

## Supporting Information

for the manuscript:

# Organic Cage Controlling Dimension and Stability of Gold Nanoparticles

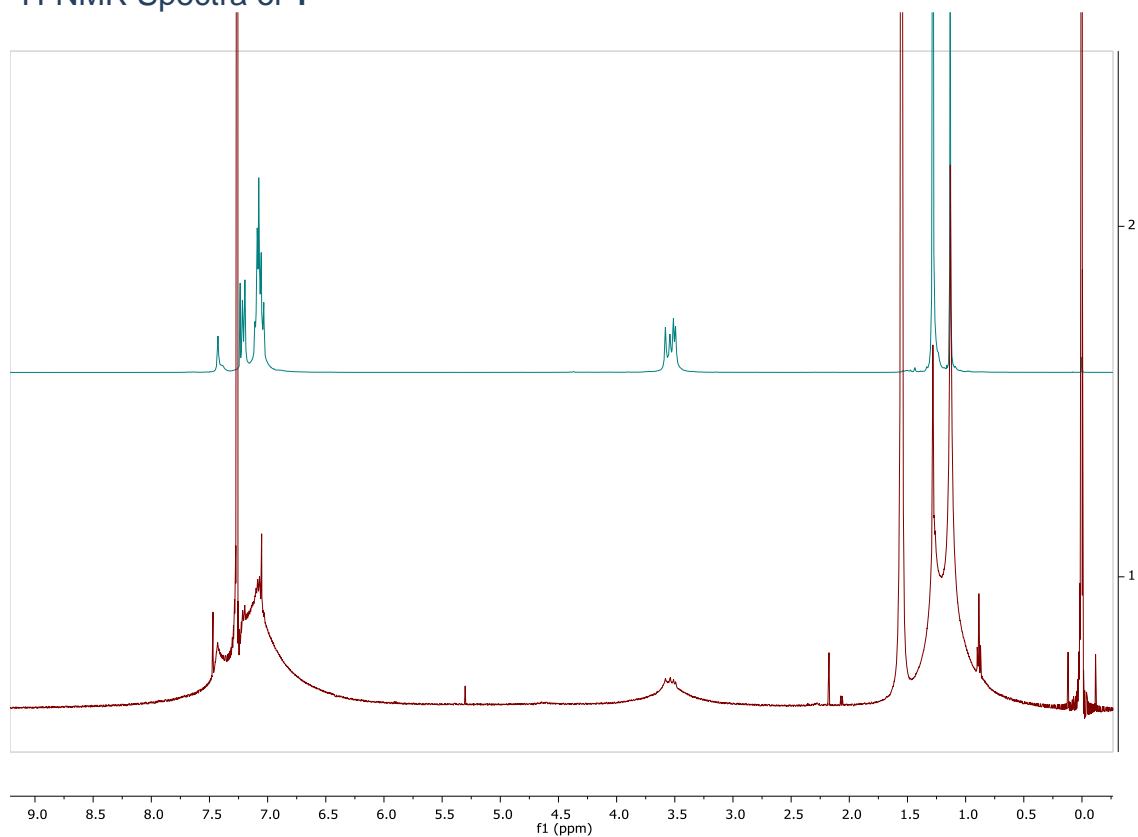
*Erich Henrik Peters and Marcel Mayor\**

## Contents

Analysis of <b>Au-1</b> .....	2
<sup>1</sup> H-NMR Spectra of <b>1</b> .....	2
TEM micrograph of <b>Au-1</b> .....	3
Thermogravimetric Analysis of <b>Au-1</b> .....	4
Materials .....	6
Equipment and Measurements .....	6
Synthesis and Analytical Data of Cage <b>1</b> and Compounds <b>3–9</b> .....	7
tris(p-(bromomethyl)phenyl)-p-(p-(triisopropylsilylethynyl)phenylethynyl)phenylmethane ( <b>7</b> ) <sup>1</sup> .....	7
bis(p-(bromomethyl)phenyl)-bis(p-tert-butylphenyl)methane ( <b>3</b> ) <sup>2</sup> .....	7
p-(tritylthiomethyl)phenyl-p-(bromomethyl)phenyl-bis(p-tert-butylphenyl)methane ( <b>4</b> ) <sup>2</sup> .....	7
p-(tritylthiomethyl)phenyl-p-(acetylthiomethyl)phenyl-bis(p-tert-butylphenyl)-methane ( <b>5</b> ) .....	8
p-(mercaptomethyl)phenyl-p(tritylthiomethyl)phenyl-bis(p-tert-butylphenyl)-methane ( <b>6</b> ) .....	10
Tris(p-(p-(p-(tritylthiomethyl)phenyl-bis(p-tert-butylphenyl)methyl)phenylmethylthiomethyl)phenyl)-p-(p-(triisopropylsilylethynyl)phenylethynyl)phenylmethane ( <b>8</b> ) .....	12
Tris(p-(p-(p-(mercaptomethyl)phenyl-bis(p-tert-butylphenyl)methyl)phenylmethylthiomethyl)phenyl)-p-(p-(triisopropylsilylethynyl)phenylethynyl)phenylmethane ( <b>9</b> ) .....	14
Cage-Type Ligand <b>1</b> .....	17
References .....	19

