

Chemistry–A European Journal

Supporting Information

Oligo-Quinolyene–Vinylene Foldamers

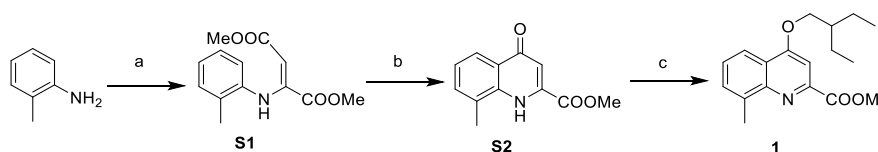
Jinhua Wang,^[a] Barbara Wicher,^[b] Victor Maurizot,^{*[a]} and Ivan Huc^{*[a, c]}

General Remarks:.....	2
Monomer Synthesis	2
Oligomer synthesis:	3
Synthesis of compounds 6-11:	5
Synthesis of compounds 14-16:	8
Synthesis of compounds 19, 19', 20 and 21:	12
UV-Vis spectra and fluorescence spectra measurements:	15
Additional figures and tables:	16
X-ray diffraction measurements:	26
NMR spectra of synthesized compounds:.....	29
References:.....	61

General Remarks: All the solvents and reagents were used as received unless otherwise specified. All chemicals were used as received from commercial suppliers without further purification unless otherwise specified. Anhydrous THF was obtained from distillation over sodium/benzophenone. Chloroform and diisopropylethylamine were distilled from calcium hydride before use. ^1H NMR, ^{13}C NMR and 2D NMR spectra were recorded on BRUKER AVANCE 300 MHz or 400 MHz spectrometers. Chemical shifts were presented in parts per million (δ , ppm) using solvent residue peaks as references (chloroform $\delta = 7.26$ ppm, dichloromethane $\delta = 5.32$ ppm, acetone $\delta = 2.05$ ppm). Coupling constants are reported as Hertz. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60-F254 plates and observed under UV light. Column chromatography purifications were carried out on Merck GEDURAN Si60 (40-63 μm). ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the European Institute of Chemistry and Biology (UMS 3033 - IECB), Pessac, France. UV-Vis spectra were recorded on Varian[®] Cary 300 Scan UV-Visible spectrophotometer at room temperature. Fluorescence spectra were recorded on HORIBA FluoroMax-4 spectrofluorometer at room temperature.

Monomer Synthesis

The synthesis of monomer **1** was achieved by following a previous procedure of similar monomer with minor modifications.¹ Compound **S1** and **S2** have been reported recently.²



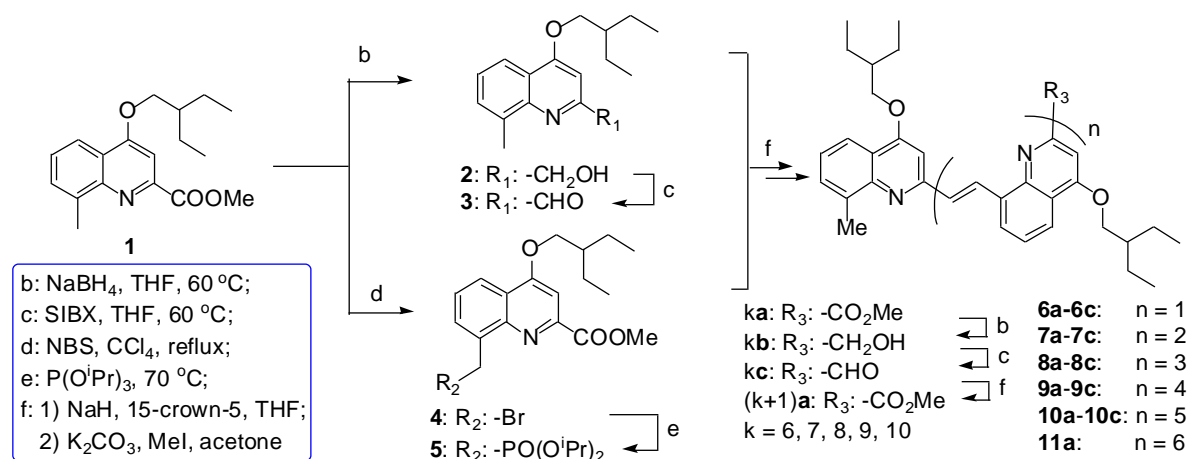
Scheme S1: Synthetic route for monomer **1**. a) dimethyl acetylenedicarboxylate, MeOH, 65 °C; b) Ph₂O, 260 °C; c) PPh₃, DIAD, 2-ethylbutanol, THF.

Compound S1 (1,4-dimethyl-2-(*o*-tolylamino)fumarate): To a 250 mL flask was added *o*-toluidine (10.0 mL, 93.3 mmol) and MeOH (200 mL), the resulting mixture was cooled with an ice bath. Dimethyl acetylenedicarboxylate (11.0 mL, 93.3 mmol) was slowly added into the flask. The ice bath was then removed, and the mixture was progressively heated to 65 °C and stirred at that temperature for 24 hours. Methanol was then removed by rotary evaporation and the resulting slurry was cooled to allow the formation of a yellow precipitate. The solid was filtered and washed with cold methanol and then dried under vacuum to yield a yellow solid (10.6 g, 45.6%). ^1H NMR (300 MHz, CDCl₃): δ 9.54 (s, 1 H), 7.20 (d, $J = 7.8$ Hz, 1 H), 7.12-7.00 (m, 2 H), 6.74 (d, $J = 7.8$ Hz, 1 H), 5.39 (s, 1 H), 3.75 (s, 3 H), 3.66 (s, 3 H), 2.35 (s, 3 H) ppm; ^{13}C NMR (75 MHz, CDCl₃): δ 170.3, 164.9, 149.0, 130.8, 130.3, 126.6, 124.8, 121.3, 92.9, 52.8, 51.3, 17.9 ppm.

Compound S2 (methyl-8-methyl-4-oxo-1,4-dihydroquinoline-2-carboxylate): Diphenyl ether (160 mL) was added to a 500 mL flask equipped with a heating mantle and then heated to reach the boiling point. Compound **S1** (10.0 g, 40.1 mmol) was added as a solid into the boiling diphenyl ether and the mixture was kept at reflux for 15 minutes. Upon complete conversion (TLC), the mixture was allowed to cool down to room temperature. Cyclohexane (200 mL) was added to form a brown precipitate. The solid was filtered and washed with cyclohexane 3 times. The solid was collected and dried under vacuum to yield a brown powder (7.0 g, 80.0%). ^1H NMR (300 MHz, CDCl₃): δ 8.87 (s, 1 H), 8.22 (d, $J = 8.1$ Hz, 1 H), 7.51 (d, $J = 6.4$ Hz, 1 H), 7.31-7.26 (m, 2 H), 6.98 (s, 1 H), 4.05 (s, 3 H), 2.56 (s, 3 H) ppm; ^{13}C NMR (75 MHz, CDCl₃): δ 180.1, 163.8, 137.9, 135.8, 133.9, 126.5, 125.4, 124.5, 124.3, 111.8, 54.0, 16.7 ppm.

Compound 1 (methyl-4-(2-ethylbutoxy)-8-methylquinoline-2-carboxylate): To a 250 mL flask was added triphenylphosphine (7.97 g, 30.4 mmol) and **S2** (6.00 g, 27.6 mmol). The flask was flushed with N₂ and dry THF (45 mL) and 2-ethylbutanol (3.7 mL, 30.4 mmol) were added via a syringe. DIAD (6.0 mL, 30.4 mmol) was then slowly added into the flask through a dropping funnel over 20 minutes. The resulting mixture was stirred at room temperature for 17 hours. The reaction mixture was concentrated and 50 mL of methanol was added in to the resulting slurry. Cooling down helped the formation of a white precipitate. The solid was filtered and washed with cold methanol and dried to yield a white solid (5.8 g, 69.6%). ¹H NMR (300 MHz, CDCl₃): δ 8.09 (d, J = 8.3 Hz, 1 H), 7.60 (d, J = 5.6 Hz, 1 H), 7.56 (s, 1 H), 7.47 (t, J = 7.7 Hz, 1 H), 4.17 (d, J = 5.6 Hz, 2 H), 4.06 (s, 3 H), 2.87 (s, 3 H), 1.86 (m, 1 H), 1.64-1.53 (m, 4 H), 0.99 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (84 MHz, CDCl₃): δ 166.8, 163.1, 148.0, 147.8, 138.3, 130.7, 127.3, 122.6, 119.7, 100.6, 70.9, 53.2, 41.0, 23.7, 18.2, 11.4 ppm, HRMS (ESI) m/z: calcd for C₁₈H₂₄NO₃ [M+H]⁺ 302.1750, found 320.1748.

Oligomer synthesis:



Scheme S2: Synthesis of methyl functionalized oligomers **6-11**.

General procedure for the synthesis of 2-hydroxymethylquinolines: To a 100 mL flask was added the corresponding methyl ester (1 equiv.) and NaBH₄ (10 equiv.), then THF (15 mL per mmol of methyl ester) was added. The resulting mixture was heated at 50 °C. Methanol (6 mL per mmol of methyl ester) was added slowly into the mixture. After complete addition of methanol, the mixture was stirred at 50 °C and the reaction was monitored by TLC. Upon completion of the reaction (usually within one hour), the mixture was allowed to cool to room temperature. Water (10 mL per mmol of methyl ester) was added to quench the unreacted NaBH₄. Then dichloromethane was added to extract the compound (15 mL × 3) and the organic phases were combined and washed with brine. The organic layer was dried over anhydrous Na₂SO₄ and filtered. Solvents were removed to give a solid. The product was usually pure enough as indicated by ¹H NMR spectra and was used for next step without further purification.

Compound 2 (4-(2-ethylbutoxy)-2-hydroxymethyl-8-methylquinoline): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from compound **1** (1.5 g, 5 mmol). Yield: 1.6 g (quant). ¹H NMR (300 MHz, CDCl₃): δ 8.04 (d, J = 8.5 Hz, 1 H), 7.54 (d, J = 8.5 Hz, 1 H), 6.57 (s, 1 H), 4.96 (s, 1 H), 4.84 (s, 2 H), 4.07 (d, J = 5.5 Hz, 2 H), 2.78 (s, 3 H), 1.85 (m, 1 H), 1.64-1.53 (m, 4 H), 0.98 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 162.7, 158.7, 146.4, 136.0, 130.4, 125.1, 121.2, 120.0, 97.0, 70.7, 64.2, 41.0, 23.7, 18.3, 11.4 ppm, HRMS (ESI) m/z: calcd for C₁₇H₂₄NO₂ [M+H]⁺ 274.1802, found 274.1798.

General procedure for the preparation of 2-quinolinecarboxaldehydes: To a 50 mL flask was added the corresponding 2-hydroxymethylquinoline (1 equiv.) and SIBX (1.2 equiv.). Then the flask

was equipped with condenser and magnetic stirring bar. The flask was flushed with N₂. Dry THF (6 mL per mmol of corresponding 2-hydroxymethylquinoline) was added into the flask through a syringe. The mixture was heated under reflux for 1 hour under N₂. Upon completion of the reaction, the mixture was cooled down to room temperature. An aqueous solution of saturated Na₂S₂O₃ (5 mL per mmol of corresponding 2-hydroxymethylquinoline) was added to quench the reaction. Dichloromethane (15 mL per mmol of corresponding 2-hydroxymethylquinoline) was added and then the organic phase was layered in an extraction funnel. The organic phase was washed three times with a saturated Na₂CO₃ solution, dried over Na₂SO₄ and filtered. The solvent was evaporated to give a slurry. Hexane was added to precipitate the product. The precipitate was isolated by filtration and washed three times with hexane. The solid was collected and dried under vacuum to afford the aldehyde.

Compound 3 (4-(2-ethylbutoxy)-8-methylquinoline-2-carbaldehyde): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from compound **2** (1.43 g, 5.23 mmol). Yield: 1.42 g (95%). ¹H NMR (300 MHz, CDCl₃): δ 10.16 (s, 1 H), 8.11 (d, J = 8.5 Hz, 1 H), 7.63 (d, J = 7.2 Hz, 1 H), 7.51 (t, J = 7.7 Hz, 1 H), 7.38 (s, 1 H), 4.17 (d, J = 5.6 Hz, 2 H), 2.87 (s, 3 H), 1.86 (m, 1 H), 1.64-1.54 (m, 4 H), 0.99 (t, J = 7.3 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.9, 163.1, 153.1, 148.1, 138.5, 130.7, 127.9, 123.3, 120.0, 96.3, 71.1, 40.9, 23.7, 18.3, 11.3 ppm, HRMS (ESI) m/z: calcd for C₁₇H₂₂NO₂ [M+H]⁺ 272.1645, found 272.1642.

Compound 4 (methyl 8-(bromomethyl)-4-(2-ethylbutoxy)quinoline-2-carboxylate): To a 100 mL flask was added **1** (2.10 g, 7.0 mmol), NBS (1.37 g, 7.7 mmol) and AIBN (22 mg, 0.14 mmol). The flask was flushed with N₂. Then 40 mL of CCl₄ was added through a syringe. The mixture was heated under N₂ at 75 °C overnight. The reaction mixture was cooled down to room temperature and washed with brine three times. The organic layer was dried over Na₂SO₄, filtered and evaporated to give a slurry. Cyclohexane was added and white needle crystals slowly formed upon standing at room temperature. The solid was filtered and washed three times with cyclohexane. The white solid was collected and dried under vacuum (1.85 g, 69.0%). ¹H NMR (300 MHz, CDCl₃): δ 8.21 (dd, J = 8.4, 1.5 Hz, 1 H), 7.90 (dd, J = 7.2, 1.5 Hz, 1 H), 7.58 (s, 1 H), 7.56 (t, J = 7.7 Hz, 1 H), 5.31 (s, 2 H), 4.18 (d, J = 5.6 Hz, 2 H), 4.06 (s, 3 H), 1.86 (m, 1 H), 1.64-1.53 (m, 4 H), 0.99 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.5, 163.0, 148.8, 146.0, 137.0, 131.7, 127.2, 122.6, 101.0, 71.1, 53.1, 40.8, 29.5, 23.6, 11.3 ppm, ESI HRMS m/z: calcd for C₁₈H₂₃BrNO₃ [M+H]⁺ 380.0856, found 380.0852.

Compound 5 (methyl 8-((diisopropoxyphosphoryl)methyl)-4-(2-ethylbutoxy)quinoline-2-carboxylate): To a 50 mL flask was added **4** (2.36 g, 6.2 mmol). The flask was flushed with N₂ and triisopropyl phosphite (3.0 mL, 12.4 mmol) was added. The mixture was heated at 70 °C for 3 hours under N₂. The reaction mixture was cooled down to room temperature. Toluene was added to remove the excess of triisopropyl phosphite by co-evaporating under reduced pressure. The slurry was dried under high vacuum to give a white solid (2.52 g, quant). ¹H NMR (300 MHz, CDCl₃): δ 8.13 (d, J = 8.5 Hz, 1 H), 7.93 (dd, J = 7.3, 3.4 Hz, 1 H), 7.53 (s, 1 H), 7.54 (t, J = 8.2 Hz, 1 H), 4.74-4.63 (m, 2 H), 4.16 (d, J = 5.4 Hz, 2 H), 4.06 (d, J = 22.3 Hz, 2 H), 1.84 (m, 1 H), 1.61-1.53 (m, 4 H), 1.22 (d, J = 6.4 Hz, 6 H), 1.09 (d, J = 6.4 Hz, 6 H), 0.99 (t, J = 7.2 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 163.1, 148.1, 146.9, 146.8, 132.7, 132.6, 131.6, 131.5, 127.2, 127.1, 122.7, 122.6, 120.8, 120.7, 100.6, 70.7, 52.9, 41.0, 29.2, 27.3, 24.2, 23.9, 23.7, 11.4 ppm; ³¹P NMR (121 MHz, CDCl₃): δ 25.2 ppm, ESI HRMS m/z: calcd for C₂₄H₃₇NO₆P [M+H]⁺ 466.2353, found 466.2348.

General procedure for the Horner-Wadsworth-Emmons (HWE) coupling: To a dry 50 mL flask was added with the aldehyde (1 equiv.), **5** (1.1 equiv.) and NaH (2 equiv.). The atmosphere inside the flask was replaced with N₂. Dry THF (5 mL per mmol of aldehyde) and 15-crown-5 (1 equiv.) were added through syringes. The mixture was stirred at room temperature for 2 hours. Upon completion, the reaction was quenched by adding water (10 mL) and dichloromethane (25 mL). The product was extracted with dichloromethane (15 mL × 3) and the organic layers were combined, dried over Na₂SO₄, filtered, and evaporated. The residue was dried under high vacuum. To this solid was added with K₂CO₃ (1.5 equiv.) and acetone (20 mL). The mixture was stirred at room temperature for about 10 minutes before adding MeI (2 equiv.). The mixture was stirred at room temperature for 5 hours. Water was then added into the mixture to dissolve salts. Dichloromethane was added to extract the product (20 mL ×

3). The organic layers were combined and washed with brine (15 mL × 3). The organic layer was dried with Na₂SO₄, filtered, and evaporated to obtain a slurry. The residue was purified by silica gel column chromatography using cyclohexane/ethyl acetate as eluent or otherwise specified. The pure fraction was collected and the solvent was removed to yield the product as a light yellow solid.

Synthesis of compounds 6-11:

Compound 6: This compound was prepared according to the general HWE coupling procedures from aldehyde **3** (0.9 g, 3.3 mmol). Eluent for silica gel column chromatography purification was cyclohexane/ethyl acetate (12/1 vol/vol). Yield: 1.16 g (63%). ¹H NMR (300 MHz, CDCl₃): δ 9.03 (d, J = 16.8 Hz, 1 H), 8.25 (d, J = 7.6 Hz, 1 H), 8.21 (d, J = 7.8 Hz, 1 H), 8.04 (d, J = 8.4 Hz, 1 H), 7.74 (d, J = 16.8 Hz, 1 H), 7.64 (t, J = 7.8 Hz, 1 H), 7.62 (s, 1 H), 7.53 (d, J = 7.4 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.26 (s, 1 H), 4.23 (d, J = 5.9 Hz, 2 H), 4.21 (d, J = 5.8 Hz, 2 H), 4.08 (s, 3 H), 2.89 (s, 3 H), 1.93-1.84 (m, 2 H), 1.68-1.55 (m, 8 H), 1.03 (t, J = 5.5 Hz, 6 H), 1.01 (t, J = 5.7 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.7, 163.2, 162.1, 156.4, 148.4, 148.3, 146.4, 137.0, 136.0, 133.0, 130.1, 129.2, 127.5, 127.2, 124.9, 122.9, 122.0, 121.0, 119.7, 100.8, 98.4, 71.2, 70.4, 53.0, 41.1, 41.0, 23.8, 23.7, 18.4, 11.4, 11.3 ppm, HRMS (ESI) m/z: calcd for C₃₅H₄₃N₂O₄ [M+H]⁺ 555.3217, found 555.3212.

Corresponding 2-hydroxymethylquinoline of 6 (6b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from compound **6** (0.84 g, 1.51 mmol). Yield: 0.79 g (quant). ¹H NMR (300 MHz, CDCl₃): δ 9.01 (d, J = 16.5 Hz, 1 H), 8.19 (d, J = 8.2 Hz, 2 H), 8.03 (d, J = 8.2 Hz, 1 H), 7.56 (d, J = 16.5 Hz, 1 H), 7.58 (d, J = 6.2 Hz, 1 H), 7.52 (t, J = 4.8 Hz, 1 H), 7.34 (t, J = 7.3 Hz, 1 H), 7.12 (s, 1 H), 6.64 (s, 1 H), 4.91 (s, 2 H), 4.19 (d, J = 5.5 Hz, 2 H), 4.11 (d, J = 5.6 Hz, 2 H), 2.87 (s, 3 H), 1.90-1.83 (m, 2 H), 1.69-1.55 (m, 8 H), 1.04-0.98 (m, 12 H) ppm, HRMS (ESI) m/z: calcd for C₃₄H₄₃N₂O₃ [M+H]⁺ 527.3268, found 527.3266.

Corresponding 2-quinolinecarboxaldehyde of 6 (6c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes starting from 2-hydroxymethylquinoline **6b** (0.84 g, 1.51 mmol). Yield: 0.68 g (92%). ¹H NMR (300 MHz, CDCl₃): δ 10.26 (s, 1 H), 9.07 (d, J = 16.6 Hz, 1 H), 8.27 (d, J = 7.8 Hz, 1 H), 8.25 (d, J = 8.2 Hz, 1 H), 8.05 (d, J = 7.8 Hz, 1 H), 7.70 (d, J = 16.6 Hz, 1 H), 7.68 (t, J = 7.4 Hz, 1 H), 7.55 (d, J = 7.2 Hz, 1 H), 7.43 (s, 1 H), 7.35 (t, J = 8.2 Hz, 1 H), 7.21 (s, 1 H), 4.22 (d, J = 5.5 Hz, 2 H), 4.20 (d, J = 5.8 Hz, 2 H), 2.88 (s, 3 H), 1.91-1.84 (m, 2 H), 1.70-1.53 (m, 4 H), 1.06-0.98 (m, 12 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.6, 163.2, 162.3, 156.2, 153.2, 148.4, 146.8, 137.0, 136.2, 133.0, 130.2, 129.0, 128.1, 127.2, 125.0, 123.7, 122.3, 121.1, 119.7, 98.4, 96.6, 71.3, 70.4, 41.1, 41.0, 23.9, 23.8, 18.4, 11.5, 11.4 ppm, HRMS (ESI) m/z: calcd for C₃₄H₄₁N₂O₃ [M+H]⁺ 525.3112, found 525.3108.

Compound 7: This compound was prepared according to the general HWE coupling procedures from aldehyde **6c** (0.68 g, 1.29 mmol). Eluent for silica gel column chromatography purification was cyclohexane/ethyl acetate (20/1 vol/vol). Yield: 0.79 g (76%). ¹H NMR (300 MHz, CDCl₃): δ 9.12 (d, J = 16.6 Hz, 1 H), 9.08 (d, J = 16.6 Hz, 1 H), 8.24-8.18 (m, 4 H), 8.03 (d, J = 7.8 Hz, 1 H), 7.80 (d, J = 16.6 Hz, 1 H), 7.70 (d, J = 16.6 Hz, 1 H), 7.64 (m, 2 H), 7.53 (d, J = 7.4 Hz, 1 H), 7.52 (t, J = 7.4 Hz, 1 H), 7.34 (s, 1 H), 7.33 (t, J = 7.8 Hz, 1 H), 7.30 (s, 1 H), 4.26 (d, J = 5.4 Hz, 2 H), 4.21 (d, J = 5.8 Hz, 2 H), 4.14 (d, J = 5.8 Hz, 2 H), 3.87 (s, 3 H), 2.87 (s, 3 H), 1.85-1.70 (m, 3 H), 1.68-1.43 (m, 12 H), 1.05 (t, J = 7.5 Hz, 6 H), 1.02 (t, J = 7.6 Hz, 6 H), 0.92 (t, J = 7.5 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.7, 163.2, 162.2, 162.1, 157.1, 156.8, 148.4, 147.0, 146.4, 136.9, 136.1, 134.7, 133.0, 131.9, 130.2, 130.0, 129.9, 127.5, 127.4, 126.7, 125.2, 124.8, 123.0, 122.2, 121.6, 121.0, 119.7, 101.0, 98.9, 98.1, 71.2, 70.5, 53.0, 41.1, 41.0, 40.9, 23.9, 23.8, 23.6, 18.5, 11.5, 11.4, 11.3 ppm, HRMS (ESI) m/z: calcd for C₅₂H₆₂N₃O₅ [M+H]⁺ 808.4684, found 808.4674.

Corresponding 2-hydroxymethylquinoline of 7 (7b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from compound **7** (730 mg, 0.93 mmol). Yield: 0.72 g (quant). ¹H NMR (300 MHz, CDCl₃): δ 9.07 (d, J = 16.6 Hz, 1 H), 8.90 (d, J = 16.6 Hz, 1 H), 8.22-8.16 (m, 4 H), 8.03 (d, J = 7.5 Hz, 1 H), 7.69 (d, J = 16.6 Hz, 1 H), 7.68 (d, J = 16.6 Hz, 1 H), 7.58-7.49 (m, 3 H), 7.33 (t, J = 7.5 Hz, 1 H), 7.31 (s, 1 H), 7.24 (s, 1 H), 6.67 (s, 1 H), 4.86

(d, J = 3.6 Hz, 2 H), 4.50 (t, J = 3.6 Hz, 1 H), 4.24 (d, J = 5.4 Hz, 2 H), 4.18 (d, J = 5.6 Hz, 2 H), 4.12 (d, J = 5.5 Hz, 2 H), 2.86 (s, 3 H), 1.91-1.77 (m, 3 H), 1.70-1.49 (m, 12 H), 1.06-0.93 (m, 18 H) ppm.

Corresponding 2-quinolinecarboxaldehyde of 7 (7c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from compound **7b** (720 mg, 0.93 mmol). Yield: 0.70 g (96%). ¹H NMR (300 MHz, CDCl₃): δ 10.16 (s, 1 H), 9.11 (d, J = 16.5 Hz, 1 H), 9.08 (d, J = 16.5 Hz, 1 H), 8.27 (d, J = 8.3 Hz, 1 H), 8.25 (d, J = 7.2 Hz, 1 H), 8.19 (d, J = 7.8 Hz, 2 H), 8.03 (d, J = 7.8 Hz, 1 H), 7.80 (d, J = 16.5 Hz, 1 H), 7.69 (d, J = 16.5 Hz, 1 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.52 (t, J = 7.3 Hz, 1 H), 7.51 (d, J = 5.8 Hz, 1 H), 7.43 (s, 1 H), 7.33 (t, J = 7.6 Hz, 1 H), 7.28 (s, 1 H), 7.27 (s, 1 H), 4.26 (d, J = 5.2 Hz, 2 H), 4.21 (d, J = 5.7 Hz, 2 H), 4.15 (d, J = 5.4 Hz, 2 H), 2.86 (s, 3 H), 1.92-1.78 (m, 3 H), 1.68-1.47 (m, 12 H), 1.05 (t, J = 7.4 Hz, 6 H), 1.02 (t, J = 7.4 Hz, 6 H), 0.94 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.4, 163.2, 162.3, 162.2, 156.9, 156.7, 153.4, 148.4, 147.1, 146.8, 136.9, 136.3, 134.8, 133.2, 132.1, 130.2, 130.1, 129.8, 128.1, 127.5, 126.9, 125.3, 124.8, 123.7, 122.5, 122.2, 121.6, 121.0, 119.7, 98.6, 98.3, 96.7, 71.3, 70.6, 70.5, 41.0, 41.0, 23.9, 23.8, 23.7, 18.5, 11.5, 11.4 ppm, HRMS (ESI) m/z: calcd for C₅₁H₆₀N₃O₄ [M+H]⁺ 778.4578, found 778.4569.

Compound 8: This compound was prepared according to the general HWE coupling procedures from aldehyde **7c** (700 mg, 0.89 mmol). Eluent for column chromatography was cyclohexane/ethyl acetate (30/1 vol/vol). Yield: 0.62 g (65%). ¹H NMR (300 MHz, CDCl₃): δ 9.45 (d, J = 16.6 Hz, 1 H), 9.16 (d, J = 16.8 Hz, 1 H), 9.02 (d, J = 16.7 Hz, 1 H), 8.22-8.16 (m, 4 H), 7.96 (dd, J = 8.3, 1.1 Hz, 1 H), 7.82 (d, J = 7.4 Hz, 1 H), 7.76 (d, J = 5.3 Hz, 1 H), 7.72 (d, J = 16.4 Hz, 1 H), 7.71 (d, J = 16.4 Hz, 1 H), 7.68 (d, J = 16.4 Hz, 1 H), 7.57 (s, 1 H), 7.53 (dd, J = 7.8, 3.5 Hz, 1 H), 7.50 (dd, J = 7.7, 3.5 Hz, 1 H), 7.43 (d, J = 6.6 Hz, 1 H), 7.32 (s, 1 H), 7.22 (s, 1 H), 7.23-7.13 (m, 2 H), 4.26 (d, J = 5.5 Hz, 2 H), 4.19 (d, J = 5.3 Hz, 2 H), 4.17 (d, J = 5.3 Hz, 2 H), 4.05 (d, J = 5.9 Hz, 2 H), 3.74 (s, 3 H), 2.82 (s, 3 H), 1.94-1.81 (m, 4 H), 1.71-1.51 (m, 8 H), 1.05 (t, J = 7.5 Hz, 6 H), 1.03 (t, J = 7.6 Hz, 6 H), 0.97 (t, J = 7.5 Hz, 6 H), 0.84 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.6, 163.0, 162.2, 161.9, 157.0, 157.0, 156.9, 148.1, 148.0, 147.1, 136.6, 135.4, 134.6, 134.5, 132.4, 131.8, 131.2, 130.8, 130.3, 130.1, 129.7, 127.2, 127.1, 126.8, 126.6, 125.1, 125.0, 124.4, 122.6, 122.4, 122.1, 121.8, 121.5, 121.4, 120.8, 119.5, 100.8, 99.6, 99.1, 97.8, 71.0, 70.6, 70.5, 70.5, 52.8, 41.1, 41.0, 40.9, 40.7, 23.8, 23.7, 23.6, 23.3, 18.5, 11.4, 11.4, 11.3, 11.2 ppm, HRMS (ESI) m/z: calcd for C₆₉H₈₁N₄O₆ [M+H]⁺ 1061.6151, found 1061.6142.

Corresponding 2-hydroxymethylquinoline of 8 (8b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from **8** (620 mg, 0.58 mmol). Yield: 0.61 g (quant). ¹H NMR (300 MHz, CDCl₃): δ 9.45 (d, J = 16.5 Hz, 1 H), 8.66 (d, J = 16.9 Hz, 1 H), 8.85 (d, J = 16.6 Hz, 1 H), 8.22-8.16 (m, 4 H), 7.91 (dd, J = 8.2, 1.2 Hz, 1 H), 7.70 (d, J = 16.8 Hz, 1 H), 7.67 (d, J = 16.4 Hz, 1 H), 7.58 (d, J = 16.6 Hz, 1 H), 7.73 (m, 2 H), 7.54-7.47 (m, 2 H), 7.40 (d, J = 7.0 Hz, 1 H), 7.32 (s, 1 H), 7.19 (s, 1 H), 7.17 (s, 1 H), 7.11 (m, 2 H), 6.59 (s, 1 H), 4.76 (s, 2 H), 4.51 (w, 1 H), 4.23 (d, J = 5.3 Hz, 2 H), 4.25 (d, J = 5.5 Hz, 2 H), 4.08 (d, J = 5.5 Hz, 2 H), 4.02 (d, J = 5.9 Hz, 2 H), 2.80 (s, 3 H), 1.89-1.83 (m, 4 H), 1.68-1.54 (m, 8 H), 1.04 (t, J = 7.05 Hz, 6 H), 1.02 (t, J = 6.6 Hz, 6 H), 0.99 (t, J = 6.9 Hz, 6 H), 0.81 (t, J = 7.4 Hz, 6 H) ppm.

Corresponding 2-quinolinecarboxaldehyde of 8 (8c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from **8b** (0.61 g, 0.58 mmol). Yield: 0.60 g (95%). ¹H NMR (300 MHz, CDCl₃): δ 9.88 (s, 1 H), 9.64 (d, J = 16.2 Hz, 1 H), 9.17 (d, J = 16.9 Hz, 1 H), 9.14 (d, J = 16.5 Hz, 1 H), 8.22-8.14 (m, 4 H), 7.82 (dd, J = 8.3, 1.1 Hz, 1 H), 7.72-7.61 (m, 4 H), 7.56-7.48 (m, 4 H), 7.36 (d, J = 6.6 Hz, 1 H), 7.31 (s, 1 H), 7.14 (s, 1 H), 7.09 (s, 1 H), 7.12-7.05 (m, 3 H), 4.24 (d, J = 5.4 Hz, 2 H), 4.19 (d, J = 6.0 Hz, 2 H), 4.17 (d, J = 5.9 Hz, 2 H), 3.94 (d, J = 6.0 Hz, 2 H), 2.71 (s, 3 H), 1.94-1.83 (m, 4 H), 1.71-1.56 (m, 8 H), 1.06 (t, J = 6.8 Hz, 6 H), 1.03 (t, J = 7.9 Hz, 6 H), 1.01 (t, J = 7.5 Hz, 6 H), 0.76 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.5, 162.8, 162.4, 162.3, 161.6, 156.8, 156.6, 1156.5, 153.0, 147.9, 147.4, 147.1, 146.3, 136.6, 135.1, 134.9, 134.3, 131.8, 131.6, 131.4, 130.4, 130.3, 130.0, 129.5, 127.2, 126.9, 126.8, 126.5, 125.1, 125.0, 124.2, 123.1, 122.3, 122.2, 121.8, 121.5, 121.4, 120.7, 119.4, 100.3, 99.6, 97.6, 96.4, 71.1, 70.6, 41.1, 41.0, 41.0, 40.6, 23.9, 23.8, 23.7, 23.2, 18.4, 11.5, 11.4, 11.4, 11.1 ppm, HRMS (ESI) m/z: calcd for C₆₈H₇₉N₄O₅ [M+H]⁺ 1031.6045, found 1031.6037.

Compound 9: This compound was prepared according to the general HWE coupling procedures from aldehyde **8c** (600 mg, 0.58 mmol). Eluent for silica gel column chromatography was cyclohexane/ethyl acetate (25/1 vol/vol). Yield: 0.42 g (55%). ¹H NMR (300 MHz, CDCl₃): δ 9.46 (d, J = 16.4 Hz, 1 H), 9.36 (d, J = 16.6 Hz, 1 H), 9.10 (d, J = 16.8 Hz, 1 H), 8.89 (d, J = 16.6 Hz, 1 H), 8.21-8.17 (m, 2 H), 8.07 (d, J = 6.8 Hz, 1 H), 8.01 (d, J = 8.3 Hz, 1 H), 7.96 (d, J = 7.9 Hz, 1 H), 7.94 (d, J = 5.9 Hz, 1 H), 7.92 (d, J = 6.0 Hz, 1 H), 7.87 (d, J = 16.6 Hz, 1 H), 7.77 (d, J = 7.3 Hz, 1 H), 7.67-7.48 (m, 7 H), 7.35 (s, 1 H), 7.24-7.14 (m, 5 H), 4.25 (d, J = 5.5 Hz, 2 H), 2.20-4.15 (m, 6 H), 4.06 (d, J = 5.7 Hz, 2 H), 3.84 (s, 3 H), 2.85 (s, 3 H), 1.95-1.37 (m, 15 H), 1.06 (t, J = 7.4 Hz, 6 H), 0.99 (t, J = 7.4 Hz, 12 H), 0.92 (t, J = 7.5 Hz, 6 H), 0.89 (t, J = 7.5 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.7, 163.0, 162.3, 162.0, 161.9, 157.1, 157.0, 157.0, 156.9, 148.3, 148.0, 147.3, 147.0, 146.8, 146.1, 136.7, 135.4, 134.5, 134.4, 134.2, 132.9, 131.7, 131.5, 131.4, 131.2, 130.2, 130.1, 129.8, 129.7, 127.2, 127.1, 126.4, 126.2, 124.8, 124.7, 124.5, 122.6, 122.3, 122.1, 121.8, 121.7, 121.4, 121.3, 120.9, 119.7, 100.7, 100.0, 99.2, 98.6, 97.9, 71.1, 70.6, 70.5, 70.4, 53.6, 52.8, 41.2, 41.0, 40.9, 40.9, 40.8, 23.8, 23.7, 23.6, 23.6, 23.5, 18.6, 11.5, 11.4, 11.3, 11.2 ppm, HRMS (ESI) m/z: calcd for C₈₆H₁₀₀N₅O₇ [M+H]⁺ 1314.7617, found 1314.7641.

Corresponding 2-hydroxymethylquinoline of 9 (9b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from **9** (390 mg, 0.29 mmol). Yield: 0.38 g (quant). ¹H NMR (300 MHz, CDCl₃): δ 9.44 (d, J = 16.5 Hz, 1 H), 9.37 (d, J = 16.5 Hz, 1 H), 9.08 (d, J = 16.5 Hz, 1 H), 8.75 (d, J = 16.5 Hz, 1 H), 8.20 (t, J = 7.3 Hz, 2 H), 8.06 (d, J = 7.3 Hz, 1 H), 8.00 (d, J = 8.8 Hz, 1 H), 7.92 (d, J = 8.6 Hz, 2 H), 7.85 (d, J = 16.5 Hz, 1 H), 7.76 (d, J = 8.8 Hz, 1 H), 7.64-7.45 (m, 5 H), 7.34 (s, 1 H), 7.26-7.14 (m, 4 H), 7.05 (t, J = 8.0 Hz, 1 H), 6.6 (s, 1 H), 4.82 (s, 2 H), 4.22 (d, J = 4.7 Hz, 2 H), 4.21 (d, J = 5.3 Hz, 2 H), 4.16 (d, J = 5.3 Hz, 2 H), 4.06 (d, J = 5.3 Hz, 2 H), 4.04 (d, J = 5.9 Hz, 2 H), 2.85 (s, 3 H), 1.89-1.41 (m, 15 H), 1.05 (t, J = 7.5 Hz, 6 H), 1.01 (t, J = 7.5 Hz, 6 H), 0.99 (t, J = 7.7 Hz, 6 H), 0.92 (t, J = 7.6 Hz, 6 H), 0.88 (t, J = 7.8 Hz, 6 H) ppm.

Corresponding 2-quinolinecarboxaldehyde of 9 (9c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from **9b** (0.38 g, 0.29 mmol). Yield: 0.36 g (93%). ¹H NMR (300 MHz, CDCl₃): δ 9.98 (s, 1 H), 9.61 (d, J = Hz, 1 H), 9.39 (d, J = Hz, 1 H), 9.01 (d, J = Hz, 1 H), 8.21 (d, J = Hz, 1 H), 8.14 (d, J = Hz, 1 H), 8.01 (d, J = Hz, 1 H), 7.96 (d, J = Hz, 1 H), 7.93 (d, J = Hz, 2 H), 7.86 (d, J = Hz, 1 H), 7.76 (d, J = Hz, 1 H), 7.67 (d, J = Hz, 1 H), 7.59-7.45 (m, 6 H), 7.29-7.24 (m, 2 H), 7.21-7.08 (m, 4 H), 7.06 (s, 1 H), 7.05 (s, 1 H), 4.23 (d, J = Hz, 2 H), 4.19 (d, J = Hz, 2 H), 4.17 (d, J = Hz, 2 H), 4.09 (d, J = Hz, 2 H), 3.95 (d, J = Hz, 2 H), 2.83 (s, 3 H), 1.96-1.35 (m, 15 H), 1.06 (t, J = Hz, 6 H), 1.02 (t, J = Hz, 6 H), 0.94 (t, J = Hz, 6 H), 0.92 (t, J = Hz, 6 H), 0.86 (t, J = Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.7, 162.8, 162.4, 162.1, 161.8, 161.7, 157.0, 156.7, 156.6, 156.5, 152.9, 148.2, 147.4, 147.1, 146.6, 146.3, 136.7, 135.2, 134.3, 134.3, 132.1, 131.7, 131.4, 131.3, 130.0, 129.8, 129.8, 129.7, 127.5, 127.2, 126.7, 126.2, 124.8, 124.7, 124.4, 124.3, 123.1, 122.4, 122.0, 121.8, 121.7, 121.4, 121.2, 121.1, 120.9, 100.7, 99.3, 99.2, 97.8, 96.3, 71.2, 70.5, 70.4, 41.1, 41.0, 40.8, 40.8, 40.7, 23.8, 23.8, 23.5, 23.5, 23.4, 18.6, 11.5, 11.4, 11.3, 11.2, 11.2 ppm, HRMS (ESI) m/z: calcd for C₈₅H₉₈N₅O₆ [M+H]⁺ 1284.7512, found 1284.7537.

