Supporting Information

for

Dendronized polymers with ureido-pyrimidinone groups: an efficient strategy to tailor intermolecular interactions, rheology and fracture

Leon F. Scherz,[1] Salvatore Costanzo,[2,3] Qian Huang,[4] A. Dieter Schlüter[1], Dimitris Vlassopoulos[,2,3]*

[1] Department of Materials, Institute of Polymers, Swiss Federal Institute of Technology (ETH), 8093 Zurich, Switzerland

[2] Institute of Electronic Structure and Laser, Foundation for Research and Technology (FORTH), 71110 Heraklion, Crete, Greece

[3] Department of Materials Science & Technology, University of Crete, 71003 Heraklion, Crete, Greece

[4] Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs., Lyngby, Denmark

TABLE OF CONTENTS

S1 Experimental part

S1.1 General information

Unless noted otherwise, all reactions were carried out in dried Schlenk glassware, in dried solvents and in an inert nitrogen atmosphere. For reactions, the used solvents were of analytical grade and obtained from a solvent purification system by LC Technology Solutions Inc., Seabrook, NH. Chromatography solvents were purchased as technical grade and distilled once prior to use. Methacryloyl chloride (MAC) was purchased from Sigma-Aldrich (97%) and freshly distilled before use. Azobis(isobutyronitrile) (AIBN) was purchased from Fluka-Chemie AG (>98%) and recrystallized from methanol. All other chemicals were commercially obtained as reagent grade and used without further purification. Methyl ester **1a** and the succinimidyl ester **1d** were purchased from Synwit Technology Co. (both >95%), 2-phenyl-2-propyl benzodithioate (CDB, 99%) and triethylamine (>99%) were purchased from Sigma-Aldrich, 4-dimethylaminopyridine (DMAP, 99%) and lithium aluminiumhydride (2.4 M in THF) were purchased from Acros Organics. TLC analyses were performed on pre-coated aluminum sheets (silica gel 60G/UV254, 0.20 mm) from Macherey-Nagel. UV-light (254 nm) was used for detection. Column chromatography was conducted on silica gel 60 Å from Fluka (230-400 mesh particle size) as the stationary phase.

S1.2 Instrumentation

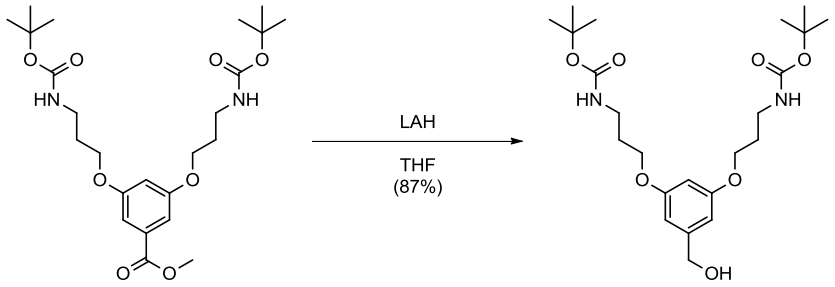
Nuclear magnetic resonance (NMR) spectroscopy. ^{1}H and ^{13}C NMR spectroscopy was performed on a Bruker AV 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometer at room temperature. Polymer spectra were recorded at 340 K to improve NMR resolution. Chemical shifts are reported as δ values (ppm) and were calibrated according to residual protons in $CDCl_3$ (7.26 ppm).

Mass spectrometry (MS). High-resolution ESI-Qq-TOF-MS was performed on a Bruker maXis (solvent, CH_2Cl_2/MeOH; ion polarity, positive; set capillary, 4500.0 V) and ESI/MALDI-FTICR-MS was performed on a Bruker solariX 94 using a THA matrix (solvent, CH_2Cl_2/MeOH; ion polarity, positive; set capillary, 4500.0 V).

Elemental analysis (EA). Combustion analysis was carried out on a Perkin-Elmer EA 240 after drying of the samples in high vacuum to constant weight.

S2 Synthetic procedures

Synthesis of 3,5-bis(3-(tert-butoxycarbonylamino)propoxy)benzyl alcohol (**1b**)



Methyl ester **1a** (1.0 equiv., 30.03 g, 62.23 mmol) was dissolved in dry THF (400 ml) and the solution was cooled to -15 °C. A 2.4 M solution of lithium aluminum hydride (LAH) in THF (2.04 equiv., 53 ml, 127.2 mmol) was diluted with THF (115 ml) and added drop wise. The reaction mixture was stirred for 2 h, after which TLC (EtOAc/hexane 1:2) confirmed the consumption of the starting material. The reaction was quenched by the sequential addition of water (4.82 ml), 15% aqueous NaOH solution (4.82 ml) and H_2O (14.46 ml), followed by continued stirring at room temperature overnight. After filtration, the volatiles were concentrated *in vacuo* and EtOAc (300 ml) was added. The solution was washed once with saturated aqueous $NaHCO_3$ solution (200 ml), once with saturated aqueous NaCl solution (200 ml), dried over $MgSO_4$ and filtered. The filtrate was concentrated before adding hexane to precipitate the desired product (**1b**) as a white solid, which was filtered off and dried *in vacuo* (24.65 g, 87%).

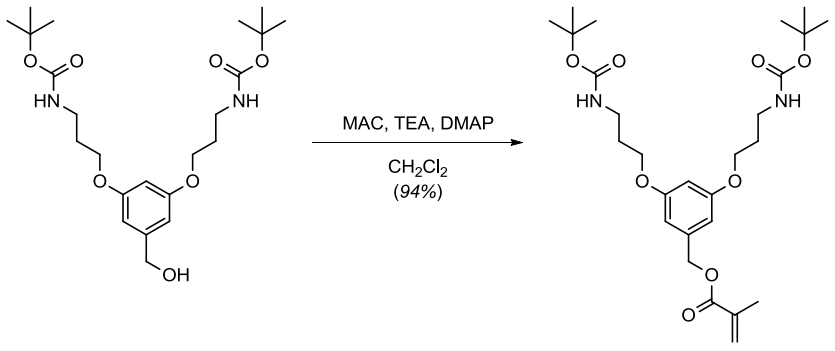
^{1}H NMR (300 MHz, $CDCl_3$) (ppm) = 6.51 (d, J = 2.2 Hz, 2H, aromatic), 6.35 (t, J = 2.3 Hz, 1H, aromatic), 4.77 (br, 2H, N*H*), 4.61 (s, 2H, BnCH_2), 3.99 (t, J = 6.0 Hz, 4H, OCH_2CH$_2$), 3.30 (q, J = 6.4 Hz, 4H, CH$_2$CH_2NH), 2.05-1.85 (m, 5H, CH_2CH$_2$NH, O*H*), 1.43 (s, 18H, ^{t}Bu).

^{13}C NMR (76 MHz, $CDCl_3$) (ppm) = 160.1, 156.0, 143.5, 105.3, 100.6, 79.2, 65.8, 65.2, 38.0, 29.5, 28.4.

HRMS (MALDI-TOF) calcd for $C_{23}H_{38}N_2NaO_7$ ([M+Na]$^+$) 477.2571; found 477.2571.

R_f: 0.30 (hexane/EtOAc 1:1).

Synthesis of 3,5-bis(3-(tert-butoxycarbonylamino)propoxy)benzyl methacrylate (**1c**)



1b **1c**

Benzyl alcohol **1b** (1.0 equiv., 24.0 g, 52.9 mmol) was added to CH_2Cl_2 (270 ml), triethylamine (TEA, 3.01 equiv., 22.2 ml, 159 mmol) and 4-dimethylaminopyridine (DMAP, 0.03 equiv., 219 mg, 1.79 mmol). After cooling of the mixture to -10 °C, a solution of methacryloyl chloride (MAC, 1.5 equiv., 7.63 ml, 79.4 mmol) in CH_2Cl_2 (50 ml) was added drop wise. After stirring in cold for 2.5 h, TLC confirmed the consumption of the staring material and the reaction was quenched and washed with saturated aqueous $NaHCO_3$ solution (2 × 200 ml) and saturated aqueous NaCl solution (100 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The obtained yellowish oil was purified by column chromatography (silica gel, 25 cm, ≈ 400 g, gradient hexane/EtOAc 3:1 → 1:1) and subsequent precipitation of the concentrated, combined product fractions into hexane to yield the title compound **1c** (26.0 g, 94%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.50 (d, J = 2.2 Hz, 2H, aromatic), 6.39 (t, J = 2.2 Hz, 1H, aromatic), 6.17-6.15 (m, 1H, *H*HC=C), 5.60-5.58 (m, 1H, H*H*C=C), 5.10 (s, 2H, BnCH_2), 4.74 (br, 2H, N*H*), 3.99 (t, J = 6.0 Hz, 4H, OCH_2CH$_2$), 3.31 (q, J = 6.2 Hz, 4H, CH$_2$CH_2NH), 2.03-1.89 (m, 7H, CH_2CH$_2$NH, CH_3), 1.44 (s, 18H, ^{t}Bu).

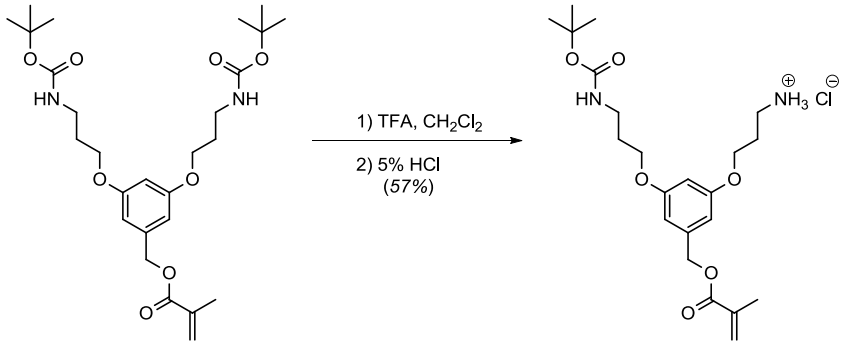
^{13}C NMR (76 MHz, $CDCl_3$) δ = 167.1, 160.0, 156.0, 138.4, 136.1, 125.9, 106.4, 100.9, 79.2, 66.2, 65.8, 37.9, 29.5, 28.4, 18.3.

HRMS (MALDI-TOF): calcd for $C_{27}H_{43}N_2O_8$ ([M+H]$^+$) 523.3014; found 523.3015.

Elemental analysis calcd (%) for $C_{27}H_{42}N_2O_8$: C 62.05, H 8.10, N 5.36, O 24.49; found: C 61.92, H 8.17, N 5.24, O 24.37.

R_f: 0.42 (hexane/EtOAc 2:1).

Synthesis of *mono*-deMG1 (**2a)**



1c **2a**

A mixture of trifluoroacetic acid (TFA, 2.6 equiv., 12.8 ml, 166.5 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a vigorously stirred solution of **1c** (1.0 equiv., 33.9 g, 64.8 mmol) in CH_2Cl_2 (320 ml) cooled to -10 °C. The reaction mixture was allowed to reach room temperature and stirring was continued with daily monitoring of the deprotection progress by TLC ($CHCl_3$/MeOH/Et_3N 10:1:0.1). After 6 d, the reaction was quenched by addition of MeOH (200 ml), concentrated and the oily residue was purified by column chromatography (same solvent mixture as for TLC). The *mono*-deprotected species was dissolved in CH_2Cl_2, washed with 5% aqueous HCl (2 x 300 ml) and dried over anhydrous $MgSO_4$. The volatiles were removed *in vacuo* to yield the title compound **2a** as a pale yellow solid (17.1 g, 57%).

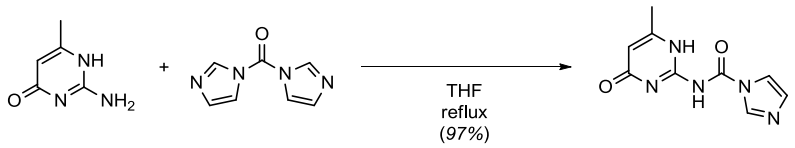
^{1}H NMR (300 MHz, DMSO–d_6) δ (ppm) = 8.07 (br, 3H, NH_3), 6.89 (t, J = 5.1 Hz, 1H, NHBoc), 6.52 (d, J = 2.1 Hz, 2H, aromatic), 6.46 (t, J = 2.3 Hz, 1H, aromatic), 6.08 (s, 1H, HHC=C), 5.72 (p, J = 1.6 Hz, 1H, HHC=C), 5.09 (s, 2H, BnCH_2), 4.04 (t, J = 6.1 Hz, 2H, OCH_2CH$_2$CH$_2$NH$_3^+$), 3.94 (t, J = 6.2 Hz, 2H, OCH_2CH$_2$CH$_2$NHBoc), 3.06 (q, J = 6.5 Hz, 2H, CH$_2$CH_2NHBoc), 2.99-2.86 (m, 2H, CH$_2$CH_2NH$_3^+$), 2.01 (p, J = 6.3, 2H, CH$_2$CH_2CH$_2$NH$_3^+$), 1.91 (s, 3H, CH_3), 1.80 (p, J = 6.4 Hz, 2H, CH$_2$CH_2CH$_2$NHBoc), 1.37 (s, 9H, ^{t}Bu).

^{13}C NMR (76 MHz, DMSO–d6) δ (ppm) = 166.3, 159.8 159.5, 155.6, 138.4, 135.7, 126.1, 106.2, 100.6, 77.5, 65.6, 65.4, 64.7, 36.9, 36.1, 29.2, 28.2, 26.8, 18.0.

HRMS (MALDI-TOF): calcd for $C_{22}H_{35}N_2O_6$ ([M+H]$^+$) 423.2490; found 423.2490.

R_f: 0.45 ($CHCl_3$/MeOH/Et_3N 10:1:0.1)

Synthesis of 2-(1-imidazolylcarbonylamino)-6-methyl-4-[1H]-pyrimidinone (**3**)



3

This compound was prepared as reported by Kaifer et al. (Organic Letters **2005**, *7*(18), 3845-3848): 6-Methylisocytosine (1.0 equiv., 3.29 g, 26.29 mmol) and 1,1´-carbonyldiimidazole (1.3 equiv., 5.60 g, 34.55 mmol) were mixed in dry THF (25 ml) and the resulting white suspension was heated to 70 °C and stirred overnight. After cooling to room temperature, the reaction was filtered and the solid was washed three times with acetone. Drying *in vacuo* afforded the UPy-imidazolide (**3**) as a white solid (5.60 g, 97%). Note: Due to its extremely low solubility in most solvents, this compound is hard to characterize.

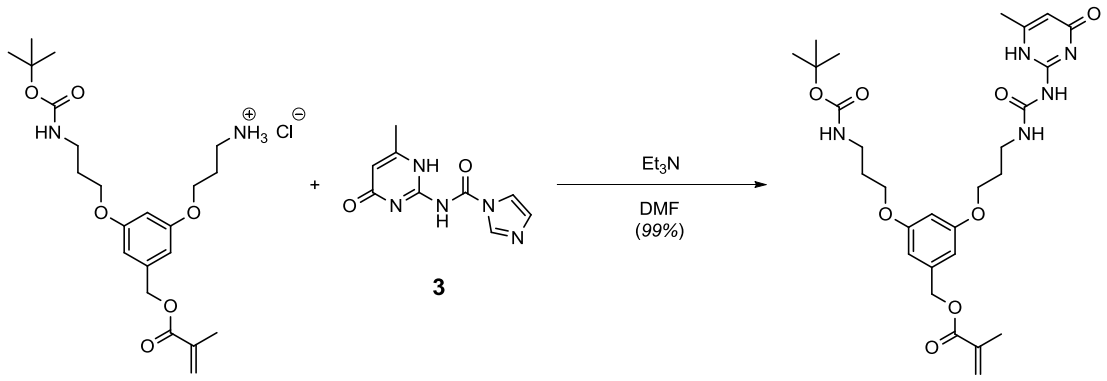
IR (ATR): ν (cm^{-1}) = 3174, 3073, 2594 (bs), 1699, 1647, 1594, 1507, 1472, 1376, 1336, 1315, 1271, 1219, 1189, 1162, 1092, 1062, 1018, 979, 909, 853, 795, 756, 643, 560, 490.

HRMS (MALDI-TOF): calcd for $C_9H_{10}N_5O_2$ ($[M+H]^+$) 220.0829; found 220.0829.

Elemental analysis calcd (%) for $C_9H_9N_5O_2$: C 49.31, H 4.14, N 31.95, O 14.60; found: C 49.21, H 4.09, N 32.18, O 14.49.

m.p.: 235-236 °C.

Synthesis of MG1-UPy (**2b**)



2a **3** **2b**

A solution of **2a** (1.0 equiv., 3.08 g, 6.74 mmol) in DMF (21 ml) and Et_3N (1.5 equiv., 1.4 ml, 10.11 mmol) was added dropwise to a vigorously stirred suspension of **3** (1.2 equiv., 1.77 g, 8.09 mmol) in DMF (24 ml) and the mixture was stirred at room temperature overnight, whereupon the reaction gradually clarified. The reaction was diluted with $CHCl_3$ (200 ml) and subsequently washed with 5% aqueous HCl (200 ml), saturated aqueous $NaHCO_3$ solution (200 ml), and saturated aqueous NaCl solution (100 ml). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo* to yield the title compound **2b** as a beige solid (3.83 g, 99%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 13.04 (br, 1H, N*H*CCH$_3$), 11.89 (br, 1H, N*H*CN), 10.28 (s, 1H, N*H*CONH), 6.50 (t, *J* = 1.7 Hz, 1H, aromatic), 6.47 (t, *J* = 1.7 Hz, 1H, aromatic), 6.40 (t, *J* = 2.3 Hz, 1H, aromatic), 6.14-6.15 (m, 1H, *H*HC=C), 5.78 (s, 1H, COC*H*), 5.58 (p, *J* = 1.5 Hz, 1H, H*H*C=C), 5.08 (s, 2H, BnC*H*$_2$), 4.77 (br, 1H, N*H*), 4.02 (t, *J* = 6.2 Hz, 2H, OC*H*$_2$CH$_2$CH$_2$NHUPy), 3.97 (t, *J* = 5.9 Hz, 2H, OC*H*$_2$CH$_2$CH$_2$NHBoc), 3.45 (q, *J* = 6.5 Hz, 2H, CH$_2$C*H*$_2$NHUPy), 3.30 (q, *J* = 6.5 Hz, 2H, CH$_2$C*H*$_2$NHBoc), 2.21 (s, 3H, HNCC*H*$_3$), 2.09 (p, *J* = 6.6 Hz, 2H, CH$_2$C*H*$_2$CH$_2$), 2.01 – 1.88 (m, 5H, CH$_2$C*H*$_2$NHBoc, H$_2$CCC*H*$_3$), 1.43 (s, 9H, ^{t}Bu).

