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Cyclodehydrogenation of hetero-oligophenylenes

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ABSTRACT

Pyrimidyl-penta-phenylbenzenes have been synthesized by Diels–Alder addition of phenylethynylpyrimidines and tetraphenylcyclopentadienones under microwave irradiation. Scholl reactions of these compounds led to two types of hetero polyaromatic hydrocarbons: (a) partial cyclization by creation of two C–C bonds *ortho* to the pyrimidine nitrogen atoms gave substituted tribenzo[e,gh,j]perimidine (N-1/3HSB) in high yields; (b) when the position 2 of the pyrimidine ring was substituted by a *tert*-butyl group, the Scholl reaction was complete and provided the first example of a diaza-hexa-*peri*-benzocoronene.

1. Introduction

Polyaryl and polycyclic hydrocarbons are currently attracting a lot of interest for their potential applications as molecular materials for electronic and optoelectronic applications. In the course of a study of the mechanical and chemical properties of molecular devices,[1] we were interested in planar heterosuperbenzene as candidates for molecular moulding,[2] metal atom manipulation,[3] electrode–molecule contact[4] or controlled rotation[5] experiments at the single molecule level. In the present contribution, the investigation of the synthesis of some pyrimidyl-penta-phenylbenzenes and the influence of the substituents on the cyclodehydrogenation reaction to access heterosuperbenzene is explored.

2. Results and discussion

2.1. Synthesis of the pyrimidyl-penta-phenylbenzenes

The general synthetic route towards (partially or fully) cyclodehydrogenated hetero-oligophenylenes is shown on Scheme 1. The propeller-like pyrimidyl-penta-phenylbenzenes were obtained by [2+4] Diels–Alder cycloaddition of tetraphenylcyclopentadienones to phenylethynylpyrimidines.

These latter were prepared by Sonogashira coupling of bromopyrimidines with ethynylbenzenes. All these syntheses were done by microwave (μw) heating, which revealed as a very efficient tool for cross-couplings and Diels–Alder reactions in terms of reaction times and yields.[6] Typically, the cross-coupling reactions were completed in less than 0.5 h in good yields (61–93%).[7–9] As pointed out by Erdélyi and Gogoll,[10] the reaction temperature was maintained just below 120 °C to avoid decomposition of the palladium catalyst. The Diels–Alder reactions, and the subsequent in-situ oxidations, were done in diphenylether at 260 °C for 45 min giving the hexaaryl compounds in 40–50% yields.

The unsubstituted (5-pyrimidyl)pentaphenylbenzene **7** was obtained in 44% yield by reaction of commercial 2,3,4,5-tetraphenylcyclopenta-2,4-dienone with 5-(phenylethynyl)pyrimidine **5** (Scheme 2).

This latter compound **5** was prepared by coupling phenylacetylene and 5-bromopyrimidine in good yield (93%), significantly higher than by conventional heating.[11–13] Similarly, the trisubstituted (5-pyrimidyl)pentaphenylbenzene **11** was obtained by [2+4] cycloaddition of 5-((4-*tert*-butylphenyl)ethynyl)pyrimidine **9** and 3,4-bis(4-*tert*-butylphenyl)-2,5-diphenylcyclopenta-2,4-dienone **10**[14–16] (Scheme 3).

The tolane **9** was synthesized from 1-*tert*-butyl-4-ethynylbenzene **8**. This latter compound[17,18] was prepared in 88% yield by cross-coupling under microwave irradiation of 1-bromo-4-*tert*-butylbenzene and trimethylsilylacetylene, and deprotection by aqueous NaOH in methanol.

The penta-*tert*-butyl propeller **13** (Scheme 4) was correspondingly synthesized by cycloaddition of **9** with the known cyclopentadienone **12**,[14,15] obtained by double Knoevenagel condensation of 4,4′-di-*tert*-butylbenzil and 1,3-bis(3,5-di-*tert*-butylphenyl)-2-propanone.

