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Dedicated to Professor Luminița Silaghi-Dumitrescu on the occasion of her 65th anniversary

SYNTHESIS AND ELECTRONIC PROPERTIES OF 3-ARYL 10*H*-PHENOTHIAZINES

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ABSTRACT. 3-Bromo 10*H*-phenothiazines, even the 10*H*-unsubstituted derivative, can be efficiently coupled with several boronic acids to give 3-aryl 10*H*-phenothiazines with good to excellent yields. Selected electronic properties (UV/Vis spectroscopy, cyclic voltammetry, DFT calculations) are discussed and correlations of the Hammett-Taft substituent parameters are established for rationalizing the transmission of the remote electronic substituent effects.

Keywords: *Cross-coupling – DFT calculations – Heterocycles – Substituent Effects – UV/Vis Spectroscopy*

INTRODUCTION

The Suzuki cross-coupling [1] is the most practical and most versatile catalytic arylation methodology and has found widespread application in biaryl formation ranging from natural product synthesis over medicinal chemistry to electronic materials. A major advantage over other Pd-catalyzed cross-coupling reactions is definitely the uneventful handling of boronic acids and boronates as robust organometallics that even do not require anhydrous reaction conditions. As a consequence, Suzuki arylations have efficiently been used for the synthesis of electroactive materials.

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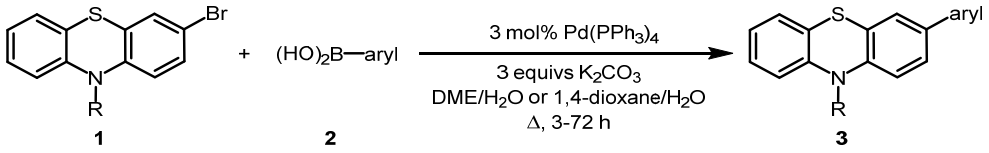
Phenothiazine, a heteroaromatic S,N-tricycle, and its derivatives have been intensively studied at the Faculty of Chemistry and Chemical Engineering at Babeş-Bolyai University in Cluj-Napoca, as witnessed by numerous publications [2]. Most interestingly, phenothiazines display low oxidation potentials, forming stable deeply colored radical cations with perfect Nernstian reversibility [3-6]. Since 2000 we have been systematically exploring the synthetic and physical organic chemistry of oligophenothiazines in linear [7] and cyclic [8] topologies. Besides the inherent electro- and photochromicity of phenothiazine conjugates [9], we became particularly interested in luminescence characteristics of π-conjugated expanded derivatives [10,11] and the peculiar behavior of (oligo)phenothiazines as potent donors in donor-acceptor conjugates, even enabling photo-induced electron transfer [12-16]. As a consequence hole transport in OLED [17], mesoporous organo silica hybrid materials [18], and chromophores in dye-sensitized solar cells can also be devised on the basis of oligophenothiazines [19-21]. Particularly interesting for nanotechnology are native (oligo)phenothiazines displaying a pronounced ability to form self-assembled monolayers on gold surfaces [22-24] as well as on zinc and iron oxide surfaces [25].

Employing Suzuki coupling as a key reaction to establish oligophenothiazines and derivatives by biaryl formation we devised borylated phenothiazines as versatile building blocks [26] that were successfully transformed in various functional 3-(hetero)arylated and 3,7-di(hetero) arylated phenothiazines [27]. Amazingly, while Suzuki coupling with N-substituted derivatives is wide spread and established the use of 3-bromo 10*H*-phenothiazine without *N*-substituent has remained unexplored. Here, we report a series of Suzuki coupling of 3-bromo 10*H*-phenothiazines with several boronic acids and selected electronic properties are discussed on the basis of UV/Vis spectroscopy, cyclic voltammetry, and DFT calculations.

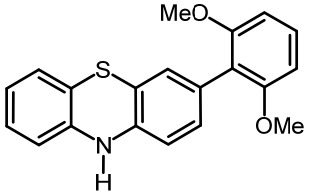
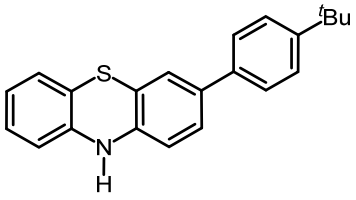
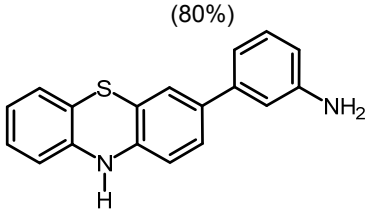
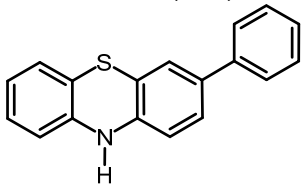
RESULTS AND DISCUSSION

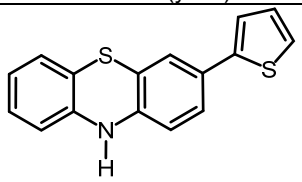
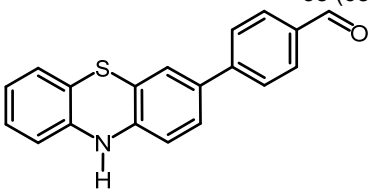
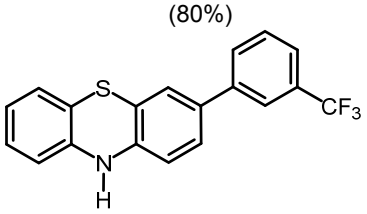
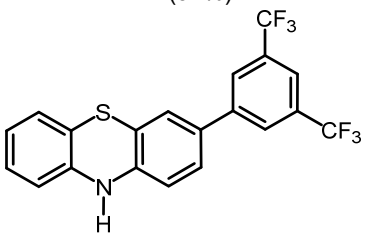
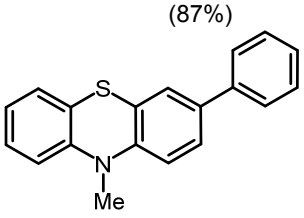
Most conveniently, we could employ standard Suzuki conditions, developed and applied in several studies [7,26], for reacting three different 3-bromo 10*H*-phenothiazines **1**, i. e. the unsubstituted derivative **1a**, the methyl (**1b**), and the *n*-hexyl derivative **1c**, with equimolar amounts of various aryl boronic acids **2** in the presence of $Pd(PPh_3)_4$ as a catalyst and potassium carbonate as a base in boiling aqueous DME or 1,4-dioxane. The resulting 3-aryl 10*H*-phenothiazines **3** were obtained as slightly colored microcrystalline solids (**3a-i**) or as a pale yellow oil (**3j**) in 56-97% yield (Scheme 1, Table1).

