Supporting Information

Solvatochromism and Side Chain Effects on Morphological Behavior of Bodipy-alt-*i*Indigo copolymers

Anup Kumar Singh[a, b, *] Gitanjali Swain[a, b], and Sarika Birajdar[a, b]

[a]Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, CSIR-Networks of Institutes for Solar Energy, Pune, 411008, India

[b]Academy of Scientific and Innovative Research (AcSIR), CSIR-Human Resource Development Centre, Ghaziabad, 201002, India

*Corresponding Author: Dr. Anup Kumar Singh, anupsinghbisen@yahoo.com

S1 Experimental Section

S1.1 Materials. Unless otherwise stated, all the chemicals and reagents were obtained commercially and used as received. All the solvents were purchased from Merk Chemicals. All the solvents used for characterization were HPLC grade. The solvents used for column chromatography purchased locally and purified by using standard procedure. Tetrahydrofuran (THF) was passed through alumina and distilled over Na/benzophenone before use. 1-bromododecane, 11-bromoundecanoic acid, 6-bromoindoline-2,3-dione, 6-bromoindolin-2-one, 2,4-dimethylpyrrole, boron trifluoride diethyl etherate, DDQ, potassium carbonate, bis(pin)diborane, $Pd(dppf)_2Cl_2$, dioxane, and triethyl amine were purchased from Aldrich chemicals.

S1.2 Structural Analysis. Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) were performed with HRMS-(ORBITRAP) mass spectrometer (Thermo Scientific, Q Exactive). ^{1}H NMR spectra were recorded with Bruker arx AV 200 MHz, AV 400 MHz, and AV 500 MHz Bruker AVANS spectrometer by using $CDCl_3$ solvent. ^{13}C NMR spectra were measured on Bruker arx 100 MHz AVANS NMR spectrometer. All chemical shifts are reported in ppm downfield to TMS at 298 K and peak multiplicities are referred as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), and multiplet (m). Analytical Thin Layer Chromatography was done on pre-coated silica gel plates (Kieselgel 60F254, Merck). Column chromatographic purifications were done with 60-120 mesh sized silica gel.

S1.3 Morphological Studies. Morphology of the copolymers was characterized using Quanta 200 3D scanning electron microscope (E-SEM). Samples for E-SEM were prepared by drop-casting a polymer solution (in chloroform) on silicon wafer and dried for 12 h at 40 ^{o}C and sputtered with gold for 30 s prior to the measurements.

S1.4 Absorption and Emission Study. UV-vis absorption spectra were recorded on SPECORD®210/PLUS, UV-visible spectrophotometer. The emission spectra were recorded on FLUOROMAX-4C research spectrofluorometer. The Stock solutions were prepared by dissolving 1mg/mL of BDP-*alt*-*i*I in various solvents.

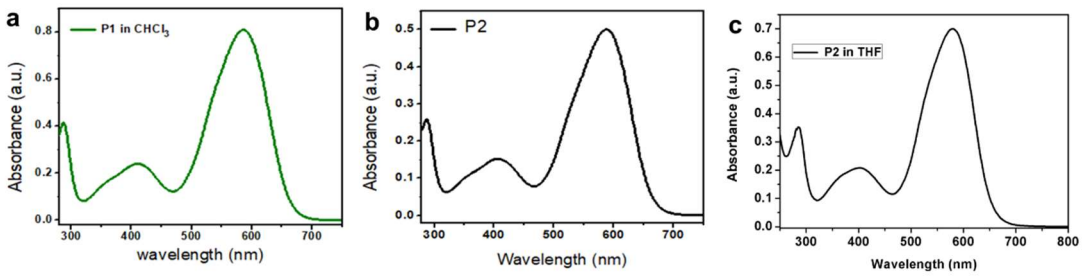


Figure S1: UV-vis spectra of copolymer P1 (a) and P2 (b) in chloroform. UV-vis spectra of P2 in 90% THF-$CHCl_3$ (c).

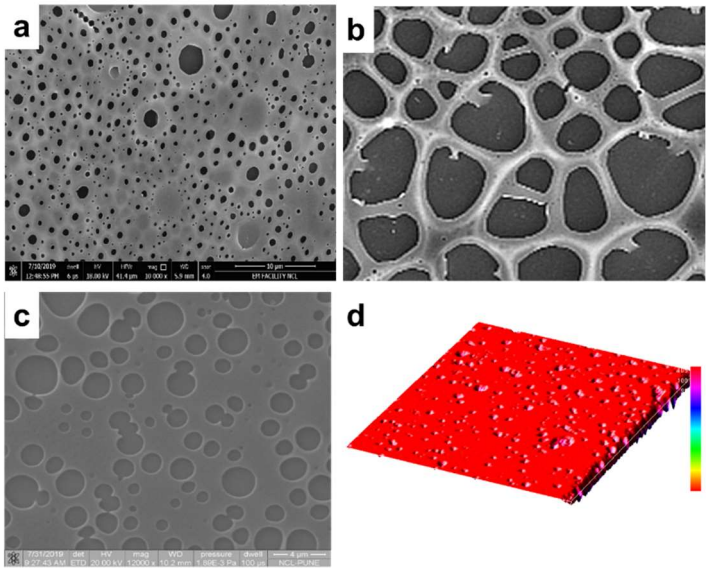
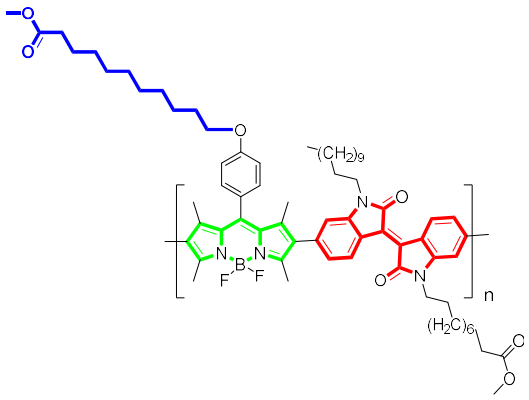


Figure S2: Scanning Electron microscopic (SEM) image of 1 mg/mL of copolymer P2 in $CHCl_3$, at t=0 min (a). SEM image of P2 in $CHCl_3$, at t=30 min (b). SEM image of P1 in 50% $CHCl_3$-THF mixture (c). 3D surface plot of P2 showing pores in 50% $CHCl_3$-THF mixture (d).

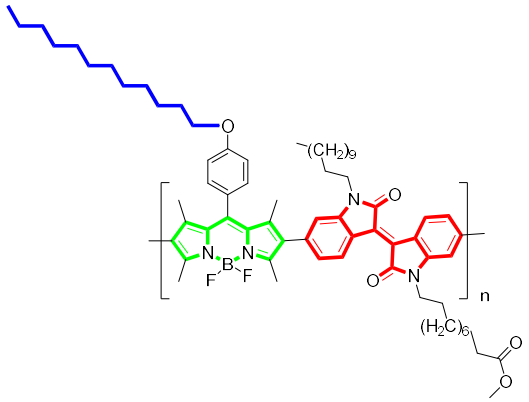
S2 Characterizations

S2.1 P2: [poly(BDP_E-*alt*-*i*I)]



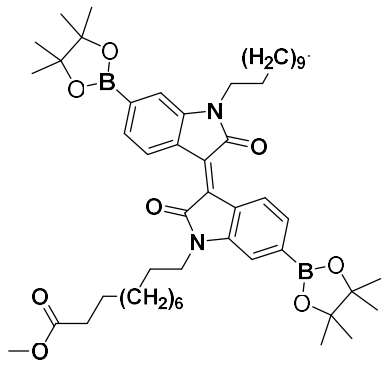
^{1}H NMR of P2 (400 MHz, $CDCl_3$, ppm): 9.20 (d, *J*=7.78 Hz, 2 H), 7.06 (d, *J*=8.24 Hz, 3 H), 6.86 (br. s., 2 H), 6.62 (br. s., 2 H), 4.02 (br. s., 2 H), 3.78 (br. s., 3 H), 3.67 (s, 6 H), 2.62 (br. s., 6 H), 2.22 - 2.35 (m, 4 H), 1.82 (d, *J*=7.79 Hz, 2 H), 1.70 (br. s., 4 H), 1.61 (br. s., 9 H), 1.46 (br. s., 10 H), 1.31 (br. s., 27 H), 1.25 (br. s., 37 H), 0.81 - 0.94 (m, 8 H). GPC (RT in THF): Mn = 8090 g·mol^{-1}, Mw = 11750 g·mol^{-1}, and PDI = 1.45 (with respect to PS standard).

S2.2 P1: [poly(BDP_{12}-*alt*-*i*I)]



^{1}H NMR of P1 (400 MHz, $CDCl_3$, ppm): 9.18 (d, *J*=8.71 Hz, 3 H), 7.06 (d, *J*=8.60 Hz, 3 H), 6.85 (br. s., 2 H), 6.62 (br. s., 2 H), 4.03 (br. s., 2 H), 3.78 (br. s., 3 H), 3.66 (s, 4 H), 2.62 (br. s., 5 H), 2.30 (t, *J*=7.06 Hz, 2 H). GPC (RT in THF): Mn = 8700 g·mol^{-1}, Mw = 12100 g·mol^{-1}, and PDI = 1.39 (against PS standard).

