Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Electrochromic Devices and Thin Film Transistor from a New Family of Ethylenedioxythiophene Based Conjugated Polymers

Zhongtao Li,[†] Yuan Zhang,[§] Amanda L. Holt,[†] Borys P Kolasa,[‡] Justin G. Wehner,[‡] Andreas Hampp,[‡] Guillermo C. Bazan,[§] Thuc-Quyen Nguyen[§] and Daniel E. Morse[*,†]

[†]*Institute for Collaborative Biotechnologies, University of California, Santa Barbara, Ca 93106, US;* [‡] *Raytheon Vision Systems, 75 Coromar Dr., Goleta, Ca 93117, USA;* [§]*Department of Chemistry and Biochemistry, Institute for Polymers and Organic Solids, University of California, Santa Barbara, Ca 93106, USA.*

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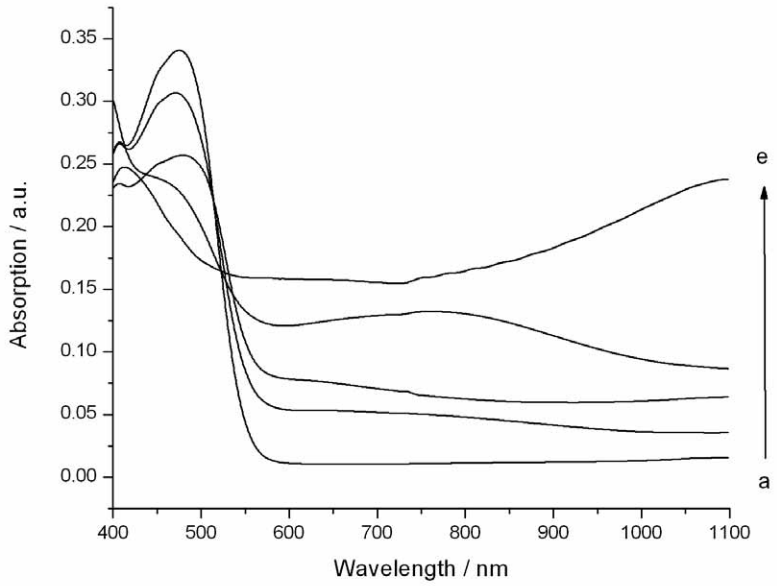
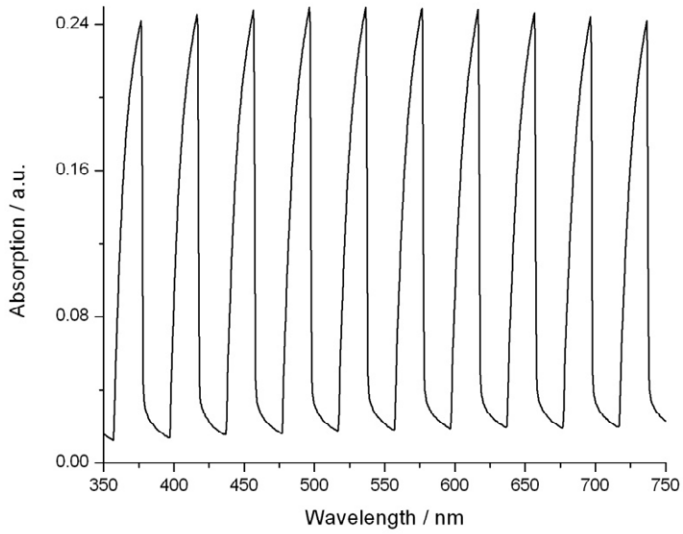
1. Electrochromic spectra and switching behavior of polymer 7c



Spectroelectrochemistry of polymer **7c** films on ITO-coated glass substrate; UV-vis-NIR absorption spectra were monitored while different potentials were applied to the films: a 0V, b 1.5V, c 2.0V, d 2.2V, e 2.5V.



Switching properties of EC devices based on polymer **6b** at 1100nm through the applied voltage switching between -2.5V and 2.5V.

2. Synthesis of compound 5a-c and 6a-c

4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole **5a**:

The 2,3-dibromobenzo[c][1,2,5]thiadiazole (500mg, 1.7mmol), tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) stannane (1.84g, 4.25mmol), $Pd(PPh_3)_4$ (63mg, 0.05 mmol), and 20ml toluene were placed in a two neck-bottle under argon. The reaction was refluxed under stirring overnight and poured into methanol and the precipitate

collected by filtration. The solid was recrystallized from dichloromethane and deep red needles of **5a** (380mg, 0.90mmol) were obtained (yield 53%). Ms molecular ion peak: 416 awu; ^{1}H NMR (500MHz $CDCl_3$), δ=8.41 (s, 2H), 6.59 (s, 2H), 4.43 (m, 4H, *J*=1.2Hz), 4.38 (m, 4H, *J*=1.35Hz); ^{13}C NMR (500MHz $CDCl_3$), δ=152.37, 141.68, 140.27, 126.65, 123.71, 113.75, 101.98, 65.01, 64.37; Anal. Calcd for $C_{18}H_{12}N_2O_4S_3$: C, 51.91; H, 2.90. Found: C, 52.11, H, 2.83.

4,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole **6a**:
5a (300mg, 0.73mmol) was dissolved in 300ml DMF and then N-bromosuccinimide (324mg, 1.82mmol) was slowly added. The mixture was stirred 3 h at room temperature. The precipitate was collected by filtration and washed three times with 50ml hot chloroform to give **6a** (220mg, 0.38mmol) as brown needles (yield 52%). Ms molecular ion peak: 574 awu; ^{1}H NMR (500MHz Dichlorobenzene-D4), δ=8.41 (s, 2H), 6.59 (s, 2H), 4.14 (m, 4H, *J*=3.3Hz), 4.03 (m, 4H, *J*=7.8Hz); Anal. Calcd for $C_{18}H_{10}Br_2N_2O_4S_3$: C, 37.65; H, 1.76. Found: C, 37.22, H, 2.23.

4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole **5b**:
The 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (600 mg, 1.09mmol), tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1.09 mg, 2.40mmol), $Pd(PPh_3)_4$ (63mg, 0.05 mmol), and 20ml toluene were placed in a two neck-bottle under argon. The mixture was refluxed under stirring overnight, and then poured into 100 ml ethyl ether. The separated organic phase was washed five times with brine, dried over magnesium sulfate and clarified by filtration, after which the solvent was removed in vacuo. The residue was purified by column chromatography on silica (50% hexane-dichloromethane) to give **5b** (580 mg, 0.86 mmol, 79%) as a yellow oil. Ms molecular ion peak: 672.2 awu; ^{1}H NMR (500MHz $CDCl_3$), δ=6.59 (s, 2H), 4.29 (t, 4H, *J*=1.6Hz), 4.26 (t, 4H, *J*=1.65Hz), 4.04 (t, 4H, *J*=6.5Hz), 1.69 (t, 4H *J*=7.8Hz), 1.34-1.28(m, 20H), 0.91 (t, 6H); ^{13}C NMR (500MHz $CDCl_3$), δ=154.8, 151.9, 141.2, 139.9, 115.9, 108.2, 100.7, 74.6, 64.7, 64.5, 31.8, 30.3, 29.4, 29.3, 25.9, 22.7, 14.1; Anal. Calcd for $C_{34}H_{44}N_2O_6S_3$: C, 60.69; H, 6.59. Found: C, 60.87, H, 6.73.

4,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole **6b**:
6a (300mg, 0.44mmol) was dissolved in 30ml THF, after which N-bromosuccinimide (168mg, 1.82mmol) was added slowly with the mixture cooled in an ice-water bath at 0℃. After allowing the mixture to warm to room temperature, it was stirred 3 h. 50ml dichloromethane was added and the solution then washed three times with water. After drying over magnesium sulfate and filtering, the solvent was removed in vacuo. The residue was purified by column chromatography on silica (50% hexane-dichloromethane) to give **6b** (320 mg, 0.38 mmol, 86%) as a highly viscous yellow oil. Ms molecular ion peak: 830.0 awu; ^{1}H NMR (500MHz CDCl3), δ=4.35 (s, 4H), 4.24 (s, 4H), 4.04 (s, 4H), 1.70 (s, 4H), 1.29-1.37 (m, 20H), 0.91 (s, 9H); ^{13}C NMR (500MHz $CDCl_3$), δ=154.7, 151.5, 139.7, 139.3, 115.3, 108.2, 88.8, 76.7, 64.7, 64.9, 64.6, 31.8, 30.2, 29.4, 29.3, 26.0, 22.7, 14.1; Anal. Calcd for $C_{34}H_{42}Br_2N_2O_6S_3$: C, 49.16; H, 5.10. Found: C, 49.38, H, 4.88.

