Electronic Supporting Information

Building liquid crystals from the 5-fold symmetrical pillar[5]arene core

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General. All reagents were used as purchased from commercial sources without further purification. Compounds **1**[1] and **8**[2] were prepared according to previously reported procedures. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference. IR spectra were recorded on a Perkin Elmer *Spectrum One*. Elemental analyses were performed by the analytical service of the ETH Zürich (Switzerland). MALDI-TOF and ESI mass spectra were recorded by the analytical service of the School of Chemistry (Strasbourg, France).

Liquid-crystalline properties. Transition temperatures (peak transitions) and enthalpies were determined with a differential scanning Mettler Toledo DSC 1 STAR^e calorimeter, under N_2, at a rate of 10 °C/min. The instrument was calibrated against indium. Optical studies were conducted using a Zeiss-Axioscope polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage.

Abbreviations: 4-(dimethylamino)pyridinium *p*-toluenesulfonate = DPTS; *N,N'*-dicyclohexylcarbodiimide = DCC.

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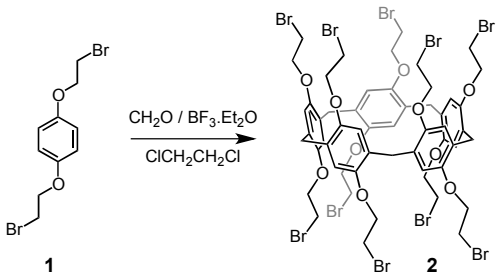
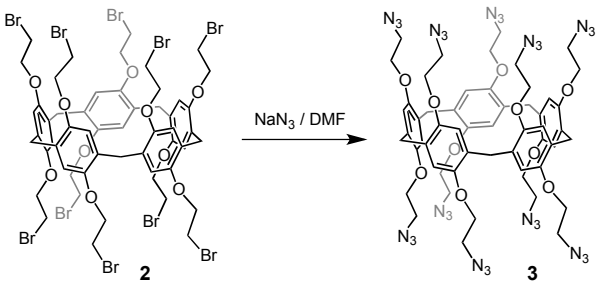
[1] Y. Ma, X. Ji, F. Xiang, X. Chi, C. Han, J. He, Z. Abliz, W. Chen and F. Huang, *Chem. Commun*., 2011, **47**, 12340.
[2] B. Dardel, D. Guillon, B. Heinrich and R. Deschenaux, *J. Mater. Chem*.,2001, **11**, 2814.

Compound 2.



$BF_3{\cdot}Et_2O$ (1.63 g, 11.5 mmol) was added to a stirred solution of **1** (3.73 g, 11.5 mmol) and paraformaldehyde (1.04 g, 34.5 mmol) in 1,2-dichloroethane (200 mL) at room temperature. After 3 h, the reaction mixture was concentrated. Column chromatography (SiO_2, cyclohexane/CH_2Cl_2 1:1) gave **2** (1.54 g, 40%). The analytical data were identical to those reported in the literature for compound **2**.[1]

Compound 3.

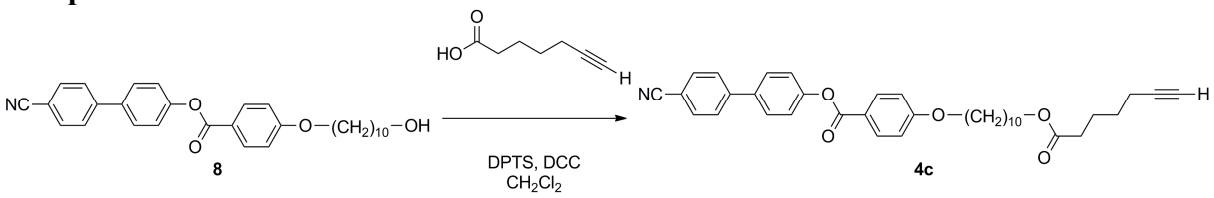


A mixture of **2** (370 mg, 0.22 mmol) and NaN_3 (172 mg, 2.64 mmol) in DMF (10 mL) was stirred for 24 h at room temperature under Ar, then H_2O (45 mL) was added. The aqueous layer was extracted with Et_2O (3 x). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave **3**[3] (278 mg, 97%) as a colourless solid that was used as received in the next step. *Caution: owing to its high number of azide residues, this compound must be handled with special care. Upon evaporation, compound **3** has never been dried under high vacuum and the use of*

[3] Compound **3** was prepared by following another synthetic route, see : X.-B. Hu, L. Chen, W. Si, Y. Yu and J.-L. Hou, *Chem. Commun*., 2011, **47**, 4694.

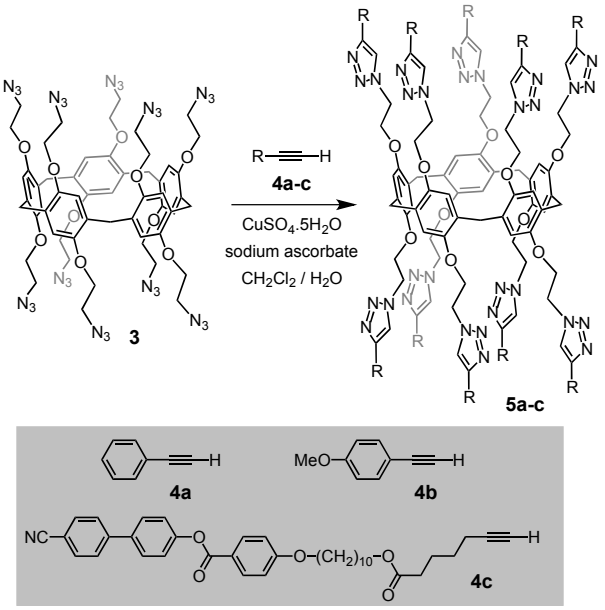
metallic spatula avoided. Furthermore, this compound has been always prepared on a small scale. IR (neat): 2089 (N_3); ^{1}H NMR (CD_2Cl_2, 300 MHz): 6.94 (s, 10 H), 4.11 (t, J = 6 Hz, 20 H), 3.82 (s, 10 H), 3.67 (t, J = 6 Hz, 20 H).

Compound 4c



To a mixture of **8** (2.00 g, 4.24 mmol), heptynoic acid (640 mg, 5.09 mmol) and DPTS (1.25 g, 4.24 mmol) in dry CH_2Cl_2 (100 mL) cooled to 0°C, was added DCC (1.31 g, 6.36 mmol). The mixture was stirred (under argon) at room temperature for 24 h, and then concentrated under vacuum. Column chromatography (SiO_2, CH_2Cl_2) followed by precipitation (the sample was dissolved in CH_2Cl_2 and the solution added dropwise to cooled MeOH) gave pure **4c** (2.23 g, 91%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.20 (d, J = 9 Hz, 2 H), 7.76 (AA'XX', J_{AX} = 9 Hz, 4 H), 7.68 (d, J = 9 Hz, 2 H), 7.38 (d, J = 9 Hz, 2 H), 7.03 (d, J = 9 Hz, 2 H), 4.11 (t, J = 7 Hz, 2 H), 4.10 (t, J = 6 Hz, 2 H), 2.38 (t, J = 7 Hz, 2 H), 2.26 (td, J = 7 Hz, J = 3 Hz, 2 H), 2.00 (t, J = 3 Hz, 1 H), 1.84 (m, 4 H), 1.61 (m, 4 H), 1.53 (m, 2 H), 1.37 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz): 173.55, 164.88, 163.73, 151.62, 144.92, 136.75, 132.69, 132.39, 128.39, 127.73, 122.61, 118.93, 114.40, 111.03 , 84.00, 68.60, 68.38, 64.54, 33.84, 29.49, 29.47, 29.36, 29.25, 29.12, 28.66, 27.90, 26.01, 25.94, 24.08, 18.18; ESI-MS: 602.70 ($[M+Na]^+$, calcd for $C_{37}H_{41}NO_5$: 579.2985); Anal. Calcd. for $C_{37}H_{41}NO_5$ (579.30): C, 76.66; H, 7.13; N, 2.42. Found: C, 76.42; H, 7.17; N, 2.39.

