

# **Regioselective Synthesis of Tetraphenyl-1,3-Butadienes with Aggregation-Induced Emission**

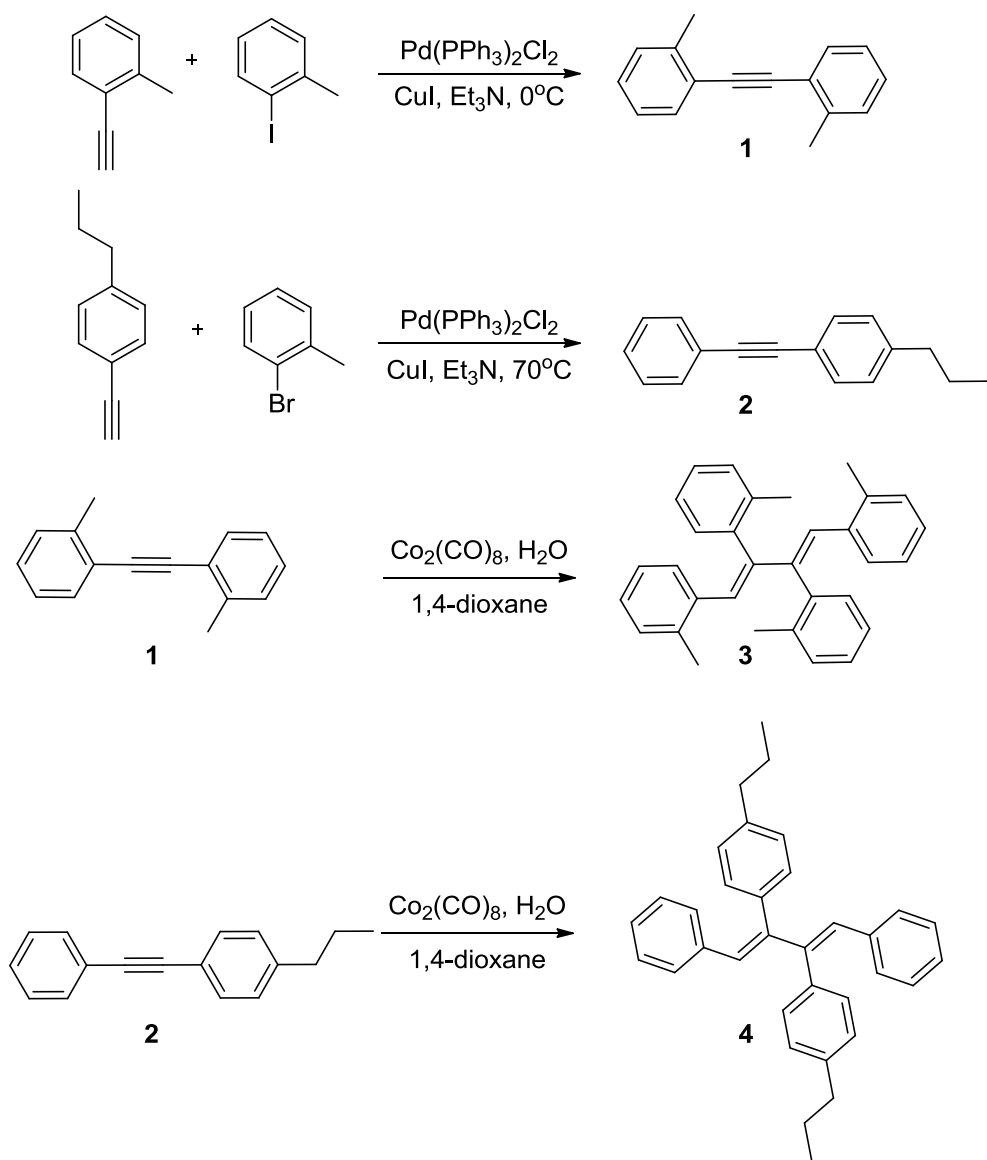
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**Scheme S1:** Synthesis of 1,3-butadienes

#### A. General Procedure

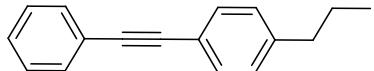
Commercially available reagents were used as received without further purification. 1,2-di-*o*-tolylethyne (**1**),<sup>1</sup> was prepared according to the literature procedures. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 600 spectrometer at 600 MHz and Bruker Avance 600 at 150 MHz respectively. Chemical shifts ( $\delta$ ) were reported as part per million (ppm) in ( $\delta$ ) scale downfield from TMS. Coupling constants ( $J$ ) were reported in

Hertz (Hz). Resonance multiplicities are described as s (singlet); d (doublet); dd (double doublet); dt (double triplet); t (triplet); td (triple doublet); tt (triple triplet); q (quartet); and m (multiplet). Chemical shifts were referenced to the residual solvent protons in  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm) in  $^1\text{H}$  NMR spectra as the internal standards, and in  $\text{CDCl}_3$  ( $\delta = 77.23$  ppm in  $^{13}\text{C}$  NMR spectra as the internal standards. Absorption spectra were recorded with a Jasco V-550 spectrometer. Photoluminescence spectra were recorded with a Hitachi F-2500 fluorescence spectrophotometer. Mass spectra were obtained on a Jeol JMS-700 Mstation and elemental analyses were performed with a Heraeus CHNO-Rapid Analyzer at the NSC Regional Instrumental Center at National Central University, Zhongli (Taiwan) and at National Cheng Kung University, Tainan (Taiwan). X-ray structural characterization of **3** was collected on a Bruker Nonius Kappa CCD diffractometer.

The PL spectra of the diene compounds and nanoaggregate mixtures were recorded on a Hitachi F-2500 fluorescence spectrophotometer. Nanoaggregate mixtures were prepared by adding water into acetonitrile solution. The concentration of all the aggregate mixtures were adjusted to  $10\ \mu\text{m}$ . PL Quantum yield value obtained in comparison to a standard. Typically the standard used for butadiene fluorescence is 9,10-diphenylanthracene.

## B. Experimental Section

### 1-(Phenylethynyl)-4-propylbenzene (2)



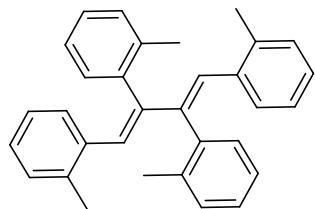
A 100 mL 2-neck flask was charged with 0.291 mg of  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.42 mmol) and 39 mg of  $\text{CuI}$  (0.21 mmol) at RT under  $\text{N}_2$ . It was evacuated/filled with  $\text{N}_2$  (3 times) and 35 mL of dry THF was added, followed by 5 mL  $\text{Et}_3\text{N}$ , 2.32 mL of the bromobenzene (4.24 g, 20.8 mmol), and 1-ethynyl-4-propylbenzene (3.0 g, 20.8 mmol). The resulting mixture was then placed in a pre-equilibrated 70°C oil bath and it was stirred for 8h. The reaction mixture was then cooled to RT and the volatiles were removed in vacuo. The mixture was washed twice with saturated  $\text{NH}_4\text{Cl}(aq)$  (150 mL), twice with  $\text{H}_2\text{O}$  (100 mL) and dried with anhydrous  $\text{MgSO}_4$ . The crude residue was purified by column chromatography ( $\text{SiO}_2$ , *n*-hexane). The solvent was rotary evaporated to yield **2**, as a colourless liquid

