

*Electronic Supplementary Information for*

**$\pi$ -Congested Poly(*paraphenylene*) from 2,2',6,6'-  
Tetraphenyl-1,1'-biphenyl: Synthesis and Structural  
Characterization**

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## Complete Reference 38

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. Montgomery, J. A.; , T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision D.02*, Gaussian, Inc.: Wallingford CT, 2004.

## General Information

The compounds used were purchased from Sigma–Aldrich, Fluka, Fisher Scientific, VWR and Acros. Field desorption mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD spectrometer, with data collected between  $m/z$  110 – 3,300. MALDI-TOF spectrometry was conducted on a Bruker Reflex IITOF spectrometer, utilizing a 337 nm nitrogen laser. Solution UV-vis absorption and emission spectra were recorded at room temperature on a Perkin-Elmer Lambda 100 spectrophotometer and J&M TIDAS spectrofluorometer, respectively. Absolute photoluminescence quantum yields (PLQY) were evaluated at 298 K on a Hamamatsu Photonic Multi-Channel Analyzer C 10027. For these techniques  $10^{-6}$  M solution in dichloromethane were used. Size-exclusion chromatography (SEC) analysis was performed with SDV (PSS) columns (106, 104, and 500 Å porosity) connected to RI and UV (254 nm) detectors against polystyrene standards, and calibrated for 1,4-poly(paraphenylene) (PPP) with THF as an eluting solvent. The high resolution mass spectrometry was performed on an ESI-Q-TOF system (maXis, BrukerDaltonics, Germany). The instrument was operated in wide pass quadrupole mode, for MS experiments, with the TOF data being collected between  $m/z$  100 – 5,000. X-ray measurements were carried out at 120 K with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$ ) on a Nonius KCCD diffractometer. The structure was solved by direct methods and refined on F by full-matrix least-squares cycles. Elemental analysis of solid samples was carried out on a Foss Heraeus Vario EL.

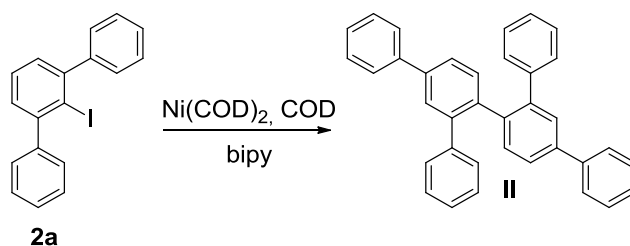
NMR measurements were recorded on a Bruker AVANCE 300, Bruker AVANCE 500 and Bruker AVANCE 700 system. For a  $^1\text{H}$  NMR spectrum (5 mm BBI z-gradient probe) 128 transients were used with an 9,3  $\mu\text{s}$  long  $90^\circ$  pulse and a 12600 Hz spectral width together with a recycling delay of 5 s. The temperature was kept at 298.3 K and regulated by a standard  $^1\text{H}$  methanol NMR sample using the topspin 3.0 software (Bruker). The proton and carbon spectra were measured in  $\text{CD}_2\text{Cl}_2$  and THF- $d_8$  at 298.3K and the spectra were referenced as follows: for the residual  $\text{CHDCl}_2$  at  $\delta(^1\text{H}) = 5.32$  ppm, THF- $d_7\text{H}$  at  $\delta(^1\text{H}) = 3.58$  ppm and THF- $d_8$  at  $\delta(^{13}\text{C})$  at 64.97 ppm (quintet). The assignment was accomplished by  $^1\text{H}, ^1\text{H}$  COSY (correlated spectroscopy) 2D method. The spectroscopic widths of the homo-nuclear 2D COSY experiments were typically 14000 Hz in both dimension (f1 and f2) and the relaxation delay 1.2s.

## Synthetic procedures

2'-iodo-1,1':3',1''-terphenyl **2** ( $R^1 = H$ ) was synthesized according to literature.<sup>1-3</sup>

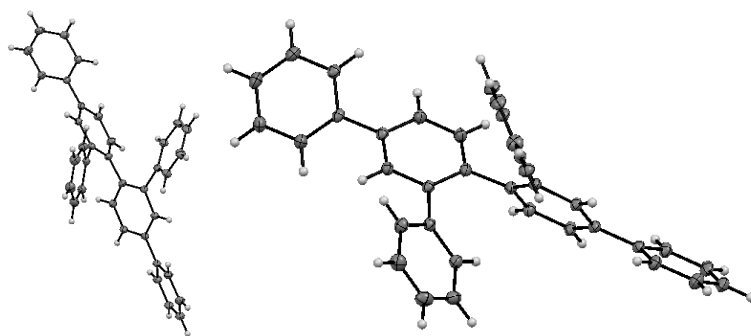
### Concept (A)

#### Yamamoto dimerization of **2a** ( $R^1 = H$ )



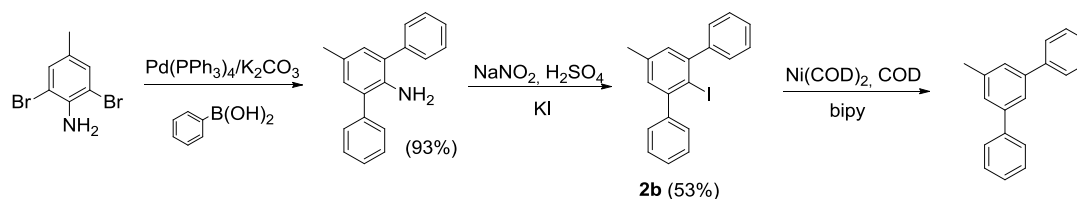
Bis(1,5-cyclooctadiene)nickel(0) (255 mg, 0.93 mmol), 1,5-cyclooctadiene (100 mg, 0.11 mL, 0.93 mmol) and 2,2'-bipyridine (145 mg, 0.93 mmol) were added to a flame-dried 100 mL Schlenk flask, dissolved in 10 mL anhydrous *N,N*-dimethylformamide and stirred for 30 min at 65 °C in the absence of light. A solution of **2a** (300 mg, 0.84 mmol) in 20 mL anhydrous toluene at 65 °C was added *via* a double-tipped needle and the resulting mixture was stirred overnight at 85 °C. The reaction was quenched by adding 1N aqueous hydrochloric acid, extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was dried with MgSO<sub>4</sub>. After having removed the solvents *in vacuo*, the residue was subjected to column chromatography (silica, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 3:1 to 2:1). **II** was obtained as a white solid (41 mg, 21%). Crystals suitable for X-ray analysis were grown by slow evaporation of a toluene solution of **II**.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz,  $\delta$ ): 6.45 – 7.65 (m, 26H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 63 MHz,  $\delta$ ): 125.1, 126.0, 126.5, 127.4, 127.9, 128.4, 128.9, 130.1, 130.3, 132.1, 132.3. FD-MS (8kV):  $m/z = 458.7$  (100%, M<sup>+</sup>). ESI-HR MS calcd for C<sub>36</sub>H<sub>26</sub> ([M+Na]<sup>+</sup>) 481.1923, found 481.1931.



**Figure 1** Different views of the X-ray crystallographic structure of **II**.<sup>4</sup>

### Yamamoto dimerization of **2b** ( $R^1 = \text{CH}_3$ )



### 5'-Methyl-[1,1':3',1''-terphenyl]-2'-amine

A 250 mL Schlenk tube was equipped with 2,6-dibromo-4-methylaniline (1.5 g, 5.66 mmol) and phenylboronic acid (2.07 g, 16.98 mmol) followed by three times evacuating and backfilling with argon. After the addition of 100 mL toluene, solid  $\text{K}_2\text{CO}_3$  (7.82 g, 56.62 mmol) and three drops of aliquat 336 the resulting mixture was degassed with argon for one hour. To this mixture  $\text{Pd}(\text{PPh}_3)_4$  (262 mg, 4 mol%) was added and it was stirred under an atmosphere of argon at 100 °C overnight. The addition of water, washing the aqueous phase three times with toluene, drying the combined organic phases with  $\text{MgSO}_4$  and evaporating of the solvent *in vacuo* resulted in a crude mixture which was subjected to column chromatography (silica, *n*-hexane/ $\text{CH}_2\text{Cl}_2$  1:2). 5'-Methyl-[1,1':3',1''-terphenyl]-2'-amine was obtained as colorless oil (1.37 g, 93%).

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 250 MHz,  $\delta$ ): 2.41 (s, 3H), 7.05 (s, 2H), 7.40 – 7.65 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 75 MHz,  $\delta$ ): 20.6, 127.6, 128.4, 129.2, 129.7, 130.8, 138.8, 140.5. FD-MS (8kV):  $m/z = 259.3$  (100%,  $\text{M}^+$ ).

### 2'-Iodo-5'-methyl-1,1':3',1''-terphenyl **2b**

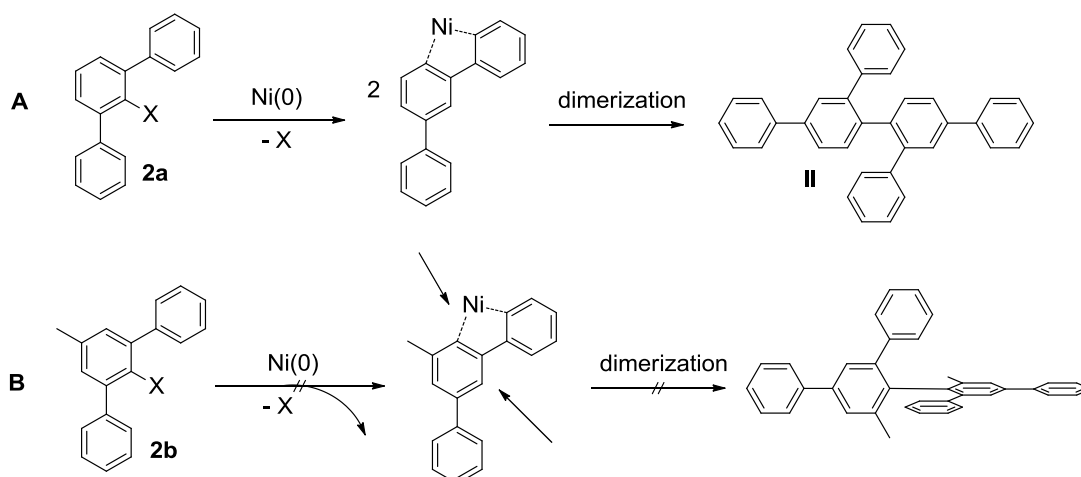
A solution of 5'-Methyl-[1,1':3',1''-terphenyl]-2'-amine (1.37 g, 5.27 mmol) in acetic acid (6.5 mL) was added dropwise to a suspension of solid  $\text{NaNO}_2$  (382 mg, 5.54 mmol) was suspended in conc. sulfuric acid (4.5 mL) at 0 °C. After vigorously stirring for one hour at 0 °C, the diazonium salt was added to a solution of  $\text{KI}$  (920 mg, 5.54 mmol) in  $\text{H}_2\text{O}$  (12 mL) at 50 °C and stirred at 70 °C for one hour. The reaction was quenched by the addition of water and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3x). The combined organic phase was dried with  $\text{MgSO}_4$ , filtered and the solvents were evaporated *in vacuo*. **2b** was obtained after column chromatographic separation (silica, *n*-hexane/ $\text{CH}_2\text{Cl}_2$  1:1 to 4:1) as a colorless oil (1.04 g, 53%).

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 250 MHz,  $\delta$ ): 2.21 (s, 3H), 7.00 (s, 2H), 7.20 – 7.32 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 75 MHz,  $\delta$ ): 21.0, 127.9, 128.3, 129.9, 131.5, 137.4, 142.6, 143.9. FD-MS (8kV):  $m/z = 370.4$  (100%,  $\text{M}^+$ ). ESI-HR MS calcd for  $\text{C}_{19}\text{H}_{15}\text{I}$  ( $[\text{M}+\text{H}]^+$ ) 371.0297, found 371.0301.

