

# Investigation of mechanochemical thianthrene-mediated aryl C-H functionalization

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# 1. Materials and methods

## 1.1. Chemicals

Unless otherwise stated, all reactants, additives, and solvents were purchased from commercial sources and used without further purification. Details of syntheses of thianthrene-S-oxide, thianthrenated salts, and functionalized products are described in the following chapters.

Sodium triflate was prepared by slowly adding sodium carbonate (1.65 g, 15.6 mmol) to triflic acid (4.66 g, 31.1 mmol) diluted by an equal volume of water (2.7 mL TfOH + 2.7 mL H<sub>2</sub>O). The obtained solution was filtered and left to evaporate to obtain crystals of an unidentified hydrate salt. The crystals were dried in an oven at 110 °C for 2 hours to obtain the anhydrous salt.

## 1.2. Milling equipment

Mechanochemical reactions were carried out using an IST500 Mixer Mill (InSolido Technologies, Zagreb, Croatia) operating at a frequency of 30 Hz. Depending on the reaction, poly(methyl-methacrylate) (PMMA) (internal volume 14.0 or 7.0 mL), teflon (internal volume 14.0 mL), or stainless steel (internal volume 14.0 mL) milling jars were used, along with stainless steel (diameter 7.0 mm, weight 1.4 g) or ZrO<sub>2</sub> (diameter 8.0 mm, weight 1.6 g) balls. Stainless steel jars were used exclusively with two stainless steel balls, while with teflon and PMMA jars only ZrO<sub>2</sub> balls were used (two for 14.0 mL vessels, one for 7.0 mL vessels).

For reactions sensitive to air (formation of thianthrene radical cation), materials were weighed in a glove box (nitrogen atmosphere). Closed reaction jars were transferred to a ball mill and the milling was performed without opening the jars.

## 1.3. *In situ* Raman monitoring

Mechanochemical monitoring was carried out using PMMA milling jars (internal volume 14.0 mL) and two stainless steel milling balls (diameter 7.0 mm, weight 1.4 g). The ball mill operated at a frequency of 30 Hz. *In-situ* Raman monitoring was performed using a portable Raman system with a PDLD (now Necsel) BlueBox laser source with the excitation wavelength of 785 nm, equipped with B&W-Tek fiber optic Raman BAC102 probe, and coupled with an OceanOptics Maya2000Pro spectrometer (with resolution of 1 cm<sup>-1</sup> or 3.5 cm<sup>-1</sup>). The probe was positioned about 4 mm under the reaction vessel. Time-resolved *in-situ* Raman spectra were collected in an automated fashion, using an in-house code in MATLAB. The same equipment was used to obtain *ex situ* Raman spectra.<sup>1</sup>

## 1.4. NMR spectroscopy

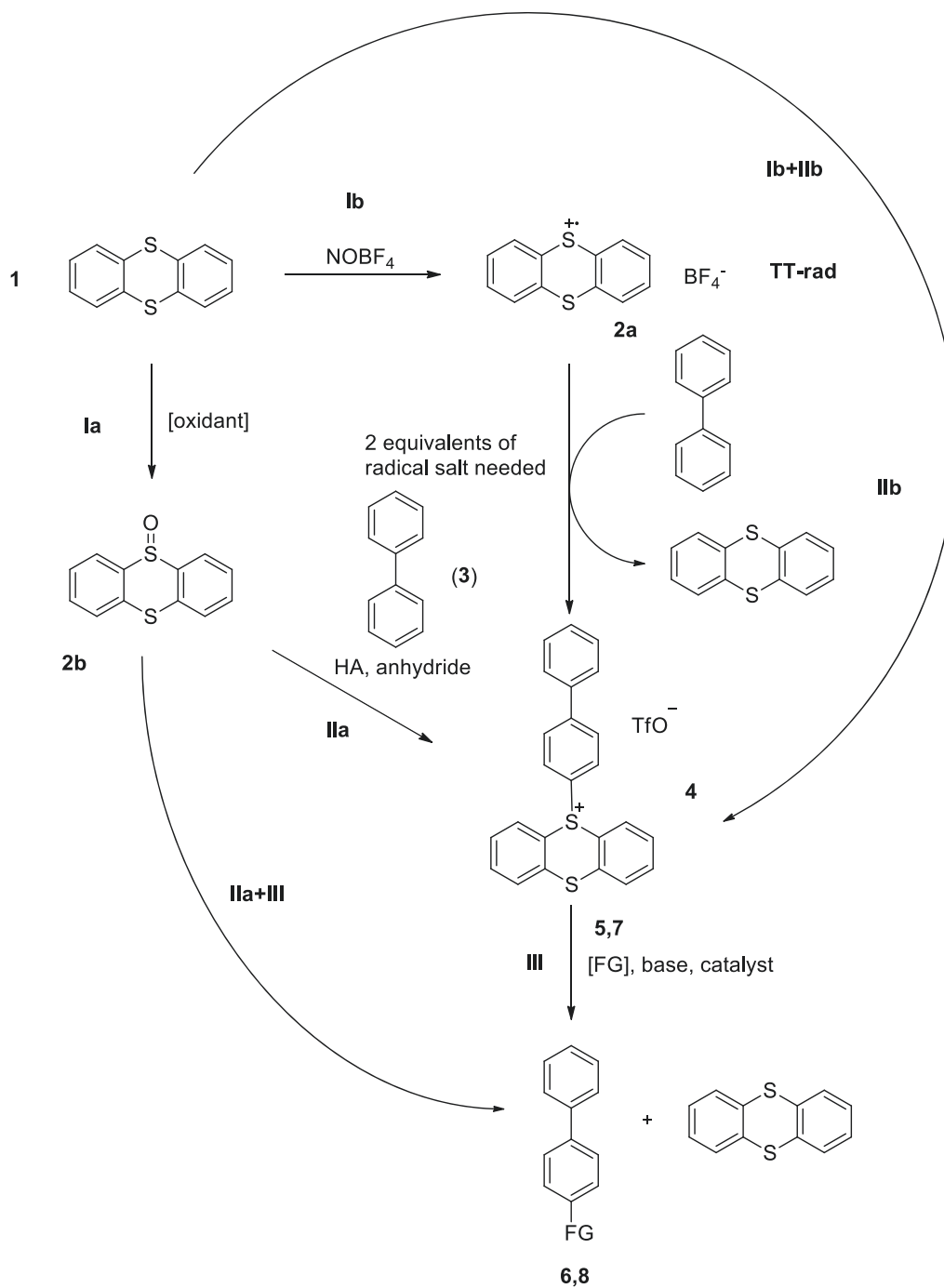
Nuclear magnetic resonance (NMR) spectra were recorded either on NMR Bruker Avance 300 MHz or Bruker Avance 600 MHz spectrometers at 25 °C. Experimental data were processed and analyzed with the program MestReNova. Chemical shifts are given in parts per million (ppm) relative to the residual solvent peak of the non-deuterated solvent (DMSO-d<sub>6</sub>: <sup>1</sup>H NMR:  $\delta$  = 2.50 ppm, or CDCl<sub>3</sub>: <sup>1</sup>H NMR:  $\delta$  = 7.26 ppm. Coupling constants (*J*) are given in Hertz (Hz).

1,3,5-Trimethoxybenzene (TMB) ( $\delta H(\text{Ar})$  = 6.09 ppm,  $\delta H(\text{CH}_3)$  = 3.77 ppm in CDCl<sub>3</sub>) was used as an internal standard for yield calculations.

### 1.5. PXRD analysis

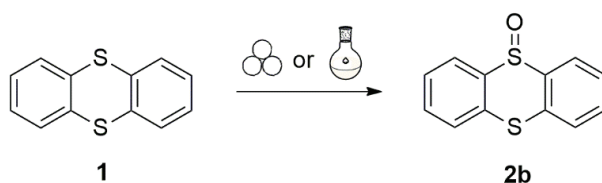
PXRD patterns were collected on a PanAlytical Aeris diffractometer (CuK $\alpha$  radiation and Ni filter where copper X-ray tube was operated at 40 kV and 7.5 mA) in Bragg-Brentano geometry, using a silicon zero-background sample holder.

### 1.6. General reaction scheme



**Scheme S1.** Reaction pathways for oxidation of thianthrene, thianthrenation of aromatic substrates, and functionalization reactions.

## 2. Thianthrene-S-oxide preparation



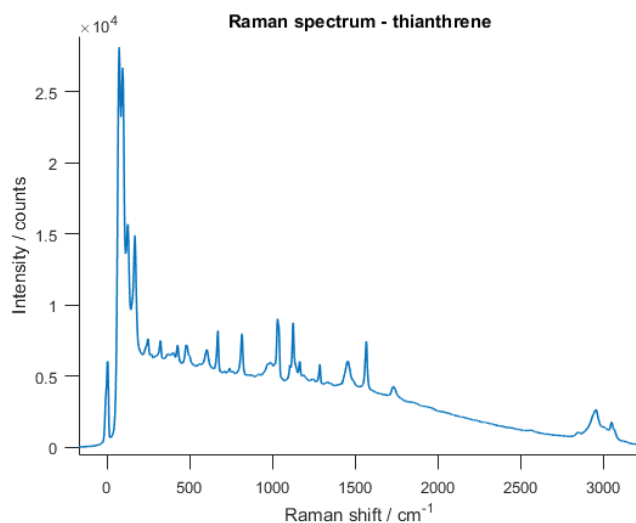
**Scheme S2.** Oxidation of thianthrene (**1**) into thianthrene-S-oxide (**2b**).