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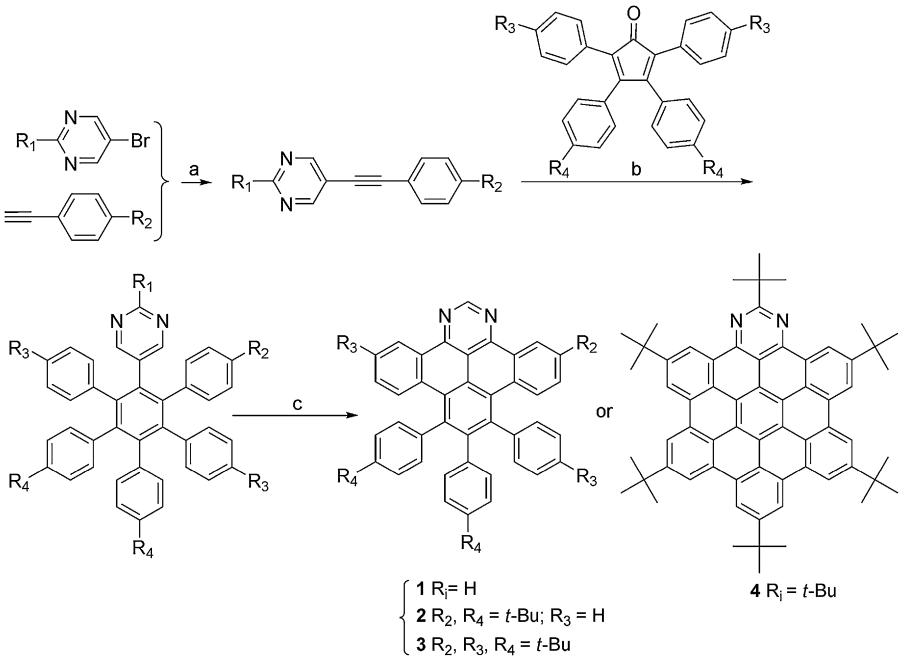


Scheme 1. General route towards pyrimidyl-penta-phenylbenzenes and their cyclodehydrogenation products. (a) Sonogashira coupling, μw; (b) [2+4] cycloaddition, Ph_2O, μw; (c) cyclodehydrogenation, $FeCl_3$, DCM, CH_3NO_2.

Finally, the fully substituted propeller **16** was obtained by condensation of **15** and **12**.

The preparation of **15** requires the synthesis of 5-bromo-2-*tert*-butylpyrimidine **14**, which was made by condensation of malondialdehyde bis(dimethylacetal) and 2,2-dimethylpropanamidine[19] to give the 2-*tert*-butylpyrimidine, subsequently brominated in position 5 by bromine in acetic acid[20] (Scheme 5).

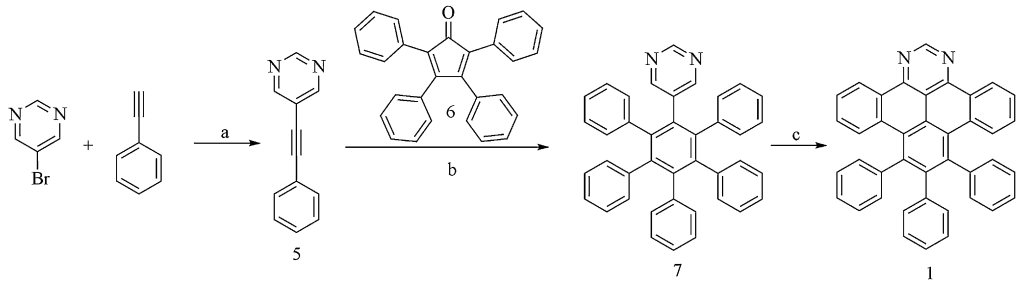
2.2. Cyclodehydrogenations

With the objective to prepare series of heterosuperbenzene, we have investigated the intramolecular Scholl reaction on these contiguous hexaarylbenzenes **7**, **11**, **13** and **16**. The Scholl reaction, i.e., the condensation of aromatics by reaction with Lewis acids, is known to be very efficient for the cyclodehydrogenation of oligophenylene compounds. Müllen and co-workers have extensively used this reaction to convert 3D-polyphenylene structures to all benzenoid 2D-hydrocarbons,[21] and in particular for the preparation of hexabenzocoronenes from hexaphenylbenzenes.[22] In this Scholl reaction, the oxidative aryl–aryl coupling is effected in general by transition metal halides such as $AlCl_3$/Cu(II), $FeCl_3$, $MoCl_5$ but also by $PhI(O_2CCF_3)_2/BF_3{\cdot}OEt_2$,[23,24] which act in the same time as oxidants and Lewis acids. This synthetic route has been recently extended by Draper and co-workers to the cyclodehydrogenation of 1,2-dipyrimidyl-3,4,5,6-tetra(4-*tert*-butylphenyl)benzene (Scheme 6).[25,26]

