Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Open Access Article. Published on 16 January 2019. Downloaded on 12/6/2025 9:07:56 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Check for updates

Cite this: *Chem. Sci.*, 2019, **10**, 3012

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 14th November 2018
Accepted 15th January 2019

DOI: 10.1039/c8sc05089a

rsc.li/chemical-science

A retro Baeyer–Villiger reaction: electrochemical reduction of [60]fullerene-fused lactones to [60]fullerene-fused ketones†

Chuang Niu,[a] Dian-Bing Zhou,[a] Yong Yang,[a] Zheng-Chun Yin[a] and Guan-Wu Wang*[ab]

A highly efficient electrochemical reduction of [60]fullerene-fused lactones to [60]fullerene-fused ketones, a formal process of retro Baeyer–Villiger reaction, has been achieved for the first time. The electrochemically generated dianionic [60]fullerene-fused lactones can be transformed into [60]fullerene-fused ketones in the presence of acetic acid in 85–91% yields. Control experiments have been performed to elucidate the reaction mechanism. The products have been characterized with spectroscopic data and single-crystal X-ray analysis. Moreover, the electrochemical properties have also been investigated.

Introduction

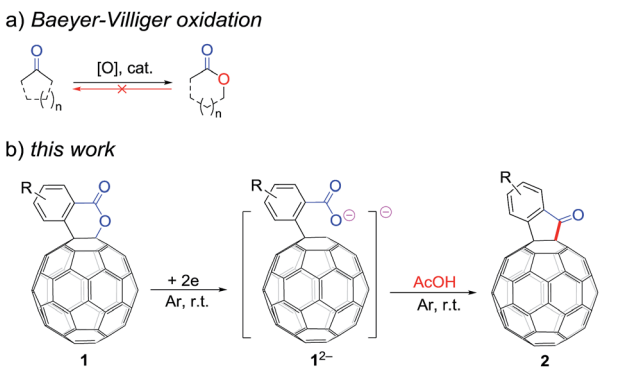
The Baeyer–Villiger oxidation is one of the most important transformations in organic synthesis, because valuable esters and lactones can be obtained directly from the corresponding ketones (Scheme 1a).[1] However, to the best of our knowledge, the retro Baeyer–Villiger reaction, that is, the direct reduction of esters/lactones to ketones accompanied by the elimination of only one oxygen atom *via* either a deoxygenative (–O) or dehydrative (–H_2O) pathway, has never been reported and remains a challenging task.[2,3]

Over the past few decades, fullerene derivatives have attracted much attention due to their potential for application in the fields of biomedical and materials science.[4] Therefore, a great diversity of synthetic protocols for functionalizing fullerenes have been developed by chemists.[5,6] Among the numerous methods, electrosynthesis has been demonstrated as a novel and efficient strategy due to its mild reaction conditions, good regioselectivity, and relatively high yields.[6]

It has been shown that electrochemically generated fullerene anions, especially singly bonded fullerene dianions, can be readily prepared and used as building blocks in the regioselective synthesis of fullerene derivatives with novel addition patterns.[6] In an attempt to protonate dianionic [60]fullerene (C_{60})-fused lactones with acetic acid (AcOH), C_{60}-fused ketones **2**,[7] rather than the expected tetrahydrofullerenes,[6i] can be surprisingly obtained in high yields (Scheme 1b). This is the first time the direct reduction of lactones to ketones, which is a formal retro reaction of Baeyer–Villiger oxidation, has been realized. Herein, we report this unprecedented retro Baeyer–Villiger reaction of C_{60}-fused lactones by the electrochemical approach.

Results and discussion

The employed C_{60}-fused lactone **1a** was synthesized according to our previous procedure.[8] Cyclic voltammetry (CV) of **1a** in *o*-dichlorobenzene (ODCB) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) showed that the first redox was an



Scheme 1 (a) Baeyer–Villiger oxidation. (b) Retro Baeyer–Villiger reaction of C_{60}-fused lactones.

