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Synthesis and Properties of Diethyl 5,10-Dihetera-5,10-dihydroindeno[2,1-*a*]indene-2,7-dicarboxylates†

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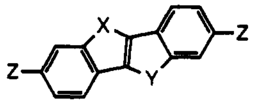
A series of six heterocyclic diesters **1b**–**6b** containing all combinations of nitrogen, sulfur, and selenium has been prepared from a common precursor, diethyl 2,2′-dinitrostilbene-4,4′-dicarboxylate. Electrochemical analysis showed oxidation potential increases in the order N < Se < S, and the same trend was observed for maxima of UV absorbance. Electrochemical oxidation of indoloindole **1b** (but not the other members of the series) generates a persistent radical cation whose properties were investigated. Diesters containing sulfur and selenium (but not nitrogen) form S_A liquid crystals. A new synthetic method leading to the indolo[1,2-*b*]indazole ring system has been found.

Introduction

Heterocyclic compounds are of increasing interest for the preparation of organic conductive,[1] magnetic,[2] and nonlinear[3] materials. Low molecular weight materials are most often prepared as charge-transfer complexes (CT) of the parent donors and acceptors.[4] In contrast, a rational design of polymeric conductive[5] and magnetic materials[6,7] requires precursors with functional groups suitable for extension of the π conjugation in a condensation process. In the present work we describe a preparation of six heterocyclic ring systems with versatile ester groups (**1b**–**6b**) at the conjugated positions 2 and 7, all from a common precursor. Spectral and electrochemical analysis of these new compounds, as well as magnetic characterization of a persistent radical salt are discussed.

Six 5,10-dihetera derivatives of 5,10-dihydroindeno[2,1-*a*]indene have been synthesized previously: 5,10-dihydroindolo[3,2-*b*]indole[8] (**1a**, R = H), [1]benzothieno[3,2-*b*][1]benzothiophene[9] (**2a**), [1]benzoselenopheno[3,2-*b*][1]benzoselenophene[10,11] (**3a**), 10H-[1]benzothieno[3,2-*b*]indole[12] (**4a**, R = H), 10H-[1]benzoselenopheno[3,2-*b*]indole[13] (**5a**, R = H), and [1]benzoselenopheno[3,2-*b*][1]benzothiophene[10] (**6a**). Some of them have been found to form complexes with electron-deficient π systems.[9,11,13,14] Polymeric compounds based on derivatives of **2b** have been applied as photoconductors in electrophotography.[15] Homopolymers obtained electrochemically from **4a** and its *N*-allyl derivative ($R = CH_2CH{=}CH_2$) are also good photoconductors.[16] The high stability of the delocalized radical cation[17] derived from 5,10-dihydro-*N*,*N*′-dimethylindolo[3,2-*b*]indole (**1a**, R = Me) is a desirable property for application as a spin-containing unit for polaronic magnetic materials.[7]



1 X=Y=NR
2 X=Y=S
3 X=Y=Se

4 X=NR, Y=S
5 X=NR, Y=Se
6 X=S, Y=Se

a Z=H
b Z=COOEt

Several synthetic routes lead to the indolo[3,2-*b*]indole (**1a**) skeleton, most of them involving formation of carbon–nitrogen bonds as the key step.[8,18–22] Reduction of *o*,*o*′-dinitrobenzil with zinc[18,19] or with stannous chloride[19] in acetic acid yields **1a**, R = H, in 30 or 32% yields, respectively. Reduction of *o*,*o*′-dinitrostilbene with triethyl phosphite yields only 2% of **1a**, R = H,[20] but reduction of 2-(*o*-nitrophenyl)indole with $P(OEt)_3$ gives a moderate yield of the product.[21] Fischer condensation of indolone and its derivatives with phenylhydrazines[22] yields **1a** and some of its derivatives.

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† Contribution No. 8770.

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The benzothieno[3,2-*b*]benzothiophene (**2a**) framework has been constructed in several ways.[9,23–29] The recently described reductive[23,24] or oxidative[24,25] cyclizations of stilbene-2,2′-disulfonyl chlorides or stilbene-2,2′-dithiols, respectively, appear to be the most convenient and efficient methods for preparation of symmetrically 2,7-disubstituted derivatives of **2a**.

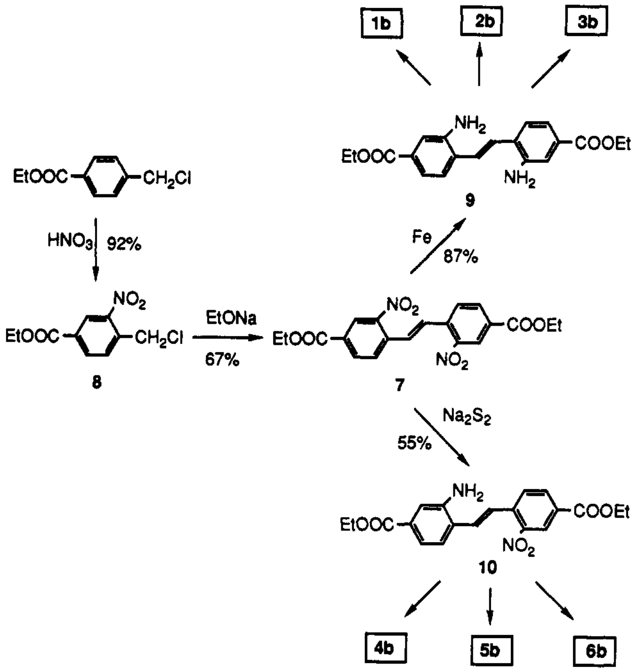
Oxidative–decarboxylative cyclization of α-[*o*-(methylseleno)phenyl]-*o*-(methylseleno)cinnamic acid or α-[*o*-(methylseleno)phenyl]-*o*-(methylthio)cinnamic acid yields benzoselenopheno[3,2-*b*]benzoselenophene (**3a**) and benzoselenopheno[3,2-*b*]benzothiophene (**6a**), respectively, in 35% yield.[10] The former was also obtained in an acid-catalyzed condensation of *o*-(methylseleno)benzaldehyde.[11]

Benzothieno[3,2-*b*]indole (**4a**) and its derivatives have been prepared from benzothiophenes[30,31] benzothiophen-3-ols,[12,32–35] and indoles.[36] Reduction of 2-(*o*-nitrophenyl)benzothiophene and 3-nitro-2-phenylbenzothiophene or decomposition of 2-(*o*-azidophenyl)benzothiophene and 3-azido-2-phenylbenzothiophene led to derivatives of benzothieno[3,2-*b*]indole in 30–60% yield.[30] Reduction of 2-(*o*-nitrophenyl)benzothiophen-3-ol with zinc was the first route to the parent **4a**.[12] Reaction of 3-hydroxybenzothiophenes[32–35] with phenylhydrazines is a convenient, moderate-yield route to a number of derivatives of **4a**. Iodine oxidation of 2-(*o*-mercaptophenyl)indole or acid-catalyzed cyclization of 2-[*o*-(methylsulfinyl)phenyl]indole also yielded **4a** in moderate yields.[36]

Benzoselenopheno[3,2-*b*]indole has been obtained by condensation of phenylhydrazine with benzoselenophen-3-one[13] or selenocyanatoacetophenone.[37]

The 2,7-disubstituted ring system **1–6**, useful for the preparation of extended π conjugation systems, is represented only by a few examples in the benzothieno[3,2-*b*]indole (**4a**) family[33] and more extensively in the benzothieno[3,2-*b*]benzothiophene (**2a**) family.[24,25] Direct electrophilic aromatic substitution (nitration and formylation) in **2a** leads to a mixture of 2- and 4-isomers.[38] However, Friedel–Crafts acetylation gives 60% of the 2-acetyl derivative.[39] Bromination of **4a** (R = H) gave 2-bromo-10H-[1]benzothieno[3,2-*b*]indole in 57% yield.[30]

Scheme I



Results and Discussion

Synthesis. The generality of heteroatom intramolecular cyclization of properly substituted stilbenes leading to simultaneous or stepwise formation of five-membered heterocyclic rings in systems **1–6** suggested that diethyl 2,2′-dinitro-(*E*)-stilbene-4,4′-dicarboxylate (**7**) would be a good choice as the precursor to esters **1b–6b**. The two nitro groups in **7** can be easily converted into sulfur and selenium derivatives suitable for the cyclizations. The ester groups are relatively stable to most of the reaction conditions, and their attachment at the 4 and 4′ positions ensures the desired substitution pattern in the final esters **1b–6b**.

The diester **7** was synthesized (Scheme I) based on an earlier report[40] of successful preparation of 4,4′-dicyano-2,2′-dinitrostilbene from 4-(chloromethyl)-3-nitrobenzonitrile. Commercially available 4-(chloromethyl)benzoic acid was converted into its ethyl ester and nitrated to yield ethyl 4-(chloromethyl)-3-nitrobenzoate (**8**). This procedure was found superior to the one in which the acid was nitrated first, and then esterified. The condensation step[40] was modified, and the ester **8** was treated with sodium ethoxide at 0–5 °C, which furnished 67% yield of the desired stilbene **7**.

The dinitrostilbene **7** was reduced with iron powder in ethanol in the presence of hydrochloric acid to yield the highly fluorescent, yellow diethyl 2,2′-diaminostilbene-4,4′-carboxylate (**9**). Reduction of **7** with 1 equiv of disodium disulfide in pyridine yielded 55% of orange diethyl 2-amino-2′-nitrostilbene-4,4′-dicarboxylate (**10**). Diamine **9** was used for preparation of diesters **1b–3b**, while nitro amine **10** was used in synthesis of **4b–6b**.

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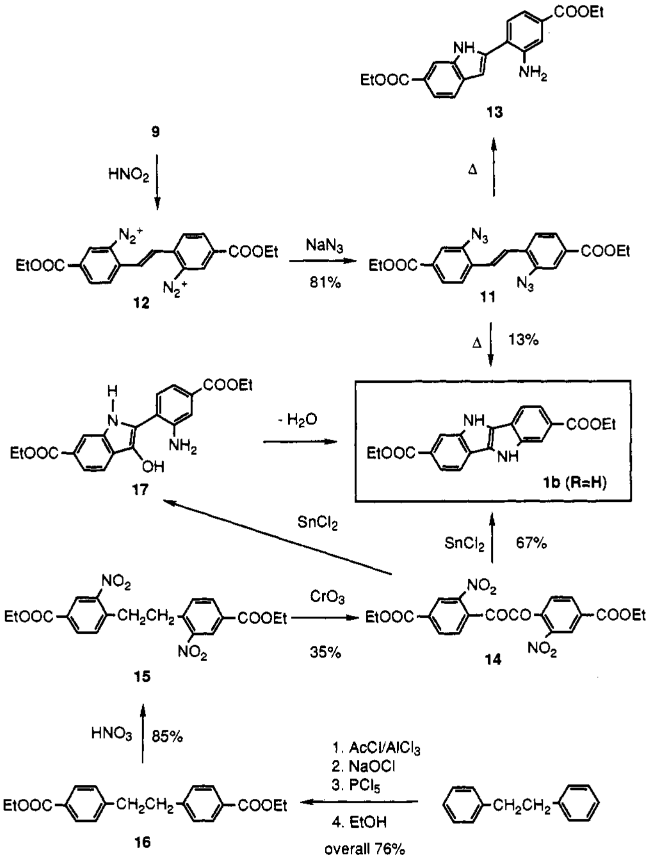
Scheme II

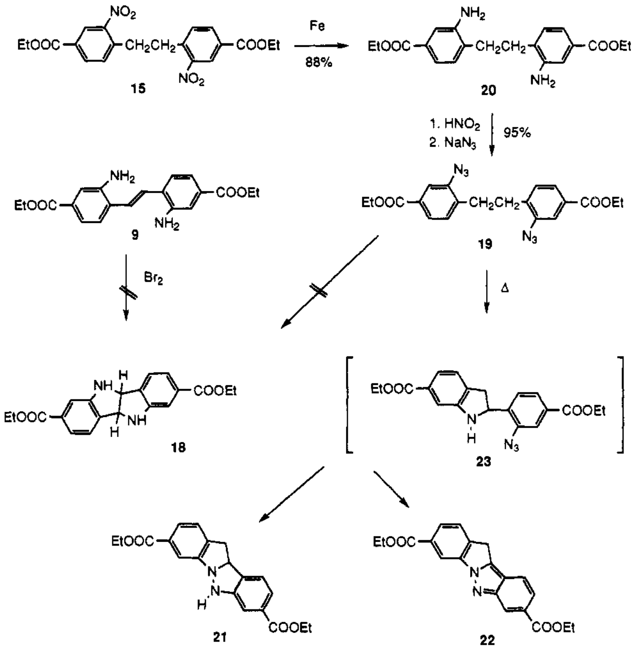


Preparation of Diethyl 5,10-Dihydroindolo[3,2-*b*]indole-2,7-dicarboxylate (1b, R = H). Diamine **9** was converted[41] to the corresponding diazide **11** via bis-diazonium salt **12** in 81% yield. Thermal decomposition of **11** at 155 °C in *o*-dichlorobenzene yielded 13% of insoluble diester **1b** (R = H). Indole **13** was identified spectroscopically as a side product of the pyrolysis (Scheme II).

