Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters
Tetrahedron Letters 45 (2004) 5367–5370

A convenient synthetic approach to bis-functionalised quaterfluorenes

Roberto Grisorio,[a] Piero Mastrorilli,[a] Cosimo Francesco Nobile,[a] Giuseppe Romanazzi,[a] Gian Paolo Suranna[a,*] and E. W. Meijer[b]

[a]*Department of Water Engineering and of Chemistry (DIAC), Polytechnic of Bari, via Orabona, 4 I-70125 Bari, Italy*
[b]*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*

Received 21 April 2004; revised 13 May 2004; accepted 17 May 2004

Abstract—$Ni(COD)_2$ promoted coupling of bromofluorenes functionalised with boronic esters or trimethylsilyl groups proves to be an efficient method for the preparation of reactive bifluorenes, which are key intermediates for the synthesis of bis-substituted oligofluorenes. The synthetic method has been exploited as a key step for the synthesis of a chiral 2,7‴-diiodo-quaterfluorene and a 2,7‴-bis-amino quaterfluorene.

Organic π-conjugated macromolecules increasingly attract industrial and scientific interest because of their potential applications in optoelectronic devices.[1] Their plastic properties, unattainable with traditional inorganic substances, can be exploited for the construction of light emitting diodes (LEDs) to be used in large area and flexible displays. In previous years synthetic efforts have been aimed at obtaining well-defined π-conjugated oligomers which, different from the corresponding polymers, can be synthesised with very high purities, indispensable for LEDs spectral stability.[2] Among them, chiral oligofluorenes are the subject of intense investigations[3] because of their strong blue and circularly polarised light emission.

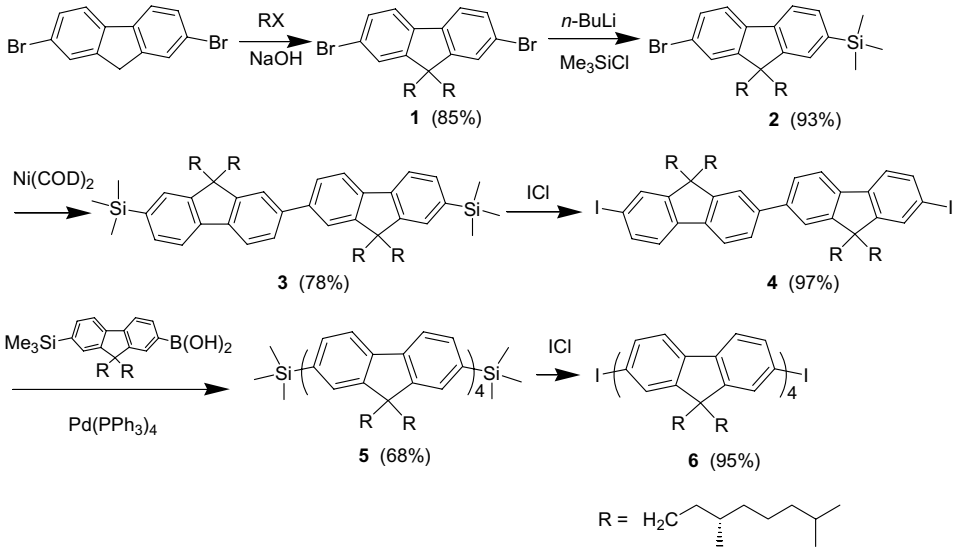
In the framework of the acknowledged procedures for the synthesis of oligofluorenes, bromination of the aromatic rings, usually carried out with $Br_2/FeCl_3$, is the crucial step for further chain growth,[4] because it provides suitable intermediates that can be used in Suzuki–Miyaura and Stille cross-couplings either as such, or after conversion into their corresponding boron or tin derivatives.[5] However, bromination may not proceed with the desired regioselectivity and can produce impurities of structural isomers, often difficult to remove,[6] which can be deleterious for the final performance of the electroluminescent device.

