Supplementary Material (ESI) for Chemical Communications

Supplementary information

Thermoresponsive Dendronized Polymers with Tunable LCST

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Content

Experimental section

Materials. Tosylated diethylene glycol monomethyl ether (Me-DEG-Ts) and tosylated triethylene glycol monoethyl ether (Et-TEG-Ts) was synthesized according to literature method.[1] Compound **2g** was synthesized according to our previous reports.[2] Tetrahydrofuran (THF) was refluxed over lithium aluminum hydride (LAH) and dichloromethane (DCM) was distilled from CaH_2 for drying. Other reagents and solvents were purchased at reagent grade and used without further purification. All reactions were run under a nitrogen atmosphere. Macherey-Nagel precoated TLC plates (silica gel 60 G/UV_{254}, 0.25 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel 60 M (Macherey-Nagel, 0.04–0.063 mm, 230–400 mesh) was used as the stationary phase for column chromatography.

Instrumentation and Measurements. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers, and chemical shifts are reported as δ values (ppm) relative to internal Me_4Si. High resolution MALDI-TOF-MS analyses were performed by the MS service of the Laboratorium für Organische Chemie, ETH Zürich, on IonSpec Ultra instruments. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. Gel Permeation Chromatography (GPC) measurements were carried out on a PL-GPC 220 instrument with 2×PL-Gel Mix-B LS column set (2×30 cm) equipped with refractive index (RI), viscosity, and light scattering (LS; 15 ^{o} and 90 ^{o} angles) detectors, and DMF (containing 1 g·L^{-1} LiBr) as eluent at 45 °C. Universal calibration was performed with poly(methyl methacrylate) standards in the range of M_p = 2680 to 3900000 (Polymer Laboratories Ltd, UK). UV/vis turbidity measurements were carried out for the lower critical solution temperature (LCST) determination on a Varian Cary 100 Bio UV/vis spectrophotometer equipped with a thermostatically regulated bath. Solutions of the dendronized polymers in de-ionized water or in PH 7 sodium phosphate buffer solution (with concentration of 0.25 wt %) were filtered with a 0.45 μm filter before adding into a cuvette (path length 1 cm), which was placed in the spectrophotometer and heated or cooled at a rate of 0.2 °C·min^{-1}. The absorptions of the solution at λ = 500 nm were recorded every minute. Surface tension of the polymers at the air-water interface was measured via pendent drop method using PAT1 (Sinterface Technologies, Berlin, Germany). For each experiment, one drop of the polymer aqueous solution (0.25 wt %) with a constant volume of 35 mm^3 was set at 22 ^{o}C. The surface tension as a function of time was then determined according to Laplace-Gauss equation. The surface tension value was selected after the equilibrium.

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[1] M. Ouchi, Y. Inoue, Y. Liu, S. Nagamune, S. Nakamura, K. Wada, T. Hakushi, *Bull. Chem. Soc. Jpn.* 1990, **63**, 1260.
[2] W. Li, A. Zhang, A. D. Schlüter, *Macromolecules*, 2008, **41**, 43-49.

Synthesis

General procedure for Williamson etherification to form G1 ester (**A**). A mixture of methyl gallate (45.6 mmol), tosylated OEG (182.3 mmol), KI (36.5 mmol), and potassium carbonate (K_2CO_3) (456.0 mmol) in dry DMF (200 mL) was stirred at 80 ^oC over 24 h. After removal of DMF in vacuo, the residue was dissolved in DCM and washed sequentially with saturated $NaHCO_3$ and brine. After drying over $MgSO_4$, purification by column chromatography with hexane/ethyl acetate (1:5, v/v) afforded the product as a colorless oil.

General procedure for synthesis of G1 alcohol (**B**). LAH (25.1 mmol) was added to a solution of G1 ester (16.7 mmol) in dry THF (100 mL) at -5 ^oC, the mixture was stirred for 30 min, then warmed to r.t. and stirred for another 3 h. The reaction was quenched by dropwise addition of water (6 mL), 10% NaOH (15 mL), and water (20 mL) successively. The resulting precipitate was filtered and THF evaporated. The residue was dissolved in DCM and washed with brine. After drying over $MgSO_4$, purification by column chromatography with DCM/MeOH (20:1, v/v) afforded the product as a colorless oil.

General procedure for synthesis of G1 macromonomer (**C**). Methacryloyl chloride (MAC) (8.65 mmol) was added dropwise to a mixture of G1 alcohol (4.32 mmol), TEA (21.60 mmol), and DMAP (0.1 g) in dry DCM (50 mL) at 0 ^oC over 5 min. The mixture was stirred for 3 h at r.t. After washing successively with aqueous $NaHCO_3$ solution and brine, the organic phase was dried over $MgSO_4$. Purification by column chromatography with DCM / MeOH (20:1, v/v) afforded the product as a colorless oil.

General procedure for synthesis of G2 acid (**D**). Compound **2g** (3.28 mmol) in dry THF (30 mL) was added dropwise to a mixture of G1 alcohol (10.81 mmol), KI (9.84 mmol), 15-crown-5 (3.28 mmol), and NaH (32.5 mmol) in dry THF (60 mL). The mixture was stirred for 24 h at r.t. before addition of MeOH to quench the excess NaH. After evaporation of solvent in vacuo, the residue was dissolved in DCM and successively washed with saturated $NaHCO_3$ and brine. After drying over $MgSO_4$, purification by column chromatography with DCM/MeOH (15:1, v/v) afforded the product as a yellow oil.

General procedure for synthesis of G2 alcohol (**E**). *N*-Methylmorpholine (4.2 mmol) and ethyl chloroformate (4.2 mmol) were added sequentially to a solution of G2 acid (0.84 mmol) in dry THF (50 mL) at -15 ^oC, and the mixture was stirred for 1 h. Then $NaBH_4$ (6.72 mmol) was added at -5 ^oC and the reaction mixture stirred for another 4 h. Water was added to quench the reaction and THF then evaporated. The residue was dissolved in DCM, and then washed successively with saturated $NaHCO_3$ and brine. After drying over $MgSO_4$, purification by column chromatography with DCM / MeOH (10:1, v/v) afforded the product as a colorless oil.

General procedure for synthesis of G2 macromonomer (**F**). MAC (3.18 mmol) was added dropwise to a mixture of G2 alcohol (0.64 mmol), TEA (3.18 mmol), and DMAP (0.15 g) in dry DCM (40 mL) at 0 ^oC over 5 min. The mixture was stirred for 5 h at r.t. and then quenched with MeOH. After washing

successively with aqueous $NaHCO_3$ solution and brine, the organic phase was dried over $MgSO_4$. Purification by column chromatography with ethyl acetate / MeOH (5:1, v/v) afforded the product as a colorless oil.

General Procedure for Polymerization in DMF Solution (**G**). The required amounts of monomer and AIBN (0.5 wt % to the monomer) were dissolved in DMF in a Schlenk tube. The solution was thoroughly deoxygenated by several freeze-pump-thaw cycles and then stirred at 60 ^{o}C for the designed time. After cooling to r.t., the polymer was dissolved in DCM and purified by silica gel column chromatography with DCM as eluent.

General Procedure for Polymerization in Bulk (**H**). The required amounts of monomer and AIBN (0.5 wt % to the monomer) were added into a Schlenk tube. The mixture was thoroughly deoxygenated by several freeze-pump-thaw cycles and then stirred at 60 ^{o}C for the designed time. The purification of the polymer followed the same process as in procedure **G**.

Methyl 3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzoate (**2a**). According to general procedure A, from methyl gallate (8.4 g, 45.6 mmol), Me-DEG-Ts (50.0 g, 182.3 mmol), KI (5.8 g, 36.5 mmol), K_2CO_3 (63.0 g, 456.0 mmol) and DMF (200 mL). **2a** was yielded as a colorless oil (19.5 g, 87%). ^{1}H NMR (CD_2Cl_2): δ 3.32–3.35 (m, 9H, CH_3), 3.48–3.55 (m, 6H, CH_2), 3.62–3.69 (m, 6H, CH_2), 3.74–3.76 (m, 2H, CH_2), 3.82–3.86 (m, 7H, CH_2 + CH_3), 4.16–4.18 (m, 6H, CH_2), 7.28 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 52.12, 58.75, 58.78, 68.93, 69.68, 70.47, 70.71, 70.75, 72.07, 72.11, 72.58, 108.65, 125.20, 142.46, 152.46, 166.54. MS: *m*/*z* calcd, 490.24; found, 513.2315 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{23}H_{38}O_{11}$, 490.55: C, 56.32; H, 7.81. Found: C, 56.13; H, 7.85.

3,4,5-Tris(2-(2-methoxyethoxy)ethoxy)benzyl alcohol (**2b**). According to general procedure B, from LAH (0.95 g, 25.1 mmol), **2a** (8.2 g, 16.7 mmol), dry THF (100 mL), water (6 mL), 10% NaOH (15 mL), and water (20 mL). **2b** was yielded as a colorless oil (7 g, 91%). ^{1}H NMR (CD_2Cl_2): δ 3.35 (s, 9H, CH_3), 3.52-3.55 (m, 6H, CH_2), 3.64-3.68 (m, 6H, CH_2), 3.75 (t, 2H, CH_2), 3.82 (t, 4H, CH_2), 4.10 (t, 2H, CH_2), 4.14 (t, 4H, CH_2), 4.56 (s, 2H, CH_2), 6.62 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 58.76, 65.11, 68.82, 69.88, 70.42, 70.68, 72.08, 72.12, 72.44, 105.99, 137.13, 137.47, 152.77. MS: *m*/*z* calcd, 462.25; found, 485.2363 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{22}H_{38}O_{10}$, 462.54: C, 57.13; H, 8.28. Found: C, 56.53; H, 8.31.

3,4,5-Tris(2-(2-methoxyethoxy)ethoxy)benzyl methacrylate (**2c**). According to general procedure C, from MAC (0.90 g, 8.65 mmol), **2b** (2.00 g, 4.32 mmol), TEA (2.19 g, 21.60 mmol), DMAP (0.1 g) and dry DCM (50 mL). **2c** was yielded as a colorless oil (2.10 g, 92%). ^{1}H NMR (CD_2Cl_2): δ 1.96 (s, 3H,CH_3), 3.35 (s, 9H, CH_3), 3.48-3.54 (m, 6H, CH_2), 3.64-3.68 (m, 6H, CH_2), 3.75 (t, 2H, CH_2), 3.83 (t, 4H, CH_2), 4.10-4.15 (m, 6H, CH_2), 5.08 (s, 2H, CH_2), 5.60 (s, 1H, CH_2), 6.13 (s, 1H, CH_2), 6.63 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ = 18.23, 58.76, 58.78, 66.46, 68.91, 69.78, 70.44, 70.69, 70.74, 72.08, 72.12, 72.46, 107.42, 125.53, 131.82, 136.57, 138.19, 152.79, 167.10. MS: *m*/*z* calcd 530.27; found

553.2627 [M + Na]$^+$. Elemental analysis (%) calcd for $C_{26}H_{42}O_{11}$, 530.61: C, 58.85; H, 7.98. Found: C, 58.26; H, 7.71.

Methyl 3,4,5-Tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzoate (**2d**). According to general procedure A, from methyl gallate (8.86 g, 48.13 mmol), Et-TEG-Ts (64.00 g, 192.53 mmol), KI (6.16 g, 38.50 mmol), K_2CO_3 (66.52 g, 481.30 mmol) and dry DMF (250 mL). **2d** was yielded as a colorless oil (26.50 g, 83%). ^{1}H NMR (CD_2Cl_2): δ 1.18–1.19 (m, 9H, CH_3), 3.46–3.51 (m, 6H, CH_2), 3.53–3.71 (m, 24H, CH_2), 3.77 (t, 2H, CH_2), 3.85–3.87 (m, 7H, CH_2 + CH_3), 4.19–4.23 (m, 6H, CH_2), 7.30 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.14, 52.12, 66.55, 68.93, 69.71, 69.96, 70.63, 70.68, 70.75, 70.78, 70.90, 72.56, 108.68, 125.20, 142.49, 152.47, 166.54. MS: *m*/*z* calcd, 664.37; found, 687.3572 [M + Na]$^+$. Elemental analysis (%) calcd for $C_{32}H_{56}O_{14,}$ 664.79: C, 57.82; H, 8.49. Found: C, 57.35; H, 8.55.

3,4,5-Tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl alcohol (**2e**). According to general procedure B, from LAH (1.28 g, 33.70 mmol), **2d** (11.20 g, 16.85 mmol), dry THF (150 mL), water (8 mL), 10% NaOH (20 mL) and water (30 mL). **2e** was yielded as a colorless oil (9.9 g, 92%). ^{1}H NMR (CD_2Cl_2): δ 1.16–1.20 (m, 9H, CH_3), 3.47–3.70 (m, 30H, CH_2), 3.76 (t, 2H, CH_2), 3.83 (t, 4H, CH_2), 4.11 (t, 2H, CH_2), 4.16 (t, 4H, CH_2), 4.56 (s, 2H, CH_2), 6.63 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.13, 65.13, 66.56, 68.86, 69.91, 69.96, 70.58, 70.70, 70.74, 70.86, 72.40, 106.15, 137.13, 137.59, 152.80. MS: *m*/*z* calcd, 636.37; found, 659.3621 [M + Na]$^+$. Elemental analysis (%) calcd for $C_{31}H_{56}O_{13,}$ 636.78: C, 58.47; H, 8.86. Found: C, 58.22; H, 8.91.

3,4,5-Tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl methacrylate (**2f**). According to general procedure C, from MAC (0.79 g, 7.54 mmol), **2e** (2.40 g, 3.77 mmol), TEA (1.91 g, 18.85 mmol), DMAP (0.15 g) and dry DCM (50 mL). **2f** was yielded as a colorless oil (2.44 g, 92%). ^{1}H NMR (CD_2Cl_2): δ 1.16-1.19 (m, 9H, CH_3), 1.96 (s, 3H, CH_3), 3.47–3.70 (m, 30H, CH_2), 3.76 (t, 2H, CH_2), 3.84 (t, 4H, CH_2), 4.11-4.16 (m, 6H, CH_2), 5.08 (s, 2H, CH_2), 5.60 (s, 1H, CH_2), 6.13 (s, 1H, CH_2), 6.63 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.15, 18.25, 66.47, 66.55, 68.89, 69.80, 69.97, 70.59, 70.68, 70.70, 70.77, 70.89, 72.46, 107.42, 125.54, 131.82, 136.56, 138.20, 152.79, 167.09. MS: *m*/*z* calcd 704.40; found 727.3862 [M + Na]$^+$. Elemental analysis (%) calcd for $C_{35}H_{60}O_{14}$, 704.85: C, 59.64; H, 8.58. Found: C, 59.87; H, 8.61.

