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Synthesis of Perylene-Tagged Internal and External Electron Donors for Magnesium Dichloride Supported Ziegler–Natta Catalysts

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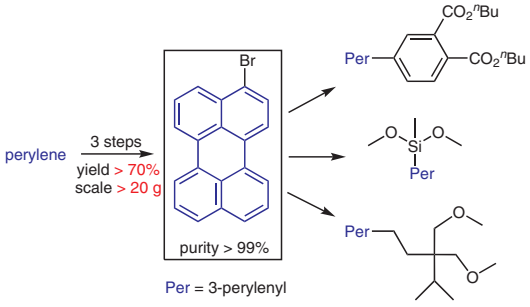

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Abstract We report on the synthesis of three perylene-tagged electron donors representing three major types – phthalates, diethers, and alkoxysilanes – which are of importance for the subsequent studies of $MgCl_2$-supported Ziegler–Natta catalysts by means of laser scanning confocal fluorescence microscopy. The obtained products were unambiguously characterized, including by X-ray crystal structure analysis; their photophysical properties (absorption and emission spectra) were investigated as well. Additionally, a reliable and convenient protocol for the multigram synthesis of the required starting material – 3-bromoperylene (PerBr) – was developed. The key step of this method was synthesis of trialkylsilyl-substituted perylenes, which were further separated by means of flash chromatography followed by conversion of the isolated 3-trialkylsilyl-substituted product to PerBr.

Key words 3-substituted perylenes, electron donors, Ziegler–Natta catalysts, emission spectra, fluorescence spectra

One of the most important milestones in chemistry and in chemical industry in the last century was the discovery of Ziegler–Natta olefin polymerization catalysts in the 1950s.[1,2] Since then, countless improvements of the Ziegler–Natta catalysts were introduced by industry, giving rise to novel systems that are chronologically combined into several generations.[3] Polymerization using supported Ziegler–Natta catalysts of the latest generations is the most important method for the industrial production of isotactic polypropylene.[4] These systems, which can be described as $TiCl_4/MgCl_2/ID/R_3Al/ED$, consist of titanium(IV) chloride, the solid support ($MgCl_2$), an aluminum alkyl cocatalyst (R_3Al), and internal (ID) and external (ED) donors. The donors are of crucial importance for achieving high polymer tacticity and regulation of the molecular weight distribution. Internal donors are used for the preparation of the supported catalyst itself, whereas external donors are added to the final catalytic system. The Ziegler–Natta catalysts most broadly used for polypropylene production are those of the fourth generation; they include dialkylphthalates as internal donors and dialkoxysilanes as external donors. In the fifth generation catalysts, the phthalates are replaced with diethers (derivatives of 1,3-dialkoxypropane) or succinates.[5]

Although Ziegler–Natta catalysts have been known for over half a century, due to their complex nature, they are still in the focus of numerous studies aiming to further elucidate the details of their structure and behavior. The mechanisms of the polymerization reactions and the catalyst structure and fragmentation have been investigated by NMR spectroscopy,[6] scanning electron microscopy (SEM),[7] transmission electron microscopy (TEM),[8] X-ray microscopy,[9] and other methods. In recent years, laser scanning confocal fluorescence microscopy (LSCFM) has been introduced as a powerful method to study fragmentation of Ziegler–Natta catalysts.[10] This method is very simple and appeared to be a faster alternative to electron microscopy.[11] For example, catalyst fragmentation was investigated by this technique by using tagged supports, but there are no examples of using perylene-tagged or other tagged electron donors in the literature (although applications of perylene-based compounds were reported in the fields of development of semiconducting materials,[12] OLEDs,[13] and cell imaging[14]). In this regard, the aim of the present work was to synthesize and characterize compounds **1**–**3** (Figure 1), representing three main types of organic electron donors, with the perylenyl fragment as the fluorescent dye. The perylene core was chosen for tagging electron donors because of its stability under polymerization conditions and high fluorescence quantum yields.[15] An additional aspect of this work was to develop a preparative method for the synthesis of the not readily available key starting material – 3-bromo-

perylene. Finally, we aimed to study the photophysical properties of **1–3** to confirm their possible use as fluorescent tags.

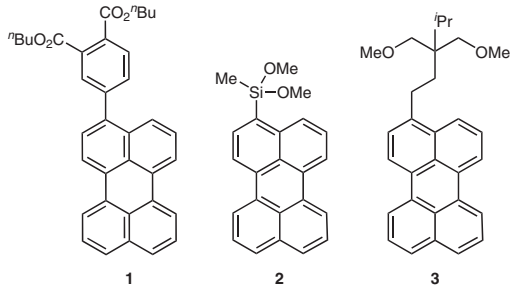
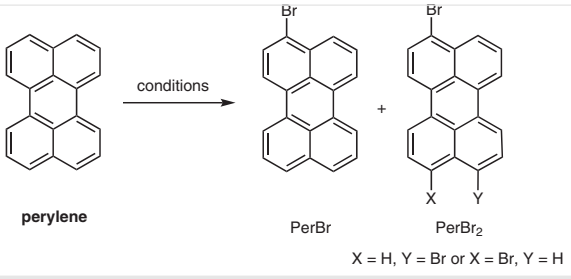


Figure 1 Electron donors to be synthesized

The synthesis of **1–3** started with the bromination of perylene[16–19] to provide the key intermediate, 3-bromoperylene (PerBr), which formed along with significant amounts of both isomeric dibromoperylenes ($PerBr_2$) (Scheme 1). Additionally, depending on the ratio of the reagents, the products are usually contaminated (up to 30%) with unreacted perylene.

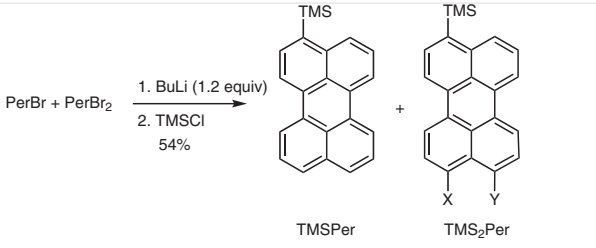


Scheme 1 Bromination of perylene

Although isolation of PerBr by recrystallization of crude mixtures of products from various solvents had been reported,[16–19] the isolated samples of PerBr were contaminated with $PerBr_2$ and unreacted perylene; that is undesirable for many applications. Furthermore, for a larger scale synthesis, all the published procedures have two major drawbacks: high dilution (up to 30 mL per mmol) and formation of the target material contaminated with $PerBr_2$ and/or unreacted perylene, which are difficult to remove using recrystallization. It should be noted that all our attempts to follow the literature purification procedures were unsuccessful; we obtained only mixtures of the desired monobromide PerBr with varied content of starting perylene and dibrominated derivatives. The plausible reason is π-stacking, a type of intermolecular interaction known for polyaromatics.[20]

