Supplementary Material (ESI) for New Journal of Chemistry

Synthesis and Characterization of Amphiphilic *o*-Phenylene Ethynylene Oligomers

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SUPPLEMENTAL INFORMATION

Supplementary Material (ESI) for New Journal of Chemistry

EXPERIMENTAL

NMR SPECTROSCOPY

NMR samples of **1** and **2** were prepared at 1.25 mm concentration in CD_3CN or $CDCl_3$. Spectra were recorded with a 400 MHz spectrometer by means of a TXI probe with Z-gradient capabilities. The temperature was maintained at 300 K for all acquisitions. One-dimensional ^1H and gradient correlated J-coupled correlation spectroscopy (GCOSY) were used.

POLARIZED OPTICAL MICROSCOPY

POM images were taken using a microscope equipped with a heated stage, crossed polarizers, a 50X objective, in transmittance mode. Samples were prepared by solvent casting of **1** and **2** from acetone solution. Annealing of a dropslide of **1** was performed using a vacuum oven, with gradual cooling from 60 °C to room temperature over 48 hours, followed by a week of standing at room temperature in order to allow formation of long-range ordered structure. A similar procedure was used with **2**, where a dropslide was gradually cooled from 130 °C to room temperature over 48 hours followed by a week of standing at room temperature.

DYNAMIC LIGHT SCATTERING

Dynamic Light Scattering experiments were performed at room temperature using an ALV unit equipped with a precision goniometer, an argon laser (λ = 514.5 nm, max. power 3 W) operated at 300 mW, and a photomultiplier. Signal from the detector was processed by a multiple tau digital correlator board and associated software. Samples of **1** and **2** were prepared both in acetonitrile and in chloroform, with 1.0 mg/mL concentration.

Measurements. ^{1}H, and ^{13}C NMR spectra for general analysis were obtained with a 400 MHz NMR spectrometer. Mass spectral data were obtained at the University of Massachusetts Amherst mass spectroscopy facility, which is supported in part by the National Science Foundation.

Materials. Reagent grade tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone. All other solvents were used as received. Trans dichlorobis (triphenylphosphine) palladium ($Pd(P\phi_3)_2Cl_2$) was purchased from Strem Chemical. Trimethylsilyl acetylene was purchased from GFS chemicals. All other reagents were used as received.

Purification. All column chromatography was performed on an automated flash chromatography system using the column sizes and solvent gradients as indicated.

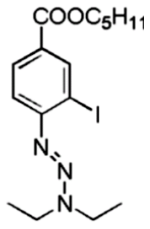
Abbreviations used: DCM (dichloromethane), TBAF (Tetra butyl ammonium fluoride), EtOAc (ethyl acetate), TEA (triethylamine), TMS (trimethylsilyl), DMAP (4-dimethylaminopyridine), EDC (1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide)

General TMS Deprotection Procedure (TBAF). One equivalent of the TMS protected compound was dissolved in DMF in a vial with stirbar. 5.0 equivalents of $KF.2H_2O$ were added, and the mixture was stirred at room temperature for 4 hours. After the reaction had completed, the mixture was filtered through paper and washed with $CHCl_3$. The filtrate was then diluted with more $CHCl_3$, washed once with water, and once with saturated aqueous CaCl2. Evaporation under vacuum gives the crude product, usually containing a small amount of residual DMF, which may be used in a Sonogashira coupling without further purification.

General Triazene Activation Procedure. This procedure was performed by microwave synthesis in Biotage 2-5 mL vials. Each vial was filled with 250 mg of triazene protected compound 0.05 eq of I_2 and of MeI ≈130 eq, a stirbar was added, and a septum crimped on. Microwave heat was applied to each tube, at a temperature of 150°C for a time of one hour. After all reactions had completed, the tubes were opened, combined, filtered through a Celite pad and washed with ethyl ether, and evaporated under a N_2 stream, and purified by flash chromatography.

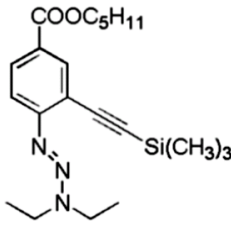
General Sonogashira Coupling Procedure. A schlenk flask with stirbar was flame dried under vacuum and backfilled with N_2 three times. To this flask were added 0.05-0.1 equivalents (based on the acetylene compound) of $Pd(P\phi_3)_2Cl_2$ and 0.1-0.2 equivalents of CuI. The 1-1.1 equivalents of the acetylene compound to 1 equivalent iodide were dissolved in separate flasks in TEA and transferred via syringe to the schlenk flask under N_2. The schlenk flask was gently degassed for 30 seconds then backfilled with N_2. The flask sealed and placed in an oil bath at 55°C for at least 6-18 hours and

checked by TLC for completeness. A precipitate should form. Once done, the reaction solution was diluted with ether, filtered through a pad of Celite and concentrated. The residue was then purified using Silica flash chromatography using the solvents indicated.



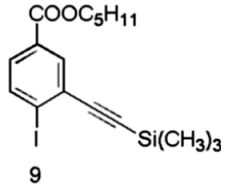
7

***N,N*-Diethyl-*N'*-(2-Iodo-4-benzoic acid) triazene (S) 2-methylbutyl ester (7)** A solution of 5.00g of **6** (14.4 mmol, 1.0 eq) and 2.83 g of DMAP (23.0 mmol, 1.6 eq) was prepared in 142 mL of DCM This solution was cooled to 0°C and 4.41 g of EDC (23.0 mmol, 1.6 eq) was added. After 20 minutes, 1.27 g of (S) 2-methylbutanol was added in 50 mL DCM. The reaction was stirred overnight, during which time the ice was allowed to melt. The mixture was evaporated, and the residue partitioned between 50 mL of water and 2 250 mL portions of DCM. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated to give crude product. Purification by flash chromatography in 20->50% DCM/Hexanes gave a light yellow oil (4.27g, 71%). ^{1}H NMR ($CDCl_3$): δ 8.50 (d, 1H, phenyl H, J = 1.8), 7.93 (dd, 1H, phenyl H, J_1 = 1.8, J_2 = 8.4), 7.38 (d, 1H, phenyl H, J = 8.4), 4.14 (m, 2H, CO_2CH_2), 3.82 (m, 4H, $N(CH_2)_2$), 1.84 (m, 1H, aliphatic), 1.53 (m, 1H, aliphatic), 1.34 (m, 7H, aliphatic 1H + $N(CH_2\text{-}C\underline{H}_3)_2$), 0.98 (m, 6H, CH_3) ppm.