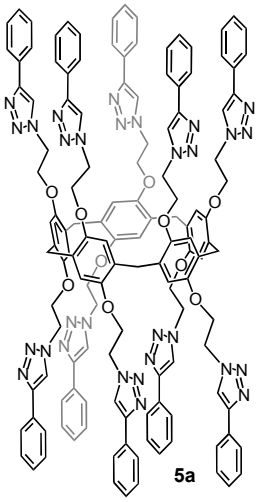
General Procedure for the click reactions.



$CuSO_4 \cdot 5H_2O$ (0.1 equiv.) and sodium ascorbate (0.3 equiv.) were added to a mixture of **3** (1 equiv.) and the appropriate terminal alkyne (11 equiv.) in CH_2Cl_2/H_2O (1:1). The resulting mixture was vigorously stirred at room temperature under Ar. After 24 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated.[4] The product was then purified as outlined in the following text.

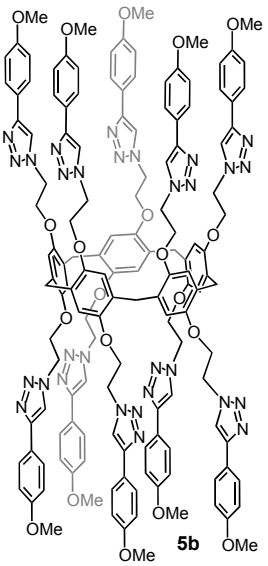
[4] The copper catalyst is easily eliminated when the product of the reaction is soluble in organic solvents as in the case of **5a-c**. The copper salts are water-soluble and most of them remain in the aqueous layer. Residual traces if any are then eliminated during the column chromatography on SiO_2. In addition, no traces of residual copper could be evidenced by mass spectrometry (when traces of copper are present, a clear peak corresponding to $[M + Cu]^+$ is observed in the mass spectrum, see: S. Cecioni, V. Oerthel, J. Iehl, M. Holler, D. Goyard, J.-P. Praly, A. Imberty, J.-F. Nierengarten and S. Vidal, *Chem. Eur. J.* 2011, **17**, 3252-3261).

Compound 5a.

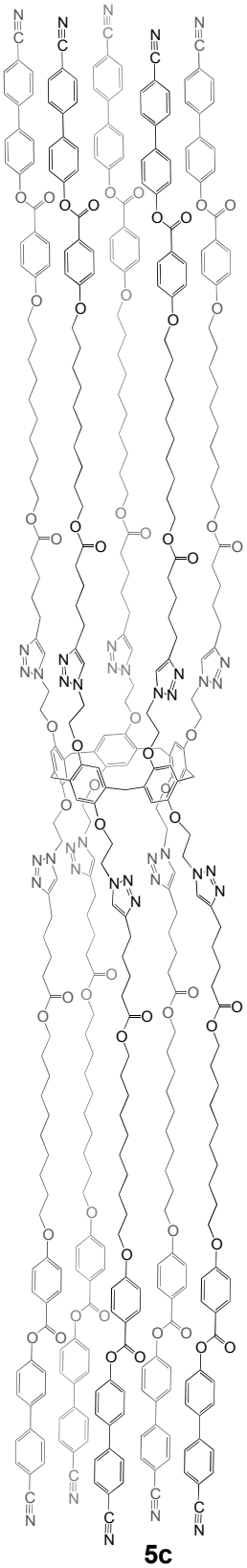


This compound was prepared from **3** (166 mg, 0.13 mmol), **4a** (146 mg, 1.43 mmol), $CuSO_4 \cdot 5H_2O$ (3.3 mg, 0.013 mmol) and sodium ascorbate (7.9 mg, 0.04 mmol) in CH_2Cl_2/H_2O (1:1, 6 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) gave **5a** (180 mg, 60%) as a colourless glassy product. ^1H NMR (CD_2Cl_2, 300 MHz): 7.92 (s, 10 H), 7.79 (m, 20 H), 7.38 (m, 20 H), 7.30 (m, 10 H), 6.55 (s, 10 H), 4.72 (m, 10 H), 4.57 (m, 10 H), 4.19 (m, 10 H), 4.05 (m, 10 H), 3.33 (s, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz,): 149.6, 147.8, 130.6, 129.0, 128.6, 128.3, 125.7, 120.3, 115.7, 67.2, 50.3, 29.7; ESI-TOF-MS: 2320.98 (M^+, calcd. for $C_{135}H_{120}N_{30}O_{10}$: 2320.9804).

Compound 5b.



This compound was prepared from **3** (198 mg, 0.152 mmol), **4b** (221 mg, 1.67 mmol), $CuSO_4 \cdot 5H_2O$ (3.8 mg, 0.015 mmol) and sodium ascorbate (9.0 mg, 0.046 mmol) in CH_2Cl_2/H_2O (1:1, 8 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) gave **5b** (350 mg, 88%) as a colourless glassy product. ^1H NMR (CD_2Cl_2, 300 MHz): 7.83 (s, 10 H), 7.72 (d, J = 7 Hz, 20 H), 6.93 (d, J = 7 Hz, 20 H), 6.57 (s, 10 H), 4.72 (m, 10 H), 4.58 (m, 10 H), 4.19 (m, 10 H), 4.04 (m, 10 H), 3.78 (s, 30 H), 3.36 (s, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 159.6, 149.5, 147.6, 128.6, 127.0, 123.3, 119.5, 115.6, 114.4, 67.2, 55.2, 50.3, 29.4; ESI-TOF-MS: 2621.1 (M^+, calcd. for $C_{145}H_{140}N_{30}O_{20}$: 2621.0860).

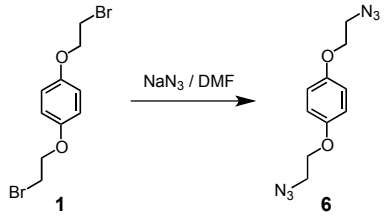


5c

Compound 5c.

