Does the Threshold Enantiomerization Route of Crowded Tetraarylethenes Involve Double Bond Rotation?

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Abstract: The chiral tetraarylvinyl propeller 1,2-bis(4-*tert*-butyl-2,6-dimethylphenyl)-1,2-dimesitylethene (**4**) was synthesized by irradiation of (4-*tert*-butyl-2,6-dimethylphenyl)mesitylketene **5**. Ethene **4** exists in two diastereomeric forms (*E* and *Z*), each existing as a racemate (i.e., (+)/(−) **4Z** and (+)/(−) **4E**). The enantiomers were resolved by chiral HPLC and the *E/Z* diastereomers were separated by (achiral) supercritical fluid chromatography. The enantiomerization process which was studied in *n*-pentadecane has a barrier of $\Delta G^{\ddagger} = 44.8 \pm 0.7$ kcal mol^{-1}. A **4Z** ⇌ **4E** interconversion was not observed under the enantiomerization conditions. Consequently, we conclude that the threshold enantiomerization process of **4** does not involve a double bond rotation. A lower limit of 48.7 kcal mol^{-1} is estimated for the barrier of the latter rotation.

Introduction

Molecular systems consisting of two or more aryl rings connected to a central frame (e.g., Ar$_3$X (X = B, N, P, CH)) usually exist in a chiral conformation in which all rings are twisted in the same sense with respect to an arbitrarily defined reference plane.[1,2] This "propeller" conformation is chiral, and the resulting two enantiomeric forms differ in the sense of twist of the rings, i.e., in their helicity. Resolution of such systems has been accomplished only in a few cases.[3] When the central frame is the ethylenic double bond, the resulting systems (e.g., Ar$_2$C=CR$_2$, Ar$_2$C=CRAr, Ar$_2$C=CAr$_2$) can be dubbed "vinyl propellers".[4] In contrast to the Ar$_3$X molecular propellers, these systems may undergo a large number of stereodynamic processes involving rotation of the aryl rings around the Ar—C= bonds, rotations around the C=C double bond, as well as skeletal rearrangements.[4-6] Crowded tetraarylvinyl propellers display high rotational barriers. Tetramesitylethene (**1**), prepared

by irradiation of dimesitylketene,[7a] exists in the solid state in a chiral propeller conformation of approximate D_2 symmetry.[7b,c] We have recently resolved **1** and determined its enantiomerization barrier.[8] This barrier is exclusively due to enthalpy ($\Delta G^{\ddagger} = 39.6$ kcal mol^{-1}, $\Delta H^{\ddagger} = 39.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 0$ cal mol^{-1} K^{-1}).[8] We also resolved the formally more crowded tetrakis(pentamethylphenyl)ethene (**2**) and found a higher enantiomerization barrier ($\Delta G^{\ddagger} = 43.1 \pm 0.1$ kcal mol^{-1}, $\Delta H^{\ddagger} = 39.6 \pm 4.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -6.7 \pm 7.9$ cal mol^{-1} K^{-1} (at 523 K)).[9] The difference was ascribed to the buttressing effects of the eight *meta* methyl groups.[9,10] The enantiomerization barriers found for **1** (39.6 kcal mol^{-1}) and **2** (43.1 kcal mol^{-1}) represent the highest values obtained so far for the helicity reversal process of polyarylvinyl propellers.

1: Ar = Mes = 2,4,6-Me$_3$C$_6$H$_2$
2: Ar = Me$_5$C$_6$

The enantiomerization (helicity reversal) process of **1** must involve ring rotations around the four aryl—C= bonds. For

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noncrowded ethenes the barrier of rotation around a double bond which involves deconjugation of the two p-orbitals to the biradical is usually substantially higher than the barrier for rotation around single bonds. The barrier of double bond rotation in simple ethenes is 62−65 kcal mol^{-1}.[11a] Barriers lower than 25 kcal mol^{-1} have been observed for sterically crowded systems such as bistricyclic ethenes while for push−pull systems even barriers as low as 10 kcal mol^{-1} have been reported.[11] The experimentally determined enantiomerization barriers of **1** and **2** are in the range of or higher than the barriers of double bond rotations of structurally related polyarylethenes, e.g., 42.8 kcal mol^{-1} for the $Z \rightarrow E$ interconversion of stilbene,[12a] and 35.2 ± 0.1 kcal mol^{-1} for the $E \rightleftharpoons Z$ interconversion of 1,2-bis(p-XC$_6$H$_4$)-1,2-diphenylethenes **3a−c**.[12b] Consequently,

