

# Synthesis of di- and monobromo(ferrocenylvinyl)cyclopropanes

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## Abstract

The Wittig olefination of ferrocene-containing chalcones leads to 1,3-dienes and their cyclodimers. The reaction of 1,3-dienes with dibromocarbene yields *gem*-dibromo(ferrocenylvinyl)cyclopropanes. Upon reductive dehalogenation with ethylmagnesium bromide they afford the corresponding monobromo derivatives. All the obtained compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis, and mass spectrometry. The structures of compounds **5a,b**, **6g**, **6h**, and **7i** were confirmed by X-ray diffraction analysis.

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## 1. Introduction

It is known that monohalogenated cyclopropanes are compounds with a great synthetic versatility as they can be used for alkylation reactions [1], elimination reactions to obtain cyclopropenes [2], as starting material for ring expansion [3], etc. In previous studies [4,5], we reported the synthesis of 1-alkyl(aryl)-1-ferrocenyl-2,2-dibromocyclopropanes and their reductive monodehalogenation using standard procedure, viz., by the action of zinc in the presence of Trilon B [6] (Scheme 1).

To obtain monohalogenated compounds from *gem*-dihalogenated ones, different methods of reduction have been employed, for example, zinc powder [6], MeLi [7], vanadium (II) chloride and diethyl phosphonate [8], tributyltin hydride [9], zinc–copper alloy [10], lithium or sodium in ethanol [11] and Grignard reagents [12].

The interest in the synthesis of vinylcyclopropanes is due to their high reactivity. Numerous inter- and intramolecular rearrangements of these compounds find applications in organic synthesis [12]. The presence of the vinyl group induces a significantly different reactivity.

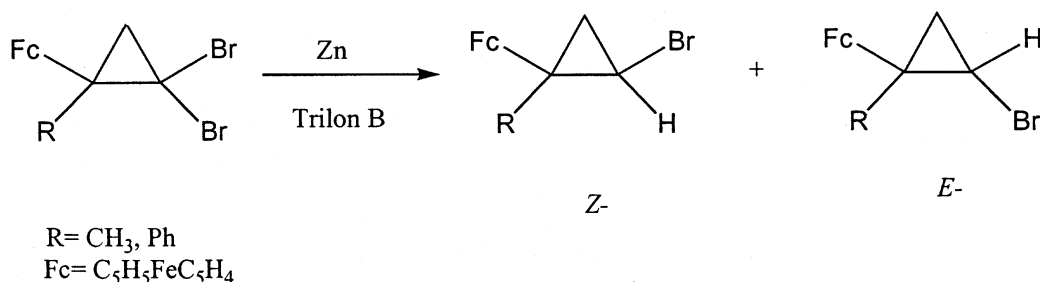
In continuation of our studies, here we report the synthesis of monobromo(ferrocenylvinyl)cyclopropanes from the *gem*-dibromides using ethylmagnesium bromide and catalytic amounts of titanium isopropoxide.

## 2. Results and discussion

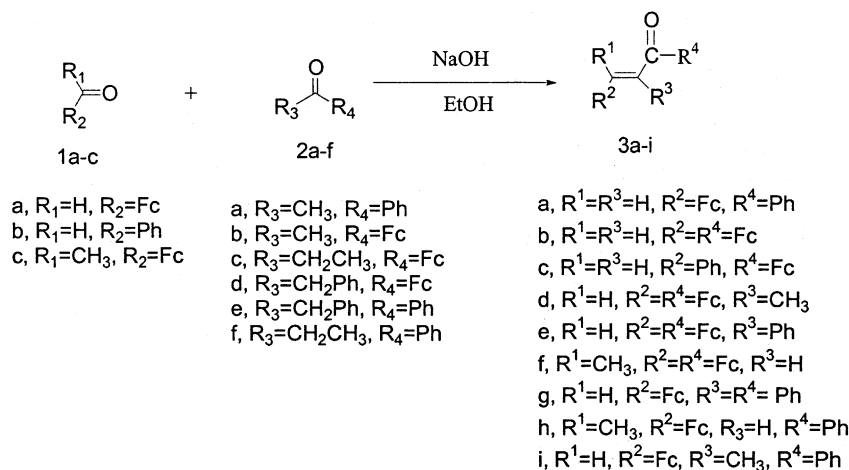
The reaction of ferrocenecarbaldehyde (**1a**), benzaldehyde (**1b**) and acetylferrocene (**1c**) with ketones **2a–f** under homogeneous conditions were carried out at room temperature in ethanol (Scheme 2). The aldehyde **1a** also reacts rapidly with acetophenone (**2a**) or acetylferrocene (**2b**) in aqueous NaOH at room temperature, the condensation products being obtained in yields 95% and 98%, respectively. All the obtained enones showed *E*-configuration [13].

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Scheme 1.



Scheme 2.

To obtain 1,3-dienes **4d–i**, the enones **3a–i** reacted with methyltriphenylphosphonium bromide in the presence of *n*-BuLi; in the case of **3a–c** ( $\text{R}^1 = \text{R}^3 = \text{H}$ ), the Diels–Alder cycloaddition products were also obtained (Scheme 3).

1,3-Dienes **4d–i** were obtained in a pure state as orange-yellow oil and were characterized by spectroscopic methods. Thus the  $^1\text{H}$  NMR spectrum of compound **4d** contained one singlet at  $\delta$  2.17 assigned to the  $\text{CH}_3$  group, two doublets at  $\delta$  5.26 and 5.52 ( $J = 1.5$  Hz) due to the vinyl protons, one singlet at  $\delta$  6.56 assigned to the proton at the double bond, as well as typical signals for the ferrocene moiety, namely, at  $\delta$  4.26 and 4.27 for the  $\text{C}_5\text{H}_5$  and at  $\delta$  4.37, 4.49, and 4.52 for the  $\text{C}_5\text{H}_4$  groups.

Autocyclization of the Wittig products **4a–c** into cyclohexenes **5a–c** occurs easily, when the  $\text{R}^4$  substituent is ferrocene or phenyl and  $\text{R}^1 = \text{R}^3 = \text{H}$ . This reaction is highly regioselective, in all the three cases studied here only one regioisomer was formed (Scheme 4).

