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Multicomponent reactions mediated by $NbCl_5$ for the synthesis of phthalonitrile-quinoline dyads: Methodology, scope, mechanistic insights and applications in phthalocyanine synthesis

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ABSTRACT

Herein, we demonstrate the efficiency of $NbCl_5$ to promote a multicomponent reaction (MCR) for the synthesis of a library of phthalonitrile-quinoline dyads, which are very useful and new functionalized building blocks for phthalocyanine (PC) synthesis. Experimental mechanistic insights on the key MCR process are described, using a deuterated reagent, clearly showing the pericyclic nature of a hetero-Diels-Alder reaction. Examples of phthalocyanine (PC) syntheses were performed in order to demonstrate the versatility of the phthalonitrile-quinoline dyads. Preliminary photophysical measurements show that our phthalonitrile library is very promising for the production of new molecular scaffolds of PC derivatives with potential applications.

1. Introduction

Phthalonitriles are the most widely used precursors for the synthesis of phthalocyanine (PC) dyes, which are used in many technological and medical applications, such as solar cells [1–3], liquid crystals [4,5], semiconductors [6–11], in photodynamic therapy (PDT) [12–16], and others [17–24]. Functionalized phthalonitriles are prepared by modifying pre-existing phthalonitriles using classical reaction approaches [25,26]. Usually they are prepared via aromatic substitution reactions (S_NAr) from substrates with good leaving groups such as NO_2, N_2^+ and halogens [25–31]. However, limitations on structural diversity are found, mainly for the synthesis of polyfunctionalized phthalonitriles and more sophisticated dyads. Another approach that has been used to functionalize phthalonitriles involves the Stille [32], Heck–Mizoroki [33,34], Suzuki–Miyaura [33,35–37], and Sonogashira reactions [33,38,39]. Many advantages are found in these last approaches such as high yields, wide substrate scope, and mild reaction conditions. However, they are not always cost competitive nor easily scaled up.

As part of our research interests on synthetic methodologies using $NbCl_5$ [40–50], we report a new approach for the functionalization of 4-formylphthalonitrile (**1**) with substituted anilines and terminal phenylacetylenes via a multicomponent reaction (MCR) promoted by $NbCl_5$ in the presence of *p*-chloranil.

Application of this strategy has enabled a facile and step efficient access to a structurally diverse collection of phthalonitrile derivatives, and in a low-cost methodology. Furthermore, we have studied and present mechanistic insights based on experiments with a deuterated phenylacetylene, demonstrating a plausible reaction mechanism not previously presented in the literature for similar MCRs. We also report the application of this methodology in the synthesis of three zinc phthalocyanine-quinoline dyads in order to demonstrate the structural variety of the compound collection. Preliminary photophysical properties of these phthalocyanine dyads were also studied.

2. Experimental

2.1. Chemicals and materials

The niobium pentachloride was supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM, Brazil) and used as received. All the other reagents were purchased from Sigma-Aldrich or Synth (Brazil) and used as supplied. Anhydrous potassium carbonate was dried at 110 °C for 12 h before use. Tetrahydrofuran was distilled over sodium/benzophenone before use, degassed by bubbling argon through it and stored over molecular sieves (4 Å). Aniline, acetonitrile, and *N*,*N*-dimethylformamide were dried with calcium hydride and distilled following standard protocols [51] and stored over molecular sieves (4 Å) under an argon atmosphere. Bis(trimethylsilyl)amine was distilled and stored over molecular sieves (4 Å) under an argon atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck

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aluminum sheets coated with silica gel 60 F_{254} and visualized with ultraviolet light (254 or 366 nm) or heating with TLC stains. Gravity column chromatography was performed on silica gel (70–230 mesh, 63–200 μM, pore size 60 Å, Merck), and flash column chromatography was performed on silica gel (230–400 mesh, 40–63 μM, pore size 60 Å, Merck).

2.2. Equipments

^{1}H NMR, ^{13}C NMR and DEPT-135 spectra were recorded on a Bruker Avance III 400 (operating at 400.15 and 100.62 MHz for ^{1}H and ^{13}C respectively) or 600 (operating at 600.23 and 150.93 MHz for ^{1}H and ^{13}C respectively) spectrometers with tetramethylsilane as the internal reference and $CDCl_3$ or $CDCl_3$/DMSO-d_6 as solvents. FT-IR spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer using KBr pellets in the range of 4000–400 cm^{-1}. UV–Vis absorption spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer using 1 cm optical length quartz cuvettes at 25 °C and tetrahydrofuran (HPLC grade) as the solvent. The fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer using 1 cm optical length cuvettes at 25 °C and degassed tetrahydrofuran (HPLC grade) as the solvent. EI-MS spectra were acquired at 70 eV on a Shimadzu GCMS-QP5000 mass spectrometer coupled with a Shimadzu GC-17A gas chromatograph. HRMS (ESI-TOF) spectra were registered in a positive ion mode on a Bruker Daltonics (Impact HD) UHR-QqTOF (Ultra-High Resolution Qq-Time-Of-Flight) mass spectrometer. HRMS (MALDI-TOF) spectra were obtained on a Bruker Daltonics Ultraflextreme MALDI-TOF/TOF mass spectrometer in positive reflector mode using α-cyano-4-hydroxycinnamic acid as the matrix. All melting points were determined on a Microquímica™ MQRPF-301 apparatus. The organic solvents were evaporated using a Büchi Rotavapor R-215 at 40 °C.

2.3. Procedure for synthesis of 4-formylphthalonitrile (1)

Phthalonitrile **1** was prepared in three steps by previously reported procedures [52,53]. Nitration of commercially available 4-bromobenzaldehyde with a mixture of H_2SO_4 and $NaNO_3$ yielded 4-bromo-3-nitrobenzaldehyde in 92% yield (11.58 g, 50.34 mmol). 3,4-Dibromobenzaldehyde was then obtained in 83% yield (10.09 g, 38.23 mmol) by the reduction with tin (II) bromide (generated *in situ* from Sn^0 and HBr), followed by diazotization and reaction with CuBr (Sandmeyer reaction). Finally, 3,4-dibromobenzaldehyde was converted into **1** by the Rosenmund-von Braun reaction (CuCN) in 60% yield (1.57 g, 10.05 mmol). Data for **1**: M.p. 138–140 °C; Literature: 138 °C [54]. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 10.13 (s, 1H, CHO), 8.34–8.29 (m, 1H), 8.24 (dd, J = 8.0, 1.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 188.3 (CHO), 138.8, 134.5, 133.8, 133.3, 120.3, 117.2, 114.6 (CN), 114.4 (CN). ^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 134.5, 133.8, 133.3. FT-IR (KBr, cm^{-1}): ν = 3105, 3071, 2878 (CHO), 2234 (C≡N), 1709 (C=O), 1597, 1381, 1194, 1096, 945, 851, 752, 530. EI-MS (m/z (%)): 156 (54) [M^+], 155 (100) [M^+ − H], 127 (38) [M^+ − CHO], 100 (21), 75 (20), 50 (25).

2.4. Procedure for synthesis of 4-(decyloxy)aniline (2g)

Aniline **2g** was prepared in two steps following reported procedures with some slight modifications [55,56].

I. Alkylation of the phenol: A mixture of 4-nitrophenol (3.48 g, 0.025 mol), K_2CO_3 (13.8 g, 0.1 mol) and 1-bromodecane (7.8 mL, 0.0375 mol) in cyclohexanone (50 mL) was stirred under reflux for 3 h. The resultant reaction mixture was filtered to separate the K_2CO_3 and then the cyclohexanone was distilled off under reduced pressure. The residue obtained was purified by silica gel column chromatography (hexane/EtOAc, 9:1 v/v) to afford a yellow oil that was crystallized from ethanol to give 1-(decyloxy)-4-nitrobenzene in 93% yield (6.48 g, 23.2 mmol).

II. Hydrogenation of the aromatic nitro group: 1-(decyloxy)-4-nitrobenzene (1 g, 3.58 mmol) was dissolved in dry THF (5 mL) and 10% Pd/C (0.1 g) was added. The reaction mixture was degassed and stirred under H_2 gas (1 atm) for 12 h at room temperature. The resultant reaction mixture was filtered through a plug of Celite, which was washed with CH_2Cl_2. The solvents were removed under vacuum and the remaining residue was purified by flash column chromatography (silica gel, hexane/EtOAc, 8:2 v/v) to afford the desired aniline **2g** in 97% yield (869 mg, 3.48 mmol). Data for **2g**: M.p. 40–41 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 6.78–6.72 (m, 2H), 6.68–6.62 (m, 2H), 3.88 (t, J = 6.6 Hz, 2H), 3.46 (s, 2H), 1.75 (dt, J = 14.8, 6.7 Hz, 2H), 1.50–1.39 (m, 2H), 1.39–1.20 (m, 12H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.63 MHz, ppm): δ 152.4, 139.8, 116.4, 115.7, 68.7, 31.9, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 116.4, 115.7, 68.7, 31.9, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1. FT-IR (KBr, cm^{-1}): ν = 3385 (NH), 3312 (NH), 2955, 2918, 2849, 1516, 1474, 1246, 1030, 827, 766, 525. EI-MS (m/z (%)): 249 (7) [M^+], 109 (100), 80 (7), 58 (8), 43 (13), 41 (17).