3,4,5-tris(2-(2-(2-(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzoic acid (**3a**). According to general procedure D, from **2g** (3.42 g, 3.28 mmol), dry THF (30 mL), **2b** (5.00 g, 10.81 mmol), KI (1.57 g, 9.84 mmol), 15-crown-5 (0.72 g, 3.28 mmol), NaH (0.78 g, 32.5 mmol) and dry THF (60 mL). **3a** was yieled as a yellow oil (3.00 g, 48%). ^{1}H NMR (CD_2Cl_2): δ 3.35 (s, 27H, CH_3), 3.53–3.83 (m, 84H, CH_2), 4.09–4.17 (m, 24H, CH_2), 4.42 (s, 6H, CH_2), 6.58 (s, 6H, CH), 7.31 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 58.76, 68.79, 68.89, 69.69, 69.83, 70.40, 70.68, 70.74, 70.88, 72.07, 72.12, 72.40, 72.54, 73.19, 106.83, 109.00, 109.07, 125.11, 134.20, 137.59, 142.59, 152.40, 152.54, 152.69, 167.89. MS: *m*/*z* calcd 1898.97; found 1921.9584 [M + Na]$^+$.

Elemental analysis (%) calcd for $C_{91}H_{150}O_{41}$, 1900.16: C57.52; H, 7.96. Found: C, 57.09; H, 7.83.

3,4,5-tris(2-(2-(2-(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl alcohol (**3b**). According to general procedure E, from *N*-Methylmorpholine (0.45 g, 4.45 mmol), ethyl chloroformate (0.46 g, 4.2 mmol), **3a** (1.6 g, 0.84 mmol), dry THF (50 mL) and $NaBH_4$ (0.25 g, 6.61 mmol). **3b** was yielded as a colorless oil (1.3 g, 82%). ^{1}H NMR (CD_2Cl_2): δ 3.30–3.34 (m, 27H, CH_3), 3.52–3.81 (m, 84H, CH_2), 4.08–4.13 (m, 24H, CH_2), 4.43 (s, 6H, CH_2), 4.53 (s, 2H, CH_2), 6.59 (s, 6H, CH), 6.61 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 58.76, 58.78, 64.93, 68.82, 69.66, 69.82, 69.89, 70.43, 70.59, 70.68, 70.72, 70.85, 72.08, 72.13, 72.43, 73.18, 106.01, 106.79, 134.19, 137.61, 152.71, 152.75. MS: *m*/*z* calcd 1884.99; found 1907.9714 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{91}H_{152}O_{40}$, 1886.18: C57.95; H, 8.12. Found: C, 57.68; H, 8.03.

3,4,5-tris(2-(2-(2-(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl methacrylate (**3c**). According to general procedure F, from MAC (0.33 g, 3.18 mmol), **3b** (1.2 g, 0.64 mmol), TEA (0.32 g, 3.18 mmol), DMAP (0.15 g) and dry DCM (40 mL). **3c** was yielded as a colorless oil (1.05 g, 85%). ^{1}H NMR (CD_2Cl_2): δ 3.30–3.35 (m, 27H, CH_3), 3.49–3.83 (m, 84H, CH_2), 4.08–4.15 (m, 24H, CH_2), 4.43 (s, 6H, CH_2), 5.07 (s, 2H, CH_2), 5.59 (s, 1H, CH_2), 6.12 (s, 1H, CH_2), 6.59 (s, 6H, CH), 6.63 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 18.51, 59.02, 59.04, 66.70, 69.00, 69.09, 69.15, 69.92, 70.08, 70.69, 70.85, 70.95, 70.98, 71.14, 72.34, 72.39, 72.69, 73.45, 106.90, 107.06, 107.64, 107.74, 125.80, 132.11, 134.43, 136.81, 137.89, 138.48, 152.98, 153.05, 153.11, 153.17, 167.32. MS: *m*/*z* 1953.01 calcd; found 1976.005 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{95}H_{156}O_{41}$, 1954.25: C58.39; H, 8.05. Found: C, 58.12; H, 7.93.

3,4,5-Tris(2-(2-(2-(3,4,5-tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzoic acid (**3d**). According to general procedure D, from **2g** (4.05 g, 3.88 mmol), dry THF (30 mL), **2e** (8.15 g, 12.80 mmol), KI (1.86 g, 11.60 mmol), 15-crown-5 (0.85 g, 3.88 mmol), NaH (0.92 g, 38.40 mmol) and dry THF (100 mL). **3d** was yielded as a yellow oil (4.7 g, 50 %). ^{1}H NMR (CD_2Cl_2): δ 1.16–1.19 (m, 27H, CH_3), 3.47–3.51 (m, 18H, CH_2), 3.55–3.70 (m, 96H, CH_2), 3.75–3.77 (m, 8H, CH_2), 3.82–3.84 (m, 16H, CH_2), 4.10 (t, 6H, CH_2), 4.13–4.18 (m, 16H, CH_2), 4.20 (t, 2H, CH_2), 4.42 (s, 6H, CH_2), 6.59 (s, 6H, CH), 7.31 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.13, 66.56, 68.76, 68.86, 69.65,69.69, 69.74, 69.83, 69.94, 70.54, 70.59, 70.66, 70.72, 70.83, 70.88, 71.07, 72.39, 72.52, 73.18, 106.82, 108.98, 125.97, 134.24, 137.55, 142.25, 152.33, 152.67, 167.71. MS: *m*/*z* calcd, 2421.34; found, 2444.335 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{118}H_{204}O_{50}$, 2422.88: C, 58.50; H, 8.49. Found: C, 57.39; H, 8.27.

3,4,5-Tris(2-(2-(2-(3,4,5-tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl alcohol (**3e**). According to general procedure E, from *N*-Methylmorpholine (0.31 g, 3.06 mmol), ethyl

chloroformate (0.34 g, 3.13 mmol), **3d** (1.50 g, 0.62 mmol), dry THF (30 mL) and $NaBH_4$ (0.19 g, 4.96 mmol). **3e** was yielded as a colorless oil (1.2 g, 81%). ^{1}H NMR (CD_2Cl_2): δ 1.16–1.19 (m, 27H, CH_3), 3.46–3.70 (m, 114H, CH_2), 3.76 (t, 8H, CH_2), 3.82–3.83 (m, 16H, CH_2), 4.09–4.14 (m, 24H, CH_2), 4.44 (s, 6H, CH_2), 4.54 (s, 2H, CH_2), 6.59 (s, 6H, CH), 6.61 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.15, 64.88, 66.55, 68.79, 69.65, 69.83, 69.89, 69.96, 70.57, 70.67, 70.70, 70.75, 70.76, 70.86, 72.42, 73.18, 105.99, 106.79, 134.19, 137.41, 137.60, 152.71, 152.73. MS: *m*/*z* calcd, 2407.36; found, 2430.355 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{118}H_{206}O_{49}$, 2408.90: C, 58.84; H, 8.62. Found: C, 58.28; H, 8.50.

3,4,5-Tris(2-(2-(2-(3,4,5-tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl methacrylate (**3f**). According to general procedure F, from MAC (0.22 g, 2.08 mmol), **3e** (1.00 g, 0.42 mmol), TEA (0.21 g, 2.08 mmol), DMAP (0.15 g) and dry DCM (40 mL). **3f** was yielded as a colorless oil (0.85 g, 83%). ^{1}H NMR (CD_2Cl_2): δ 1.17–1.19 (m, 27H, CH_3), 1.95 (s, 3H, CH_3), 3.46–3.70 (m, 114H, CH_2), 3.76 (t, 8H, CH_2), 3.83 (t, 16H, CH_2), 4.09–4.15 (m, 24H , CH_2), 4.43 (s, 6H, CH_2), 5.07 (s, 2H, CH_2), 5.59 (s, 1H, CH_2), 6.12 (s, 1H, CH_2), 6.59 (s, 6H, CH), 6.64 (s, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.15, 18.26, 66.45, 66.54, 68.81, 68.87, 69.65, 69.81, 69.84, 69.97, 70.58, 70.68, 70.70, 70.75, 70.76, 70.87, 72.43, 73.20, 106.81, 107.48, 125.57, 131.86, 134.17, 136.54, 137.63, 138.20, 152.72, 152.78, 167.07. MS: *m*/*z* calcd 2475.39; found 2498.382 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{122}H_{210}O_{50,}$ 2476.97: C, 59.16; H, 8.55. Found: C, 58.34; H, 8.35.

Poly(3,4,5-Tris(2-(2-methoxyethoxy)ethoxy)benzyl methacrylate) [**PG1(MD)**]. According to general procedure G from **2c** (0.50 g, 0.94 mmol), AIBN (2.5 mg) and DMF (0.4 mL), polymerization for 4 h yielded **PG1(MD)** as colorless gel (0.14 g, 28%). ^{1}H NMR (CD_2Cl_2): δ 0.83–1.06 (m, 3H, CH_3), 1.90 (br, 2H, CH_2), 3.29–3.32 (m, 9H, CH_3), 3.47–3.49 (m, 6H, CH_2), 3.62 (br, 6H, CH_2), 3.74 (br, 6H, CH_2), 4.06 (br, 6H, CH_2), 4.81 (br, 2H, CH_2), 6.55 (br, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 58.72, 67.03, 68.84, 69.74, 70.41, 70.66, 70.80, 72.05, 72.11, 72.40, 72.48, 72.92, 107.16, 130.86, 130.96, 138.04, 152.77. The signals from the polymer backbone were so broad that they disappeared in the baseline. Elemental analysis (%) calcd for $(C_{26}H_{42}O_{11})_n$ $(530.61)_n$: C, 58.85; H, 7.98. Found: C, 62.74; H, 7.59.

Poly(3,4,5-Tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl methacrylate) [**PG1(ET)**]. According to general procedure H from **2f** (0.50 g, 0.71 mmol) and AIBN (2.5 mg), polymerization for 3 h yielded **PG1(ET)** as colorless gel (0.34 g, 68%). ^{1}H NMR (CD_2Cl_2): δ 0.86 (br, 2H, CH_3), 1.13–1.18 (m, 10H, CH_3 + CH_3), 3.43–3.64 (m, 30H, CH_3), 3.74 (br, 6H, CH_2), 4.06 (br, 6H, CH_2), 4.80 (br, 2H, CH_2), 6.53 (br, 2H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.22, 45.24, 66.49, 68.83, 69.75, 69.95, 70.55, 70.62, 70.70, 70.80, 72.48, 106.94, 130.83, 137.97, 152.76. The signals from the polymer backbone were so broad that they disappeared in the baseline. Elemental analysis (%) calcd for $(C_{35}H_{60}O_{14})_n$ $(704.85)_n$: C, 59.64; H, 8.58. Found: C, 58.88; H, 8.55.

Poly(3,4,5-tris(2-(2-(2-(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl methacrylate) [**PG2(MD)**]. According to general procedure H from **3c** (0.49 g, 0.25 mmol) and AIBN (2.5 mg), polymerization for 24 h yielded **PG2(MD)** as colorless gel (0.3 g, 61%). ^{1}H NMR (CD_2Cl_2): δ 3.27–3.32 (m, 27H, CH_3), 3.47–3.74 (m, 84H, CH_2), 4.04 (br, 24H, CH_2), 4.35 (br, 6H, CH_2), 6.52 (br, 8H, CH).^{13}C NMR (CD_2Cl_2): δ 58.72, 68.83, 69.65, 69.78, 70.38, 70.56, 70.65, 72.04, 72.09, 72.44, 73.08, 106.59, 134.15, 137.58, 152.70. The signals from the polymer backbone were so broad that they disappeared in the baseline. Elemental analysis (%) calcd for $(C_{95}H_{156}O_{41})_n$ $(1948.21)_n$: C, 58.57; H, 7.76. Found: C, 57.58; H, 8.01.

Poly(3,4,5-Tris(2-(2-(2-(3,4,5-tris(2-(2-(2 ethoxyethoxy)ethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl methacrylate) [**PG2(ET)**]. According to general procedure H from **3f** (0.76 g, 0.31 mmol) and AIBN (3.8 mg), polymerization for 24 h yielded **PG2(ET)** as colorless gel (0.47 g, 62%). ^{1}H NMR (CD_2Cl_2): δ 1.12–1.13 (m, 27H, CH_3), 3.43 –3.75 (m, 138H, CH_2), 4.05 (br, 24H, CH_2), 4.37 (br, 6H, CH_2), 6.52 (br, 8H, CH). ^{13}C NMR (CD_2Cl_2): δ 15.23, 66.47, 68.87, 69.68, 69.81, 69.95, 70.54, 70.63, 70.70, 70.82, 72.45, 73.11, 106.56, 134.13, 137.63, 152.71. The signals from the polymer backbone were so broad that they disappeared in the baseline. Elemental analysis (%) calcd for $(C_{122}H_{210}O_{50})_n$ $(2476.97)_n$: C, 59.16; H, 8.55. Found: C, 58.45; H, 8.43.

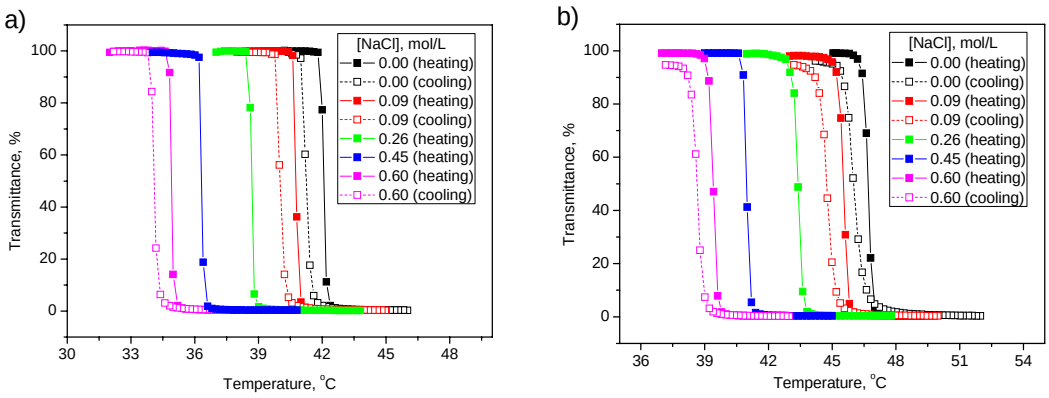

Figure S1. Plots of the temperature against the transmittance of PG1(MD) (a) and PG2(MD) (b) in 20 mM sodium phosphate buffer solution (0.25 wt%, PH 7.0) with the presence of different concentration of sodium chloride.

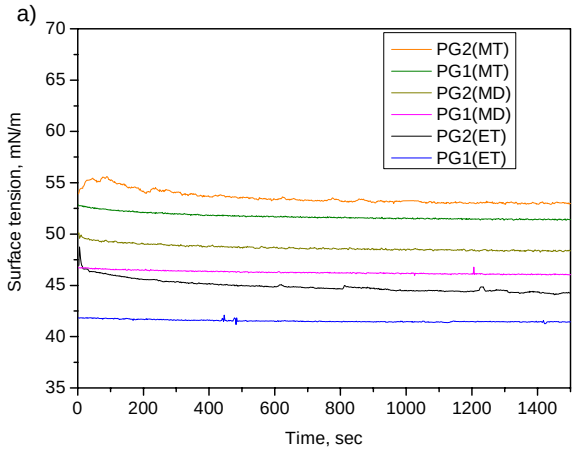

Figure S2. Surface tension *vs* time for pendant drops formed at air–water interface from 0.25 wt% aqueous solutions of **PG1(ET)**, **PG2(ET)**, **PG1(MD)**, **PG2(MD)**, **PG1(MT)** and **PG2(MT)**.