8

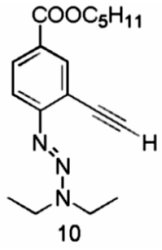
***N,N*-Diethyl-*N'*-(2-trimethylsilanylethynyl-4-benzoic acid) triazene (S) 2-methylbutyl ester (8)** The general Sonogashira coupling procedure described above was used to prepare this compound. 1.93 g of **7** (4.61 mmol, 1.0 eq), 162 mg of $Pd(P\phi_3)_2Cl_2$ (0.23 mmol, 0.05 eq), and 9 mg CuI (0.05 mmol, 0.01 eq) were combined in a 100 mL schlenk flask with 31 mL TEA. TMS acetylene (0.974 mL/0.697 g, 6.92 mmol, 1.5 eq) was added to the solution. Reaction was stirred overnight at room temperature. After completion, the reaction solution was filtered through Celite with ether to wash, evaporated, and purified with flash chromatography in 0%->20% EtOAc/hexanes to give a light yellow oil (1.60 g, 90%). ^{1}H NMR($CDCl_3$): δ 8.143 (d, 1H, phenyl H, J = 1.8), 7.899 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.451 (d, 1H, phenyl H, J = 8.4), 4.152 (m, 2H, CO_2CH_2), 3.83 (m, 4H, $N(CH_2)_2$), 1.87 (m, 1H, aliphatic), 1.53 (m, 1H, aliphatic), 1.31 (m, 7H, aliphatic 1H + $N(CH_2\text{-}C\underline{H}_3)_2$), 0.98 (m, 6H, CH_3), 0.25 (s, 9H, $Si(CH_3)_3$) ppm.



9

(S) 2-methylbutyl 3-trimethylsilanylethynyl 4-iodo benzoate (9) The general Triazene Activation Procedure described above was used to prepare this compound. 580 mg of **8** (1.29 mmol, 1.0 eq) and 33 mg of I_2 (0.13 mmol, 0.1 eq) were dissolved in 10 mL of CH_3I, divided into 2 Biotage vials, and each portion was microwaved for 1 hour at 150 °C. Reaction was worked up as described above, and purified with flash chromatography in 0%->30% EtOAc/hexanes to give a light yellow oil (572 mg, 92%). ^{1}H NMR($CDCl_3$): δ 8.066 (d, 1H, phenyl H, J = 1.8), 7.927 (d, 1H, phenyl H, J = 8.4), 7.607 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 4.156 (m, 2H, CO_2CH_2), 1.85 (m, 1H, aliphatic), 1.51 (m, 1H, aliphatic), 1.27 (m, 1H, aliphatic), 0.98 (m, 6H, CH_3), 0.30 (s, 9H, $Si(CH_3)_3$) ppm.

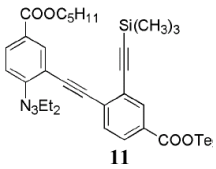
***N,N*-Diethyl-*N'* (3- ethynyl 4-benzoic acid) triazene (S) 2-methylbutyl ester (10)**



10

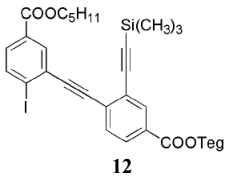
The general TMS deprotection procedure, listed above, was used to prepare this compound. 290 mg of **8** (0.801 mmol, 1.0 eq) and 376 mg of KF.$2H_2O$ (4.0 mmol, 5.0 eq) were dissolved in 5 mL of DMF and stirred for 4 hours. The mixture was diluted with 50 mL $CHCl_3$ and washed with 25 mL of H_2O and 25 mL of saturated $CaCl_2$ before evaporation to give a yellow oil which was taken directly on to **11** without further purification.

Triazene-C^5-Es-TMS (11) This compound was prepared using the general Sonogashira coupling procedure described above. 0.801 mmol of **10** and 393 mg of **3** (0.801 mmol, 1.0 eq) were coupled in 20 mL of 1:1 TEA/THF using 28 mg (0.042 mmol, 0.05 eq) of $Pd(P\phi_3)_2Cl_2$ and 1.5 mg (0.008 mmol, 0.01 eq) of CuI as described in the general procedure. The product was purified by flash chromatography in 0%->60% EtOAc/hex to give an orange oil (398 mg, 73%). ^{1}H NMR($CDCl_3$): δ 8.238 (d, 1H, phenyl H, J = 1.8), 8.185 (d, 1H, phenyl H, J = 1.8), 7.976 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.945 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.537 (d, 1H, phenyl H, J = 8.4), 7.526 (d, 1H, phenyl H, J = 8.4), 4.48 (m, 2H, CO_2CH_2), 4.156 (m, 2H, CO_2CH_2), 3.86 (m, 6H, CH_2), 3.70 (m, 6H, CH_2), 3.54 (m, 2H, CH_2), 3.381 (s, 3H, OCH_3), 1.88 (m, 1H, aliphatic), 1.54 (m, 1H, aliphatic), 1.30 (m, 7H, aliphatic 1H + $N(CH_2\text{-}C\underline{H}_3)_2$), 0.98 (m, 6H, CH_3), 0.27 (s, 9H, $Si(CH_3)_3$) ppm.



