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PREPARATION OF CYAN DYES FROM 6-DIETHYLAMINOBENZO[*b*]FURAN-2-CARBOXALDEHYDE

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6-Diethylaminobenzo[*b*]furan-2-carboxaldehyde was synthesized in four steps and 48% overall yield starting from 4-diethylaminosalicylaldehyde. Five cyan dyes were made from this aldehyde using malononitrile dimer and 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran. The crystal structures of two dyes are included.

Keywords: Benzofuran; dyes; malononitrile dimer; polyene

As part of a program to discover new organic nonlinear optical dyes for electro-optic devices, several "push–pull" dyes[1] based on the benzofuran ring system were synthesized (Fig. 1). These dyes are composed of various lengths of olefin linkage between the electron donor diethylamino group and the electron acceptor tricyano-ligand at each end of the molecule. The electron acceptors used to complete the dyes were malononitrile dimer or 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF).

The benzofuran aldehydes, **11**[2–6] and **14**, were prepared as shown in Scheme 1. Deprotonation of commercially available 4-diethylaminosalicylaldehyde (**7**)[7] with potassium *tert*-butoxide and alkylation with diethyl bromomalonate in dimethylformamide gave the cyclized alcohol **8**.[8,9] Dehydration and decarboxylation of **8** was carried out by brief treatment in hot polyphosphoric acid to give the benzofuran ester **9**.[10] In working up this reaction, it was essential to keep the aqueous reaction mixture cold while slowly neutralizing with cold aqueous sodium hydroxide to prevent hydrolysis of the product. (The amount of aqueous sodium hydroxide necessary to neutralize a known quantity of polyphosphoric acid was previously determined.)

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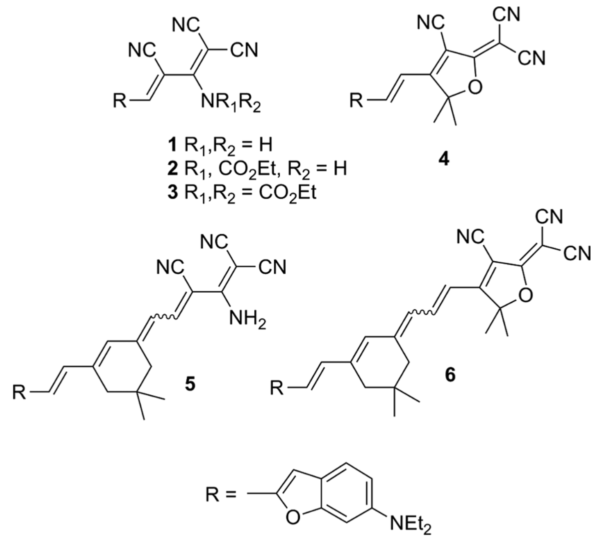
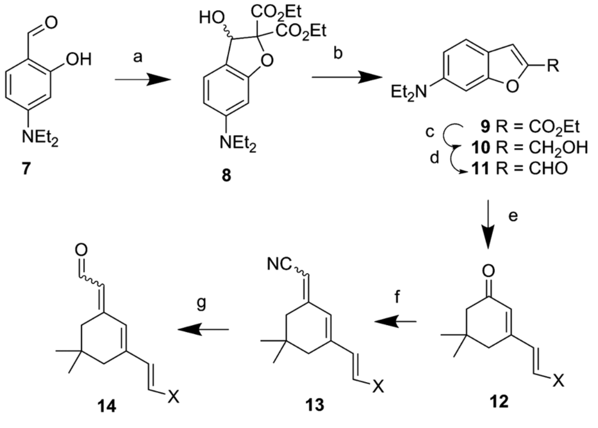


Figure 1. Chemical structures of the dyes.

The ester **9** was reduced with lithium tetrahydroaluminate to the alcohol **10** and then oxidized to aldehyde **11** with 2,3,4,5-tetrachlorobenzoquinone (*p*-chloranil), a sequence previously reported by Chen and Fox.[4]

Continuing onward, Knoevenagel condensation of aldehyde **10** with isophorone gave the ketone **12**.[11] Lithioacetonitrile[12–14] was best prepared by adding



X = 6-diethylaminobenzo[*b*]furan-2-yl

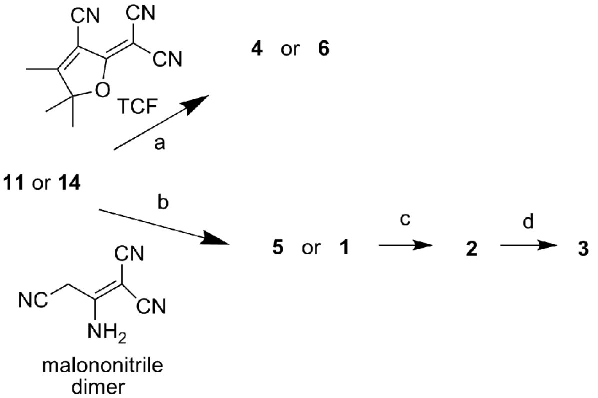
Reagents and conditions: a) KO*t*Bu, diethyl bromomalonate, DMF; b) PPA, 100 °C; c) LAH, THF; d) *p*-chloranil, $CHCl_3$, 40 °C; e) isophorone, NaOH, H_2O, EtOH; f) 1. MeCN, LDA, THF, –78 °C, 2. HOAc, reflux; g) 1. DIBAL, PhMe, –78 °C, 2. H_2O, SiO_2, oxalic acid, rt.

