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Synthesis of Core-Modified Third-Generation Light-Driven Molecular Motors

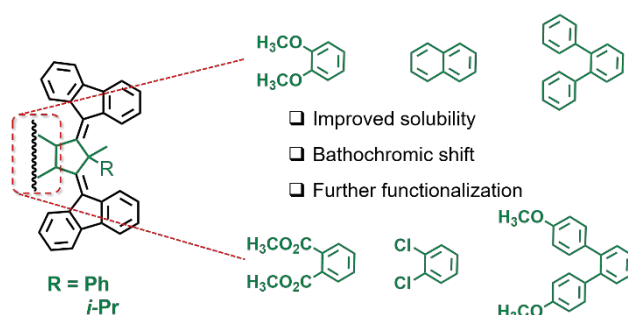
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KEYWORDS: light-driven rotary motors, molecular machines, core-substituted motors, third-generation molecular motors.

ToC GRAPHIC:



ABSTRACT:

The synthesis and characterization of a series of light-driven third-generation molecular motors featuring various structural modifications at the central aromatic core are presented. We explore a number of substitution patterns, such as 1,2-dimethoxybenzene, naphthyl, 1,2-dichlorobenzene, 1,1':2',1''-terphenyl, 4,4''-dimethoxy-1,1':2',1''-terphenyl, and 1,2-dicarbomethoxybenzene, considered essential for designing future responsive systems. In many cases, the synthetic routes for both synthetic intermediates and motors reported here are modular, allowing for their post-functionalization. The structural modifications introduced in the core of the motors result in improved solubility and a bathochromic shift of the absorption maxima. These features, in combination with a structural design that presents remote functionalization of the stator with respect to the fluorene rotors, make these novel motors particularly promising as light-responsive actuators in covalent and supramolecular materials.

INTRODUCTION

The field of molecular machines and motors has experienced amazing developments enabling a transition from molecules to dynamic molecular systems.^{1,2,11–15,3–10} One reason for this development relies on the promise that the integration of these artificial molecular tools into functional materials provides the opportunity for dynamic, responsive and adaptive properties.^{16–18} Moreover, the possibility to perform work upon applying an external stimulus in the form of chemical energy or light^{7,19} represents an appealing perspective for material science. In this context, light-driven rotary molecular motors represent promising candidates for further investigation due to their ability to undergo 360° unidirectional rotary motion upon irradiation.^{20–25} Recent examples of molecular motors embedded in light-responsive polymer networks,^{26,27} surfaces,²⁸ and metal organic frameworks^{29–31} (MOFs) have shown some of the future directions of stimuli-responsive materials. In order to advance the field and envision further opportunities to explore, fundamental work on the design and synthesis of novel molecular motor structures is paramount.

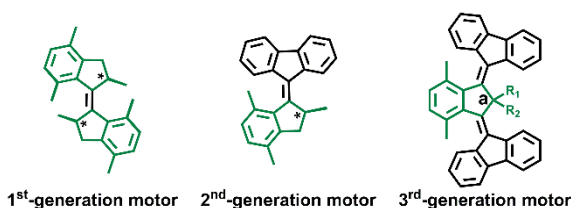


Figure 1. General chemical structure of first- (left), second- (center) and third-generation (right) molecular motors.

The light-driven molecular motors developed in our group are based on overcrowded alkenes that undergo 360° unidirectional rotary motion thanks to a unique interplay between point and helical chirality.^{32–34} These molecular systems are classified into three generations, depending on the number of stereogenic centers, which control the unidirectionality of the rotary motion.³⁴ First- and second-generation molecular motors possess two³⁵ and one

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2
3 stereogenic center,³⁶ respectively, while the recently developed third-generation molecular
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5 motors^{37,38} are *meso*-structures. General chemical structures of first-, second- and third-
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7 generation motors are shown in Figure 1.
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10 Third-generation molecular motors can be considered as a combination of two second-
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12 generation motors with opposite helicity.^{37,38} They feature one center of pseudo-asymmetry
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14 (denoted with the letter **a** in Figure 1) that allows for the unidirectional rotary motion of the
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16 parallel rotors with respect to the central aromatic core, meaning that one rotor rotates
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18 clockwise and the other anti-clockwise.^{37,38} Drawing a parallel with the macroscopic world, the
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20 fluorene rotors rotate similarly to the left and right wheels of a car from the perspective of the
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22 driver. This peculiar feature makes this generation of motors particularly appealing for
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24 locomotion and cargo transport applications, since the combination of the unidirectional rotary
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26 motions of the two rotors should result in unidirectional translation, as conceptually
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28 demonstrated with the nanocar.³⁹
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33 Previous investigations on light-driven third-generation motors carried out in our group
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35 focused on *i*) the introduction of the concept of unidirectional rotary motion in achiral light-
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37 driven molecular motors,³⁷ and *ii*) the consequences of structural variations on speed and
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39 unidirectionality.³⁸ Concerning *ii*, particular attention was dedicated to the role of the
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41 substituents at the pseudo-asymmetric carbon atom, while no synthetic work was carried out
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43 on the central aromatic core that presented either a benzene or *p*-xylene moiety. Reliable
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45 procedures for the modification of the core of these motors are highly desirable, as it would
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47 greatly facilitate their incorporation into functional materials. We now report the synthesis and
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49 characterization of a library of core-modified third-generation light-driven molecular motors
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51 (Chart 1). Most of the new motors (**2-7** and **9**) present either the methyl, phenyl (Me,Ph) or
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53 methyl, *iso*-propyl (Me,*i*-Pr) combination of substituents at the pseudo-asymmetric carbon
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55 atom. These combinations of substituents have been reported to lead to 70% and 100%
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unidirectionality, respectively.³⁸ The octadecyl, phenyl (C_{18} ,Ph) combination was installed in motor **8**, instead. The replacement of the Me substituent with more sterically hindered C_{18} should result in an increase in unidirectionality from 70 to 78%.³⁸ Despite this modest effect, our major motivation for the C_{18} ,Ph combination was its potential use to facilitate the deposition of third generation motors onto solid supports, since long alkyl chains are typically responsible for more favorable molecule-surface interactions. We focused on a number of motifs for the central aromatic core, such as 1,2-dimethoxybenzene (**2**), naphthyl (**3**), 1,2-dichlorobenzene (**4**), 1,1':2',1''-terphenyl (**5**), 4,4''-dimethoxy-1,1':2',1''-terphenyl (**6**), and 1,2-dicarbomethoxybenzene (**9**). Therefore, what distinguishes these motors from previous examples is the presence of substituents on the central aromatic cores, which results in 1) bathochromic shifts of the absorption maxima, and 2) ample possibilities for further functionalization/integration into light-responsive systems/materials and surface anchoring.

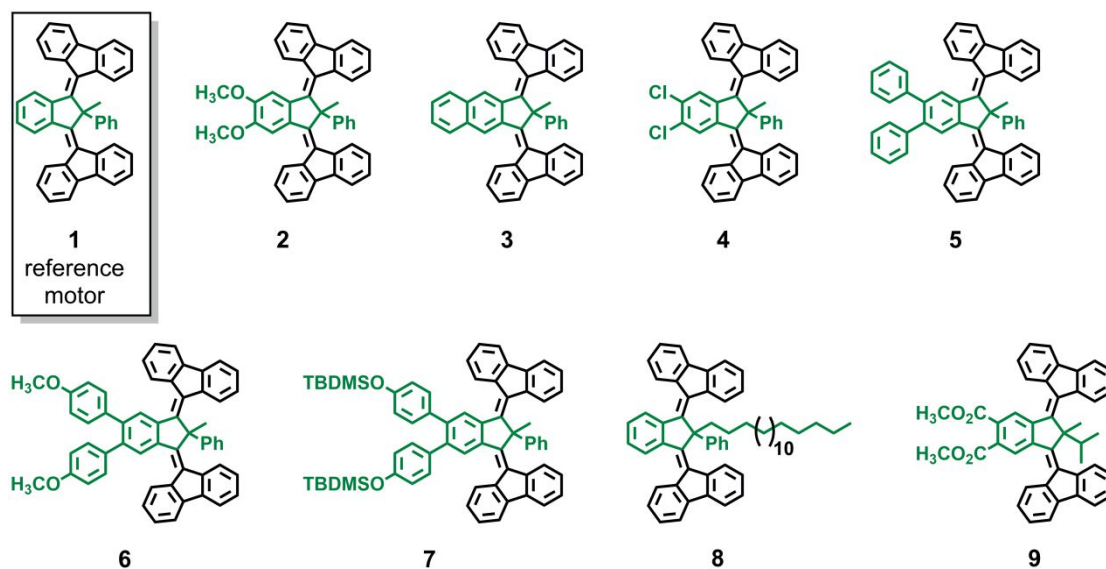
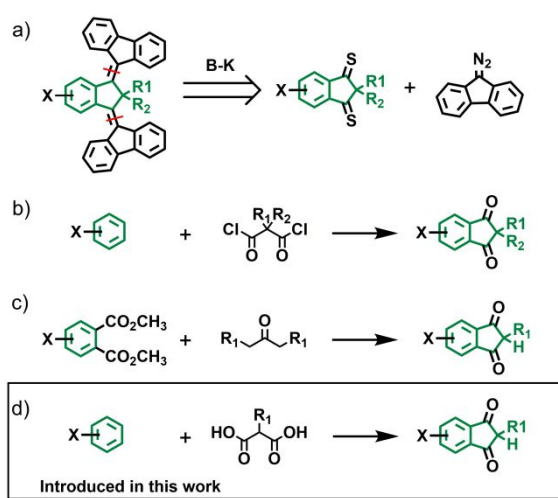


Chart 1. Chemical structures of the third-generation motors presented here.