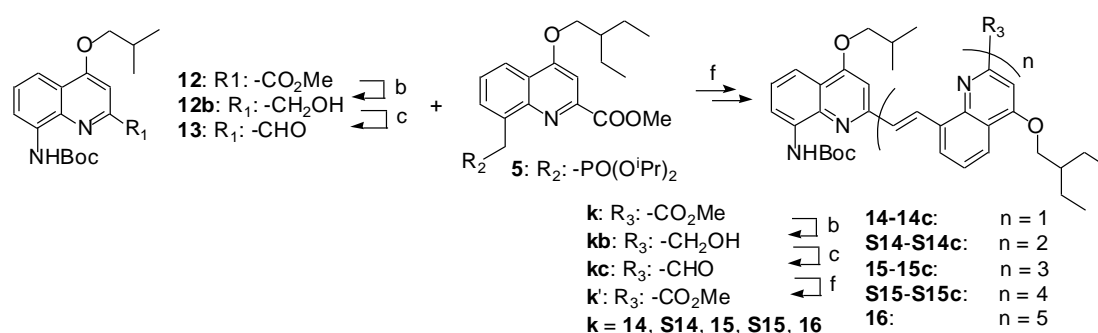
Compound 10: This compound was prepared according to the general HWE coupling procedures from aldehyde **9c** (0.36 g, 0.28 mmol). Eluent for silica gel column chromatography was cyclohexane/ethyl acetate (25/1 vol/vol). Yield: 0.23 g (52%). ¹H NMR (300 MHz, CDCl₃): δ 9.36 (d, J = 16.4 Hz, 1 H), 9.30 (d, J = 16.4 Hz, 1 H), 9.29 (d, J = 16.4 Hz, 1 H), 9.13 (d, J = 16.4 Hz, 1 H), 8.94 (d, J = 16.5 Hz, 1 H), 8.14 (d, J = 5.9 Hz, 1 H), 8.08 (d, J = 7.1 Hz, 1 H), 8.04-7.90 (m, 7 H), 7.84-7.70 (m, 5 H), 7.66 (d, J = 6.8 Hz, 1 H), 7.60-7.54 (m, 2 H), 7.49 (d, J = 6.6 Hz, 1 H), 7.37-7.29 (m, 4 H), 7.24-7.16 (m, 4 H), 4.22 (d, J = 5.8 Hz, 2 H), 4.17-4.10 (m, 10 H), 3.84 (s, 3 H), 2.87 (s, 3 H), 1.91-1.44 (m, 18 H), 1.03 (t, J = 7.3 Hz, 6 H), 0.99 (t, J = 7.4 Hz, 12 H), 0.96 (t, J = 7.4 Hz, 6 H), 0.93 (t, J = 7.4 Hz, 6 H), 0.90 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.7, 163.0, 162.0, 157.1, 157.0, 156.8, 148.1, 147.1, 146.9, 146.1, 163.7, 135.5, 134.4, 134.2, 134.1, 133.0, 131.6, 131.4, 131.3, 131.1, 131.0, 130.8, 130.2, 129.8, 129.6, 127.3, 127.1, 126.7, 126.5, 126.2, 124.9, 124.5, 122.7, 122.0, 121.8, 121.4, 120.9, 119.7, 100.8, 99.5, 99.3, 99.0, 98.5, 98.0, 71.1, 70.6, 70.5, 52.9, 41.0, 40.9, 40.8, 23.7, 23.7, 23.6, 23.5, 18.6, 11.4, 11.3, 11.3 ppm, HRMS (ESI) m/z: calcd for C₁₀₃H₁₁₉N₆O₈ [M+H]⁺ 1568.9118, found 1568.9151.

Corresponding 2-hydroxymethylquinoline of 10 (10b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from **10** (0.2 g, 0.12 mmol). Yield: 0.19 g (quant). ¹H NMR (300 MHz, CDCl₃): δ 9.38 (d, J = 16.4 Hz, 1 H), 9.33 (d, J = 16.4 Hz, 1 H), 9.23 (d, J = 16.4 Hz, 1 H), 9.13 (d, J = 16.4 Hz, 1 H), 8.81 (d, J = 16.4 Hz, 1 H), 8.14 (d, J = 7.8 Hz, 1 H), 8.07 (d, J = 7.8 Hz, 1 H), 8.02-7.86 (m, 4 H), 7.79-7.72 (m, 2 H), 7.69-7.47 (m, 3 H), 7.33 (s, 1 H), 7.22-7.11 (m, 5 H), 6.63 (s, 1 H), 4.83 (s, 2 H), 4.22-4.07 (m, 12 H), 2.86 (s, 3 H), 1.89-1.43 (m, 18 H), 1.05-0.85 (m, 36 H) ppm.

Corresponding 2-quinolinecarboxaldehyde of 10 (10c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from **10b** (0.19 g, 0.12 mmol). Yield: 0.18 g (91%). ¹H NMR (300 MHz, CDCl₃): δ 10.00 (s, 1 H), 9.31 (d, J = 16.1 Hz, 1 H), 9.36 (d, J = 16.4 Hz, 1 H), 9.18 (d, J = 16.4 Hz, 1 H), 9.11 (d, J = 16.4 Hz, 1 H), 9.02 (d, J = 16.4 Hz, 1 H), 8.13 (d, J = 7.8 Hz, 1 H), 8.05-7.88 (m, 6 H), 7.82-7.80 (m, 2 H), 7.75-7.64 (m, 3 H), 7.59-7.49 (m, 3 H), 7.37 (t, J = 7.9 Hz, 1 H), 7.32 (s, 2 H), 7.25-7.15 (m, 5 H), 7.10 (s, 1 H), 7.08 (s, 1 H), 4.20-4.09 (m, 10 H), 4.02 (d, J = 5.8 Hz, 2 H), 2.88 (s, 3 H), 1.89-1.40 (m, 18 H), 1.04-0.86 (m, 36 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.6, 162.9, 162.2, 162.1, 161.9, 161.8, 157.1, 157.0, 156.7, 156.5, 153.0, 148.3, 147.2, 147.1, 147.0, 146.4, 136.7, 135.4, 134.4, 134.0, 132.4, 131.6, 131.3, 131.1, 130.9, 130.5, 129.8, 129.7, 127.6, 126.8, 126.7, 126.5, 126.3, 124.8, 124.5, 124.3, 123.2, 122.0, 121.4, 121.2, 120.9, 119.7, 100.0, 99.6, 99.0, 98.9, 98.1, 96.4, 71.3, 70.5, 41.1, 41.0, 40.9, 40.8, 40.7, 31.7, 23.8, 23.7, 23.6, 23.5, 22.8, 18.6, 14.2, 11.4, 11.4, 11.3, 11.2, HRMS (ESI) m/z: calcd for C₁₀₂H₁₁₇N₆O₇ [M+H]⁺ 1538.9012, found 1538.9036.

Compound 11: This compound was prepared according to the general HWE coupling procedures from aldehyde **10c** (0.19 g, 0.12 mmol). Purification was achieved by silica gel column chromatography (eluent: cyclohexane/ethyl acetate 30/1 vol/vol) Yield: 115 mg (41%). ¹H NMR (300 MHz, CDCl₃): δ 9.34-9.26 (m, 4 H), 9.23 (d, J = 16.4 Hz, 1 H), 9.14 (d, J = 16.4 Hz, 1 H), 8.95 (d, J = 16.6 Hz, 1 H), 8.15 (m, 2 H), 8.07-1.96 (m, 5 H), 7.92-7.36 (m, 16 H), 7.20-7.02 (m, 3 H), 4.24-4.15 (m, 14 H), 3.85 (s, 3 H), 2.86 (s, 3 H), 1.90-1.77 (m, 7 H), 1.62-1.43 (m, 28 H), 1.12-0.93 (m, 42 H) ppm, HRMS (ESI) m/z: calcd for C₁₂₀H₁₃₈N₇O₉ [M+H]⁺ 1822.0584, found 1822.0619.

Synthesis of compounds 14-16:



b: NaBH₄, THF, 60 °C; c: SIBX, THF, 60 °C; f: 1) NaH, 15-crown-5, THF; 2) K₂CO₃, MeI, acetone

Scheme S3: Synthesis of Boc-protected amine quinoline oligovinylenes.

Compound 13: This compound was prepared from **12**⁸ according the general procedures of 2-hydroxymethylquinolines and 2-quinolinecarboxaldehydes.

The corresponding 2-hydroxymethylquinoline **12b** (*tert*-butyl (2-(hydroxymethyl)-4-isobutoxyquinolin-8-yl)carbamate): Yield: 1.84 g (94%). ¹H NMR (300 MHz, CDCl₃): δ 8.72 (s, 1 H), 8.43 (d, J = 7.8 Hz, 1 H), 7.80 (d, J = 7.8 Hz, 1 H), 7.44 (t, J = 8.0 Hz, 1 H), 6.66 (s, 1 H), 4.87 (s, 2 H), 3.95 (d, J = 6.4 Hz, 2 H), 3.66 (w, 1 H), 2.27 (m, 1 H), 1.58 (s, 9 H), 1.13 (d, J = 6.6 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 162.7, 158.9, 153.0, 137.7, 134.4, 126.0, 120.9, 115.7, 114.7, 98.0, 80.7, 77.6, 77.2, 76.7, 75.0, 65.0, 28.6, 28.3, 19.4 ppm.

Compound 13 (tert-butyl (2-formyl-4-isobutoxyquinolin-8-yl)carbamate): Yield 1.6 g (93%). ¹H NMR (300 MHz, CDCl₃): δ 10.17 (s, 1 H), 9.00 (s, 1 H), 8.49 (d, J = 7.8 Hz, 1 H), 7.84 (d, J = 7.8 Hz, 1 H), 7.59 (t, J = 7.8 Hz, 1 H), 7.36 (s, 1 H), 4.04 (d, J = 6.5 Hz, 2 H), 2.28 (m, 1 H), 1.60 (s, 9 H), 1.13 (d, J = 6.6 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 193.7, 163.1, 152.8, 151.7, 138.7, 136.0, 129.2, 123.1, 115.7, 114.5, 96.9, 81.0, 77.6, 77.2, 76.7, 75.4, 28.5, 28.3, 19.4 ppm; HRMS (ESI) m/z: calcd for C₁₉H₂₅N₂O₄ [M+MeOH+H]⁺ 377.2071, found 377.2093

Compound 14: This compound was prepared according the general HWE coupling reaction between compounds **13** (1.03 g, 3 mmol) and **5**. The compound was purified by precipitation in DCM/hexane (1/5 vol/vol). Yield: 1.35 g (73%). ¹H NMR (300 MHz, CDCl₃): δ 9.15 (s, 1 H), 8.81 (d, J = 16.6 Hz, 1 H), 8.39 (d, J = 7.8 Hz, 1 H), 8.25-8.23 (m, 2 H), 7.80 (d, J = 16.6 Hz, 1 H), 7.78 (d, J = 7.8 Hz, 1 H), 7.66 (t, J = 7.8 Hz, 1 H), 7.62 (s, 1 H), 7.42 (t, J = 8.0 Hz, 1 H), 7.34 (s, 1 H), 4.21 (d, J = 5.6 Hz, 2 H), 4.11 (d, J = 6.4 Hz, 2 H), 4.09 (s, 3 H), 2.40-2.26 (m, 1 H), 1.93-1.81 (m, 1 H), 1.69-1.54 (m, 2 H), 1.60 (s, 9 H), 1.18 (d, J = 6.3 Hz, 6 H), 1.01 (t, J = 7.2 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.6, 163.2, 162.1, 155.8, 153.1, 148.3, 146.3, 139.0, 135.7, 135.0, 132.8, 129.6, 127.6, 127.5, 126.0, 123.0, 122.3, 120.8, 115.0, 114.4, 100.9, 98.2, 80.4, 74.8, 71.2, 53.1, 41.0, 28.6, 28.4, 23.8, 19.5, 11.4 ppm, HRMS (ESI) m/z: calcd for C₃₇H₄₆N₃O₆ [M+H]⁺ 628.3381, found 628.3380.

Corresponding 2-hydroxymethylquinoline of 14 (14b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from **14** (1.38 g, 2.19 mmol). Yield: 1.3 g (quant). ¹H NMR (300 MHz, CDCl₃): δ 9.14 (s, 1 H), 8.82 (d, J = 16.7 Hz, 1 H), 8.39 (d, J = 7.5 Hz, 1 H), 8.21-8.17 (m, 2 H), 7.78 (d, J = 8.3 Hz, 1 H), 7.56 (d, J = 16.7 Hz, 1 H), 7.55 (t, J = 7.8 Hz, 1 H), 7.41 (t, J = 8.0 Hz, 1 H), 7.17 (s, 1 H), 6.67 (s, 1 H), 4.91 (s, 2 H), 4.11 (d, J = 5.6 Hz, 2H), 4.07 (d, J = 6.4 Hz, 2 H), 2.35-2.26 (m, 1 H), 1.88-1.81 (m, 1 H), 1.60 (s, 9 H), 1.65-1.52 (m, 4 H), 1.16 (d, J = 6.7 Hz, 6 H), 1.00 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 162.7, 162.3, 159.8, 155.6, 153.1, 145.3, 139.0, 134.9, 134.0, 131.6, 129.8, 127.0, 126.0, 125.4, 122.7, 121.7, 120.8, 115.0, 114.4, 98.5, 97.6, 80.4, 74.7, 70.9, 64.7, 41.0, 28.6, 28.4, 23.8, 19.5, 11.4 ppm.

Corresponding 2-quinolinecarboxaldehyde of 14 (14c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from **14b** (1.31 g, 2.19 mmol). Yield: 1.13 g (86%). ¹H NMR (300 MHz, CDCl₃): δ 10.27 (s, 1 H), 9.19 (s, 1 H), 9.08 (d, J = 16.7 Hz, 1 H), 8.42 (d, J = 7.32 Hz, 1 H), 8.28-8.25 (m, 2 H), 7.79 (d, J = 8.4 Hz, 1 H), 7.70 (t, J = 7.8 Hz, 1 H), 7.66 (d, J = 16.7 Hz, 1 H), 7.43 (t, J = 8.1 Hz, 1 H), 7.43 (s, 1 H), 7.16 (s, 1 H), 4.21 (d, J = 5.6 Hz, 2 H), 4.08 (d, J = 6.33 Hz, 2 H), 2.37-2.28 (m, 1 H), 1.93-1.83 (m, 1 H), 1.61 (s, 9 H), 1.64-1.61 (m, 4 H), 1.18 (d, J = 6.6 Hz, 6 H), 1.01 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.5, 163.2, 162.4, 155.2, 153.3, 153.1, 146.7, 139.1, 135.9, 135.0, 131.9, 129.3, 128.1, 127.1, 126.1, 123.8, 122.6, 120.8, 115.1, 114.4, 99.3, 96.7, 80.5, 74.8, 71.3, 40.9, 28.6, 28.4, 23.7, 19.5, 11.4 ppm, HRMS (ESI) m/z: calcd for C₃₆H₄₄N₃O₅ [M+H]⁺ 598.3276, found 598.3275.

Boc-trimer S14: This compound was prepared according the general HWE coupling reaction from aldehyde **14c** (1.13 g, 1.89 mmol). The compound was purified by precipitation in DCM/hexane (1/5 vol/vol). Yield: 1.21 g (72%). ¹H NMR (300 MHz, CDCl₃): δ 9.20 (s, 1 H), 9.11 (d, J = 16.6 Hz, 1 H), 9.07 (d, J = 16.6 Hz, 1 H), 8.38 (d, J = 7.6 Hz, 1 H), 8.27-8.18 (m, 4 H), 7.82-7.76 (m, 2 H), 7.69 (d, J = 16.8 Hz, 1 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.63 (s, 1 H), 7.53 (t, J = 7.7 Hz, 1 H), 7.40 (t, J = 8.1 Hz, 1 H), 7.34 (s, 1 H), 7.31 (s, 1 H), 4.27 (d, J = 5.3 Hz, 2 H), 4.21 (d, J = 5.5 Hz, 2 H), 3.99 (d, J = 6.5 Hz, 2 H), 3.84 (s, 3 H), 2.22-2.11 (m, 1 H), 1.96-1.84 (m, 2 H), 1.75-1.55 (m, 8 H), 1.55 (s, 9 H), 1.05 (t, J = 7.6 Hz, 6 H), 1.02 (t, J = 7.3 Hz, 6 H), 1.01 (d, J = 7.1 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.6, 163.2, 162.3, 162.1, 157.0, 156.1, 153.2, 148.4, 146.4, 139.0, 136.0, 134.9, 134.4, 132.7, 131.2, 130.6, 130.1, 127.5, 127.4, 126.9, 125.8, 125.2, 123.0, 122.5, 122.3, 121.6, 120.7, 115.0, 114.4, 101.0, 98.9, 98.7, 80.3, 74.7, 71.2, 70.6, 53.0, 41.1, 41.0, 28.6, 28.3, 23.8, 23.7, 19.3, 11.5, 11.4 ppm, HRMS (ESI) m/z: calcd for C₅₄H₆₅N₄O₇ [M+H]⁺ 881.4849, found 881.4847.

Corresponding 2-hydroxymethylquinoline of Boc-trimer S14 (S14b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from **S14** (1.21 g, 1.37 mmol). Yield: 1.05 g (95%). ¹H NMR (300 MHz, CDCl₃): δ 9.19 (s, 1 H), 8.99 (d, J = 16.8 Hz, 1 H), 8.92 (d, J = 16.6 Hz, 1 H), 8.37 (d, J = 7.2 Hz, 1 H), 8.21-8.16 (m, 4 H), 7.77 (dd, J =

8.3, 1.2 Hz, 1 H), 7.69 (d, J = 16.6 Hz, 1 H), 7.67 (d, J = 16.8 Hz, 1 H), 7.54 (t, J = 7.1 Hz, 1 H), 7.52 (t, J = 7.1 Hz, 1 H), 7.39 (d, J = 16.1 Hz, 1 H), 7.30 (s, 1 H), 7.24 (s, 1 H), 6.67 (s, 1 H), 4.83 (s, 2 H), 4.24 (d, J = 5.4 Hz, 2 H), 4.11 (d, J = 5.5 Hz, 1 H), 4.04 (d, J = 6.4 Hz, 2 H), 2.32-1.98 (m, 2 H), 1.74-1.54 (m, 12 H), 1.53 (s, 9 H), 1.07 (d, J = 6.8 Hz, 6 H), 1.03 (t, J = 7.9 Hz, 6 H), 1.00 (t, J = 7.4 Hz, 6 H) ppm.

Corresponding 2-quinolinecarboxaldehyde of Boc-trimer S14 (S14c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from **S14b** (1.05 g, 1.23 mmol). Yield: 0.98 g (93%). ¹H NMR (300 MHz, CDCl₃): δ 10.13 (s, 1 H), 9.19 (s, 1 H), 9.12 (d, J = 16.5 Hz, 1 H), 9.03 (d, J = 16.7 Hz, 1 H), 8.38 (d, J = 7.4 Hz, 1 H), 8.27 (d, J = 8.3 Hz, 1 H), 8.28 (d, J = 7.1 Hz, 1 H), 8.21 (d, J = 6.9, 1 H), 8.18 (d, J = 7.6 Hz, 1 H), 7.80 (d, J = 16.8 Hz, 1 H), 7.78 (d, J = 4.7 Hz, 1 H), 7.70 (d, J = 16.7 Hz, 1 H), 7.69 (t, J = 7.9, 1 H), 7.53 (t, J = 15.6 Hz, 1 H), 7.41 (t, J = 8.0 Hz, 1 H), 7.42 (s, 1 H), 7.29 (s, 1 H), 7.28 (s, 1 H), 4.02 (d, J = 6.4 Hz, 2 H), 4.27 (d, J = 5.5 Hz, 2 H), 4.21 (d, J = 5.6 Hz, 2 H), 2.27-2.19 (m, 1 H), 1.94-1.84 (m, 2 H), 1.68-1.51 (m, 8 H), 1.51 (s, 9 H), 1.08 (d, J = 6.7 Hz, 6 H), 1.06 (t, J = 7.4 Hz, 6 H), 1.01 (t, J = 7.4 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.3, 163.2, 162.3, 162.2, 156.9, 156.0, 153.3, 153.1, 147.1, 146.8, 139.0, 136.1, 134.9, 134.6, 132.9, 131.4, 130.7, 129.8, 128.1, 127.4, 127.1, 125.8, 125.3, 123.7, 122.6, 122.5, 121.6, 120.7, 115.0, 114.4, 98.8, 98.6, 96.7, 80.2, 74.7, 71.3, 70.6, 41.1, 40.9, 28.5, 28.4, 23.9, 23.7, 19.4, 11.5, 11.3 ppm, HRMS (ESI) m/z: calcd for C₅₃H₆₃N₄O₆ [M+H]⁺ 851.4742, found 851.4741.

Compound 15: This compound was prepared according the general HWE coupling reaction from aldehyde **S14c** (0.98 g, 1.15 mmol). The compound was purified by precipitation in DCM/hexane (1/5 vol/vol). Yield: 0.94 g (72%). ¹H NMR (300 MHz, CDCl₃): δ 9.48 (d, J = 16.5 Hz, 1 H), 9.13 (s, 1 H), 9.10 (d, J = 17.9 Hz, 1 H), 8.97 (d, J = 16.9 Hz, 1 H), 8.29 (d, J = 7.3 Hz, 1 H), 8.22-8.18 (m, 4 H), 7.95 (d, J = 8.1 Hz, 1 H), 7.75-7.70 (m, 4 H), 7.54-7.50 (m, 4 H), 7.42 (d, J = 7.9 Hz, 1 H), 7.29 (s, 1 H), 7.22-7.15 (m, 3 H), 4.27 (d, J = 5.1 Hz, 2 H), 4.18-4.16 (m, 4 H), 3.89 (d, J = 6.2 Hz, 2 H), 3.77 (s, 3 H), 2.17-2.07 (m, 1 H), 1.94-1.80 (m, 3 H), 1.74-1.51 (m, 12 H), 1.57 (s, 9 H), 1.05 (t, J = 7.5 Hz, 6 H), 1.02 (t, J = 7.4 Hz, 6 H), 0.98 (t, J = 7.4 Hz, 6 H), 0.90 (d, J = 6.6 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 166.6, 163.0, 162.3, 161.9, 157.1, 157.0, 156.0, 153.2, 148.0, 146.1, 138.8, 135.2, 134.7, 132.4, 131.4, 131.2, 130.5, 127.4, 127.1, 126.7, 125.4, 125.1, 125.0, 122.6, 122.5, 122.4, 122.0, 121.6, 121.5, 120.5, 114.8, 113.4, 100.7, 99.8, 99.0, 98.4, 80.2, 74.4, 71.2, 70.7, 70.6, 52.8, 41.1, 41.0, 40.9, 28.6, 28.2, 23.8, 23.7, 23.7, 19.2, 11.4, 11.4 ppm, HRMS (ESI) m/z: calcd for C₇₁H₈₄N₅O₈ [M+H]⁺ 1134.6314, found 1134.6331.

Corresponding 2-quinolinecarboxaldehyde of 15 (15c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes starting from **15** (0.8 g, 0.7 mmol) by two steps. Yield: 0.75 g (89%). ¹H NMR (300 MHz, CDCl₃): δ 9.91 (s, 1 H), 9.61 (d, J = 16.3 Hz, 1 H), 9.10 (d, J = 16.7 Hz, 1 H), 9.04 (d, J = 19.8 Hz, 1 H), 8.25-8.13 (m, 4 H), 7.85 (d, J = 7.8 Hz, 1 H), 7.71-7.50 (m, 5 H), 7.33 (d, J = 7.8 Hz, 1 H), 7.29 (s, 1 H), 7.18-7.10 (m, 4 H), 4.25 (d, J = 5.5 Hz, 2 H), 4.20 (d, J = 5.6 Hz, 2 H), 4.16 (d, J = 5.9 Hz, 2 H), 3.80 (d, J = 6.7 Hz, 2 H), 2.06-1.84 (m, 4 H), 1.70-1.54 (m, 12 H), 1.56 (s, 9 H), 1.06 (t, J = 7.4 Hz, 6 H), 1.02 (t, J = 7.4 Hz, 6 H), 1.01 (t, J = 7.4 Hz, 6 H), 0.83 (d, J = 6.7 Hz, 6 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 194.6, 162.9, 162.4, 162.3, 161.6, 156.7, 155.9, 153.1, 153.0, 147.4, 147.1, 146.4, 138.6, 135.0, 134.8, 134.7, 134.0, 131.8, 131.5, 131.1, 130.6, 130.4, 130.2, 127.4, 127.0, 126.9, 126.6, 125.2, 125.1, 124.9, 123.2, 122.5, 122.4, 122.0, 121.5, 120.4, 114.6, 114.2, 100.4, 99.4, 98.2, 96.4, 80.2, 74.2, 71.4, 70.6, 70.6, 41.0, 41.0, 40.7, 28.6, 28.2, 23.9, 23.8, 23.7, 23.6, 19.2, 19.1, 11.5, 11.4, 11.4, 11.3 ppm, HRMS (ESI) m/z: calcd for C₇₀H₈₂N₅O₇ [M+H]⁺ 1104.6209, found 1104.6226.

Boc-pentamer S15: This compound was prepared according the general HWE coupling reaction from aldehyde **15c** (0.75 g, 0.68 mmol). The compound was purified by silica gel column chromatography (eluent: cyclohexane/ethyl acetate 20/1 vol/vol). Yield: 0.38 g (52%). ¹H NMR (300 MHz, CDCl₃): δ 9.42 (d, J = 16.6 Hz, 1 H), 9.35 (d, J = 16.4 Hz, 1 H), 9.18 (s, 1 H), 9.02 (d, J = 16.8 Hz, 1 H), 8.88 (d, J = 16.7 Hz, 1 H), 8.36 (d, J = 7.2 Hz, 1 H), 8.21-8.18 (m, 2 H), 8.05 (d, J = 7.3 Hz, 1 H), 8.02 (d, J = 8.4 Hz, 1 H), 7.96 (d, J = 8.2 Hz, 1 H), 7.90-7.80 (m, 3 H), 7.72-7.60 (m, 5 H), 7.56 (s, 1 H), 7.51 (t, J = 7.8 Hz, 1 H), 7.35-7.18 (m, 9 H), 4.24 (d, J = 5.6 Hz, 2 H), 4.19 (d, J = 5.6 Hz, 2 H), 4.15 (d, J = 5.7 Hz, 2 H), 4.07 (d, J = 5.8 Hz, 2 H), 4.02 (d, J = 6.5 Hz, 2 H), 3.83 (s, 3 H), 2.25-2.17

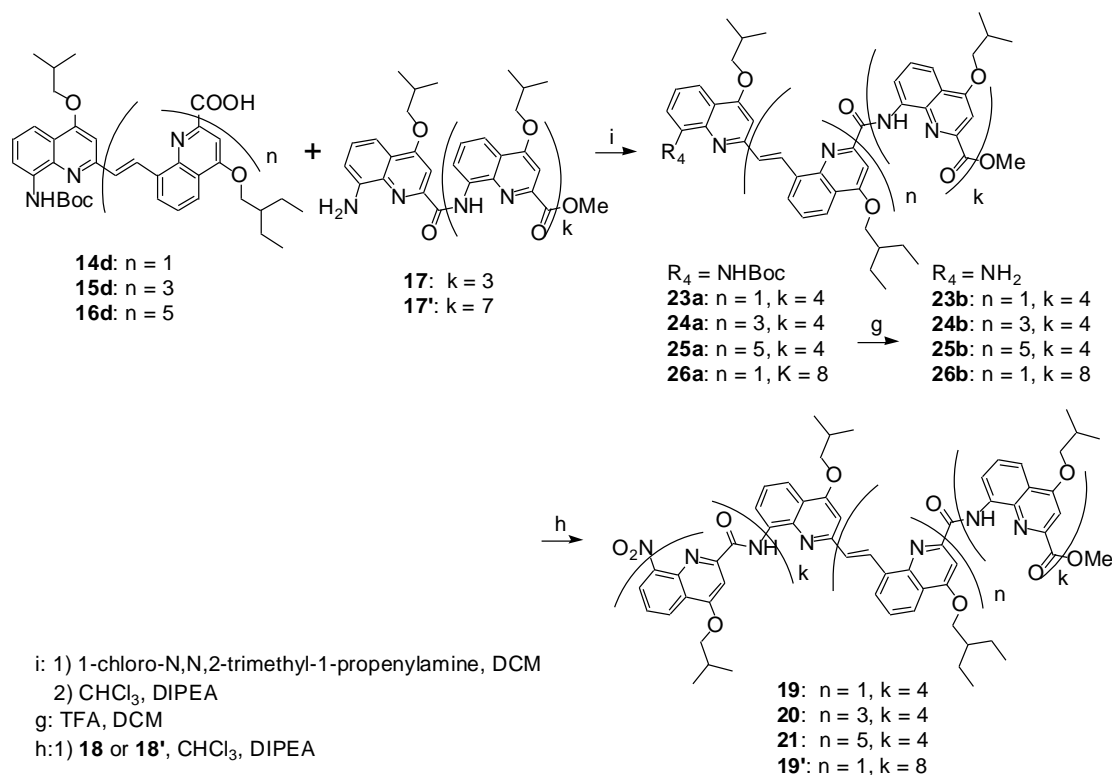
(m, 1 H), 1.96-1.54 (m, 20 H), 1.58 (s, 9 H), 1.08-0.83 (m, 30 H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 166.7, 163.0, 162.3, 162.1, 162.0, 157.2, 157.1, 156.9, 156.2, 153.2, 148.0, 147.3, 147.0, 146.8, 146.1, 138.9, 135.4, 134.8, 134.4, 134.2, 134.1, 132.9, 131.5, 131.3, 130.9, 130.7, 130.4, 129.9, 127.3, 127.2, 126.6, 126.4, 125.5, 124.8, 124.5, 122.6, 122.4, 122.2, 122.1, 121.8, 121.5, 121.3, 120.6, 114.8, 114.4, 100.7, 99.9, 99.3, 98.7, 98.4, 80.2, 74.6, 71.1, 70.7, 70.6, 52.8, 41.0, 41.0, 40.9, 40.8, 28.6, 28.3, 23.8, 23.7, 23.7, 23.5, 19.3, 11.4, 11.4, 11.3, 11.3 ppm, HRMS (ESI) m/z : calcd for $\text{C}_{88}\text{H}_{103}\text{N}_6\text{O}_9$ $[\text{M}+\text{H}]^+$ 1387.7781, found 1387.7816.

Corresponding 2-hydroxymethylquinoline of Boc-pentamer S15 (S15b): This compound was prepared according to the general procedure for the synthesis of 2-hydroxymethylquinolines from **S15** (0.38 g, 0.27 mmol). Yield: 0.37 g (quant). ^1H NMR (300 MHz, CDCl_3): δ 9.40 (d, $J = 16.5$ Hz, 1 H), 9.38 (d, $J = 16.5$ Hz, 1 H), 9.18 (s, 1 H), 9.01 (d, $J = 16.8$ Hz, 1 H), 8.74 (d, $J = 16.6$ Hz, 1 H), 8.34 (d, $J = 7.7$ Hz, 1 H), 8.20 (d, $J = 8.2$ Hz, 1 H), 8.19 (d, $J = 7.5$ Hz, 1 H), 8.03 (d, $J = 5.4$ Hz, 1 H), 8.01 (d, $J = 6.9$ Hz, 1 H), 7.93 (d, $J = 8.2$ Hz, 1 H), 7.88 (d, $J = 5.5$ Hz, 1 H), 7.84 (d, $J = 16.5$ Hz, 1 H), 7.81 (d, $J = 8.1$ Hz, 1 H), 7.67-7.47 (m, 6 H), 7.32 (t, $J = 8.1$ Hz, 1 H), 7.27 (s, 1 H), 7.23-7.16 (m, 5 H), 7.10 (t, $J = 7.8$ Hz, 1 H), 6.61 (s, 1 H), 4.81 (s, 2 H), 4.21 (d, $J = 5.5$ Hz, 4 H), 4.07 (d, $J = 5.3$ Hz, 2 H), 4.05 (d, $J = 4.7$ Hz, 2 H), 4.00 (d, $J = 6.6$ Hz, 2 H), 2.27-2.18 (m, 1 H), 1.92-1.49 (m, 20 H), 1.07-0.96 (m, 24 H), 0.89 (t, $J = 7.4$ Hz, 6 H) ppm.

Corresponding 2-quinolinecarboxaldehyde of Boc-pentamer S15 (S15c): This compound was prepared according to the general procedure for the synthesis of 2-quinolinecarboxaldehydes from **S15b** (0.37 g, 0.27 mol). Yield: 0.36 g (95%). ^1H NMR (300 MHz, CDCl_3): δ 9.98 (s, 1 H), 9.54 (d, $J = 16.3$ Hz, 1 H), 9.34 (d, $J = 16.6$ Hz, 1 H), 9.15 (s, 1 H), 8.99 (d, $J = 16.6$ Hz, 1 H), 8.92 (d, $J = 16.8$ Hz, 1 H), 8.35 (d, $J = 7.0$ Hz, 1 H), 8.22 (d, $J = 8.2$ Hz, 1 H), 8.14 (d, $J = 6.5$ Hz, 1 H), 7.99 (d, $J = 7.9$ Hz, 2 H), 7.90 (d, $J = 6.3$ Hz, 1 H), 7.87 (d, $J = 7.2$ Hz, 1 H), 7.78 (d, $J = 16.4$ Hz, 1 H), 7.73 (d, $J = 8.2$ Hz, 1 H), 7.64-7.48 (m, 6 H), 7.33 (t, $J = 8.0$ Hz, 1 H), 7.31 (s, 1 H), 7.26-7.13 (m, 3 H), 7.11 (s, 1 H), 7.09 (s, 1 H), 7.07 (s, 1 H), 4.22 (d, $J = 5.9$ Hz, 2 H), 4.20 (d, $J = 5.9$ Hz, 2 H), 4.09 (d, $J = 5.8$ Hz, 2 H), 4.02 (d, $J = 6.6$ Hz, 2 H), 3.98 (d, $J = 5.8$ Hz, 2 H), 2.28-2.17 (m, 1 H), 1.94-1.38 (m, 20 H), 1.59 (s, 9 H), 1.08-0.99 (m, 18 H), 0.95 (t, $J = 7.4$ Hz, 6 H), 0.87 (t, $J = 7.4$ Hz, 6 H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 194.6, 162.8, 162.4, 162.2, 161.9, 161.8, 157.0, 156.8, 156.5, 156.2, 153.2, 153.0, 147.4, 147.1, 146.6, 146.4, 138.9, 135.9, 135.3, 134.8, 134.3, 134.0, 132.2, 131.7, 131.4, 131.2, 130.7, 130.6, 130.1, 129.8, 127.5, 127.3, 127.0, 126.4, 125.7, 125.4, 124.8, 124.3, 123.2, 122.5, 122.2, 122.0, 121.9, 121.5, 121.3, 121.2, 120.6, 114.8, 114.4, 100.4, 99.4, 99.2, 98.3, 96.4, 80.2, 74.6, 71.3, 70.6, 41.0, 40.9, 40.8, 34.4, 30.5, 29.6, 28.6, 28.4, 23.8, 23.5, 23.4, 21.3, 19.3, 11.4, 11.4, 11.3, 11.2 ppm, HRMS (ESI) m/z : calcd for $\text{C}_{87}\text{H}_{101}\text{N}_6\text{O}_8$ $[\text{M}+\text{H}]^+$ 1357.7675, found 1357.7717.

Compound 16: This compound was prepared according the general HWE coupling reaction from aldehyde **S15c** (0.32 g, 0.23 mmol). The compound was purified by silica gel column chromatography (eluent: cyclohexane/ethyl acetate 20/1 vol/vol). Yield: 0.17 g (36%). ^1H NMR (300 MHz, CDCl_3): δ 9.34 (d, $J = 16.6$ Hz, 1 H), 9.31 (d, $J = 16.2$ Hz, 1 H), 9.28 (d, $J = 16.4$ Hz, 1 H), 9.19 (s, 1 H), 9.06 (d, $J = 16.7$ Hz, 1 H), 8.93 (d, $J = 16.7$ Hz, 1 H), 8.36 (d, $J = 6.5$ Hz, 1 H), 8.13 (d, $J = 6.8$ Hz, 1 H), 8.09 (d, $J = 6.7$ Hz, 1 H), 8.03-7.99 (m, 4 H), 7.94-7.56 (m, 12 H), 7.39 (d, $J = 15.7$ Hz, 1 H), 7.34-7.15 (m, 12 H), 4.23 (d, $J = 5.8$ Hz, 2 H), 4.17 (d, $J = 5.5$ Hz, 6 H), 4.12 (d, $J = 5.6$ Hz, 2 H), 3.98 (d, $J = 6.4$ Hz, 2 H), 3.84 (s, 3 H), 2.21-2.12 (m, 1 H), 1.93-1.77 (m, 5 H), 1.66-1.44 (m, 29 H), 1.08-0.86 (m, 36 H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 166.6, 162.1, 157.2, 156.9, 156.2, 153.2, 148.1, 147.0, 146.2, 134.8, 134.3, 131.5, 130.9, 127.2, 127.1, 126.7, 125.5, 124.7, 122.4, 122.1, 121.8, 121.2, 120.7, 114.8, 114.4, 100.8, 99.4, 98.4, 80.2, 74.6, 71.2, 70.7, 52.9, 40.9, 28.6, 28.3, 23.7, 23.6, 22.8, 19.3, 11.4, 11.3 ppm, HRMS (ESI) m/z : calcd for $\text{C}_{105}\text{H}_{122}\text{N}_7\text{O}_{10}$ $[\text{M}+\text{H}]^+$ 1641.9281, found 1641.9285.

Synthesis of compounds 19, 19', 20 and 21:



Scheme S4: Synthesis of compound **19** (**19'**)-**21**.

General procedure for the saponification of methyl esters to obtain the carboxylic acids: To a round bottom flask were added the methyl ester (1 equiv.) and sodium hydroxide (10 equiv.), then tetrahydrofuran (2 mL) and methanol (0.2 mL). The mixture was stirred at room temperature for about 2 hours. Upon completion of the reaction (TLC), an aqueous citric acid solution (5% w/vol) was added to adjust the pH to around 3. Usually the product precipitated out from the solution. The precipitate was filtered and washed with water three times. The solid was collected and was dried under high vacuum to obtain a yellow solid.

Corresponding free carboxylic acid of 14 (14d): This compound was prepared according to general saponification procedure from **14** (75 mg, 0.12 mmol). Yield: 65 mg (87%). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.12 (s, 1 H), 8.76 (d, $J = 16.4$ Hz, 1 H), 8.43 (d, $J = 7.8$ Hz, 1 H), 8.29 (d, $J = 9.5$ Hz, 1 H), 8.26 (d, $J = 7.2$ Hz, 1 H), 7.80 (d, $J = 8.3$ Hz, 1 H), 7.71 (t, $J = 7.9$ Hz, 1 H), 7.71 (s, 1 H), 7.55 (d, $J = 16.4$ Hz, 1 H), 7.44 (t, $J = 8.1$ Hz, 1 H), 7.08 (s, 1 H), 4.25 (d, $J = 5.6$ Hz, 2 H), 4.07 (d, $J = 6.4$ Hz, 2 H), 2.34-2.28 (m, 1 H), 1.94-1.82 (m, 1 H), 1.68-1.51 (m, 13 H), 1.17 (d, $J = 6.7$ Hz, 6 H), 1.02 (t, $J = 7.4$ Hz, 6 H) ppm, HRMS (ESI) m/z : calcd for $\text{C}_{36}\text{H}_{42}\text{N}_3\text{O}_6$ $[\text{M}-\text{H}]^-$ 612.3068, found 612.3063.

Corresponding free carboxylic acid of 15 (15d): This compound was prepared according to general saponification procedure from **15** (36 mg, 0.031 mmol). Yield: 30 mg (85%). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.68 (d, $J = 16.2$ Hz, 1 H), 9.10 (d, $J = 16.9$ Hz, 1 H), 8.93 (s, 1H), 8.79 (d, $J = 16.1$ Hz, 1 H), 8.21 (d, $J = 7.2$ Hz, 4 H), 8.13 (d, $J = 7.4$ Hz, 1 H), 7.81 (d, $J = 8.3$ Hz, 1 H), 7.65 (d, $J = 16.3$ Hz, 1 H), 7.60-7.49 (m, 6 H), 7.43 (d, $J = 16.3$ Hz, 1 H), 7.30 (d, $J = 8.1$ Hz, 1 H), 7.13-7.02 (m, 6 H), 4.24-4.19 (m, 6 H), 3.73 (d, $J = 6.7$ Hz, 2 H), 1.97-1.88 (m, 4 H), 1.68-1.58 (m, 12 H), 1.07-0.99 (m, 18 H), 0.78 (d, $J = 6.7$ Hz, 6 H) ppm, HRMS (ESI) m/z : calcd for $\text{C}_{70}\text{H}_{82}\text{N}_5\text{O}_8$ $[\text{M}+\text{H}]^+$ 1120.6158, found 1120.6208.

Corresponding free carboxylic acid of 16 (16d): This compound was prepared according to general saponification procedure from **16** (92 mg, 0.056 mmol). Yield: 75 mg (83%). $^1\text{H NMR}$ (300

MHz, CDCl₃): δ 9.38 (d, J = 16.5 Hz, 1 H), 9.36 (d, J = 16.3 Hz, 1 H), 9.16 (d, J = 16.2 Hz, 1 H), 9.18 (s, 1 H), 8.99 (d, J = 16.8 Hz, 1 H), 8.72 (d, J = 16.4 Hz, 1 H), 8.35 (d, J = 6.8 Hz, 1 H), 8.11 (d, J = 6.6 Hz, 1 H), 7.97 (d, J = 6.7 Hz, 4 H), 7.87 (d, J = 7.4 Hz, 1 H), 7.82 (d, J = 6.5 Hz, 1 H), 7.74 (d, J = 7.8 Hz, 1 H), 7.68-7.30 (m, 11 H), 7.22-7.07 (m, 5 H), 7.00 (s, 1 H), 6.97 (s, 1 H), 6.91 (s, 1 H), 4.19-4.12 (m, 8 H), 3.96 (d, J = 6.0 Hz, 4 H), 2.20-2.11 (m, 1 H), 1.92-1.82 (m, 5 H), 1.66-1.37 (m, 31 H), 1.02-0.83 (m, 36 H) ppm, HRMS (ESI) m/z: calcd for C₁₀₄H₁₂₀N₇O₁₀ [M+H]⁺ 1627.9125, found 1627.9177.

