SYNTHETIC APPROACHES TO REGIOREGULAR UNSYMMETRICAL DIALKOXY SUBSTITUTED POLY(1,4-PHENYLENE ETHYNYLENE)S

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I. Synthesis of monomers 1 and 2 for preparation of regiorandom PPEs.

Experimental procedures for the preparation of **1** and **2** according to the synthetic route shown in Figure S-1 are provided below.

4-Dodecyloxyphenol, 13b. NaH (12.96 g, 540 mmol), was added over 30 min to a stirred solution of 1,4-hydroquinone (60 g, 545.5 mmol) in anhydrous DMF (900 mL) under N_2 and the mixture was stirred for 20 min. 1-Bromododecane (134.46 g, 540 mmol) was added dropwise over 10 min and the mixture was stirred for 18 h. The resulting dark brown solution was acidified with 10% aqueous HCl and poured into CH_2Cl_2 (400 mL). The organic layer was extracted with 10% aqueous HCl (2 × 200 mL) and the solvent was removed under reduced pressure. The residue was recrystallized twice from EtOH, and once from hexane, to afford **13b** (40 g, 26 % yield) as a white solid, m.p. 79°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.7-6.8 (m, 4H, Ar-H), 4.5-5.0 (bs, 1H, OH), 3.88 (t, $^3J_{HH}$ = 6.61 Hz, 2H, -OCH$_2$-), 1.7-1.8 (m, 2H, C-2 -CH$_2$-), 1.2-1.5 (m, 18H), 0.85 (t, $^3J_{HH}$ = 6.7 Hz, 3H, -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.49, 149.57 (Ar C-O), 116.26, 115.9 (Ar C-H), 69.06 (-OCH$_2$-), 32.17, 29.92, 29.89, 29.85, 29.66, 29.60, 26.29, 22.94, 14.38. IR (*v*, cm^{-1}): 3436, 3364 (O-H), 3034, 2953 (Ar C-H str), 2915, 2870,
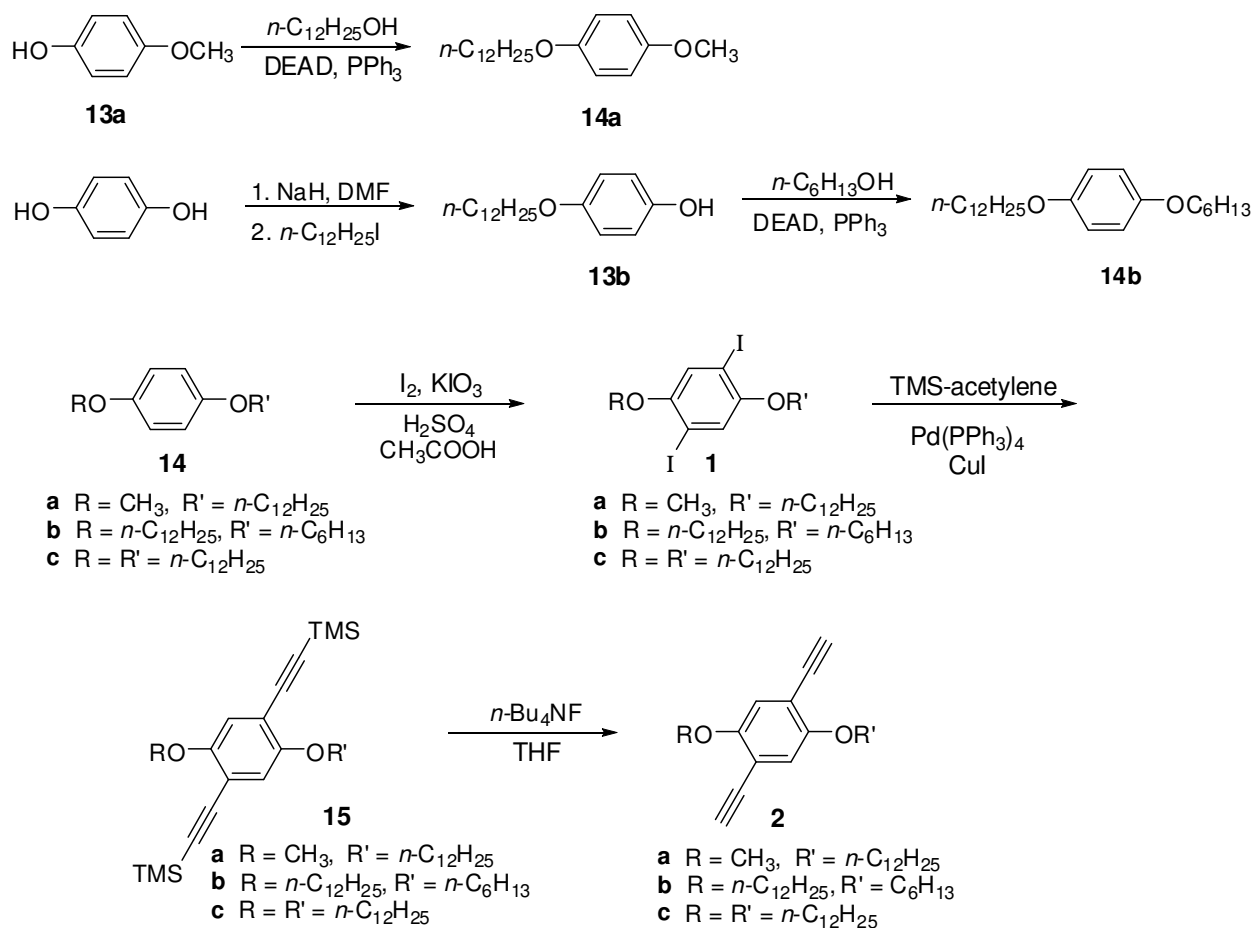
Figure S-1. Synthesis of diiodo (**1**) and dialkyne (**2**) monomer for the synthesis of regiorandom

