DOI: 10.1002/asia.200700099

Synthesis of Functionalized *o*-, *m*-, and *p*-Terphenyl Derivatives by Consecutive Cross-Coupling Reactions of Triazene-Substituted Arylboronic Esters

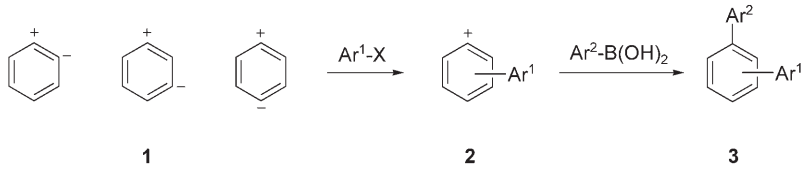
Ching-Yuan Liu, Andrey Gavryushin, and Paul Knochel*[a]

Abstract: Triazene-substituted arylboronic esters were prepared readily from the corresponding aryl magnesium derivatives and shown to function as a new class of donor–acceptor-substituted coupling reagents. The selective functionalization of these aromatic derivatives led to a wide variety of terphenyl derivatives in which the original bifunctional unit (often further substituted with another functional group) formed the central aromatic ring. The functionalized terphenyl derivatives were formed in two efficient cross-coupling steps from the triazene-substituted boronic esters: Suzuki cross-coupling with an aryl halide was followed by $BF_3{\cdot}OEt_2$-induced palladium-catalyzed coupling of the diazonium salt generated in situ from the triazene with an arylboronic acid.

Keywords: boronic esters · cross-coupling · synthetic methods · terphenyls · triazenes

Introduction

The preparation and selective transformation of bimetallic[1] aromatic and heteroaromatic reagents has become an interesting challenge in organic synthesis.[2] Many of the resulting polyfunctional oligoaryl compounds exhibit important pharmaceutical or optoelectronic properties.[3] Terphenyl derivatives have also attracted much interest from organic chemists as a result of their potential application in optical,[4] electrical,[5] and liquid-crystal[6] devices. We envisaged that aromatic derivatives represented by synthons of type **1**, which display donor and acceptor reactivity, would serve as versatile and efficient reagents for the preparation of compounds of type **2** and **3** through successive cross-coupling reactions with Ar^1–X (X = Br or I) and Ar^2–$B(OH)_2$ (Scheme 1). Herein, we describe the development of new synthetic methods for the preparation of functionalized terphenyl derivatives. Such compounds have been reported to show potent hepatoprotective activity.[7]



1 2 3

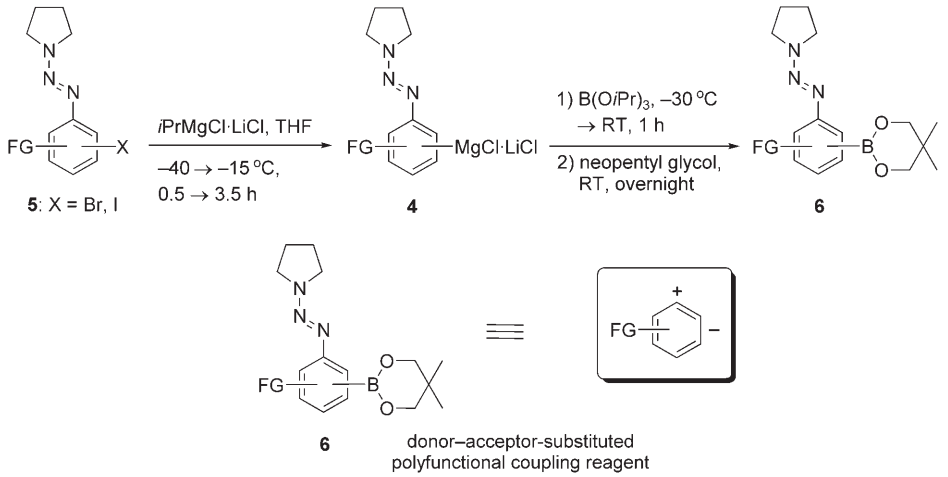
Scheme 1. Consecutive cross-coupling reactions of reagents represented by the synthons **1** to give terphenyl derivatives **3**.

