Supporting Information

Nonconductive ferrofluids from permanently magnetic nanoplatelets hybridized with polar phosphonic ligands

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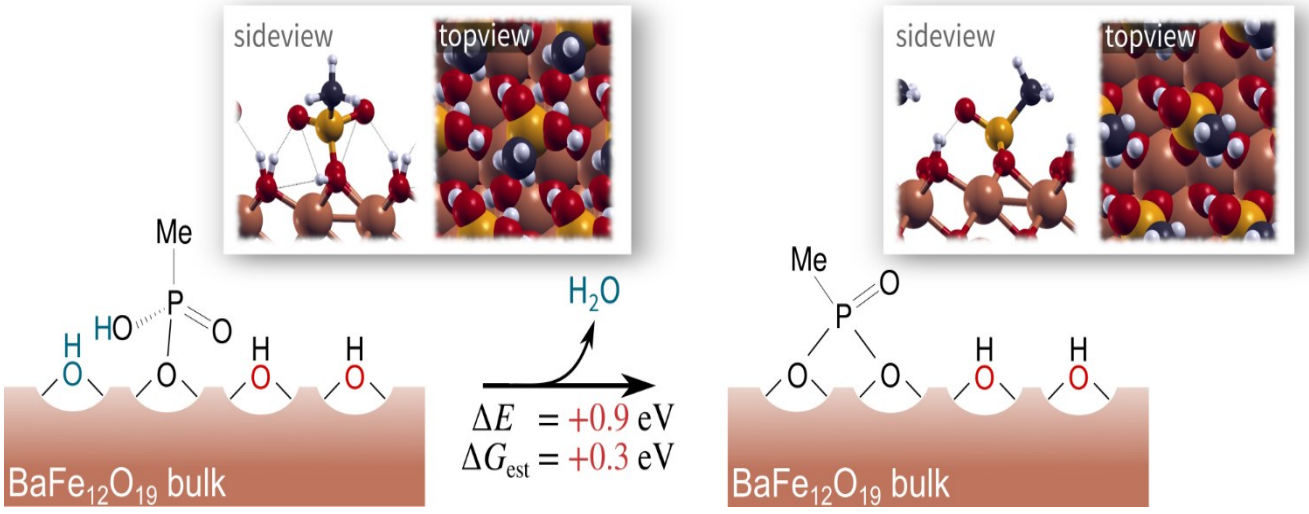


Figure S1 The energetics for the formation of the bidentate mode obtained with DFT calculations.

Synthesis and characterization of polar ligands

General information

All chemicals were purchased from commercial sources and used without further purification. CH_2Cl_2 and MeCN were dried and distilled using conventional methods, dry dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from commercial sources. All samples were dried in the vacuum oven nüve EV 018 under vacuum (1 Torr) for at least 8 hours. Melting points were measured on NAGEMA PHMK 05 and they are not corrected. Carbon, hydrogen, and nitrogen content was determined using 2400 series II CHN analyzer (PerkinElmer). The accuracy of C, H and N determination under the used conditions is <0.3 weight %. Determination of phosphorus, sulfur and bromine content was done by dissolving the samples in methanol (VWR Chemicals) and analyzing the solution by XEPOS P X-ray fluorescence spectrometer (SPECTRO Analytical Instruments). ^{1}H, ^{13}C, CRAPT, gCOSY, gHSQCAD and gHMBCAD spectra were measured on Varian Gemini 300 (operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C). Chemical shifts are given in δ-units (ppm) and are referenced to solvent signal. Fourier-transformed infrared (FTIR) spectra were recorded on a spectrometer Nicolet 6700 (Thermo Scientific, USA) using a standard MIR source, KBr beamsplitter, and Deuterated alanine doped Tri-Glycine Sulphate (DTGS) detector. The spectra resulted from 256 scans collected at 2 cm^{-1} resolution. The sample was deposited on KBr window from stock solution in toluene in the concentration 10^{-2} mol/l and demountable liquid cell (PIKE) was used as sample holder. Data were processed and analyzed using the OMNIC™ spectroscopy software suite (Thermo Electron Corp.). Substance purities and courses of the reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F_{254} on aluminium-backed sheets (Merck) and analysed at 254 and 365 nm. Column chromatography was carried out on silica gel 60 with particle size 0.063 – 0.200 mm (Merck).

High-performance liquid chromatography (HPLC) analyses were carried out using an Agilent 1260 Infinity II HPLC system (Agilent Technologies, USA), which consisted of a quaternary gradient solvent pump, an autosampler, a column thermostat and a diode array detector with continual spectrum acquisition. OpenLab CDS (Chromatography Data Systems) software was used for system control and data acquisition. Column Poroshell 120 PFP (150 x 4.6 mm i.d.) with 4 µm superficially porous silica gel particles substituted with pentafluorophenyl ligand was used as the stationary phase. The experiments were performed at 40 °C with the mobile-phase flow rate of 1 $mL \cdot min^{-1}$ and 3 µL sample injection. Mobile phase comprised of acetonitrile and 20 mM sodium phosphate buffer with pH of 6.5; the ratio of acetonitrile and buffer differed for individual samples in order to optimize the separation of target solute and its impurities. The samples were prepared at a concentration of 0.2 $mg \cdot mL^{-1}$ by dissolving the compounds in acetonitrile/water 1/1 (*v*/*v*). Deionized water used for buffer preparation was prepared on ULTRAPUR water purification system purchased from Watrex (Czechia) and acetonitrile (for HPLC - gradient grade) was purchased from VWR International (Czechia).

The synthesis protocol is shown in Scheme S1.

Synthesis of 2-(6-bromohexyl)isoindoline-1,3-dione **1** (1)

Phthalimide (11.8 g, 0.08 mol) and K_2CO_3 (33.2 g, 0.24 mol) were placed in a round-bottom flask, which was repeatedly evacuated and filled with argon. DMF (60 mL, dry) and 1,6-dibromohexane were further poured into the flask and the reaction mixture was stirred for 23 h under argon atmosphere. The reaction was quenched with demineralized H_2O (100 mL) and stirred until all components were dissolved. Subsequently, EtOAc (100 mL) and brine (100 mL) were added, and the organic phase was separated. The aqueous phase was extracted with EtOAc (2x 50 mL) and the combined organic layers were further washed with brine (5x 50 mL) and dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, 2-(6-bromohexyl)isoindoline-1,3-dione **1** was obtained via a column chromatography (SiO_2, first washed with hexane, eluent hexane:EtOAc 5:1 *v*/*v*) as a white solid (22.1 g, 89%).

Analytical data for **1** (1)

The analytical data were in agreement with the literature.

Synthesis of 2-(10-bromodecyl)isoindoline-1,3-dione **2** (1)

Phthalimide (11.8 g, 0.08 mol) and K_2CO_3 (33.2 g, 0.24 mol) were placed in a round-bottom flask, which was repeatedly evacuated and filled with argon. DMF (60 mL, dry) and 1,10-dibromodecane were further poured into the flask and the reaction mixture was stirred for 45 h under argon atmosphere. Subsequently, EtOAc (200 mL) and demineralized H_2O (200 mL) were added, and the organic phase was separated. The aqueous phase was extracted with EtOAc (2x 100 mL) and the combined organic layers were further washed with brine (5x 50 mL) and dried over $MgSO_4$. After the solvent evaporation on a

rotary vacuum evaporator, 2-(10-bromodecyl)isoindoline-1,3-dione **2** was obtained via a column chromatography (SiO_2, first washed with hexane, eluent hexane:EtOAc 5:1 → 4:1 *v*/*v*) as a white solid (25.16 g, 86%).

Analytical data for **2**

The analytical data were in agreement with the literature (2).

Synthesis of diethyl (6-(1,3-dioxoisoindolin-2-yl)hexyl)phosphonate **3** (3)

2-(6-Bromohexyl)isoindoline-1,3-dione **1** (21.6 g, 69.6 mmol) was dissolved in triethyl phosphite (60 mL, 0.348 mol) in a round-bottom flask. The reaction mixture was stirred and heated to 150 °C for 22 h. Subsequently, the mixture was cooled down and the unreacted triethyl phosphite was distilled off using vacuum distillation. Diethyl (6-(1,3-dioxoisoindolin-2-yl)hexyl)phosphonate **3** was obtained as colourless oil (25.06 g, 98%).

Analytical data for **3**

The analytical data were in agreement with the literature (4).

Synthesis of diethyl (10-(1,3-dioxoisoindolin-2-yl)decyl)phosphonate **4** (3)

2-(10-Bromodecyl)isoindoline-1,3-dione **2** (24.8 g, 67.7 mmol) was dissolved in triethyl phosphite (58 mL, 0.338 mol) in a round-bottom flask. The reaction mixture was stirred and heated to 150 °C for 18 h. Subsequently, the mixture was cooled down and the unreacted triethyl phosphite was distilled off using vacuum distillation. Diethyl (10-(1,3-dioxoisoindolin-2-yl)decyl)phosphonate **4** was obtained as colourless oil (26.18 g, 91%).

Analytical data for **4**

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.81 – 7.73 (m, 2H, Ar-*H*), 7.68 – 7.60 (m, 2H, Ar-*H*), 4.12 – 3.93 (m, 4H, OCH_2CH_3), 3.60 (t, *J* = 7.3 Hz, 2H, CH_2N), 1.73 – 1.43 (m, 8H, 4x CH_2), 1.35 – 1.14 (m, 10H, 5x CH_2), 1.25 (t, *J* = 7.1 Hz, 6H, OCH_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ ^{13}C NMR (75 MHz, cdcl$_3$) δ 168.33 (s, *C*=O), 133.75 (s, Ar *C*H), 132.10 (s, Ar *C*q), 123.04 (s, Ar *C*H), 61.27 (d, *J* = 6.8 Hz, OCH_2CH_3), 37.95 (s, CH_2N), 30.49 (d, *J* = 17.0 Hz, $PCH_2CH_2CH_2$), 29.30 (s), 29.19 (s), 29.04 (s), 28.94 (s), 28.49 (s), 26.75 (s), 26.53 (s, 5x CH_2, $PCH_2CH_2CH_2CH_2$, two of the signals in the range 29.30 – 26.53 ppm that could not be directly determined represent a doublet), 24.67 (s, CH_2), 22.32 (d, *J* = 5.4 Hz, $PCH_2CH_2CH_2$), 16.41 (d, *J* = 6.3 Hz, OCH_2CH_3). See the spectrum in Figure S2.

Synthesis of diethyl (6-aminohexyl)phosphonate **5** (5)

Diethyl (6-(1,3-dioxoisoindolin-2-yl)hexyl)phosphonate **3** (11.4 g, 31.0 mmol) was dissolved in EtOH (120 mL) in a round-bottom flask. Hydrazine monohydrate (2.3 mL, 46.5 mmol) was further added into the flask and the reaction mixture was refluxed for 2 h. Once cooled down, the solvent was evaporated on a rotary vacuum evaporator. The crude mixture was dissolved in aqueous NaOH solution (10%, 300 mL), which was subsequently extracted with CH_2Cl_2 (3x 50 mL). The combined organic layers were dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, diethyl (6-aminohexyl)phosphonate **5** was obtained as colourless oil (7.45 g, ca 100%).

Analytical data for **5** (5)

The analytical data were in agreement with the literature.

Synthesis of diethyl (10-aminodecyl)phosphonate **6** (5)

Diethyl (10-(1,3-dioxoisoindolin-2-yl)decyl)phosphonate **4** (5.0 g, 11.8 mmol) was dissolved in EtOH (50 mL) in a round-bottom flask. Hydrazine monohydrate (0.89 mL, 17.7 mmol) was further added into the flask and the reaction mixture was refluxed for 2 h. Once cooled down, the solvent was evaporated on a rotary vacuum evaporator. The crude mixture was dissolved in aqueous NaOH solution (10%, 150 mL), which was subsequently extracted with CH_2Cl_2 (3x 50 mL). The combined organic layers were dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, diethyl (10-aminodecyl)phosphonate **6** was obtained as colourless oil (3.33 g, 96%).

Analytical data for **6**

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 4.13 – 3.94 (m, 4H, OCH_2CH$_3$), 2.67 (t, J = 7.3 Hz, 2H, CH_2NH$_2$), 1.75 – 1.39 (m, 6H, 3x CH_2), 1.27 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3), 1.35 – 1.18 (m, 12H, 6x CH_2).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 61.34 (d, J = 6.8 Hz, O*C*H$_2$CH$_3$), 41.19 (s, *C*H$_2$NH$_2$), 30.52 (d, J = 17.0 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.43 (s), 29.27 (s), 29.24 (s), 29.00 (s), 28.99 (s), 26.78 (s), 26.51 (s), 24.65 (s, 6x *C*H$_2$, PCH$_2$CH$_2$CH$_2$, two of the signals in the range 29.43 – 24.65 ppm that could not be directly determined represent a doublet), 22.31 (d, J = 5.5 Hz, PCH$_2$*C*H$_2$CH$_2$), 16.41 (d, J = 6.3 Hz, OCH$_2$*C*H$_3$). See the spectrum in Figure S3.

Synthesis of 1-(dodecylsulfonyl)-4-fluorobenzene **8** (6)

4-Fluorobenzenesulfonyl chloride (10.64 g, 54.7 mmol), $NaHCO_3$ (9.19 g, 0.109 mol), $Na_2SO_3 \cdot 7H_2O$ (26.2 g, 0.104 mol) and demineralized H_2O (68 mL) were stirred in a round-bottom flask and heated to 100 °C for 3.5 h. The reaction mixture was cooled down to the room temperature, 1-iodododecane (40.5 mL, 0.164 mol) and tetrabutylammonium iodide (1.21 g, 3.28 mmol) were added and the mixture was further heated to 100 °C for 18 h. Once cooled down, more demineralized H_2O was added, and the reaction mixture was extracted with CH_2Cl_2 (3x 100 mL). The combined organic layers were washed with brine (150 mL) and dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, 1-(dodecylsulfonyl)-4-fluorobenzene **8** was obtained via a column chromatography (SiO_2, first washed with hexane, eluent hexane:EtOAc 20:1 → 10:1 *v*/*v*) as a white solid (11.07 g, 62%).

Analytical data for **8**

M.p. 58.0 – 60.0 °C (hexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.92 (dd, J = 8.9, 5.1 Hz, 2H, Ar-*H*), 7.24 (dd, J = 8.5, 8.7 Hz, 2H, Ar-*H*), 3.14 – 3.00 (m, 2H, SO$_2$CH_2), 1.77 – 1.62 (m, 2H, SO$_2$CH$_2$CH_2), 1.42 – 1.14 (m, 18H, 9x CH_2), 0.87 (t, J = 6.7 Hz, 3H, CH_3). See the spectrum in Figure S4.

^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 165.75 (d, J = 256.2 Hz, Ar *C*F), 135.28 (d, J = 3.5 Hz, Ar *C*q), 130.90 (d, J = 9.7 Hz, Ar *C*H), 116.53 (d, J = 22.7 Hz, Ar *C*H), 56.47 (s, SO$_2$*C*H$_2$), 31.86 (s, *C*H$_2$), 29.55 (s, *C*H$_2$), 29.52 (s, *C*H$_2$), 29.42 (s, *C*H$_2$), 29.28 (s, *C*H$_2$), 29.19 (s, *C*H$_2$), 28.96 (s, *C*H$_2$), 28.21 (s, *C*H$_2$), 22.67 (s, SO$_2$CH$_2$*C*H$_2$), 22.64 (s, *C*H$_2$), 14.08 (s, *C*H$_3$).