The diester **1b** (R = H) was also obtained from diethyl 2,2′-dinitrobenzil-4,4′-dicarboxylate (**14**), a derivative of 2,2′-dinitrobenzil.[18,19] This specific precursor for **1b** was prepared by chromic acid oxidation[42] of bibenzyl derivative **15**, prepared in five steps from bibenzyl via diethyl bibenzyl-4,4′-dicarboxylate (**16**) in 65% overall yield. The oxidations of **15** to **14** with cerium ammonium nitrate[43] and selenium dioxide[44] were not successful.

Reduction of benzil **14** to **1b** was accomplished using stannous chloride in a mixture of acetic acid and hydrochloric acid.[19] When 10% excess of $SnCl_2$ was used and the reaction was carried out for 1 h, only 23% of **1b** was isolated as an insoluble product. The major product of the reaction was identified spectroscopically as indole **17**. This result is in agreement with the literature[19] report of an analogous product, as an intermediate in the synthesis of **1a**. However, **17** does not oxidize in air[19] to the corresponding keto indole.[45] Resubmission of the indole **17** to the reaction conditions furnished more **1b**. Diester **1b** was obtained in 67% yield when benzil **14** was treated with excess $SnCl_2$ at 80 °C for 5 h. The stannous chloride method was found to be superior to the zinc/acetic acid method[18,19] where a relatively long reflux time was necessary. Diester **1b** is a high melting, yellow-green powder which is insoluble in most organic solvents but can be recrystallized from pyridine. The diester **1b** (R = H) was converted into its *N*,*N*′-dimethyl derivative **1b** (R = Me) by reaction with methyl iodide in the presence of excess potassium hydride in THF.

Scheme III



Two approaches to the tetrahydroindoloindole **18** were briefly studied (Scheme III). Thermal decomposition of diazide **19**, obtained from diamine **20** in a standard way,[41] gave almost equal amounts of two major products, but none of the expected **18**. NMR analysis of each of the two products shows the presence of two nonequivalent benzene rings. Based on further information obtained from IR and mass spectroscopy, structures **21** and **22** were assigned (Scheme III). Decomposition of *o*-alkylaryl azides where the β C–H bond is activated (e.g., an alkyl group) leads to formation of indolines via a nitrene insertion mechanism.[46] However, with a nitrogen atom in the β position the assisted decomposition of the azide occurs at much lower temperatures and formation of an N–N bond results.[47] The nitrogen atom may be part of another ring system (e.g., pyridine)[48] or a secondary anilinic nitrogen (but not an aliphatic amine).[49] The formation of diethyl 5,11a-dihydro-11*H*-indolo[1,2-*b*]indazole-3,8-dicarboxylate (**21**) and diethyl 1*H*-indolo[1,2-*b*]indazole-3,8-dicarboxylate (**22**) can be explained by a two-stage decomposition of diazide **19** via intermediate **23** (Scheme III). Thus thermal decomposition of azide **19** appears to be a new method of preparation of the indoloindazole ring system. This ring

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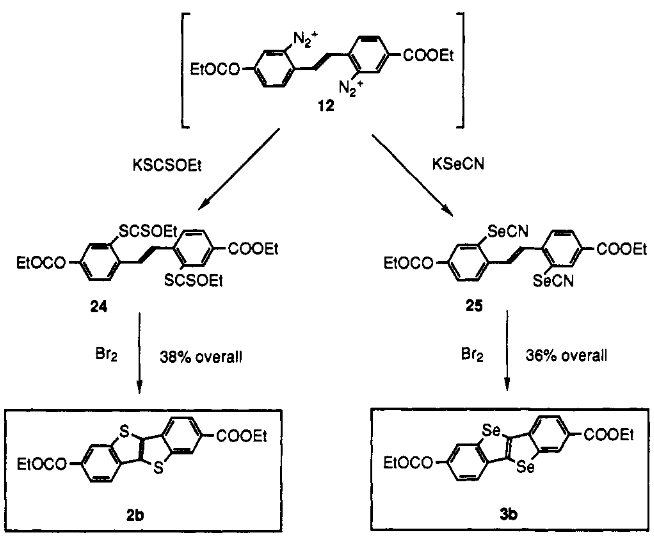
Scheme IV



system has, to our knowledge, been reported only once in the literature.[50] Addition of bromine to diaminostilbene **9** in either pyridine or acetic acid did not lead to formation of the desired **18**.

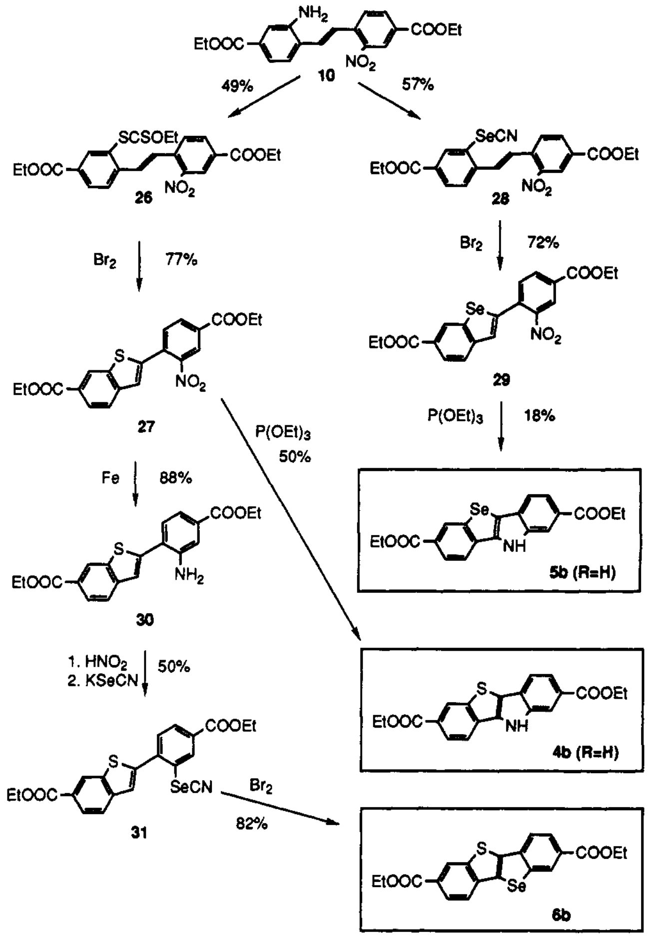
Preparation of Diethyl Benzothieno[3,2-*b*]benzothiophene-2,7-dicarboxylate (2b). The diaminostilbene **9** was converted[51] into bis-xanthate **24** via bis-diazonium salt **12** in 49% yield (Scheme IV). Treatment of crude **24** with bromine in acetic acid[24] yielded ester **2b** in 38% overall yield. The reaction proceeds presumably via a sulfenyl bromide intermediate resulting from the oxidative cleavage of the xanthate.

Preparation of Diethyl Benzoselenopheno[3,2-*b*]benzoselenophene-2,7-dicarboxylate (3b). Bis-diazonium salt **12** was converted[52] into bis-selenocyanate **25**, which without purification was treated with bromine in acetic acid in a manner analogous to the preparation of **2b** to yield **3b** in 36% overall yield (Scheme IV). The formation of **3b** apparently involves oxidative cleavage of the Se–CN bond and formation of a selenyl bromide,[53] which adds to the C=C bond[54] eliminating HBr.

Preparation of Diethyl Benzothieno[3,2-*b*]indole-2,7-dicarboxylate (4b). Amine **10** was diazotized and converted[51] to xanthate **26**, which was treated with bromine in acetic acid to form benzothiophene **27** in 38% overall yield. Nitro compound **27** was refluxed with 2 equiv of triethyl phosphite[30] to give **4b** (R = H) in 50% yield (Scheme V). This quite insoluble yellowish product was converted into its *N*-methyl derivative **4b** (R = Me) by reaction with methyl iodide in the presence of excess KH.

Preparation of Diethyl Benzoselenopheno[3,2-*b*]indole-2,7-dicarboxylate (5b). Amine **10** was diazotized and converted[52] into selenocyanate **28**, which was treated with bromine in acetic acid to yield 41% overall of benzoselenophenone **29** (Scheme V). The diester **29** was refluxed with 2 equiv of triethyl phosphite to produce a consistently low 18% yield of diester **5b** (R = H), which, after partial purification, was converted into its *N*-methyl derivative **5b** (R = Me).

Scheme V



Preparation of Diethyl Benzoselenopheno[3,2-*b*]benzothiophene-2,7-dicarboxylate (6b). Nitrophenylbenzothiophene **27** was reduced with iron in ethanol to the corresponding amine **30**, which was diazotized and converted[52] into selenocyanate **31**. The crude selenocyanate was treated with bromine in acetic acid to yield diester **6b** in 36% overall yield.

Thermal Properties

The heterocyclic diesters **1b–6b** (R = Me) all melt above 200 °C. Compounds **2b**, **3b**, and **6b**, i.e. those which do not contain nitrogen atoms, are liquid crystals and display a smectic A phase whose range appears to be a function of the size of the heteroatom (Table I). The phase is widest for **2b**, which contains the smaller sulfur atoms (Figure 1). Formation of a mesophase by the esters resembles the thermal behavior of some aromatic diesters e.g., diethyl terphenyl-4,4″-dicarboxylate,[55] which also forms S_A phases.

Spectroscopy

Chemical shifts in proton NMR spectra of compounds **1b–6b** are easily assigned based on the coupling patterns.

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Table I. Thermal Analysis[a] of Mesogenic Diethyl 5,10-Dihetera-5,10-dihydroindeno[2,1-*a*]indene-2,7-dicarboxylates

	X	Y	*K*		(Δ*H*)	S_A[b]		(ΔH)	I
2b	S	S		219	(9.1)		304	(2.5)	
3b	Se	Se		238	(10.0)		287	(1.8)	
6b	S	Se		220	(9.0)		287	(1.9)	

[a] Temperatures of crystal-smectic A (K-S_A) and smectic A-isotropic (S_A-I) phase transitions are expressed in °C and their enthalpies in kcal/mol. [b] Assignment of the S_A phase is based on comparison of the smectic textures with photomicrographs in Demus, D., Richter, L.; *Textures of Liquid Crystals*; VEB: Leipzig, GDR, 1978.