(4.22 g, 19.15 mmol, yield 92%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.61 (dd,  $J_m = 1.2$  Hz,  $J_o = 7.8$  Hz, 2H), 7.54 (d,  $J = 7.8$  Hz, 2H), 7.41-7.37 (m, 3H), 7.22 (d,  $J = 7.8$  Hz, 2H), 2.66 (t,  $J = 7.5$  Hz, 2H), 1.72 (q,  $J = 7.8$  Hz, 2H), 1.02 (t,  $J = 7.8$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  143.1, 131.9, 131.8, 131.5, 131.4, 128.6, 128.5, 128.2, 127.9, 123.5, 120.4, 119.0, 89.6, 88.7, 37.9, 24.2, 13.7. HRMS (FAB+) m/z for  $\text{C}_{17}\text{H}_{16}$  220.1252, found 220.1251.

### Synthesis of dimers

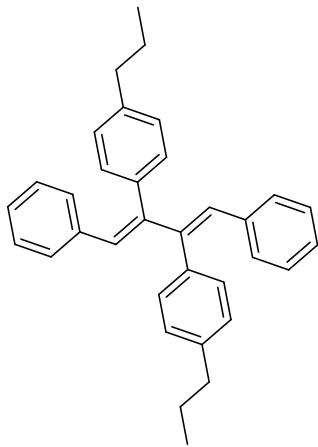
A mixture of  $\text{Co}_2(\text{CO})_8$  (20 mol %),  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (2 mmol) and the alkyne (1 mmol) in 1,4-dioxane (4 mL) were heated to reflux at 110°C for 18h. After completion, the reaction mixture was concentrated by a rotary evaporator and extracted with water, dried over  $\text{MgSO}_4$ . The residue was purified by column chromatography on silica gel using hexane as eluent to afford white solid.

### 2,2',2'',2'''-((1E,3E)-Buta-1,3-diene-1,2,3,4-tetrayl)tetrakis(methylbenzene) (3)



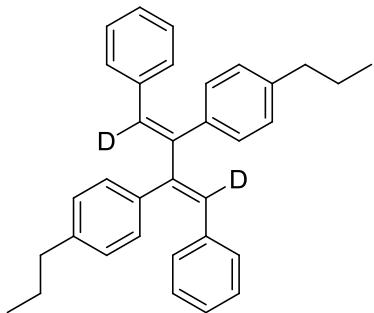
White solid (0.248 g, 0.598 mmol, yield 60%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.26-7.22 (m, 8H), 7.00 (d,  $J = 7.4$  Hz, 2H), 6.93 (t,  $J = 7.4$  Hz, 2H), 6.75 (t,  $J = 7.5$  Hz, 2H), 6.61 (d,  $J = 7.8$  Hz, 2H), 6.36 (d,  $J = 6.9$  Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 2.06 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  143.6, 138.8, 136.8, 136.5, 136.2, 130.8, 130.5, 130.1, 129.6, 129.1, 127.9, 127.3, 126.6, 125.9, 125.2, 19.8, 19.7, 19.4. HRMS (FAB+) m/z for  $\text{C}_{32}\text{H}_{30}$  414.2348, found 414.2350.

### 4,4'-(1E,3E)-1,4-Diphenylbuta-1,3-diene-2,3-diyl)bis(propylbenzene) (4)



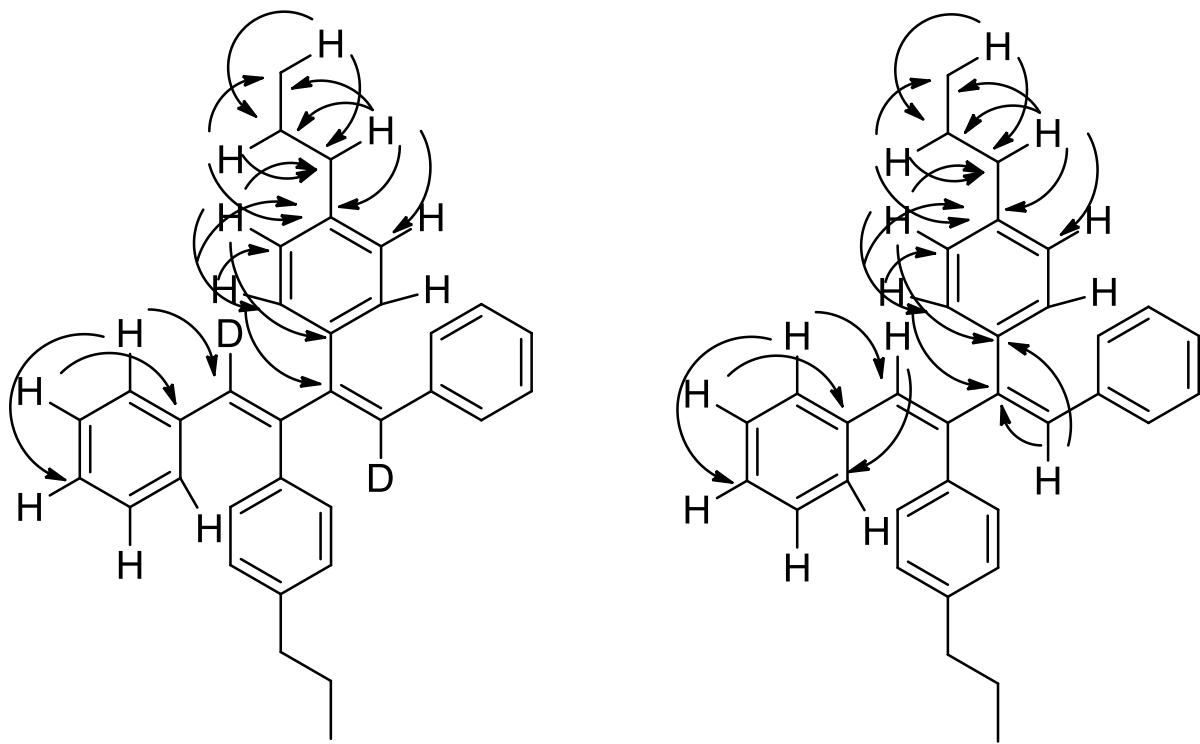
White solid (0.257 g, 0.580 mmol, yield 58%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.20 (m, 8H), 7.01-7.00 (m, 6H), 6.75-6.74 (m, 4H), 6.30 (s, 2H), 2.66 (t,  $J$  = 7.5 Hz, 4H), 1.71 (q,  $J$  = 7.4 Hz, 4H), 0.97 (t,  $J$  = 7.3 Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  145.8, 141.6, 137.5, 136.9, 131.4, 130.1, 129.5, 128.9, 127.7, 126.4, 37.8, 24.4, 13.6. HRMS (FAB+) m/z for  $\text{C}_{34}\text{H}_{34}$  442.2661, found 442.2658.

