

## Supporting Information

# Shape-Persistent Fluorescent Tetraphenylmethane Dendrimers

Julio I. Urzúa,<sup>a,†</sup> María Regueira,<sup>a</sup> Massimo Lazzari<sup>b</sup> and Mercedes Torneiro<sup>a,\*</sup>

<sup>a</sup> Departamento de Química Orgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.

<sup>b</sup> Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Física, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.

mercedes.torneiro@usc.es

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## General methods and materials

All reagents were used as purchased from commercial sources without further purification. Solvents were dried using standard techniques prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone, methylene chloride was distilled from calcium hydride and piperidine from phosphorus pentoxide. All reactions involving oxygen or moisture sensitive compounds were carried out under a dry argon (L-50) atmosphere using oven-dried glassware. Reaction temperatures refer to external bath temperatures. Organic extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated using a rotary evaporator. Reactions were monitored by thin-layer chromatography using aluminum-backed silica gel plates (0.2 mm thickness); the chromatograms were visualized with ultraviolet light (254 nm). Preparative TLC was performed with silica gel 60  $F_{254}$  glass plates (Merk, 20x20 cm). Flash chromatography was performed with silica gel (230-400 mesh). Preparative-scale size-exclusion chromatography (SEC) was performed with BioRad Bio-beads SX-1 using a glass column (4 x 150 cm) under gravity flow.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AMX-500 (11.74 T, 500 MHz for  $^1\text{H}$  and 126 MHz for  $^{13}\text{C}$ ) and Bruker WM-250 (5.87 T, 250 MHz for  $^1\text{H}$  and 63 MHz for  $^{13}\text{C}$ ) NMR spectrometers using the residual proton or carbon signal of the deuterated solvent as an internal standard. Distortionless Enhancement by Polarization Transfer (DEPT) was used to assign carbon types. Low resolution mass spectra were acquired on a Hewlett-Packard HP5988A electron impact (EI) quadrupole mass spectrometer. High resolution mass spectra were acquired on an Autospec Micromass electron impact (EI) spectrometer. MALDI-TOF mass spectra were recorded on a Bruker Ultraflex III TOF/TOF spectrometer using dithranol/AgTFA as the matrix. Elemental analysis was performed on a macro sample CHNS Leco TruSpec CHNS model apparatus. Analytical-scale SEC (GPC) and micropreparative SEC were performed at room temperature in a PL-GPC 50 Integrated GPC/SEC System (Agilent) with a PLgel 3  $\mu\text{m}$  MIXED-E (100-30000 Da) column calibrated by polystyrene standards and a differential refractometer as detector, with THF as eluent (1.0 mL/min). Dynamic light scattering was recorded in an ALV-5000 digital full correlator (ALV, Langen, Germany) at a scattering angle  $\theta = 90^\circ$  using an Sapphire CDRH HP 488-500 (Coherent) laser operating at  $\lambda = 488$  nm and 10 mW at 30 °C. Data analysis was performed using the CONTIN inverse Laplace fitting routine. The resulting distribution of radii was normalized by mass. Sample solutions for DLS were prepared in pure THF at 1 mg/mL, were filtered through 0.2  $\mu\text{m}$  porosity PTFE filters, and were allowed to equilibrate for 1 day. The morphology of aggregates was examined using Zeiss model ULTRA Plus Field Emission Scanning Electron Microscopy (FE-SEM). Samples were prepared by spin coating 20  $\mu\text{L}$  of solution previously filtered through 0.45  $\mu\text{m}$  porosity PTFE filters at 1 mg/mL concentration onto a silicon wafer Silicon wafers (5 x 5 mm) were first cleaned in an ultrasonic bath for 15 min with acetone and Milli-Q water 1/1 (v/v). AFM experiments were performed for the same samples on a Multimode Nanoscope III (Digital Instrument), with a Cantilever NCHR (10 nm diameter) in dynamic no contact mode. UV-vis spectra were recorded in a Thermo Scientific Evolution 300 spectrophotometer, and fluorescence studies were performed on a Agilent Varian Cary Eclipse fluorimeter. In both cases quartz Hellma cells were used (1 cm). Quantum yields were determined by the comparative method,<sup>1</sup> using quinine sulfate 0.5 M in  $\text{H}_2\text{SO}_4$  as the standard.<sup>2</sup>

## Synthetic procedures

**Trimethyl((4-(tris(4-methoxyphenyl)methyl)phenyl)ethynyl)silane (7).** A Schlenk tube equipped with a stirring bar was charged with **6**<sup>3</sup> (267 mg, 0.55 mmol), CuI (20 mg, 0.11 mmol) and (Ph<sub>3</sub>P)<sub>4</sub>Pd (63 mg, 0.055 mmol). Anhydrous THF (10 mL), piperidine (0.8 mL, 7.11 mmol) and trimethylsilylacetylene (0.4 mL, 2.74 mmol) were added under argon. The Schlenk tube was sealed with a teflon screw cap and the reaction mixture was stirred at 60 °C for 12 h. The resulting mixture was allowed to reach rt and concentrated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and washed with a saturated solution of NH<sub>4</sub>Cl (3 x 20 mL). The combined organic layer was dried and concentrated to give a residue, which was purified by flash chromatography (5% EtOAc/hexanes) to give **3** as a white solid [205 mg, 0.88 mmol, Rf= 0.60 (30% EtOAc/hexanes), 77%]. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 7.38 (2H, d, J=8.5 Hz, Ar), 7.17 (2H, d, J=8.5 Hz, Ar), 7.09 (6H, d, J=8.9 Hz, Ar<sub>OMe</sub>), 6.80 (6H, d, J=8.9 Hz, Ar<sub>OMe</sub>), 3.80 (9H, s, OMe), 0.27 (9H, s, TMS). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz) δ 157.4 (C), 148.1 (C), 138.9 (C), 131.9 (CH), 130.9 (CH), 130.7 (CH), 120.3 (C), 112.6 (CH), 105.0 (C), 93.97 (C), 62.8 (C), 55.0 (CH<sub>3</sub>), 0.0 (CH<sub>3</sub>). **MS** (CI, m/z, %) 507 ([MH]<sup>+</sup>, 94), 506 ([M]<sup>+</sup>, 36), 435 ([MH-TMS]<sup>+</sup>, 8). **EA** (C<sub>33</sub>H<sub>34</sub>O<sub>3</sub>Si) calcd. C 78.22%, H 6.76%; found C 78.36%, H 7.07%.

**(4-(tris(4-methoxyphenyl)methyl)phenyl)ethyne (3).** An aqueous solution of sodium hydroxide (10 mL, 1.0 M) was added to a solution of **7** (480 mg, 0.95 mmol) in THF (25 mL) and the reaction mixture was stirred for 12 h. Then, HCl (40 mL, 10%) was added and the aqueous layer was extracted with EtOAc (3 x 25 mL). The combined organic layer was dried and concentrated to give a residue, which was purified by flash chromatography (10% EtOAc/hexanes) to give **3** as a white solid [400 mg, 0.92 mmol, Rf= 0.55 (30% EtOAc/hexanes), 98%]. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 7.39 (2H, d, J=8.4 Hz, Ar), 7.18 (2H, d, J=8.4 Hz, Ar), 7.09 (6H, d, J=8.9 Hz, Ar<sub>OMe</sub>), 6.80 (6H, d, J=8.9 Hz, Ar<sub>OMe</sub>), 3.79 (9H, s, OMe), 3.06 (1H, s, C≡C-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz) δ 157.6 (C), 148.6 (C), 139.0 (C), 132.0 (CH), 131.3 (CH), 131.0 (CH), 119.5 (C), 112.8 (CH), 83.7 (C), 77.0 (CH), 62.9 (C), 55.3 (CH<sub>3</sub>). **MS** (EI, m/z, %) 434 (M<sup>+</sup>, 99), 327 ([M-C<sub>7</sub>H<sub>7</sub>O]<sup>+</sup>, 100). **HRMS** (EI) calcd. For C<sub>30</sub>H<sub>26</sub>O<sub>3</sub><sup>+</sup> (M<sup>+</sup>) 434.1882, found 434.1881.