### 2.1. Solution synthesis

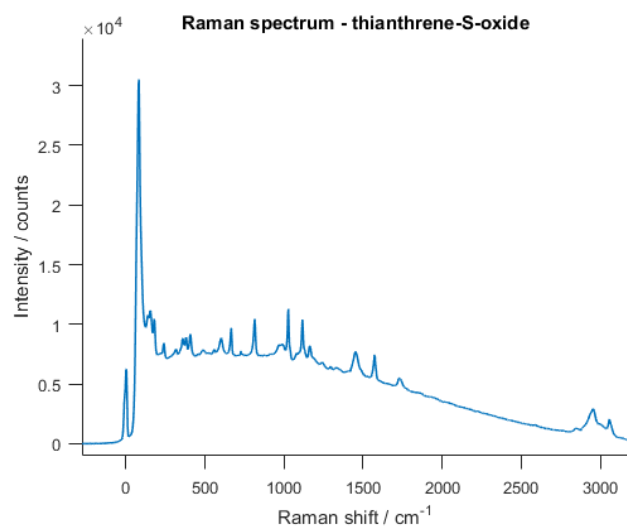
Solution synthesis was performed following a published procedure.<sup>2</sup> Thianthrene (**1**) (23.1 mmol, 5.00 g), aluminium nitrate nonahydrate (1.1 equiv., 9.49 g), KBr (0.05 equiv., 136.5 mg), citric acid (2.1 equiv., 9.49 g) and SiO<sub>2</sub> (7.00 g) were added to a round-bottom flask equipped with a magnetic stirring bar. Dichloromethane (125 mL) was also added to the reaction flask. The mixture was stirred overnight at room temperature. The resulting mixture was filtered, and the filtration residue was washed with dichloromethane. The filtrate was dried over sodium sulfate and the solvent was removed by vacuum distillation. The product was obtained as white powder (4.95 g, 92 %) with a tinge of yellow due to the adsorbed NO<sub>2</sub> formed in the reaction. (<sup>1</sup>H NMR (**2b**): δ/ ppm: 7.95 – 7.92 (m, 2H), 7.64 – 7.62 (m, 2H), 7.57 – 7.54 (m, 2H), 7.45 – 7.42 (m, 2H).)

### 2.2. Solid-state synthesis with *in situ* Raman monitoring

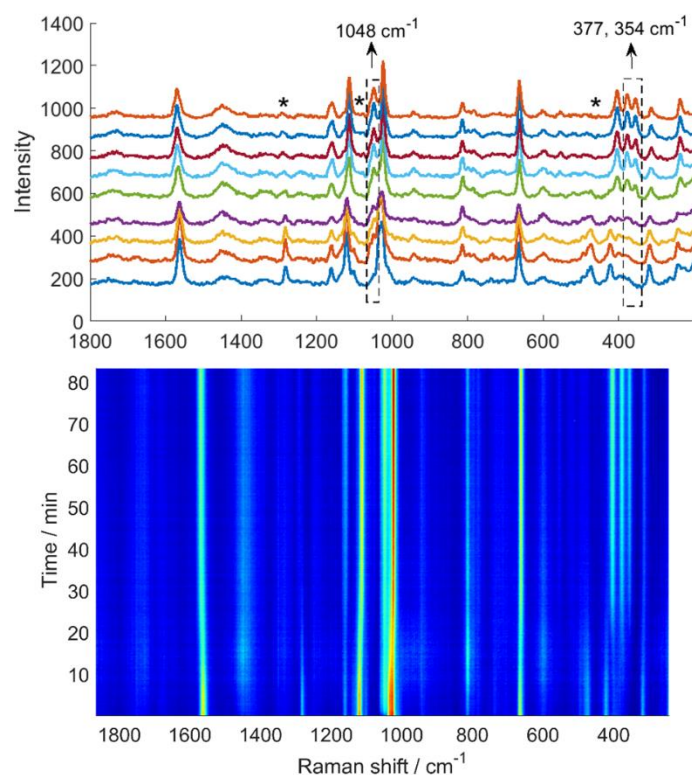
**1** (0.46 mmol, 100 mg), aluminium nitrate nonahydrate (1.1 equiv., 189.82 mg), KBr (0.05 equiv., 2.74 mg), citric acid (1.5 equiv., 132.57 mg) and SiO<sub>2</sub> (ca. 140 mg) were added to a 14 mL PMMA jar with 2 SS balls (mass 1.4 g). Milling was conducted for 80 min at 30 Hz with *in situ* Raman monitoring (**Figures S1-S3**). After the reaction was complete, the product purified of inorganic residues was analyzed by <sup>1</sup>H NMR to confirm that all **1** was consumed (**Figure S9**), as well as by PXRD analysis for phase purity (**Figure S5**).



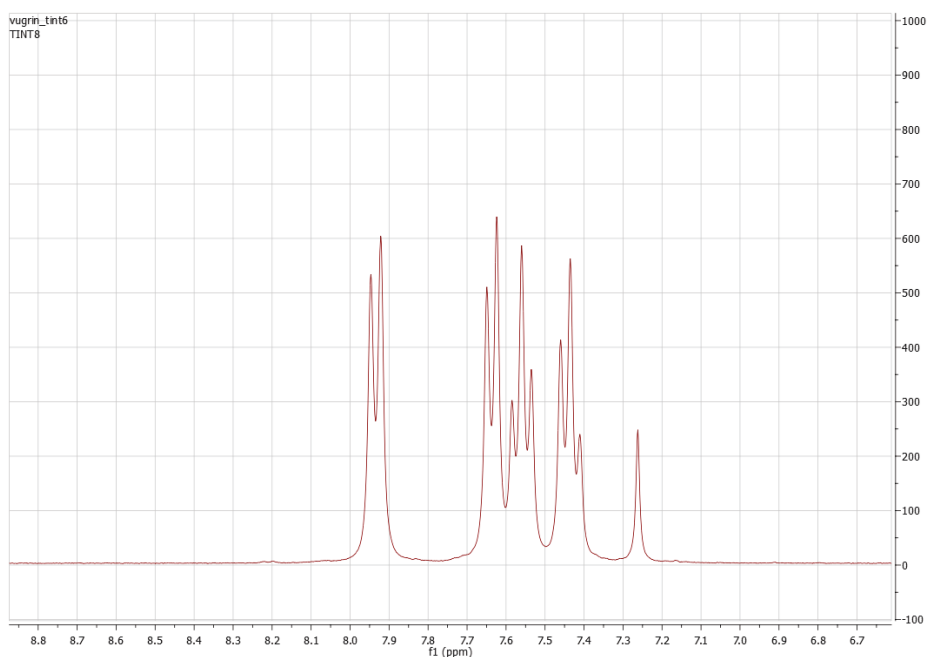
**Figure S1.** Raman spectrum of commercially obtained thianthrene.



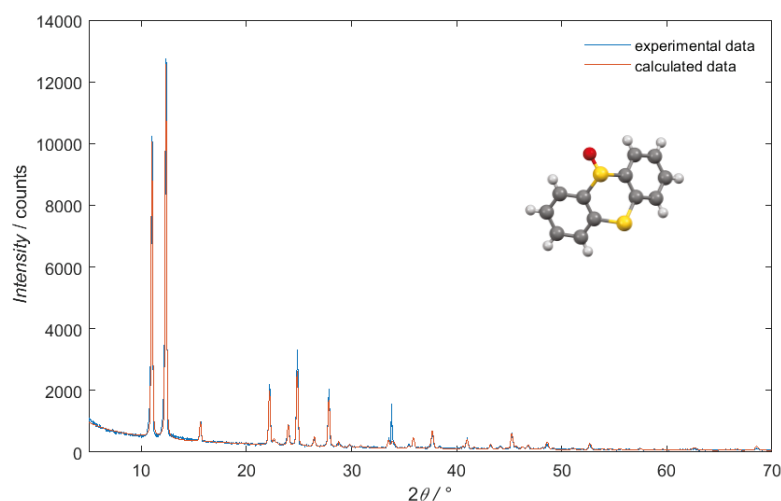
**Figure S2.** Raman spectrum of **2b** obtained by solution synthesis.



**Figure S3.** Time-resolved 2D plot of mechanochemical thianthrene oxidation during 80 min of milling at 30 Hz using PMMA jars (internal volume 14 mL) with two SS milling balls (1.4 g). The formation of thianthrene-S-oxide (signals at 1048, 377, and 354  $\text{cm}^{-1}$ ) in the solid state starts in 20 min, with complete thianthrene consumption after 80 min.



**Figure S4.** Aromatic region of the  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of **2b** obtained by milling for 80 minutes.

