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Porous molecular networks formed by self-assembly of positively-charged trigonal building blocks at the liquid/solid interfaces

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Contents

1. Details of STM Investigations.

All STM investigations were performed at 22–26 °C using a Nanoscope IIIa or IIId (Digital Instruments Inc.) with an external pulse/function generator (model Agilent 33220A) with negative sample bias. All STM images were acquired in the constant current mode. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.20 or 0.25 mm).

Prior to imaging, a compound under investigation was dissolved in commercially available 1-phenyloctane (PO, TCI) or 1,2,4-trichlorobenzene (TCB, Aldrich) at various solute concentrations, and a drop of a solution of a *tris*-(3,5-didecyl-2-hydroxybenzylidene)triaminoguanidinium salt (6~8 μL) was applied on a freshly cleaved surface of HOPG (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH or Advanced Ceramics Inc., Cleveland, USA). The STM investigations were then performed at the liquid/solid interface. By changing the tunneling parameters during the STM imaging, namely, the voltage applied to the substrate and the average tunneling current, it was possible to switch from the visualization of the adsorbate layer to that of the underlying HOPG substrate. This enabled us to correct for drift effects by the use of SPIP software (Image Metrology A/S).

2. Additional STM Images.

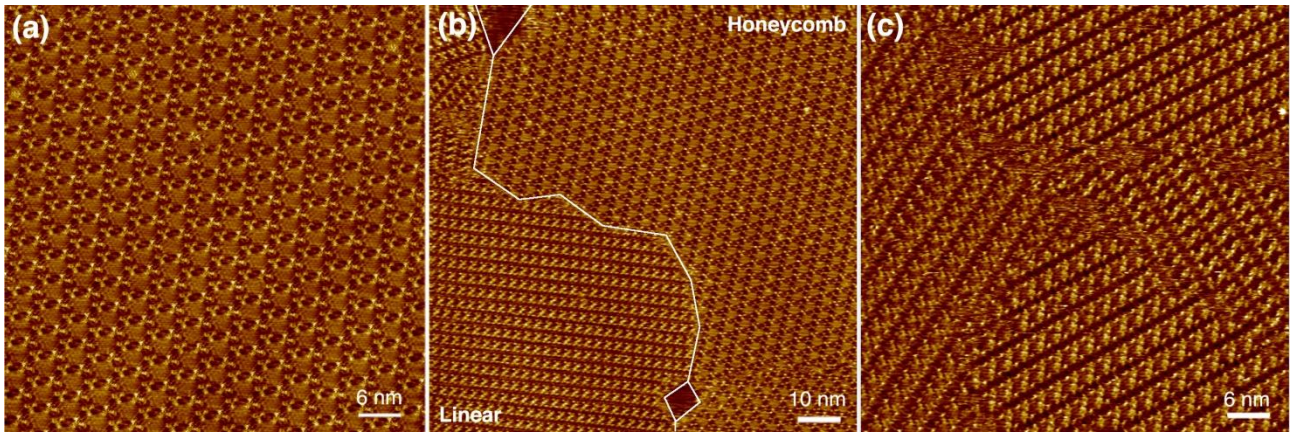


Fig. S1. A set of typical STM images for **1a** observed at the 1-phenyloctane/graphite surface. Images were collected at a concentration of (a) 3.0×10^{-6} M, (b) 1.2×10^{-5} M, and (c) 1.0×10^{-4} M. Tunneling parameters; I_{set} = 0.20 nA and V_{set} = –0.50 V for (a), I_{set} = 0.21 nA and V_{set} = –0.30 V for (b), and I_{set} = 0.30 nA and V_{set} = –0.55 V for (c). The white lines in (b) indicate the domain boundaries between the porous honeycomb and non-porous linear structures.

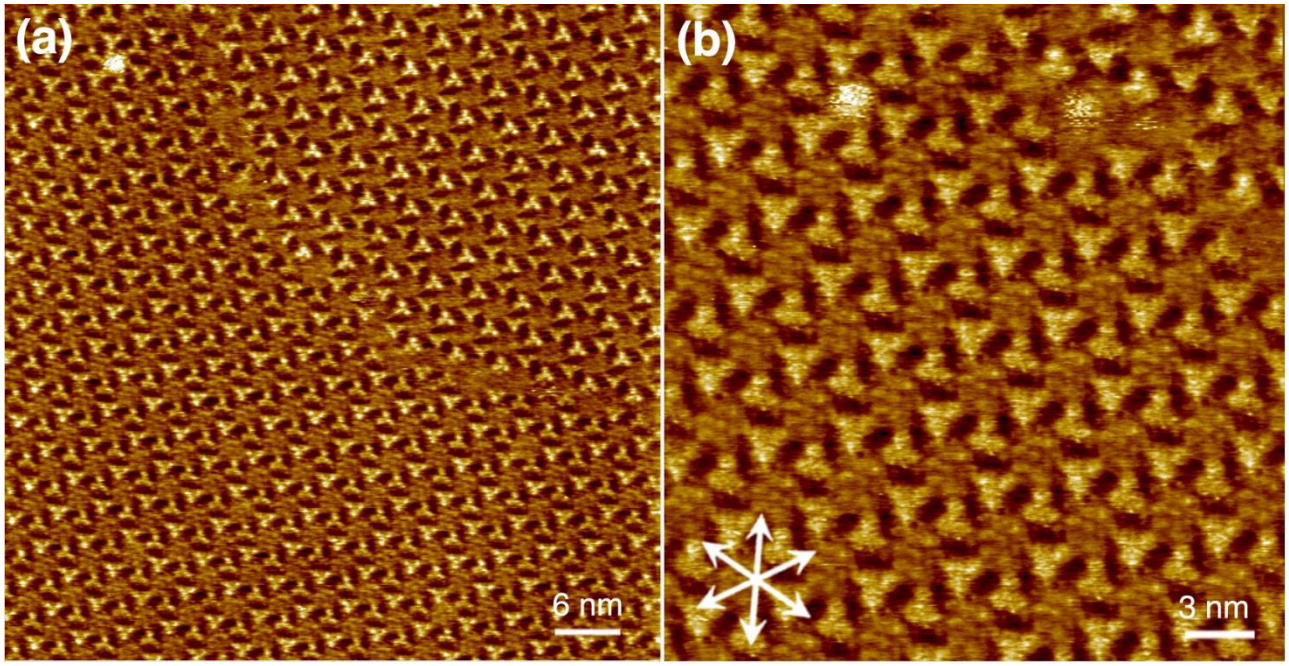


Fig. S2. STM images of monolayers formed by **1a** at the TCB/graphite interface (concentration; 1.0×10^{-4} M, tunneling parameters; I_{set} = 0.20 nA and V_{set} = –0.50 mV for both images).

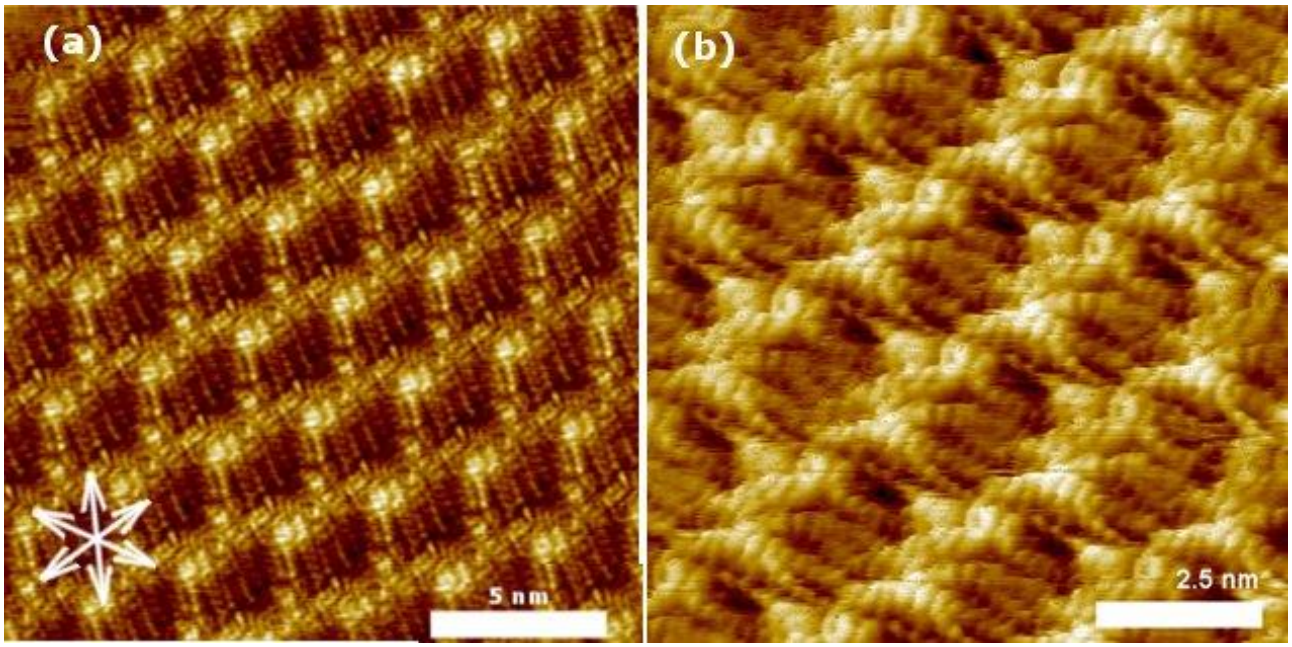


Fig. S3. STM images of monolayers formed by **2** at the 1-phenyloctane/graphite interface (concentration; 1.8×10^{-6} M, tunneling parameters; I_{set} = 0.15 nA and V_{set} = –0.35 V for (a) and I_{set} = 0.20 nA and V_{set} = –0.30 V for (b)). Unit cell parameters: a = 2.8 ± 0.1 nm, b = 3.1 ± 0.1 nm, γ = 120 ± 4°