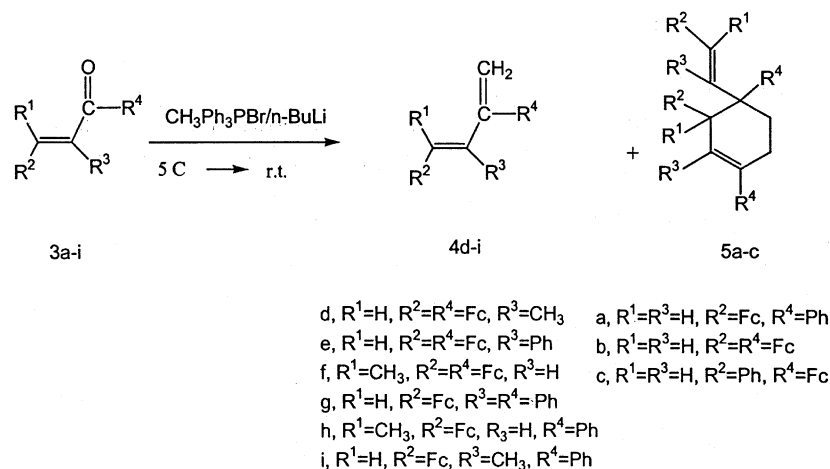
In the  $^1\text{H}$  NMR spectrum of the cyclohexene **5a**, we observed multiplets at  $\delta$  2.0–2.4 assigned to the methylene groups of the cyclohexene ring, one doublet at  $\delta$  3.73 (d, 2H,  $J = 5.3$  Hz) assigned to the methine group of the cyclohexene ring, two doublets at  $\delta$  5.7 (d, 1H,  $J = 14$  Hz,  $\text{HC}=\text{CH}$ ) and 5.88 (d, 1H,  $J = 14$  Hz,  $\text{HC}=\text{CH}$ ) assigned to vinylic protons, one doublet at

$\delta$  6.64 (d, 2H,  $J = 5.7$  Hz) due to the proton at the double bond of the cyclohexene ring. The cyclooligomerization occurs stereospecifically and the cyclooligomers **5a–c** were obtained in only one *endo*-isomeric form, which was confirmed by X-ray diffraction analysis of compounds **5a** and **5b** (Figs. 1 and 2).

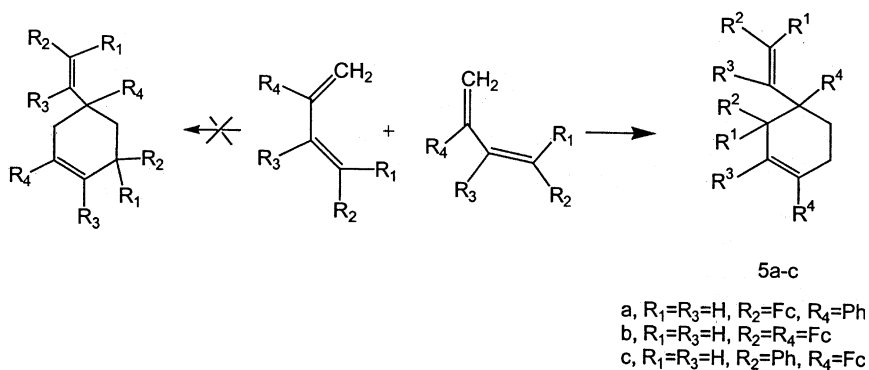
The cyclopropanation of the dienes **4d–i** was carried out at room temperature using bromoform in 40% aqueous NaOH in the presence of  $[\text{BnN}^+\text{Et}_3]\text{Cl}^-$  as a phase transfer catalyst (Scheme 5) to give *gem*-dibromocyclopropanes **6d–i** regioselectively as a single product in each case, the addition dibromocyclopropane occurring to the less substituted double bond ( $^1\text{H}$  NMR data).

In the  $^1\text{H}$  NMR spectrum of compound **6d**, the following signals were observed: two doublets at  $\delta$  1.49 and 2.08 ppm ( $J = 7.5$  Hz) assigned to the protons of the  $\text{CH}_2$  group of the cyclopropane ring, one broad singlet at  $\delta$  2.33 assigned to the  $\text{CH}_3$  group, two singlets at  $\delta$  4.16 and 4.21 for the  $\text{C}_5\text{H}_5$  and four signals at  $\delta$  4.13, 4.29, 4.70 and 4.52 for the  $\text{C}_5\text{H}_4$  groups of the ferrocene units, and one singlet at  $\delta$  5.96 for the proton at the double bond. The structures of *gem*-dibromocyclopropanes **6g** and **6h** were confirmed by X-ray diffraction analysis (Figs. 3 and 4).

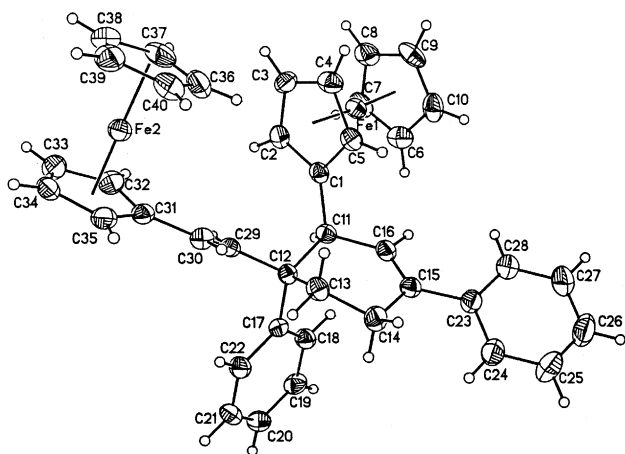
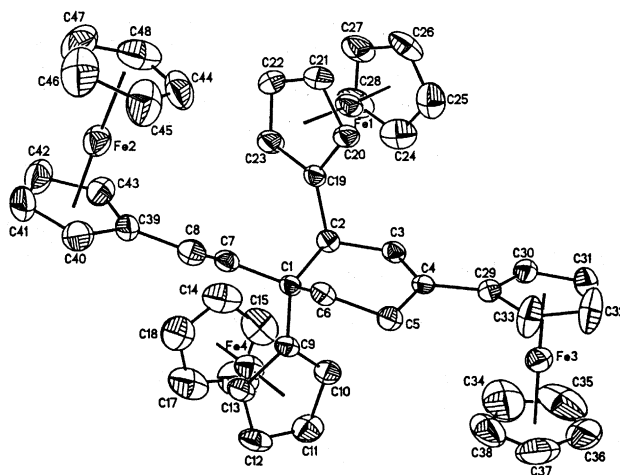
Reduction of 2,2-dibromo-1-(2-ferrocenylvinyl)cyclopropanes **6d,g–i** with ethylmagnesium bromide in the



Scheme 3.

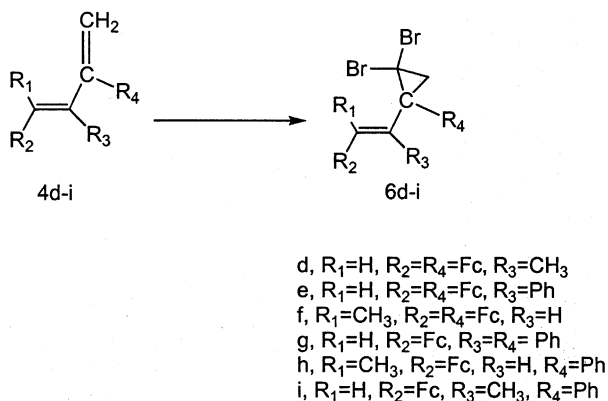


Scheme 4.

Fig. 1. General view of compound **5a**. Selected bond lengths/Å: C<sub>15</sub>–C<sub>16</sub>=1.325 and C<sub>29</sub>–C<sub>30</sub>=1.305.Fig. 2. General view of compound **5b**. Selected bond lengths/Å: C<sub>3</sub>–C<sub>4</sub>=1.325 and C<sub>7</sub>–C<sub>8</sub>=1.326.

presence of titanium isopropoxide in THF occurred without opening of the three-membered ring and resulted in a mixture of *Z*- and *E*-isomeric monobromides (3:1) **7d,g-i** (Scheme 6).

