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Ultrasound assisted Bradsher reaction in aqueous and non-aqueous media: First use of ultrasounds in electrophilic aromatic cyclisation leading to polyacenes

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ABSTRACT

The present work describes the first use of ultrasounds in the Bradsher cyclisation of activated and non-activated *ortho*-formyl diarylmethanes. This reaction is also the first example of electrophilic, aromatic cyclisation assisted by ultrasounds which leads to pure polycyclic, fused aromatic hydrocarbons containing 3 and 4 fused rings in excellent yields. The reaction proceeds not only in aqueous but also in non-aqueous media at milder conditions (room temperature) and in much shorter reaction times than in conventional protocols.

1. Introduction

The aim of our project was investigation of the ultrasounds effect on efficiency of the electrophilic aromatic cyclisation reaction and in particular of the Bradsher reaction, leading to formation of a new benzene ring in the fused, polycyclic, aromatic and heteroaromatic systems. So far, this research problem has not been sufficiently explored, both in respect to the Bradsher reaction itself and to aromatic, electrophilic cyclisation reactions in general. In the literature, only a few reports are found that describe the formation of aromatic compounds under sonochemical conditions: indole [1], pyrazole [2], pyridine [3–5] and imidazole [6] rings. A bit richer is the family of multicomponent reactions promoted by ultrasounds that enable synthesis of nonaromatic rings, present in 1,3-dihydroindole-2-one [7], coumarine [8], chromene [9], xanthene [10], 7,10,11,12-tetrahydrobenzo[c]acridin-8(9*H*)-ones [11], phenoxazine [12] and others. According to the SciFidner® database, the Bradsher reaction has never been carried out under sonochemical conditions.

The Bradsher reaction, being an intramolecular modification of the Friedel-Crafts reaction, is an important method for the synthesis of polycyclic, fused aromatic hydrocarbons **III** and **IV** (Scheme 1). This reaction, for the first time developed by Bradsher in 1940, is based on the acid-catalysed cyclodehydration of *ortho*-formyl or *ortho*-acyl substituted diarylmethanes **I** leading to polyacenes **III** [13,14]. Recently, we have developed a modification of the Friedel-Crafts/Bradsher reaction using *O*-protected *ortho*-acetal substituted diarylmethanols **II** as substrates to synthesis of RO-functionalised polyacenes **IV** (Scheme 1) [15–22]. In our modification, we had to employ very mild reaction conditions due to a possibility of formation of two, reactive benzylic and dibenzylic carbocations derived from the acetal and ArI(ArII)CHOR[3] moieties in **II**. We used 1 N HCl, MeOH/H_2O at 25 °C which were the mildest reaction conditions ever used in this type of S_EAr cyclisation.

The original Bradsher reaction usually requires long reaction times and harsh conditions which may be illustrated by a typical cyclisation of *ortho*-bromophenyl *ortho*-benzylphenyl ketone to 9-*ortho*-bromophenylanthracene (34% HBr-CH_3COOH, 150 °C, 4 days, 69–80% yields) [13]. Although, efficiency of the Bradsher

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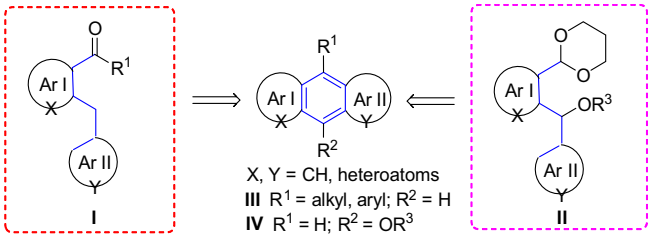


Scheme 1. Synthesis of polycyclic, fused aromatic hydrocarbons **III** and **IV** via the Bradsher reaction.

reaction is often satisfactory, competitive processes and low yields constitute sometimes serious synthetic problems [23–26]. The Bradsher reaction usually proceeds at high temperatures above 100 °C. Some reactions require even higher temperatures (200–230 °C) and must be carried out in sealed tubes for several hours [27–29].

A number of acidic catalysts, such as HBr [13,27,30–34], HCl [35–37], H_2SO_4 [26,38–40], H_3PO_4 [41], polyphosphoric acid (PPA) [34,42–46], TfOH [6,47–49], $MeSO_3H$ [50] IPy_2BF_4/HBF_4 [51], $FeCl_3x6H_2O$ [3], $AlCl_3$ [52], $In(OTf)_3$ [28,53,54], $BF_3{\cdot}Et_2O$ [55], Amberlyst ®15 [23–26,56], Amberlite® IR120 [26,57,58] has been employed in the Bradsher reactions. These reactions were carried out in various solvents, such as benzene [23–25], toluene [28,35,55], DCM [49,50], DCE [26], AcOEt [37], AcOH [13,27] without or in the presence of small amounts of water.

The high temperature, long reaction times, inconvenient solvents, use of sealed pressure tubes and formation of competitive products are indeed serious disadvantages of the Bradsher reaction which we decided to overcome in the present investigations.

2. Experimental

2.1. Materials and apparatus

All organic solvents were purchased from commercial sources. All chemicals used in this work, were purchased from Aldrich, Ark Pharm, Frontier Scientific or Alfa Aesar and were used without further purification. The ^1H NMR and ^{13}C NMR spectra were measured on a Brucker AV 200, AV 500 and AV 600 spectrometer in $CDCl_3$ and C_6D_6 with chemical shift (δ) given in ppm relative to TMS as internal standard. All the mass spectra of pure compounds were recorded on Finnigan MAT 95 double focusing (BE geometry) mass spectrometer (Finnigan MAT, Bremen, Germany). Standard, low-resolution EI mass spectra were obtained using electron energy of 70 eV, accelerating voltage of 4.6 kV, and ion source temperature of 250 °C. Samples were introduced via a direct insertion probe, heated from 30 to 300 °C. Accurate mass measurements were performed by a peak matching technique using perfluorokerosene as an internal standard at a resolving power of 10.000 (10% valley definition). Melting points were measured using Boetius apparatus. Thin layer chromatography (TLC) was performed on precoated Merck 60 (F_{254} 60) silica gel plates with fluorescent indicator, with detection by means of UV light at 254 and 360 nm. Column chromatography was done on Merck silica gel (Kieselgel 60, 230–400 mesh). IR spectra were taken on a FT-IR spectrometer ATI Mattson model Infinity AR60 in KBr pellets and reported in cm^{-1}. Elemental analysis was determined by using a EuroVector analizator model 301. Ultrasonication was performed by Ultrasonic processor model GEX 600 with the resonance frequency of 20 kHz and power 600 W, equipped with a coupler and a stepped titanium alloy microtip Ti-6Al-4V (diameter 6 mm, length 113 mm, amplitude 75 μm, volume 10–50 mL). The cyclisation reactions were carried out in open vessels (thick-walled glass tube). Dry and oxygen free solvents: THF and CH_2Cl_2 were taken from MB SPS-800 (MBRAUN Solvent Purification System). Syntheses of *ortho*-formyl diarylmethane derivatives were performed on the vacuum line under argon flow.

2.2. Experimental procedures

2.2.1. General procedure for the preparation of ortho-formyl diarylmethanes **3** via the Suzuki-Miyaura reaction

A Schlenk flask (25 mL) containing a biphasic mixture of oxygen free THF (10 mL) and aqueous 2 M solution of K_2CO_3 (4 mL) was immersed in the oil bath. Then, *ortho*-formyl aromatic boronic acid **1** (2.40 mmol), benzylic type halide **2** (2.20 mmol) and $Pd(PPh_3)_4$ (0.06 mmol) were added and the temperature of the oil bath was maintained at 80 °C. The mixture was vigorously stirred at this temperature for 24 h under argon atmosphere. Then, it was allowed to cool down, washed with H_2O (8 mL) and extracted with ethyl acetate (3x10 mL). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed in vacuum and crude product was purified by column chromatography over silica gel using a mixture of petroleum ether/acetone (20/1) as eluent.

