

SUPPORTING INFORMATION

for

Electrofluorochromic Detection of Cyanide Anion with A Benzothiadiazole-Containing Conjugated Copolymer

Guoqiang Ding,^a Hui Zhou,^b Jianwei Xu,^{*b} and Xuehong Lu^{*a}

^a School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

^b Institute of Materials Research and Engineering, 3 Research Link, 117602, Singapore
Email: asxhlu@ntu.edu.sg; jw-xu@imre.a-star.edu.sg

S1. Materials

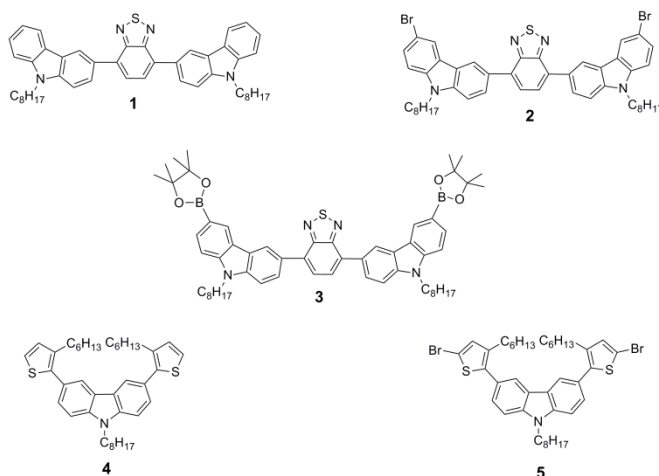
3,6-Dibromocarbazole and 3-bromocarbazole were purchased from TCI and used as received. 1-Bromooctane, 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester), 3-hexylthiophene-2-boronic acid pinacol ester, [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl₂), Aliquat[®] 336, N-bromosuccinimide (NBS), bis(pinacolato)diborane, *p*-xylene, acetonitrile (ACN, anhydrous), polypropylene carbonate (PC), poly(methyl methacrylate) (PMMA, M_w = 120,000 g/mol) and ferrocene were purchased from Aldrich and used as received. Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) was purchased from Strem Chemical Inc. and used as received. 3,6-Dibromo-9-octylcarbazole¹ and 3-bromo-9-octylcarbazole² were synthesized according to literatures.

S2. Chemical characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400-MHz NMR spectrometer in deuterated chloroform (CDCl₃) at room temperature using

tetramethylsilane (TMS) as an internal standard. Operating frequencies of the NMR spectrometer were 400.13 MHz (^1H) and 100.61 MHz (^{13}C). Size exclusion chromatography (SEC) analyses were carried out on a Waters 2690 system using THF as eluent and polystyrene standards. Mass spectroscopy of the compounds was measured by Finnigan LCQ Mass Spectrometer. Elemental analysis of the polymer was conducted on an Elementar Vario Micro Cube for C, H, N and S determination. Absorption (ABS) spectra of the polymer were measured using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectra of the polymer were recorded using a Perkin Elmer LS-55 fluorescence spectrometer.

S3. Synthesis



Compound 1. To a 50 mL Schlenk tube 3-bromo-9-octylcarbazole (716.6 mg, 2.00 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (388.1 mg, 1.00 mmol), Aliquat[®] 336 (0.15 g) and toluene (8 mL) were added. After all the monomers were dissolved, Na_2CO_3 aqueous solution (2 M, 6 mL) was added. Followed by degassing of the mixture, $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 0.01 mmol) was added and then the tube was sealed by a rubber stopper. The mixture was stirred and refluxed at 110 °C for 24 h. After reaction, the organic layer was separated and

then the solvent was removed under reduced pressure. The crude product was purified over silica gel column chromatography using hexane/dichloromethane (DCM) (3:2) as eluent. The final product was obtained as brightly orange solid (95%). ^1H NMR (ppm): δ = 8.72 (s, 2H), 8.21 (d, 2H), 8.15 (d, 2H), 7.93 (s, 2H), 7.58 (d, 2H), 7.51 (t, 2H), 7.46 (d, 2H), 7.28 (t, 2H), 4.37 (t, 4H), 1.94 (m, 4H), 1.27-1.46 (m, 20H), 0.88 (t, 6H). ^{13}C NMR (ppm): δ = 155.1, 141.4, 140.9, 133.8, 128.9, 128.3, 127.5, 126.2, 123.7, 123.6, 121.6, 121.0, 119.4, 109.3, 109.1, 43.7, 32.2, 30.1, 29.8, 29.6, 29.4, 27.7, 23.0, 14.4. MS (ESI) m/z for $\text{C}_{46}\text{H}_{50}\text{N}_4\text{S}$: calcd, 690.4; found, 690.4.