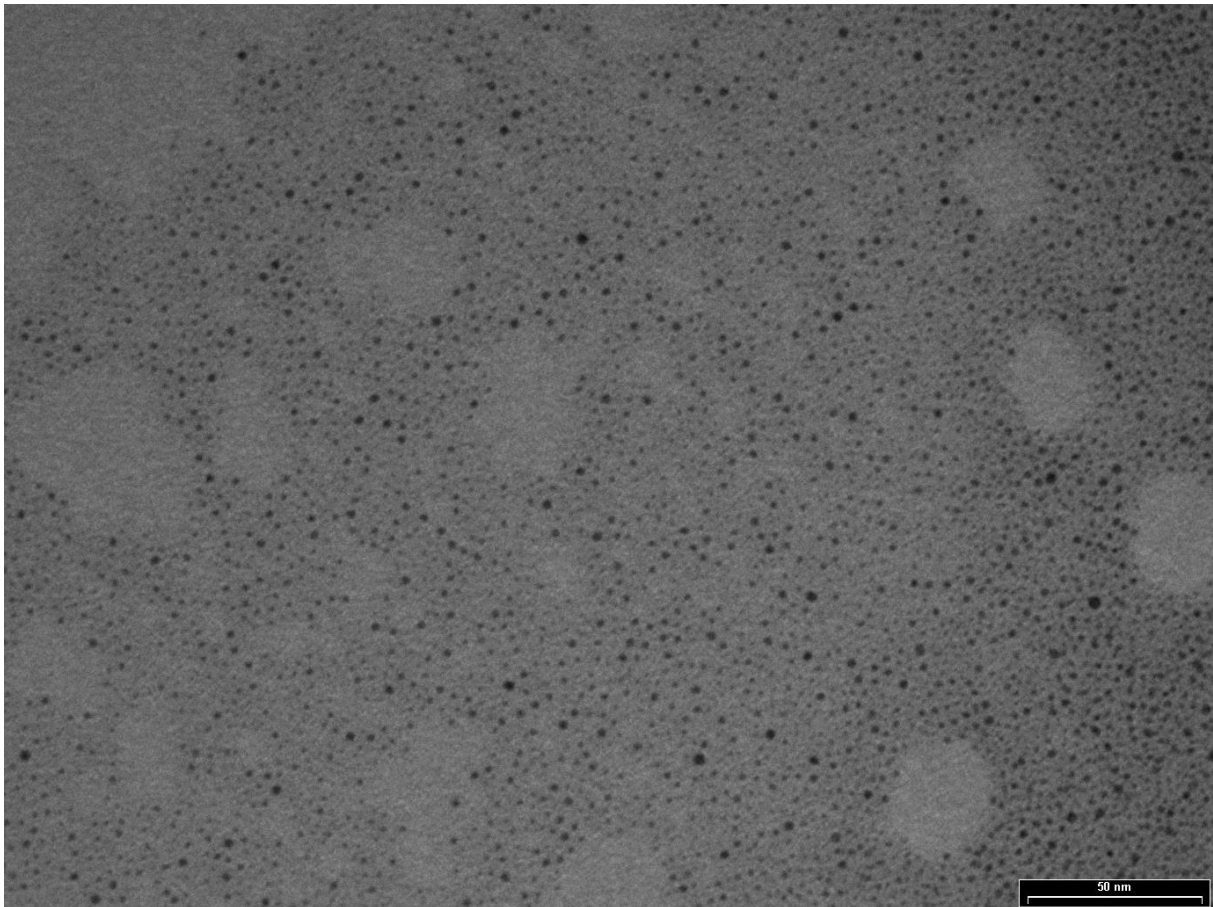
## Analysis of Au-1

### <sup>1</sup>H-NMR Spectra of 1



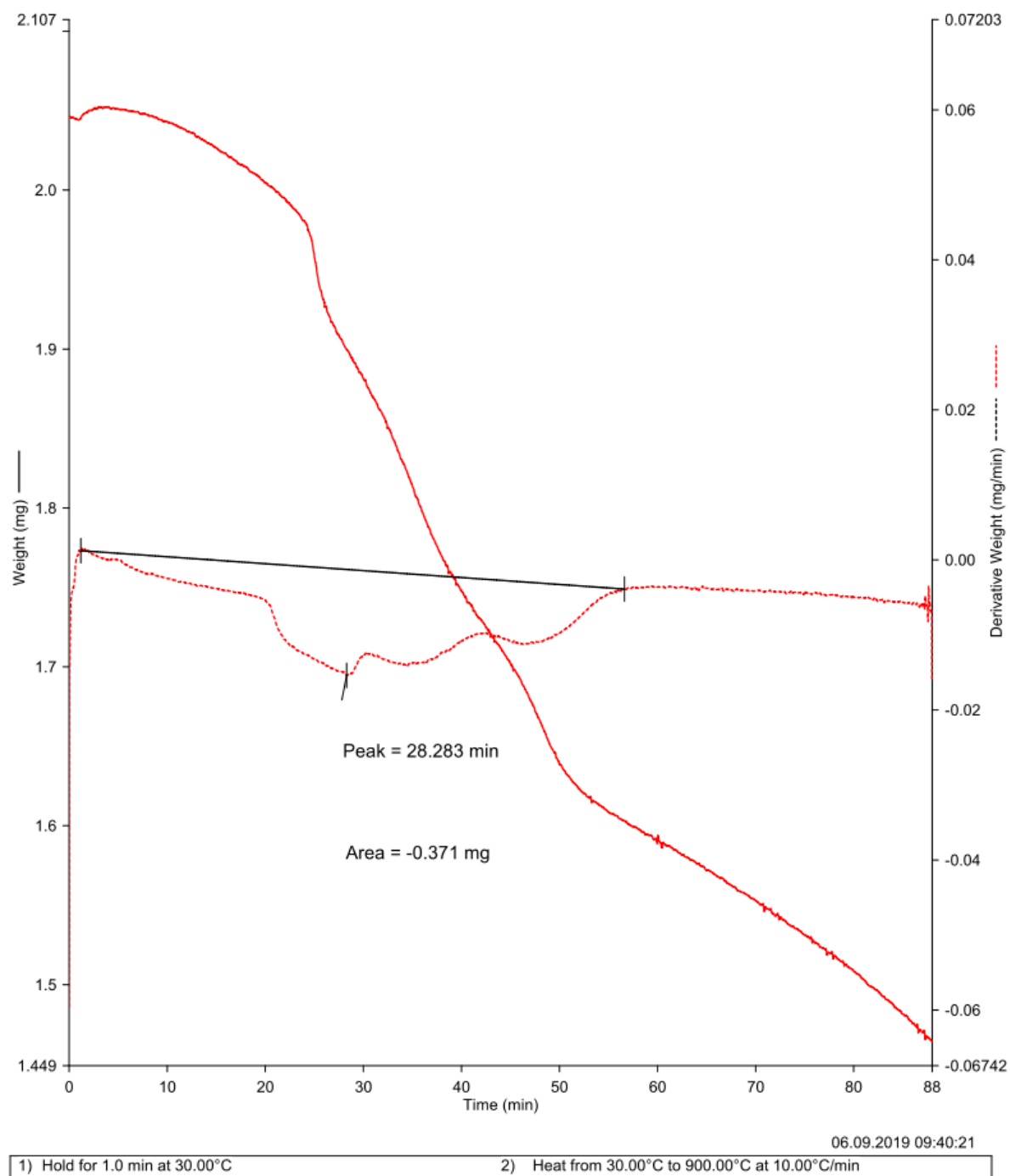
**Fig. S1** <sup>1</sup>H NMR spectrum of cage **1** (blue) and **Au-1** (red). The close similarity corroborates the coating of the Au NP by the ligand. The characteristic line-broadening caused by the restricted tumbling motion documents the immobilization of the ligand on the NP surface.

TEM micrograph of **Au-1**



**Fig. S2.** Representative TEM micrograph of **Au-1**

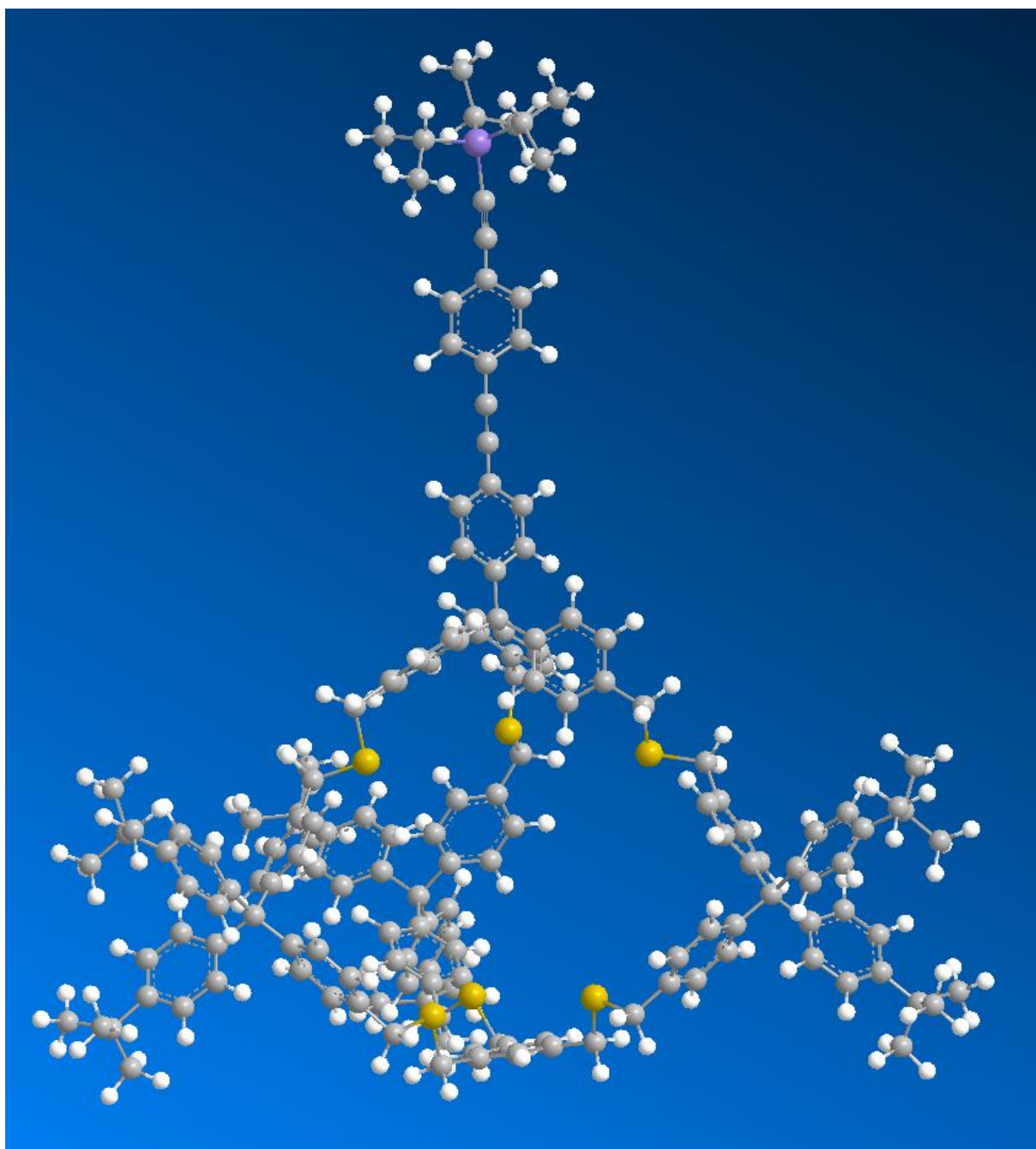
## Thermogravimetric Analysis of Au-1



**Fig. S3.** TGA mass loss trace for Au-1.

**Table S1.** Ligand-to-gold ratio as taken from TGA and TEM images.

Au-1	m(1) [mg]	M(1) [g/mol]	n(1) [mol]	m <sub>Au</sub> [mg]	n <sub>Au</sub> [mol]	M <sub>Au</sub> [g mol <sup>-1</sup> ]	n <sub>Au</sub> /n(1)
TGA	2.053	2325.58	1.60·10 <sup>-7</sup>	1.682	8.54·10 <sup>-6</sup>	196.97	53.5



**Fig. S4.** Chem3D MM2 simulation render of **1**.

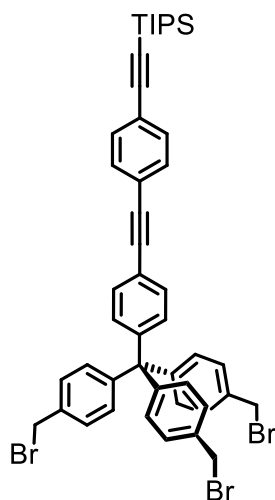
## Materials

All commercially available starting materials were of reagent grade and used as received, unless stated differently. Absolute THF was purchased from Acros, stored over 4 Å molecular sieves, pre-dried with CaH, handled under argon and freshly distilled over sodium before each use. Pure CH<sub>2</sub>Cl<sub>2</sub> was purchased from J. T. Baker. Pure toluene was purchased from Acros. Pure DMF was purchased from Acros Organics. *tert*-butylmethylether (TBME), *c*-hexane, ethyl acetate (EtOAc), and CH<sub>2</sub>Cl<sub>2</sub> from Biosolve were used for purification and were of technical grade. Column chromatography was carried out on SiliaFlash P60 (particle size 40–63 μm) from SiliCycle. SEC for the purification of AuNPs mono-, di- and trimers was performed manually using Bio-Rad Bio-Beads S-X1 (operating range 600–14 000 g mol<sup>-1</sup>) with CH<sub>2</sub>Cl<sub>2</sub> or toluene as eluent. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

## Equipment and Measurements

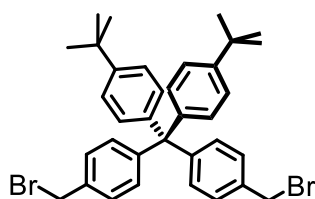
<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DPX 400 instrument (<sup>1</sup>H resonance 400 MHz, <sup>13</sup>C resonance 101 MHz) or a Bruker DRX 500 instrument (<sup>1</sup>H resonance 500 MHz, <sup>13</sup>C resonance 126 MHz) at 298 K. The chemical shifts (δ) are reported in ppm and are referenced to the residual proton signal of the deuterated solvent (Chloroform-*d*: 7.26 ppm) for <sup>1</sup>H spectra or the carbon of the solvent (Chloroform-*d*: 77.1 ppm) for <sup>13</sup>C spectra. The coupling constants (*J*) are given in Hertz (Hz), the multiplicities are denoted as: s (singlet), d (duplet), t (triplet), m (multiplet), and br (broad). High-resolution mass spectra (HRMS) were measured as HR-ESI-ToF-MS with a Maxis 4G instrument from Bruker or a Bruker UltraFlex II – MALDI-ToF-MS. For purification of the ligands, a (automated) Shimadzu Prominence System was used with SDV preparative columns from Polymer Standards Service (two Showdex columns in series, 20 mm × 600 mm each, exclusion limit: 30 000 g mol<sup>-1</sup>) with chloroform as eluent. UV–vis measurements were recorded on a Jasco V-770 spectrophotometer using 117.100F-QS cuvettes from Hellma Analytics (10 mm light path). TEM was performed on a Philips CM100 TEM at 80 kV using copper grids (Cu-400HD) from Pacific Grid Tech. TGA was measured on a Mettler Toledo TGA/SDTA851<sup>e</sup> with a heating rate of 10 °C min<sup>-1</sup>.