The reaction products *E*/*Z*-**7i** can be easily separated by chromatography on alumina. In the <sup>1</sup>H NMR spectrum of **7i**(*E*) two doublets of doublets at δ 1.73 and 1.92 assigned to the protons of the methylene group



Scheme 5.

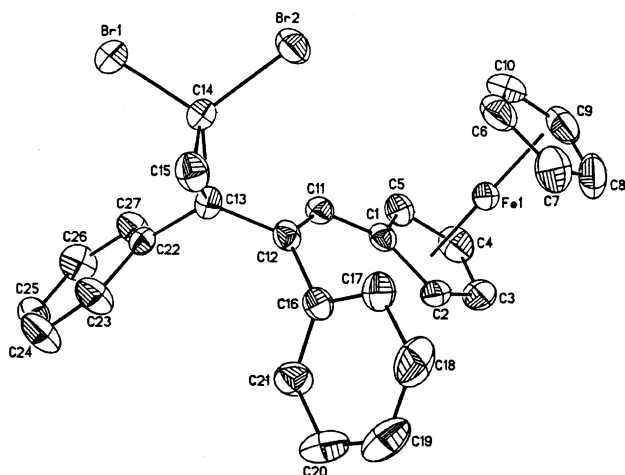


Fig. 3. General view of compound **6g**. Selected bond lengths/Å: C<sub>14</sub>–Br<sub>1</sub>=1.918; C<sub>14</sub>–Br<sub>2</sub>=1.920; C<sub>11</sub>–C<sub>12</sub>=1.347; C<sub>14</sub>–C<sub>15</sub>=1.497; C<sub>15</sub>–C<sub>13</sub>=1.531.

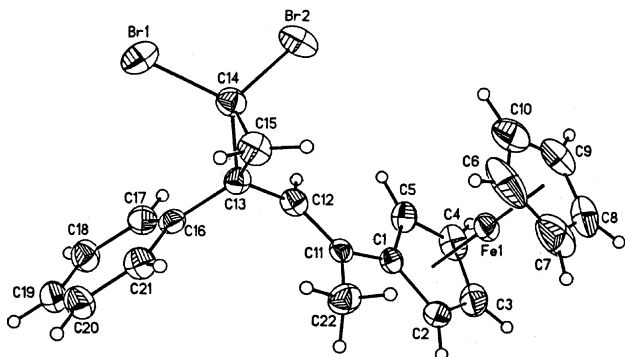


Fig. 4. General view of compound **6h**. Selected bond lengths/Å: C<sub>14</sub>–Br<sub>1</sub>=1.909; C<sub>14</sub>–Br<sub>2</sub>=1.924; C<sub>11</sub>–C<sub>12</sub>=1.327; C<sub>14</sub>–C<sub>15</sub>=1.428; C<sub>15</sub>–C<sub>13</sub>=1.534.

(AB part of the ABM spin system) were observed. The <sup>1</sup>H NMR spectrum of the isomer **7i(Z)** contained the same pattern of signals but at δ 1.48 and 1.93. One can see that the difference in the chemical shifts of the protons A and B ( $\Delta\delta_Z = \delta_B - \delta_A = 0.45$  ppm) for the isomer **7i(Z)** is larger than that for the **7i(E)** isomer

( $\Delta\delta_E = \delta_B - \delta_A = 0.19$  ppm). Similar differences have also been observed in the <sup>1</sup>H NMR spectra of the *Z*- and *E*-isomers of the compounds **7g,h**.

We carried out X-ray structural analysis of single crystals of **7i(E)**, which allowed us to assign more reliably the stereochemistry of the cyclopropane ring (Fig. 5).

### 3. Experimental

IR spectra were recorded on a Nicolet FT-IR Magna 700 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on a Varian Unity 500 instrument operating at 500 and 125 MHz, respectively. For both <sup>1</sup>H and <sup>13</sup>C, chemical shifts are expressed in ppm relative to tetramethylsilane (TMS 0.00 ppm) used as an internal standard. FAB<sup>+</sup> mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer. X-ray crystallographic data were collected at room temperature on a Siemens P/4 diffractometer.

#### 3.1. General procedure for the preparation of enones (**3a–i**)

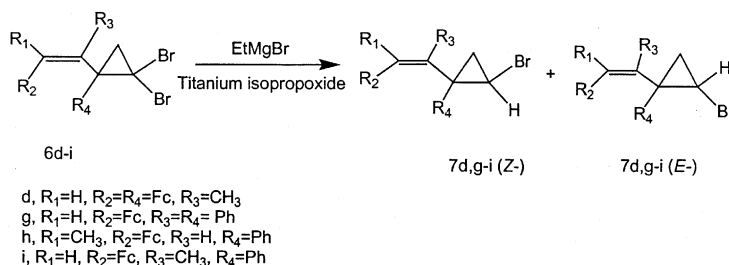
The synthesis conditions and characterization of enones **3a–i** were reported in [13,14]

To a mixture of the aldehyde or ketone **1a,c** (1 mmol) and a ketone **2a–f** (1 mmol) were dissolved in ethanol, and NaOH 40% was added, the mixture was stirred for 24 h and chromatographed on alumina (Brockmann activity III) using hexane as eluent.

#### 3.2. General procedure for the preparation of dienes (**4d–i**)

To a solution of methyltriphenylphosphonium bromide (1.07 g, 3 mmol) in anhydrous THF (30 ml) a 2.5 M solution of *n*-BuLi in *n*-hexane (1.2 ml, 3 mmol) is added under nitrogen with cooling in an ice bath. The reaction is left for 45 min, then a solution of the respective ketone (2 mmol) in a minimum amount of THF is added to the yellowish suspension, and the reaction mixture was kept at room temperature for 4 h, then several drops of H<sub>2</sub>O are added and the reaction mixture is distributed in a CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O system. The reaction products are purified by column chromatography on neutral alumina using *n*-hexane as the eluent.

Compound (**4d**), yield 0.27 g (32%), yellow oil; MS *m/z* (%): 436 (100).  $\nu_{\max}$  (film)/cm<sup>-1</sup>: 1598 (C=C), 878 (C=CH<sub>2</sub>);  $\delta_H$  (300 MHz, CDCl<sub>3</sub>): 2.17 (3H, s, CH<sub>3</sub>), 4.26 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.27 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.37 (4H, t, *J*=1.8 Hz, C<sub>5</sub>H<sub>4</sub>), 4.49 (2H, t, *J*=1.5 Hz, C<sub>5</sub>H<sub>4</sub>), 4.52 (2H, t, *J*=1.5 Hz, C<sub>5</sub>H<sub>4</sub>), 5.26 (1H, d, *J*=1.5 Hz, =CH<sub>2</sub>), 5.52 (1H, d, *J*=1.5 Hz, =CH<sub>2</sub>), 6.56 (1H, s, =CH);  $\delta_C$  (75 MHz, CDCl<sub>3</sub>): 18.2 (CH<sub>3</sub>), 68.0 (C<sub>5</sub>H<sub>4</sub>), 68.3 (C<sub>5</sub>H<sub>4</sub>), 68.5 (C<sub>5</sub>H<sub>4</sub>), 68.7 (C<sub>5</sub>H<sub>4</sub>), 69.3 (C<sub>5</sub>H<sub>4</sub>),



Scheme 6.

