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Synthesis of a novel twisted π -conjugated macrocycle *via* double Friedel–Crafts reaction and its physical properties†

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We synthesized a cyclic molecule from diarylalkynes and Meldrum's acid derivatives as the methylenation reagent *via* double Friedel–Crafts reaction. Single-crystal X-ray structure analysis confirmed the twisted structure of the molecule. We also investigated their physical properties and homoconjugation by UV-Vis, photoluminescence, DFT and TD-DFT calculations.

In recent years, three-dimensional π -conjugated macrocycles exhibiting geometric structures¹ have been synthesized. Besides compounds with zero Gaussian curvature, such as carbon nanotubes and cycloparaphenylenes (CPPs),² twisted macrocycles³ are formed from combined special structures that can significantly alter their electronic, optical and chemical properties, and thus have received much attention. For example, the Möbius band is a well-known topological structure discovered independently by the German mathematicians and astronomers Möbius and Johanlestein in 1858,⁴ and macrocycles with the Möbius ring structure have been successfully synthesized recently.⁵ Besides, infinity-shaped or figure-eight molecules,⁶ molecular cages,⁷ and Penrose stairs⁸ have been widely reported so far. Twisted macrocycles have potential applications in various advanced technologies, such as fluorescent sensor,⁹ luminescent material¹⁰ and host–guest chemistry.¹¹

The typical cyclic π -conjugated molecules are composed of sp^2 carbon skeleton, allowing for the delocalization of π -electrons across the molecules.¹² Generally, the introduction of sp^3 carbons typically disrupts the π -conjugation. Therefore, examples where a π -conjugated macrocycle includes sp^3 carbons without cleavage of

the π -conjugation are rare.¹³ The flexibility provided by tetrahedron structure of sp^3 carbons facilitates the design of a wide variety of cyclic molecular structures, and thus it is also necessary to use a method for ensuring the coherence of the π -conjugated structure over sp^3 carbon atoms.

One effective approach to extend the π -conjugated system over sp^3 carbons is homoconjugation,¹⁴ where the π -conjugated system is extended across σ -bond(s) *via* through-space interaction instead of through-bond interaction.¹⁵ To achieve effective homoconjugation, a twisted or rigid structure is often necessary for keeping the molecular configuration to obtain the largest orbital overlap.¹⁴ Furthermore, based on previous researches, diarylmethane is the classic structure for realizing homoconjugation.¹⁶ Therefore, we hypothesised that if diarylmethane moieties can bridge two rigid π -conjugated structures, it is possible to build a π -conjugated system that includes sp^3 carbons without cleavage of the π -conjugation. Our recent research opens up the possibility of this assumption. We recently developed Meldrum's acid derivatives as cyclisation reagents capable of double C–C bond formation to synthesise fluorene derivatives from biaryl derivatives without using a catalyst (Fig. 1(a)).¹⁷ Owing to the existence of electron-donating amino groups, this reaction occurs at the C4–H and C4'–H positions of the biaryl, resulting in the formation of cyclic fluorene compound. We planned to synthesise a novel cyclic molecule **3** using this reaction: the diarylalkynes **1**, which serve as the rigid parts,¹⁸ are bridged by sp^3 carbon atoms from Meldrum's acid derivative (Fig. 1(b)). We expected that the π -conjugated structure of the entire molecule could be constructed with homoconjugation whereas the cyclic π -conjugated structure is hybridized by sp^3 carbon atoms (Fig. 1(c)).

We then investigated the synthesis of twisted macrocycle using our reported reaction.¹⁷ Treatment of amino group-containing diarylalkyne **1** with 2.5 equivalents of Meldrum's acid derivative **2** in dichloroethane at 120 °C for 12 h gave cyclic molecule **3** in 69% yield (Scheme 1).