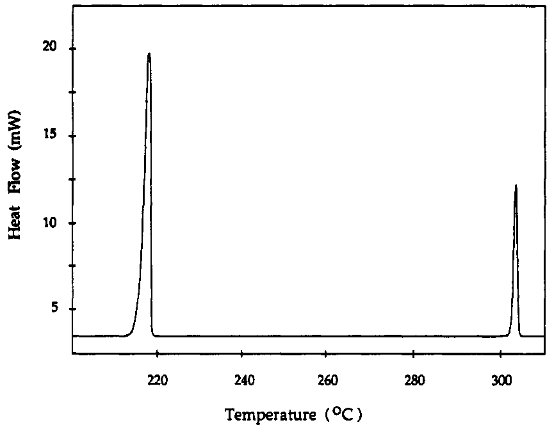
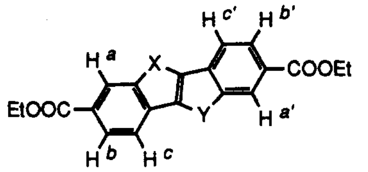


Figure 1. Differential scanning calorimetry of **2b**. Scan rate 5 °C/min.

Table II. ^{1}H NMR of Diethyl 5,10-Dihetera-5,10-dihydroindeno[2,1-*a*]indene-2,7-dicarboxylates



	X	Y	a	a′	b	b′	c	c′	NMe
1b	NMe	NMe	8.13		7.81–7.85				4.05
2b	S	S	8.63		7.93		8.13		–
3b	Se	Se	8.68		7.87		8.14		–
4b	NMe	S	8.22	8.60	7.78	7.91	8.10	8.10	4.24
5b	NMe	Se	8.18	8.60	7.68	7.87	8.07	8.09	4.20
6b	S	Se	8.64	8.66	7.92	7.85	8.11	8.13	–

Each ring system has three aromatic proton resonances: typically two sets of doublets and a doublet of doublets with typical coupling constants of 8.3 and 1.5 Hz. Ester **1b** is the only exception, and the two high-field aromatic proton resonances overlap. Assignment of the chemical shifts of the series is shown in Table II.[56]

The strongest absorption maxima in the electronic spectra (Table III) of the diesters **1b**–**6b** appear between 331 nm (for **2b**) and 354 nm (for **1a**). The longest wavelength absorptions are relatively strong, and the maxima appear between 367 nm (for **2b**) and 426 nm (for **1a**). *N*-Methyl compounds and N-anions show a bathochromic shift as compared to the NH compounds **1b**, **4b**, and **5b** (R = H). The trend is shown for **4b** in Figure 2.

Table III. Electronic Spectra of Diethyl 5,10-Dihetera-5,10-dihydroindeno[2,1-*a*]indene-2,7-dicarboxylates[a]

	X	Y	UV [λ_{max} (log ϵ_{max})]	emission[b]
1b	NMe	NMe	255 (4.44), 250 (4.23), 284 (4.65), 339 (4.56) s, 354 (4.73), 411 (4.10), 426 (4.10)	459, 479
1b	NH	NH	224 (4.34), 244 (4.25), 277 (4.55), 336 (4.54) s, 350 (4.65), 390 (4.23), 407 (4.19)	436, 459
2b	S	S	221 (4.64), 242 (4.29), 267 (4.36), 317 (4.59) s, 331 (4.67), 350 (4.08), 367 (4.24)	387, 401
3b	Se	Se	226 (4.68), 250 (4.16), 274 (4.19), 313 (4.37) s, 324 (4.62), 339 (4.67), 365 (3.98), 382 (4.15)	none
4b	NMe	S	223 (4.45), 249 (4.34), 267 (4.47), 331 (4.56) s, 341 (4.64), 379 (4.10), 395 (4.16)	421, 439
4b	NH	S	222 (4.50), 245 (4.36), 264 (4.38), 328 (4.47) s, 340 (4.53), 369 (4.25), 385 (4.29)	411, 427
4b	N⁻	S[c,d]	223 (4.50), 271 (4.41), 296 (4.50), 329 (4.20) s, 374 (4.62), 440 (4.05), 460 (4.05)	[e]
5b	NMe	Se	225 (4.50), 252 (4.37), 269 (4.43), 332 (4.55) s, 346 (4.66), 386 (4.08), 402 (4.16)	429, 449
5b	NH	Se	224 (4.48), 250 (4.32), 266 (4.39), 330 (4.54) s, 344 (4.61), 376 (4.15), 391 (4.21)	420, 438
5b	N⁻	Se[c,d]	230 (4.36), 271 (4.28), 295 (4.33), 330 (4.18) s, 377 (4.49), 441 (3.91), 463 (3.91)	[e]
6b	S	Se	223 (4.64), 247 (4.22), 269 (4.26), 309 (4.35), 320 (4.60), 335 (4.67), 358 (4.02), 374 (4.20)	396, 414

[a] Spectra recorded in THF at four concentrations. [b] Excitation at the peak of the strongest absorption. [c] Approximate values. [d] Anions obtained by treatment of the solution of the appriopriate NH compounds with excess NaH and sonication for 15 min. Measured for two concentrations. [e] Not measured.

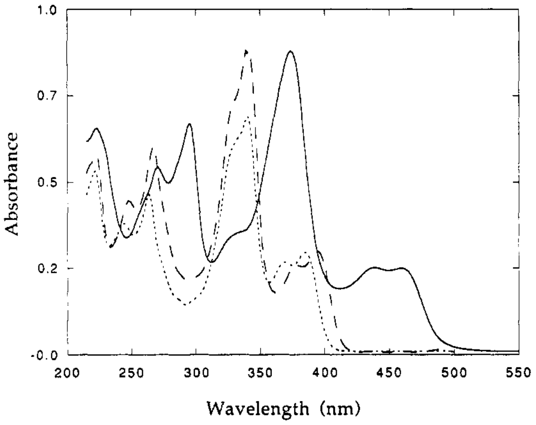


Figure 2. Absorption spectra of **4b**, R = H (- - -); **4b** R = Me (– – –); and **4b**, R = H N-anion (—) in THF. The anion was prepared by treatment of the solution of **4b**, R = H, with excess NaH and sonication for 15 min.

All compounds except for **3b** are fluorescent (Table III). Ester **1b** shows the strongest fluorescence, and esters **2b** and **6b** show relatively weak fluorescence, presumably due to a heavy atom effect. A typical emission spectrum is shown for **5b** in Figure 3.

Electrochemistry

Cyclic voltammetry of the series **1b**–**6b** shows that the first one-electron oxidation is reversible for compounds containing nitrogen, and the potential increases in the order **1b** < **5b** < **4b** (Table IV).

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(56) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley and Sons: New York, 1981. Appendix f, p 236.

Table IV. First Oxidation Potentials[a] of Diethyl 5,10-Dihetera-5,10-dihydroindeno[2,1-*a*]indene-2,7-dicarboxylates as Determined by Cyclic Voltametry

	X	Y	$E_{1/2}$(V)	i_a/i_c	ΔE (mV)
1b	NMe	NMe	0.75	1.0	83
2b	S	S	1.59	0.80	91
3b	Se	Se	1.37	I[b]	-
4b	NMe	S	1.16	1.0	91
5b	NMe	Se	1.09	0.96	87
6b	S	Se	1.48	I	-

[a] Versus Ag^0/AgCl electrode and referenced to ferrocene (+0.35 V). [b] Irreversible.

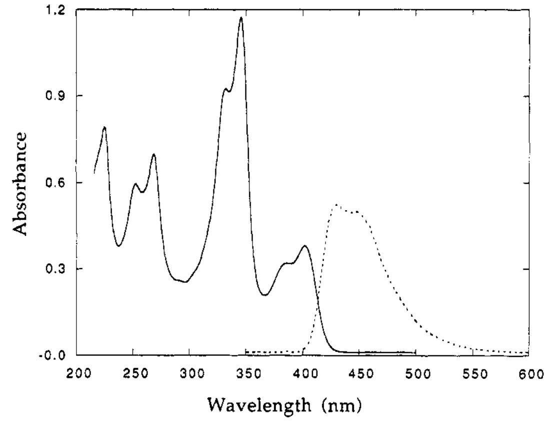

Figure 3. Absorption (—) and normalized emission (- - -) spectra of **5b** (R = Me).

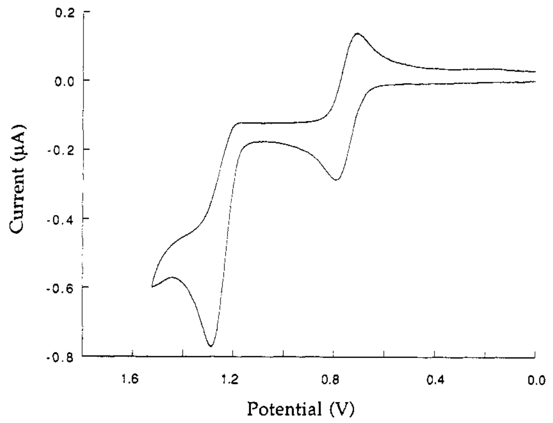

Figure 4. Cyclic voltammetry of **1b** (R = Me) in CH_2Cl_2. Scan rate 100 mV/s.

Benzothienobenzothiophene **2b** is oxidized at the highest potential, and the process is quasireversible. Oxidation of selenium-containing compounds **3b** and **6b** is irreversible. The oxidation potential within the series is a function of the heteroatom and increases in order N < Se < S. Under our conditions the second electron oxidations are irreversible and visible only for the nitrogen-containing compounds (R = Me): **1b** (1.33 V), **4b** (1.64 V), and **5b** (1.53 V). A typical CV pattern is shown for **1b** (R = Me) in Figure 4.

Energies of the longest wavelength absorptions in the series of diesters **1b–6b** vary linearly with their first oxidation potentials (Figure 5). It appears that as the HOMO–LUMO gap decreases, the HOMO rises within the series. Simple calculations using the PM3 method (Spartan 1.0 program) support this model, but also indicate significant although smaller changes in the LUMO energies.

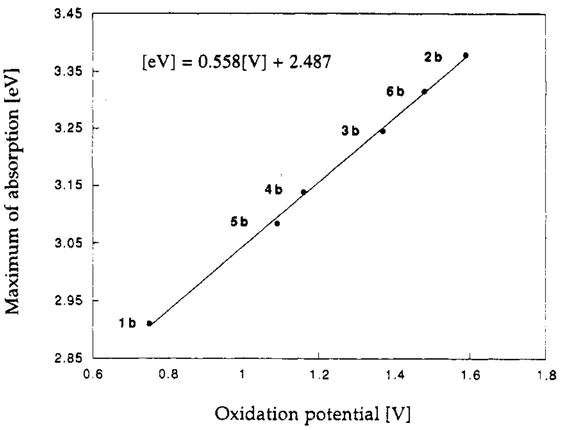

Figure 5. Maxima of long wavelength absorption versus the first oxidation potential in **1b–6b** series.

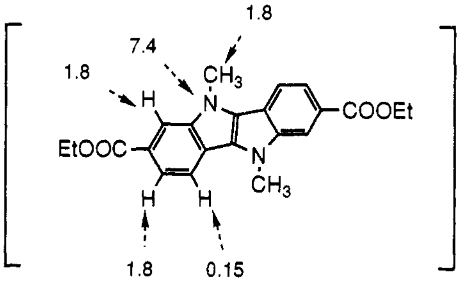

Figure 6. Radical cation **32** with indicated hyperfine coupling constants (G).

Radical Cation of 1b (R = Me)

Electrochemical oxidation of diethyl 5,10-dihydro-*N*,*N*′-dimethylindolo[3,2-*b*]indole-2,7-dicarboxylate (**1b**, R = Me) in methylene chloride in the presence of tetrabutylammonium perchlorate (0.1 M) produced a microcrystalline precipitate of black-green radical cation perchlorate **32** (Figure 6). Electrolysis of a dilute solution of **1b** resulted in full oxidation of the starting material and formation of perchlorate salt **32** with a 1:1 stoichiometry. In contrast, oxidation of a more concentrated solution furnished a black solid with a more typical[57] 2:1 stoichiometry, in which every second molecule of **1b** was converted into radical cation. The result is supported by coulometry and elemental analysis, although, it was not possible to obtain an analytically pure sample of **32** with 1:1 stoichiometry. Both salts are insoluble in THF but sparingly soluble in methylene chloride, giving green solutions that are relatively stable to water and air. A methylene chloride solution of **32** shows a broad, low-intensity absorption band in the visible region. The mixed valence salt gives a UV-vis spectrum that appears to be a superposition of **1b** and the radical **32** (Figure 7).

