

ARTICLE

Received 3 Jan 2014 | Accepted 25 Jun 2014 | Published 22 Jul 2014

DOI: 10.1038/ncomms5508

# Intramolecular C-F and C-H bond cleavage promoted by butadienyl heavy Grignard reagents

Heng Li<sup>1</sup>, Xiao-Ye Wang<sup>1</sup>, Baosheng Wei<sup>1</sup>, Ling Xu<sup>1</sup>, Wen-Xiong Zhang<sup>1</sup>, Jian Pei<sup>1</sup> & Zhenfeng Xi<sup>1,2</sup>

Organomagnesium compounds (Grignard reagents) are among the most useful organometallic reagents and have greatly accelerated the advancement of synthetic chemistry and related sciences. Nevertheless, heavy Grignard reagents based on the metals calcium, strontium or barium are not widely used, mainly due to their rather inert heavy alkaline-earth metals and extremely high reactivity of their corresponding Grignard-type reagents. Here we report the generation and reaction chemistry of butadienyl heavy Grignard reagents whose extremely high reactivity is successfully tamed. Facile synthesis of perfluoro- $\pi$ -extended pentalene and naphthalene derivatives is realized by the *in situ* generated heavy Grignard reagents via intramolecular C-F/C-H bond cleavage. These obtained perfluorodibenzopentalene and perfluorodinaphthopentalene derivatives show low-lying LUMO levels, with one being the lowest value so far among all pentalene derivatives. Our results set an exciting example for the meaningful synthetic application of heavy Grignard reagents.

<sup>1</sup>Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Haidian, Beijing 100871, China. <sup>2</sup>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, China. Correspondence and requests for materials should be addressed to Z.X. (email: zfxi@pku.edu.cn).

For the development of organomagnesium compounds (Grignard reagents (RMgX)), Grignard was awarded with the Nobel prize in 1912. Since then, organomagnesium compounds have greatly accelerated the advancement of synthetic chemistry and related subjects<sup>1</sup>. Nevertheless, the organometallic chemistry of heavy Grignard reagents (RAeX, Ae = Ca, Sr and Ba) is still in its infancy due to the rather inert heavy alkaline-earth metals and extremely high ionicity and reactivity of Ae–C bonds<sup>2–7</sup>. The enormous reactivity of generated Ae–C bonds easily led to side reactions and obstructed the application of heavy Grignard reagents<sup>8–12</sup>.

Prior efforts to develop useful reaction chemistry and synthetic applications of heavy alkaline-earth species were conducted. Unexpected results have displayed charming reactivity of Ae–X bonds (X = P, N and C). Westerhausen *et al.*<sup>13,14</sup> reported the first synthetic application in which the enhanced reactivity was exhibited by the reactions between alkaline-earth metal phosphanides (Ae–P bonding) and diphenylbutadiynes. As for Mg[P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, *cis*-addition to the C≡C bond of diphenylbutadiynes occurred. However, the corresponding derivatives of heavy alkaline-earth metals, calcium, strontium and barium could undergo further reactions. Barrett *et al.*<sup>15</sup> set an encouraging precedent for the C–F bond activation promoted by Ca–N bonding species. The cleavage of C–F bond in a trifluoromethyl group was observed. In addition, deprotonation, oligomerization and Kumada-type cross-coupling reaction of arylcalcium halides were developed by Westerhausen and colleagues<sup>16–18</sup>.

The above mentioned literature reports demonstrate preliminary but exciting reaction chemistry of heavy alkaline-earth reagents bearing Ae–P or Ae–N bonds. With the aim of exploring this area, especially in the generation and synthetic applications of heavy Grignard reagents containing Ae–C bonds, design and development of new strategies are of great challenge and demand.

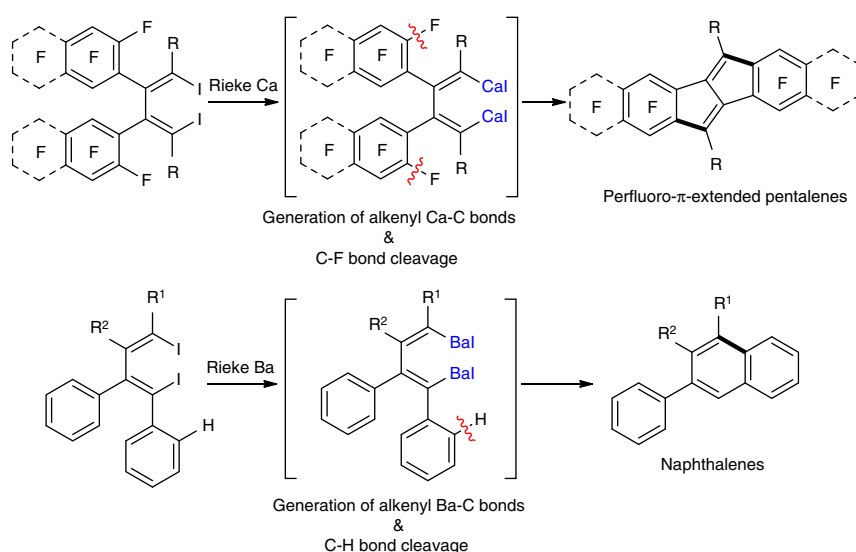
We consider that the extremely high reactivity of heavy Grignard reagents might be tamed by intramolecular nucleophilic aromatic substitution or coordination stabilization. Thus, here in this work (Fig. 1), the highly reactive heavier alkaline-earth metals are *in situ* prepared by the Rieke procedure, and the corresponding alkenyl Ae–C bonds are formed by the reaction between Rieke Ae and alkenyl iodides<sup>19</sup>. Subsequently, the

reactions of heavy Grignard reagents containing alkenyl Ae–C bonds and the conjugated diene moiety are investigated. The successful intramolecular nucleophilic aromatic substitution is mainly due to the butadienyl organo-di-heavy Grignard reagents (double Ae–C bonds) and the formation of stable five(six)-membered rings. Intramolecular C–F and C–H bond cleavage leads to perfluoro- $\pi$ -extended pentalene and naphthalene derivatives, respectively. Pentalene derivatives have attracted much recent attention because of their potential applications as organic conjugated materials. However, access to these compounds is generally very difficult. These obtained compounds exhibit the lowest unoccupied molecular orbital (LUMO) levels in reported pentalene derivatives, showing great potential in electron-accepting materials.

## Results

**Synthesis of perfluoro- $\pi$ -extended pentalene derivatives.** In recent years, dibenzopentalene derivatives have attracted considerable attentions because of their unique planar structures, antiaromatic characters and promising application in organic materials science<sup>20,21</sup>. Several reliable methods for the synthesis of dibenzopentalene derivatives were designed and reported<sup>22–30</sup>. In case of dinaphthopentalene derivatives, Kawase *et al.*<sup>31</sup> reported the unique synthesis and application in organic thin-film transistors. Introducing F atoms onto organic  $\pi$ -conjugated systems is an effective way to lower the energy levels, which can tune the electron transport properties<sup>32,33</sup>. Therefore, novel approaches for the synthesis of fluorodibenzopentalene and fluorodinaphthopentalene derivatives should be extremely attractive. Dibenzopentalene and dinaphthopentalene derivatives own a 6-5-5-6 fused ring system, which might be constructed by 2,3-phenyl-substituted 1,3-butadiene species. We have reported the facile synthesis of dibenzopentalene dianion from 1,4-dithio-1,3-butadienes and Ba[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (ref. 34). With this result in hand, we envisioned a novel approach from 1,4-diiodo-1,3-butadienes to perfluoro- $\pi$ -extended pentalenes through C–F bond cleavage<sup>35–37</sup>.

First, 2,3-perfluoroaryl-substituted 1,4-diiodo-1,3-butadienes **1** (**1a**: R = *n*-Pr; **1b**: R = *n*-Bu; **1c**: R = *n*-Oct; **1d**: R = (CH<sub>2</sub>)<sub>3</sub>Ph; **1e**: R = Cy; **1f**: R = Ph) were prepared in good isolated yields by modifying the procedures reported by Tilley and colleagues<sup>38,39</sup>,



**Figure 1 | Heavy Grignard reagents.** Generation and application of butadienyl organo-di-heavy Grignard reagents for the synthesis of perfluoro- $\pi$ -extended pentalenes and naphthalenes via C–F/C–H cleavage.