The structure of the obtained cyclic molecule **3** was confirmed using ¹H nuclear magnetic resonance (NMR) spectroscopy (Fig. S14, ESI†), ¹³C NMR (Fig. S15, ESI†), high resolution

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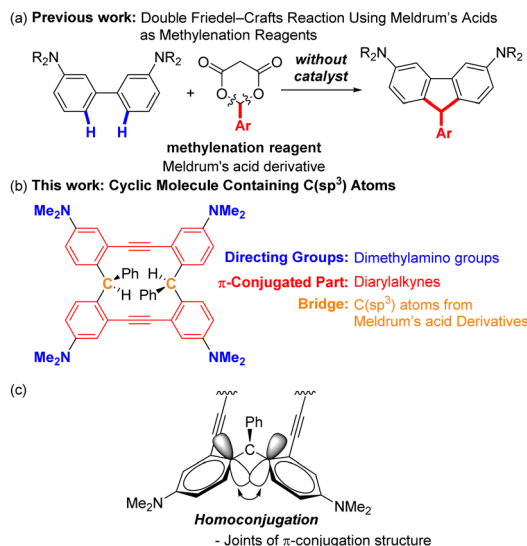
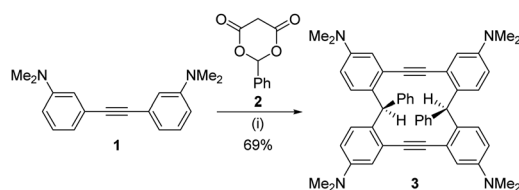


Fig. 1 (a) Double Friedel–Crafts reaction using Meldrum's acids as methylation reagents; (b) design of cyclic molecule containing sp³ carbon atoms; (c) utilization of homoconjugation for π -conjugation.

mass spectrometry (HRMS) (ESI⁺), and single-crystal X-ray crystallography (Fig. 2 and Fig. S2–S4, ESI⁺). In ¹H NMR spectrum, the methine proton of **3** is observed in downfield (7.09 ppm, Fig. S14, ESI⁺) compared to that of 4,4'-(phenyl-methylene)bis(*N,N*-dimethylaniline) (Leuco Malachite Green, 5.39 ppm).¹⁹ This result is probably attributed to the deshielding effect of the alkyne moieties.

Single-crystal X-ray crystallography revealed that the crystal packing structure of **3** is composed of the pair of enantiomers (Fig. S2, ESI⁺). For each enantiomer, the two diarylalkyne parts have the same axial chirality, which served as the basis for naming the enantiomers (*R_a,R_a*)-**3** and (*S_a,S_a*)-**3** (Fig. 2 and Fig. S1, ESI⁺).²⁰ Furthermore, product **3** exhibits a twisted cyclic structure. Although the two phenyl groups derived from **2** could have been in the same or opposite direction, they were found to be in the same direction (Fig. 2(c) and (f)). This finding may be attributed to steric repulsion between the phenyl group and phenyl methine moiety. The four *ortho*-phenylene moieties and two C≡C triple bonds were almost planar and straight, respectively.

Furthermore, the interconversion between two enantiomers of **3** was investigated by density functional theory (DFT) calculations (Method: B3LYP/6-31G(d), for the details, see ESI⁺). We found the interconversion between two enantiomers of **3** was a racemization which proceeds through a transient intermediate of the transition



Scheme 1 Synthesis of twisted macrocycle **3**. Reagents and conditions: (i) **2** (2.5 equiv.), ClCH₂CH₂Cl, 120 °C, 6 h.

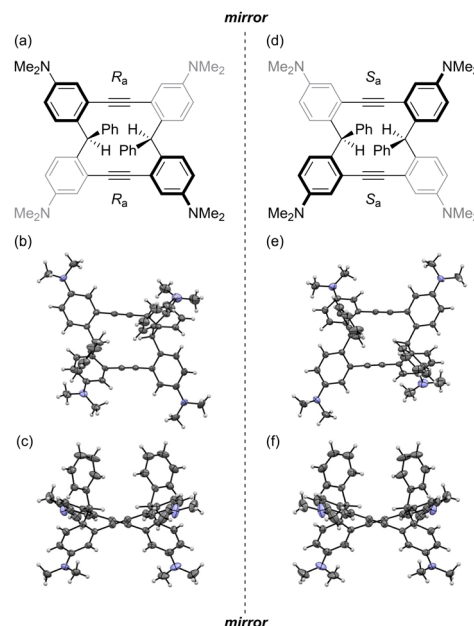


Fig. 2 Structures of (*R_a,R_a*)-**3** and (*S_a,S_a*)-**3**. (a) Structure of (*R_a,R_a*)-**3**; (b) top view of (*R_a,R_a*)-**3**; (c) front view of (*R_a,R_a*)-**3**; (d) structure of (*S_a,S_a*)-**3**; (e) top view of (*S_a,S_a*)-**3**; (f) front view of (*S_a,S_a*)-**3**. The thermal ellipsoids are drawn at 50% probability in the ORTEP drawings.