## Synthesis and Analytical Data of Cage **1** and Compounds **3–9**



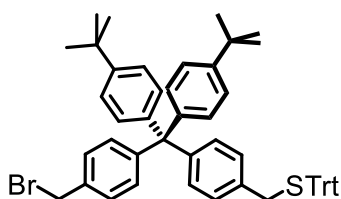
tris(p-(bromomethyl)phenyl)-p-(p-(triisopropylsilylethynyl)phenylethynyl)phenylmethane (**7**)<sup>1</sup>

Compound **7** was synthesized as described in Ref. 1.



bis(p-(bromomethyl)phenyl)-bis(p-tert-butylphenyl)methane (**3**)<sup>2</sup>

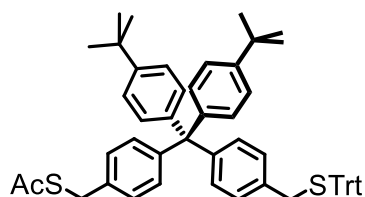
Compound **3** was synthesized as described in Ref. 2.



p-(tritylthiomethyl)phenyl-p-(bromomethyl)phenyl-bis(p-tert-butylphenyl)methane (**4**)<sup>2</sup>

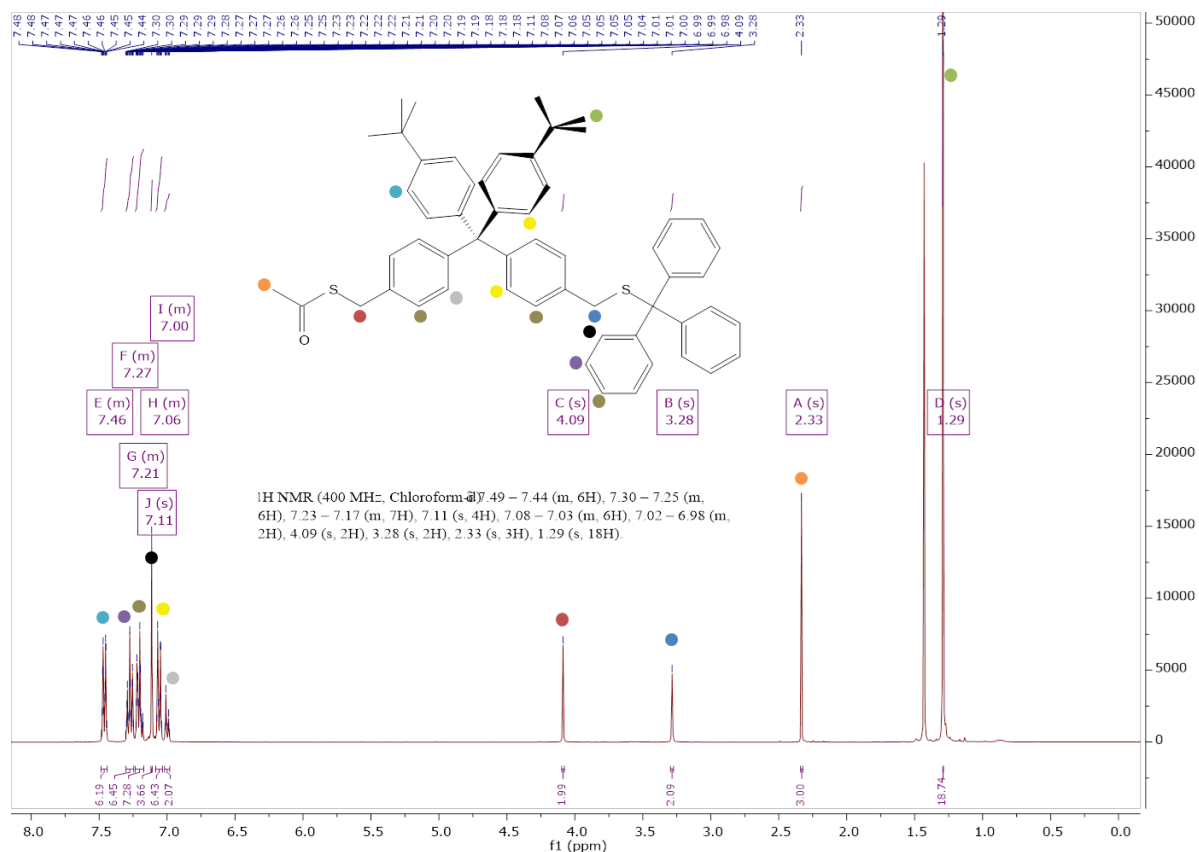
In a 250 ml flask, compound **3** (2.75 g, 4.45 mmol, 1 eq.) was dissolved in 100 ml freshly distilled THF in. Tritylthiol (1.27 g, 4.45 mmol, 1 eq.) was added to the solution which was then bubbled with argon for 15 minutes. NaH (60% dispersion in mineral oil, 200 mg, 5.03 mmol, 1.1 eq.) was added to the flask. The mixture was stirred at rt for 2 hours, quenched by careful addition of minimum amounts of water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The crude product was subjected to automated column chromatography (c-hexane: CH<sub>2</sub>Cl<sub>2</sub> 10:1 and 2:1) to afford compound **4** (1.22 g, 1.50 mmol, 34%) as a white foam. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.48 - 7.43 (m, 5H), 7.30 (s, 4H), 7.26 (d, J = 1.7 Hz, 6H), 7.24 - 7.18 (m, 7H), 7.15 (d, J = 8.4

Hz, 2H), 7.08 -7.04 (m, 5H), 7.00 (d, J = 8.3 Hz, 2H), 4.47 (s, 2H), 3.28 (s, 2H), 1.29 (s, 18H).

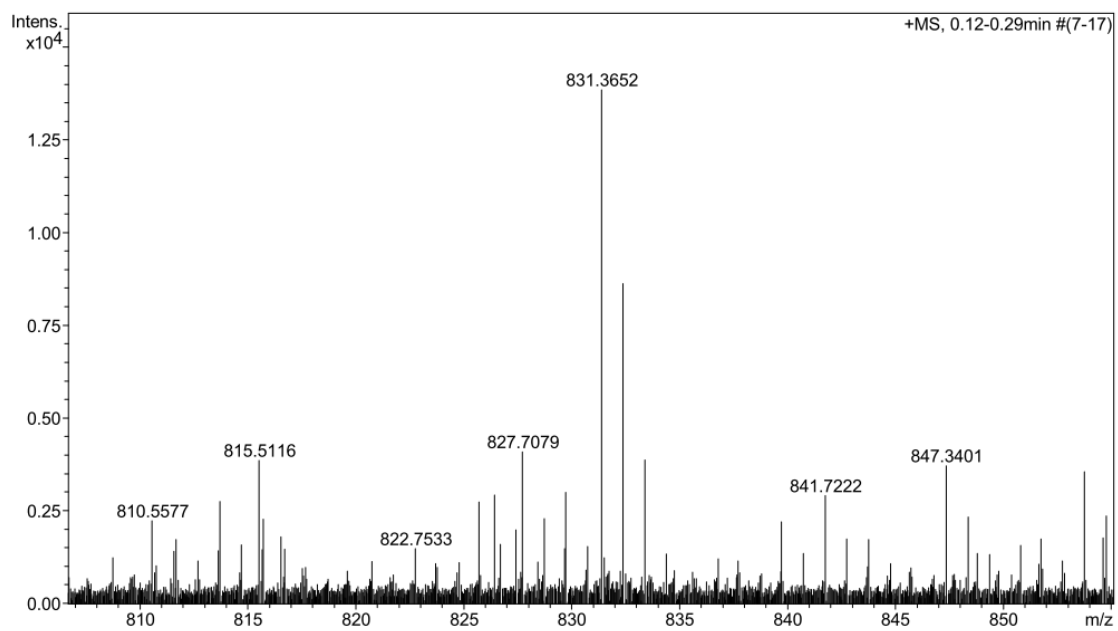
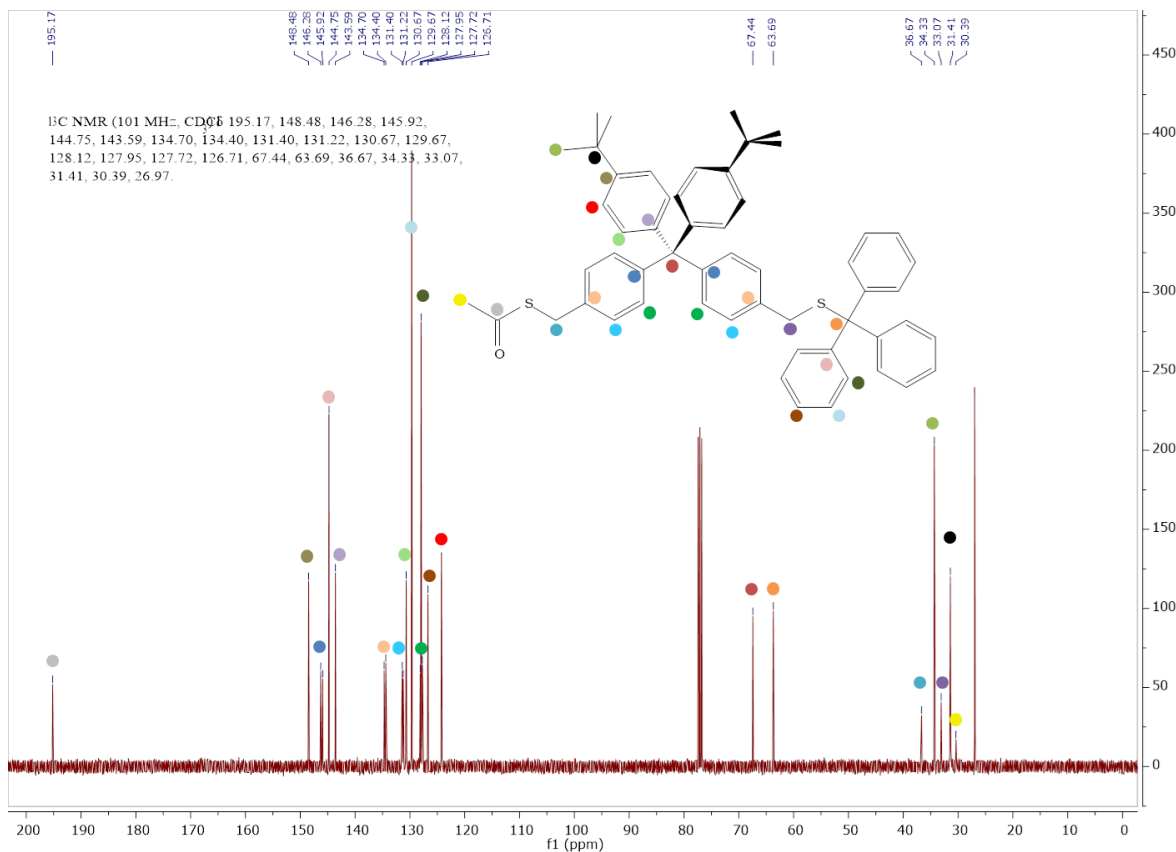


p-(tritylthiomethyl)phenyl-p-(acetylthiomethyl)phenyl-bis(p-tert-butylphenyl)-methane (5)

