

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

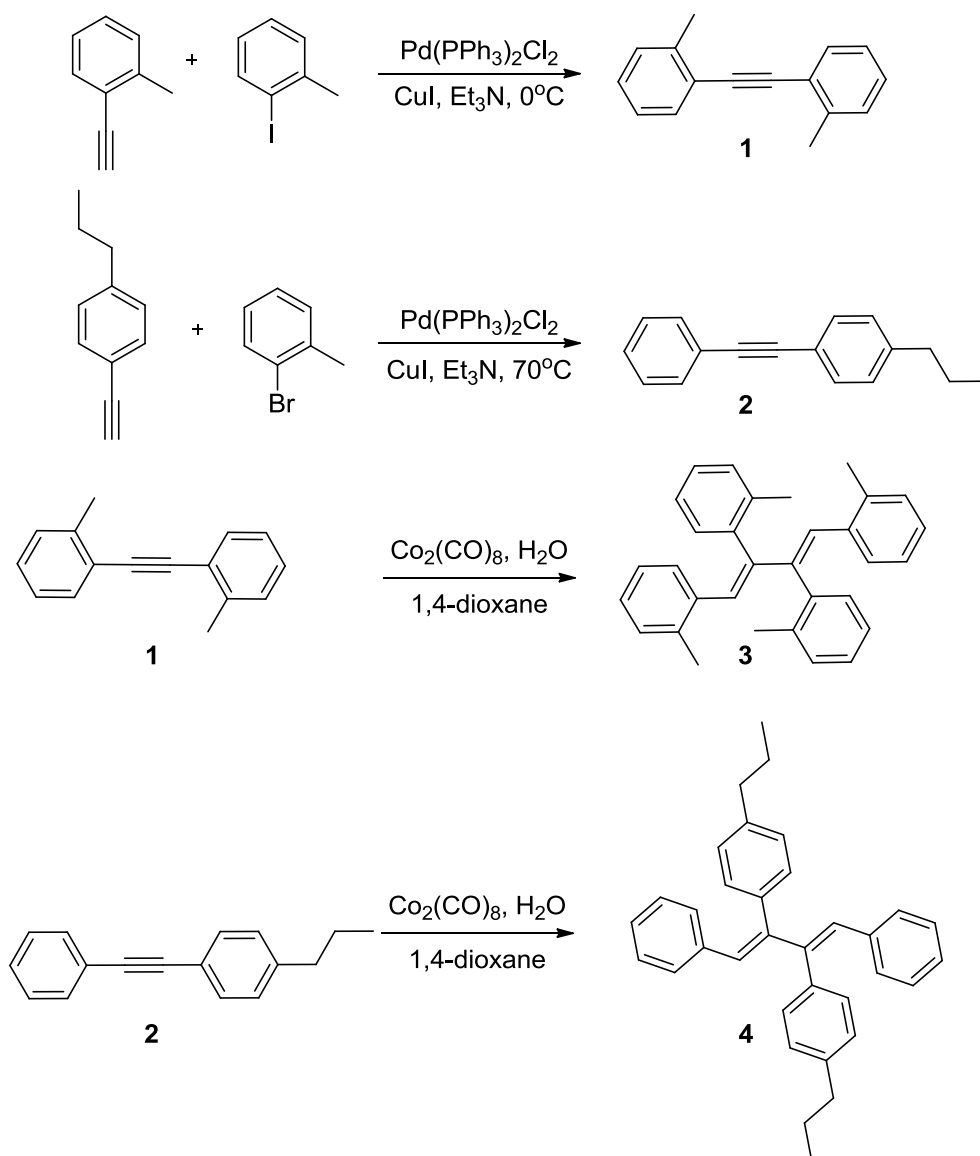
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**Scheme S<sub>1</sub>:** Synthesis of 1,3-butadienes

## A. General Procedure

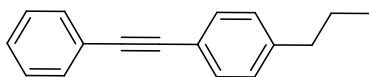
Commercially available reagents were used as received without further purification. 1,2-di-*o*-tolylethyne (**1**),<sup>1</sup> was prepared according to the literature procedures. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 600 spectrometer at 600 MHz and Bruker Avance 600 at 150 MHz respectively. Chemical shifts (δ) were reported as part per million (ppm) in (δ) 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 CDCl<sub>3</sub> ( $\delta$  = 7.26 ppm) in <sup>1</sup>H NMR spectra as the internal standards, and in CDCl<sub>3</sub> ( $\delta$  = 77.23 ppm) in <sup>13</sup>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 into acetonitrile solution. The concentration of all the aggregate mixtures were adjusted to 10  $\mu$ 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**)



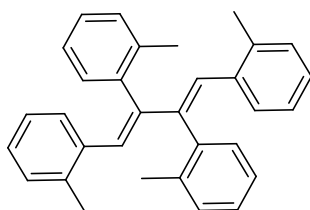
A 100 mL 2-neck flask was charged with 0.291 mg of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.42 mmol) and 39 mg of CuI (0.21 mmol) at RT under N<sub>2</sub>. It was evacuated/filled with N<sub>2</sub> (3 times) and 35 mL of dry THF was added, followed by 5 mL Et<sub>3</sub>N, 2.32 mL of the bromobenzene (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 NH<sub>4</sub>Cl(aq) (150 mL), twice with H<sub>2</sub>O (100 mL) and dried with anhydrous MgSO<sub>4</sub>. The crude residue was purified by column chromatography (SiO<sub>2</sub>, *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

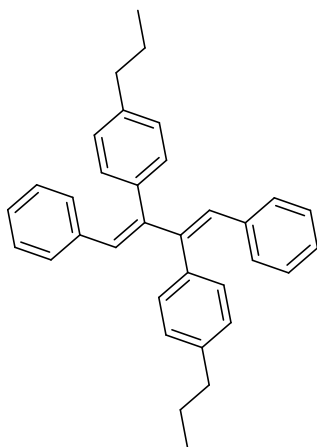
A mixture of  $\text{Co}_2(\text{CO})_8$  (20 mol %),  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (2 mmol) and the alkyne (1 mmol) in 1,4-dioxane (4 mL) were heated to reflux at  $110^\circ\text{C}$  for 18h. After completion, the reaction mixture was concentrated by a rotary evaporator and extracted with 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'''-((1*E*,3*E*)-Buta-1,3-diene-1,2,3,4-tetrayl)tetrakis(methylbenzene) (3)