4,4'-(1E,3E)-1,4-Diphenylbuta-1,3-diene-2,3-diyl)bis(propylbenzene (4')

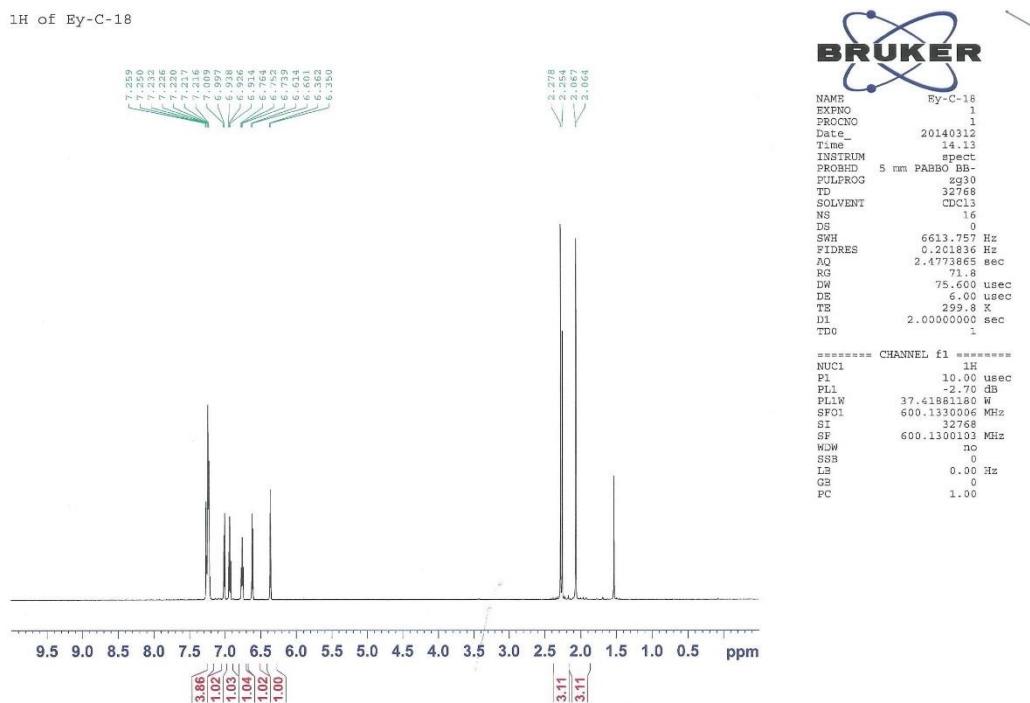


White solid (0.249 g, 0.560 mmol, yield 56%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.20 (m, 8H), 7.01-7.00 (m, 6H), 6.74-6.73 (m, 4H), 2.65 (t,  $J$  = 7.8 Hz, 4H), 1.71 (q,  $J$  = 7.4 Hz, 4H), 0.97 (t,  $J$  = 7.2 Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  145.7, 141.6, 137.4, 136.9, 130.1, 129.4, 128.9, 127.7, 126.4, 37.8, 24.4, 13.6. HRMS (FAB+) m/z for  $\text{C}_{34}\text{H}_{32}\text{D}_2$  442.2786, found 442.2785.

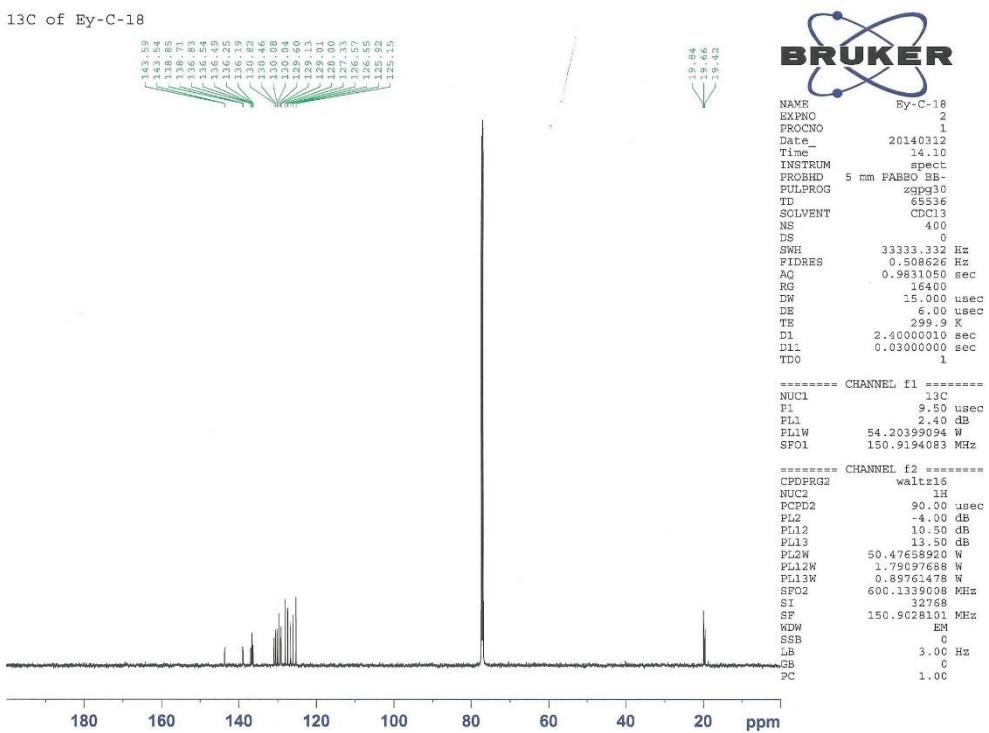
### C. HMBC and HMQC correlation figures