4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole **5c**:
The 4,7-dibromo-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole (600mg, 0.90mmol), tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (900mg, 1.98mmol), $Pd(PPh_3)_4$ (63mg, 0.05 mmol), and 20ml toluene were placed in a two neck-bottle under argon. The mixture was refluxed under stirring overnight, and then poured into 100 ml ethyl ether. The organic phase separated and was washed five times with brine. After drying over magnesium sulfate and filtering, the solvent was removed in vacuo. The residue was purified by column chromatography on silica (50% hexane-dichloromethane) to give **5c** (570 mg, 0.73 mmol, 81%) as a yellow oil.

Ms molecular ion peak: 784.3 awu; ^{1}H NMR (500MHz $CDCl_3$), δ=6.42(s, 2H), 4.30 (t, 4H, *J*=3.8Hz), 4.25 (t, 4H, *J*=1.55Hz), 4.04 (t, 4H *J*=7.8Hz), 1.70 (m, 4H, *J*=6.5Hz), 1.34-1.28(m, 36H), 0.91 (t, 6H, *J*=7.5Hz). ^{13}C NMR (500MHz $CDCl_3$), δ=154.8, 151.9, 141.2, 139.9, 115.9, 108.2, 100.7, 74.6, 64.7, 64.5, 31.9, 30.3, 29.7, 29.6, 29.5, 29.4, 25.9, 22.7, 14.1, Anal. Calcd for $C_{42}H_{60}N_2O_6S_3$: C, 64.25; H, 7.70. Found: C, 64.50, H, 7.98.

4,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole **6c**:

5c (300mg, 0.38mmol) was dissolved in 30ml THF while being cooled with an ice-water bath. N-bromosuccinimide (146mg, 0.84mmol) was then added slowly. The mixture was allowed to warm to room temperature and stirred 3 h. 50ml dichloromethane was added and the organic phase then washed three times with water. After drying over magnesium sulfate and filtering, the solvent was removed in vacuo. The residue was purified by column chromatography on silica (50% hexane-dichloromethane) to give **6c** (292 mg, 0.31 mmol, 82%) as a highly viscous yellow oil. Ms molecular ion peak: 942.2 awu; ^{1}H NMR (500MHz CDCl3), δ=4.35 (s, 3H), 4.24 (s, 5H), 4.05 (s, 4H), 1.70 (m, 4H), 1.29-1.37 (m, 36H), 0.91 (s, 9H); ^{13}C NMR (500MHz $CDCl_3$), δ=154.8, 151.5, 139.7, 139.4, 115.3, 108.2, 88.8, 74.6, 65.0, 64.9, 64.5, 31.9, 30.3, 29.7, 29.7, 29.5, 29.4, 29.3, 26.0, 22.7, 14.2; Anal. Calcd for $C_{42}H_{58}Br_2N_2O_6S_3$: C, 53.50; H, 6.20. Found: C, 53.21, H, 6.67.