Synthesis of diethyl (10-((4-(methylsulfonyl)phenyl)amino)decyl)phosphonate **9**

1-(Methylsulfonyl)-4-fluorobenzene **7** (commercial compound, 1.19 g, 6.82 mmol) and diethyl (10-aminodecyl)phosphonate **6** (4.00 g, 13.6 mmol) were dissolved in dry DMSO (15 mL) in a round-bottom flask. The reaction mixture was stirred and heated to 130 °C for 3 h. Subsequently, the mixture was cooled down to the room temperature and poured to demineralized H_2O (150 mL), followed by the extraction with CH_2Cl_2 (3x 50 mL). The combined organic layers were dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, diethyl (10-((4-(methylsulfonyl)phenyl)amino)decyl)phosphonate **9** was obtained via a column chromatography (SiO_2, first washed with CH_2Cl_2, eluent CH_2Cl_2:MeOH 50:1 *v*/*v*) as a white solid (1.48 g, 49%).

Analytical data for **9**

M.p. 42.0 – 48.0 °C ($CHCl_3$/MeOH).

Anal. calcd. for $C_{21}H_{38}NO_5PS$: C, 56.36; H, 8.56; N, 3.13; O, 17.87; P, 6.92; S, 7.16. Found: C, 56.14; H, 8.45; N, 2.98; P, 6.92; S, 6.44; Br, <0.02.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.65 (d, J = 8.8 Hz, 2H, Ar-*H*), 6.58 (d, J = 8.9 Hz, 2H, Ar-*H*), 4.16 – 3.94 (m, 4H, OCH_2CH$_3$), 3.13 (t, J = 7.1 Hz, 2H, CH_2NH), 2.97 (s, 3H, SO$_2$CH_3), 1.82 – 1.45 (m, 6H, 3x CH_2), 1.45 – 1.15 (m, 12H, 6x CH_2), 1.30 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3). See the spectrum in Figure S5.

^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 152.38 (s, Ar *C*q), 129.22 (s, Ar *C*H), 126.74 (s, Ar *C*q), 111.56 (s, Ar *C*H), 61.36 (d, J = 6.6 Hz, O*C*H$_2$CH$_3$), 45.05 (s, SO$_2$*C*H$_3$), 43.27 (s, *C*H$_2$NH), 30.50 (d, J = 17.0 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.39 (s), 29.25 (s), 29.20 (s), 29.09 (s), 28.98 (s), 26.96 (s), 26.56 (s), 24.70 (s, 6x *C*H$_2$, PCH$_2$CH$_2$CH$_2$, two of the signals in the range 29.39 – 24.70 ppm that could not be directly determined represent a doublet), 22.32 (d, J = 5.4 Hz, PCH$_2$*C*H$_2$CH$_2$), 16.45 (d, J = 6.3 Hz, OCH$_2$*C*H$_3$).

Synthesis of diethyl (6-((4-(dodecylsulfonyl)phenyl)amino)hexyl)phosphonate **10**

1-(Dodecylsulfonyl)-4-fluorobenzene **8** (2.77 g, 8.43 mmol) and diethyl (6-aminohexyl)phosphonate **5** (4.00 g, 16.9 mmol) were dissolved in dry DMSO (28 mL) in a round-bottom flask. The reaction mixture was stirred and heated to 130 °C for 2 h. Subsequently, the mixture was cooled down to the room temperature and poured to demineralized H_2O (200 mL), followed

by the extraction with CH_2Cl_2 (3x 50 mL). The combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, diethyl (6-((4-(dodecylsulfonyl)phenyl)amino)hexyl)phosphonate **10** was obtained via a column chromatography (SiO_2, two rounds, first round with eluent CH_2Cl_2:MeOH 100:1 → 30:1 *v*/*v*, second round with eluent CH_2Cl_2:EtOAc 2:1 *v*/*v*) as a white solid (1.55 g, 34%).

Analytical data for **10**

M.p. 41.0 – 42.0 °C ($CHCl_3$/MeOH).

Anal. calcd. for $C_{28}H_{52}NO_5PS$: C, 61.62; H, 9.60; N, 2.57; O, 14.66; P, 5.68; S, 5.87. Found: C, 61.52; H, 9.38; N, 2.29; P, 5.52; S, 6.06; Br, <0.06.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.62 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.59 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 4.36 (t, *J* = 5.2 Hz, 1H, N*H*), 4.16 – 3.98 (m, 4H, OCH_2CH$_3$), 3.15 (dd, *J* = 12.6, 6.9 Hz, 2H, CH_2NH), 3.05 – 2.93 (m, 2H, SO_2CH_2), 1.81 – 1.54 (m, 10H, 5x CH_2), 1.51 – 1.37 (m, 4H, 2x CH_2), 1.31 (t, *J* = 7.1 Hz, 6H, OCH_2CH_3), 1.36 – 1.15 (m, 16H, 8x CH_2), 0.86 (t, *J* = 6.7 Hz, 3H, CH_3). See the spectrum in Figure S6.

^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 152.28 (s, Ar *C*q), 129.98 (s, Ar *C*H), 125.37 (s, Ar *C*q), 111.56 (s, Ar *C*H), 61.42 (d, *J* = 6.9 Hz, O*C*H_2CH$_3$), 56.80 (s, SO_2CH_2), 43.11 (s, *C*H_2NH), 31.86 (s, *C*H_2), 30.11 (d, *J* = 16.1 Hz, $PCH_2CH_2CH_2$), 29.55 (s), 29.54 (s), 29.45 (s), 29.29 (s), 29.25 (s), 29.04 (s), 28.82 (s), 28.29 (s), 26.44 (s), 24.57 (s, 9x *C*H_2, P*C*$H_2CH_2CH_2$, two of the signals in the range 29.55 – 24.57 ppm that could not be directly determined represent a doublet; one signal was overlapped), 22.92 (s, *C*H_2), 22.64 (s, *C*H_2), 22.30 (d, *J* = 5.4 Hz, $PCH_2CH_2CH_2$), 16.47 (d, *J* = 6.3 Hz, OCH_2CH_3), 14.08 (s, *C*H_3).

Synthesis of diethyl (10-((4-nitrophenyl)amino)decyl)phosphonate **12**

1-Iodo-4-nitrobenzene **11** (commercial compound, 905 mg, 3.64 mmol), CuI (138 mg, 0.727 mmol) and proline (167 mg, 1.45 mmol) were placed in a round-bottom flask, which was repeatedly evacuated and filled with argon. Dry DMSO (4 mL) was poured into the flask and the mixture was stirred for 10 min under the argon atmosphere. Subsequently, diethyl (10-aminodecyl)phosphonate **6** (3.2 g, 10.9 mmol) was added to the flask and the reaction mixture was further stirred for 3 days under argon atmosphere. Finaly, the mixture was poured into aqueous NaOH solution (1M, 400 mL), followed by the extraction with EtOAc (3x 50 mL). The combined organic layers were washed with demineralized H_2O (100 mL), brine (100 mL) and dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, diethyl (10-((4-nitrophenyl)amino)decyl)phosphonate **12** was obtained via a column chromatography (SiO_2, eluent CH_2Cl_2:EtOAc 2:1 *v*/*v*) as yellow oil (1.27 g, 84%).

Analytical data for **12**

Anal. calcd. for $C_{20}H_{35}N_2O_5P$: C, 57.96; H, 8.51; N, 6.76; O, 19.30; P, 7.47. Found: C, 57.55; H, 8.31; N, 6.51; P, 7.43; Br, <0.03.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 8.04 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 6.49 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 4.82 (t, *J* = 4.7 Hz, 1H, N*H*), 4.18 – 3.95 (m, 4H, OCH_2CH$_3$), 3.16 (dt, *J* = 7.1, 5.7 Hz, 2H, CH_2NH), 1.78 – 1.46 (m, 6H, 3x CH_2), 1.37 – 1.23 (m, 12H, 6x CH_2), 1.29 (t, *J* = 11.6 Hz, 6H, OCH_2CH_3). See the spectrum in Figure S7.

^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 153.62 (s, Ar *C*q), 137.50 (s, Ar *C*q), 126.41 (s, Ar *C*H), 110.81 (s, Ar *C*H), 61.39 (d, *J* = 6.8 Hz, O*C*H_2CH$_3$), 43.34 (s, *C*H_2NH), 30.48 (d, *J* = 16.9 Hz, $PCH_2CH_2CH_2$), 29.36 (s), 29.21 (s), 29.16 (s), 29.02 (s), 28.96 (s), 26.92 (s), 26.52 (s), 24.65 (s, 6x *C*H_2, P*C*$H_2CH_2CH_2$, two of the signals in the range 29.36 – 24.65 ppm that could not be directly determined represent a doublet), 22.30 (d, *J* = 5.4 Hz, $PCH_2CH_2CH_2$), 16.44 (d, *J* = 6.4 Hz, OCH_2CH_3).

Synthesis of (10-((4-(methylsulfonyl)phenyl)amino)decyl)phosphonic acid **a**

Diethyl (10-((4-(methylsulfonyl)phenyl)amino)decyl)phosphonate **9** (1.28 g, 2.86 mmol) was placed in a round-bottom flask, which was repeatedly evacuated and filled with argon. Dry CH_2Cl_2 (80 mL) and trimethylsilyl bromide (1.9 mL, 14.3 mmol) were further poured into the flask and the reaction mixture was stirred for 3 days under argon atmosphere. Subsequently, the mixture was evaporated on a rotary vacuum evaporator and repeatedly dissolved in CH_2Cl_2 (3x 50 mL) and evaporated. Similar process was then repeated with MeOH (3x 50 mL). The crude mixture was then heated with demineralized H_2O (100 mL) to 100 °C for 2 h. Once cooled down to the room temperature, (10-((4-(methylsulfonyl)phenyl)amino)decyl)phosphonic acid **a** was filtered off as a white precipitate (973 mg, 87%). The purity of a was determined by HPLC as 99.9%.

Analytical data for **a**

M.p. 143.5 – 145.0 °C (H_2O).

Anal. calcd. for $C_{17}H_{30}NO_5PS$: C, 52.16; H, 7.72; N, 3.58; O, 20.43; P, 7.91; S, 8.19. Found: C, 52.44; H, 7.46; N, 3.32; P, 8.42; S, 8.39; Br, 0.03.

^{1}H NMR (300 MHz, CD_3OD, 298 K) δ 7.60 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.66 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 3.13 (t, *J* = 7.0 Hz, 2H, CH_2NH), 3.00 (s, 3H, SO_2CH_3), 1.77 – 1.49 (m, 6H, 3x CH_2), 1.49 – 1.24 (m, 12H, 6x CH_2).

^{13}C NMR (75 MHz, CD_3OD, 298 K) δ 153.47 (s, Ar *C*q), 128.75 (s, Ar *C*H), 124.97 (s, Ar *C*q), 110.85 (s, Ar *C*H), 43.71 (s, SO_2CH_3), 42.48 (s, CH_2NH), 30.32 (d, *J* = 16.7 Hz, $PCH_2CH_2CH_2$), 29.23 (s), 29.09 (s), 29.03 (s), 28.84 (s), 28.55 (s), 27.59 (s), 26.73 (s), 25.76 (s, 6x CH_2, $PCH_2CH_2CH_2$, two of the signals in the range 29.23 – 25.76 ppm that could not be directly determined represent a doublet), 22.49 (d, *J* = 5.2 Hz, $PCH_2CH_2CH_2$). See the spectrum in Figure S8.

IR (film, MeOH): 3374(m) ν(NH);

2922(s), 2862(m), 2847(m) ν(CH), 1476(m), 1456(m) $\delta(CH_3)$+ $\delta(CH_3)$;

3000-2400 ν(POH);

Ar: 3017(m), 1600(s), 1495(m), 1288(m), 1091(m), 824(m),776(m);

1322(m) $\nu_A(SO_2)$, 1133(s), 1137(s) $\nu_S(SO_2)$, 967(m) ν(POH), 535(m) $\beta(SO_2)$.

Synthesis of (6-((4-(dodecylsulfonyl)phenyl)amino)hexyl)phosphonic acid **b**

Diethyl (6-((4-(dodecylsulfonyl)phenyl)amino)hexyl)phosphonate **10** (1.37 g, 2.51 mmol) was placed in a round-bottom flask, which was repeatedly evacuated and filled with argon. Dry MeCN (90 mL) and trimethylsilyl bromide (1.7 mL, 12.8 mmol) were further poured into the flask and the reaction mixture was stirred for 3 days under argon atmosphere. Subsequently, the mixture was evaporated on a rotary vacuum evaporator and repeatedly dissolved in CH_2Cl_2 (3x 50 mL) and evaporated. Similar process was then repeated with MeOH (3x 50 mL). The crude mixture was then heated with MeCN (100 mL) to 82 °C for 2 h. Once cooled down to the room temperature, (6-((4-(dodecylsulfonyl)phenyl)amino)hexyl)phosphonic acid **b** was filtered off as a white precipitate in a form of hydrobromide salt (1.23 g, 86%).

Analytical data for **b**

M.p. 199.5 – 203.0 °C (MeCN).

Anal. calcd. for $C_{24}H_{45}BrNO_5PS$: C, 50.52; H, 7.95; N, 2.45; O, 14.02; P, 5.43; S, 5.62; Br, 14.00. Found: C, 50.66; H, 7.57; N, 2.32; P, 5.24; S, 6.16; Br, 14.10.

^{1}H NMR (300 MHz, CD_3OD, 298 K) δ 7.77 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 7.10 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 3.27 (t, *J* = 7.5 Hz, 2H, CH_2NH), 3.18 – 3.10 (m, 2H, SO_2CH_2), 1.80 – 1.55 (m, 8H, 4x CH_2), 1.54 – 1.42 (m, 4H, 2x CH_2), 1.41 – 1.21 (m, 18H, 9x CH_2), 0.89 (t, *J* = 6.6 Hz, 3H, CH_3). See the spectrum in Figure S9.

^{13}C NMR (75 MHz, CD_3OD, 298 K) δ 148.63 (s, Ar *C*q), 129.71 (s, Ar *C*q, Ar *C*H), 115.57 (s, Ar *C*H), 55.66 (s, SO_2CH_2), 45.80 (s, CH_2NH), 31.63 (s, CH_2), 29.80 (d, *J* = 16.4 Hz, $PCH_2CH_2CH_2$), 29.29 (s), 29.16 (s), 29.02 (s), 28.94 (s), 28.70 (s), 27.76 (s), 27.29 (s), 25.97 (s), 25.46 (s, 9x CH_2, $PCH_2CH_2CH_2$, two of the signals in the range 29.29 – 25.46 ppm that could not be directly determined represent a doublet; two signals were overlapped), 22.57 (s, CH_2), 22.33 (d, *J* = 4.4 Hz, $PCH_2CH_2CH_2$), 22.30 (s, CH_2), 13.02 (s, CH_3).

IR (film, MeOH): 3378(m) ν(NH);

2934(m), 2912(s), 2868(m), 2848(m) ν(CH), 1468(m) $\delta(CH_3)$+ $\delta(CH_3)$, 1405(m) $\delta(CH_2)$ (P-CH_2), 717(m) $(CH_2)_n$;

3000-2400 ν(POH);

Ar: 3013(m), 1601(s), 1499(m), 1287(m), 1090(m), 824(m), 784(m);

1221(m) ν(P=O), 1310(m) $\nu_A(SO_2)$, 1142(s), 1134(s) $\nu_S(SO_2)$, 997(m) ν(POH), 540(m) $\beta(SO_2)$.