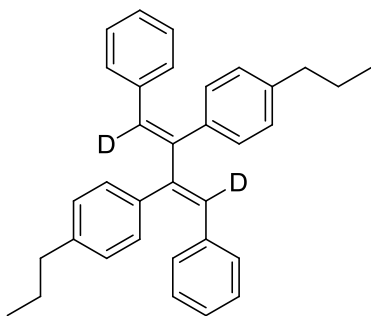
White solid (0.248 g, 0.598 mmol, yield 60%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.26-7.22 (m, 8H), 7.00 (d,  $J = 7.4$  Hz, 2H), 6.93 (t,  $J = 7.4$  Hz, 2H), 6.75 (t,  $J = 7.5$  Hz, 2H), 6.61 (d,  $J = 7.8$  Hz, 2H), 6.36 (d,  $J = 6.9$  Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 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'-((1*E*,3*E*)-1,4-Diphenylbuta-1,3-diene-2,3-diyl)bis(propylbenzene) (4)



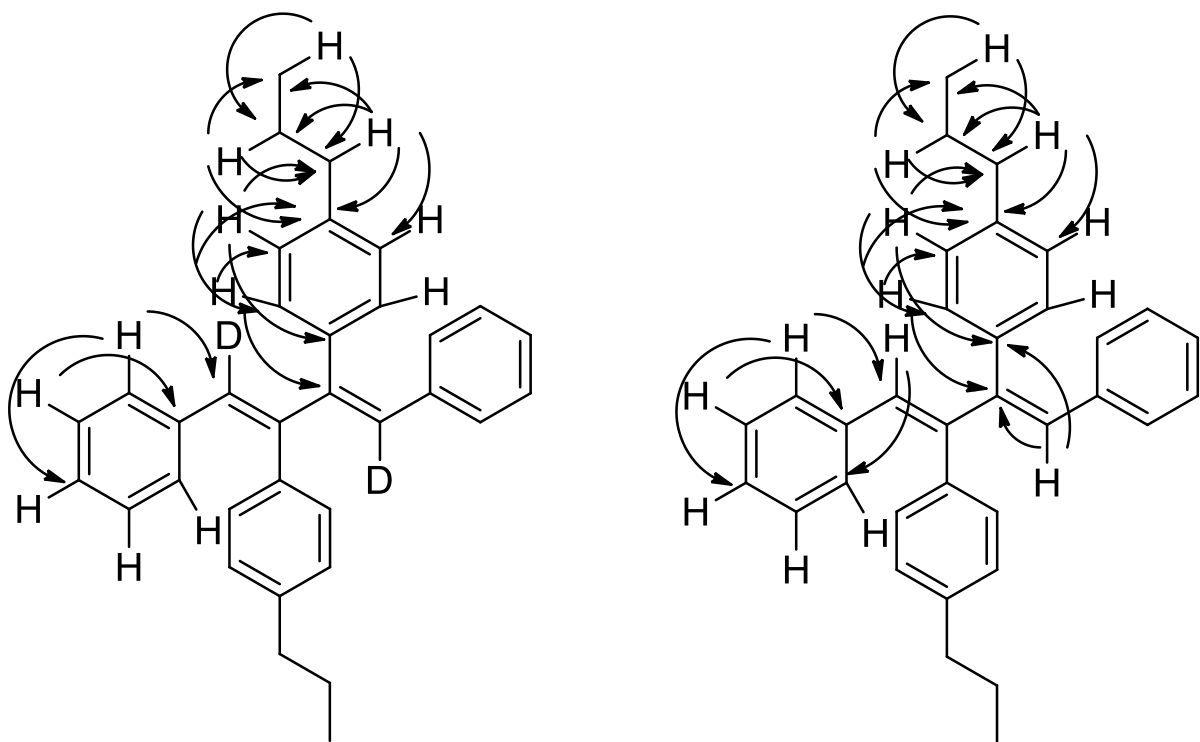
White solid (0.257 g, 0.580 mmol, yield 58%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.20 (m, 8H), 7.01-7.00 (m, 6H), 6.75-6.74 (m, 4H), 6.30 (s, 2H), 2.66 (t,  $J = 7.5$  Hz, 4H), 1.71 (q,  $J = 7.4$  Hz, 4H), 0.97 (t,  $J = 7.3$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 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')



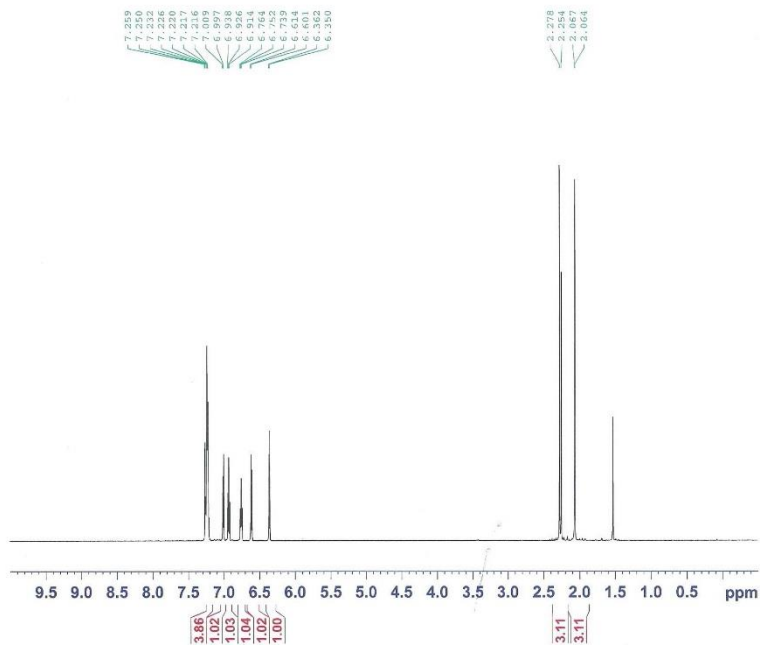
White solid (0.249 g, 0.560 mmol, yield 56%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.20 (m, 8H), 7.01-7.00 (m, 6H), 6.74-6.73 (m, 4H), 2.65 (t,  $J = 7.8$  Hz, 4H), 1.71 (q,  $J = 7.4$  Hz, 4H), 0.97 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  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