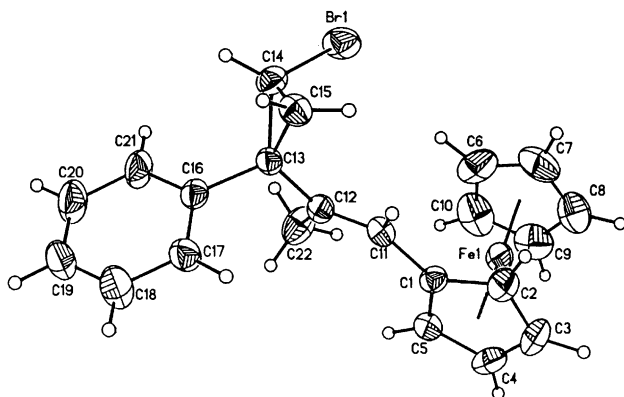


Fig. 5. General view of compound **7i(E)**. Selected bond lengths/Å: C<sub>14</sub>–Br=1.912; C<sub>11</sub>–C<sub>12</sub>=1.323; C<sub>13</sub>–C<sub>14</sub>=1.510; C<sub>14</sub>–C<sub>15</sub>=1.498 and C<sub>15</sub>–C<sub>13</sub>=1.487.

68.9 (C<sub>5</sub>H<sub>5</sub>), 69.6 (C<sub>5</sub>H<sub>5</sub>), 82.8 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 85.7 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 110.1 (=CH<sub>2</sub>), 125.9 (=C(Fc)H), 135.1 (=C–CH<sub>3</sub>), 150.4 (Fc–C=CH<sub>2</sub>). Found: C, 68.80; H, 5.49. Calc. for C<sub>25</sub>H<sub>24</sub>Fe<sub>2</sub>: C, 68.81; H, 5.54%.

Compound (**4e**), yield 0.09 g (9%), yellow oil; MS *m/z* (%): 498 (37), 227 (100).  $\nu_{\max}$  (film)/cm<sup>-1</sup>: 1598 (C=C), 878 (C=CH<sub>2</sub>);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 3.76 (2H, t, *J*=1.9 Hz, C<sub>5</sub>H<sub>4</sub>), 4.06 (2H, t, *J*=1.9 Hz, C<sub>5</sub>H<sub>4</sub>), 4.09 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.11 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.21 (2H, t, *J*=1.9 Hz, C<sub>5</sub>H<sub>4</sub>), 4.34 (2H, t, *J*=1.9 Hz, C<sub>5</sub>H<sub>4</sub>), 4.94 (1H, d, *J*=1.9 Hz, =CH<sub>2</sub>), 5.49 (1H, d, *J*=1.9 Hz, =CH<sub>2</sub>), 6.75 (1H, s, =CH), 7.24 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 67.9 (C<sub>5</sub>H<sub>4</sub>), 68.5 (C<sub>5</sub>H<sub>4</sub>), 68.7 (C<sub>5</sub>H<sub>4</sub>), 69.0 (C<sub>5</sub>H<sub>5</sub>), 69.2 (C<sub>5</sub>H<sub>4</sub>), 69.5 (C<sub>5</sub>H<sub>4</sub>), 69.5 (C<sub>5</sub>H<sub>4</sub>), 81.6 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 86.1 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 114.4 (=CH<sub>2</sub>), 126.9 (=C(Fc)H), 127.5 (Ph), 129.7 (Ph), 132.0 (Ph), 139.44 (Ph<sub>ipso</sub>), 140.9 (=C–Ar), 148.7 (Fc–C=CH<sub>2</sub>). Found: C, 72.25; H, 5.23. Calc. for C<sub>30</sub>H<sub>26</sub>Fe<sub>2</sub>: C, 72.29; H, 5.25%.

Compound (**4f**), yield 0.26 g (30%), orange crystals, m.p. 97–98 °C; MS *m/z* (%): 436 (100).  $\nu_{\max}$  (KBr)/cm<sup>-1</sup>: 1594 (C=C), 882 (C=CH<sub>2</sub>);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 2.18 (3H, d, *J*=1.4 Hz, CH<sub>3</sub>), 4.15 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.17 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.23 (2H, t, *J*=2.0 Hz, C<sub>5</sub>H<sub>5</sub>), 4.28 (2H, t, *J*=2.0 Hz, C<sub>5</sub>H<sub>4</sub>), 4.38 (2H, t, *J*=1.9 Hz, C<sub>5</sub>H<sub>4</sub>), 4.49 (2H, t, *J*=1.9 Hz, C<sub>5</sub>H<sub>4</sub>), 4.96 (1H, t, *J*=1.6 Hz, =CH<sub>2</sub>), 5.46 (1H, d, *J*=1.9 Hz, =CH), 6.49 (1H, t, *J*=1.6 Hz, =CH);  $\delta_{\text{C}}$  (75 MHz,

CDCl<sub>3</sub>): 20.5 (CH<sub>3</sub>), 68.0 (C<sub>5</sub>H<sub>4</sub>), 68.1 (C<sub>5</sub>H<sub>4</sub>), 68.2 (C<sub>5</sub>H<sub>4</sub>), 68.4 (C<sub>5</sub>H<sub>5</sub>), 68.4 (C<sub>5</sub>H<sub>4</sub>), 68.8 (C<sub>5</sub>H<sub>4</sub>), 68.9 (C<sub>5</sub>H<sub>5</sub>), 69.0 (C<sub>5</sub>H<sub>4</sub>), 86.7 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 88.5 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 116.4 (=CH<sub>2</sub>), 122.6 (=CH), 135.1 (=C–CH<sub>3</sub>), 143.8 (Fc–C=CH<sub>2</sub>). Found: C, 768.85; H, 5.52. Calc. for C<sub>25</sub>H<sub>24</sub>Fe<sub>2</sub>: C, 68.81; H, 5.54%.