^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm) = 173.0, 167.1, 160.3, 160.0, 156.7, 156.0, 148.3, 138.2, 136.2, 125.9, 106.7, 106.5, 106.3, 101.0, 79.2, 66.2, 65.8, 65.7, 38.0, 37.1, 29.5, 29.2, 28.4, 18.9, 18.4.

HRMS (MALDI-TOF): calcd for $C_{28}H_{40}N_5O_8$ ([M+H]$^+$) 574.2877; found 574.2872.

Polymerization of macromonomers **1c** and **2b**

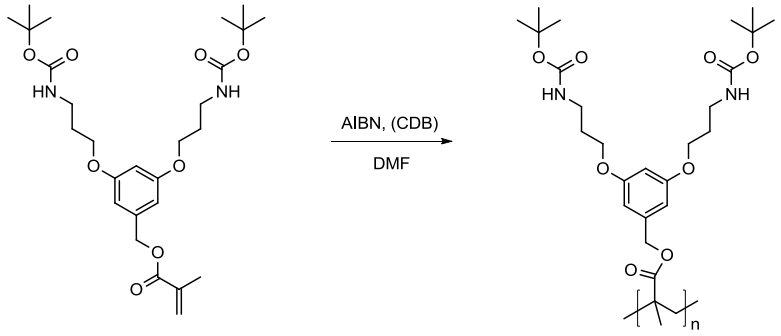
General Procedure A: *Controlled Radical Polymerization (RAFT),* $P_n \approx 40$. The desired amounts of macromonomers **1c** and **2b** were placed in a Schlenk tube equipped with a magnetic stir bar under N_2 atmosphere, followed by addition of 0.1M solutions of azobis(isobutyronitrile) (AIBN; 0.025 equiv.) and cumyl dithiobenzoate (CDB; 0.025 equiv.) in DMF. The reaction was diluted with DMF to arrive at a final concentration of 1.0 $g \cdot ml^{-1}$. After homogenization and thorough degassing by several freeze-pump-thaw cycles, the polymerization mixture was placed in a preheated oil bath (65 °C), and the reaction was stirred at this temperature for a predetermined amount of time under N_2. The reaction was stopped by removing the flask from the oil bath and rapid cooling in liquid N_2. DMF (5 ml) was added to dissolve the mixture and the polymer was obtained by repeated precipitation into cold MeOH (200 ml). After decanting the supernatant, freeze-drying of the gummy residue from a mixture of 1,4-dioxane and water (V/V 10:1) afforded the polymer as a pink foam.

General Procedure B: *Free Radical Polymerization (FRP),* larger P_n. The desired amounts of macromonomers **1c** and **2b** were placed in a Schlenk tube equipped with a magnetic stir bar under N_2 atmosphere, followed by addition of a 0.1M solution of azobis(isobutyronitrile) (AIBN; 0.002 equiv.) in DMF. The reaction was diluted with DMF to arrive at a final concentration of 0.25-0.50 $g \cdot ml^{-1}$ as specified in Table 1 of the main text. After homogenization and thorough degassing by several freeze-pump-thaw cycles, the polymerization mixture was placed in a preheated oil bath (65 °C), and the reaction was stirred at this temperature for a predetermined amount of time under N_2. The reaction was stopped by removing the flask from the oil bath and rapid cooling in liquid N_2. DMF (5 ml) was added to dissolve the mixture and the polymer was obtained by repeated precipitation into cold MeOH (200 ml). After decanting the supernatant, freeze-drying of the gummy residue from a mixture of 1,4-dioxane and water (V/V 10:1) afforded the polymer as a colorless foam.

Formula for the Calculation of UPy-Contents in the Copolymers with g = 1:

$$f_{UPy} = \frac{1}{1 + \frac{I_{Boc}}{9}} \cdot 100\%$$

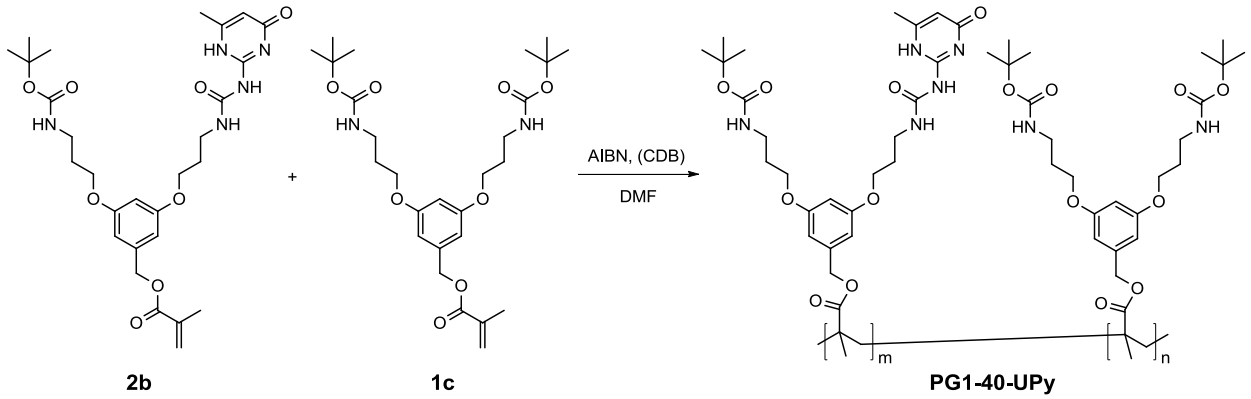
Homopolymerization of **1c** (Synthesis of **PG1-40-UPy0**)



1c **PG1-40-UPy0**

Synthesis of **PG1-40-UPy0**. Following *General Procedure A*, **1c** (3.00 g, 5.74 mmol), AIBN (1.15 ml), and CDB (1.15 ml) were dissolved in DMF (0.70 ml) and polymerized for 20 h. The final product (2.49 g, 83%) was obtained as a fluffy, pink foam.

Copolymerization of **1c** and **2b** (Synthesis of **PG1-P_n-UPy(*f*)**)



2b **1c** **PG1-40-UPy**

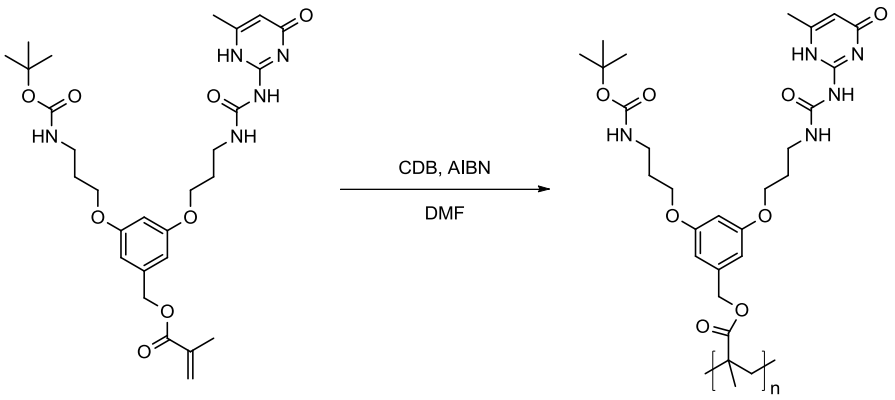
Synthesis of **PG1-40-UPy5**. Following *General Procedure A*, **1c** (1.54 g, 2.95 mmol), **2b** (0.19 g, 0.33 mmol), AIBN (0.73 ml), and CDB (0.73 ml) were dissolved in DMF (0.27 ml) and polymerized for 19 h. The final product (1.53 g, 88%) was obtained as a fluffy, pink foam.

Synthesis of **PG1-40-UPy10**. Following *General Procedure A*, **1c** (1.33 g, 2.55 mmol), **2b** (0.36 g, 0.64 mmol), AIBN (0.71 ml), and CDB (0.71 ml) were dissolved in DMF (0.28 ml) and polymerized for 19 h. The final product (1.39 g, 82%) was obtained as a fluffy, pink foam.

Synthesis of **PG1-40-UPy25**. Following *General Procedure A*, **1c** (1.00 g, 1.93 mmol), **2b** (1.10 g, 1.93 mmol), AIBN (0.86 ml), and CDB (0.86 ml) were dissolved in DMF (0.40 ml) and polymerized for 18 h. The final product (1.68 g, 80%) was obtained as a dense, pink foam.

Synthesis of **PG1-40-UPy33**. Following *General Procedure A*, **1c** (0.43 g, 0.82 mmol), **2b** (0.97 g, 1.64 mmol), AIBN (0.55 ml), and CDB (0.55 ml) were dissolved in DMF (0.30 ml) and polymerized for 16 h. The final product (1.30 g, 92%) was obtained as a dense, pink foam.

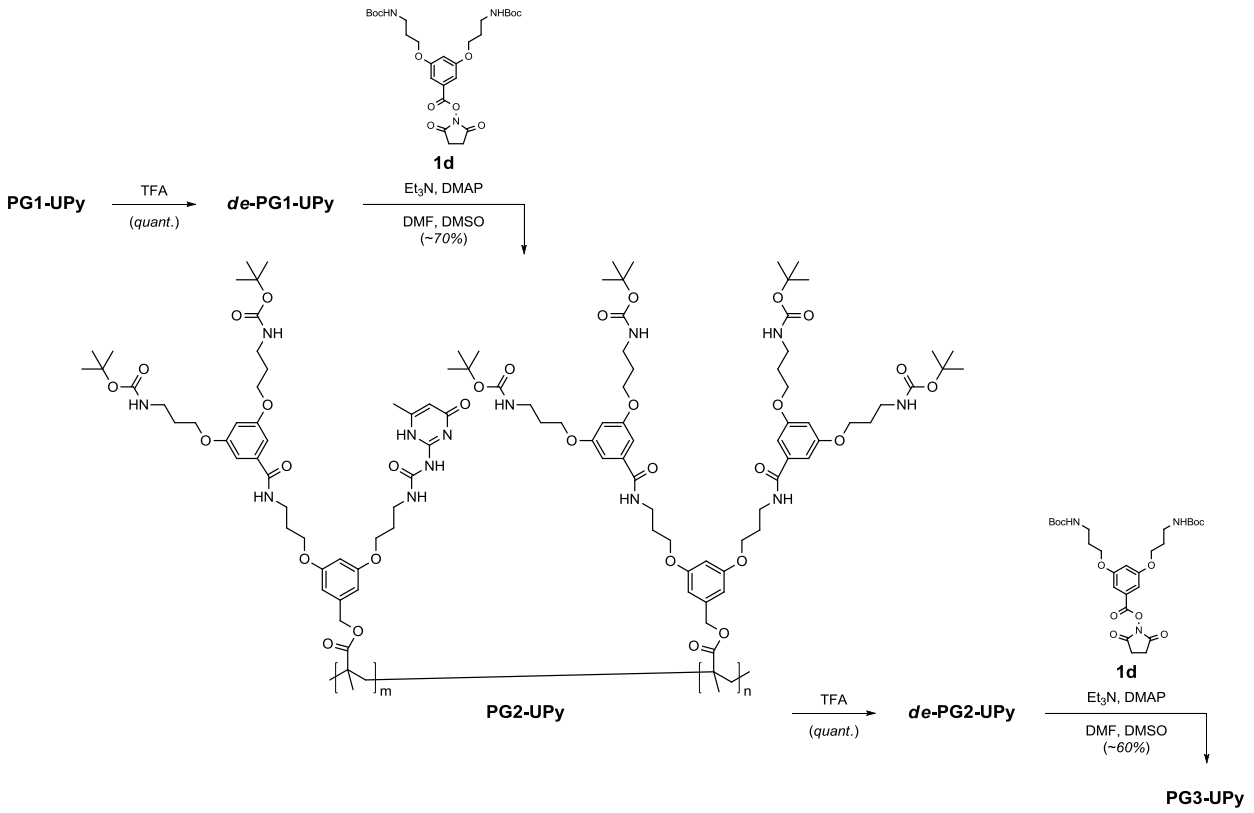
Homopolymerization of **2b** (Synthesis of **PG1-40-UPy50**)



2b **PG1-40-UPy50**

Synthesis of **PG1-40-UPy50**. Following *General Procedure A*, **2b** (0.74 g, 1.29 mmol), AIBN (0.32 ml), and CDB (0.32 ml) were dissolved in DMF (0.10 ml) and polymerized for 14 h. The initially homogeneous polymerization mixture solidified over the course of the reaction. After 14 h, the reaction was stopped by removing the flask from the oil bath and rapid cooling in liquid N_2. $CHCl_3$ (10 ml) was added to the flask, the polymer was suspended with heating to 60 °C, transferred into a glass frit (Por. 3) and hot filtered. Washing with hot $CHCl_3$ was repeated three times (3 × 20 ml). Drying *in vacuo* afforded the polymer (0.64 g, 87%) as a pink, granular solid.

Post-polymerization dendronization (**PG*g*+1-UPy**)



General Procedure C: *Boc Deprotection*. TFA (20 equiv per amine) was slowly added to PG*g* at -10 °C and the mixture was allowed to warm to room temperature overnight. Excess TFA was removed from the resulting solution by repeated addition of methanol and evaporation to dryness (5 × 20 ml). The solid residue was taken up in water and freeze-dried to yield *de*PG*g* quantitatively as a colorless foam.

General Procedure D: *Dendronization*. *de*PG*g* (1.0 equiv., c = 0.5 mmol·ml^{-1}) and DMAP (0.3 equiv. per amine) were dissolved in a mixture of DMF and DMSO. Et_3N (2.0 equiv. per amine) was slowly added and the mixture was cooled to -10 °C. Activated ester **1d** (3.0 equiv. per amine) was added in cold and the mixture was subsequently allowed to reach room temperature. Two further additions of **1d** (1.0 equiv. per amine each) were performed at 2 d intervals. The mixture was stirred for a predetermined amount of time (PG2: ≈7 d; PG3: ≈21 d) before the polymer was precipitated into cold Et_2O thrice. After column filtration over silica gel, freeze-drying of the gummy residue from 1,4-dioxane (10 ml) afforded PG*g*+1 as a colorless foam.

Synthesis of **PG2-40-UPy0**. Following *General Procedure C*, PG1-40-UPy0 (0.63 g, 1.20 mmol) was mixed with TFA (6.50 ml). Following *General Procedure D*, *de*PG1-40-UPy0 (0.66 g, 1.20 mmol), DMAP (83 mg) and Et_3N (0.63 ml) were dissolved in DMF (7.00 ml), followed by batchwise addition of **1d** (6.40 g, 11.3 mmol). After 11 d, the final product (1.06 g, 72%) was obtained as a colorless foam.

Synthesis of **PG2-40-UPy5**. Following *General Procedure C*, PG1-40-UPy5 (0.23 g, 0.43 mmol) was mixed with TFA (3.00 ml). Following *General Procedure D*, *de*PG1-40-UPy5 (0.24 g, 0.43 mmol), DMAP (32 mg) and Et_3N (0.25 ml) were dissolved in DMF/DMSO (4.00/0.50 ml), followed by batchwise addition of **1d** (2.50 g, 4.36 mmol). After 12 d, the final product (0.37 g, 70%) was obtained as a colorless foam.

Synthesis of **PG2-40-UPy25**. Following *General Procedure C*, PG1-40-UPy25 (0.23 g, 0.41 mmol) was mixed with TFA (3.00 ml). Following *General Procedure D*, *de*PG1-40-UPy25 (0.24 g, 0.41 mmol), DMAP (30 mg) and Et_3N (0.23 ml) were dissolved in DMF/DMSO (4.00/0.50 ml), followed by batchwise addition of **1d** (1.90 g, 3.36 mmol). After 7 d, the final product (0.30 g, 69%) was obtained as a colorless foam.

Synthesis of **PG2-40-UPy50**. Following *General Procedure C*, PG1-40-UPy50 (0.16 g, 0.28 mmol) was mixed with TFA (2.00 ml). Following *General Procedure D*, *de*PG1-40-UPy50 (0.16 g, 0.28 mmol), DMAP (20 mg) and Et_3N (0.16 ml) were dissolved in DMF/DMSO (3.50/1.00 ml), followed by batchwise addition of **1d** (1.30 g, 2.30 mmol). After 8 d, the final product (0.18 g, 70%) was obtained as a colorless foam.