2.2.2. Procedures for the preparation of fused, polycyclic (hetero) aromatic hydrocarbons **4**

2.2.2.1. ***Procedure A1*** *for the preparation of* ***4a***, ***4b***, ***4c*** *and* ***4h*** *using ultrasounds and HCl_{aq}/acetone medium.* A solution of *ortho*-formyl diarylmethane **3** (0.40 mmol) in acetone (14 mL) was placed in the thick-walled glass tube (50 mL). The titanium alloy microtip was immersed in the reaction mixture to the height of 2.5 cm. Then, the aqueous solution of HCl_{aq} (6.5 M, 14 mL) (v/v = 1/1) was added and the resulting mixture was sonicated (amplitude 26.3 μm (35%), pulse on/off 2 s, 25 °C). The room temperature was set on the processor automatically and was maintained using water bath. The reaction mixture was sonicated until disappearance of the starting material (monitoring by TLC, Tables 4 and 6). After the reaction was completed, the reaction mixture was poured into $NaHCO_{3aq}$ (20 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After filtration, ethyl acetate was removed in vacuum and the crude product was purified by column chromatography over silica gel with a mixture of petroleum ether/acetone (10/1) to afford the corresponding anthracenes **4**.

2.2.2.2. ***Procedure A2*** *for the preparation of* ***4a*** *and* ***4b*** *under silent conditions in HCl_{aq}/acetone medium.* A solution of *ortho*-formyl diarylmethane **3** (0.40 mmol) in acetone (14 mL) was placed in the round-bottomed flask (50 mL). Then, the aqueous solution of HCl_{aq} (6.5 M, 14 mL) (v/v = 1/1) was added. The reaction mixture was stirred at the room temperature until disappearance of the starting material (monitoring by TLC, Table 6). Then, the reaction mixture was poured into $NaHCO_{3aq}$ (20 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After filtration, ethyl acetate was removed in vacuum and the crude product was purified by column chromatography over silica gel with a mixture of petroleum ether/acetone (10/1) to afford the corresponding anthracenes **4**.

2.2.2.3. ***Procedure B1*** *for the preparation of* ***4d***, ***4e***, ***4f***, ***4g***, ***4i*** *and* ***4j*** *using ultrasounds and HCl_{aq}/acetone medium.* A solution of *ortho*-formyl diarylmethane **3** (0.40 mmol) in acetone (6 mL) was placed in the glass tube (50 mL). The titanium microtip was immersed in the reaction mixture to the height of 2.5 cm. Then, the aqueous solution of HCl_{aq} (6.5 M, 6 mL) (v/v = 1/1) was added and the resulting mixture was sonicated (amplitude 18.8 μm (25%), pulse on/off 2 s, 25 °C). The room temperature was set on the processor

automatically and was maintained using water bath. The reaction mixture was sonicated until disappearance of the starting material (monitoring by TLC, Tables 4 and 6). Then, the reaction mixture was poured into $NaHCO_{3aq}$ (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After filtration, ethyl acetate was removed in vacuum and the crude product was purified by column chromatography over silica gel with a mixture of petroleum ether/acetone (10/1) to afford the corresponding anthracenes **4**.

2.2.2.4. ***Procedure B2*** *for the preparation of* ***4e***, ***4f*** *and* ***4j*** *under silent conditions in HCl_{aq}/acetone medium.* A solution of *ortho*-formyl diarylmethane **3** (0.40 mmol) in acetone (6 mL) was placed in the round-bottomed flask (50 mL). Then, the aqueous solution of HCl_{aq} (6.5 M, 6 mL) (v/v = 1/1) was added. The reaction mixture was stirred at the room temperature until disappearance of the starting material (monitoring by TLC, Table 6). Then, the reaction mixture was poured into $NaHCO_{3aq}$ (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After filtration, ethyl acetate was removed in vacuum and the crude product was purified by column chromatography over silica gel with a mixture of petroleum ether/acetone (10/1) to afford the corresponding anthracenes **4**.

2.2.2.5. ***Procedure C1*** *for the preparation of* ***4a***, ***4b***, ***4d***, ***4f***, ***4g***, ***4j*** *using ultrasounds and $FeCl_3/CH_2Cl_2$ nonaqueous medium.* A solution of *ortho*-formyl diarylmethane **3** (0.40 mmol) in CH_2Cl_2 (25 mL) was placed in the glass tube (50 mL). The titanium microtip was immersed in the reaction mixture to the height of 2.5 cm. Then, the $FeCl_3$ (0.04 mmol) was added and the resulting mixture was sonicated (amplitude 26.3 μm (35%), pulse on/off 2 s, 25 °C). The room temperature was set on the processor automatically and was maintained using water bath. The reaction mixture was sonicated until disappearance of the starting material (monitoring by TLC, Tables 2 and 6). Then, the reaction mixture was poured into 1 M $NaOH_{aq}$ (5 mL), and extracted with CH_2Cl_2 (3 × 7 mL). The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After filtration, CH_2Cl_2 was removed in vacuum and the crude product was purified by column chromatography over silica gel with a mixture of petroleum ether/acetone (10/1) to afford anthracenes **4**.

2.2.2.6. ***Procedure C2*** *for the preparation of* ***4b***, ***4d***, ***4f***, ***4j*** *under silent conditions in $FeCl_3/CH_2Cl_2$ nonaqueous medium.* A solution of *ortho*-formyl diarylmethane **3** (0.40 mmol) in CH_2Cl_2 (25 mL) was placed in the round-bottomed flask (50 mL). Then, the $FeCl_3$ (0.04 mmol) was added and the resulting mixture was stirred at the room temperature until disappearance of the starting material (monitoring by TLC, Table 6). Then, the reaction mixture was poured into 1 M $NaOH_{aq}$ (2 mL), and extracted with CH_2Cl_2 (3 × 7 mL). The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After filtration, CH_2Cl_2 was removed in vacuum and the crude product was purified by column chromatography over silica gel with a mixture of petroleum ether/acetone (10/1) to afford anthracenes **4**.

2.3. Representative spectral data

*2.3.1. 2-Benzylbenzaldehyde (**3a**)*

Yield: 65%. Light yellow oil; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 4.47 (s, 2H, CH_2), 7.17–7.34 (m, 6H, 6xH_{Ar}), 7.38–7.60 (m, 2H, 2xH_{Ar}), 7.88 (dd, 1H, $^4J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 10.27 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 36.79, 125.07, 125.78, 127.36, 127.36, 127.57, 127.57, 130.45, 130.85, 132.71, 139.09, 141.77, 141.77, 191.19; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{14}H_{12}O$: 196.08882; Found: 196.08876; MS (EI, 70 eV) *m/z* (%) 196 [M^+, 100], 178 [M^+, $-H_2O$, 84], 165.1 [M^+, 63]; Anal. calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16; Found C, 85.59; H, 5.97.

*2.3.2. 2-(Naphth-2-yl-methyl)benzaldehyde (**3b**)*

Yield: 59%. Light yellow oil; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 4.62 (s, 2H, CH_2), 7.27–7.37 (m, 2H, 2xH_{Ar}), 7.41–7.55 (m, 4H, 4xH_{Ar}), 7.58 (s, 1H, H_{Ar}), 7.73–7.86 (m, 3H, 3xH_{Ar}), 7.89 (dd, 1H, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 2.0 Hz, H_{Ar}), 10.31 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 36.97, 124.34, 124.91, 125.87, 125.96, 126.18, 126.18, 126.44, 127.02, 130.51, 130.91, 131.06, 132.40, 132.72, 132.77, 136.69, 141.60, 191.23; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{18}H_{14}O$: 246.10447; Found: 246.10438; MS (EI, 70 eV) *m/z* (%) 246 [M^+, 94], 228 [M^+, $-H_2O$, 100], 215 [M^+, $-CH_2O$, –H, 55], 118 [M^+, $-C_{10}H_8$, 30]; Anal. calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73; Found: C, 87.52; H, 5.59.

