Supporting Information for

Functionalized Poly(3-hexylthiophene)s via Lithium-Bromine Exchange

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Contents

Characterization

Data for poly(3-bromo-4-hexylthiophene) (1). After following the previous literature (Li, Y.; Vamvounis, G.; Holdcroft, S. *Macromolecules* **2001**, 34, 141-143), yellow polymer was obtained with 99% yield based on 100% bromination. Four different batches of Br-P3HTs were used throughout the paper. #1 (33,000 g/mol, M_w/M_n = 2.05, starting from commercial P3HT with 41,000 g/mol, M_w/M_n = 2.16), #2 (27,000 g/mol, M_w/M_n = 1.82, starting from commercial P3HT with 28,000 g/mol, M_w/M_n = 1.86), #3 (26,000 g/mol, M_w/M_n = 1.80, starting from commercial P3HT with 28,000 g/mol, M_w/M_n = 1.86), and #4 (39,000 g/mol, M_w/M_n = 1.99, starting from commercial P3HT with 33,000 g/mol, M_w/M_n = 2.03)). Anal. Calcd for $C_{10}H_{13}BrS$ (#4): C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 48.38; H, 5.09; N, 0.38; Br, 33.40; S, 12.35.

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)] (3a). Starting from Br-P3HT #3 (30 mg, M_n 26,000 g/mol, M_w/M_n = 1.80) and using methanol (excess) as an electrophile, **3a** was obtained (14.4 mg, average repeat unit molecular weight 187.58 g/mol, 62 % yield). GPC: M_n 15,000 g/mol, M_w/M_n = 3.01; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04–6.98 (m, 0.73H), 2.86–2.62 (bm, 2H), 1.69 (bm, 2H), 1.43–1.28 (bm, 6H), 0.91 (bm, 3H); IR (cm^{-1}): 1726 (C-Br), 1458 (thiophene); Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 66.33; H, 7.43; N, 0.39; Br, 6.65; S, 16.69.

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)] (3b). Starting from Br-P3HT #3 (30 mg, M_n 26,000 g/mol, M_w/M_n = 1.80) and using methanol (excess) as an electrophile, **3b** was obtained (16.5 mg, average repeat unit molecular weight 172.59 g/mol, 78 % yield). GPC: M_n 28,000 g/mol, M_w/M_n = 9.43; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 0.92H), 2.81–2.57 (bm, 2H), 1.71 (bm, 2H), 1.44–1.35 (bm, 6H), 0.91 (bm, 3H); IR (cm^{-1}): 1725 (C-Br), 1463 (thiophene); Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 71.06; H, 8.33; N, 0.27; Br, 1.02; S, 16.92.

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)] (3c). Starting from Br-P3HT #3 (30 mg, M_n 26,000 g/mol, M_w/M_n = 1.80) and using methanol (excess) as an electrophile, **3c** was obtained (17.9 mg, average repeat unit molecular weight 171.01 g/mol, 86 % yield). GPC: M_n 41,000 g/mol, M_w/M_n = 7.39; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 0.94H), 2.81–2.57 (bm, 2H), 1.71 (bm, 2H), 1.44–1.35 (bm, 6H), 0.91 (bm, 3H); IR (cm^{-1}): 1725 (C-Br), 1464 (thiophene); Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 71.57; H, 8.59; N, < 0.02; Br, 0.64; S, 17.53.

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)] (3d). Starting from Br-P3HT #3 (30 mg, M_n 26,000 g/mol, M_w/M_n = 1.80) and using methanol (excess) as an electrophile, **3d** was obtained (18.9 mg, average repeat unit molecular weight 169.44 g/mol, 91 % yield). GPC: M_n 24,000 g/mol, M_w/M_n = 13.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 0.96H), 2.81–2.57 (bm, 2H), 1.71 (bm, 2H), 1.44–1.35 (bm, 6H), 0.91 (bm, 3H); IR (cm^{-1}): 1726 (C-Br), 1464 (thiophene); Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 71.53; H, 8.27; N, 0.39; Br, 0.42; S, 17.38.

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(3-hexylthiophene-4-*d*)] (4). Starting from Br-P3HT #2 (30 mg, M_n 27,000 g/mol, M_w/M_n = 1.82) and using methanol-d4 (excess) as

an electrophile, **4** was obtained (average repeat unit molecular weight 171.72 g/mol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 0.24H), 2.81–2.57 (bm, 2H), 1.71 (bm, 2H), 1.44–1.35 (bm, 6H), 0.92 (bm, 3H).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(1-(4-hexylthiophen-3-yl)ethan-1-one)] (5). Starting from Br-P3HT #2 (30 mg, M_n 27,000 g/mol, M_w/M_n = 1.82) and using acetic anhydride (10 eq., 0.116 mL) as an electrophile, **5** was obtained (26.0 mg, average repeat unit molecular weight 196.24 g/mol, quantitative yield). GPC: M_n 22,000 g/mol, M_w/M_n = 3.86; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06–7.00 (bm, 0.34H), 2.81–2.56 (bm, 2H), 2.21 (bs, 1.81H), 1.68 (bm, 2H), 1.41–1.31 (bm, 6H), 0.87 (bm, 3H); IR (cm^{-1}):1686 (carbonyl), 1458 (thiophene); UV-vis (CH_2Cl_2): λ_{max} 277, 379 nm; Fluorescence (CH_2Cl_2): λ_{max} 549 nm (Ex. 350 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(1-(4-hexylthiophen-3-yl)hexan-1-one)] (6). Starting from Br-P3HT #1 (30 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) and using hexanoic anhydride (10 eq., 0.28 mL) as an electrophile, **6** was obtained (27.7 mg, average repeat unit molecular weight 231.46 g/mol, 98% yield). GPC: M_n 64,000 g/mol, M_w/M_n = 3.13; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04–6.98 (bm, 0.33H), 2.78–2.56 (bm, 2H), 2.44–2.28 (bm, 1.28H), 1.68–1.54 (bm), 1.39–1.28 (bm), 0.87–0.86 (bm); IR (cm^{-1}): 1688 (carbonyl), 1464 (thiophene); UV-vis (CH_2Cl_2): λ_{max} 256, 386 nm; Fluorescence (CH_2Cl_2): λ_{max} 551 nm (Ex. 350 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(1-(4-hexylthiophen-3-yl)-3-methylbutan-1-one)] (7). Starting from Br-P3HT #1 (30 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) and using isovaleric anhydride (10 eq., 0.245 mL) as an electrophile, **7** was obtained (27.3 mg, average repeat unit molecular weight 220.59 g/mol, quantitative yield). GPC: M_n 64,000 g/mol, M_w/M_n = 2.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04–6.98 (bm, 0.35H), 2.77–2.60 (bm, 2H), 2.34–2.33 (bm, 1.16H), 2.10 (bm), 1.68–1.58 (bm, 2H), 1.42–1.27 (bm), 0.85–0.83 (bm); IR (cm^{-1}): 1688 (carbonyl), 1465 (thiophene); UV-vis (CH_2Cl_2): λ_{max} 387 nm; Fluorescence (CH_2Cl_2): λ_{max} 554 nm (Ex. 350 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(2,2,2-trifluoro-1-(4-hexylthiophen-3-yl)ethan-1-one)] (8). Starting from Br-P3HT #1 (31.1 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) and using trifluoroacetic anhydride (10 eq., 0.176 mL) as an electrophile, **8** was obtained (28.7 mg, average repeat unit molecular weight 220.87 g/mol, quantitative yield). GPC: M_n 33,000 g/mol, M_w/M_n = 5.50; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07–6.99 (bm, 0.41H), 2.76–2.60 (bm, 2H), 1.68–1.60 (bm, 2H), 1.41–1.29 (bm, 6H), 0.88 (bm, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.38 (bm); IR (cm^{-1}): 1798 (carbonyl), 1202 (CF_3), 1157 (CF_3); UV-vis (CH_2Cl_2): λ_{max} 278, 387 nm; Fluorescence (CH_2Cl_2): λ_{max} 576 nm (Ex. 350 nm); Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Calcd for $C_{12}H_{13}F_3OS$: C, 54.95; H, 5.00; F, 21.73; O, 6.10; S, 12.22. Found: C, 59.88; H, 6.12; N, < 0.02; Br, 3.55; F, 11.67; S, 13.62.

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-((4-hexylthiophen-3-yl)(phenyl)methanone)] (9). Starting from Br-P3HT #1 (30 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) and using benzoic anhydride (10 eq., 277 mg pre-dissolved in 1 mL THF) as an electrophile, **9** was obtained (25.6 mg, average repeat unit molecular weight 230.39 g/mol, 91% yield). GPC: M_n 55,000 g/mol, M_w/M_n = 2.04; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.32 (bm, 2.69H), 6.98–6.73 (bm, 0.36H), 2.80–2.29 (bm, 2H), 1.68–1.51 (bm, 2H), 1.40–1.19 (bm, 6H), 0.90–0.82 (bm, 3H); IR (cm^{-1}): 1663 (carbonyl), 1597 (phenyl), 1449 (thiophene); UV-vis (CH_2Cl_2): λ_{max} 250, 279, 397 nm; Fluorescence (CH_2Cl_2): λ_{max} 562 nm (Ex. 360 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-((4-hexylthiophen-3-yl)(p-tolyl)methanone)] (10). Starting from Br-P3HT #1 (30 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) using 4-methylbenzoic anhydride (10 eq., 311 mg pre-dissolved in 1 mL THF) as an electrophile, **10** was obtained (30.5 mg, average repeat unit molecular weight 238.35 g/mol based on x = 0.37, y = 0.06, z = 0.57, quantitative yield). GPC: M_n 62,000 g/mol, M_w/M_n = 1.83; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.05 (bm), 6.98–6.75 (bm, 0.37H), 2.79–2.33 (bm), 1.70–1.10 (bm, 8H), 0.90–0.81 (bm, 3H); IR (cm^{-1}): 1660 (carbonyl), 1605 (phenyl), 1457 (thiophene); UV-vis (CH_2Cl_2): λ_{max} 266, 390 nm; Fluorescence (CH_2Cl_2): λ_{max} 566 nm (Ex. 360 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-((4-hexylthiophen-3-yl)(4-methoxyphenyl)methanone)] (11). Starting from Br-P3HT #1 (30 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) and using 4-methoxybenzoic anhydride (10eq., 350 mg pre-dissolved in 1 mL THF) as an electrophile, **11** was obtained (31.1 mg, average repeat unit molecular weight 259.78 g/mol, 98% yield). GPC: M_n 63,000 g/mol, M_w/M_n = 1.84; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (bm, 0.65H), 7.41 (bm, 0.65H), 6.97 (bm, 0.27H), 6.80 (bm, 1.30H), 3.82 (bs, 1.94H), 2.79–2.33 (bm, 2H), 1.68–1.17 (bm, 8H), 0.89–0.81 (bm, 3H); IR (cm^{-1}): 1655 (carbonyl), 1598 (methoxy phenyl), 1509 (methoxy phenyl), 1460 (thiophene); UV-vis (CH_2Cl_2): λ_{max} 286, 397 nm; Fluorescence (CH_2Cl_2): λ_{max} 557 nm (Ex. 365 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(1-(4-hexylthiophen-3-yl)butan-1-ol)] (12). Starting from Br-P3HT #2 (30 mg, M_n 27,000 g/mol, M_w/M_n = 1.82) and using butyraldehyde (10eq., 0.11 mL) as an electrophile, **12** was obtained (22.5 mg, average repeat unit molecular weight 216.47 g/mol, 85% yield). GPC: M_n 18,000 g/mol, M_w/M_n = 4.19; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (bm, 0.32H), 4.78 (bm, 0.51H), 2.92–2.54 (bm, 2H), 1.88 (bm, 1.02H), 1.69–1.31 (bm, 9.02H), 0.88 (bm, 4.53H); IR (cm^{-1}): 3436 (hydroxyl), 1464 (thiophene); UV-vis ($CHCl_3$): λ_{max} 258, 360 nm; Fluorescence ($CHCl_3$): λ_{max} 536 nm (Ex. 330 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-((4-hexylthiophen-3-yl)(4-methoxyphenyl)methanol)] (13). Starting from Br-P3HT #1 (30 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) and using 4-methoxybenzaldehyde (10 eq., 0.15 mL) as an electrophile, **13** was obtained (26.6 mg, average repeat unit molecular weight 256.00 g/mol, 85% yield). GPC: M_n 57,000 g/mol, M_w/M_n = 4.24; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (bm), 6.97 (bm, 0.32H), 6.82 (bm), 5.94 (bs), 3.84 (bs), 3.77 (bm), 2.75–2.27 (bm, 2H), 1.65–1.04 (bm, 8H), 0.86–0.81 (bm, 3H); IR (cm^{-1}): 3497 (hydroxyl), 1599 (methoxy phenyl), 1510 (methoxy phenyl), 1463 (thiophene); UV-vis (CH_2Cl_2): λ_{max} 276, 297, 349 nm; Fluorescence (CH_2Cl_2): λ_{max} 532 nm (Ex. 335 nm).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-((4-hexylthiophen-3-yl)(5-methylfuran-2-yl)methanol)] (14). Starting from Br-P3HT #2 (30 mg, M_n 27,000 g/mol, M_w/M_n = 1.82) and using 5-methylfurfural (10 eq., 0.12 mL) as an electrophile, **14** was obtained (31 mg, average repeat unit molecular weight 232.53 g/mol, quantitative yield). GPC: M_n 14,000 g/mol, M_w/M_n = 1.99; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98–6.88 (bm, 0.37H), 6.04–5.59 (bm), 2.79–2.35 (bm, 2H), 2.26 (bs), 1.67–1.24 (bm, 8H), 0.86 (bm, 3H); IR (cm^{-1}): 3445 (hydroxyl), 1684 (furan), 1511 (furan), 1458 (thiophene).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-((4-hexylthiophen-3-yl)trimethylsilane)] (15). Starting from Br-P3HT #1 (30 mg, M_n 33,000 g/mol, M_w/M_n = 2.05) and using trimethylsilyl chloride (10 eq., 0.155 mL) as an electrophile, **15** was obtained (20.8 mg, average repeat

unit molecular weight 212.02 g/mol, 80% yield). GPC: M_n 32,000 g/mol, M_w/M_n = 5.83; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (bs, 0.37H), 2.85–2.50 (bm, 2H), 1.68–1.58 (bm, 2H), 1.41–1.28 (bm, 6H), 0.87 (bm, 3H), 0.16 (bm); IR (cm^{-1}): 1465 (thiophene), 837 (Si-C).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(3-fluoro-4-hexylthiophene)] (16). Starting from Br-P3HT #3 (30 mg, M_n 26,000 g/mol, M_w/M_n = 1.80) and using *N*-fluorobenzenesulfonimide (10 eq., 0.386 mg pre-dissolved in 2 mL THF), **16** was obtained (22 mg, average repeat unit molecular weight 180.70 g/mol, 99% yield). GPC: M_n 17,000 g/mol, M_w/M_n = 1.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (bm, 0.30H), 2.79–2.59 (bm, 2H), 1.65 (bm, 2H), 1.40–1.33 (bm, 6H), 0.90 (bm, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -123.60 (bs); IR (cm^{-1}): 1464 (thiophene); UV-vis ($CHCl_3$): λ_{max} 266, 419 nm; UV-vis (thin film): λ_{max} 491 nm; Fluorescence ($CHCl_3$): λ_{max} 554 nm (Ex. 380 nm); Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Calcd for $C_{10}H_{13}FS$: C, 65.18; H, 7.11; F, 10.31; S, 17.40. Found: C, 60.19; H, 6.56; N, 0.64; Br, 1.11; F, 8.81; S, 14.57.

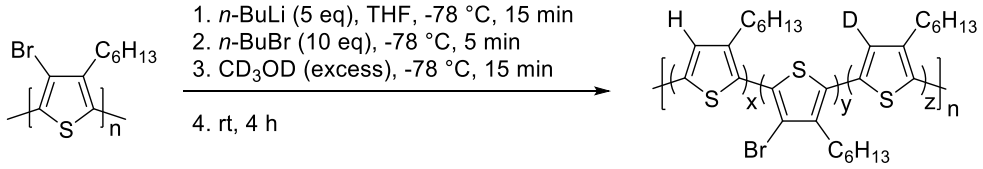
Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(3-azido-4-hexylthiophene)] (17). Starting from Br-P3HT #2 (30 mg, M_n 27,000 g/mol, M_w/M_n = 1.82) and using *p*-toluenesulfonyl azide solution (11-15 % (w/w) in toluene, 10 eq., 2.06 mL added based on the assumption of 13 % (w/w) in toluene) as an electrophile, followed by either glacial acetic acid (10 eq., 0.068 mL) or HCl (10 eq., 3 M, 0.4 mL) quenching, **17** was obtained (29.1 mg from HCl quenching). IR (cm^{-1}): 2105 (azide), 1457 (thiophene). As a result of acidic workup and excess tosyl azide, hydrazoic acid might be formed, and thus, cautions need to be taken. When a large reaction scale needs to be performed, aqueous workup can also be carried out, according to the literature (Gavenonis, J.; Tilley, T. D. *Organometallics* **2002**, 21, 5549-5563).

Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(1-(4-hexylthiophen-3-yl)-4-(phenoxymethyl)-1*H*-1,2,3-triazole)] (18). Starting from the crude mixture of **17** (12.7 mg) with AcOH quenching, **18** was obtained (24 mg). IR (cm^{-1}): 1599 (triazole), 1494 (phenyl), 1457 (thiophene).

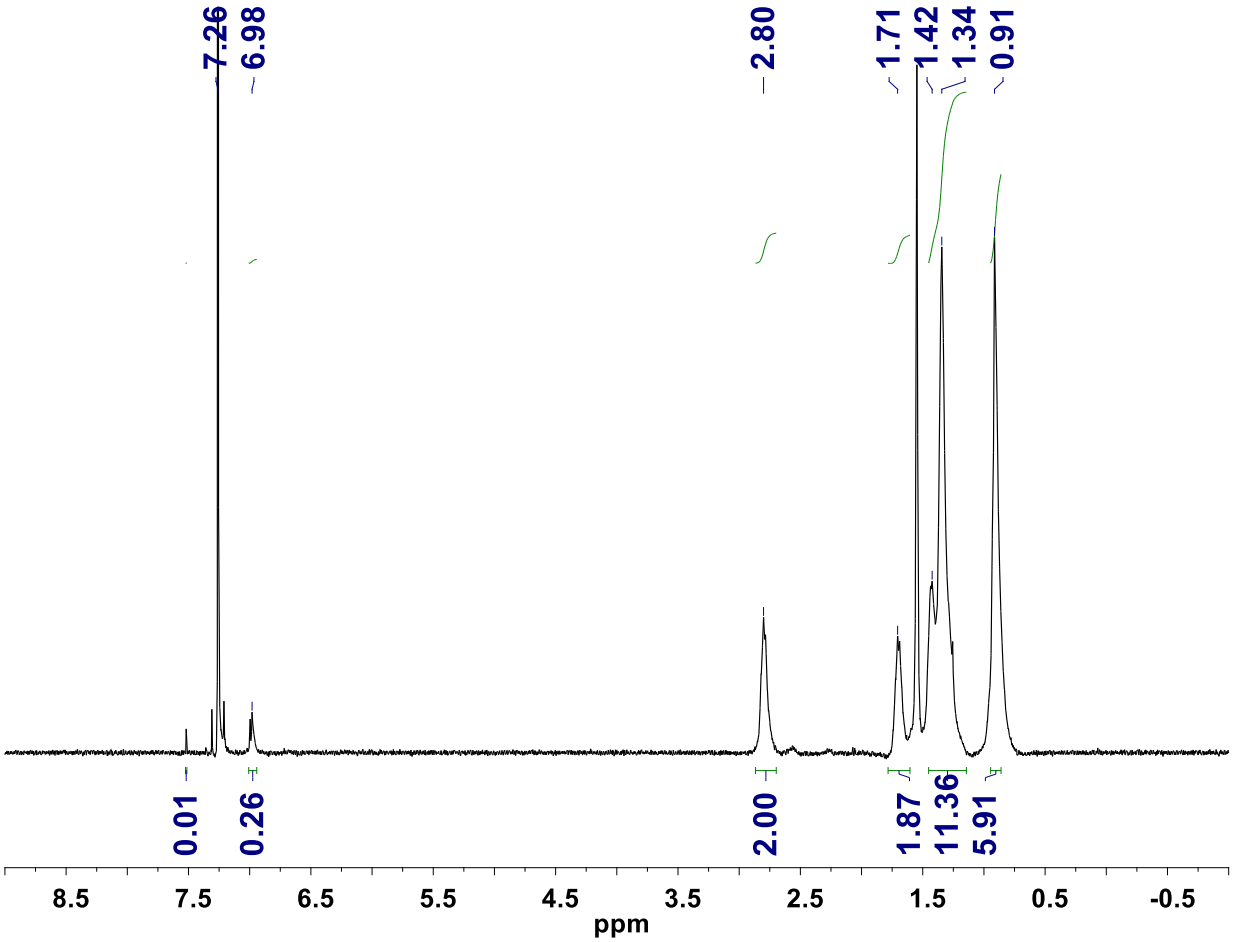
Data for poly[(3-hexylthiophene)-*ran*-(3-bromo-4-hexylthiophene)-*ran*-(4,4-difluoro-3-(4-hexylthiophen-3-yl)-4,5,6,7-tetrahydro-3*H*-benzo[3,4]cycloocta[1,2-*d*][1,2,3]triazole)] (19). Starting from Br-P3HT #2 (30 mg, M_n 27,000 g/mol, M_w/M_n = 1.82), the crude mixture of **17** was obtained, then difluorobenzocyclooctyne (**20**) was added to the mixture, resulting in **19** (39 mg). GPC: M_n 13,000 g/mol, M_w/M_n = 2.59; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (bm), 7.40 (bm), 6.98 (bm), 6.77 (bm), 2.79–2.41 (bm), 2.06 (bm), 1.66–1.30 (bm), 0.86 (bm); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.58 (bm), -90.06 (bm); IR (cm^{-1}): 1611–1570 (triazole), 1493 (phenyl), 1458 (thiophene).

