

Supporting Information for

Turning Pd-Catalysed Direct C–H Arylation of Thiophene Derivatives into Green: Industrial Wastewater as an Effective Reaction Medium

Stefano Nejrrotti,*^a Barbara Centrella,^a Davide Gallo,^{a,b} Claudia Barolo,^{a,c,d} Matteo Bonomo*^a

a Department of Chemistry, NIS and INSTM Reference Centre, Università degli Studi di Torino, via Pietro Giuria 7, 10126 Torino, Italy.

b Ahlstrom Italia S.p.A., via Stura 98, 10075 Mathi (TO), Italy.

c Istituto di Scienza, Tecnologia e Sostenibilità per lo Sviluppo dei Materiali Ceramici (ISSMC-CNR), via Granarolo 64, 48018 Faenza (RA), Italy.

d ICxT Interdepartmental Center, Università Degli Studi di Torino, Lungo Dora Siena 100, Torino, 10153, Italy.

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General information

All reagents and solvents were purchased from Merck, TCI or VWR, and were used as received, without further purification. Type II water was obtained with a reverse osmosis system, coupled with a nuclear-grade ion exchange resin. "Industrial wastewater" was the condensation water from the industrial process by Ahlstrom Italia SpA, disposed of as hazardous waste with European Waste Catalogue (EWC) Code 16 10 01. Reactions were performed using standard laboratory glassware, at open air; heating was provided through an oil bath. Flash column chromatography was performed on a Biotage SP1 chromatographer, using Biotage Sfar columns. R_f values refer to TLC carried out on silica gel plates. ^1H and ^{13}C NMR spectra were recorded on a Jeol ECZR600 spectrometer, working at 14.1 T (^1H operating frequency: 600 MHz), in CDCl_3 , using Wilmad high throughput Class B Glass NMR tubes. The residual solvent peak was used as an internal reference (CHCl_3 , ^1H : 7.26 ppm; CDCl_3 , ^{13}C : 77.16 ppm). Multiplicity is reported as follows: s (singlet), d (doublet), t (triplet), m (multiplet). UV-Vis spectra were recorded on a Cary 300 Bio spectrophotometer, in CH_2Cl_2 solution. Fluorescence measurements were recorded using a HORIBA Jobin Yvon Fluorolog2 fluorimeter. The excitation wavelength was set at the absorption peak in the visible region, previously recorded at the UV-Vis spectra. Diluted solutions with absorbance around or lower 0.1 absorbance units were used to avoid the presence of aggregates. ESI-MS spectra were recorded using a LTQ Orbitrap (Thermo Scientific) spectrometer, with electrospray interface and ion trap as mass analyser. The flow injection effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas. The following parameters were used: Api Source ESI, Source Voltage 5 kV, Source Current 0.05 μA , Sheath Gas Flow Rate 1.0 arb, Aux Gas Flow Rate 20.00 arb, Sweep Gas Flow Rate 0 arb, Capillary Voltage 32 V, Capillary Temp 275.00 $^\circ\text{C}$, Tube Lens Voltage 75 V; Detector Orbitrap: Resolution 30 000 and Scan range 100–1500. ICP-AES was performed on an Agilent 5800 spectrometer, in three replicates for each compound; values are reported with a 0.05 confidence interval. The samples were prepared by MW-assisted digestion of around 20 mg of compound in 5 mL of HNO_3 . Melting point was determined using a Stuart SMP3 instrument, setting a heating rate of 2 $^\circ\text{C min}^{-1}$.

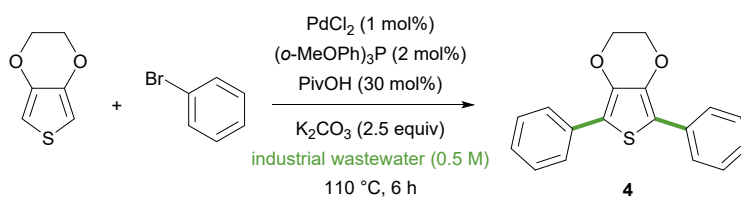
Green metrics formulas

$$E - factor = \frac{\sum reagents + \sum solvents - product}{product}$$

$$RME = \frac{product}{\sum reagents}$$

$$gRME = \frac{product}{\sum reagents + \sum solvents}$$

Synthesis of 2,5-diphenyl-3,4-ethylenedioxythiophene, **4**



A vial was charged with palladium(II) chloride (0.01 equiv, 0.1 mmol, 17.7 mg), tris(2-methoxyphenyl)phosphine (0.02 equiv, 0.2 mmol, 70 mg), pivalic acid (0.3 equiv, 3 mmol, 306 mg), and potassium carbonate (2.5 equiv, 25 mmol, 3.455 g). Then, industrial wastewater (20 mL) was added and the vial was stirred for 2 min, before adding 3,4-ethylenedioxythiophene (1 equiv, 10 mmol, 1.06 mL) and bromobenzene (2.5 equiv, 25 mmol, 2.63 mL). The mixture was stirred at 110 °C for 6 h, then it was cooled down. Water (15 mL) and ethanol (15 mL) were added to induce the precipitation of product **4**, which was recovered through filtration. The crude product was triturated with a mixture of ethanol (15 mL) and dichloromethane (2 mL) to obtain pure **4** as a yellow solid (2.178 g, 74% yield). ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.77–7.74 (m, 4H), 7.40–7.36 (m, 4H), 7.24–7.21 (m, 2H), 4.37 (s, 4H).¹ Pd content (ICP-AES): 1.2 ± 0.3 ppm.