### Dimerization

Bis(1,5-cyclooctadiene)nickel(0) (183 mg, 0.67 mmol), 1,5-cyclooctadiene (72 mg, 0.08 mL, 0.67 mmol) and 2,2'-bipyridine (104 mg, 0.67 mmol) were added to a flame-dried 50 mL Schlenk flask, dissolved in 7.2 mL anhydrous *N,N*-dimethylformamide and stirred for 30 min at 65 °C in the absence of light. A solution of **2b** (225 mg, 0.61 mmol) in 14.4 mL anhydrous toluene at 65 °C was added *via* a double-tipped needle and the resulting mixture was stirred overnight at 85 °C. The reaction was quenched by adding 1N aqueous hydrochloric acid, extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was dried with MgSO<sub>4</sub>. After having removed the solvents *in vacuo*, the residue was subjected to column chromatography (silica, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 3:1) and dehalogenated starting material (5'-methyl-1,1':3',1''-terphenyl) was obtained.

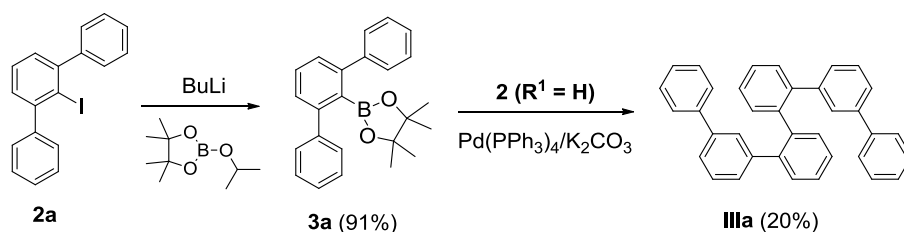
FD-MS (8kV):  $m/z = 244.1$  (100%, M<sup>+</sup>).



**Scheme 1** Plausible reaction mechanism of the *Yamamoto* dimerization of **2a** and **2b**.

In situation A, a migration of the active Ni<sup>0</sup> complex to the less hindered  $\pi$ -face of **2a** occurs, followed by the C-C bond formation at the 4'-position of **2a**. Whereas in case of **2b** (B), the migration of the active Ni<sup>0</sup> complex does not result in a less hindered situation since both positions (indicated by arrows) are considerably shielded for the C-C bond formation, which results finally in dehalogenation of **2b**.

### Suzuki-Miyaura dimerization of **3a** ( $R^1 = H$ , $R^2 = H$ )



### 2-([1,1':3',1''-Terphenyl]-2'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3a**

2'-Iodo-1,1':3',1''-terphenyl **2a** (1 g, 2.81 mmol) was added to a flame-dried 50 mL Schlenk flask and dissolved in 12.5 mL anhydrous Et<sub>2</sub>O under an argon atmosphere. To the resulting solution was added dropwise *n*BuLi (2.11 mL, 3.37 mmol, 1.6 M in hexane) at room temperature and stirred for additional two hours. The solution was subsequently cooled to -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.04 g, 1.15 mL, 5.61 mmol) was added with a syringe. After warming up to room temperature overnight, the reaction mixture was quenched with 1N aqueous hydrochloric acid, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x), the combined organic phases were dried with MgSO<sub>4</sub> and filtered. The solvents were evaporated *in vacuo* and the residue was subjected to column chromatography (silica, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1 to 1:2) yielding **3a** as a white crystalline solid (900 mg, 91%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz,  $\delta$ ): 0.76 (s, 12H), 7.18 – 7.40 (m, 13H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz,  $\delta$ ): 25.1, 84.1, 127.5, 127.8, 127.9, 128.4, 128.9, 129.6, 130.0, 143.8, 146.8. FD-MS (8kV):  $m/z = 355.1$  (100%, M<sup>+</sup>). ESI-HR MS calcd for C<sub>24</sub>H<sub>25</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 357.2026, found 357.2035.

### Dimerization

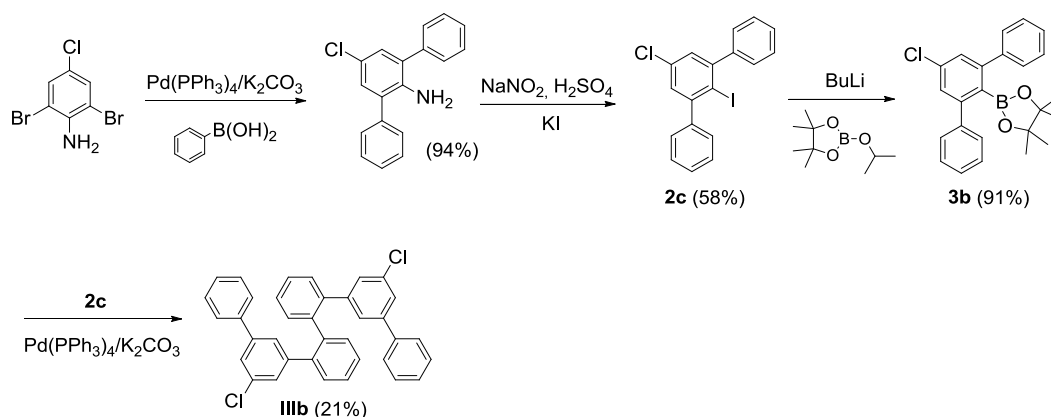
**Table 1** Optimization of the reaction conditions for the sterically hindered Suzuki-Miyaura coupling towards **III**.

Entry	Catalyst System	<i>T</i> (°C)	<i>t</i> (h)	Base	Yield (%) <sup>[a]</sup>
1	[Pd <sub>2</sub> dba <sub>3</sub> ] + S-Phos	100	24	K <sub>3</sub> PO <sub>4</sub>	– <sup>[b]</sup>
2	[Pd(OAc) <sub>2</sub> ] + PPh <sub>3</sub>	100	24	K <sub>3</sub> PO <sub>4</sub>	– <sup>[b]</sup>
3	[Pd(PPh <sub>3</sub> ) <sub>4</sub> ]	100	24	K <sub>3</sub> PO <sub>4</sub>	– <sup>[b]</sup>
4	[Pd(PPh <sub>3</sub> ) <sub>4</sub> ]	100	24	Cs <sub>2</sub> CO <sub>3</sub>	– <sup>[b]</sup>
5	[Pd(PPh <sub>3</sub> ) <sub>4</sub> ] + aliquat 336	100	24	Na <sub>2</sub> CO <sub>3</sub>	– <sup>[b]</sup> , <sup>[c]</sup>
<b>6</b>	<b>[Pd(PPh<sub>3</sub>)<sub>4</sub>] + aliquat 336</b>	<b>100</b>	<b>24</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>20</b>

<sup>[a]</sup>Yield of the isolated, analytically pure compound. <sup>[b]</sup>No product was detected. <sup>[c]</sup>Na<sub>2</sub>CO<sub>3</sub> was used as a 2M aqueous solution.

A 100 mL Schlenk tube was equipped with 2-([1,1':3',1''-terphenyl]-2'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3a** (300 mg, 0.84 mmol) and 2'-iodo-1,1':3',1''-terphenyl **2a** (300 mg, 0.84 mmol) followed by three times evacuating and backfilling with argon. After the addition of 30 mL toluene, aqueous 2M K<sub>2</sub>CO<sub>3</sub> solution (15 mL) and three drops of aliquat 336 the resulting mixture was degassed with argon for one hour. To this mixture Pd(PPh<sub>3</sub>)<sub>4</sub> (39 mg, 4 mol%) was added and it was stirred under an atmosphere of argon at 100 °C overnight. After the addition of water, washing the aqueous phase three times with toluene, drying the combined organic phases with MgSO<sub>4</sub> and evaporating of the solvent *in vacuo*, the crude mixture was subjected to column chromatography (silica, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1). 1,1':3',1'':2'',1''':2''',1''':3''',1''''-sexiphenyl **IIIa** was obtained as a white solid (39 mg, 20%).  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz, δ): 6.48 – 7.59 (m, 26H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 63 MHz, δ): 125.1, 126.0, 126.5, 127.4, 127.9, 128.4, 128.9, 130.1, 130.3, 132.1, 132.3. FD-MS (8kV): *m/z* = 458.3 (100%, M<sup>+</sup>). ESI-HR MS calcd for C<sub>36</sub>H<sub>26</sub> ([M+H]<sup>+</sup>) 459.2113, found 459.2121.

### Suzuki-Miyaura dimerization of **3b** (R<sup>1</sup> = Cl, R<sup>2</sup> = Cl)



### 5'-Chloro-[1,1':3',1''-terphenyl]-2'-amine

A 250 mL Schlenk tube was equipped with 2,6-dibromo-4-chloroaniline (6.0 g, 21.03 mmol) and phenylboronic acid (6.41 g, 52.56 mmol) followed by three times evacuating and backfilling with argon. After the addition of 150 mL toluene, solid K<sub>2</sub>CO<sub>3</sub> (43.6 g, 315.39 mmol) and three drops of aliquat 336 the resulting mixture was degassed with argon for one hour. To this mixture Pd(PPh<sub>3</sub>)<sub>4</sub> (729 mg, 3 mol%) was added and it was stirred under an atmosphere of argon at 100 °C overnight. The addition of water, washing the aqueous phase three times with toluene, drying the combined organic phases with MgSO<sub>4</sub> and



evaporating of the solvent *in vacuo* resulted in a crude mixture which was subjected to column chromatography (silica, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 2:). 5'-chloro-[1,1':3',1''-terphenyl]-2'-amine was obtained as colorless oil (5.55 g, 94%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz, δ): 6.98 (s, 2H), 7.23 – 7.41 (m, 10H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, δ): 122.7, 128.1, 129.4, 129.5, 129.6, 139.0, 140.2. FD-MS (8kV): *m/z* = 278.1 (100%, M<sup>+</sup>).

#### 5'-Chloro-2'-iodo-1,1':3',1''-terphenyl **2c**

To a suspension of 5'-chloro-[1,1':3',1''-terphenyl]-2'-amine (5.55 g, 19.84 mmol) in concentrated hydrochloric acid (15 mL) was added dropwise to a solution of NaNO<sub>2</sub> (1.49 g, 21.62 mmol) in H<sub>2</sub>O (6.6 mL) at 0 °C. After vigorously stirring for 1.5 hours at 0 °C, the diazonium salt was added to a solution of KI (27.43 g, 165.25 mmol) in H<sub>2</sub>O (37.5 mL) and stirred at room temperature overnight. The reaction was quenched by the addition of aqueous Na<sub>2</sub>SO<sub>3</sub> solution and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x). The combined organic phase was dried with MgSO<sub>4</sub>, filtered and the solvents were evaporated *in vacuo*. The residue was recrystallized from EtOH, yielding **2c** as a colorless oil (4.50 g, 58%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz, δ): 7.34 (s, 2H), 7.37 – 7.56 (m, 10H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, δ): 100.4, 101.5, 128.4, 128.5, 128.8, 129.6, 144.5, 149.9. FD-MS (8kV): *m/z* = 389.3 (100%, M<sup>+</sup>). ESI-HR MS calcd for C<sub>18</sub>H<sub>12</sub>ClI ([M+H]<sup>+</sup>) 390.9750, found 390.9763.

#### 2-(5'-Chloro-[1,1':3',1''-terphenyl]-2'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3b**

5'-Chloro-2'-iodo-1,1':3',1''-terphenyl **2c** (1 g, 2.56 mmol) was added to a flame-dried 50 mL Schlenk flask and dissolved in 12.5 mL anhydrous Et<sub>2</sub>O under an argon atmosphere. To the resulting solution was added dropwise *n*BuLi (1.92 mL, 3.07 mmol, 1.6 M in hexane) at room temperature and stirred for additional two hours. The solution was subsequently cooled to -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (947 mg, 1.05 mL, 5.11 mmol) was added with a syringe. After warming up to room temperature overnight, the reaction mixture was quenched with 1N aqueous hydrochloric acid, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x), the combined organic phases were dried with MgSO<sub>4</sub> and filtered. The solvents were evaporated *in vacuo* and the residue was subjected to column chromatography (silica, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1 to 1:2) yielding **3b** as a white crystalline solid (910 mg, 91%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz, δ): 0.75 (s, 12H), 7.17 – 7.42 (m, 12H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, δ): 25.3, 84.1, 127.7, 127.9, 128.0, 128.4, 128.9, 129.6, 130.0, 143.8, 146.8. FD-MS

(8kV):  $m/z = 389.9$  (100%,  $M^+$ ). ESI-HR MS calcd for  $C_{24}H_{25}BClO_2$  ( $[M+H]^+$ ) 391.1636, found 391.1655.