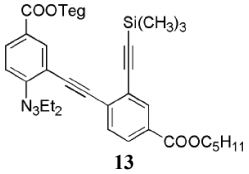
11

I-C^5-Es-TMS (12) The general Triazene Activation Procedure described above was used to prepare this compound. 871 mg of **11** (1.28 mmol, 1.0 eq) and 65 mg of I_2 (0.257 mmol, 0.30 eq) were dissolved in 9 mL of CH_3I, divided into 2 Biotage vials, and each portion was microwaved for 1 hour at 150 °C. Reaction was worked up as described above, and purified with flash chromatography in 0%->20% acetone/$CHCl_3$ to give an orange oil (506 mg, 56%). ^{1}H NMR($CDCl_3$): δ 8.204 (d, 1H, phenyl H, J = 1.8), 8.176 (d, 1H, phenyl H, J = 1.8), 8.008 (d, 1H, phenyl H, J = 8.4), 7.992 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.691 (d, 1H, phenyl H, J = 8.4), 7.688 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 4.50 (m, 2H, CO_2CH_2), 4.187 (m, 2H, CO_2CH_2), 3.86 (m, 2H, CH_2), 3.70 (m, 6H, CH_2), 3.51 (m, 2H, CH_2), 3.385 (s, 3H, OCH_3), 1.87 (m, 1H, aliphatic), 1.51 (m, 1H, aliphatic), 1.28 (m, 1H, aliphatic), 0.98 (m, 6H, CH_3), 0.28 (s, 9H, $Si(CH_3)_3$) ppm.



12

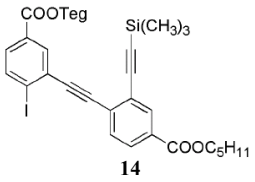
Triazene-Es-C^5-TMS (13) This compound was prepared using the general Sonogashira coupling procedure described above. 1.97 mmol of **4** and 816 mg of **9** (1.97 mmol, 1.0 eq) were coupled in 40 mL of 1:1 TEA/THF using 69 mg (0.098 mmol, 0.05 eq) of $Pd(P\phi_3)_2Cl_2$ and 3.8 mg (0.019 mmol, 0.01 eq) of CuI as described in the general procedure. The product was purified by flash chromatography in 0%->60% EtOAc/hex to give an orange oil (398 mg, 73%). ^{1}H NMR($CDCl_3$): δ



13

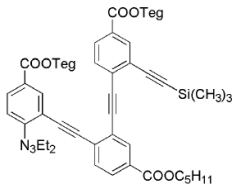
8.263 (d, 1H, phenyl H, J = 1.8), 8.154 (d, 1H, phenyl H, J = 1.8), 7.979 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.932 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.532 (d, 1H, phenyl H, J = 8.4), 7.522 (d, 1H, phenyl H, J = 8.4), 4.48 (m, 2H, CO_2CH_2), 4.17 (m, 2H, CO_2CH_2), 3.82 (m, 6H, CH_2), 3.68 (m, 6H, CH_2), 3.54 (m, 2H, CH_2), 3.36 (s, 3H, OCH_3), 1.88 (m, 1H, aliphatic), 1.54 (m, 1H, aliphatic), 1.30 (m, 7H, aliphatic 1H + $N(CH_2\text{-}C\underline{H}_3)_2$), 0.98 (m, 6H, CH_3), 0.28 (s, 9H, $Si(CH_3)_3$) ppm.

I-Es-C^5-TMS (14) The general Triazene Activation Procedure described above was used to prepare this compound. 978 mg of **13** (1.44 mmol, 1.0 eq) and 73 mg of I_2 (0.288 mmol, 0.20 eq) were dissolved in 10 mL of CH_3I, divided into 2 Biotage vials, and each portion was microwaved for 1 hour at 150 ^oC. Reaction was worked up as described above, and purified with flash chromatography in 0%->20% acetone/$CHCl_3$ to give an orange oil (506 mg, 56%). ^1H NMR($CDCl_3$): δ 8.202 (d, 1H, phenyl H, J = 1.8), 8.173 (d, 1H, phenyl H, J = 1.8), 8.002 (d, 1H, phenyl H, J = 8.4), 7.976 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.699 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.685 (d, 1H, phenyl H, J = 8.4), 4.49 (m, 2H, CO_2CH_2), 4.19 (m, 2H, CO_2CH_2), 3.84 (m, 2H, CH_2), 3.70 (m, 6H, CH_2), 3.52 (m, 2H, CH_2), 3.37 (s, 3H, OCH_3), 1.88 (m, 1H, aliphatic), 1.52 (m, 1H, aliphatic), 1.30 (m, 1H, aliphatic), 1.0 (m, 6H, CH_3), 0.29 (s, 9H, $Si(CH_3)_3$) ppm.



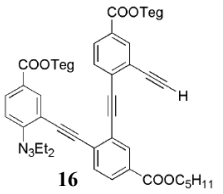
14

Triazene-Es-C^5-Es-TMS (15) This compound was prepared by the general Sonogashira procedure described above. 111 mg of **4** (284 µmol, 1.0 eq), 200 mg of **12** (284 µmol, 1.0 eq), 10.0 mg of $Pd(P\phi_3)_2Cl_2$ (14 µmol, 0.05 eq), and 0.6 mg CuI (3 µmol, 0.01 eq) were coupled in a Schlenk flask in 15 mL TEA and 30 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->20% acetone/$CHCl_3$ to obtain an orange solid (350 mg, 87%). ^1H NMR ($CDCl_3$): δ 8.294 (d, 1H, phenyl H, J = 1.8), 8.252 (d, 1H, phenyl H, J = 1.8), 8.179 (d, 1H, phenyl H, J = 1.8), 8.015 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.987 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.897 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.621 (d, 1H, phenyl H, J = 8.4), 7.593 (d, 1H, phenyl H, J = 8.4), 7.522 (d, 1H, phenyl H, J = 8.4), 4.50 (m, 4H, CO_2CH_2), 4.20 (m, 2H, CO_2CH_2), 3.70 (m, 20H, CH_2), 3.52 (m, 4H, CH_2), 3.37 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 1.88 (m, 1H, aliphatic), 1.54 (m, 1H, aliphatic), 1.30 (m, 7H, aliphatic 1H + $N(CH_2\text{-}C\underline{H}_3)_2$), 0.98 (m, 6H, CH_3), 0.29 (s, 9H, $Si(CH_3)_3$) ppm.



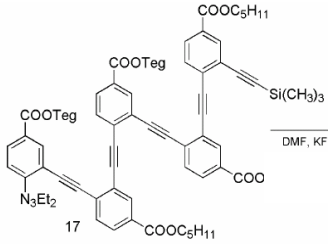
15

Triazene-Es-C5-Es-≡-H (16) The general TMS deprotection procedure, listed above, was used to prepare this compound. 257 mg of **8** (265 µmol, 1.0 eq) and 125 mg of $KF.2H_2O$ (1330 µmol, 5.0 eq) were dissolved in 5 mL of DMF and stirred for 4 hours. The mixture was diluted with 25 mL $CHCl_3$ and washed with 15 mL of H_2O and 15 mL of saturated $CaCl_2$ before evaporation to give an orange oil which was taken directly on to **17** without further purification.