3. ^{1}H and ^{13}C NMR spectra

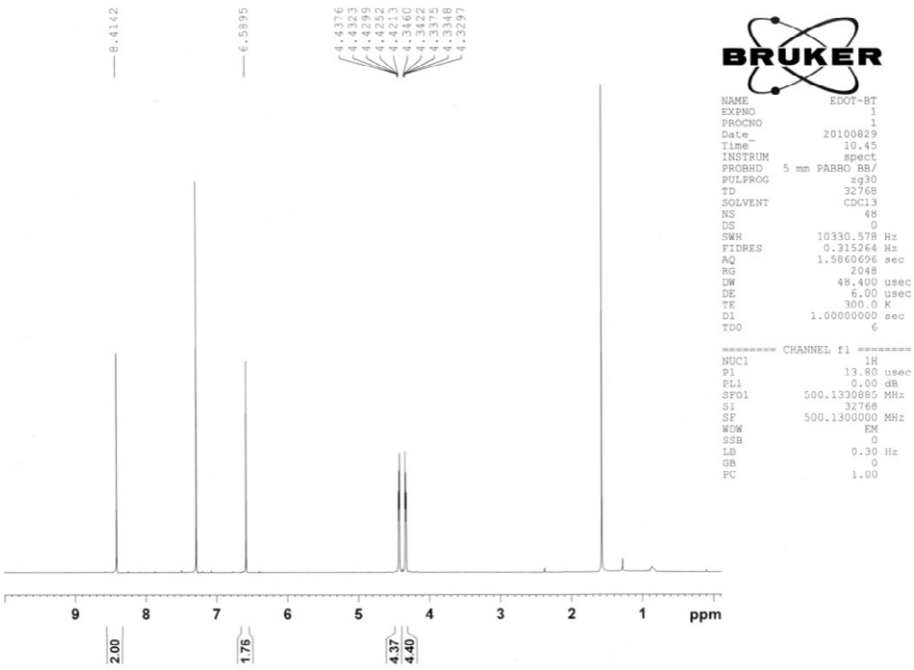


Figure S1. ^{1}H NMR of **5a** in $CDCl_3$

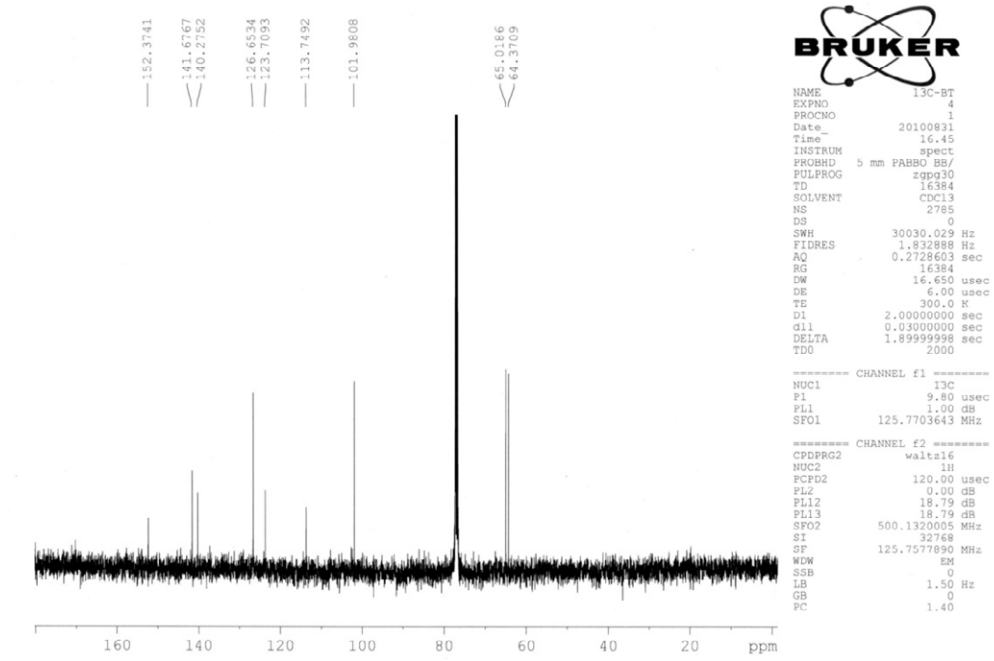


Figure S2. ^{13}C NMR of **5a** in $CDCl_3$

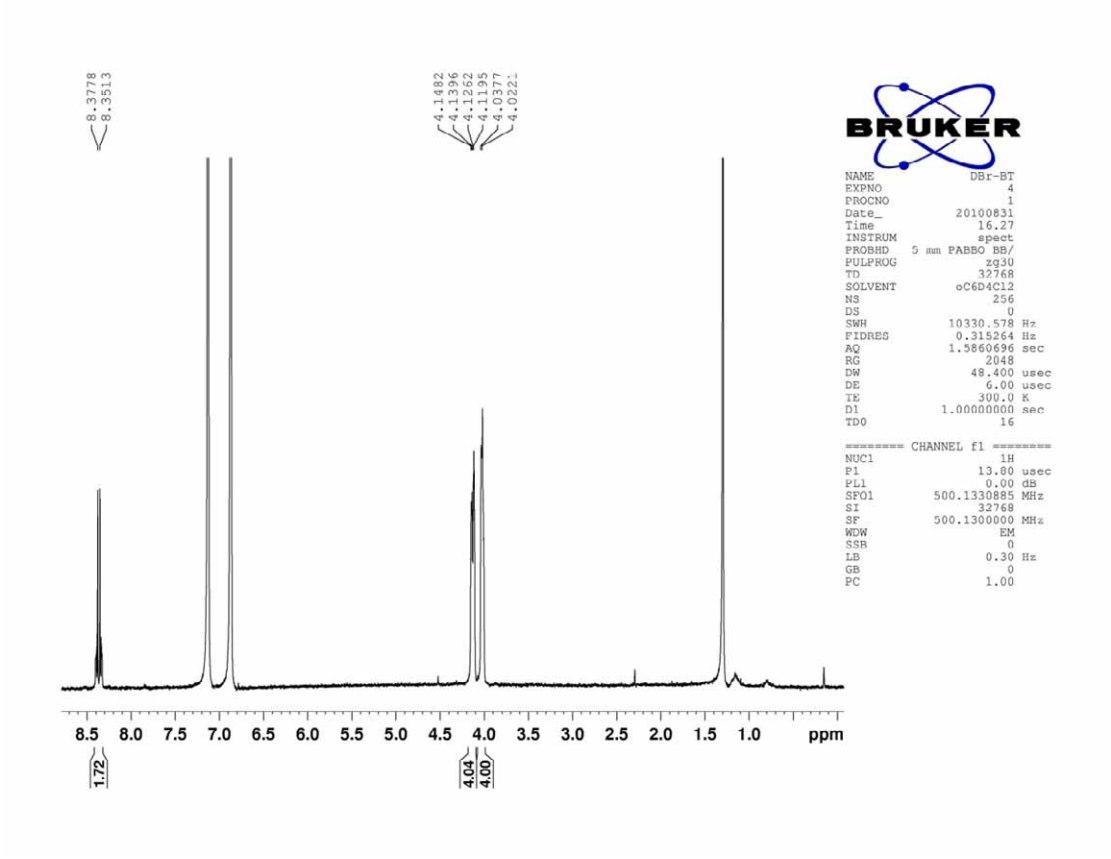


Figure S3. ^{1}H NMR of **6a** in dichlorobenzene-D4

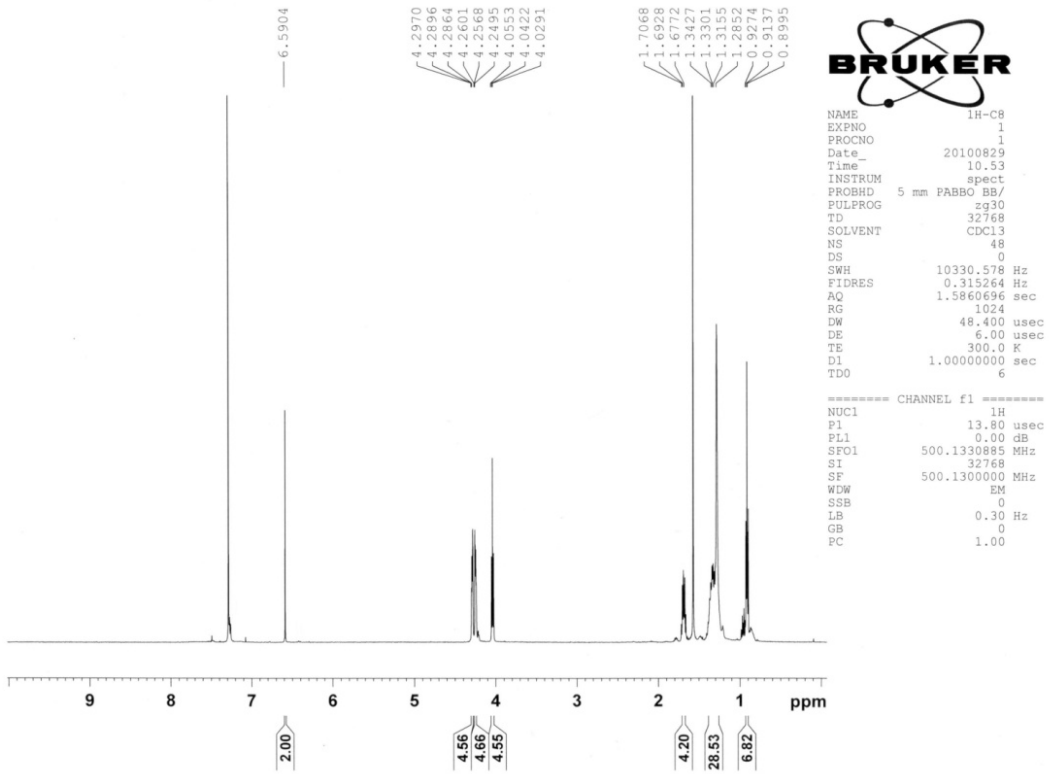