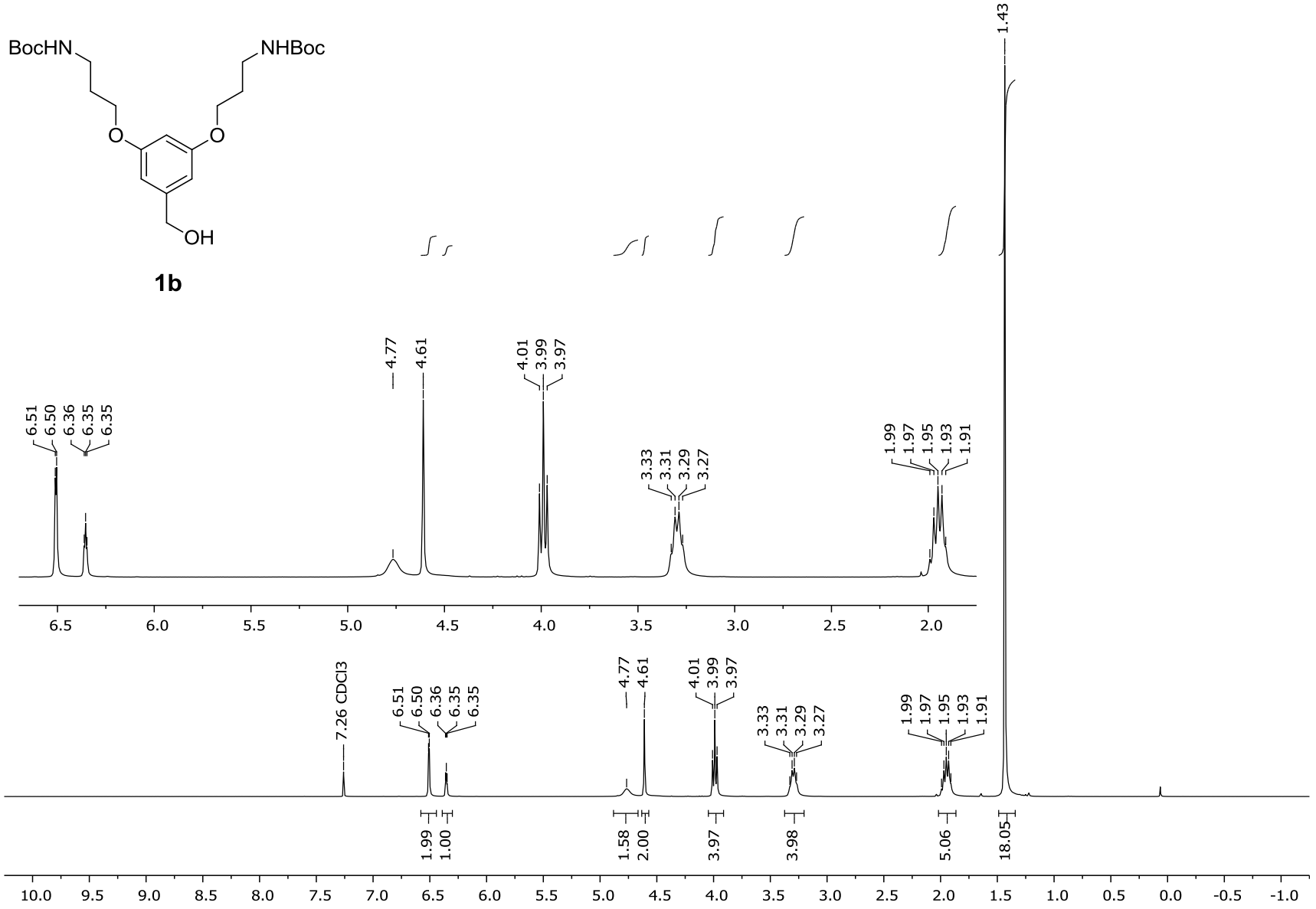
Synthesis of **PG3-UPy0**. Following *General Procedure C*, PG2-40-UPy0 (0.31 g, 0.26 mmol) was mixed with TFA (6.60 ml). Following *General Procedure D*, *de*PG2-40-UPy0 (0.33 g, 0.26 mmol), DMAP (38 mg) and Et_3N (0.29 ml) were dissolved in DMF (6.20 ml), followed by batchwise addition of **1d** (2.93 g, 5.18 mmol). After 20 d, the final product (0.55 g, 81%) was obtained as a colorless foam.

Synthesis of **PG3-40-UPy5**. Following *General Procedure C*, PG2-40-UPy5 (0.14 g, 0.12 mmol) was mixed with TFA (5.00 ml). Following *General Procedure D*, *de*PG2-40-UPy5 (0.15 g, 0.12 mmol), DMAP (9 mg) and Et_3N (0.21 ml) were dissolved in DMF/DMSO (3.50/0.50 ml), followed by batchwise addition of **1d** (1.37 g, 2.42 mmol). After 30 d, the final product (0.24 g, 77%) was obtained as a colorless foam.

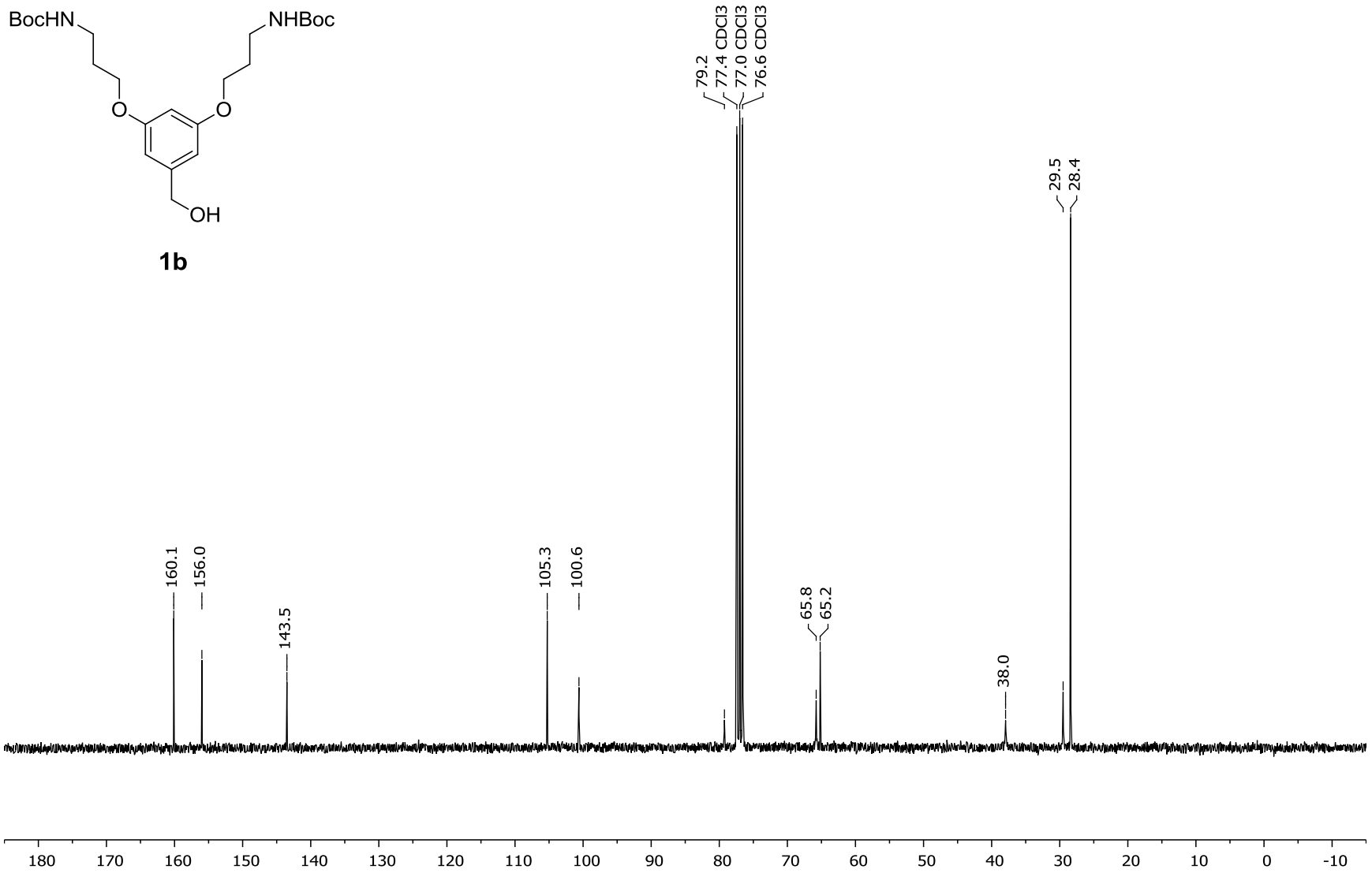
Synthesis of **PG3-40-UPy25**. Following *General Procedure C*, PG2-40-UPy25 (85 mg, 0.08 mmol) was mixed with TFA (4.00 ml). Following *General Procedure D*, *de*PG2-40-UPy25 (88 mg, 0.08 mmol), DMAP (6 mg) and Et_3N (0.14 ml) were dissolved in DMF/DMSO (3.00/0.60 ml), followed by batchwise addition of **1d** (1.35 g, 2.38 mmol). After 14 d, the final product (0.14 g, 85%) was obtained as a colorless foam.

Synthesis of **PG3-40-UPy50**. Following *General Procedure C*, PG2-40-UPy50 (79 mg, 0.08 mmol) was mixed with TFA (3.00 ml). Following *General Procedure D*, *de*PG2-40-UPy50 (81 mg, 0.08 mmol), DMAP (6 mg) and Et_3N (0.10 ml) were dissolved in DMF/DMSO (2.80/1.60 ml), followed by batchwise addition of **1d** (0.78 g, 1.36 mmol). After 18 d, the final product (0.11 g, 78%) was obtained as a colorless foam.

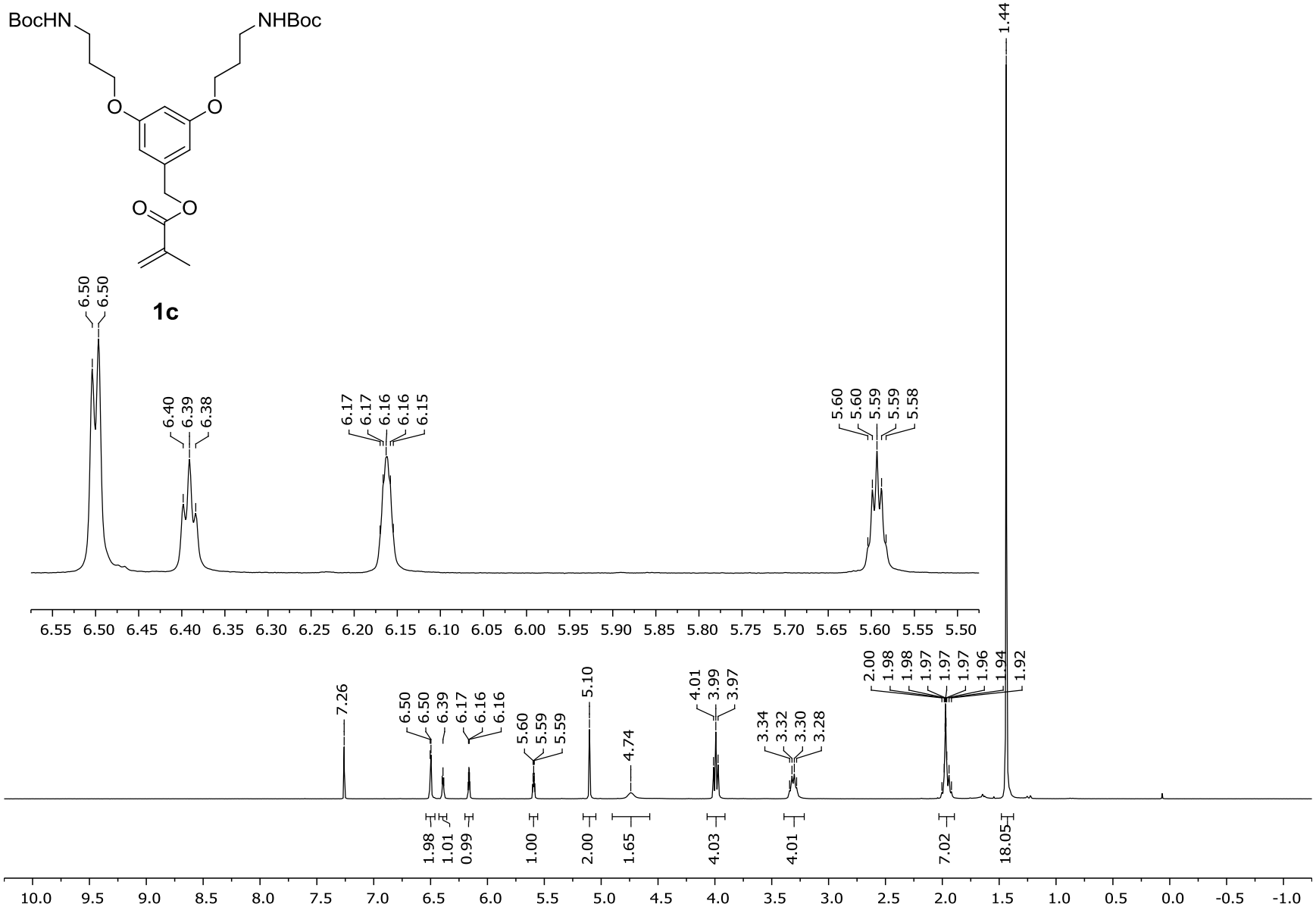
S3 NMR Spectra: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **1b**:



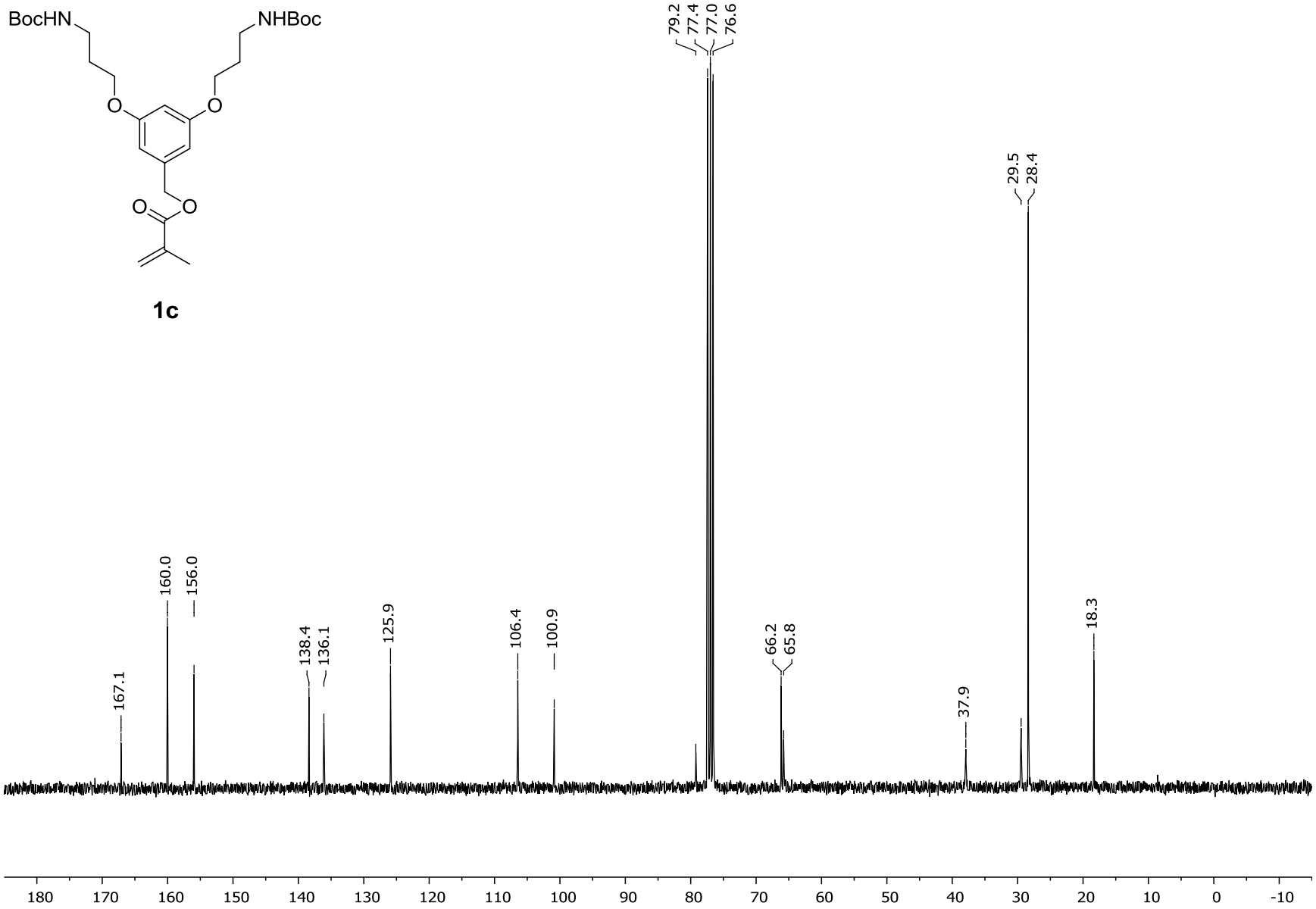
^{13}C NMR spectrum ($CDCl_3$, 76 MHz) of compound **1b**:



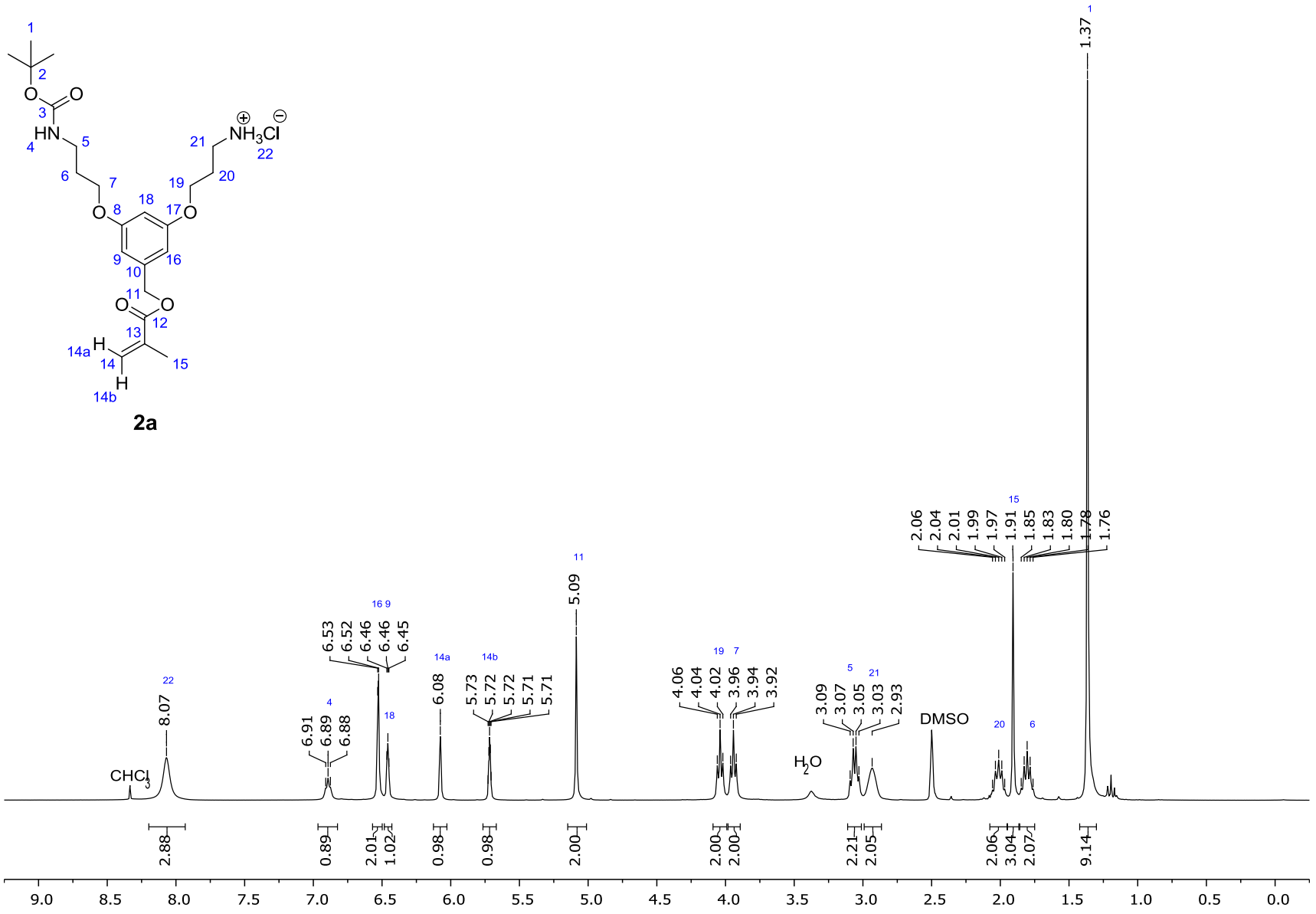
^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **1c**:



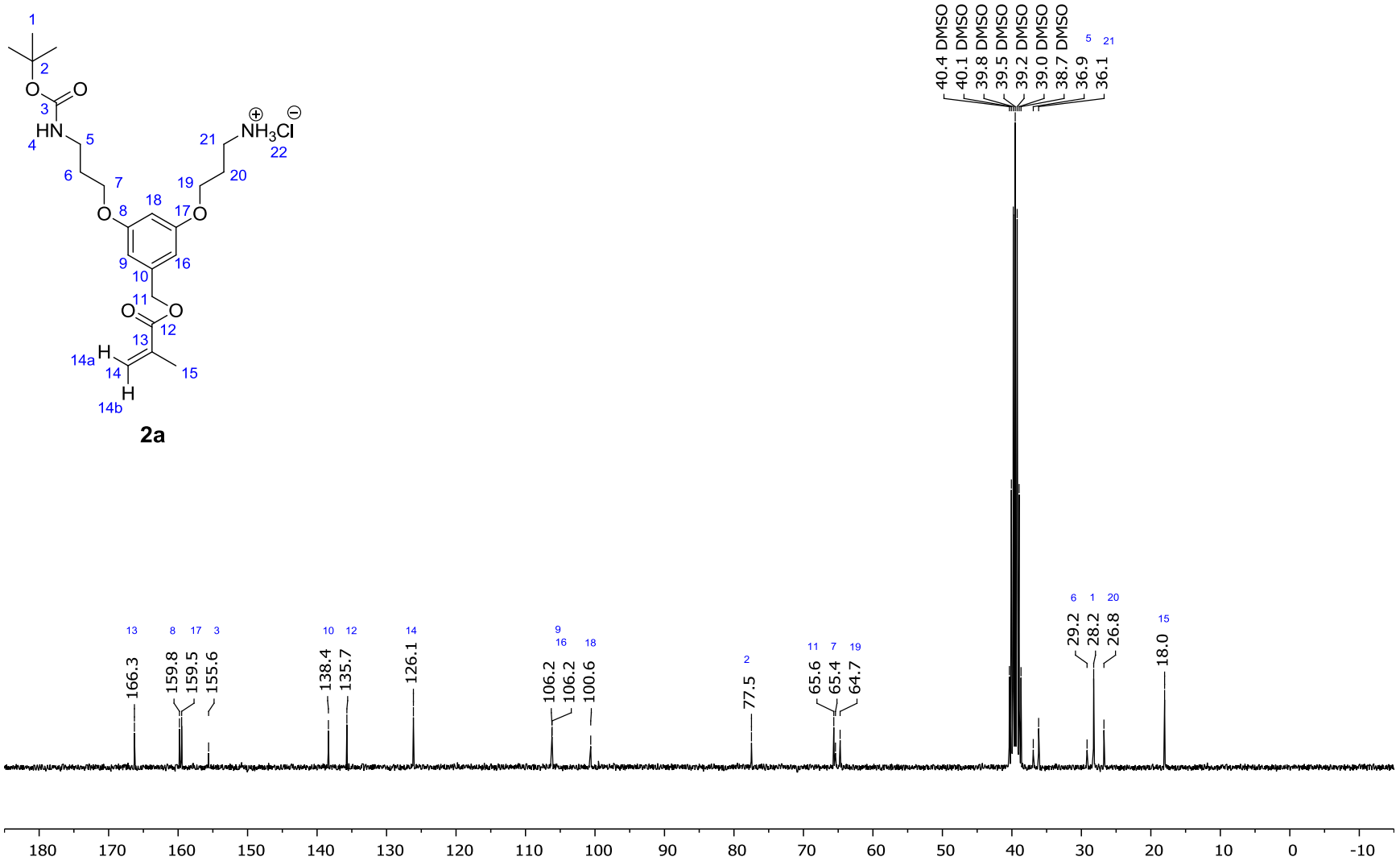
^{13}C NMR spectrum ($CDCl_3$, 76 MHz) of compound **1c**:



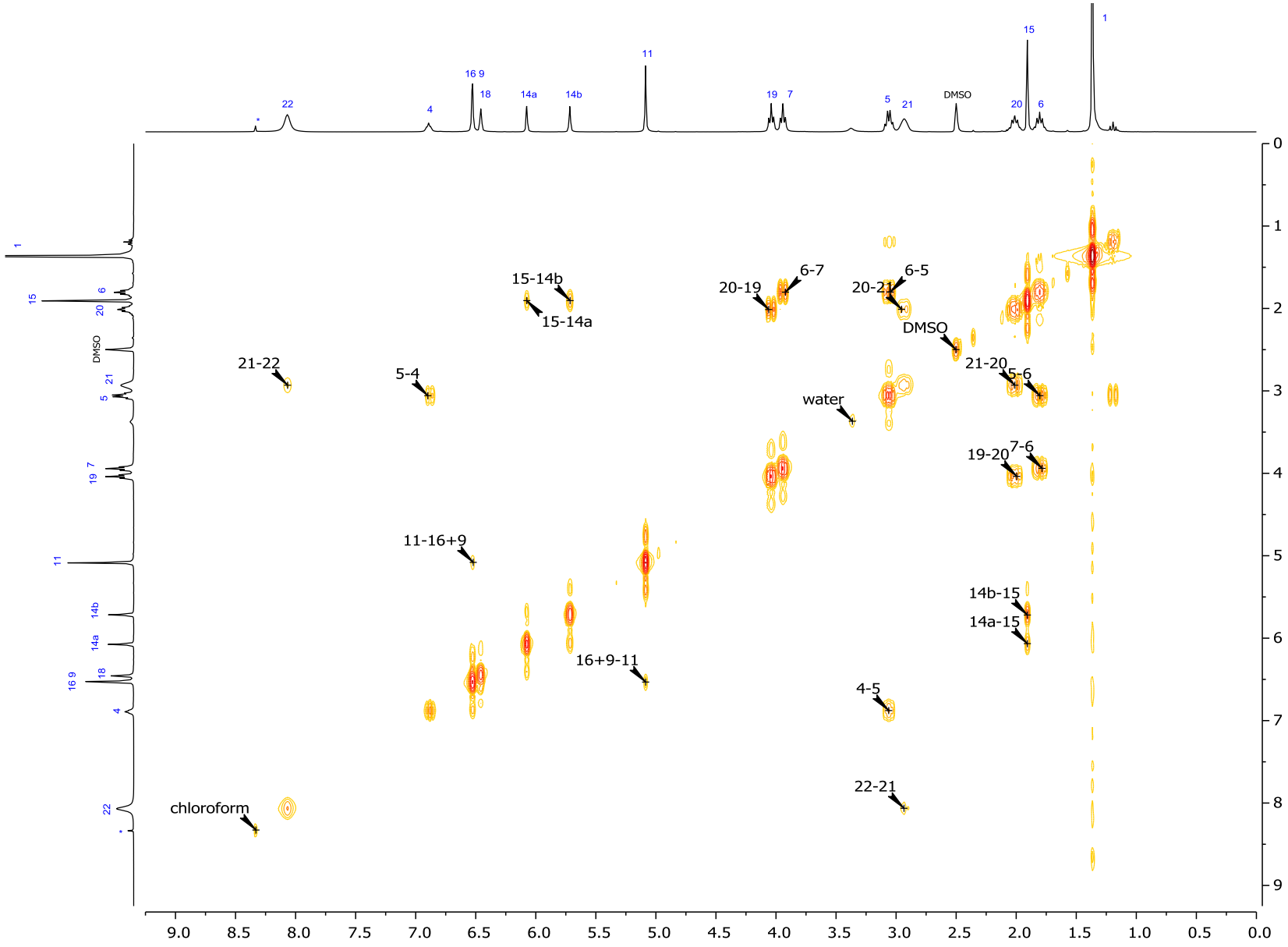
^{1}H NMR spectrum (DMSO-d6, 300 MHz) of compound **2a**:



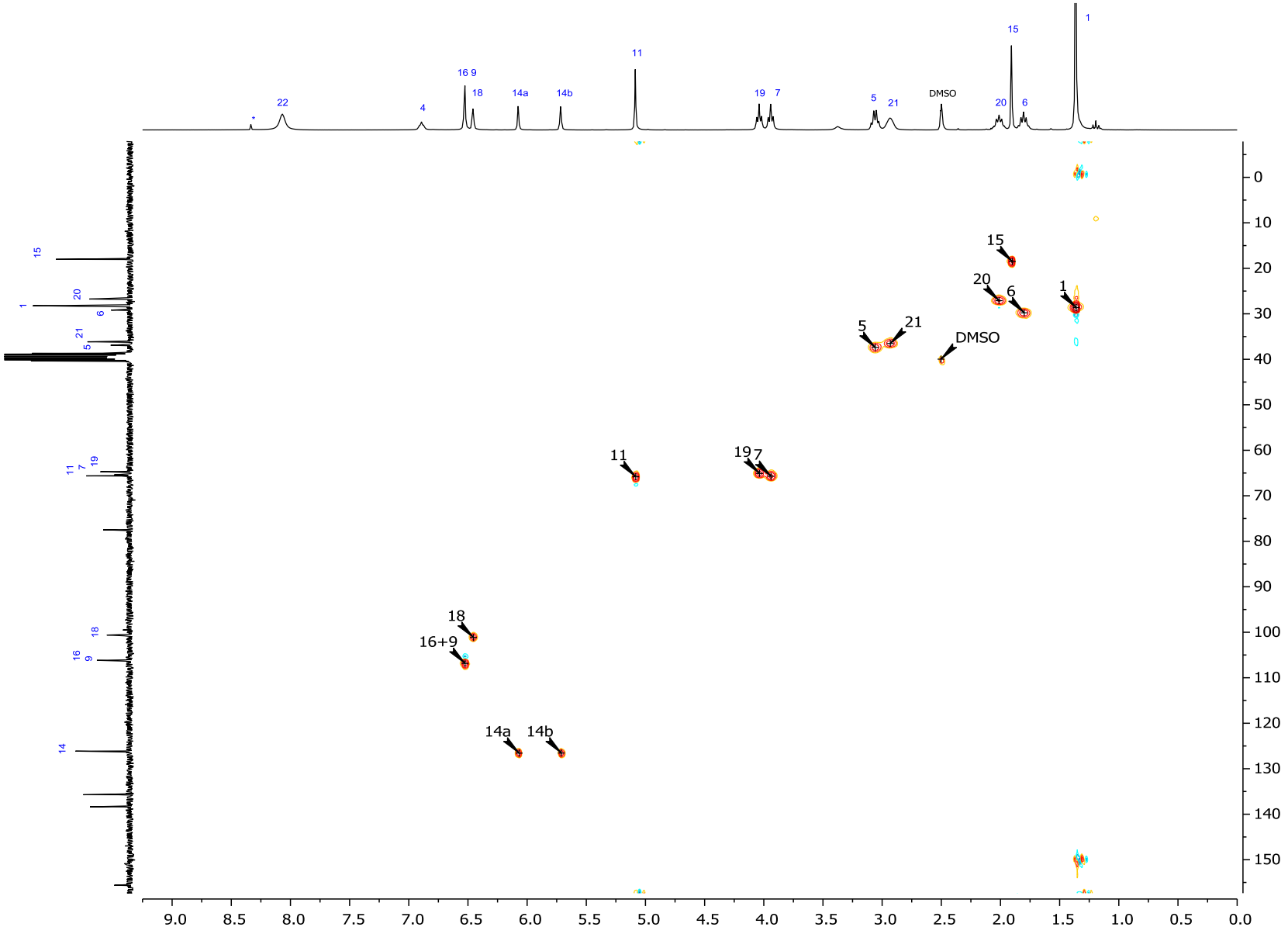
^{13}H NMR spectrum (DMSO-d6, 76 MHz) of compound **2a**:



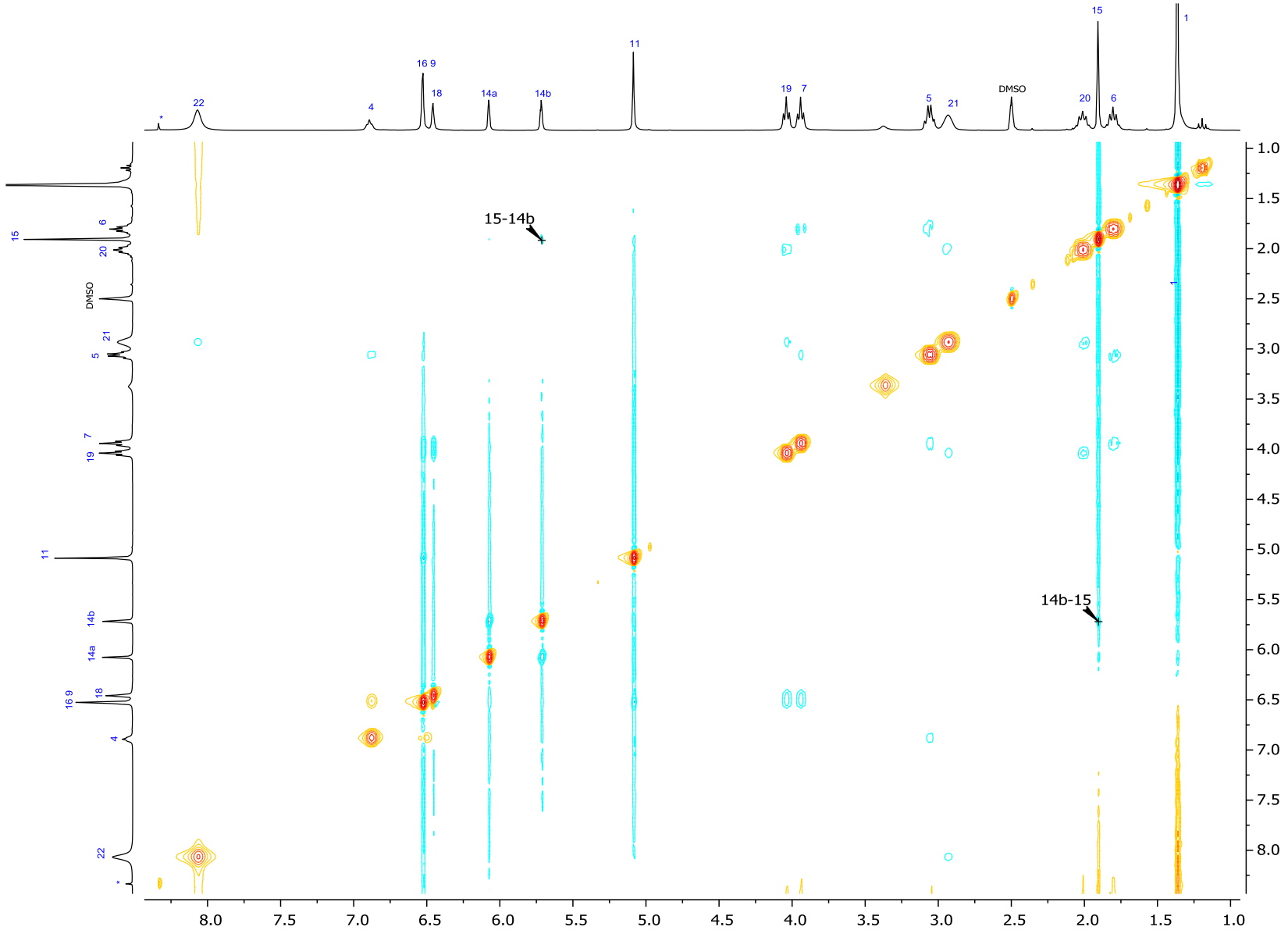
^{1}H-^{1}H COSY NMR spectrum (DMSO-d6) of compound **2a**:



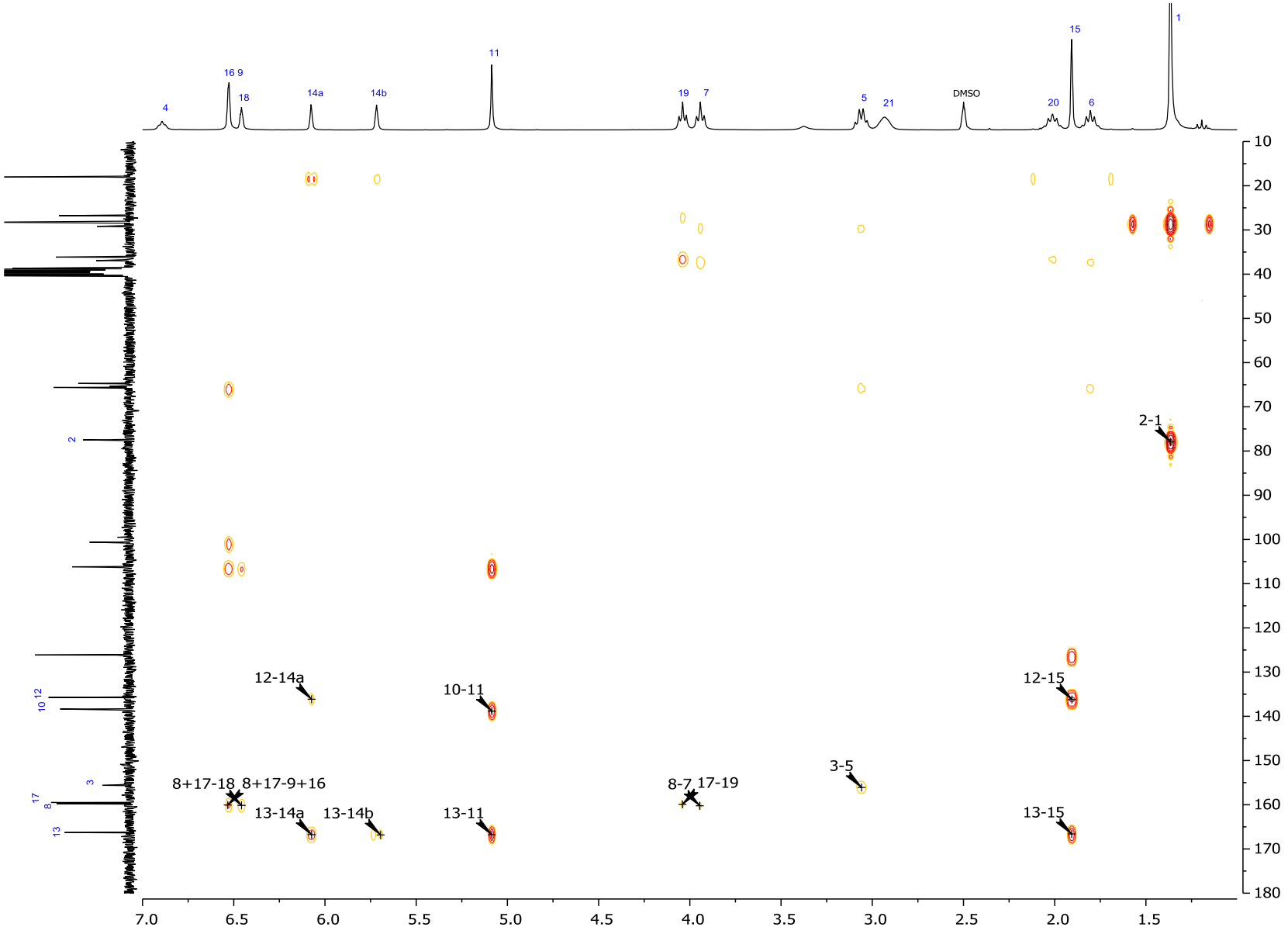
^{1}H-^{13}C HSQC NMR spectrum (DMSO-d6) of compound **2a**:



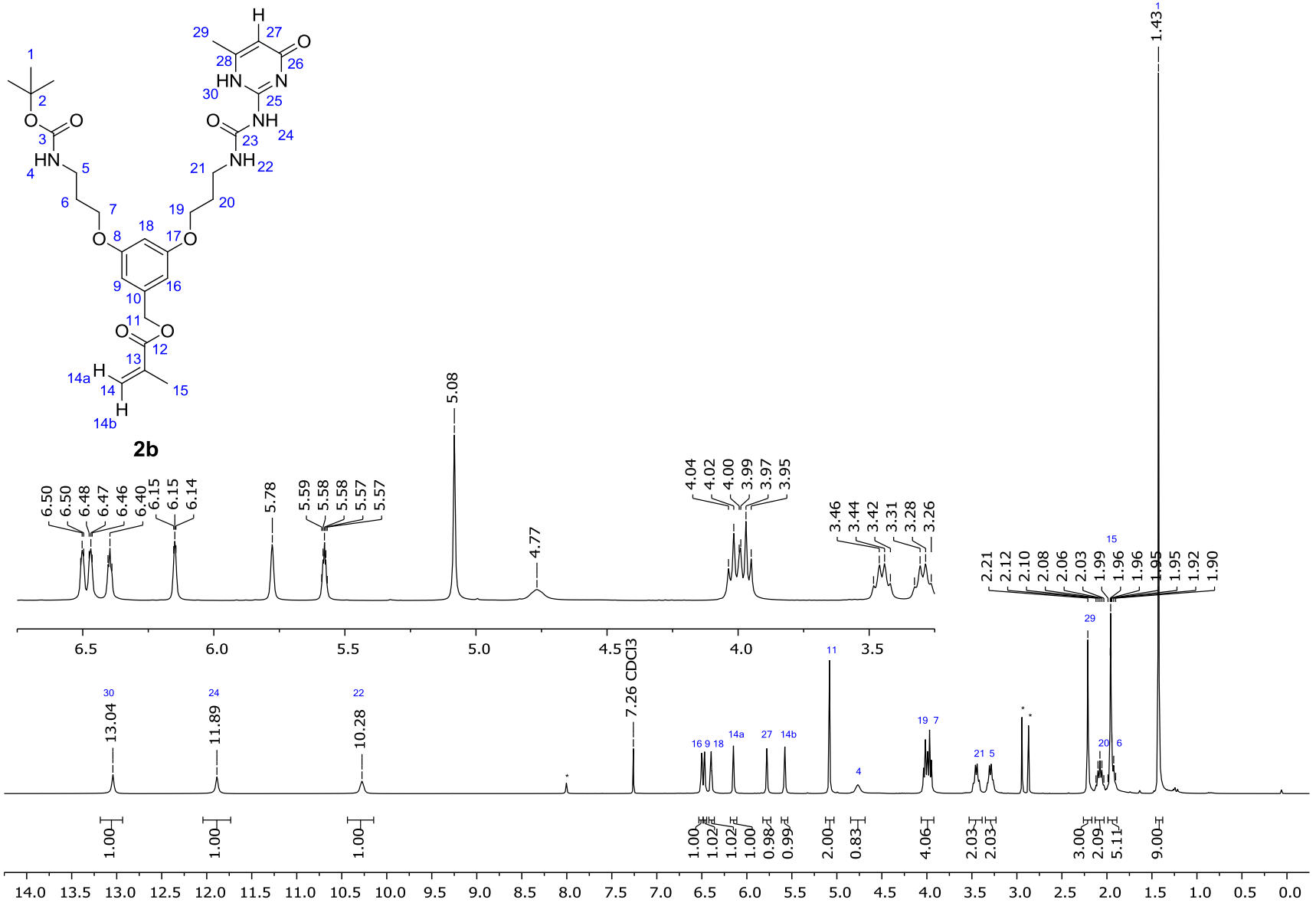
^{1}H-^{1}H NOESY NMR spectrum (DMSO-d6) of compound **2a**:



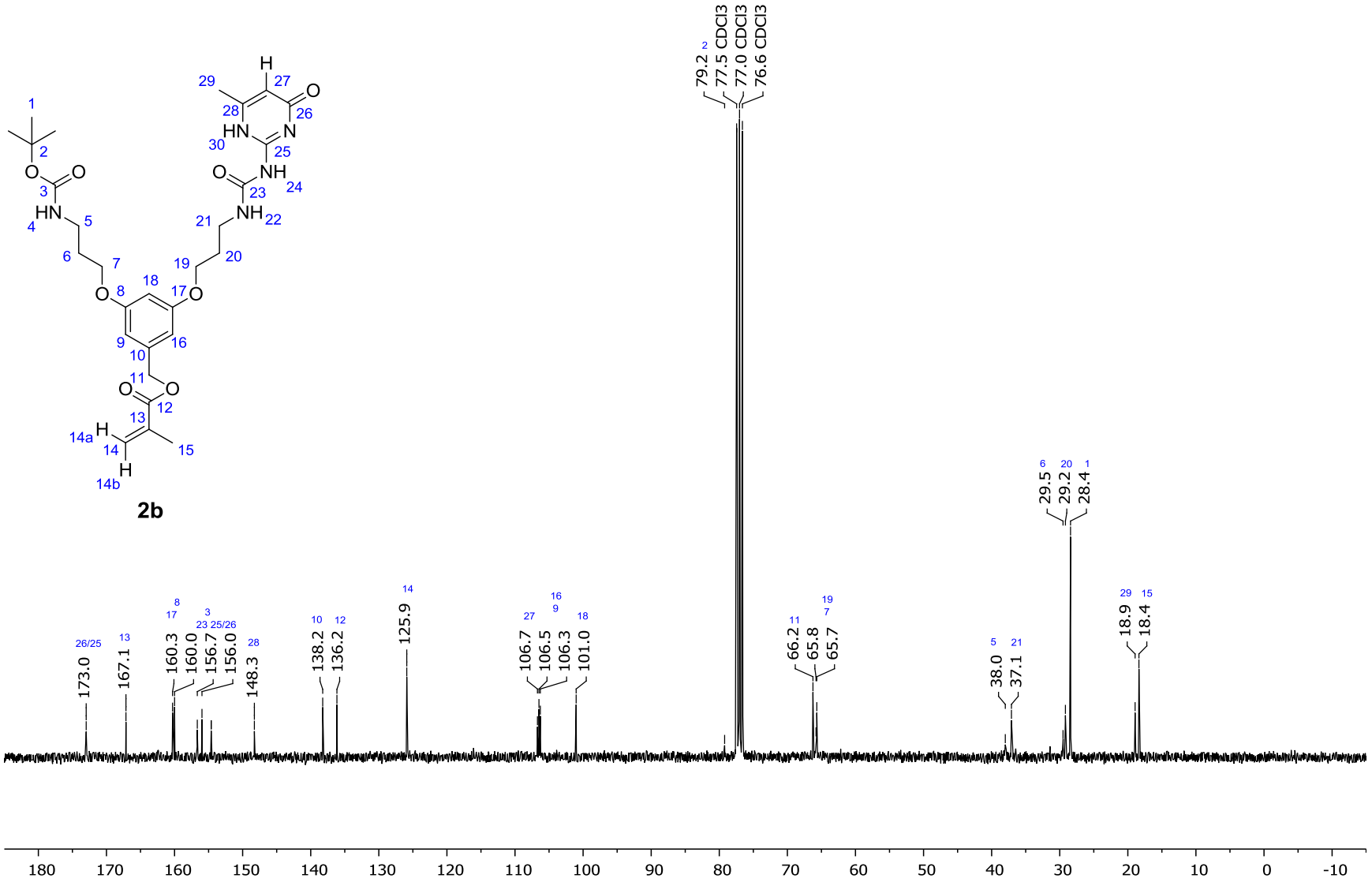
^{1}H-^{13}C HMBC NMR spectrum (DMSO-d6) of compound **2a**:



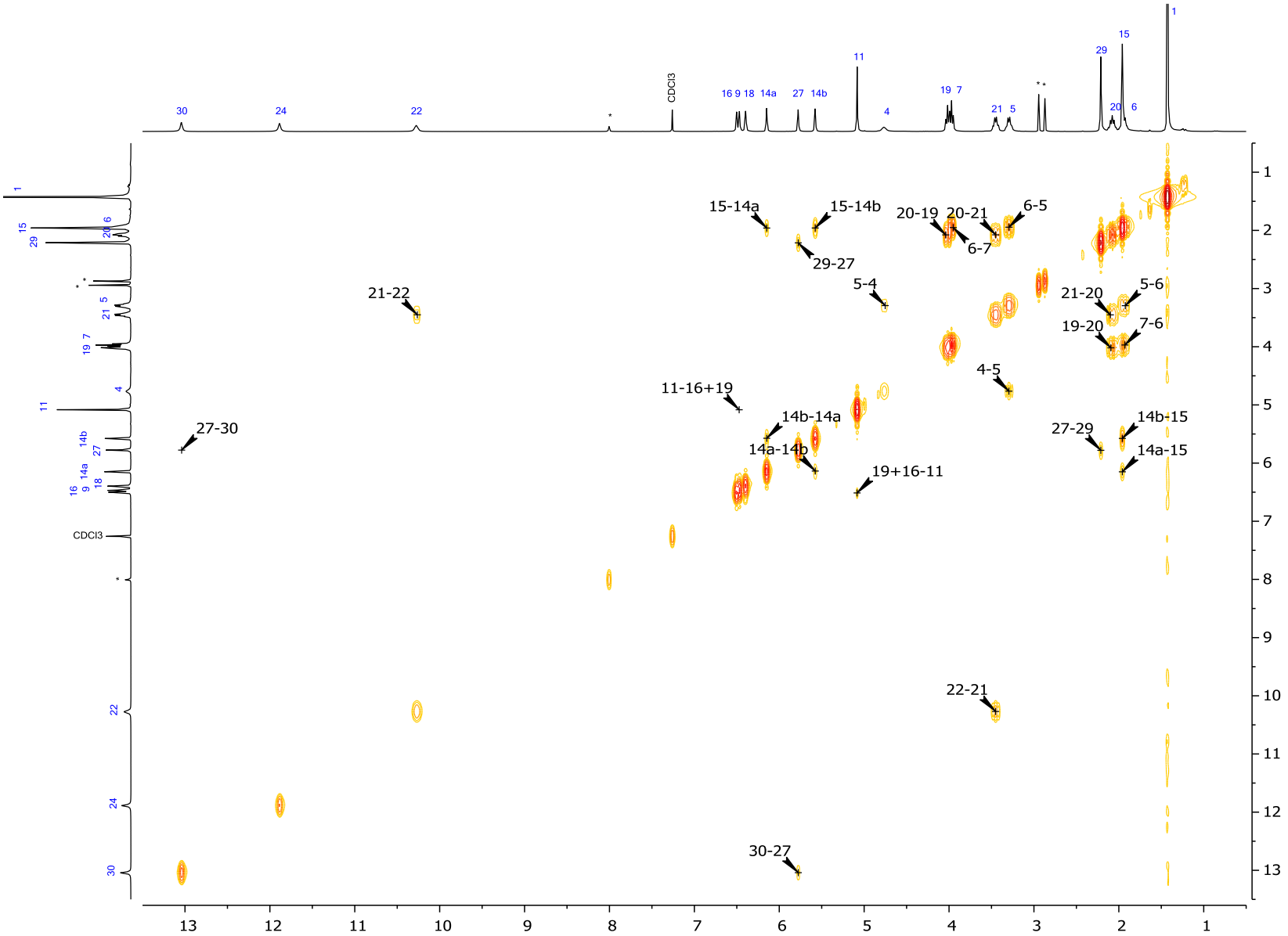
^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **2b**:



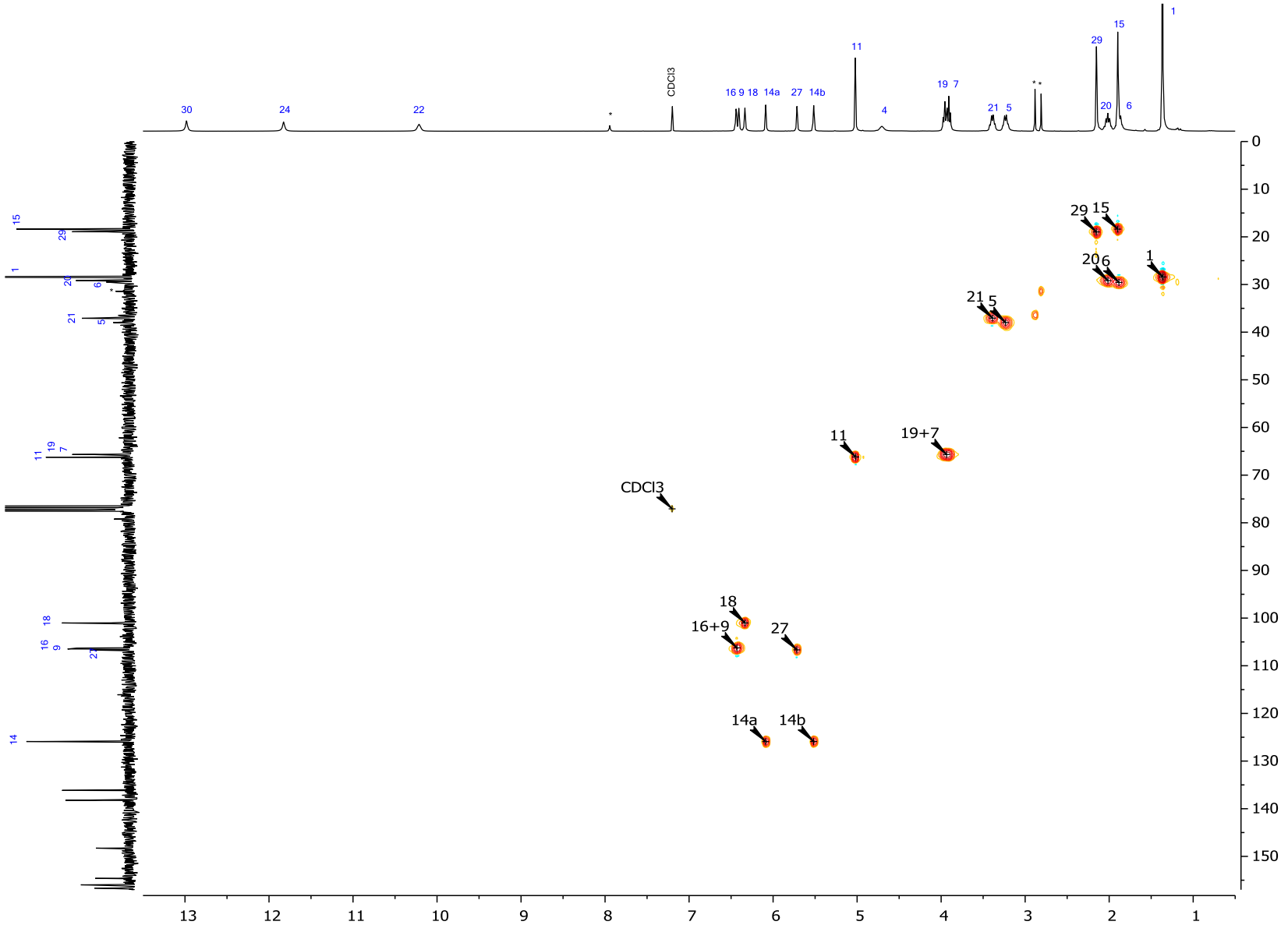
^{13}H NMR spectrum ($CDCl_3$, 76 MHz) of compound **2b**:



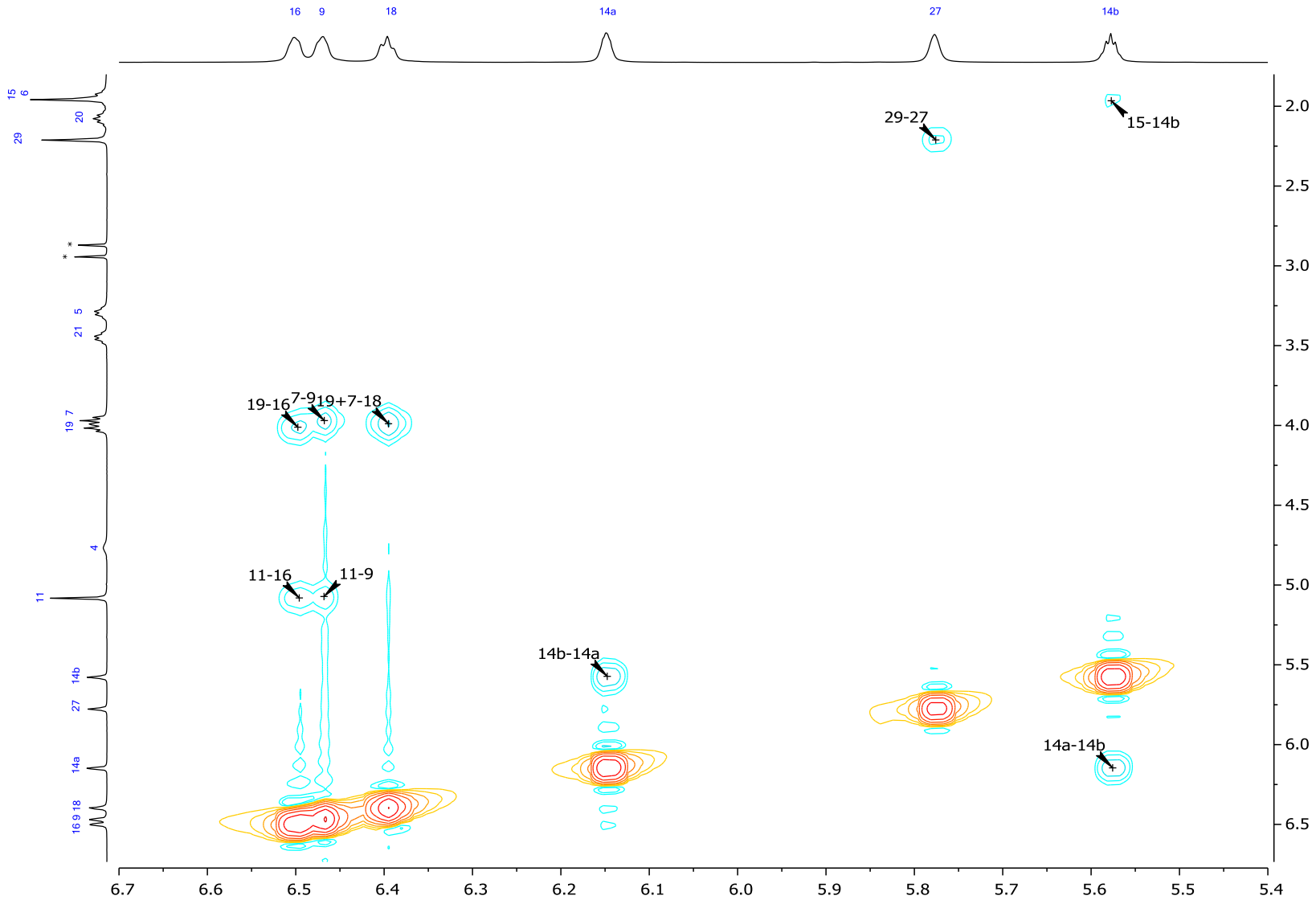
^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 300 MHz) of compound **2b**:



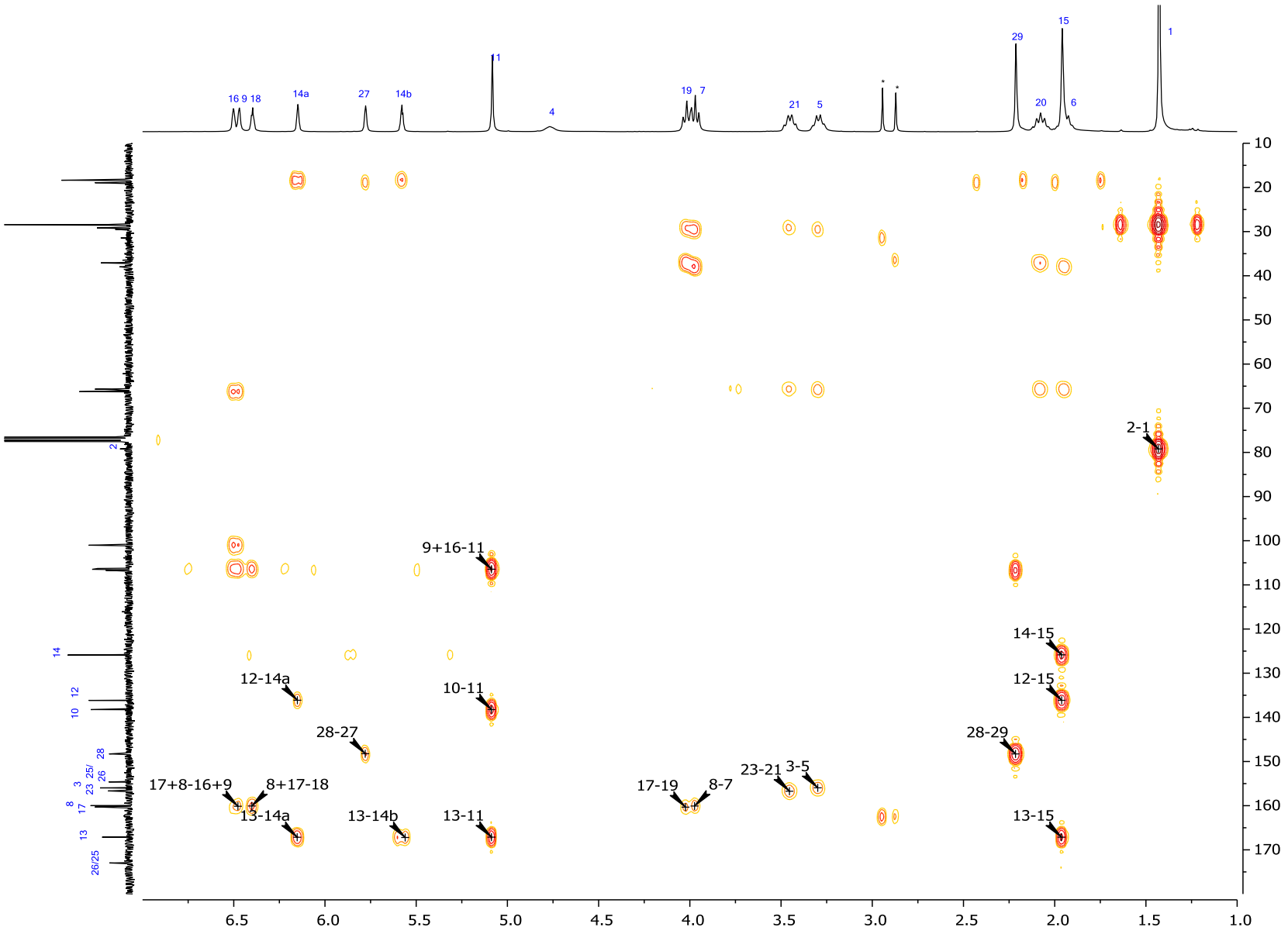
^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$, 300 MHz, 76 MHz) of compound **2b**:



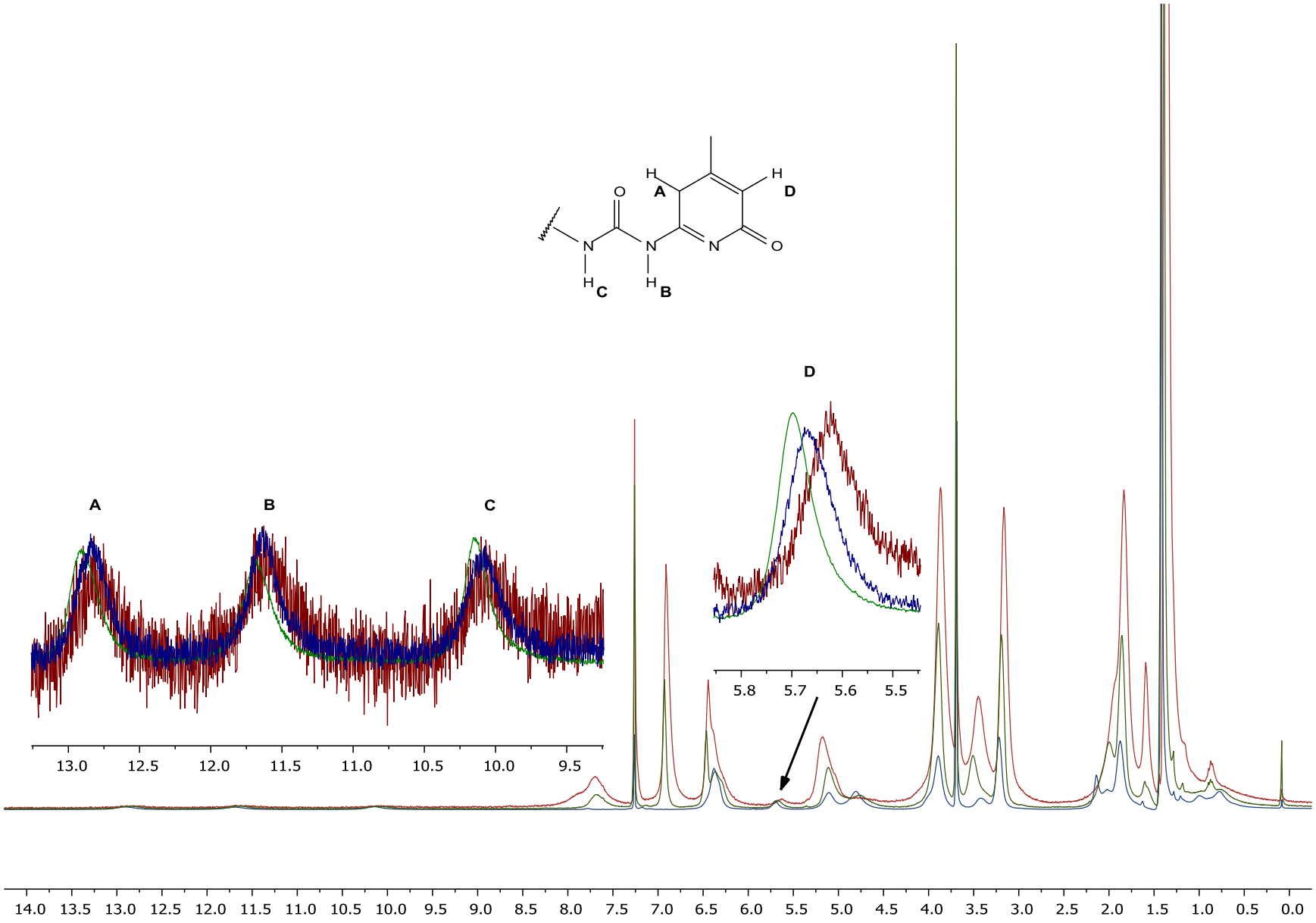
^{1}H-^{13}C NOESY NMR spectrum ($CDCl_3$, 300 MHz, 76 MHz) of compound **2b**:



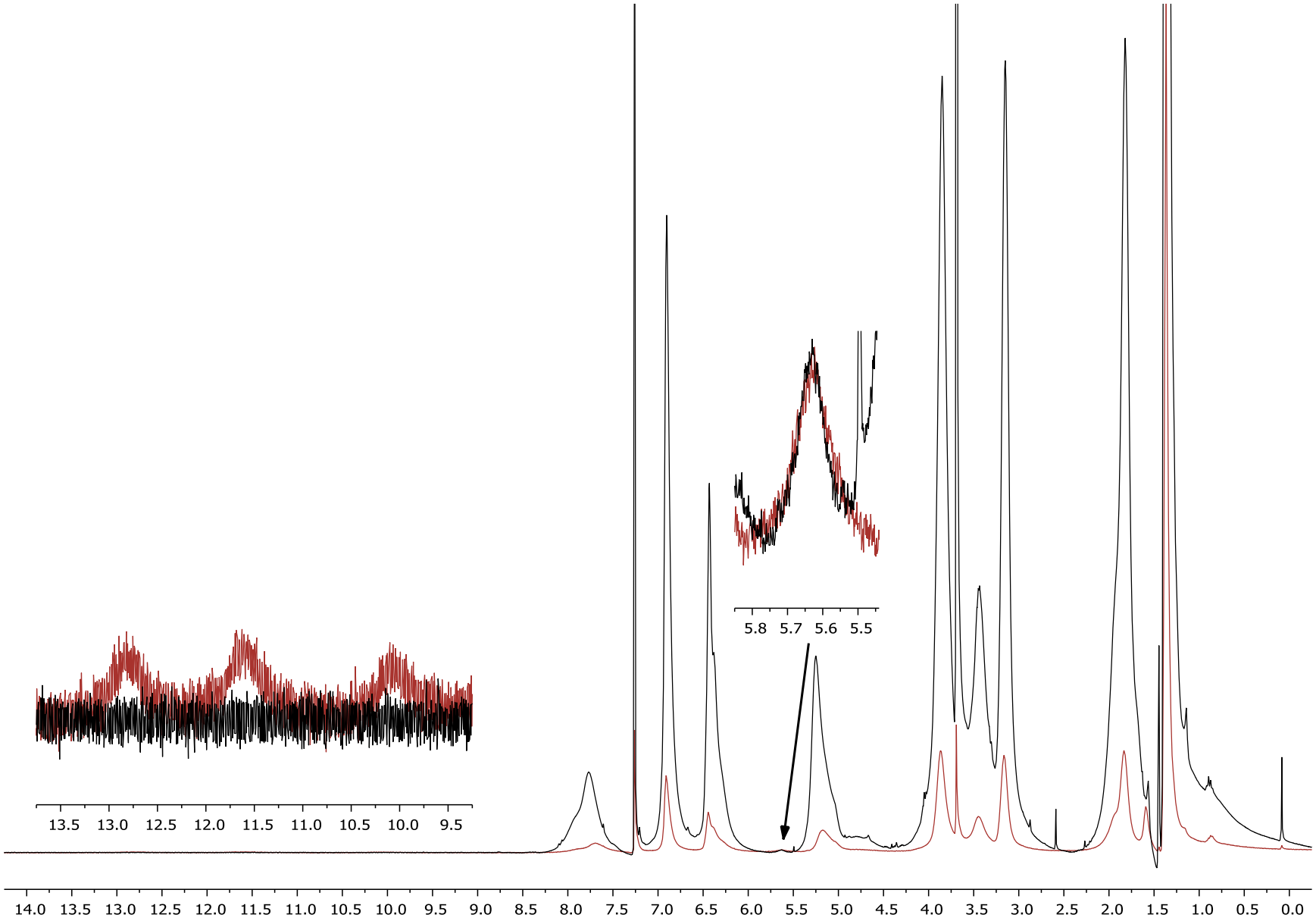
^{1}H-^{13}C HMBC NMR spectrum ($CDCl_3$, 300 MHz, 76 MHz) of compound **2b**:



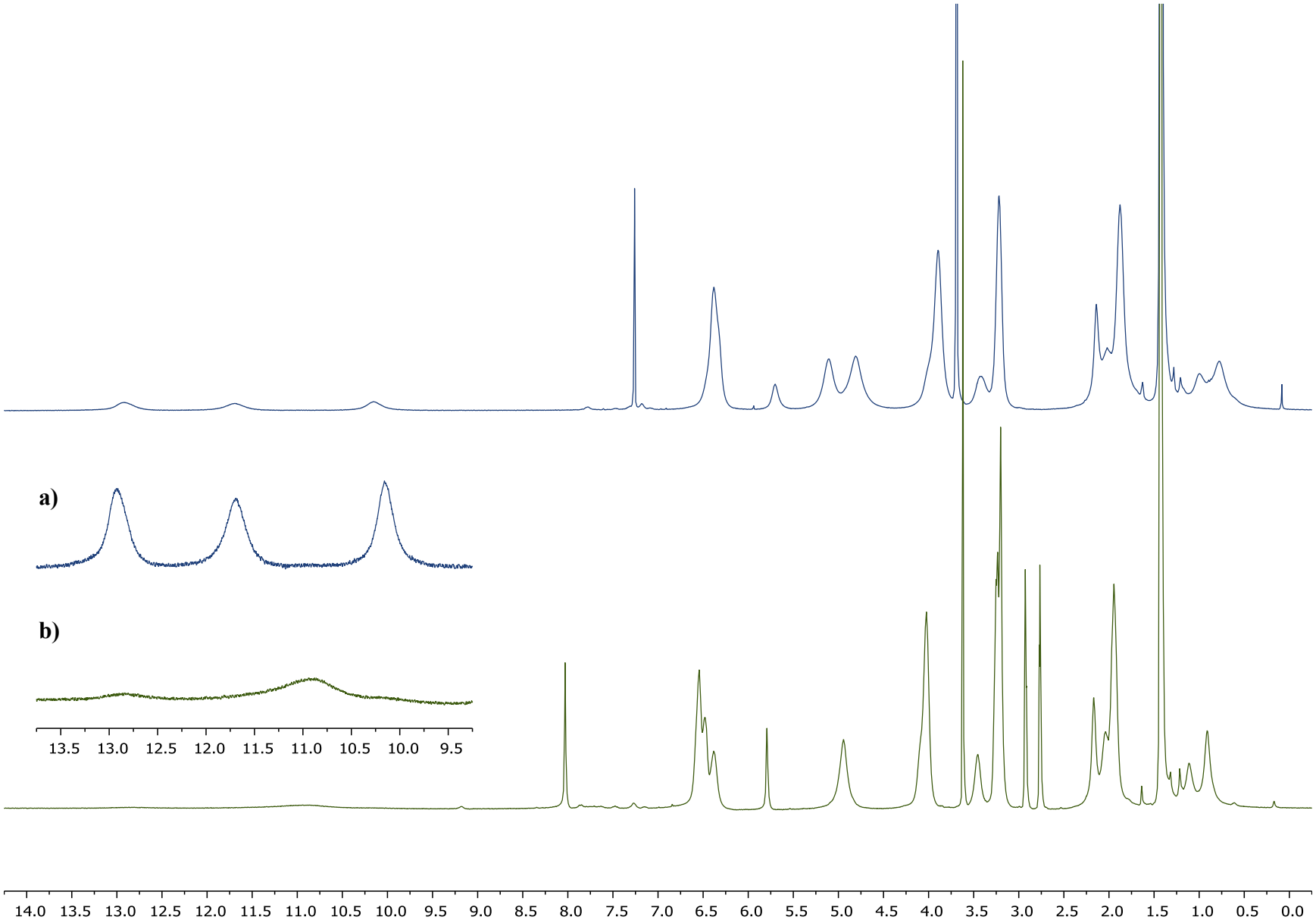
^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **PG1-40-UPy25** (olive), **PG2-40-UPy25** (blue) and **PG3-40-UPy25** (red):



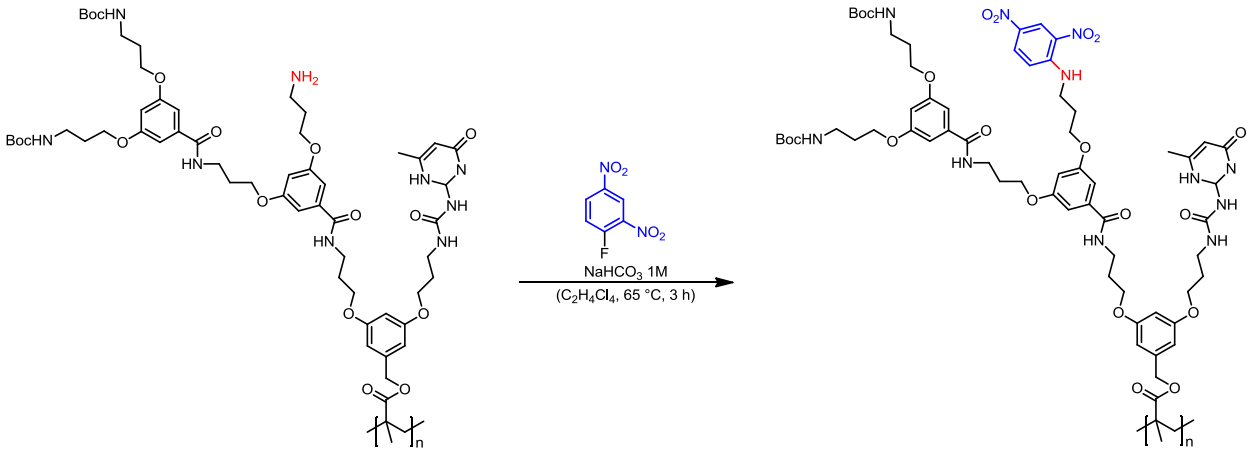
^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **PG3-40-UPy5** (black) and **PG3-40-UPy25** (red):



Comparison of the ^{1}H NMR spectra of **PG1-40-UPy25** recorded in (**a, blue**) $CDCl_3$ and (**b, olive**) DMF-d6:



S4 Supplementary procedure for quantification of structure perfection



Scheme 1. Schematic representation of the UV-labeling reaction of unreacted amines (defect sites) using 1-Fluoro-2,4-dinitrobenzene (Sanger's reagent).