### D. $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR spectra details

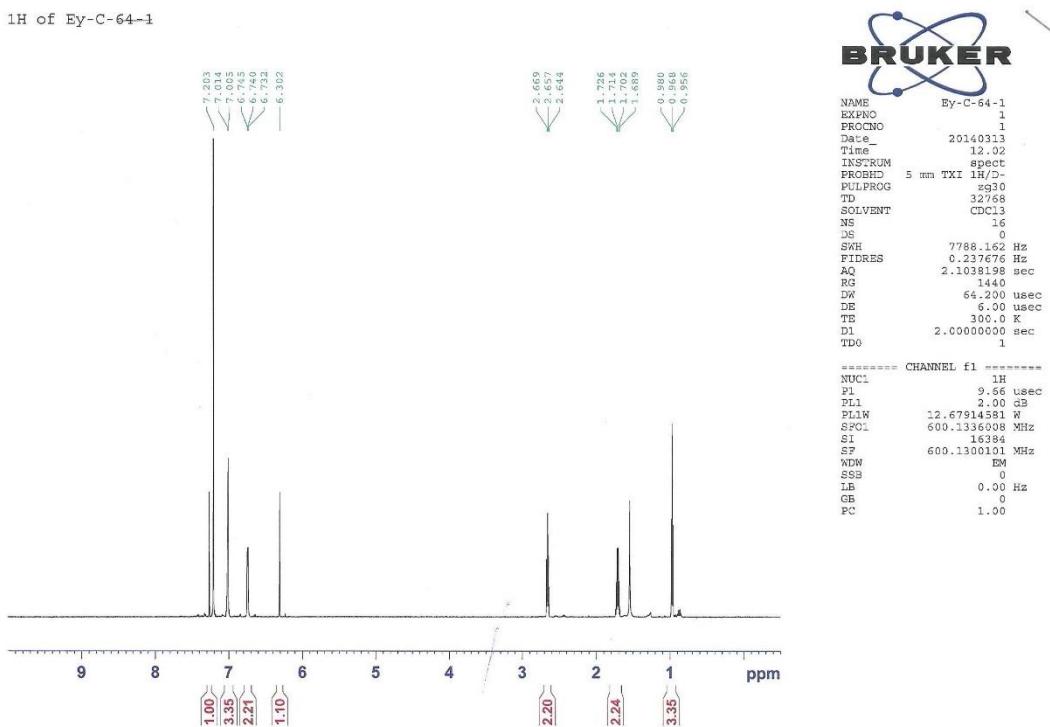


<sup>13</sup>C of Ey-C-18



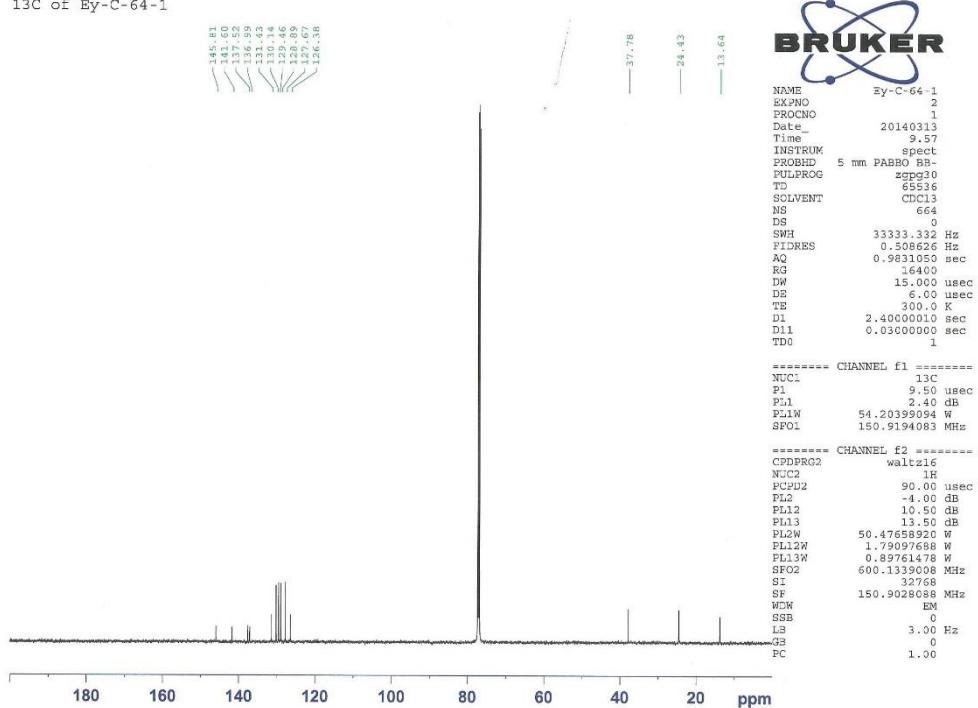
<sup>13</sup>C-NMR of compound 3

<sup>1</sup>H of Ey-C-64-1



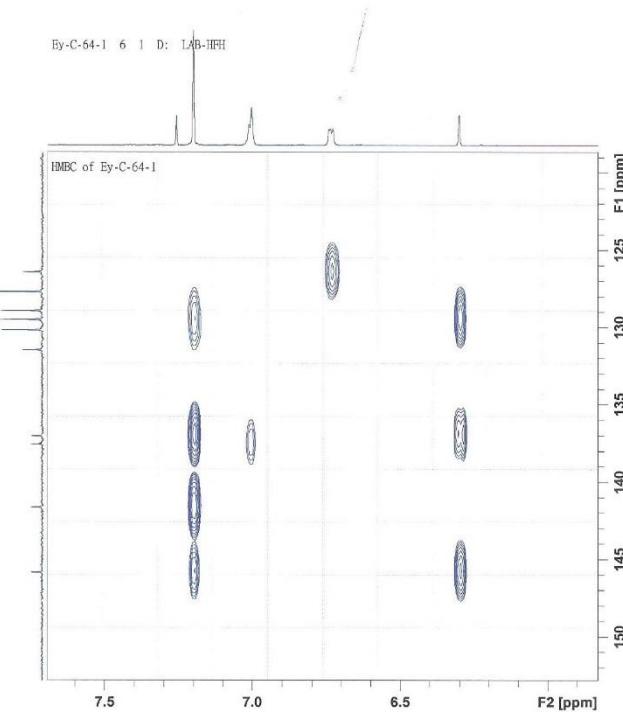
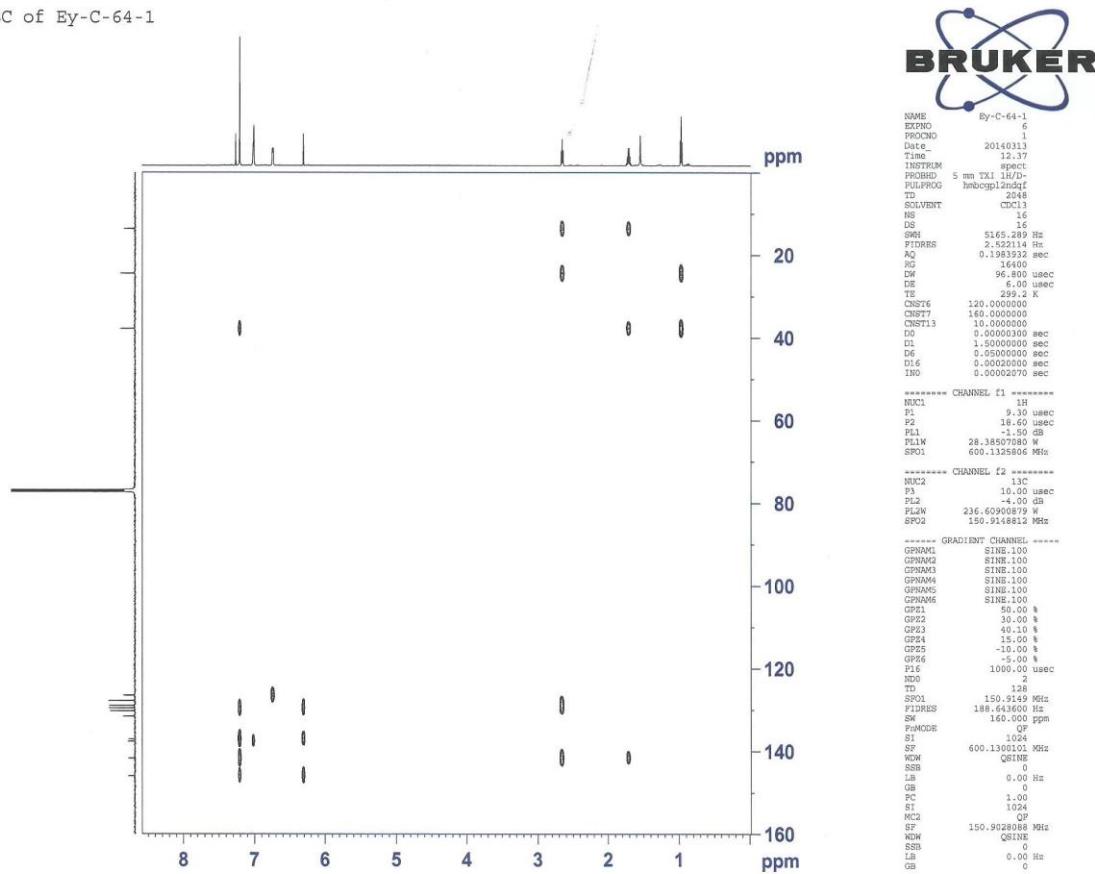
<sup>1</sup>H-NMR of compound 4

