

Supporting information

**Synthesis and Properties of Oligo[n]cruciforms: Nanosized Sterically Encumbered Tetraethynylphenyl-Homologated Fluorophores.**

Abdelaziz Al Ouahabi,<sup>†</sup> Paul N. W. Baxter,<sup>\*,†</sup> Jean-Paul Gisselbrecht,<sup>‡</sup> André De Cian,<sup>§</sup> Lydia Brelot,<sup>§</sup> Nathalie Kyritsakas-Gruber.<sup>§,||</sup>

<sup>†</sup>Institut Charles Sadron, CNRS UPR 022, 6 Rue de Loess, F-67083 Strasbourg, France.

<sup>‡</sup>Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide and <sup>§</sup>Service de Radiocristallographie, CNRS UMR 7177, <sup>||</sup>Current address: Laboratoire de Chimie de Coordination Organique, CNRS UMR 7140, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg, France.

## S1. Supporting Information; Table of Contents.

**S1.** Supporting Information; Table of Contents. p 2.

**S2.** Supporting Information; General Experimental Methods. p 5.

**S3.** Supporting Information; Synthetic Procedures and Characterization Data for **7 - 9, 11, 14** and **15** and UV/visible spectrum of **10**. p 8.

**S4.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4-iodo-2,5-bis-triisopropylsilylethynyl-bromobenzene (**7**) in  $\text{CDCl}_3$  at 26 °C: 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum). p 13.

**S5.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4-iodo-2,5-bis-triisopropylsilylethynyl-bromobenzene (**7**) in  $\text{CDCl}_3$  at 26 °C: 200 - 0 ppm (upper), and expansion of aliphatic region showing TIPS carbons (lower spectrum). p 14.

**S6.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-bromobenzene (**8**) in  $\text{CDCl}_3$  at 25 °C: 10 - 0 ppm (upper), and expanded aromatic region (lower spectrum). p 15.

**S7.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-bromobenzene (**8**) in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm. p 16.

**S8.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-bromobenzene (**8**) in  $\text{CDCl}_3$ : Expansion of aromatic/ethynyl region (upper), and TIPS carbons (lower spectrum). p 17.

**S9.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-iodobenzene (**9**) in  $\text{CDCl}_3$  at 25 °C: 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum). p 18.

**S10.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-iodobenzene (**9**) in  $\text{CDCl}_3$  at 25 °C. p 19.

**S11.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-iodobenzene (**9**) in  $\text{CDCl}_3$  at 25 °C: Magnification of aromatic region (upper), and expansion of aliphatic region showing TIPS carbons (lower spectrum). p 20.

**S12.** 500.13 MHz  $^1\text{H}$  NMR spectra of 1,4-diethynyl-2,5-bis-triisopropylsilylethynylbenzene (**11**) (upper spectrum) in  $\text{CDCl}_3$  at 25 °C, and 100.61 MHz  $^{13}\text{C}$  NMR (lower spectrum) in  $\text{CDCl}_3$  at 26 °C. p 21.

- S13.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25 °C: 10 - 0 ppm. p 22.
- S14.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25 °C: Expansion of aromatic region (upper), and TIPS protons in aliphatic region (lower spectrum). p 23.
- S15.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl-region (lower spectrum). p 24.
- S16.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25 °C: Expansion of closely situated peaks in aromatic region (upper), and ethynyl-region (lower spectrum). p 25.
- S17.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  at 25 °C. p 26.
- S18.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  at 25 °C: expansion of aromatic region (upper spectrum), and expansion of aliphatic region, showing TIPS peaks (left) and TMS peak (right: lower spectrum). p 27.
- S19.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  at 25 °C. p 28.
- S20.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  25 °C: Aromatic and acetylenic region (upper), and magnification of part of aromatic region (lower spectrum) showing peak at 125.46 ppm on left side of peak at 125.44 ppm. p 29.
- S21.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  25 °C: Expansion of aliphatic region showing TIPS carbons. p 30.
- S22.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25 °C: 10 - 0 ppm. p 31.
- S23.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25 °C: Expansion of closely situated peaks in aromatic region (upper), and TIPS peaks (lower spectrum). p 32.
- S24.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25 °C (200 - 0 ppm). p 33.
- S25.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25 °C: Expansion of aromatic region (upper), and ethyne-region (lower spectrum). p 34.
- S26.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25 °C. p 35.
- S27.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25 °C. Upper spectrum: Expansion of aliphatic region showing TIPS signals (left) and TMS signal (right); Lower spectrum: Expansion of aromatic region. p 36.
- S28.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm (upper), and expansion of ethynyl-region (lower spectrum). p 37.

**S29.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25 °C: Magnification of part of aromatic region (upper), and expansion of aliphatic-region showing TIPS peaks (lower spectrum). p 38.

**S30.** 400.13 MHz  $^1\text{H}$  NMR spectra of 2-iodo-4-triisopropylsilylethynyl-trimethylsilylethynylbenzene (**14**) in  $\text{CDCl}_3$  at 25 °C: 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum). p 39.

**S31.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 2-iodo-4-triisopropylsilylethynyl-trimethylsilylethynylbenzene (**14**) in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum). p 40.

**S32.** 400.13 MHz  $^1\text{H}$  NMR spectra of 2-iodo-4-triisopropylsilylethynyl-ethynylbenzene (**15**) in  $\text{CDCl}_3$  at 24 °C: 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum). p 41.

**S33.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 2-iodo-4-triisopropylsilylethynyl-ethynylbenzene (**15**) in  $\text{CDCl}_3$  at 24 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum). p 42.

**S34.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4,4',4''-tris-(triisopropylsilylethynyl)-dehydrotribenzo[12]annulene (**5**) in  $\text{CD}_2\text{Cl}_2$  at 22 °C: 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum). p 43.

**S35.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4,4',4''-tris-(triisopropylsilylethynyl)-dehydrotribenzo[12]annulene (**5**) in  $\text{CD}_2\text{Cl}_2$  at 22 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum). p 44.

**S36.** 500.13 MHz  $^1\text{H}$  NMR spectra of 4,4',4''-triethynyl-dehydrotribenzo[12]annulene (**16**) in  $\text{CD}_2\text{Cl}_2$  at 25 °C: 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum). p 45.

**S37.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4,4',4''-triethynyl-dehydrotribenzo[12]annulene (**16**) in  $\text{CD}_2\text{Cl}_2$  at 24 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum). p 46.

**S38.** Supporting information; X-ray Experimental for **1**. p 47.

**S39.** Supporting information; Full-page thermal ellipsoid plot of X-ray crystal structure of **1**. p 48.

## S2. Supporting information; General Experimental Methods.

Standard inert atmosphere and Schlenk techniques were employed for reactions conducted under argon. Starting materials **6**,<sup>14</sup> **10**,<sup>16</sup> and **13**<sup>22</sup> were prepared as described. The alkynes TMSA (trimethylsilylacetylene) and TIPSA (triisopropylsilylacetylene), **12**, and the catalysts CuI, [PdCl<sub>2</sub>(dppf)].CH<sub>2</sub>Cl<sub>2</sub><sup>39</sup> were obtained from commercial sources. The PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was prepared by heating PdCl<sub>2</sub> and PPh<sub>3</sub> (1 : 2.5 molar ratio) in DMSO.<sup>40</sup> Triethylamine and toluene used in the Sonogashira reactions were deoxygenated by bubbling with argon for 0.5 h directly prior to use. The Et<sub>2</sub>O in the bromine/iodine metatheses was freshly distilled over Na/benzophenone under argon. The heptane used in the spectroscopic studies was purchased from PROLABO (Normapur grade; >99.0%), with an H<sub>2</sub>O content <0.01%, and was used without further purification. All silica chromatography was performed on Geduran Silica gel (Si 60, 40-63 μm) purchased from Merck. Through-bond proton connectivities were determined by <sup>1</sup>H - <sup>1</sup>H COSY, and through-space proton connectivities by NOESY and ROESY spectroscopy. All <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced either to the CHCl<sub>3</sub> solvent peaks (at 7.26 and 77.0 ppm respectively) or the CH<sub>2</sub>Cl<sub>2</sub> solvent peaks (at 5.32 and 54.0 ppm respectively).

All the UV-visible spectra and solution luminescence emission spectra of **1** - **5** and **16** were recorded in heptane at 20 - 25 °C. The solid state luminescence emission spectra of **1** - **5** and **16** were recorded at 20 - 25 °C as evaporated thin films on a quartz disc. The evaporated thin films were prepared from either pentane solution (**1**, **3**, **5** and **10**) or CH<sub>2</sub>Cl<sub>2</sub> solutions/suspensions (**2**, **4** and **16**). All emission spectra were corrected for the instrumental response. In order to verify if the emission shape and energy varied with excitation wavelength, the fluorescence spectra were obtained using high and low energy excitation wavelengths which in the case of the solution measurements corresponded to absorption maxima of the respective UV-visible spectra. The excitation wavelengths used to record the solution and solid state emission spectra and the solution concentrations are shown in the Table 4 below.

**Table 4.** Luminescence emission experimental data: excitation wavelengths and solution concentrations.

Compound no.	$\lambda_{\text{excitation}}$ [nm] (solution)	$\lambda_{\text{excitation}}$ [nm] (thin film)	concentration of heptane solution [mol/L]
<b>1</b>	275 <sup>a</sup>	286	$2 \times 10^{-5}$
	286	372 <sup>a</sup>	
<b>2</b>	273	273	$5 \times 10^{-5}$
	289 <sup>a</sup>	386 <sup>a</sup>	
<b>3</b>	273	300	$7 \times 10^{-5}$
	285 <sup>a</sup>	356 <sup>a</sup>	
<b>4</b>	275	287	$1 \times 10^{-5}$
		377 <sup>a</sup>	
<b>5</b>	254	318	$5 \times 10^{-4}$
	367 <sup>a</sup>	400 <sup>a</sup>	
<b>10</b>	273 <sup>a</sup>	251	$4 \times 10^{-6}$
	321	273 <sup>a</sup>	
<b>16</b>	308 <sup>a</sup>	301	$9 \times 10^{-7}$
	362	410	

<sup>a</sup>excitation wavelengths used for emission spectra and data displayed in Figures and Table of publication

In all emission spectra, only minimal changes in the shape of the curves were observed; the  $\lambda(\text{max.})$  varying by  $\leq 2$  nm upon excitation at different wavelengths, showing that re-absorption effects were negligible in these measurements.

The experimental conditions used to measure the luminescence quantum yields are shown in Table 5 below. All luminescence measurements concerning the phenyleneethynylene oligomers were performed in air-equilibrated heptane, and those of anthracene in argon-degassed ethanol at 20 - 25 °C. In the case of the quantum yield oxygen quenching investigations on **4**, the luminescence spectra of each of the solutions were measured in air-equilibrated heptane, then bubbled with argon for 10 minutes and the luminescence directly re-measured.

**Table 5.** Experimental conditions used for luminescence quantum yield measurements.

Monomer/ Oligomer	Luminescence standard	Excitation $\lambda$ (nm)	Absorbance bandpass (nm)	Excitation monochromator (nm)	Emission monochromator (nm)
<b>1</b>	anthracene	339	2	5	2
<b>2</b>	anthracene	339	2	5	2
<b>3</b>	anthracene	339	2	5	2
<b>4</b>	anthracene	339	2	2	2
<b>5</b>	quinine hemisulfate monohydrate in 0.5 M a.q. H <sub>2</sub> SO <sub>4</sub>	307, 318	2	5	2
<b>10</b>	anthracene	320	2	4	2

Infrared spectra were recorded as compressed powders and the thermochemical TGA measurements performed under an atmosphere of argon. The DSC measurements were recorded using an N<sub>2</sub> flow of 20 mL/minute and a heating rate of 2 °C/minute. Melting point measurements were performed using an internally calibrated heating stage supported on an optical microscope, and using a heating rate of 10 °C/minute up to 5 - 10 °C below the phase transition and 0.5 °C/minute over the phase transition. Compounds **1 - 5** and **16** were stable at ambient temperature, and in particular, **1 - 5** were photostable and could be stored on the bench over several years with no visible sign of decomposition.

### References (Contd.)

- 39) Corain, B.; Longato, B.; Favero, G.; Ajò, D.; Pilloni, G.; Russo, U.; Kreissl, F. R. *Inorg. Chim. Acta.* **1989**, *157*, 259.
- 40) Brumbaugh, J. S.; Sen, A. *J. Am. Chem. Soc.* **1988**, *110*, 803.

### S3. Supporting Information; Synthetic Procedures and Characterization Data for 7 - 9, 11, 14 and 15 and UV/visible spectrum of 10.

#### **4-iodo-2,5-bis-triisopropylsilylethynyl-bromobenzene (7):**

To a dried, argon filled 500mL 2-necked flask fitted with an alcohol thermometer, vacuum/Argon inlet adaptor and rubber septum, containing **6** (4.138g,  $6.94 \times 10^{-3}$  mol), was added Et<sub>2</sub>O (150 mL) via syringe. The stirred suspension was cooled to  $-78$  °C (acetone/CO<sub>2</sub> bath) and *n*-BuLi (4.2 mL, 1.67 mol/L in cyclohexane,  $7.01 \times 10^{-3}$  mol) added at a rate which maintained the internal temperature at  $-74$  °C. During addition, the suspended solid dissolved. The resulting yellow solution was stirred at  $-74$  °C for 2 h, during which time a suspended solid re-appeared. In a separate dried Schlenk was prepared a solution of 1,2-diiodoethane (2.86g,  $1.01 \times 10^{-2}$  mol) in Et<sub>2</sub>O (24 mL) under argon, and this syringed into the reaction solution at a rate which ensured that the internal temperature did not rise above  $-70$  °C (all suspended solids dissolved), and the reaction stirred at  $-78$  °C for 4 h, then allowed to warm to ambient temperature with continued stirring overnight. The reaction solution was extracted with water ( $3 \times 70$  mL), dried (anhydrous MgSO<sub>4</sub>), gravity filtered and the solvent distilled off at atmospheric pressure on a waterbath. The residue was dried under vacuum and chromatographed on Silica eluting with hexane, then recrystallized from absolute ethanol and air-dried to afford **7** (3.380g, 76%) as a dusty white solid (Mp. =  $137.0 - 138.3$  °C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz, 26 °C):  $\delta$  = 7.902 (s, 1H; pH3), 7.632 (s, 1H; pH6), 1.154 (s, 21H; 5-Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.142 ppm (m, 21H; 2-Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.61 MHz, 26 °C):  $\delta$  = 142.7, 135.8, 131.1, 126.7, 124.9, 106.5, 103.0, 99.8, 99.0, 97.9, 18.70 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.65 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.30 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.27 ppm (CH(CH<sub>3</sub>)<sub>2</sub>). IR (thin film): 2942 (m), 2889 (w), 2864 (m), 2161 (w) (C≡C), 1457 (s), 1056 (m), 995 (m), 883 (s), 807 (vs), 677 (s), 662 cm<sup>-1</sup> (s). EI MS: *m/z* (%): 644.2 (19) [*M*<sup>+</sup>], 601.2 (100) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>7</sub>]. calcd. for C<sub>28</sub>H<sub>44</sub>BrISi<sub>2</sub>: 644.1. High Res. ESI MS: *m/z* (%): 707.0491 (100) [*M* + Cu<sup>+</sup>]. calcd. for C<sub>28</sub>H<sub>44</sub>BrCuISi<sub>2</sub>: 707.0483.

#### **4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-bromobenzene (8):**

Following the general procedure for Sonogashira couplings, a mixture of **7** (3.380g,  $5.25 \times 10^{-3}$  mol), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.159g,  $2.27 \times 10^{-4}$  mol) and trimethylsilylacetylene (1.0 mL, 0.695g, 7.08



$\times 10^{-3}$  mol) in toluene (100 mL), and CuI (0.159g,  $8.35 \times 10^{-4}$  mol) in Et<sub>3</sub>N (8 mL) were stirred for 7 d in the dark at ambient temperature. All solvent was subsequently removed from the reaction under reduced pressure on a waterbath, and the residue extracted with pentane (5  $\times$  40 mL). The combined pentane washings were gravity filtered, the solvent distilled off on a waterbath and the remaining oil chromatographed on four consecutive columns of Silica, eluting with pentane. The product thus obtained was dried under vacuum (80 °C, 0.01 mmHg) to afford **8** (2.475g, 77%) as a pale honey-colored oil that slowly crystallized upon standing (Mp. = 62.0 - 65.8 °C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz, 25 °C):  $\delta$  = 7.650 (s, 1H; phH6), 7.553 (s, 1H; phH3), 1.143 (s, 42H; 2,5-Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 0.234 ppm (s, 9H; Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.61 MHz, 25 °C):  $\delta$  = 137.3, 136.2, 126.5, 125.3, 124.9, 124.5, 103.7 (-C $\equiv$ ), 103.5 (-C $\equiv$ ), 101.7 (-C $\equiv$ ), 99.8 (-C $\equiv$ ), 98.8 (-C $\equiv$ ), 98.4 (-C $\equiv$ ), 18.75 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.65 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.2 (CH(CH<sub>3</sub>)<sub>2</sub>), -0.2 ppm (Si(CH<sub>3</sub>)<sub>3</sub>). IR (thin film): 2943 (m), 2891 (w), 2865 (m), 2160 (w) (C $\equiv$ C), 1468 (m), 1250 (m), 997 (m), 899 (m), 882 (m), 857 (s), 841 (vs), 825 (vs), 770 (m), 760 (m), 677 (s), 662 cm<sup>-1</sup> (s). EI MS: *m/z* (%): 614.3 (57) [*M*<sup>+</sup>], 571.3 (100) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>7</sub>], 529.2 (73) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>7</sub> - C<sub>3</sub>H<sub>6</sub>]. calcd. for C<sub>33</sub>H<sub>53</sub>BrSi<sub>3</sub>: 614.3. High Res. ESI MS: *m/z* (%): 677.1923 (100) [*M* + Cu<sup>+</sup>]. calcd. for C<sub>33</sub>H<sub>53</sub>BrCuSi<sub>3</sub>: 677.1914.

#### **4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-iodobenzene (9):**

To a dried, argon filled 500mL 2-necked flask fitted with an alcohol thermometer, vacuum/Argon inlet adaptor and rubber septum, and containing **8** (2.475g,  $4.03 \times 10^{-3}$  mol), was added Et<sub>2</sub>O (140 mL) via syringe. The stirred solution was cooled to -78 °C (acetone/CO<sub>2</sub> bath) and *n*-BuLi (3.0 mL, 1.6 mol/L in hexanes,  $4.80 \times 10^{-3}$  mol) added at a rate which maintained the internal temperature below -74 °C. The solution was then stirred at -78 °C for 1.5 h. In a separate dried Schlenk was prepared a solution of 1,2-diiodoethane (3.00g,  $1.06 \times 10^{-2}$  mol) in Et<sub>2</sub>O (20 mL) under argon, and this syringed into the reaction solution at a rate which ensured that the internal temperature did not rise above -70 °C. The reaction was stirred at -78 °C for a further 4 h, then allowed to warm to ambient temperature with continued stirring. The reaction solution was extracted with water (4  $\times$  50 mL), and the combined aqueous phases extracted with Et<sub>2</sub>O (20 mL). The combined organic phases were then dried (anhydrous MgSO<sub>4</sub>), gravity filtered and the

solvent distilled off at atmospheric pressure on a waterbath. The residue was further dried in a stream of air and chromatographed on five consecutive columns of Silica eluting with pentane. The product thus isolated was dried under vacuum (0.01 mmHg) to afford **9** (2.121g, 80%) as an oil that crystallized to a soft cream solid (Mp. = 57.0 - 59.3 °C).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz, 25 °C):  $\delta$  = 7.905 (s, 1H; pH6), 7.509 (s, 1H; pH3), 1.156 (s)/1.141 (s); (42H; 2,5-Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 0.233 ppm (s, 9H; Si(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.61 MHz, 25 °C):  $\delta$  = 142.4, 136.4, 129.7, 126.3, 125.3, 107.0, 103.3, 101.8, 100.0, 99.7, 98.3, 97.9, 18.75 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.71 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.2 (CH(CH<sub>3</sub>)<sub>2</sub>), -0.2 ppm (Si(CH<sub>3</sub>)<sub>3</sub>). IR (thin film): 2943 (m), 2890 (w), 2864 (m), 2154 (w) (C≡C), 1463 (m), 1250 (m), 897 (m), 882 (m), 854 (s), 840 (vs), 823 (s), 767 (m), 758 (m), 667  $\text{cm}^{-1}$  (vs). High Res. ESI MS:  $m/z$  (%): 723.1763 (100) [ $M + \text{Cu}^+$ ]. calcd. for  $\text{C}_{33}\text{H}_{53}\text{CuISi}_3$ : 723.1790.

#### **1,4-bis-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynylbenzene (10):**

UV-vis (heptane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 246sh (16526), 251sh (23565), 259 (59778), 265 (69419), 274 (185531), 284 (22504), 290 (24675), 296 (28422), 302 (34204), 308 (39881), 315 (29858), 321 (47073), 334 (4824), 342 (3642), 350 nm (3409  $\text{M}^{-1}\text{cm}^{-1}$ ).

#### **1,4-diethynyl-2,5-bis-triisopropylsilylethynylbenzene (11):**

To a stirred solution of **10** (1.840g,  $2.91 \times 10^{-3}$  mol) in  $\text{Et}_2\text{O}$  (150 mL) and MeOH (30 mL) was added powdered  $\text{K}_2\text{CO}_3$  (0.451g,  $3.26 \times 10^{-3}$  mol), and the mixture was stirred at ambient temperature in the dark for 4 d. A white suspended solid formed during stirring. All solvent was removed under reduced pressure on a waterbath, and the residue suspended in water, filtered under vacuum and washed with excess deionized water, then MeOH (3 × 5 mL) and air dried. The product was finally recrystallized from abs. EtOH to afford **11** (1.098g, 77%) as colorless micro-needles. (Mp. = 163.0 - 164.5 °C).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500.13 MHz, 25 °C):  $\delta$  = 7.579 (s, 2H; pH3/6), 3.322 (s, 2H; -C≡CH), 1.135 ppm (s, 42H; Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.61 MHz, 26 °C):  $\delta$  = 136.1, 126.0, 124.9, 103.5 (-C≡), 98.1 (-C≡), 82.9 (-C≡), 81.1 (-C≡), 18.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 11.3 ppm (CH(CH<sub>3</sub>)<sub>2</sub>). UV-vis (heptane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 226 (10662), 237 (16206), 242sh (19122), 249 (43401), 255 (52104), 262

(128195), 277 (14786), 283 (17959), 288 (22421), 293 (27484), 299 (30756), 306 (27089), 312 (45791), 322sh (3407), 329 (3122), 336 (1746), 344 nm ( $2856 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (KBr disc): 3287 (vs) ( $\equiv\text{C-H}$ ), 2943 (vs), 2889 (s), 2865 (vs), 2157 (m) ( $\text{C}\equiv\text{C}$ ), 1480 (vs), 1461 (s), 1376 (m), 1191 (m), 997 (m), 910 (s), 883 (s), 840 (vs), 685 (vs), 638 (s),  $587 \text{ cm}^{-1}$  (m). EI MS:  $m/z$  (%): 486.3 (23) [ $M^+$ ], 443.2 (100) [ $M^+ - \text{C}_3\text{H}_7$ ]. calcd. for  $\text{C}_{32}\text{H}_{46}\text{Si}_2$ : 486.3. High Res. ESI MS:  $m/z$  (%): 549.2451 [ $M + \text{Cu}^+$ ] (100). calcd. for  $\text{C}_{32}\text{H}_{46}\text{CuSi}_2$ : 549.2429.

#### **2-iodo-4-triisopropylsilylethynyl-trimethylsilylethynylbenzene (14):**

To a dried, argon filled 1 L 2-necked flask fitted with an alcohol thermometer, vacuum/argon inlet adaptor and rubber septum, and containing **13** (17.662g,  $4.07 \times 10^{-2}$  mol), was added  $\text{Et}_2\text{O}$  (500 mL) via syringe. The stirred solution was cooled to  $-78 \text{ }^\circ\text{C}$  (acetone/ $\text{CO}_2$  bath) and  $n\text{-BuLi}$  (35 mL, 1.4 mol/L in hexanes,  $4.90 \times 10^{-2}$  mol) added at a rate which maintained the internal temperature below  $-70 \text{ }^\circ\text{C}$ . The resulting pale yellow solution was then stirred at  $-78 \text{ }^\circ\text{C}$  for 1.5 h. A solution of 1,2-diiodoethane (14.00g,  $4.97 \times 10^{-2}$  mol) in  $\text{Et}_2\text{O}$  (25 mL) under argon was prepared in a separate dried Schlenk, and syringed into the reaction solution at a rate which ensured that the internal temperature did not rise above  $-70 \text{ }^\circ\text{C}$ . The reaction was stirred at  $-78 \text{ }^\circ\text{C}$  for a further 3 h, then allowed to warm to ambient temperature with continued stirring. The reaction solution was extracted with water ( $2 \times 100 \text{ mL}$ ), and the combined aqueous phases extracted with  $\text{Et}_2\text{O}$  (100 mL). The combined organic phases were then dried (anhydrous  $\text{MgSO}_4$ ), gravity filtered and the solvent distilled off at atmospheric pressure on a waterbath. The remaining oil was chromatographed on two consecutive columns of Silica eluting with heptane. The product thus obtained was finally heated at  $80 \text{ }^\circ\text{C}$  in a stream of air to drive off residual volatiles, to afford **14** (18.531g, 95%) as a pale honey-colored oil.