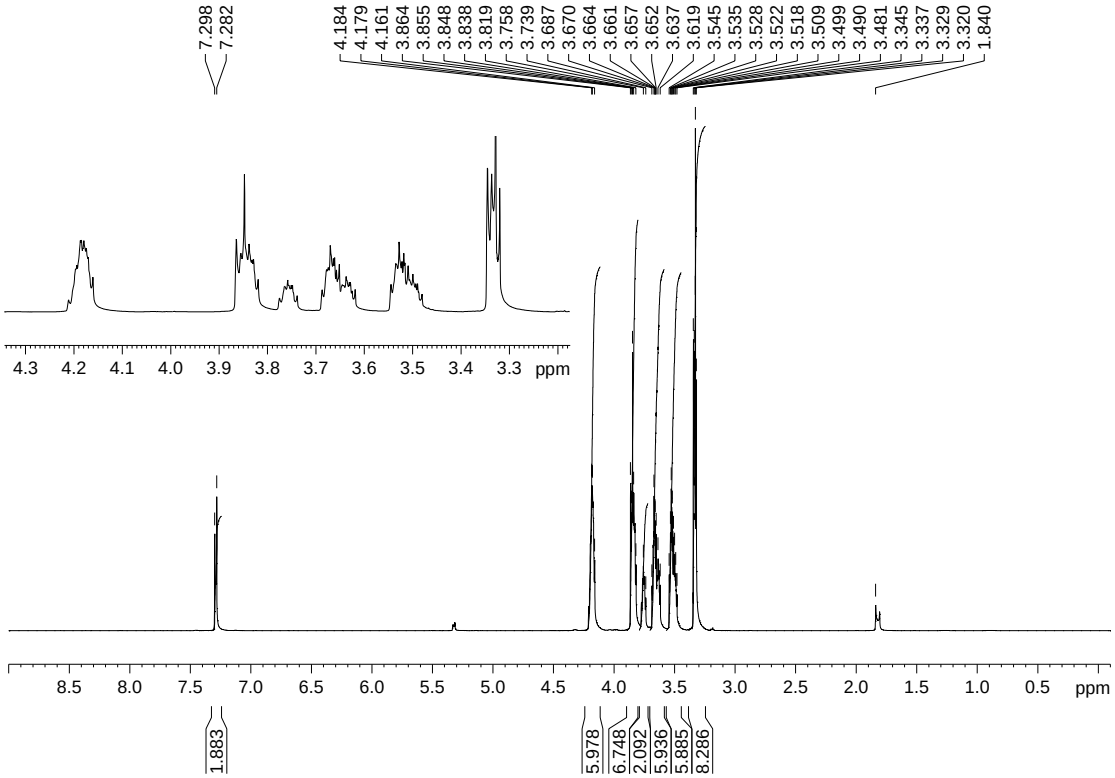

Figure S3. ^{1}H NMR spectrum of compound **2a** in CD_2Cl_2.

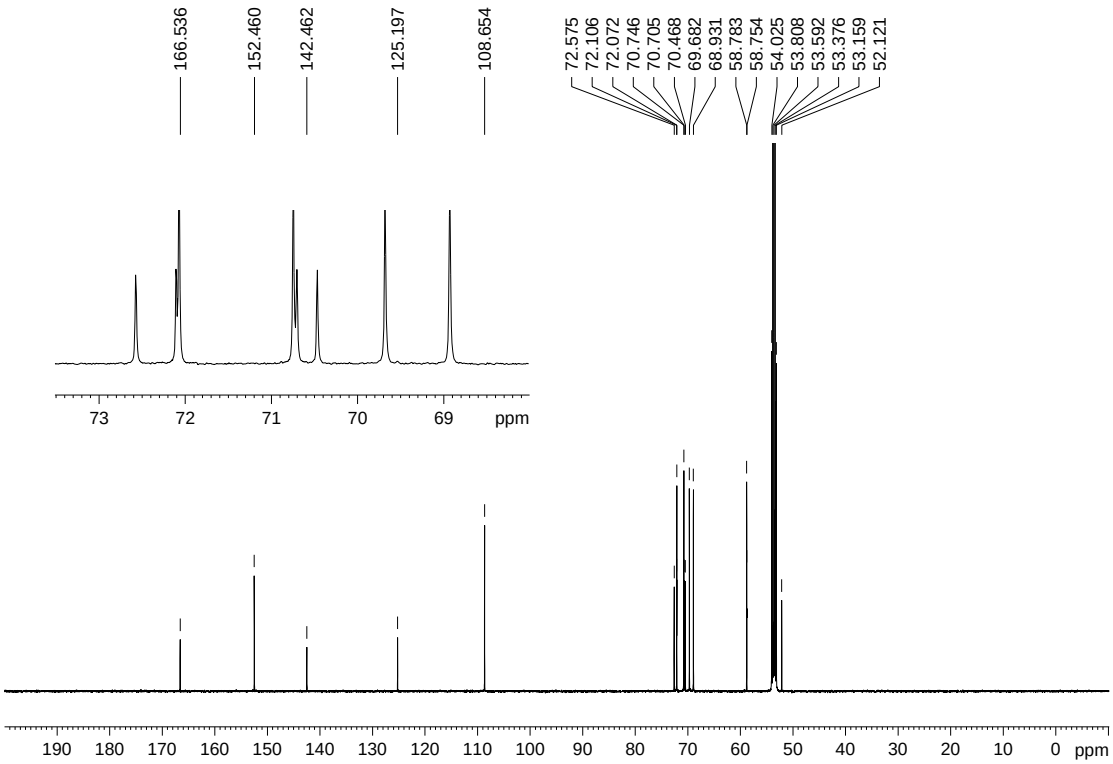

Figure S4. ^{13}C NMR spectrum of compound **2a** in CD_2Cl_2.

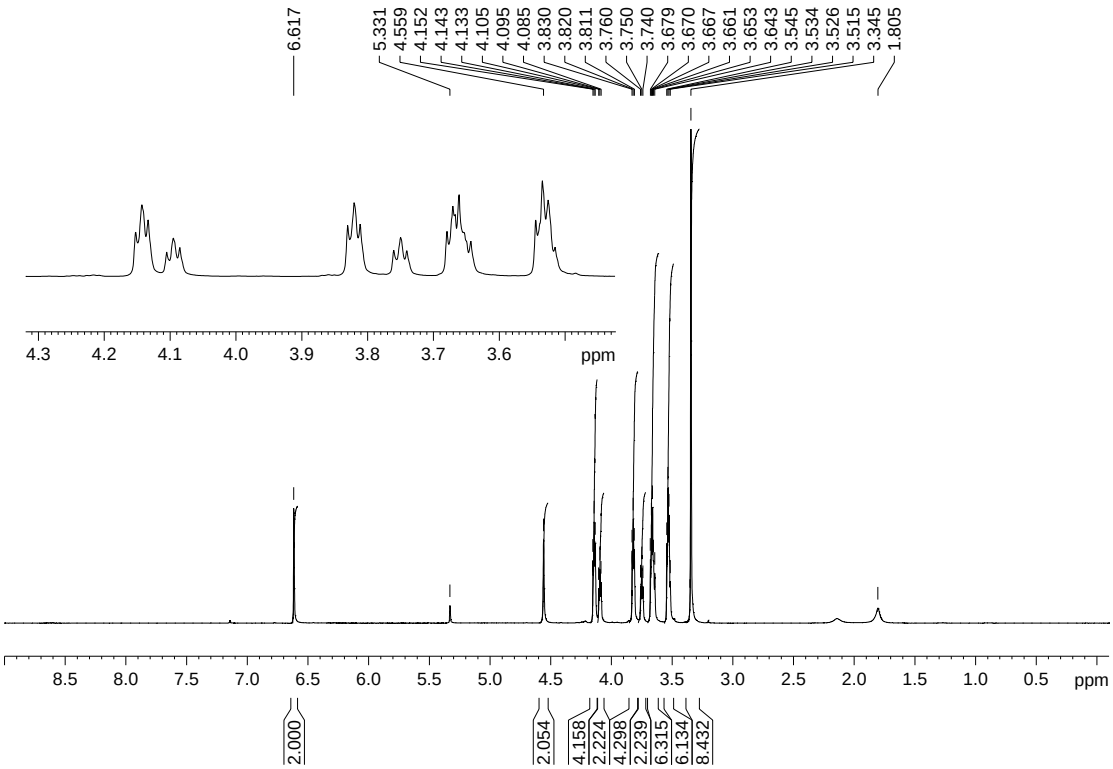

Figure S5. ^{1}H NMR spectrum of compound **2b** in CD_2Cl_2.

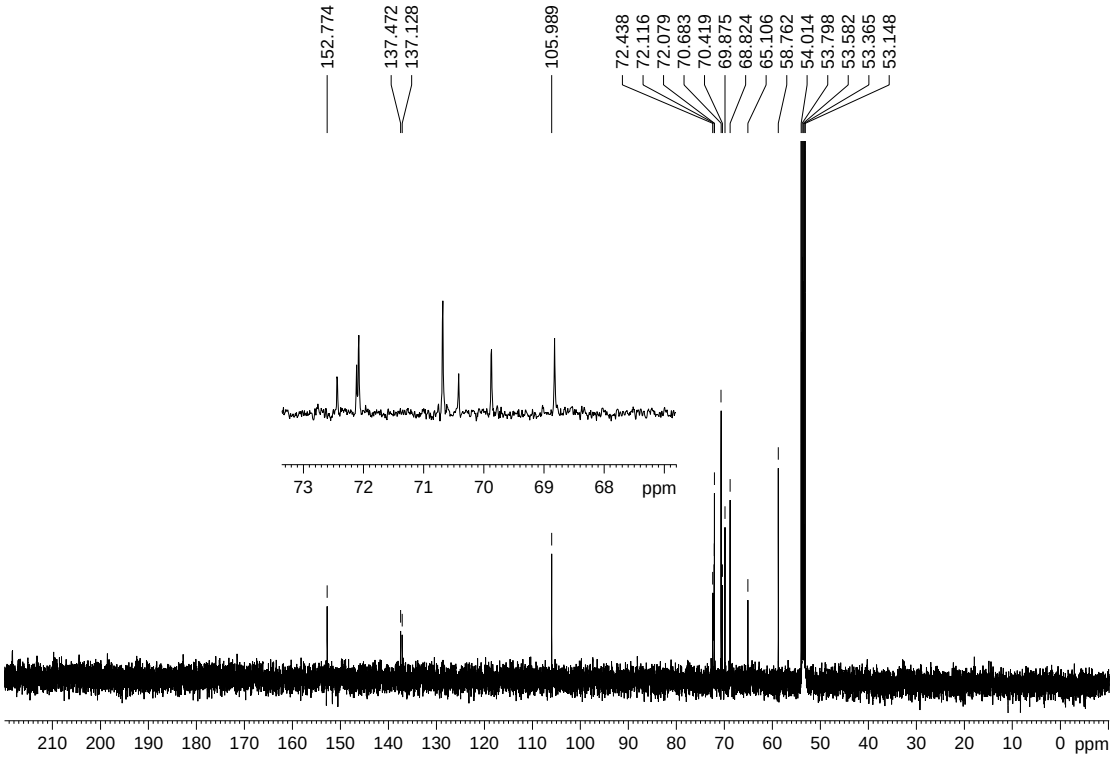

Figure S6. ^{13}C NMR spectrum of compound **2b** in CD_2Cl_2.

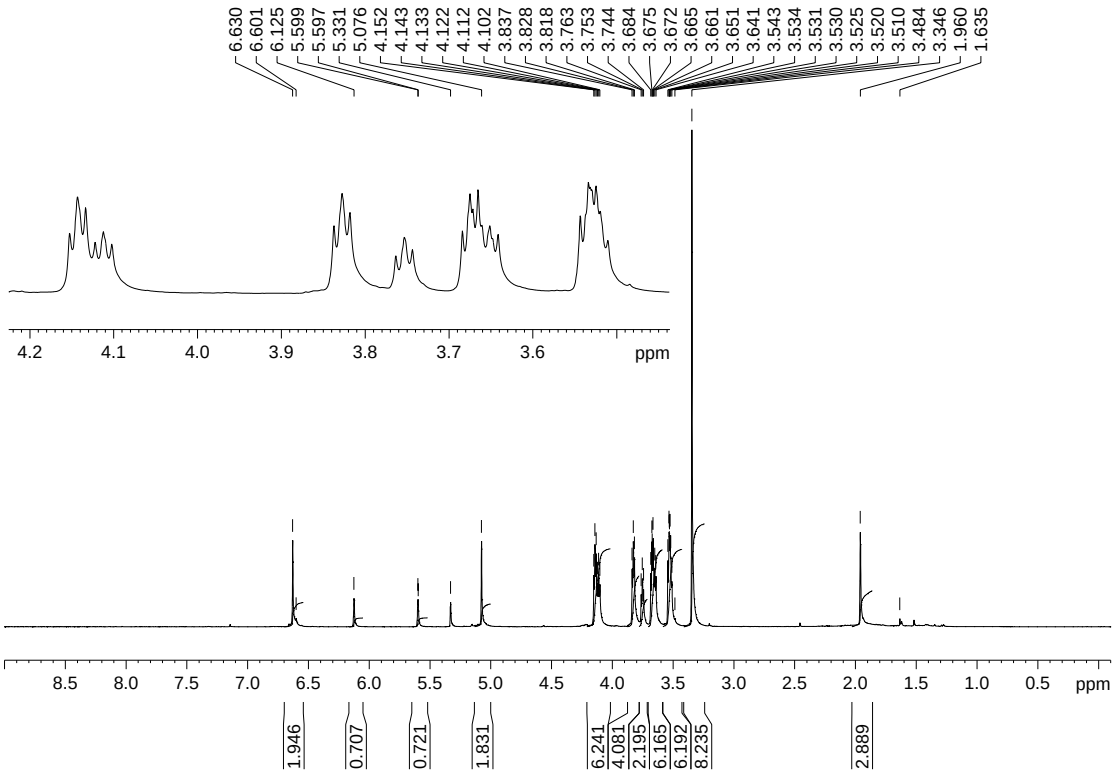

Figure S7. ^{1}H NMR spectrum of compound **2c** in CD_2Cl_2.