General procedure for Boc-amine deprotection: To a dry flask was the Boc-protected amine compound (1 equiv.) and 3 mL of dry dichloromethane. Trifluoroacetic acid (TFA, 1 mL) was added into the solution. The mixture was stirred at room temperature for 2 hours. Dichloromethane (15 mL) was further added to dilute the solution and the solution was washed with water and saturated NaHCO₃ aqueous solution three times. The organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. The resulting solid was used without any further purification.

General procedure for the acid chloride coupling: To a dry 25 mL flask was added the corresponding carboxylic acid (1 equiv.). Then the flask was sealed with septum and flushed with N₂. Dry chloroform (5 mL) was added into the flask to dissolve the solid under N₂. Then oxalyl chloride (when there is no acid sensitive functional group presented, 5 equiv.) or 1-chloro-N,N,2-trimethyl-1-propenylamine (Ghosez's reagent, when acid sensitive Boc groups are present, 1.5 equiv.) was added. The mixture was stirred at room temperature under N₂ for 2 hours. Upon completion of the activation, the solvent was removed under high vacuum and the residue was dried under high vacuum for 3 hours. To a separate dry flask was added the corresponding amine (0.95 eq). The flask was sealed with a septum and flushed with N₂. Then dry DIPEA (2 equiv.) and 2 mL of dry chloroform were added. The acid chloride was removed from the vacuum line, placed under N₂, and dissolved into a minimum amount of dry chloroform. The acid chloride solution was transferred into the flask containing the amine and the resulting mixture was stirred at room temperature under N₂ overnight. Then the reaction was quenched by adding water. Dichloromethane was added to extract the product. Depending on the purity of the crude, either precipitation with DCM/methanol or silica gel column chromatography (eluent: dichloromethane/ethyl acetate) was used to purify the compound.

Compound 23a: This compound was prepared according to the general acid chloride coupling between the carboxylic acid **14d** (70 mg, 0.114 mmol) and amine **17** (90 mg, 0.0912 mmol). Activation of acid to acid chloride was done with 1-chloro-N,N,2-trimethyl-1-propenylamine. Purification was achieved by silica gel chromatography. Yield: 135 mg (87%). ¹H NMR (300 MHz, CDCl₃): δ 11.91 (s, 1H), 11.82 (s, 1 H), 11.72 (s, 1 H), 11.49 (s, 1 H), 8.64 (s, 1 H), 8.50 (d, J = 6.7 Hz, 1 H), 8.36 (d, J = 7.8 Hz, 1 H), 8.32 (d, J = 8.6 Hz, 1 H), 8.28 (d, J = 7.4 Hz, 1 H), 8.23 (d, J = 7.3 Hz, 1 H), 8.09 (d, J = 8.5 Hz, 1 H), 8.06 (d, J = 7.6 Hz, 1 H), 7.85 (d, J = 6.8 Hz, 1 H), 7.80 (d, J = 8.5 Hz, 1 H), 7.67 (d, J = 7.6 Hz, 1 H), 7.62 (d, J = 7.5 Hz, 2 H), 7.47 (d, J = 16.2 Hz, 1 H), 7.40-7.19 (m, 6 H), 7.09-6.98 (m, 2 H), 6.87 (s, 1 H), 6.82 (s, 1 H), 6.62 (d, J = 16.6 Hz, 1 H), 6.47 (s, 1 H), 6.20 (s, 1 H), 4.54-4.49 (m, 1 H), 4.51 (d, J = 9.0 Hz, 2 H), 4.33-4.27 (m, 2 H), 4.11-3.93 (m, 5 H), 3.68 (d, J = 6.6 Hz, 2 H), 3.17 (s, 3 H), 2.57-2.07 (m, 6 H), 1.85-1.71 (m, 4 H), 1.59 (s, 9 H), 1.34-1.07 (m, 30 H), 0.70 (d, J = 6.6 Hz, 3 H), 0.59 (d, J = 6.7 Hz, 3 H) ppm, HRMS (ESI) m/z: calcd for C₉₃H₁₀₂N₁₁O₁₄ [M+H]⁺ 1597.7636, found 1597.7646.

Compound 23b: This compound was prepared from **23a** according to the general Boc-amine deprotection procedure from **23a** (130 mg, 0.081 mmol). Yield 120 mg (95%). ¹H NMR (300 MHz, CDCl₃): δ 11.93 (s, 1 H), 11.89 (s, 1 H), 11.76 (s, 1 H), 11.58 (s, 1 H), 8.54 (d, J = 8.0 Hz, 1 H), 8.40 (d, J = 7.6 Hz, 1 H), 8.29 (d, J = 7.6 Hz, 1 H), 8.24 (d, J = 8.1 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 8.05 (d, J = 8.5 Hz, 1 H), 7.83 (d, J = 6.0 Hz, 1 H), 7.81 (d, J = 7.1 Hz, 1 H), 7.74 (d, J = 16.8 Hz, 1 H), 7.64 (t, J = 7.9 Hz, 1 H), 7.48 (t, J = 7.9 Hz, 1 H), 7.40 (t, J = 8.1 Hz, 1 H), 7.39 (s, 1 H), 7.36-7.28 (m, 2 H), 7.23 (s, 1H), 7.20-7.10 (m, 1 H), 7.02 (t, J = 7.9 Hz, 1 H), 6.85 (s, 1H), 6.81 (s, 1H), 6.74 (d, J = 7.4 Hz, 1 H), 6.50 (d, J = 16.5 Hz, 1 H), 6.48 (s, 1 H), 6.22 (s, 1H), 4.55-4.47 (m, 3 H), 4.35-4.27 (m, 2 H), 4.12-3.92 (m, 5 H), 3.68 (d, J = 6.3 Hz, 2 H), 3.18 (s, 3 H), 2.57-2.08 (m, 6 H), 1.87-1.70 (m, 4 H), 1.37-1.23 (m, 18 H), 1.19-1.13 (m, 6 H), 1.10 (t, J = 6.3 Hz, 6 H), 0.70 (d, J = 6.7 Hz, 3 H), 0.60 (d, J = 6.7 Hz, 3 H) ppm.

Compound 19: This compound was prepared according to the general acid chloride coupling between the acid chloride **18** (123 mg, 0.12 mmol) and amine **23b** (120 mg, 0.08 mmol). Activation of acid to acid chloride was done with oxalyl chloride. Purification was achieved by silica gel chromatography. Yield: 120 mg (75%). ¹H NMR (400 MHz, CDCl₃): δ 11.30 (s, 1 H), 11.20 (s, 1 H), 11.14 (s, 1 H), 11.01 (s, 1 H), 10.97 (s, 1 H), 10.84 (s, 1 H), 10.78 (s, 1 H), 10.72 (s, 1 H), 8.24 (d, J = 8.2 Hz, 1 H), 8.19 (d, J = 7.5 Hz, 1 H), 8.15 (d, J = 7.7 Hz, 1 H), 8.14 (d, J = 7.5 Hz, 1 H), 8.07 (d, J = 7.5 Hz, 1 H), 7.96 (d, J = 8.3 Hz, 1 H), 7.91 (d, J = 7.5 Hz, 1 H), 7.84 (d, J = 8.2 Hz, 1 H), 7.53 (d, J = 7.9 Hz, 1 H), 7.40 (d, J = 7.7 Hz, 1 H), 7.38 (d, J = 7.9 Hz, 1 H), 7.30 (t, J = 7.8 Hz, 1 H), 7.01 (s, 1 H), 6.63 (s, 1 H), 6.61 (s, 1 H), 6.50 (s, 1 H), 6.27 (s, 1 H), 5.88 (s, 1 H), 5.40 (s, 1 H), 5.08 (s, 1 H), 2.94 (s, 3 H), 1.04 (t, J = 7.9 Hz, 6 H) ppm; ¹³C NMR (200 MHz, CDCl₃): δ 163.9, 163.5, 163.3, 163.2, 163.2, 163.0, 162.9, 162.4, 162.1, 161.8, 161.6, 161.0, 161.0, 160.8, 160.8, 160.6, 160.2, 159.8, 159.8, 153.4, 150.6, 150.4, 150.0, 149.2, 148.8, 148.6, 148.2, 145.4, 145.0, 144.6, 139.9, 139.1, 139.1, 139.0, 138.6, 138.4, 138.3, 137.9, 137.8, 137.2, 134.6, 133.9, 133.8, 133.8, 133.7, 133.7, 133.5, 133.3, 132.6, 128.3, 127.6, 127.3, 127.2, 126.8, 126.7, 126.2, 126.1, 125.3, 124.6, 124.4, 124.0, 123.3, 122.6, 122.4, 122.1, 121.9, 121.8, 121.6, 121.3, 120.7, 117.4, 117.4, 117.3, 117.2, 116.9, 116.8, 116.5, 116.4, 116.4, 116.3, 116.1, 115.6, 115.2, 114.8, 100.4, 100.4, 100.0, 99.5, 98.8, 98.1, 98.0, 97.9, 97.8, 76.0, 75.8, 75.7, 75.6, 75.5, 75.2, 75.0, 74.9, 71.8, 52.0, 41.6, 28.8, 28.8, 28.8, 28.7, 28.7, 28.6, 28.5, 28.5, 24.2, 24.1, 19.6, 19.6, 19.6, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 19.2, 11.6 ppm, HRMS (ESI) m/z: calcd for C₁₄₄H₁₄₈N₁₉O₂₂ [M+H]⁺ 2496.1074, found 2496.1087.

Compound 24a: This compound was prepared according to the general acid chloride coupling between the carboxylic acid of **15** (30 mg, 0.026) and amine **17** (20 mg, 0.02). Activation of acid to acid chloride was done with 1-chloro-N,N,2-trimethyl-1-propenylamine. Purification was done by silica gel column chromatography (eluent: DCM/ethyl acetate 15/1 vol/vol). Yield: 35 mg (82%). ¹H NMR (300 MHz, CDCl₃): δ 11.62 (s, 1 H), 11.60 (s, 1 H), 11.47 (s, 1 H), 11.36 (s, 1 H), 8.82 (s, 1 H), 8.70 (d, J = 16.3 Hz, 1 H), 8.50 (d, J = 16.7 Hz, 1 H), 8.33 (d, J = 7.4 Hz, 1 H), 8.22-8.08 (m, 4 H), 8.01-7.91 (m, 3 H), 7.84 (d, J = 7.3 Hz, 1 H), 7.74-7.60 (m, 3 H), 7.54-7.34 (m, 6 H), 7.24-7.06 (m, 6 H), 6.98 (t, J = 7.9 Hz, 1 H), 6.87 (s, 1 H), 6.80 (d, J = 6.1 Hz, 1 H), 6.75 (d, J = 7.9 Hz, 1 H), 6.67 (s, 1 H), 6.58 (s, 1 H), 6.40 (s, 1 H), 6.22 (s, 1 H), 6.07 (s, 1 H), 4.47-4.42 (m, 1 H), 4.24-3.68 (m, 12 H), 3.66-3.62 (m, 2 H), 3.46-3.41 (m, 1 H), 3.02 (s, 3 H), 2.52-2.12 (m, 7 H), 1.92-1.56 (m, 15 H), 1.37-1.34 (m, 6 H), 1.29-0.98 (m, 42 H), 0.56 (d, J = 6.4 Hz, 3 H), 0.34 (d, J = 6.3 Hz, 3 H), HRMS (ESI) m/z: calcd for C₁₂₇H₁₄₀N₁₃O₁₆ [M+H]⁺ 2104.0569, found 2104.0586.

Compound 20: This compound was prepared according to the general acid chloride coupling between the acid chloride **18** (60 mg, 0.059 mmol) and the corresponding amine **24b** (40 mg, 0.0199 mmol). Activation of acid to acid chloride was done with oxalyl chloride. Purification was achieved by silica gel chromatography and crystallization with dichloromethane/methanol (1/4 vol/vol). Yield: 20 mg (33%). ¹H NMR (300 MHz, CD₂Cl₂/MeOH-D₃ (4/6 vol/vol)) δ 11.28 (s, 1 H), 11.10 (s, 2 H), 11.07 (s, 1 H), 11.06 (s, 1 H), 10.92 (s, 1 H), 10.84 (s, 1 H), 8.24 – 8.17 (m, 2 H), 7.93 (d, J = 7.4 Hz, 1 H), 7.91 – 7.86 (m, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 7.75 – 7.55 (m, 10 H), 7.49 (dd, J = 8.3, 1.5 Hz, 3 H), 7.38 (t, J = 8.0 Hz, 2 H), 7.33 – 7.17 (m, 5 H), 7.16 – 6.96 (m, 11 H), 6.92 (s, 1 H), 6.74 (t, J = 7.9 Hz, 1 H), 6.60 (t, J = 7.7 Hz, 1 H), 6.46 (d, J = 7.5 Hz, 1 H), 6.37 (s, 1 H), 6.36 (s, 1 H), 6.27 (s, 1 H), 6.21 (s, 1 H), 6.15 (d, J = 7.3 Hz, 1 H), 5.85 (d, J = 7.1 Hz, 1 H), 5.70 (s, 1 H), 5.62 (s, 1 H), 4.65 (s, 1 H), 4.35 – 4.07 (m, 11 H), 3.96 – 3.35 (m, 15 H), 2.86 (s, 3 H), 2.42 – 1.59 (m, 28 H), 1.32 – 0.97 (m, 108 H). HRMS (ESI) m/z: calcd for C₁₇₈H₁₈₆N₂₁O₂₄ [M+H]⁺ 3003.4041, found 3003.4087.

Compound 25a: This compound was prepared according to the general acid chloride coupling between the carboxylic acid of **16** (50 mg, 0.03 mmol) and amine **17** (20 mg, 0.02 mmol). Activation of acid to acid chloride was done with 1-chloro-N,N,2-trimethyl-1-propenylamine. Purification was done by silica gel column chromatography (eluent: DCM/ethyl acetate 15/1 vol/vol). Yield: 32 mg (78%). ¹H NMR (300 MHz, CDCl₃) δ 11.62 (s, 1 H), 11.60 (s, 1 H), 11.45 (s, 1 H), 11.34 (s, 1 H), 9.24 (s, 1 H), 9.03 (d, J = 16.6 Hz, 1 H), 8.86 (d, J = 17.7 Hz, 1 H), 8.76 (d, J = 16.3 Hz, 1 H), 8.66 (d, J = 16.3 Hz, 1 H), 8.40 (d, J = 7.7 Hz, 1 H), 8.30 (d, J = 7.5 Hz, 1 H), 8.21 – 8.11 (m, 4 H), 8.02 – 7.85 (m, 6 H), 7.81 – 7.61 (m, 10 H), 7.54 – 7.31 (m, 10 H), 7.24 – 7.05 (m, 6 H), 6.95 (s, 1 H), 6.92 (s, 1 H), 6.88 (s, 1 H), 6.78 (m, 3 H), 6.67 (s, 1 H), 6.59 (s, 1 H), 6.58 (t, J = 7.4 Hz, 1 H), 6.37 (s, 1 H), 6.26 (s,

1 H), 6.02 (s, 2 H), 4.36 – 3.54 (m, 24 H), 3.01 (s, 3 H), 2.52 – 2.83 (m, 12 H), 1.62 (s, 9 H), 1.33 – 0.92 (m, 54 H). HRMS (ESI) m/z: calcd for C₁₆₁H₁₇₈N₁₅O₁₈ [M+H]⁺ 2610.3502, found 2610.3562.

Compound 21: This compound was prepared according to the general acid chloride coupling between the acid chloride **18** (60 mg, 0.059 mmol) and corresponding amine **25b** (40 mg, 0.0159 mmol). Activation of acid to acid chloride was done with oxalyl chloride. Purification was achieved by silica gel chromatography and crystallization with dichloromethane/methanol. Yield: 15 mg (27%). ¹H NMR (300 MHz, CD₂Cl₂) shows multiple sets of signals. ¹H NMR (300 MHz, CD₂Cl₂) δ 12.09-10.84 (m, 8 H, CONH), 8.50-5.81 (m, 53 H, Ar-H), 4.29-3.33 (m, 21 H), 3.16-2.88 (m, 3 H), 2.40-0.63 (m, 155 H) ppm. HRMS (ESI) m/z: calcd for C₂₁₂H₂₂₄N₂₃O₂₆ [M+2H]²⁺ 1755.3524, found 1755.3685.

Compound 26a: This compound was prepared according to the general acid chloride coupling between the carboxylic acid of **14** (94 mg, 0.152 mmol) and amine **17'** (150 mg, 0.076 mmol). Activation of acid to acid chloride was done with 1-chloro-N,N,2-trimethyl-1-propenylamine. Purification was achieved by silica gel column chromatography (eluent: DCM/ethyl acetate 15/1 vol/vol). Yield: 115 mg (85%). ¹H NMR (300 MHz, CDCl₃) δ 11.33 (s, 1 H), 11.24 (s, 2 H), 10.83 (s, 1 H), 10.80 (s, 1 H), 10.74 (s, 1 H), 10.72 (s, 1 H), 10.70 (s, 1 H), 8.53 (s, 1 H), 8.18 (d, J = 7.6 Hz, 1 H), 8.10 (dd, J = 7.7, 1.3 Hz, 1 H), 8.08 (dd, J = 7.7, 1.3 Hz, 1 H), 8.05 – 7.90 (m, 5 H), 7.88 (dd, J = 8.0, 1.5 Hz, 1 H), 7.82 (dd, J = 8.3, 1.3 Hz, 1 H), 7.78 (dd, J = 8.4, 1.2 Hz, 1 H), 7.71 (ddd, J = 9.5, 8.3, 1.3 Hz, 2 H), 7.53 – 7.44 (m, 3 H), 7.36 (dd, J = 7.8, 1.3 Hz, 1 H), 7.35 (s, 1 H), 7.33 (s, 1 H), 7.29 – 6.90 (m, 12 H), 6.87 (s, 1 H), 6.72 (s, 1 H), 6.59 (s, 1 H), 6.52 (s, 1 H), 6.38 (s, 1 H), 6.35 (s, 1 H), 6.35 (d, J = 15.4 Hz, 1 H), 6.32 (s, 1 H), 6.18 (s, 1 H), 6.17 (s, 1 H), 5.88 (s, 1 H), 4.19 (m, 2 H), 4.09 – 3.73 (m, 16 H), 3.64 (d, J = 6.3 Hz, 2 H), 2.95 (s, 3 H), 2.88 (t, J = 7.9 Hz, 1 H), 2.50 – 2.09 (m, 9 H), 2.01 – 1.89 (m, 1 H), 1.56 (s, 9 H), 1.33 – 1.01 (m, 54 H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 163.8, 162.8, 162.7, 162.7, 162.6, 162.6, 162.4, 162.2, 162.0, 161.5, 161.2, 161.0, 160.6, 159.6, 159.4, 159.3, 154.0, 153.0, 150.2, 150.0, 149.0, 149.0, 148.8, 148.6, 148.6, 145.1, 144.1, 138.7, 138.2, 138.0, 137.9, 137.5, 137.4, 137.4, 134.2, 134.0, 133.6, 133.4, 133.4, 133.3, 132.9, 132.8, 132.7, 132.6, 130.6, 127.6, 127.5, 126.9, 126.8, 126.8, 126.0, 125.7, 125.6, 125.6, 125.4, 122.9, 122.4, 122.3, 122.0, 121.9, 121.6, 121.5, 121.4, 120.4, 117.1, 117.0, 116.8, 116.7, 116.6, 116.2, 116.1, 116.0, 115.8, 115.6, 114.6, 114.4, 100.1, 99.7, 98.9, 98.6, 97.7, 97.6, 97.5, 80.0, 75.5, 75.3, 75.2, 75.2, 75.0, 74.8, 73.4, 71.2, 52.0, 40.8, 28.6, 28.3, 28.3, 28.2, 28.2, 28.2, 27.8, 23.8, 23.6, 19.8, 19.8, 19.7, 19.6, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.0, 18.7, 11.5, 11.2 ppm; HRMS (ESI) m/z: calcd for C₁₄₉H₁₅₈N₁₉O₂₂ [M+H]⁺ 2566.1857, found [M+H]⁺ 2566.1995.

Compound 19': This compound was prepared according to the general acid chloride coupling between the acid chloride **18'** (113 mg, 0.056 mmol) and amine **26b** (70 mg, 0.028 mmol). Activation of acid to acid chloride was done with oxalyl chloride. Purification was achieved by silica gel chromatography (eluent: DCM/ethyl acetate 15/1 vol/vol). Yield: 120 mg (75%). ¹H NMR (300 MHz, CDCl₃): δ 11.07 (s, 1 H), 11.03 (s, 1 H), 10.70 (s, 2 H), 10.45 (s, 1 H), 10.39 (s, 1 H), 10.28 (s, 1 H), 10.27 (s, 1 H), 10.15 (s, 1 H), 10.12 (s, 2 H), 10.11 (s, 1 H), 10.04 (s, 1 H), 9.95 (s, 2 H), 9.94 (s, 1 H), 8.17 (dd, J = 8.2, 1.5 Hz, 1 H), 7.94 – 7.71 (m, 7 H), 7.60 – 7.39 (m, 15 H), 7.24 – 6.68 (m, 30 H), 6.61 (m, 4 H), 6.37 (s, 2 H), 6.35 (s, 1 H), 6.19 (s, 1 H), 6.17 (s, 1 H), 6.05 (s, 1 H), 6.00 (d, J = 7.1 Hz, 1 H), 5.91 (s, 1 H), 5.90 (s, 1 H), 5.87 (s, 2 H), 5.85 (s, 1 H), 5.82 (s, 1 H), 5.75 (s, 1 H), 5.45 (s, 1 H), 5.07 (s, 1 H), 4.64 (s, 1 H), 4.02 – 3.37 (m, 36 H), 3.15 (s, 2 H), 2.80 (s, 3 H), 2.40 – 1.90 (m, 21 H), 1.66 (m, 3 H), 1.24 – 0.97 (m, 108 H) ppm; HRMS (ESI) m/z: calcd for C₂₅₆H₂₆₁N₃₅O₃₈ [M+2H]²⁺ 2217.4811, found 2217.5043.

UV-Vis spectra and fluorescence spectra measurements:

The UV-Vis spectra of compounds **1**, **6-11** were measured at room temperature in chloroform. Stock solutions (1×10⁻³ mol/L) of the above compounds were prepared by dissolving calculated amount of

those compounds in chloroform. The solutions used for measurement of UV-Vis spectra (1×10^{-5} mol/L) were obtained by diluting 100 times the stock solutions with chloroform. The spectra were corrected for chloroform absorption. The cell path was 1 cm. Fluorescence spectra were measured with the solutions of above compounds in chloroform (1×10^{-5} mol/L) using 365 nm as excitation wavelength and the EX/EM slit with were all 1/1 nm.

Additional figures and tables:

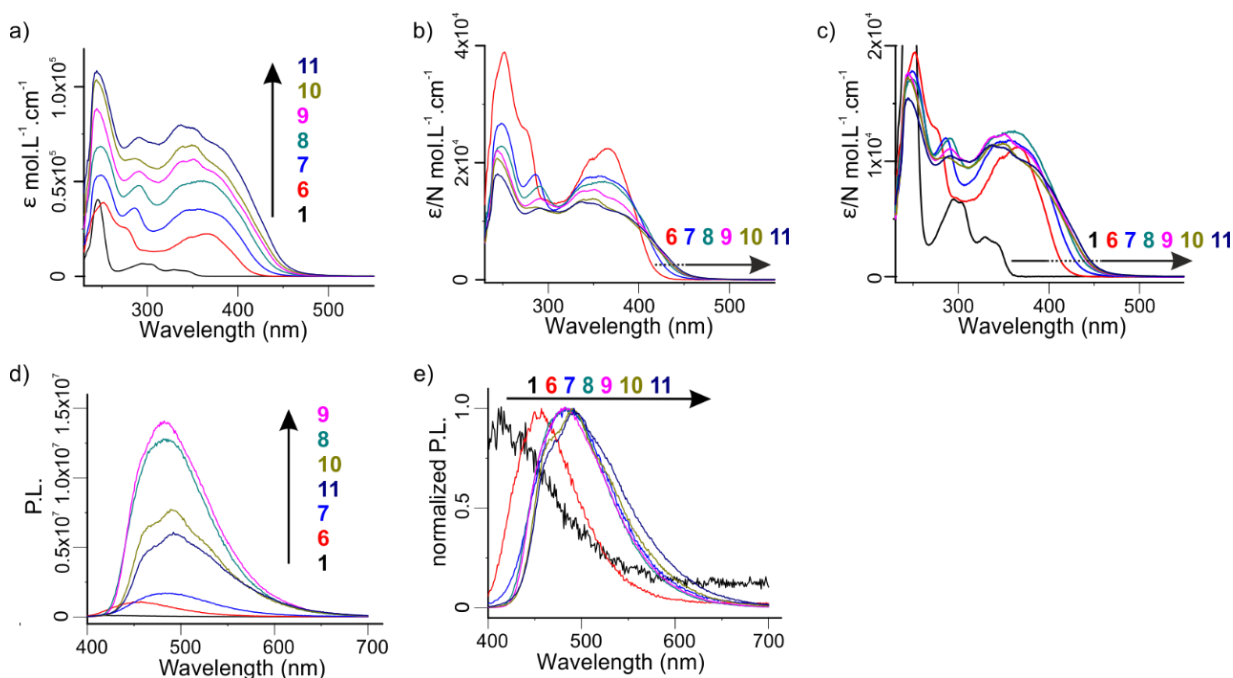


Figure S1: a) UV-vis absorption spectra of **1** and **6-11**; b) molar extinction coefficients of **6-11** divided by number of double bonds; c) molar extinction coefficients of **1, 6-11** divided by number of aromatic rings; d) fluorescence spectra of **1** and **6-11**; e) normalized fluorescence spectra of **1** and **6-11**.

compound	1	6	7	8	9	10	11
Emission maximum	410 nm	457 nm	483 nm	484 nm	486 nm	489 nm	492 nm

Table S1: Fluorescence emission maximum of compounds **1** and **6-11**.

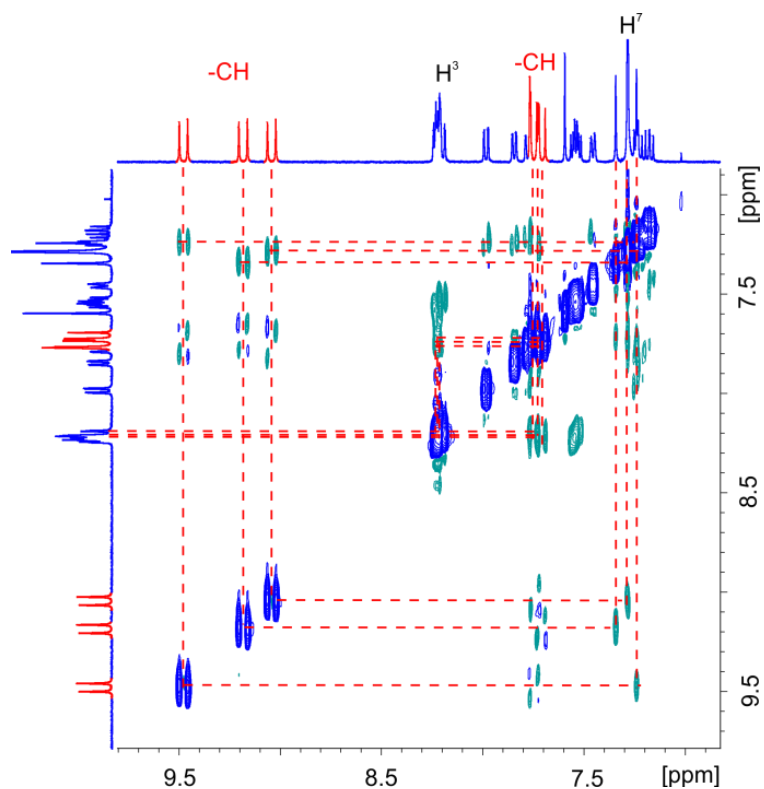


Figure S2: Excerpt from ^1H - ^1H NOESY spectrum of **8** in CDCl_3 at 298 K (400 MHz) indicating the correlations between vinyl protons and aromatic protons.

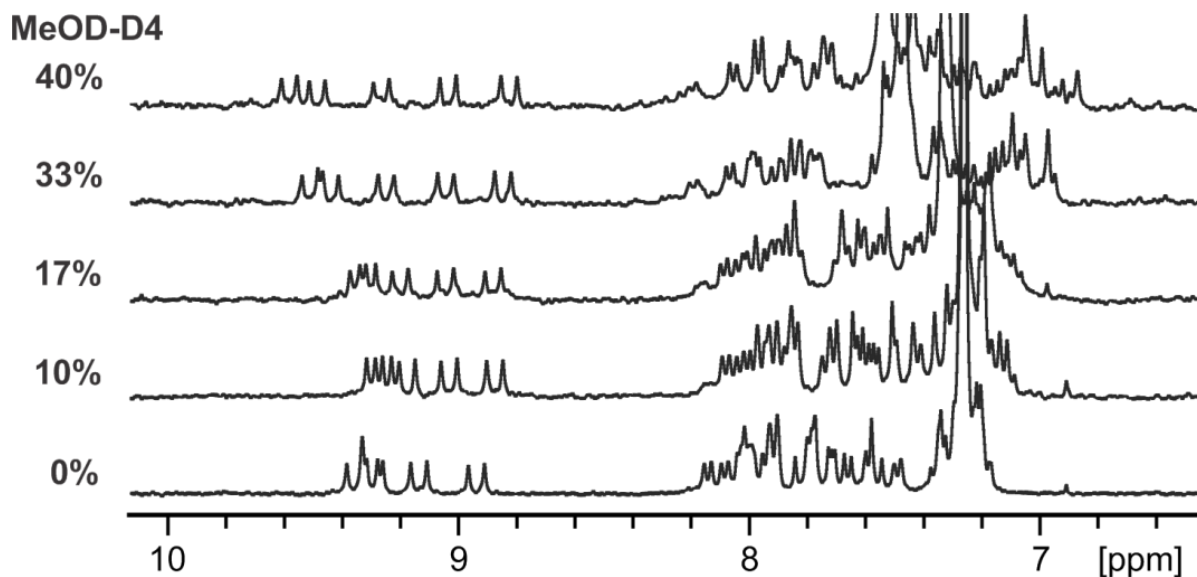


Figure S3: Part of the ^1H -NMR spectra (300 MHz) of **10** in CDCl_3 containing different proportions of CD_3OD (vol/vol %) showing the vinyl and aromatic region.

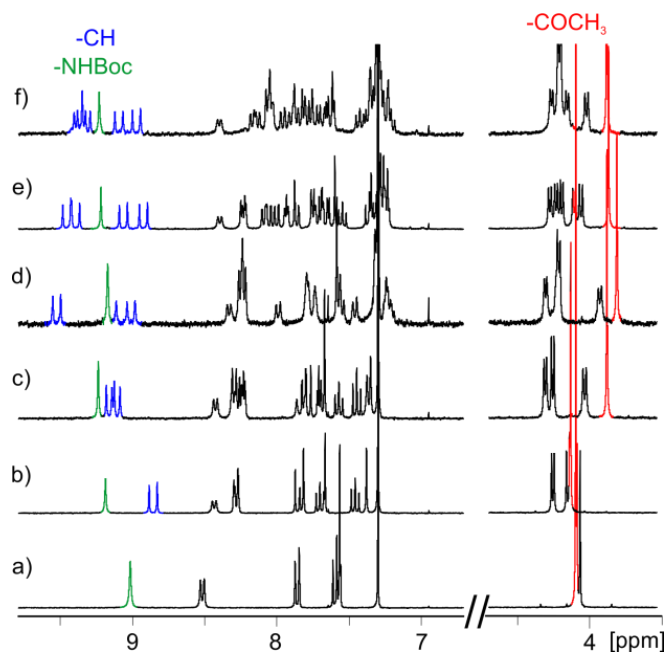


Figure S4: Part of the ^1H NMR spectra (300 MHz) of **12** and **14**, **S14**, **15**, **S15**, **16** showing the vinyl, aromatic and terminal groups at 298 K for a) **12**, b) **14**, c) **S14**, d) **15**, e) **S15**, f) **16**.

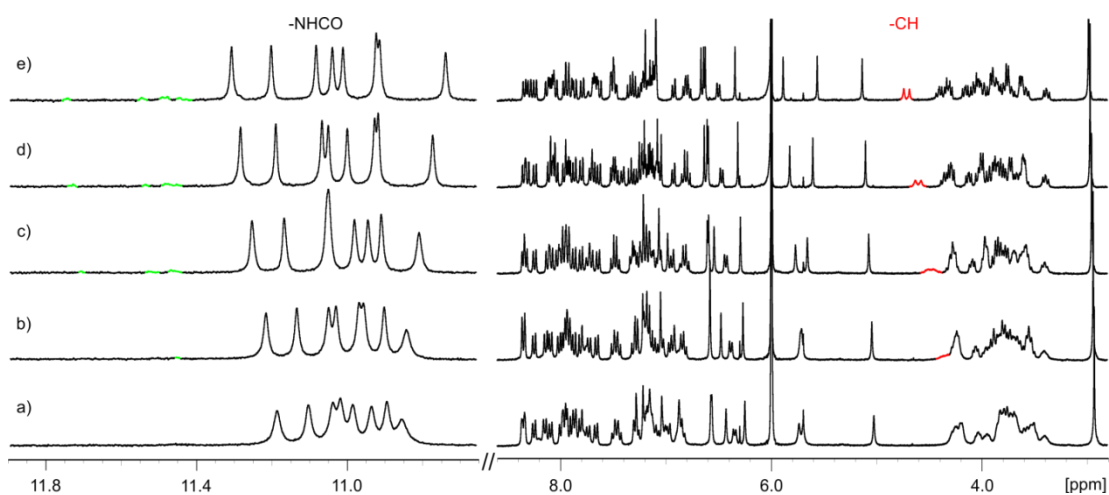


Figure S5: Part of the ^1H NMR spectra (300 MHz) of **19** in $\text{C}_2\text{D}_2\text{Cl}_4$ showing the amide and aromatic resonances at different temperatures: a) 268 K, b) 283 K, c) 303 K, d) 323 K, e) 343 K.

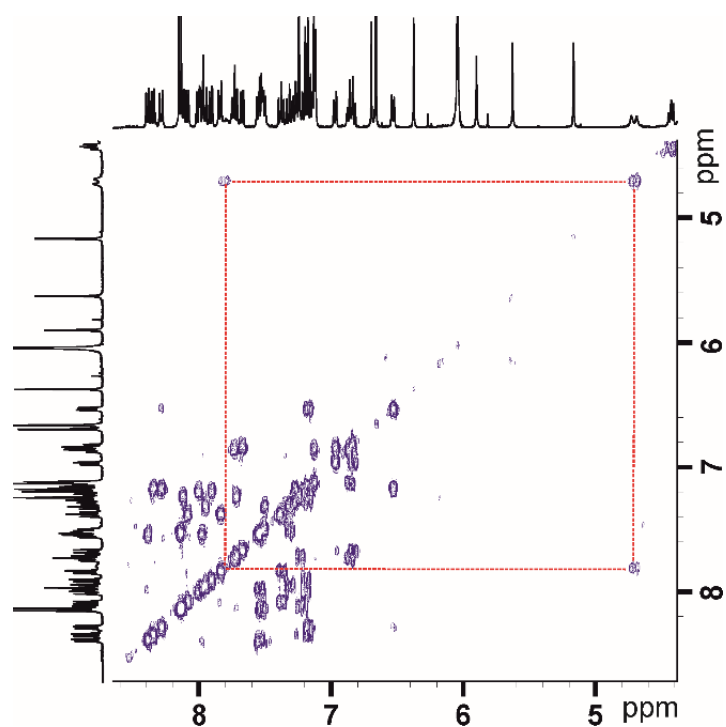


Figure S6: Excerpt from the ^1H - ^1H COSY spectrum of **19** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 333 K (400 MHz) indicating the correlations between vinyl protons.

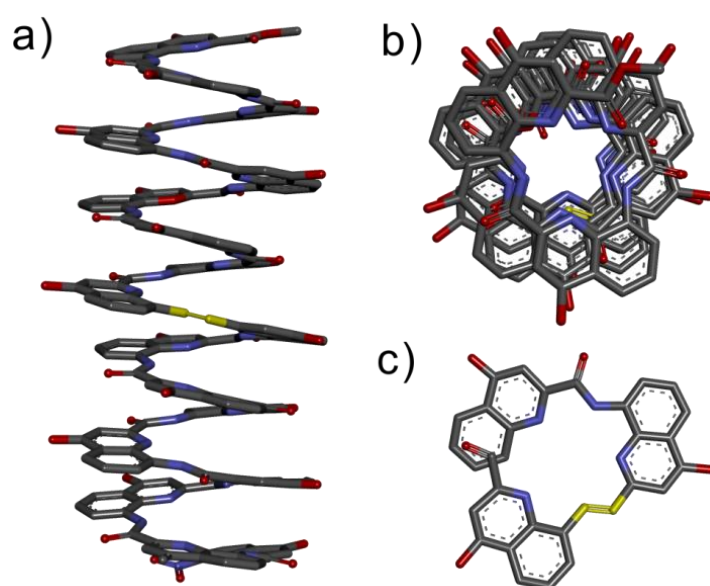


Figure S7: Crystal structure of compound **19'** showing a) the side view; b) top view and c) the conformation of the vinyl function. All side chains and hydrogens are removed for clarity; the vinylene was highlighted with yellow color.

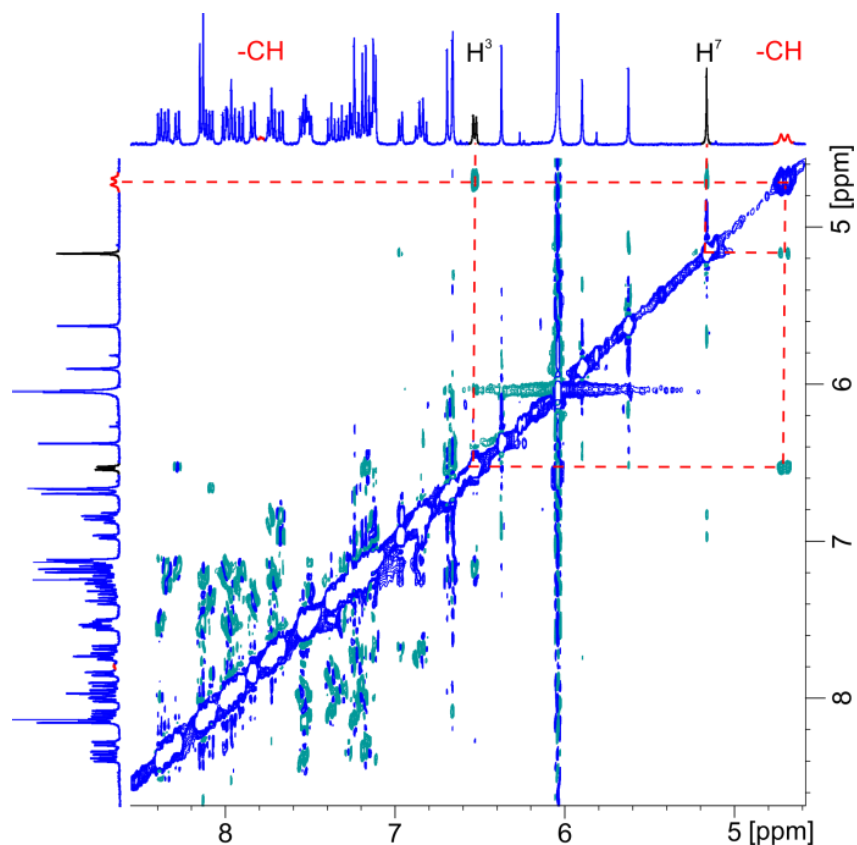


Figure S8: Excerpt from the ^1H - ^1H NOESY spectrum of **19** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 333 K (400 MHz) indicating correlations between vinyl protons and aromatic protons.

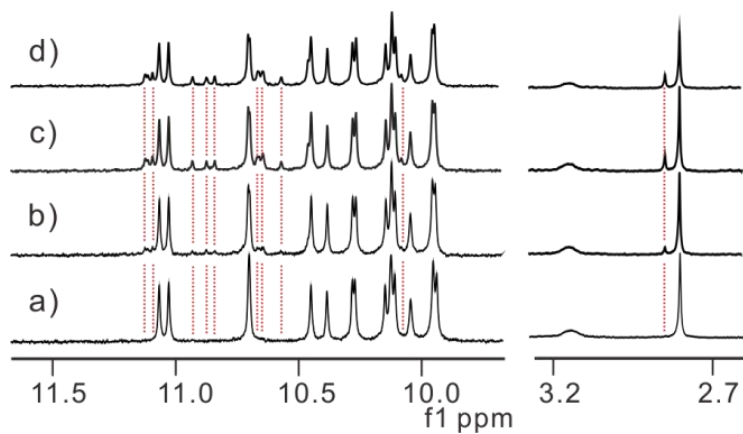


Figure S9: Part of the ^1H NMR spectra of **19'** obtained after freshly dissolving a crystal and measured after a) 6 minutes, b) 5 hours, c) 21 hours and d) 72 hours, only the amide region and methyl ester region are shown.