Results and Discussion

Preparation of Arylboronic Esters with a Triazene Functionality

Recently, we developed a general reaction for halogen–magnesium exchange with the mixed Mg/Li reagent *i*PrMgCl·LiCl.[8] Aryl bromides and iodides undergo an efficient halogen–magnesium exchange with this reagent under very mild conditions. The exchange reaction is compatible with many functional groups, including triazenes. Accordingly, we prepared a variety of aryl magnesium reagents of type **4** from the corresponding bromo- or iodophenyl triazenes **5** (Scheme 2). Borylation of the aryl magnesium reagents **4** then gave arylboronic esters **6** with a triazene moiety. Compounds of type **6** are useful reagents for the selective func-

[a] Dr. C.-Y. Liu, Dr. A. Gavryushin, Prof. Dr. P. Knochel
Department Chemie und Biochemie
Ludwig-Maximilians-Universität München
Butenandtstrasse 5–13, Haus F, 81377 München (Germany)
Fax: (+49) 89-2180-77680
E-mail: paul.knochel@cup.uni-muenchen.de

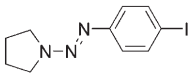
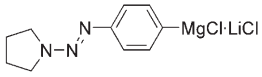
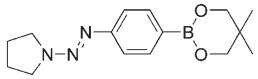
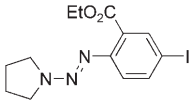
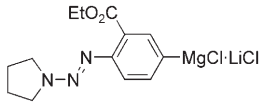
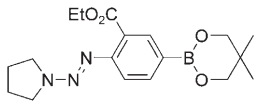
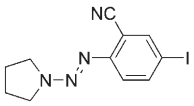
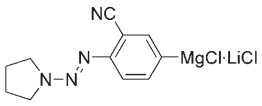
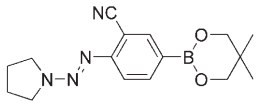
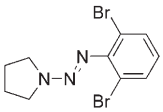
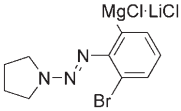
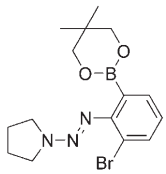
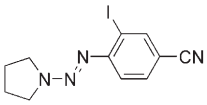
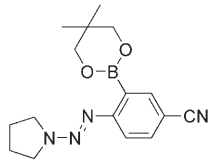
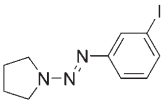
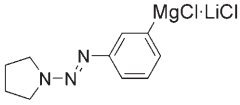
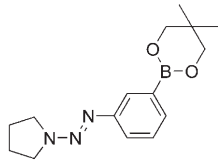


Scheme 2. Preparation of boronic esters **6** with a triazene functionality. FG = functional group.

tionalization of aromatic derivatives through two successive cross-coupling reactions.

Thus, the Grignard reagents **8a–f** prepared from the readily available bromo- or iodoaryl triazenes **7a–f** were treated with triisopropyl borate (1.2 equiv) followed by neopentyl glycol (1.25 equiv) to give the desired triazene-substituted arylboronic esters **9a–f** (55–86%; Table 1).

Table 1. Synthesis of arylboronic esters **9** with a triazene moiety by the treatment of Grignard reagents **8** with triisopropyl borate and neopentyl glycol.

Entry	7	T [°C], t [h][a]	8	9[b]	Yield [%][c]
1	 **7a**	–30, 1	 **8a**	 **9a**	86
2	 **7b**	–40, 0.5	 **8b**	 **9b**	78
3	 **7c**	–40, 0.5	 **8c**	 **9c**	83
4	 **7d**	–15, 5	 **8d**	 **9d**	55
5	 **7e**	–40, 0.7	 **8e**	 **9e**	65
6	 **7f**	–30, 1	 **8f**	 **9f**	86

[a] Temperature and reaction time for the halogen–magnesium exchange of **7**. [b] Transformation of the Grignard reagent **8** into the arylboronic ester **9**: $B(OiPr)_3$ was added to **8** at –30 °C, and the reaction mixture was warmed to room temperature, then stirred at room temperature for a further 1 h. Neopentyl glycol was then added at room temperature, and the reaction mixture was stirred overnight. [c] Yield of the analytically pure product.

