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ARTICLE

## Stepwise Synthesis and Characterization of Germa[4], [5], [8], and [10]pericyclines

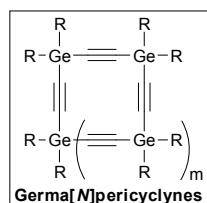
Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The stepwise syntheses of germa[*N*]pericyclines, including the [5]pericyclines, and their characterization are described. The yields of germa[4] and [8]pericyclines were improved significantly compared to those obtained in previous studies. The routes reported herein afforded the novel germa[5] and [10]pericyclines, which were characterized by X-ray crystallography, UV-Vis spectroscopy, and fluorescence emission spectroscopy. A unique fluorescence emission was observed for the large germa[10]pericycline ring.



### Previous studies

Single-step synthesis from **1a–b**  
Unselective synthesis  
*N* = 4, 6, 8 of (even [*N*])

### This study

•Stepwise, selective synthesis  
•Synthesis of [5]pericyclines (odd [*N*])

Fig 1 Germa[*N*]pericyclines

## Introduction

The acetylene unit, especially as polyynes, has long been focused in material science, and as building blocks of peculiar structural molecules in synthetic, and physical organic chemistry.<sup>1,2</sup> In recent decades, cyclic skipped polyynes compounds called [*N*]pericyclines,<sup>3–7</sup> which are composed of *N* acetylenic units, have received a growing amount of attention. As the reduced bond angles of the vertex sp<sup>3</sup> atoms in pericyclines are considered to reinforce the through-space interaction between skipped alkynes, such characteristics result in unique electronic and optical properties. To develop pericycline chemistry facilitating the hyperconjugation of alkynes<sup>8</sup> and the heavy atom effect of vertexes, we previously reported the synthesis and characterization of germa[*N*]pericyclines, novel pericyclines containing the group

14 element germanium (Fig 1).<sup>9</sup> It was demonstrated that such compounds were efficient building blocks for incorporation in functional materials and polymers. However, our previous one-step synthesis unselectively afforded [4], [6], and [8]pericyclines in low yields. Moreover, this method was not suitable for the preparation of [5]pericyclines, containing an odd number of germanium atoms. Since the small [4] and [5]pericyclines are expected to show specific properties due to their reduced vertex angles, their syntheses and characterization are of particular interest. In contrast, germa[8]pericyclines were revealed to display unique fluorescence emission patterns in fluorescence spectra and we believed that such interesting behaviour was worthy of investigation through the synthesis of large ring germapericyclines. We herein report the improved stepwise synthesis of germa[*N*]pericyclines, including germa[4], [5], [8], and [10]pericyclines, and their characterizations by X-ray crystallography, UV-Vis spectroscopy, and fluorescence spectroscopy.

## Results and discussion

We first performed the stepwise synthesis of germapericyclines from diethynylgermanes **1a–b**.<sup>9</sup> To monoanions of **1a–b**, generated by the addition of *n*-butyllithium, was added 0.5 eq of the appropriate germanium dichloride to give trimeric compounds **2a–b** (Scheme 1). Monoacetylation of **2a–b** with ethyl magnesium bromide followed by coupling with 1 eq of the germanium dichloride and subsequent ethynylation afforded tetragermanes **3a–b**. With precursors **2** and **3** in hand, we conducted the macrocyclization reaction to give the germapericyclines. Slow addition of diphenylgermanium dichloride to dilithiated **2a** via a syringe pump afforded **4a** and **5a** in 12% and 23% yields, respectively. Addition over 5 min via a dropping funnel gave **4a** and **5a** in only 4% and 17%, respectively. The overall yields of

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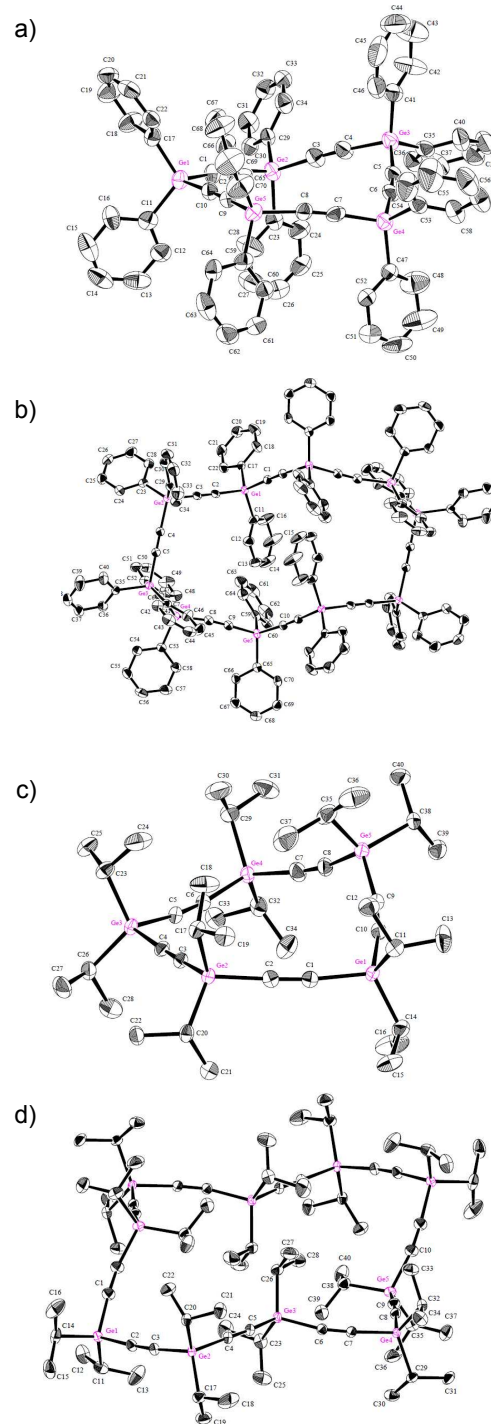
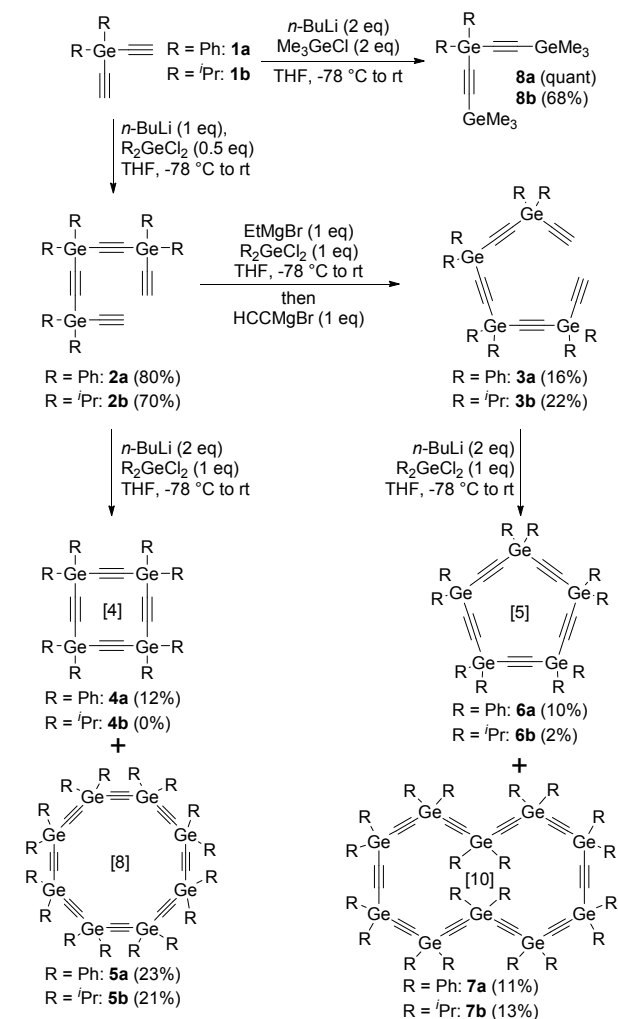
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† Electronic Supplementary Information (ESI) available: NMR, UV-visible, fluorescence emission spectra, CV (DPV), and crystallographic data of CCDC 1057090–1057093. See DOI: 10.1039/x0xx00000x