state TS-**3**. The energy barrier is about 7.5 kcal mol^{−1} (Fig. 3). Compared with previous researches,^{8b,c,21} this relatively lower energy barrier makes the racemization proceed easily at room temperature.^{22,23}

DFT calculations were performed to verify the hypothesis whether homoconjugation provided by diarylmethane moieties can construct continuous π -conjugated systems containing sp³ carbons. Interestingly, the results of the calculations show that there is an overlap of π -orbitals at the *ipso*-carbon atoms on the aromatic rings (yellow circle in Fig. 4(a)) and the

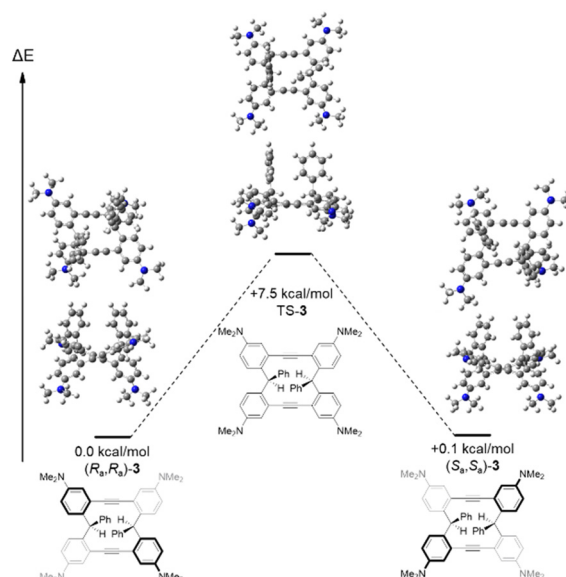


Fig. 3 Energy diagram of the interconversion between two enantiomers.



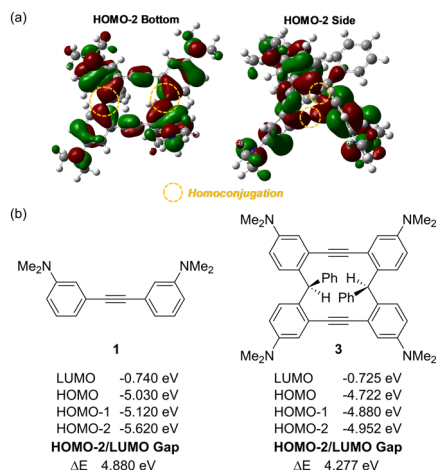


Fig. 4 (a) HOMO-2 orbital of **3** and homoconjugation (left: bottom view; right: side view); (b) the energies of LUMO, HOMO, HOMO-1, and HOMO-2 and HOMO-2/LUMO energy gaps of **1** and **3** calculated by the B3LYP/6-31G(d) level of theory.

HOMO-2/LUMO energy gap of **3** is smaller than that of **1** (Fig. 4(b)). These results indicate that a weak homoconjugation at the HOMO-2 level exists in **3**.

To further validate the effect of homoconjugation on the HOMO-2 level, we measured the UV-Vis and fluorescence spectra of the twisted macrocycle **3** and its precursor **1** (Fig. S5 and Table S10, ESI†). In 0.01 mM dichloromethane solution, **3** exhibited a maximum absorption at 271 nm and small absorption peaks at 222 and 347 nm. Precursor **1** exhibited a maximum absorption at 266 nm and small absorption peaks at 219 and 338 nm. By comparing the absorption spectra of **1** and **3**, a slight red shift was detected (219 to 222, 266 to 271, and 338 to 348 nm). The red shift observed in the UV-Vis spectra was also observed in the fluorescence spectra of **1** and **3** (406 to 415 nm).