$$p\text{-XC}_6\text{H}_4\text{C(Ph)}{=}\text{C(Ph)C}_6\text{H}_4\text{X-}p$$
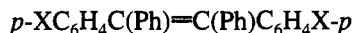
3: X = Me (a), MeO (b), CN (c)

the possibility that the rotation of the aryl rings in **1** is preceded by breaking the π bond (see below) or even that for these crowded systems the double bond rotation has a lower barrier than the single bond rotations required for the helicity reversal process cannot be *a priori* unequivocally excluded. The present work intends to answer the question of whether the two processes are mechanisticaly connected, and if they are not connected which one of them has the higher barrier.

Enantiomerization and Diastereomerization Pathways of Vicinal *Para*-Disubstituted Tetraarylvinyl Propellers. A tetraphenylethene disubstituted in the *para* positions of vicinal rings should exist in four stereoisomeric forms (two enantiomeric pairs): $+Z/-Z$ and $+E/-E$.[13] Several different enantiomerization and diastereomerization routes are available for such systems (Figure 1). Two of them apply if the rotations around the Ar−C and the C=C bonds are independent. The first and simplest enantiomerization pathway for the system involves helicity reversal by rotations around the Ar−C bonds, most likely by a correlated rotation[1] of the four rings via a four-ring flip mechanism[4b,8,14] (Figure 1, route a). This process interconverts the $+Z \rightleftharpoons -Z$ and $+E \rightleftharpoons -E$ enantiomeric pairs. Second, rotation around the double bond which is not accompanied by rotations around Ar−C bonds should result in a change of the *E/Z* configuration of the double bond with retention of the helicity (i.e., $+Z \rightleftharpoons +E$ and $-Z \rightleftharpoons -E$, route b). Alternatively, the aryl rotations may be accompanied by or coupled to a double bond rotation process. Thus, a third possibility is that a rate-determining opening of the double bond yields a biradical intermediate which then may undergo
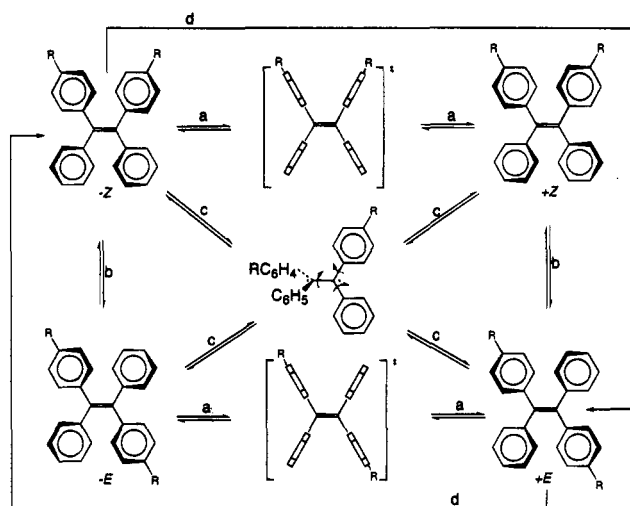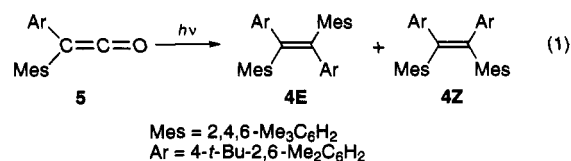
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(13) In this paper the "+" and "−" designations indicate the two possible helicity senses of the propellers, according to the arbitrary convention described in ref 2b. The dextrorotatory and levorotatory material (at 780 nm) obtained in the resolution experiments will be designated by the usual plus and minus signs enclosed in brackets (i.e., "(+)" and "(−)"). The absolute configuration (+ or −) of the resolved enantiomers of **4** (see text) and the *(E)* or *(Z)* configurations at the double bond are at present unknown.

