JOC The Journal of Organic Chemistry

Article

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Tin-Functionalized Azobenzenes as Nucleophiles in Stille Cross-Coupling Reactions

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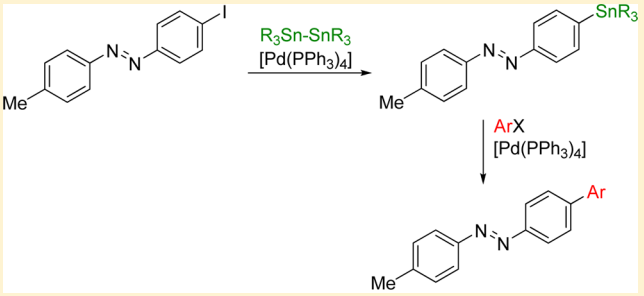
Supporting Information

ABSTRACT: The metalation of azobenzene by halogen−metal exchange typically leads to a reduction of the azo group to give hydrazine derivatives as major byproducts, instead of the desired metalated azobenzene species. In cross-coupling reactions, azobenzenes therefore usually serve as electrophiles, which greatly limits the scope of the reaction. To solve this problem, we have developed a mild and fast method to stannylate azobenzenes in high yields. This research shows that these stannylated azobenzenes can be used as nucleophilic components in Stille cross-coupling reactions with aryl bromides. The cross-coupling products were obtained in high yields ranging from 70 to 93%. With this reversal of the nucleophilic and electrophilic components, cross-coupling products are now accessible in which the aromatic rings coupled to the azobenzene bear functional groups that are sensitive to metalation.



INTRODUCTION

Azobenzene and its derivatives are bistable systems (with their *trans* and their *cis* form)[1] that are comparatively resistant to photobleaching[2] and thermal decomposition.[3] Therefore, they are widely used as effective photoswitchable units in molecular systems and polymers[4] with potential applications ranging from biochemical[5] and medical uses,[6] to photoswitchable bulk materials,[7] to smart surfaces[8] and lithographic applications.[9] A further interest lies in their potential to couple both mechanical and photochemical work in one molecule.[1a,7,10] The effective functionalization of azobenzenes, which enables their connection to other functional molecules or tuning photophysical properties, is therefore essential.

The most versatile approach to functionalize aromatic rings to form CC bonds is by transition-metal-catalyzed cross-coupling methods. While the use of halogen- or pseudohalogen-functionalized azobenzenes as the electrophilic component in this type of reaction is an established synthetic route,[11] there are hardly any nucleophilic azobenzenes known. While a metalation *ortho* to the azo group is facilitated by directed *ortho*-metalation,[12] yields are typically low. Moreover, this feature cannot be used for the synthesis of *para*-substituted analogues. For *para*-substituted azobenzenes, pinacol borane substituted azobenzene derivatives have been described that served as a nucleophile in Suzuki cross-coupling reactions.[13] Lithiated species can be prepared in situ by halogen−metal exchange, but the reported yields are very low (maximal 42% for *para*[14] and 47% for *ortho*[15]). For Grignard compounds, a patent exists that reports the synthesis of the symmetrical *para*-magnesiated azobenzene.[16] However, elemental magnesium in combination with ammonium chloride has been successfully used for the reduction of *ortho*-, *meta*-, and *para*-halogenated azobenzenes to the halogenated hydrazine analogues in 75−91% yield.[17] However, no other metallic groups in the *para* position that can be used for cross-coupling reactions have been described to date.[18]

The main synthetic challenge of preparing *para*-metalated azobenzenes is their low tolerance toward reductive reaction conditions: Most protocols for introducing nucleophilic functional groups are based on deprotonation followed by transmetalation. Alternatively, and as in the case of azobenzenes, a halogen−metal exchange on compounds such as the *para*-halogenated azobenzene **1** with an organolithium reagent to the 4-lithioazobenzene **2** can be used, followed by a transmetalation with the desired metal chloride or semimetal chloride (Scheme 1). However, a prominent side reaction that is impossible to avoid using the highly nucleophilic alkylorganolithium reagents is the reduction of the azo group to hydrazine derivatives (**3** and **4**).[19]

In this work, an easy-to-use methodology to obtain tin functionalized azobenzene derivatives in very high yields[18] and their applicability for Stille cross-coupling reactions is presented.

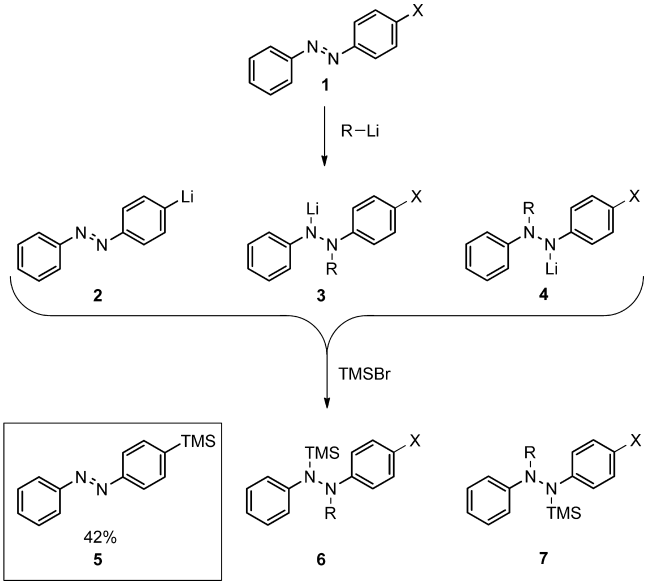
RESULTS AND DISCUSSION

Although stannylation reactions of arenes are most often performed by a transmetalation from the corresponding organolithium or organomagnesium compounds, another method for introducing trialkyl tin groups is by a cross-coupling reaction.[20] In such a reaction, an aryl halide is treated with a distannane, $R_3Sn-SnR_3$, using a transition-metal catalyst. For the

Received: December 4, 2013
Published: February 6, 2014

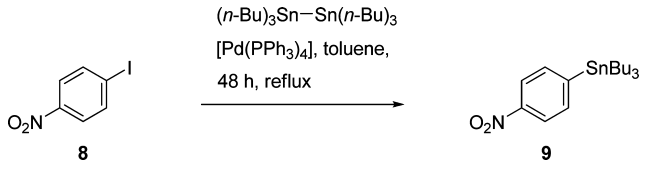
   dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719−1728

Scheme 1. Halogen–Lithium Exchange (Left); Concomitant Reduction of the Azobenzene 1 to Hydrazine Derivatives 6 and 7 (Middle and Right)[14,19]



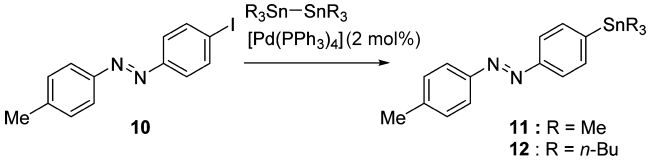
stannylation of nitrophenyl iodide **8**,[21] *n*-hexabutyldistannane as the electrophile and $[Pd(PPh_3)_4]$ as the catalyst in toluene at reflux conditions, a similar reaction had been reported to give product **9** in a yield of 63% (Scheme 2).

