Electronic Supplementary Information

Stereoselective synthesis of amino-substituted cyclopentafullerenes promoted by magnesium perchlorate/ferric perchlorate

Wan Ma,‡a Kun Wang,‡a Cheng Huang,‡a Hui-Juan Wang,b Fa-Bao Li,*a Rui Sun,a Li Liu,a Chao-Yang Liu,*b and Abdullah M. Asiri*c

a Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei Key Laboratory of Polymer Materials, Key Laboratory of Green Preparation and Application for Functional Materials, Ministry of Education, and School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, People’s Republic of China

E-mail: lfb0615@hubu.edu.cn

b State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Center for Magnetic Resonance, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, People’s Republic of China

E-mail: chyliu@wipm.ac.cn

c Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

‡These authors contributed equally to this work.
Optimization of reaction conditions for arylamines/secondary amines S4-S6
NOESY spectra of trans/cis-3ad and trans/cis-3ba S7-S8
1H NMR spectra for reaction mixture S9
Experimental details and spectra data S10-S33
Typical MALDI-TOF MS of cyclopentafulerenes S34-S35
Typical UV-vis spectra of cyclopentafulerenes S36
1H NMR spectrum of compound trans-3aa S37
13C NMR spectrum of compound trans-3aa S37-S38
1H NMR spectrum of compound cis-3aa S38
13C NMR spectrum of compound cis-3aa S39
1H NMR spectrum of compound trans-3ab S40
13C NMR spectrum of compound trans-3ab S40-S41
1H NMR spectrum of compound cis-3ab S41
13C NMR spectrum of compound cis-3ab S42
1H NMR spectrum of compound trans/cis-3ac S43
NOESY spectrum of trans/cis-3ac S43
13C NMR spectrum of compound trans/cis-3ac S44
1H NMR spectrum of compound trans-3ad S45
13C NMR spectrum of compound trans-3ad S45-S46
1H NMR spectrum of compound cis-3ad S46
13C NMR spectrum of compound cis-3ad S47
1H NMR spectrum of compound trans-3ae S48
13C NMR spectrum of compound trans-3ae S48-S49
1H NMR spectrum of compound cis-3ae S49
13C NMR spectrum of compound cis-3ae S50
1H NMR spectrum of compound trans-3af S51
13C NMR spectrum of compound trans-3af S51-S52
1H NMR spectrum of compound cis-3af S52
13C NMR spectrum of compound cis-3af S53
1H NMR spectrum of compound trans-3ba S54
13C NMR spectrum of compound trans-3ba S54-S55
1H NMR spectrum of compound cis-3ba S55
13C NMR spectrum of compound cis-3ba S56
1H NMR spectrum of compound trans-3ca S57
13C NMR spectrum of compound trans-3ca S57-S58
1H NMR spectrum of compound cis-3ca S58
13C NMR spectrum of compound cis-3ca S59
1H NMR spectrum of compound trans/cis-3da S60
13C NMR spectrum of compound trans/cis-3da S60-S61
1H NMR spectrum of compound cis-5aa S61
13C NMR spectrum of compound cis-5aa S62
1H NMR spectrum of compound cis-5ab S63
13C NMR spectrum of compound cis-5ab S63-S64
H NMR spectrum of compound cis-5ac
13C NMR spectrum of compound cis-5ac
H NMR spectrum of compound cis-5ad
13C NMR spectrum of compound cis-5ad
H NMR spectrum of compound cis-5ae
13C NMR spectrum of compound cis-5ae
H NMR spectrum of compound cis-5af
13C NMR spectrum of compound cis-5af
H NMR spectrum of compound cis-5ag
13C NMR spectrum of compound cis-5ag
H NMR spectrum of compound cis-5ba
13C NMR spectrum of compound cis-5ba
H NMR spectrum of compound cis-5ca
13C NMR spectrum of compound cis-5ca
H NMR spectrum of compound trans-6aa
13C NMR spectrum of compound trans-6aa
H NMR spectrum of compound trans-6ad
13C NMR spectrum of compound trans-6ad
H NMR spectrum of compound trans-6ae
13C NMR spectrum of compound trans-6ae
H NMR spectrum of compound cis-7
13C NMR spectrum of compound cis-7
H NMR spectrum of compound cis/trans-ortho-8
13C NMR spectrum of compound cis/trans-ortho-8
NOESY spectrum of cis/trans-ortho-8

S3
Optimization of reaction conditions for arylamines/secondary amines

Table S1 Optimization of reaction conditions for the reaction of C\textsubscript{60} with cinnamaldehyde 1a and aniline 2a\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Molar ratio\textsuperscript{b}</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Yield (%) of cis-3aa\textsuperscript{c}</th>
<th>Yield (%) of trans-3aa\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:5:5:1</td>
<td>180</td>
<td>120</td>
<td>15 (68)</td>
<td>6 (27)</td>
</tr>
<tr>
<td>2</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:10:1</td>
<td>180</td>
<td>60</td>
<td>16 (52)</td>
<td>13 (42)</td>
</tr>
<tr>
<td>3</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:20:20:1</td>
<td>180</td>
<td>40</td>
<td>12 (50)</td>
<td>11 (46)</td>
</tr>
<tr>
<td>4</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:10:3</td>
<td>180</td>
<td>30</td>
<td>22 (54)</td>
<td>18 (44)</td>
</tr>
<tr>
<td>5</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:10:4</td>
<td>180</td>
<td>60</td>
<td>33 (75)</td>
<td>10 (23)</td>
</tr>
<tr>
<td>6</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:10:5</td>
<td>180</td>
<td>40</td>
<td>26 (74)</td>
<td>8 (23)</td>
</tr>
<tr>
<td>7</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:15:10:4</td>
<td>180</td>
<td>40</td>
<td>27 (59)</td>
<td>16 (35)</td>
</tr>
<tr>
<td>8</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:5:10:4</td>
<td>180</td>
<td>120</td>
<td>2 (20)</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:15:4</td>
<td>180</td>
<td>30</td>
<td>22 (56)</td>
<td>15 (38)</td>
</tr>
<tr>
<td>10</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:5:4</td>
<td>180</td>
<td>60</td>
<td>11 (61)</td>
<td>4 (22)</td>
</tr>
<tr>
<td>11</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:10:4</td>
<td>160</td>
<td>70</td>
<td>20 (67)</td>
<td>9 (30)</td>
</tr>
<tr>
<td>12\textsuperscript{d}</td>
<td>Mg(ClO\textsubscript{4})\textsubscript{2}</td>
<td>1:10:10:4</td>
<td>180</td>
<td>90</td>
<td>32 (78)</td>
<td>8 (20)</td>
</tr>
<tr>
<td>13</td>
<td>AlCl\textsubscript{3}</td>
<td>1:10:10:4</td>
<td>180</td>
<td>60</td>
<td>8 (36)</td>
<td>3 (14)</td>
</tr>
<tr>
<td>14</td>
<td>Fe(ClO\textsubscript{4})\textsubscript{3}·xH\textsubscript{2}O</td>
<td>1:10:10:4</td>
<td>180</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>Mn(OAc)\textsubscript{3}·2H\textsubscript{2}O</td>
<td>1:10:10:4</td>
<td>180</td>
<td>150</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>CuCl\textsubscript{2}</td>
<td>1:10:10:4</td>
<td>180</td>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>Cu(OAc)\textsubscript{2}</td>
<td>1:10:10:4</td>
<td>180</td>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Unless otherwise indicated, all reactions were performed in o-dichlorobenzene (ODCB) under air conditions. \textsuperscript{b}Molar ratio refers to C\textsubscript{60}/1a/2a/additive. \textsuperscript{c}Isolated yield; those in parentheses were based on consumed C\textsubscript{60}. \textsuperscript{d}The reaction was conducted under nitrogen atmosphere.
Table S2 Optimization of reaction conditions for the reaction of C₆₀ with cinnamaldehyde 1a and diethylamine 4a

![Reaction Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Molar ratio</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Yield (%) of cis-5aa</th>
<th>Yield (%) of trans-6aa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg(ClO₄)₂</td>
<td>1:10:10:4:0</td>
<td>100</td>
<td>90</td>
<td>18 (58)</td>
<td>12 (39)</td>
</tr>
<tr>
<td>2</td>
<td>Mg(ClO₄)₂</td>
<td>1:10:10:2:0</td>
<td>100</td>
<td>90</td>
<td>29 (55)</td>
<td>22 (42)</td>
</tr>
<tr>
<td>3</td>
<td>Mg(ClO₄)₂</td>
<td>1:10:10:1:0</td>
<td>100</td>
<td>90</td>
<td>36 (55)</td>
<td>25 (38)</td>
</tr>
<tr>
<td>4</td>
<td>Mg(ClO₄)₂</td>
<td>1:10:10:0.5:0</td>
<td>100</td>
<td>60</td>
<td>37 (63)</td>
<td>20 (34)</td>
</tr>
<tr>
<td>5</td>
<td>Mg(ClO₄)₂</td>
<td>1:10:10:0.2:0</td>
<td>100</td>
<td>60</td>
<td>18 (40)</td>
<td>26 (58)</td>
</tr>
<tr>
<td>6</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:10:0.5:0.5</td>
<td>100</td>
<td>50</td>
<td>28 (53)</td>
<td>14 (26)</td>
</tr>
<tr>
<td>7</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:15:0.5:0.5</td>
<td>100</td>
<td>50</td>
<td>40 (59)</td>
<td>17 (25)</td>
</tr>
<tr>
<td>8</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.5:0.5</td>
<td>100</td>
<td>35</td>
<td>40 (70)</td>
<td>7 (12)</td>
</tr>
<tr>
<td>9</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:25:0.5:0.5</td>
<td>100</td>
<td>30</td>
<td>38 (72)</td>
<td>7 (13)</td>
</tr>
<tr>
<td>10</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:15:20:0.5:0.5</td>
<td>100</td>
<td>35</td>
<td>35 (81)</td>
<td>6 (14)</td>
</tr>
<tr>
<td>11</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:15:20:0.5:0.2</td>
<td>100</td>
<td>15</td>
<td>31 (45)</td>
<td>18 (26)</td>
</tr>
<tr>
<td>12</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.5:0.5</td>
<td>100</td>
<td>20</td>
<td>32 (41)</td>
<td>12 (15)</td>
</tr>
<tr>
<td>13</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.5:0.1</td>
<td>100</td>
<td>40</td>
<td>40 (69)</td>
<td>9 (16)</td>
</tr>
<tr>
<td>14</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td><strong>1:10:20:0.5:0.5</strong></td>
<td>80</td>
<td>60</td>
<td>40 (80)</td>
<td>8 (16)</td>
</tr>
<tr>
<td>15</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.5:0.5</td>
<td>60</td>
<td>110</td>
<td>15 (79)</td>
<td>trace</td>
</tr>
<tr>
<td>16</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.5:0.5</td>
<td>80</td>
<td>60</td>
<td>39 (78)</td>
<td>8 (16)</td>
</tr>
<tr>
<td>17</td>
<td>Mg(ClO₄)₂</td>
<td>1:10:20:0.5:0.5</td>
<td>80</td>
<td>40</td>
<td>25 (76)</td>
<td>4 (12)</td>
</tr>
<tr>
<td>18</td>
<td>Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.0:0.5</td>
<td>80</td>
<td>60</td>
<td>29 (35)</td>
<td>21 (25)</td>
</tr>
<tr>
<td>19</td>
<td>Mg(ClO₄)₂/CuCl₂</td>
<td>1:10:20:0.5:0.5</td>
<td>80</td>
<td>60</td>
<td>18 (50)</td>
<td>10 (28)</td>
</tr>
<tr>
<td>20</td>
<td>Mg(ClO₄)₂/CuCl₂·H₂O</td>
<td>1:10:20:0.5:0.5</td>
<td>80</td>
<td>45</td>
<td>20 (65)</td>
<td>8 (26)</td>
</tr>
<tr>
<td>21</td>
<td>Mg(ClO₄)₂/DMAP</td>
<td>1:10:20:0.5:0.5</td>
<td>80</td>
<td>70</td>
<td>30 (51)</td>
<td>11 (19)</td>
</tr>
<tr>
<td>22</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.5:0.5</td>
<td>80</td>
<td>60</td>
<td>39 (80)</td>
<td>5 (10)</td>
</tr>
<tr>
<td>23</td>
<td>Mg(ClO₄)₂/Fe(ClO₄)₃·xH₂O</td>
<td>1:10:20:0.5:0.5</td>
<td>80</td>
<td>60</td>
<td>22 (71)</td>
<td>6 (19)</td>
</tr>
</tbody>
</table>