$^1\text{H}$  of Ey-C-18



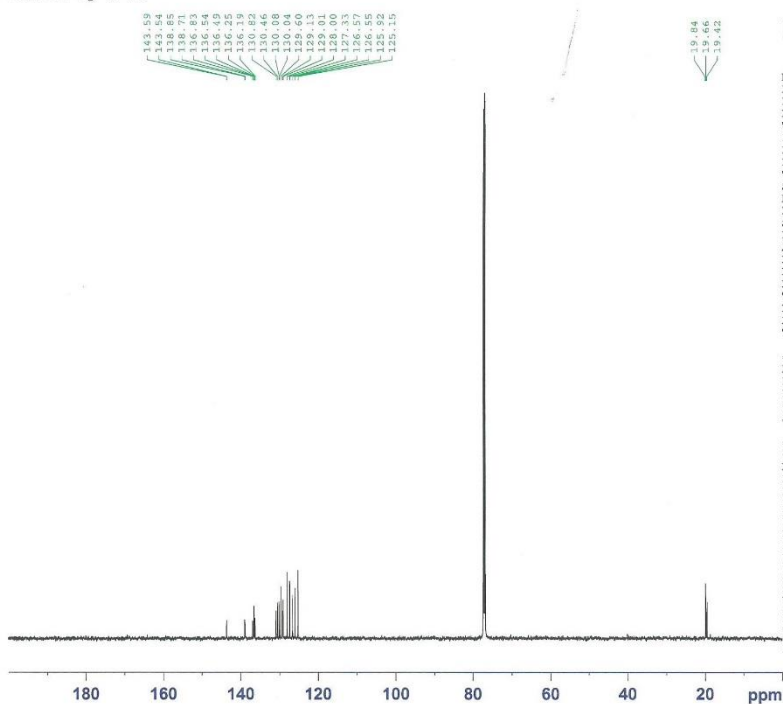
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PROCNO    1
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PULPROG   zg30
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SOLVENT   CDCl3
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DS         0
SWH        6613.757 Hz
FIDRES     0.201836 Hz
AQ         2.4773865 sec
RG         71.8
DW         75.600 usec
DE         6.00 usec
TE         299.8 K
D1         2.00000000 sec
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$^1\text{H}$ -NMR of compound 3

13C of Ey-C-18



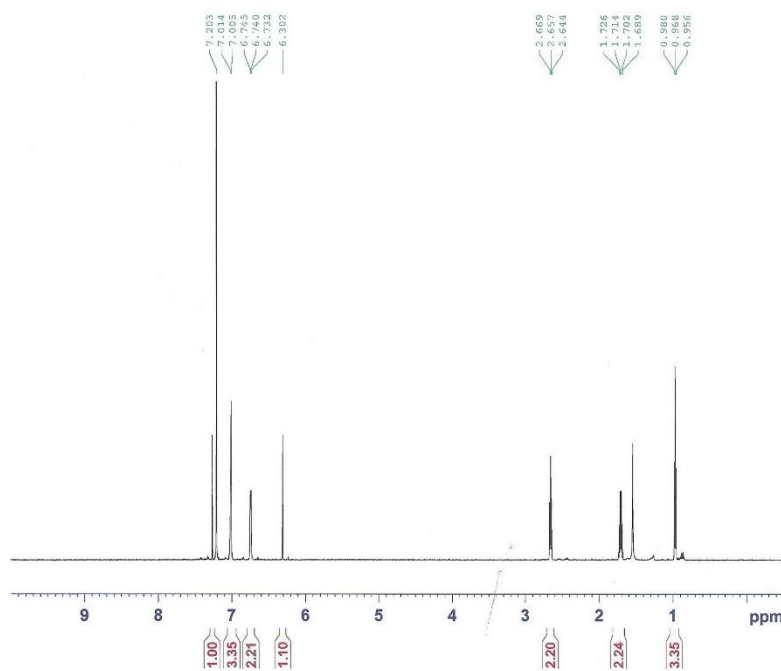
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FIDRES 0.508626 Hz  
AQ 0.9831050 sec  
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DE 6.00 usec  
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D1 2.40000010 sec  
D11 0.03000000 sec  
TD0 1

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PL13 13.50 dB  
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### $^{13}\text{C}$ -NMR of compound 3