Here we report the use of the Yamamoto coupling reaction for a simple and high-yielding synthesis of the 2,7′-bis(trimethylsilyl)-{9,9,9′,9′-tetrakis[(*S*)-3,7-dimethyloctyl]-7,2′-bifluorene (**3**) and of the 2,2′-{9,9,9′,9′-tetrakis[(*S*)-3,7-dimethyloctyl]-2,2′-bifluoren-7,7′-diyl}-bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane) (**8**), which are high-value intermediates for the preparation of new quaterfluorene derivatives. Compound **4** has in fact been successfully used for the synthesis of the new 2,7‴-diiodo-9,9,9′,9′,9″,9″,9‴,9‴-octakis[(*S*)-3,7-dimethyloctyl]-7,2′;7′,2″;7″,2‴-quaterfluorene (**6**) whereas **8** has been the building block for the obtainment of the new 2,7‴-bis-amino-9,9,9′,9′,9″,9″,9‴,9‴-octakis[(*S*)-3,7-dimethyloctyl]-7,2′;7′,2″;7″,2‴-quaterfluorene (**11**).

The interest for new efficient synthetic approaches for the obtainment of bis-functionalised oligofluorenes is justified by the facile modulation of their optical and charge injection properties by means of the introduction of specific end groups.[7] For instance, the presence of reactive iodides in **6** makes it the ideal substrate for further functionalisation in order to create cross-linkable or supramolecular polymers, while the amines in

Keywords: Oligofluorenes; Ni(0) promoted coupling; Amines; Boronic esters.
* Corresponding author. Tel.: +39-0805963603; fax: +39-0805963611; e-mail: surannag@poliba.it

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.05.074

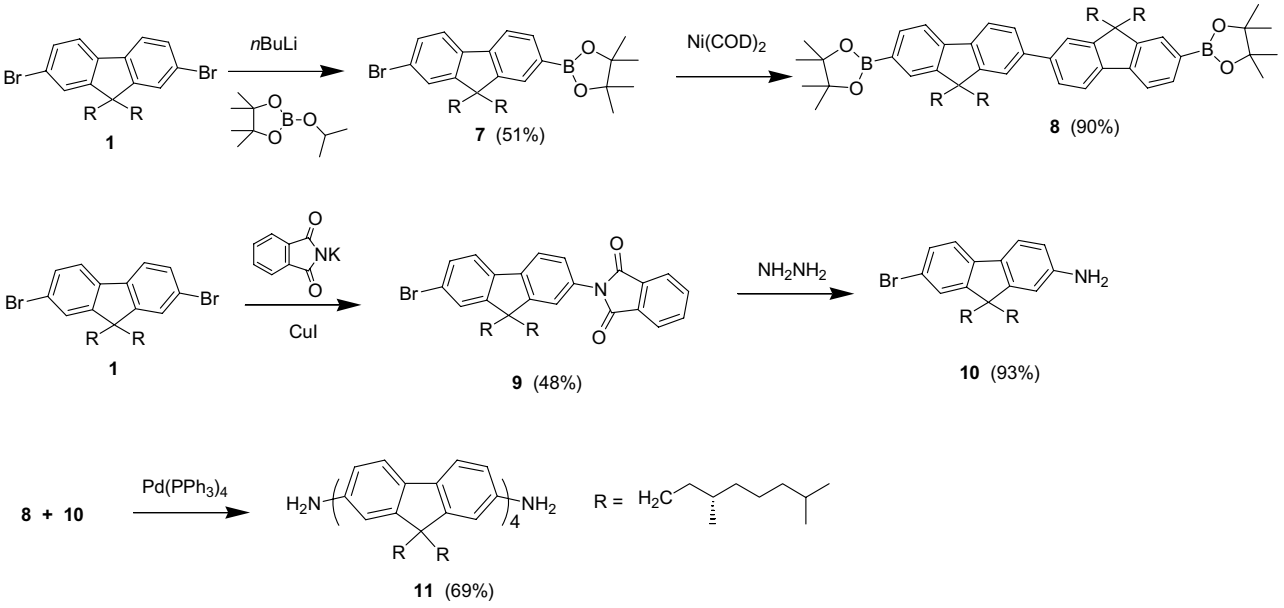


Scheme 1. Synthesis of **6**.