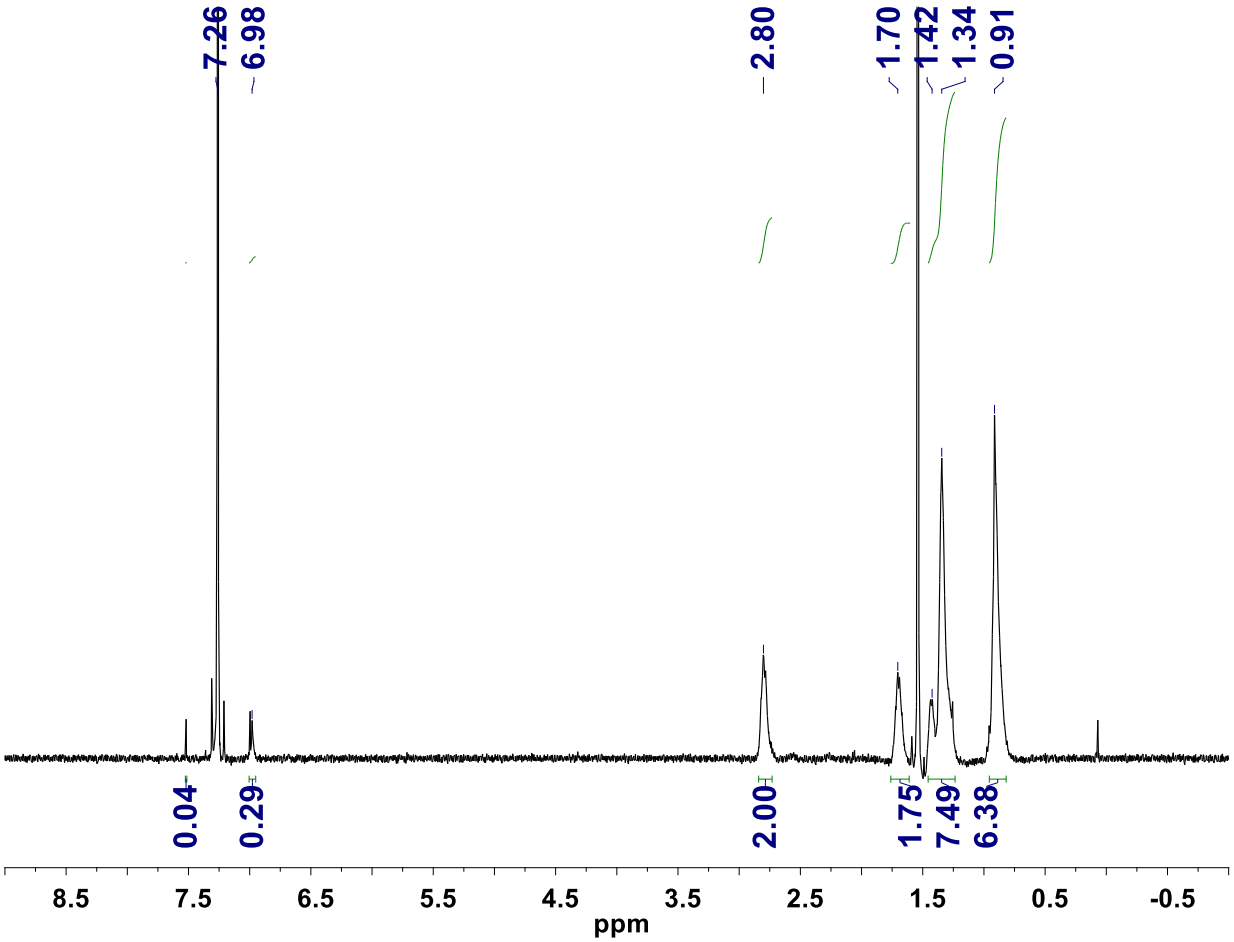
Control Experiments with *n*-Butyl Bromide

In the deuterated methanol quenching experiment (**4**), there were 24% proton (H) back at the 4-position of P3HT. Although this proton might come from E2-elimination of *n*-butyl bromide by lithiated P3HT, our control experiments described in the following scheme showed that E2-elimination did not occur.



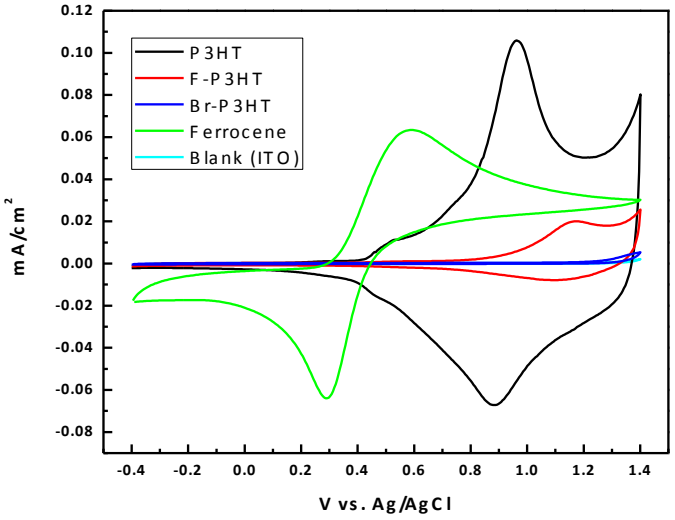
The key experimental design is to add 10 equivalent of *n*-BuBr after Li-Br has occurred and before quenching with deuterated methanol. If E2-elimination would occur, there could be more protons back at the 4-position than 24% which is without *n*-BuBr addition. The *n*-BuBr used here was purified by stirring it for 4 hours under K_2CO_3, followed by distillation in order to remove any proton impurities. Two independent reactions with the identical reaction condition were carried out in order to best assess whether E2-elimination would occur or not. Two NMR spectra are shown in the below.


7.26
6.98
2.80
1.71
1.42
1.34
0.91
0.01
0.26
2.00
1.87
11.36
5.91
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
ppm



The recovered 4-position protons appeared at 6.98 ppm, and after subtracting ^{13}C-^{1}H coupling satellite overlapped with the 4-position proton peak, we have seen that 25% protons are back in both independent experiments. This 25% is almost identical to the reaction in the paper (24%) without the addition of *n*-butyl bromide; that is, E2-elimination did not occur, and the recovered proton could be attributed to other proton sources as described in the paper. We think that at a low temperature (-78 ^{o}C) it would be hard to undergo E2 elimination, and subsequent electrophiles are much more reactive enough to quench all the polylithiates.

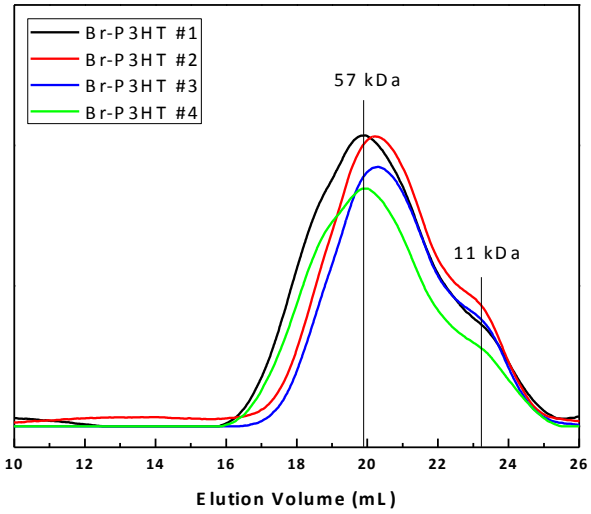
Cyclic Voltammetry Data



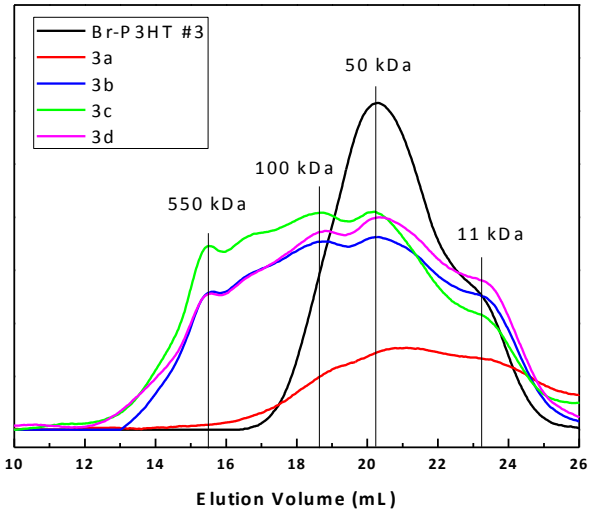
Cyclic voltammetry curves of P3HT (black), F-P3HT (red), Br-P3HT (blue), ferrocene (light green), and blank measured on bare ITO (light blue).

Gel Permeation Chromatography Traces

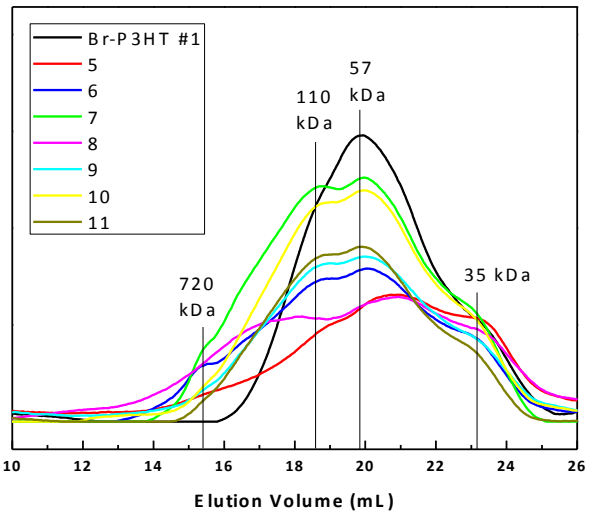
All the Gel Permeation Chromatography (GPC) traces are plotted here. First, Br-P3HT from batch #1 to batch #4 is shown below. All Br-P3HT traces exhibit similar shape. Number-averaged molecular weights of a few peaks are indicated.



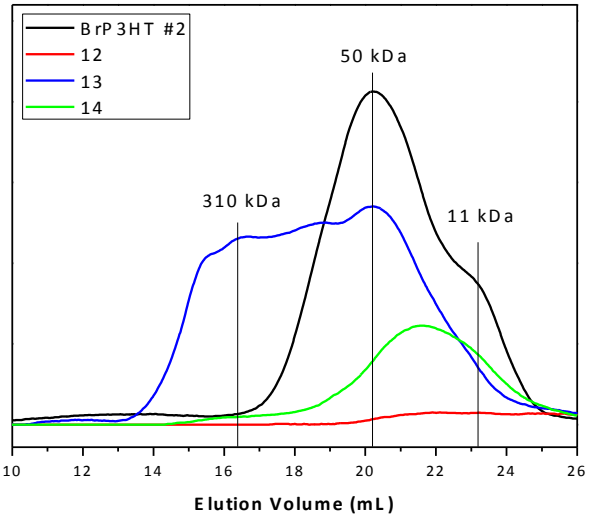
The GPC traces of compound **3a** – **3d** are plotted below. Their starting Br-P3HT #3 is also shown together. Number-averaged molecular weights of a few peaks are indicated.



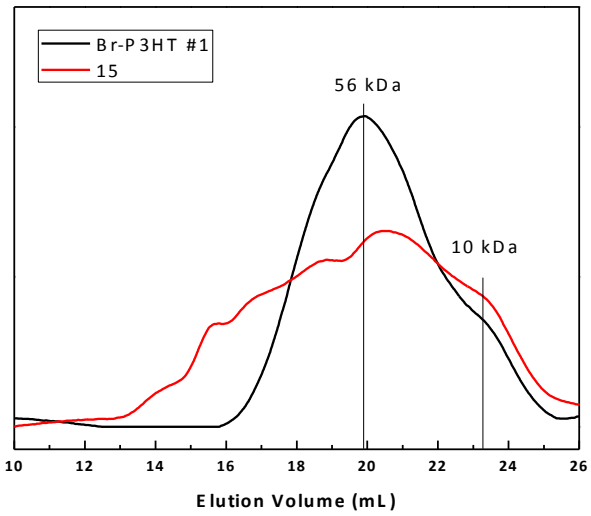
The GPC traces of ketone-functionalized P3HT (**5** – **11**) are shown below. The most frequently used Br-P3HT (#1 for ketone-functionalized P3HT) is plotted together for comparison. Number-averaged molecular weights of a few peaks are indicated.

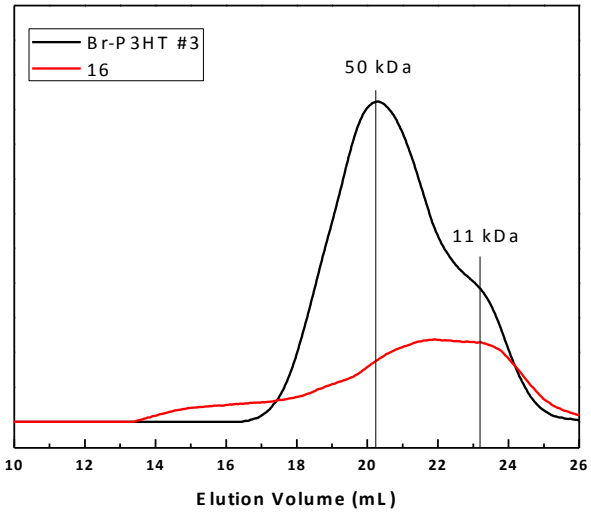


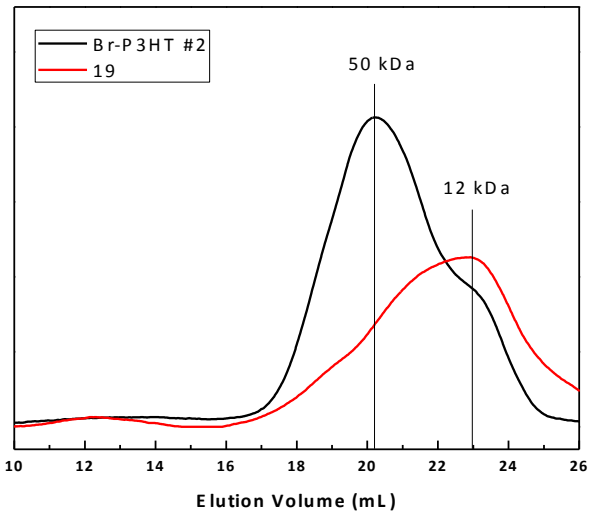
The GPC traces of secondary alcohol-functionalized P3HT (**12** – **14**) are shown below. The most frequently used Br-P3HT (#2 for secondary alcohol-functionalized P3HT) is plotted together for comparison. Number-averaged molecular weights of a few peaks are indicated.



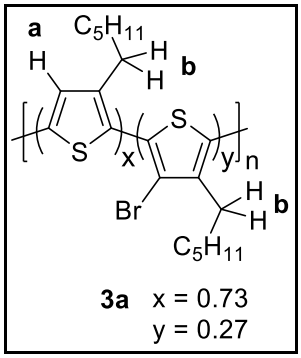
The GPC traces of 15, 16, and 19 are plotted below with their corresponding starting polymer Br-P3HT.


Br-P3HT #1
15
56 kDa
10 kDa
10
12
14
16
18
20
22
24
26
Elution Volume (mL)


Br-P3HT #3
16
50 kDa
11 kDa
10
12
14
16
18
20
22
24
26
Elution Volume (mL)


Br-P3HT #2
19
50 kDa
12 kDa
10
12
14
16
18
20
22
24
26
Elution Volume (mL)

^{1}H and ^{19}F NMR Spectra



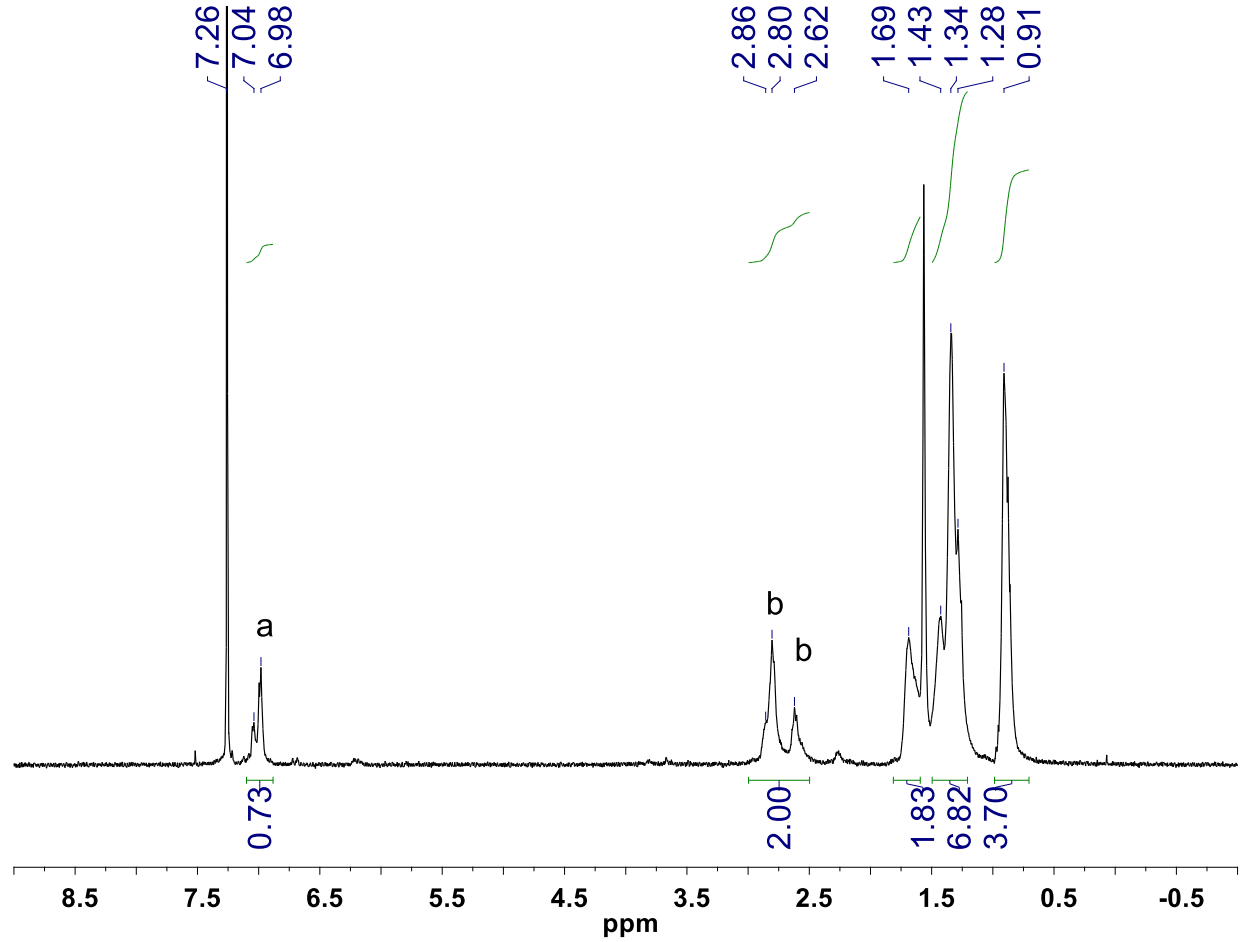
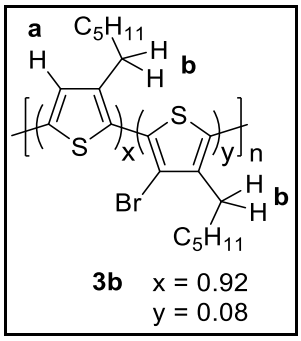


Figure S1. Compound **3a**.