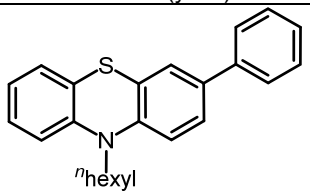


Scheme 1

Table 1. Experimental details of the synthesis of 3-aryl 10*H*-phenothiazines **3**.

Entry	3-bromo-10*H*-phenothiazine **1**	aryl boronic acid **2**	Time *t*	3-aryl 10*H*-phenothiazines **3** (yield)[a]
1	R = H (**1a**) [28]	aryl = 2,6(MeO)$_2$C$_6$H$_3$ (**2d**)	12 h	 **61d** **3a** (78%)
2	**1a**	aryl = *p*-^{t}BuC$_6$H$_4$ (**2b**)	48 h	 **61b** **3b** (80%)
3	**1a**	aryl = *m*-H$_2$NC$_6$H$_4$ (**2e**)	45 h	 **61e** **3c** (78%)
4	**1a**	aryl = Ph (**2a**)	16 h	 **61a** **3d** (67%)

Entry	3-bromo-10*H*-phenothiazine **1**	aryl boronic acid **2**	Time *t*	3-aryl 10*H*-phenothiazines **3** (yield)[a]
5	**1a**	aryl = 2-thienyl (**2h**)	22 h	 **61h** **3e** (68%)
6	**1a**	aryl = $OHCC_6H_4$ (**2c**)	72 h	 **61c** **3f** (80%)
7	**1a**	aryl = *m*-$F_3CC_6H_4$ (**2f**)	25 h	 **61f** **3g** (97%)
8	**1a**	aryl = 3,5-$(F_3C)_2C_6H_3$ (**2g**)	12 h	 **61g** **3h** (87%)
9	R = Me (**1b**) [29]	**2a**	3 h	 **61i** **3i** (83%)

Entry	3-bromo-10*H*-phenothiazine **1**	aryl boronic acid **2**	Time *t*	3-aryl 10*H*-phenothiazines **3** (yield)[a]
10[b]	R = *n*hexyl (**1c**) [30]	**2a**	25 h	 **61j** **3j** (56%)

[a]Isolated yield after chromatography on silica gel. [b]The reaction was conducted in a degassed mixture of 1,4-dioxane (8 mL) and water (4 mL).

The structural assignments are in excellent agreement with the ^{1}H and ^{13}C NMR resonances for phenothiazine typical NMR spectra [31]. Although the slightly colored appearance of the solids indicated a propensity to facile air oxidation, no special precautions had to be taken for preparing the NMR spectra samples. Most characteristically, the proton resonances of the NH-signals of the compounds **3a-h**, recorded in d^6-DMSO, appear as distinct singlets between δ 8.6-8.8. The resonances of the methyl (**3i**) and methylene protons (**3j**) that are directly adjacent to the electronegative 10-nitrogen core appear in the spectra recorded in $CDCl_3$ as a singlet at δ 3.38 or as a triplet at δ 3.95, respectively. Likewise in the IR spectra of compounds **3a-h** the bands between 3300 and 3400 cm^{-1} can be unambiguously assigned to the distinct NH stretch vibrations [32], which are absent in the spectra of compounds **3i** and **3j**. For the latter CH stretch vibrations are clearly observed between 2900 and 3000 cm^{-1}. For all derivatives **3** the base peak in the mass spectra is the molecule peak, indicating the peculiar stability of phenothiazinyl radical cations. The most characteristic fragmentation pattern is the α-cleavage of the methyl or hexyl substituent adjacent to the nitrogen atom in the spectra of phenothiazines **3i** and **3j**.

Selected electronic properties of the 3-aryl 10*H*-phenothiazines **3** were determined by recording UV/Vis spectra and cyclic voltammograms (Table 2). For comparison the same data were measured for phenothiazine (**4**), 10-methyl 10*H*-phenothiazine (**5**), and 10-*n*-hexyl 10*H*-phenothiazine (**6**).

In the UV/Vis spectra all phenothiazines **3** display two distinct absorption bands, an intense band between 254 and 287 nm and a variable weaker longer wavelength absorption that varies with the aryl substitution pattern between 318 and 402 nm. As a consequence of the electron withdrawing substituent effect at the remote *p*-position on the 3-aryl moiety this latter absorption band obviously arises from pronounced charge transfer characteristics. This finding and interpretation is in good agreement with the electronic properties

of a series of 3-(hetero)aryl substituted 10-*n*-hexyl 10*H*-phenothiazines [27c]. Comparison of two consanguineous series reveals the electronic effect of *N*-substitution. The longest wavelength absorption in the UV/Vis spectra of phenothiazine (**4**), 10-methyl 10*H*-phenothiazine (**5**), and 10-*n*-hexyl 10*H*-phenothiazine (**6**) appears at 320, 310, and 311 nm, respectively. The same trend is found for 3-phenyl derivatives where the NH derivative **3d** displays the most redshifted maximum at 335 nm, for the hexyl derivative **3j** this band is found at 322 nm and for the methyl derivative **3i** the maximum appears at 318 nm. Assuming a charge transfer character of this band with phenyl being a weak acceptor moiety, the NH derivative **3d** with represents the most pronounced donor character followed by the hexyl derivative **3j** and the methylated compound **3i**. While the correlation between methyl and hexyl substitution is logical, the NH effect is counterintuitive at first sight. However, considering the pseudoequatorial orientation of the small H atom in the butterfly conformation of phenothiazine an efficient overlap of the nitrogen lone pair with the annelated benzo cores can be assumed [33]. Alkyl substituents must adopt pseudoaxial orientations due to steric interactions. Hence, the overlap of the nitrogen lone pair with the π-systems is considerably diminished.

