SUPPORTING INFORMATION

Carborane-stilbene dyads: influence of the substituents and cluster isomers on the photoluminescence properties†

A. Ferrer-Ugalde, a# J. Cabrera-González, a E. J. Juárez-Pérez, a# F. Teixidor, a E. Pérez-Inestrosa, b,c J. M. Montenegro, b,c R. Sillanpää, d M. Haukka and d R. Núñez* a

a Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus U.A.B., 08193, Bellaterra, Barcelona, Spain. E-mail: rosario@icmab.es
b Universidad de Málaga, IBIMA, Department of Organic Chemistry, 29071-Malaga, Spain.
c Andalusian Centre for Nanomedicine and Biotechnology-BIONAND, Parque Tecnológico de Andalucía, 29590-Málaga, Spain.
d Department of Chemistry, University of Jyväskylä, FIN-40014, Jyväskylä, Finland.

† A. Ferrer-Ugalde current address: School of Chemistry and Chemical Engineering. Queen’s University of Belfast, David Keir Building, Belfast, BT9 5AG, United Kingdom; E. J. Juárez-Pérez current address: Energy Materials and Surface Sciences Unit (EMSS), Okinawa Institute of Science and Technology Graduate University (OIST), 1919-1 Tancha, Onna-son, Okinawa, 904-0495, Japan
Figure Captions and Tables

**Fig. S1** Ortep plot of the solid-state structure of 6.

**Fig. S2** Ortep plot of the solid-state structure of 7.

**Fig. S3** Packing of 9 along crystallographic c-axis.

**Fig. S4** Packing of 12 along crystallographic a-axis.

**Fig. S5** Packing of 13 along crystallographic c-axis.

**Fig. S6** Packing of 14 along crystallographic a-axis.

**Fig. S7** Packing of 15 on crystallographic ab-plane.

**Fig. S8** Emission spectra of 10 in solution (THF) and solid. $\lambda_{\text{exc}} = 310$ nm (left). Emission spectra of 10 in solution (THF), solid and thin film. $\lambda_{\text{exc}} = 310$ nm (right).

**Fig. S9** Emission spectra of 10 in solution (THF), solid and thin film at $\lambda_{\text{exc}} = 310$ nm (left). Fluorescence emission of 10 in different THF/H$_2$O ratio at $\lambda_{\text{exc}} = 320$ nm (right).

**Fig. S10** Absorbance and excitation spectra of 10 and 14 in THF and H$_2$O/THF 97:3.

**Table S1** Selected bond lengths (Å).

**Table S2** Selected crystallographic data for compounds 6, 7, 9 and 12-15.

**Table S3** Weak hydrogen bonds in 6 and 7.

**Table S4** Molecular orbital contribution (%) for the fragments constituting every compound.

**NMR Spectra**
Experimental Part

Instrumentation.

Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The $^1$H NMR (300.13 MHz), $^{11}$B{$^1$H} and $^{11}$B NMR (96.29 MHz) and $^{13}$C{$^1$H} NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded in CDCl$_3$ or CD$_3$COCD$_3$ solutions at 25ºC. Chemical shift values for $^{11}$B{$^1$H} NMR spectra were referenced to external BF$_3$·OEt$_2$, and those for $^1$H and $^{13}$C{$^1$H} NMR were referenced to SiMe$_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz. MALDI-TOF-MS mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF [N2 laser; $\lambda_{exc}$ 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. UV-Vis spectra were recorded on Shimadzu UV-1700 Pharmaspec spectrophotometer, in 0.1 cm cuvettes, using solutions of compounds with 10$^{-6}$ mol·L$^{-1}$ of concentration. The fluorescence emission spectra were recorded in a JASCO FP-750 spectrofluorometer and a FLS 920 from Edinburgh Instruments using a 450W Xe lamp as excitation source. Samples were prepared in spectroscopic grade solvents and adjusted to a response within the linear range. No fluorescent contaminants were detected on excitation in the wavelength region of experimental interest. Fluorescence quantum yields were determined by comparison with styrene or stilbene as reference, and corrected for the refractive index of the solvent, cyclohexane for styrene (n = 1.426) and methylecyclohexane for stilbene (n = 1.422). Samples were prepared in such a way as to obtain an absorbance of 0.1–0.2 at the excitation wavelength to avoid internal reabsorption effects in the posterior emission.$^1$ The quantum yield for $i$ was determined by $\Phi_i = \left[ (F_i \cdot A_{R_i} \cdot n_{i}^3) / (F_{R} \cdot A_{i} \cdot n_{R}^3) \right] \cdot \Phi_R$, where $f_i = 1$-
10 to F are the integrated intensities, A the absorbances and n the refractive indices.\textsuperscript{2}