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both **4a** (10%) and **5a** (18%) from **1a** via the stepwise route were significantly improved in comparison to the previous one-step syntheses (3% and 10% for **4a** and **5a**, respectively). In addition, the [8]pericycylene **5b** was isolated from **2b** in 15% overall yield via the stepwise route, compared to 13% yield in a single step synthesis. The isolation of [4]pericycylene **4b** was not successful via the stepwise approach. For the successful preparation of the germa[5]pericyclines **6a–b** and [10]pericyclines **7a–b** from **3a–b**, high-dilution reaction conditions were required. Considering the unsuccessful result to synthesize **4b**, the low yield of **6b** could be attributed to the presence of the bulky isopropyl groups suppressing formation of the cyclic species. For comparison, reference compounds **8a–b** were also prepared by masking **1a–b** with the trimethylgermyl group.

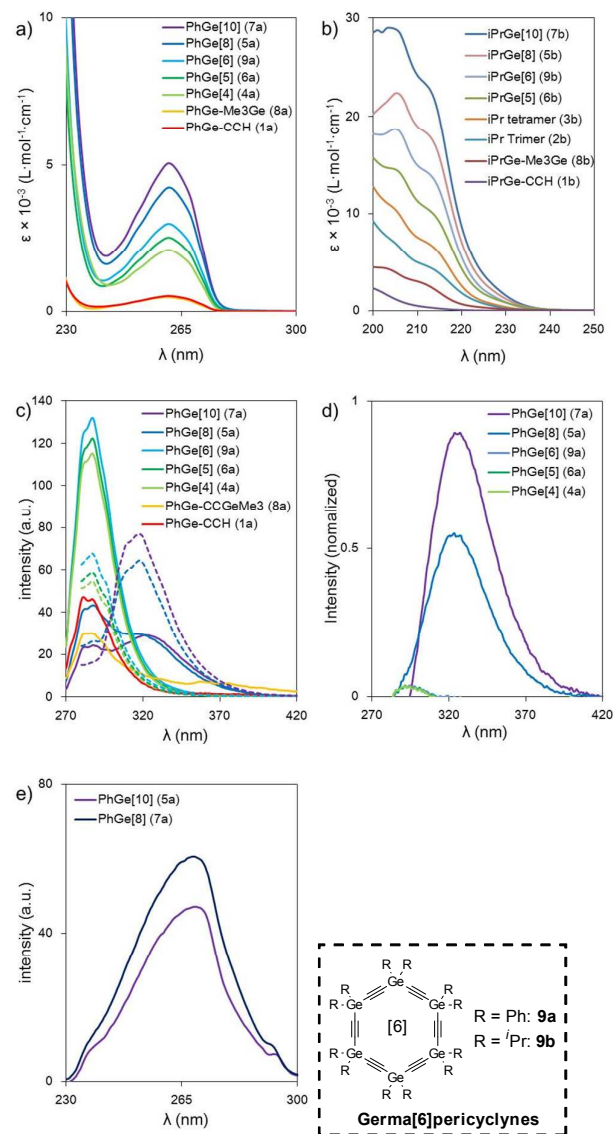


**Fig 2** ORTEP drawing of germa[5] and [10]pericyclines; a) **6a**; b) **7a**; c) **6b**; d) **7b**.

Following their first successful synthesis, X-ray crystallography of the germa[5] **6a–b** and [10]pericyclines **7a–b** was carried out (Fig 2). [5]Pericyclines **6a–b** displayed envelope conformations, while [4]pericycylene **4a** was previously found to be planar.<sup>9</sup> The smallest C–Ge–C angles of **6a–b** were comparable to **4a** (**4a**: 103.66(10),<sup>9</sup> **6a**: 104.1(3)°,