Table 2. Selected UV/Vis spectroscopic and electrochemical data of 3-aryl 10*H*-phenothiazines **3** and reference phenothiazines **4**-**6** and selected Hammett-Taft substituent parameters $\sigma_{p/m}$, σ_R, and σ_R^+ (UV/Vis spectra recorded in DMSO; cyclic voltammetry recorded in 0.1 M dichloromethane solution of NBu_4PF_6 as an electrolyte, Pt working electrode and Pt counter electrode *vs* Ag/AgCl reference electrode, ferrocene as internal standard ($E_{1/2}^{0/+1}$ = 450 mV) [34], scan rate *v* = 100 mV/s, *T* = 20 °C).

3-aryl 10*H*-phenothiazines **3**	Absorption λ_{max} [nm]	$E_{1/2}^{0/+1}$ [mV]	$E_{1/2}^{+1/+2}$ [mV]	$E_{1/2}^{0/-1}$ [mV]	$\sigma_{p/m}$	σ_R	σ_R^+
3a	262, 322	542	1170	-	-	-	-
3b	270, 333	587	1185	-	-0.20[a]	-0.16[a]	-0.26[a]
3c	265, 329	589	784 (irr)	-	-0.16[b]	-0.18[b]	-0.16[b]
3d	268, 335	611	1153	-	0.00[c]	0.00[c]	0.00[c]
3e	265sh, 287, 346	-	-	-	-	-	-
3f	284, 402	671	1267	-1802 (irr)	0.42[d]	0.23[d]	0.72[d]
3g	265, 328[e]	-	-	-	-	-	-
3h	271, 340, 372	-	-	-	-	-	-
3i	265, 318[e]	741	-	-	-	-	-
3j	268, 322	701	-	-	-	-	-

3-aryl 10*H*-phenothiazines **3**	Absorption λ_{max} [nm]	$E_{1/2}^{0/+1}$ [mV]	$E_{1/2}^{+1/+2}$ [mV]	$E_{1/2}^{0/-1}$ [mV]	$\sigma_{p/m}$	σ_R	σ_R^+
4	254, 320[f] [34]	624	-	-	-	-	-
5	254, 310[e]	764	-	-	-	-	-
6	256, 311	728	-	-	-	-	-

[a]Substituent parameter *p*-^{t}Bu. [b]Substituent parameter *m*-NH_2. [c]Substituent parameter H. [d]Substituent parameter *p*-CHO. [e]Recorded in $CHCl_3$. [f]Recorded in acetonitrile.

This assignment is additionally supported by the first reversible oxidation potentials $E_{1/2}^{0/+1}$, which are also lowest for the NH derivatives **3d** (611 mV) and **4** (624 mV) in both consanguineous series. Likewise the potentials of the hexyl derivatives appear anodically shifted at 701 (**3j**) and 728 mV (**6**), and for the methyl substitution in compounds **3i** and **5** the oxidation is shifted most anodically to 741 and 764 mV, respectively. All this underlines the peculiar and very electron rich character of NH phenothiazine substituents as potent donors.

For scrutinizing the remote electronic substituent effect on the oxidation of the phenothiazinyl core we recorded redox potentials of another consanguineous series of derivatives (**3b-d**, and **3f**) bearing substituents in *p*- and *m*-positions of the phenyl ring. For these substituents suitable Hammett σ-parameters are available, however, out of curiosity we also were interested to determine the effect of the 2,6-dimethoxy substitution (**3a**) on the first oxidation potential. Indeed the lowest oxidation potential is found for the 2,6-dimethoxy derivative **3a**. From ESR measurements of the radical cation of 1,3-dimethoxy benzene it is known that the methoxy substituents can considerably accommodate spin density [36]. Although twofold *ortho*-methoxy substitution causes a torsional angle of 52° in a related biphenyl [37], an efficient stabilization of the phenothiazinyl radical cation by the remote substituents can be assumed. Besides first oxidations at potentials between 542 and 671 mV with Nernstian behavior (Figure 1) the derivatives **3a-d**, and **3f** also display second oxidations, which are also reversible in arrange between 1170 and 1267 mV, with exception of the *m*-aniline derivative **3c**. In that case the second oxidation occurs, due to the similarity of the ionization potentials of phenothiazine (7.02 eV) and aniline (7.55 eV) [38], at considerable lower potential, also causing irreversible consecutive reactions of the dication, such as dimerization or deprotonation [39]. The appearance of a reduction wave for compound **3f** at a cathodic potential of -1802 mV can be assigned to the irreversible reduction in the phenothiazinyl expanded benzaldehyde. This reduction is considerably

anodically shifted in comparison to benzaldehyde (E_{red} = -2581 mV, measured in a 0.1 M solution of NBu_4ClO_4 as an electrolyte in sulfolane vs. $Ag/AgClO_4$ at a scan rate v = 167 mV/s, T = 50 °C) [40], presumably to due to the extended conjugation of the π-system.