(14) Early calculations on tetraphenylethene (Stegemeyer, H.; Rapp, W. *Ber. Bunsenges. Phys. Chem.* **1971**, *76*, 1665) had indicated that the preferred rotational mechanism involves correlated rotation of the four rings via a transition state in which the rings are perpendicular to the double bond plane (a four-ring flip mechanism). See also ref 4b.
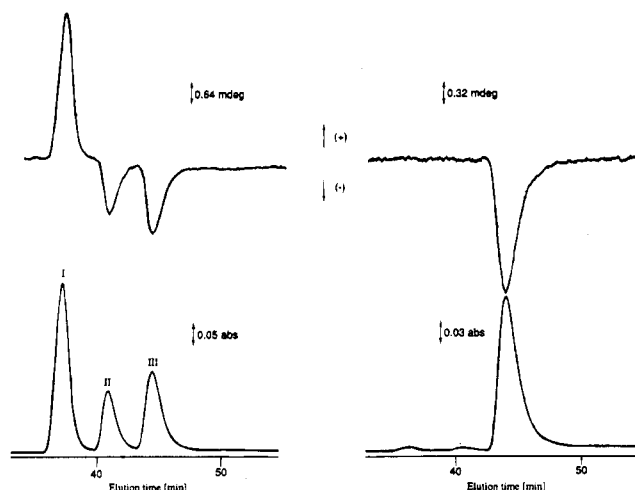
Figure 1. Possible enantiomerization and diastereomerization pathways of a tetraarylethene disubstituted at the *para* positions of two vicinal rings. (a) Helicity reversal by four-ring flip rotation of the Ar−C bonds. In the ideal transition state the four rings are perpendicular to the double bond plane. (b) Double bond rotation retaining the helicity of the system. (c) Double bond rotation followed by helicity reversal of the two diarylmethyl subunits in the diradical intermediate. This process interconverts the four stereoisomeric forms. (d) Combined helicity reversal and double bond rotation.

relatively "fast" internal rotations around the Ar−C bonds. If the intermediate is sufficiently long lived, the helicity of each Ar$_2$C subunit may be either retained or reversed, and any of the four stereoisomeric forms may be obtained after reformation of the double bond. This route therefore results in homomerization, enantiomerization, and diastereomerization (Figure 1, path c). A fourth possible pathway involves concerted single-step coupled Ar−C and double bond rotations leading to both helicity reversal and $E \rightleftharpoons Z$ interconversion. This process results exclusively in the diastereomerizations $+Z \rightleftharpoons -E$ and $-Z \rightleftharpoons +E$ without any accompanying enantiomerization (path d).

Structural Considerations and Synthesis of (*E/Z*)-1,2-Bis-(4-*tert*-butyl-2,6-dimethylphenyl)-1,2-dimesitylethenes. In order to monitor both the helicity reversal and the double bond rotation processes it is necessary to desymmetrize the tetraarylethene **1** by introducing a "tag" substituent. In order to minimally perturb both the ground state and the rotational transition state we modified **1** by replacing two p-Me groups on vicinal rings by two p-t-Bu groups (cf. **4**). This desymmetrization results in lowering the D_2 symmetry of **1** to C_2. Ethene **4** should exist in two diastereomeric forms (**4Z** and **4E**) each existing in two enantiomeric forms (+**4Z**/−**4Z**, +**4E**/−**4E**). The enantiomerization process can be followed by studying the (+**4Z**/−**4Z** (or +**4E**/−**4E**)) interconversions, while a **4Z** $\rightleftharpoons$ **4E** interconversion will indicate that a double bond rotation (i.e., diastereomerization) process is taking place.

For the preparation of **4** we irradiated (4-*tert*-butyl-2,6-dimethylphenyl)mesitylketene **5** (eq 1). The irradiation af-

$$\text{Ar}\big\backslash_{\text{Mes}}{=}\text{C}{=}\text{O} \xrightarrow{h\nu} \text{Ar}\big\backslash_{\text{Mes}}{=}\big/^{\text{Mes}}_{\text{Ar}} + \text{Ar}\big\backslash_{\text{Mes}}{=}\big/^{\text{Ar}}_{\text{Mes}} \qquad (1)$$

5   **4E**   **4Z**

Mes = 2,4,6-Me$_3$C$_6$H$_2$
Ar = 4-t-Bu-2,6-Me$_2$C$_6$H$_2$

forded a 1.1:1 mixture of **4Z** and **4E**, although we do not know if **4E** or **4Z** is formed in excess.[13] Partial separation of the two diastereomers was achieved by column chromatography. The 400-MHz ^{1}H NMR spectrum of a mixture of **4Z** and **4E** partially