Scheme 2. Stannylation of *p*-Nitrophenyl Bromide (8) with Hexa-*n*-butyldistannane to 9 in 63% Yield[21]



To establish reaction conditions for a stannylation of azobenzene using such a cross-coupling reaction, initially those same reaction conditions for azobenzene **10** as the electrophilic component were used and hexamethyldistannane as electrophile. Compound **11** could be isolated in a yield of 46% (Table 1, entry 1): the trimethylstannylazobenzene **11** proved stable to pH neutral silica gel, and therefore, it could be easily purified by removal of the catalyst with a filtration column. This product **11** was then used as a calibrant for the development of a gas chromatographic (GC) method which allowed us to monitor the reaction and optimize it efficiently. The reaction was performed in different solvents at different temperatures with $[Pd(PPh_3)_4]$ as catalyst (Table 1). For the thermal reactions at 70 °C, the reaction progress was monitored in regular intervals, and the time given in Table 1 represents the time when no further conversion was observed. The reaction turned out to be highly temperature and solvent dependent. For all solvents, a reaction temperature of 70 °C using conventional heating led to significantly longer reaction times than heating to 150 °C in the microwave. (Compare Table 1, entries 2–7, with entries 8 to 13, respectively.) At 70 °C, DMF and DMSO turned out to be very suitable for the reaction to give a full conversion and a GC yield of 91% and 84%, respectively (Table 1, entries 2 and 3). Although pyridine and toluene as solvents led

Table 1. Optimization of the Stannylation of 4-Iodo-4′-methylazobenzene (10) with 2 mol % of $[Pd(PPh_3)_4]$ as Catalyst



entry	R	solvent	*T* (°C)	time	yield[a] (%)
1	Me	toluene	reflux[b]	48 h	46[c]
2	Me	DMF	70[b]	9 h	91
3	Me	DMSO	70[b]	13 h	84
4	Me	pyridine	70[b]	11 h	54
5	Me	toluene	70[b]	14 h	64
6	Me	dioxane	70[b]	12 h	39
7	Me	THF	70[b]	16 h	43
8	Me	DMF	150[d]	10 min	21
9	Me	DMSO	150[d]	10 min	27
10	Me	pyridine	150[d]	10 min	82
11	Me	toluene	150[d]	10 min	>99
					95[c]
12	Me	dioxane	150[d]	10 min	94
13	Me	THF	150[d]	10 min	>99
14	*n*-Bu	toluene	150[d]	35 min	74[c]

[a]GC yield unless noted otherwise; calibrated with the product **11** using triisoprobylbenzene as the internal calibration standard. [b]Conventional heating. [c]Isolated yield. [d]Microwave heating.

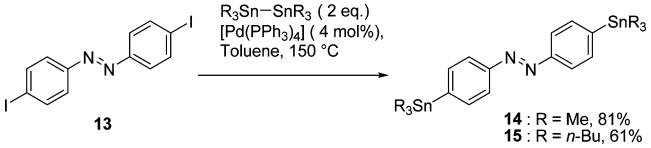
to adequate yields (54%, entry 5 and 64% entry 1, respectively), starting material could still be observed. Dioxane and THF as solvents led to the lowest yields under those reaction conditions (39% and 43%, entries 6 and 7) and did not lead to a full conversion of the starting material. However, in all reactions no side products were observed, only the starting material **10** and product **11**. As byproduct formation was not a significant issue at 70 °C, and in order to reduce the reaction time and increase the product yield, the reaction was performed at higher temperatures in a sealed reaction vessel in a microwave at 150 °C (Table 1, entries 8–13). For each solvent, the reaction was stopped after 10 min; the mixture was analyzed by GC to determine the conversion of the starting material. Although no decomposition or side products could be observed under any of the reaction conditions, there were significant differences with respect to conversion compared to the reactions performed at 70 °C. Under the microwave conditions, DMF and DMSO, which were the most suitable solvents for conventional heating at 70 °C, only led to low yields of 21% and 27% (Table 1, entries 8 and 9). Toluene and THF, on the other hand, led to an almost quantitative product yield of >99% each, respectively (Table 1, entries 11 and 13). The same was true for dioxane and pyridine (Table 1, entries 12 and 10). The optimized conditions for the monostannylation of azobenzene in toluene (Table 1, entry 11) were transferred to the coupling reaction of *n*-hexabutyldistannane to azobenzene in toluene in the microwave to give **12**. Although THF also led to a quantitative yield for the stannylation, toluene was selected because this solvent does not carry the risk of forming explosive peroxides when stored.[22] The stannylation of **10** to give **12** was monitored by thin layer chromatography because we could not observe a signal in GC/MS. After 10 min, the reaction was incomplete, presumably due to the lower reactivity of

dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719–1728

$(n\text{-Bu})_3\text{Sn}-\text{Sn}(n\text{-Bu}_3)$ as compared to the sterically more accessible $Me_3Sn-SnMe_3$. The reaction time in the microwave was therefore increased to 35 min. Although the product could be isolated in an adequate yield of 74% (Table 1, entry 14), the purification required a Kugelrohr distillation at very high temperatures of 180 °C and a pressure of 9.4×10^{-2} mbar, which probably led to a partial decomposition of the material.

Having established high-yielding reaction conditions, 4,4′-bis(iodo)azobenzene (**13**) was stannylated with both hexamethyldistannane and *n*-hexabutyldistannane to give products **14** and **15** (Scheme 3). As for the monostannylated species, the

Scheme 3. Distannylation of 4,4′-Bis(iodo)azobenzene (13) with 4 mol % of $[Pd(PPh_3)_4]$ as a Catalyst to Products 14 and 15



bis-trimethylstannylated azobenzene (**14**) was obtained in a very good yield of 81%. For the bis(tri-*n*-butyl)stannylated species **15**, the isolated yield was somewhat lower, at 61%. Whereas the methylstannylated azobenzenes could be purified by filtration on silica and subsequent evaporation of the hexamethyldistannane without a noticeable loss of yield, **15** had to be performed by Kugelrohr distillation. We assume that this process caused the observed lower yield for this product.

With both the trimethylstannyl- and tri-*n*-butylstannylazobenzenes **11** and **12** in hand, we explored their usefulness in Stille cross-coupling reactions with various aromatic bromides as reaction partners (Table 2). All of these Stille coupling reactions were performed at a moderate temperature of 70 °C. The reaction progress was monitored by GC/MS, and the reaction was terminated when no starting material could be detected any more. Initially, all reactions were performed with the trimethylstannylazobenzene **11** as the nucleophile. As expected, the use of electron-deficient benzene derivatives gave excellent yields: *para*-bromonitrobenzene (**16**) was fully converted within 6 h, giving the product **17** in a yield of 89% (Table 2, entry 1). Similarly, the electron-deficient *para*-cyanobenzene bromide **18** and *para*-bromophenyl methyl ketone **19** required only a short reaction time of 8 h to give the products **20** and **21** in good yields of 82% and 87%, respectively. The reaction worked equally well for electron-rich aromatic cycles. Although the electrophile **24** bears an aldehyde group, the furan heterocycle is very electron rich, which explains the longer reaction time of 16 h which was required for this compound, and a yield of 73% of **25** could be isolated. Electron-rich electrophiles typically required longer reaction times of more than 19 h (compare, for example, 3-methoxy bromide **28**, 2,4-dimethoxide **29**, and benzodioxolyl bromide **30** with bromobenzene **22**; Table 2, entries 7, 8, 9, and 4), but the furan ester **27** showed a full conversion after only 14 h and could be isolated in a yield of 84% (Table 2, entry 6). In reactions with bromothiophenes, 2-bromothiophene (**34**) gave **35** with a yield of 88% in only 11 h, which is significantly faster compared to the less reactive[23] 3-bromothiophene (**36**) with a reaction time of 14 h to give **37** in an isolated yield of 83%. (Table 2, entries 10, and 11). The *para*-bromoaniline **38** showed full conversion to product **39** after 19 h with a yield of 72%.

Stille cross-coupling reactions with the tri-*n*-butylstannyl azobenzene derivative were also performed with the electron-deficient *para*-nitrophenyl bromide (**16**) and the electron-rich 3-methoxyphenyl bromide (**28**). As this starting material, tri-*n*-butylstannyl azobenzene could not be observed by our GC/MS, the reaction was monitored by thin-layer chromatography. The yields with this nucleophile were significantly lower than the product yield with the methylstannylated species: Product **17** could only be isolated in a yield of 71% (18% lower than with nucleophile **11**), and product **31** gave only a yield of 54% (25% lower than with nucleophile **11**) (Table 2, entries 1 (b) and 7 (b)). We attribute this to the lower reactivity of the nucleophile **12** to the increased sterical hindrance of the *n*-butyl groups as compared to the methyl groups.

Several of the aryl bromides were used for the Stille coupling reactions in this work are highly sensitive to typical metalation reactions using organolithium or organomagnesium reagents. For example, nitrophenyl bromide and cyanophenyl bromide (**16**, **18**) are unstable when treated with *n*-butyllithium, and the aldehyde-, ketone-, and ester-functionalized aryl bromides (**19**, **24**, and **26**[24]) would be attacked by the butyl nucleophile and be reduced. To circumvent this problem, protection groups can be used, but as this increases the number of steps in a synthesis, and causes more waste, it is advantageous if protection groups can be avoided in a synthetic process. With our newly developed stannylated azobenzenes, aromatic bromides bearing these sensitive functional groups (nitro, cyano, carbonyl) can now be used as the much more easily accessible electrophilic cross-coupling partner for a carbon−carbon bond formation with an azobenzene. The carbonyl functionalized arylbromides gave yields from 73 to 87% (Table 2 entries 3, 5, and 6).