For further elucidating the remote substituent effect the first oxidation potentials $E_{1/2}^{0/+1}$ of the four derivatives **3b-d**, and **3f** of the consanguineous series bearing *p*- and *m*-phenyl substituents were subjected to Hammett-Taft correlation analyses with the parameters $\sigma_{p/m}$, σ_R, and σ_R^+ [41]. The obtained correlations gave for $\sigma_{p/m}$: $E_{1/2}^{0/+1}$ = 138.16 $\sigma_{p/m}$ + 612.43 [mV] (R^2 = 0.9981); for σ_R: $E_{1/2}^{0/+1}$ = 203.8 σ_R + 620.1 [mV] (R^2 = 0.9717); and for σ_R^+: $E_{1/2}^{0/+1}$ = 88.117 σ_R^+ + 607.89 [mV]; (R^2 = 0.992). This indicates that the remote electronic effect is transmitted by both resonance and inductive effects, however, with a dominance imposed by the stabilization of positive charges as a consequence of the generation of radical cations.

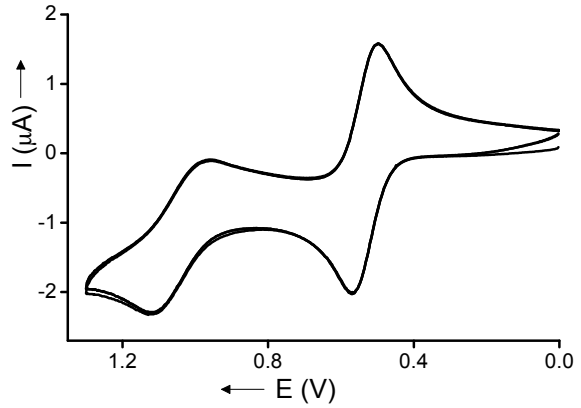


Figure 1. Cyclic voltammogram of compound **3d** (recorded in 0.1 M dichloromethane solution of NBu_4PF_6 as an electrolyte, Pt working electrode and Pt counter electrode *vs* Ag/AgCl reference electrode, ferrocene as internal standard, scan rate v = 100 mV/s, T = 20 °C).

Additional insight in the electronic structure of 3-aryl substituted 10*H*-phenothiazines was obtained by quantum chemical calculations for the four representative structures **3b-d**, and **3f** on the DFT level of theory (B3LYP 6–31 G*) [42]. The HOMO energies of the geometry optimized structures were considered for correlation studies, both with $\sigma_{p/m}$, σ_R, and σ_R^+ [41], and the experimentally obtained first oxidation potentials $E_{1/2}^{0/+1}$ of the corresponding compounds **3b-d**, and **3f** (Table 3).

Table 3. Computed HOMO energies (B3LYP 6–31 G*), first oxidation potentials $E_{1/2}^{0/+1}$, and selected Hammett-Taft substituent parameters $\sigma_{p/m}$, σ_R, and σ_R^+ of structures **3b-d**, and **3f**.

Structure	$\sigma_{p/m}$	σ_R	σ_R^+	$E_{1/2}^{0/+1}$ [mV]	E_{HOMO} [eV]
3b	-0.20[a]	-0.16[a]	-0.26[a]	587	-4.925
3c	-0.16[b]	-0.18[b]	-0.16[b]	589	-4.890
3d	0.00[c]	0.00[c]	0.00[c]	611	-4.969
3f	0.42[d]	0.23[d]	0.72[d]	671	-5.177

[a]Substituent parameter *p*-^{t}Bu. [b]Substituent parameter *m*-NH_2. [c]Substituent parameter H. [d]Substituent parameter *p*-CHO.

The correlations of the Hammett-Taft substituent parameters $\sigma_{p/m}$, σ_R, and σ_R^+ with the calculated HOMO energies are reasonable with R^2 between 0.953 and 0.966, as already established with the first oxidation potentials $E_{1/2}^{0/+1}$. The correlation between the HOMO energies and the first oxidation potentials $E_{1/2}^{0/+1}$ fits even better (R^2 = 0.98). Therefore, it should be possible to predict the oxidation potentials of congeners of compounds **3** by employing the calculated HOMO energies in the following equation:

$$E_{1/2}^{0/+1} = -301.73\ E_{HOMO} - 891.23\ [mV]\ (R^2 = 0.98),$$

where E_{HOMO} is given in [eV].

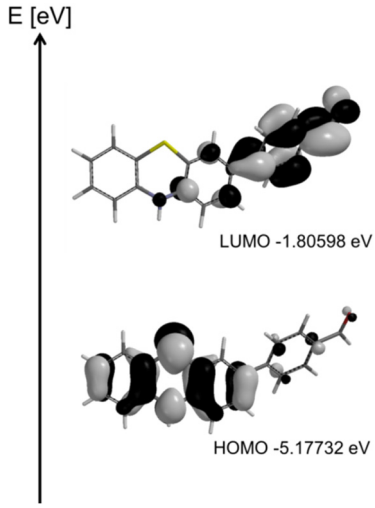


Figure 2. Frontier molecular orbitals, HOMO (bottom) and LUMO (top) of structure **3f**.

A closer inspection of the Kohn-Sham frontier molecular orbitals indicates that the longest-wavelength electronic absorption bands that can be assigned to arise from states with considerable HOMO to LUMO transitions that possess significant charge-transfer character. In particular, for the formyl substituted derivative **3f** this charge-transfer character becomes apparent, where the HOMO displays phenothiazine-centered coefficient density and the LUMO coefficients are predominantly localized in the formylphenyl moiety (Figure 2).

CONCLUSIONS

In summary we could show that the Suzuki coupling of 3-bromo 10*H*-phenothiazines, in particular with the 10-unsubstituted derivative, with several boronic acids proceeds very efficiently and can be employed for the rapid access of various 3-(hetero)aryl 10*H*-phenothiazines. Extensive UV/Vis spectroscopic measurements and cyclic voltammetry as well as DFT calculations have revealed that the electronic properties of these derivatives can be correlated with Hammett-Taft parameters indicating a significant contribution of resonance in transmitting the electronic substituent from the remote substituent position by virtue on the effect of the first oxidation potential. For further exploitation of the insights in the electronic structure extracted from DFT calculations, especially with 10-unsubstituted phenothiazines as donors, underline a considerable charge-transfer character from the phenothiazine to most favorably an electron acceptor at the remote substituent position. This is particularly interesting for devising novel types of light-harvesting dyes for organic photovoltaics. Further studies in these directions are currently underway.