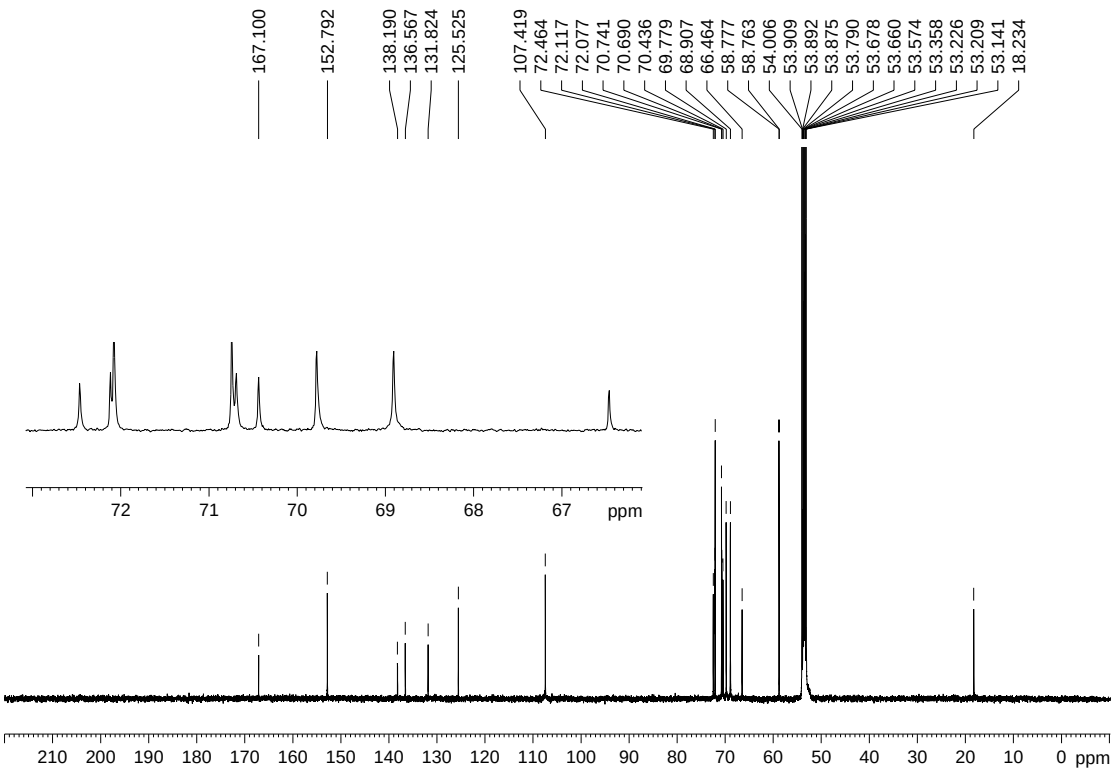

Figure S8. ^{13}C NMR spectrum of compound **2c** in CD_2Cl_2.

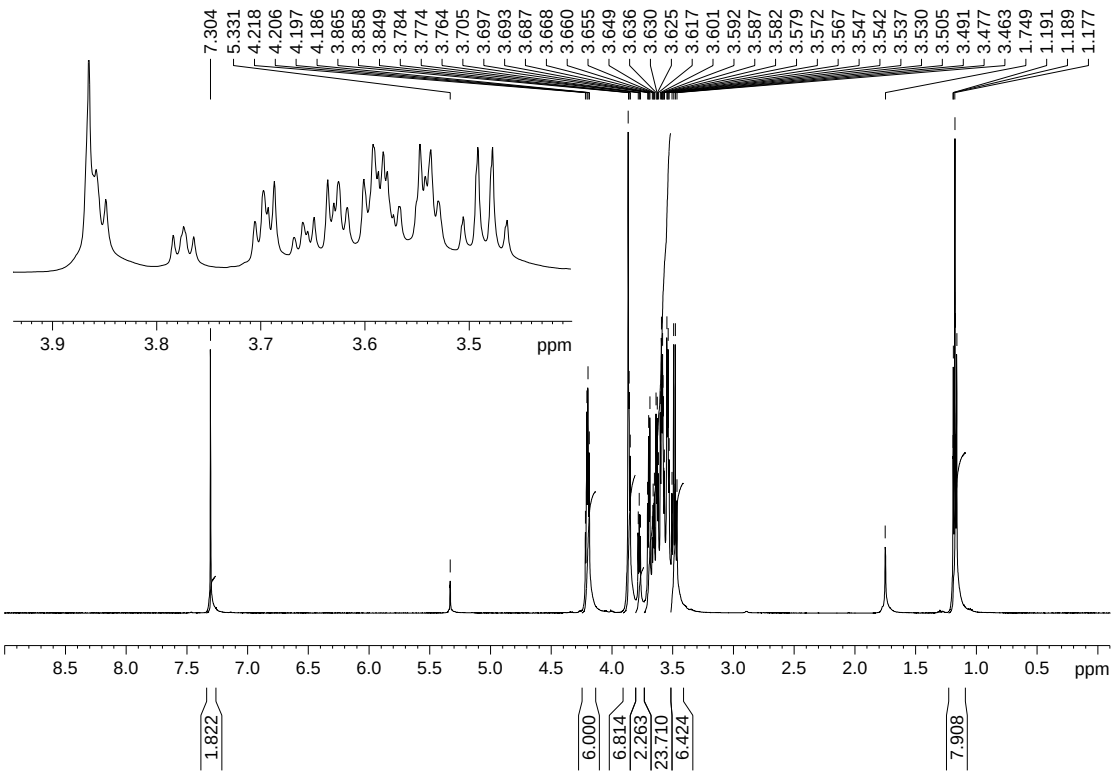

Figure S9. ^{1}H NMR spectrum of compound **2d** in CD_2Cl_2.

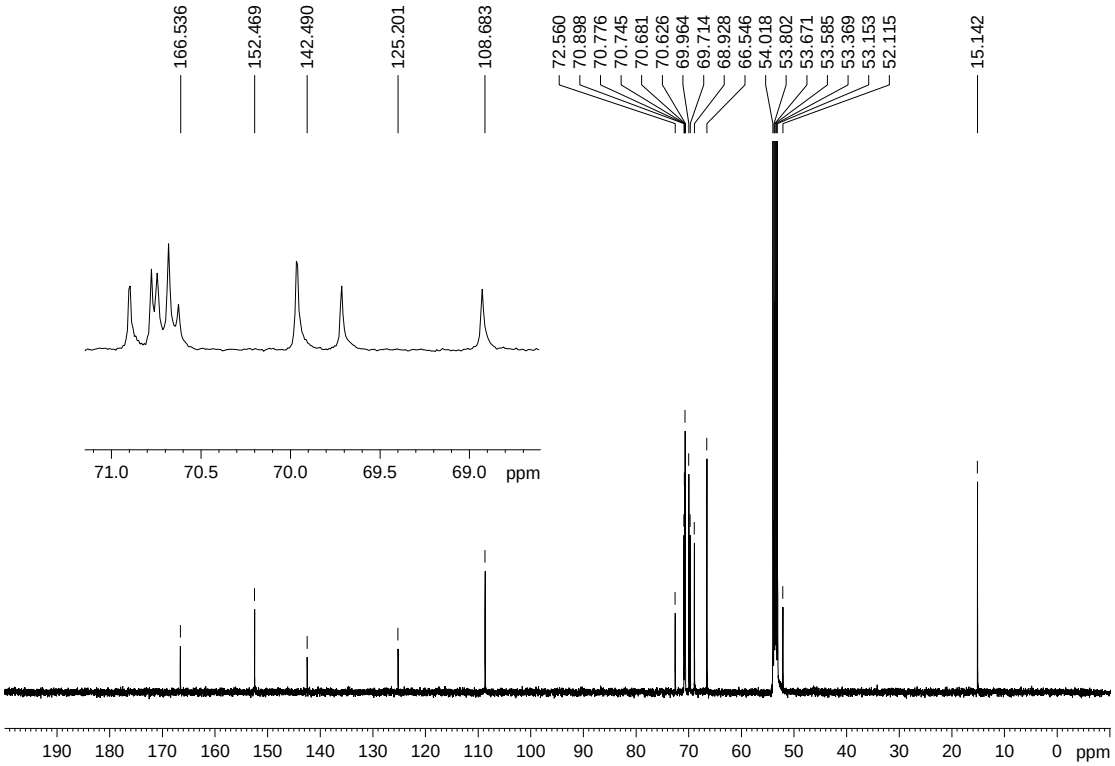

Figure S10. ^{13}C NMR spectrum of compound **2d** in CD_2Cl_2.

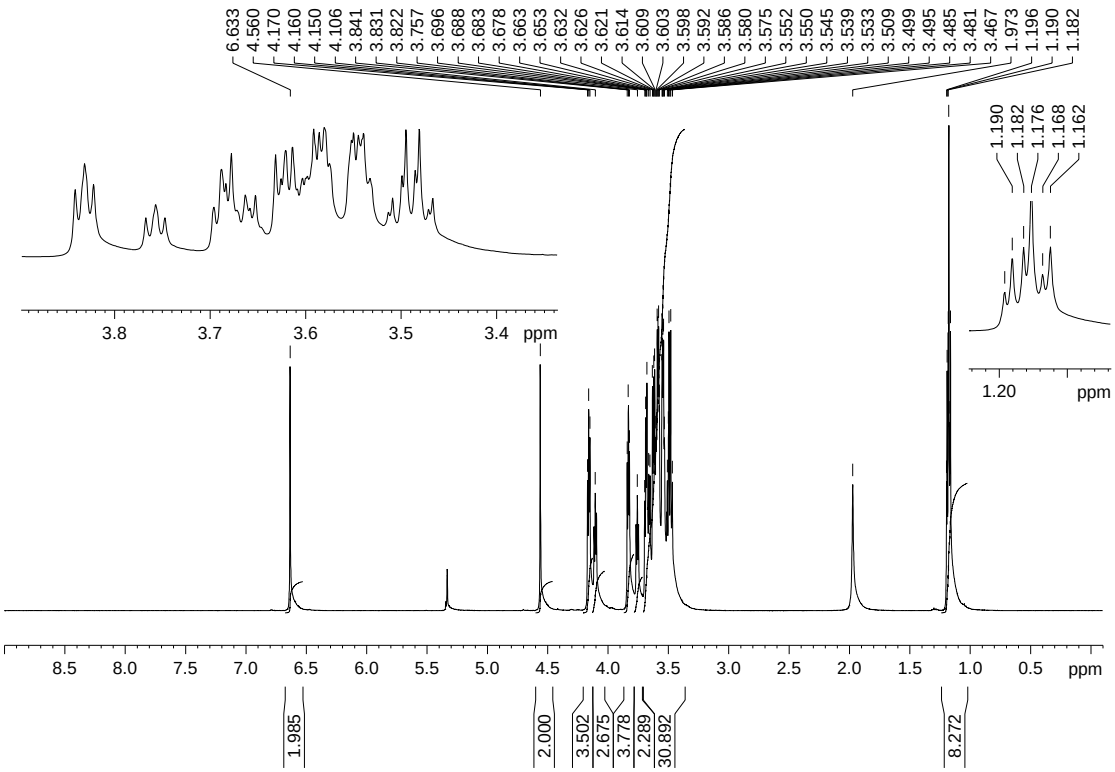

Figure S11. ^{1}H NMR spectrum of compound **2e** in CD_2Cl_2.

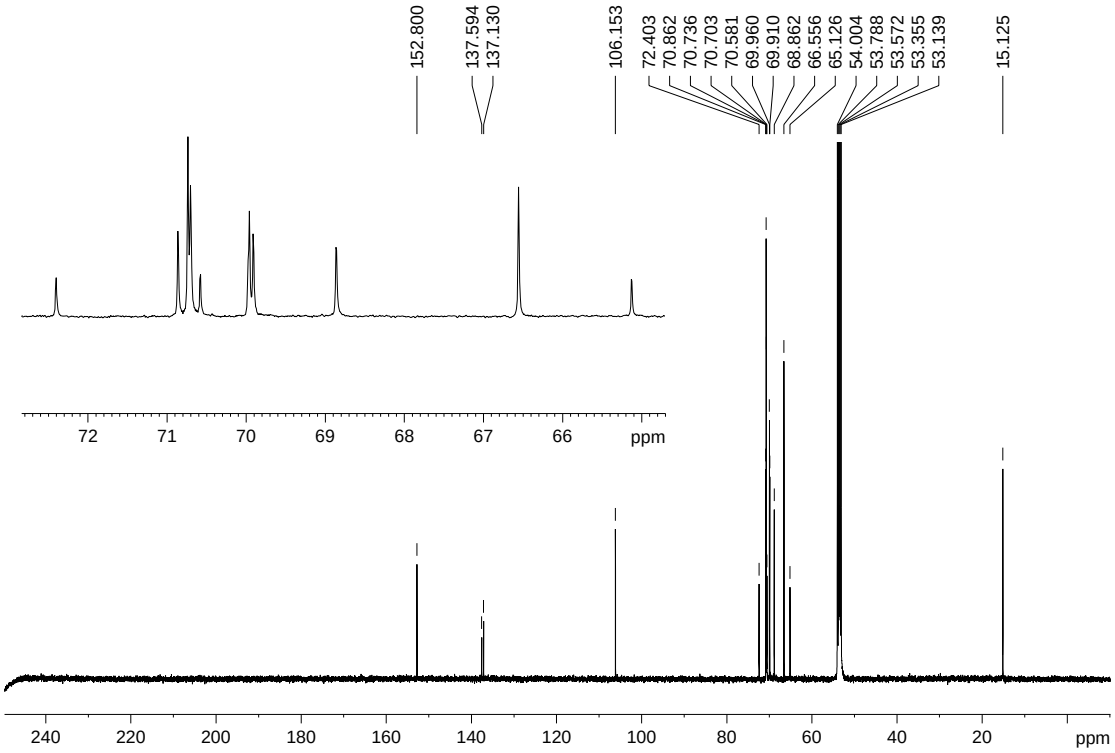

Figure S12. ^{13}C NMR spectrum of compound **2e** in CD_2Cl_2.

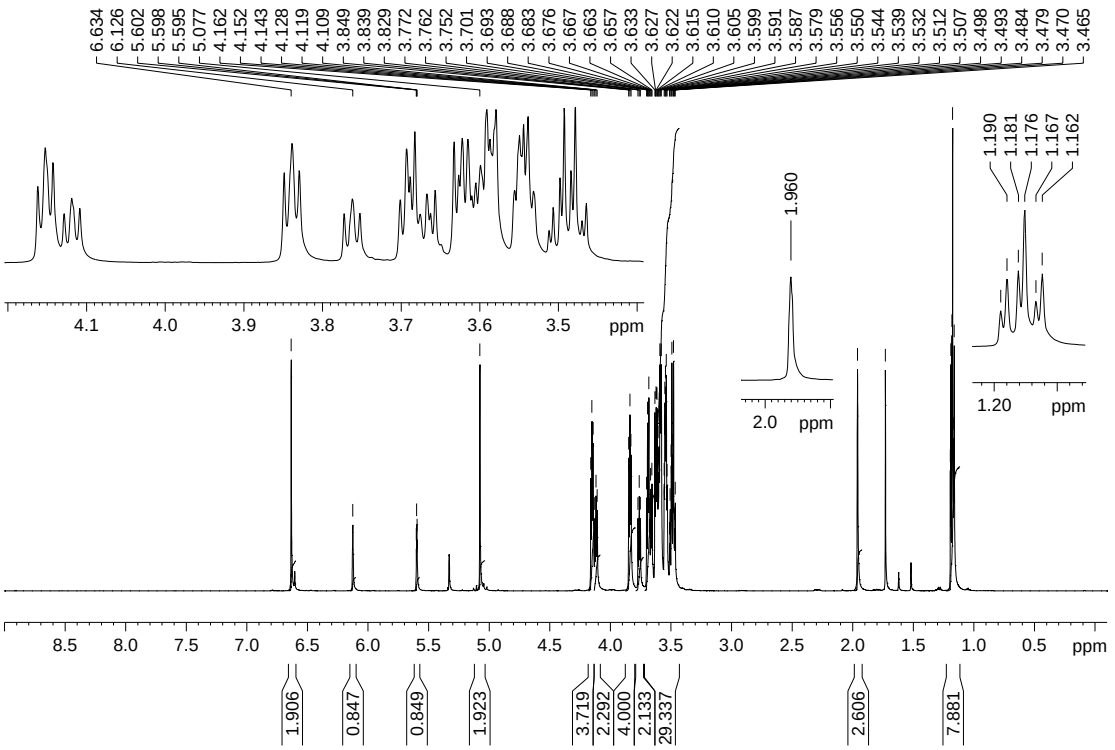

Figure S13. ^{1}H NMR spectrum of compound **2f** in CD_2Cl_2.