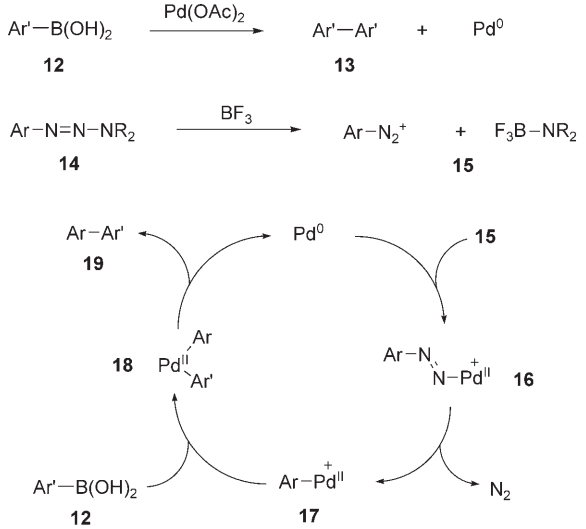
Preparation of Polyfunctional Biaryl Triazenes by Suzuki Cross-Coupling

All new triazene-substituted arylboronic esters **9** underwent Suzuki cross-coupling reactions[9] smoothly. In the absence of Lewis acids,[10] the triazene moiety is in general fairly compatible with the reaction conditions of the Suzuki coupling. Accordingly, the treatment of the boronic ester **9a** with a range of aryl bromides and iodides in the presence of $[Pd(PPh_3)_4]$ (3 mol%) and K_3PO_4 (2 equiv) in dioxane/water (10:1) at 100°C for 4–6 h furnished the expected functionalized aryl triazenes **10a–e** in 61–89% yield (Table 2, entries 1–5). The arylboronic esters **9b** and **9c**, which contain an additional functional group, also underwent efficient cross-coupling reactions with a variety of aryl halides to provide the triazenes **10f–h** (70–89%; Table 2, entries 6–8) and **10i–k** (52–72%; entries 9–11), respectively. Coupling reactions of the functionalized boronic esters **9d** and **9e**, which contain a triazene substituent in the *ortho* position, proceeded to completion in 2–6 h at 100°C to give the triazenes **10l–p** in 46–86% yield (Table 2, entries 12–16). Finally, not only arylboronic esters in which the triazene substituent is in the *para* or *ortho* position undergo successful Suzuki coupling reactions: Compound **9f** also reacted with bromomesitylene and 5-bromopyrimidine to afford the desired triazenes **10q** (62%; Table 2, entry 17) and **10r** (80%; Table 2, entry 18), respectively.

Synthesis of Polyfunctional *o*-, *m*-, and *p*-Terphenyl Derivatives from Biaryl Triazenes