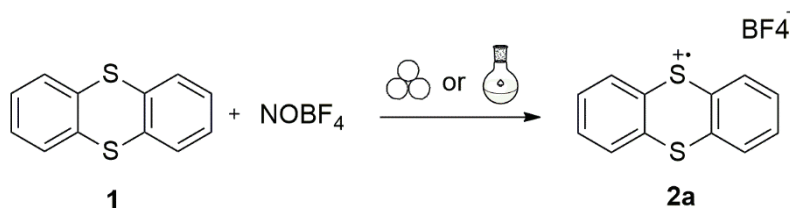


**Figure S5.** Diffractogram of **2b** obtained by solid-state synthesis; Rietveld refinement against literature data (Refcode: PEFMUK01).

### 2.3. Multigram synthesis in a planetary mill

**1** (0.023 mol, 5.00 g), aluminium nitrate nonahydrate (1.1 equiv., 9.49 g), KBr (0.05 equiv., 137 mg), citric acid (1.5 equiv., 6.63 g) and  $\text{SiO}_2$  (7.0 g) were added to a 100 mL SS planetary mill jar with 20 SS balls (mass 1.4 g). Milling was conducted for 6 h at 600 rpm. Solidified reaction mixture was then broken in small pieces and sonicated in 100 mL DCM until all material was powdered. Resulting mixture was filtered over Celite and washed once with DCM. Filtrate was dried over anhydrous sodium sulfate and the liquid was removed using rotavap to yield **2b** as a white solid (5.059 g, 94.9 %) with a mild yellow tinge and the odour of nitrogen dioxide.

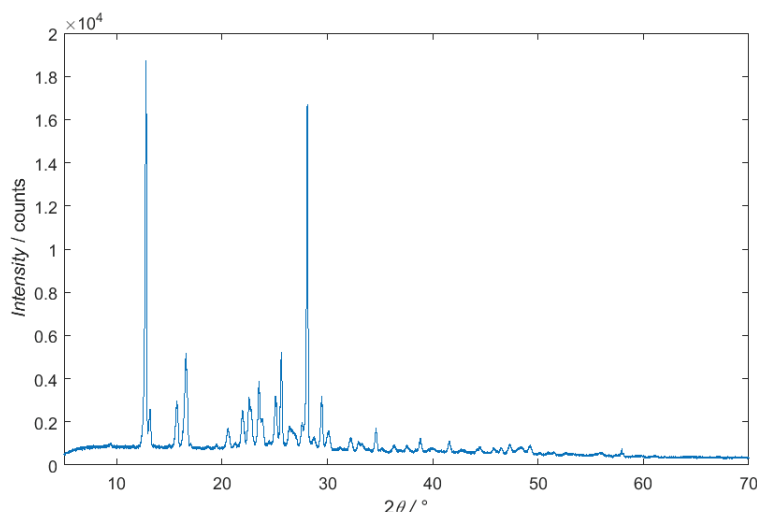
### 3. Thianthrene radical cation preparation



**Scheme S3.** Formation of thianthrene radical cation (**2a**).<sup>3</sup>

#### 3.1. Solution synthesis

**1** (2.36 mmol, 510 mg) and NOBF<sub>4</sub> (2.48 mmol, 290 mg) were weighed in a nitrogen-filled glove box and transferred into a round-bottom glass flask. MeCN (40 mL), dried by molecular sieves and stored under Ar, was added using a syringe. The reaction mixture was then stirred at room temperature. The solution changed immediately from colorless to dark purple. After 1 h of stirring, diethyl ether (120 mL) dried by molecular sieves and kept under Ar was added. The resulting precipitate was filtered under Ar stream and washed with diethyl ether until the filtrate was discolored. The isolated dark purple material was dried in a vacuum oven for 5 h at room temperature. Powder diffraction pattern (**Figure S6**) was obtained from a sample exposed to DCM vapors for several hours, which was measured under a Kapton film.

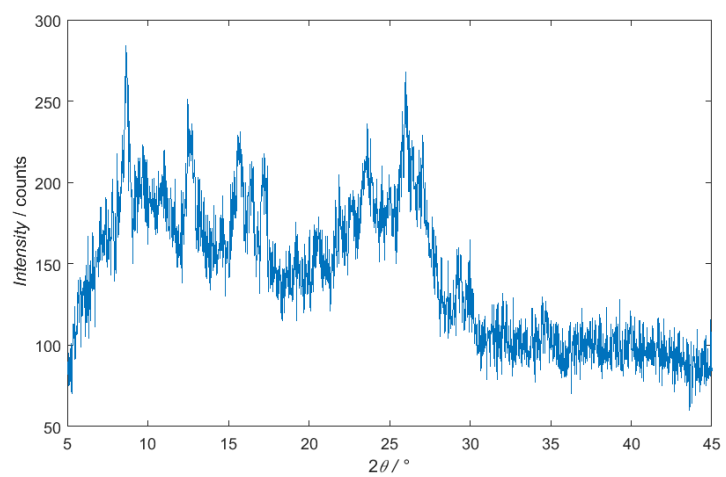


**Figure S6.** Powder diffraction pattern of **2a**.

#### 3.2. Solid-state synthesis attempts

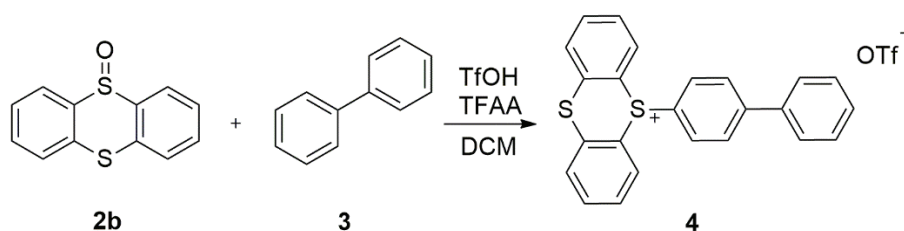
**1** (0.46 mmol, 100 mg) and NOBF<sub>4</sub> (0.46 mmol, 54 mg) were added to a 14 mL PMMA jar with 2 SS balls (mass 1.4 g). Milling was conducted for 60 min at 30 Hz. Deep blue colour appeared immediately, even prior to grinding, but the PXRD pattern showed only loss of crystallinity of the starting materials, no signals related to the expected product (**Figure S7**, compare with **Figure S6**).





**Figure S7.** Predominantly amorphous diffraction pattern of a sample prepared by grinding thianthrene and NOBF<sub>4</sub>.

## 4. Biphenyl thianthrenation

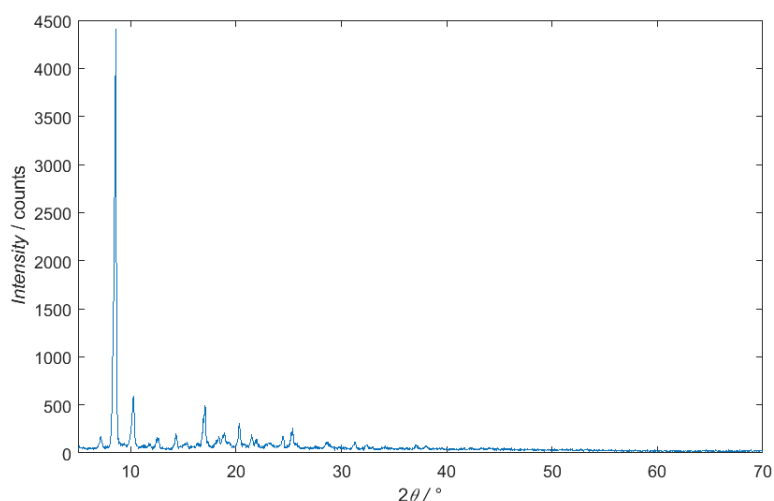


**Scheme S4.** Typical reaction conditions for biphenyl thianthrenation.<sup>4</sup>

### 4.1. Solution synthesis

Biphenyl thianthrenium triflate (**4**) was prepared by following a slightly modified literature procedure.<sup>4</sup> **2b** (6.46 mmol, 1,50 g) and **3** (1 equiv., 0,99 g) were added to a round flask connected to a Schlenk line and equipped with a stirring bar. The flask was evacuated and filled with Ar three times. 26 mL MeCN dried over molecular sieves was added using a syringe. The mixture was then cooled to  $-40\text{ }^{\circ}\text{C}$ . Subsequently, triflic acid (2 equiv., 1,15 mL) and trifluoroacetic anhydride (3 equiv., 2,7 mL) were added to the flask using syringes. The mixture was then stirred for 1 h at  $-40\text{ }^{\circ}\text{C}$ . During that period color changed first to purple, and then to brown. Afterwards, the mixture was warmed to room temperature and stirred for another hour. Then 65 mL saturated sodium bicarbonate solution was poured into the mixture. MeCN was then removed under reduced pressure, and the resulting mixture was diluted with 65 mL water and 130 mL DCM. The mixture was then transferred to a separatory funnel, the organic layer was separated, and the aqueous layer was extracted thrice with 195 mL DCM. Organic layers were joined, dried over sodium sulfate and the solvent was removed under reduced pressure to yield the raw product as a red viscous mass prone to form foam.