Scheme 1. Synthesis of the aldehydes.

the hexyllithium into the solution of acetonitrile in tetrahydrofuran rather than the reverse. Addition of lithioacetonitrile to **12** at −78 °C gave an intermediate β-hydroxynitrile, which was difficult to characterize. Thus, the crude product from this reaction was refluxed in glacial acetic acid to give the unsaturated nitrile **13** as an almost 1:1 mixture of geometric isomers.[15] Finally, **13** was reduced with di*iso*butylaluminum hydride to give aldehyde **14**. Both aldehydes **11** and **14** were obtained as oils that were difficult to purify completely for accurate combustion analyses; nevertheless, they reacted readily with the nucleophilic acceptor groups.

The final reactions to prepare the dyes are shown in Scheme 2. Dyes **4** and **6** were made by condensation of **11** and **14** with the TCF acceptor in the presence of piperidinium acetate. Dyes **1** and **5** were made by refluxing ethanol solutions of the aldehydes **11** and **14** with malononitrile dimer and piperidinium acetate. In dyes **5** and **6**, the *cis*/*trans* ratio changed from nearly 50%, established at the preparation of **13**, to an 85% *trans*/15% *cis* mixture. This isomerization phenomena has been observed previously with other related dyes.[15,16] The amino group of **1** could be further functionalization by reaction with ethyl chloroformate. When using triethylamine, the monoethoxycarbonyl derivative **2** was obtained. Reaction of **1** with excess ethyl chloroformate and pyridine yielded the diethoxycarbonyl derivative **3**. The curious behavior of malononitrile dimer derivatives to acylation was described previously by Vanmaele.[17,18] Similar attempts to prepare the corresponding ethoxycarbonyl derivatives of **5** appeared to be successful by thin-layer chromatographic (TLC) analysis of the reaction mixtures. However, attempts to isolate and purify the products failed, possibly because of hydrolytic instability.[19]

The λ_{max} for the dyes dissolved in methylene chloride are collected in Table 1. In the series of dyes **1**–**3**, there is a progressive bathochromic shift caused by acylation of the nitrogen atom of **1**.[17,18] The longer length conjugation is probably responsible for the blue appearance of **5** as compared to the red color of **1**.[1] There is a bathochromic shift when the conjugation of **4** is extended to **6**. The malononitrile



Reagents and conditions: a) piperidinium acetate, EtOH or CH_2Cl_2, heat; b) EtOH,reflux; c) $ClCO_2Et$, TEA, CH_2Cl_2, 0 °C; d) $ClCO_2Et$, pyridine, CH_2Cl_2, 0 °C.

Scheme 2. Preparations of the dyes.

Table 1. λ_{max} of **1**–**6** in methylene chloride solution

Compound	λ_{max} (nm)
1	550
2	599
3	655
4	662
5	624
6	697

dimer is a weaker electron acceptor group compared to TCF (compare **1** to **4** and **5** to **6**). Only when the amino group is acylated twice does the malononitrile dimer derivative approach the electron-accepting strength of the TCF acceptor (compare **3** to **4**).

The crystal structure of malononitrile[19,20] dye **5**, Fig. 2, is composed of one molecule with a nearly planar conformation and the second with a slight twist from planarity at the trinitrile end. The planar structure has the transoid conformation (Fig. 3, and the nonplanar is *cis*oid. The crystal structure of the TCF dye[21–25] **6** (Fig. 4) shows a planar conformation along the polyene backbone with the benzofuran ring rotated 180° as compared to **5**. The TCF group resides in the transoid conformation.

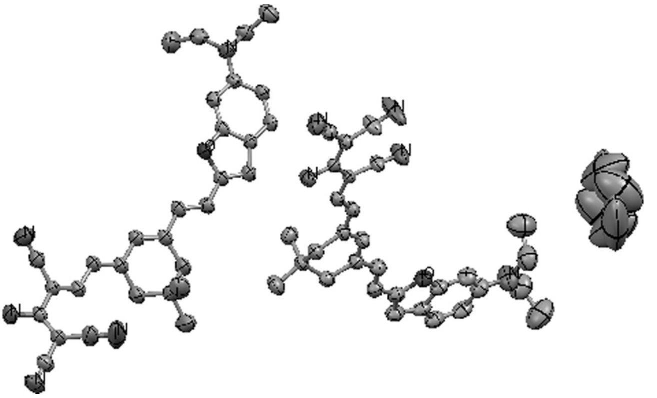


Figure 2. The molecular structure of the asymmetric unit of **5**. Hydrogen atoms are not shown, and only the heteroatoms are labeled. Displacement ellipsoids are drawn at the 50% probability level. The toluene solvent molecule shows rotational disorder and occupies a special position.