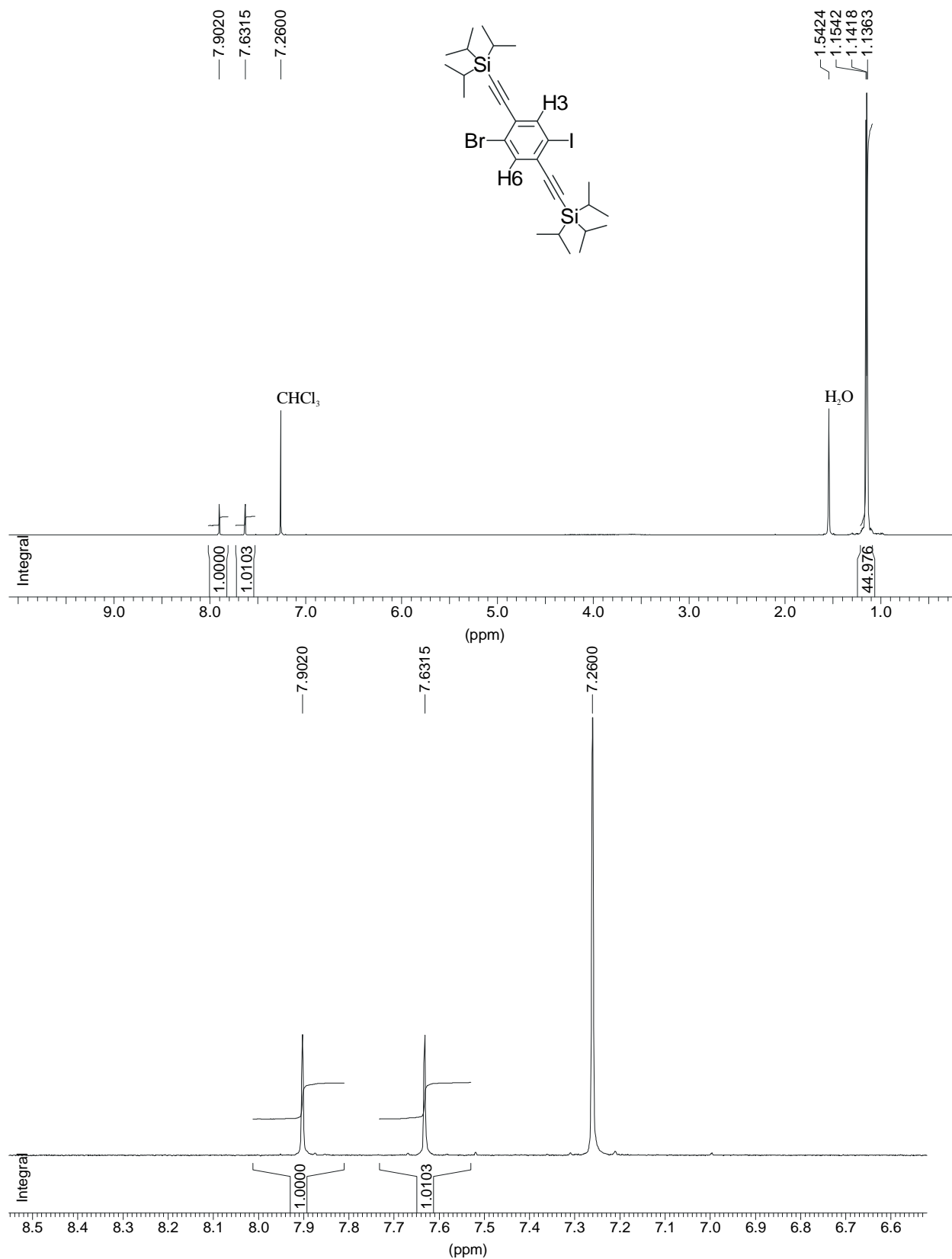
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz,  $25 \text{ }^\circ\text{C}$ ):  $\delta = 7.925$  (m, 1H; H3), 7.363 (m, 2H; H5, H6), 1.119 (m, 21H;  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 0.284 ppm (s, 9H;  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.61 MHz,  $25 \text{ }^\circ\text{C}$ ):  $\delta = 141.6$ , 132.0, 131.2, 129.4, 124.7, 106.2, 104.7, 100.7, 100.5, 94.4, 18.6 ( $\text{CH}(\text{CH}_3)_2$ ), 11.2 ( $\text{CH}(\text{CH}_3)_2$ ),  $-0.3$  ppm ( $\text{Si}(\text{CH}_3)_3$ ). IR (thin film): 2957 (m), 2943 (m), 2892 (w), 2864 (m), 2162 (m) ( $\text{C}\equiv\text{C}$ ), 1465 (m), 1249 (m), 1035 (m), 996 (m), 882 (m), 854 (vs), 842 (vs), 829 (vs), 793 (s), 759 (m), 675 (s),  $661 \text{ cm}^{-1}$  (s). High Res. ESI MS:  $m/z$  (%): 543.0490 (100) [ $M + \text{Cu}^+$ ]. calcd. for  $\text{C}_{22}\text{H}_{33}\text{CuSi}_2$ : 543.0456.

**2-iodo-4-triisopropylsilylethynyl-ethynylbenzene (15):**

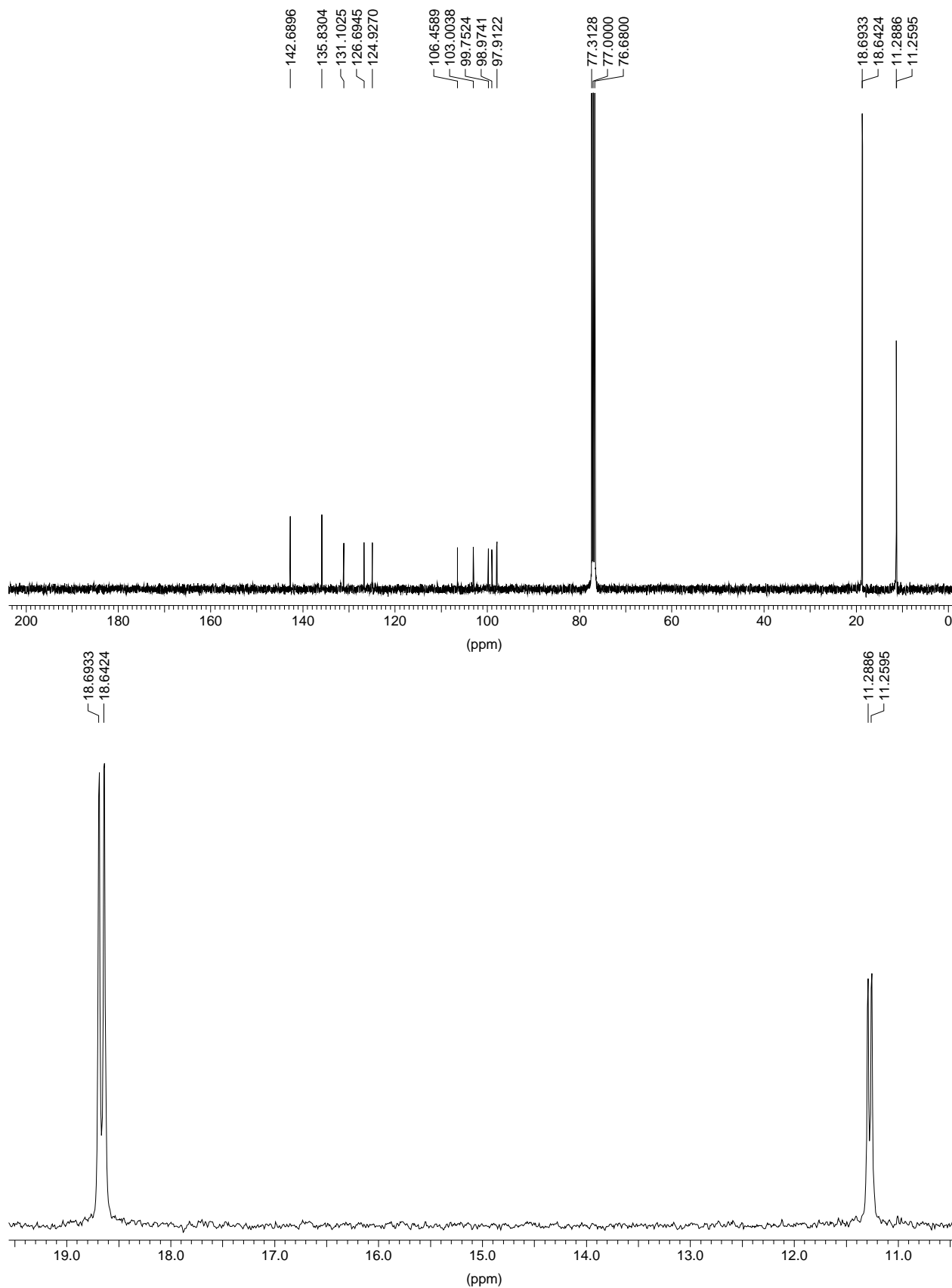
To a stirred solution of **14** (4.343g,  $9.04 \times 10^{-3}$  mol) in THF (30 mL) and MeOH (50 mL) was added powdered  $K_2CO_3$  (0.635g,  $4.59 \times 10^{-3}$  mol). The mixture was stirred at ambient temperature in the dark for 14 h, by which time all the **14** had been consumed, as judged by TLC (Silica/heptane) sampling. All solvent was then removed under reduced pressure at ambient temperature to yield an oily residue, which was partitioned between pentane (150 mL) and water (100 mL). The aqueous phase was further extracted with pentane ( $2 \times 20$  mL) and the combined organic extracts dried (anhydrous  $MgSO_4$ ), gravity filtered and the solvent removed under reduced pressure at ambient temperature. The remaining oil was chromatographed on three consecutive columns of Silica, eluting with heptane. The product exhibits some heat sensitivity, turning orange-brown upon removal of the solvent under reduced pressure on a waterbath at 75 °C. However, final purification could be achieved upon passage down a short column of Silica, eluting with pentane. The solvent was removed under reduced pressure at ambient temperature and the product dried in a stream of air to afford **15** (3.617g, 98%) as a viscous pale-orange oil.

$^1H$  NMR ( $CDCl_3$ , 400.13 MHz, 24 °C):  $\delta$  = 7.939 (d,  $^4J(3,5) = 1.0$  Hz, 1H; H3), 7.413 (d,  $^3J(6,5) = 7.7$  Hz, 1H; H6), 7.383 (dd,  $^3J(5,6) = 8.0$  Hz,  $^4J(5,3) = 1.4$  Hz, 1H; H5), 3.473 (s, 1H;  $-C\equiv CH$ ), 1.121 ppm (m, 21H;  $Si(CH(CH_3)_2)_3$ ).  $^{13}C$  NMR ( $CDCl_3$ , 100.61 MHz, 24 °C):  $\delta$  = 141.7, 132.7, 131.3, 128.5, 125.3, 104.5, 99.8, 94.7, 84.9, 82.6, 18.6 ( $CH(CH_3)_2$ ), 11.2 ppm ( $CH(CH_3)_2$ ). IR (thin film): 3300 (m) ( $\equiv C-H$ ), 2941 (s), 2890 (m), 2864 (s), 2158 (m) ( $C\equiv C$ ), 1586 (m), 1465 (s), 1212 (m), 1034 (m), 996 (m), 881 (vs), 828 (s), 738 (s), 674 (vs), 653  $cm^{-1}$  (vs). High Res. ESI MS:  $m/z$  (%): 471.0121 (20) [ $M + Cu^+$ ]. calcd. for  $C_{19}H_{25}CuISi$ : 471.0061.

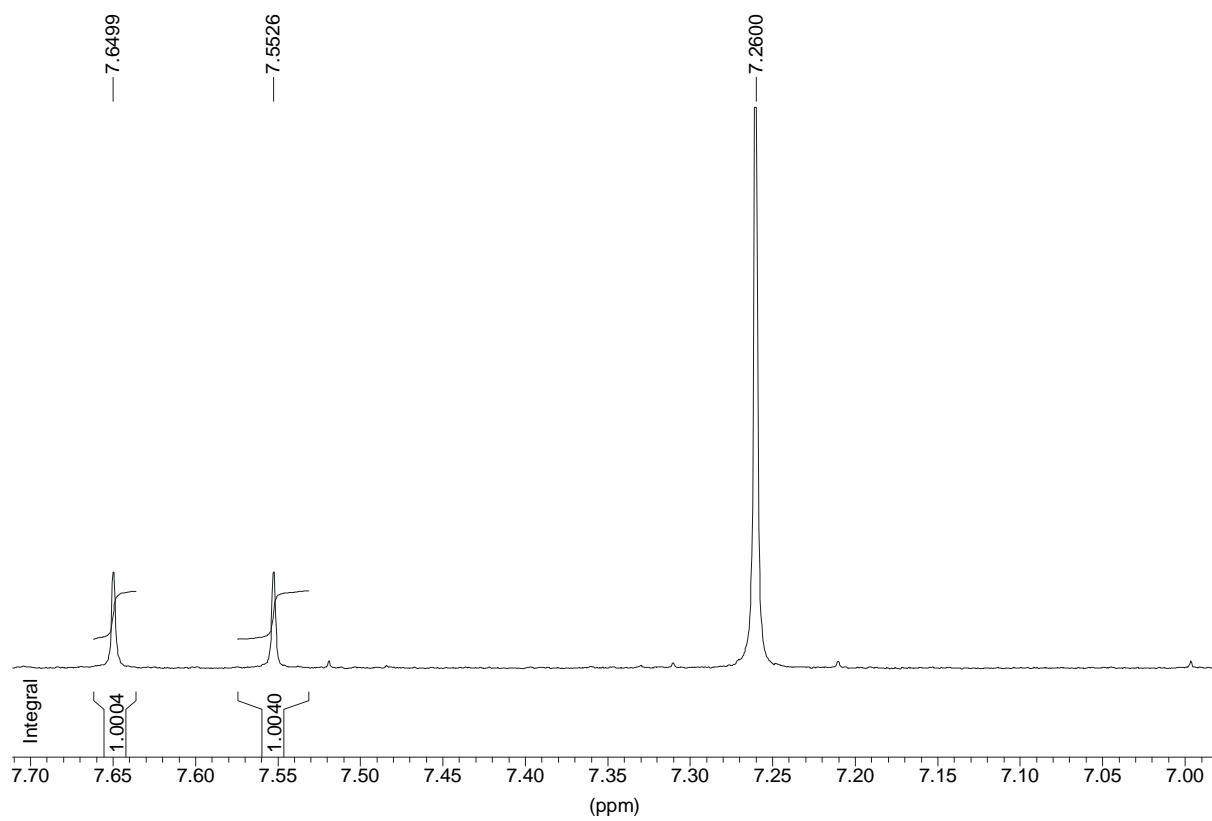
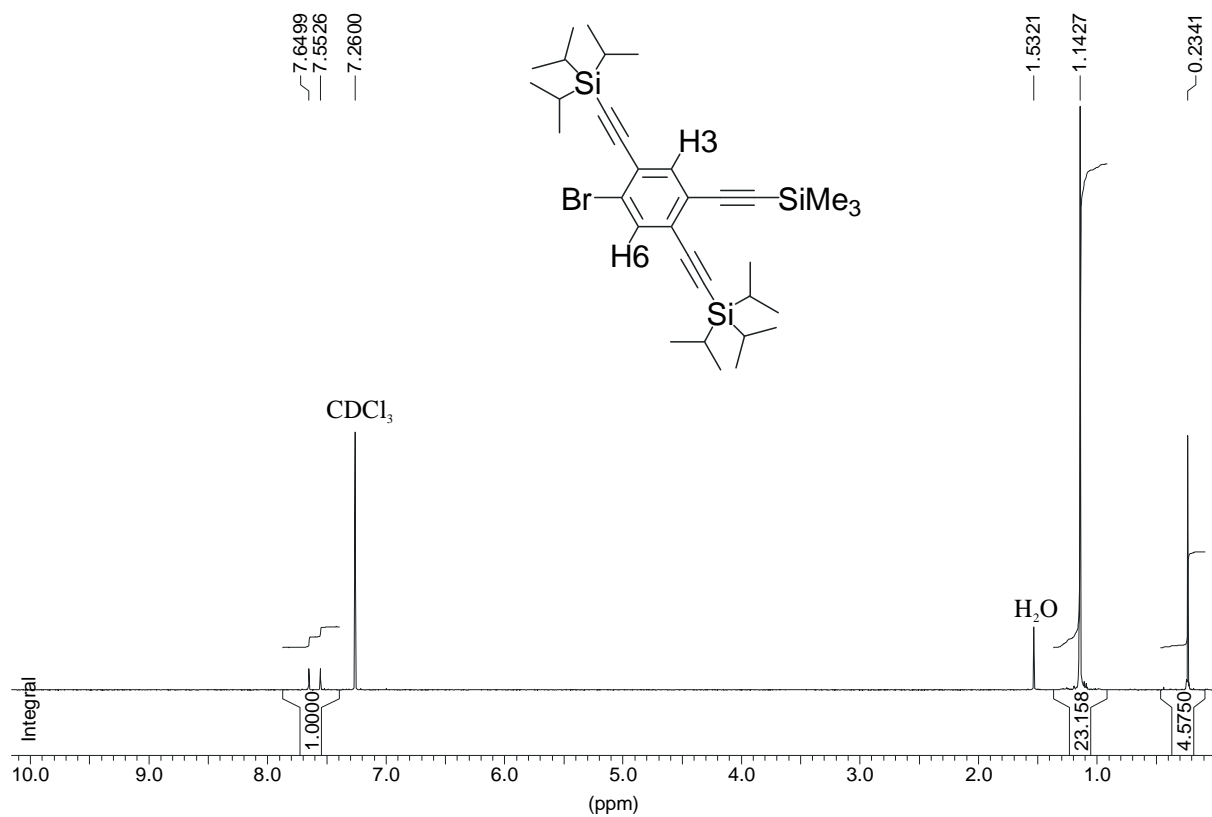
**S4.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4-iodo-2,5-bis-triisopropylsilylethynyl-bromobenzene (**7**) in  $\text{CDCl}_3$  at 26  $^\circ\text{C}$ : 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum).



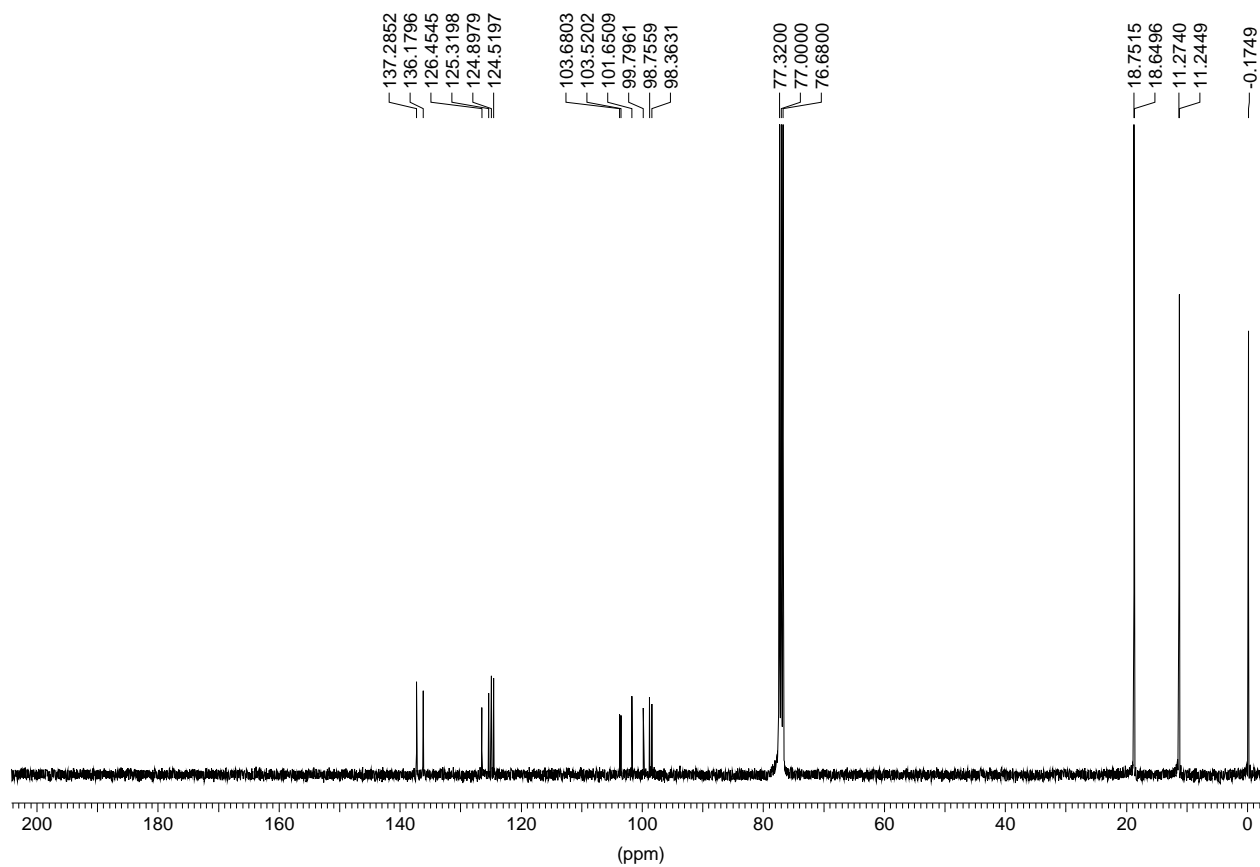
**S5.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4-iodo-2,5-bis-triisopropylsilylethynyl-bromobenzene (**7**) in  $\text{CDCl}_3$  at 26 °C: 200 - 0 ppm (upper), and expansion of aliphatic region showing TIPS carbons (lower spectrum).



**S6.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-bromobenzene (**8**) in  $\text{CDCl}_3$  at 25 °C: 10 - 0 ppm (upper), and expanded aromatic region (lower spectrum).