The aggregates of 10 and 14 were obtained by adding water to THF solutions of both compounds and stirring.\textsuperscript{3-5} The solid state (powder and films) fluorescence emission measurements were carried out in an Edinburgh Instrument FLS920 fluorometer, using a 450 W Xe lamp as excitation source and a Starna 20-C support for solid samples. The excitation wavelength used was 310 nm and the spectra were registered using 2 nm excitation and emission slits opening and a dwell time of 0.2 s. For the preparation of films a drop of a solution of 10 and 14 was evaporated over a short path length demountable Starna 20C cell and then the emission spectra were registered.

**X-ray Structure Determinations.**

The crystals of 6, 7, 9, 12, 13, 14, and 15 were immersed in cryo-oil, mounted in MiTeGen loops, and measured at 120-123 K. The X-ray diffraction data were collected on a Rigaku Oxford Diffraction Supernova diffractometer using Cu Kα (λ = 1.54184 Å) radiation or on a Nonius Kappa ApexII diffractometer using Mo Kα (λ = 0.71073 Å) radiation. The Denzo/Scalepack\textsuperscript{6} or CrysAlisPro\textsuperscript{7} program packages were used for cell refinements and data reductions. The structures were solved by direct methods or by charge flipping method using the SHELXS-97\textsuperscript{8} or Superflip\textsuperscript{9} programs. A multi-scan or Gaussian absorption correction (SADABS\textsuperscript{10} or CrysAlisPro\textsuperscript{7}) was applied to structural data of 6, 7, 12, 14, and 15. Structural refinements were carried out using SHELXL-97 or SHELXL-2014\textsuperscript{8} programs. The unit cell of structures 9 and 12 contained two independent molecules. In structure 9, carbon atoms in the double bond between the aromatic rings in one of the stilbene ligands were disordered over two sites. Structure 12 was refined as a racemic twin. The BASF value was refined to 0.017. In all structures the hydrogen atoms were positioned geometrically and constrained to ride on their
parent atoms with C-H = 0.95-0.99 Å, B-H 1.12 Å, and U_{iso} = 1.2-1.5 \cdot U_{eq} (parent atom). Crystallographic details are summarized in Table 2 and Table S2. Selected bond lengths are given in Table S1. The codes for structures 6-15 are CCDC 1507869-1507875

**Calculations.**

Ground-state calculations were carried out by using hybrid DFT (B3LYP functional) and Ahlrichs def2-TZV basis set\(^{11, 12}\) as implemented in the ORCA 3.0.1 package\(^{13}\). Partial density of state (PDOS) of the fragments fluorophore (styrenyl or stilbenyl), carboranyl substituent (Me or Ph) and carborane cage (o-, m- or p-carborane) and their orbital composition analysis (Mulliken type with 0.5 eV of FWHM) were obtained using Multiwfn 3.3.7\(^{14, 15}\). Probability (60 %) isodensity for the HOMO – LUMO 3D contour plots of the compounds were obtained using Gabedit\(^{16}\).

**Characterization of compounds 3-16**

The IR spectra show typical \(\nu (B-H)\) strong bands for closo clusters between 2565 and 2592 cm\(^{-1}\). The \(^1\)H NMR spectra of 3-16 show one singlet in a region from \(\delta 3.06\) to 3.49 ppm due to the C_c-CH\(_2\) protons, which is slightly upfield shifted (0.1-0.2 ppm) in the m-derivatives with regard to o-isomers. For compounds 3-4 the vinyl protons appear in the region 5.28-6.74 ppm as a set of three resonances, similar to their analogous o-carborane derivatives 1-2\(^{17}\). These signals disappear completely after the Heck reaction, corroborating the formation of compounds 9-16, in which a resonance attributed to the two alkene protons is observed in the range 7.03-7.14 ppm. The \(^{13}\)C NMR spectra of 3-16 show one resonance in the range 40.34-42.95 ppm attributed to the C_c-CH\(_2\) carbons, whereas compounds 5-8 show one signal at around 93 ppm attributed to C-I. All the
stilbene-containing carboranes 9-16 show resonances in the aromatic region from $\delta$ 120 to 140 ppm.