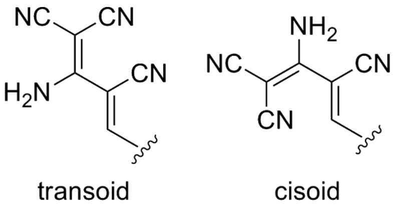


Figure 3. Conformations of the acceptor end of **5** in the solid state.

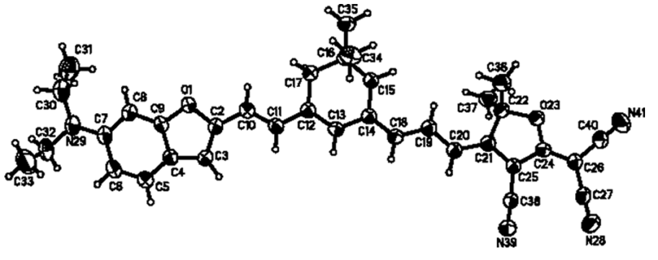


Figure 4. The molecular structure of the symmetric unit of **6** in ORTEP format showing the atom numbering scheme. The hydrogen atoms are drawn as small spheres of arbitrary radii. Only one major conformation of the disordered diethylamino group is shown.

EXPERIMENTAL

The melting points were collected on an electrothermal capillary melting-point apparatus and are not corrected. All NMR data were collected on a Bruker Avance II 300-MHz spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz). Nuclear magnetic resonance data (free-induction decays) were processed using NUTS software from Acorn NMR (Livermore, CA). All spectra are referenced to solvent or tetramethylsilane. The transmission ultraviolet—visible (UV-vis) spectra for compounds dissolved in CH_2Cl_2 were obtained with a Cary 5 near infrared (NIR)–vis-UV spectrophotometer and quartz cuvettes. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

Malononitrile dimer was prepared according to the procedures of Taylor and Hartke[26] or Mittelbach.[27] Piperidinium acetate and the TCF acceptor were prepared according to literature procedures.[28,29] The 2,3,5,6-tetrachloro-1,4-benzoquinone (*p*-chloranil, 99%) was purchased from Sigma-Aldrich (Milwuakee) and recrystallized from toluene before use. The 4-(diethylamino)salicylaldehyde (**7**, 98%) was purchased from Sigma-Aldrich and purified before use: 50 g was dissolved in 500 mL Et_2O and magnetically stirred with 5 g Darco G-60. After 1 h, the mixture was filtered through diatomaceous earth, and the solvent was rotary evaporated to give the product as a tan amorphous crystal. All other reagents were obtained commercially and used as received.

Racemic Diethyl 3-Hydroxy-6-diethylamino-2,3-dihydrobenzo[*b*]furan-2,2-dicarboxylate (8)

A 1-L round-bottomed flask equipped with mechanical stirrer and internal thermometer was charged with 400 mL anhydrous dimethylformamide (DMF) and 50 g **7** (0.26 mol) were added. An endotherm of 7 °C occurred while the solids dissolved. The solution was then cooled to 5 °C with an ice bath. In one portion, 32 g KO*t*Bu (0.286 mol, 1.1 equiv) was added, and the temperature climbed to 20 °C then slowly fell back to 10 °C. After 5 min, the potassium salt of the 4-diethylaminosalicylaldehyde precipitated. In a gentle stream, 74.57 g diethyl bromomalonate (0.312 mol, 1.2 equiv) was added using an addition funnel over 15 min. After ~10 g of the bromide had been added, the solids broke up and stirring resumed. The temperature peaked at 29 °C, and the cooling bath was removed. The mixture was stirred at rt for 1 h. The mixture was poured into 2 L distilled H_2O containing 16.42 mL glacial HOAc (0.286 mol, 1.1 equiv). A brown oil separated initially and after stirring for several hours became a tan solid. The crude product was collected on a coarse-porosity glass frit. The title compound was obtained as white microcrystals from hexanes/EtOAc (75 g, 83%). Mp 87–89 °C. δ_H ($CDCl_3$): 7.19 (d, $J = 9.1$ Hz, 1H), 6.33–6.27 (m, 2H), 5.79 (d, $J = 8.3$ Hz, 1H), 4.43–4.14 (m, 4H), 3.32 (q, $J = 7.1$ Hz, 4H), 2.22 (d, $J = 8.4$ Hz, OH), 1.32 (t, $J = 7.1$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 6H); δ_C ($CDCl_3$): 166.77, 165.73, 160.83, 150.93, 126.15, 112.23, 106.29, 93.89, 93.38, 62.64, 62.56, 44.84, 14.23, 14.07, 12.59. Elemental analysis calculated for $C_{18}H_{25}NO_6$: C, 61.52; H, 7.17; N, 3.99. Found: C, 61.62; H, 7.22; N, 3.97.

