# A Novel Approach to Stilbenoid Dendrimer Core Synthesis

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**Abstract:** A new synthetic protocol for the one-pot, stereoselective synthesis of 1,3,5-tris[(*E*)-4-halostyryl]benzene and 1,2,4,5-tet-rakis[(*E*)-4-halostyryl]benzene derivatives as stilbenoid dendrimer cores via palladium-catalyzed Hiyama cross-coupling of aryl tri- or tetrahalides with 1,3-bis[(*E*)-4-halostyryl]disiloxanes is described.

Key words: cross-coupling, palladium catalyst, stilbenoid dendrimer cores, silicon derivatives

Dendrimers are repeatedly branched, monodisperse macromolecules built of a central core and repeated sequences (dendrons).<sup>1</sup> The number describing the dendrimer generation is defined by the number of branching points between the periphery and the core. The degree of branching in a dendrimer increases with successive generations so that high generation dendrimers are globular in shape and possess high functional group densities at their periphery.

Various dendritic systems have been studied in view of their prospective applications as low-dielectric materials,<sup>2</sup> catalysts,<sup>3</sup> unimolecular micelles,<sup>4</sup> sensors,<sup>5</sup> efficient light-harvesting antennae<sup>6</sup> and potential drug-delivery systems.<sup>7</sup>

Dendrimers with polyconjugated branches represent an important group within this class of materials and hence they are interesting because of their electrical, optical, nonlinear optical, electroluminescent and photophysical properties. For example, such compounds have been successfully used as charge-transporting<sup>8</sup> and light-emitting materials.9 Arylalkene-based dendrimers have been one of the most widely studied families of dendrimers with trans-stilbenyl moieties within the branching framework playing a major role in the structures.<sup>10</sup> Stilbene units can make the core or can be elements of the dendrons or both.<sup>1d,10</sup> Stilbenoid dendrimers offer a number of advantages over the linear poly(p-phenylenevinylene) (PPV). Due to their highly branched structures, such dendrimers are expected to be less aggregated and hence, should not suffer from fluorescence quenching due to intermolecular interactions.<sup>11</sup> Dendrimers with photoreversible stilbene core undergo mutual cis-trans isomerization in organic solvents to give photostationary state mixture of cis and trans isomers. The photocyclization reaction does not take place in the second or higher generation dendrimers probably due to the steric effect of the bulky dendron groups.

SYNLETT 2008, No. 19, pp 3026–3030 Advanced online publication: 12.11.2008 DOI: 10.1055/s-0028-1083630; Art ID: G24008ST © Georg Thieme Verlag Stuttgart · New York Despite rapid advances in the potential application of dendrimers, their syntheses are still confined to the divergent<sup>12a</sup> or convergent<sup>12b</sup> synthetic strategies. There are two main convergent strategies reported for obtaining (*E*)-stilbenyl-based dendrimers. The first strategy is based on the Wittig<sup>10</sup> or Horner–Wadsworth–Emmons-type chemistry,<sup>13a–13c</sup> whereas the second is based on the Heck<sup>9a,b,13d,e</sup> or Suzuki<sup>13f,g</sup> palladium-catalyzed-type chemistry. Recently, an alternative approach to stilbenyl dendrons has been reported, which is based on the Ramberg– Backlund reaction.<sup>14</sup> Depending on the substituents, the Wittig–Horner reaction in stilbenoid series sometimes exhibits a low percent of Z isomer (2–5%).<sup>10</sup>

The palladium-catalyzed and fluoride-promoted crosscoupling of unsaturated organosilicon compounds with aryl halides (Hiyama coupling) has been recently employed as a mild and efficient alternative to the well-established Heck, Stille and Suzuki reactions, taking into account the commercial availability, high stability and low toxicity of the silicon derivatives.<sup>15</sup>

Therefore, we wish to report herein the first, unprecedented, one-pot palladium-catalyzed Hiyama-type strategy for the stereoselective synthesis of 1,3,5-tris[(*E*)-4-halostyryl]benzene and 1,2,4,5-tetrakis[(*E*)-4-halostyryl]benzene derivatives as stilbenoid dendrimer cores using aryl tri(or tetra)halides and appropriate 1,3-bis[(*E*)-4-halostyryl]disiloxanes. These compounds can be easily transformed into the first or higher generation dendrimers via the wellknown reactions like those of Heck, Hiyama, Stille or Suzuki.

