

**Supporting Information** for *Org. Lett.*

**Donor-Acceptor Substituted Phenylethenyl Bithiophenes: Highly Efficient and Stable Nonlinear Optical Chromophores**

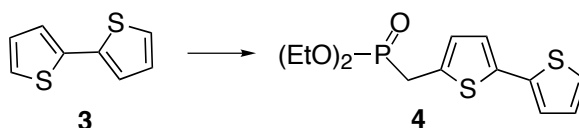
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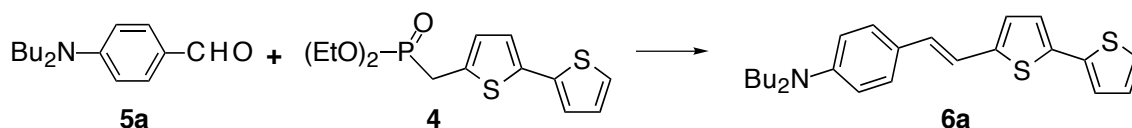
**Syntheses**

*General.* Reagents and (anhydrous) solvents were purchased from *Fluka*, *Aldrich*, and *Lancaster*, and used without purification. Flash chromatography (FC) was performed on E. Merck 60, 230–400 mesh silica gel. Thin layer chromatography (TLC) was performed with 0.25 mm E. Merck silica gel 60 F<sub>25</sub> plates and visualized by UV (254 or 350 nm) and cerium ammonium molybdate. *All chemicals, some of them such as tetracyanoethylene and the chromophores are hazardous, should be handled with great care.*

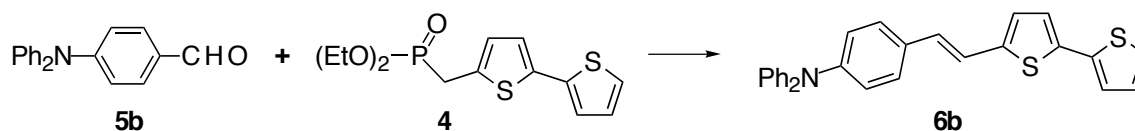


Diethyl (2,2'-bithien-5-yl)methylphosphonate (4). At  $-76^{\circ}$ , a soln. of *n*-BuLi (15 ml, 2.35 M in hexane, 35 mmol) was added slowly to a stirred soln. of bithiophene (**3**, 6 g, 35 mmol) in anhydrous THF (140 ml) under N<sub>2</sub>. After stirring at  $-76^{\circ}$  for 1.5 h, the slightly blue soln. was transferred via a double end needle to a stirred suspension of CuI (6.67 g, 35 mmol) in THF (4 ml) at ca.  $-40^{\circ}$ . The yellow mixture was stirred at  $0^{\circ}$  for 1 h. The resulting clear brown soln. was treated with diethyl iodomethylphosphonate (8.757 g, 31.5 mmol) and then with anhydrous DMSO (30 ml), and heated at  $56^{\circ}\text{C}$  for 20 h. THF was evaporated, and the residue was diluted with AcOEt (600 ml), treated with an aq. soln. of Na<sub>2</sub>S (3%, 140 ml). The organic layer was washed with 3x150 ml H<sub>2</sub>O, and dried over Na<sub>2</sub>SO<sub>4</sub>. FC (AcOEt) gave **4** (7.32 g, 73%) as a brown oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.19 (dd, *J* = 5.0, 1.0, 1 H); 7.12 (br. d, *J* = 3.7, 1 H); 7.01 (d, *J* = 3.7, 1 H); 6.99 (dd, *J* = 5.3, 3.7, 1 H); 6.88 (t, *J* =

3.7, 1 H); 4.10 (dt,  $J = 15.3, 7.2, 4$  H); 3.33 (d,  $J = 20.9, 2$  H); 1.30 (t,  $J = 7.2, 6$  H).  $^{13}\text{C-NMR}$  (75 Hz,  $\text{CDCl}_3$ ): 145.04, 136.30, 136.08, 134.37, 129.74, (128.93, 128.75), (126.62, 126.55), 122.18, (62.73, 62.60), (29.99, 27.14), (16.50, 16.38).  $^{31}\text{P-NMR}$  (81 MHz,  $\text{CDCl}_3$ ): 24.22. EI-MS  $m/z$ : 361 (51,  $\text{M}^+$ ), 224.1 (100,  $[\text{M}-(\text{EtO})_2\text{PO}]^+$ ).