Ethyl 6-Diethylaminobenzo[*b*]furan-2-oate (9)

A 1-L beaker was charged with 410 g polyphosphoric acid (PPA) followed by 81.9 g **8** (0.23 mol). The mixture was heated on a hotplate to 100 °C and mechanically stirred with a steel spatula by hand. The color became bright yellow, and gas that evolved caused foaming. After 30 min, the yellow color noticeably changed to tan, and ^1H NMR of an aliquot of the reaction mixture dissolved in DMSO-d_6 showed that all the starting material was consumed and the reaction was complete. Water (1 L) was added, and the mixture was dissolved to give a clear solution. The mixture was transferred to a 3-L beaker, magnetically stirred, and cooled in an ice bath while a previously prepared, cold solution of 205 g NaOH dissolved in 1 L H_2O was added in a gentle stream. Care was taken to keep the internal temperature below 20 °C to prevent ester hydrolysis. The resulting pH was ~5, and a brown oil separated. The mixture was extracted twice with 500-mL portions of Et_2O. After drying over anhydrous $MgSO_4$, the solution was evaporated to half the volume and diluted with an equal volume of hexanes. The mixture was filtered through SiO_2 to remove some polar impurities. Evaporation of the filtrate gave the title compound as a pale yellow oil (51.6 g, 86%). No further purification was performed. δ_H ($CDCl_3$): 7.43 (dd, $J = 8.9$ and 0.6 Hz, 1H), 7.40 (d, $J = 1.0$ Hz, 1H), 6.77 (m, 1H), 6.74 (dd, $J = 8.7$ and 2.3 Hz, 1H), 4.40 (q, $J = 7.2$ Hz, 2H), 3.41 (q, $J = 7.0$ Hz, 4H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.19 (t, $J = 6.9$ Hz, 6H); δ_C ($CDCl_3$): 159.62, 158.48, 148.46, 142.79, 122.80, 115.84, 114.38, 110.55, 92.93, 60.62, 44.72, 14.25, 12.26. Elemental analysis calculated for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 70.01; H, 7.40, 5.33.

2-Hydroxymethyl-6-diethylaminobenzo[*b*]furan (10)

A 1-L round-bottomed flask equipped with magnetic stirbar was charged with 400 mL anhydrous tetrahydrofuran (THF). The flask was stirred and purged with N_2 while 10.56 g lithium aluminum hydride (0.278 mol, 1.75 equiv) was added over 10 min. A reflux condenser was attached to the flask, and an addition funnel with N_2 bubbler was connected on top of the condenser. The funnel was charged with a solution of 41.58 g **9** (0.159 mol) in 100 mL anhydrous THF. The ester was added over 20 min. The mixture was then refluxed until TLC showed complete consumption of the ester (30 min). The mixture was cooled in an ice bath and carefully quenched with 10.56 mL H_2O followed by 10.56 mL 15% NaOH and finally 31.68 mL H_2O. After stirring 1 h, the mixture was filtered through diatomaceous earth. The filtrate was washed with 100 mL brine, and the organic phase was separated and dried over anhydrous $MgSO_4$. The solvent was stripped at the rotovap to give 30.3 g of the title compound as a pale yellow oil (87%). No further purification was performed. δ_H ($CDCl_3$): 7.28 (d, $J = 8.5$ Hz, 1H), 6.75 (d, $J = 1.8$ Hz, 1H), 6.65 (dd, $J = 8.8$ and 2.1 Hz, 1H), 6.42 (s, 1H), 4.60 (s, 2H), 3.31 (q, $J = 7.4$ Hz, Hz, 4H), 3.2 (bs, OH), 1.12 (t, $J = 7.1$ Hz, 6H); δ_C ($CDCl_3$): 157.38, 154.09, 146.54, 121.14, 117.84, 110.16, 104.08, 95.09, 57.89, 45.13, 12.47. Elemental analysis calculated for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.06; H, 7.92; N, 6.34.

6-Diethylaminobenzo[*b*]furan-2-carboxaldehyde (11)

A 2-L round-bottomed flask equipped with magnetic stirbar was charged with 36.53 g 2,3,5,6-tetrachloro-1,4-benzoquinone (0.149 mmol, 1.1 equiv) and 900 mL $CHCl_3$. An addition funnel was attached, and 29.48 g **10** (0.135 mol) dissolved in 100 mL $CHCl_3$ were added over 20 min. The mixture heated to 40 °C for 8 h. After this time, TLC showed the alcohol was completely consumed. The dark mixture was cooled to rt, and the precipitated 2,3,5,6-tetrachloro-1,4-hydroquinone [32.44 g (97%), mp 235–238 °C (HOAc), δ_H (DMSO): 10.21 (bs, 2 OH); δ_C (DMSO): 144.11, 120.74] was filtered. The solvent was stripped at the rotovap, and 500 mL 50% hexanes/Et_2O were added. The supernatant was decanted away from some dark residues on the flask wall. The solution was then chromatographed on silica gel to give the title compound as a yellow-brown oil (22.56 g, 77%). δ_H ($CDCl_3$): 9.63 (s, 1H), 7.50 (d, $J = 9.2$, 1H), 7.41 (d, $J = 1.0$, 1H), 6.77 (dd, $J = 8.9$ and 2.3 Hz, 1H), 6.71 (d, $J = 2.0$ Hz, 1H), 3.45 (q, $J = 7.2$ Hz, 4H), 1.23 (t, $J = 7.1$ Hz, 6H); δ_C ($CDCl_3$): 177.79, 159.92, 151.33, 150.14, 124.18, 116.08, 111.49, 92.73, 45.22, 12.66.