The $^{11}$B{$^1$H} NMR resonances of $o$-carborane derivatives appear in the typical closo region,\textsuperscript{18} from $\delta$ -3.59 to -10.55 ppm, with the general pattern 2:8 for Ph-$o$-carborane derivatives and 1:1:4:4 or 1:1:8 for Me-$o$-carborane derivatives. Additionally, resonances for $m$-carborane derivatives appear in the region from $\delta$ -5.09 to -13.73 ppm with patterns 1:1:6:2 or 2.6:2. Elemental analyses and MALDI-TOF spectrometry also confirmed the structures of all these compounds (see Experimental Part).
Compound 6 crystallized in the orthorhombic space group Pbca, whereas compound 7 crystallized in the monoclinic space group P2₁/n. Both compounds show weak intramolecular interactions. The iodine substituent (I1) of the iodobenzyl group is involved in a very weak hydrogen bond with the adjacent B7-H7 unit (B7⋯I1: 3.977(3) Å, #1: -½-x, -y, -½+z) in 6, and with the adjacent B(10)-H(10) (B10⋯I1: 3.853(3) Å, #2: ½-x, ½-y, ½-z) in 7 (Table S3). Structure of 9 consists of two independent molecules. The organic moieties are connected through series of very weak C-H⋯π contacts between the stilbene ligands in 9 (Fig. S3) and in 12 (Fig. S4) where the stilbene group is acting as a terminal substituent. Unlike 9, in 12 the carborane ends of the molecules are pushed further apart by the CH₃ groups. In compound 13 the stilbene ligands are forming parallel stacks with very weak π⋯π interactions (Fig. S5). The chains are pulled together via interactions between the carborane units giving an overall zig-zag structure. In 14 the phenyl substituents on carbon C2 force the carborane
ends of the molecules apart; reducing the direct contacts between carborane cages (Fig. S6). In compound 15 the stilbene ligands are well separated and not involved even in weak in π-interactions (Fig. S7).

**Fig. S3** Packing of 9 along crystallographic c-axis.

**Fig. S4** Packing of 12 along crystallographic a-axis.
Fig. S5 Packing of 13 along crystallographic c-axis.

Fig. S6 Packing of 14 along crystallographic a-axis.
**Fig. S7** Packing of 15 on crystallographic ab-plane.
Fig. S8 Emission spectra of 10 and 14 in solution (THF) and solid at $\lambda_{\text{exc}} = 310$ nm.

Fig. S9 Emission spectra of 10 in solution (THF), solid and thin film at $\lambda_{\text{exc}} = 310$ nm (left). Fluorescence emission of 10 in different THF/H$_2$O ratios at $\lambda_{\text{exc}} = 320$ nm (right).
**Fig S10.** Absorbance and excitation spectra of 10 and 14 in THF and H₂O/THF 97:3, respectively.
Table S1. Selected bond lengths (Å).

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>7</th>
<th>9A</th>
<th>9B</th>
<th>12A</th>
<th>12B</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-C(13)</td>
<td>1.527(3)</td>
<td>1.536(3)</td>
<td>1.531(2)</td>
<td>1.535(2)</td>
<td>1.537(9)</td>
<td>1.543(8)</td>
<td>1.531(2)</td>
<td>1.527(2)</td>
<td>1.5407(14)</td>
</tr>
<tr>
<td>C(2)-C(20)</td>
<td>1.504(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(17)-I(1)</td>
<td>2.105(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)-I(1)</td>
<td></td>
<td></td>
<td>2.100(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(20)</td>
<td></td>
<td></td>
<td>1.521(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(21)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5216(15)</td>
</tr>
<tr>
<td>C(2)-C(21)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(20)-C(21)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(20)-C(28)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(28)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)-C(28)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(20)-C(28)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(21)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)-C(21)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(20)-C(20)$^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# Symmetry transformations used to generate equivalent atoms: 
- #1: -x+2,-y,-z+2, 
- #2: -x,-y,-z, 
- #3: -x,-y+2,-z

$^a$
Table S2. Selected crystallographic data for compounds 6, 7, 9 and 12-15.