<sup>13</sup>C of EY-C-64-1

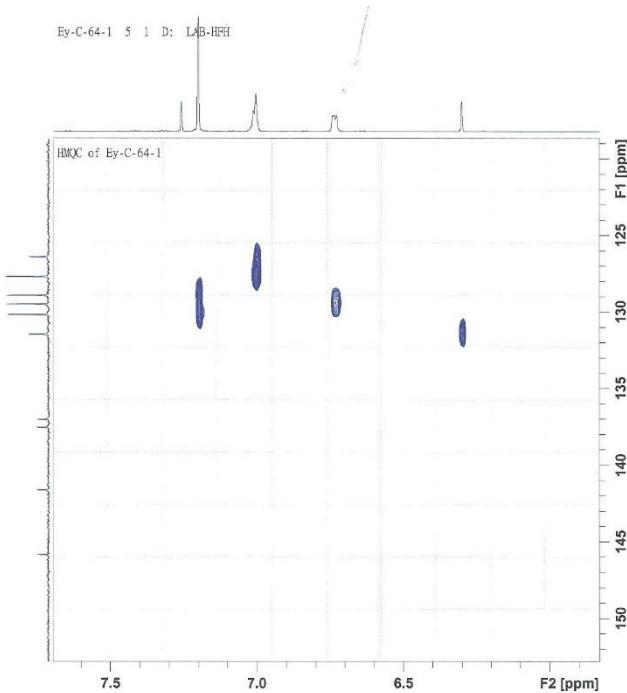


<sup>13</sup>C-NMR of compound 4

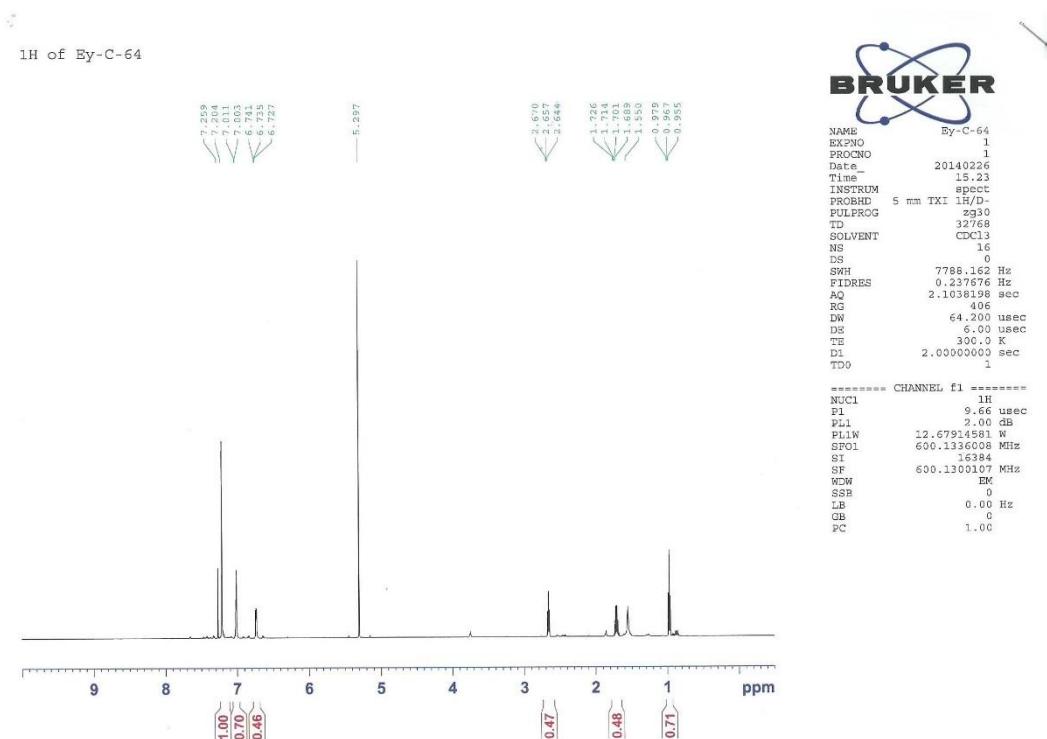
HMBC of Ey-C-64-1



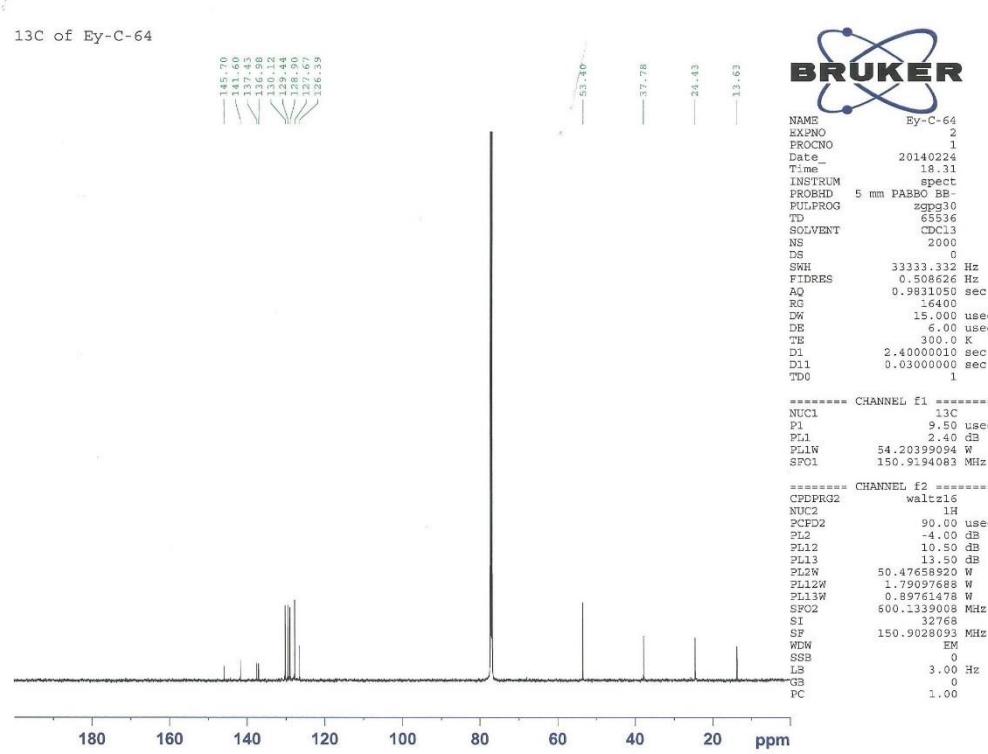