The product was purified by dissolving it in 20 mL DCM, cooling the solution to  $-20\text{ }^{\circ}\text{C}$ , and adding 20 mL diethyl ether, also cooled down to  $-20\text{ }^{\circ}\text{C}$ , in 1 mL portions, and with vigorous mixing and scraping the beaker with a spatula. The product was obtained in the form of off-white crystals that were subsequently dried in a vacuum oven at room temperature to remove the remaining diethyl ether. Final yield was 2.78 g, 82 %. <sup>1</sup>H NMR spectrum was assigned according to the lit.: <sup>1</sup>H NMR (**4**) (500 MHz, CD<sub>3</sub>CN, 298 K,  $\delta$ / ppm: 8.41 (d,  $J = 7.9$  Hz, 2H), 7.94 (d,  $J = 7.9$  Hz, 2H), 7.89 (t,  $J = 7.9$  Hz, 2H), 7.83 (t,  $J = 7.6$  Hz, 2H), 7.73–7.66 (m, 2H), 7.59–7.53 (m, 2H), 7.47–7.36 (m, 3H), 7.22–7.16 (m, 2H).<sup>4</sup>



**Figure S8.** Diffraction pattern of **4**, obtained from DCM/diethyl ether.

#### 4.2. Optimization of conditions for solid-state synthesis

Thianthrenation of biphenyl was studied under different experimental conditions and using various materials for activation in a vibratory ball mill. Tables S1 and S2 list the experiments performed in a IST 500 mixer mill, using PMMA milling jars of 14 mL at 30 Hz. The synthesis of thianthrenium salt was carried out at room temperature, and without excluding contact with air. Yields were determined using NMR spectra of raw reaction mixtures for experiments performed in PMMA jars, and using crude isolated products for experiments performed in teflon jars. Isolation was performed similarly to the procedure after the solution synthesis, with the adjusted scale, and removing MeCN omitted, as it was not present in the system. Yields were determined for the raw product.

**Table S1.** Optimization of conditions for mechanochemical thianthrenation of biphenyl: combinations of acids and anhydrides.<sup>a</sup>

Entry	Acid	Anhydride	Notes	Yield (%) <sup>b</sup>
1	TfOH (2 eq.)	TFAA (3 eq.)	Teflon jar	73
2	TfOH (2 eq.)	TFAA (3 eq.)	Teflon jar, 0.215 mmol scale	63
3	TfOH (2 eq.)	TFAA (3 eq.)		66
4	TfOH (3 eq.)	TFAA (2 eq.)		24
5	TfOH (1 eq.)	TFAA (1 eq.)		34
6	TfOH (0.2 eq.)	TFAA (1 eq.)		43
7	-	TFAA (2 eq.)		14
8	-	TFAA (1.2 eq.)		7.6
9	H <sub>2</sub> SO <sub>4</sub> (1 eq.)	Ac <sub>2</sub> O (3 eq.)	Teflon jar	5.2

<sup>a</sup>Reaction setup: mixer mill, 30 Hz, 14mL PMMA jar, two ZrO<sub>2</sub> milling balls (1.6 g), 120 min, air, r.t, **2b** (0.43 mmol), **3** (1 equiv.). <sup>b</sup>NMR yield determined using an internal standard.

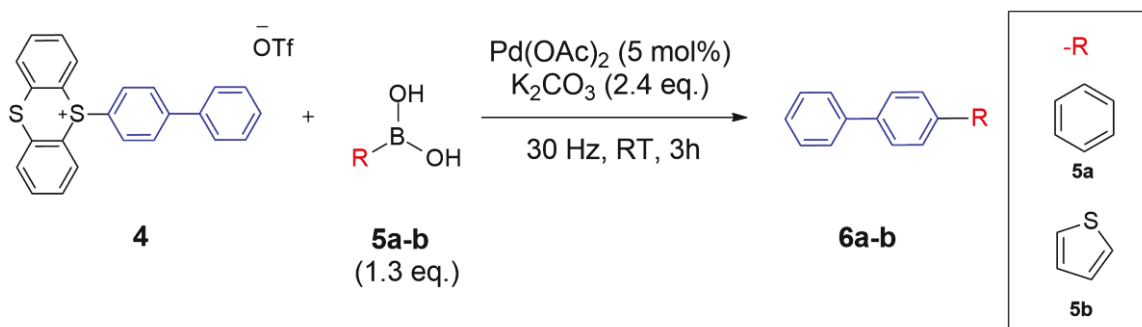
**Table S2.** Optimization of conditions for mechanochemical thianthrenation of biphenyl: combinations of acids and anhydrides with solid additives.<sup>a</sup>

Entry	Acid	Anhydride	Additive	Notes	Yield (%) <sup>b</sup>
1	TfOH (2 eq.)	TFAA (3 eq.)	NaOTf (500 mg)	Teflon jar	86
2	TfOH (1 eq.)	TFAA (2 eq.)	NaOTf (500 mg)	Teflon jar	32
3	TfOH (0.5 eq.)	TFAA (1.1 eq.)	NaOTf (500 mg)	Teflon jar	4.7
4	TfOH (2 eq.)	TFAA (3 eq.)	Na <sub>2</sub> SO <sub>4</sub> (300 mg)		49
5	TfOH (2 eq.)	TFAA (3 eq.)	NaBF <sub>4</sub> (300 mg)		47
6	TfOH (0.2 eq.)	TFAA (1.1 eq.)	NaBF <sub>4</sub> (300 mg)	0.215 mmol scale	6.9
7	TfOH (2 eq.)	TFAA (3 eq.)	SiO <sub>2</sub> (200 mg)	0.215 mmol scale	16
8	TfOH (1 eq.)	TFAA (1 eq.)	SiO <sub>2</sub> (200 mg)	0.215 mmol scale	2.4
9	TfOH (1 eq.)	TFAA (1 eq.)	Al <sub>2</sub> O <sub>3</sub> (200 mg)	0.215 mmol scale	Traces
10	TfOH (1 eq.)	TFAA (1 eq.)	NaCl (100 mg)	0.215 mmol scale	ND
11	TfOH (1 eq.)	TFAA (1 eq.)	TiO <sub>2</sub> (100 mg)	0.215 mmol scale	3.1
12	H <sub>2</sub> SO <sub>4</sub> (1 eq.)	Ac <sub>2</sub> O (3 eq.)	NaOTf (500 mg)	Teflon jar	21
13	H <sub>2</sub> SO <sub>4</sub> (1 eq.)	-	NaBF <sub>4</sub> (300 mg)		Traces
14	H <sub>2</sub> SO <sub>4</sub> (1 eq.)	-	SiO <sub>2</sub> (100 mg)	0.215 mmol scale	ND
15	H <sub>2</sub> SO <sub>4</sub> (1 eq.)	-	Na <sub>2</sub> SO <sub>4</sub> (100 mg)		ND

<sup>a</sup>Reaction setup: mixer mill, 30 Hz, 14mL PMMA jar, two ZrO<sub>2</sub> milling balls (1.6 g), 120 min, air, r.t, **2b** (0.43 mmol), **3** (1 equiv.). <sup>b</sup>NMR yield determined using an internal standard.

## 5. Functionalization of thianthrenated biphenyl salt in the solid state

### 5.1. Suzuki-Miyaura-type functionalization



**Scheme S5.** Formation of a new C-C bond from **4** and boronic acid substrates **5a-b** in a ball mill.

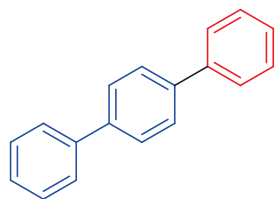
#### Procedure:

**4** (0.1 mmol, 51.86 mg), **5a-b** (1.3 equiv.), base (2.4 equiv.) and Pd catalyst (5 mol%) were added together into a 7 mL PMMA jar equipped with one  $\text{ZrO}_2$  ball (1.6 g). Milling frequency was 30 Hz, and duration of milling was 3 h. After the milling crude reaction mixtures were processed by dissolving in dichloromethane, filtrating over Celite, and removing the solvent under reduced pressure. TMB was used as an internal standard to determine yields.

**Table S3.** Optimization of reaction conditions for mechanochemical Suzuki-Miyaura reaction.<sup>a</sup>

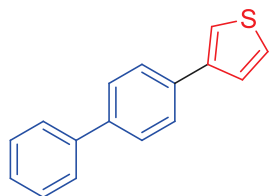
Entry	R-B(OH) <sub>2</sub>	Catalyst	Base	Notes	Yield (%) <sup>b</sup>
1	5a	$\text{Pd}(\text{PPh}_3)_4$	$\text{K}_2\text{CO}_3$		90
2	5a	$\text{Pd}(\text{Cl})_2$	$\text{K}_2\text{CO}_3$		74
3	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$		72
4	5a	-	$\text{K}_2\text{CO}_3$		ND
5	5b	$\text{Pd}(\text{Cl})_2$	$\text{K}_2\text{CO}_3$		28
6	5b	$\text{Pd}(\text{PPh}_3)_4$	$\text{K}_2\text{CO}_3$		63
7	5b	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$		54
8	5a	$\text{Pd}(\text{OAc})_2$	$\text{KHCO}_3$		30
9	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_3\text{PO}_4 \times \text{H}_2\text{O}$		14
10	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	2.0 equiv. base	62
11	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	4.0 equiv. base	84
12	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	6.0 equiv. base	50
13	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	<i>i</i> -PrOH, 10 $\mu\text{L}$	44
14	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	NaCl, 100 mg	39
15	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	1.0 equiv PhB(OH) <sub>2</sub>	73
16	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	1.1 equiv PhB(OH) <sub>2</sub>	57
17	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	1 % catalyst, 16 h reaction, 0.5 mmol scale	18
18 <sup>c</sup>	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	One pot synthesis – 1 <sup>o</sup>	Traces
19 <sup>d</sup>	5a	$\text{Pd}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	One pot synthesis – 2 <sup>o</sup>	53