RESULTS AND DISCUSSION

The key step in the synthesis of overcrowded alkene-based third-generation molecular motors is the Barton-Kellogg olefination (B-K reaction).^{37,38} This approach is shown in Scheme

1a, where disconnection at the level of the overcrowded alkene moieties results in two building blocks: an indanedithione and a diazo compound. The high stability of indanedithiones deriving from the 1,3-indanedione skeleton with a quaternary carbon atom in the α -position to the two thiocarbonyl moieties, as well as that of 9-diazo fluorene, makes this combination of reactants particularly convenient. Both can be stored as stable synthetic intermediates without the necessity to generate them *in situ* or use them immediately after purification. The use of indanedithiones which can be directly prepared from the diketone precursors shifts the attention to the synthesis of 1,3-indanedione derivatives. In previous studies,^{37,38} we have successfully prepared these compounds using Friedel-Crafts acylation of electron-rich aromatic compounds (Scheme 1b), or NaH-induced Claisen condensation between a dimethyl phthalate-type derivative and symmetrical ketones with two methylene groups at the α position (Scheme 1c).^{40,41} In the present study, we predominantly applied the Claisen condensation approach in view of its more widely compatible reaction conditions. However, we also adopted a third synthetic strategy consisting of Friedel-Crafts acylation with malonic acids in polyphosphoric acid⁴¹ (PPA) (Scheme 1d). Although less general than the Claisen condensation,⁴⁰ the PPA-strategy can save many synthetic steps with certain core designs.

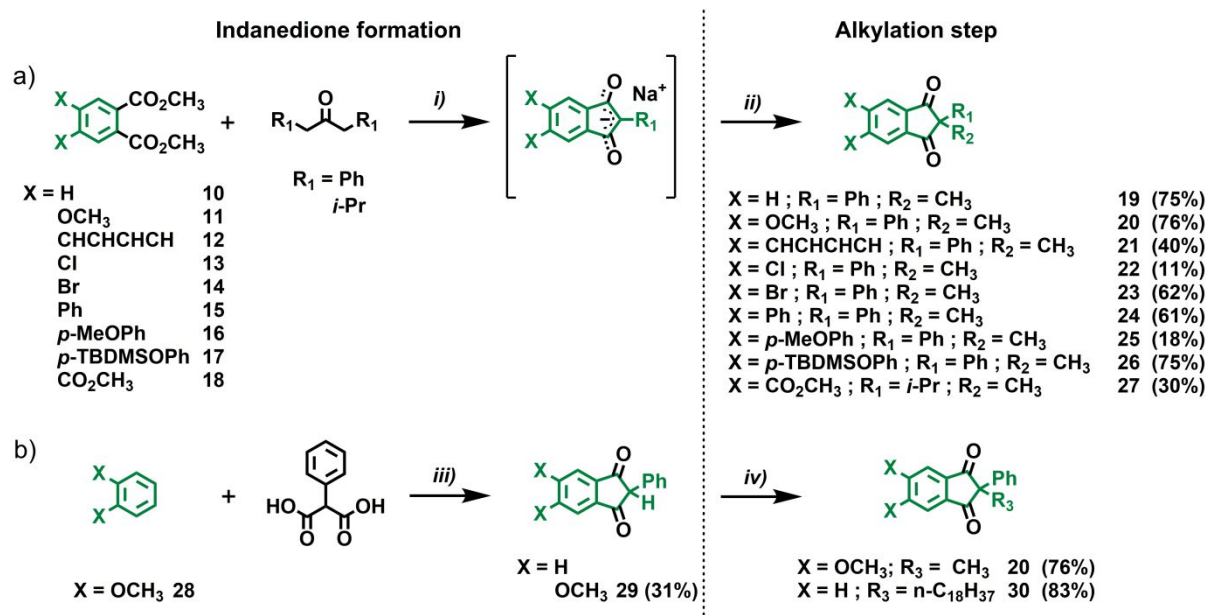


Scheme 1. (a) Retrosynthetic approach for third-generation motors. Approaches for the synthesis of 1,3-indanedione derivatives based on (b) Friedel-Crafts acylation with acyl

chlorides, (c) NaH-induced Claisen condensation, and (d) PPA-induced Friedel-Crafts acylation with malonic acids.

Synthesis of motor cores

As indicated, in most cases we followed the Claisen condensation approach⁴⁰ for preparing the required 1,3-indanediones. Starting from the corresponding dimethyl phthalate-derivatives **10–18**, the NaH-induced cyclization reaction with commercially available 1,3-diphenyl-2-propanone or 2,6-dimethyl-4-heptanone in toluene at 110 °C was performed (Scheme 2a, *i*). The reaction mixtures turned into deep red suspensions at different reaction times (1–5 d), depending on the dimethyl phthalate starting material used. The red precipitates corresponded to the sodium salts of the cyclized products (intermediates between brackets in Scheme 2a), which were not soluble in toluene. Different from our previous reports on third-generation motors,^{37,38} in the present procedure we did not isolate the neutral compounds by treating the Na-salts with hydrochloric acid (HCl). Simple filtration of the red suspensions allowed for obtaining the crude Na-salts, which were then subjected to alkylation with methyl iodide (MeI) in acetone at 60 °C (Scheme 2a, *ii*). These reactions were conducted in the presence of mixtures of Aliquat 336 and potassium fluoride (KF) on celite, as their combination had previously been shown to favor C-alkylation of the enolates over the competing O-alkylation.^{37,38} Core structures **19–27** were obtained in good yields (from 30% to 76%), with the only exceptions of **22** and **25** (11% and 18%, respectively), after chromatographic purification on silica (Scheme 2a).

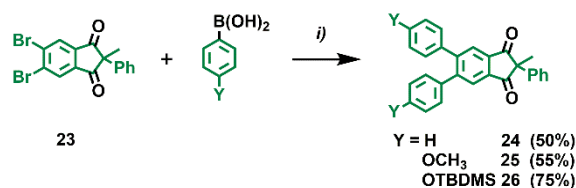


Scheme 2. Synthesis of motor cores applying (a) the Claisen condensation approach, followed by filtration of the crude Na-salts and immediate methylation; (b) the PPA-induced Friedel-Crafts acylation, followed by alkylation of the isolated intermediate. Reaction conditions: *i*) diester (1 eq), 1,3-diphenyl-2-propanone or 2,6-dimethyl-4-heptanone (1.5 eq.), NaH 60 wt% (2 eq.), Toluene, 110 °C, 1–5 d depending on the starting material; *ii*) MeI (2 eq.), Aliquat 336 (0.05 eq.), KF on celite (0.05 eq.), acetone, 60 °C, o/n; *iii*) Phenylmalonic acid (1.5 eq.), PPA (115% H_3PO_4 basis), 90 °C, mechanical stirring, o/n; *iv*) MeI or 1-iodooctadecane (2 eq.), Aliquat 336 (0.05 eq.), KF on celite (0.05 eq.), acetone, 60 °C, o/n.

Given the laborious synthetic routes to obtain starting diester **11** (4 steps),^{42,43} we attempted the direct PPA-induced double Friedel-Crafts acylation of commercially available 1,2-dimethoxybenzene **28** (Scheme 2b). Encouraged by a related functionalization with *iso*-propylmalonic acid,⁴⁴ we slightly adapted the reaction conditions to phenylmalonic acid. Gratifyingly, we successfully obtained **29** in 31% yield after a simple extraction-recrystallization sequence. Alkylation of **29** with MeI afforded motor core unit **20** after chromatographic purification (Scheme 2b, *iv*). It must be emphasized that applying this route is particularly convenient to access **20**, since it shortens the synthesis from 6 steps (4 steps

account for the preparation of **11**) to only 2 steps. Finally, alkylation of 2-phenyl-1H-indene-1,3(2H)-dione³⁸ with 1-iodooctadecane afforded **30** in 83% yield (Scheme 2b, *iv*).

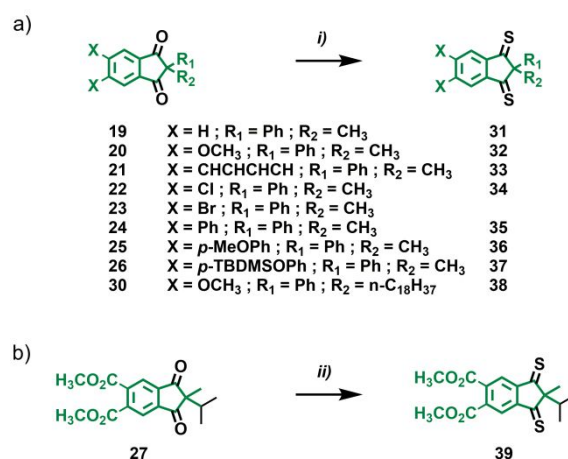
A particularly convenient aspect of some of our synthetic routes to these core structures is their modularity, as additional substituents can be introduced *via* both the dimethyl phthalate as well as core building blocks. Bromo-substituted dimethyl phthalate **14** or 1,3-indanedione **23** could be converted into derivatives **15–17** or **24–26**, respectively, by means of Suzuki–Miyaura cross-coupling reaction with phenyl-boronic acids catalyzed by palladium-tetrakis(triphenylphosphine) ($\text{Pd}(\text{PPh}_3)_4$). Details on the preparation of **14** can be found in the experimental section, while here we briefly discuss the post-modification of **23** (Scheme 3). Applying the Suzuki–Miyaura cross-coupling on this core structure, **24–26** were obtained in 50–75% yield (Scheme 3). While the same reaction on **14** consistently afforded the corresponding esters **15–17** in higher yields (see experimental section), the post-modification of **23** has the additional advantage of diversifying these syntheses after the NaH-induced Claisen condensation, which represents the critical step in the preparation of these core units. Hence, direct modification of **14** is the best option if the target is one molecular design only; alternatively, post-modification of **23** is more convenient when the screening of multiple molecular designs is desired.



Scheme 3. Suzuki-Miyaura cross coupling reaction on indanedione core **23** with phenylboronic acid, 4-methoxyphenylboronic acid, and 4-(*tert*-butyldimethylsilyloxy)phenylboronic acid affording **24**, **25**, and **26**, respectively. Reaction conditions: *i*) boronic acid (2.2 eq.), $\text{Pd}(\text{PPh}_3)_4$ (10 mol%), toluene, 110 °C, 18 h.