(*E*)-3-(2-(6-(Diethylamino)benzo[*b*]furan-2-yl)vinyl)-5,5-dimethylcyclohex-2-enone (12)

A 250-mL round-bottomed flask equipped with magnetic stirbar and reflux condenser was charged with 8.4 g **11** (39 mmol), 5.34 g isophorone (39 mmol, 1 equiv), and 50 mL EtOH. Over 5 min, a solution of 1.55 g NaOH (39 mmol, 1 equiv) in 5 mL H_2O was added dropwise. The mixture was heated to reflux for 15 min and then allowed to cool to rt. The mixture was poured into 200 mL H_2O and neutralized with 2.2 mL glacial HOAc (39 mmol, 1 equiv). The mixture was extracted three times with 100-mL portions of Et_2O. The organic phases were collected and washed once with 100 mL H_2O followed by 100 mL brine. The organic phase was dried over anhydrous $MgSO_4$ and rotary evaporated to a crude orange solid. Recrystallization from heptane gave 12.07 g of the title compound as orange needles (93%). Mp 102–104 °C. δ_H ($CDCl_3$): 7.33 (d, $J = 9.0$ Hz, 1H), 6.93 (d, $J_{ab} = 15.7$ Hz, 1H), 6.81 (d, $J_{ab} = 16.2$ Hz, 1H), 6.71 (d, $J = 1.8$ Hz, 1H), 6.66 (dd, $J = 8.7$ and 2.3 Hz, 1H), 6.66 (s, 1H), 6.08 (s, 1H), 3.41 (q, $J = 7.1$ Hz, 4H), 2.42 (s, 2H), 2.29 (s, 2H), 1.20 (t, $J = 6.9$ Hz, 6H), 1.09 (s, 6H); δ_C ($CDCl_3$): 200.12, 158.26, 154.77, 151.71, 147.76, 127.41, 126.54, 122.59, 121.77, 118.15, 109.99, 109.55, 93.35, 51.55, 45.09, 38.99, 33.41, 28.66, 12.72. Elemental analysis calculated for $C_{22}H_{27}NO_2$: C, 78.23; H, 8.00; N, 4.15. Found: C, 78.21; H, 8.06; N, 4.13.

(*E* and *Z*)-2-(3-((*E*)-2-(6-(Diethylamino)benzo[*b*]furan-2-yl)vinyl)-5,5-dimethylcyclohex-2-enylidene)acetonitrile (13)

A 1-L round-bottomed flask equipped with magnetic stirbar and 200-mL addition funnel was charged with 200 mL anhydrous THF and 13.3 g anhydrous MeCN (320 mmol, 9 equiv). The apparatus was protected by N_2 bubbler and cooled in a dry ice/acetone bath. The addition funnel was charged with 126 mL of 2.3 M hexyllithium in hexanes (290 mmol, 8 equiv), which were added over 30 min. During the addition, the lithioacetonitrile precipitated as a white solid. After 20 min, a new addition funnel was equipped and charged with a previously prepared solution of 12.07 g **12** (36 mmol) in 30 mL anhydrous THF. The ketone solution was run in over 20 min. The cooling bath was then removed, and the mixture was stirred at rt overnight. A saturated aqueous solution of NH_4Cl (100 mL) and 250 mL Et_2O was added, and the mixture was vigorously stirred. The organic layer was separated and washed with 100 mL H_2O followed by 100 mL brine. The organic layer was dried over anhydrous $MgSO_4$ and rotary evaporated to an orange oil, which was the intermediate β-hydroxynitrile. The oil was dissolved in 200 mL glacial HOAc in a 500-mL round-bottomed flask and refluxed for 5 h. After this time, the reaction was complete by TLC. The glacial HOAc and other volatiles were rotary evaporated, leaving a crude orange solid. Recrystallization from MeCN gave the title compound as orange needles (7.75 g, 60%). Mp 138–140 °C. δ_H ($CDCl_3$): 7.32 (d, $J = 8.7$ Hz, 1H), 7.03–6.25 (m, 6H), 5.12 (s, 0.54 H, *trans*), 4.95 (s, 0.44 H, *cis*), 3.42 (q, $J = 7.0$ Hz, 4H, *cis*), 3.41 (q, $J = 7.0$ Hz, 4H, *trans*), 2.49–2.21 (m, 4H), 1.22 (t, $J = 7.0$ Hz, 3H, *cis*), 1.21 (t, $J = 7.0$ Hz, 3H, *trans*), 1.06–0.98 (m, 6H); δ_C ($CDCl_3$): 158.19, 157.69, 152.46, 152.41, 147.56, 145.01, 144.67, 128.69, 128.36, 126.91, 124.70, 121.55, 121.49, 119.94, 119.77, 118.64, 118.56, 110.00, 107.96, 107.87, 93.83, 93.69, 93.32, 91.89, 45.21, 44.87, 42.28, 39.03, 38.93, 31.42, 31.26, 28.37, 28.32, 12.82. Elemental analysis calculated for $C_{24}H_{28}N_2O$: C, 79.96; H, 7.83; N, 7.77. Found: C, 79.84; H, 7.91; N, 7.90.