Synthesis of (10-((4-(dodecylsulfonyl)phenyl)amino)decyl)phosphonic acid **c**

Diethyl (10-((4-(dodecylsulfonyl)phenyl)amino)decyl)phosphonate **d** (1.69 g, 2.81 mmol) was placed in a round-bottom flask, which was repeatedly evacuated and filled with argon. Dry CH_2Cl_2 (120 mL) and trimethylsilyl bromide (2.1 mL, 15.7 mmol) were further poured into the flask and the reaction mixture was stirred for 3 days under argon atmosphere. Subsequently, the mixture was evaporated on a rotary vacuum evaporator and repeatedly dissolved in CH_2Cl_2 (3x 50 mL) and evaporated. Similar process was then repeated with MeOH (3x 50 mL). The crude mixture was then heated with MeCN (100 mL) to 82 °C

for 2 h. Once cooled down to the room temperature, (10-((4-(dodecylsulfonyl)phenyl)amino)decyl)phosphonic acid **c** was filtered off as a white precipitate in a form of hydrobromide salt (1.54 g, 87%).

Analytical data for **c**

M.p. 175.0 – 180.0 °C (MeCN).

Anal. calcd. for $C_{28}H_{53}BrNO_5PS$: C, 53.67; H, 8.53; N, 2.24; O, 12.77; P, 4.94; S, 5.12; Br, 12.75. Found: C, 54.80; H, 8.11; N, 2.25; P, 5.19; S, 5.70; Br, 10.34.

^{1}H NMR (300 MHz, DMSO, 298 K) δ 7.46 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 6.63 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 3.10 – 2.96 (m, 4H, C*H*$_2$NH, SO_2CH_2), 1.60 – 1.37 (m, 8H, 4x C*H*$_2$), 1.37 – 1.06 (m, 30H, 15x C*H*$_2$), 0.82 (t, *J* = 6.7 Hz, 3H, C*H*$_3$). See the spectrum in Figure S10.

^{13}C NMR (75 MHz, DMSO, 298 K) δ 153.24 (s, Ar *C*q), 129.85 (s, Ar *C*H), 123.85 (s, Ar *C*q), 111.44 (s, Ar *C*H), 55.85 (s, SO_2CH_2), 42.75 (s, *C*H$_2$NH), 31.73 (s, *C*H$_2$), 30.49 (d, *J* = 15.9 Hz, $PCH_2CH_2CH_2$), 29.47 (s), 29.43 (s), 29.29 (s), 29.14 (s), 29.11 (s), 28.85 (s), 28.78 (s), 27.80 (s), 27.03 (s), 26.96 (s, 13x *C*H$_2$, P*C*H$_2$CH$_2$CH$_2$, two of the signals in the range 29.47 – 26.96 ppm that could not be directly determined represent a doublet; five signals were overlapped), 23.11 (d, *J* = 5.1 Hz, $PCH_2CH_2CH_2$), 23.07 (s, *C*H$_2$), 22.54 (s, *C*H$_2$), 14.39 (s, *C*H$_3$).

IR (film, MeOH): 3349(m) ν(NH);

2917(s), 2848(m) ν(CH), 1472(m), 1466(m) $\delta(CH_3)$+ $\delta(CH_3)$, 1417(m) $\delta(CH_2)$ (P-CH_2),717(m) $(CH_2)_n$;

3000-2400 ν(POH);

Ar: 3013(m), 1598(m), 1575(m), 1290(m), 1089(m), 821(m), 790(m), 771(m);

1234(w) ν(P=O), 1318(m) $\nu_A(SO_2)$, 1143(s) $\nu_S(SO_2)$, 952(m) ν(POH), 540(m) $\beta(SO_2)$.

Synthesis of diethyl (10-((4-(dodecylsulfonyl)phenyl)amino)decyl)phosphonate **d**

1-(Dodecylsulfonyl)-4-fluorobenzene **8** (1.84 g, 5.59 mmol) and diethyl (10-aminodecyl)phosphonate **6** (3.28 g, 11.2 mmol) were dissolved in dry DMSO (18 mL) in a round-bottom flask. The reaction mixture was stirred and heated to 130 °C for 2.5 h. Subsequently, the mixture was cooled down to the room temperature and poured to demineralized H_2O (150 mL), followed by the extraction with CH_2Cl_2 (3x 50 mL). The combined organic layers were dried over $MgSO_4$. After the solvent evaporation on a rotary vacuum evaporator, diethyl (10-((4-(dodecylsulfonyl)phenyl)amino)decyl)phosphonate **d** was obtained via a column chromatography (SiO_2, eluent CH_2Cl_2:EtOAc 2:1 *v*/*v*) as a white solid (1.81 g, 54%). The purity of d was determined by HPLC as 98.9%.

Analytical data for **d**

M.p. 49.5 – 51.0 °C ($CHCl_3$/MeOH).

Anal. calcd. for $C_{32}H_{60}NO_5PS$: C, 63.86; H, 10.05; N, 2.33; O, 13.29; P, 5.15; S, 5.33. Found: C, 63.71; H, 9.89; N, 2.09; P, 5.31; S, 5.32; Br, <0.03.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.63 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.59 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 4.26 (br s, 1H, N*H*), 4.18 – 3.99 (m, 4H, O*CH*$_2$CH$_3$), 3.15 (t, *J* = 7.1 Hz, 2H, C*H*$_2$NH), 3.05 – 2.95 (m, 2H, SO_2CH_2), 1.80 – 1.49 (m, 10H, 5x C*H*$_2$), 1.31 (t, *J* = 7.1 Hz, 6H, OCH$_2$C*H*$_3$), 1.45 – 1.15 (m, 28H, 14x C*H*$_2$), 0.87 (t, *J* = 6.7 Hz, 3H, C*H*$_3$). See the spectrum in Figure S11.

^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 152.31 (s, Ar *C*q), 129.99 (s, Ar *C*H), 125.38 (s, Ar *C*q), 111.56 (s, Ar *C*H), 61.36 (d, *J* = 6.7 Hz, O*CH*$_2$CH$_3$), 56.81 (s, SO_2CH_2), 43.31 (s, *C*H$_2$NH), 31.87 (s, *C*H$_2$), 30.53 (d, *J* = 16.9 Hz, $PCH_2CH_2CH_2$), 29.56 (s), 29.54 (s), 29.46 (s), 29.41 (s), 29.30 (s), 29.27 (s), 29.25 (s), 29.21 (s), 29.16 (s), 29.04 (s), 29.00 (s), 28.29 (s), 26.99 (s), 26.60 (s), 24.74 (s, 13x *C*H$_2$, P*C*H$_2$CH$_2$CH$_2$, two of the signals in the range 29.56 – 24.74 ppm that could not be directly determined represent a doublet), 22.92 (s, *C*H$_2$), 22.65 (s, *C*H$_2$), 22.34 (d, *J* = 5.4 Hz, $PCH_2CH_2CH_2$), 16.47 (d, *J* = 6.3 Hz, OCH$_2$C*H*$_3$), 14.09 (s, *C*H$_3$).

Synthesis of (10-((4-nitrophenyl)amino)decyl)phosphonic acid **e**

Diethyl (10-((4-nitrophenyl)amino)decyl)phosphonate **12** (1.26 g, 3.04 mmol) was placed in a round-bottom flask, which was repeatedly evacuated and filled with argon. Dry CH_2Cl_2 (80 mL) and trimethylsilyl bromide (2.0 mL, 15.2 mmol) were further poured into the flask and the reaction mixture was stirred for 3 days under argon atmosphere. Subsequently, the mixture was evaporated on a rotary vacuum evaporator and repeatedly dissolved in CH_2Cl_2 (3x 50 mL) and evaporated. Similar process was then repeated with MeOH (3x 50 mL). The crude mixture was then heated with MeCN (100 mL) to 82 °C for 2 h. Once

cooled down to the room temperature, (10-((4-nitrophenyl)amino)decyl)phosphonic acid **e** was filtered off as a pale yellow precipitate in a form of hydrobromide salt (1.10 g, 82%).

Analytical data for **e**

M.p. 140.0 – 143.0 °C (MeOH/MeCN).

Anal. calcd. for $C_{16}H_{28}BrN_2O_5P$: C, 43.75; H, 6.42; N, 6.38; O, 18.21; P, 7.05; Br, 18.19. Found: C, 43.99; H, 6.13; N, 5.94; P, 6.70; Br, 18.60.

^{1}H NMR (300 MHz, CD_3OD, 298 K) *δ* 8.09 (d, *J* = 9.3 Hz, 2H, Ar-*H*), 6.81 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 3.23 (t, *J* = 7.3 Hz, 2H, C*H*$_2$NH), 1.82 – 1.49 (m, 6H, 3x C*H*$_2$), 1.49 – 1.23 (m, 12H, 6x C*H*$_2$). See the spectrum in Figure S12.

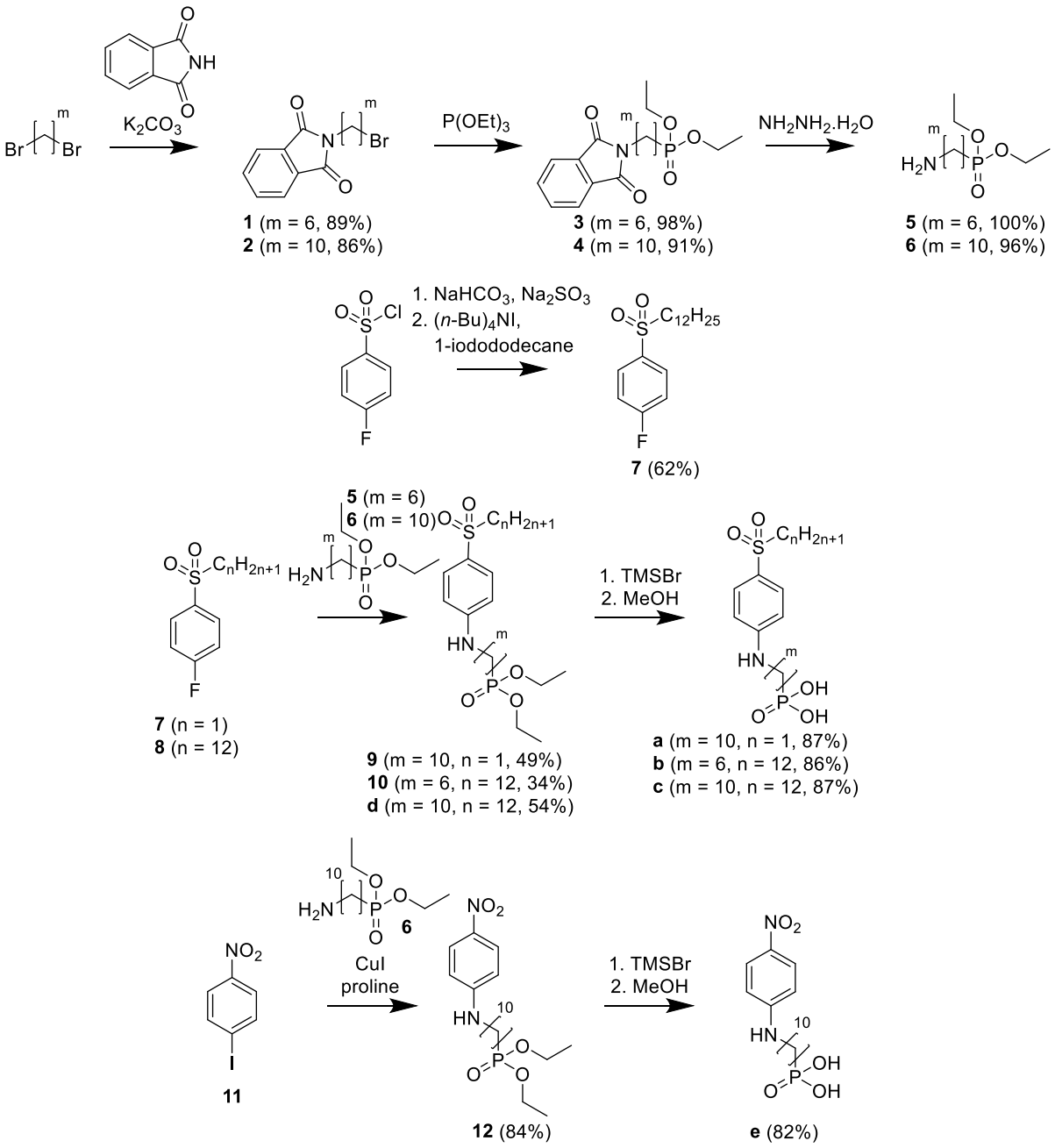
^{13}C NMR (75 MHz, CD_3OD, 298 K) *δ* 152.32 (s, Ar *C*q), 138.28 (s, Ar *C*q), 125.82 (s, Ar *C*H), 112.61 (s, Ar, *C*H), 44.19 (s, *C*H$_2$NH), 30.13 (s), 29.16 (s), 28.99 (s), 28.81 (s), 27.29 (s), 26.57 (s), 25.46 (s, 6x *C*H$_2$, PC*H*$_2$CH$_2$CH$_2$, PCH$_2$C*H*$_2$CH$_2$, PCH$_2$CH$_2$C*H*$_2$, two pairs of signals in the range 30.13 – 25.46 ppm that could not be directly determined represent two doublets; three signals were overlapped), 22.34 (d, *J* = 5.2 Hz, PCH$_2$*C*H$_2$CH$_2$).

IR (film, MeOH): 3400(m) ν(NH);

2927(m), 2854(m) ν(CH), 1469(m)δ(CH_3)+ δ(CH_3);

Ar: 1601(s), 1503(s), 1306(s), 1186(m), 1111(m);

1535(s) ν(NO_2), 1320(s) ν(NO_2), 856(m) β (NO_2), 985(m) ν(POH)



Scheme S1 Syntheses of polar ligands.