1H of Ey-C-64-1

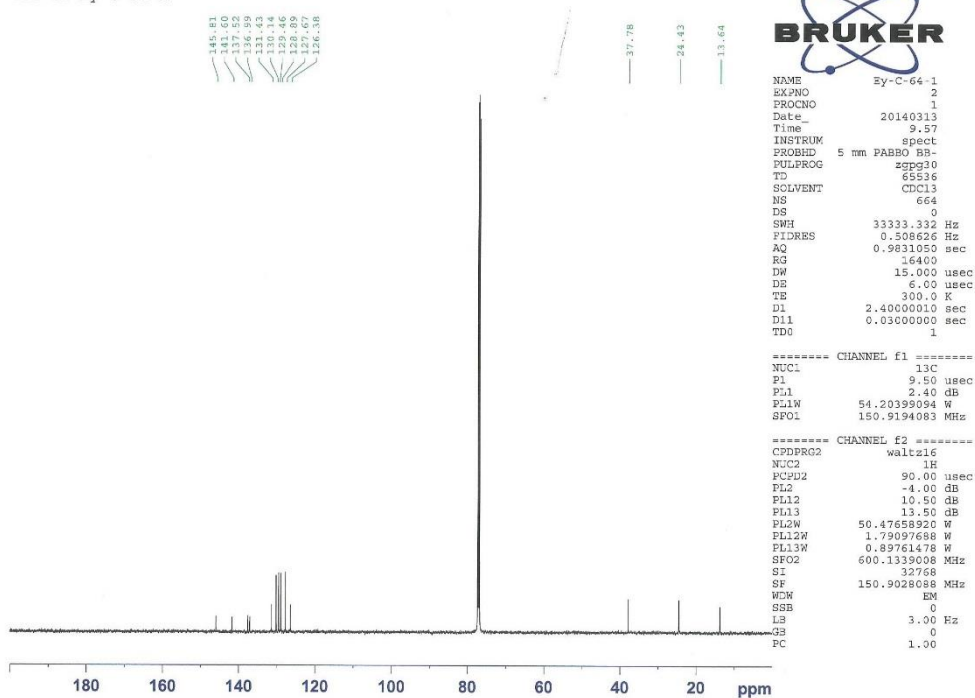


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PROCNO 1  
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RG 1440  
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TE 300.0 K  
D1 2.00000000 sec  
TD0 1

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### $^1\text{H}$ -NMR of compound 4