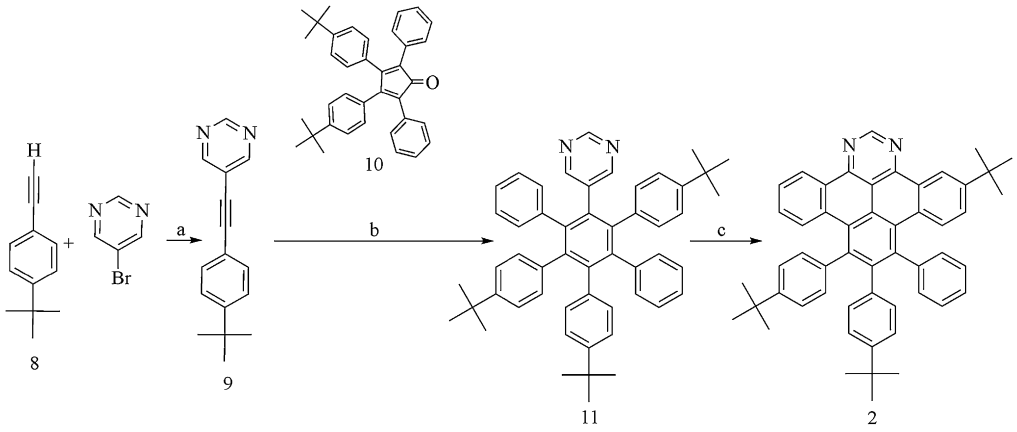
Remarkably, whereas Scholl cyclodehydrogenation by $AlCl_3$/$CuCl_2$ in CS_2 gave solely the fully cyclized heterosuperbenzene N-HSB, the reaction employing a milder catalyst ($FeCl_3$/nitromethane/DCM) gave a mixture of N-HSB (35%) and of 'half-cyclized' N-1/2HSB (32%). Surprisingly, treatment of N-1/2HSB by $FeCl_3$, or under forcing conditions by $AlCl_3/CuCl_2$, did not give N-HSB, which indicates that the partially cyclodehydrogenated compound is not a parent intermediate of the heterosuperbenzene in this reaction. It is worth noting that some partially cyclodehydrogenated oligophenylenes can be fully cyclodehydrogenated to give HBC in quantitative yield and without chlorination.[27]

2.3. Scholl reaction on the hexaarylbenzenes 7, 11, 13 and 16

Attempts to cyclodehydrogenate these four compounds by $AlCl_3/CuCl_2$ in CS_2 or $MoCl_5$ in dichloromethane in various conditions gave invariably fully insoluble products, containing polychlorinated products as shown by mass spectroscopy. For **7** and **11**, it is possible that the presence of unsubstituted phenyl groups in *para*-position to the central benzene favours oligomerization. Furthermore the pyrimidine could maintain some solubility to the reaction intermediates by complexation with the aluminium, which would favour the polymerization and the chlorination. And



Scheme 2. Reagents and conditions: (a) DIPA, PPh_3, $PdCl_2(PPh_3)_2$, CuI, DMF, μw, 115 °C, 93%; (b) Ph_2O, 260 °C, 44%; (c) $FeCl_3/CH_3NO_2$, DCM, 94%.



Scheme 3. Reagents and conditions: (a) DIPA, PPh_3, $PdCl_2(PPh_3)_2$, CuI, DMF, μw, 115 °C, 61%; (b) Ph_2O, 260 °C, 52%; (c) $FeCl_3/CH_3NO_2$, DCM, 90%.