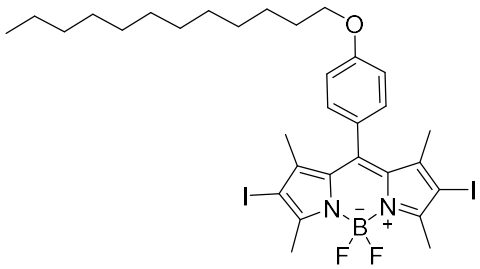
S2.3 M1: Methyl (E)-11-(1'-dodecyl-2,2'-dioxo-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-1-yl)undecanoate



^{1}H NMR of M1 (400 MHz, $CDCl_3$, ppm): 9.16 (d, J=7.7 Hz, 2H), 7.5 (d, J=7.8 Hz, 2H), 7.17 (s, 2H), 3.78 (d, J=7.1 Hz, 4H), 3.67 (s, 3H), 2.3 (t, J= 7.0 (x2) Hz, 2H), 1.67 (m, 6H), 1.38 (s, 24 H), 0.87 (t, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 174.42, 167.78, 167.68, 143.99, 143.02, 132.47, 131.23, 129.12, 129.01, 128.87, 124.57, 124.26, 120.51, 114.65, 113.22, 113.12, 84.17, 84. 12, 77.32, 76.68, 51.45, 40.22,

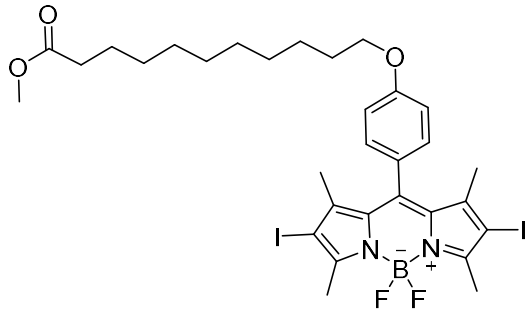
40.06, 34.10, 31.89, 29.60, 29.52, 29.32, 27.61, 27.51, 27.37, 26.99, 24.84, 22.66, 14.09.

S2.4 M2: 10-(4-(Dodecyloxy)phenyl)-5,5-difluoro-2,8-diiodo-1,3,7,9-tetramethyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine



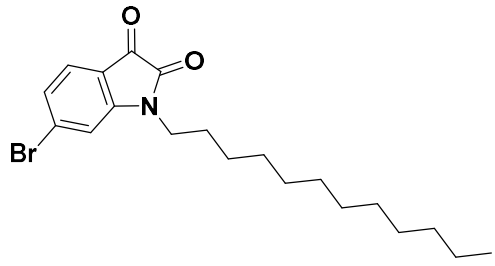
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.12 (d, J= 8.5 Hz, 2H), 7.03 (d, 8.5 Hz, 2H), 4.03 (t, J= 6.7 Hz (x2), 2H), 2.63 (m, 6H), 1.84 (m, 2H), 1.49 (m, 9H), 1.3 (m), 0.89 (t, J=8.0 Hz (x2), 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 160.58, 156.96, 145.84, 142.20, 132.20, 129.48, 126.89, 115.84, 85.96, 68.73, 32.39, 30.14, 30.12, 30.07, 30.04, 29.90, 29.83, 29.68, 26.52, 23.16, 17.65, 16.47, 14.60.

S2.5 M3: Methyl 11-(4-(5,5-difluoro-2,8-diiodo-1,3,7,9-tetramethyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)phenoxy)undecanoate



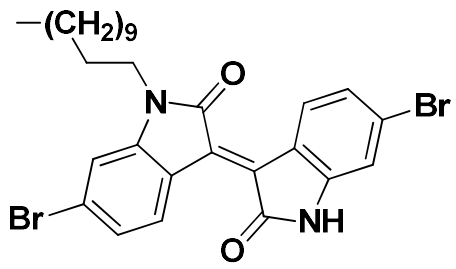
^{1}H NMR of M3 (200 MHz, $CDCl_3$, ppm): 7.13 (d, J= 8.5 Hz, 2H), 7.02 (d, 8.5 Hz, 2H), 4.02 (t, J= 6.7 Hz (x 2), 2H), 3.67 (s), 2.63 (m, 6H, 2.32 (t, 2H), 1.82 (m, 2H), 1.48 (m, 7H), 1.3 (m), 0.89 (t, J=8.0 Hz (x 2), 3H).

S2.6 R1: 6-bromo-1-dodecylindoline-2,3-dione



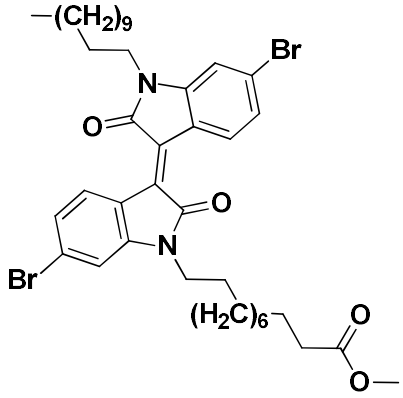
^{1}H NMR of R1 (200 MHz, $CDCl_3$, ppm): 7.46 (d, J= 8.0 Hz, 1H), 7.28 (s, 1H), 7.06 (d, J= 8.0 Hz, 1H), 3.69 (t, J= 8.0 Hz, 2H), 1.70 (d, 8.0 Hz, 2H), 1.36-1.26 (m, 18 H), 0.88 (t, J=7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 182.33, 157.93, 151.83, 133.49, 126.76, 126.34, 116.23, 113.72, 40.45, 31.86, 29.55, 29.49, 29.42, 29.29, 29.13, 27.14, 26.64, 14.08.

S2.7 R2: (E)-6,6'-dibromo-1-dodecyl-[3,3'-biindolinylidene]-2,2'-dione



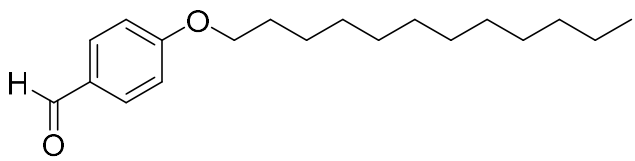
^{1}H NMR of R2 (400 MHz, $CDCl_3$, ppm): 9.14 (dd, J= 8.6, 8.6 Hz 2H), 7.71 (s, br, 1H, -NH), 7.19 (dd, J= 8.5, 1.7 Hz, 2H), 6.97 (dd, J= 10.0, 1.8 Hz, 2H), 3.74 (t, J= 7.3 Hz, 2H), 1.69 (m, br, 2H), 1.44-1.19 (m, 18 H), 0.89 (t, J=8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 180.93, 145.87, 143.21, 131.46, 131.11, 126.71, 125.24, 120.32, 112.61, 111.39, 40.30, 31.90, 29.61, 29.55, 29.49, 29.26, 27.37, 26.98, 22.68, 14.11.

S2.8 R3: Methyl (E)-11-(6,6'-dibromo-1'-dodecyl-2,2'-dioxo-[3,3'-biindolinylidene]-1-yl)undecanoate



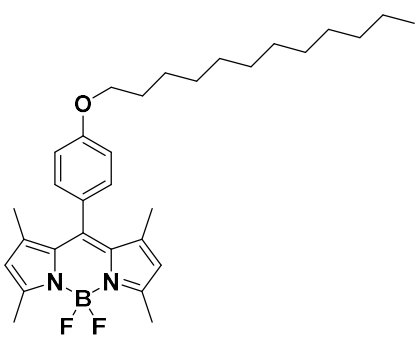
^{1}H NMR of R3 (200 MHz, $CDCl_3$, ppm): 9.07 (d, J=8.6 Hz, 2H), 7.16 (d, J=8.6 Hz, 2H), 6.92 (s, 2H), 3.72 (t, J=7.3(x2) Hz, 4H), 3.67 (s, 3H), 2.3 (t, J=7.5(x2), 2H), 1.64 (m, 7H), 1.35 (m, br, 8H), 1.28 (m, br, 10 H), 1.26 (m, br, 12H), 0.88 (t, J=6.5(x2) Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 174.28, 167.68, 145.75, 132.60, 131.18, 126.71, 125.10, 120.40, 111.27, 51.42, 40.23, 34.07, 29.58, 29.53, 29.48, 29.38, 29.31, 29.24, 29.20, 29.17, 29.08, 27.35, 26.95, 26.94, 24.91, 22.66, 14.10.