Synthesis and characterization of the motors.

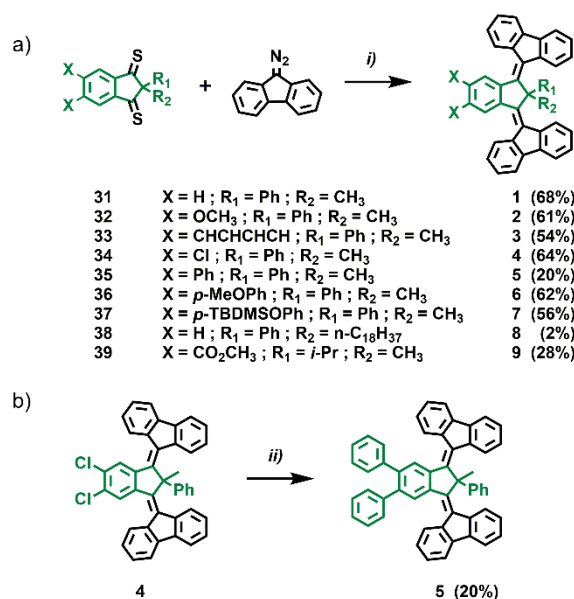
With the 1,3-indanedione derivatives **19–27** and **30** in hand, we then focused on their conversion into indanedithiones, which in some cases was not straightforward. Previous work on third-generation motors highlighted the importance of using mixtures of phosphorous pentasulfide (P_2S_5) and Lawesson's reagent (LR) in boiling toluene.^{37,38} We found that this mixture was necessary in most cases, while treating **20** with only LR sufficed to achieve full conversion (Scheme 4a). This behavior was attributed to the electron-donating effect of the methoxy-substituents. Unfortunately, core unit **23** could not be successfully converted into its corresponding indanedithione, probably due to the electron-withdrawing effect of the two bromine substituents. Besides electronic effects, steric hindrance may also play a role in the 1,3-indanedione→indanedithione conversion. For example, when **30** was subjected to the reaction conditions of Scheme 4a, we obtained a mixture of unreacted **30** as well as mono- and di-substituted (**38**) products that could not be fully separated by chromatography. *Tert*-butyldimethylsilyl- (TBDMS) protecting groups, which are of interest for potential post-functionalization of the motors due to their ease of removal, were found to be particularly inert and survive indanedithione formation. Finally, core **27** could not be converted to indanedithione **39** with the reaction conditions reported in Scheme 4a. We could, however, obtain **39** by reacting **27** in the presence of LR under microwave irradiation for 4 h, albeit in very low yield (8%) (Scheme 4b). These conditions were unsuccessful with **23**, as we only recovered unreacted starting material. Thioketones **31–39** were characterized by 1H NMR to ensure full conversion and were directly (without isolation) used in the subsequent Barton-Kellogg olefination (B-K reaction).



Scheme 4. Preparation of the indanedithiones starting from the corresponding substituted 1,3-indanediones, applying (a) conventional heating and (b) microwave irradiation. Reaction conditions: *i*) P₂S₅ (4 eq.), LR (4 eq.), toluene, 110 °C, o/n; *ii*) LR (8 eq.), toluene, 110 °C, 4 h, microwave irradiation.

B-K reactions were run starting from toluene solutions of indanedithiones **31–39** at room temperature, followed by the addition of solid diazofluorene (Scheme 5a). The typical green-blue toluene solutions of **31–39** turned red immediately upon addition of diazofluorene, and the progress of these reactions was monitored by TLC. Desulfurizing agent hexamethylphosphorous triamide (HMPT) was added when no traces of starting indanedithione were detected and the resulting mixtures were heated up to 90 °C and stirred overnight (Scheme 5a). Motors **1–9** (**1** had previously been reported) were obtained after chromatographic purification. Following the same strategy of post-functionalization previously discussed for core **23**, we highlight the possibility to also access motor **5** *via* post-modification of **4** by direct two-fold catalytic cross-coupling with phenyllithium (Ph-Li) (Scheme 5b). Attempts at preparing **6** *via* similar post modification of **4** resulted in negligible conversions as judged by crude product ¹H-NMR analysis. This justified the choice of the higher yielding B-K reaction to obtain **6** and **7**.

All newly synthesized motors were obtained as powders with colors ranging from orange to deep red, depending on the nature of the core substitution. The core-modified light-driven third-generation motors **2–9** are significantly more soluble than reference motor **1** in halogenated solvents and a number of other organic solvents (acetone, THF, diethyl ether, and ethyl acetate). The presence of substituents at distal positions in the molecular structures with respect to the overcrowded alkene moieties probably results in favored solvation.



Scheme 5. Synthesis of core-modified third-generation molecular motors *via* (a) Barton-Kellogg olefination and (b) direct catalytic cross-coupling post-modification of motor **4** with phenyllithium to yield motor **5**. Reaction conditions: *i*) Diazofluorene (2.5 eq.), toluene, RT, 4–18 h. HMPT (2 eq.), 90 °C, 18 h; *ii*) Dichloro[1,3-bis(2,6-di-3-pentylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) (Pd-PEPPSI-IPent catalyst, 5 mol%), dry toluene, 40 °C, 5 min. Slow addition (1 h) of PhLi (2.5 eq. in 1 mL dry toluene), 40 °C.

Previous work on third-generation molecular motors revealed that the substituents at the pseudo-asymmetric carbon atom **a** (Figure 1) define the number of isomers potentially accessible from one motor structure.³⁸ The steric hindrance of these substituents was found to be the key structural parameter.³⁸ The two substituents at carbon **a** are placed one each in a

pseudo-equatorial and pseudo-axial orientation, and can interconvert their positions through thermal conformational isomerization. Depending on the steric hindrance exerted by the two substituents, the two conformational isomers are not degenerate, with one being energetically preferred. The more stable isomer for reference motor **1** was reported to be the one with the phenyl ring in the pseudo-axial position (*s*-isomer), more remote from the two fluorene moieties.³⁸ This allows the phenyl ring to have more spatial freedom. The ratio between the two isomers with the phenyl ring placed pseudo-axially (*s*-isomer) and pseudo-equatorially (*r*-isomer), respectively, was determined to be 2:1 at room temperature by integrating the two different singlets corresponding to the methyl substituent in the ¹H NMR spectrum of **1**.³⁸ The singlet of the methyl group of the *s*-isomer was more downfield shifted compared to that of the *r*-isomer.³⁸ The two isomers also possess different local asymmetry with respect to the two fluorene moieties and, as a result, third-generation motors with this Me,Ph substitution pattern at carbon **a** are not fully unidirectional. The 2:1 isomer distribution of reference motor **1** means that roughly 67% of the motor population rotate in one direction, while the remaining 33% rotate in the opposite direction, resulting in 34% net unidirectional rotation. The thermal interconversion between the two isomers was confirmed by the observation of signal coalescence in temperature-dependent (TD) NMR studies.³⁸ Replacing the phenyl substituent with the more sterically demanding *iso*-propyl group resulted in exclusive formation of one isomer only. As a result, third-generation motors featuring Me,*i*-Pr substitution on carbon **a** are fully unidirectional, the NMR spectra are characterized by much sharper signals and no coalescence phenomena are observed in TD-NMR studies.^{37,38} The newly synthesized third-generation motors **2–9** perfectly fit into this qualitative description. The ¹H NMR spectra of motors **2–8**, with the Me,Ph substitution pattern, show two almost overlapping singlets for the methyl substituent at room temperature. Moreover, these motors show signal coalescence upon heating/cooling of NMR samples (see SI for ¹H NMR spectra measured at 90 °C and -45 °C).

Measuring ^1H NMR spectra at $-45\text{ }^\circ\text{C}$ for motors **2–8** allows to separate the singlets of the methyl group of the *r*- and *s*-isomers and ultimately determine their degree of unidirectionality at the specific temperature (Table S1). The *s*-isomer, with the methyl group in the pseudo-equatorial position, was the more stable isomer for **2–8**, as suggested by the more intense downfield shifted signal (*vide supra*).³⁸ Hence, motors **2–8** show preferred directional rotary motion, in line with previous findings.^{37,38} Motor **9**, with the Me,*i*-Pr combination, instead, possesses a ^1H NMR spectrum characterized by sharp signals and only one resonance for both the methyl and *iso*-propyl group (see SI), and hence should undergo fully unidirectional rotary motion.

Third-generation molecular motors possess the highest speed of rotation among the three generations of artificial molecular motors (ultra-fast rotary motion). The unidirectional rotary cycle is composed of a photochemical E–Z isomerization (PEZ) followed by subsequent thermal helix inversion (THI).³⁴ This sequence covers the first 180-degree rotation, while another PEZ-THI combination completes the rotary cycle.³⁴ Assuming a high enough photon flux, the THI is considered the rate-limiting step of the rotary cycle, and thus defines the rotary speed of our molecular motors. The ultra-fast rotary motion of third generation molecular motors implies very low thermal activation barriers for THI.³⁸ While the unidirectionality of the rotary motion is controlled by the substituents on carbon **a**, the speed of rotation is mainly governed by the central aromatic core. The limited steric hindrance exerted by the central aromatic core on the fluorene moieties, especially in the case of the unsubstituted benzene core, is the main reason for the high rotary speed. Earlier studies confirmed the ultra-fast rotary motion looking at motor structures that featured the *p*-xylene core and desymmetrized fluorine rotors.³⁷ The lack of readily available *p*-xylene derivatives simultaneously functionalized with two ester moieties in the 1,2-positions and two identical substituents in the 4,5-positions, prevented direct measurement of the ultra-fast rotary motion. The temperatures required for

studying the rotation of motors **2–9** (below $-110\text{ }^{\circ}\text{C}$) are instrumentally inaccessible and/or not compatible with the melting point of many organic solvents. Congruously, any attempt at studying the unidirectional rotary motions of motors **2–9** by ^1H NMR at $-80\text{ }^{\circ}\text{C}$ via *in situ* irradiation with 365 nm, 395 nm, or 405 nm light did not afford any change in their ^1H NMR spectra (see SI). Hence, we anticipate that **2–9** undergo ultra-fast rotary motion by their close structural resemblance to previous third-generation molecular motors.^{37,38} On one hand, this represents a challenge to address in the future for a rigorous physico-chemical understanding of the behavior of these molecules using transient spectroscopy methods, which is part of an upcoming study. On the other hand, it also makes this class of photochemically-driven compounds particularly promising for the preparation of light-responsive materials and actuators, since their use should result in a much faster actuation of the polymeric or supramolecular ensembles they will be embedded in.

