Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Direct synthesis of poly(*p*-phenyleneethynylene)s from calcium carbide

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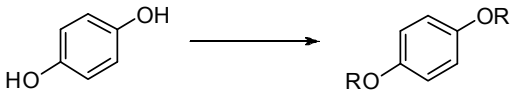
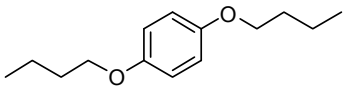
Contents

General: All reagents were purchased from Sigma-Aldrich, Fluka® (Switzerland) or Merck® (Germany) and used without further purification. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F-254 pre-coated plastic TLC plates from EM Science. Visualization was performed with a 254 nm ultraviolet lamp. Gel column chromatography was carried out with silica gel (60, 230-400 mesh) from ICN Silitech. Elemental (C, H, N) analysis was performed on PE 2400 series II (Perkin-Elmer, USA). The ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 or Bruker 400 in $CDCl_3$ and DMSO-d_6. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards: chloroform (δ 7.26 for ^{1}H, δ 77.00 for ^{13}C) and DMSO-d_6 (δ2.50 for ^{1}H, δ 39.52 for ^{13}C). Coupling constants (J) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triple), q (quartet), bs (broad singlet), m (multiplet). Fourier transform infrared spectra were acquired on Nicolet 6700 FT-IR spectrometer equipped with a mercury-cadminum telluride (MCT) detector (Nicolet, USA). All polymer solutions were filtered through 0.45 μm syringe filters prior to use. All polymer solutions were filtered through 0.45 μm syringe filters prior to use. Polymer molecular weights were determined by Waters 600 controller chromatograph equipped two HR (waters), column (HR1 and HR4) at 35 ^{0}C and a reflective index detector (waters 2414). Tetrahydrofuran was used as an eluent with the flow rate of 1.0 mL/min (3 mg/mL sample concentrations). Sample injection volume was 50 μL. Polystyrenes (996–188,000 Da.) were used as standards for calibration. The UV-Visible spectra were obtained from Varian Cary 50 UV-Vis spectrophotometer (Varian, USA) using $CHCl_3$ and DMSO as a solvent. Fluorescence emission spectra were acquired by using Perkin Elmer precisely LS 45.

General procedure for preparation of 1,4-dialkoxybenzene (procedure A) (a–d): To a stirred suspension of KOH (4.5 equiv.) and hydroquinone (1 equiv.) in dried DMF or DMSO was added dropwise alkyl bromide (4 equiv.). The mixture was stirred at room temperature for overnight. The mixture was extracted three times with CH_2Cl_2. The combined organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide product.

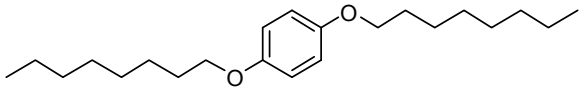


Synthesis of 1,4-dibutoxybenzene (a)[1]



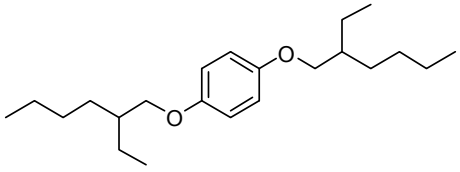
Synthesis as declared in procedure A using hydroquinone (2.00 g, 18.16 mmol), *n*-butyl bromide (9.95 g, 72.64 mmol), KOH (4.58 g, 81.72 mmol) in DMF (15 mL). The mixture was poured into 300 mL of cool water and the organic layer was filtered, washed with cool water many times, and dried over a steam bath to afford **a** (3.06 g, 76%) as a light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 4H), 3.92–3.89 (t, 4H), 1.77–1.70 (m, 4H), 1.52–1.43 (m, 4H), 0.98–0.94 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.7, 115.9, 68.9, 32.0, 19.7, 14.3.

Synthesis of 1,4-bis(octyloxy)benzene (b)[2]



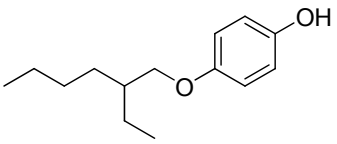
Synthesis as declared in procedure A using hydroquinone (2.00 g, 18.16 mmol), *n*-octyl bromide (14.03 g, 72.64 mmol), KOH (4.59 g, 81.72 mmol) in DMF (15 mL) to afford **b** (3.05 g, 50%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 4H), 3.91–3.87 (t, 4H), 1.78–1.71 (m, 4H), 1.47–1.40 (m, 4H), 1.32–1.28 (m, 16H), 0.90–0.86 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.7, 115.9, 69.2, 32.3, 29.9, 29.9, 29.7, 26.5, 23.1, 14.6.

Synthesis of 1,4-bis(2-ethylhexyloxy)benzene (c)[3]



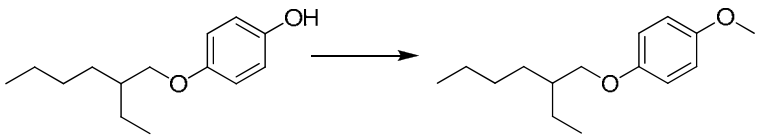
Synthesis as declared in procedure A using hydroquinone (2.00 g, 18.16 mmol), 2-ethylhexyl bromide (14.03 g, 72.64 mmol), KOH (4.59 g, 81.72 mmol) in dried DMSO (15 mL) to afford **c** (5.59 g, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 4H), 3.79 (d, 4H), 1.69 (dd, 2H), 1.56–1.21 (m, 16H), 1.06–0.85 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.7, 115.6, 71.5, 39.8, 30.8, 29.4, 24.1, 23.3, 14.3, 11.3.

Synthesis of 4-(2-ethylhexyloxy)phenol (d)



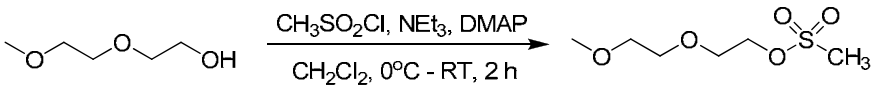
Synthesis as declared in procedure A using hydroquinone (1.00 g, 9.08mmol), 2-ethylhexyl bromide (0.58 g, 3.02 mmol), KOH (3.40 g, 60.4 mmol) in dried DMSO (10 mL) to afford **d** (0.51 g, 76%) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, 4H), 5.20 (s, 1H), 3.78 (d, 2H), 1.73–1.67 (m, 1H), 1.53–1.38 (m, 4H), 1.33–1.31 (m, 4H), 0.94–0.91 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 149.3, 116.1, 115.8, 71.5, 39.5, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1.

Synthesis of 1-(2-ethylhexyloxy)-4-methoxybenzene (e)[4]



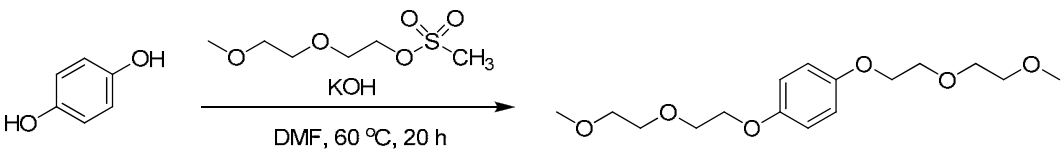
To a stirred solution of **d** (0.51 g, 2.31 mmol) in dried THF (15 mL) was charged with MeI (0.98 g, 6.94 mmol) and then added NaH (0.11 g, 4.62 mmol). The reaction mixture was stirred for 12 h at 70 ^{0}C and finally dropped with MeOH (5 mL). The reaction mixture was extracted with CH_2Cl_2 (3×50) and the combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide **e** (0.46 g, 84%) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 4H), 3.86-3.65 (m, 5H), 1.75–1.69 (m, 1H), 1.57–1.30 (m, 8H), 0.96–0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.7, 152.2, 114.5, 113.6, 70.3, 54.7, 38.5, 29.6, 28.1, 22.9, 22.1, 13.0, 10.1.

Synthesis of 2-(2-methoxyethoxy)ethylmethanesulfonate (f)



To a stirred solution of Diethyleneglycol monomethylether (10.38 g, 86.31 mmol) and DMAP in CH_2Cl_2 (150 mL) was charged with triethylamine (25.00 mL, 178 mmol). The reaction mixture was stirred at 0 ^{0}C for 10 min and then dropwise with mesylchloride (10.92 g, 95.2 mmol) which was dissolved with CH_2Cl_2 (50 mL). The reaction mixture was stirred at room temperature for 2 h. The mixture was extracted with CH_2Cl_2 (3×50) and the combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide **f** (15.47 g, 90%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.33 (t, 2H), 3.72 (t, 2H), 3.60 (t, 2H), 3.49 (t, 2H), 3.32 (s, 3H), 3.02 (s, 3H).

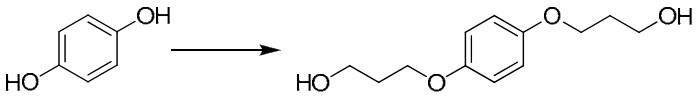
Synthesis of 1,4-bis(2-(2-methoxyethoxy)ethoxy)benzene (g)[5]



To a stirred solution of hydroquinone (1.53 g, 13.89 mmol) and KOH (2.44 g, 43.5 mmol) in DMF (30 mL) was added with **f** (5.81 g, 29.3 mmol). The reaction mixture was stirred at 60 ^{0}C for 20 h. The reaction mixture was extracted with CH_2Cl_2/0.1

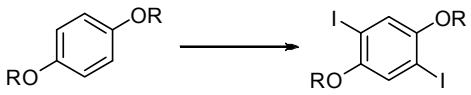
M HCl and the combined organic phase was washed with water (10×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide **g** (4.21 g, 96%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (s, 4H), 4.05 (t, 4H), 3.79 (t, 4H), 3.68 (t, 4H), 3.54 (t, 4H), 3.35 (s, 6H).

Synthesis of 3,3'-(1,4-phenylenebis(oxy))dipropan-1-ol (h)[6]

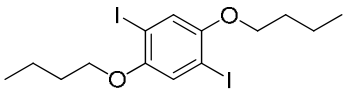


To a stirred suspension of K_2CO_3 (22.6 g, 163.47mmol) and hydroquinone (3 g, 27.24mmol) in MeCN (20 mL) was added dropwise 3-chloropropan-1-ol (12.88 g, 136.23mmol). The mixture was refluxed overnight. The mixture was extracted with CH_2Cl_2 (3×200) and the combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide **h** (6.16 g, 100%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 4H), 4.09–4.06 (t, 4H), 3.87–3.84 (t, 4H), 2.05–1.99 (m, 4H), 1.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.0, 115.4, 66.5, 60.5, 31.9.

General procedure for preparation of 2,5-diiodo-1,4-dialkoxybenzene(procedure B) (1a–1c, 1f): To a stirred of 2,5-dialkylbenzene **(1a–1c, 1f)** (1 equiv.) in MeOH at temperature below 15 ^{0}C was added dropwise iodine(I)chloride (4 equiv.) and the mixture was stirred reflux for 1 day under pressure of N_2. The mixture was extracted three times with CH_2Cl_2. The combined extract was washed with aqueous $Na_2S_2O_3$, water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide product.

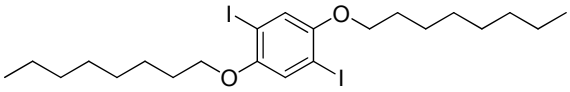


Synthesis of 1,4-dibutoxy-2,5-diiodobenzene (1a)[7]



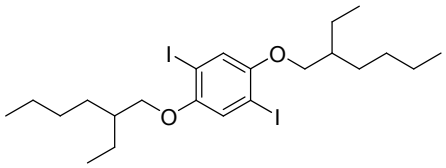
Synthesis as declared in procedure B using **a** (4.00 g, 17.99 mmol), iodine(I)chloride (12.76 g, 78.61 mmol) in MeOH (30 mL) to afford **1a** (6.29 g, 74%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 2H), 3.95–3.92 (t, 4H), 1.82–1.75 (m, 4H), 1.58–1.49 (m, 4H), 1.00–0.96 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 123.2, 86.6, 70.4, 31.6, 19.6, 14.1.

Synthesis of 1,4-diiodo-2,5-bis(octyloxy)benzene (1b)[3,7]



Synthesis as declared in procedure B using **b** (3.00 g, 8.98mmol), iodine(I)chloride (6.37 g, 39.25mmol) in MeOH (20 mL) to afford **1b** (1.89 g, 36%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 2H), 3.94–3.91 (t, 4H), 1.83–1.75 (m, 4H), 1.54–1.44 (m, 4H), 1.39–1.24 (m, 16H), 0.89 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 122.9, 86.4, 70.4, 31.8, 29.3, 29.2, 29.2, 26.0, 22.7, 14.1.