poly(phenylene ethynylene).

2849, 1606, 1512, 1454, 1395, 1370, 1297, 1237 (C-O str.), 1169, 1104, 1037, 1007, 826, 768.

HRMS: calc. for $C_{18}H_{30}O_2$ = 278.22458, obs. = 278.22513, Δ = 2.0 ppm.

4-Dodecyloxyanisole, 14a.[1] A suspension of 4-methoxyphenol (12.4 g, 100 mmol),

K_2CO_3 (16.6 g, 120 mmol) and 1-bromododecane (29.8 g, 120 mmol) in degassed DMF (75 mL)

was heated at 80°C for 18 h. The reaction mixture was cooled, diluted with chloroform (100 mL)

and washed with 10% HCl (3 × 150 mL). The organic extracts were dried over $MgSO_4$ and the

solvent was removed at under reduced pressure. The residue was recrystallized from methanol to

afford **14a** (15.01, 51.4 % yield) as white flakes, m.p. = 216-217 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.85 (s, 4H, Ar-H), 3.90 (t, [3]J_{HH} = 6.7 Hz, 2H, -OCH$_2$-), 3.77 (s, 3H, -OCH$_3$), 1.70-1.82 (m, 2H), 1.20-1.51 (m, 18H), 0.89 (t, [3]J_{HH} = 6.6 Hz, 3H, -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.47, 153.14 (Ar C1,4), 115.24, 114.43 (Ar C2,3,5,6), 68.52 (-O-CH$_2$-), 55.57 (-O-CH$_3$), 31.77, 31.61, 29.52, 29.25, 29.21, 29.15, 25.91, 25.73, 22.68, 22.61, 14.11. IR (v, cm^{-1}): 2954, 2933 (Ar C-H str.), 2918, 2873, 2849, 1539, 1509, 1474, 1440, 1359, 1293, 1219 (C-O str.), 1036, 901, 826, 743, 529. HRMS: *calc.* for C$_{19}$H$_{32}$O$_2$ = 292.24023, *obs.* = 292.24237, Δ = 7.3 ppm.