TD-DFT calculations (B3LYP/6-311++G(d,p)) were carried out. Based on stimulated UV-Vis spectra of **1** (Fig. S9, ESI†) and **3** (Fig. S10, ESI†), **3** exhibited a maximum absorption at 292 nm and small absorption peaks at 370 nm. Precursor **1** exhibited a maximum absorption at 303 nm and small absorption peaks at 246 nm. The redshift was also observed in the TD-DFT calculations. Electronic transitions related to HOMO-2 were listed in Table S25 (ESI†) (precursor **1**) and Table S26 (ESI†) (product **3**). We found that excited states involving HOMO-2 (Fig. S9, ESI† marked in red) of precursor **1** has relatively higher oscillator strength. About product **3**, excited states involving HOMO-2 (Fig. S10, ESI† marked in red) of product **3** shows medium contribution to the overall absorption. Therefore, TD-DFT calculations illustrate explicitly the significant contribution of the HOMO-2 level to the absorption spectrum. This result also supports the existence of homoconjugation at the HOMO-2 level of product **3**.

In summary, we successfully synthesised a cyclic molecule with a twisted topological structure from electron-rich diarylalkynes and Meldrum's acid derivatives *via* a double Friedel-Crafts reaction. This is a special example of a sp^3 carbon-

bridged twisted cyclic π -conjugated molecule with maintaining the π -conjugated system by homoconjugation. Single-crystal X-ray structural analysis revealed that this molecule exists as a mixture of enantiomers in a single crystal unit. In the absorption and fluorescence spectra of the twisted macrocycle, a red shift was observed compared to that of the diarylalkyne precursor. The DFT and TD-DFT calculations can explain this red shift and the existence of homoconjugation. This research demonstrates the versatility and potential of sp^3 carbon atoms in complex π -conjugated systems, providing a new method for construction of new π -conjugated macrocycle bridged sp^3 carbon atoms by homoconjugation.

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Data availability

The data supporting this article have been included as part of the ESI†. Crystallographic data for compound **3** has been deposited at the CCDC 2335048† and can be obtained from <https://www.ccdc.cam.ac.uk/>.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- Reviews: (a) J. F. Stoddart, *Chem. Soc. Rev.*, 2009, **38**, 1521; (b) Y. Segawa, D. R. Levine and K. Itami, *Acc. Chem. Res.*, 2019, **52**, 2760; Books: (c) A. T. Balaban, *From Chemical Topology to Three-Dimensional Geometry*, Springer, New York, NY, 2006; (d) A. Kerber, R. Laue, M. Meringer, C. Rücker and E. Schymanski, *Mathematical Chemistry and Chemoinformatics*, De Gruyter, Berlin, Boston, 2014.
- Reviews: (a) E. J. Leonhardt and R. Jasti, *Nat. Rev. Chem.*, 2019, **3**, 672; (b) J. Wang, X. Zhang, H. Jia, S. Wang and P. Du, *Acc. Chem. Res.*, 2021, **54**, 4178; (c) D. Imoto, A. Yagi and K. Itami, *Precis. Chem.*, 2023, **1**, 516.
- (a) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 3350; (b) K. C. Sahoo, M. A. Majewski, M. Stepień and H. Rath, *J. Org. Chem.*, 2017, **82**, 8317; (c) I. Casademont-Reig, T. Woller, J. Contreras-García, M. Alonso, M. Torrent-Sucarrat and E. Matito, *Phys. Chem. Chem. Phys.*, 2018, **20**, 2787; (d) Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, *Science*, 2019, **365**, 272; (e) K. J. Weiland, T. Brandl, K. Atz, A. Prescimone, D. Häussinger, T. Šolomek and M. Mayor, *J. Am. Chem. Soc.*, 2019, **141**, 2104; (f) A. Ghosh, S. Dash, A. Srinivasan, C. H. Suresh,