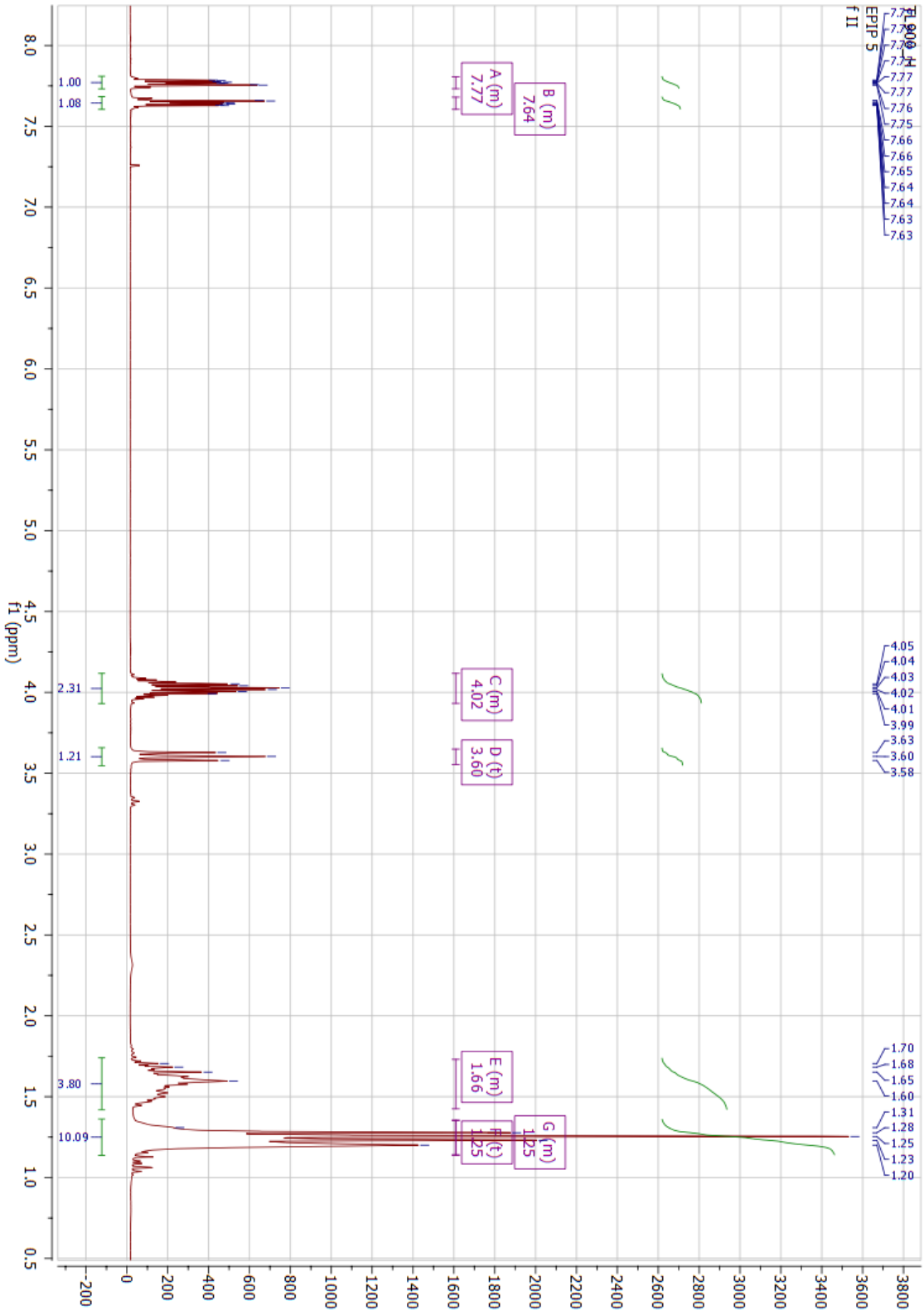


Figure S2 1H NMR (300 MHz, CDCl3, 298 K) spectrum of compound **4**.

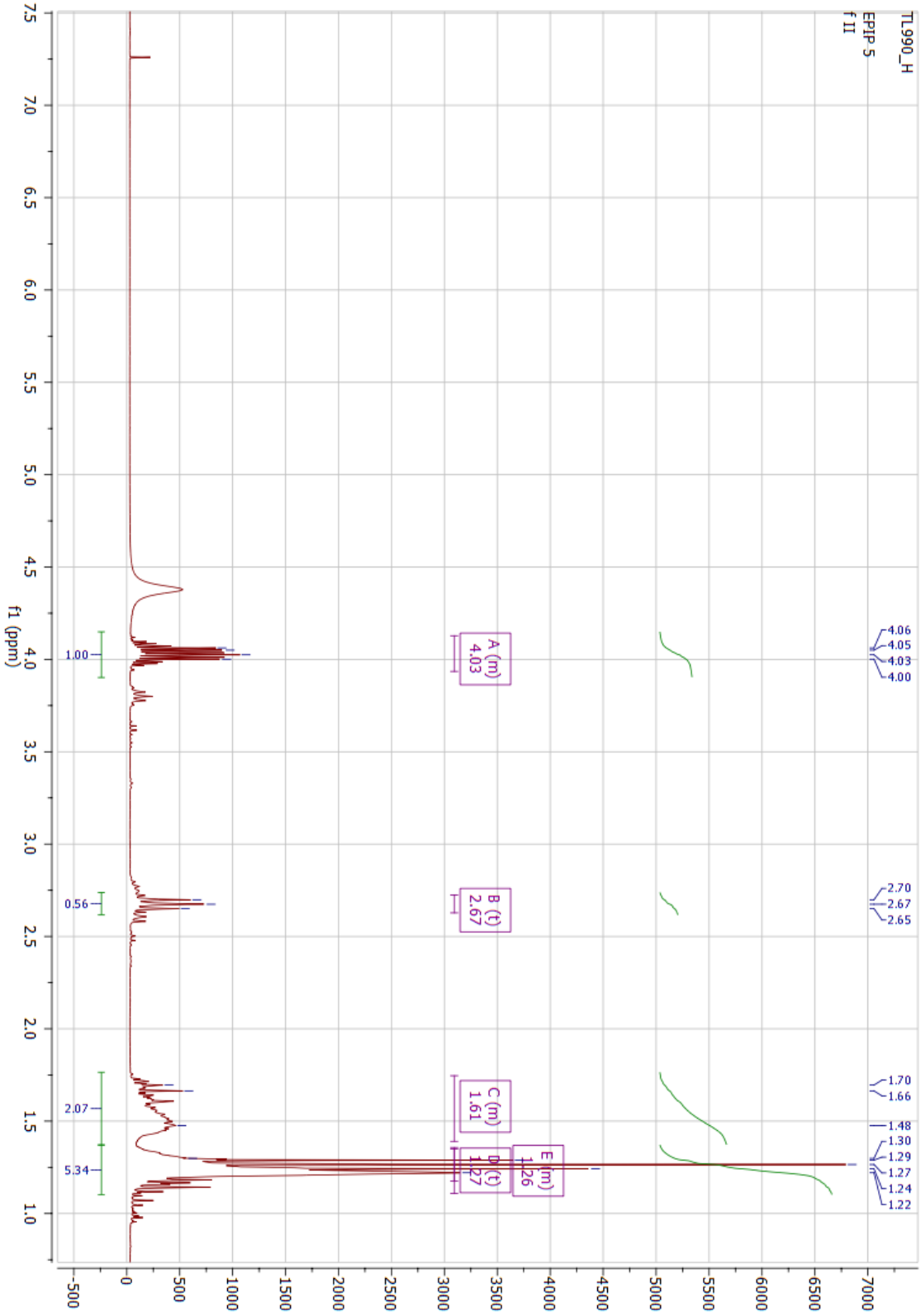


Figure S3 1H NMR (300 MHz, CDCl3, 298 K) spectrum of compound **6**.

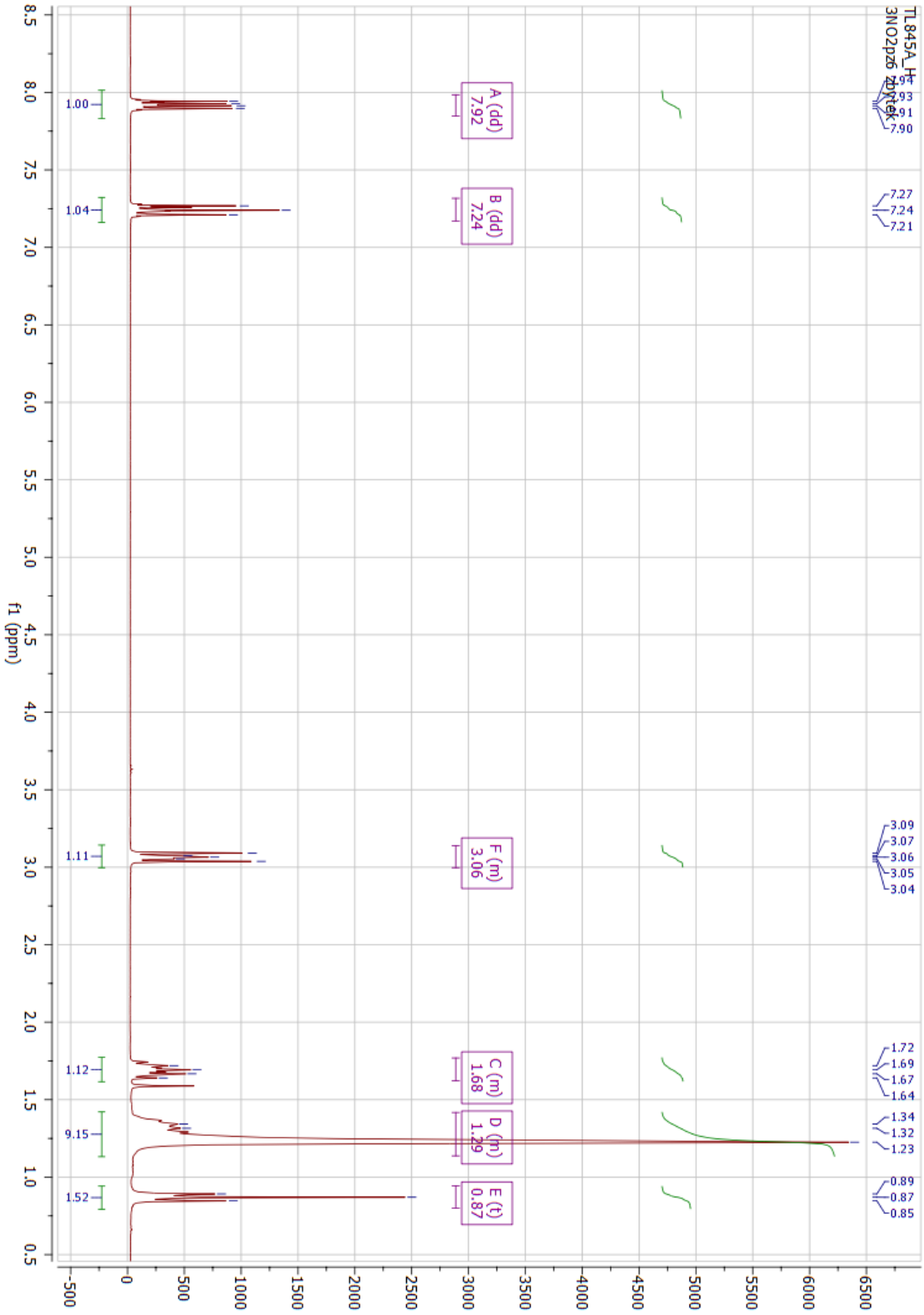


Figure S4 1H NMR (300 MHz, CDCl3, 298 K) spectrum of compound **8**.

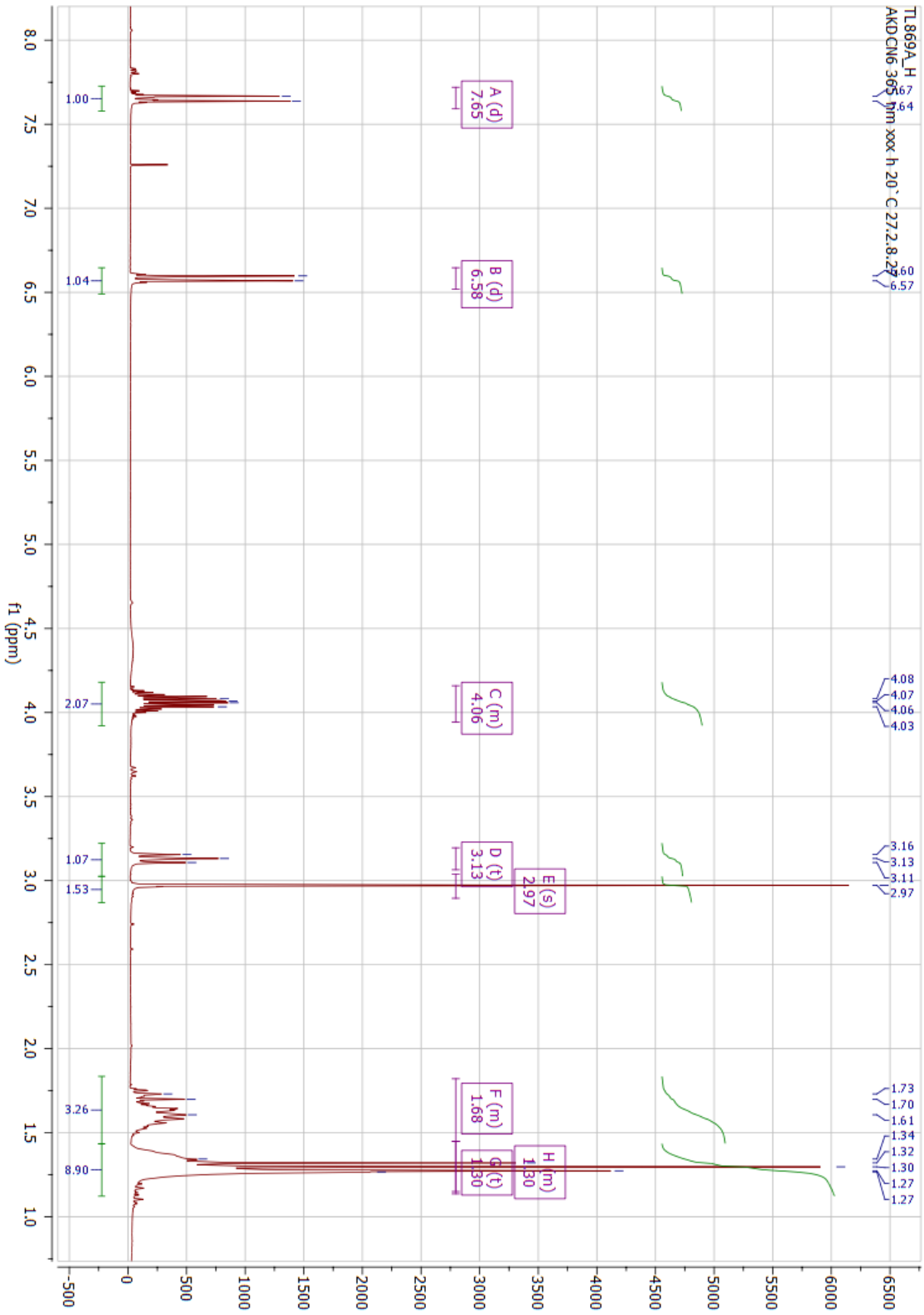


Figure S5 1H NMR (300 MHz, CDCl3, 298 K) spectrum of compound **9**.