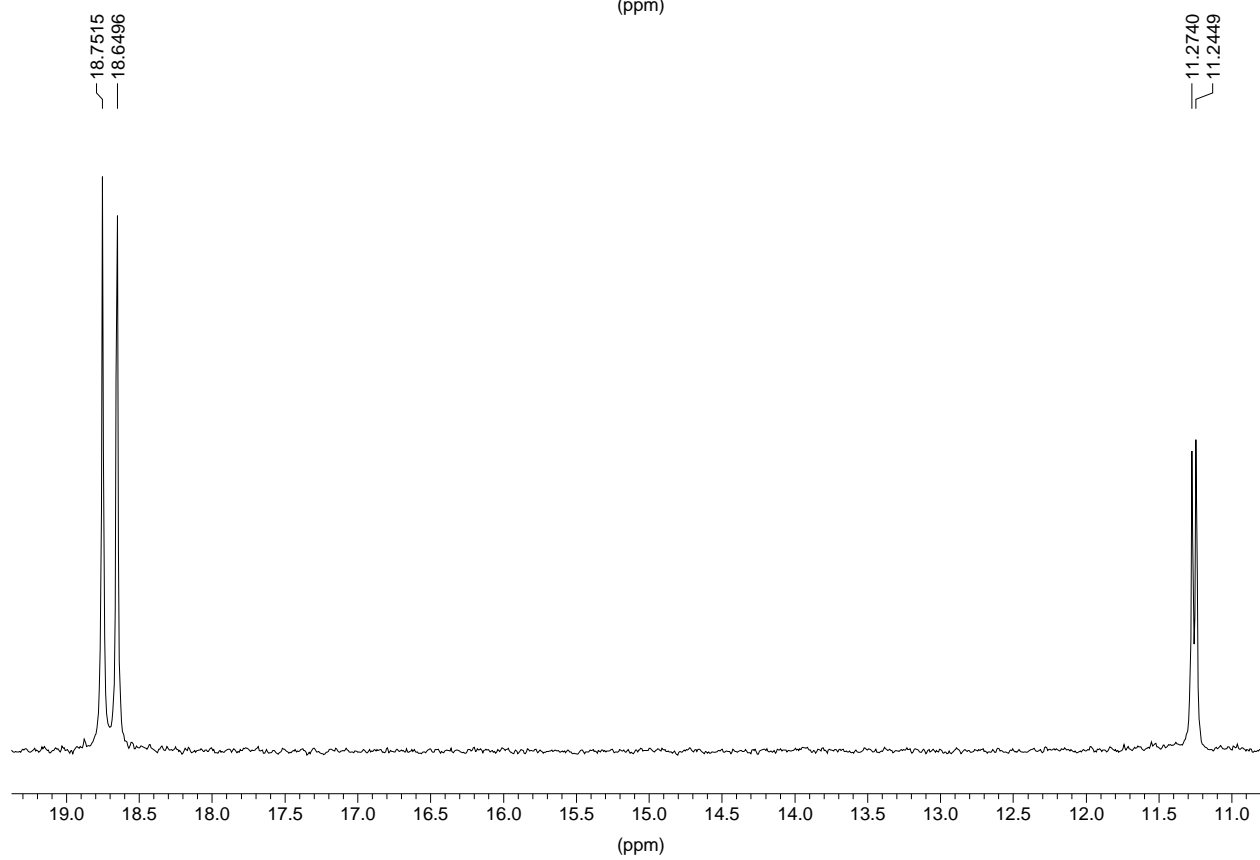
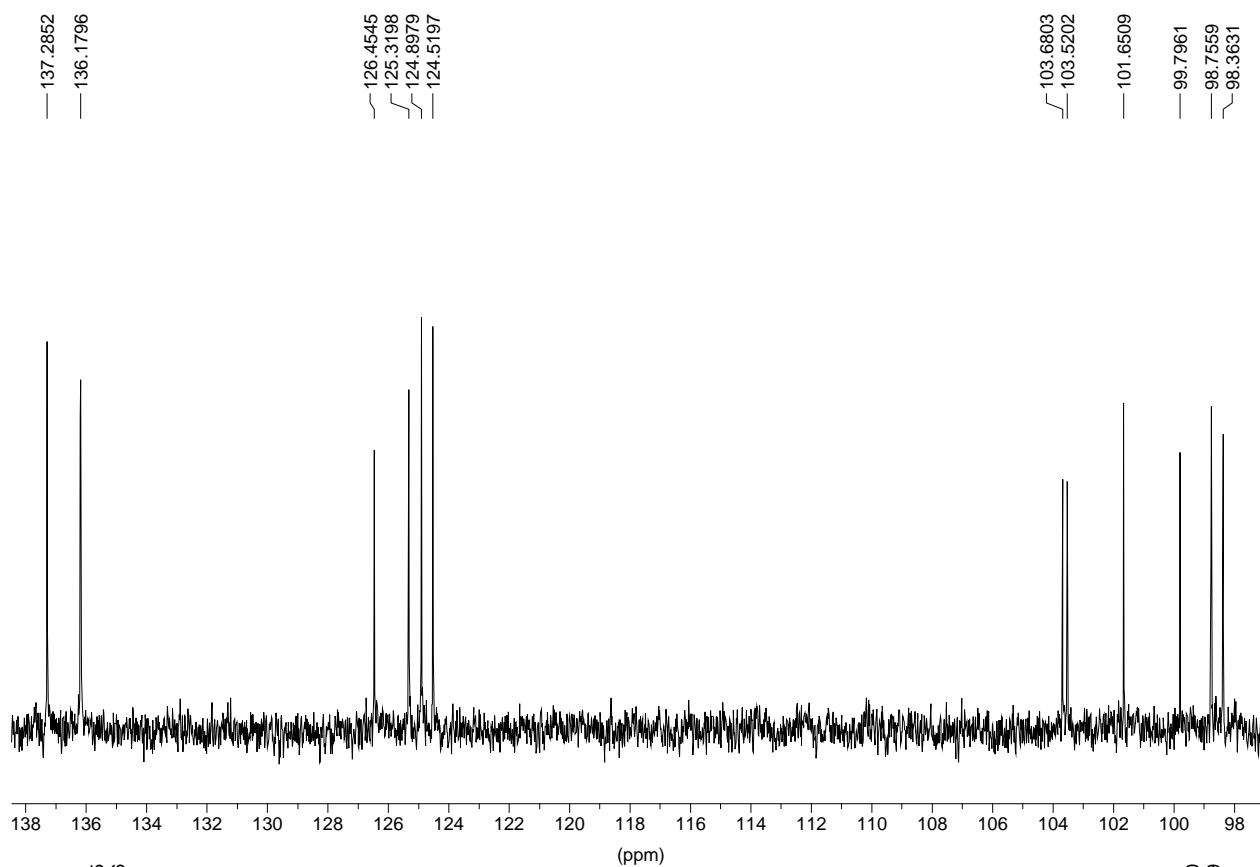


**S7.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-bromobenzene (**8**)  
in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm.

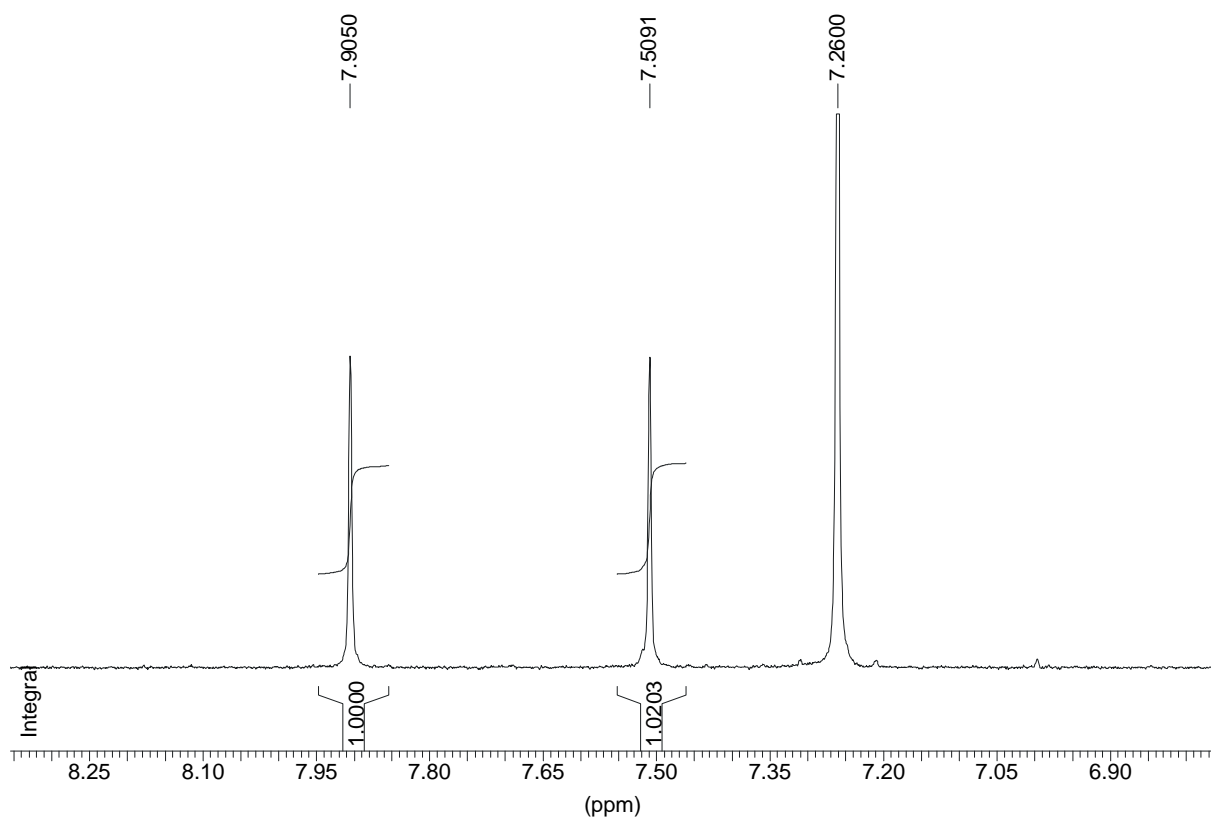
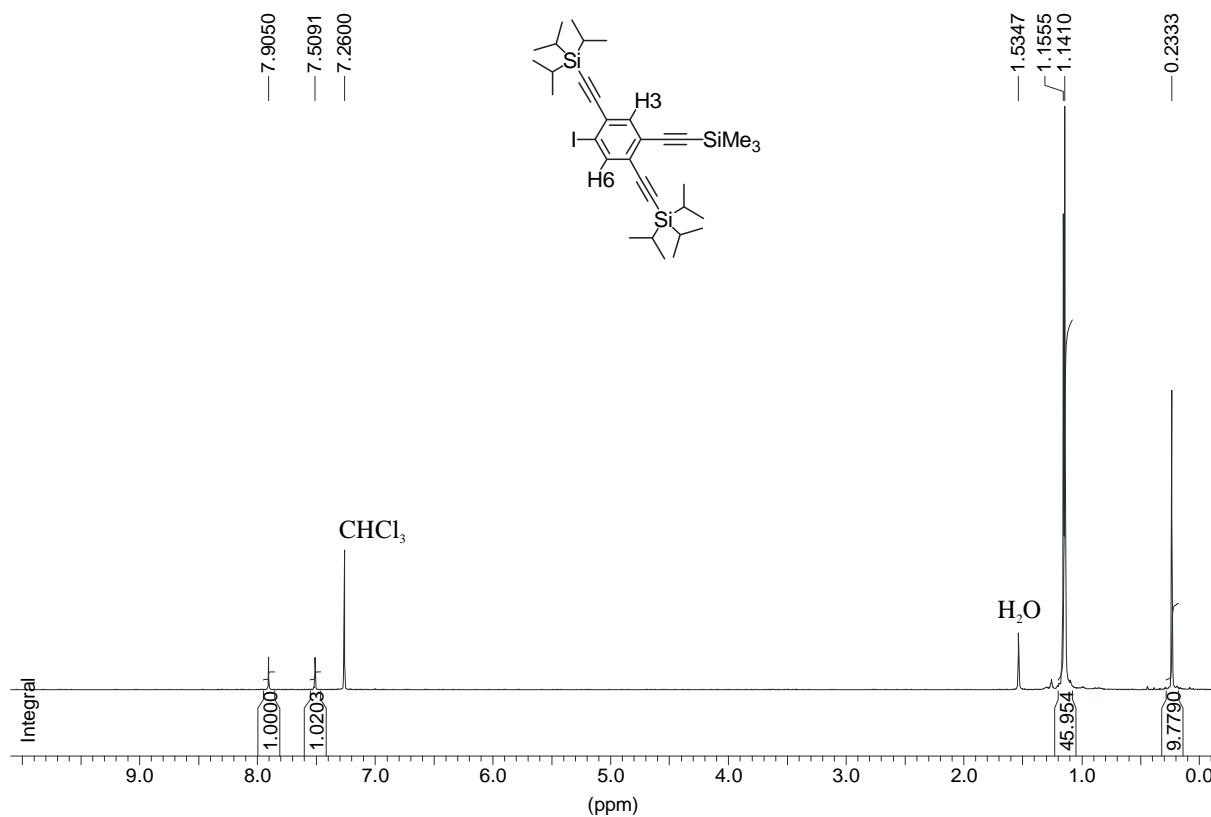




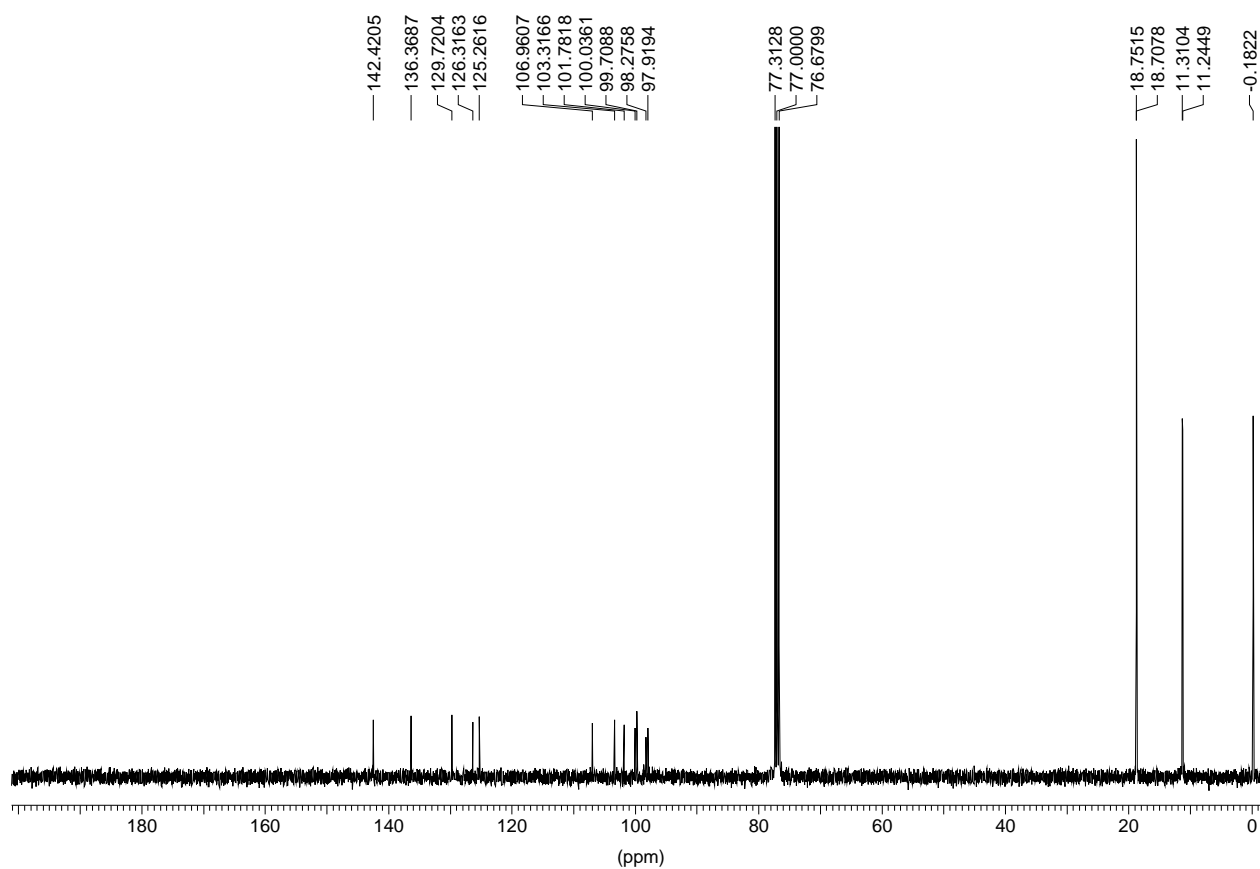
**S8.**  $^{13}\text{C}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-bromobenzene (**8**) in  $\text{CDCl}_3$ :  
Expansion of aromatic/ethynyl region (upper), and TIPS carbons (lower spectrum).



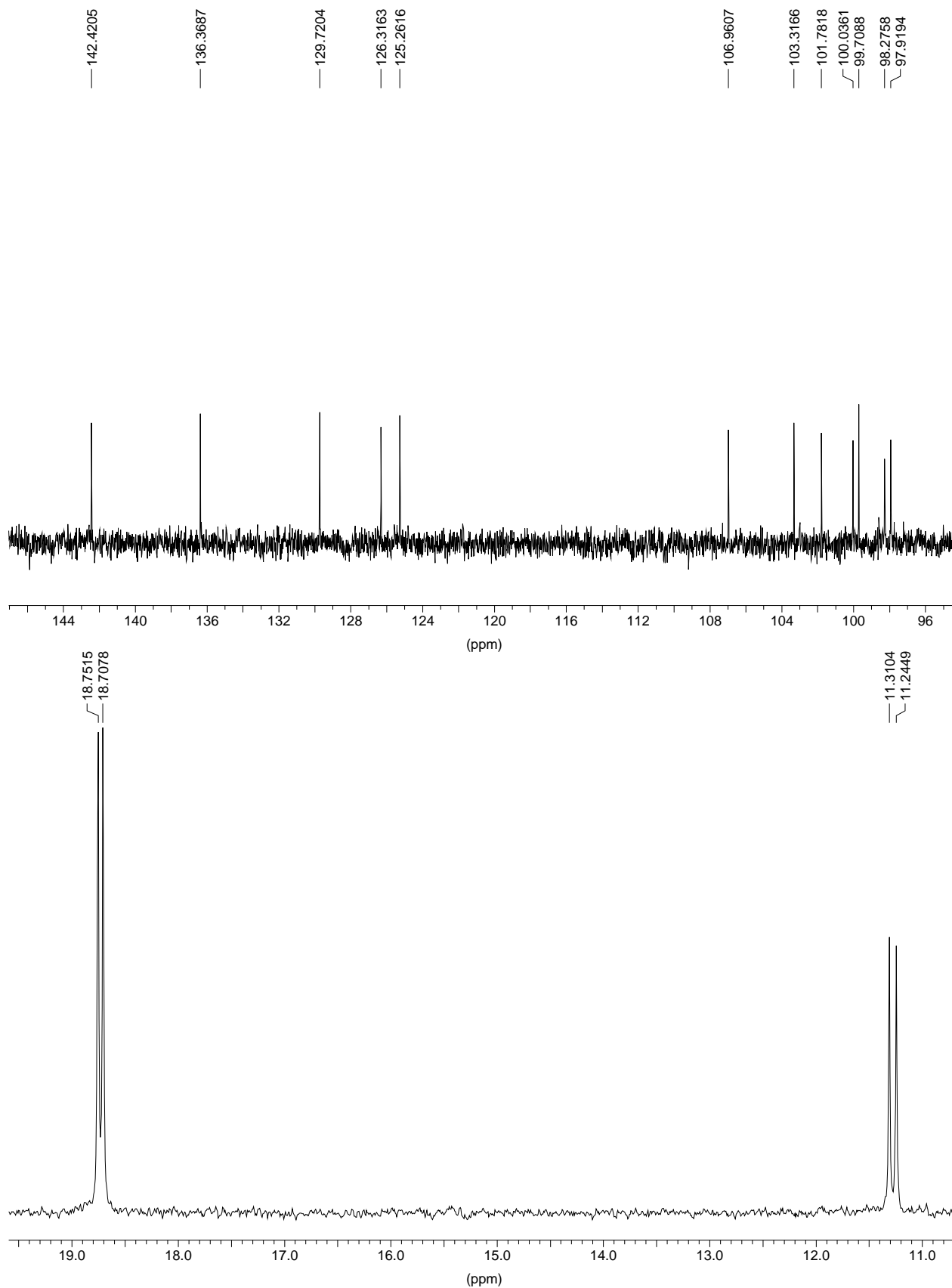
**S9.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-iodobenzene (**9**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum).



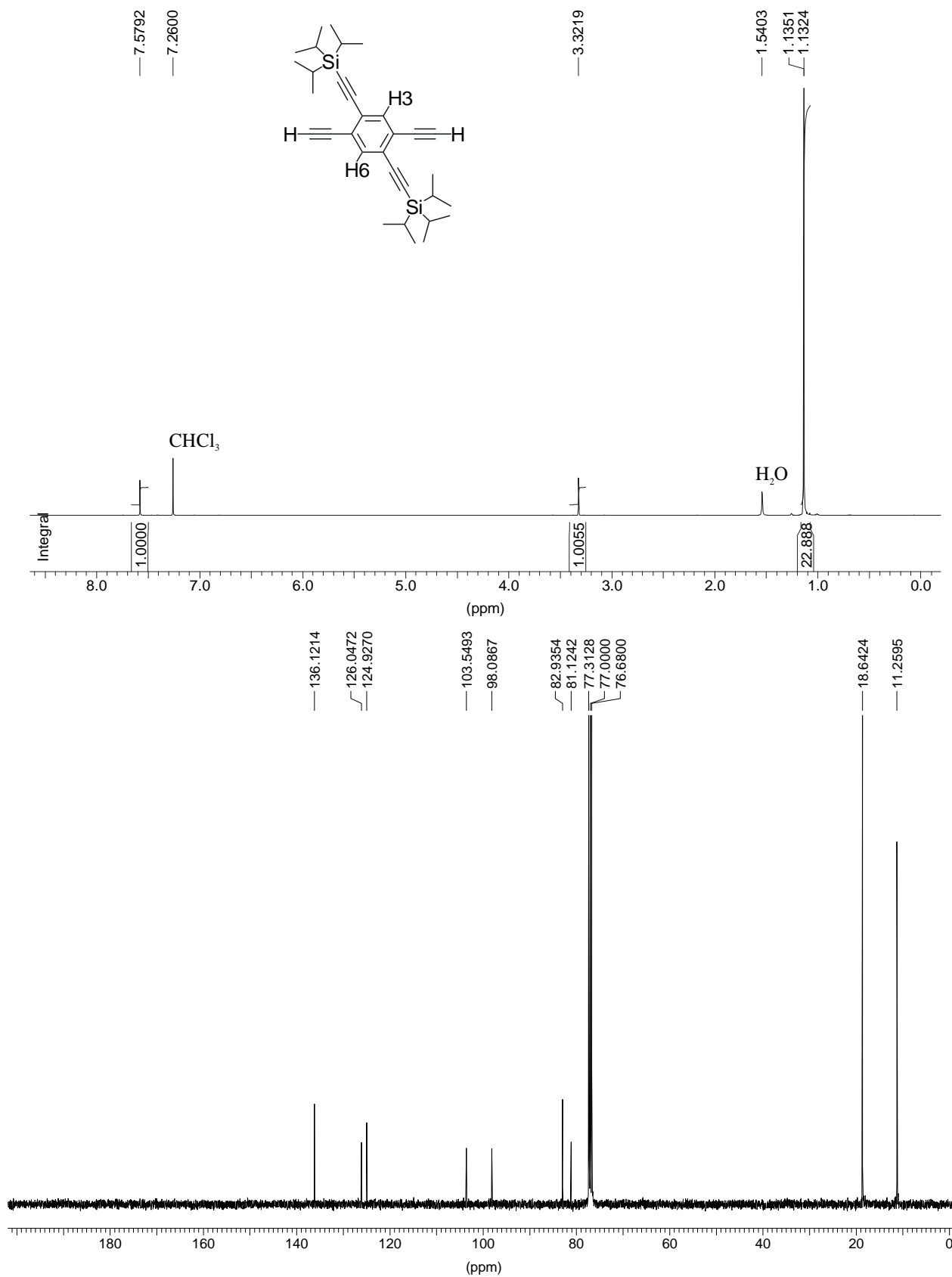
**S10.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-iodobenzene (**9**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ .

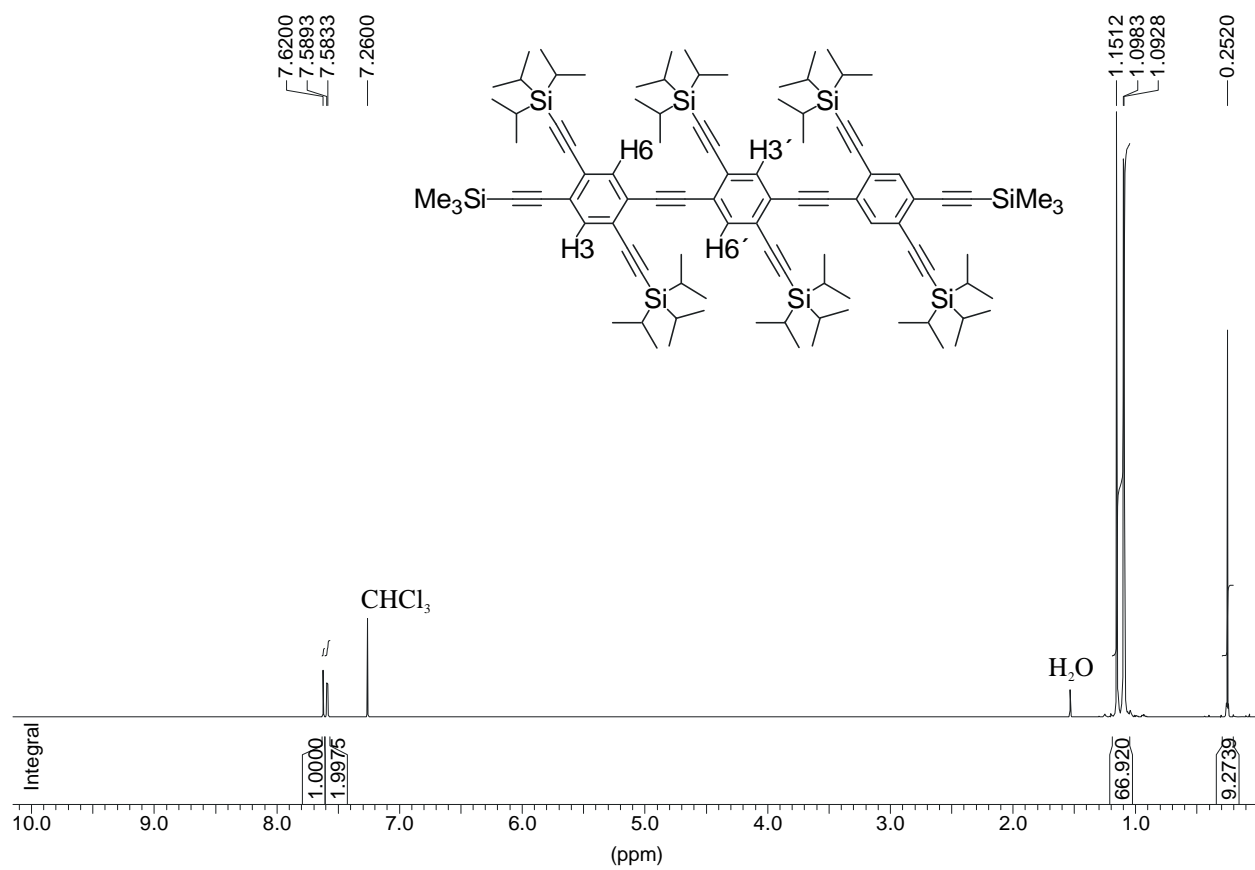


**S11.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4-trimethylsilylethynyl-2,5-bis-triisopropylsilylethynyl-iodobenzene (**9**) in  $\text{CDCl}_3$  at 25 °C: Magnification of aromatic region (upper), and expansion of aliphatic region showing TIPS carbons (lower spectrum).

