Characterization of 2-Chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (EDOT-Cl)

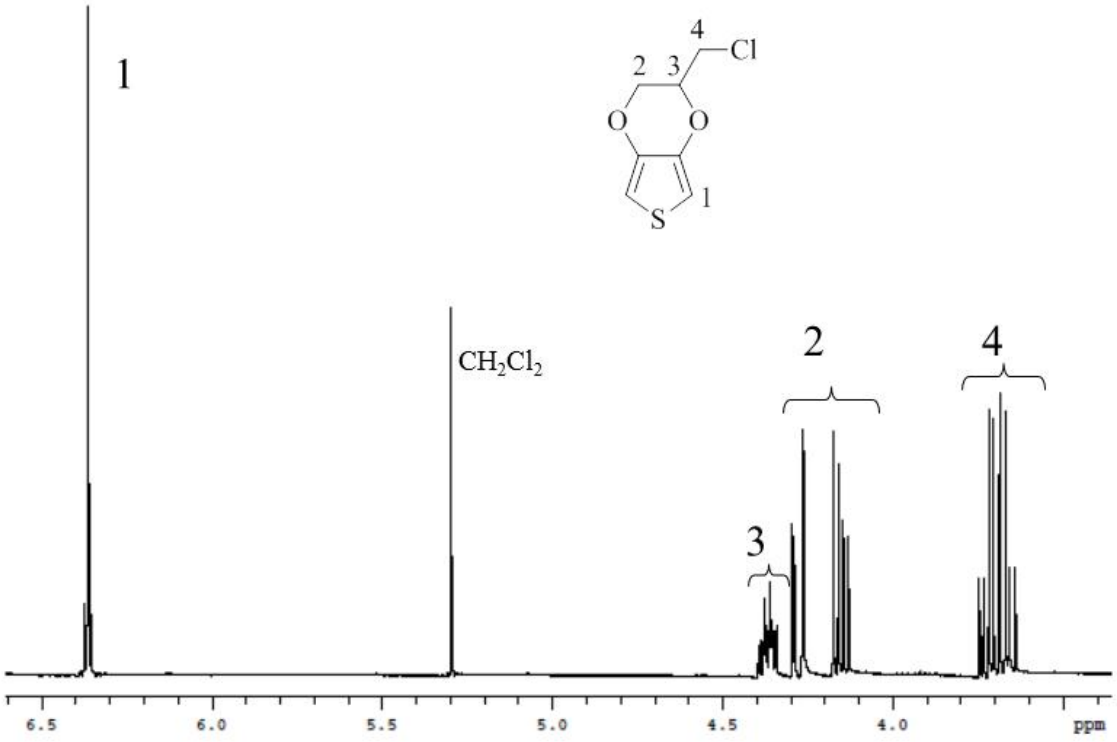
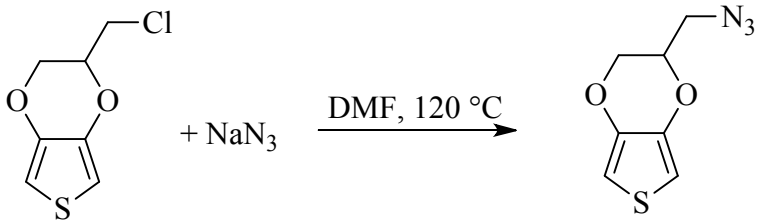


Figure 1S. ^{1}H-NMR spectrum in $CDCl_3$ (400 MHz) of 2-Chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (EDOT-Cl)

^{1}H NMR ($CDCl_3$): δ = 6.37 (m, 2H, C*H*S), 4.36 (m, 1H, CH-O), 4.29 (dd, J_1= 12.0 Hz, J_2= 2.4 Hz,1H, CH_2-O) 4.15 (dd, J_1= 12.0 Hz, J_2= 6.0 Hz,1H, CH_2-O), 3.72 (dd, J_1= 11.6 Hz, J_2= 5.2 Hz, 1H, CH_2-Cl), 3.66 (dd, J_1= 11.6 Hz, J_2= 7.2 Hz,1H, CH_2-Cl); ^{13}C NMR ($CDCl_3$): δ = 141.16, 140.71, 100.12, 100.11, 72.84, 65.55, 41.31.