16

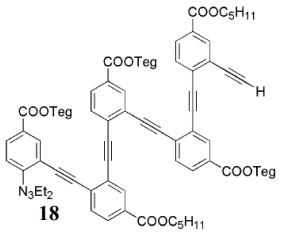
Triazene-Es-C^5-Es-Es-C^5-TMS (17) This compound was prepared by the general Sonogashira procedure described above. 265 µmol of **16** (1.0 eq),



17

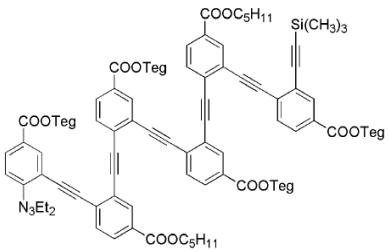
187 mg of **14** (265 µmol, 1.0 eq), 9.3 mg of $Pd(P\phi_3)_2Cl_2$ (14 µmol, 0.05 eq), and 0.5 mg CuI (2.7 µmol, 0.01 eq) were coupled in a Schlenk flask in 15 mL TEA and 30 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->30% acetone/$CHCl_3$ to obtain an orange solid (158 mg, 38%). ^{1}H NMR ($CDCl_3$): δ 8.299 (d, 1H, phenyl H, J = 1.8), 8.158 (d, 2H, phenyl H, J = 1.8), 8.118 (d, 1H, phenyl H, J = 1.8), 8.088 (d, 1H, phenyl H, J = 1.8), 8.008 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.941 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.910 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.867 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.900 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.699 (d, 1H, phenyl H, J = 8.4), 7.569 (d, 1H, phenyl H, J = 8.4), 7.557 (d, 2H, phenyl H, J = 8.4), 7.424 (d, 1H, phenyl H, J = 8.4), 4.48 (m, 4H, CO_2CH_2), 4.42 (m, 2H, CO_2CH_2), 4.16 (m, 4H, CO_2CH_2), 3.70 (m, 28H, CH_2), 3.52 (m, 6H, CH_2), 3.369 (s, 3H, OCH_3), 3.348 (s, 3H, OCH_3), 3.343 (s, 3H, OCH_3), 1.84 (m, 2H, aliphatic), 1.52 (m, 2H, aliphatic), 1.30 (m, 8H, aliphatic 2H + $N(CH_2\text{-}C\underline{H}_3)_2$), 0.98 (m, 12H, CH3), 0.27 (s, 9H, $Si(CH_3)_3$)) ppm.

Triazene-Es-C^5-Es-Es-C^5-≡-H (18) The general TMS deprotection procedure, listed above, was used to prepare this compound. 158 mg of **17** (107 µmol, 1.0 eq) and 47 mg of $KF.2H_2O$ (500 µmol, 4.7 eq) were dissolved in 5 mL of DMF and stirred for 4 hours. The mixture was diluted with 25 mL $CHCl_3$ and washed with 15 mL of H_2O and 15 mL of saturated $CaCl_2$ before evaporation to give an orange oil which was taken directly on to **1** or to **19** without further purification.



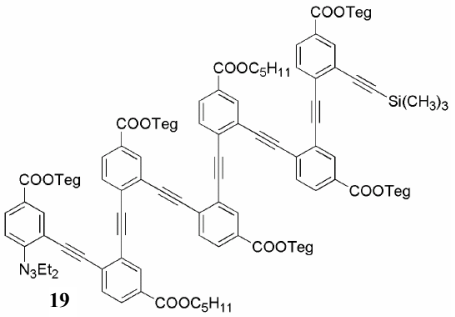
18

Triazene-Es-C^5-Es-Es-C^5-Es-TMS (1) This compound was prepared by the general Sonogashira procedure described above. 70 µmol of **18** (1.0 eq), 77 mg of **3** (77 µmol, 1.1 eq), 2.4 mg of $Pd(P\phi_3)_2Cl_2$ (4 µmol, 0.05 eq), and 0.1 mg CuI (0.7 µmol, 0.01 eq) were coupled in a Schlenk flask in 15 mL TEA and 30 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->40% acetone/$CHCl_3$ to obtain an orange solid (74 mg, 59%). ^{1}H NMR ($CDCl_3$): δ 8.179 (d, 1H, phenyl H, J = 1.8), 8.107 (d, 1H, phenyl H, J = 1.8), 8.057 (d, 1H, phenyl H, J = 1.8), 8.022 (d, 1H, phenyl H, J = 1.8), 8.008 (d, 1H, phenyl H, J = 1.8), 7.948 (d, 1H, phenyl H, J = 1.8), 7.919 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.863 (dd, 5H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.625 (d, 1H, phenyl H, J = 8.4), 7.522 (d, 1H, phenyl H, J = 8.4), 7.477 (d, 1H, phenyl H, J = 8.4), 7.416 (d, 1H, phenyl H, J = 8.4), 7.403 (d, 1H, phenyl H, J = 8.4), 7.368 (d, 1H, phenyl H, J = 8.4), 4.48 (m, 6H, CO_2CH_2), 4.41 (m, 2H, CO_2CH_2), 4.12 (m, 6H, CO_2CH_2), 3.70 (m, 34H, CH_2), 3.52 (m, 10H, CH_2), 3.365 (s, 3H, OCH_3), 3.360 (s, 3H, OCH_3), 3.350 (s, 3H, OCH_3), 3.338 (s, 3H, OCH_3), 1.84 (m, 2H, aliphatic), 1.52 (m, 2H, aliphatic), 1.30 (m, 8H, aliphatic 2H + $N(CH_2\text{-}C\underline{H}_3)_2$), 0.98 (m, 12H, CH_3), 0.28 (s, 9H, $Si(CH_3)_3$)) ppm. ^{13}C NMR ($CDCl_3$): δ 165.64 (CO_2), 165.19 (CO_2), 165.09 (CO_2), 165.04 (CO_2), 165.00 (CO_2), 164.95 (CO_2), 155.55 (C-N_3Et_2), 135.021, 133.202, 133.084, 133.015, 132.723, 132.390, 132.144, 132.050, 131.702, 130.573, 130.538, 129.848, 129.825, 129.629, 129.485, 129.444, 129.387, 129.327, 129.298, 129.247, 129.106, 129.006, 128.966, 128.886, 125.736, 125.581, 125.397, 125.344, 125.246, 124.923, 117,451, 116,356, 102,303, 100,006 (C≡), 99,953 (C≡), 94.963 (C≡), 94.820 (C≡), 94.335 (C≡), 94.116 (C≡), 94.096 (C≡), 92.246 (C≡), 92.119 (C≡), 91.940 (C≡), 91.873 (C≡), 71.887, 70.623, 70.594,



