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N-Arylbenzo[*b*]phenothiazines as Reducing Photoredox Catalysts for Nucleophilic Additions of Alcohols to Styrenes: Shift towards Visible Light

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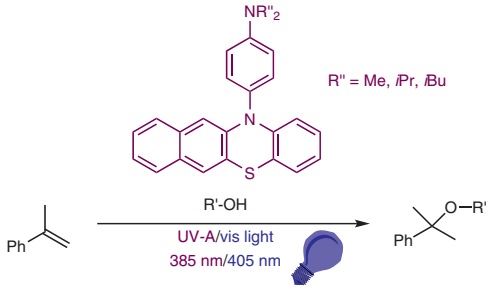

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Abstract *N*-Phenylphenothiazines are an important class of photoredox catalysts because they are synthetically well accessible, they allow the tuning of the optoelectronic properties by different substituents, and they have strong reduction properties for activation of alkenes. One of the major disadvantages of *N*-phenylphenothiazines, however, is the excitation at 365 nm in the UV-A light range. We synthesized three differently dialkylamino-substituted *N*-phenylbenzo[*b*]phenothiazines as alternative photoredox catalysts and applied them for the nucleophilic addition of alkohols to α-methyl styrene. The additional benzene ring shift the absorbance bathochromically and allows performing the photocatalyses by excitation at 385 nm and 405 nm. This type of photoredox catalysis tolerates other functional groups, as representatively shown for alcohols as substrates with C–C and C–N triple bonds.

Key words photochemistry, LED, styrene, photocatalysis, alcohol

Over the last decade, photoredox catalysis has become a powerful method in modern synthetic organic chemistry. Light, preferably in the visible range, provides enough energy to overcome activation barriers of reactions by alternative pathways that are not accessible by the conventional thermal approach.[1] Photoredox catalysis complements the available synthetic methods by so far unknown transformations and thereby overcomes limits of current synthetic methods.[2] The majority use transition-metal complexes mainly with ruthenium due to their photophysical properties and their (photo)chemical robustness. In order to enhance the sustainability by the combination of using light from energy-saving LEDs and nonmetallated photoredox catalysts, organic dyes are important alternatives, for instance, eosin Y,[3] rhodamine 6G,[4] mesityl[5] and aminoacridinium,[6] naphthyochromenones,[7] and 4,6-dicyanobenzenes.[8] However, there is not *one* single organic photoredox catalyst for different types of organic reactions. Instead, each organic photoredox catalyst has its own reactivity profile and substrate scope. In order to apply organic dyes in advanced photoredox catalysts in a versatile way, it is beneficial that modifications can be made to the core structure in order to tune optical and redox properties.[8,9] *N*-Phenylphenothiazines[10] (Figure 1) meet these criteria. They are important new photoredox catalysts because they (i) are easily synthetically accessible, (ii) they allow the introduction of electron-donating or electron with-drawing groups at the core or at the phenyl group to tune the optoelectronic properties, (iii) they are strongly reducing photoredox catalysts, and (iv) they are photochemically stable.[11,12] We recently used the strong reductive power of *N*-phenylphenothiazines to activate inert SF_6 and to obtain pentafluorosulfanylated organic compounds.[13] One of the major disadvantages of *N*-phenylphenothiazines, however, is the excitation at 365 nm in the UV-A light range that may cause undesired side reactions. *N*-Phenylbenzo[*b*]phenothiazines are important alternatives as their unsubstituted core structure was applied for ATRA polymerization.[14] We present herein differently dialkylamino-substituted *N*-phenylbenzo[*b*]phenothiazines **1**–**3** as strongly reducing photoredox catalysts for the nucleophilic addition of alcohols to α-methyl styrene **7** (Figure 1). The condensation with an additional benzene ring yields a bathochromically shifted excitation wavelength and should allow running the photocatalysis at 385 nm and even at the border to visible light (405 nm).