Study of the single-crystal X-ray structures of some of the newly synthesized motors highlighted that the core-modifications introduced in the design of **2–9** resulted in significant variations compared to the previous systems. We obtained single crystals of motors **2**, **4** and **5** by slow diffusion of hexane (anti-solvent) into a concentrated 1,2-dichloroethane (solvent) solution of **2**, **4** and **5**.⁴⁵ The crystal structures of motors **4** and **5** are shown in Figure 2a and 2b, respectively, while that of **2** is shown in Figure S88 due to its similarity to the X-ray structure of **4**. Regardless of the presence of both possible isomers (Me,Ph substituents) in solution, all motors crystallized as one single isomer. The same behavior had also been observed in previous investigations,³⁸ with reference **1** crystallizing with the phenyl substituent in the pseudo-axial orientation. While in the single crystals of **4** the phenyl substituent is placed pseudo-axial and has more spatial freedom (Figure 2a), in the crystals of **5** we observed the opposite isomer featuring a pseudo-equatorial phenyl ring (Figure 2b). Interestingly, the two aromatic rings of the 1,1':2',1''-terphenyl system in **5** do not possess the same dihedral angle

(45.54(17)° and 58.57(16)°) with respect to the central aromatic core, which removes the symmetry plane of the molecule in the single crystal.

Finally, further shifting of the absorption spectra of light-triggered molecular motors towards the visible and near-IR region is also highly desirable and of particular attention in recent motor designs.^{31,46–49} The introduction of two methoxy groups in the core of motor **2** resulted in a bathochromic shift of 32 nm compared to **1** (Figure 2c). This was already well visible in the appearance of the two motors in the solid state: while **1** is an orange powder, **2** is deeply red colored. However, while increasing the electron density by means of electron donating substituents proved to be beneficial in this respect, preliminary studies towards electron-withdrawing substituents showed only a modest or no effect (see SI).

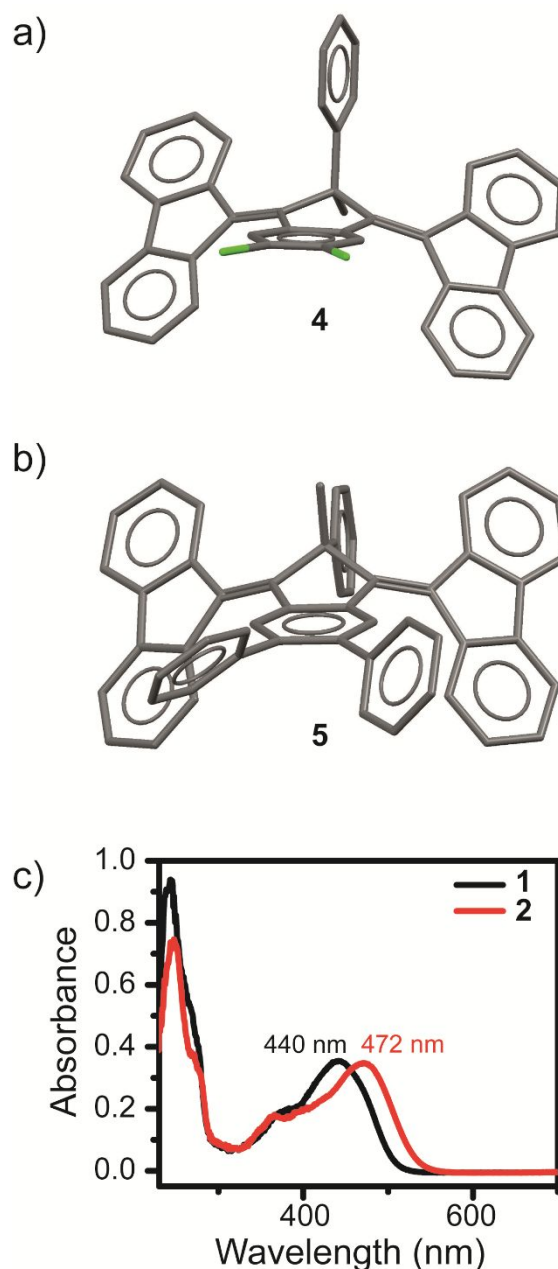


Figure 2. (a) Single-crystal X-ray structure of motor **4**. (b) Single-crystal X-ray structure of motor **5**. Hydrogen atoms are omitted for clarity in the crystal structures. Carbon atoms are depicted in grey, chlorine atoms in green. (c) UV-vis spectrum of reference motor **1** (black trace) and motor **2** (red trace) in CH_2Cl_2 (25 °C, 5×10^{-6} M, optical path 1 cm).

CONCLUSIONS

In conclusion, the synthesis and characterization of several new light-driven third-generation molecular motors with different designs of the central aromatic core and

functionalities is reported. While in previous efforts the focus was exclusively on benzene- and *p*-xylene-type cores, in this investigation a number of moieties were explored, such as 1,2-dimethoxybenzene (**2**), naphthyl (**3**), 1,2-dichlorobenzene (**4**), 1,1':2',1''-terphenyl (**5**), 4,4''-dimethoxy-1,1':2',1''-terphenyl (**6**), and 1,2-dicarbomethoxybenzene (**9**). We present modular and scalable synthetic routes, which further offer the possibility to post-functionalize synthetic intermediates and motors. This aspect is particularly beneficial in case screening of different molecular designs is required to optimize the structure for a specific task. The structural modifications introduced in the newly synthesized motors resulted in an improved solubility compared to reference motor **1**, as well as a bathochromic shift of the absorption spectra. Hence, the core-modifications presented here offer ample opportunity for application/incorporation of these motors in light-responsive materials. In particular, the functionalization of the cores at the distal side with respect to the fluorene rotors makes the design of model motors **2–9** highly promising for ongoing research towards cargo transport and locomotion along tracks.

EXPERIMENTAL SECTION

Instrumentation:

Microwave reactions were performed on a Discover SP Microwave Synthesizer.

Column chromatography was performed using a Grace Reveleris instrument.

¹H NMR and ¹³C NMR spectra were recorded either on a Varian Mercury Vx 400 MHz (100 MHz for ¹³C), Varian Oxford AS 500 MHz (125 MHz for ¹³C) or a Bruker 600 MHz (150 MHz for ¹³C) NMR spectrometers. Chemical shifts are given in ppm (δ) values relative to the solvent (for CDCl₃: ¹H δ: 7.26 and ¹³C δ: 77.16; for Cl₂DCCDCl₂: ¹H δ: 6.00 and ¹³C δ: 73.78). Splitting patterns are labelled as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; h, heptet; m, multiplet.

UV-vis absorption spectra were recorded on a Jasco V-630 or a Hewelett-Packard 8453 spectrometer.

Infrared spectra were recorded on a Perkin Elmer Spectrum One 1600 FT-IR spectrometer or a Perkin Elmer Spectrum Two FT-IR spectrometer, equipped with a Perkin Elmer Universal ATR Sampler Accessory.

High Resolution Mass Spectra (HR-MS) were recorded on an LTQ Orbitrap XL.

Single-crystals were mounted on a cryoloop and placed in the nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and processing was carried out using the Bruker APEX3 software suite.⁵⁰ A multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*).⁵⁰ The structure was solved either using *SHELXS*⁵¹ (LP18006) or *SHELXT*⁵² (18005, 18011), and refinement was performed using *SHELXL*.⁵¹ The hydrogen atoms were generated by geometrical considerations, constrained by idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms.

Materials:

Compound **10** was purchased from TCI. Compound **28** was purchased from Sigma-Aldrich. All other commercially available products were purchased from either TCI, Combi Blocks or Sigma-Aldrich, and used as received.

General method A: procedure for esterification. The desired dicarboxylic acid (1 eq) was loaded in a round bottom flask and dissolved/suspended MeOH (2.2 mL per mmol of acid) at 0 °C. Then, SOCl₂ (4 eq) was added dropwise via syringe. The reaction mixture was heated under to reflux and left overnight. After being cooled to room temperature, the volatiles were removed. The crude mixture was dissolved in DCM and washed with water (2 × 100 mL). The

organic phase was then dried over MgSO_4 , filtered and evaporated to achieve the desired esters. All products were used in the next step without further purification.

General method B: NaH-induced procedure for the core preparation. The appropriate diester (1 eq) and ketone (2 eq) were weighed in a round bottom flask and dissolved in toluene (2 mL per mmol of diester). Sodium hydride on oil (60 wt%) (2 eq) was added in small portions with a spatula. The resulting suspension was stirred for 5 minutes at room temperature under nitrogen, then heated at reflux for 1-5 days. The starting white-grey suspensions turned deep red upon reacting. The mixtures were cooled down to room temperature. The precipitate was filtered, washed with pentane, and dried. The dried solid (powder) was loaded with KF on celite (50 wt%) (0.02 eq) and methyl-N,N,N-trioctan-1-ammonium (0.02 eq) in a round bottom flask. Acetone (same volume as toluene) was added and the mixture was stirred for 5 minutes at room temperature under nitrogen. Methyl iodide (2 eq) or 1-iodooctadecane (2 eq) was added and the reaction mixture was heated at reflux overnight. The reaction mixture changed color from deep red to yellow upon reacting. The solvent was removed and the crude material was dissolved in CH_2Cl_2 and H_2O . The organic phase was washed ($\times 3$) with H_2O , dried over MgSO_4 , filtered. The solvent was removed and the crude material purified by column chromatography (SiO_2 , gradient from 100% pentane to pentane/EtOAc mixtures).