[a]Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Center for Excellence in Molecular Synthesis of CAS, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: gwang@ustc.edu.cn

[b]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

† Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization data, the NMR spectra, and CVs of **2a–i** and **3a** (PDF). X-ray crystallographic data for **2f** (CIF). CCDC 1856172. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc05089a

This journal is © The Royal Society of Chemistry 2019

Open Access Article. Published on 16 January 2019. Downloaded on 12/6/2025 9:07:56 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

irreversible one-electron transfer process with an E_{pc} of −0.60 V (A) *versus* a saturated calomel electrode (SCE), and the second redox was chemically quasi-reversible on the CV timescale with E_{pc} at −1.14 V (B) (Fig. 1a), indicating that the compound underwent a chemical reaction process after receiving one electron. The heterolytic cleavage of the C_{60}–O bond occurred to provide the ring-opened radical anion **1a**$^{\bullet-}$, in which the negative charge and unpaired electron were distributed on the fullerene skeleton and/or the carbonyl group, respectively (*vide infra*), once **1a** acquired one electron. Upon acceptance of the second electron, a singly bonded dianionic species **1a**$^{2-}$, in which one negative charge was located at the carboxylate group and another one was distributed on the fullerene cage, was formed.[9] These ring-opened structures were further confirmed by the visible/near-infrared (Vis/NIR) study of **1a**$^{\bullet-}$ and **1a**$^{2-}$, which were obtained by controlled potential electrolysis (CPE) at −0.90 V and −1.34 V, respectively. The Vis/NIR spectra of **1a**$^{\bullet-}$ and **1a**$^{2-}$ (Fig. 1b) showed strong absorption bands at λ = 986 and 652 nm, which were in excellent agreement with those of the singly bonded anions of a C_{60}-fused oxazoline (λ = 963, and 645 nm),[9c] a C_{60}-fused sultone (λ = 983 and 648 nm),[9d] and a C_{60}-fused indoline (λ = 966 and 648 nm).[9e]

Controlled potential electrolysis of **1a** (0.015 mmol) in 15.0 mL of anhydrous ODCB solution containing 0.1 M TBAP was carried out at −1.34 V to obtain **1a**$^{2-}$ under an argon atmosphere at ambient temperature (∼25 °C). With an aim to protonate **1a**$^{2-}$, AcOH (10 equiv.) was added, and the reaction mixture was stirred at room temperature for 30 min. To our surprise, an intriguing product, C_{60}-fused ketone **2a**, was obtained in 91% yield. Importantly, this unexpected dehydrative retro Baeyer–Villiger reaction could be extended to other C_{60}-fused lactones, and the results are summarized in Table 1. C_{60}-fused lactones with electron-donating groups including the methyl and methoxy groups as well as electron-withdrawing groups such as the chloro and carbonyl groups at different positions of the aromatic ring afforded **2a–g** in excellent yields of 86–91%. Detailed comparisons of these results showed that the electronic properties (entries 1–4 *vs.* entries 5–7) and locations (entry 1 *vs.* entry 2, entry 3 *vs.* entry 4, and entry 5 *vs.* entry 6) of the substituents on the phenyl ring had little effect on the product yields, indicating that the ring-closure of **1a–g**$^{2-}$ to afford **2a–g** was a highly efficient process. In addition, when the di-substituted substrate with two methoxy groups was employed, the corresponding product **2h** could also be obtained smoothly in 85% yield. Finally, C_{60}-fused lactone **1i** with no substituent on the phenyl ring gave the simplest C_{60}-fused ketone **2i** in 90% yield.