The syntheses of *N*-phenylbenzo[*b*]phenothiazines **1**–**3** (Scheme 1) start with the condensation of naphthalene-2,3-diol (**9**) with 2-aminobenzothiol (**10**) to 12*H*-ben-

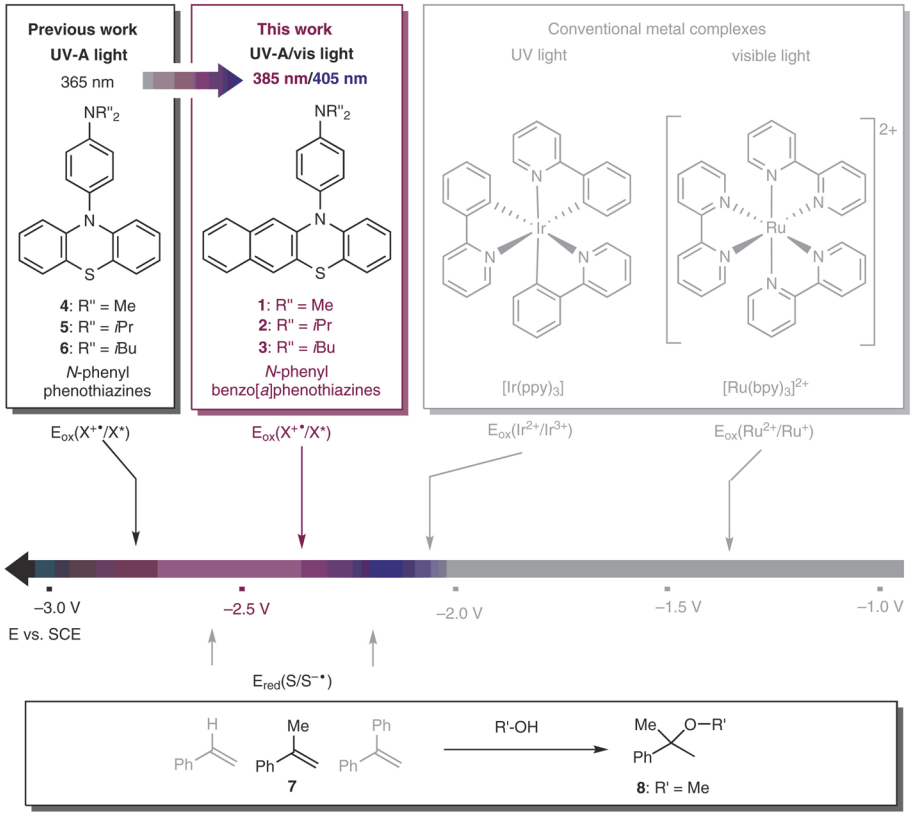
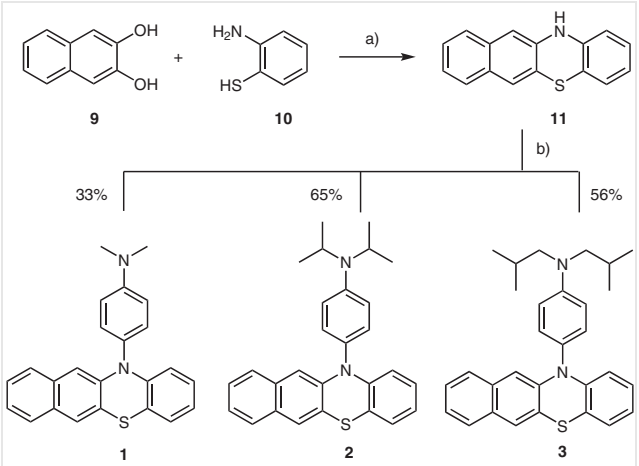


Figure 1 *N*-Phenylbenzo[*b*]phenothiazines **1–3** in comparison with *N*-phenylphenothiazines **4–6**,[11] conventional transition-metal complexes as photoredox catalysts, their oxidation potentials, and the reduction potentials of differently substituted olefin substrates, in particular **7**, for nucleophilic addition of alcohols to products with Markovnikov selectivity, like **8**.

zo[*b*]phenothiazine (**11**)[15] as the core chromophore structure. Subsequent Hartwig–Buchwald aminations with the corresponding dialkylamino-substituted phenyl bromides yield the target compounds **1**,[16] **2**,[17] and **3**[18] in sufficient yields of 33–65%.