**Trimethyl((4-(tris(4-iodophenyl)methyl)phenyl)ethynyl)silane (4).** A round bottom flask equipped with a stirring bar and a condenser was charged with **5**<sup>4</sup> (1.0 g, 1.21 mmol), CuI (50 mg, 0.24 mmol) and (Ph<sub>3</sub>P)<sub>4</sub>Pd (140 mg, 0.12 mmol). Anhydrous THF (100 mL) was added under argon and the mixture was heated at reflux until obtaining a homogeneous solution, which was cooled to rt. Then, trimethylsilylacetylene (0.13 mL, 0.97 mmol) was added and the resulting mixture was stirred at rt for 1 h and then concentrated. CHCl<sub>3</sub> (50 mL) was added to the resulting solid residue and the mixture was refluxed for 3 h. The suspended solid was collected by filtration to recover **5** (50 mg, 5%) and the filtrate was concentrated to give a residue, which was purified by flash chromatography (hexanes) to give **4** as a white solid [336 mg, 0.42 mmol, Rf= 0.57 (hexanes), 35%]. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 7.57 (6H, d, J=8.6 Hz, Ar<sub>I</sub>), 7.36 (2H, d, J=8.5 Hz, Ar), 7.08 (2H, d, J=8.5 Hz, Ar), 6.88 (6H, d, J=8.6 Hz, Ar<sub>I</sub>), 0.24 (9H, s, TMS). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz) δ 145.5 (C), 145.1 (C), 136.9 (CH), 132.6 (CH), 131.5 (CH), 130.4 (CH), 121.3 (C), 104.3 (C), 94.9 (C), 92.4 (C), 64.1 (C), 0.10 (CH<sub>3</sub>). **EA** (C<sub>30</sub>H<sub>25</sub>I<sub>3</sub>Si) calcd. C 45.36%, H 3.17%; found C 45.43%, H 3.31%.

**Dendrimer 1.** A Schlenk tube equipped with a stirring bar was charged with **5**<sup>4</sup> (181 mg, 0.22 mmol), freshly prepared **3** (477 mg, 1.1 mmol), CuI (8 mg, 0.044 mmol) and (Ph<sub>3</sub>P)<sub>4</sub>Pd (102 mg, 0.088 mmol). Anhydrous THF (15 mL) and piperidine (0.33 mL, 2.86 mmol) were added under argon. The Schlenk tube was sealed with a teflon screw cap and the reaction mixture was stirred at 80 °C during 12 h. The resulting mixture was allowed to reach rt and concentrated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed with a saturated solution of NH<sub>4</sub>Cl (3 x 30 mL). The organic layer was dried and concentrated to give a residue, which was purified by flash chromatography (90-100% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give **1** as a white solid [405 mg, 0.20 mmol, Rf= 0.60 (80% CH<sub>2</sub>Cl<sub>2</sub>/hexanes), 90%]. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.40 (16H, m, Ar), 7.17 (16H, m, Ar), 7.07 (24H, d, J=8.9 Hz, Ar<sub>OMe</sub>), 6.78 (24H, d, J=8.9 Hz, Ar<sub>OMe</sub>), 3.79 (36H, s, OMe). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz) δ 157.5 (C), 148.0 (C), 145.8 (C), 139.0 (C), 131.9 (CH), 130.9 (CH), 130.6 (CH), 121.2 (C), 120.31 (C), 112.7 (CH), 89.7 (C), 88.8 (C), 62.8 (C), 55.1 (CH<sub>3</sub>). **MS** (MALDI-TOF, m/z) 2374 ([MAG + 3THF]<sup>+</sup>), 2302 ([MAG + 2THF]<sup>+</sup>), 2230 ([MAG + THF]<sup>+</sup>), 2158 (MAG<sup>+</sup>), 1943 ([M-C<sub>7</sub>H<sub>7</sub>O]<sup>+</sup>), 1541 ([M-C<sub>36</sub>H<sub>29</sub>O<sub>3</sub>]<sup>+</sup>). **EA** (C<sub>145</sub>H<sub>116</sub>O<sub>12</sub>) calcd. C 84.93%, H 5.70%; found C 84.86%, H 5.58%.

**TMS-Protected Dendron 8.** A Schlenk tube equipped with a stirring bar was charged with **3** (1.2 g, 2.76 mmol), **4** (556 mg, 0.70 mmol), CuI (13 mg, 0.07 mmol) and (Ph<sub>3</sub>P)<sub>4</sub>Pd (243 mg, 0.21 mmol). Anhydrous THF (20 mL) and piperidine (1.05 mL, 9.1 mmol) were added under argon. The Schlenk tube was sealed with a teflon screw cap and the reaction mixture was stirred at 80 °C during 12 h. The resulting mixture was allowed reach rt and concentrated. The residue was dissolved in EtOAc (20 mL) and washed with a

saturated solution of  $\text{NH}_4\text{Cl}$  (3 x 20 mL). The organic layer was dried and concentrated to give a residue, which was purified by flash chromatography (80%  $\text{CH}_2\text{Cl}_2$ /hexanes) to give **8** as a white solid [918 mg, 0.56 mmol, Rf= 0.42 (70%  $\text{CH}_2\text{Cl}_2$ /hexanes), 80%].  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  7.39 (14H, m, Ar), 7.21 (14H, m, Ar), 7.11 (18H, d,  $J=8.0$  Hz,  $\text{Ar}_{\text{OMe}}$ ), 6.80 (18H, d,  $J=8.0$  Hz,  $\text{Ar}_{\text{OMe}}$ ), 3.79 (27H, s, OMe), 0.26 (9H, s, TMS).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 63 MHz)  $\delta$  157.8 (C), 148.4 (C), 146.1 (C), 139.4 (C), 132.3 (CH), 131.4 (CH), 131.3 (CH), 131.2 (CH), 131.0 (CH), 121.7 (C), 120.8 (C), 113.1 (CH), 90.1 (C), 89.2 (C), 65.1 (C), 63.2 (C), 55.5 ( $\text{CH}_3$ ), 0.31 (TMS). **MS** (MALDI-TOF,  $m/z$ ) 1822 ( $\text{MAG}^+$ ), 1607 ( $[\text{M}-\text{C}_7\text{H}_7\text{O}]^+$ ).

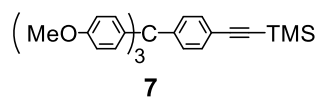
**Dendron 9.** TBAF (0.4 mL, 0.396 mmol, 1.0 M in THF) was added to a solution of **8** (179 mg, 0.10 mmol) in anhydrous THF (20 mL) and the reaction mixture was stirred for 12 h under argon. The resulting mixture was concentrated and the residue was dissolved in EtOAc (10 mL) and washed with a saturated solution of  $\text{NH}_4\text{Cl}$  (3 x 15 mL). The organic layer was dried and concentrated to give a residue, which was purified by flash chromatography (70%  $\text{CH}_2\text{Cl}_2$ /hexanes) to give **9** as a white solid [100 mg, 0.064 mmol Rf= 0.37 (70%  $\text{CH}_2\text{Cl}_2$ /hexanes), 98%].  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  7.43 (14H, m, Ar), 7.21 (14H, d,  $J=7.3$  Hz, Ar), 7.11 (18H, d,  $J=8.9$  Hz,  $\text{Ar}_{\text{OMe}}$ ), 6.81 (18H, d,  $J=8.9$  Hz,  $\text{Ar}_{\text{OMe}}$ ), 3.80 (27H, s, OMe), 3.09 (1H, s,  $\text{C}\equiv\text{CH}$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 63 MHz)  $\delta$  157.6 (C), 148.2 (C), 145.8 (C), 139.2 (C), 132.1 (CH), 131.2 (CH), 131.1 (CH), 130.9 (CH), 130.8 (CH), 121.5 (C), 120.6 (C), 112.8 (CH), 89.9 (C), 88.9 (C), 83.4 (C), 77.7 (CH), 64.9 (C), 63.0 (C), 55.3 ( $\text{CH}_3$ ).