The structures of products **2a–i** were unambiguously characterized by MALDI-TOF MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV-vis spectrometry. All mass spectra of these products exhibited the correct $[M]^+$ peaks. Their ^{1}H NMR spectra displayed the expected chemical shifts as well as the splitting patterns for all protons. The ^{13}C NMR spectra of **2a–i** exhibited no more than 30 peaks in the range of 135–159 ppm for the 58 sp^2-carbons of the fullerene cage and two peaks at 70–80 ppm for the two sp^3-carbons of the fullerene skeleton, consistent with the C_s symmetry of their molecular structures. Their UV-vis spectra exhibited a peak at 430–432 nm, which corresponds to the diagnostic absorption of 1,2-adducts of C_{60} at the [6,6]-junction. The structures of products were unambiguously confirmed by the single-crystal X-ray diffraction analysis of **2f** as an example (Fig. 2).[10]

During the screening of the added acids, it was intriguingly found that different amounts of trifluoroacetic acid (TFA) afforded different products. When **1a**$^{2-}$ was treated with 1 equiv. of TFA, **2a** could also be obtained in 90% yield, but required a long reaction time of 12 h. However, when **1a**$^{2-}$ was reacted with 3 equiv. of TFA for only 3 min, hydrofullerene **3a** was obtained in 89% yield (Scheme 2a). The structure of **3a** was established by its spectral data, particularly the singlet at δ_H = 6.89 ppm for the diagnostic fullerenyl proton in its ^{1}H NMR spectrum.[6f,i,j,9a,e,11] Additional control experiments showed that treatment of **3a** with 1 equiv. of sodium hydride (NaH) in a mixture of ODCB and CH_3CN (4 : 1) at room temperature under an argon atmosphere provided **2a** in 71% yield (Scheme 2b). The reported pK_a values of TFA, *t*-BuC_{60}H, PhCO_2H, and AcOH in DMSO were 3.45, 5.7, 11.1, and 12.3, respectively.[12] Although their corresponding pK_a values in ODCB or a mixture of ODCB and CH_3CN are unavailable, it is reasonable to assume that the relative pK_a values of the same order are retained in these solvent systems. Therefore, it is expected that TFA would first protonate the carboxylate anion and then the fullerenyl anion. When only 1 equiv. of TFA was added, the carboxylate anion of **1a**$^{2-}$ would be preferably protonated, and subsequent

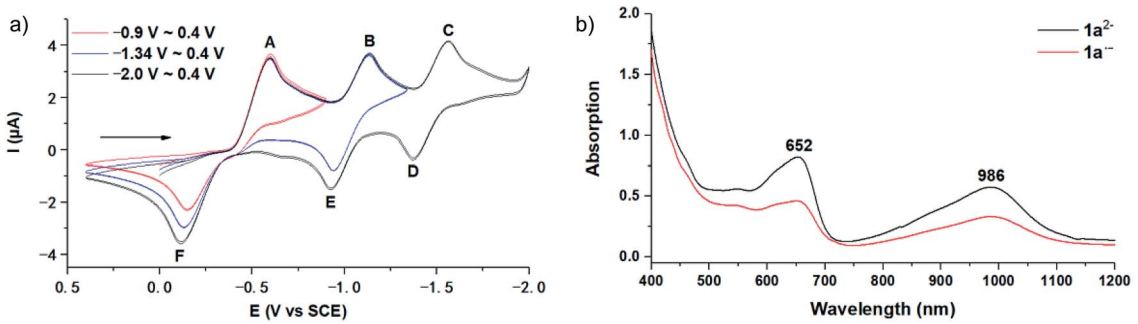
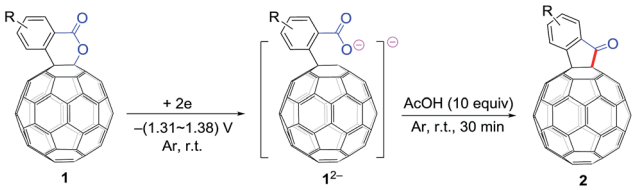
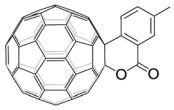
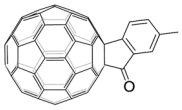
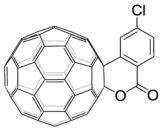
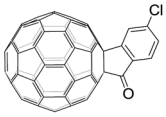
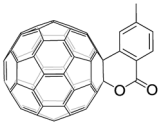
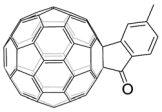
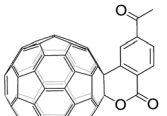
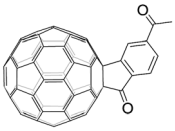
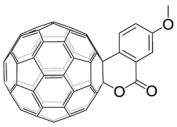
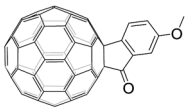
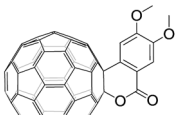
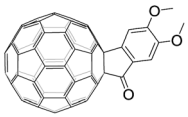
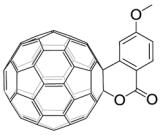
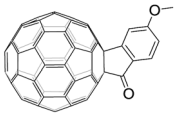
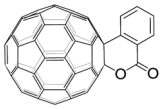
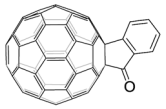
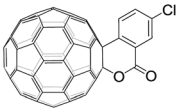
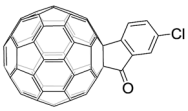