1-Dodecyloxy-4-hexyloxybenzene, 14b. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.82 (s, 4H, Ar-H), 3.93 (t, [3]J_{HH} = 6.5 Hz, 4H,-OCH$_2$-), 1.68-1.80 (m, 4H), 1.2-1.5 (m, 24H), 0.84-0.94 (m, 6H, 2 -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.16 (Ar C1,4), 115.34 (Ar C2,3,5,6), 68.62 (2 -OCH$_2$-), 31.91, 31.61, 29.66, 29.63, 29.58, 29.41, 29.39, 29.35, 26.05, 25.73, 22.68, 22.61, 14.11, 14.03. IR (v, cm^{-1}): 2932 (Ar C-H str.), 2917, 2870, 2848, 1510, 1474, 1463, 1395, 1381, 1284, 1240 (C-O str.), 1113, 1031, 1008, 996, 826, 771. HRMS: calc. for C$_{24}$H$_{42}$O$_2$ = 362.31848, obs. = 362.32083, Δ = 6.5 ppm.

4-Dodecyloxy-2,5-diiodoanisole, 1a.[1] A solution of dialkoxybenzene **14a** (7.67 g, 26.3 mmol), I$_2$ (7.65 g, 29.9 mmol), KIO$_3$ (2.57 g, 12 mmol), H$_2$O (14 mL) and H$_2$SO$_4$ (3.5 mL) in acetic acid (150 mL) was heated at 70 °C for 24 h. The reaction mixture was cooled, diluted with CH$_2$Cl$_2$ (200 mL) and washed with aqueous Na$_2$SO$_3$ solution. The combined extracts were washed with 10% aqueous NaOH (2 × 150 mL), dried over MgSO$_4$, and solvent was removed under reduced pressure. The residue was recrystallized twice from ethanol to afford diiodide **1a** (5.06 g, 35.2% yield) as white needles, m.p. = 62-64 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.18 (s, 1H, Ar-H), 7.17 (s, 1H, Ar-H), 3.92 (t, [3]J_{HH} = 6.4 Hz, 2H, -OCH$_2$-), 3.90 (s, 3H, -OCH$_3$), 1.72-

1.87 (m, 2H), 1.22-1.56 (m, 18H), 0.89 (t, $^3J_{HH}$ = 6.6 Hz, 3H, -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.88, 153.78 (Ar C1,4), 122.7, 121.80 (Ar C3,6), 86.14, 86.56 (Ar C2,5), 66.50 (-O-CH$_2$-), 53.57 (-O-CH$_3$), 29.78, 27.53, 27.50, 27.45, 27.83, 27.25, 27.21, 23.91, 20.55, 11.99. IR (v, cm^{-1}): 2913 (Ar C-H str.), 2848, 1483, 1469, 1462, 1434, 1381, 1349, 1266, 1212 (C-O str.), 1180, 1065, 1051, 1022, 994, 958, 921, 848, 813, 778, 757, 737, 716. HRMS: *calc*. for C$_{19}$H$_{30}$O$_2$I$_2$ = 544.03353, *obs*. = 544.03631, Δ = 5.1 ppm. Elemental Analysis: Theoretical = C 41.93%, H 5.56%, O 5.88%, I 46.63%; Found = C 41.99%, H 5.56%, O 5.97%, I 46.68%.

1-Dodecyloxy-4-hexyloxy-2,5-diiodobenzene, 1b. (5.24 g, 80% yield) white solid, m.p. 42-44 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.18 (s, 2H, Ar-H), 3.92 (t, $^3J_{HH}$ = 6.4 Hz, 4H, -OCH$_2$-), 1.74-1.86 (m, 4H), 1.20-1.58 (m, 24H), 0.84-0.96 (m, 6H, 2 × -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.68 (Ar C1,4), 122.99 (Ar C3,6), 86.54 (Ar C2,5), 70.57 (-OCH$_2$-), 32.16, 31.7, 29.89, 29.83, 29.8, 29.6, 29.5, 29.38, 29.35, 26.26, 25.95, 22.94, 22.82, 14.38, 14.28. IR (v, cm^{-1}): 2943, 2924 (Ar C-H str.), 2847, 2359, 1485, 1456, 1387, 1348, 1264, 1209 (C-O str.), 1053, 1013, 1004, 993, 936, 850, 794. HRMS: calc. for C$_{24}$H$_{40}$O$_2$I$_2$ = 614.11178, obs. = 614.11330, Δ = 2.5 ppm. Elemental analysis: Theoretical = C 46.92 %, H 6.56 %, O 5.21 %, I 41.31 % Found = C 46.83 %, H 6.47 %, O 5.29 %, I 41.05 %.