(*E* and *Z*)-2-(3-((*E*)-2-(6-(Diethylamino)benzo[*b*]furan-2-yl)vinyl)-5,5-dimethylcyclohex-2-enylidene)acetaldehyde (14)

A 500-mL round-bottomed flask equipped with a magnetic stirbar was charged with 7.75 g **13** (22 mmol) and 250 mL toluene. The mixture was cooled in a dry ice / acetone bath. A 100-mL addition funnel and N_2 bubbler were equipped, and the funnel was charged with 32 mL 1 M di*iso*butylaluminum hydride in hexanes (32 mmol, 1.5 equiv), which was added over 1 h. The mixture was stirred at rt for 12 h. After this time, a paste of 30 g SiO_2 and 10 mL H_2O was added, followed by 1 g oxalic acid dihydrate. The mixture was stirred another 12 h to allow complete hydrolysis of the imine intermediate. The mixture was filtered through celite to remove insolubles. The organic phase was separated and washed with 100 mL H_2O followed by 100 mL brine. After drying over anhydrous $MgSO_4$, the solvent was rotary evaporated, leaving an orange oil. The crude product was chromatographed on SiO_2 (hexanes/EtOAc) to obain 6.92 g of the title compound as an orange oil (88%). δ_H ($CDCl_3$): 10.22 (d, $J = 8.2$ Hz, 0.37 Hz, *cis*), 10.01 (d, $J = 8.4$ Hz, 0.63 H, *trans*), 7.32 (d, $J = 8.6$ Hz, 1H), 7.02–6.89 (m, 1H), 6.75–6.33 (m, 4H), 5.94 (d, $J = 8.4$ Hz, 0.66 H, *trans*), 5.74 (d, $J = 8.4$ Hz, 0.52 H, *cis*), 3.41 (q, $J = 7.0$ Hz, 4H), 2.71–2.26 (m, 4H), 1.21 (t, $J = 7.0$ Hz, 6H), 1.08–0.99

(m, 6H); δ_C ($CDCl_3$): 190.76, 189.73, 158.12, 158.10, 156.45, 156.15, 152.51, 152.48, 147.58, 145.66, 145.54, 129.99, 129.09, 128.79, 127.15, 125.21, 122.63, 121.54, 119.86, 119.68, 118.57, 110.00, 108.07, 108.00, 93.72, 46.37, 45.21, 39.47, 39.18, 39.07, 31.37, 31.27, 29.23, 28.58, 28.45, 22.89, 14.31, 12.82.

2-Amino-4-(6-(diethylamino)benzo[*b*]furan-2-yl)buts-1,3-diene-1,1,3-tricarbonitrile (1)

A 250-mL round-bottomed flask equipped with magnetic stirbar and reflux condenser was charged with 2.14 g **11** (10 mmol), 1.30 g malononitrile dimer (1 equiv), and 50 mL EtOH. The mixture was heated briefly to dissolve all the solids. In one portion, 1.4 g piperidinium acetate (1 equiv) was added, and the mixture was refluxed for 1 h. After cooling to rt, the mixture was poured into 500 mL H_2O, causing a dark solid to precipitate. The solid was collected on a medium-porosity glass frit. After air-drying on the frit, 2.32 g of the title compound were obtained as a dark green powder, which was shown to be a monohydrate by combustion analysis (66%). Mp 180–182 °C. $\lambda_{max} = 550$ nm. δ_H (DMSO): 8.85 (bs, NH_2), 7.78 (s, 1H), 7.64 (s, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 6.87 (dd, $J = 9.3$ and 1.9 Hz, 1H), 6.70 (d, $J = 1.1$ Hz, 1H), 3.48 (q, $J = 7.0$ Hz, 4H), 1.16 (t, $J = 7.0$ Hz, 6H); δ_H (DMSO): 165.95, 159.71, 149.92, 146.67, 137.11, 124.05, 121.56, 116.66, 115.58, 111.69, 93.35, 91.24, 48.72, 44.37, 12.35. Elemental analysis calculated for $C_{19}H_{17}N_5O \cdot H_2O$: C, 65.32; H, 5.48; N, 20.04. Found: C, 65.82; H, 4.86; N, 20.47.