**Dendrimer 2.** A Schlenk tube equipped with a stirring bar was charged with **5** (41 mg, 0.048 mmol), freshly prepared **9** (380 mg, 0.23 mmol), CuI (2 mg, 0.0092 mmol) and  $(\text{Ph}_3\text{P})_4\text{Pd}$  (21 mg, 0.018 mmol). Anhydrous THF (10 mL) and piperidine (0.062 mL, 0.62 mmol) were added under argon. The Schlenk tube was sealed with a teflon screw cap and the reaction mixture was stirred at 80 °C during 12 h. The resulting mixture was allowed to reach rt and concentrated. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (20 mL) and washed with a saturated solution of  $\text{NH}_4\text{Cl}$  (3 x 30 mL). The organic layer was dried and concentrated to give a residue, which was purified by SEC (Bio-Beads SX-1, THF) and flash chromatography (1-10% THF/ $\text{CH}_2\text{Cl}_2$ ) to give **2** as a white solid [280 mg, 0.041 mmol, Rf= 0.60 (1% THF/  $\text{CH}_2\text{Cl}_2$ ), 65%].  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.40 (64H, m, Ar), 7.18 (64H, m, Ar), 7.08 (72H, d,  $J=8.9$  Hz,  $\text{Ar}_{\text{OMe}}$ ), 6.78 (72H, d,  $J=8.9$  Hz,  $\text{Ar}_{\text{OMe}}$ ), 3.80 (108H, s, OMe).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 63 MHz)  $\delta$  158.1 (C), 148.7 (C), 146.4 (C), 139.7 (C), 132.6 (CH), 131.7 (CH), 131.6 (CH), 131.5 (CH), 131.3 (CH), 122.0 (C), 121.1 (C), 113.4 (CH), 90.4 (C), 89.9 (C), 89.5 (C), 65.5 (C), 63.5 (C), 55.8 ( $\text{CH}_3$ ). **MS** (MALDI-TOF,  $m/z$ ) 13869 ( $\text{M}_2\text{Ag}^+$ , calcd. 13868), 6988 ( $\text{MAG}^+$ ), 6774 ( $[\text{M}-\text{C}_7\text{H}_7\text{O}]^+$ , calcd. 6673), 6372 ( $[\text{M}-\text{C}_{36}\text{H}_{29}\text{O}_3]^+$ , calcd. 6371).

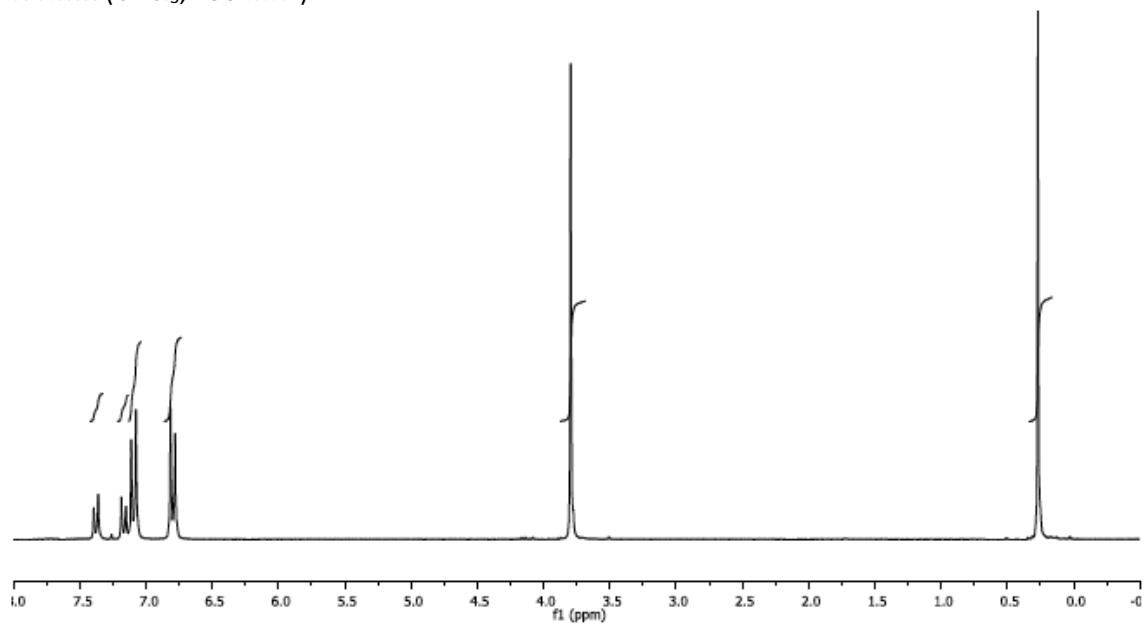
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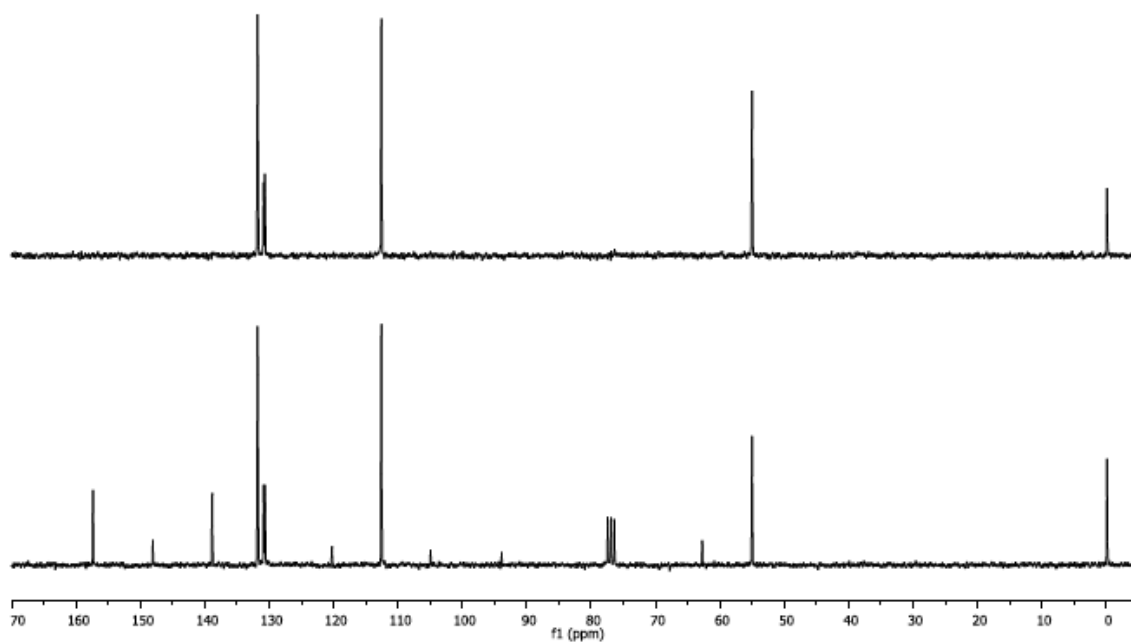
# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR/DEPT spectra

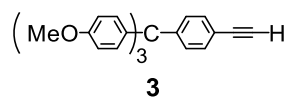


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)

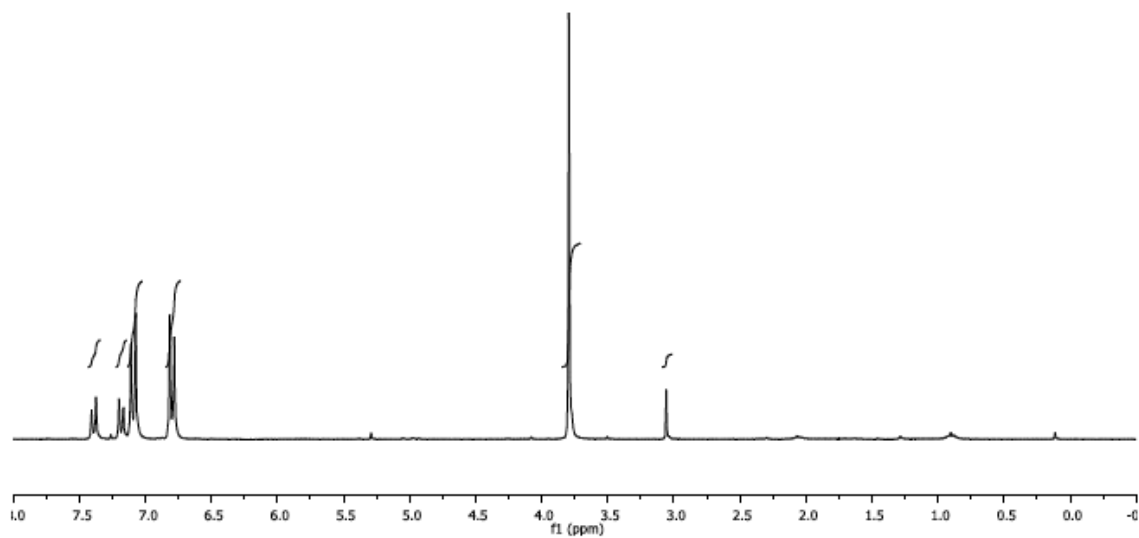


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 63 MHz)