EPR spectra of **32** (Figure 8) in methylene chloride solution show a regular pattern of 25 lines which can be simulated (Figure 8) using the coupling constants shown in Figure 6. The parent radical cation[17] is also a stable solid. However, the presence of the two ester groups[58] and their push-pull[59] interactions with the nitrogens appear to enhance the stability of **32**. Evidence for the interaction

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(57) Braam, J. M.; Carlson, C. D.; Stephens, D. A.; Rehan, A. E.; Compton, S. J.; Williams, J. M. *Inorg. Synth.* **1986**, *24*, 132.

(58) Kosower, E. M.; Poziomek, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5515.

(59) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.

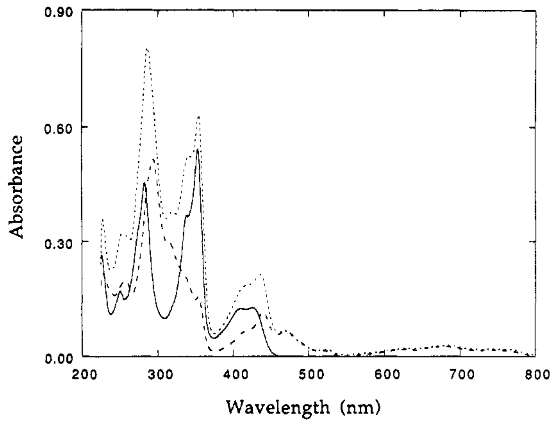

Figure 7. UV-vis absorption spectra of **1b**, R = Me, in THF (—) and its radical cation perchlorate **32**: 2:1 salt (- - -) and 1:1 salt (— — —) in CH_2Cl_2.

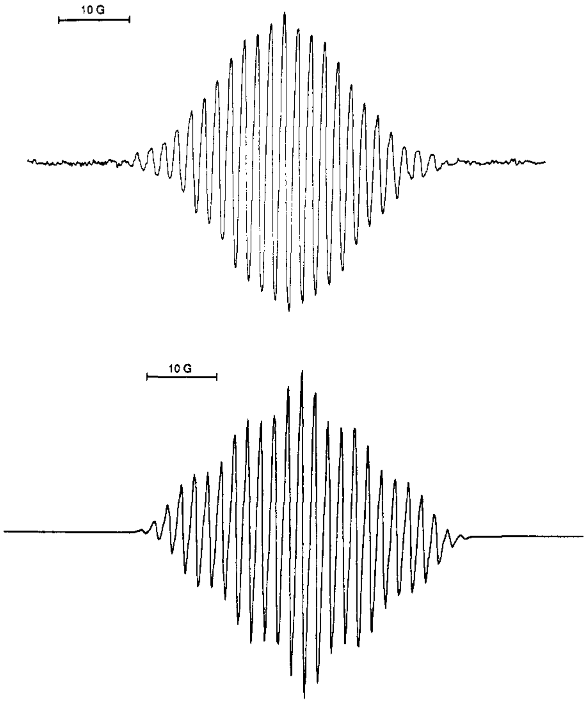

Figure 8. EPR spectra of radical cation **32**: (upper) measured in CH_2Cl_2 (g = 2.0037), (lower) simulated.

may be found in the magnitude of N coupling constants in the parent radical cation (6 G)[17] vs the diester **32** (7.4 G). This result is in agreement with a proposal[58] of internal polarization and resulting higher α spin density on the nitrogen. The radical cation is electrochemically relatively stable with a pK_{dis} value of 8.8 (pK_{dis} = ($E_1 - E_2$)/0.059). Magnetic susceptibility measurements in the range of 1.8–300 K and 0–5.5 T revealed that both the 1:1 and 2:1 salts of **32** are antiferromagnetically coupled in the solid state.

Chemical oxidation[17] of **1b**, R = Me, with lead tetraacetate in acetic acid was not successful, and the green color attributable to **32** was present only for a very short time.

Summary

The series **1–6** was studied thermally, spectroscopically, and electrochemically. Diethyl 5,10-dihydro-5,10-dimethylindolo[3,2-*b*]indole-2,7-dicarboxylate (**1b**) was found to form stable radical cation **32**. The results suggest that the indoloindole unit may be an especially promising candidate for incorporation into the polaronic ferromagnet design.[7] Preliminary efforts along these lines have been quite encouraging, and results of these studies will be reported separately.[60]

Table V. Electronic Spectra of 2,7-Bis(ethoxycarbonyl)-5,10-dihydro-5,10-dimethylindolo[3,2-*b*]indol-5-ium Perchlorate[a] (32)

salt	UV-vis [λ_{max} (log ϵ_{max})]
2:1[b]	227 (4.51), 253 (4.48), 287 (4.90), 341 (4.70) s, 355 (4.78), 415 (4.23) s, 436 (4.30), 469 (3.80), 522 (3.24), 634 (3.31), 683 (3.43), 754 (3.25)
1:1[c]	227 (4.3), 258 (4.3), 295 (4.7), 317 (4.5) s, 412 (3.8) s, 440 (4.1), 470 (3.8), 518 (3.2), 632 (3.3), 681 (3.4), 753 (3.2)

[a] Spectra recorded in CH_2Cl_2. [b] Measured at four concentrations. [c] Approximate values.

Experimental Section

Melting points and boiling points are uncorrected. NMR spectra were obtained on a JEOL JNM-GX 400 in $CDCl_3$ and referenced to TMS (^{1}H spectra) or $CDCl_3$ (^{13}C spectra) unless specified otherwise. IR spectra were recorded on a Perkin-Elmer 1600 instrument in KBr unless specified otherwise. UV-vis absorption spectra were obtained on a Cary 2200 spectrophotometer in THF and CH_2Cl_2 (radical cation **32**). Emission spectra were recorded on SPF-500C SLM spectrophotometer in THF unless specified otherwise. Mass spectroscopy was done on a ZAB 7070 instrument in the Chemistry Department of the University of California, Riverside. Elemental analyses were performed in Atlantic Microlab, Norcross, GA and Galbraith Laboratories, Knoxville, TN (selenium-containing samples). Electrochemical analysis was done using a Princeton Applied Research, and the preparative electrooxidation was accomplished with a Bioanalytical System instrument. The ESR spectrum was obtained on Varian E-line Century Series (X-band, 9.2 GHz). Magnetic measurements were done using a Quantum Design MPMS SQUID magnetometer. Samples of **1b–6b** (R = Me) for thermal and spectroscopic study were purified by vacuum sublimation (200 °C/0.1 Torr).

Cyclic Voltammetry. An electrochemical cell equipped with a 1-mm platinum microelectrode (working), a platinum counter-mm electrode (Torr), and a silver chloride reference electrode (silver wire electrolyzed in concd hydrochloric acid at 1.5 V) and containing vacuum-dried tetrabutylammonium perchlorate (171 mg, 0.50 mmol) was purged with argon. Dried and deoxygenated methylene chloride (5 mL) was injected through a septum followed by the heterocyclic compound (5 μmol). The measurements were conducted at scan rates from 0.1–0.7 V/s. At the end of the analysis, ferrocene (5 μmol) was added and a CV was run with a rate of 0.2 V/s to reference the sample. Results are collected in Table IV.

Diethyl 5,10-Dihydroindolo[3,2-*b*]indole-2,7-dicarboxylate (1b, R = H). Method A (from 14). Benzil **14** (2.70 g, 6.1 mmol) was suspended in warm acetic acid (40 mL) and a filtered solution of stannous chloride (19 g, 84 mmol) in acetic acid (50 mL) and hydrochloric acid (19 mL) was added at once. The mixture was stirred at 80 °C for 5 h and the resulting fine yellow precipitate was filtered off, washed with acetic acid, dilute hydrochloric acid, water, and ethanol. Drying at 110 °C gave 1.44 g (67% yield) of yellow-green powder, which was recrystallized (pyridine, 110 mL) to give 0.78 g of the product. **Method B (from 11).** A suspension of diazide **11** (1.0 g, 2.5 mmol) in freshly distilled 1,2-dichlorobenzene (40 mL) was stirred and heated at 155 °C overnight under an atmosphere of dry argon. The dark reaction mixture was cooled and filtered, and the resulting solid was washed with chloroform to give 0.11 g (13% yield) of yellow-green product: mp dec >370 °C; IR 3312, 1682, 1600, 1278, 1253, 1209, 762 cm^{-1}; EIMS, m/z 351 (M + 1, 28), 350 (M, 100), 294

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(60) Kaszynski, P.; Dougherty, D. A., unpublished results.

(21). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.51; H, 5.13; N, 7.96.

Diethyl 5,10-Dihydro-*N*,*N'*-dimethylindolo[3,2-*b*]indole-2,7-dicarboxylate (1b, R = Me). Crude diester **1b**, R = H (0.50 g), was suspended in dry THF (60 mL), and excess potassium hydride (35% in oil, 1.0 mL) was added. The mixture was stirred and gently refluxed for 30 min, and methyl iodide (2 mL) was added in four portions over a period of 48 h, under an atmosphere of dry argon. The yellow reaction mixture was carefully poured into dilute hydrochloric acid, the resulting yellow precipitate was filtered off, washed with hexanes, and dried to give 0.4 g of crude product. The product was purified on a silica gel column (methylene chloride/ethyl acetate, 3:1), and recrystallized (chlorobenzene) to yield 0.28 g (51% yield) of yellow-green crystals: mp 250–251 °C; ^{1}H NMR δ 1.46 (t, J = 7.1 Hz, 6H), 4.05 (s, 6H), 4.44 (q, J = 7.1 Hz, 4H), 7.81–7.85 (m, 4H), 8.13 (s, 2H); ^{13}C NMR δ 14.47, 31.62, 60.87, 111.72, 116.84, 117.19, 119.46, 124.22, 128.57, 140.96, 167.49; IR 1703, 1497, 1322, 1272, 1246, 758 cm^{-1}; EIMS, *m/z* 379 (M + 1, 21), 378 (M, 82), 364 (43), 350 (63), 336 (49), 322 (100), 308 (41), 307 (59). Anal. Calcd for $C_{22}H_{22}N_2O_4$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.65; H, 5.73; N, 7.47.