11, could facilitate, as electron-donor groups, the hole injection by raising the HOMO energy level.[8]

The synthesis of **6** is depicted in Scheme 1 and started from the commercially available 2,7-dibromo-fluorene, which was reacted with (*S*)-3,7-dimethyloctyl-bromide in a NaOH aqueous solution to afford **1** in 85% yield. Minor impurities of mono-alkyl derivatives (<1%), the presence of which may lead to keto-defects under LEDs operating conditions, have been removed by treating **1** with an excess solution of ^{t}BuOK in THF.[9] Subsequent lithiation with one equiv of *n*-BuLi and reaction with trimethylsilyl chloride yielded **2** in 93% yield. The $Ni(COD)_2$-promoted dimerisation of **2** gave the 2,7′-bistrimethylsilyl-bifluorene **3**[10] in 80% yield, which was transformed into the corresponding bis-iodide **4**[11] by ICl in 97% yield. It can therefore be concluded that the Yamamoto coupling conditions are tolerant towards trimethylsilyl groups, which can be used as protective moieties during C–C linkage step and easily converted into reactive iodides. Submitting **4** to a Suzuki reaction with two equiv of 2-trimethylsilyl-9,9-bis[(*S*)-3,7-dimethyloctyl]-fluoren-7-yl-boronic acid[2] and treating the obtained quaterfluorene derivative **5**[12] with ICl afforded the 2,7‴-diiodo-quaterfluorene derivative **6**.[13]

We have tested the reactivity of **6** in the synthesis of **11**, which has been achieved via copper catalysed amino-dehalogenation of **6** with potassium phthalimide[14] followed by reaction with hydrazine. However, unsatisfactory yields in the first step (less than 10%), directed our efforts towards an alternative approach, namely the



Scheme 2. Synthesis of **11**.

Pd-catalysed Suzuki coupling reaction between the bis(boronate) **8**[15] and the 2-bromo-7-aminofluorene derivative **10** (Scheme 2).

The synthesis of **8**[16] is depicted in Scheme 2. The lithiation of **1** with 1 equiv of *n*-BuLi, followed by treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, gave the boronic ester **7**, which was submitted to a $Ni(COD)_2$ promoted Yamamoto coupling reaction. The Yamamoto aryl–aryl coupling is usually employed in synthetic procedures to achieve several types of π-conjugated polymers; to the best of our knowledge, this is the first example of a Yamamoto coupling reaction[17] of aryl bromides bearing boronic ester moieties.[18] The potential risks of transmetallation, and consequent polymerisation could in fact dissuade from the use of $Ni(COD)_2$ in the presence of boron derivatives,[19] although the fact that the Yamamoto coupling does not involve the use of a base, encouraged our choice. The reaction afforded **8** in 90% yield and can thus be considered a powerful and general tool for increasing the oligomeric unit, while preserving reactive groups, like boronates.

Compound **10** was obtained in two steps starting from **1** (Scheme 2). The copper catalysed amino-dehalogenation of **1** with 1 equiv of potassium phthalimide yielded 48% of **9**,[20] which was reacted with $NH_2NH_2{\cdot}H_2O$ giving **10**[21] in 93% yield. Compound **11**[22] was synthesised in good yield by reacting 2 equiv of **10** with **8** in the above cited Suzuki coupling.

In conclusion, we have described the synthesis of two new quaterfluorenes. In both cases the synthesis of the bifluorenyl 'core' used for the subsequent reactions with 2 equiv of suitable end-cappers was achieved by a $Ni(COD)_2$ promoted coupling of suitable bromofluorenes (**2** or **7**). The proposed strategy represents a valid alternative to bromination and subsequent functionalisation of bifluorenes and bears a high potential as a simple and high-yielding method for the preparation of reactive fluorene oligomers.

Acknowledgements

This work was financially supported by the FIRB project MICROPOLYS. The authors are indebted to Dr. Giuseppe Ciccarella (University of Lecce) for conducting the APCI-mass spectrometric measurements and to Dr. Antonino Rizzuti for useful discussions.