Compound **2**. NBS (373.8 mg, 2.1 mmol) was added into the solution of compound **1** (689.0 mg, 1.00 mmol) dissolved in DCM (20 mL), and the mixture was stirred overnight at room temperature. After reaction, the solvent was removed under reduced pressure and the crude product was purified over silica gel column chromatography using hexane/dichloromethane (DCM) (3:2) as eluent. The final product was obtained as brightly orange solid (85%). ^1H NMR (ppm): δ = 8.67 (s, 2H), 8.31 (s, 2H), 8.16 (d, 2H), 7.91 (s, 2H), 7.57 (d, 4H), 7.32 (d, 2H), 4.33 (t, 4H), 1.91 (m, 4H), 1.27-1.46 (m, 20H), 0.87 (t, 6H). ^{13}C NMR (ppm): δ = 155.0, 141.1, 140.0, 133.6, 129.3, 128.9, 128.3, 128.2, 125.3, 123.7, 122.7, 121.8, 112.3, 110.7, 109.4, 43.8, 32.2, 30.1, 29.7, 29.5, 29.4, 27.8, 23.0, 14.4. MS (ESI) m/z for $\text{C}_{46}\text{H}_{48}\text{N}_4\text{SBr}_2$: calcd, 848.2; found, 848.2.

Compound **3**. A mixture of compound **2** (848.8 mg, 1.00 mmol), bis(pinacolato)diborane (533.3 mg, 2.10 mmol), potassium acetate (KOAc) (588.8 mg, 6.00 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (73.2 mg, 0.10 mmol) in degassed DMF (20 mL) was stirred overnight at 80 °C under nitrogen atmosphere. After cooled to room temperature, water and chloroform (CHCl_3) were added to the mixture, and the separated organic layer was washed with brine and water and dried over anhydrous MgSO_4 . After the removal of the solvent under reduced pressure, the residue was

purified over silica gel column chromatography using hexane/dichloromethane (DCM) (3:2) as eluent to give compound **3** as a brightly orange solid (65%). ^1H NMR (ppm): δ = 8.82 (s, 2H), 8.73 (s, 2H), 8.18 (d, 2H), 7.97 (d, 2H), 7.92 (s, 2H), 7.57 (d, 2H), 7.44 (d, 2H), 4.36 (t, 4H), 1.93 (m, 4H), 1.27-1.47 (m, 44H), 0.88 (t, 6H). ^{13}C NMR (ppm): δ = 155.0, 143.5, 140.9, 133.7, 132.8, 129.4, 128.4, 128.3, 127.6, 125.9, 124.0, 123.3, 121.9, 109.2, 108.7, 43.7, 32.2, 30.1, 29.8, 29.6, 29.4, 27.7, 25.3, 23.0, 14.4. MS (ESI) m/z for $\text{C}_{58}\text{H}_{72}\text{N}_4\text{SO}_4\text{B}_2$: calcd, 942.5; found, 942.5.