For the purpose of our work we needed multigram quantities of pure PerBr. After failures with purification by recrystallization, we tried to use column chromatography, but the poor solubility of perylene derivatives and close R_f values for all the compounds shown in Scheme 1 made this kind of purification ineffective. Therefore, we needed to develop a new protocol for large-scale preparation of 3-bromoperylene, since it is the starting material for all three target donors. The idea was to modify the perylene core with a substituent that would increase solubility, so that flash chromatography could be easily applied to separate mixtures of the substituted perylenes. An additional requirement was that this new functional group could be changed back to a halogen atom in good yield. An example of such a group is a trialkylsilyl moiety, which should improve the solubility of the products, but can be easily replaced with bromine by treatment with NBS under suitable conditions.[21]

Before modification of a mixture of the bromide and dibromides, we decided to conduct the bromination of perylene with a maximum yield of monobromo derivative and reduce the content of the starting perylene to an as low as possible level. Having varied the bromination conditions, we found that the addition of 1.3 equivalents of NBS gave an 8:1 mixture of PerBr and $PerBr_2$ with a small trace (<1%) of perylene (as judged by GC). To obtain a mixture of the corresponding TMS derivatives, i.e., TMSPer and TMS_2Per, the obtained mixture of PerBr and $PerBr_2$ was treated with a slight excess of ^{n}BuLi in THF followed by the addition of an excess of TMSCl (Scheme 2).

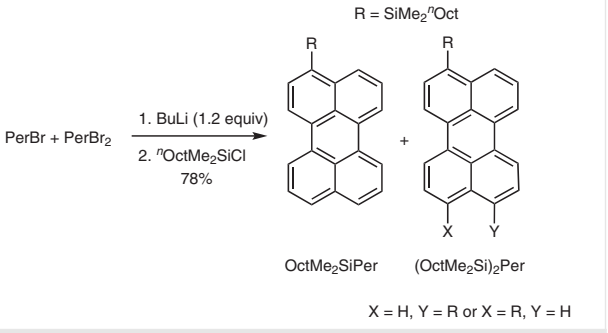


Scheme 2 Synthesis of trimethylsilyl-substituted perylene

Actually, this mixture of the TMS-substituted perylenes showed much higher solubility in the common solvents than the corresponding bromo derivatives, but the differences between the R_f values of the components were not high enough for easy and effective purification of multigram samples by flash chromatography. Nevertheless, a smaller sample of TMSPer successfully isolated in this manner was found to react with NBS to give PerBr in almost quantitative yield.

To develop a more practical procedure, the solubility of the substituted perylene derivatives to be separated should be increased dramatically. Synthesis of similar silylated perylenes bearing a longer alkyl chain at silicon could be a solution to this problem (Scheme 3). $OctMe_2SiPer$ and $(OctMe_2Si)_2Per$ were found to be significantly more soluble in all common solvents than the TMS-substituted ana-

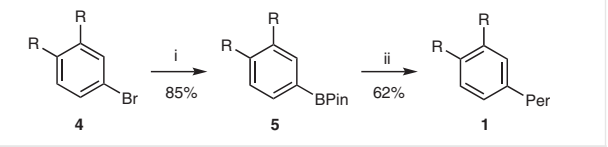
logues, and so their separation could be performed on a multigram scale. As before, $OctMe_2SiPer$ reacted with NBS in CH_2Cl_2 to form PerBr in almost quantitative yield.



Scheme 3 Synthesis of (octyldimethylsilyl)-substituted perylene

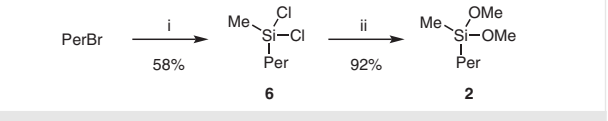
Thus, we have developed a new three-step protocol that can be used for large-scale preparation of 3-bromoperylene. This procedure gave analytically pure PerBr in >70% overall yield starting from a 25 gram sample of perylene.

Synthesis of the perylene-tagged dibutylphathalate **1** is illustrated in Scheme 4. Bromination of phthalic anhydride with bromine in aqueous NaOH[22] followed by esterification with ^{n}BuOH gave **4**, which was then borylated with $(BPin)_2$ via the Miyaura protocol[23] in the presence of 5 mol% of $Pd(OAc)_2/2Ph_3P$ and anhydrous KOAc. The boronic acid ester **5** was introduced into the $Pd(PPh_3)_4$-catalyzed Suzuki–Miyaura reaction[24] with PerBr to give the desired coupling product **1**.



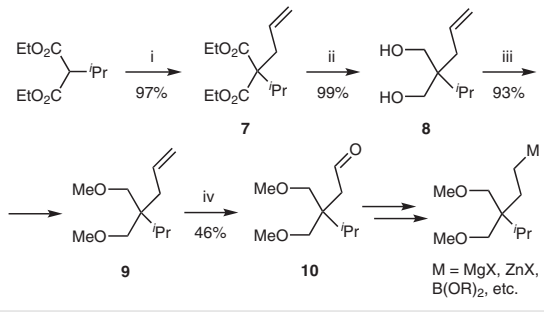
Scheme 4 Synthesis of diester **1** (R = $CO_2{}^n$Bu). *Reagents and conditions*: (i) $(BPin)_2$, $Pd(OAc)_2$, Ph_3P, KOAc, THF; (ii) $Pd(PPh_3)_4$, K_2CO_3, toluene–EtOH–H_2O.

Synthesis of the perylene-tagged silane-based donor **2** was carried out via reaction of 3-perylenyllithium with $MeSiCl_3$[25] followed by substitution of the chlorine atoms at silicon with OMe moieties by treatment with methanol–pyridine (Scheme 5). The crude chlorosilane **6** was recrystallized from methylcyclohexane to give almost pure material in 58% yield. The final product **2** was also purified by recrystallization from methylcyclohexane.

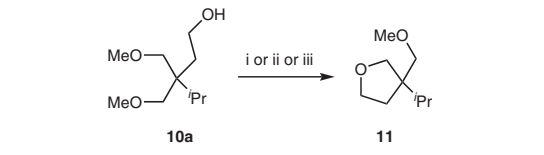


Scheme 5 Synthesis of silylated perylene **2**. *Reagents and conditions*: (i) ^{n}BuLi, $MeSiCl_3$; (ii) MeOH, pyridine.