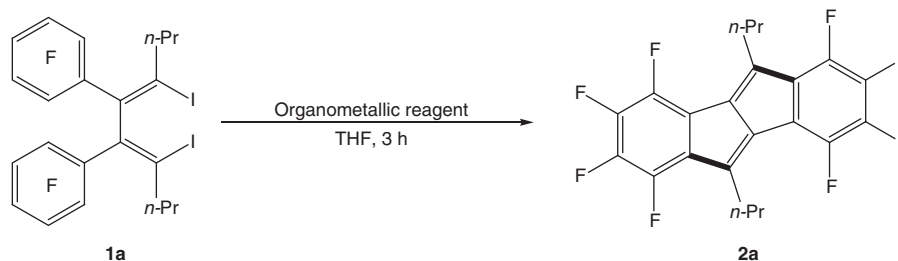
via iodination of zirconacyclopentadienes. Similarly, the 2,3-perfluoronaphthyl-substituted butadiene derivative **1g** was also obtained (see the Methods). As shown in Table 1, when **1a** was treated with *n*-BuLi, the expected perfluorodibenzopentalene derivative **2a** was observed. However, the yield was rather low. Obviously, more reactive organometallic reagents were needed to cleave the C–F bonds. In 2005, Niemeyer and colleagues<sup>40</sup> described the first heavy alkaline-earth metal C<sub>6</sub>F<sub>5</sub> species in which short heavy alkaline-earth metal–fluorine bonds were observed. After screening various organometallic reagents including Rieke metals of alkaline earth metals, in which Rieke Mg was generated by the reaction between MgCl<sub>2</sub> and K<sup>41</sup>, Rieke Ca/Ba were prepared by the reaction between CaI<sub>2</sub>/BaI<sub>2</sub> and lithium biphenylide<sup>9,10</sup>, we found that Ca–C bond was the best for this C–F cleavage reaction. Other organometallic reagents gave no products or lower yields. These results demonstrated that heavy Grignard reagents exhibited excellent reactivity. The optimal reaction conditions were found to be Rieke Ca (3.0 equiv) in tetrahydrofuran (THF) at –95 °C for 3 h. Under these optimized conditions, perfluorodibenzopentalene derivative **2a** was obtained in 52% isolated yield.

The scope of C–F bond activation by Ca heavy Grignard reagents was investigated under the optimized reaction conditions and the results are summarized in Fig. 2a. After formation of alkenylcalcium iodides, C–F cleavage took place twice, generating the perfluorodibenzopentalenes **2a–c** in moderate isolated yields. The corresponding substituents at the 5- and 10-positions were propyl, butyl and octyl groups. The solubility of perfluorodibenzopentalenes **2a–c** could be regulated by the variable carbon chains, which is very important for use as organic materials. The 1,4-diiodo-1,3-butadienes **1d** and **1e** containing terminal phenyl and cyclohexyl groups also afforded their corresponding perfluorodibenzopentalenes **2d** and **2e**, respectively. When the reaction between 1,4-phenyl-substituted 1,4-diiodo-1,3-butadiene **1f** and Rieke Ca was carried out, the C–F cleavage process gave the perfluorodibenzopentalene **2f** in 31% yield, along with a fulvene derivative (see the Supplementary

Figs 1,2). In addition, the reaction of 2,3-perfluoronaphthyl-substituted butadiene derivative **1g** was investigated. The perfluorodibenzopentalene **2g** was obtained in 21% isolated yield due to the relatively high reactivity of C–F bonds of perfluoronaphthyl substituents. As expected, use of the relatively mild organolithium reagent afforded **2g** in 37% isolated yield. Single crystals of **2e** and **2g** suitable for X-ray structural analysis were obtained from hexane and chlorobenzene solutions, respectively (see Fig. 2b,c and Supplementary Figs 3 and 4). The molecular structure of **2e** revealed a planar structure. A large bond alternation was observed within the pentalene core. This study on the synthesis and structural characterization of perfluoro- $\pi$ -extended pentalenes **2a–g** is the first example among all reports on pentalene derivatives. Meanwhile, this is the first C–F bond cleavage promoted by heavy Grignard reagents.

**Properties of perfluoro- $\pi$ -extended pentalene derivatives.** The photophysical and electrochemical properties of compounds **2a**, **2f** and **2g** were investigated and the results are summarized in Table 2. As shown in Fig. 3a, these compounds exhibited two main absorption bands with vibrational fine structures. The absorption maximum of **2g** showed a significant red-shift of ~50 nm compared with those of **2a** and **2f**, presumably due to the enlarged  $\pi$ -conjugated plane. The optical bandgaps of **2a**, **2f** and **2g** were estimated from the absorption onsets (440 nm for **2a**; 469 nm for **2f**; 522 nm for **2g**) to be 2.82, 2.65 and 2.38 eV, respectively. The above results indicate that the photophysical properties of these pentalene derivatives can be effectively modulated by structural modifications. In cyclic voltammetry experiment (Fig. 3b), reversible reductive waves were observed, revealing electron-accepting abilities of these compounds. The LUMO energy levels of compounds **2a** and **2g** estimated from the reductive onsets showed almost the same values, while compound **2f** showed a low LUMO level of –3.56 eV, which is the lowest value among reported pentalene derivatives<sup>26–28,31</sup>. These features make them potential as good electron-accepting