Compound (**4g**), yield 0.62 g (80%), yellow oil, MS *m/z* (%): 390 (100).  $\nu_{\max}$  (film)/cm<sup>-1</sup>: 1679 (C=C), 817 (C=CH<sub>2</sub>);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 3.62 (2H, t, *J*=1.8, 2.04 Hz, C<sub>5</sub>H<sub>4</sub>), 4.02 (2H, t, *J*=1.8, 2.04 Hz, C<sub>5</sub>H<sub>4</sub>), 4.01 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.82 (1H, d, *J*=1.5 Hz, =CH<sub>2</sub>), 5.12 (1H, d, *J*=1.5 Hz, =CH<sub>2</sub>), 6.18 (1H, s, =CH), 7.26 (10H, m, Ar);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 68.6 (C<sub>5</sub>H<sub>4</sub>), 69.0 (C<sub>5</sub>H<sub>5</sub>), 69.5 (C<sub>5</sub>H<sub>4</sub>), 82.3 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 116.2 (=CH<sub>2</sub>), 127.0 (=C(Fc)H), 127.2 (Ph), 128.0 (Ph), 128.9 (Ph), 129.9 (Ph), 139.3 (Ph<sub>ipso</sub>), 140.6 (Ph<sub>ipso</sub>), 142.6 (=C–Ar), 152.5 (=C–Ph). Found: C, 768.85; H, 5.52. Calc. for C<sub>26</sub>H<sub>22</sub>Fe<sub>1</sub>: C, 79.99; H, 5.68%.

Compound (**4h**), yield 0.34 g (44%), yellow oil, MS *m/z* (%): 328 (100).  $\nu_{\max}$  (film)/cm<sup>-1</sup>: 1622 (C=C), 895 (C=CH<sub>2</sub>);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 2.03 (3H, s, CH<sub>3</sub>), 4.10 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.25 (5H, s, C<sub>5</sub>H<sub>4</sub>), 4.46 (2H, s, C<sub>5</sub>H<sub>4</sub>), 5.17 (1H, s, =CH<sub>2</sub>), 5.59 (1H, s, =CH<sub>2</sub>), 6.43 (1H, s, =CH). 7.28 (4H, dd, *J*=2.5, 7.6 Hz, Ph), 7.42 (1H, d, *J*=7.5 Hz, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 17.2 (CH<sub>3</sub>), 65.7 (C<sub>5</sub>H<sub>4</sub>), 68.7 (C<sub>5</sub>H<sub>4</sub>), 69.0 (C<sub>5</sub>H<sub>5</sub>), 88.3 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 114.7 (=CH<sub>2</sub>), 122.8 (=CH), 126.6 (Ph), 127.4 (Ph), 128.2 (Ph), 136.6 (Ph<sub>ipso</sub>), 141.3 (=C–CH<sub>3</sub>), 145.3 (=C–Ph). Found: C, 76.88; H, 6.12. Calc. for C<sub>21</sub>H<sub>20</sub>Fe<sub>1</sub>: C, 76.82; H, 6.14%.

Compound (**4i**), yield 0.34 g (53%), yellow oil, MS *m/z* (%): 328 (100).  $\nu_{\max}$  (film)/cm<sup>-1</sup>: 1615 (C=C), 884 (C=CH<sub>2</sub>);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 2.04 (3H, s, CH<sub>3</sub>), 4.08 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.21 (2H, t, *J*=1.8 Hz, C<sub>5</sub>H<sub>4</sub>), 4.33 (2H, t, *J*=1.8 Hz, C<sub>5</sub>H<sub>4</sub>), 5.11 (1H, d, *J*=1.4 Hz, =CH<sub>2</sub>), 5.28 (1H, d, *J*=1.4 Hz, =CH<sub>2</sub>), 6.11 (1H, s, =CH), 7.31 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 16.7 (CH<sub>3</sub>), 68.6 (C<sub>5</sub>H<sub>4</sub>), 69.0 (C<sub>5</sub>H<sub>5</sub>), 69.5 (C<sub>5</sub>H<sub>4</sub>), 82.6 (C<sub>5</sub>H<sub>4</sub><sub>ipso</sub>), 112.1 (=CH<sub>2</sub>), 127.1 (=CH), 127.9 (Ph), 128.5 (Ph), 134.4 (Ph<sub>ipso</sub>), 141.9 (=C–CH<sub>3</sub>), 153.3 (=C–Ph). Found: C, 76.78; H, 6.10. Calc. for C<sub>21</sub>H<sub>20</sub>Fe<sub>1</sub>: C, 76.82; H, 6.14%.

Compound (**5a**), yield 0.012 g (20%), yellow crystals, m.p. 187–188 °C; MS *m/z* (%): 628 (77), 524 (15), 442

(12), 390 (12), 314 (100).  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1639 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 2.0 (1H, m,  $\text{CH}_2$ ), 2.07 (1H, m,  $\text{CH}_2$ ), 2.35 (1H, m,  $\text{CH}_2$ ), 2.40 (1H, m,  $\text{CH}_2$ ), 3.73 (2H, d,  $J=5.7$  Hz, CH), 4.07 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.10 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.13 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.16 (H, 2s,  $\text{C}_5\text{H}_4$ ), 4.26 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.39 (2H, s,  $\text{C}_5\text{H}_4$ ), 5.70 (1H, d,  $J=14$  Hz,  $\text{CH}=\text{CH}$ ), 5.88 (1H, d,  $J=14$  Hz,  $\text{HC}=\text{CH}$ ), 6.64 (2H, d,  $J=5.7$  Hz,  $\text{CH}=\text{CH}$ ), 7.20 (10H, m, 2Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 24.7 ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_2$ ), 41.4 (C–Fc), 51.8 (CH), 68.0 ( $\text{C}_5\text{H}_4$ ), 68.4 ( $\text{C}_5\text{H}_4$ ), 68.5 ( $\text{C}_5\text{H}_5$ ), 68.9 ( $\text{C}_5\text{H}_4$ ), 69.0 ( $\text{C}_5\text{H}_5$ ), 69.3 ( $\text{C}_5\text{H}_4$ ), 87.5 ( $\text{C}_5\text{H}_4$  ipso), 98.2 ( $\text{C}_5\text{H}_4$  ipso), 122.8 ( $=\text{CH}$ ), 133.9 ( $=\text{CH}$ ), 125.8 (Ph), 126.4 (Ph), 126.9 (Ph), 127.6 (Ph), 128.4 (Ph), 130.0 (Ph), 131.6 ( $\text{Ph}_{\text{ipso}}$ ), 136.2 ( $\text{Ph}_{\text{ipso}}$ ), 137.8, ( $\text{Ph}_{\text{ipso}}$ ), 138.2 ( $=\text{CH}$ ), 142.3 ( $=\text{C}(\text{Fc})$ ). Found: C, 76.48; H, 5.73. Calc. for  $\text{C}_{40}\text{H}_{36}\text{Fe}_2$ : C, 76.43; H, 5.77%.

Compound (5b), yield 0.109 g (13%), yellow crystals, m.p. 150–151 °C; MS (FAB<sup>+</sup>)  $m/z$  844.  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1646 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 2.10 (2H, m,  $\text{CH}_2$ ), 2.44 (2H, m,  $\text{CH}_2$ ), 3.48 (1H, d,  $J=3.1$  Hz, CH), 4.15 (36H, m, 4Fc), 6.04 (1H, d,  $J=3.1$  Hz,  $=\text{CH}$ ), 6.16 (1H, d,  $J=12$  Hz,  $\text{HC}=\text{CH}$ ), 6.25 (1H, d,  $J=12$  Hz,  $\text{HC}=\text{CH}$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 42.9 ( $\text{CH}_2$ ), 44.0 ( $\text{CH}_2$ ), 46.4 (CH), 46.7 (C–Fc), 68.8 (4Fc), 70.4 ( $\text{C}_5\text{H}_4$  ipso), 71.0 ( $\text{C}_5\text{H}_4$  ipso), 71.1 ( $\text{C}_5\text{H}_4$  ipso), 71.3 ( $\text{C}_5\text{H}_4$  ipso), 122.2 ( $=\text{CH}$ ), 124.2 ( $=\text{CH}$ ), 132.8 ( $=\text{CH}(\text{Fc})$ ), 136.2 ( $=\text{C}(\text{Fc})$ ). Found: C, 68.24; H, 5.23. Calc. for  $\text{C}_{48}\text{H}_{44}\text{Fe}_4$ : C, 68.25, H, 5.25%.