References and notes

1. Müller, D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829, and references cited therein.
2. Geng, Y.; Culligan, S.; Trajkovska, A.; Wallace, J.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542.
3. Geng, Y.; Trajkovska, A.; Katsis, D.; Ou, J. J.; Culligan, S. W.; Chen, S. H. J. *J. Am. Chem. Soc.* **2002**, *124*, 8337.
4. Ding, J.; Day, M.; Robertson, G.; Roovers, J. *Macromolecules* **2002**, *35*, 3474.
5. Babudri, F.; Farinola, G.; Naso, F. *J. Mater. Chem.* **2004**, *14*, 11.
6. Zhou, X. H.; Yan, J. C.; Pei, J. *Org. Lett.* **2003**, *5*, 3543.
7. Miteva, T.; Meisel, A.; Knoll, W.; Nohofer, H. G.; Scherf, U.; Müller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater.* **2001**, *13*, 565.
8. Beaupré, S.; Leclerc, M. *Macromolecules* **2003**, *36*, 8986.
9. Craig, M. R.; de Kok, M. M.; Hofstraat, J. W.; Schenning, A. P. H. J.; Meijer, E. W. *J. Mater. Chem.* **2003**, *13*, 2861.
10. *Synthesis of* **3**: A mixture of **2** (4.80 g, 8.0 mmol), $Ni(COD)_2$ (2.64 g, 9.6 mmol), bipyridine (1.50 g, 9.6 mmol) and COD (0.86 g, 8.0 mmol) in toluene (50.0 mL) was stirred at 80 °C overnight. After cooling to room temperature, the solution was filtered on a Celite plug washing the residue with petroleum ether (bp 40–60 °C). After solvent evaporation, the crude was purified by flash chromatography (silica gel, petroleum ether bp 40–60 °C) to yield **3** (80%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.82 (m, 2H), 7.73–7.76 (m, 2H), 7.62–7.67 (m, 4H), 7.51–7.56 (m, 4H), 1.99–2.15 (m, 8H), 1.40–1.52 (m, 4H), 1.02–1.27 (m, 24H), 0.54–0.97 (m, 48H), 0.32 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 150.1, 141.6, 140.7, 140.3, 138.9, 131.8, 127.7, 126.0, 121.5, 120.0, 119.0, 54.9, 39.2, 37.4, 36.6, 32.9, 30.6, 30.5, 27.9, 24.7 (two overlapping signals), 22.7, 22.6, 19.6, 19.5, −0.8.
11. *Synthesis of* **4**: To a solution of **3** (2.20 g, 2.1 mmol) in CH_2Cl_2 (12.0 mL), a 1.0 M ICl solution (4.5 mL, 4.5 mmol) was slowly added at 0 °C in 30′, and the mixture was stirred for a further 60′ at room temperature. The reaction was quenched with an aqueous $Na_2S_2O_3$ solution (10% wt), added dropwise until discolouration was observed. After extraction with methylene chloride and solvent evaporation, the crude residue was purified by flash chromatography (silica gel, petroleum ether bp 40–60 °C) to yield **4** (97%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, $J = 7.95$ Hz, 2H), 7.69–7.73 (m, 4H), 7.63 (d, $J = 7.95$ Hz, 2H), 7.58 (s, 2H), 7.51 (d, $J = 7.63$ Hz, 2H), 1.99–2.15 (m, 8H), 1.40–1.52 (m, 4H), 1.02–1.27 (m, 24H), 0.54–0.97 (m, 48H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 150.8, 141.1, 140.5, 139.5, 139.4, 135.9, 132.1, 126.3, 121.5, 120.0, 92.5, 55.3, 39.2, 37.5, 37.4, 36.7, 36.5, 32.8, 30.5, 27.9, 24.7, 22.7, 22.6, 19.6, 19.5.
12. *Synthesis of* **5**: A mixture of **4** (0.86 g, 0.6 mmol), 2-trimethylsilyl-9,9-bis[(*S*)-3,7-dimethyloctyl]-fluoren-7-yl-boronic acid (0.84 g, 1.5 mmol), $Pd(PPh_3)_4$ (60.0 mg, 5×10^{-2} mmol), toluene (14.0 mL) and 2.0 M Na_2CO_3 solution (5.0 mL) was stirred at 90 °C for 2 days. After cooling to room temperature, petroleum ether (bp 40–60 °C) was added. The organic layer was separated and dried over Na_2SO_4. After solvent evaporation, the crude residue was purified by flash chromatography (silica gel, petroleum ether bp 40–60 °C) to yield **5** (68%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.82 (m, 6H), 7.72 (d, $J = 7.13$ Hz, 2H), 7.60–7.68 (m, 12H), 7.48–7.53-(m, 4H), 1.87–2.15 (m, 16H), 1.37–1.51 (m, 8H), 1.02–1.27 (m, 48H), 0.54–0.97 (m, 96H), 0.32 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 151.3, 150.8, 150.5, 141.5, 140.7, 140.5, 140.2, 139.2, 138.9, 138.6, 131.8, 131.2, 128.2, 127.5, 127.0, 126.3, 125.5, 121.5, 119.9, 119.1, 118.8, 55.0, 54.8, 39.2, 37.5, 36.6, 32.8, 30.7, 30.5, 27.9, 24.7, 22.7, 22.6, 19.5, −0.9.
13. *Synthesis of* **6**: To a solution of **5** (1.00 g, 0.5 mmol) in CH_2Cl_2 (4.0 mL), a 1.0 M ICl solution (1.0 mL, 1.0 mmol)