S2.9 R4: 4-(Dodecyloxy)benzaldehyde



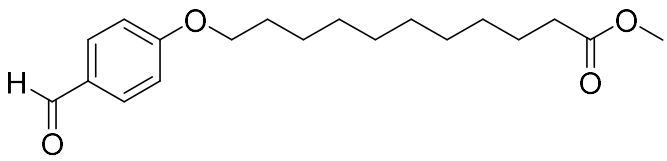
^{1}H NMR of R4 (200 MHz, $CDCl_3$, ppm): 7.16 (d, *J*=8.46 Hz, 2 H), 7.00 (d, *J*=8.59 Hz, 2 H), 5.98 (s, 2 H), 4.01 (t, *J*=6.51 Hz, 2 H), 2.56 (s, 6 H), 1.71 - 1.92 (m, 2 H), 1.44 (s, 6 H), 1.28 (s, 14 H), 0.84 - 0.93 (m, 3 H). LC-HRMS: m/z calcd for $C_{31}H_{43}BF_2N_2O$ $[M+H]^+$: 509.3470; found: 509.3467.

S2.10 R5: 10-(4-(Dodecyloxy)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine



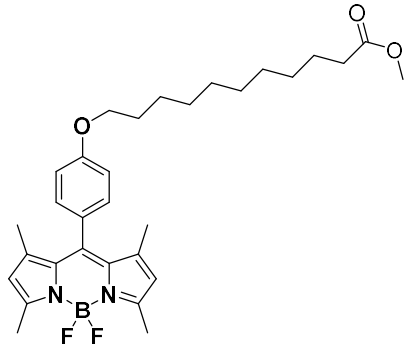
^{1}H NMR of R5 (200 MHz, $CDCl_3$, ppm): 7.16 (d, *J*=8.46 Hz, 2 H), 7.00 (d, *J*=8.59 Hz, 2 H), 5.98 (s, 2 H), 4.01 (t, *J*=6.51 Hz, 2 H), 2.56 (s, 6 H), 1.71 - 1.92 (m, 2 H), 1.44 (s, 6 H), 1.28 (s, 14 H), 0.84 - 0.93 (m, 3 H). LC-HRMS: m/z calcd for $C_{31}H_{43}BF_2N_2O$ $[M+H]^+$: 509.3470; found: 509.3467.

S2.11 R6: Methyl 11-(4-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)phenoxy)undecanoate



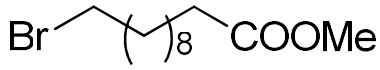
^{1}H NMR of R6 (400 MHz, $CDCl_3$, ppm): 9.84 (s, 1 H), 7.81 (d, *J*=8.84 Hz, 2 H) 6.96, (d, *J*=8.72 Hz, 2 H), 4.01 (t, *J*=6.51 Hz, 2 H), 3.63 (s), 2.87 (t, 2H), 1.71 - 1.93 (m, 3 H), 1.36 - 1.58 (m, 4 H), 1.27 (s, 13 H), 0.81 - 0.95 (m, 3 H).

S2.10 R7: Methyl 11-(4-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)phenoxy)undecanoate



^{1}H NMR of R7 (400 MHz, $CDCl_3$, ppm): 7.15 (d, *J*=8.72 Hz, 2 H), 7.00 (d, *J*=8.72 Hz, 2 H), 5.98 (s, 2 H), 4.00 (t, *J*=6.57 Hz, 2 H), 3.68 (s, 4 H), 2.56 (s, 6 H), 2.32 (t, *J*=7.45 Hz, 2 H), 1.73 - 1.93 (m, 2 H), 1.40 - 1.47 (m, 6 H), 1.26 - 1.35 (m, 10 H), 0.75 - 0.94 (m, 3 H).

S2.11 Methyl-11-bromo-undecanoate



^{1}H NMR of Methyl-11-bromo-undecanoate (400 MHz, $CDCl_3$, ppm): 3.66 (s, 3 H), 3.40 (t, *J*=6.88 Hz, 2 H), 2.30 (t, *J*=7.52 Hz, 2 H), 1.74 - 1.96 (m, 2 H), 1.61 (t, *J*=7.20 Hz, 2 H), 1.20 - 1.49 (m, 12 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 174.25, 51.38, 34.03, 33.95, 32.76, 29.28, 29.12, 28.66, 28.09, 24.86.