Compound (5c), yield 0.37 g (67%), yellow crystals, m.p. 181–182 °C; MS  $m/z$  (%): 628 (100).  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1598 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 2.11 (2H, m,  $\text{CH}_2$ ), 2.44 (2H, m,  $\text{CH}_2$ ), 3.73 (1H, d,  $J=3.5$  Hz, CH), 4.07 (18H, m, 2Fc), 5.7 (1H, d,  $J=14$  Hz,  $\text{HC}=\text{CH}$ ), 5.88 (1H, d,  $J=14$  Hz,  $\text{HC}=\text{CH}$ ), 6.64 (1H, d,  $J=3.5$  Hz,  $=\text{CH}$ ), 7.24 (10H, m, 2Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 25.40 ( $\text{CH}_2$ ), 30.7 ( $\text{CH}_2$ ), 45.2 (CH), 46.9 (C–Ph), 67.5 ( $\text{C}_5\text{H}_4$ ), 67.6 ( $\text{C}_5\text{H}_4$ ), 68.8 (2 $\text{C}_5\text{H}_5$ ), 69.5 ( $\text{C}_5\text{H}_4$ ), 69.7 ( $\text{C}_5\text{H}_4$ ), 70.3 ( $\text{C}_5\text{H}_4$ ), 70.9 ( $\text{C}_5\text{H}_4$ ), 89.8 (2  $\text{C}_5\text{H}_4$  ipso), 125.0 (Ph), 125.8 (Ph), 126.8 (Ph), 127.6 (Ph), 127.9 (Ph), 128.3 (Ph), 134.5 ( $=\text{CH}$ ), 135.8 ( $\text{Ph}_{\text{ipso}}$ ), 136.3 ( $=\text{CH}$ ), 141.8 ( $\text{Ph}_{\text{ipso}}$ ), 146.3 ( $=\text{CH}(\text{Ph})$ ), (Ph), 146.5 ( $=\text{C}(\text{Ph})$ ). Found: C, 76.44; H, 5.73. Calc. for  $\text{C}_{40}\text{H}_{36}\text{Fe}_2$ : C, 76.43; H, 5.77%.

### 3.3. General procedure for the synthesis of gem-dibromo(ferrocenyl)cyclopropanes (6d–i)

The diene 4d–i (1 mmol) is added to bromoform (0.43 ml, 5 mmol), a phase-transfer catalyst, and a 40% solution of sodium hydroxide (3 ml), and the mixture was vigorously stirred at room temperature. The reaction mixture is distributed in a  $\text{CH}_2\text{Cl}_2$ – $\text{H}_2\text{O}$  system. The target products are purified by column chromatography on neutral alumina using *n*-hexane as the eluent.

Compound (6d), yield 0.51 g (85%), yellow crystals, m.p. 145–146 °C; MS  $m/z$  (%): 608 (37.5), 606 (21.25),

326 (100%).  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1444 (C=C– $\text{CH}_3$ );  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 1.49 (1H, d,  $J=7.5$  Hz,  $\text{CH}_2$ ), 2.08 (1H, d,  $J=7.5$  Hz,  $\text{CH}_2$ ), 2.33 (3H, s,  $\text{CH}_3$ ), 4.16 (10H, s, 2 $\text{C}_5\text{H}_5$ ), 4.21 (10H, s, 2 $\text{C}_5\text{H}_5$ ), 4.13 (2H, s, 2 $\text{C}_5\text{H}_4$ ), 4.29 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.70 (2H, s, 2 $\text{C}_5\text{H}_4$ ), 4.52 (2H, s, 2 $\text{C}_5\text{H}_2$ ), 5.96 (1H, s,  $=\text{CH}$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 19.6 ( $\text{GH}_3$ ), 36.1 ( $\text{CH}_2$ ), 36.5 (C–Fc), 43.4 (C–Br), 68.5 (2 Fc), 89.8 ( $\text{C}_5\text{H}_4$  ipso), 126.2 ( $=\text{C}(\text{Fc})\text{H}$ ), 135.3 ( $=\text{C}-\text{CH}_3$ ). Found: C, 51.44; H, 3.93. Calc. for  $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{Fe}_2$ : C, 51.35; H, 3.97%.

Compound (6e), yield 0.3 g (45%), orange crystals, m.p. 144–146 °C; MS  $m/z$  (%): 670, (32)  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1622 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 1.26 (2H, s,  $\text{CH}_2$ ), 3.56 (2H, s,  $\text{C}_5\text{H}_4$ ), 3.62 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.12 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.24 (10H, s, 2 $\text{C}_5\text{H}_5$ ), 6.46 (1H, s,  $=\text{CH}$ ), 7.22 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 30.5 ( $\text{CH}_2$ ), 41.2 (CBr<sub>2</sub>), 57.1 (C–Fc), 65.9 ( $\text{C}_5\text{H}_4$ ), 66.1 ( $\text{C}_5\text{H}_4$ ), 66.1 ( $\text{C}_5\text{H}_4$ ), 67.5 ( $\text{C}_5\text{H}_5$ ), 67.9 ( $\text{C}_5\text{H}_5$ ), 84.1 ( $\text{C}_5\text{H}_4$  ipso), 87.1 ( $\text{C}_5\text{H}_4$  ipso), 126.8 ( $=\text{C}(\text{Fc})\text{H}$ ), 127.3 (Ph), 127.8: (Ph), 131.2 (Ph), 136.6 ( $\text{Ph}_{\text{ipso}}$ ), 136.7 ( $=\text{C}-\text{Ph}$ ). Found: C, 55.43; H, 3.93. Calc. for:  $\text{C}_{31}\text{H}_{26}\text{Br}_2\text{Fe}_2$ : C, 55.55; H, 3.91%.