**6b**: 103.58(13)°), while the largest C–Ge–C angles were 107.6(3)° for **6a** and 109.12(19)° for **6b**, respectively. The Ge–C≡C angles were found to vary between 170.2(8)° and 178.6(6)° (**6a**), and between 165.9(4)° and 177.0(4)° (**6b**). From these results, it could be concluded that **6a–b** exhibited greater strain than methylated sila[5]pericyclines (average C–X–C and X–C≡C angles: 106.0° and 175.1° (**6a**), 106.2° and 172.2° (**6b**), *c.f.* 106.1° and 177.2° (Me-sila[5])<sup>4f</sup>), and were not bent to the extent of **4a** (103.8° and 172.3°). In contrast, [10]pericyclines **7a–b** were present in zigzag forms,<sup>9</sup> with **7a** displaying intramolecular π–π interactions between the phenyl rings present in its cavity. From X-ray data, the estimated distance between phenyl rings in the cavity of **7a** was approximately 3.5–3.8 Å with full ring overlap while that of **5a** was 3.5 Å with only partial overlap.

$\lambda_{\text{ex}} = 273.5$  nm (dashed lines), (d) normalized differential spectra based on **1a**,  $\lambda_{\text{ex}} = 260$  nm, (e) excitation spectra, **5a**:  $\lambda_{\text{ex}} = 321.5$  nm, **7a**:  $\lambda_{\text{ex}} = 320$  nm.



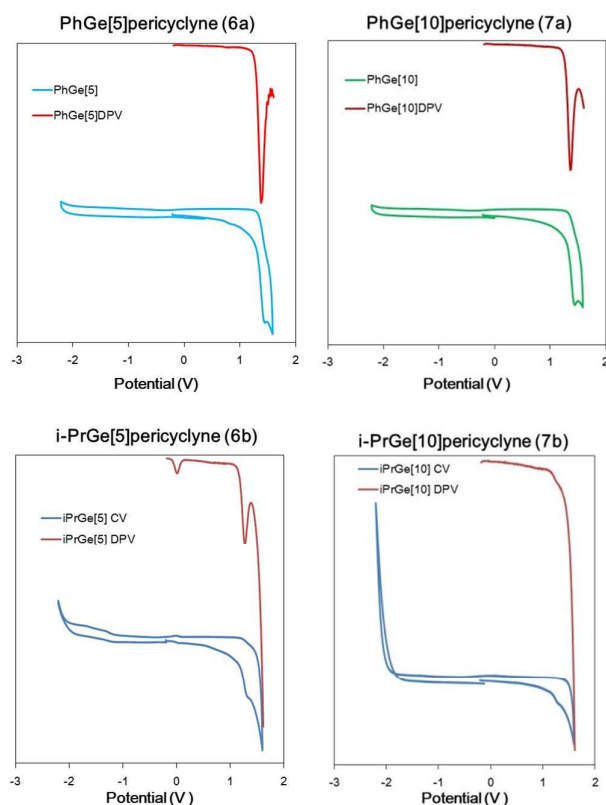
**Fig 3** UV-visible spectra: (a): 0.1 mM in CH<sub>2</sub>Cl<sub>2</sub>, (b): 0.1 mM in hexane; and fluorescence emission spectra: (c): 0.1 mM in CH<sub>2</sub>Cl<sub>2</sub>.  $\lambda_{\text{ex}} = 260$  nm (solid lines),

UV-Vis and fluorescence emission spectra of [5]pericyclines **6a–b** and [10]pericyclines **7a–b** were recorded in dichloromethane and hexane, and were compared to a range of other germapericyclines.<sup>9</sup> Both **6a** and **7a** showed comparable absorption maxima (261 nm,  $\epsilon = 2540$  (**6a**), 5070 (**7a**), ), to the other phenyl germapericyclines<sup>9</sup> (Fig 3a, see supporting information for detail). In addition, it was observed that the  $\epsilon$  values increased with an increase in the number of benzene rings. Although it is expected that **6a** and **7a** also have absorption bands at short wavelengths, measurement was problematic due to solubility issues. In the UV-Vis spectra of hexane-soluble **6b** and **7b** (Fig 3b), shoulders were observed at 205 nm ( $\epsilon = 14500$  (**6b**), 28900 (**7b**)), and 213 nm ( $\epsilon = 10600$  (**6b**), 23200 (**7b**)), as reported for [6]pericycline **9b** and [8]pericycline **5b**<sup>9</sup> (for detailed values, see supporting information). When compared to compound **8b** (203 nm:  $\epsilon = 4330$ , 210 nm:  $\epsilon = 2994$ ) and **1b**,<sup>9</sup> where no such peaks were present, these shoulders could be assigned to the internal germanium-substituted alkynes, as observed for the silapericyclines.<sup>4g</sup> It appeared that ring size did not affect the spectra,<sup>10</sup> however, a small bathochromic shift between compounds **8b** and **7b** (Fig 3b) suggested the influence of cyclic structures or ring strain.<sup>4f</sup>

Strain within the alkyne structure could also be estimated by Raman spectroscopy.<sup>11</sup> According to the reported trends, [4]pericycline **4a** was found to contain the most-strained alkynes (**4a**: 2107 cm<sup>-1</sup>) followed by [5]pericycline (**6a**: 2110 cm<sup>-1</sup>) among the phenyl compounds, while the values for [6], [8], [10]pericyclines were comparable (**9a**: 2114, **5a**: 2112,<sup>9</sup> **7a**: 2113 cm<sup>-1</sup>). However, isopropyl compounds gave opposite results, with the band for [5]pericycline (**6b**: 2103 cm<sup>-1</sup>), found at a higher wavenumber than comparable [6], [8], and [10]pericyclines (**9b**: 2099, **5b**: 2098, **7b**: 2098 cm<sup>-1</sup>). The reason is not clear so far because of few referential examples.