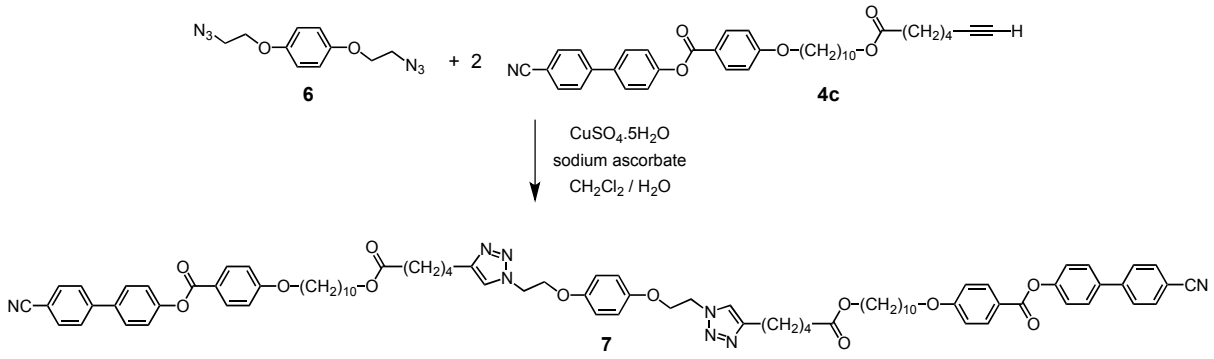
This compound was prepared from **3** (83 mg, 0.064 mmol), **4c** (408 mg, 0.704 mmol), $CuSO_4 \cdot 5H_2O$ (2.0 mg, 0.007 mmol) and sodium ascorbate (4.0 mg, 0.019 mmol) in CH_2Cl_2/H_2O (1:1, 8 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2.5% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **5c** (369 mg, 81%) as a colourless glassy product. IR (neat): 2226 (C≡N), 1727 (C=O); ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.04 (d, J = 7 Hz, 20 H), 7.64 (AA'XX', J_{AX} = 7 Hz, 40 H), 7.57 (d, J = 7 Hz, 20 H), 7.53 (s, 10 H), 7.23 (d, J = 7 Hz, 20 H), 6.89 (d, J = 7 Hz, 20 H), 6.56 (s, 10 H), 4.70 (m, 20 H), 4.20 (m, 10 H), 4.10 (m, 10 H), 3.94 (t, J = 6 Hz, 20 H), 3.91 (t, J = 6 Hz, 20 H), 3.21 (s, 10 H), 2.61 (m, 20 H), 2.19 (m, 20 H), 1.70 (m, 20 H), 1.56 (m, 60 H), 1.37 (m, 20 H), 1.22 (m, 100 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 173.5, 164.8, 163.7, 151.6, 149.4, 148.0, 144.8, 136.7, 132.6, 132.3, 131.5, 128.3, 127.7, 122.5, 121.3, 121.2, 118.8, 114.4, 111.0, 68.3, 67.1, 64.5, 50.1, 33.9, 29.7, 29.5, 29.4, 29.2, 29.1, 28.9, 28.6, 26.0, 25.9, 25.3, 24.5; MALDI-TOF-MS: 2388.8 ($[M+3Na]^{3+}$, m/z calcd. for $C_{425}H_{470}N_{40}O_{60}Na_3$: 2389.1667); Anal. Calcd. for $C_{425}H_{470}N_{40}O_{60}$ (7098.62): C, 71.91; H, 6.67; N, 7.89. Found: C, 71.66; H, 6.84; N, 7.62.

Compound 6.



A mixture of **1** (389 mg, 1.2 mmol) and NaN_3 (195 mg, 3.0 mmol) in DMF (8 mL) was stirred at room temperature for 20 h under Ar, then H_2O (40 mL) was added. The aqueous layer was extracted with Et_2O (3 x) and the combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave **6** (273 mg, 92%) as a colourless oil that was used as received in the next step. *Caution: owing to its high nitrogen content, this compound must be handled with special care. Upon evaporation, compound* ***6*** *has never been dried under high vacuum and the use of metallic spatula avoided. Furthermore, this compound has been always prepared on a small scale.* IR (neat): 2105 (N_3); ^{1}H NMR ($CDCl_3$, 300 MHz): 6.88 (s, 4 H), 4.12 (t, J = 5 Hz, 4 H), 3.58 (t, J = 5 Hz, 4 H).

Compound 7.



A mixture of **6** (72 mg, 0.288 mmol), **4c** (418 mg, 0.720 mmol), $CuSO_4 \cdot 5H_2O$ (7 mg, 0.029 mmol) and sodium ascorbate (17 mg, 0.086 mmol) in CH_2Cl_2/H_2O (1:1, 10 mL) was vigorously stirred at room temperature. After 24 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated. Column chromatography (SiO_2, CH_2Cl_2 containing 1.7% of methanol) gave

7 (370 mg, 91%) as a colourless solid. IR (neat): 2226 (C≡N), 1725 (C=O); ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.07 (d, J = 7 Hz, 4 H), 7.67 (AA'XX', J_{AX} = 7 Hz, 8 H), 7.61 (d, J = 7 Hz, 4 H), 7.42 (s, 2 H), 7.26 (d, J = 7 Hz, 4 H), 6.93 (d, J = 7 Hz, 4 H), 6.73 (s, 4 H), 4.59 (t, J = 6 Hz, 4 H), 4.20 (t, J = 6 Hz, 4 H), 3.98 (t, J = 6 Hz, 4 H), 3.96 (t, J = 6 Hz, 4 H), 2.63 (m, 4 H), 2.25 (m, 4 H), 1.75 (m, 4 H), 1.60 (m, 8 H), 1.53 (m, 4 H), 1.41 (m, 4 H), 1.25 (m, 20 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 173.6, 164.8, 163.7, 152.71, 151.6, 144.8, 136.7, 132.6, 132.3, 128.3, 127.7, 122.6, 121.2, 118.9, 115.8, 114.4, 111.0, 68.4, 67.1, 64.5, 34.0, 29.5 , 29.4, 29.3, 29.2, 29.1, 28.6, 26.0, 25.9, 25.3, 24.5; ESI-TOF-MS: 1407.79 ($[M+H]^+$, calcd. for $C_{84}H_{95}N_8O_{12}$: 1407.7069); Anal. Calcd. for $C_{84}H_{95}N_8O_{12}$ (1407.71): C, 71.67; H, 6.73; N, 7.96. Found: C, 71.39; H, 6.69; N, 7.85.

Fig. S1. IR spectra of compounds **3**, **5a**, **5b** and **5c**. The IR spectra of **5a-c** confirmed that no unreacted azide (2089 cm^{-1}) residues remain in the final products.