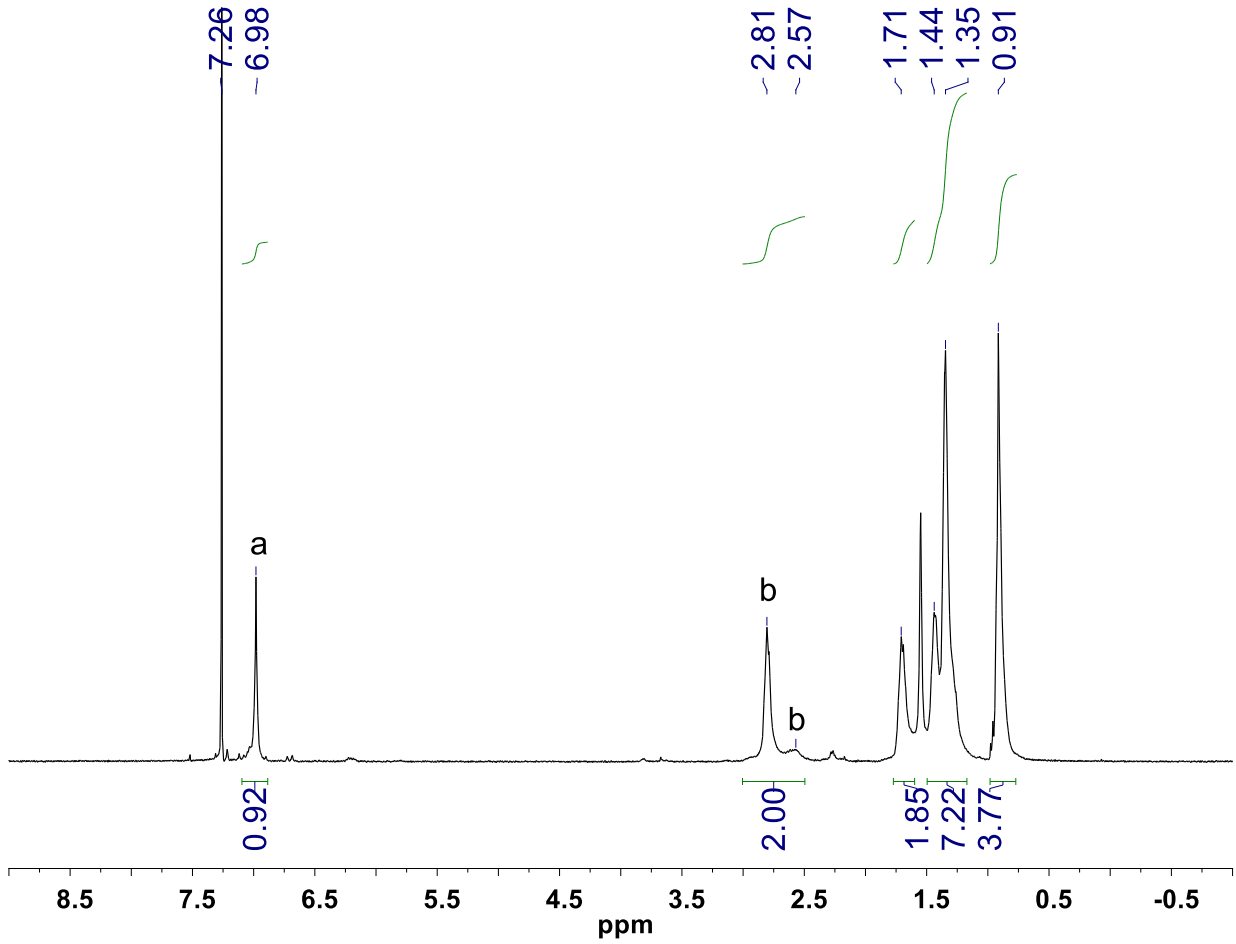
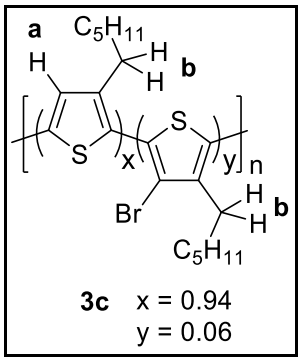


Figure S2. Compound **3b**.



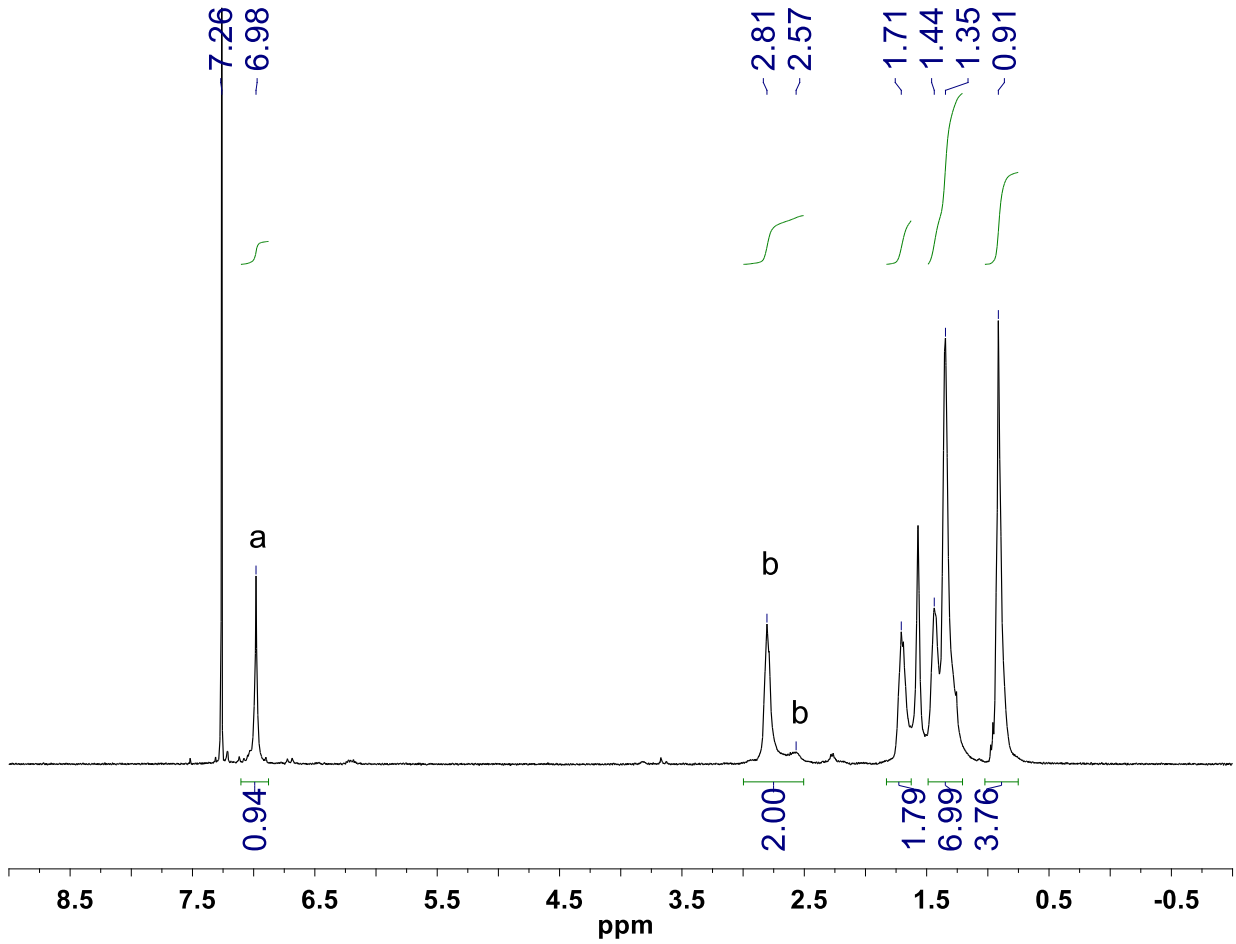
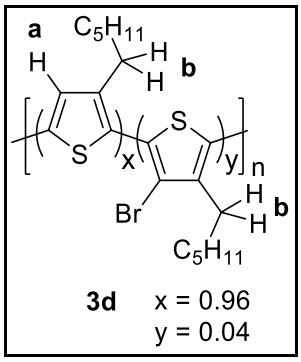


Figure S3. Compound **3c**.



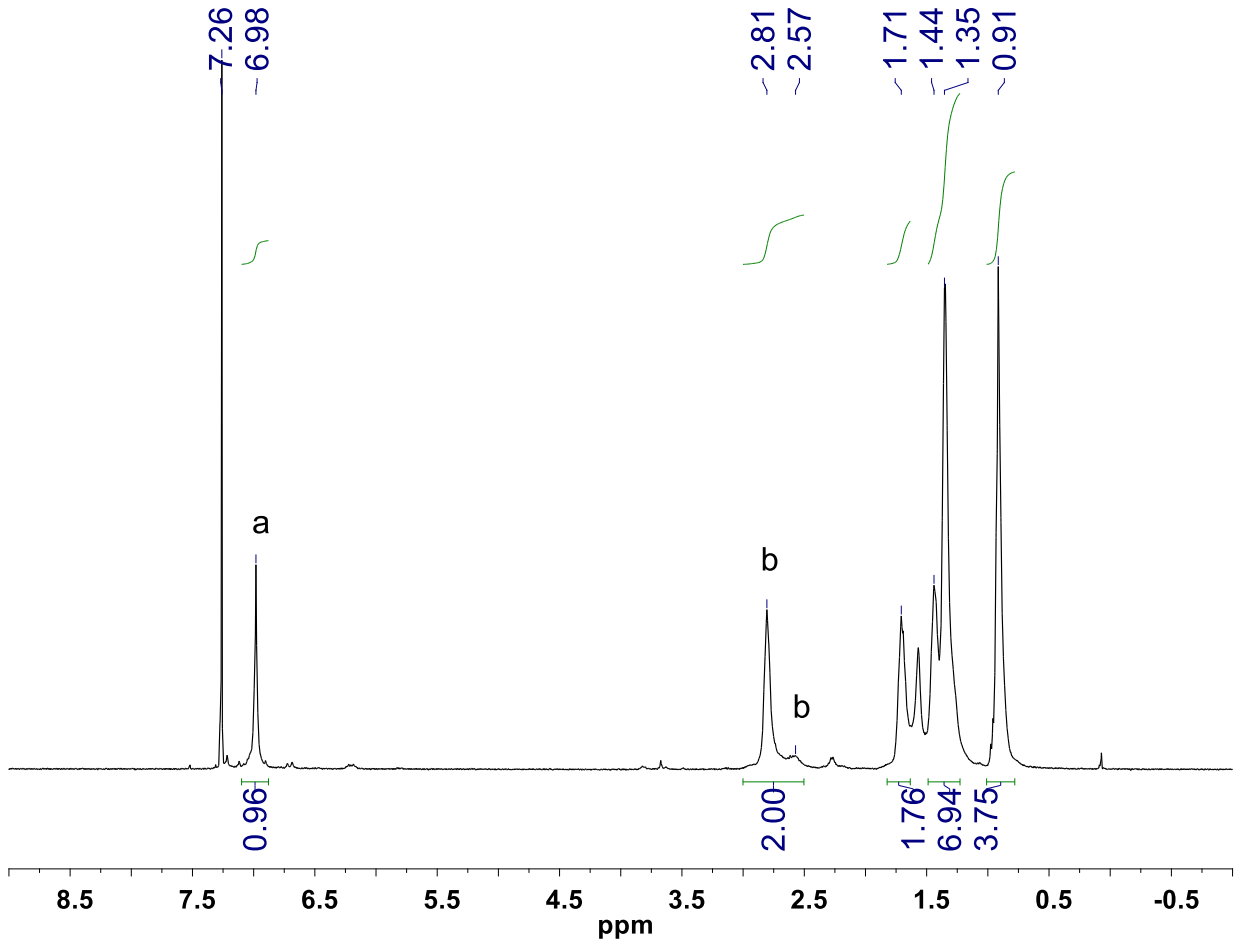
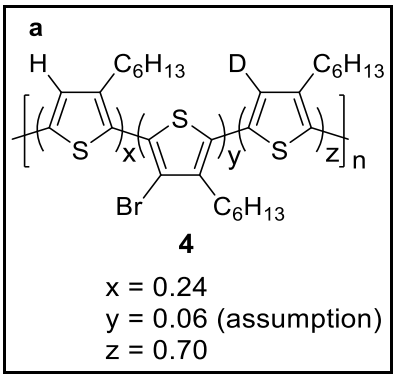


Figure S4. Compound **3d**.



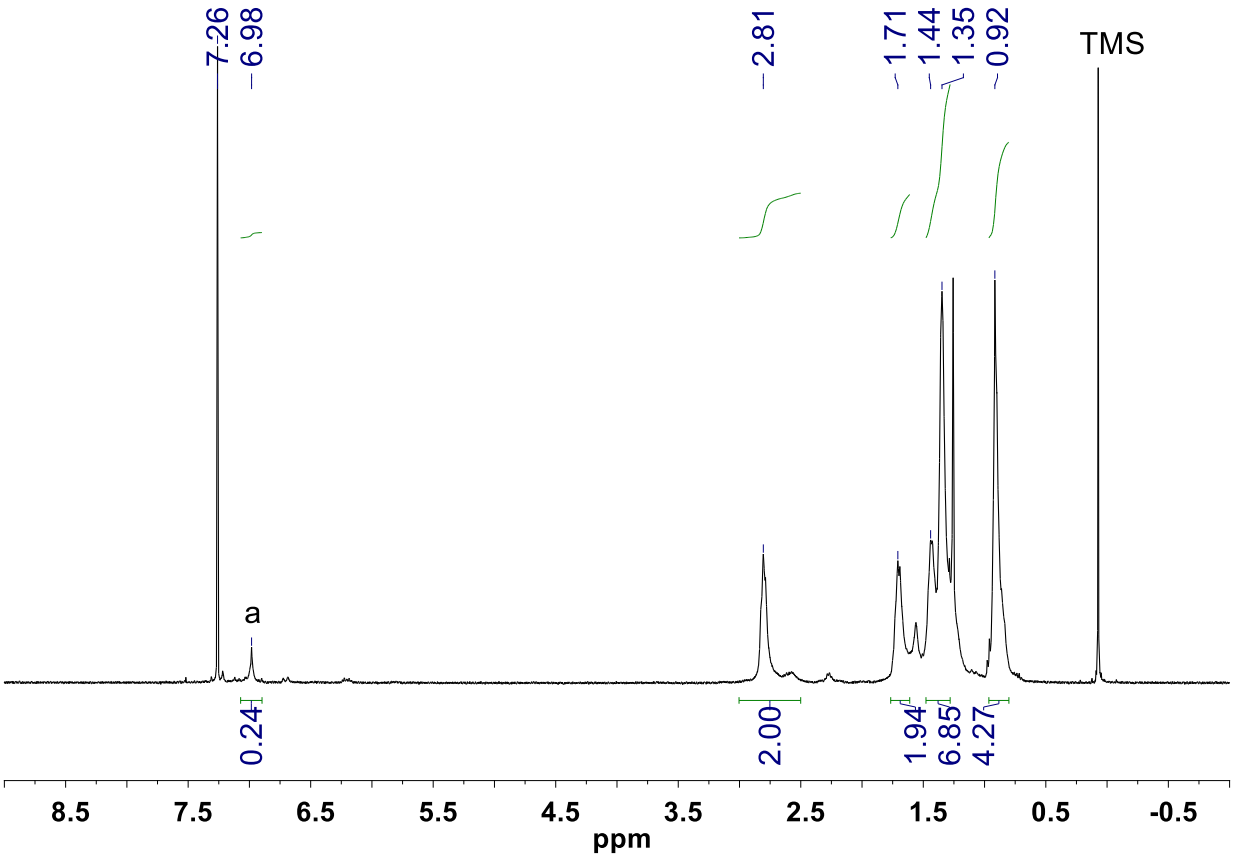
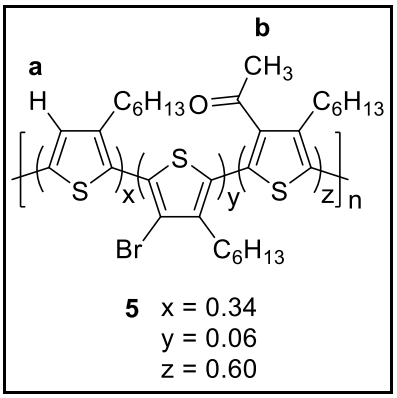


Figure S5. Compound **4**.



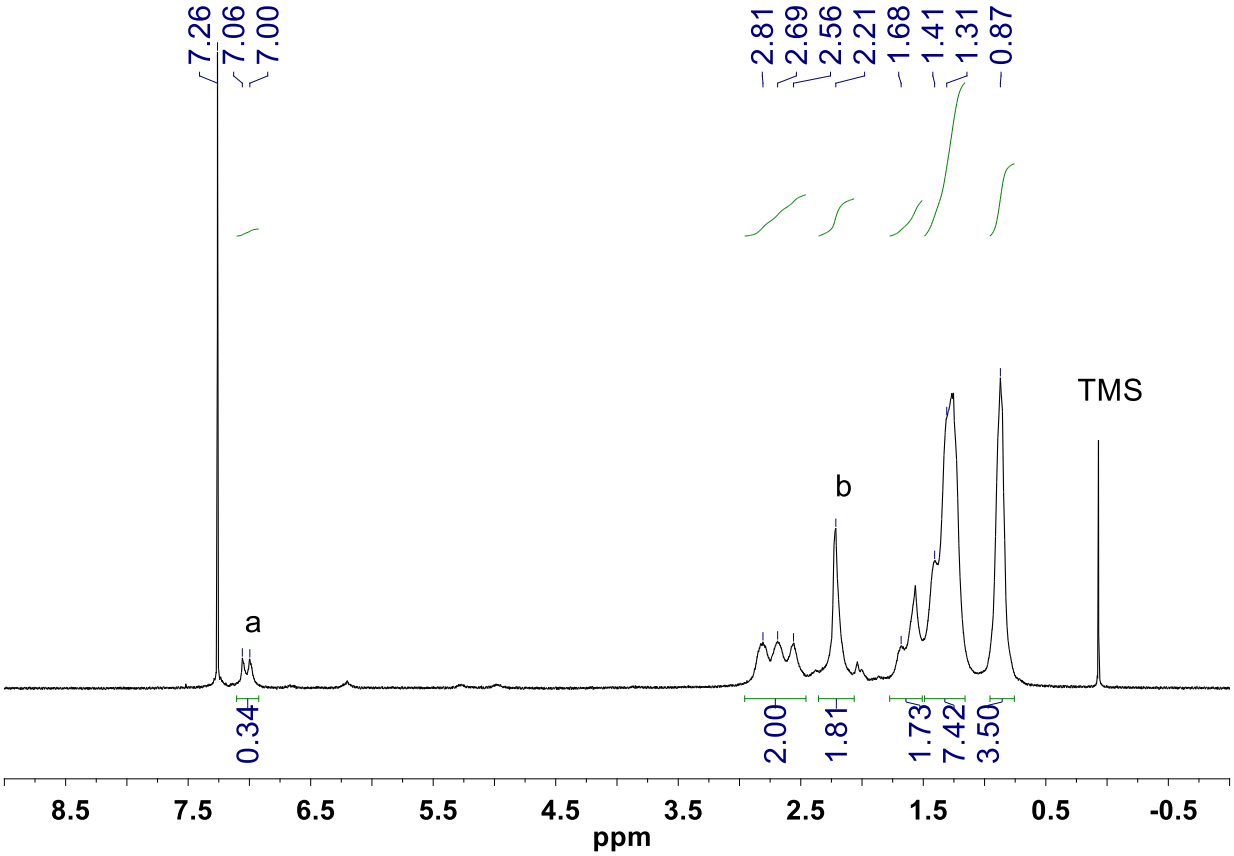


Figure S6. Compound **5**.

