

SUPPORTING INFORMATION to the paper

# “Unexpected Formation of a Cyclic Vinylene Sulfate in the Synthesis of Ethynyl-substituted Acenes”

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## Experimental

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**Fig. S2:** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>), aromatic region

## Supplementary Spectra of **4**

**Fig. S3:** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  
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## Supplementary Spectra of **6**

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**Fig. S26:** Photo-luminescence quantum yield measurements of **4**, **6** and **7**

## References

## Experimental

### Materials and Methods

The reagents (Triisopropylsilyl)acetylene, and sulfuric acid (95-98% assay) were obtained commercially from Acros and ACP respectively. 6,13-Pentacenedione and *n*-hexyllithium (2.3 M solution in hexane) were obtained commercially from Sigma-Aldrich. All solvents were of at least reagent grade and dried if necessary. FTIR spectra were collected using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were run on a Varian Mercury 300 MHz NMR spectrometer. HR-APCI spectra were run on a Finnigan LCQ/DUO mass spectrometer. UV-Vis-NIR spectra were measured with a JASCO V-670 spectrometer using quartz cuvettes. Fluorescence spectra were obtained using a Varian Cary Eclipse spectrophotometer.

### X-ray Measurements

X-ray crystallographic data were collected on yellow needles at 100 K, which were mounted on a loop fiber. Data were collected using a Bruker SMART diffractometer equipped with an APEX II CCD detector, a graphite monochromator and Cu K $\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation source. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 x 512 pixel mode. The data were scanned using Bruker's SMART program and integrated using Bruker's SAINT software. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degree scan in 33 frames over four different parts of the reciprocal space (132 frames total). The structure was solved by direct methods using SHELXS-97 and refined by least-squares methods using SHELXL-97 incorporated in the SHELXTL suite of programs.<sup>i</sup>

### Electrochemical Measurements

All electrochemical measurements were performed at room temperature with a CHI-760C or BASi Epsilon electrochemical workstation. Saturated solutions of the analyte in anhydrous DCM containing 0.5 M supporting electrolyte (Bu<sub>4</sub>NPF<sub>6</sub>) were prepared and deaerated by sparging with N<sub>2</sub> gas for 15 min. A typical three-electrode setup was used including a platinum working electrode, Ag wire reference electrode, and a platinum wire auxiliary electrode. Ferrocene was used in all cases as an internal standard and potentials quoted are versus ferrocene ( $E_{1/2} = 0.40 \text{ V vs. Ag wire}$ ).<sup>ii</sup>

### DFT Calculations

GAUSSIAN 09W was used for Density Functional Theory Calculations (DFT) calculations on molecules with density functional theory at the B3LYP/6-31G(d,p) level of theory.<sup>iii</sup>

### PLQY Measurements

PLQY data was calculated based on:  $PLQY_X = PLQY_{ST}(\text{Grad}_X/\text{Grad}_{ST})(n_X^2/n_{ST}^2)$ , Anthracene PLQY = 0.36 in cyclohexane<sup>iv</sup>, cyclohexane refractive index = 1.426 at 20°C, toluene refractive index = 1.496 at 20°C.

$$PLQY_X = 0.36(m_X/307957)(1.496^2/1.426^2)*100\%$$
$$PLQY_4 = 0.9\%, PLQY_6 = 38.6\%, PLQY_7 = 9.9\%$$

### Synthesis and Characterization

**1:** 6,13-Bis(triisopropylsilylethynyl)pentacene was prepared from pentacene-6,13-dione following a modified literature procedure. Under an atmosphere of Nitrogen, 0.22 mL of *n*-butyllithium (0.50 mmol, 2.3 M solution in hexane) was added dropwise to 90 mg (0.50 mmol) of triisopropylsilyl acetylene at 0 °C. The mixture was kept at 0 °C for another 40 min before it was combined with 1.2 mL of dry THF, followed by 6,13-pentacenequinone (20 mg, 0.065 mmol). The mixture was warmed to room temperature and stirred overnight. The reaction was combined with water (75 mL) saturated with NH<sub>4</sub>Cl and then extracted with DCM (75 mL). The organic phase was retained; removing the solvent and then combining the residue with hexanes. The mixture was poured onto a silica plug and washed with 200 ml DCM:hexanes (1:3) and then eluted with 200 mL DCM:hexanes (1:1). The resulting white solid was then dissolved in 10 mL acetone, and then combined with five drops of a tin(II) chloride dihydrate solution (37 mg (0.17 mmol) SnCl<sub>2</sub>·2H<sub>2</sub>O in 100 ml 10% v/v H<sub>2</sub>SO<sub>4</sub> in water). The reaction vessel was covered with aluminum foil and then the mixture was stirred overnight. The resulting blue mixture was then dissolved in hexane, washed with water and saturated sodium bicarbonate solution and then dried over magnesium sulfate. The hexane solution is then poured on to a silica plug, which is flushed with hexane (200 mL), followed by 1:4 DCM/hexane to elute a deep blue solid (~38 mg, 91%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.30 (s, 4H), 7.99 (dd,  $J = 9, 3 \text{ Hz}$ , 4H), 7.43 (dd,  $J = 9, 3 \text{ Hz}$ , 4H), 1.38 (m, 42H) ppm.<sup>v</sup>

**4:** (*E*)-2-styrylanthracene-9,10-dione was prepared from 2-amino-9,10-anthraquinone following a modified literature procedure. Under an atmosphere of nitrogen, 9,10-anthraquinone-2-yl triflate<sup>vi</sup> (5.3 g, 0.015 mol) was added to DME (20 ml) and H<sub>2</sub>O (150 mL) containing K<sub>2</sub>CO<sub>3</sub> (20.8 g, 0.150 mol) the mixture was stirred while sparging with nitrogen for 0.5 hours. Trans-2-phenylvinylboronic acid (2.28 g, 0.0154 mol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.61 g, 0.53 mmol) were then added and the mixture was stirred while refluxing for 24 hours. The resulting precipitate was filtered off, washed with water and hexanes. The crude material was dried, dissolved in DCM (~ 500 mL) and the red solution was filtered from undissolved residue. The volume of the solvent was reduced by rotary evaporation upon which the desired product crystallized in several fractions. A combined yield was 4.1 g (89%). Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a saturated solution of **4** in 50:50 DCM/MeOH. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 8.44 (d, *J* = 0.5 Hz, 1H), 8.36 (m, 3H), 7.92 (dd, *J* = 9, 3 Hz, 1H), 7.85 (m, 2H), 7.61 (m, 2H), 7.44 (m, 4H), 7.26 (d, *J* = 16.5 Hz, 1H) ppm.<sup>vii</sup>

**6 and 7:** Under an atmosphere of Nitrogen, 0.83 mL of *n*-hexyllithium (1.9 mmol, 2.3 M solution in hexane) was added dropwise to 349 mg (1.9 mmol) of triisopropylsilyl acetylene at 0 °C. The mixture was kept at 0 °C for one hour before it was combined with (*E*)-2-styrylanthracene-9,10-dione **4** (99 mg, 0.32 mmol) followed by 8 mL of dry Et<sub>2</sub>O. The mixture was warmed to room temperature and stirred overnight. The reaction was combined with water (100 mL) saturated with NH<sub>4</sub>Cl and then extracted with hexanes (100 mL). The mixture was poured onto a silica plug and washed with 200 ml DCM:hexanes (1:3) and then eluted with 200 mL DCM:hexanes (1:1), providing 79 mg (37%) of the intermediate **5** which was used without purification in the next step.

Intermediate **5** was dissolved in 15 mL acetone, and then combined with 20 drops of a tin(II) chloride dihydrate solution (37 mg (0.17 mmol) SnCl<sub>2</sub>·2H<sub>2</sub>O in 100 ml 10% v/v H<sub>2</sub>SO<sub>4</sub> in water). The reaction vessel was covered with aluminum foil and then the mixture was stirred overnight. The resulting yellow mixture was then poured into hexane (100 mL), washed with water and saturated sodium bicarbonate solution and then dried over magnesium sulfate. The hexane solution was then poured onto a silica plug and eluted with hexane (200 mL), providing **6**, 18 mg (24%). After removal of **6**, a DCM:Hexane mixture (1:3, amount) was poured onto the plug used to elute **7**, 66 mg (76%).

An alternative procedure for the synthesis of **6** in better yield is also provided:

**6:** The dihydroxy intermediate **5** was dissolved in hexanes and then combined with 0.6 mL of a tin(II) chloride dihydrate solution (900 mg SnCl<sub>2</sub>·2H<sub>2</sub>O in 2 ml 10% v/v HCl in water). The reaction vessel was covered with aluminum foil and then the mixture was stirred overnight. The resulting yellow mixture was then poured into hexane (100 mL), washed with water and saturated sodium bicarbonate solution and then dried over magnesium sulfate. hexane solution is then poured on to a silica and eluted with additional hexane (200 mL), providing **6**, 144 mg (83%).