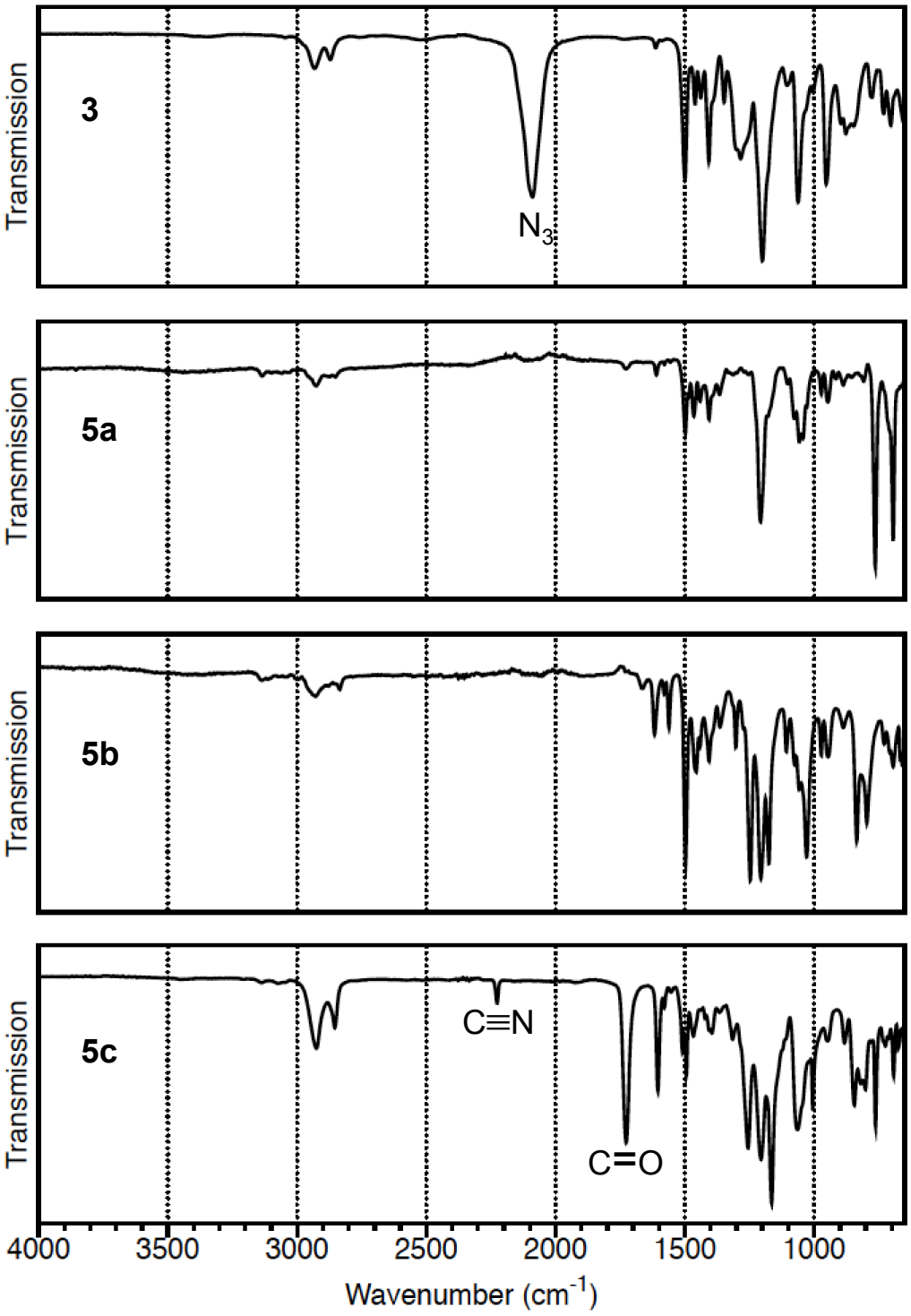


Fig. S2. ^{1}H NMR spectra (300 MHz, CD_2Cl_2) of compounds **3**, **5a** and **5b**.

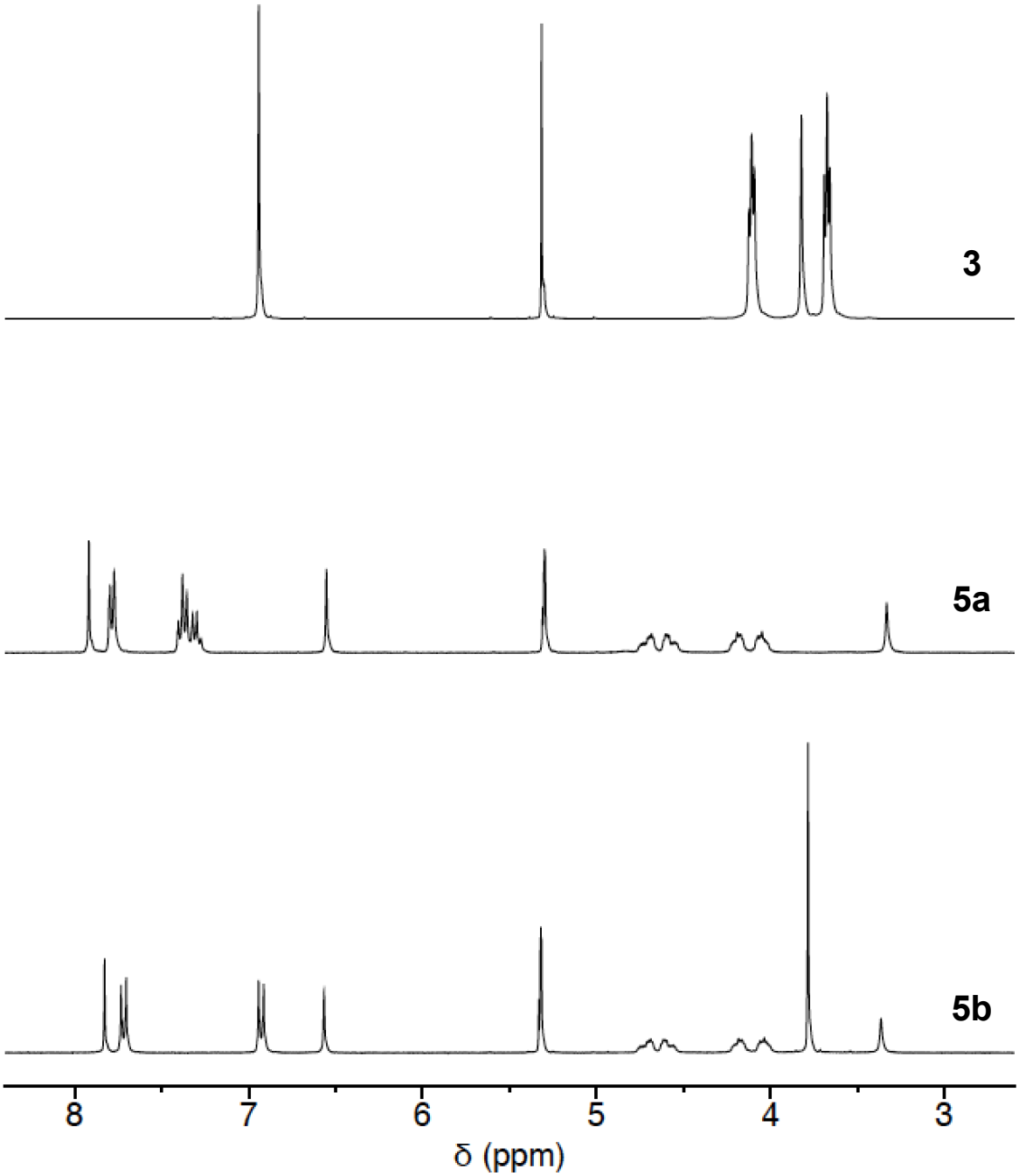
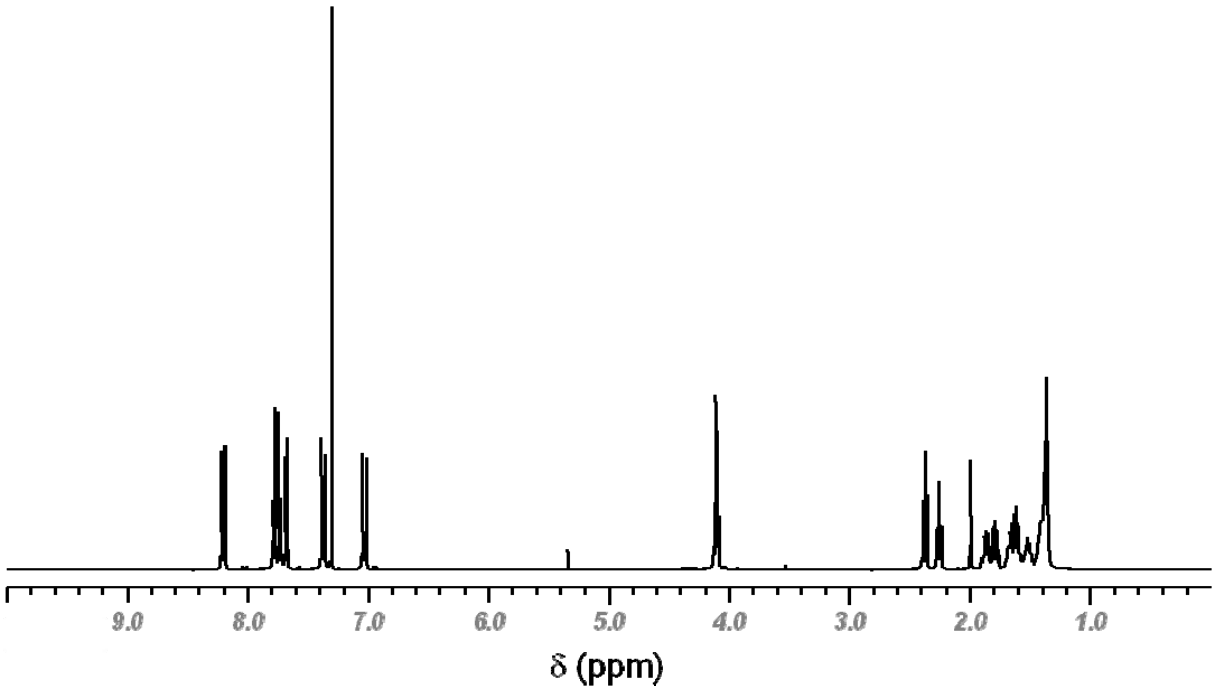