Figure 2. Chiral HPLC chromatogram of **4**. Low trace: UV absorption (at 254 nm). Upper trace: optical activity of the eluted solution (at 780 nm). Left: resolution of racemic **4Z** and **4E**. Fraction I (dextrorotatory) contains a mixture of (+)**4Z** and (+)**4E**. Fractions II and III are levorotatory and can be assigned as (−)**4Z** and (−)**4E** or vice versa. Right: isolated fraction III.
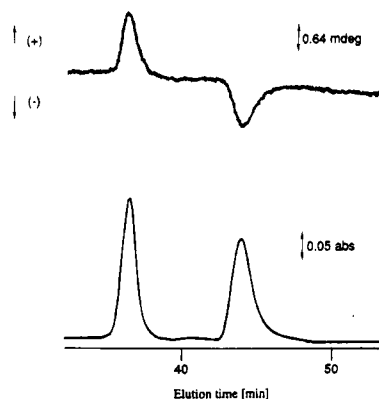

Figure 3. HPLC chromatogram of fraction III after heating for 20 h at 553 K in *n*-pentadecane. Low trace: UV absorption (at 254 nm). Upper trace: optical activity of the eluted solution (at 780 nm).

Table 1. Racemization Data of Fraction III of **4** in *n*-Pentadecane

temp (K)	time (h)	ee (%)	k_{enant} (s^{-1})
528	5	87.4	
	10	76.9	3.01×10^{-6}
	24	56.6	
	32	47.8	
533	4	82.4	
	8	74.0	4.57×10^{-6}
	15	58.8	
	24	43.7	
538	2	86.7	
	4	78.0	6.74×10^{-6}
	8	62.5	
	12	52.9	
543	2	81.2	
	4	73.5	9.95×10^{-6}
	8	55.3	
	11	44.5	

enriched by either isomer displays separate *tert*-butyl signals for the two diastereomers (δ 1.20 and 1.21 ppm) as well as for most of the methyl and aromatic protons. The aromatic signals of the *tert*-butyl substituted rings appear as pair of doublets, as previously observed in triarylethenols.[4a] Such splitting is the result of the long-range *meta* coupling of the aromatic protons. No splitting is observed for the aromatic signals of the mesityl rings since any such splitting is hidden due to broadening by unresolved long-range coupling with the *p*-Me group. The ^{1}H NMR spectrum of the diastereomers is in full agreement with a "frozen" propeller conformation of C_2 symmetry in which pairs of *ortho* methyls and aromatic protons within a given ring reside in diastereotopic environments (see Experimental Section).

Resolution and Enantiomerization of 4. A ca. 1:1 mixture of **4E** and **4Z** was resolved using the chiral stationary phase cellulose tris(3,5-dimethylphenylcarbamate) and isooctane as eluent. In order to obtain a complete resolution five columns connected in tandem were used. Three fractions were obtained (I, II, and III, Figure 2). Fraction I corresponded to dextrorotatory material (a mixture of (+)**4Z** and (+)**4E**), while fractions II and III corresponded to levorotatory material and therefore can be assigned as either II: (−)**4Z**, III: (−)**4E** or II: (−)**4E**, III: (−) **4Z**.[13] Heating a sample of fraction I in *n*-pentadecane at 528 K resulted in the formation of II and III at similar rates indicating similar enantiomerization barriers for **4Z** and **4E**, as expected. The enantiomerization of ethene **4** was followed by heating the levorotatory fraction III (i.e., either (−)**4Z** or (−)-**4E**) in pentadecane at 528, 533, 538, and 543 K. As shown in Figure 3, this resulted in an increase in intensity of fraction I, while no compound corresponding to fraction II was formed. From the racemization data collected in Table 1, a barrier of $\Delta G^{\ddagger} = 44.8 \pm 0.7$ kcal mol^{-1} ($\Delta H^{\ddagger} = 44.2 \pm 0.34$ kcal mol^{-1}, $\Delta S^{\ddagger} = -1.15 \pm 0.66$ eu (at 500 K))[15] was calculated for the enantiomerization process.

These experiments clearly demonstrate that the enantiomerization process is *not* accompanied by a simultaneous (−)**4Z** ⇌ (−)**4E** diastereomerization. By symmetry considerations, it can be concluded also that the (+)**4Z** ⇌ (+)**4E** process, although "hidden" since the two diastereomers are not separated

under the chromatographic conditions, is not taking place. The enantiomerization observed is compatible with a "pure" ring rotation process (route a) which interconverts the pair of compounds (−)**4Z** ⇌ (+)**4Z** and (−)**4E** ⇌ (+)**4E**. However, since under the resolution conditions (+)**4Z** and (+)**4E** appear as a single fraction (fraction I), the observed growth of fraction I with time can also be interpreted as resulting from a process in which the ring and double bond rotations are coupled leading to the exchanges (−)**4Z** ⇌ (+)**4E** and (+)**4Z** ⇌ (−)**4E** (route d in Figure 1).