**6:** Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a saturated solution of **6** in 50:50 DCM/MeOH. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 8.70 (d, *J* = 3.0 Hz, 1H), 8.62 (m, 3H), 7.88 (dd, *J* = 9, 3 Hz, 1H), 7.61 (m, 4H), 7.44 (t, *J* = 9.0 Hz, 2H), 7.33 (m, 3H), 1.31 (m, 36H), 0.90 (m, 6H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 139.03, 137.64, 134.59, 131.96, 130.68, 130.21, 129.88, 129.08, 129.00, 128.51, 127.37, 126.88, 120.44, 120.36, 107.41, 106.91, 105.11, 104.93, 20.62, 20.55, 13.46, 13.41 ppm. FT-IR (neat): 3058 (w), 3028 (w), 2941 (s), 2889 (w), 2862 (s), 2162 (w), 2124 (m), 1676 (m), 1591 (m), 1496 (w), 1460 (s), 1426 (w), 1379 (s), 1328 (w), 1294 (w), 1244 (w), 1216 (m), 1155 (w), 1132 (w), 1073 (w), 1043 (m), 1016 (w), 995 (m), 953 (m), 918 (w), 881 (s), 839 (w), 814 (m), 773 (m), 761 (m), 746 (m), 671 (s), 658 (s), 621 (m), 583 (m), 548 (w), 506 (w), 488 (w), 460 (w), 443 (w) cm<sup>-1</sup>. HR-APCIMS (*m/z*) for C<sub>44</sub>H<sub>57</sub>Si<sub>2</sub> [M + H]<sup>+</sup>: calculated 641.39933 found 641.39719. mp: 162-166°C.

**7:** Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a saturated solution of **7** in 50:50 DCM/MeOH. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 8.75 (d, *J* = 1.5 Hz, 1H), 8.66 (m, 1H), 8.19 (d, *J* = 9 Hz, 2H), 7.90 (dd, *J* = 9, 1.5 Hz, 1H), 7.66 (m, 4H), 7.45 (t, *J* = 9 Hz, 2H), 7.35 (m, 3H), 1.35 (m, 42H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 147.55, 147.42, 136.95, 135.80, 132.55, 132.45, 131.52, 131.24, 130.67, 128.85, 128.15, 128.07, 127.82, 127.31, 127.19, 126.69, 126.18, 125.71, 125.43, 125.34, 122.62, 118.65, 106.82, 102.55, 18.94, 18.21 ppm. FT-IR (neat): 3029 (w), 2942 (s), 2865 (s), 2145 (w), 1649 (m), 1560 (w), 1496 (w), 1462 (m), 1402 (s), 1383 (w), 1289 (w), 1216 (s), 1186 (m), 1151 (s), 1038 (m), 1018 (w), 999 (m), 956 (s), 920 (w), 909 (w), 882 (s), 826 (w), 814 (w), 793 (s), 759 (m), 746 (m), 732 (w), 671 (w), 662 (s), 624 (m), 602 (w), 575 (w), 552 (w), 511 (m), 488 (w), 462 (w) cm<sup>-1</sup>. HR-APCIMS (*m/z*) for C<sub>44</sub>H<sub>57</sub>OSi<sub>2</sub> [M – SO<sub>3</sub> + H]<sup>+</sup>: calculated 657.39425 found 657.39150. T<sub>dec.</sub> >120°C.

### Supplementary Spectra of 1

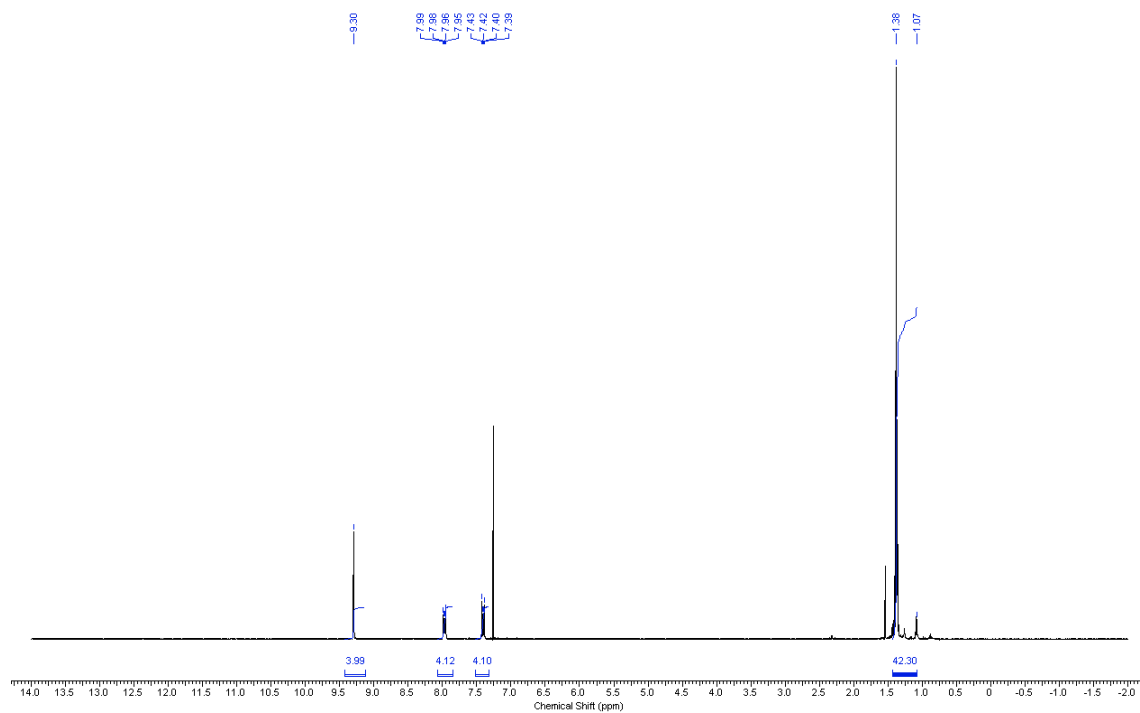


Fig. S1:  $^1\text{H-NMR}$  of **1** (300 MHz,  $\text{CDCl}_3$ )

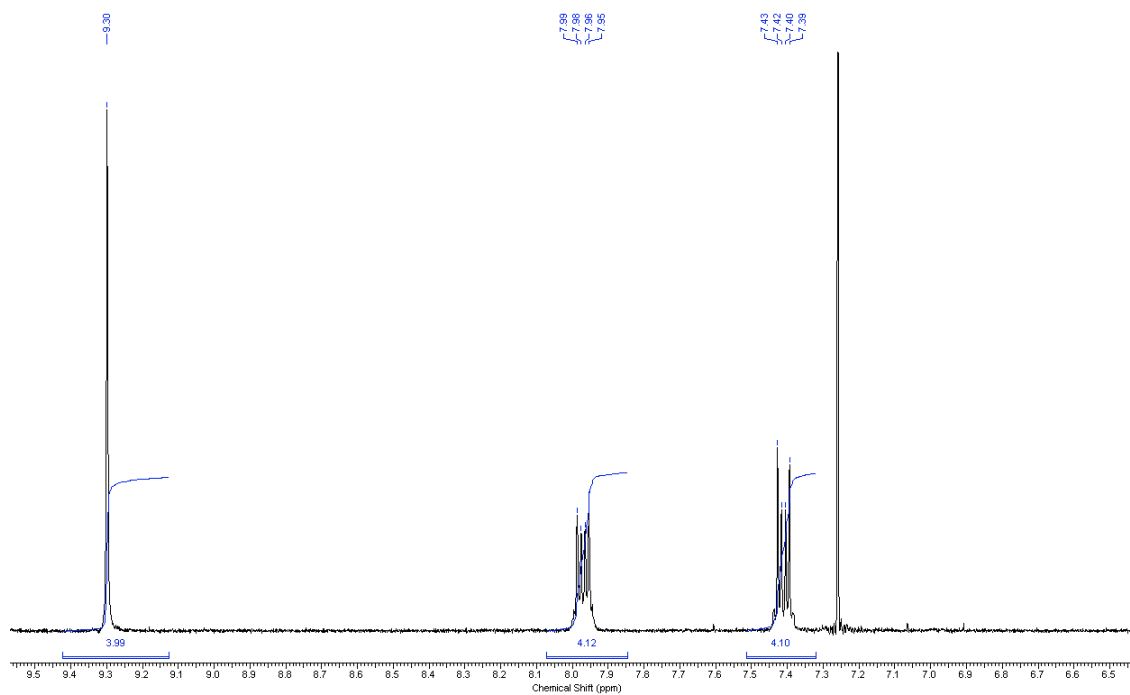


Fig. S2:  $^1\text{H-NMR}$  of **1** (300 MHz,  $\text{CDCl}_3$ ), aromatic region