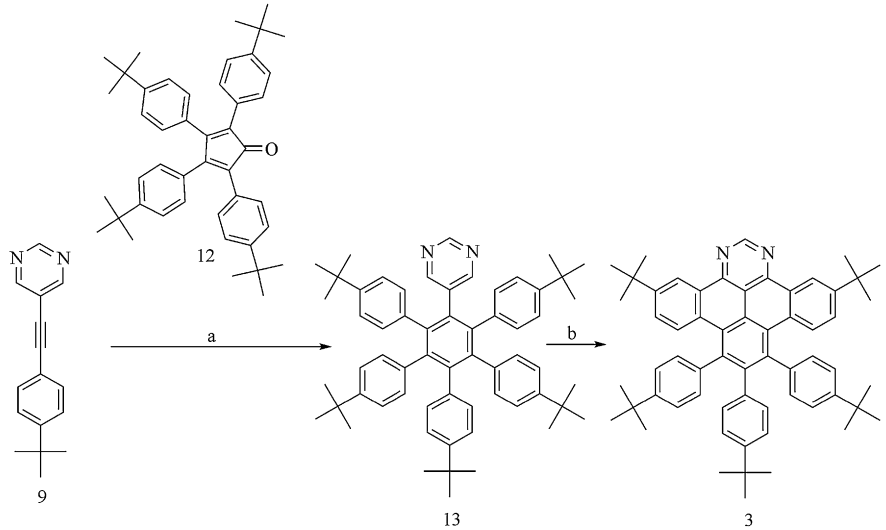
the presence of a dipole in the reaction products due to the pyrimidine ring decreases further the solubility of the final oligomers. The impossibility to fully cyclodehydrogenate **13** in the conditions used to prepare N-HSB from the very similar 1,2-dipyrimidyl-3,4,5,6-tetra(4-*tert*-butylphenyl)benzene (Scheme 6) is very puzzling. In contrast, reaction of **7**, **11** and **13** in dichloromethane with $FeCl_3$/nitromethane gave very good yields of partially cyclodehydrogenated **1** (94%), **2** (90%) and **3** (85%), respectively (Scheme 1). In this reaction, and very similarly to what is observed for bipyrimidines (Scheme 6), the only C–C bonds that have been created are those in *ortho* position with respect to the pyrimidine nitrogen, leading to tribenzo[e,gh,j]perimidine cores (N-1/3HSB according to Draper's nomenclature).[26] The cyclodehydrogenation mechanisms are therefore probably similar and could involve arenium intermediates and/or the coordination of the iron.[24] Very similarly to what was observed with N-1/2HSB, attempts to complete the cyclodehydrogenation of these N-1/3HSB by reaction with $AlCl_3$ or $FeCl_3$ were unsuccessful. In contrast, reaction of the per-*tert*-butylated **16** with $FeCl_3$, in the same conditions as above for **7**, **11**, **13**, provided the *N*-heterosuperbenzene **4** in 60% yield. The substitution of the hydrogen atom in position 2 in the pyrimidine ring (in **13**) by a *tert*-butyl group (in **16**) has a profound effect on the reactivity of these compounds. This substitution by a bulky, electron donating group has several consequences: (a) it increases the pyrimidine nucleophilicity, (b) blocks the position 2 and could hinder oligomerization at this position, (c) increases the solubility of reagents, intermediates and products, and (d) prevents complexation by the nitrogen atoms by steric crowding. At this stage, further work is required to unveil the cyclodehydrogenation mechanisms leading to these very different chemical behaviours.

In conclusion, pyrimidyl-penta-phenylbenzenes have been synthesized by Diels–Alder addition of phenylethynylpyrimidines and tetraphenylcyclopentadienones under microwave irradiation. Scholl reactions of these compounds (ferric chloride/nitromethane/dichloromethane) led to two types of hetero polyaromatic hydrocarbons: (a) partial cyclization by creation of two C–C bonds *ortho* to the pyrimidine nitrogen atoms gave substituted tribenzo[e,gh,j]perimidine (N-1/3HSB) in high yields; (b) when the position 2 of the pyrimidine ring was substituted by a *tert*-butyl group, the Scholl reaction was complete and provided the first example of a diaza-hexa-*peri*-benzocoronene.

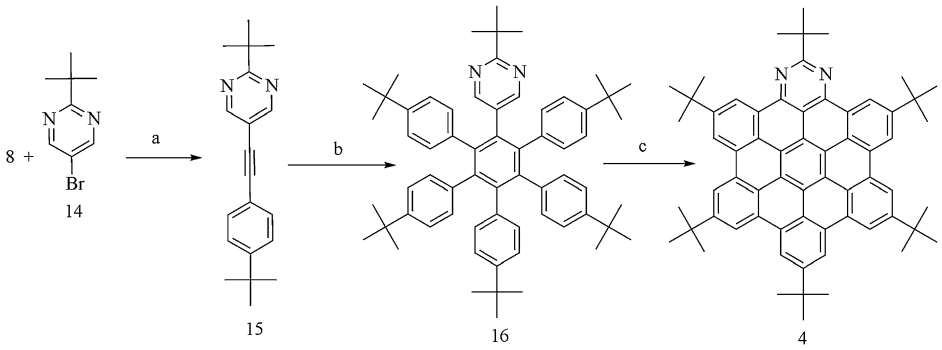
3. Experimental

3.1. General

^1H and ^{13}C NMR spectra were recorded with a Bruker WF-250/300 MHz in $CDCl_3$ or CD_2Cl_2 solutions at 20 °C using solvent residue as the internal standard ($CDCl_3$ at δ_H: 7.25 ppm, δ_C: 77.0 ppm, CD_2Cl_2 at δ_H: 5.30 ppm, δ_C: 53.8 ppm). Mass Spectroscopy was performed with a Nermag R10-R10 (DCI). Elemental analyses were done by the Service d'Analyse de l'ICSN (Paris) and by the Service



Scheme 4. Reagents and conditions: (a) Ph_2O, 260 °C, 46%; (b) $FeCl_3/CH_3NO_2$, DCM, 85%.