[(2-Dodecyloxy-5-methoxy-1,4-phenylene)di-2,1-ethynediyl]bis[trimethylsilane], 15a. Diiodide **1a** (1.5 g, 2.76 mmol) was added to a stirred solution of PdCl$_2$(PPh$_3$)$_2$ (96 mg, 140 μmol) and CuI (26 mg, 136 μmol) in a mixture of piperidine (9 mL) and toluene (6 mL). The mixture was degassed by freeze-pump-thaw and back-filling with argon. Trimethylsilylacetylene (0.86 mL, 6.07 mmol) was added dropwise over 10 min and the mixture was stirred for 2 h. CH$_2$Cl$_2$ (100 mL) was added and the mixture was flushed through silica plug. The solvent was removed under reduced pressure to afford **15a** (0.97 g, 73% yield) as a pale brown solid, m.p.

71-73 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.90 (s, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 3.95 (t, $^{3}J_{HH} =$ 6.1 Hz, 2H, -O-CH$_2$-), 3.90 (s, 3H, -OCH$_3$), 1.70-1.85 (m, 2H), 1.2-1.6 (m, 18H), 0.89 (t, $^{3}J_{HH} =$ 6.6 Hz, 3H, -CH$_3$), 0.25 (s, 18H, 2 × -Si(CH$_3$)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 154.05, 154 (Ar C2,5), 117.68, 115.49 (aromatic C3,6), 113.95, 113.27 (Ar C1,4), 100.84, 100.18 (-C≡C-), 69.40 (-O-CH$_2$-), 56.3(-O-CH$_3$), 31.87, 29.59, 29.39, 29.31, 25.98, 25.68, 22.65, 14.08. IR (v, cm^{-1}): 2955, 2922 (Ar C-H str.), 2852, 2372, 2347, 2151 (C≡C str.), 1540, 1495, 1467, 1398, 1386, 1271, 1247, 1222, 1200 (C-O str.), 1176, 1032, 939, 877, 838, 757. HRMS: calc. for C$_{29}$H$_{48}$O$_2$Si$_2$ = 484.31929, obs. = 484.32047, Δ = 2.4 ppm.

[(2-Dodecyloxy-5-hexyloxy-1,4-phenylene)di-2,1-ethynediyl]bis[trimethylsilane],

15b. (79% yield) dark brown solid, m.p. 42-43°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.89 (s, 2H, Ar-H), 3.95 (t, $^{3}J_{HH}$ = 6.3 Hz, 4H, -O-CH$_2$-), 1.70-1.85 (m, 4H), 1.2-1.6 (m, 24H), 0.84-0.94 (m, 6H, 2 × -CH$_3$), 0.25 (s, 18H, 2 × -Si (CH$_3$)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.98 (Ar C2,5), 117.15 (aromatic C3,6)), 113.89 (Ar C1,4), 101.04, 100.05 (-C≡C-), 69.40 (-O-CH$_2$-), 31.9, 31.59, 29.67, 29.63, 29.43, 29.34, 29.27, 26.01, 25.68, 22.68, 22.62, 14.11, 14.06. IR (v, cm^{-1}): 2954, 2922 (Ar C-H str.), 2852, 2153 (C≡C str.), 1495, 1467, 1406, 1379, 1271, 1247, 1222, 1200 (C-O str.), 1176, 1025, 939, 877, 838, 757. HRMS: calc. for C$_{34}$H$_{58}$O$_2$Si$_2$ = 554.39754, obs. = 554.39898, Δ = 2.6 ppm.