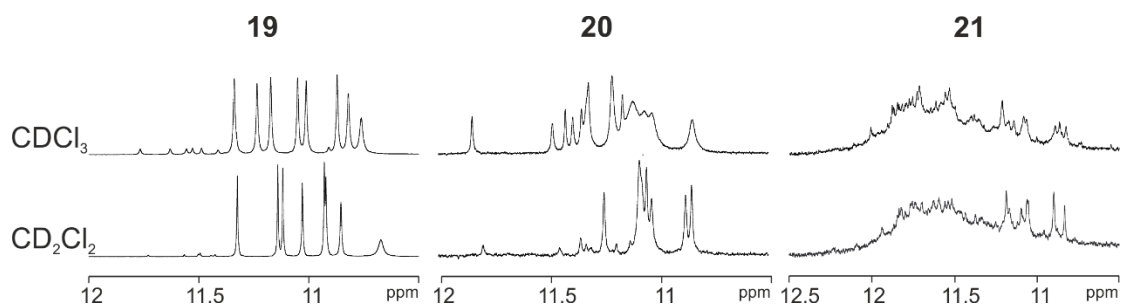


Figure S10: Part of the ^1H NMR spectra (400 MHz) of **19**, **20** and **21** in CDCl_3 and CD_2Cl_2 showing the amide region.

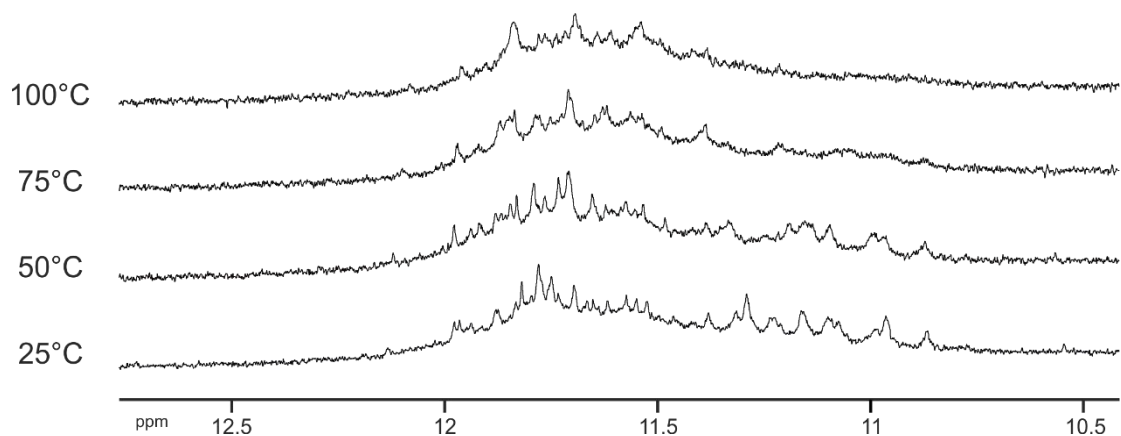


Figure S11: Part of the ^1H NMR spectra (400 MHz) of **21** in $\text{C}_2\text{D}_2\text{Cl}_4$ at different temperatures showing the amide region.

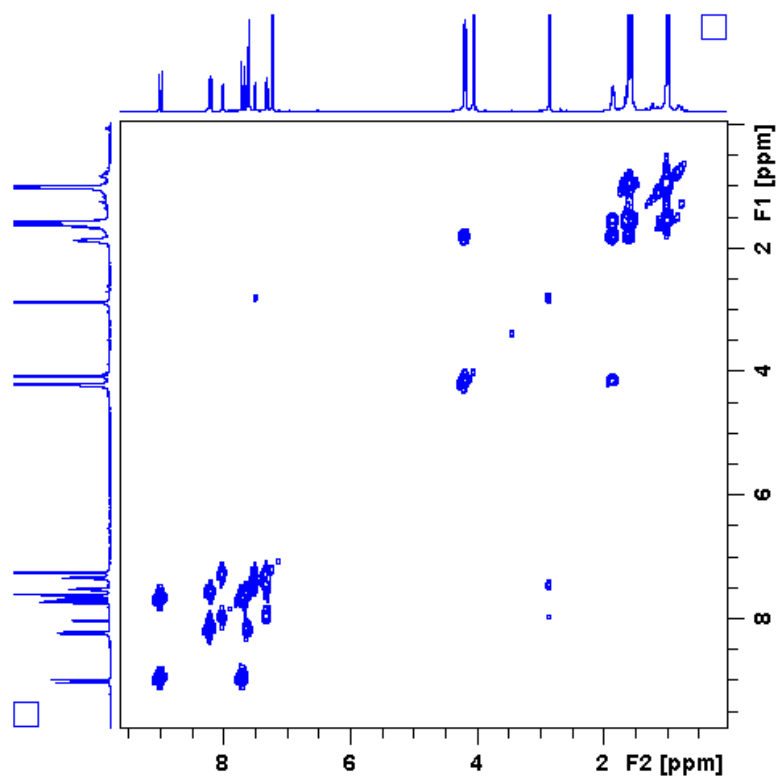


Figure S12: 2D COSY NMR spectrum (CDCl_3 , 400 MHz, 5 mM) of compound **6**.

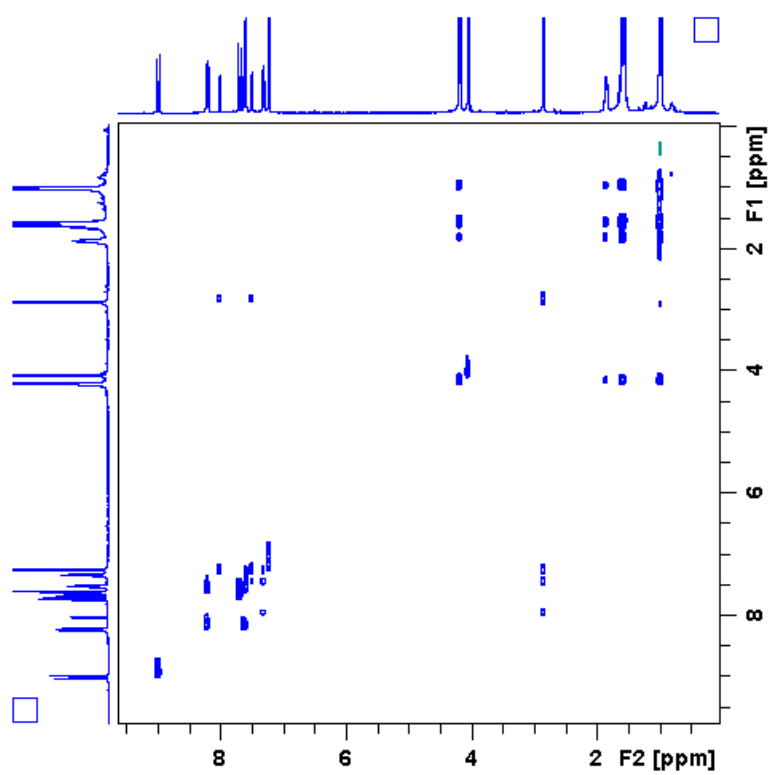


Figure S13: 2D TOCSY NMR spectrum (CDCl_3 , 400 MHz, 5 mM) of compound **6**.

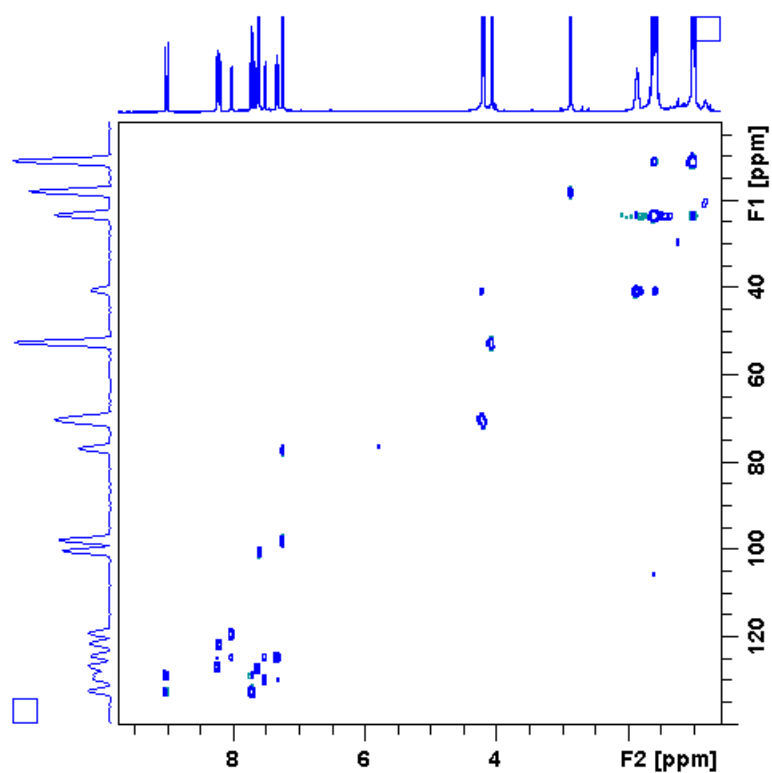


Figure S 14: 2D HSQC NMR spectrum (CDCl₃, 400 MHz, 5 mM) of compound 6.

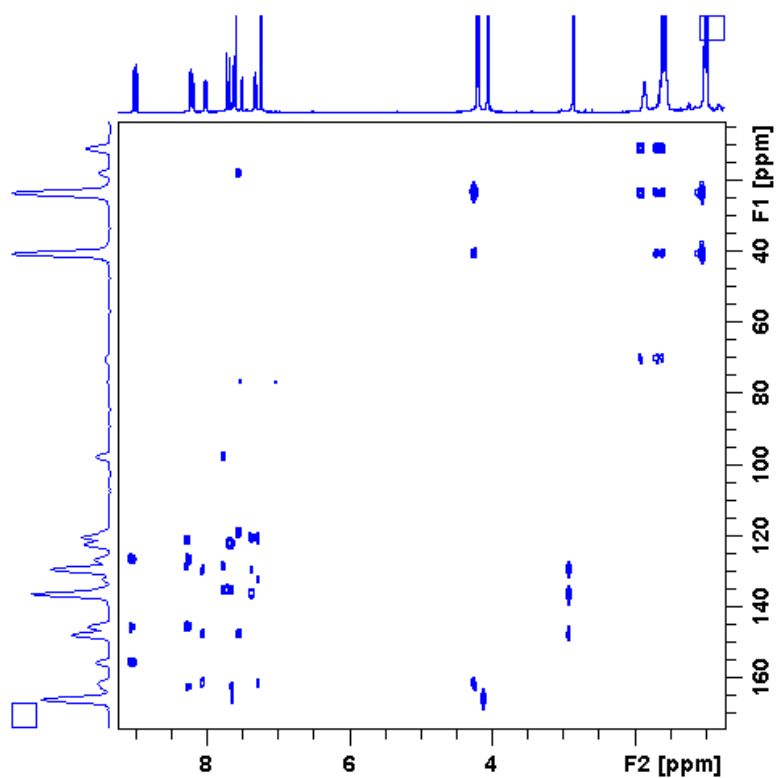


Figure S15: 2D HMBC NMR spectrum (CDCl₃, 400 MHz, 5 mM) of compound 6.

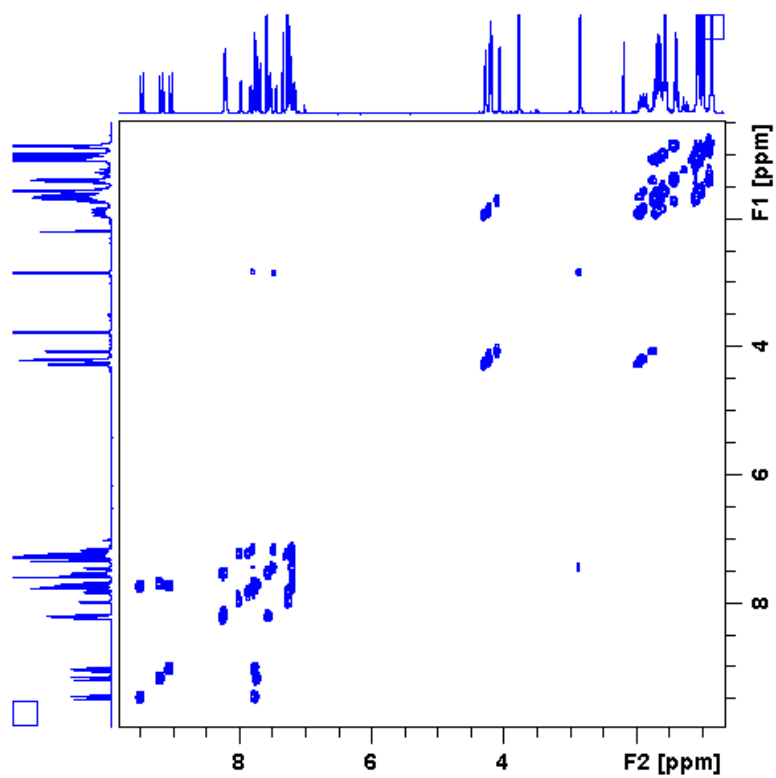


Figure S 16: 2D COSY NMR spectrum(CDCl₃, 400 MHz, 2 mM) of compound **8**.

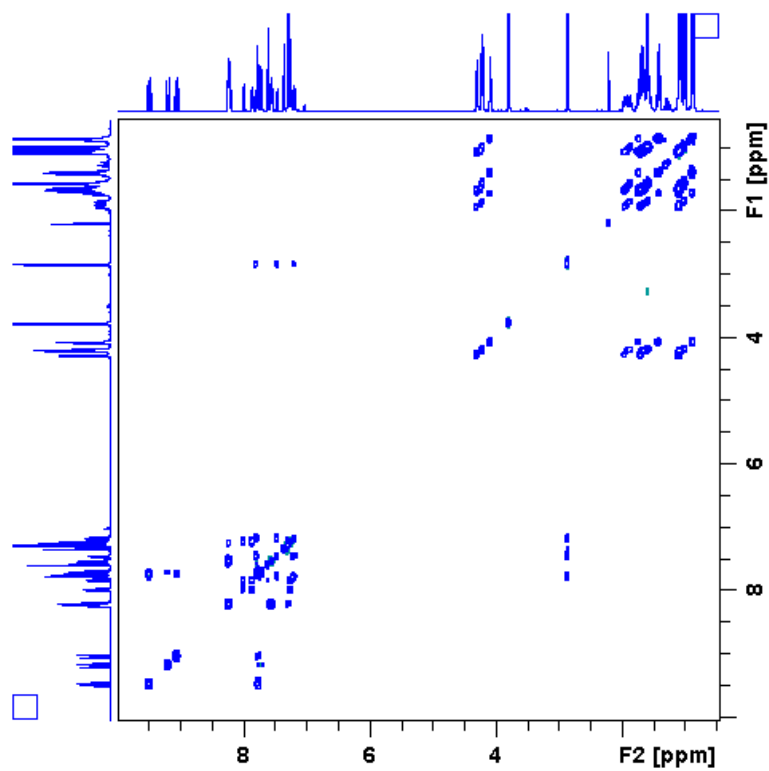


Figure S17: 2D TOCSY NMR spectrum (CDCl₃, 400 MHz, 2 mM) of compound **8**.

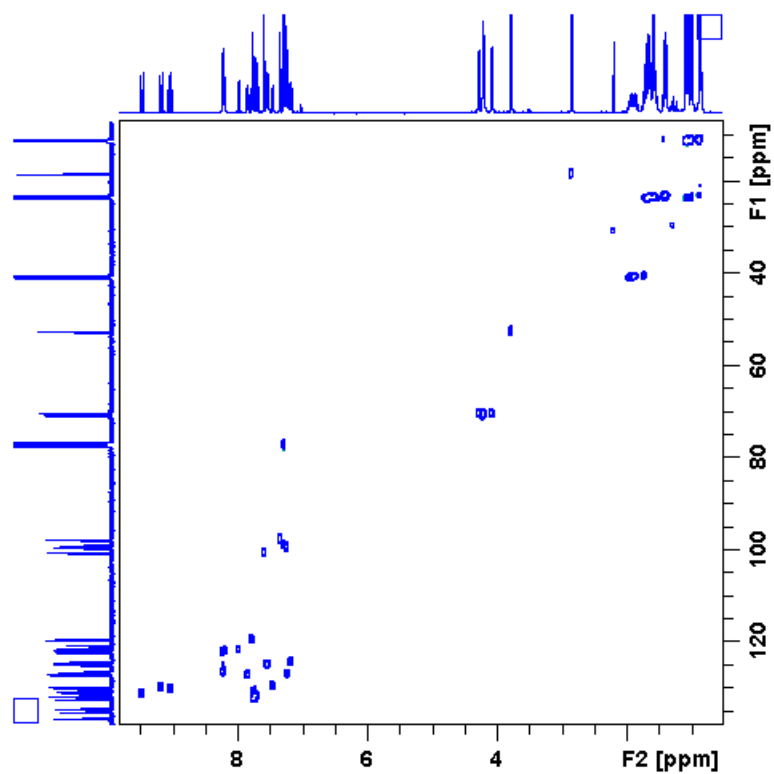


Figure S18: 2D HSQC NMR spectrum (CDCl₃, 400 MHz, 2 mM) of compound **8**.

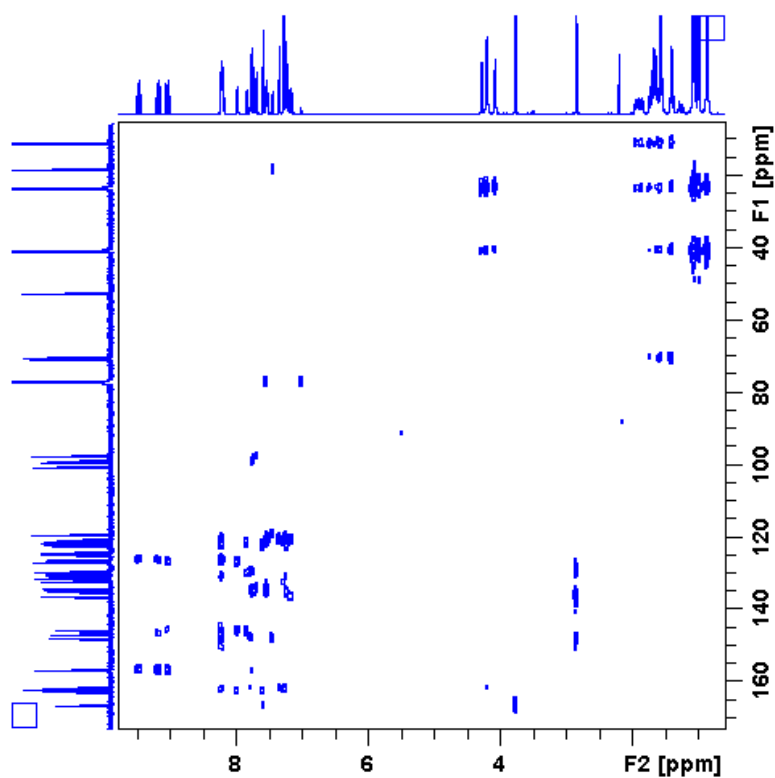


Figure S19: 2D HMBC NMR spectrum (CDCl₃, 400 MHz, 2 mM) of compound **8**.

X-ray diffraction measurements:

The X-ray diffraction measurements for **6**, **19**, **19'** and **20** were carried out on a Rigaku FRX rotating anode (2.9 kW) diffractometer at the IECB x-ray facility (CNRS UMS 3033 – INSERM US001). The CuK α radiation monochromated with high flux Osmic Varimax HF mirrors was used for data collection. The x-ray source is equipped with a Dectris Pilatus 200K detector and partial chi goniometer. All crystals were kept at 100(2) K during data collection. The Rigaku CrystalClear suite³ was used to index and integrate data with a multiscan absorption correction. Structures were solved with the ShelXT⁴ structure solution program using Intrinsic Phasing and using Olex2⁵ were refined with the ShelXL⁶ refinement package using Least Squares minimization.

Despite a lot of attempts, only tiny crystals were obtained for **6**. The single crystal used for data collection has the longest dimension around 30 μm thus a diffraction limit at about 1 \AA . The Squeeze⁷ procedure was employed to remove disordered solvents molecules that could not be reliably modelled from the structures **19** and **20**. For search and analysis of solvent accessible voids in the structures default parameters were used: grid 0.20 \AA , probe radius 1.2 \AA and number of steps 6. Calculated total potential solvent accessible void volume and electron counts per unit cell were 1687 \AA^3 and 590, and 3592 and 808, for **19** and **20**, respectively. For **19'** a solvent mask was calculated using Olex2⁵ and 1176 electron was found in a volume of 3374 \AA^3 per unit cell.

For **6** all atoms were refined with anisotropic displacement parameters and, the position of all H-atoms were determined. In the structure of **20** only backbones, and in the structures of **19** and **19'** backbone, solvent, and some side chains were refined with ADPs. In **20** H atoms of backbone were only localized but not refined. For **19** and **19'** the positions of backbone hydrogen atoms, chloroform and dichloromethane molecules and O-H groups for methanol molecules were determined. All H atoms were refined in the riding-model approximation, with Uiso(H)=1.2Ueq(CH, CH₂, NH) and Uiso(H)=1.5Ueq(OH). DFIX, AFIX and EADP instructions were employed to model geometry of the molecules and temperature parameters.

The final cif files were checked using IUCR's checkcif algorithm. Due to the characteristics of the crystals, i.e. large volume fractions of disordered solvent molecules, weak diffraction intensity, incompleteness of the data and moderate resolution, a number of A - level and B - level alerts remain in the check cif file. These alerts are inherent to the data and refinement procedures and do not reflect errors. Rather, they illustrate the limited practicality of the checkcif tool for medium size molecule crystallography. They are explicitly listed below and have been divided into two groups. The first group illustrates weak quality of the data and refinement statistics if compared to that expected for small molecule structures from highly diffracting crystals. The second group is connected to decisions made during refinement and explained below.

Group 1:

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
PLAT023_ALERT_3_A Resolution (too) Low [sin(theta)/Lambda < 0.6].
PLAT084_ALERT_3_A High wR2 Value (i.e. > 0.25) 0.54 Report
PLAT934_ALERT_3_A Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..
PLAT023_ALERT_3_B Resolution (too) Low [sin(theta)/Lambda < 0.6]..
PLAT082_ALERT_2_B High R1 Value
PLAT220_ALERT_2_B NonSolvent Resd 1 C Ueq(max)/Ueq(min)

PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors
PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors
PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds
PLAT992_ALERT_5_B Repd & Actual _reflns_number_gt Values Differ

Group 2:

PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s)
PLAT202_ALERT_3_A Isotropic non-H Atoms in Anion/Solvent
As mentioned above, not all atoms were refined with ADPs

PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing)
DIFMN02_ALERT_2_B The minimum difference density is

As mentioned above, not all H-atoms were localized, but they were used in SFAC calculation

PLAT430_ALERT_2_A Short Inter D...A Contact

PLAT430_ALERT_2_B Short Inter D...A Contact

These alerts concern contacts with solvent molecules which positions were poorly determined

PLAT097_ALERT_2_B Large Reported Max. (Positive) Residual Density 0.97 eA-3

PLAT098_ALERT_2_B Large Reported Min. (Negative) Residual Density -0.93 eA-3

Unmodeled electron density in proximity to the side chains

PLAT306_ALERT_2_B Isolated Oxygen Atom

Unrecognized electron density was introduced to the refinement as dummy oxygen atoms

Identification code	6	19	19'	20
Chemical formula	C ₃₅ H ₄₂ N ₂ O ₄	C ₁₄₄ H ₁₄₇ N ₁₉ O ₂₂ ·4(CH ₃ OH)·CHCl ₃ · (solvent)*	C ₂₅₆ H ₂₆₀ N ₃₅ O ₃₈ ·C ₆ H ₅ Cl·7(CH ₂ Cl) 2)·(solvent)**	C ₁₇₈ H ₁₈₅ N ₂₁ O ₂₄ ·4(CH ₃ OH)·3(O) **·(solvent)*
Formula weight	554.70	2743.33	5142.01	3178.63
Temperature (K)	100 (2)	100 (2)	100 (2)	100 (2)
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions (Å, °)	a=20.8273 (9), α=90	a=19.3650 (5), α=76.670 (2)	a=28.242 (7), α=90	a=17.1889 (5), α=90
	b=13.2306 (4), β=99.508 (4)	b=27.6825 (5), β=80.410 (2)	b=32.207 (7), β=114.173 (6)	b=72.303 (3), β=103.933 (3)
	c=11.3733 (4), γ=90	c=29.8129 (6), γ=81.832 (2)	c=33.646 (9), γ=90	c=29.7568 (9), γ=90
Volume (Å ³)	3090.9 (2)	15244.2 (6)	27921 (12)	35894 (2)
Z	4	4	4	8
Density (calculated) (Mg m ⁻³)	1.192	1.195	1.223	1.176
Absorption coefficient (mm ⁻¹)	0.61	1.14	1.94	0.66
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Crystal size (mm)	0.03 × 0.02 × 0.01	0.10 × 0.05 × 0.03	0.20 × 0.10 × 0.07	0.20 × 0.06 × 0.03
Completeness	99.5 (up to 51.10°)	97.2 (up to 54.24°)	97.2 (up to 65.08°)	99.7 (up to 57.90°)
Reflections collected	13241	81340	163848	205725
Reflections observed [<i>I</i> > 2σ(<i>I</i>)]	2768	29564	33497	35326
<i>R</i> _{int}	0.020	0.032	0.085	0.071
Data/parameters/restraints	3317/411/27	36198/2968/116	46303/3086/112	49779/3243/210
Goodness-of-fit on F ²	1.06	2.50	1.67	2.56
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	0.0804, 0.2127	0.1842, 0.5189	0.1357, 0.3896	0.2349, 0.5876
R indices (all data)	0.0927, 0.2242	0.1970, 0.5355	0.1568, 0.4196	0.2588, 0.6093
Largest diff. peak and hole	0.60, -0.72	1.12, -1.00	1.11, -1.12	0.97, -0.92
CCDC #	2018566	2018567	2018568	2018569

*The squeeze procedure was used to removed severely disordered solvent molecules

**Unrecognized electron density was introduced to the refinement as dummy oxygen atoms

NMR spectra of synthesized compounds:

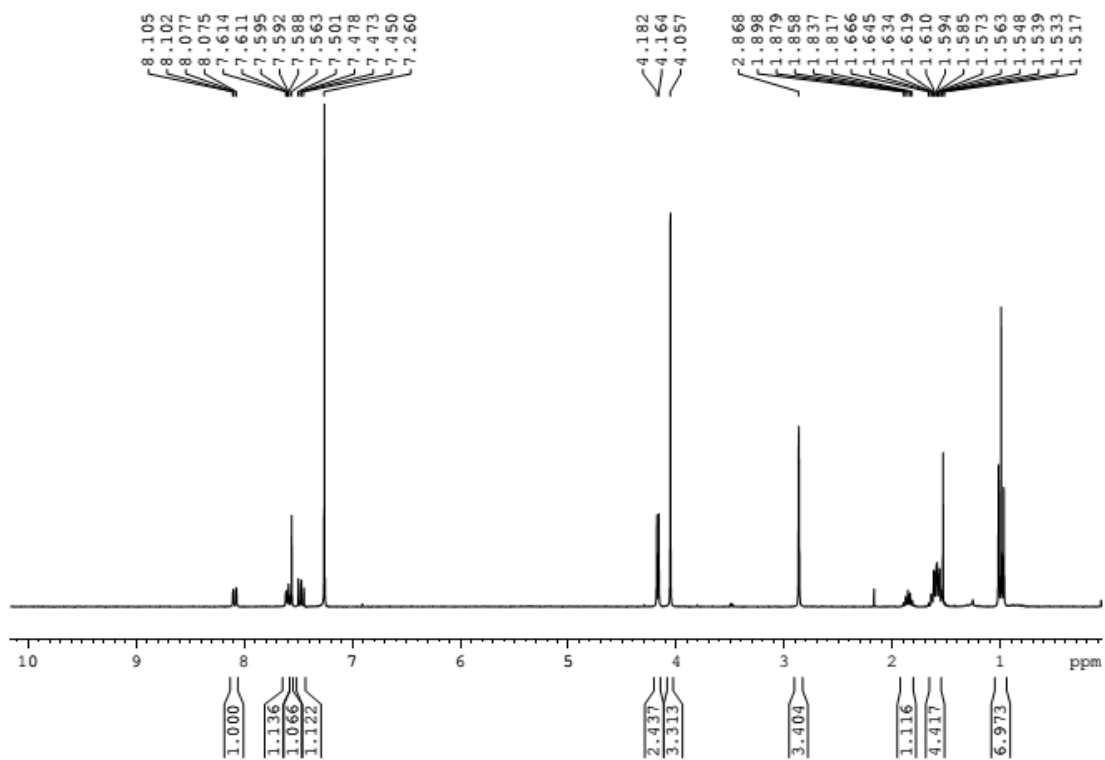


Figure S20: ¹H NMR of **1** in CDCl₃ (300 MHz).

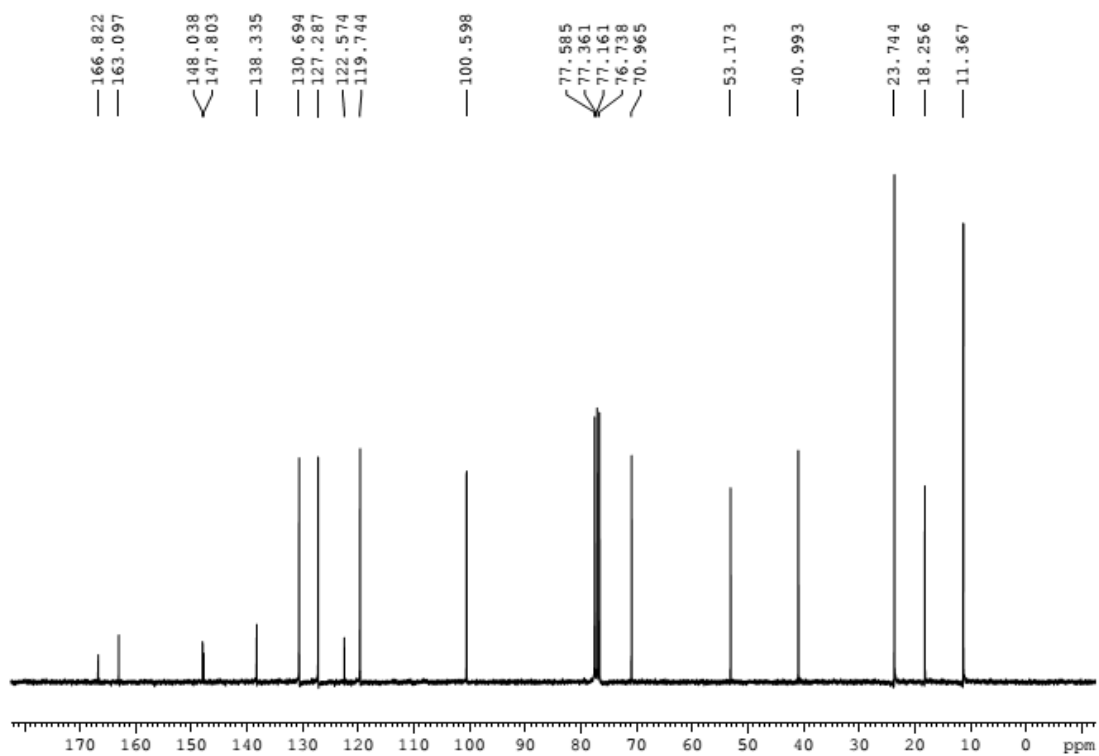


Figure S21: ^{13}C NMR of **1** in CDCl_3 (75 MHz).

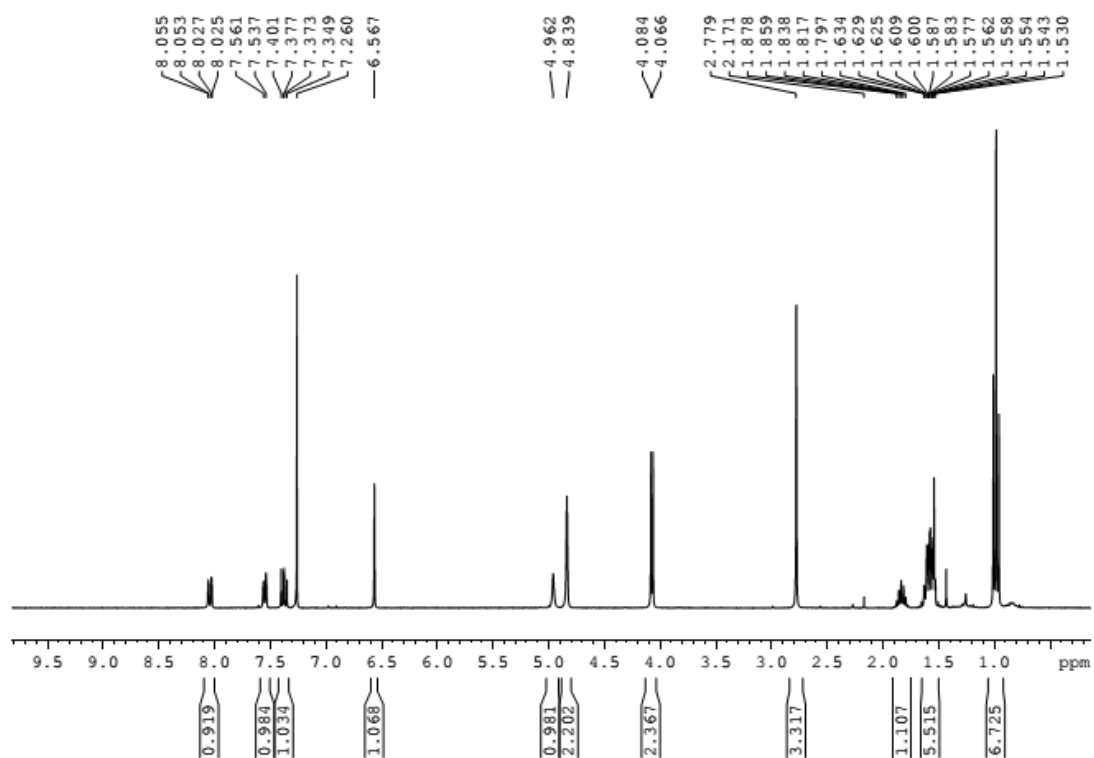


Figure S22: ^1H NMR of **2** in CDCl_3 (300 MHz).

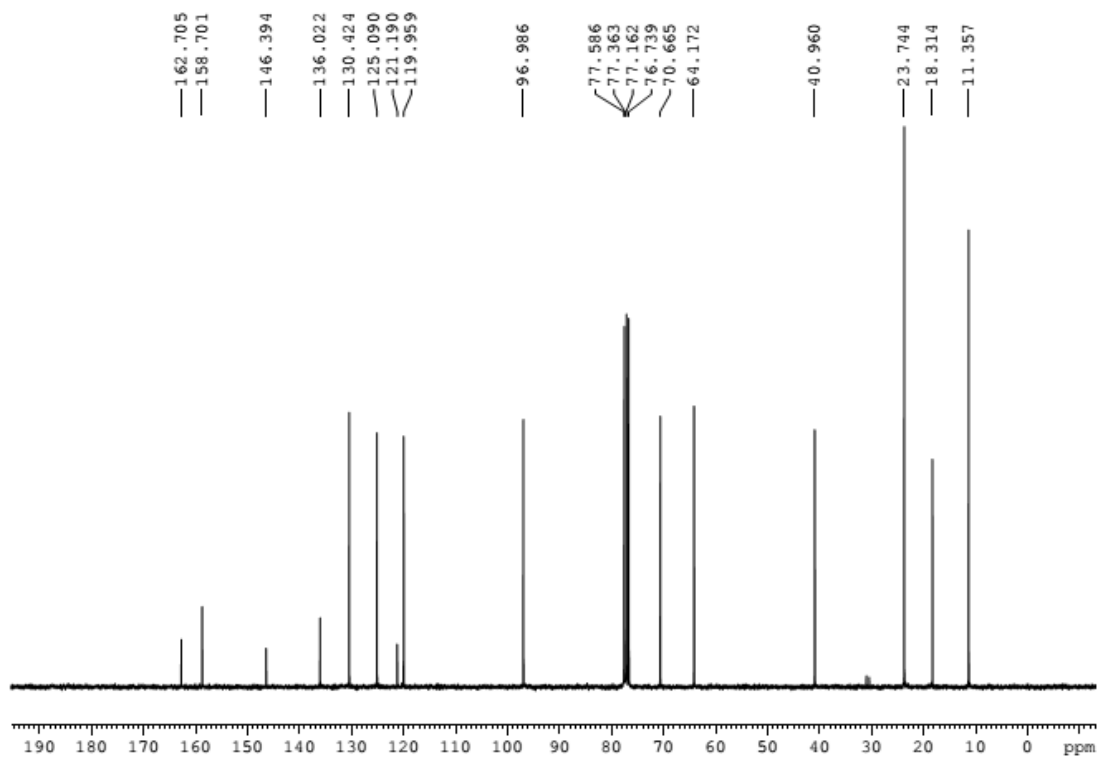


Figure S23: ^{13}C NMR of **2** in CDCl_3 (75 MHz).

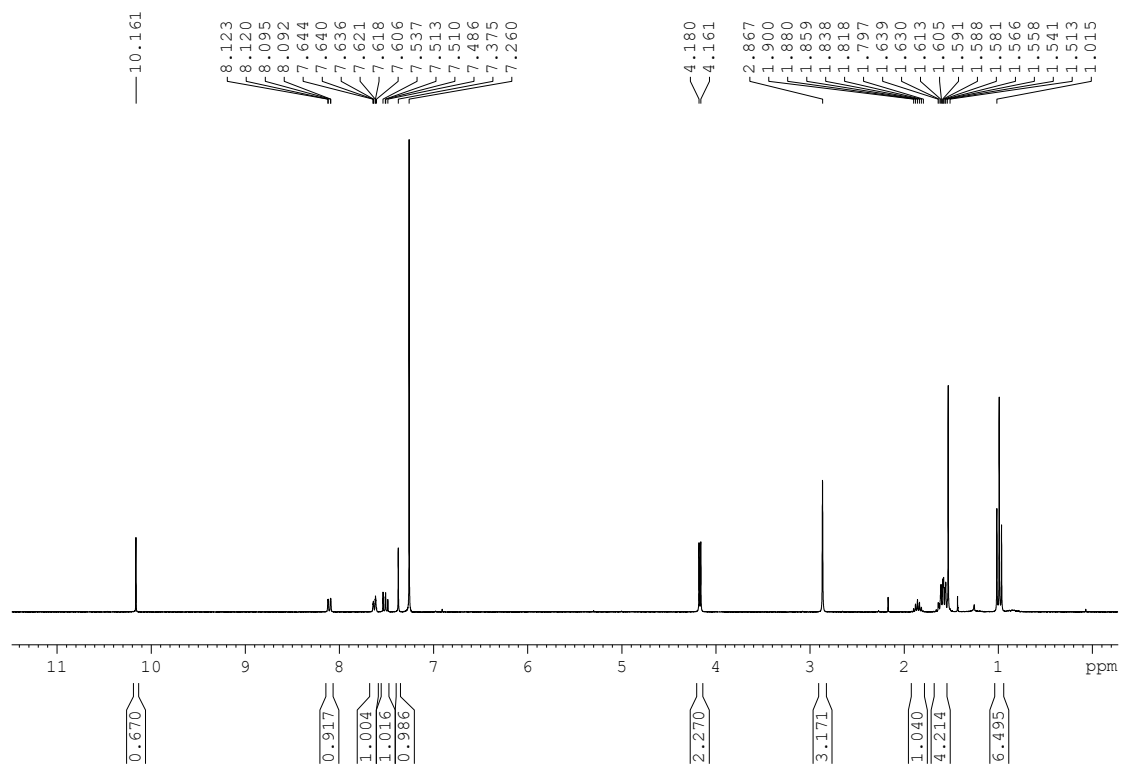


Figure S24: ^1H NMR of **3** in CDCl_3 (300 MHz).