CONCLUSION

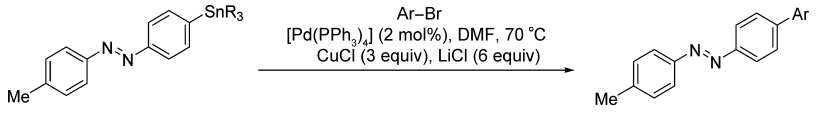
In conclusion, we have developed a highly efficient methodology to prepare mono- and distannylated azobenzene derivatives with tri-*n*-butylstannyl and trimethylstannyl substituents. This reaction involves a palladium-catalyzed cross-coupling reaction with reagents of the type $R_3Sn-SnR_3$ and the easily accessible iodinated azobenzene derivatives as starting materials. It was also shown that such tin-functionalized azobenzenes are effective nucleophiles in Stille cross-coupling reactions with a range of functionalized aryl bromides. Electron-rich and electron-deficient electrophiles were efficiently cross-coupled in similarly high yields ranging from 70 to 93%. Of particular interest are electrophiles FG−Ar−Br with functional groups (FG) such as aldehydes, ketones, or nitro groups. Previously, corresponding nucleophiles, FG−Ar−M, could be reacted with the easily accessible azobenzene halides using established procedures. However, such compounds FG−Ar−M can be difficult to prepare in this form if a metalation procedure would lead to an attack of the nucleophile on these electrophilic functional groups. Because azobenzene stannanes are now available, these electrophiles can be used as the much more easily accessible electrophilic component. This newly established method therefore complements the established procedures by introducing a new synthon for nucleophilic azobenzenes.

EXPERIMENTAL SECTION

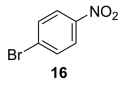
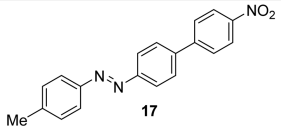
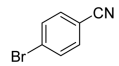
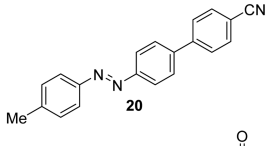
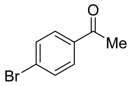
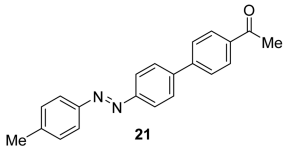
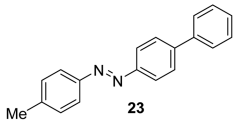
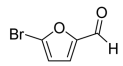
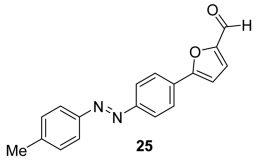
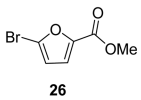
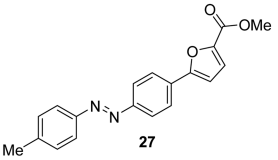
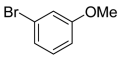
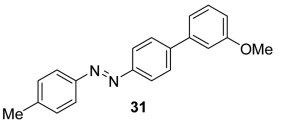
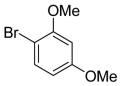
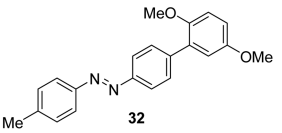
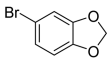
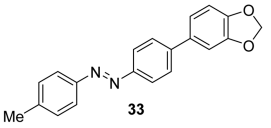
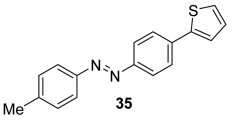
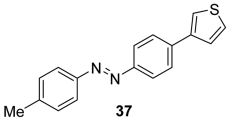
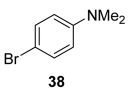
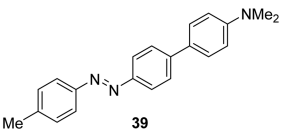
All reagents used were commercially available and used without further purification. For their purities see the Supporting Information. All solvents that were used in the stannylation and Stille reactions were dried prior to use. For the exact drying procedures see Supporting Information.

dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719−1728

Table 2. Stille Coupling of Various Aryl Bromides with 4-Methyl-4′-(trimethylstannyl)azobenzene (11) or 4-Methyl-4′-(tri-*n*-butylstannyl)azobenzene (12)



11 : R = Me
12 : R = *n*-Bu

Entry	Electrophile	Product	t/h	Yield [%]
1	 **16**	 **17**	6 17	89[a] 71[b]
2	 **18**	 **20**	8	82
3	 **19**	 **21**	8	87
4	 **22**	 **23**	12	93
5	 **24**	 **25**	16	73
6	 **26**	 **27**	14	84
7	 **28**	 **31**	19 25	79[a] 54[b]
8	 **29**	 **32**	26	70
9	 **30**	 **33**	24	70
10	 **34**	 **35**	11	88
11	 **36**	 **37**	14	83
12	 **38**	 **39**	19 h	72

[a]Reaction with 4-methyl-4′(trimethylstannyl)azobenzene. [b]Reaction with tri-*n*-butylstannylazobenzene.

All preparations for the stannylation reactions were performed in a nitrogen-filled glovebox and carried out in a sealed vial under nitrogen. All Stille couplings were carried out using standard Schlenk techniques under a nitrogen atmosphere.

All NMR spectra were recorded on a 500 MHz spectrometer (with respect to the proton resonance). ^{1}H NMR and ^{13}C NMR spectra were referenced against the solvent residual proton signals (^{1}H) or the solvent itself (^{13}C). ^{119}Sn NMR spectra were referenced externally against $CDCl_3$.

The exact assignment of the peaks was performed by two-dimensional NMR spectroscopy such as ^{1}H COSY, ^{1}H/^{13}C HSQC, or ^{1}H/^{13}C HMBC when possible.

All microwave syntheses were performed on a Biotage Initiator+ SP Wave (Organic Synthesis Mode). The temperature was measured with an external IR sensor during microwave heating.

Due to the toxicity of organotin compounds,[25] certain precautions should be observed: All manipulations should be performed in a well-vented fume cupboard, wearing standard eye protection, lab coats, and nitrile gloves with the following specification: EN374-1:2003 "Protection against chemical splash."

Care needs to be taken to observe proper disposal procedures for all waste products, according to the health and safety procedures in place. Under no circumstances should these compounds be disposed of in the drains or allowed to leak in any other way into the environment.

Representative Procedure for the Optimization of the Stannylation of 4-Iodo-4′-methylazobenzene. *Thermal Syntheses.* A solution of 4-iodo-4′-methylazobenzene (177 mg, 550 μmol), hexamethyldistannane (180 mg, 550 μmol), [Pd(PPh$_3$)$_4$] (12.7 mg, 2 mol %), and the internal reference 1,3,5-triisopropylbenzene (112 mg, 550 μmol) in toluene (4 mL) was heated to 70 °C. In regular intervals, a sample (0.1 mL) was taken from the reaction vial and filtered through a short column of silica (5 × 3 mm; eluent: DCM) and a PTFE syringe filter (pore size = 45 μm) before the sample was analyzed by GC.

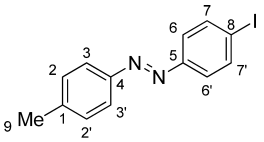
For all other reaction conditions, the parameters were varied as specified in Table 1.

Microwave syntheses. A solution of 4-iodo-4′-methylazobenzene (177 mg, 0.55 mmol), hexamethyldistannane (180 mg, 0.55 mmol), [Pd(PPh$_3$)$_4$] (12.7 mg, 2 mol %), and the internal reference 1,3,5-triisopropylbenzene (112 mg, 550 μmol) in toluene (4 mL) was heated to 150 °C in a microwave apparatus. Every 10 min, a sample (0.1 mL) was taken from the reaction vial and filtered through a short column of silica (5 × 3 mm; eluent: DCM) and a PTFE syringe filter (pore size = 45 μm), before the sample was analyzed by GC.