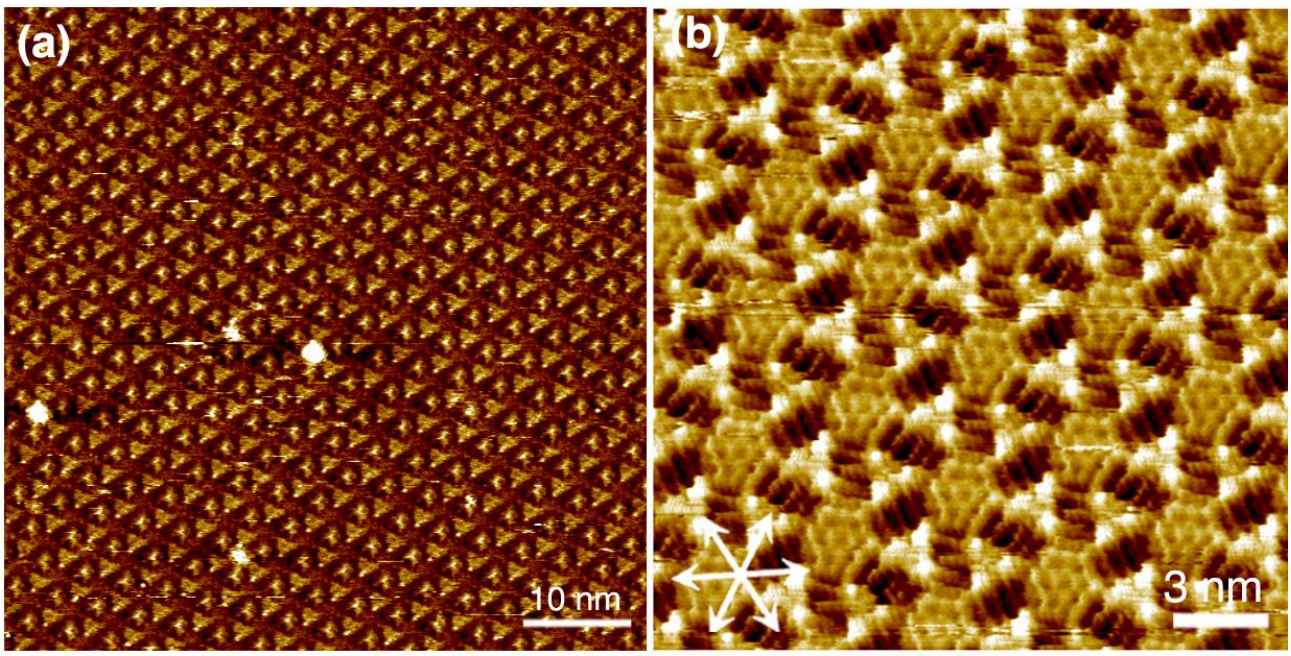


Fig. S4. STM images of monolayers formed by **1b** at the 1-phenyloctane/graphite interface (concentration; 3.2×10^{-6} M, tunneling parameters; I_{set} = 0.10 nA and V_{set} = –0.47 V for (a) and I_{set} = 30 pA and V_{set} = –0.32 V for (b)).

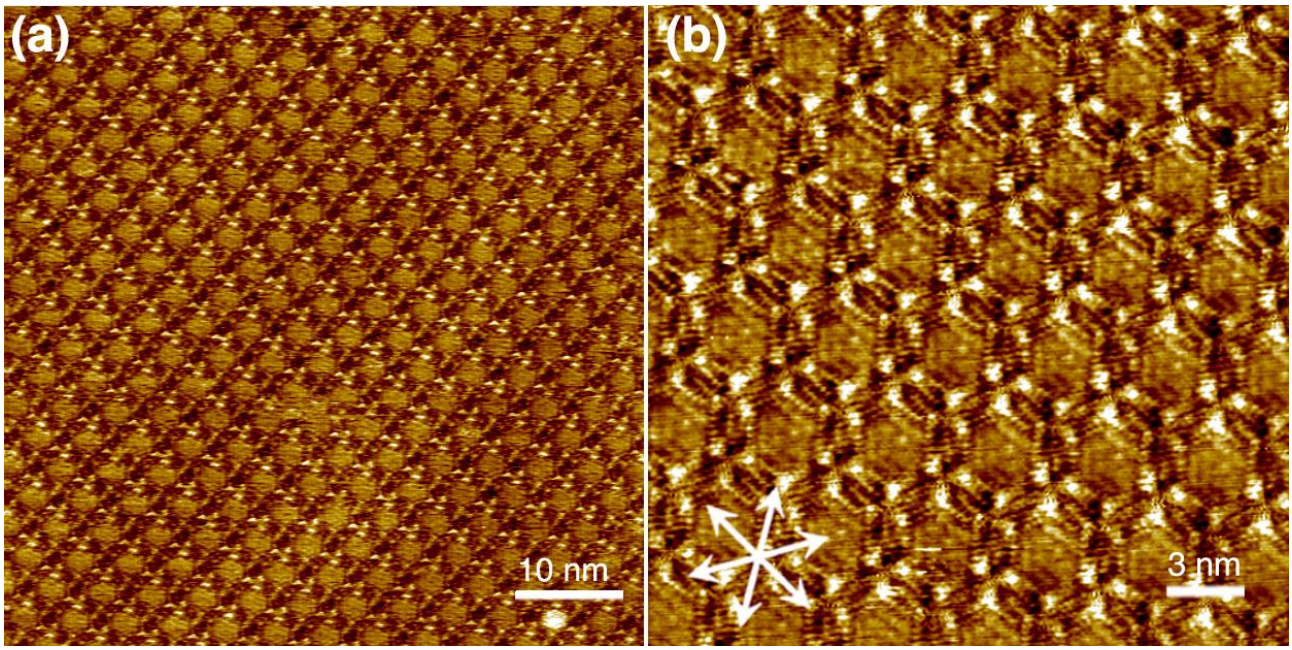


Fig. S5. STM images of monolayers formed by **1c** at the 1-phenyloctane/graphite interface (concentration; 3.0×10^{-6} M, tunneling parameters; I_{set} = 0.23 nA and V_{set} = –0.29 mV for (a) and I_{set} = 0.22 nA and V_{set} = –0.20 V for (b)).

3. Theoretical Simulations of Model Compound.

All theoretical calculations were performed with the Gaussian 09 package. A geometry optimization of cation $\mathbf{1}^+$ was performed by the B3LYP functional with the 6-31g(d) bases set. The geometry of this sss-isomer was fixed to C_{3h}. Representative frontier molecular orbitals were calculated using optimized geometry of cation $\mathbf{1}^+$ (Fig. S6).

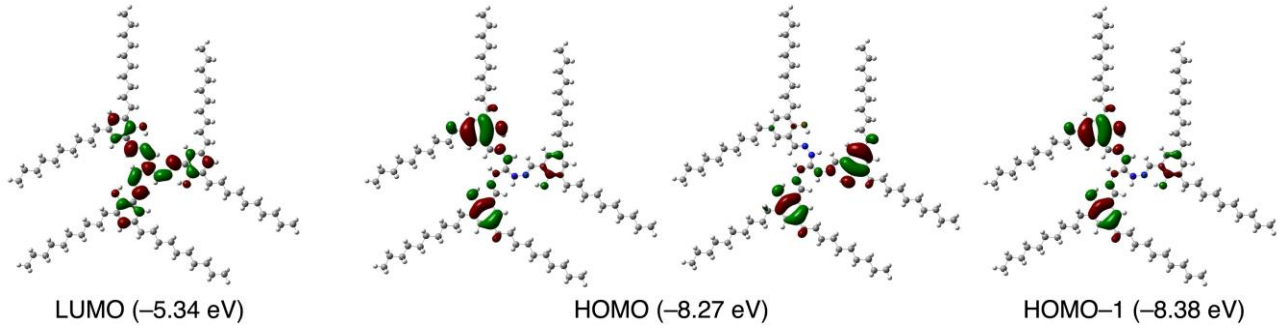


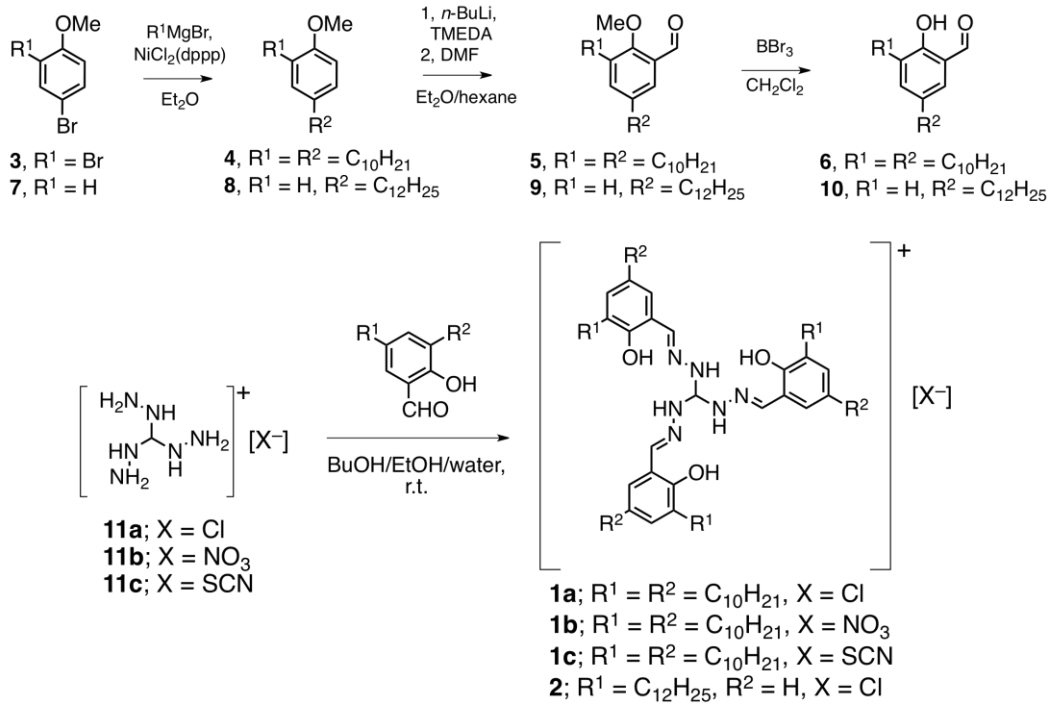
Fig. S6. Representative frontier molecular orbitals for *tris*-(3,5-didecyl-2-hydroxybenzylidene)triaminoguanidinium cation calculated at the B3LYP/6-31g(d) level of theory.

4. Synthesis of Triaminoguandinium Salts.

General. All solvents were distilled or passed through activated alumina and copper catalyst in a Glass Contour solvent purification system prior use. All commercially available reagents were used as received.