EXPERIMENTAL SECTION

All reactions were carried out in flame-dried Schlenk flasks under nitrogen. Reagents and catalyst were purchased as reagent grade and were used without further purification. Solvents were dried and distilled by standard procedures [43]. 3-Bromo 10*H*-phenothiazines **1** were prepared according published procedures [28-30]. Column chromatography: silica gel 60, mesh 70–230. TLC: silica gel plates. Melting points: uncorrected values. ^{1}H and ^{13}C NMR spectra: d_6-DMSO, d_6-acetone, or $CDCl_3$ (locked to Me4Si). The assignments of quaternary C, CH, CH_2 and CH_3 were made with the aid of DEPT spectra. Elemental analyses were carried out in the Microanalytical Laboratories of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität, Heidelberg, Germany.

Electrochemistry: Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed CH_2Cl_2 at room temperature and at scan rates of 100, 250, 500, and 1000 mVs^{-1}. The electrolyte was Bu_4NPF_6 (0.025 M). The working electrode was a 1 mm platinum disk, the counter-electrode was a platinum wire, and the reference electrode was an Ag/AgCl electrode. The potentials were corrected to the internal standard of Fc/Fc^+ in CH_2Cl_2 ($E_{1/2}^{0/+1}$ = 450 mV) [34].

General procedure (GP) for the synthesis of 3-aryl 10*H*-phenothiazines 3

In a 50 mL Schlenk flask with a magnetic stir bar 3-bromo-10*H*-phenothiazine **1** (1.0 equiv), aryl boronic acid **2** (1.1 equiv), $Pd(PPh_3)_4$ (40 mg, 0.03 mmol), K_2CO_3 (159 mg, 1.15 mmol), DME (10 mL), and water (5 mL) were placed and degassed with nitrogen for 5 min (for experimental details see Table 4). The light brown suspension was heated to reflux under nitrogen for the time indicated. After cooling to room temp the reaction mixture was extracted with dichloromethane (2 x 50 mL) and the combined organic layers with water (2 x 50 mL). The combined organic layers were dried (anhydrous $MgSO_4$), the solvents were removed in vacuo and the residue was purified by flash chromatography on silica gel (ether/pentane) to give the 3-aryl phenothiazines **3**.

Table 4. Experimental details of the synthesis of 3-aryl 10*H*-phenothiazines **3**.

Entry	3-bromo-10*H*-phenothiazine **1**	aryl boronic acid **2**	3-aryl 10*H*-phenothiazines **3** (yield)
1[a]	349 mg (1.25 mmol) of **1a**	254 mg (1.40 mmol) of 2,6-dimethoxyphenyl boronic aid (**2a**)	330 mg (78%) of **3a**
2[b]	224 mg (0.80 mmol) of **1a**	157 mg (0.88 mmol) of 4-*tert*-butylphenyl boronic acid (**2b**)	214 mg (80%) of **3b**
3[c]	305 mg (1.10 mmol) of **1a**	193 mg (1.21 mmol) of 3-aminophenyl boronic acid (**2c**)	249 mg (78%) of **3c**
4[d]	321 mg (1.15 mmol) of **1a**	155 mg (1.27 mmol) of phenyl boronic acid (**2d**)	213 mg (67%) of **3d**
5[e]	327 mg (1.17 mmol) of **1a**	160 mg (1.30 mmol) of 2-thienyl boronic acid (**2e**)	226 mg (68%) of **3e**
6[f]	270 mg (0.97 mmol) of **1a**	160 mg (1.06 mmol) of 4-formylphenyl boronic acid (**2f**)	239 mg (80%) of **3f**
7[g]	311 mg (1.12 mmol) of **1a**	234 mg (1.23 mmol) of 3-(trifluoromethyl) phenyl boronic acid (**2g**)	373 mg (97%) of **3g**
8[a]	151 mg (0.54 mmol) of **1a**	154 mg (0.59 mmol) of 3,5-bis(trifluoromethyl) phenyl boronic acid (**2h**)	194 mg (87%) of **3h**

Entry	3-bromo-10*H*-phenothiazine **1**	aryl boronic acid **2**	3-aryl 10*H*-phenothiazines **3** (yield)
9[h]	292 mg (1.00 mmol) of 3-bromo-10-methyl-10*H*-phenothiazin (**1b**)	134 mg (1.10 mmol) of phenyl boronic acid (**2d**)	240 mg (83%) of **3i**
10[g,i]	362 mg (1.00 mmol) of 3-brom-10-hexyl-10*H*-phenothiazin (**1c**)	121 mg (1.00 mmol) of phenyl boronic acid (**2d**)	201 mg (56%) of **3j**

[a]Reaction time of 12 h. [b]Reaction time of 48 h. [c]Reaction time of 45 h. [d]Reaction time of 16 h. [e]Reaction time of 22 h. [f]Reaction time of 72 h. [g]Reaction time of 25 h. [h]Reaction time of 3 h. [i]The reaction was conducted in a degassed mixture of 1,4-dioxane (8 mL) and water (4 mL).

3-(2,6-Dimethoxyphenyl)-10*H*-phenothiazine (3a)

According to the GP and after chromatography on silica gel (ether/pentane 1:2) 330 mg (78%) of compound **3a** were obtained as a rose powder, R_f (diethyl ether/pentane 1:2) = 0.30, Mp 204-205 °C.