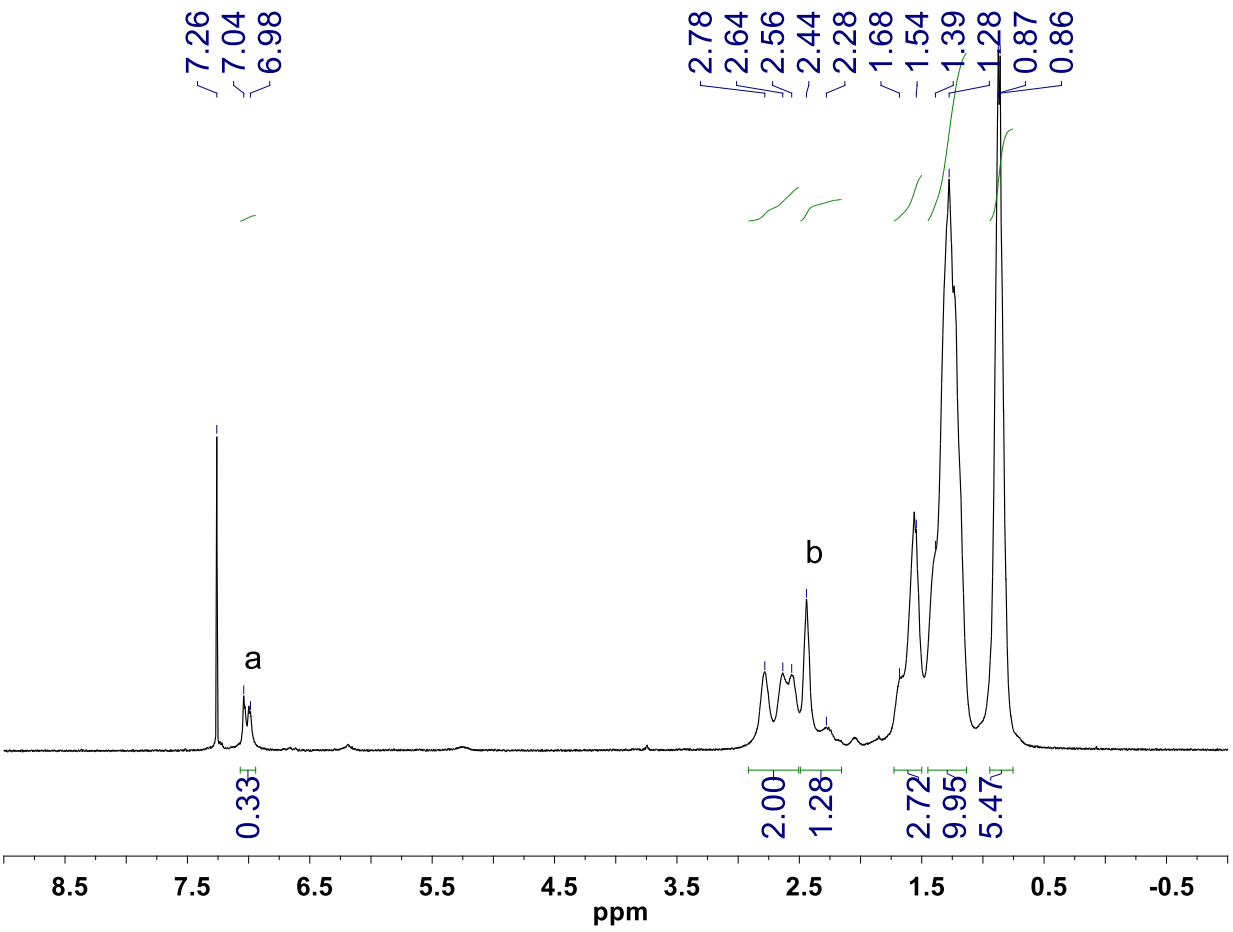
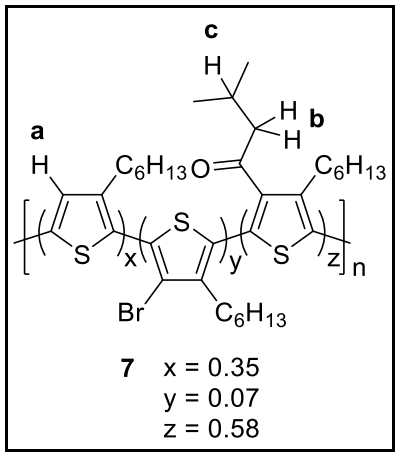


Figure S7. Compound **6**.



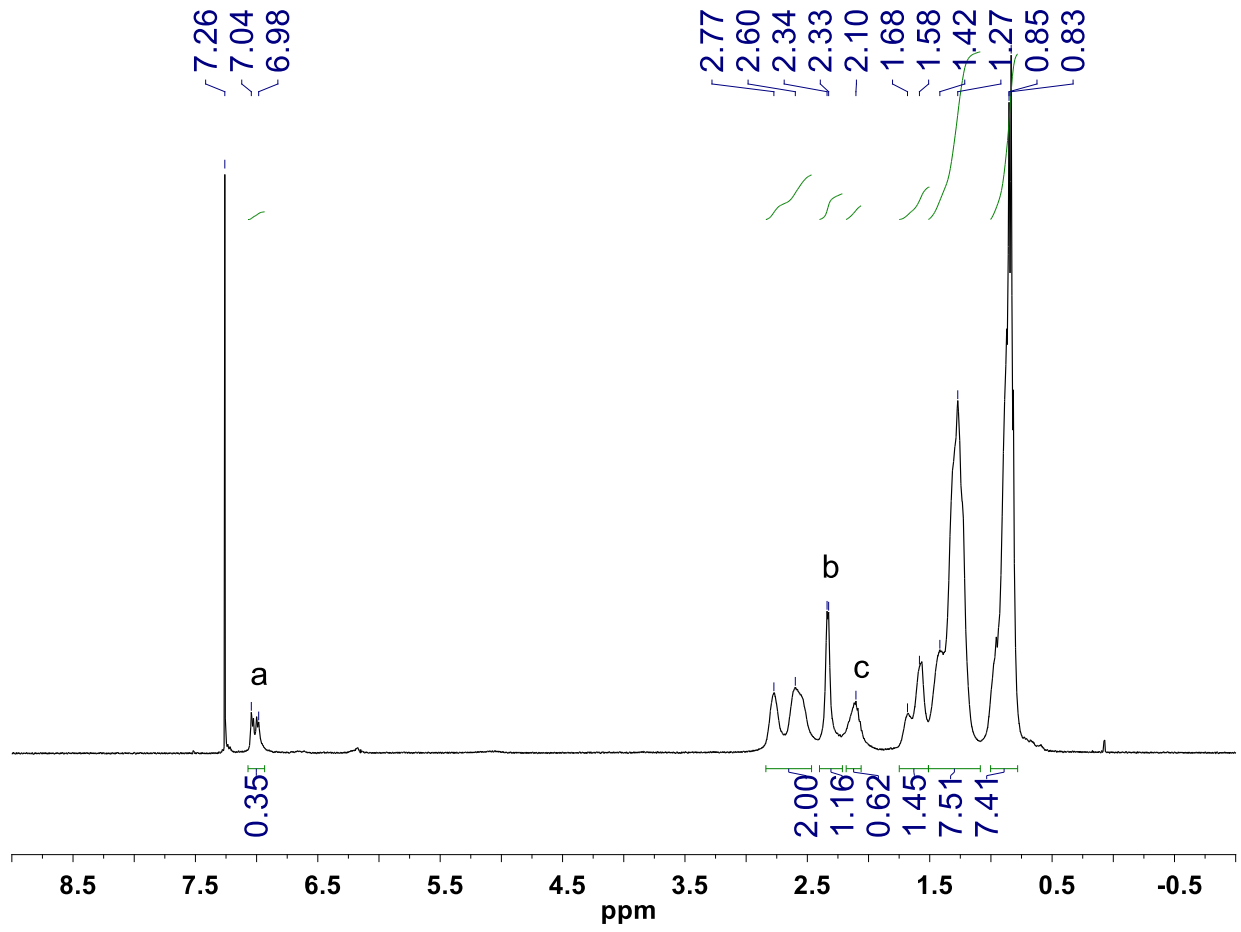
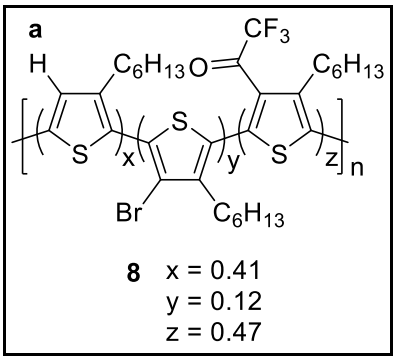


Figure S8. Compound **7**.



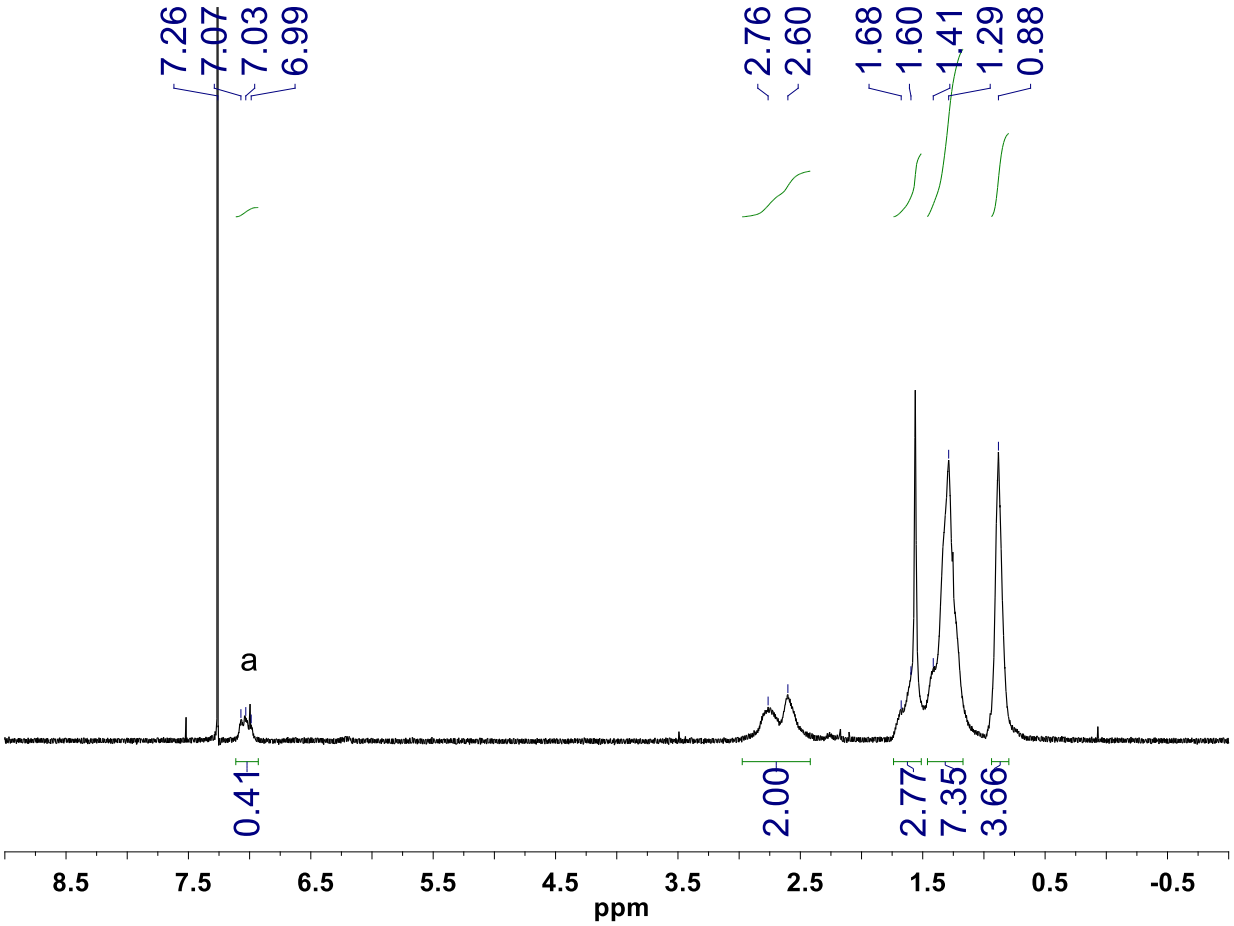
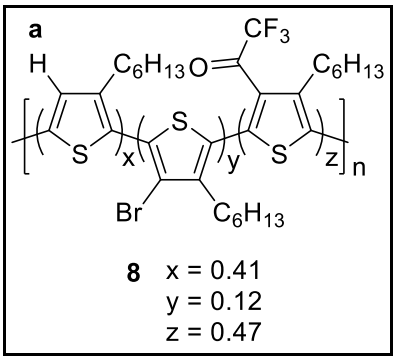


Figure S9. Compound **8**.



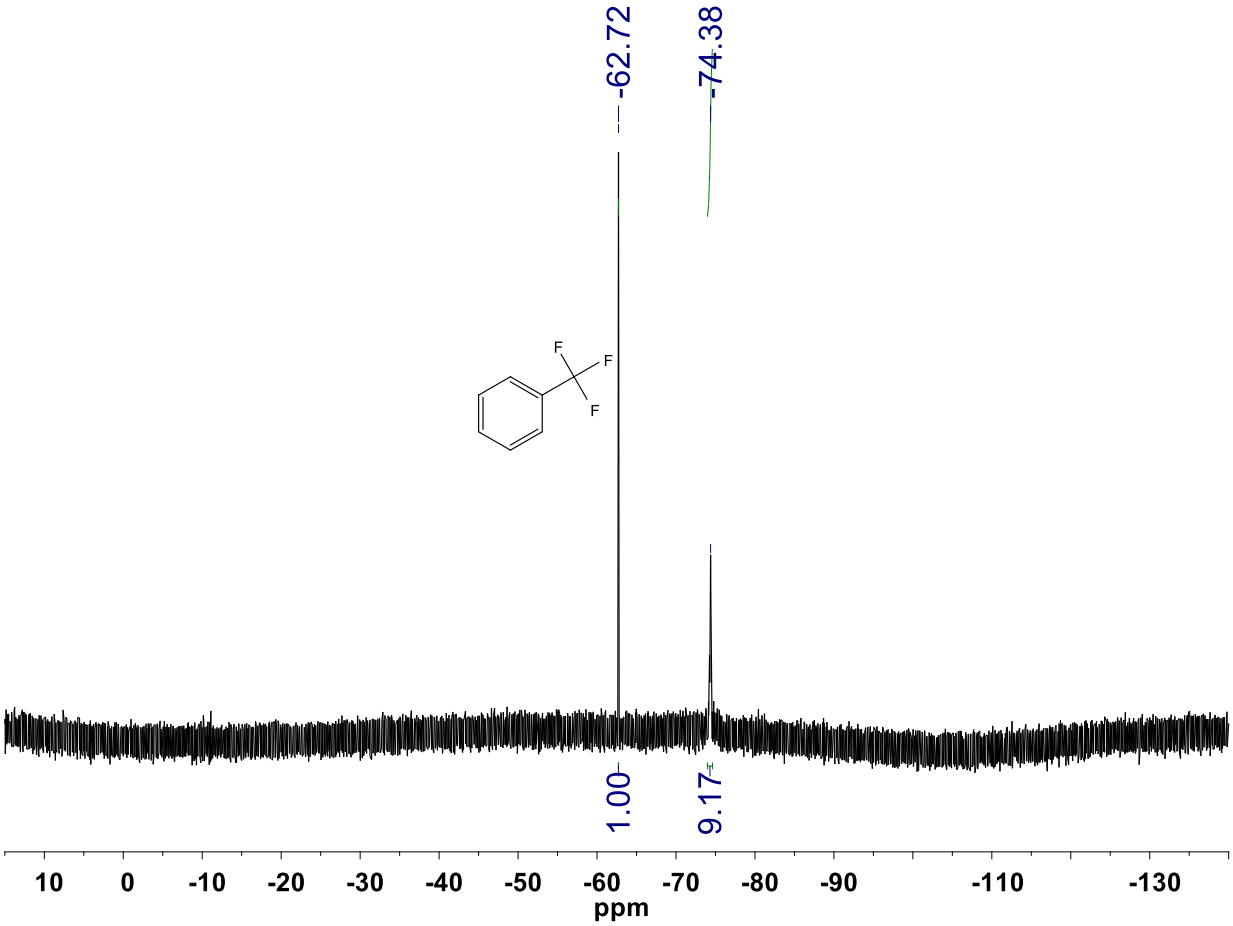


Figure S10. Compound **8** (^{19}F NMR).

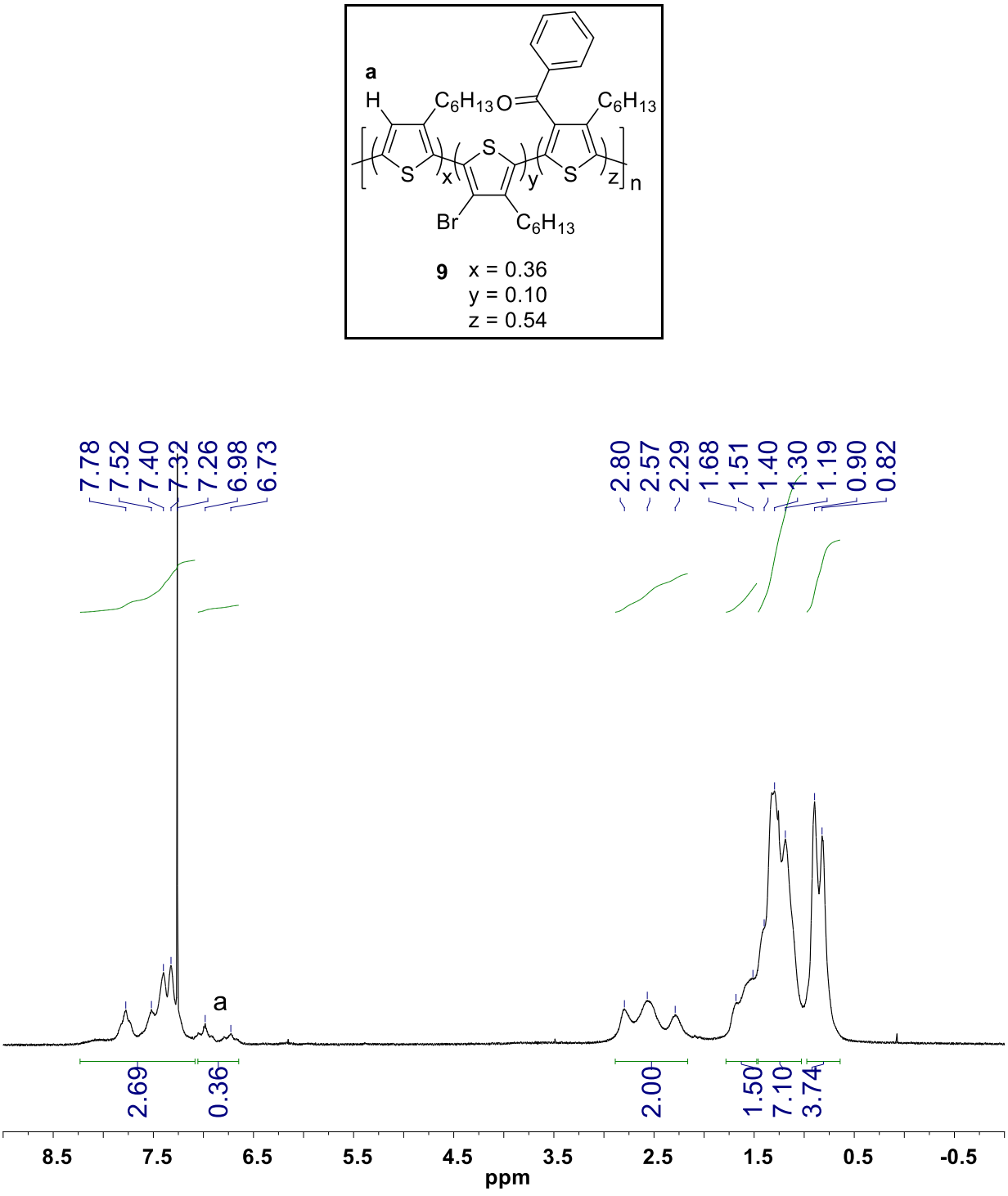


Figure S11. Compound **9**.