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were measured on a Brucker UltraShield Plus 400 spectrometer. Chloroform-*d*, 1,1,2,2-tetrachloroethan-d_2 and tetrahydrofurane-d_8 were used as solvent, the spectra were referenced to residual solvent proton signals in the ^{1}H NMR spectra (7.26, 6.00, and 3.58 ppm) and to the solvent carbons in the ^{13}C NMR spectra (77.0 and 74.0 ppm for chloroform-*d* and 1,1,2,2-tetrachloroethan-d_2), respectively. Preparative HPLC was undertaken with JAI LC-9204 chromatograph using 600 mm × 40 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as the eluent. Other spectra were recorded by the use of the following instruments: IR spectra, JACSCO FT/IR-410, Nicolet Avatar360 ESP; MS spectra, ThermoFisher Scientific LTQ-Orbitrap XL; elemental analysis, HERAEUS CHNO-Rapid.

Scheme S1. Synthesis of *tris*-(3,5-Didecyl-2-hydroxybenzylidene)triaminoguanidinium Salts **1a**–**c** and *tris*-(5-Dodecyl-2-hydroxybenzylidene)triaminoguanidinium Chloride **2**.



Synthesis of 2,4-Didecylanisole (4).[1] Under an argon atmosphere, a solution of 1-bromodecane (12.0 mL, 57.5 mmol) in ether (30 mL) was added dropwise to a suspension of magnesium (1.61 g, 66.3 mmol) in ether (20 mL) at room temperature. The mixture was allowed to reflux for 1.5 h.

To a mixture of 2,4-dibromoanisole (6.00 g, 22.6 mmol) and $NiCl_2$(dppp) (124 mg, 0.229 mmol) in ether (70 mL), the Grignard reagent prepared above was added dropwise. After addition, the mixture was allowed to reflux for 17 h. Additional $NiCl_2$(dppp) (62.8 mg, 0.116 mmol) was added to the mixture. After further refluxing for 5 h, the reaction was quenched by addition of an aqueous solution of HCl (1 M, 8.5 mL). The organic phase was washed with water, a saturate aqueous solution of $NaHCO_3$, brine, and dried over $MgSO_4$. After evaporation of the solvent under vacuum, the residue was subjected to silica gel column chromatography (hexane/AcOEt = 100/1) to give a colorless oil (2.27 g) containing **4** and mono-alkylated anisole (ca. 9/1 ratio estimated by ^{1}H NMR spectrum). This mixture was used without further purification for the next step. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 6.98–6.93 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.60–1.50 (m, 4H), 1.40–1.20 (m, 28H), 0.89 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 155.5, 134.7, 131.1, 129.9, 126.2, 55.4, 35.2, 31.9, 31.8, 30.2, 30.0, 29.7, 29.6, 29.4, 22.7, 14.1; IR (NaCl) 2924, 2853, 2995, 1551, 1466, 1250, 1038, 807 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{49}O$ ($[M+H]^+$): 389.3783, found: 389.3772.

Synthesis of 3,5-Didecyl-2-methoxybenzaldehyde (5). Under an argon atmosphere, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 1.35 mL, 8.94 mmol) was added dropwise to a solution of *n*-BuLi (32.5 mL, 0.27 M, 8.8 mmol) in hexane and ether (1/5 volumetric ratio) at –80 °C. After stirring at –80 °C for 1 h, 2,4-didecylanisole (**4**, 2.27 g, 5.10 mmol) was added to the mixture. The mixture was allowed to warm up to 0 °C. After stirring at 0 °C for 13 h, DMF (0.93 mL, 12 mmol) was added to the reaction mixture. Further stirring at room temperature for 6 h, the reaction was quenched by addition of water (10 mL) and an aqueous solution of HCl (1 M, 20 mL). The mixture was stirred at 45 °C for 3 h. The product was extracted with ether, and the extract was washed with water, a saturate aqueous solution of $NaHCO_3$, and brine, and dried over $MgSO_4$. After removal of the solvents under vacuum, purification was performed by using silica gel column chromatography (from hexane to hexane/AcOEt = 4/1) and recycling HPLC to furnish 3,5-didecyl-2-methoxybenzaldehyde (**5**, 634 mg, 30%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 10.36 (s, 1H), 7.49 (d, *J* = 2.4 Hz 1H), 7.25 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.63–1.50 (m, 4H), 1.40–1.20 (m, 28H), 0.91–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 190.6, 159.6, 139.0, 136.8, 136.7, 128.9, 126.0, 64.1, 35.2, 31.9, 31.3,

30.7, 29.60, 29.57, 29.56, 29.47, 29.44, 29.3, 29.23, 29.16, 22.7, 14.1; IR (NaCl) 2925, 2854, 2750, 1691, 1603, 1475, 1467, 1251, 1216, 1140, 1012, 888, 722 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{48}O_2Na$ ($[M+Na]^+$): 439.3552, found: 439.3539.

Synthesis of 3,5-Didecyl-2-hydroxybenzaldehyde (6). Under an argon atmosphere, to a solution of 3,5-didecyl-2-methoxybenzaldehyde (**5**, 634 mg, 1.54 mmol) in CH_2Cl_2 (15 mL), a solution of BBr_3 (1 M, 2.6 mL, 3 mmol) in CH_2Cl_2 was added dropwise at –40 °C. After stirring at 0 °C for 3 h, the reaction was stopped by the addition of MeOH (6 mL). The reaction mixture was poured into ice water. The product was extracted with CH_2Cl_2. The organic phases were washed with water, a saturate aqueous solution of $NaHCO_3$, brine, and dried over $MgSO_4$. After evaporation of the solvent, purification was performed by using silica gel column chromatography (hexane/AcOEt = 9/1) to give 3,5-didecyl-2-hydroxybenzaldehyde (**6**, 548 mg, 90%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ 11.08 (s, 1H), 9.84 (s, 1H), 7.20 (s, 1H), 7.17 (s, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.63–1.50 (m, 4H), 1.40–1.20 (m, 28H), 0.91–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 196.8, 157.9, 137.7, 133.7, 131.2, 130.4, 120.0, 34.8, 31.9, 31.5, 29.6, 29.5, 29.3, 29.2, 22.7, 14.1; IR (NaCl) 3143, 2924, 2854, 2735, 1657, 1619, 1604, 1461, 1323, 1264, 1215, 1160, 995, 875, 721 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{47}O_2$ ($[M+H]^+$): 403.3576, found: 403.3559.

Synthesis of Triaminoguanidinium Salts. Triaminoguanidium chloride **11a** and triaminoguanidinium nitrate **11b** were prepared following literature procedures.[2]

Synthesis of Triaminoguanidinium Thiocyanate 11c. Guanidinium thiocyanate (5.5 g, 50 mmol) was dissolved in dioxane (15 mL) and the mixture was refluxed for 5 min. The aqueous solution of $N_2H_4 \cdot H_2O$ (64%, 11 mL, 0.17 mol) and dioxane (5 mL) were added to a dropping funnel. After dropwise addition of the solution for 1 h, the reaction was refluxed for further 4 h. When pH value of the mixture became 8-9, the solvent was removed under vacuum. The residue was washed with EtOH to give triaminoguanidinum thiocyanate (**11c**, 6.5 g, 60%) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) δ 8.64 (s, 3H), 6.54 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6, 20 °C) δ 159.02, 129.55; IR (KBr) 3340, 3256, 2810, 2069, 1686, 1335, 978, 744, 638, 563 cm^{-1}; Anal. calcd for $C_2H_9N_7S \cdot 1/5H_2O$: C, 14.40; N, 58.78; H, 5.68; found: C, 14.60; N, 58.98; H, 5.60.

Synthesis of *tris*-(3,5-Didecyl-2-hydroxybenzylidene)triaminoguanidinium Chloride (1a). Under an argon atmosphere, to a solution of **6** (181 mg, 0.45 mmol) in *tert*-butanol (4.0 mL), a solution of triaminoguanidinium chloride (19.8 mg, 140 mmol) in a mixture of ethanol and water (4.0 mL, 3/2 volumetric ratio) and a drop of an aqueous solution of HCl (1 M) were added. After

stirring at r.t. for 6 d, yellow precipitates were formed. The precipitate was collected by filtration and washed with hexane to afford **1a** (73.4 mg, 41%) as a lime yellow wax. mp 71–72 °C; ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C) δ 8.35 (s, 3H), 7.05 (d, *J* = 2.0 Hz, 3H), 6.94 (d, *J* = 2.0 Hz, 3H), 2.70 (t, *J* = 7.6 Hz, 6H), 2.59 (t, *J* = 7.6 Hz, 6H), 1.76–1.58 (m, 12H), 1.50–1.25 (84H) 1.00–0.88 (m, 18H); ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 80 °C) δ 153.9, 133.7, 132.7, 130.4, 128.4, 117.0, 99.7, 35.0, 31.9, 31.4, 29.71, 29.66, 29.63, 29.60, 29.56, 29.54, 29.49, 29.29, 29.27, 22.6, 14.0; IR (KBr) 3368, 3154, 2955, 2924, 2851, 1622, 1604, 1533, 1468, 1257, 1151, 866, 721 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{82}H_{141}N_6O_3$ ([M–Cl]$^+$): 1258.1065, found: 1258.1060.

Synthesis of *tris*-(3,5-Didecyl-2-hydroxybenzylidene)triaminoguanidinium Nitrate (1b). Under an argon atmosphere, to a solution of **6** (104 mg, 0.258 mmol) in *tert*-butanol (2.0 mL), a solution of triaminoguanidinium nitrate (14.2 mg, 81.5 mmol) in a mixture of ethanol and water (2.0 mL, 3/2 volumetric ratio) and a drop of an aqueous solution of HNO_3 (1 M) were added. After stirring at r.t. for 9 d, yellow precipitates were formed. The precipitate was collected and washed several times with *iso*-propanol to give **1b** (56.6 mg, 50%) as a pale yellow solid. mp 77–79 °C; ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C) δ 8.29 (s, 3H), 7.05 (s, *J* = 2.0 Hz, 3H), 6.95 (s, *J* = 2.0 Hz, 3H), 2.72 (t, *J* = 7.6 Hz, 6H), 2.60 (t, *J* = 7.6 Hz, 6H), 1.80–1.60 (m, 12H), 1.50–1.30 (m, 84H), 1.00–0.90 (m, 18H); ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 80 °C) δ 153.9, 148.4, 133.7, 132.5, 130.3, 128.2, 117.2, 35.0, 31.9, 31.4, 29.74, 29.66, 29.63, 29.60, 29.57, 29.49, 29.29, 29.27, 22.6, 14.0; IR (KBr) 3367, 3125, 3016, 2955, 2921, 2851, 1620, 1604, 1533, 1468, 1301, 1257, 1151, 1027, 866, 721 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{82}H_{141}N_6O_3$ ([M–NO_3]$^+$): 1258.1065, found: 1258.1044.