Fig. 1 (a) Cyclic voltammograms of compound **1a** (1.0 mM) shown within different potential windows. The CVs recorded in ODCB containing 0.1 M TBAP starting from 0.0 V toward the negative potential with a scan rate of 50 mV s^{-1}. The arrows indicate the scan direction for the cyclic voltammetric measurements. (b) Vis/NIR spectra of **1a**$^{\bullet-}$ (red) and **1a**$^{2-}$ (black) in ODCB (0.25 mM).

Open Access Article. Published on 16 January 2019. Downloaded on 12/6/2025 9:07:56 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Table 1 Results for the reaction of dianionic **1a–i**$^{2-}$ with AcOH[a]



Entry	C_{60}-fused lactone **1**	Potential (V)	Product **2**	Yield[b] (%)	Entry	C_{60}-fused lactone **1**	Potential (V)	Product **2**	Yield[b] (%)
1	 **1a**	−1.34	 **2a**	91	6	 **1f**	−1.31	 **2f**	90
2	 **1b**	−1.38	 **2b**	90	7	 **1g**	−1.38	 **2g**	88
3	 **1c**	−1.38	 **2c**	89	8	 **1h**	−1.36	 **2h**	85
4	 **1d**	−1.38	 **2d**	91	9	 **1i**	−1.36	 **2i**	90
5	 **1e**	−1.38	 **2e**	86					

[a] All the reactions were performed with 0.015 mmol of **1a–i**$^{2-}$ and 0.150 mmol of acetic acid at room temperature (~25 °C) for 30 min under an argon atmosphere. [b] Isolated yield.

intramolecular cyclization by the attack of the fullerenyl anion to the formed carboxyl group afforded C_{60}-fused ketone **2a**. In comparison, when excess amounts (3 equiv.) of TFA were added, both the carboxylate anion and the fullerenyl anion were protonated to give hydrofullerene **3a** as the most stable 1,2-adduct. On the other hand, 1 equiv. of NaH would selectively deprotonate the more acidic fullerenyl proton rather than the carboxyl group of **3a**, followed by a cyclization process to provide **2a**.

Based on the above results and previous literature,[9] a plausible reaction mechanism for the formation of **2** is depicted in Scheme 3. Firstly, C_{60}-fused lactone **1** is electrochemically reduced with a cleavage of the C–O bond to generate ring-opened dianionic **1**$^{2-}$. Since AcOH is the weakest acid in the order of the above-mentioned acids (TFA, *t*-BuC_{60}H, PhCO_2H and AcOH), only the carboxylate anion of dianion **1**$^{2-}$ seems to be protonated even in the presence of excess AcOH to give monoanion **4**. Finally, intermediate **4** undergoes intramolecular cyclization accompanied by the removal of the hydroxide ion, which is assisted by the neutralization with another molecule of AcOH, to provide product **2**.