Detail on synthesis and characterization of 2-Azidomethyl-2,3-dihydro-thieno[3,4-b][1,4] dioxine (EDOT-N_3)



Sodium azide (176,8 mg, 2,72 mmol) was added to a solution of 2-Chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (EDOT-Cl) (258 mg, 1,36 mmol) in DMF (15 mL) under nitrogen atmosphere. The reaction mixture was stirred at 120°C for 3h. The solvent was removed under

vacuum and the residual sodium azide removed adding 30 mL of water subsequently extracted with diethylether (3 x 30 mL). The organic fractions were washed with water (30 mL) and dried on sodium sulfate. Removing the solvent under vacuum 2-Azidomethyl-2,3-dihydro-thieno[3,4-b][1,4] dioxine (EDOT-N_3) was obtained as a yellow oil (yield = 95%)

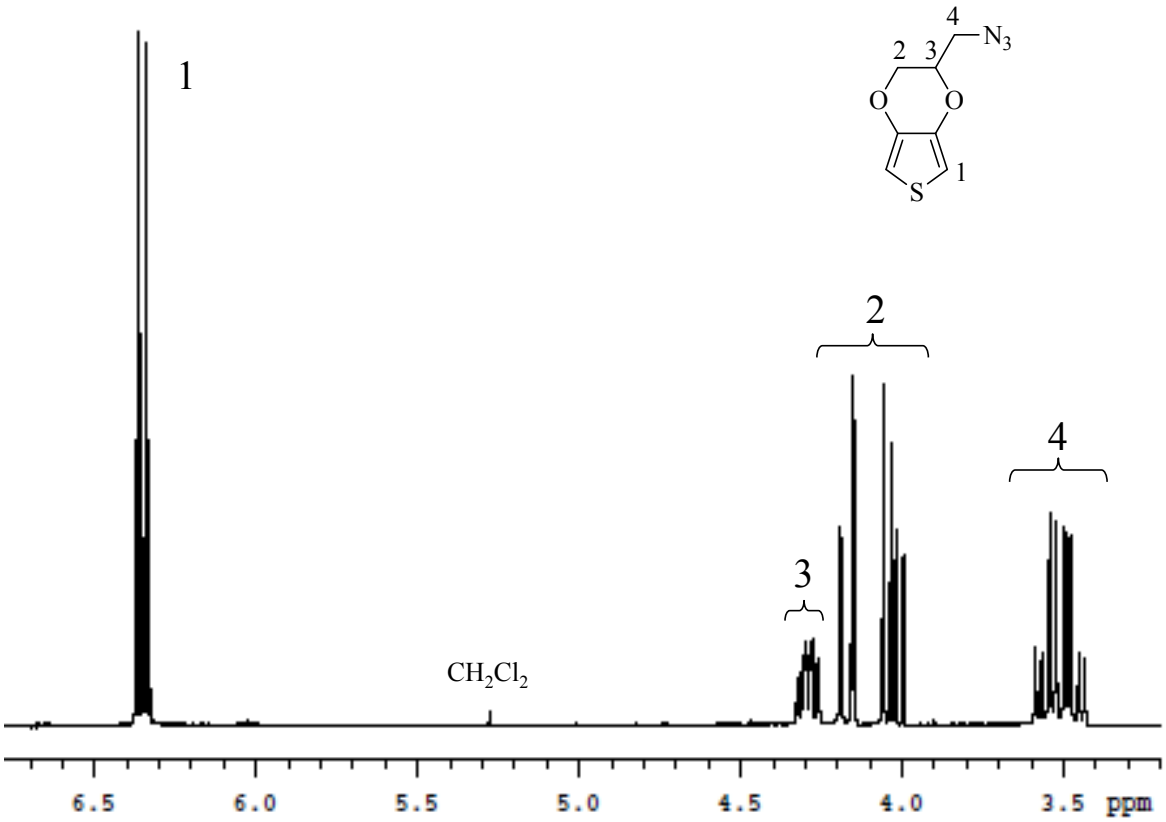


Figure 2S. ^{1}H-NMR spectrum in $CDCl_3$ (400 MHz) of 2-Azidomethyl-2,3-dihydro-thieno[3,4-b][1,4] dioxine (EDOT-N_3)

^{1}H-NMR ($CDCl_3$, 300MHz): 6.36 (AB-system, J_{AB} = 3.7 Hz, 2H, CH-S), 4.30 (m, 1H, CH-O), 4.18 (dd, J_1=11.7 Hz, J_2= 2.3 Hz,1H, CH_2-O), 4.04 (dd, J1= 11.7 Hz, J2= 6.9 Hz,1H, CH_2-O), 3.56 (dd, J_1= 13.1 Hz, J_2= 6.0 Hz, 1H, CH_2-N_3), 3.47 (dd, J_1= 13.1 Hz, J_2= 5.2 Hz,1H, CH_2-N_3); ^{13}C NMR ($CDCl_3$): δ = 141.0, 140.6, 100.21, 100.04, 72.4, 65.7, 50.5.