Sample preparation:

The UV-labeled polymer samples were prepared following a slightly modified procedure previously reported by Zhang et al. (*Angew. Chem. Int. Ed.* **2011**, *50*, 737-740). The procedure is described exemplarily for the classic PG2-40-UPy25 sample: PG2-40-UPy25 (20.9 mg) was weighed in a 10 ml round bottom flask and dissolved in 1,1,2,2-tetrachloroethane (0.29 mL). After addition of $NaHCO_3$ (0.1 M solution, 0.36 mL) and Sanger's reagent (0.20 mL, 43 mM in 1,1,2,2-tetrachloroethane), the flask was sealed with a rubber sept and the reaction mixture was heated to 65 °C for 3 h with stirring. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and successively washed with saturated Na_2CO_3 solution (5 mL), water (5 mL) and brine (5 mL). After concentration of the organic layer *in vacuo*, the residue was dissolved in a minimum amount of CH_2Cl_2 and precipitated into Et_2O. The precipitation step was repeated twice. After freeze-drying from 1,4-dioxane, 2,4-dinitroaniline-labeled PG2-40-UPy25 (19 mg, 91%) was obtained as a slightly yellow foam.

Quantification of dendronization:

The quantitative UV experiments were performed on a UV-670 UV/Vis spectrophotometer from JASCO by using 10 mm quartz cuvettes. The UV-labelled polymers were dissolved in 1,1,2,2-tetrachloroethane with concentrations of about 2.641×10^{-4} mol/L (repeat unit). The extinction coefficient of 2,4-dinitroaniline moiety ($\varepsilon = 1.64 \times 10^4$ L·mol^{-1}cm^{-1}) was taken from a previous report. The concentration of the dinitroanilino moieties, which is also considered as the concentration of unconverted terminal amino groups (supposing all the unreacted amino groups in the dendronization were labeled by treating with Sanger's reagent), was calculated according to the Lambert-Beer law (Equation 1):

$$c = \frac{A}{\varepsilon \cdot l} \qquad \text{(Equation 1)}$$

In this equation, l denotes the inside width of the UV cuvettes (1.0 cm) and A denotes the absorbance at 357 nm. The structure perfection X for the conversion from *de*-PG1 to PG2 was therefore calculated as $X = 1\text{-}(c/c_0) \times 100\%$, in which c denotes the concentration of 2,4-dinitroanilino moieties, and c_0 denotes the concentration of total termini in the starting material (de-PG1). The UV-Vis spectra of the labeled UPy DPs are shown in Figure S1. The results for the degree of coverage (*i.e.* the perfection of the dendronization) X were calculated from the absorption of labeled dendronized polymers at 357 nm and are summarized in Table S1:

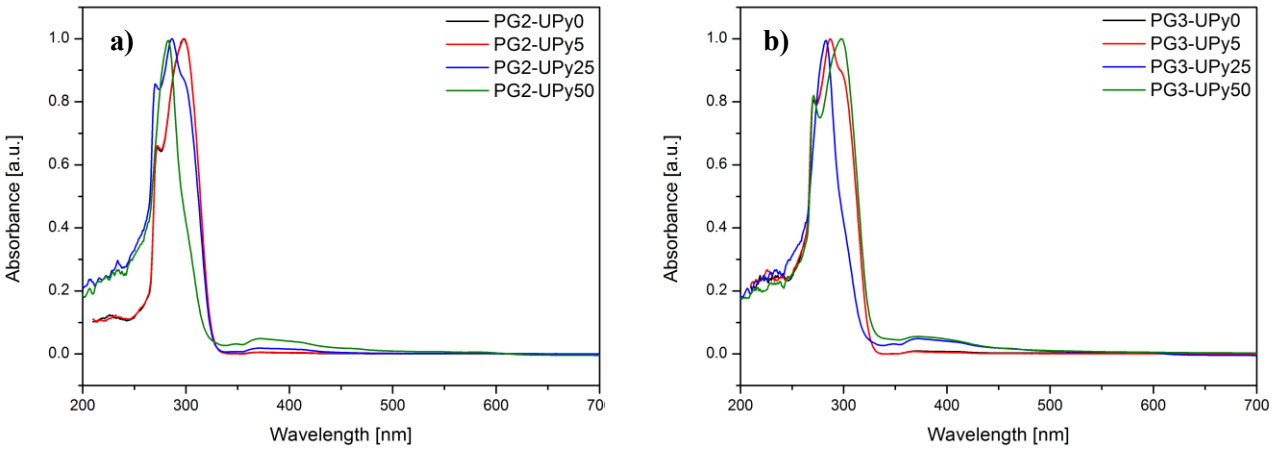


Figure S1. Normalized UV-Vis spectra of Sanger-labeled DPs with (**a**) $g = 2$ and (**b**) $g = 3$. Black, 0 mol% UPy; red, 5 mol% UPy; blue, 25 mol% UPy; olive, 50 mol% UPy.

Table S1. Summarized results of the DP labeling experiments.

Entry	Sample	c [mol/L]	c_0 [mol/L]	A (at 357 nm)	X [%]
1	PG2-UPy0	$5.46463 \cdot 10^{-6}$	0.002740379	0.08962	99.8
2	PG2-UPy5	$3.35134 \cdot 10^{-6}$	0.001645352	0.05496	99.8
3	PG2-UPy25	$1.27622 \cdot 10^{-6}$	0.00039615	0.02093	99.7
4	PG2-UPy50	$5.17634 \cdot 10^{-6}$	0.000583636	0.084892	99.1
5	PG3-UPy0	$2.4311 \cdot 10^{-6}$	0.001470096	0.03987	99.8
6	PG3-UPy5	$8.33537 \cdot 10^{-7}$	0.000725956	0.01367	99.9
7	PG3-UPy25	$6.26902 \cdot 10^{-6}$	0.000826725	0.102812	99.2
8	PG3-UPy50	$6.72707 \cdot 10^{-6}$	0.000739682	0.110324	99.1

S5 Supplementary GPC traces

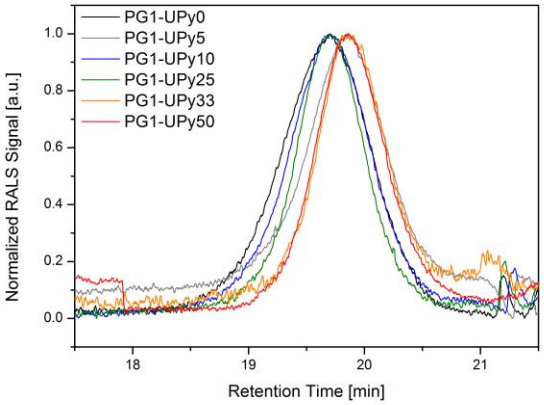


Figure S2. DMF GPC elution traces of PG1 comprising 0-50 mol% UPy in their side chains.

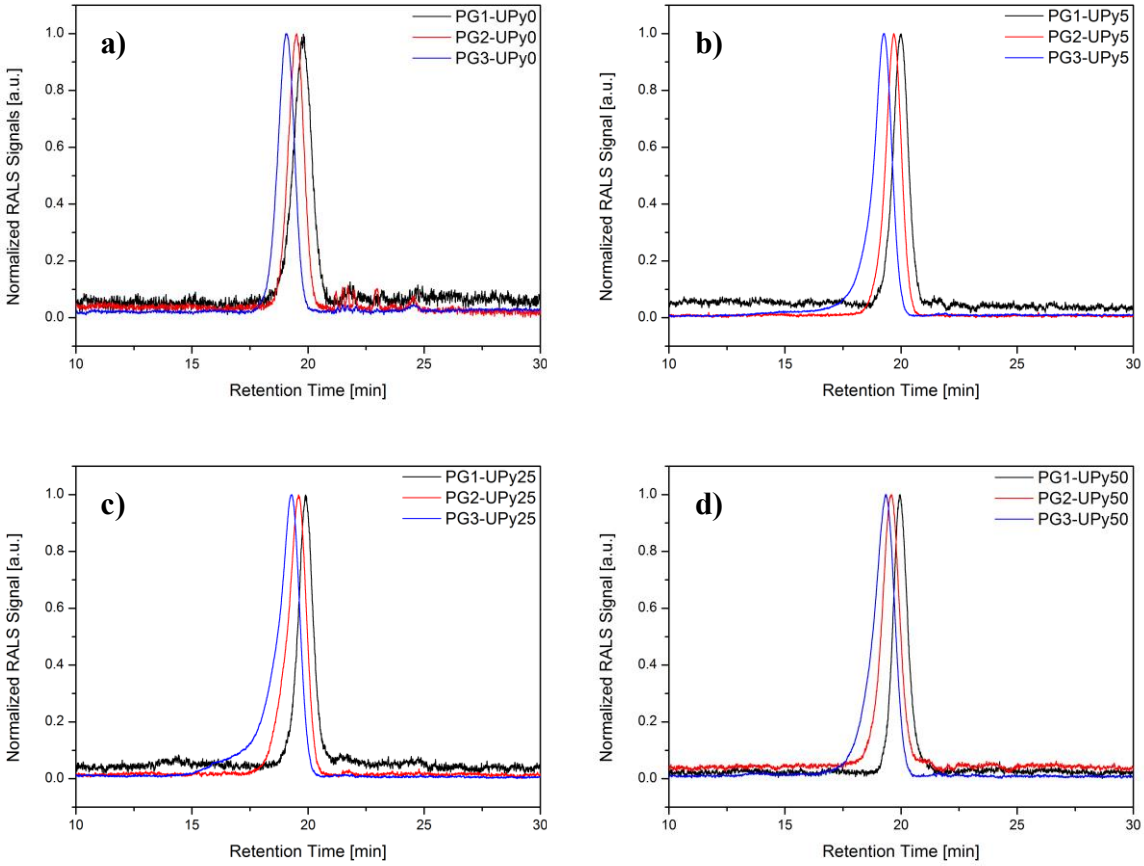


Figure S3. GPC elution traces of PG1-3 in DMF containing (**a**) 0 mol% UPy, (**b**) 5 mol% UPy, (**c**) 25 mol% UPy, and (**d**) 50 mol% UPy. The elution peak maxima shift towards shorter retention times with increasing polymer generation, irrespective of the degree of UPy-functionalization, consistently.

S6 Supplementary DSC traces

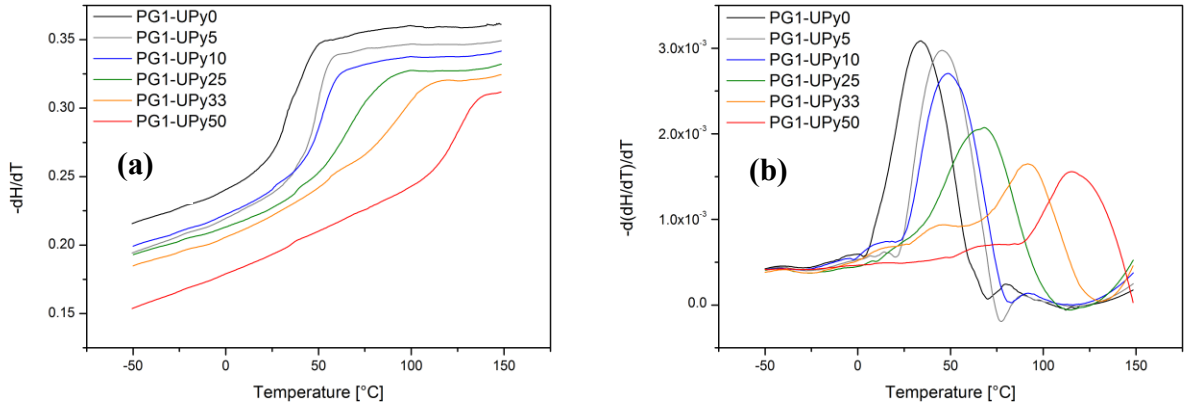


Figure S4. (**a**) Second heating DSC thermograms for the first-generation DPs comprising 0 – 50% UPy normalized by the sample weight. In (**b**), the differentiated traces are shown to better visualize the shift and broadening of the glass transition.

Table S2. Summary of the determined T_g values for PG1-3-UPy(f) with $P_n \approx 40$. [a] Standard deviations of 3 individual measurements.

	PG1		**PG2**		**PG3**	
UPy [%]	T_g [°C]	SD[a] [°C]	T_g [°C]	SD[a] [°C]	T_g [°C]	SD[a] [°C]
0	37.7	1.8	64.1	0.7	69.4	0.8
5	50.9	2.9	67.5	1.3	70.7	0.5
10	53.6	1.1	-	-	-	-
25	69.0	0.8	74.5	0.6	75.2	0.7
33	94.4	1.0	-	-	-	-
50	127.7	1.7	92.4	0.7	83.4	0.7

S7 Supplementary TGA traces

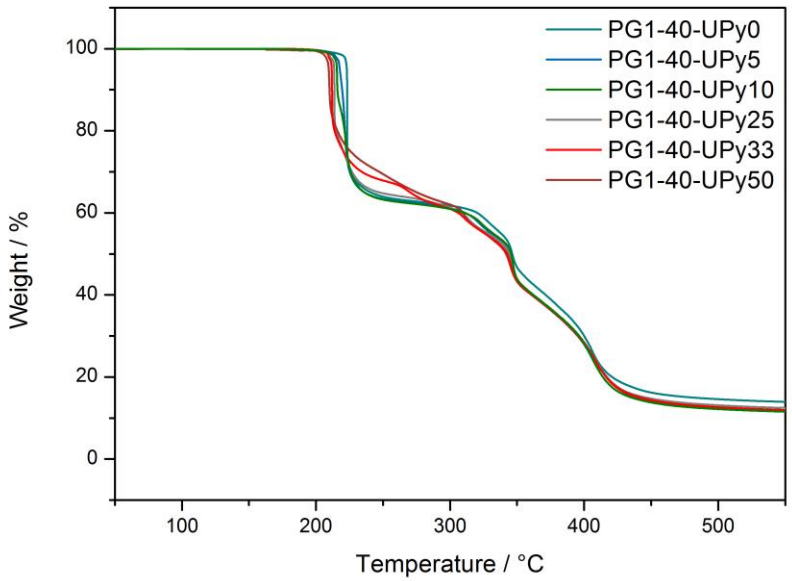


Figure S5. Thermal degradation of PG1-40 with degrees of UPy-functionalization ranging from 0 – 50%. All measurements were performed at a heating rate of 20 °C min^{-1} in N_2.

S8 Ageing effects and annealing protocol

Dendronized polymers (DPs) are synthesized in dilute environment. After synthesis, they are freeze-dried in order to remove solvent. The freeze-dried systems are out of equilibrium as density gradients originate in such materials after solvent removal. When temperature of freeze-dried samples is increased above T_g, the outermost branches of DPs tend to interpenetrate each other in order to minimize intermolecular density gradients. This interdigitation process is slow and the time required to approach an equilibrium state depends on the initial conditions of the pristine samples and the particular protocol used for sample preparation. For this reason, rheological properties of DPs melts depend on the history of the samples.

In previous work (Costanzo et al., Macromolecules **2016**, *49*, 7054-7068), we used a specific protocol for equilibration of the samples (henceforth referred to as protocol 1): we loaded the samples into the rheometer at $T_g + 30$ °C and, after a short time for thermal stabilization of the specimen and rheometric tools (20 min), we monitored the time evolution of the dynamic moduli. We assumed equilibrated structure when both moduli reached plateau values over time. With this protocol we obtained consistent linear mastercurves and shift factors for different samples of same generation. However, such protocol is impracticable for nonlinear rheological measurements. Particularly for uniaxial extension, specimens easily break and need to be replaced at every transient startup test. Moreover, the amount of sample needed for fresh specimens at each measurement is much larger than the typical quantities available from the lab synthesis of DPs (100-150 mg). Therefore, we treated the UPy-functionalized samples with a different protocol (henceforth referred to as protocol 2) compared to classic DPs. More specifically we attempted to erase the previous sample history through thermal annealing at high temperature for long time. To this end, we annealed all the samples in vacuum at the highest possible temperature (100 °C) for 8 days, compatibly with chemical stability of DPs. Then, we started with rheological measurements directly after the necessary time for thermal stabilization of the specimen and rheometric tools (approximately 20 min). With such a procedure, we could obtain reproducibility of both linear and nonlinear data, irrespective of the fact that some of the samples were recycled from previous measurements, as demonstrated in Figure 2 of the main text.