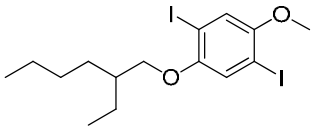
Synthesis of 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene(1c)[3,8]



Synthesis as declared in procedure B using **c** (0.50 g, 1.49mmol), iodine(I)chloride (1.07 g, 5.96mmol) in MeOH (35 mL) to afford **1c** (0.69 g, 79%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 2H), 3.80 (d, 4H), 1.72 (dt, 2H), 1.59–1.38

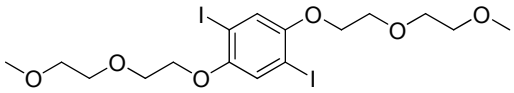
(m, 8H), 1.36–1.24 (m, 8H), 0.91 (t, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 121.9, 85.6, 71.9, 39.0, 30.0, 28.6, 23.5, 22.5, 13.6, 10.8.

Synthesis of1-(2-ethylhexyloxy)-2,5-diiodo-4-methoxybenzene (1d)[9]



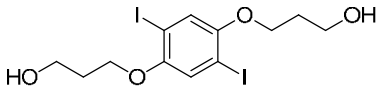
A solution of **e** (0.15 g, 0.65 mmol), H_5IO_6 (0.07 g, 0.33mmol) and I_2 (0.33 g, 1.30 mmol) in 1.5 mL acetic acid, 1 mL sulfuric acid and 2 mL water was stirred at 70 ^{0}C for 12 h under pressure of N_2. After cooling, the mixture was extracted with CH_2Cl_2 (3×50). The organic layer was washed with aqueous $Na_2S_2O_3$, water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide **1d** (0.19 g, 60%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 1H), 7.16 (s, 1H), 3.82 (d, 5H), 1.79–1.68 (m, 1H), 1.60–1.40 (m, 4H), 1.36–1.28 (m, 4H), 0.97–0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3, 153.2, 122.6, 121.7, 86.3, 85.6, 72.5, 57.3, 39.6, 30.6, 29.2, 24.1, 23.1, 14.2, 11.3.

Synthesis of1,4-diiodo-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene (1e)[10]



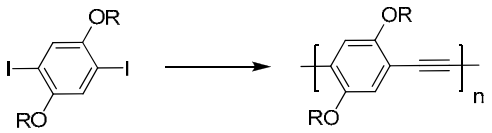
A solution of **g** (0.50 g, 1.59 mmol), H_5IO_6 (0.18 g, 0.79 mmol) and I_2 (0.80 g, 3.18 mmol) in 4.5 mL acetic acid, 3 mL sulfuric acid and 6 mL water was stirred at 70 ^{0}C for 12 h. After cooling, the mixture was extracted with CH_2Cl_2 (3×50). The organic layer was washed with aqueous $Na_2S_2O_3$, water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide **1e** (0.59 g, 66%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 2H), 4.12–4.10 (t, 4H), 3.89–3.87 (t, 4H), 3.79–3.76 (t, 4H), 3.59–3.57 (t, 4H), 3.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 123.8, 86.6, 72.3, 71.3, 70.6, 69.8, 60.7, 59.3.

Synthesis of 3,3'-(2,5-diiodo-1,4-phenylene)bis(oxy)dipropan-1-ol (1f)[11]

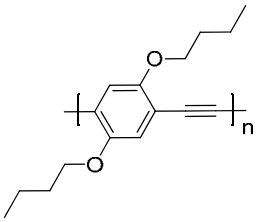


Synthesis as declared in procedure B using **h** (1.50 g, 5.64 mmol), iodine(I)chloride (4.57 g, 28.18 mmol) in MeOH (15 mL) to afford **1f** (2.64 g, 98%) as a white solid. ^{1}H NMR (400MHz, DMSO): δ 7.33 (s, 2H), 4.52 (s, 2H), 4.03–4.00 (t, 4H), 3.60–3.57 (t, 4H), 1.86–1.80 (m, 4H). ^{13}C NMR (101 MHz, DMSO): δ 152.3, 122.4, 86.9, 66.8, 57.3, 32.1.

General procedure for polymerization of aryl diiodides (procedure C) (2a–2f)): A 100 mL round bottom flask with a magnetic stir bar was charged with aryl diiodides (1 equiv.), palladium catalyst (0.05 equiv.), copper catalyst (0.1 equiv.), triphenylphosphine (0.1 equiv.), calcium carbide (6 equiv.) in 1:2 mixture of base and solvent. All reactions were carried out under positive pressure of N_2 filled in rubber balloons. The mixture was stirred at room temperature for 20 hours. The solution was then filtrated with cotton wool by methylene chloride as eluent, concentrated to a small volume and precipitated by dropping the solution into 150 mL of methanol. The precipitate that formed was collected by centrifuge, washed repeatedly with methanol and evaporated under vacuum.

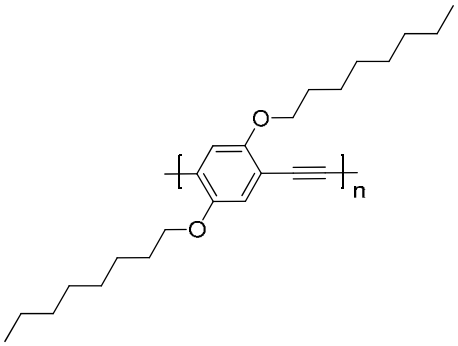


Synthesis of poly(1,4-dibutoxy-*p*-phenyeneethynylene) (2a)[12]



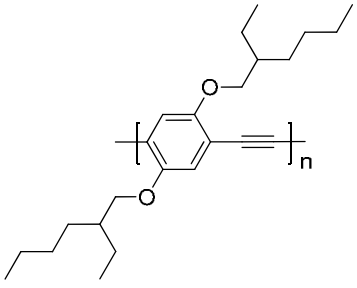
Synthesis as declared in procedure C using **1a** (150 mg, 0.31 mmol), palladium(II)acetate (3.37 mg, 0.015 mmol), copper iodide (5.90 mg, 0.031 mmol), triphenylphosphine (8.13mg, 0.031 mmol), calcium carbide (119.22mg, 1.86 mmol) and DBU (2 mL) in THF (4 mL) to afford **2a** (53.48 mg, 71%) as a yellow orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (br, 2H), 4.04 (br, 4H), 1.83 (br, 4H), 1.55 (br, 4H), 0.99 (br, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.9, 117.7, 114.7, 91.9, 69.8, 31.7, 19.6, 14.2. FTIR (cm^{-1}): 2954, 2929, 2869, 2200, 2157, 1768, 1721, 1595. GPC (vs. polystyrene standards in tetrahydrofuran): M_w = 20,168, M_w/M_n = 2.3, DP_n = 36.

Synthesis of poly(1,4-bis(octyloxy)-*p*-phenyleneethynylene) (2b)[3,12,13]



Synthesis as declared in procedure C using **1b** (100 mg, 0.17 mmol), palladium(II)acetate (1.9 mg, 0.008 mmol), copper iodide (3.24 mg, 0.017 mmol), triphenylphosphine (4.46 mg, 0.017 mmol), calcium carbide (65.38 mg, 1.02 mmol) and DBU (1 mL) in THF (2 mL) to afford **2b** (47.27 mg, 78%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (br, 2H), 4.01 (br, 4H), 1.83 (br, 4H), 1.49 (br, 4H), 1.27 (br, 16H), 0.86 (br, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.7, 117.6, 114.5, 91.6, 69.9, 32.0, 29.6, 29.5, 29.5, 26.2, 22.8, 14.2. FTIR (cm^{-1}): 2922, 2850, 2186, 2157, 1733, 1597. GPC (vs. polystyrene standards in tetrahydrofuran): M_w = 40,972, M_w/M_n = 2.40, DP_n = 48.

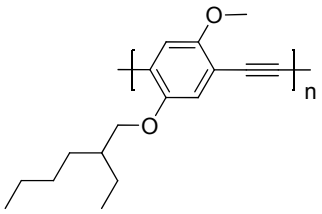
Synthesis of poly(1,4-bis(2-ethylhexyloxy)-*p*-phenyleneethynylene) (2c)[3,14]



Synthesis as declared in procedure C using **1c** (100 mg, 0.17 mmol), palladium(II)acetate (1.9 mg, 0.008 mmol), copper iodide (3.24 mg, 0.017 mmol), triphenylphosphine (4.46 mg, 0.017 mmol), calcium carbide (65.38 mg, 1.02 mmol) and DBU (0.5 mL) in THF (1 mL) to afford **2c** (50.36 mg, 83%) as a yellow fiber. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (s, 2H), 3.89 (s, 4H), 1.81 (s, 2H), 1.53 (s, 8H), 1.33 (s, 8H), 0.98 (s, 5H), 0.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 153.6, 116.6, 114.1,

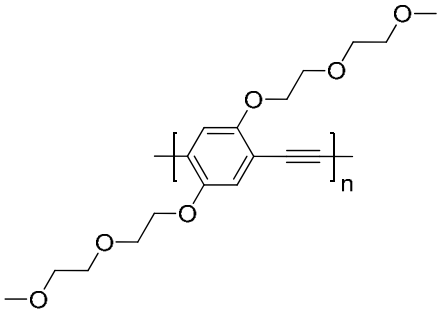
91.5, 71.9, 39.5, 30.5, 29.0, 23.9, 22.9, 13.9, 11.2. FTIR (cm^{-1}): 2954, 2921, 2869, 2855, 2203, 2159, 1642, 1592. Found: C, 80.86; H, 10.11. Calc. for $C_{12}H_{18}O$: C, 80.84; H, 10.18%. GPC (vs. polystyrene standards in tetrahydrofuran): M_w = 91300, M_w/M_n= 2.00, DP_n = 128.

Synthesis of poly(1-(2-ethylhexyloxy)-4-methoxy-*p*-phenyleneethynylene) (2d)



Synthesis as declared in procedure C using **1d** (100 mg, 0.20 mmol), palladium(II)acetate (2.25 mg, 0.01 mmol), copper iodide (3.81 mg, 0.02 mmol), triphenylphosphine (5.25 mg, 0.02 mmol), calcium carbide (76.92 mg, 1.20 mmol) and DBU (1.34 mL) in THF (2.66 mL) to afford **2d** (48.28 mg, 93%) as a yellow-green powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (s, 1H),3.90 (br, 4H),1.80 (br, 1H),1.73-1.19 (br, 8H), 0.96-0.88 (br, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 153.7, 117.0, 115.1, 91.5, 71.7, 56.3, 39.5, 30.4, 29.0, 23.8, 22.9, 13.9, 11.1. FTIR (cm^{-1}): 2954, 2924, 2872, 2855, 2198, 2159, 1663, 1642, 1603, 1546. Found: C, 79.05; H, 8.59. Calc. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%. GPC (vs. polystyrene standards in tetrahydrofuran): M_w = 26,915, M_w/M_n= 2.21, DP_n = 47.

Synthesis of poly(1,4-bis(2-(2-methoxyethoxy)ethoxy)-*p*-phenyleneethynylene) (2e)



Synthesis as declared in procedure C using **1e** (100 mg, 0.18 mmol), palladium(II)acetate (2.02 mg, 0.009 mmol), copper iodide (3.43 mg, 0.018 mmol), triphenylphosphine (4.72 mg, 0.018 mmol), calcium carbide (69.23 mg, 1.08 mmol) and DBU (1.16 mL) in THF (2.24 mL) to afford **2e** (52.43 mg, 87%) as an orange film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (s, 2H), 4.24 (br, 4H), 3.92 (br, 4H), 3.77 (br, 4H), 3.53 (br, 4H), 3.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.13, 118.55, 115.15, 91.98, 72.53, 71.49, 70.22, 59.49. FTIR (cm^{-1}): 2921, 2872, 2817, 2198, 2159, 1721, 1666, 1633, 1600. Found: C, 64.17; H, 6.92. Calc. for C_3H_4O: C, 64.27; H, 7.19%. GPC (vs. polystyrene standards in tetrahydrofuran): M_w = 26,975, M_w/M_n= 1.56, DP_n = 51.

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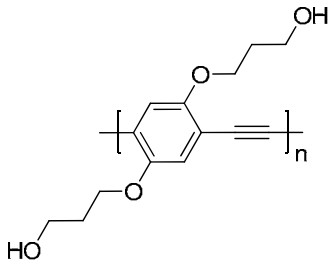
Synthesis of poly(1,4-bis(oxy)dipropan-1-ol-*p*-phenyleneethynylene) (2f)



Synthesis as declared in procedure C using **1f** (100 mg, 0.21 mmol), palladium(II)acetate (2.36 mg, 0.01 mmol), copper iodide (4.00 mg, 0.02 mmol), triphenylphosphine (5.51 mg, 0.02 mmol), calcium carbide (80.77 mg, 1.26 mmol) and DBU

(1.33 mL) in THF (2.66 mL) to afford **2f (**48.40 mg, 93%) as a dark-orange solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.15 (s, 2H), 4.57 (br, 4H), 4.14 (br, 4H), 3.64 (br, 4H), 1.91 (br, 4H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 152.9, 116.9, 113.6, 91.6, 66.2, 57.4, 32.2. FTIR (cm^{-1}): 3313, 2929, 2874, 2184, 2159, 1735, 1713, 1598.