^{1}H NMR (d_6-DMSO, 300 MHz), δ3.64 (s, 6 H), 6.66-6.83 (m, 7 H), 6.90 (m_c, 1 H), 6.98 (m_c, 1 H), 7.23 (t, J = 8.4 Hz, 1 H), 8.59 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ 55.8 (CH_3),104.5 (CH), 113.9 (CH), 114.6 (CH), 115.5 (C_{quat}), 116.6 (C_{quat}), 117.9 (C_{quat}), 121.8 (CH), 126.4 (CH), 127.6 (CH), 127.7 (C_{quat}), 128.4 (CH), 128.8 (CH), 130.2 (CH), 140.7 (C_{quat}), 142.4 (C_{quat}), 157.3 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 336 (21), 335 (M^+, 100), 289 (14). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3381 (m), 3000 (w), 2935 (w), 2834 (w), 2182 (w), 1891 (w), 1579 (s), 1504 (w), 1469 (vs), 1428 (s), 1377 (w), 1303 (s), 1265 (m), 1246 (vs), 1171 (w), 1107 (vs), 1033 (w), 1024 (w), 886 (w), 819 (w), 789 (w), 745 (m). UV/VIS (DMSO), λ_{max} [nm] (ε): 262 (38400), 322 (6400). Anal. calcd. for $C_{20}H_{17}NO_2S$ (335.4): C 71.62, H 5.11, N 4.18, S 9.56; Found: C 71.57, H 5.39, N 4.02, S 9.13.

3-(4-*tert*-Butylphenyl)-10*H*-phenothiazine (3b)

According to the GP and after chromatography on silica gel (ether/pentane 1:1) 214 mg (80 %) of compound **3b** were obtained as a rose powder, R_f (diethyl ether) = 0.90, Mp 253-255 °C.

^{1}H NMR (d_6-DMSO, 300 MHz), δ 1.27 (s, 12 H), 6.67-6.77 (m, 3 H), 6.90-7.00 (m, 2 H), 7.17 (d, J = 1.8 Hz, 1 H), 7.26 (dd, J = 1.8 Hz, J = 8.3 Hz, 1 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 8.4 Hz, 2 H), 8.66 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ31.2 (CH_3), 34.3 (C_{quat}), 114.6 (CH), 114.8 (CH), 116.3 (C_{quat}), 117.1 (C_{quat}), 121.9 (CH), 124.0 (CH), 125.5 (CH), 125.7 (CH), 125.8 (CH), 126.4 (CH), 127.7 (CH), 133.8 (C_{quat}), 136.5 (C_{quat}), 141.3 (C_{quat}), 141.9 (C_{quat}), 149.3 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 332 (24), 331 (M^+, 100), 317 (13), 316 (52), 301 (27). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3372 (m, br), 2961 (m), 1605 (w), 1577 (w), 1460 (m, sh), 1471 (vs), 1431 (w), 1307 (m), 1269 (w), 1125 (w),

1034 (w), 813 (s), 744 (s). – UV/VIS (DMSO), λ_{max} [nm] (ε): 270 (36600), 333 (8400). HRMS calcd. for $C_{22}H_{21}NS$: 331.1394; Found: C: 331.1423.

3-(10*H*-Phenothiazin-3-yl)phenylamine (3c)

According to the GP and after chromatography on silica gel (ether/pentane 1:1) 249 mg (78%) of compound **3c** were obtained as a greenish brown powder, R_f (diethyl ether) = 0.46, Mp 193-194 °C.

^{1}H NMR (d_6-DMSO, 300 MHz), δ 5.06 (s, 2 H), 6.49 (m_c, 1 H), 6.65-6.76 (m, 5 H), 6.90-7.07 (m, 4 H), 7.18 (dd, *J* = 1.8 Hz, *J* = 8.3 Hz, 1 H), 8.64 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ 111.4 (CH), 112.8 (CH), 113.7 (CH), 114.6 (CH), 114.7 (CH), 116.3 (C_{quat}), 116.9 (C_{quat}), 121.9 (CH), 124.0 (CH), 125.7 (CH), 126.4 (CH), 127.7 (CH), 129.4 (CH), 134.8 (C_{quat}), 139.9 (C_{quat}), 141.2 (C_{quat}), 141.9 (C_{quat}), 149.2 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 291 (19), 290 (M^+, 100), 289 (25), 258 (10). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3362 (vs), 3049 (m), 1602 (vs), 1576 (vs), 1471 (vs), 1424 (vs), 1379 (w), 1305 (vs), 1253 (w), 1224 (m), 1169 (w), 1155 (w), 1125 (w), 1078 (w), 1033 (w), 994 (w), 864 (m), 820 (s), 783 (vs), 746 (vs), 688 (s), 656 (m). UV/VIS (DMSO), λ_{max} [nm] (ε): 265 (41800), 329 (10700). Anal. calcd. for $C_{18}H_{14}N_2S$ (290.4): C 74.45, H 4.86, N 9.65, S 11.04; Found: C 74.18, H 4.81, N 9.49, S 10.78.

3-Phenyl-10*H*-phenothiazine (3d)

According to the GP and after chromatography on silica gel (ether/pentane 1:25) 213 mg (67 %) of compound **3d** were obtained as a rose powder, R_f (diethyl ether) = 0.75, Mp 217-218 °C.

^{1}H NMR (d_6-DMSO, 300 MHz), δ 6.67-6.77 (m, 3 H), 6.91-6.99 (m, 2 H), 7.20 (d, *J* = 1.8 Hz, 1 H), 7.27-7.31 (m, 2 H), 7.38 (t, *J* = 7.3 Hz, 2 H), 7.55 (d, *J* = 7.4 Hz, 2 H), 8.68 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ 114.6 (CH), 114.9 (CH), 116.3 (C_{quat}), 117.2 (C_{quat}), 122.0 (CH), 124.3 (CH), 125.8 (CH), 126.0 (CH), 126.4 (CH), 126.9 (CH), 127.7 (CH), 128.9 (CH), 133.8 (C_{quat}), 139.3 (C_{quat}), 141.5 (C_{quat}), 141.8 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 276 (20), 275 (M^+, 100), 274 (25). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3362 (vs), 3055 (w), 1881 (w), 1601 (m), 1576 (m), 1487 (s), 1469 (vs), 1424 (m), 1382 (w), 1305 (m), 1273 (w), 1155 (w), 1125 (w), 1078 (w), 1032 (w), 884 (w), 819 (s), 758 (vs), 749 (vs), 689 (s). UV/VIS (DMSO), λ_{max} [nm] (ε): 268 (35800), 335 (8000). HRMS calcd. for $C_{18}H_{13}NS$ (275.3): 275.0768; Found: 275.0776.