*2.3.3. 2-(6-(Naphth-2-yl-methyl)benzo[d][1,3]dioxol-5-yl)acetaldehyde (**3c**)*

Yield: 82%. White solid; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 4.49 (s, 2H, CH_2), 6.01 (s, 2H, OCH_2O), 6.72 (s, 1H, H_{Ar}), 7.27 (dd, 1H, $^3J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 8.0 Hz, H_{Ar}), 7.36 (s, 1H, H_{Ar}), 7.39–7.49 (m, 2H, 2xH_{Ar}), 7.51 (s, 1H, H_{Ar}), 7.69–7.82 (m, 3H, 3xH_{Ar}), 10.19 (s, 1H, CHO); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.51 (s, 2H, CH_2), 6.03 (s, 2H, OCH_2O), 6.74 (s, 1H, H_{Ar}), 7.30 (dd, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 7.38 (s, 1H, H_{Ar}), 7.42–7.49 (m, 2H, 2xH_{Ar}), 7.53 (s, 1H, H_{Ar}), 7.73–7.83 (m, 3H, 3xH_{Ar}), 10.21 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 37.66, 102.07, 108.96, 111.31, 125.70, 126.25, 126.98, 127.01, 127.63, 127.68, 128.42, 128.62, 132.18, 133.60, 137.82, 140.40, 147.12, 152.62, 189.63; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{19}H_{14}O_3$: 290.09429; Found: 290.09434; MS (EI, 70 eV) *m/z* (%) 290 [M^+, 100], 273 [M^+, –OH, 92], 231 [M^+, –CHO, $-OCH_2$, 32], 215 [M^+, –CHO, $-OCH_2O$, 32], 162 [M^+, $-C_{10}H_8$, 18], 88 [M^+, $-C_{10}H_7$, $-OCH_2O$, –CHO, 18]; Anal. calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86; Found: C, 78.61; H, 4.89.

*2.3.4. 2-(3,5-dimethoxybenzyl)benzaldehyde (**3d**)*

Yield: 66%. Yellow oil; ^{1}H NMR (C_6D_6, 500 MHz): δ (ppm) = 3.26 (s, 6H, 2xOCH_3), 4.16 (s, 2H, CH_2), 6.32 (s, 3H, 3xH_{Ar}), 6.90–6.95 (m, 2H, 2xH_{Ar}), 7.00–7.05 (m, 1H, H_{Ar}), 7.51 (d, 1H, $^3J_{H-H}$ = 5.0 Hz, H_{Ar}), 10.00 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 38.98, 55.48, 55.48, 99.27, 108.18, 127.68, 132.29, 132.95, 134.31, 135.15, 143.61, 143.76, 162.30, 162.30, 192.56; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{16}H_{16}O_3$: 256.10994; Found: 256.11003; MS (EI, 70 eV) *m/z* (%) 256 [M^+, 100], 238 [M^+, $-H_2O$, 80]; Anal. calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29; Found: C, 75.07; H, 6.35.

*2.3.5. 2-(3,4,5-Trimethoxybenzyl)benzaldehyde (**3e**)*

Yield 90%. White solid; m.p. 86 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 3.73 (s, 6H, 2 x OCH_3), 3.77 (s, 3H, OCH_3), 4.34 (s, 2H, CH_2), 6.33 (s, 2H, 2xH_{Ar}), 7.22 (d, 1H, $^3J_{H-H}$ = 8.0 Hz, H_{Ar}), 7.36 (t, 1H, $^3J_{H-H}$ = 8.0 Hz, H_{Ar}), 7.51 (dt, 1H, $^4J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 8.0 Hz, H_{Ar}), 7.81 (dd, 1H, $^4J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 8.0 Hz, H_{Ar}), 10.20 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 36.98, 54.72, 54.72, 59.51, 104.58, 104.58, 125.78, 130.13, 131.02, 132.66, 134.70, 135.11, 141.51, 151.96, 151.96, 191.22; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd. for $C_{17}H_{18}O_3$: 286.12051; Found: 286.12072; MS (EI, 70 eV) *m/z* (%) 286 [M^+, 100], 269 [M^+, –O, –H, 36], 255 [M^+, –OMe, 50], 211 [M^+, –Me, –OMe, –CHO, 20], 181 [M^+, –CHO, $-C_6H_4$, 14]; Anal. calcd for $C_{17}H_{18}O_3$: C, 71.31; H, 6.34; Found: C, 71.42; H, 6.39.

*2.3.6. 6-(3,4,5-Trimethoxybenzyl)benzo[d][1,3]dioxole-5-carbaldehyde (**3f**)*

Yield: 91%. White solid; m.p. 110 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 3.78 (s, 6H, 2xOCH_3), 3.80 (s, 3H, OCH_3), 4.28 (s, 2H, CH_2), 6.04 (s, 2H, OCH_2O), 6.33 (s, 2H, 2xH_{Ar}), 6.68 (s, 1H, H_{Ar}), 7.34 (s, 1H, H_{Ar}), 10.15 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 37.53, 55.88, 55.88, 60.64, 101.83, 105.39, 105.39, 108.75, 110.79, 128.27, 135.65, 136.32, 140.13, 146.82, 152.32, 153.16, 153.16, 189.41; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for: $C_{18}H_{18}O_6$: 330.11034; Found: 330.11027; MS (EI, 70 eV) *m/z* (%) 330 [M^+, 100], 313 [M^+, –OH, 35], 299 [M^+, –CH_2O, –H, 49], 282 [M^+, -OMe, –OH, 29], 266 [M^+, –Me, –OMe, –CHO, 25], 240 [M^+, –CHO, -2xMe, –OCH_3, 15], 196 [M^+, –CHO, –$C_6H_2(OMe)_3$, 35]; Anal. calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49; Found: C, 65.42; H, 5.57.

*2.3.7. 4-Methoxy-2-(3,4,5-trimethoxybenzyl)benzaldehyde (**3g**)*

Yield: 93%. White solid; m.p. 100 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 3.72 (s, 6H, 2xOCH_3), 3.76 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 4.26 (s, 2H, CH_2), 6.29 (s, 2H, 2xH_{Ar}), 7.05 (d, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 7.15 (d, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 7.34 (s, 1H, H_{Ar}), 10.18 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 37.04, 55.22, 55.76, 55.76, 60.55, 105.37, 105.37, 114.21, 120.50, 132.54, 134.43, 134.89, 136.09, 136.32, 153.04, 153.04, 158.33, 191.54; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{18}H_{20}O_5$: 316.13107; Found: 316.13061; MS (EI, 70 eV) *m/z* (%) 316 (M^+, 100), 298 [M^+, –H_2O, 39], 285 [M^+, –CH_2O, –H, 60], 226 [M^+, -4xMe, –CH_2O, 23], 120 [M^+, -Me, $C_6H_2(OMe)_3$, 28]; Anal. calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37; Found C, 68.42; H, 6.45.

*2.3.8. 3-Benzylthiophene-2-carbaldehyde (**3h**)*

Yield: 64%. Light yellow oil; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 4.33 (s, 2H, CH_2), 6.94 (d, 1H, H_{Ar}), 7.20 (s, 1H, H_{Ar}), 7.21 (s, 1H, H_{Ar}), 7.23–7.25 (m, 1H, H_{Ar}), 7.31–7.33 (m, 2H, 2xH_{Ar}), 7.61 (d, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 34.14, 126.60,128.54, 128.72, 128.72, 131.33, 131.33, 134.54, 137.95, 139.07, 149.92, 182.28; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{12}H_{10}OS$: 202.04524; Found: 202.04508; MS (EI, 70 eV) *m/z* (%) 202 [M^+, 100], 96 [M^+, –CHO, –C_6H_5, 14]; Anal. calcd for $C_{12}H_{10}OS$: C, 71.26; H, 4.98; S, 15.85; Found: C, 71.09; H, 5.14; S, 15.61.