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

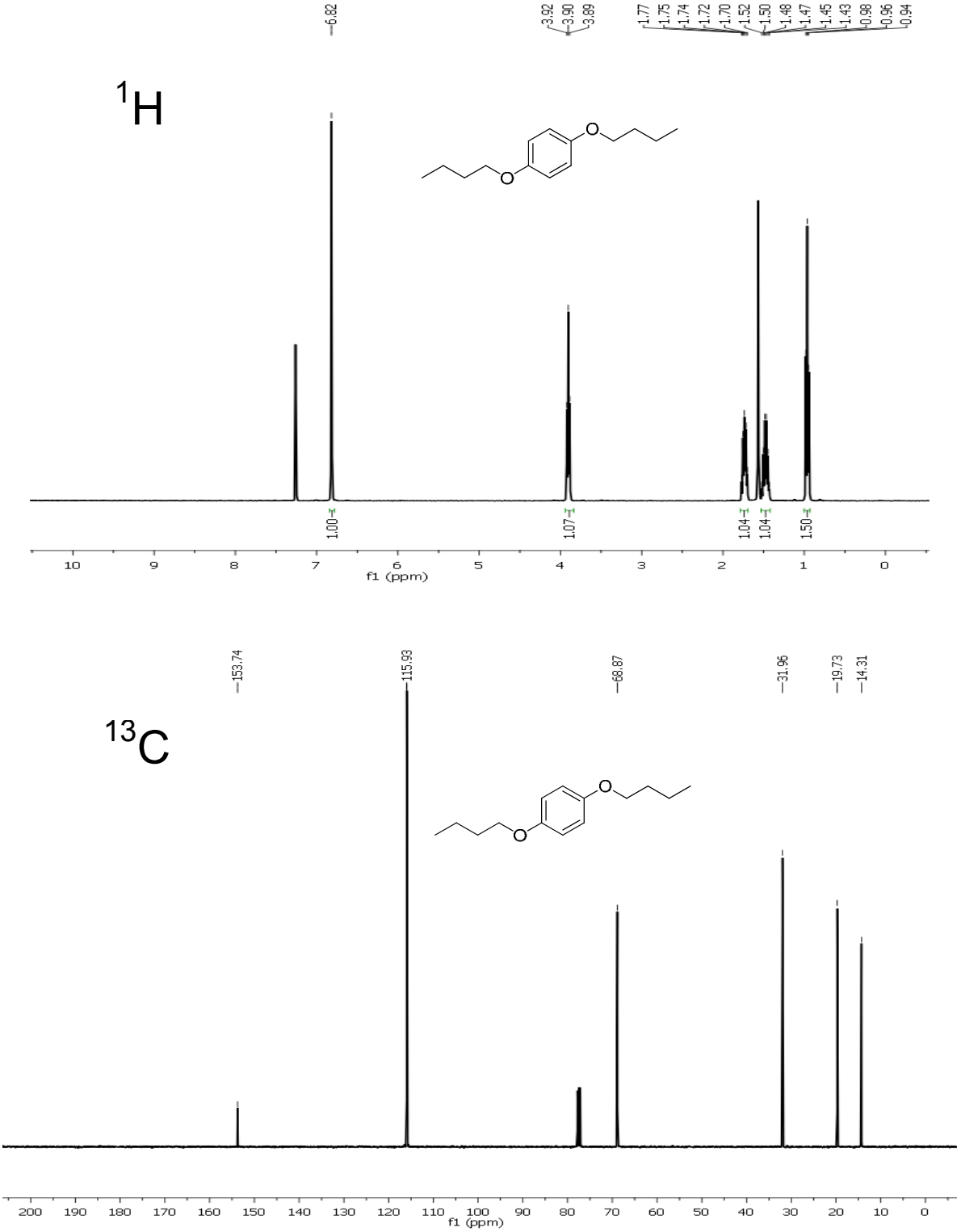


Figure S1 ^{1}H and ^{13}C NMR spectra of compound **a**

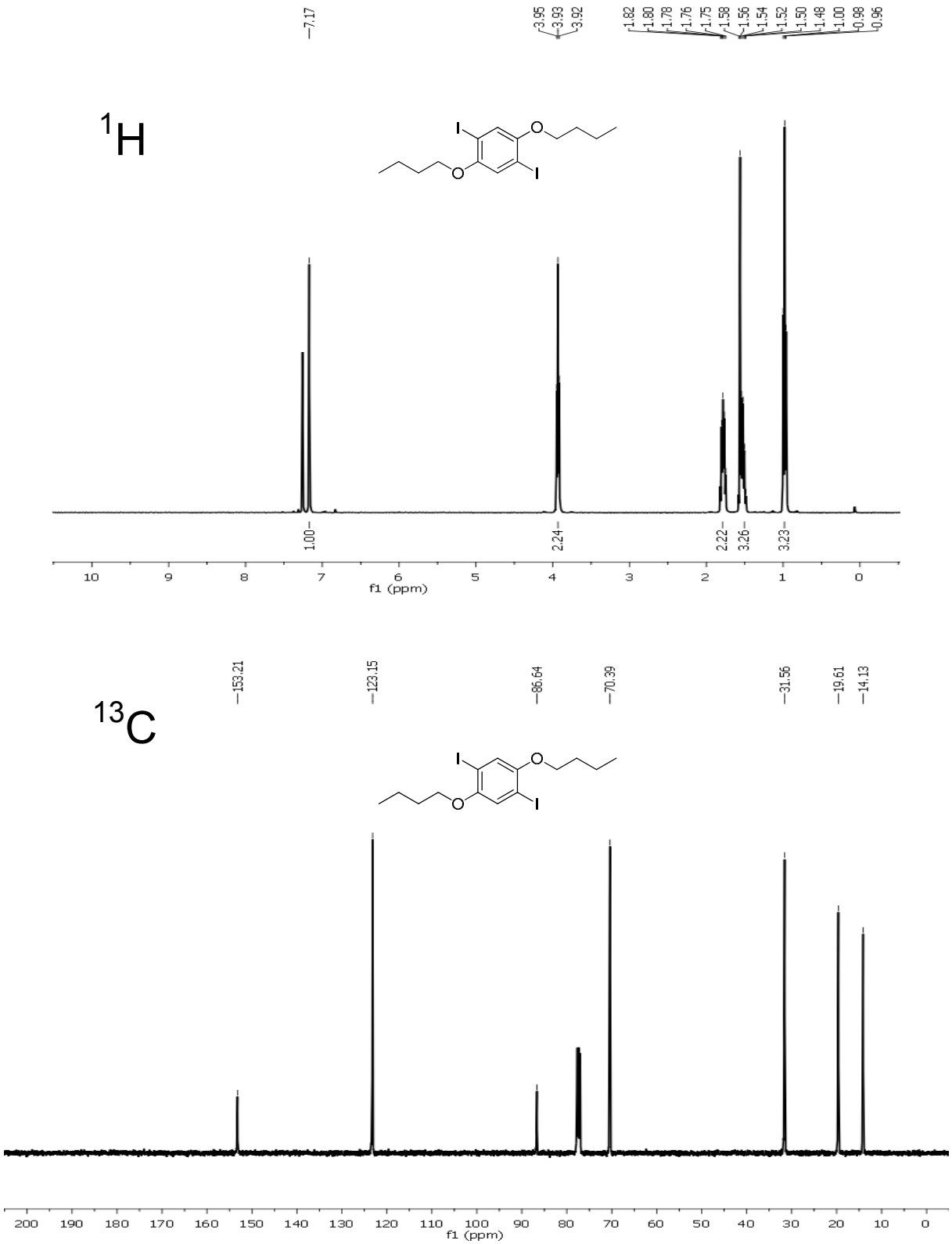


Figure S2 ^{1}H and ^{13}C NMR spectra of compound **1a**

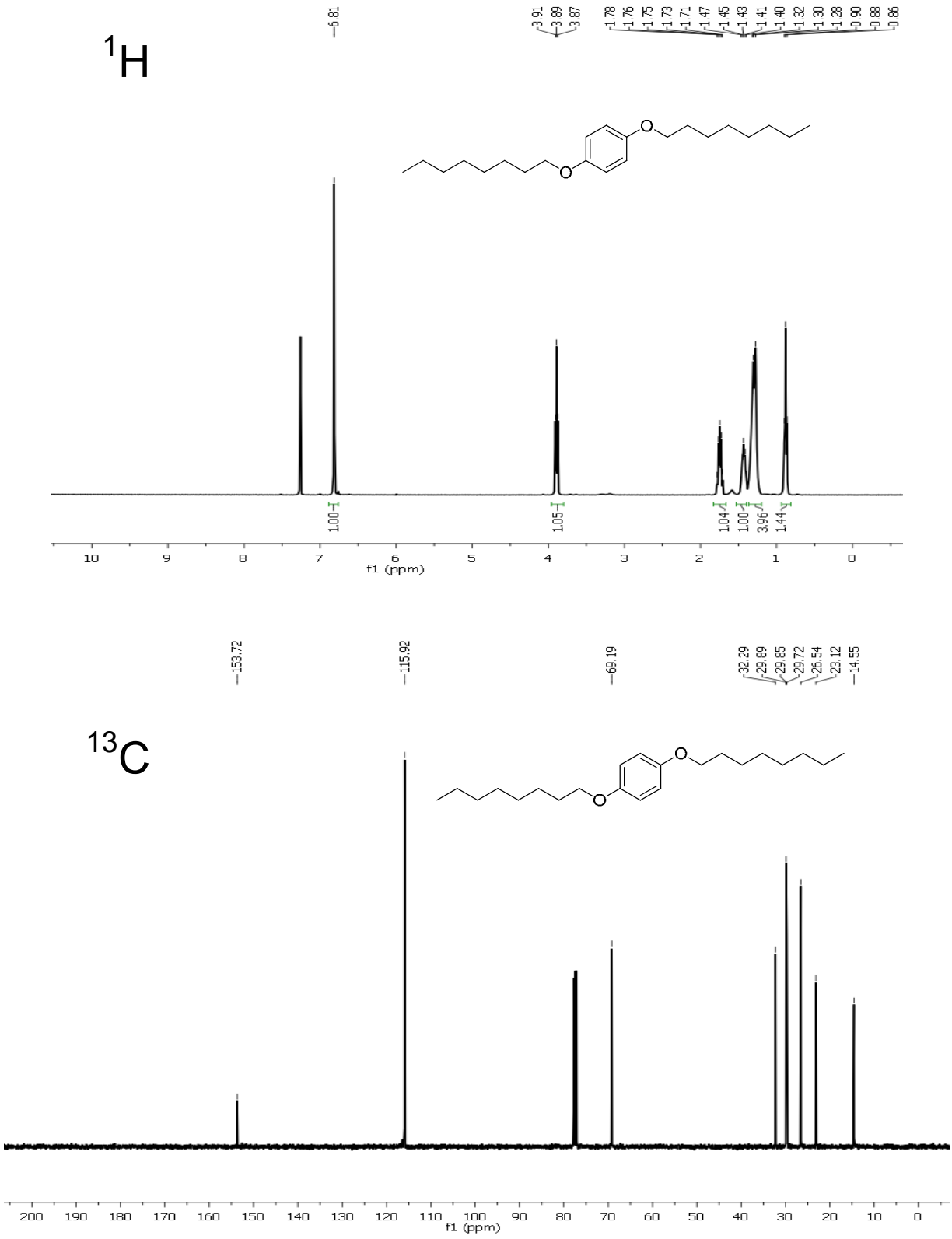


Figure S3 ^{1}H and ^{13}C NMR spectra of compound **b**

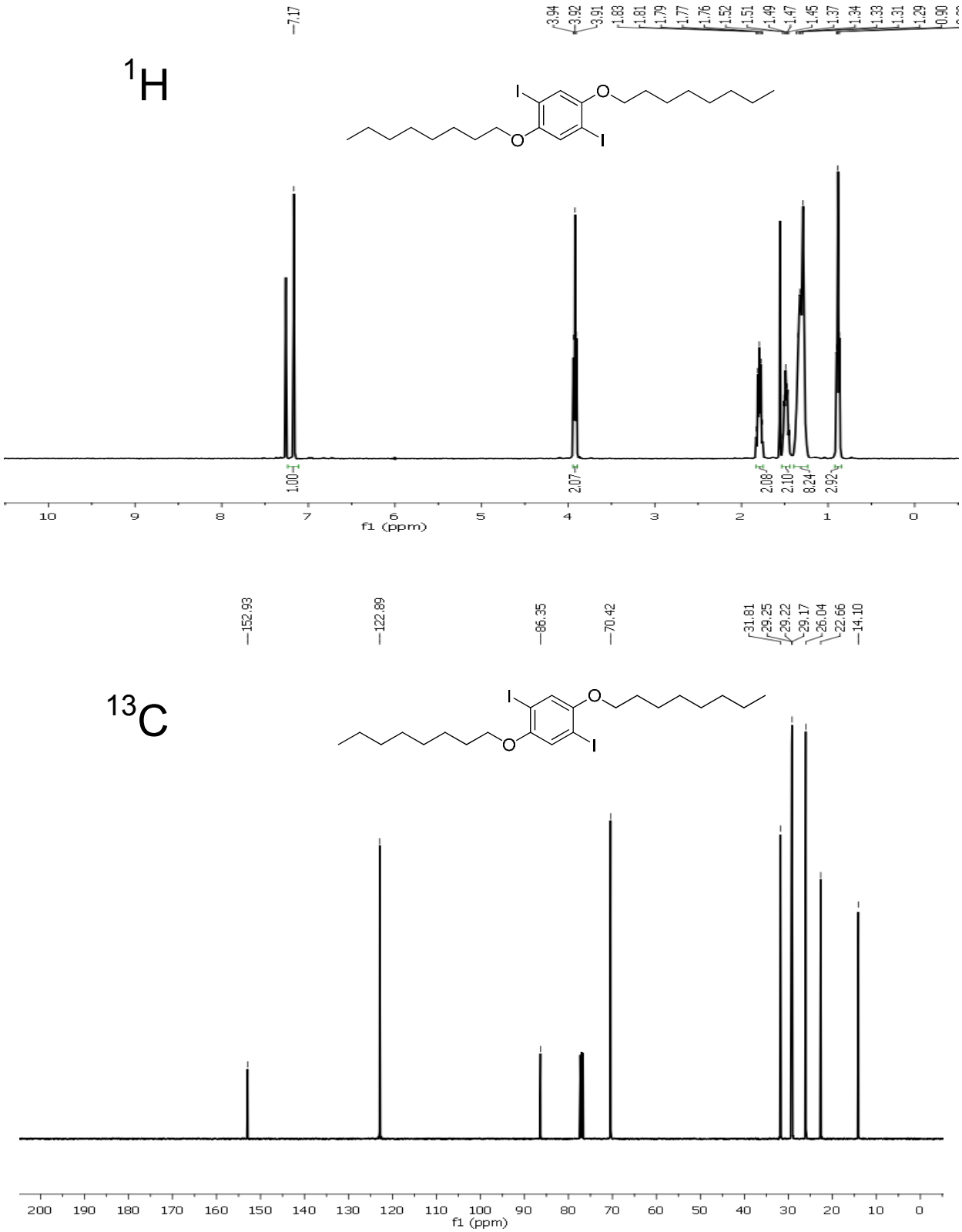


Figure S4 ^{1}H and ^{13}C NMR spectra of compound **1b**

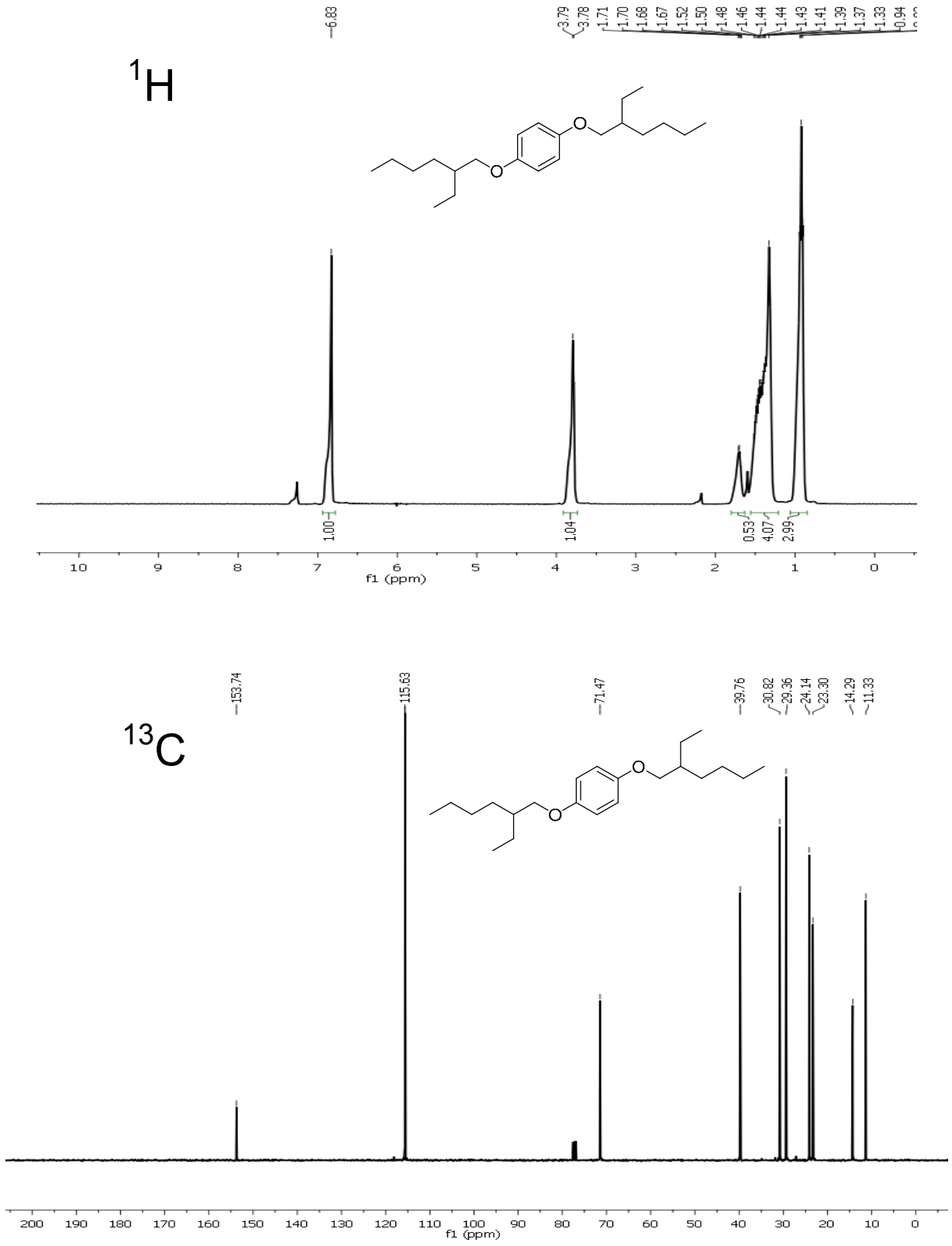


Figure S5 ^{1}H and ^{13}C NMR spectra of compound **c**

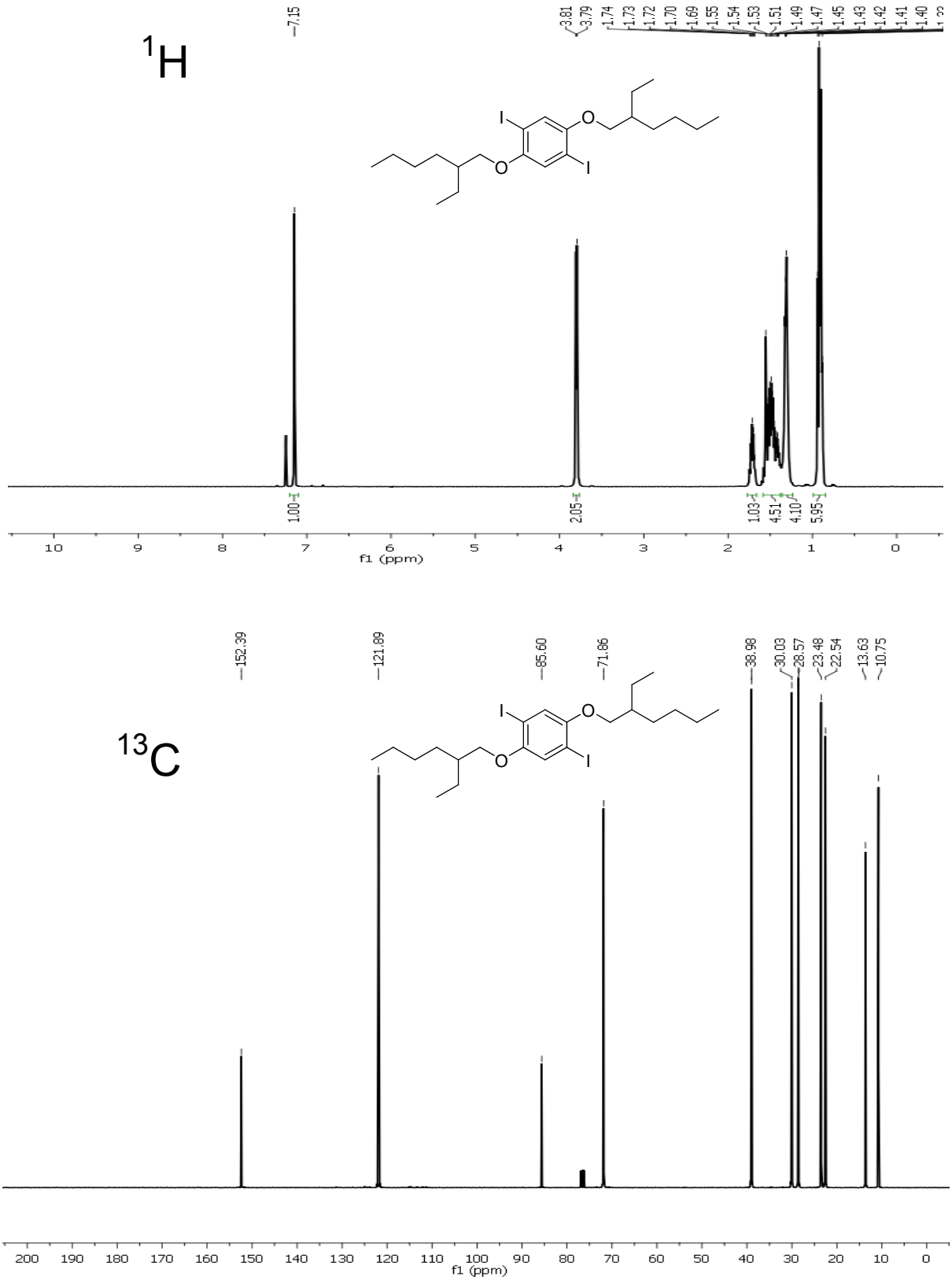