Ethyl 1,1,3-Tricyano-4-(6-(diethylamino)benzo[*b*]furan-2-yl)buta-1,3-dien-2-ylcarbamate (2)

A 100-mL round-bottomed flask equipped with magnetic stirbar was charged with 1 g **1** (3 mmol), 300 mg triethylamine (TEA; 6 mmol, 2 equiv), and 20 mL CH_2Cl_2. The mixture was cooled in an ice bath while 327 mg ethyl chloroformate (1 equiv) were added dropwise. After stirring 30 min, the mixture was poured into 100 mL H_2O. The organic phase was separated and washed with 50 mL saturated aqueous $NaHCO_3$ and then 50 mL brine. The organic phase was dried over anhydrous $MgSO_4$ and rotary evaporated to 1.43 g of a dark residue. Recrystallization of the crude product from a mixture of MeOH and H_2O gave 370 mg of the title compound as copper-colored microcrystals (31%). Mp 172–175 °C. $\lambda_{max} = 599$ nm. δ_H ($CDCl_3$): 7.62–7.44 (m, 4H), 6.79 (dd, $J = 9.1$ and 2.3 Hz, 1H), 6.67 (d, $J = 1.9$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.49 (q, $J = 7.4$ Hz, 4H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 6H); δ_C ($CDCl_3$): 161.86, 161.13, 151.52, 150.89, 147.89, 136.52, 124.50, 123.81, 118.54, 115.54, 113.23, 112.87, 112.75, 92.46, 92.18, 65.79, 64.26, 45.58, 14.38, 12.79. Elemental analysis calculated for $C_{22}H_{21}N_5O_3$: C, 65.50; H, 5.25; N, 17.36. Found: C, 65.29; H, 5.41; N, 17.47.

Diethyl 1,1,3-Tricyano-4-(6-(diethylamino)benzo[*b*]furan-2-yl)buta-1,3-dien-2-yldicarbamate (3)

A 50-mL round-bottomed flask equipped with magnetic stirbar was charged with 500 mg **1** (1.5 mmol), 20 mL CH_2Cl_2, and 2.37 g pyridine (30 mmol, 20 equiv).

The burgundy-colored mixture was cooled in an ice bath, and 1.3 g ethyl chloroformate (12 mmol, 8 equiv) was added dropwise over 30 min. The color of the reaction became brilliant blue. After stirring 30 min further, the mixture was poured into 100 mL H_2O. The organic layer was separated and washed with 50 mL saturated aqueous Na_2CO_3 and finally 50 mL brine. The organic phase was dried over anhydrous $MgSO_4$ and rotary evaporated to a 620 mg of a purple residue. Recrystallization from EtOH gave the title compound as metallic green crystals. Mp 80–82 °C. $\lambda_{max} = 655$ nm. δ_H ($CDCl_3$): 7.65–7.40 (m, 3H), 6.82 (dd, $J = 9.0$ and 2.0 Hz, 1H), 6.64 (s, 1H), 4.38 (q, $J = 7.2$ Hz, 4H), 3.52 (q, $J = 7.2$ Hz, 4H), 1.35 (t, $J = 7.2$ Hz, 6H), 1.28 (t, $J = 7.2$ Hz, 6H); δ_C ($CDCl_3$): 162.74, 159.28, 152.51, 149.94, 148.46, 133.87, 125.19, 119.66, 114.94, 113.69, 112.49, 112.35, 95.59, 91.92, 65.15, 45.78, 14.28, 12.89. Elemental analysis calculated for $C_{25}H_{25}N_5O_5$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.79; H, 5.43; N, 14.49.

(*E*)-2-(3-Cyano-4-(2-(6-(diethylamino)benzo[*b*]furan-2-yl)vinyl)-5,5-dimethylfuran-2(5*H*)-ylidene)malononitrile (4)

A 50-mL round-bottomed flask equipped with a magnetic stirbar and reflux condenser was charged with 1.3 g **11** (6 mmol), 1.19 g TCF (1 equiv), and 25 mL EtOH. The mixture was heated briefly to dissolve all the solids. In one portion, 867 mg piperdidinium acetate (1 equiv) was added, and the mixture was refluxed for 1 h. After cooling to rt, the green microcrystalline powder was filtered on a medium-porosity glass frit (2.1 g, 88%). No further purification was necessary. Mp 275–277 °C. $\lambda_{max} = 662$ nm. δ_H ($CDCl_3$): 7.53 (d, $J = 15.5$ Hz, 1H), 7.45 (d, $J = 9.0$ Hz, 1H), 7.17 (s, 1H), 6.81 (d, $J = 15.5$ Hz, 1H), 6.76 (dd, $J = 9.0$ and 2.3 Hz, 1H), 6.67 (d, $J = 1.7$ Hz, 1H), 3.49 (q, $J = 7.1$ Hz, 4H), 1.75 (s, 6H), 1.28 (t, $J = 7.4$ Hz, 6H). Elemental analysis calculated for $C_{24}H_{22}N_4O_2$: C, 72.34; H, 5.57; N, 14.06. Found: C, 72.50: H, 5.46; N, 14.07.