*2.3.9. 3-(3,4,5-Trimethoxybenzyl)thiophene-2-carboxaldehyde (**3i**)*

Yield: 79%. White solid; m.p. 84 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 3.78 (s, 6H, 2xOCH_3), 3.79 (s, 3H, OCH_3), 4.24 (s, 2H, CH_2), 6.37 (s, 2H, 2xH_{Ar}), 6.92 (d, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 7.62 (d, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 10.05 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 34.54, 55.92, 55.92, 60.69, 105.46, 105.46, 131.20, 134.48,134.68, 136.49, 137.77, 149.63, 153.24, 153.24, 182.18; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{15}H_{16}O_4S$: 292.07693; Found: 292.07819; MS (EI, 70 eV) *m/z* (%) 292 [M^+, 100], 261 [M^+, -OMe, 20], 217 [M^+, –CHO, -Me, -OMe, 18], 202 [M^+, –CHO, -2xMe, -OMe, 10]; Anal. calcd for $C_{15}H_{16}O_4S$: C, 61.63; H, 5.52; S, 10.97; Found: C, 61.51; H, 5.47; S, 10,69.

*2.3.10. 2-(Benzo[b]thien-2-ylmethyl)benzaldehyde (**3j**)*

Yield: 55%. Yellow oil; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 4.68 (s, 2H, CH_2), 6.96 (s, 1H, H_{Ar}), 7.18–7.35 (m, 2H, 2xH_{Ar}), 7.36–7.67 (m, 4H, 4xH_{Ar}), 7.70–7.76 (d, 1H, $^3J_{H-H}$ = 8.0 Hz, H_{Ar}), 7.82–7.88 (d, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}) 10.24 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 32.19, 120.79, 120.88, 121.80, 122.54, 122.96, 126.32, 130.15, 131.75, 132.47, 132.77, 138.46, 138.68, 140.14, 142.97, 191.14; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{16}H_{12}OS$: 252.06089; Found: 252.06021; MS (EI, 70 eV) *m/z* (%) 252 [M^+, 100], 234 [M^+, –H_2O, 58], 118 [M^+, –C_8H_5S (benzothiophene), 62]. Anal. calcd for $C_{16}H_{12}OS$: C, 76.16; H, 4.79; S, 12.71; Found: C, 76.14; H, 4.68; S, 12.83.

*2.3.11. Anthracene (**4a**)*

Yield: 78%. Yellow solid; m.p. >200 °C; IR (KBr) cm^{-1}: 3048, 2923, 2853, 1620, 1532, 1447, 1315, 1271, 1146, 997, 956, 883, 726, 601; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.42–7.49 (m, 4H, 4xH_{Ar}), 7.96–8.03 (m, 4H, 4xH_{Ar}), 8.42 (s. 2H, 2xH_{Ar}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 124.07, 124.07, 124.07, 124.07, 124.94, 124.94, 126.89, 126.89, 126.89, 126.89, 130.39, 130.39, 130.39, 130.39; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{14}H_{10}$: 178.07825; Found: 178.07811; MS (EI, 70 eV) *m/z* (%) 178 [M^+, 100]; Anal. calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66; Found: C, 94.42; H, 5.59.

*2.3.12. Tetraphene (**4b**)*

Yield: 81%. Yellow solid; m.p. 154 °C; IR (KBr) cm^{-1}: 3047, 2923, 2853, 1623, 1499, 1475, 1338, 1238, 954, 897, 885, 812, 746, 688; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.50–7.88 (m, 7H, 7xH_{Ar}), 8.00–8.15 (m, 2H, 2xH_{Ar}), 8.35 (s, 1H, H_{Ar}), 8.82 (d, 1H, $^3J_{H-H}$ = 8.0 Hz, H_{Ar}), 9.16 (s, 1H, H_{Ar}); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.53–7.60 (m, 2H, 2xH_{Ar}), 7.61–7.67 (m, 2H, 2xH_{Ar}), 7.70 (dt, 1H, $^3J_{H-H}$ = 10.0 Hz, $^4J_{H-H}$ = 5.0 Hz, H_{Ar}), 7.80 (d, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 7.87 (d, 1H, $^4J_{H-H}$ = 5.0 Hz, H_{Ar}), 8.03–8.17 (m, 2H, 2xH_{Ar}), 8.37 (s, 1H, H_{Ar}), 8.85 (d, 1H, $^4J_{H-H}$ = 5.0 Hz, H_{Ar}), 9.17 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 121.62, 123.01, 125.77, 125.88, 125.88, 126.85, 126.92, 127.15, 127.41, 127.41, 127.82, 127.82, 128.52, 128.69, 128.92, 130.60, 131.98, 132.04; HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{18}H_{12}$: 228.09390; Found: 228.09323; MS (EI, 70 eV) *m/z* (%) 228 [M^+, 100]; Anal. calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30; Found: C, 94.58; H, 5.57.

*2.3.13. Tetrapheno[9,10-d][1,3]dioxole (**4c**)*

Yield: 72%. Yellow solid; m.p. 192 °C; IR (KBr) cm^{-1}: 3050, 2960, 2908, 1471,1458, 1259, 1202, 1109, 1036, 945, 885, 840, 885, 803, 750, 568, 552; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 6.07 (s, 2H, OCH_2O), 7.25 (s, 1H, H_{Ar}), 7.33 (s, 1H, H_{Ar}), 7.59 (dt, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 7.60 (d, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 7.66 (dt, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 7.72 (d, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 7.84 (d, 1H, $^3J_{H-H}$ = 12.0 Hz, H_{Ar}), 8.14 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 101.00, 102.54, 103.23, 120.24, 122.50, 125.50, 126.21, 126.48, 126.89, 126.89, 127.51, 128.42, 129.41, 129.44, 130.19, 131.67, 147.84, 147.92; HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{19}H_{12}O_2$: 272.08373; found: 272.08417; MS (EI, 70 eV) *m/z* (%) 272 [M^+, 100]; Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44; Found: C, 83.54; H, 4.67.

*2.3.14. 1,3-Dimethoxyanhtracene (**4d**)*

Yield: 91%. Yellow solid; m.p. 70 °C; IR (KBr) cm^{-1}: 3046, 3023, 2997, 2964, 2936, 2902, 2826, 1636, 1627, 1570, 1546, 1450, 1418, 1369, 1345, 1312, 1279, 1247, 1201, 1153, 1136, 1093, 1043, 941, 886, 816, 735, 594, 529; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 3.96 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 6.46 (d, 1H, H_{Ar}), 6.82 (d, 1H, H_{Ar}), 7.41 (dt, 1H, $^4J_{H-H}$ = 5.0 Hz, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 7.47 (dt, 1H, $^4J_{H-H}$ = 5.0 Hz, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 7.93 (d, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 8.01 (d, 1H, $^4J_{H-H}$ = 5.0 Hz, H_{Ar}), 8.21 (s, 1H, H_{Ar}), 8.74 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 55.38, 55.70, 96.27, 97.44, 121.26, 122.23, 123.78, 124.27, 125.86, 127.37, 128.90, 129.94, 132.69, 133.12, 156.68, 157.77; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{16}H_{14}O_2$: 238.09938; Found: 238.09954; MS (EI, 70 eV) *m/z* (%) 238 [M^+, 100], 223 [M^+, -Me, 18]; Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; Found: C, 80.49; H, 5.96.