Compound **4**. To a 50 mL Schlenk tube 3,6-dibromo-9-octylcarbazole (437.2 mg, 1.00 mmol), 3-hexylthiophene-2-boronic acid pinacol ester (588.5 mg, 2.00 mmol), Aliquat[®] 336 (0.15 g) and toluene (8 mL) were added. After all the monomers were dissolved, Na_2CO_3 aqueous solution (2 M, 6 mL) was added. Followed by degassing of the mixture, $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 0.01 mmol) was added and then the tube was sealed by a rubber stopper. The mixture was stirred and refluxed at 110 °C for 24 h. After reaction, the organic layer was separated and then the solvent was removed under reduced pressure. The crude product was purified over silica gel column chromatography using hexane as eluent. The final product was obtained as colorless oil (92%). ^1H NMR (ppm): δ = 8.10 (d, 2H), 7.45 (s, 2H), 7.32 (d, 2H), 7.27 (d, 2H), 7.03 (d, 2H), 4.31 (t, 2H), 2.75 (t, 4H), 1.90 (m, 2H), 1.68 (m, 4H), 1.26-1.43 (m, 22H), 0.85 (t, 9H). ^{13}C NMR (ppm): δ = 141.4, 139.4, 139.0, 132.8, 130.0, 123.9, 122.3, 121.3, 120.6, 110.0, 43.7, 32.2, 32.1, 31.5, 30.1, 29.8, 29.7, 29.6, 29.4, 29.3, 27.8, 27.3, 23.0, 14.4. MS (ESI) m/z for $\text{C}_{40}\text{H}_{53}\text{NS}_2$: calcd, 611.4; found, 611.3.

Compound **5**. NBS (373.8 mg, 2.1 mmol) was added in portions to the solution of compound **4** (612.0 mg, 1.00 mmol) in CHCl_3 /acetic acid (5 mL / 5 mL) at 0 °C in 1 h. The mixture was then stirred at 0 °C for 1 more hour and then at room temperature overnight. Then water and CHCl_3 was added into the mixture. The organic layer were separated and washed with NaOH

aqueous solution, and then dried over magnesium sulfate. After the solvent was removed under reduced pressure, the crude product was purified over silica gel column chromatography using hexane as eluent. The final product was obtained as colorless oil (72%). ^1H NMR (ppm): δ = 8.06 (s, 2H), 7.48 (d, 2H), 7.42 (d, 2H), 6.97 (s, 2H), 7.32 (t, 2H), 2.63 (t, 4H), 1.91 (m, 2H), 1.62 (m, 4H), 1.25-1.44 (m, 22H), 0.86 (t, 9H). ^{13}C NMR (ppm): δ = 140.8, 140.7, 139.3, 132.4, 128.0, 125.0, 123.2, 121.8, 109.9, 109.3, 43.8, 32.2, 32.0, 31.3, 30.1, 29.7, 29.6, 29.5, 29.4, 29.0, 27.7, 27.3, 23.0, 14.4. MS (ESI) m/z for $\text{C}_{40}\text{H}_{51}\text{NS}_2\text{Br}_2$: calcd, 769.2; found, 769.2.

Polymer **P**. To a 25 mL Schlenk tube compound **3** (471.5 mg, 0.50 mmol), compound **5** (384.9 mg, 0.50 mmol), Aliquat[®] 336 (0.10 g) and toluene (4 mL) were added. After all the monomers were dissolved, Na_2CO_3 aqueous solution (2 M, 3 mL) was added. Followed by degassing of the mixture, $\text{Pd}(\text{PPh}_3)_4$ (5.8 mg, 0.005 mmol) was added and then the tube was sealed by a rubber stopper. The mixture was stirred and refluxed at 110 °C for 72 h. After reaction, the organic layer was separated and then the solvent was removed under reduced pressure. The crude product was dissolved in a very small amount of chloroform and then dropped into excess methanol (100 mL) for precipitation. The obtained precipitate was filtered and dried under vacuum. The precipitate was finally washed with acetone using a Soxhlet extractor for 2 days and dried in a vacuum oven at 40 °C for 2 days. Then the final product (**P**) was obtained as orange solid (87%). ^1H NMR (ppm): δ = 8.77 (m, 2H), 8.45 (m, 2H), 8.26 (m, 2H), 8.17 (m, 2H), 7.91 (m, 2H), 7.81 (m, 2H), 7.33-7.64 (m, 10H), 4.32 (m, 6H), 2.79 (m, 4H), 1.92 (m, 6H), 1.61 (m, 4H), 1.29 (m, 42H), 0.89 (m, 15H). ^{13}C NMR (ppm): δ = 143.2, 141.3, 140.8, 140.5, 139.5, 133.7, 129.7, 129.2, 128.4, 127.9, 126.7, 126.3, 125.9, 125.0, 124.6, 124.0, 123.7, 123.4, 121.8, 121.6, 118.0, 109.5, 109.3, 109.1, 43.8, 32.2, 32.1, 31.5, 29.8, 29.7, 29.6,

29.5, 29.1, 27.7, 23.0, 14.4. Anal Calcd for C₈₆H₉₉N₅S₃: C, 79.5; H, 7.7; N, 5.4; S, 7.4. Found: C, 78.8; H, 7.4; N, 5.3; S, 7.4.