**Table 1 | Optimization of the C–F bond cleavage reaction conditions.**

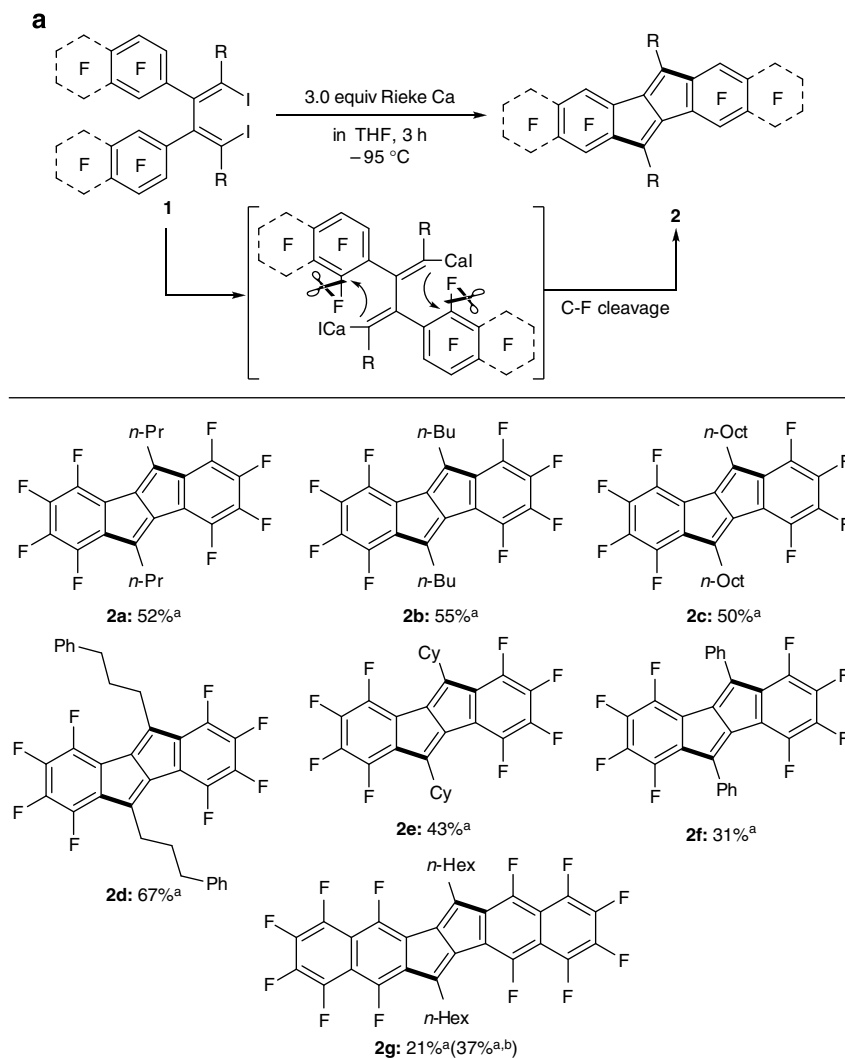


Entry	Organometallic reagent	Reaction temperature	Isolated yield
1	2.0 equiv <i>n</i> -BuLi*	–78 °C to 70 °C	5%
2	2.0 equiv Lithium biphenylide	–78 °C to 70 °C	0%
3	2.0 equiv Rieke Mg <sup>†</sup>	–78 °C to 70 °C	0%
4	2.0 equiv Rieke Mg <sup>‡</sup>	70 °C	Messy
5	2.0 equiv Rieke Ca <sup>†</sup>	–78 °C to r.t.	0%
6	2.0 equiv Rieke Ca <sup>‡</sup>	–78 °C to r.t.	Messy
7	2.0 equiv Rieke Ca <sup>‡</sup>	–78 °C	25%
8	2.0 equiv Rieke Ca <sup>‡</sup>	–95 °C	40%
9	3.0 equiv Rieke Ca <sup>‡</sup>	–95 °C	52%
10	4.0 equiv Rieke Ca <sup>‡</sup>	–95 °C	33%
11	3.0 equiv Rieke Ba <sup>‡</sup>	–95 °C	37%

\*Et<sub>2</sub>O/hexane was used instead of THF.

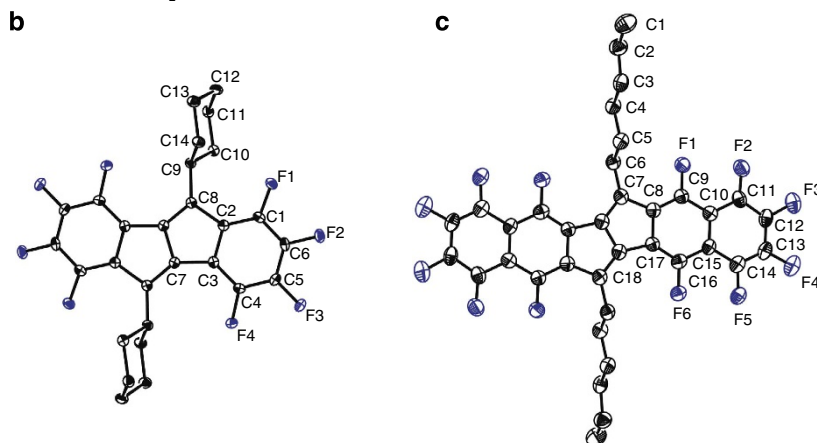
<sup>†</sup>Rieke metal was prepared by the reaction between AeI<sub>2</sub> and K.

<sup>‡</sup>Rieke metal was prepared by the reaction between AeI<sub>2</sub> and lithium biphenylide.



<sup>a</sup> Yields refer to isolated yields after purification.

<sup>b</sup> 2.0 equiv of *n*-BuLi in Et<sub>2</sub>O/Hexane, -78 °C to r.t., 3 h.



**Figure 2 | Scope and structure of perfluoro- $\pi$ -extended pentalene derivatives.** (a) Scope of C-F bond activation via heavy Grignard reagents.

(b) Thermal ellipsoid plot of perfluorodibenzopentalene **2e** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. (c) Thermal ellipsoid plot of perfluorodinaphthopentalene **2g** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. The whole molecule of **2g** was disordered. The major part was shown above.

and transporting materials. All the compounds are non-emissive, which is a common phenomenon in  $4n$   $\pi$ -electron systems<sup>42</sup>.

To investigate the influence of introducing F atoms onto the pentalene derivatives and their electronic properties, we performed density functional theory calculations on compounds

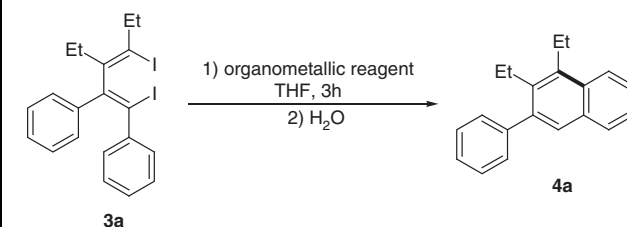
**2a-F**, **2f-F** and **2g-F**, together with model compounds **2a-H**, **2f-H** and **2g-H** without F atoms on the backbone (Fig. 3c). The optimized geometries of all the compounds proved to be fully planar, in agreement with the single crystal structures. In consistence with the experimental results, the LUMO levels of compounds **2a-F** and **2g-F** are similar, while the HOMO level of **2g-F** are 0.4 eV higher than that of **2a-F**. This trend is also true in the case of **2a-H** and **2g-H**, meaning that extending  $\pi$ -conjugated plane along the long axis of pentalene derivatives mainly raised the HOMO levels, with LUMO levels almost

**Table 2 | Summary of the photophysical and electrochemical properties of compounds 2a, 2f and 2g.**

Compound	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{onset}}^{\text{abs}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{HOMO}}$ (eV)
<b>2a</b>	267	440	2.82	-3.32	-6.14
<b>2f</b>	272	469	2.65	-3.56	-6.21
<b>2g</b>	317	522	2.38	-3.33	-5.71