General method D: procedure for indanedithione preparation with conventional heating. The appropriate indanedione (1 eq) was added to an oven-dried round bottom flask under nitrogen. Dry toluene (5 mL per mmol) was added, followed by the addition of P_4S_{10} (4 eq) and Lawesson's reagent (4 eq). The resulting suspension was heated overnight at reflux and monitored with TLC. When full conversion was not achieved overnight, additional P_4S_{10} (4 eq) was added and the reaction kept under reflux for additional 24 hours. The reaction mixture was cooled down to room temperature. The suspension was filtered over a short pad of celite, and the filtered solution (green in most cases) was evaporated. The crude product was immediately

1
2
3 purified with column chromatography (SiO_2 , gradient from 100% pentane to 90:10
4 pentane/EtOAc). In many cases the desired indanedithione was not obtained in 100% purity
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6 due to the presence of other products deriving from non-complete conversion or unknown
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8 impurities. Using these slightly impure indanedithiones in the following Barton-Kellogg
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10 olefinations never affected the outcome of the reactions, hence they did not undergo further
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12 purification.
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17 **General method E: procedure for preparation of indanedithione 39 with microwave**
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19 **heating.** Indanedione **27** (400 mg; 1.26 mmol) was loaded into a 25 mL microwave vial and
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21 dissolved in toluene (10 mL). Lawesson's reagent (8 eq; 4.06 g; 10.05 mmol) was added and
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23 the vial was sealed. The resulting suspension was sonicated for 5 min. The reaction mixture
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25 was heated at 110 °C for 4 hours under microwave irradiation. The suspension was filtered over
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27 a short pad of celite, and the filtered solution was evaporated. The crude product was
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29 immediately purified with column chromatography (SiO_2 , gradient from 100% pentane to 95:5
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31 pentane/EtOAc). Indanedithione **39** was almost always obtained in mixtures with unreacted **27**
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33 and product of single-conversion. Prolonged reaction times resulted in degradation of **39** and/or
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35 no further conversion.
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40 **General method F: procedure for the Barton-Kellogg olefination.** The appropriate
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42 indanedithione (1 eq) was dissolved in toluene (5 mL per mmol of indanedithione). Next, 9-
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44 diazo-9H-fluorenone⁵³ (2.5 eq) was added and the resulting mixture was stirred at room
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46 temperature under a nitrogen atmosphere for 8 hours. Hexamethylphosphanetriamine (2 eq)
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48 was added. The mixture was heated at 90 °C overnight. The volatiles were evaporated under
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50 reduced pressure. The residue was adsorbed on celite and purified by column chromatography
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52 (SiO_2 , gradient pentane/ CH_2Cl_2 ; 0–100%).
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56 **General method G: procedure for the Suzuki couplings.** The appropriate di-bromo
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58 derivative (1 eq) and boronic acid (2.5 eq) were weighed in a round bottom flask and
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dissolved/suspended in toluene (30 mL per mmol of di-bromo derivative) was added. An 8 M aqueous solution of K_2CO_3 (21 eq) was added to the organic phase. The mixture was degassed for 15 minutes by bubbling nitrogen. Palladium(0) tetrakis(triphenylphosphine) (0.1 eq) was added. The reaction mixture was heated at reflux overnight. The reaction mixture was cooled down and loaded into a separatory funnel. The toluene layer was separated, and the aqueous layer washed with CH_2Cl_2 ($\times 3$). All the organic phases were dried over $MgSO_4$ and filtered. After solvents removal, the crude materials were purified by column chromatography (SiO_2 , gradient pentane/EtOAc; 0–50%).

dimethyl 4,5-dimethoxyphthalate (11). Synthesized according to literature procedures.^{42,43} 1H -NMR ($CDCl_3$, 600 MHz, δ): 7.15 (s, 2H), 3.90 (s, 6H), 3.84 (s, 6H). ^{13}C -NMR $\{^1H\}$ ($CDCl_3$, 150 MHz, δ): 167.9, 150.7, 125.2, 111.4, 56.2, 52.6. FT-IR (dry powder) (cm^{-1}): 3018 (*C-H*), 2955 (*C-H*), 1709 (*C=O*). HR-MS (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}O_6Na$ 276.0683; found 276.0680 (0.8 ppm). M_p 86.2–87.1 °C.

dimethyl 4,5-dichlorophthalate (13). Synthesized with general method A. (white solid; 15.8 g; 60.3 mmol; 91% yield). 1H -NMR ($CDCl_3$, 600 MHz, δ): 7.78 (s, 2H), 3.88 (s, 6H). ^{13}C -NMR $\{^1H\}$ ($CDCl_3$, 150 MHz, δ): 166.0, 135.8, 131.4, 131.0, 53.1. FT-IR (dry powder) (cm^{-1}): 3096 (*C-H*), 3037 (*C-H*), 2956 (*C-H*), 1720 (*C=O*). HR-MS (m/z): $[M+H]^+$ calcd for $C_{10}H_9Cl_2O_4$ 262.9872; found 262.9873 (0.2 ppm). M_p 44.5–46 °C.

dimethyl 4,5-dibromophthalate (14). 1,2-dibromo-4,5-dimethyl-benzene (5 g; 18.94 mmol) was weighed in a custom-made teflon beaker equipped with a teflon cap. The compound was suspended in 35 mL of a 30 wt% HNO_3 aqueous solution. A stirring bar was added and the teflon beaker was sealed with the teflon cap. The teflon reactor was inserted into an autoclave. The autoclave was placed on top of a hot plate previously set at 170 °C. The reaction was left overnight, after which it was cooled down to room temperature. The teflon reactor was extracted from the autoclave and the reaction mixture was poured into a pH 14 aqueous solution

(200 mL). The resulting solution was filtered (folded paper filter). The filtered solution was acidified with concentrated (37 wt %) HCl to induce precipitation (addition of HCl significantly developed heat; cool down the mixture during acidification). The precipitate was filtered (Buchner filter) and dried. The obtained white solid (1,2-dibromophthalic acid) was then subjected to esterification following general method A. (white solid; 4.3 g; 12.3 mmol; 65% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 7.96 (s, 2H), 3.91 (s, 6H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 166.1, 134.1, 132.0, 128.4, 53.2. FT-IR (dry powder) (cm⁻¹): 2953 (C-H), 2923 (C-H), 2852 (C-H), 1730 (C=O). HR-MS (*m/z*): [M+H]⁺ calcd for C₁₀H₉Br₂O₄ 352.8842; found 352.8841 (0.2 ppm). M_p 72.6-74.3 °C.

dimethyl [1,1':2',1''-terphenyl]-4',5'-dicarboxylate (15). Synthesized with general method G and purified by column chromatography (SiO₂, gradient pentane/EtOAc; 0–50%). (off-white solid; 2.12 g; 6.12 mmol; 63% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 7.80 (s, 2H), 7.24-7.23 (m, 6H), 7.15-7.13 (m, 4H), 3.94 (s, 6H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 168.0, 143.6, 139.7, 131.4, 130.9, 129.8, 128.3, 127.5, 52.8. FT-IR (dry powder) (cm⁻¹): 2955 (C-H), 1721 (C=O). HR-MS (*m/z*): [M+Na]⁺ calcd for C₂₂H₁₈O₄Na 369.1097; found 369.1094 (0.9 ppm). M_p 108.8-110.1 °C.

dimethyl 4,4''-dimethoxy-[1,1':2',1''-terphenyl]-4',5'-dicarboxylate (16). Synthesized with general method G and purified by column chromatography (SiO₂, gradient pentane/EtOAc; 0–50%). (off-white solid; 7.05 g; 17.3 mmol; 81% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 7.74 (s, 2H), 7.07-7.06 (AA'BB' system, 4H), 6.79-6.77 (AA'BB' system, 4H), 3.93 (s, 6H), 3.78 (s, 6H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 168.1, 159.1, 143.0, 132.2, 131.3, 130.9, 130.5, 113.8, 55.3, 52.8. FT-IR (dry powder) (cm⁻¹): 2955 (C-H), 2841 (C-H), 1722 (C=O). HR-MS (*m/z*): [M+Na]⁺ calcd for C₂₄H₂₂O₆Na 429.1309; found 429.1303 (1.4 ppm). M_p 113.6-115.1 °C.

dimethyl 4,4''-bis((tert-butyldimethylsilyl)oxy)-[1,1':2',1''-terphenyl]-4',5'-dicarboxylate (17). Synthesized with general method G and purified by column chromatography (SiO₂, gradient pentane/EtOAc; 0–30%). (transparent oil; 6.7 g; 11.03 mmol; 97% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 7.75 (s, 2H), 6.99-6.98 (AA'BB' system, 4H), 6.71-6.69 (AA'BB' system, 4H), 3.93 (s, 6H), 0.97 (s, 18H), 0.18 (s, 12H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 168.2, 155.3, 143.2, 132.9, 131.2, 130.9, 130.4, 120.8, 120.0, 116.0, 52.8, 25.8, 25.8, 18.4, -4.28. FT-IR (dry liquid) (cm⁻¹): 2954 (C-H), 2930 (C-H), 2858 (C-H), 1728 (C=O), 1244 (Si-O). HR-MS (*m/z*): [M+H]⁺ calcd for HR-MS C₃₄H₄₇O₆Si₂ 607.2906; found 607.2887 (3.1 ppm).

tetramethyl benzene-1,2,4,5-tetracarboxylate (18). Synthesized with general method A. (white solid; 25 g; 75.1 mmol; 95% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 8.07 (s, 2H), 3.94 (s, 12H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 166.5, 134.4, 129.8, 53.2. FT-IR (dry powder) (cm⁻¹): 2956 (C-H), 1720 (C=O). HR-MS (*m/z*): [M+Na]⁺ calcd for C₁₄H₁₄O₈Na 333.0581; found 333.0579 (0.6 ppm). M_p 137.1-138.9 °C.