<sup>a</sup>Reaction setup: mixer mill, 30 Hz, 7mL PMMA jar, one  $\text{ZrO}_2$  milling ball (1.6 g), 3 h, air, r.t., **4** (0.1 mmol), **5a-b** (1.3 equiv.), Pd catalyst (5 mol%), base (2.4 equiv.). mol% is calculated with the respect to **4**. <sup>b</sup>NMR yield determined using internal standard. <sup>c</sup>One-step one-pot reaction: 14 mL teflon jar, two  $\text{ZrO}_2$  milling balls (1.6 g). 1st step: 3 h, air, r.t., **2** (0.43 mmol), biphenyl (1 equiv.), TFAA (3 equiv.), **5a** (1.3 equiv.),  $\text{K}_2\text{CO}_3$  (6.4 equiv.), and  $\text{Pd}(\text{OAc})_2$  (5 mol%). <sup>d</sup>Two step one-pot reaction: 14 mL teflon jar, two  $\text{ZrO}_2$  milling balls (1.6 g). 1<sup>st</sup> step: 3 h, air, r.t., milling of **2b** (0.43 mmol), **3** (1 equiv.), TfOH (2 equiv.), and TFAA (3 equiv.), 2<sup>nd</sup> step: in the same jar, milling for 3 h after addition of **5a** (1.3 equiv.),  $\text{K}_2\text{CO}_3$  (6.4 equiv.), and  $\text{Pd}(\text{OAc})_2$  (5 mol%).



**p-terphenyl, 6a**

$^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ / ppm = 7.36 (t,  $J$  = 7.4 Hz, 2H), 7.46 (m, 4H), 7.65 (d,  $J$  = 7.2 Hz, 4H), 7.68 (s, 4H).<sup>5</sup>



**3-([1,1'-biphenyl]-4-yl)thiophene, 6b**

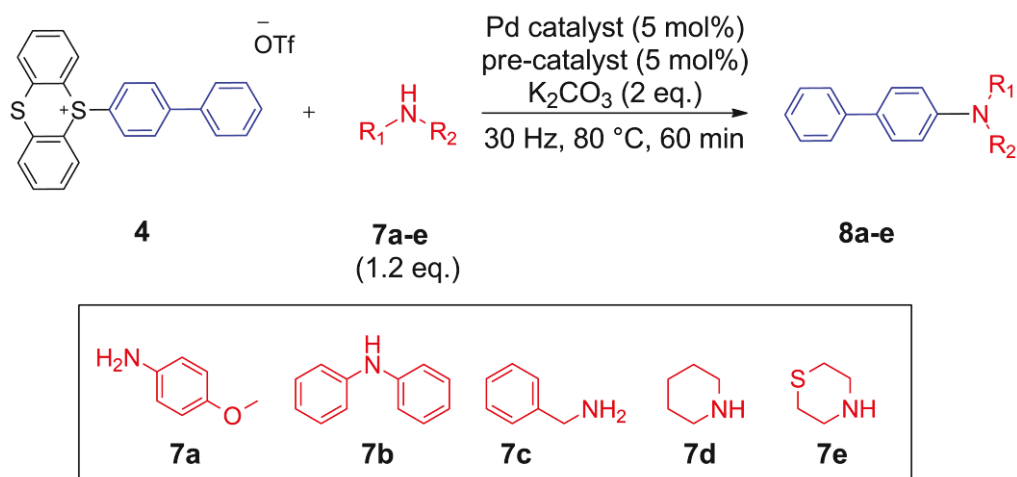
$^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ / ppm = 7.71-7.61 (m, 6H), 7.51-7.40 (m, 5H), 7.38-7.33 (m, 1H).<sup>6</sup>

Kinetics was monitored by *ex situ*  $^1\text{H}$  NMR spectroscopy for the standard reaction setup (**Table S3, entry 3**). Small samples were taken from the reaction mixture after 1, 2, and 3 h, and processed as described above. Reaction was continued immediately after collecting 1 h and 2 h samples, and stopped after 3 h.

**Table S4.** Time dependence of yield of Suzuki-Miyaura reaction for product **6a**.

$t$ / h	Yield (%)
1	51
2	74
3	79

## 5.2. Buchwald-Hartwig-type functionalization



**Scheme S6.** Formation of a new C-N bond using **4** and amines **7a-e** in a ball mill.

## Procedure:

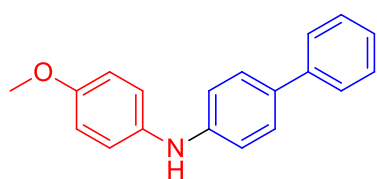
**4** (0.193 mmol, 100 mg), amines **7a-e** (1.2 equiv.), base (2 equiv.), co-catalyst tBuXPhosPdG3 (5 mol %), and catalyst Pd(OAc)<sub>2</sub> (5 mol %), were added into a 14 mL SS jar along with two SS milling balls (1.4 g). The milling frequency was 30 Hz and the duration of milling was 60 min. Increased temperatures (40 °C, 80 °C, 100 °C) were achieved using a heat gun. Room temperature reactions were performed in PMMA jars.

For all synthetic procedures, crude reaction mixtures were processed by dissolving in dichloromethane, filtering over Celite, and removing the solvent under reduced pressure. TMB was used as an internal standard.

**Table S5.** Buchwald-Hartwig reaction in a ball mill. Attempts to optimize reaction conditions.<sup>a</sup>

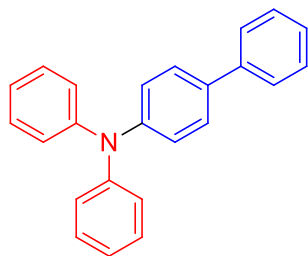
Entry	Aniline	Notes	Yield (%) <sup>b</sup>
1	<b>8a</b>	40 °C	59
2	<b>8a</b>	0.1 mmol scale, RT, PMMA jar (7 mL)	16
3	<b>8a</b>	tBuOK	73
4	<b>8a</b>	0.1 mmol scale, tBuOK, PMMA jar (7 mL)	9.7
5	<b>8a</b>	0.1 mmol scale, tBuXPhosPdG3 not added, PMMA jar (7 mL), RT	ND
6	<b>8a</b>	0.1 mmol scale, tBuXPhosPdG3 and base not added, PMMA jar (7 mL), RT	ND
7	<b>8a</b>	0.1 mmol scale, Pd(OAc) <sub>2</sub> not added, PMMA jar (7 mL), RT	23
8	<b>8a</b>	0.1 mmol scale, Pd(OAc) <sub>2</sub> not added, tBuOK, PMMA jar (7 mL), RT	24
9	<b>8a</b>	0.1 mmol scale, no Pd cat., BaTiO <sub>3</sub> (3.7 eq), PMMA jar (7 mL), RT	ND
10	<b>8a</b>	0.1 mmol scale, no Pd cat., BaTiO <sub>3</sub> (3.7 eq), MeCN (5 μL), PMMA jar (7 mL), RT	ND
11	<b>8a</b>	0.5 mmol scale, 1 mol% Pd catalysts	37
12	<b>8e</b>	0.1 mmol scale, PMMA jar (7 mL), RT	3.4
13	<b>8d</b>	0.1 mmol scale, PMMA jar (7 mL), RT	2.3
14	<b>8d</b>	100 °C	5.6

<sup>a</sup>Reaction conditions (unless noted otherwise): mixer mill, 30 Hz, 7mL SS jar, two SS milling balls (1.4 g), 60 min, air, 80 °C, **4** (0.1 mmol), **7a-e** (1.2 equiv.), Pd catalyst (5 mol%), base (2 equiv.). <sup>b</sup>NMR yield determined using an internal standard.