*Unless otherwise indicated, all reactions were performed in chlorobenzene under air conditions. "Molar ratio refers to C₆₀/1a/4a/Mg(ClO₄)₂/other additive. Isolated yield; those in parentheses were based on consumed C₆₀. The reaction was conducted under nitrogen atmosphere. The reaction was carried out in o-dichlorobenzene (10 mL)."
The reaction was conducted in toluene (10 mL).
Figure S1. NOESY (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of trans-3ad.

Figure S2. NOESY (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of cis-3ad, and the nuclear Overhauser effect between the two methine protons is indicated by the curved arrow.
Figure S3. NOESY (500 MHz, CS₂/DMSO-d₆) spectrum of trans-3ba.

Figure S4. NOESY (500 MHz, CS₂/DMSO-d₆) spectrum of cis-3ba, and the nuclear Overhauser effect between the two methine protons is indicated by the curved arrow.
Figure S5. (a) $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of the reaction mixture of C$_{60}$, cinnamaldehyde (1a), aniline (2a), and Mg(ClO$_4$)$_2$ for 1 h under the optimized conditions. (b) $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of the reaction mixture of C$_{60}$, cinnamaldehyde (1a), aniline (2a), and Mg(ClO$_4$)$_2$ for 0 h under the optimized conditions.
Experimental details and spectra data

General procedure for the synthesis of amino-substituted cyclopentafullerenes

3. C_{60} (36.0 mg, 0.05 mmol), cinnamaldehydes 1 (0.50 mmol), arylamines 2 (0.50 mmol) and Mg(ClO_4)_2 (44.7 mg, 0.20 mmol) were added to a 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. After they were completely dissolved in 6 mL of o-dichlorobenzene by sonication, the resulting solution was put into an oil bath preset at 180 °C and stirred under air conditions. Thin-layer chromatography (TLC) was employed to carefully monitor the reaction and to stop the reaction at the designated time. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent evaporation in vacuo was completed, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to afford first unreacted C_{60} and then amino-substituted cyclopentafullerenes 3.

Cyclopentafullerenes trans-3aa and cis-3aa: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 2a (46 μL, 0.50 mmol) and Mg(ClO_4)_2 (44.7 mg, 0.20 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 60 min afforded first unreacted C_{60} (20.1 mg, 56%) and then trans-3aa (4.7 mg, 10%, R_f = 0.68), cis-3aa (15.2 mg, 33%, R_f = 0.59) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. trans-3aa: ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.59 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.01 (t, J = 7.9 Hz, 2H), 6.92 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 8.5 Hz, 1H), 6.52 (t, J = 7.2 Hz, 1H), 5.73 (dd, J = 8.0, 5.3 Hz, 1H), 5.59 (dd, J = 14.4, 4.5 Hz, 1H), 3.80-3.73 (m, 1H), 2.92 (dd,
J = 12.7, 4.5 Hz, 1H); $^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) (all 1C unless indicated) 
$\delta$ 154.97, 154.26, 152.57, 152.53, 145.71, 145.60, 145.22 (2C), 145.08, 144.62, 144.30, 144.24, 144.22, 144.16, 144.09, 144.01 (2C), 143.98, 143.74, 143.61, 143.45, 143.37 (2C), 143.28 (5C), 143.10, 142.69, 142.55 (2C), 142.49, 141.12, 141.05, 140.75, 140.60, 140.52 (2C), 140.43, 140.28, 140.25, 140.23, 140.17, 140.10, 139.98 (3C), 139.80, 139.72, 139.63, 138.37, 137.68, 137.52, 137.45, 136.74, 135.81, 134.41, 134.14, 133.25, 127.79 (2C, aryl C), 127.56 (2C, aryl C), 127.04 (2C, aryl C), 126.10 (aryl C), 115.87 (aryl C), 111.84 (2C, aryl C), 76.15 (sp$^3$-C of C$_{60}$), 73.40 (sp$^3$-C of C$_{60}$), 63.50, 55.37, 35.15; FT-IR $\nu$/cm$^{-1}$ (KBr) 3395, 3042, 1599, 1498, 1456, 1426, 1313, 1251, 1183, 1152, 1077, 869, 783, 746, 694, 599, 570, 527; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$/nm 256, 310, 431; HRMS (ESI) $m/z$: [M]$^-$ Calcd for C$_{75}$H$_{15}$N 929.1205; Found 929.1183. *cis*-3aa: $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) $\delta$ 7.57 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.00-6.96 (m, 2H), 6.83 (d, J = 7.7 Hz, 2H), 6.49 (t, J = 7.3 Hz, 1H), 6.05 (dd, J = 9.8, 3.5 Hz, 1H), 5.84-5.79 (m, 1H), 4.98 (dd, J = 13.9, 4.4 Hz, 1H), 3.67-3.59 (m, 1H), 3.01-2.97 (m, 1H); $^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) (all 1C unless indicated) $\delta$ 154.76, 153.09, 152.94, 152.54, 145.85, 145.79, 145.55, 145.06 (2C), 145.04, 144.18, 144.09, 144.07, 143.97, 143.95, 143.91, 143.86 (3C), 143.66, 143.56, 143.30, 143.19, 143.16, 143.10, 142.99 (2C), 142.96 (2C), 142.55, 142.35, 142.29 (2C), 140.94, 140.84, 140.52, 140.48 (2C), 140.41 (2C), 140.22 (2C), 140.11, 140.00, 139.86, 139.84, 139.75, 139.63, 139.60 (2C), 139.38, 137.72, 137.53 (2C), 137.08, 135.68, 134.33, 134.22, 133.56, 132.62, 127.50 (4C, aryl C), 127.09 (2C, aryl C), 126.05 (aryl C), 115.58 (aryl C), 111.90 (2C,
aryl C), 74.07 (sp$^3$-C of C$_{60}$), 73.84 (sp$^3$-C of C$_{60}$), 64.54, 54.35, 34.58; FT-IR $\nu$/cm$^{-1}$ (KBr) 3399, 3028, 2881, 1599, 1500, 1456, 1428, 1317, 1252, 1226, 1185, 1150, 1070, 1015, 746, 693, 664, 571, 526; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$/nm 257, 311, 430; HRMS (MALDI-TOF) m/z: [M]$^-$ Calcd for C$_{75}$H$_{15}$N 929.1205; Found 929.1202.