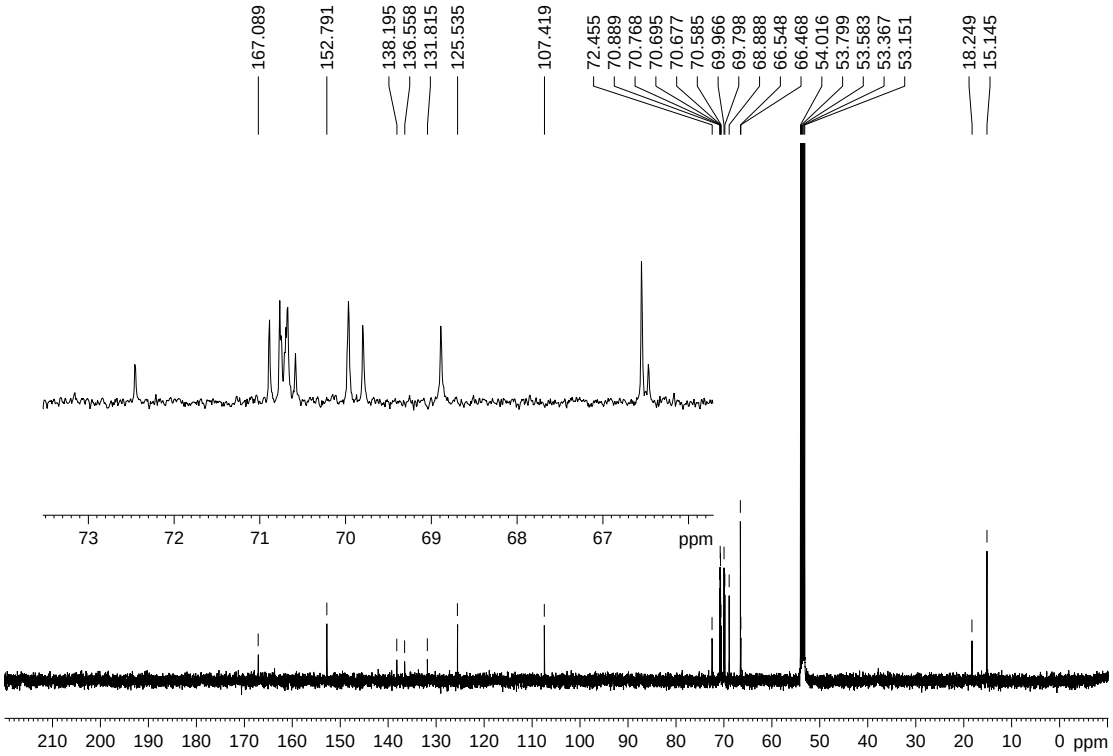

Figure S14. ^{13}C NMR spectrum of compound **2f** in CD_2Cl_2.

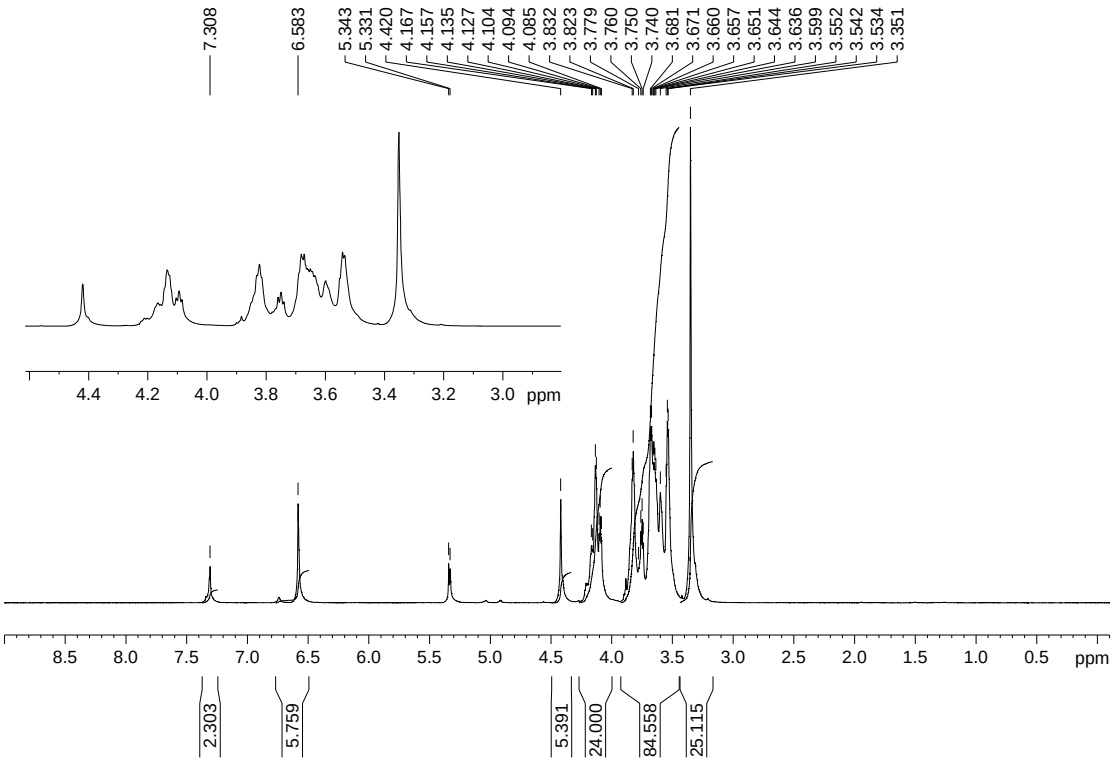

Figure S15. ^{1}H NMR spectrum of compound **3a** in CD_2Cl_2.

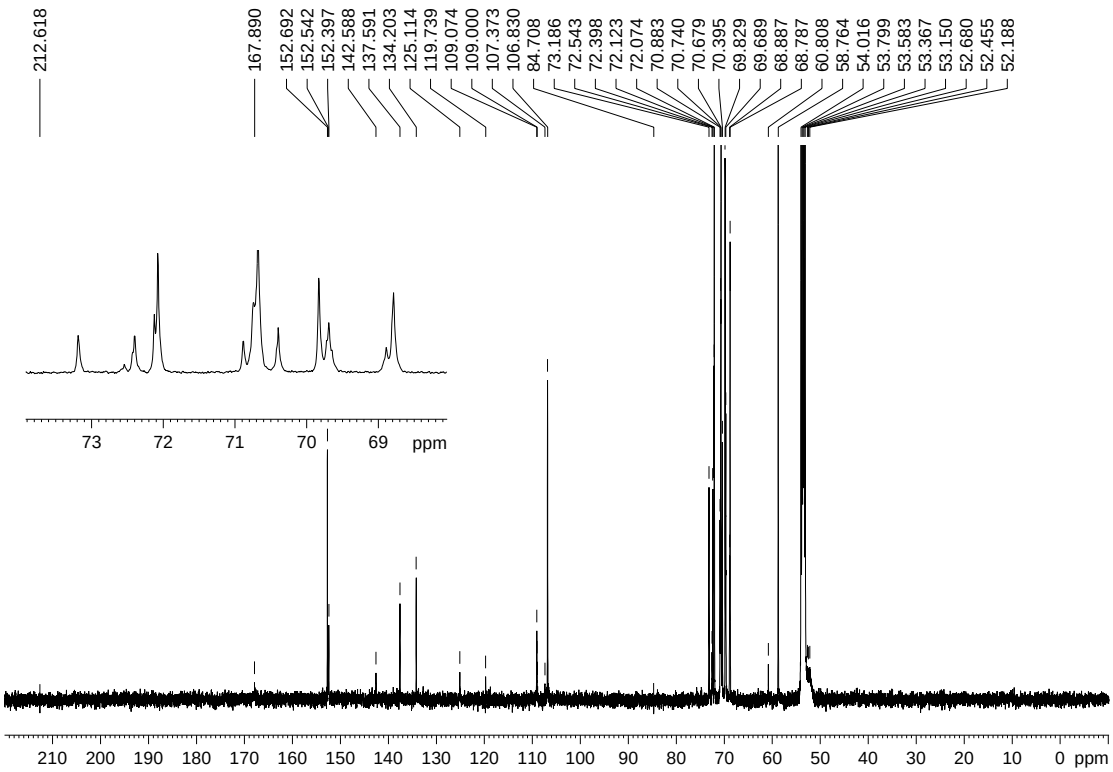

Figure S16. ^{13}C NMR spectrum of compound **3a** in CD_2Cl_2.

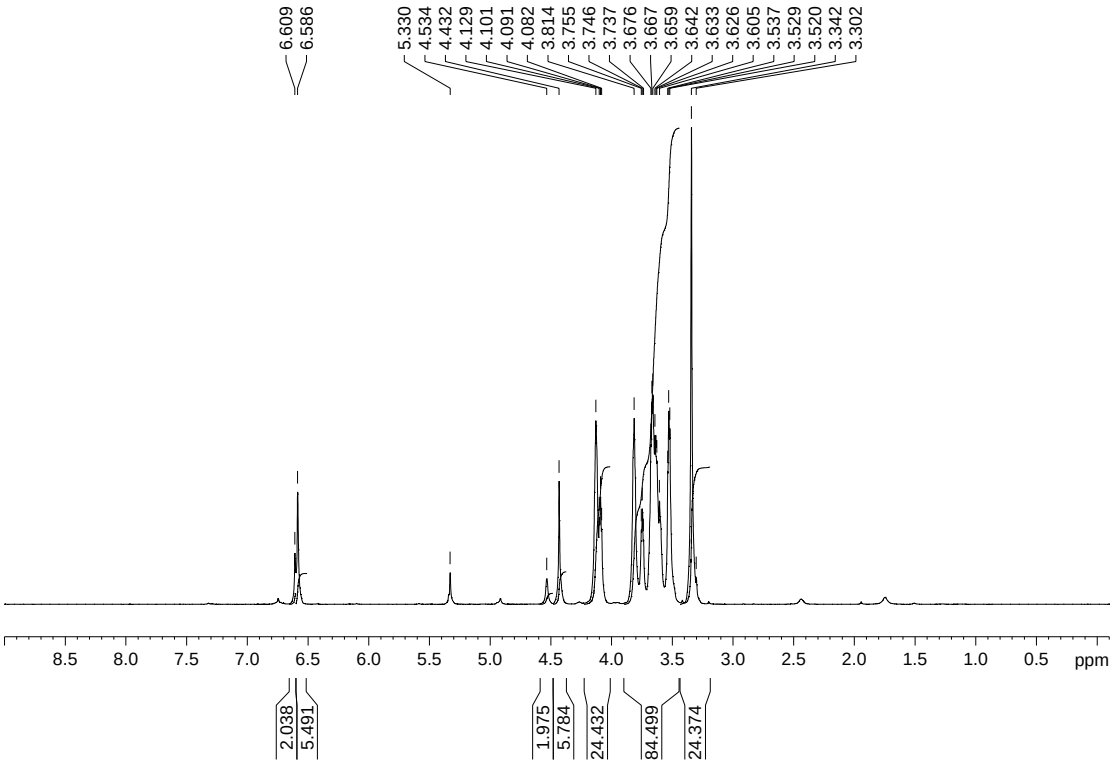

Figure S17. ^{1}H NMR spectrum of compound **3b** in CD_2Cl_2.

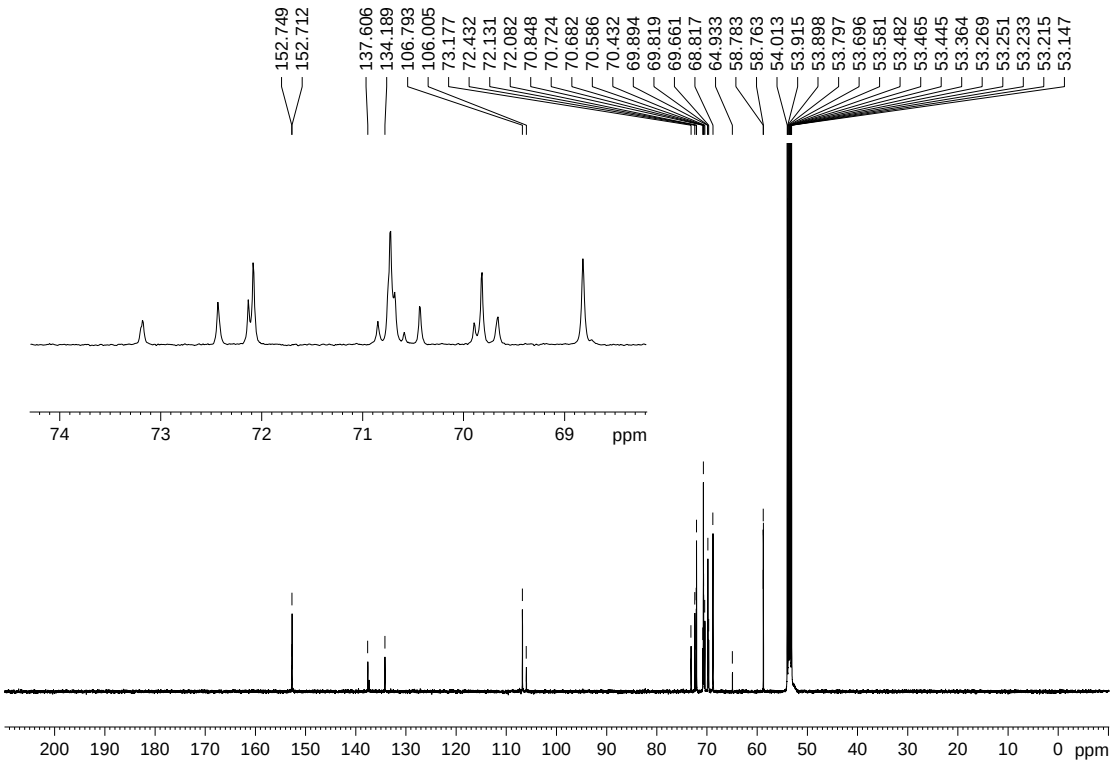

Figure S18. ^{13}C NMR spectrum of compound **3b** in CD_2Cl_2.