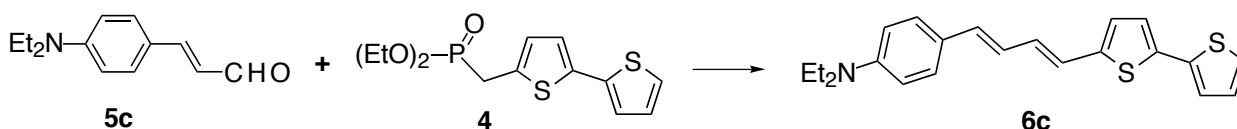


*N,N*-Dibutyl-4-[(*E*)-2-(2,2'-bithien-5-yl)-1-ethenyl] aniline (**6a**). A soln. of **4** (1.142 g, 3.609 mmol) and 4-(dibutylamino)benzaldehyde (**5a**, 720 mg, 3.085 mmol) in THF (25 ml) was added to a mixture of NaH (55% in miner oil, 200 mg, 4.15 mmol) and 15-crown-5 (40 mg, 0.18 mmol) at r.t. The suspension was stirred for 4 h, diluted with toluene, washed with  $\text{H}_2\text{O}$  (3 x 80 ml), dried over  $\text{Na}_2\text{SO}_4$ . FC (toluene) gave **6a** (1.22 g, 100%) as an orange fluorescent solid.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 7.32 (dt,  $J = 8.8, 2.4, 2$  H); 7.18 (dd,  $J = 5.1, 1.1, 1$  H); 7.15 (dd,  $J = 3.6, 1.1, 1$  H); 7.04 (d,  $J = 3.7, 1$  H); 7.01 (dd,  $J = 5.1, 3.7, 1$  H); 6.95 (d,  $J = 16.0, 1$  H); 6.85 (d,  $J = 3.8, 1$  H); 6.82 (d,  $J = 16.0, 1$  H); 6.61 (dt,  $J = 8.9, 2.5, 2$  H); 3.29 (t,  $J = 7.6, 4$  H); 1.63–1.50 (m, 4 H); 1.44–1.26 (m, 2 H); 0.97 (t,  $J = 7.3, 6$  H).  $^{13}\text{C-NMR}$  (75 Hz,  $\text{CDCl}_3$ , DEPT): 147.91 (s), 143.34 (s), 137.91 (s), 134.46 (s), 129.00 (d), 127.81 (d), 127.67 (2d), 125.21 (d), 124.09 (d), 123.97 (d + s), 123.23 (d), 116.72 (d), 111.68 (2d), 50.79 (t), 29.51 (t), 20.36 (t), 14.01 (q). EI-MS  $m/z$ : 395 (100,  $\text{M}^+$ ), 352 (77), 310 (38), 295 (32). Anal. calc. for  $\text{C}_{24}\text{H}_{29}\text{NS}_2$ : C 72.86, H 7.39, N 3.54, S 16.21; found: C 72.95, H 7.40, N 3.25, S 16.13.

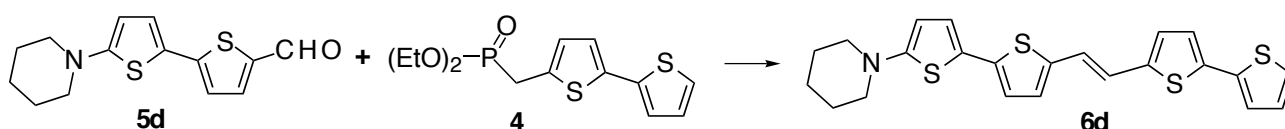


*N,N*-Diphenyl-4-[(*E*)-2-(2,2'-bithien-5-yl)-1-ethenyl] aniline (**6b**). Similar to **6a**, from **4** and **5b** in 100% yield. Yellow fluorescent solid.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 7.32 (dt,  $J = 8.7, 2.5, 2$  H); 7.26 (br. t,  $J = 7.8, 4$  H); 7.20 (dd,  $J = 5.1, 1.1, 1$  H); 7.17 (dd,  $J = 3.6, 1.1, 1$  H); 7.10 (br. d,  $J = 8.7, 4$  H); 7.07–7.02 (m, 6 H); 7.01 (dd,  $J = 5.1, 3.6, 1$  H); 6.91 (d,  $J = 3.8, 1$  H); 6.83 (d,  $J = 16.0, 1$  H).  $^{13}\text{C-NMR}$  (75 Hz,  $\text{CDCl}_3$ , DEPT): 147.54 (2s), 147.48 (s), 142.37 (s), 137.68 (s), 135.67 (s), 131.00 (s),