**Cyclopentafullerenes trans-3ab and cis-3ab:** According to the general procedure, the reaction of C$_{60}$ (36.0 mg, 0.05 mmol) with 1a (63 $\mu$L, 0.50 mmol), 2b (61.6 mg, 0.50 mmol) and Mg(ClO$_4$)$_2$ (44.7 mg, 0.20 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 40 min afforded first unreacted C$_{60}$ (21.4 mg, 59%) and then trans-3ab (6.7 mg, 14%, $R_f = 0.68$), cis-3ab (10.5 mg, 22%, $R_f = 0.59$) as amorphous brown solid with CS$_2$/CH$_2$Cl$_2$ as eluent (V/V = 10/1): mp > 300 °C. **trans-3ab:** $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) $\delta$ 7.58 (d, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 6.9$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 6.87 (d, $J = 8.9$ Hz, 2H), 6.61 (d, $J = 8.9$ Hz, 2H), 6.35 (d, $J = 8.0$ Hz, 1H), 5.65 (dd, $J = 7.8$, 5.7 Hz, 1H), 5.57 (dd, $J = 14.3$, 4.4 Hz, 1H), 3.76-3.70 (m, 1H), 3.62 (s, 3H), 2.94-2.90 (m, 1H); $^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) (all 1C unless indicated) $\delta$ 154.96, 154.19, 152.60, 152.50, 149.97, 145.45, 145.11 (2C), 145.02, 144.54, 144.18, 144.12 (2C), 144.04, 143.98, 143.91 (2C), 143.86, 143.63, 143.51, 143.39, 143.27, 143.25, 143.18 (2C), 143.16, 143.14 (2C), 143.00, 142.58, 142.47, 142.45, 142.38, 141.00, 140.96, 140.66, 140.49, 140.42 (2C), 140.32, 140.19, 140.14, 140.12, 140.07, 139.99, 139.88 (2C), 139.84, 139.69, 139.62 (2C), 139.53, 138.26, 137.57, 137.41, 137.36, 136.65, 135.63, 134.34, 134.02, 133.08, 127.69 (2C, aryl C), 126.93 (2C, aryl C), 125.98 (aryl C), 113.05 (2C, aryl C), 113.03 (2C, aryl C), 75.96 (sp$^3$-C of C$_{60}$), 73.30 (sp$^3$-C of C$_{60}$), 64.34, 55.20, 53.89, 35.01; FT-IR $\nu$/cm$^{-1}$ (KBr) 3419,
Cyclopentafullerenes trans/cis-3ac: According to the general procedure, the reaction of C₆₀ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 2c (70 μL, 0.50 mmol) and Mg(ClO₄)₂ (44.7 mg, 0.20 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 30 min afforded first unreacted C₆₀ (29.8 mg, 83%) and then trans/cis-3ac (7.9 mg,
16%, \textit{trans/cis} = 1/5.6, R\textsubscript{f} = 0.66) as an amorphous brown solid with CS\textsubscript{2} as eluent: mp > 300 °C. \textit{cis-3ac}: \textsuperscript{1}H NMR (500 MHz, CS\textsubscript{2}/DMSO-d\textsubscript{6}) \(\delta\) 7.54 (d, \(J = 7.5\) Hz, 2H), 7.26 (t, \(J = 7.6\) Hz, 2H), 7.18 (t, \(J = 7.4\) Hz, 1H), 6.76 (s, 2H), 5.26-5.20 (m, 1H), 4.79 (dd, \(J = 13.7, 4.2\) Hz, 1H), 3.65 (d, \(J = 12.2\) Hz, 1H), 3.43 (q, \(J = 12.4\) Hz, 1H), 2.92-2.88 (m, 1H), 2.42 (s, 6H), 2.21 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CS\textsubscript{2}/DMSO-d\textsubscript{6}) (all 1C unless indicated) \(\delta\) 154.46, 153.65, 152.49, 150.94, 146.47, 145.66, 145.25, 145.21, 144.83, 144.43, 144.31 (2C), 144.25 (2C), 144.14, 144.10, 144.02, 143.98, 143.86, 143.73, 143.68, 143.40, 143.34 (3C), 143.21, 143.14 (2C), 142.62, 142.59, 142.54, 142.48, 141.14, 141.09, 140.75, 140.70, 140.67, 140.60, 140.51, 140.45, 140.36, 140.24 (3C), 140.08, 140.03, 139.89, 139.81 (2C), 139.70 (2C), 137.99, 137.75, 137.50, 137.39, 135.53, 135.30, 134.19, 133.43, 132.97 (aryl C), 130.02 (aryl C), 128.61 (2C, aryl C), 128.35 (2C, aryl C), 127.71 (2C, aryl C), 127.09 (2C, aryl C), 126.17 (aryl C), 73.80 (sp\textsuperscript{3}-C of C\textsubscript{60}), 73.10 (sp\textsuperscript{3}-C of C\textsubscript{60}), 68.70, 54.82, 36.51, 19.41, 17.78 (2C); FT-IR \(\nu/cm^{-1}\) (KBr) 3419, 3027, 2951, 2895, 1599, 1482, 1429, 1372, 1303, 1228, 1186, 1070, 1027, 906, 854, 762, 695, 667, 597, 571, 527; UV-vis (CHCl\textsubscript{3}) \(\lambda_{\text{max}}/nm\) 257, 310, 431; HRMS (MALDI-TOF) \(m/z\): [M]\textsuperscript{-} Calcd for C\textsubscript{78}H\textsubscript{21}N 971.1674; Found 971.1673.

\textbf{Cyclopentafullerenes trans-3ad and cis-3ad:} According to the general procedure, the reaction of C\textsubscript{60} (36.0 mg, 0.05 mmol) with 1\textsubscript{a} (63 \(\mu\)L, 0.50 mmol), 2d (53.6 mg, 0.50 mmol) and Mg(ClO\textsubscript{4})\textsubscript{2} (44.7 mg, 0.20 mmol) in \(o\)-dichlorobenzene (6 mL) at 180 °C for 60 min afforded first unreacted C\textsubscript{60} (22.3 mg, 62%) and then \textit{trans-3ad} (3.1 mg, 7%, R\textsubscript{f} = 0.47), \textit{cis-3ad} (13.1 mg, 28%, R\textsubscript{f} = 0.29) as amorphous brown solid with
CS\textsubscript{2} as eluent: mp > 300 °C. \textit{trans-3ad}: \textsuperscript{1}H NMR (500 MHz, CS\textsubscript{2}/DMSO-\textit{d}_6) \textit{\delta} 7.58 (d, \textit{J} = 7.2 Hz, 2H), 7.29 (t, \textit{J} = 7.6 Hz, 2H), 7.20 (t, \textit{J} = 7.4 Hz, 1H), 6.85 (d, \textit{J} = 8.5 Hz, 2H), 6.81 (d, \textit{J} = 8.5 Hz, 2H), 6.12-6.10 (m, 1H), 5.67 (dd, \textit{J} = 7.2, 5.3 Hz, 1H), 5.50 (dd, \textit{J} = 14.3, 4.5 Hz, 1H), 3.76-3.70 (m, 1H), 2.96 (dd, \textit{J} = 12.6, 4.6 Hz, 1H), 2.18 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CS\textsubscript{2}/DMSO-\textit{d}_6) (all 1C unless indicated) \textit{\delta} 155.02, 154.30, 152.67, 152.59, 145.63, 145.21 (2C), 145.10, 144.64, 144.29, 144.24, 144.22, 144.14, 144.08, 144.01 (2C), 143.97, 143.74, 143.62, 143.48, 143.42, 143.36 (2C), 143.29 (3C), 143.27, 143.25, 143.10, 142.69, 142.56 (2C), 142.48, 141.11, 141.05, 140.76, 140.59, 140.52 (2C), 140.43, 140.29, 140.25, 140.23, 140.18, 140.10, 139.98 (3C), 139.79, 139.72, 139.63, 138.36, 137.67, 137.51, 137.43, 136.76, 135.76, 134.42, 134.13, 133.21, 128.06 (2C, aryl C), 127.78 (2C, aryl C), 127.03 (2C, aryl C), 126.08 (aryl C), 123.98 (aryl C), 112.01 (2C, aryl C), 76.18 (sp\textsuperscript{3}-C of C\textsubscript{60}), 73.40 (sp\textsuperscript{3}-C of C\textsubscript{60}), 63.77, 55.35, 35.13, 19.24; FT-IR \textit{\nu}/cm\textsuperscript{-1} (KBr) 3396, 3019, 2948, 1617, 1516, 1456, 1383, 1303, 1249, 1185, 885, 807, 695, 670, 527; UV-vis (CHCl\textsubscript{3}) \textit{\lambda}_{max}/nm 257, 309, 431; HRMS (ESI) \textit{m/z}: [M]+ Calcd for C\textsubscript{76}H\textsubscript{17}N 943.1361; Found 943.1338. \textit{cis-3ad}: \textsuperscript{1}H NMR (500 MHz, CS\textsubscript{2}/DMSO-\textit{d}_6) \textit{\delta} 7.56 (d, \textit{J} = 7.4 Hz, 2H), 7.29 (t, \textit{J} = 7.6 Hz, 2H), 7.20 (t, \textit{J} = 7.4 Hz, 1H), 6.82 (d, \textit{J} = 8.4 Hz, 2H), 6.72 (d, \textit{J} = 8.4 Hz, 2H), 5.77-5.71 (m, 1H), 5.26 (d, \textit{J} = 9.9 Hz, 1H), 4.93 (dd, \textit{J} = 13.8, 4.4 Hz, 1H), 3.58-3.50 (m, 1H), 3.07-3.02 (m, 1H), 2.16 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CS\textsubscript{2}/DMSO-\textit{d}_6) (all 1C unless indicated) \textit{\delta} 154.64, 152.93, 152.73, 152.36, 145.70, 145.43, 144.89, 144.86, 144.84, 143.98, 143.87 (2C), 143.78, 143.74, 143.72, 143.66 (3C), 143.46, 143.37, 143.27, 143.10, 142.99, 142.97, 142.90, 142.81, 142.78, 142.76 (2C), 142.36,
142.17, 142.09 (2C), 140.74, 140.64, 140.33, 140.29 (2C), 140.22 (2C), 140.03 (2C), 139.92, 139.81, 139.68, 139.64, 139.42 (3C), 139.18, 137.53, 137.32, 137.31, 136.88, 135.50, 134.13, 134.03, 133.37, 132.37, 127.83 (2C, aryl C), 127.35 (2C, aryl C), 126.95 (2C, aryl C), 125.92 (aryl C), 123.52 (aryl C), 111.90 (2C, aryl C), 73.92 (sp\textsuperscript{3}-C of C\textsubscript{60}), 73.66 (sp\textsuperscript{3}-C of C\textsubscript{60}), 64.66, 54.18, 34.47, 18.97; FT-IR ν/cm\textsuperscript{-1} (KBr) 3413, 3024, 2908, 1614, 1515, 1455, 1426, 1356, 1295, 1249, 1223, 1185, 1141, 1011, 807, 761, 696, 666, 653, 571, 527; UV-vis (CHCl\textsubscript{3}) \(\lambda_{\text{max}}\)/nm 257, 310, 430; HRMS (ESI) \(m/z\): [M] - Calcd for C\textsubscript{76}H\textsubscript{17}N 943.1361; Found 943.1335.