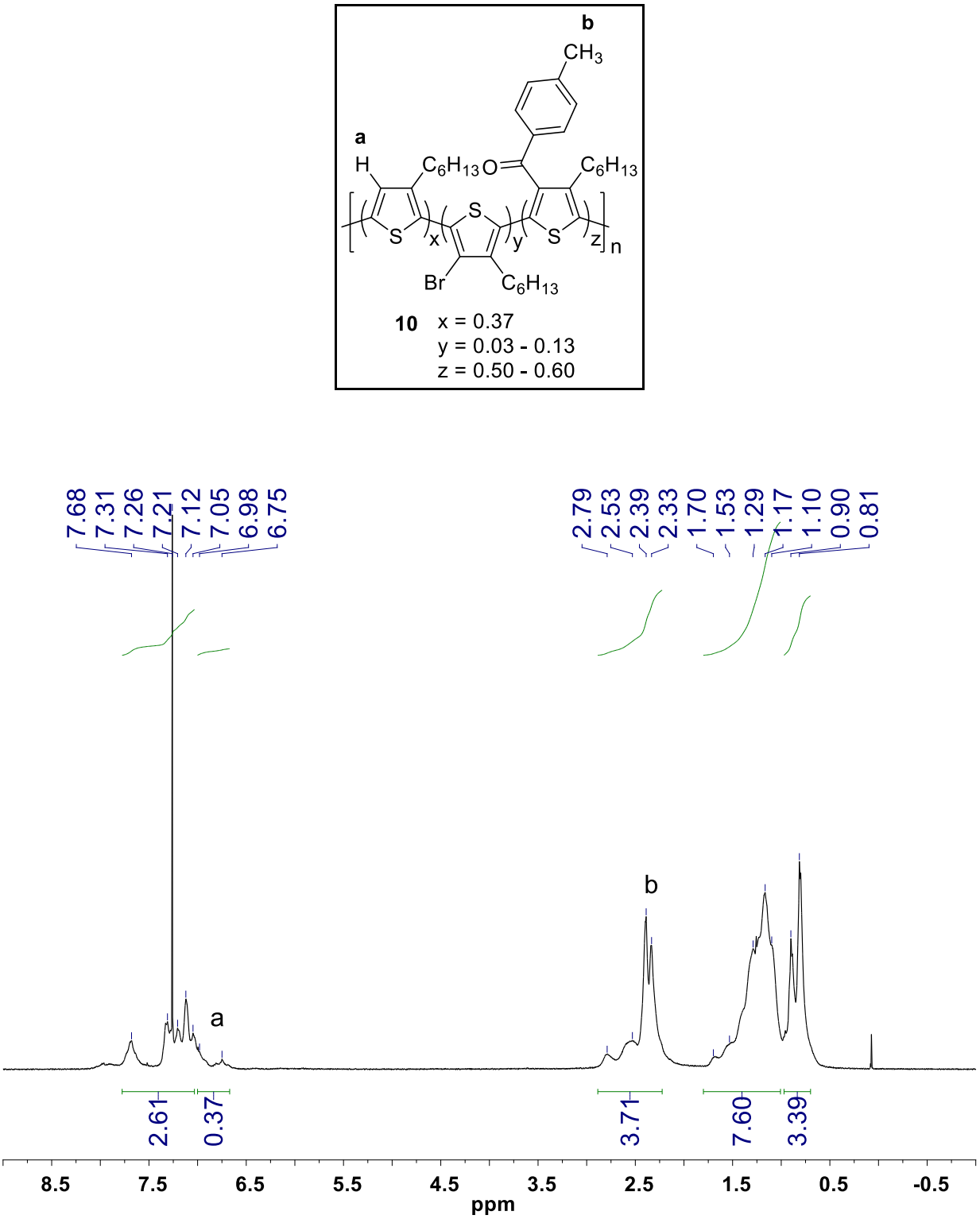


Figure S12. Compound **10** (Integration value based on 57 % conversion).

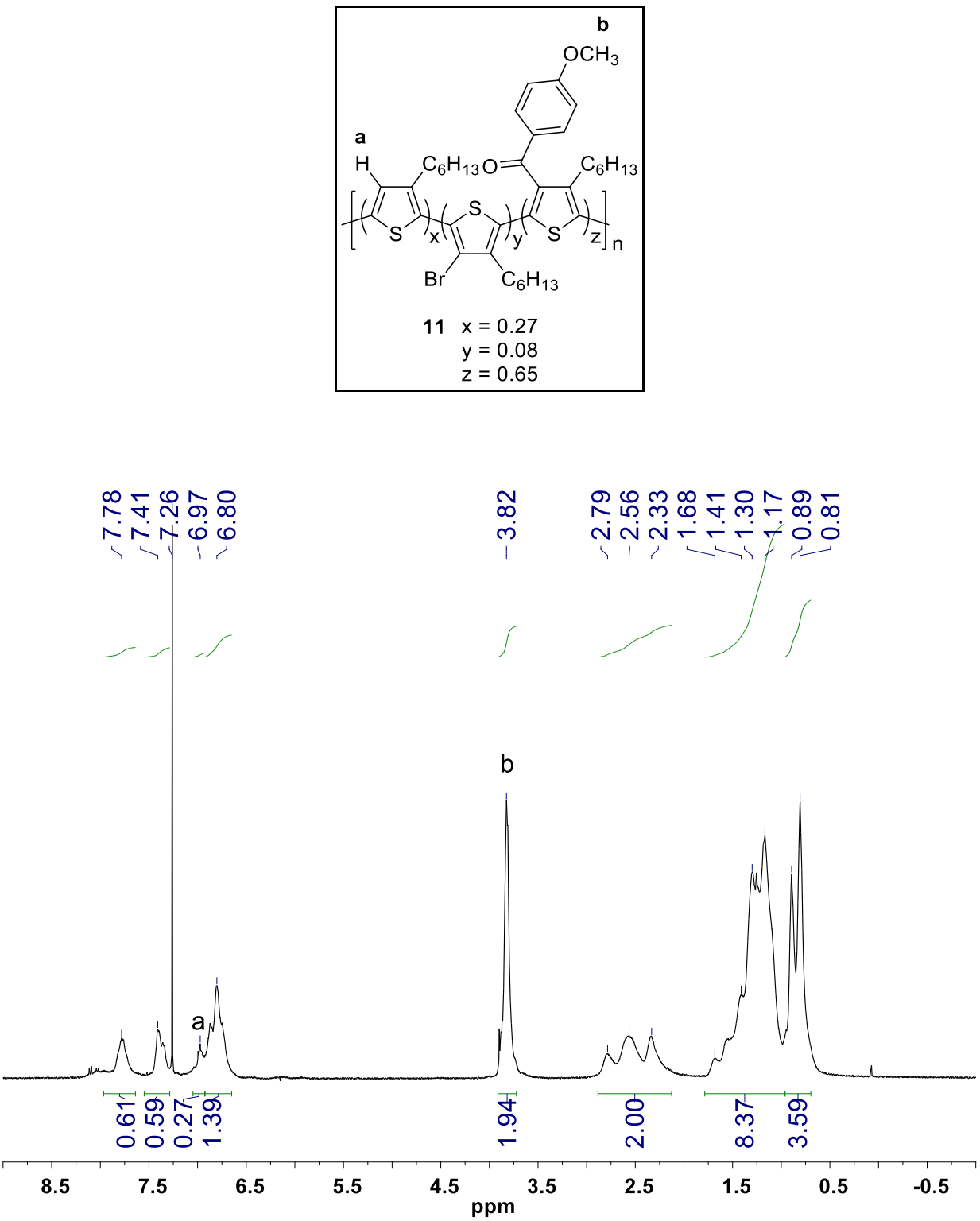
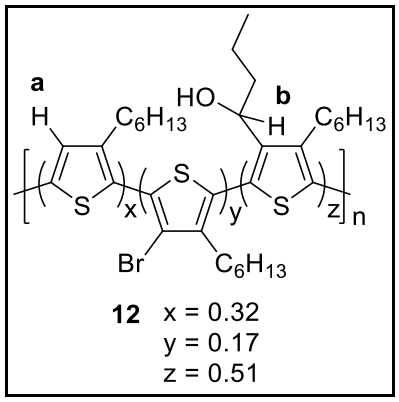


Figure S13. Compound **11**.



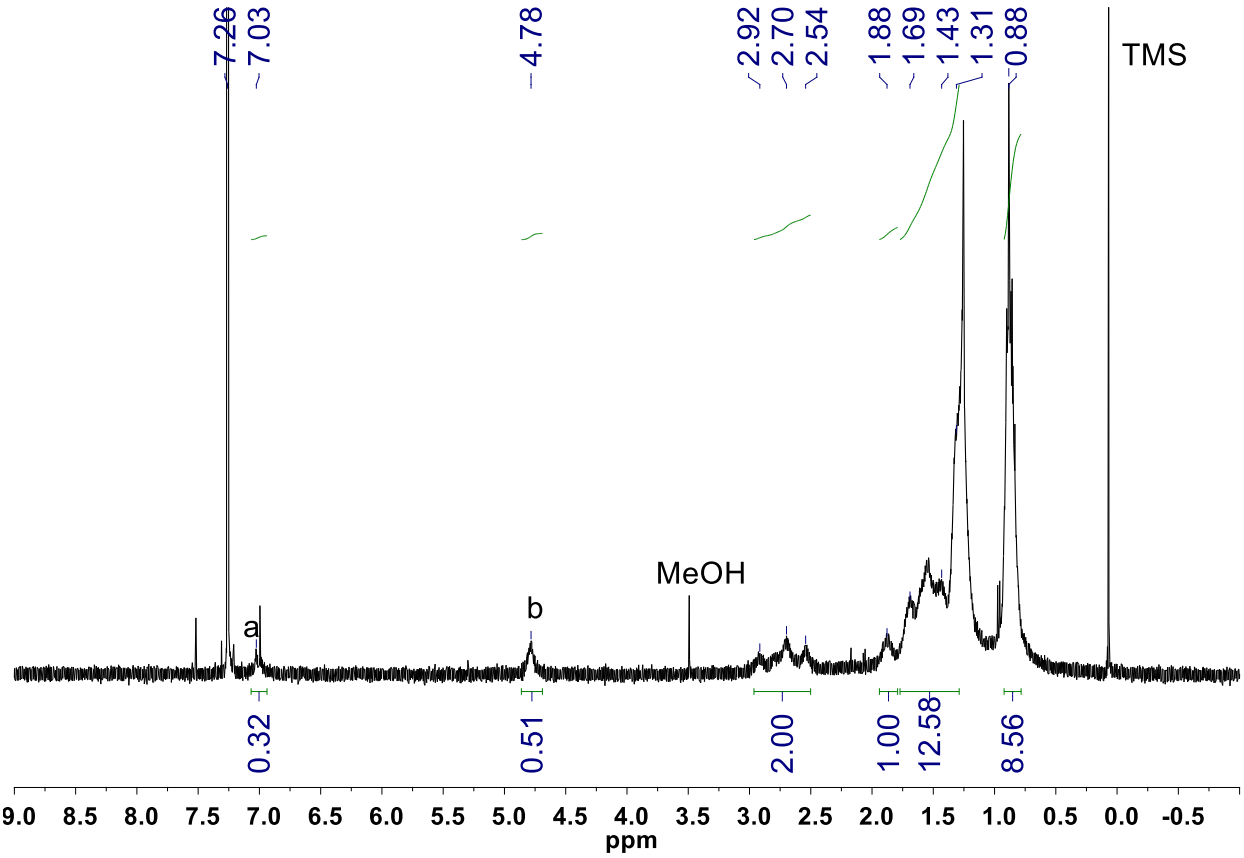


Figure S14. Compound **12**.

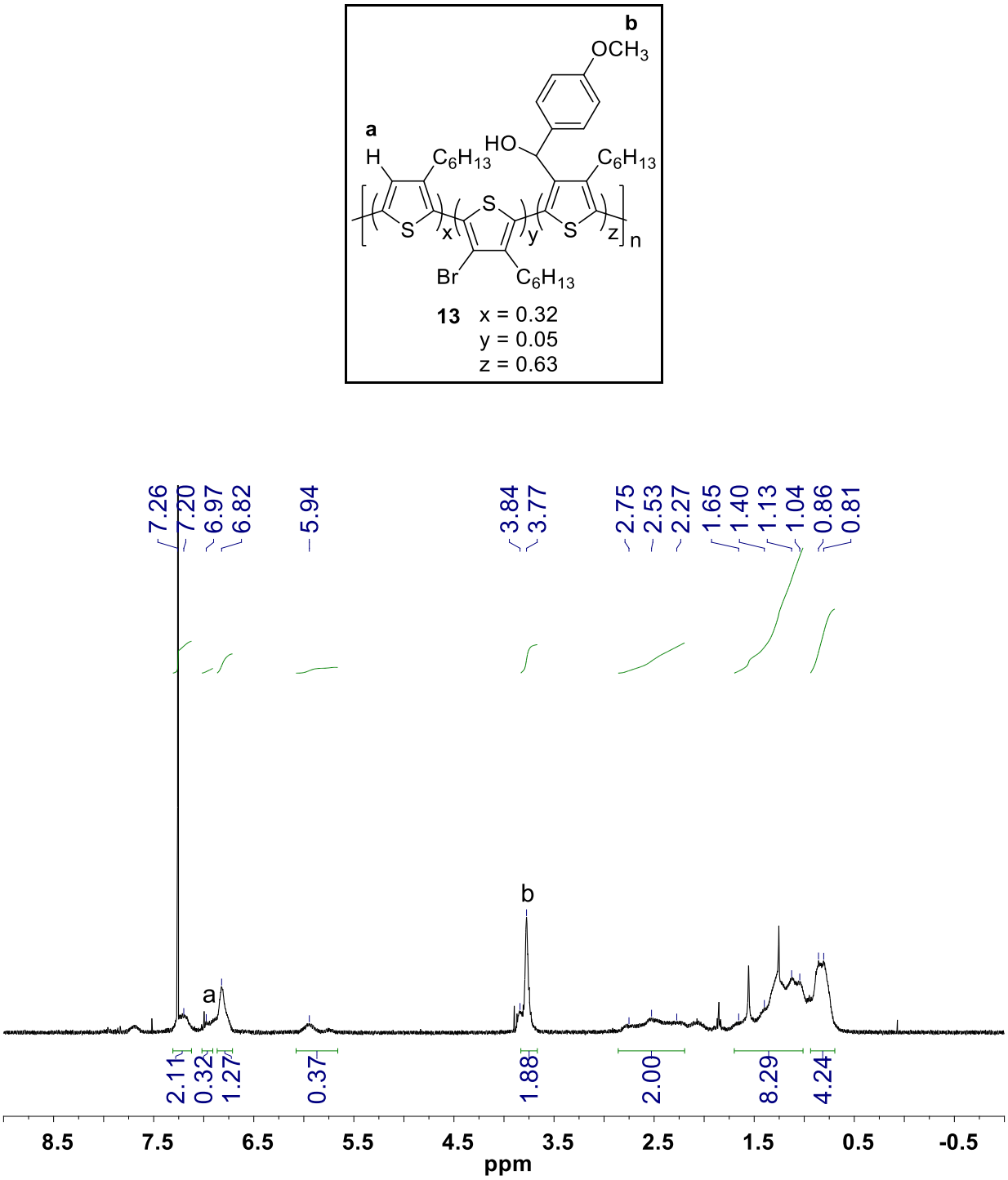
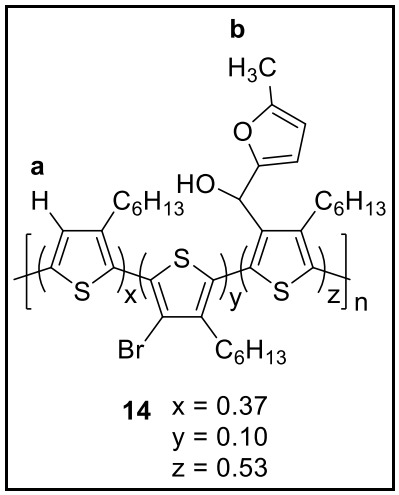


Figure S15. Compound **13**.



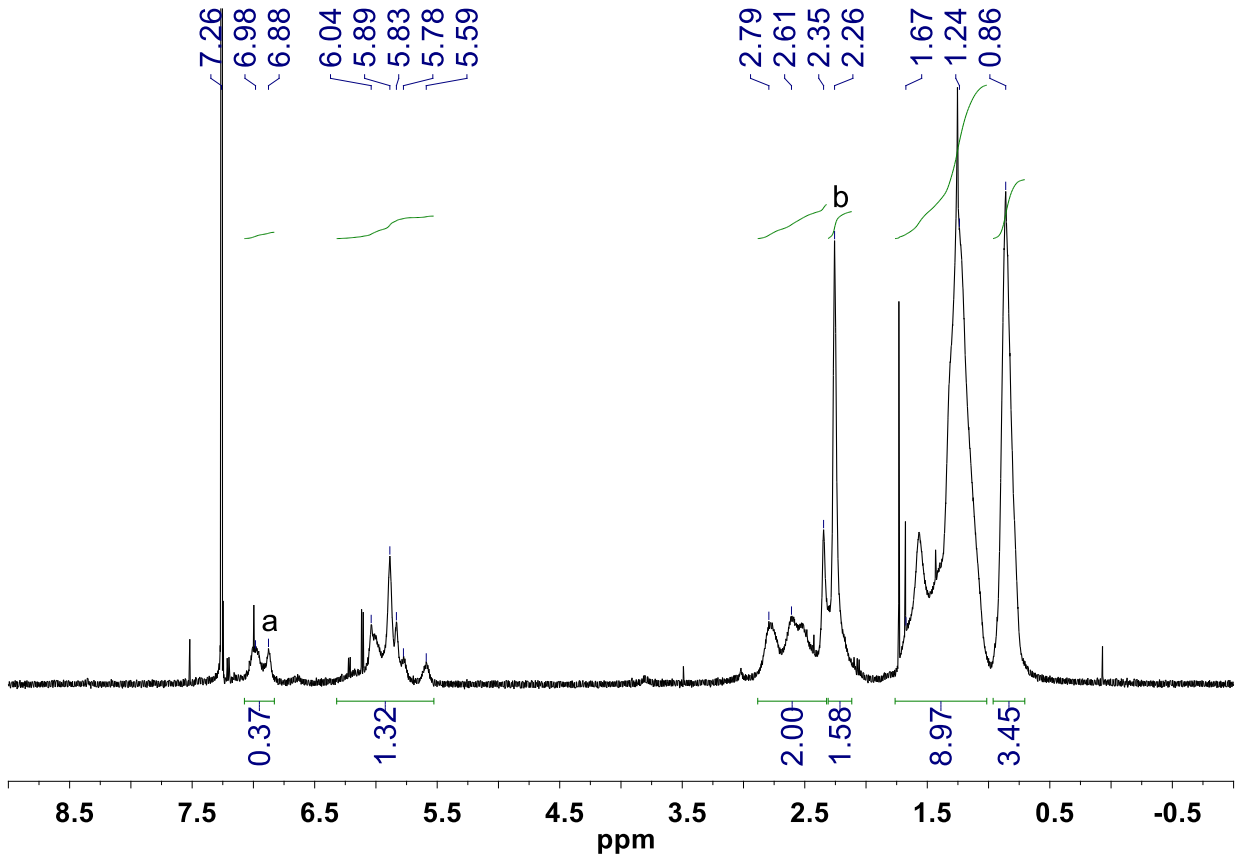
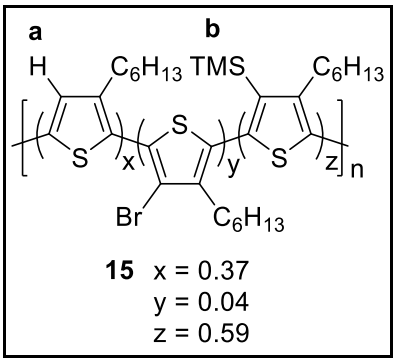


Figure S16. Compound **14**.