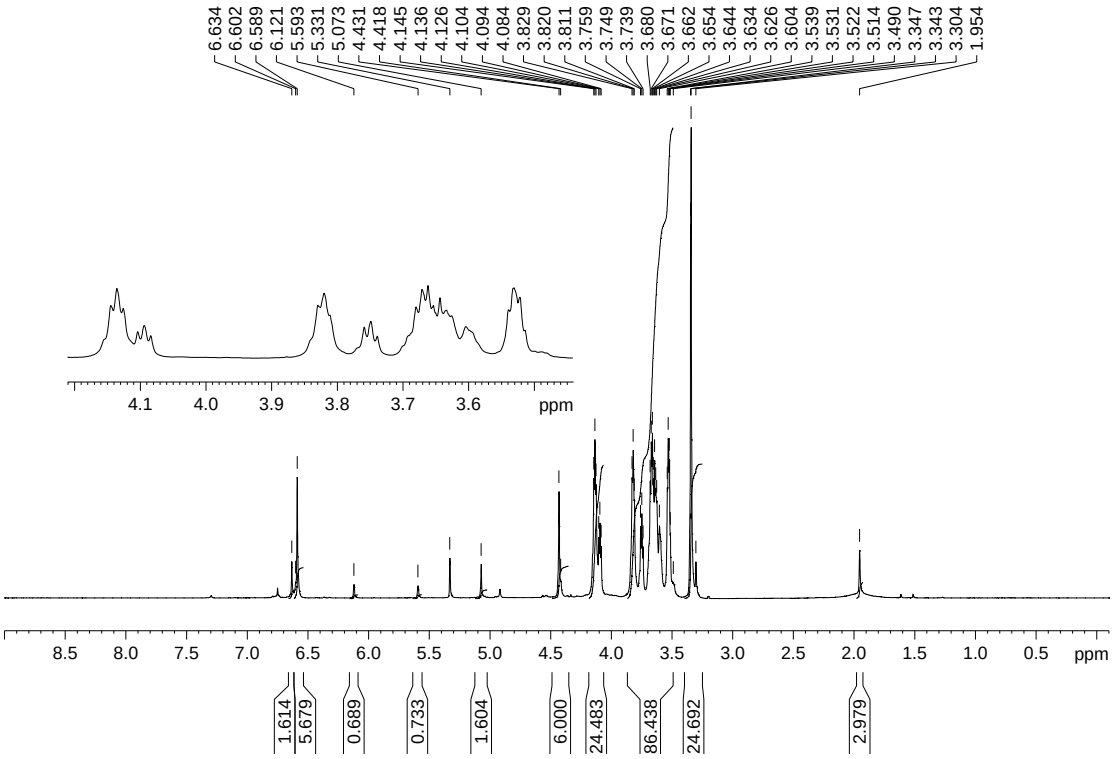

Figure S19. ^{1}H NMR spectrum of compound **3c** in CD_2Cl_2.

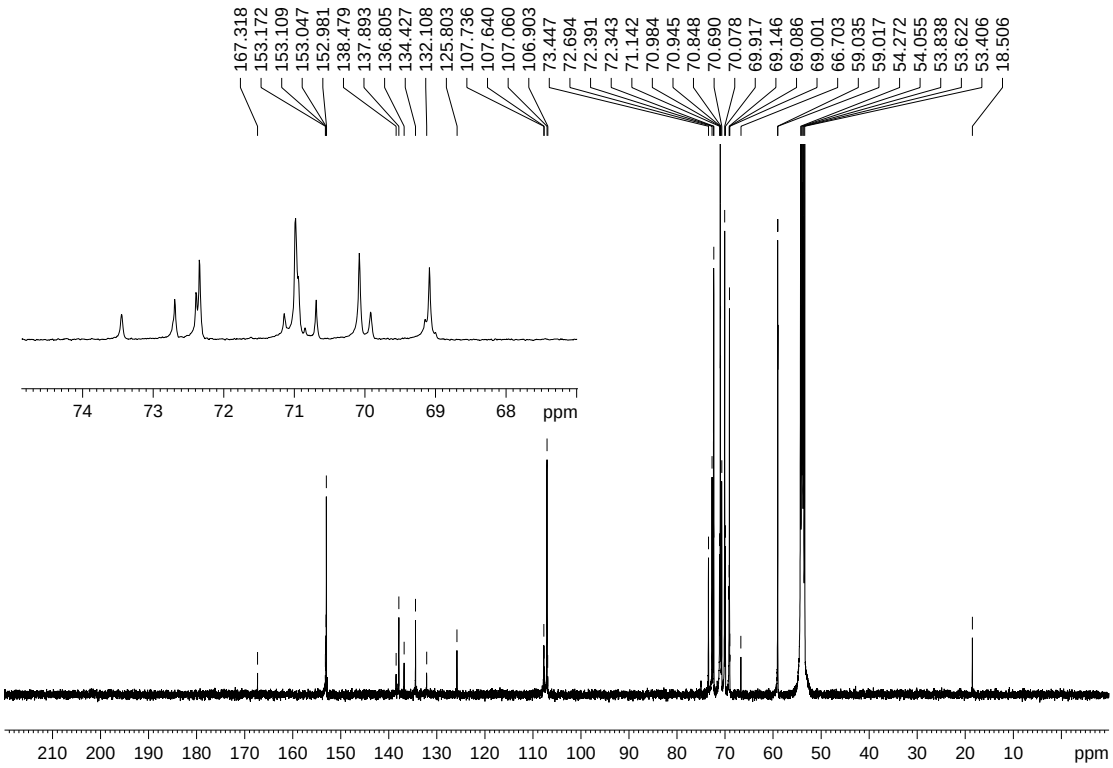

Figure S20. ^{13}C NMR spectrum of compound **3c** in CD_2Cl_2.

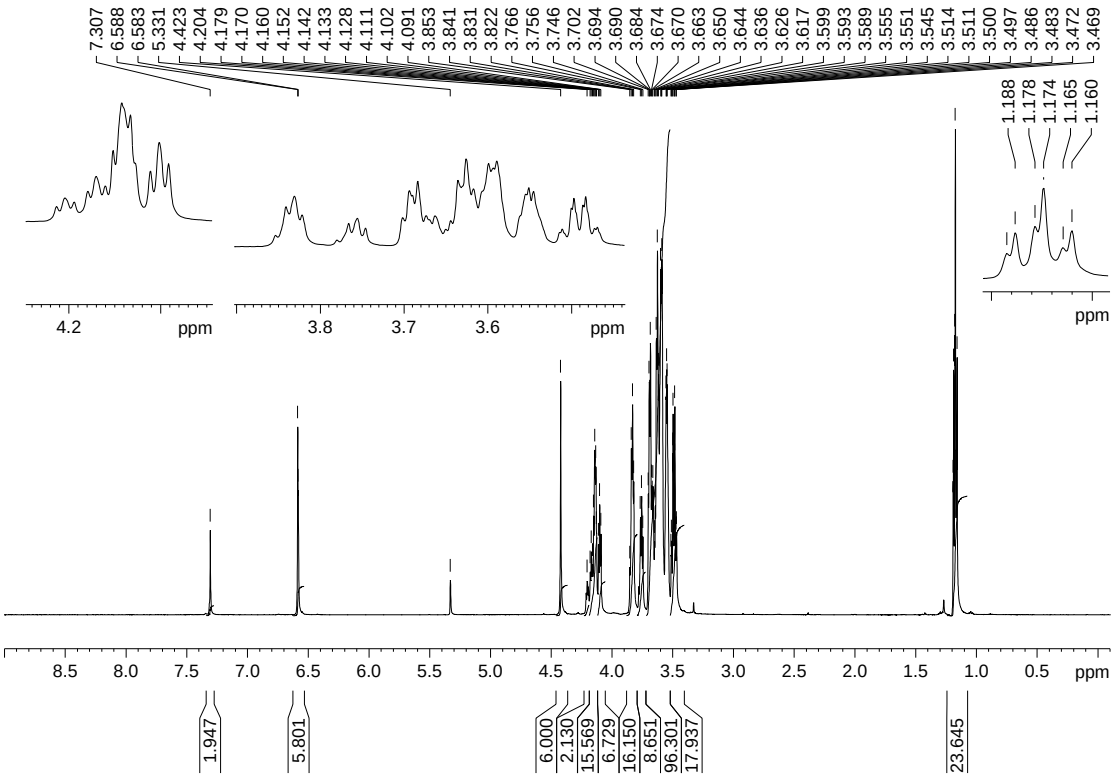

Figure S21. ^{1}H NMR spectrum of compound **3d** in CD_2Cl_2.

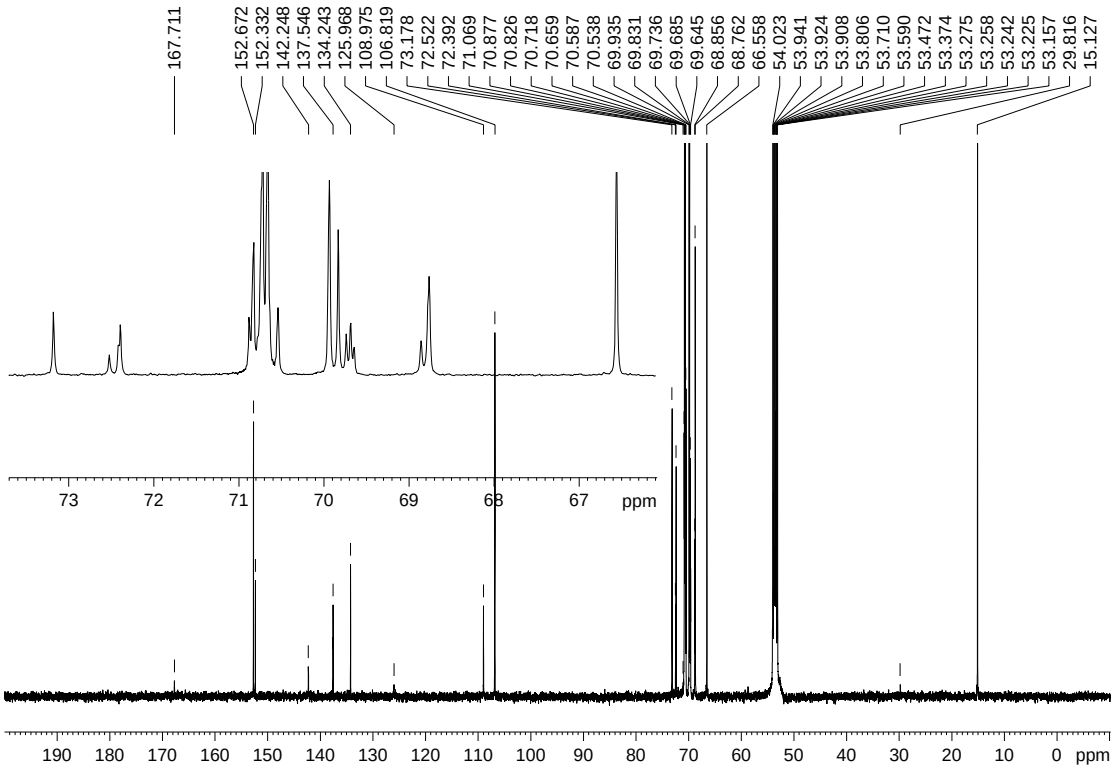

Figure S22. ^{13}C NMR spectrum of compound **3d** in CD_2Cl_2.

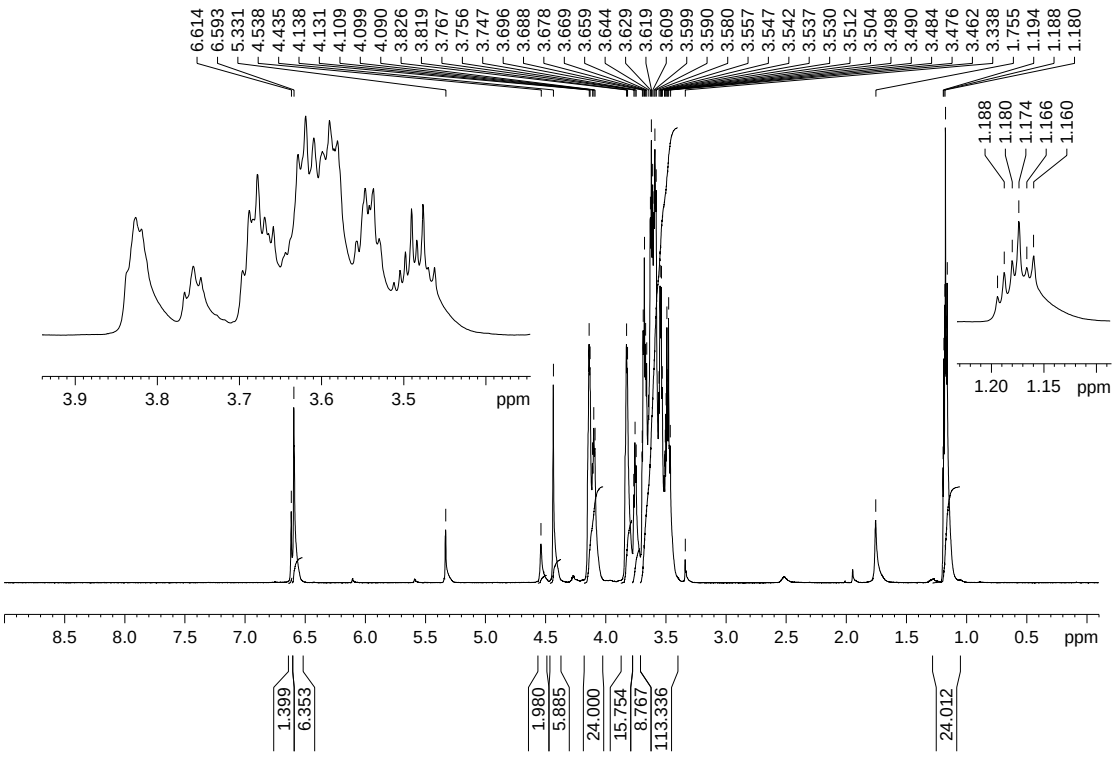

Figure S23. ^{1}H NMR spectrum of compound **3e** in CD_2Cl_2.