In order to unequivocally distinguish between these possibilities, we separated the two diastereomeric racemates ((+)/(−)-**4Z** and (+)/(−)**4E**) by supercritical fluid chromatography (SFC) using the achiral octadecyl-bonded silica gel as the stationary phase and CO_2 as the mobile phase. Both diastereomers were completely separated (Figure 4). The resolved fraction III displayed a single peak in the SFC as expected. After a solution of this fraction in *n*-pentadecane was heated at 553 K for 20 h, substantial (95.2%) racemization of the sample was observed as indicated by the increase of fraction I in the HPLC chromatogram. However, no $E \rightleftharpoons Z$ diastereomerization took place judged from the SFC (Figure 4). These experiments rule out pathway d and indicate that *no double bond rotation is involved in the threshold rotational pathway of the system*. Examination of the sample by SFC showed no detectable diastereomerization even after 48 h in *n*-pentadecane at 553 K. Assuming that ≥10% diastereomerization could have been detected under these conditions, we estimate a lower limit of 48.7 kcal mol^{-1} for the barrier of the double bond rotation.

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(15) The error in the enthalpy and entropy terms is probably high due to the relatively narrow temperature range of the enantiomerization studies.
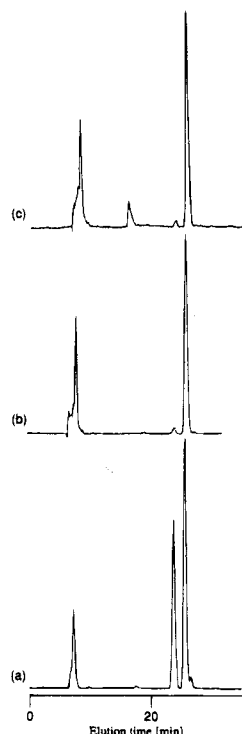
Figure 4. Supercritical fluid chromatographic analysis: (a) mixture of racemic **4Z** and **4E**; (b) resolved fraction III; (c) racemized fraction III after heating for 20 h at 553 K. The ratio between the two diastereomers remains unchanged after the racemization of the sample indicating that no double bond rotation took place.

The larger double bond barrier observed for **4** as compared with those of the less crowded tetraarylethenes **3a–c**[12b] could be due to a ground state effect, a transition state effect, or both. The ethene unit in some crowded ethenes adopts a nonplanar (folded or twisted) geometry and this ground state effect reduces the barrier considerably.[11] However, according to X-ray crystallography the double bond of **1** shows only a small departure from planarity (the C–C=C–C (cis) torsional angle is 4.4°),[7b,c] the steric crowding in the ground state being mainly relieved by elongation of the double bond. We do not expect a significant difference between the ground state geometries of **1** and **4**. Although the double bond torsional angle in tetraphenylethene is slightly higher (ca. 8°),[16] this ground state effect should reduce the barrier in tetraphenylethene and its p-X substituted derivatives **3a–c** only slightly compared with **1**, **2**, and **4**. This effect should be compensated by the lower Ar–C torsion angles in tetraphenylethene (average 48°)[16] compared with **1** (54.6°)[7b] which reduces the relative ground state energy of the former due to conjugation. Hence, the difference is most likely due to a combination of steric and electronic effects on the diradical transition state. The effect of the *para* substituents in ethenes **3** is negligible,[12b] and this should also apply for our systems. Decreasing the torsional angles of the rings with the Ar(C$_{ipso}$)–C–Ar(C$_{ipso}$) unit in the transition state will stabilize the developing biradical by conjugation. However, the *ortho* substituents present in **4** should make this decrease more energetically costly, raising the energy of the transition state. This effect should be the major source of the barrier since, in spite of the presence of two aryl groups on the radical, the barrier is still higher for **4** than for stilbene, which in turn is higher than that deduced for tetraphenylethene.[12b]

The aryl–C rotational mechanism most likely involves a correlated rotation of the four rings via a four-ring flip

mechanism.[4b,8] Surprisingly, the rotational barrier of **4** ($\Delta G^{\ddagger}$ = 44.8 kcal mol^{-1}) is higher than the barriers found for **1** ($\Delta G^{\ddagger}$ = 39.6 kcal mol^{-1}) and **2** ($\Delta G^{\ddagger}$ = 43.1 kcal mol^{-1}). The larger rotational barrier is not due to increased ground state conjugation of the aryl rings with the double bond. Clearly, the transition state for the rotation of **4** is the most crowded and a possible explanation for its high barrier is that the bulky *tert*-butyl groups reduce the flexibility of the ring to allow the alleviation of the repulsive steric interactions in the transition state.

