–e**.

Fortunately, we succeeded in obtaining a single crystal of chiral fullerene derivative **2c** obtained by slow evaporation from a mixture of CS₂/hexane (black and shiny crystals), which allowed us to determine unambiguously its absolute configuration by X-ray diffraction analysis. The diffraction data revealed that the new stereocenter formed at the C3

Table 2: (*S,S*)-*f*-Binaphane-catalyzed [3+2] cycloaddition of allenolates **1a–e** to [60]fullerene.^[a]

					
Entry	Allenolate	R ¹ , R ²	Product	Conv. ^[b,c] (yield)	<i>er</i> (<i>ee</i>) ^[b]
1	1a	Me, Et	(<i>S</i>)- 2a	49 (40)	94:6 (88)
2	1b	Et, Et	(<i>S</i>)- 2b	36 (25)	96:4 (92)
3	1c	<i>i</i> Pr, Et	(<i>S</i>)- 2c	23 (15)	88:12 (76)
4	1d	Ph, Et	(<i>R</i>)- 2d ^[d]	19 (10)	>99:<1 (99)
5	1e	Ph, Bn	(<i>R</i>)- 2e ^[d]	42 (33)	89:11 (78)

[a] A solution of (*S,S*)-*f*-Binaphane (10 mol%) and allenolate **1a–e** (0.016 mmol) in dry toluene (1 mL) was stirred for 15 min and then [60]fullerene (0.017 mmol) was added and the resulting mixture was stirred for 2 h at RT under Ar atmosphere. [b] Determined by HPLC analysis. [c] Based on consumed [60]fullerene. [d] The cases in which R¹ = Ph, the priority of substituents changes and leads to an *R* configuration.

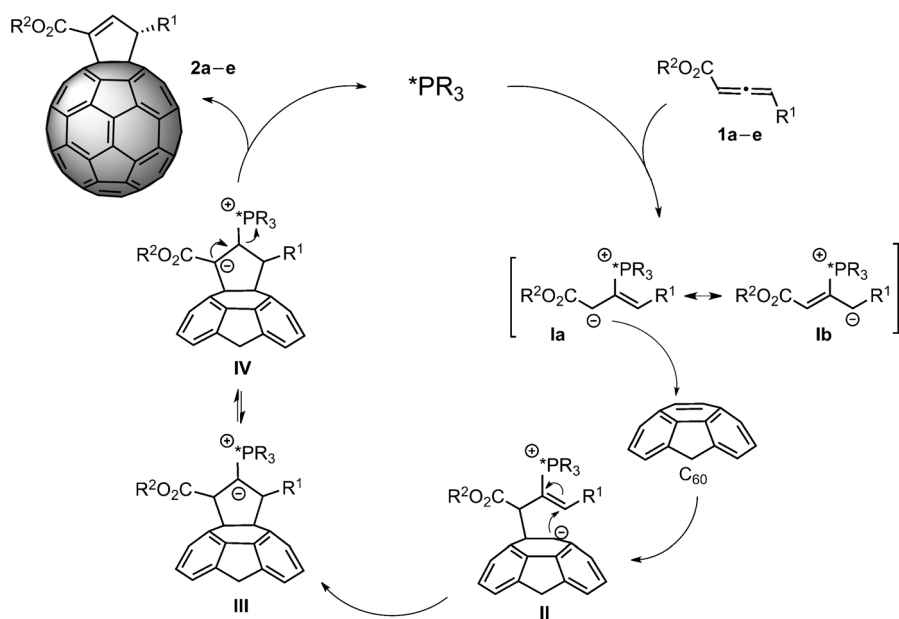


Figure 2. Mechanism for the phosphine-catalyzed [3+2] cycloaddition of allenates **1a–e** to [60]fullerene.