### Dimerization

A 100 mL Schlenk tube was equipped with 2-(5'-Chloro-[1,1':3,1''-terphenyl]-2'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3b** (300 mg, 0.77 mmol) and 5'-Chloro-2'-iodo-1,1':3,1''-terphenyl **2c** (300 mg, 0.77 mmol) followed by three times evacuating and backfilling with argon. After the addition of 30 mL toluene, aqueous 2M  $K_2CO_3$  solution (15 mL) and three drops of aliquat 336 the resulting mixture was degassed with argon for one hour. To this mixture  $Pd(PPh_3)_4$  (35 mg, 4 mol%) was added and it was stirred under an atmosphere of argon at 100 °C for two days. After the addition of water, washing the aqueous phase three times with toluene, drying the combined organic phases with  $MgSO_4$  and evaporating of the solvent *in vacuo*, the crude mixture was subjected to column chromatography (silica, *n*-hexane/ $CH_2Cl_2$  4:1). 5',5''-dichloro-1,1':3,1''-2'',1''':2''',1''':3''',1''''-sexiphenyl **IIIb** was obtained as a white solid (42 mg, 21%). Crystals suitable for X-ray analysis were grown by slow evaporation of a  $CH_2Cl_2/MeOH$  solution of **IIIb**.

$^1H$  NMR ( $CD_2Cl_2$ , 250 MHz,  $\delta$ ): 5.91 (d,  $J = 7.5$  Hz, 2H), 6.30 (d,  $J = 10$  Hz, 2H), 6.53 (s, 4H) 6.67 – 7.47 (m, 16H).  $^{13}C$  NMR ( $CD_2Cl_2$ , 63 MHz,  $\delta$ ): 125.3, 126.2, 126.6, 127.4, 127.9, 128.4, 128.9, 130.3, 130.5, 142.1, 142.3. FD-MS (8kV):  $m/z = 525.1$  (100%,  $M^+$ ). ESI-HR MS calcd for  $C_{36}H_{24}Cl_2$  ( $[M+H]^+$ ) 527.1333, found 527.1322.

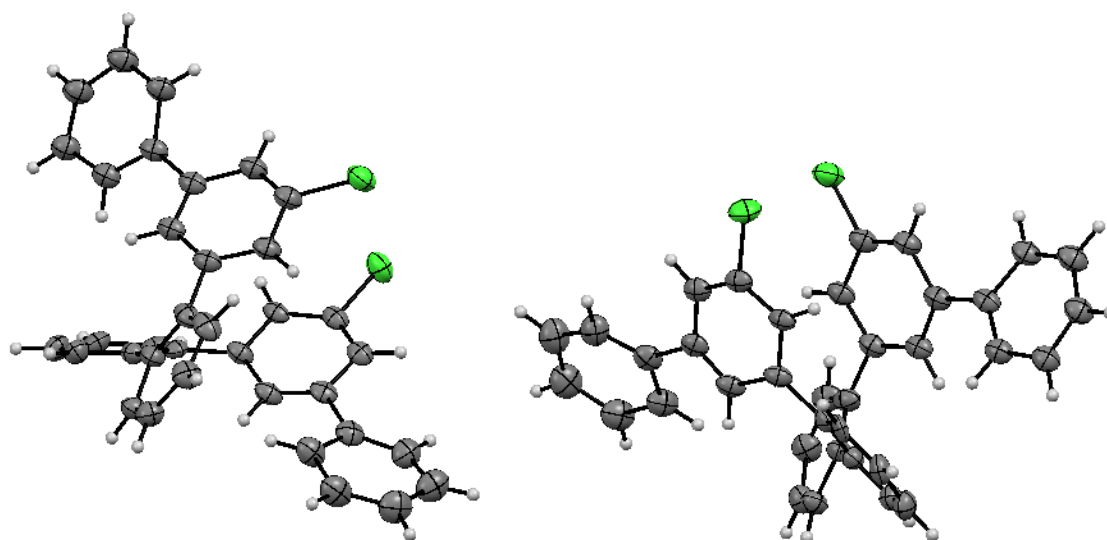
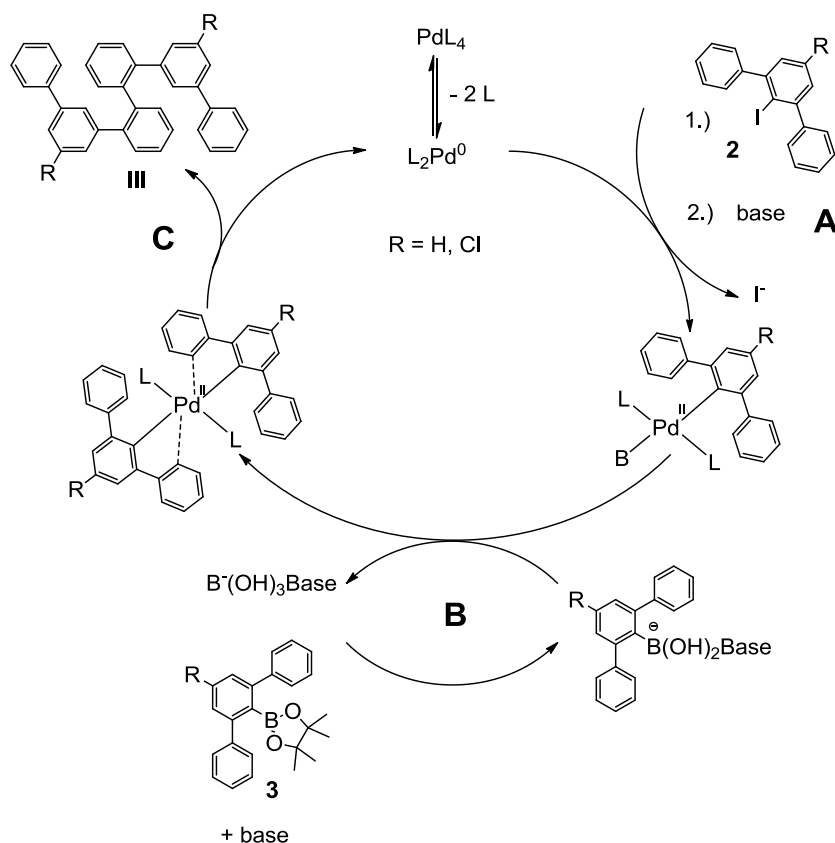


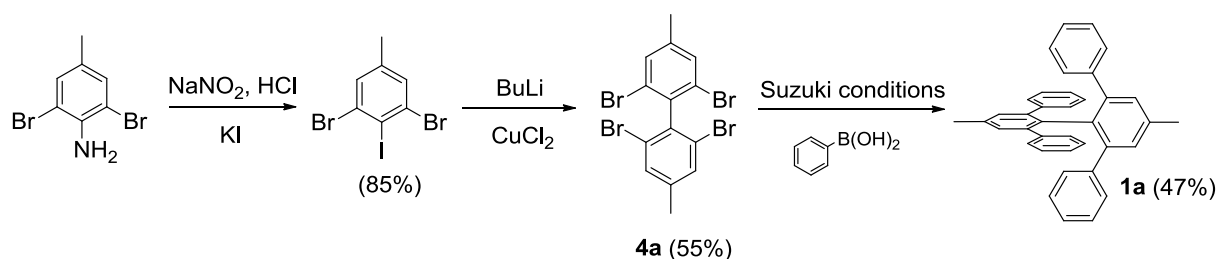
Figure 2 Different views of the X-ray crystallographic structure of **IIIb**.<sup>5</sup>



**Scheme 2** Proposed catalytic cycle for the *Suzuki-Miyaura* cross-coupling towards **III**. A) oxidative addition and reaction with the base; B) C-H activation during transmetalation; C) reductive elimination.

## Concept (B)

### Attachment of peripheral phenyl rings towards **1a**



#### *1,3-Dibromo-2-iodo-5-methylbenzene*

To a suspension of 2,6-dibromo-4-methylaniline (6.00 g, 22.65 mmol) in concentrated hydrochloric acid (15 mL) was added dropwise a solution of NaNO<sub>2</sub> (1.72 g, 24.91 mmol) in H<sub>2</sub>O (7.8 mL) at 0 °C. After vigorously stirring for 2 hours at 0 °C, the diazonium salt was added to a solution of KI (31.32 g, 188.64 mmol) in H<sub>2</sub>O (44 mL) and stirred at room temperature overnight. The reaction was quenched by the addition of aqueous Na<sub>2</sub>SO<sub>3</sub> solution and the mixture was extracted with

CH<sub>2</sub>Cl<sub>2</sub> (3x). The combined organic phase was dried with MgSO<sub>4</sub>, filtered and the solvents were evaporated *in vacuo*. The residue was recrystallized from EtOH, yielding 1,3-Dibromo-2-iodo-5-methylbenzene as a white solid (7.23 g, 85%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz, δ): 2.30 (s, 3H), 7.47 (s, 2H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, δ): 21.4, 107.6, 131.4, 131.8, 135.8. FD-MS (8kV): *m/z* = 375.6 (100%, M<sup>+</sup>).

#### 2,2',6,6'-Tetrabromo-4,4'-dimethyl-1,1'-biphenyl **4a**

1,3-Dibromo-2-iodo-5-methylbenzene (4.2 g, 11.18 mmol) and anhydrous CuCl<sub>2</sub> (9.0 g, 67.05 mmol) was added to a flame-dried 100 mL Schlenk flask and suspended in 37 mL anhydrous Et<sub>2</sub>O under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*BuLi (7.54 mL, 12.07 mmol, 1.6 M in hexane) was added dropwise over 2.5 hours. After warming up to room temperature overnight, the reaction mixture was quenched with aqueous NH<sub>4</sub>Cl solution, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x), the combined organic phases were dried with MgSO<sub>4</sub> and filtered. The solvents were evaporated *in vacuo* and the residue was subjected to column chromatography (silica, *n*-hexane) yielding **4a** as a white crystalline solid (1.53 g, 55%). Cr

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz, δ): 2.43 (s, 6H), 7.55 (s, 4H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, δ): 20.9, 124.4, 132.8, 142.2, 153.6. FD-MS (8kV): *m/z* = 498.1 (100%, M<sup>+</sup>). Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>Br<sub>4</sub>: C 33.78%, H 2.02%. Found: C 33.51%, H 1.95%.

#### 4,4'-Dimethyl-2,2',6,6'-tetraphenyl-1,1'-biphenyl **1a**

**Table 2** Optimization of the reaction conditions for the sterically hindered *Suzuki-Miyaura* coupling towards **1a**.