Conclusions. The threshold enantiomerization pathway of the vinyl propeller **4** involves purely ring rotations. The barrier for the double bond rotation is significantly higher.

Experimental Section

The irradiation experiment was performed using a 80-W Hanau mercury vapor lamp (Q-81) through a quartz glass filter. For the resolution experiment a JASCO PU-980 HPLC apparatus using a JASCO 875-UV and Shodex OR-1 detectors were used. Five columns connected in tandem of cellulose tris(3,5-dimethylphenylcarbamate) (25 x 0.46 (i.d.) cm x 5) were used as the stationary phase. The flow was 0.5 mL/min and the pressure was 63 kg cm^{-2}.

The separation of the *E* and *Z* isomers of **4** was carried out by supercritical fluid chromatography (SFC). SFC was performed on a column (25 x 0.46 (i.d.) cm) packed with octadecyl bonded silica gel (JASCO Finepack SIL C18T-5, particle size 5 μm) using supercritical CO$_2$ as the mobile phase (flow rate: 1.0 mL/min). The fluid pressure at the bottom of the column was controlled at 210 kg cm^{-2}, and the column temperature was kept at 40 °C.

(4-*tert*-Butyl-2,6-dimethylphenyl)mesitylketene (5). The ketene was prepared by a modification of a previously published procedure.[17] To an ice-cooled solution of (4-*tert*-butyl-2,6-dimethylphenyl)mesitylacetic acid (0.9 g, 2.66 mmol)[18] dissolved in dry toluene (12 mL) were added thionyl chloride (0.3 mL) and pyridine (two drops). The solution was allowed to attain room temperature and then heated slowly to reflux. After reflux for 4.5 h, the solution was decanted from the precipitated pyridinium hydrochloride, and the solvent was evaporated, yielding 0.7 g (82%) of crude product. After dissolution in hot dry petroleum ether 60–80 °C, the solution was treated with Norite, yielding on cooling yellow crystalline solid (0.48 g, 56%), mp 140.5–141 °C. IR (nujol) νcco 2099.9 cm^{-1}. Anal. Calcd for C$_{23}$H$_{28}$O: C, 86.20; H, 8.81. Found: C, 86.45; H, 9.06.

1,2-Bis(4-*tert*-butyl-2,6-dimethylphenyl)-1,2-dimesitylethene (4). Ketene **5** (60 mg) was dissolved in hexane (70 mL) and the solution was irradiated for 1 h with stirring under nitrogen. After evaporation of the solvent, a mixture with a 1.1:1 ratio of the two *t*-Bu signals was observed. The residue was chromatographed (silica, 230–400 mesh, eluent: hexane) yielding the crude product (28.5 mg, 52%), mp 241–243 °C (mp 246 °C for one of the pure isomers fractionated by SFC).

^{1}H NMR (CDCl$_3$, 400 MHz, RT) diastereomer A: δ 1.20 (s, 18H, *t*-Bu), 1.71 (s, 12H, Me), 1.84 (s, 6H, Me), 1.89 (s, 6H, Me), 2.16 (s, 6H, Me), 6.53 (br s, 2H, Mes-H), 6.60 (br s, 2H, Mes-H), 6.62 (d, *J* = 2.1 Hz, 2H, Ar-H), 6.73 (d, *J* = 2.1 Hz, 2H, Ar-H). ^{1}H NMR (CDCl$_3$, 400 MHz, RT) diastereomer B: δ 1.21 (s, 18H, *t*-Bu), 1.68 (s, 6H, Me), 1.70 (s, 6H, Me), 1.83 (s, 6H, Me), 1.90 (s, 6H, Me), 2.16 (s, 6H, Me), 6.49 (br s, 2H, Mes-H), 6.59 (br s, 2H, Mes-H), 6.67 (d, *J* = 2.1 Hz, 2H, Ar-H), 6.75 (d, *J* = 2.1 Hz, 2H, Ar-H). HRMS calcd for C$_{44}$H$_{56}$ *m/z* 584.4382, found *m/z* 584.4374 for the diastereomeric mixture and 584.4387 for the isolated pure diastereomer.

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