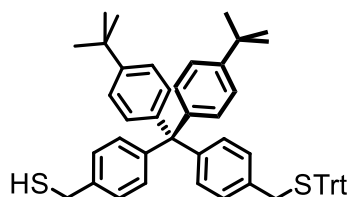
In a 100 ml flask, **4** (1.22 g, 1.50 mmol, 1 eq.) was dissolved in 50 ml dry DMF. Potassium thioacetate (0.343 g, 3.00 mmol, 2 eq.) was added and the mixture was stirred for 30 minutes after which time the mixture was diluted in excess TBME and washed five times with water to remove the DMF. The mixture was dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated to dryness and subjected to column chromatography (c-hexane: CH<sub>2</sub>Cl<sub>2</sub> 1:1) to give asymmetrically protected side-chain **5** as a green foam (1.13 g, 1.40 mmol, 93%). <sup>1</sup>H-NMR (400 MHz, Chloroform-d) δ 7.49 – 7.44 (m, 6H), 7.30 – 7.25 (m, 6H), 7.23 – 7.17 (m, 7H), 7.11 (s, 4H), 7.08 – 7.03 (m, 6H), 7.02 – 6.98 (m, 2H), 4.09 (s, 2H), 3.28 (s, 2H), 2.33 (s, 3H), 1.29 (s, 18H). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>) δ 195.17, 148.48, 146.28, 145.92, 144.75, 143.59, 134.70, 134.40, 131.40, 131.22, 130.67, 129.67, 128.12, 127.95, 127.72, 126.71, 67.44, 63.69, 36.67, 34.33, 33.07, 31.41, 30.39. HRMS (ESI-ToF): m/z = [M+Na]<sup>+</sup> calcd. for C<sub>56</sub>H<sub>56</sub>OS<sub>2</sub>Na<sup>+</sup>: 831.3665, found: 831.3652.





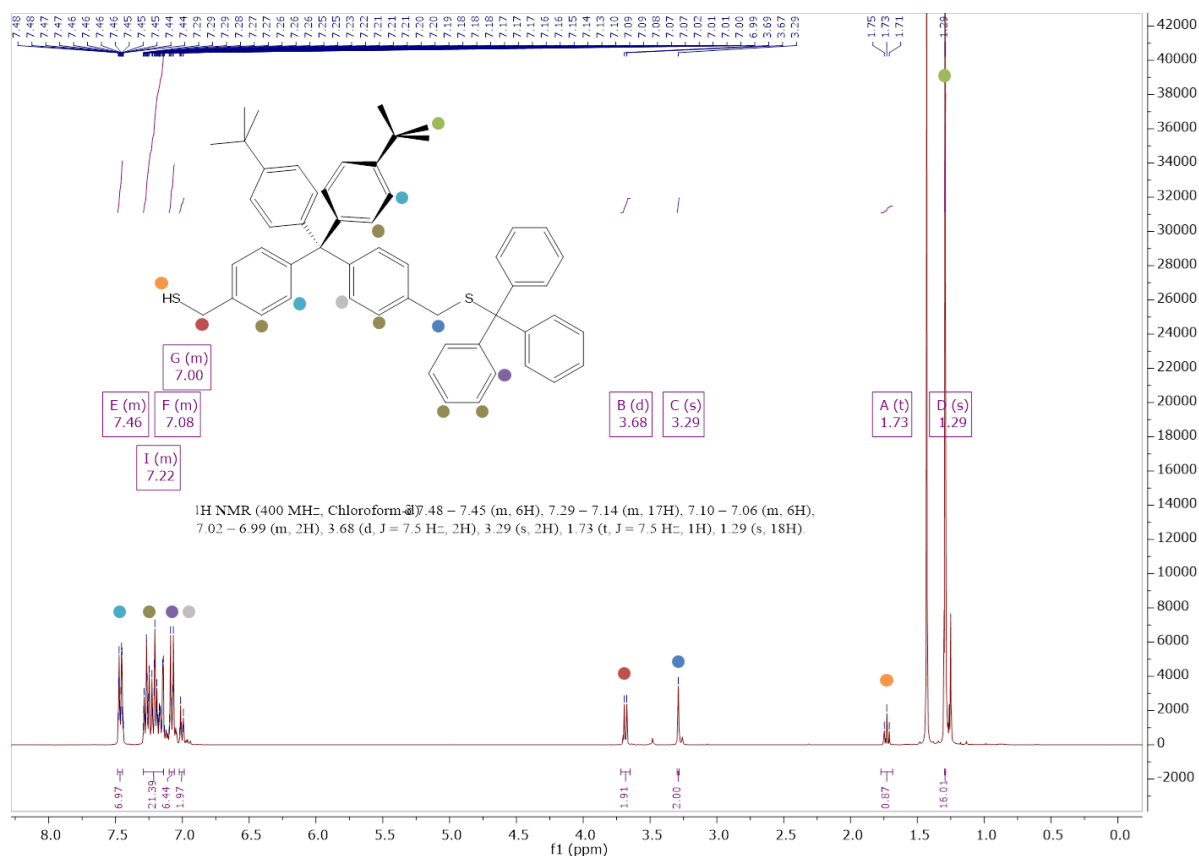


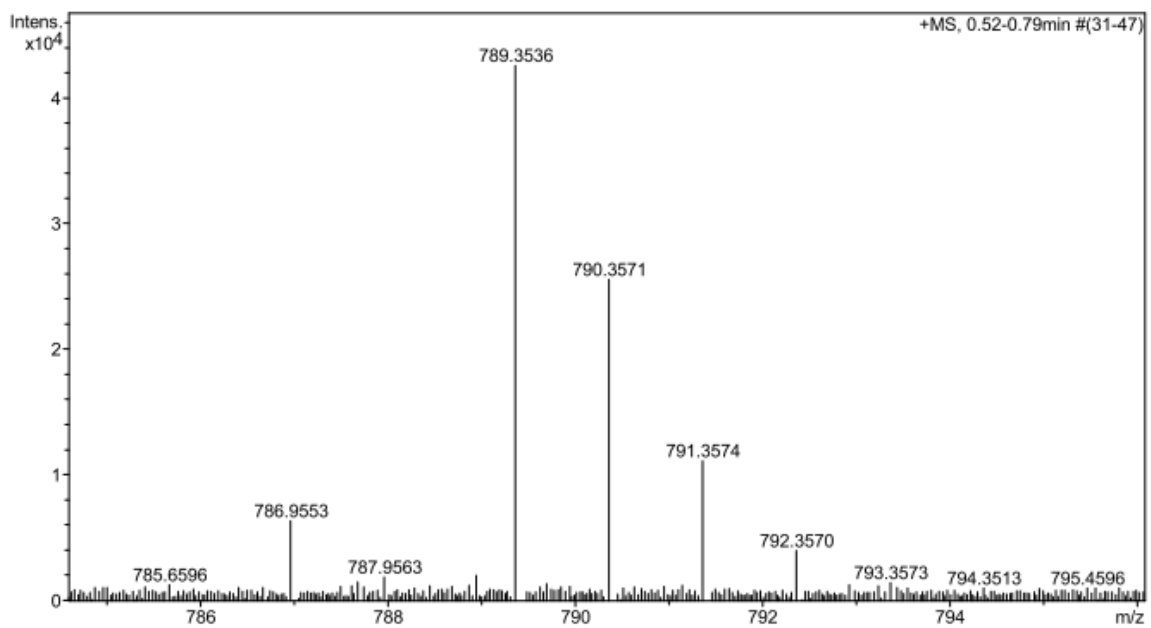
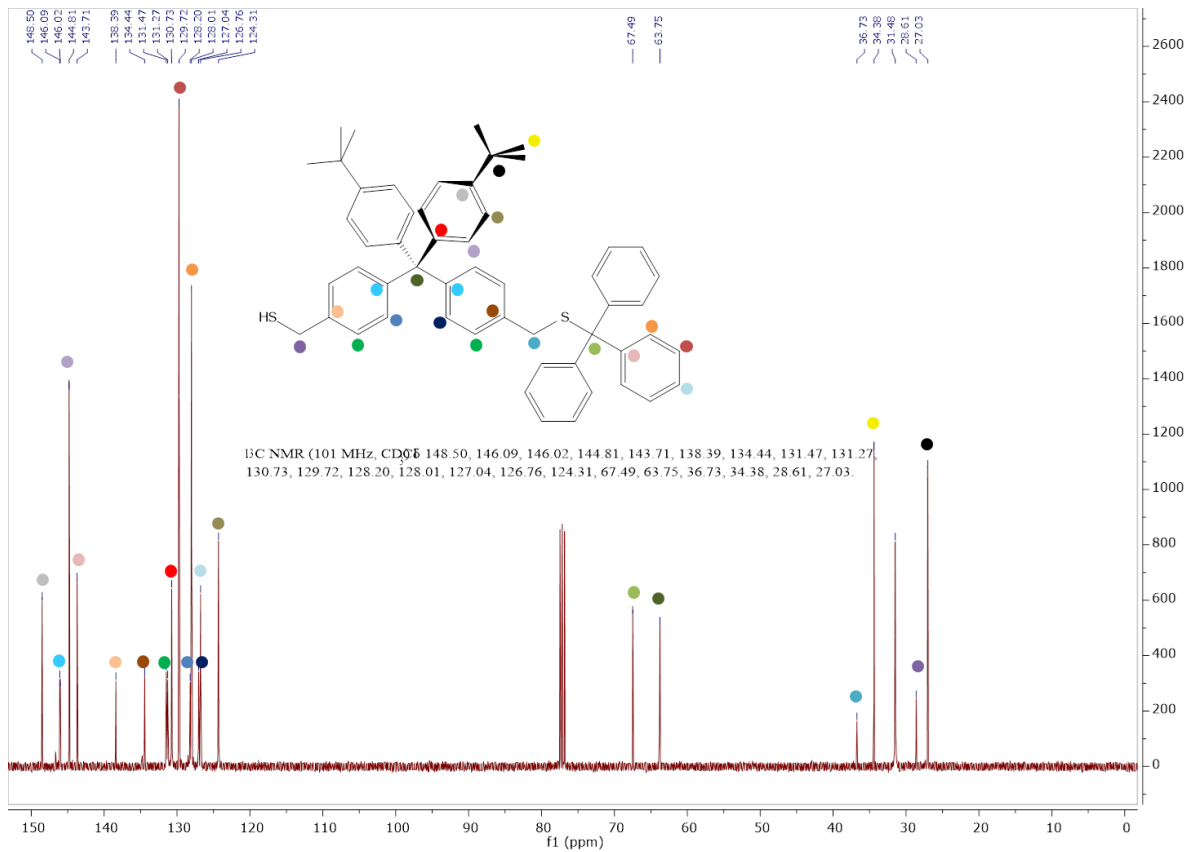
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	z
831.3652	1	C <sub>56</sub> H <sub>56</sub> NaO <sub>2</sub> S <sub>2</sub>	100.00	831.3665	1.2	1.5	10.1	28.5	even	1+