Green metrics calculation for compound **4**

Materials employed					
1) Reaction		2) Work-up		3) Purification	
EDOT	1.422 g	H ₂ O	15 g	EtOH	11.8 g
PhBr	3.925 g	EtOH	11.8 g	DCM	2.7 g
K ₂ CO ₃	3.455 g	<i>sum</i>	26.8 g	<i>sum</i>	14.5 g
PdCl ₂	0.0177 g	Product obtained 4 2.178 g			
(<i>o</i> -MeOPh) ₃ P	0.070 g				
PivOH	0.306 g				
<i>reagents sum</i>	9.196 g				
H ₂ O	20 g				
<i>total sum</i>	29.196 g				

E-factor: (29.196 + 26.8 + 14.5 – 2.178) / 2.178 = 31

RME: 2.178 / 9.196 = 0.237

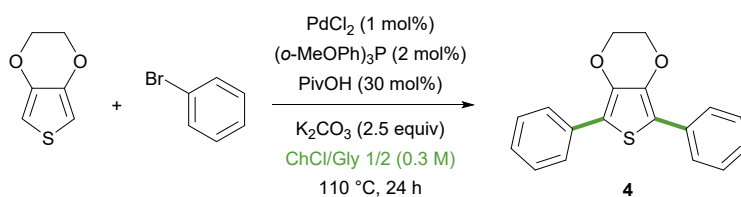
gRME: 2.178 / (29.196 + 26.8 + 14.5) = 0.031

if reaction water is not considered as waste (see the main text for the discussion)

E-factor: (9.196 + 26.8 + 14.5 – 2.178) / 2.178 = 22

gRME: 2.178 / (9.196 + 26.8 + 14.5) = 0.043

Green metrics calculation for the synthesis of compound **4** through direct C–H arylation in DES



Numbers and calculations from the work by Zani *et al.*¹

Materials employed					
1) Reaction		2) Work-up		3) Purification	
EDOT	0.213 g	H ₂ O	1 g	EtOH	3.95 g
PhBr	0.589 g	EtOH	8.79 g	<i>sum</i>	3.954 g
K ₂ CO ₃	0.518 g	<i>sum</i>	9.79 g		
PdCl ₂	0.0027 g				
(<i>o</i> -MeOPh) ₃ P	0.011 g				
PivOH	0.046 g				
<i>reagents sum</i>	1.380 g				
ChCl/Gly	5.89 g				
<i>total sum</i>	7.27 g				

Product obtained	
4	0.396 g

E-factor: $(7.27 + 9.79 + 3.954 - 0.396) / 0.396 = 52$

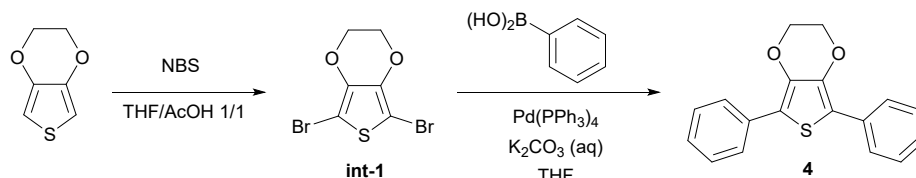
RME: $0.396 / 1.380 = 0.287$

gRME: $0.396 / (7.27 + 9.79 + 3.954) = 0.019$

Green metrics calculation for the synthesis of compound **4** through Suzuki-Miyaura cross-coupling

The 2-steps synthesis from commercially available reagents involves the bromination of EDOT and the subsequent Suzuki-Miyaura coupling with phenyl boronic acid.^{2,3}

The total amount of waste (or of reagents and solvents used) from the first step was normalized to the final amount of the target product **4** (normalized waste). For the liquid/liquid extraction and for the recrystallization of the second step, plausible amount of solvent were considered.



Step 1 – Bromination – Materials employed

1) Reaction		2) Work-up	
EDOT	1.42 g	H ₂ O	100 g
NBS	3.74 g	<i>sum</i>	100 g
<i>reagents sum</i>	5.16 g		
THF	17.8 g		
AcOH	21 g		
<i>total sum</i>	43.96 g		

Product obtained	
int-1	2.6 g

Waste (step 1): 43.96 + 100 – 2.6 = 141.36 g

Normalization factor (int-1 used in step 2 / int-1 obtained from step 1): 12.7 / 2.6 = 4.88

Normalized waste: 141.36 * 4.88 = 689.84 g

Normalized reagents sum: 5.16 * 4.88 = 25.18 g

Normalized global (reagents + solvents) sum: 143.96 * 4.88 = 792.52 g

Step 2 – Suzuki coupling – Materials employed

1) Reaction		2) Work-up		3) Purification	
int-1	12.7 g	chloroform	74.5 g	methanol	39.6 g
PhB(OH) ₂	11.4 g	H ₂ O	30 g	<i>sum</i>	39.6 g
K ₂ CO ₃	13.8 g	<i>sum</i>	104.5 g		
Pd(PPh ₃) ₄	0.392 g				
<i>reagents sum</i>	38.292 g				
THF	44.5 g				
H ₂ O	50 g				
<i>sum</i>	132.8 g				

Product obtained	
4	7.91 g

Waste (step 2): 132.8 + 104.5 + 39.6 – 7.91 = 269 g

Waste (step 1 + 2): 689.84 + 269 = 958.8 g

Overall E-factor (step 1 + 2): 958.8 / 7.91 = 121

Overall reagents sum (step 1 + 2): $25.18 + 38.292 = 63.5 \text{ g}$

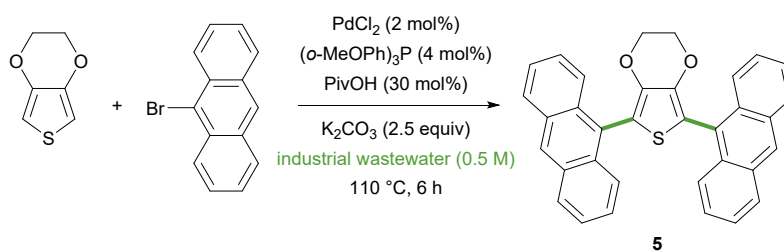
Global sum (step 2): $132.8 + 104.5 + 39.6 = 276.9 \text{ g}$