For all other reaction conditions, the parameters were varied as specified in Table SI 1 (Supporting Information).

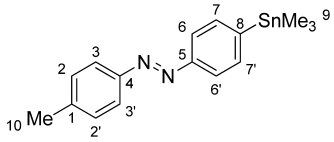
dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719−1728

*4-Iodo-4′-methylazobenzene (**10**).*[26]



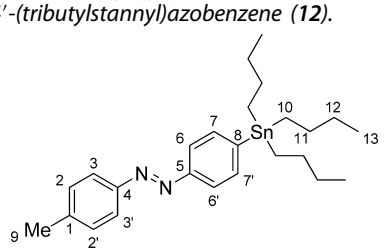
This compound has also been synthesized by J. Tour and co-workers using a different method.[26] *para*-Toluidine (26.0 g, 243 mmol) was dissolved in DCM (100 mL) at 20 °C. A solution of K_2SO_5 (300 g, 488 mmol) in water (600 mL) was added, and the reaction was stirred for 4 h at 20 °C. The dark green organic phase was separated and washed with 1 M hydrochloric acid (2 × 150 mL), a saturated aqueous solution of hydrogen carbonate (1 × 150 mL), and water (1 × 200 mL). The organic phase was dried over magnesium sulfate. After evaporation of the solvent and without further purification, a solution of 4-iodoaniline (53.2 g, 243 mmol) in acetic acid (250 mL) was added to the crude product and stirred for 16 h at 20 °C. The precipitate was separated by filtration and dissolved in DCM (50 mL). The solution was washed 1 M hydrochloric acid (2 × 150 mL), a saturated solution of hydrogen carbonate in water (1 × 150 mL), and water (1 × 200 mL). The combined organic phases were dried over magnesium sulfate. After evaporation of the solvent, 42.3 g (54%, lit.[26] 93%) of an orange solid was obtained. Mp: 160 °C (lit.[27] mp 160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.86 (d, ^3J = 8.5 Hz, 2 H, H-3,3′), 7.83 (d, ^3J = 8.5 Hz, 2 H, H-7,7′), 7.64 (d, ^3J = 8.5 Hz, 2 H, H-6,6′), 7.32 (d, ^3J = 8.5 Hz, 2 H, H-2,2′), 2.45 (s, 3H, H-9) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 152.0 (C-5), 150.6 (C-4), 142.0 (*C-1*), 138.3 (C-7,7′), 129.8 (C-2,2′), 124.4 (C-6,6′), 123.0 (C-3,3′), 97.2 (*C-8*), 21.5 (*C-9*) ppm. IR (ATR): 3021 (w), 2978 (w), 2912 (w), 1600 (m), 1381 (m), 1105 (m), 1065 (m), 830 (s), 763 (s), 711 (s), 512 (s) cm^{-1}. HRMS (CI-sector) *m/z*: $[M + H]^+$ calcd for $[C_{13}H_{11}N_2I + H]^+$ 323.0045, found 323.0050.

*4-Methyl-4′-(trimethylstannyl)azobenzene (**11**).*



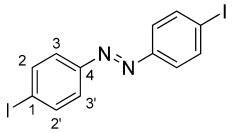
4-Iodo-4′-methylazobenzene (3.00 g, 9.31 mmol), hexamethyldistannane (3.05 g, 9.31 mmol), and $[Pd(PPh_3)_4]$ (215 mg, 186 μmol, 2 mol %) were dissolved in toluene (19 mL). The reaction vessel was heated to 170 °C for 10 min in a microwave. The solvent was evaporated, and the crude product was purified by filtration through silica with cyclohexane/ethyl acetate (v/v, 2/3). The solvent and the remaining hexamethyldistannane were evaporated at 6.4 × 10^{-2} mbar and 70 °C over the course of 17 h. 3.12 g (95%) of red solid was obtained. Mp: 62 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.87 (d, ^3J = 8.2 Hz, 2 H, H-3, 3′), 7.84 (d, ^3J = 8.3 Hz, 2 H, H-6, 6′), 7.66 (d, ^3J = 8.3 Hz, 2 H, H-7,7′), 7.32 (d, ^3J = 8.2 Hz, 2 H, H-2, 2′), 2.45 (s, 3 H, H-10), 0.35 (s, 9 H, H-9) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): 152.7 (*C-5*), 150.9 (*C-4*), 146.7 (*C-8*), 141.5 (*C-1*), 136.6 (*C-7, 7′*), 129.7 (*C-2, 2′*), 122.9 (*C-6, 6′*) 122.9 (*C-3, 3′*), 21.5 (*C-10*) −9.5 (*C-9*) ppm. ^{119}Sn NMR (187 MHz, $CDCl_3$): −25.25 ppm. IR (ATR): 3023 (w), 2980 (w), 2910 (w), 1600 (w), 1380 (w), 1156 (m), 1065 (m), 1010 (m), 830 (s), 783 (s), 711 (s), 526 (s) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + H]^+$ calcd for $[C_{16}H_{20}N_2Sn + H]^+$ 361.0721, found 361.0735.

*4-Methyl-4′-(tributylstannyl)azobenzene (**12**).*



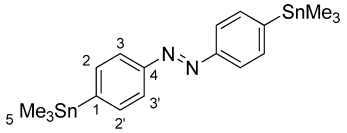
4-Iodo-4′-methylazobenzene (1.00 g, 3.10 mmol), hexa-*n*-butyldistannane 1.80 g (3.10 mmol), and $[Pd(PPh_3)_4]$ (64.3 g, 55.0 μmol, 2 mol %) were dissolved in toluene (19 mL). The reaction vessel was heated to 150 °C for 35 min in a microwave apparatus, and then the solvent was evaporated. The crude product was dissolved in DCM and filtered over a short plug of silica. The solvent was evaporated, and the remaining oil was purified by Kugelrohr distillation (9.43 × 10^{-2} mbar, 150 °C, 20 min). The residue was dissolved in DCM and filtered over a short plug of silica. After evaporation of the solvent, 998 mg (74%) of a red oil was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): 7.87 (d, ^3J = 8.1 Hz, 2 H, H-3, 3′), 7.86 (d, ^3J = 8.2 Hz, 2 H, H-6, 6′), 7.65 (d, ^3J = 8.2 Hz, 2 H, H-7,7′), 7.33 (d, ^3J = 8.1 Hz, 2 H, H-2, 2′), 2.34 (s, 3 H, H-9), 1.66−1.49 (m, 6 H, H-11), 1.41−1.32 (m, 6 H, H-12), 1.19−1.05 (m, 6 H, H-10), 0.91 (t, ^3J = 7.3 Hz, 9 H, H-13) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): 152.7 (*C-5*), 150.9 (*C-4*), 146.7 (*C-8*), 141.3 (*C-1*), 137.1 (*C-7, 7′*), 129.7 (*C-2, 2′*), 122.9 (*C-6,6′*) 122.8 (*C-3,3′*), 29.1 (*C-11*), 27.4 (*C-12*), 21.5 (*C-9*), 13.7 (*C-13*), 9.7 (*C-10*) ppm. ^{119}Sn NMR (187 MHz, $CDCl_3$): −39.9 ppm. IR (ATR): 3020 (w), 2955 (s), 2921 (s), 2870 (m), 2852 (m), 1600 (w), 1462 (m), 1376 (m), 1964 (m), 1013 (m), 960 (m), 873 (m), 829 (s), 658 (s) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + H]^+$ calcd for $[C_{25}H_{38}N_2Sn + H]^+$ 487.2130, found 487.2149.