Fig. S3. ^{1}H and ^{13}C NMR spectra (400 MHz (^{1}H) and 100 MHz (^{13}C), $CDCl_3$) of compound **4c**.



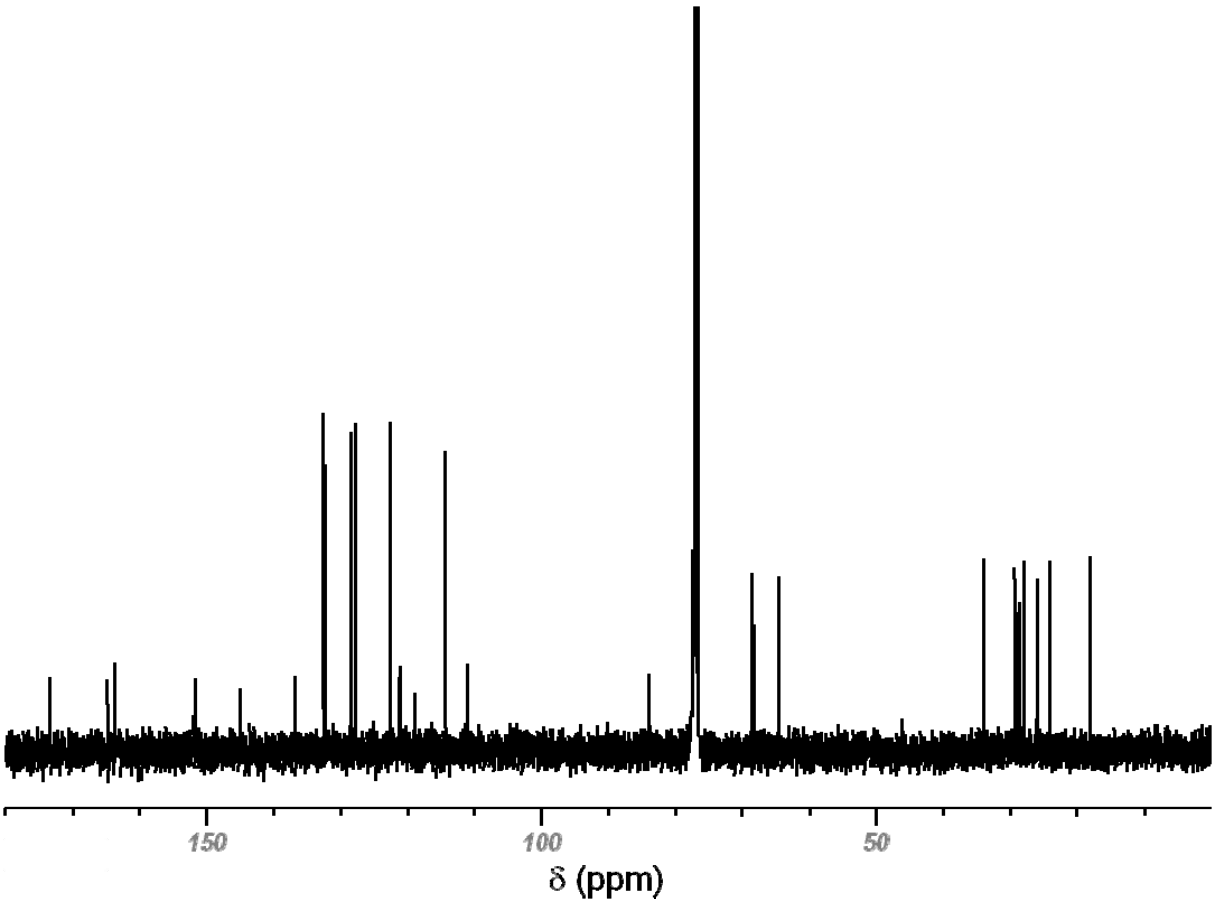


Fig. S4. Differential scanning thermogram of compound **4c** registered during the second heating-cooling cycle.