Diethyl [1]Benzothieno[3,2-*b*][1]benzothiophene-2,7-dicarboxylate (2b). Diamine **9** (5.00 g, 14 mmol) was stirred with concd hydrochloric acid (10 mL) for 30 min. Water (15 mL) was added, and the resulting yellow paste of the hydrochloride was cooled in an ice-bath. A solution of $NaNO_2$ (2.15 g, 31 mmol) in water (14 mL) was slowly added at temperatures below 5 °C. The resulting clear-yellow solution of the bis-diazonium salt **12** was stirred for 30 min, and the pH was adjusted to *ca.* 4.5 by addition of sodium acetate (20%, 18 mL). A catalytic[61] amount of $NiCl_2 \cdot 6H_2O$ was added, followed by a solution of potassium ethyl xanthate (6.1 g, 38 mmol) in water (15 mL) at 5 °C. The resulting suspension was allowed to slowly warm to room temperature and stirred for 1 h. Chloroform was added, and the organic phase was separated, dried, and passed through a short silica gel column (chloroform). The solvent was evaporated, and the residue was recrystallized from a small amount of ethanol to yield 4.5 g of about 90% pure bis-xanthate **24**: mp 125–134 °C; ^{1}H NMR δ (major peaks) 1.29 (t, J = 7.1 Hz, 6H), 1.41 (t, J = 7.1 Hz, 6H), 4.40 (q, J = 7.1 Hz, 4H), 4.58 (q, J = 7.1 Hz, 4H), 7.62 (s, 2H), 7.84 (d, J = 8.3 Hz, 2H), 8.13 (dd, J_1 = 8.3 Hz, J_2 = 1.7 Hz, 2H), 8.21 (d, J = 1.7 Hz, 2H); ^{13}C NMR δ (major peaks) 13.58, 14.28, 61.35, 70.64, 126.54, 129.79, 129.89, 130.71, 131.71, 137.87, 144.41, 165.25, 210.70; IR 1717, 1289, 1261, 1023, 768 cm^{-1}; CIMS, *m/z* 566 (M + 2H, 22), 443 (72), 415 (64), 387 (100), 386 (71), 355 (66), 341 (51). Without further purification the crude xanthate (4.5 g) was suspended in warm acetic acid (150 mL) and bromine (1 M in CCl_4, 25 mL) was added, the mixture was refluxed for 1 h and cooled, and the white-yellow precipitate was filtered off. The solid (2.32 g) was washed with ethanol, dried, and passed through a short silica gel column (chloroform). The solvent was evaporated, and the solid was recrystallized (chlorobenzene) to yield 2.07 g (38% overall yield) of white cotton-like crystals: mp 215 °C; ^{1}H NMR δ 1.46 (t, J = 7.1 Hz, 6H), 4.45 (q, J = 7.1 Hz, 4H), 7.93 (d, J = 8.3 Hz, 2H), 8.13 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 2H), 8.63 (d, J = 1.5 Hz, 2H); ^{13}C NMR δ 14.39, 61.33, 121.61, 125.98, 126.12, 127.70, 135.89, 136.06, 142.41, 166.15; IR 1721, 1275, 1228, 1022, 761 cm^{-1}; EIMS, *m/z* 385 (M + 1, 23), 384 (M, 100), 283 (39). Anal. Calcd for $C_{20}H_{16}S_2O_4$: C, 62.48; H, 4.20; S, 16.68. Found: C, 62.35; H, 4.21; S, 16.64.

Diethyl [1]Benzoselenopheno[3,2-*b*][1]benzoselenophene-2,7-dicarboxylate (3b). A yellow solution of the bis-diazonium salt **12** was prepared from diamine **9** (1.05 g, 3 mmol), and the pH was adjusted to *ca.* 4.5. Potassium selenocyanate (0.93 g, 6.5 mmol) dissolved in water (5 mL) was slowly added at a temperature below 5 °C, and the evolution of nitrogen began immediately. The foamy suspension of the resulting bis-selenocyanate was stirred at 5–10 °C for 30 min, and the product was dissolved in chloroform. The organic layer was separated, dried, and passed through a layer of silica gel, and the eluent was evaporated to give crude (1.0 g) bis-selenocyanate **25**: ^{1}H NMR δ 1.43 (t, J = 7.1 Hz, 6H), 4.43 (q, J = 7.1 Hz, 4H), 7.52 (s, 2H), 7.89 (d, J = 8.2 Hz, 2H), 8.18 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 2H), 8.48 (d, J = 1.6 Hz, 2H). The solid (1.0 g) was suspended in acetic acid (40 mL) and bromine (1 M in CCl_4, 4 mL) was added. The mixture was slowly brought to reflux and then cooled. The resulting solid was filtered off, washed with ethanol, and dried to give 0.52 g of white-gray product. The diester was passed through a short silica gel column (CH_2Cl_2) and recrystallized (chlorobenzene) to yield 0.51 g (36% overall yield based on diamine **9**) of yellowish cotton-like crystals of **3b**: mp 234–235 °C; ^{1}H NMR δ 1.45 (t, J = 7.1 Hz, 6H), 4.45 (q, J = 7.1 Hz, 4H), 7.87 (d, J = 8.2 Hz, 2H), 8.14 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 2H), 8.68 (d, J = 1.3 Hz, 2H); ^{13}C NMR δ 14.39, 61.33, 123.82, 126.68, 127.51, 128.58, 137.07, 140.77, 141.42, 166.09; IR 1716, 1275, 1226, 762 cm^{-1}; EIMS, *m/z* 482 (33), 481 (21), 480 (100), 479 (21), 478 (92), 477 (34), 476 (52), 452 (54). Anal. Calcd for $C_{20}H_{16}Se_2O_4$: C, 50.22; H, 3.37; Se, 33.02. Found: C, 50.13; H, 3.37; Se, 32.92.

Diethyl 10*H*-[1]Benzothieno[3,2-*b*]indole-2,7-dicarboxylate (4b, R = H). Benzothiophene **27** (0.40 g, 1 mmol) and freshly distilled triethyl phosphite (0.35 mL, 2.04 mmol) were stirred at 170 °C under argon atmosphere for 12 h. The resulting dark-red mixture was cooled, and 50% aqueous ethanol (5 mL) was added. Precipitated solid was filtered off and boiled with ethanol (10 mL), and the crude material (0.19 g) was recrystallized (chlorobenzene) to give 0.18 g (50% yield) of light yellow powder: mp 253 °C; ^{1}H NMR δ 1.45 (t, J = 7.1 Hz, 6H), 4.45 (q, J = 7.1 Hz, 4H), 7.83 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.96 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 8.14 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 8.31 (d, J = 1.5 Hz, 1H), 8.63 (d, J = 1.5 Hz, 1H), 8.93 (s, 1H); IR 3283, 1713, 1680, 1289, 1243, 1224 cm^{-1}; EIMS, *m/z* 368 (M + 1, 22), 367 (M, 100). Anal. Calcd for $C_{20}H_{17}NSO_4$: C, 65.37; H, 4.67; N, 3.81; S, 8.73. Found: C, 65.16; H, 4.71; N, 3.80; S, 8.83.

Diethyl *N*-Methyl-10*H*-[1]benzothieno[3,2-*b*]indole-2,7-dicarboxylate (4b, R = Me). Indole **4b** R = H (92 mg, 0.25 mmol), was suspended in dry THF, and excess potassium hydride (30% in mineral oil) was added, followed by methyl iodide (0.5 mL). The mixture was stirred and refluxed for 1 h, cooled, and poured into dilute hydrochloric acid. The resulting solid was taken up in chloroform, the organic layer was separated, dried (Na_2SO_4), and filtered through a silica gel plug. The filtrate was evaporated, and the resulting yellow solid was recrystallized (hexane–benzene) to give 85 mg (89% yield) of bright yellow product: mp 215 °C; ^{1}H NMR δ 1.45 (t, J = 7.1 Hz, 3H), 1.46 (t, J = 7.1 Hz, 3H), 4.24 (s, 3H), 4.44 (q, J = 7.1 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 7.78 (dd, J_1 = 8.2 Hz, J_2 = 0.6 Hz, 1H), 7.91 (dd, J_1 = 8.5 Hz, J_2 = 1.2 Hz, 1H), 8.10 (m, 2H), 8.22 (d, J = 0.6 Hz, 1H), 8.60 (d, J = 1.2 Hz, 1H); ^{13}C NMR δ 14.37, 14.43, 31.67, 60.98, 61.17, 111.96, 118.07, 119.10, 119.65, 120.63, 124.30, 125.30, 125.40, 126.22, 126.35, 129.40, 139.77, 141.35, 143.18, 166.22, 167.17; IR 1701, 1262, 1236, 1109, 756 cm^{-1}; EIMS, *m/z* 382 (M + 1, 25), 381 (M, 100), 325 (25). Anal. Calcd for $C_{21}H_{19}NSO_4$: C, 66.12; H, 5.02; N, 3.67; S, 8.41. Found: C, 66.00; H, 5.07; N, 3.73; S, 8.51.

Diethyl 10*H*-[1]Benzoselenopheno[3,2-*b*]indole-2,7-dicarboxylate (5b, R = H). The ester was prepared in 18% yield from benzoselenophene **29** (0.88 g, 2 mmol) as described for **4b**, R = H: mp 260–262 °C; ^{1}H NMR δ 1.45 (t, J = 7.1 Hz, 3H), 1.46 (t, J = 7.1 Hz, 3H), 4.44 (q, J = 7.1 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 7.77 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.96 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 8.16 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 8.32 (d, J = 1.5 Hz, 1H), 8.66 (d, J = 1.5 Hz, 1H), 9.03 (s, 1H); IR 3286, 1706, 1681, 1285, 1244, 1221, 761 cm^{-1}; EIMS, *m/z* 417 (25), 416 (21), 415 (100), 413 (47), 314 (35). Anal. Calcd for $C_{20}H_{17}NSeO_4$: C, 57.80; H, 4.14; N, 3.38; Se, 19.06. Found: C, 58.54; H, 4.18; N, 3.48; Se, 18.49.

Diethyl *N*-Methyl-10*H*-[1]benzoselenopheno[3,2-*b*]indole-2,7-dicarboxylate (5b, R = Me). The ester was prepared in 87% yield as described for **4b**, R = Me, and recrystallized from chloroform: mp 205 °C; ^{1}H NMR δ 1.44 (t, J = 7.1 Hz, 3H), 1.45 (t, J = 7.1 Hz, 3H), 4.20 (s, 3H), 4.42 (q, J = 7.1 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 7.68 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 8.07 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 1H), 8.09 (dd, J_1 = 8.3 Hz, J_2 = 0.7 Hz, 1H), 8.18 (d, J = 0.7 Hz, 1H), 8.60 (d, J = 1.5 Hz, 1H); ^{13}C NMR δ 14.37, 14.44, 31.89, 60.98, 61.20, 111.98, 115.43, 119.52, 120.71, 121.30, 125.32, 126.00, 126.35, 126.94, 129.19, 132.32, 141.07, 141.25, 142.75, 166.13, 167.24; IR 1706, 1259, 1234, 762 cm^{-1}; EIMS, *m/z* 430 (19), 429 (100), 427 (44). Anal. Calcd

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(61) Warning! See *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 1050.

for $C_{21}H_{19}NSeO_4$: C, 58.88; H, 4.47; N, 3.27; Se, 18.43. Found: C, 58.72; H, 4.56; N, 3.18; Se, 17.94.

Diethyl [1]Benzoselenopheno[3,2-*b*][1]benzothiophene-2,7-dicarboxylate (6b). (Aminophenyl)benzothiophene **30** (0.74 g, 2 mmol) was stirred with concd hydrochloric acid (1 mL) for 1 h, water (3 mL) was added, and the yellow suspension of the hydrochloride was cooled in an ice-bath. A solution of sodium nitrite (152 mg) in water (5 mL) was added at a temperature below 5 °C. The mixture was stirred for 30 min, pH was adjusted to *ca.* 4.5 using sodium acetate (20%, 4 mL), and a solution of potassium selenocyanate (360 mg) in water (3 mL) was added at ice-bath temperature. The resulting suspension was stirred at room temperature for 1 h, and the solid was filtered, dried, dissolved in methylene chloride, and passed through a short silica gel column. The solvent was evaporated leaving 0.48 g of crude selenocyanate **31** which, after recrystallization (benzene–hexane), melted at 124–125 °C: ^{1}H NMR δ 1.44 (t, J = 7.1 Hz, 3H), 1.45 (t, J = 7.1 Hz, 3H), 4.44 (q, J = 7.1 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 7.42 (s, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H), 8.11 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 1H), 8.13 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 1H), 8.58 (d, J = 1.5 Hz, 1H), 8.61 (d, J = 1.7 Hz, 1H); IR 1730, 1716, 1296, 1274, 1233, 1127, 762 cm^{-1}; EIMS, *m/z* 460 (33), 459 (100), 457 (56), 432 (88), 430 (62), 414 (42). The crude selenocyanate (0.48 g) was suspended in acetic acid (10 mL). Bromine (1 M in CCl_4, 1 mL) was added, and the mixture was refluxed for 1 h. The mixture was cooled, and the resulting precipitate was filtered off and washed with methanol to give 356 mg (82% yield or 41% overall) of white cotton-like product **6b**. An analytical sample was obtained by passing a solution through a short silica gel column using chloroform as an eluent followed by recrystallization from chloroform: mp 214 °C; ^{1}H NMR δ 1.45 (t, J = 7.1 Hz, 3H), 1.46 (t, J = 7.1 Hz, 3H), 4.44 (q, J = 7.1 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 7.85 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 8.11 (dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, 1H), 8.13 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 1H), 8.64 (s, 1H), 8.66 (d, J = 1.5 Hz, 1H); ^{13}C NMR δ 14.38 (2C), 61.33 (2C), 122.26, 123.06, 125.80, 126.12, 126.62, 127.53, 127.58, 128.74, 134.49, 138.13, 138.31, 138.50, 141.37, 142.28, 166.06, 166.19; IR 1719, 1277, 1227, 762 cm^{-1}; EIMS, *m/z* 434 (37), 433 (32), 432 (100), 430 (65), 429 (38), 428 (47), 387 (56), 331 (69), 329 (59), 286 (81), 284 (51), 283 (32), 206 (56). Anal. Calcd for $C_{20}H_{16}SSeO_4$: C, 55.69; H, 3.74; S, 7.43; Se, 18.31. Found: C, 55.41; H, 3.62; S, 7.50; Se, 18.80.