*4,4′-Bis(iodo-)azobenzene (**13**).*[28]



This compound has also been synthesized by Roncali and co-workers.[28] For the preparation of the catalyst, copper chloride (5.00 g, 45.7 mmol) was dissolved in pyridine (50 mL), and the mixture was stirred for 30 min at 20 °C. An insoluble residue which remained was removed by filtration before addition of 4-iodoaniline (14.3 g, 65.3 mmol) in one portion to the solution. The reaction mixture was stirred for 9 h at 20 °C while air was bubbled through the reaction mixture with the help of a frit. Then, diethyl ether (150 mL) was added, and the organic phase was washed with water (3 × 200 mL), 2 M aqueous hydrochloride acid (2 × 200 mL), and water (1 × 100 mL). The organic phase was dried over sodium sulfate. After evaporation of the solvent, the crude product was recrystallized from ethanol to give 8.64 g (61%, lit.[28] 87%) of a red solid. Mp: 210 °C (lit.[28] mp 210−211 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.07 (d, ^3J = 8.7 Hz, 4 H, H-2, 2′), 7.79 (d, ^3J = 8.7 Hz, 4 H, H-3,3′) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): 151.8 (*C-4*), 138.4 (*C-2, 2′*), 124.5 (*C-3, 3′*), 98.1 (*C-1*) ppm. IR (ATR): 3078 (w), 1560 (m), 1573 (m), 1469 (m), 1393 (m), 1156 (m), 1051 (m), 1001 (m), 833 (s), 539 (s) cm^{-1}. HRMS (CI-sector) *m/z*: $[M + H]^+$ calcd for $[C_{12}H_8N_2I_2 + H]$ 434.8855, found 434.8848.

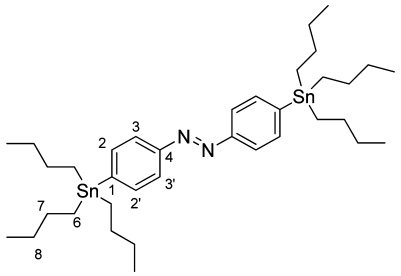
*4,4′-Bis(trimethylstannyl)azobenzene (**14**).*



4,4′-*Bis*(iodo)azobenzene (1.00 g, 2.30 mmol), hexamethyldistannane (1.15 g, 4.61 mmol), DMSO (2 mL), and $[Pd(PPh_3)_4]$ (106 μg, 92.0 μmol, 4 mol %) were dissolved in toluene (19 mL). The reaction vessel was heated to 150 °C for 10 min in a microwave apparatus. Then the solvent was evaporated, and the crude product was purified by filtration on silica with DCM. The solvent was evaporated, and the remaining hexamethyldistannane was evaporated at 5.3 × 10^{-2} mbar and 70 °C over 39 h. 946 mg (81%) of red solid was obtained. Mp: 54 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.87 (d, ^3J = 8.2 Hz, 4 H, H-3, 3′), 7.65 (d, ^3J = 8.2 Hz, 4 H, H-2, 2′), 0.34 (s, 18 H, H-5) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): 152.8 (*C-4*), 147.1 (*C-1*), 136.6 (*C-2, 2′*), 122.0 (*C-3, 3′*), −9.4 (*C-5*) ppm. ^{119}Sn NMR (187 MHz, $CDCl_3$): δ = −25.20 ppm. IR (ATR): 3067 (w), 3024 (w), 2987 (w), 2917 (w), 1925 (w), 1437 (m), 1383 (m), 1306 (m), 1067 (m), 1011 (m), 831 (s), 761 (s), 583 (s), 508 (s) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + H]^+$ calcd for $[C_{18}H_{26}N_2Sn_2 + H]^+$ 511.0213, found 511.0227.

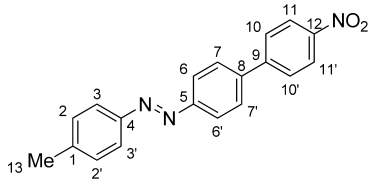
dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719−1728

*4,4′-Bis(tributylstannyl)azobenzene (**15**).*



4,4′-*Bis*(iodo)azobenzene (1.00 g, 2.30 mmol), hexa-*n*-butyldistannane (2.67 g, 4.60 mmol), DMSO (2 mL), and [$Pd(PPh_3)_4$] (106 mg, 92.0 μmol, 4 mol %) were dissolved in toluene (19 mL). The reaction vessel was heated to 150 °C for 60 min in a microwave apparatus. The solvent was evaporated. The crude product was dissolved in DCM and filtered over a short plug of silica. The solvent was evaporated, and the remaining oil was purified by removing the byproducts by Kugelrohr distillation (7.93×10^{-2} mbar, 150 °C, 30 min). The residue was dissolved in DCM and filtered over a short plug of silica. 1.07 g (61%) of a red oil was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): 7.85 (d, ^3J = 8.2 Hz, 4H, H-3, 3′), 7.64 (d, ^3J = 8.2 Hz, 4H, H-2, 2′), 1.66−1.49 (m, 12H, H-7), 1.41−1.32 (m, 12 H, H-8), 1.19−1.05 (m, 12 H, H-6), 0.91 (t, ^3J = 7.3 Hz, 18 H, H-9) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): 152.7 (*C-4*), 147.0 (*C-1*), 137.1 (*C-3, 3′*), 121.8 (*C-2, 2′*), 29.1 (*C-7*), 27.4 (*C-8*), 13.7 (C-9), 9.7 (*C-6*) ppm. ^{119}Sn NMR (187 MHz, $CDCl_3$): −40.0 ppm. IR (ATR): 3074 (w), 2955 (s), 2922 (s), 2850 (s), 1921 (w), 1462 (m), 1376 (m), 1064 (m), 1012 (m), 830 (s) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + H]^+$ calcd for $[C_{36}H_{62}N_2Sn_2 + H]^+$ 763.3030, found 763.3023.

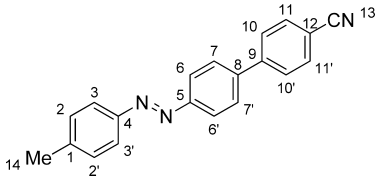
*4-(4-Nitrophenyl)-4′-methylazobenzene (**17**).*



Method A. 4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), *para*-nitrophenyl bromide (113 mg, 0.557 mmol), [$Pd(PPh_3)_4$ (12.9 mg, 0.011 mmol, 2 mol %), copper chloride (165 mg, 1.67 mmol,] 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 6 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The product was recrystallized from EtOH. Orange crystals (157 mg, 89%) were obtained.

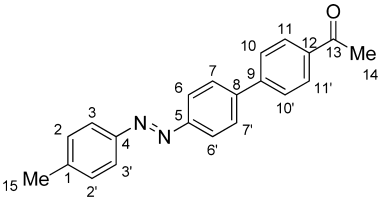
Method B. 4-Methyl-4′-(tri-*n*-butylstannyl)azobenzene (270 mg, 0.557 mmol), *para*-nitrophenyl bromide (113 mg, 0.559 mmol), [$Pd(PPh_3)_4$] (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 17 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The solvent was evaporated. The crude product was recrystallized from cyclohexane. An orange solid (125 mg, 71%) was obtained. Mp: 104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 8.24 (d, ^3J = 8.9 Hz, 2 H, H-11, 11′), 7.93 (d, ^3J = 8.7 Hz, 2H, H-6, 6′), 7.78 (d, ^3J = 8.2 Hz, 2H, H-3,3′), 7.71 (d,^3J = 8.9 Hz, 2H, H-10, 10′), 7.68 (d, ^3J = 8.7 Hz, 2H, H-7, 7′), 7.26 (d, ^3J = 8.2 Hz, 2 H, H-2, 2′), 2.37 (s, 3 H, H-13) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 152.8 (*C-5*), 150.8 (*C-4*), 147.4 (*C-12*), 146.6 (*C-9*), 142.1 (*C-8*), 140.6 (*C-1*), 129.8 (*C-2, 2′*), 128.1 (*C-7, 7′*), 127.9 (*C-10, 10′*), 124.2 (*C-11, 11′*), 123.5 (*C-6, 6′*), 123.0 (*C-3, 3′*), 21.6 (*C-13*) ppm. IR (ATR): 3023 (w), 2979 (w), 2912 (w), 1382 (m), 1067 (m), 832 (m), 1065 (m), 832 (s), 760 (s), 583 (s), 520 (s) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + H]^+$ calcd for $[C_{19}H_{15}N_3O_2 + H]^+$ 318.1237, found 318.1245.