Supplementary Spectra of 4

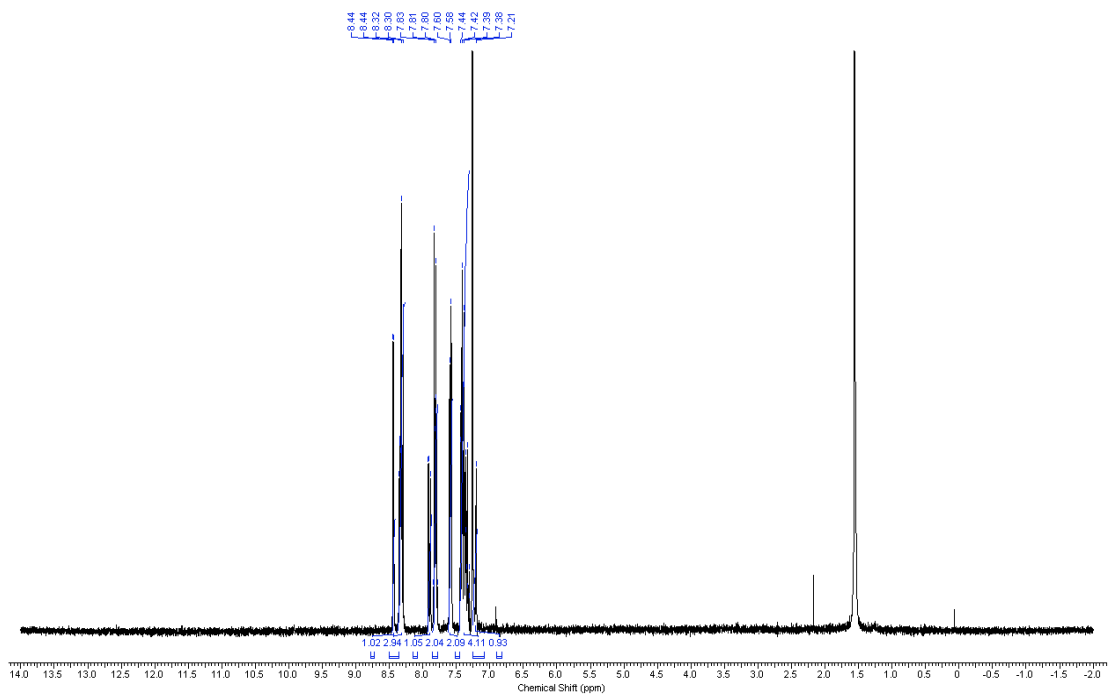


Fig. S3:  $^1\text{H-NMR}$  of 4 (300 MHz,  $\text{CDCl}_3$ )

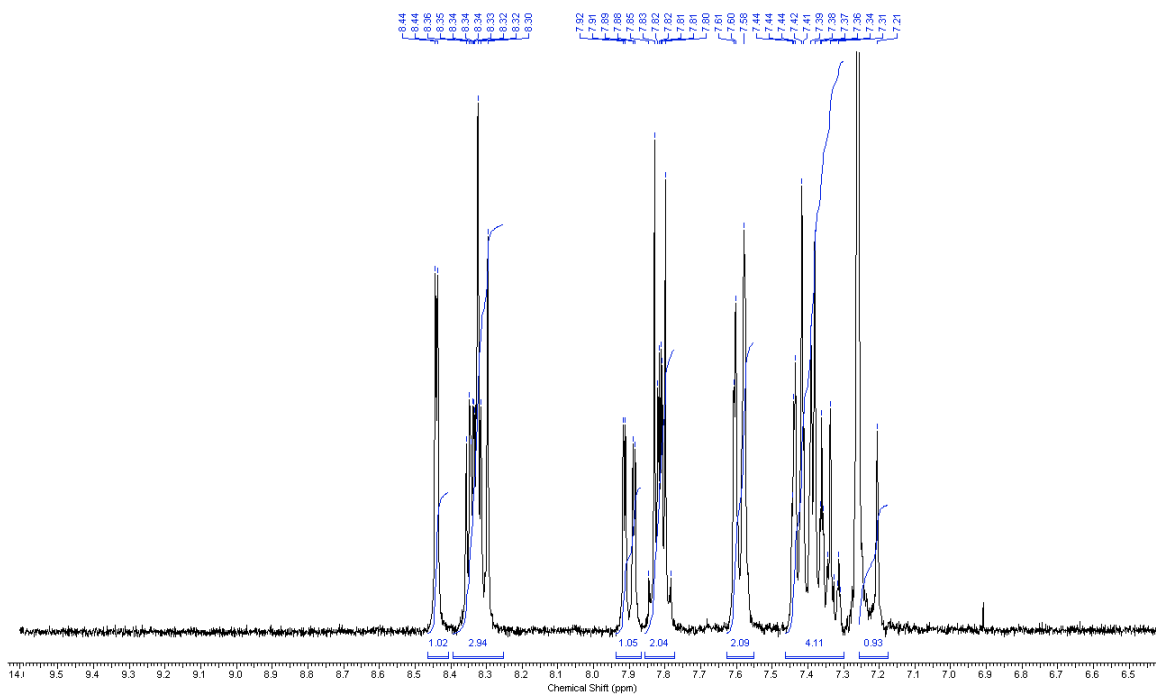


Fig. S4:  $^1\text{H-NMR}$  of 4 (300 MHz,  $\text{CDCl}_3$ ), aromatic region

### Supplementary Spectra of 6

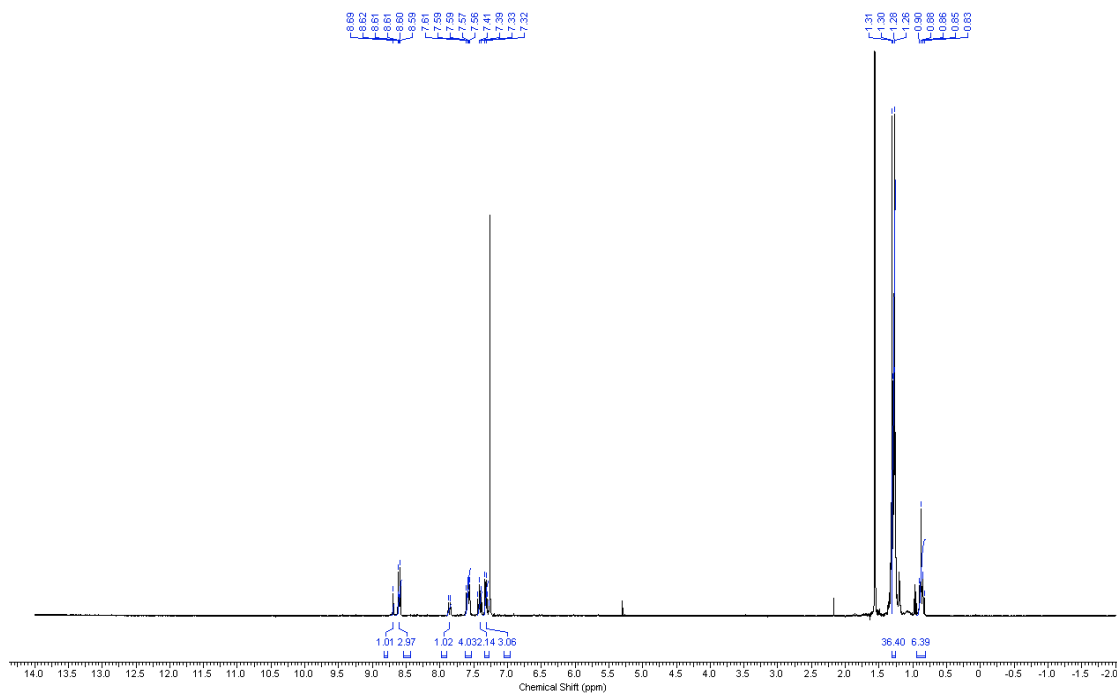


Fig. S5:  $^1\text{H-NMR}$  of **6** (300 MHz,  $\text{CDCl}_3$ )