Synthesis of *tris*-(3,5-Didecyl-2-hydroxybenzylidene)triaminoguanidinium Thiocyanate (1c). Under an argon atmosphere, a solution of triaminoguanidinium thiocyanate (13.3 mg, 81.5 mmol) in a mixture of ethanol and water (2.0 mL, 3/2 volumetric ratio) was added to a solution of **6** (98.2 mg, 0.243 mmol) in *tert*-butanol (2.0 mL). After stirring at r.t. for 9 d, yellow precipitates were formed. The precipitate was collected by filtration and washed several times with *iso*-propanol. Recrystallization from a mixture of CH_2Cl_2/*iso*-propanol afforded **1c** (53.7 mg, 50%) as a pale yellow solid. mp 77–79 °C; ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C) δ 8.30 (s, 3H), 7.05 (d, *J* = 2.0 Hz, 3H), 6.95 (d, *J* = 2.0 Hz, 3H), 2.72 (t, *J* = 7.2 Hz, 6H), 2.60 (t, *J* = 7.2 Hz, 6H), 1.85–1.25 (m, 84H), 1.00–0.90 (m, 18H); ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 80 °C) δ 153.9, 148.4, 133.7, 132.5, 130.3, 128.2, 117.2, 99.7, 35.0, 31.9, 31.4, 29.74, 29.66, 29.63, 29.60, 29.56, 29.49, 29.29, 29.27, 22.6, 14.0; IR (KBr) 3367, 3142, 2920, 2850, 1620, 1604, 1532, 1468, 1301, 1256, 1151, 866, 721 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{82}H_{141}N_6O_3$ ([M–SCN]$^+$): 1258.1065, found: 1258.1044.

Synthesis of 4-Dodecylanisole (8). Under an argon atmosphere, a solution of freshly distilled 1-bromododecane (10.0 g, 40.0 mmol) in ether (30 mL) was added dropwise to a suspension of magnesium (1.06 g, 44.0 mmol) in ether (20 mL) at room temperature. After the addition, the mixture was refluxed for 1.5 h.

To a mixture of 4-bromoanisole (3.47 g, 18.6 mmol) and $NiCl_2$(dppp) (0.111 g, 20.5 mmol) in ether (20 mL), the Grignard reagent prepared above (15 mL, 1.2 M, 18.5 mmol) was added dropwise. After the addition, the mixture was refluxed for 5 h, the reaction was quenched by addition of an aqueous solution of HCl (3 M, 8.5 mL). The organic phase was washed with water, a saturate aqueous solution of $NaHCO_3$, brine, and dried over $MgSO_4$. After evaporation of the solvent under vacuum, the residue was subjected to silica gel column chromatography (EtOAc/Hex = 1/1) to give 4-dodecylanisole (**8**, 4.47g, 79%) as a yellow oil. All spectra of 4-dodecylanisole agreed with those in a previous report.[3]

Synthesis of 5-Dodecyl-2-methoxybenzaldehyde (9). Under an argon atmosphere, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 0.5 mL, 3.3 mmol) was added drop wise to a solution of *n*-BuLi (1.9 mL, 1.6 M, 3.0 mmol) in hexane diluted by ether (10 mL) at –80 °C. After stirring at –80 °C for 30 min, 4-dodecylanisole (502 mg, 1.82 mmol) was added to the mixture. The mixture was allowed to warm up to 0 °C. After stirring at 0 °C for 6 h, DMF (0.2 mL, 2.6 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 6 h. The reaction was quenched by addition of water (2 mL) and an aqueous solution of HCl (2 M, 2 mL). After refluxing for 2 h, the product was extracted with ether. The extract was washed with water, a saturate aqueous solution of $NaHCO_3$, and brine, and dried over $MgSO_4$. The evaporation of the solvent gave 5-dodecylanisaldehyde (**9**, 41 mg, 75%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 10.46 (s, 1H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 2.59–2.57 (m, 2H), 1.27–1.21 (m, 20H), 0.91–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 30°C) δ 190.2, 160.3, 136.1, 135.4, 128.1, 124.8, 111.8, 55.9, 34.9, 32.1, 31.6, 29.85, 29.81, 29.79, 29.72, 29.62, 29.5, 29.3, 22.8, 14.3. IR (KBr) 3460, 2985, 2918, 2850, 1682, 1612, 1498, 1471, 1259, 1190, 1167, 1024, 1060, 833 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{32}O_2Na$ ($[M+Na]^+$): 327.2295, found: 327.2298.

Synthesis of 5-Dodecyl-2-hydroxybenzaldehyde (10). Under an argon atmosphere, to a solution of 5-dodecylanisaldehyde (**9**, 328 mg, 1.08 mmol) in CH_2Cl_2 (5 mL) at –78 °C, BBr_3 (2.0 mL, 1 M in CH_2Cl_2, 2 mmol) was added. The resulting mixture was stirred at r.t. for 4 h. MeOH (5 mL) was added to the mixture at 0 °C. The resulting brown-red solution was poured into ice. The product

was extracted with CH_2Cl_2, and organic phase was washed with water and saturated aqueous solution of $NaHCO_3$, brine, and dried over anhydrous $MgSO_4$. The volatiles were removed under vacuum, and the residue was purified by silica gel column chromatography (EtOAc/Hex = 1/1) yielding 5-dodecylsalicylaldehyde (**10**, 231 mg, 74%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 10.83 (s, 1H), 9.87 (s, 1H), 7.35 (dd, *J* = 8.4 Hz and 2.3 Hz, 1H), 7.36–7.33 (m, 1H), 6.91 (d, 1H, *J* = 8.2 Hz), 2.61–2.59 (m, 2H), 1.27–1.25 (m, 20H), 0.90–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 30 °C) δ 196.8, 159.9, 137.6, 134.5, 133.0, 120.6, 117.6, 34.9, 32.1, 31.6, 29.9, 29.81, 29.79, 29.72, 29.61, 29.5, 29.3, 22.8, 14.3. The ^{1}H NMR spectrum agrees with previous reports.[4]

Synthesis of *tris*-(5-Dodecyl-2hydroxybenzylidene)triaminoguanidinium Chloride (2). Triaminoguanidinium chloride (15.8 mg, 0.112 mmol) was suspended in a mixture of H_2O and EtOH (0.4 mL, 3:2 ratio) and acidified with HCl (0.5 M) to a pH-value of 3. After addition of a solution of 5-dodecylsalicylaldehyde (110 mg, 0.418 mmol) in butanol (0.4 mL), the mixture was stirred at r.t. for 24 h. The colour of the solution turned to yellow under formation of white colored fine particles. After filtration, the yellowish powder was dried under reduced pressure to afford **2** (47 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 3H), 9.87 (3H), 8.48 (s, 3H), 7.12–7.08 (m, 3H), 7.00–6.95 (m, 3H), 6.87–6.83 (m, 3H), 2.47 (t (br), 6H), 1.55 (s, 12H), 1.27-1.25 (m, 60H), 0.88 (t, *J* = 8.5 Hz, 9H). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.91 (s, 3H), 10.09 (s, 3H), 9.02 (s, 3H), 7.90 (s, 3H), 7.14 (dd, *J* = 2.1 Hz, *J* = 8.4 Hz, 3H), 6.90 (d, *J* = 8.4 Hz, 3H), 2.55 (t, *J* = 8.1 Hz, 6H), 1.59–1.57 (m, 6H), 1.21 (s, 60H) 0.83–0.81 (t, *J* = 8.5 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.3, 148.6, 147.9, 133.0, 132.4, 126.4, 119.0, 116.1, 34.31, 31.24, 31.13, 29.00, 28.96, 28.95, 28.83, 28.65, 28.57, 22.0, 13.9. IR (KBr) 3604, 3491, 3360, 3128, 2956, 2920, 2850, 1643, 1610, 1500, 1466, 1346, 1267, 1165, 1095, 970, 831, 725 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{58}H_{93}N_6O_3$ ($[M\text{-}Cl]^+$): 921.7304, found: 921.7292.

5. ^{1}H and ^{13}C NMR Spectra of Synthetic Intermediates.

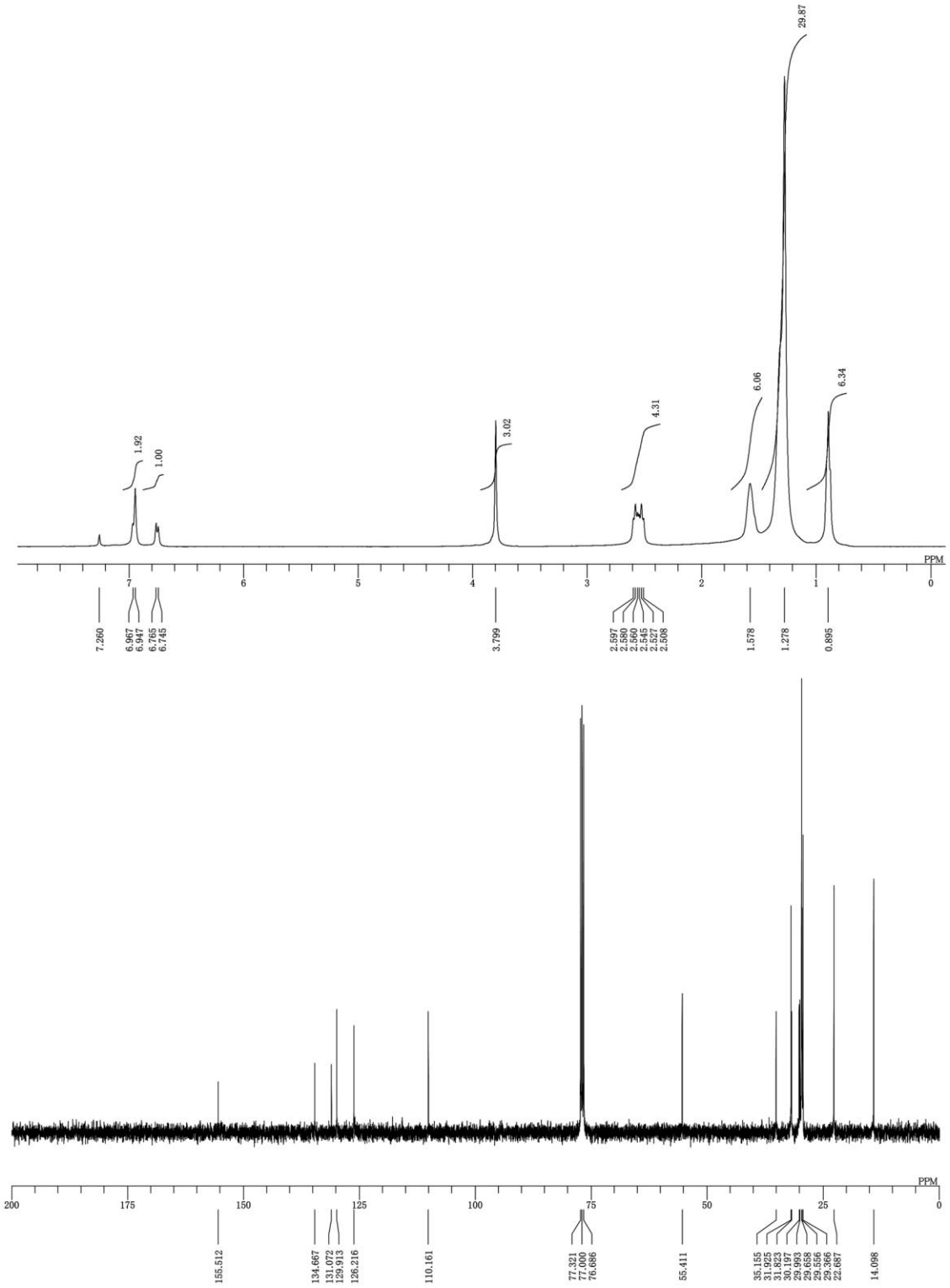


Fig. S7. ^{1}H and ^{13}C NMR spectra of **4** in $CDCl_3$ at 30 °C.