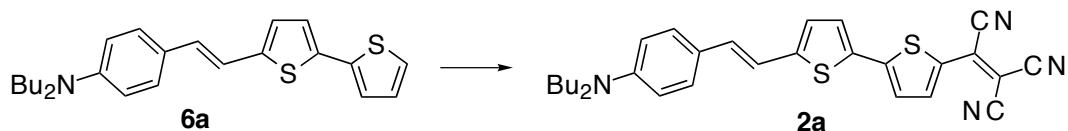
129.38 (4d), 128.00 (d), 127.95 (d), 127.25 (2d), 126.62 (d), 124.65 (4d), 124.42 (d), 124.19 (d), 123.63 (d), 123.51 (2d), 123.19 (2d), 120.03 (d). EI-MS  $m/z$ : 435 (100,  $M^+$ ). Anal. calc. for  $C_{28}H_{21}NS_2$ : C 77.20, H 4.86, N 3.22, S 14.72; found: C 77.40, H 5.15, N 3.11, S 14.50.



*N,N*-Diethyl-4-[(1*E*, 3*E*)-4-(2,2'-bithien-5-yl)-1,3-butadienyl] aniline (6c). Similar to **6a**, from **4** and **5c** in 82% yield. Orange fluorescent solid.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 7.29 (br. d,  $J = 8.9$ , 2 H); 7.18 (dd,  $J = 5.1$ , 1.1, 1 H); 7.15 (dd,  $J = 3.6$ , 1.1, 1 H); 7.03 (d,  $J = 3.7$ , 1 H); 7.00 (dd,  $J = 5.1$ , 3.6, 1 H); 6.82 (d,  $J = 3.8$ , 1 H); 6.72 (dd,  $J = 14.7$ , 10.2, 1 H); 6.68 (dd,  $J = 14.6$ , 10.2, 1 H); 6.62 (br. d,  $J = 8.9$ , 2 H); 6.61 (d,  $J = 14.7$ , 1 H); 6.56 (d,  $J = 14.5$ , 1 H); 3.36 (q,  $J = 7.1$ , 4 H); 1.17 (z,  $J = 7.1$ , 6 H).  $^{13}\text{C-NMR}$  (75 Hz,  $\text{CDCl}_3$ , DEPT): 147.49 (s), 142.77 (s), 137.81 (s), 135.25 (s), 133.64 (d), 130.38 (d), 127.92 (3d), 125.89 (d), 124.71 (s), 124.25 (d), 124.21 (d), 123.96 (d), 123.46 (d), 122.62 (d), 111.70 (2d), 44.46 (t), 12.72 (q). EI-MS  $m/z$ : 365 (100,  $M^+$ ), 350 (60,  $[M-\text{Me}]^+$ ).

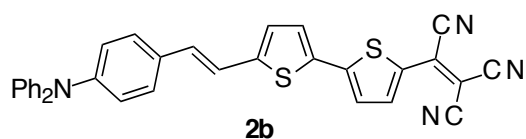


5-Piperidinyl-5'-[(*E*)-2-(2,2'-bithien-5-yl)-1-ethenyl]-2,2'-bithiophene (6d). Similar to **6a**, from **4** and **5d**. After FC, the product was further purified by crystallization from toluene. Pink fluorescent solid. Yield: 40%.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ): 7.20 (dd,  $J = 5.1$ , 1.1, 1 H); 7.16 (dd,  $J = 3.6$ , 1.1, 1 H); 7.04 (d,  $J = 3.7$ , 1 H); 7.01 (dd,  $J = 5.1$ , 3.6, 1 H); 6.93 (d,  $J = 15.7$ , 1 H); 6.89 (d,  $J = 3.9$ , 1 H); 6.88 (d,  $J = 4.0$ , 1 H); 6.86 (d,  $J = 3.8$ , 1 H); 6.85 (d,  $J = 15.8$ , 1 H); 6.81 (d,  $J = 3.7$ , 1 H); 5.98 (d,  $J = 4.0$ , 1 H); 3.15 (t,  $J = 5.6$ , 4 H); 1.72 (q,  $J = 5.7$ , 4 H); 1.60–1.54 (m, 2 H).  $^{13}\text{C-NMR}$  (125 Hz,  $\text{CDCl}_3$ , DEPT): 159.54 (s), 141.69 (s), 139.01 (s), 137.88 (s), 137.55 (s), 135.74 (s), 127.89 (d), 127.45 (d), 126.66 (d), 124.38 (d), 124.20 (d), 123.59 (2d), 122.76 (s), 121.63 (d), 121.44 (d), 120.07 (d), 104.70 (d), 52.15 (t), 25.19 (t), 23.72 (t). EI-MS  $m/z$ : 439 (100,  $M^+$ ).