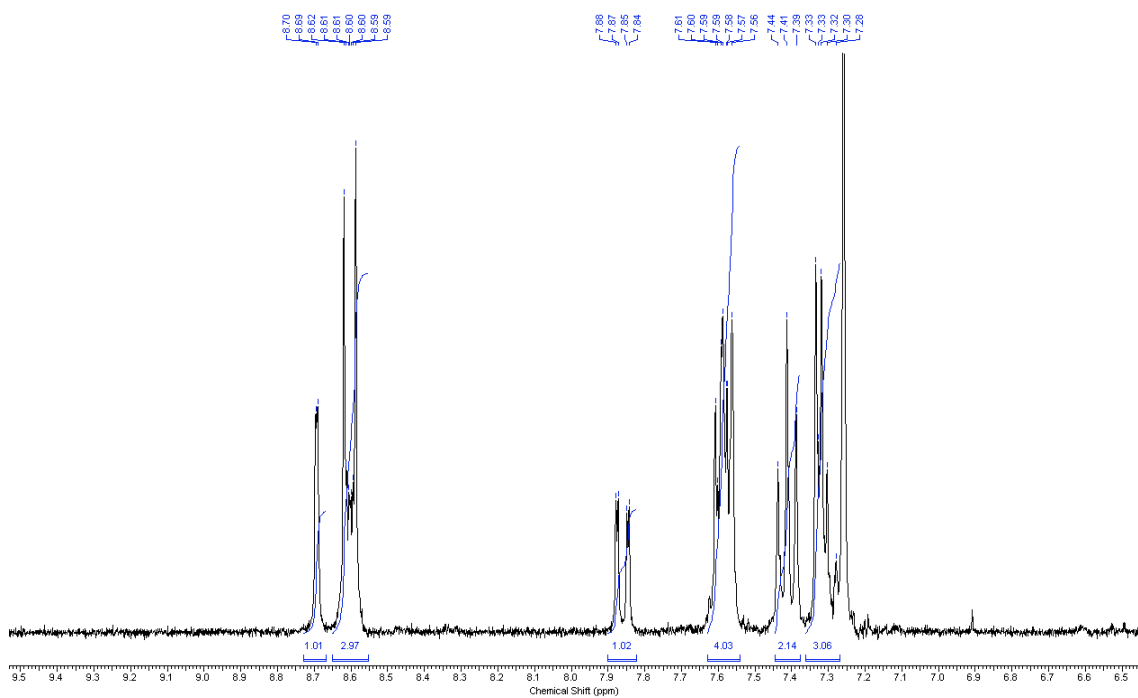


Fig. S6:  $^1\text{H-NMR}$  of **6** (300 MHz,  $\text{CDCl}_3$ ), aromatic region

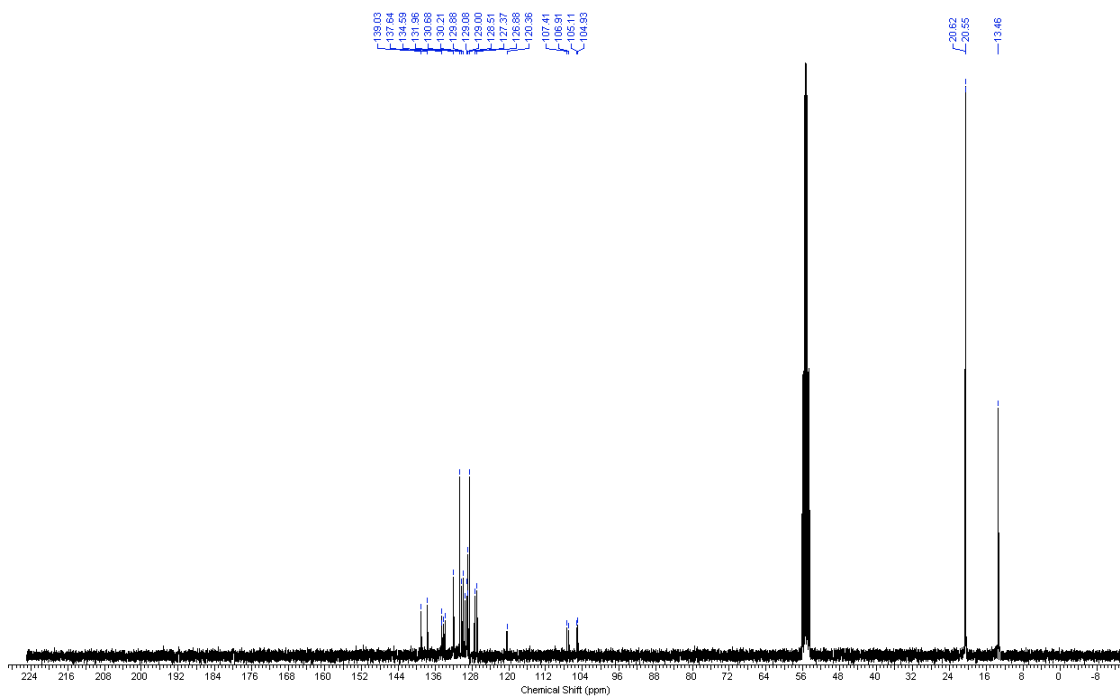


Fig. S7:  $^{13}\text{C}$ -NMR of 6 (75 MHz,  $\text{CDCl}_3$ )