Overall global sum (step 1 + 2): $792.52 + 276.9 = 1069.4 \text{ g}$

Overall RME (step 1 + 2): $7.91 / 63.5 = 0.125$

Overall gRME (step 1 + 2): $7.91 / 1069.4 = 0.0074$

Synthesis of 2,5-di(anthracene-9-yl)-3,4-ethylenedioxythiophene, **5**



A vial was charged with palladium(II) chloride (0.02 equiv, 0.04 mmol, 7.8 mg), tris(2-methoxyphenyl)phosphine (0.04 equiv, 0.08 mmol, 28 mg), pivalic acid (0.3 equiv, 0.6 mmol, 61 mg), potassium carbonate (2.5 equiv, 5 mmol, 691 mg), and 9-bromoanthracene (2.5 equiv, 5 mmol, 1.286 g). Then, industrial wastewater (4 mL) was added and the vial was stirred for 2 min, before adding 3,4-ethylenedioxythiophene (1.0 equiv, 2 mmol, 0.212 mL). The mixture was stirred at 110 °C for 6 h, then it was cooled down. Water (10 mL) was added and the mixture was filtered. The solid crude product was triturated with a mixture of ethanol (10 mL) and dichloromethane (2 mL) to obtain pure **5** as a yellow solid (633 mg, 64% yield). ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.57 (s, 2H), 8.25 (dt, *J* = 8.7, 1.0 Hz, 4H), 8.08 (d, *J* = 8.4 Hz, 4H), 7.62–7.58 (m, 4H), 7.55–7.52 (m, 4H), 4.25 (s, 4H).⁴ Pd content (ICP-AES): 5.4 ± 1.2 ppm.

Green metrics calculation for compound **5**

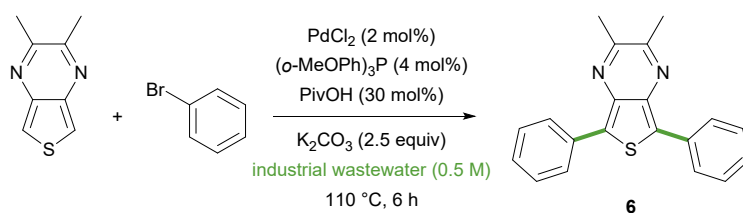
Materials employed					
1) Reaction		2) Work-up		3) Purification	
EDOT	0.284 g	H ₂ O	10g	EtOH	7.9 g
ArBr	1.286 g	<i>sum</i>	10 g	DCM	2.7 g
PdCl ₂	0.0078 g			<i>sum</i>	10.6 g
(o-MeOPh) ₃ P	0.028 g				
PivOH	0.061 g				
K ₂ CO ₃	0.691 g				
<i>reagents sum</i>	2.358 g				
H ₂ O	4 g				
<i>sum</i>	6.358 g				
Product obtained					
		5	0.633 g		

E-factor: (6.358 + 10 + 10.6 – 0.633) / 0.633 = 42

RME: 0.633 / 2.358 = 0.268

gRME: 0.633 / (6.358 + 10 + 10.6) = 0.024

Synthesis of 5,7-diphenyl-2,3-dimethylthieno[3,4-*b*]pyrazine, **6**



A vial was charged with palladium(II) chloride (0.02 equiv, 0.04 mmol, 7.8 mg), tris(2-methoxyphenyl)phosphine (0.04 equiv, 0.08 mmol, 28 mg), pivalic acid (0.3 equiv, 0.6 mmol, 61 mg), potassium carbonate (2.5 equiv, 5 mmol, 691 mg), and 2,3-dimethylthieno[3,4-*b*]pyrazine (1.0 equiv, 2 mmol, 328 mg). Then, industrial wastewater (4 mL) was added and the vial was stirred for 2 min, before adding bromobenzene (2.5 equiv, 5 mmol, 0.525 mL). The mixture was stirred at 110 °C for 6 h, then it was cooled down. Water (4 mL) was added and the mixture was filtered. The solid crude product was triturated with a mixture of ethanol (4 mL) to obtain pure **6** as a brown solid (557 mg, 88% yield). **Mp** 107–109 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.22–8.18 (m, 4H), 7.49–7.45 (m, 4H), 7.36–7.31 (m, 2H), 2.66 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 153.1 (Cq), 139.3 (Cq), 133.6 (Cq), 130.4 (Cq), 129.0 (CH), 128.1 (CH), 127.7 (CH), 23.9 (CH₃). **HRMS** (ESI, positive mode) *m/z*: [M+H]⁺ calcd for C₂H₁₇N₂S⁺ 317.1107; found 317.1104. Pd content (ICP-AES): 6.5 ± 2.3 ppm.

Green metrics calculation for compound **6**

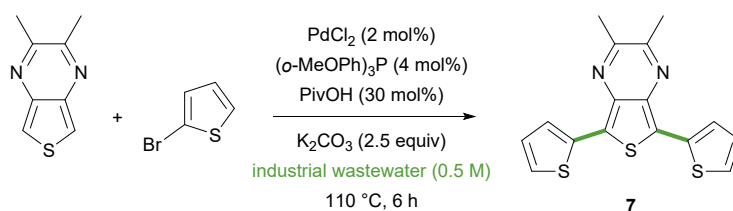
Materials employed					
1) Reaction		2) Work-up		3) Purification	
TP	0.328 g	H ₂ O	4 g	EtOH	3.2 g
PhBr	0.785 g		<i>sum</i> 4 g	<i>sum</i>	3.2 g
PdCl ₂	0.0078 g	Product obtained 6 0.557 g			
(<i>o</i> -MeOPh) ₃ P	0.028 g				
PivOH	0.061 g				
K ₂ CO ₃	0.691 g				
<i>reagents sum</i>	1.901 g				
H ₂ O	4 g				
<i>sum</i>	5.901 g				