**Cyclopentafullerenes trans-3ae and cis-3ae:** According to the general procedure, the reaction of C\textsubscript{60} (36.0 mg, 0.05 mmol) with \textbf{1a} (63 \(\mu\)L, 0.50 mmol), \textbf{2e} (63.8 mg, 0.50 mmol) and Mg(ClO\textsubscript{4})\textsubscript{2} (44.7 mg, 0.20 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 30 min afforded first unreacted C\textsubscript{60} (25.1 mg, 70%) and then trans-3ae (5.1 mg, 11%, \(R_f = 0.64\)), cis-3ae (6.3 mg, 13%, \(R_f = 0.45\)) as amorphous brown solid with CS\textsubscript{2} as eluent: mp > 300 °C. **trans-3ae:** \(^1\)H NMR (500 MHz, CS\textsubscript{2}/DMSO-\textsubscript{d\textsubscript{6}}) \(\delta\) 7.59 (d, \(J = 7.2\) Hz, 2H), 7.30 (t, \(J = 7.6\) Hz, 2H), 7.21 (t, \(J = 7.4\) Hz, 1H), 7.08 (d, \(J = 8.3\) Hz, 1H), 6.96 (d, \(J = 9.1\) Hz, 2H), 6.92 (d, \(J = 9.1\) Hz, 2H), 5.71 (dd, \(J = 8.0, 5.4\) Hz, 1H), 5.58 (dd, \(J = 14.4, 4.5\) Hz, 1H), 3.80-3.73 (m, 1H), 2.90 (dd, \(J = 12.5, 4.3\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CS\textsubscript{2}/DMSO-\textsubscript{d\textsubscript{6}}) (all 1C unless indicated) \(\delta\) 154.40, 153.75, 152.04, 151.99, 145.07, 144.83 (2C), 144.65, 144.17 (2C), 143.90, 143.85, 143.83, 143.77, 143.70, 143.62 (2C), 143.59, 143.33, 143.19, 142.98 (2C), 142.90 (4C), 142.85, 142.71 (2C), 142.28, 142.16 (2C), 142.09, 140.72, 140.67, 140.37, 140.21, 140.13 (2C), 140.03, 139.82 (3C), 139.75, 139.70, 139.58 (3C), 139.40, 139.33, 139.23,
137.98, 137.29, 137.12, 137.07, 136.25, 135.43, 134.01, 133.70, 132.90, 127.40 (2C, aryl C), 126.92 (2C, aryl C), 126.79 (2C, aryl C), 125.87 (aryl C), 119.40 (aryl C), 112.62 (2C, aryl C), 75.71 (sp$^3$-C of C$_{60}$), 72.96 (sp$^3$-C of C$_{60}$), 63.11, 54.95, 34.66; FT-IR ν/cm$^{-1}$ (KBr) 3395, 3023, 2898, 2361, 1598, 1495, 1457, 1384, 1311, 1182, 1094, 903, 813, 761, 697, 615, 528; UV-vis (CHCl$_3$) λ$_{max}$/nm 256, 311, 431; HRMS (ESI) m/z: [M]$^-$ Calcd for C$_{75}$H$_{14}$ClN 963.0815; Found 963.0753. cis-3ae: $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) δ 7.57 (d, $J = 7.4$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 7.3$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 6.52 (d, $J = 9.5$ Hz, 1H), 5.84-5.78 (m, 1H), 4.99 (dd, $J = 13.9$, 4.3 Hz, 1H), 3.62 (q, $J = 12.6$ Hz, 1H), 2.98-2.94 (m, 1H); $^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) (all 1C unless indicated) δ 154.68, 153.15, 152.99, 152.56, 145.81, 145.54, 145.19, 145.16 (2C), 144.77, 144.30, 144.21, 144.19, 144.06 (3C), 143.99 (2C), 143.96, 143.75, 143.65, 143.42, 143.31, 143.29, 143.23, 143.11 (4C), 142.66, 142.46, 142.42 (2C), 141.07, 140.97, 140.65, 140.61 (2C), 140.55, 140.47, 140.34, 140.33, 140.22, 140.13, 140.00, 139.96, 139.87, 139.73 (2C), 139.70, 139.50, 137.86, 137.68 (2C), 137.21, 135.75, 134.44, 134.29, 133.67, 132.84, 127.61 (2C, aryl C), 127.27 (2C, aryl C), 127.18 (2C, aryl C), 126.15 (aryl C), 119.48 (aryl C), 113.11 (2C, aryl C), 74.08 (sp$^3$-C of C$_{60}$), 73.95 (sp$^3$-C of C$_{60}$), 64.53, 54.38, 34.52; FT-IR ν/cm$^{-1}$ (KBr) 3402, 3057, 3024, 2954, 1597, 1494, 1457, 1426, 1401, 1313, 1249, 1182, 1137, 1093, 1068, 1009, 813, 781, 762, 695, 668, 597, 571, 527; UV-vis (CHCl$_3$) λ$_{max}$/nm 257, 313, 430; HRMS (ESI) m/z: [M]$^-$ Calcd for C$_{75}$H$_{14}$ClN 963.0815; Found 963.0748.
Cyclopentafullerenes trans-3af and cis-3af: According to the general procedure, the reaction of C$_{60}$ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 2f (86.0 mg, 0.50 mmol) and Mg(ClO$_4$)$_2$ (44.7 mg, 0.20 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 50 min afforded first unreacted C$_{60}$ (26.4 mg, 73%) and then trans-3af (4.4 mg, 9%, $R_f = 0.80$), cis-3af (6.2 mg, 12%, $R_f = 0.63$) as amorphous brown solid with CS$_2$ as eluent: mp > 300 °C. trans-3af: $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) $\delta$ 7.59 (d, $J = 7.4$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.12 (d, $J = 8.5$ Hz, 1H), 7.08 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.70 (dd, $J = 8.2, 5.4$ Hz, 1H), 5.58 (dd, $J = 14.4, 4.5$ Hz, 1H), 3.80-3.73 (m, 1H), 2.89 (dd, $J = 12.7, 4.5$ Hz, 1H); $^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) (all 1C unless indicated) $\delta$ 154.40, 153.77, 152.06, 151.98, 145.09, 144.85 (2C), 144.67, 144.60, 144.19, 143.93, 143.88, 143.85, 143.79, 143.72, 143.64 (2C), 143.61, 143.35, 143.21, 143.01 (2C), 142.93 (5C), 142.88, 142.74, 142.31, 142.19 (2C), 142.11, 140.75, 140.69, 140.39, 140.24, 140.16 (2C), 140.06, 139.84 (3C), 139.77, 139.73, 139.61 (3C), 139.43, 139.35, 139.25, 138.01, 137.31, 137.15, 137.10, 136.27, 135.46, 134.03, 133.72, 132.94, 129.78 (2C, aryl C), 127.42 (2C, aryl C), 126.82 (2C, aryl C), 125.90 (aryl C), 113.15 (2C, aryl C), 106.84 (aryl C), 75.73 (sp$^3$-C of C$_{60}$), 72.98 (sp$^3$-C of C$_{60}$), 63.03, 54.97, 34.66; FT-IR ν/cm$^{-1}$ (KBr) 3399, 3023, 2884, 2799, 1592, 1493, 1457, 1427, 1395, 1311, 1249, 1184, 1075, 929, 810, 763, 695, 570, 528; UV-vis (CHCl$_3$) $\lambda_{max}$/nm 257, 312, 431; HRMS (ESI) $m/z$: [M]$^+$ Calcd for C$_{75}$H$_{14}$BrN 1007.0310; Found 1007.0259. cis-3af: $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) $\delta$ 7.57 (d, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.05 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 6.57 (d, $J = 9.4$ Hz,
(1H), 5.83-5.78 (m, 1H), 4.99 (dd, \( J = 13.9 \), 4.2 Hz, 1H), 3.63 (q, \( J = 12.6 \) Hz, 1H), 3.10-2.93 (m, 1H); \(^{13}\)C NMR \((125 \text{ MHz, } \text{CS}_2/\text{DMSO-}d_6)\) (all 1C unless indicated) \( \delta \)

154.59, 153.08, 152.91, 152.50, 145.72, 145.46, 145.11 (2C), 145.09 (2C), 144.22, 144.11 (2C), 143.98 (3C), 143.91 (3C), 143.68, 143.58, 143.34, 143.23, 143.21, 143.16, 143.03 (4C), 142.59, 142.39, 142.34 (2C), 140.99, 140.90, 140.58, 140.53 (2C), 140.47, 140.39, 140.27, 140.25, 140.14, 140.05, 139.93, 139.88, 139.79, 139.66 (2C), 139.62, 139.43, 137.78, 137.62 (2C), 137.13, 135.68, 134.36, 134.22, 133.60, 132.78, 130.05 (2C, aryl C), 127.55 (2C, aryl C), 127.14 (2C, aryl C), 126.12 (aryl C), 113.56 (2C, aryl C), 106.75 (aryl C), 73.99 (sp\(^3\)-C of C\(_{60}\)), 73.87 (sp\(^3\)-C of C\(_{60}\)), 64.33, 54.29, 34.42; FT-IR ν/cm\(^{-1}\) (KBr) 3403, 3064, 3026, 2950, 2883, 1591, 1492, 1457, 1426, 1398, 1311, 1248, 1182, 1139, 1071, 1008, 810, 781, 761, 695, 653, 570, 526; UV-vis (CHCl\(_3\)) \( \lambda_{\text{max}}/\text{nm} \) 257, 312, 430; HRMS (ESI) \( m/z \): [M]\(^{-}\) Calcd for C\(_{75}\)H\(_{14}\)BrN 1007.0310; Found 1007.0251.