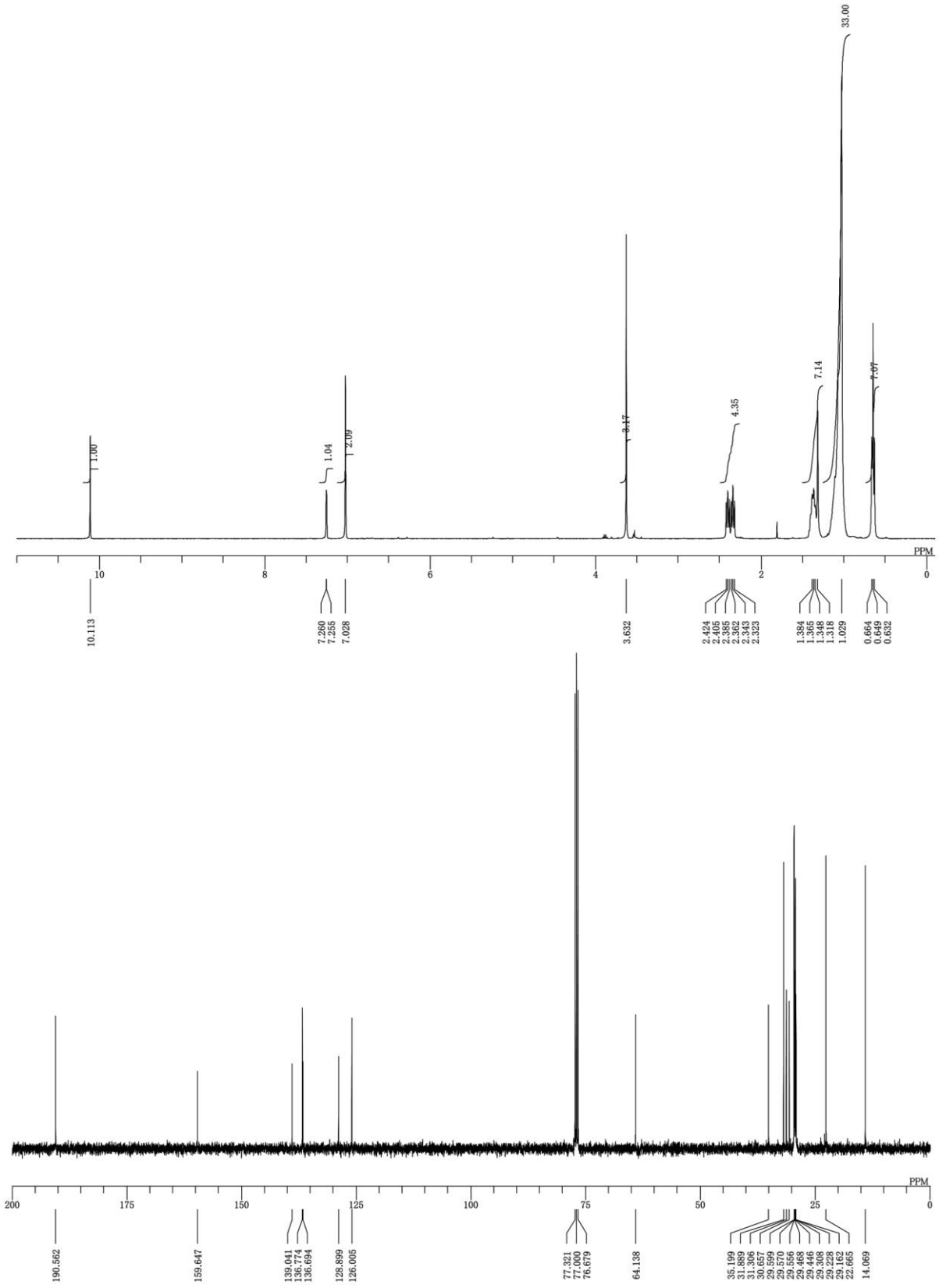


Fig. S8. ^{1}H and ^{13}C NMR spectra of **5** in $CDCl_3$ at 30 °C.

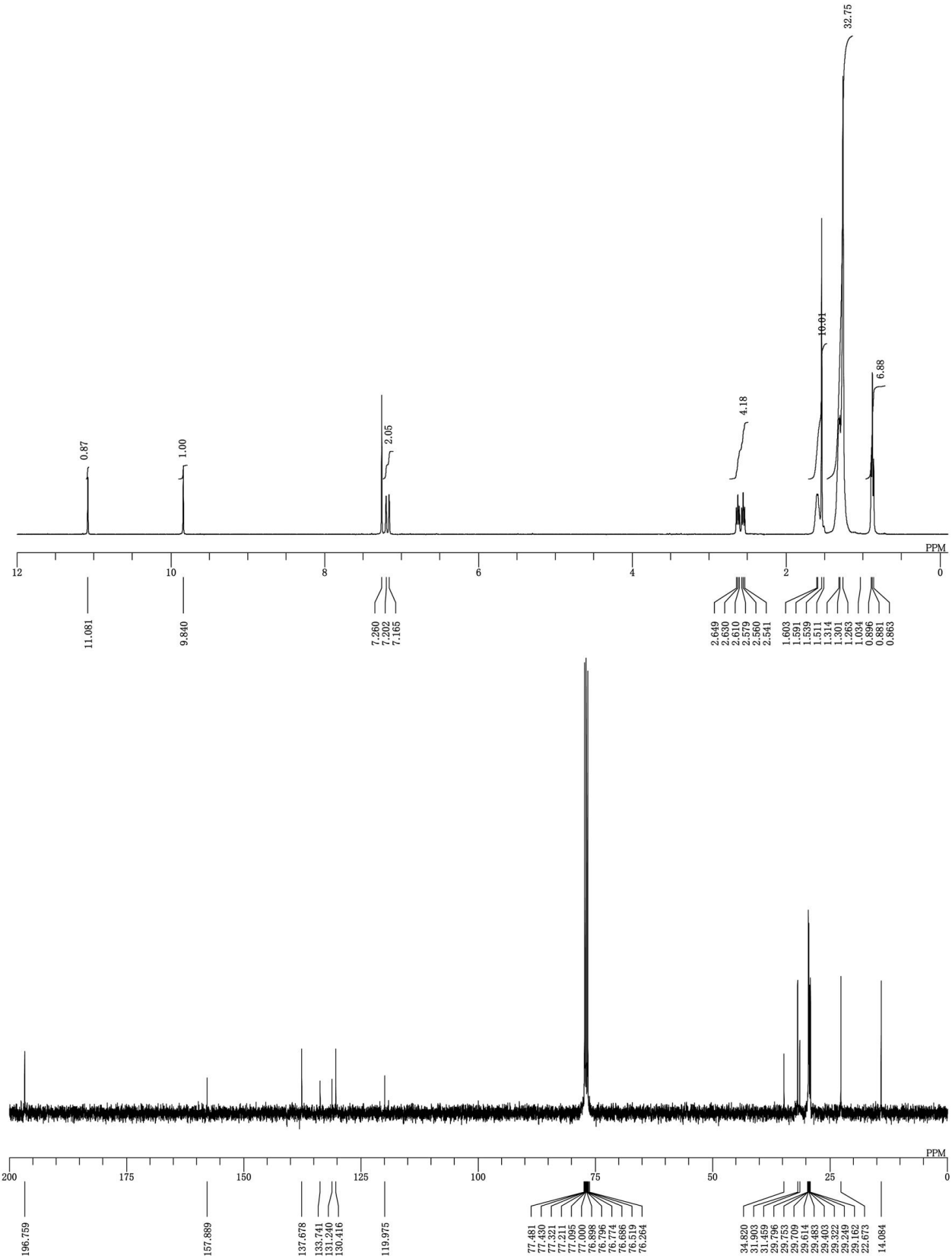


Fig. S9. ^{1}H and ^{13}C NMR spectra of **6** in $CDCl_3$ at 30 °C.