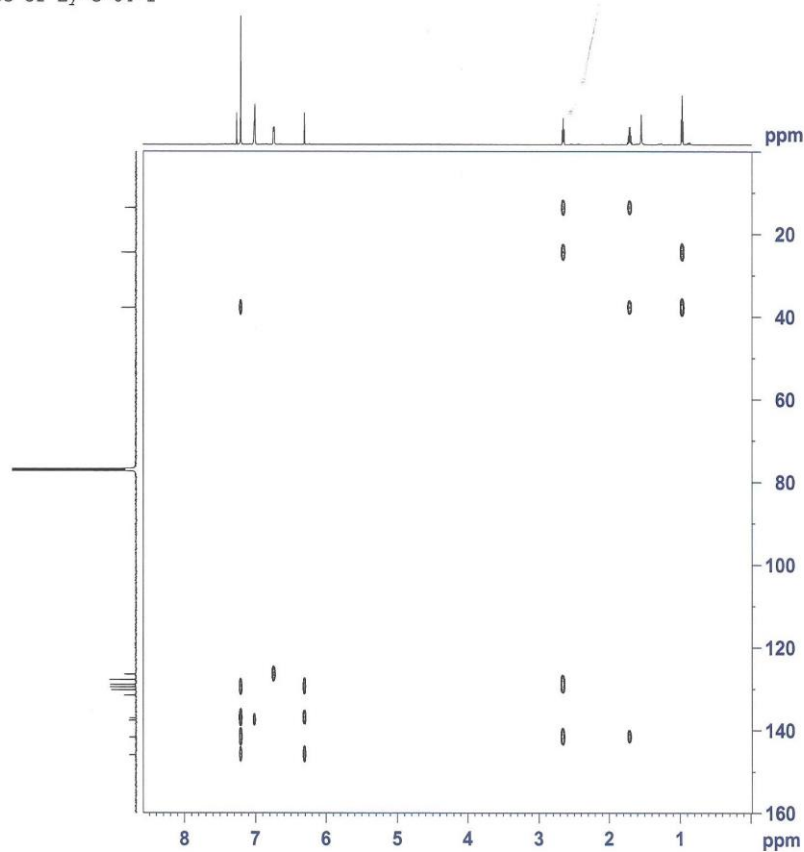
<sup>13</sup>C of Ey-C-64-1



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



HMBC of By-C-64-1



```

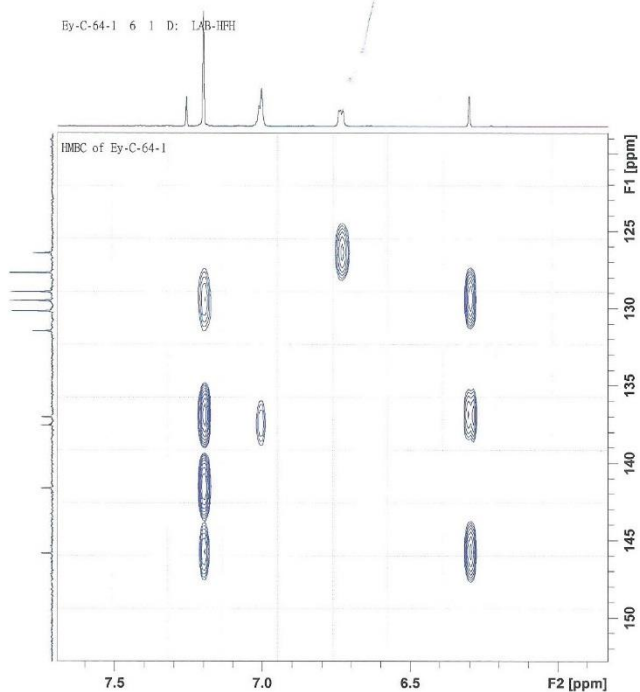
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TE         299.2 K
CNS16     120.0000000
CHET7     140.0000000
CNS13     10.0000000
DO         0.0000300 sec
DL         1.5000000 sec
D6         0.0500000 sec
D1.6      0.0002000 sec
RG         0.0000270 sec

----- CHANNEL f1 -----
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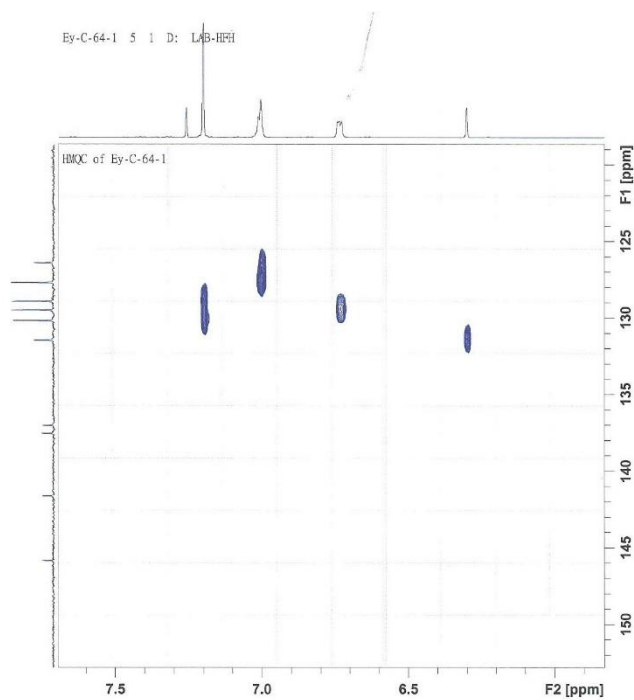
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GPNAM2     SINE.100
GPNAM3     SINE.100
GPNAM4     SINE.100
GPNAM5     SINE.100
GPNAM6     SINE.100
GPE1       50.00 %
GPE2       30.00 %
GPE3       40.10 %
GPE4       15.00 %
GPE5       -10.00 %
GPE6       -5.00 %
P16        1000.00 usec
ND0         2
TD          128
SFO1       150.9149 MHz
FIDRES     188.643600 Hz