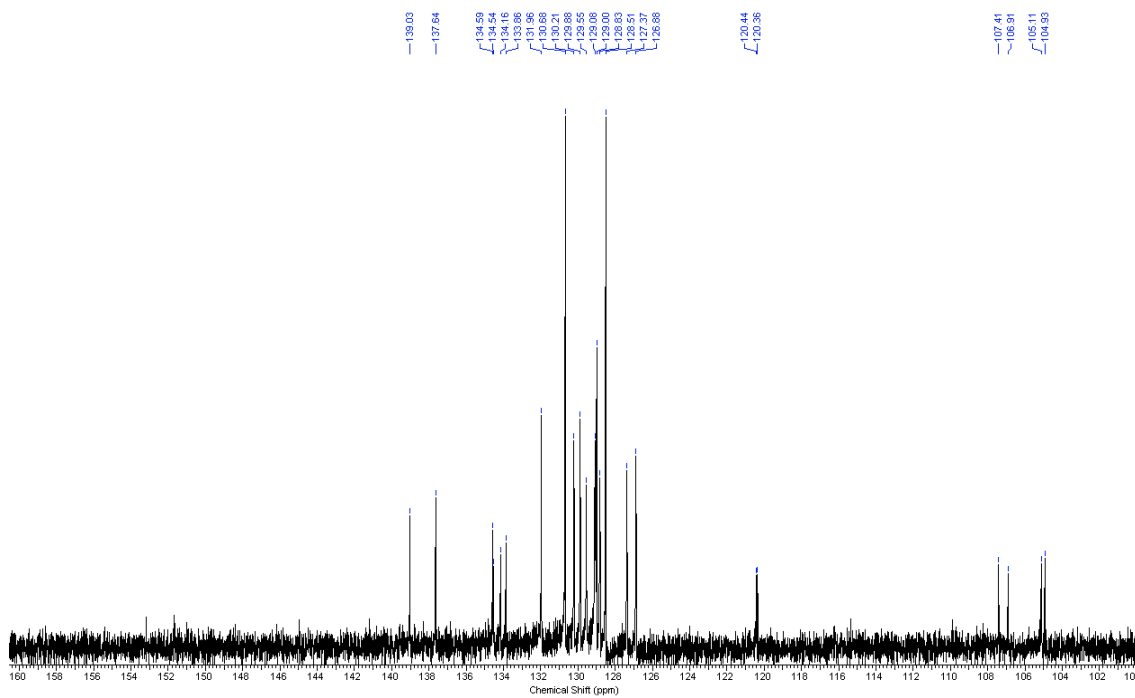


Fig. S8:  $^{13}\text{C}$ -NMR of 6 (75 MHz,  $\text{CDCl}_3$ ), aromatic region

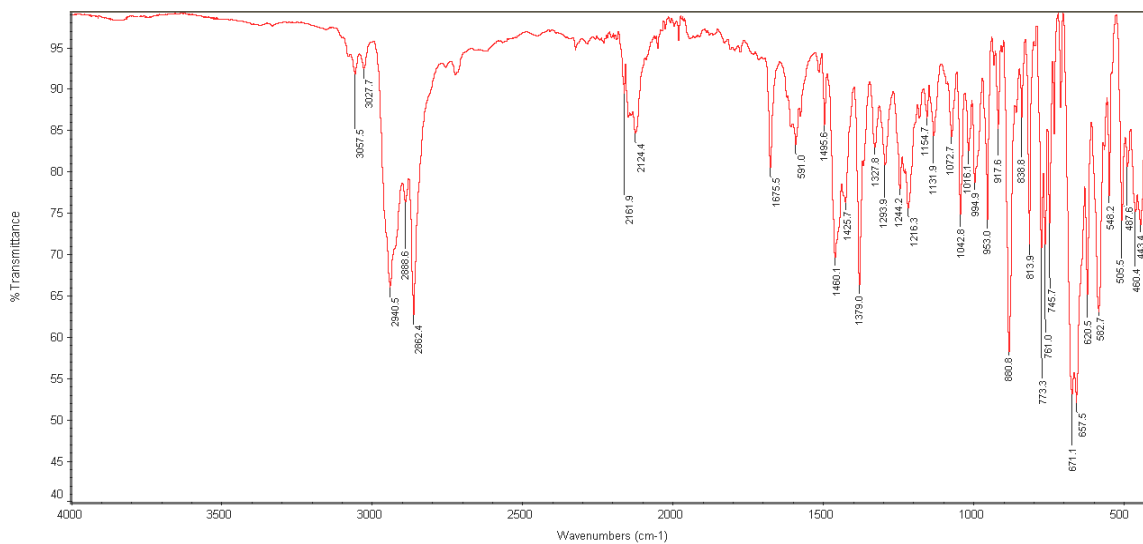
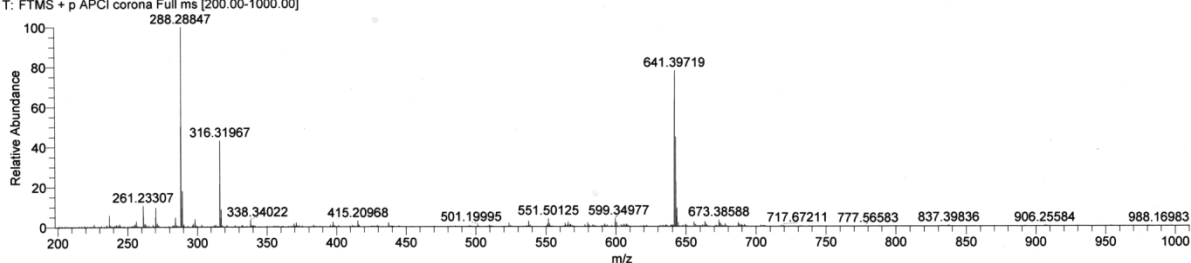


Fig. S9: ATR-FTIR of 6 (neat solid).

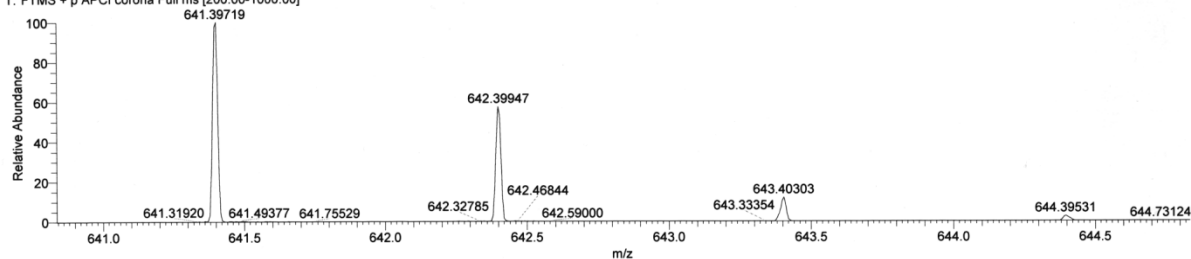
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7/25/2011 9:39:49 AM

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 SB: 8 0.06-0.14

T: FTMS + p APCI corona Full ms [200.00-1000.00]

m/z = 641.38427-641.41170

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
641.39719	192253.7	100.00	31040.96	1.00	641.39933	-2.14	18.5	C <sub>44</sub> H <sub>57</sub> Si <sub>2</sub>
					641.41418	-16.99	23.5	C <sub>49</sub> H <sub>53</sub>
					641.35980	37.38	24.5	C <sub>47</sub> H <sub>49</sub> Si
					641.45370	-56.52	17.5	C <sub>46</sub> H <sub>61</sub> Si
					641.32028	76.91	30.5	C <sub>50</sub> H <sub>41</sub>
					641.30543	91.76	25.5	C <sub>45</sub> H <sub>45</sub> Si <sub>2</sub>

Fig. S10: HR-APCI MS of 6.



Supplementary Spectra of 7

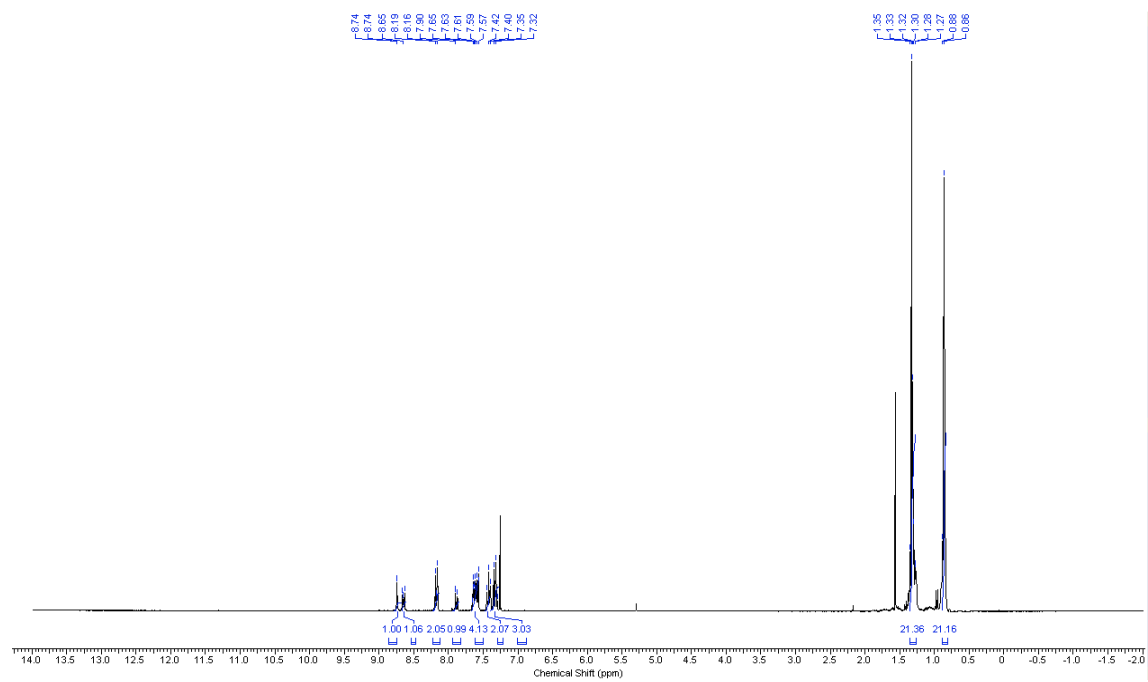


Fig. S11:  $^1\text{H-NMR}$  of 7 (300 MHz,  $\text{CDCl}_3$ )