The fluorescence emission maxima of the germa[5]pericycline **6a** were found to be similar to the [4] and [6]pericyclines (**4a** and **9a**) ( $\lambda = 282, 288$  nm) (Fig 3c).<sup>9</sup> However, unlike [4], [5], and [6]pericyclines (**4a**, **6a**, and **9a**), [10]pericyclines **7a** also displayed emission at 318 nm as well as [8]pericyclines **5a**. This difference was displayed clearly in the normalized differential spectra (Fig 3d). Changing the excitation wavelength from 260 to 273.5 nm increased the emission intensities of **5a** and **7a** at approximately 320 nm, whereas no significant changes were observed for **4a**, **6a**, or **9a**. Because As the characteristic emissions could be assigned to absorption around 265 nm (Fig 3e), the emissions were likely derived from the excimer, by intramolecular π–π stacking of the benzene rings, as indicated in Fig 2b. It is expected that the larger ring size of **7a** compared to **5a** allows stronger π–π interactions. Fluorescence emission quantum yields were not recorded because the emissions were observed at only short wavelength.

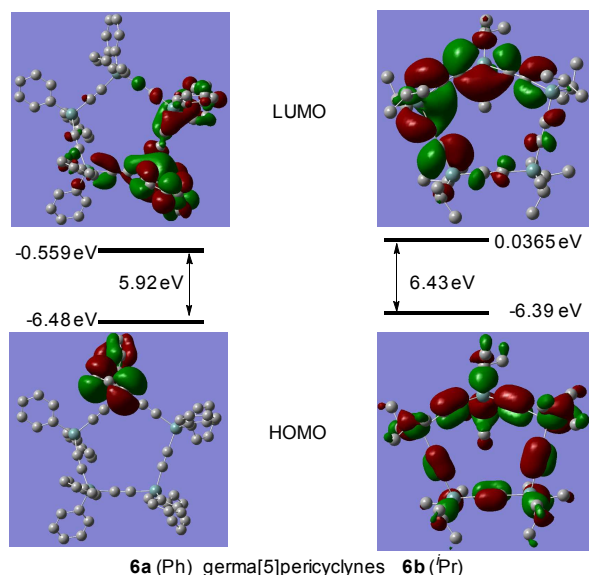




**Fig 4** Cyclic and differential pulse voltammograms of germa[5] and [10]pericyclines **6a–b** and **7a–b** (1.0 mM in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub> solution; scan rate = 0.1 V s<sup>-1</sup>).

From cyclic voltammetry and differential pulse voltammetry (DPV) (Fig 4), oxidation potentials ( $E_{\text{ox}}^{\text{DPV}} = 1.38$  V (**6a**, Ph-[5]), 1.36 V (**7a**, Ph-[10]), 1.27 V (**6b**, *i*-Pr-[5]), and 1.26 V (**7b**, *i*-Pr-[10])) were found to be comparable to those previously reported for the germa[4], [6], and [8]pericyclines.<sup>9</sup> In addition, the oxidation potentials of isopropyl compounds **6b** and **7b** were found to be smaller than those of the corresponding phenyl compounds **6a** and **7a**.

DFT calculations for germa[5]pericyclines **6a–b** (Fig 5) show the through-space interactions between alkynes in the LUMO of **6b**. Delocalized orbitals between the alkyne moieties and the phenyl groups through the germanium atoms are also shown for **6a**. As was the case for the [6]pericyclines,<sup>9</sup> out-of-plane HOMOs are found in **6b**, while the [4]pericyclines<sup>9</sup> display in-plane orbitals. In contrast, the orbitals of **6a** are located close to the benzene rings.



**6a** (Ph) germa[5]pericyclines **6b** (Pr)

**Fig 5** Molecular orbitals for the germa[5]pericyclines **6a** and **6b** obtained by DFT calculations (Gaussian 09 B3LYP/6-31G(d,p))

## Conclusions

Germa[4], [5], [8], and [10]pericyclines were synthesized via a stepwise route, giving an improvement in yield over our previously reported one-step synthetic route. Novel germa[5] and [10]pericyclines were characterized by X-ray crystallography, cyclic voltammetry, UV-Vis spectroscopy, and fluorescence emission spectroscopy. The unique fluorescence behaviour of phenylgerma[10]pericycylene is reported, and the frontier orbitals of [5]pericyclines were estimated by DFT calculations. Our improved synthesis and optical investigation of cyclic skipped oligo-alkyne compounds may open the door to further studies into the chemistry and design of functional organic-inorganic hybrid materials.

## Experimental

### General Procedures

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a JEOL JNM-ECP500 spectrometer (500 MHz for <sup>1</sup>H NMR and 126 MHz for <sup>13</sup>C NMR). Chemical shifts are reported as  $\delta$  values in ppm and calibrated with respect to the residual solvent peak (CDCl<sub>3</sub>,  $\delta$  7.26 for <sup>1</sup>H NMR and  $\delta$  77.00 for <sup>13</sup>C NMR) or tetramethylsilane ( $\delta$  0 for <sup>1</sup>H NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad peak), and m (complex multiplet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were measured using a JASCO FT-IR-4200 spectrometer. Mass spectra were recorded using a JEOL JMS-700 MStation [EI (70 eV), CI, FAB, and ESI]. X-ray crystal analyses were performed using a Rigaku R-Axis RAPID/S imaging plate diffractometer. Raman spectra were obtained using a JASCO laser Raman spectrophotometer, NRS-2100. The

cyclic voltammetry measurements of the compounds were performed using a BAS electrochemical analyser ALS612D in dichloromethane containing *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte at 298 K (100 mV s<sup>-1</sup>). The glassy carbon working electrode was polished using BAS polishing alumina suspension and rinsed with water before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to Ag/AgNO<sub>3</sub> and normalized with respect to Fc/Fc<sup>+</sup>. Flash column chromatography was performed using Merck Silica gel 60. The progress of the reactions was monitored by silica gel thin layer chromatography (TLC) (Merck TLC Silica gel 60 F<sub>254</sub>) with iodine/silica gel stain. The purification of the mixture of germapericyclines was performed using a LC-908 recycling preparative high-performance liquid chromatography (HPLC) equipped with a JAIGEL 2H-40 column (chloroform elution) made by Japan Analytical Industry Co., Ltd. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical, which was further dehydrated over activated molecular sieves 4A. Density functional theory (DFT) calculations were performed using the Gaussian09, and the geometries of the molecules were optimized by employing the B3LYP density functionals and the 6-31G(d,p) basis set in this series of calculations.