### HMBC of compound 4



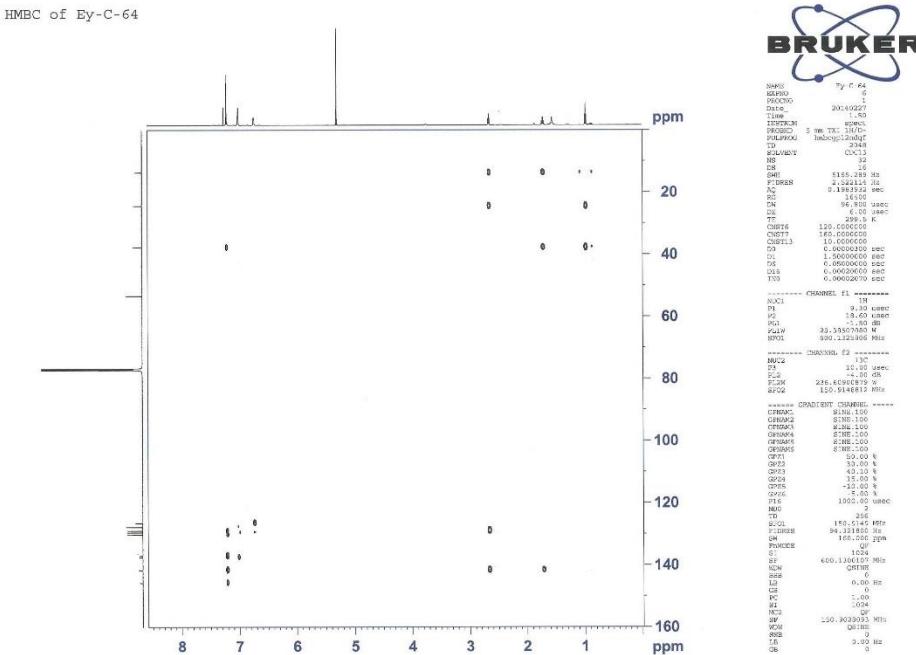
### HMQC of compound 4



### <sup>1</sup>H-NMR of compound 4'

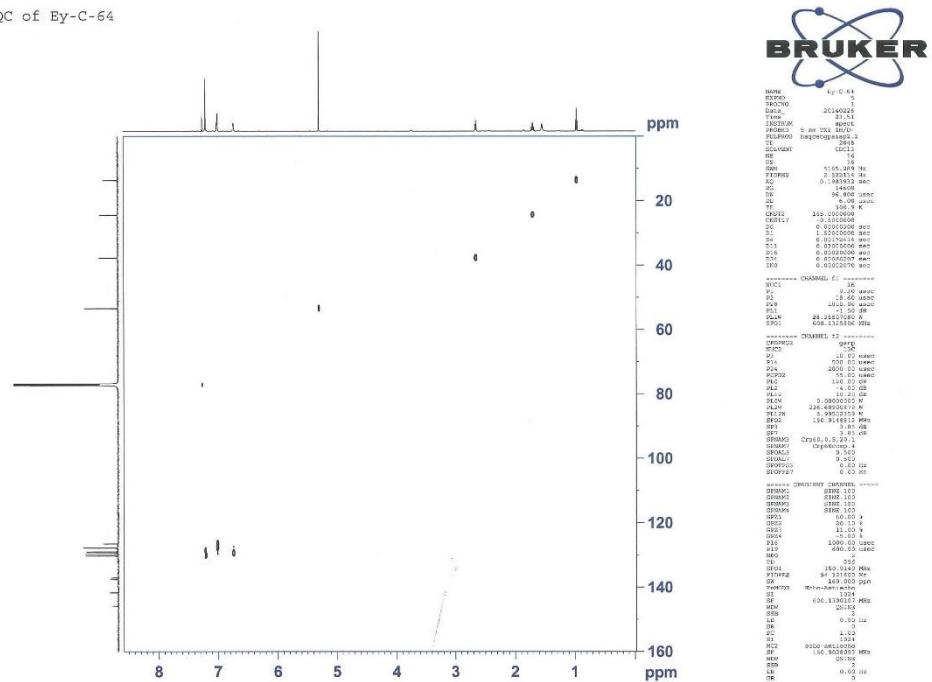


### <sup>13</sup>C-NMR of compound 