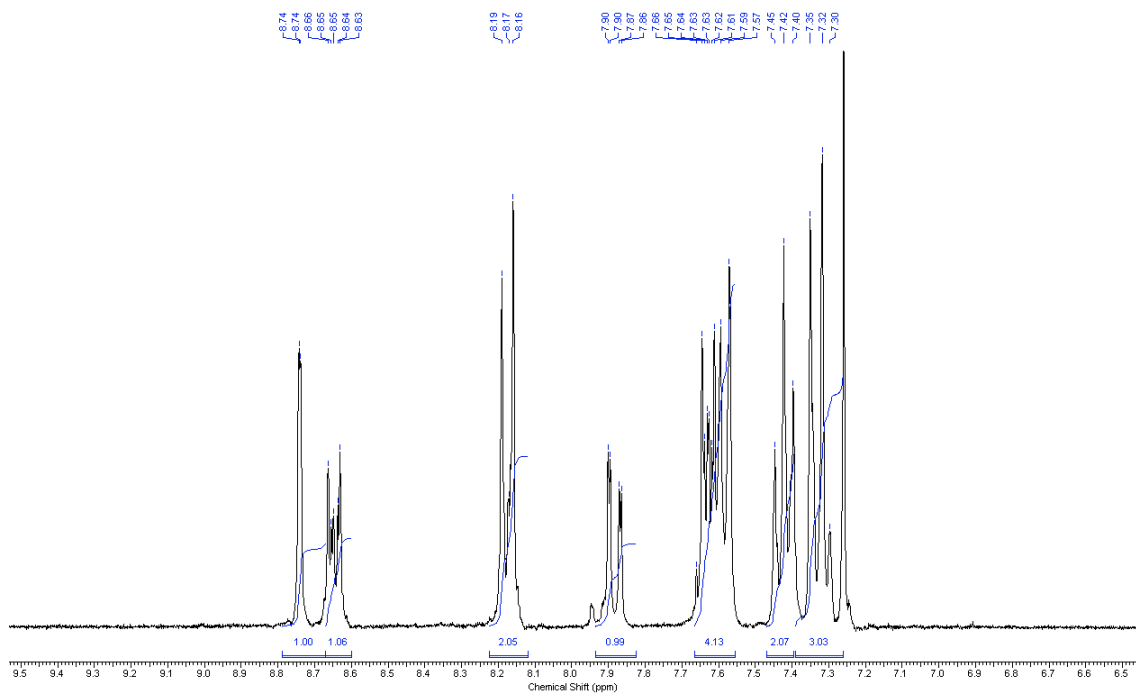
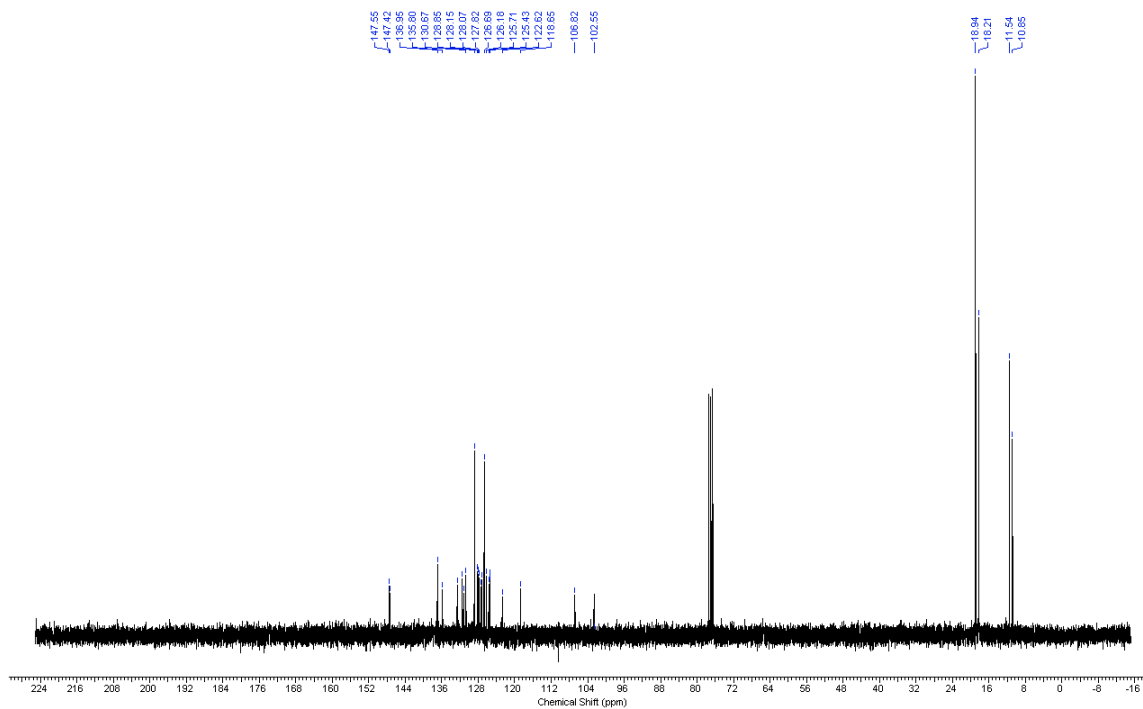
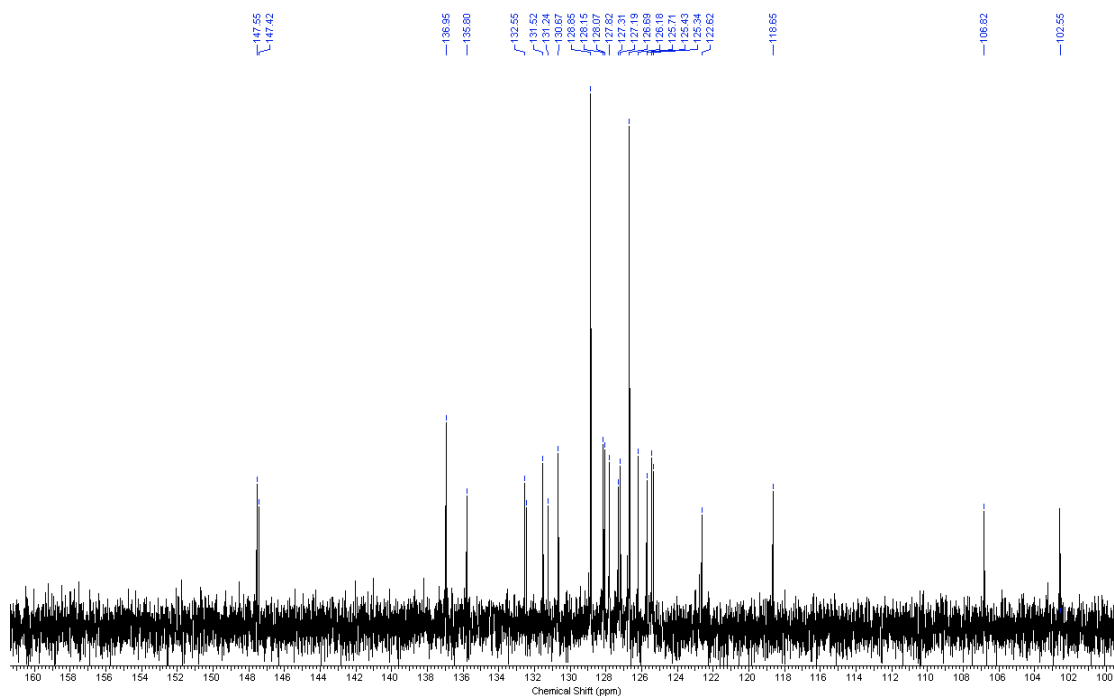


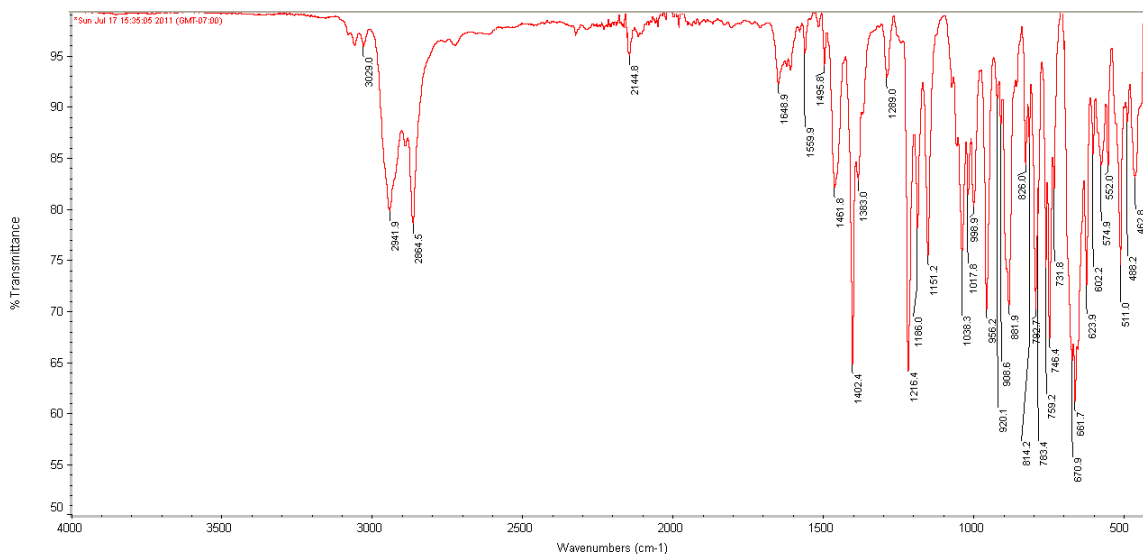
Fig. S12:  $^1\text{H-NMR}$  of 7 (300 MHz,  $\text{CDCl}_3$ ), aromatic region.