HOMO, highly occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

**Table 3 | Optimization of the C-H bond cleavage reaction conditions.**

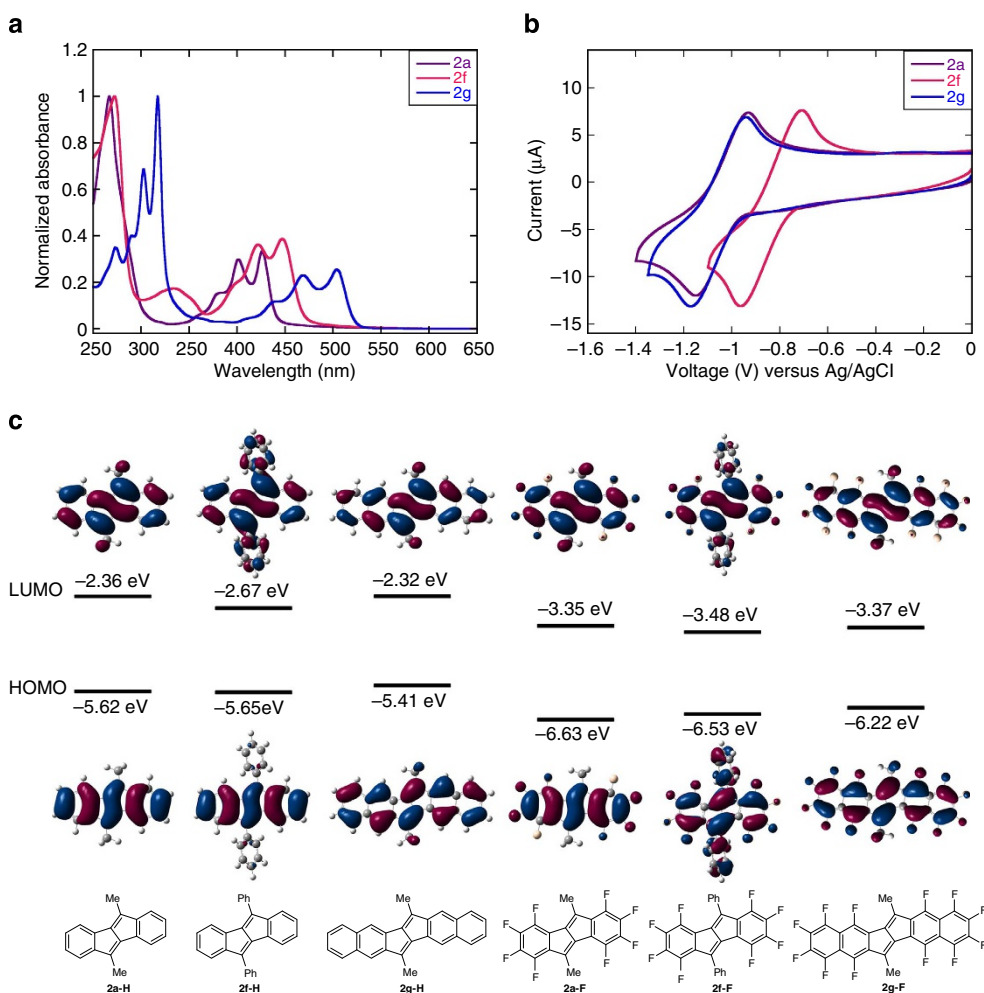


Entry	Organometallic reagent	Reaction temperature	Isolated yield
1	4.0 equiv <i>t</i> -BuLi	-78 °C to r.t.	Trace
2	2.0 equiv Lithium biphenylide	-78 °C to r.t.	0%
3	2.0 equiv Rieke Mg <sup>†</sup>	-78 °C to r.t.	Trace
4	2.0 equiv Rieke Ca <sup>†</sup>	-78 °C to r.t.	54%
5	2.0 equiv Rieke Ba <sup>†</sup>	-78 °C to r.t.	74%

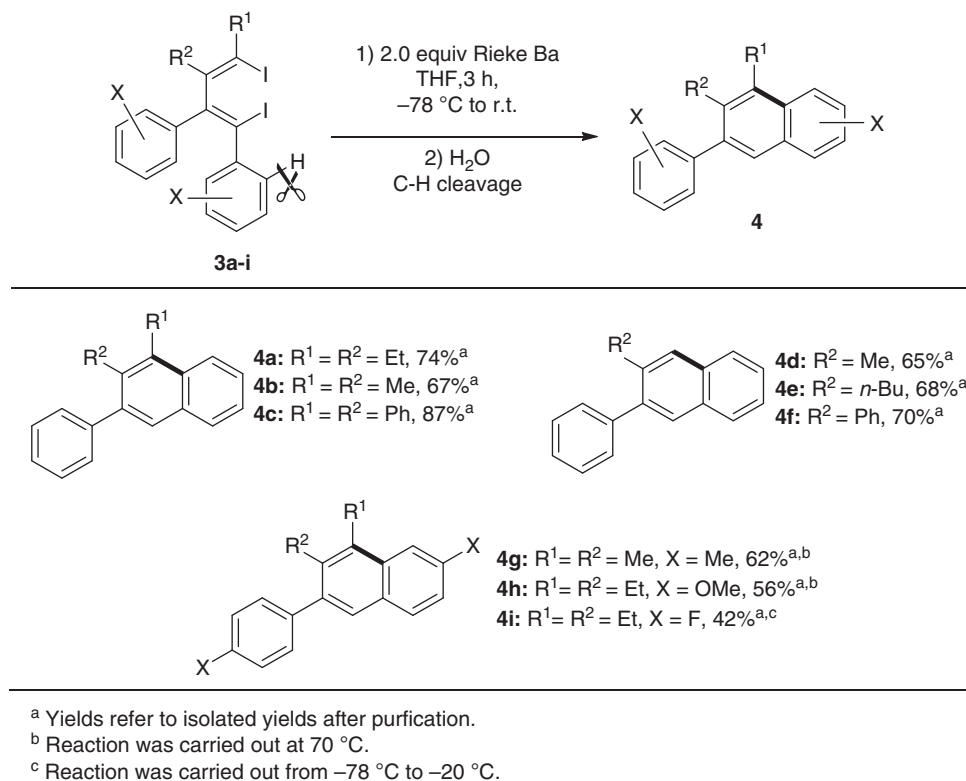
r.t., room temperature

<sup>†</sup>Rieke metal was prepared by the reaction between  $\text{AeI}_2$  and K.

<sup>‡</sup>Rieke metal was prepared by the reaction between  $\text{AeI}_2$  and lithium biphenylide.



**Figure 3 | Properties of perfluoro- $\pi$ -extended pentalene derivatives **2a**, **2f** and **2g**.** (a) Normalized absorption spectra of **2a** (purple), **2f** (pink) and **2g** (blue) in  $\text{CHCl}_3$  solutions ( $1 \times 10^{-5}$  M). (b) Cyclic voltammograms of **2a** (purple), **2f** (pink) and **2g** (blue) in *o*-dichlorobenzene (1 mM) with 0.1 M *n*-Bu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte (scan rate:  $100 \text{ mV s}^{-1}$ ). (c) Density functional theory-calculated molecular orbitals and energy levels at the B3LYP/6-311 + G(d,p) level of theory.



**Figure 4 | Naphthalene derivatives.** Scope of naphthalene derivatives.

unchanged. On the other hand, replacing the alkyl chains with phenyl rings at the 5- and 10-positions resulted in delocalized orbitals and lowered LUMO levels. Compared with the model compounds **2a-H**, **2f-H** and **2g-H**, the perfluoro- $\pi$ -extended pentalene derivatives **2a-F**, **2f-F** and **2g-F** showed lowered HOMO and LUMO levels by  $\sim 1.0$  eV. Therefore, the introduction of F atoms onto the pentalene backbones significantly lowered the orbital energy levels and the electronic properties of these perfluoro- $\pi$ -extended pentalene derivatives can be finely tuned by varying the substituents at the 5- and 10-positions.

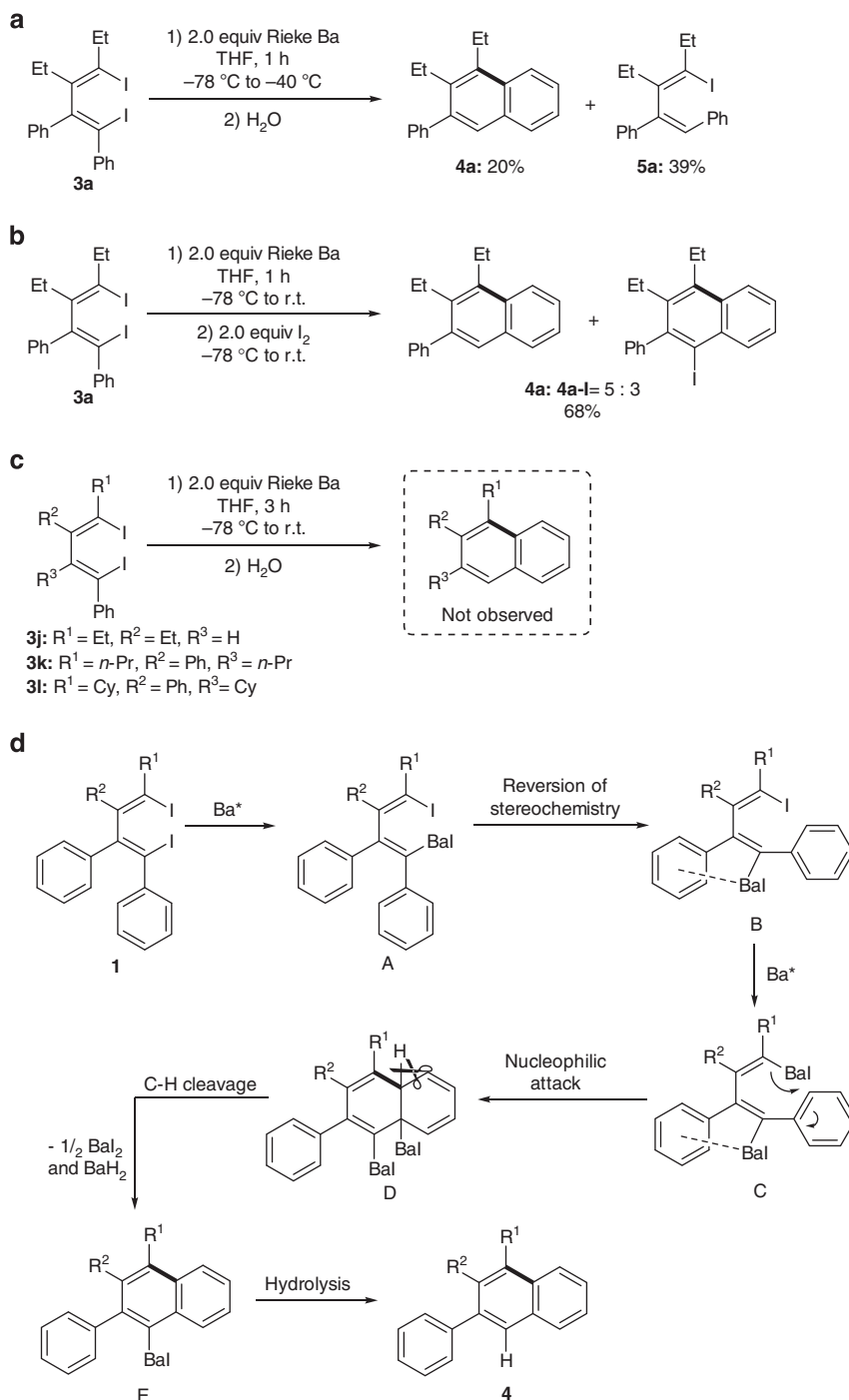
**Synthesis of naphthalene derivatives.** Naphthalene derivatives are very attractive because of their applications in medicinal chemistry and material science<sup>43–47</sup>. Application of organometallic reagents could greatly expand the synthesis of naphthalene derivatives. Inspired by the above C–F activation and synthesis of perfluoro- $\pi$ -extended pentalenes derivatives, we envisioned a similar approach might be possible to cleave aryl C–H bonds of the aryl group at the fourth position. We initiated our study with the aryl-substituted 1,4-diiodo-1,3-butadienes on treatment with various organometallic reagents.