SW         160.000 ppm
FACOR      0
SI         1024
SF         600.130101 MHz
RG         0
WDW         EM
SSB         0
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MC2        0
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By-C-64-1 6 1 D: LAB-JFH

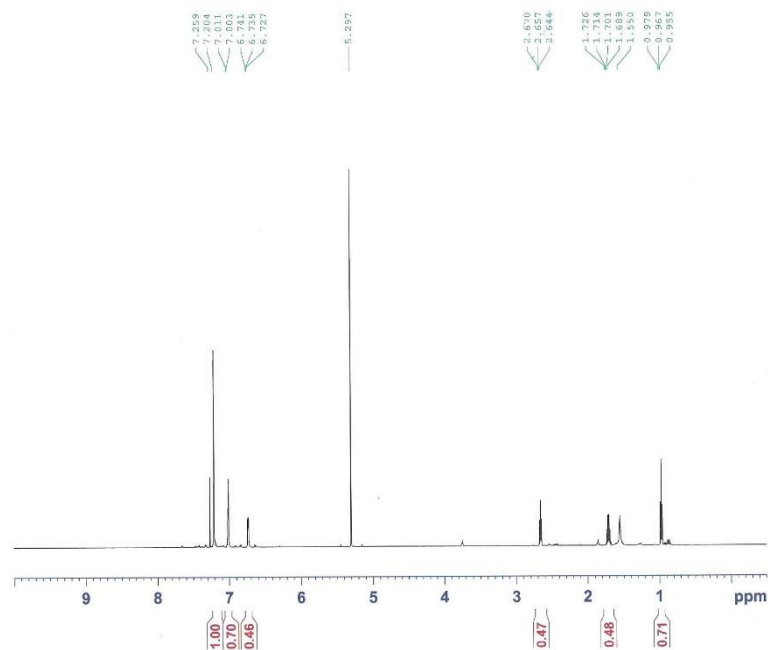


## HMBC of compound 4



## HMQC of compound 4

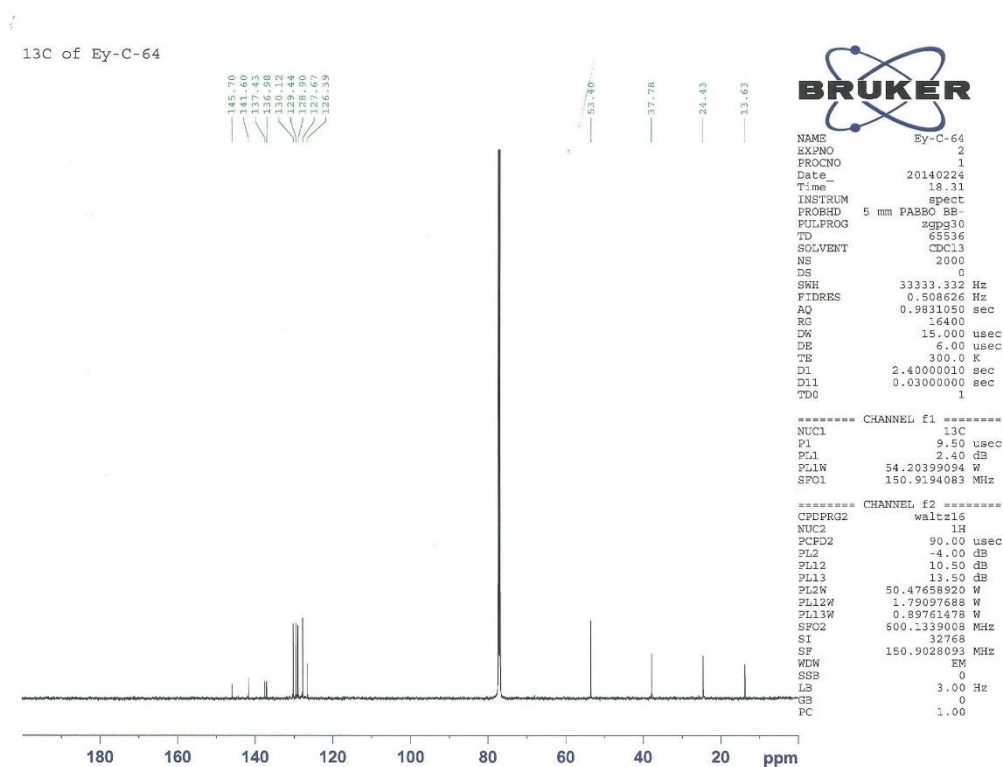
<sup>1</sup>H of By-C-64



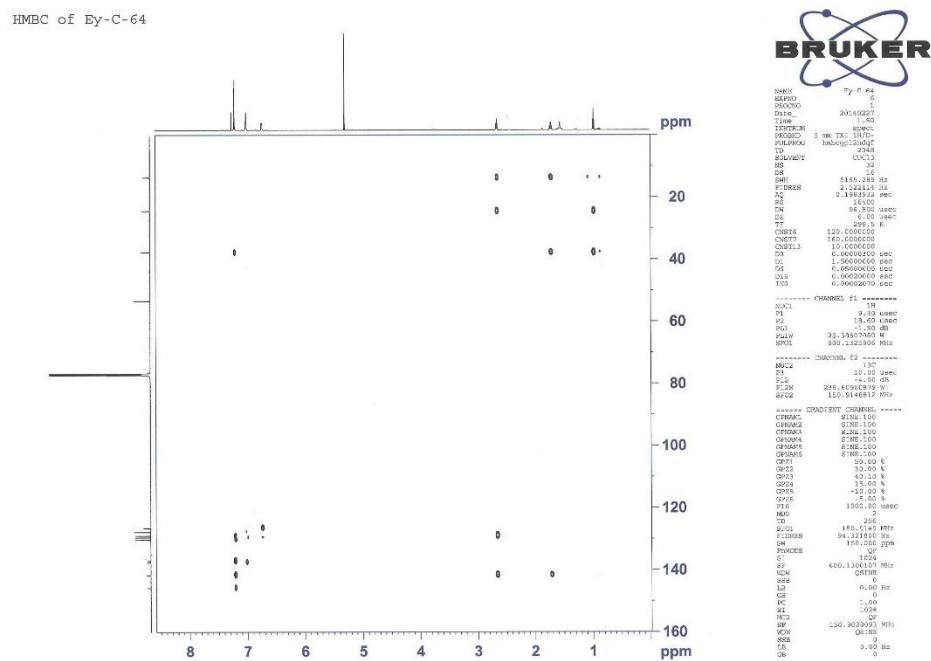
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FIDRES 0.237576 Hz  
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RG 406  
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DE 6.00 usec  
TE 300.0 K  
D1 2.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
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SI 36384  
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# <sup>1</sup>H-NMR of compound 4'

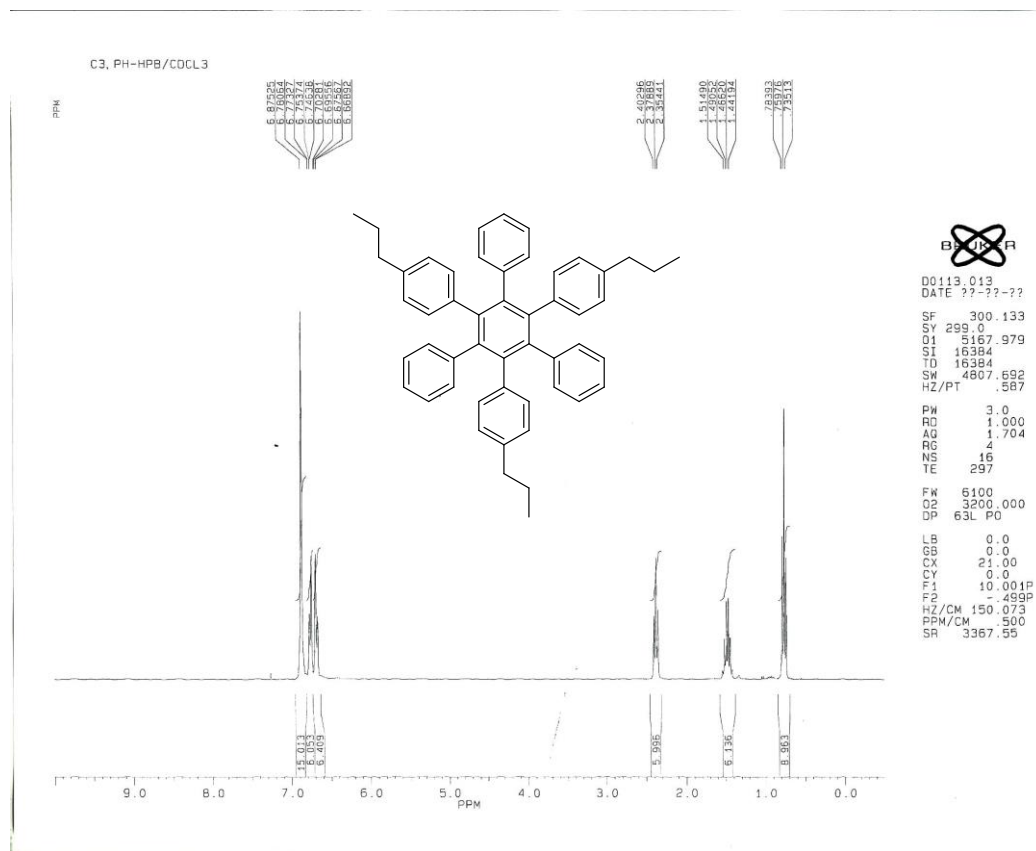