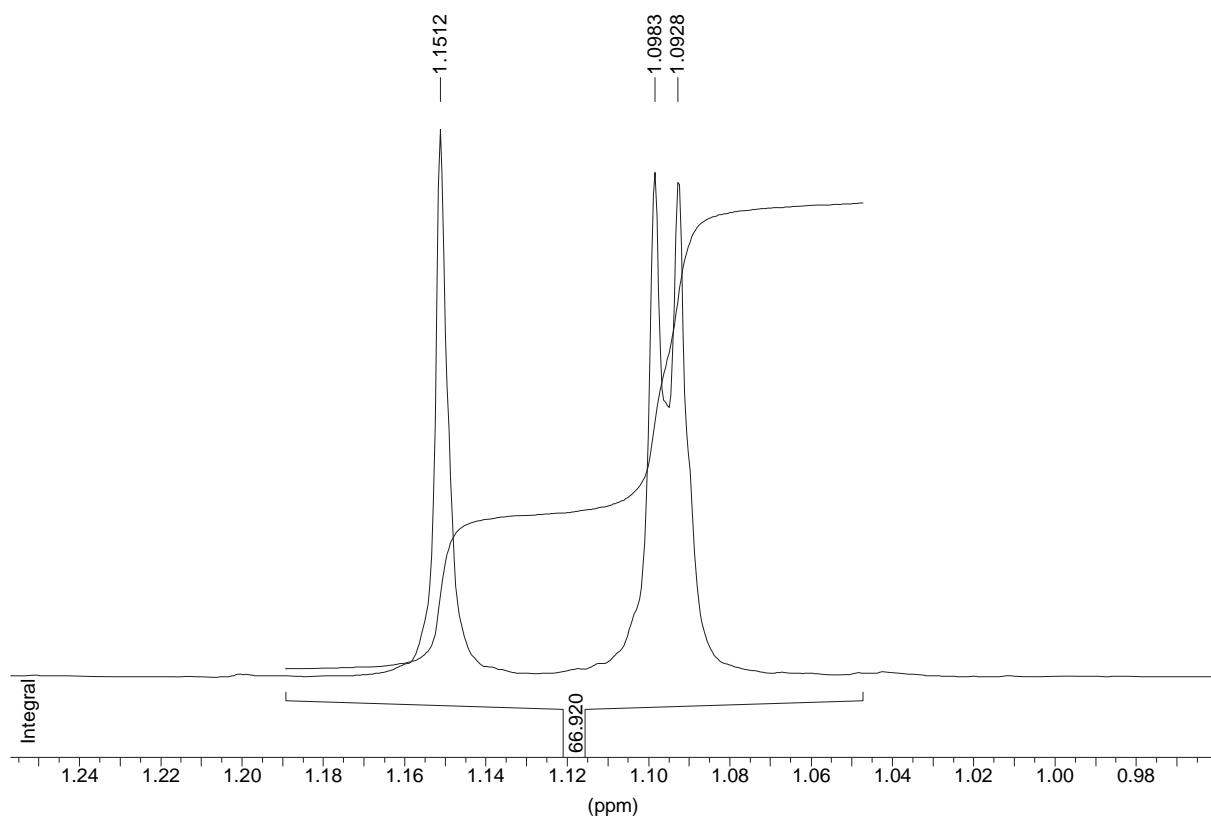
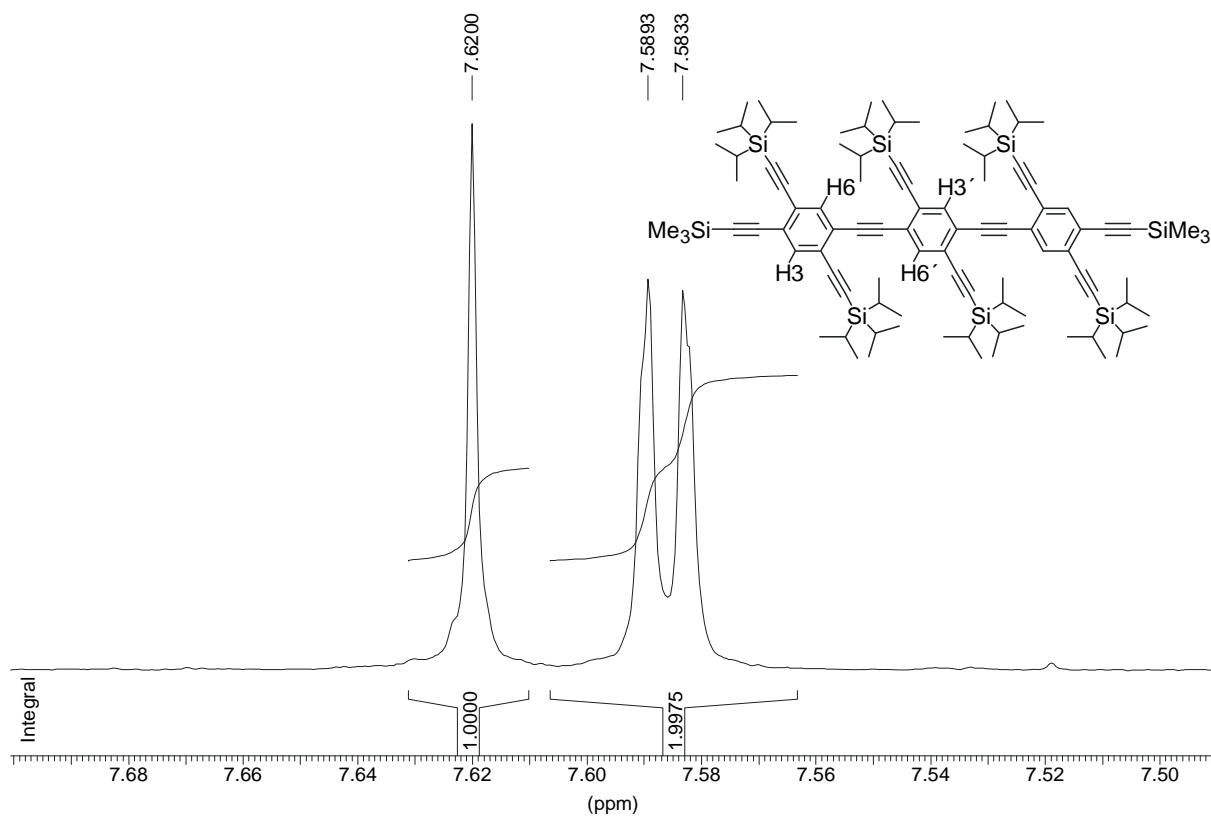


**S12.** 500.13 MHz  $^1\text{H}$  NMR spectra of 1,4-diethynyl-2,5-bis-triisopropylsilylbenzene (**11**) (upper spectrum) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ , and 100.61 MHz  $^{13}\text{C}$  NMR (lower spectrum) in  $\text{CDCl}_3$  at 26  $^\circ\text{C}$ .

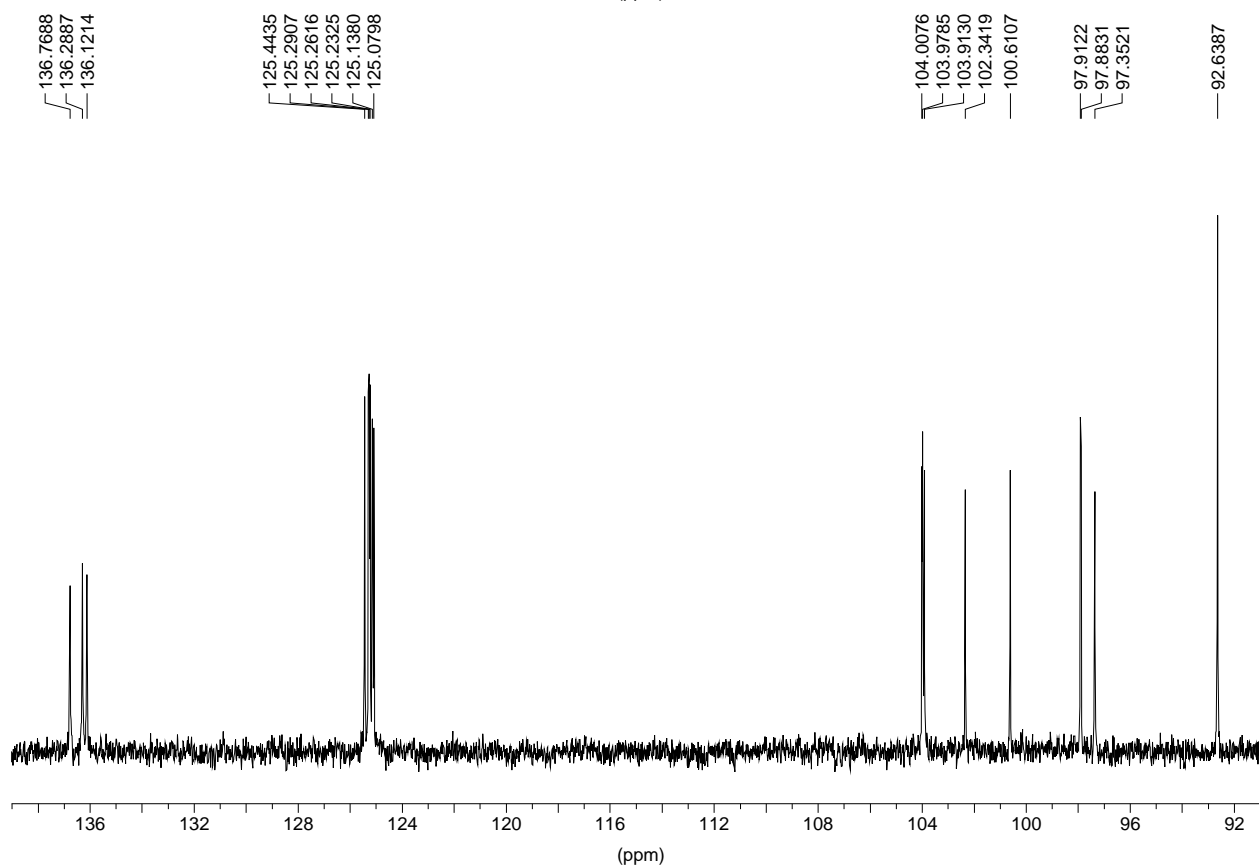
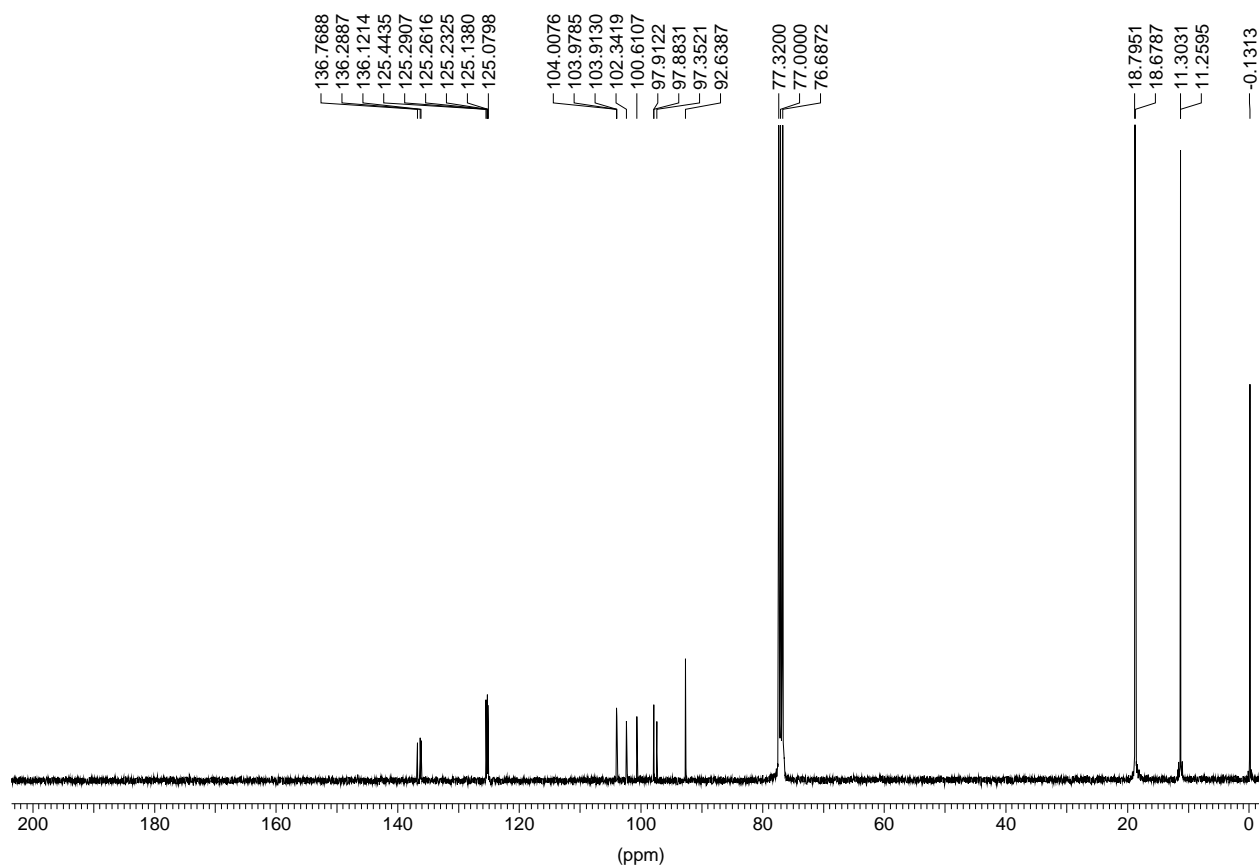


**S13.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : 10 - 0 ppm.

**S14.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : Expansion of aromatic region (upper), and TIPS protons in aliphatic region (lower spectrum).

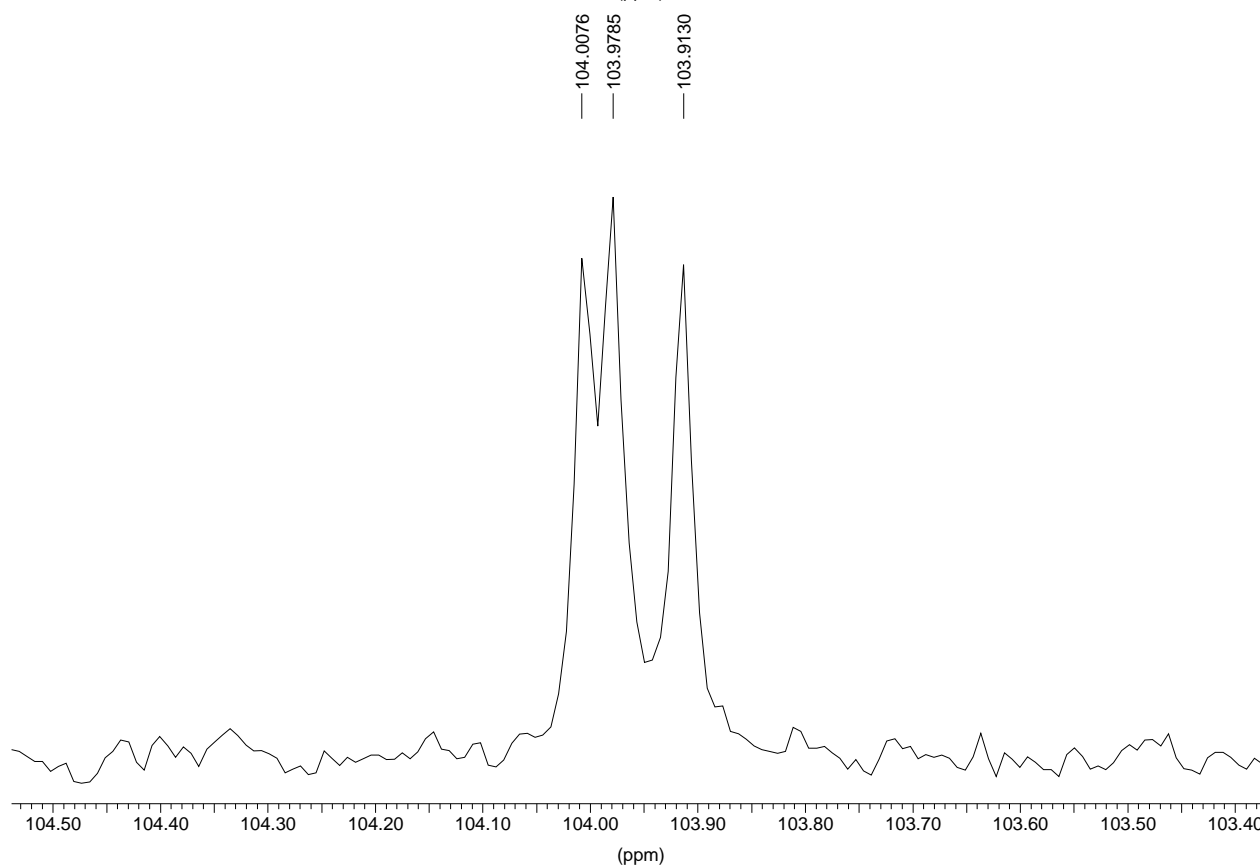
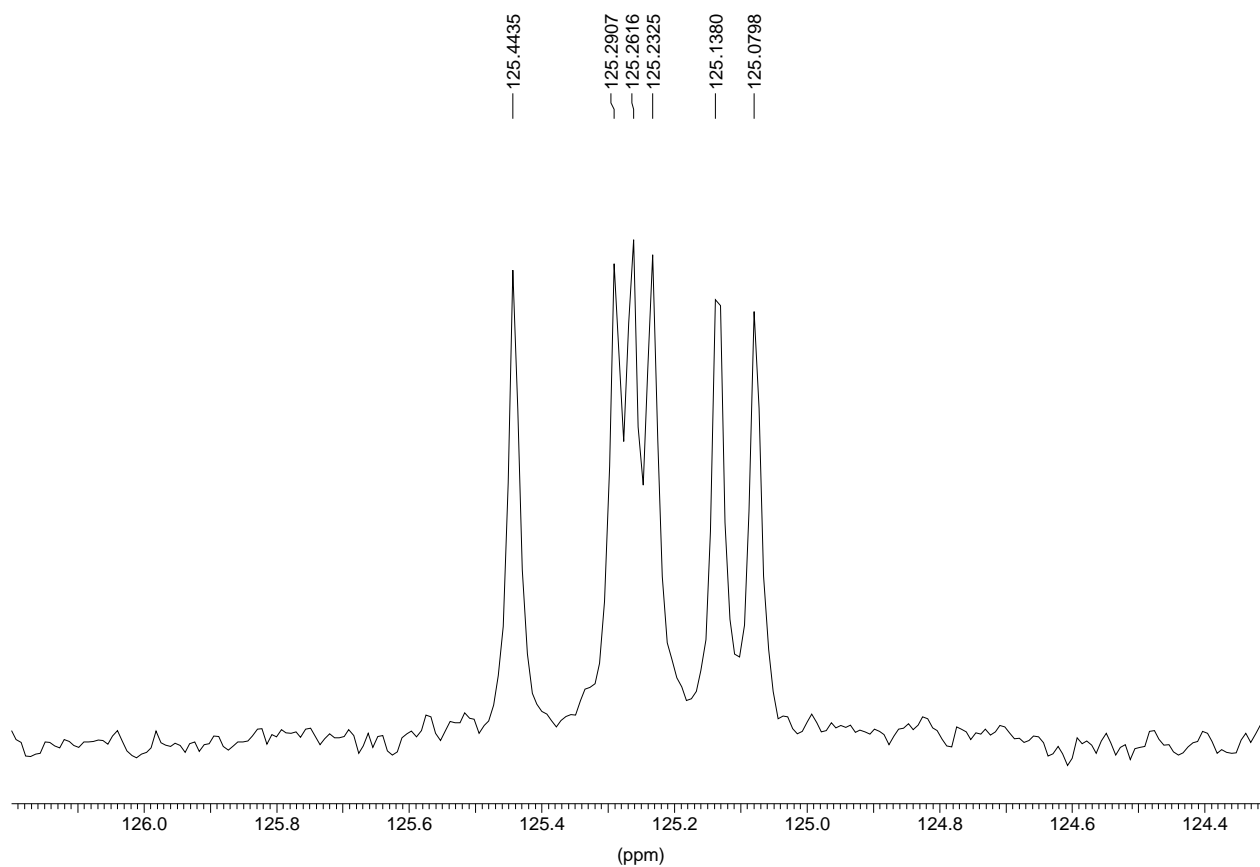


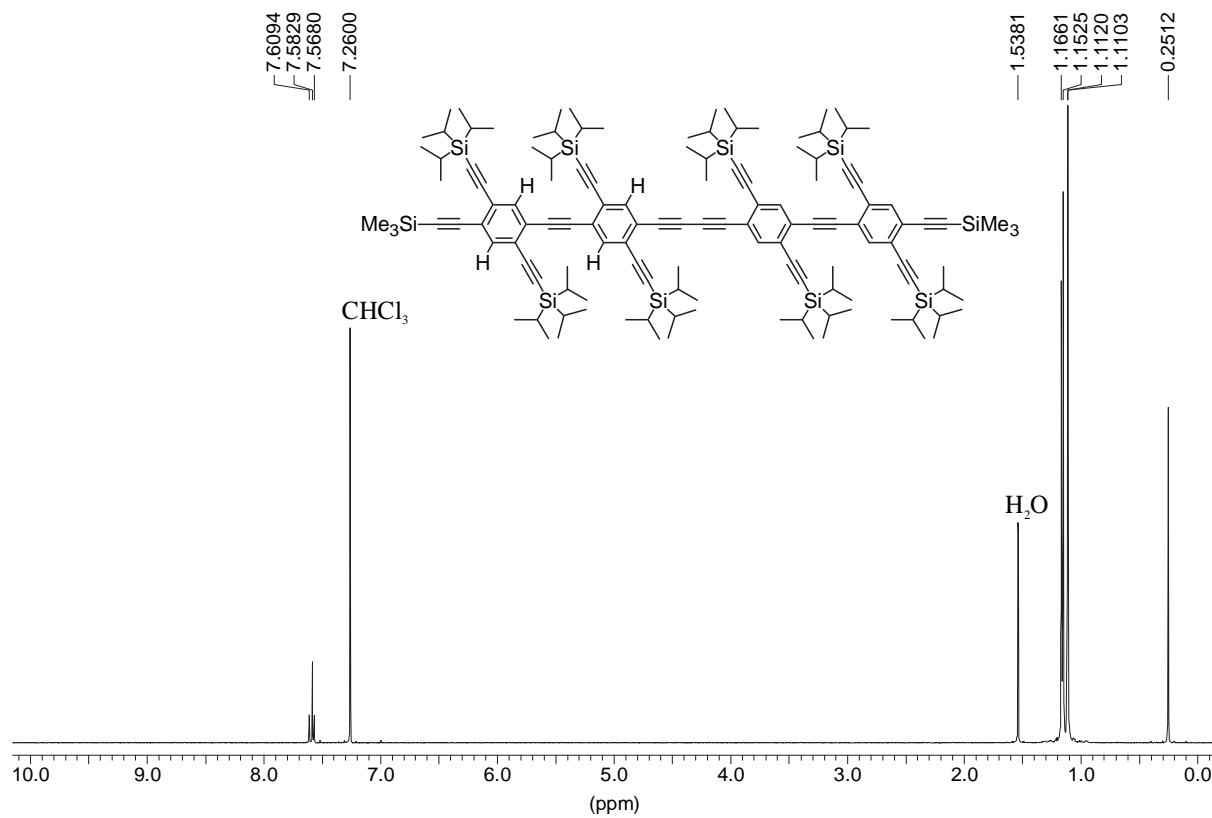
**S15.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl-region (lower spectrum).