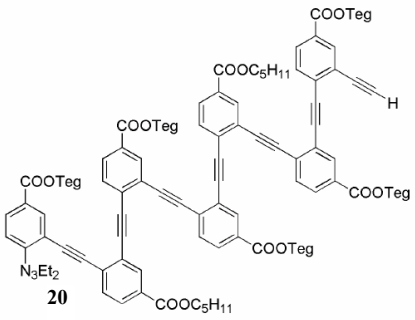
1

70.552, 70.511, 69.927, 69.830, 69.156, 69.083, 69.052, 64.343, 64.291, 63.900, 58.984, 49.322, 42.095, 34.218, 34.171, 26.084, 16.491, 16.414, 14.315, 11.277, 11.205, 11.184, 10.886, 0.023 ($Si(CH_3)_3$) ppm. MALDI *m/z* = 1786 ($m + Na^+$), 1803 ($m + K^+$).



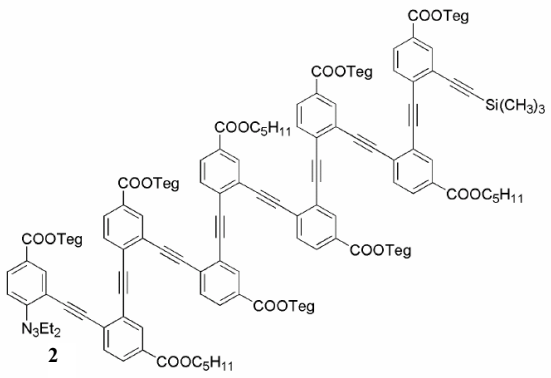
19

Triazene-Es-C^5-Es-Es-C^5-Es-Es-TMS (19) This compound was prepared by the general Sonogashira procedure described above. 107 µmol of **18** (1.0 eq), 83 mg of **5** (107 µmol, 1.0 eq), 3.8 mg of $Pd(P\phi_3)_2Cl_2$ (5.4 µmol, 0.05 eq), and 0.2 mg CuI (1.1 µmol, 0.01 eq) were coupled in a Schlenk flask in 15 mL TEA and 30 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->40% acetone/$CHCl_3$ to obtain an orange solid (94 mg, 43%). ^1H NMR ($CDCl_3$): δ 8.172 (d, 1H, phenyl H, J = 1.8), 8.116 (d, 1H, phenyl H, J = 1.8), 8.078 (d, 1H, phenyl H, J = 1.8), 7.980 (d, 1H, phenyl H, J = 1.8), 7.900 (d, 1H, phenyl H, J = 1.8), 7.875 (d, 1H, phenyl H, J = 1.8), 7.853 (d, 1H, phenyl H, J = 1.8), 7.825 (d, 2H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.756 (d, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.720 (d, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.681 (d, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.362 (d, 2H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.596 (d, 1H, phenyl H, J = 8.4), 7.474 (d, 1H, phenyl H, J = 8.4), 7.447 (d, 1H, phenyl H, J = 8.4), 7.378 (d, 1H, phenyl H, J = 8.4), 7.312 (d, 1H, phenyl H, J = 8.4), 7.292 (d, 1H, phenyl H, J = 8.4), 7.272 (d, 1H, phenyl H, J = 8.4) [only downfield side of doublet visible], 4.48 (m, 10H, CO_2CH_3), 4.10 (m, 4H, CO_2CH_3), 3.8 (m, 6H, CH_2), 3.7 (m, 36H, CH_2), 3.5 (m, 12H, CH_2), 3.368 (s, 6H, OCH_3), 3.353 (s, 3H, OCH_3), 3.345 (s, 3H, OCH_3), 3.340 (s, 3H, OCH_3), 1.84 (m, 2H, aliphatic), 1.52 (m, 2H, aliphatic), 1.3 (m, 8H, aliphatic 2H + $N(CH_2\text{-}CH_3)_2$), 0.98 (m, 12H, CH_3), 0.29 (s, 9H, $Si(CH_3)_3$) ppm.



20

Triazene-Es-C^5-Es-Es-C^5-Es-Es-≡-H (20) The general TMS deprotection procedure, listed above, was used to prepare this compound. 94 mg of **19** (45.8 µmol, 1.0 eq) and 21 mg of $KF.2H_2O$ (229 µmol, 5.0 eq) were dissolved in 2 mL of DMF and stirred for 4 hours. The mixture was diluted with 10 mL $CHCl_3$ and washed with 5 mL of H_2O and 5 mL of saturated $CaCl_2$ before evaporation to give an orange oil which was taken directly on to **2** without further purification.