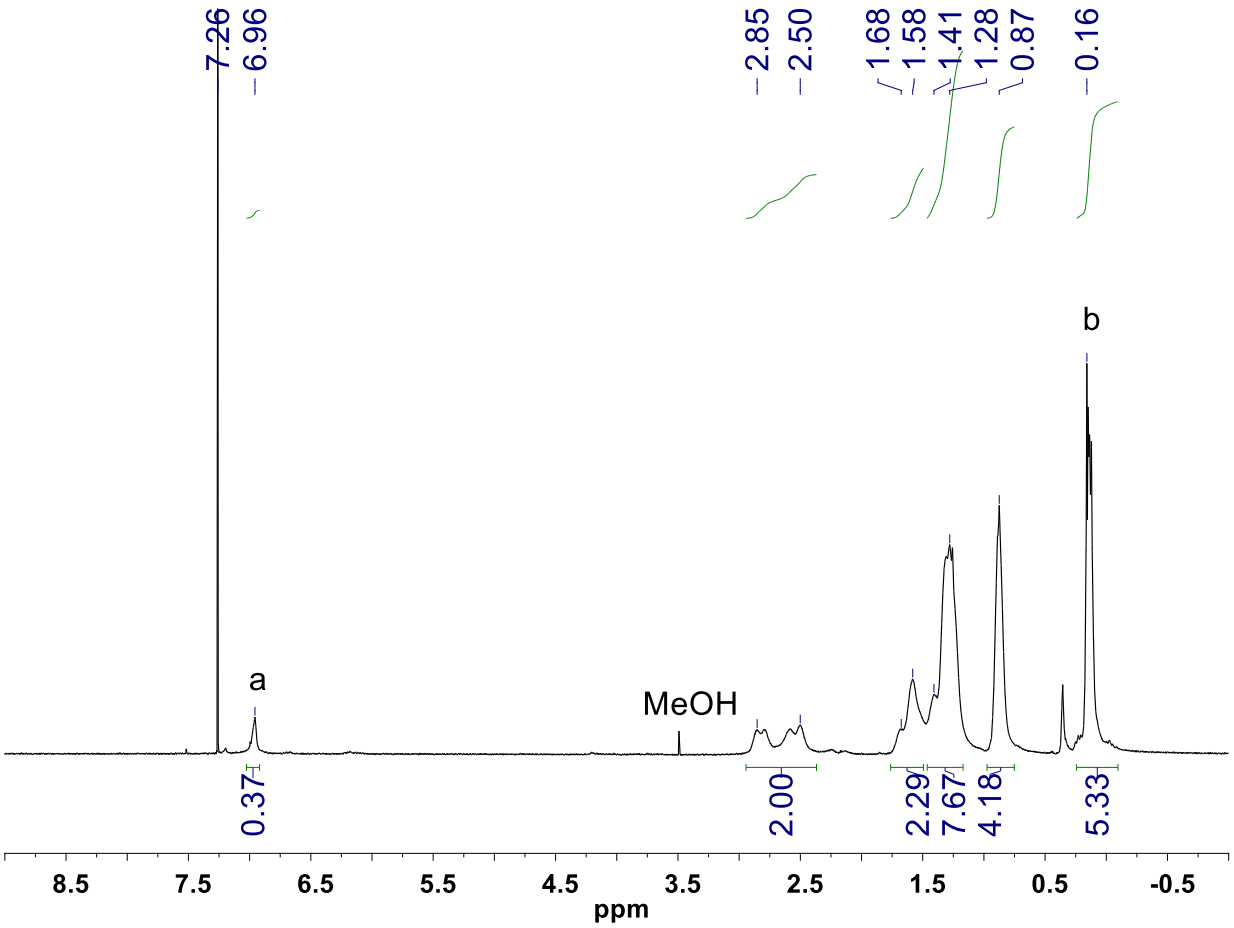


Figure S17. Compound **15**.

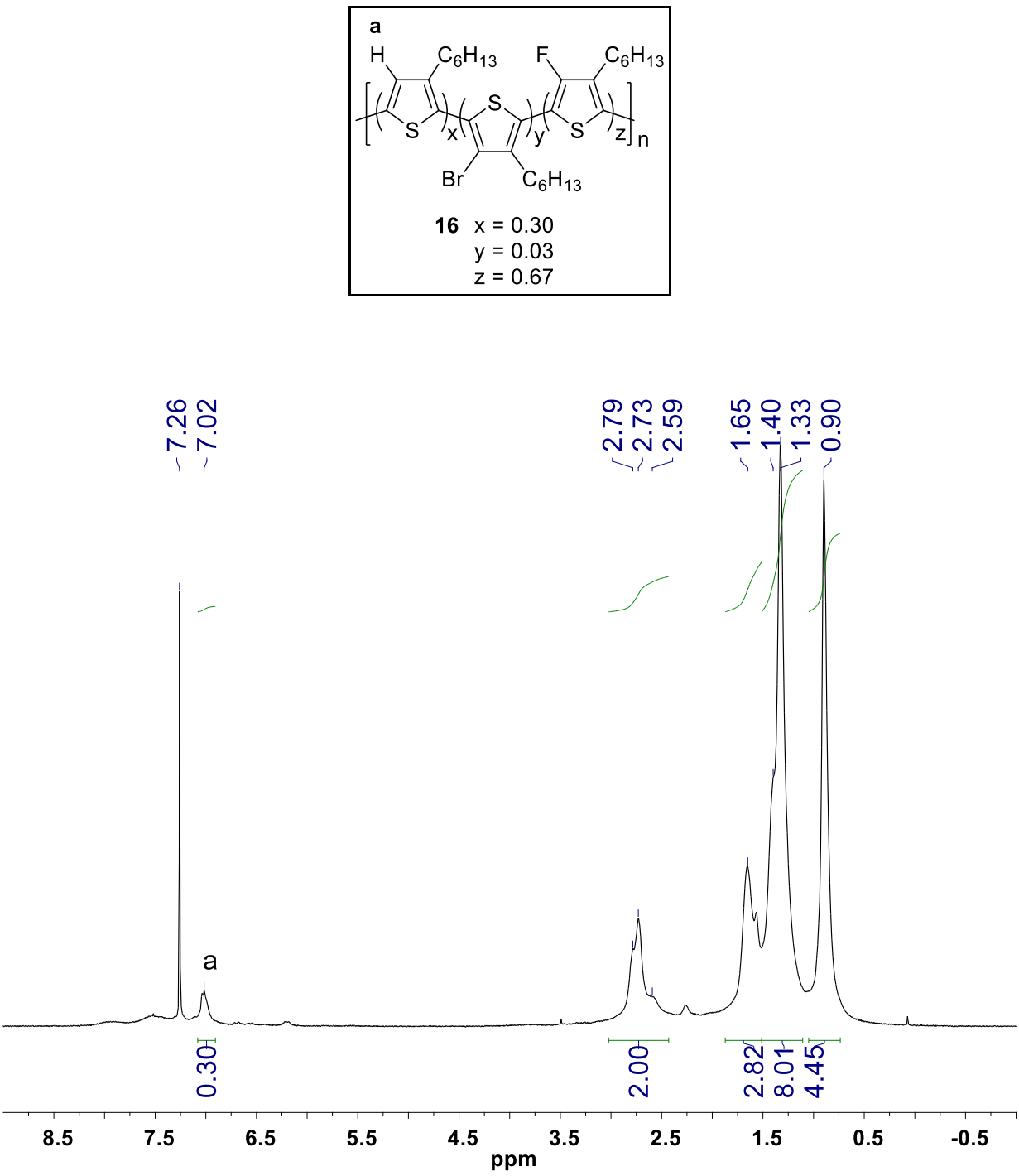
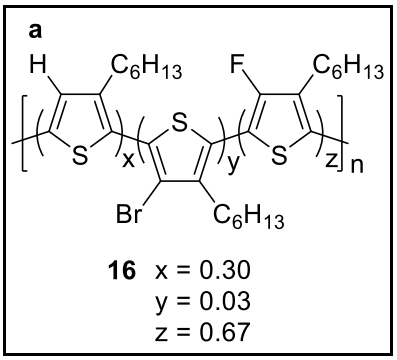


Figure S18. Compound **16**.



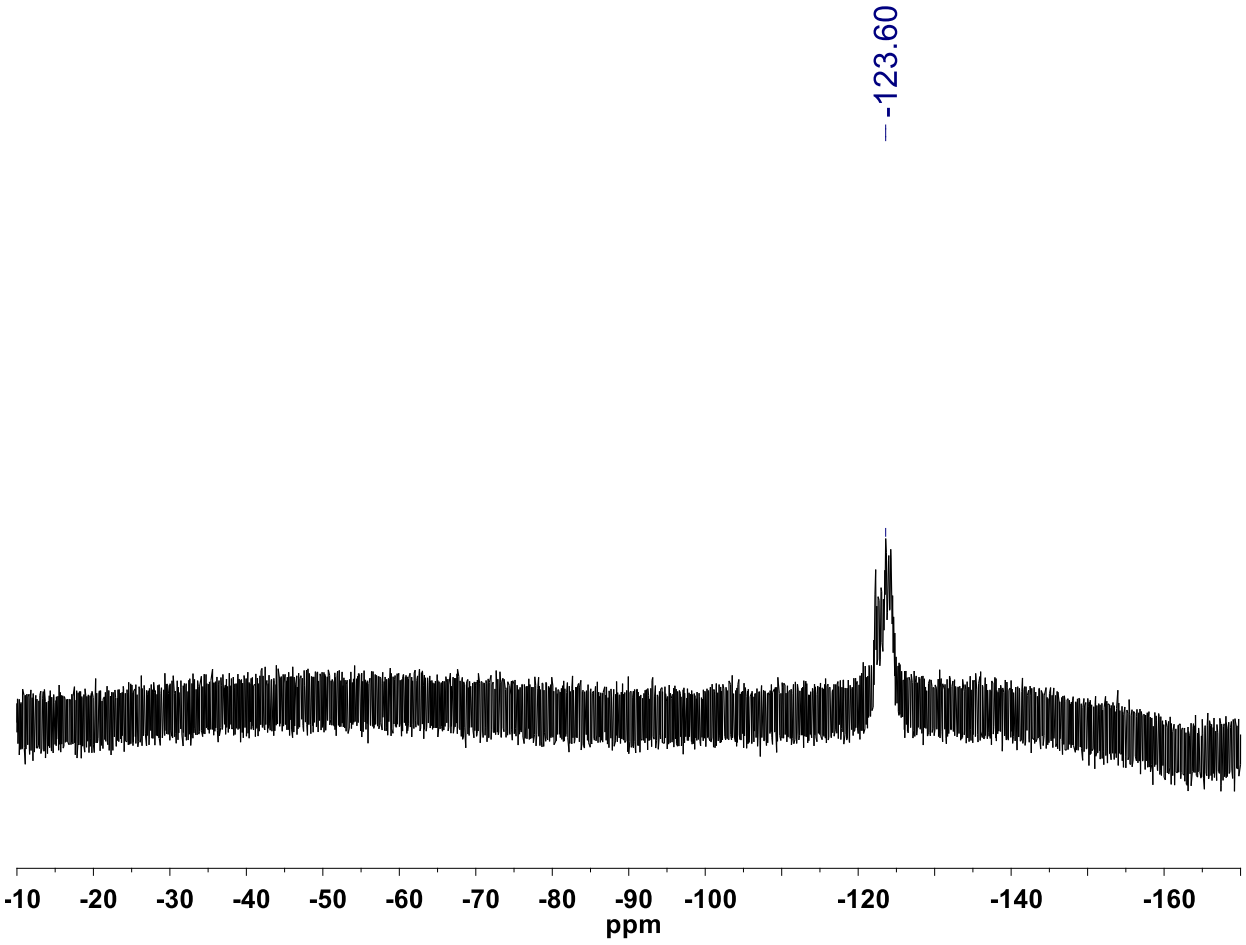
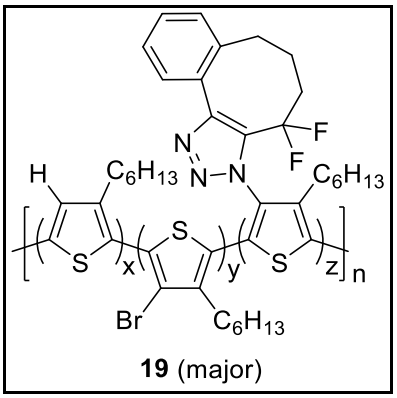


Figure S19. Compound **16** (^{19}F NMR).



19 (major)

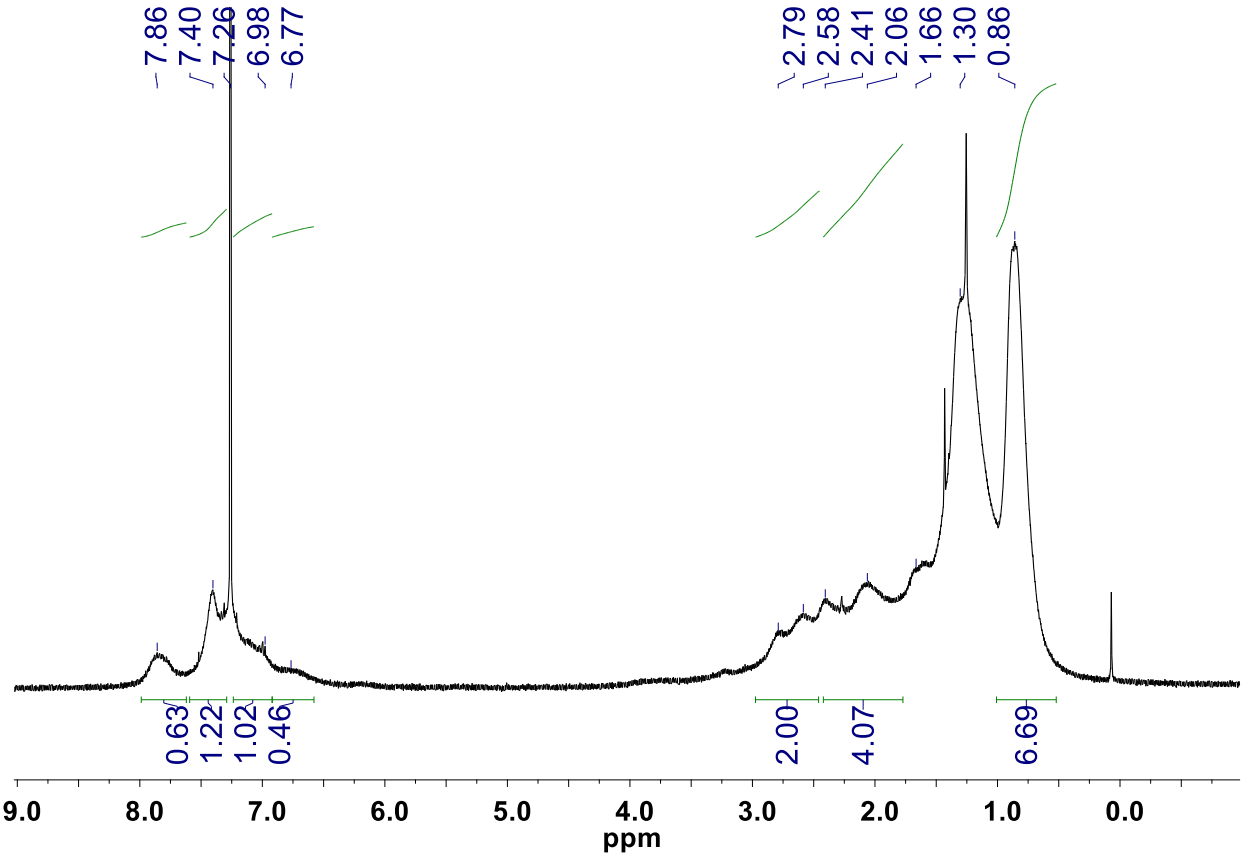
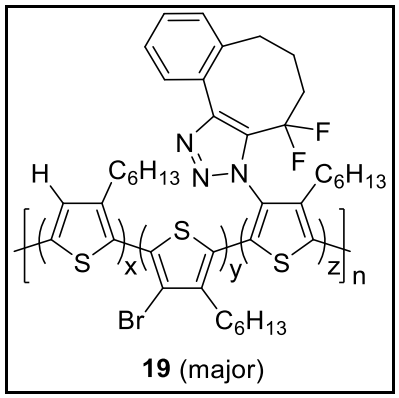


Figure S20. Compound **19**.