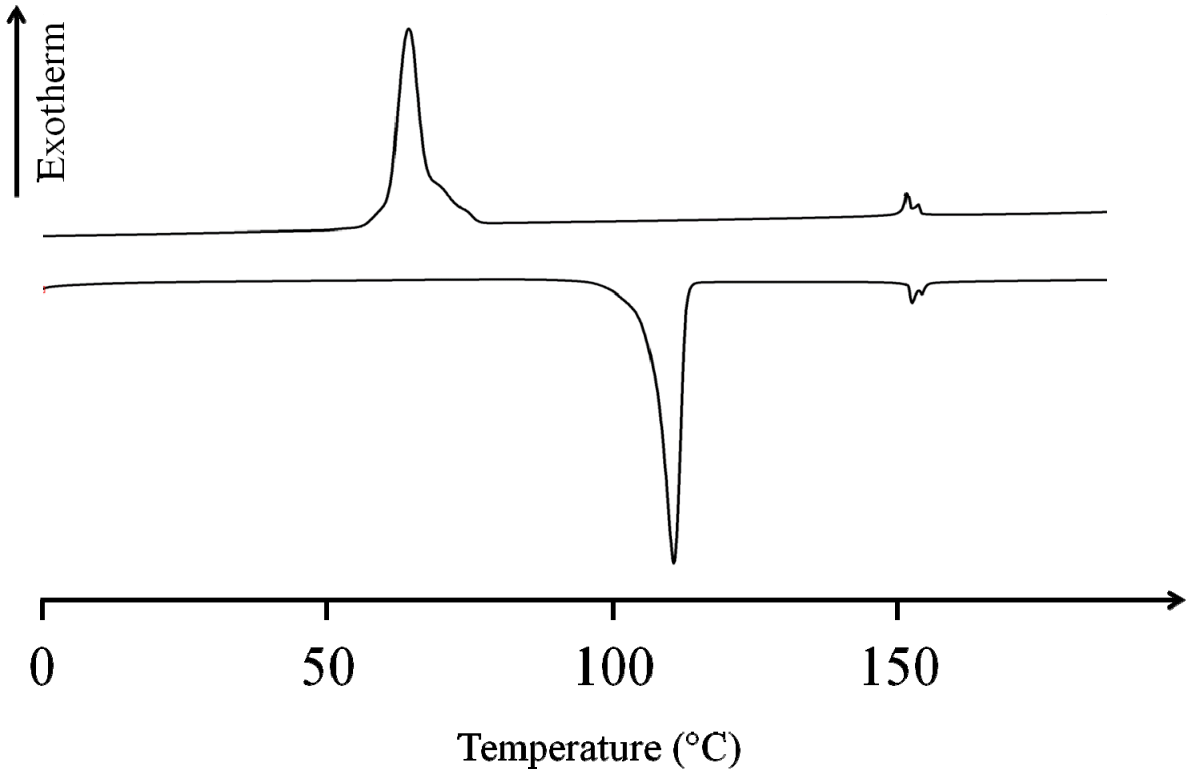


Fig. S5. ^{1}H NMR spectra (300 MHz, CD_2Cl_2) of compounds **5c** and **7**.

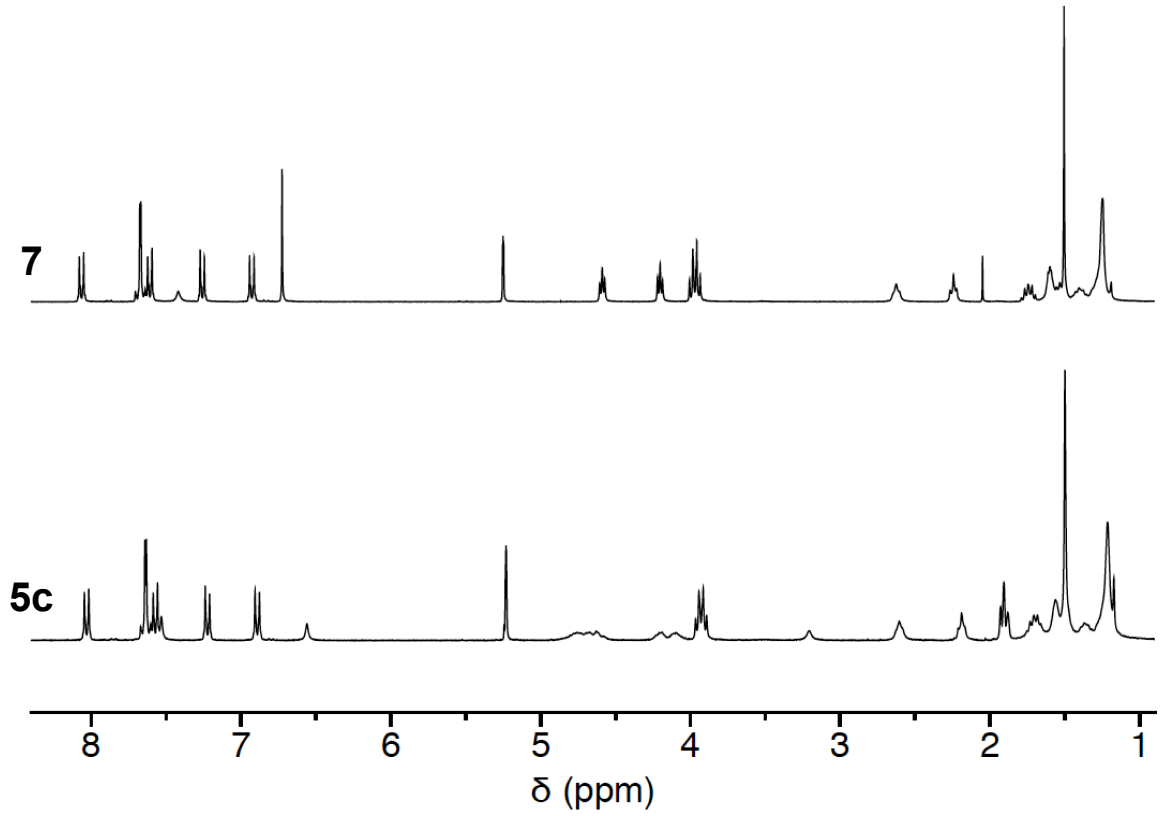


Fig. S6. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compounds **5a** and **5b**.