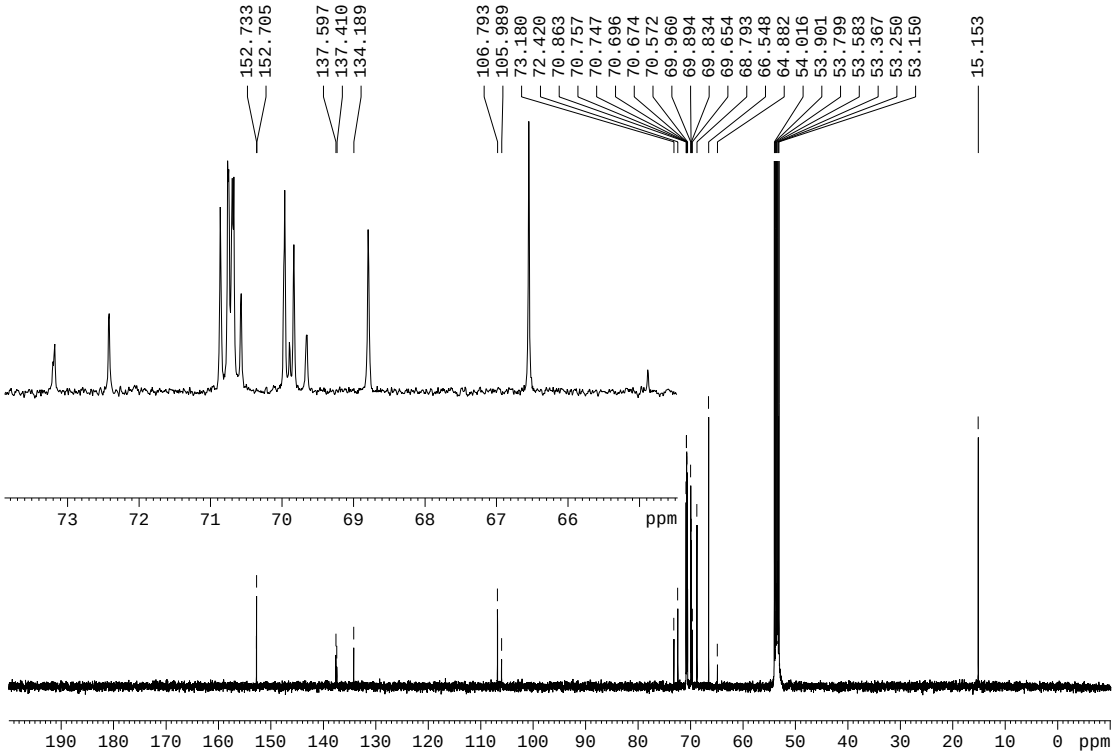

Figure S24. ^{13}C NMR spectrum of compound **3e** in CD_2Cl_2.

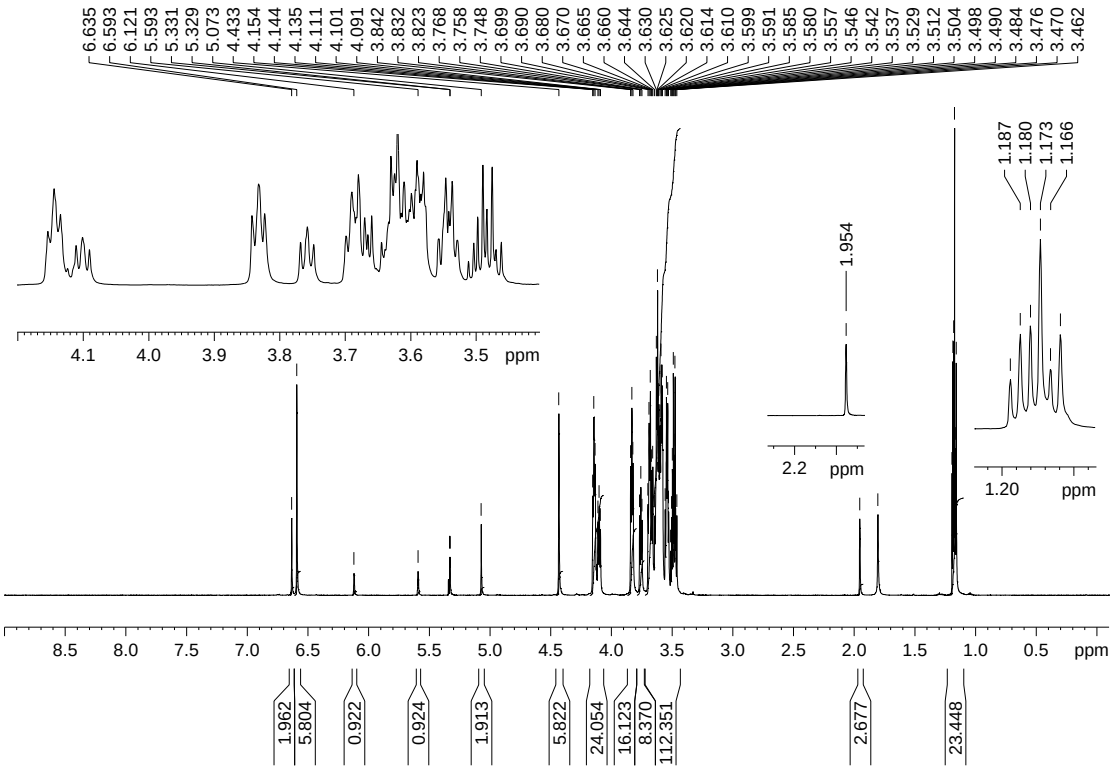

Figure S25. ^{1}H NMR spectrum of compound **3f** in CD_2Cl_2.

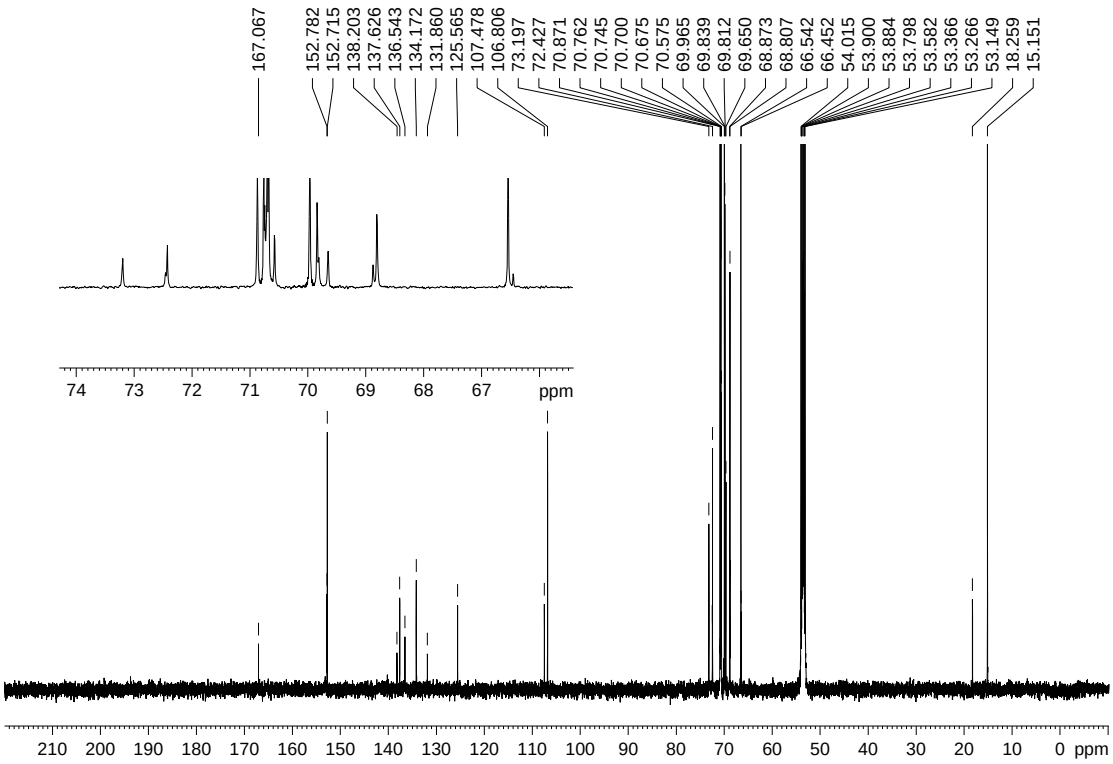

Figure S26. ^{13}C NMR spectrum of compound **3f** in CD_2Cl_2.

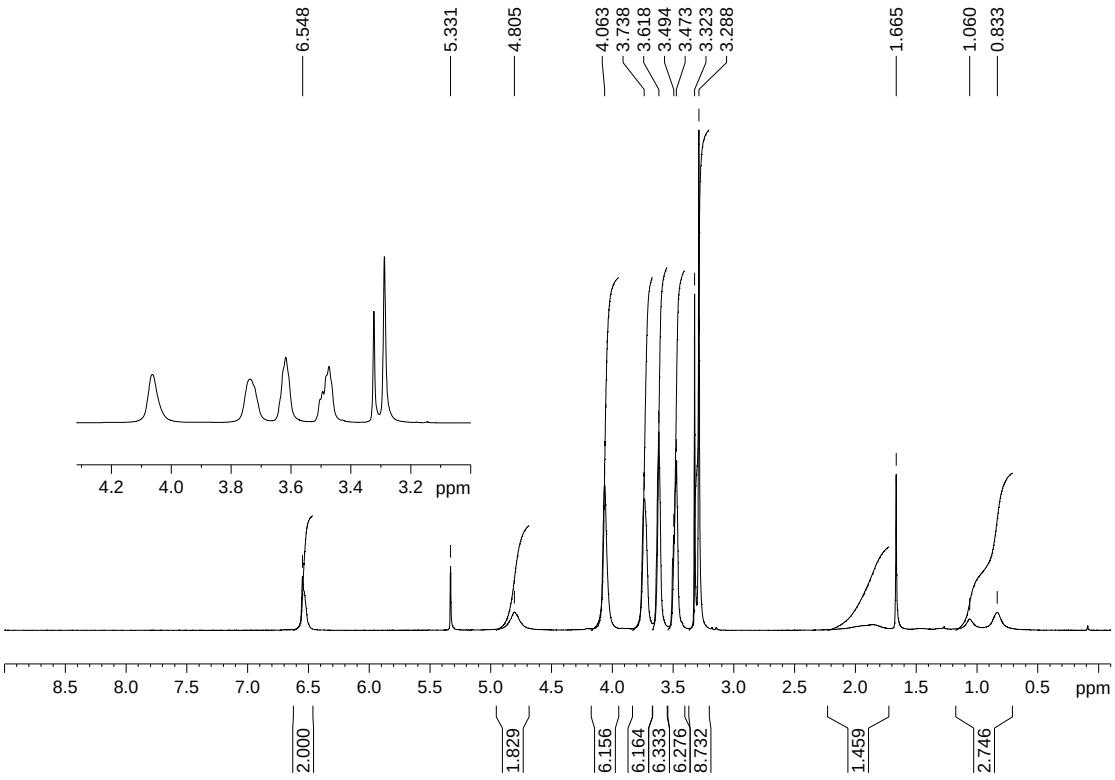

Figure S27. ^{1}H NMR spectrum of **PG1(MD)** in CD_2Cl_2.

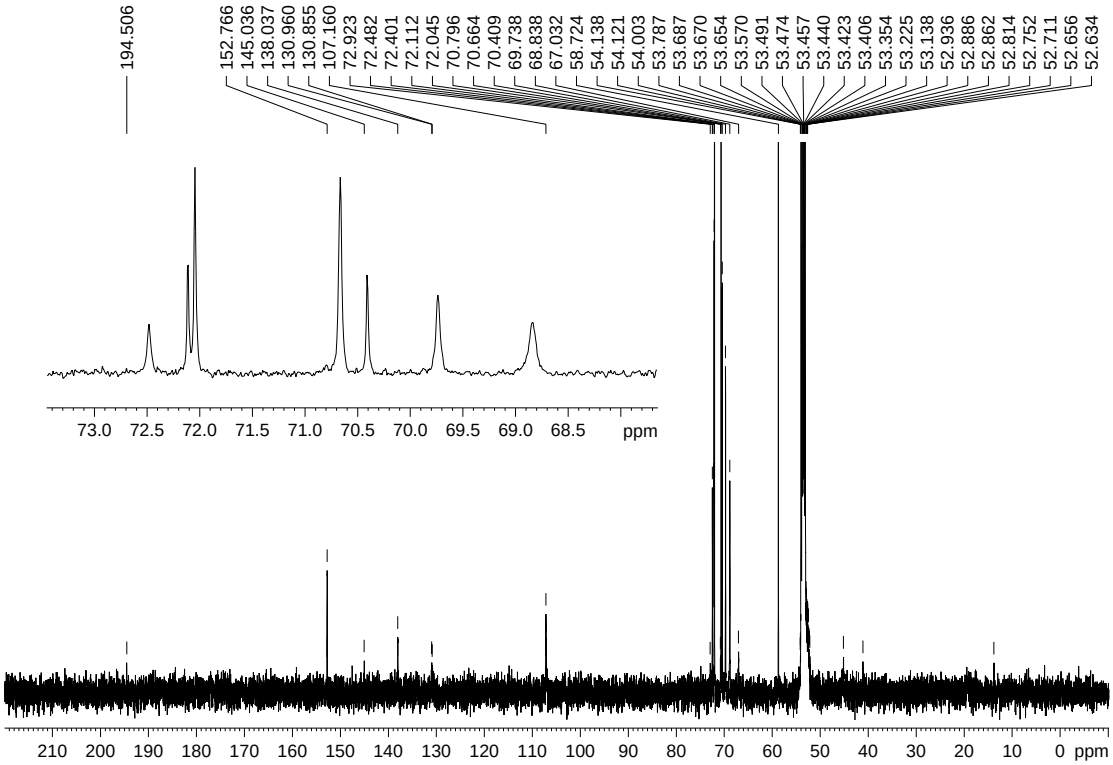

Figure S28. ^{13}C NMR spectrum of **PG1(MD)** in CD_2Cl_2.

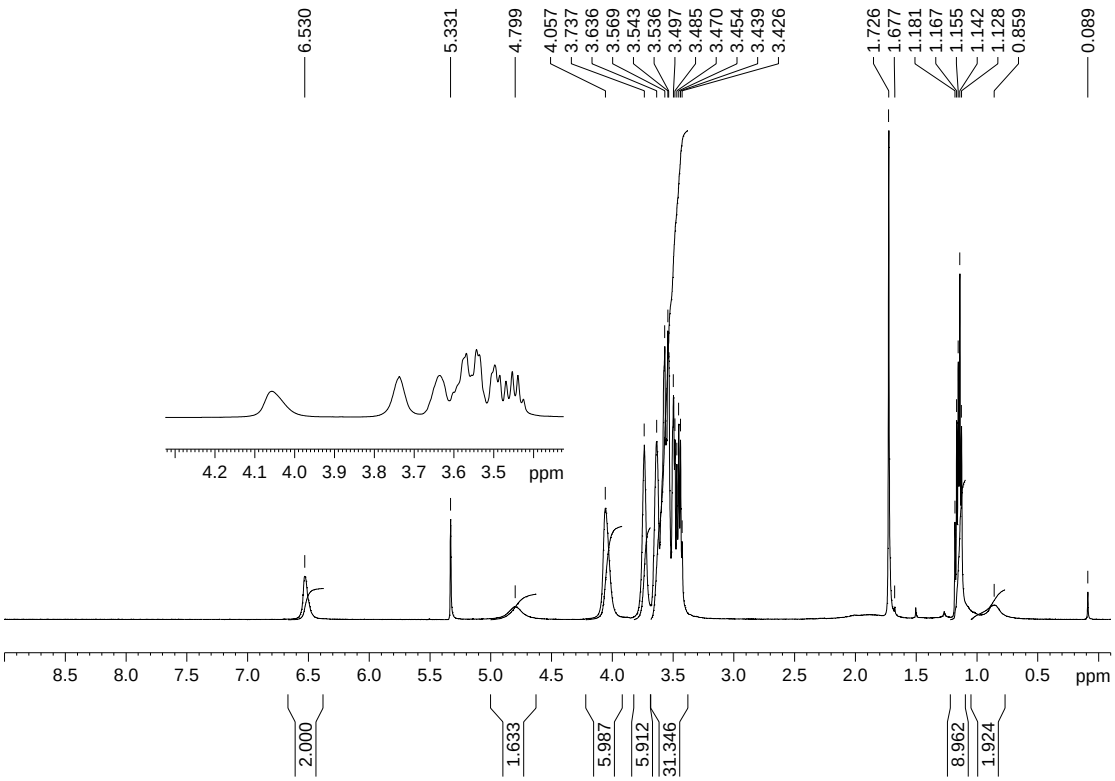

Figure S29. ^{1}H NMR spectrum of **PG1(ET)** in CD_2Cl_2.