Figure S6 ^{1}H and ^{13}C NMR spectra of compound **1c**

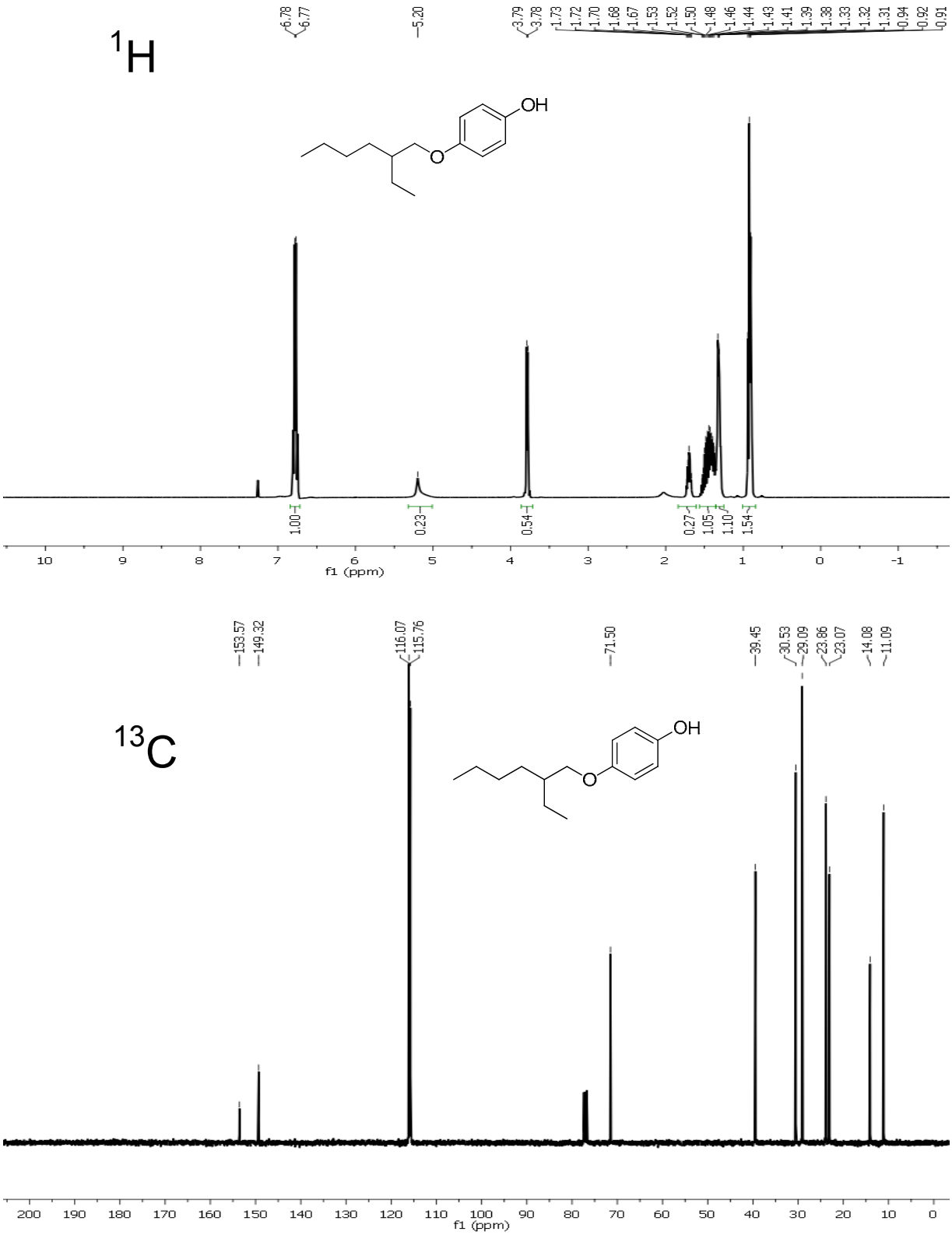


Figure S7 ^{1}H and ^{13}C NMR spectra of compound **d**

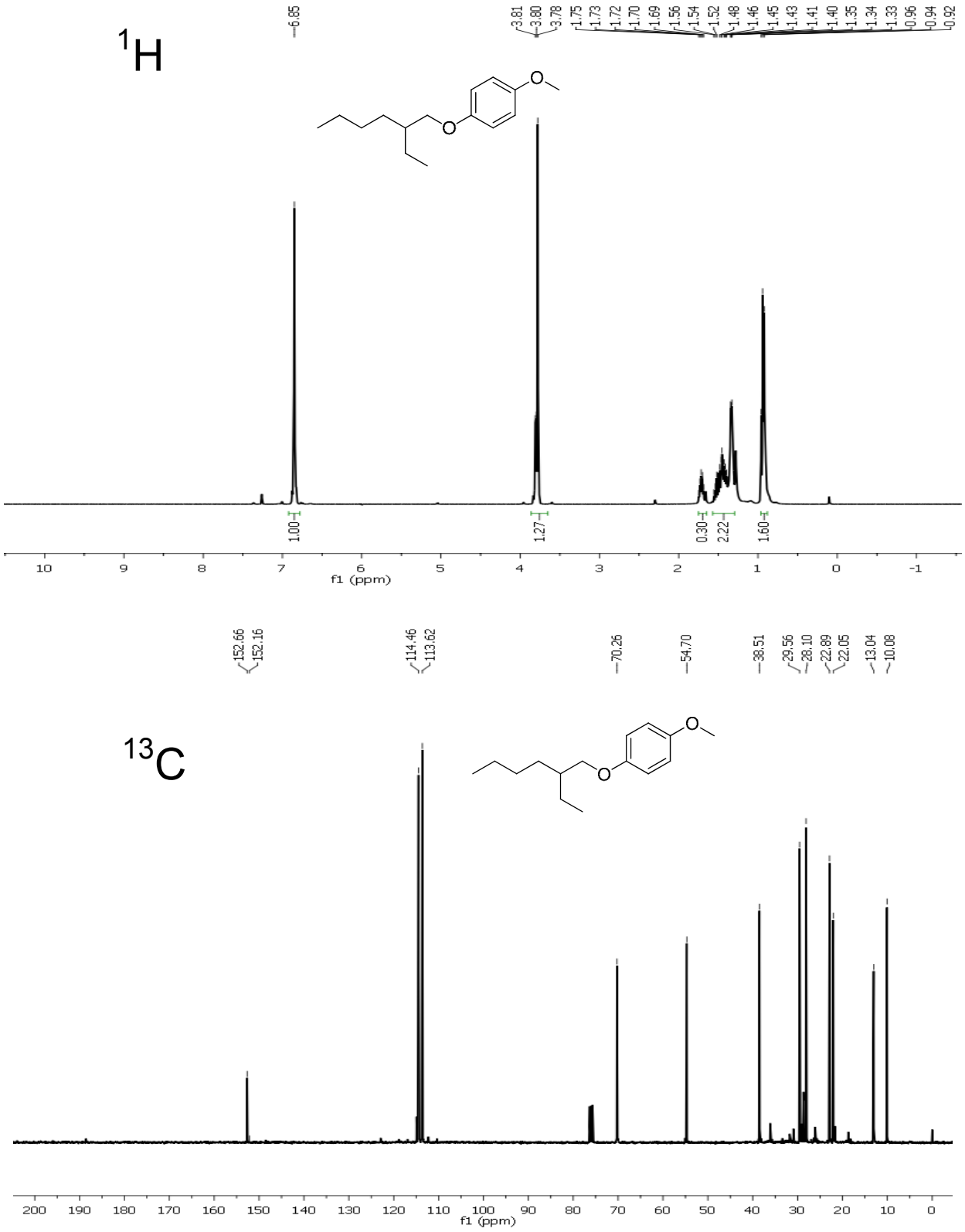


Figure S8 ^{1}H and ^{13}C NMR spectra of compound **e**

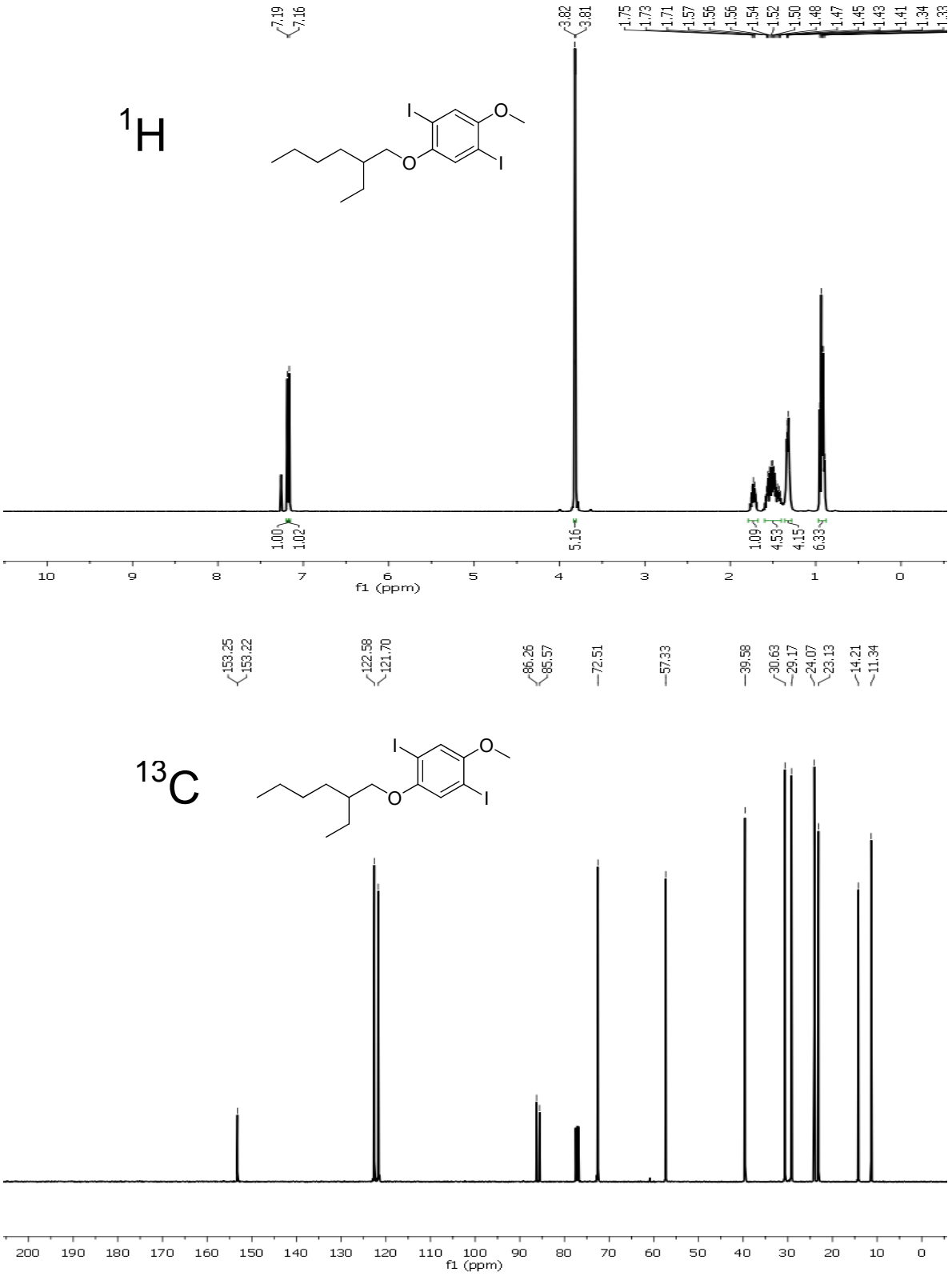


Figure S9 ^{1}H and ^{13}C NMR spectra of compound **1d**

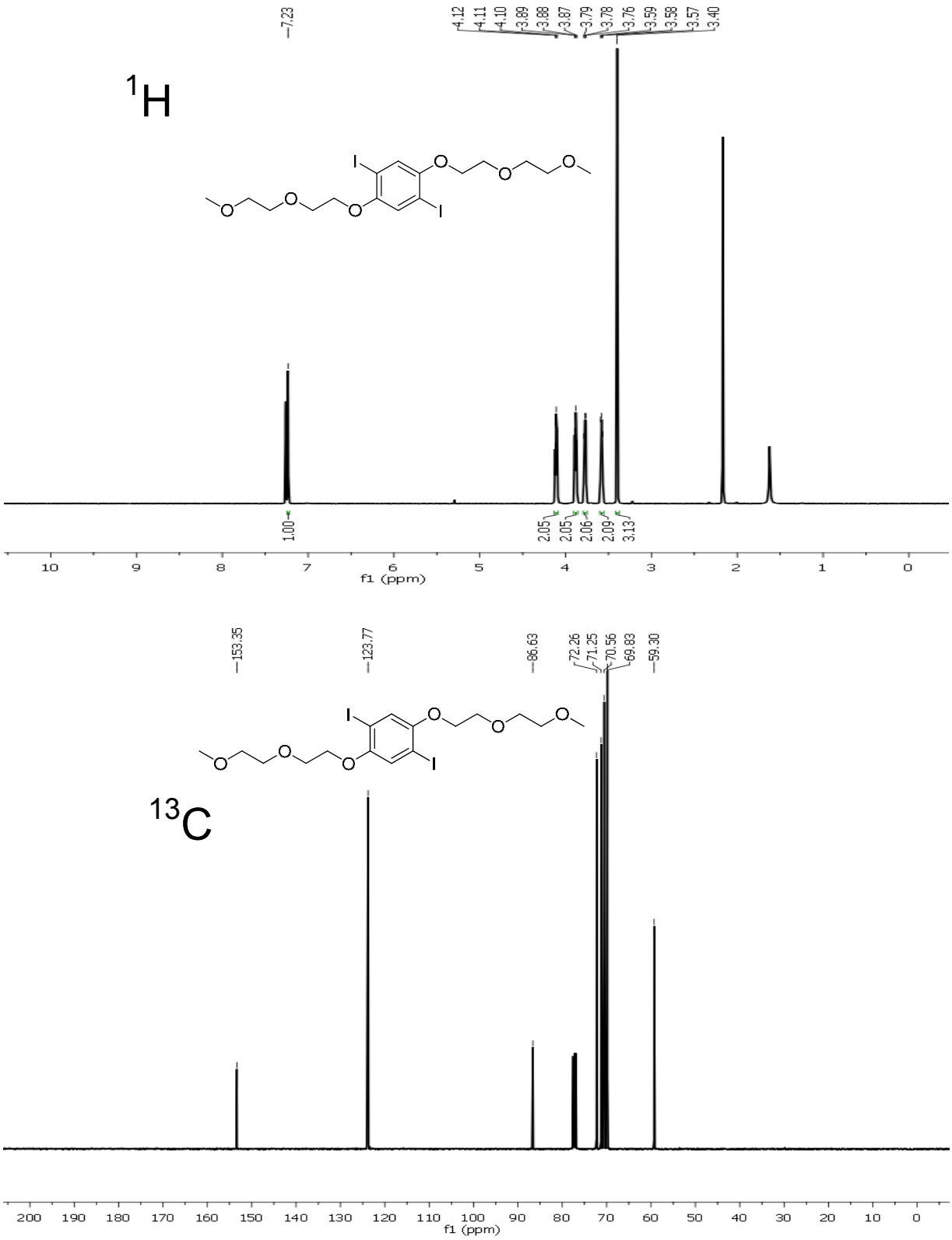


Figure S10 ^{1}H and ^{13}C NMR spectra of compound **1e**

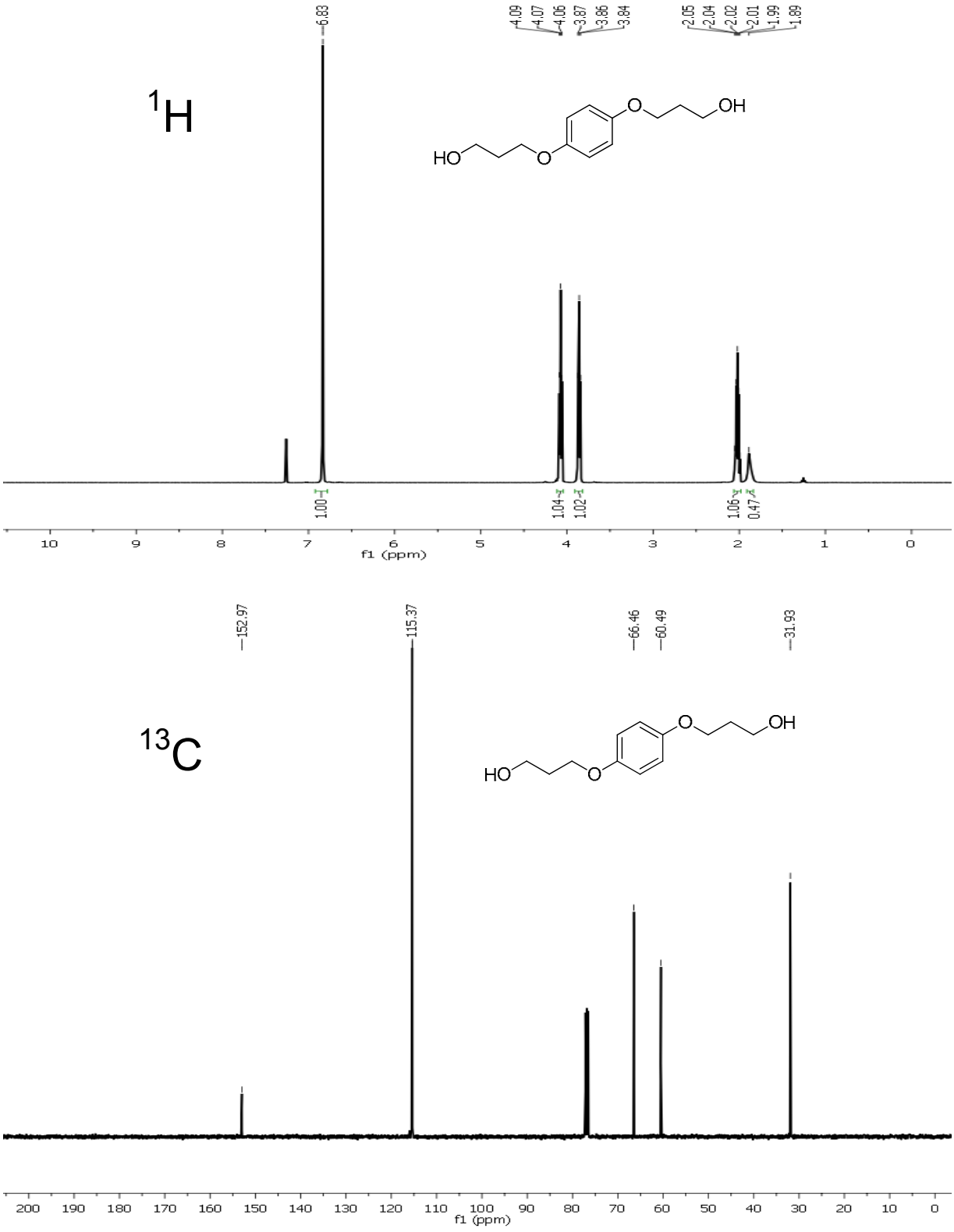


Figure S11 ^{1}H and ^{13}C NMR spectra of compound **g**

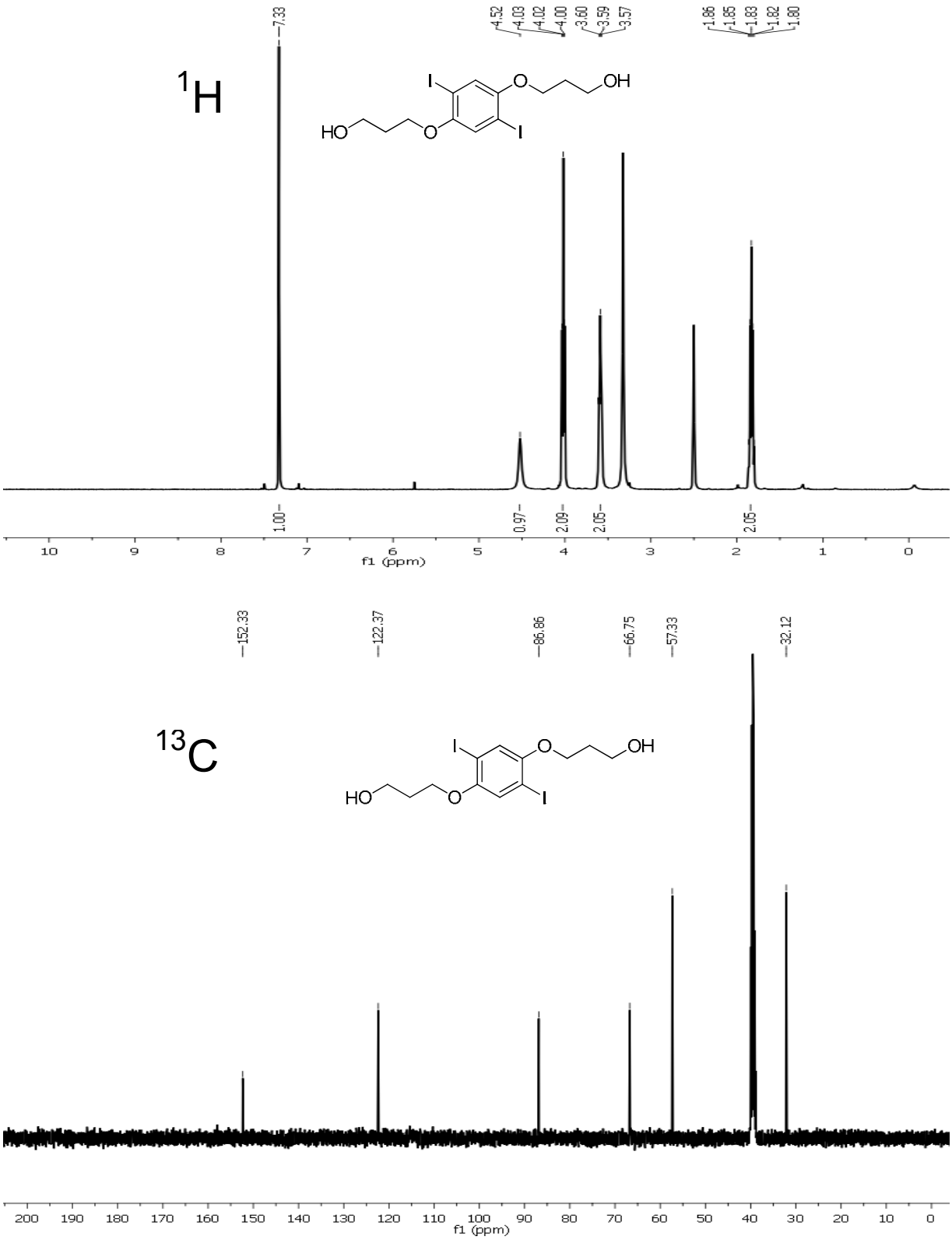