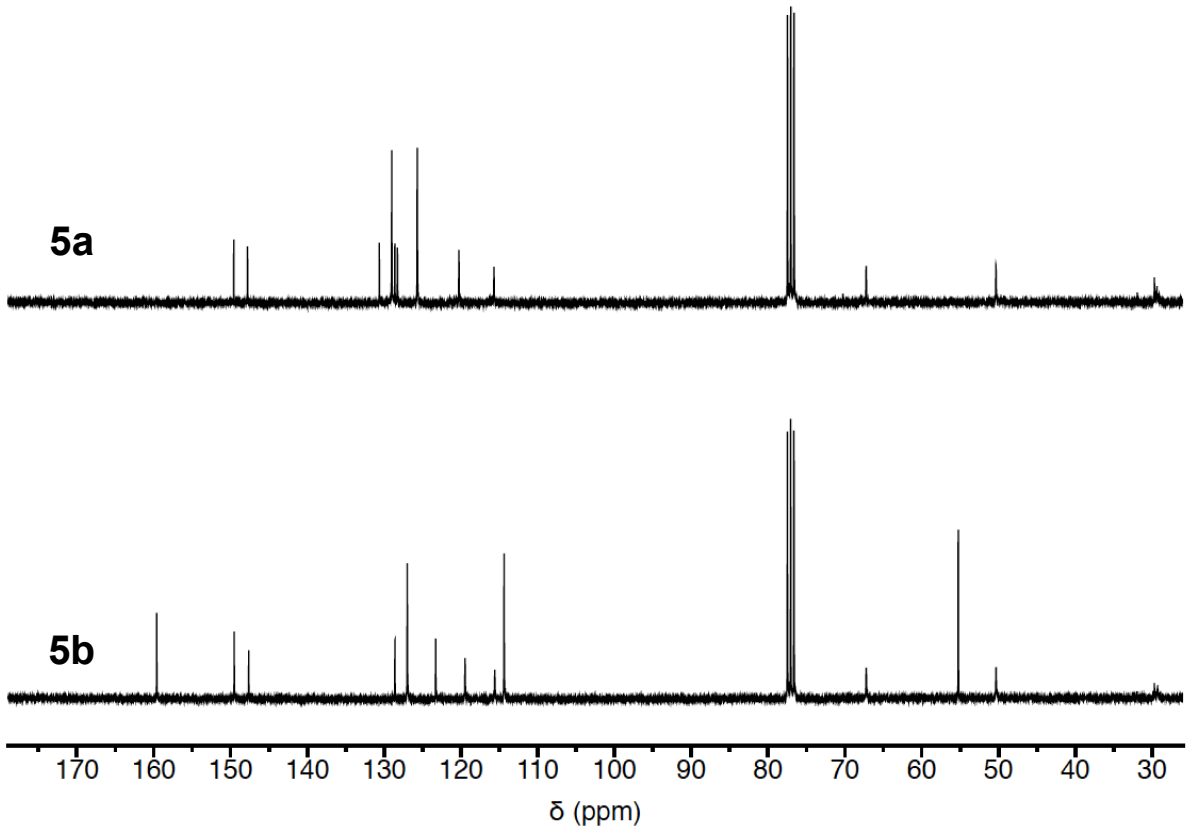


Fig. S7. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of compounds **5c** and **7**.

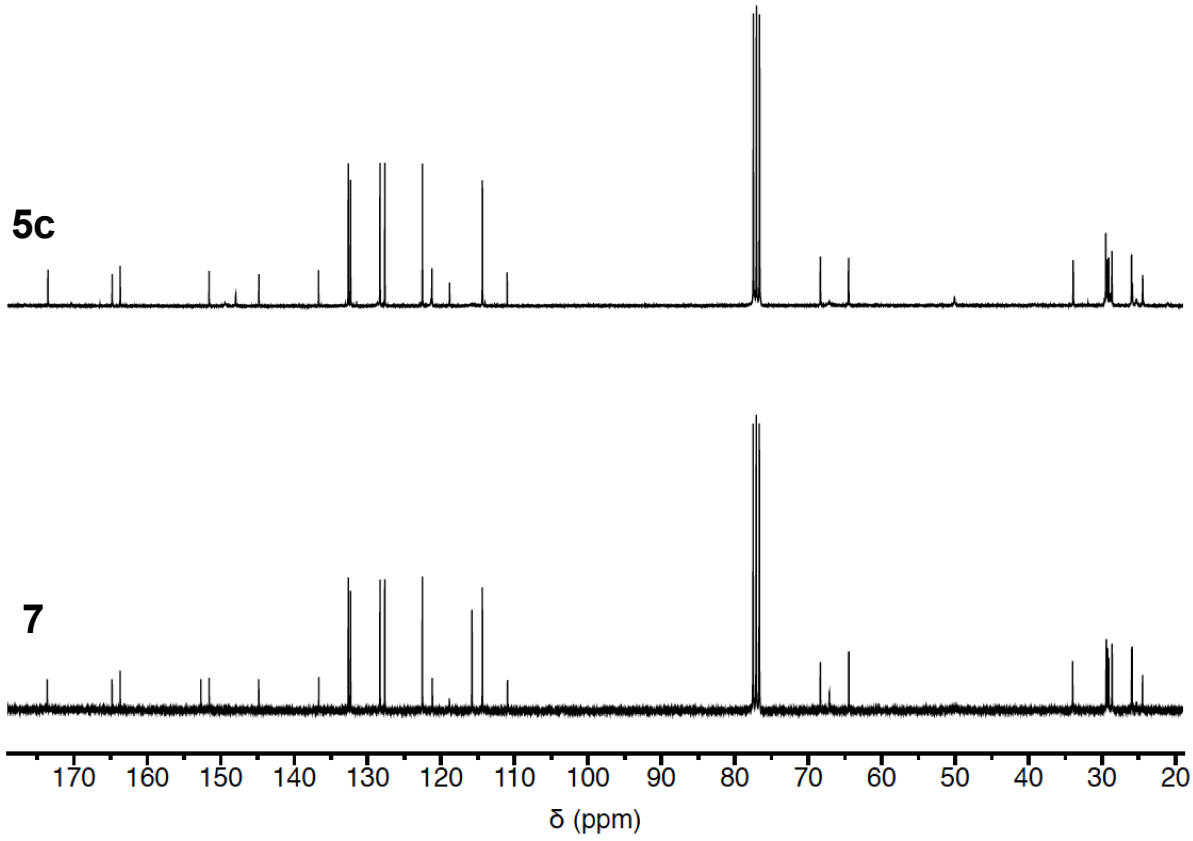


Fig. S8. HPLC traces on a GPC column (PLgel, CH_2Cl_2) obtained for compounds **5a**, **5b**, **5c** and **7**.