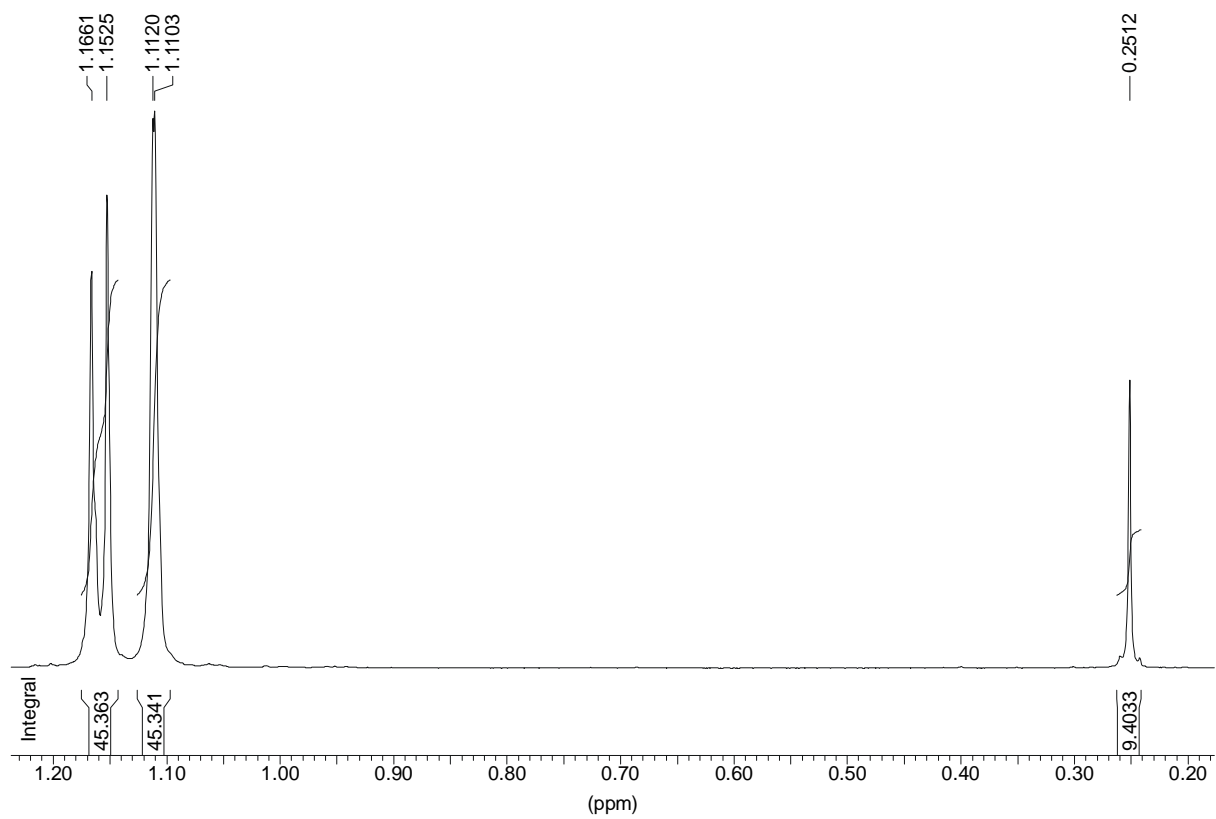
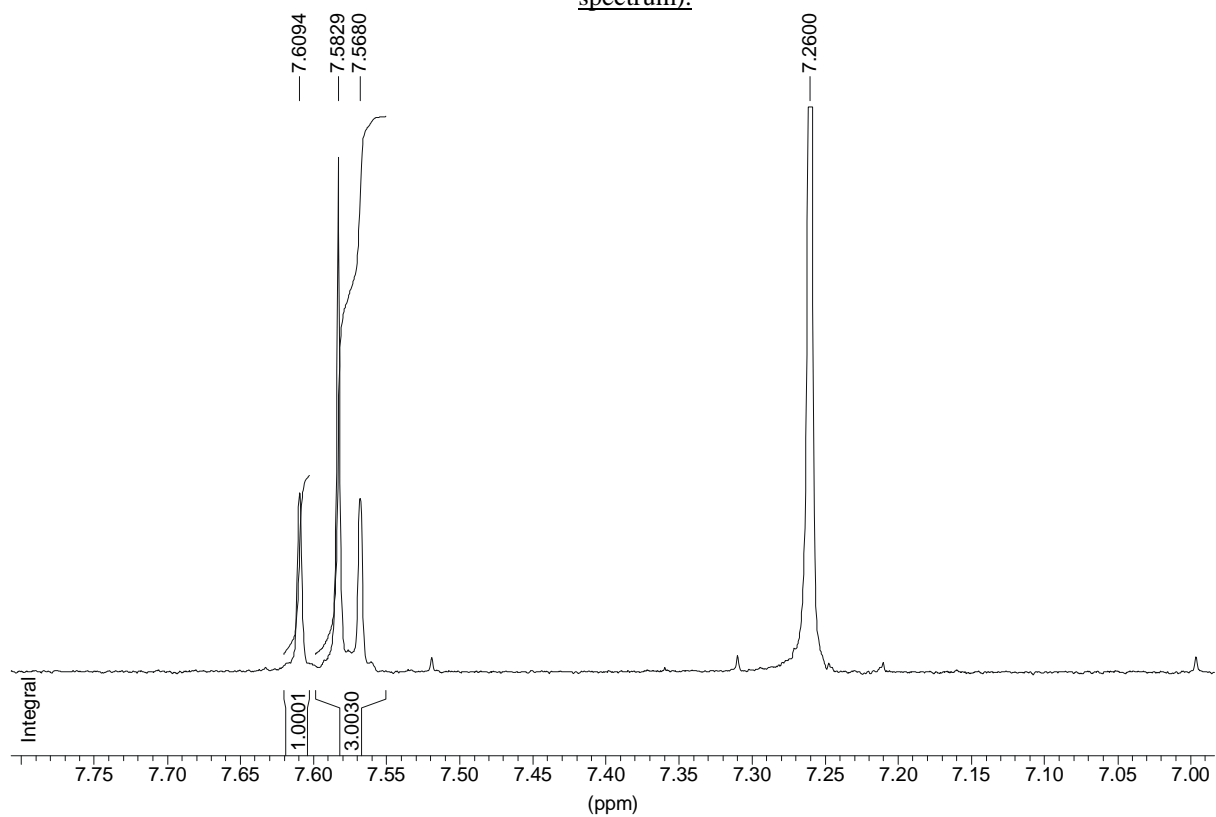


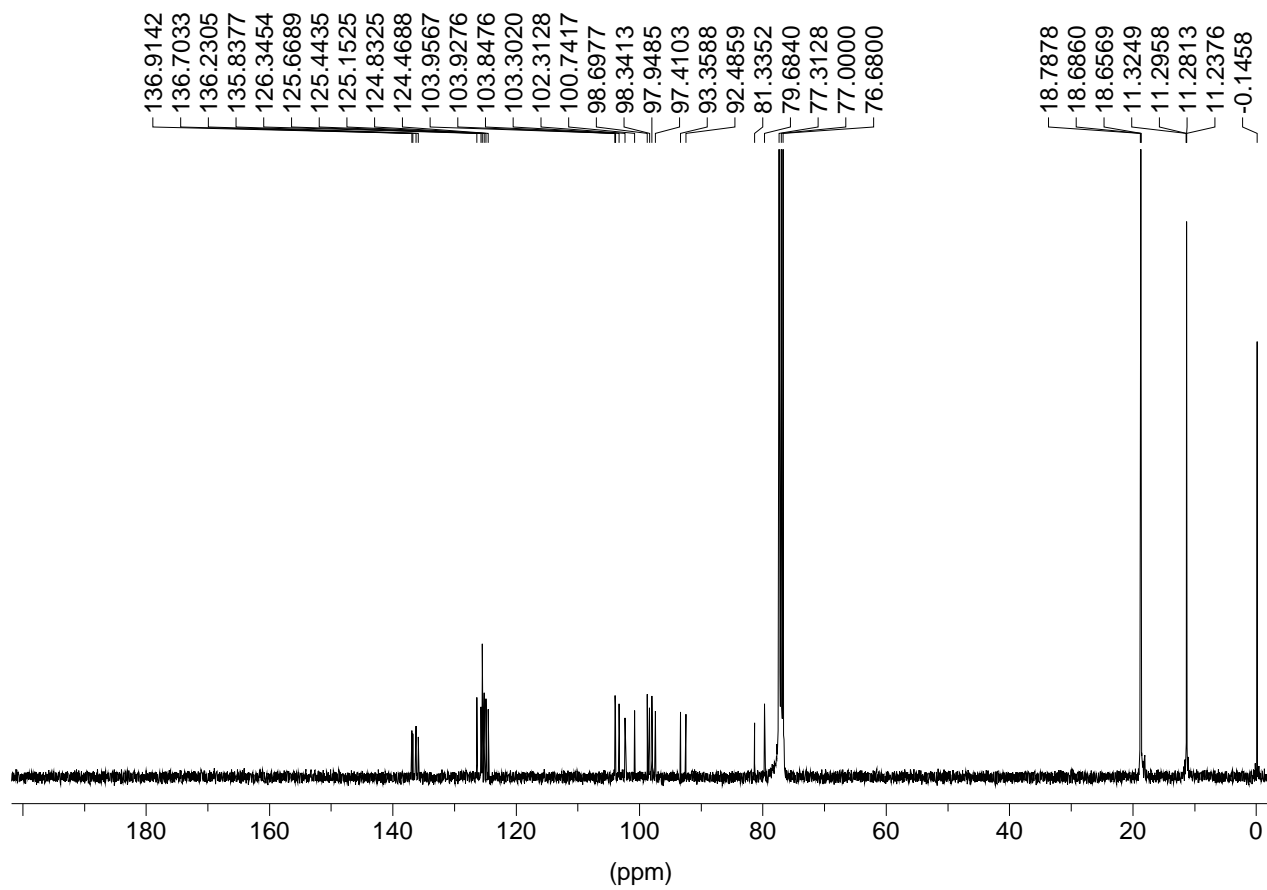
**S16.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[3]cruciform (**1**) in  $\text{CDCl}_3$  at 25 °C: Expansion of closely situated peaks in aromatic region (upper), and ethynyl-region (lower spectrum).



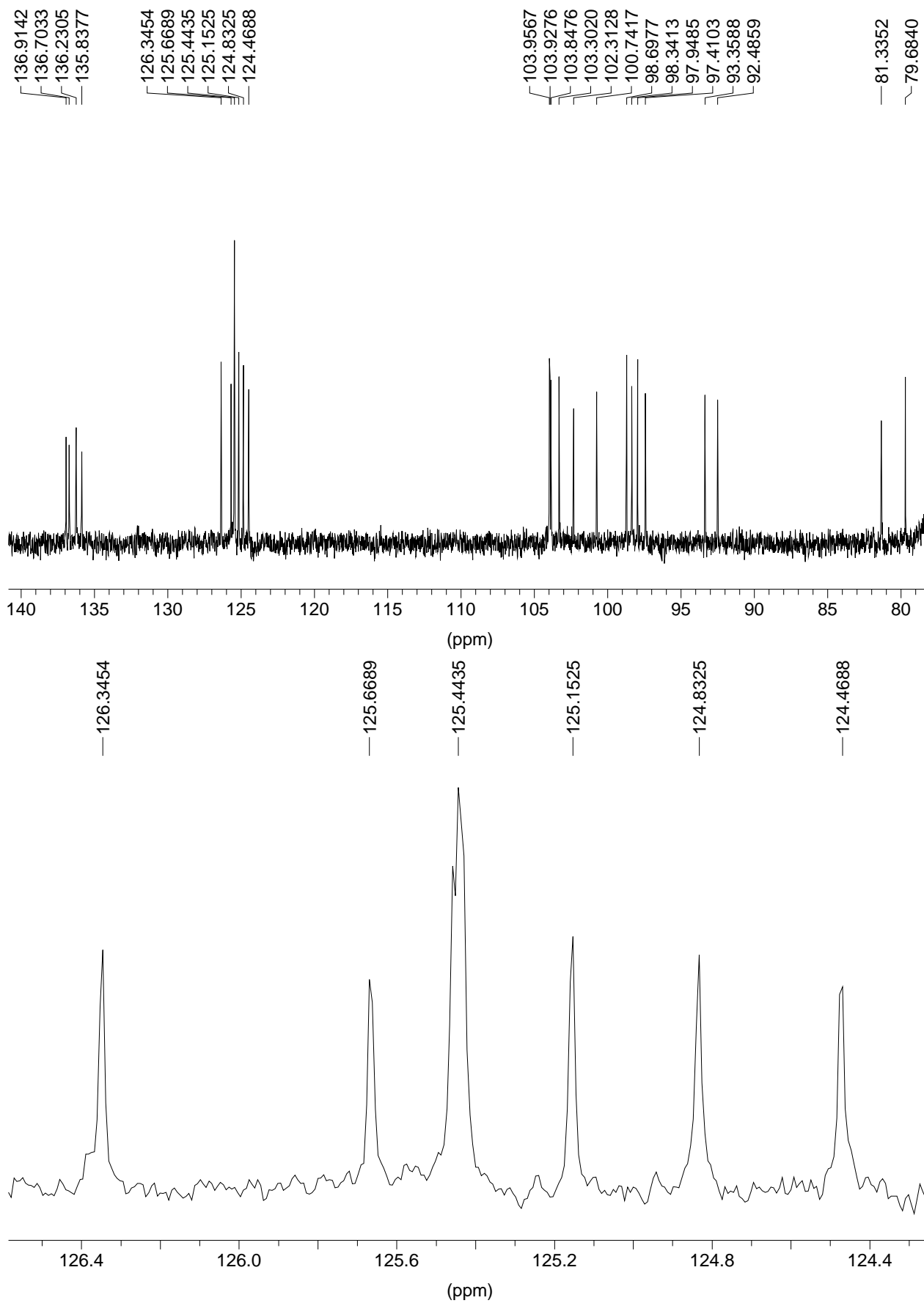
**S17.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ .

**S18.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : expansion of aromatic region (upper spectrum), and expansion of aliphatic region, showing TIPS peaks (left) and TMS peak (right: lower spectrum).

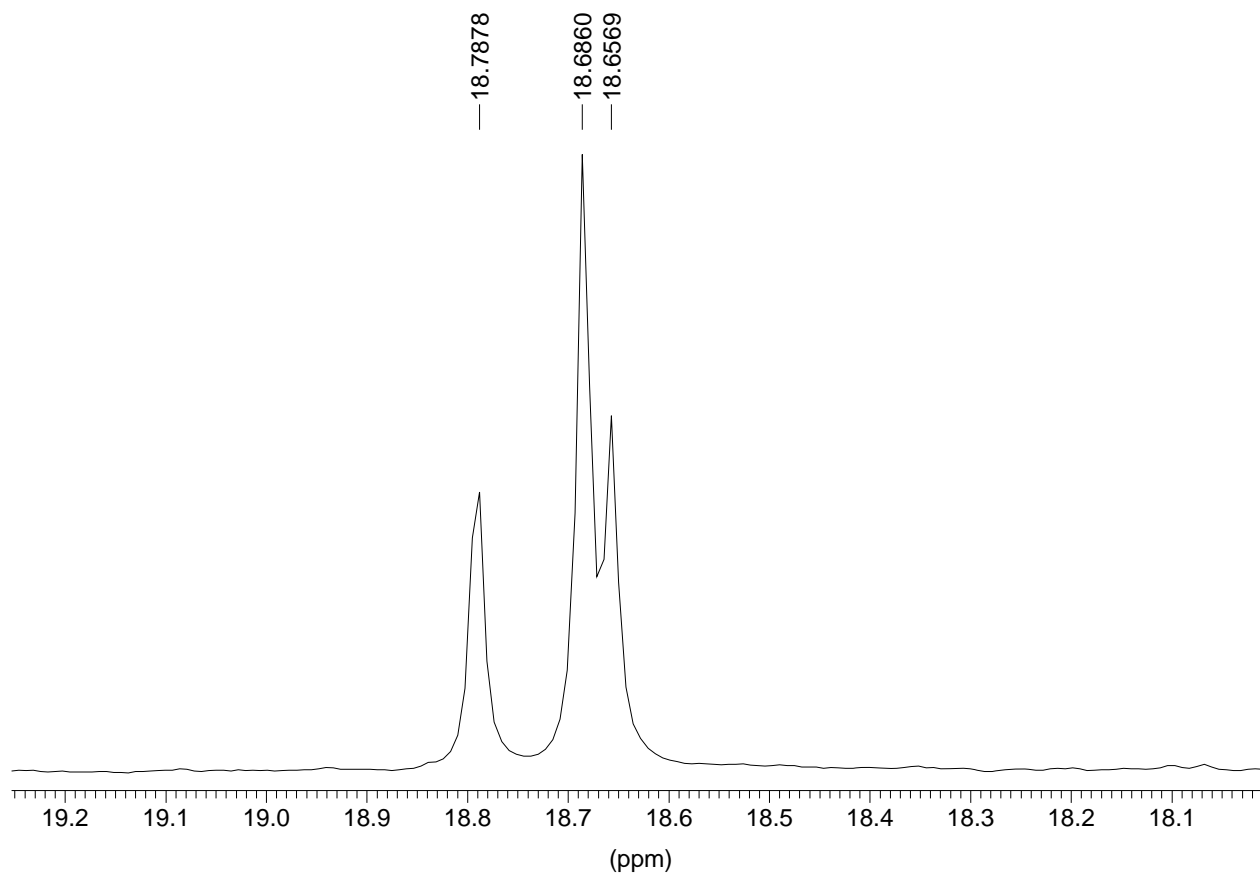
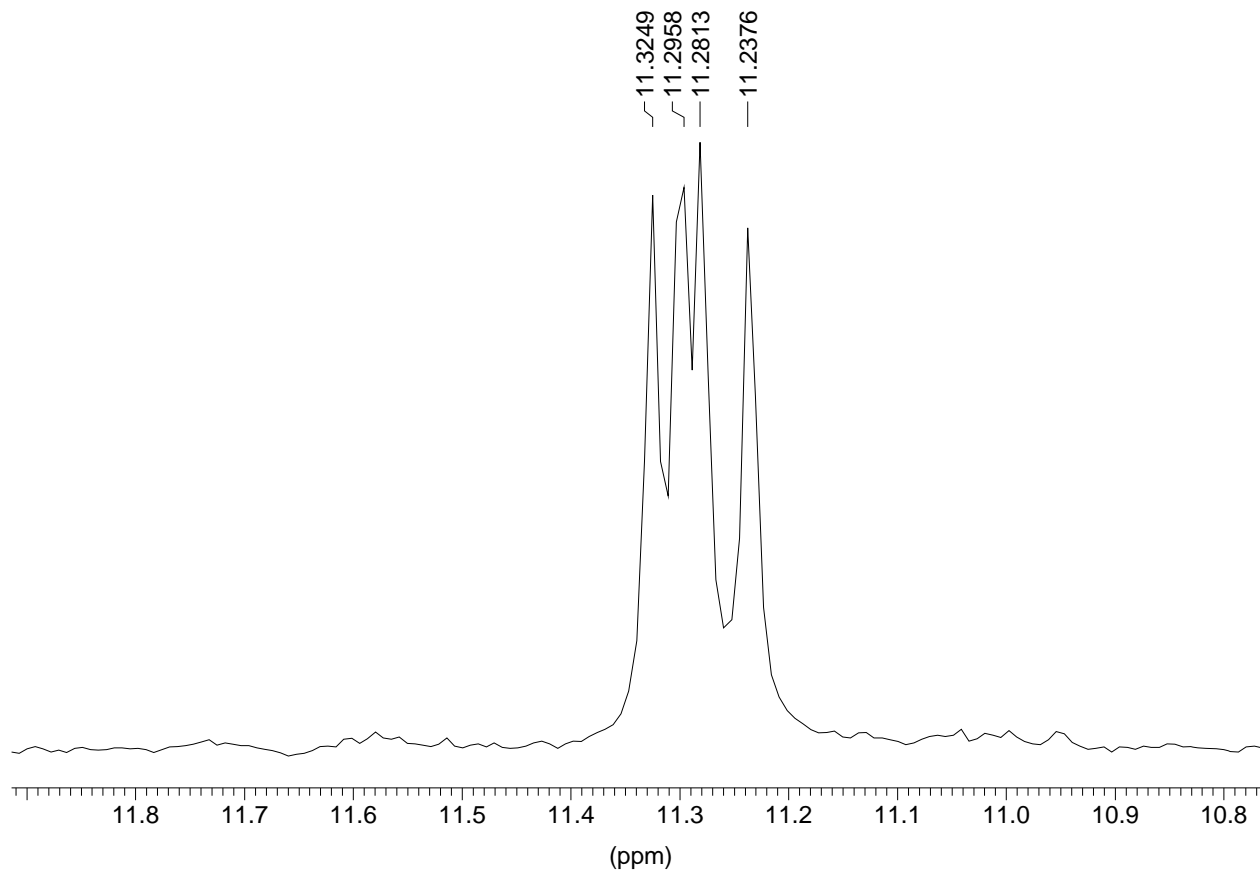


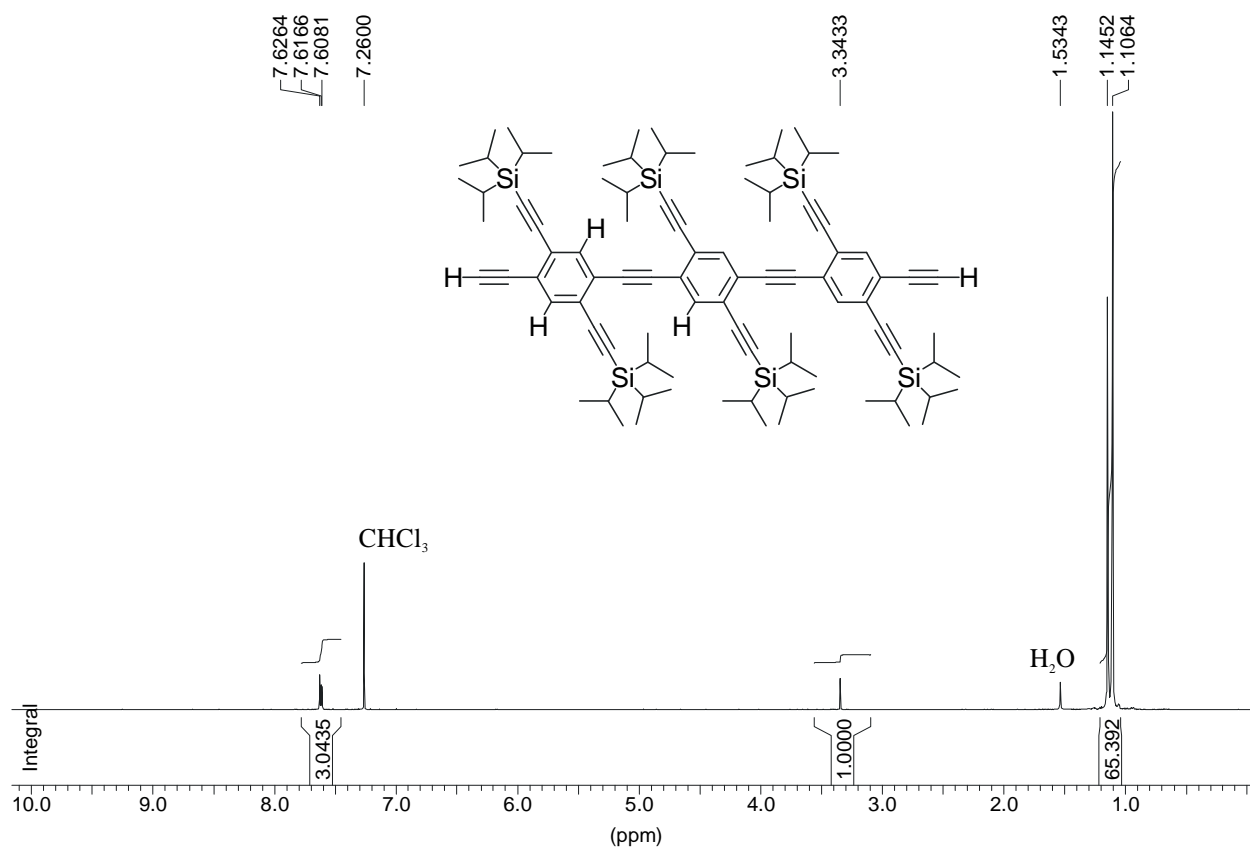
**S19.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  at 25 °C.

**S20.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$ , 25 °C: Aromatic and acetylenic region (upper), and magnification of part of aromatic region (lower spectrum) showing peak at 125.46 ppm on left side of peak at 125.44 ppm.

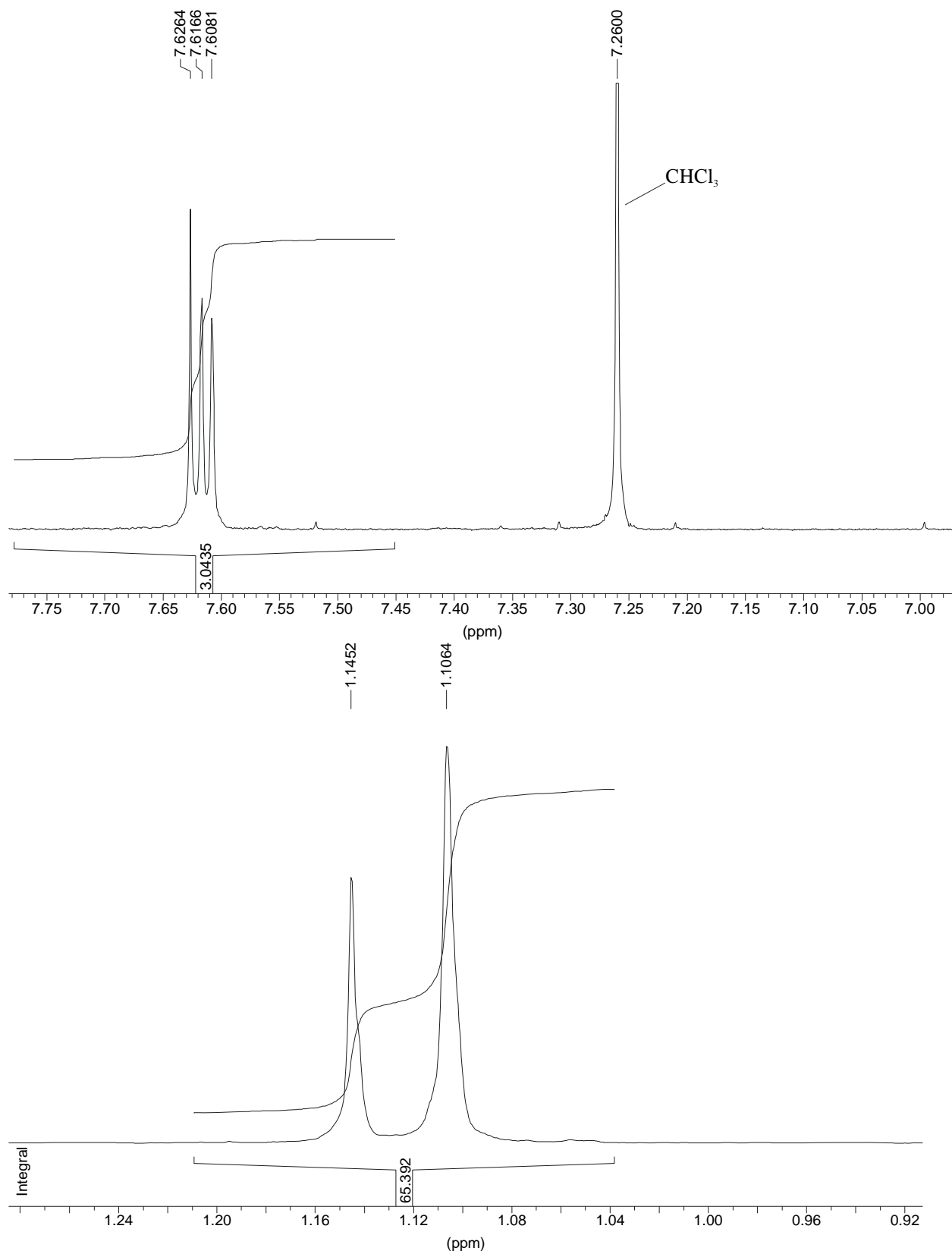


**S21.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[4]cruciform (**2**) in  $\text{CDCl}_3$  25  $^\circ\text{C}$ : Expansion of aliphatic region  
showing TIPS carbons.