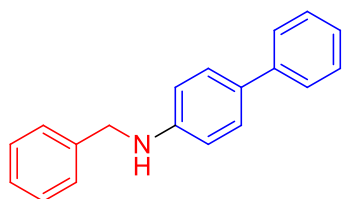
**N-(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine, **8a****

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ/ppm = 7.87 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.92 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H).<sup>7</sup>



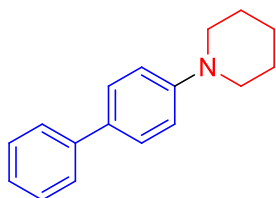
**4-(*N,N*-diphenyl)aminobiphenyl, 8b**

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.03 (t,  $J$  = 7.5 Hz, 2H), 7.14 (d,  $J$  = 8.7 Hz, 6H), 7.27 (t,  $J$  = 7.4 Hz, 4H), 7.30 (t,  $J$  = 7.5 Hz, 1H), 7.42 (t,  $J$  = 8.1 Hz, 2H), 7.48 (d,  $J$  = 8.8 Hz, 2H), 7.57 (d,  $J$  = 7.1 Hz, 2H).<sup>8</sup>



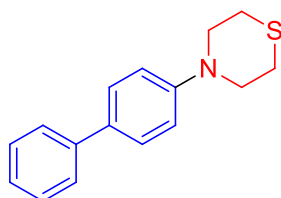
**4-(*N*-benzyl)aminobiphenyl, 8c**

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.64 (dd,  $J$  = 11.7 Hz,  $J$  = 4.6 Hz, 4H), 7.51-7.47 (m, 4H), 7.40 (t,  $J$  = 7.4 Hz, 1H), 7.24 (dd,  $J$  = 8.2 Hz, 7.5 Hz, 2H), 6.78 (t,  $J$  = 7.3 Hz, 1H), 6.73-6.70 (m, 2H), 4.42 (s, 2H), 4.13 (s, 1H).<sup>9</sup>



**1-(4-phenyl)phenylpiperidine, 8d**

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.51-7.42 (m, 4H), 7.36-7.30 (m, 2H), 7.23-7.18 (m, 1H), 7.03-6.98 (m, 2H), 3.16 (t,  $J$  = 5.0 Hz, 4H), 1.69-1.54 (m, 6H).<sup>10</sup>



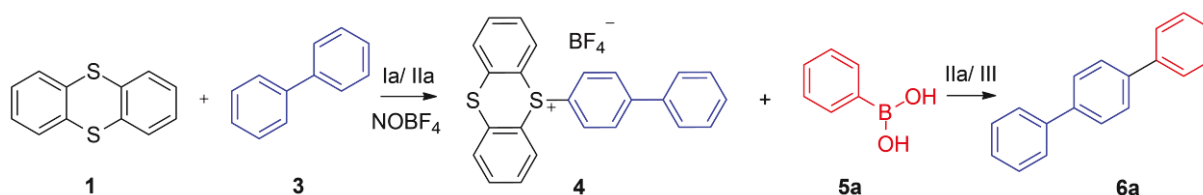
***N*-(4-phenyl)phenylthiomorpholine, 8e**

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.54 (d,  $J$  = 7.3 Hz, 2H), 7.50 (d,  $J$  = 8.7 Hz, 2H), 7.41-7.37 (m, 2H), 7.27 (t,  $J$  = 7.3 Hz, 1H), 6.93 (d,  $J$  = 8.6 Hz, 2H), 3.57 (t,  $J$  = 4.8 Hz, 4H), 2.73 (t,  $J$  = 4.8 Hz, 4H).<sup>11</sup>



## 6. One pot-reactions

### 6.1. Thianthrenation *via* nitrosonium tetrafluoroborate



**Scheme S9.** Synthesis attempt of **6a** from thianthrene and  $\text{NOBF}_4$ .

#### Procedure:

**Step Ib. 1** (0.43 mmol),  $\text{NOBF}_4$  (2.2 equiv.) and **3** (1 equiv.) were added into a teflon jar (14.0 mL internal volume) along with two  $\text{ZrO}_2$  milling balls (1.6 g). The mixture was milled at 30 Hz for 3 h.

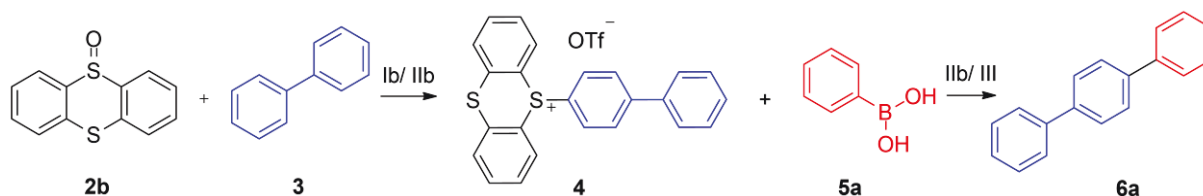
**Step IIb.** After taking crude samples for NMR analysis and breaking the mixture that was glued to the milling balls, **5a** (1.3 equiv.),  $\text{Pd}(\text{OAc})_2$  (5 %), and  $\text{K}_2\text{CO}_3$  (2.4 equiv.) were added to the mixture, which was then milled for another 3 h. The final mixture was processed by dissolving in dichloromethane, filtering over Celite and removing the solvent under reduced pressure. TMB was used as an internal standard. The product was not detected.

In the second experiment TfOH (0.5 equiv.) was added to the mixture, and the amount of the base was increased accordingly.

**Table S8.** Experimental conditions for one-pot synthesis of **5a**.

Entry	TfOH (equiv.)	Note	Yield (%)
1 (Ib.)	-	Material stuck on the milling ball, forming a blue "snow ball"	ND
2 (Ib.)	0.5	Dark blue "snow ball" with a white envelope	ND
3 (IIb.)	-	-	ND
4 (IIb.)	-	$\text{K}_2\text{CO}_3$ (2.65 equiv)	ND

### 6.2. One-pot Suzuki-type reactions starting from thianthrene-S-oxide



**Scheme S10.** Formation **6a** in two steps from **2b** without isolating the thianthrenium salt **4**.

## Procedures:

**One-step one-pot reaction:** **2b** (0.43 mmol), **3** (1 equiv.), TFAA (3 equiv.), **5a** (1.3 equiv.), K<sub>2</sub>CO<sub>3</sub> (6.4 equiv.), and Pd(OAc)<sub>2</sub> (5 mol%) were added into a 14 mL teflon jar equipped with two ZrO<sub>2</sub> milling balls (1.6 g). The mixture was milled for 3 h at 30 Hz, without excluding contact with air, and then processed by dissolving in dichloromethane, filtering over Celite and removing the solvent under reduced pressure. TMB was used as an internal standard. The product was detected only in traces (**Table S3**, entry 22).

**Two-step one-pot reaction:** **2b** (0.43 mmol), **3** (1 equiv.), TfOH (2 equiv.), and TFAA (3 equiv.) were added into a 14 mL teflon jar equipped with two ZrO<sub>2</sub> milling balls (1.6 g). The mixture was milled for 3 h at 30 Hz, without excluding contact with air. After that period **5a** (1.3 equiv.), K<sub>2</sub>CO<sub>3</sub> (6.4 equiv.), and Pd(OAc)<sub>2</sub> (5 mol%) were introduced to the reaction mixture, and milling was continued for another 3h. The reaction mixture was processed by dissolving in dichloromethane, filtering over Celite and removing the solvent under reduced pressure. TMB was used as an internal standard. <sup>1</sup>H NMR yield (*p*-terphenyl) = 53%.

## 7. NMR spectra

### 7.1. Thianthrene-S-oxide preparation

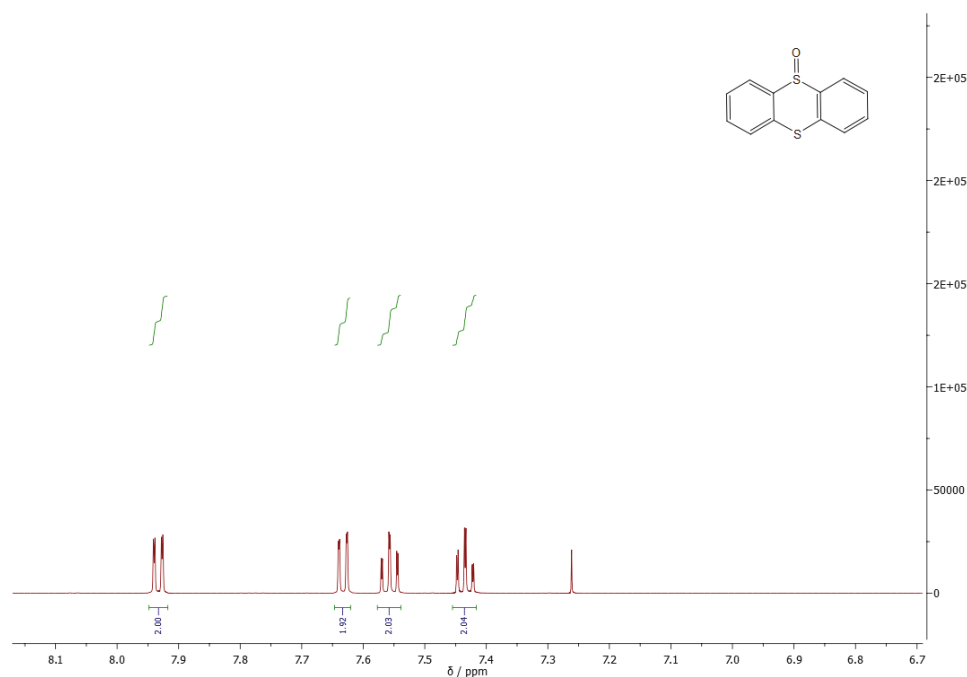


Figure S9. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of thianthrene-S-oxide (**2b**).