Since 1,3-bis[(*E*)-4-halostyryl]disiloxanes **1–3** (Scheme 1) as starting compounds can be easily prepared with high yield from inexpensive 1,3-divinyltetramethyldisiloxane and halostyrenes using the ruthenium-catalyzed silylative cross-coupling reaction, this sequence of reactions, i.e. silylative coupling (also called *trans*-silylation or silyl group transfer)<sup>16</sup>–desilylative coupling (Hiyama) is expected to be an attractive alternative for the synthesis of stilbenoid dendrimer cores.

The silylative coupling of 1,3-divinyltetramethyldisiloxane with *para*-halosubstituted styrenes was examined in an open system under a gentle stream of argon. The reaction was effectively catalyzed by the ruthenium catalyst [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (1 mol% per silyl group) and CuCl as a co-catalyst (2 mol%) in dioxane at 100 °C for 16 hours. The exclusive formation of the *E*-isomer of 1,3bis[(*E*)-4-halostyryl]disiloxanes **1–3** (Table 1) was confirmed by <sup>1</sup>H NMR. The use of the catalyst or co-catalyst



Scheme 1

**Table 1** Synthesis of 1,3-Bis[(E)-4-halostyryl]tetramethyldisilox-anes via Silylative Cross-Coupling of 1,3-Divinyltetramethyldisilox-ane with 4-Halostyrenes<sup>a,17</sup>

Entry	Time (h)	Product	Conversion (ArX) (%)	Yield (%) <sup>b</sup>
1	24	1°	84	_
2	8	1	54	-
3	16	1	>99	87
4	16	2	>99	91
5	16	3	>99	93

<sup>a</sup> Reaction conditions: [Si]/[ArX]/[TBAF]/[RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>]/ CuCl = 1:4:2.4:0.01:0.02, dioxane, 100 °C.

<sup>b</sup> Isolated yields of products.

<sup>c</sup> [Ru]:/[Si] = 1:200.

in lower amounts (0.5 mol% per silyl group) required longer reaction time (24–48 h) and gave the desired product in low yield (Table 1, entry 1). On the other hand, a lower amount of catalyst led to significant amounts of monosubstituted 1,3-divinyltetramethyldisiloxane (1styryl-3-vinyltetramethyldisiloxane). In the second step of the one-pot silylative coupling–desilylative coupling sequence, this monosubstituted compound yielded some by-products.

It is worth noting that the best results were observed when the co-catalyst was added to the reaction mixture a few minutes after beginning of the reaction.

The synthesized 1,3-bis[(*E*)-4-bromostyryl]disiloxane (**2**) thus obtained was next used for the palladium-catalyzed desilylative coupling reaction with 1,3,5-tribromobenzene in the synthesis of 1,3,5-tris[(*E*)-4-bromostyryl]benzene (**5**) (Scheme 2). The reaction was performed in an open system under a gentle flow of argon in the presence of  $[Pd_2(dba)_3]$  (1 mol% per silyl group) and TBAF as an activator at 30 °C for 24 hours.

Unfortunately, under these reaction conditions (30–40  $^{\circ}$ C), the expected product was not observed, whereas at



55 °C a low conversion of 1,3,5-tribromobenzene was detected (ca. 20%). By increasing the temperature to 80 °C the reaction was complete in 16 hours. Due to the presence of bromine substituents in both substrates, a mixture of linear and branched polymers was isolated (Scheme 2, Table 2).