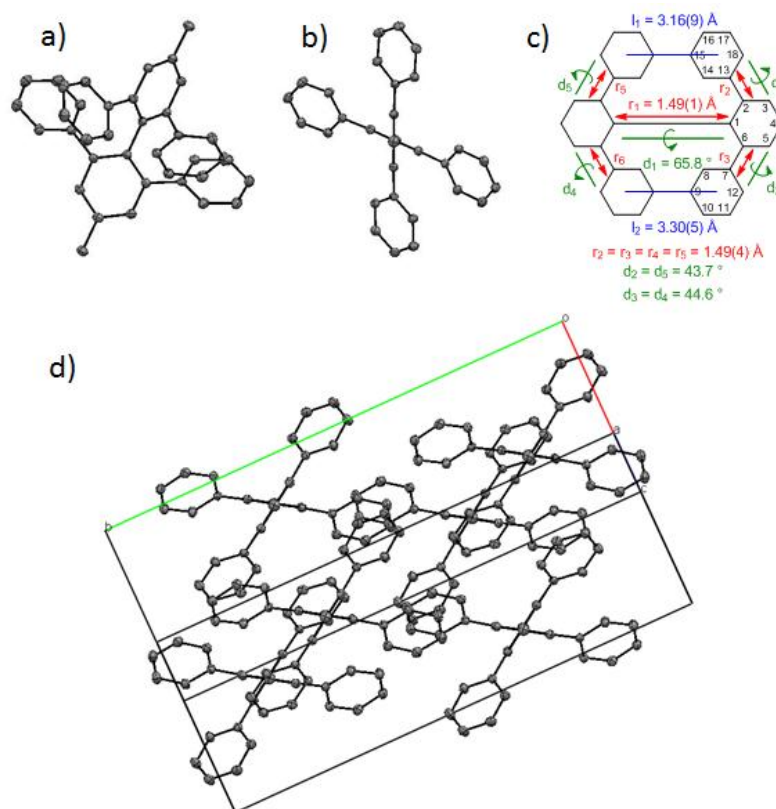
Entry	Catalyst System	<i>T</i> (°C)	<i>t</i> (h)	Base	Yield (%) <sup>[a]</sup>
1	[Pd <sub>2</sub> dba <sub>3</sub> ] + S-Phos	100	24	K <sub>3</sub> PO <sub>4</sub>	20 <sup>[b]</sup>
2	[Pd(OAc) <sub>2</sub> ] + PPh <sub>3</sub>	100	24	K <sub>3</sub> PO <sub>4</sub>	– <sup>[c]</sup>
3	[Pd(PPh <sub>3</sub> ) <sub>4</sub> ]	100	24	K <sub>3</sub> PO <sub>4</sub>	12
4	[Pd(PPh <sub>3</sub> ) <sub>4</sub> ]	100	24	Cs <sub>2</sub> CO <sub>3</sub>	23
5	[Pd(PPh <sub>3</sub> ) <sub>4</sub> ] + aliquat 336	100	24	Na <sub>2</sub> CO <sub>3</sub>	33 <sup>[d]</sup>
<b>6</b>	<b>[Pd(PPh<sub>3</sub>)<sub>4</sub>] + aliquat 336</b>	<b>100</b>	<b>24</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>47</b>

<sup>[a]</sup>Yield of the isolated, analytically pure compound. <sup>[b]</sup>The purification was complicated by a large amount of dehalogenated **4a**. <sup>[c]</sup>No product was detected. <sup>[d]</sup>Na<sub>2</sub>CO<sub>3</sub> was used as a 2M aqueous solution.

A 50 mL Schlenk tube was equipped with 2,2',6,6'-tetrabromo-4,4'-dimethyl-1,1'-biphenyl **4a** (150 mg, 0.30 mmol) and phenylboronic acid **5a** (220 mg, 1.81 mmol) followed by three times evacuating and backfilling with argon. After the addition of 30 mL toluene, solid K<sub>2</sub>CO<sub>3</sub>

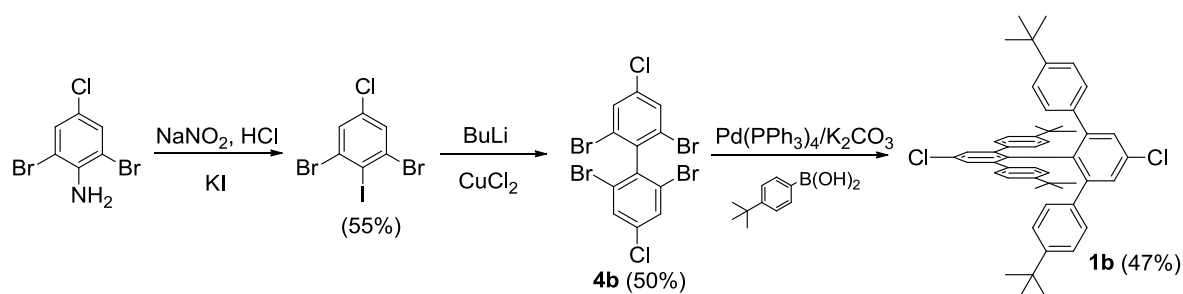
(1.67 g, 12.05 mmol) and three drops of aliquat 336 the resulting mixture was degassed with argon for 1.5 hours. To this mixture Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 2.5 mol%) was added and it was stirred under an atmosphere of argon at 100 °C for two days. After the addition of water, washing the aqueous phase three times with toluene, drying the combined organic phases with MgSO<sub>4</sub> and evaporating of the solvent *in vacuo*, the crude mixture was subjected to column chromatography (silica, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 4:1). Finally the product fraction was recrystallized from *n*-hexane, yielding **1a** as a white, crystalline solid (69 mg, 47%). Crystals suitable for X-ray analysis were grown by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/MeOH solution of **1a**.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, δ): 2.38 (s, 6H), 6.63 (d, *J* = 10 Hz, 8H), 6.99 (m, 12H), 7.11 (t, *J*<sub>1</sub> = *J*<sub>2</sub> = 5 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 176 MHz, 323 K, δ): 21.1, 125.6, 127.1, 129.2, 130.6, 132.9, 137.0, 141.7, 142.0. FD-MS (8kV): *m/z* = 486.7 (100%, M<sup>+</sup>). Anal. Calcd. for C<sub>38</sub>H<sub>30</sub>: C 93.79%, H 6.21%. Found: C 93.48%, H 5.92%.



**Figure 3** Different views of the X-ray crystallographic structure of **1a**. a) Top view. b) Side view along the 4,4'-positions. c) Characteristic metrics of **1a**. d) View of the Asymmetric unit along the 4,4'-positions (all views: hydrogen atoms omitted for clarity).<sup>6</sup>

## Attachment of peripheral phenyl rings towards **1b**



### 1,3-Dibromo-5-chloro-2-iodobenzene

To a suspension of 2,6-dibromo-4-chloroaniline (10.00 g, 35.04 mmol) in concentrated hydrochloric acid (19 mL) was added dropwise to a solution of NaNO<sub>2</sub> (2.64 g, 38.20 mmol) in H<sub>2</sub>O (12 mL) at 0 °C. After vigorously stirring for 2 hours at 0 °C, the diazonium salt was added to a solution of KI (48.46 g, 291.91 mmol) in H<sub>2</sub>O (68 mL) and stirred at room temperature overnight. The reaction was quenched by the addition of aqueous Na<sub>2</sub>SO<sub>3</sub> solution and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x). The combined organic phase was dried with MgSO<sub>4</sub>, filtered and the solvents were evaporated *in vacuo*. The residue was recrystallized (3x) from EtOH, yielding 1,3-dibromo-5-chloro-2-iodobenzene as a off-white needles (7.64 g, 55%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz,  $\delta$ ): 2.30 (s, 3h), 7.47 (s, 2H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz,  $\delta$ ): 107.6, 131.4, 131.8, 135.8. FD-MS (8kV):  $m/z$  = 395.7 (100%, M<sup>+</sup>).

### 2,2',6,6'-Tetrabromo-4,4'-dichloro-1,1'-biphenyl **4b**

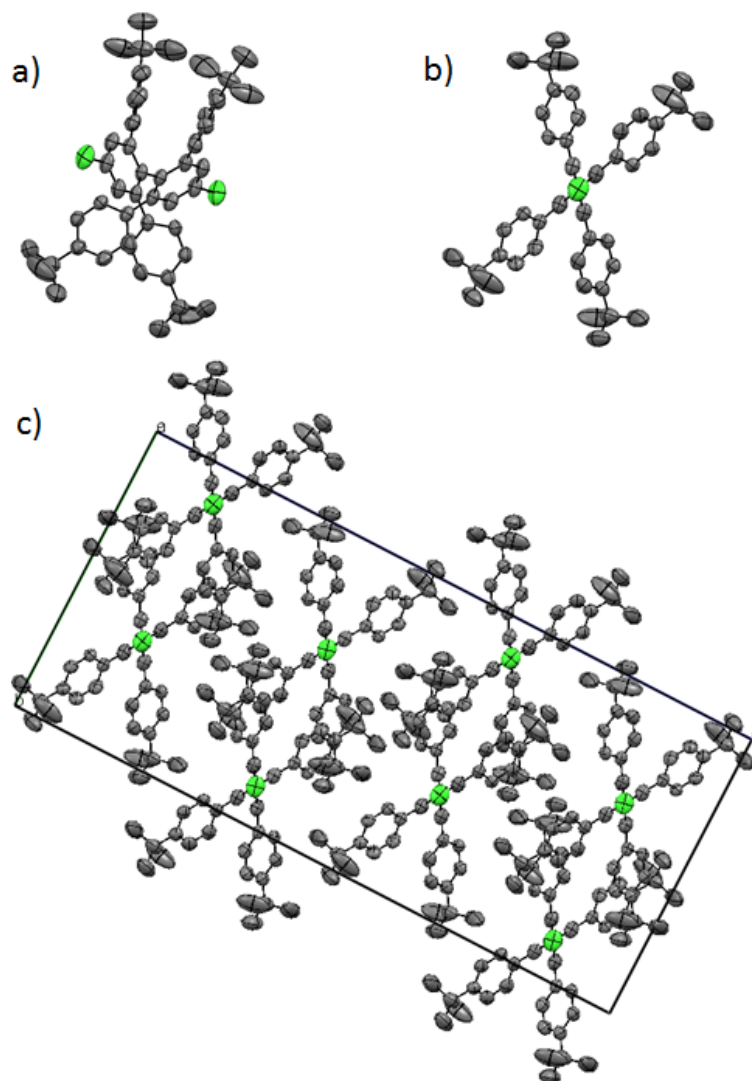
1,3-dibromo-5-chloro-2-iodobenzene (3.5 g, 8.83 mmol) and anhydrous CuCl<sub>2</sub> (7.1 g, 53.00 mmol) was added to a flame-dried 100 mL Schlenk flask and suspended in 28 mL anhydrous Et<sub>2</sub>O under an argon atmosphere. The resulting mixture was cooled to -78 °C and *n*BuLi (5.96 mL, 9.54 mmol, 1.6 M in hexane) was added dropwise over 2.5 hours. After warming up to room temperature overnight, the reaction mixture was quenched with aqueous NH<sub>4</sub>Cl solution, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x), the combined organic phases were dried with MgSO<sub>4</sub> and filtered. The solvents were evaporated *in vacuo* and the residue was subjected to column chromatography (silica, *n*-hexane) yielding **4b** as a white crystalline solid (1.91 g, 50%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz,  $\delta$ ): 7.77 (s, 4H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz,  $\delta$ ): 124.8, 132.2, 136.2 (3 out of 4 expected). FD-MS (8kV):  $m/z$  = 539.3 (100%, M<sup>+</sup>). Anal. Calcd. for C<sub>12</sub>H<sub>4</sub>Br<sub>4</sub>Cl<sub>2</sub>: C 26.76%, H 0.75%. Found: C 26.92%, H 0.88%.

#### *4,4'-Dichloro-2,2',6,6'-tetraphenyl-1,1'-biphenyl* **1b**

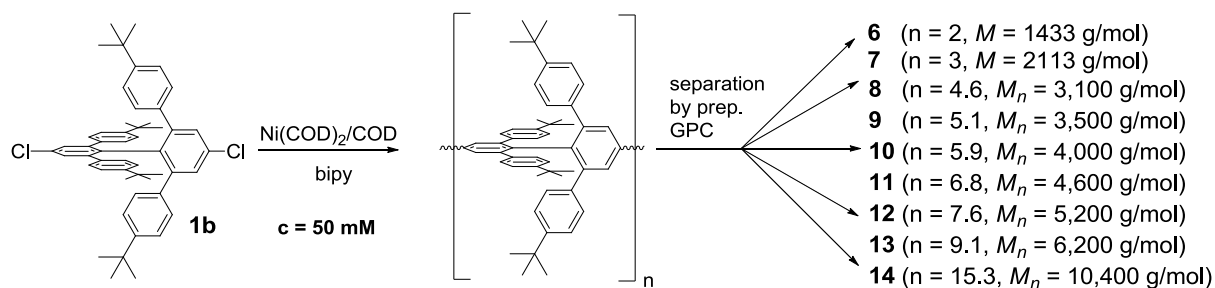
A 50 mL Schlenk tube was equipped with 2,2',6,6'-tetrabromo-4,4'-dichloro-1,1'-biphenyl **4b** (1.0 g, 1.86 mmol) and (4-(tert-butyl)phenyl)boronic acid **5b** (1.98 g, 11.14 mmol) followed by three times evacuating and backfilling with argon. After the addition of 55 mL toluene, solid K<sub>2</sub>CO<sub>3</sub> (10.26 g, 74.26 mmol) and three drops of aliquat 336 the resulting mixture was degassed with argon for 2 hours. To this mixture Pd(PPh<sub>3</sub>)<sub>4</sub> (215 mg, 2.5 mol%) was added and it was stirred under an atmosphere of argon at 100 °C for four days. After the addition of water, washing the aqueous phase three times with toluene, drying the combined organic phases with MgSO<sub>4</sub> and evaporating of the solvent *in vacuo*, the crude mixture was subjected to column chromatography (silica, petrolether/CH<sub>2</sub>Cl<sub>2</sub> 20:1). Finally the product fraction was crystallized from petrolether/CH<sub>2</sub>Cl<sub>2</sub> solution, yielding **1b** as a white, crystalline solid (654 mg, 47%). Crystals suitable for X-ray analysis were grown by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution of **1b**.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz, δ): 1.23 (s, 36H), 6.38 (d, *J* = 10 Hz, 8H), 6.91 (d, *J* = 10 Hz, 8H), 7.05 (s, 4H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, δ): 31.3, 34.6, 124.7, 128.9, 129.4, 133.7, 133.8, 137.4, 144.3, 149.9. FD-MS (8kV): *m/z* = 753.4 (100%, M<sup>+</sup>). Anal. Calcd. for C<sub>52</sub>H<sub>56</sub>Cl<sub>2</sub>: C 83.06%, H 7.51%. Found: C 82.98%, H 7.13%.