### 7.2. Thianthrenium salt preparation

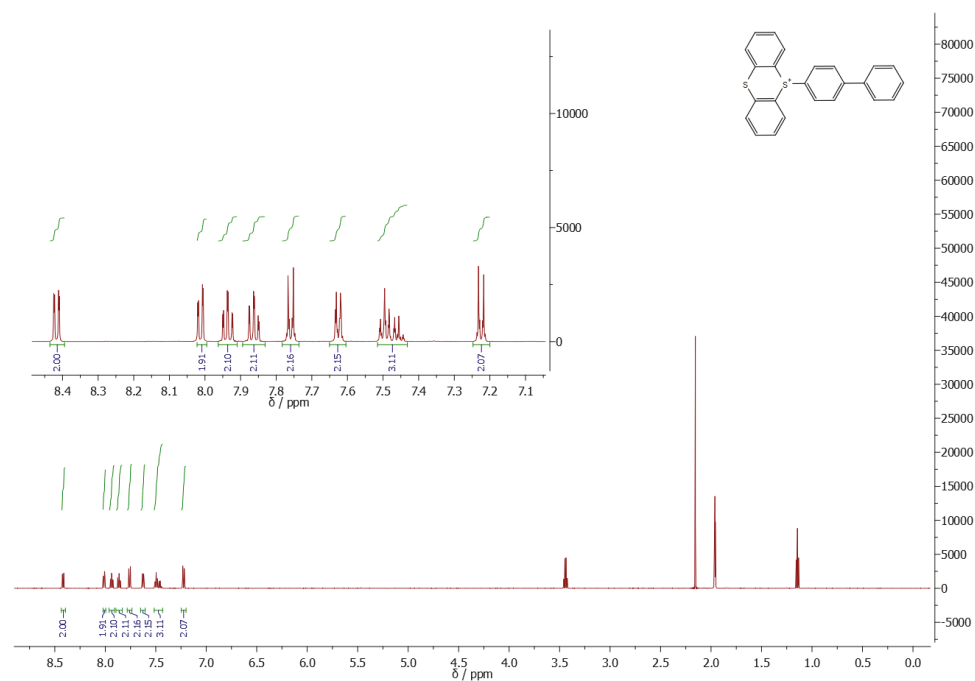
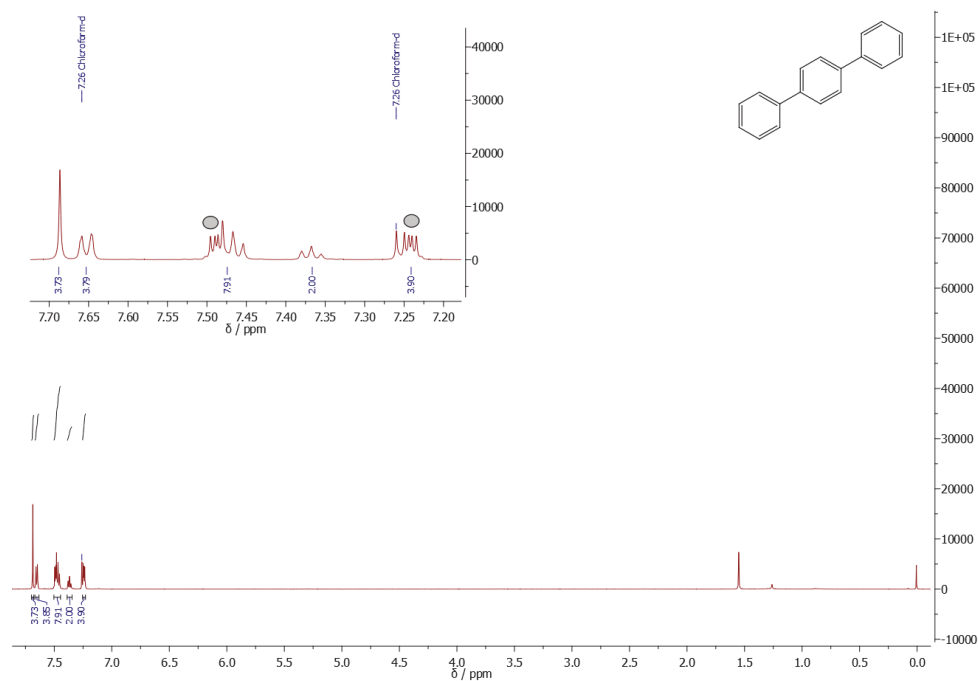
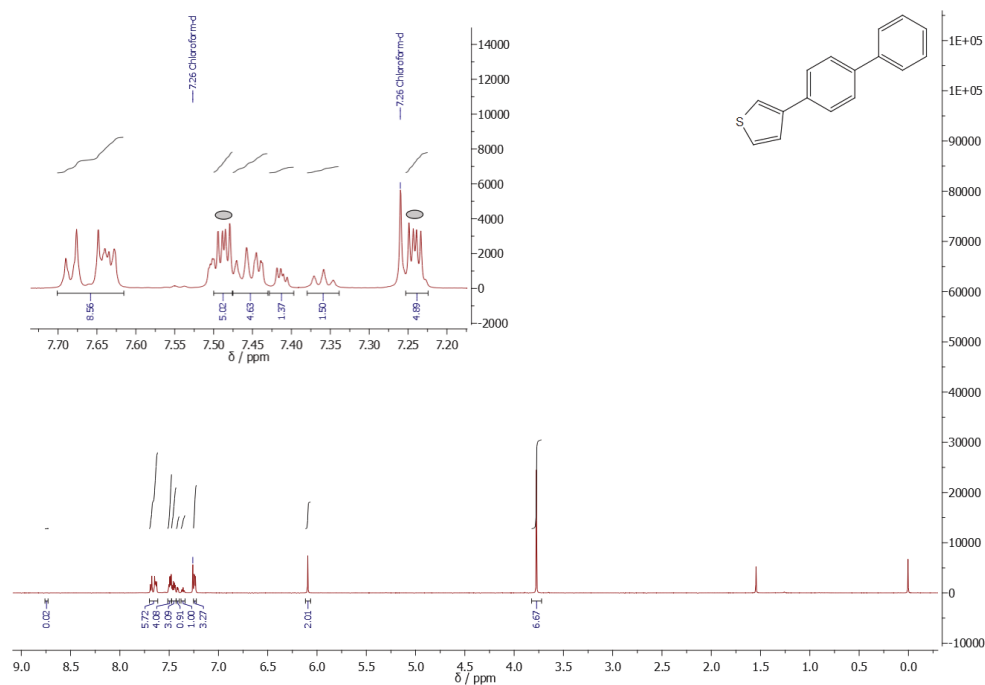


Figure S10. <sup>1</sup>H NMR spectrum (600 MHz, CD<sub>3</sub>CN) of S-biphenylthianthrenium triflate (**4**).

### 7.3. Suzuki-type functionalization

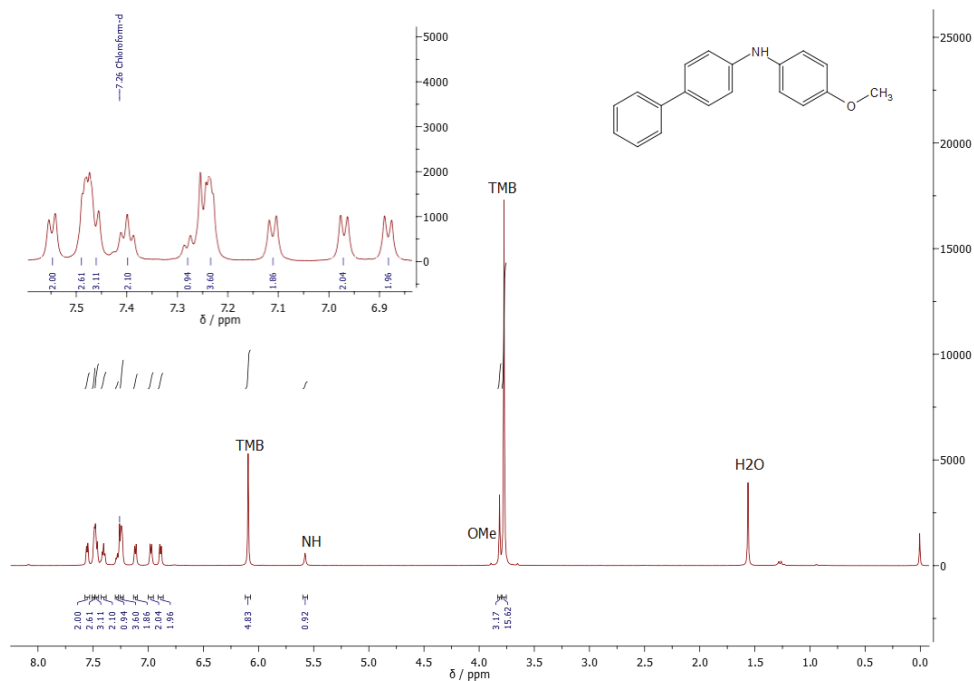


**Figure S11.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of **6a** after purification. Grey circles indicate the presence of thianthrene.