Scheme 5. Reagents and conditions: (a) DIPA, PPh_3, $PdCl_2(PPh_3)_2$, CuI, DMF, μw, 115 °C, 78%; (b) Ph_2O, 260 °C, 62%; (c) $FeCl_3/CH_3NO_2$, DCM, 60%.

d'Analyse du LCC (Toulouse). Note that, as observed by others, the carbon analysis of extended polyaromatic compounds **1**–**3** is inaccurate, due to incomplete combustion. The cyclopentadienones **10** and **12** were prepared according to Refs. 14 and 15. THF was distilled from Na/benzophenone. Dichloromethane was distilled over calcium hydride. Nitromethane was dried on molecular sieves prior use. Other solvents and reagents were used as obtained in the best quality available. The microwave heating was carried out in closed vials with a CEM-Discover monomode microwave apparatus under the conditions (power, temperature, time) given here. After completion of the reaction, the vessel was cooled down rapidly to 60 °C.

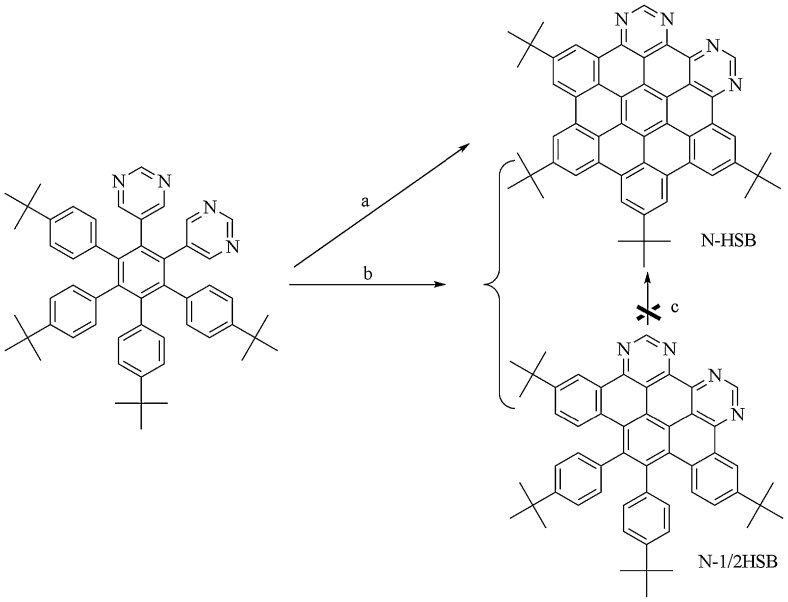
3.2. Synthesis of 5-phenylethynylpyrimidine 5

A mixture of 102 mg of phenylacetylene (1 mmol) and 159 mg (1 mmol) 5-bromopyrimidine in 0.5 mL of dry DMF was degassed and 1.5 mL of dry DIPA, triphenylphosphine (23 mg, 0.087 mmol), $Pd(P(C_6H_5)_3)Cl_2$ (15 mg, 0.021 mmol) and CuI (4 mg, 0.02 mmol) were added and the mixture was irradiated at 150 W, 115 °C, 25 min. After cooling the brown-orange coloured suspension was extracted with 2×50 mL ether and washed with 2×25 mL saturated NH_4Cl, 2×25 mL water then dried with $MgSO_4$. The crude product was further purified by chromatographic column in silica gel using DCM as eluent. Drying under vacuum in ice gave pale yellow powder. Yield: 167 mg (93%).

^{1}H NMR (250 MHz, CD_2Cl_2): δ=7.41 (m, 3H, Ar–H), 7.57 (m, 2H, Ar–H), 8.86 (s, 2H, H4, H6), 9.11 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=82.6, 95.9, 119.8, 121.9, 128.6, 129.4, 131.8, 156.8, 158.7; MS (CI, NH_3): *m*/*z* calcd for $C_{12}H_8N_2$: 180.0; found: 181 [M^++1]. Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.55. Found: C, 79.88; H, 4.44; N, 14.55.

3.3. Synthesis of 1-*tert*-butyl-4-ethynylbenzene 8

To a degassed mixture of 3 g of 1-bromo-4-*tert*-butylbenzene (14.08 mmol), 485 mg of $Pd(P(C_6H_5)_3)_4$ (3%), 160 mg of CuI (6%) in 10 mL DIPA and 30 mL dry THF was added 2 mL of TMSA (1.38 g, 14 mmol). The mixture was irradiated at 150 W, 33 min, 110 °C. After cooling the mixture was filtered over Celite; the Celite was washed with diethylether until colourless and the solvent evaporated under vacuum. The residue was then dissolved in ether, washed with HCl 1%, brine then dried on $MgSO_4$. Purification by chromatography using hexane as eluent yielded 3.08 g of (4-*tert*-butylphenylethynyl)-trimethylsilane, which was then dissolved in 150 mL of methanol. To this solution was added 14 mL of aqueous 2.5 M NaOH. After 15 min of stirring the mixture was acidified to neutrality with 1 M HCl.