Our recently published *N*-phenylphenothiazines are strongly reducing photoredox catalysts, able to activate SF_6 for pentafluorosulfanylations, but they have to excited at 365 nm. In principle, irradiations that are more selective are realized by shifting the excitation of the photoredox catalyst from the UV-A range into the bathochromic direction. Irradiations at 385 nm and 405 nm LEDs gain selectivity because this is outside the typical n–π^* absorption range of carbonyl-substituted substrates. This is an important goal because it improves the tolerance of other functional groups in the substrates. With the extension of the aromatic system of the core structure of benzo[*b*]phenothiazines a significant bathochromic shift of the absorption bands is achieved. A high electronic ground-state potential is combined with a relatively small S_0–S_1 gap E_{00}. The UV/Vis absorbance of **1–3** show additional broad bands ranging from 350–420 nm that are not observable with *N*-phenylphenothiazines **4–6** (Figure 2). Cyclic voltammetry of **1–3** show two fully reversible potentials that can be assigned to the formation of the radical cation and further to the dication, respectively (Figure 2). The benzo condensation has no significant influence on the first oxidation potential $E_{ox}(\mathbf{X}^{+\bullet}/\mathbf{X})$



Scheme 1 Synthesis of *N*-phenylbenzo[*b*]phenothiazines **1–3**. *Reagents and conditions*: a) naphthalene-2,3-diol, 2-aminobenzothiol (1.00 equiv), 1,2,4-trichlorobenzene, overnight, 200 °C; b) aryl halogenide (1.50 equiv), NaO*t*-Bu (2.50 equiv), tricyclohexylphosphine (0.07 equiv), $Pd_2(dba)_3$ (0.05 equiv), toluene, overnight, 120 °C.

that were observed in the range between 0.51–0.58 V, in comparison to 0.49–0.57 V for **4**–**6**[11] (Table 1). Due to the red-shifted absorbance, however, the singlet excitation energies E_{00} for **1**–**3** at 2.8–3.0 eV are lower in comparison to 3.1–3.5 eV for **4**–**6**.[11] As result, the oxidation potentials of **1**–**3** in the excited states $E_{ox}(\mathbf{X}^{+\bullet}/\mathbf{X}^{*})$ are also reduced to –2.3 to –2.4 V in comparison to –2.5 to –3.0 eV for **4**–**6**.[11] Most importantly, these potentials are still sufficient to activate α-methyl styrene (**7**) as representative aromatic substrate by reduction to the radical anion. According to literature, such strongly reducing potentials are achieved by merging photocatalysis and electrocatalysis,[20] or by using the acridine radical as photocatalyst.[21]

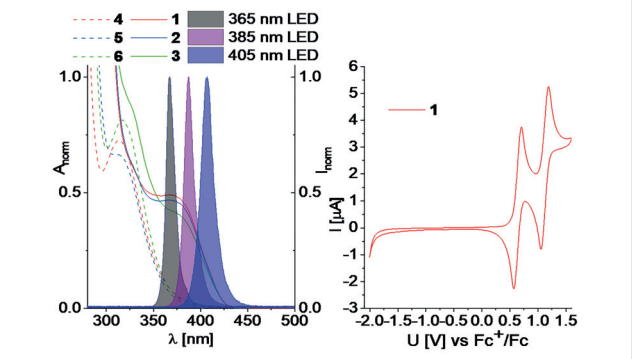


Figure 2 Normalized UV/Vis absorption of *N*-phenylbenzo[*b*]phenothiazines **1**–**3** in comparison to *N*-phenylphenothiazines **4**–**6** and normalized emission of the 365 nm, 386 nm, and 405 nm LEDs (left) and representative cyclic voltagram of **2** (right)