**Fig. S13:**  $^{13}\text{C}$ -NMR of **7** (75 MHz,  $\text{CDCl}_3$ ).



**Fig. S14:**  $^{13}\text{C}$ -NMR of **7** (75 MHz,  $\text{CDCl}_3$ ), aromatic region.

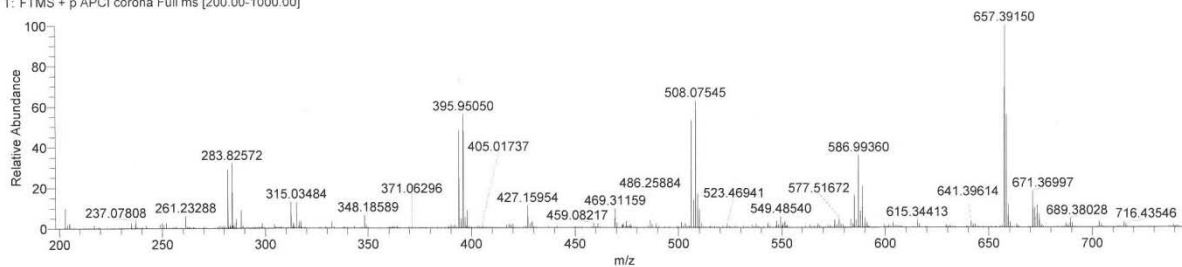


**Fig. S15:** ATR-FTIR of **7** (neat solid).

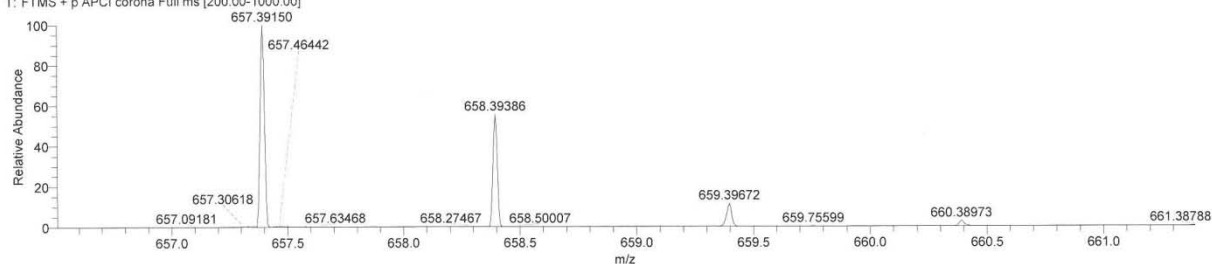
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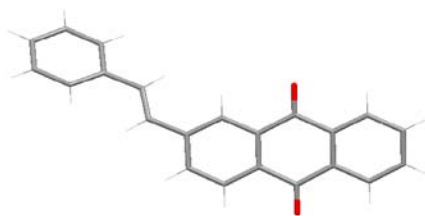
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m/z = 657.37732-657.40339

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
657.39150	1006192.8	100.00	31634.23	1.00	657.39110	0.39	23.5	C <sub>48</sub> H <sub>53</sub> Si
					657.39425	-2.75	18.5	C <sub>44</sub> H <sub>57</sub> O <sub>2</sub> Si <sub>2</sub>
					657.39448	-2.98	18.5	C <sub>45</sub> H <sub>57</sub> S <sub>2</sub> Si
					657.39762	-6.12	13.5	C <sub>41</sub> H <sub>61</sub> O <sub>2</sub> Si <sub>2</sub>
					657.39785	-6.35	13.5	C <sub>42</sub> H <sub>61</sub> S <sub>2</sub> Si
					657.40099	-9.49	8.5	C <sub>38</sub> H <sub>65</sub> O <sub>2</sub> Si <sub>2</sub>

**Fig. S16:** HR-APCI MS of **7**.

**X-ray crystallographic analysis**



**Fig. S17:** X-Ray Crystal structure of **4**

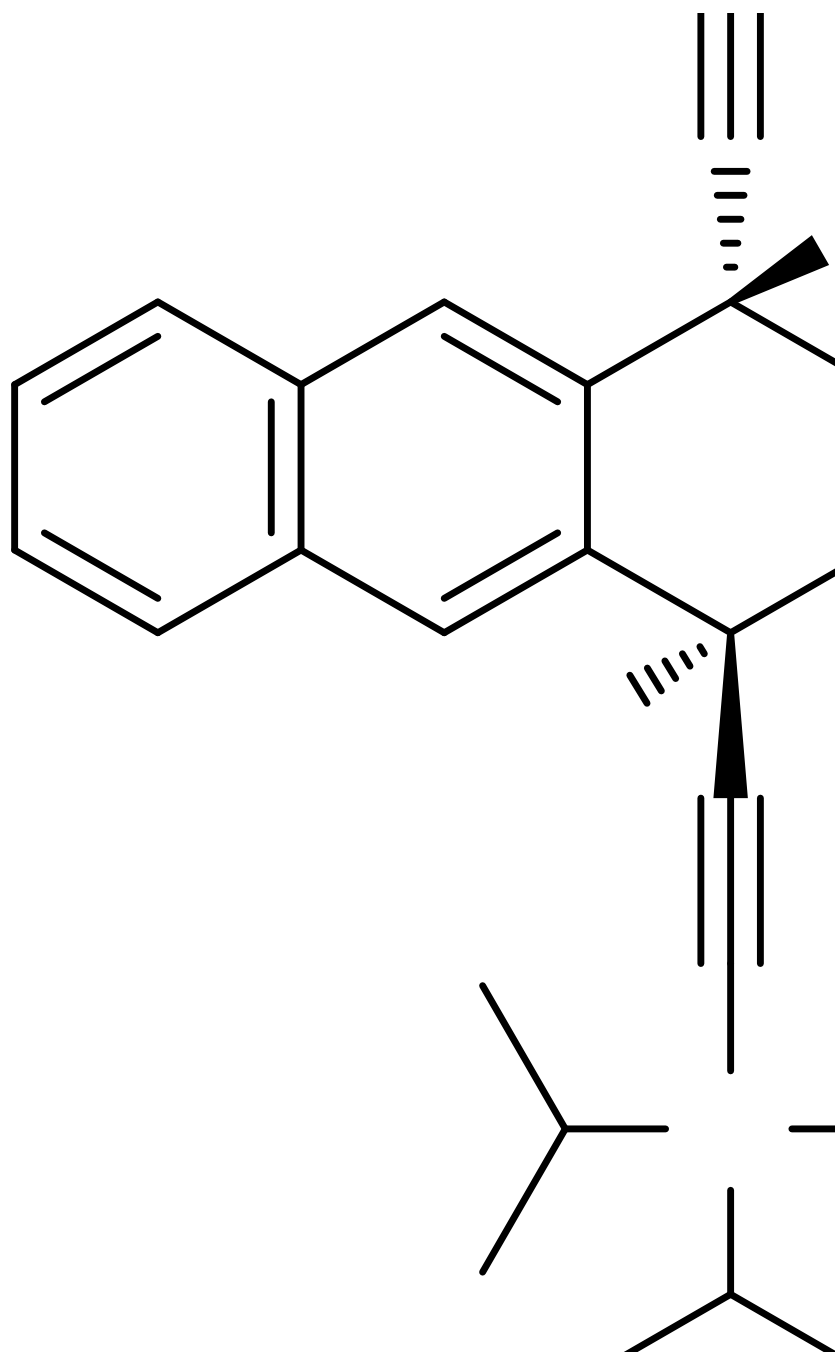
**Table 1:** X-Ray Crystallographic Data of **4**

Compound reference	<b>4</b>
Chemical formula	C <sub>22</sub> H <sub>14</sub> O <sub>2</sub>
Formula Mass	310.33
Crystal system	Orthorhombic
<i>a</i> /Å	4.7611(2)
<i>b</i> /Å	13.0291(6)
<i>c</i> /Å	23.9530(10)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Unit cell volume/Å <sup>3</sup>	1485.87(12)
Temperature/K	100
Space group	<i>P</i> 212121
No. of formula units per unit cell, <i>Z</i>	4
No. of reflections measured	24965
No. of independent reflections	2853
<i>R</i> <sub>int</sub>	0.046
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0345
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0963
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.0370
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0990

**Table 2:** UB3LYP 6-31G(d,p) calculated energies in eV

Compound	HOMO	LUMO	Gap	Total Energy
<b>9</b>	-1.355	-5.814	4.459	-66393.154
<b>1'</b>	-6.627	-8.772	2.146	-64324.378
<b>1</b>	-2.730	-4.629	1.899	-62267.371
<b>5</b>	-1.487	-5.522	4.035	-66425.171
<b>6</b>	-2.290	-5.048	2.758	-62299.871
<b>7'</b>	-6.498	-8.481	1.984	-64356.506
<b>7</b>	-2.496	-5.368	2.872	-81321.184
<b>8'</b>	-6.825	-8.036	1.211	-64356.200
<b>8</b>	-2.483	-5.391	2.908	-81321.190