Figure S4. ^{1}H NMR of **5b** in $CDCl_3$

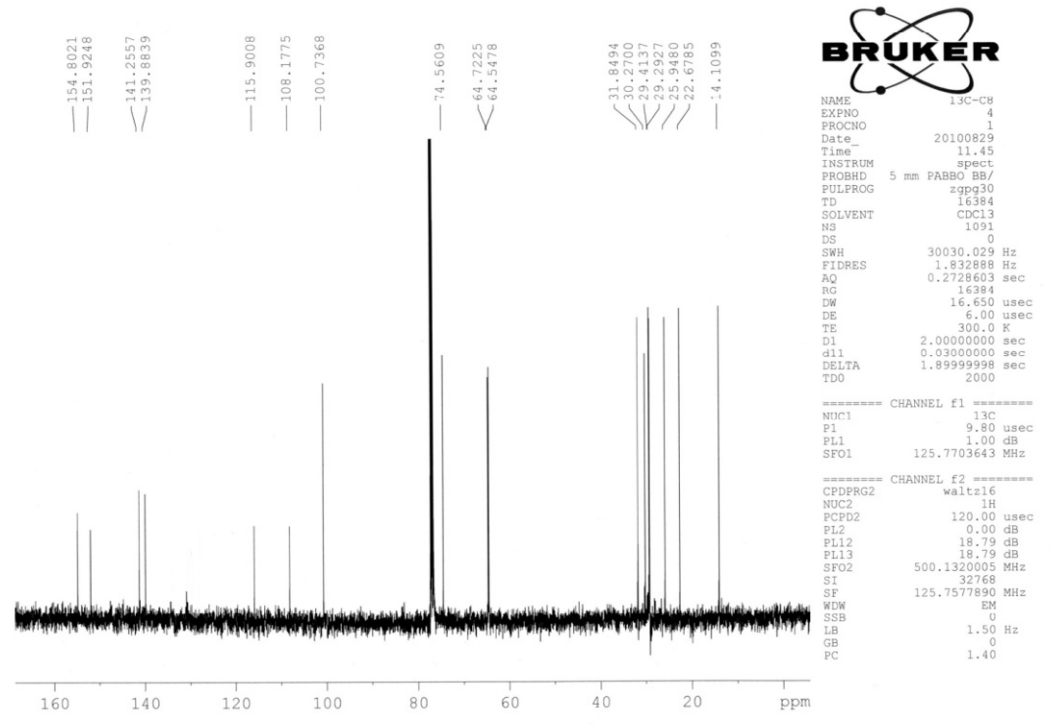


Figure S5. ^{13}C NMR of **5b** in $CDCl_3$

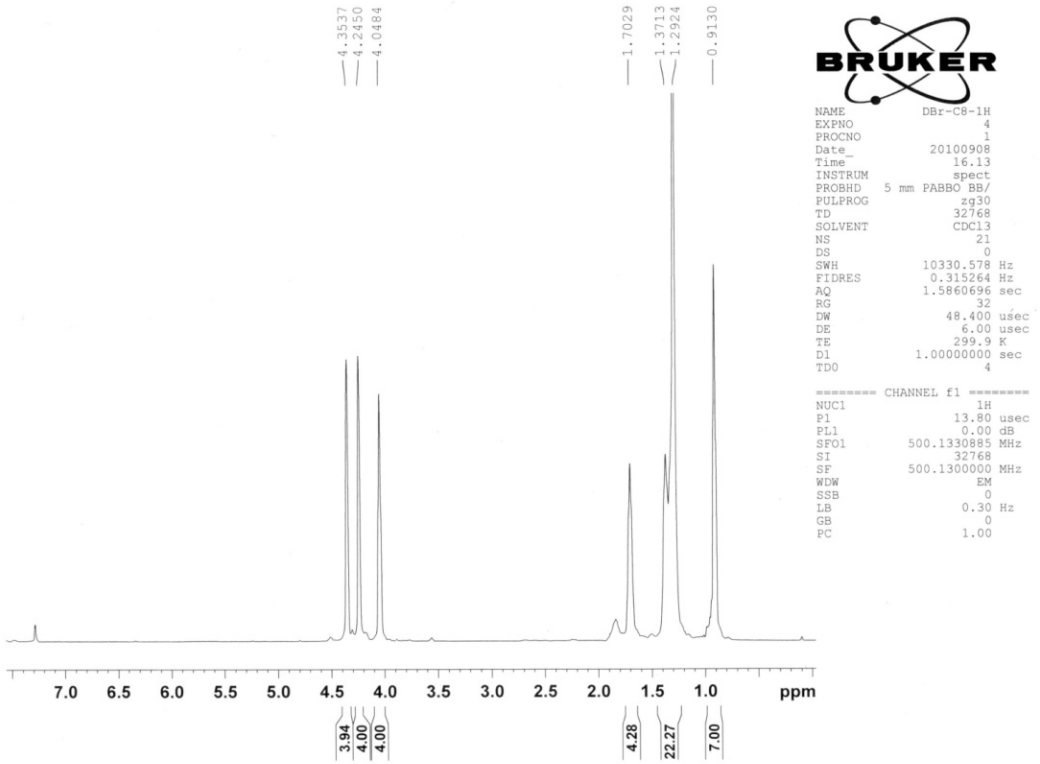


Figure S6. ^{1}H NMR of **6b** in $CDCl_3$

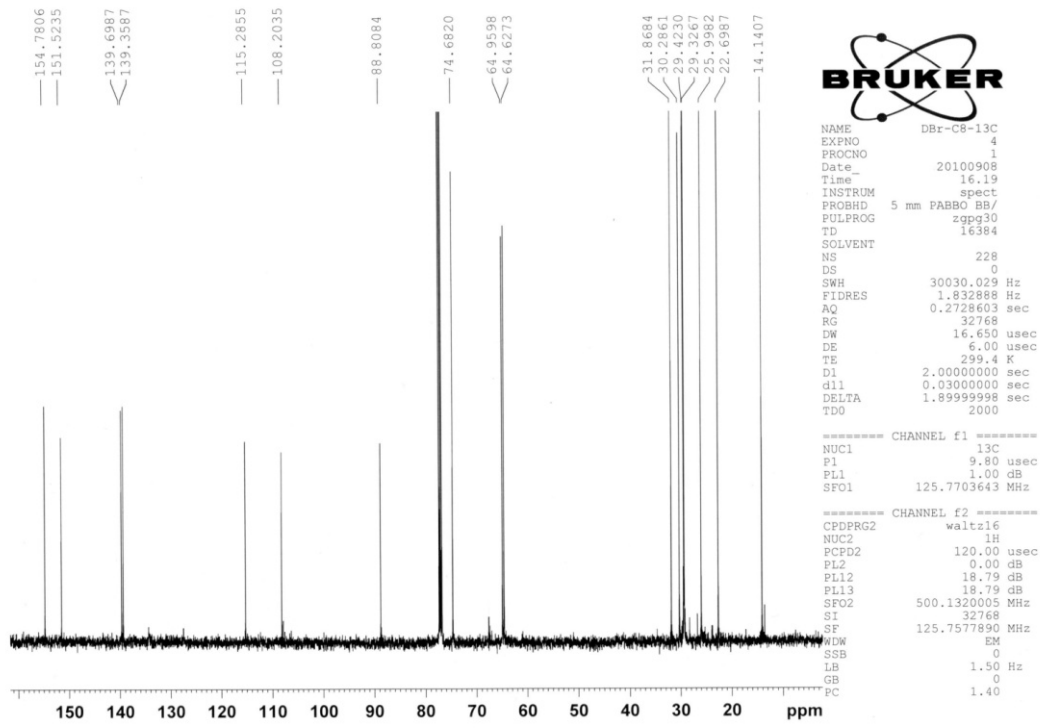


Figure S7. ^{13}C NMR of **6b** in $CDCl_3$

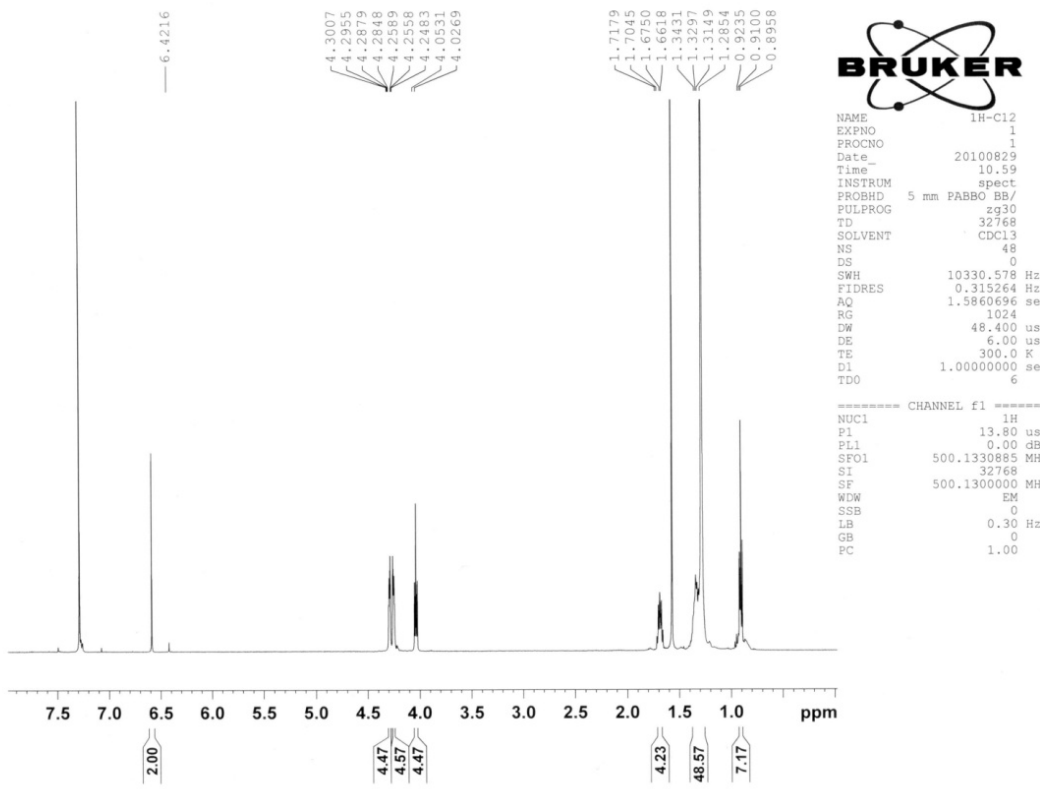