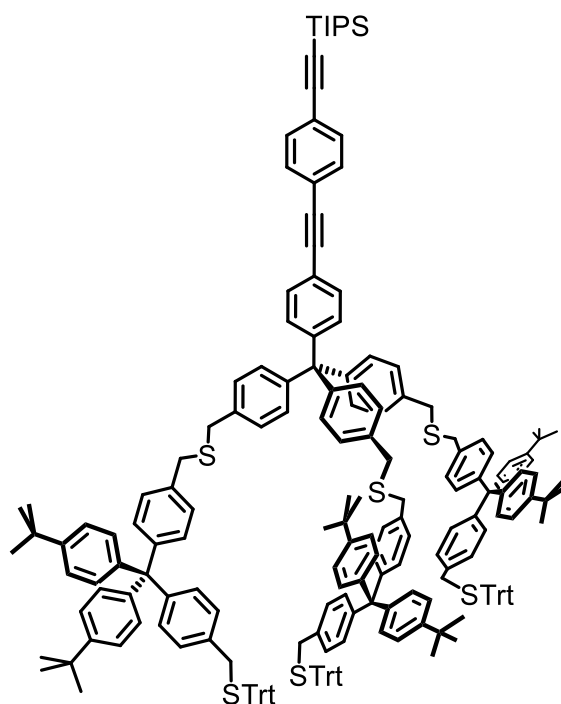
p-(mercaptomethyl)phenyl-p(tritylthiomethyl)phenyl-bis(p-tert-butylphenyl)-methane  
(6)

In a 100 ml flask, **5** (939 mg, 1.16 mmol, 1 eq.) was dissolved in 30 ml MeOH:THF 1:1 and degassed with argon for 20 minutes after which time  $K_2CO_3$  (321 mg, 2.32 mmol 2 eq.) was added. The mixture was stirred for 4 hours and thereafter acidified by addition of 10% aqueous HCl (50 ml). The mixture was extracted three times with  $CH_2Cl_2$ , dried over  $Na_2SO_4$  and subjected to automated column chromatography (c-hexane:  $CH_2Cl_2$  gradient 4:1 to 1:1) to afford thiol **6** as a white foam (854 mg, 1.11 mmol, 96%).  $^1H$  NMR (400 MHz, Chloroform-d)  $\delta$  7.48 – 7.45 (m, 6H), 7.29 – 7.14 (m, 17H), 7.10 – 7.06 (m, 6H), 7.02 – 6.99 (m, 2H), 3.68 (d,  $J = 7.5$  Hz, 2H), 3.29 (s, 2H), 1.73 (t,  $J = 7.5$  Hz, 1H), 1.29 (s, 18H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  148.50, 146.09, 146.02, 144.81, 143.71, 138.39, 134.44, 131.47, 131.27, 130.73, 129.72, 128.20, 128.01, 127.04, 126.76, 124.31, 67.49, 63.75, 36.73, 34.38, 28.61, 27.03. HRMS (ESI-ToF):  $m/z = [M+Na]^+$  calcd. for  $C_{54}H_{54}S_2Na^+$ : 789.3559, found: 789.3536.



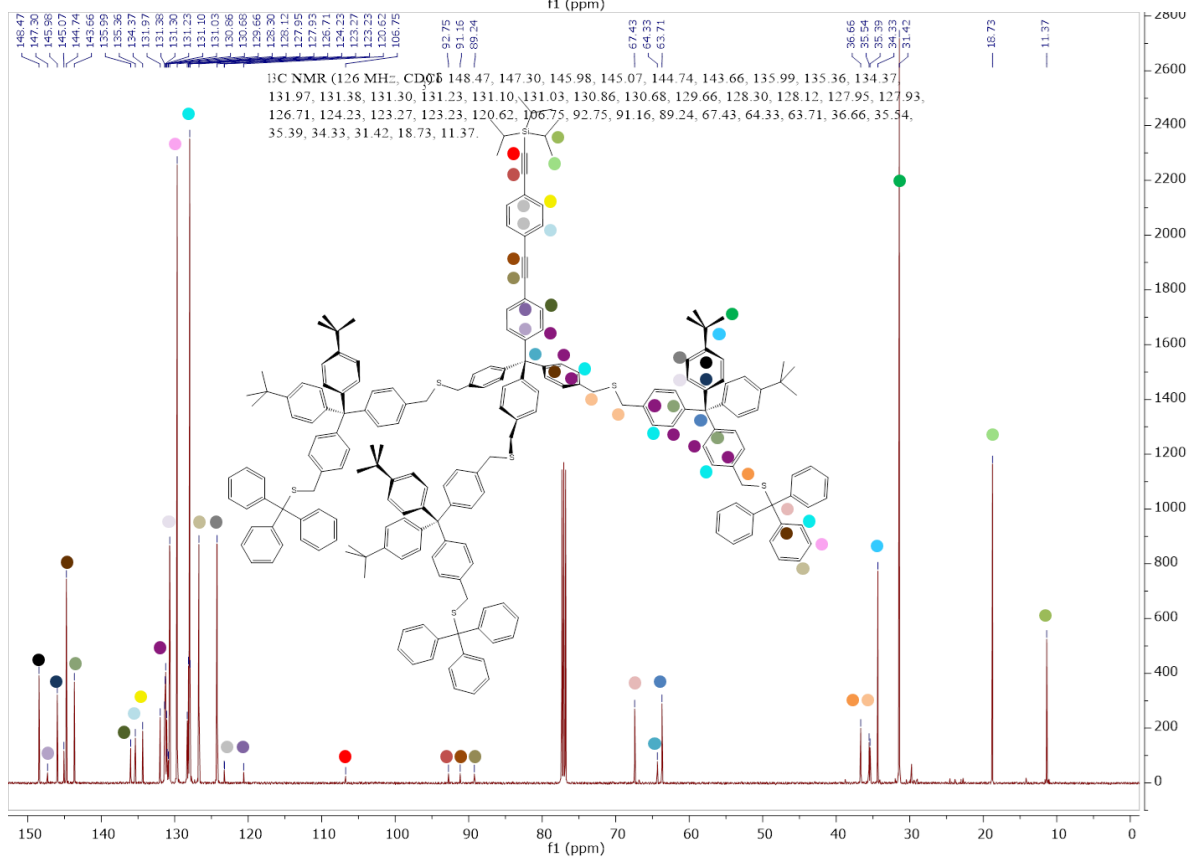
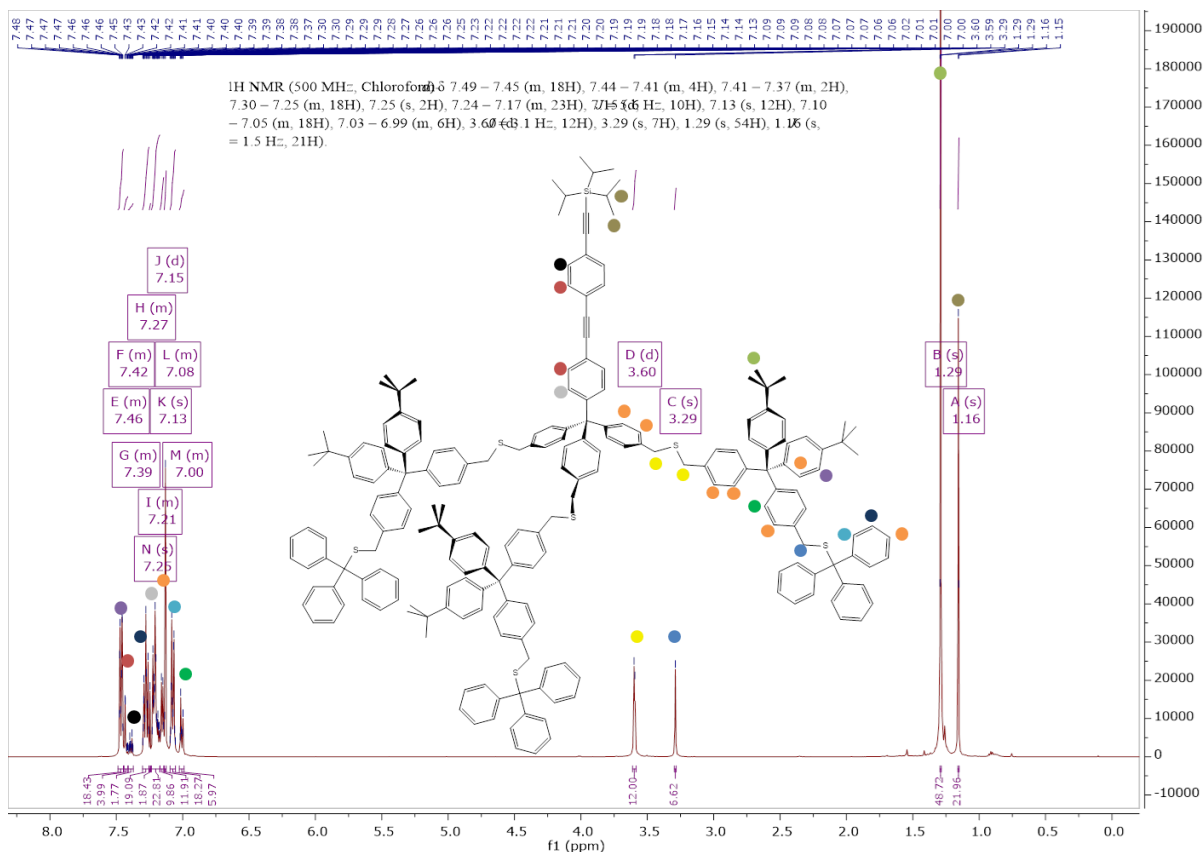