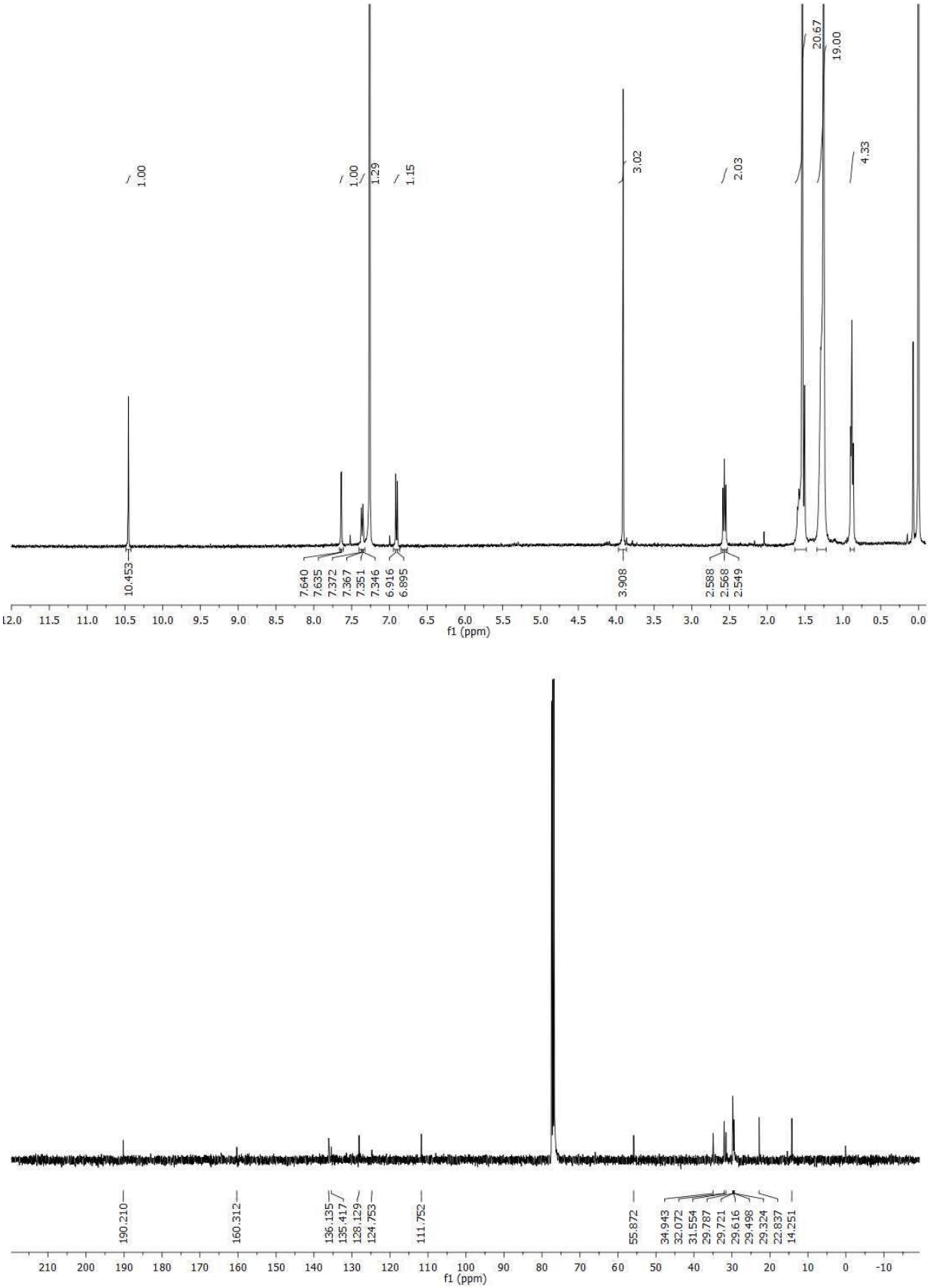


Fig. S10. ^{1}H and ^{13}C NMR spectrum of **9** in $CDCl_3$ at 30 °C.

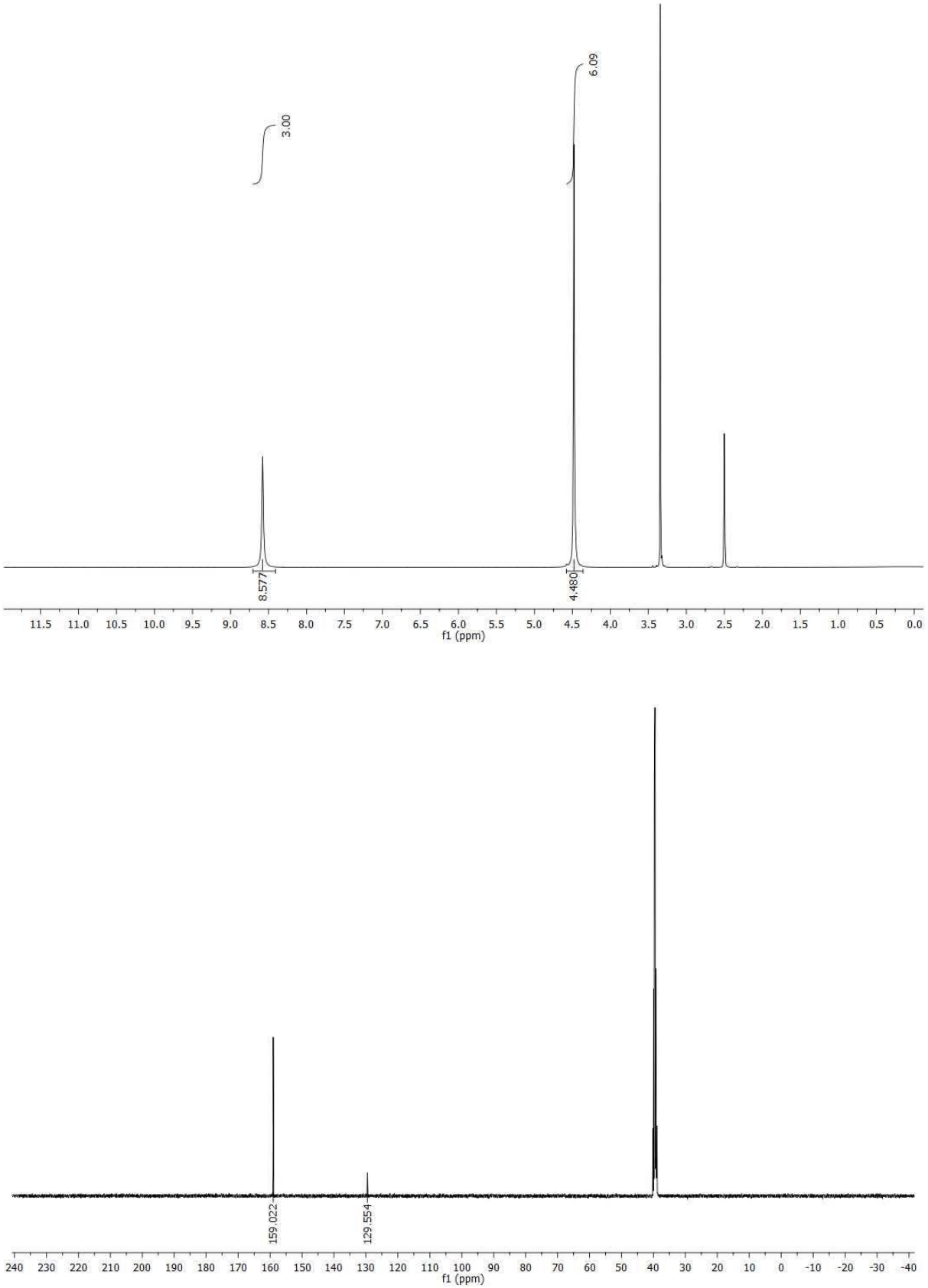


Fig. S11. ^{1}H and ^{13}C NMR spectrum of **11c** in DMSO-d_6 at 20 °C.

6. ^{1}H and ^{13}C NMR Spectra of *tris*-(3,5-Didecyl-2-hydroxybenzylidene)triaminoguanidinium Salts.

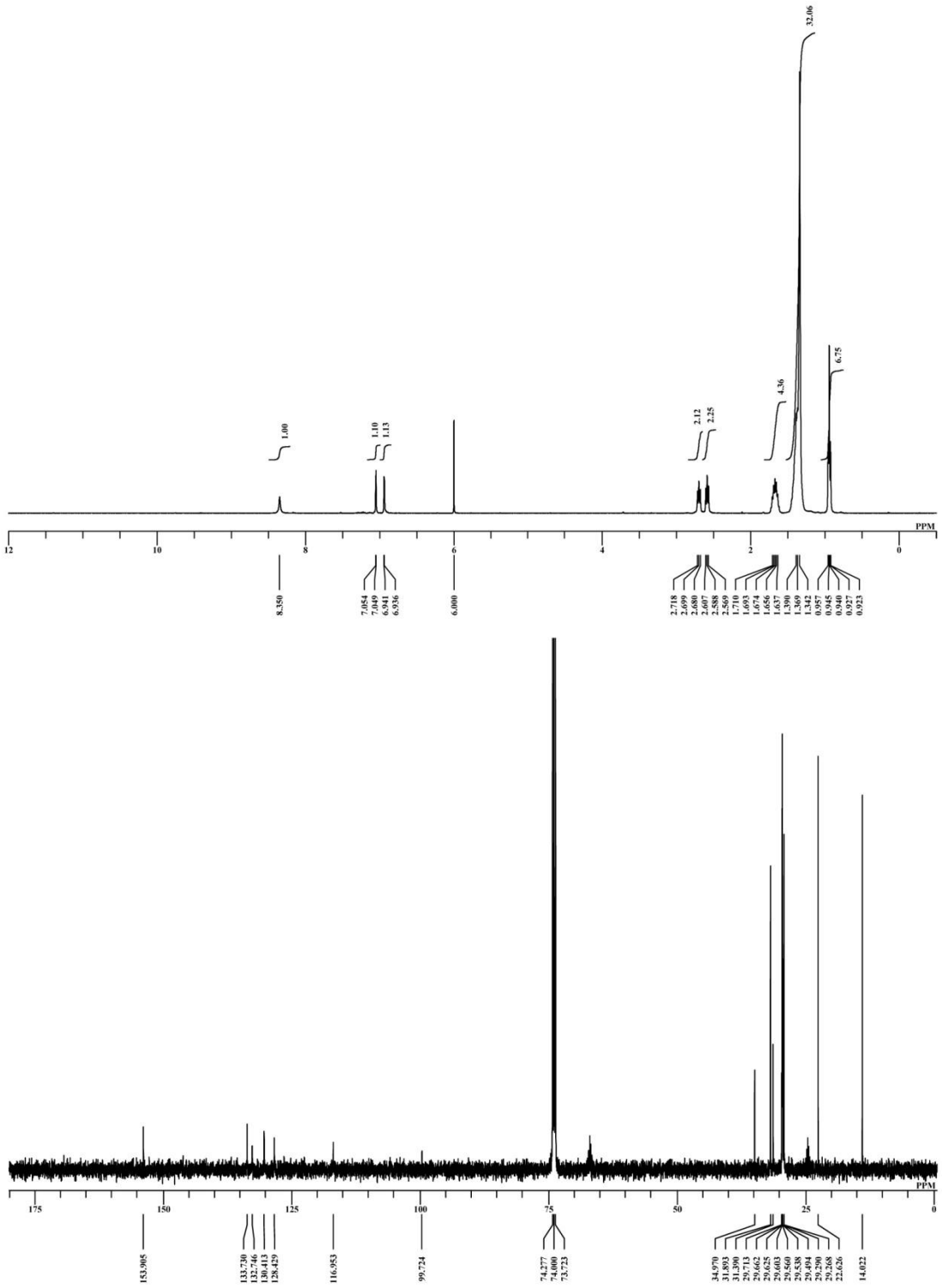


Fig. S12. ^{1}H and ^{13}C NMR spectra of **1a** in tetrachloroethane-d_2 at 80 °C.