2.5. General procedure for the MCRs, and the synthesis of phthalonitrile derivatives 4

To a 15-mL glass pressure tube (Ace tube®, back seal, Aldrich Z181064) with magnetic stirring, were added sequentially *p*-chloranil (135.2 mg, 0.55 mmol), $NbCl_5$ (67.5 mg, 0.25 mmol, 50 mol%) and anhydrous CH_3CN (1 mL) under an argon atmosphere. To this mixture was added a previously prepared solution of 4-formylphthalonitrile (**1**) (78.1 mg, 0.50 mmol), anilines (**2a-g**) (0.50 mmol) and phenylacetylenes (**3a-i**) (0.55 mmol) in 4 mL of anhydrous CH_3CN under argon. The tube was closed and the resulting mixture was stirred at 100 °C in an oil bath for 24 h. After cooling to room temperature, the resultant reaction mixture was quenched with H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with sat. aqueous $NaHCO_3$ (3 × 20 mL) and H_2O (3 × 50 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum. Two different methods for purification were used:

Method 1: the residue was chromatographed on silica gel (70–230 mesh) and eluted with CH_2Cl_2/hexane (9:1, v/v). After solvent removal, the product was sonicated with ethanol (10 mL) for 20 min, followed by cooling in a refrigerator for 12 h, filtration, and dried under vacuum at room temperature.

Method 2: the residue was sonicated with ethanol (10 mL) for 20 min, followed by cooling in a refrigerator for 12 h, and filtration. This was repeated two more times with ethanol (10 mL) and once with pentane/EtOAc (7:3, v/v; 10 mL). Finally, the product was dried under vacuum at room temperature.

The same procedure was used when the multicomponent reaction was performed in the absence of *p*-chloranil.

2.5.1. 4-(4-Phenylquinolin-2-yl)phthalonitrile (4a)

The MCR was carried out according to the general procedure with aniline (**2a**) (46.6 mg, 0.50 mmol) and phenylacetylene (**3a**) (57.3 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4a** in 40% yield (66.9 mg, 0.202 mmol). When the same reaction was carried out in the absence of *p*-chloranil, compound **4a** was obtained in 29% yield (48.6 mg, 0.147 mmol). A similar result (43.1 mg, 0.130 mmol, yield 26%) was observed when the MCR was performed in the absence of *p*-chloranil at room temperature for 96 h. Data for **4a**: M.p. 240–241 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.77 (d, J = 1.7 Hz, 1H), 8.59 (dd, J = 8.3, 1.8 Hz, 1H), 8.26 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.86–7.80 (m, 2H), 7.63–7.55 (m, 6H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 151.8, 150.5, 148.8, 144.3, 137.6, 133.9, 132.5, 131.4, 130.5, 130.4, 129.5, 128.9, 128.8, 127.9, 126.5, 125.9, 118.4, 116.5, 115.6, 115.4.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.62 MHz,

ppm): δ 133.9, 132.5, 131.4, 130.5, 130.4, 129.5, 128.9, 128.8, 127.9, 125.9, 118.4. FT-IR (KBr, cm^{-1}): ν = 3115, 3076, 3051, 2234 (C≡N), 1589, 1489, 1416, 1362, 1217, 924, 887, 854, 766, 698, 579, 528. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{14}N_3^+$ $[M + H]^+$: 332.1182; Found: 332.1195.

2.5.2. 4-(6-Fluoro-4-phenylquinolin-2-yl)phthalonitrile (4b)

The MCR was carried out according to the general procedure with 4-fluoroaniline (**2b**) (56.1 mg, 0.50 mmol) and phenylacetylene (**3a**) (57.3 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4b** in 76% yield (132.5 mg, 0.379 mmol). When the same reaction was carried out in the absence of *p*-chloranil, compound **4b** was obtained in 42% yield (74.1 mg, 0.212 mmol). Data for **4b**: M.p. 238–239 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.74 (d, *J* = 1.8 Hz, 1H), 8.56 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.30–8.23 (m, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.85 (s, 1H), 7.63–7.51 (m, 7H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 161.4 (*J* = 250.4 Hz), 151.3, 150.0, 146.0, 144.0, 137.2, 134.0, 133.0, 132.9, 132.4, 131.3, 129.3, 129.2, 129.0, 127.5, 127.4, 121.0, 120.7, 118.9, 116.6, 115.7, 115.5, 115.4, 109.5, 109.3.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.62 MHz, ppm): δ 134.0, 133.0, 132.9, 132.4, 131.3, 129.3, 129.2, 129.0, 121.0, 120.7, 118.9, 109.5, 109.3. FT-IR (KBr, cm^{-1}): ν = 3115, 3076, 3049, 2234 (C≡N), 1626, 1591, 1493, 1364, 1234, 1198, 826, 773, 702, 527. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{13}FN_3^+$ $[M + H]^+$: 350.1088; Found: 350.1098.

2.5.3. 4-(6-Chloro-4-phenylquinolin-2-yl)phthalonitrile (4c), and the scale-up experiment

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and phenylacetylene (**3a**) (57.3 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4c** in 80% yield (147.4 mg, 0.403 mmol). When the same reaction was carried out in the absence of *p*-chloranil, compound **4c** was obtained in 49% yield (90.5 mg, 0.247 mmol). In the absence of $NbCl_5$, phthalonitrile **4c** was obtained in 6% yield (11.0 mg, 0.03 mmol).

The same procedure was used to scale up this MCR. In this case, a 100-mL glass pressure tube (Ace tube®, back seal, Aldrich Z566241) was used, and the following amounts of reagents were used: 4-chloroaniline (**2c**) (325.4 mg, 2.50 mmol), 4-formylphthalonitrile (**1**) (390.4 mg, 2.50 mmol), phenylacetylene (**3a**) (286.6 mg, 2.75 mmol), *p*-chloranil (676.2 mg, 2.75 mmol), $NbCl_5$ (337.7 mg, 1.25 mmol), and CH_3CN (25 mL). Yield: 70% (640.2 mg, 1.75 mmol). Data for **4c**: M.p. 261–262 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.75 (d, *J* = 1.7 Hz, 1H), 8.57 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 2.3 Hz, 1H), 7.86 (s, 1H), 7.76 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.67–7.58 (m, 3H), 7.57–7.51 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 152.0, 149.8, 147.2, 143.9, 137.0, 134.0, 132.4, 132.0, 131.5, 131.4, 129.3, 129.2, 129.0, 127.2, 124.7, 119.1, 116.6, 115.8, 115.4, 115.3.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.62 MHz, ppm): δ 134.0, 132.4, 132.0, 131.5, 131.4, 129.3, 129.2, 129.0, 124.7, 119.1. FT-IR (KBr, cm^{-1}): ν = 3117, 3080, 2235 (C≡N), 1587, 1483, 1362, 1152, 883, 822, 777, 706, 527. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{13}ClN_3^+$ $[M + H]^+$: 366.0793; Found: 366.0802.

2.5.4. 4-(6-Methoxy-4-phenylquinolin-2-yl)phthalonitrile (4d)

The MCR was carried out according to the general procedure with 4-methoxyaniline (**2d**) (61.6 mg, 0.50 mmol) and phenylacetylene (**3a**) (57.3 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4d** in 75% yield (135.1 mg, 0.374 mmol). When the same reaction was carried out in the absence of *p*-chloranil, compound **4d** was obtained in 52% yield (94.5 mg, 0.261 mmol). Data for **4d**: M.p. 197–198 °C. ^{1}H NMR ($CDCl_3$, 600.23 MHz, ppm): δ 8.73 (d, *J* = 1.8 Hz, 1H), 8.55 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.15 (d, *J* = 9.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.79 (s, 1H), 7.62–7.54 (m, 5H), 7.47 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 150.93 MHz, ppm): δ 159.0, 149.4, 148.8, 145.0, 144.5, 138.0, 133.9, 132.1, 131.9, 131.1, 129.2, 128.9, 128.8, 127.7, 123.1, 118.7, 116.5, 115.6, 115,5, 115,1, 103.6, 55.6.^{13}C NMR (DEPT-135) ($CDCl_3$, 150.93 MHz, ppm): δ 133.9, 132.1, 131.9, 131.1, 129.2, 128.9, 128.8, 123.1, 118.7, 103.6, 55.6. FT-IR (KBr, cm^{-1}): ν = 3113, 3078, 3051, 2949, 2824, 2234 (C≡N), 1626, 1599, 1493, 1368, 1265, 1223, 1042, 854, 826, 700, 528. HRMS (ESI-TOF): *m/z* calcd. for $C_{24}H_{16}N_3O^+$ $[M + H]^+$: 362.1288; Found: 362.1307.

2.5.5. 4-(6-Nitro-4-phenylquinolin-2-yl)phthalonitrile (4e)

The MCR was carried out according to the general procedure with 4-nitroaniline (**2e**) (69.1 mg, 0.50 mmol) and phenylacetylene (**3a**) (57.3 mg, 0.55 mmol), and purified by method 2 to afford the phthalonitrile **4e** in 55% yield (103.6 mg, 0.275 mmol). When the same reaction was carried out in the absence of *p*-chloranil, compound **4e** was obtained in 41% yield (77.8 mg, 0.207 mmol). Data for **4e**: M.p. > 300 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.91 (d, *J* = 2.5 Hz, 1H), 8.80 (d, *J* = 1.2 Hz, 1H), 8.63 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.58 (dd, *J* = 9.2, 2.5 Hz, 1H), 8.40 (d, *J* = 9.3 Hz, 1H), 8.06–7.97 (m, 2H), 7.72–7.62 (m, 3H), 7.62–7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 154.9, 152.7, 146.3, 143.0, 136.0, 134.0, 132.6, 132.1, 131.6, 129.8, 129.3, 125.5, 123.8, 122.9, 119.7, 116.7, 116.5, 115.1.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.62 MHz, ppm): δ 134.0, 132.6, 132.1, 131.6, 129.8, 129.3, 123.8, 122.9, 119.7. FT-IR (KBr, cm^{-1}): ν = 3105, 3080, 3051, 2235 (C≡N), 1620, 1591, 1551, 1485, 1410, 1342, 1084, 841, 810, 766, 746, 704, 527. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{13}N_4O_2^+$ $[M + H]^+$: 377.1033; Found: 377.1042.