3-Thiophen-2-yl-10*H*-phenothiazine (3e)

According to the GP and after chromatography on silica gel (ether/pentane 1:4) 226 mg (68%) of compound **3e** were obtained as golden brown crystals that were sensitive to oxidation in solution, R_f (diethyl ether/pentane 1:4) = 0.24, Mp 220-222 °C.

^{1}H NMR (d_6-DMSO, 300 MHz), δ 6.66-6.77 (m, 3 H), 6.90-7.06 (m, 3 H), 7.18 (d, *J* = 1.8 Hz, 1 H), 7.24 (dd, *J* = 1.8 Hz, *J* = 8.1 Hz, 1 H), 7.32 (m_c, 1 H), 7.40 (m_c, 1 H), 8.71 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ 114.6 (CH), 114.8 (CH), 116.0 (C_{quat}), 117.3 (C_{quat}), 122.1 (CH), 122.4 (CH), 123.0 (CH), 124.5 (CH), 125.1 (CH), 126.4 (CH), 127.8 (CH), 127.85 (C_{quat}), 128.5 (CH), 141.4 (C_{quat}), 141.6 (C_{quat}), 142.9 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 282 (20), 281 (M^+, 100), 280 (17), 249 (24), 248 (14), 236 (14), 204 (11). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3362 (vs), 3070 (w), 1603 (w), 1576 (m), 1532 (w), 1471 (vs), 1428 (s), 1389 (w), 1298 (s), 1259 (w), 1211 (w), 1153 (w), 1125 (w), 1076 (w), 1033 (w), 930 (w), 879 (w), 811 (vs), 751 (vs), 693 (s). UV/VIS (DMSO), λ_{max} [nm] (ε): 265 (19000, sh), 287 (21900), 346 (8700). HRMS calcd. for $C_{16}H_{11}NS_2$: 281.0332; Found: 281.0349.

4-(10*H*-Phenothiazin-3-yl)-benzaldehyde (3f)

According to the GP and after chromatography on silica gel (ether/pentane 1:2) 239 mg (80%) of compound **3b** were obtained as an intense yellow powder, R_f (diethyl ether/pentane 1 : 2) = 0.10, Mp 202 °C.

^{1}H NMR (d_6-DMSO, 300 MHz), δ 6.67-6.78 (m, 3 H), 6.91-6.99 (m, 2 H), 7.33 (d, *J* = 1.7 Hz, 1 H), 7.40 (dd, *J* = 1.8 Hz, *J* = 8.3 Hz, 1 H), 7.80 (d, *J* = 8.3 Hz, 2 H), 7.90 (d, *J* = 8.3 Hz, 2 H), 8.80 (s, 1 H), 9.98 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ 114.7 (CH), 114.9 (CH), 116.1 (C_{quat}), 117.4 (C_{quat}), 122.2 (CH), 124.7 (CH), 126.2 (CH), 126.4 (CH), 126.6 (CH), 127.8 (CH), 130.3 (CH), 132.1 (C_{quat}), 134.6 (C_{quat}), 141.3 (C_{quat}), 142.5 (C_{quat}), 144.9 (C_{quat}), 192.6 (CH). MS (EI+, 70 eV) *m/z* (%): 304 (17), 303 (M^+, 100), 274 (22), 273 (15), 241 (19). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3435 (s, br), 2924 (w), 2852 (w), 1691 (s), 1598 (vs), 1575 (s), 1521 (w), 1491 (m), 1471 (vs), 1435 (w), 1387 (w), 1308 (s), 1272 (m), 1218 (m), 1175 (s), 1079 (w), 1033 (w), 836 (m), 811 (s), 750 (s). UV/VIS (DMSO), λ_{max} [nm] (ε): 284 (24700), 402 (11400). Anal. calcd. for $C_{19}H_{13}NOS$ (303.4): C 75.22, H 4.32, N 4.62, S 10.57; Found: C 75.29, H 4.37, N 4.53, S 10.28.

3-(3-Trifluoromethylphenyl)-10*H*-phenothiazine (3g)

According to the GP and after chromatography on silica gel (ether/pentane 1:2) 373 mg (97%) of compound **3g** were obtained as a light yellow powder, R_f (diethyl ether/pentane 1:2) = 0.30, Mp 217 °C

^{1}H NMR (d_6-DMSO, 300 MHz), δ 6.67-6.77 (m, 3 H), 6.90-7.01 (m, 2 H), 7.32-7.39 (m, 2 H), 7.57-7.62 (m, 2 H), 7.87 (m_c, 2 H), 8.74 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ 114.7 (CH), 114.9 (CH), 116.2 (C_{quat}), 117.4 (C_{quat}), 122.1 (CH), 122.2 (m_c, CH), 123.4 (m_c, CH), 124.6 (CH), 126.2 (m_c, C_{quat}), 126.3 (CH), 126.4 (CH), 127.8 (CH), 129.8 (CH), 129.9 (d, *J* = 28 Hz,

C_{quat}), 130.0 (CH), 132.0 (C_{quat}), 140.3 (C_{quat}), 141.5 (C_{quat}), 142.2 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 344 (22), 343 (M^+, 100), 342 (16), 311 (17). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3435 (m, br), 3363 (s), 2928 (w), 1602 (w), 1577 (w), 1479 (s), 1448 (m), 1422 (m), 1382 (w), 1335 (vs), 1303 (w), 1293 (w), 1263 (w), 1174 (vs), 1111 (s), 1074 (m), 1043 (m), 877 (w), 798 (s), 756 (s), 694 (m). UV/VIS ($CHCl_3$), λ_{max} [nm] (ε): 265 (34000), 328 (6800). Anal. calcd. for $C_{19}H_{12}F_3NS$ (343.4): C 66.46, H 3.52, N 4.08; Found: C 66.46, H 3.26, N 4.03.