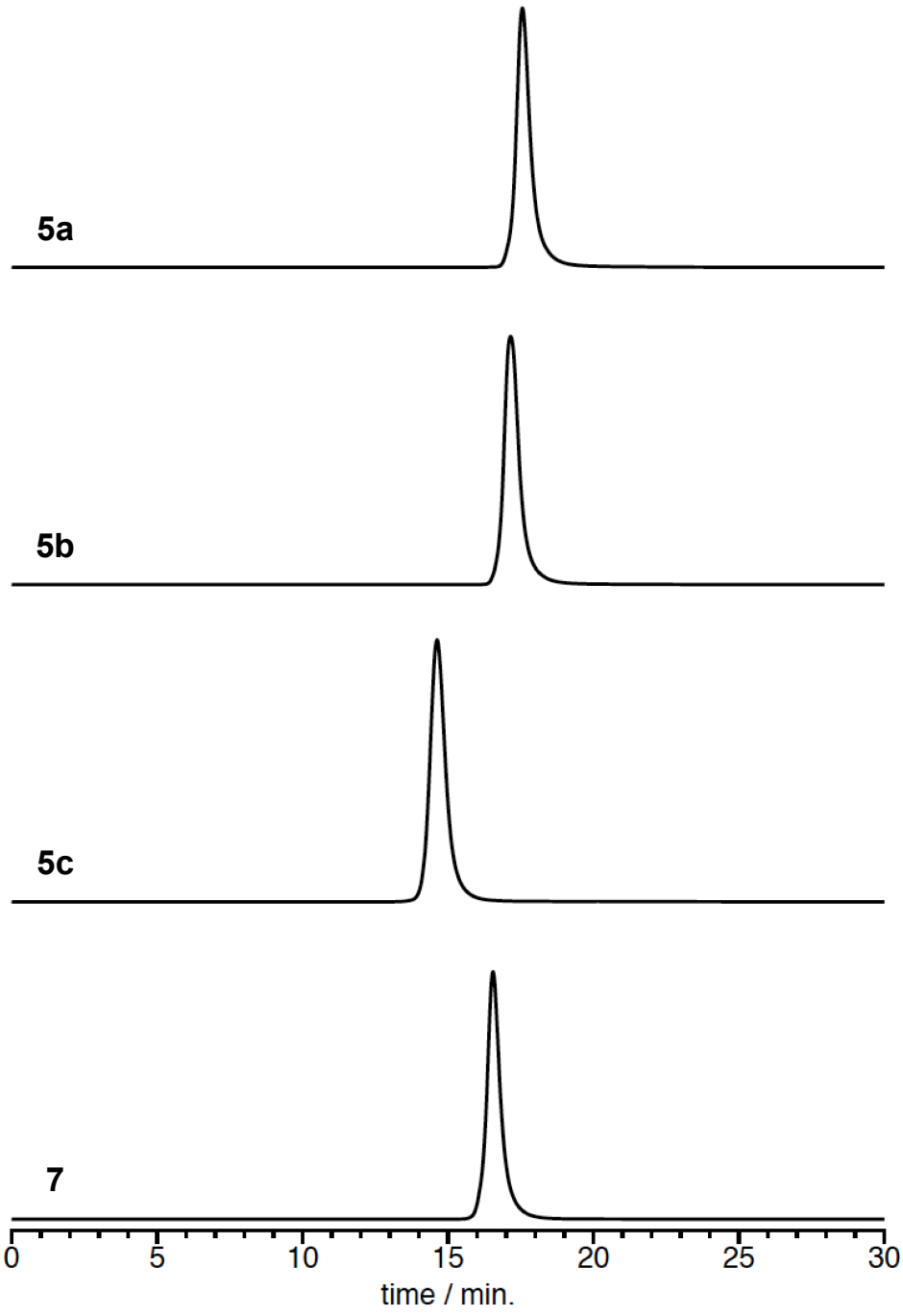


Fig. S9. Maldi-mass spectrum of compound **5c**

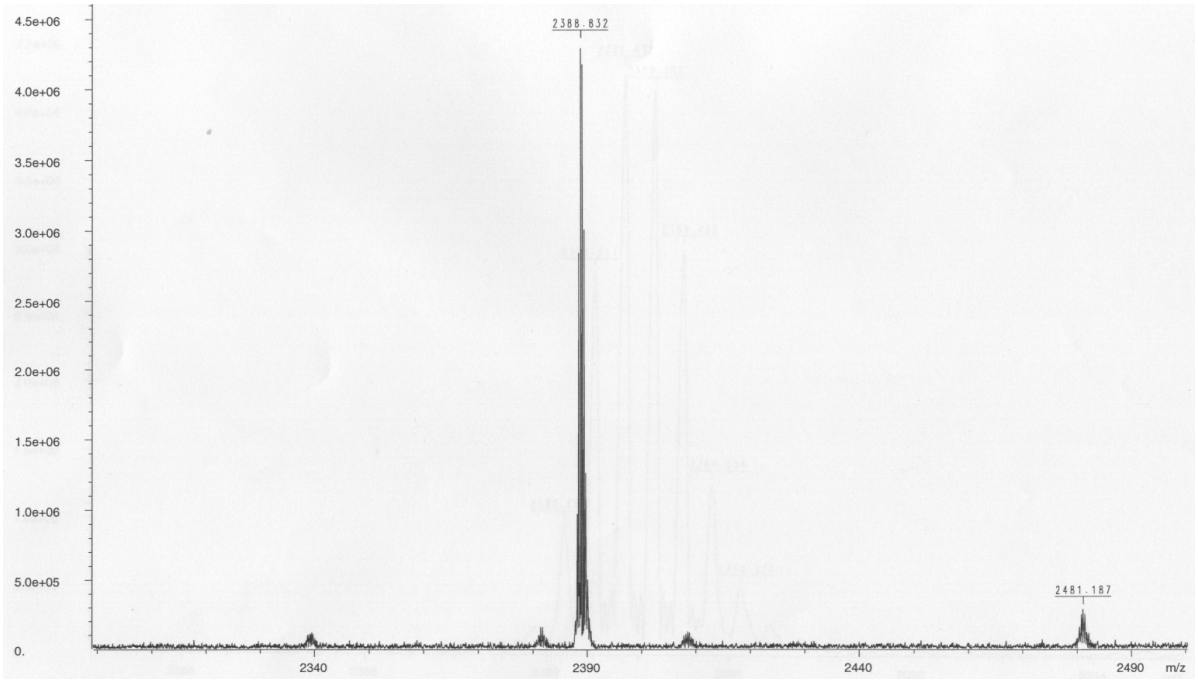


Fig. S10. ESI-mass spectrum of compound **7**

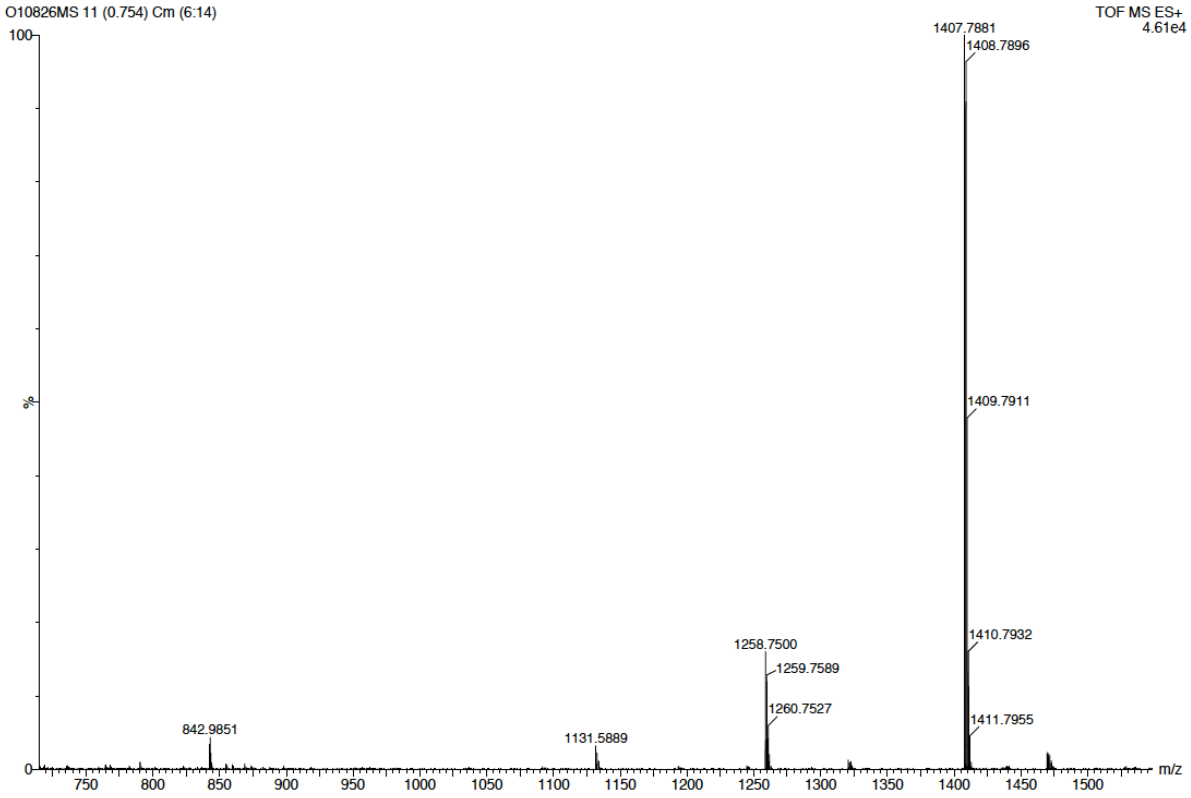


Fig. S11. Calculated structure of compound **5c**. The molecular modeling has been performed with *Spartan'10* Macintosh Parallel Edition (Wavefunction Inc., USA) at the MMFF level.