**Cyclopentafullerenes trans-3ba and cis-3ba:** According to the general procedure, the reaction of C\(_{60}\) (36.0 mg, 0.05 mmol) with 1b (88.1 mg, 0.50 mmol), 2a (46 μL, 0.50 mmol) and Mg(ClO\(_4\))\(_2\) (44.7 mg, 0.20 mmol) in \( o \)-dichlorobenzene (6 mL) at 180 °C for 40 min afforded first unreacted C\(_{60}\) (25.2 mg, 70%) and then trans-3ba (4.6 mg, 10%, \( R_f = 0.77 \)), cis-3ba (7.8 mg, 16%, \( R_f = 0.67 \)) as amorphous brown solid with \text{CS}_2/\text{CH}_2\text{Cl}_2 as eluent \( (V/V = 10/1) \): mp > 300 °C. trans-3ba: \(^1\)H NMR \((500 \text{ MHz, } \text{CS}_2/\text{DMSO-}d_6)\) \( \delta \)

7.49 (d, \( J = 8.6 \) Hz, 2H), 7.01 (t, \( J = 7.7 \) Hz, 2H), 6.91 (d, \( J = 8.2 \) Hz, 2H), 6.80 (d, \( J = 8.2 \) Hz, 2H), 6.75 (d, \( J = 8.0 \) Hz, 1H), 6.52 (t, \( J = 7.2 \) Hz, 1H), 5.72-5.70 (m, 1H), 5.54 (dd, \( J = 14.3 \), 4.3 Hz, 1H), 3.74-3.68 (m, 1H), 3.71 (s, 3H), 2.88
(dd, \( J = 12.6, 4.3 \) Hz, 1H); \(^{13}\)C NMR (125 MHz, CS\(_2\)/DMSO-\(d_6\)) (all 1C unless indicated) \( \delta \) 156.77 (aryl C), 154.88, 154.28, 152.58, 152.40, 145.52, 145.42, 144.98 (2C), 144.89, 144.59, 144.06, 143.99 (2C), 143.92, 143.85, 143.77 (2C), 143.73, 143.52, 143.39, 143.23, 143.12, 143.03 (6C), 142.86, 142.46, 142.33 (2C), 142.28, 140.88, 140.81, 140.52, 140.36, 140.28 (2C), 140.20, 140.06, 140.03, 139.98 (2C), 139.87, 139.76 (2C), 139.72, 139.56, 139.53, 139.41, 138.11, 137.51, 137.36, 137.18, 135.59, 134.11, 133.85, 133.04, 128.49 (2C, aryl C), 128.30 (aryl C), 127.36 (2C, aryl C), 115.63 (aryl C), 112.24 (2C, aryl C), 111.60 (2C, aryl C), 75.89 (sp\(^3\)-C of C\(_{60}\)), 73.41 (sp\(^3\)-C of C\(_{60}\)), 63.21, 54.53, 53.83, 35.23; FT-IR \( \nu/cm^{-1} \) (KBr) 3395, 2922, 2851, 1601, 1507, 1461, 1427, 1311, 1251, 1180, 1149, 1034, 829, 746, 690, 666, 570, 527; UV-vis (CHCl\(_3\)) \( \lambda_{\text{max}}/\text{nm} \) 257, 308, 431; HRMS (ESI) \( m/z \): [M]\(^{-}\) Calcd for C\(_{76}\)H\(_{17}\)NO 959.1310; Found 959.1257. \textit{cis-3ba}: \(^{1}\)H NMR (500 MHz, CS\(_2\)/DMSO-\(d_6\)) \( \delta \) 7.47 (d, \( J = 8.6 \) Hz, 2H), 6.97 (t, \( J = 7.8 \) Hz, 2H), 6.83-6.79 (m, 4H), 6.47 (t, \( J = 7.3 \) Hz, 1H), 6.15 (d, \( J = 9.3 \) Hz, 1H), 5.83-5.78 (m, 1H), 4.93 (dd, \( J = 13.8, 4.4 \) Hz, 1H), 3.71 (s, 3H), 3.58 (q, \( J = 12.6 \) Hz, 1H), 2.96-2.92 (m, 1H); \(^{13}\)C NMR (125 MHz, CS\(_2\)/DMSO-\(d_6\)) (all 1C unless indicated) \( \delta \) 156.63 (aryl C), 154.52, 153.10, 152.89, 152.42, 145.55 (2C), 145.32, 144.82, 144.76 (2C), 143.88 (2C), 143.80, 143.77, 143.65, 143.63, 143.56 (2C), 143.54, 143.38, 143.28, 143.00, 142.87 (2C), 142.81, 142.71 (2C), 142.67 (2C), 142.26, 142.07, 142.03, 142.01, 140.65, 140.55, 140.19 (3C), 140.13 (2C), 139.96 (2C), 139.83, 139.72, 139.56 (2C), 139.50, 139.36, 139.32 (2C), 139.11, 137.50, 137.20 (2C), 136.86, 134.05, 133.89, 133.20, 132.36, 128.17 (2C, aryl C), 127.27 (2C, aryl C), 127.14 (aryl C), 115.32 (aryl C), 112.26 (2C, aryl
C), 111.64 (2C, aryl C), 73.86 (sp^3-C of C_{60}), 73.77 (sp^3-C of C_{60}), 64.24, 53.76, 53.43, 34.62; FT-IR ν/cm\(^{-1}\) (KBr) 3391, 3022, 2946, 2889, 2826, 1601, 1508, 1457, 1430, 1308, 1251, 1180, 1033, 747, 687, 651, 525; UV-vis (CHCl\(_3\)) λ\(_{\text{max}}/\text{nm}\) 256, 308, 430; HRMS (ESI) \(m/z\): [M] – Calcd for C\(_{76}\)H\(_{17}\)NO 959.1310; Found 959.1256.

**Cyclopentafullerenes trans-3ca and cis-3ca:** According to the general procedure, the reaction of C\(_{60}\) (36.0 mg, 0.05 mmol) with 1c (88.6 mg, 0.50 mmol), 2a (46 μL, 0.50 mmol) and Mg(ClO\(_4\))\(_2\) (44.7 mg, 0.20 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 40 min afforded first unreacted C\(_{60}\) (21.3 mg, 59%) and then trans-3ca (7.6 mg, 16%, \(R_f = 0.71\)), cis-3ca (10.9 mg, 22%, \(R_f = 0.65\)) as amorphous brown solid with CS\(_2\)/CH\(_2\)Cl\(_2\) as eluent (V/V = 10/1): mp > 300 °C. trans-3ca: \(^1\)H NMR (500 MHz, CS\(_2\)/DMSO-\(d_6\)) δ 8.16 (d, \(J = 8.6\) Hz, 2H), 7.87 (d, \(J = 8.6\) Hz, 2H), 7.02 (t, \(J = 7.8\) Hz, 2H), 6.93-6.89 (m, 3H), 6.53 (t, \(J = 7.2\) Hz, 1H), 5.83-5.77 (m, 2H), 3.85-3.79 (m, 1H), 2.98 (dd, \(J = 12.6, 4.5\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CS\(_2\)/DMSO-\(d_6\)) (all 1C unless indicated) δ 154.17, 153.01, 152.05, 150.98, 145.26, 145.08, 144.90 (2C), 144.84, 144.22 (2C), 143.97, 143.91, 143.85, 143.78, 143.73, 143.66 (2C), 143.63 (2C), 143.28, 143.20, 143.06, 142.98 (4C), 142.91 (3C), 142.78, 142.35, 142.23, 142.12, 142.02, 140.77, 140.71, 140.42, 140.25, 140.19, 140.15, 140.07, 139.90, 139.86 (2C), 139.68 (2C), 139.62, 139.54, 139.50, 139.41, 139.39, 139.29, 138.10, 137.38, 137.21, 137.11, 135.33, 134.43, 134.24, 132.77, 128.65 (2C, aryl C), 127.28 (2C, aryl C), 121.69 (2C, aryl C), 115.66 (aryl C), 111.50 (2C, aryl C), 75.88 (sp^3-C of C\(_{60}\)), 72.58 (sp^3-C of C\(_{60}\)), 63.17, 54.45, 34.77; FT-IR ν/cm\(^{-1}\) (KBr) 3394, 2954, 2883, 1600, 1519, 1501, 1427, 1344, 1315, 1252, 1184, 855, 748, 694, 670, 570, 527;
UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub>/nm 257, 313, 431; HRMS (ESI) m/z: [M]<sup>+</sup> Calcd for C<sub>75</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> 974.1055; Found 974.0982. cis-3ca: <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/DMSO-<i>d</i><sub>6</sub>) δ 8.16 (d, <i>J</i> = 8.5 Hz, 2H), 7.85 (d, <i>J</i> = 8.5 Hz, 2H), 6.98 (t, <i>J</i> = 7.8 Hz, 2H), 6.84 (d, <i>J</i> = 8.0 Hz, 2H), 6.49 (t, <i>J</i> = 7.2 Hz, 1H), 6.29 (d, <i>J</i> = 9.5 Hz, 1H), 5.92-5.86 (m, 1H), 5.19 (dd, <i>J</i> = 13.8, 4.4 Hz, 1H), 3.68 (q, <i>J</i> = 12.7 Hz, 1H), 3.03-2.99 (m, 1H); <sup>13</sup>C NMR (125 MHz, CS<sub>2</sub>/DMSO-<i>d</i><sub>6</sub>) (all 1C unless indicated) δ 154.18, 151.89, 151.79, 151.57, 145.41, 145.39, 145.06, 144.81, 144.73, 144.66, 144.22, 143.76 (2C), 143.72, 143.56 (2C), 143.50 (3C), 143.36, 143.21, 143.13, 142.96, 142.92 (2C), 142.84, 142.72 (3C), 142.58 (2C), 142.22, 142.03, 141.84 (2C), 140.59, 140.49, 140.14 (3C), 140.04, 139.99, 139.86, 139.75 (2C), 139.58, 139.49, 139.40 (2C), 139.21 (2C), 139.18, 139.04, 137.42, 137.24, 137.18, 136.77, 134.31, 133.82, 133.61, 132.21, 128.43 (2C, aryl C), 127.20 (2C, aryl C), 121.70 (2C, aryl C), 115.31 (aryl C), 111.55 (2C, aryl C), 73.68 (sp<sup>3</sup>-C of C<sub>60</sub>), 72.92 (sp<sup>3</sup>-C of C<sub>60</sub>), 64.05, 53.16, 34.00; FT-IR ν/cm<sup>-1</sup> (KBr) 3394, 2921, 2851, 1597, 1515, 1462, 1428, 1343, 1314, 1252, 1181, 1147, 1104, 1011, 852, 779, 747, 693, 593, 570, 525; UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub>/nm 257, 307, 430; HRMS (ESI) m/z: [M]<sup>+</sup> Calcd for C<sub>75</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> 974.1055; Found 974.0985.