We also explored the possibility for the retro Baeyer–Villiger reaction of C_{60}-fused lactones by utilization of their radical monoanions with **1a** as an example. The irreversible first redox process in the CV of **1a** (Fig. 1a) hinted that its lactone moiety would rupture to provide the ring-opened **1a**$^{\bullet-}$ after receiving one electron. The Vis/NIR spectrum of **1a**$^{\bullet-}$ showed significantly lower intensities at 986 and 652 nm than that of **1**$^{2-}$ at the same concentration (Fig. 1b), suggesting that only some of **1a**$^{\bullet-}$ had a ring-opened structure with the negative charge distributed on the fullerene skeleton. The synthesis of **2a** by the reaction of **1a**$^{\bullet-}$ with 10 equiv. of AcOH was attempted, yet **2a** could be obtained in only 54% yield (Scheme 4), much lower than that (91%) from the reaction of **1**$^{2-}$. The exact reaction

Open Access Article. Published on 16 January 2019. Downloaded on 12/6/2025 9:07:56 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

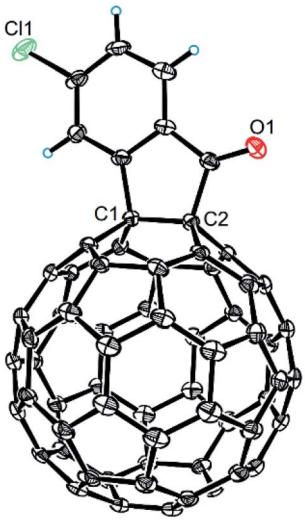
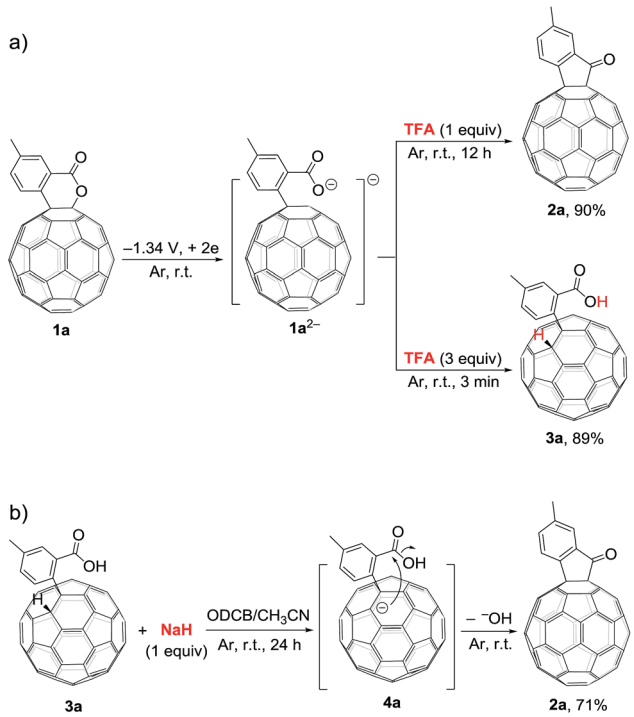


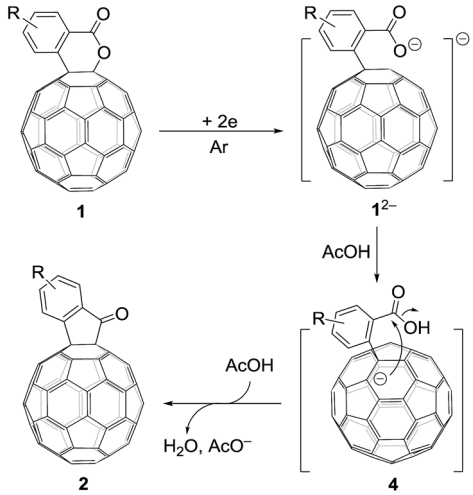
Fig. 2 ORTEP diagram for one enantiomer of **2f** with thermal ellipsoids shown at 50% probability. The toluene molecule is omitted for clarity.

pathway leading to **2a** is not clear and currently under investigation. Therefore, the retro Baeyer–Villiger reaction of C_{60}-fused lactones was much more efficiently achieved through their dianionic intermediates rather than with their radical monoanionic species.