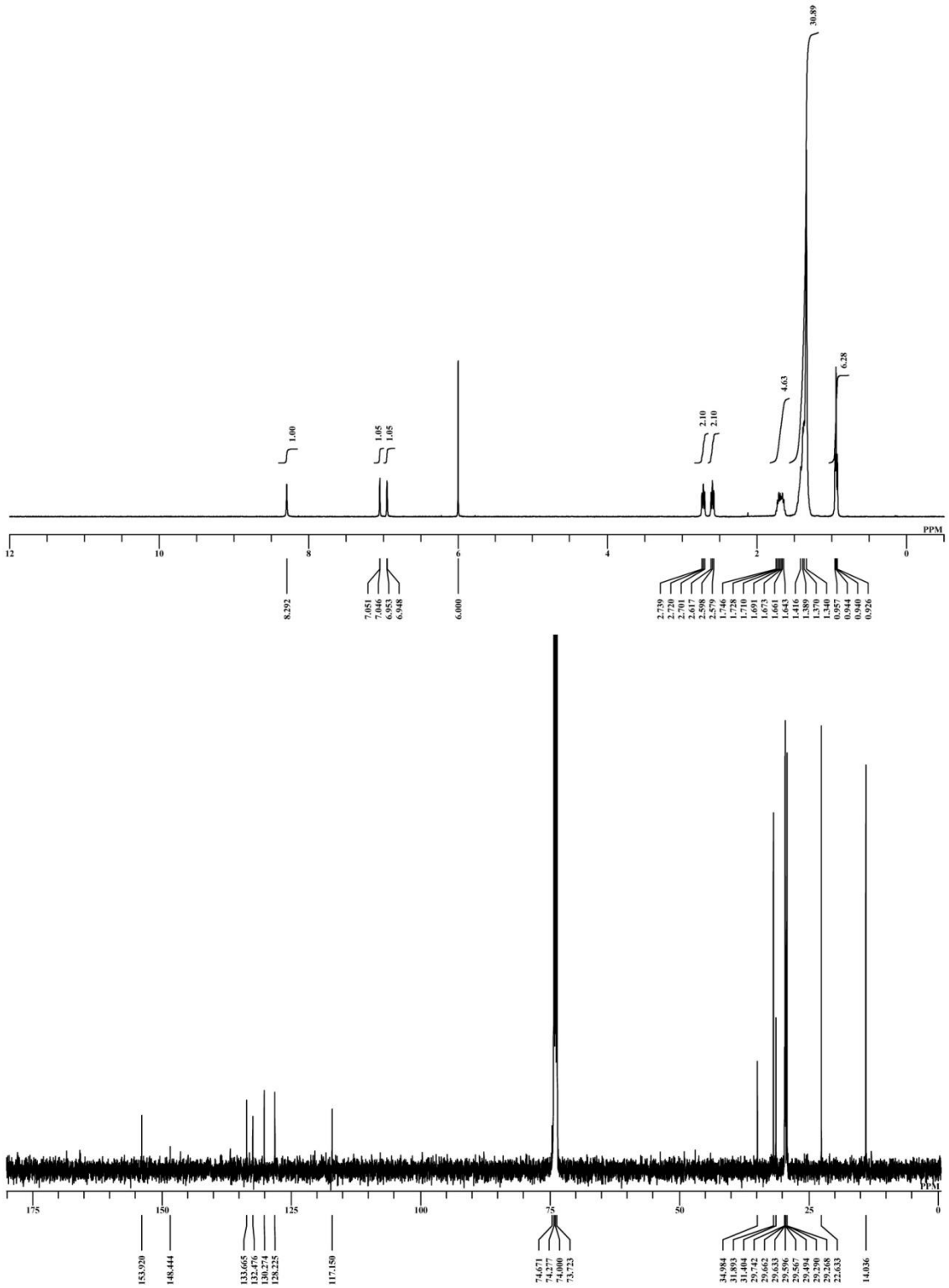


Fig. S13. ^{1}H and ^{13}C NMR spectra of **1b** in tetrachloroethane-d_2 at 80 °C.

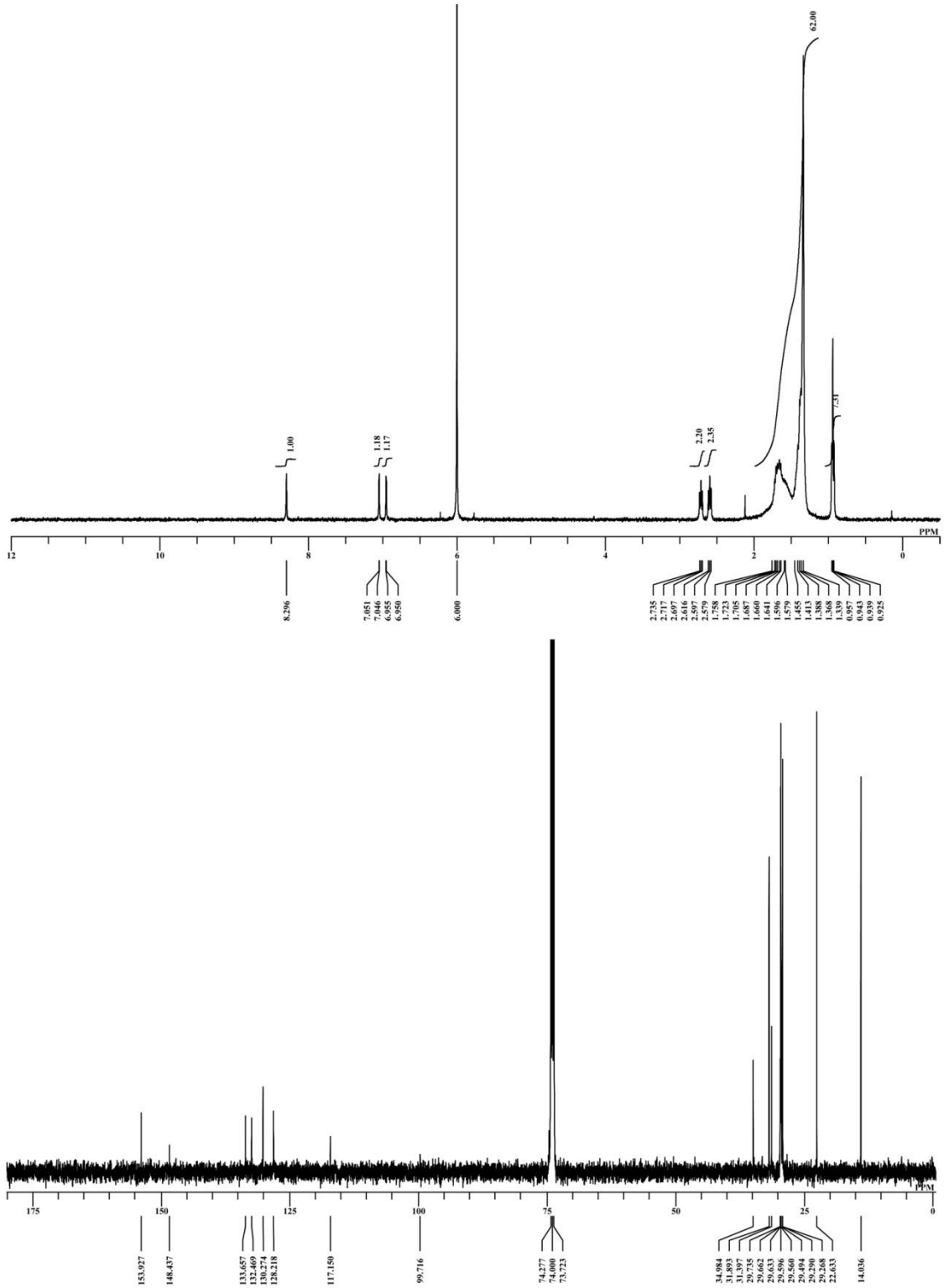


Fig. S14. ^{1}H and ^{13}C NMR spectra of **1c** in tetrachloroethane-d_2 at 80 °C.

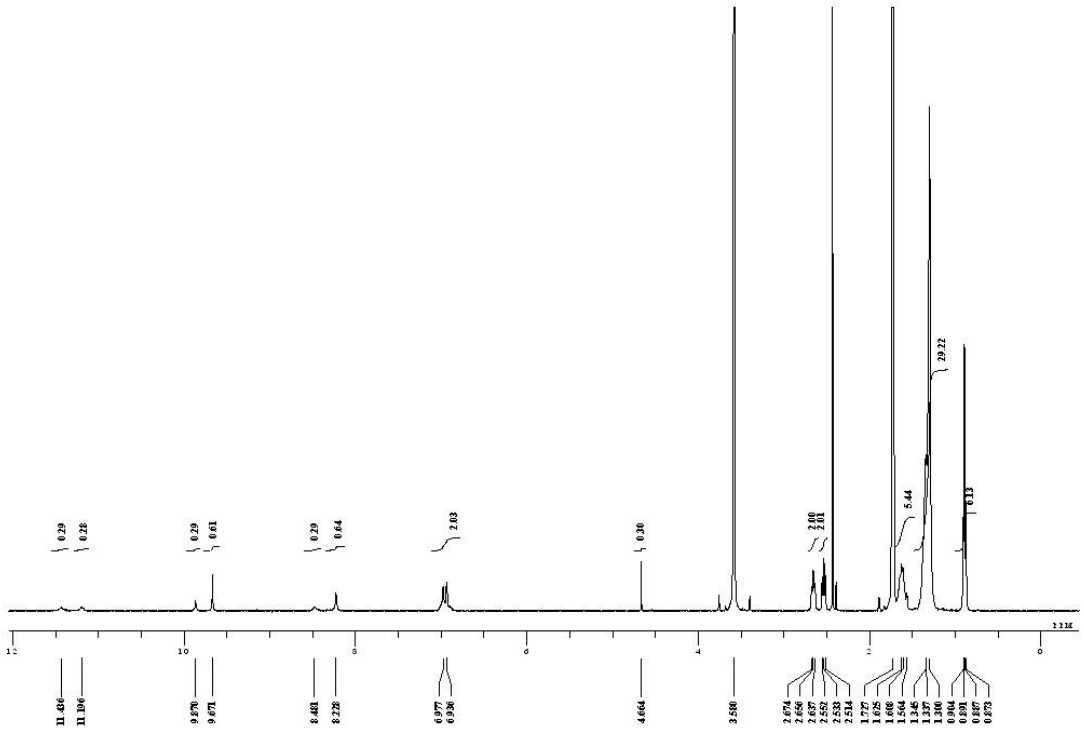


Fig. S15. ^{1}H NMR spectrum of **1b** in tetrahydrofuran-d_8 at 30 °C.