**Cyclopentafullerenes trans/cis-3da:** According to the general procedure, the reaction of C<sub>60</sub> (36.0 mg, 0.05 mmol) with 1c (71 μL, 0.50 mmol), 2a (46 μL, 0.50 mmol) and Mg(ClO<sub>4</sub>)<sub>2</sub> (44.7 mg, 0.20 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 40 min afforded first unreacted C<sub>60</sub> (30.2 mg, 84%) and then trans/cis-3ca (6.1 mg, 13%, trans/cis = 1/4, <i>R</i><sub>f</sub> = 0.73) as amorphous brown solid with CS<sub>2</sub> as eluent: mp > 300 °C. cis-3da: <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/DMSO-<i>d</i><sub>6</sub>) δ 7.92 (br.s, 2H), 7.47 (t, <i>J</i> =...
7.3 Hz, 2H), 7.34 (t, \(J = 7.1\) Hz, 1H), 6.95 (t, \(J = 7.6\) Hz, 2H), 6.81 (d, \(J = 8.0\) Hz, 2H), 6.45 (t, \(J = 7.1\) Hz, 1H), 6.20 (d, \(J = 9.5\) Hz, 1H), 5.77-5.70 (m, 1H), 5.01 (d, \(J = 7.5\) Hz, 1H), 3.84-3.76 (m, 1H), 1.16 (d, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CS\(_2\)/DMSO-d\(_6\)) (all 1C unless indicated) \(\delta\) 157.64, 154.80, 153.21, 152.60, 146.26, 146.08, 145.62, 145.14, 145.06, 144.76, 144.17, 144.01, 143.92 (3C), 143.87 (2C), 143.72, 143.57, 143.30 (2C), 143.12 (2C), 143.06, 143.00 (2C), 142.95, 142.91, 142.79, 142.56, 142.39 (2C), 142.25, 140.94, 140.90, 140.53, 140.49, 140.37, 140.34, 140.14, 140.03 (2C), 140.01, 139.97, 139.81 (3C), 139.71 (2C), 139.53, 139.46, 137.93, 137.91, 137.69, 137.55 (2C), 135.62, 133.57, 133.38, 132.25, 128.88 (2C, aryl C), 127.43 (2C, aryl C), 127.17 (2C, aryl C), 125.98 (aryl C), 115.41 (aryl C), 111.57 (2C, aryl C), 73.83 (sp\(^3\)-C of C\(_{60}\)), 71.26 (sp\(^3\)-C of C\(_{60}\)), 68.28, 59.49, 40.96, 12.14; FT-IR \(\nu\)/cm\(^{-1}\) (KBr) 3407, 3012, 2883, 1599, 1501, 1455, 1429, 1384, 1311, 1252, 1185, 1144, 939, 748, 670, 527; UV-vis (CHCl\(_3\)) \(\lambda_{max}/\text{nm}\) 256, 310, 431; HRMS (ESI) \(m/z\): [M]\(^{-}\) Calcd for C\(_{76}\)H\(_{17}\)N 943.1361; Found 943.1302.

**General Procedure for the Synthesis of Cyclopentafulerenes 5.** A mixture of C\(_{60}\) (36.0 mg, 0.05 mmol), cinnamaldehydes 1 (0.50 mmol), secondary amines 4 (1.00 mmol), Mg(ClO\(_4\))\(_2\) (5.6 mg, 0.025 mmol) and Fe(ClO\(_4\))\(_3\)·xH\(_2\)O (8.9 mg, 0.025 mmol) was added to a 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. After they were completely dissolved in 10 mL of chlorobenzene by sonication, the resulting solution was put into an oil bath preset at 80 °C and stirred under air conditions. Thin-layer chromatography (TLC) was employed to carefully monitor the reaction and to stop the reaction at the designated time. The reaction
mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent evaporation in vacuo was completed, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to afford first unreacted C$_{60}$ and then cyclopentafulerenes 5.

**Cyclopentafulerene cis-5aa and Fulleropyrrolidine trans-6aa:** According to the general procedure, the reaction of C$_{60}$ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 4a (103 μL, 1.00 mmol), Mg(ClO$_4$)$_2$ (5.6 mg, 0.025 mmol) and Fe(ClO$_4$)$_3$·xH$_2$O (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 60 min afforded first unreacted C$_{60}$ (17.9 mg, 50%) and then cis-5aa$^1$ (18.3 mg, 40%, $R_f = 0.82$) and trans-6aa$^{2,3}$ (3.8 mg, 8%, $R_f = 0.24$) as amorphous brown solid with CS$_2$ as eluent: mp > 300 °C.

**Cyclopentafulerene cis-5ab and Fulleropyrrolidine trans-6ab:** According to the general procedure, the reaction of C$_{60}$ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 4b (137 μL, 1.00 mmol), Mg(ClO$_4$)$_2$ (5.6 mg, 0.025 mmol) and Fe(ClO$_4$)$_3$·xH$_2$O (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 55 min afforded first unreacted C$_{60}$ (22.7 mg, 63%) and then cis-5ab (13.9 mg, 30%, $R_f = 0.97$) and trans-6ab$^3$ (trace, $R_f = 0.68$) as amorphous brown solid with CS$_2$ as eluent: mp > 300 °C. $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) δ 7.58 (d, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 5.04 (dd, $J = 12.5$, 4.5 Hz, 1H), 4.86 (dd, $J = 13.4$, 4.5 Hz, 1H), 3.60 (q, $J = 12.6$ Hz, 1H), 3.06 (br.s, 2H), 2.99-2.93 (m, 2H), 2.89-2.84 (m, 1H), 1.71-1.61 (m, 2H), 1.56-1.50 (m, 2H), 0.91-0.86 (m, 6H); $^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) (all 1C unless indicated) δ 155.39, 154.80, 153.00, 152.70,
146.17, 145.78, 145.40, 145.23, 144.81, 144.49, 144.43, 144.41, 144.34 (2C), 144.24, 144.19, 144.09, 144.03, 144.01, 143.85, 143.52, 143.45, 143.39 (2C), 143.35, 143.30 (2C), 143.17, 142.84, 142.70, 142.61, 142.52, 141.36, 141.20, 140.84, 140.79 (2C), 140.68, 140.61, 140.48 (2C), 140.39, 140.33, 140.20, 140.16, 139.99, 139.95 (2C), 139.85, 139.78, 138.15, 137.70, 137.64, 137.44, 136.09 (aryl C), 134.40, 134.00, 133.16, 132.61, 127.77 (2C, aryl C), 127.22 (2C, aryl C), 126.22 (aryl C), 75.07, 74.31, 73.36, 55.42, 29.59, 21.01 (2C), 10.72 (2C); FT-IR ν/cm⁻¹ (KBr) 2958, 2926, 2865, 2793, 1516, 1459, 1427, 1376, 1189, 1088, 1013, 759, 696, 573, 547, 527; UV-vis (CHCl₃) λ_max/nm 257, 311, 431; HRMS (MALDI-TOF) m/z: [M]⁻ Calcd for C₇₅H₂₃N 937.1831; Found 937.1832.

Cyclopentafullerene cis-5ac and Fulleropyrrolidine trans-6ac: According to the general procedure, the reaction of C₆₀ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 4c (169 μL, 1.00 mmol), Mg(ClO₄)₂ (5.6 mg, 0.025 mmol) and Fe(ClO₄)₃·xH₂O (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 50 min afforded first unreacted C₆₀ (17.4 mg, 48%) and then cis-5ac (21.5 mg, 45%, R_f = 0.97) and trans-6ac (trace, R_f = 0.84) as amorphous brown solid with CS₂ as eluent: mp > 300 °C. cis-5ac: ¹H NMR (500 MHz, CS₂/DMSO-d₆) δ 7.57 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 7.0 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 5.03-4.99 (m, 1H), 4.84-4.81 (m, 1H), 3.57 (q, J = 12.6 Hz, 1H), 3.09 (br.s, 2H), 2.94 (br.s, 2H), 2.87-2.83 (m, 1H), 1.63-1.61 (m, 2H), 1.45 (br.s, 2H), 1.33-1.26 (m, 4H), 0.87 (t, J = 7.1 Hz, 6H); ¹³C NMR (125 MHz, CS₂/DMSO-d₆) (all 1C unless indicated) δ 155.40, 154.90, 153.13, 152.77, 146.22, 145.88, 145.45, 145.28, 144.88, 144.54, 144.49, 144.46, 144.39 (2C),
144.28, 144.23, 144.15, 144.08 (2C), 143.91, 143.57, 143.51, 143.46, 143.44, 143.39, 143.35 (2C), 143.21, 142.89, 142.76, 142.67, 142.57, 141.41, 141.25, 140.88, 140.85 (2C), 140.73, 140.62, 140.55, 140.53, 140.43, 140.39, 140.25, 140.21, 139.99 (3C), 139.94, 139.84, 138.15, 137.73, 137.70, 137.48, 136.17, 134.41, 134.07, 133.25, 132.64, 127.83 (2C, aryl C), 127.28 (2C, aryl C), 126.26 (aryl C), 75.13, 74.32, 73.34, 55.49, 29.78 (2C), 29.42, 19.43 (2C), 13.06 (2C); FT-IR ν/cm⁻¹ (KBr) 2954, 2925, 2858, 1539, 1498, 1458, 1427, 1372, 1269, 1221, 1185, 1013, 896, 828, 760, 695, 573, 527; UV-vis (CHCl₃) λ_max/nm 257, 311, 431; HRMS (MALDI-TOF) m/z: [M]⁻ Calcd for C₇₇H₂₇N 965.2144; Found 965.2142.