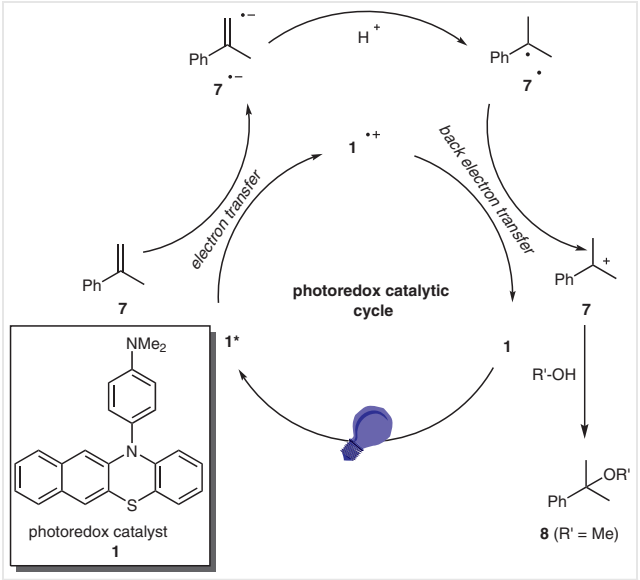
Table 1 Oxidation Potentials $E_{ox}(\mathbf{X}^{+\bullet}/\mathbf{X})$ and $E_{ox}(\mathbf{X}^{2+}/\mathbf{X}^{+\bullet})$, Singlet Excitation Energies E_{00}, and Estimated Excited-State Oxidation Potentials $E_{ox}(\mathbf{X}^{+\bullet}/\mathbf{X}^{*})$ of *N*-Phenylbenzo[*b*]phenothiazines **1**–**3**

	1	**2**	**3**
$E_{ox}(\mathbf{X}^{+\bullet}/\mathbf{X})$[a] (V)	0.58	0.55	0.51
$E_{ox}(\mathbf{X}^{2+}/\mathbf{X}^{+\bullet})$[a] (V)	1.04	1.04	1.04
E_{00} (eV)[b]	3.0	3.0	2.8
$E_{ox}(\mathbf{X}^{+\bullet}/\mathbf{X}^{*})$ (V)	–2.4	–2.4	–2.3
ε_{385nm} ($M^{-1}cm^{-1}$)	4,300	4,600	4,100
ε_{405nm} ($M^{-1}cm^{-1}$)	2,100	2,300	2,100

[a] Converted from the ferrocene scale into the SCE scale: +0.38 V.[19]
[b] E_{00} was estimated by the intersection of the normalized absorbance and fluorescence.

Photoredox catalysis were performed with α-methyl styrene (**7**) and different alcohols (R′OH) as nucleophiles. α-Methyl styrene (**7**) bears one phenyl group and is thereby an activated olefin with respect to its reduction potential $E_{red}(S/S^{-\bullet})$ between that of 1,1-diphenylethylene ($E_{red}(S/S^{-\bullet})$ = –2.3 V) and styrene ($E_{red}(S/S^{-\bullet})$ = –2.6 V). Notably, a diphenylethylene derivative has been applied as substrate for enantioselective intramolecular alkoxylation by naphthalene dicarboxylates.[22] According to Rehm–Weller, the driving force of this initial electron transfer is estimated according to $\Delta G = E_{ox} - E_{red} - E_{00}$ (omitting the Coulomb interaction energy E_c). For **1**–**3**, the driving force ΔG for the photoinduced electron transfer to **7** lie in the range between –0.2 eV and +0.3 eV, thus not clearly exergonic, close to borderline cases.

In previous studies, the photoredox catalytic methoxylation of **7** by *N*-phenylphenothiazines was restricted to 365 nm excitation because the extinction of **4**–**6** at higher wavelengths is too low. Our newly synthesized benzofused derivatives **1**–**3** allow excitation by LEDs at 385 nm and even at 405 nm because the spectral overlap of the absorbances with the emission of the 385 nm (and 405 nm) LEDs is sufficient (Figure 2). After such excitation of the photoredox catalysts **1**–**3** an electron transfer to the substrate **7** yields the charge separated state (Scheme 2). The resulting radical anion **7** is rapidly protonated to the neutral radical **7** that undergoes the back electron transfer to the cation **7**. The latter intermediate is the strong electrophile that reacts with alcohols (like MeOH in the simplest case) as weak nucleophiles to the final addition product (like **8**). In contrast to our previous result with *N*,*N*-dimethylaminopyrene as photoredox catalyst,[23] the alkoxylations with *N*-phenylbenzo[*b*]phenothiazines do not require the addition of trimethylamine as electron shuttle for efficient back electron transfer. Both, the photoinduced charge separation by electron transfer and the regeneration of the catalyst by back electron transfer works without an additive, which is a significant advantage.