Figure S12 ^{1}H and ^{13}C NMR spectra of compound **1f**

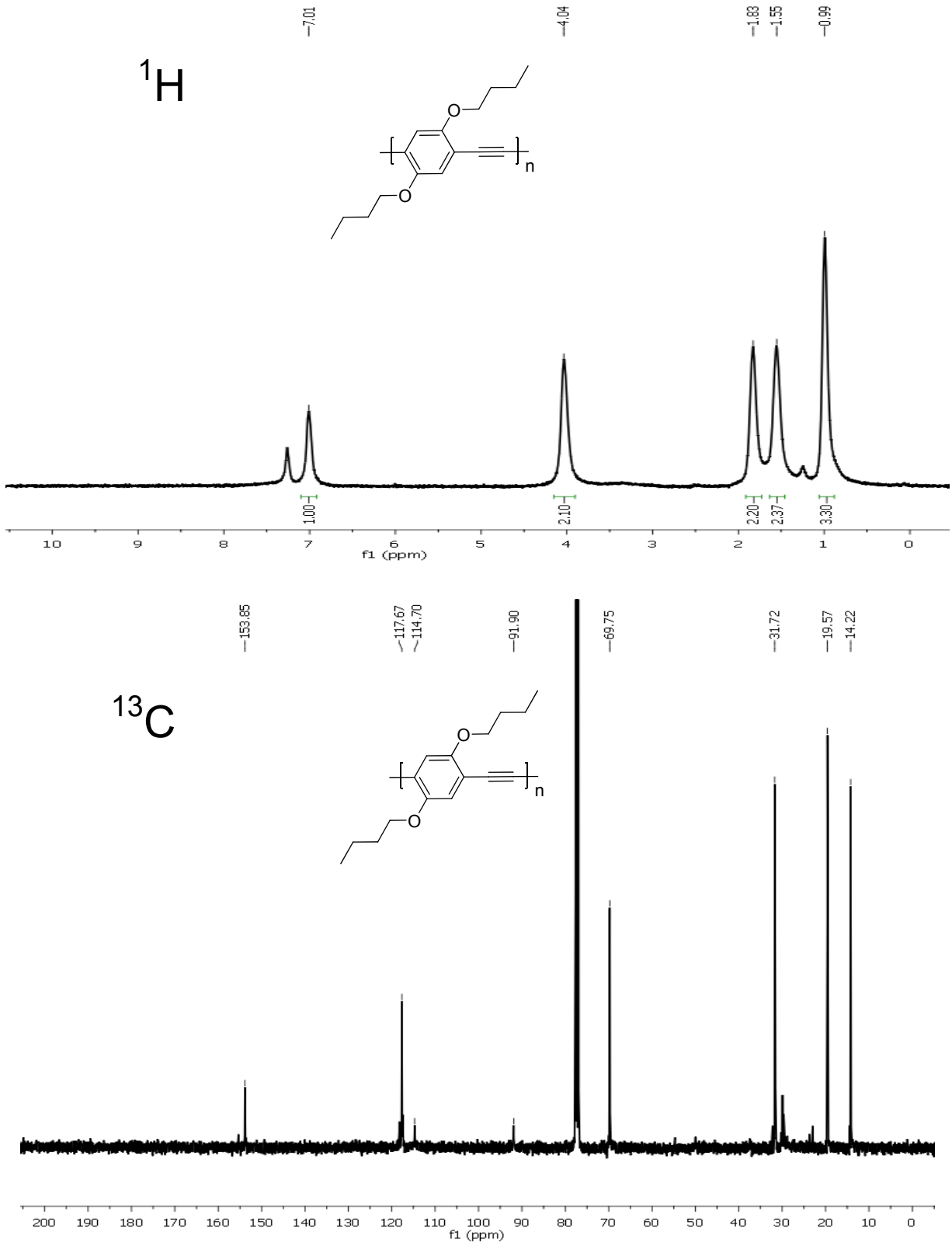


Figure S13 ^{1}H and ^{13}C NMR spectra of PPE **2a**

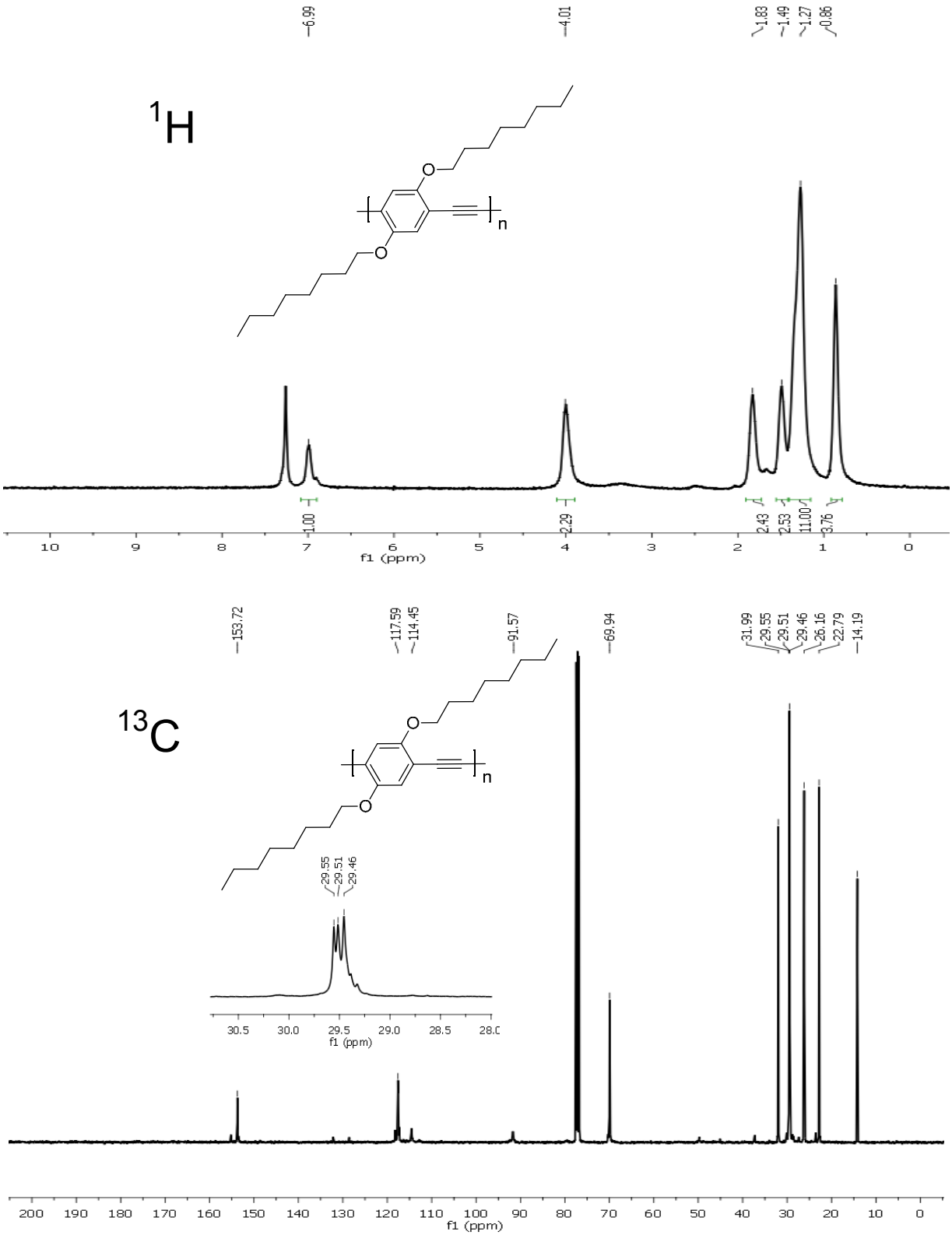


Figure S14 ^{1}H and ^{13}C NMR spectra of PPE **2b**

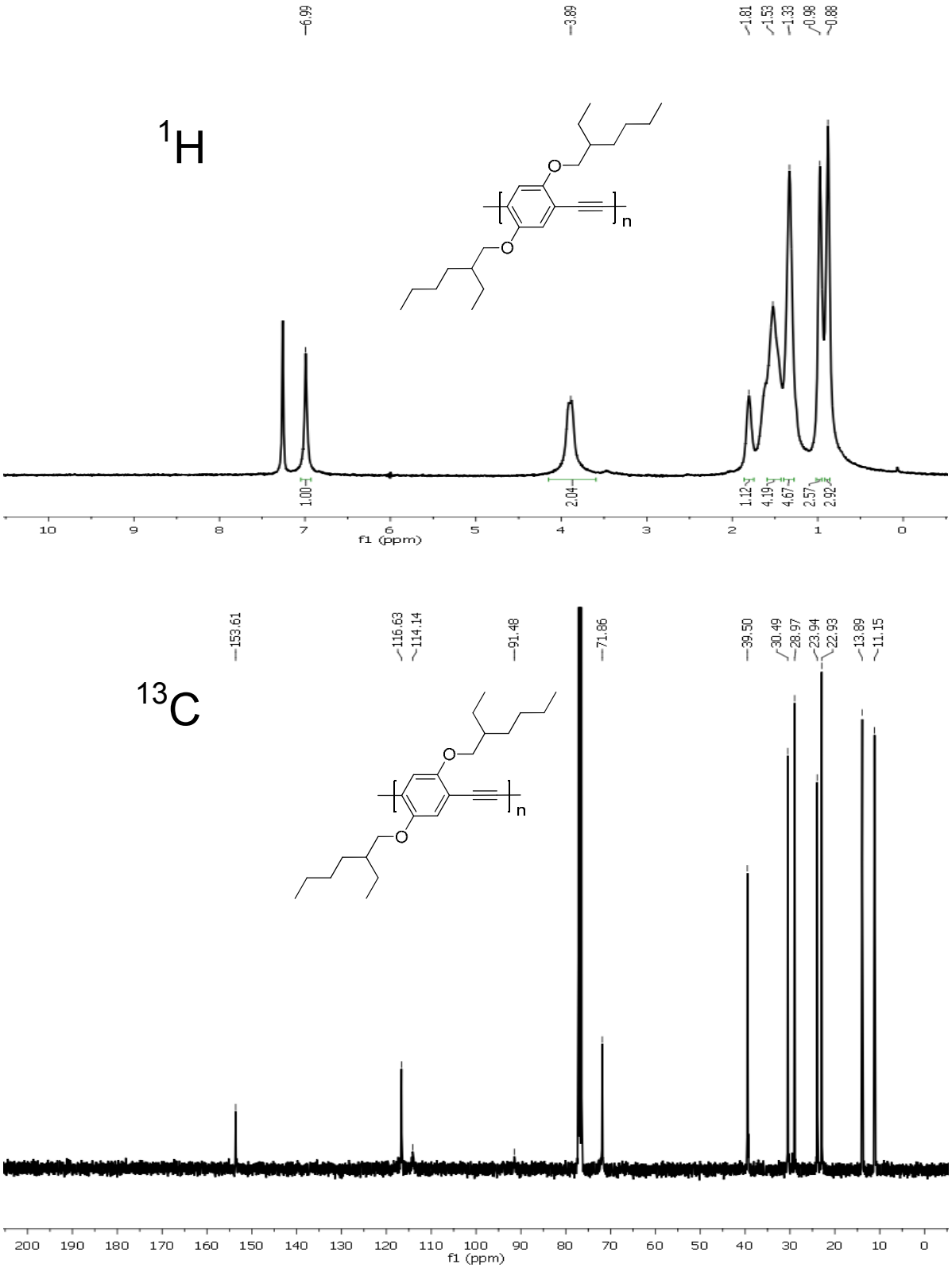


Figure S15 ^{1}H and ^{13}C NMR spectra of PPE **2c**

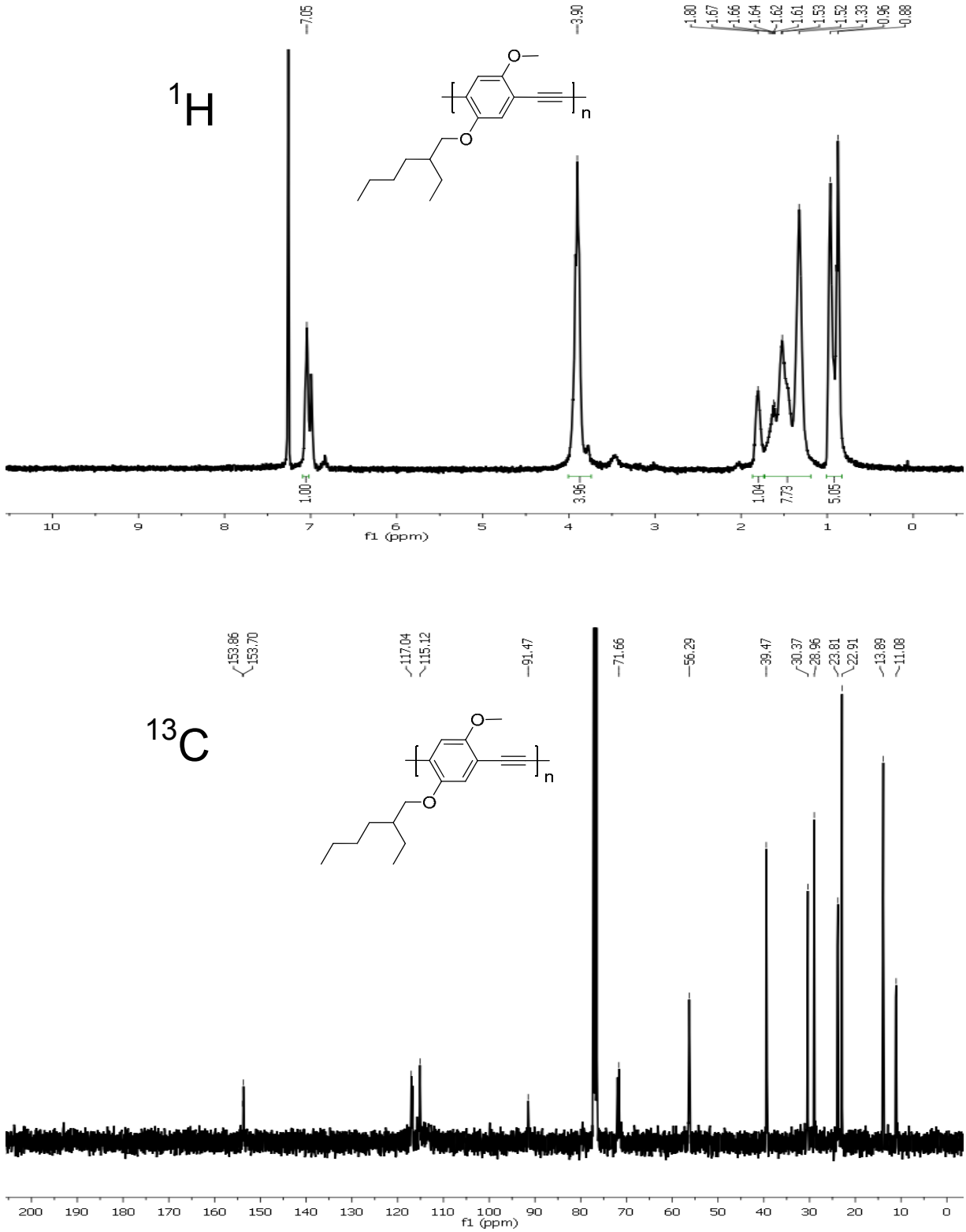


Figure S16 ^{1}H and ^{13}C NMR spectra of PPE **2d**

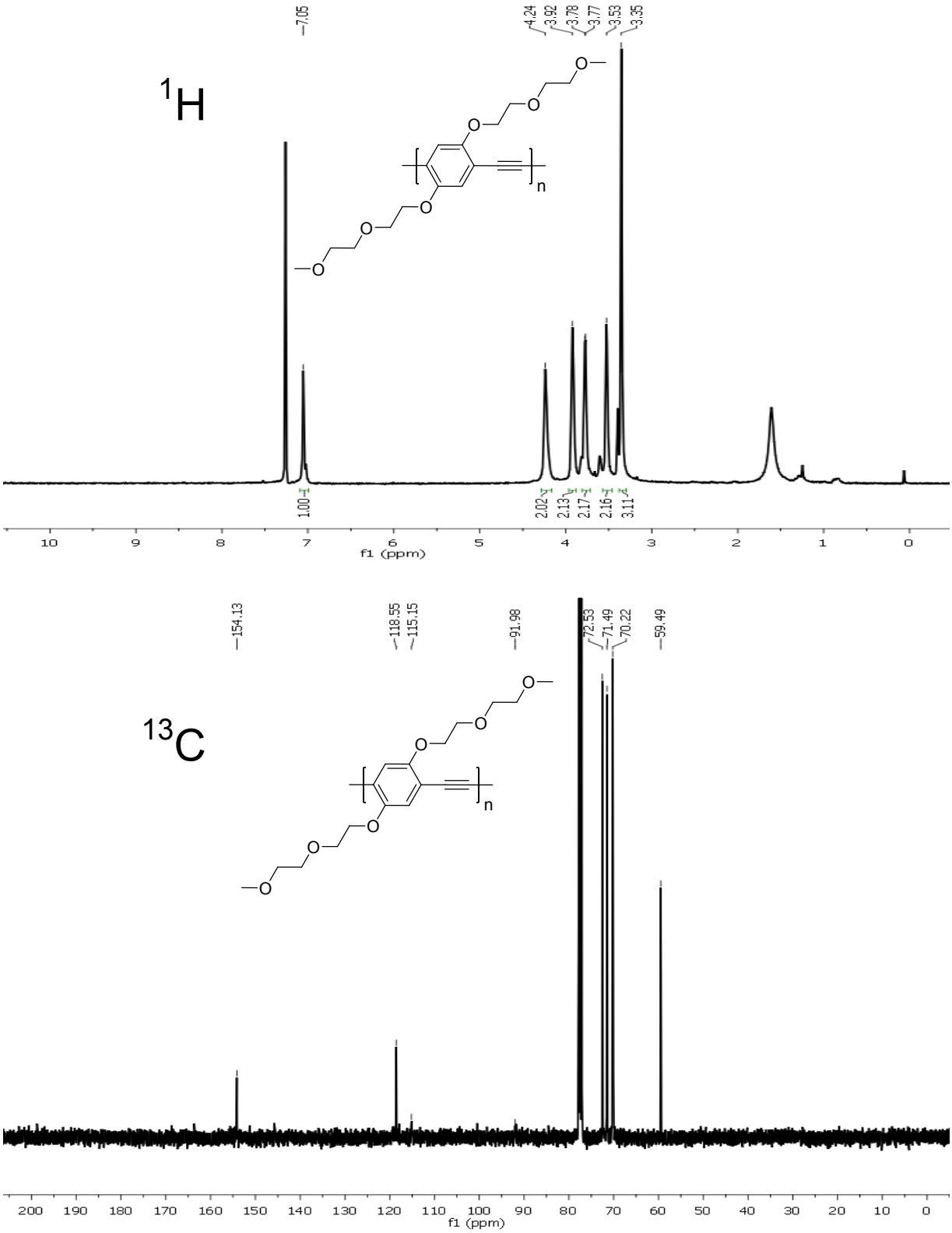


Figure S17 ^{1}H and ^{13}C NMR spectra of PPE **2e**

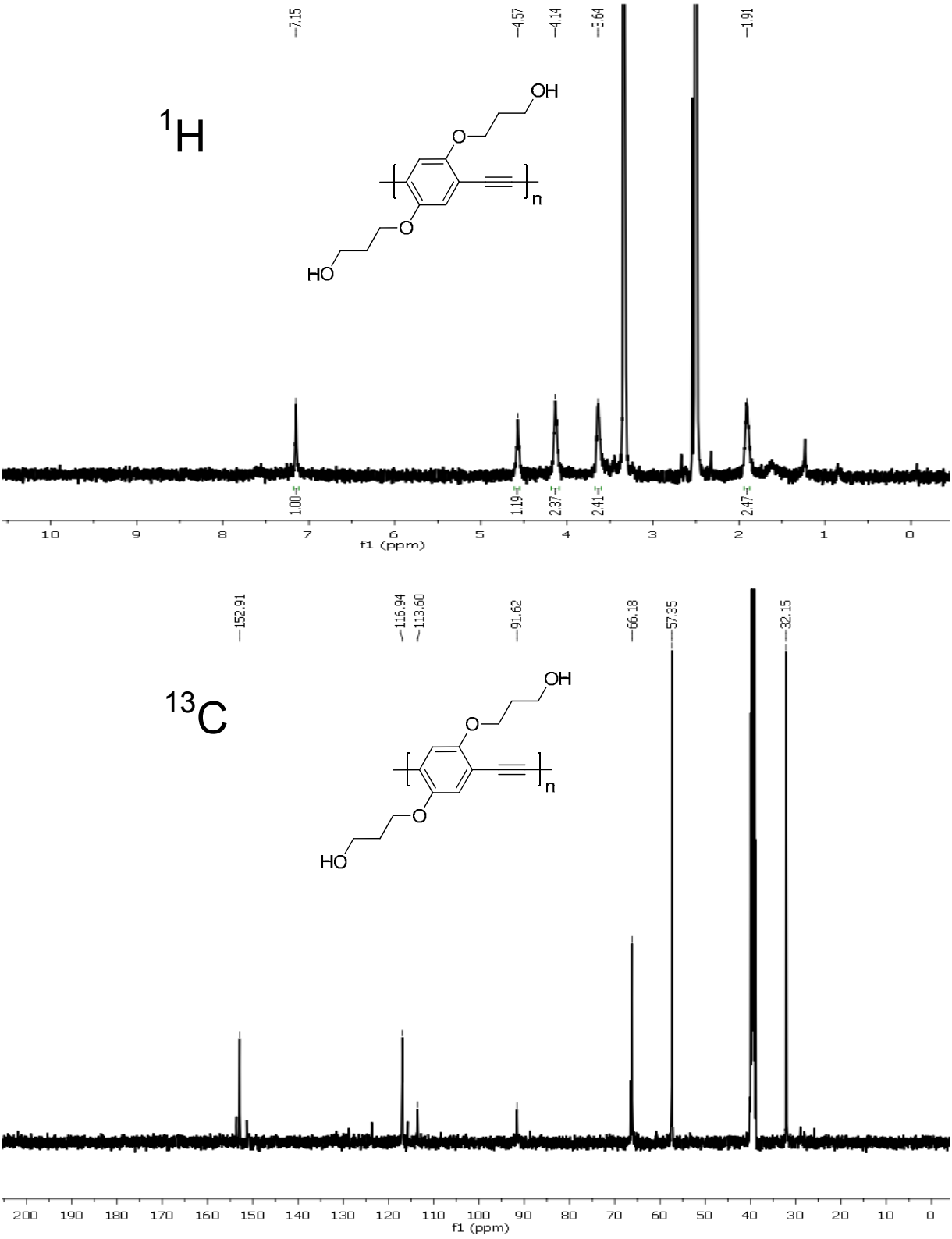