2

Triazene-Es-C^5-Es-Es-C^5-Es-Es-C^5-Es-TMS (2) This compound was prepared by the general Sonogashira procedure described above. 45.8 µmol of **20** (1.0 eq), 33 mg of **12** (45.8 µmol, 1.0 eq), 1.6 mg of $Pd(P\phi_3)_2Cl_2$ (2.3 µmol, 0.05 eq), and 0.1 mg CuI (0.5 µmol, 0.01 eq) were coupled in a Schlenk flask in 15 mL TEA and 30 mL THF. The reaction was heated at 55°C overnight, worked up as

described in the general procedure, and purified by flash chromatography in 0->40% acetone/$CHCl_3$ to obtain an orange solid (55 mg, 47%). ^{1}H NMR (CD_3CN): δ 7.949 (d, 1H, phenyl H, J = 1.8), 7.855 (d, 1H, phenyl H, J = 1.8), 7.821 (d, 1H, phenyl H, J = 1.8), 7.773 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.761 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.753 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.722 (d, 2H, phenyl H, J = 1.8), 7.710 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.562 (d, 1H, phenyl H, J = 1.8), 7.545 (d, 1H, phenyl H, J = 1.8), 7.526 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.524 (d, 1H, phenyl H, J = 8.4), 7.463 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.451 (d, 1H, phenyl H, J = 1.8), 7.440 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.397 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.370 (dd, 1H, phenyl H, J_1 = 1.8 J_2 = 8.4), 7.346 (d, 1H, phenyl H, J = 8.4), 7.326 (d, 1H, phenyl H, J = 8.4), 7.325 (d, 1H, phenyl H, J = 1.8), 7.265 (d, 1H, phenyl H, J = 8.4), 7.099 (d, 1H, phenyl H, J = 8.4), 7.079 (d, 2H, phenyl H, J = 8.4), 7.058 (d, 1H, phenyl H, J = 8.4), 6.950 (d, 1H, phenyl H, J = 8.4), 4.40 (m, 12H, CO_2CH_2), 4.10 (m, 6H, CO_2CH_2), 3.60 (m, 64H, CH_2), 3.311 (s, 3H, OCH_3), 3.297 (s, 3H, OCH_3), 3.292 (s, 3H, OCH_3), 3.260 (s, 3H, OCH_3), 3.240 (s, 3H, OCH_3), 3.224 (s, 3H, OCH_3), 1.8 (m, 3H, aliphatic), 1.5 (m, 3H, aliphatic), 1.2 (m, 9H, aliphatic 3H + $N(CH_2\text{-}CH_3)_2$), 1.0 (m, 18H, CH_3), 0.25 (m, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 165.693, 165.251, 165.150, 165.092, 165.060, 165.012, 155.608, 135.074, 133.255, 133.138, 133.068, 132.776, 132.443, 132.197, 132.104, 131.755, 130.626, 130.591, 129.901, 129.878, 129.538, 129.497, 129.440, 129.380, 129.352, 129.300, 129.159, 129.060, 129.019, 128.940, 125.789, 125.634, 125.450, 125.397, 125.299, 124.976, 117.505, 116.409, 102.356, 100.059, 95.016, 94.873, 94.389, 94.170, 94.149, 92.299, 92.172, 91.994, 91.926, 71.940, 70.676, 70.647, 70.605, 70.564, 69.981, 69.883, 69.209, 69.136, 69.105, 64.396, 64.344, 63.953, 59.037, 49.375, 42.148, 34.271, 34.224, 26.137, 16.544, 16.467, 14.367, 11.258, 10.939, 0.055 ppm. MALDI *m/z* = 2581 ($m + Na^+$), 2598 ($m + K^+$).

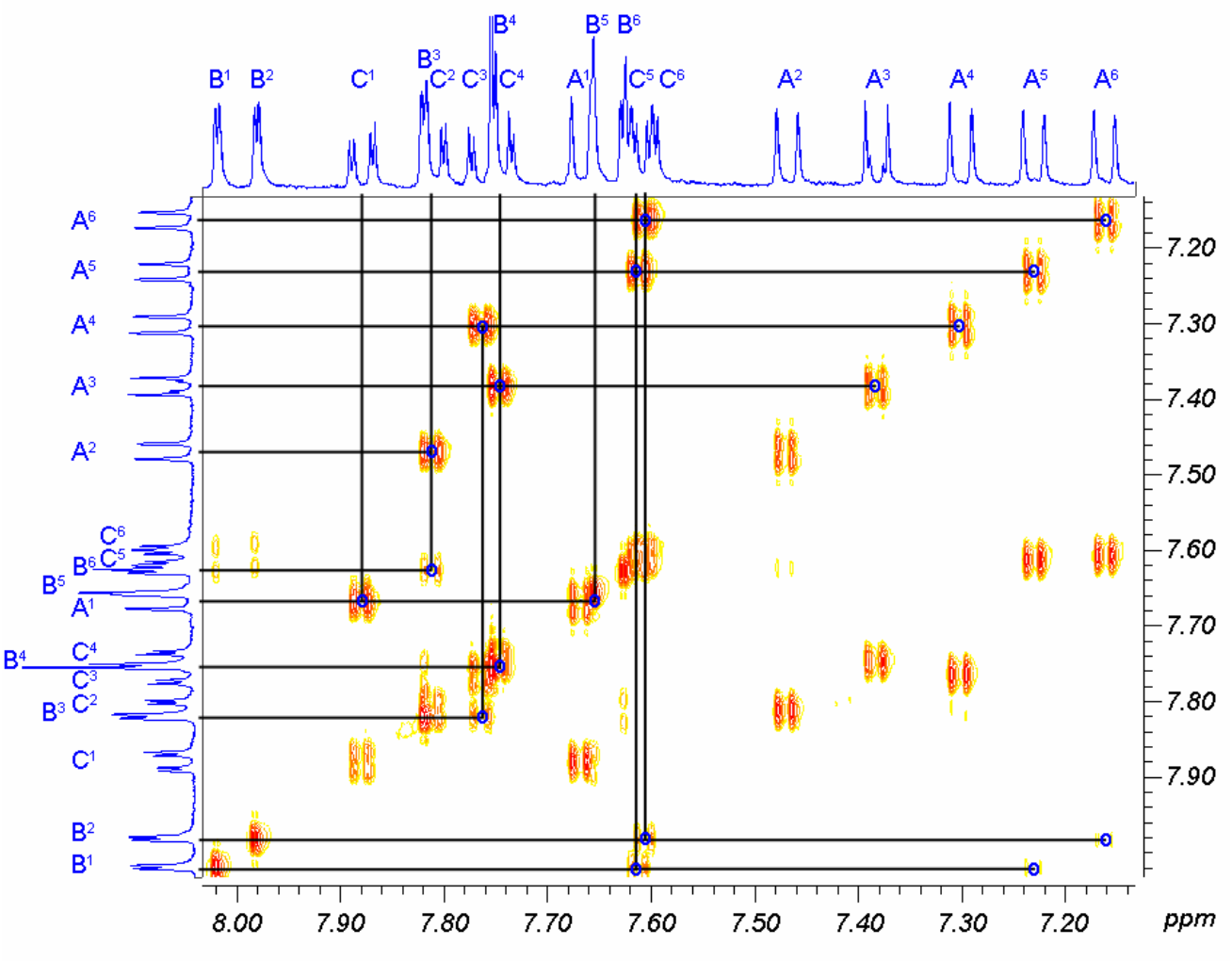


Figure S1: Aromatic region of GCOSY of **1** in CD_3CN, 1.25 mm.