# <sup>13</sup>C-NMR of compound 4'

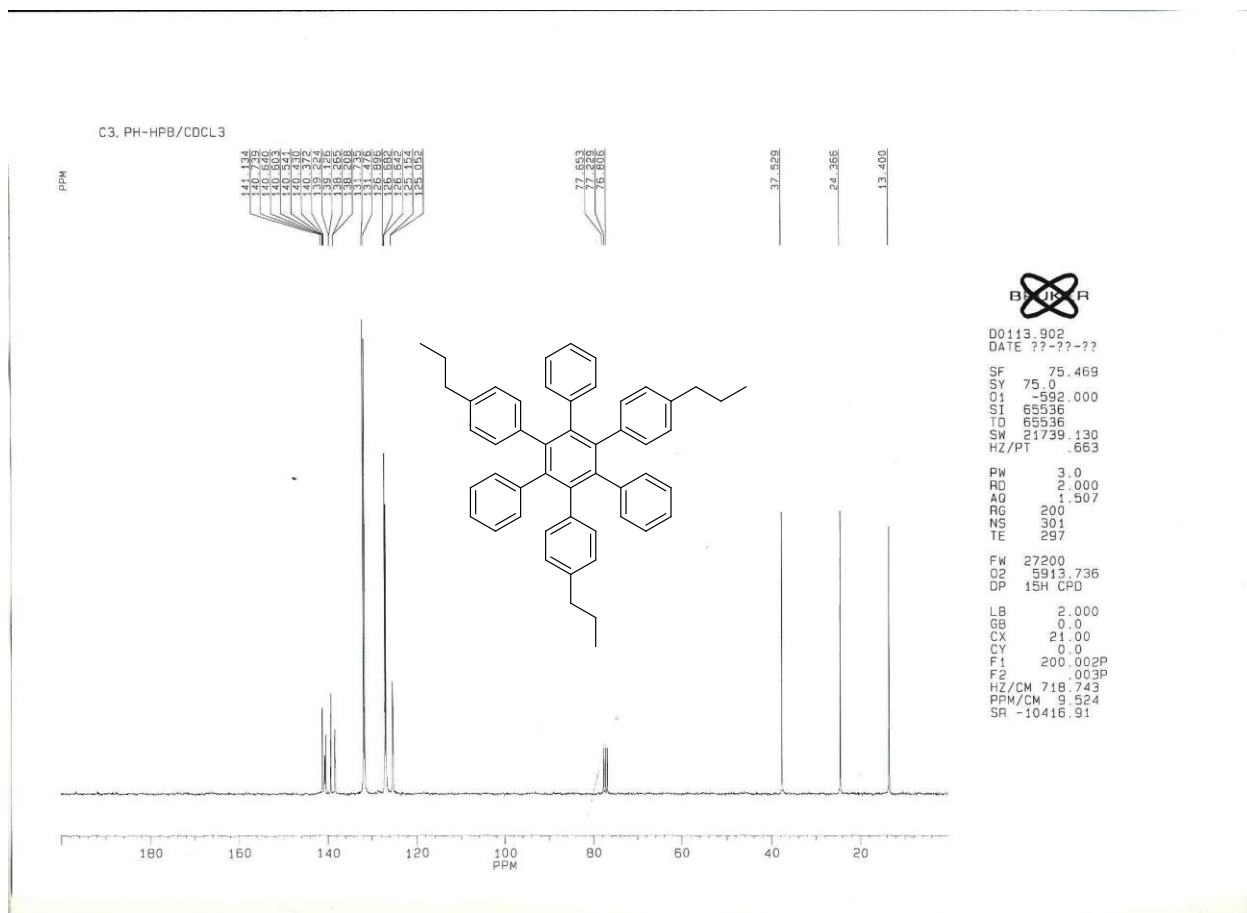


# HMBC of compound 4'

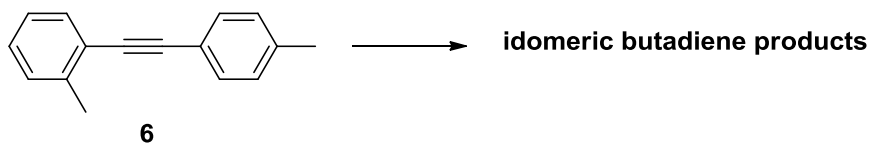




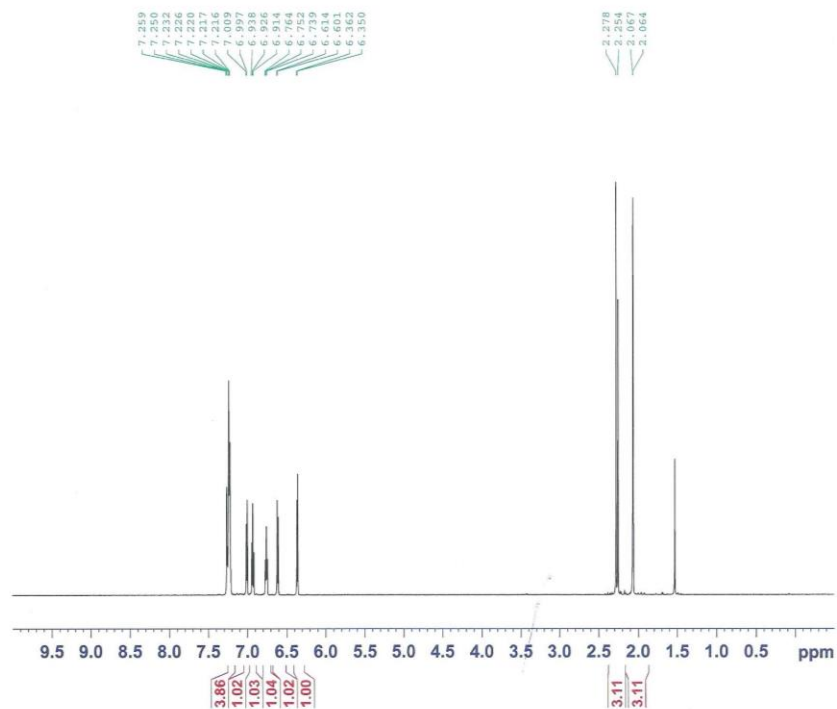
$^1\text{H}$  NMR spectrum of trimer (hexaphenylbenzene (HPB)) from **3**



$^{13}\text{C}$ -NMR spectrum of trimer (hexaphenylbenzene (HPB)) from **3**



<sup>1</sup>H of Ey-C-18



**BRUKER**

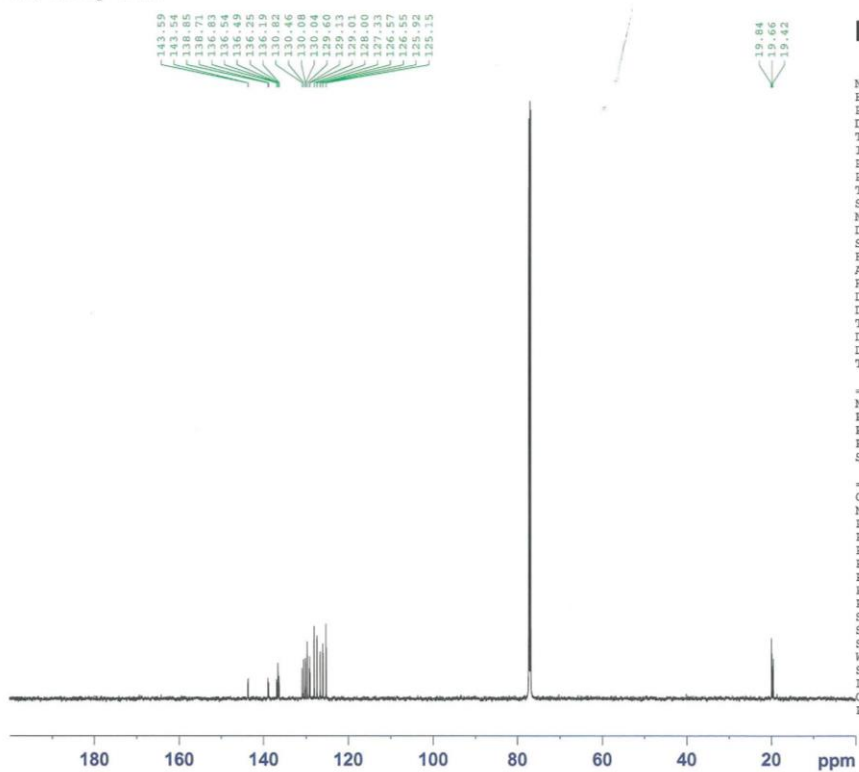
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SOLVENT    CDCl3
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DS         0
SWH        6613.757 Hz
FIDRES     0.201836 Hz
AQ         2.4773865 sec
RG         71.8
DW         75.600 usec
DE         6.00 usec
TE         299.8 K
D1         2.00000000 sec
TD0        1

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SFO1       600.1330006 MHz
SI         32768
SF         600.1300103 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.00
  