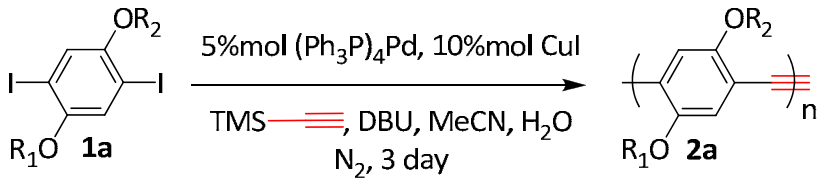


Figure S18 ^{1}H and ^{13}C NMR spectra of PPE **2f**



A 100 mL round bottom flask with a magnetic stir bar was charged with 1,4-dibutoxy-2,5-diiodobenzene **1a** (150.0 mg, 0.31 mmol), TMS-acetylene (36.53 mg, 0.37 mmol), $Pd(PPh_3)_4$ (17.34 mg, 0.015 mmol), CuI (5.90 mg, 0.031 mmol), DBU (0.28 g, 1.86 mmol) in $MeCN/H_2O$. The solution was stirred at room temperature under N_2 atmosphere for 3 days. After the reaction proceeded completely, the reaction mixture was then filtrated through a cotton wool and washed with CH_2Cl_2. The filtered was evaporated under vacuum and precipitated by dropping the solution into 150 mL of MeOH. The precipitate that formed was collected by centrifuge, washed repeatedly with MeOH and evaporated under vacuum to give poly(1,4-dibutoxy-*p*-phenyleneethynylene) **2a** (75.5 mg, 100%) as yellow-green powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02–6.91 (d, 2H), 4.04 (s, 4H), 1.84–1.83 (d, 4H), 1.57–1.56 (d, 4H), 1.00 (s, 6H). GPC (vs. polystyrene standards in tetrahydrofuran): M_w = 9,669 Da, M_w/M_n= 2.30, DP_n = 17.

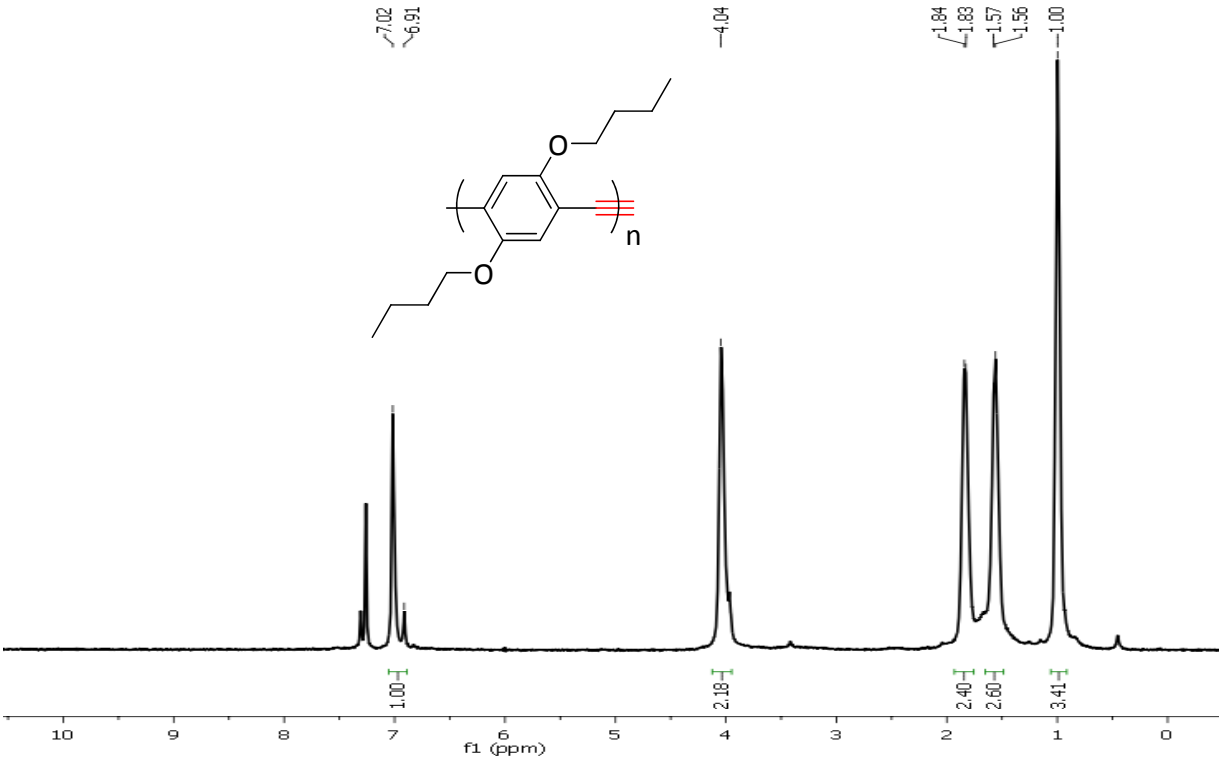