Scheme 6. Reagents and conditions from Refs. 25 and 26. (a) $AlCl_3$, $CuCl_2$, CS_2, rt, 49%; (b) $FeCl_3/CH_3NO_2$, DCM, rt; N-HSB (35%)+N-1/2HSB (32%); (c) $AlCl_3/CuCl_2$ or $FeCl_3$.

Then the product was extracted with hexane (3×150 mL) and washed with water (100 mL), dried over $MgSO_4$, giving 1.96 g of pure **8** as orange oil (yield for the two steps: 88%). Analyses and spectroscopic data were in agreement with the literature.[17,18]

3.4. Synthesis of 9

To a degassed solution of **8** (158 mg, 1 mmol) and 5-bromopyrimidine (156 mg, 1 mmol) in 0.5 mL DMF and 1.5 mL dry DIPA were added triphenylphosphine (23 mg, 0.087 mmol), $Pd(P(C_6H_5)_3)Cl_2$ (15 mg, 0.0213 mmol) and CuI (4 mg, 0.021 mmol). The mixture was irradiated at 150 W, 115 °C, 25 min. After cooling the brown-orange suspension was extracted with 2×50 mL ether and filtered. The solution was washed with saturated NH_4Cl (2×25 mL), water (2×25 mL) and finally dried over $MgSO_4$. The crude product was purified by chromatography (silica gel, eluent: DCM/ethylacetate 5%). Yield: 145 mg of pale yellow powder (61%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.33 (s, 9H, *tert*-Bu), 7.29 (d, $^3J_{H-H}$=8.7 Hz, 2H, Ar–H), 7.51 (d, $^3J_{H-H}$=8.7 Hz, 2H, Ar–H), 8.84 (s, 2H, H4, H6), 9.09 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=31.0, 81.8, 96.1, 118.8, 120.6, 125.6, 131.4, 131.8, 152.9, 156.6, 158.5; MS (CI, NH_3): *m*/*z* calcd for $C_{16}H_{16}N_2$: 236.1; found: 237 [M^++1]. Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.32; N, 11.85. Found: C, 81.19; H, 6.99; N, 11.87.

3.5. Synthesis of 15

To a degassed mixture of 158 mg (1 mmol) of 1-*tert*-butyl-4-ethynylbenzene (**8**), 5-bromo-2-*tert*-butylpyrimidine (**14**) (215 mg, 1 mmol) in 0.5 mL of dry DMF and 1.5 mL of dry DIPA were added triphenylphosphine (23 mg, 0.087 mmol), $Pd(P(C_6H_5)_3)Cl_2$ (15 mg, 0.021 mmol) and CuI (4 mg, 0.02 mmol), and the mixture was irradiated at 150 W, 115 °C, 25 min. After cooling the brown suspension was extracted with 2×50 mL of diethylether, filtered and washed with 2×25 mL saturated NH_4Cl, 2×25 mL water then dried with $MgSO_4$. The crude product was further purified by chromatographic column in silica gel using a gradient of petroleum ether/DCM as eluent (0–20% DCM). Yield: 205 mg (77%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.30 (s, 9H, *tert*-Bu), 1.37 (s, 9H, *tert*-Bu), 7.39 (d, $^3J_{H-H}$=8.7 Hz, 2H, Ar–H), 7.47 (d, $^3J_{H-H}$=8.7 Hz, 2H, Ar–H), 8.75 (s, 2H, H4, H6); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=29.2, 30.8, 82.5, 94.9, 116.2, 119.1, 125.6, 131.4, 152.6, 158.2, 175.6; MS (CI, NH_3): *m*/*z* calcd for $C_{20}H_{24}N_2$: 292.4; found: 293.3 [M^++1]. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.38; H, 8.39; N, 9.21.

3.6. General procedure for the synthesis of 7, 11, 13 and 16

A mixture of phenylethynylpyrimidine (0.2 mmol) and cyclopentadienone (0.2 mmol) in diphenylether (1.5 g) was irradiated at 300 W, 260 °C, 45 min. After cooling, the dark-red mixture was diluted with dichloromethane (1 mL), poured in methanol (50 mL) and stirred; the off white precipitate was filtered, washed with methanol and vacuum dried. The product was recrystallized by partial evaporation (24 h) of a mixture of DCM (2.5 mL) and ethanol (5 mL).