^{1}H and ^{13}C NMR

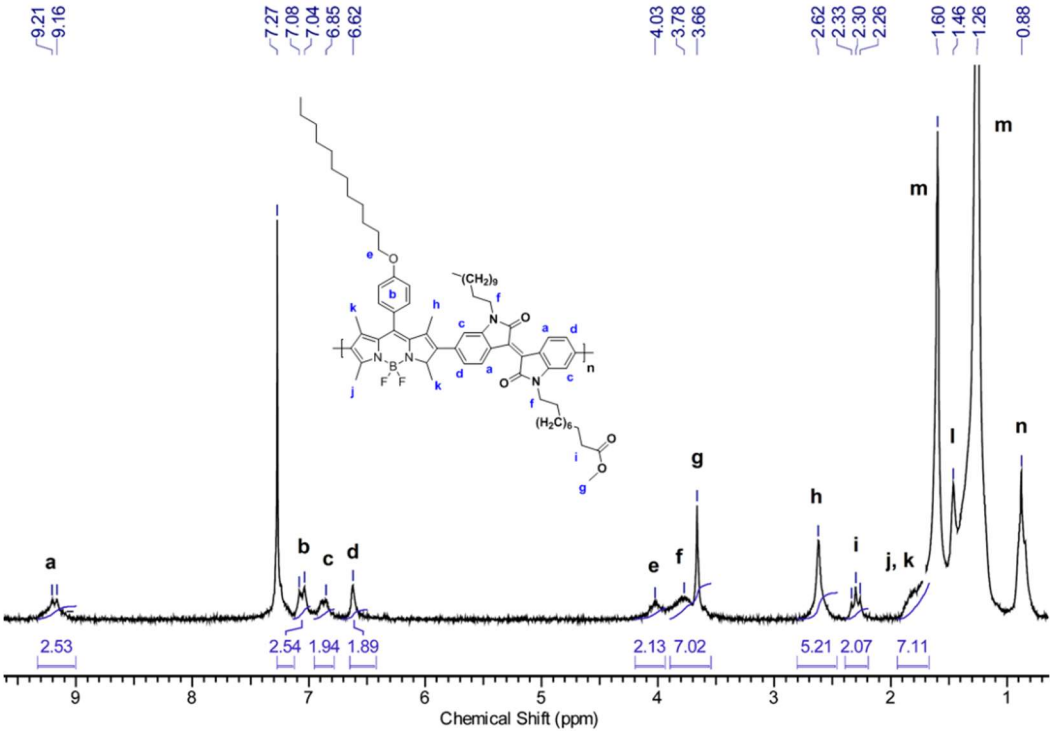


Figure S4: ^{1}H NMR (400 MHz) of polymer P1 in $CDCl_3$

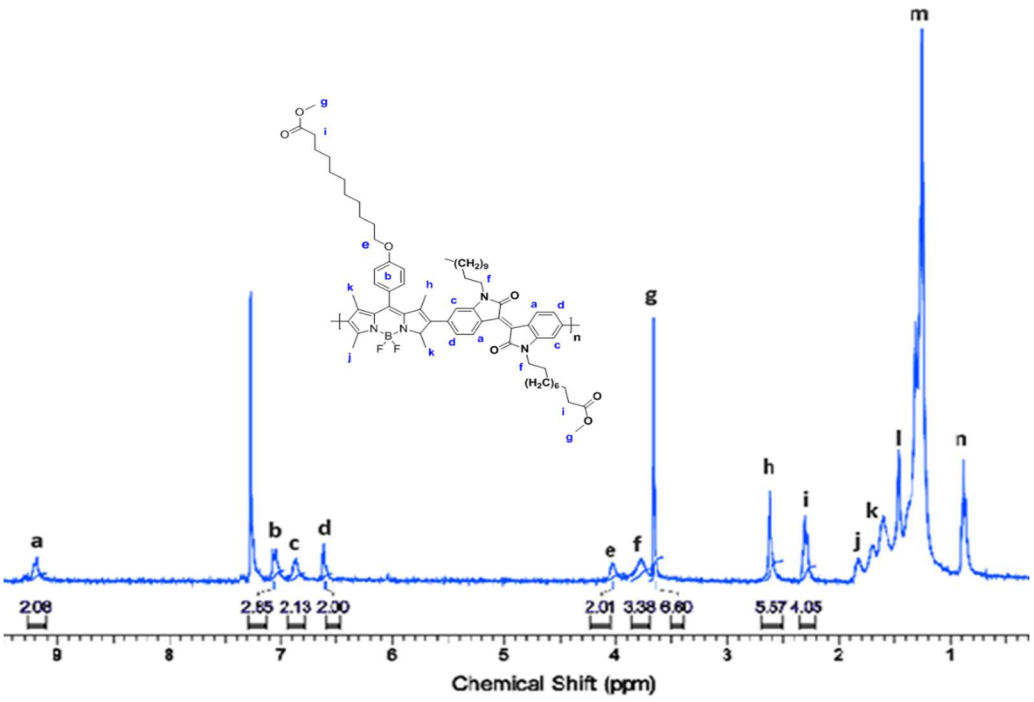


Figure S5: ^{1}H NMR (400 MHz) spectrum of polymer P2 in $CDCl_3$

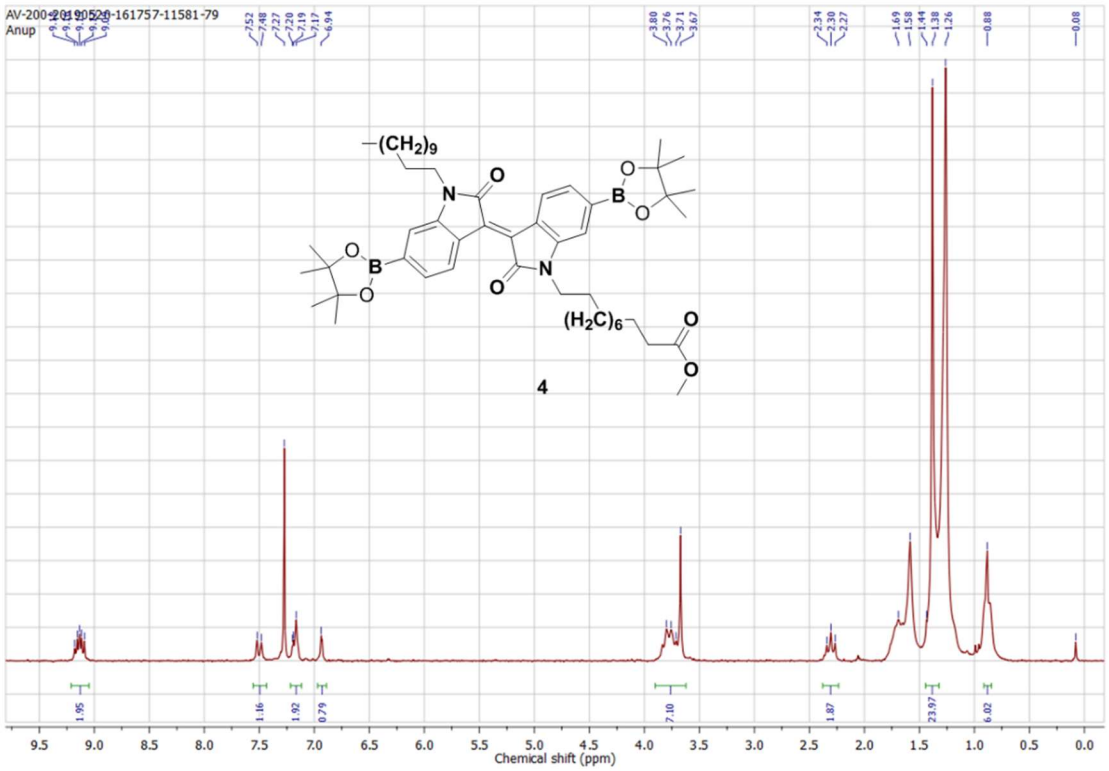


Figure S6: ^{1}H NMR (400 MHz) spectrum of monomer M1 in $CDCl_3$

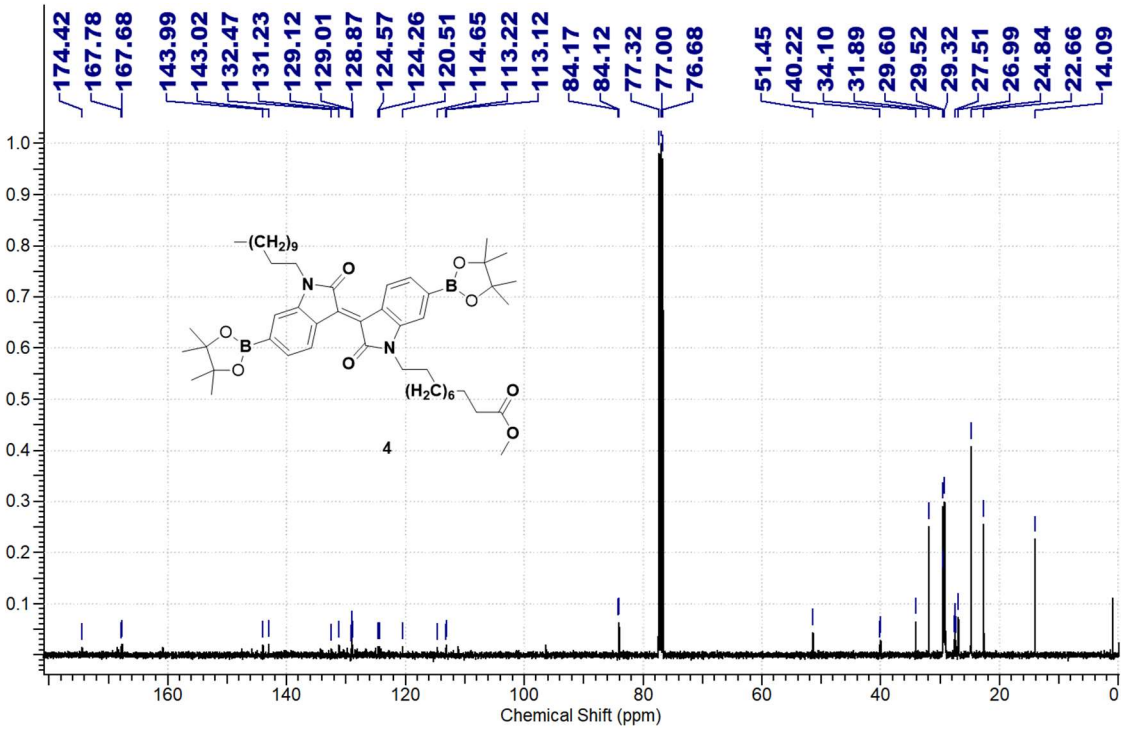