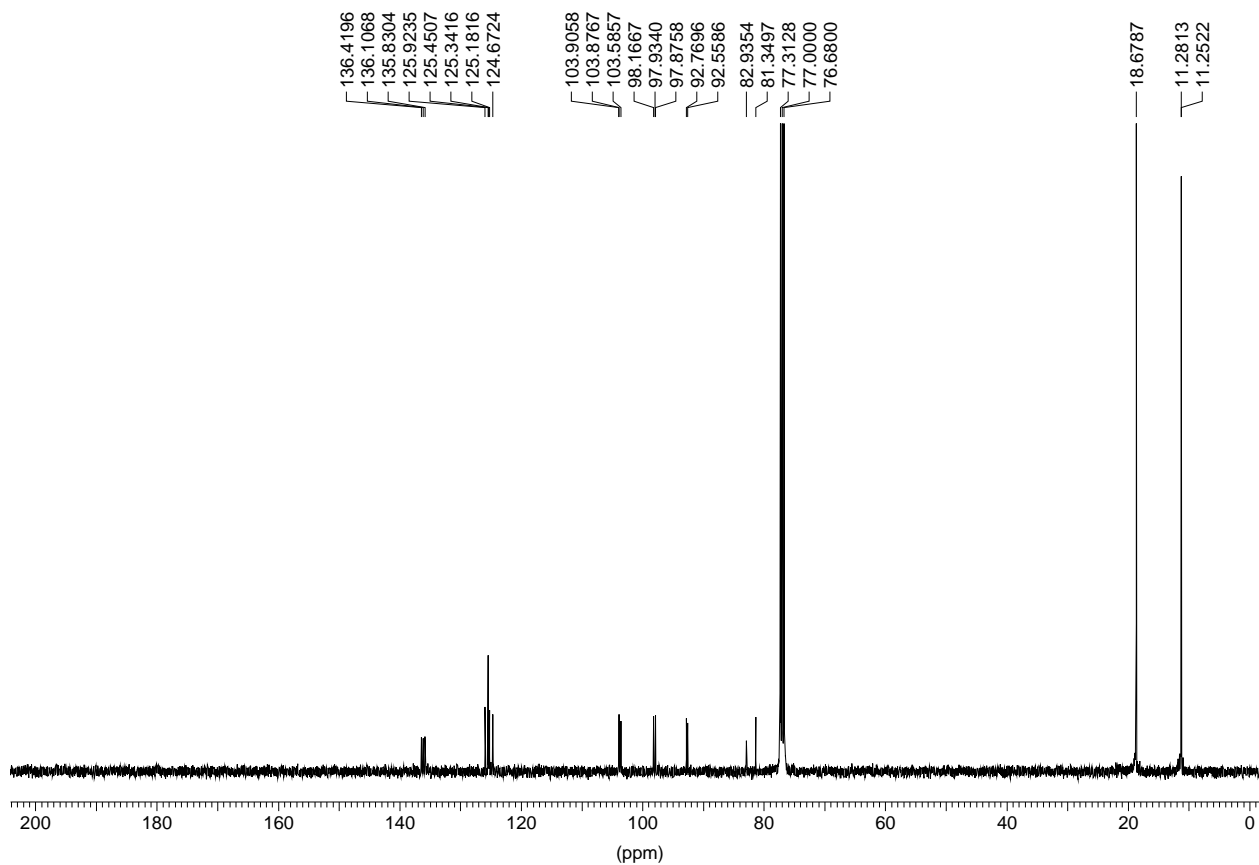


**S22.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : 10 - 0 ppm.

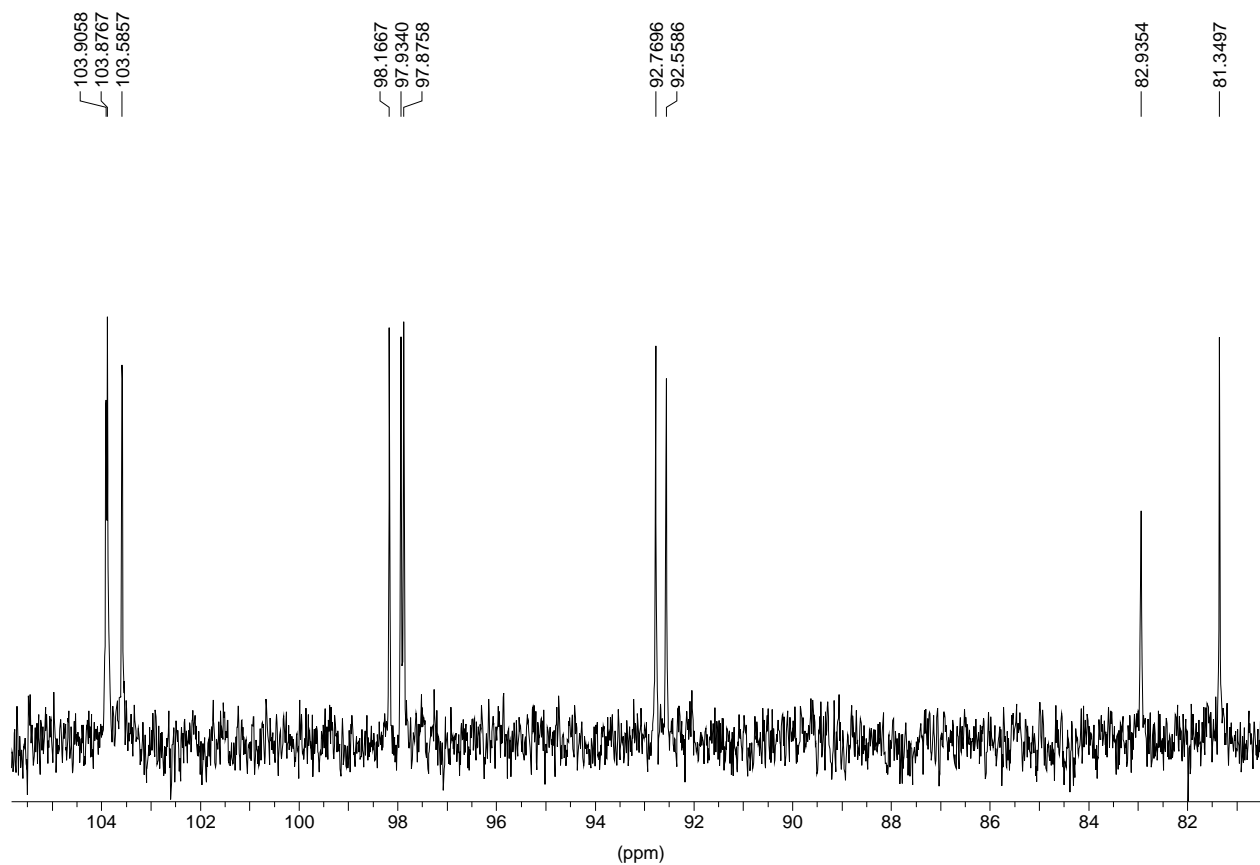
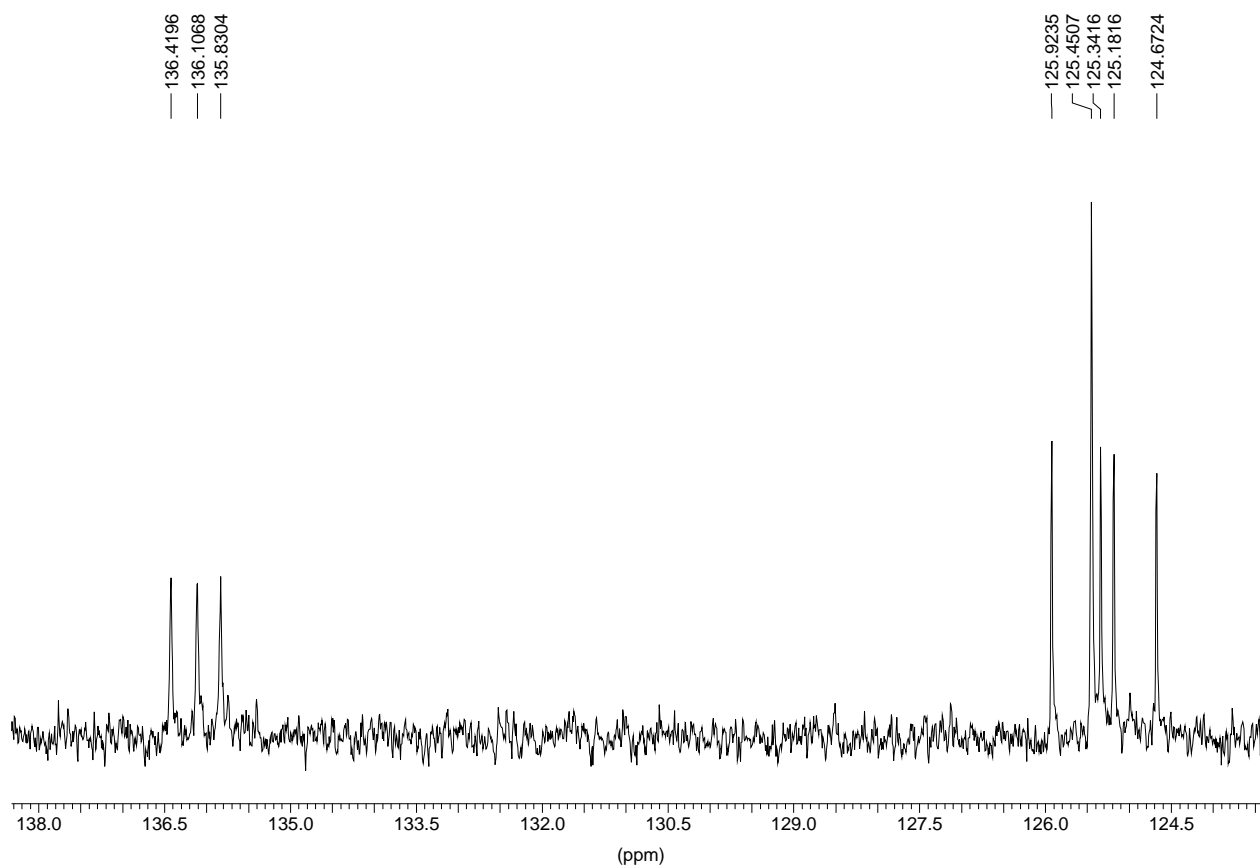
**S23.** 400.13 MHz  $^1\text{H}$  NMR spectra of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : Expansion of closely situated peaks in aromatic region (upper), and TIPS peaks (lower spectrum).

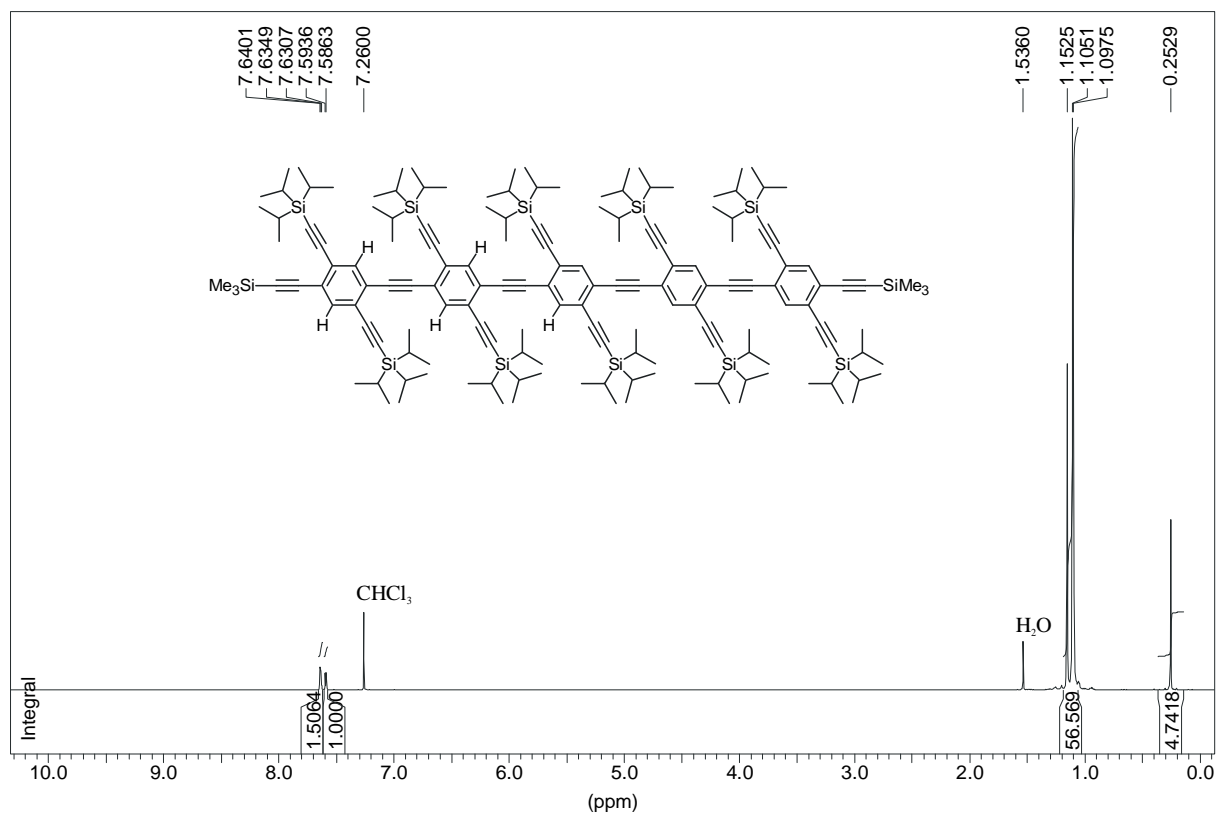




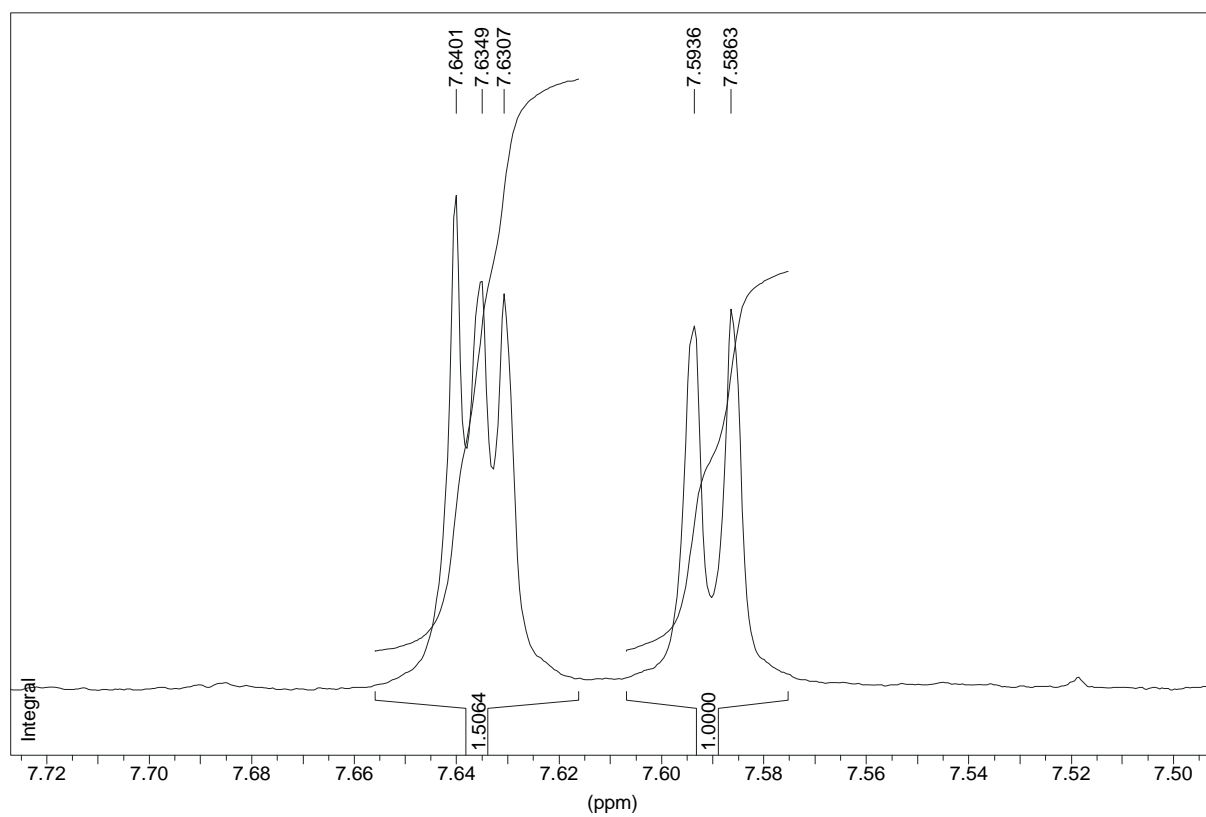
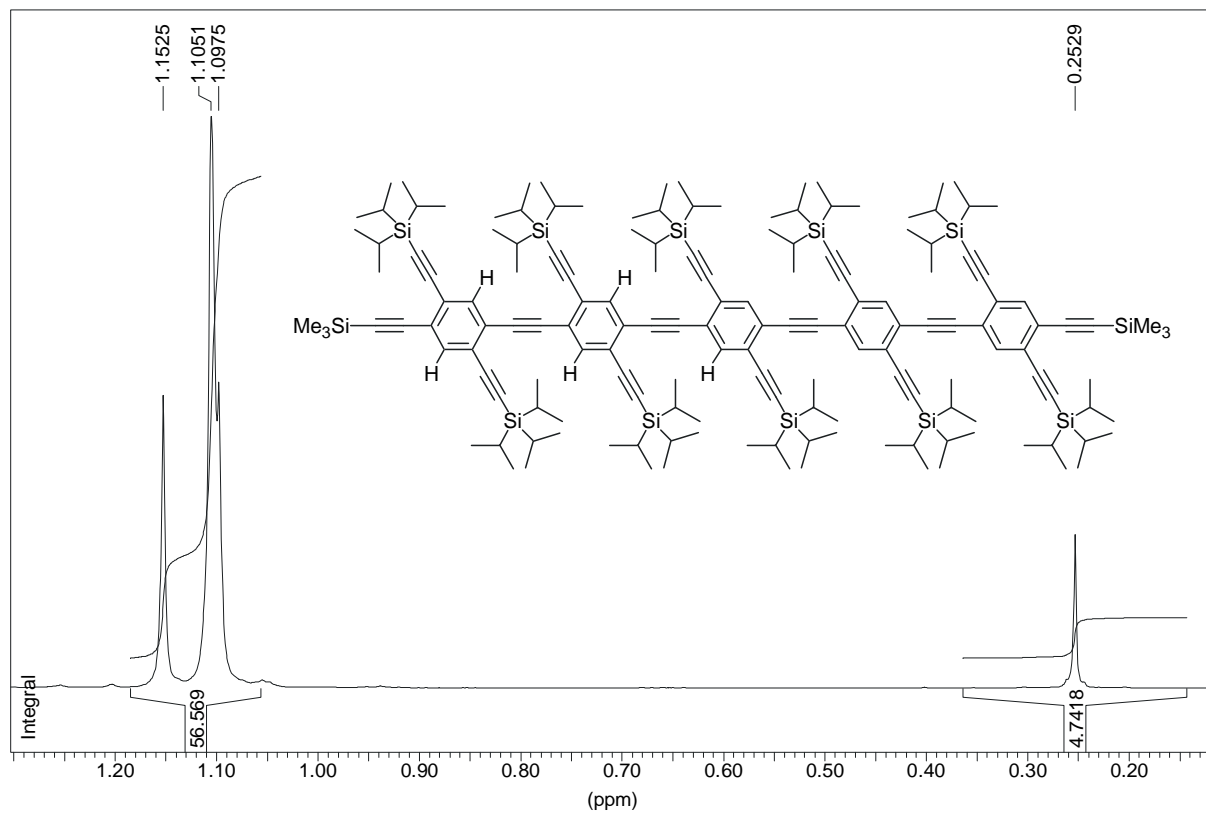
**S24.** 100.61 MHz  $^{13}\text{C}$  NMR spectrum of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25 °C (200 - 0 ppm).

**S25.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[3]cruciform (**3**) in  $\text{CDCl}_3$  at 25 °C: Expansion of aromatic region (upper), and ethyne-region (lower spectrum).