E-factor: (5.901 + 4 + 3.2 – 0.557) / 0.557 = 22

RME: 0.557 / 1.901 = 0.293

gRME: 0.557 / (5.901 + 4 + 3.2) = 0.043

Synthesis of 5,7-di(thien-2-yl)-2,3-dimethylthieno[3,4-*b*]pyrazine, **7**



A vial was charged with palladium(II) chloride (0.02 equiv, 0.04 mmol, 7.8 mg), tris(2-methoxyphenyl)phosphine (0.04 equiv, 0.08 mmol, 28 mg), pivalic acid (0.3 equiv, 0.6 mmol, 61 mg), potassium carbonate (2.5 equiv, 5 mmol, 691 mg), and 2,3-dimethylthieno[3,4-*b*]pyrazine (1.0 equiv, 2 mmol, 328 mg). Then, industrial wastewater (4 mL) was added and the vial was stirred for 2 min, before adding 2-bromothiophene (2.5 equiv, 5 mmol, 0.290 mL). The mixture was stirred at 110 °C for 6 h, then it was cooled down. Water (4 mL) was added and the mixture was filtered. The solid crude product was triturated with a mixture of ethanol (10 mL) to obtain pure **7** as a red solid (611 mg, 93% yield). ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.63 (dd, *J* = 3.7, 1.1 Hz, 2H), 7.36 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.10 (dd, *J* = 5.1, 3.7 Hz, 2H), 2.67 (s, 6H).⁵ Pd content (ICP-AES): 6.3 ± 1.6 ppm.

Green metrics calculation for compound **7**

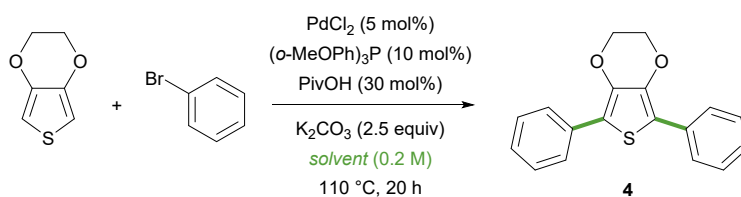
Materials employed					
1) Reaction		2) Work-up		3) Purification	
TP	0.328 g	H ₂ O	4 g	EtOH	7.9 g
ThBr	0.489 g	<i>sum</i>	4 g	<i>sum</i>	7.9 g
PdCl ₂	0.0078 g	Product obtained 7 0.611 g			
(<i>o</i> -MeOPh) ₃ P	0.028 g				
PivOH	0.061 g				
K ₂ CO ₃	0.691 g				
<i>reagents sum</i>	1.605 g				
H ₂ O	4 g				
<i>sum</i>	5.605 g				