*2.3.15. 1,2,3-Trimethoxyanhtracene (**4e**)*

Yield: 72%. Light yellow solid; m.p. 86 °C; IR (KBr) cm^{-1}: 3049, 3004, 2966, 2930, 2831, 1627, 1565, 1540, 1471, 1462, 1450, 1421, 1355, 1311, 1285, 1236, 1204, 1133, 1092, 1031, 1000, 941, 913, 888, 751, 601; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 4.00 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 4.13 (s, 3H, OCH_3), 7.02 (s, 1H, H_{Ar}),

7.37–7.42 (m, 2H, 2xH_{Ar}), 7.89–8.02 (m, 2H, 2xH_{Ar}), 8.22 (s, 1H, H_{Ar}), 8.59 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 54.56, 60.04, 60.16, 99.58, 119.07, 122.84, 123.08, 123.38, 124.10, 126.27, 127.22, 128.25, 129.07, 130.54, 139.33, 145.79, 151.83; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{17}H_{16}O_3$: 268.10994; Found: 268.11043. MS (EI, 70 eV) *m/z* (%) 268 [M^+,100], 253 [M^+, -Me, 55], 238 [M^+, -2xMe, 6]; Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; Found: C, 76.08; H, 6.09.

*2.3.16. 6,7,8-Trimethoxyanthra[2,3-d][1,3]dioxole (**4f**)*

Yield: 85%. Light yellow solid; m.p. 153 °C; IR (KBr) cm^{-1}: 3052, 2970, 2940, 2830, 1631, 1603, 1555, 1476, 1460, 1419, 1354, 1310, 1280, 1233, 1215, 1161, 1101, 1036, 998, 947, 913, 879, 802, 690, 556; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 3.97 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.10 (s, 3H, OCH_3), 6.01 (s, 2H, OCH_2O), 6.93 (s, 1H, H_{Ar}), 7.11 (s, 1H, H_{Ar}), 7.20 (s, 1H, H_{Ar}), 7.98 (s, 1H, H_{Ar}), 8.34 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 54.51, 59.96, 60.10, 99.34, 99.62, 100.72, 101.62, 117.62, 121.65, 126.66, 127.23, 128.81, 128.81, 145.62, 146.00, 146.54, 151,29, 151,29; HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{19}H_{12}O_2$: 312.09977; Found: 312.09991; MS (EI, 70 eV) *m/z* (%) 312 [M^+, 100], 297 [M^+, -Me, 40], 183 [M^+, 16]; Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16; Found: C, 69.05; H, 5.31.

*2.3.17. 1,2,3,7-Tetramethoxyanhtracene (**4g**)*

Yield: 81%. Light yellow solid; m.p. >200 °C; IR (KBr) cm^{-1}: 3007, 2939, 2830, 1629, 1541, 1470, 1450, 1418, 1353, 1320, 1230, 1202, 1176, 1145, 1129, 1099, 1037, 1025, 996, 904, 889, 836, 803, 729, 600; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 3.94 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 4.11 (s, 3H, OCH_3), 6.99 (s, 1H, H_{Ar}), 7.12 (dd, 1H, $^3J_{H-H}$ = 10.0 Hz, $^4J_{H-H}$ = 2.0 Hz, H_{Ar}), 7.20 (m, 1H, H_{Ar}), 7.79 (d, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 8.13 (s, 1H, H_{Ar}), 8.44 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 53.96, 54.51, 59.99, 60.08, 99.80, 102.86, 117.03, 118.97, 122.87, 123.37, 126.68, 126.96, 127.86, 129.94, 145.44, 146.99, 151.00, 155.38; HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{18}H_{18}O_4$: 298.12051; Found: 298.12037; MS (EI, 70 eV) *m/z* (%) 298 [M^+, 100], 283 [M^+, -Me, 34], 169 (12); Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08; Found: C, 72.18; H, 6.15.

*2.3.18. 6,7,8-Trimethoxynaphtho[2,3]thiophene (**4i**)*

Yield: 58%. Light yellow solid; m.p. 102 °C; IR (KBr) cm^{-1}: 3085, 2939, 2833, 1624, 1601, 1563, 1479, 1464, 1436, 1410, 1384, 1297, 1263, 1240, 1221, 1204, 1144, 1108, 1044, 1017, 997, 910, 870, 746, 670, 626; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 3.98 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 4.08 (s, 3H, OCH_3), 7.01 (s, 1H, H_{Ar}), 7.34 (m, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 7.45 (m, 1H, $^3J_{H-H}$ = 6.0 Hz, H_{Ar}), 8.13 (s, 1H, H_{Ar}), 8.56 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 54.54, 59.98, 60.16, 100.43, 113.52, 118.95, 126. 51, 121.54, 127.19, 135.11, 137.50, 139.21, 145.51, 151.17; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{15}H_{14}O_3S$: 274.06637; Found: 274.06698; MS (EI, 70 eV) *m/z* (%) 274 [M+, 100], 259 [M^+, -Me, 42], 244 [M^+, -2 x Me, 3], 216 (33); Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14; S, 11.69; Found: C, 65.64; H, 5.16; S, 11.74.

*2.3.19. Benzo[d]naphtho[2,3-b]thiophene (**4j**)*

Yield: 72%. White solid; m.p. 160 °C; IR (KBr) cm^{-1}: 1586, 1492, 1451, 1415, 1371, 1332, 1312, 1267, 1129, 1014, 953, 876, 766, 754, 728, 676; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.50–7.62 (m, 4H, 4xH_{Ar}), 7.89 (d, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 7.97 (d, 1H, $^3J_{H-H}$ = 5.0 Hz, H_{Ar}), 8.10 (d, 1H, $^3J_{H-H}$ = 10.0 Hz, H_{Ar}), 8.30 – 8.34 (m, 1H, H_{Ar}), 8.34 (s, 1H, H_{Ar}), 8.68 (s, 1H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 120.07, 120.68, 122.01, 122.91, 124.59, 125.22, 126.03, 126.03, 127.12, 127.75, 128.47, 130.87, 132.60, 135.18, 137.71, 140.17; HRMS (EI, 70 eV): *m/z* $[M]^+$ Calcd for $C_{16}H_{10}S$: 234.05032; Found: 234.05044; MS (EI, 70 eV) *m/z* (%) 234 [M^+, 100]; Anal. Calcd for $C_{16}H_{10}S$: C, 82.02; H, 4.30; S, 13.68; Found: C, 81.97; H, 4.51; S, 13.74.

3. Results and discussion

ortho-Formyl diarylmethanes **3**, key substrates in the Bradsher cyclisation reaction, were obtained in the Suzuki-Miyaura [59] cross-coupling of substituted and unsubstituted *ortho*-formyl phenylboronic acids **1a–c** and 3-formyl thienyl 2-boronic acid **1d** with bromides and chlorides of the benzyl type **2a–e**, in the presence of palladium tetrakis-triphenylphosphine $Pd(PPh_3)_4$, as a catalyst and aqueous solution of 2 M K_2CO_3, in THF, at 80 °C. Due to high sensitivity of the palladium catalyst to O_2, all the reactions had to be carried out under argon atmosphere in Schlenk flasks (Table 1).

Thus, methoxy substituted *ortho*-formyl diarylmethanes **3d–g**, **3i** favoring S_EAr cyclisations and diarylmethanes **3a–c**, **3h**, **3j** unsubstituted in the Ar II fragment, were obtained in good to high yields (Table 1).