- S. Peruncheralathan and T. K. Chandrashekar, *Org. Chem. Front.*, 2019, **6**, 3746; (g) Y. Li, A. Yagi and K. Itami, *J. Am. Chem. Soc.*, 2020, **142**, 3246; (h) M. Rickhaus, M. Jirasek, L. Tejerina, H. Gotfredsen, M. D. Peeks, R. Haver, H.-W. Jiang, T. D. W. Claridge and H. L. Anderson, *Nat. Chem.*, 2020, **12**, 236. Reviews: (i) M. Stępień, N. Sprutta and L. Latos-Grażyński, *Angew. Chem., Int. Ed.*, 2011, **50**, 4288; (j) M. Rickhaus, M. Mayor and M. Juriček, *Chem. Soc. Rev.*, 2016, **45**, 1542; (k) B. Szyzsko, M. J. Bialek, E. Pacholska-Dudziak and L. Latos-Grażyński, *Chem. Rev.*, 2017, **117**, 2839; (l) M. A. Majewski and M. Stępień, *Angew. Chem., Int. Ed.*, 2019, **58**, 86; (m) M. Hasegawa, Y. Nojima and Y. Mazaki, *ChemPhotoChem*, 2021, **5**, 10421058; (n) S. M. Bachrach, *J. Org. Chem.*, 2023, **88**, 7962.
- 4 J. H. E. Cartwright and D. L. González, *Math. Intell.*, 2016, **38**, 69.
- 5 Single-stranded Möbius molecules: (a) D. Ajami, O. Oeckler, A. Simon and R. Herges, *Nature*, 2003, **426**, 819; (b) Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2008, **47**, 681; (c) G. R. Schaller, F. Topić, K. Rissanen, Y. Okamoto, J. Shen and R. Herges, *Nat. Chem.*, 2014, **6**, 608; (d) G. Naulet, L. Sturm, A. Robert, P. Dechambenoit, F. Röhricht, R. Herges, H. Bock and F. Durola, *Chem. Sci.*, 2018, **9**, 8930; (e) Y.-Y. Fan, D. Chen, Z.-A. Huang, J. Zhu, C.-H. Tung, L.-Z. Wu and H. Cong, *Nat. Commun.*, 2018, **9**, 3037; (f) J. S. Moore, X. Jiang, S. D. Laffoon, D. Chen, S. Pérez-Estrada, A. S. Danis, J. Rodríguez-López, M. A. García-Garibay and J. Zhu, *J. Am. Chem. Soc.*, 2020, **142**, 6493; (g) Z. Luo, X. Yang, K. Cai, X. Fu, D. Zhang, Y. Ma and D. Zhao, *Angew. Chem., Int. Ed.*, 2020, **59**, 14854; (h) J. Malinčič, S. Gaikwad, J. P. Mora-Fuentes, M.-A. Boillat, A. Prescimone, D. Häussinger, A. G. Campaña and T. Šolomek, *Angew. Chem., Int. Ed.*, 2022, **61**, e202208591. Double-stranded Möbius Molecules: (i) S. Nishigaki, Y. Shibata, A. Nakajima, H. Okajima, Y. Masumoto, T. Osawa, A. Muranaka, H. Sugiyama, A. Horikawa, H. Uekusa, H. Koshino, M. Uchiyama, A. Sakamoto and K. Tanaka, *J. Am. Chem. Soc.*, 2019, **141**, 14955. Möbius carbon nanobelt: (j) Y. Segawa, T. Watanabe, K. Yamanoue, M. Kuwayama, K. Watanabe, J. Pirillo, Y. Hijikata and K. Itami, *Nat. Synth.*, 2022, **1**, 535; (k) W. Fan, T. M. Fukunaga, S. Wu, Y. Han, Q. Zhou, J. Wang, Z. Li, X. Hou, H. Wei, Y. Ni, H. Isobe and J. Wus, *Nat. Synth.*, 2023, **2**, 880.