**Figure 4** Different views of the X-ray crystallographic structure of **1b**. a) Top view. b) Side view along the 4,4'-positions. c) View of the Asymmetric unit along the 4,4'-positions (all views: hydrogen atoms omitted for clarity).<sup>7</sup>

## Polymerization

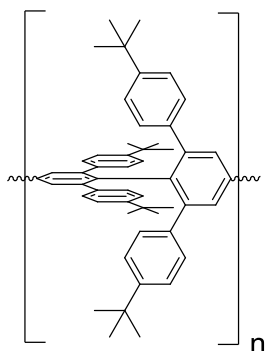


Bis(1,5-cyclooctadiene)nickel(0) (121 mg, 0.44 mmol), 1,5-cyclooctadiene (47 mg, 0.05 mL, 0.44 mmol) and 2,2'-bipyridine (69 mg, 0.44 mmol) were added to a flame-dried 10 mL microwave vial, dissolved in 1.6 mL anhydrous *N,N*-dimethylformamide, sealed and stirred



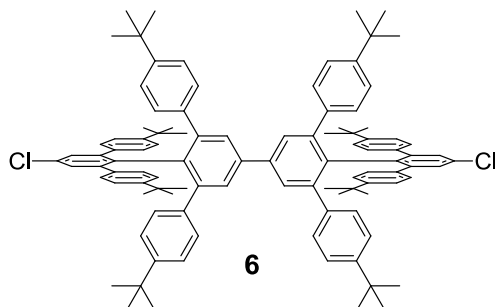
for 30 min at 65 °C in the absence of light. A solution of **1b** (150 mg, 0.20 mmol) in 2.4 mL anhydrous toluene at 65 °C was added *via* a double-tipped needle and the resulting mixture was heated in a CEM microwave at 300 W and activated cooling, keeping the temperature at 110 °C for two days. The reaction mixture was precipitated in 150 mL MeOH/conc. HCl (10:1) and stirred for 2 hours resulting in a white solid after filtration (119 mg, 79%). The polymer was separated by preparative size-exclusion chromatography (BioBeads S-X1, CHCl<sub>3</sub>) to allow isolation of **6** (25 mg, 9%), **7** (18 mg, 5%), **8** (10 mg, 2%), **9** (11 mg, 2%), **10** (8 mg, 1%), **11** (8 mg, 1%), **12** (5 mg, 0.5%), **13** (4 mg, 0.3%) and **14** (30 mg, 2%). Analytical SEC profiles of the isolated fractions are shown in Figure 8. Compounds **6** – **9** were identified by mass spectrometry, while their NMR were complicated and broadened.

### Polymer



<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz,  $\delta$ ): 1.29 (br s, CH<sub>3</sub>), 6.56 (br m, CH<sub>peripheral</sub>), 7.04 (br m, CH<sub>peripheral</sub>), 7.48 (br s, CH<sub>central</sub>), 7.50 (br s, CH<sub>central</sub>). SEC (eluent: THF, poly(*paraphenylene*) calibration):  $M_n$  = 10,400 g/mol, PDI = 1.42.

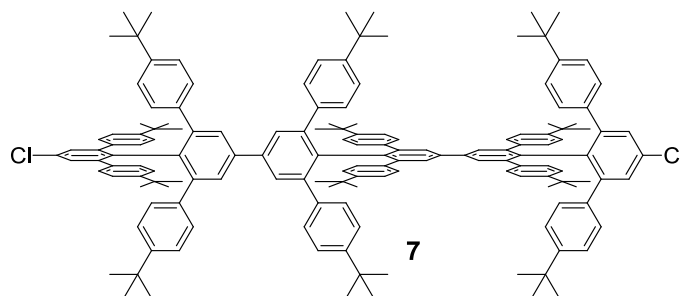
### Dimer **6**



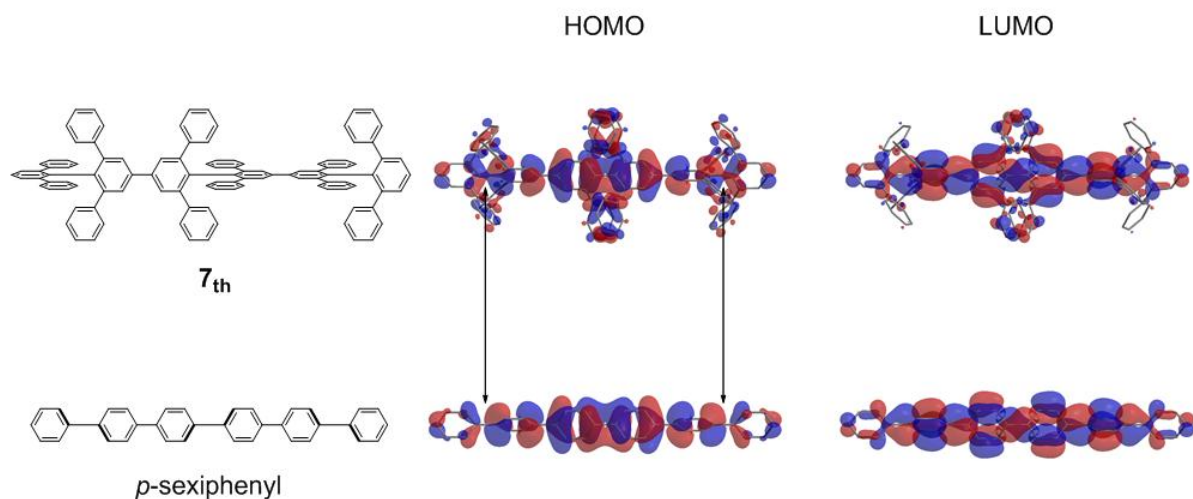
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 700 MHz,  $\delta$ ): 1.34 (s, 36H), 1.35 (s, 36H), 6.57 (dd,  $J_1$  = 6 Hz,  $J_2$  = 2.5 Hz, 16H), 7.03 (t,  $J_1$  =  $J_2$  = 7.5 Hz 16H), 7.19 (s, 4H), 7.51 (s, 4H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 63 MHz,

$\delta$ ): 33.0, 33.1, 33.6, 36.0, 36.2, 115.9, 122.1, 122.5, 123.7, 123.9, 124.3, 126.6, 129.8, 130.3, 131.0, 131.1, 132.5, 132.6, 136.2. FD-MS (8kV):  $m/z = 1434.4$  (100%,  $M^+$ ). MALDI-TOF MS (dithranol):  $m/z = 1435.82$  (100%)  $[M+H]^+$ . ESI-HR MS calcd for  $C_{104}H_{112}Cl_2$  ( $[M+Na]^+$ ) 1453.8039, found 1453.7991.

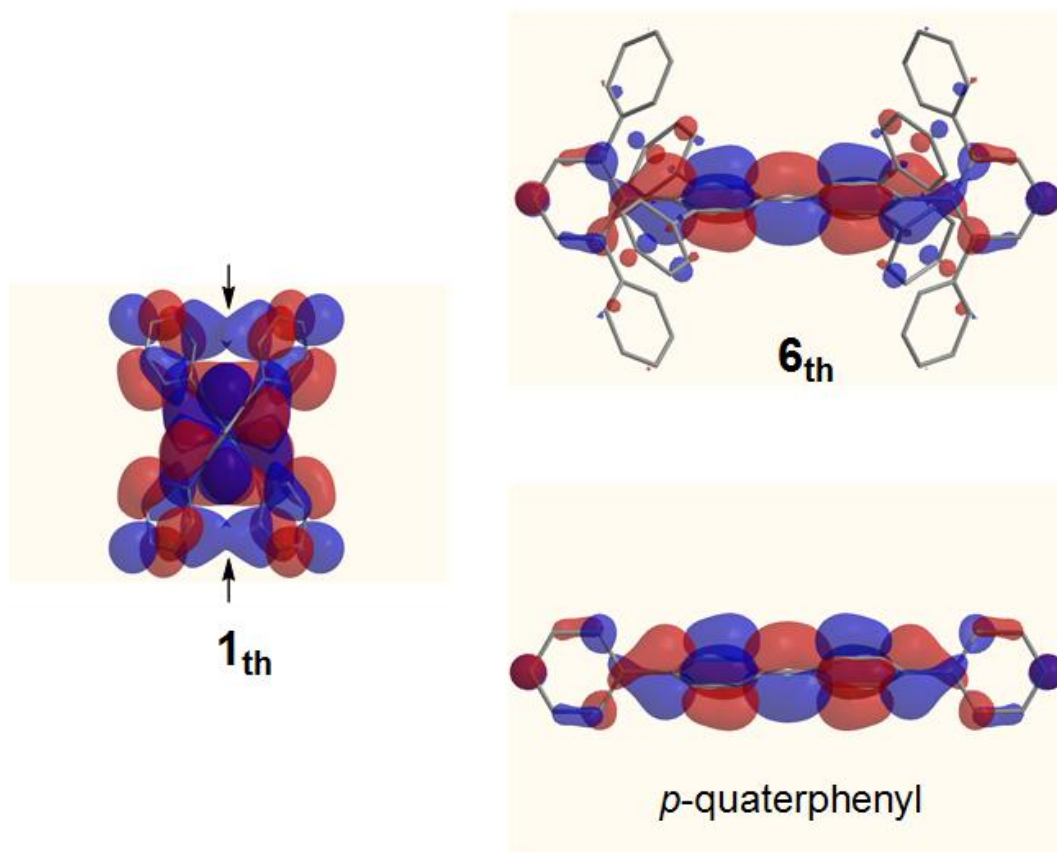
### Trimer **7**



$^1H$  NMR ( $CD_2Cl_2$ , 700 MHz,  $\delta$ ): 1.33 (s, 36H), 1.34 (s, 36H), 1.35 (s, 36H), 6.57 (dd,  $J_1 = 6$  Hz,  $J_2 = 2.2$  Hz, 16H), 6.63 (d,  $J = 8$  Hz, 8H), 7.03 (m, 24H), 7.19 (s, 4H), 7.53 (s, 8H).  $^{13}C$  NMR ( $CD_2Cl_2$ , 176 MHz,  $\delta$ ): 29.2, 29.7, 31.1, 34.2, 118.5, 124.2, 124.3, 125.0, 127.6, 128.6, 128.7, 128.8, 129.0, 130.7, 133.0, 133.9, 134.3, 134.5, 134.9, 137.3, 137.6, 138.3, 138.6, 138.8, 139.2, 142.8, 142.9, 144.0, 148.9, 149.0, 149.4, 153.7. FD-MS (8kV):  $m/z = 2113.4$  (100%,  $M^+$ ). MALDI-TOF MS (dithranol):  $m/z = 2114.34$  (100%)  $[M+H]^+$ . ESI-HR MS calcd for  $C_{156}H_{168}Cl_2$  ( $[M+Na]^+$ ) 2134.2421, found 2134.2405.