On the basis of this method, we developed a new synthetic route to terphenyl derivatives. Palladium-catalyzed cross-coupling reactions of functionalized aryl triazenes **10** with arylboronic acids through $BF_3{\cdot}OEt_2$-induced decomposition of the triazene according to a procedure described by Tamao and co-workers[11] led to terphenyl derivatives **11**. Thus, the treatment of the aryl triazenes **10a**, **10e**, **10h**, and **10k** with 3-methoxybenzeneboronic acid (2 equiv) in the presence of $Pd(OAc)_2$ (10 mol%) and $BF_3{\cdot}OEt_2$ (1.5 equiv) in methanol/diethyl ether (2:1) at 0°C for 3–5 h produced the polyfunctional *p*-terphenyl derivatives **11a** (65%; Table 3, entry 1), **11b** (63%; Table 3, entry 2), **11c** (78%; Table 3, entry 3), and **11d** (72%, Table 3, entry 4). The compatibility of sensitive functional groups, such as aldehyde, ester, and nitrile groups, with the presence of a Lewis acid in these reactions was particularly encouraging. Furthermore, cross-coupling reactions of **10p** with 3-methoxybenzeneboronic acid and 4-formylbenzeneboronic acid at 0°C afforded the polyfunctional *o*-terphenyl derivatives **11e** (72%; Table 3, entry 5) and **11f** (65%; Table 3, entry 6) after 5 and 11 h, respectively. Similar coupling reactions occurred readily between the aryl triazene **10q** and both 3-methoxybenzeneboronic acid and 4-formylbenzeneboronic acid to provide the *m*-terphenyls **11g** (73%; Table 3, entry 7) and **11h** (80%; Table 3, entry 8).

A tentative mechanism for the $BF_3{\cdot}OEt_2$-induced cross-coupling reaction involves the formation of a diazonium salt **15** (Scheme 3). The reaction of $Pd(OAc)_2$ with the excess arylboronic acid **12** gives Pd^0 along with the biaryl species **13** as a by-product. Boron trifluoride induces the decomposition of the aryl triazene **14** and generates the diazonium salt **15**, which reacts with Pd^0 to form the aryl diazopalladium(II) species **16**. Following the loss of nitrogen, transmetalation of the aryl palladium(II) intermediate **17** with the arylboronic acid **12** leads to the diaryl palladium(II) species **18**, which undergoes reductive elimination to afford the product **19** and regenerate Pd^0.



Scheme 3. A plausible mechanism for the palladium-catalyzed cross-coupling reaction of aryl triazenes with arylboronic acids in the presence of $BF_3{\cdot}OEt_2$.

Conclusions

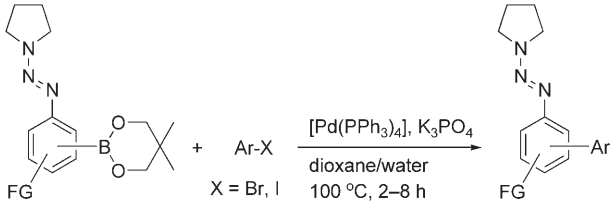
In summary, we have prepared a number of triazene-substituted arylboronic esters as a new class of donor–acceptor-substituted coupling reagents. To demonstrate the versatility of these reagents, which are readily available from the corresponding aryl magnesium species, we employed them the preparation of functionalized terphenyl derivatives. Studies toward the extension of this methodology are currently under way in our laboratories.

Experimental Section

General

All reactions were carried out under argon by using standard Schlenk techniques. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 300, Bruker AMX 600, or Varian VXR 400 S instrument. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak ([D_1]chloroform: $\delta_H = 7.24$ ppm, $\delta_C = 77.0$ ppm; [D_6]benzene: $\delta_H = 7.16$ ppm, $\delta_C = 128.0$ ppm; [D_6]acetone: $\delta_H = 2.04$ ppm, $\delta_C = 206.7$ ppm). IR spectra were recorded on a Perkin–Elmer 1420 infra-

Table 2. Synthesis of polyfunctional aryl triazenes **10** by Suzuki cross-coupling reactions of arylboronic esters **9** with aryl halides.[a]