To synthesize the target electron donor **3**, we decided to use a cross-coupling reaction[26] between PerBr and a suitable organometallic reagent (Scheme 6). First, according to Scheme 6, aldehyde **10** was synthesized and then used as a precursor in a number of attempts to prepare the corresponding alkyl halide, from which an organometallic reagent could be obtained. Unfortunately, our attempts to convert **10** (after reduction to alcohol **10a** with $NaBH_4$) to the corresponding alkyl bromide or iodide failed, since the only obtained compound was the product of the rearrangement shown in Scheme 7. As a result, **11** was isolated in almost quantitative yield in all three cases.

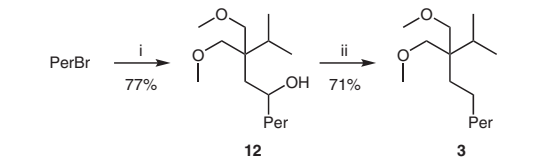


Scheme 6 Synthesis of aldehyde **10**. *Reagents and conditions*: (i) NaH, AllBr; (ii) LAH; (iii) NaH, MeI; (iv) $OsO_4/NaIO_4$.



Scheme 7 Cyclization of **10a** to **11**. *Reagents and conditions*: (i) MsCl, Et_3N, then KBr; (ii) MsCl, Et_3N, then KI; (iii) Ph_3P, CBr_4.

After this failure, we decided to carry out addition of perylenyllithium (derived from PerBr) to aldehyde **10**, followed by catalytic reduction of alcohol **12** thus formed (Scheme 8). This addition was performed as expected, but the subsequent reduction of **12** with hydrogen over Pd/C resulted in partial hydrogenation of the perylene aromatic core. Alternatively, the so-called ionic hydrogenation was



Scheme 8 Synthesis of **3**. *Reagents and conditions*: (i) ^{n}BuLi, then **9**; (ii) Et_3SiH, Ac^FOH ($Ac^F = CF_3C(O)$).

used,[27] and the desired electron donor **3** was obtained in good yield. It should be noted that the main side product of the ionic hydrogenation was a cyclic ether similar to **11**, presumably formed via trapping of the intermediate benzyl cation by oxygen from one of the two methoxy groups.

The molecular structure of **3** was determined by X-ray crystallography (Figure 2). Single crystals of this compound were grown from methylcyclohexane. As confirmed by crystallography analysis, the perylenyl moiety is not planar. The central six-membered ring is twisted with dihedral angles of 0.5° and 3.2° related to the C(7A)–C(6A)–C(19A)–C(18A) and C(3A)–C(4A)–C(11A)–C(12A) carbon atoms.

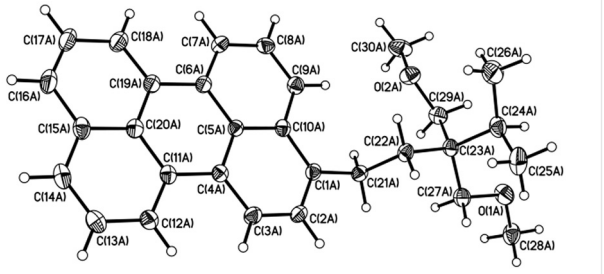


Figure 2 Molecular structure of **3** (thermal ellipsoids drawn at the 50% probability level). Selected bond lengths (Å) are C(1A)–C(21A), 1.511(3); C(1A)–C(2A), 1.366(3); C(2A)–C(3A), 1.402(3); C(3A)–C(4A), 1.379(3); C(4A)–C(11A), 1.474(3); C(4A)–C(5A), 1.428(3); C(5A)–C(10A), 1.433(3).

In the crystal state, each independent molecule forms a centrosymmetric stacking dimer (Figure 3). The distances between the average planes of the polyaromatic fragments in the dimers of molecules A and B are 3.44 and 3.47 Å, respectively. The shortest interatomic distances (Å) in the dimers are: C(1A)···C(5A)$_{2-x,-y,-z}$, 3.432(3); C(3A)···C(9A)$_{2-x,-y,-z}$, 3.466(4); C(1B)···C(5B)$_{1-x,1-y,-z}$, 3.466(3); and C(3B)···C(9B)$_{1-x,1-y,-z}$, 3.496(4).

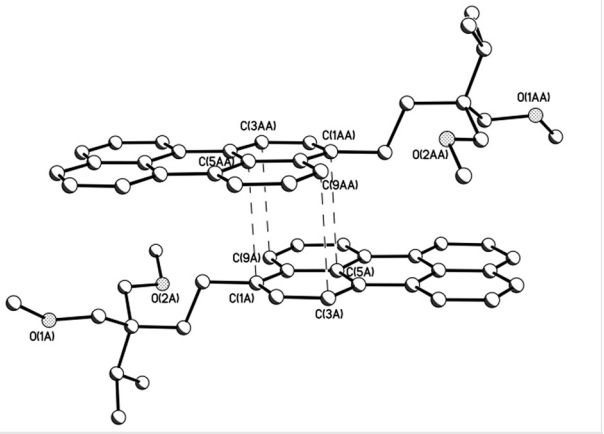


Figure 3 Molecular structure of the stacking dimer of **3**

The molecular structure of TMS_2Per as established by X-ray crystallography is shown in Figure 4. Suitable crystals of the compound were obtained from a methylcyclohexane solution. The central six-membered ring is twisted with dihedral angles 8.1° and 9.9° related to the C(9)–C(8)–C(18)–C(19) and C(5)–C(6)–C(16)–C(15) carbon atoms. In the crystal state, each independent molecule forms a stacking polymer (Figure 5). Fragment of crystal packing: ladder shape stack with interplane distance of 3.33 Å, shortest C···C contacts of C(9)···C(15A)$_{x-1,y,z}$ 3.389(6) Å and C(9)···C(14A)$_{x-1,y,z}$ 3.412(6), and distance between centroids of the polycyclic fragments of 7.02 Å.

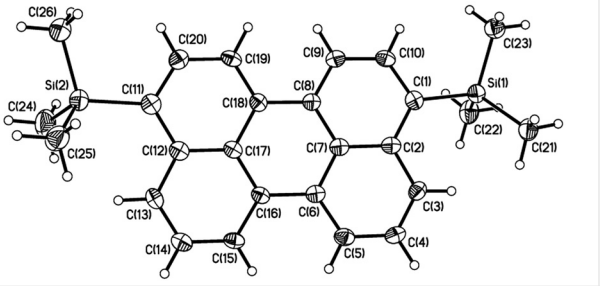


Figure 4 Molecular structure of TMS_2Per (thermal ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) are C(1)–Si(1), 1.883(4); C(11)–Si(2), 1.885(4); C(1)–C(2), 1.432(6); C(1)–C(10), 1.384(5); C(2)–C(7), 1.441(5); C(7)–C(8), 1.422(5); C(8)–C(9), 1.382(5); C(8)–C(18), 1.472(5); C(9)–C(10), 1.404(5).