As shown in Table 3, treatment of **3a** with *t*-BuLi or Rieke Mg afforded a trace amount of the naphthalene product **4a** (ref. 41). When **3a** was treated with Rieke Ca, **4a** was obtained in 54% isolated yield<sup>9</sup>. Among the four different organometallic reagents, the barium reagent gave the best result with 74% isolated yield of **4a**<sup>10</sup>. In this reaction, the C–H bond of the aryl group at the fourth position was cleaved.

As shown in Fig. 4, the substrate scope was examined using Ba heavy Grignard reagent (R<sub>Ba</sub>I). Naphthalene derivatives **4a-f** were obtained in excellent isolated yields. Both electron-donating and electron-withdrawing groups on the phenyl rings of 1,4-diiodo-1,3-butadienes **1** were applicable.

To obtain more evidence for understanding the C–H cleavage reaction mechanism, we then attempted several experiments. First, we conducted the reaction at  $-40$  °C. Hydrolysis of the reaction mixture afforded **4a** in 20% yield, along with the monoiodo 1,3-butadiene **5a** in 39% yield, which is useful for understanding the reversion of stereochemistry at the terminal carbon bonding with a phenyl group and a Ba atom (Fig. 5a)<sup>48</sup>. We also tried the trapping experiment by the addition of I<sub>2</sub> to the reaction mixture. As a result, product **4a** protonated by ether cleavage and the iodo-substituted naphthalene derivative **4a-I** was obtained<sup>49</sup>. The formation of **4a-I** strongly indicates that naphthylbarium species was an intermediate in this process resulting in the desired product **4a** (Fig. 5b). As shown in Fig. 5c, we next investigated the substitution effect of this reaction process using **3j** with no substituent at the third position, the corresponding naphthalene product was not observed. To further research the intramolecular coordination stabilization of aromatic ring at the third position, aryl-substituted 1,4-diiodo-1,3-butadienes **3k** and **3l** containing more steric propyl and cyclohexyl groups were tried to react with Rieke Ba. Formation of their corresponding naphthalene products were not observed. Thus, the aryl group on the third position is necessary.

Based on all the above experiments, a proposed mechanism for the formation of **4** is given in Fig. 5d. First, the intermediate **A** containing a Ba–C bond was formed<sup>50</sup>. Next, the reversion of stereochemistry at the terminal carbon bonding with a phenyl group and a Ba atom occurred due to the coordination of the Ba atom to the third positioned phenyl ring<sup>51–53</sup>. The generation of **5a** at low temperature experiment also indicates the formation of intermediate **B**. After the generation of a second Ba–C bond, the subsequent intramolecular nucleophilic aromatic substitution would occur, generating the species **D**. Next, **D** converted to the naphthylbarium species **E** via C–H bond cleavage, while the BaI<sub>2</sub> and BaH<sub>2</sub> were removed from **D**. Iodination of **E** could



**Figure 5 | Mechanistic consideration.** (a) Low-temperature experiment. (b) Trapping experiment with I<sub>2</sub>. (c) Effect of substitution pattern. (d) Proposed mechanism for the formation of **4**.

afford **4a-I**. Finally, hydrolysis of intermediate **E** gave the naphthalene product.

## Discussion

We have disclosed novel reaction chemistry of heavy Grignard reagents bearing conjugated diene moiety. The high reactivity of heavy Ae–C bond was successfully tamed by intramolecular nucleophilic aromatic substitution or intramolecular coordination stabilization, obstructing side reactions to a great degree. Both of the C–F/C–H bond activation process set an exciting example for the meaningful synthetic application of heavy Grignard reagents.

More importantly, a series of important perfluorodibenzopentene and perfluorodinaphthopentene derivatives were firstly synthesized, which showed the lowest LUMO levels among reported pentene systems, exhibiting high potential as *n*-type semiconducting materials.

## Methods

**General methods.** All reactions were carried out under a slightly positive pressure of dry and oxygen-free argon by using standard Schlenk line techniques. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. <sup>1</sup>H and <sup>13</sup>C

NMR spectra were recorded on a Bruker-400 spectrometer (FT, 400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ) and a Bruker-500 spectrometer (FT, 500 MHz for  $^1\text{H}$ ; 125 MHz for  $^{13}\text{C}$ ) at room temperature.  $^{19}\text{F}$  NMR data was obtained on a Bruker-500 spectrometer with 2,2,2-trifluoroethanol as the external standard. Chemical shifts were reported in units (p.p.m.) by assigning TMS (2,2,2-trifluoroethanol) resonance in the  $^1\text{H}$  NMR ( $^{19}\text{F}$  NMR) spectrum as 0.00 p.p.m. High-resolution mass spectra were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Micro elemental analyses were performed on an Elemental Analyzer vario EL apparatus. Rieke Mg, Rieke Ca and Rieke Ba were prepared according to literature methods<sup>9,10,41</sup>. Rieke Mg was generated by the reaction between  $\text{MgCl}_2$  and K, and Rieke Ca/Ba were prepared by the reaction between  $\text{CaI}_2/\text{BaI}_2$  and lithium biphenylide. The characterization data for **1**, **2**, **4** and **5a** are described in the Supplementary Methods. The aryl-substituted 1,4-diiodo-1,3-butadienes **3** are synthesized by the reported procedure<sup>38</sup>. The procedures for **1**, **2**, **4** and **5a** are described below. All of the NMR spectra can be found in the Supplementary Figs 5–69.