Figure S8. ^{1}H NMR of **5c** in $CDCl_3$

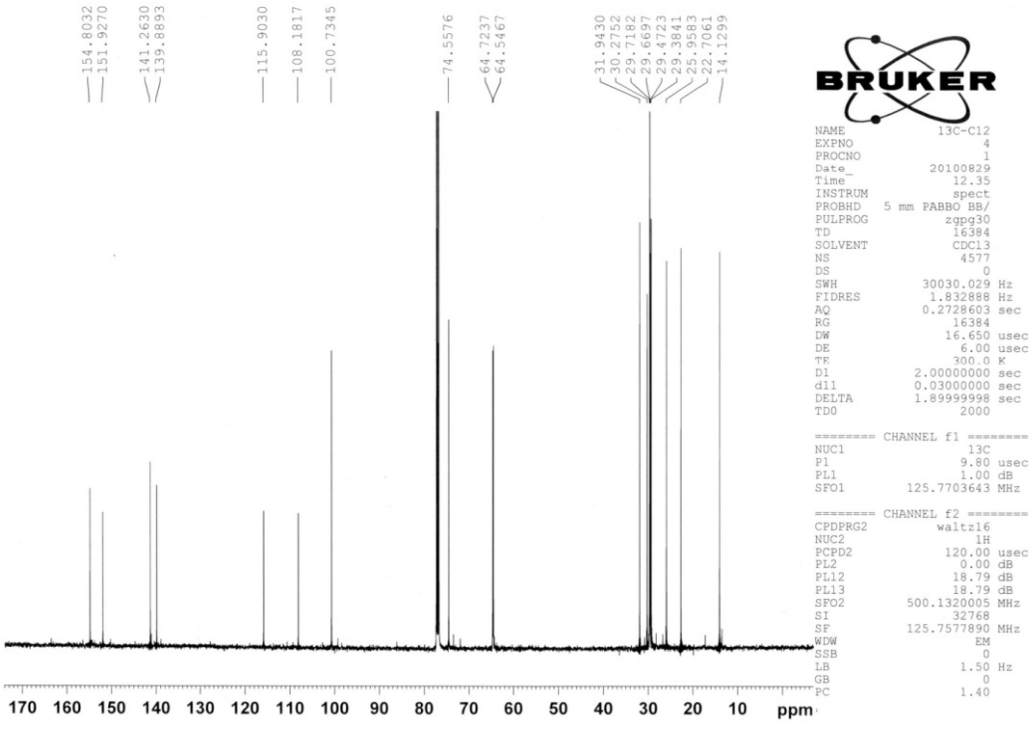


Figure S9. ^{13}C NMR of **5c** in $CDCl_3$

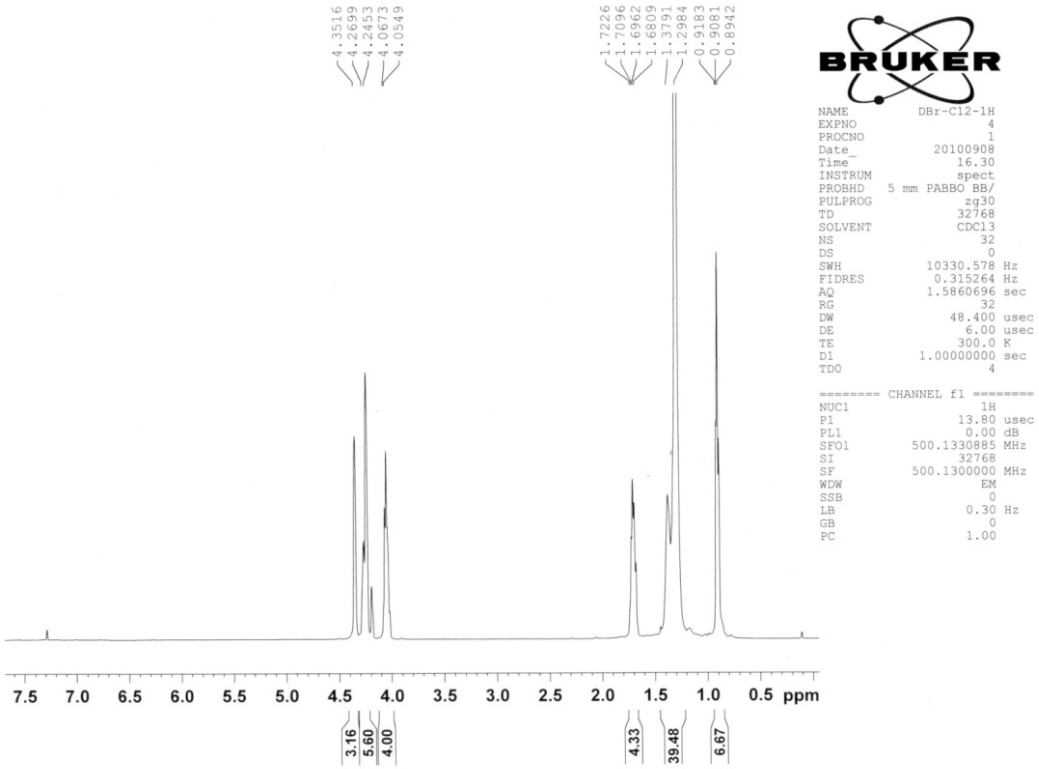


Figure S10. ^{1}H NMR of **6c** in $CDCl_3$

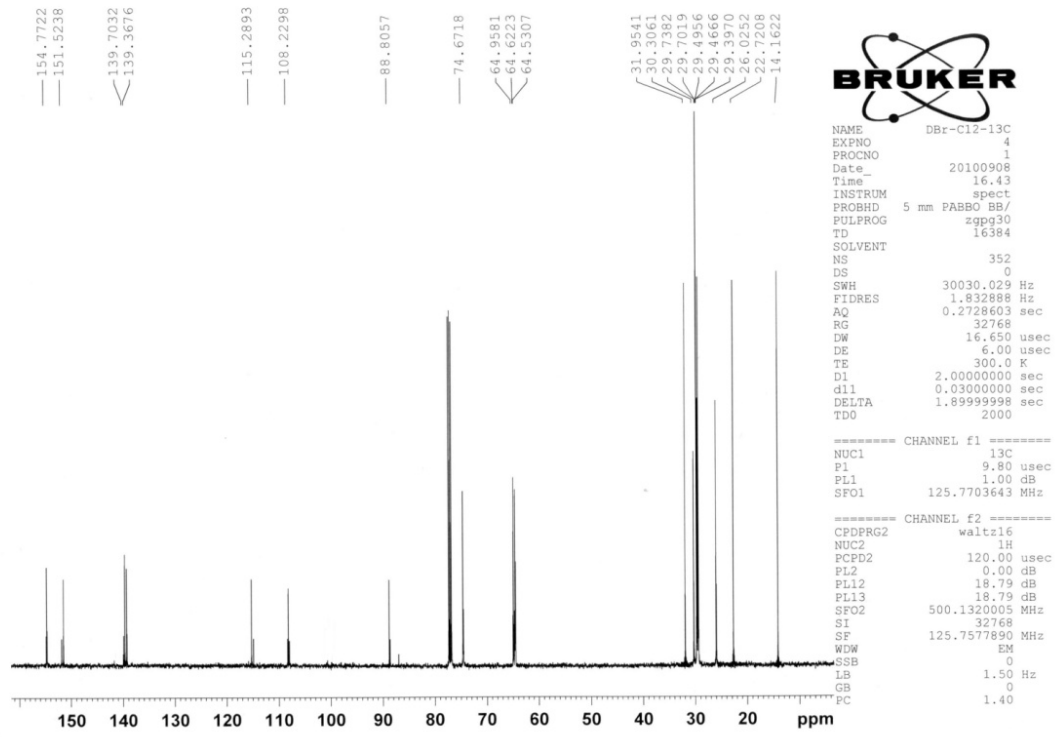


Figure S11. ^{13}C NMR of **6c** in $CDCl_3$

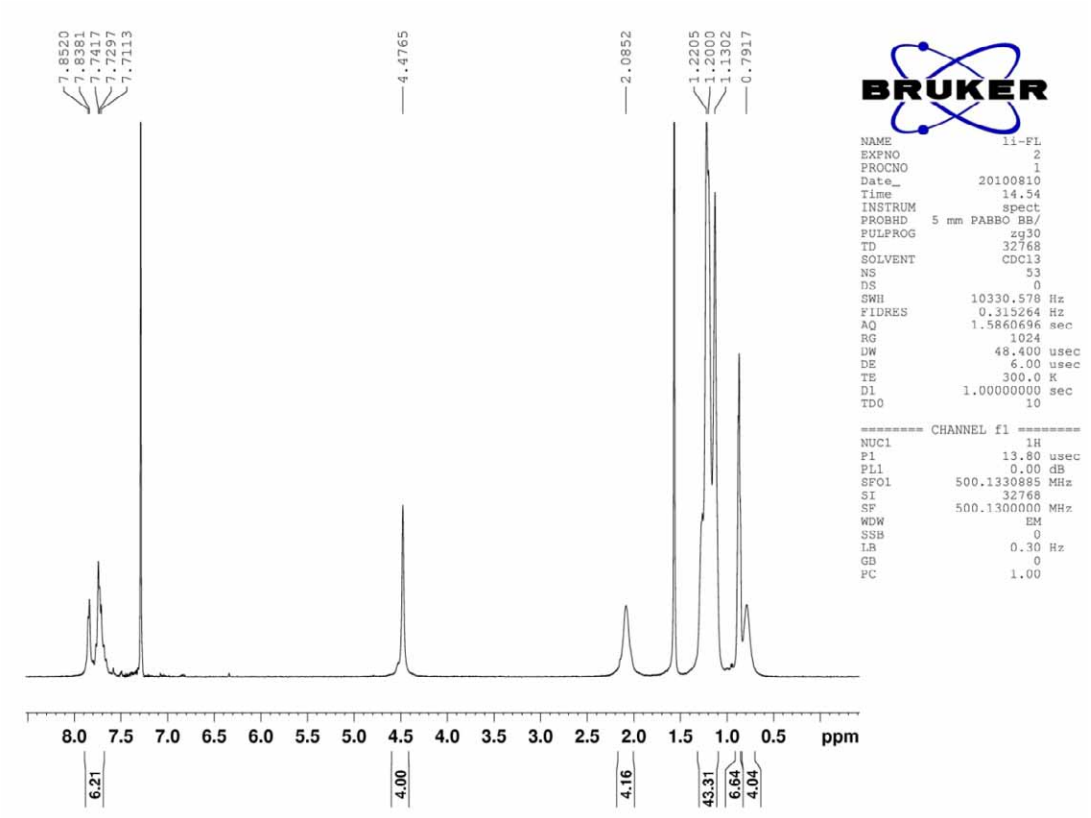