Diethyl 2,2′-Dinitro-(*E*)-stilbene-4,4′-dicarboxylate (7). Nitro ester **8** (169.5 g, 0.70 mol) was dissolved in anhydrous ethanol (1000 mL), and sodium ethoxide (21% in ethanol, 260 mL, 0.70 mol) was added dropwise over a period of 45 min at ice-bath temperature under argon atmosphere. The mixture was stirred for 30 min at low temperature and then slowly brought to reflux. After 30 min the mixture was cooled, and the yellow precipitate was filtered and washed with ethanol. The solid was suspended in water (500 mL), filtered, washed with ethanol, and dried to give crude product which melted at 191–192 °C. The crude product was dissolved in warm chloroform and filtered. Ethanol was added to the filtrate, and the mixture was concentrated and cooled in ice. The resulting yellow crystalline solid was filtered and dried to give 97.6 g (67% yield) of ester **7** mp 196–197 °C; ^{1}H NMR δ 1.45 (t, J = 7.1 Hz, 6H), 4.46 (q, J = 7.1 Hz, 4H), 7.67 (s, 2H), 7.90 (d, J = 8.2 Hz, 2H), 8.32 (dd, J_1 = 8.2 Hz, J_2 = 1.7 Hz, 2H), 8.69 (d, J = 1.7 Hz, 2H); ^{13}C NMR δ 14.25, 61.99, 126.11, 129.24, 129.78, 131.61, 134.01, 135.78, 147.83, 164.13; IR 1728, 1616, 1526, 1360, 1288, 1262, 1021, 760 cm^{-1}; EIMS, *m/z* 414 (M, 5), 369 (37), 223 (56), 207 (100), 191 (48). Anal. Calcd for $C_{20}H_{18}N_2O_8$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.84; H, 4.33; N, 6.73.

Ethyl 4-(Chloromethyl)-3-nitrobenzoate[62] (8). Method A. 4-(Chloromethyl)benzoic acid (124.4 g, 0.73 mol) was refluxed with thionyl chloride (100 mL) for 3 h. Excess $SOCl_2$ was evaporated, dry ethanol (300 mL) was carefully added, and the mixture was refluxed for 30 min. Ethanol was evaporated and the crude product was short-path distilled (110 °C/0.4 Torr). The distillate was transferred to a three-necked flask and cooled in an ice-bath, and a chilled mixture of nitric acid (68%, 225 mL) and sulfuric acid (96%, 265 mL) was added dropwise, maintaining the temperature below 10 °C. The ice-bath was replaced with a water-bath, and the mixture was stirred at room temperature for 3–5 h until starting material was no longer detectable by GC. The mixture was diluted with ice–water, and the oily yellow product was separated. The aqueous layer was extracted with chloroform. Combined organic fractions were dried ($MgSO_4$), solvent evaporated, and the residue short-path distilled (145 °C/0.4 Torr) to yield 163.2 g (92% overall yield) of pure ester. **Method B.** A chilled mixture of nitric acid (68%, 30 mL) and sulfuric acid (96%, 35 mL) was added dropwise to stirred, powdery 4-(chloromethyl)benzoic acid (25.0 g, 0.147 mol) at a temperature below 10 °C. The pale-yellow suspension was stirred at room temperature for 2 h and diluted with ice–water. The precipitate was filtered, washed with water, and dried. Crude acid was refluxed with thionyl chloride, excess $SOCl_2$ was evaporated, and the resulting acid chloride was treated with anhydrous ethanol. The mixture was refluxed for 30 min, ethanol was evaporated, and the oily residue was fractionally distilled to give (3.60 g, 12% yield; 100–105 °C/0.4 Torr) of ethyl 4-(chloromethyl)benzoate and 26.31 g (73% overall yield; 146–150 °C/0.8 Torr, lit.[62] 170–174 °C/4 Torr) of yellow viscous ethyl 4-(chloroethyl)-3-nitrobenzoate: ^{1}H NMR δ 1.38 (t, J = 7.1 Hz, 3H), 4.39 (q, J = 7.1 Hz, 2H), 4.95 (s, 2H), 7.75 (d, J = 8.1 Hz, 1H), 8.23 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 1H), 8.60 (d, J = 1.7 Hz, 1H); ^{13}C NMR δ 14.13, 42.27, 61.94, 126.05, 131.65, 131.91, 134.04, 136.40, 147.87, 163.88; IR (neat) 1726, 1538, 1350, 1293, 1258 cm^{-1}.

Diethyl 2,2′-Diamino-(*E*)-stilbene-4,4′-dicarboxylate (9). Concd hydrochloric acid (9 mL) was added over a period of 2 h to a stirred and gently refluxed suspension of dinitrostilbene **7** (8.00 g) and iron powder (9 g) in ethanol (150 mL). After 3 h, the warm dark reaction mixture was poured into 5% $NaHCO_3$ (500 mL). The dark precipitate was filtered, the dry solid was boiled with chloroform (150 mL), and the hot mixture was filtered. The solid was washed with two more portions of hot chloroform, and the combined filtrates were evaporated. The resulting yellow product was recrystallized (chloroform–ethanol) to give 5.90 g (87% yield) of pure diamine: mp 191–192 °C; ^{1}H NMR δ 1.39 (t, J = 7.1 Hz, 6H), 3.93 (br s, 4H), 4.36 (q, J = 7.1 Hz, 4H), 7.12 (s, 2H), 7.41 (s, 2H), 7.46 (s, 4H); ^{13}C NMR δ 14.33, 60.92, 117.25, 120.17, 126.62, 127.07, 127.72, 130.70, 143.94, 166.50; IR 3480, 3389, 1697, 1631, 1321, 1304, 1245, 764 cm^{-1}; EIMS, *m/z* 355 (M + 1, 15), 354 (100). Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.74; H, 6.26; N, 7.96.

Diethyl 2-Amino-2′-nitro-(*E*)-stilbene-4,4′-dicarboxylate (10). Dinitrostilbene **7** (10.35 g, 25 mmol) was dissolved in warm pyridine (100 mL), and a solution of sodium sulfide nonahydrate (6.0 g, 25 mmol) and sulfur (0.80 g, 25 mmol) in water (30 mL) was added. The dark red reaction mixture was stirred and gently refluxed for 5 h, cooled, and placed in a freezer. The resulting red-orange crystals were filtered off, and washed with ethanol and water to yield 6.27 g (mp 161–166 °C) of crude product. The amine was recrystallized from toluene and subsequently from pyridine to give 5.30 g (55% yield) of red-orange product (mp 174–176 °C) used in the further transformations. An analytical sample was obtained using column chromatography (silica gel, CH_2Cl_2–ethyl acetate 5:1): mp 179–180 °C; ^{1}H NMR δ 1.40 (t, J = 7.1 Hz, 3H), 1.43 (t, J = 7.1 Hz, 3H), 4.05 (br s, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 7.23 (d, J = 15.9 Hz, 1H), 7.42 (s, 1H), 7.46 (s, 2H), 7.56 (d, J = 15.9 Hz, 1H), 7.84 (d, J = 8.3 Hz, 1H), 8.24 (dd, J_1 = 8.3 Hz, J_2 = 1.7 Hz, 1H), 8.60 (d, J = 1.7 Hz, 1H); ^{13}C NMR δ 14.26, 14.30, 61.02, 61.86, 117.65, 120.14, 125.65, 126.06, 126.38, 127.91, 128.32, 130.54, 130.70, 131.57, 133.52, 136.68, 144.48, 147.82, 164.34, 166.31; IR 3463, 3378, 1712, 1695, 1292, 1248, 767 cm^{-1}; CIMS, *m/z* 386 (MH − 1, 25), 385 (MH, 100), 384 (M, 25). Anal. Calcd for $C_{20}H_{20}N_2O_6$: C, 62.49; H, 5.24; N, 7.29. Found: C, 62.53; H, 5.34; N, 7.27.

Diethyl 2,2′-Diazido-(*E*)-stilbene-4,4′-dicarboxylate (11). The bis-diazonium salt **12** was prepared as described for the preparation of **2b**. Without adjusting the pH of the mixture, a solution of sodium azide (20% excess) in water was slowly added at temperatures below 6 °C. The mixture was stirred at ice-bath temperature for 1 h, and the resulting yellow product was filtered off, washed with water, and dried. The crude diazide was dissolved in chloroform and passed through a short silica gel plug. The yellow filtrate was evaporated and the solid residue

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was washed with warm ethanol to give 81% yield of yellow crystals of the diazide **11**: mp 153–154 °C dec; ^{1}H NMR δ 1.42 (t, J = 7.1 Hz, 6H), 4.40 (q, J = 7.1 Hz, 4H), 7.39 (s, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.81 (s, 2H); ^{13}C NMR δ 14.28, 61.35, 119.59, 125.52, 125.81, 126.46, 131.07, 132.50, 137.94, 165.36; IR 2134, 1718, 1413, 1302, 1255, 1124, 766 cm^{-1}; EIMS, *m/z* 406 (M, 12), 352 (45), 350 (100), 277 (51), 249 (47). Anal. Calcd for $C_{20}H_{18}N_6O_4$: C, 59.11; H, 4.46; N, 20.68. Found: C, 59.11; H, 4.46; N, 20.71.

Ethyl 2-[2-Amino-4-(ethoxycarbonyl)phenyl]indole-6-carboxylate (13). The mother liquor from the preparation of **1b** (method B) was passed through a silica gel plug and washed with hexanes to elute dichlorobenzene. The organic products were eluted with methylene chloride–ethyl acetate mixture (3:1), the solvent was evaporated, and the dark red solid residue (0.24 g) was purified on a silica gel column. The isolated product was recrystallized (CCl_4) to give yellowish fine crystals: mp 162–163 °C; ^{1}H NMR δ 1.40 (t, J = 7.1 Hz, 3H), 1.41 (t, J = 7.1 Hz, 3H), 4.25 (br s, 2H), 4.37 (q, J = 7.1 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 6.84 (d, J = 1.8 Hz, 1H), 7.47 and 7.50 (AB, J = 8.0 Hz, 2H), 7.49 (s, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 8.21 (s, 1H), 9.22 (br s, 1H); ^{13}C NMR δ 14.29, 14.39, 60.81, 61.12, 102.50, 113.34, 117.71, 120.00, 120.06, 121.30, 122.16, 124.35, 129.13, 130.99, 132.29, 135.69, 138.29, 143.97, 166.44, 167.67; IR 3369, 1718, 1695, 1619, 1281, 1216, 764 cm^{-1}; EIMS, *m/z* 353 (M + 1, 23), 352 (M, 100).