3-(3,5-Bis-trifluoromethylphenyl)-10*H*-phenothiazine (3h)

According to the GP and after chromatography on silica gel (ether/pentane 1:2) 194 mg (87%) of compound **3h** were obtained as a light green powder, R_f (diethyl ether/pentane 1:2) = 0.34, Mp 199 °C

^{1}H NMR (d_6-DMSO, 300 MHz), δ 6.67 (d, *J* = 7.7 Hz, 1 H), 6.73-6.77 (m, 2 H), 6.92 (m_c, 1 H), 6.98 (m_c, 1 H), 7.48-7.51 (m, 2 H), 7.94 (s, 1 H), 8.22 (s, 2 H), 8.81 (s, 1 H). ^{13}C NMR (d_6-DMSO, 75 MHz), δ 114.7 (CH), 114.8 (CH), 116.2 (C_{quat}), 117.6 (C_{quat}), 120.0 (m_c, CH), 123.5 (d, *J* = 271 Hz, C_{quat}), 122.3 (CH), 125.0 (CH), 126.3 (m_c, CH), 126.4 (CH), 126.8 (CH), 127.8 (CH), 130.3 (C_{quat}), 130.9 (quat, *J* = 32 Hz, CH), 141.3 (C_{quat}), 141.8 (C_{quat}), 142.8 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 412 (22), 411 (M^+, 100), 410 (13), 379 (16). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3435 (s, br), 2927 (w), 1605 (w), 1578 (w), 1478 (m), 1465 (m), 1377 (s), 1280 (vs), 1184 (m), 1130 (s), 1067 (w), 899 (w), 881 (w), 749 (w), 682 (w). UV/VIS (DMSO), λ_{max} [nm] (ε): 271 (27300), 340 (7100), 372 (7000). Anal. calcd. for $C_{20}H_{11}F_6NS$ (411.3): C 58.40, H 2.70, N 3.40; Found: C 58.55, H 2.39, N 3.36.

10-Methyl-3-phenyl-10*H*-phenothiazine (3i)

According to the GP and after concentration of the extraction solvents 240 mg (83%) of compound **3i** were obtained as colorless crystals, Mp 126-127 °C.

^{1}H NMR ($CDCl_3$, 300 MHz), δ 3.38 (s, 3 H), 6.83 (m_c, 2 H), 6.93 (m_c, 1 H), 7.15 (d, *J* = 7.5 Hz, 2 H), 7.19-7.31 (m, 1 H), 7.37-7.42 (m, 4 H), 7.52 (d, *J* = 7.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 35.3 (CH_3), 114.1 (CH), 114.2 (CH), 122.5 (CH), 123.1 (C_{quat}), 123.8 (C_{quat}), 125.6 (CH), 126.1 (CH), 126.5 (CH), 126.9 (CH), 127.2 (CH), 127.5 (CH), 128.8 (CH), 135.6 (C_{quat}), 140.0 (C_{quat}), 145.1 (C_{quat}), 145.6 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 290 (20), 289 (M^+, 100), 275 (13), 274 (59), 144 (15). IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3436 (m, br), 1629 (w, br), 1602 (w), 1577 (w), 1464 (vs), 1335 (m), 1260 (m), 1142 (w), 1042 (w), 873 (w), 810 (w), 762 (m), 750 (m), 697 (w). UV/VIS ($CHCl_3$), λ_{max} [nm] (ε): 265 (31200), 318 (7200). Anal. calcd. for $C_{19}H_{15}NS$ (289.4): C 78.86, H 5.22, N 4.84, S 11.08; Found: C 78.50, H 5.24, N 4.81, S 11.03.

10-Hexyl-3-phenyl-10*H*-phenothiazine (3j)

According to the GP and after chromatography on silica gel (pentane) 201 mg (56%) of compound **3j** were obtained as a light yellow oil, R_f (pentane) = 0.31.

^{1}H NMR (d_6-acetone, 300 MHz), δ 0.84 (m_c, 3 H), 1.28 (m_c, 4 H), 1.45 (m_c, 2 H), 1.79 (m_c, 2 H), 3.95 (t, J = 7.0 Hz, 2 H), 6.93 (m_c, 1 H), 7.00-7.08 (m, 2 H), 7.13-7.22 (m, 2 H), 7.29 (m_c, 1 H), 7.38-7.48 (m, 4 H), 7.59 (m_c, 2 H). ^{13}C NMR (d_6-acetone, 75 MHz), δ 14.2 (CH_3), 23.2 (CH_2), 27.1 (CH_2), 27.5 (CH_2), 32.1 (CH_2), 47.8 (CH_2), 116.6 (CH), 116.8 (CH), 123.3 (CH), 125.1 (C_{quat}), 126.0 (C_{quat}), 126.1 (CH), 126.7 (CH), 127.1 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 129.6 (CH), 136.1 (C_{quat}), 140.6 (C_{quat}), 145.5 (C_{quat}), 146.0 (C_{quat}). MS (EI+, 70 eV) *m/z* (%): 360 (30), 359 (M^+, 100), 288 (35), 275 (19), 274 (79), 256 (13). IR (Film), $\tilde{\nu}$ [cm^{-1}]: 2954 (s), 2927 (s), 2855 (m), 1599 (m), 1576 (m), 1508 (w), 1483 (m), 1462 (vs), 1443 (m), 1395 (w), 1332 (m), 1293 (w), 1250 (s), 1133 (w), 1105 (w), 818 (m), 761 (vs), 747 (s), 697 (s). UV/VIS (CH_2Cl_2), λ_{max} [nm] (ε): 236 (20400), 268 (37300), 322 (8100). Anal. calcd. for $C_{24}H_{25}NS$ (359.5): C 80.17, H 7.01, N 3.89, S 8.92; Found: C 80.40, H 7.07, N 4.07, S 8.86.

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