Scheme 2 Proposed mechanism for the nucleophilic addition of alcohols R′OH to substrate **7** yielding product **8** using **1** as photoredox catalyst

The yields of **8** after irradiation by the 385 nm LED with **1** and **2** as photoredox catalyst are 58% and 48%, respectively (Table 2). The yields are lower but still in a similar range than the yields obtained by standard 365 nm irradiation. Irradiations by the 405 nm LED yield very low amounts of product **8** (4% and 2%) due to yield reduced extinction coefficient of **1** and **2** at this wavelength. The best photoredox catalyst within this small set of differently substituted *N*-phenylbenzo[*b*]phenothiazines is **3** that delivers yields of 88% by 385 nm irradiation, which is even higher than the yield by 365 nm irradiation, and remarkable 24% by 405 nm irradiation, respectively. These results show a clear improvement of this type of photoredox catalysis, since the previously applied irradiation at 365 nm is very close to direct activation of substrates and thereby the limit of photocatalysis.

Table 2 Yields of Photoredox Catalytic Methoxylations of α-Methylstyrene (**7**, 180 mM) to Product **8**[a]

LED (nm)	Yield of **1** (%)	Yield of **2** (%)	Yield of **3** (%)
365	76	89	62
385	58	48	88
405	5	4	24

[a] Conditions: photoredox catalyst (**1**, **2**, or **3**, 10 mol%), MeOH (1.00 mL), 35 °C, 65 h irradiation at 365 nm, 385 nm, or 405 nm.

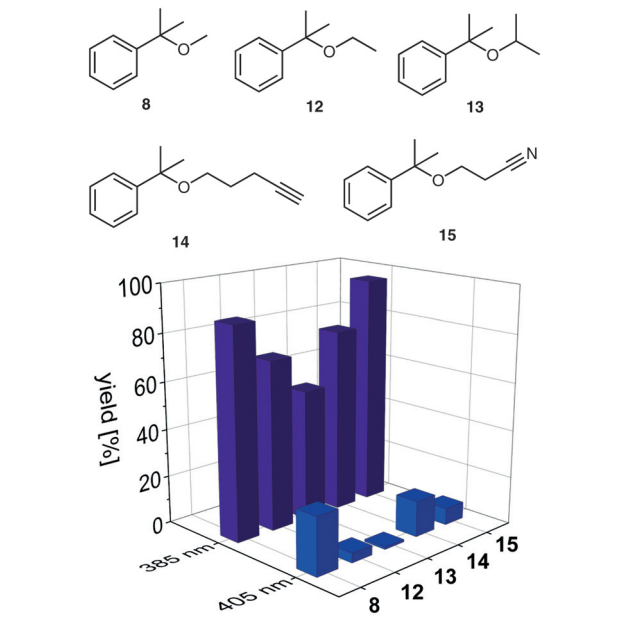


Figure 3 Product scope **8**, **12–15** for the photoredox catalytic conversion of α-methylstyrene (**7**) with methanol, ethanol, isopropanol, pent-4-yn-1-ol, and **2**-hydroxypropanenitrile, and yields of products **8** and **12–15**. *Reagents and conditions*: **3** (10 mol%) R′OH (0.75 mL), 35 °C, 65 h irradiation at 385 nm or 405 nm.

To widen the substrate scope of this photoredox catalysis ethanol, isopropanol, pent-4-yn-1-ol, and 2-hydroxypropanenitrile were used as alternative alcohols for the nucleophilic addition to substrate **7** (Figure 3 and Table 3). These reactions were performed with the photoredox catalyst **3** that was previously identified as the best one. The yields of products **8**, **12**, and **13** after 385 nm irradiation in the presence of MeOH, EtOH, and *i*-PrOH drop from 88% over 71% to 55%. This drop can be assigned to the increasing stering demand in this series of alcohols and supports the proposed nucleophilic addition mechanism (Scheme 2). The products **14** and **15** are formed in remarkable yields of 77% and 96%, respectively, and representatively show that this type of photoredox catalysis tolerates other functional groups, in particular C–C and C–N triple bonds, due to the selective irradiation wavelength.