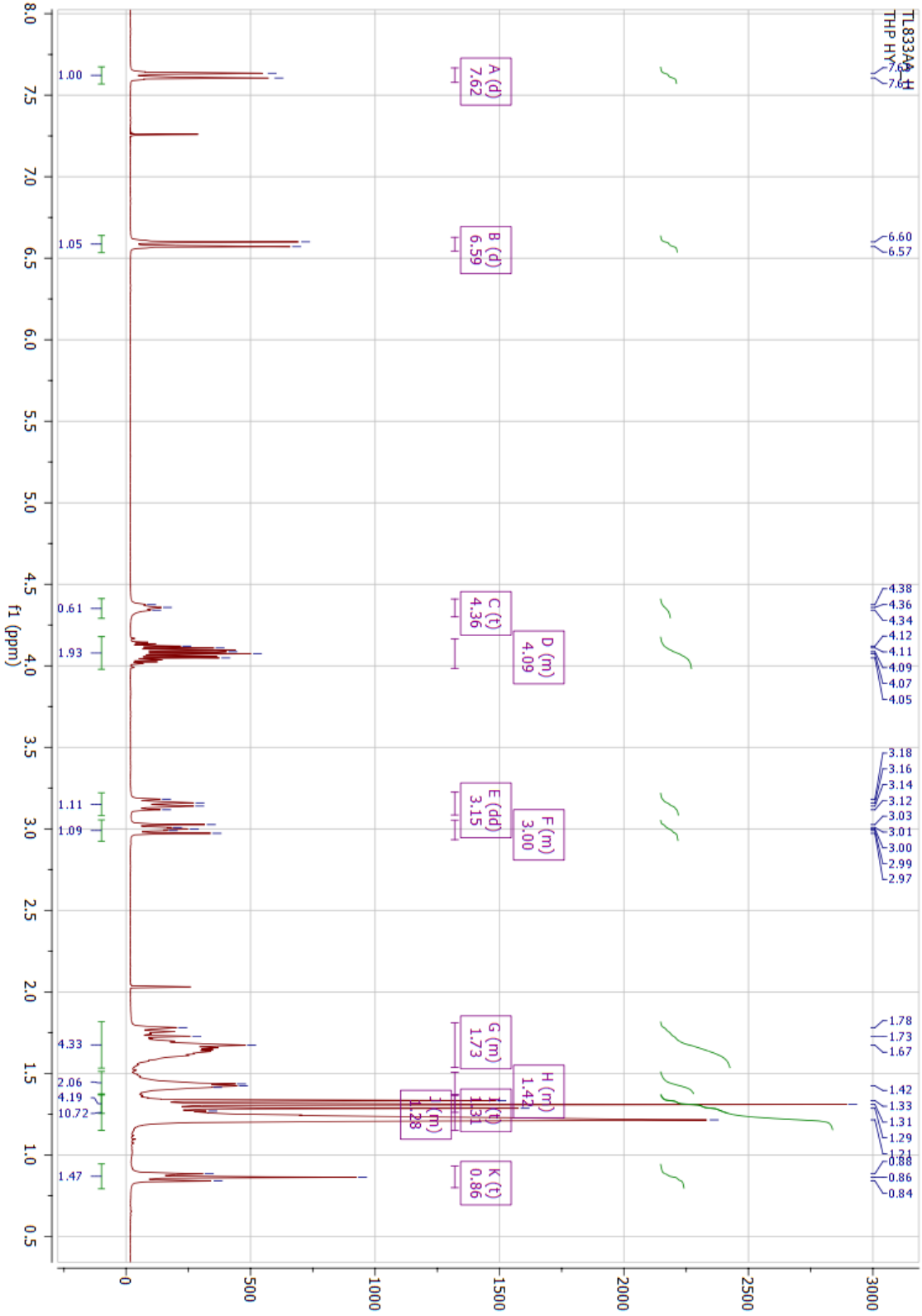


Figure S6 1H NMR (300 MHz, CDCl3, 298 K) spectrum of compound **10**.

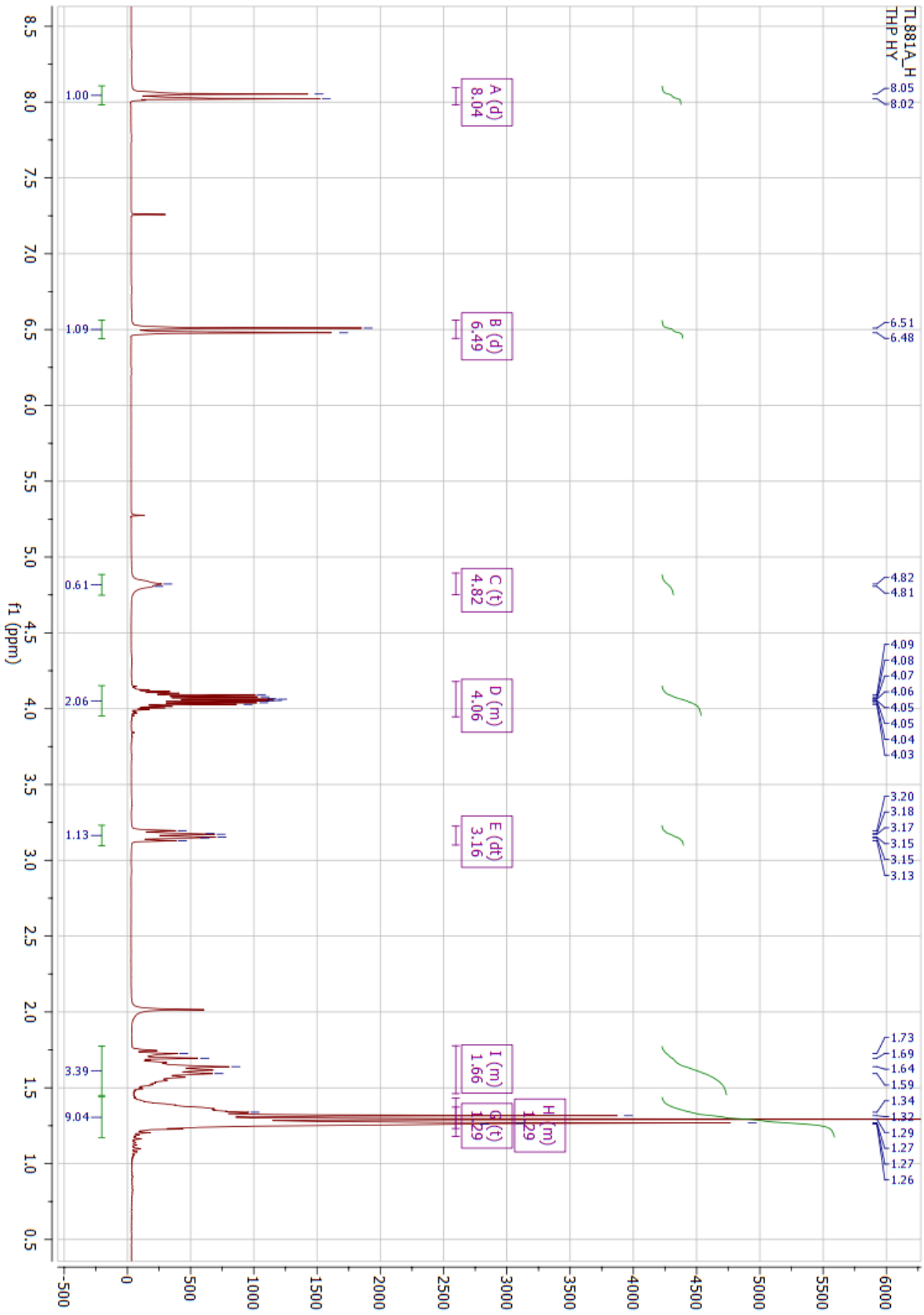


Figure S7 1H NMR (300 MHz, CDCl3, 298 K) spectrum of compound **12**.

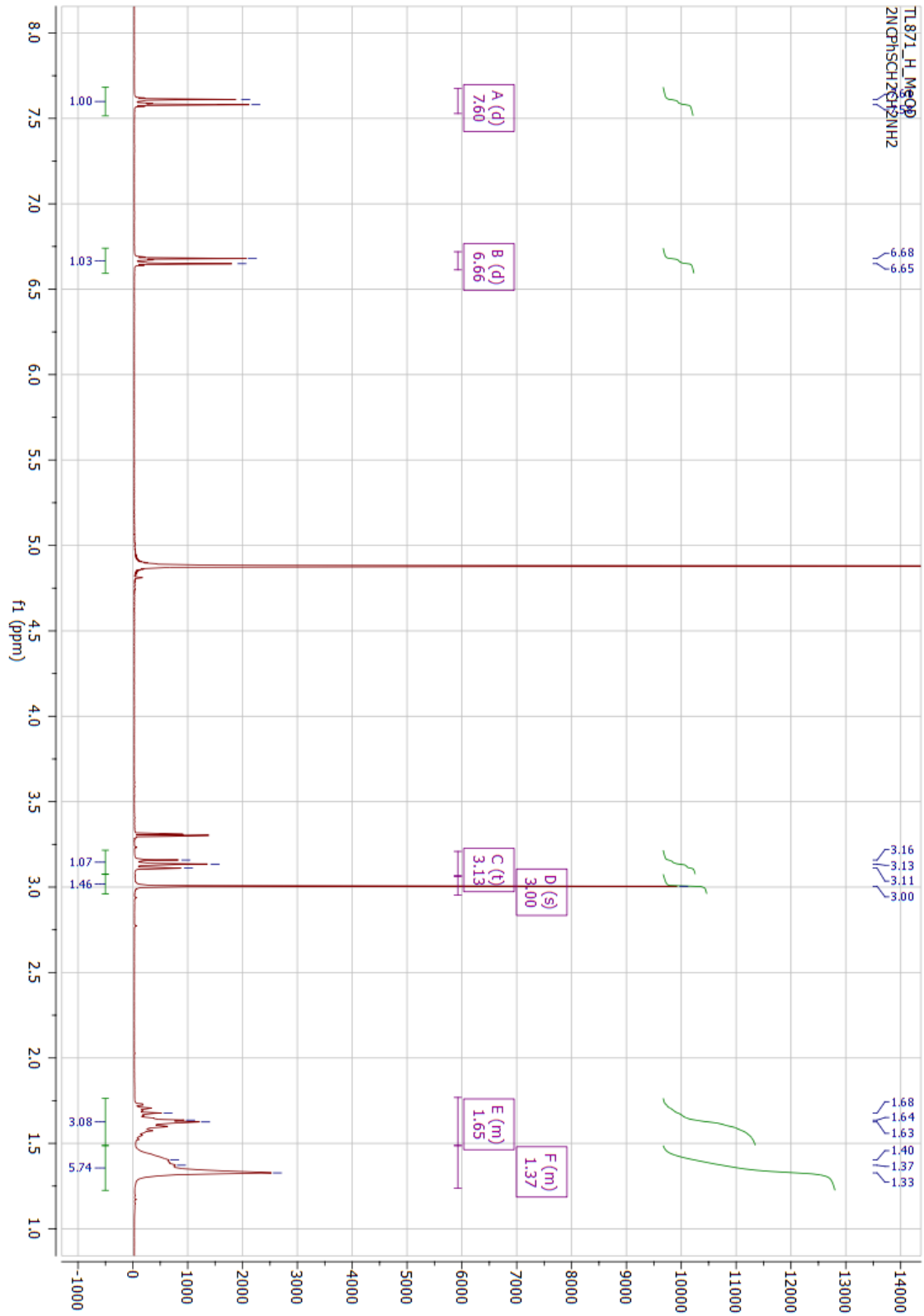


Figure S8 1H NMR (300 MHz, CD3OD, 298 K) spectrum of compound **a**.

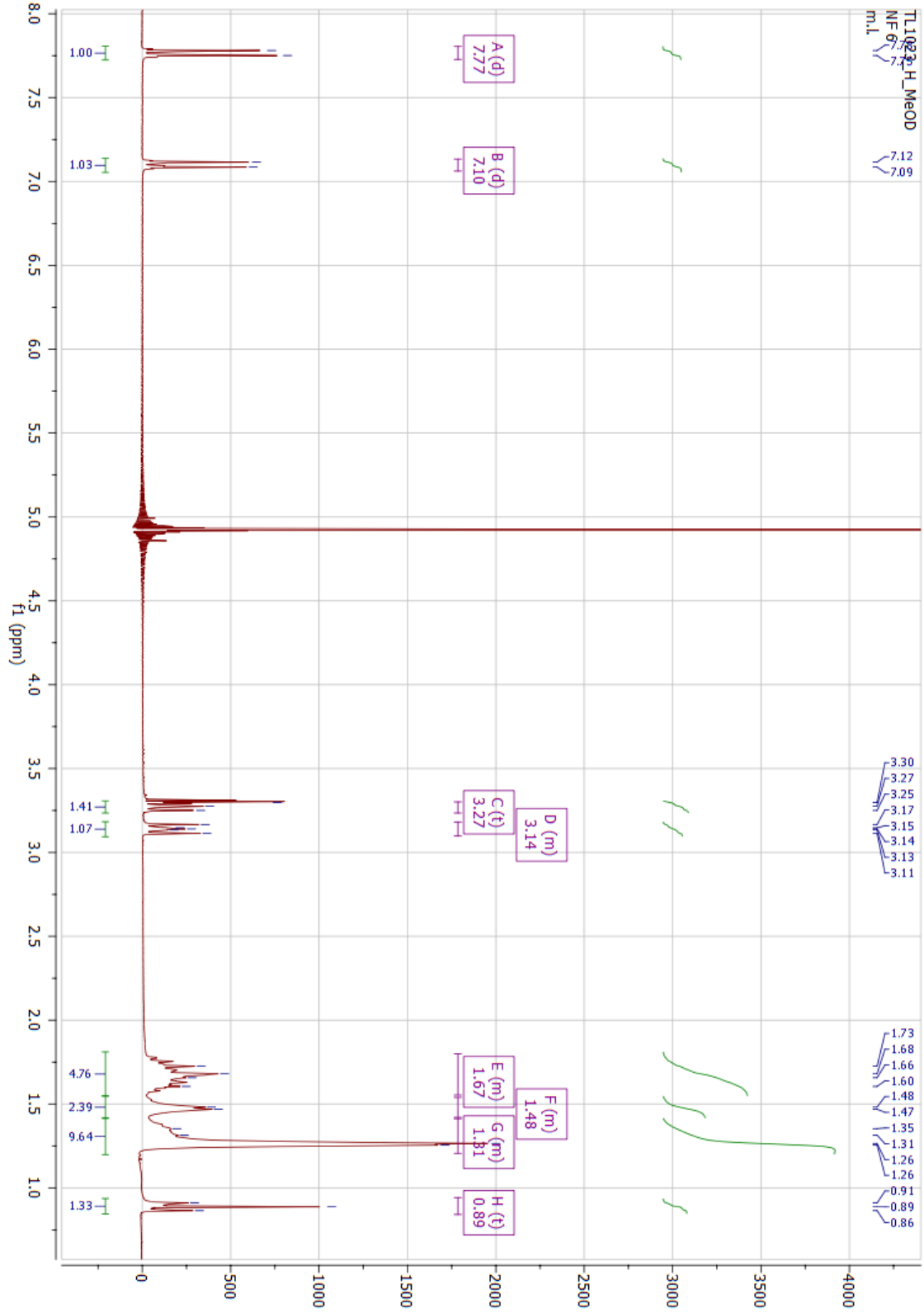


Figure S9 1H NMR (300 MHz, CD3OD, 298 K) spectrum of compound **b**.