2-{5'-[2-(E)-(4-dibutylaminophenyl)-1-ethenyl]-2,2'-bithien-5-yl}-1,1,2-ethylenetricarbonitrile (2a).

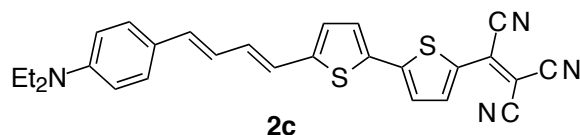
A soln. of BuLi (0.30 ml, 2.1 M in hexane, 0.63 mmol) was added to a soln. of **6a** (239 mg, 0.604 mmol) in THF (5 ml) at  $-76^\circ$  under  $N_2$ . The soln. was stirred at  $-76^\circ$  to  $0^\circ$  for 1.5 h, recooled to  $-76^\circ$ , treated in one portion with a soln. of tetracyanoethylene (94.48 mg, 737  $\mu$ mole) in THF (1.3 ml), stirred at  $-76^\circ$  to r.t. for ca. 2 h. THF was removed under vacuum, and the residue was dissolved in  $CHCl_3$ , neutralized with 0.1 N HCl, washed with 4 x  $H_2O$ , dried over  $Na_2SO_4$ . FC (toluene) gave **2a** as a dark green solid (242 mg, 80%).  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 7.94 (d,  $J = 4.4$ , 1 H); 7.42 (d,  $J = 4.0$ , 1 H); 7.34 (d,  $J = 8.9$ , 2 H); 7.28 (d,  $J = 4.4$ , 1 H); 6.98 (d,  $J = 4.0$ , 1 H); 6.97 (d,  $J = 16.0$ , 1 H); 6.92 (d,  $J = 16.0$ , 1 H); 6.62 (d,  $J = 9.0$ , 2 H); 3.31 (t,  $J = 7.6$ , 4 H); 1.65–1.54 (m, 4 H); 1.43–1.31 (m, 4 H); 0.97 (t,  $J = 7.3$ , 6 H).  $^{13}C$ -NMR (75 Hz,  $CDCl_3$ , DEPT): 152.99 (s), 150.99 (s), 148.81 (s), 141.59 (d), 133.13 (d), 131.72 (s), 131.11 (s), 130.77 (s), 130.22 (d), 128.58 (2d), 126.41 (d), 124.67 (d), 122.89 (s), 115.25 (d), 112.97 (s), 112.91 (s), 112.60 (s), 111.66 (2d), 79.13 (s), 50.80 (t), 29.49 (t), 20.33 (t), 13.99 (q). EI-MS  $m/z$ : 496 (1.6,  $M^+$ ), 471 (1.7), 453 (1.9), 428 (1.6), 149 (3.9), 86 (56), 84 (86), 49 (100). Anal. calc. for  $C_{29}H_{28}N_4S_2$ : C 70.13, H 5.68, N 11.28, S 12.91; found: C 70.28, H 5.86, N 11.04, S 12.78.



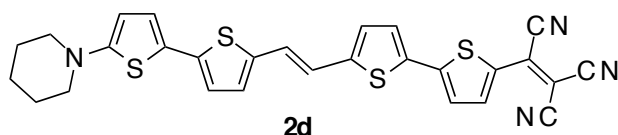
2-{5'-[2-(E)-(4-diphenylaminophenyl)-1-ethenyl]-2,2'-bithien-5-yl}-1,1,2-ethylenetricarbonitrile (2b)

Similar to **2a**, in 45% yield. Dark green solid.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 7.97 (d,  $J = 4.4$ , 1 H); 7.43 (d,  $J = 4.0$ , 1 H); 7.34 (br. d,  $J = 8.7$ , 2 H); 7.31 (d,  $J = 4.4$ , 1 H); 7.32–7.25 (m, 4 H); 7.18–7.02 (m, 10 H); 6.98 (d,  $J = 16.1$ , 1 H).  $^{13}C$ -NMR (75 Hz,  $CDCl_3$ , DEPT): 152.50 (s), 149.39 (s), 148.58 (s), 147.15 (2s), 141.54 (d), 132.11 (s), 131.93 (s), 131.87 (d), 131.24 (s), 129.91 (d), 129.44 (4d), 128.24 (s), 127.82 (2d), 127.44 (d), 125.07 (4d), 125.00 (d), 123.70 (2d), 122.59 (2d), 118.46 (d),