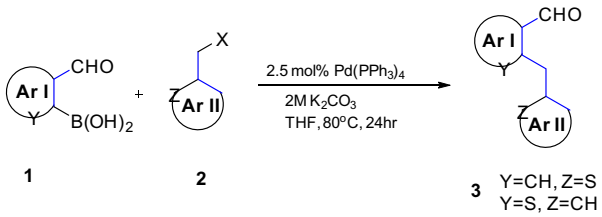
The next step of our project was optimization of the ultrasounds assisted Bradsher cyclisation reaction of **3**. First, we carried out a series of experiments, in which we subjected a less reactive *ortho*-formyl diarylmethane **3b** with the unsubstituted ArII fragment, to the Bradsher reaction in aqueous solutions of various inorganic (HCl_{aq}, HBr_{aq}, H_2SO_{4aq}) and organic (CH_3COOH) proton acids, in aqueous solution of inorganic, acidic salt ($NaHSO_{4aq}$) as well as in nonaqueous medium (methylene chloride, DCM) containing Lewis acids ($FeCl_3$, $InCl_3$, $ZrCl_4$,$Cu(OTf)_2$) or acidic ion-exchange resin (Amberlite® IR120) (Table 2). The best results for aqueous media were obtained with HCl_{aq} and for nonaqueous ones with $FeCl_3$. In case of HCl_{aq}, the reaction required a larger excess of acid (230 equiv.) to afford **4b** in 95% yield. Interestingly, quite a small increase of the HCl amount, from 200 to 230 equiv., resulted in a great rise of the yield from 10 to 95%. (Table 2, entry 2, 3). The use of $FeCl_3$ (0.1–1.0 equiv.) in nonaqueous medium (DCM) gave the cyclic product **4b** in 93–95% yields. The reaction time was dependent on the amount of $FeCl_3$ used. The bigger amounts of the Lewis acid, the shorter reaction times (from 40 min to less than 1 min) were achieved (Table 2, entry 7, 8, 9). Other combinations of acidic components, solvents, reaction times and temperature gave low yields of **4b** (Table 2, entries 1, 2, 10–14). All experiments presented in Table 2 were carried out at the amplitude of 26.3 μm (35%).

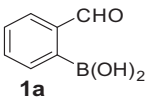
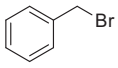
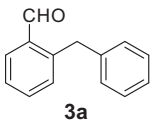
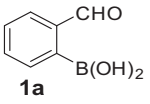
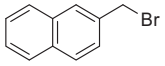
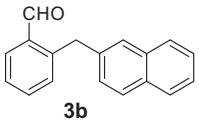
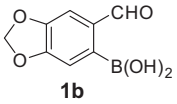
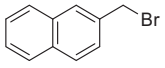
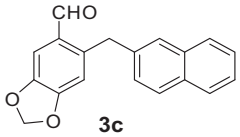
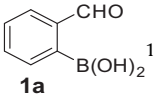
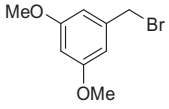
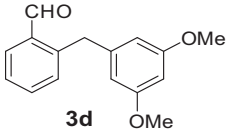
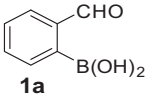
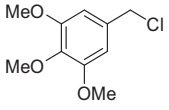
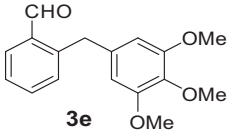
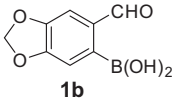
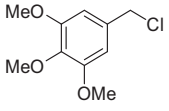
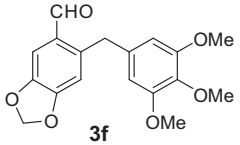
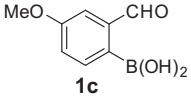
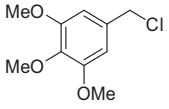
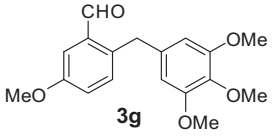
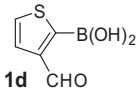
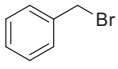
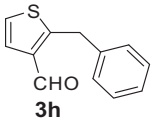
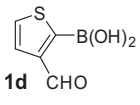
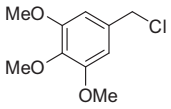
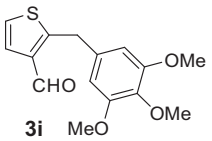
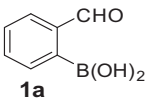
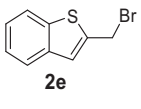
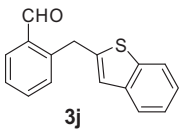
In the second series of experiments, we optimized solvent, a ratio of solvent/HCl_{aq} and amount of HCl using *ortho*-diarylmethane **3e**, as the reactive compound in electrophilic, aromatic cyclisation (Table 3). For the aqueous solutions of HCl, we applied 21–42 mL of H_2O/1 mmol of *ortho*-formyl diarylmethane, while in the literature only 9 mL of H_2O/1 mmol was engaged [37]. For aqueous solutions of HBr, 1.5 mL of water per 1.0 mmol of *ortho*-formyl diarylmethane was usually employed [13]. It is worth mentioning that in the Bradsher reaction, HCl was rarely used (ethanolic solution [56], 3 N aqueous solution in a mixture with AcOEt [37] and 3.08 N ethereal solution [35]) and the corresponding products were obtained in very differentiated yields.

We also tried to carry out the Bradsher reaction without acid hoping that ultrasounds would bring energy sufficient for cyclisation (Table 3, entry 1). Unfortunately, the cyclisation of the product **4e** did not occur and only the substrate **3e** was recovered from the reaction mixture.

In the next experiments, we increased amounts of water and HCl and found that the cyclisation proceeded faster and more effectively when a bigger amount of acid was present in the reaction mixture. Application of HCl in the range of 100–200 equiv.

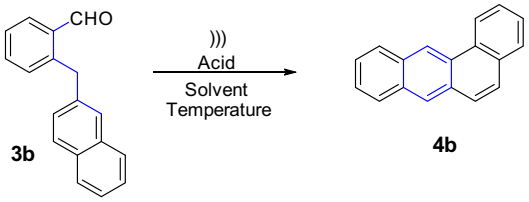
Table 1
Synthesis of *ortho*-formyl diarylmethanes **3a**–**j**.



Entry	Substrate 1	Substrate 2	Product 3	Yield (%)[a]
1	 **1a**	 **2a**	 **3a**	63
2	 **1a**	 **2b**	 **3b**	59
3	 **1b**	 **2b**	 **3c**	82
4	 **1a**	 **2c**	 **3d**	66
5	 **1a**	 **2d**	 **3e**	90
6	 **1b**	 **2d**	 **3f**	91
7	 **1c**	 **2d**	 **3g**	93
8	 **1d**	 **2a**	 **3h**	64
9	 **1d**	 **2d**	 **3i**	79
10	 **1a**	 **2e**	 **3j**	55

[a] Isolated yields.

Table 2
Selection of the relevant acid in the ultrasound assisted Bradsher cyclisation of **3b** to **4b** in aqueous and non-aqueous media.



Entry	Acid	Equiv. of acid[b]	Solvent	Time [min.]	Temperature [°C]	Yield[c] [%]
1[a]	HCl_{aq}	100	Acetone	40 min	25	2
2[a]	HCl_{aq}	200	Acetone	40 min	25	15
3[a]	HCl_{aq}	230	Acetone	40 min	25	95
4[a]	HBr_{aq}	180	Acetone	40 min	25	51
5[a]	H_2SO_{4aq}	200	Acetone	40 min	25	9
6[a]	CH_3COOH	350	acetone	40 min	25	9
7	$FeCl_3$	0.1	CH_2Cl_2	40 min	25	93
8	$FeCl_3$	0.5	CH_2Cl_2	1 min	25	93
9	$FeCl_3$	1.0	CH_2Cl_2	<1 min	25	95
10	$ZrCl_4$	1.0	CH_2Cl_2	50 min	25–50	0
11	$InCl_3$	1.0	CH_2Cl_2	40 min	25–50	0
12	Amberlite®	–	CH_2Cl_2	40 min	25–50	0
13[a]	$NaHSO_{4aq}$	200	Acetone	40 min	25–50	0
14	$Cu(OTf)_2$	1.0	CH_2Cl_2	40 min	25–50	0

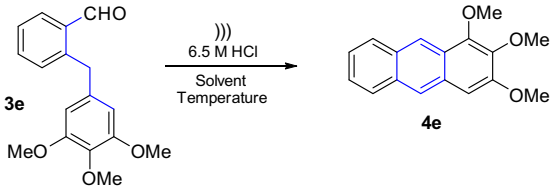
[a] $V_{acidaq}/v_{solvent} - 1/1$.
[b] Calculated on pure acid.
[c] Based on the ^1H NMR spectra.

led to the formation of **4e** in 90–94% yield within less than 1 min. (Table 3, entry 5). Therefore, in the general protocol we used 100 equiv. of HCl. It is worth mentioning that the use of larger amounts of HCl_{aq} (200 equiv.) was beneficial in case of **4e** because of the immediate precipitation of the pure product within less than 1 min. (Table 3, entry 8 and 9). Finally, cyclisation of **3e** was carried out in other solvents, such as MeOH, acetone, CH_3CN and CH_2Cl_2. The best yields of **4e** were obtained in acetone (90%) and CH_3CN (95%). However, acetone is much cheaper and greener than acetonitrile and this was the reason why we chose acetone in our general protocol. All experiments presented in Table 3 were carried out at the amplitude of 18.8 μm (25%).