Compound (6f), yield 1.8 mg (43%), yellow crystals, m.p. 147–149 °C; MS  $m/z$  (%): 608 (29), 528 (22), 446 (19), 326 (100).  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1636 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 1.49 (2H, m,  $\text{CH}_2$ ), 2.16 (3H, s,  $\text{CH}_3$ ), 4.13 (2H, m,  $\text{C}_5\text{H}_4$ ), 4.16 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.19 (5H, s,  $\text{C}_5\text{H}_5$ ) 4.29 (2H, m,  $\text{C}_5\text{H}_4$ ), 4.47 (2H, m,  $\text{C}_5\text{H}_4$ ), 5.96 (1H, s,  $=\text{CH}$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 18.7 ( $\text{CH}_3$ ), 34.6 (CBr<sub>2</sub>), 35.1 ( $\text{CH}_2$ ), 46.8 (C–Fc), 65.1 ( $\text{C}_5\text{H}_4$ ), 65.5 ( $\text{C}_5\text{H}_4$ ) 68.4 ( $\text{C}_5\text{H}_5$ ), 68.7 ( $\text{C}_5\text{H}_5$ ), 87.41 ( $\text{C}_5\text{H}_4$  ipso), 122.6 ( $=\text{CH}$ ), 130.92 ( $=\text{C}-\text{CH}_3$ ). Found: C, 46.56; H, 3.63. Calc. for  $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{Fe}_2$ : C, 46.59; H, 3.60%.

Compound (6g), yield 0.37 g (67%), orange crystals, m.p. 147–148 °C; MS  $m/z$  (%): 562 (100).  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1631 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 2.10 (2H, m,  $\text{CH}_2$ ), 4.19 (9H, s, Fc), 6.58 (1H, s,  $=\text{CH}$ ), 7.25 (10H, s, 2 Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 34.1 ( $\text{CH}_2$ ), 40.0 (C–Fc), 43.7 (CBr<sub>2</sub>), 70.8 (Fc), 86.8 ( $\text{C}_5\text{H}_4$  ipso), 127.2 ( $=\text{CH}$ ), 127.9 (Ph), 128.3 (Ph), 129.7 (Ph), 130.0 (Ph), 139.8 ( $\text{Ph}_{\text{ipso}}$ ), 141.0 ( $=\text{C}-\text{Ph}$ ). Found: C, 57.66; H, 3.93. Calc. for  $\text{C}_{27}\text{H}_{22}\text{Br}_2\text{Fe}_1$ : C, 57.68; H, 3.94%.

Compound (6h), yield 0.17 g (35%), yellow crystals, m.p. 90–91 °C; MS  $m/z$  (%): 500 (100).  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 1618 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 1.67 (3H, s,  $\text{CH}_3$ ), 1.9 (1H, d,  $J=6$  Hz,  $\text{CH}_2$ ), 2.55 (1H, d,  $J=9$  Hz,  $\text{CH}_2$ ), 4.34 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.62 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.84 (2H, s,  $\text{C}_5\text{H}_4$ ), 6.04 (1H, s,  $=\text{CH}$ ), 7.23 (5H, m, Ar);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ): 16.5 ( $\text{CH}_3$ ), 34.7 ( $\text{CH}_2$ ), 37.4 (CBr<sub>2</sub>), 37.8 (C–Ph), 67.1 ( $\text{C}_5\text{H}_4$ ), 70.1 ( $\text{C}_5\text{H}_4$ ), 71.9 ( $\text{C}_5\text{H}_5$ ), 89.8 ( $\text{C}_5\text{H}_4$  ipso), 125.3 ( $=\text{CH}$ ), 127.0 (Ph), 128.2 (Ph), 128.6 (Ph), 137.0 ( $\text{Ph}_{\text{ipso}}$ ), 141.4 ( $=\text{C}-\text{CH}_3$ ). Found: C, 52.80; H, 3.98. Calc. for  $\text{C}_{22}\text{H}_{20}\text{Br}_2\text{Fe}$ : C, 52.83; H, 4.03%.

Compound (6i), yield 0.36 g (73%), yellow crystals, m.p. 97–98 °C; MS  $m/z$  (%): 500 (100).  $\nu_{\max}$  (KBr)/

cm<sup>-1</sup>: 1620 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 2.07 (3H, s, CH<sub>3</sub>), 2.2 (1H, s, CH<sub>2</sub>), 2.37 (1H, s, CH<sub>2</sub>), 4.13 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.26 (2H, s, C<sub>5</sub>H<sub>4</sub>), 4.38 (2H, s, C<sub>5</sub>H<sub>4</sub>), 6.26 (1H, s, =CH), 7.25 (5H, m, Ar);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 17.4 (CH<sub>3</sub>), 34.4 (CBr<sub>2</sub>), 35.4 (CH<sub>2</sub>), 48.6 (C-Ph), 69.1 (C<sub>5</sub>H<sub>4</sub>), 69.4 (C<sub>5</sub>H<sub>5</sub>), 69.9 (C<sub>5</sub>H<sub>4</sub>), 88.8 (C<sub>5</sub>H<sub>4</sub>ipso), 126.0 (=CH), 126.7 (Ph), 127.2 (Ph), 128.0 (Ph), 134.9 (Ph<sub>ipso</sub>), 140.9 (=C-CH<sub>3</sub>). Found: C, 52.80; H, 3.98. Calc. for C<sub>22</sub>H<sub>20</sub>Br<sub>2</sub>Fe: C, 52.83; H, 4.03%.

#### 3.4. General procedure for the obtaining of the mono-bromo(ferrocenyl)cyclopropanes (7d,g-i)

1 mmol of the dibromo(ferrocenyl)cyclopropane (6d-i) was added to a solution of 1.2 mmol of ethyl magnesium bromide in dry THF and some drops of titanium isopropoxide. The mixture was stirred in an inert atmosphere for 3 h at room temperature, and quenched by addition of water (100 ml). The organic layer was separated, washed with water (2×20 ml) and benzene was evaporated in vacuo. The residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (hexane-ethyl acetate, 3:1) to give the compounds Z-,E-7d,g-i.

Z-,E-Compound (7d) (3:1), yield 0.39 g (75 %), yellow oil; MS *m/z* (%): 528 (100).  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup>: 1444;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 1.62 (1H, t, *J*=4.8 Hz, CH<sub>2</sub>), 1.76 (1H, t, *J*=4.8 Hz, CH<sub>2</sub>), 2.06 (3H, s, CH<sub>3</sub>), 3.26 (1H, dd, *J*=3.0, 4.5 Hz, CH<sub>2</sub>), 4.07 (2H, m, C<sub>5</sub>H<sub>4</sub>), 4.14 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.15 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.19 (2H, m, C<sub>5</sub>H<sub>4</sub>), 4.24 (2H, m, C<sub>5</sub>H<sub>4</sub>), 4.36 (5H, s, C<sub>5</sub>H<sub>4</sub>), 6.21 (1H, s, =CH);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 18.8 (CH<sub>3</sub>), 28.8 (CH<sub>2</sub>), 32.4 (CHBr), 34.6 (C-Fc), 66.3 (C<sub>5</sub>H<sub>4</sub>), 66.9 (C<sub>5</sub>H<sub>4</sub>), 67.1 (C<sub>5</sub>H<sub>4</sub>), 67.3 (C<sub>5</sub>H<sub>4</sub>), 68.2 (C<sub>5</sub>H<sub>4</sub>), 68.5 (C<sub>5</sub>H<sub>5</sub>), 68.8 (C<sub>5</sub>H<sub>5</sub>), 68.9 (C<sub>5</sub>H<sub>4</sub>), 69.3 (C<sub>5</sub>H<sub>4</sub>), 82.0 (C<sub>5</sub>H<sub>4</sub>ipso), 90.0 (C<sub>5</sub>H<sub>4</sub>ipso), 126.1 (=C(Fc)H), 135.5 (=C-CH<sub>3</sub>). Found: C, 58.89; H, 4.98. Calc. for C<sub>26</sub>H<sub>25</sub>BrFe<sub>2</sub>: C, 59.00; H, 4.76%.