*4-(4-Cyanophenyl-) 4′-methylazobenzene (**20**).*



4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 4-bromobenzonitrile (101 mg, 0.557 mmol), [$Pd(PPh_3)_4$] (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 8 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The product was purified by column chromatography on silica with toluene as eluent. The solvent was evaporated, and an orange solid (136 mg, 82%) was obtained. Mp: 207 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 8.01 (d, ^3J = 8.7 Hz, 2H, 6, 6′), 7.86 (d, ^3J = 8.2 Hz, 2H, 3, 3′), 7.81−7.74 (m, 6 H, H-7, 7′, 10, 10′, 11, 11′), 7.36 (d, ^3J = 8.2 Hz, 2H, 2,2′), 2.45 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2) (due to significant signal overlap in the ^{1}H NMR spectrum, it was impossible to assign all ^{13}C NMR signals using HMQC and HMBC): 152.7 (*C-5*), 150.9 (*C-4*), 144.65, 142.4 (*C-1*), 141.3, 132.8 (*C-2, 2′*), 123.0, 128.2, 127.9, 123.5 (*C-6, 6′*), 123.0 (*C-3, 3′*), 118.9, 111.6, 21.4 (*C-14*) ppm. IR (ATR): 3071 (w), 3045 (w), 2925 (w), 2225 (m), 1598 (m), 1417 (m), 1378 (m), 1233 (m), 1208 (m), 1158 (m), 1109 (m), 1003 (m), 830 (s), 718 (m), 639 (m), 546 (s) cm^{-1}. HRMS (CI-sector) *m/z*: $[M + H]^+$ calcd for $[C_{20}H_{15}N_3 + H]^+$ 298.1344, found 298.1347.

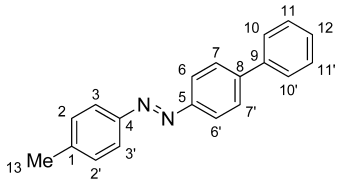
*4-(4-Acetylphenyl)-4′-methylazobenzene (**21**).*



4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 4-bromoacetophenone (111 mg, 0.557 mmol), [$Pd(PPh_3)_4$] (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 8 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The solvent was evaporated. The crude product was purified by column chromatography with toluene as eluent. An orange solid (152 mg, 87%) was obtained. Mp: 186 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 8.05 (d, ^3J = 8.6 Hz, 2 H, H-11, 11′), 8.01 (d, ^3J = 8.7 Hz, 2 H, H-6, 6′), 7.86 (d, ^3J = 8.1 Hz, 2 H, H-3, 3′), 7.82 (d, ^3J = 8.7 Hz, 2 H, H-7, 7′), 7.79 (d, ^3J = 8.6 Hz, 2 H, H-10, 10′), 7.36 (d, ^3J = 8.1 Hz, 2 H, H-2, 2′), 2.63 (s, 3 H, H-14), 2.45 (s, 3 H, H-15) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 197.7 (*C-13*), 152.75 (*C-5*), 151.2 (*C-4*), 144.9 (*C-9*), 142.50 (*C-8*), 142.4 (*C-1*), 136.8 (*C-12*), 130.2 (*C-2, 2′*), 129.3 (*C-11, 11′*), 128.4 (*C-7, 7′*), 127.6 (*C-10, 10′*), 123.7 (*C-6, 6′*), 123.2 (*C-3, 3′*), 26.9 (*C-14*), 21.6 (*C-15*) ppm. IR (ATR): 3348 (w), 3027 (w), 2917 (w), 2859 (w), 1925 (w), 1674 (s), 1599 (m), 1355 (m), 1231 (m), 957 (m), 824 (s), 720 (m) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + Na]^+$ calcd for $[C_{21}H_{18}N_2O + Na]^+$ 337.1311, found 337.1318.

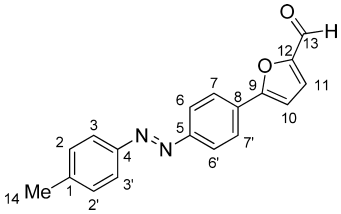
dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719−1728

*4-Phenyl-4′-methylazobenzene (**23**).*



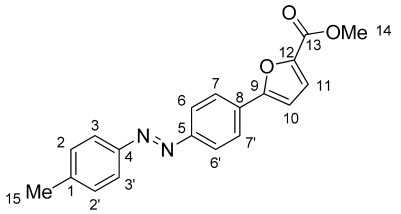
4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), bromobenzene (87,5 mg, 0.557 mmol), $[Pd(PPh_3)_4]$ (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 10 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The solvent was evaporated. The crude product was purified by column chromatography with toluene as eluent. The solvent was evaporated, and an orange solid (141 mg, 93%) was obtained. Mp: 198 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.99 (d, ^3J = 8.7 Hz, 2 H, H-6, 6′), 7.86 (d, ^3J = 8.1 Hz, 2 H, H-3, 3′), 7.78 (d, ^3J = 8.7 Hz, 2 H, H-7, 7′), 7.70 (dd, J = 8.5, 1.2 Hz, 2 H, H-10, 10′), 7.49 (t, ^3J = 8.5 Hz, 2 H, H-11, 11′), 7.42−7.38 (m, 1 H, H-12), 7.36 (d, ^3J = 8.1 Hz, 2 H, H-2, 2′), 2,45 (s, 3 H, H-15) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 152.2 (*C-5*), 151.24 (*C-4*), 143.8 (*C-8*), 142.3 (*C-1*), 140.5 (*C-9*), 130.2 (*C-2, 2′*), 129.3 (*C-11, 11′*), 128.3 (*C-12*), 128.1 (*C-7, 7′*), 127.5 (*C-10, 10′*), 123.6 (*C-6, 6′*), 123.2 (*C-3, 3′*), 21.6 (C-13) ppm. IR (ATR): 3023.7 (w), 2914 (w), 1599 (m), 1483 (m), 1405 (m), 1157 (m) 847 (s), 763 (s), 687 (s) cm^{-1}. HRMS (CI-sector) *m/z*: $[M + H]^+$ Calcd for $[C_{19}H_{16}N_2 + H]^+$ 273.1392; Found 273.1391.

*4-(2-Furanyl-5-aldehyde)-4′-methylazobenzene (**25**).*



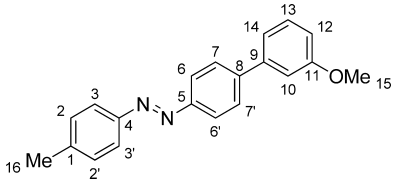
4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 2-bromo-5-furaldehyde (97.5 mg, 0.557 mmol), $[Pd(PPh_3)_4]$ (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 16 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The product was purified by column chromatography with DCM as eluent. The solvent was evaporated, and an orange solid (155 mg, 73%) was obtained. Mp: 163 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 9.67 (s, 1 H, H-13) 7.98 (m, 4 H, H-6,6′,7,7′), 7.85 (d, ^3J = 8.2 Hz, 2 H,H- 3,3′), 7.38−7.34 (m, 3 H, 2, 2′, H-11), 6.99 (d, ^3J = 3.7 Hz, 1 H, H-12), 2.45 (s, 3 H, H-14) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 177.3 (*C-13*), 158.4 (*C-9*), 153.0 (*C-12*), 152.7 (*C-5*), 150.9 (*C-4*), 142.5 (*C-1*), 131.0 (C-8), 129.0 (*C-2, 2′*), 127.9 (C-11), 126.0 (*C-7, 7′*), 123.5 (*C-6, 6′*), 123.1 (*C-3, 3′*), 109.1 (*C-10*), 21.4 (*C-15*) ppm. IR (ATR): 3137 (w), 3057 (w), 2922 (w), 2852 (w), 1683 (s), 1477 (s), 1257 (s), 1151 (s), 1104 (s), 1040 (s), 966 (s), 815 (s), 546 (m), 529 (m) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + Na]^+$ calcd for $[C_{18}H_{14}N_2O_2 + Na]^+$ 313.0947, found 313.0956.