2.5.6. 4-(6-Ethyl-4-phenylquinolin-2-yl)phthalonitrile (4f)

The MCR was carried out according to the general procedure with 4-ethylaniline (**2f**) (61.8 mg, 0.50 mmol) and phenylacetylene (**3a**) (57.3 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4f** in 75% yield (135.3 mg, 0.376 mmol). Data for **4f**: M.p. 215–216 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.75 (d, *J* = 1.6 Hz, 1H), 8.56 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.80 (s, 1H), 7.75–7.66 (m, 2H), 7.64–7.51 (m, 5H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.63 MHz, ppm): δ 150.9, 149.8, 147.6, 144.5, 144.4, 137.8, 133.9, 132.4, 131.6, 131.3, 130.3, 129.4, 128.8, 126.5, 123.4, 118.4, 116.5, 115.5, 115.4, 115.3, 29.2, 15.4.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 133.9, 132.4, 131.6, 131.3, 130.3, 129.4, 128.8, 123.4, 118.4, 29.2, 15.4. FT-IR (KBr, cm^{-1}): ν = 3074, 2965, 2230 (C≡N), 1597, 1585, 1489, 1414, 845, 700, 523. HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{18}N_3^+$ $[M + H]^+$: 360.1495; Found: 360.1498.

2.5.7. 4-(6-(Decyloxy)-4-phenylquinolin-2-yl)phthalonitrile (4g)

The MCR was carried out according to the general procedure with 4-(decyloxy)aniline (**2g**) (124.7 mg, 0.50 mmol) and phenylacetylene (**3a**) (57.3 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4g** in 76% yield (185.1 mg, 0.379 mmol). Data for **4g**: M.p. 128–130 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.73 (d, *J* = 1.2 Hz, 1H), 8.55 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 (s, 1H), 7.65–7.51 (m, 5H), 7.47 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.79 (dt, *J* = 14.9, 6.4 Hz, 2H), 1.50–1.41 (m, 2H), 1.39–1.21 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.63 MHz, ppm): δ 158.5, 149.2, 148.7, 144.8, 144.5, 138.0, 133.9, 132.1, 131.8, 131.0, 129.2, 128.9, 128.8, 127.7, 123.3, 118.6, 116.4, 115.6, 155.5, 115.0, 104.3, 68.4, 31.9, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 133.9, 132.1, 131.8, 131.0, 129.2, 128.9, 128.8, 123.3, 118.6, 104.3, 68.4, 31.9, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. FT-IR (KBr, cm^{-1}): ν = 3078, 3049, 2918, 2851, 2234 (C≡N), 1622, 1599, 1489, 1470, 1369, 1223, 1036, 860, 825, 702, 527. HRMS (ESI-TOF): *m/z* calcd. for $C_{33}H_{34}N_3O^+$ $[M + H]^+$: 488.2696; Found: 488.2703.

2.5.8. 4-(6-Methoxy-4-(4-pentylphenyl)quinolin-2-yl)phthalonitrile (4h)

The MCR was carried out according to the general procedure with 4-

methoxyaniline (**2d**) (61.6 mg, 0.50 mmol) and 1-ethynyl-4-pentylbenzene (**3b**) (97.7 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4h** in 70% yield (150.9 mg, 0.350 mmol). Data for **4h**: M.p. 177–178 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.70 (d, J = 1.5 Hz, 1H), 8.52 (dd, J = 8.3, 1.7 Hz, 1H), 8.12 (d, J = 9.2 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.76 (s, 1H), 7.51–7.43 (m, 3H), 7.42–7.36 (m, 2H), 7.28–7.23 (m, 1H), 3.83 (s, 3H), 2.74 (t, J = 7.8 Hz, 2H), 1.73 (quint, J = 7.4 Hz, 2H), 1.46–1.34 (m, 4H), 0.95 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 158.9, 149.4, 148.9, 145.0, 144.5, 143.9, 135.2, 133.9, 132.1, 131.9, 131.0, 129.1, 128.9, 127.8, 122.9, 118.7, 116.4, 115.6, 115.5, 115.0, 103.8, 55.6, 35.8, 31.6, 31.1, 22.6, 14.1.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.62 MHz, ppm): δ 133.9, 132.1, 131.9, 131.0, 129.1, 129.0, 122.9, 118.7, 103.8, 55.6, 35.8, 31.6, 31.1, 22.6, 14.1. FT-IR (KBr, cm^{-1}): ν = 3084, 3034, 2994, 2951, 2924, 2859, 2239 (C≡N), 2230 (C≡N), 1620, 1595, 1493, 1470, 1225, 1042, 847, 831, 523. HRMS (ESI-TOF): *m/z* calcd. for $C_{29}H_{26}N_3O^+$ $[M + H]^+$: 432.2070; Found: 432.2088.

2.5.9. 4-(6-(Decyloxy)-4-(4-pentylphenyl)quinolin-2-yl)phthalonitrile (4i)

The MCR was carried out according to the general procedure with 4-(decyloxy)aniline (**2g**) (124.7 mg, 0.50 mmol) and 1-ethynyl-4-pentylbenzene (**3b**) (97.7 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4i** in 81% yield (226.9 mg, 0.407 mmol). Data for **4i**: M.p. 145–147 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.72 (br s, 1H), 8.54 (dd, J = 8.2, 1.4 Hz, 1H), 8.13 (d, J = 9.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.77 (s, 1H), 7.53–7.35 (m, 5H), 7.25 (d, J = 2.2 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 1.87–1.69 (m, 4H), 1.51–1.23 (m, 18H), 0.95 (t, J = 6.8 Hz, 3H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.63 MHz, ppm): δ 158.4, 149.2, 148.8, 144.9, 144.6, 143.8, 135.2, 133.9, 132.1, 131.8, 131.0, 129.1, 128.9, 127.8, 123.2, 118.6, 116.4, 115.6, 115.5, 115.0, 104.5, 68.3, 35.8, 31.9, 31.6, 31.1, 29.6, 29.4, 29.3, 29.1, 26.1, 22.7, 22.6, 14.1, 14.0.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 133.9, 132.1, 131.8, 131.0, 129.1, 128.9, 123.2, 118.6, 104.5, 68.3, 35.8, 31.9, 31.6, 31.1, 29.6, 29.4, 29.3, 29.1, 26.1, 22.7, 22.6, 14.1, 14.0. FT-IR (KBr, cm^{-1}): ν = 3040, 2924, 2853, 2226 (C≡N), 1618, 1597, 1493, 1261, 1215, 1126, 1032, 825, 525. HRMS (ESI-TOF): *m/z* calcd. for $C_{38}H_{44}N_3O^+$ $[M + H]^+$: 558.3479; Found: 558.3483.

2.5.10. 4-(6-Chloro-4-(4-pentylphenyl)quinolin-2-yl)phthalonitrile (4j)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and 1-ethynyl-4-pentylbenzene (**3b**) (97.7 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4j** in 80% yield (174.9 mg, 0.401 mmol). Data for **4j**: M.p. 224–226 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.74 (d, J = 1.6 Hz, 1H), 8.56 (dd, J = 8.2, 1.7 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 8.01–7.92 (m, 2H), 7.85 (s, 1H), 7.74 (dd, J = 9.0, 2.3 Hz, 1H), 7.51–7.36 (m, 4H), 2.76 (t, J = 7.8 Hz, 2H), 1.74 (quint, J = 7.4 Hz, 2H), 1.48–1.34 (m, 4H), 0.96 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.63 MHz, ppm): δ 152.0, 149.9, 147.2, 144.4, 143.9, 134.2, 134.0, 133.8, 132.4, 131.9, 131.4, 129.3, 129.1, 127.2, 124.8, 119.1, 116.6, 115.8, 115.4, 115.3, 35.8, 31.6, 31.1, 22.6, 14.1.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 134.0, 132.4, 131.9, 131.4, 129.3, 129.1, 124.8, 119.1, 35.8, 31.6, 31.1, 22.6, 14.1. FT-IR (KBr, cm^{-1}): ν = 3080, 2924, 2857, 2234 (C≡N), 1595, 1483, 1362, 1155, 827, 525. HRMS (ESI-TOF): *m/z* calcd. for $C_{28}H_{23}ClN_3^+$ $[M + H]^+$: 436.1575; Found: 436.1573.