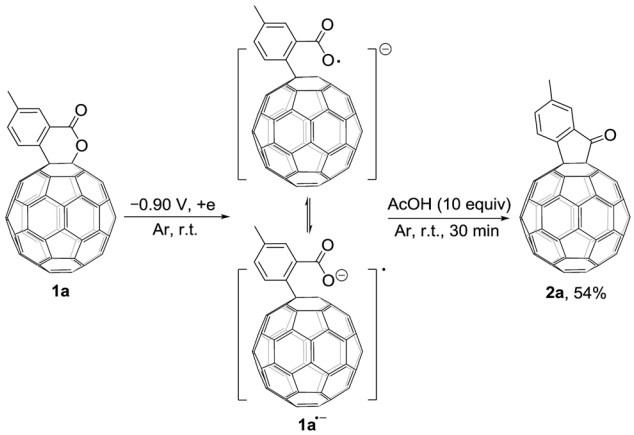
The half-wave reduction potentials of C_{60}-fused ketones **2a–i** and hydrofullerene **3a** along with those of C_{60} were investigated by CV and are summarized in Table 2. All of their electrochemical properties were quite similar and showed two



Scheme 2 Control experiments.



Scheme 3 Proposed reaction mechanism for the formation of C_{60}-fused ketones from C_{60}-fused lactones.



Scheme 4 Synthesis of **2a** by the reaction of **1a**$^{\bullet-}$ with AcOH.

reversible redox processes. As shown in Table 2, the first reduction potentials of products **2a–i** and **3a** were more negative than that of C_{60}, indicating that they possess higher LUMO

Table 2 Half-wave reduction potentials (V) of C_{60} and compounds **2a–f** and **3a**[a]

Compd	E_1	E_2
C_{60}	−1.076	−1.460
2a	−1.121	−1.503
2b	−1.127	−1.522
2c	−1.125	−1.520
2d	−1.128	−1.522
2e	−1.106	−1.495
2f	−1.104	−1.500
2g	−1.103	−1.490
2h	−1.117	−1.499
2i	−1.111	−1.483
3a	−1.130	−1.518

[a] *Versus* ferrocene/ferrocenium. Experimental conditions: 1.0 mM compound and 0.1 M TBAP in anhydrous ODCB; reference electrode: SCE; working electrode: Pt disc; auxiliary electrode: Pt wire; scan rate: 50 mV s^{-1}.

Open Access Article. Published on 16 January 2019. Downloaded on 12/6/2025 9:07:56 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

energy levels than C_{60} and may have potential for application in organic photovoltaic devices as acceptors.[13]

Conclusions

In summary, we have achieved a highly efficient synthesis of various C_{60}-fused ketones from C_{60}-fused lactones for the first time *via* electrochemical reduction, an unprecedented dehydrative retro Baeyer–Villiger reaction. The present protocol shows advantages of mild reaction conditions, a short reaction time, excellent product yields, and remarkable functional group tolerance. Moreover, control experiments have been performed to elucidate the plausible reaction mechanism for the formation of C_{60}-fused ketones. The electrochemical properties of the synthesized C_{60}-fused ketones have been characterized and may be utilized in solar cell devices.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

We are thankful for financial support from the National Natural Science Foundation of China (21572211) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000).

Notes and references

1 For selected reviews, see: (*a*) G. R. Krow, *Org. React.*, 1993, **43**, 251; (*b*) G. Strukul, *Angew. Chem., Int. Ed.*, 1998, **37**, 1198; (*c*) G.-J. ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Chem. Rev.*, 2004, **104**, 4105.