9: FG = CO_2Et, CN, Br, H

10

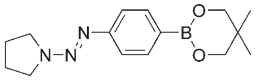
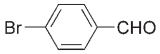
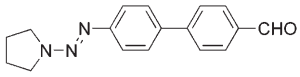
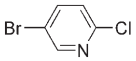
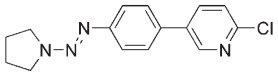
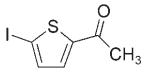
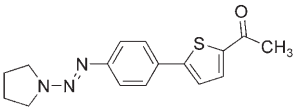
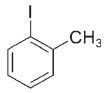
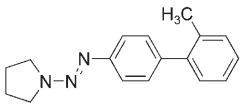
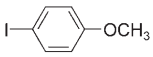
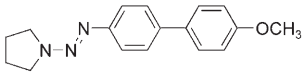
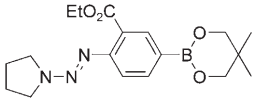
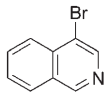
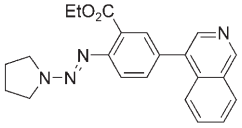
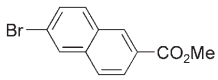
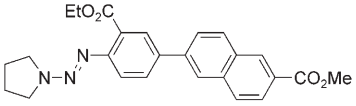
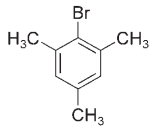
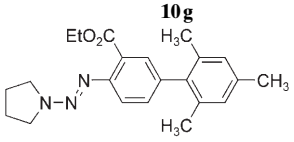
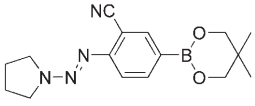
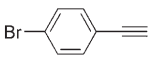
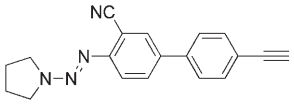
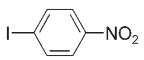
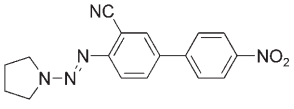
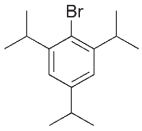
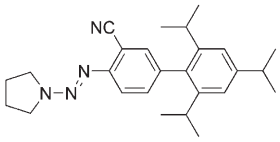
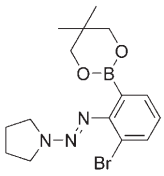
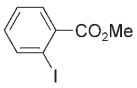
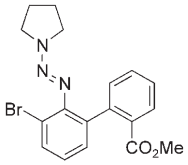
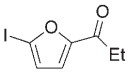
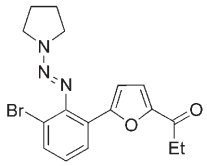
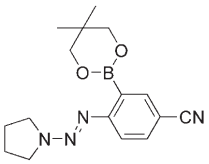
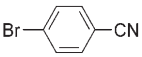
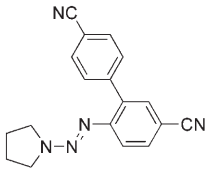
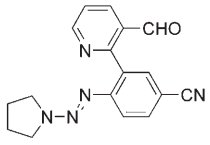
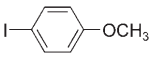
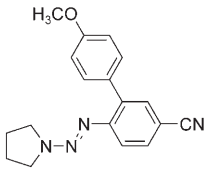
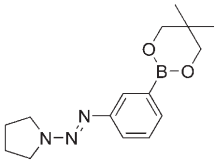
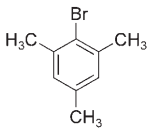
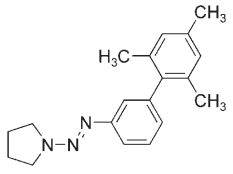
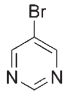
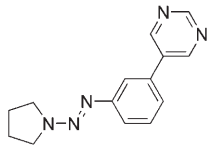
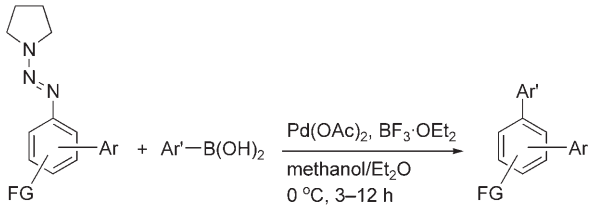
Entry	**9**	Aryl halide	Product[b]	Yield [%]
1	 **9a**		 **10a**	80
2	**9a**		 **10b**	70
3	**9a**		 **10c**	89
4	**9a**		 **10d**	75
5	**9a**		 **10e**	61
6	 **9b**		 **10f**	89
7	**9b**		 **10g**	70
8	**9b**		 **10h**	89
9	 **9c**		 **10i**	55
10	**9c**		 **10j**	72