2.5.11. 4-(4-(4-Butylphenyl)-6-chloroquinolin-2-yl)phthalonitrile (4k)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and 1-butyl-4-ethynylbenzene (**3c**) (91.6 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4k** in 73% yield (154.3 mg, 0.366 mmol). Data for **4k**: M.p. 224–225 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.74 (d, J = 0.9 Hz, 1H), 8.57 (dd, J = 8.2, 1.3 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 8.04–7.91 (m, 2H), 7.85 (s, 1H), 7.74 (dd, J = 9.0, 2.0 Hz, 1H), 7.52–7.36 (m, 4H), 2.77 (t, J = 7.7 Hz, 2H), 1.73 (quint, J = 7.6 Hz, 2H), 1.46 (sext, J = 7.4 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.63 MHz, ppm): δ 152.0, 149.9, 147.2, 144.3, 143.9, 134.2, 134.0, 133.8, 132.4, 131.9, 131.4, 129.3, 129.1, 127.3, 124.8, 119.1, 116.6, 115.8, 115.4, 115.3, 35.5, 33.6, 22.4, 14.0.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 134.0, 132.4, 131.9, 131.4, 129.3, 129.1, 124.8, 119.1, 35.5, 33.6, 22.4, 14.0. FT-IR (KBr, cm^{-1}): ν = 3080, 3034, 2957, 2930, 2858, 2232 (C≡N), 1595, 1483, 1155, 825, 523. HRMS (ESI-TOF): *m/z* calcd. for $C_{27}H_{21}ClN_3^+$ $[M + H]^+$: 422.1419; Found: 422.1422.

2.5.12. 4-(4-(4-(tert-Butyl)phenyl)-6-chloroquinolin-2-yl)phthalonitrile (4l)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and 1-(*tert*-butyl)-4-ethynylbenzene (**3d**) (90.7 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4l** in 79% yield (166.9 mg, 0.395 mmol). Data for **4l**: M.p. 298–300 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.74 (d, J = 1.4 Hz, 1H), 8.56 (dd, J = 8.2, 1.6 Hz, 1H), 8.19 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.85 (s, 1H), 7.75 (dd, J = 9.0, 2.3 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.63 MHz, ppm): δ 152.5, 152.0, 149.8, 147.2, 143.9, 134.0, 133.8, 132.4, 131.9, 131.4, 129.1, 127.2, 126.0, 124.8, 119.1, 116.6, 115.8, 115.4, 115.3, 31.3.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.63 MHz, ppm): δ 134.0, 132.4, 131.9, 131.4, 129.1, 126.0, 124.8, 119.1, 31.3. FT-IR (KBr, cm^{-1}): ν = 3084, 2951, 2904, 2868, 2235 (C≡N), 1597, 1483, 1362, 1157, 849, 827, 600, 525. HRMS (ESI-TOF): *m/z* calcd. for $C_{27}H_{21}ClN_3^+$ $[M + H]^+$: 422.1419; Found: 422.1418.

2.5.13. 4-(6-Chloro-4-(4-methoxyphenyl)quinolin-2-yl)phthalonitrile (4m)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and 1-ethynyl-4-methoxybenzene (**3e**) (74.9 mg, 0.55 mmol), and purified by method 2 to afford the phthalonitrile **4m** in 78% yield (155.3 mg, 0.392 mmol). Data for **4m**: M.p. dec. above 280 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm) δ 8.74 (d, J = 1.6 Hz, 1H), 8.57 (dd, J = 8.2, 1.8 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.97 (dd, J = 5.2, 3.0 Hz, 2H), 7.83 (s, 1H), 7.75 (dd, J = 9.0, 2.3 Hz, 1H), 7.51–7.46 (m, 2H), 7.16–7.11 (m, 2H), 3.95 (s, 3H). FT-IR (KBr, cm^{-1}): ν = 3233, 3078, 2941, 2845, 2237 (C≡N), 1593, 1514, 1483, 1263, 1180, 1032, 824, 569, 523. HRMS (ESI-TOF): *m/z* calcd. for $C_{24}H_{15}ClN_3O^+$ $[M + H]^+$: 396.0898; Found: 396.0905.

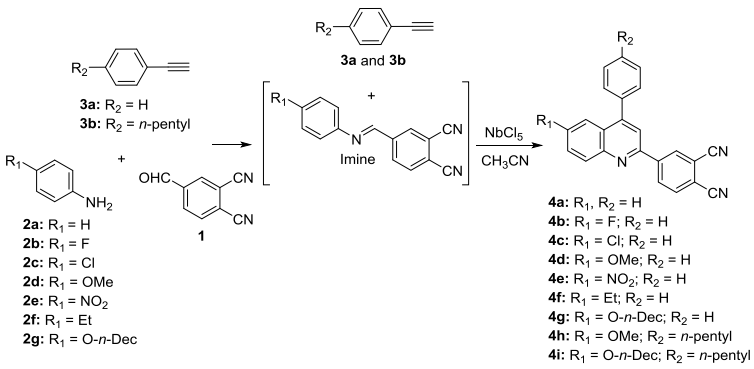
2.5.14. 4-(6-Chloro-4-(4-methylphenyl)quinolin-2-yl)phthalonitrile (4n)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and 1-ethynyl-4-methylbenzene (**3f**) (65.9 mg, 0.55 mmol), and purified by method 2 to afford the phthalonitrile **4n** in 80% yield (152.7 mg, 0.402 mmol). Data for **4n**: M.p. 272–274 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.74 (d, J = 1.6 Hz, 1H), 8.56 (dd, J = 8.3, 1.7 Hz, 1H), 8.19 (d, J = 9.0 Hz, 1H), 7.99–7.93 (m, 2H), 7.84 (s, 1H), 7.75 (dd, J = 9.0, 2.3 Hz, 1H), 7.46–7.39 (m, 4H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 152.0, 149.8, 147.2, 143.9, 139.4, 134.0, 133.9, 132.4, 131.9, 131.4, 129.7, 129.3, 127.3, 124.8, 119.0, 116.6, 115.8, 115.4, 21.4.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.62 MHz, ppm): δ 134.0, 132.4, 131.9, 131.4, 129.7, 129.3, 124.8, 119.0, 21.4. FT-IR (KBr, cm^{-1}): ν = 3080, 2920, 2232 (C≡N), 1595, 1483, 1153, 856, 845, 814, 525. HRMS (ESI-TOF): *m/z* calcd. for $C_{24}H_{15}ClN_3^+$ $[M + H]^+$: 380.0949; Found: 380.0949.

2.5.15. 4-(6-Chloro-4-(4-fluorophenyl)quinolin-2-yl)phthalonitrile (4o)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and 1-ethynyl-4-fluorobenzene (**3g**) (66.7 mg, 0.55 mmol), and purified by method 2 to afford the phthalonitrile **4o** in 79% yield (152.4 mg, 0.397 mmol). Data for **4o**: M.p. > 300 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.74 (d,

Table 1
Synthesis of phthalonitriles **4a-i**.[a]



Entry	Aniline	Product	R_1	R_2	Yield (%)[f]
1[b]	**2a**	**4a**	H	H	0
2[c]	**2a**	**4a**	H	H	26
3[d]	**2a**	**4a**	H	H	29
4	**2a**	**4a**	H	H	40
5[d]	**2b**	**4b**	F	H	42
6	**2b**	**4b**	F	H	76
7[e]	**2c**	**4c**	Cl	H	6
8[d]	**2c**	**4c**	Cl	H	49
9	**2c**	**4c**	Cl	H	80
10[d]	**2d**	**4d**	OMe	H	52
11	**2d**	**4d**	OMe	H	75
12[d]	**2e**	**4e**	NO_2	H	41
13	**2e**	**4e**	NO_2	H	55
14	**2f**	**4f**	Et	H	75
15	**2g**	**4g**	O-*n*-Dec	H	76
16	**2d**	**4h**	OMe	*n*-pentyl	70
17	**2g**	**4i**	O-*n*-Dec	*n*-pentyl	81

[a] Conditions: 4-formylphthalonitrile (**1**) (0.50 mmol), aniline derivatives (**2a-g**) (0.50 mmol), phenylacetylenes (**3a**, **3b**) (0.55 mmol), $NbCl_5$ (50 mol%), *p*-chloranil (0.55 mmol) in CH_3CN (5 mL) were heated in a glass pressure tube at 100 °C for 24 h.
[b] The reaction was carried out in the absence of $NbCl_5$ and *p*-chloranil at room temperature.
[c] The reaction was carried out in the absence of *p*-chloranil at room temperature for 96 h.
[d] The reaction was carried out in the absence *p*-chloranil.
[e] The reaction was carried out in the absence of $NbCl_5$.
[f] Isolated yields.

J = 1.5 Hz, 1H), 8.57 (dd, *J* = 8.2, 1.7 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.83 (s, 1H), 7.77 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.56–7.50 (m, 2H), 7.35–7.29 (m, 2H). FT-IR (KBr, cm^{-1}): ν = 3076, 2234 (C≡N), 1597, 1514, 1483, 1364, 1240, 1165, 847, 829, 825, 527. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{12}ClFN_3^+$ $[M + H]^+$: 384.0698; Found: 384.0703.