E-factor: (5.605 + 4 + 7.9 - 0.611) / 0.611 = 28

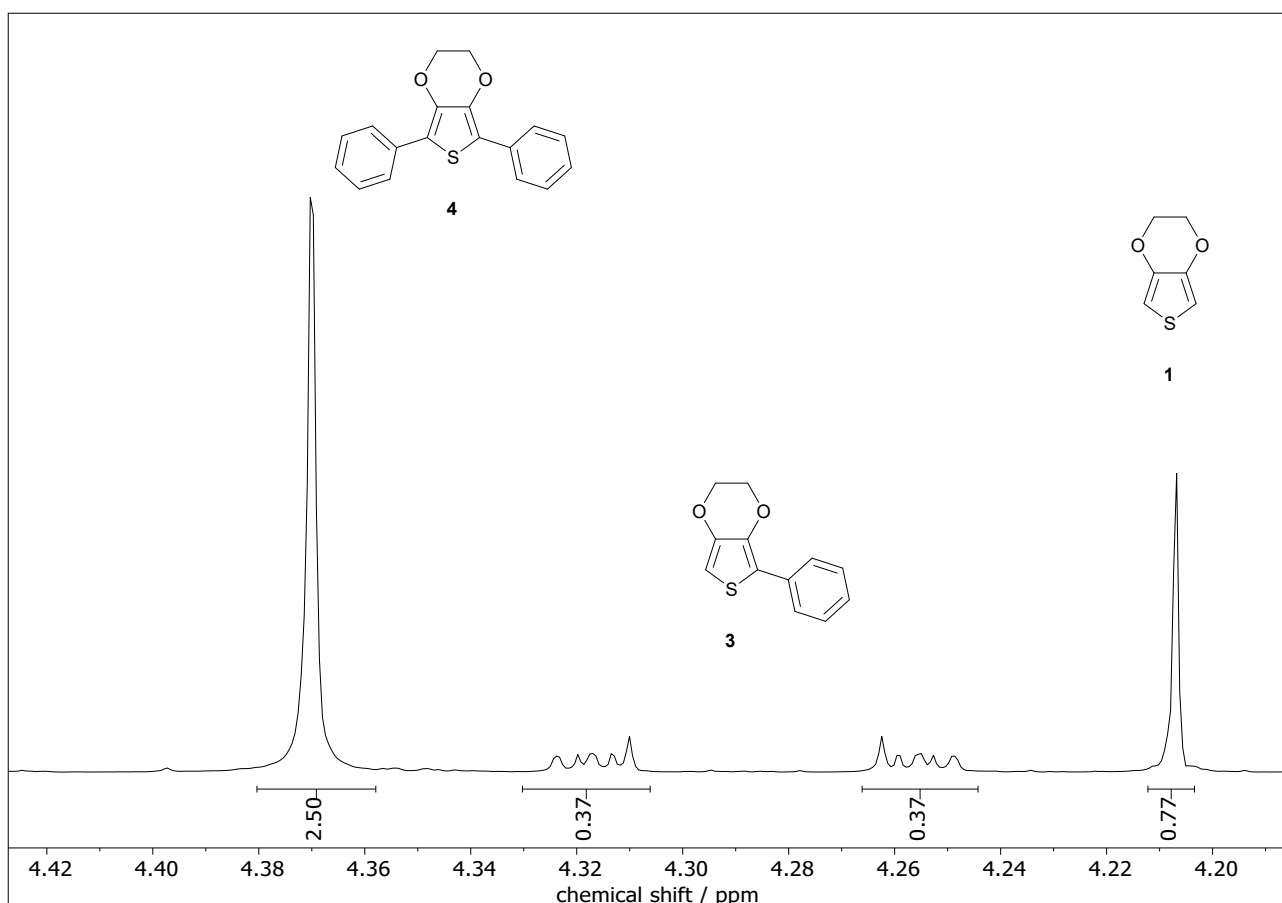
RME: 0.611 / 1.605 = 0.381

gRME: 0.611 / (5.605 + 4 + 7.9) = 0.035

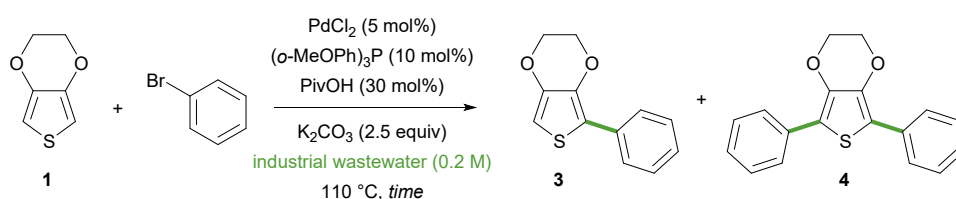
Procedure for the screening of solvents in the synthesis of compound **4** (Table 1)



A vial was charged with palladium(II) chloride (0.05 equiv, 0.025 mmol, 4.4 mg), tris(2-methoxyphenyl)phosphine (0.1 equiv, 0.05 mmol, 17.6 mg), pivalic acid (0.3 equiv, 0.075 mmol, 15.3 mg), and potassium carbonate (2.5 equiv, 1.25 mmol, 173 mg). Then, the solvent (2.5 mL) was added and the vial was stirred for 2 min, before adding 3,4-ethylenedioxythiophene (1.0 equiv, 0.5 mmol, 53 μ L) and bromobenzene (2.5 equiv, 1.25 mmol, 132 μ L). The mixture was stirred at 110 °C for 20 hours, then it was cooled down and extracted three times with 5 mL of CH₂Cl₂; the combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was dissolved in CDCl₃ and analysed through ¹H NMR to determine the relative ratio between compounds **1**, **3** and **4**, by using the methylenic protons in the EDOT structure (**1**, 4H at δ = 4.37 ppm; **3**, 2H at δ = 4.32 ppm, 2H at δ = 4.25 ppm; **4**, 4H at δ = 4.21 ppm). The spectrum of the reaction performed in glycerol (Table 1, entry 2) is reported as a representative example:

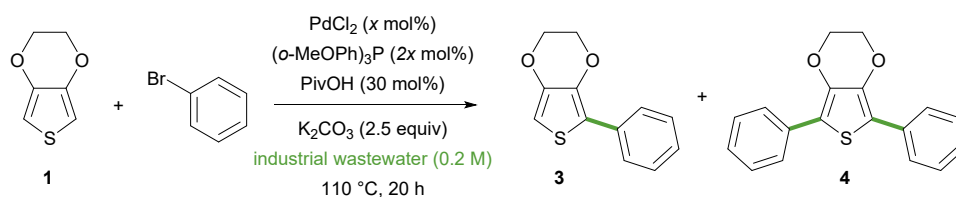


Kinetic study for the synthesis of compound 4 (Figure 1)



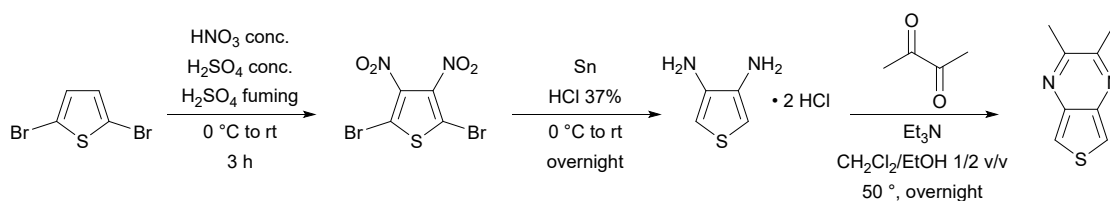
A vial was charged with palladium(II) chloride (0.05 equiv, 0.025 mmol, 4.4 mg), tris(2-methoxyphenyl)phosphine (0.1 equiv, 0.05 mmol, 17.6 mg), pivalic acid (0.3 equiv, 0.075 mmol, 15.3 mg), and potassium carbonate (2.5 equiv, 1.25 mmol, 173 mg). Then, the solvent (2.5 mL) was added and the vial was stirred for 2 min, before adding 3,4-ethylenedioxythiophene (1.0 equiv, 0.5 mmol, 53 μ L) and bromobenzene (2.5 equiv, 1.25 mmol, 132 μ L). The mixture was stirred at 110 °C for different times (see Figure 1), then it was rapidly cooled down by flushing the vial externally with cold water. The mixture was extracted three times with 5 mL of CH₂Cl₂; the combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was analysed by ¹H NMR to determine the relative ratio between compounds **1**, **3** and **4**.