4-Dodecyloxy-2,5-diethynylanisole, 2a. Tetra-*n*-butylammonium fluoride (1.15 g, 4.41 mmol) was added dropwise to a solution of bis(trimethylsilane) **15a** (970 mg, 2.41 mmol) in dry THF (15 mL) and the mixture was stirred overnight and poured into H$_2$O (50 mL). The mixture was extracted with CH$_2$Cl$_2$ (100 mL), the combined extracts were dried over MgSO$_4$ and the solvent was removed under reduced pressure. The residue was recrystallized from ethanol to give diethyne **2a** (0.59 g, 85% yield) as a pale yellow solid, m.p. 71-73 °C. ^{1}H NMR (300 MHz,

CDCl$_3$): δ 6.97 (s, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 3.97 (t, $^3J_{H1-H2}$ = 6.6 Hz, 2H, -OCH$_2$-), 3.85 (s, 3H, -OCH$_3$), 3.38 (s, 1H, -C≡H), 3.36 (s, 1H, -C≡H), 1.70-1.85 (m, 2H), 1.2-1.6 (m, 18H), 0.89 (t, $^3J_{HH}$ = 6.6 Hz, 3H, -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 154.52 (Ar C1,4), 118.09, 116.14 (Ar C3,6), 113.56, 112.73 (Ar C2,5), 82.81, 79.95 (-C≡C-), 69.85 (-OCH$_2$-), 56.6 (-O-CH$_3$), 32.15, 29.87, 29.81, 29.58, 29.55, 29.33, 29.29, 26.11, 22.92, 22.81, 14.36. IR (ν, cm^{-1}): 3278 (≡C-H str.), 2943, 2918 (Ar C-H str.), 2846, 2105 (C≡C str.), 1497, 1459, 1383, 1273, 1214 (C-O str.), 1198, 1057, 1046, 1027, 1013, 985, 863. HRMS: calc. for C$_{23}$H$_{32}$O$_2$ = 340.24023, obs. = 340.24301, Δ = 8.2 ppm. Elemental Analysis: Theoretical = C 81.13%, H 9.47%, O 9.40%; Found = C 80.66 %, H 9.35 %, O 9.66 %.

1-Dodecyloxy-2,5-diethynyl-4-hexyloxybenzene, 2b. (69% yield) pale yellow solid, m.p. 62°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.95 (s, 2H, Ar-H), 3.97 (t, $^3J_{H1-H2}$ = 6.6 Hz, 4H, -OCH$_2$-), 3.33 (s, 2H, -C≡H), 1.74-1.85 (m, 4H), 1.2-1.53 (m, 24H), 0.83-0.94 (m, 6H, 2 × -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 154.16 (Ar C1,4), 117.90, 117.86 (Ar C3,6), 113.41 (Ar C2,5), 82.65, 82.61 (-C≡C-), 69.85 (-O-CH$_2$-), 32.15, 31.73, 29.87, 29.81, 29.79, 29.58, 29.55, 29.33, 29.29, 26.11, 25.79, 22.92, 22.81, 14.36, 14.25. IR (ν, cm^{-1}): 3283 (≡C-H str.), 2957, 2940, 2919 (Ar C-H str.), 2871, 2848, 2159 (C≡C str.), 1499, 1468, 1462, 1384, 1272, 1217 (C-O str.), 1198, 1057, 1046, 1028, 1000, 985, 863. HRMS: calc. for C$_{28}$H$_{42}$O$_2$ = 410.31848, obs. = 410.30775, Δ = 6.2 ppm. Elemental analysis: Theoretical = C 81.90 %, H 10.31 %, O 7.79 %, Found = C 81.89 %, H 10.42 %, O 7.87 %.