2.5.16. Methyl 4-(6-chloro-2-(3,4-dicyanophenyl)quinolin-4-yl)benzoate (4p)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and methyl 4-ethynylbenzoate (**3h**) (97.9 mg, 0.55 mmol), and purified by method 2 to afford the phthalonitrile **4p** in 57% yield (120.5 mg, 0.284 mmol). Data for **4p**: M.p. 281–283 °C. ^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 8.76 (d, *J* = 1.4 Hz, 1H), 8.57 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.30–8.25 (m, 2H), 8.22 (d, *J* = 9.1 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.87 (s, 1H), 7.83 (d, *J* = 2.2 Hz, 1H), 7.78 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.65–7.60 (m, 2H), 4.02 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): δ 166.5, 152.0, 148.6, 147.1, 143.6, 141.4, 134.4, 134.0, 132.4, 132.1, 131.7, 131.4, 130.9, 130.2, 129.5, 126.7, 124.3, 118.9, 116.7, 116.0, 115.3, 52.5.^{13}C NMR (DEPT-135) ($CDCl_3$, 100.62 MHz, ppm): δ 134.0, 132.4, 132.1, 131.7, 131.4, 130.2, 129.5, 124.3, 118.9, 52.5. FT-IR (KBr, cm^{-1}): ν = 3078, 2955, 2237 (C≡N), 1728 (C=O), 1593, 1483, 1288, 1119, 854, 827, 708, 525. HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{15}ClN_3O_2^+$ $[M + H]^+$: 424.0847; Found: 424.0852.

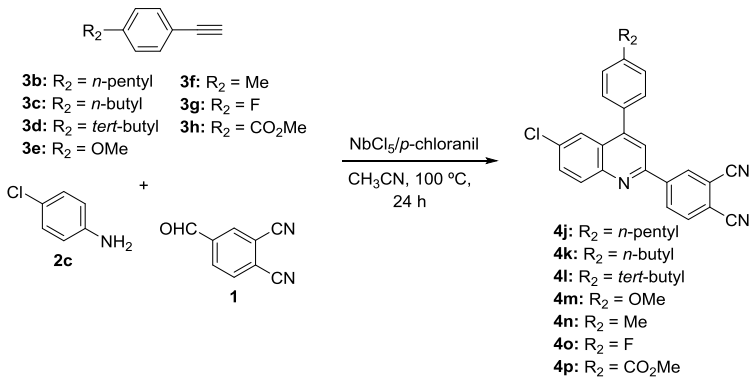
2.5.17. 4-(6-Chloro-4-phenylquinolin-2-yl-3-d)phthalonitrile (4q)

The MCR was carried out according to the general procedure with 4-chloroaniline (**2c**) (65.1 mg, 0.50 mmol) and phenylacetylene-*d* (**3i**) (56.7 mg, 0.55 mmol), and purified by method 1 to afford the phthalonitrile **4q** in 74% yield (135.6 mg, 0.369 mmol). Data for **4q**: M.p. 260–261 °C. ^{1}H NMR ($CDCl_3$, 600.23 MHz, ppm): δ 8.75 (d, *J* = 1.7 Hz, 1H), 8.57 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 2.3 Hz, 1H), 7.76 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.64–7.57 (m, 3H), 7.56–7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 150.93 MHz, ppm): δ 152.0, 149.7, 147.2, 143.8, 136.9, 134.0, 132.4, 132.0, 131.5, 131.4, 129.3, 129.2, 129.1, 127.2, 124.7, 118.8 (*J* = 25.0 Hz), 116.6, 115.8, 115.4, 115.3.^{13}C NMR (DEPT-135) ($CDCl_3$, 150.93 MHz, ppm): δ 134.0, 132.4, 132.0, 131.5, 131.4, 129.3, 129.2, 129.1, 124.7. FT-IR (KBr, cm^{-1}): ν = 3115, 3080, 3055, 2234 (C≡N), 1599, 1537, 1481, 1358, 1086, 826, 766, 746, 704, 573, 527. HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{12}DClN_3^+$ $[M + H]^+$: 367.0855; Found: 367.0865.

2.6. General procedure for the synthesis of zinc phthalocyanine-quinoline dyads (5a-c)

ZnPCs **5a-c** were synthesized following previously reported procedures with minor modifications [57]. To a 15-mL glass pressure tube (Ace pressure tube®, back seal, Aldrich Z181064) equipped with a

Table 2
Synthesis of phthalonitriles **4j-p**.[a]



Entry	Acetylene	Product	R_2	Yield (%)[b]
1	**3b**	**4j**	*n*-pentyl	80
2	**3c**	**4k**	*n*-butyl	73
3	**3d**	**4l**	*tert*-butyl	79
4	**3e**	**4m**	OMe	78
5	**3f**	**4n**	Me	80
6	**3g**	**4o**	F	79
7	**3h**	**4p**	CO_2Me	57

[a] Conditions: $NbCl_5$ (50 mol%), *p*-chloranil (0.55 mmol), 4-formylphthalonitrile (**1**) (0.50 mmol), 4-chloroaniline (**2c**) (0.50 mmol) and phenylacetylene derivatives (**3b**-**h**) (0.55 mmol) in CH_3CN (5 mL) at 100 °C for 24 h.
[b] Isolated yields.

magnetic stir bar and rubber septum, were added sequentially phthalonitrile derivatives (**4g-i**) (0.09 mmol), $Zn(OTf)_2$ (8.3 mg, 22.5 μmol, 0.25 equiv), HMDS (76 μL, 4.0 equiv) and DMF (200 μL) under an argon atmosphere at room temperature. The tube was closed and the resulting mixture was stirred at 130 °C under light protection for 24 h. After cooling to room temperature, 5 mL of methanol was added, and the solid was filtered under vacuum and washed with methanol.

2.6.1. Zinc phthalocyanine-quinoline 5a

The crude solid obtained from phthalonitrile **4g** (43.9 mg, 0.09 mmol) was purified by flash column chromatography (silica gel, 230–400 mesh), eluting initially with dichloromethane/toluene/ethyl acetate (4:4:2, v/v/v) to remove fluorescent impurities and then with toluene/ethyl acetate/methanol (6:3:1, v/v/v) to elute the product. Evaporation of the elute gave a solid which was dissolved in a small amount of chloroform, methanol was added afterwards, and the solution was stored at room temperature overnight. The green solid obtained was filtered, washed with methanol, and then dried under vacuum to afford the pure ZnPC **5a** (24.5 mg, 12.15 μmol, 54%). Data for **5a**: ^{1}H NMR ($CDCl_3$/DMSO-d_6 = 2:1, 400.15 MHz, ppm): δ 9.63–9.11 (m, 6H), 8.91–8.43 (m, 8H), 8.33–7.98 (m, 14H), 7.91–7.74 (m, 10H), 7.49–6.96 (m, 10H), 4.01–3.66 (m, 8H), 1.92–1.73 (m, 8H), 1.62–1.26 (m, 56H), 1.02–0.90 (m, 12H). UV–Vis (THF): λ_{max}/nm (log ε) = 695 (5.59), 626 (4.89), 357 (5.14). FT-IR (KBr, cm^{-1}): ν = 2922, 2853, 1618, 1589, 1545, 1491, 1385, 1356, 1225, 1095, 910, 831, 748, 702. HRMS (MALDI-TOF): *m/z* calcd. for $C_{132}H_{133}N_{12}O_4Zn^+$ $[M + H]^+$: 2013.9859; Found: 2013.9837.