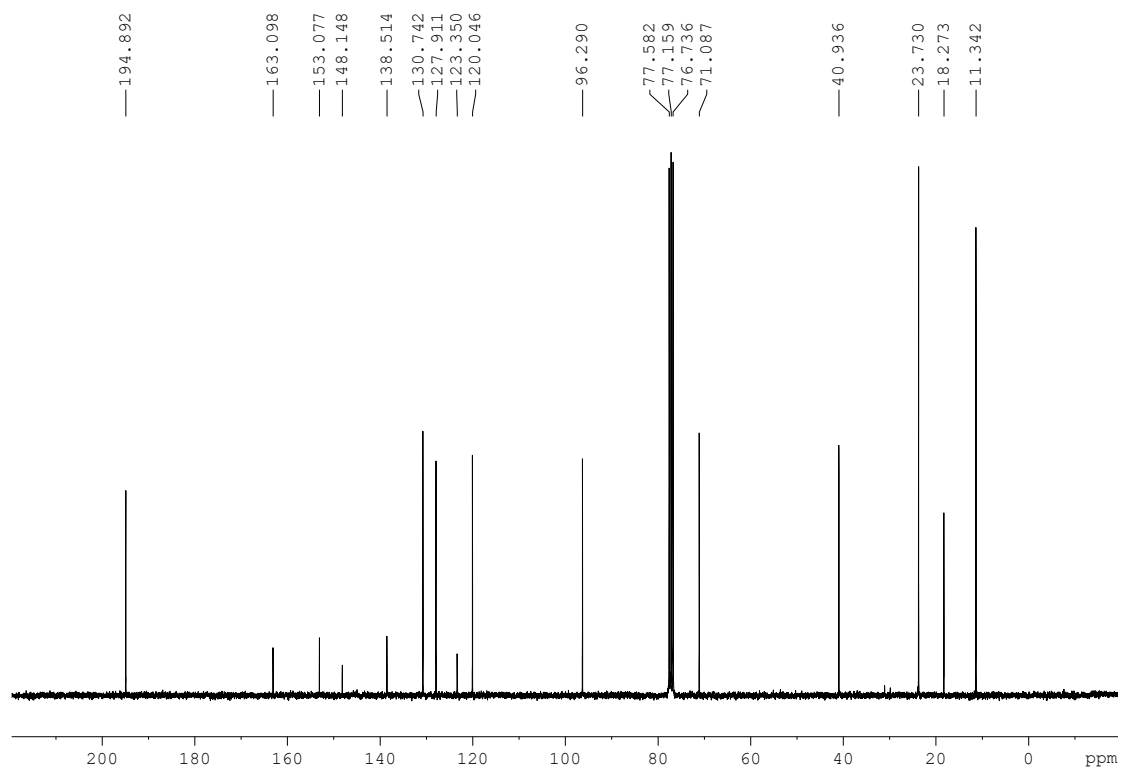


Figure S25: ^{13}C NMR of **3** in CDCl_3 (75 MHz).

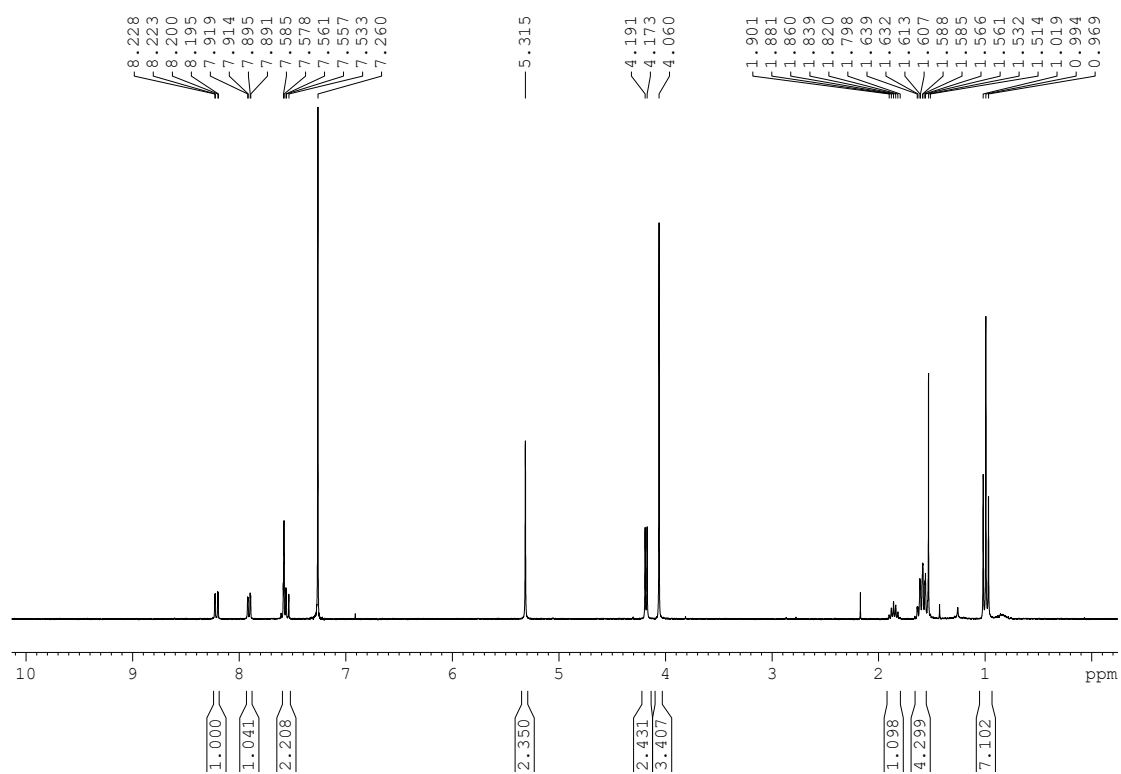


Figure S26: ^1H NMR of **4** in CDCl_3 (300 MHz).

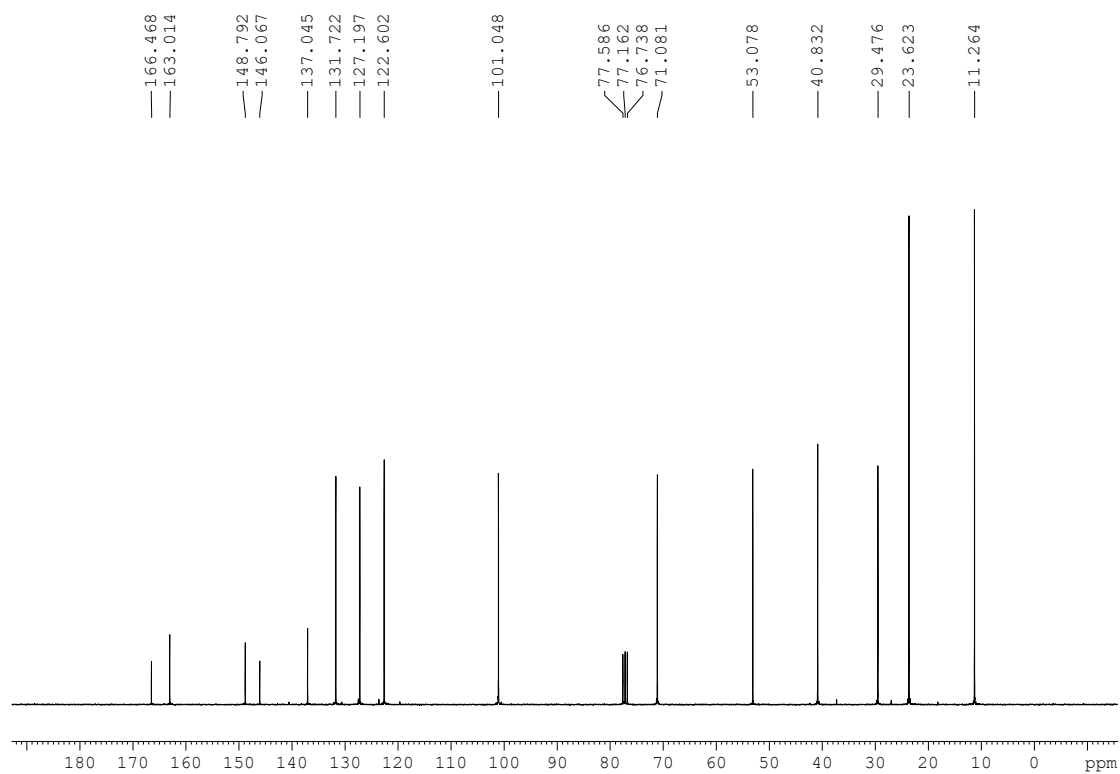


Figure S27: ^{13}C NMR of **4** in CDCl_3 (75 MHz).

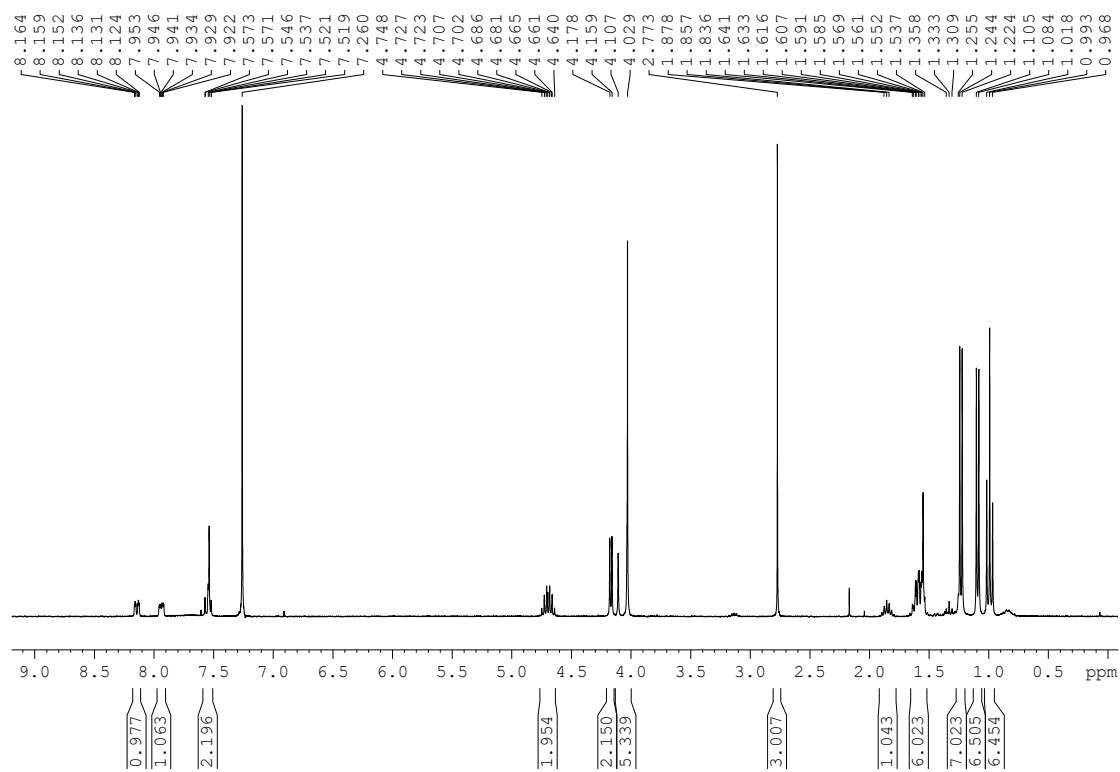


Figure S28: ^1H NMR of **5** in CDCl_3 (300 MHz).

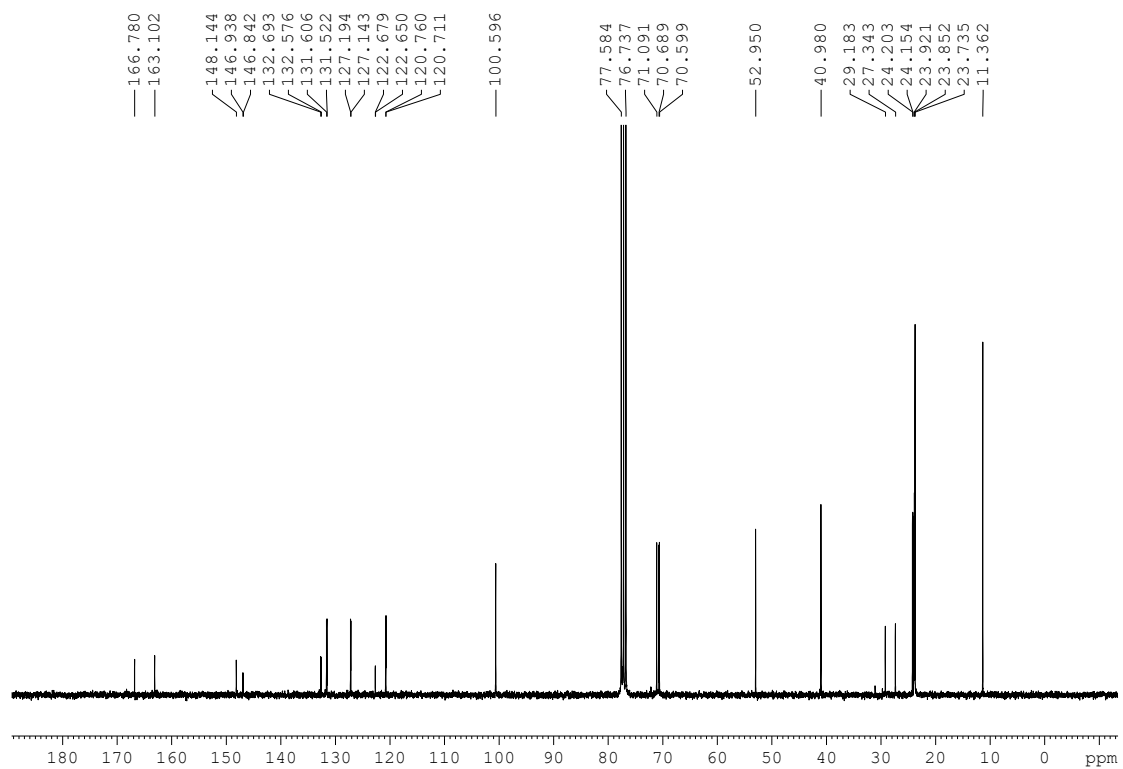


Figure S29: ^{13}C NMR of **5** in CDCl_3 (75 MHz).

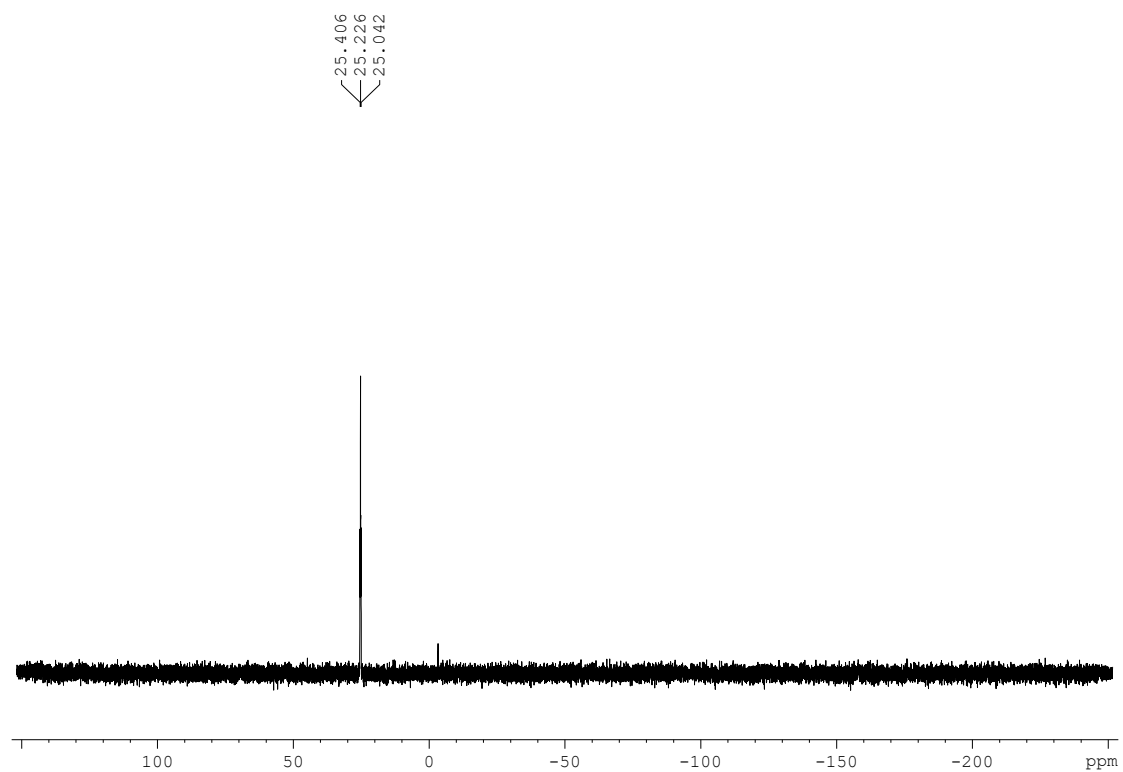


Figure S30: ^{31}P NMR of **5** in CDCl_3 (121 MHz).

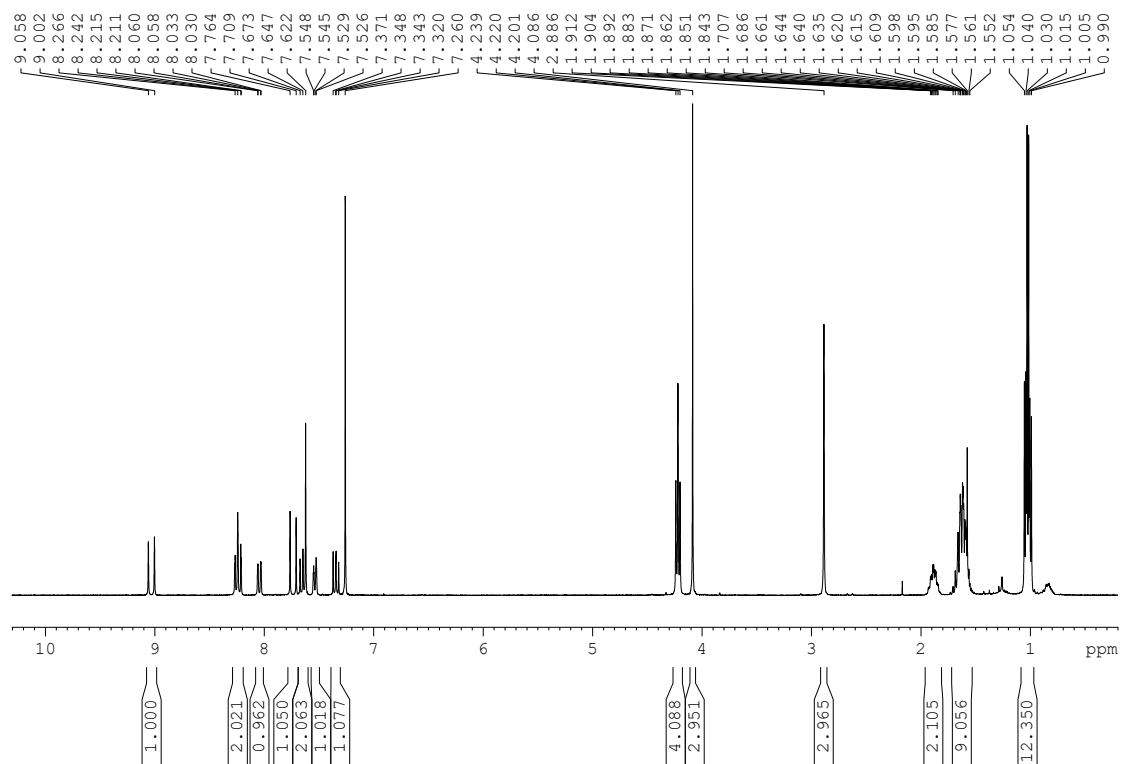


Figure S31: ^1H NMR of **6** in CDCl_3 (300 MHz).

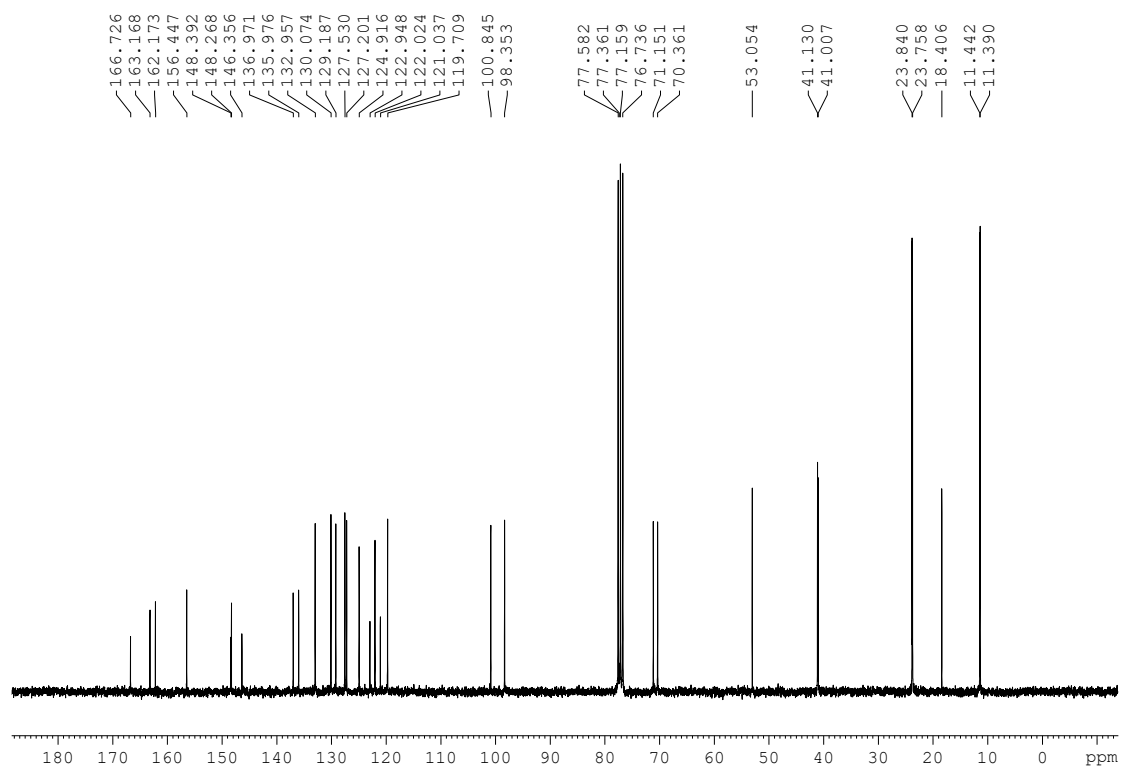


Figure S32: ^{13}C NMR of **6** in CDCl_3 (75 MHz).

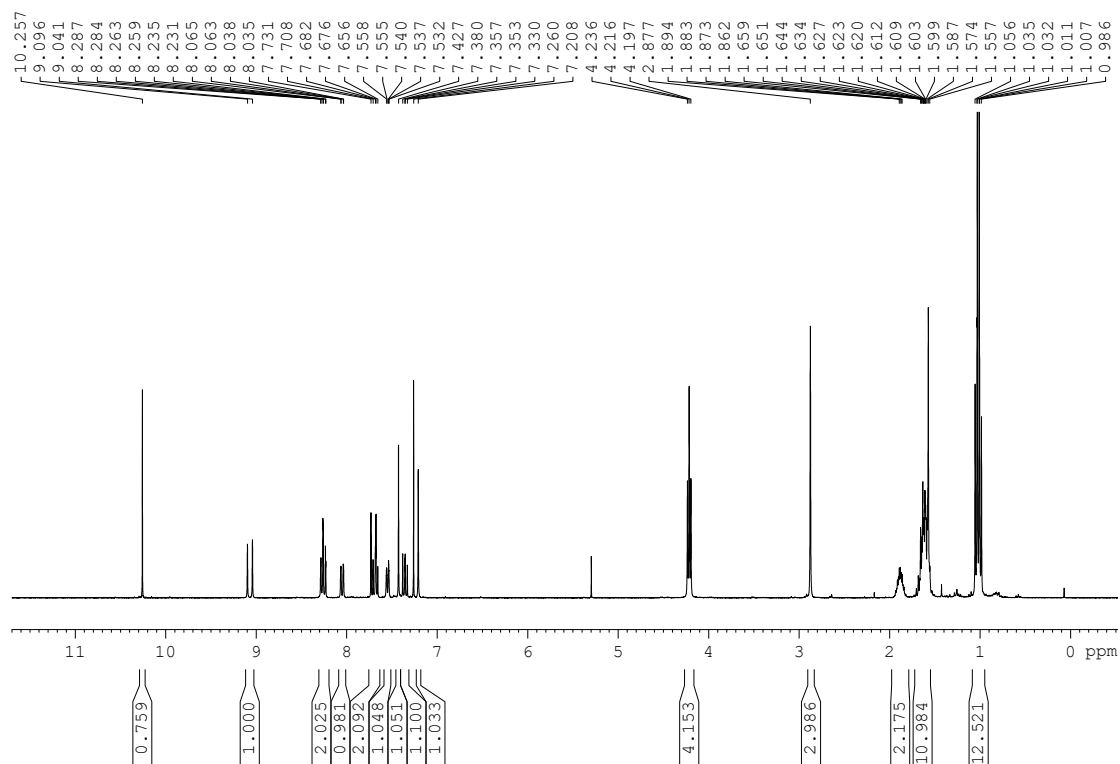


Figure S33: ^1H NMR of **6c** in CDCl_3 (300 MHz).

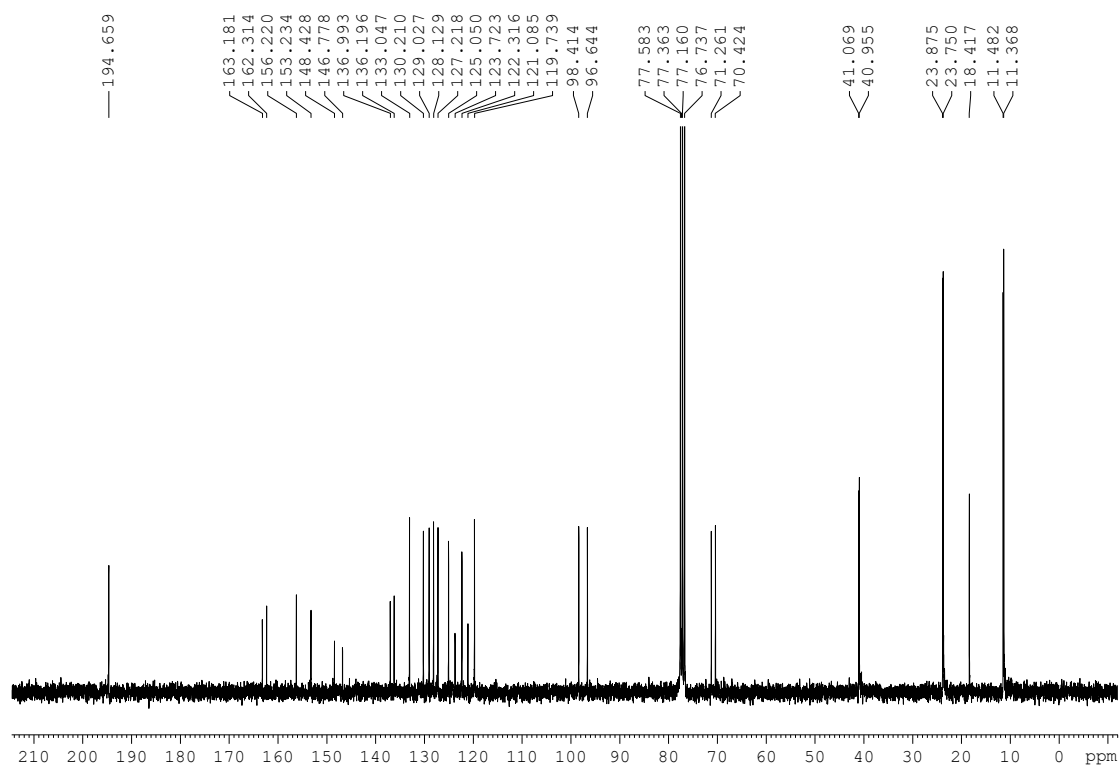


Figure S34: ^{13}C NMR of **6c** in CDCl_3 (75 MHz).

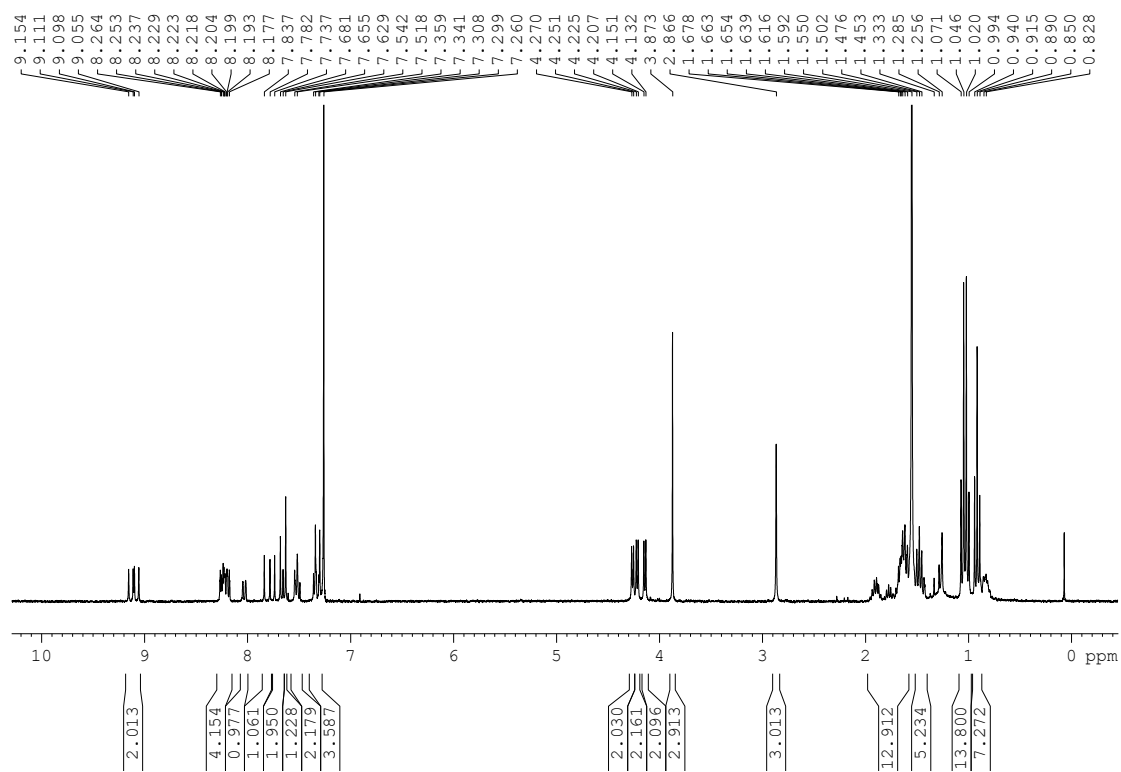


Figure S35: ^1H NMR of **7** in CDCl_3 (300 MHz).

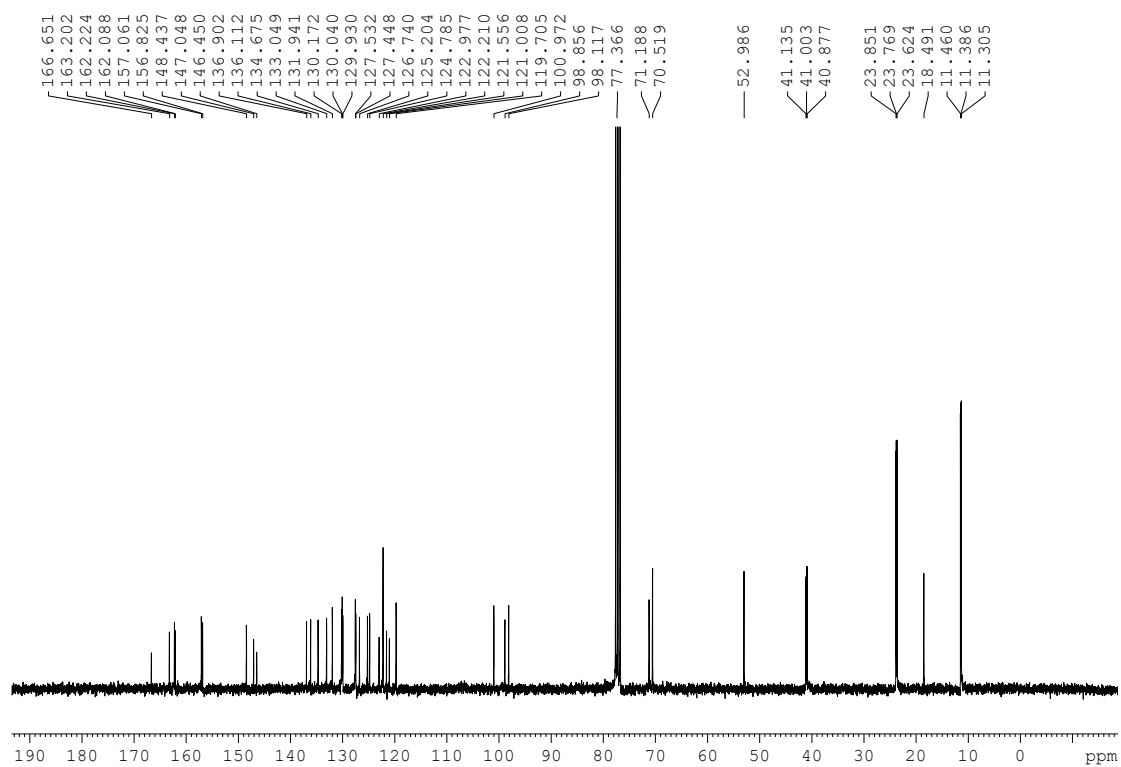


Figure S36: ^{13}C NMR of **7** in CDCl_3 (75 MHz).

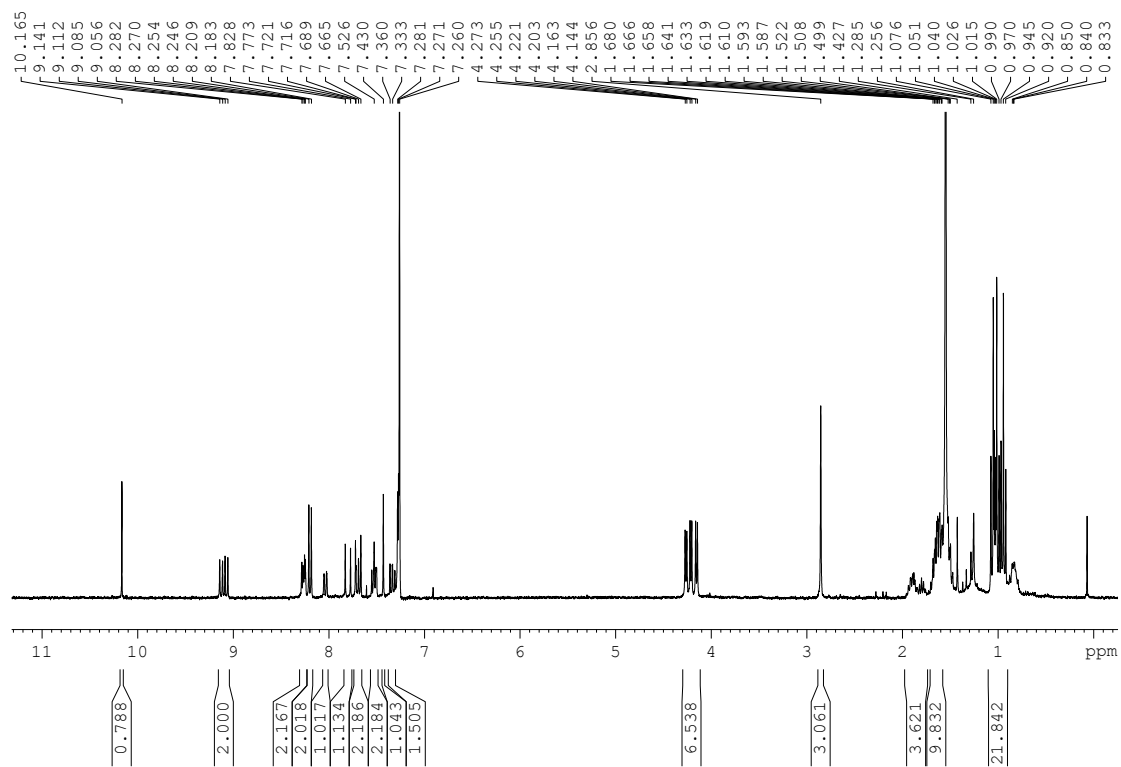


Figure S37: ^1H NMR of **7c** in CDCl_3 (300 MHz).

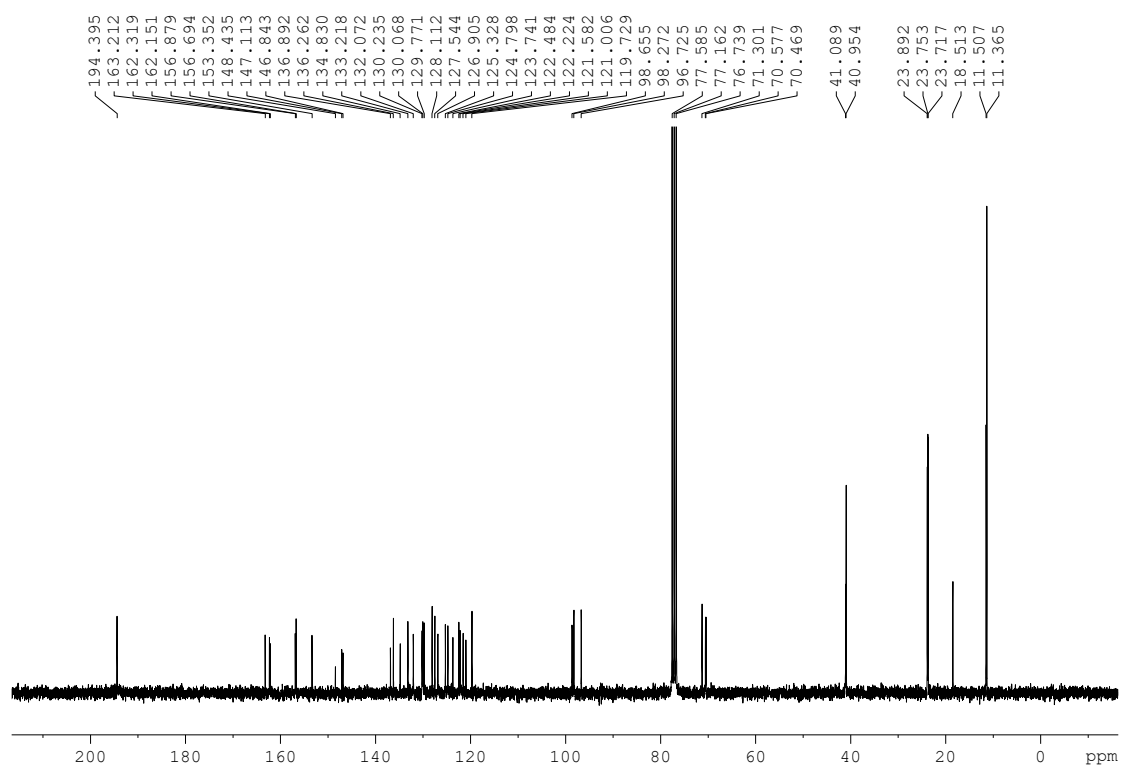


Figure S38: ^{13}C NMR of **7c** in CDCl_3 (75 MHz).

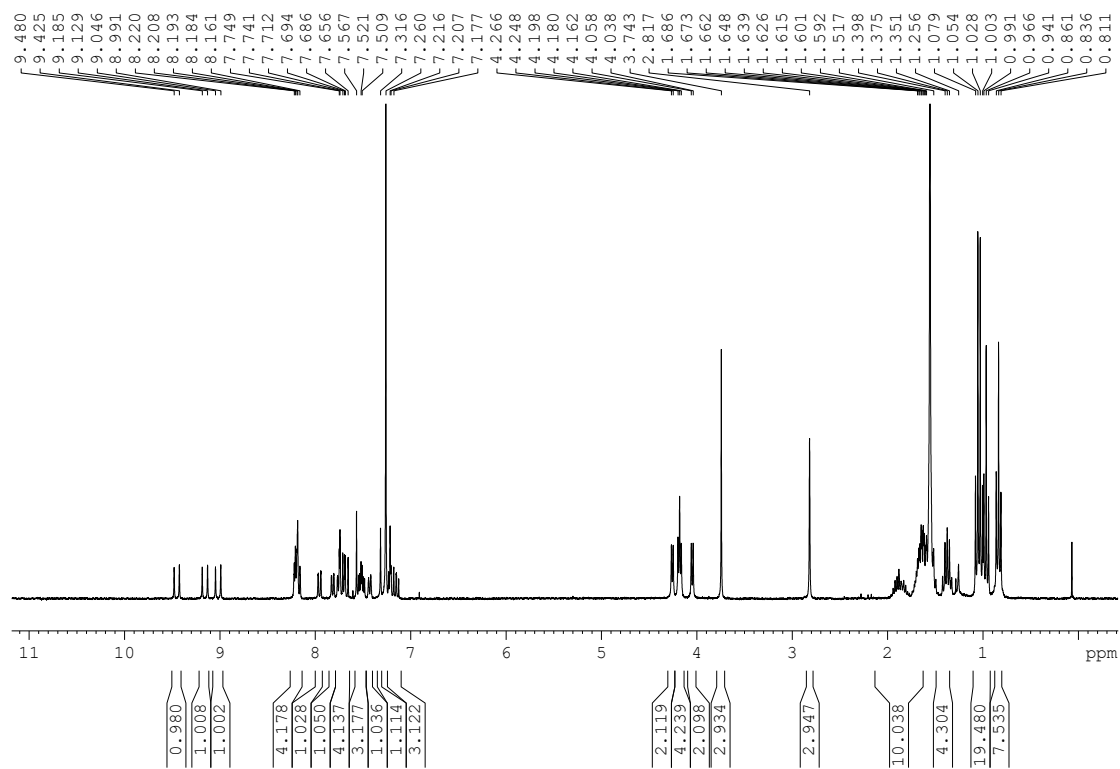


Figure S39: ^1H NMR of **8** in CDCl_3 (300 MHz).