Study on the catalyst loading for the synthesis of compound 4



A vial was charged with palladium(II) chloride (0.005–0.02 equiv), tris(2-methoxyphenyl)phosphine (0.01–0.04 equiv), pivalic acid (0.3 equiv, 0.075 mmol, 15.3 mg), and potassium carbonate (2.5 equiv, 1.25 mmol, 173 mg). Then, industrial wastewater (2.5 mL) was added and the vial was stirred for 2 min, before adding 3,4-ethylenedioxythiophene (1.0 equiv, 0.5 mmol, 53 μ L) and bromobenzene (2.5 equiv, 1.25 mmol, 132 μ L). The mixture was stirred at 110 °C for 20 hours, then it was cooled down and extracted three times with 5 mL of CH₂Cl₂; the combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was dissolved in CDCl₃ and analysed through ¹H NMR to determine the relative ratio between compounds **1**, **3** and **4**. Results: relative ratio **1/3/4** of 0/0/100 at 0.02 equiv Pd; 1/7/92 at 0.01 equiv Pd; 8/30/62 at 0.005 equiv Pd.

Synthesis of 2,3-dimethylthieno[3,4-*b*]pyrazine



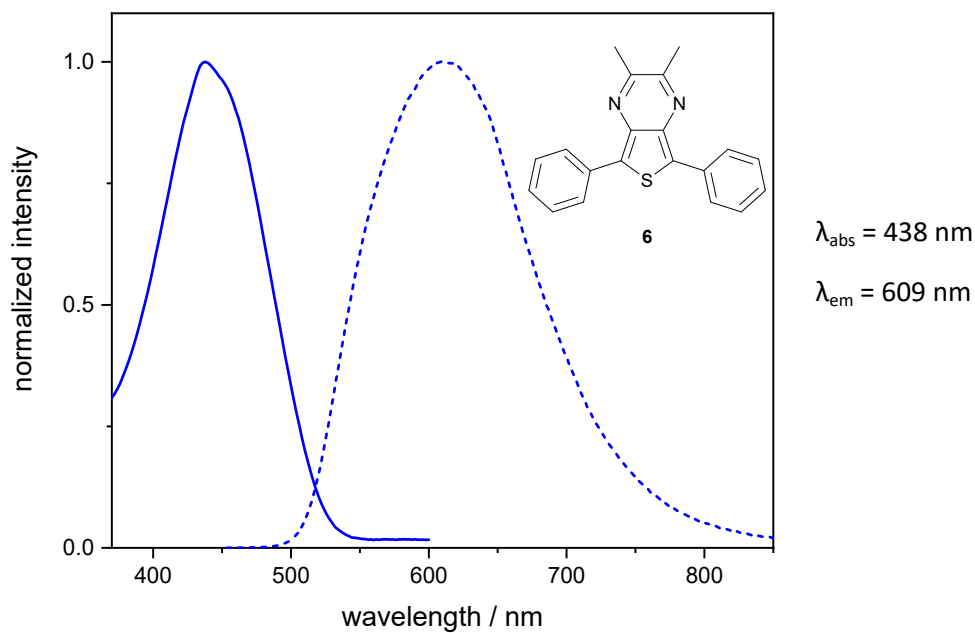
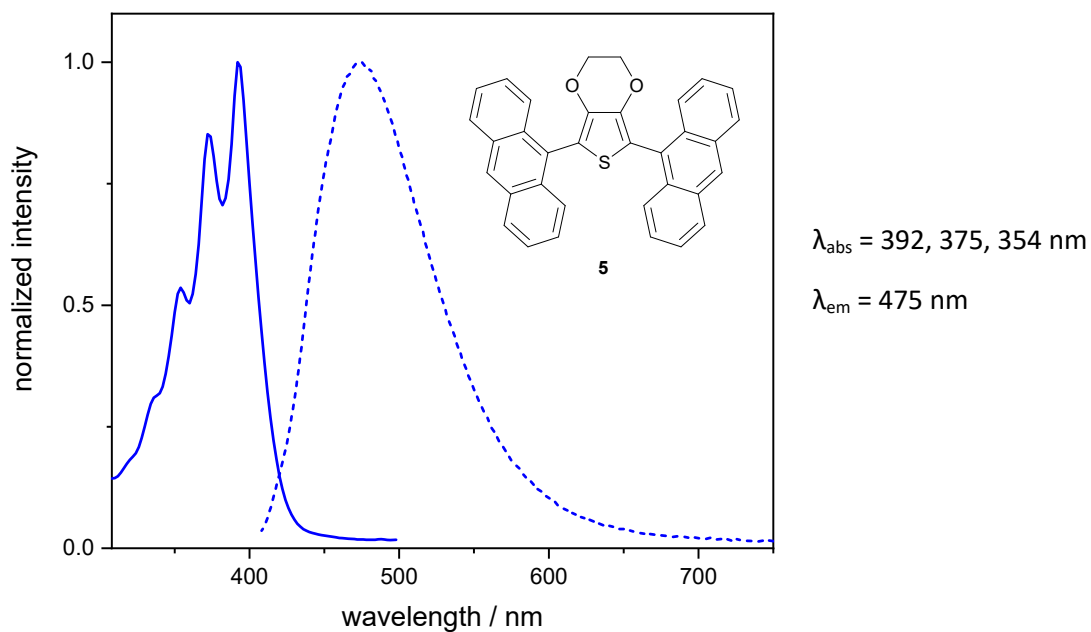
To a 3-neck flask, equipped with a condenser, concentrated sulfuric acid (38 mL), fuming sulfuric acid (58 mL) and concentrated nitric acid (32 mL) were added while keeping the mixture cold with an ice bath. The mixture was stirred in the ice bath for 20 min to ensure complete cooling, then 2,5-dibromothiophene (90 mmol, 21.78 g, 10.1 mL) was slowly added and the mixture was stirred with the ice bath for 10 min, then it was allowed to reach room temperature and stirred for 3 hours. After that time, the mixture was poured into ice and the formation of a yellow solid was observed. The yellow solid, 2,5-dibromo-3,4-dinitrothiophene, was filtered and used for the next step without further purification (22.40 g, 75% yield).