2.6.2. Zinc phthalocyanine-quinoline 5b

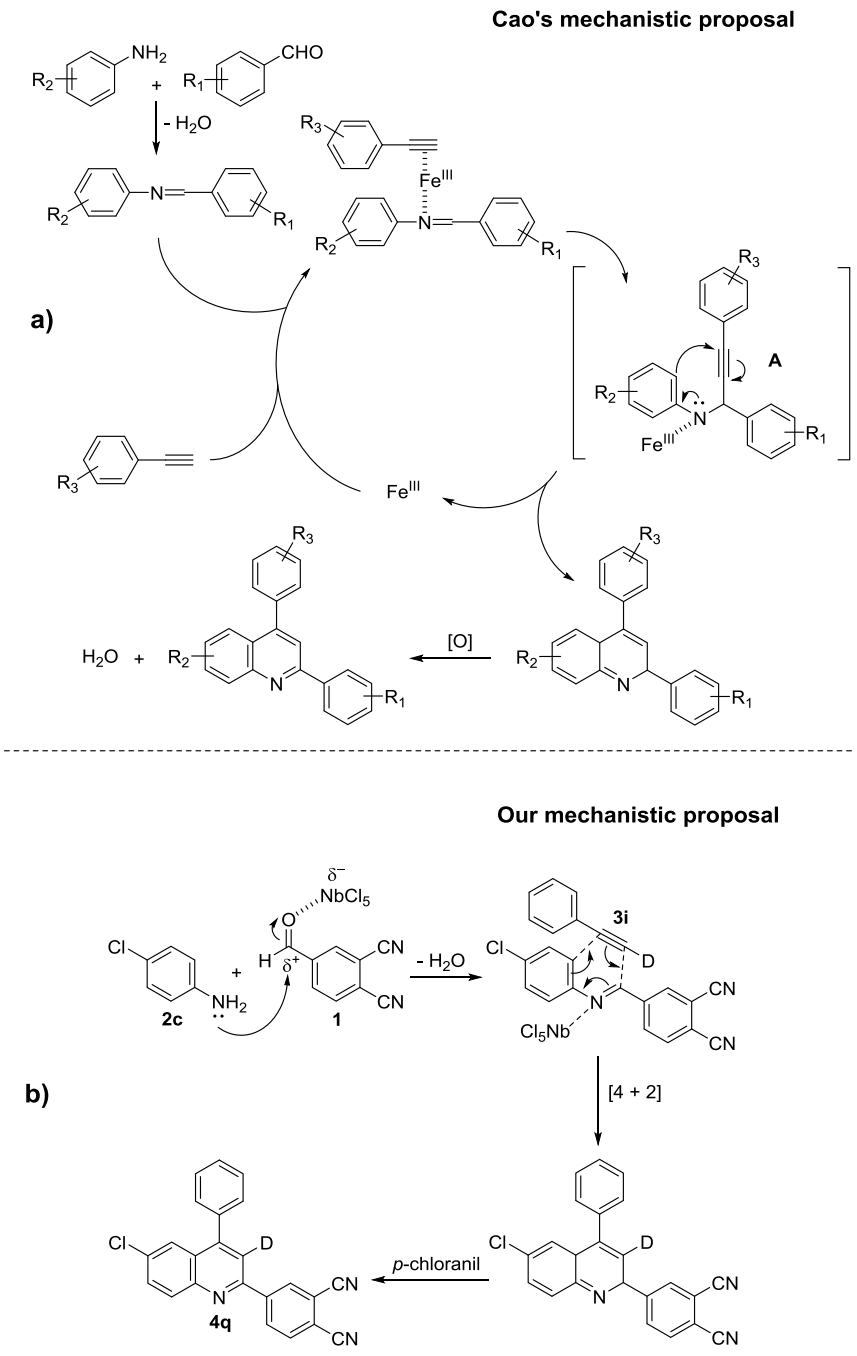
The crude solid obtained from phthalonitrile **4h** (38.8 mg, 0.09 mmol) was purified by flash column chromatography (silica gel, 230–400 mesh), eluting initially with toluene/ethyl acetate (8:2, v/v) to remove fluorescent impurities and then with toluene/ethyl acetate/methanol (7:2:1, v/v/v) to elute the product. Evaporation of the elute gave a solid which was dissolved in a small amount of chloroform, methanol was added afterwards, and the solution was stored at room temperature overnight. The green solid obtained was filtered, washed with methanol, and then dried under vacuum to afford the pure ZnPC **5b** (25.9 mg, 14.45 μmol, 64%). Data for **5b**: ^{1}H NMR ($CDCl_3$/DMSO-d_6 = 2:1, 400.15 MHz, ppm): δ 9.71–9.14 (m, 6H), 8.99–8.42 (m, 8H), 8.35–8.02 (m, 9H), 7.89–7.57 (m, 12H), 7.51–6.98 (m, 9H), 4.00–3.58 (m, 12H), 3.09–2.81 (m, 8H), 2.08–1.82 (m, 8H), 1.68–1.38 (m, 16H), 1.13–0.91 (m, 12H). UV–Vis (THF): λ_{max}/nm (log ε) = 695 (5.50), 626 (4.77), 355 (5.05). FT-IR (KBr, cm^{-1}): ν = 2926, 2853, 1620, 1589, 1545, 1493, 1385, 1356, 1227, 1095, 903, 831, 750. HRMS (MALDI-TOF): *m/z* calcd. for $C_{116}H_{101}N_{12}O_4Zn^+$ $[M + H]^+$: 1789.7355; Found: 1789.7329.

2.6.3. Zinc phthalocyanine-quinoline 5c

The crude solid obtained from phthalonitrile **4i** (50.2 mg, 0.09 mmol) was purified by flash column chromatography (silica gel, 230–400 mesh), eluting initially with dichloromethane/toluene/ethyl acetate (6:2:2, v/v/v) to remove fluorescent impurities and then with toluene/ethyl acetate/methanol (7:2:1, v/v/v) to elute the product. Evaporation of the elute gave a solid which was dissolved in a small amount of chloroform, methanol was added afterwards, and the solution was stored at room temperature overnight. The green solid obtained was filtered, washed with methanol, and then dried under vacuum to afford the pure ZnPC **5c** (30.0 mg, 13.06 μmol, 58%). Data for **5c**: ^{1}H NMR ($CDCl_3$/DMSO-d_6 = 2:1, 400.15 MHz, ppm): δ 9.77–9.10 (m, 6H), 9.05–8.42 (m, 8H), 8.39–8.01 (m, 9H), 7.97–7.75 (m, 7H), 7.67–7.53 (m, 5H), 7.51–7.02 (m, 9H), 4.10–3.68 (m, 8H), 3.02–2.82 (m, 8H), 2.13–1.75 (m, 16H), 1.68–1.24 (m, 72H), 1.15–0.90 (m, 24H). UV–Vis (THF): λ_{max}/nm (log ε) = 695 (5.63), 626 (4.92), 355 (5.19). FT-IR (KBr, cm^{-1}): ν = 2924, 2853, 1618, 1589, 1545, 1493, 1385, 1356, 1223, 1095, 910, 829, 748. HRMS (MALDI-TOF): *m/z* calcd. for $C_{152}H_{173}N_{12}O_4Zn^+$ $[M + H]^+$: 2294.2989; Found: 2294.3037.

2.7. Aggregation studies

The aggregation behaviour of ZnPCs **5a-c** was investigated in THF using UV–Vis spectroscopy (Fig. 3 and Figs. S1 and S2). Different concentrations of zinc phthalocyanines **5a-c** were prepared and the absorbances measured.



Scheme 1. a) Mechanism proposed by Cao et al. [62]; **b**) Our mechanistic proposal based on experiment.

2.8. Fluorescence measurements

The values of Φ_F were obtained by comparing the areas under the fluorescence spectra of the samples (ZnPCs **5a-c**) with the area under the fluorescence spectrum of the standard (unsubstituted ZnPC) (see SI, Fig. S3 and Table S1) [58]. A solution of each compound was prepared in THF and the absorbances at the excitation wavelength (λ_{ex} = 630 nm) were adjusted to be 0.05 for comparison. Dissolved oxygen was removed from the solutions by bubbling argon. The calculation was performed by Eq. (1):

$$\Phi_F = \Phi_F^{Std} \times \frac{F \times A_{Std}}{F_{Std} \times A} \quad (1)$$

In Eq. (1), Φ_F^{Std} is the fluorescence quantum yield of the standard (for unsubstituted ZnPC is 0.25 in THF) [58], F and F_{Std} are the areas under the fluorescence emission curves of the sample and standard, respectively. A and A_{Std} are the absorbances of the sample and standard, respectively, at the excitation wavelength (λ_{ex} = 630 nm).

2.9. Molar absorption coefficient (ε)

The values for ε were obtained from the data of Fig. 3 and Figs. S1 and S2. All the graphs of absorbance against concentration for each band are in agreement with the Lambert-Beer's law (see SI, Tables S2–S4), affording straight lines with $R^2 > 0.99$. In each graph, the slope of this line is the molar absorptivity (ε) divided by the optical path length, as described in Eq. (2) [59]:

$$A = \varepsilon \times c \times l \quad (2)$$

In Eq. (2), A is the absorbance, c is the concentration and l is the optical

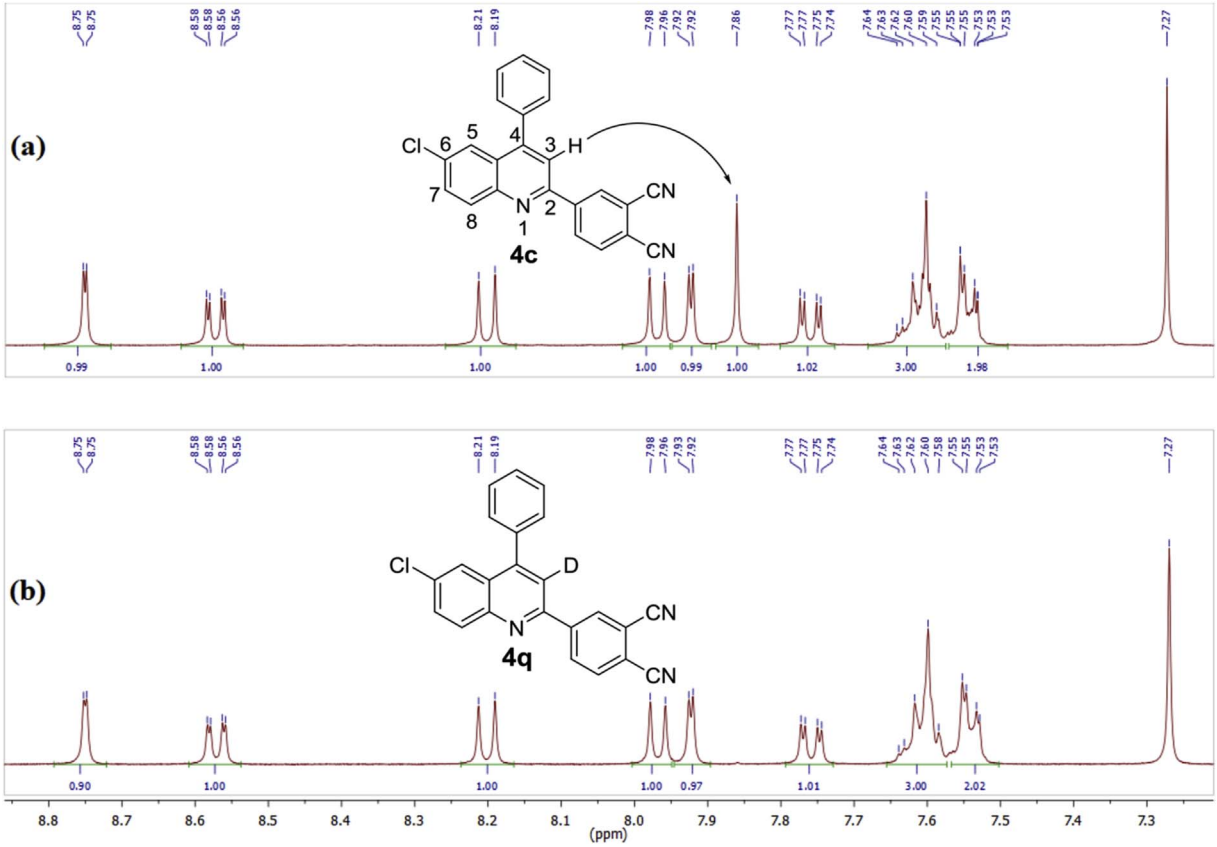


Fig. 1. Comparison of ^{1}H NMR (400 MHz) spectra in $CDCl_3$ of **4c** (**a**) and **4q** (**b**).

path length, respectively.