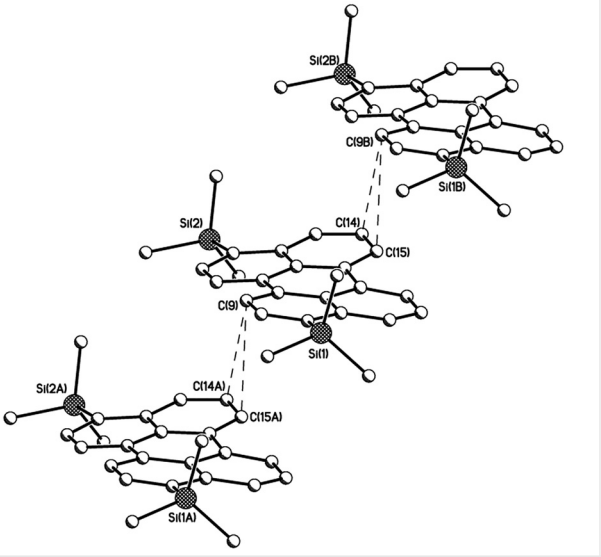


Figure 5 Molecular structure of stacking polymer of TMS_2Per

The UV-vis absorption and fluorescence behavior of perylene and its derivatives was studied in acetonitrile solution. The absorption spectra of the compounds are shown in Figure 6; the quantitative data are summarized in Table 1. UV-vis absorptions of perylene and its derivatives display very similar profiles: the spectra contain a strong

absorption maximum at about 250 nm, with a more or less pronounced shoulder, as well as a strong absorption at 330-450 nm with a vibronic structure. As one could expect, introduction of substituents at the third position of perylene led to a bathochromic shift in the absorption maxima compared to unsubstituted perylene; the largest shift (10 nm) was observed for **1**.

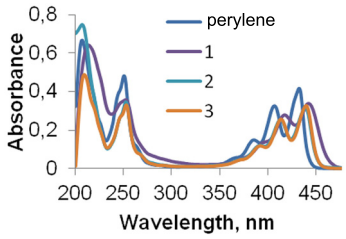


Figure 6 Absorption spectra of donors **1–3** and perylene in MeCN (10^{-5} M) at 20 °C

Table 1 Optical Properties of Donors **1–3** and Perylene in MeCN (10^{-5} M) at 20 °C

Compound	λ_{max}[a] (nm)	λ_{max}[b] (nm)	Stokes shift[c] ($\times 10^5$ cm^{-1})	Φ_f[d]
perylene	432	442	10	0.67
1	442	474	3.1	0.81
2	439	451	8.3	0.75
3	440	452	8.3	0.91

[a] Maximum of absorption spectra.
[b] Maximum of emission spectra (λ_{exc} = 250 nm).
[c] Stokes shift.
[d] Fluorescence quantum yield.

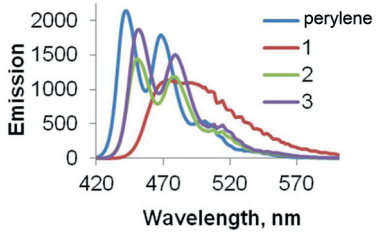


Figure 7 Emission spectra of donors **1–3** and PerBr in MeCN (10^{-5} M) at 20 °C

The fluorescence emission properties of perylene and its derivatives are shown in Figure 7; the quantitative data are summarized in Table 1. All compounds show intense photoluminescence in solution; along with this, we observed red-shift fluorescence for all the compounds in comparison to perylene. The perylenyl derivatives, except for **1**, exhibit a very similar emission profile, which is close to perylene and appears as a mirror image of the absorption spectrum. In the case of **1**, we observed a lower resolution of the vibronic structure in the emission spectra, suggesting electronic communication between the perylene and phenyl units. The emission quantum yields (Φ_f) are in the range of 0.67–0.91.

We developed a reliable and reproducible method for the preparation of multigram quantities of 3-bromoperylene via a three-step protocol starting from unsubstituted perylene with an overall yield as high as 70%. The key step of this protocol was the synthesis of trialkylsilyl-substituted perylenes, which were further separated by means of flash chromatography. The desired mono(trialkylsilyl)perylene was converted into the corresponding bromide. In addition, three perylene-based electron donors (which are examples of three main types of donors: phthalates, diethers, and alkoxysilanes) were successfully synthesized from the thus obtained 3-bromoperylene; the solid-state structure of one target compound was examined by means of X-ray crystallography. Furthermore, we recorded absorption and emission spectra as well as calculated emission quantum yields for all electron donors obtained. The structure and photophysical properties make the electron donors ideal candidates for labeling $MgCl_2$-supported Ziegler–Natta catalysts for subsequent investigation of their properties by means of fluorescence spectroscopy methods.

All reagents were obtained from commercial sources and used as received. Hydrocarbon solvents were dried over 4 Å MS for at least 24 h prior to use. Ethereal solvents were stored over solid KOH for 24 h, then refluxed over and distilled from sodium-benzophenone. MeOH was stored over 3 Å MS for 48 h prior to use. Flash chromatography was carried out on silica gel 60 (40–63 μm). NMR spectra were recorded on Bruker Avance 400 MHz and Bruker Avance II 600 MHz spectrometers at r.t. unless otherwise stated. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with a diamond UATR sampling accessory. Absorptions are reported as values in cm^{-1} followed by the relative intensity: s = strong, m = medium, w = weak. Melting points were measured on a Buchi B-545 instrument. Absorption spectra were recorded on a Hitachi U-1900 spectrophotometer. Emission spectra were recorded on a Hitachi F-7000 luminescence spectrometer; samples were placed in a standard quartz cuvette with a spectral path length of 10 mm. Spectral measurements were carried out for solutions of PerBr and **1–3** in MeCN (10^{-6} M). Quantum yields were calculated by the reference dye (rhodamine B) method from the absorbance and the integrated luminescence intensities. HRMS spectra were measured on an Orbitrap Elite instrument.