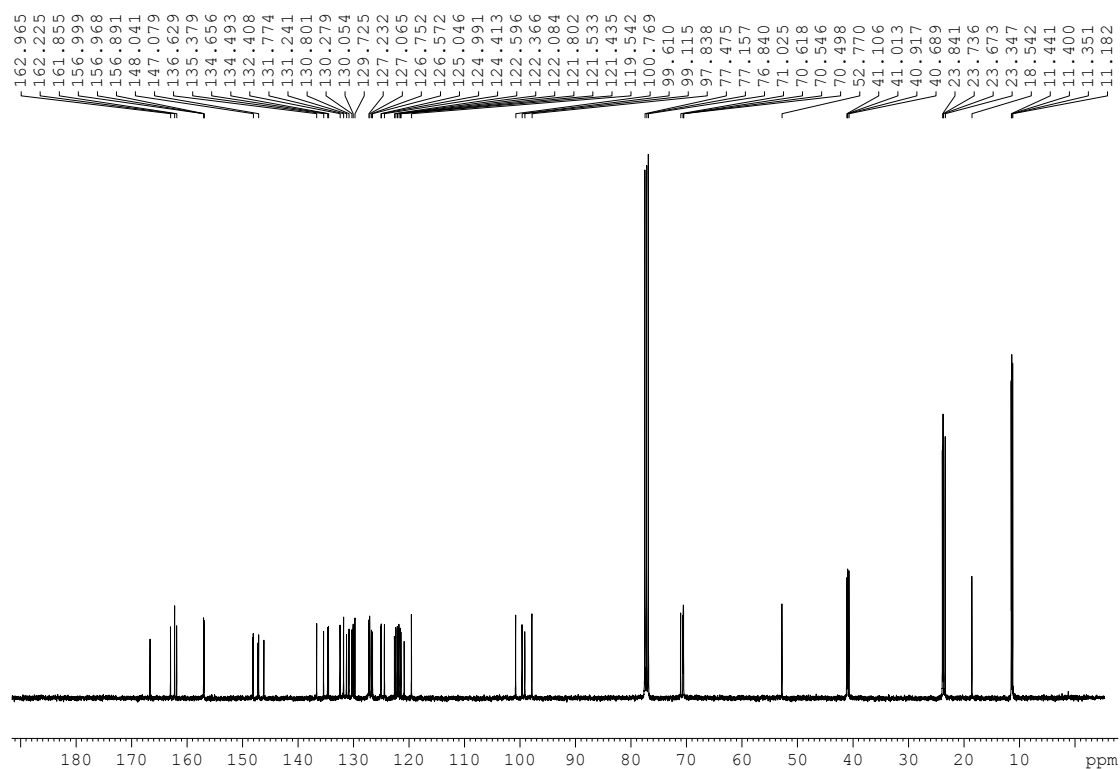


Figure S40: ^{13}C NMR of **8** in CDCl_3 (75 MHz).

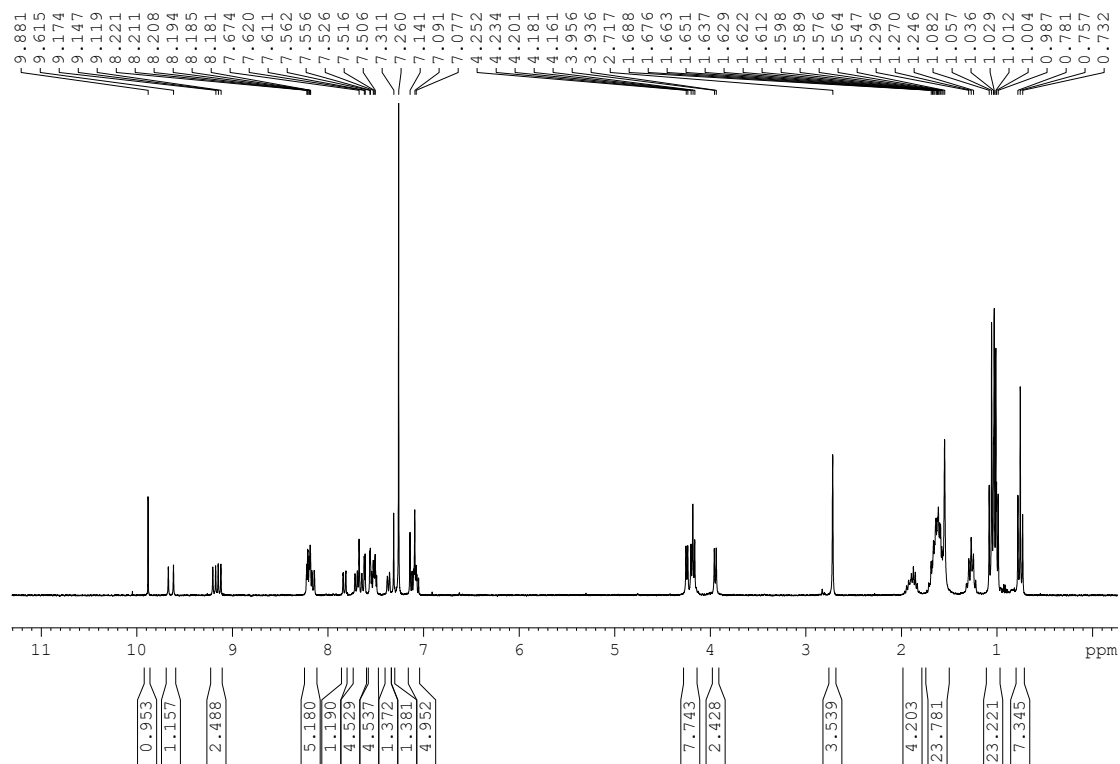


Figure S41: ^1H NMR of **8c** in CDCl_3 (300 MHz).

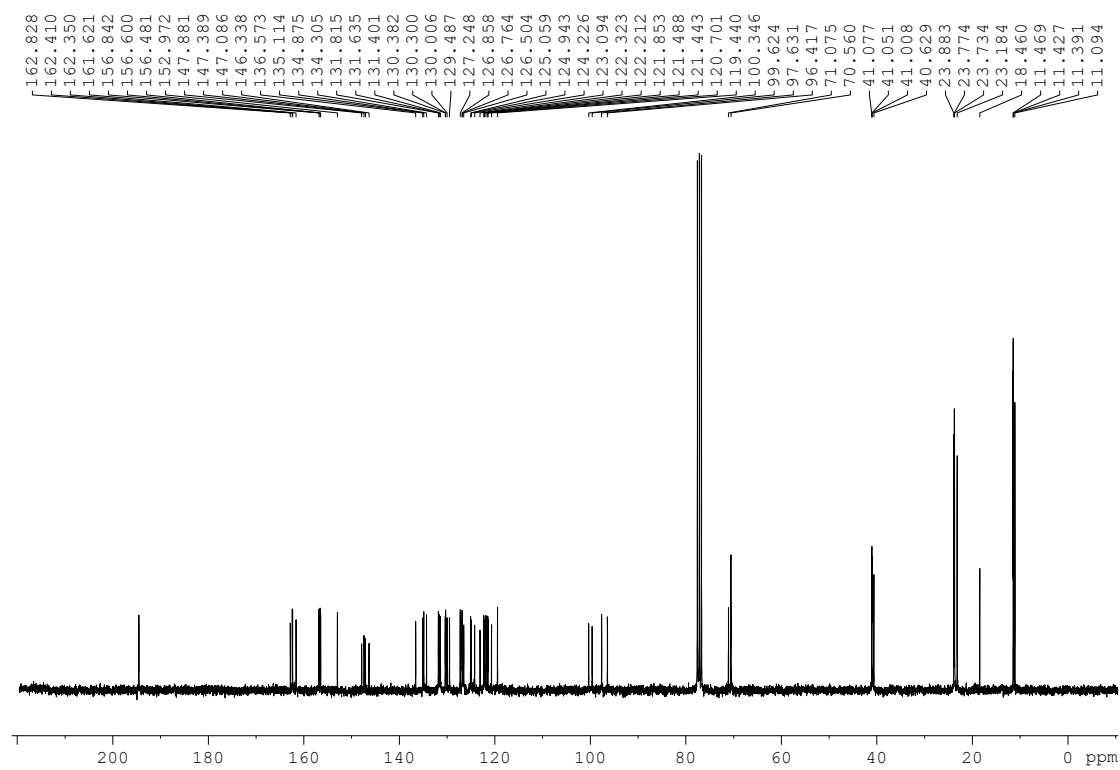


Figure S42: ^{13}C NMR of **8c** in CDCl_3 (75 MHz).

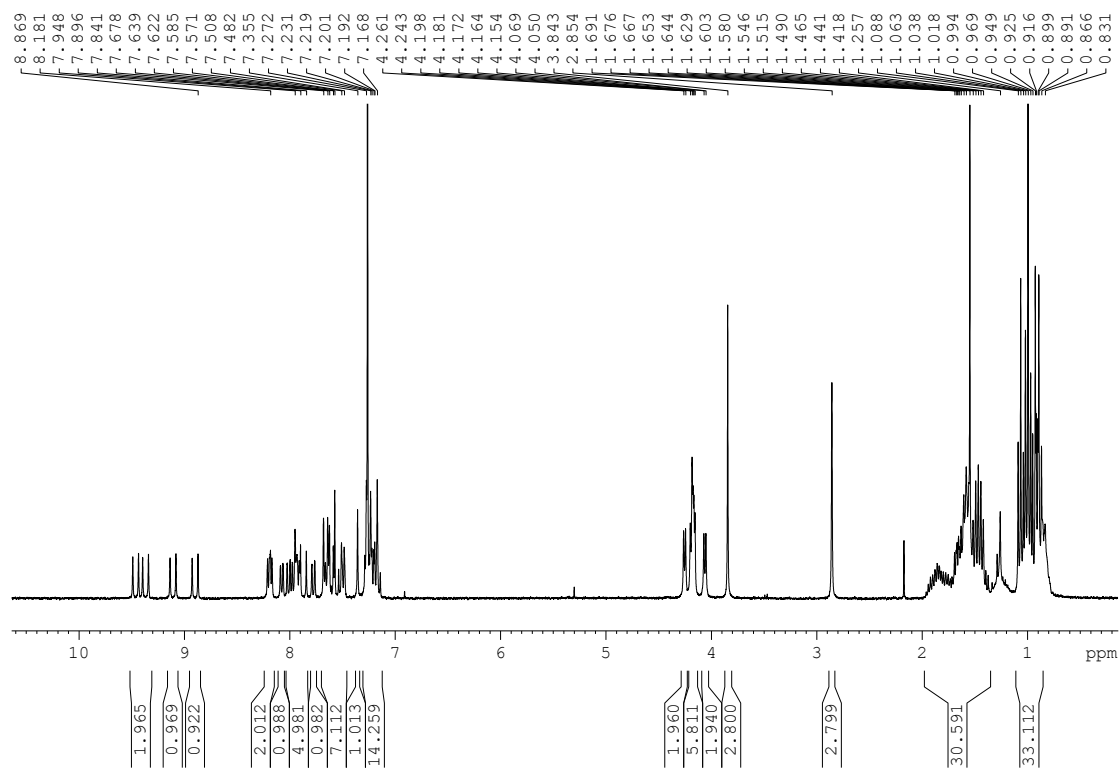


Figure S43: ^1H NMR of **9** in CDCl_3 (300 MHz).

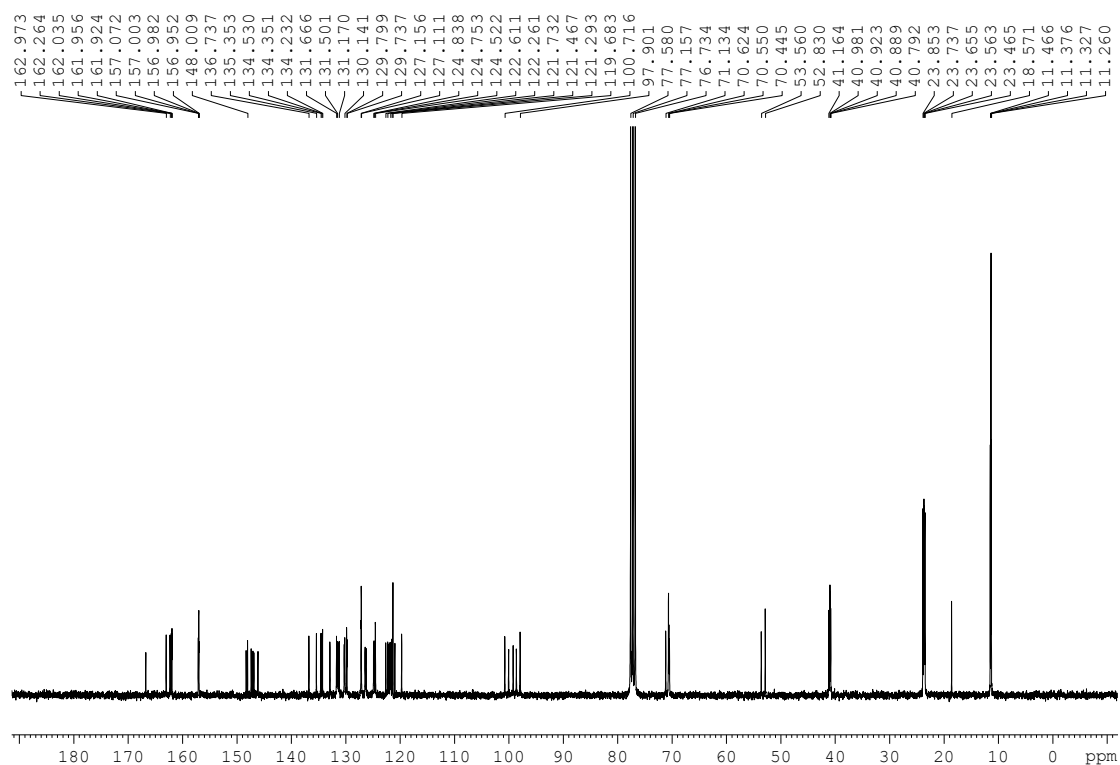


Figure S44: ^{13}C NMR of **9** in CDCl_3 (75 MHz).

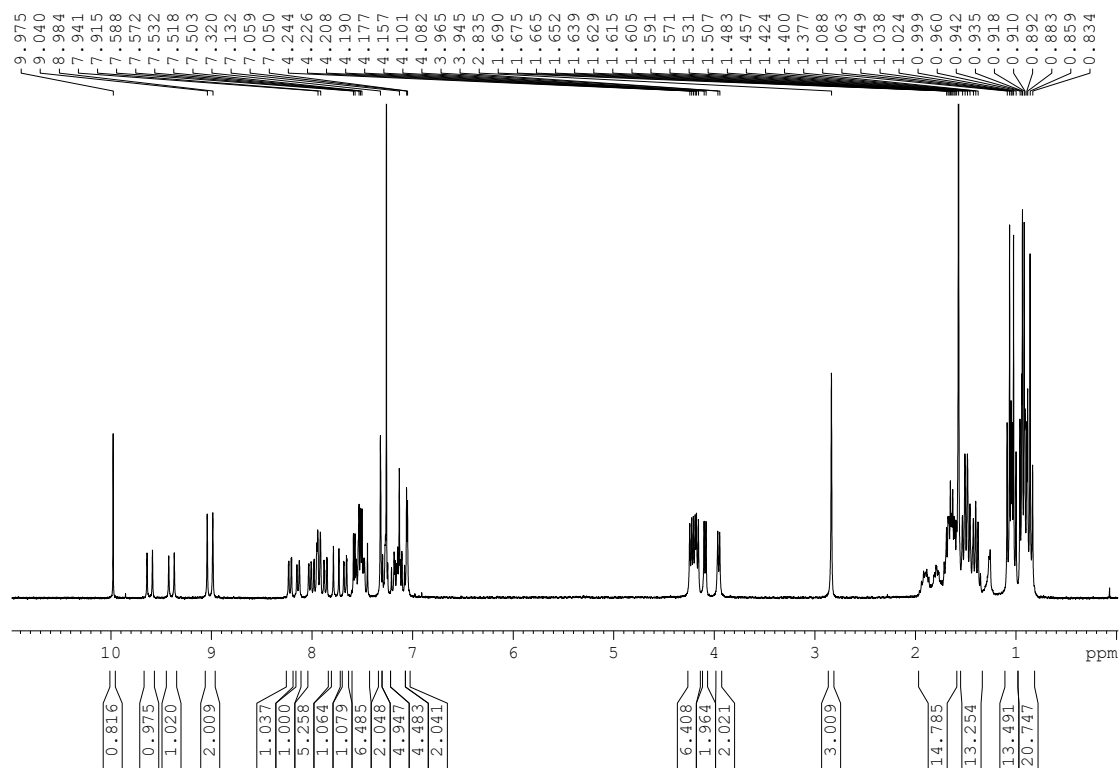


Figure S45: ^1H NMR of **9** in CDCl_3 (300 MHz).

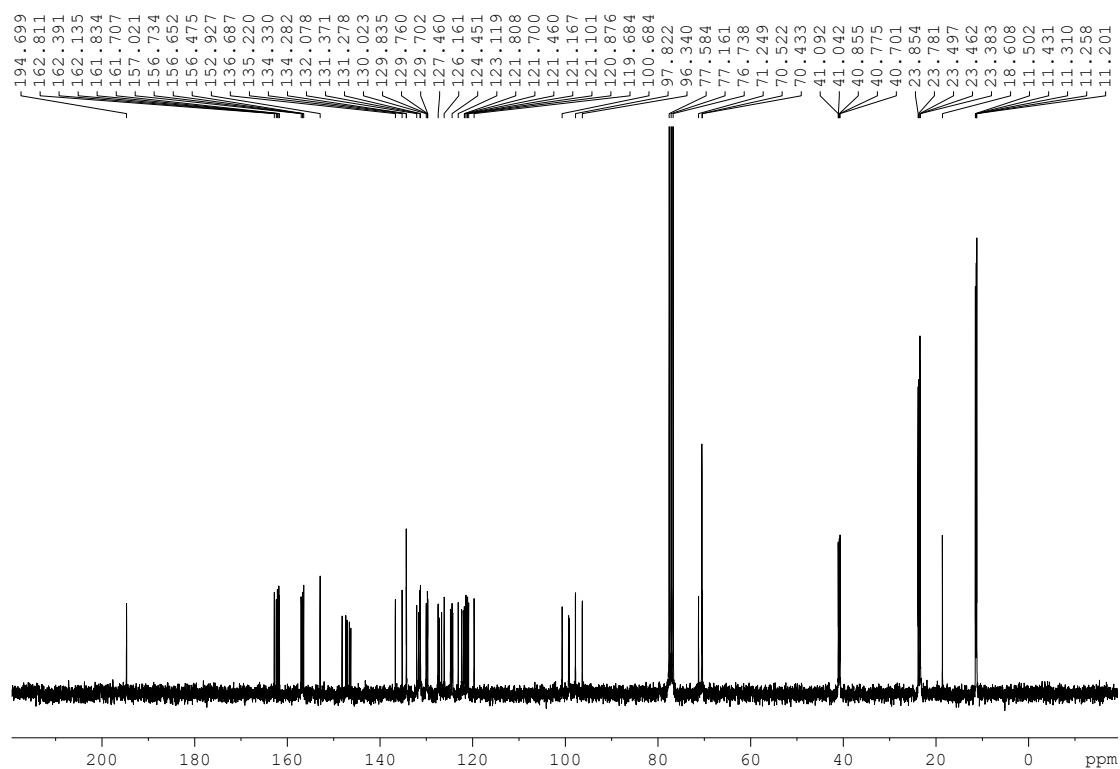


Figure S46: ^{13}C NMR of **9** in CDCl_3 (75 MHz).

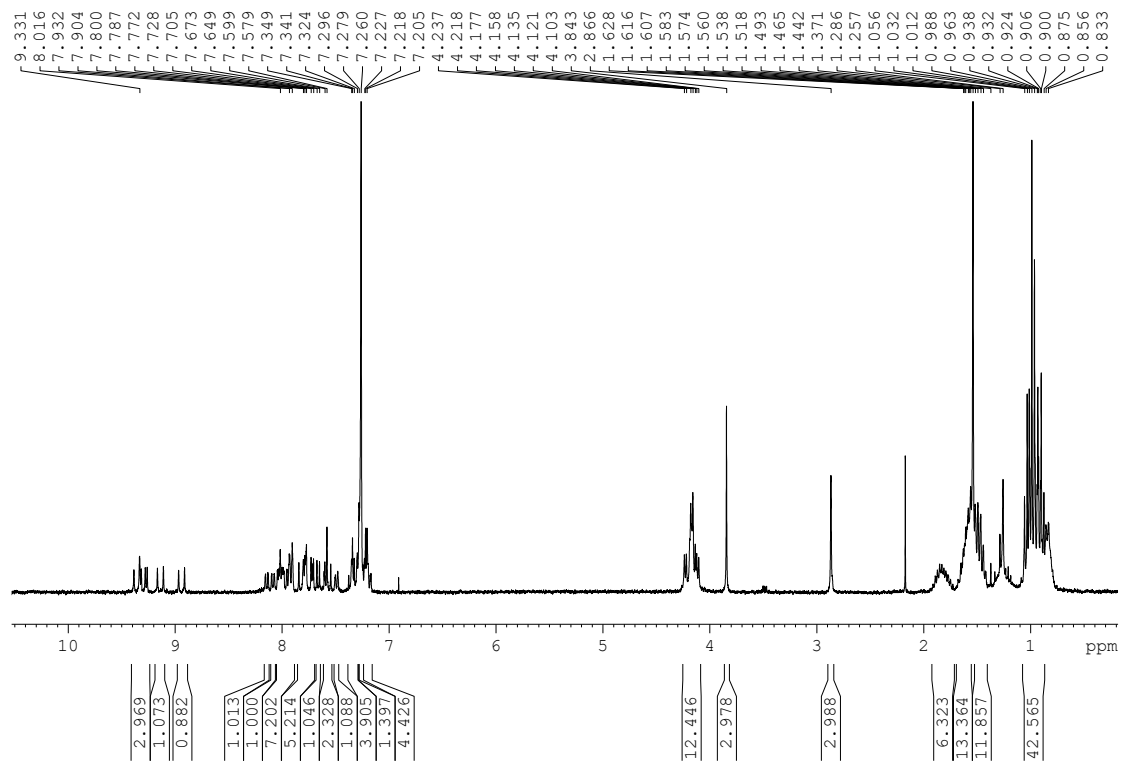


Figure S47: ^1H NMR of **10** in CDCl_3 (300 MHz).

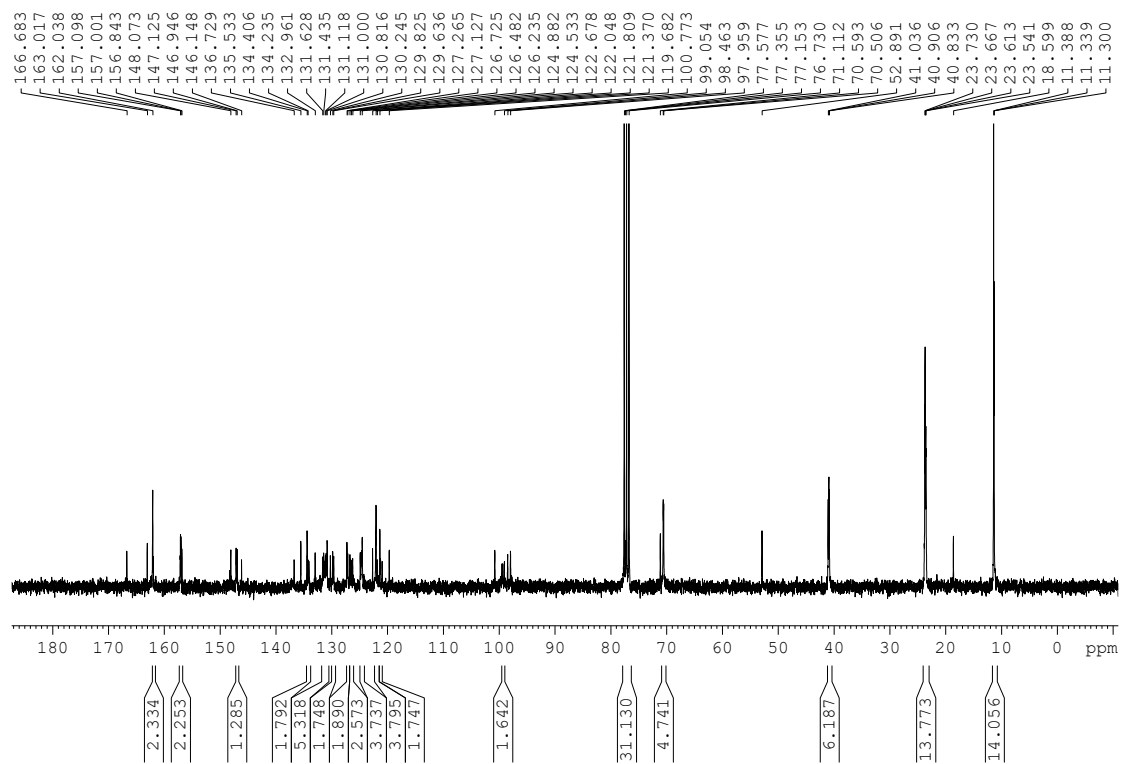


Figure S48: ^{13}C NMR of **10** in CDCl_3 (75 MHz).

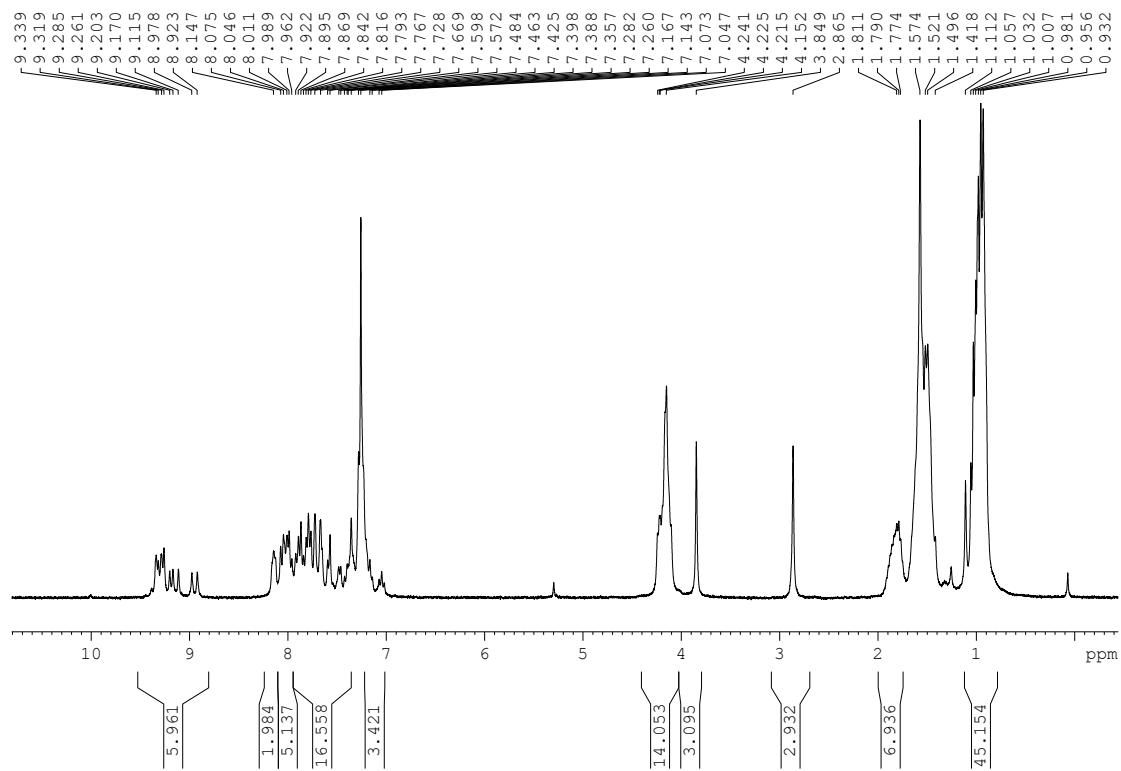


Figure S49: ^1H NMR of **11** in CDCl_3 (300 MHz).

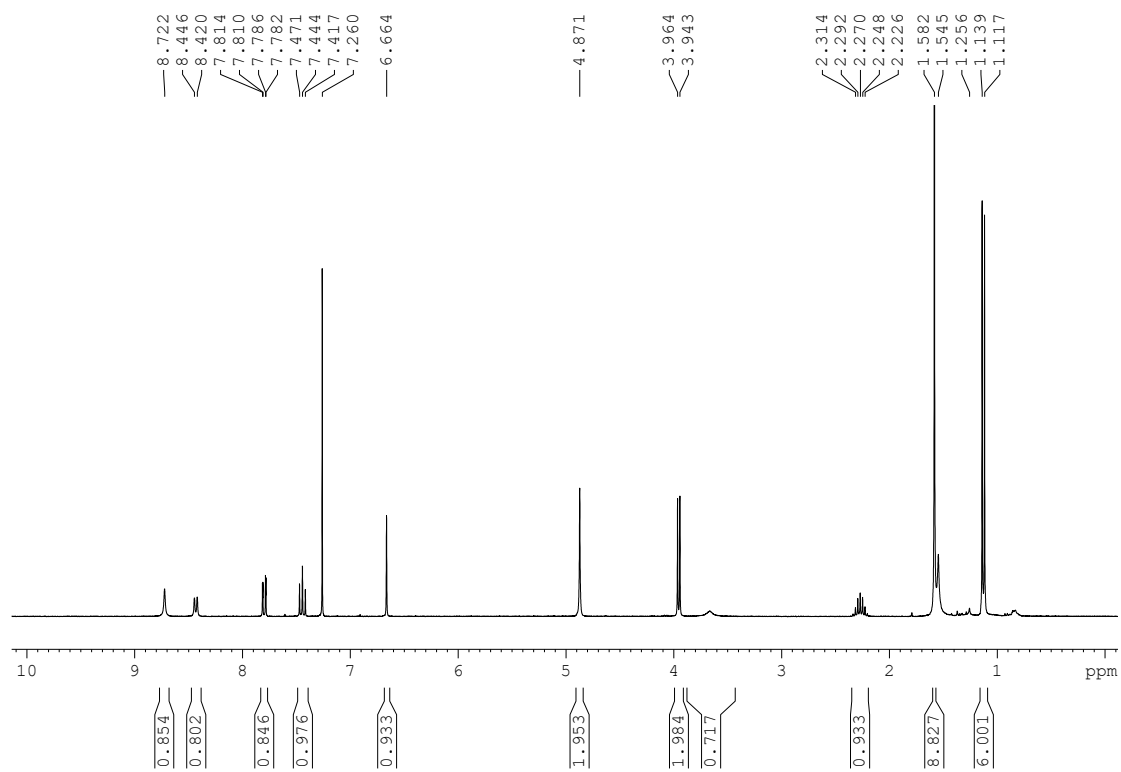


Figure S50: ^1H NMR of **12b** in CDCl_3 (300 MHz).

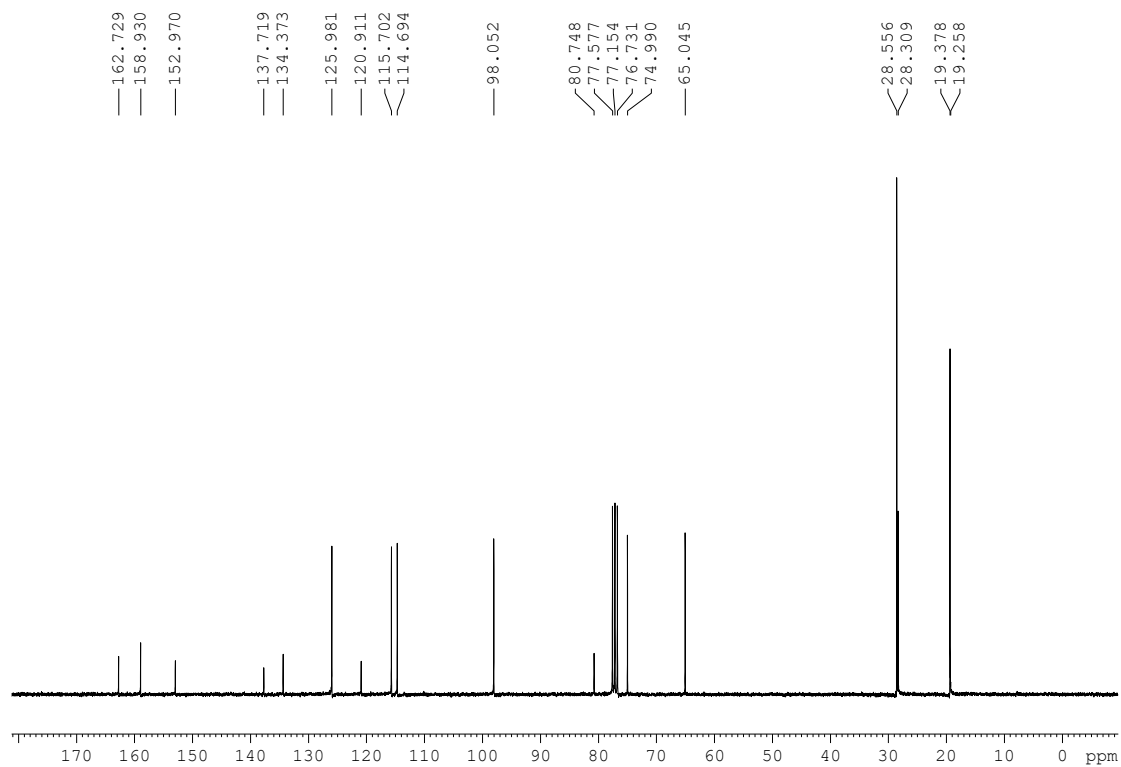


Figure S51: ^{13}C NMR of **12b** in CDCl_3 (75 MHz).

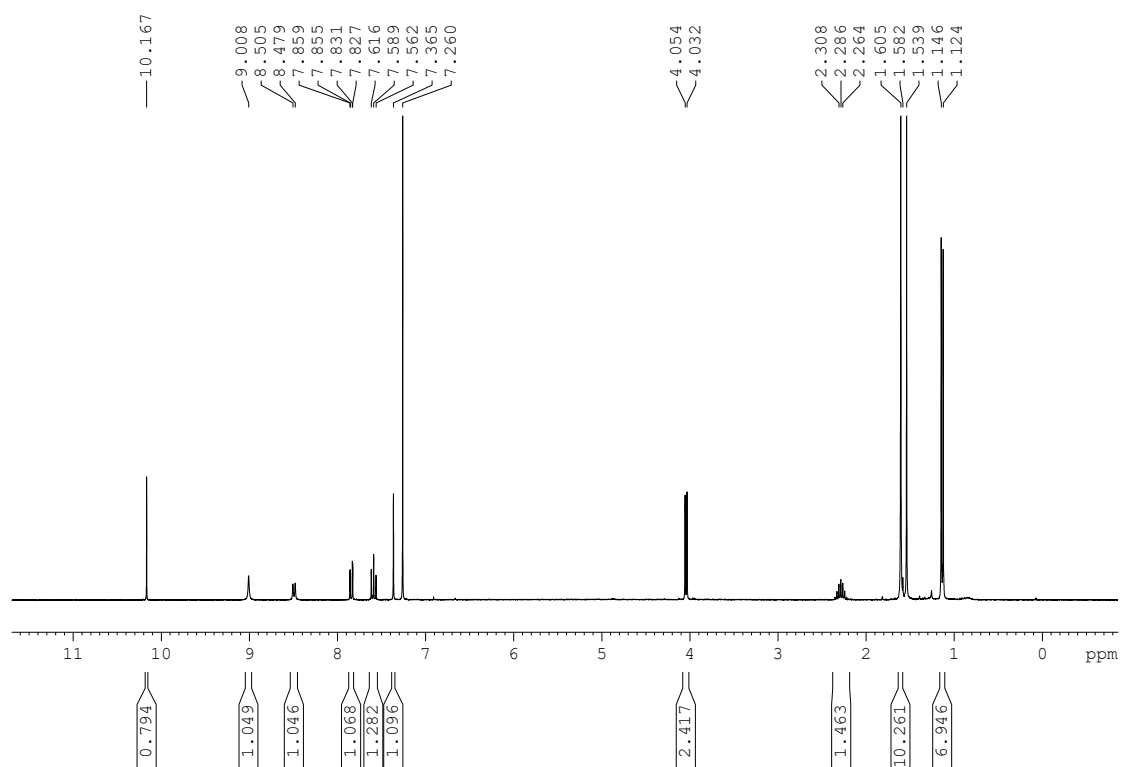


Figure S52: ^1H NMR of **13** in CDCl_3 (300 MHz).

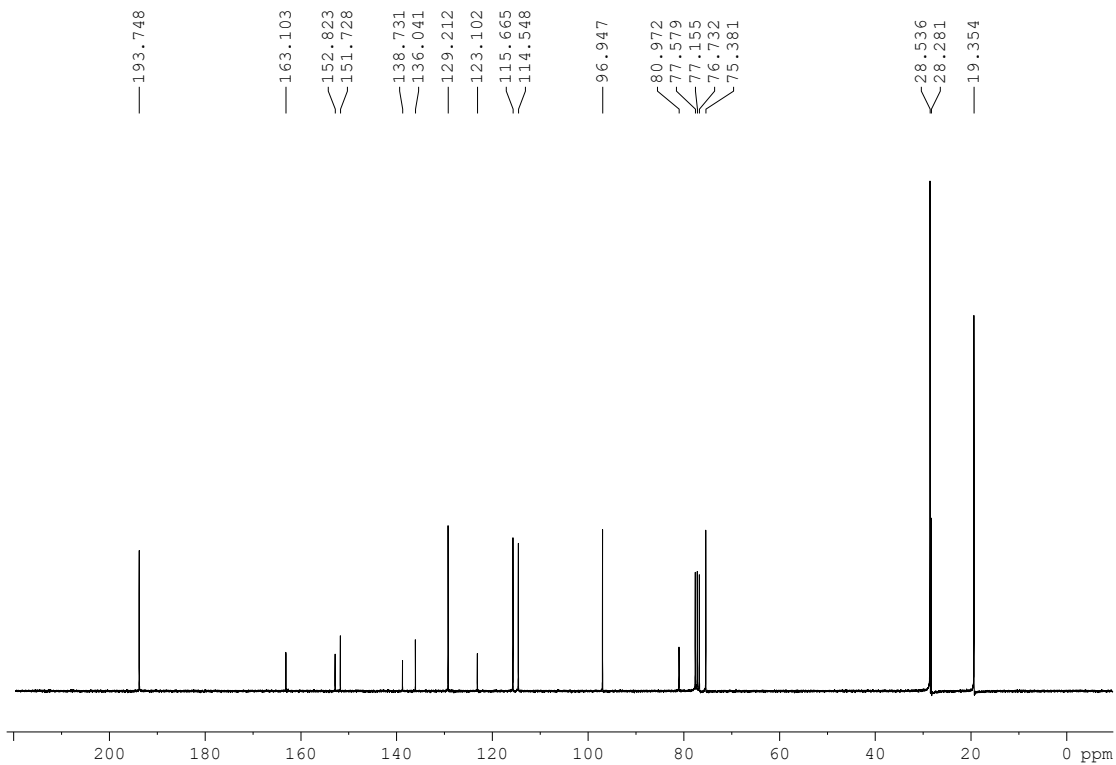


Figure S53: ^{13}C NMR of **13** in CDCl_3 (75 MHz).