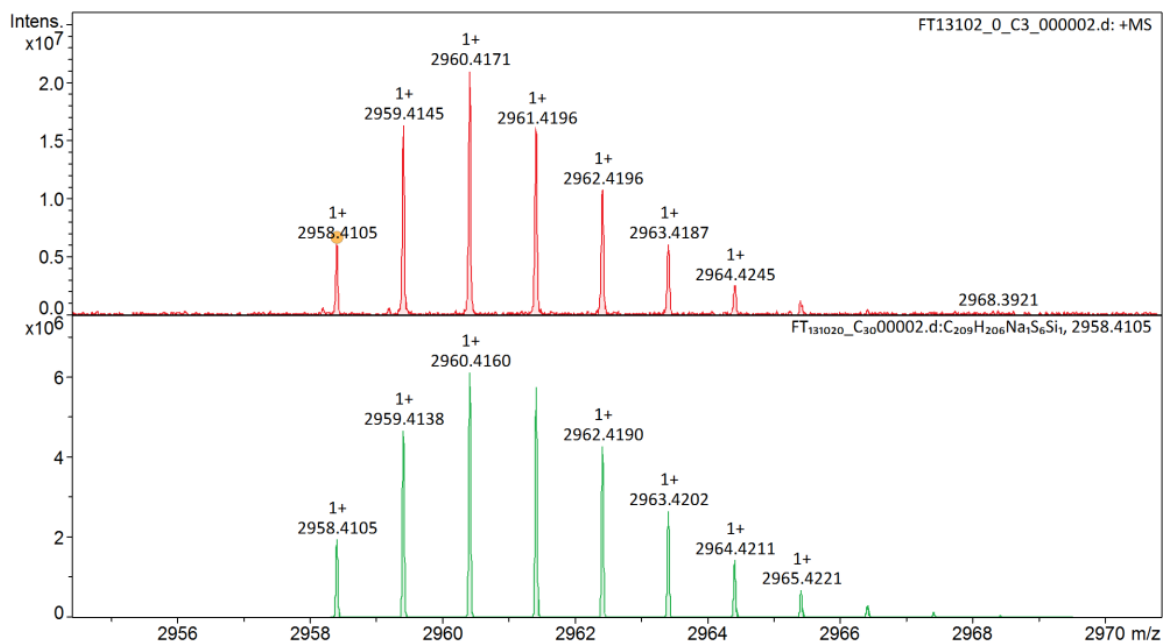
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	z
789.3536	1	C <sub>54</sub> H <sub>54</sub> NaS <sub>2</sub>	100.00	789.3559	2.4	3.0	8.1	27.5	even	1+



Tris(p-(p-(p-(tritylthiomethyl)phenyl-bis(p-tert-butylphenyl)methyl)phenylmethylthio-methyl)phenyl)-p-(p-(triisopropylsilylethynyl)phenylethynyl)phenylmethane (**8**)

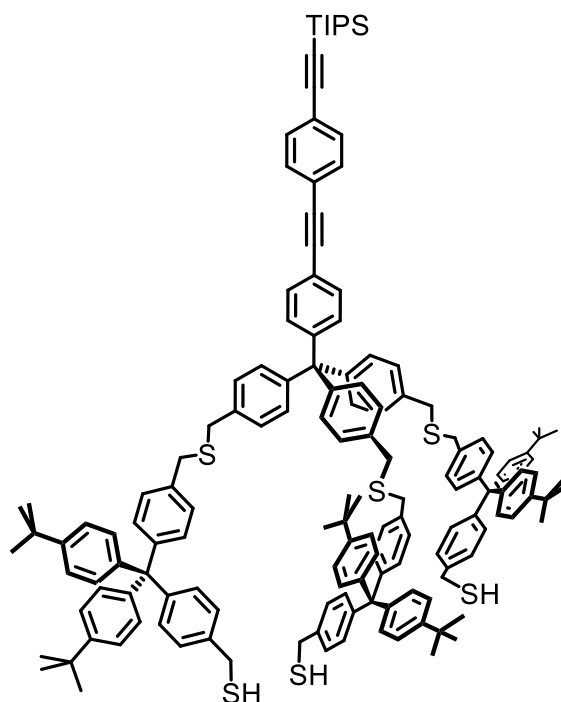
In a 25 ml flask, tribromide **7** (100 mg, 0.114 mmol, 1 eq.) and thiol **6** (350 mg, 0.456 mmol, 4 eq.) were dissolved in 10 ml dry THF and bubbled with argon for 30 minutes. NaH (60% dispersion in mineral oil, 50 mg, 1.25 mmol, 11 eq.) was added and the mixture was stirred at rt for 15 hours after which the reaction was quenched by careful addition of minimum amounts of water. The mixture was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated over a silica plug (CH<sub>2</sub>Cl<sub>2</sub>) and evaporated to dryness. Isolation by automated GPC (chloroform) gave S-protected cage precursor **8** as a yellow solid (279 mg, 0.096 mmol, 84%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 18H), 7.44 – 7.41 (m, 4H), 7.41 – 7.37 (m, 2H), 7.30 – 7.25 (m, 18H), 7.25 (s, 2H), 7.24 – 7.17 (m, 23H), 7.15 (d, *J* = 5.6 Hz, 10H), 7.13 (s, 12H), 7.10 – 7.05 (m, 18H), 7.03 – 6.99 (m, 6H), 3.60 (d, *J* = 3.1 Hz, 12H), 3.29 (s, 6H), 1.29 (s, 54H), 1.16 (s, 21H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.47, 147.30, 145.98, 145.07, 144.74, 143.66, 135.99, 135.36, 134.37, 131.97, 131.38, 131.30, 131.23, 131.10, 131.03, 130.86, 130.68, 129.66, 128.30, 128.12, 127.95, 127.93, 126.71, 124.23, 123.27, 123.23, 120.62, 106.75, 92.75, 91.16, 89.24, 67.43, 64.33, 63.71, 36.66, 35.54, 35.39, 34.33, 31.42, 18.73, 11.37. HRMS (MALDI-ToF): *m/z* = [M+Na]<sup>+</sup> calcd. for C<sub>209</sub>H<sub>206</sub>S<sub>6</sub>SiNa<sup>+</sup>: 2958.4105, found: 2958.4105.





Evaluation Spectra / Validation Formula:

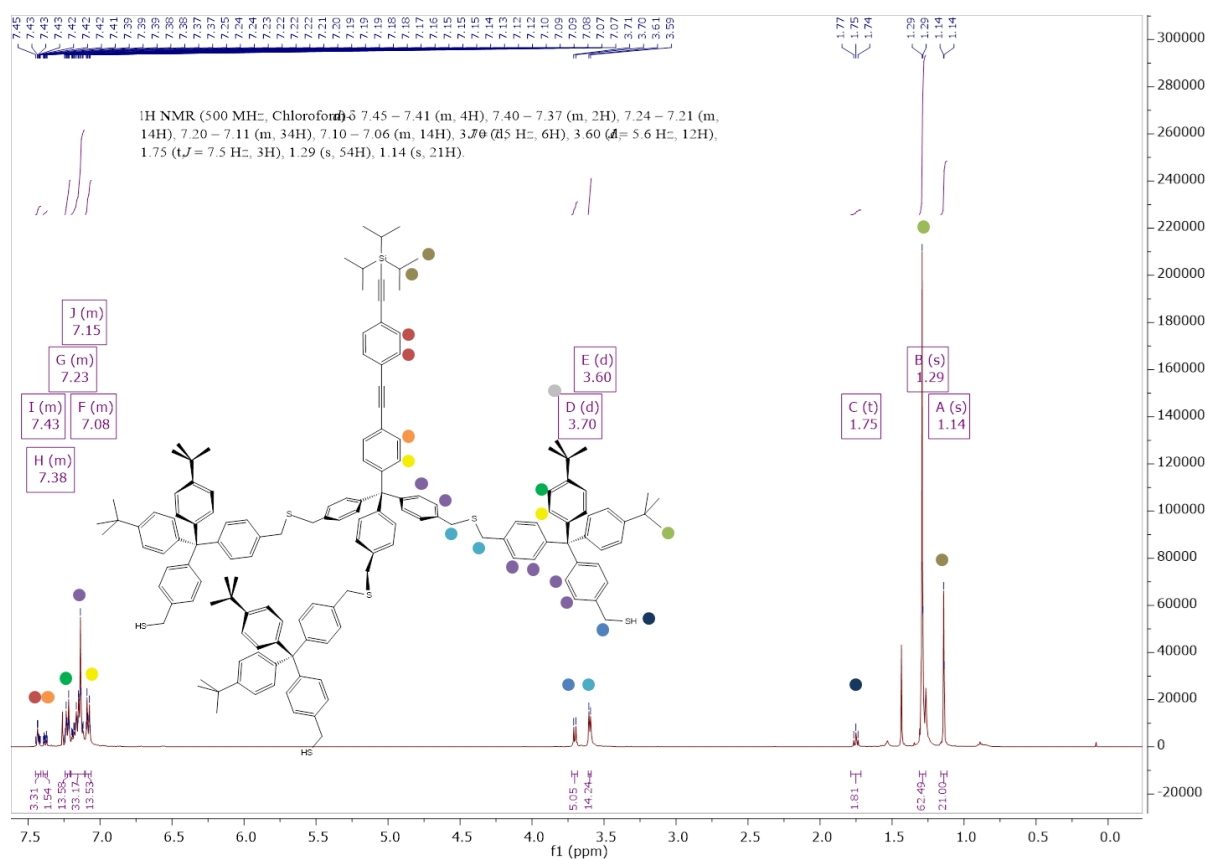
#	Ion Formula	Adduct	m/z	z	Meas. m/z	mSigma	N-Rule	err [mDa]	err [ppm]
1	C <sub>209</sub> H <sub>206</sub> NaS <sub>6</sub> Si	M+Na	2958.4105	1+	2958.4105	102.4	ok	-0.0	-0.0