**bis((ethynyldiphenylgermyl)ethynyl)diphenylgermane (2a).** *n*-Butyllithium (1.63 M in hexane, 3.21 mL, 5.24 mmol) was added dropwise to a stirred solution of diethynyldiphenylgermane **1a**<sup>9</sup> (1.45 g, 5.24 mmol) in THF (52 mL) at -78 °C under a nitrogen atmosphere. After 2 h, dichlorodiphenylgermane (744 mg, 2.50 mmol) was added at the same temperature. Then the reaction mixture was warmed up to ambient temperature and stirred for 13 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane/dichloromethane = 10/1 to 3/1) to afford **2a** (1.57 g, 80%). White solid; R<sub>f</sub> value 0.3 (hexane/dichloromethane = 3/1); m.p. 123.7–124.6 °C; IR (KBr, disc) ν<sub>max</sub> 3273, 3070, 3028, 2035, 1485, 1433, 1095, 736 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73–7.70 (m, 12H), 7.44–7.37 (m, 18H), 2.60 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 133.8, 133.7, 133.3, 133.2, 130.1, 130.1, 128.6, 128.5, 107.8, 107.4, 95.3, 82.6; LRMS (ESI, M = C<sub>44</sub>H<sub>32</sub>Ge<sub>3</sub>) *m/z* = 801 [M+Na]<sup>+</sup>; Anal. Calcd for C<sub>44</sub>H<sub>32</sub>Ge<sub>3</sub>: C, 67.87; H, 4.14. Found: C, 67.69, H, 3.97.

**bis((ethynyldiisopropylgermyl)ethynyl)diisopropylgermane (2b).** *n*-Butyllithium (1.63 M in hexane, 9.04 mL, 14.73 mmol) was added dropwise to a stirred solution of diethynyldiisopropylgermane **1b**<sup>9</sup> (3.07 g, 14.73 mmol) in THF (150 mL) at -78 °C under a nitrogen atmosphere. After 2 h, dichlorodiisopropylgermane<sup>5</sup> (1.61 g, 7.02 mmol) was added at the same temperature. Then the reaction mixture was warmed up to ambient temperature and stirred for 16 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was

extracted with ether, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane to hexane/dichloromethane = 5/1) to afford **2b** (2.81 g, 70%). Colorless oil; R<sub>f</sub> value 0.16 (hexane); IR (NaCl, neat) ν<sub>max</sub> 3292, 2944, 2865, 2032, 1463, 1005, 878, 668 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.32 (s, 2H), 1.48–1.37 (m, 6H), 1.20–1.17 (m, 36H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 107.8, 106.3, 93.9, 83.5, 18.8, 18.74, 18.70, 16.7, 16.6; LRMS (ESI, M = C<sub>26</sub>H<sub>44</sub>Ge<sub>3</sub>) *m/z* = 597 [M+Na]<sup>+</sup>.

**3,3,6,6,9,9,12,12-octaphenyl-3,6,9,12-tetragermatetradeca-1,4,7,10,13-pentayne (3a).** Ethylmagnesium bromide (0.97 M in THF, 1.58 mL, 1.53 mmol) was added dropwise to a stirred solution of **2a** (1.19 g, 1.53 mmol) in THF (15 mL) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred for 1 h at the same temperature, and then the reaction mixture was warmed up to ambient temperature and stirred for 2 h. The reaction mixture was cooled down to -78 °C and dichlorodiphenylgermane (414 mg, 1.39 mmol) was added. The reaction mixture was warmed up to ambient temperature and stirred for 17 h. The reaction mixture was cooled down to 0 °C and ethynylmagnesium bromide (0.5 M in THF, 3.48 mL, 1.74 mmol) was added. After that, the reaction mixture was warmed up to ambient temperature and stirred for 9 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The mixture was extracted with dichloromethane and washed with brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (hexane/dichloromethane = 4/1 to 3/1) to afford **3a** (233 mg, 16%). White solid; R<sub>f</sub> value 0.26 (hexane/dichloromethane = 2/1); m.p. 132.6–134.9 °C; IR (KBr, disc) ν<sub>max</sub> 3275, 3069, 3045, 2035, 1484, 1432, 1095 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73–7.69 (m, 16H), 7.43–7.35 (m, 24H), 2.586 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 133.8, 133.7, 133.4, 133.1, 130.1, 130.0, 128.6, 128.5, 107.9, 107.7, 107.4, 95.2, 82.6; LRMS (ESI, M = C<sub>58</sub>H<sub>42</sub>Ge<sub>4</sub>) *m/z* = 1053 [M+Na]<sup>+</sup>. Anal. Calcd For C<sub>58</sub>H<sub>42</sub>Ge<sub>4</sub>: C, 67.67; H, 4.11. Found: C, 67.58; H, 4.18.

**3,3,6,6,9,9,12,12-octaisopropyl-3,6,9,12-tetragermatetradeca-1,4,7,10,13-pentayne (3b).** Ethylmagnesium bromide (0.97 M in THF, 12.76 mL, 12.38 mmol) was added dropwise to a stirred solution of **2b** (7.11 g, 12.38 mmol) in THF (123 mL) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred for 1 h at the same temperature, then the reaction mixture was warmed up to ambient temperature and stirred for 2 h. The reaction mixture was cooled down to -78 °C and dichlorodiisopropylgermane<sup>9</sup> (2.58 g, 11.23 mmol) was added. The reaction mixture was again warmed up to ambient temperature. After 14 h, the reaction mixture was cooled down to 0 °C. Ethynylmagnesium bromide (0.5 M in THF, 28.13 mL, 14.07 mmol) was added to the mixture, and was stirred for 1h at the same temperature. Then the mixture was warmed up to ambient temperature and stirred for 7 h. The reaction mixture was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was

extracted with ether and washed with brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (hexane/dichloromethane = 20/1 to 10/1) to afford **3b** (2.30 g, 27%). Colorless oil;  $R_f$  value 0.11 (hexane/dichloromethane = 10/1); IR (NaCl, neat)  $\nu_{\max}$  3292, 2944, 2864, 2032, 1463, 1004, 878, 668  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.32 (s, 2H), 1.47–1.36 (m, 8H), 1.20–1.17 (m, 48H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  108.0, 107.2, 106.2, 93.9, 83.5, 18.8, 18.8, 18.7, 16.7, 16.6; LRMS (ESI,  $M = \text{C}_{34}\text{H}_{58}\text{Ge}_4$ )  $m/z = 779$  [ $M+\text{Na}$ ] $^+$ .