Z-,E-Compound (7g) (3:1), yield 0.09 g (20%), yellow oil; MS *m/z* (%): 484 (40), 432 (40), 403 (68), 337 (100).  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 1446;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 1.48 (1H, d, *J*=5.2 Hz, CH<sub>2</sub>), 2.21 (1H, d, *J*=5.2 Hz, CH<sub>2</sub>), 3.54 (1H, dd, *J*=3.19, 5.2 Hz, CHBr), 4.04 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.31 (4H, m, C<sub>5</sub>H<sub>4</sub>), 6.02 (1H, s, =CH), 7.25 (10H, m, 2Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 23.3 (CH<sub>2</sub>), 29.4 (CHBr), 40.0 (C-Fc), 68.6 (C<sub>5</sub>H<sub>4</sub>), 68.9 (C<sub>5</sub>H<sub>4</sub>), 70.0 (C<sub>5</sub>H<sub>5</sub>), 70.3 (C<sub>5</sub>H<sub>4</sub>), 71.1 (C<sub>5</sub>H<sub>4</sub>), 82.2 (C<sub>5</sub>H<sub>4</sub>ipso), 124.1 (Ph), 124.5 (Ph), 126.0 (Ph), 126.6 (=CH), 126.8 (Ph), 127.9 (Ph), 128.0 (Ph), 128.2 (Ph), 128.3 (Ph), 128.6 (Ph), 129.9 (Ph), 138.8 (Ph<sub>ipso</sub>), 140.3 (Ph<sub>ipso</sub>), 143.5 (=C-Ph). Found: C, 67.15; H, 4.67. Calc. for C<sub>27</sub>H<sub>23</sub>BrFe<sub>1</sub>: C, 67.09; H, 4.79%.

Z-,E-Compound (7h) (3:1), yield 0.16 g (40%), yellow oil; MS *m/z* (%): 422 (35), 341 (100).  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup>: 1444;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 1.52 (1H, *J*=6.9 Hz, CH<sub>2</sub>), 1.68 (1H, t, *J*=6.9 Hz, CH<sub>2</sub>), 3.53 (1H, dd, *J*=4.2, 6.9 Hz, CHBr), 4.15 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.18 (2H, s,

C<sub>5</sub>H<sub>4</sub>), 4.38 (2H, m, C<sub>5</sub>H<sub>4</sub>), 6.32 (1H, s, =CH), 7.19 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 17.8 (CH<sub>3</sub>), 24.1 (CH<sub>2</sub>), 26.7 (CHBr), 40.4 (C-Ph), 68.6 (C<sub>5</sub>H<sub>4</sub>), 68.8 (C<sub>5</sub>H<sub>4</sub>), 69.1 (C<sub>5</sub>H<sub>5</sub>), 69.1 (C<sub>5</sub>H<sub>4</sub>), 69.7 (C<sub>5</sub>H<sub>4</sub>), 82.7 (C<sub>5</sub>H<sub>4</sub>ipso), 126.6 (=CH), 126.6 (Ph), 127.9 (Ph), 128.0 (Ph), 128.3 (Ph), 134.2 (Ph<sub>ipso</sub>), 142.4 (=C-CH<sub>3</sub>). Found: C, 62.65; H, 5.07. Calc. for C<sub>22</sub>H<sub>21</sub>BrFe: C, 62.61; H, 5.01%.

E-Compound (7i), yield 0.05 g (13%), orange crystals, m.p. 95–96 °C; MS *m/z* (%): 422 (40), 341 (100).  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 1448;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 1.73 (1H, dd, *J*=1.4, 6.3 Hz, CH<sub>2</sub>), 1.93 (1H, dd, *J*=1.4, 6.3 Hz, CH<sub>2</sub>), 1.98 (3H, s, CH<sub>3</sub>), 3.59 (1H, dd, *J*=1.4, 6.3 Hz, CHBr), 4.22 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.30 (2H, s, C<sub>5</sub>H<sub>4</sub>), 4.46 (2H, m, C<sub>5</sub>H<sub>4</sub>), 6.37 (1H, s, =CH), 7.27 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 17.8 (CH<sub>3</sub>), 24.1 (CH<sub>2</sub>), 26.7 (CHBr), 40.4 (C-Ph), 68.9 (C<sub>5</sub>H<sub>4</sub>), 69.2 (C<sub>5</sub>H<sub>5</sub>), 69.1 (C<sub>5</sub>H<sub>4</sub>), 69.8 (C<sub>5</sub>H<sub>4</sub>), 82.9 (C<sub>5</sub>H<sub>4</sub>ipso), 126.1 (=CH), 126.6 (Ph), 127.9 (Ph), 128.0 (Ph), 134.3 (Ph<sub>ipso</sub>), 142.5 (CH<sub>3</sub>). Found: C, 62.62; H, 5.01. Calc. for C<sub>22</sub>H<sub>21</sub>BrFe: C, 62.61; H, 5.01%.

Z-Compound (7i), yield 0.03 g (9%), red crystals, m.p. 93–95 °C; MS *m/z* (%): 422 (40), 341 (100).  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 1446;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 1.48 (1H, dd, *J*=1.4, 6.3 Hz, CH<sub>2</sub>), 1.93 (1H, dd, *J*=1.4, 6.3 Hz, CH<sub>2</sub>), 1.98 (3H, s, CH<sub>3</sub>), 3.59 (1H, dd, *J*=1.4, 6.3 Hz, CHBr), 4.24 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.32 (2H, s, C<sub>5</sub>H<sub>4</sub>), 4.48 (2H, m, C<sub>5</sub>H<sub>4</sub>), 6.42 (1H, s, =CH), 7.27 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>): 17.8 (CH<sub>3</sub>), 24.1 (CH<sub>2</sub>), 26.7 (CHBr), 40.4 (C-Ph), 68.9 (C<sub>5</sub>H<sub>4</sub>), 69.2 (C<sub>5</sub>H<sub>5</sub>), 69.2 (C<sub>5</sub>H<sub>4</sub>), 69.8 (C<sub>5</sub>H<sub>4</sub>), 82.8 (C<sub>5</sub>H<sub>4</sub>ipso), 126.1 (=CH), 126.6 (Ph), 127.9 (Ph), 128.1 (Ph), 134.3 (Ph<sub>ipso</sub>), 142.5 (=C-CH<sub>3</sub>). Found: C, 62.62; H, 5.01. Calc. for C<sub>22</sub>H<sub>21</sub>BrFe: C, 62.61; H, 5.01%.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 229832 for compound 5a, No. 229833 for compound 5b, No. 229834 for compound 6g, No. 232399 for compound 6h, and No. 229835 for compound 7i(E). Copies of this information may be obtained free of charge from The Director, CCDC 12 Union Road Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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