Under standard desilylative coupling conditions in the absence of 1,3,5-tribromobenzene, compound **2** underwent at 80 °C desilylative homocoupling to poly(phenylenevinylene) derivatives with high yield (>99%) and stereoselectivity (>99% E).<sup>18</sup> This unexpected result can be of interest in the synthesis of (E)-poly(phenylenevinylene) derivatives and needs further investigations.

The reaction performed with 1,3-bis[(*E*)-4-halostyryl]disiloxanes **1** and **3** and under the optimum conditions provided almost quantitative yields (90–96%) of the desired 1,3,5-tris[(*E*)-4-styryl]benzene (**4**) and 1,3,5-tris[(*E*)-4chlorostyryl]benzene (**6**; Table 2). Similarly to the reactions with 1,3,5-tribromobenzene, the palladium-catalyzed coupling of the 1,3-bis[(*E*)-4-halostyryl]disiloxanes **1–3** with 1,2,4,5-tetraiodobenzene in the presence of TBAF and Pd<sub>2</sub>(dba)<sub>3</sub> (1 mol% per silyl group) catalyst proceeded stereoselectively to give satisfactory yields of the desired 1,2,4,5-tetrakis[(*E*)-4-halostyryl]benzenes **7– 9** (Table 2).

The compounds **1–3** underwent the desilylative coupling reaction (Hiyama coupling) with 1,2,4,5-tetraiodobenzene at 30 °C because of the higher reactivity of iodo-substituted substrates. This reaction required a small excess of silyl compounds (at least 10% per iodo substituent) and TBAF (20% per silyl group). The reaction needed at least 1 mol% catalyst loading ([Pd<sub>2</sub>(dba)<sub>3</sub>]) per silyl group for exclusive formation of the expected products. The use of a higher amount of palladium catalyst, or a higher temperature of the reaction significantly reduced the reaction time. Under the above specific reaction conditions, the desired 1,2,4,5-tetrakis[(*E*)-4-halostyryl]benzenes **7–9** were obtained with high yield and stereoselectivity (Table 2).



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The results of the catalytic study prompted us to perform experiments aiming at a design of the one-pot reaction system without isolation of 1,3-bis[(E)-4-halostyryl]disiloxanes 1-3 (Scheme 3). In the first step, the unsaturated organosilicon precursors were synthesized using ruthenium hydride catalyzed silvlative coupling of 1,3-divinyltetramethyldisiloxane with styryl halides. Then, the post-reaction mixture was treated with an appropriate tri(or tetra)halobenzene under standard Hiyama crosscoupling conditions (Scheme 3, Table 2). A twofold excess of 4-halostyrene relative to divinyltetramethyldisiloxane (per silyl group) was found enough to complete with the silvlative coupling reaction of both vinyl groups and in these conditions homopolymerization of halostyrene was not observed. These optimal conditions applied to the one-pot synthesis of 4, and 6–9 provided very high yields (72–95%) and stereoselectivity (>99%). Noticeably, the yields were only slightly lower than those obtained in the two-step process with isolation of 1,3bis[(E)-4-halostyryl]disiloxanes 1–3 (Table 2). 1,3,5-Tris[(E)-4-halostyryl]benzene 4 and 6 and 1,2,4,5-tetrakis[(E)-4-halostyryl]benzene 7–9 were isolated via column chromatography with silica gel (THF-EtOAc).

The structure of the products 1-4 and 6-9 was confirmed by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and EI-MS spectroscopy. The presence of (*E*)-vinylene functionality was unambiguously confirmed by the appearance of FT-IR bands attributable to the CH bending of *trans*-vinylene at 956–986 cm<sup>-1</sup>. Unfortunately, the corresponding <sup>1</sup>H NMR signals (J = 15.9-19.2 Hz) fell in the region of aromatic protons and could not be assigned for some products (**4**, **6** and **7**). The MALDI-MS spectra of poly(phenylenevinylene) (Scheme 2) in dithranol as a matrix revealed only shortchain polymers (6–20-mer).