**Figure 5** HOMO and LUMO orbitals of **7<sub>th</sub>** (a), and *p*-sexiphenyl (b). Left: molecular structures, middle: HOMO orbitals, right: LUMO orbitals (isocounter value: 0.015 [a.u.] for all molecular orbitals).



**Figure 6** LUMO orbitals of **1<sub>th</sub>**, **6<sub>th</sub>**, and *p*-quaterphenyl (isocounter value: 0.010 [a.u.] for LUMO of **1<sub>th</sub>**, 0.026 [a.u.] for LUMO of **6<sub>th</sub>** and *p*-quaterphenyl).

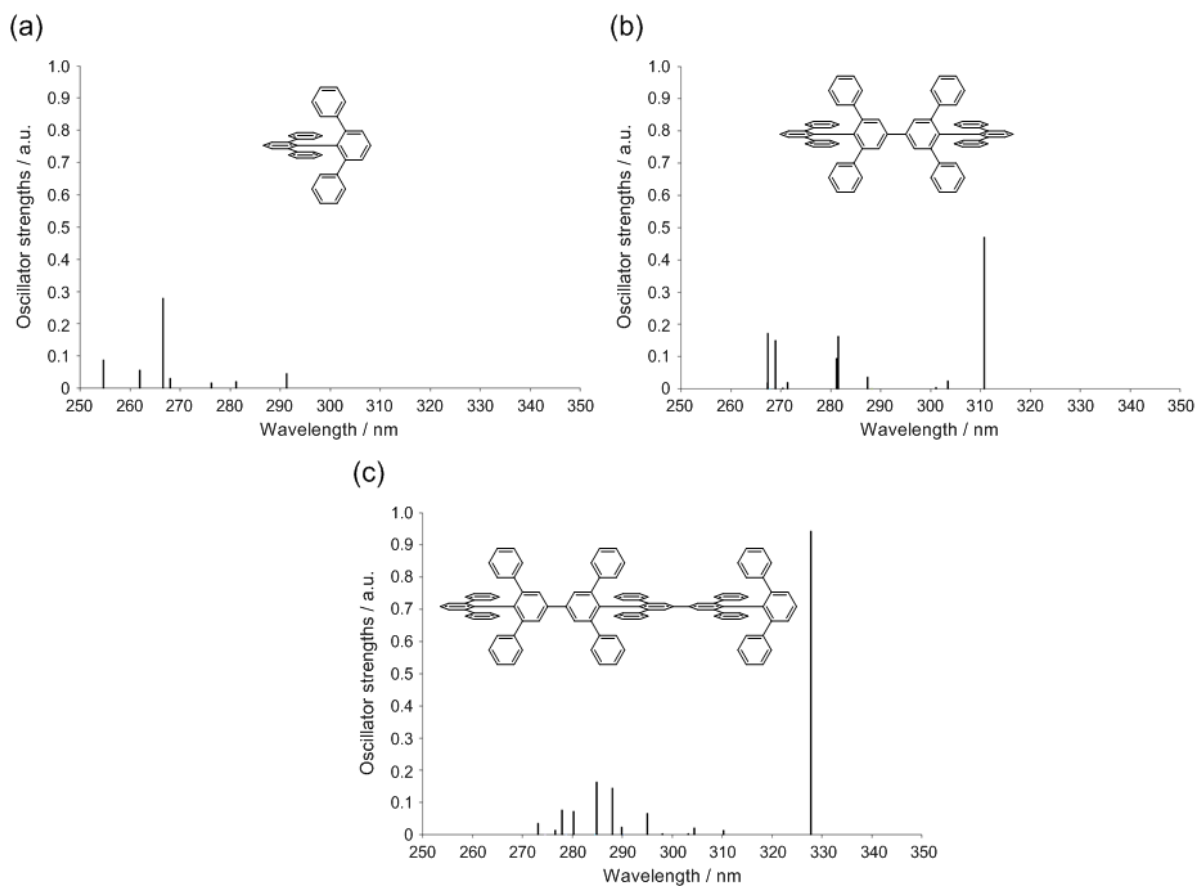


Figure 7 TD-DFT calculations of  $1_{th}$  (a),  $6_{th}$  (b), and  $7_{th}$  (c) (B3LYP/6-31G\*// B3LYP/6-31G\*).

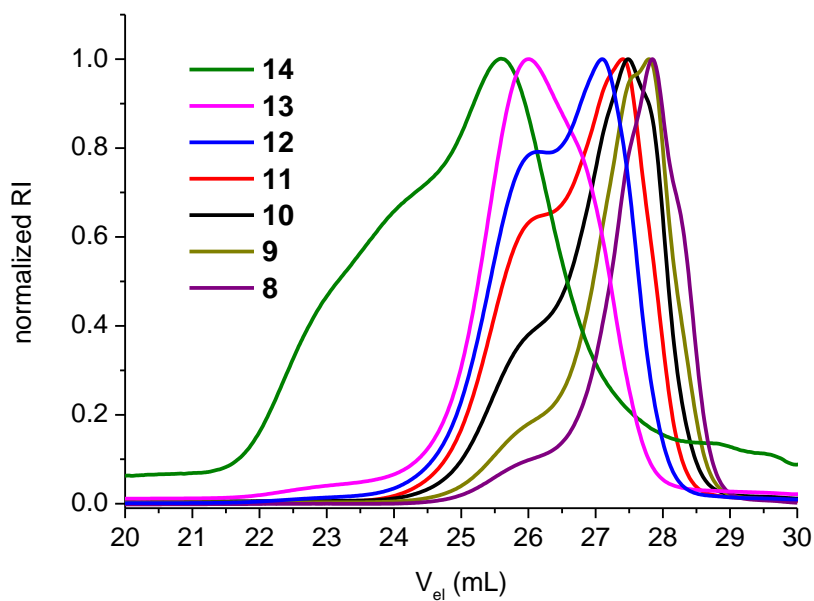
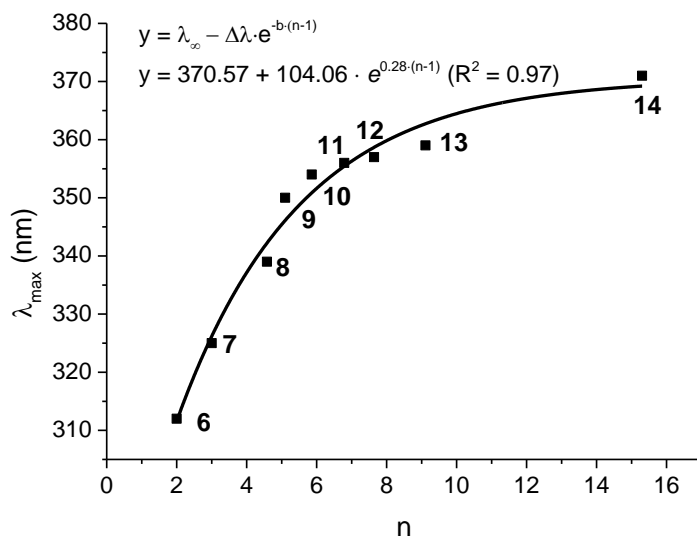
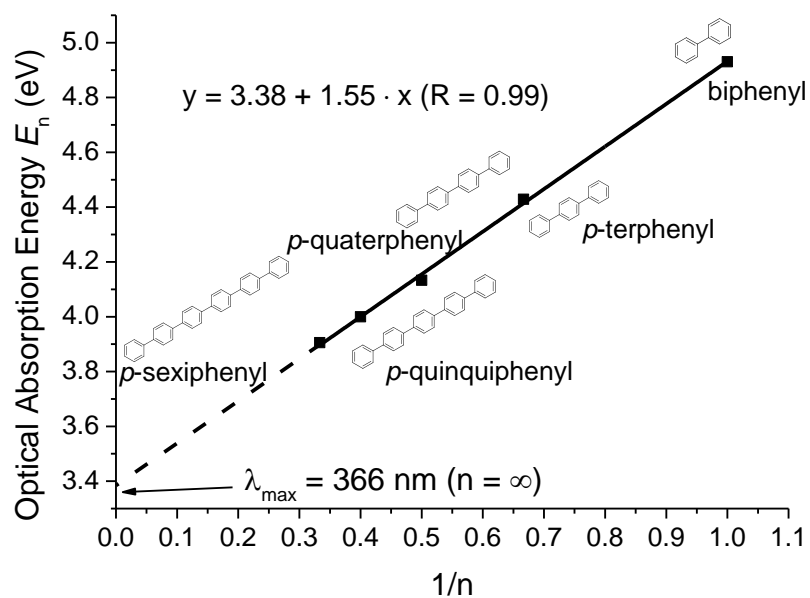


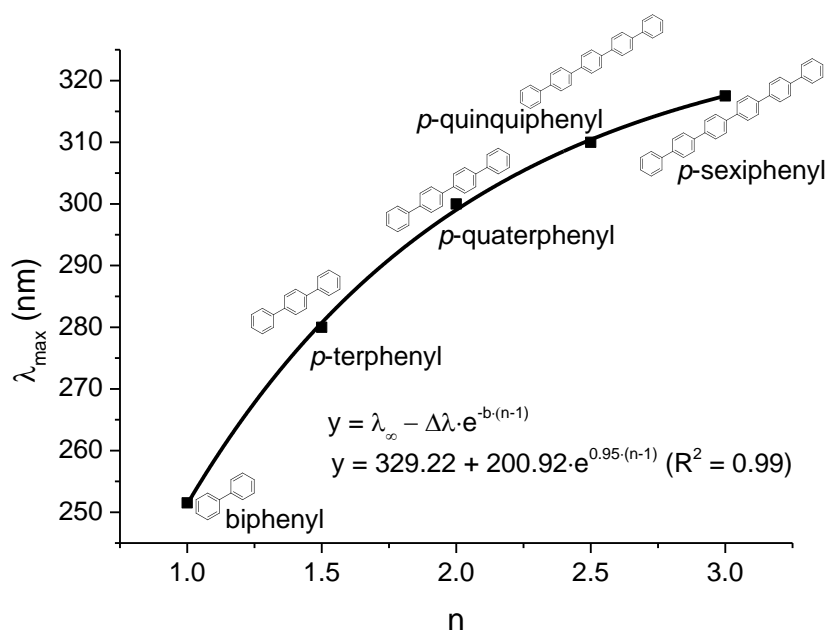
Figure 8 SEC analysis of 8-14.



**Figure 9** Plot of the absorption maxima ( $\lambda_{\max}$ ) of **6-14** with the number of the repeating units. The curve corresponds to the exponential fit.<sup>8</sup>



**Figure 10** Correlation of the optical absorption energy ( $E_n$ ) of unsubstituted PPP with the inverse number of the repeating units and the linear equation (for all spectra:  $10^{-6} \text{ M}$  in  $\text{CHCl}_3$ ).<sup>9</sup>



**Figure 11** Correlation of the absorption maxima ( $\lambda_{\max}$ ) of unsubstituted PPP with the number of the repeating units. The curve corresponds to the exponential fit (for all spectra:  $10^{-6}$  M in  $\text{CHCl}_3$ ).<sup>8,9</sup>