**Synthesis of octaphenylgerma[4]pericyclyne (4a) and hexadecaphenylgerma[8]pericyclyne (5a) from 2a.** To a stirred solution of **2a** (450 mg, 0.58 mmol) in THF (36 mL) was added *n*-butyllithium (1.60 M in hexane, 0.72 mL, 1.16 mmol) dropwise at  $-78$  °C under nitrogen atmosphere. After 1.5 h, dichlorodiphenylgermane (0.12 mL, 0.58 mmol) was added dropwise over 1 h with syringe pump at the same temperature, and the mixture was stirred at room temperature for 16 h. The reaction was quenched with ammonium chloride saturated aqueous solution at 0 °C. The mixture was extracted with dichloromethane and was washed with brine. The combined organic layer was dried over magnesium sulfate, and was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/dichloromethane = 4/1) and recycling preparative HPLC to afford germa[4]pericyclyne **4a** (70 mg, 12%) as a white powder and germa[8]pericyclyne **5a** (130 mg, 23%) as a white powder.<sup>9</sup>

**Synthesis of hexadecaisopropylgerma[8]pericyclyne (5b) from 2b.** To a stirred solution of **2b** (2.36 g, 4.11 mmol) in THF (205 mL) was added *n*-butyllithium (1.63 M in hexane, 5.04 mL, 8.22 mmol) at  $-78$  °C under nitrogen atmosphere. After 2 h, 1:0.11 inseparable mixture of dichlorodiisopropylgermane<sup>9</sup> and chlorotriisopropylgermane (1.05 g, of mixture, 4.11 mmol for  $^i\text{Pr}_2\text{GeCl}_2$ ) was added at the same temperature, and the reaction mixture was warmed up to room temperature. After 34 h, the reaction was quenched with saturated ammonium chloride aqueous solution at 0 °C. The mixture was extracted with dichloromethane and was washed with brine. The combined organic layers were dried over magnesium sulfate, and were concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (hexane/dichloromethane = 15/1 to 5/1) and recycling preparative HPLC to afford **5b** (653 mg, 21%) as a white powder.<sup>9</sup>

**Synthesis of decaphenylgerma[5]pericyclyne (6a) and icosaphenylgerma[10]pericyclyne (7a).** To a stirred solution of **3a** (675 mg, 0.66 mmol) in THF (32 mL) was added *n*-butyllithium (1.63 M in hexane, 0.85 mL, 1.38 mmol) dropwise at  $-78$  °C under nitrogen atmosphere. After 2 h, dichlorodiphenylgermane (215 mg, 0.72 mmol) was added at the same temperature, and the reaction mixture was warmed up to ambient temperature. After 46 h, the reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with dichloromethane and washed with brine. The combined

organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (dichloromethane/hexane = 1/3 to 1/1.5) and recycling preparative HPLC to afford **6a** (80 mg, 10%) and **7a** (90 mg, 11%).

**Decaphenylgerma[5]pericyclyne (6a, CCDC: 1057090).** Colorless crystal;  $R_f$  value 0.33 (hexane/dichloromethane = 2/1); m.p. 271.7–273.0 °C; IR (KBr, disc)  $\nu_{\max}$  3070, 3049, 1485, 1433, 1095, 735, 695  $\text{cm}^{-1}$ ; Raman  $\nu_{\max}$  2110  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72–7.68 (m, 20H), 7.43–7.35 (m, 30H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9, 133.3, 129.9, 128.5, 107.1; LRMS (ESI,  $M = \text{C}_{70}\text{H}_{50}\text{Ge}_5$ )  $m/z = 1277$  [ $M+\text{Na}$ ] $^+$ . Recrystallization for X-ray crystallographic analysis was carried out using dichloromethane and hexane.

**Icosaphenylgerma[10]pericyclyne (7a, CCDC: 1057091).** Colorless crystal;  $R_f$  value 0.16 (dichloromethane/hexane = 1/2); m.p. 213.2–215.0 °C; IR (KBr, disc)  $\nu_{\max}$  3070, 3049, 1485, 1434, 1095, 736, 694  $\text{cm}^{-1}$ ; Raman  $\nu_{\max}$  2113  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68–7.66 (m, 40H), 7.34–7.27 (m, 60H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  133.7, 133.4, 129.9, 128.5, 107.8; LRMS (ESI,  $M = \text{C}_{140}\text{H}_{100}\text{Ge}_{10}$ )  $m/z = 2530$  [ $M+\text{Na}$ ] $^+$ . Recrystallization for X-ray crystallographic analysis was carried out using dichloromethane and hexane.

**Synthesis of decaisopropylgerma[5]pericyclyne (6b) and icosaisopropylgerma[10]pericyclyne (7b).** To a stirred solution of **3b** (1.05 g, 1.38 mmol) in THF (280 mL) was added *n*-butyllithium (1.60 M in hexane, 1.90 mL, 3.04 mmol) dropwise at  $-78$  °C under nitrogen atmosphere. After 2 h, dichlorodiisopropylgermane<sup>5</sup> (381 mg, 1.66 mmol) was added at the same temperature, and the reaction mixture was warmed up gradually to ambient temperature. After 40 h, the reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with dichloromethane and washed with brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (dichloromethane/hexane = 1/20 to 1/5) and recycling preparative HPLC to afford **6b** (31 mg, 2%) and **7b** (164 mg, 13%).