Table 3 Yields of Photoredox Catalytic Methoxylations of α-Methylstyrene (**7**, 180 mM) to Products **8**, **12–15**[a]

LED (nm)	Yield of **8** (%)	Yield of **12** (%)	Yield of **13** (%)	Yield of **14** (%)	Yield of **15** (%)
385	88	71	55	77	96
405	24	4	1	15	7

[a] Conditions: **3** (10 mol%), alcohol (1.00 mL), 35 °C, 65 h irradiation at 385 nm or 405 nm.

In conclusion, the synthesized *N*-benzophenothiazine-based catalysts **1–3** show a significantly redshifted absorbance in comparison to conventional *N*-phenylphenothiazines, allow excitation at 385 nm (and even at 405 nm), and provide an excited-state reduction potential of $E^* = -2.4$ V vs SCE. Although this potential is diminished compared to conventional *N*-phenylphenothiazines, it is clearly sufficient for alkoxylations of α-methylstyrene (**7**) by photoredox catalytic nucleophilic additions. Using photoredox catalyst **3**, the addition of MeOH to **7** gives higher yields when irradiated at 385 nm compared to conventional 365 nm. The excitation at 385 nm (and 405 nm) allows reactions that are more selective because other functional groups are not excited. Hence, this improved photoredox catalysis tolerates other functional groups, as representatively shown for alcohols with C–C and C–N triple bonds.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1304-4575.

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(15) **Experimental Procedure**
Compounds **9** (8.00 g, 50.0 mmol) and **10** (6.25 g, 50.0 mmol) were dissolved in 1,2,4-trichlorobenzene (25 mL), heated to 200 °C, and stirred overnight. After cooling, the product mixture was diluted with *n*-hexane, and the crystalline **11** was collected by filtration, washed with fresh *n*-hexane and EtOH, and obtained as yellow powder (5.02 g, 20.2 mmol, 40%). ^{1}H NMR (500 MHz, DMSO): δ = 8.99 (br s, 1 H), 7.57 (t, *J* = 8.6 Hz, 2 H), 7.49 (s, 1 H), 7.31–7.27 (m, 1 H), 7.20–7.16 (m, 1 H), 7.04–6.96 (m, 3 H), 6.78–6.73 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.60, 139.13, 133.31, 129.69, 127.54, 126.56, 126.22, 126.09, 125.89, 124, 123.53, 121.31, 119.91, 115.69, 114.67, 107.97 ppm. ESI-HRMS: *m/z* calcd: 249.0612 [M$^+$]; found: 249.0603 [M$^+$].

(16) **Experimental Procedure**
Compound **11** (250 mg, 1.00 mmol, 1.00 equiv), 4-bromo-*N*,*N*-dimethylaniline (300 mg, 1.50 mmol, 1.50 equiv), NaO*t*-Bu (240 mg, 2.50 mmol, 2.50 equiv), tricyclohexylphosphine (20.0 mg, 0.07 mmol, 0.07 equiv), and Pd_2dba_3 (46 mg, 0.05 mmol, 0.05 equiv) were dissolved in anhydrous toluene (0.26 M). The reaction mixture was stirred under reflux and inert atmosphere overnight and cooled to r.t. The solvent was removed under vacuum. Compound **1** was purified by column chromatography (hexane/CH_2Cl_2 = 5:1, silica gel, R_f = 0.34) and obtained as yellow solid (123 mg, 0.330 mmol, 33%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.7 Hz, 1 H), 7.43 (s, 1 H), 7.33 (d, *J* = 8.2 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.21–7.15 (m, 2 H), 7.03 (d, *J* = 7.5 Hz, 1 H), 6.94 (d, *J* = 8.7 Hz, 2 H), 6.85 (t, *J* = 7.15 Hz, 1 H), 6.77 (t, *J* = 7.2 Hz, 1 H), 6.47 (s, 1 H), 6.27 (d, *J* = 8.0 Hz, 1 H), 3.09 (s, 6 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.19, 143.96, 142.56, 133.36, 131.52, 130.10, 129.37, 126.93, 126.89, 126.42, 126.21, 125.92, 124.27, 124.03, 122.22, 121.65, 119.0, 116.0, 114.04, 110.88, 40.71 ppm. ESI-HRMS: *m/z* calcd: 368.1347 [M$^+$]; found: 368.1332 [M$^+$].