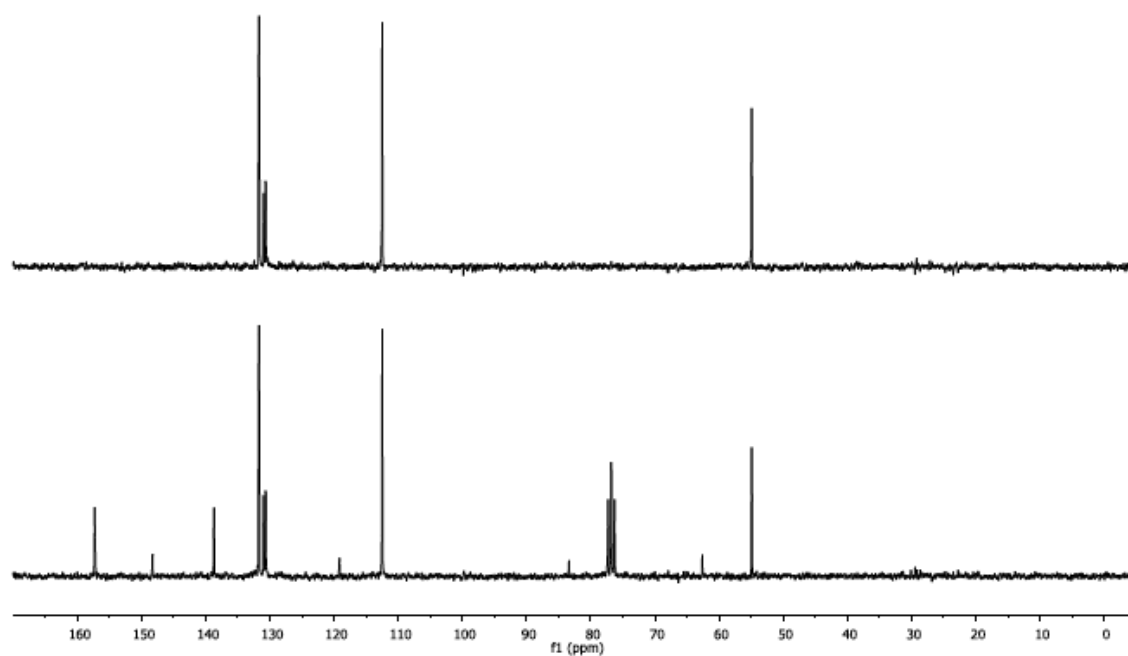


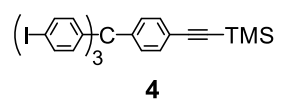


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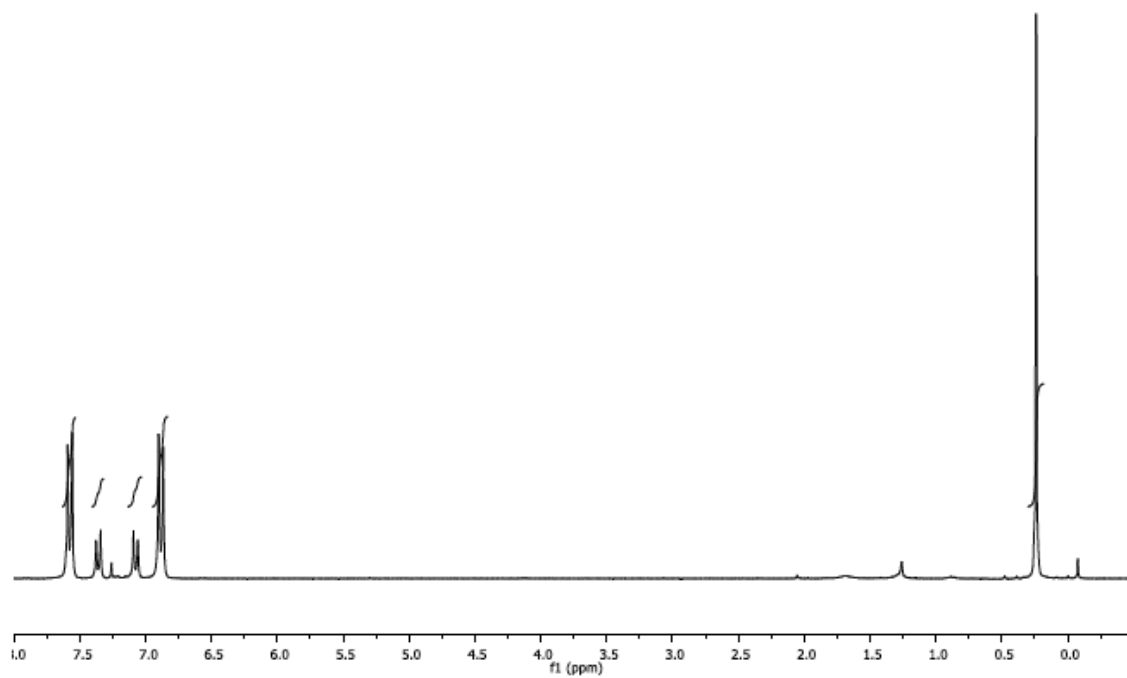


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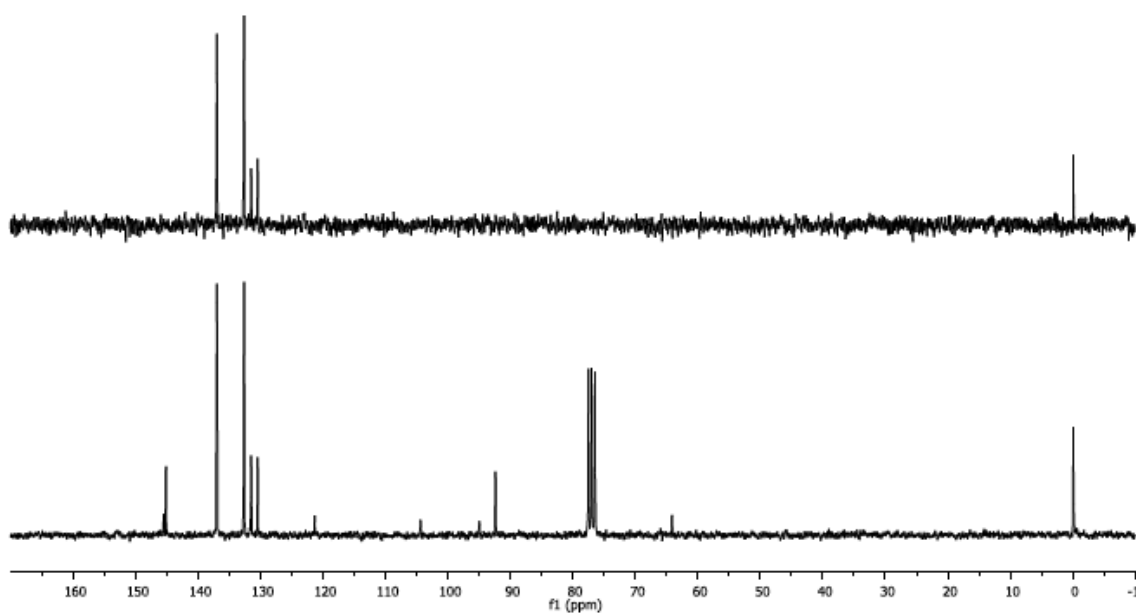