Figure S12. ^{1}H NMR of **2** in $CDCl_3$

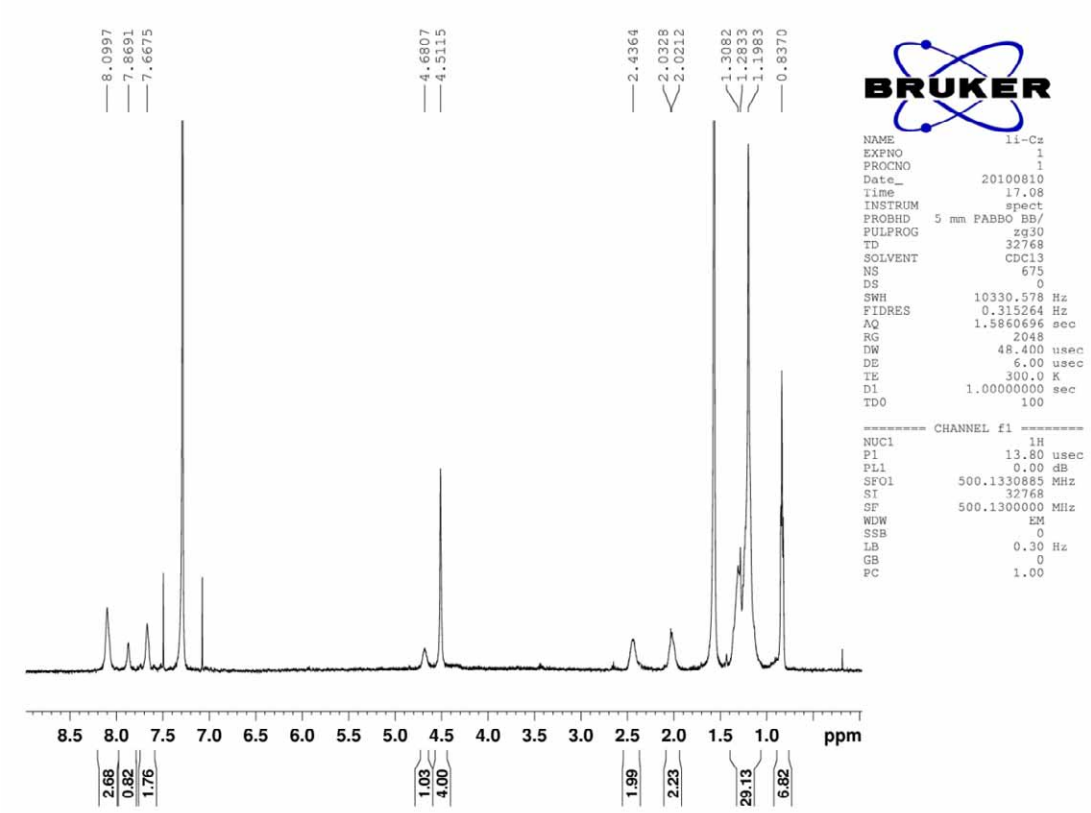


Figure S13. ^{1}H NMR of **4** in $CDCl_3$

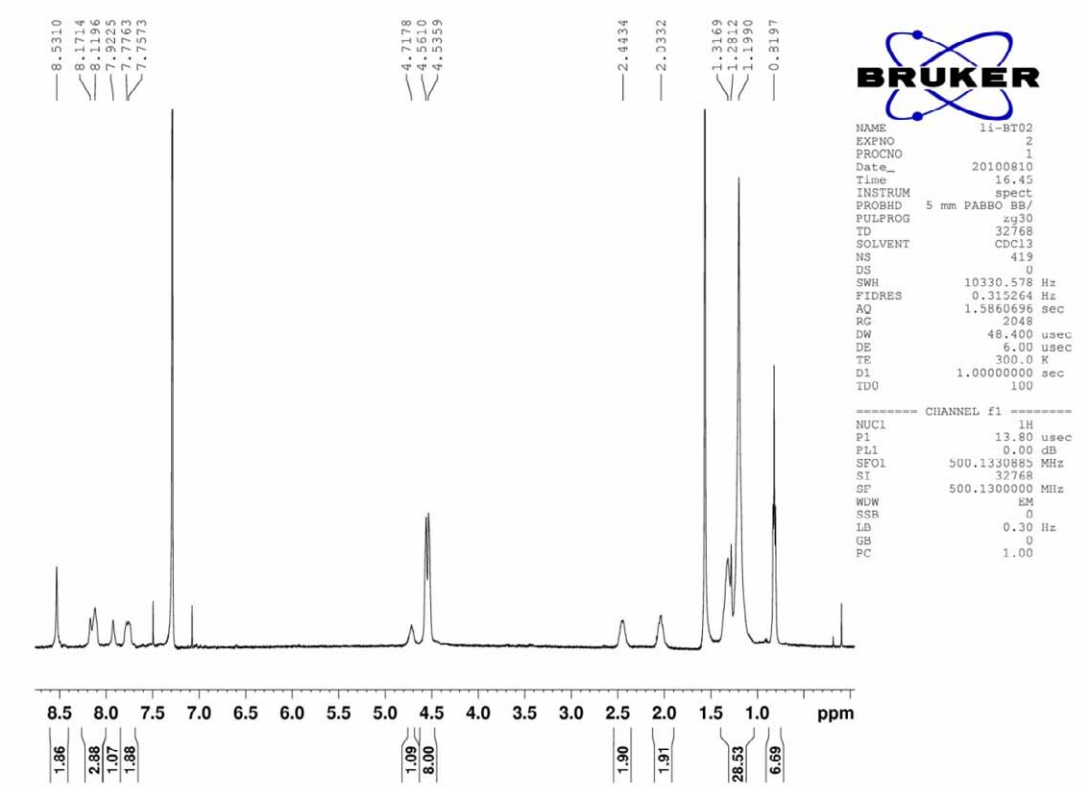


Figure S14. ^{1}H NMR of **7a** in $CDCl_3$

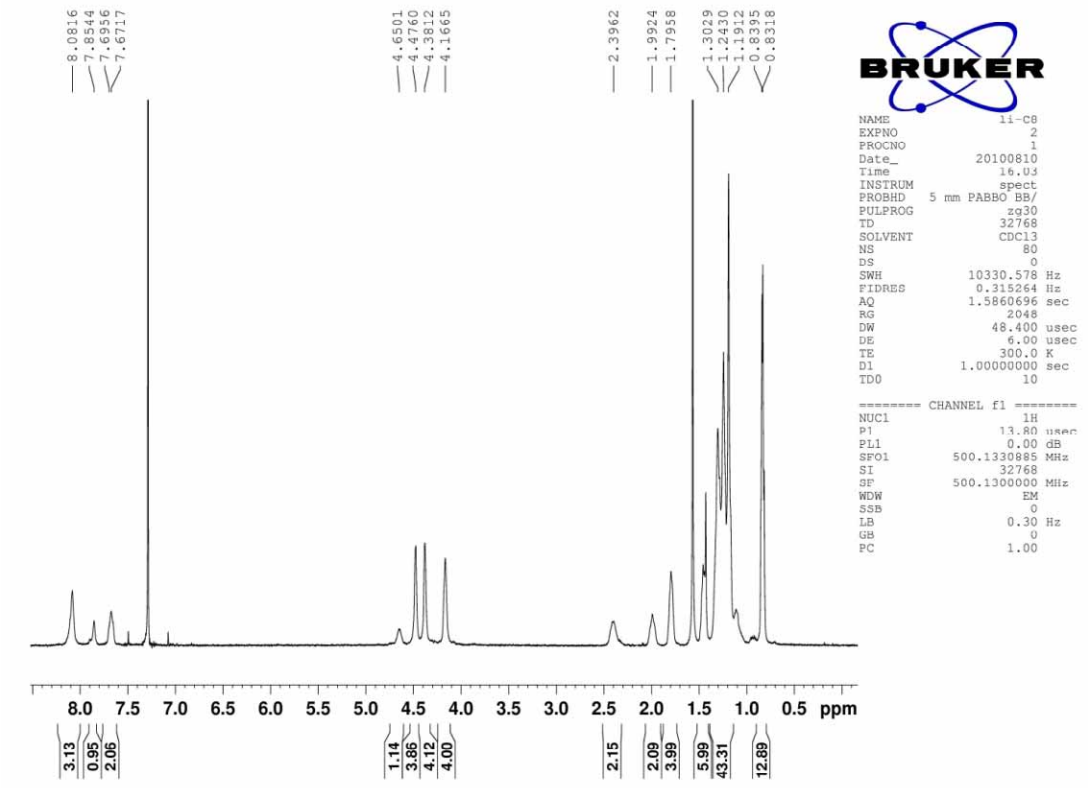


Figure S15. ^{1}H NMR of **7b** in $CDCl_3$