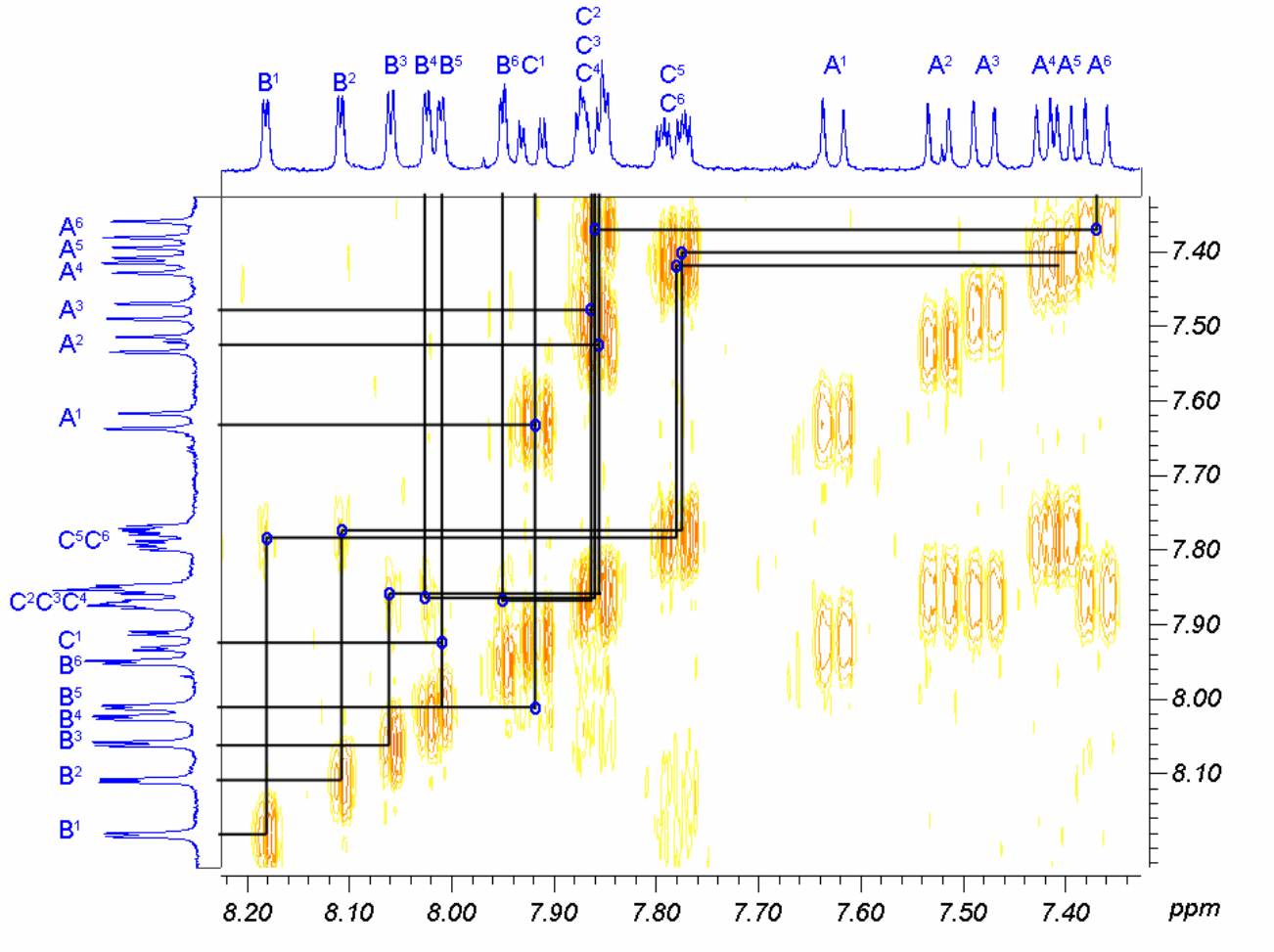


Figure S2: Aromatic region of GCOSY of **1** in $CDCl_3$, 1.25 mm.