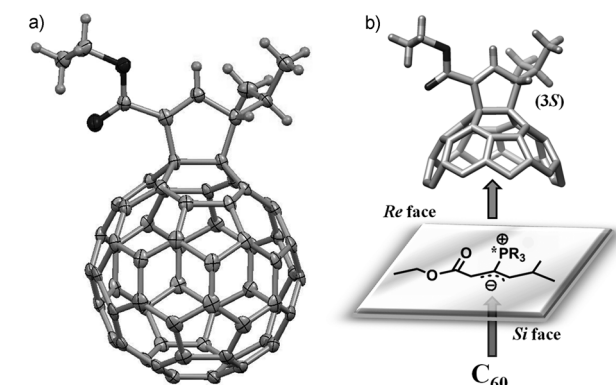


Figure 3. [a] X-ray analysis of a single crystal of **2c**. An *S* configuration was determined for the C3 carbon atom. [b] The resulting enantiomer is consistent with an attack by [60]fullerene to the enantiotopic *Si* face of the prochiral carbon of the allenate.

carbon atom of the cyclopentene ring presented an *S* configuration (Figure 3a).^[29]

The determined crystal structure was chiral belonging to $P2_1$ space group and, therefore, only one enantiomer was present. This analysis confirmed the structure of (3*S*)-1-ethoxycarbonyl-3-isopropyl-1-cyclopenteno[4,5:1,2][60]fullerene, which features a double bond between carbons C1–C2 with a bond length of 1,328 Å and the absolute configuration of C3 corresponding to the *S* enantiomer (see also SI).

The formation of cyclopentenofullerenes presenting an absolute *S* configuration at C3 reveals the shielding of the *Re* face by the phosphine **III** and the resulting approaching of the [60]fullerene occurs from the *Si* face of the prochiral carbon atom C3 in the allenates (Figure 3b).

As expected, both enantiomers of cyclopentene derivative **2a** gave rise to mirror images in the circular dichroism (CD)

spectra due to the perturbation of an asymmetric group onto the former symmetric C_{60} chromophore. The resulting Cotton effect at ≈ 430 nm (Figure 4a), associated to the UV/Vis band typically found for all [60]fullerene monoadducts, has been used as an empirical way to assign the absolute configuration of chiral fullerene derivatives.^[14,30] Although the reasoning that leads to a definition of a *sector rule* for fullerene derivatives was correct, and all the known examples reported so far have substantially confirmed the accurate of this rule, an oversight has probably been the reason for the final inversion of the signs reported in the literature.^[14]

On the other hand, the availability of a direct method to assign the absolute configuration of new chiral fullerene derivatives based on easily accessible spectral data (CD spectra) may be extremely helpful in the

absence of X-ray analysis. Therefore, the unambiguous determination of the absolute configuration of chiral fullerene derivatives by X-ray diffraction in this and other recent

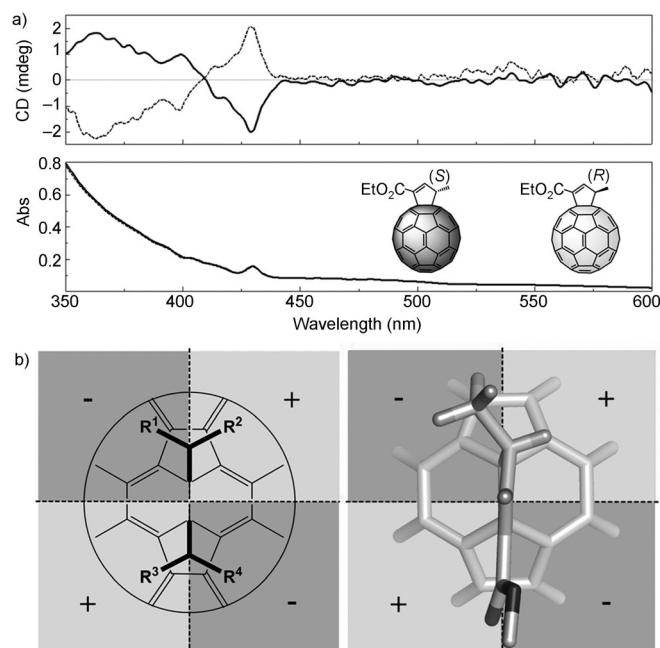


Figure 4. [a] Circular dichroism and UV-Vis spectra for both enantiomers of **2a** (concentration, 4×10^{-4} M in dichloromethane).^[33] [b] Corrected *sector rule* for the assignment of absolute configuration of chiral fullerenes derivatives. A plane tangent to the [60]fullerene sphere at the attacked 6–6 single bond is divided in four sectors by two other planes: one that goes through the 6–6 bond and the second one which bisects the 6–6 single bond. The observation of a negative peak at 430 (as it is the case for compounds **2a** labelled in solid line) is consistent with the location of the largest group in a negative sector (upper left or down right sector) and *viceversa*.

work^[31] is a good opportunity for an accurate redefinition of the amended *sector rule* (Figure 4b, and for more details see SI).