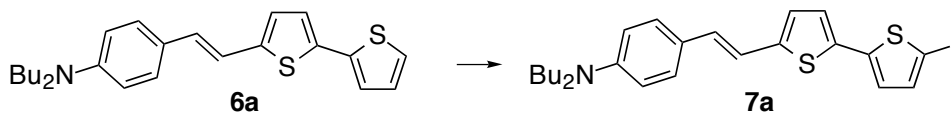
112.80 (s), 112.73 (s), 112.36 (s), 80.32 (s). EI-MS  $m/z$ : 536 (11,  $M^+$ ), 511 (21), 44 (100). Anal. calc. for  $C_{33}H_{20}N_4S_2$ : C 73.85, H 3.76, N 10.44, S 11.95; found: C 73.59, H 4.24, N 10.10.



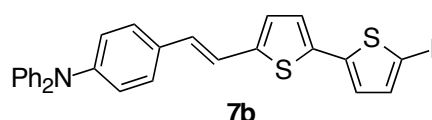
2-{5'-[4-(1*E*,3*E*)-(4-diethylaminophenyl)-1,3-butadienyl]-2,2'-bithien-5-yl}-1,1,2-ethylenetricarbonitrile (2c). Similar to **2a**, in 44% yield. Dark green solid.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 7.95 (d,  $J = 4.4$ , 1 H); 7.41 (d,  $J = 4.0$ , 1 H); 7.31 (d,  $J = 9.0$ , 2 H); 7.28 (d,  $J = 4.4$ , 1 H); 6.95 (d,  $J = 4.3$ , 1 H); 6.87 (dddd,  $J = 15.2, 7.3, 2.8$ , 1 H); 6.79–6.59 (m, 5 H); 3.39 (q,  $J = 7.1$ , 4 H); 1.19 (t,  $J = 7.1$ , 6 H).  $^{13}C$ -NMR (75 Hz,  $CDCl_3$ , DEPT): 152.70 (s), 150.06 (s), 148.06 (s), 141.53 (d), 136.82 (d), 134.36 (d), 131.86 (s), 131.80 (s), 130.87 (s), 130.15 (d), 128.48 (2d), 126.90 (d), 124.85 (d), 124.01 (2s overlapped), 123.04 (d), 121.17 (d), 112.88 (s), 112.53 (s), 111.59 (2d), 79.52 (s), 44.46 (2t), 12.67 (2q). Anal. calc. for  $C_{27}H_{22}N_4S_2$ : C 69.50, H 4.75, N 12.01, S 13.74; found: C 69.68, H 4.95, N 11.98, S 13.61.



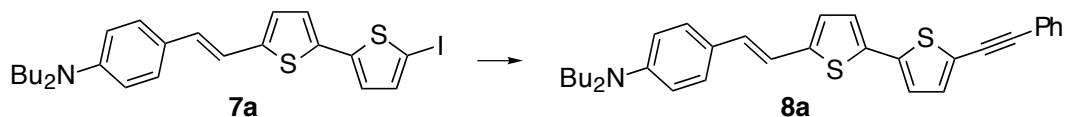
2-{5'-[2-(*E*)-(5'-piperidiny)-2,2'-bithien-5-yl]-1-ethenyl}-2,2'-bithien-5-yl}-1,1,2-ethylenetricarbonitrile (2d). Similar to **2a**, in 8% yield. Dark green solid. It was sparsely soluble in  $CHCl_3$  and other less polar solvents. Although easier to dissolve in polar solvent such as DMPU, DMSO, and DMF, it rapidly decomposed in the presence of air and day light, as evidenced by the colour change from dark green to deep red. EI-MS  $m/z$ : 540 (1.5,  $M^+$ ), 149 (1.1), 84 (100). High resolution MS: calc. for  $C_{28}H_{20}N_4S_4$ : 540.0568; found: 540.0549.