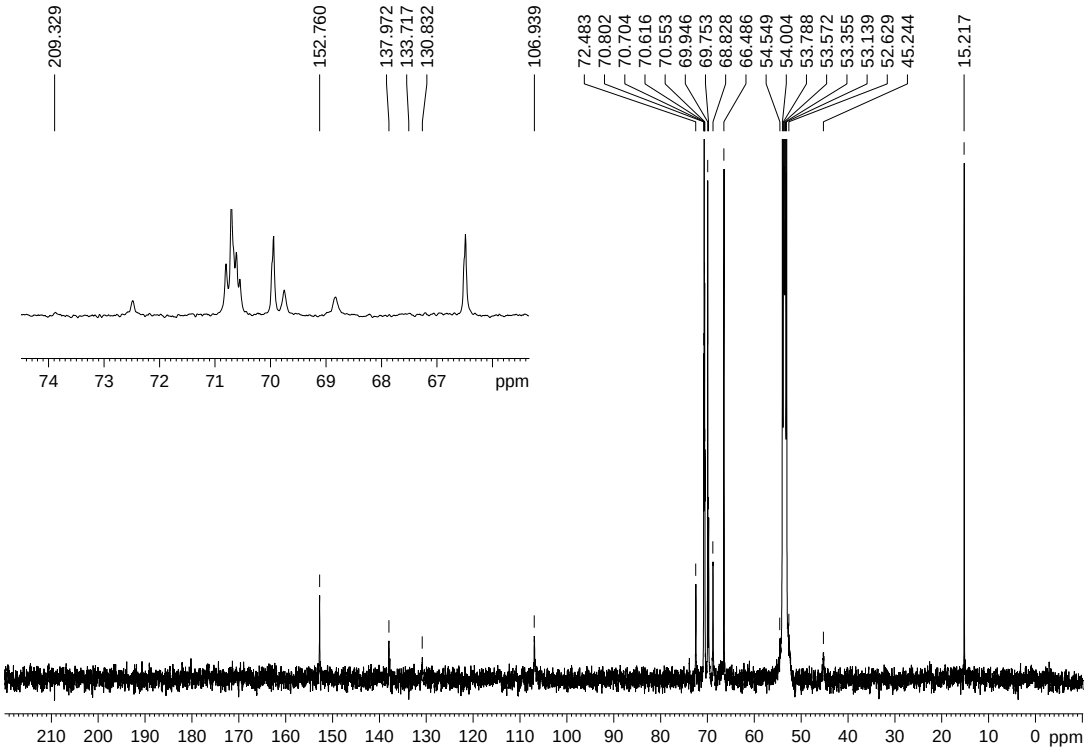

Figure S30. ^{13}C NMR spectrum of **PG1(ET)** in CD_2Cl_2.

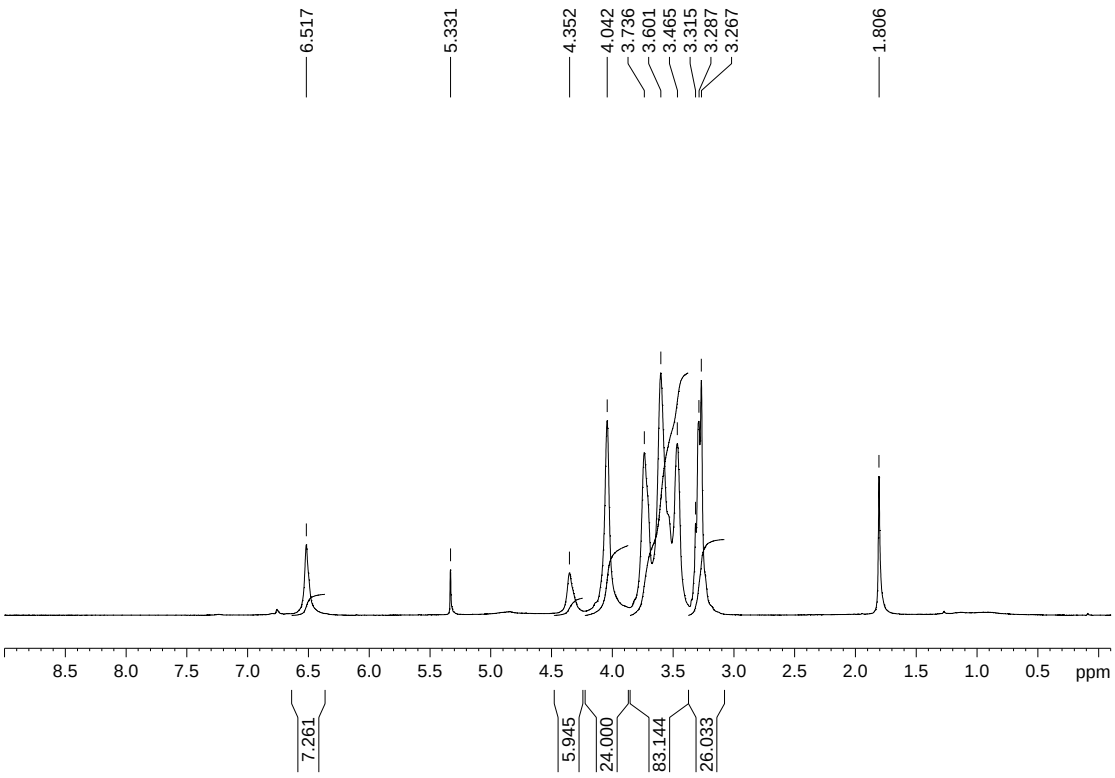

Figure S31. ^{1}H NMR spectrum of **PG2(MD)** in CD_2Cl_2.

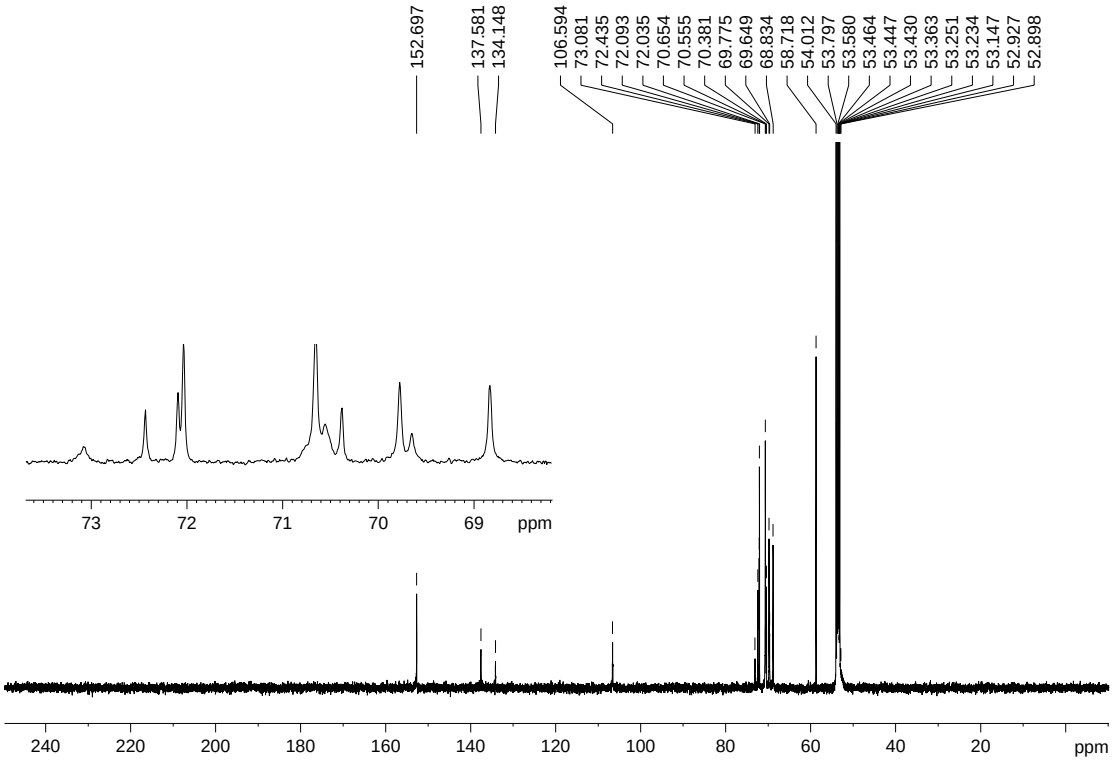

Figure S32. ^{13}C NMR spectrum of **PG2(MD)** in CD_2Cl_2.

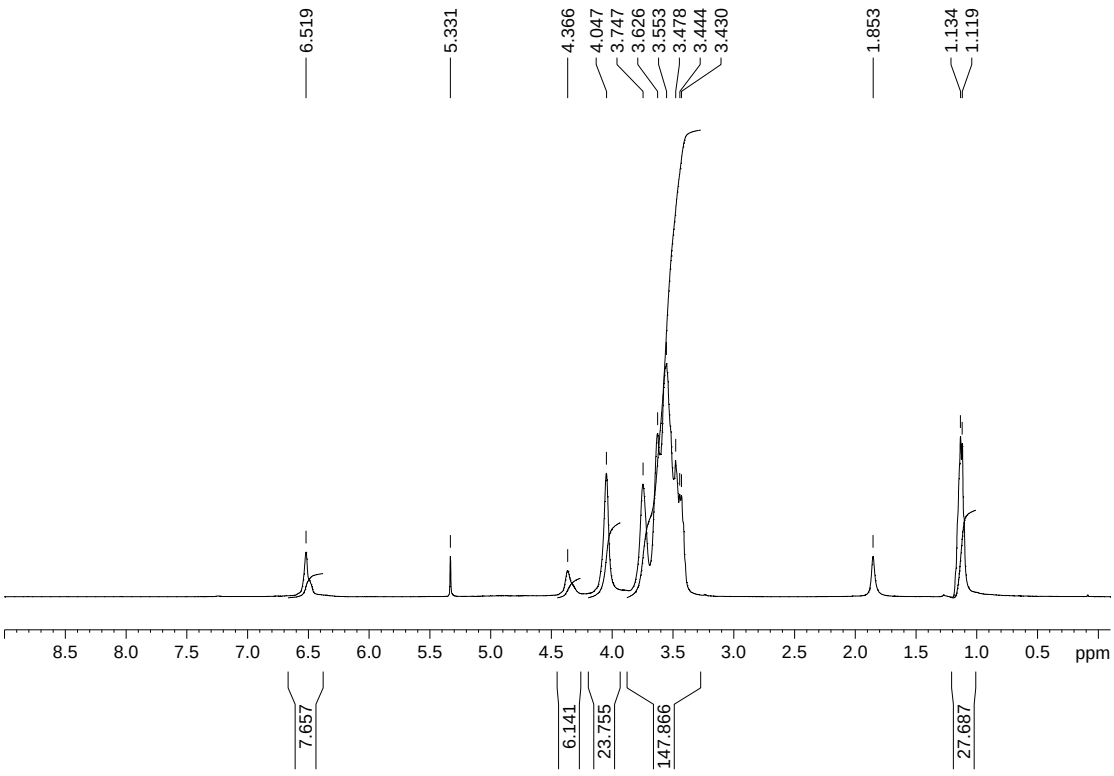

Figure S33. ^{1}H NMR spectrum of **PG2(ET)** in CD_2Cl_2.

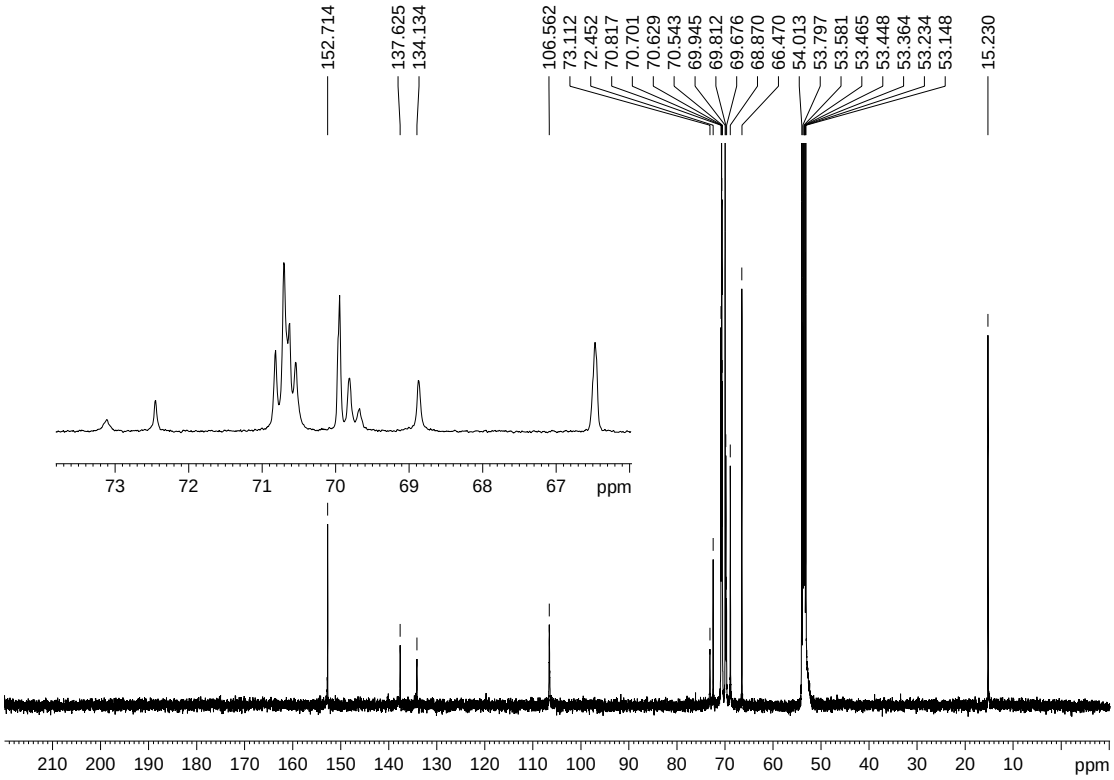

Figure S34. ^{13}C NMR spectrum of **PG2(ET)** in CD_2Cl_2.