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>7</th>
<th>9</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>fW</td>
<td>436.32</td>
<td>374.25</td>
<td>350.49</td>
<td>412.55</td>
<td>520.74</td>
<td>644.87</td>
<td>520.74</td>
</tr>
<tr>
<td>temp (K)</td>
<td>123(2)</td>
<td>123(2)</td>
<td>123(2)</td>
<td>120(2)</td>
<td>123(2)</td>
<td>123(2) K</td>
<td>123(2)</td>
</tr>
<tr>
<td>â(Å)</td>
<td>0.71073</td>
<td>1.54184</td>
<td>0.71073</td>
<td>1.54178</td>
<td>0.71073</td>
<td>1.54184 Å</td>
<td>1.54184</td>
</tr>
<tr>
<td>cryst syst</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>Pbca</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁</td>
<td>P2₁/c</td>
<td>P2₁/c</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.0897(2)</td>
<td>7.75300(10)</td>
<td>11.9556(3)</td>
<td>11.4530(10)</td>
<td>6.6255(2)</td>
<td>14.4906(3)</td>
<td>12.0182(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>21.1818(5)</td>
<td>17.9867(3)</td>
<td>7.5223(2)</td>
<td>7.2953(6)</td>
<td>28.5036(10)</td>
<td>12.2981(2)</td>
<td>12.79780(10)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>22.1298(4)</td>
<td>11.8559(2)</td>
<td>45.0299(9)</td>
<td>27.575(2)</td>
<td>8.0673(3)</td>
<td>10.38440(10)</td>
<td>10.95890(10)</td>
</tr>
<tr>
<td>ß(deg)</td>
<td>90</td>
<td>98.493(2)</td>
<td>92.6080(10)</td>
<td>97.317(8)</td>
<td>95.529(2)</td>
<td>91.1570(10)</td>
<td>113.436(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>3792.04(15)</td>
<td>1635.19(4)</td>
<td>4045.51(17)</td>
<td>2285.2(3)</td>
<td>1516.43(9)</td>
<td>1850.19(5)</td>
<td>1546.50(4)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ρ calc (Mg/m³)</td>
<td>1.529</td>
<td>1.520</td>
<td>1.151</td>
<td>1.199</td>
<td>1.14</td>
<td>1.158</td>
<td>1.118</td>
</tr>
<tr>
<td>μ(Mo Kα) (mm⁻¹)</td>
<td>1.684</td>
<td>15.173</td>
<td>0.057</td>
<td>0.438</td>
<td>0.054</td>
<td>0.404</td>
<td>0.367</td>
</tr>
<tr>
<td>No. reflns.</td>
<td>22686</td>
<td>21644</td>
<td>41836</td>
<td>14078</td>
<td>5247</td>
<td>25257</td>
<td>38438</td>
</tr>
<tr>
<td>Unique reflns.</td>
<td>3704</td>
<td>3447</td>
<td>7837</td>
<td>7331</td>
<td>2968</td>
<td>3902</td>
<td>3255</td>
</tr>
<tr>
<td>GOOF (F²)</td>
<td>1.046</td>
<td>1.044</td>
<td>1.015</td>
<td>1.050</td>
<td>1.049</td>
<td>1.064</td>
<td>1.057</td>
</tr>
<tr>
<td>Rint</td>
<td>0.0281</td>
<td>0.0423</td>
<td>0.0399</td>
<td>0.0915</td>
<td>0.0216</td>
<td>0.0599</td>
<td>0.0357</td>
</tr>
<tr>
<td>R1 (I ≥ 2σ)</td>
<td>0.0226</td>
<td>0.0287</td>
<td>0.0541</td>
<td>0.0980</td>
<td>0.0487</td>
<td>0.0627</td>
<td>0.0430</td>
</tr>
<tr>
<td>wR2 (I ≥ 2σ)</td>
<td>0.0491</td>
<td>0.0769</td>
<td>0.1345</td>
<td>0.2676</td>
<td>0.1277</td>
<td>0.1735</td>
<td>0.1213</td>
</tr>
</tbody>
</table>

* R1 = Σ||F₀| - |Fc||Σ|F₀|, wR2 = [Σ[w(F₀² - Fc²)²]/Σ[w(F₀²)²]]¹/².

Table S3. Weak hydrogen bonds in 6 and 7.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>D-H</th>
<th>H⋯A</th>
<th>D⋯A</th>
<th>D-H⋯A</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>B7⋯I1¹</td>
<td>1.12</td>
<td>3.316</td>
<td>3.977(3)</td>
<td>118.7</td>
</tr>
<tr>
<td>7</td>
<td>B10⋯I1²</td>
<td>1.12</td>
<td>3.207</td>
<td>3.853(3)</td>
<td>117.4</td>
</tr>
</tbody>
</table>