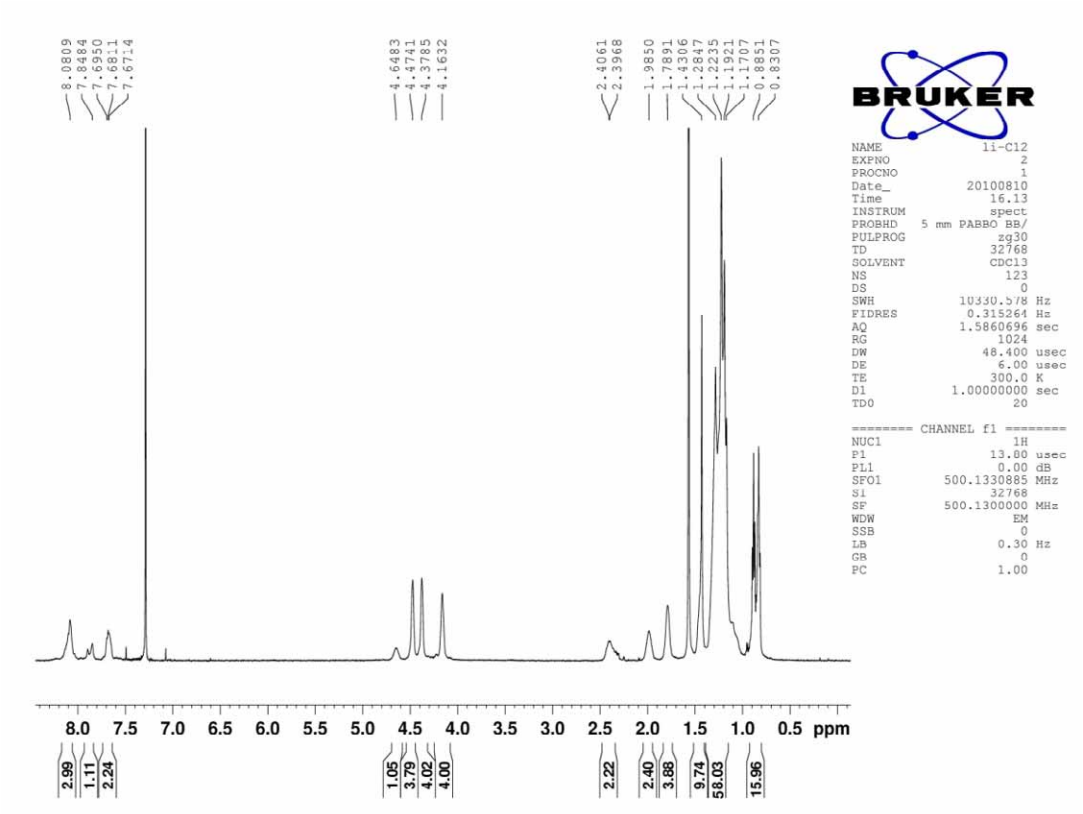


Figure S16. ^{1}H NMR of **7c** in $CDCl_3$

4. Cyclic voltammetry data for polymer 2, 4 and 7a-c

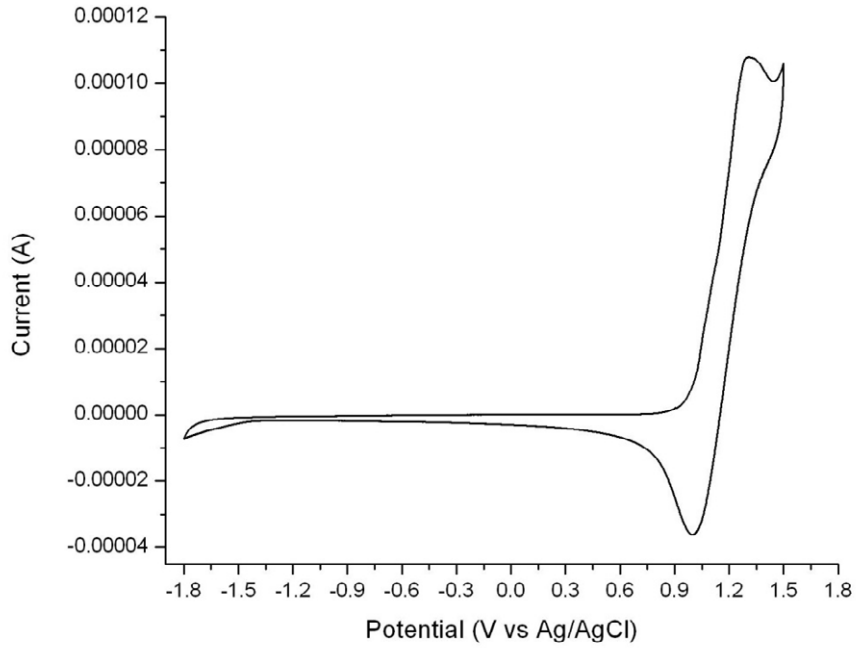


Figure S17. Cyclic voltammetry curves of polymer **2** obtained with a drop-cast polymer film under 0.1 M

TBAP/acetonitrile electrolyte solution scanned at a rate of 100 mV/s.