S4. Cyclic voltammetry and spectroelectrochemical characterization

Polymer **P** was dissolved in *p*-xylene (20 mg/mL) and then spin-coated (1000 rpm) onto indium tin oxide (ITO) electrodes laminated on poly(ethylene terephthalate) (PET) substrates (ITO/PET, 100 Ω/sq) to form **P**/ITO/PET. The thickness of the spin-coated film was controlled at around 100 nm, which was measured using an Alpha-Step IQ surface profiler. The cyclic voltammetry (CV) of **P**/ITO/PET was carried out in a three-electrode cell, with platinum (Pt) wire as counter electrode, silver (Ag) wire as reference electrode, and 0.1 M LiClO₄/ACN as electrolyte, respectively, using an Autolab PGSTAT302 electrochemical workstation. In spectroelectrochemical characterization, **P**/ITO/PET was placed in a three-electrode cell with Pt wire as counter and Ag wire as reference electrode, respectively, and with 0.1 M LiClO₄/ACN as electrolyte in a quartz cuvette, and tested using the same Autolab electrochemical workstation with the Shimadzu UV-3600 UV-vis-NIR spectrophotometer for absorption spectra, and with the Perkin Elmer LS-55 fluorescence spectrometer for PL spectra. For both electrochemical and spectroelectrochemical characterization, the pseudo-reference silver wire was calibrated vs. Fc/Fc⁺ by dissolving ferrocene in the electrolyte solution.

S5. Figures

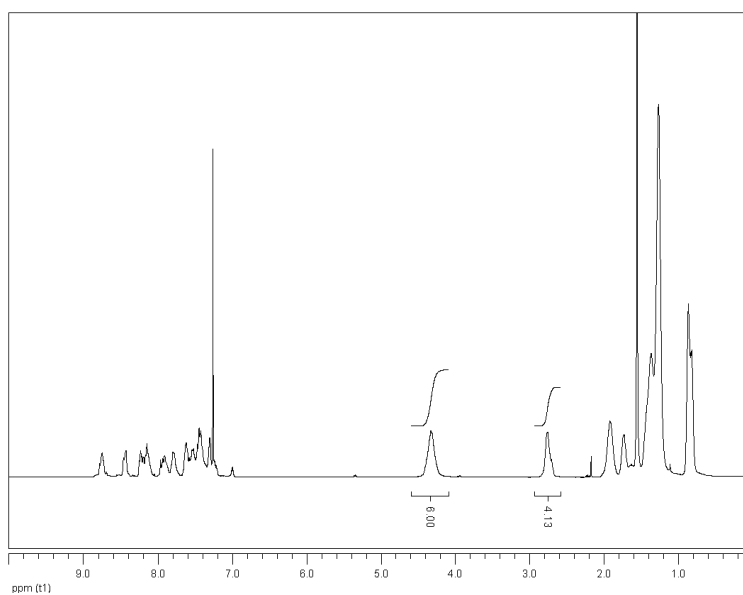


Fig. S1 ^1H NMR spectra of copolymer **P** in CDCl_3 .