5,6-dimethoxy-2-methyl-2-phenyl-1H-indene-1,3(2H)-dione (20). Synthesized with general method B and purified by column chromatography (SiO₂, gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (off-white solid; 882 mg; 2.98 mmol; 76% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 7.32 (s, 2H), 7.28-7.15 (m, 5H), 3.96 (s, 6H), 1.63 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 201.0, 156.4, 138.4, 136.5, 129.4, 128.8, 128.8, 128.8, 127.6, 126.7, 103.9, 57.6, 56.8, 20.0. FT-IR (dry powder) (cm⁻¹): 3012 (C-H), 2979 (C-H), 2959 (C-H), 1688 (C=O). HR-MS (*m/z*): [M+H]⁺ calcd for C₁₈H₁₈O₄ 297.1121; found 297.1120 (0.5 ppm). M_p 168.2-170.7 °C.

2-methyl-2-phenyl-1H-cyclopenta[b]naphthalene-1,3(2H)-dione (21). Synthesized with general method B and purified by column chromatography (SiO₂, gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (off-white solid; 1.24 g; 4.33 mmol; 40% yield). ¹H-NMR

(CDCl₃, 600 MHz, δ): 8.58 (s, 2H), 8.12-8.11 (m, 2H), 7.73-7.71 (m, 2H), 7.39-7.38 (m, 2H), 7.31-7.23 (m, 3H), 1.78 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 202.3, 138.2, 136.9, 136.3, 130.7, 129.8, 128.9, 127.7, 126.9, 125.2, 59.6, 20.3. FT-IR (dry powder) (cm⁻¹): 2979 (C-H), 2934 (C-H), 2867 (C-H), 1688 (C=O). HR-MS (*m/z*): [M+H]⁺ calcd for C₂₀H₁₆O₂ 287.1067; found 287.1065 (0.5 ppm). M_p 113.1-115.6 °C.

5,6-dichloro-2-methyl-2-phenyl-1H-indene-1,3(2H)-dione (22). Synthesized with general method B and purified by column chromatography (SiO₂, gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (off-white solid; 1.01 g; 3.31 mmol; 11% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 8.07 (s, 2H), 7.28-7.21 (m, 5H), 1.66 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 199.7, 141.6, 140.1, 137.2, 129.1, 128.1, 126.7, 125.7, 58.5, 20.3. FT-IR (dry powder) (cm⁻¹): 2929 (C-H), 1709 (C=O). HR-MS (*m/z*): [M+H]⁺ calcd for C₁₆H₁₂Cl₂O₂ 305.0131; found 305.0129 (0.4 ppm). M_p 104.9-106.8 °C.

5,6-dibromo-2-methyl-2-phenyl-1H-indene-1,3(2H)-dione (23). Synthesized with general method B and purified by column chromatography (SiO₂, gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (off-white solid; 4.0 g; 10.15 mmol; 62% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 8.25 (s, 2H), 7.27-7.21 (m, 5H), 1.66 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 199.8, 140.5, 137.1, 134.5, 129.1, 129.1, 129.0, 128.1, 126.7, 58.4, 20.2. FT-IR (dry powder) (cm⁻¹): 3072 (C-H), 2934 (C-H), 1707 (C=O). HR-MS (*m/z*): [M+H]⁺ calcd for C₁₆H₁₂Br₂O₂ 392.9120; found 392.9189 (0.4 ppm). M_p 145.6-147.1 °C.

2-methyl-2,5,6-triphenyl-1H-indene-1,3(2H)-dione (24). Synthesized with general method B and purified by column chromatography (SiO₂, gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (off-white solid; 1.26 g; 3.25 mmol; 61% yield). Synthesized also with general method G and purified by column chromatography (SiO₂, gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (off-white solid; 900 mg; 2.32 mmol; 50 % yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 8.07 (s, 2H), 7.41-7.39 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.23 (m,

7H), 7.16-7.14 (m, 4H), 1.76 (s, 3H). ^{13}C -NMR $\{^1\text{H}\}$ (CDCl_3 , 150 MHz, δ): 201.8, 149.2, 140.3, 139.7, 138.1, 129.7, 129.0, 128.4, 128.1, 127.8, 126.9, 125.9, 58.6, 20.3. FT-IR (dry powder) (cm^{-1}): 3060 (C-H), 1707 (C=O). HR-MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{22}\text{O}_2$ 389.1536; found 389.1534 (0.4 ppm). M_p 195.3-197.2 $^\circ\text{C}$.

5,6-bis(4-methoxyphenyl)-2-methyl-2-phenyl-1H-indene-1,3(2H)-dione (25). Synthesized with general method B (off-white solid; 2.07 g; 0.53 mmol; 18% yield) and purified by column chromatography (SiO_2 , gradient from 100% pentane to 7:3 pentane/EtOAc mixture). Synthesized also with general method G and purified by column chromatography (SiO_2 , gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (off-white solid; 950 mg; 2.12 mmol; 55 % yield). ^1H -NMR (CDCl_3 , 600 MHz, δ): 8.02 (s, 2H), 7.40-7.39 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.10-7.09 (AA'BB' system, 4H), 6.82-6.80 (AA'BB' system, 4H), 3.80 (s, 6H), 1.75 (s, 3H). ^{13}C -NMR $\{^1\text{H}\}$ (CDCl_3 , 150 MHz, δ): 201.9, 159.5, 148.7, 140.0, 138.2, 132.2, 131.0, 129.0, 127.7, 126.9, 125.7, 114.0, 58.5, 55.4, 20.2. FT-IR (dry powder) (cm^{-1}): 3059 (C-H), 2961 (C-H), 1701 (C=O). HR-MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{25}\text{O}_4$ 449.1747; found 449.1738 (2.0 ppm). M_p 196.2-198.7 $^\circ\text{C}$.

5,6-bis(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-methyl-2-phenyl-1H-indene-1,3(2H)-dione (26). Synthesized with general method G and purified by column chromatography (SiO_2 , gradient from 100% pentane to 8:2 pentane/EtOAc mixture). (off-white solid; 622 mg; 0.96 mmol; 75% yield). ^1H -NMR (CDCl_3 , 600 MHz, δ): 8.02 (s, 2H), 7.40-7.39 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.02-7.01 (AA'BB' system, 4H), 6.74-6.73 (AA'BB' system, 4H), 1.75 (s, 3H), 0.98 (s, 18H), 0.19 (s, 12H). ^{13}C -NMR $\{^1\text{H}\}$ (CDCl_3 , 150 MHz, δ): 201.9, 155.8, 148.9, 140.0, 138.2, 132.8, 131.0, 129.6, 129.0, 128.9, 127.7, 126.9, 125.6, 120.2, 58.5, 25.8, 20.2, 18.4, -4.3. FT-IR (dry powder) (cm^{-1}): 2931 (C-H), 2858 (C-H), 1703 (C=O), 1266 (Si-O). HR-MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{40}\text{H}_{49}\text{O}_4\text{Si}_2$ 649.3164; found 649.3147 (2.6 ppm). M_p 134.2-136.5 $^\circ\text{C}$.

dimethyl 2-isopropyl-2-methyl-1,3-dioxo-2,3-dihydro-1H-indene-5,6-dicarboxylate (27).

Synthesized with general method B and purified by column chromatography (SiO₂, gradient from 100% pentane to 7:3 pentane/EtOAc mixture). (yellow solid; 3.07 g; 9.65 mmol; 30% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 8.25 (s, 2H), 3.96 (s, 6H), 2.16 (h, *J* = 6 Hz, 1H), 1.27 (s, 3H), 0.91 (d, *J* = 6 Hz, 6H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 203.5, 166.4, 142.7, 138.6, 123.9, 57.5, 53.4, 34.7, 18.1, 17.4. FT-IR (dry powder) (cm⁻¹): 2957 (*C-H*), 2876 (*C-H*), 1729 (*C=O*), 1710 (*C=O*). HR-MS (*m/z*): [M+H]⁺ calcd for C₁₇H₁₉O₆ 319.1176; found 319.1175 (0.4 ppm). M_p 92.2-94.6 °C.

5,6-dimethoxy-2-phenyl-1H-indene-1,3(2H)-dione (29). Synthesized adapting a literature procedure.⁴⁴ (off-white solid; 7.78 g; 27.5 mmol; 31% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 7.40 (s, 2H), 7.34-7.28 (m, 3H), 7.18-7.16 (m, 2H), 4.20 (s, 1H), 4.04 (s, 6H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 197.4, 156.3, 138.0, 133.9, 129.1, 128.8, 127.9, 103.8, 59.6, 56.9. FT-IR (dry powder) (cm⁻¹): 3006 (*C-H*), 2946 (*C-H*), 1686 (*C=O*). HR-MS (*m/z*): [M+H]⁺ calcd for C₁₇H₁₅O₄ 283.0965; found 283.0961 (1.3 ppm). M_p 101.2-103.5 °C.

2-octadecyl-2-phenyl-1H-indene-1,3(2H)-dione (30). Synthesized with general method B applying only the alkylation part on 2-phenyl-1H-indene-1,3(2H)-dione³⁸ and purified by column chromatography (SiO₂, gradient from 100% pentane to 9:1 pentane/EtOAc mixture). (off-white solid; 2.89 g; 6.09 mmol; 83% yield). ¹H-NMR (CDCl₃, 600 MHz, δ): 8.03-8.02 (m, 2H), 7.86-7.85 (m, 2H), 7.42-7.40 (m, 2H), 7.30-7.28 (m, 2H), 7.24-7.22 (m, 1H), 2.25 (t, *J* = 9 Hz, 2H), 1.30-1.13 (m, 35H), 0.88 (t, *J* = 6 Hz, 3H). ¹³C-NMR {¹H} (CDCl₃, 150 MHz, δ): 202.2, 142.2, 137.4, 136.0, 128.9, 127.7, 127.0, 123.7, 62.5, 36.5, 32.1, 30.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.3, 25.4, 22.8, 14.3. FT-IR (dry powder) (cm⁻¹): 2949 (*C-H*), 2916 (*C-H*), 2850 (*C-H*), 1705 (*C=O*). HR-MS (*m/z*): [M+H]⁺ calcd for C₃₃H₄₇O₂ 475.3571; found 475.3557 (2.9 ppm). M_p 63.2-64.3 °C.