In conclusion, we have developed a new, efficient, and highly stereoselective, one-pot synthetic methodology for the construction of 1,3,5-tris[(*E*)-4-halostyryl]benzene and 1,2,4,5-tetrakis[(*E*)-4-halostyryl]benzene derivatives as stilbenoid dendrimer core based on the palladium-catalyzed Hiyama cross-coupling of 1,3-bis[(*E*)-4-halostyryl]disiloxanes or the sequential silylative coupling, Hiyama cross-coupling of 1,3-divinyltetramethyldisiloxane with halosubstituted arenes. The availability of the starting materials, simplicity of the experimental technique and the possibility of the use of aryl bromides are favorable features of this new catalytic approach to obtain the stereodefined stilbenoid dendrimer core.

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 Table 2
 Synthesis of 1,3,5-Tris(or 1,2,4,5-Tetrakis)[(E)-4-halostyryl]benzene Derivatives<sup>a,19</sup>

$\begin{pmatrix} Me \\ X \\ H, Br, Cl \end{pmatrix} \xrightarrow{H} 0 \xrightarrow{Pd_2(dba)_3} 0 \xrightarrow{R^2} R^1 = H; R^2 = R^3 = 0 \xrightarrow{H} 0 $								
Entry	Aryl halide	Х	Time (h)	Product	Yield (%) <sup>b</sup>			
1	1,3,5-C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub>	Н	16	4	95 (93)°			
2	1,3,5-C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub>	Br	16	5	polymer			
3	1,3,5-C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub>	Cl	48	6	96 (90)			
4	1,2,4,5-C <sub>6</sub> H <sub>2</sub> I <sub>4</sub>	Н	24	7	77 (72)			
5	1,2,4,5-C <sub>6</sub> H <sub>2</sub> I <sub>4</sub>	Br	24	8	93 (95)			
6	$1,2,4,5-C_6H_2I_4$	Cl	24	9	81 (78)			

<sup>a</sup> Silylative coupling conditions: dioxane (0.25 M), 100 °C, 16 h, [Si]/[ArX]/[RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>]/[CuCl] = 1:2:0.01:0.02; Hiyama coupling conditions: dioxane (0.25 M), 80 °C, [Si]/[ArBr<sub>3</sub>]/[TBAF]/[Pd<sub>2</sub>(dba)<sub>3</sub>] = 1:0.25:1.2:0.01,  $Sil(ArL)/(TDAF)/(Pd_2(dba)_3) = 1:0.25:1.2:0.01$ 

 $[Si]/[ArI_4]/[TBAF]/[Pd_2(dba)_3] = 1:0.2:1.2:0.01, 30 \ ^{\circ}C.$ 

<sup>b</sup> Isolated yields of products.

<sup>c</sup> The yield of the 'one-pot' reaction is given in parenthesis.



#### Scheme 3

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- (17) Typical Procedure for the Synthesis of 1,3-Bis[(E)-4halostyryl]disiloxanes: The glass reactor (10-mL, twonecked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, argon bubbling tube and thermostated oil bath) was evacuated and flushed with argon. [RuH(Cl)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (47.6 mg, 0.05 mmol), 1,3divinyltetramethyldisiloxane (0.5 g, 2.5 mmol), styrene or 4-bromo(or chloro)styrene (10 mmol) and anhyd dioxane (5 mL) were added to the reactor. Then the reaction mixture was stirred and heated at 100 °C under argon flow. After 5 min, copper(I) chloride (CuCl; 9.9 mg, 0.1 mmol) was added as a co-catalyst. The synthesis process was carried out for the next 16 h. After the reaction was completed (GC-MS analysis) the volatiles were evaporated under vacuum and the crude product was chromatographed on silica gel (eluent: hexane-EtOAc, 10:1) to afford the analytically pure products.