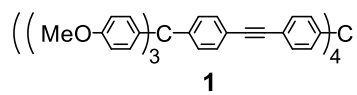


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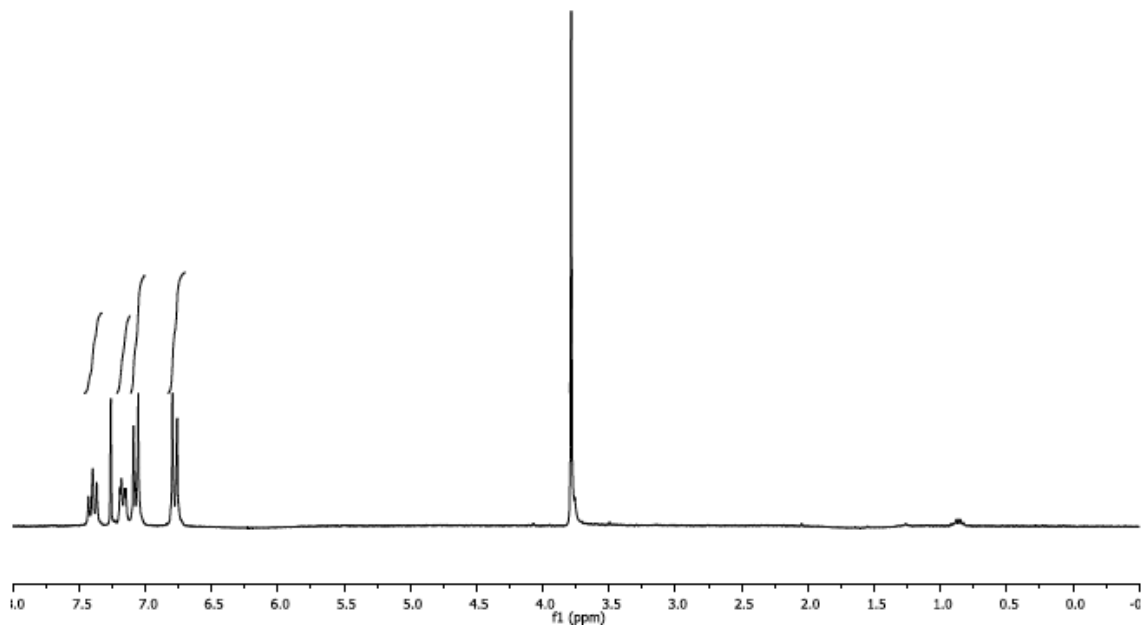


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz)

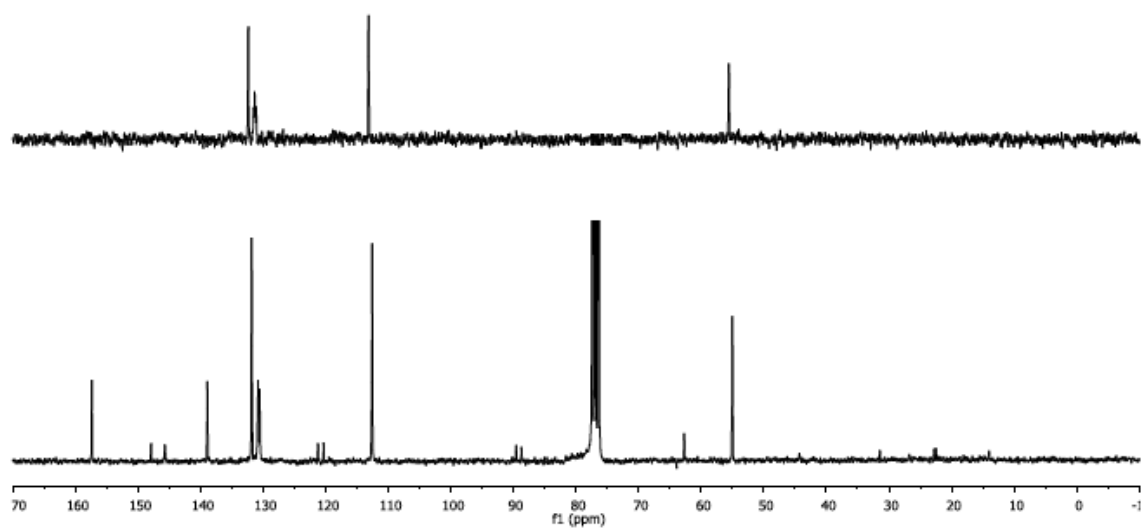




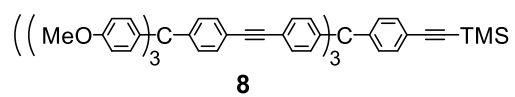
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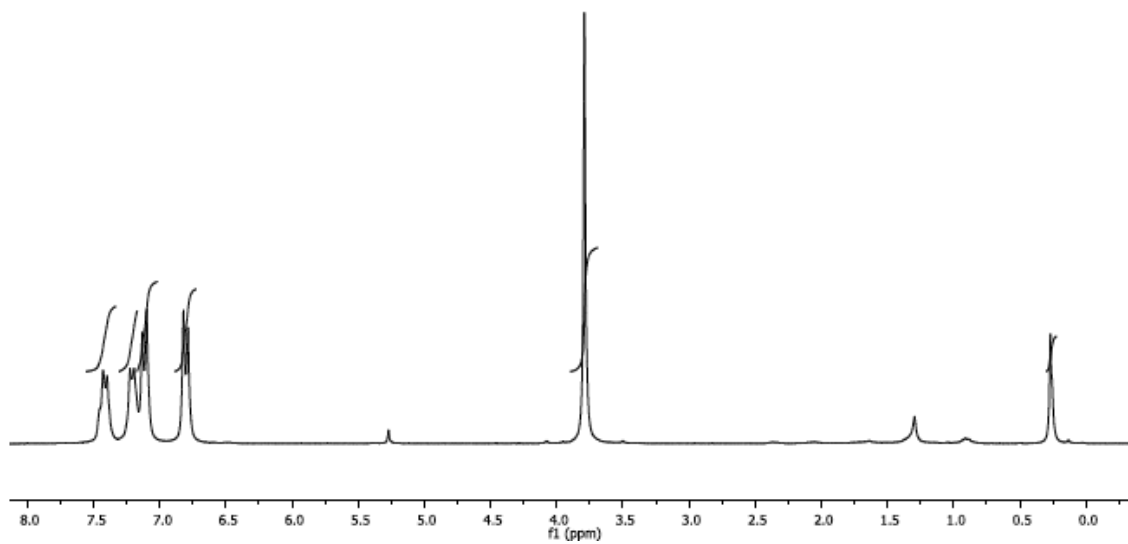
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz)