was slowly added at 0 °C in 30′, and the resulting mixture was stirred for a further 60′ at room temperature. The reaction was quenched with an aqueous $Na_2S_2O_3$ solution (10% wt), added dropwise until discolouration was observed. After extraction with methylene chloride and solvent evaporation, the crude residue was purified by flash chromatography (silica gel, petroleum ether bp 40–60 °C) to yield **6** in 95% as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.87 (m, 24H), 1.90–2.14 (m, 16H), 1.34–1.50 (m, 8H), 1.00–1.27 (m, 48H), 0.56–0.98 (m, 96H).

14. Lindley, J. *Tetrahedron* **1984**, *40*, 1433.
15. Any attempt aimed at obtaining the corresponding bis-trimethylstannyl or bis-boronic acid derivatives by means of lithiation of **4** and subsequent reaction with Me_3SnCl or $B(O^iPr)_3$, respectively, was unsuccessful because of difficulties in removing byproducts.
16. *Synthesis of* **8**: A mixture of **7** (2.20 g, 3.4 mmol), $Ni(COD)_2$ (1.20 g, 4.0 mmol), bipyridine (0.63 g, 4.0 mmol) and COD (0.36 g, 3.4 mmol) in toluene (20.0 mL) was stirred at 80 °C overnight. After cooling to room temperature, the solution was filtered on a Celite plug with petroleum ether as eluent. Upon evaporating off the solvent, the residue was purified with a short silica gel plug with CH_2Cl_2 as eluent to yield **8** in 90% as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.89 (m, 8H), 7.58–7.67 (m, 4H), 1.99–2.15 (m, 8H), 1.40–1.52 (m, 28H), 1.02–1.27 (m, 24H), 0.54–0.97 (m, 48H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 150.3, 144.1, 141.0, 140.0, 133.8, 128.5, 126.2, 121.7, 120.3, 119.0, 83.7, 55.0, 39.2, 36.6, 36.5, 32.9, 30.6, 27.1, 24.9, 24.6, 22.7, 19.6, 19.5.
17. Yamamoto, T.; Wakabayashi, S.; Osakada, K. *J. Organomet. Chem.* **1992**, *428*, 223.
18. Recently, it has been demonstrated that the Yamamoto coupling can also tolerate unprotected arylamine functions: Güntner, R.; Asawapirom, U.; Forster, M.; Schmitt, C.; Stiller, B.; Tiersch, B.; Falcou, A.; Nothofer, H.-G.; Scherf, U. *Thin Solid Films* **2002**, *417*, 1.
19. Tang, Z. Y.; Hu, Q. S. *J. Am. Chem. Soc.* **2004**, *126*, 3058.
20. *Synthesis of* **9**: A mixture of **1** (5.00 g, 8.3 mmol), CuI (1.58 g, 8.3 mmol) and potassium phthalimide (1.53 g, 8.3 mmol) in DMA (130.0 mL) was refluxed for 2 days. After cooling to room temperature, water was added to the reaction mixture and the products extracted with petroleum ether. The organic phase was washed with brine and dried over Na_2SO_4. After solvent evaporation, the crude residue was purified by flash chromatography (silica gel, petroleum ether bp 40–60 °C/CH_2Cl_2 = 100:0, 75:25 then 50:50) to yield **9** (48%) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–8.02 (m, 2H), 7.78–7.85 (m, 3H), 7.59–7.63 (d, J = 8.58 Hz, 1H), 7.43–7.52 (m, 4H), 1.99–2.15 (m, 4H), 1.40–1.52 (m, 2H), 1.02–1.27 (m, 12H), 0.54–0.97 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 153.3, 151.0, 139.7, 139.4, 134.4, 131.8, 130.9, 130.1, 126.2, 125.1, 123.7, 121.5, 121.3, 121.1, 120.1, 55.5, 39.2, 37.5, 37.2, 36.7, 36.5, 32.9, 32.8, 30.6, 30.4, 27.9, 24.6, 24.5, 22.7, 22.6, 19.5; IR (CsI): ν [cm^{-1}] 2927, 2867, 1778, 1728, 1612, 1456, 1372, 1230, 813, 715.
21. *Synthesis of* **10**: To a solution of **9** (0.98 g, 1.5 mmol) in ethanol (60.0 mL), $NH_2NH_2{\cdot}H_2O$ (73.0 mg, 1.5 mmol) was added in one portion. The mixture was refluxed for 3 h. After cooling to room temperature, the solution was filtered. After solvent evaporation, the residue was purified by passage through a short silica gel plug using CH_2Cl_2 as eluent, to yield **10** (93%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.48 (m, 4H), 6.62–6.70 (m, 2H), 3.85 (s, 2H), 1.99–2.15 (m, 4H), 1.40–1.52 (m, 2H), 1.02–1.27 (m, 12H), 0.54–0.97 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) 152.3, 152.0, 146.2, 140.7, 131.4, 129.7, 125.7, 120.6, 119.6, 119.0, 114.1, 109.6, 54.9, 39.2, 37.8, 37.7, 36.6, 32.9, 30.4, 27.9, 24.6, 24.5, 22.7, 22.6, 19.5; IR (CsI): ν [cm^{-1}] 3477, 3382, 2927, 2867, 1733, 1616, 1456, 1373, 1215, 809.
22. *Synthesis of* **11**: a mixture of **8** (0.51 g, 0.45 mmol), **10** (0.49 g, 0.90 mmol), $Pd(PPh_3)_4$ (0.10 g, 9×10^{-2} mmol), toluene (5.0 mL), ethanol (1.0 mL) and a 2.0 M Na_2CO_3 solution (2.0 mL) was refluxed for 2 days. After the solution was cooled to room temperature, diethyl ether was added. The organic layer was separated, washed with water and dried over Na_2SO_4. After solvent evaporation, the residue was purified by flash chromatography (silica gel, petroleum ether/CH_2Cl_2 = 2:1) to yield **11** in 69% as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.86 (m, 4H), 7.51–7.71 (m, 16H), 6.70–6.75 (m, 4H), 1.88–2.19 (m, 16H), 1.39–1.50 (m, 8H), 1.02–1.26 (m, 48H), 0.56–0.99 (m, 96H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 151.7, 150.4, 140.8, 140.4, 140.2, 139.9, 138.9, 126.0, 121.5, 121.0, 120.6, 119.8, 118.4, 114.1, 109.9, 55.0, 54.7, 39.3, 37.4, 36.7, 32.9, 30.6, 27.8, 24.7, 22.6, 19.6; IR (CsI): ν [cm^{-1}] 3476, 3364, 2926, 2867, 1716, 1619, 1585, 1461, 1366, 1261, 1040, 812, 740; MS (APCI): m/z calculated: 1809.54, found: 1810.6 (M^+ + H).