1,3-Bis[(E)-4-bromostyryl]tetramethyldisiloxane (2): mp 56-60 °C. IR (KBr): 799.5, 844.8, 985.3, 1055.5, 1253.5, 1485.7, 1604.6, 2956.9, 3020.3 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta =$ 0.24 (s, 12 H, SiMe), 6.41 (d, J = 19.1 Hz, 2 H, SiCH=), 6.86 (d, J = 19.2 Hz, 2 H, PhCH=), 7.27 (d, J = 7.6 Hz, 4 H,  $BrC_6H_4$ ), 7.43 (d, J = 8.3 Hz, 4 H,  $BrC_6H_4$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 0.9, 121.9, 127.9, 129.4, 131.5, 136.9, 142.9. MS (EI): *m/z* (%rel. int.) = 496 (7) [M<sup>+</sup>], 415 (32), 297 (60), 133 (100), 117 (37), 73 (50). HRMS: m/z [M<sup>+</sup>] calcd for C<sub>20</sub>H<sub>24</sub><sup>79</sup>Br<sup>81</sup>BrOSi<sub>2</sub>: 495.9712; found: 495.9685. 1,3-Bis[(E)-4-chlorostyryl)tetramethyldisiloxane (3): mp 51-54 °C. IR (KBr): 800.6, 845.1, 985.6, 1056.4, 1254.2, 1488.9, 1564.5, 1606.2, 2957.6, 3024.3 cm<sup>-1</sup>. <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta = 0.25$  (s, 12 H, SiMe), 6.40 (d, J = 19.2 Hz, 2 H, SiCH=), 6.88 (d, J = 19.2 Hz, 2 H, PhCH=), 7.28 (d, J = 8.8 Hz, 4 H,  $ClC_6H_4$ ), 7.34 (d, J = 8.8 Hz, 4 H,  $ClC_6H_4$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 0.9, 127.6, 128.6, 129.2, 133.7, 136.5, 142.8. MS (EI): m/z (%rel. int.) = 406 (21) [M<sup>+</sup>], 281 (90), 253 (100), 227 (59), 133 (98), 117 (62), 73 (98). HRMS: m/z [M<sup>+</sup>] calcd for C<sub>20</sub>H<sub>24</sub><sup>35</sup>Cl<sub>2</sub>OSi<sub>2</sub>: 406.0743; found: 406.0746.

(18) Synthesis of PPV from 1,3-Bis[(*E*)-4-bromostyryl]tetramethyldisiloxane: [Pd<sub>2</sub>(dba)<sub>3</sub>] (9.16 mg, 0.01 mmol), dioxane (4 mL), 1,3-bis[(*E*)-4-bromostyryl]tetramethyldisiloxane (2; 248 mg, 0.5 mmol), and tetrabutylammonium fluoride (320 mg, 1.2 mmol) were placed in an evacuated and flushed with argon, 10-mL flask. The mixture was heated at 80 °C for 12 h under an argon atmosphere. The degree of conversion of the substrates was estimated by GC and TLC analyses. Then the reaction mixture was cooled and the precipitated solid was filtered and washed extensively with acetone.

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(19) Typical Procedure for the One-Pot Synthesis of 1,3,5-Tris- or 1,2,4,5-Tetrakis[(E)-4-halostyryl)benzenes and Spectroscopic Data of Selected Products: The glass reactor (10-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, argon bubbling tube and thermostated oil bath) was evacuated and flushed with argon. [RuH(Cl)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (9.52 mg, 0.01 mmol), 1,3-divinyltetramethyldisiloxane (0.1 g, 0.5 mmol), styrene or 4-bromo(or chloro)styrene (2.0 mmol) and anhyd dioxane (2 mL) were added to the reactor. Then the reaction mixture was stirred and heated at 100 °C under argon flow. After 5 min, CuCl (1.98 mg, 0.02 mmol) was added as a co-catalyst. The synthesis process was carried out for the next 24 h. After the reaction was completed (GC-MS or GC and TLC analyses), palladium catalyst [Pd<sub>2</sub>,dba)<sub>3</sub>] (9.16 mg, 0.01 mmol), TBAF (320 mg, 1.2 mmol), dioxane (3 mL) and respective haloarene [1,3,5tribromobenzene (78.7 mg, 0.25 mmol) or 1,2,4,5-tetraiodobenzene (116 mg, 0.2 mmol)] were added and the mixture was heated at 80 °C (30 °C for 1,2,4,5-tetraiodobenzene) for 16-48 h under an argon atmosphere. The degree of conversion of the substrates was estimated by GC and TLC analyses. The final product was separated using chromatography column with silica (THF-EtOAc). 1,3,5-Tris[(E)-4-chlorostyryl]benzene (6): mp 216–220 °C. IR (KBr): 806.3, 841.7, 960.2, 1090.4, 1490.7, 1585.1, 1668.2, 2924.2, 2957.7, 3024.9 cm<sup>-1</sup>. <sup>1</sup>H NMR