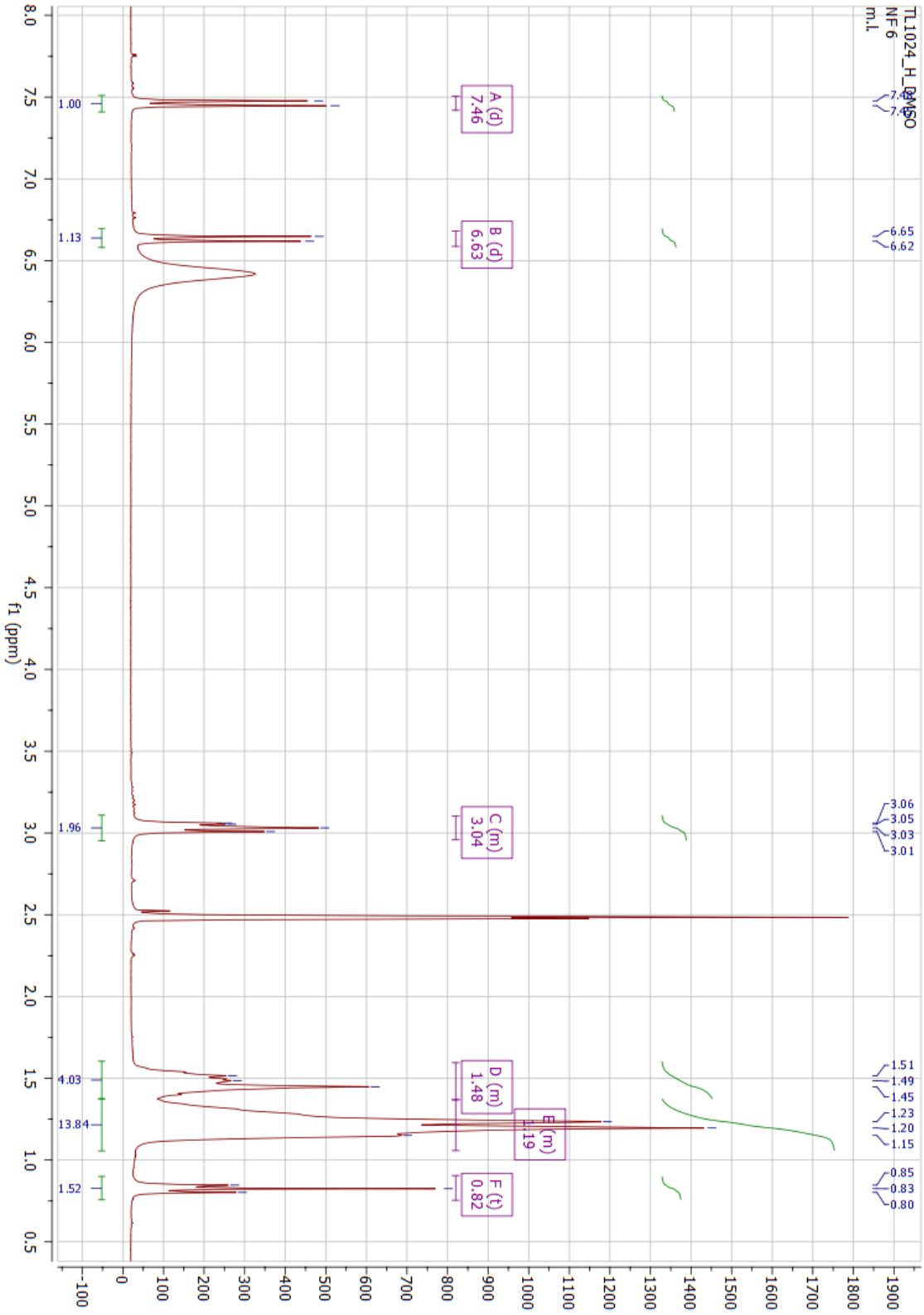


Figure S10 1H NMR (300 MHz, DMSO, 298 K) spectrum of compound **c**.

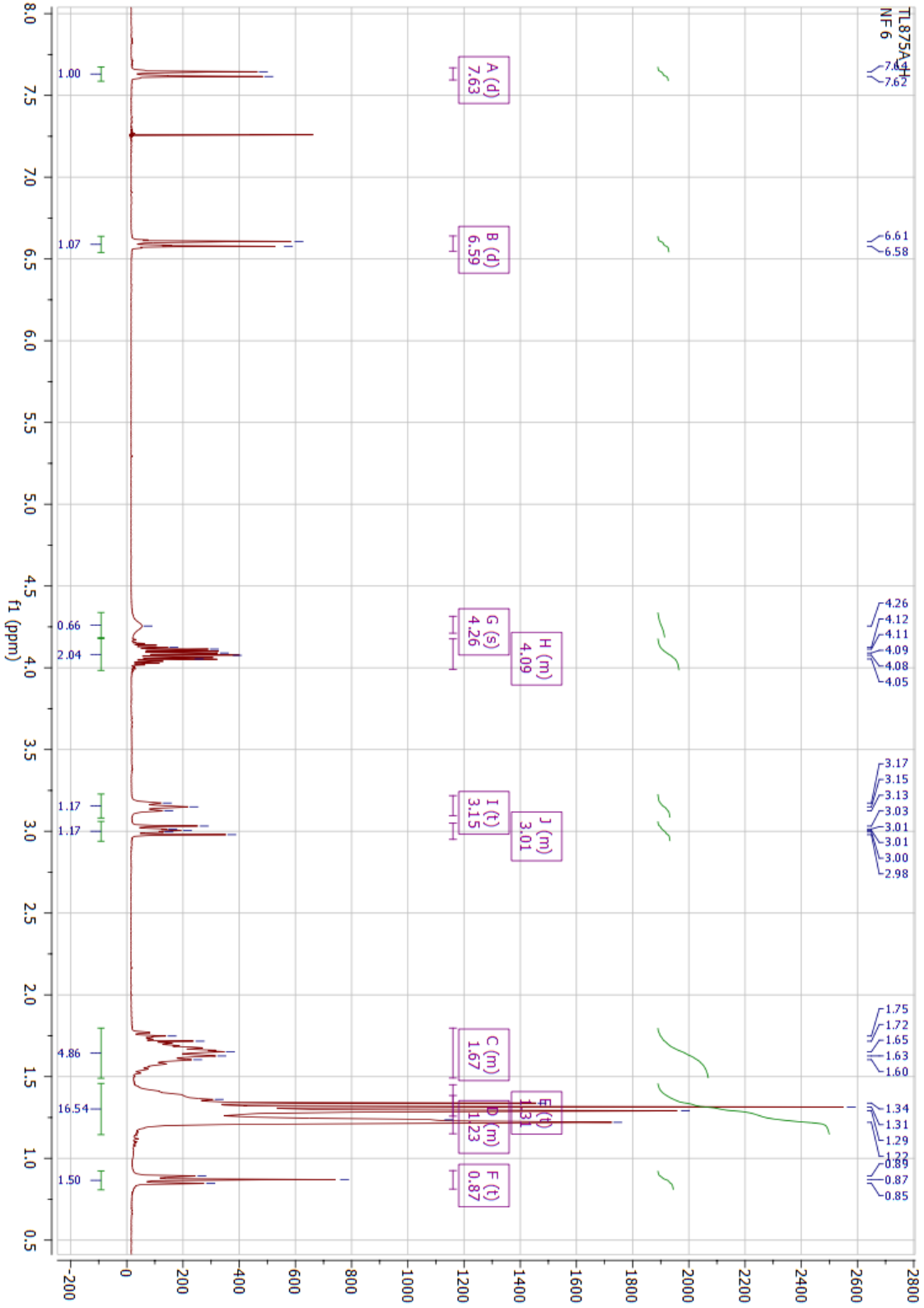


Figure S11 1H NMR (300 MHz, CDCl3, 298 K) spectrum of compound **d**.

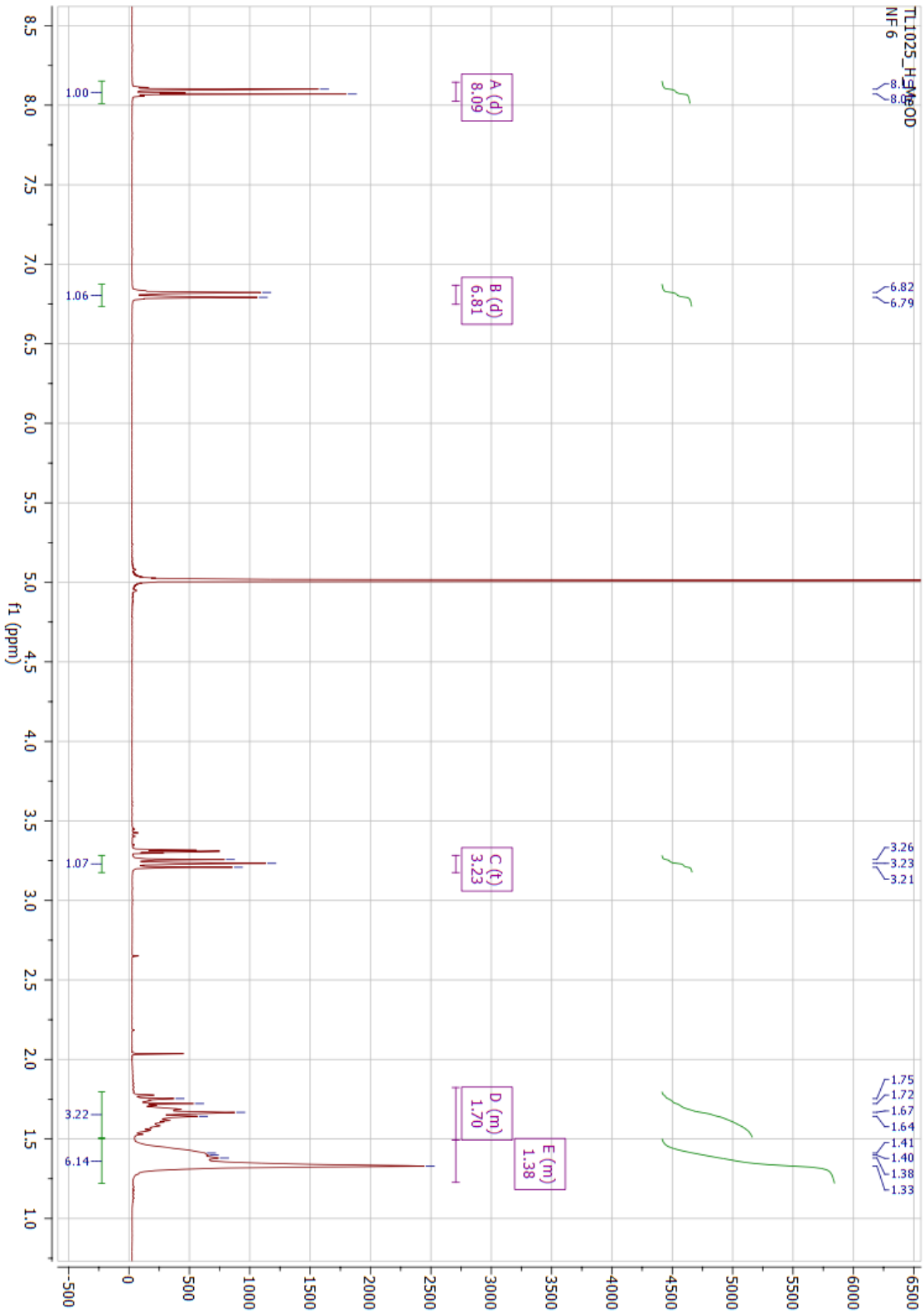


Figure S12 1H NMR (300 MHz, CD3OD, 298 K) spectrum of compound **e**.

Purity of polar ligands

HPLC analyses of the prepared phosphonic acids **b**, **c** and **e** revealed that these compounds contain a significant amount of an unwanted impurity, see Figure S13. This impurity was subsequently identified as an adduct of hydrobromic acid and acetonitrile by comparing retention time of the impurity with an in-house prepared MeCN·xHBr adduct, see Figure S14. The adduct was prepared using the following protocol: The mixture of HBr (aqueous concentrated, 5 mL) in MeCN (50 mL) was heated in a round-bottom flask for 3.5 h at 82 °C. After cooling down to the room temperature, MeCN·xHBr adduct was filtered off as a white precipitate.

Nevertheless, it is important to mention that only HBr was present in the samples **b**, **c** and **e** (check elemental analyses), MeCN·xHBr adduct was formed during the HPLC analyses, since MeCN was used as a sample solvent. The undesired HBr was undoubtedly produced in the final reaction step by the degradation of trimethylsilyl bromide, and its presence is practically unavoidable when using this synthetic procedure.

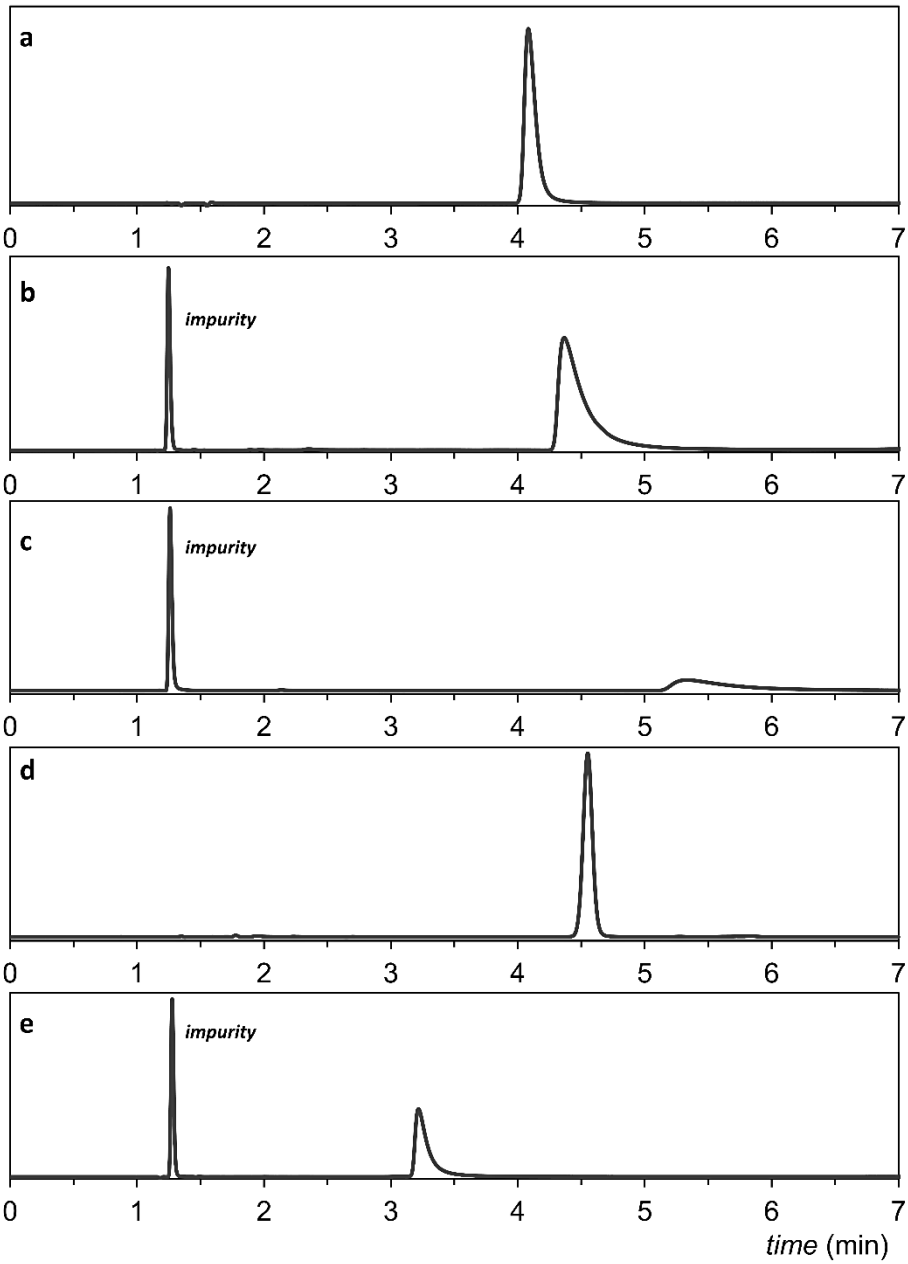


Figure S13 HPLC analyses of compounds a-e recorded at 210 nm. The mobile phase used for the analyses were: (a) 70/30 buffer/acetonitrile, (b) 40/60 buffer/acetonitrile, (c) and (d) 30/70 buffer/acetonitrile, (e) 60/40 buffer/acetonitrile.