¹: -½-x, -y, -½+z, ²: ½-x, ½-y, ½-z
Table S4. Molecular orbital contribution (%) for the fragments constituting every compound.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Carborane</th>
<th>Orbital type</th>
<th>Energy (eV)</th>
<th>Ph/Me</th>
<th>Styrenyl/stilbene</th>
<th>o-\text{m-/p-carboranyl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>o-Me</td>
<td>LUMO</td>
<td>-1.48</td>
<td>0.10</td>
<td>96.70</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-6.47</td>
<td>0.10</td>
<td>98.20</td>
<td>1.70</td>
</tr>
<tr>
<td>2</td>
<td>o-Ph</td>
<td>LUMO</td>
<td>-1.52</td>
<td>58.90</td>
<td>18.87</td>
<td>22.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-6.42</td>
<td>0.30</td>
<td>98.03</td>
<td>1.72</td>
</tr>
<tr>
<td>3</td>
<td>m-Me</td>
<td>LUMO</td>
<td>-1.31</td>
<td>0.10</td>
<td>97.03</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-6.32</td>
<td>0.02</td>
<td>98.27</td>
<td>1.71</td>
</tr>
<tr>
<td>4</td>
<td>m-Ph</td>
<td>LUMO</td>
<td>-1.34</td>
<td>1.39</td>
<td>94.84</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-6.32</td>
<td>0.30</td>
<td>98.13</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td>p-Me</td>
<td>LUMO</td>
<td>-1.32</td>
<td>0.20</td>
<td>96.35</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-6.29</td>
<td>0.02</td>
<td>98.17</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>p-Ph</td>
<td>LUMO</td>
<td>-1.32</td>
<td>0.89</td>
<td>95.00</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-6.30</td>
<td>0.10</td>
<td>98.14</td>
<td>1.74</td>
</tr>
<tr>
<td>9</td>
<td>o-Me</td>
<td>LUMO</td>
<td>-1.90</td>
<td>0.10</td>
<td>98.10</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-5.94</td>
<td>0.02</td>
<td>99.20</td>
<td>0.78</td>
</tr>
<tr>
<td>10</td>
<td>o-Ph</td>
<td>LUMO</td>
<td>-1.82</td>
<td>2.85</td>
<td>94.84</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-5.85</td>
<td>0.14</td>
<td>99.06</td>
<td>0.80</td>
</tr>
<tr>
<td>11</td>
<td>m-Me</td>
<td>LUMO</td>
<td>-1.78</td>
<td>0.00</td>
<td>98.15</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-5.85</td>
<td>0.01</td>
<td>99.31</td>
<td>0.68</td>
</tr>
<tr>
<td>12</td>
<td>m-Ph</td>
<td>LUMO</td>
<td>-1.80</td>
<td>0.04</td>
<td>98.06</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>-5.83</td>
<td>0.00</td>
<td>99.15</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Substituents</td>
<td>LUMO</td>
<td>HOMO</td>
<td>Angle</td>
<td>Energy</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>--------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>2 x o-Me</td>
<td>-2.02</td>
<td>-6.01</td>
<td>0.11</td>
<td>97.74</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>2 x o-Ph</td>
<td>-2.00</td>
<td>-5.97</td>
<td>1.22</td>
<td>95.42</td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2 x m-Me</td>
<td>-1.97</td>
<td>-5.95</td>
<td>0.02</td>
<td>97.58</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2 x m-Ph</td>
<td>-1.92</td>
<td>-5.91</td>
<td>0.07</td>
<td>96.83</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- LUMO and HOMO values are in eV.
- Angle is in degrees.
- Energy is in kcal/mol.
- The values represent the electronic properties of the substituted compounds.

**Formula:**
- LUMO: Highest Occupied Molecular Orbital
- HOMO: Lowest Unoccupied Molecular Orbital
- Energy: Relative energy of the molecule compared to a reference state.
NMR Spectra

**Compound 3**

$^1$H NMR (CDCl$_3$, TMS)

$^1$H{$^13$B} NMR (CDCl$_3$, TMS)
$^{11}$B{$^{1}$H} NMR (CD$_3$COCD$_3$, BF$_3$·Et$_2$O)

$^{13}$C{$^{1}$H} NMR (CD$_3$COCD$_3$, TMS)
Compound 4

$^1$H NMR (CDCl$_3$, TMS)

$^1$H{${}^{11}$B} NMR (CDCl$_3$, TMS)
$^{11}$B$\{^1$H$\}$ NMR (CDCl$_3$, BF$_3$·Et$_2$O)

$^{13}$C$\{^1$H$\}$ NMR (CDCl$_3$, TMS)
Compound 5

$^1$H NMR (CDCl$_3$, TMS)