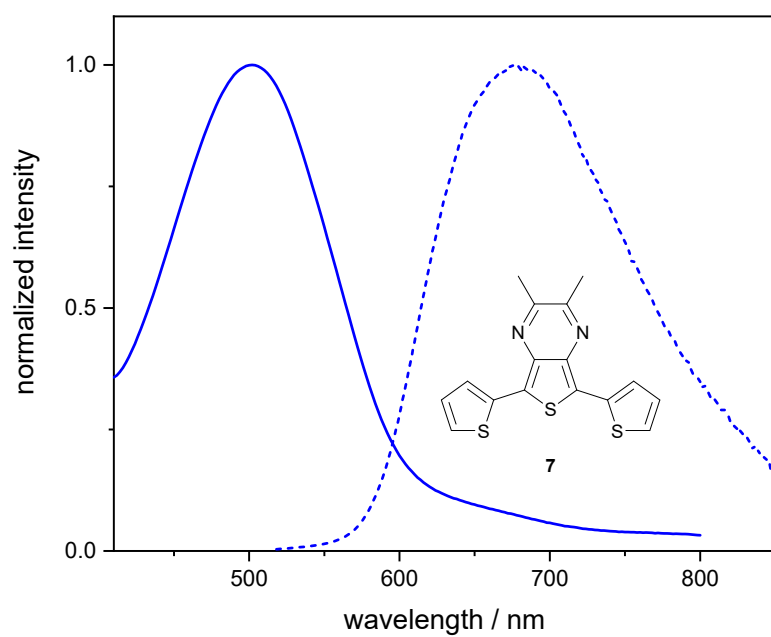
2,5-dibromo-3,4-dinitrothiophene (1.0 equiv, 40 mmol, 13.28 g) was added to a flask containing concentrated hydrochloric acid (250 mL). Tin (7.0 equiv, 280 mmol, 33.2 g) was added portionwise over 30 minutes, while keeping the mixture cold with an ice bath. The mixture allowed to reach room temperature and stirred overnight, then it was transferred into a freezer ($-18\text{ }^\circ\text{C}$) and kept there for 2–3 hours, observing the formation of a yellow solid. The yellow solid, 2,3-diaminothiophene dihydrochloride, was filtered, washed with cold acetonitrile and cold diethyl ether, and used for the next step without further purification (4.79 g, 64% yield).

To a solution of 2,3-diaminothiophene dihydrochloride (1.0 equiv, 16 mmol, 3.0 g) and 2,3-butanedione (1.1 equiv, 17.6 mmol, 1.54 mL) in $\text{CH}_2\text{Cl}_2/\text{EtOH}$ 1/2 v/v (0.07 M, 230 mL, of which 77 CH_2Cl_2 and 153 EtOH), triethylamine (4.0 equiv, 64 mmol, 8.92 mL) was added and the mixture was stirred at $50\text{ }^\circ\text{C}$ overnight. Then, water was added and the mixture was extracted three times with EtOAc; the combined organic layers were dried over anhydrous Na_2SO_4 , filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography to afford pure 2,3-dimethylthieno[3,4-*b*]pyrazine as a tan solid (1.476 g, 56% yield). R_f 0.26 (80/20 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ (ppm): 7.79 (s, 2H), 2.63 (s, 2H).⁶