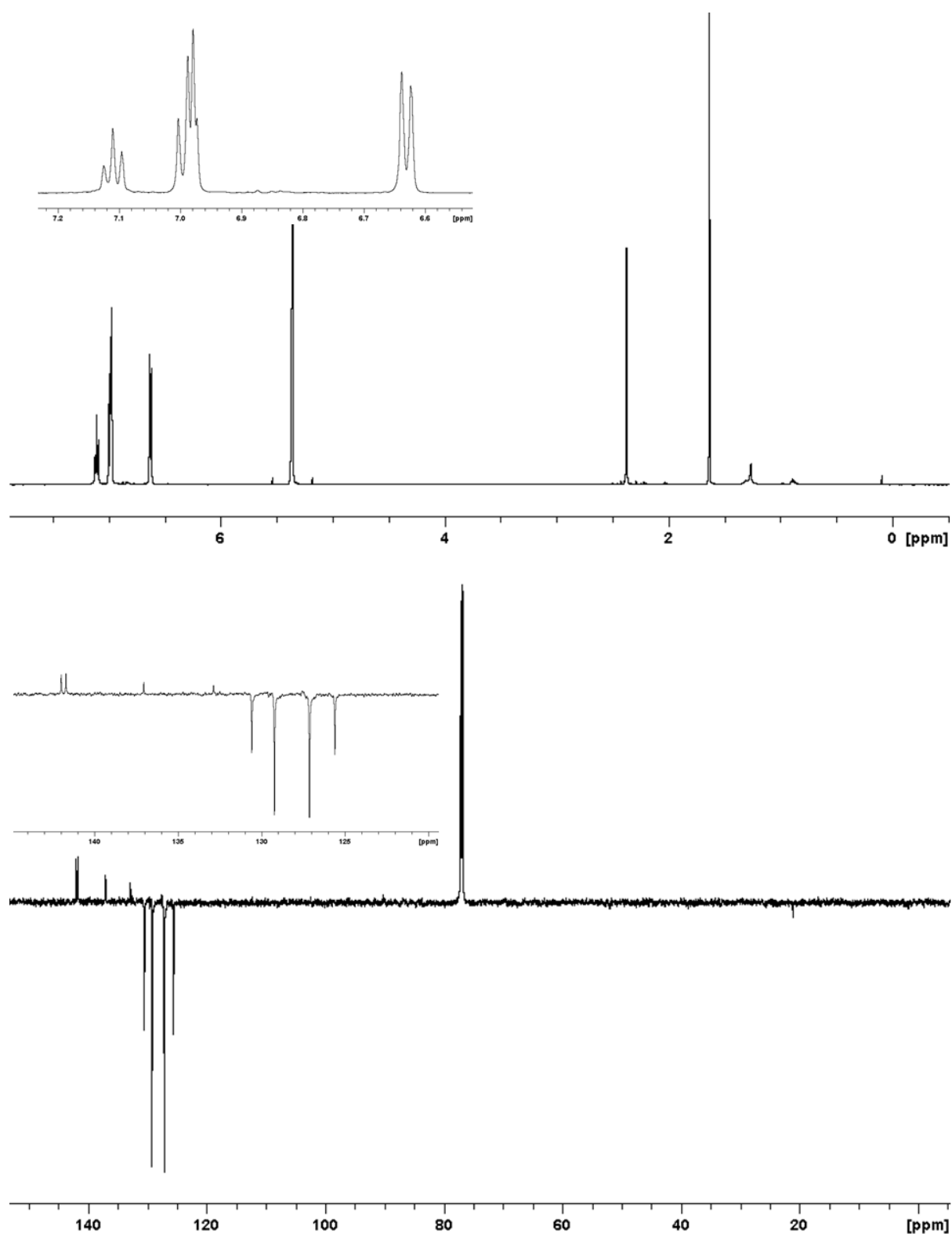


Figure 12  $^1\text{H}$  (top) and  $^{13}\text{C}$  spinecho (bottom) NMR spectra of **1a**.

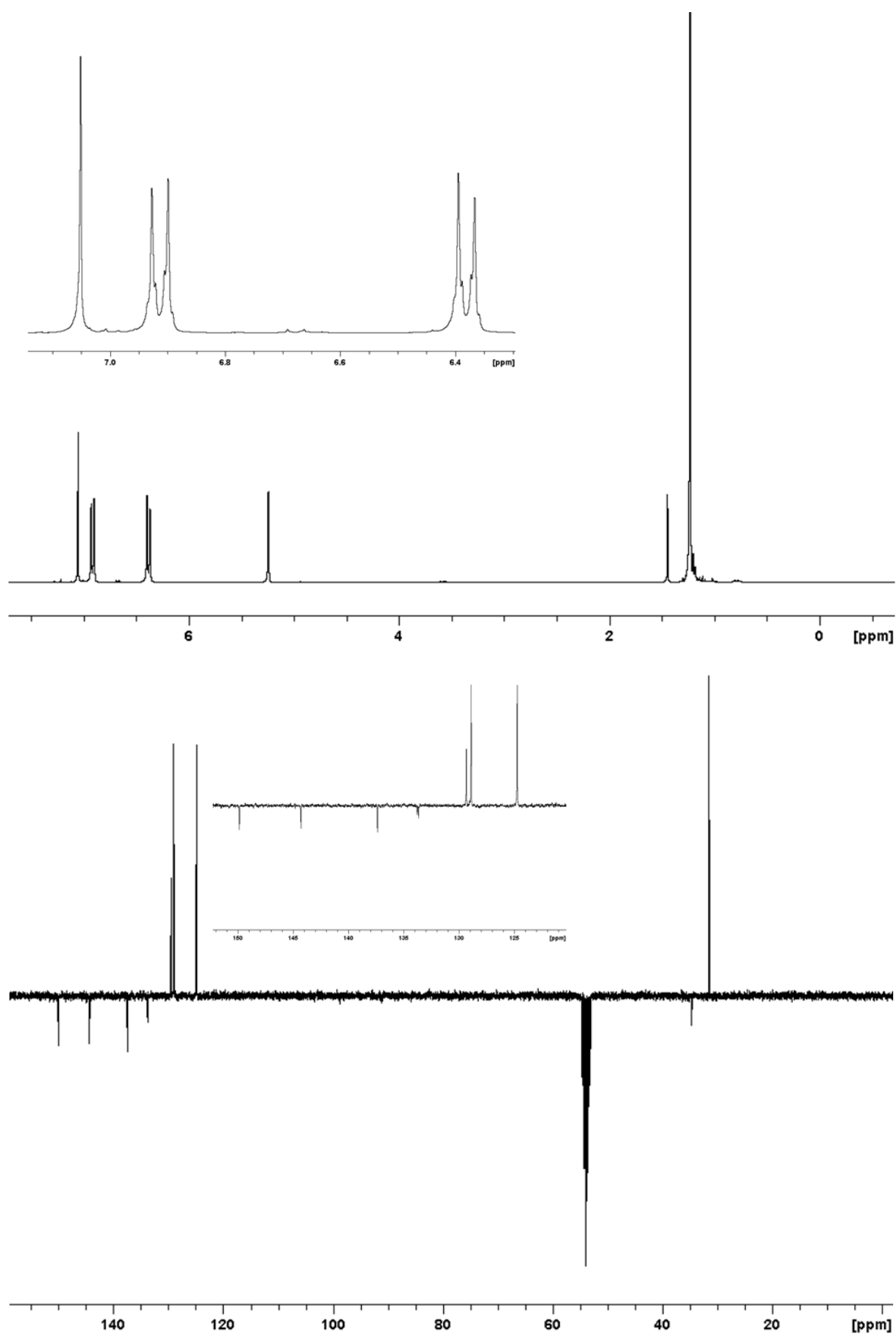
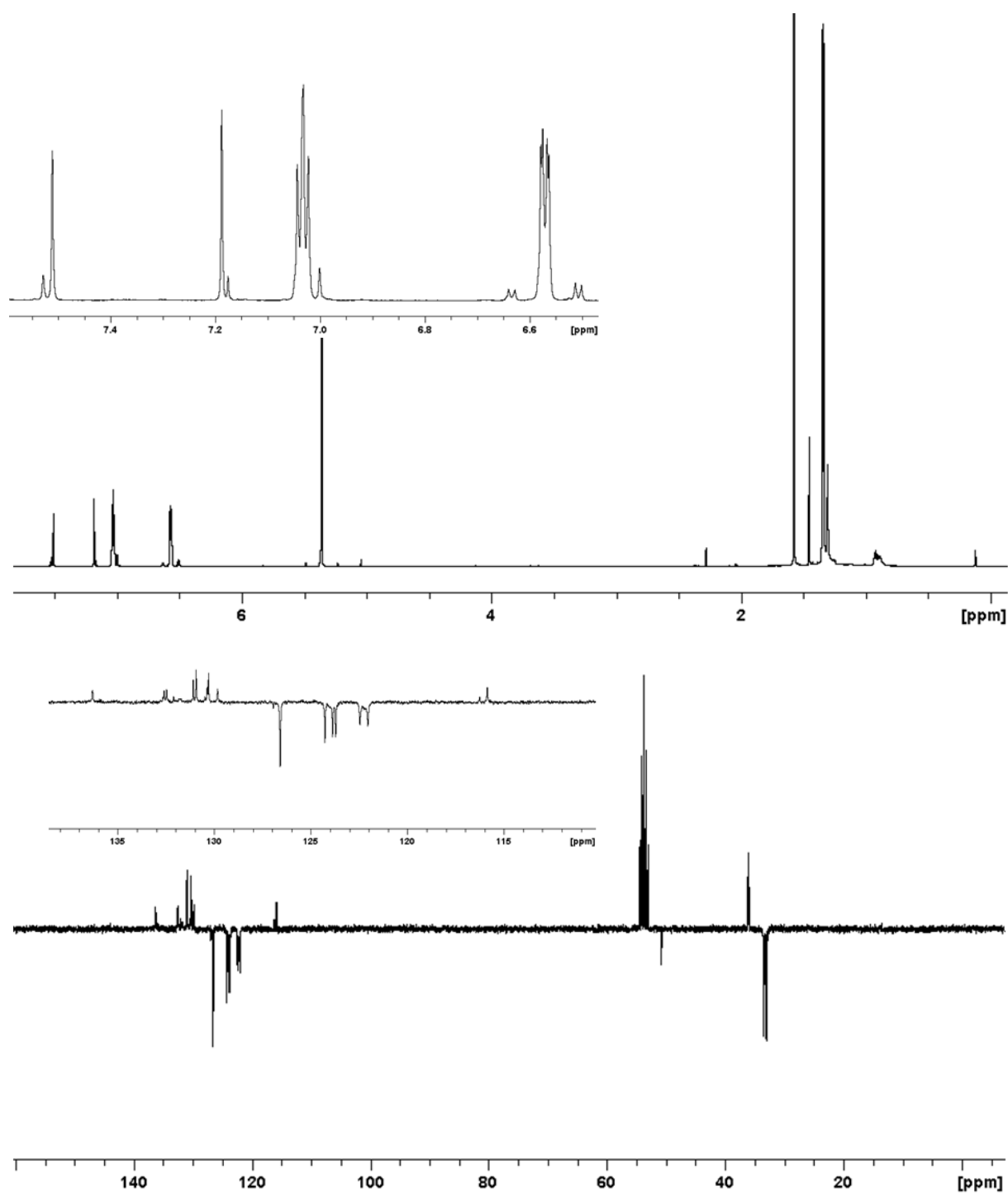


Figure 13  $^1\text{H}$  (top) and  $^{13}\text{C}$  spinecho (bottom) NMR spectra of 1b.