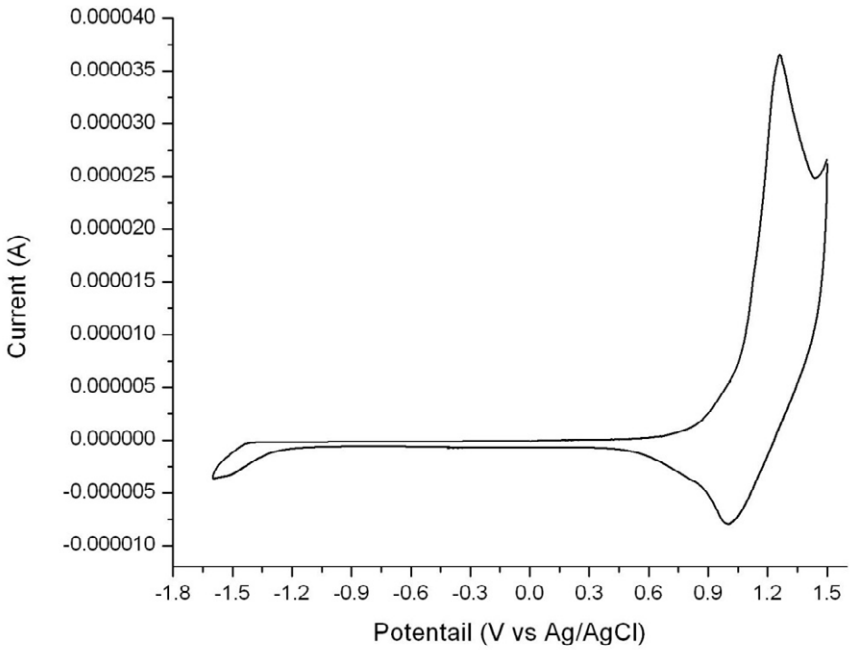


Figure S18. Cyclic voltammetry curves of the polymer **4** obtained with a drop-cast polymer film under 0.1 M TBAP/acetonitrile electrolyte solution scanned at a rate of 100 mV/s.

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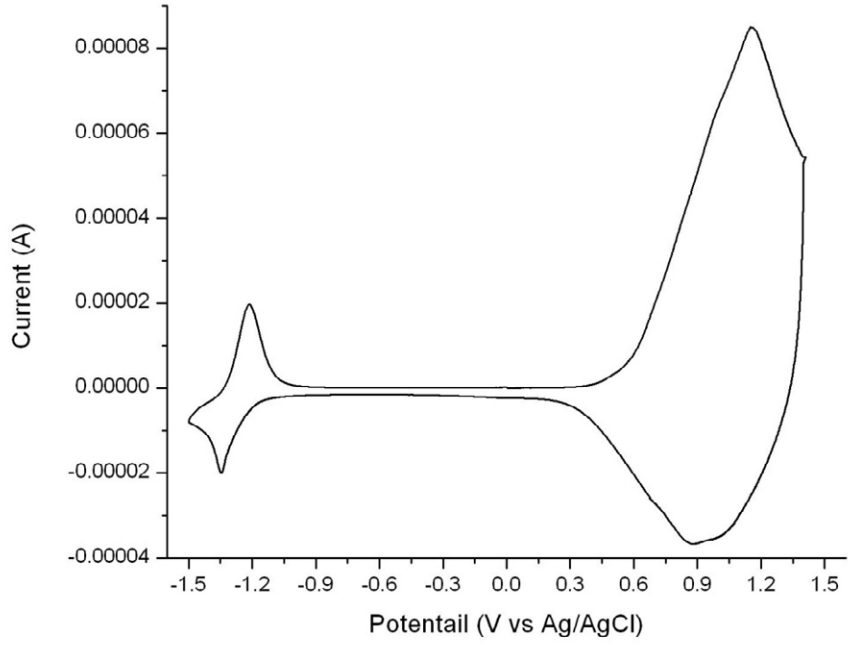

Figure S19. Cyclic voltammetry curves of polymer **7a** obtained with a drop-cast polymer film under 0.1 M TBAP/acetonitrile electrolyte solution scanned at a rate of 100 mV/s..

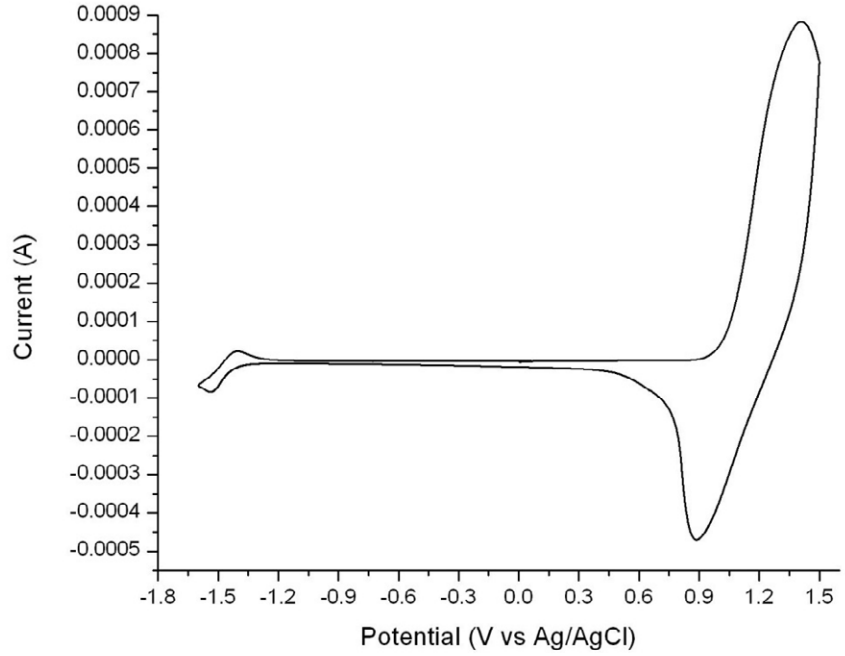

Figure S19. Cyclic voltammetry curves of polymer **7b** obtained with a drop-cast polymer film under 0.1 M TBAP/acetonitrile electrolyte solution scanned at a rate of 100 mV/s.

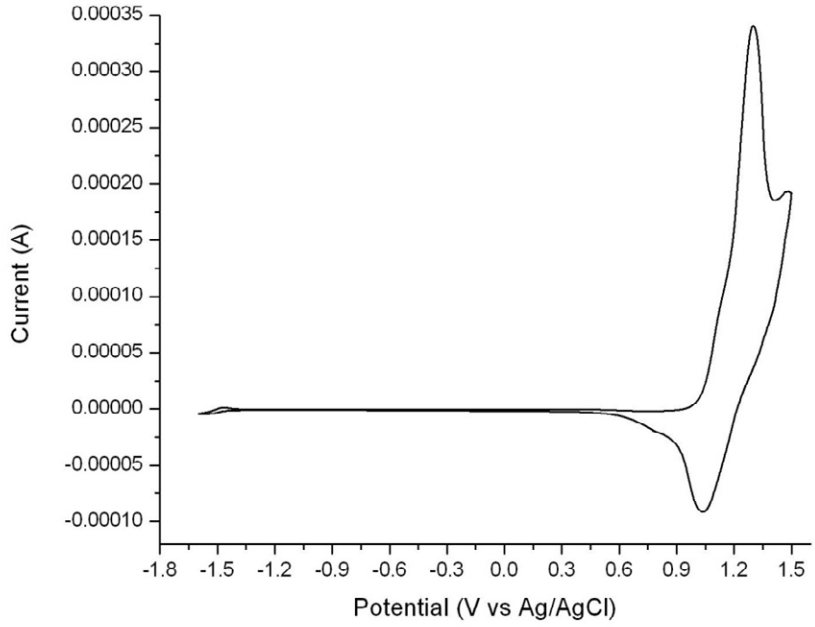

Figure S19. Cyclic voltammetry curves of polymer **7c** obtained with a drop-cast polymer film under 0.1 M TBAP/acetonitrile electrolyte solution scanned at a rate of 100 mV/s.