In the third series of experiments, we examined impact of intensity of the cavitation process which depended on the amplitude of vibration of the ultrasound microtip at a fixed frequency. In our experiments involving cyclisation of non-activated *ortho*-formyl diarylmethane **3b** to **4b** and activated one **3e** to **4e**, we used amplitudes of vibrations in the range of 3.8–26.3 μm. In Table 4, we showed that the more intensive cavitation process led to higher yields of both **4b** and **4d**. In case of non-activated *ortho*-formyl diarylmethane **3b**, the highest yield 93% was obtained at the amplitude 26.3 μm. In case of activated substrate **3e**, the highest yield was gained at the lower amplitude 18.8 μm.

The next step of our project was the ultrasound assisted Bradsher cyclisation of the remaining substrates **3** under previously established conditions (Table 5). In case of non-activated diarylmethanes **3a-c** and **3h**, ultrasound pulses were generated every 2 s at room temperature, in a mixture of acetone/6.5 M HCl_{aq}

Table 3
Optimization of solvent, a ratio of solvent/HCl_{aq} and amount of HCl in the ultrasound assisted Bradsher cyclisation of **3e** leading to **4e**.



Entry	Solvent	Solvent/HCl_{aq} (v_s/v_{HClaq})	Equiv. of HCl[a]	Reaction time [min]	Temperature [°C]	Yield[b] [%]
1	Acetone	1/–	–	32 min	25–50	0
2	Acetone	1/1	0.5	25 min	25	0
3	Acetone	1/1	5	25 min	25	15
4	Acetone	1/1	50	25 min	25	63
5	Acetone	1/1	100	<1 min	25	90
6	Acetone	1/2	130	<1 min	25	90
7	Acetone	1/6	170	<1 min	25	94
8	Acetone	1/10	200	<1 min	25	92
9	Acetone	1/20	200	<1 min	25	90
10	Acetonitrile	1/1	100	<1 min	25	95
11	Methanol	1/1	100	<1 min	25	44
12	Methylene chloride	1/1	100	<1 min	25	34

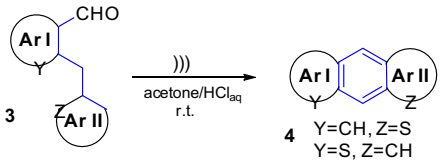
[a] Calculated on pure acid.
[b] Based on the ^1H NMR spectra.

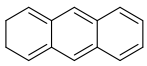
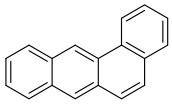
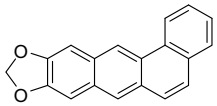
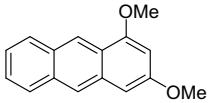
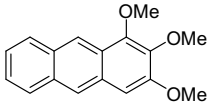
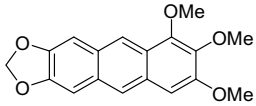
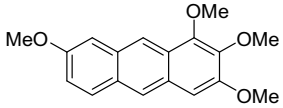
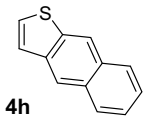
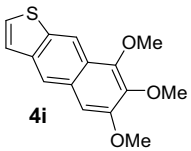
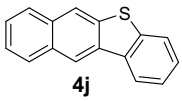
Table 4
Influence of the ultrasound amplitude on effectivness of the Bradsher cyclisation of *ortho*-formyl diarylmethane **3b** to **4b** and **3e** to **4e**.

Entry	Amplitude (μm)/(%)	Cyclisation conditions of **3b**	Yield[a] of **4b** [%]	Cyclisation conditions of **3e**	Yield[b] of **4e** [%]
1	3.8/(5%)	6.5 M HCl (230 equiv.)/acetone, 40 min	0	6.5 M HCl (100 equiv.)/acetone, 15 s	25
2	11.3/(15%)		31		61
3	18.8/(25%)		55		96
4	26.3/(35%)		93		96

[a, b] Based on the ^1H NMR spectra.

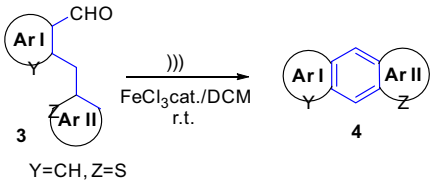
Table 5
The Bradsher cyclisation products **4a–j** obtained in aqueous medium (procedure A1 for **3a–c**, **3h**; procedure B1 for **3d–g**, **3i–j**).

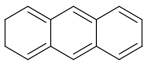
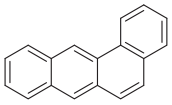
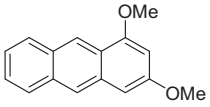
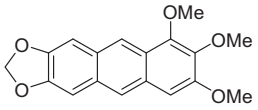
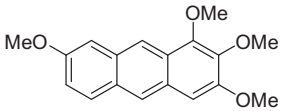
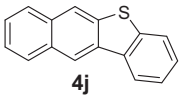


Entry	*ortho*-Formyl diarylmethanes 3	Products 4	Amplitude (μm)/(%)	Time [min]	Yield [%][a]/[%][b]
1	**3a**	 **4a**	26.3/(35%)	40 min	90/78
2	**3b**	 **4b**	26.3/(35%)	40 min	95/81
3	**3c**	 **4c**	26.3/(35%)	40 min	90/72
4	**3d**	 **4d**	18.8/(25%)	<1 min	Quant./91
5	**3e**	 **4e**	18.8/(25%)	<1 min	88/72
4	**3f**	 **4f**	18.8/(25%)	<1 min	93/85
5	**3g**	 **4g**	18.8/(25%)	<1 min	92/81
7	**3h**	 **4h**	26.3/(35%)	40 min	No reaction
8	**3i**	 **4i**	18.8/(25%)	<1 min	74/58
9	**3j**	 **4j**	18.8/(25%)	25 min	82/72

[a] Based on the ^{1}H NMR spectra.
[b] Isolated yields.

Table 6
The Bradsher cyclisation products **4a**, **4b**, **4d**, **4f**, **4g**, **4j** obtained in non-aqueous medium (procedure C1).



Entry	*ortho*-Formyl diarylmethanes 3	Products 4	Amplitude (μm)/(%)	Time [min]	Yield [%][a]/[%][b]
1	**3a**	 **4a**	26.3/(35%)	60 min	72/58
2	**3b**	 **4b**	26.3/(35%)	40 min	93/78
3	**3d**	 **4d**	26.3/(35%)	5 min	Quant./84
4	**3f**	 **4f**	26.3/(35%)	5 min	89/70
5	**3g**	 **4g**	26.3/(35%)	5 min	95/87
6	**3j**	 **4j**	26.3/(35%)	5 min	95/75

[a] Based on the ^{1}H NMR spectra.
[b] Isolated yields.