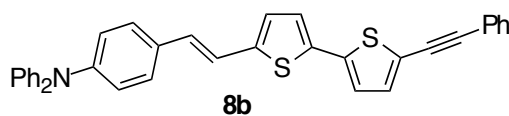
*N,N*-Dibutyl-4-[(*E*)-2-(5'-iodo-2,2'-bithien-5-yl)-1-ethenyl] aniline (**7a**). A soln. of BuLi (0.55 ml, 2.32 M in hexane, 1.28 mmol) was added to a soln. of **6a** (512 mg, 1.29 mmol) in THF (10 ml) at  $-76^{\circ}$  under  $N_2$ . The brown-orange soln. was stirred at  $-76^{\circ}$  for 10 min. The cooling bath was removed, and the mixture was warmed to  $0^{\circ}$  for ca. 15 min, re-cooled to  $-76^{\circ}$ , treated with a soln. of  $I_2$  (355 mg, 1.39 mmol) in THF (5 ml) in one portion, stirred at  $-76^{\circ}$  for ca. 20 min. The brown soln. was diluted with toluene, washed with diluted aq.  $Na_2S_2O_3$  and then  $H_2O$  (3x), and dried over  $Na_2SO_4$ . FC (toluene) gave **7a** as a yellow solid (681 mg, 93%).  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 7.30 (d,  $J = 8.8$ , 2 H); 7.13 (d,  $J = 3.8$ , 1 H); 6.97 (d,  $J = 3.8$ , 1 H); 6.92 (d,  $J = 15.7$ , 1 H); 6.83 (d,  $J = ca. 3.8$ , 1 H); 6.81 (d,  $J = ca. 15.7$ , 1 H); 6.80 (d,  $J = 3.8$ , 1 H); 6.60 (d,  $J = 8.9$ , 2 H); 3.28 (t,  $J = 7.6$ , 4 H); 1.62–1.52 (m, 4 H); 1.43–1.24 (m, 4 H); 0.96 (t,  $J = 7.3$ , 6 H).  $^{13}C$ -NMR (75 Hz,  $CDCl_3$ , DEPT): 148.00 (s), 143.92 (s), 143.84 (s), 137.70 (d), 133.14 (s), 129.44 (d), 127.75 (2d), 125.16 (d), 124.57 (d), 124.49 (d), 123.80 (s), 116.44 (d), 111.66 (2d), 71.26 (s), 50.79 (2t), 29.51 (2t), 20.37 (2t), 14.02 (2q). EI-MS  $m/z$ : 521 (10,  $M^+$ ), 478 (6), 395 (10), 352 (8), 86 (65), 84 (100). Anal. calc. for  $C_{24}H_{28}NS_2I$ : C 55.27, H 5.41, N 2.69; found: C 56.61, H 5.48, N 2.61.



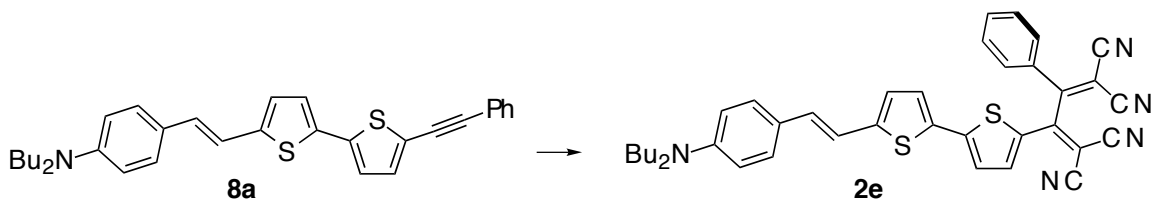
*N,N*-Diphenyl-4-[(*E*)-2-(5'-iodo-2,2'-bithien-5-yl)-1-ethenyl] aniline (**7b**). Similar to **7a**, from **6b** in 82% yield.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 7.31 (br. d,  $J = 8.6$ , 2 H); 7.29–7.23 (m, 4 H); 7.14 (d,  $J = 3.8$ , 1 H); 7.10 (br. d,  $J = 7.5$ , 4 H); 7.09–7.03 (m, 5 H); 6.99 (d,  $J = 3.8$ , 1 H); 6.89 (d,  $J = 3.8$ , 1 H); 6.83 (d,  $J = 16.0$ , 1 H); 6.82 (d,  $J = 3.8$ , 1 H).  $^{13}C$ -NMR (75 Hz,  $CDCl_3$ , DEPT): 147.55 (s), 147.45 (2s), 143.52 (s), 142.86 (s), 137.74 (d), 134.27 (s), 130.75 (s), 129.31 (4d), 128.39 (d), 127.24 (2d), 126.45 (d), 124.82 (d), 124.63 (4d), 124.58 (d), 123.35 (2d), 123.18 (2d), 119.69 (d), 71.75 (s). EI-MS  $m/z$ : 561 (86,  $M^+$ ), 435 (100,  $[M-I+1]^+$ ). Anal. calc. for  $C_{28}H_{20}NS_2I$ : C 59.89, H 3.59, N 2.49; found: C 61.84, H 4.26, N 2.43.