**Cyclopentafullerene cis-5ad and Fulleropyrrolidine trans-6ad:** According to the general procedure, the reaction of C₆₀ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 4d (129 μL, 1.00 mmol), Mg(ClO₄)₂ (5.6 mg, 0.025 mmol) and Fe(ClO₄)₃·xH₂O (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 15 min afforded first unreacted C₆₀ (14.3 mg, 40%) and then *cis-5ad* (20.1 mg, 42%, R_f = 0.88) and *trans-6ad*³ (4.4 mg, 9%, R_f = 0.10) as amorphous brown solid with CS₂ as eluent: mp > 300 °C. *cis-5ad:* ¹H NMR (500 MHz, CS₂/DMSO-d₆) δ 7.59 (d, J = 7.2 Hz, 2H), 7.32-7.28 (m, 4H), 7.22-7.13 (m, 4H), 5.08 (d, J = 11.2 Hz, 1H), 4.85 (d, J = 12.6 Hz, 1H), 4.31 (d, J = 13.3 Hz, 1H), 4.13 (d, J = 13.3 Hz, 1H), 3.62 (q, J = 12.5 Hz, 1H), 2.95-2.93 (m, 1H), 2.78 (s, 3H); ¹³C NMR (125 MHz, CS₂/DMSO-d₆) (all 1C unless indicated) δ 155.33, 154.68, 152.93, 152.71, 145.94, 145.88, 145.51, 145.38, 144.96, 144.55 (3C), 144.47 (2C), 144.35, 144.30, 144.23, 144.19, 144.13, 143.97, 143.64, 143.60, 143.55, 143.51, 143.48, 143.43 (2C), 143.33, 142.92, 142.83,
142.77, 142.63, 141.45, 141.33, 140.98, 140.92 (2C), 140.82, 140.73, 140.62, 140.57,
140.52, 140.45, 140.33, 140.28, 140.15, 140.13, 140.07, 140.06, 139.93, 138.19,
137.98, 137.86, 137.61, 137.44, 136.17, 134.58, 134.41, 133.36, 132.88, 127.93 (2C,
aryl C), 127.36 (4C, aryl C), 126.98 (2C, aryl C), 126.35 (aryl C), 125.94 (aryl C),
75.83, 74.24, 73.57, 55.39, 29.06; FT-IR ν/cm\(^{-1}\) (KBr) 3027, 2922, 2848, 2787, 1602,
1538, 1494, 1454, 1427, 1359, 1217, 1184, 1071, 1027, 967, 907, 739, 696, 573, 527;
UV-vis (CHCl\(_3\)) λ\(_{\text{max}}/\text{nm}\) 257, 310, 431; HRMS (MALDI-TOF) m/z: [M]\(^-\) Calcd for
C\(_{77}\)H\(_{19}\)N 957.1518; Found 957.1515.

**Cyclopentafullerene cis-5ae and Fulleropyrrolidine trans-6ae:** According to the
general procedure, the reaction of C\(_{60}\) (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50
mmol), 4e (192 μL, 1.00 mmol), Mg(ClO\(_4\))\(_2\) (5.6 mg, 0.025 mmol) and
Fe(ClO\(_4\))\(_3\)·xH\(_2\)O (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 150
min afforded first unreacted C\(_{60}\) (18.1 mg, 50%) and then trans-6ae\(^3\) (5.9 mg, 11%, R\(_f\)
= 0.89) and cis-5ae (15.4 mg, 30%, R\(_f\) = 0.75) as amorphous brown solid with CS\(_2\) as
eluent: mp > 300 °C. **cis-5ae:** ¹H NMR (500 MHz, CS\(_2\)/DMSO-d\(_6\)) δ 7.58 (d, J = 7.3
Hz, 2H), 7.38 (d, J = 7.1 Hz, 4H), 7.30 (t, J = 7.7 Hz, 2H), 7.22-7.12 (m, 7H), 5.08
(dd, J = 12.6, 4.5 Hz, 1H), 4.76 (dd, J = 13.5, 4.4 Hz, 1H), 3.96-3.92 (m, 2H), 3.66 (q,
J = 12.6 Hz, 1H), 3.03-2.99 (m, 1H); ¹³C NMR (125 MHz, CS\(_2\)/DMSO-d\(_6\)) (all 1C
unless indicated) δ 154.40, 154.12, 151.95, 151.42, 145.26, 145.22, 144.84, 144.72,
144.14, 143.96, 143.88, 143.82 (2C), 143.76, 143.67, 143.61, 143.59, 143.52, 143.45,
143.25, 142.99, 142.95, 142.85, 142.81, 142.74 (3C), 142.66, 142.18 (2C), 142.07,
141.94, 140.72, 140.65, 140.33, 140.25 (2C), 140.14, 140.06, 139.99, 139.88 (2C),
Cyclopentafullerene cis-5af: According to the general procedure, the reaction of C₆₀ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 4f (108 μL, 1.00 mmol), Mg(ClO₄)₂ (5.6 mg, 0.025 mmol) and Fe(ClO₄)₃·xH₂O (8.9 mg, 0.025 mmol) in ODCB (6 mL) at 180 °C for 120 min afforded first unreacted C₆₀ (20.6 mg, 57%) and then cis-5af (8.5 mg, 18%, Rₛ = 0.87) as amorphous brown solid with CS₂ as eluent: mp > 300 °C. cis-5af: $^1$H NMR (500 MHz, CS₂/DMSO-$d_6$) $\delta$ 7.64 (d, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.13 (t, $J = 7.9$ Hz, 2H), 7.06 (d, $J = 8.4$ Hz, 2H), 6.65 (t, $J = 7.2$ Hz, 1H), 6.19 (dd, $J = 12.3$, 4.5 Hz, 1H), 5.07 (dd, $J = 13.4$, 4.4 Hz, 1H), 3.97 (q, $J = 12.5$ Hz, 1H), 3.35 (s, 3H), 2.93-2.89 (m, 1H); $^{13}$C NMR (125 MHz, CS₂/DMSO-$d_6$) (all 1C unless indicated) $\delta$ 154.20, 154.00, 152.80, 152.35, 148.49 (aryl C), 145.35, 145.29, 145.20 (2C), 145.02, 144.40, 144.35, 144.32 (2C), 144.28, 144.19, 144.14, 144.10 (2C), 143.89, 143.81, 143.52, 143.48 (2C), 143.38, 143.33, 143.25 (3C), 142.73, 142.62, 142.55, 142.51, 141.28, 141.18, 140.79, 140.76 (2C), 140.69, 140.54, 140.47, 140.39, 140.30 (2C), 140.14, 140.11, 140.02, 139.97, 139.91, 139.77 (2C), 138.16 (2C), 137.81, 137.43, 135.81, 134.43, 134.34,
133.59, 132.83, 127.81 (2C, aryl C), 127.73 (2C, aryl C), 127.25 (2C, aryl C), 126.31 (aryl C), 116.81 (aryl C), 112.61 (2C, aryl C), 73.86, 73.77, 71.60, 54.28, 33.06, 31.81; FT-IR ν/cm⁻¹ (KBr) 3026, 2807, 1594, 1503, 1426, 1400, 1314, 1242, 1184, 1156, 1121, 1089, 1009, 963, 748, 693, 572, 526; UV-vis (CHCl₃) λ max/nm 256, 307, 430; HRMS (MALDI-TOF) m/z: [M]⁻ Calcd for C₇₆H₁₇N 943.1361; Found 943.1362.

**Cyclopentafullerene cis-5ag:** According to the general procedure, the reaction of C₆₀ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), 4g (126 μL, 1.00 mmol), Mg(ClO₄)₂ (5.6 mg, 0.025 mmol) and Fe(ClO₄)₃·xH₂O (8.9 mg, 0.025 mmol) in ODCB (6 mL) at 180 °C for 100 min afforded first unreacted C₆₀ (27.2 mg, 76%) and then cis-5ag (6.8 mg, 14%, Rᵣ = 0.91) as amorphous brown solid with CS₂ as eluent: mp > 300 °C. *cis-5ag:* ¹H NMR (500 MHz, CS₂/DMSO-d₆) δ 7.64 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.63 (t, J = 6.9 Hz, 1H), 6.19 (dd, J = 12.1, 3.9 Hz, 1H), 5.05 (dd, J = 13.3, 3.9 Hz, 1H), 4.14-4.07 (m, 1H), 3.94 (q, J = 12.3 Hz, 1H), 3.76-3.69 (m, 1H), 2.99-2.96 (m, 1H), 1.31 (t, J = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CS₂/DMSO-d₆) (all 1C unless indicated) δ 154.18, 153.71, 152.73, 152.14, 146.12 (aryl C), 145.05 (3C), 144.91, 144.77, 144.11, 144.05, 144.02 (2C), 143.97, 143.89, 143.84, 143.81 (2C), 143.61, 143.52, 143.18 (3C), 143.09, 143.04, 142.98, 142.93, 142.90, 142.45, 142.32, 142.24 (2C), 140.99, 140.89, 140.48 (3C), 140.40, 140.27, 140.17, 140.11, 140.02 (2C), 139.85 (2C), 139.71, 139.69, 139.61, 139.47, 139.40, 137.80 (2C), 137.54, 137.13, 135.55, 134.09, 134.05, 133.32, 132.31, 127.58 (4C, aryl C), 127.03 (2C, aryl C), 126.12 (aryl C), 116.54 (aryl C), 113.40 (2C, aryl C), 73.56 (2C), 70.78, 54.06,
32.21, 12.38; FT-IR ν/cm$^{-1}$ (KBr) 3028, 2968, 2923, 2848, 1595, 1539, 1497, 1456, 1427, 1373, 1305, 1268, 1231, 1189, 1157, 1122, 1094, 1009, 745, 696, 573, 527;
UV-vis (CHCl$_3$) $\lambda_{\text{max}}$/nm 257, 310, 431; HRMS (MALDI-TOF) $m/z$: [M]$^-$ Calcd for C$_{77}$H$_{19}$N 957.1518; Found 957.1516.

**Cyclopentafullerene cis-5ba and Fulleropyrrolidine trans-6ba:** According to the general procedure, the reaction of C$_{60}$ (36.0 mg, 0.05 mmol) with 1b (81.1 mg, 0.50 mmol), 4a (103 μL, 1.00 mmol), Mg(ClO$_4$)$_2$ (5.6 mg, 0.025 mmol) and Fe(ClO$_4$)$_3$:xH$_2$O (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 120 min afforded first unreacted C$_{60}$ (21.3 mg, 59%) and then cis-5ba$^{1,4}$ (16.2 mg, 34%, R$_f$ = 0.31) and trans-6ba$^{2,3}$ (trace, R$_f$ = 0.06) as amorphous brown solid with CS$_2$ as eluent: mp > 300 °C.

**Cyclopentafullerene cis-5ca and Fulleropyrrolidine trans-6ca:** According to the general procedure, the reaction of C$_{60}$ (36.0 mg, 0.05 mmol) with 1c (88.6 mg, 0.50 mmol), 4a (103 μL, 1.00 mmol), Mg(ClO$_4$)$_2$ (11.2 mg, 0.05 mmol) and Fe(ClO$_4$)$_3$:xH$_2$O (17.8 mg, 0.05 mmol) in chlorobenzene (10 mL) at 80 °C for 35 min afforded first unreacted C$_{60}$ (6.8 mg, 19%) and then cis-5ca$^1$ (6.4 mg, 13%, R$_f$ = 0.15) and trans-6ca$^{2,3}$ (20.0 mg, 42%, R$_f$ = 0.12) as amorphous brown solid with CS$_2$ as eluent: mp > 300 °C.