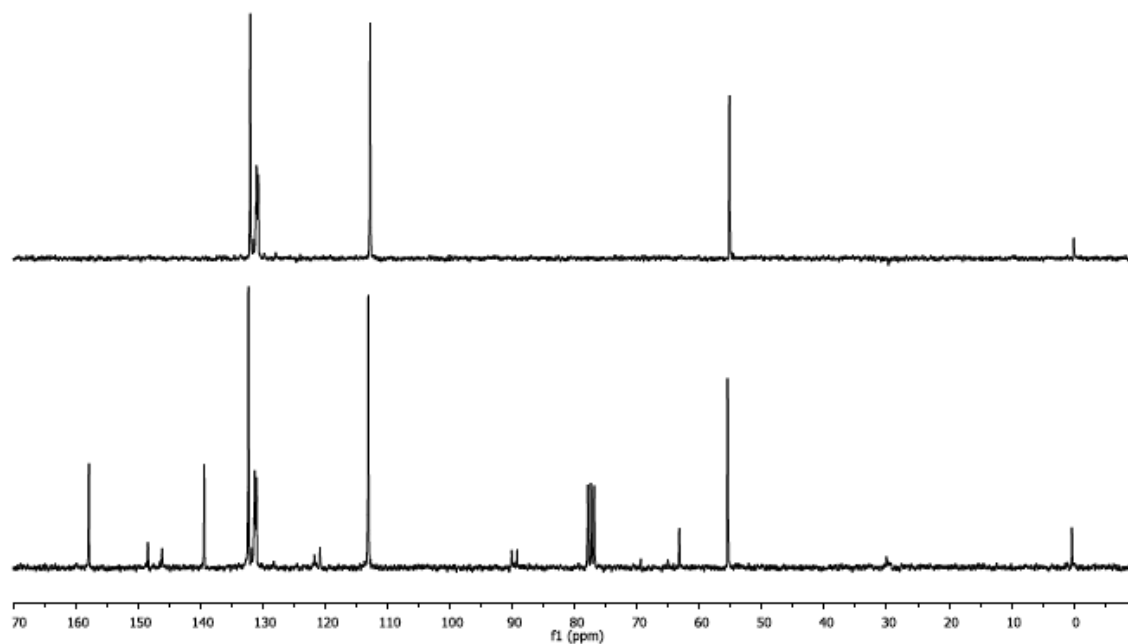


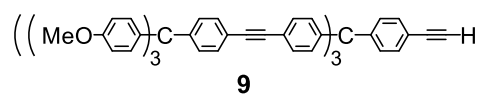


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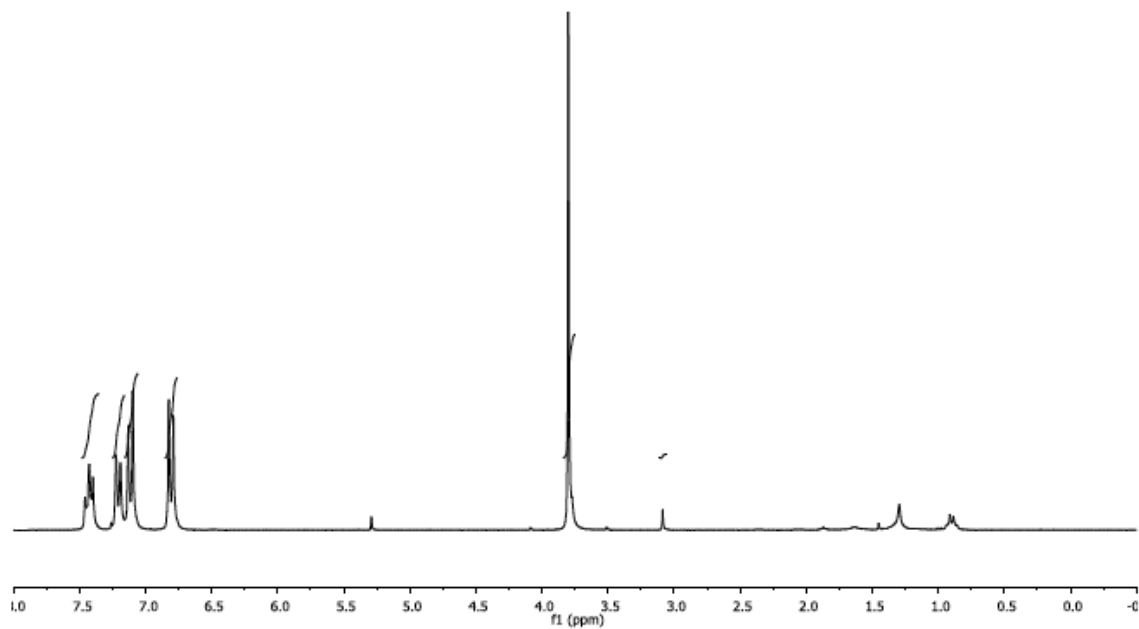


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 63 MHz)

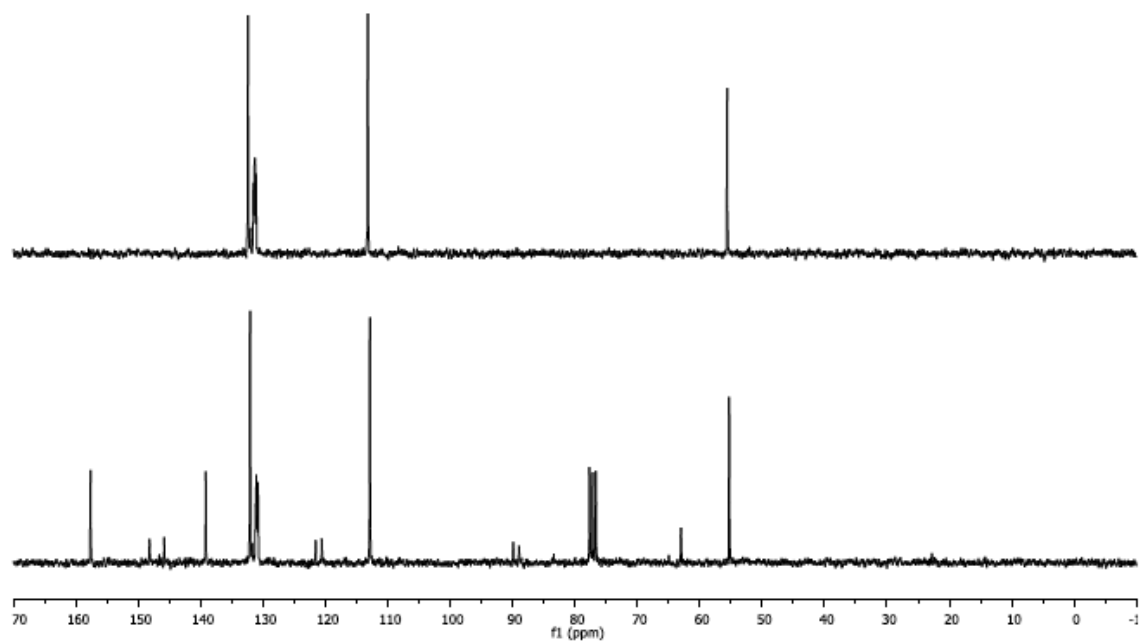


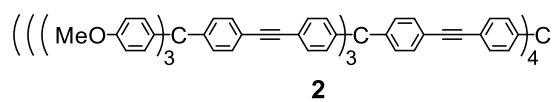


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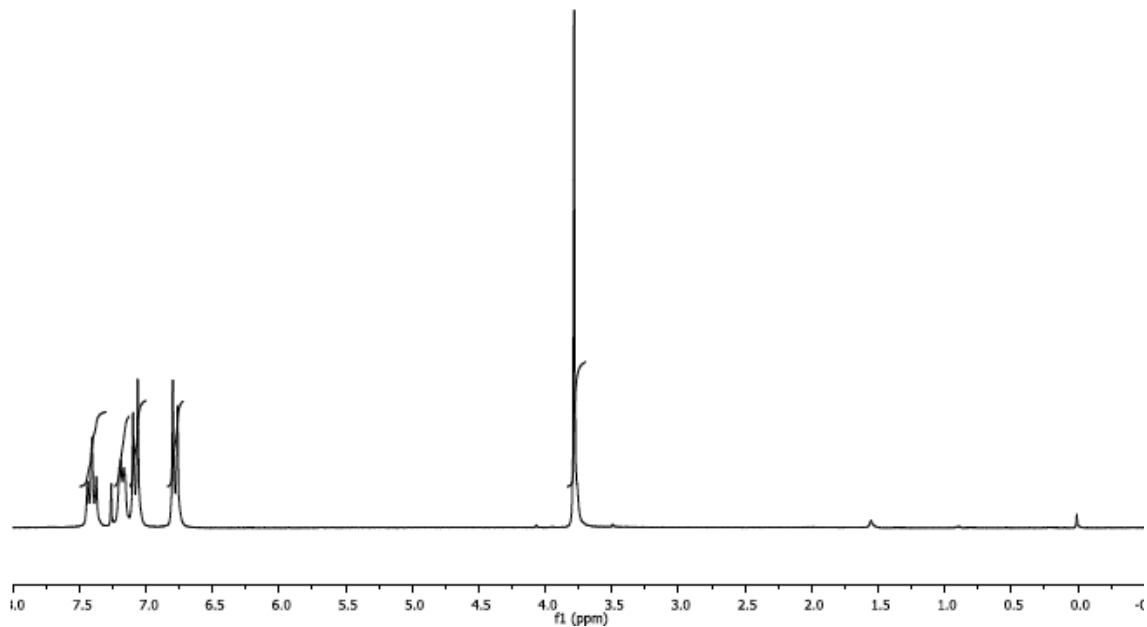