II. Analysis of mixture of products obtained from formylation of 7b.

Formylation of monoiodobenzene **7b** (TiCl$_4$, CHCl$_2$OCH$_3$) at low temperature (-15 to -40 °C) afforded a mixture of productsColumn chromatography followed by NMR and mass spectral analysis of individual components indicated the formation of: benzaldehyde **12** (61% conversion), together with 1,4-dialkoxy-2,5-diiodobenzene (6%), 1,4-dialkoxybenzene (3%), 2,5-dialkoxy-benzaldehyde (18%) and 2,5-dialkoxy-3-iodobenzaldehyde (12%), Figure S-2. . ^{1}H NMR spectra of the crude product mixtures are provided in Figure S-3.
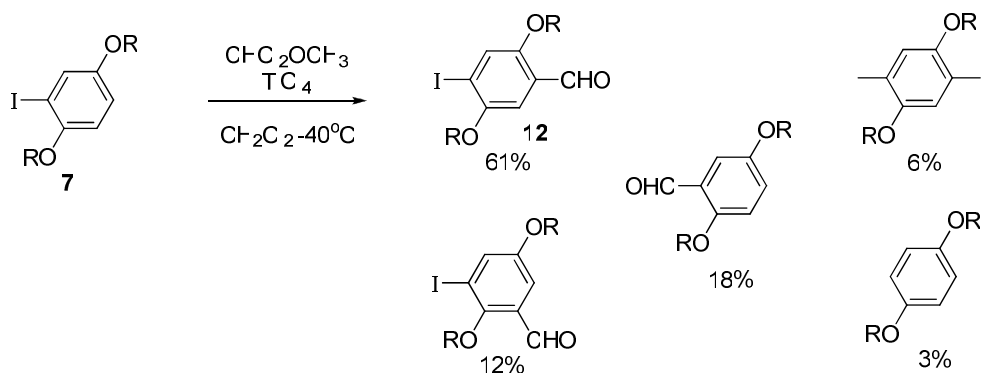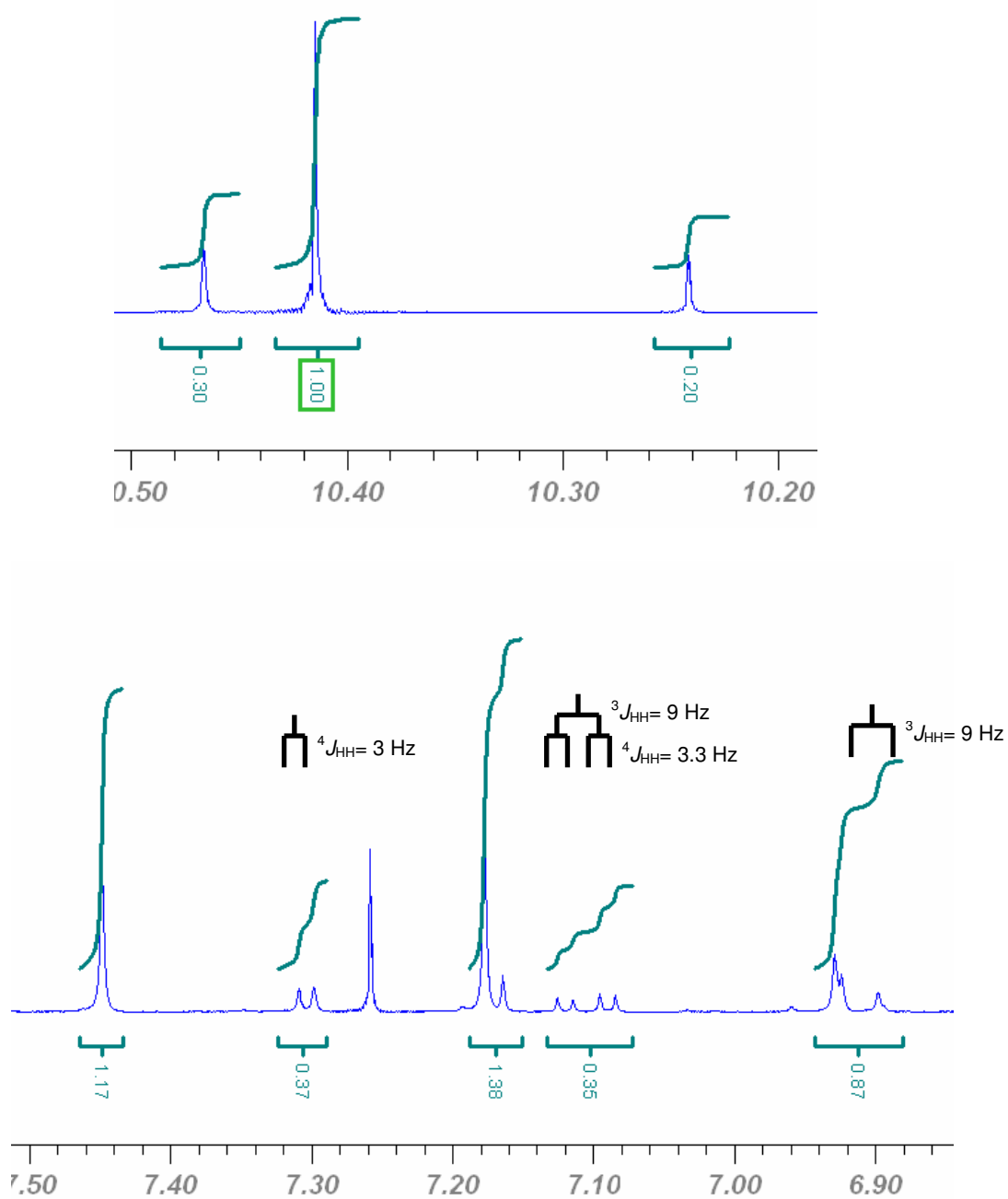