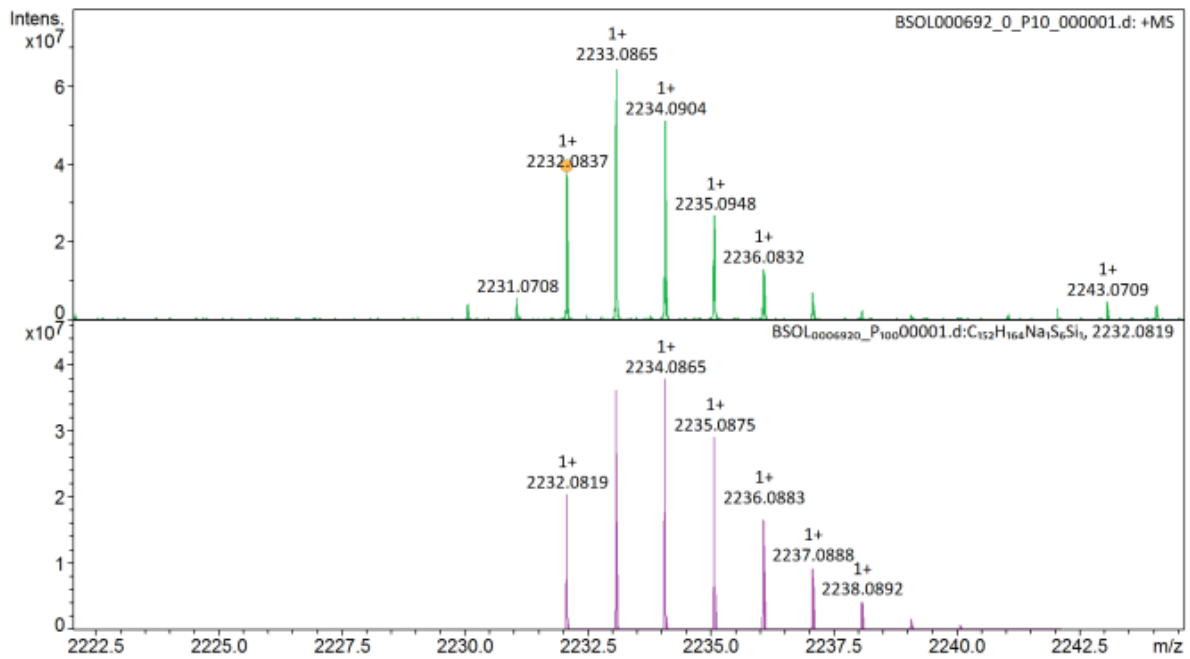
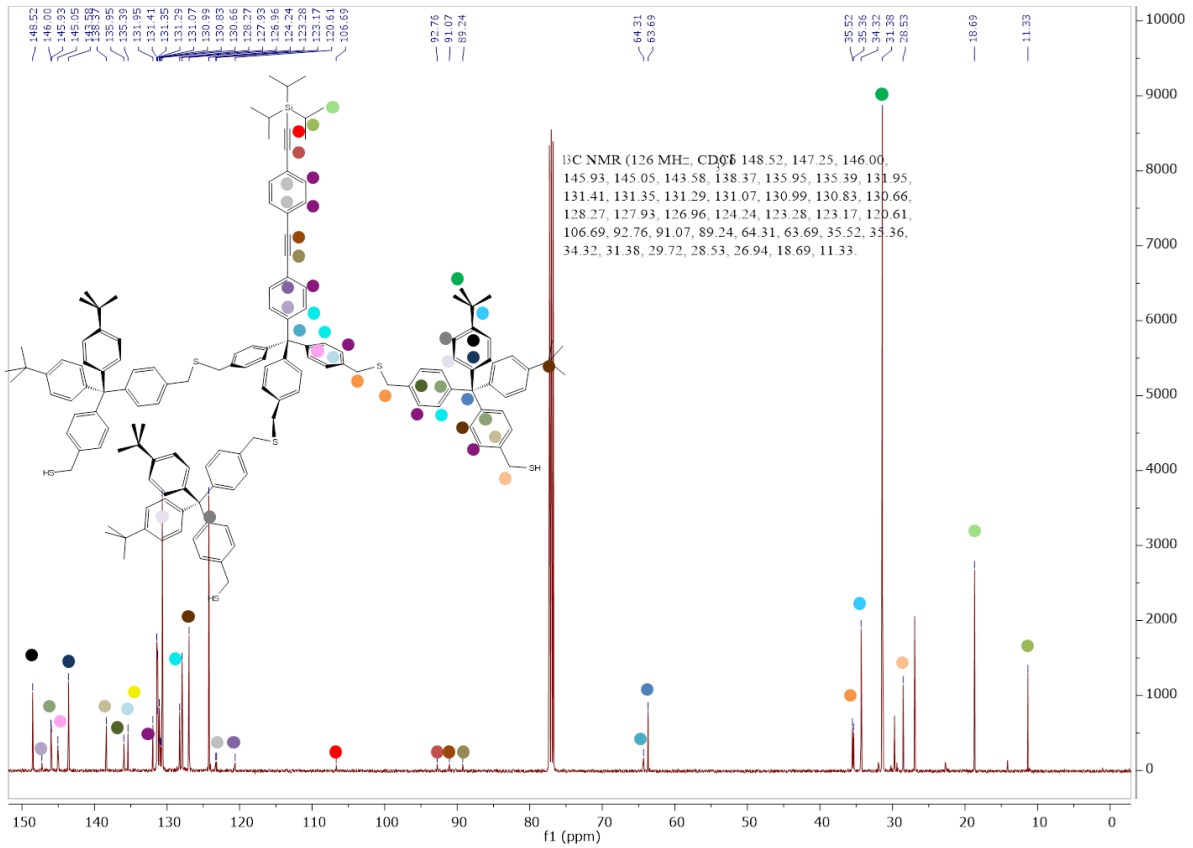


Tris(p-(p-(p-(mercaptomethyl)phenyl-bis(p-*tert*-butylphenyl)methyl)phenylmethylthio-methyl)phenyl)-p-(p-(triisopropylsilylethynyl)phenylethynyl)phenylmethane (**9**)

In a dry, degassed 25 ml flask, cage precursor **8** (576 mg, 0.196 mmol, 1 eq.) and SiEt<sub>3</sub>H (0.20 ml, 0.745 mmol, 3.8 eq.) were dissolved in 20 ml CH<sub>2</sub>Cl<sub>2</sub> and degassed for 30 minutes. The deprotection was started upon addition of 0.8 ml TFA (4 vol-%) which was visible from the color change to bright orange. The mixture was stirred until

the color had faded, indicating completion of the reaction (5 minutes) and quenched by addition of saturated aqueous NaHCO<sub>3</sub>. The phases were separated and the aqueous phase extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. Purification was performed by column chromatography (c-hexane: CH<sub>2</sub>Cl<sub>2</sub> gradient 4:1 to 1:1) to yield cage precursor trithiol **9** (404 mg, 0.183 mmol, 93%) as a white solid. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 4H), 7.40 – 7.37 (m, 2H), 7.24 – 7.21 (m, 14H), 7.20 – 7.11 (m, 34H), 7.10 – 7.06 (m, 14H), 3.70 (d, *J* = 7.5 Hz, 6H), 3.60 (d, *J* = 5.6 Hz, 12H), 1.75 (t, *J* = 7.5 Hz, 3H), 1.29 (s, 54H), 1.14 (s, 21H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.52, 147.25, 146.00, 145.93, 145.05, 143.58, 138.37, 135.95, 135.39, 131.95, 131.41, 131.35, 131.29, 131.07, 130.99, 130.83, 130.66, 128.27, 127.93, 126.96, 124.24, 123.28, 123.17, 120.61, 106.69, 92.76, 91.07, 89.24, 64.31, 63.69, 35.52, 35.36, 34.32, 31.38, 28.53, 18.69, 11.33. HRMD (MALDI-ToF): *m/z* = [M+Na]<sup>+</sup> calcd. for C<sub>152</sub>H<sub>164</sub>S<sub>6</sub>SiNa<sup>+</sup>: 2232.0819, found: 2232.0837.