Diethyl 2,2′-Dinitrobenzil-4,4′-dicarboxylate (14). Dinitrobibenzyl **15** (30.0 g, 72 mmol) was suspended in acetic acid (700 mL) and chromium trioxide (50 g) was added. The mixture was stirred at 75–80 °C for 6 h, and more CrO_3 (14 g) was added. Progress of the oxidation was monitored by ^{1}H NMR. The mixture was stirred and heated overnight, cooled, and diluted with water (2.5 L). The product was extracted with chloroform, and the extract was washed with $KHCO_3$, dried, and filtered through silica gel. The resulting clear yellow solution was evaporated, and the resulting solid was washed with ethanol to give 11.8 g of yellow product with mp 220–223 °C. The crude product was recrystallized (acetic acid) to give 11.2 g (35% yield) of the diketone: mp 226–228 °C; ^{1}H NMR δ 1.47 (t, J = 7.1 Hz, 6H), 4.50 (q, J = 7.1 Hz, 4H), 7.76 (d, J = 7.8 Hz, 2H), 8.54 (d, J = 7.8 Hz, 2H), 8.91 (s, 2H); ^{13}C NMR δ 14.23, 62.42, 124.89, 129.38, 134.51, 135.63, 135.75, 147.33, 163.56, 186.41; IR 1720, 1538, 1343, 1288, 1255, 1194 cm^{-1}; EIMS, *m/z* 399 (M – EtO, 6), 223 ($^1/_2$M + 1, 12), 222 ($^1/_2$M, 100). Anal. Calcd for $C_{20}H_{16}N_2O_{10}$: C, 54.06; H, 3.63; N, 6.31. Found: C, 54.04; H, 3.66; N, 6.32.

Diethyl 2,2′-Dinitrobibenzyl-4,4′-dicarboxylate (15). A chilled mixture of nitric acid (68%, 90 mL) and sulfuric acid (96%, 105 mL) was added dropwise to stirred solid diester **16** (60.0 g, 0.20 mol) at a temperature below 10 °C. During the addition the powdery diester slowly formed a yellow cake. When the addition was complete the reaction mixture was stirred at room temperature for 3 h and poured onto ice. Yellow precipitate was filtered off, washed with water, and dried. Crude product was boiled with ethanol (500 mL), cooled, filtered, dried, and recrystallized (nitrobenzene, 400 mL) to give 70.8 g (85% yield) of yellow crystals: mp 191 °C; ^{1}H NMR δ 1.43 (t, J = 7.1 Hz, 6H), 3.32 (s, 4H), 4.43 (q, J = 7.1 Hz, 4H(), 7.48 (d, J = 8.1 Hz, 2H), 8.19 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 2H), 8.61 (d, J = 1.7 Hz, 2H); ^{13}C NMR δ 14.26, 34.25, 61.83, 126.05, 130.60, 132.70, 133.75, 139.96, 149.15, 164.33; IR 1719, 1530, 1344, 1289, 1268, 1259, 1150, 756, 712, 678 cm^{-1}; EIMS, *m/z* 371 (M – EtO, 20), 208 ($^1/_2$M, 100), 192 (51), 164 (48). Anal. Calcd for $C_{20}H_{20}N_2O_8$: C, 57.69; H, 4.84; N, 6.73. Found: C, 57.66; H, 4.86; N, 6.71.

Diethyl Bibenzyl-4,4′-dicarboxylate[63] (16). Acetyl chloride (43 mL, 0.60 mol) was added dropwise to a stirred suspension of aluminum chloride (90.0 g, 0.67 mol) in a solution of bibenzyl (50.0 g, 0.274 mol) in hexanes (400 mL). During the addition the temperature was allowed to rise above 40 °C, and the fine suspension of $AlCl_3$ gradually changed to a viscous cake, which eventually solidified. When the addition was complete the reaction mixture was stirred and refluxed an additional 3 h, cooled, and poured into a mixture of ice and hydrochloric acid. The yellow solid was filtered and treated with concd hydrochloric acid (150 mL) and water (50 mL) to decompose the remaining complex. The crude 4,4′-diacetylbibenzyl[64] was added to an aqueous solution of potassium hypochlorite (prepared from 350 g of calcium hypochlorite[65,66]) and dioxane (200 mL), and the mixture was stirred and gently heated. The reaction, which started at about 70 °C, was maintained at 75–80 °C for 3 h, during which all solid dissolved. Excess hypochlorite was destroyed with sodium sulfite, and the warm reaction mixture was filtered. The filtrate was acidified with hydrochloric acid and chilled, and the resulting fine white precipitate was filtered, washed with water, and dried at 120 °C to give 68.6 of fine white powder of bibenzyl-4,4′-dicarboxylic acid.[64] The crude diacid (68.6 g) was reacted with PCl_5 (118 g), and the resulting clear yellow solution was refluxed for 30 min. The resulting $POCl_3$ was distilled off under water aspirator vacuum, and the crude crystalline diacid chloride was carefully treated with dry ethanol (250 mL). The mixture was refluxed for 30 min and evaporated, and the solid residue was dissolved in chloroform, filtered, and evaporated. The product was recrystallized (ethanol–chloroform) to give 68.5 g (76% overall yield) of white crystals: mp 97–98 °C (lit.[63] mp 100 °C); ^{1}H NMR δ 1.38 (t, J = 7.1 Hz, 6H), 2.98 (s, 4H), 4.36 (q, J = 7.1 Hz, 4H), 7.18 (d, J = 8.2 Hz, 4H), 7.94 (d, J = 8.2 Hz, 4H); ^{13}C NMR δ 14.30, 37.36, 60.77, 128.32, 128.44, 129.65, 146.33, 166.52.

Ethyl 2-[2-Amino-4-(ethoxycarbonyl)phenyl]-3-hydroxyindole-6-carboxylate (17). Dinitrobenzil **14** (1.00 g, 2.25 mmol) was reduced with $SnCl_2$ as described for **1b** (method A). After 1 h of stirring and heating (80 °C) the resulting yellow suspension was cooled and filtered to give 0.18 g (23% yield) of indoloindole **1b**. The filtrate was diluted with water, cooled in a refrigerator and the resulting yellow precipitate of **17** was filtered off and dried: mp 185 °C dec; ^{1}H NMR (CD_3OD) δ 1.38 (t, J = 7.1 Hz, 3H), 1.39 (t, J = 7.1 Hz, 3H), 4.35 (q, J = 7.1 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 1H), 7.65–7.68 (m, 3H), 7.76 (d, J = 1.5 Hz, 1H), 8.03 (s, 1H); ^{13}C NMR δ (CD_3OD) 14.58, 14.69, 61.87, 62.26, 114.70, 118.33, 120.36, 121.69, 122.81, 123.71, 124.98, 125.38, 127.43, 130.38, 131.30, 135.13, 135.88, 141.35, 167.78, 169.43; IR 3366, 1715, 1683, 1282, 1212, 767 cm^{-1}; CIMS, *m/z* 370 (MH + 1, 20), 369 (MH, 100), 368 (M, 54).

Diethyl 2,2′-Diazidobibenzyl-4,4′-dicarboxylate (19). Diamine **20** (5.00 g, 14.0 mmol) was suspended in a mixture of ethanol (35 mL), water (10 mL), and concd hydrochloric acid (6.5 mL). The mixture was stirred for 45 min, the resulting paste was cooled in an ice-bath, and a solution of sodium nitrite (2.05 g) in water (8 mL) was added dropwise at a temperature below 5 °C. The almost clear yellow solution of the bis-diazonium salt was stirred for 30 min, and a solution of sodium azide (2.1 g) in water (8 mL) was slowly added at a temperature below 7 °C. The resulting white cake of the product was stirred for 45 min and filtered. The product was well washed with water followed by alcohol and dried. Crude azide was dissolved in a small amount of chloroform and passed through a silica gel plug. The silica gel was washed with chloroform in such a way that the orange band was not eluted. The eluate was evaporated and the resulting solid washed with warm ethanol to give 5.45 g (95% yield) of white diazide: mp 114–115 °C; ^{1}H NMR δ 1.40 (t, J = 7.1 Hz, 6H), 2.88 (s, 4H), 4.39 (q, J = 7.1 Hz, 4H), 7.10 (d, J = 7.8 Hz, 2H), 7.68 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 2H), 7.79 (d, J = 1.5 Hz, 2H); ^{13}C NMR δ 14.28, 31.51, 61.20, 118.98, 125.75, 130.14, 130.53, 137.41, 138.58, 165.67; IR 2146, 1718, 1294, 1254, 775, 750 cm^{-1}; EIMS, *m/z* 408 (M, 8), 353 (28), 352 (100), 351 (25), 350 (28), 279 (81). Anal. Calcd for $C_{20}H_{20}N_6O_4$: C, 58.81; H, 4.94; N, 20.58. Found: C, 58.85; H, 4.93; N, 20.51.

Diethyl 2,2′-Diaminobibenzyl-4,4′-dicarboxylate (20). The dinitrobibenzyl **15** (9.25 g, 22 mmol) was reduced with iron powder (10 g) as described for preparation of **9**. The crude diamine (7.70 g) was recrystallized (chloroform–ethanol) to give 7.00 g (88% yield) of pale yellow crystals: mp 139–140 °C; ^{1}H NMR δ 1.38 (t, J = 7.1 Hz, 6H), 2.85 (s, 4H), 3.70 (br s, 4H), 4.34 (q, J = 7.1

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(66) 3 L of Chlorox instead of KOCl was also used for the oxidation with a similar result.

Hz, 4H), 7.05 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 1.5 Hz, 2H), 7.39 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 2H); ^{13}C NMR δ 14.31, 30.60, 60.76, 116.60, 120.15, 129.59 (2C), 130.69, 144.31, 166.72; IR 3365, 3215, 1703, 1297, 1242 cm^{-1}; EIMS, m/z 356 (M, 17), 178 ($^1/_2$M, 100). Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.39; H, 6.79; N, 7.86. Found: C, 67.44; H, 6.80; N, 7.85.

Pyrolysis of Diethyl 2,2′-Diazidobibenzyl-4,4′-dicarboxylate (19). A solution of diazide **19** (1.50 g) in anhydrous *o*-dichlorobenzene (20 mL) was stirred and heated at 155 °C for 5 h under argon atmosphere. The solvent was removed and the resulting dark residue was passed through a silica plug using methylene chloride–ethyl acetate (3:1) mixture as an eluent. Evaporation of the solvent left 0.95 g of dark brown solid which upon recrystallization (ethanol) gave 0.59 g of a brown-yellow mixture of two major components in an approximate 1:1 ratio (estimated by NMR). A fraction of the mixture was separated on a silica gel column initially using chloroform and then methylene chloride–ethyl acetate (3:1) mixture. White-yellow products were recrystallized from a benzene–hexane mixture (compound **21**) or ethanol (compound **22**).

Diethyl 5,11a-Dihydro-11*H*-indolo[1,2-*b*]indazole-3,8-dicarboxylate (21): mp 185–186 °C; ^{1}H NMR δ 1.35 (t, J = 7.1 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H), 3.45–3.57 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 5.40 (d, J = 8.1 Hz, 1H), 6.3 (br, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.26 (d, J = 7.8 Hz, 1H), 7.62 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.81 (s, 1H); ^{13}C NMR δ 14.24, 14.31, 34.15, 60.81, 60.97, 69.80, 115.21, 117.15, 122.26, 124.25, 125.03, 125.68, 130.60, 131.45, 133.09, 139.64, 147.83, 154.01, 166.07, 166.53; IR 3297, 1722, 1704, 1429, 1288, 1212, 758 cm^{-1}; EIMS, m/z 354 (17), 353 (23), 352 (100), 350 (50). Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.16; H, 5.72; N, 7.95. Found: C, 68.12; H, 5.69; N, 7.92.