(230 equiv.), in a ratio of 1/1(v/v), at the higher amplitude 26.3 μm, within 40 min (Procedure A1), while activated diarylmethanes **3d–g** and **3i** were sonicated in a mixture of acetone/6.5 M HCl_{aq} (100 equiv.), in a ratio of 1/1 (v/v), at the lower amplitude 18.8 μm within shorter reaction time, i.e. less than 1 min (Procedure B1). Although unsubstituted diarylmethane **3j** was not activated by MeO groups, it easily cyclized with a lesser amount of HCl_{aq} (100 equiv.) at lower amplitude (Procedure B1).

We have also conducted a series of ultrasound assisted Bradsher cyclizations of *ortho*-formyl diarylmethanes **3** in non-aqueous medium - $FeCl_3$/DCM. The solution of *ortho*-formyl diarylmethane **3**, $FeCl_3$ (0.1 equiv.) in DCM was sonicated with the titanium microtip. Ultrasounds were generated every 2 s at room temperature at the amplitude of 26.3 μm (35%) (Procedure C1). In case of non-activated substrates **3a** and **3b**, the cyclisation process proceeded much longer (60 min and 40 min, respectively) than in case of activated ones **3d**, **3f** and **3g** (5 min). The heteroaromatic substrate **3j** also easily cyclized to **4j** within 5 min. All polyacenes **4** were obtained in good to excellent 58–87% yields (Table 6).

In the final set of experiments, we present a comparison of effectivness of the Bradsher reaction, which was assisted (Procedures A1, B1, C1) and non-assisted (Procedures A2, B2, C2) by ultrasounds (Table 7, silent conditions: substrate **3**/acid/solvent/stirring at 25 °C). The reaction involved both less reactive *ortho*-formyl diarylmethanes **3a** and **3b**, unsubstituted in the ArII fragment and the very reactive representatives **3e** and **3f**, due to the presence of electron rich ArII fragment which promoted electrophilic, aromatic substitution (Table 7).

In general, application of ultrasounds significantly shortened the reaction times compared to silent conditions and in case of *ortho*-formyl diarylmethanes **3a** and **3b** without MeO-subtituents, reacting under aqueous conditions (acetone/HCl_{aq}), the shortening was 13-fold from 510 to 520 min. to 40 min. In non-aqueous medium (DCM) using Lewis acid ($FeCl_3$), the shortening of the reaction time for **3b** was 3-fold from 130 min. to 40 min. and significantly differed from the reaction times observed for aqueous media. In case of reactive *ortho*-formyl diarylmethane **3e**, when a large excess of HCl (100–200 equiv.) was used, the ultrasounds contribution was negligible (Table 7, entry 4 and 5). Application of only 50 equiv. of HCl extended the reaction times from less than 1 min to 100 min for **3e** and showed a significant influence of ultrasounds (Table 7, entry 4–6). The similar effect was observed for **3f**.

Table 7
Comparison of effectivness of the Bradsher reaction carried out with and without use of ultrasounds for *ortho*-formyl diarylmethanes with MeO-subtituents **3e**, **3f** and for the unsubstituted *ortho*-formyl diarylmethanes **3a**, **3b**, **3j** (procedures A1 and A2 for **3a-b**; procedures B1 and B2 for **3e**, **3f**, **3j**; procedures C1 and C2 for **3b**, **3f**, **3j**).

Entry	Substrate (**3**)	Acid/Solvent	Equiv. of acid[b]	Product (**4**)	Ultrasonic irradiation			Silent conditions	
					Amplitude (μm)/(%)	Time [min]	Yield[c] [%]	Time [min]	Yield[c] [%]
1[a]	**3a**	HCl_{aq}/acetone	230	**4a**	26.3/(35%)	40 min	90	520 min	84
2[a]	**3b**	HCl_{aq}/acetone	230	**4b**	26.3/(35%)	40 min	95	510 min	94
3	**3b**	$FeCl_3$/DCM	0.1	**4b**	26.3/(35%)	40 min	93	130 min	85
4[a]	**3e**	HCl_{aq}/acetone	200	**4e**	18.8/(25%)	<1 min	95	<1 min	93
5[a]	**3e**	HCl_{aq}/acetone	100	**4e**	18.8/(25%)	<1 min	94	<1 min	95
6[a]	**3e**	HCl_{aq}/acetone	50	**4e**	18.8/(25%)	100 min	95	750 min	85
7[a]	**3f**	HCl_{aq}/acetone	50	**4f**	18.8/(25%)	100 min	93	750 min	81
8	**3f**	$FeCl_3$/DCM	0.1	**4f**	26.3/(35%)	5 min	95	10 min	87
9[a]	**3j**	HCl_{aq}/acetone	100	**4j**	18.8/(25%)	25 min	82	450 min	84
10	**3j**	$FeCl_3$/DCM	0.1	**4j**	26.3/(35%)	5 min	89	10 min	91

[a] $V_{HClaq}/V_{aceton} - 1/1$.
[b] Calculated on a pure acid.
[c] Based on the ^1H NMR spectra.

Under nonaqueous conditions ($FeCl_3$/DCM), *ortho*-formyl diarylmethanes **3f** and **3j** cyclized 2 times faster (10 min. for silent conditions versus 5 min. for ultrasounds) (Table 7, entry 8 and 10).

A special case among activated aryl groups ArII (Scheme 1) constitutes 3,5-dimethoxyphenyl group having a particular preference in the electrophilic aromatic cyclisation reaction of *ortho*-formyl diarylmethane **3d** due to the fact that preferred 2 and 6 positions are situated in the *ortho* positions to both MeO groups. The compound **3d** was stable during synthesis, workup with AcOEt and purification using column chromatography over silica gel with petroleum ether/acetone as an eluent. However, dissolution of the sample of **3d** in $CDCl_3$ caused under silent conditions unprecedented, spontaneous cyclisation to **4d** in the NMR tube within 15 min at room temperature (c.a. 50% conversion) probably due to trace amounts of hydrochloric acid present in the solvent. Preparative sonication of the $CHCl_3$ solution (reagent grade, without deacidification) gave quantitatively **4d** in 100% purity within 10 min (pulse on/off - 2 s, amplitude 26.3 μm). Sonication of the acetone solution of **3d** under the same reaction conditions recovered the substrate. In the presence of excess of HCl_{aq}, cyclisation of **3d** occurred immediately within less than 1 min. (Table 5). Introduction of the third methoxy substituent in 3,4,5-trimethoxyphenyl group of **3e**, caused prolongation of the sonication time from 10 min. for **3d** to more than 1 h for **3e** (76% conversion). The *ortho*-formyl diarylmethane **3e** unlike **3d** did not cyclise both in $CDCl_3$ and $CHCl_3$ solutions under silent conditions. In sonicated HCl_{aq} solutions, however, the reaction was very fast and no significant difference in reaction times was observed (less than 1 min for **3d** and **3e**, Table 5).

4. Conclusions

This work meets the demands for softening of the harsh reaction conditions of the Bradsher reaction, which usually proceeds at high temperatures, within long reaction times in the presence of strong acids and cannot be applied to substrates which could decompose at these conditions. We were successful to carry out this reaction at room temperature in both aqueous medium (HCl_{aq}/acetone) and in non-aqueous medium $FeCl_3$/DCM and to significantly shorten reaction times both for activated and non-activated *ortho*-formyl diarylmethanes which gave the corresponding cyclic products in high yields. These results were gained by the first use of ultrasounds in the Bradsher reaction and in electrophilic aromatic cyclisation, in general, leading to polyacenes containing 3 and 4 fused aromatic and heteroaromatic rings. Moreover, the obtained result for aqueous medium (HCl_{aq}/acetonitrile) outline alternative direction of further improvements of our conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ultsonch.2016.07.010.

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