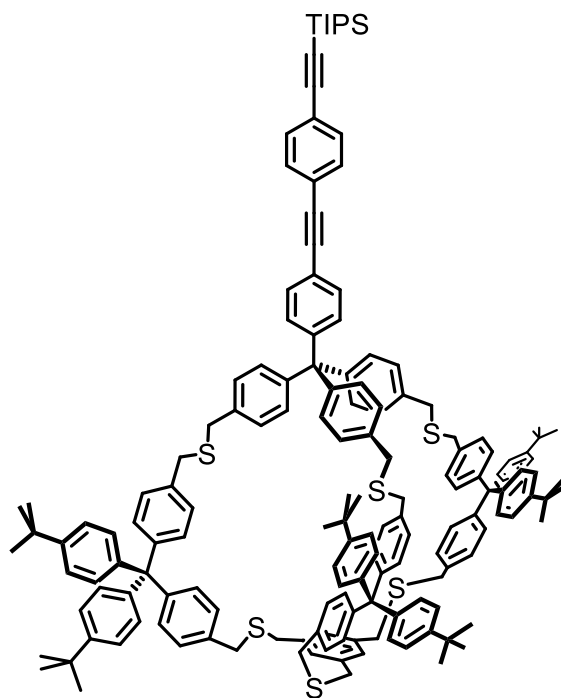




**Evaluation Spectra / Validation Formula:**

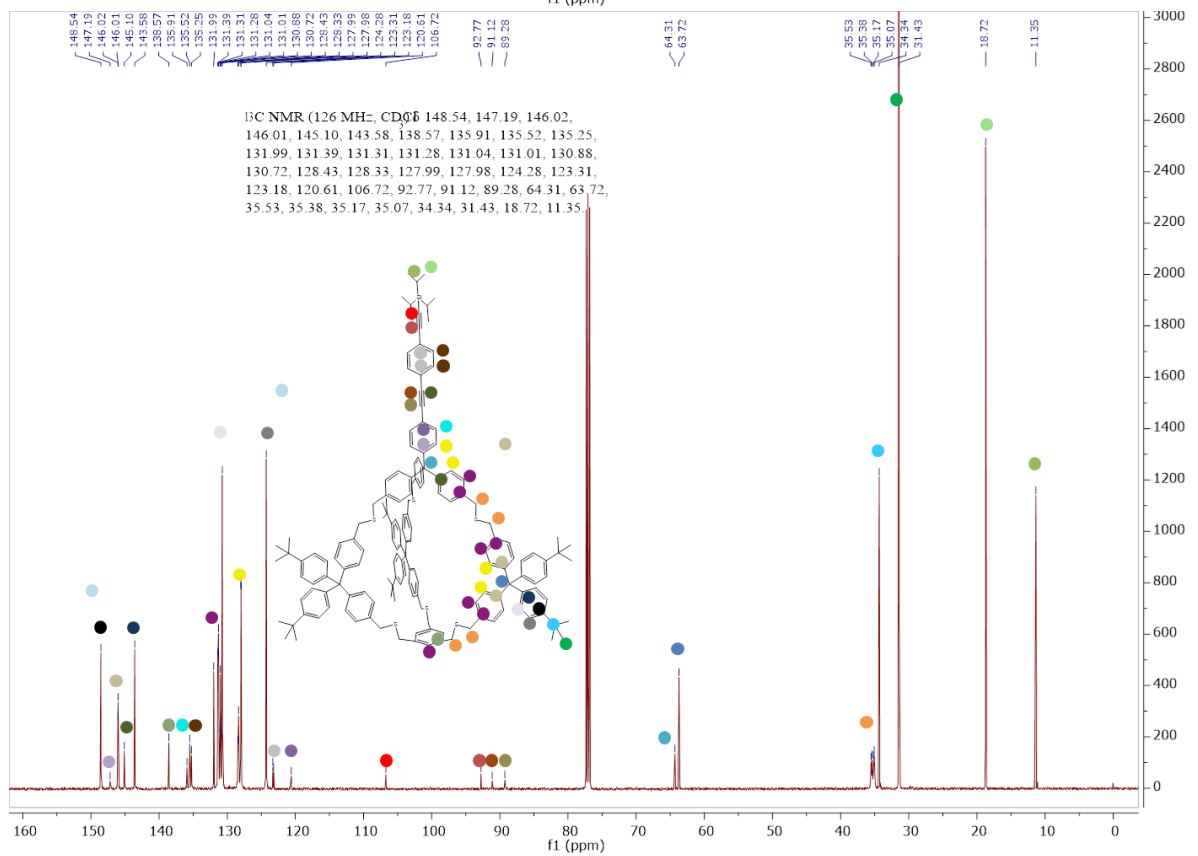
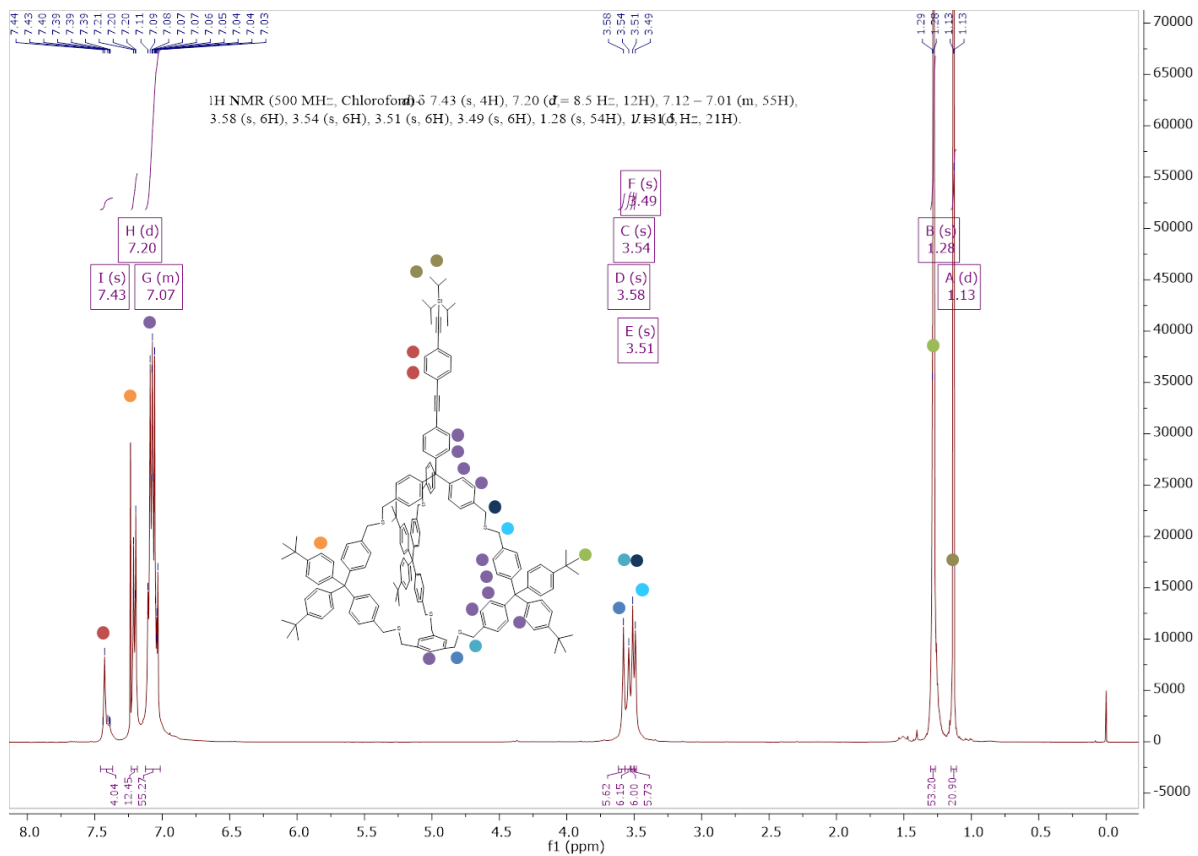
#	Ion Formula	Adduct	m/z	z	Meas. m/z	mSigma	N-Rule	err [mDa]	err [ppm]
1	C <sub>152</sub> H <sub>164</sub> Na <sub>6</sub> Si <sub>6</sub>	M+Na	2232.0819	1+	2232.0837	177.6	ok	-1.8	-0.8

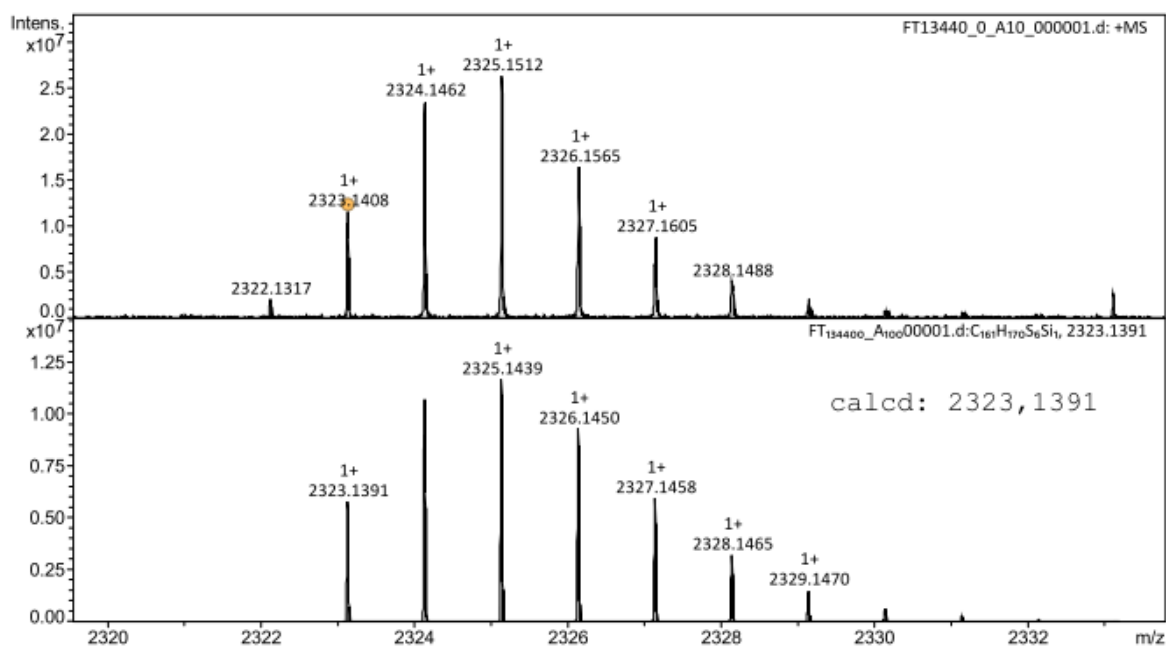




### Cage-Type Ligand 1

In a 250 ml flask, trithiol **9** (175 mg, 0.079 mmol, 1 eq.) and 1,3,5-tris(bromo-methyl)benzene (28 mg, 0.079 mmol, 1 eq.) were dissolved in 200 ml dry THF and degassed with an argon stream for 30 minutes. NaH (60% dispersion in mineral oil, 30 mg, 0.751 mmol, 9.5 eq.) was added and the reaction mixture was allowed to stir at rt for 3 days. The reaction was quenched upon careful addition of minimum amounts of water, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed in vacuo. The crude was filtrated over a silica plug (CH<sub>2</sub>Cl<sub>2</sub>) and cage **1** was isolated by automated GPC (chloroform) to give a colorless solid (95 mg, 0.041 mmol, 52%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 4H), 7.20 (d, *J* = 8.5 Hz, 12H), 7.12 – 7.01 (m, 55H), 3.58 (s, 6H), 3.54 (s, 6H), 3.51 (s, 6H), 3.49 (s, 6H), 1.28 (s, 54H), 1.14 – 1.12 (m, 21H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.54, 147.19, 146.02, 146.01, 145.10, 143.58, 138.57, 135.91, 135.52, 135.25, 131.99, 131.39, 131.31, 131.28, 131.04, 131.01, 130.88, 130.72, 128.43, 128.33, 127.99, 127.98, 124.28, 123.31, 123.18, 120.61, 106.72, 92.77, 91.12, 89.28, 64.31, 63.72, 35.53, 35.38, 35.17, 35.07, 34.34, 31.43, 18.72, 11.35. HRMS (MALDI-ToF): *m/z* = [M]<sup>+</sup> calcd. for C<sub>161</sub>H<sub>170</sub>S<sub>6</sub>Si<sup>+</sup>: 2323.1391, found: 2323.1408.





Evaluation Spectra / Validation Formula:

#	Ion Formula	Adduct	m/z	z	Meas. m/z	mSigma	N-Rule	err [mDa]	err [ppm]
1	C161H170S6Si	M	2323.1391	1+	2323.1408	213.8	ok	-1.7	-0.7

## References

1. E. H. Peters and M. Mayor, *Eur. J. Inorg. Chem.*, 2020, **2020**, 2325–2334.
2. M. Lehmann, E. H. Peters and M. Mayor, *Chem. – Eur. J.*, 2016, **22**, 2261–2265.