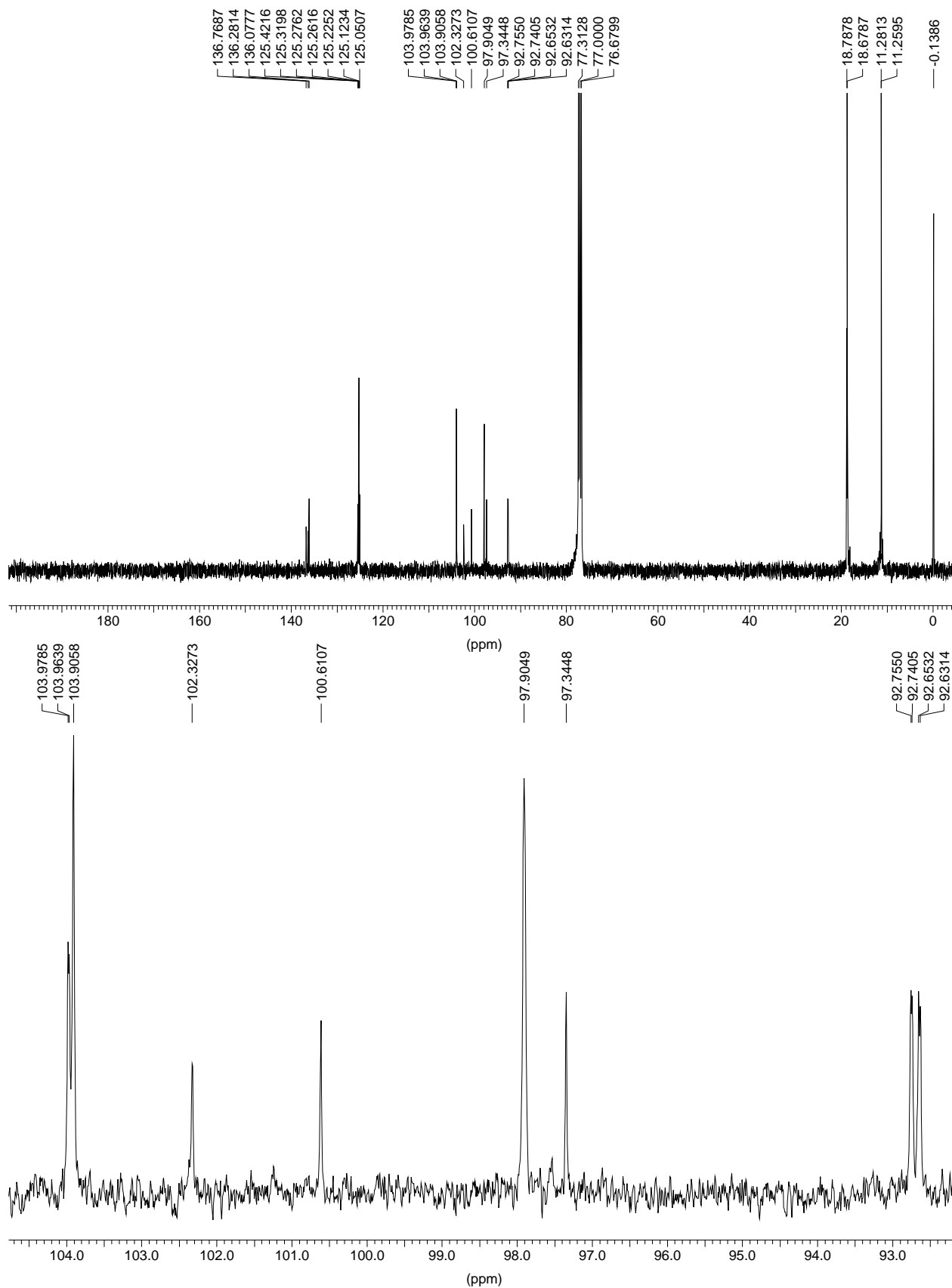


**S26.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ .

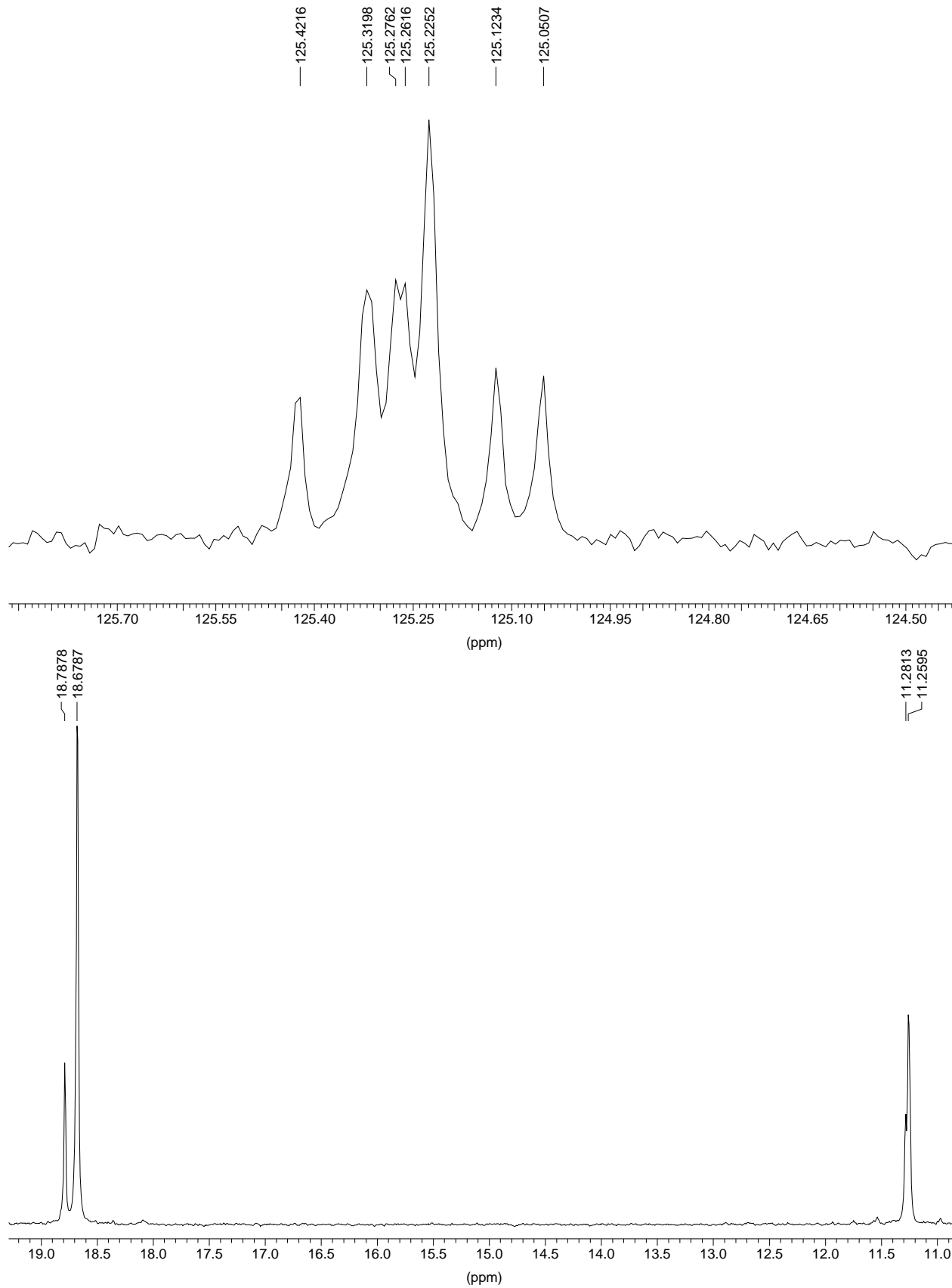
**S27.** 400.13 MHz  $^1\text{H}$  NMR spectrum of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ . Upper spectrum: Expansion of aliphatic region showing TIPS signals (left) and TMS signal (right); Lower spectrum: Expansion of aromatic region.



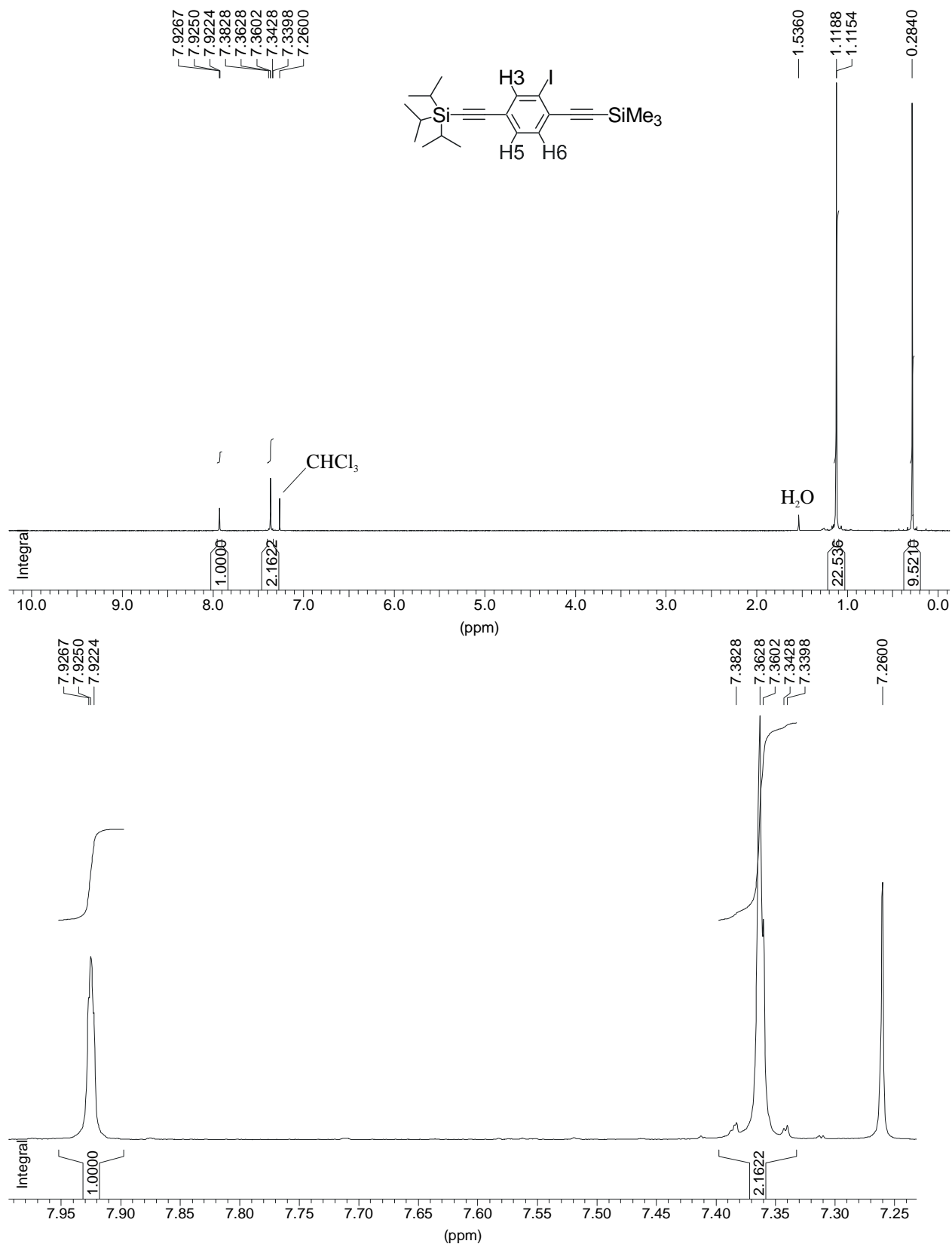
**S28.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm (upper), and expansion of ethynyl-region (lower spectrum).



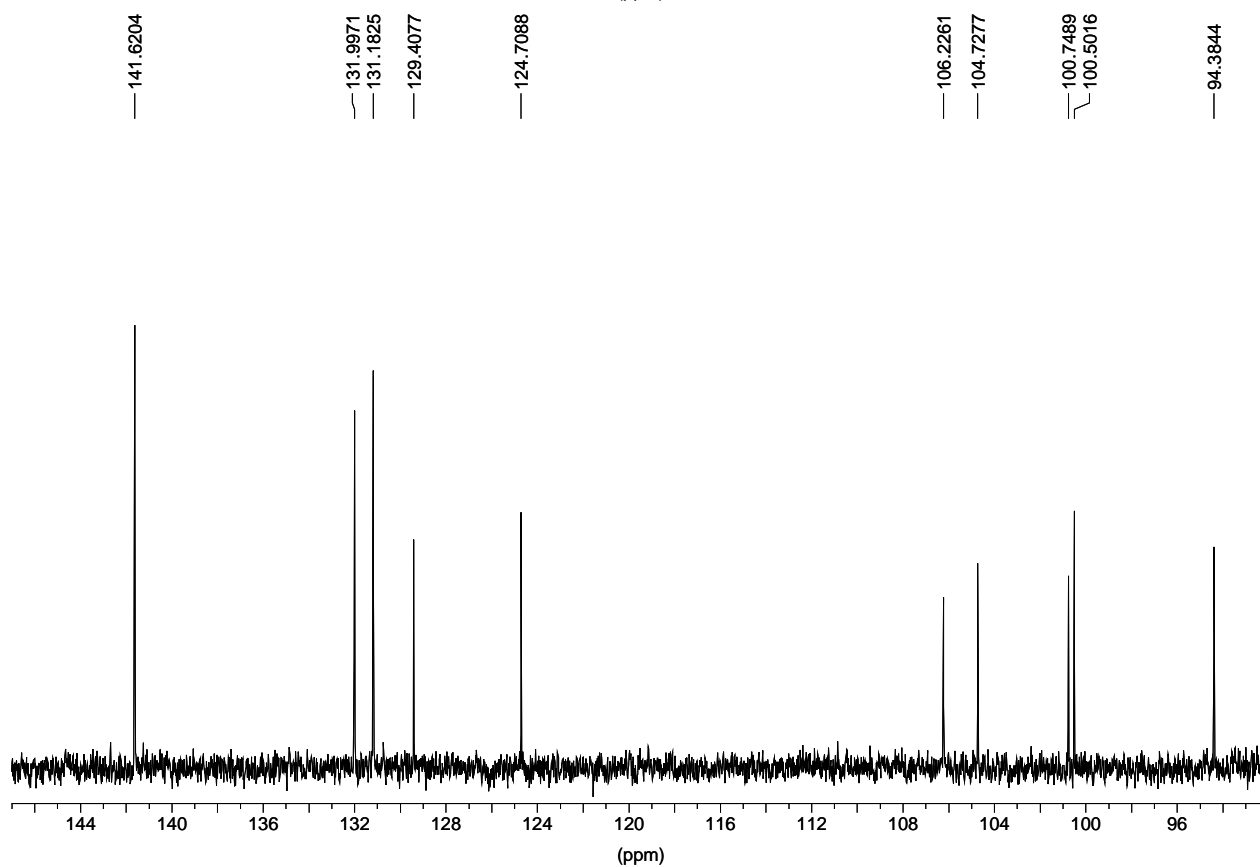
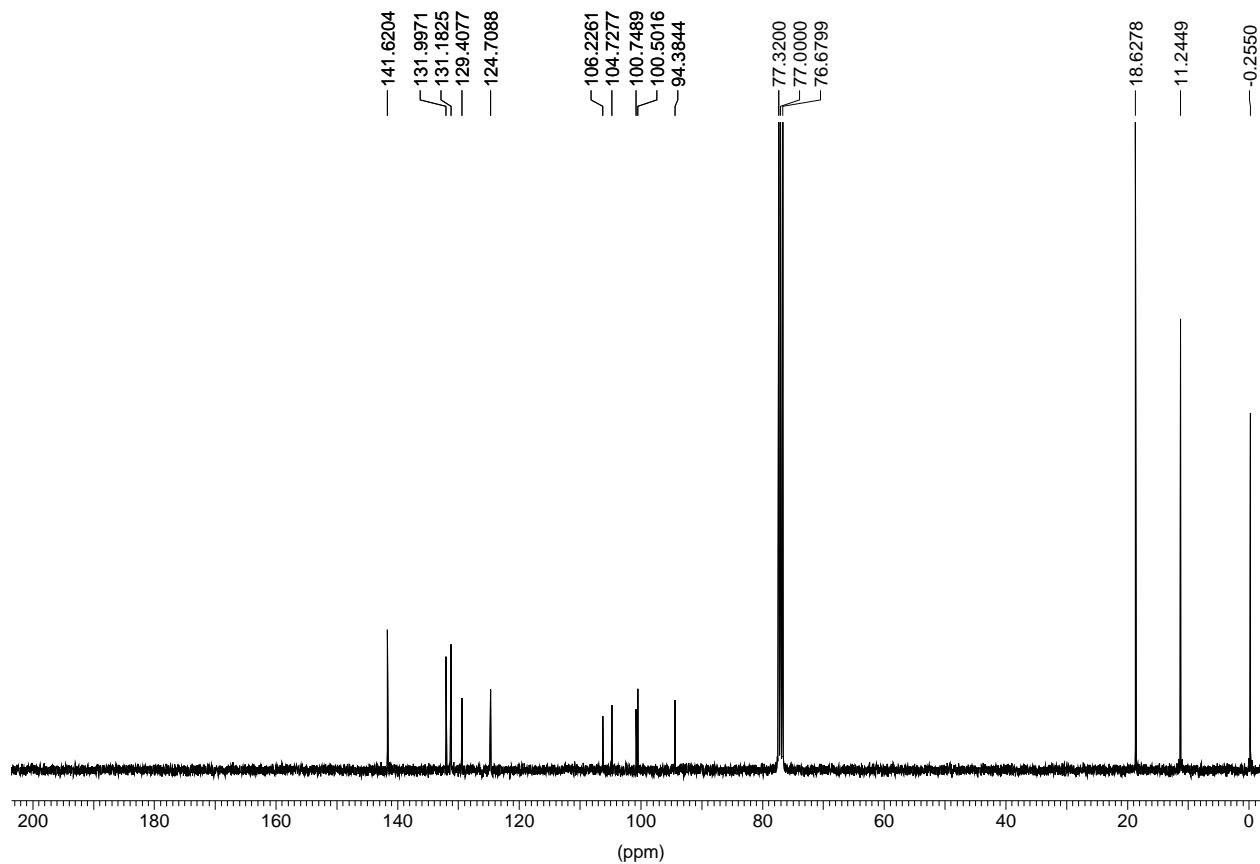
**S29.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of Oligo[5]cruciform (**4**) in  $\text{CDCl}_3$  at 25 °C: Magnification of part of aromatic region (upper), and expansion of aliphatic-region showing TIPS peaks (lower spectrum).



**S30.** 400.13 MHz  $^1\text{H}$  NMR spectra of 2-iodo-4-triisopropylsilylethynyl-trimethylsilylethynylbenzene (**14**) in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum).

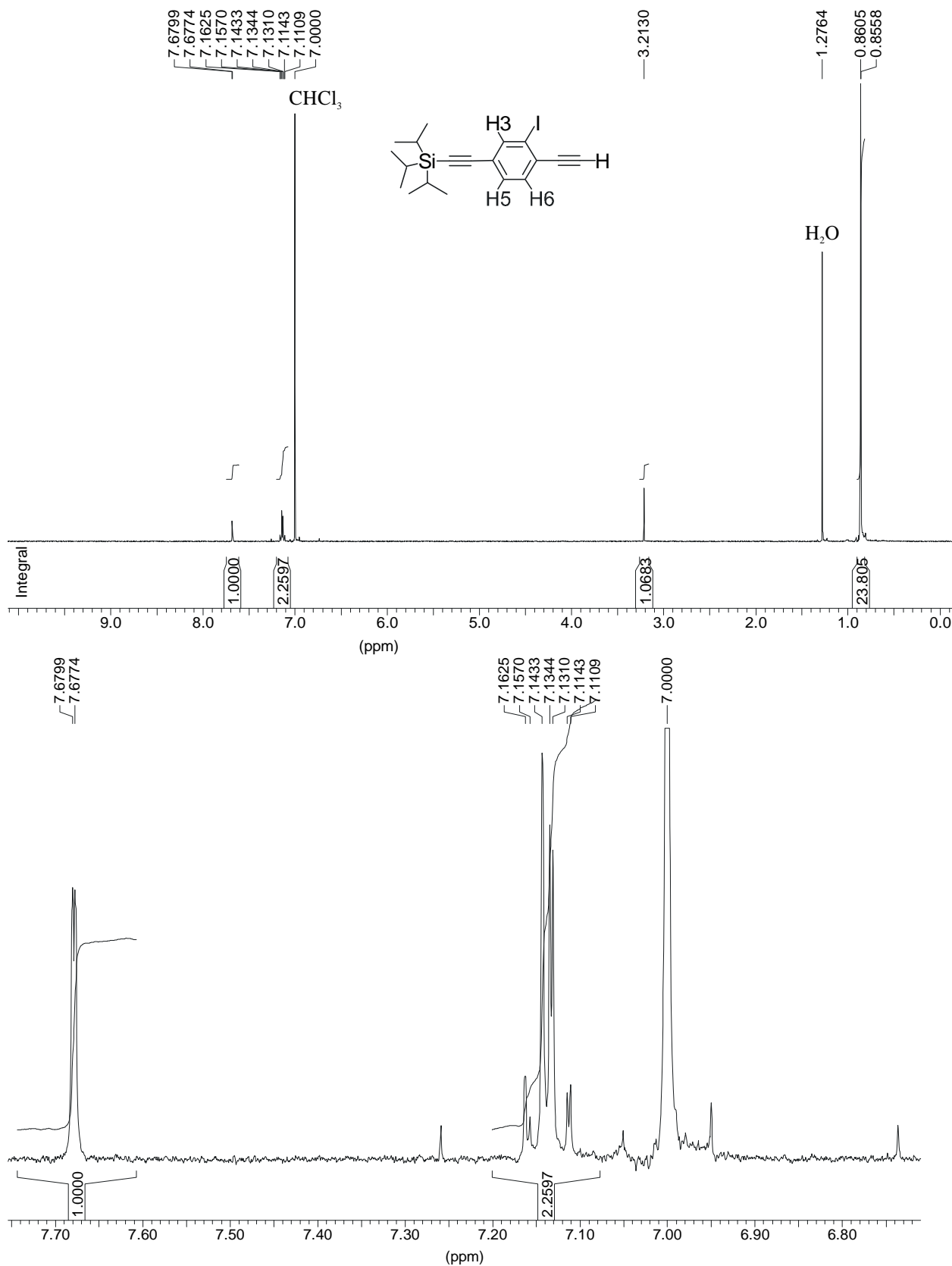


**S31.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 2-iodo-4-triisopropylsilylethynyl-trimethylsilylethynylbenzene (**14**) in  $\text{CDCl}_3$  at 25 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum).

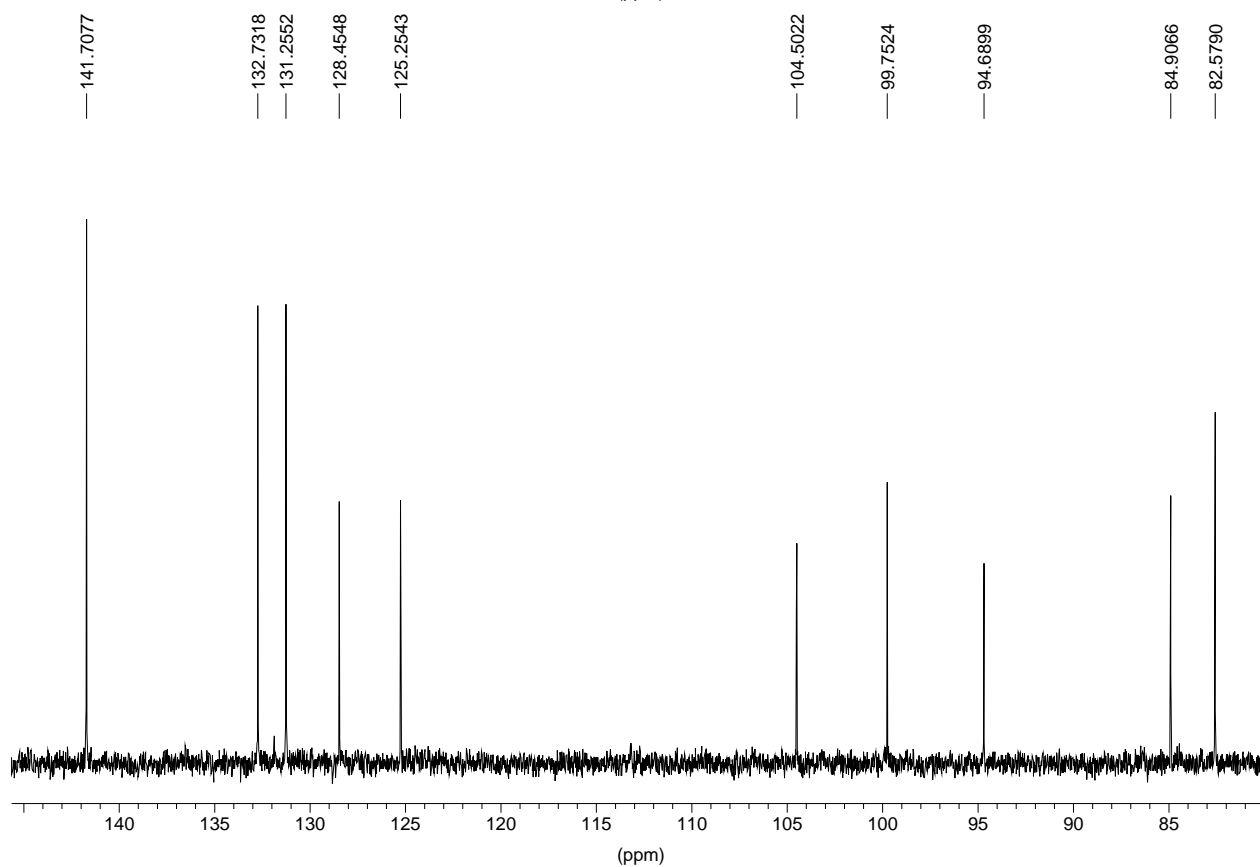
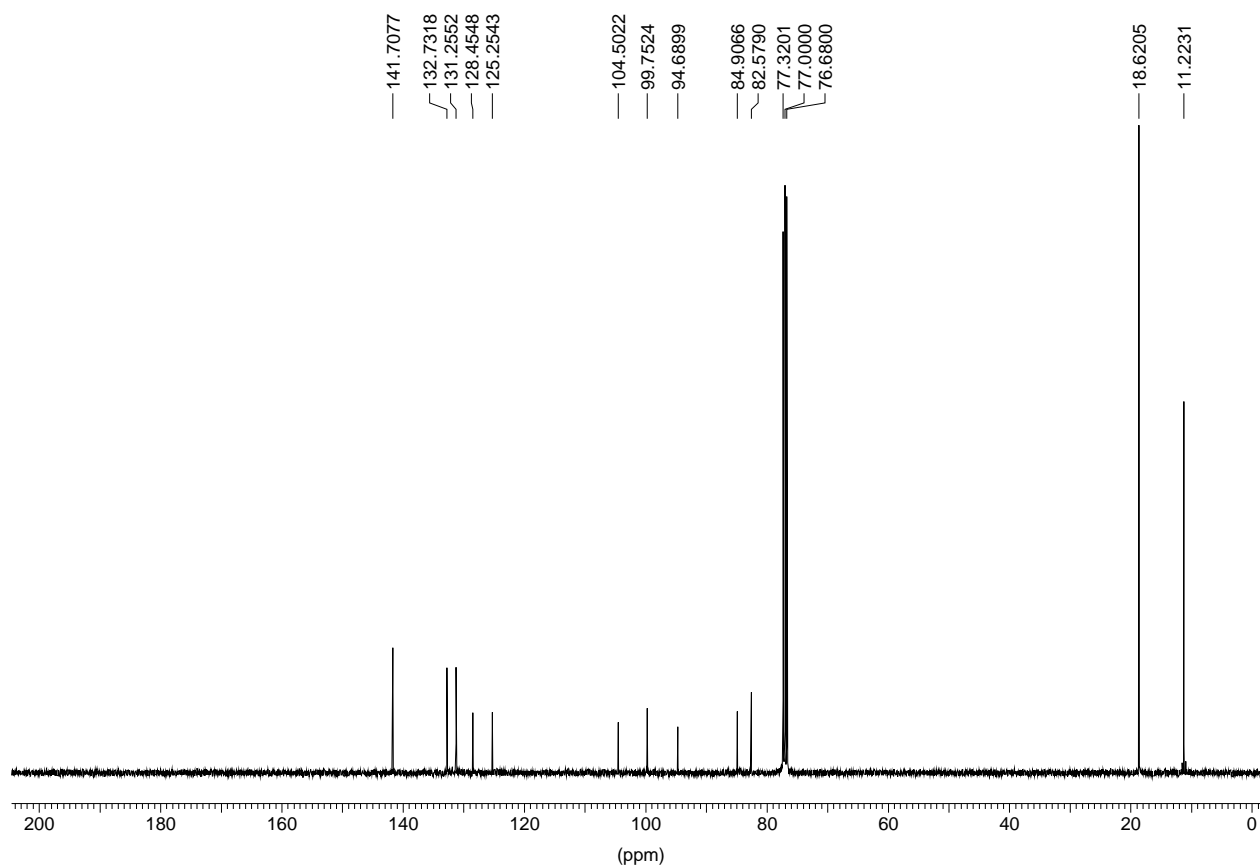