Figure S-2. Formylation of **7b**.

Figure S-3: ^{1}H NMR spectra of crude reaction mixture obtained upon formylation of 7b. Top, formyl (-C*H*O) region of the spectrum. Bottom, aromatic region.

III. Alternate approach to prepare 4-iodophenylacetylene A-B type monomers

In addition to the schemes described in Figures 3-5 for the synthesis of 4-iodophenylacetylene (**13**), we also attempted to prepare these A-B type monomers by a shorter approach. This approach was designed to avoid the tosylation and detosylation step used in the previous scheme to regioselectively monoiodinate the benzene ring. This approach involved monoiodination of the symmetrical dialkoxybenzene **2** followed by Frieldel-Crafts acetylation followed by regioselective dealkylation of the alkoxyl group adjacent to the ketone substitutuent[12], Figure S-4.
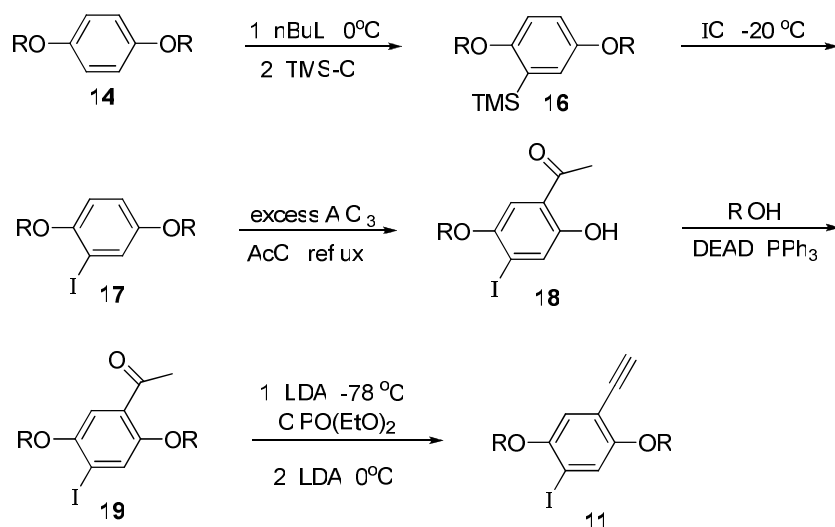

Figure S-4. Synthesis of 4-iodophenylacetylene (**13**) monomer by Friedel-Crafts acylation and regioselective dealkylation.

Iodination of the symmetrical dialkoxy benzene **2** was achieved by lithiation followed by reaction with trimethylsilane chloride to afford the trimethylsilyl derivative **15**, followed by treatment with iodine monochloride. Treatment of the resulting iodobenzene **16** with excess AlCl₃ and acetyl chloride at reflux, led to the formation of a mixture of products, including the desired product **17** with the hydroxyl group adjacent to the acetyl group. However, the mixture

also contained substantial amounts of the regioisomer in which dealkylation had taken place adjacent to the iodo subsubstituent and non-acetylated phenols. The separation of the mixture was tedious and provided product **17** in a low yield. The tetrasubstituted compound **18** could be obtained by attaching the desired second chain using Mitsunobu coupling. Negishi Tour phosphonation-elimination of **18** would provide the iodoalkyne monomer **13**. Overall, this approach was not efficient due to the tedious separation of the mono-iodinated product **16**, and the undesired cleavage of the alkyl side chains on the carbon at the 4 position. Apart from these reasons, the Neigishi-Tour reaction was not suitable for base sensitive side chains on the aromatic ring.

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