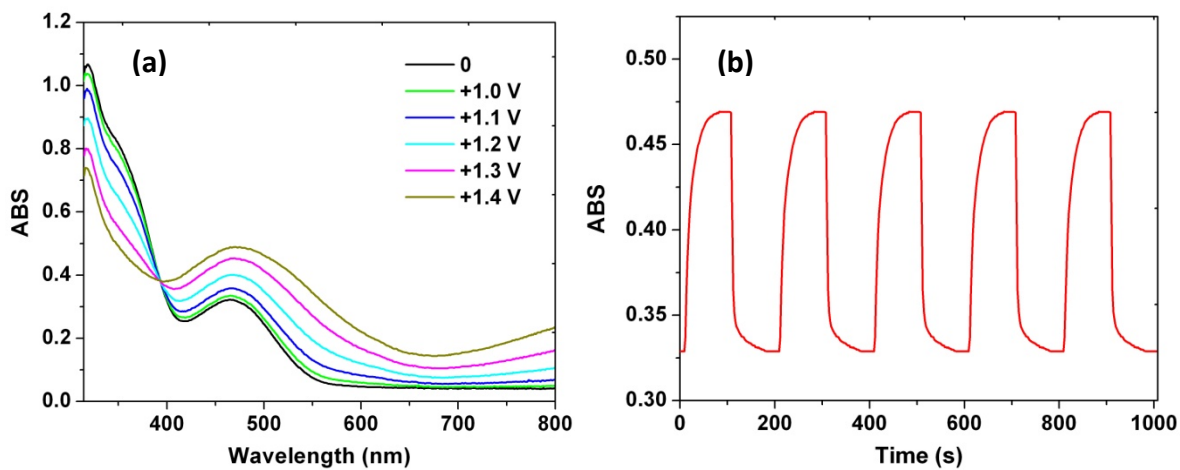


Fig. S2 (a) Absorption spectra under different potentials, and (b) absorption–time profiles ($\lambda_{\text{monitor}} = 465$ nm, switching between 1.4 V and -1.0 V with 200 s per cycle) of **P**/ITO/PET in 0.1 M $\text{LiClO}_4/\text{ACN}$.

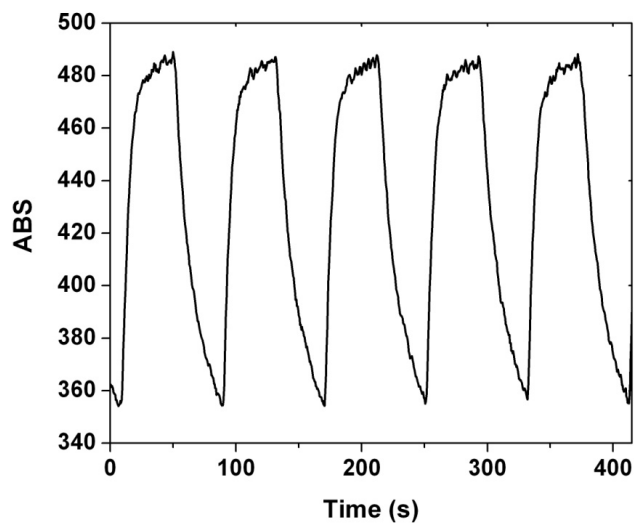


Fig. S3 PL intensity–time profiles ($\lambda_{\text{exc}} = 465 \text{ nm}$, $\lambda_{\text{monitor}} = 580 \text{ nm}$; switching between 1.0 V and -1.0 V with 80 s per cycle) of **P**/ITO/PET in 0.1 M $\text{LiClO}_4/\text{ACN}$ (**R**) with 10^{-4} M TBACN.

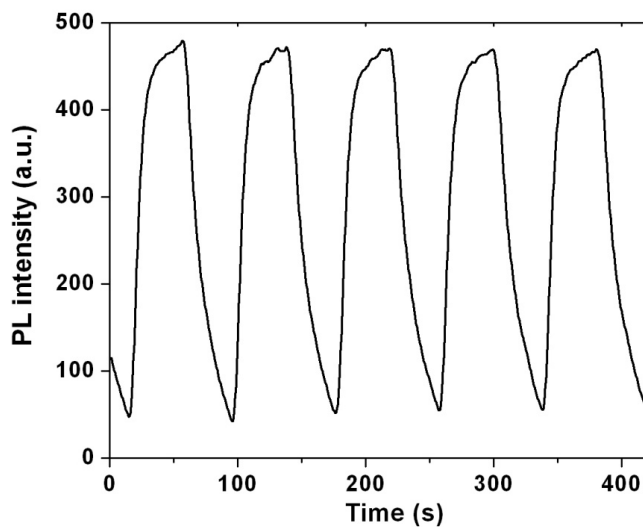


Fig. S4 PL intensity–time profiles ($\lambda_{\text{exc}} = 465 \text{ nm}$, $\lambda_{\text{monitor}} = 580 \text{ nm}$; switching between 1.2 V and -1.0 V with 80 s per cycle in 0.1 M $\text{LiClO}_4/\text{ACN}$, **R**) of **P**/ITO/PET that was taken out from **R** + TBACN (10^{-4} M) and washed with ACN before this switching test.