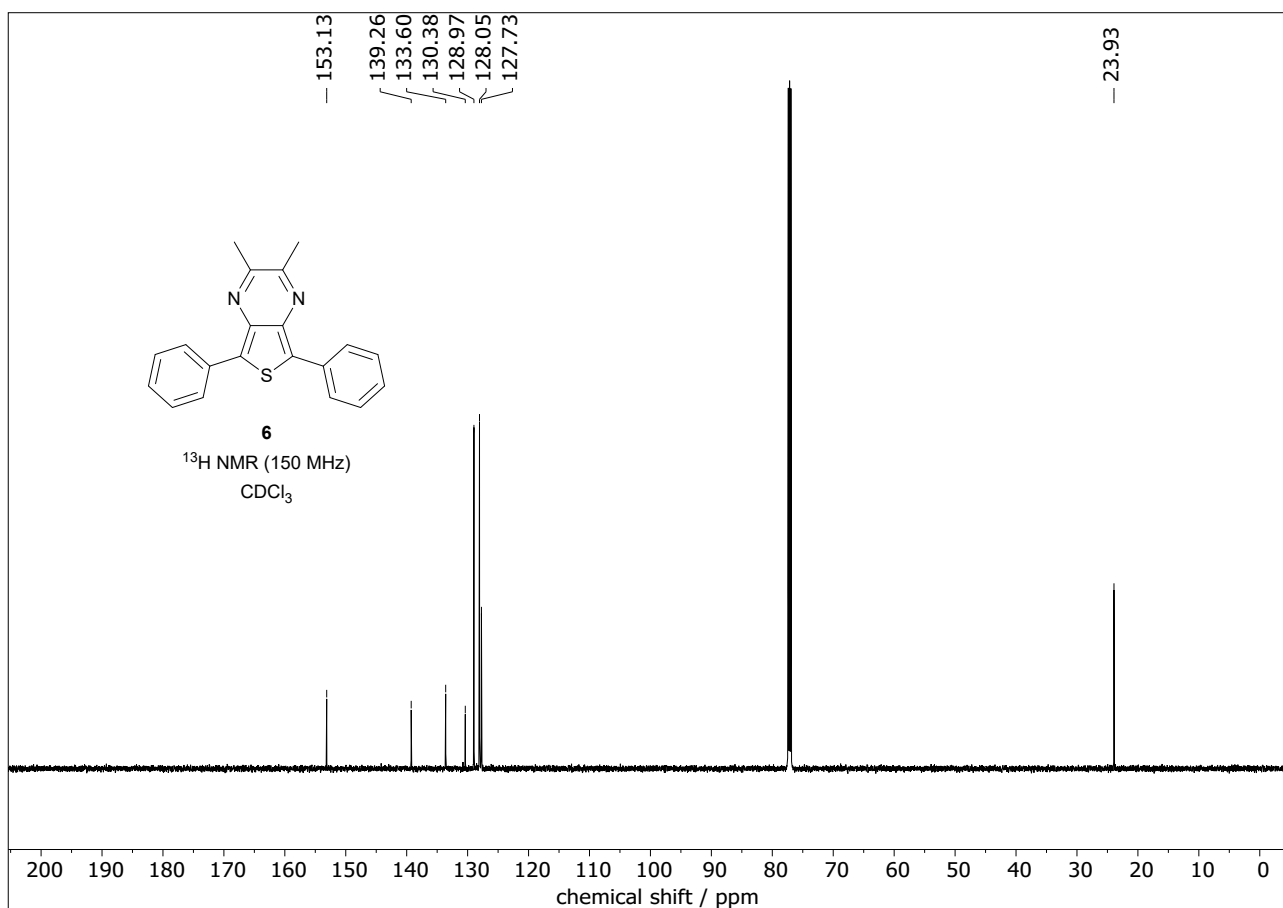
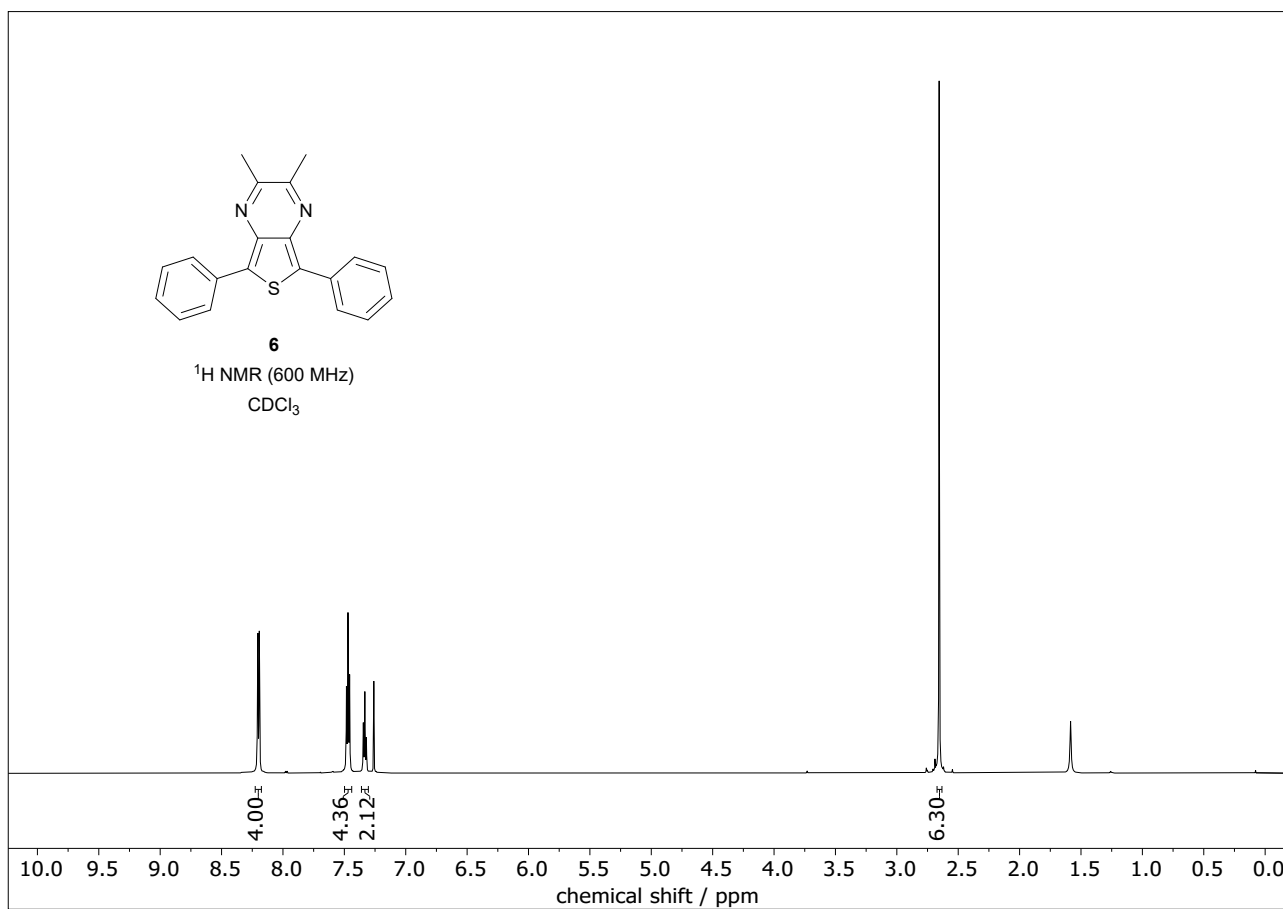
Optical characterisation of compounds 5–7

All absorption (solid line) and emission (dashed line) spectra were recorded in CH₂Cl₂. Absorption spectra were normalized to the peak used as excitation wavelength to acquire the fluorescence spectrum. Emission spectra were normalized to the maximum peak.





NMR spectra of compound 6



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