**Synthesis of 1a-f. A typical procedure for 1a.** To a THF (60 ml) solution of  $\text{Cp}_2\text{ZrCl}_2$  (2.4 mmol, 700 mg) at  $-78^\circ\text{C}$  was added dropwise *n*-BuLi (4.8 mmol, 1.6 M, 3.0 ml) with a syringe. After the addition was completed, the reaction mixture was stirred at  $-78^\circ\text{C}$  for 1 h. Next, 1-perfluorophenyl-2-propylacetylene (4.0 mmol, 936 mg) was added, and the reaction mixture was warmed up to  $50^\circ\text{C}$  and stirred at this temperature for 3 h. The mixture was cooled to  $0^\circ\text{C}$ , and CuCl (198 mg, 2.0 mmol) and  $\text{I}_2$  (1.016 g, 4.0 mmol) were added. The solution was warmed up to  $25^\circ\text{C}$  and kept at this temperature for 1 h. After that, the reaction mixture was quenched with 3 N HCl and the resulting mixture was extracted with diethyl ether for three times then washed with  $\text{NaHCO}_3(\text{aq})$ ,  $\text{Na}_2\text{S}_2\text{O}_5(\text{aq})$  and brine. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was subjected to  $\text{SiO}_2$  column using hexane as the eluent. 2,3-Diperfluorophenyl-1,4-diiodo-1,3-butadiene derivative **1a** was synthesized in 80% yield (1,155 mg).

**Synthesis of 1g.** To a toluene (60 ml) solution of  $\text{Cp}_2\text{ZrCl}_2$  (2.4 mmol, 700 mg) at  $-78^\circ\text{C}$  was added dropwise *n*-BuLi (4.8 mmol, 1.6 M, 3.0 ml) with a syringe. After the addition was completed, the reaction mixture was stirred at  $-78^\circ\text{C}$  for 1 h. Next, 1-perfluoronaphthyl-2-hexylacetylene (4.0 mmol, 1,448 mg) was added, and the reaction mixture was warmed up to  $80^\circ\text{C}$  and stirred at this temperature for 6 h. The mixture was cooled to  $0^\circ\text{C}$ , and CuCl (198 mg, 2.0 mmol) and ICl (648 mg, 4.0 mmol) were added. The solution was warmed up to  $25^\circ\text{C}$  and kept at this temperature for 3 h. After that, the reaction mixture was quenched with 3 N HCl and the resulting mixture was extracted with diethyl ether for three times then washed with  $\text{NaHCO}_3(\text{aq})$ ,  $\text{Na}_2\text{S}_2\text{O}_5(\text{aq})$  and brine. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was subjected to  $\text{SiO}_2$  column using hexane as the eluent. 2,3-Diperfluoronaphthyl-1,4-diiodo-1,3-butadiene Derivative **1g** was synthesized in 51% yield (998 mg).

**Synthesis of 2a-f and 2f'. A typical procedure for 2a.** Rieke calcium (0.3 mmol), prepared from lithium biphenylide (0.6 mmol) and excess  $\text{CaI}_2$  (0.48 mmol, 141 mg) in THF (3 ml), was cooled to  $-95^\circ\text{C}$ . Then, to a THF (5 ml) solution of 2,3-diperfluorophenyl-1,4-diiodo-1,3-butadiene **1a** (0.1 mmol, 72 mg) at  $-95^\circ\text{C}$  was added dropwise Rieke calcium solution via a syringe over 1 h. After the addition was completed, the reaction mixture was stirred at  $-95^\circ\text{C}$  for 2 h. After that, the reaction mixture was quenched with  $\text{H}_2\text{O}$  and the resulting mixture was extracted with ethyl acetate for three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was purified by HPLC using hexane as the eluent. Perfluorodibenzopentalene derivative **2a** was synthesized in 52% yield (22 mg).

**Synthesis of 2g.** To an  $\text{Et}_2\text{O}$  (5 ml) and hexane (5 ml) solution of 2,3-diperfluoronaphthyl-1,4-diiodo-1,3-butadiene **1g** (0.1 mmol, 98 mg) at  $-78^\circ\text{C}$  was added dropwise *n*-BuLi (0.2 mmol, 1.6 M, 0.13 ml) with a syringe. After the addition was completed, the reaction mixture was allowed to room temperature and stirred for 3 h. Next, the reaction mixture was quenched with  $\text{H}_2\text{O}$  and the resulting mixture was extracted with ethyl acetate for three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was subjected to thin layer chromatography using hexane as the eluent. After that, the resulting powders need to be rinsed by chloroform. Perfluorodinaphthopentalene derivative **2g** was synthesized in 37% yield (25 mg).

**Synthesis of 4a-f. A typical procedure for 4a.** Rieke barium (0.5 mmol), prepared from lithium biphenylide (1 mmol) and excess  $\text{BaI}_2$  (0.55 mmol, 215 mg) in THF (10 ml), was cooled to  $-78^\circ\text{C}$ . Next, the corresponding 1,4-diiodo-1,3-butadiene derivative **3** (0.25 mmol) was added. After the addition was completed, the reaction mixture was allowed to room temperature and stirred at room temperature for 3 h. After that, the reaction mixture was quenched with  $\text{H}_2\text{O}$  and the resulting mixture was extracted with ethyl acetate for three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude

product, which was subjected to  $\text{SiO}_2$  column using hexane as the eluent. Naphthalene derivative **4a** was synthesized in 74% yield (48 mg).

**Synthesis of 4g-h. A typical procedure for 4g.** Rieke barium (0.5 mmol), prepared from lithium biphenylide (1 mmol) and excess  $\text{BaI}_2$  (0.55 mmol, 215 mg) in THF (10 ml), was warmed to  $70^\circ\text{C}$ . Next, the corresponding 1,4-diiodo-1,3-butadiene derivative **3** (0.25 mmol) was added. After the addition was completed, the reaction mixture was stirred at  $70^\circ\text{C}$  for 3 h. After that, the reaction mixture was quenched with  $\text{H}_2\text{O}$  and the resulting mixture was extracted with ethyl acetate for three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was subjected to  $\text{SiO}_2$  column using hexane as the eluent. Naphthalene derivative **4g** was synthesized in 62% yield (40 mg).

**Synthesis of 4i.** Rieke barium (0.5 mmol), prepared from lithium biphenylide (1 mmol) and excess  $\text{BaI}_2$  (0.55 mmol, 215 mg) in THF (10 ml), was cooled to  $-78^\circ\text{C}$ . Next, the corresponding 1,4-diiodo-1,3-butadiene derivative **3** (0.25 mmol) was added. After the addition was completed, the reaction mixture was allowed to  $-20^\circ\text{C}$  and stirred at  $-20^\circ\text{C}$  for 3 h. After that, the reaction mixture was quenched with  $\text{H}_2\text{O}$  and the resulting mixture was extracted with ethyl acetate for three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was subjected to  $\text{SiO}_2$  column using hexane as the eluent. Naphthalene derivative **4i** was synthesized in 42% yield (31 mg).

**Synthesis of 5a.** Rieke barium (0.5 mmol), prepared from lithium biphenylide (1 mmol) and excess  $\text{BaI}_2$  (0.55 mmol, 215 mg) in THF (10 ml), was cooled to  $-78^\circ\text{C}$ . Next, the corresponding 1,4-diiodo-1,3-butadiene derivative **3** (0.25 mmol) was added. After the addition was completed, the reaction mixture was allowed to  $-40^\circ\text{C}$  and stirred at  $-40^\circ\text{C}$  for 1 h. After that, the reaction mixture was quenched with  $\text{H}_2\text{O}$  and the resulting mixture was extracted with ethyl acetate for three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was subjected to  $\text{SiO}_2$  column using hexane as the eluent. 1-Iodo-1,3-butadiene derivative **5a** was synthesized in 39% yield (39 mg).

**Synthesis of 4a and 4a-I.** Rieke barium (0.5 mmol), prepared from lithium biphenylide (1 mmol) and excess  $\text{BaI}_2$  (0.55 mmol, 215 mg) in THF (10 ml), was cooled to  $-78^\circ\text{C}$ . Then, the corresponding 1,4-diiodo-1,3-butadiene derivative **3** (0.25 mmol) was added. After the addition was completed, the reaction mixture was allowed to room temperature and stirred at room temperature for 1 h. After that, to the reaction mixture was added  $\text{I}_2$  (0.5 mmol, 127 mg) and the resulting mixture was extracted with ethyl acetate for three times. The extract was dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated *in vacuo* to give crude product, which was subjected to  $\text{SiO}_2$  column using hexane as the eluent. **4a** and **4a-I** was synthesized in 68% yield (53 mg).