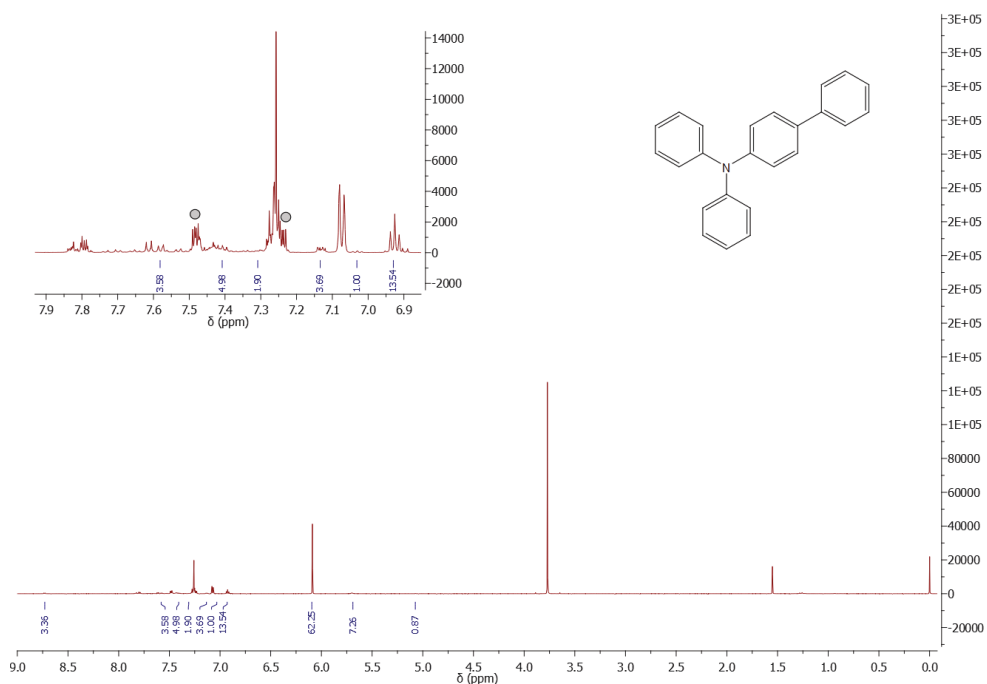


**Figure S12.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of **6b**. Grey circles indicate the presence of thianthrene. Internal standard (TMB) is also visible in the spectra.

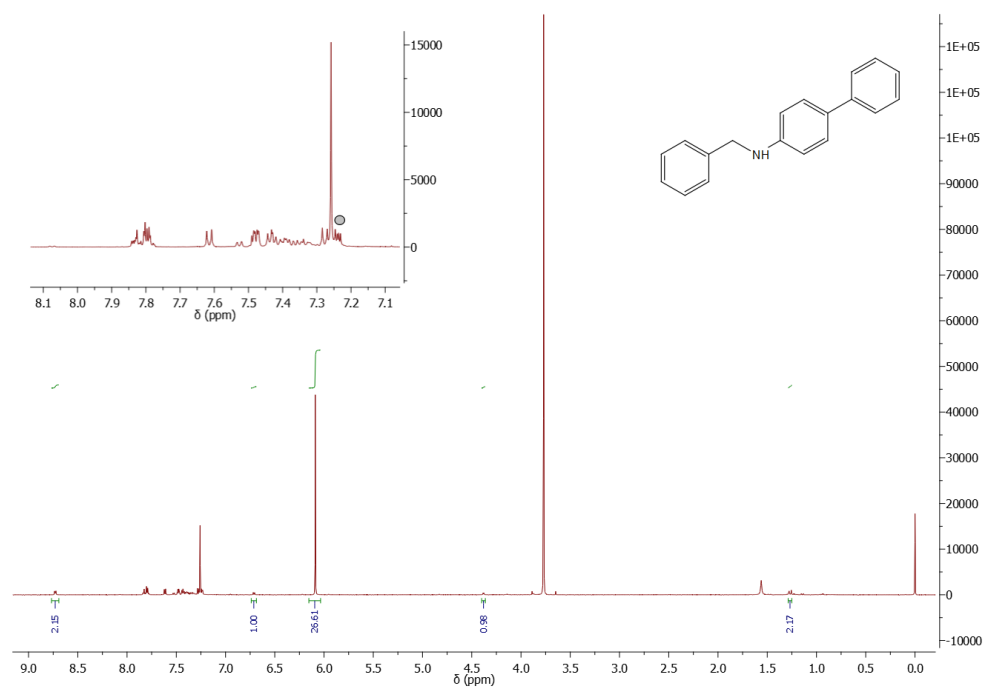
## 7.4. Buchwald-Hartwig-type functionalization



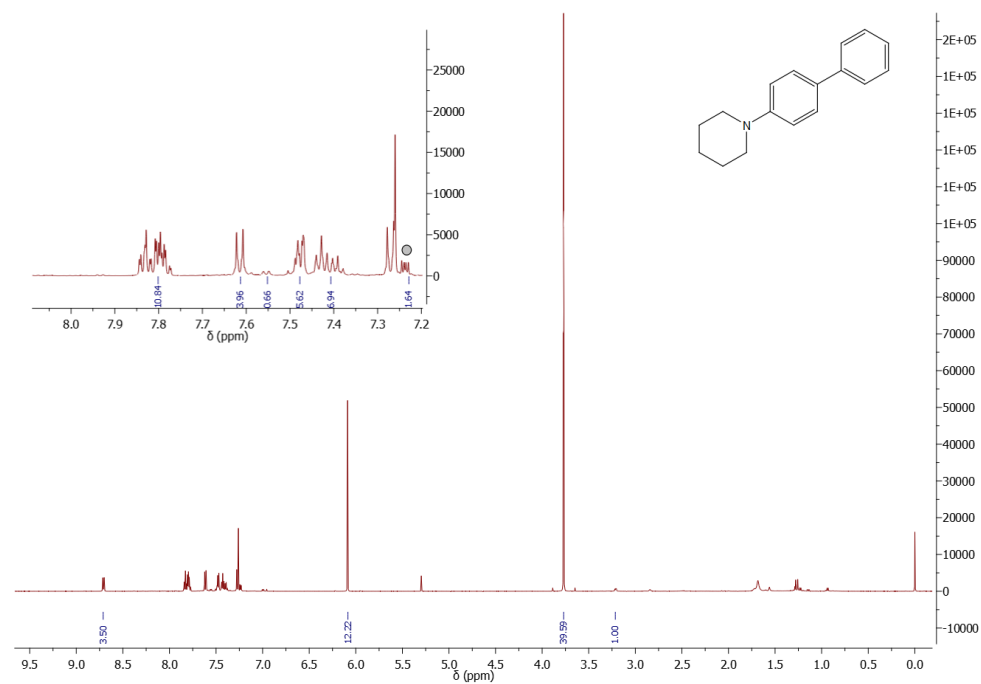
**Figure S13.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of a reaction mixture containing **8a**. Internal standard (TMB) is also visible in the spectra.



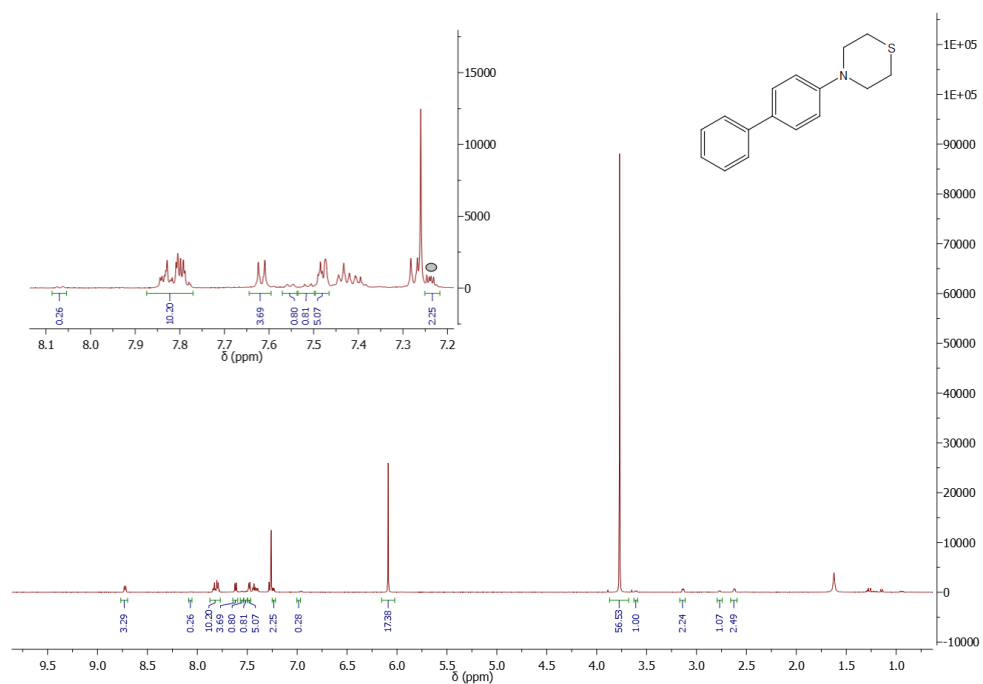
**Figure S14.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of a reaction mixture **8b**. Grey circles indicate the presence of thianthrene. Internal standard (TMB) is also visible in the spectra.



**Figure S15.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of a reaction mixture containing **8c**. Gray circle indicates the presence of thianthrene. Internal standard (TMB) is also visible in the spectra.



**Figure S16.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of a reaction mixture containing **8d**. Gray circle indicates the presence of thianthrene. Internal standard (TMB) is also visible in the spectra.



**Figure S17.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of a reaction mixture containing **8e**. Gray circle indicates the presence of thianthrene. Internal standard (TMB) is also visible in the spectra.

## 8. References

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