Bromoperylene (PerBr)

Mixture of Brominated Perylenes

To a suspension of perylene (25.0 g, 100 mmol, 1 equiv) in DMF (1000 mL) a solution of NBS (23.0 g, 130 mmol, 1.3 equiv) in DMF (400 mL) was added via a syringe pump for 10 h. The obtained mixture was stirred overnight at r.t. and poured into water (2000 mL). The precipitate obtained was filtered off on a glass frit (G3) and was subsequently washed with EtOH (100 mL), Et_2O (100 mL), and finally with CH_2Cl_2 (3 × 100 mL). The obtained solid was dried under vacuum, yielding a mixture of brominated perylenes; yield: 29.8 g (90%); 89% of 3-bromoperylene by GC-MS; yellow solid.

Bromoperylene (PerBr) via OctMe$_2$SiPer; Method A

OctMe$_2$SiPer

To a suspension of the brominated perylenes (12.4 g, 36.7 mmol, 1 equiv) in anhyd THF (500 mL), 2.5 M ^{n}BuLi in hexanes (17.6 mL, 44.1 mmol, 1.2 equiv) was added dropwise at –80 °C. The reaction mixture was stirred for 1 h at this temperature, and then dimethyl(*n*-octyl)silyl chloride (9.87 g, 47.7 mmol, 1.3 equiv) was added and the obtained suspension was stirred overnight at r.t. Thereafter the resulting mixture was carefully poured into water (1000 mL) and the obtained two-phase mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography (silica gel, *n*-hexane/CH_2Cl_2, 4:1). This procedure gave OctMe$_2$SiPer; yield: 12.2 g (78%); yellow solid; mp 100.5–100.9 °C.

IR (neat): 3048w, 2955w, 2919m, 2851w, 1590w, 1457w, 1383w, 1246m, 1063w, 1002m, 846m, 809s, 763s, 682m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15–8.19 (m, 3 H), 8.12 (d, *J* = 7.5 Hz, 1 H), 7.95 (d, *J* = 8.3 Hz, 1 H), 7.64–7.69 (m, 3 H), 7.48–7.52 (m, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 1.22–1.42 (m, 12 H), 0.99–1.03 (m, 2 H), 0.88 (t, *J* = 6.9 Hz, 3 H), 0.50 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5, 137.5, 134.5, 134.1, 132.2, 131.8, 131.4, 131.2, 128.7, 128.5, 127.9, 127.6, 126.51, 126.49, 126.0, 120.3, 120.1, 119.9, 119.3, 33.6, 31.9, 29.3, 24.1, 22.7, 16.5, 14.1, –1.5.

HRMS: *m*/*z* calcd for $C_{30}H_{34}Si$: 422.2430; found: 422.2448.

PerBr from OctMe$_2$SiPer

To a solution of OctMe$_2$SiPer (4.50 g, 10.6 mmol, 1 equiv) in CH_2Cl_2 (100 mL) a solution of NBS (1.90 g, 10.6 mmol, 1 equiv) in CH_2Cl_2 (60 mL) was added for 15 min at –30 °C. The reaction mixture was stirred overnight at r.t. The precipitate obtained was filtered off on a glass frit (G3) and was washed with CH_2Cl_2 (3 × 50 mL). The obtained solid was dried under vacuum, yielding PerBr; yield: 3.56 g (quant.); yellow solid.

Bromoperylene (PerBr) via TMSPer; Method B

TMSPer

To a suspension of the brominated perylenes (1.36 g, 4.43 mmol, 1 equiv) in anhyd THF (50 mL), 2.5 M ^{n}BuLi in hexanes (1.95 mL, 4.87 mmol, 1.1 equiv) was added dropwise at –80 °C. The reaction mixture was stirred for 1 h at this temperature; then TMSCl (0.62 mL, 4.87 mmol, 1.1 equiv) was added, and the obtained suspension was stirred overnight at r.t. Thereafter the resulting mixture was carefully poured into water (100 mL) and the obtained two-phase mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography (silica gel, *n*-hexane/THF, 4:1). This procedure gave TMSPer; yield: 0.78 g (54%); yellow solid; mp 181.2–181.7 °C.

IR (neat): 3047w, 2952w, 2895w, 1497w, 1247w, 1062w, 1002w, 857m, 824s, 808s, 763s, 666m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15–8.19 (m, 3 H), 8.11 (d, *J* = 7.4 Hz, 1 H), 7.95 (d, *J* = 8.2 Hz, 1 H), 7.65–7.69 (m, 3 H), 7.43–7.52 (m, 3 H), 0.51 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 138.1, 134.6, 133.9, 132.3, 131.9, 131.4, 131.2, 128.7, 128.6, 128.2, 128.0, 127.7, 128.6 (overlapping resonances), 126.1, 120.4, 120.2, 120.0, 119.4, 0.2.

HRMS: *m*/*z* calcd for $C_{23}H_{20}Si$: 324.1334; found: 324.1346.

PerBr from TMSPer

To a solution of TMSPer (1.00 g, 3.08 mmol, 1 equiv) in CH_2Cl_2 (50 mL), a solution of NBS (0.55 g, 3.08 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added for 15 min at –30 °C. The reaction mixture was stirred overnight at r.t. The precipitate obtained was filtered off on a glass frit (G3) and was washed with CH_2Cl_2 (3 × 10 mL). The obtained solid was dried in vacuum, yielding PerBr; yield: 1.02 g (quant.); yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 7.5 Hz, 1 H), 8.18 (d, *J* = 7.5 Hz, 1 H), 8.14 (d, *J* = 7.5 Hz, 1 H), 8.07 (d, *J* = 8.4 Hz, 1 H), 7.97 (d, *J* = 8.2 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.69 (d, *J* = 8.2 Hz, 2 H), 7.56 (t, *J* = 8.0 Hz, 1 H), 7.47 (td, *J* = 7.8, 5.1 Hz, 2 H).

HRMS: *m*/*z* calcd for $C_{20}H_{11}Br$: 330.0044; found: 330.0017.

Dibutyl 4-Bromophthalate (4)

To a suspension of 4-bromophthalic acid (25.0 g, 102 mmol, 1 equiv) in toluene (400 mL), ^{n}BuOH (100 mL, 1.09 mol, 10 equiv) and H_2SO_4 (2 mL) were added. The reaction mixture was refluxed using a Dean–Stark head for 2 h and then cooled to r.t. Thereafter the resulting mixture was carefully poured into water (300 mL), and the obtained two-phase mixture was extracted with toluene (2 × 100 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by vacuum distillation (138–140 °C, 0.7 mbar) to give **4**.

Yield: 28.0 g (78%); colorless oil.

IR (neat): 2960m, 2935w, 2874w, 1723s, 1589w, 1254s, 1122s, 1088s, 1068s, 939m, 890w, 838m, 767m, 696w cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 1 H), 7.61 (m, 2 H), 4.28 (q, *J* = 6.5 Hz, 4 H), 1.60–1.78 (m, 4 H), 1.32–1.48 (m, 4 H), 0.86–1.02 (m, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.4, 168.2, 134.2, 133.6, 131.5, 130.5, 130.3, 125.3, 65.7, 65.5, 30.33, 30.32, 19.0, 13.5.