4'

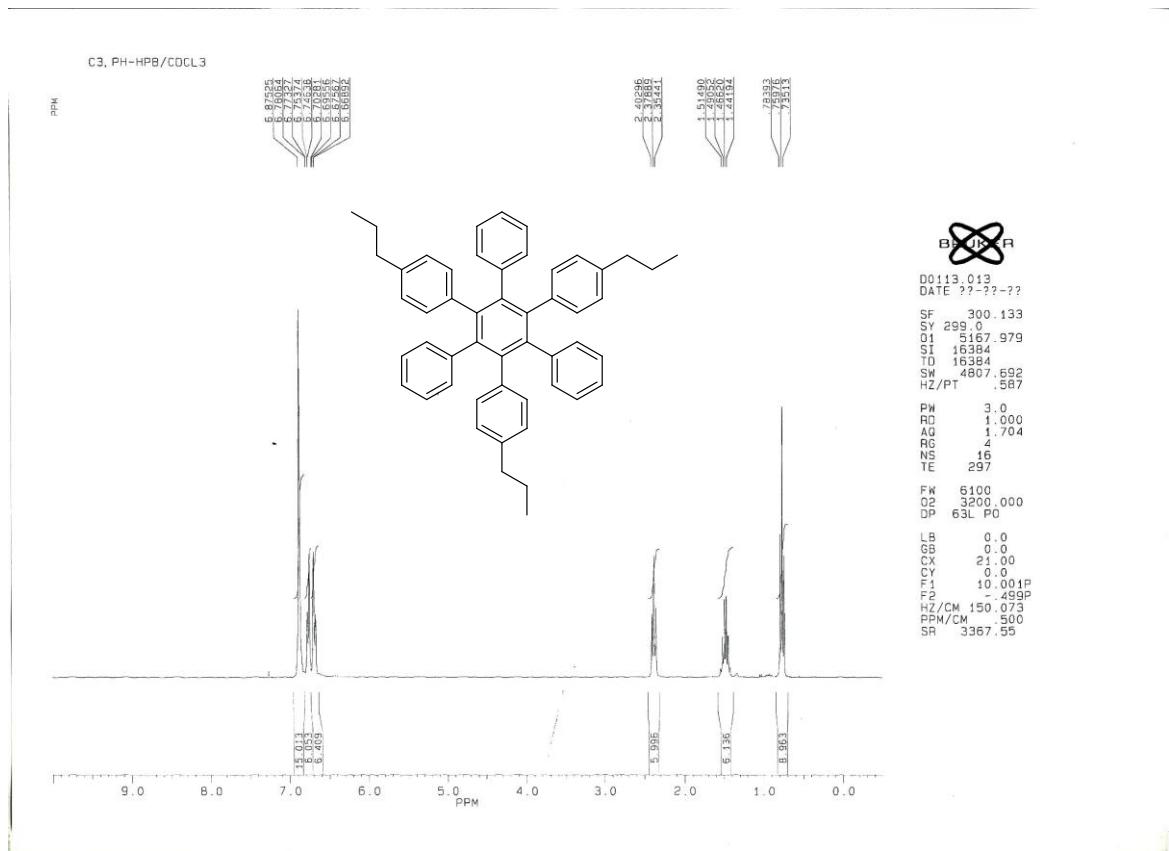


### HMBC of compound 4'

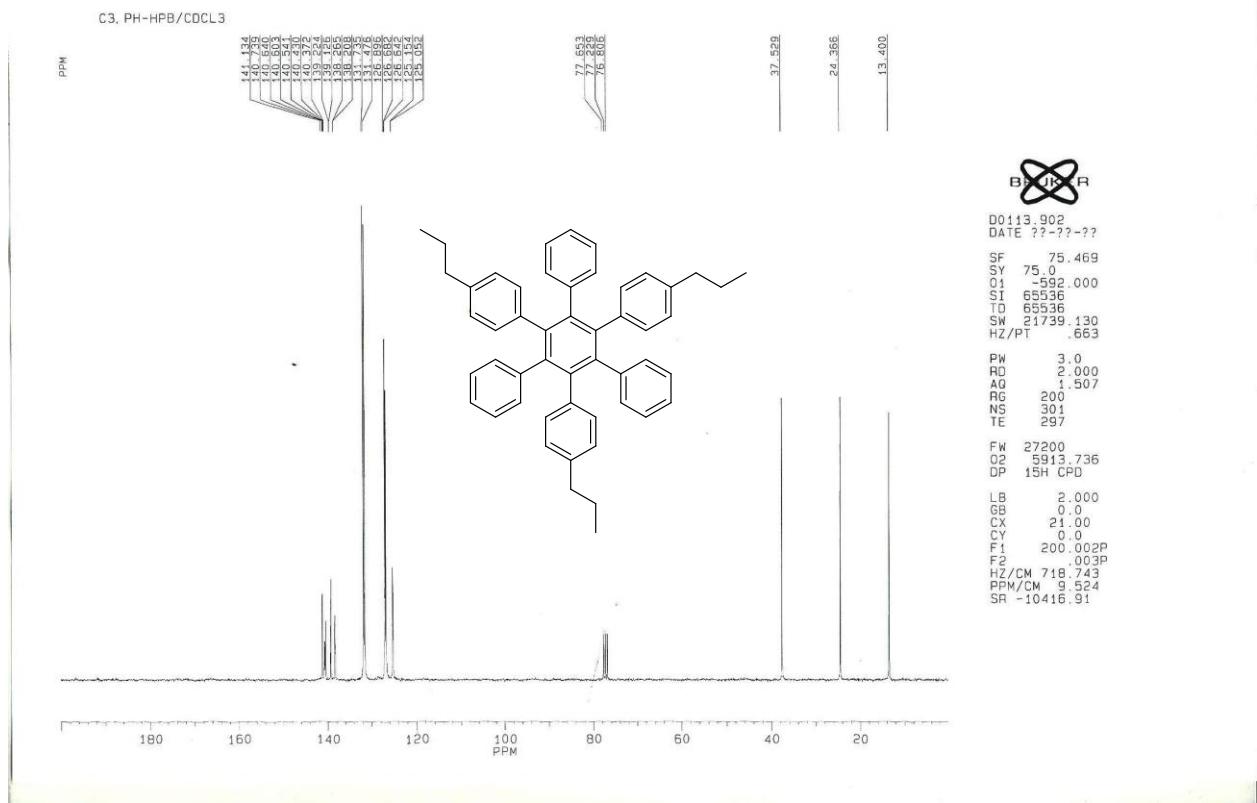
### HMDS of Ey-C-64



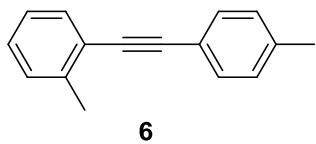
### HMQC of compound 4'