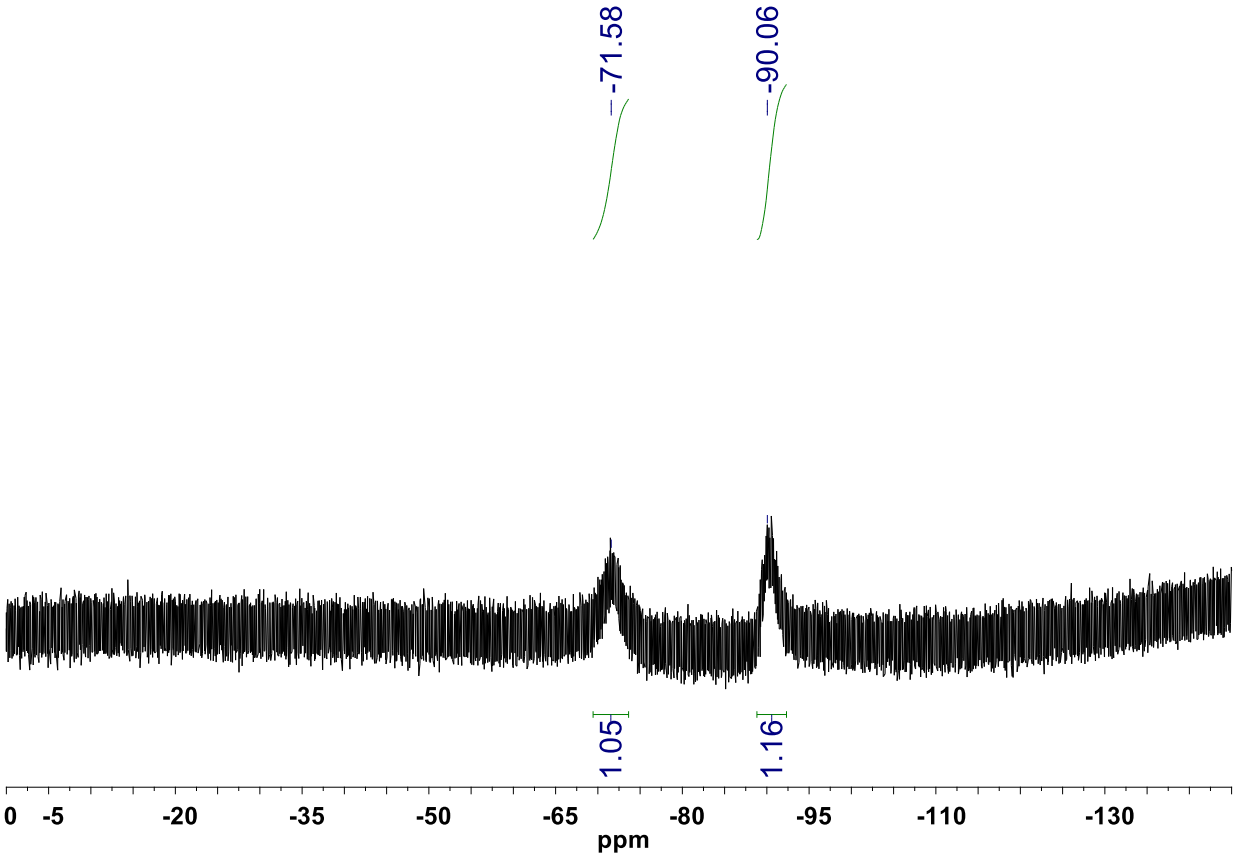
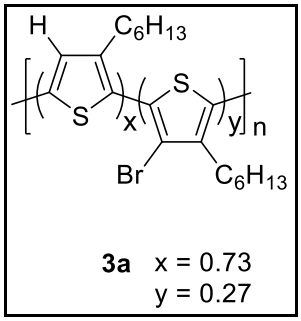
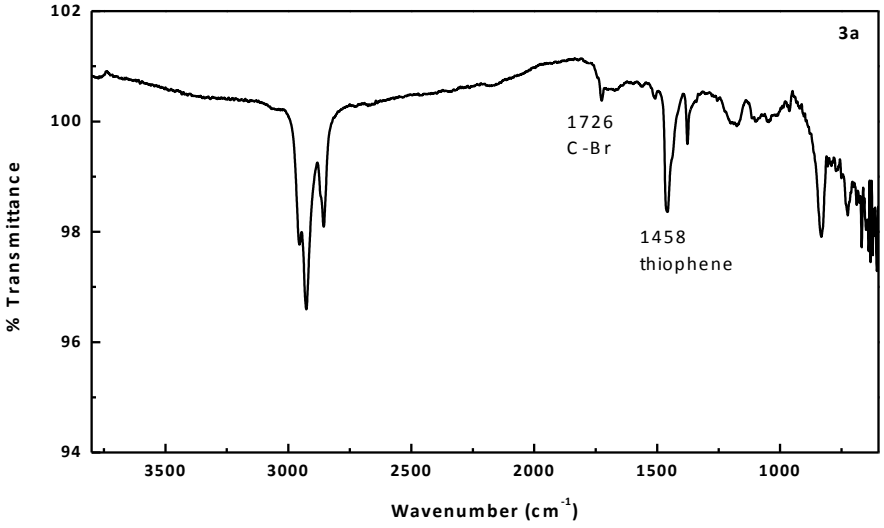


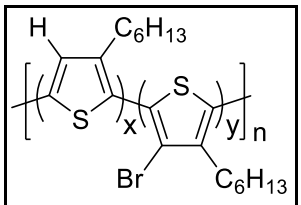
Figure S21. Compound **19**.

IR Spectra

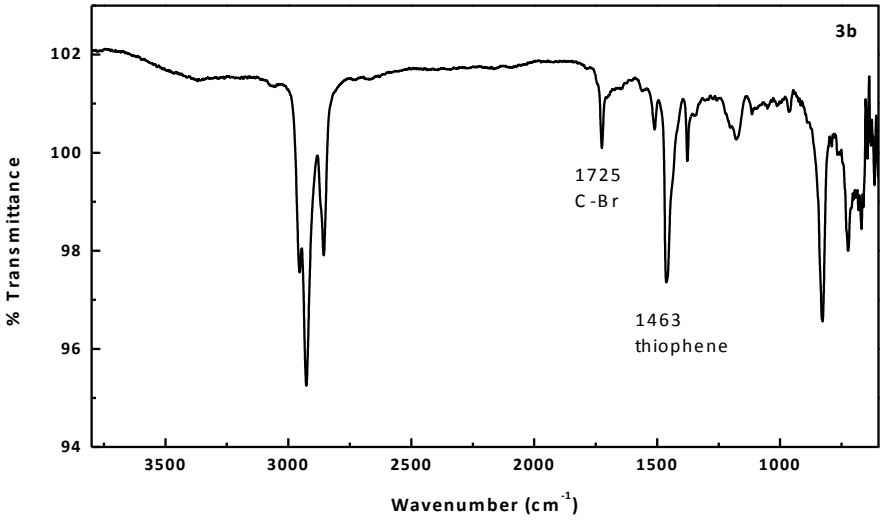


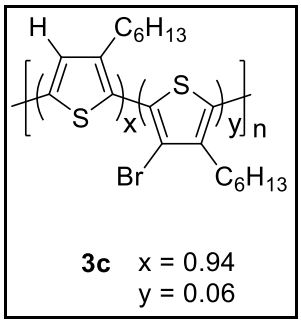
3a x = 0.73
y = 0.27



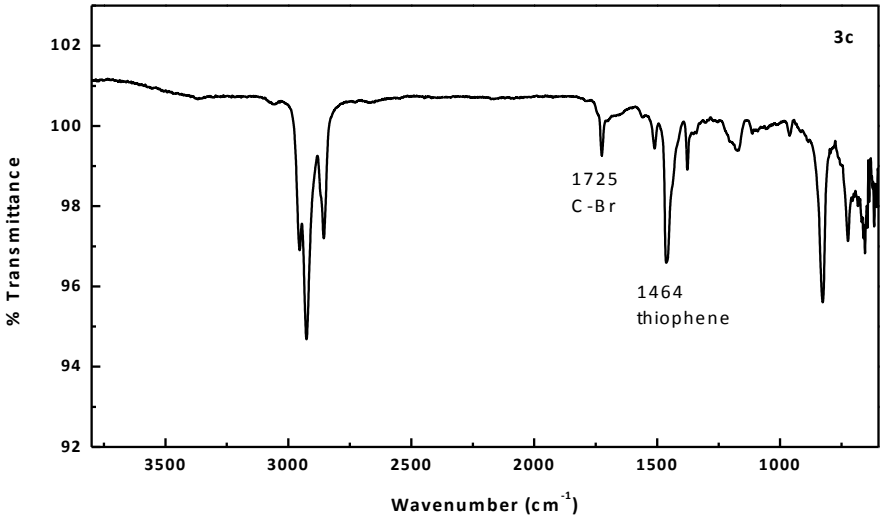

H
C6H13
S
S
x
y
n
Br
C6H13

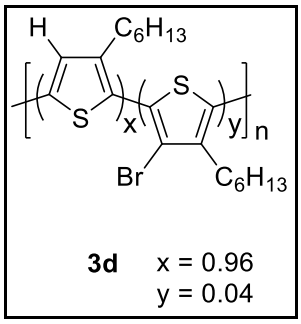
3b x = 0.92
y = 0.08


3b
102
100
98
96
94
% Transmittance
1725
C-Br
1463
thiophene
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

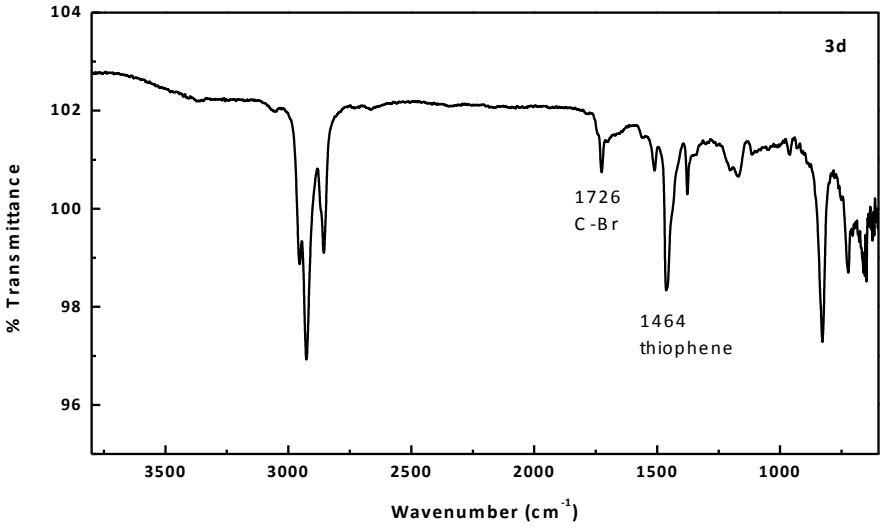

H
C6H13
S
S
x
y
n
Br
C6H13

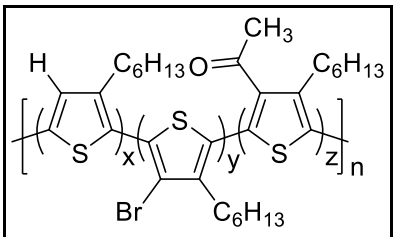
3c x = 0.94
y = 0.06


3c
% Transmittance
102
100
98
96
94
92
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
1725
C-Br
1464
thiophene

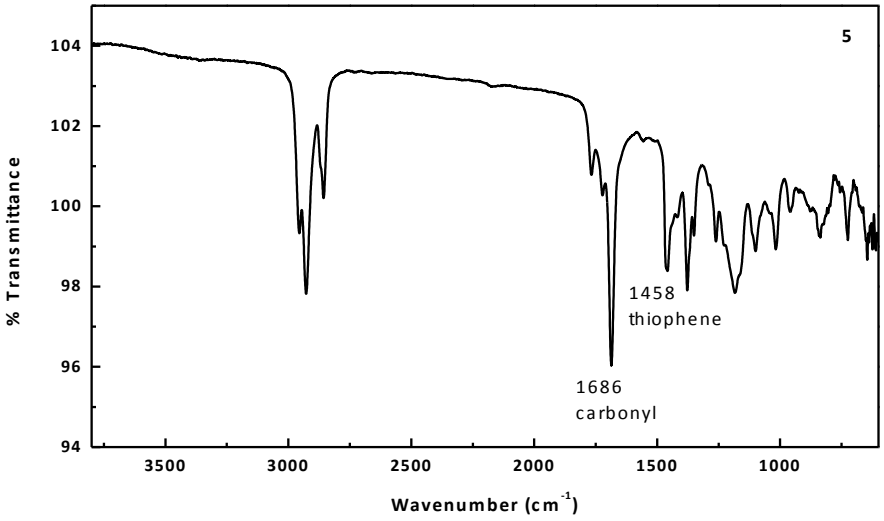

H
C6H13
S
S
x
y
n
Br
C6H13

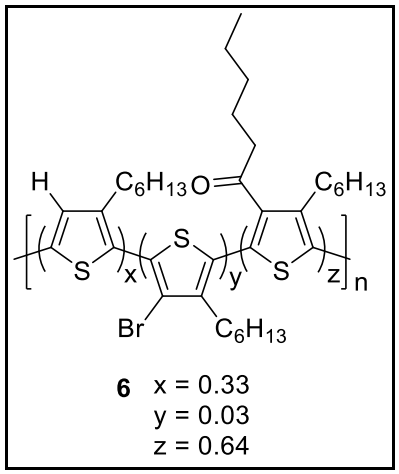
3d x = 0.96
y = 0.04


3d
% Transmittance
104
102
100
98
96
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
1726
C-Br
1464
thiophene