Figure S7: ^{13}C NMR (100 MHz) spectrum of monomer M1 in $CDCl_3$

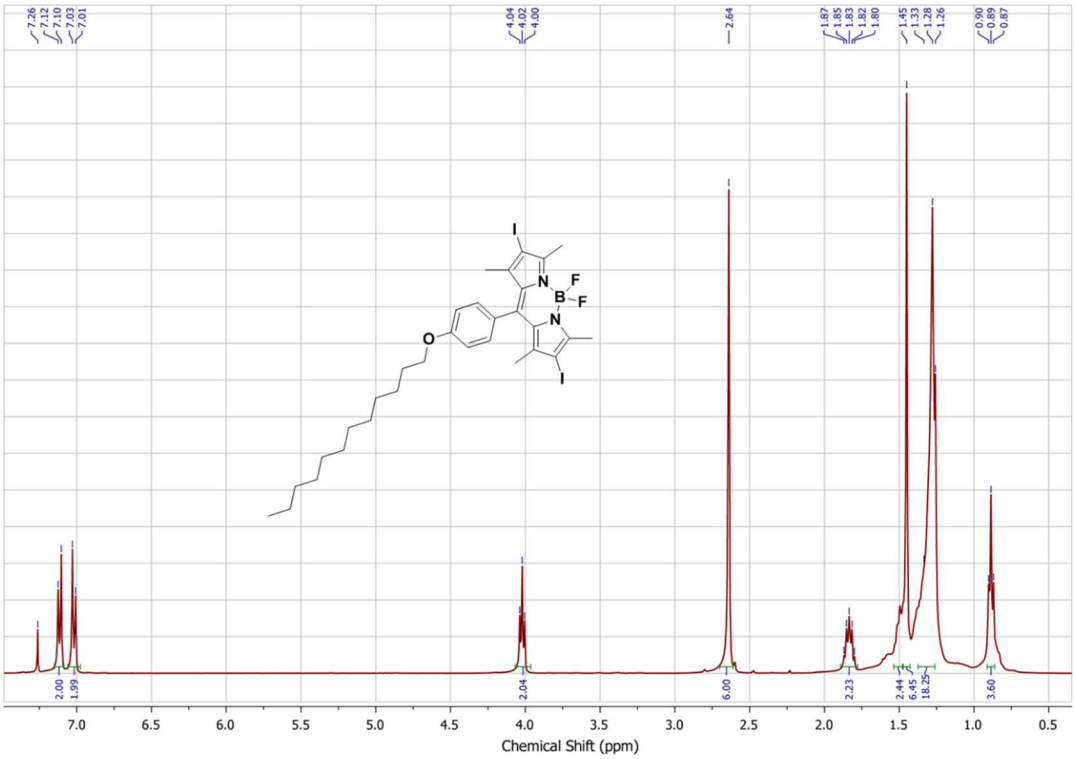


Figure S8: ^{1}H NMR (400 MHz) spectrum of monomer M2 in $CDCl_3$

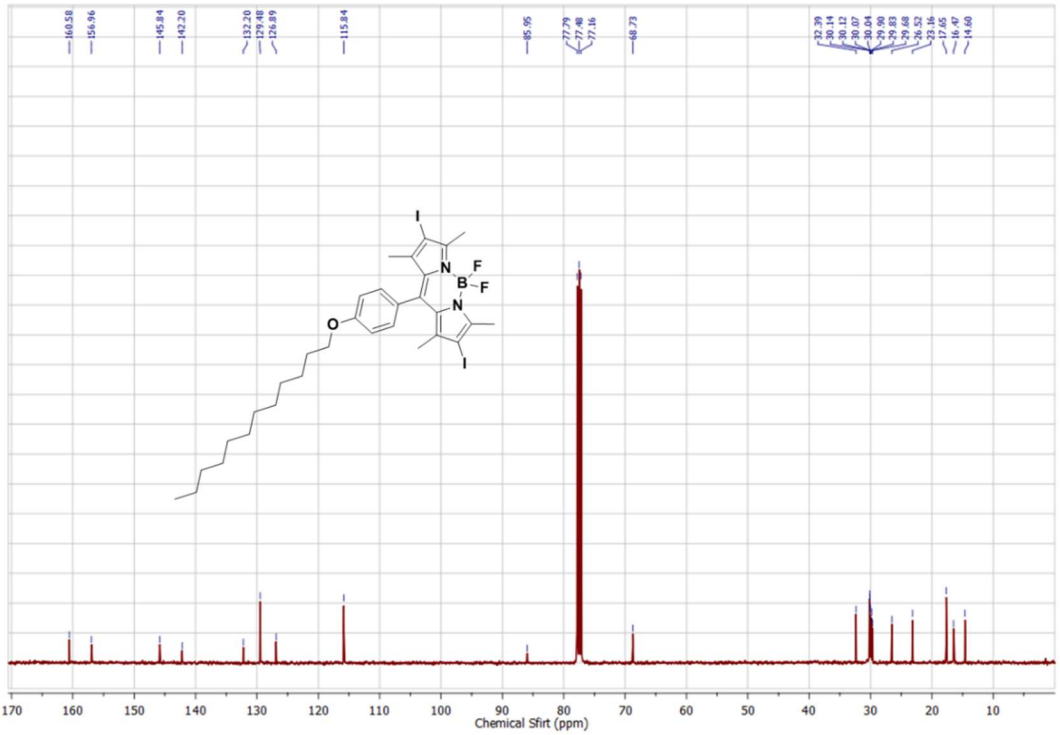


Figure S9: ^{13}C NMR (100 MHz) spectrum of monomer M2 in $CDCl_3$

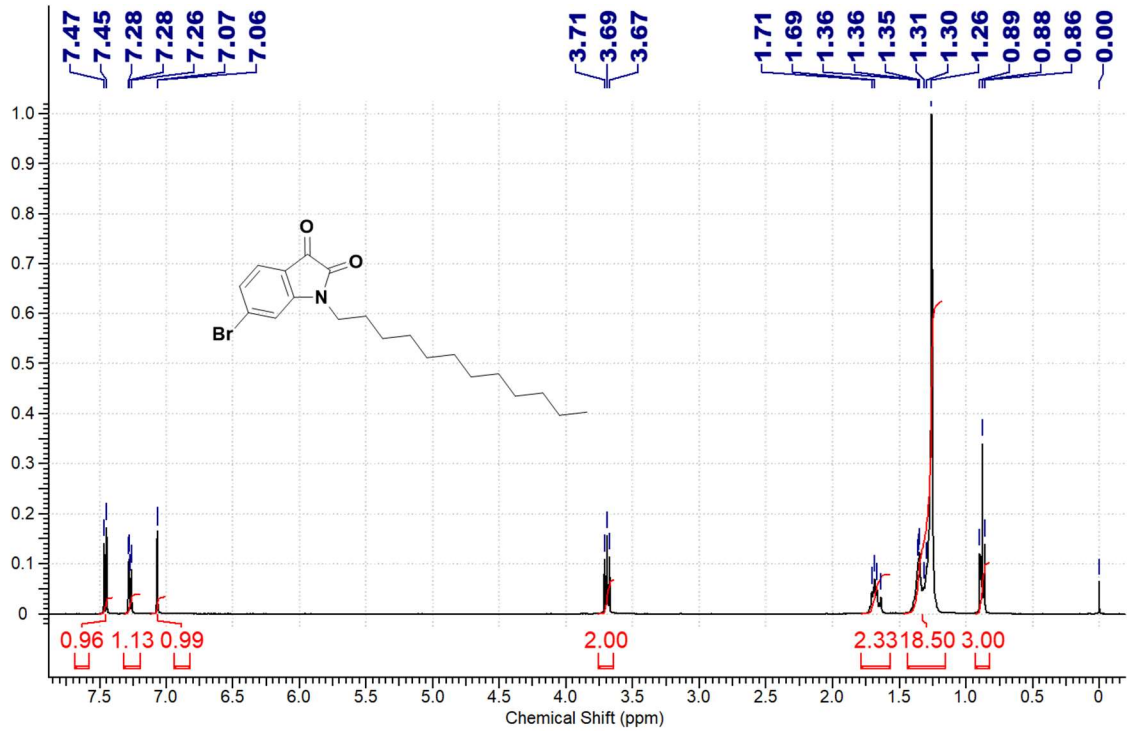


Figure S10: ^{1}H NMR (400 MHz) spectrum of compound R1 in $CDCl_3$

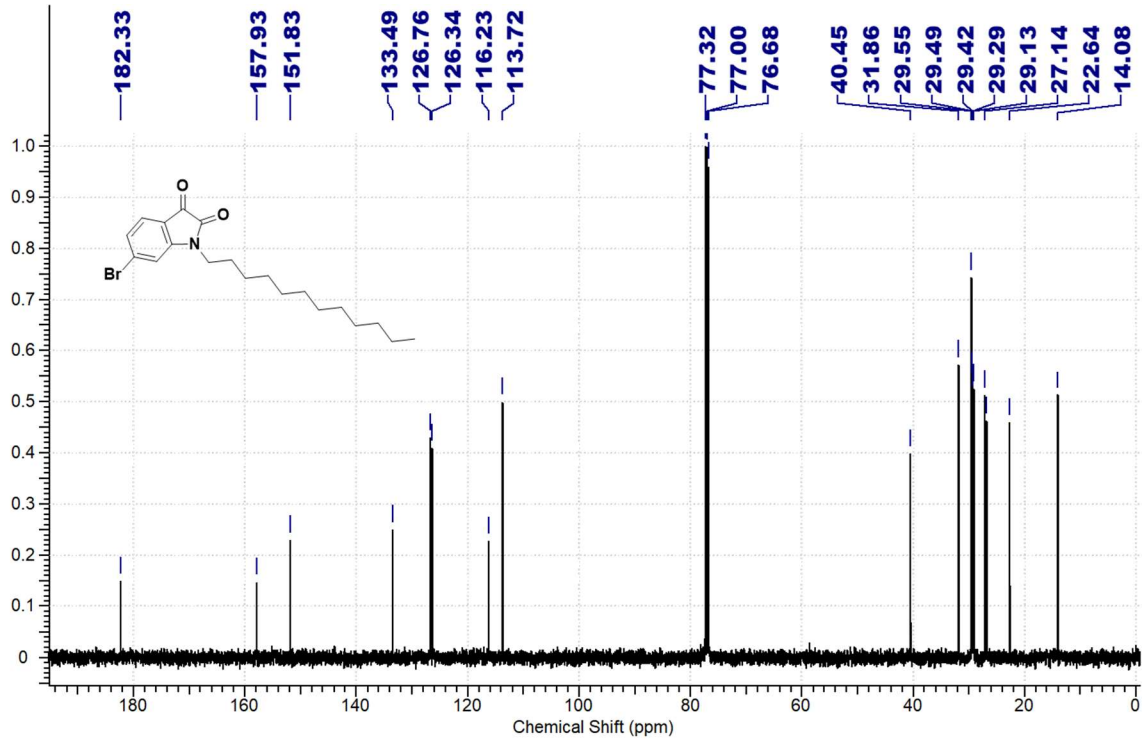