Table 2. (Continued)

Entry	9	Aryl halide	Product[b]	Yield [%]
11	**9c**		 **10k**	52
12	 **9d**		 **10l**	54
13	**9d**		 **10m**	46
14	 **9e**		 **10n**	83
15	**9e**		 **10o**	75
16	**9e**		 **10p**	86
17	 **9f**		 **10q**	62
18	**9f**		 **10r**	80

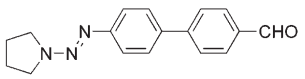
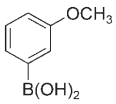
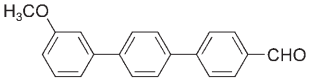
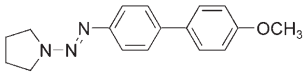
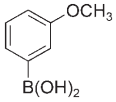
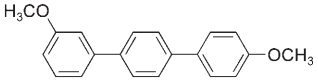
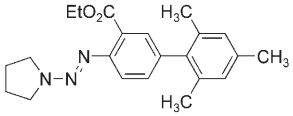
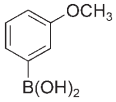
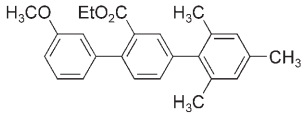
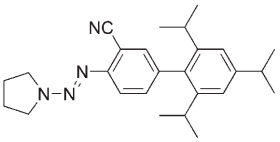
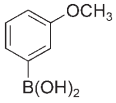
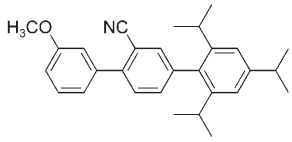
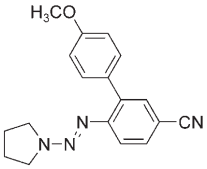
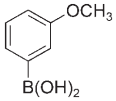
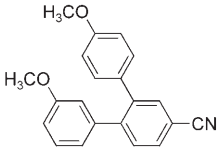
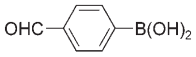
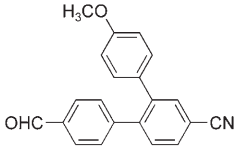
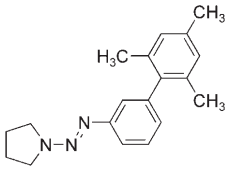
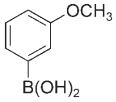
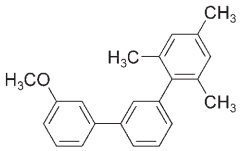
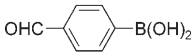
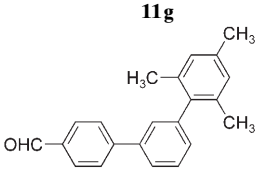
[a] Reaction conditions: **9** (1 equiv), aryl halide (1.2 equiv), $[Pd(PPh_3)_4]$ (3 mol%), K_3PO_4 (2.0 equiv), dioxane/water (10:1 *v*/*v*), 100 °C, 2–8 h. [b] Yield of the analytically pure product.

Table 3. Synthesis of polyfunctional *o*-, *m*-, *p*-terphenyl derivatives **11** by palladium-catalyzed cross-coupling reactions of aryl triazenes **10** with arylboronic acids in the presence of $BF_3{\cdot}OEt_2$.[a]



10
FG = CO_2Et, CN, Br, H

11

Entry	**10**	Arylboronic acid	Product	Yield [%][b]
1	 **10a**		 **11a**	65
2	 **10e**		 **11b**	63
3	 **10h**		 **11c**	78
4	 **10k**		 **11d**	72
5	 **10p**		 **11e**	72
6	**10p**		 **11f**	65
7	 **10q**		 **11g**	73
8	**10q**		 **11h**	80