2 The terminology of "retro Baeyer–Villiger reaction" in retrosynthetic analyses of complex molecules appeared in the literature. See: (*a*) L. A. Paquette, M. J. Wyvratt, O. Schallner, D. F. Schneider, W. J. Begley and R. M. Blankenship, *J. Am. Chem. Soc.*, 1976, **98**, 6744; (*b*) L. A. Paquette, M. J. Wyvratt, O. Schallner, J. L. Muthard, W. J. Begley, R. M. Blankenship and D. Balogh, *J. Org. Chem.*, 1979, **44**, 3616; (*c*) D. Enders and M. Knopp, *Tetrahedron*, 1996, **52**, 5805.

3 The indirect retro Baeyer–Villiger reaction *via* multiple steps has been reported. See: J.-M. Dollat, J.-L. Luche and P. Crabbé, *J. Chem. Soc., Chem. Commun.*, 1997, 761.

4 For selected reviews, see: (*a*) E. Nakamura and H. Isobe, *Acc. Chem. Res.*, 2003, **36**, 807; (*b*) L. Sánchez, N. Martín and D. M. Guldi, *Angew. Chem., Int. Ed.*, 2005, **44**, 5374; (*c*) C. Thilgen and F. Diederich, *Chem. Rev.*, 2006, **106**, 5049; (*d*) F. Giacalone and N. Martín, *Chem. Rev.*, 2006, **106**, 5136; (*e*) Y. Matsuo and E. Nakamura, *Chem. Rev.*, 2008, **108**, 3016; (*f*) B. C. Thompson and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58; (*g*) D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski and N. Martín, *Chem. Soc. Rev.*, 2009, **38**, 1587; (*h*) J. L. Delgado, P.-A. Bouit, S. Filippone, M. Á. Herranz and N. Martín, *Chem. Commun.*, 2010, **46**, 4853; (*i*) M. D. Tzirakis and M. Orfanopoulos, *Chem. Rev.*, 2013, **113**, 5262; (*j*) S.-E. Zhu, F. Li and G.-W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 7535; (*k*) B. M. Illescas, J. Rojo, R. Delgado and N. Martín, *J. Am. Chem. Soc.*, 2017, **139**, 6018. For a recent example of biological applications, see: (*l*) J. Luczkowiak, A. Muñoz, M. Sánchez-Navarro, R. Ribeiro-Viana, A. Ginieis, B. M. Illescas, N. Martín, R. Delgado and J. Rojo, *Biomacromolecules*, 2013, **14**, 431.

5 For selected reviews, see: (*a*) M. Murata, Y. Murata and K. Komatsu, *Chem. Commun.*, 2008, 6083; (*b*) G. C. Vougioukalakis, M. M. Roubelakis and M. Orfanopoulos, *Chem. Soc. Rev.*, 2010, **39**, 817; (*c*) K. Itami, *Chem. Rec.*, 2011, **11**, 226; (*d*) G.-W. Wang and F.-B. Li, *Curr. Org. Chem.*, 2012, **16**, 1109; (*e*) E. E. Maroto, M. Izquierdo, S. Reboredo, J. Marco-Martínez, S. Filippone and N. Martín, *Acc. Chem. Res.*, 2014, **47**, 2660; (*f*) L. Gan, *Chem. Rec.*, 2015, **15**, 189.

6 For selected examples of electrosyntheses, see: (*a*) C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 1993, **115**, 8505; (*b*) P. L. Boulas, Y. Zuo and L. Echegoyen, *Chem. Commun.*, 1996, 1547; (*c*) K. M. Kadish, X. Gao, E. Van Caemelbecke, T. Suenobu and S. Fukuzumi, *J. Phys. Chem. A*, 2000, **104**, 3878; (*d*) O. Lukoyanova, C. M. Cardona, M. Altable, S. Filippone, Á. Martín-Domenech, N. Martín and L. Echegoyen, *Angew. Chem., Int. Ed.*, 2006, **45**, 7430; (*e*) M. Zheng, F.-F. Li, L. Ni, W.-W. Yang and X. Gao, *J. Org. Chem.*, 2008, **73**, 3159; (*f*) W.-W. Yang, Z.-J. Li and X. Gao, *J. Org. Chem.*, 2010, **75**, 4086; (*g*) F.-F. Li, A. Rodríguez-Fortea, P. Peng, G. A. Campos Chavez, J. M. Poblet and L. Echegoyen, *J. Am. Chem. Soc.*, 2012, **134**, 7480; (*h*) H.-L. Hou, Z.-J. Li and X. Gao, *Org. Lett.*, 2014, **16**, 712; (*i*) Y. Xiao and G. Wang, *Chin. J. Chem.*, 2014, **32**, 699; (*j*) H.-S. Lin, Y. Matsuo, J.-J. Wang and G.-W. Wang, *Org. Chem. Front.*, 2017, **4**, 603.