In case of phosphonic acid **a**, we successfully managed to remove the unwanted HBr. Once was the corresponding hydrobromide salt heated in water, HBr passed quantitatively into water, while the pure ligand **a** remained undissolved. Unfortunately, this purification procedure could not be used for the other relevant ligands (**b**, **c** and **e**), therefore, these compounds were further used in the form of hydrobromide salts.

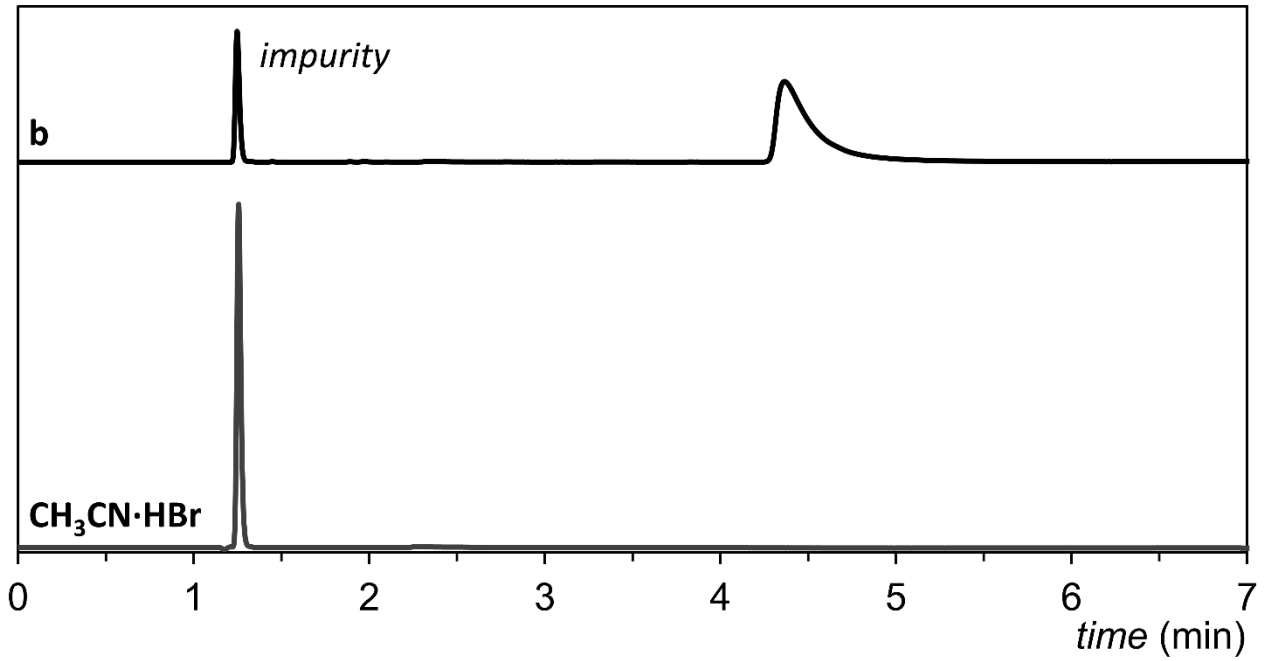


Figure S14 Comparison of HPLC analysis of phosphonic acid b and in-house prepared adduct of hydrobromic acid and acetonitrile recorded at 210 nm. The mobile phase was 40/60 buffer/acetonitrile.

Nominal surface density of the ligands for the hybridization

During the synthesis of polar ligands, HBr evolved as a side product and was not completely removed during the purification processes, as described above. The nominal densities of 3 and 10 molecules/nm^2 were roughly estimated from the total surface calculated from the average size of the NPLs. If we consider, the ligands' purity the nominal densities were slightly lower than 3 or 10 molecules/nm^2 (Table S1). 3 molecules/nm^2 represent the maximum theoretical density for a monolayer assembly (see Calculation section in main document). Therefore, for the hybrid samples hybridized with $\leq$3 molecules/nm^2, we expect the ligands to assemble in a monolayer. The large excess of 10 molecules/nm^2 may accelerate the surface reaction and favour a multilayer assembly of the ligands.

Table S1. Nominal surface densities of the ligands considering their phase purity. The ligands' structures are shown in Figure 2.

Ligand	Purity (%)	Actual nominal density for ~10 molecules/nm^2	Actual nominal density for ~3 molecules/nm^2
a	99.9[a]	9.99	2.99
b	85.8[b]	8.58	2.57
c	87.1[b]	8.71	2.61
d	98.9[a]	9.89	2.97
e	81.6[b]	8.16	2.54

[a] Determined by HPLC.

[b] Calculated theoretical amount of phosphonic acid in the corresponding hydrobromide salt.

The selection procedure of the solvent with low polarity

The suspension of core BHF NPLs (c = 2 mg/mL) in 0.001 M aqueous HNO3 (10 mL) was mixed with the solution of (6-((4-(hexyl(methyl)amino)phenyl)sulfonyl)hexyl)phosphonic acid hydrobromide (polar ligand) in a selected solvent with relatively low polarity (10 mL) in a round-bottom flask. The concentration of the polar ligand corresponded to the surface coverage of NPLs with 2.5 or 8 molecules/nm^2. The resulting mixture was continuously shaken by hand and its behavior was monitored visually. The best results were achieved using 1-hexanol (Figure S15).

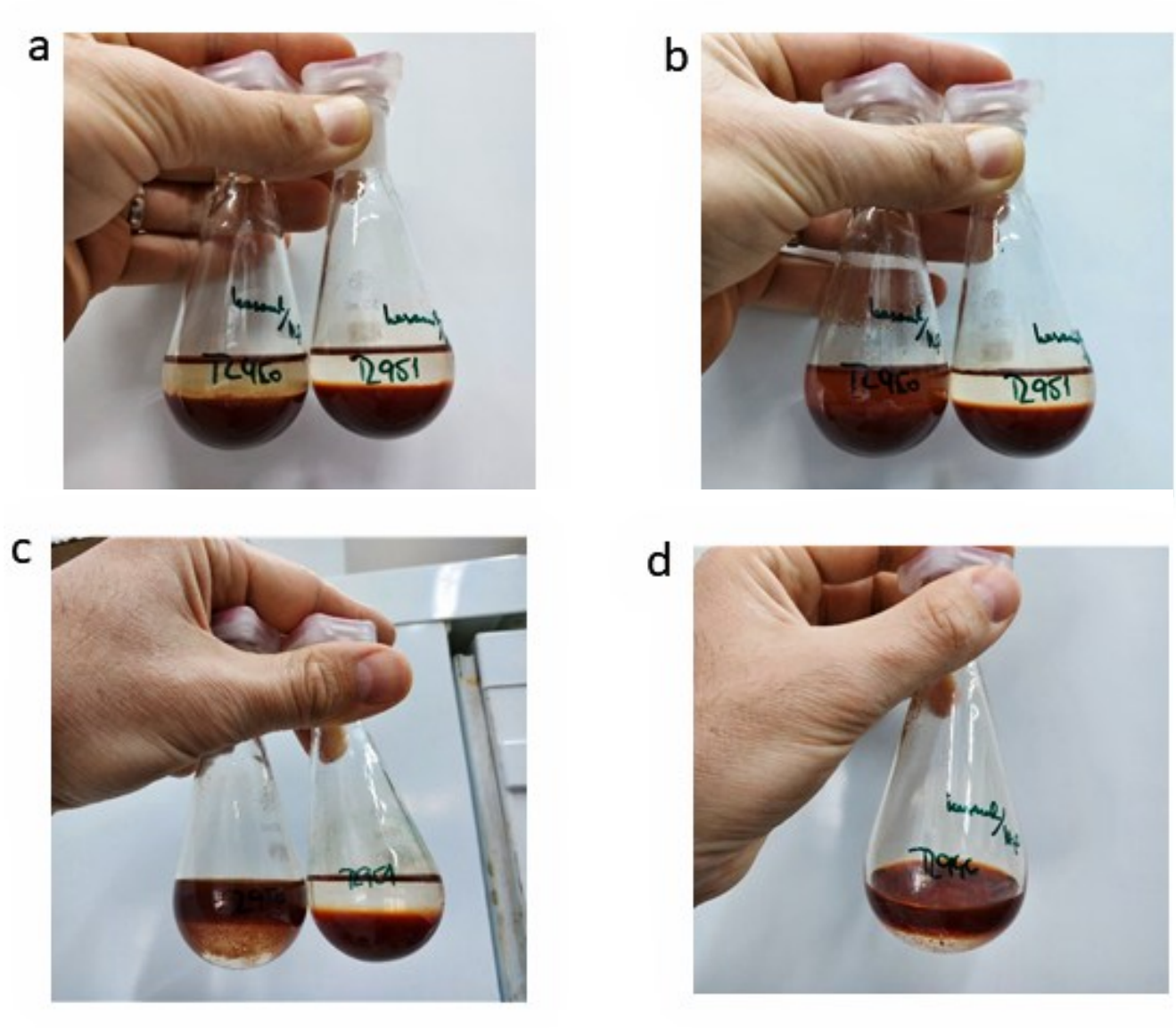


Figure S15 Hybridization test of the BHF NPL in the biphasic system 1-hexanol/water: (a) left flask the NPLs suspension/ligand solution (2.5 molecules/nm^2), right flask the NPLs suspension/pure 1-hexanol (t = 0 min); (b) left flask the NPLs suspension/ligand solution (2.5 molecules/nm^2), right flask the NPLs suspension/pure 1-hexanol (t = 15 min, after shaking); (c) left flask the NPLs suspension/ligand solution (2.5 molecules/nm^2), right flask the NPLs suspension/pure 1-hexanol (t = 72 h, after shaking); (d) the NPL suspension/ligand solution (8 molecules/nm2), (t = 72 h, after shaking).

Electrokinetic measurements

Figure S16 shows examples of measuring the zeta potential of the same hybrid NPLs in two different solvents, methanol and 1-hexanol. Figure S16a shows a phase plot for the sample measured in methanol with a regular saw-like behaviour. The saw-like behaviour is a result of the electrophoretic mobility of the NPLs under an a.c. electric field. From the phase plot, the zeta potential was calculated with the peak at –25.6 and a narrow distribution of ± 0.8 mV (Figure S16b). Figure S16c shows a phase plot of the NPLs dispersed in 1-hexanol, where the phase difference oscillates around 0 rad, indicating that the particles are not responding to the electric field. From Figure S16c the zeta potential was calculated, Figure S16d. The zeta-potential distribution is extremely wide, indicating that the NPLs suspended in hexanol have zero surface charge.

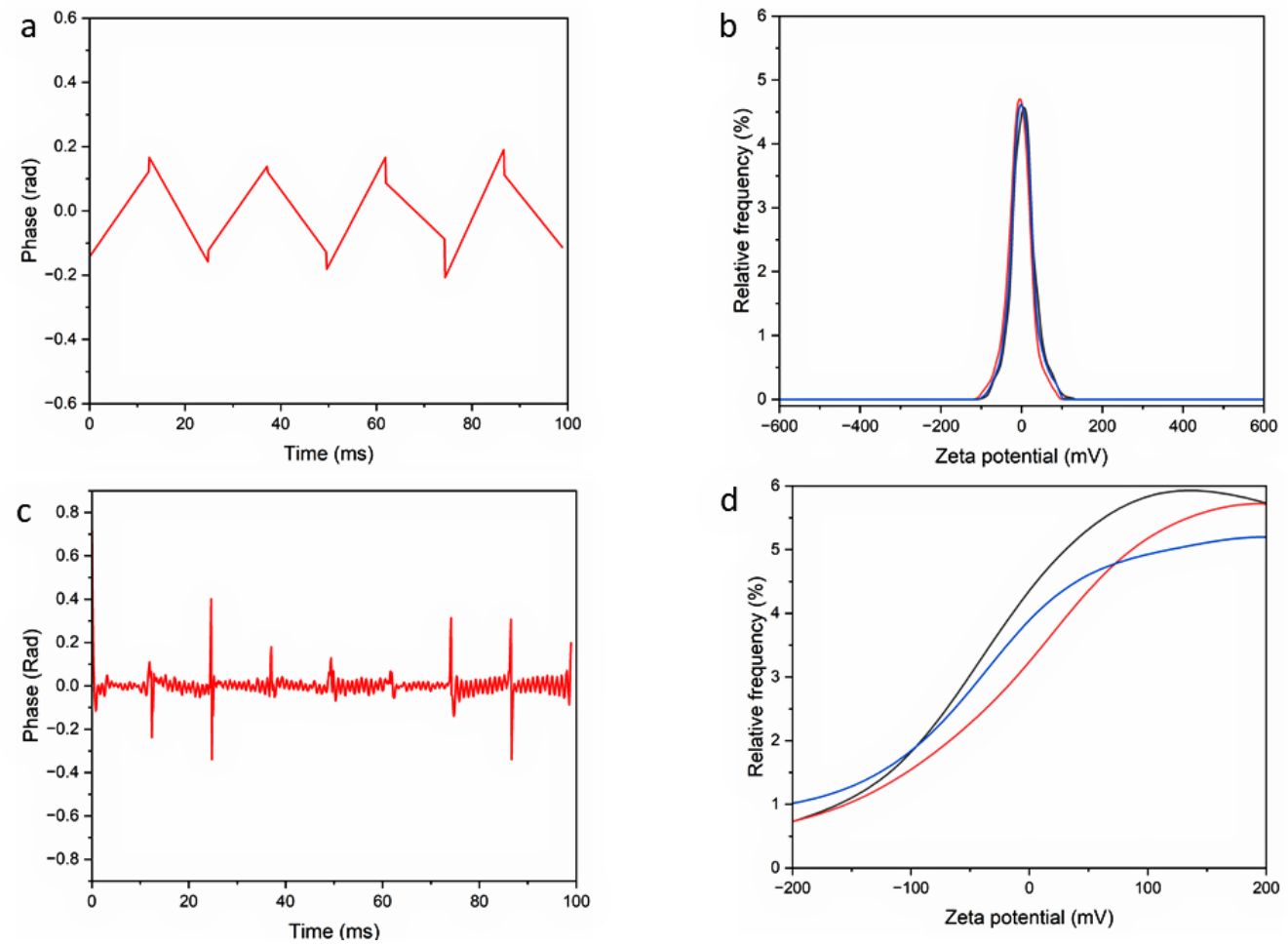


Figure S16 (a) phase plot and (b) zeta potential distribution of BHF-10**c**-H-120C dispersed in methanol. (c) phase plot and (d) zeta potential distribution of BHF-10**c**-H-120C dispersed in 1-hexanol.

Determination of the fraction of nonmagnetic phases with thermal analyses

The nonmagnetic thermally decomposable phases in the core BHF NPLs samples were: the adsorbed water and CO_2 from air, and the nitrate from the nitric acid solution used for washing and dispersing the as-synthesized BHF. An additional secondary phase, present in minor fractions, i.e., ≤ 1.5 wt.%, in some of the batches was $BaCO_3$. For the synthesis, a surplus of Ba is needed and its product, $BaCO_3$, is, in major part, dissolved and washed with a nitric acid solution. However, some minor fractions remain. $BaCO_3$ decomposes above 600 °C to BaO (s) and CO_2 (g). The total mass of nonmagnetic phases in the core NPLs was calculated from the mass loss obtained directly from the TGA up to 600 °C and the mass of $BaCO_3$, was calculated from the mass loss above 600 °C.