3.6.1. Compound **7**

Yield 44%; ^{1}H NMR (300 MHz, CD_2Cl_2): δ=6.80–7.00 (m, 25H, Ar–H), 8.2 (s, 2H, H4, H6), 8.60 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=125.8, 126.2, 126.9, 127.5, 129.3, 131.5, 133.3, 135.1, 139.8, 140.3, 140.5, 142.0, 141.0, 155.6, 158.0, 206.8; MS (CI, NH_3): *m*/*z* calcd for $C_{40}H_{28}N_2$: 536.6; found: 537 [M^++1]. Anal. Calcd for $C_{40}H_{28}N_2$: C, 89.52; H, 5.26; N, 5.22. Found: C, 88.09; H, 5.26; N, 5.04.

3.6.2. Compound **11**

Yield 52%; ^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.12 (br m, 27H, 3×*tert*-Bu), 6.70–6.97 (m, 20H, Ar–H), 8.14 (s, 2H, H4, H6), 8.59 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=31.2, 34.3, 123.6, 124.2, 124.2, 126.1, 126.8, 127.4, 131.1, 131.3, 131.5, 131.6, 135.4, 136.8, 137.4, 137.6, 140.2, 140.6, 140.8, 141.3, 142.4, 148.4, 149.1, 155.4, 158.0; MS (CI, NH_3): *m*/*z* calcd for $C_{52}H_{48}N_2$: 700.4; found: 701.4 [M^++1]. Anal. Calcd for $C_{52}H_{52}N_2$: C, 88.59; H, 7.43; N, 3.57. Found: C, 88.42; H, 7.21; N, 3.27.

3.6.3. Compound **13**

Yield: 46%; ^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.10 (s, 45H, 5×*tert*-Bu), 6.70–6.77 (m, 10H, Ar–H), 6.84–6.90 (m, 6H, Ar–H), 6.937 (br d, $^3J_{H-H}$=8.4 Hz, 4H, Ar–H), 8.16 (s, 2H, H4, H6), 8.59 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=31.6, 34.7, 124.1, 124.6, 131.5, 131.7, 137.5, 138.1, 141.3, 141.7, 148.8, 149.4, 155.8, 158.5; MS (CI, NH_3): *m*/*z* calcd for $C_{60}H_{68}N_2$: 817.2; found: 817 [M+]. Anal. Calcd for $C_{60}H_{68}N_2$: C, 88.18; H, 8.39; N, 3.43. Found C, 87.72; H, 8.33; N, 3.29.

3.6.4. Compound **16**

Yield: 62%; ^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.08–1.11 (m, 54H, 6×*tert*-Bu), 6.72–6.75 (m, 10H, Ar–H), 6.83–6.93 (m, 10H, Ar–H), 8.04 (s, 2H, H4, H5); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=29.8, 31.3, 31.6, 124.0, 124.5, 131.5, 134.4, 137.7, 138.1, 141.5, 142.4, 148.8, 149.2, 157.8, 173.9; MS (CI, NH_3): *m*/*z* calcd for $C_{64}H_{76}N_2$: 872.6; found: 873.7 [M^++1]. Anal. Calcd for $C_{64}H_{76}N_2$: C, 88.02; H, 8.77; N, 3.21. Found: C, 88.03; H, 8.35; N, 3.15.

3.7. General procedure for cyclodehydrogenation of 7, 11, 13 and 16

The hexaaryl compound was dissolved in anhydrous DCM. A stream of argon saturated with DCM was bubbled into the solution during the reaction to reduce chlorination. A solution of anhydrous $FeCl_3$ (1:30 mol ratio) in anhydrous nitromethane was quickly added. After a reaction time of 90 min, the reaction was quenched with methanol. Part of the dichloromethane was removed under reduced pressure. The precipitate was filtered and washed with aqueous HCl and methanol.

3.7.1. Compound **1**

Yield 94%; product was precipitated with methanol; ^{1}H NMR (300 MHz, CD_2Cl_2): δ=6.90 (m, 5H, Ar–H), 7.17 (m, 12H, Ar–H), 7.61 (m, 4H, Ar–H), 9.40 (d, $^3J_{H-H}$=9 Hz, 2H, Ar–H), 9.75 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=125.2, 125.4, 126.3, 126.6, 127.0, 127.1, 128.2, 128.9, 129.7, 130.5, 131.3, 131.8, 134.1, 139.8, 140.4, 142.7, 152.9, 155.6; MS (CI, CH_4): *m*/*z* calcd for $C_{40}H_{24}N_2$: 532.2; found: 533.2 [M^++1]. Anal. Calcd for $C_{40}H_{24}N_2$: C, 90.20; H, 4.54; N, 5.26. Found: C, 89.75; H, 4.73; N, 4.93. *Rf*: 0.52 in dichloromethane, silica gel.