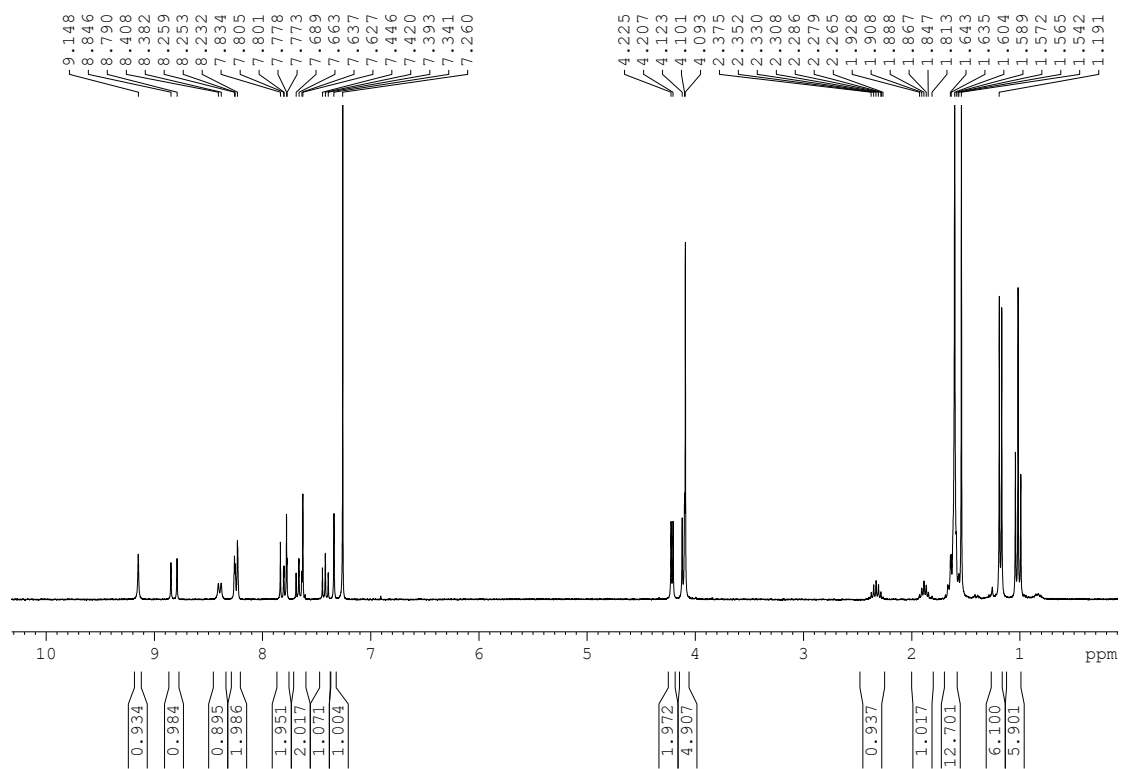


Figure S54: ^1H NMR of **14** in CDCl_3 (300 MHz).

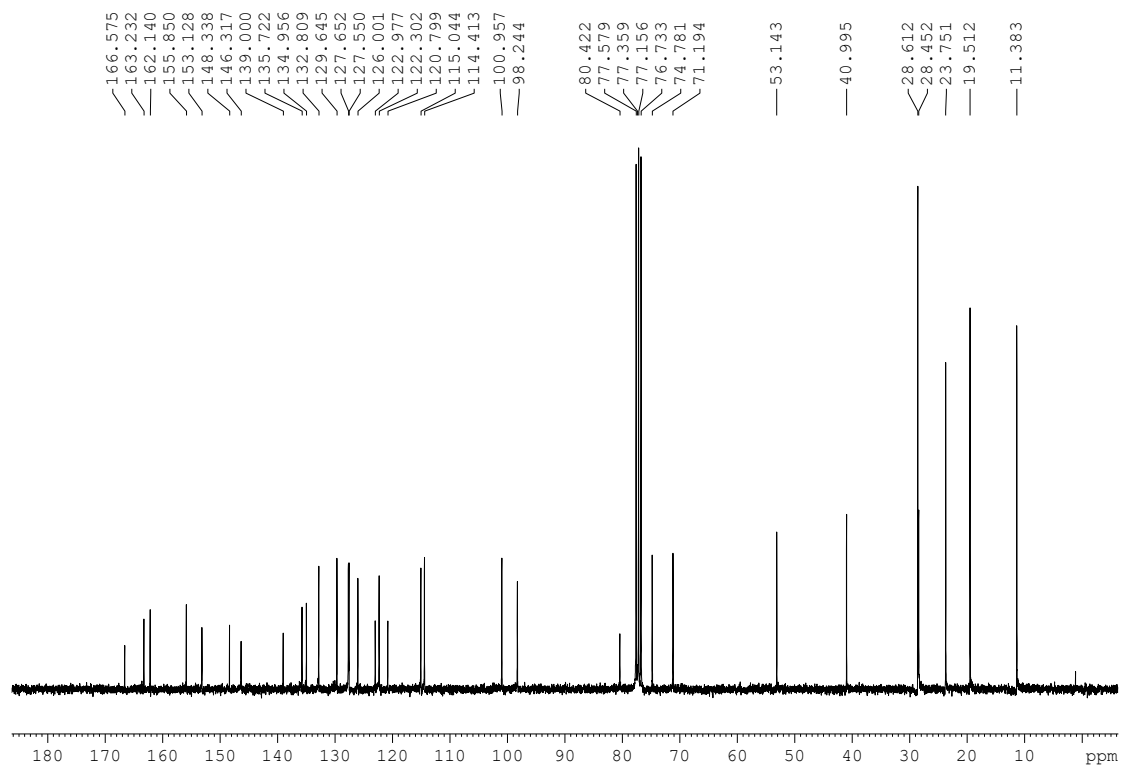


Figure S55: ¹³C NMR of **14** in CDCl₃ (75 MHz).

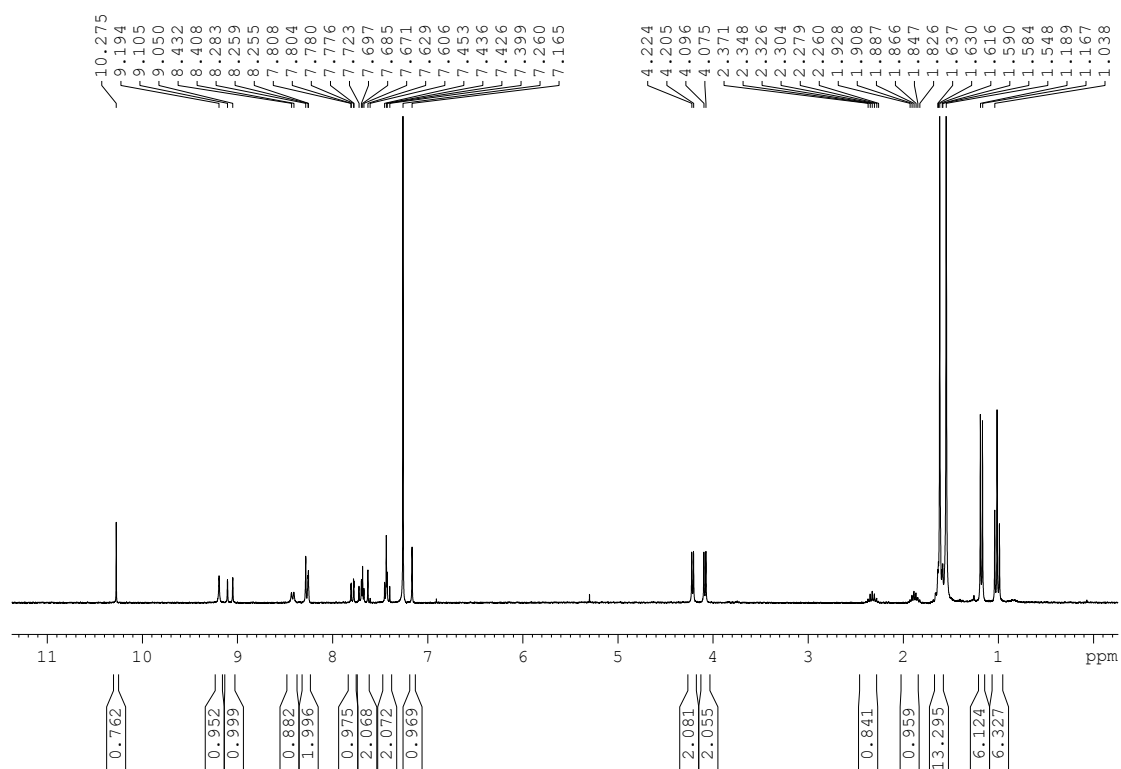


Figure S 56: ¹H NMR of **14c** in CDCl₃ (300 MHz).

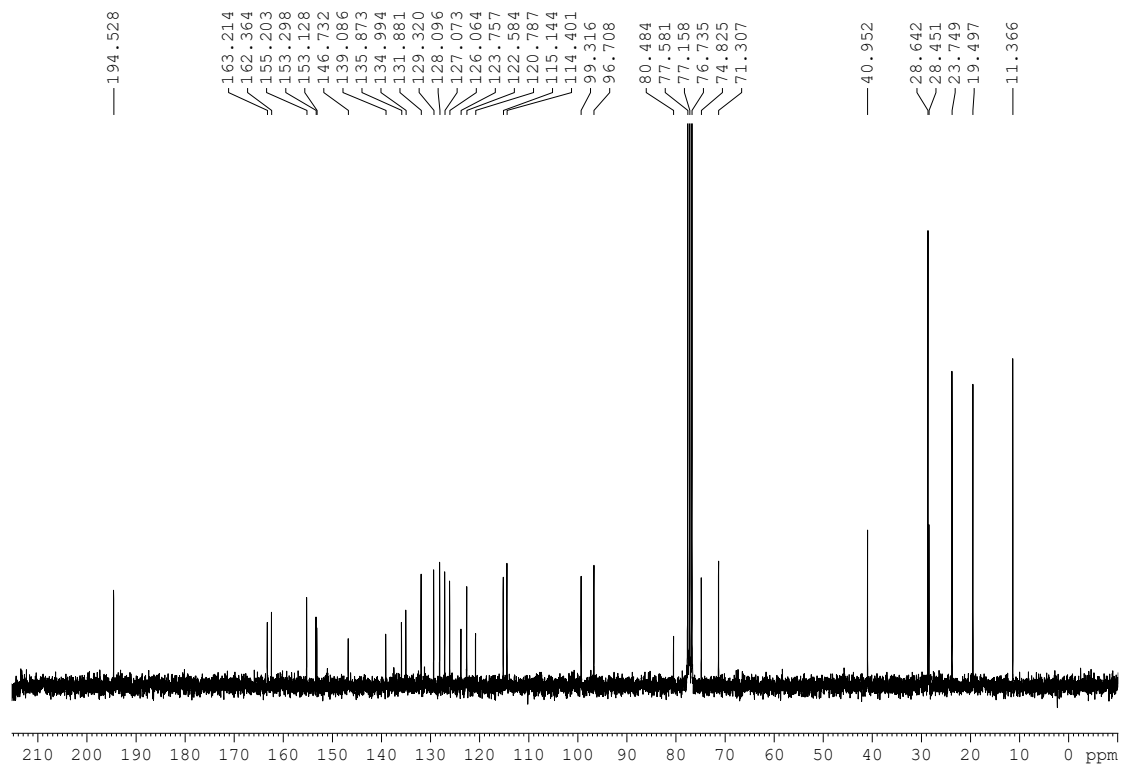


Figure S57: ^{13}C NMR of **14c** in CDCl_3 (75 MHz).

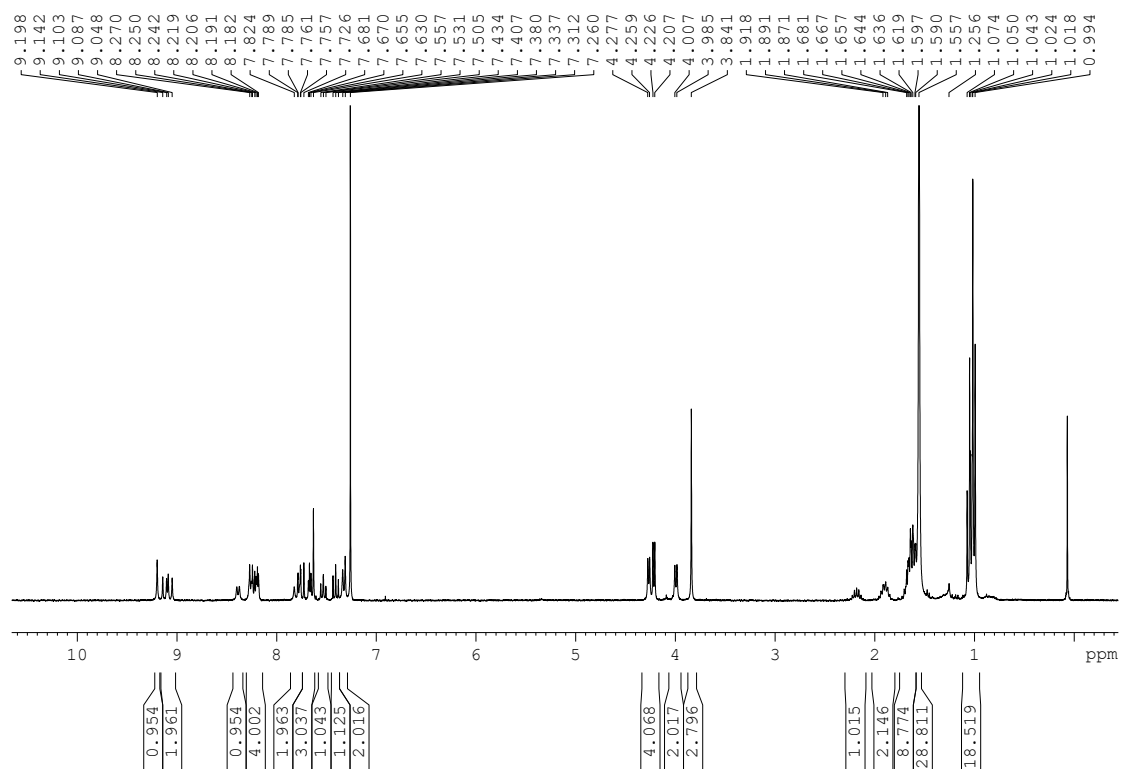


Figure S58: ^1H NMR of **S14** in CDCl_3 (300 MHz).

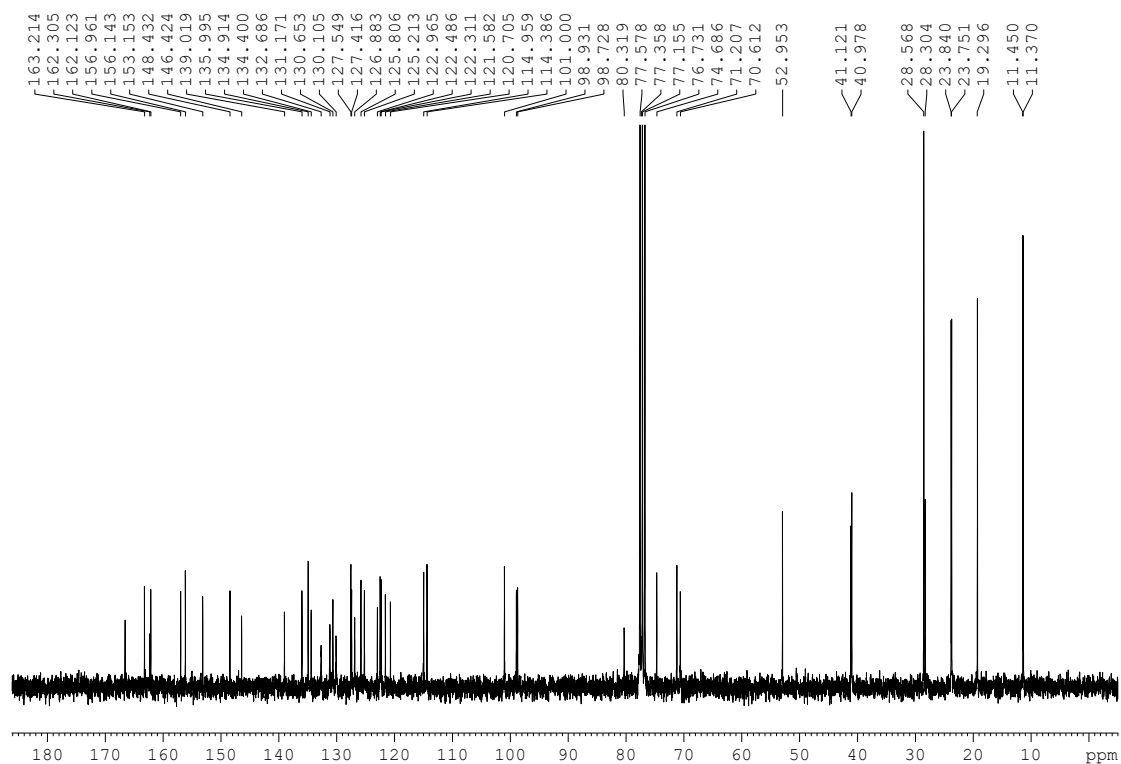


Figure S59: ^{13}C NMR of **S14** in CDCl_3 (75 MHz).

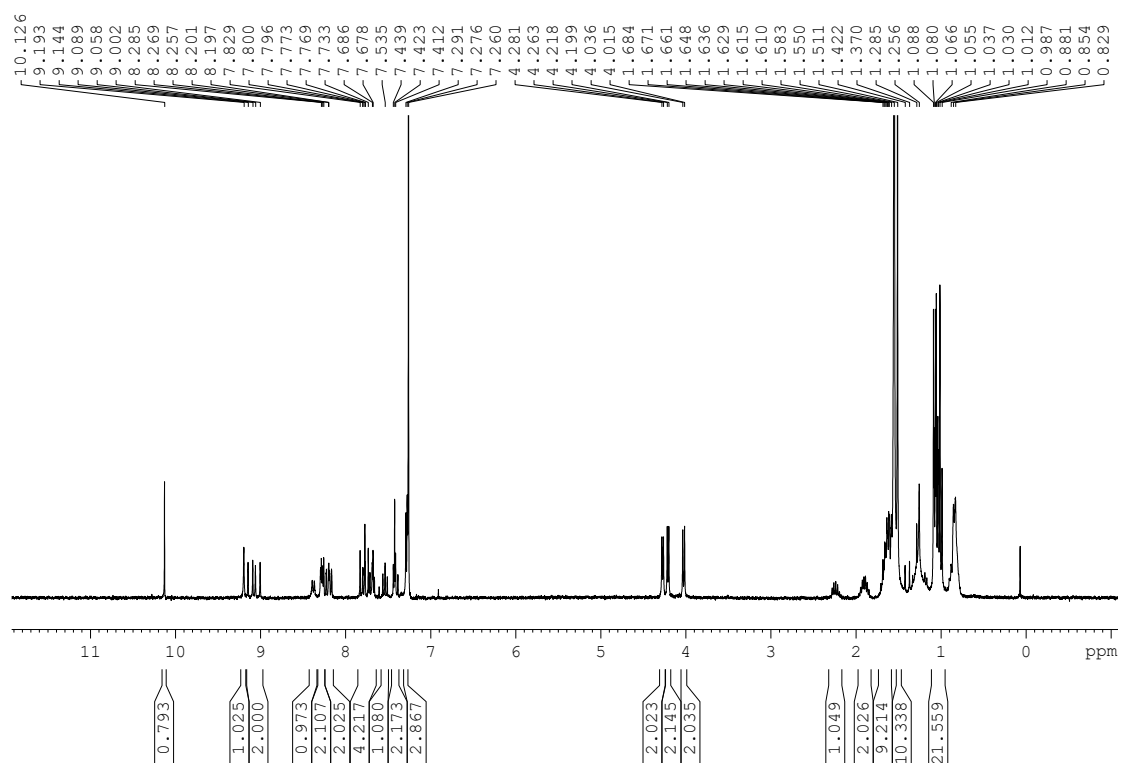


Figure S60: ^1H NMR of **S14c** in CDCl_3 (300 MHz).

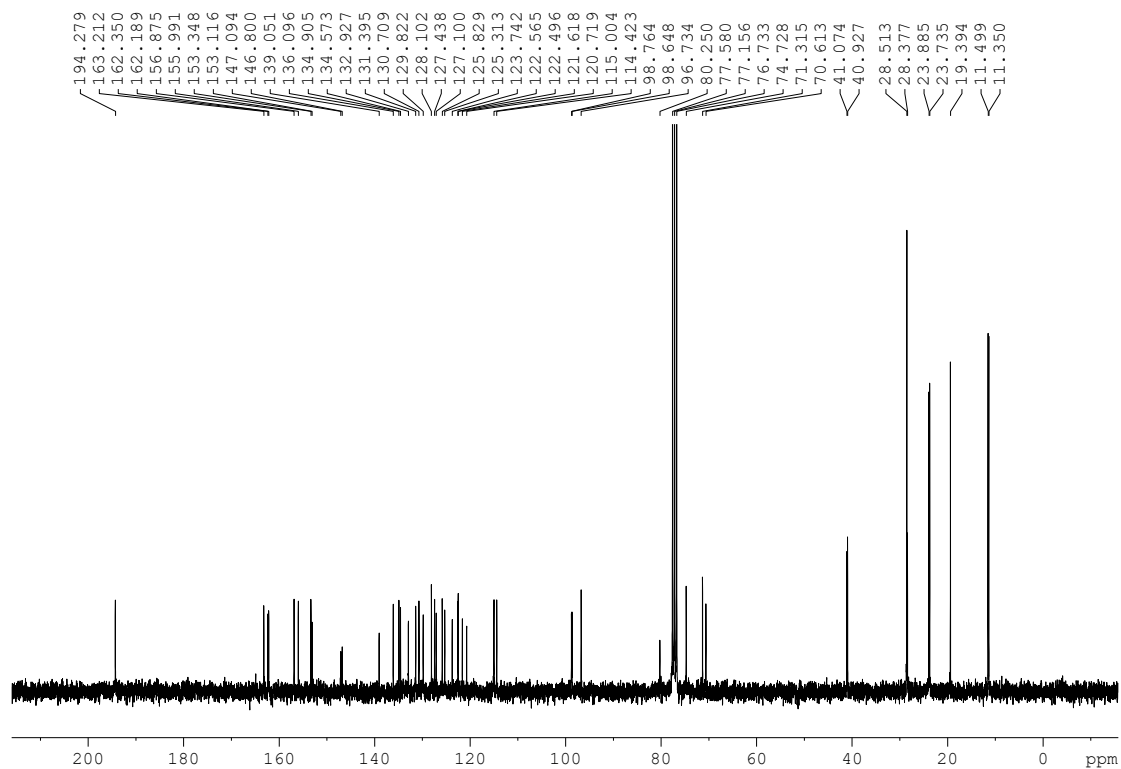


Figure S61: ^{13}C NMR of **S14c** in CDCl_3 (75 MHz).

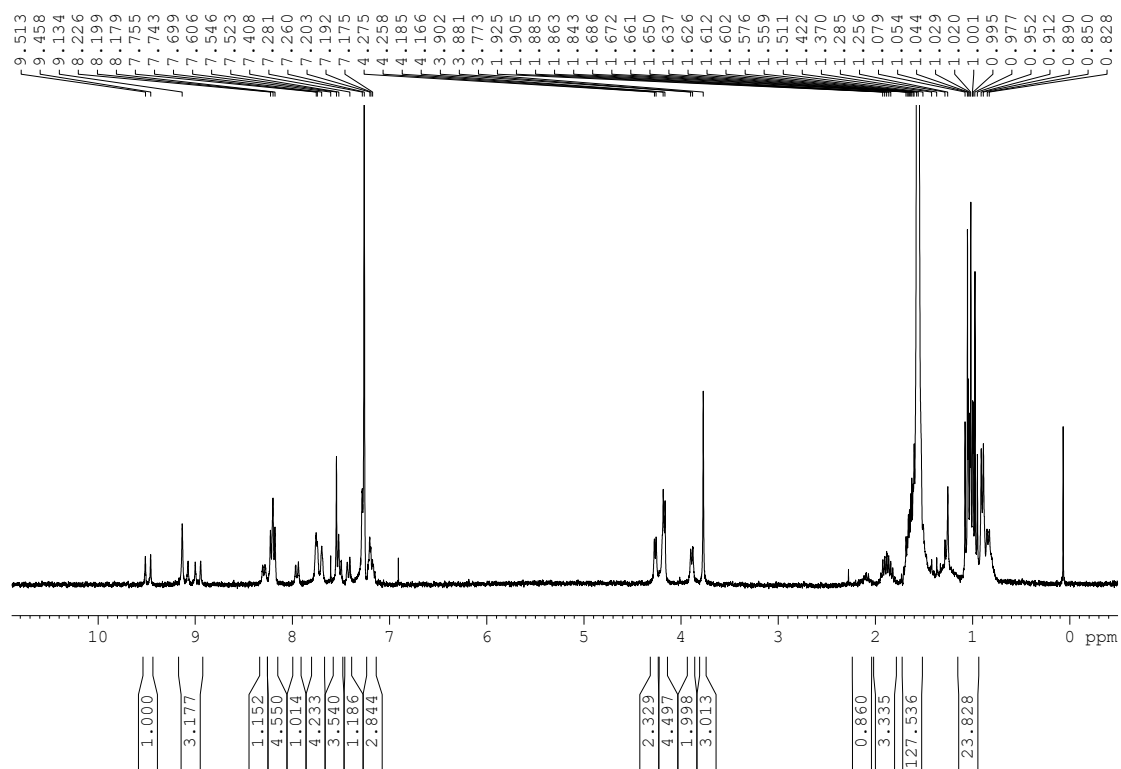


Figure S62: ^1H NMR of **15** in CDCl_3 (300 MHz).

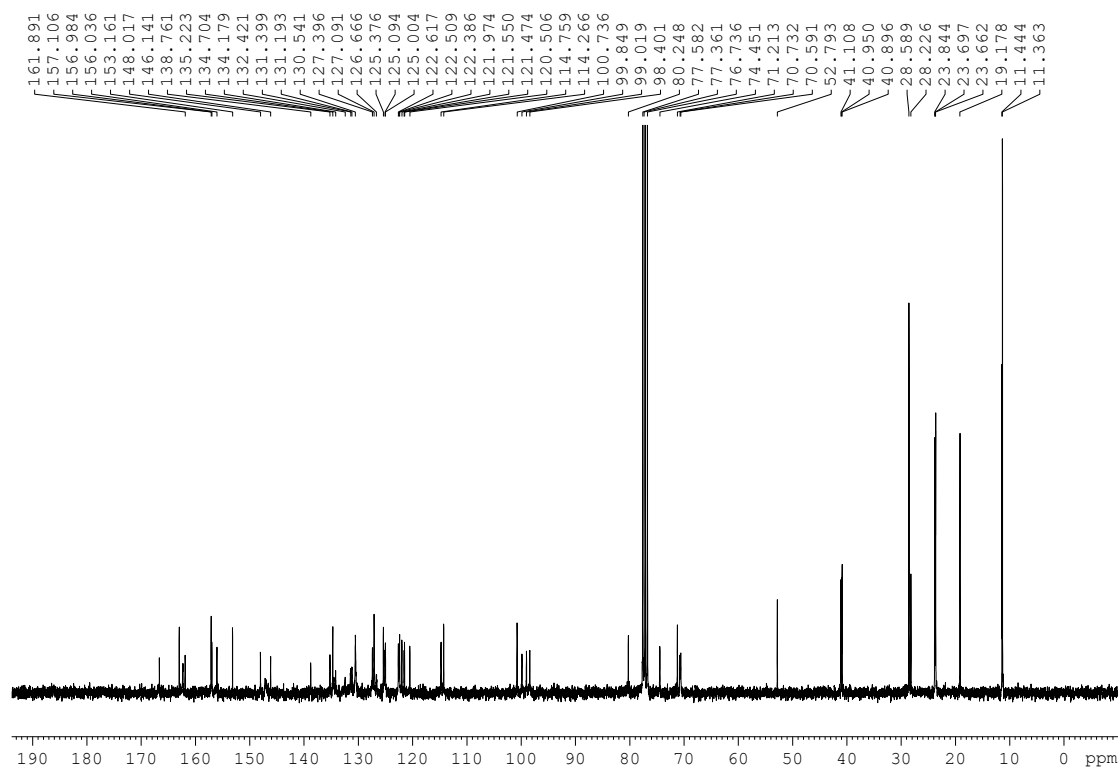


Figure S63: ^{13}C NMR of **15** in CDCl_3 (75 MHz).

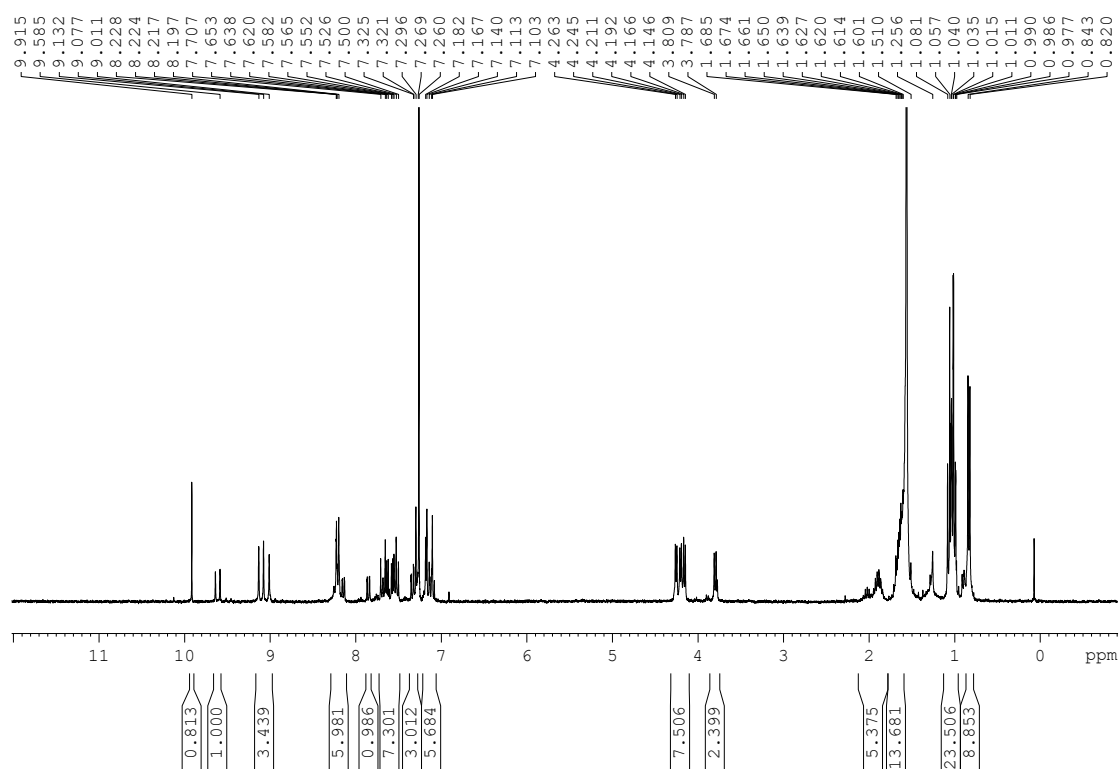


Figure S64: ^1H NMR of **15c** in CDCl_3 (300 MHz).

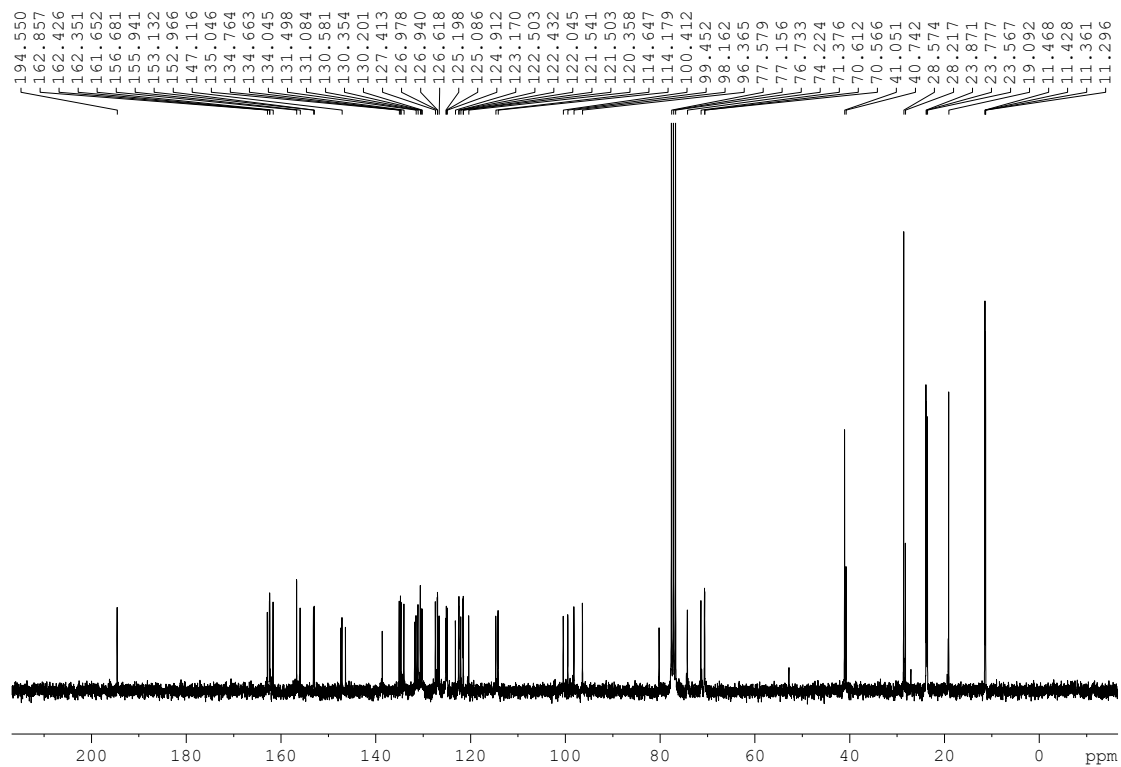


Figure S65: ^{13}C NMR of **15c** in CDCl_3 (75 MHz).

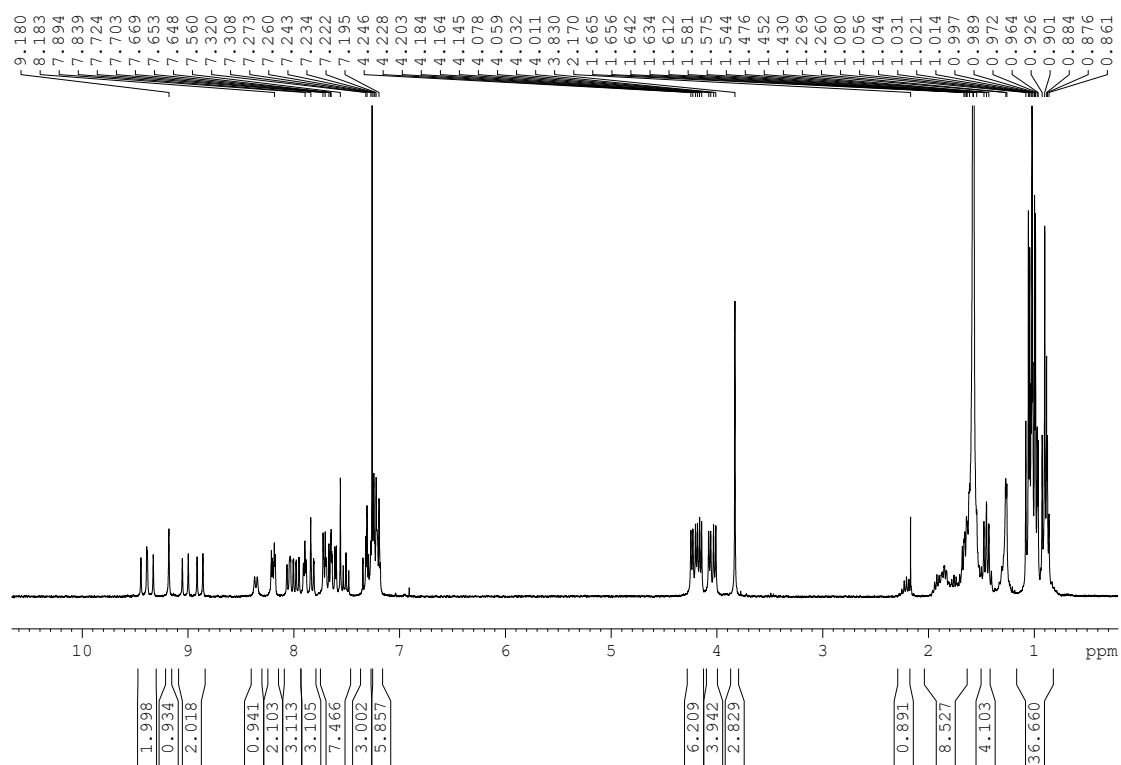


Figure S66: ^1H NMR of **S15** in CDCl_3 (300 MHz).

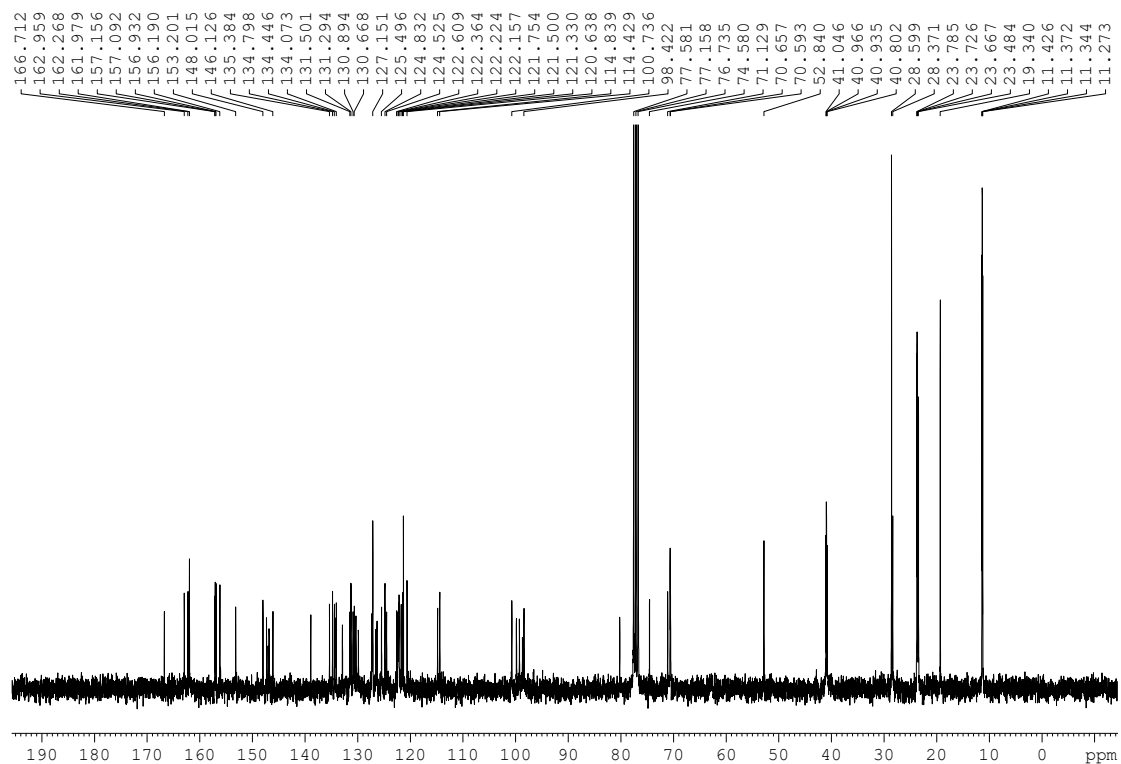


Figure S67: ^{13}C NMR of **S15** in CDCl_3 (75 MHz).

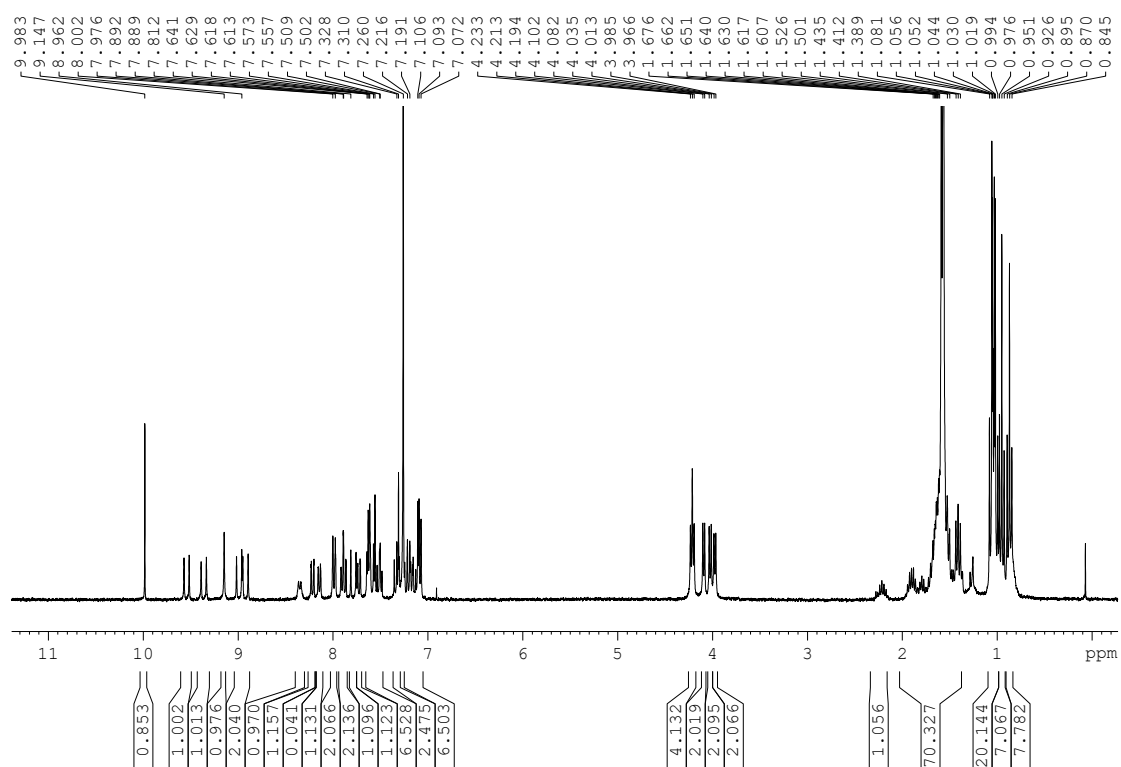


Figure S68: ^1H NMR of **S15c** in CDCl_3 (300 MHz).