```

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

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



NAME Ey-C-18  
EXPNO 2  
PROCNO 1  
Date\_ 20140312  
Time\_ 14.10  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 400  
DS 0  
SWH 33333.332 Hz  
FIDRES 0.508626 Hz  
AQ 0.9831050 sec  
RG 16400  
DW 15.000 usec  
DE 6.00 usec  
TE 299.9 K  
D1 2.40000010 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 <sup>13</sup>C  
P1 9.50 usec  
PL1 2.40 dB  
PL1W 54.20399094 W  
SFO1 150.9194083 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 <sup>1</sup>H  
PCPD2 90.00 usec  
PL2 -4.00 dB  
PL12 10.50 dB  
PL13 13.50 dB  
PL2W 50.47658920 W  
PL12W 1.79097688 W  
PL13W 0.89761478 W  
SFO2 600.1339008 MHz  
SI 32768  
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SSB 0  
LB 3.00 Hz  
GB 0  
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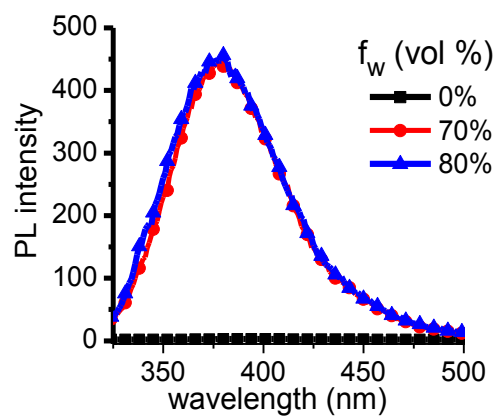
<sup>13</sup>C-NMR spectrum of the mixture of isomeric butadiene from **6**



### E. X-ray Crystallographic data

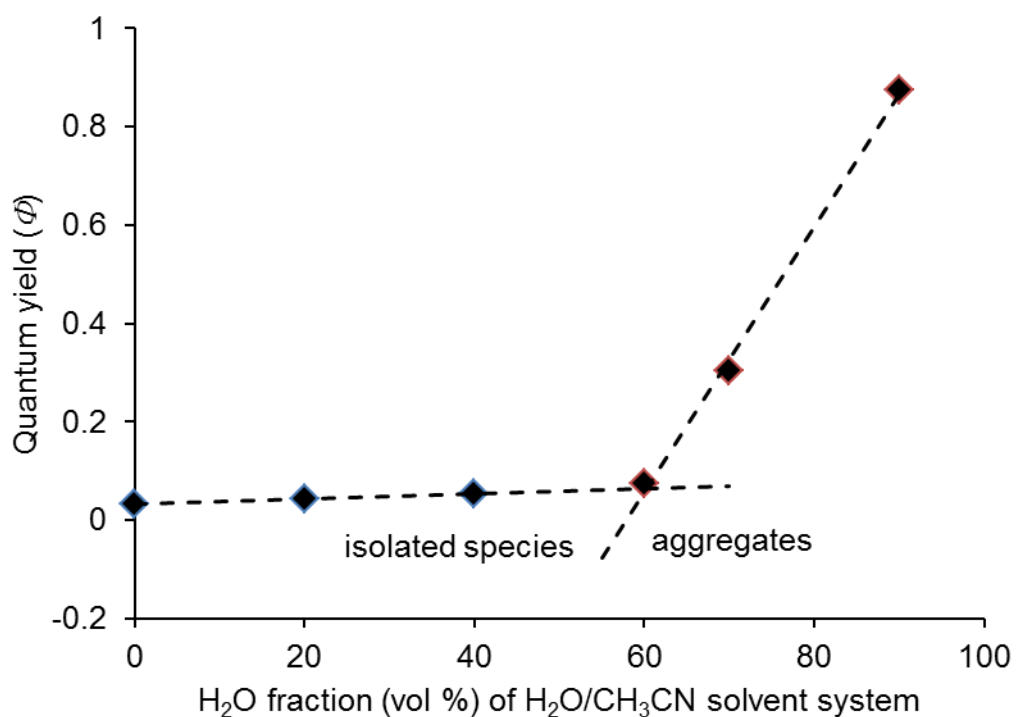
2,2',2'',2'''-((1*E*,3*E*)-Buta-1,3-diene-1,2,3,4-tetrayl)tetrakis(methylbenzene) (**3**) was studied by single crystal X-ray diffraction method. Complete cif file for compound **3** has been deposited with the Cambridge Crystallographic Data Centre, CCDC Deposit # 888658. Copies of the data can be obtained, 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.