Figure S11: ^{13}C NMR (100 MHz) spectrum of compound R1 in $CDCl_3$

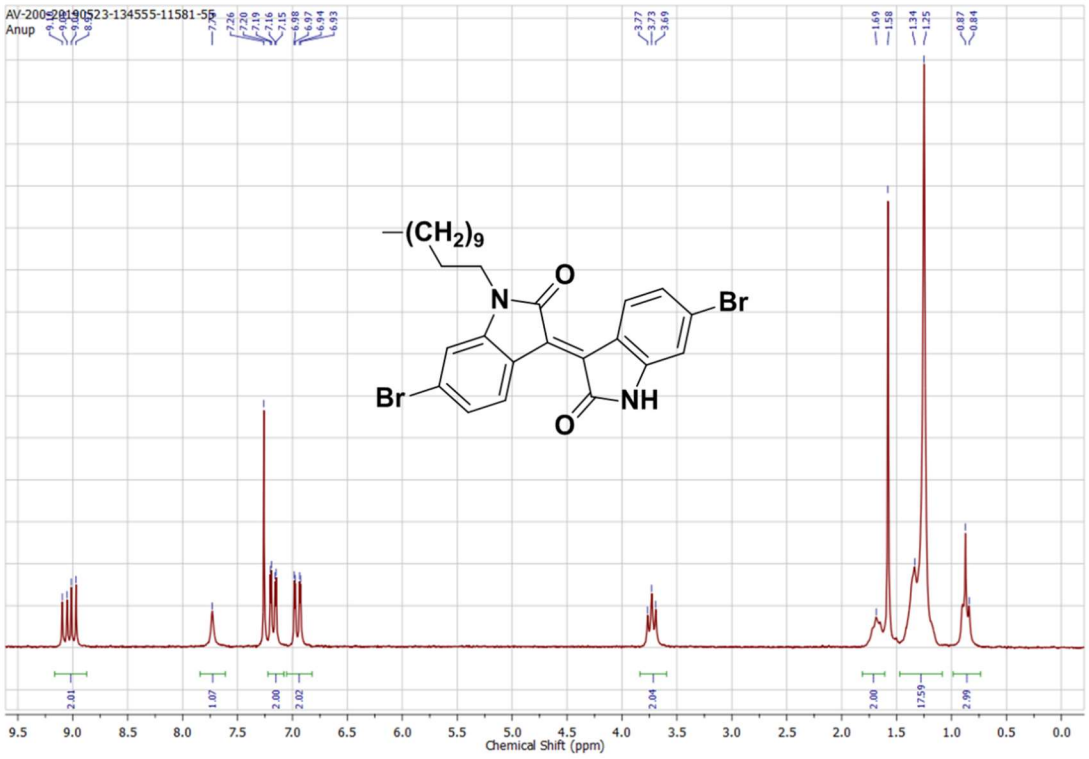


Figure S12: ^{1}H NMR (200 MHz) spectrum of compound R2 in $CDCl_3$

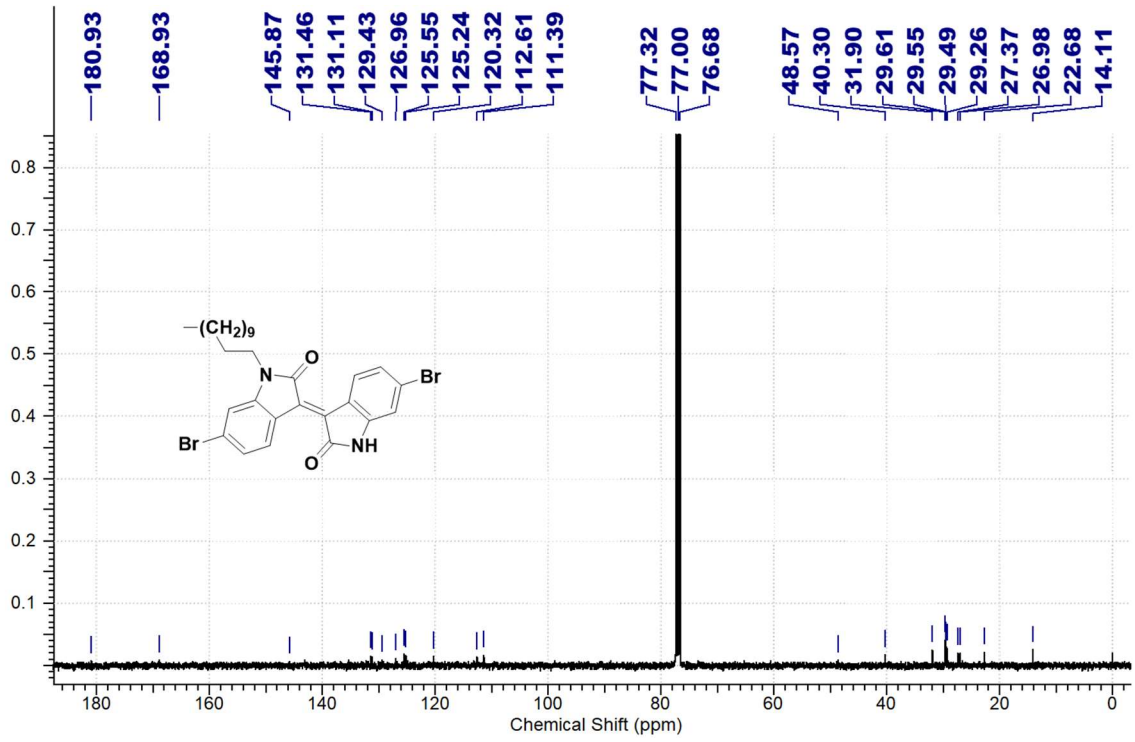


Figure S13: ^{13}C NMR (100 MHz) spectrum of Compound R2 in $CDCl_3$

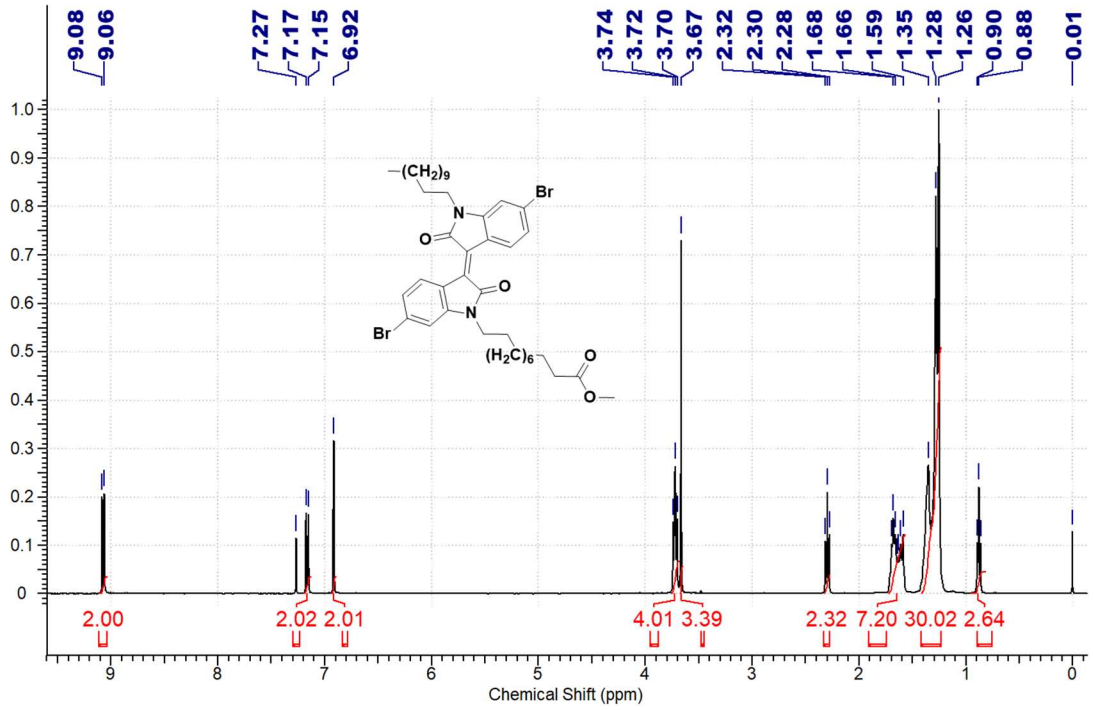


Figure S14: ^{1}H NMR (400 MHz) spectrum of Compound R3 in $CDCl_3$