**X-ray crystallographic analysis.** Single crystals suitable for X-ray diffraction were grown from hexane (**2f**, **2e** and **1a**) or chlorobenzene (**2g**) solution. Data collections were performed at 100 K for **2f**, **2e** and **1a** on a SuperNova diffractometer, using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data of **2g** was performed at 100 K on a SuperNova diffractometer, using graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Using Olex2 (ref. 54), these structures were solved with the ShelXS and refined with the ShelXL<sup>55</sup> refinement package using Least Squares minimization. Refinement was performed on  $F^2$  anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. In the case of **2g**, the whole molecule was disordered and treated with 61 and 39% occupancy. The disordered part1 and part2 are related by local two-fold axis, which is equivalent to a local mirror plane perpendicular to the plane of the figure. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). The thermal ellipsoid plot in the Fig. 2b,c and Supplementary Figs 2–4 and 70 were drawn by Ortep-3 v1.08 (ref. 56). See Supplementary Table 1 and Supplementary Data 1–4 for the crystal data details of **2f**, **2e**, **2g** and **1a**.

**Photophysical and electrochemical details.** Absorption spectra was recorded on PerkinElmer Lambda 750 ultraviolet-visible spectrometer in  $\text{CHCl}_3$  solutions ( $1 \times 10^{-5} \text{ M}$ ). Cyclic voltammetry was performed on BASi Epsilon workstation and measurements were carried out in dichlorobenzene (1 mM) containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte (scan rate:  $100 \text{ mV s}^{-1}$ ). Glassy carbon electrode was used as a working electrode, a platinum sheet as a counter electrode and Ag/AgCl as a reference electrode.



**Computational details.** Density functional theory calculations were performed at the B3LYP/6-311 + G(d,p) level using the Gaussian 09 software package<sup>57</sup>. See Supplementary Table 2 for the Cartesian coordinates.