$^1$H$^{(11)}$B NMR (CDCl$_3$, TMS)
$^{11}$B\{$^1$H\} NMR (CDCl$_3$, BF$_3$·Et$_2$O)

$^{13}$C\{$^1$H\} NMR (CDCl$_3$, TMS)
Compound 6

$^1$H NMR (CDCl$_3$, TMS)

$^1$H{$^{11}$B} NMR (CDCl$_3$, TMS)
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl$_3$, BF$_3$·Et$_2$O)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$, TMS)
Compound 7

$^1$H NMR (CDCl$_3$, TMS)

$^1$H$^{[^1]}$B NMR (CDCl$_3$, TMS)
$^{11}\text{B}^{[\text{H}]}$ NMR (CDCl$_3$, BF$_3$·Et$_2$O)

$^{13}\text{C}^{[\text{H}]}$ NMR (CDCl$_3$, TMS)
Compound 8

$^1$H NMR (CDCl$_3$, TMS)

$^1$H{$_{^{13}}$B} NMR (CDCl$_3$, TMS)
$^{11}\text{B} \{^1\text{H}\}$ NMR (CDCl$_3$, BF$_3$·Et$_2$O)

$^{13}\text{C} \{^1\text{H}\}$ NMR (CDCl$_3$, TMS)
Compound 9

$^1\text{H}$ NMR (CDCl$_3$, TMS)

$^1\text{H}$$^{11\text{B}}$ NMR (CDCl$_3$, TMS)
$^{11}$B{$^1$H} NMR (CDCl$_3$, BF$_3$·Et$_2$O)

$^{13}$C{$^1$H} NMR (CDCl$_3$, TMS)
Compound 10

$^1$H NMR (CDCl$_3$, TMS)

$^1$H$^{^{11}}$B NMR (CDCl$_3$, TMS)
\(^{11}\text{B}\{^1\text{H}\}\) NMR (CDCl\(_3\), BF\(_3\)-Et\(_2\)O)

\(^1\text{H}\) NMR (CDCl\(_3\), TMS)

**Compound 11**

\(^1\text{H}\) NMR (CDCl\(_3\), TMS)
$^1$H{$^{11}$B} NMR (CDCl$_3$, TMS)

$^{11}$B{$^1$H} NMR (CDCl$_3$, BF$_3$·Et$_2$O)

34
$^{13}$C{\textsuperscript{1}H} NMR (CDCl$_3$, TMS)

Compound 12

$^1$H NMR (CDCl$_3$, TMS)
$^1$H/$^{11}$B NMR (CDCl$_3$, TMS)

$^{11}$B/$^1$H NMR (CDCl$_3$, BF$_3$·Et$_2$O)
$^{13}$C{$^1$H} NMR (CDCl$_3$, TMS)

Compound 13

$^1$H NMR (CDCl$_3$, TMS)
$^1$H{$^{11}$B} NMR (CDCl$_3$, TMS)

$^{11}$B{$^1$H} NMR (CDCl$_3$, BF$_3$·Et$_2$O)
$^{13}$C-$^1$H NMR (CDCl$_3$, TMS)

**Compound 14**

$^1$H NMR (CDCl$_3$, TMS)
$^1$H{$^{11}$B} NMR (CDCl$_3$, TMS)

$^{11}$B{$^1$H} NMR (CDCl$_3$, BF$_3$·Et$_2$O)

Sili
gre
e
gre
ase

wat
er

B-H

H gre
ease

H gre
ease

B-H
$^{13}$C{$^1$H} NMR (CDCl$_3$, TMS)

Compound 15

$^1$H NMR (CDCl$_3$, TMS)
$^1$H{$^{11}$B} NMR (CDCl$_3$, TMS)

$^{11}$B{$^1$H} NMR (CDCl$_3$, BF$_3$·Et$_2$O)
13C{1H} NMR (CDCl₃, TMS)

Compound 16

1H NMR (CDCl₃, TMS)
$^1$H{$^{11}$}B NMR (CDCl$_3$, TMS)

$^{11}$B{$^1$}H NMR (CDCl$_3$, BF$_3$·Et$_2$O)
$^{13}$C\{$^1$H\} NMR (CDCl$_3$, TMS)

\[
\begin{align*}
42.96 & \\
75.67 & \\
79.57 & \\
126.56 & \\
127.77 & \\
128.25 & \\
128.44 & \\
128.53 & \\
130.24 & \\
135.29 & \\
136.39 & \\
136.61 &
\end{align*}
\]
References