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 63 MHz)

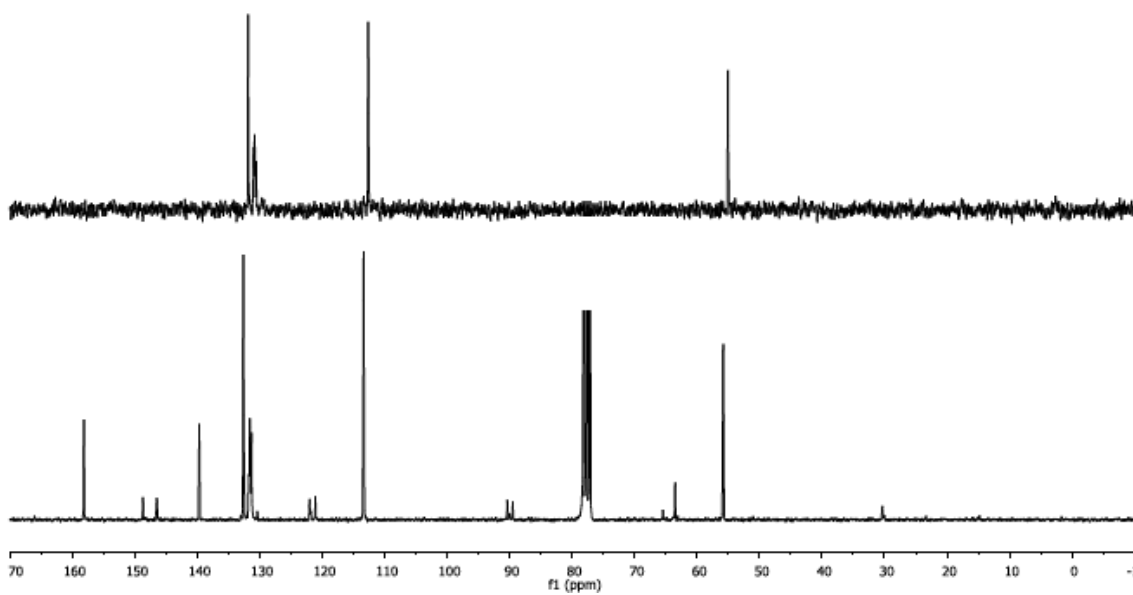




<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)



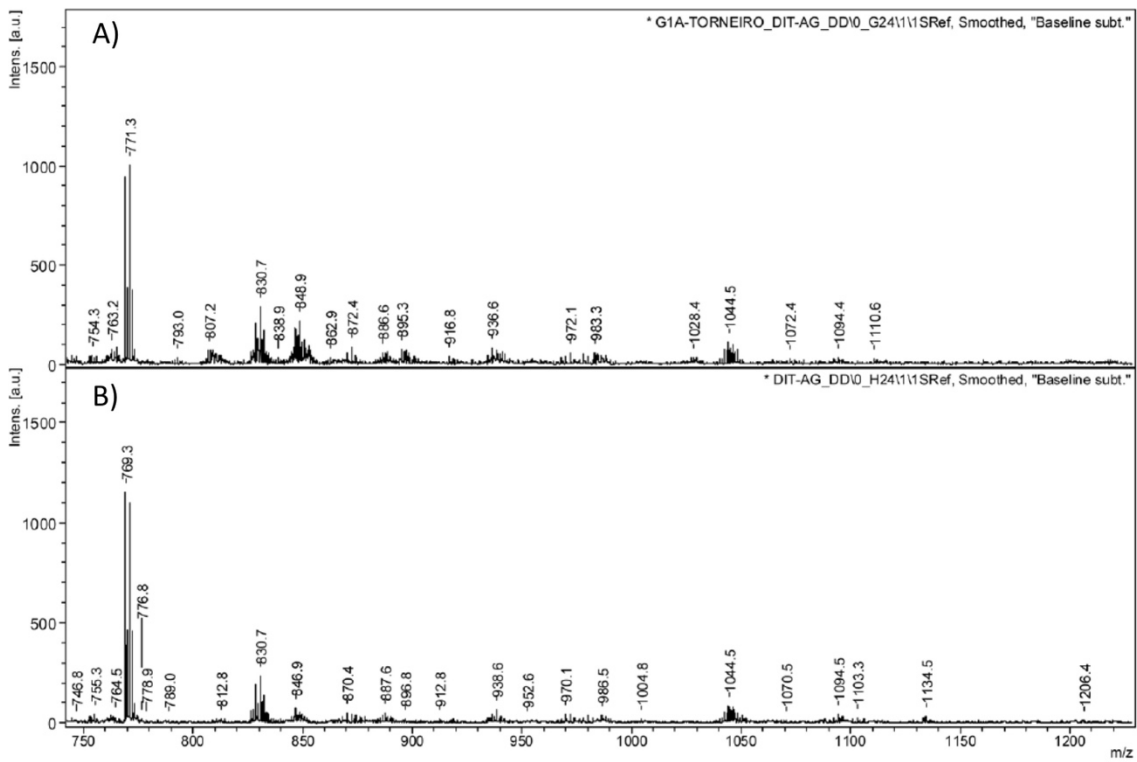
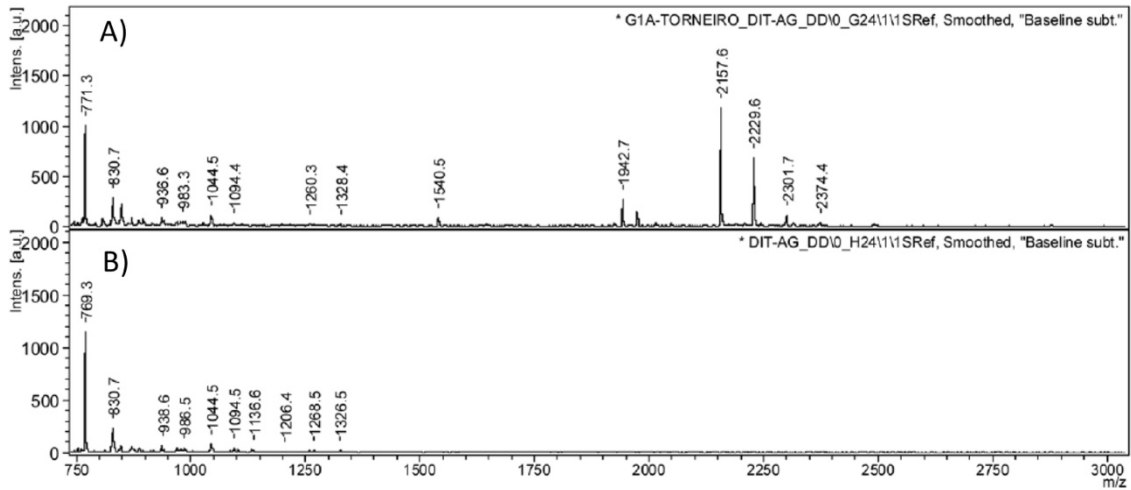
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz)