## References

- Seyferth, D. The Grignard reagents. *Organometallics* **28**, 1598–1605 (2009).
- Hanusa, T. P. Non-cyclopentadienyl organometallic compounds of calcium, strontium and barium. *Coord. Chem. Rev.* **210**, 329–367 (2000).
- Alexander, J. S. & Ruhlandt-Senge, K. Not Just heavy “Grignards”: recent advances in the organometallic chemistry of the alkaline earth metals calcium, strontium and barium. *Eur. J. Inorg. Chem.* **2002**, 2761–2774 (2002).
- Westerhausen, M., Gärtner, M., Fischer, R. & Langer, J. Aryl calcium compounds: syntheses, structures, physical properties, and chemical behavior. *Angew. Chem. Int. Ed.* **46**, 1950–1956 (2007).
- Westerhausen, M. Heavy Grignard reagents—synthesis and reactivity of organocalcium compounds. *Coord. Chem. Rev.* **252**, 1516–1531 (2008).
- Smith, J. D. Organometallic compounds of the heavier s-block elements—What next? *Angew. Chem. Int. Ed.* **48**, 6597–6599 (2009).
- Harder, S. Geminal dianions stabilized by phosphonium substituents. *Coord. Chem. Rev.* **255**, 1252–1267 (2011).
- Alexander, J. S. & Ruhlandt-Senge, K. Barium triphenylmethanide: an examination of anion basicity. *Angew. Chem. Int. Ed.* **40**, 2658–2660 (2001).
- Wu, T.-C., Xiong, H. & Rieke, R. D. Organocalcium chemistry: preparation and reactions of highly reactive calcium. *J. Org. Chem.* **55**, 5045–5051 (1990).
- Yanagisawa, A., Habaue, S., Yasue, K. & Yamamoto, H. Allylbarium reagents: unprecedented regio- and stereoselective allylation reactions of carbonyl compounds. *J. Am. Chem. Soc.* **116**, 6130–6141 (1994).
- Yanagisawa, A., Takahashi, H. & Arai, T. Reactive barium-promoted reformatsky-type reaction of  $\alpha$ -chloroketones with aldehydes. *Chem. Commun.* 580–581 (2004).
- Yanagisawa, A., Suzuki, T., Koide, T., Okitsu, S. & Arai, T. Selective propargylation of carbonyl compounds and imines with barium reagents. *Chem. Asian J.* **3**, 1793–1800 (2008).
- Westerhausen, M., Digeser, M. H., Nöth, H., Seifert, T. & Pfitzner, A. A unique barium-carbon bond: mechanism of formation and crystallographic characterization. *J. Am. Chem. Soc.* **120**, 6722–6725 (1998).
- Westerhausen, M. *et al.* 2,5-diphenyl-3,4-bis(trimethylsilyl)-1-phosphacyclopentadienide as a ligand at calcium, strontium and tin(II). *Inorg. Chem.* **38**, 3207–3214 (1999).
- Barrett, A. G. M., Crimmin, M. R., Hill, M. S., Hitchcock, P. B. & Procopiou, P. A. Trifluoromethyl coordination and C-F bond activation at calcium. *Angew. Chem. Int. Ed.* **46**, 6339–6342 (2007).
- Gärtner, M., Görls, H. & Westerhausen, M. Heteroleptic phenylcalcium derivatives via metathesis reactions of  $\text{PhCa}(\text{thf})_4\text{I}$  with potassium compounds. *Organometallics* **26**, 1077–1083 (2007).
- Fischer, R. *et al.* THF solvates of extremely soluble bis(2,4,6-trimethylphenyl)calcium and tris(2,6-dimethoxyphenyl)-dicalcium iodide. *Angew. Chem. Int. Ed.* **46**, 1618–1623 (2007).
- Langer, J., Köhler, M., Görls, H. & Westerhausen, M. Arylcalcium halides as substrates in Kumada-type cross-coupling reactions. *J. Organomet. Chem.* **751**, 563–567 (2014).
- Rieke, R. D. Preparation of organometallic compounds from highly reactive metal powders. *Science* **246**, 1260–1264 (1989).
- Saito, M. Synthesis and reaction of dibenzo[*a,e*]pentalene. *Symmetry* **2**, 950–969 (2010).
- Hopf, H. Pentalenes—From highly reactive antiaromatics to substrates for material science. *Angew. Chem. Int. Ed.* **52**, 12224–12226 (2013).
- Saito, M., Nakamura, M., Tajima, T. & Yoshioka, M. Reduction of phenyl silyl acetylenes with lithium: unexpected formation of a dilithium dibenzopentalenide. *Angew. Chem. Int. Ed.* **46**, 1504–1507 (2007).
- Levi, Z. U. & Tilley, T. D. Versatile synthesis of pentalene derivatives via the Pd-catalyzed homocoupling of haloynes. *J. Am. Chem. Soc.* **131**, 2796–2797 (2009).
- Xu, F., Peng, L., Orita, A. & Otera, J. Dihalo-substituted dibenzopentalenes: their practical synthesis and transformation to dibenzopentalene derivatives. *Org. Lett.* **14**, 3970–3973 (2012).
- Hashmi, A. S. K. *et al.* Gold-catalyzed synthesis of dibenzopentalenes—Evidence for gold vinylidenes. *Adv. Synth. Catal.* **354**, 555–562 (2012).
- Maekawa, T., Segawa, Y. & Itami, K. C-H activation route to dibenzo[*a,e*]pentalenes: annulation of arylacetylenes promoted by  $\text{PdCl}_2\text{-AgOTf-o-chloranil}$ . *Chem. Sci.* **4**, 2369–2373 (2013).
- Chen, C. *et al.* Dibenzopentalenes from  $\text{B}(\text{C}_6\text{F}_5)_3$ -induced cyclization reactions of 1,2-bis(phenylethynyl)benzenes. *Angew. Chem. Int. Ed.* **52**, 5992–5996 (2013).
- Zhao, J., Oniwa, K., Asao, N., Yamamoto, Y. & Jin, T. Pd-catalyzed cascade cross-over annulation of *o*-alkynylarylhalides and diarylacetylenes leading to dibenzo[*a,e*]pentalenes. *J. Am. Chem. Soc.* **135**, 10222–10225 (2013).
- Zhu, C. *et al.* Stabilization of anti-aromatic and strained five-membered rings with a transition metal. *Nat. Chem.* **5**, 698–703 (2013).
- London, G. *et al.* Pentalenes with novel topologies: exploiting the cascade carbopalladation reaction between alkynes and *gem*-dibromoolefins. *Chem. Sci.* **5**, 965–972 (2014).
- Kawase, T. *et al.* Dinaphthopentalenes: pentalene derivatives for organic thin-film transistors. *Angew. Chem. Int. Ed.* **49**, 7728–7732 (2010).
- Facchetti, A. *et al.* Building blocks for n-type organic electronics: regiochemically modulated inversion of majority carrier sign in perfluoroarene-modified polythiophene semiconductors. *Angew. Chem. Int. Ed.* **42**, 3900–3903 (2003).
- Sakamoto, Y. *et al.* Perfluoropentalene: high-performance p-n junctions and complementary circuits with pentalene. *J. Am. Chem. Soc.* **126**, 8138–8140 (2004).
- Li, H., Wei, B., Xu, L., Zhang, W.-X. & Xi, Z. Barium dibenzopentalenide as a main-group metal  $\eta^8$  complex: facile synthesis from 1,4-dithio-1,3-butadienes and  $\text{Ba}[\text{N}(\text{SiMe}_3)_2]_2$ , structural characterization, and reaction chemistry. *Angew. Chem. Int. Ed.* **52**, 10822–10825 (2013).
- Amii, H. & Uneyama, K. C-F bond activation in organic synthesis. *Chem. Rev.* **109**, 2119–2183 (2009).
- Clot, E. *et al.* C-F and C-H bond activation of fluorobenzenes and fluoropyridines at transition metal centers: how fluorine tips the scales. *Acc. Chem. Res.* **44**, 333–348 (2011).
- Stahl, T., Klare, H. F. T. & Oestreich, M. Main-group Lewis acids for C-F bond activation. *ACS Catal.* **3**, 1578–1587 (2013).
- Xi, C., Huo, S., Afifi, T. H., Hara, R. & Takahashi, T. Remarkable effect of copper chloride on diiodination of zirconacyclopentadienes. *Tetrahedron Lett.* **38**, 4099–4102 (1997).
- Johnson, S. A. *et al.* Regioselective coupling of pentafluorophenyl substituted alkynes: mechanistic insight into the zirconocene coupling of alkynes and a facile route to conjugated polymers bearing electron-withdrawing pentafluorophenyl substituents. *J. Am. Chem. Soc.* **125**, 4199–4211 (2003).
- Hauber, S.-O., Lissner, F., Deacon, G. B. & Niemeyer, M. Stabilization of aryl-calcium, -strontium, and -barium compounds by designed steric and  $\pi$ -bonding encapsulation. *Angew. Chem. Int. Ed.* **44**, 5871–5875 (2005).
- Rieke, R. D. & Bales, S. E. Activated Metals. IV. Preparation and reactions of highly reactive magnesium metal. *J. Am. Chem. Soc.* **96**, 1775–1781 (1974).
- Chase, D. T. *et al.* Electron-accepting 6,12-diethynylindeno[1,2-*b*]fluorenes: synthesis, crystal structures, and photophysical properties. *Angew. Chem. Int. Ed.* **50**, 11103–11106 (2011).
- Viswanathan, G. S., Wang, M. & Li, C.-J. A highly regioselective synthesis of polysubstituted naphthalene derivatives through gallium trichloride catalyzed alkyne-aldehyde coupling. *Angew. Chem. Int. Ed.* **41**, 2138–2141 (2002).
- Kabalka, G. W., Ju, Y. & Wu, Z. A new titanium tetrachloride mediated annulation of  $\alpha$ -aryl-substituted carbonyl compounds with alkynes: a simple and highly efficient method for the regioselective synthesis of polysubstituted naphthalene derivatives. *J. Org. Chem.* **68**, 7915–7917 (2003).
- Yoshikawa, E. & Yamamoto, Y. Palladium-catalyzed intermolecular controlled insertion of benzyne-benzyne-alkene and benzyne-alkyne-alkene—Synthesis of phenanthrene and naphthalene derivatives. *Angew. Chem. Int. Ed.* **39**, 173–175 (2000).
- Zhou, H., Xing, Y., Yao, J. & Chen, J. Sulfur-assisted propargyl-allenyl isomerizations and electrocyclizations for the convenient and efficient synthesis of polyfunctionalized benzenes and naphthalenes. *Org. Lett.* **12**, 3674–3677 (2010).
- Feng, C. & Loh, T.-P. Palladium-catalyzed bisolefination of C-C triple bonds: a facile method for the synthesis of naphthalene derivatives. *J. Am. Chem. Soc.* **132**, 17710–17712 (2010).
- Knorr, R., Lattke, E. & Räßle, E. Der konformative *ortho*-effekt bei *o*-tolylstilbenen und deren vinylithiumderivaten. *Chem. Ber.* **114**, 1581–1591 (1981).
- Fischer, R., Gärtner, M., Görls, H. & Westerhausen, M. Synthesis of 2,4,6-trimethylphenylcalcium iodide and degradation in THF solution. *Angew. Chem. Int. Ed.* **45**, 609–612 (2006).
- Köhler, M., Görls, H., Langer, J. & Westerhausen, M. 1-Alkenylcalcium iodide: synthesis and stability. *Eur. Chem. J.* **20**, 5237–5239 (2014).
- Harder, S. & Lutz, M. The phosphonium dibenzylidene anion as a ligand in organobarium chemistry. *Organometallics* **16**, 225–230 (1997).
- Westerhausen, M. *et al.* Synthesis of strontium and barium bis[tris(trimethylsilyl)methyl]zincates] via the transmetalation of bis[tris(trimethylsilyl)methyl]zinc. *Organometallics* **20**, 893–899 (2001).
- Loh, C., Seuppel, S., Görls, H., Krieck, S. & Westerhausen, M. Structural evidence of strong calcium- $\pi$  interactions to aryl substituents stabilized by coexistent agostic bonds to alkyl groups. *Organometallics* **33**, 1480–1491 (2014).
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42**, 339–341 (2009).
- Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* **A64**, 112–122 (2008).
- Farrugia, L. J. ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI). *J. Appl. Cryst.* **30**, 565–566 (1997).
- Frisch, M. J. *et al.* Gaussian 09. Revision B.01 (Gaussian, Inc., 2010).

### Acknowledgements

This work was supported by the Major State Basic Research Development Program (2012CB821600) and Natural Science Foundation of China. We also thank Professor Xiang Hao of ICCAS for useful discussions and comments on the the refinement of X-ray data.

### Author contributions

Z.X. conceived and supervised the project. H.L. and B.W. planned and carried out the experiment work. H.L. recorded all NMR data. L.X. and W.-X.Z. solved all X-ray structures. X.-Y.W. conducted the photophysical and electrochemical study of perfluorodibenzopentalene and perfluorodinaphthopentalene derivatives. X.-Y.W. conceived the theoretical work and conducted theoretical computations. Z.X., J.P. and W.-X.Z. drafted the paper. All authors discussed the results and contributed to the preparation of the final manuscript.

### Additional information

**Accession codes:** The X-ray crystal structure information is available at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-993609 (**2f**), CCDC-1001290 (**2e**), CCDC-953857 (**2g**) and CCDC-953855 (**1a**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supplementary Information** accompanies this paper at <http://www.nature.com/naturecommunications>

**Competing financial interests:** The authors declare no competing financial interests.

**Reprints and permission** information is available online at <http://npg.nature.com/reprintsandpermissions/>

**How to cite this article:** Li, H. *et al.* Intramolecular C–F and C–H bond cleavage promoted by butadienyl heavy grignard reagents. *Nat. Commun.* 5:4508 doi: 10.1038/ncomms5508 (2014).