The fractions of phosphonic ligands were determined by evaluating the ligand decomposition step from 220 to 1000°C. Using this range, we avoided the low-temperature processes, drying, and condensation that occur below the decomposition temperature. We assumed that the mass loss at this temperature range was a result of the decomposition of the organic part of the ligand. Thus, the fraction of the ligand was calculated by comparing the mass loss of coted BHFs and the mass loss of pure ligands.

Example of thermal analysis for the BHF-10**c**-H-120C sample

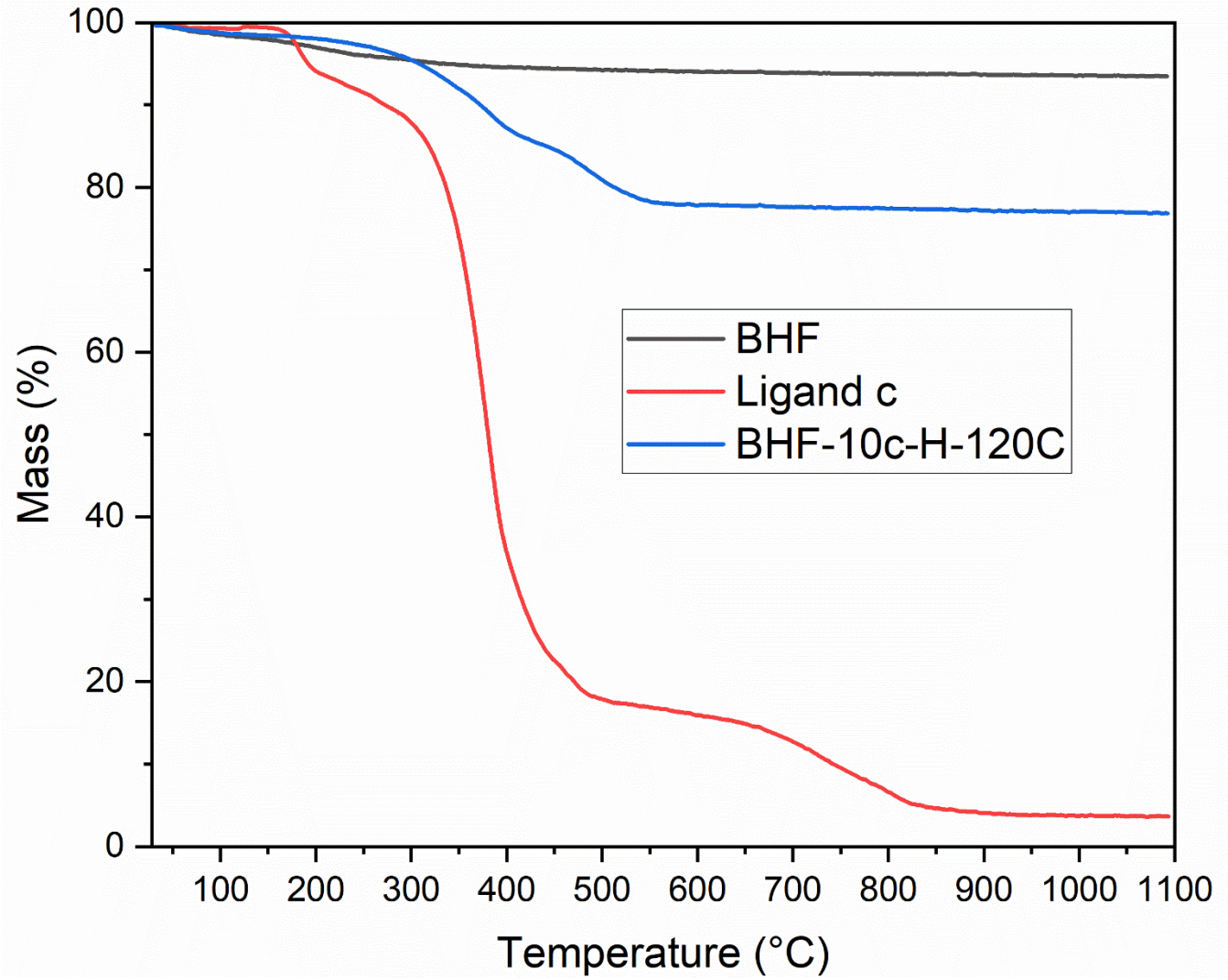


Figure S17 TGA and DSC curves for the core BHF NPLs, ligand c, and hybrid NPLs.

XPS results

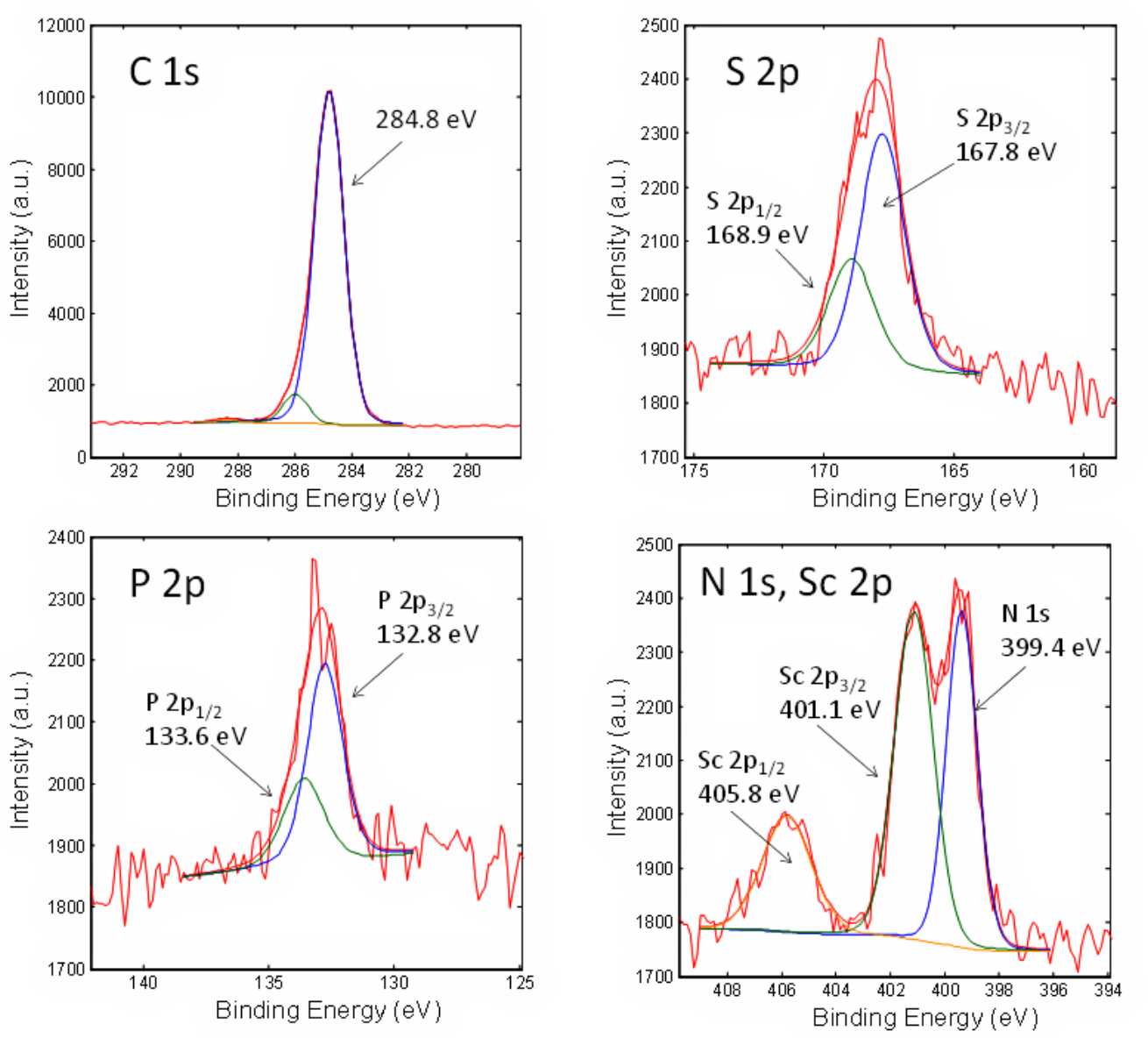


Figure S18 The high-energy resolution XPS spectra of C 1s, S 2p, P 2p, N 1s, and Sc 2p of the sample BHF-10**c**-H-120C.

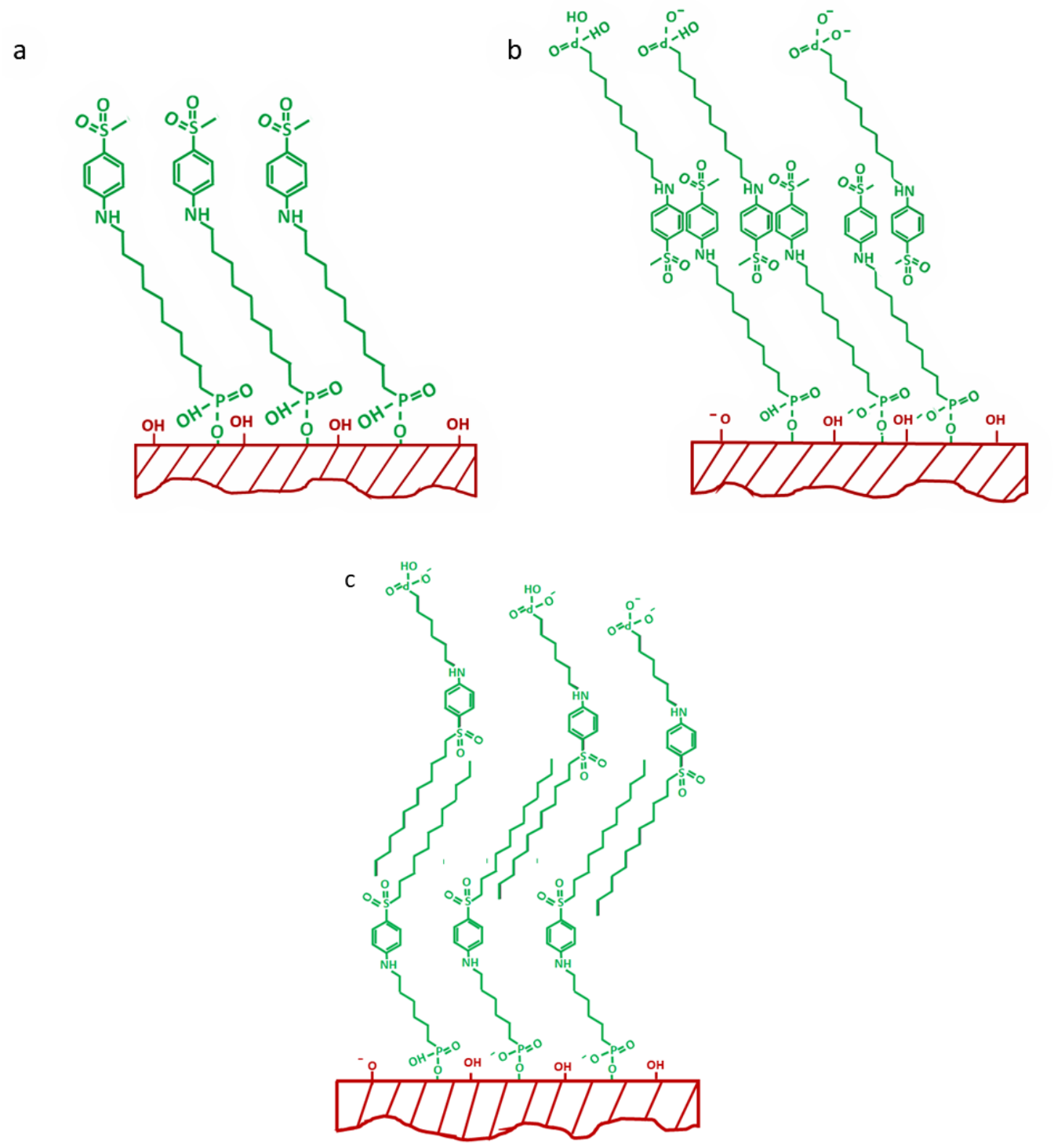


Figure S19 Schematic representation of possible assembly of an exemplary phosphonic ligand a at a metal-oxide surface: (a) monolayer assembly with monodentate binding in low-polar solvents and (b & c) a bilayer assembly in polar solvents via (b) π-π interactions and (c) hydrophobic interactions (ligand **b**).

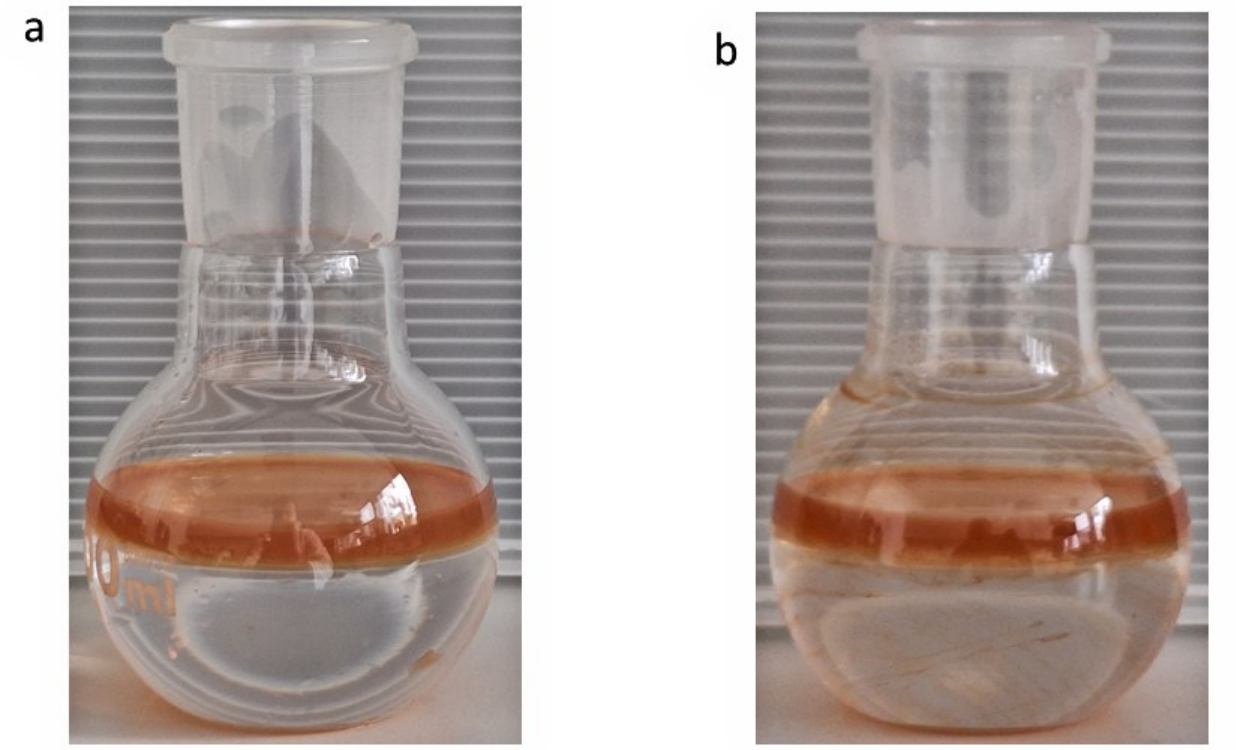


Figure S20 Photos of the brown 1-hexanol FF and transparent nitric acid solution (a) before and (b) after the stirring at room temperature for 24 h.

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