- 6 (a) Z. Zhang, W.-Y. Cha, N. J. Williams, E. L. Rush, M. Ishida, V. M. Lynch, D. Kim and J. L. Sessler, *J. Am. Chem. Soc.*, 2014, **136**, 7591; (b) K. Senthikumar, M. Kondratowicz, T. Lis, P. J. Chmielewski, J. Cybinska, J. L. Zafra, J. Casado, T. Vives, J. Crassous, L. Favereau and M. Stępień, *J. Am. Chem. Soc.*, 2019, **141**, 7421; (c) A. Robert, G. Naulet, H. Bock, N. Vanthuyne, M. Jean, M. Giorgi, Y. Carissan, C. Aroulanda, A. Scalabre, E. Pouget, F. Durola and Y. Coquerel, *Chem. – Eur. J.*, 2019, **25**, 14364; (d) L. H. Wang, N. Hayase, H. Sugiyama, J. Nogami, H. Uekusa and K. Tanaka, *Angew. Chem., Int. Ed.*, 2020, **59**, 17951; (e) T. A. Schaub, E. A. Prantl, J. Kohn, M. Bursch, C. R. Marshall, E. J. Leonhardt, T. C. Lovell, L. N. Zakharov, C. K. Brozek, S. R. Waldvogel, S. Grimme and R. Jasti, *J. Am. Chem. Soc.*, 2020, **142**, 8763; (f) W. Fan, T. Matsuno, Y. Han, X. Wang, Q. Zhou, H. Isobe and J. Wu, *J. Am. Chem. Soc.*, 2021, **143**, 15924; (g) C. Li, Z. Huang, Y. Hu, W. Liang, R. Su, M. Chen, L. Zhou, D. Wu, G. Gao and J. You, *Org. Lett.*, 2021, **23**, 3746; (h) M. Krzeszewski, H. Ito and K. Itami, *J. Am. Chem. Soc.*, 2022, **144**, 862; (i) M. Hasegawa, C. Hasegawa, Y. Nagaya, K. Tsubaki and Y. Mazaki, *Chem. – Eur. J.*, 2022, **28**, e2022022; (j) K. Wypych, M. Dimitrova, D. Sundholm and M. Pawlicki, *Org. Lett.*, 2022, **24**, 4876; (k) L.-H. Wang, J. Nogami, Y. Nagashima and K. Tanaka, *Org. Lett.*, 2023, **25**, 4225; (l) A. Artigas, Y. Carissan, D. Hagebaum-Reignier, H. Bock, F. Durola and Y. Coquerel, *Chem. – Eur. J.*, 2024, e202401016.
- 7 (a) K. Matsui, Y. Segawa, T. Namikawa, K. Kamada and K. Itami, *Chem. Sci.*, 2012, **4**, 84; (b) T. Matsushima, S. Kikkawa, I. Azumaya and S. Watanabe, *ChemistryOpen*, 2018, **7**, 278; (c) N. Hayase, J. Nogami, Y. Shibata and K. Tanaka, *Angew. Chem., Int. Ed.*, 2019, **58**, 9439; (d) Y. Ni, F. Gordillo-Gómez, M. P. Alvarez, Z. Nan, Z. Li, S. Wu, Y. Han, J. Casado and J. Wu, *J. Am. Chem. Soc.*, 2020, **142**, 12730; (e) J. Zhu, Y. Han, Y. Ni, S. Wu, Q. Zhang, T. Jiao, Z. Li and J. Wu, *J. Am. Chem. Soc.*, 2021, **143**, 14314; (f) A. Basavarajappa, M. D. Ambhorea and V. G. Anand, *Chem. Commun.*, 2021, **57**, 4299.
- 8 (a) L. S. Penrose and R. Penrose, *Br. J. Psychol.*, 1958, **49**, 31; (b) W. Nakanishi, T. Matsuno, J. Ichikawa and H. Isobe, *Angew. Chem., Int. Ed.*, 2011, **50**, 6048; (c) Z. He, E. Wang, J. W. Y. Lam, Y. Li, Z. Lin and B. Z. Tang, *ChemPlusChem*, 2015, **80**, 1245.
- 9 H. Nie, Q.-H. Li, S. Zhang, C.-M. Wang, W.-H. Lin, K. Deng, L.-J. Shu, Q.-D. Zeng and J.-H. Wan, *Org. Chem. Front.*, 2021, **8**, 6806.
- 10 (a) H. Tanaka, Y. Inoue and T. Mori, *ChemPhotoChem*, 2018, **2**, 386. Review: (b) J.-L. Ma, Q. Peng and C.-H. Zhao, *Chem. – Eur. J.*, 2019, **25**, 15441.
- 11 (a) H. Abe, T. Yoneda, Y. Ohishi and M. Inouye, *Chem. – Eur. J.*, 2016, **22**, 18944; (b) Y. Xu, S. Gsanger, M. B. Minameyer, I. Imaz, D. Maspoch, O. Shyshov, F. Schwer, X. Ribas, T. Drewello, B. Meyer and M. von Delius, *J. Am. Chem. Soc.*, 2019, **141**, 18500; (c) J. Wang, Y.-Y. Ju, K.-H. Low, Y.-Z. Tan and J. Liu, *Angew. Chem., Int. Ed.*, 2021, **60**, 11814.