**Decaisopropylgerma[5]pericyclyne (6b, CCDC: 1057092).** Colorless crystal;  $R_f$  value 0.16 (hexane/dichloromethane = 10/1); m.p. 74.4–76.1 °C; IR (KBr, disc)  $\nu_{\max}$  2944, 2887, 2863, 1463, 1003, 670  $\text{cm}^{-1}$ ; Raman  $\nu_{\max}$  2103  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.40 (sept, 10H,  $J = 7.5$  Hz), 1.19 (d, 60H,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  106.8, 19.0, 16.5; LRMS (ESI,  $M = \text{C}_{40}\text{H}_{70}\text{Ge}_5$ )  $m/z = 937$  [ $M+\text{Na}$ ] $^+$

**Icosaisopropylgerma[10]pericyclyne (7b, CCDC: 1057093).** Colorless crystal;  $R_f$  value 0.11 (hexane/dichloromethane = 10/1); m.p. 49.2–50.5 °C; IR (KBr, disc)  $\nu_{\max}$  2945, 2887, 2864, 1463, 1006, 669  $\text{cm}^{-1}$ ; Raman  $\nu_{\max}$  2093  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.39 (sept, 20H,  $J = 7.5$  Hz), 1.17 (d, 120H,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  107.2, 18.8, 16.7; LRMS (ESI,  $M = \text{C}_{80}\text{H}_{140}\text{Ge}_{10}$ )  $m/z = 1851$  [ $M+\text{Na}$ ] $^+$

**Diphenylbis(trimethylgermyl)ethynylgermane (8a).** *n*-Butyllithium (1.63 M in hexane, 2.44 mL, 3.97 mmol) was added dropwise to a stirred solution of diethynyldiphenylgermane **1a**<sup>9</sup> (500 mg, 1.81 mmol) in THF (18

mL) at  $-78\text{ }^{\circ}\text{C}$  under nitrogen atmosphere. After 2 h, chlorotrimethylgermane (609 mg, 3.97 mmol) was added at the same temperature, and the reaction mixture was warmed up to ambient temperature and stirred for 8 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at  $0\text{ }^{\circ}\text{C}$ . The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane to hexane/dichloromethane = 10/1) to afford **8a** (927 mg, quant.). White solid;  $R_f$  value 0.13 (hexane/dichloromethane = 20/1); m.p.  $86.6\text{--}87.3\text{ }^{\circ}\text{C}$ ; IR (KBr, disc)  $\nu_{\text{max}}$  3066, 3051, 2979, 2911, 2102, 1483, 1430, 1240, 1092,  $835\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69–7.67 (m, 4H), 7.40–7.38 (m, 6H), 0.40 (s, 18H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  134.7, 133.7, 129.6, 128.3, 116.6, 103.2, 0.16; LRMS (ESI,  $M = \text{C}_{24}\text{H}_{28}\text{Ge}$ )  $m/z = 533$   $[\text{M}+\text{Na}]^+$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{28}\text{Ge}_3$ : C, 51.78; H, 5.53. Found: C, 51.61; H, 5.52.

**Diisopropylbis(trimethylgermyl)ethynylgermane (8b).** To a stirred solution of **1b**<sup>9</sup> (750 mg, 3.59 mmol) in THF (35 mL) was added *n*-butyllithium (1.63 M in hexane, 4.85 mL, 7.90 mmol) dropwise at  $-78\text{ }^{\circ}\text{C}$  under nitrogen atmosphere. After 2 h, chlorotrimethylgermane (1.21 g, 7.90 mmol) was added at the same temperature, and the reaction mixture was warmed up to ambient temperature. After 2 h, the reaction was quenched with a saturated aqueous solution of ammonium chloride at  $0\text{ }^{\circ}\text{C}$ . The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layers were dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane to dichloromethane/hexane = 1/10) and recycling preparative HPLC to afford **8b** (1.08 g, 68%). Colorless oil;  $R_f$  value 0.14 (hexane); IR (NaCl, neat)  $\nu_{\text{max}}$  2944, 2865, 1464, 1241, 1004, 833, 768,  $667\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.38 (sept, 2H,  $J = 7.5\text{ Hz}$ ), 1.16 (d, 12H,  $J = 7.5\text{ Hz}$ ), 0.34 (s, 18H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  115.1, 104.2, 18.9, 16.7, 0.04, 0.02, 0.00; LRMS (ESI,  $M = \text{C}_{16}\text{H}_{32}\text{Ge}_3$ )  $m/z = 465$   $[\text{M}+\text{Na}]^+$

## Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research on Innovative Areas "New Polymeric Materials Based on Element-Blocks (no. 2401)" of MEXT (No. 15H00750 for H. T. and No. 25102531 for K. K.), CREST-JST Japan for K. K. and the Tokuyama Science Foundation for K. T. We also thank Profs Naoki Aratani and Hiroko Yamada (CV and DPV), Mr. Kazuo Fukuda, Ms. Yoshiko Nishikawa (MS measurement), Mr. Fumio Asanoma (Elemental analysis) and Mr. Shohei Katao (X-ray crystallographic analysis) of NAIST.

## Notes and references

- 1 *Acetylene Chemistry: Chemistry, Biology, and Material Science*, ed. F. Diederich, P. J. Stang and R. R. Tykwinski, Wiley-VCH, Weinheim, 2005.