(*E* and *Z*)-2-Amino-5-(3-((E)-2-(6-(diethylamino)benzo[*b*]furan-2-yl)vinyl)-5,5-dimethylcyclohex-2-enylidene)penta-1,3-diene-1,1,3-tricarbonitrile (5)

A 50-mL round-bottomed flask equipped with magnetic stirbar and reflux condenser was charged with 1 g **14** (2.8 mmol), 363 mg malononitrile dimer (1 equiv), and 15 mL EtOH. The mixture was heated briefly to dissolve all the solids. In one portion, 400 mg piperidinium acetate (1 equiv) were added, and the mixture was heated to reflux. After 1 h, the mixture was cooled to rt, and the precipitate was filtered on a medium-porosity glass frit. After vacuum drying, 1.17 g of the title compound was obtained as a green microcrystalline powder (90%). The compound could be recrystallized from MeCN or toluene to give the title compound as copper-colored microcrystals. Mp 163–165 °C. $\lambda_{max} = 624$ nm. δ_H ($CDCl_3$): 8.65 (d, $J = 11.7$ Hz, 0.15 H, *cis*), 8.42 (d, $J = 12.7$ Hz, 0.85 H, *trans*), 7.33 (d, $J = 8.5$ Hz, 1H), 7.02–6.91 (m, 1H), 6.80–6.45 (m, 6H), 5.88 (bs, NH_2), 3.44 (q, $J = 7.4$ Hz, 4H), 2.50 (s, 2H), 2.39 (s, 2H), 1.22 (t, $J = 7.0$ Hz, 6H), 1.06 (s, 6H). Elemental analysis calculated for $C_{30}H_{31}N_5O$: C, 75.44; H, 6.54; N, 14.66. Found: C, 75.51; H, 6.48; N, 14.62.

(*E* and *Z*)-2-(3-Cyano-4-(3-(3-((*E*)-2-(6-(diethylamino)benzo[*b*]furan-2-yl)vinyl)-5,5-dimethylcyclohex-2-enylidene)prop-1-enyl)-5,5-dimethylfuran-2(5*H*)-ylidene)malononitrile (6)

A 50-mL round-bottomed flask equipped with magnetic stirbar was charged with 1 g **14** (2.8 mmol), 547 mg TCF (1 equiv), and 15 mL CH_2Cl_2. The mixture was heated briefly to dissolve all the solids. One portion of 400 mg piperidinium acetate (1 equiv) was added, and the mixture was heated to 40 °C for 2 h. During this time, a dark purple solid precipitated. After cooling to rt, the solid was collected on a medium-porosity glass frit. After washing with EtOH, the product was air-dried on the frit (1 g, 67%). The product was recrystallized from MeCN to give the title compound as microscopic purple needles. Mp 243–245 °C. $\lambda_{max} = 697$ nm. δ_H ($CDCl_3$): 8.26 (dd, $J = 15.1$ and 13.7 Hz, 0.15 H, *cis*), 7.99 (dd, $J = 15.1$ and 12.5 Hz, 0.85 H, *trans*), 7.33 (d, $J = 8.6$ Hz, 1H), 7.05–6.59 (m, 5H), 6.48–6.09 (m, 3H), 3.43 (q, $J = 6.7$ Hz, 4H), 2.43 (s, 2H), 2.37 (s, 2H), 1.72–1.67 (m, 6H), 1.22 (t, $J = 7.0$ Hz, 6H), 1.08–1.03 (m, 6H). Elemental analysis calculated for $C_{33}H_{34}N_4O_2$: C, 76.42; H, 6.61; N, 10.80. Found: C, 76.71; H, 6.66, N, 10.57.

X-Ray Structure Determination of 5 and 6

Some selected data and refinement details are collected in Table 2. CCDC 736600 (**5**) and CCDC 737420 (**6**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing

Table 2. Crystal structure data and refinement details for compounds **5** and **6**

Compound	5	6
Empirical formula	$C_{30}H_{31}N_5O$	$C_{33}H_{34}N_4O_2$
Formula weight	477.60	544.68
Temperature (K)	296	223(2)
Crystallization solvent	Toluene	Acetonitrile
Crystal system	Triclinic	Monoclinic
Space group	P1	$P2_1/n$
Unit cell dimensions (Å, °) a	10.0455(5)	8.8392(2)
B	14.2645(7)	14.8729(3)
C	20.6577(11)	23.5183(5)
α	89.0130(10)	90
β	79.9670(10)	95.2460(10)
γ	79.2660(10)	90
Volume (Å^3)	2863.5(3)	3078.87(11)
Z	2	4
Density (g/cm^3)	1.153	1.175
Crystal size (mm)	$0.06 \times 0.18 \times 0.35$ mm^3	$0.21 \times 0.04 \times 0.03$ mm^3
Reflections collected	33504	5111
Independent reflections	12902	5161
Completeness (%)	98.1	91.7
Data/restraints/parameters	12902 / 0 / 697	5161 / 0 / 398
Goodness of fit on F^2	0.797	1.049
Final R [I > 2sigma(I)]	$R_1 = 0.0486$, $wR_2 = 0.1509$	$R_1 = 0.0407$, $wR_2 = 0.0988$

data_request@ccdc.cam.ac.uk, or by contacting the CCDC at 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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