Diethyl 11*H*-Indolo[1,2-*b*]indazole-3,8-dicarboxylate (22): mp 174–175 °C; ^{1}H NMR δ 1.43 (t, J = 7.1 Hz, 6H), 4.14 (s, 2H), 4.41 (q, J = 7.1 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 7.61 (d, J = 7.9 Hz, 1H), 7.64 and 7.66 (AB, J = 8.9 Hz, 2H), 8.04 (d, J = 7.9 Hz, 1H), 8.48 (s, 1H), 8.53 (s, 1H); ^{13}C NMR δ 14.27, 14.31, 28.85, 61.06, 61.47, 113.31, 118.87, 119.39, 121.52, 121.95, 125.94, 128.16, 128.66, 131.20, 137.33, 139.41, 140.29, 152.52, 165.47, 166.78; IR 1718, 1711, 1282, 1251, 1210, 1089, 1075, 760 cm^{-1}; EIMS, m/z 351 (M + 1, 25), 350 (100), 277 (56). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.65; H, 5.25; N, 7.98.

Ethyl 2-[4-(Ethoxycarbonyl)-2-nitrophenyl]benzothiophene-6-carboxylate (27). Amine **10** (3.68 g, 9.6 mmol) was stirred with concd hydrochloric acid (6 mL) for 30 min, water (8 mL) was added, and the resulting suspension was cooled in an ice-bath. Sodium nitrite (0.70 g, 10.1 mmol) in water (5 mL) was added dropwise at a temperature below 5 °C. The yellow suspension was stirred at the ice-bath temperature for 45 min and then a cold aqueous solution of sodium acetate (20%, 20 mL) was added followed by a few crystals[61] of $NiCl_2$. The mixture was stirred for 10 min at 5 °C and potassium ethyl xanthate (2.0 g, 12.5 mmol) in water (5 mL) was added. The resulting orange-brown suspension was slowly warmed up to room temperature (most nitrogen evolved at about 15 °C) and stirred for 45 min, and the resulting brown gluey organic product was dissolved in methylene chloride. The organic phase was separated, dried, and filtered through a silica gel plug, which was washed with more methylene chloride. The filtrate was evaporated, and the residue was crystallized (hexane–benzene, 10%) to yield 2.28 g (49% yield) of crude diethyl 2-[(ethoxythiocarbonyl)thio]-2′-nitrostilbene-4,4′-dicarboxylate (**26**): mp 96–98 °C; ^{1}H NMR δ 1.29 (t, J = 7.1 Hz, 3H), 1.42 (t, J = 7.1 Hz, 3H), 1.44 (t, J = 7.1 Hz, 3H), 4.41 (q, J = 7.1 Hz, 2H), 4.44 (q, J = 7.1 Hz, 4H), 4.58 (q, J = 7.1 Hz, 2H), 7.59 (d, J = 15.9 Hz, 1H), 7.69 (d, J = 15.9 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 8.17 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 1H), 8.23 (d, J = 1.7 Hz, 1H), 8.27 (dd, J_1 = 8.3 Hz, J_2 = 1.7 Hz, 1H), 8.64 (d, J = 1.7 Hz, 1H); ^{13}C NMR δ 13.50, 14.25 (2C), 61.40, 61.85, 70.68, 126.00, 126.78, 127.52, 128.77, 129.99, 131.07, 131.16, 131.77, 131.96, 133.71, 136.06, 137.73, 143.86, 147.87, 164.15, 165.13, 210.14; IR 1716, 1283, 1261, 1219, 766 cm^{-1}; CIMS, m/z 491 (MH + 1, 28), 490 (MH, 100), 489 (M, 25). The crude xanthate **26** (2.12 g, 4.35 mol) was suspended in acetic acid (30 mL), and a solution of bromine in CCl_4 (1 M, 5 mL) was added. The resulting mixture was stirred and gently refluxed for 1.5 h, cooled, and poured into water. The organic products were extracted with methylene chloride and the extract was washed with $NaHCO_3$, dried, and evaporated. The yellow residue was passed through a short silica gel column using methylene chloride as an eluent, the eluate was evaporated, and the yellow-orange residue (1.65 g) was recrystallized (ethanol–benzene, 5%) to give 1.35 g (77% yield or 38% overall based on amine **10**) of yellow crystals: mp 126–127 °C; ^{1}H NMR δ 1.43 (t, J = 7.1 Hz, 3H), 1.44 (t, J = 7.1 Hz, 3H), 4.43 (q, J = 7.1 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 7.39 (s, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 8.05 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 8.27 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 1H), 8.46 (d, J = 1.5 Hz, 1H), 8.57 (s, 1H); ^{13}C NMR δ 14.21, 14.32, 61.18, 62.04, 123.96, 124.19, 124.25, 125.11, 125.71, 127.38, 131.84, 131.86, 132.48, 132.62, 140.09, 140.20, 142.79, 149.22, 163.94, 166.24; IR 1718, 1708, 1536, 1295, 1282, 1235 cm^{-1}; EIMS, m/z 400 (M + 1, 24), 399 (M, 100), 354 (31). Anal. Calcd for $C_{20}H_{17}NO_6S$: C, 60.14; H, 4.29; N, 3.51; S, 8.03. Found: C, 60.15; H, 4.29; N, 3.52; S, 7.95.

Ethyl 2-[4-(Ethoxycarbonyl)-2-nitrophenyl]benzoselenophene-6-carboxylate (29). Diazonium salt prepared from nitroamine **10** (3.84 g, 10 mmol) as described for **27** was treated with a cold aqueous solution of sodium acetate (20%, 15 mL) to adjust the pH of the mixture to above 4. Potassium selenocyanate (1.58 g, 11 mmol) in water (5 mL) was slowly added at a temperature below 5 °C. The mixture was stirred for 30 min at ice-bath temperature and warmed to room temperature, and the resulting selenocyanate was filtered off. The crude dry product was dissolved in chloroform, passed through a silica gel plug, and washed with chloroform in such a way that the red band remained on the gel. The eluent was evaporated and the residue was recrystallized (chloroform–benzene) to give 2.71 g (57% yield) of crude diethyl 2-nitro-2′-(selenocyanato)-(*E*)-stilbene-4,4′-dicarboxylate (**28**): mp 145–149 °C; ^{1}H NMR δ 1.43 (t, J = 7.1 Hz, 3H), 1.44 (t, J = 7.1 Hz, 3H), 4.43 (q, J = 7.1 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 7.50 (d, J = 15.9 Hz, 1H), 7.70 (d, J = 15.9 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 8.17 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 8.33 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 1H), 8.48 (s, 1H), 8.68 (s, 1H); ^{13}C NMR δ 14.25 (2C), 61.73, 61.97, 100.34, 122.49, 126.11, 127.92, 129.15, 129.80, 131.56, 131.97, 132.09 (2C), 134.05, 135.72, 136.91, 143.03, 147.80, 164.10, 164.56; IR 1726, 1532, 1286, 1265, 767 cm^{-1}; EIMS, m/z 474 (10), 472 (7), 429 (16), 192 (21), 191 (100). Crude selenocyanate **28** (2.71 g, 5.7 mmol) was suspended in acetic acid (35 mL), and a solution of bromine in CCl_4 (1 M, 7 mL) was added. The resulting mixture was stirred and gently refluxed for 1 h, cooled, and poured into water. The organic products were extracted with methylene chloride, and the extract was washed with 5% $NaHCO_3$, dried, and evaporated. The yellow residue was passed through a short silica gel column using methylene chloride as an eluent, the eluate was evaporated, and the residue was recrystallized (benzene–hexane) to give 2.12 g of product with mp 102–104 °C. One more recrystallization gave 1.84 g (72% yield or 41% overall based on amine **10**) of yellow crystals: mp 105–106 °C; ^{1}H NMR δ 1.43 (t, J = 7.1 Hz, 3H), 1.44 (t, J = 7.1 Hz, 3H), 4.43 (q, J = 7.1 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 7.54 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 8.27 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 8.47 (d, J = 1.5 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR δ 14.22, 14.32, 61.19, 62.03, 125.06, 125.70, 126.06, 127.02, 127.17, 127.89, 131.67, 132.59, 132.65, 134.01, 142.19, 143.08, 145.19, 148.85, 163.98, 166.20; IR 1722, 1702, 1532, 1265, 1234, 764 cm^{-1}; EIMS, m/z 449 (22), 448 (25), 447 (100), 445 (48), 430 (26), 402 (28), 400 (19). Anal. Calcd for $C_{20}H_{17}NO_6Se$: C, 53.82; H, 3.84; N, 3.14; Se, 17.69. Found: C, 53.78; H, 3.85; N, 3.06; Se, 17.20.

Ethyl 2-[2-Amino-4-(ethoxycarbonyl)phenyl]benzothiophene-6-carboxylate (30). Nitrobenzothiophene **27** (1.00 g, 2.5 mmol) and iron powder (1.5 g) were suspended in ethanol (25 mL) and warmed, and concd hydrochloric acid (1.5 mL) was slowly added. The mixture was stirred and refluxed for 2 h, cooled, and filtered. The yellow filtrate was diluted with water, the organic products were extracted with methylene chloride, washed with $NaHCO_3$, and dried, and the solvent was evaporated. The resulting yellow residue (0.86 g, mp 140–142 °C) was recrystallized (ethanol–benzene) to give 0.81 g (88% yield) of the amine **30**: mp 141–2 °C; ^{1}H NMR δ 1.40 (t, J = 7.1 Hz, 3H), 1.44 (t, J = 7.1 Hz, 3H), 4.26 (br s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 4.43

(q, J = 7.1 Hz, 2H), 7.42 (d, J = 8.5 Hz, 1H), 7.48 (dd, J_1 = 7.2 Hz, J_2 = 1.7 Hz, 1H), 7.49 (s, 1H), 7.54 (s, 1H), 7.81 (d, J = 8.3 Hz, 1H), 8.05 (dd, J_1 = 8.5 Hz, J_2 = 1.7 Hz, 1H), 8.57 (s, 1H); ^{13}C NMR δ 14.31, 14.36, 61.06, 62.13, 117.08, 119.53, 122.77, 123.22, 123.26, 124.17, 125.54, 126.61, 130.94, 131.60, 139.37, 143.43, 144.14, 144.62, 166.27, 166.53; IR 3441, 3355, 1707, 1280, 1238, 767 cm^{-1}; EIMS, m/z 370 (M + 1, 23), 369 (M, 100). Anal. Calcd for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18; N, 3.79; S, 8.68. Found: C, 64.97; H, 5.18; N, 3.84; S, 8.76.

Preparative Electrochemistry. A solution of diethyl 5,10-dihydro-*N,N'*-dimethylindolo[3,2-*b*]indole-2,7-dicarboxylate (**1b**, R = Me, 18 mg, 0.05 mmol, for preparation of 1:1 salt, and 94 mg, 0.25 mmol for preparation of 2:1) and 0.1 M tetrabutylammonium perchlorate in methylene chloride (50 mL) was electrolyzed at constant potential (0.9 V) under an atmosphere of dry argon until the appropriate amount of the current was passed through. The resulting black precipitate was filtered off, washed with dry THF, and dried to yield black-green radical ion.

Radical Cation Perchlorate 32 (1:1 salt): IR 3500 (br), 1704, 1364, 1288, 1253, 1093, 1020, 764 cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_2O_8Cl$: C, 55.29; H, 4.64; N, 5.86. Found: C, 54.14; H, 4.67; N, 5.77.

Radical Cation Perchlorate 32 (2:1 salt): IR 3500 (br), 1706, 1364, 1275, 1252, 1134, 1091, 1021, 910, 761 cm^{-1}. Anal. Calcd for $C_{44}H_{44}N_4O_{12}Cl$: C, 61.71; H, 5.18; N, 6.54. Found: C, 61.51; H, 5.15; N, 6.53.

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