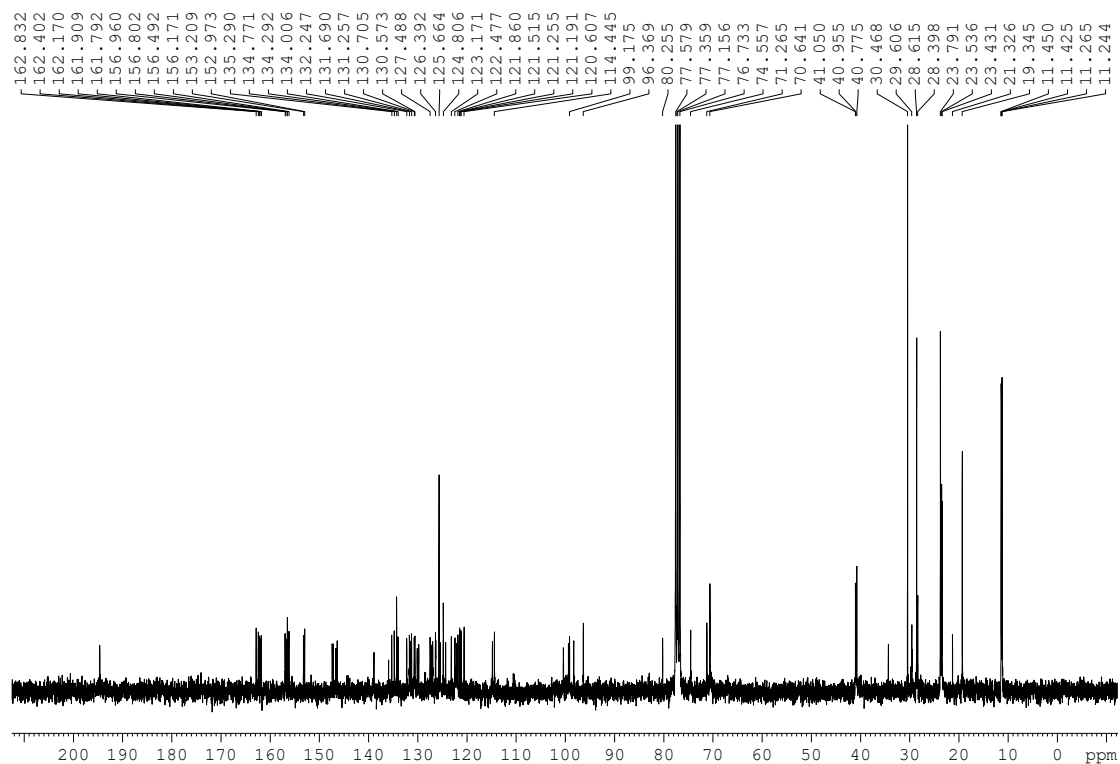


Figure S69: ^{13}C NMR of **S15c** in CDCl_3 (75 MHz).

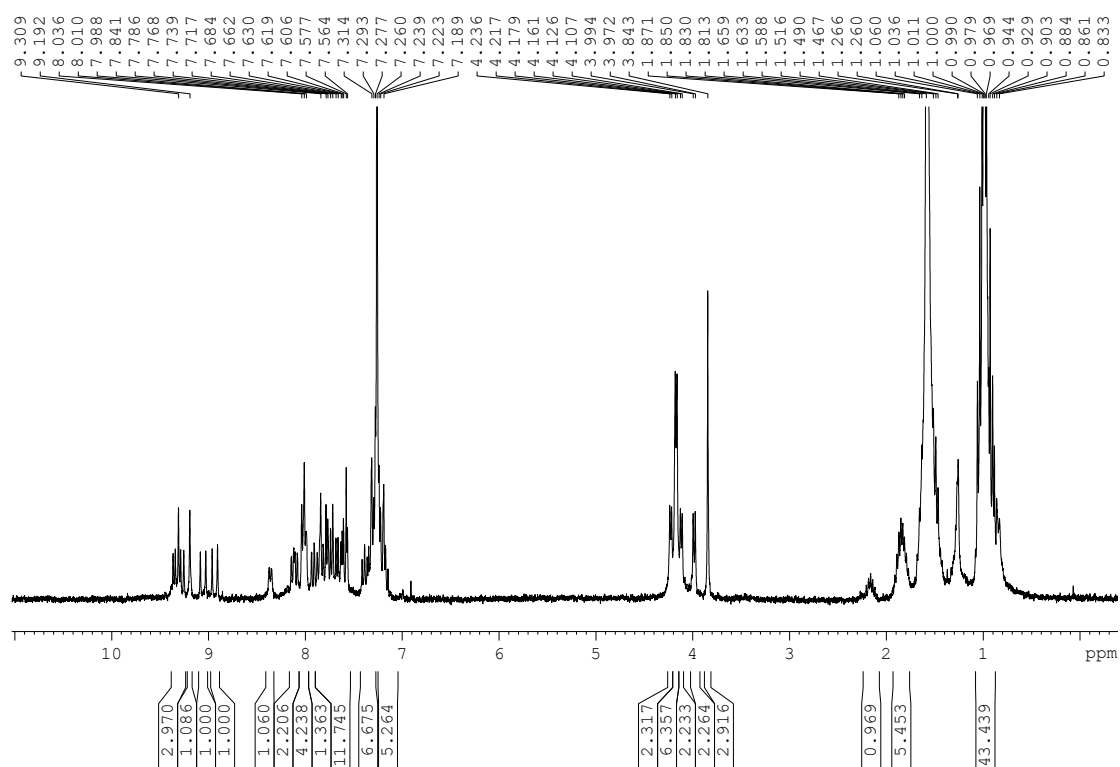


Figure S70: ^1H NMR of **16** in CDCl_3 (300 MHz).

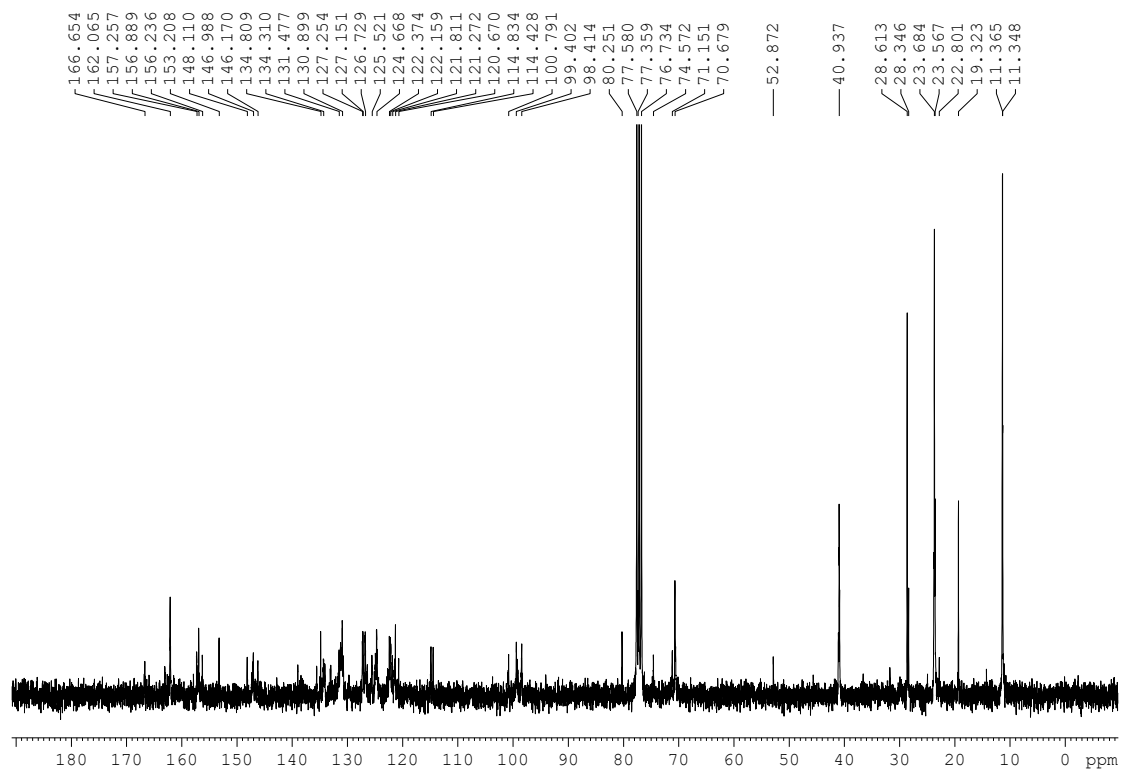


Figure S71: ^{13}C NMR of **16** in CDCl_3 (75 MHz).

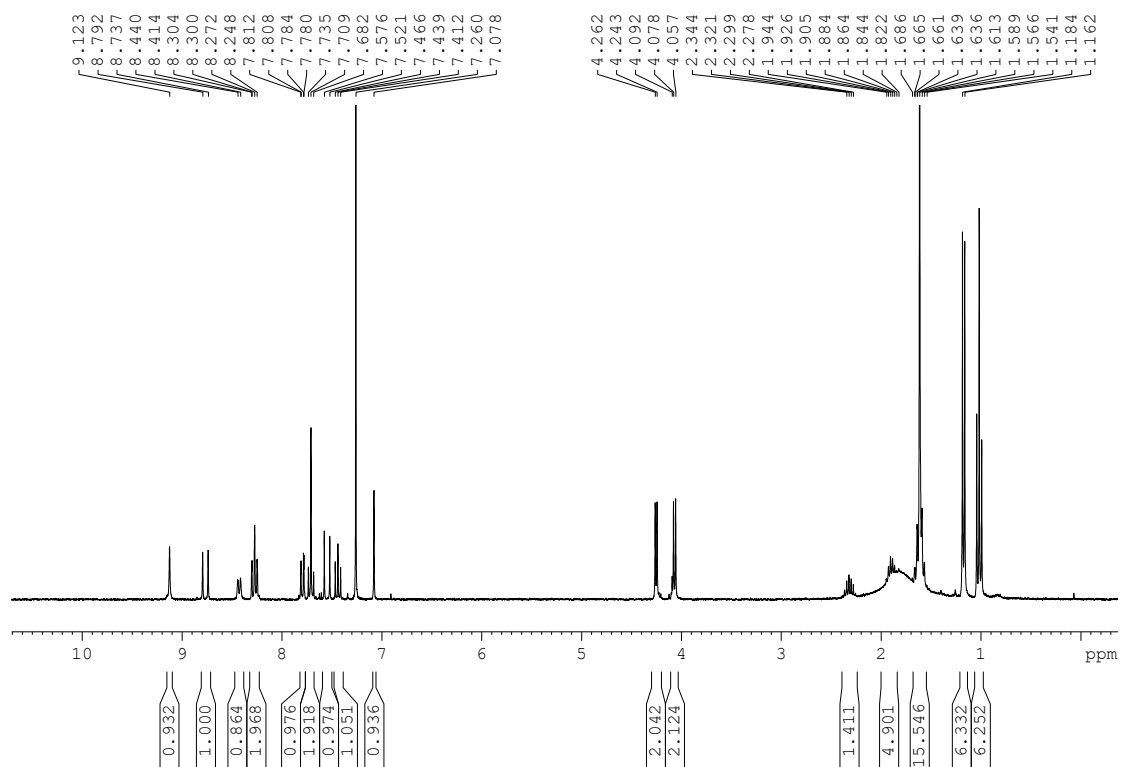


Figure S72: ^1H NMR of **14d** in CDCl_3 (300 MHz).

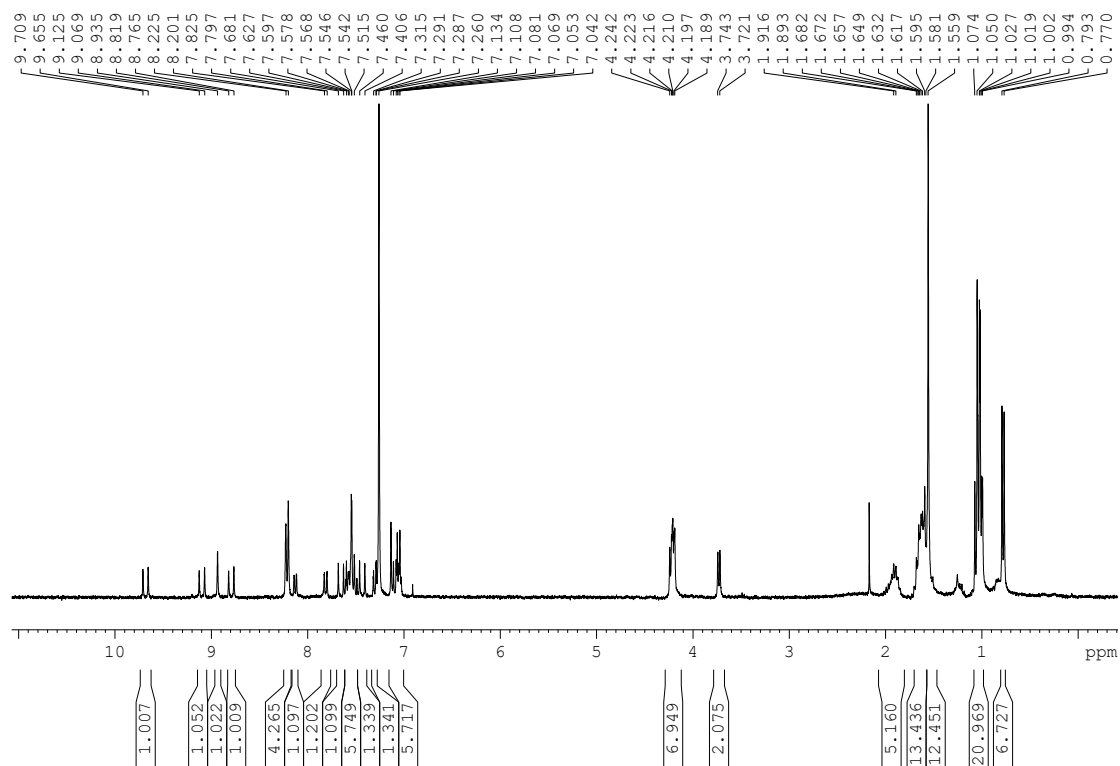


Figure S73: ^1H NMR of **15d** in CDCl_3 (300 MHz).

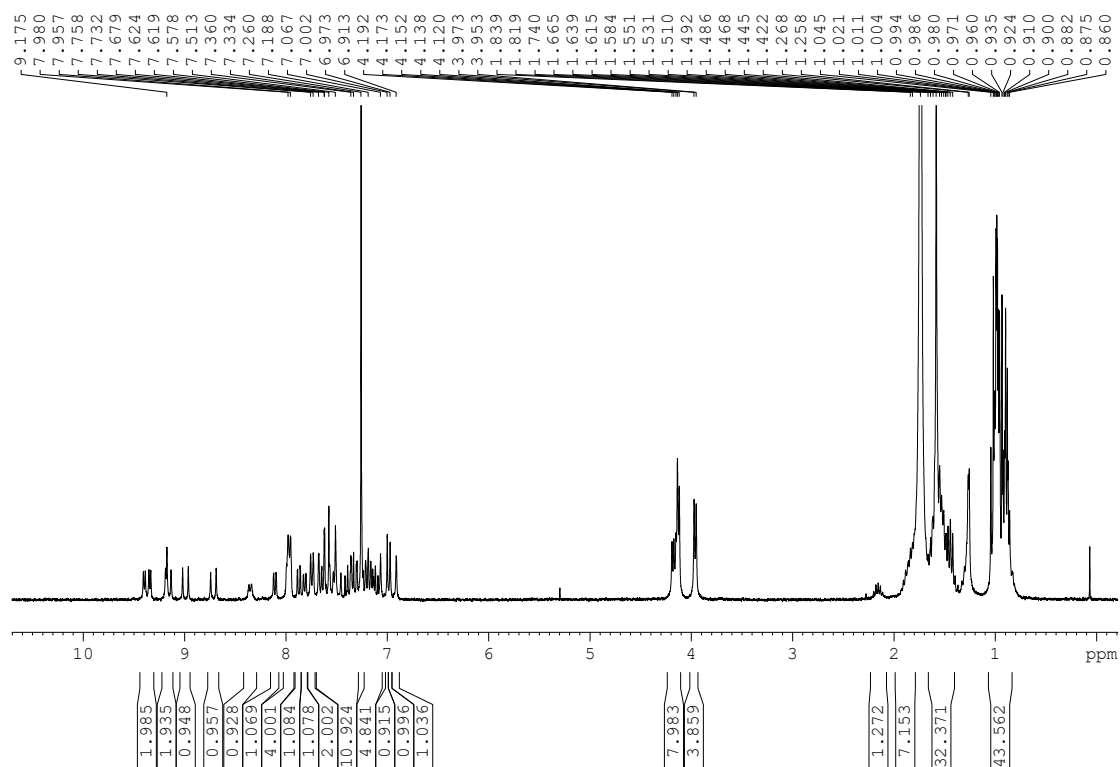


Figure S74: ^1H NMR of **16d** in CDCl_3 (300 MHz).

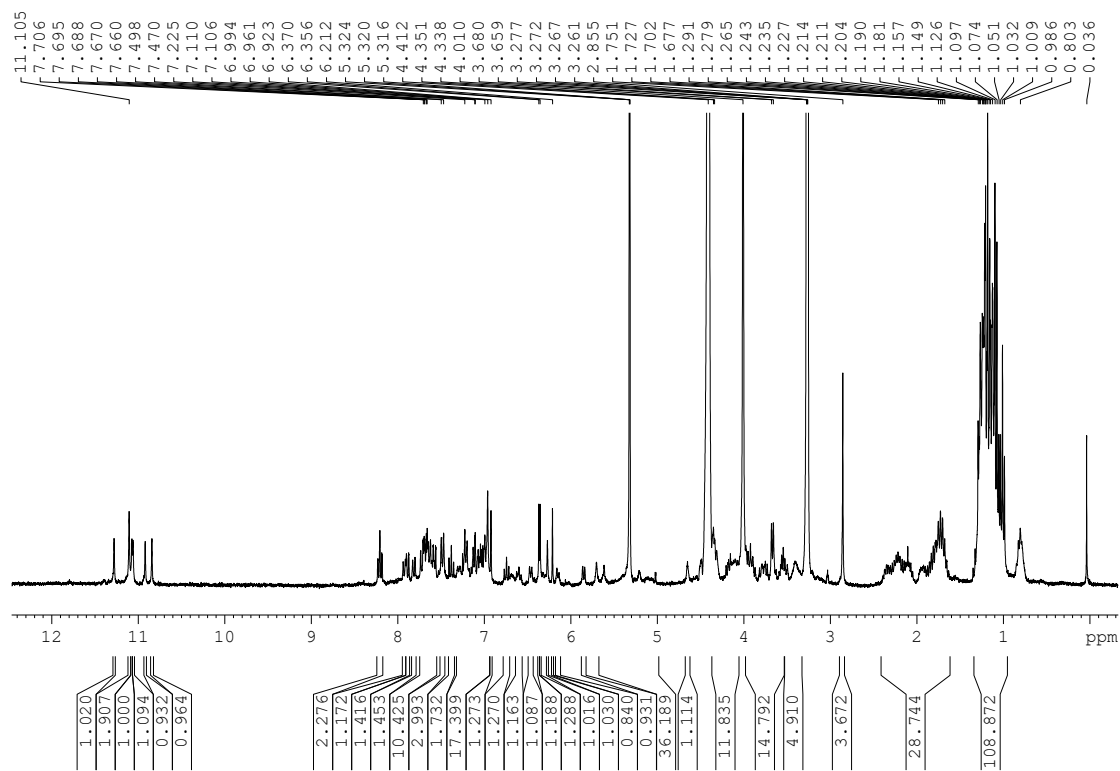


Figure S75: ^1H NMR of **20** in $\text{CD}_2\text{Cl}_2/\text{MeOH-D}_3$ (vol/vol 4/6) (300 MHz).

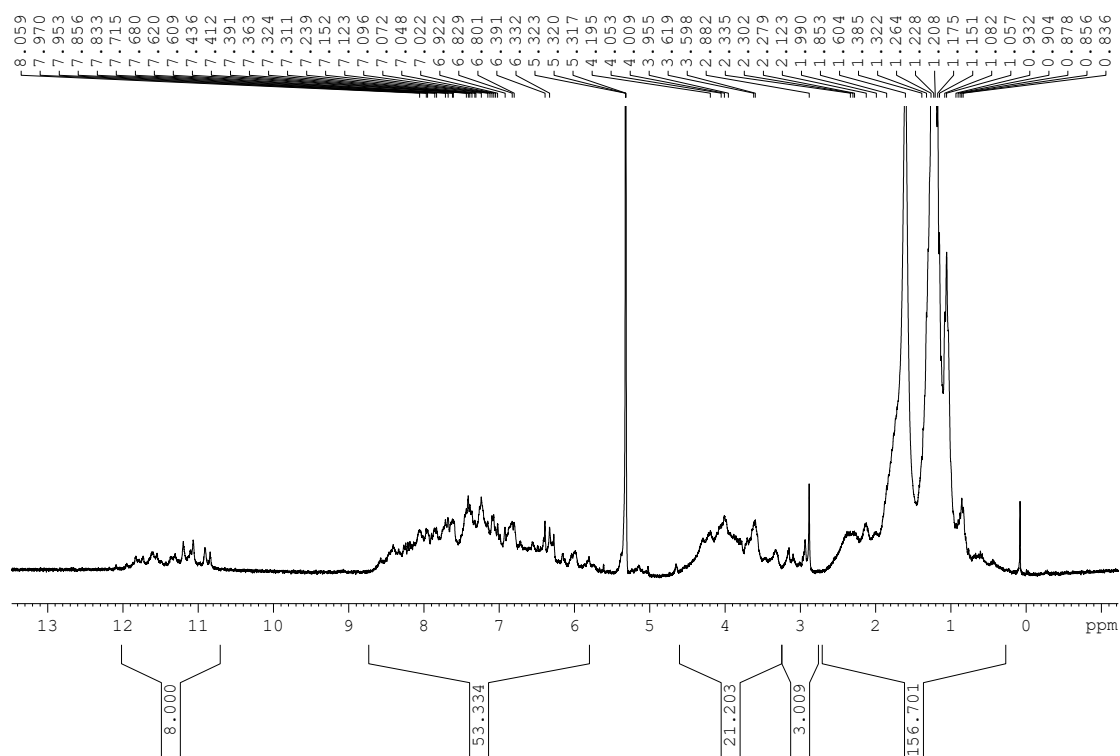


Figure S76: ^1H NMR of **21** in CD_2Cl_2 (300 MHz).

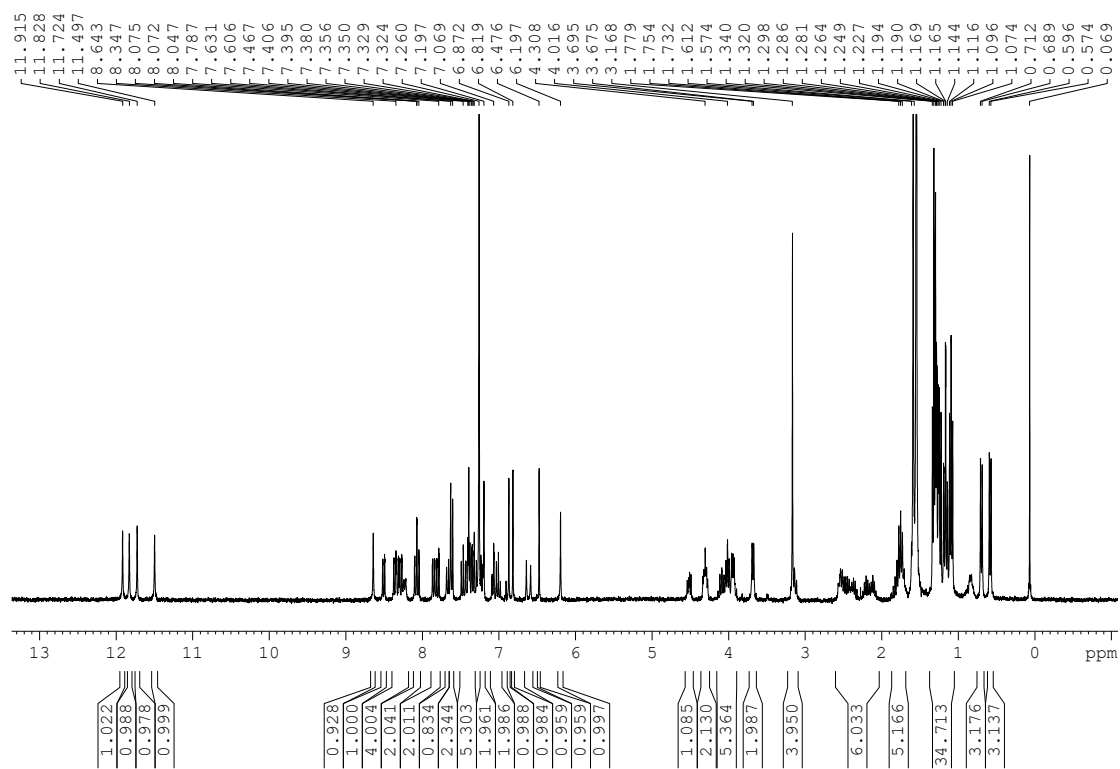


Figure S77: ^1H NMR of **23a** in CDCl_3 (300 MHz).

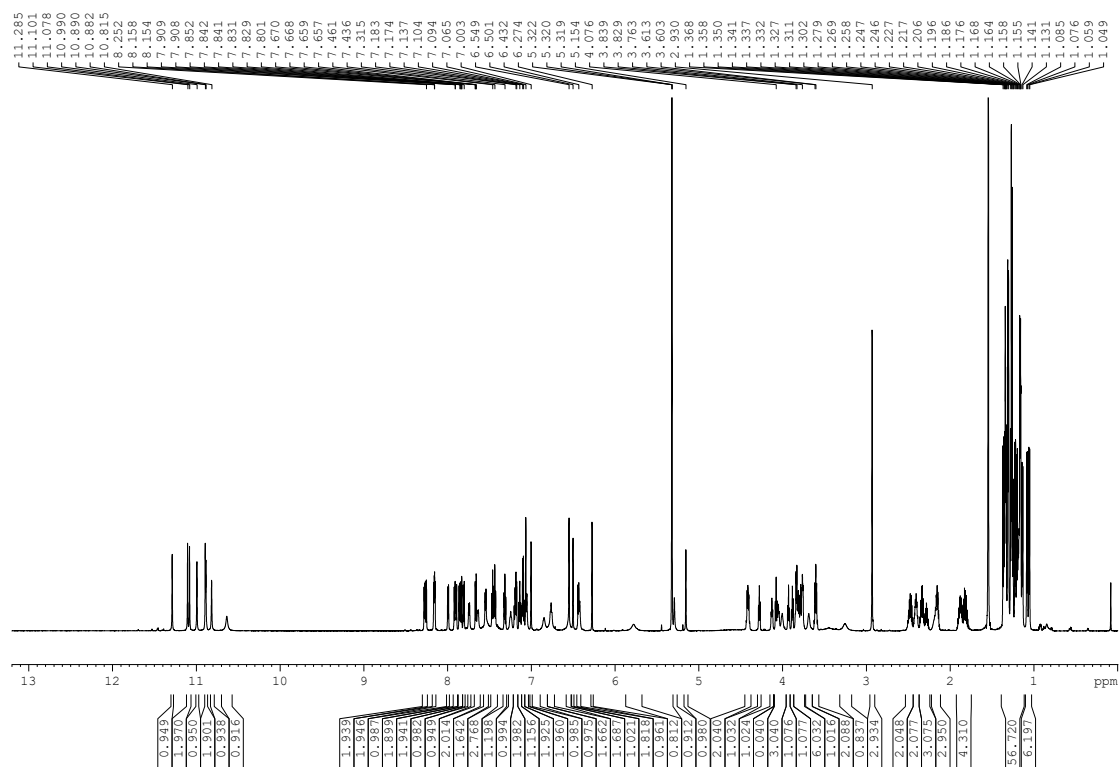


Figure S78: ^1H NMR of **19** in CD_2Cl_2 (700 MHz).

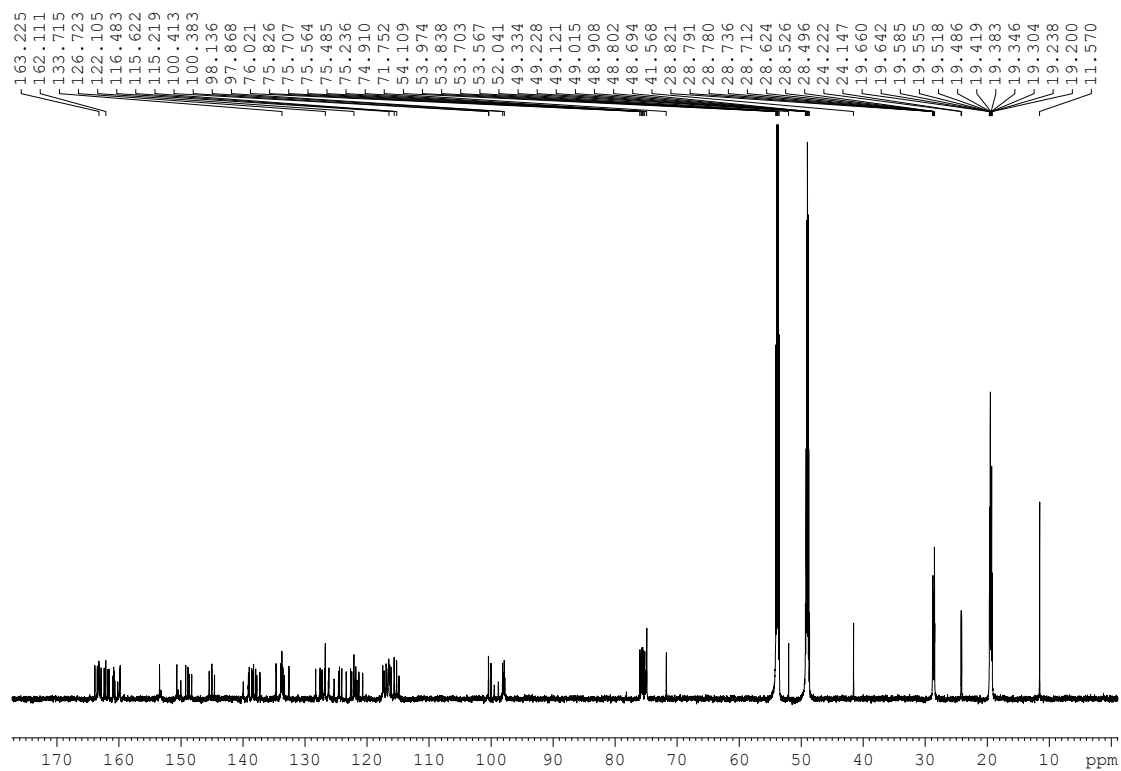


Figure S79: ^{13}C NMR of **19** in CD_2Cl_2 (200 MHz).

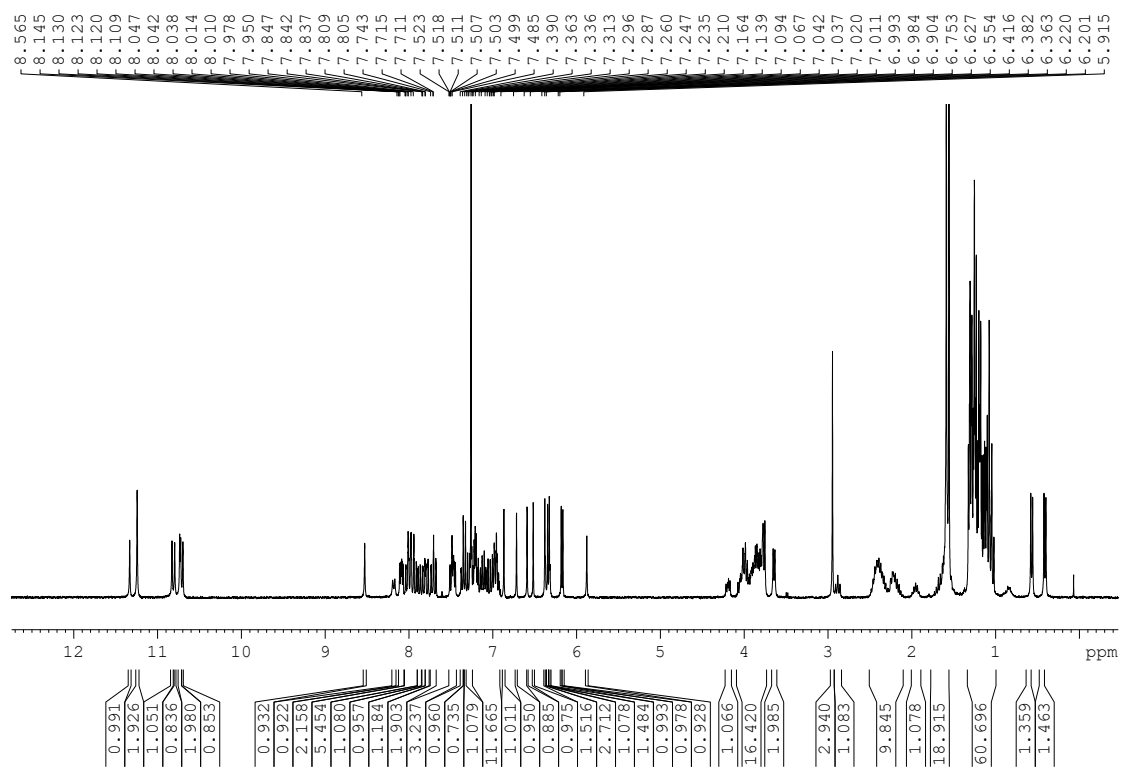


Figure S80: ^1H NMR of **26a** in CDCl_3 (300 MHz).

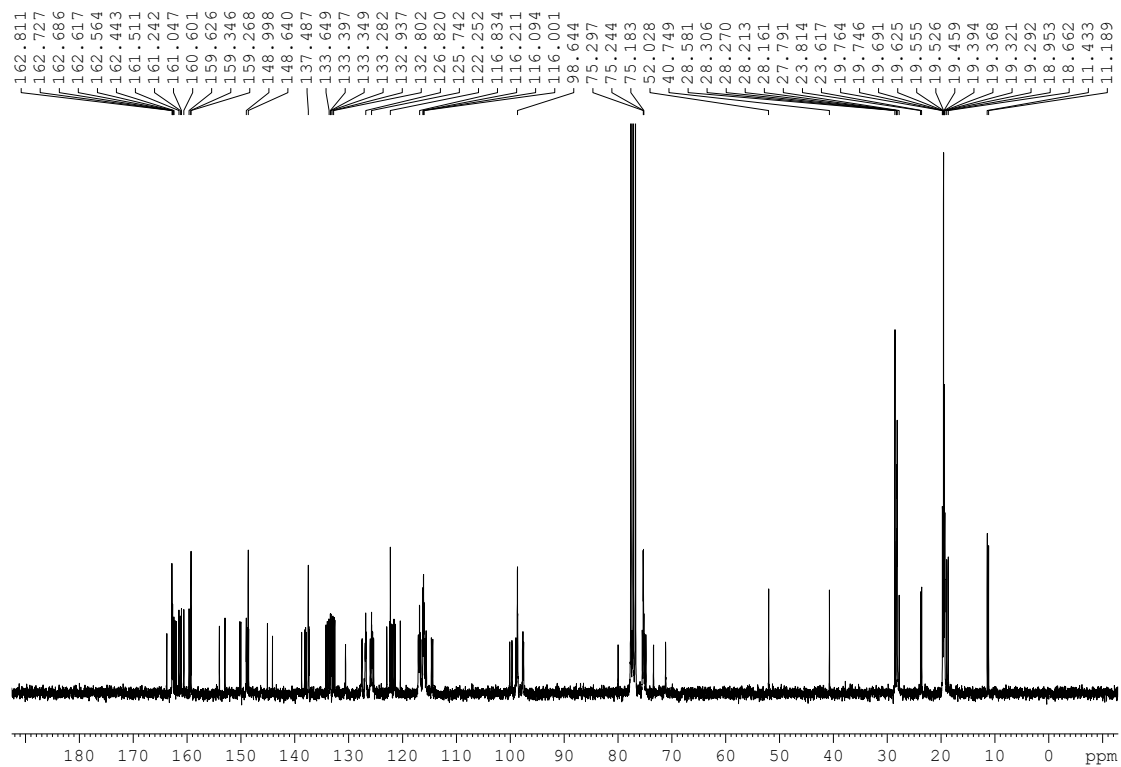


Figure S81: ^{13}C NMR of **26a** in CDCl_3 (75 MHz).

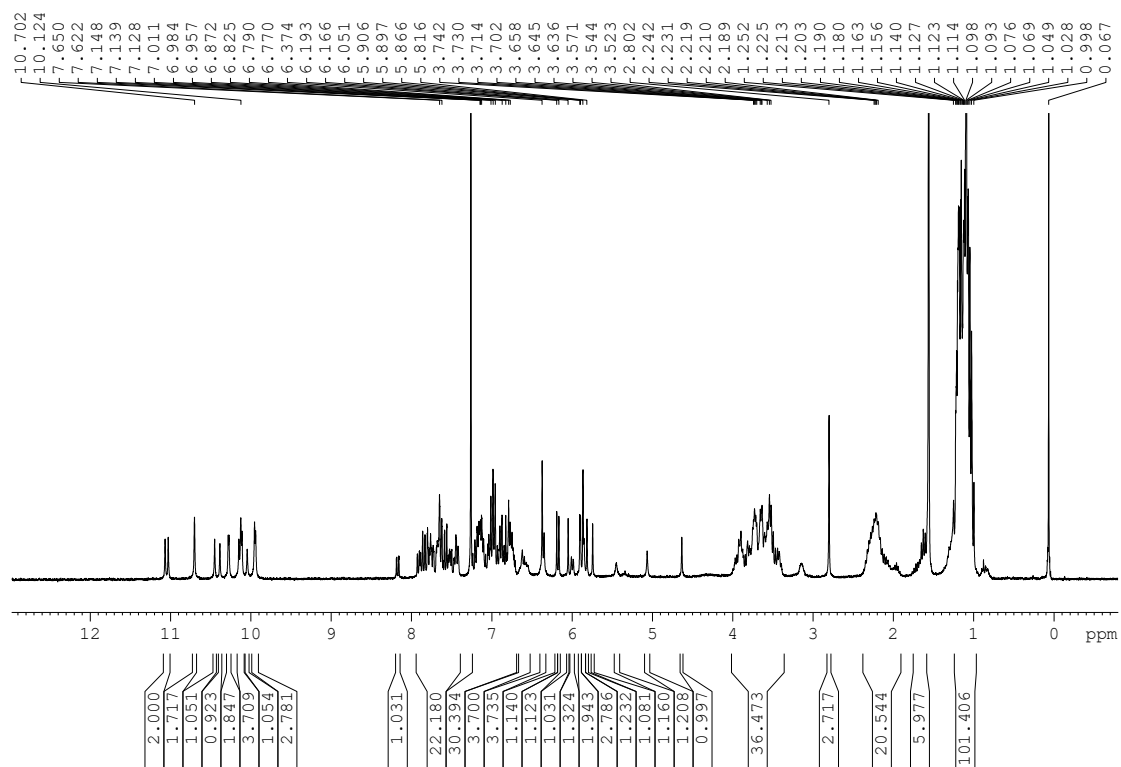


Figure S82: ^1H NMR of **19'** in CDCl_3 (300 MHz).

References:

- (1) T. Qi, T. Deschrijver, I. Huc, *Nat. Protocols* **2013**, 8, 693-708.
- (2) T. Yan, F. Li, J. Tian, L. Wang, Q. Luo, C. Hou, Z. Dong, J. Xu, J. Liu, *ACS Appl. Mater. Interfaces* **2019**, 11, 30566-30574.
- (3) CrystalClear-SM Expert 2.1 (Rigaku 2013) Software, Version 5.6.2.0, Tokyo, Japan.
- (4) G. M. Sheldrick, *Acta Cryst.* **2015**, A71, 3-8.
- (5) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, 42, 339-341.
- (6) G. M. Sheldrick, *Acta Cryst.* **2015**, C71, 3-8.
- (7) A. L. Spek, *Acta. Cryst.* **2015**, C71, 9-18.
- (8) K. Srinivas, B. Kauffmann, C. Dolain, J.-M. Léger, L. Ghosez and I. Huc, *J. Am. Chem. Soc.* **2008**, 130, 13210-13211.