HRMS: *m*/*z* calcd for $C_{16}H_{21}BrO_4$: 356.0623; found: 356.0591.

Compound 5

To a solution of Ph_3P (0.83 g, 3.16 mmol, 0.1 equiv) in anhyd THF (350 mL), $Pd(OAc)_2$ (0.35 g, 1.56 mmol, 0.05 equiv), **4** (11.3 g, 31.6 mmol, 1 equiv), bis(pinacolato)diboron [$(BPin)_2$; 8.84 g, 34.8 mmol, 1.1 equiv], and KOAc (9.30 g, 94.8 mmol, 3 equiv) were added. The obtained suspension was refluxed for 12 h, then carefully poured into water (500 mL); the obtained two-phase mixture was extracted with Et_2O (3 × 250 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography (silica gel, *n*-hexane/ethyl acetate, 10:1), giving **5**.

Yield: 9.50 g (85%); yellow viscous oil.

IR (neat): 2961w, 2935w, 2875w, 1724s, 1359s, 1256s, 1099s, 1068s, 964m, 851s, 710m, 669m cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.92 (dd, *J* = 7.7, 1.0 Hz, 1 H), 7.68 (d, *J* = 7.7 Hz, 1 H), 4.28 (td, *J* = 6.8, 1.5 Hz, 4 H), 1.63–1.78 (m, 4 H), 1.42 (dq, *J* = 15.0, 7.5 Hz, 5 H), 1.33 (s, 13 H), 0.94(t, *J* = 7.3 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.7, 167.6, 137.0, 134.8, 134.3, 131.5, 127.9, 84.4, 83.5, 64.2, 65.42, 65.38, 30.5, 30.4, 24.7, 19.0, 13.6.

HRMS: *m*/*z* calcd for $C_{22}H_{33}BO_6$: 404.2370; found: 404.2352.

Dichloro(methyl)(perylen-3-yl)silane (6)

To a suspension of PerBr (9.43 g, 28.5 mmol, 1 equiv) in anhyd THF (900 mL), 2.5 M ^{n}BuLi in hexanes (11.4 mL, 28.5 mmol, 1 equiv) was added dropwise at –80 °C. The reaction mixture was stirred for 1 h at

this temperature, then trichloro(methyl)silane (14.0 mL, 114 mmol, 4 equiv) was added, and the obtained suspension was stirred overnight at r.t. Thereafter the resulting mixture was evaporated to dryness, and the residue was redissolved in toluene (300 mL). The resulting suspension was filtered through a pad of Celite 503 and then evaporated to dryness. The residue was recrystallized from toluene and the obtained precipitate was filtered off on a glass frit (G3), washed with cold toluene (3 × 10 mL), and then dried under vacuum yielding **6**.

Yield: 6.04 g (58%); yellow solid; mp 217.0–217.8 °C.

IR (neat): 2961w, 2935w, 2875w, 1724s, 1359s, 1256s, 1099s, 1068s, 964m, 851s, 710m, 669m cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.27 (m, 3 H), 8.14 (dd, *J* = 7.9, 3.2 Hz, 2 H), 7.93 (d, *J* = 7.7 Hz, 1 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.58 (t, *J* = 7.9 Hz, 1 H), 7.44–7.53 (m, 2 H), 1.24 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$, 55 °C): δ = 135.0, 130.4, 129.6, 129.1 (three overlapped resonances), 128.5, 128.2, 127.3, 127.2, 126.8, 126.6, 121.5, 120.9, 120.6, 118.9. 6.9. (Due to the very low solubility of the compound in $CDCl_3$, even at elevated temperatures, we were not able to detect all carbons in the ^{13}C NMR spectrum.)

HRMS: *m*/*z* calcd for $C_{21}H_{14}Cl_2Si$: 364.0242; found: 364.0261.

Diethyl 2-Allyl-2-isopropylmalonate (7)

To a suspension of NaH (6.23 g, 260 mmol, 1.05 equiv) in anhyd THF (1000 mL), diethyl 2-isopropylmalonate (50.0 g, 247 mmol, 1 equiv) was added dropwise for 10 min at 0 °C. The resulting mixture was stirred at this temperature for 30 min, then allyl bromide (31.5 g, 260 mmol, 1.05 equiv) was added dropwise, and the reaction mixture was stirred overnight at r.t. Thereafter the resulting mixture was carefully poured into water (2000 mL), and the obtained two-phase mixture was extracted with Et_2O (3 × 300 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. This procedure gave **7**; yield: 58.5 g (97%); colorless oil.

IR (neat): 3080w, 2980w, 2939w, 2880w, 1724s, 1640w, 1465w, 1369w, 1275m, 1226s, 1136m, 1042s, 918m, 858w cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.74 (ddt, *J* = 17.1, 10.0, 7.2 Hz, 1 H), 4.91–5.16 (m, 2 H), 4.17 (q, *J* = 7.1 Hz, 4 H), 2.64 (d, *J* = 7.2 Hz, 2 H), 2.30 (spt, *J* = 6.9 Hz, 1 H), 1.24 (t, *J* = 7.2 Hz, 6 H), 0.98 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.7, 133.5, 118.1, 61.7, 60.7, 38.1, 31.7, 18.4, 14.1.

HRMS: *m*/*z* calcd for $C_{13}H_{22}O_4$: 242.1518; found: 242.1533.

Compound 8

To a suspension of LAH (27.4 g, 723 mmol, 3 equiv) in anhyd Et_2O (1500 mL), **7** (58.5 g, 241 mmol, 1 equiv) was added dropwise for 1 h at 0 °C. The reaction mixture was stirred for 4 h at r.t., then carefully quenched with water (60 mL). The resulting suspension was filtered through a pad of Celite 503. The organic layer was separated, dried over Na_2SO_4, and then evaporated to dryness. This procedure gave **8**; yields 38.0 g (quant.); colorless oil.

IR (neat): 3349s, 3076w, 2961m, 2935m, 2883m, 1638w, 1440m, 1388m, 1175w, 1036s, 995s, 911s cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.74–5.93 (m, 1 H), 4.97–5.16 (m, 2 H), 3.75 (d, *J* = 10.9 Hz, 2 H), 3.65 (d, *J* = 10.8 Hz, 2 H), 2.40 (s, 2 H), 2.13 (d, *J* = 7.5 Hz, 2 H), 1.83–1.98 (m, 1 H), 0.89 (d, *J* = 7.0 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 134.9, 117.5, 67.7, 43.1, 34.2, 28.4, 17.03.