<sup>1</sup>H NMR spectrum of trimer (hexaphenylbenzene (HPB)) from 3

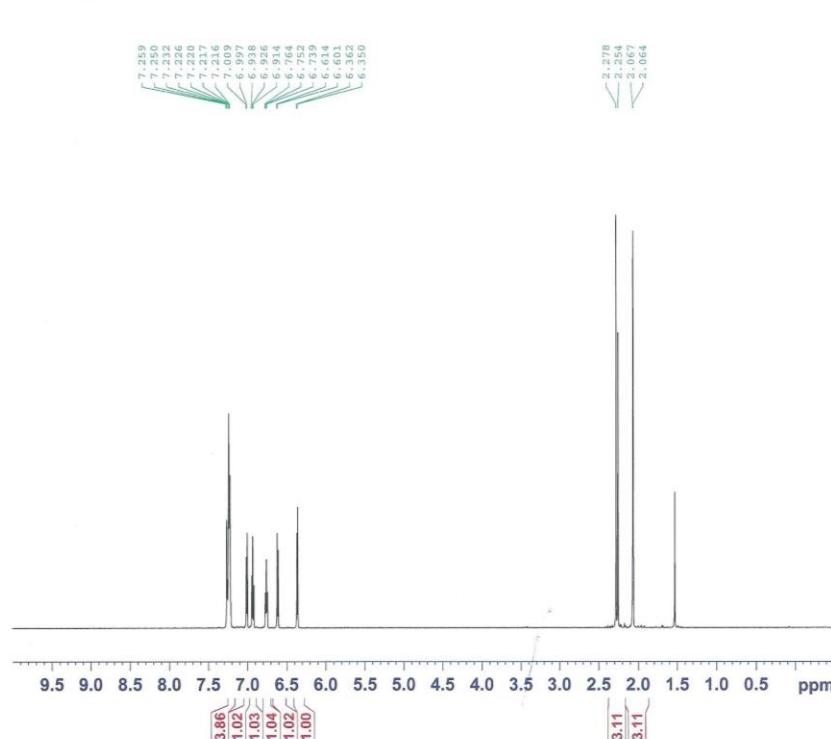


<sup>13</sup>C-NMR spectrum of trimer (hexaphenylbenzene (HPB)) from **3**



idomeric butadiene products

1H of EY-C-18



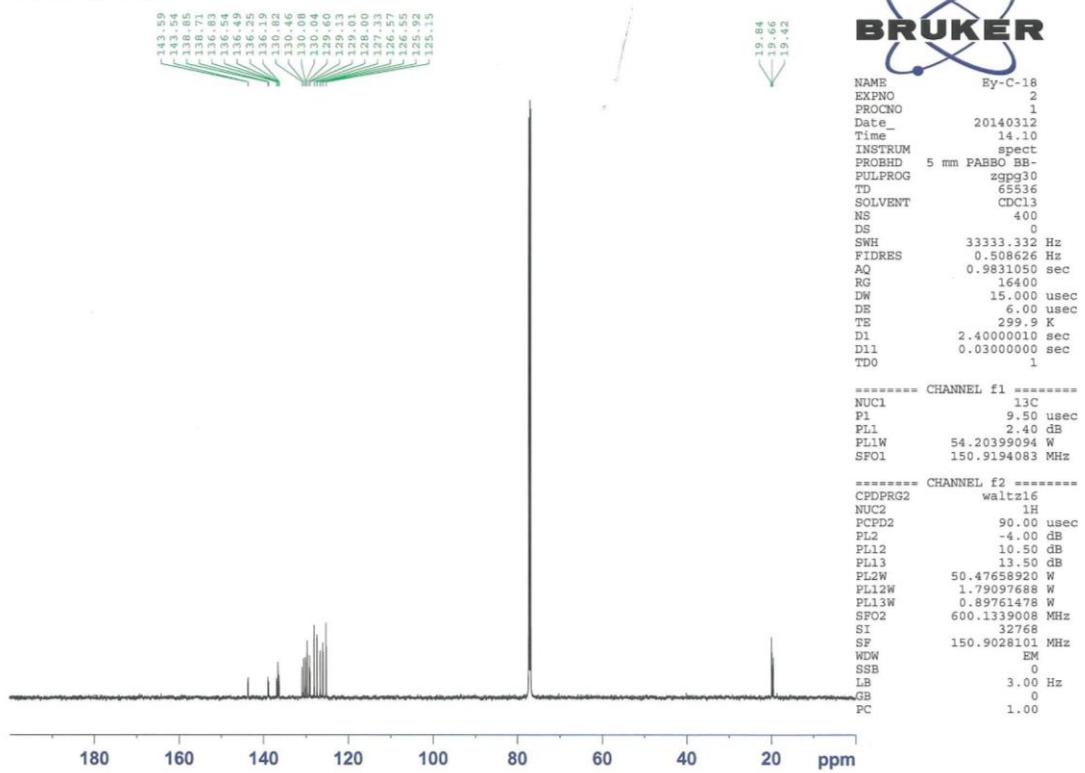
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 Time 14.13  
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 DS 0  
 SWH 6613.757 Hz  
 FIDRES 0.201836 Hz  
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 RG 71.8  
 DW 75.600 usec  
 DE 6.00 usec  
 TE 299.8 K  
 D1 2.0000000 sec  
 TDO 1

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*

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 P1C1 10.00 usec  
 PL1 -2.70 dB  
 PL1W 37.41881180 W  
 SF01 600.1330000 MHz  
 SI 32768  
 SF 600.1300103 MHz  
 WDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 FC 1.00

<sup>1</sup>H-NMR spectrum of the mixture of isomeric butadiene from **6**

13C of Ey-C-18

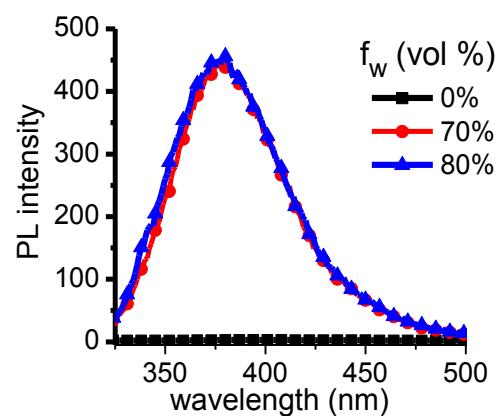


13C-NMR spectrum of the mixture of isomeric butadiene from 6

## **E. X-ray Crystallographic data**

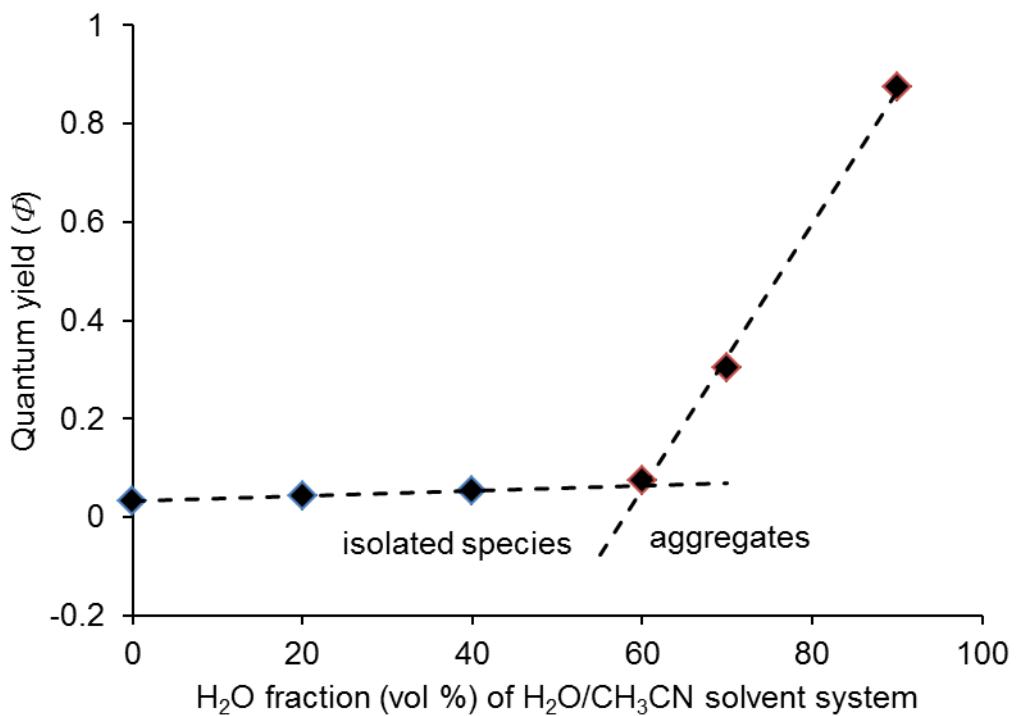
2,2',2'',2'''-((1*E*,3*E*)-Buta-1,3-diene-1,2,3,4-tetrayl)tetrakis(methylbenzene) (**3**) was studied by single crystal X-ray diffraction method. Complete cif file for compound **3** has been deposited with the Cambridge Crystallographic Data Centre, CCDC Deposit # 888658. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## F. PL Spectra of **4** in Water/Acetonitrile



water/acetonitrile solvent mixtures with different volume percents of water (0 vol %, 70 vol %, and 80 vol % of water in acetonitrile). Concentration of **4**: 10  $\mu$ M.

**G. Photoluminescence Quantum Yields of 4 vs. Solvent Composition of the Water/Acetonitrile Mixture**



**References**

(1) Busacca, C. A.; Farber, E.; DeYoung, J.; Campbell, S.; Gonnella, N. C.; Grinberg, N.; Haddad, N.; Lee, H.; Ma, S.; Reeves, D.; Shen, S.; Senanayake, C. H. *Org. Lett.* **2009**, *11*, 5594-5597.