(17) **Experimental Procedure**
Compound **11** (250 mg, 1.00 mmol, 1.00 equiv), 4-bromo-*N*,*N*-diisopropylaniline (1.42 mL, 384 mg, 1.50 mmol, 1.50 equiv), NaO*t*-Bu (240 mg, 2.50 mmol, 2.50 equiv), tricyclohexylphosphine (20.0 mg, 0.07 mmol, 0.07 equiv), and Pd_2dba_3 (46 mg, 0.05 mmol, 0.05 equiv) were dissolved in anhydrous toluene (0.26 M). The reaction mixture was stirred under reflux and inert atmosphere overnight and cooled to r.t. The solvent was removed under vacuum. Compound **2** was purified by column chromatography (hexane/CH_2Cl_2 = 1:2, silica gel, R_f = 0.4) and obtained as yellow solid (275 mg, 0.648 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.8 Hz, 1 H), 7.43 (s, 1 H), 7.35 (d, *J* = 7.9 Hz, 1 H), 7.23–7.15 (m, 4 H), 7.06 (d, *J* = 8.9 Hz, 1 H), 7.03 (d, *J* = 6.0 Hz, 3 H), 6.87 (t, *J* = 7.4 Hz, 1 H), 6.78 (t, *J* = 7.4 Hz, 1 H), 6.52 (s, 1 H), 6.32 (d, *J* = 7.2 Hz, 1 H), 3.93 (hept, 2 H), 1.36 (d, *J* = 6.8 Hz, 12 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.19, 143.98, 142.54, 133.38, 130.91, 130.11, 129.72, 126.96, 126.89, 126.42, 126.22, 125.88, 124.25, 124.01, 122.29, 121.64, 119.02, 118.79, 116.30, 110.93, 47.70, 21.47 ppm. ESI-HRMS: *m/z* calcd: 424.1973 [M$^+$]; found: 424.1948 [M$^+$].

(18) **Experimental Procedure**
Compound **11** (250 mg, 1.00 mmol, 1.00 equiv), 4-bromo-*N*,*N*-diisobutylaniline (299 mg, 1.05 mmol, 1.05 equiv), NaO*t*-Bu (240 mg, 2.50 mmol, 2.50 equiv), tricyclohexylphosphine (20 mg, 0.07 mmol, 0.07 equiv), and Pd_2dba_3 (46.0 mg, 0.05 mmol, 0.05 equiv) were dissolved in anhydrous toluene (0.26 M). The reaction mixture was stirred under reflux and inert atmosphere overnight and cooled to r.t. The solvent was removed under vacuum. Compound **3** was purified by column chromatography (hexane, silica, R_f = 0.3) and obtained as white solid (256 mg, 0.566 mmol, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.0 Hz, 1 H), 7.43 (s, 1 H), 7.35 (d, *J* = 7.10 Hz, 1 H), 7.22–7.14 (m, 4 H), 7.02 (d, *J* = 7.25 Hz, 1 H), 6.90–6.75 (m, 4 H), 6.51 (s, 1 H), 6.32 (d, *J* = 8.10 Hz, 1 H), 3.25 (d, *J* = 7.21 Hz, 4 H), 2.20 (hept, *J* = 6.70 Hz, 2 H), 0.99 (d, *J* = 6.55 Hz, 12 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.09, 144.11, 142.68, 133.39, 131.31, 130.09, 128.06, 126.96, 126.89, 126.39, 126.21, 125.84, 124.24, 123.97, 122.30, 121.59, 118.97, 116.31, 113.89, 110.91, 60.65, 26.57, 20.67 ppm. ESI-HRMS: *m/z* calcd: 452.2286 [M$^+$]; found: 452.2269 [M$^+$].

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