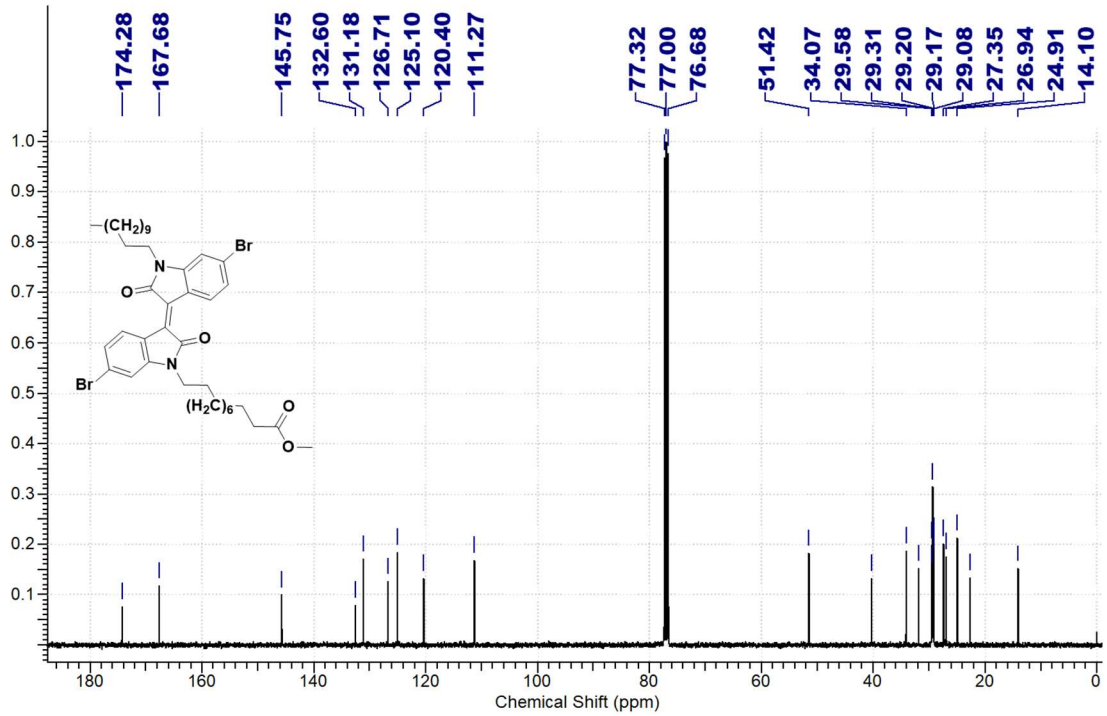


Figure S15: ^{13}C NMR (100 MHz) spectrum of Compound R3 in $CDCl_3$

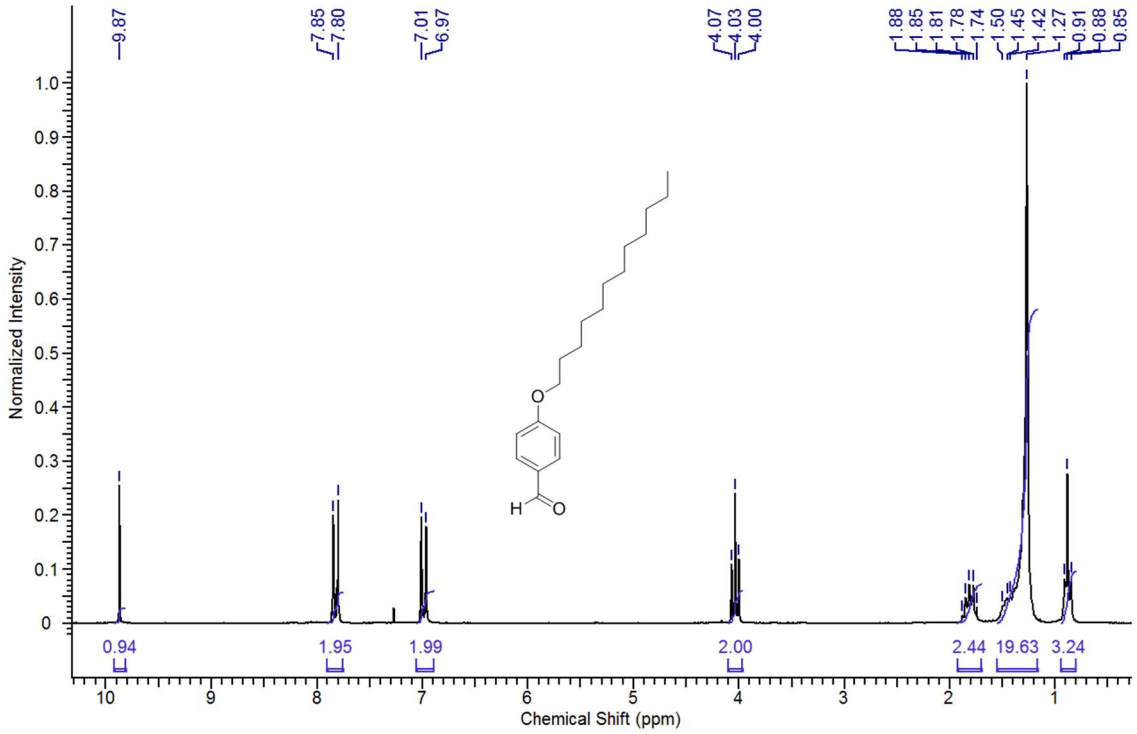


Figure S16: ^{1}H NMR (200 MHz) spectrum of Compound R4 in $CDCl_3$

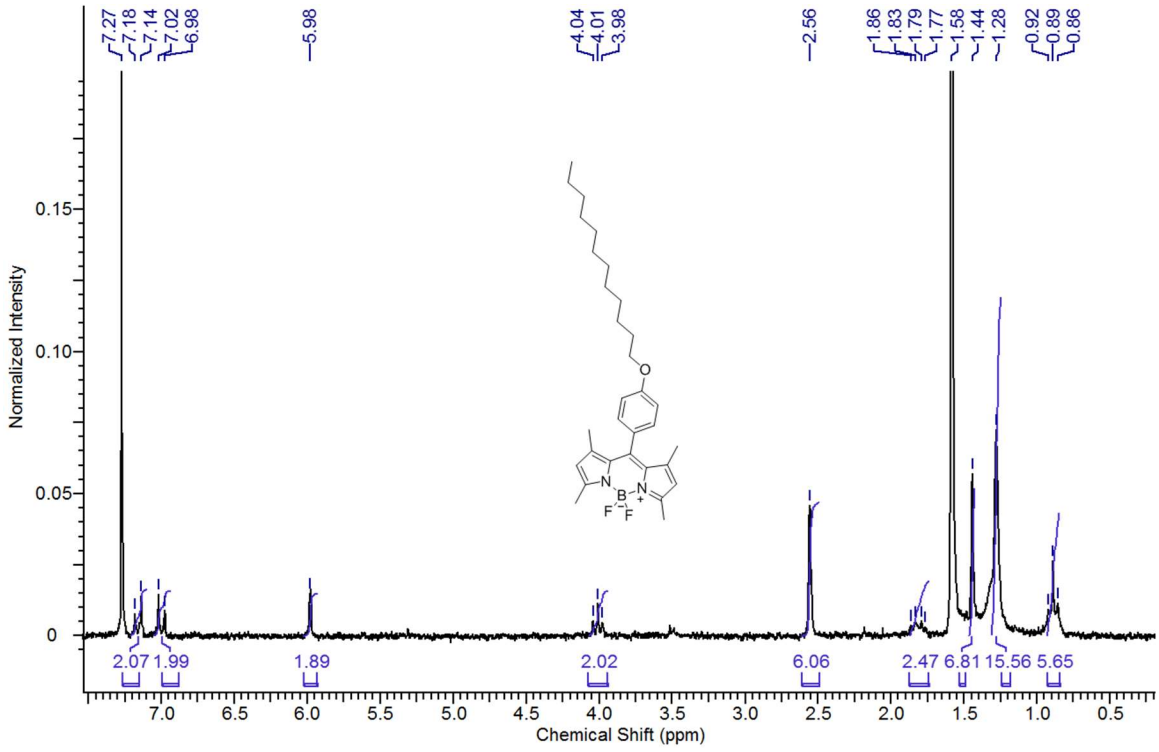


Figure S17: ^{1}H NMR (200 MHz) spectrum of Compound R5 in $CDCl_3$

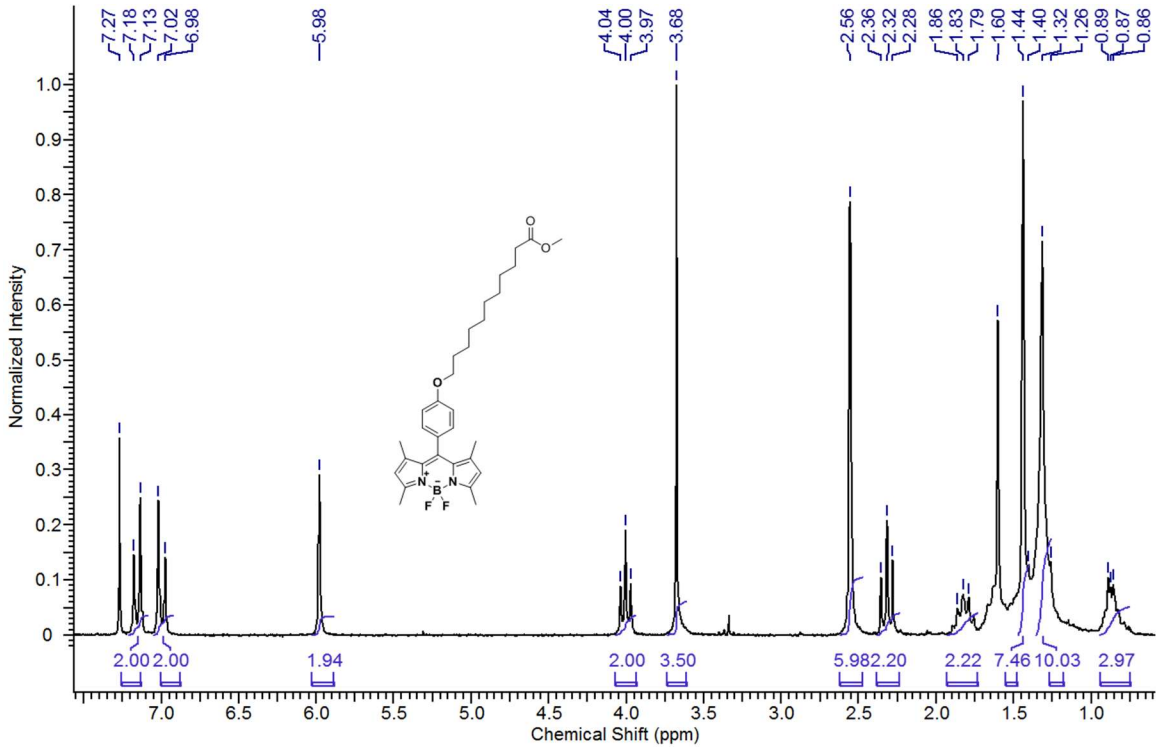


Figure S18: ^{1}H NMR (200 MHz) spectrum of Compound R7 in $CDCl_3$