**Reaction of C$_{60}$ with Cinnamaldehyde (1a) and Triethylamine in the Presence of Mg(ClO$_4$)$_2$.** By following the same experimental procedure as for the reaction of C$_{60}$ with amines 2/4, the reaction of C$_{60}$ (36.0 mg, 0.05 mmol) with 1a (63 μL, 0.50 mmol), triethylamine (69 μL, 0.50 mmol) and Mg(ClO$_4$)$_2$ (44.7 mg, 0.20 mmol) in o-
dichlorobenzene (6 mL) at 180 °C for 60 min afforded first unreacted C$_{60}$ (20.6 mg, 57%) and then cis-5aa$^1$ (9.9 mg, 22%, R$_f$ = 0.82) and trans-6aa$_{2,3}$ (1.5 mg, 3%, R$_f$ = 0.24) as amorphous brown solid with CS$_2$ as eluent: mp > 300 °C.

**Cyclopentafullerene cis-7:** By following the same experimental procedure as for the reaction of C$_{60}$ with amines 2/4, the reaction of cis-3aa (11.6 mg, 0.0125 mmol) with benzoyl chloride (29 μL, 0.250 mmol) and DMAP (7.6 mg, 0.0625 mmol) in chlorobenzene (5 mL) at 120 °C for 24 h afforded first unreacted cis-3aa (2.3 mg, 20%, R$_f$ = 0.98) and then cis-7 (10.2 mg, 79%, R$_f$ = 0.36) as an amorphous brown solid (mp > 300 °C) with CS$_2$/CH$_2$Cl$_2$ as eluent (V/V = 10/1). cis-7: \(^1\)H NMR (500 MHz, CS$_2$/DMSO-$d_6$) $\delta$ 7.48 (d, $J$ = 7.4 Hz, 2H), 7.28-7.17 (m, 7H), 7.10-7.00 (m, 6H), 5.12 (dd, $J$ = 13.6, 4.2 Hz, 1H), 3.47-3.40 (m, 1H), 2.90-2.86 (m, 1H); \(^{13}\)C NMR (125 MHz, CS$_2$/DMSO-$d_6$) (all 1C unless indicated) $\delta$ 169.84 (C=O), 156.28, 153.70, 152.86, 152.21, 145.64 (2C), 145.59, 145.22, 145.04, 144.70, 144.61, 144.56 (3C), 144.46, 144.39 (3C), 144.25, 144.02, 143.87, 143.72, 143.66, 143.57, 143.50, 143.49, 143.42, 143.04, 142.91, 142.79 (2C), 141.48 (2C), 141.23, 141.03 (3C), 140.96, 140.91, 140.79, 140.69, 140.57, 140.34, 140.24, 140.16, 140.11, 140.03, 139.95, 139.60 (aryl C), 138.21, 138.10, 137.83, 137.82, 135.88 (aryl C), 135.02, 134.89, 134.54, 134.32, 132.43 (aryl C), 129.80 (2C, aryl C), 128.07 (aryl C), 128.01 (2C, aryl C), 127.78 (2C, aryl C), 127.39 (2C, aryl C), 127.03 (2C, aryl C), 126.61 (aryl C), 126.51 (aryl C), 126.39 (2C, aryl C), 74.43, 73.36, 66.37, 54.32, 33.29; FT-IR ν/cm$^{-1}$ (KBr) 2920, 2849, 1644, 1593, 1491, 1453, 1426, 1337, 1267, 1218, 1180, 1155, 1108, 1073, 1016, 783, 762, 734, 697, 574, 527; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$/nm 257, 310,
HRMS (MALDI-TOF) \( m/z: [M]^− \) Calcd for \( \text{C}_{82}\text{H}_{19}\text{NO} \) 1033.1467; Found 1033.1468.

**Cyclopentafullerene 8:** By following the same experimental procedure as for the reaction of \( \text{C}_{60} \) with amines 2/4, the reaction of cis-3aa (11.6 mg, 0.0125 mmol) with paraformaldehyde (0.8 mg, 0.0250 mmol) and TsOH-H\(_2\)O (2.4 mg, 0.0125 mmol) in chlorobenzene (5 mL) at 40 °C for 1.5 h afforded first unreacted cis-3aa (2.5 mg, 22%, \( R_f = 0.98 \)) and then 8 (7.5 mg, 63%, cis-ortho-8/trans-ortho-8 = 10.5/1, \( R_f = 0.86 \)) as an amorphous brown solid (mp > 300 °C) with CS\(_2/\text{CH}_2\text{Cl}_2\) as eluent (V/V = 10/1).

cis-ortho-8: \(^1\)H NMR (500 MHz, CS\(_2/\text{DMSO-}d_6\)) \( \delta \) 7.63 (d, \( J = 7.4 \) Hz, 2H), 7.31 (t, \( J = 7.7 \) Hz, 2H), 7.24-7.16 (m, 2H), 7.11 (t, \( J = 8.0 \) Hz, 1H), 6.91-6.82 (m, 2H), 5.84 (dd, \( J = 12.4, 4.6 \) Hz, 1H), 5.56 (d, \( J = 10.6 \) Hz, 1H), 4.95-4.87 (m, 1H), 4.67 (d, \( J = 10.6 \) Hz, 1H), 3.91 (q, \( J = 12.8 \) Hz, 1H), 3.03-2.98 (m, 1H); \(^{13}\)C NMR (125 MHz, CS\(_2/\text{DMSO-}d_6\)) (all 1C unless indicated) \( \delta \) 154.55, 154.38, 152.87, 152.08, 146.08, 145.79, 145.71, 145.63, 145.26, 144.88, 144.75 (3C), 144.70, 144.63 (2C), 144.49, 144.47, 144.33, 144.17 (2C), 144.01, 143.88 (2C), 143.85 (2C), 143.72, 143.67 (2C), 143.12, 143.03 (2C), 142.99, 141.68, 141.60, 141.22 (2C), 141.14, 141.10, 140.90 (2C), 140.77, 140.75, 140.66, 140.60, 140.55, 140.40 (2C), 140.37, 140.23, 140.18, 138.74, 138.35, 138.21, 137.89, 136.03, 135.24, 134.83, 133.84, 133.69, 128.17 (2C, aryl C), 127.52 (2C, aryl C), 126.55 (aryl C), 126.38 (aryl C), 124.04 (aryl C), 123.73 (aryl C), 120.03 (aryl C), 118.07 (aryl C), 74.90, 74.18, 73.69, 66.54, 55.12, 32.35; FT-IR \( \nu/cm^{-1} \) (KBr) 2919, 2849, 1603, 1491, 1455, 1427, 1270, 1225, 1179, 1056,
1030, 921, 750, 697, 575, 526; UV-vis (CHCl₃) λ_max/nm 257, 307, 431; HRMS (MALDI-TOF) m/z: [M]⁻ Calcd for C₇₆H₁₇NO 959.1310; Found 959.1311.

Transformation of cis-3aa in the Presence of Mg(ClO₄)₂. By following the same experimental procedure as for the reaction of C₆₀ with amines 2/4, the reaction of cis-3aa (18.6 mg, 0.02 mmol) with Mg(ClO₄)₂ (9.0 mg, 0.04 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 60 min afforded first trans-3aa (4.3 mg, 24%, R_f = 0.68) and then unreacted cis-3aa (11.5 mg, 62%, R_f = 0.59) as amorphous brown solid with CS₂ as eluent: mp > 300 °C.

Transformation of trans-3aa in the Presence of Mg(ClO₄)₂. By following the same experimental procedure as for the reaction of C₆₀ with amines 2/4, the reaction of trans-3aa (18.6 mg, 0.02 mmol) with Mg(ClO₄)₂ (9.0 mg, 0.04 mmol) in o-dichlorobenzene (6 mL) at 180 °C for 60 min afforded first C₆₀ (1.3 mg, 9%) and then unreacted trans-3aa (1.7 mg, 8%, R_f = 0.68), cis-3aa (7.4 mg, 40%, R_f = 0.59) as amorphous brown solid with CS₂ as eluent: mp > 300 °C.

References


Typical MALDI-TOF MS of cyclopentafullerenes
MALDI-TOF MS of compound cis-7

MALDI-TOF MS of compound cis-ortho-8
Typical UV-vis spectra of cyclopentafullerenes
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3aa

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3aa
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3aa
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *cis*-3aa
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $trans$-$3ab$

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $trans$-$3ab$
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *cis-3ab*
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3ab
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans/cis-3ac

NOESY (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of trans/cis-3ac
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans/cis-3ac
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *trans*-3ad

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *trans*-3ad
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $cis$-$3ad$
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $cis$-$3ad$
\(^1\)H NMR (500 MHz, CS\(_2\)/DMSO-\(d_6\)) spectrum of compound trans-3ae

\(^{13}\)C NMR (125 MHz, CS\(_2\)/DMSO-\(d_6\)) spectrum of compound trans-3ae
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3ae
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3ae
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3af

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3af
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3af
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3af
$^{1}$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3ba

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3ba
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3ba
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3ba
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3ca

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-3ca
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-3ca
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $cis$-3ca
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans/cis-3da

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans/cis-3da
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *cis-5aa*
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5aa
$^{1}H$ NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ab

$^{13}C$ NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ab
$^{1}$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-$\textit{5ac}$
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound \textit{cis-5ac}
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ad

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ad
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ae
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$_d_6$) spectrum of compound \textit{cis-5ae}
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $cis$-$5af$

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $cis$-$5af$
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ag
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *cis-5ag*
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ba

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ba
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-5ca
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $cis$-5ca
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $trans$-$6aa$

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $trans$-$6aa$
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-6ad
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *trans-6ad*
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $trans$-$6ae$

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound $trans$-$6ae$
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound trans-6ca
$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound *trans-6ca*
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-7

$^{13}$C NMR (125 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis-7
$^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) spectrum of compound cis/trans-ortho-8
NOESY (500 MHz, CS₂/DMSO-d₆) spectrum of cis/trans-ortho-8

¹³C NMR (125 MHz, CS₂/DMSO-d₆) spectrum of compound cis/trans-ortho-8