*4-(5-Methylcarboxylate-2-furanyl)-4′-methylazobenzene (**27**).*



4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 5-bromo-2-furancarboxylic acid methyl ester (114 mg, 0.557 mmol), $[Pd(PPh_3)_4]$ (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 14 h. After the reaction mixture had cooled to 20 °C, chloroform (40 mL) was added, and the mixture was extracted with water (3 × 150 mL). The combined organic phases were dried over sodium sulfate. The product was purified by column chromatography with toluene as eluent. The solvent was evaporated, and an orange solid (185 mg, 84%) was obtained. Mp: 161 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.98 (d, ^3J = 8.8 Hz, 2 H, H-7, 7′), 7.93 (d, ^3J = 8.8 Hz, 2 H, H-6, 6′), 7.85 (d, ^3J = 8.3 Hz, 2 H, H-3, 3′), 7.35 (d, ^3J = 8.3 Hz, 2 H, H 2, 2′), 7.28 (d, ^3J = 3.6 Hz, 1 H, H-11), 6.90 (d, ^3J = 3.6 Hz, 1 H, H-10), 3.91 (s, 3 H, H-14), 2.45 (s, 3 H, H-15) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 159.3 (*C-13*), 156.98 (*C-12*), 152.9 (*C-8*), 151.2 (*C-4*), 144.7 (*C-9*), 142.6 (*C-1*), 131.8 (*C-5*), 130.2 (*C-2, 2′*), 125.8 (*C-7, 7′*), 123.7 (*C-6, 6′*), 123.4 (*C-3, 3′*), 120.3 (*C-11*), 108.6 (*C-10*), 52.2 (*C-14*), 21.6 (*C-15*) ppm. IR (ATR): 3403 (w), 3243 (w), 3122 (w), 3034 (w), 2954 (m), 2848 (2), 1703 (s), 1527 (m), 1299 (s) 1133 (s), 1027 (m), 992 (m), 923 (m), 808 (s), 759 (s), 553 (s) cm^{-1}. HRMS (ESI-FTMS) *m/z*: $[M + Na]^+$ calcd for $[C_{19}H_{16}N_2O_3 + Na]^+$ 343.1053, found 343.1062.

*4-(3-Methoxyphenyl-) 4′-methylazobenzene (**31**).*



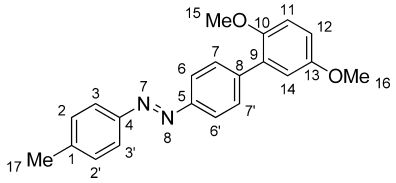
Method A. 4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 1-bromo-5-methoxybenzene (104 mg, 0.557 mmol), $[Pd(PPh_3)_4]$ (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 19 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The solvent was evaporated, and the crude product was purified by column chromatography with toluene as solvent. An orange solid (133 mg, 79%) was obtained.

Method B. 4-Methyl-4′-(tri-*n*-butylstannyl)azobenzene (270 mg, 0.557 mmol), 1-bromo-5-methoxybenzene (104 mg, 0.557 mmol), $[Pd(PPh_3)_4]$ (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 25 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The solvent was evaporated. The crude product was purified by Kugelrohr distillation (150 °C, 9.74 × 10^{-2} mbar) for 30 min. The residue was purified by column chromatography. An orange solid (91 mg, 54%) was obtained. Mp: 81 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.99 (d, ^3J = 8.7 Hz, 2 H, H-6, 6′), 7.87 (d, ^3J = 8.1 Hz, 2 H, H - 3, 3′), 7.78 (d, ^3J = 8.7 Hz, 1 H, H-7, 7′), 7.40 (t, ^3J = 7.9 Hz, 1 H, H-13), 7.36 (d, ^3J = 8.1 Hz,

dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719−1728

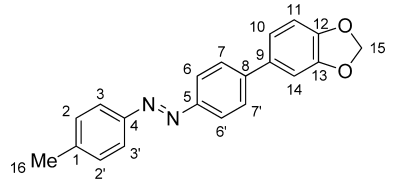
2 H, H-2, 2′), 7.28 (ddd, J = 8.2, 2.6, 0.9 Hz, 1 H, H-14), 7.22 (dd, J = 2.6 Hz, 0.9 Hz, 1 H, H-10), 6.95 (ddd, J = 8.2, 2.6, 0.9 Hz, 1 H, H-12), 3.88 (s, 3 H, H-15), 2.46 (s, 3 H, H-16) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 160.6 (*C*-11), 152.3 (*C*-5), 151.3 (*C*-4), 143.7 (*C*-8), 142.7 (*C*-1), 142.0 (*C*-9), 130.3 (C-10), 130.2 (*C*-13), 128.2 (*C*-7, 7′), 123.6 (*C*-6, 6′), 123.2 (*C*-3, 3′), 120.0 (C-2,2′), 113.7 (*C*-12), 113.2 (*C*-10), 55.7 (C-15), 21.6 (*C*-16) ppm. IR (ATR): 3080 (w), 3009 (w), 2947 (m), 2844 (m), 1925 (w), 1598 (s), 1583 (s), 1480 (s), 1295 (s), 1213 (s), 1152 (s), 1023 (s), 846 (s), 836 (s), 823 (s) 780 (s), 736 (m), 692 (s)545 (s) cm^{-1}. HRMS (CI-sector) m/z: [M + H]$^+$ calcd for [$C_{20}H_{18}N_2O$ + H]$^+$ 303.1497, found 303.1500.

*4-(2,5-Methoxyphenyl)-4′-methylazobenzene (**32**).*



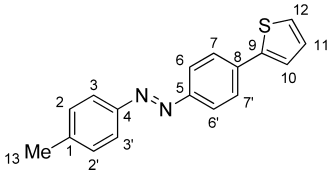
4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 1-bromo-2,5-dimethoxybenzene (120 mg, 0.557 mmol), [Pd(PPh$_3$)$_4$] (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 26 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The crude product was purified by column chromatography with toluene as solvent. The solvent was evaporated, and an orange solid (137 mg, 74%) was obtained. Mp: 74 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.94 (d, ^3J = 8.7 Hz, 2 H, H-6, 6′), 7.86 (d, ^3J = 8.3 Hz, 2 H, H-3, 3′), 7.70 (d, ^3J = 8.7 Hz, 2 H, H-7, 7′), 7.36 (d, ^3J = 8.3 Hz, 2 H, H-2, 2′), 6.98 (d, ^3J = 8.9 Hz, 1 H, H-11), 6.97 (d, ^4J = 2.9 Hz, 1 H, H-14), 6.91 (dd, J = 8.9, 3.2 Hz, 1 H, H-12), 3.82 (s, 3 H, H-15), 3.79 (s, 3 H, H-16), 2.46 (s, 3 H, H-17) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 154.7 (*C*-10), 152.3 (*C*-5), 151.3 (*C*-13), 151.2 (*C*-4), 142.6 (*C*-1), 142.0 (*C*-8), 131.1 (*C*-7, 7′), 130.6 (*C*-2, 2′), 130.2 (C-9), 123.6 (*C*-3, 3′), 123.1 (*C*-6, 6′), 117.3 (*C*-14), 114.5 (*C*-12), 113.6 (*C*-11), 57.0 (*C*-15), 56.6 (*C*-16), 22.0 (*C*-17) ppm. IR (ATR): 3093 (w), 3001 (w), 2954 (m), 2830 (m), 1593 (m), 1488 (s), 1459 (s), 1296 (m), 1208 (s), 1178 (s), 1023 (s), 1010 (s), 852 (s), 811 (s), 727 (s). HRMS (CI-sector) m/z: [M + H]$^+$ calcd for [$C_{21}H_{20}N_2O_2$ + H]$^+$ 333.1603, found 333.1604.