7 For the synthesis of other C_{60}-fused ketones, see: (*a*) S.-C. Chuang, A. Islam, C.-W. Huang, H.-T. Shih and C.-H. Cheng, *J. Org. Chem.*, 2003, **68**, 3811; (*b*) W. Zhang, J. K. Sprafke, M. Ma, E. Y. Tsui, S. A. Sydlik, G. C. Rutledge and T. M. Swager, *J. Am. Chem. Soc.*, 2009, **131**, 8446; (*c*) B. Hu, T.-X. Liu, P. Zhang, Q. Liu, J. Bi, L. Shi, Z. Zhang and G. Zhang, *Org. Lett.*, 2018, **20**, 4801.

8 G.-W. Wang and B. Zhu, *Chem. Commun.*, 2009, 1769.

9 (*a*) G.-W. Wang, F.-B. Li and T.-H. Zhang, *Org. Lett.*, 2006, **8**, 1355; (*b*) W.-W. Yang, Z.-J. Li, F.-F. Li and X. Gao, *J. Org. Chem.*, 2011, **76**, 1384; (*c*) W.-W. Chang, Z.-J. Li, W.-W. Yang and X. Gao, *Org. Lett.*, 2012, **14**, 2386; (*d*) R. Liu, F. Li, Y. Xiao, D.-D. Li, C.-L. He, W.-W. Yang, X. Gao and G.-W. Wang, *J. Org. Chem.*, 2013, **78**, 7093; (*e*) Y. Xiao, S.-E. Zhu, D.-J. Liu, M. Suzuki, X. Lu and G.-W. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 3006; (*f*) J.-J. Wang, H.-S. Lin, C. Niu and G.-W. Wang, *Org. Biomol. Chem.*, 2017, **15**, 3248.

10 The CCDC number of compound **2f** is 1856172. For more details, see the ESI.†

 This journal is © The Royal Society of Chemistry 2019

Open Access Article. Published on 16 January 2019. Downloaded on 12/6/2025 9:07:56 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

11 For other selected hydrofullerenes, see: (*a*) M. Izquierdo, S. Osuna, S. Filippone, A. Martín-Domenech, M. Solà and N. Martín, *J. Org. Chem.*, 2009, **74**, 1480; (*b*) M. Izquierdo, S. Osuna, S. Filippone, A. Martín-Domenech, M. Solà and N. Martín, *J. Org. Chem.*, 2009, **74**, 6253.

12 For selected examples, see: (*a*) F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456; (*b*) P. J. Fagan, P. J. Krusic, D. H. Evans, S. A. Lerke and E. Johnston, *J. Am. Chem. Soc.*, 1992, **114**, 9697.

13 For selected examples, see: (*a*) Y. Matsuo, A. Iwashita, Y. Abe, C.-Z. Li, K. Matsuo, M. Hashiguchi and E. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 15429; (*b*) C.-P. Chen, C. Luo, C. Ting and S.-C. Chuang, *Chem. Commun.*, 2011, **47**, 1845; (*c*) M. Hashiguchi, N. Obata, M. Maruyama, K. S. Yeo, T. Ueno, T. Ikebe, I. Takahashi and Y. Matsuo, *Org. Lett.*, 2012, **14**, 3276.