- 12 Reviews: (a) P. von Ragué Schleyer, *Chem. Rev.*, 2001, **101**, 1115; (b) T. M. Krygowski and M. K. Cyrański, *Chem. Rev.*, 2001, **101**, 1385; (c) N. Martin and L. T. Scott, *Chem. Soc. Rev.*, 2015, **44**, 6397; Book: (d) M. Solà, A. I. Boldyrev, M. K. Cyrański, T. M. Krygowski and G. Merino, *Aromaticity and Antiaromaticity: Basics and Applications*, John Wiley & Sons Ltd, 2023.
- 13 (a) L. T. Scott, G. J. DeCicco, J. L. Hyun and G. Reinhardt, *J. Am. Chem. Soc.*, 1983, **105**, 7760; (b) L. T. Scott, M. J. Cooney, D. W. Rogers and K. Dejiroongruang, *J. Am. Chem. Soc.*, 1988, **110**, 7244; (c) C. Lepetit, B. Silvi and R. Chauvin, *J. Phys. Chem. A*, 2003, **107**, 464; (d) Y. Miyazawa, Z. Wang, M. Matsumoto, S. Hatano, I. Antol, E. Kayahara, S. Yamago and M. Abe, *J. Am. Chem. Soc.*, 2021, **143**, 7426.
- 14 (a) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, 1954, **76**, 18; (b) L. T. Scott, *Pure Appl. Chem.*, 1986, **58**, 105. Review: (c) R. V. Williams, *Chem. Rev.*, 2001, **101**, 1185.
- 15 J. Liu, H. Zhang, L. Hu, J. Wang, J. W. Y. Lam, L. Blancafort and B. Z. Tang, *J. Am. Chem. Soc.*, 2022, **144**, 7901.
- 16 (a) S. Clementi, V. Mancini and G. Marino, *J. Chem. Soc. D*, 1970, 1457; (b) J. O. Barcina, M. d R. C. Heras, M. Mba, R. G. Aspe and N. Herrero-García, *J. Org. Chem.*, 2009, **74**, 7148; (c) H. Zhang, X. Zheng, N. Xie, Z. He, J. Liu, N. L. C. Leung, Y. Niu, X. Huang, K. S. Wong, R. T. K. Kwok, H. H. Y. Sung, I. D. Williams, A. Qin, J. W. Y. Lam and B. Z. Tang, *J. Am. Chem. Soc.*, 2017, **139**, 16264.
- 17 Z. Jiang, K. Sekine and Y. Kuninobu, *Chem. Commun.*, 2022, **58**, 843.
- 18 S. Toyota, *Chem. Rev.*, 2010, **110**, 5398.
- 19 M. Söderström, C. Matt and L. R. Odell, *ACS Omega*, 2023, **8**, 4320.
- 20 L. C. Cross and W. Klyne, *Pure Appl. Chem.*, 1976, **45**, 11.
- 21 E. L. Eliel, S. H. Wilen and M. P. Doyle, *Basic Organic Stereochemistry*, Wiley, New York, 2001.
- 22 Chiral-stationary phase HPLC for the racemic resolution of product 3 has been tried. However, the two enantiomers of product 3 could not be isolated successfully. IA-3, IB N-3, IC-3, ID-3, IE-3, IF-3, IG-3, IH-3 and IJ-3 columns with various kinds of eluents (tetrahydrofuran, *n*-hexane, ethyl acetate, dichloromethane, chloroform, diethylamine and their combination) have been tried.
- 23 We measured the circular dichroism (CD) spectra of 10⁻⁴ M DCM solution of the mixtures of 3 and (+)-10-camphorsulfonic acid ((+)-CSA) or (–)-CSA with different ratio. Comparing with spectra of (+)-CSA and (–)-CSA solution, red shift and enhancement of the ellipticity were observed (Fig. S21, ESI†). These results indicated that the addition of the chiral additive induced the chirality of 3.