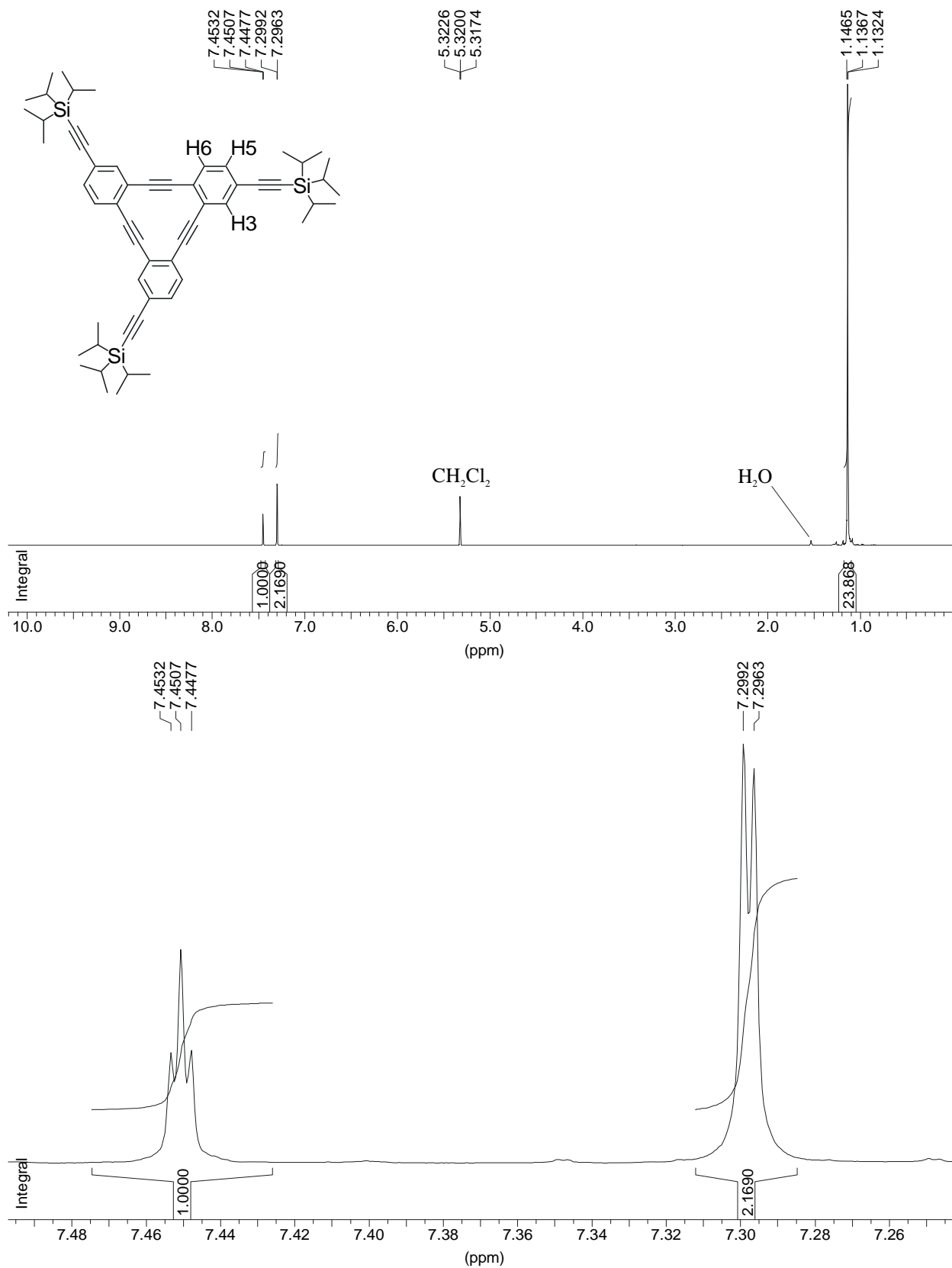
**S32.** 400.13 MHz  $^1\text{H}$  NMR spectra of 2-iodo-4-triisopropylsilyl-ethynylbenzene (**15**) in  $\text{CDCl}_3$  at 24  $^\circ\text{C}$ : 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum).



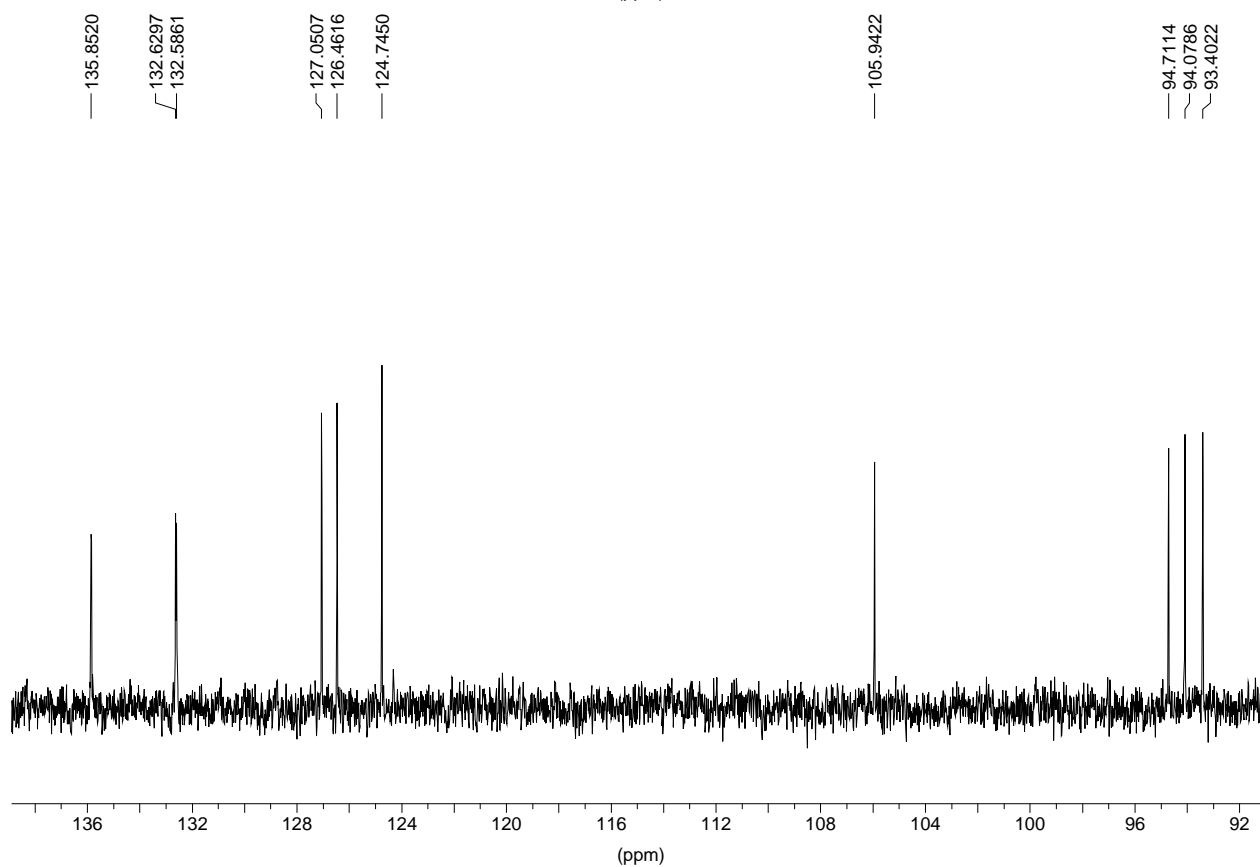
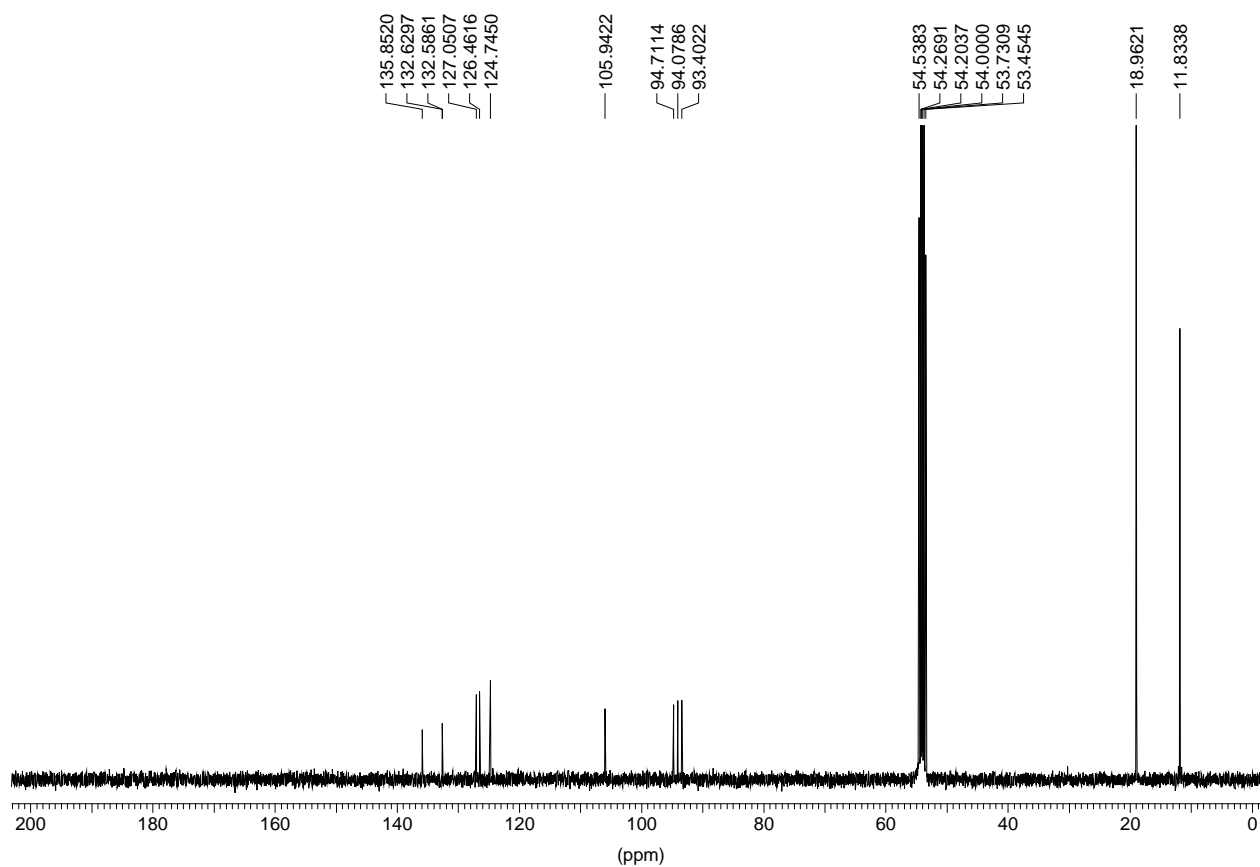
**S33.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 2-iodo-4-triisopropylsilylethynyl-ethynylbenzene (**15**) in  $\text{CDCl}_3$  at 24 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum).



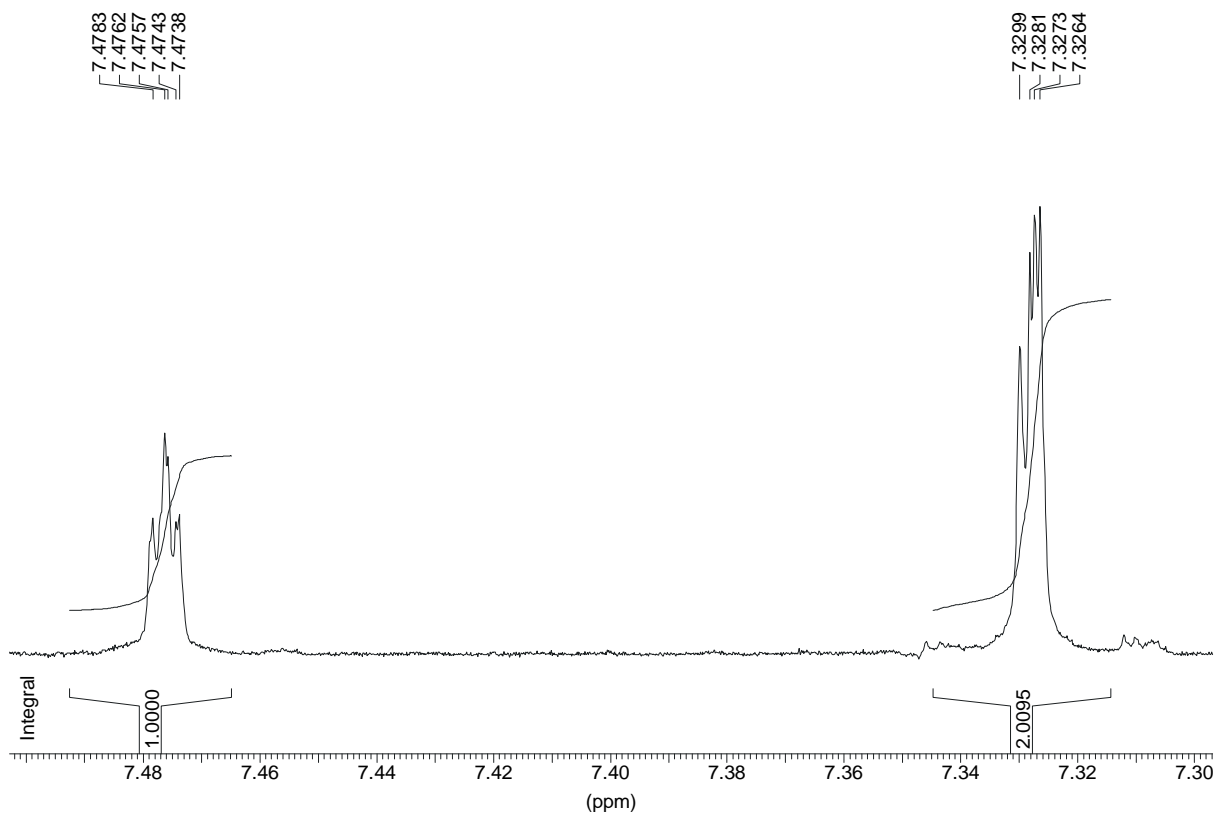
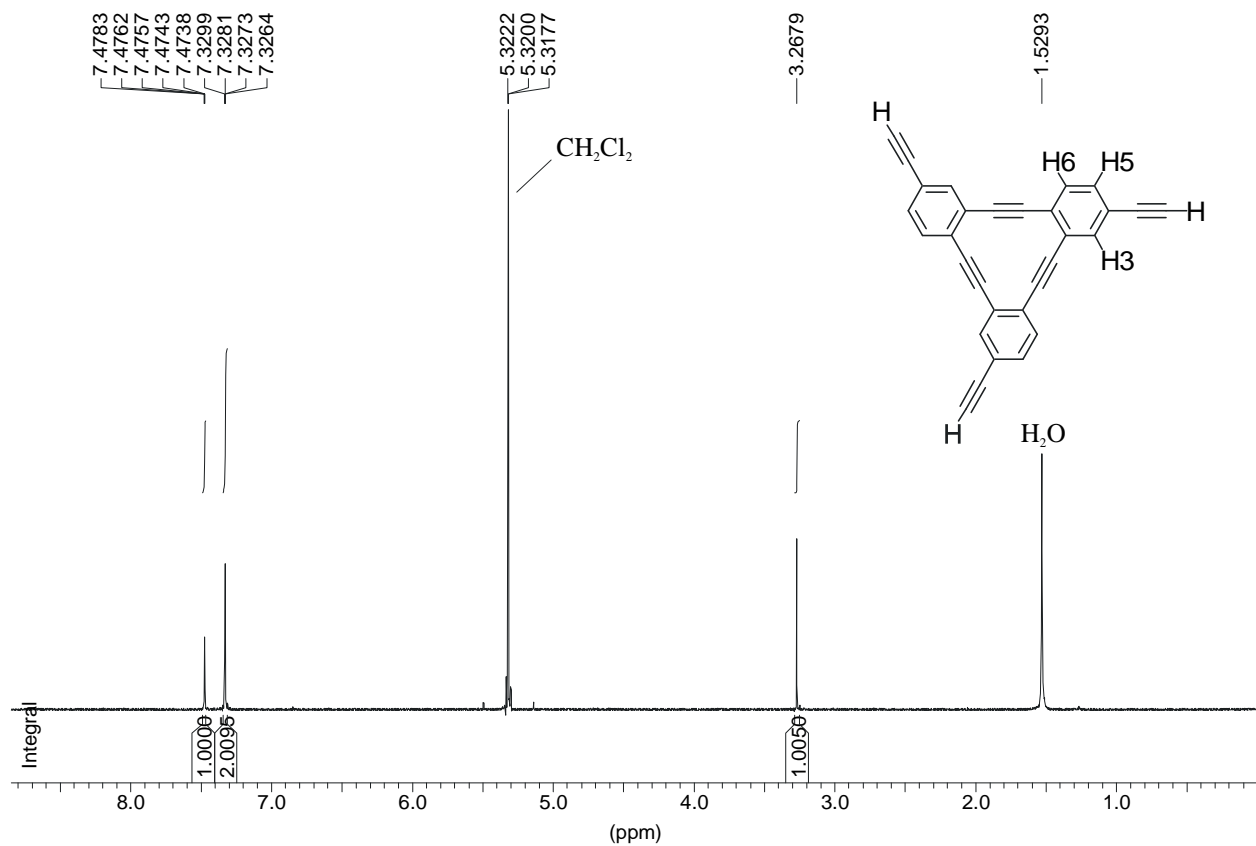
**S34.** 400.13 MHz  $^1\text{H}$  NMR spectra of 4,4',4''-tris-(triisopropylsilyl)ethynyl)-dehydrotribenzo[12]annulene (**5**) in  $\text{CD}_2\text{Cl}_2$  at 22 °C: 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum).



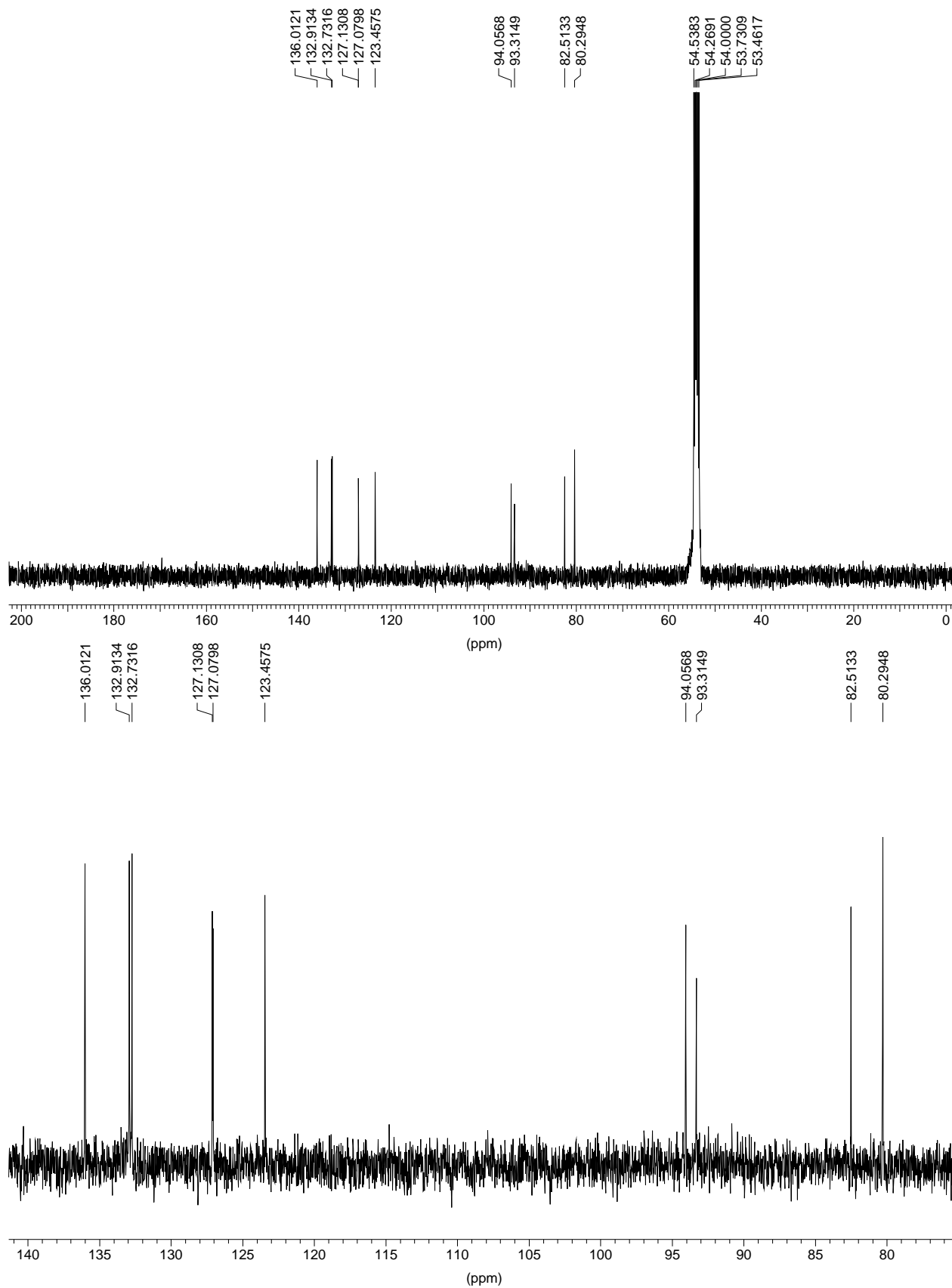
**S35.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4,4',4''-tris-(triisopropylsilylethynyl)-dehydrotribenzo[12]annulene (**5**) in  $\text{CD}_2\text{Cl}_2$  at 22 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum).



**S36.** 500.13 MHz  $^1\text{H}$  NMR spectra of 4,4',4''-triethynyl-dehydrotribenzo[12]annulene (**16**) in  $\text{CD}_2\text{Cl}_2$  at 25  $^\circ\text{C}$ : 10 - 0 ppm (upper), and expansion of aromatic region (lower spectrum).



**S37.** 100.61 MHz  $^{13}\text{C}$  NMR spectra of 4,4',4''-triethynyl-dehydrotribenzo[12]annulene (**16**) in  $\text{CD}_2\text{Cl}_2$  at 24 °C: 200 - 0 ppm (upper), and expansion of aromatic/ethynyl region (lower spectrum).



### S38. Supporting information; X-ray Experimental for 1.

Suitable crystals of **1** were obtained as yellow prisms by slow, partial evaporation of a near-saturated heptane solution of the compound at ambient temperature. The crystals were placed in oil, and a single crystal was selected, mounted on a glass fiber and placed in a low-temperature N<sub>2</sub> stream. X-ray diffraction data collection was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal-detector distance was 36 mm. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structure was solved by Direct methods using the program SHELXS-97.<sup>41a</sup> The refinement and all further calculations were carried out using SHELXL-97.<sup>41b</sup> The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F<sup>2</sup>. Crystallographic data: crystal size 0.16 × 0.14 × 0.14 mm, space group C2/c, monoclinic crystal system, scan range 2.86° ≤ 2θ ≤ 57.38°,  $a = 47.6120(15)$ ,  $b = 14.9290(5)$ ,  $c = 14.7370(5) \text{ \AA}$ ,  $\beta = 97.930(2)^\circ$ ,  $V = 10374.9(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 0.994 \text{ g cm}^{-3}$ ,  $\mu = 0.143 \text{ mm}^{-1}$ , 13327 unique reflections at 173(2) K of which 8169 were taken as observed [ $I > 2\sigma(I)$ ],  $R_{\text{int}} = 0.0368$ ,  $RI[I > 2\sigma(I)] = 0.0724$ ,  $wR2(\text{all data}) = 0.1923$ ,  $Goof = 1.027$ . The asymmetric unit contains half a molecule, of which the trimethylsilyl group and two isopropyl groups are disordered over two positions.

#### References (Contd.)

41) a) Sheldrick, G. M. "SHELXS-97 Program for Crystal Structure Determination", *Acta Crystallogr.* **1990**, *A46*, 467-473; b) Sheldrick, G. (1999) "SHELXL-97", Universität Göttingen, Göttingen, Germany.