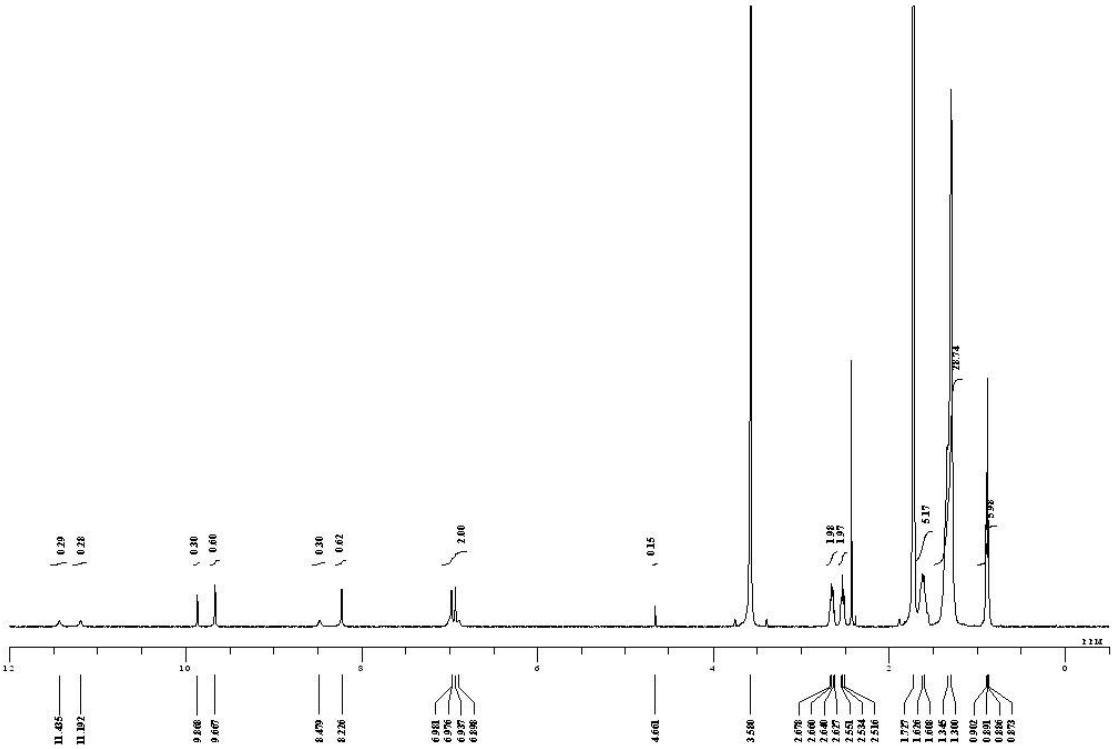


Fig. S16. ^{1}H NMR spectrum of **1c** in tetrahydrofuran-d_8 at 30 °C.

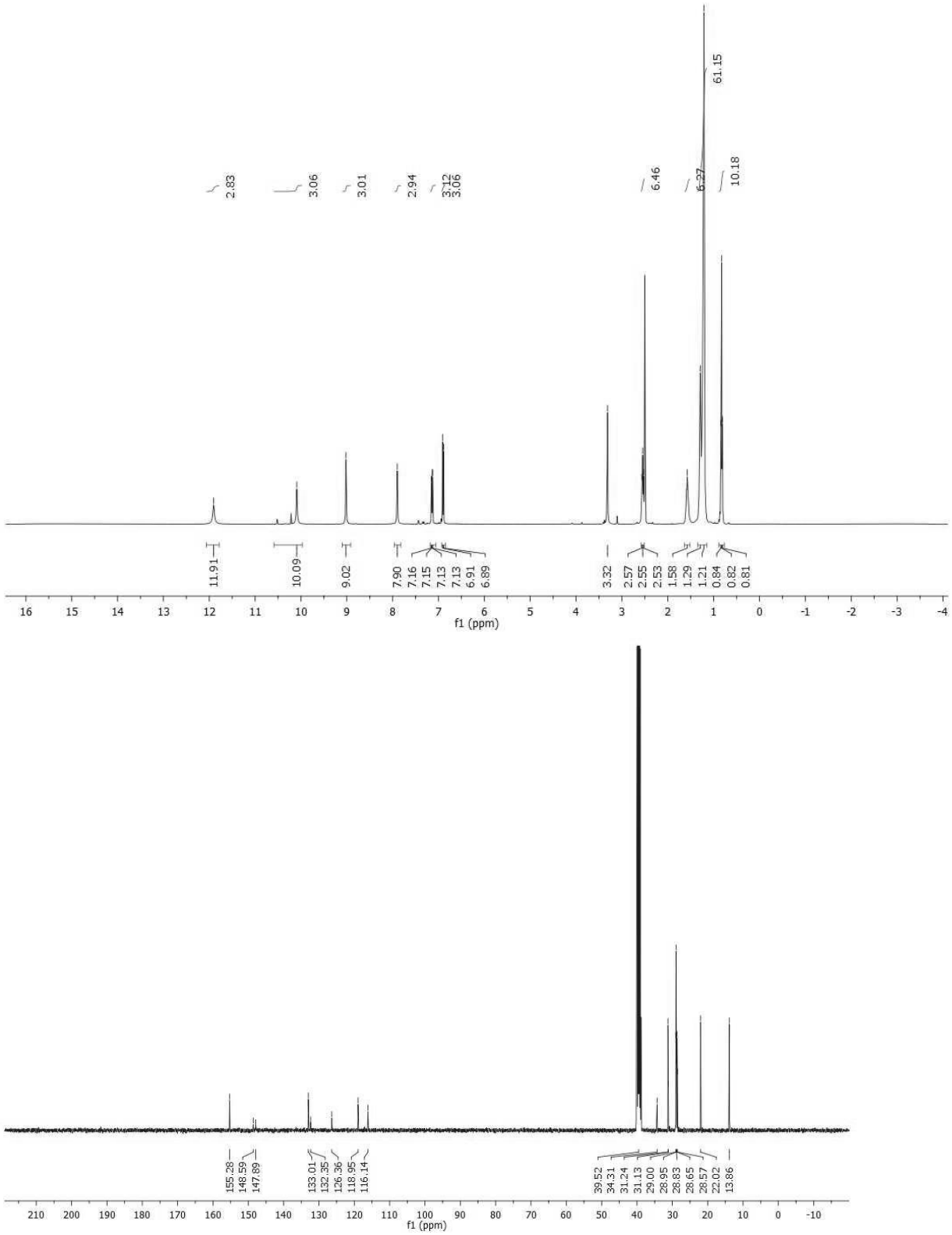


Fig. S17. ^{1}H and ^{13}C NMR spectrum of **2** in DMSO-d_6 at 30 °C.

7. NOESY NMR Spectra of *tris*-(3,5-Didecyl-2-hydroxybenzylidene)triaminoguanidinium Nitrate.

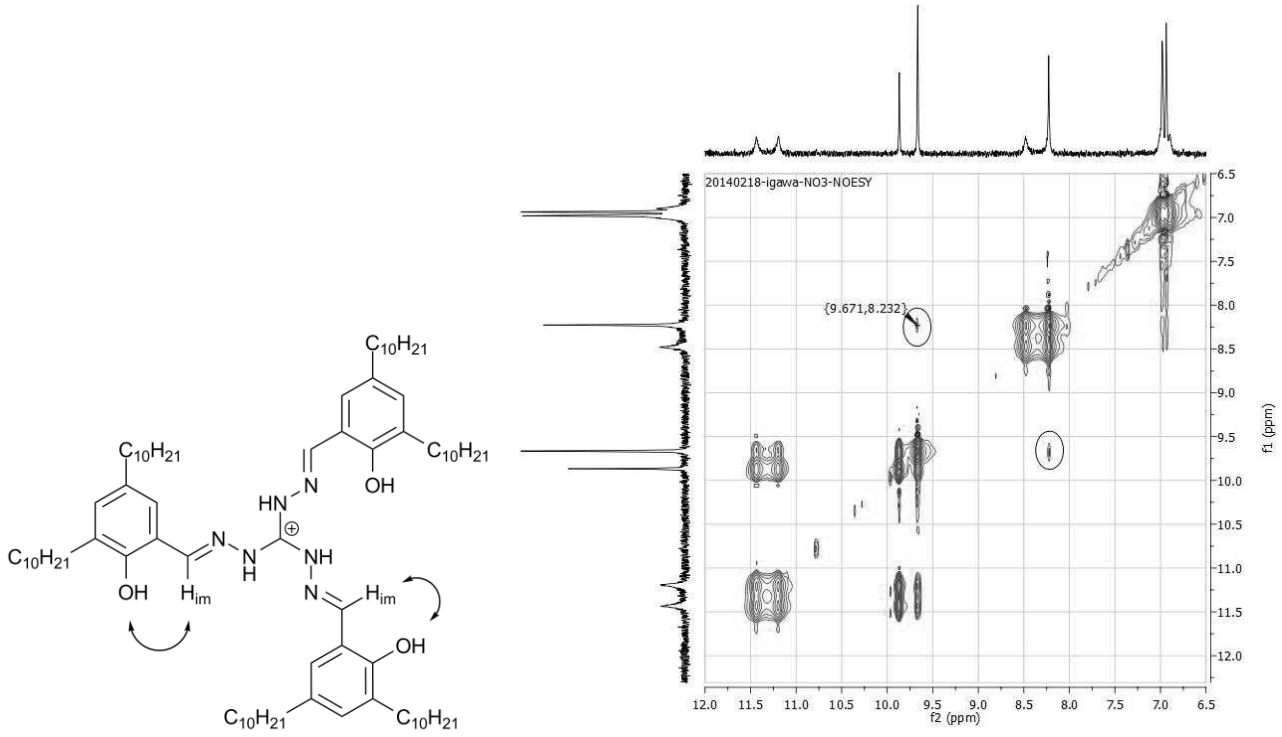


Fig. S18. NOESY NMR spectrum of **1b** in tetrahydrofuran-d_8 at 30 °C: aromatic region with highlighted cross peak between imine signal and OH signal as a result of *saa*-conformation.

8. References

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