(CDCl<sub>3</sub>):  $\delta$  = 7.09 (d, *J* = 15.9 Hz, 3 H, C<sub>6</sub>H<sub>3</sub>C*H*=), 7.20– 7.45 (m, 15 H, ClC<sub>6</sub>H<sub>4</sub>CH=), 7.65 (s, 3 H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 124.8, 125.4, 127.6, 128.1, 128.8, 133.3, 135.5, 137.7. MS (EI): *m*/*z* (%rel. int.) = 486 (8) [M<sup>+</sup>], 364 (56), 350 (47), 220 (49), 205 (100), 73 (57). HRMS: *m*/*z* [M<sup>+</sup>] calcd for C<sub>30</sub>H<sub>21</sub><sup>35</sup>Cl<sub>3</sub>: 486.0709; found: 486.0694.

**1,2,4,5-Tetrakis**[*(E)*-**4-bromostyryl]benzene** (**8**): mp 265–268 °C. IR (KBr): 798.9, 845.4, 956.6, 1008.5, 1072.1, 1258.5, 1487.9, 1587.4, 1682.4, 1725.1, 2924.1, 2957.9, 3049.3 cm<sup>-1</sup>. <sup>1</sup>H NMR (THF- $d_8$ ):  $\delta = 7.19$  (d, J = 16.0 Hz, 4 H, C<sub>6</sub>H<sub>2</sub>CH=), 7.50–7.58 (m, 16 H, BrC<sub>6</sub>H<sub>4</sub>), 7.67 (d, J = 16.1 Hz, 4 H, BrC<sub>6</sub>H<sub>4</sub>CH=), 7.98 (s, 2 H, C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C NMR (THF- $d_8$ ):  $\delta = 121.9$ , 125.0, 127.2, 129.1, 130.9, 132.4, 136.3, 137.6. MS (EI): m/z (%rel. int.) = 802 (5) [M<sup>+</sup>], 633 (14), 308 (20), 196 (32), 185 (64), 91 (95), 57 (100). Anal. Calcd for C<sub>38</sub>H<sub>26</sub>Br<sub>4</sub>: C, 56.89; H, 3.27. Found: C, 56.58; H, 3.03.

**1,2,4,5-Tetrakis**[*(E)*-**4-chlorostyryl]benzene (9**): mp 242–246 °C. IR (KBr): 808.2, 853.3, 960.3, 1012.2, 1091.7, 1492.4, 1592.4, 1667.7, 1686.8, 2924.6, 2955.8, 3027.2 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.96$  (d, J = 16.2 Hz, 4 H, C<sub>6</sub>H<sub>2</sub>CH=), 7.06–7.17 (m, 16 H, ClC<sub>6</sub>H<sub>4</sub>), 7.44 (d, J = 16.2 Hz, 4 H, ClC<sub>6</sub>H<sub>4</sub>CH=), 7.87 (s, 2 H, C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 126.4$ , 127.1, 129.3, 129.7, 130.2, 134.2, 136.1, 138.9. MS (EI, %rel. int.): m/z = 622 (6) [M<sup>+</sup>], 248 (32), 178 (51), 139 (68), 125 (100). Anal. Calcd for C<sub>38</sub>H<sub>26</sub>Cl<sub>4</sub>: C, 73.09; H, 4.20. Found: C, 72.81; H, 4.01.