In some cases, indanedithiones **31-39** were not obtained in 100% purity. Hence, we only report their ¹H NMR spectra. However, the impurities present in **31-39** did not affect the subsequent B-K olefinations to obtain motors **1-9**.

5,6-dimethoxy-2-methyl-2-phenyl-1H-indene-1,3(2H)-dithione (32). Synthesized with general method D and purified by column chromatography (SiO₂, gradient from 100% pentane to 9:1 pentane/EtOAc). (green solid; 180 mg; 0.55 mmol; 33% yield). ¹H-NMR (CDCl₃, 300 MHz, δ): 7.40 (s, 2H), 7.21-7.17 (m, 5H), 4.09 (s, 6H), 1.92 (s, 3H).

2-methyl-2-phenyl-1H-cyclopenta[b]naphthalene-1,3(2H)-dithione (33). Synthesized with general method D and purified by column chromatography (SiO₂, gradient from 100% pentane to 90:10 pentane/EtOAc). (green solid; 576 mg; 1.81 mmol; 52% yield). ¹H-NMR (CDCl₃, 300 MHz, δ): 8.63 (s, 2H), 8.15-8.12 (m, 2H), 7.72-7.69 (m, 2H), 7.22-7.12 (m, 5H), 2.00 (s, 3H).

5,6-dichloro-2-methyl-2-phenyl-1H-indene-1,3(2H)-dithione (34). Synthesized with general method D and purified by column chromatography (SiO₂, gradient from 100% pentane to 9:1 pentane/EtOAc). (green solid; 275 mg; 0.81 mmol; 32% yield). ¹H-NMR (CDCl₃, 400 MHz, δ): 8.15 (s, 2H), 7.24-7.15 (m, 5H), 1.91 (s, 3H).

2-methyl-2,5,6-triphenyl-1H-indene-1,3(2H)-dithione (35). Synthesized with general method D and purified by column chromatography (SiO₂, gradient from 100% pentane to 9:1 pentane/EtOAc). The compound was not obtained in high purity. (green solid; 120 mg; 2.85 mmol; 35% yield). ¹H-NMR (CDCl₃, 400 MHz, δ): 8.14 (s, 2H), 7.31-7.29 (m, 10H), 7.25-7.22 (m, 5H), 2.01 (s, 3H).

5,6-bis(4-methoxyphenyl)-2-methyl-2-phenyl-1H-indene-1,3(2H)-dithione (36). Synthesized with general method D and purified by column chromatography (SiO₂, gradient from 100% pentane to 9:1 pentane/EtOAc). (green solid; 113 mg; 0.23 mmol; 45% yield). ¹H-NMR (CDCl₃, 400 MHz, δ): 8.05 (s, 2H), 7.28-7.21 (m, 5H), 7.16-7.14 (AA'BB' system, 4H), 6.83-6.80 (AA'BB' system, 4H), 3.81 (s, 6H), 1.96 (s, 3H).

5,6-bis(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-methyl-2-phenyl-1H-indene-1,3(2H)-

dione (37). Synthesized with general method D and purified by column chromatography (SiO₂, gradient from 100% pentane to 95:5 pentane/EtOAc). (green solid; 200 mg; 0.29 mmol; 48% yield). ¹H-NMR (CDCl₃, 400 MHz, δ): 8.06 (s, 2H), 7.25-7.20 (m, 5H), 7.08-7.06 (AA'BB' system, 4H), 6.75-6.73 (AA'BB' system, 4H), 1.97 (s, 3H), 0.98 (s, 18H), 0.19 (s, 12H).

dimethyl 2-isopropyl-2-methyl-1,3-dioxo-2,3-dihydro-1H-indene-5,6-dicarboxylate (27).

Synthesized with general method E and purified by column chromatography (SiO₂, gradient from 100% pentane to 9:1 pentane/EtOAc). However, this procedure afforded singly converted product in all attempts, with the only exception of one case in which desired **39** was obtained (green solid; 181 mg; 0.51 mmol; 33% yield). ¹H-NMR (CDCl₃, 400 MHz, δ): 8.27 (s, 2H), 3.96 (m, 6H), 2.41 (h, *J* = 7 Hz, 1H), 1.52 (s, 3H), 0.86 (d, *J* = 7 Hz, 6H).

Motor 2. Synthesized with general method F and purified by column chromatography (SiO₂, gradient pentane/CH₂Cl₂; 0–100%). (deep red solid; 200 mg; 0.34 mmol; 61% yield). ¹H-NMR (Cl₂DCCDCl₂, 500 MHz, 90 °C, δ) (signals of the main isomer): 8.41 (d, *J* = 6 Hz, 2H), 7.80 (d, *J* = 6 Hz, 2H), 7.72 (d, *J* = 6 Hz, 2H), 7.68 (d, *J* = 6 Hz, 2H), 7.65 (s, 2H), 7.30 (t, *J* = 6Hz, 3H), 7.27 (t, *J* = 6Hz, 3H), 7.18 (t, *J* = 6Hz, 3H), 7.13 (t, *J* = 6Hz, 3H), 3.86 (s, 6H), 2.44 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 125 MHz, -45 °C, δ): 160.7, 157.2, 154.3, 152.2, 150.2, 149.7, 142.2, 140.9, 140.4, 140.1, 139.6, 139.5, 138.9, 137.6, 137.4, 137.3, 132.9, 130.4, 128.7, 128.6, 128.0, 127.5, 127.3, 127.2, 127.0, 126.8, 126.7, 126.7, 126.6, 126.2, 126.0, 125.8, 123.6, 119.9, 119.6, 119.5, 119.4, 110.7, 105.4, 71.4, 68.7, 56.9, 56.7, 56.6, 23.4, 19.4. HR-MS (*m/z*): [M+H]⁺ calcd for C₄₄H₃₃O₂ 593.2475; found 593.2461 (2.3 ppm). UV-Vis (CH₂Cl₂) λ_{max}, nm (ε): 247 (149200), 471 (69400). M_p 260-262 °C. Single crystals for XRD were obtained from slow diffusion of hexane (anti-solvent) into a saturated solution of 1,2-dichloroethane (solvent).

Motor 3. Synthesized with general method F and purified by column chromatography (SiO₂, gradient pentane/CH₂Cl₂; 0–100%). (orange solid; 395 mg; 0.678 mmol; 54% yield). ¹H-NMR

(Cl₂DCCDCl₂, 500 MHz, 90 °C, δ): 8.72 (s, 2H), 8.64 (d, J = 6 Hz, 2H), 7.84-7.82 (m, 4H), 7.80-7.78 (m, 2H), 7.71 (d, J = 6 Hz, 2H), 7.68-7.67 (m, 2H), 7.57-7.55 (m, 4H), 7.73 (t, J = 6 Hz, 3H), 7.29-7.26 (m, 3H), 7.15-7.12 (m, 5H), 2.48 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 125 MHz, -45 °C, δ): 159.5, 156.6, 144.0, 141.8, 141.6, 140.6, 140.2, 140.1, 140.00, 139.6, 139.4, 137.5, 135.6, 134.3, 134.0, 133.5, 133.5, 132.0, 130.9, 129.5, 129.0, 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.5, 127.3, 127.2, 126.5, 126.4, 126.2, 125.2, 125.0, 123.1, 122.9, 119.6, 119.5, 119.4, 118.8, 70.0, 67.6, 20.1, 19.7. HR-MS (m/z): [M+H]⁺ calcd for C₄₆H₃₁ 583.2420; found 583.2410 (1.8 ppm). UV-Vis (CH₂Cl₂) λ_{max} , nm (ϵ): 244 (239352), 400 (94064). M_p > 300 °C.

Motor 4. Synthesized with general method F and purified by column chromatography (SiO₂, gradient pentane/CH₂Cl₂; 0–100%). (orange solid; 313 mg; 0.52 mmol; 64% yield). ¹H-NMR (Cl₂DCCDCl₂, 500 MHz, 90 °C, δ) (signals of the main isomer): 8.35 (d, J = 6 Hz, 2H), 8.32 (s, 2H), 7.73-7.68 (m, 5H), 7.63 (d, J = 6 Hz, 2H), 7.34 (t, J = Hz, 3H), 7.26 (t, J = 6 Hz, 3H), 7.21 (t, J = 6 Hz, 3H), 7.10 (t, J = 6 Hz, 3H), 2.42 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 125 MHz, -45 °C, δ): 157.1, 154.4, 154.2, 147.2, 144.6, 140.8, 140.4, 140.3, 140.2, 139.8, 139.6, 138.5, 138.4, 137.1, 135.3, 135.0, 134.4, 134.0, 133.1, 132.7, 130.7, 130.4, 129.6, 128.8, 128.3, 128.2, 128.1, 127.9, 127.7, 127.5, 126.6, 126.4, 125.4, 125.3, 124.4, 123.5, 123.3, 122.8, 120.3, 120.2, 119.8, 119.6, 119.5, 119.0, 70.7, 68.5, 19.7, 18.9. HR-MS (m/z): [M+H]⁺ calcd for C₄₂H₂₇Cl₂ 601.1484; found 601.1481 (0.5 ppm). UV-Vis (CH₂Cl₂) λ_{max} , nm (ϵ): 241 (156766), 441 (59518). M_p 269-271 °C. Single crystals for XRD were obtained from slow diffusion of hexane (antisolvent) into a saturated solution of 1,2-dichloroethane (solvent).