See following page for diagrams of the compounds in Table 2



**Fig. S18:** Diagrams of the compounds in Table 2

Supplementary Figures

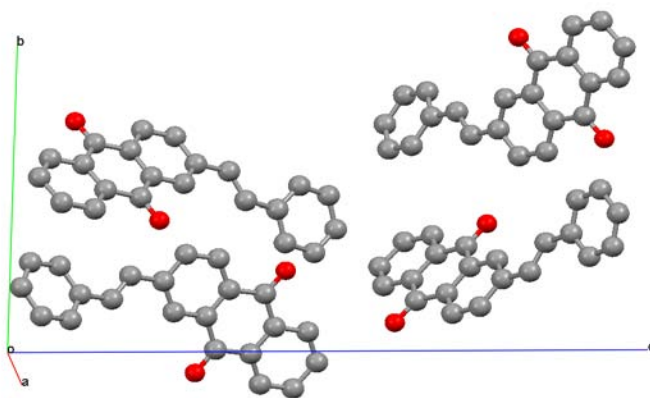


Fig. S19: Crystal packing of 4 – hydrogen atoms omitted for clarity

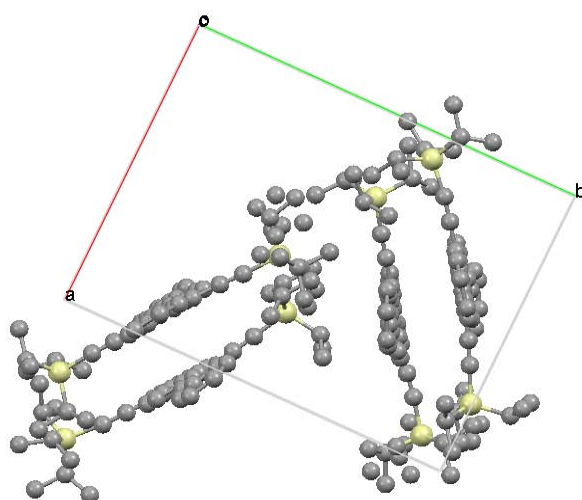


Fig. S20: Crystal packing of 6 – hydrogen atoms omitted for clarity

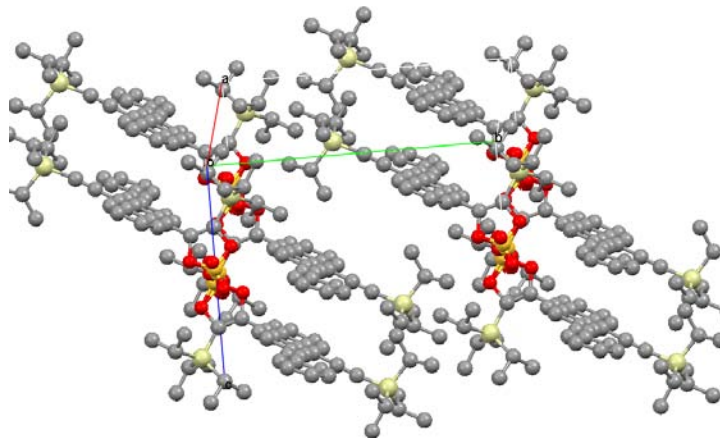
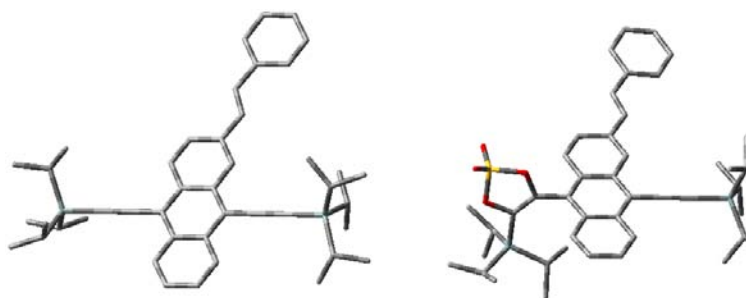
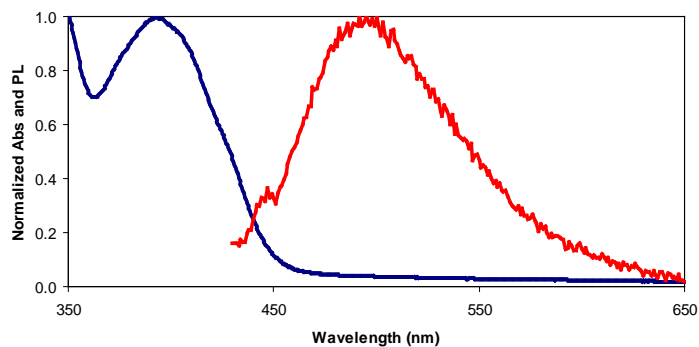


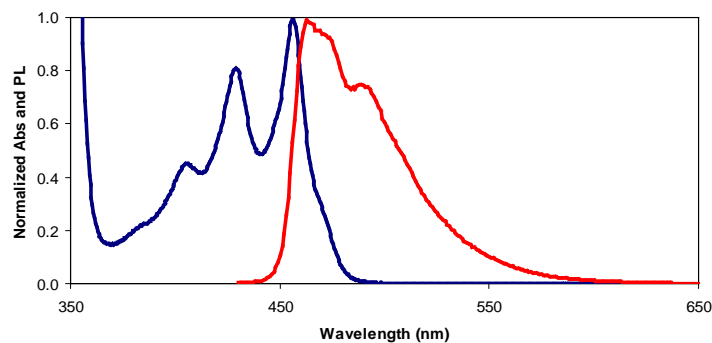
Fig. S21: Crystal packing of 7 – hydrogen atoms omitted for clarity



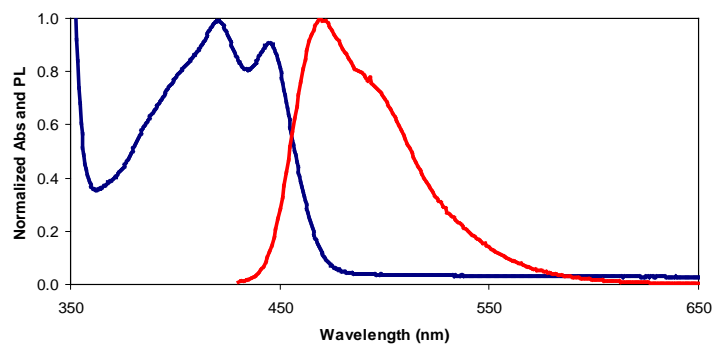
**Fig. S22:** B3LYP/6-31G(d,p) optimized molecular structures of **6** and **7**.



**Fig. S23:** UV-Vis absorption ( $\lambda = 393$  nm) and emission (490 nm, PLQY<sub>4</sub> = 1%) spectra of **4** in toluene



**Fig. S24:** UV-Vis absorption ( $\lambda = 405, 429, 456$  nm) and emission (463 nm, PLQY<sub>6</sub> = 39%) spectra of **6** in toluene



**Fig. S25:** UV-Vis absorption ( $\lambda = 421, 446$  nm) and emission (472 nm, PLQY<sub>7</sub> = 10%) spectra of **7** in toluene

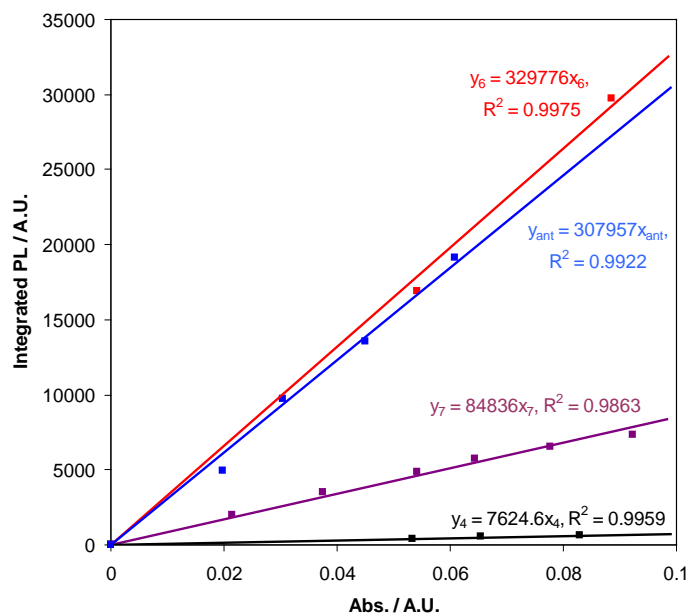


Fig. S26: Photoluminescence quantum yield measurements of **4**, **6** and **7** and anthracene standard **ant**.

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