Interestingly, following protocol 1 (loading at $T_g + 30$ °C and equilibration into the rheometer) leads to different equilibration state with respect to thermal annealing of protocol 2. Figure S6 shows the equilibration performed on pristine samples (before annealing) of PG1-40-UPy5 and PG1-40-UPy10 following protocol 1. Equilibration was performed at approximately 30 °C above T_g.

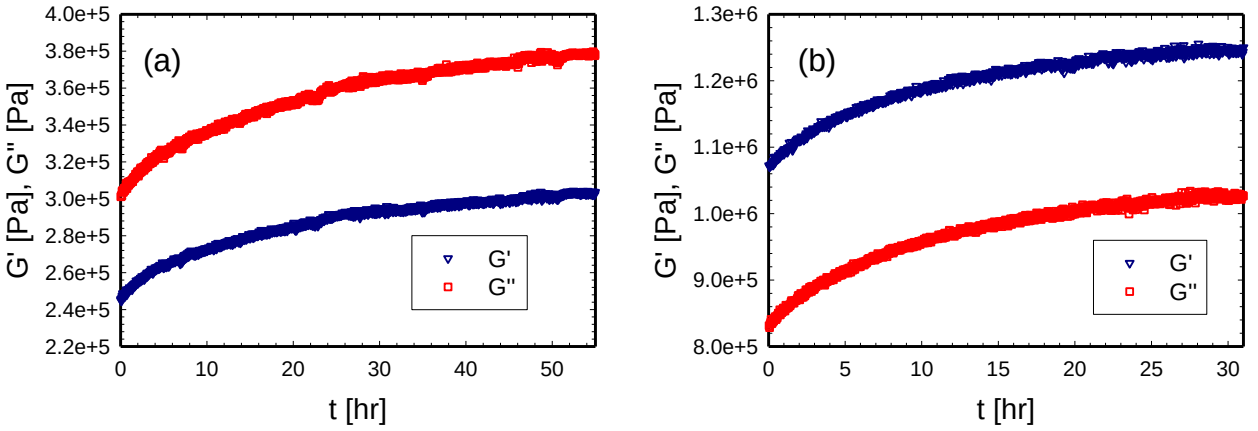


Figure S6: (a) Equilibration of the sample PG1-40-UPy5 at 80 °C and (b) equilibration of the sample PG1-40-UPy10 performed at 80 °C.

After equilibration as in Figure S6, we proceeded with linear rheological measurements. The linear mastercurves obtained with protocol 1 are shown in Figure S7 along with those from protocol 2, at the same reference temperature. Horizontal shift between the mastercurves obtained with the two procedures is evident, as indicated also from the respective position of the minima of the loss factors.

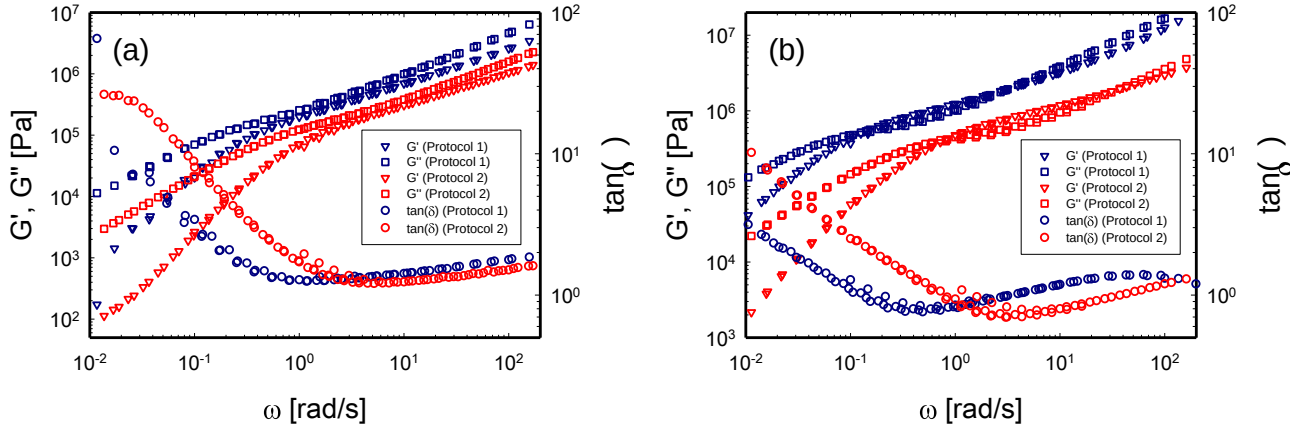


Figure S7: (a) mastercuves of the sample PG1-40-UPy5 with thermal annealing (Protocol 1) and equilibration (Protocol 2). Mastercurves are at T_{ref} = 90 °C in both cases. (b) Mastercuves of the sample PG1-40-UPy10 with thermal annealing (Protocol 1) and equilibration (Protocol 2). Mastercurves are at T_{ref} = 90 °C in both cases.

We argue that the horizontal shift cannot be attributed to residual solvent trapped in the systems. Indeed, the quantity of remaining solvent after synthesis was found negligible, as demonstrated from the NMR spectra. We can speculate that, interdigitation process as induced from protocol 1 is incomplete and leads

the system to a metastable equilibrium where the hydrogen bonding units (UPy and Boc) are not all associated and the free branches act as diluent, speeding up molecular dynamics. On the other hand, protocol 2 brings to an equilibrium state where all hydrogen bonding groups are associated. In such a situation molecular dilution is suppressed and dynamics slowed down. Moreover, extra bonding does not bring a significant contribution to the elastic plateau modulus which is almost identical in the two cases (conversely to dilution in amorphous polymers by molecular solvents).

The effect of annealing on the dynamics is further confirmed in Figure S8 where we report dynamic frequency sweep tests carried out on the unfunctionalized pristine sample PG1-40 at different times from loading. From Figure S8a, one can observe horizontal shifting of dynamic moduli as the annealing proceeds. The fact that the shift is mainly horizontal is ascertained by considering the evolution of the loss factor (Figure S8b).

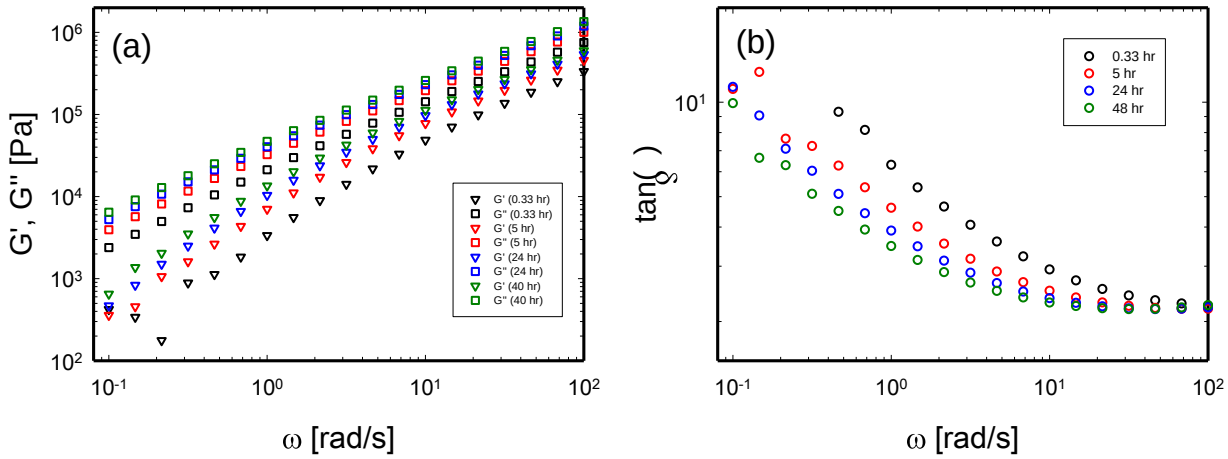


Figure S8: ageing of the sample PG1-40. (a) dynamic moduli as a function of angular frequency, ω at different times after loading into the rheometer (tests are performed at the same strain value, 4% and temperature, 80 °C). (b) Corresponding loss factor, tan(δ).

In order to be consistent with measurements on UPy DPs, the sample PG1-40 has been treated according to protocol 2 and the corresponding LVE re-measured.

S9 Time temperature superposition (TTS)

UPy-DPs are expected to be thermo-rheologically complex as the temperature dependence of the characteristic time scale for supramolecular associations is different compared to the other relaxation processes of the system (dictated by molecular friction). In principle, time-temperature superposition is not applicable to thermorheologically complex materials. However, by observing the shape of the frequency-dependent dynamic moduli at different temperatures, one can see that data can be adequately superimposed in order to obtain apparent mastercurves.

In such a case, the procedure for TTS is based on a two dimensional minimization approach. First, we superimpose the curves of tan(δ) at different temperatures in such a way to minimize the sum of distances between two neighbouring points. The reason for first shifting tan(δ) is that the shift of the loss factor is only horizontal. After horizontal shifting of tan(δ), the curves of elastic and viscous moduli are vertically shifted according to the same criterion. In order to apply this procedure we use the software TA Orchestrator (TA instruments, USA). The horizontal apparent shift factors to build the mastercurves of Figure 3 of the main text are reported in Figure S9.

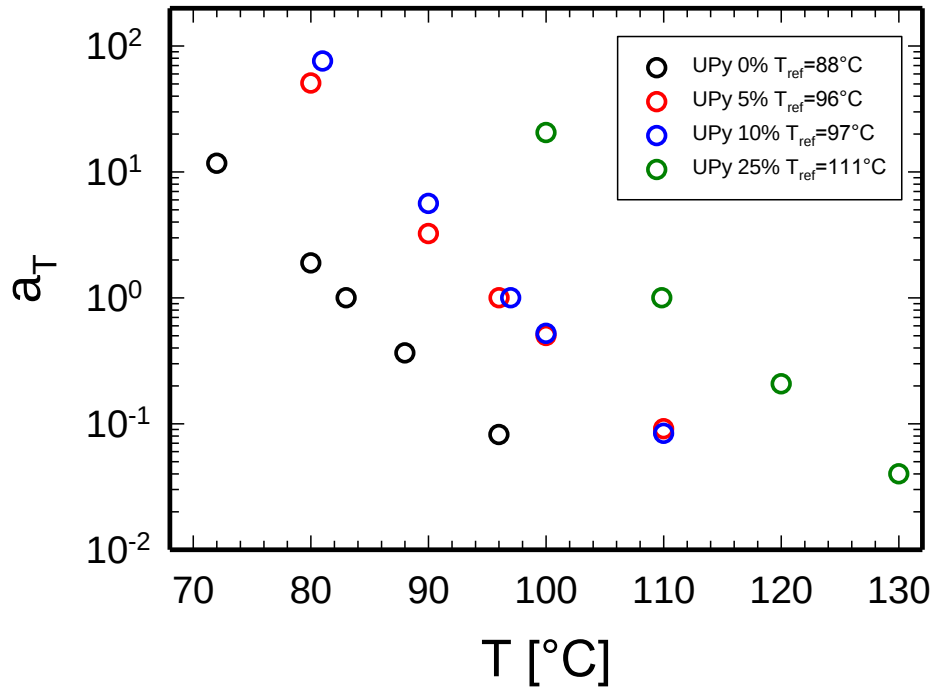


Figure S9: Horizontal shift factors obtained in order to build the mastercurves of Figure 3 of the main text at $T_{ref} = T_g + 45$ °C.

Vertical shift factors are of the order of unity. The failure of TTS for UPy-functionalized samples is confirmed by the Van-Gurp-Palmen plots of the different samples (Figure S10). The scattering of the data points at different temperatures increases around the minimum of the phase angle as the UPy

content is increased. This region corresponds to the intermediate frequency range, namely to the elastic plateau region.

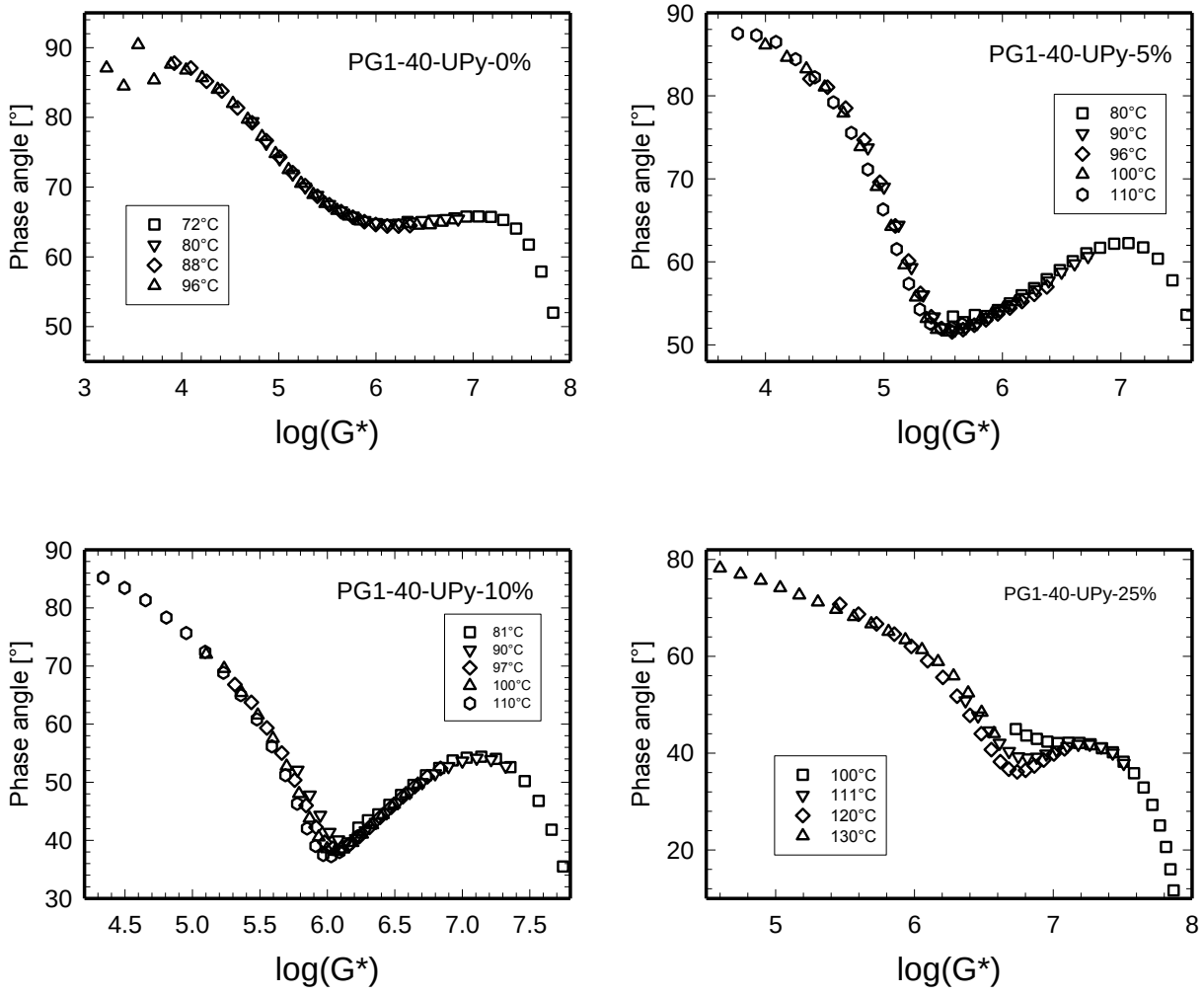


Figure S10: Van Gurp-Palmen plots for PG1-40-UPy samples.

S10 Evaluation of the terminal relaxation time

The characteristic time of PG1-40-UPy5 as evaluated in Figure S11 is $\tau_D = 75 \pm 10\ s$ at T = 80 °C.
The characteristic time of PG1-40-UPy10 as evaluated in Figure S11 is $\tau_D = 800 \pm 100\ s$ at T = 81 °C.

.

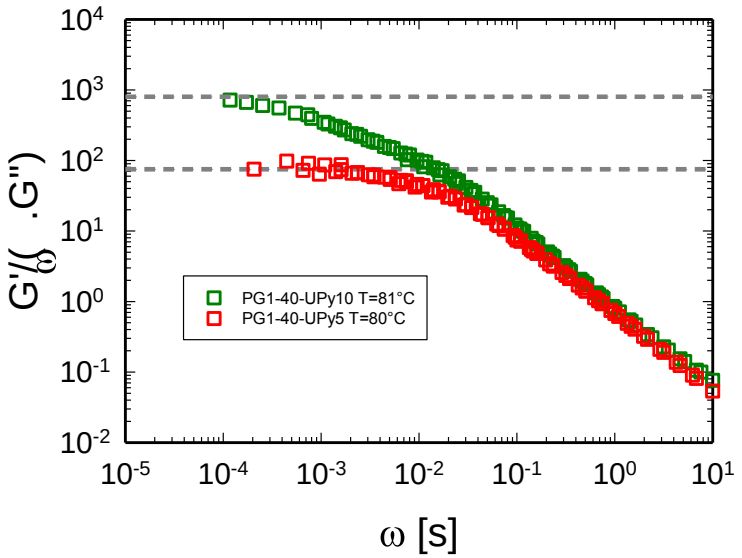


Figure S11: Evaluation of the terminal relaxation time of PG1-40-UPy5 at T = 80 °C and PG1-40-UPy10 at T = 81 °C.

S11 Other rheological data

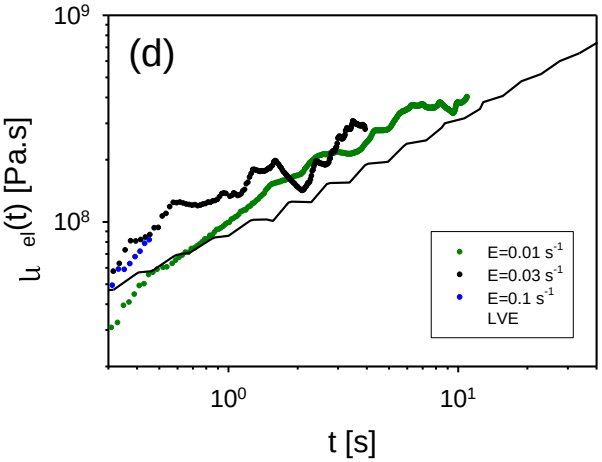


Figure S12: Extensional measurements on the sample PG1-40-UPy25. Extensional rates are indicated with the symbol E.