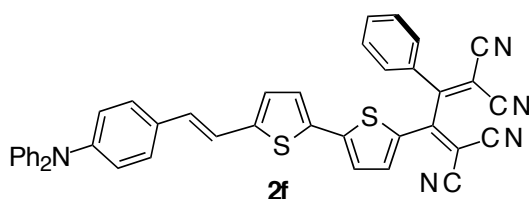
*N,N*-Dibutyl-4-[(*E*)-2-(5'-phenylethynyl-2,2'-bithien-5-yl)-1-ethenyl] aniline (**8a**). At r.t., a soln. of phenylacetylene (26 mg, 0.25 mmole) in THF (1 ml) was added to a stirred mixture of **7a** (120 mg, 0.23 mmole), tris(dibenzylideneacetone)dipalladium(0) (3.16 mg, 3.45  $\mu$ mole), and CuI (1.314 mg, 6.902  $\mu$ mole) in  $N_2$ , followed by addition of triethylamine (96  $\mu$ l, 0.69 mmole). The deep brown solution was stirred at r.t. for 48 h. THF was removed in vacuum, and the residue was dissolved in toluene, washed with  $H_2O$  (2x), and dried over  $Na_2SO_4$ . FC (toluene) gave **8a** as an orange/brown solid (112 mg, 98%). The mass spectrum showed it contaminated with a small amount of **7a**. The material was used for the next step without further purification.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 7.54–7.49 (m, 2 H); 7.36–7.29 (m, 5 H); 7.16 (d,  $J = 3.8$ , 1 H); 7.05 (d,  $J = 3.8$ , 1 H); 7.03 (d,  $J = 3.8$ , 1 H); 6.93 (d,  $J = 16.4$ , 1 H); 6.85 (d,  $J = 3.8$ , 1 H); 6.82 (d,  $J = 16.1$ , 1 H); 6.60 (d,  $J = 8.9$ , 2 H); 3.28 (t,  $J = 7.5$ , 4 H); 1.63–1.53 (m, 4 H); 1.42–1.30 (m, 4 H); 0.96 (t,  $J = 7.3$ , 6 H).  $^{13}C$ -NMR (75 Hz,  $CDCl_3$ , DEPT): 148.00 (s), 144.11 (s), 139.42 (s), 133.66 (s), 132.86 (d), 132.51 (d), 131.37 (2d), 129.45 (d), 128.44 (s), 128.38 (2d), 127.76 (2d), 125.30 (d), 124.66 (d), 123.81 (s), 122.96 (d), 121.40 (s), 116.48 (d), 111.66 (2d), 94.17 (s), 82.88 (s), 50.78 (2t), 29.50 (2t), 20.35 (2t), 14.00 (2q). EI-MS  $m/z$ : 495 (50,  $M^+$ ), 452 (20), 410 (13), 394 (20), 205 (13), 202 (14), 86 (70), 84 (100).



*N,N*-Diphenyl-4-[(*E*)-2-(5'-phenylethynyl-2,2'-bithien-5-yl)-1-ethenyl] aniline (**8b**). Similar to **8a**, from **7b** in 84% yield.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 7.54–7.49 (m, 3 H); 7.37–7.23 (m, 8 H); 7.17 (d,  $J = 3.8$ , 1 H); 7.14–7.01 (m, 11 H); 6.92 (d,  $J = 3.8$ , 1 H); 6.84 (d,  $J = 16.5$ , 1 H).  $^{13}C$ -NMR (75 Hz,  $CDCl_3$ , DEPT): 147.56 (s), 147.45 (2s), 143.04 (s), 139.06 (s), 134.83 (s), 132.86 (d), 132.51 (d), 131.39 (2d), 130.77 (s), 129.31 (4d), 128.44 (d), 128.40 (2d), 127.25 (2d), 126.60 (d), 124.67 (d), 124.63 (4d), 123.36 (2d), 123.33 (d), 123.18 (2d), 122.87 (s), 121.85 (s), 119.75 (d), 94.35 (s), 82.75 (s). EI-MS  $m/z$ : 561 (7, [**7b**] $^+$ ), 535 (100,  $M^+$ ), 435 (17).