[a] Reaction conditions: **10** (1 equiv), arylboronic acid (2 equiv), $Pd(OAc)_2$ (10 mol%), $BF_3{\cdot}OEt_2$ (1.5 equiv), methanol/diethyl ether (2:1 *v*/*v*), 0 °C, 3–12 h. [b] Yield of the analytically pure product.

red spectrometer. Mass spectra were recorded on a Finnigan MAT 95 Q spectrometer. Column chromatography was performed on Merck silica gel 60 (230–400 mesh ASTM). THF was dried with sodium/benzophenone and distilled. Reactions were monitored by gas chromatography (GC, GC–MS) or thin-layer chromatography (TLC) of hydrolyzed aliquots.

Syntheses

Typical procedure for the preparation of bromo- or iodophenyl triazenes (TP1): A solution of $NaNO_2$ (1.3 g, 19 mmol) in cold water (40 mL) was added dropwise to a solution cooled in an ice bath of the corresponding aniline (18.1 mmol) in concentrated HCl (7.2 mL). The resulting solution of the diazonium salt was stirred at 0 °C for 30 min and then added rapidly to a solution of the pyrrolidine (2.6 g, 36.2 mmol) and K_2CO_3 (12.5 g, 90.5 mmol) in acetonitrile/water (1:2, 25 mL). The reaction mixture was stirred for 30 min at 0 °C, then was extracted with CH_2Cl_2 (3×50 mL). The organic layer was washed twice with brine, dried ($MgSO_4$), filtered, and concentrated by evaporation. Purification by flash chromatography furnished the product **7b**, **7c**, or **7f**.

Typical procedure for the preparation of triazene-substituted arylboronic esters (TP2): *i*PrMgCl·LiCl (5.5 mmol, 2.0 M in THF) was added slowly to a solution of **7** (5 mmol) in THF (3.3 mL) at −40 or −15 °C, and the reaction mixture was stirred at low temperature for 0.5–5 h. When GC analysis of a hydrolyzed reaction aliquot indicated the complete conversion of **7** into the corresponding Grignard reagent, a solution of $B(OiPr)_3$ 1.4 mL, 6 mmol) in THF (1 mL) was added. The resulting mixture was stirred at low temperature for 1 h and then warmed to room temperature and stirred for a further 2 h. Neopentylglycol (650 mg, 6.25 mmol) was then added, and the reaction mixture was stirred at room temperature for 12 h. Aqueous NH_4Cl (10 mL) was then added, and the aqueous phase was extracted with CH_2Cl_2 (2×30 mL). The organic fractions were washed with brine (50 mL), dried (Na_2SO_4), and concentrated in vacuo. Purification by flash chromatography furnished the product **9**.

Typical procedure for the Suzuki cross-coupling of arylboronic esters **9** with aryl halides (TP3): The arylboronic ester **9** (1 mmol) and the aryl halide (1.2 mmol) were dissolved in dioxane/water (10:/1, 11 mL) in a nitrogen-flushed sealed tube, and then K_3PO_4 (2 mmol) and $[Pd(PPh_3)_4]$ (3 mol%) were added. The reaction mixture was stirred at 100 °C for 2–8 h and then cooled to room temperature. Aqueous NH_4Cl (25 mL) was added, and the aqueous phase was extracted with diethyl ether (3× 20 mL). The organic fractions were washed with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography furnished the aryl triazene **10**.

Typical procedure for the preparation of *o*-, *m*-, and *p*-terphenyl derivatives (TP4): $BF_3{\cdot}OEt_2$ (0.75 mmol) was added dropwise to a solution of the aryl triazene **10** (0.5 mmol), phenylboronic acid (1 mmol), and $Pd(OAc)_2$ (10 mol%) in methanol/diethyl ether (2:1, 6 mL) at 0 °C, and the resulting mixture was stirred at 0 °C for 3–12 h. When thin-layer chromatography indicated complete consumption of the aryl triazene, water (5 mL) was added, and the aqueous phase was extracted with ethyl acetate (2×10 mL). The organic fractions were washed with brine (20 mL), dried (Na_2SO_4), and concentrated in vacuo. Purification by flash chromatography furnished the product **11**.