*4-(5-1,3-Benzodioxolyl)-4′-methylazobenzene (**33**).*



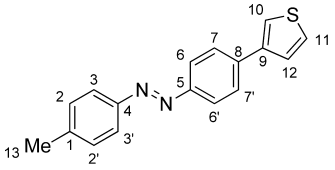
4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 5-bromo-1,3-benzodioxole (112 mg, 0.557 mmol), [Pd(PPh$_3$)$_4$] (12.9 mg, 0.011 mmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 24 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with water (3 × 150 mL). The combined organic phases were dried over sodium sulfate. The crude product was purified by column chromatography with toluene as solvent. A red solid (123 mg, 70%) was obtained. Mp: 144 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.95 (d, ^3J = 8.5 Hz, 2 H, 6,6′), 7.84 (d, ^3J = 8.2 Hz, 2 H, 3,3′), 7.69 (d, ^3J = 8.5 Hz, 2 H, 7,7′), 7.35 (d, ^3J = 8.2 Hz, 2 H, 2,2′), 7.19–7.16 (m, 2 H, H-11, 14), 6.84 (d, ^3J = 7.8 Hz, 1 H, H-10), 6.03 (s, 2 H, H-15), 2.45 (s, 3 H, H-16) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 151.7 (*C*-5), 151.0 (*C*-4), 148.5 (*C*-12), 147.9 (*C*-13), 143.3 (*C*-8), 141.9 (*C*-1), 134.5 (*C*-9), 129.9 (*C*-2, 2′), 127.5 (*C*-7, 7′), 123.3 (*C*-3, 3′), 122.9 (*C*-6, 6′), 121.0 (*C*-11), 108.7 (*C*-10), 107.5 (*C*-14), 101.7 (*C*-15), 21.4 (*C*-16) ppm. IR (ATR): 3022 (w), 2912 (w), 2859 (w), 2720 (w), 1920 (w), 1696 (m), 1477 (m), 1242 (m), 1307 (m), 823 (s), 731 (m), 547 (m) cm^{-1}. HRMS (CI-sector) m/z: [M + H]$^+$ calcd for [$C_{20}H_{16}N_2O_2$ + H]$^+$ 317.1290, found 317.1291.

*4-(2-Thiophene-yl)-4′-methylazobenzene (**35**).*



4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 2-bromothiophene (90.8, 0.557 mmol), [Pd(PPh$_3$)$_4$] (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 11 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The crude product was dissolved in DCM and filtered through a short plug of silica. The solvent was evaporated and dried at 5 × 10^{-2} mbar for 19 h. An orange solid (173 mg, 88%) was obtained. Mp: 153 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.93 (d, J = 8.7 Hz, 2 H, H-6,6′), 7.84 (d, J = 8.2 Hz, 1H, H-3, 3′), 7.78 (d, J = 8.7 Hz, 2 H, H-7, 7′), 7.46 (dd, J = 3.6, 1.1 Hz, 1 H, H-10), 7.38 (dd, J = 5.1, 1.1 Hz, 1 H, H-12), 7.35 (d, J = 8.2 Hz, 1H, H- 2,2′), 7.14 (dd, J = 5.1, 3.6 Hz, 1 H, H-11), 2.45 (s, 3 H, H-13) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 152.1 (*C*-5), 151.2 (*C*-4), 143.8 (*C*-9), 142.3 (*C*-1), 137.0 (*C*-8), 130.2 (*C*-2), 128.8 (*C*-11), 126.7 (*C*-7), 126.3 (*C*-12), 124.5 (*C*-10), 123.8 (*C*-6), 123.2 (*C*-3), 21.6 (*C*-13) ppm. IR (ATR): 3104 (w), 3027 (w), 2914 (m), 2856 (m), 1928 (w), 1735 (m), 1598 (m), 1157 (m), 1110 (m), 1011 (m), 846 (s), 824 (s), 780 (s), 728 (s), 690 (m), 531 (s) cm^{-1}. HRMS (CI-sector) m/z: [M + H]$^+$ calcd for [$C_{17}H_{14}N_2S$ + H]$^+$ 279.0956, found 279.0953.

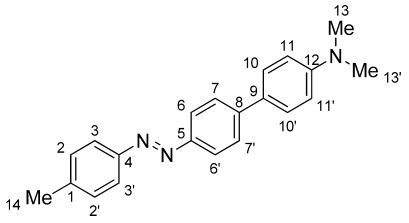
*4-(3-Thiophene-yl)-4′-methylazobenzene (**37**).*



4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 3-bromothiophene (90.8 mg, 0.557 mmol), [Pd(PPh$_3$)$_4$] (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 14 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The crude product was dissolved in DCM (5 mL) and filtered through a short plug of silica. The solvent was evaporated, and the product was dried at 5 × 10^{-2} mbar for 21 h. An orange solid (164 mg, 83%) was obtained. Mp: 178 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.95 (d, J = 8.7 Hz, 2 H, H-6, 6′), 7.84 (d, J = 8.1 Hz, 2 H, H-3, 3′), 7.78 (d, J = 8.7 Hz, 2 H, H-7, 7′), 7.62 (dd, J = 2.9, 1.4 Hz, 1 H, H-10), 7.50 (dd, J = 5.0, 1.4 Hz, 1 H, H-11), 7.46 (dd, J = 5.0, 2.9 Hz, 1 H, H-12), 7.35 (d, J = 8.1 Hz, 2 H, H-2, 2′), 2.45 (s, 3 H, H-13). ^{13}C NMR (125 MHz, CD_2Cl_2): 152.0 (*C*-5), 151.2 (*C*-4), 142.2 (*C*-1), 141.8 (*C*-9), 138.4 (*C*-8), 130.2 (*C*-2), 127.3 (*C*-7), 127.0 (*C*-12), 126.6 (*C*-11), 123.7 (*C*-6), 123.1 (*C*-3), 121.8 (*C*-10), 21.6 (*C*-13) ppm. IR (ATR): 3104 (w), 3027 (w), 2914 (m), 2856 (m), 1928 (w), 1735 (m), 1598 (m), 1157 (m), 1110 (m), 1011 (m), 846 (s), 824 (s), 780 (s), 728 (s), 690 (m), 531 (s) cm^{-1}. HRMS (CI-sector) m/z: [M + H]$^+$ calcd for [$C_{17}H_{14}N_2S$ + H]$^+$ 279.0956, found 279.0951.

dx.doi.org/10.1021/jo402598u | J. Org. Chem. 2014, 79, 1719–1728

*4-(4-N,N-Dimethylaminophenyl)-4′-methylazobenzene (**39**).*



4-Methyl-4′-(trimethylstannyl)azobenzene (200 mg, 0.557 mmol), 4-bromo-*N*,*N*-dimethylaniline (111 mg, 0.557 mmol), $[Pd(PPh_3)_4]$ (12.9 mg, 11.2 μmol, 2 mol %), copper chloride (165 mg, 1.67 mmol, 3 equiv), and lithium chloride (142 mg, 3.34 mmol, 6 equiv) were dissolved in DMF (15 mL). The reaction mixture was heated to 70 °C for 19 h. After the reaction mixture had cooled to 20 °C, chloroform (80 mL) was added, and the mixture was extracted with 2 M hydrochloric acid (2 × 150 mL), a saturated sodium carbonate solution (1 × 150 mL), and water (1 × 150 mL). The combined organic phases were dried over sodium sulfate. The solvent was evaporated, and the crude product was purified by column chromatography with toluene as solvent. An orange solid (126 mg, 72%) was obtained. Mp: 124 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.93 (d, ^3J = 8.6 Hz, 2 H, H-6, 6′), 7.83 (d, ^3J = 8.3 Hz, 2 H, H-3, 3′), 7.73 (d, ^3J = 8.6 Hz, 1 H, H-7, 7′), 7.60 (d, ^3J = 8.9 Hz, 2 H, H-10, 10′), 7.36 (d, ^3J = 8.0 Hz, 2 H, H-2, 2′), 7.36 (d, ^3J = 8.9 Hz, 2 H, H-11, 11′), 3.01 (s, 6 H, H-13), 2.44 (s, 3 H, H-14) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2):[2] 151.3 (C-5), 151.2 (C-4), 150.9 (C-12), 143.9 (C-8), 141.9 (C-1), 130.1 (C-2,2′), 129.7 (C-9), 128.0 (C-7,7′), 126.7 (C-10,10′), 123.6 (C-6,6′), 123.0 (C-7,7′), 112.9 (C-11,11′), 40.6 (C-13,13′), 21.6 (C-14) ppm. IR (ATR): 3031 (w), 2921 (w), 2852 (w), 2801 (w), 1591 (m), 1537 (m), 1492 (m), 1364 (m), 1286 (m), 1210 (m), 1153 (m), 950 (m), 826 (s), 812 (s) 716 (m) cm^{-1}. HRMS (CI-sector) *m*/*z*: $[M + H]^+$ calcd for $[C_{21}H_{21}N_3 + H]^+$ 316.1814, found 316.1809.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

GC calibration, purities of the compounds used, drying procedures for the solvents, and ^{1}H and ^{13}C NMR spectra for all compounds This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported by the Special Research Area 677 “Function by Switching” of the Deutsche Forschungsgemeinschaft (DFG), Project C10.

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