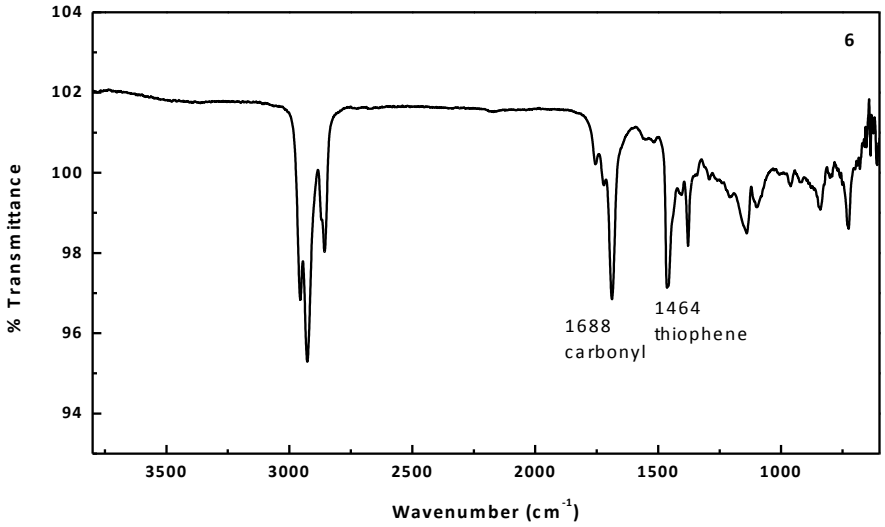


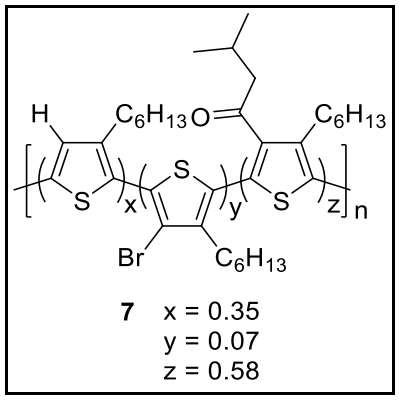
5 x = 0.34
y = 0.06
z = 0.60



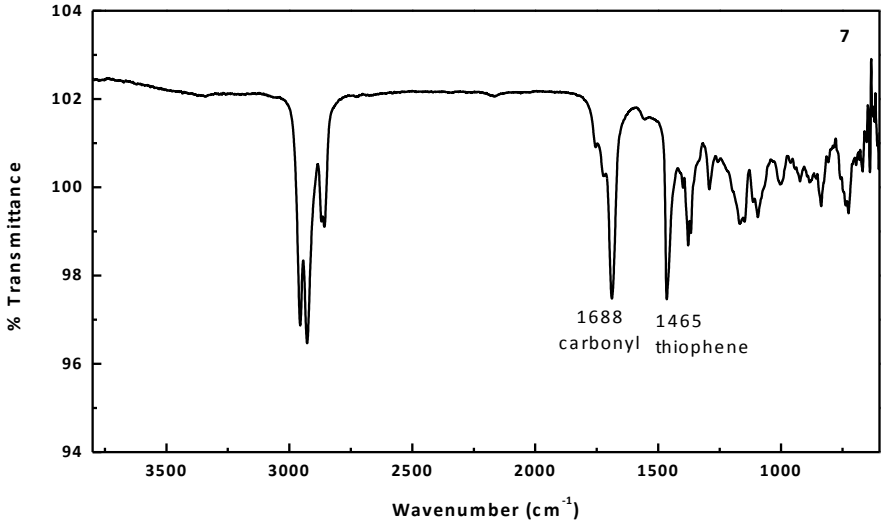


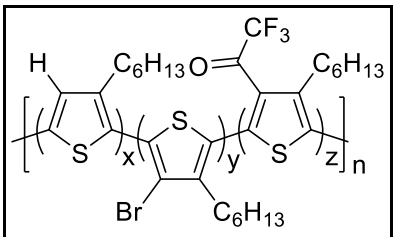
6 x = 0.33
y = 0.03
z = 0.64



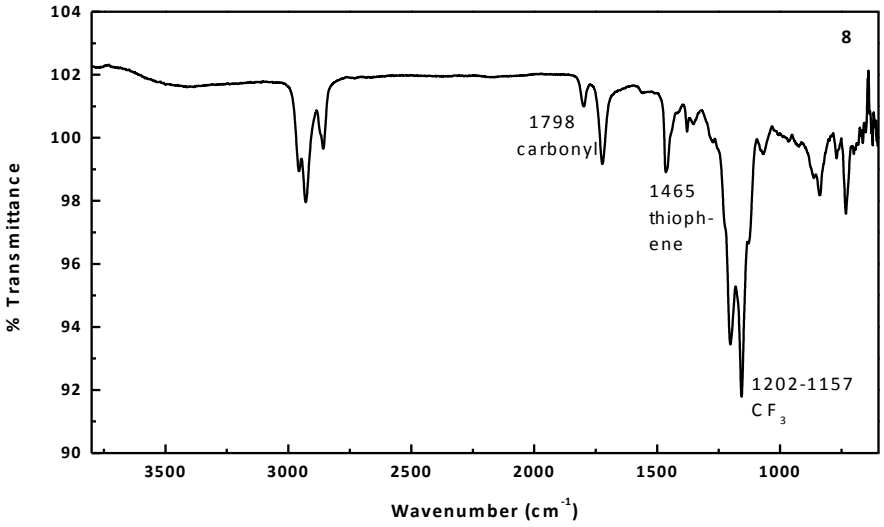


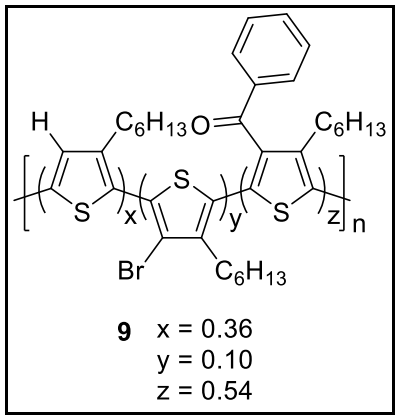
7 x = 0.35
y = 0.07
z = 0.58



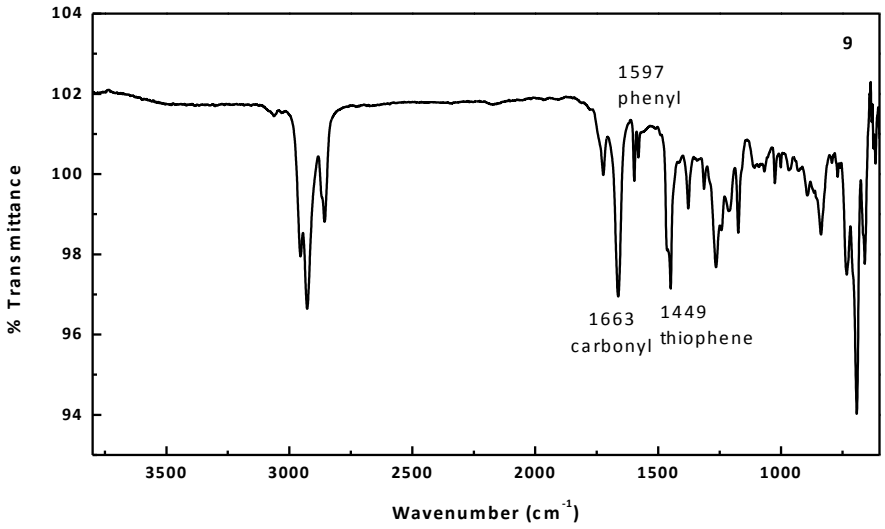


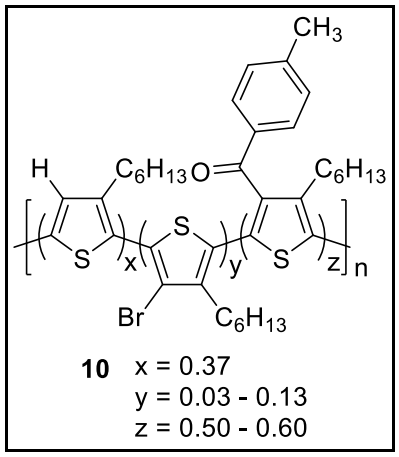
8 x = 0.41
y = 0.12
z = 0.47



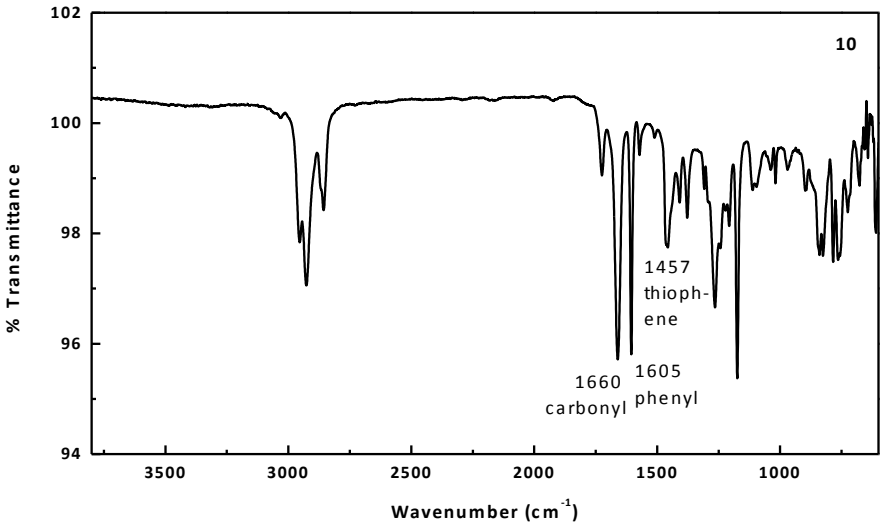


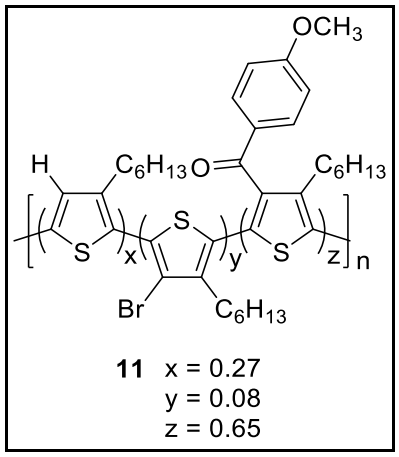
9 x = 0.36
y = 0.10
z = 0.54



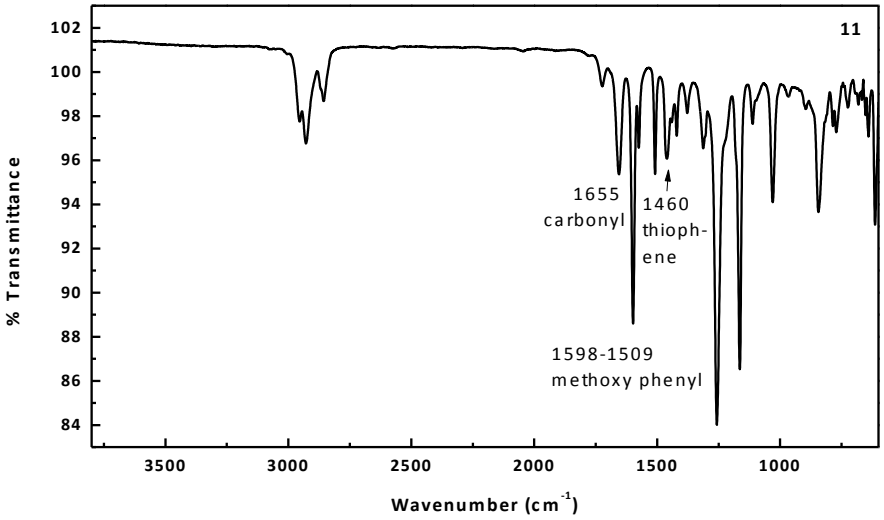


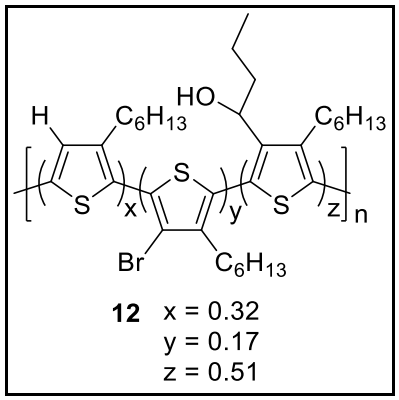
10 x = 0.37
y = 0.03 - 0.13
z = 0.50 - 0.60



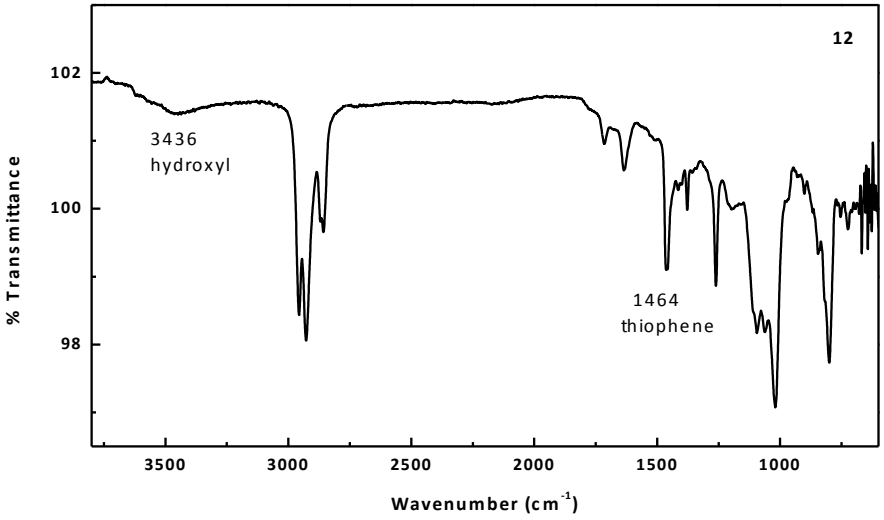


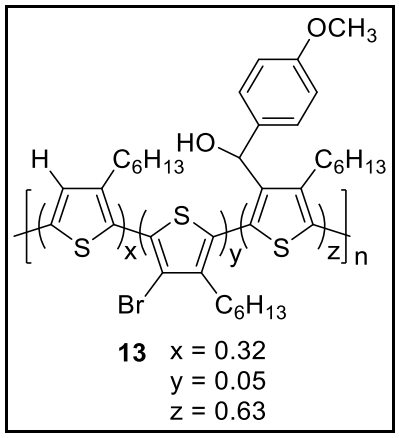
11 x = 0.27
y = 0.08
z = 0.65



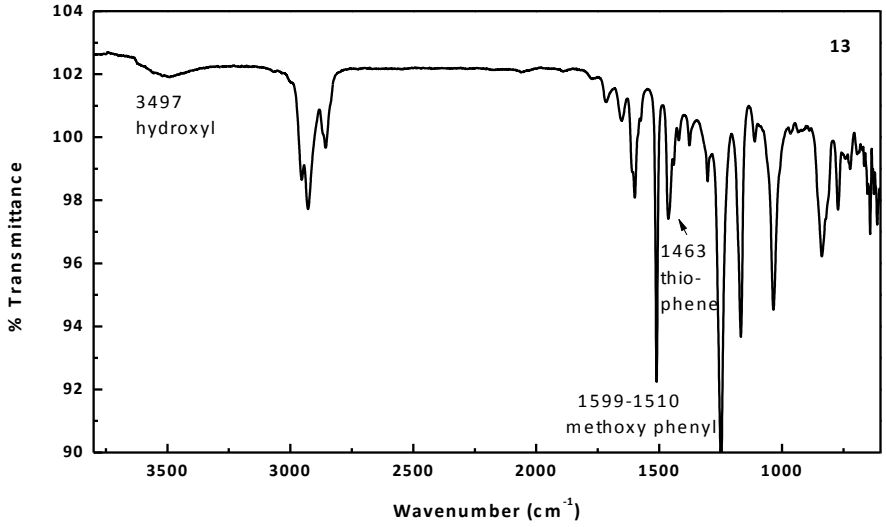


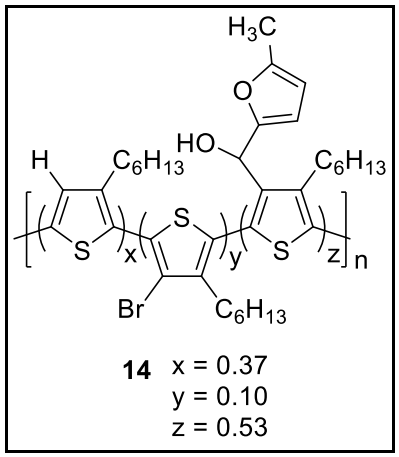
12 x = 0.32
y = 0.17
z = 0.51



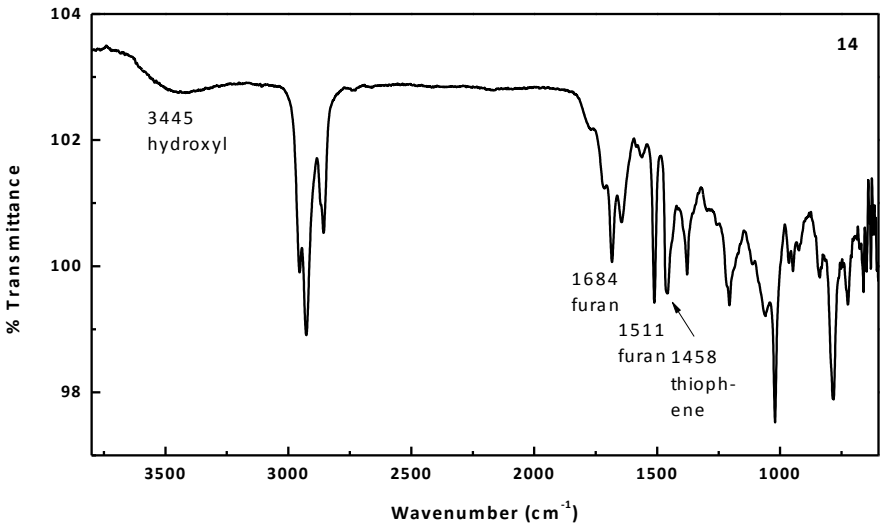


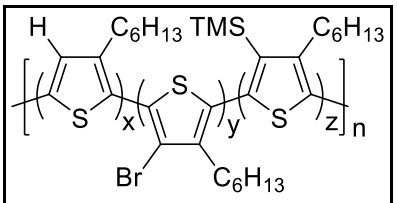
13 x = 0.32
y = 0.05
z = 0.63



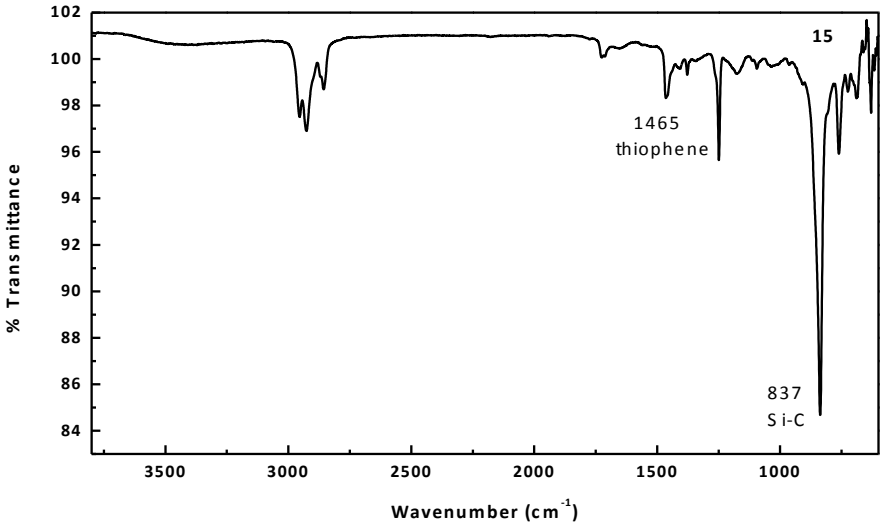


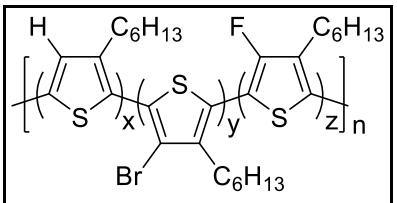
14 x = 0.37
y = 0.10
z = 0.53



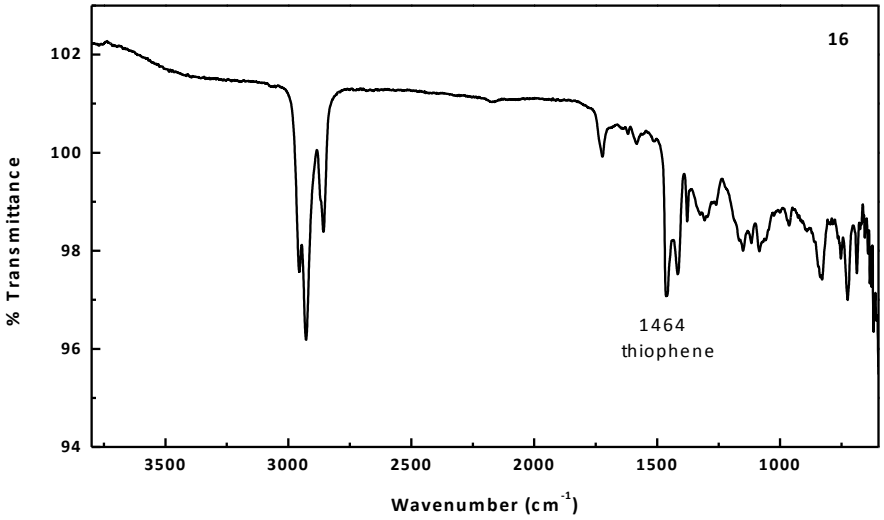


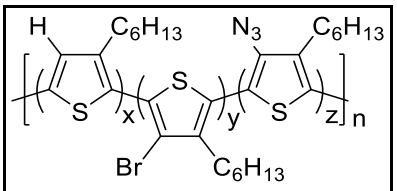
15 x = 0.37
y = 0.04
z = 0.59



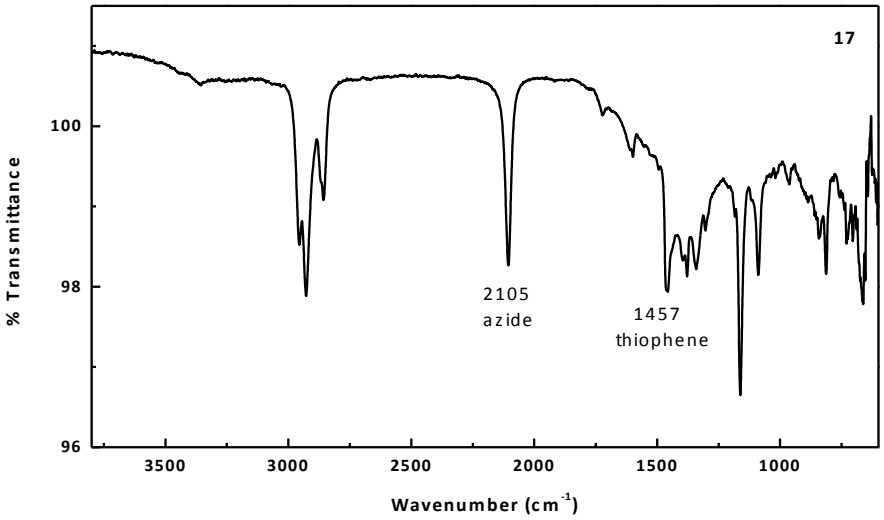


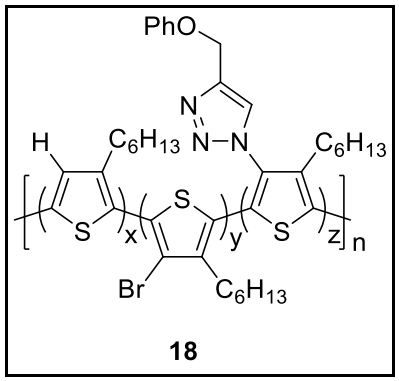
16 x = 0.30
y = 0.03
z = 0.67



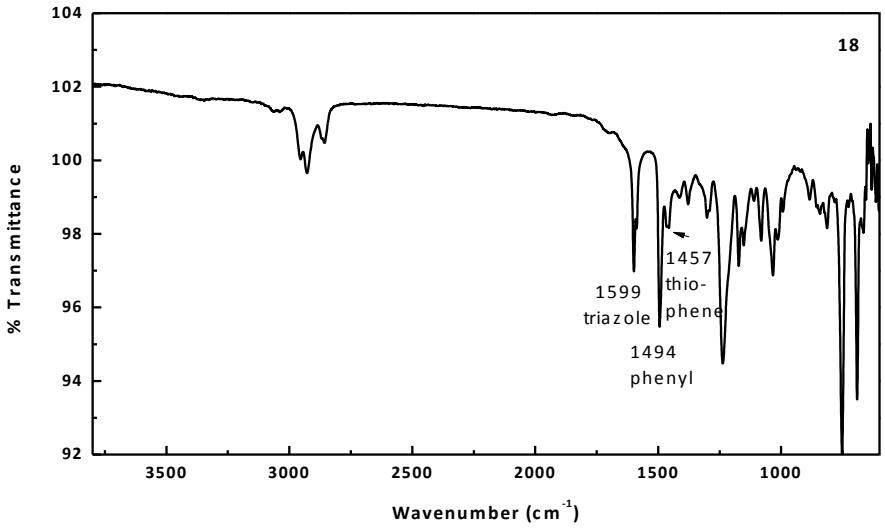

H
C6H13
N3
C6H13
S
S
S
x
y
z
n
Br
C6H13

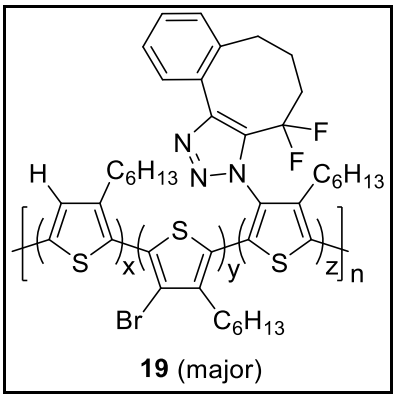
17


17
100
98
96
% Transmittance
2105
azide
1457
thiophene
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

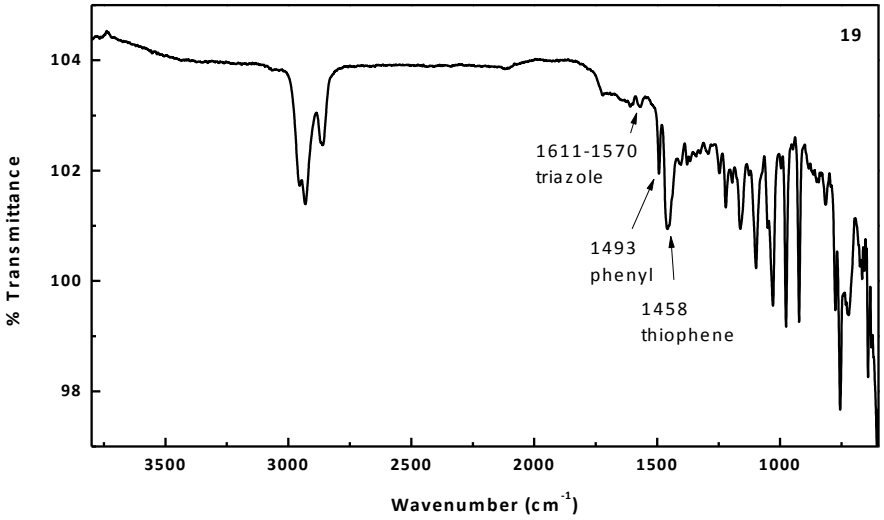

PhO
N
N
N
H
C6H13
C6H13
S
S
S
x
y
z
n
Br
C6H13

18


18
% Transmittance
Wavenumber (cm-1)
104
102
100
98
96
94
92
3500
3000
2500
2000
1500
1000
1599
triazole
1494
phenyl
1457
thio-
phene


N
F
F
H
C_6H_{13}
N–N
C_6H_{13}
S
S
x
y
S
z
n
Br
C_6H_{13}

19 (major)


19
104
102
100
98
% Transmittance
1611-1570
triazole
1493
phenyl
1458
thiophene
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})