HRMS: *m*/*z* calcd for $C_9H_{18}O_2$: 158.1307; found: 158.1321.

Compound 9

To a suspension of NaH (12.1 g, 504 mmol, 2.1 equiv) in anhyd THF (1000 mL), **8** (38.0 g, 240 mmol, 1 equiv) was added dropwise for 10 min at 0 °C. The resulting mixture was stirred at this temperature for 30 min, then MeI (85.2 g, 600 mmol, 2.5 equiv) was added dropwise, and the reaction mixture was stirred overnight at r.t. Thereafter the resulting mixture was carefully poured into water (2000 mL), and the obtained two-phase mixture was extracted with Et_2O (3 × 300 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. This procedure gave **9**; yield: 41.4 g (93%); colorless oil.

IR (neat): 3075w, 2977w, 2921w, 2875m, 2809w, 1638w, 1459w, 1386w, 1199w, 1108s, 997w, 959w, 910m cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.75–5.92 (m, 1 H), 4.89–5.10 (m, 2 H), 3.28 (s, 6 H), 3.24 (s, 4 H), 2.09 (d, *J* = 7.4 Hz, 2 H), 1.77 (spt, 1 H), 0.89 (d, *J* = 7.0 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 135.7, 116.6, 75.1, 59.0, 43.1, 36.1, 30.6, 17.7.

HRMS: *m*/*z* calcd for $C_{11}H_{22}O_2$: 186.1620; found: 186.1596.

Compound 10

To a solution of **9** (41.4 g, 220 mmol, 1 equiv) and OsO_4 (570 mg, 2.2 mmol, 0.01 equiv) in a THF–water mixture (800 mL, 3:1), $NaIO_4$ (100 g, 470 mmol, 2.1 equiv) was added in small portions for 45 min. The resulting suspension was additionally stirred for 2 h, then filtered through a pad of Celite 503. The filtrate was extracted with Et_2O (3 × 300 mL) and the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by fractional distillation under reduced pressure. This procedure gave **10**; yield: 18.9 g (46%); colorless oil; bp 88 °C/2 mbar.

IR (neat): 2963w, 2925w, 2879w, 2812w, 2749w, 1716s, 1462w, 1391w, 1199m, 1105s, 963m cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, *J* = 3.2 Hz, 1 H), 3.36 (s, 4 H), 3.27 (s, 6 H), 2.30 (d, *J* = 3.2 Hz, 2 H), 1.89 (spt, *J* = 7.0 Hz, 1 H), 0.87 (d, *J* = 7.0 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 202.9, 74.2, 58.9, 45.8, 44.8, 30.4, 17.2.

HRMS: *m*/*z* calcd for $C_{10}H_{20}O_3$: 188.1412; found: 188.1422.

Compound 10a

To a solution of **10** (3.00 g, 16.0 mmol, 1 equiv) in THF (30 mL) and MeOH (15 mL), $NaBH_4$ (0.90 g, 24.0 mmol, 1.5 equiv) was added in small portions at r.t. The resulting mixture was stirred overnight, diluted with brine, and extracted with Et_2O (2 × 30 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. This procedure gave **10a**; yield: 2.60 g (86%); colorless oil.

IR (neat): 3400w, 2960w, 2922m, 2876m, 2809w, 1460w, 1450w, 1385w, 1198m, 1106s, 1035m, 1011m, 958m cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (br.s, 1 H), 3.53–3.56 (m, 2 H), 3.21–3.30 (m, 10 H), 1.77–1.88 (m, 1 H), 1.55–1.58 (m, 2 H), 0.79 (d, *J* = 7.0 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.0, 59.0, 58.4, 42.3, 35.6, 30.2, 17.0.

HRMS: *m*/*z* calcd for $C_{10}H_{22}O_3$: 190.1569; found: 190.1558.

Compound 11

To a solution of **10a** (1.50 g, 7.90 mmol, 1 equiv) in CH_2Cl_2 (35 mL), Et_3N (1.12 g, 11.1 mmol, 1.4 equiv) was added. The resulting mixture was cooled to 0 °C and MsCl (1.17 g, 10.2 mmol, 1.3 equiv) was added dropwise and the mixture was stirred for 2 h at the same temperature. Brine (50 mL) was added to the mixture and the organic layer was separated, dried over Na_2SO_4, and then evaporated to dryness. The residue was redissolved in DMF (30 mL) and KI (3.72 g, 22.0 mmol, 3 equiv) was added in portions. The resulting viscous reaction mixture was stirred at 65 °C for 20 min, poured into brine (100 mL), and extracted with hexane (2 × 50 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography (silica gel, *n*-hexane/Et_2O, 5:1). This procedure gave **11**; yield: 0.80 g (68%); yellow oil.

IR (neat): 2961m, 2930w, 2873m, 2810w, 1466w, 1389w, 1368w, 1200m, 1177m, 1108s, 1072m, 1047m, 965m, 942m, 921m cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.72–3.81 (m, 2 H), 3.60–3.62 (m, 1 H), 3.52–3.54 (m, 1 H), 3.29 (s, 3 H), 3.25–3.27 (m,2 H), 1.76–1.86 (m, 1 H), 1.57–1.73 (m, 2 H), 0.89 (d, *J* = 7.0 Hz, 3 H), 0.88 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.2, 74.4, 68.3, 59.1, 50.3, 32.6, 32.0, 18.6, 18.4.

HRMS: *m*/*z* calcd for $C_9H_{18}O_2$: 158.1307; found: 158.1319.

Compound 12

To a suspension of PerBr (13.0 g, 39.3 mmol, 1 equiv) in anhyd THF (500 mL), 2.5 M ^{n}BuLi in hexanes (16.0 mL, 39.3 mmol, 1 equiv) was added dropwise at –80 °C. The reaction mixture was stirred for 1 h at this temperature, then **10** (8.13 g, 43.2 mmol, 1.1 equiv) was added dropwise, and the obtained suspension was stirred overnight at r.t. Thereafter the resulting mixture was carefully poured into water (500 mL), and the obtained two-phase mixture was extracted with CH_2Cl_2 (3 × 500 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography (silica gel, *n*-hexane/CH_2Cl_2, 1:1). This procedure gave **12**; yield: 13.0 g (77%); yellow solid; mp 146.8–147.3 °C.