2-{5'-{(E)-2-[4-(Dibutylamino)phenyl]-1-ethenyl}-2,2'-bithien-5-yl}-3-phenyl-1,3-butadiene-1,1,4,4-tetracarbonitrile (2e). A mixture of **8a** (99 mg, 0.20 mmol) and tetracyanoethylene (27.6 mg, 0.216 mmol) in  $\text{CHCl}_3$  (2 ml) was stirred in  $\text{N}_2$  for 48 h, and then concentrated. FC ( $\text{CHCl}_3$ ) gave **2e** (87 mg, 69%) as a dark green solid.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 7.78 (br. d,  $J = 7.2$ , 2 H); 7.70 (d,  $J = 4.5$ , 1 H); 7.66 (br. d,  $J = 7.3$ , 1 H); 7.57 (br. t,  $J = 7.1$ , 2 H); 7.37 (d,  $J = 4.0$ , 1 H); 7.33 (d,  $J = 8.9$ , 2 H); 7.26 (d,  $J = 4.5$ , 1 H); 6.97 (d,  $J = 16.4$ , 1 H); 6.96 (d,  $J = 4.0$ , 1 H); 6.92 (d,  $J = 16.4$ , 1 H); 6.62 (d,  $J = 8.9$ , 2 H); 3.30 (t,  $J = 7.6$ , 4 H); 1.64–1.53 (m, 4 H); 1.43–1.30 (m, 4 H); 0.97 (t,  $J = 7.3$ , 6 H).  $^{13}\text{C-NMR}$  (75 Hz,  $\text{CDCl}_3$ , DEPT): 166.87 (s), 155.44 (s), 152.27 (s), 150.02 (s), 148.66 (s), 139.24 (d), 134.73 (d), 132.63 (d), 131.21 (s), 131.17 (s), 131.03 (s), 129.98 (2d), 129.55 (d), 129.43 (2d), 128.42 (2d), 126.20 (d), 125.04 (d), 123.01 (s), 115.40 (d), 113.37 (s), 112.44 (s), 111.68 (s), 111.64 (2d), 111.08 (s), 87.71 (s), 75.44 (s), 50.79 (2t), 29.48 (2t), 20.33 (2t), 13.99 (2q). EI-MS  $m/z$ : 623 (100,  $\text{M}^+$ ), 580 (65), 538 (45), 312 (24), 269 (49). Anal. calc. for  $\text{C}_{38}\text{H}_{33}\text{N}_5\text{S}_2$ : C 73.16, H 5.33, N 11.23, S 10.21; found: C 72.84, H 5.74, N 10.94, S 10.02.



2-{5'-{(E)-2-[4-(Diphenylamino)phenyl]-1-ethenyl}-2,2'-bithien-5-yl}-3-phenyl-1,3-butadiene-1,1,4,4-tetracarbonitrile (2f). Similar to **2e**, from **8b** in 60% yield.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ): 7.77 (t,  $J = 7.5$ , 2 H); 7.72 (d,  $J = 4.4$ , 1 H); 7.67 (t,  $J = 7.5$ , 1 H); 7.58 (t,  $J = 8.0$ , 2 H); 7.38 (d,  $J = 4.0$ , 1 H); 7.33 (d,  $J = 8.7$ , 2 H); 7.30–7.26 (m, 5 H); 7.12 (d,  $J = 7.5$ , 4 H); 7.08–7.02 (m, 6 H); 6.97 (d,  $J = 16.0$ , 1 H).  $^{13}\text{C-NMR}$  (125 Hz,  $\text{CDCl}_3$ , DEPT): 166.70 (s), 155.73 (s), 151.73 (s), 148.52 (s), 148.41 (s), 147.20 (2s), 139.15 (d), 134.80 (d), 132.10 (s), 131.66 (s), 131.39 (d), 131.10 (s), 130.02 (2d), 129.64 (s), 129.42 (4d+2d), 129.28 (d), 127.72 (2d), 127.27 (d), 125.35 (d), 124.99 (4d), 123.61 (2d),



122.72 (2d), 118.62 (d), 113.17 (s), 112.23 (s), 111.62 (s), 111.05 (s), 87.76 (s), 76.35 (s). EI-MS *m/z*: 663 (15, M<sup>+</sup>), 84 (35), 44 (100). Anal. cacl. for C<sub>42</sub>H<sub>25</sub>N<sub>5</sub>S<sub>2</sub>: C 75.99, H 3.80, N 10.55, S 9.66; found: C 75.99, H 4.07, N 10.51, S 9.53.