3.7.2. Compound **2**

Yield 90%; product was precipitated with methanol; ^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.15 (s, 9H, *tert*-Bu), 1.26 (s, 9H, *tert*-Bu), 1.45 (s, 9H, *tert*-Bu), 6.69 (d, $^3J_{H-H}$=8.4 Hz, 2H, Ar–H), 6.90 (d, $^3J_{H-H}$=8.4 Hz, 2H, Ar–H), 6.96 (d, $^3J_{H-H}$=8.4 Hz, 2H, Ar–H), 7.21–7.28 (m, 8H, Ar–H), 7.33 (dd, $^3J_{H-H}$=9.0 Hz, $^4J_{H-H}$=2.3 Hz, 1H, Ar–H), 7.59 (d, $^3J_{H-H}$=6.9 Hz, 1H, Ar–H), 7.64 (d, $^3J_{H-H}$=9 Hz, 1H, Ar–H), 7.79 (d, $^3J_{H-H}$=8.4 Hz, 1H, Ar–H), 9.41 (d, $^3J_{H-H}$=6.9 Hz, 1H, Ar–H), 9.48 (d, $^4J_{H-H}$=2.4 Hz, 1H, Ar–H), 9.76 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=30.9, 30.0, 30.1, 123.0, 124.8, 125.1, 126.5, 126.9, 127.1, 128.1, 128.8, 129.5, 129.9, 130.7, 131.2, 131.3, 137.3, 139.8, 150.1, 155.3; MS (CI, CH_4): *m*/*z* calcd for $C_{52}H_{48}N_2$: 700.4; found: 701.4 [M^++1]. Anal. Calcd for $C_{52}H_{48}N_2$: C, 89.0; H, 6.90; N, 4.00. Found: C, 88.12; H, 7.01; N, 3.80. *Rf*: 0.45 in dichloromethane, silica gel.

3.7.3. Compound ***3***

Yield: 85%; product was precipitated with methanol; ^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.14 (s, 9H, *tert*-Bu), 1.27 (s, 18H, 2×*tert*-Bu), 1.47 (s, 18H, 2×*tert*-Bu), 6.58 (d, $^3J_{H-H}$=8.3 Hz, 2H), 6.87 (d, $^3J_{H-H}$= 8.4 Hz, 2H, Ar–H), 6.93 (d, $^3J_{H-H}$=8.3 Hz, 4H, Ar–H), 7.19 (d, $^3J_{H-H}$=8.5 Hz, 4H, Ar–H), 7.49 (dd, $^3J_{H-H}$=9.1 Hz, $^4J_{H-H}$=2.1 Hz, 2H, Ar–H), 7.83 (d, $^3J_{H-H}$=9.1 Hz, 2H, Ar–H), 9.43 (d, $^4J_{H-H}$=2.1 Hz, 2H, Ar–H), 10.09 (s, 1H, H2); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=29.7, 34.4, 35.2, 123.1, 125.1, 129.9, 130.4, 130.5, 130.9, 138.1, 138.9, 139.0, 139.8, 141.5, 150.3, 158.8; MS (CI, CH_4): *m*/*z* calcd for $C_{60}H_{64}N_2$: 812.5; found: 812.6 [M^+]. Anal. Calcd for $C_{60}H_{64}N_2$: C, 88.62; H, 7.93; N, 3.44. Found: C, 88.36; H, 7.72; N, 4.19. R_f: 0.70 in dichloromethane, silica gel.

3.7.4. Compound ***4***

Yield: 60%; product was further purified using column chromatography, silica gel, petroleum ether–dichloromethane (4: 1); ^{1}H NMR (300 MHz, CD_2Cl_2): δ=1.75 (s, 9H, *tert*-Bu), 1.85 (s, 27H, 3×*tert*-Bu), 1.93 (s, 18H, 2×*tert*-Bu), 9.41 (br s, 6H, Ar–H), 9.56 (d, $^4J_{H-H}$=1.8 Hz, 2H, Ar–H), 10.11 (d, $^4J_{H-H}$=1.8 Hz, 2H, Ar–H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ=30.6, 31.7, 31.8, 125.9, 126.7, 128.5, 129.1, 130.3, 131.3, 132.3, 148.4, 150.0, 150.3, 166.2; MS (CI, CH_4): *m*/*z* calcd for $C_{64}H_{64}N_2$: 860.5; found: 861.7 [M^++1]. Anal. Calcd for $C_{64}H_{64}N_2$: C, 89.26; H, 7.49; N, 3.25. Found: C, 88.74; H, 7.04; N, 3.64. R_f: 0.83 in petroleum ether–dichloromethane (4:1), silica gel.

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