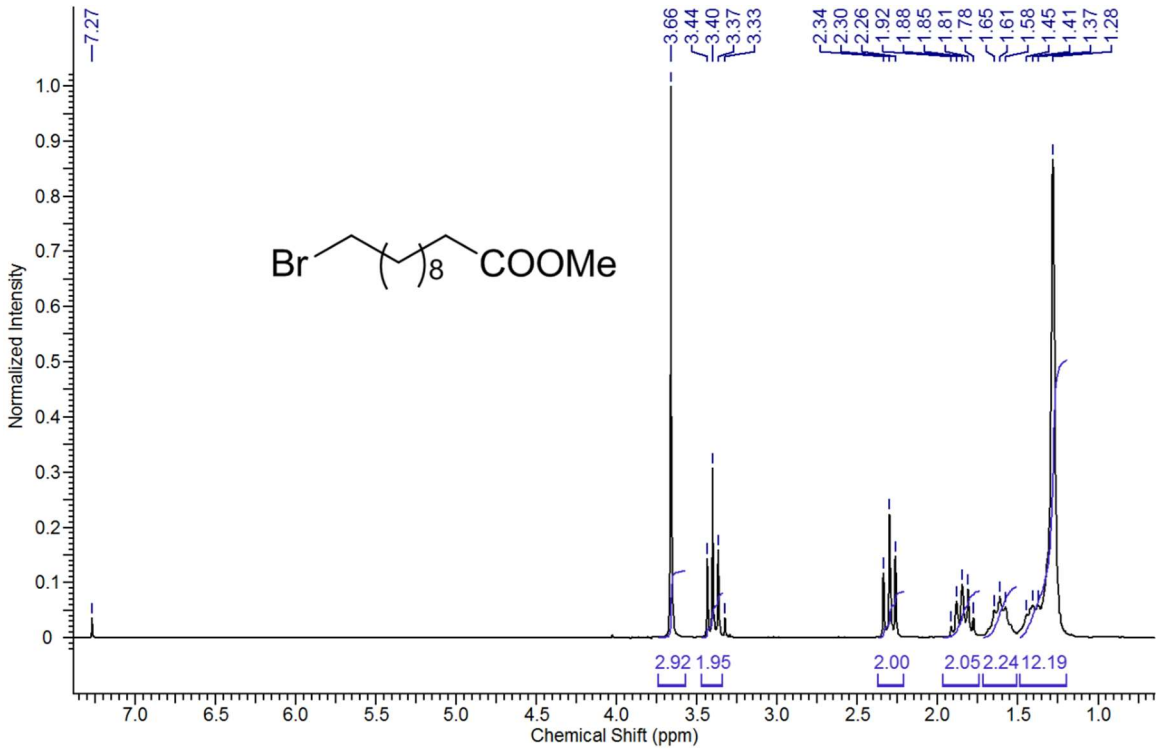


Figure S19: ^{1}H NMR (200 MHz) spectrum of methyl 11-bromoundecanoate in $CDCl_3$.

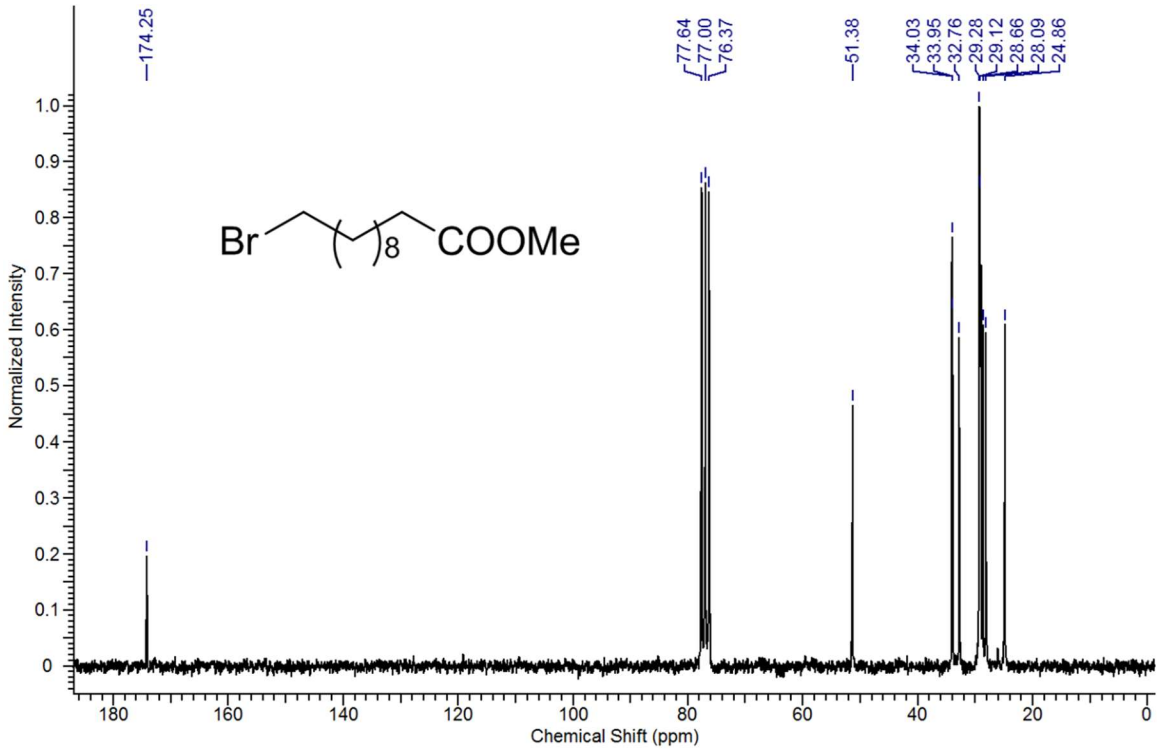


Figure S20: ^{13}C NMR (50 MHz) spectrum of methyl 11-bromoundecanoate in $CDCl_3$.

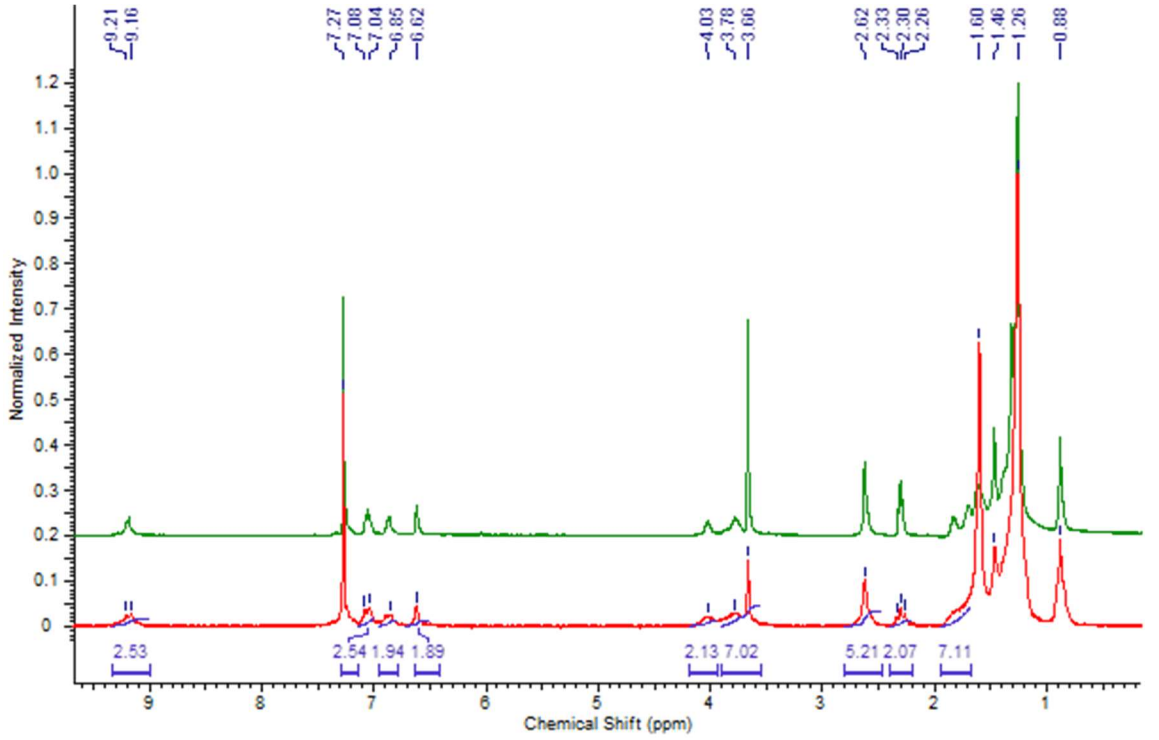


Figure S21: ^{1}H NMR (400 MHz) spectrums of polymers P1 (red) and P2 (green) in $CDCl_3$.