Provided that all cyclopenteno[4,5:1,2][60]fullerene derivatives (**2**) formed from (*S,S*)-*f*-Binaphane **III** feature a negative Cotton effect (solid line, Figure 4a and SI), in agreement with the corrected *sector rule*, an *S* configuration of the C3 carbon atom of the cyclopentene ring is assigned.^[32] Conversely, an *R* configuration is assigned to the cyclopenteno[4,5:1,2][60]fullerene derivative resulting from, for example, the use of (*R*)-Binaphane **II** as catalyst, which gave a positive Cotton effect (see Table 1 and SI).

In summary, we have described the first asymmetric organocatalytic synthesis onto fullerenes to obtain new, stable and versatile chiral carbocyclic derivatives which have been fully characterized by spectroscopic and electrochemical techniques. [60]Fullerene has thus been successfully used as a benchmark to develop a novel organocatalytic system to promote the enantioselective [3+2] cycloaddition of allenates. Furthermore, X-ray analysis of an optically pure cyclopenteno[60]fullerene has allowed us to ascertain the chemical structure and, most importantly, the assignment of the absolute configuration of the new stereocenter at C3 in compound **2c** (*S* configuration) through the attack of the [60]fullerene unit to the phosphine-containing 1,3-dipole from the *Si* face. Furthermore, based on these experimental findings, the *sector rule* for the absolute configuration of chiral [60]fullerene derivatives has been amended. The aforementioned results pave the way for the application of fullerenes in fields where chirality is a key issue such as in bio-medical applications, as well as in the thus far less-explored materials science where chirality has recently been shown to impact some physical properties.^[34]

Received: February 13, 2013

Published online: April 11, 2013

Keywords: [60]fullerene · 1,3-dipolar cycloaddition · asymmetric catalysis · enantioselectivity · organocatalysis