2.10. Photobleaching studies

A solution of ZnPCs **5a-c** in THF with an absorbance near 1 was irradiated in the dark with a white LED lamp (30 W) (see SI, Fig. S4) in periods of 1 min (10 irradiations), 5 min (4 irradiations), 10 min (3 irradiations), and 30 min (2 irradiations), totaling 2 h. After each irradiation time, the UV–Vis spectrum was measured in order to observe the possible photobleaching by reduction of the photosensitizer concentration (Fig. 5 and Figs. S5 and S6).

3. Results and discussion

3.1. Synthesis of phthalonitrile derivatives (*4a-q*)

Phthalonitrile **1** was used in the reactions with substituted anilines **2a-g** and phenylacetylenes **3a**,**b** in MCRs promoted by $NbCl_5$, for the preparation of the phthalonitriles **4a-i** (Table 1).

We initially tested 4-formylphthalonitrile (**1**) and phenylacetylene (**3a**) as substrates, for exploring the aniline substrate scope. When the MCR was carried out with aniline (**2a**) in the absence of $NbCl_5$ and *p*-chloranil at room temperature for 24 h, the desired phthalonitrile (**4a**) was not obtained (Table 1, entry 1). The formation of an imine (an intermediate isolable in this MCR) was detected. When the same MCR was carried out in the presence of $NbCl_5$ at room temperature for 96 h, the phthalonitrile **4a** was obtained in 26% yield (entry 2). A similar result (29%) was observed when the MCR was performed at 100 °C for 24 h (entry 3). However, when $NbCl_5$ and *p*-chloranil were used together also at 100 °C for 24 h, the compound **4a** was obtained in 40% yield (entry 4). Interestingly, when the MCR was carried out with the aniline **2c** and *p*-chloranil (without $NbCl_5$), the phthalonitrile **4c** was obtained in 6% yield (entry 7). Similar results had already been reported by Leardini et al. [60,61] for the synthesis of 2,4-diphenylquinolines from imines and phenylacetylene under oxidising conditions. It is also clear from Table 1 that anilines which contain either electron-donating or electron-withdrawing groups can be both tolerated in this MCR (entries 5, 6 and 8–17) with no evident changes in yields. For example, the MCRs carried out with the substituted anilines **2b-e** in the presence of the $NbCl_5$/*p*-chloranil system at 100 °C for 24 h provided the phthalonitriles **4b-e** in yields ranging from 55 to 80% (entries 6, 9, 11 and 13). These results are better than those obtained using only $NbCl_5$ under the same conditions (41–52%, Table 1, entries 5, 8, 10 and 12). In addition, the MCRs carried out with the anilines **2f**,**g** and phenylacetylene (**3a**) or **2d**,**g** and 1-ethynyl-4-pentylbenzene (**3b**) in the presence of the $NbCl_5$/*p*-chloranil system at 100 °C for 24 h afforded the compounds **4f-i** in 70–81% yields (entries 14–17).

Subsequently, we used 4-formylphthalonitrile (**1**) and 4-chloroaniline (**2c**) as model substrates for exploring the phenylacetylene substrate scope (Table 2).

Product **4c** was selected due to its efficiency in the MCR, as previously demonstrated (80%, Table 1, entry 9). It was found that substituted phenylacetylenes (**3b-g**) were suitable substrates for this MCR (Table 2), and the expected phthalonitriles (**4j-o**) were obtained in 73–80% yields (Table 2, entries 1–6) using the $NbCl_5$/*p*-chloranil system at 100 °C for 24 h. Notably, when phenylacetylene **3h** (R_2 = CO_2Me) was used in the MCR under the same conditions, the phthalonitrile **4p** was obtained in only 57% yield (entry 7), possibly due to the strong electron-withdrawing and mesomeric effect of the ester group. Furthermore, we have successfully performed a scaled-up experiment of **1** (2.5 mmol) with **2c** and **3a** in the same conditions established in Table 1 and entry 9, and obtained 640.2 mg of **4c** in 70% yield (see Section 2.5.3).

Intriguingly, the literature on similar MCRs suggests that this reaction proceeds by a stepwise pathway involving the propargylamine **A** as a key intermediate (Scheme 1a) [62–70], or by a concerted pathway

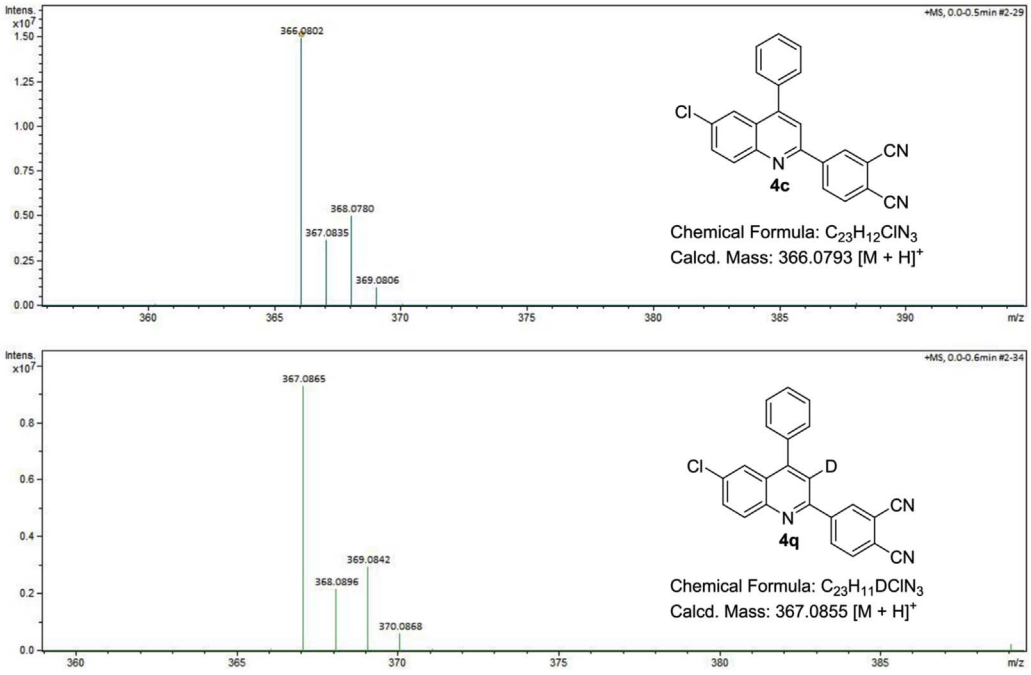


Fig. 2. Comparison of HRMS spectra of **4c** (**a**) and **4q** (**b**).

(not proven) [61,71].

To obtain our own insight on the mechanism of this MCR, a deuterium labelling experiment using phenylacetylene-*d* (99% atom D) (**3i**) with 4-formylphthalonitrile (**1**) and 4-chloroaniline (**2c**) was carried out under the same reaction conditions, as described in Table 2. To our delight, the deuterated phthalonitrile **4q** was obtained as a single product in 74% yield, showing that rupture of the C-D bond does not occur during the MCR (Scheme 1b). Thus, we propose the initial formation of an imine between formylphthalonitrile **1** and the substituted anilines **2** catalysed by $NbCl_5$. This is followed by a hetero-Diels-Alder reaction with the phenylacetylenes **3** also catalysed by $NbCl_5$. Finally, the dihydroquinoline intermediate is oxidised by *p*-chloranil to the phthalonitrile-quinoline dyads **4**.

As illustrated in the ^{1}H NMR spectrum of phthalonitrile **4c** (Fig. 1a), the H-3 signal of the quinoline nucleus appearing at δ 7.86 ppm (singlet, 1H) is absent in the spectrum of the deuterium-labelled phthalonitrile **4q** (Fig. 1b). The structure of **4q** was confirmed by HRMS with a molecular ion peak at *m/z* 367.0865 [M (deuterated) + H]$^+$ (Fig. 2b).

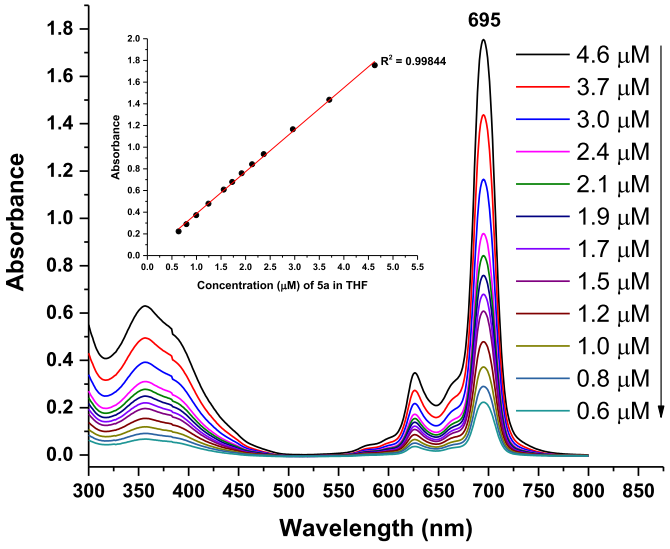


Fig. 3. Aggregation behaviour of ZnPc **5a** in THF at different concentrations. The inset plots the Q band absorption at 695 nm vs. the concentration of **5a**.