Figure S19 ^{1}H NMR spectra of PPE **2a** from TMS acetylene

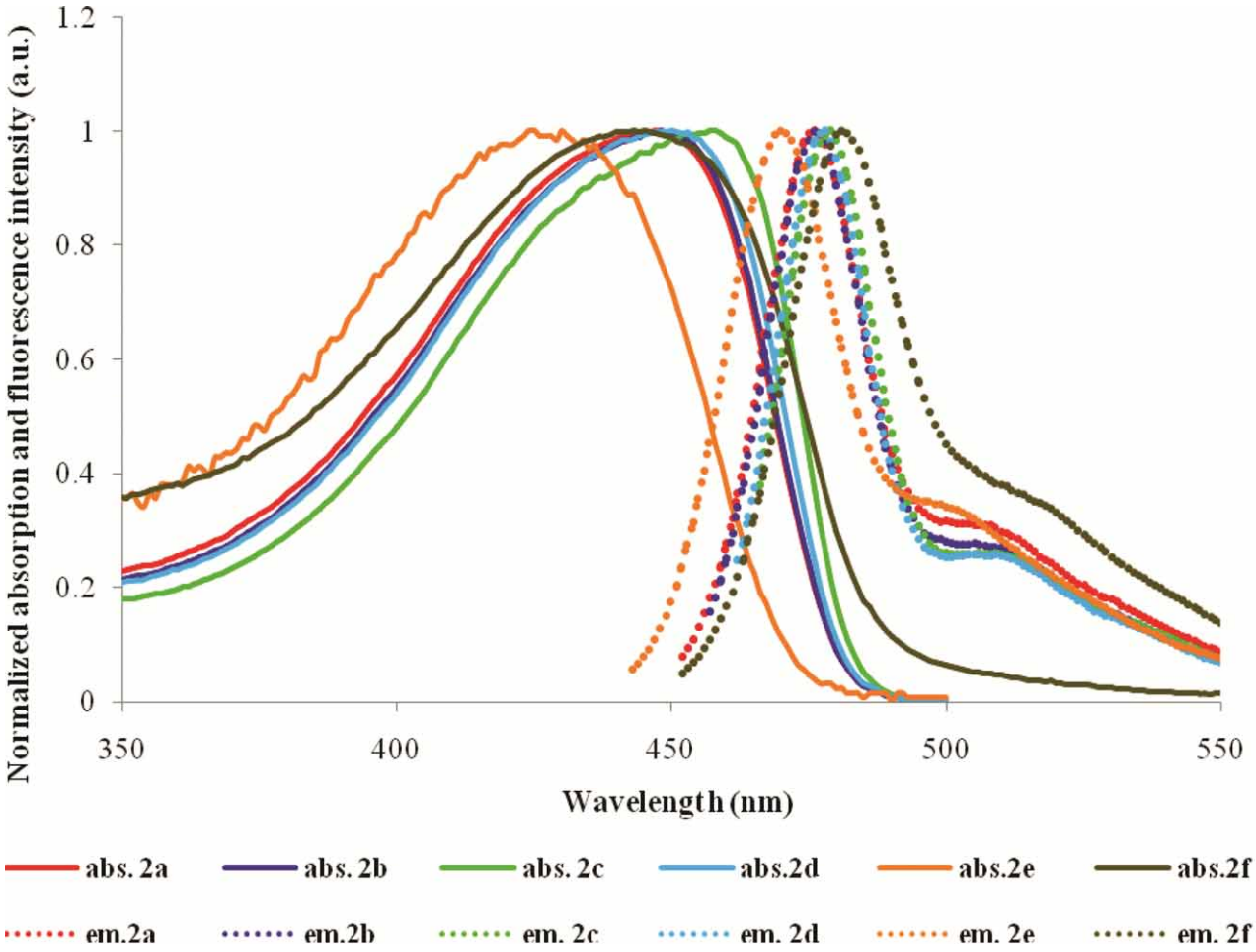


Figure S20 Normalized absorption and emission spectra of **2a–2e** in $CHCl_3$ and **2f** in DMSO.

Table S1. Appearances of **2a-2f**

Entry	PPEs	Precipitance	Solution	Under black-light
1	**2a**: R_1=R_2= $O(CH_2)_3CH_3$			
2	**2b**: R_1=R_2= $O(CH_2)_7CH_3$			
3	**2c**: R_1=R_2=$OCH_2CH(CH_2CH_3)((CH_2)_3CH_3)$			
4	**2d**: R_1= OMe R_2=$OCH_2CH(CH_2CH_3)((CH_2)_3CH_3)$			
5	**2e**: R_1=R_2= $O(CH_2)_2O(CH_2)_2OCH_3$			
6	**2f**: R_1=R_2= $O(CH_2)_3OH$			

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