Motor 5. Motor 4 (108 mg; 0.18 mmol) and **Pd-PEPPSI-IPent** complex (5 mol %) were dissolved in toluene (4 mL) in a dried Schlenk flask under N₂. The mixture was stirred at 40 °C for 5 min. Subsequently, a toluene solution (1 mL) of PhLi (2.5 eq.) was added over 1 h by use of a syringe pump. After complete addition, MeOH (1 mL) was added to quench the remaining PhLi. The reaction mixture was transferred to a round-bottom flask, celite was

added, and the solvents evaporated in vacuo. Purification with column chromatography (SiO₂, elution in gradient from 100% Pentane to 100% DCM) afforded motor **5** (red solid; 25 mg; 0.036 mmol; 20% yield). Synthesized also with general method F (50 mg; 0.072 mmol; 20% yield from **24**). ¹H-NMR (Cl₂DCCDCl₂, 500 MHz, 90 °C, δ) (signals of the main isomer): 8.63 (d, *J* = 6 Hz, 2H), 8.30 (s, 2H), 7.80 (d, *J* = 6 Hz, 3H), 7.69-7.64 (m, 6H), 7.31-7.11 (m, 20H), 2.50 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 125 MHz, -45 °C, δ): 159.8, 156.6, 147.0, 144.6, 141.5, 141.3, 140.5, 140.2, 140.1, 140.0, 139.9, 139.8, 139.6, 139.1, 137.5, 135.6, 133.2, 132.7, 131.9, 131.4, 129.8, 129.8, 129.3, 128.9, 128.7, 128.5, 128.3, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 127.0, 126.9, 126.6, 126.3, 126.2, 126.1, 125.1, 123.7, 123.3, 119.6, 119.4, 118.9, 70.7, 68.6, 19.9, 19.4. HR-MS (*m/z*): [M+H]⁺ calcd for C₅₄H₃₇ 685.2890; found 685.2881 (1.3 ppm). UV-Vis (CH₂Cl₂) λ_{max}, nm (ε): 246 (209192), 391 (63390), 449 (86394). M_p > 300 °C. Single crystals for XRD were obtained from slow diffusion of hexane (antisolvent) into a saturated solution of 1,2-dichloroethane (solvent).

Motor 6. Synthesized with general method F and purified by column chromatography (SiO₂, gradient pentane/CH₂Cl₂; 0–100%). (red solid; 108 mg; 0.14 mmol; 62% yield). ¹H-NMR (Cl₂DCCDCl₂, 500 MHz, 90 °C, δ) (signals of the main isomer): 8.62 (d, *J* = 6 Hz, 2H), 8.25 (s, 2H), 7.79 (d, *J* = 6 Hz, 2H), 7.68 (d, *J* = 6 Hz, 2H), 7.64 (d, *J* = 6 Hz, 2H), 7.29 (t, *J* = Hz, 3H), 7.25 (t, *J* = 6 Hz, 3H), 7.18 (t, *J* = 6 Hz, 3H), 7.15 (d, *J* = 6 Hz, 4H), 7.12 (t, *J* = 6 Hz, 3H), 6.80 (d, *J* = 6 Hz, 4H), 3.82 (s, 6H), 2.49 (s, 3H). ¹³C-NMR {¹H} (CDCl₃, 125 MHz, -45 °C, δ): 160.0, 158.1, 158.0, 156.9, 146.6, 144.2, 141.4, 141.0, 140.8, 140.6, 139.9, 139.7, 139.5, 139.2, 137.5, 135.6, 132.8, 132.7, 132.6, 132.4, 131.7, 131.0, 130.9, 130.5, 128.7, 127.6, 127.4, 127.2, 126.7, 126.3, 126.2, 125.1, 123.7, 123.3, 119.5, 119.4, 113.2, 70.6, 68.5, 55.3, 19.8, 19.5. HR-MS (*m/z*): [M+H]⁺ calcd for C₅₆H₄₁O₂ 745.3101; found 745.3088 (1.7 ppm). UV-Vis (CH₂Cl₂) λ_{max}, nm (ε): 244 (206000), 395 (69400), 450 (84200). M_p 268-270 °C.

Motor 7. Synthesized with general method F and purified by column chromatography (SiO₂, gradient pentane/CH₂Cl₂; 0–100%). (red solid; 120 mg; 0.13 mmol; 56% yield). ¹H-NMR (Cl₂DCCDCl₂, 500 MHz, 90 °C, δ) (signals of the main isomer): 8.62 (d, *J* = 6 Hz, 2H), 8.26 (s, 2H), 7.79 (d, *J* = 6 Hz, 2H), 7.68 (d, *J* = 6 Hz, 2H), 7.65 (d, *J* = 6 Hz, 2H), 7.30 (t, *J* = Hz, 3H), 7.25 (t, *J* = 6 Hz, 3H), 7.18 (t, *J* = 6 Hz, 3H), 7.12 (t, *J* = 6 Hz, 3H), 7.09 (d, *J* = 6 Hz, 4H), , 6.72 (d, *J* = 6 Hz, 4H), 2.49 (s, 3H), 1.03 (s, 18 H), 0.23 (s, 12H). ¹³C-NMR {¹H} (CDCl₃, 125 MHz, -45 °C, δ): 160.1, 156.9, 154.4, 154.3, 146.6, 144.2, 141.3, 141.1, 140.6, 139.9, 139.9, 139.7, 139.5, 139.2, 137.5, 135.6, 133.5, 133.3, 132.8, 132.3, 131.5, 131.0, 130.9, 128.7, 127.6, 127.4, 127.2, 126.6, 126.2, 123.4, 119.7, 119.5, 119.4, 70.7, 68.5, 29.9, 25.6, 19.8, 19.6, 18.2, -4.4. HR-MS (*m/z*): [M+H]⁺ calcd for C₆₆H₆₅O₂Si₂ 945.4518; found 945.4505 (1.4 ppm). UV-Vis (CH₂Cl₂) λ_{max}, nm (ε): 246 (178420), 396 (59400), 451 (72400). M_p 248-251.6 °C.

Motor 8. Synthesized with general method F, after column chromatography (SiO₂, gradient pentane/DCM: 0% - 100%) and preparative TLC (SiO₂, pentane/EtOAc 98:2) (orange solid; 32 mg; 0.041 mmol; 2% yield from **30**). ¹H-NMR (CDCl₃, 500 MHz, -45 °C, δ): 8.45 (d, *J* = 8.0 Hz, 2H), 8.24-8.22 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.71-7.67 (m, 4H), 7.39-7.25 (m, 11H), 7.15 (t, *J* = 8 Hz, 2H), 7.19 (t, *J* = 8 Hz, 2H), 3.04 (m, 2H), 1.23 (m, 20H), 1.01 (m, 2H), 0.87 (m, 5H), 0.74 (m, 2H), 0.67 (m, 2H), 0.56 (m, 2H), 0.44 (m, 2H), 0.34 (m, 2H). ¹³C-NMR {¹H} (CDCl₃, 125 MHz, -45 °C, δ): 155.1, 148.7, 141.0, 140.0, 139.8, 138.8, 137.4, 133.3, 130.5, 129.1, 128.5, 127.5, 127.4, 127.4, 126.8, 126.1, 126.0, 123.5, 119.4, 119.3, 72.06, 32.1, 30.7, 29.9, 29.9, 29.9, 29.8, 29.6, 29.6, 29.5, 29.0, 28.9, 27.9, 24.7, 22.9, 14.5. HR-MS (*m/z*): [M+H]⁺ calcd for C₅₉H₆₃ 771.4924; found 771.4912 (1.5 ppm). UV-Vis (CH₂Cl₂) λ_{max}, nm (ε): 241 (105922), 453 (40224). M_p 194.2-196.6 °C.

Motor 9. Synthesized with general method F and purified by column chromatography (SiO₂, gradient pentane/CH₂Cl₂; 0–100%). (orange solid; 90 mg; 0.146 mmol; 28% yield). ¹H-NMR (CDCl₃, 600 MHz, 25 °C, δ): 8.44 (s, 2H), 8.20 (d, *J* = 6 Hz, 2H), 8.01 (d, *J* = 6 Hz, 2H), 7.77

(d, $J = 6$ Hz, 2H), 7.73 (d, $J = 6$ Hz, 2H), 7.39 (t, $J = 6$ Hz, 2H), 7.34-7.30 (m, 6H), 7.13 (t, $J = 6$ Hz, 2H), 3.89 (s, 6H), 3.01 (h, $J = 6$ Hz, 1H), 2.39 (s, 3H), 1.07 (d, $J = 6$ Hz, 6H). [HMPA present in the sample due to a strong interaction with the compound; the doublet at 2.65 in the ^1H -NMR spectrum belongs to HMPA] ^{13}C -NMR $\{^1\text{H}\}$ (CDCl_3 , 125 MHz, -45°C , δ): 167.8, 155.8, 150.2, 145.2, 140.9, 139.7, 139.6, 138.1, 136.1, 134.3, 131.1, 129.1, 128.9, 128.3, 128.2, 127.8, 127.3, 126.7, 126.4, 125.2, 123.5, 120.0, 119.7, 119.6, 75.0, 70.0, 53.3, 39.9, 28.8, 24.2. HR-MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{35}\text{O}_4$ 615.2530; found 615.25174(2.0 ppm). UV-Vis (CH_2Cl_2) λ_{max} , nm (ϵ): 238 (196366), 374 (49228), 440 (65830). $M_p > 300^\circ\text{C}$.

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SUPPORTING INFORMATION

List of all synthesized compounds, ^1H NMR and ^{13}C NMR spectra, UV-Vis spectra of motors **1-9**, FT-IR spectra, Crystal Structure of motors **2**, **4** and **5**, TD- ^1H NMR experiments with motor **6**, ^1H NMR *in situ* irradiation experiments at -80°C with motor **6**.

Crystallographic data of **2** (CIF).

Crystallographic data of **4** (CIF).

Crystallographic data of **5** (CIF).

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