**Figure 14**  $^1\text{H}$  (top) and  $^{13}\text{C}$  spinecho (bottom) NMR spectra of **6**.

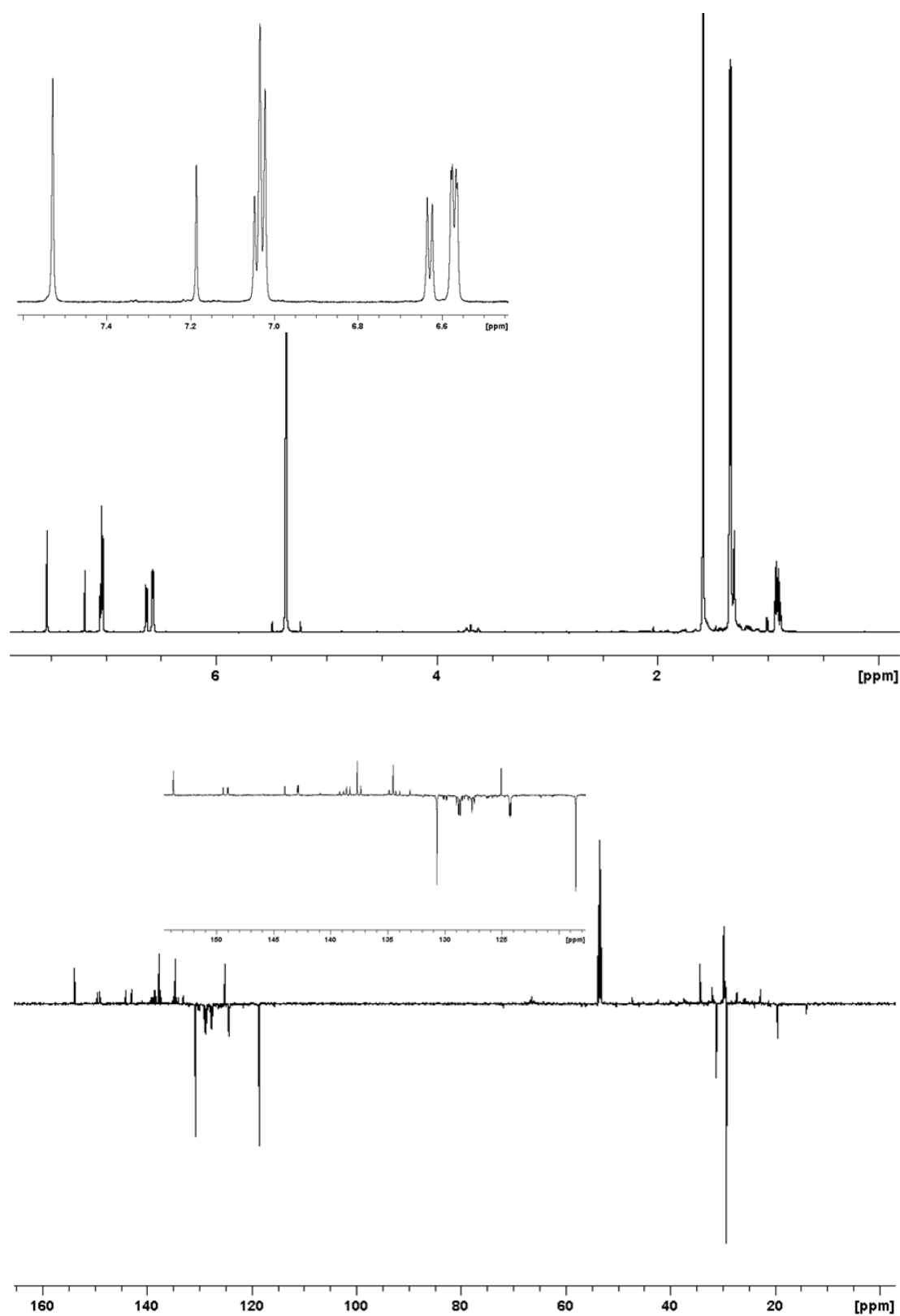
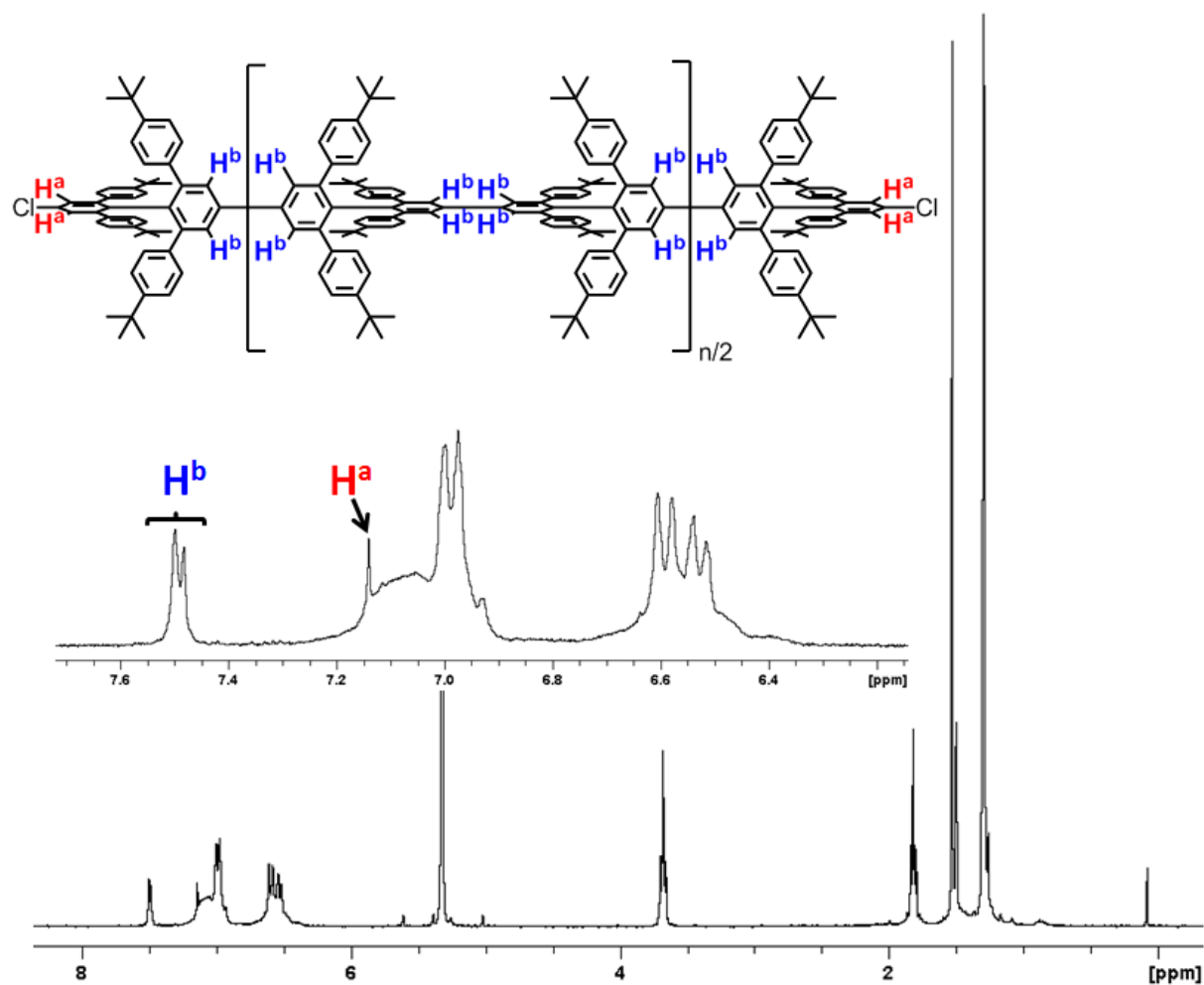
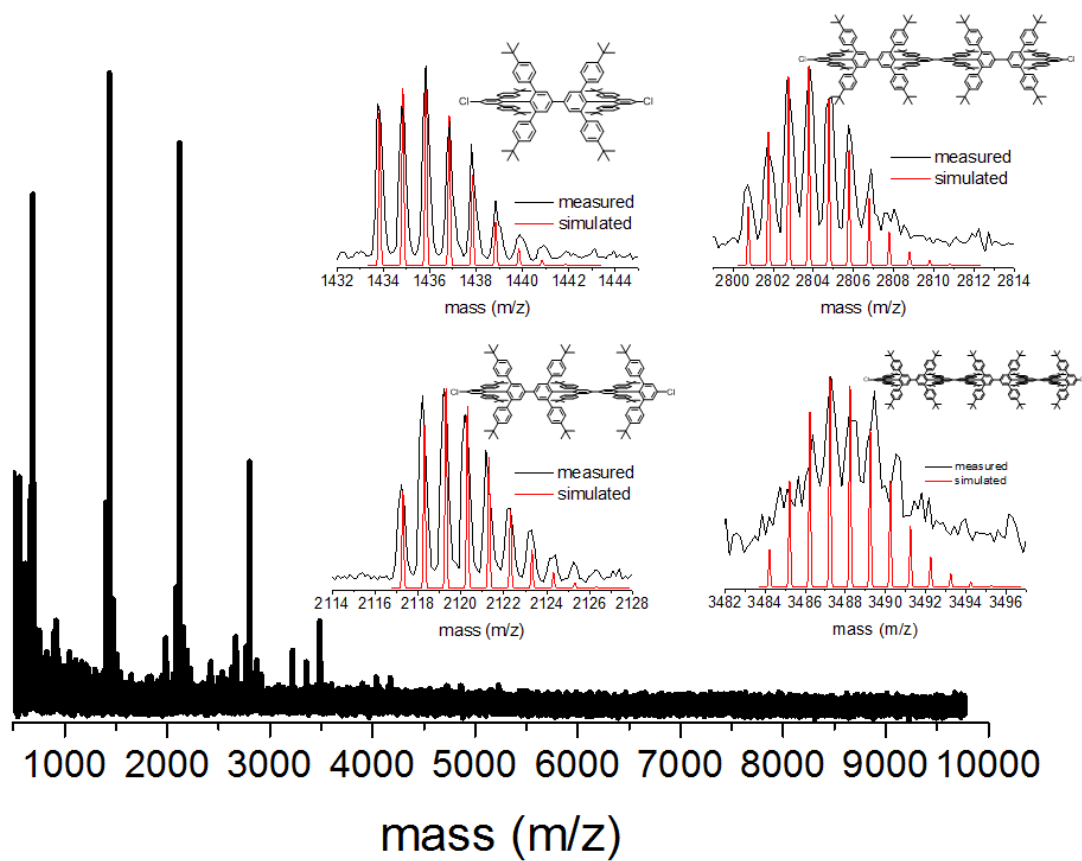


Figure 15  $^1\text{H}$  (top) and  $^{13}\text{C}$  spinecho (bottom) NMR spectra of 7.



**Figure 16**  $^1\text{H}$  NMR spectrum of the isolated polymer after *Yamamoto* coupling. Inset: Zoom into the aromatic region of the spectrum together with the structure of a polymer chain with highlighted 3,5- and 3',5'-protons and the respective assignment.



**Figure 17** MALDI-TOF MS of the isolated polymer after *Yamamoto* coupling. Inset: Measured (black line) and simulated (red line) isotopic pattern of the dimer, trimer, tetramer and pentamer.

## References

1. S. Ozasa, Y. Fujioka, J. Kikutake and E. Ibuki, *Chem. Pharm. Bull.*, 1983, **31**, 1572-1581.
2. Y. Fujioka, S. Ozasa, K. Sato and E. Ibuki, *Chem. Pharm. Bull.*, 1985, **33**, 22-29.
3. L. Tong, H. Lau, D. M. Ho and R. A. Pascal, *J. Am. Chem. Soc.*, 1998, **120**, 6000-6006.
4. Crystal data for **II** (CCDC 918310 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)): Single crystals of **II** were obtained by slow evaporation of a dichloromethane solution. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON (A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7).  $C_{36}H_{26}$ ,  $M = 458.60$ , triclinic, P-1,  $a = 9.9080(2)$ ,  $b = 10.7787(3)$ ,  $c = 12.7321(3)$  Å,  $\alpha = 97.6691(12)$ ,  $\beta = 94.7545(14)$ ,  $\gamma = 115.8972(11)^\circ$ .  $R = 0.0482$ ,  $R_w = 0.0590$ .
5. Crystal data for **IIIb** (CCDC 918311 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)): Single crystals of **IIIb** were obtained by slow evaporation of a dichloromethane/methanol solution. The unit cell contains 16  $CH_3OH$  molecules. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON (A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7).  $C_{36.5}H_{25}Cl_3$ ,  $M = 569.96$ , monoclinic, P21/c,  $a = 7.5317(7)$ ,  $b = 21.0519(9)$ ,  $c = 17.7743(8)$  Å,  $\beta = 94.802(5)^\circ$ .  $R = 0.0464$ ,  $R_w = 0.0571$ .
6. Crystal data for **1a** (CCDC 918312 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)): Single crystals of **1a** were obtained by slow evaporation of a dichloromethane/methanol solution. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON (A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7).  $C_{38}H_{30}$ ,  $M = 486.66$ , monoclinic, C2/c,  $a = 7.3789(2)$ ,  $b = 22.1571(8)$ ,  $c = 16.3043(5)$  Å,  $\beta = 102.0571(18)^\circ$ .  $R = 0.0423$ ,  $R_w = 0.0502$ .
7. Crystal data for **1b** (CCDC 918313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)): Single crystals of **1b** were obtained by slow evaporation of a dichloromethane solution. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON (A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7).  $C_{52}H_{56}Cl_2$ ,  $M = 751.92$ , orthorhombic, Fddd,  $a = 13.8723(4)$ ,  $b = 17.3314(3)$ ,  $c = 37.5890(5)$  Å,  $\beta = 90.0000(00)^\circ$ .  $R = 0.0601$ ,  $R_w = 0.0766$ .

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