- 2 (a) R. Gleiter and D. B. Werz, *Chem. Rev.*, 2010, **110**, 4447–4488; (b) S. Ijadi-Maghsoodi, Y. Pang, and T. J. Barton, *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 955–965; (c) R. J. P. Corriu, C. Guerin, B. Henner, A. Jean and H. Mutin, *J. Organomet. Chem.* 1990, **396**, C35–C38; (d) A. W. M. Lee, A. B. W. Yeung, M. S. M. Yuen, H. Zhang, X. Zhao and W. Y. Wong, *Chem. Commun.*, 2000, 75–76. (e) W.-Y. Wong, A. W.-M. Lee, C.-K. Wong, G.-L. Lu, H. Zhang, T. Mo, and K.-T. Lam, *New J. Chem.*, 2002, **26**, 354–360; (f) W.-Y. Wong, C.-K. Wong, G. L. Lu, K. W. Cheah, J. X. Shi and Z. Lin, *J. Chem. Soc. Dalton Trans.*, 2002, 4587–4594; (g) W.-Y. Wong, S.-Y. Poon, A. W.-M. Lee, J.-X. Shia and K.-W. Cheah, *Chem. Commun.*, 2004, 2420–2421; (h) W.-Y. Wong, S.-Y. Poon, J.-X. Shi and K.-W. Cheah, *J. Polym. Sci. A: Polym. Chem.*, 2006, **44**, 4804–4824; (i) W.-Y. Wong, S.-Y. Poon, J.-X. Shi and K.-W. Cheah, *Inorg. Organomet. Polym. Mater.*, 2007, **17**, 189–200.
- 3 (a) V. Maraval and R. Chauvin, *Chem. Rev.*, 2006, **106**, 5317–5343; (b) A. de Meijere and S. I. Kozhushkov, *Top. Curr. Chem.*, 1999, **201**, 1–42.
- 4 (Sila[N]pericyclines) (a) H. Sakurai, Y. Eriyama, A. Hosomi, Y. Nakadaira and C. Kabuto, *Chem. Lett.*, 1984, **13**, 595–598; (b) R. Gleiter, W. Schäfer and H. Sakurai, *J. Am. Chem. Soc.*, **1985**, **107**, 3046–3050; (c) R. Bortolin, B. Parbhoo and S. S. D. Brown, *J. Chem. Soc., Chem. Commun.*, 1988, 1079–1081; (d) R. Bortolin, S. S. D. Brown and B. Parbhoo, *Inorg. Chim. Acta*, 1989, **158**, 137–139; (e) E. Hengge and A. Baumegeger, *J. Organomet. Chem.*, 1989, **369**, C39–C42; (f) A. Baumegeger, E. Hengge, S. Gamper, E. Hardtweck and R. Janoschek, *Monatsh. Chem.*, 1991, **122**, 661–671; (g) M. Unno, T. Saito and H. Matsumoto, *Chem. Lett.*, **1999**, **28**, 1235–1236. (h) M. Unno, T. Saito and H. Matsumoto, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 2407–2413.
- 5 (Carbo[N]pericyclines) (a) L. T. Scott, G. J. DeCicco, J. L. Hyun and G. Reinhardt, *J. Am. Chem. Soc.*, 1983, **105**, 7760–7761; (b) L. T. Scott, G. J. DeCicco, J. L. Hyun and G. Reinhardt, *J. Am. Chem. Soc.*, 1985, **107**, 6546–6555; (c) L. Maurette, C. Tedeschi, E. Sermot, M. Soleilhavoup, F. Hussain, B. Donnadiou and R. Chauvin, *Tetrahedron*, 2004, **60**, 10077–10098; (d) O. V. Shishkin, R. I. Zubatyuk, V. V. Dyakonenko, C. Lepetit and R. Chauvin, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6837–6848; (e) L. Leroyer, C. Lepetit, A. Rives, V. Maraval, N. Saffon-Merceron, D. Kandaskalov, D. Kieffer and R. Chauvin, *Chem.–Eur. J.*, 2012, **18**, 3226–3240; (f) A. Rives, I. Baglai, C. Barthes, V. Maraval, N. Saffon-Merceron, A. Saquet, Z. Voitenko, Y. Volovenko and R. Chauvin, *Chem. Sci.* 2015, **6**, 1139–1149.
- 6 (Phospha[N]pericyclines) (a) L. T. Scott and M. Unno, *J. Am. Chem. Soc.*, 1990, **112**, 7823–7825; (b) G. Märkl, T. Zollitsch, P. Kreimeier, M. Prinzhorn, S. Reithinger and E. Eibler, *Chem.–Eur. J.* 2000, **6**, 3806–3820; (c) S. G. A. van Assema, P. B. Kraikivskii, S. N. Zelinskii, V. V. Saraev, G. B. de Jong, F. J. J. de Kanter, M. Schakel, J. C. Slootweg and K. Lammertsma, *J. Organomet. Chem.*, 2007, **692**, 2314. (d) S. G. A. van Assema, G. Bas de Jong, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, A. L. Spek, M. Lutz and K. Lammertsma, *Eur. J. Org. Chem.* 2007, 2404–2412.
- 7 (Theoretical studies of pericyclines comprising other elements) (a) A. I. Boldyrev, V. V. Zhdankin, J. Simons and P. J. Stang, *J. Am. Chem. Soc.*, 1992, **114**, 10569–10572; (b) D. B. Werz and R. Gleiter, *Org. Lett.*, 2004, **6**, 589–592.
- 8 (a) R. Gleiter and G. Habershauer, *Aromaticity and Other Conjugation Effects*, Wiley-VCH, Weinheim, 2012; (b) R. Gleiter, D. Kratz, W. Schäfer and V. Schehlmann, *J. Am. Chem. Soc.*, 1991, **113**, 9258–9264; (c) E. Göransson, R. Emanuelsson, K. Jorner, T. F. Markle, L. Hammarström and H. Ottosson, *Chem. Sci.*, 2013, **4**, 3522–3532.



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Journal Name

- 9 H. Tanimoto, T. Nagao, Y. Nishiyama, T. Morimoto, F. Iseda, Y. Nagato, T. Suzuka, K. Tsutsumi and K. Kakiuchi, *Dalton Trans.*, 2014, **43**, 8338–8373.
- 10 S. Eisler, R. McDonald, G. R. Loppnow and R. R. Tykwinski, *J. Am. Chem. Soc.*, 2000, **122**, 6917–6928.
- 11 A. Lucotti, M. Tommasini, W. A. Chalifoux, D. Fazzi, G. Zerbina and R. R. Tykwinski, *J. Raman Spectrosc.*, 2012, **43**, 95–101.