After optimizing the methodology and testing the scope, and elucidating the mechanism of this $NbCl_5$ mediated MCR, we decided to demonstrate the versatility of some of the phthalonitrile-quinoline dyads for the synthesis of the PCs **5a-c**.

3.2. Synthesis of zinc phthalocyanine-quinoline dyads (5a-c)

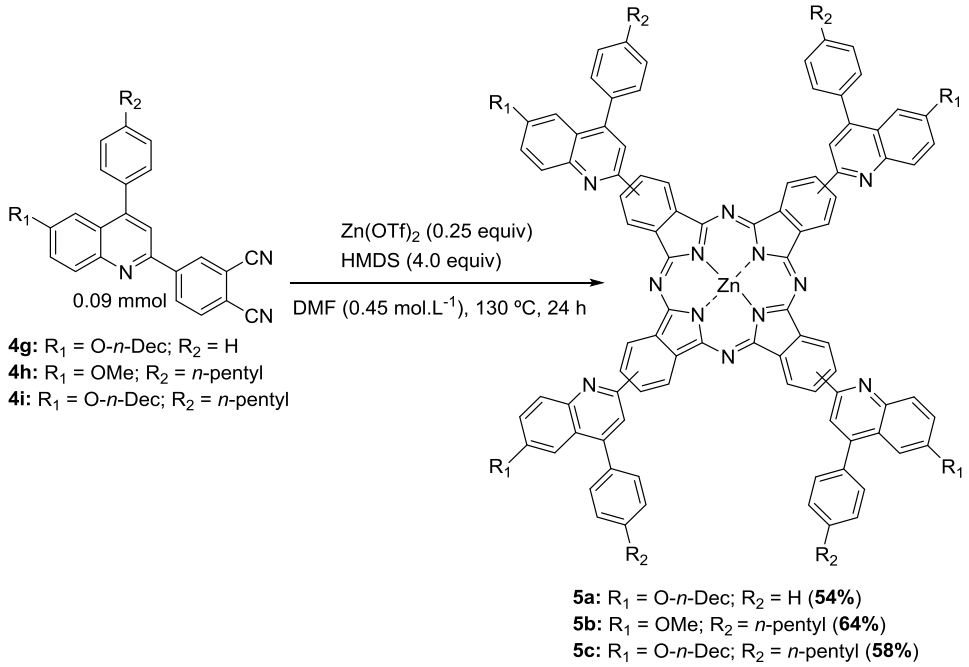
ZnPCs **5a-c** were prepared by cyclotetramerization of phthalonitriles **4g-i**, respectively, in the presence of $Zn(OTf)_2$ and HMDS, in DMF at 130 °C for 24 h (Scheme 2) [57]. The compounds **5a-c** were obtained in 54–64% yields as non-separable regioisomeric mixtures. Phthalonitriles **4g-i** do not yield PCs using standard methodologies such as heating with $Zn(OAc)_2$ in DMAE.

The ^{1}H NMR spectra of ZnPCs **5a-c** (see SI, Figs. S60–62) show that the peaks are broadened due to the presence of regioisomers and the slight aggregation in solution at the concentrations used for the NMR. The structures of ZnPCs **5a-c** were confirmed by MALDI-TOF mass spectrometric analyses (see SI, Figs. S82–84). In order to measure the preliminary photophysical properties of these new dyads, aggregation, fluorescence and photodegradation studies were performed as described below.

3.3. Aggregation, photobleaching, and photophysical properties of the zinc phthalocyanine-quinoline dyads (5a-c)

The UV–Vis spectra of dyads **5a-c** show intense Q band absorption in THF at 695 nm. Compared with the unsubstituted Zinc (II) phthalocyanine (666 nm), the Q-band absorption of ZnPCs **5a-c** are red-shifted by 29 nm, showing the effect of the extended π-system (quinoline moieties).

The aggregation behaviour of the ZnPCs **5a-c** was studied by concentration-dependent UV–Vis spectral measurements in THF at room temperature. As observed for compound **5a** (Fig. 3), the intensity of the Q-band absorption increased with the concentration without producing new bands (normally blue-shifted). The bands perfectly followed



Scheme 2. Synthesis of zinc phthalocyanine-quinoline dyads (**5a-c**).

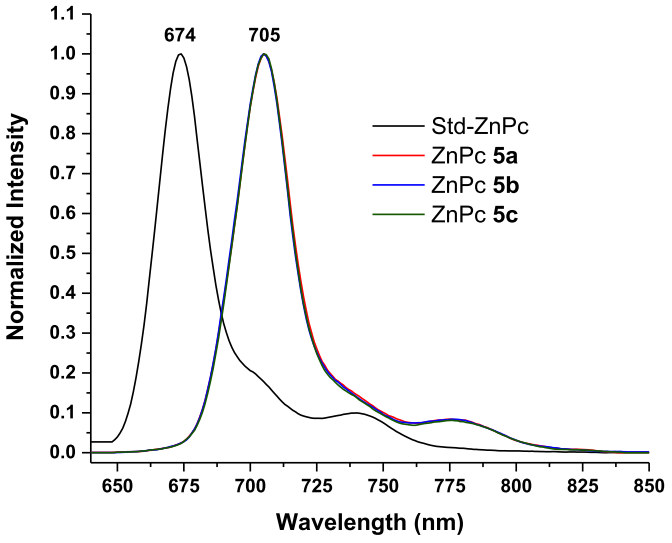


Fig. 4. Normalized emission spectra for Std-ZnPc (black line), **5a** (red line), **5b** (blue line) and **5c** (green line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

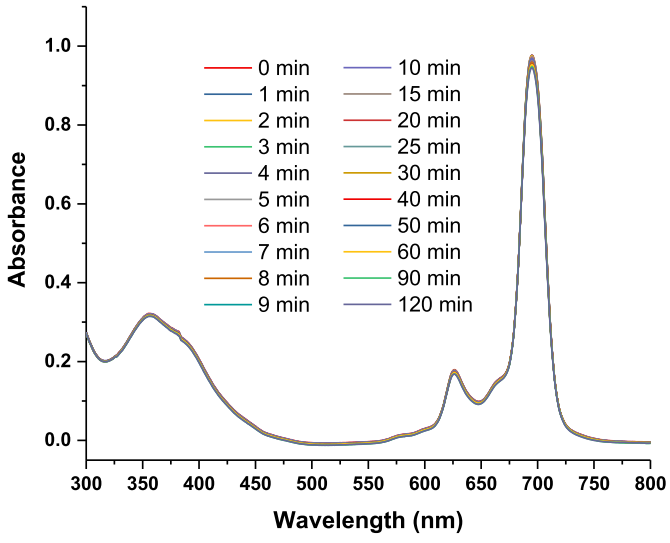


Fig. 5. Photobleaching study of ZnPc **5a** in THF.

Lambert-Beer's law (Fig. 3 inset plot), suggesting no aggregation in this solvent at the concentrations tested. A similar behaviour was found for ZnPCs **5b** and **5c** (see SI, Figs. S1 and S2).

Fluorescence measurements were studied under identical conditions in degassed THF at room temperature (Fig. 4). Upon excitation at 630 nm, fluorescence emissions at 705 nm were found for all compounds, with the quantum yields of 0.16 (ZnPC **5a**) and 0.15 (ZnPCs **5b** and **5c**) relative to ZnPC standard (Φ_F = 0.25 in THF) [58], and Stokes shifts of 10 nm (Table 3).

The photobleaching studies (example in Fig. 5 for ZnPC **5a**) were also performed in THF, and the ZnPCs **5a-c** showed no significant degradation after irradiation for 2 h with a white LED lamp (30 W) (see SI, Figs. S5 and S6).

Table 3
Photophysical parameters of ZnPCs **5a-c** in THF.

ZnPc	λ (nm) (log ε)	λ_{em} [a] (nm)	Stokes (nm)	Φ_F [b]
5a	357 (5.14), 626 (4.89), 695 (5.59)	705	10	0.16
5b	355 (5.05), 626 (4.77), 695 (5.50)	705	10	0.15
5c	355 (5.19), 626 (4.92), 695 (5.63)	705	10	0.15

[a] Excited at 630 nm. All the emission analyses were carried out in degassed THF at room temperature.
[b] Relative to Std-ZnPc in THF as the reference (Φ_F = 0.25) [58].

4. Conclusions

We have demonstrated the versatility of $NbCl_5$ as a very efficient Lewis acid for the promotion of MCRs between anilines, 4-formylphthalonitrile and phenylacetylenes. We have also demonstrated

that this MCR goes by a pericyclic hetero-Diels-Alder reaction. The methodology describes the scope, and the scalability for the production of the phthalonitrile-quinoline dyad (**4c**) on a 600 mg-scale. To show the versatility of our library, we have also synthesized three new phthalocyanine derivatives, and measured their photophysical properties which show good potential for applications in photonics.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.12.065.

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