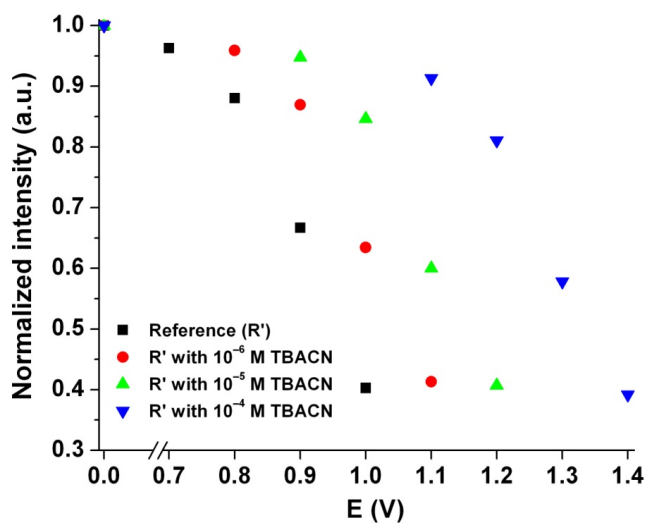


Fig. S5 Normalized PL intensities ($\lambda_{\text{exc}} = 465 \text{ nm}$ and $\lambda_{\text{monitor}} = 580 \text{ nm}$) of P/ITO/PET under different potentials in ACN/H₂O (1:1, volume/volume) with 0.1 M LiClO₄ and different concentrations (0, 10⁻⁶, 10⁻⁵ and 10⁻⁴ M) of TBACN. Reference (R') refers to ACN/H₂O (1:1, volume/volume) with 0.1 M LiClO₄ without TBACN.

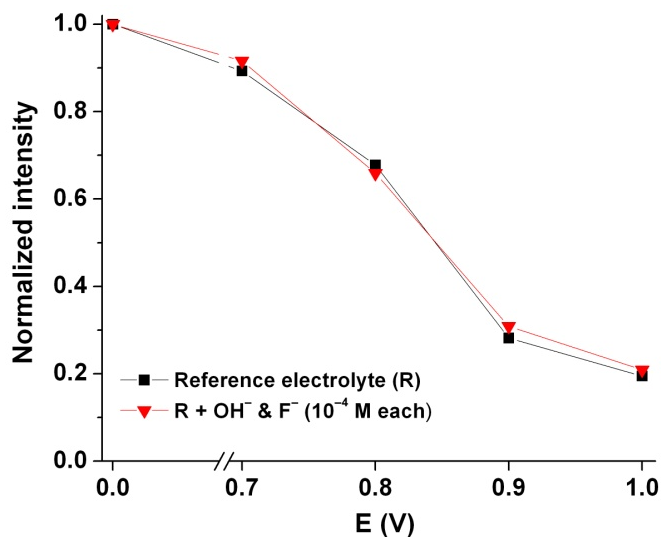


Fig. S6 Normalized PL intensities ($\lambda_{\text{exc}} = 465 \text{ nm}$ and $\lambda_{\text{monitor}} = 580 \text{ nm}$) of **P**/ITO/PET as a function of potential, E. The two curves were obtained using the reference electrolyte (**R**) as well as **R** + TBA-based anions (OH^- and F^- , 10^{-4} M each).

References

1. Y. Li, J. Ding, M. Day, Y. Tao, J. Lu and M. D'iorio, *Chem. Mater.*, 2004, **16**, 2165.
2. R. Grisorio, A. Dell'Aquila, G. Romanazzi, G. P. Suranna, P. Mastrorilli, P. Cosma, D. Acierno, E. Amendola, G. Ciccarella and C. F. Nobile, *Tetrahedron*, 2006, **62**, 627.