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–164.
- [2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354–358.
- [3] S. Iijima, *Nature* **1991**, *354*, 56–58.
- [4] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666–669.
- [5] J. L. Delgado, M. A. Herranz, N. Martín, *J. Mater. Chem.* **2008**, *18*, 1417–1426.
- [6] A. Hirsch, M. Bettreich, *Fullerenes, Chemistry and Reaction*, Wiley-VCH, Weinheim, **2005**.
- [7] a) C. Thilgen, F. Diederich, *Chem. Rev.* **2006**, *106*, 5049–5135; b) C. Thilgen, I. Gosse, F. Diederich, *Top. Stereochem.* **2003**, *23*, 1–124.
- [8] S. Filippone, E. E. Maroto, A. Martín-Domenech, M. Suarez, N. Martín, *Nat. Chem.* **2009**, *1*, 578–582.
- [9] E. E. Maroto, A. de Cózar, S. Filippone, Á. Martín-Domenech, M. Suarez, F. P. Cossío, N. Martín, *Angew. Chem.* **2011**, *123*, 6184–6188; *Angew. Chem. Int. Ed.* **2011**, *50*, 6060–6064.
- [10] K. Sawai et al., *J. Am. Chem. Soc.* **2011**, *133*, 17746–17752.
- [11] E. E. Maroto, S. Filippone, A. Martín-Domenech, M. Suarez, N. Martín, *J. Am. Chem. Soc.* **2012**, *134*, 12936–12938.
- [12] a) D. W. C. MacMillan, *Nature* **2008**, *455*, 304–308; b) E. N. Jacobsen, D. W. C. MacMillan, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 20618–20619.
- [13] M. Sampath, T.-P. Loh, *Chem. Sci.* **2010**, *1*, 739–742.
- [14] S. R. Wilson, L. Qingyi, C. Jingrong, W. Yunhui, C. J. Welch, D. I. Schuster, *Tetrahedron* **1996**, *52*, 5131–5142.
- [15] L.-W. Ye, J. Zhou, Y. Tang, *Chem. Soc. Rev.* **2008**, *37*, 1140–1152.
- [16] C. Zhang, X. Lu, *J. Org. Chem.* **1995**, *60*, 2906–2908.
- [17] B. J. Cowen, S. J. Miller, *Chem. Soc. Rev.* **2009**, *38*, 3102–3116.
- [18] G. Zhu, Z. Chen, Q. Jiang, D. Xiao, P. Cao, X. Zhang, *J. Am. Chem. Soc.* **1997**, *119*, 3836–3837.
- [19] a) A. Marinetti, A. Voituriez, *Synlett* **2010**, 174–194; b) Y. Fujiwara, G. C. Fu, *J. Am. Chem. Soc.* **2011**, *133*, 12293–12297; c) M. Steurer, L. K. Jensen, D. Worgull, K. A. Jørgensen, *Chem. Eur. J.* **2012**, *18*, 76–79; d) X. Han, F. Zhong, Y. Wang, Y. Lu, *Angew. Chem.* **2012**, *124*, 791–794; *Angew. Chem. Int. Ed.* **2012**, *51*, 767–770.
- [20] a) B. F. O'Donovan, P. B. Hitchcock, M. F. Meidine, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Commun.* **1997**, 81–82; b) L.-W. Guo, X. Gao, D.-W. Zhang, S.-H. Wu, H.-M. Wu, *Chin. J. Chem.* **2002**, *20*, 1430–1433.
- [21] D. Xiao, X. Zhang, *Angew. Chem.* **2001**, *113*, 3533–3536; *Angew. Chem. Int. Ed.* **2001**, *40*, 3425–3428.
- [22] The different order in the addition of the reagents affects to the formation of bisadducts, for more details see SI.
- [23] N. Martín, M. Altable, S. Filippone, Á. Martín-Domenech, L. Echegoyen, C. M. Cardona, *Angew. Chem.* **2006**, *118*, 116–120; *Angew. Chem. Int. Ed.* **2006**, *45*, 110–114.
- [24] A solution of (*S,S*)-*f*-Binaphane (10 mol%) and allenolate **1a** (0.016 mmol) in dry toluene (1 mL) was stirred for 15 min and then [60]fullerene (0.017 mmol) was added and the resulting mixture was stirred for 2 h at RT under Ar atmosphere.
- [25] L. Echegoyen, L. E. Echegoyen, *Acc. Chem. Res.* **1998**, *31*, 593–601.
- [26] J. Heinze, *Angew. Chem.* **1984**, *96*, 823–840; *Angew. Chem. Int. Ed. Eng.* **1984**, *23*, 831–847.
- [27] N. Martín, L. Sánchez, B. Illescas, I. Pérez, *Chem. Rev.* **1998**, *98*, 2527–2547.
- [28] a) Y. Xia, Y. Liang, Y. Chen, M. Wang, L. Jiao, F. Huang, S. Liu, Y. Li, Z.-X. Yu, *J. Am. Chem. Soc.* **2007**, *129*, 3470–3471; b) T. Dudding, O. Kwon, E. Mercier, *Org. Lett.* **2006**, *8*, 3643–3646; c) E. Mercier, B. Fonovic, C. Henry, O. Kwon, T. Dudding, *Tetrahedron Lett.* **2007**, *48*, 3617–3620; d) Y. Liang, S. Liu, Y. Xia, Y. Li, Z.-X. Yu, *Chem. Eur. J.* **2008**, *14*, 4361–4373.
- [29] CCDC 902793 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [30] *Sector rule* used up to now to assign the absolute configuration on the basis of the Cotton effect at 430 nm, even though well justified and rationalized, presents an oversight in its conclusion and should be amended also in the light of these results.
- [31] S. Campidelli, P. Bourgun, B. Guinchin, J. Furrer, H. Stoeckli-Evans, I. M. Saez, J. W. Goodby, R. Deschenaux, *J. Am. Chem. Soc.* **2010**, *132*, 3574–3581.
- [32] It is worth noting that in cases R¹ = Ph (Table 2, entries 4 and 5), the priorities of substituents change and lead to an *R* configuration in the product.
- [33] Both enantiomers were separated previously by semipreparative HPLC using Regis WHELK-O1 5/100 25 cm × 10.0 mm column, hexane/2-propanol 92:8, flow rate 4 mL min⁻¹.
- [34] Y. Hizume, K. Tashiro, R. Charvet, Y. Yamamoto, A. Saeki, S. Seki, T. Aida, *J. Am. Chem. Soc.* **2010**, *132*, 6628–6629.