IR (neat): 3452w, 3050w, 2952w, 2896w, 2815w, 1589w, 1386m, 1185w, 1098s, 1063m, 971m, 822m, 766s cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.30 (m, 4 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.84 (d, *J* = 7.9 Hz, 1 H), 7.66 (dd, *J* = 7.8, 5.4 Hz, 2 H), 7.39–7.55 (m, 3 H), 5.51 (d, *J* = 10.3 Hz, 1 H), 3.59–3.79 (m, 2 H), 3.51 (s, 3 H), 3.36–3.48 (m, 5 H), 1.96–2.10 (m, 2 H), 1.80 (dd, *J* = 15.3, 10.4 Hz, 1 H), 0.86 (d, *J* = 7.0 Hz, 3 H), 0.88 (d, *J* = 7.0 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.8, 134,6, 131.7, 131.4 (three overlapped resonances), 129.9, 128.9, 128.5, 127.6, 127.3, 126.5, 126.4, 126.2, 123.4, 123.0, 120.3, 120.1, 119.9, 119.8, 76.1, 73.9, 66.3, 59.2, 59.1, 44.2, 43.1, 31.7, 17.2, 17.0.

HRMS: *m*/*z* calcd for $C_{30}H_{32}O_3$: 440.2351; found: 440.2381.

Compound 1

To a solution of K_2CO_3 (9.90 g, 71.6 mmol, 2 equiv) in water (600 mL), PerBr (10.8 g, 32.6 mmol, 1 equiv), **5** (14.5 g, 35.8 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (2.07 g 1.79 mmol, 0.05 equiv) and MeOH (100 mL) were added. The obtained suspension was refluxed for 10 h, then carefully poured into water (500 mL), and the obtained two-phase mixture was extracted with toluene (3 × 350 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography (silica gel, *n*-hexane/CH_2Cl_2, 3:1). The obtained oil was triturated with MeOH (30 mL). The formed precipitate was filtered off on a glass frit (G3), washed with CH_2Cl_2 (3 × 10 mL), and then dried under vacuum, yielding **1**; yield: 11.8 g (62%); yellow solid; mp 115.9–116.4 °C.

IR (neat): 2958w, 2933w, 2873w, 1721s, 1601w, 1280s, 1243s, 1122s, 1069s, 828m, 809s, 766s cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.21 (m, 4 H), 7.80–7.94 (m, 2 H), 7.59–7.76 (m, 4 H), 7.36–7.54 (m, 4 H), 4.26–4.43 (m, 4 H), 1.66–1.84 (m, 4 H), 1.37–1.54 (m, 4 H), 0.88–1.05 (m, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7, 167.3, 143.8, 137.3, 134.4, 132.9, 132.3, 132.1, 131.4, 131.4, 130.9, 130.6, 130.6, 130.0, 129.1, 128.8, 128.3, 127.9, 127.8, 127.6, 126.8, 126.4, 126.4, 125.0, 120.4, 120.3, 120.3, 119.6, 77.3, 76.7, 65.7, 65.6, 30.6, 30.5, 19.2, 19.1, 13.7, 13.7.

HRMS: *m*/*z* calcd for $C_{36}H_{32}O_4$: 528.2301; found: 528.2317.

Compound 2

To a solution of **6** (9.00 g, 24.6 mmol, 1 equiv) in toluene (300 mL), MeOH (18.0 mL) was added dropwise at 0 °C. To the obtained solution pyridine (4.00 mL, 51.2 mmol, 1 equiv) was added dropwise, and the reaction mixture was stirred for 6 h at r.t. Thereafter the obtained suspension was evaporated to dryness, and the residue was extracted with boiling methylcyclohexane (400 mL). The obtained solution was evaporated to dryness, yielding **2**; yield: 8.05 g (92%); yellow solid; mp 149.6–149.9 °C.

IR (neat): 3048w, 2937w, 2834w, 1591w, 1498w, 1384w, 1256w, 1187w, 1067s, 1003w, 811s, 761s, 686m cm^{-1}.

^1H NMR (400 MHz, CD_2Cl_2): δ = 8.18–8.29 (m, 4 H), 8.15 (d, *J* = 8.3 Hz, 1 H), 7.90 (d, *J* = 7.4 Hz, 1 H), 7.72 (t, *J* = 8.2 Hz, 2 H), 7.45–7.60 (m, 3 H), 3.63 (s, 6 H), 0.49 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.4, 135.6, 134.5, 133.4, 131.6, 131.5, 131.3, 130.9, 128.6, 128.5, 128.3, 127.8, 127.8, 126.9, 126.6, 126.5, 120.7, 120.3, 120.1, 119.3, 50.6, –3.8.

HRMS: *m*/*z* calcd for $C_{23}H_{23}O_2Si$: 356.1233; found: 356.1211.

Compound 3

To a solution of **12** (13.0 g, 29.5 mmol, 1 equiv) in CH_2Cl_2 (400 mL), Et_3SiH (23.5 mL, 148 mmol, 5 equiv) was added. To the obtained solution trifluoroacetic acid (12.0 mL, 148 mmol, 5 equiv) was added dropwise at –20 °C. The reaction mixture was stirred for 6 h at r.t. Thereafter the resulting mixture was carefully poured into water (500 mL), and the obtained two-phase mixture was extracted with CH_2Cl_2 (3 × 300 mL). The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by column chromatography (silica gel, *n*-hexane/CH_2Cl_2, 1:1). This procedure gave **3**; yield: 8.80 g (71%); yellow solid; mp 136.0–136.7 °C.

IR (neat): 2965w, 2927w, 2869w, 1387m, 1189w, 1098s, 975w, 826m, 813s, 772s, 756s cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.05–8.27 (m, 4 H), 7.96 (d, *J* = 8.4 Hz, 1 H), 7.64 (t, *J* = 7.6 Hz, 2 H), 7.38–7.56 (m, 3 H), 7.33 (d, *J* = 7.7 Hz, 1 H), 3.43 (s, 4 H), 3.40 (s, 6 H), 2.94–3.09 (m, 2 H), 1.96 (spt, *J* = 6.8 Hz, 1 H), 1.64–1.82 (m, 2 H), 0.96 (d, *J* = 7.0 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.0, 134.6, 133.0, 131.6, 131.5, 131.5, 129.2, 129.0, 128.5, 127.5, 127.1, 126.7, 126.5, 126.4, 126.1, 124.0, 120.1, 120.0, 119.9, 119.5, 77.3, 76.7, 75.3, 59.1, 43.0, 33.4, 30.7, 28.0, 17.8.

HRMS: *m*/*z* calcd for $C_{23}H_{23}O_2Si$: 424.2402; found: 424.2431.

Crystallographic Data

CCDC-1848244 (**3**) and CCDC-1848243 (TMS_2Per) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611085.

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