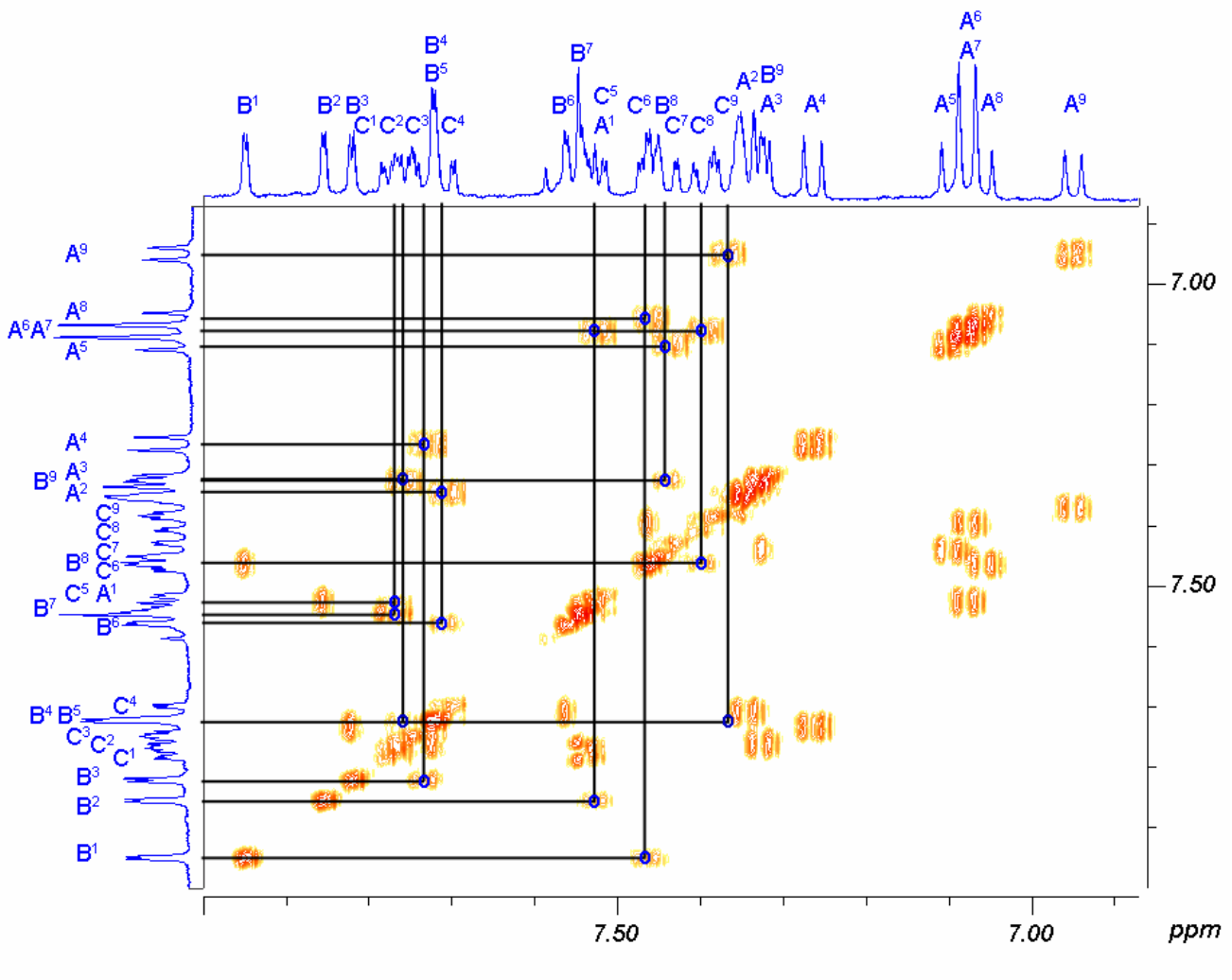


Figure S3: Aromatic region of GCOSY of **2** in CD_3CN, 1.25 mm.

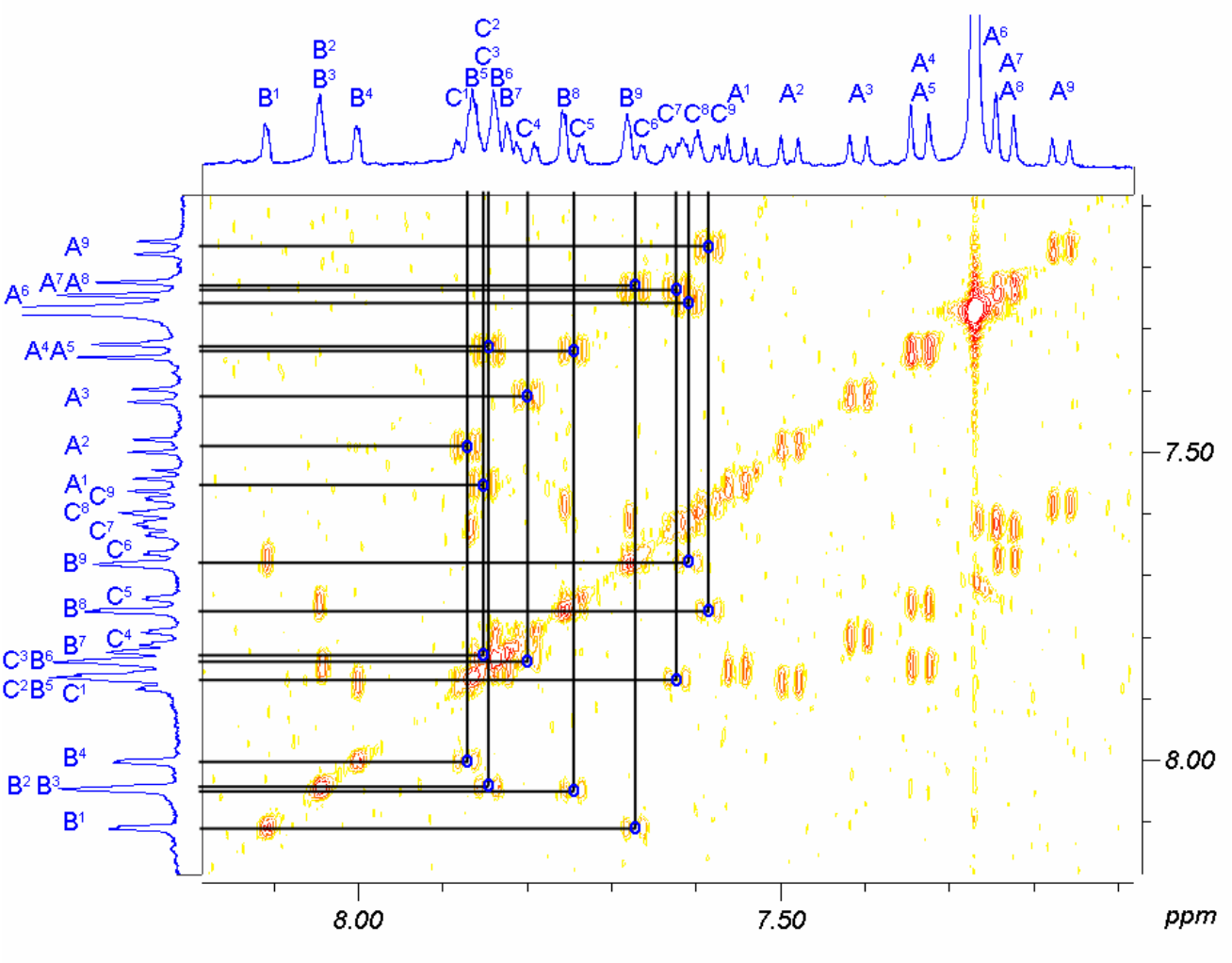


Figure S4: Aromatic region of GCOSY of **2** in $CDCl_3$, 1.25 mm.