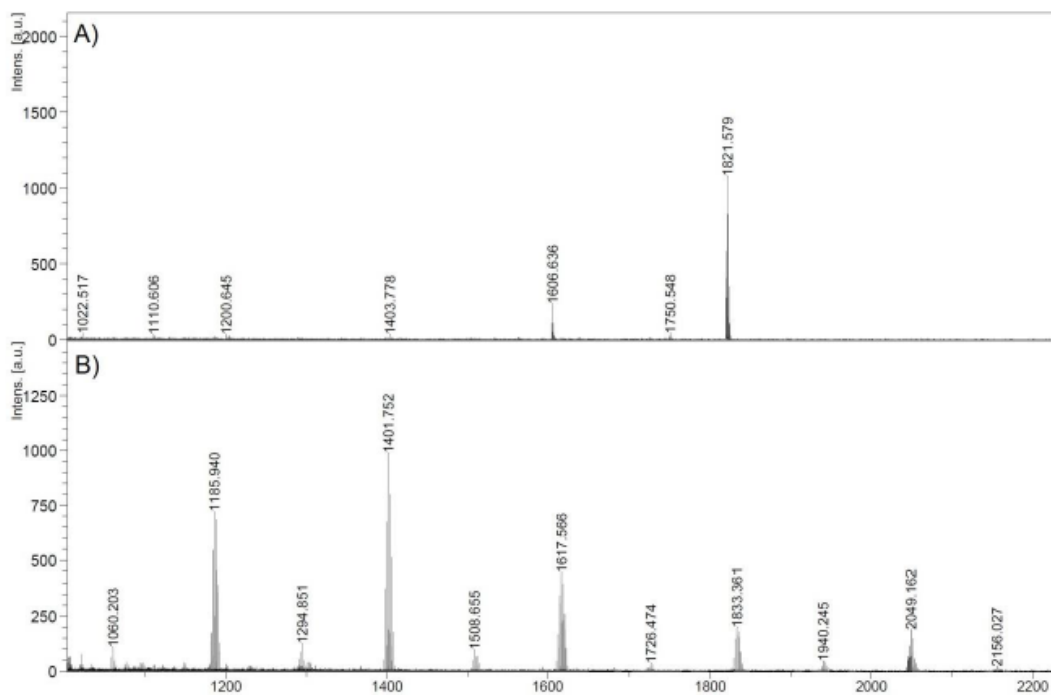
# MALDI-TOF mass spectra

A) Sample; B) matrix.

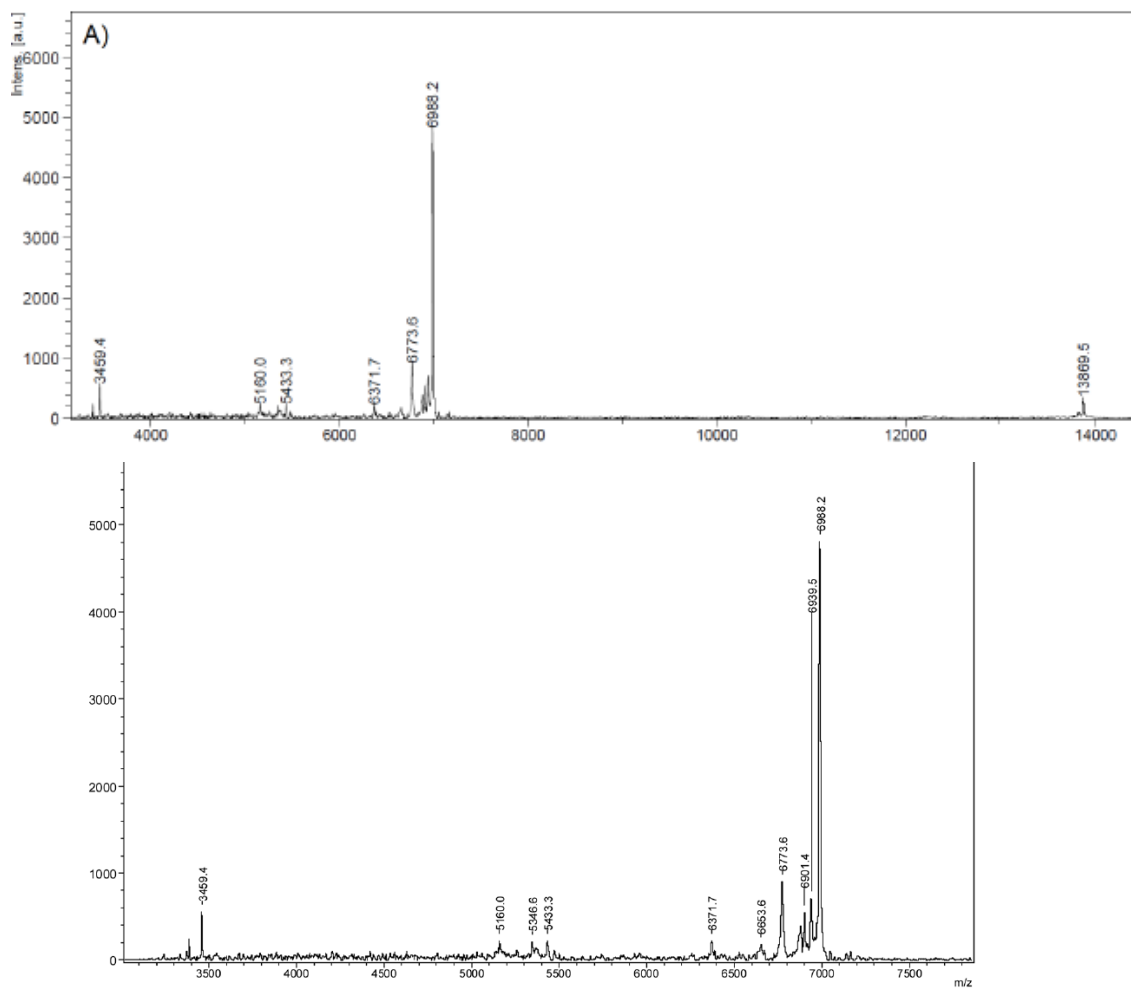
## Dendrimer 1



## Dendron 8



## Dendrimer 2



## DLS analysis of 2

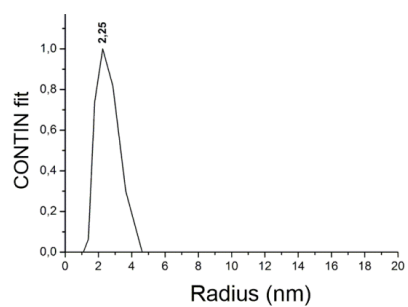
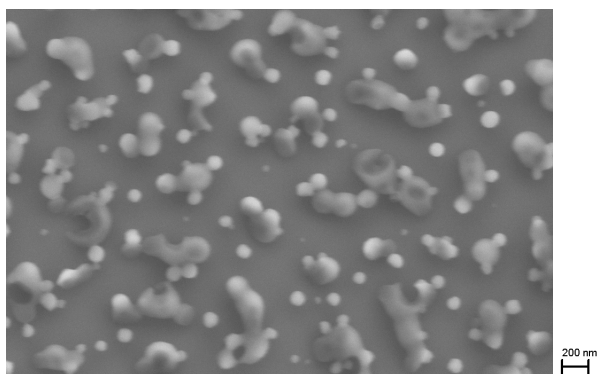


Figure S1. Size distribution from DLS of 2.

## SEM and AFM images of 2

A)



B)

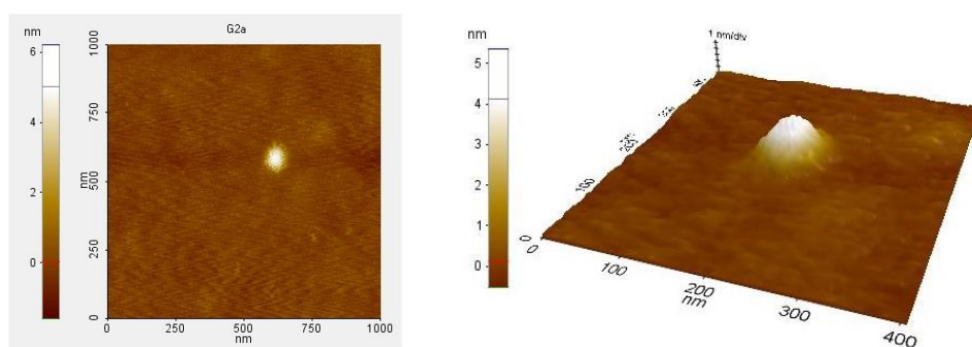


Figure S2. A) SEM image of 2. B) AFM image of 2 (left) and 3D projection (right).