9a: Prepared according to TP2 from 1-(4-iodophenylazo)pyrrolidine[12] (**7a**; 1.51 g, 5 mmol), *i*PrMgCl (2.8 mL, 1.1 equiv, 2.0 M in THF), $B(OiPr)_3$ (1.4 mL, 6 mmol), and neopentylglycol (650 mg, 6.25 mmol). Reaction conditions: −30 °C, 1 h; 25 °C, 2 h; 25 °C, 12 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded (4-(5,5-dimethyl-[1,3,2]dioxaborinan-2-yl)phenyl)pyrrolidin-1-yldiazene (**9a**; 1.23 g, 86%) as a white powder. M.p.: 209.0–210.5 °C; IR (KBr): $\tilde{\nu}$ = 2959 (w), 2930 (w), 2876 (w), 1699 (w), 1596 (m), 1476 (m), 1412 (m), 1391 (m), 1338 (m), 1293 (s), 1245 (s), 1154 (m), 1128 (s), 844 cm^{-1} (s); ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 3.76 (br s, 4H), 3.74 (s, 4H), 2.00 (br s, 4H), 1.00 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 153.3, 134.6, 119.5, 72.3, 31.9, 23.8, 21.9 ppm; MS (70 eV, EI): *m*/*z* (%): 287 (13) $[M]^+$, 217 (10), 189 (100), 147 (6), 121 (15), 103 (6), 69 (17); HRMS (EI): *m*/*z* calcd for $C_{15}H_{22}BN_3O_2$: 287.1805; found: 287.1810.

7b: Prepared according to TP1 from 2-carbethoxy-4-iodoaniline[13] (5.3 g, 18.1 mmol), concentrated HCl (7.2 mL), $NaNO_2$ (1.3 g, 19 mmol), pyrrolidine (2.6 g, 36.2 mmol), and K_2CO_3 (12.5 g, 90.5 mmol). Reaction conditions: 0 °C, 0.5 h; 25 °C, 0.5 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 2:1) yielded 1-(2-carbethoxy-4-iodophenylazo)-pyrrolidine (**7b**; 5.9 g, 87%) as a yellow solid. M.p.: 95.1–96.1 °C; IR (KBr): $\tilde{\nu}$ = 2976 (w), 2876 (w), 1718 (s), 1573 (w), 1467 (m), 1416 (m), 1362 (m), 1312 (w), 1225 (m), 1072 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.87 (d, J = 2.0 Hz, 1H), 7.63 (dd, J = 8.8, 2.0 Hz, 1H), 7.14 (d, J = 8.8 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.85 (br s, 2H), 3.63 (br s, 2H), 1.98 (br s, 4H), 1.32 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.9, 149.7, 140.0, 137.7, 128.2, 121.0, 87.7, 61.0, 50.9, 46.6, 23.8, 23.4, 14.2 ppm; MS (70 eV, EI): *m*/*z* (%): 373 (17) $[M]^+$, 303 (87), 247 (100), 203 (5), 148 (10), 120 (14), 75 (10); HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}IN_3O_2$: 373.0287; found: 373.0245.

9b: Prepared according to TP2 from **7b** (373 mg, 1 mmol), *i*PrMgCl (0.55 mL, 1.1 equiv, 2.0 M in THF), $B(OiPr)_3$ (0.28 mL, 1.2 mmol), and neopentylglycol (130 mg, 1.25 mmol). Reaction conditions: −40 °C, 0.5 h; 25 °C, 2 h; 25 °C, 12 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:2) yielded 5-(5,5-dimethyl[1,3,2]dioxaborinan-2-yl)-2-(pyrrolidin-1-ylazo)benzoic acid ethyl ester (**9b**; 280 mg, 78%) as a brown solid. M.p.: 142.6–143.7 °C; IR (KBr): $\tilde{\nu}$ = 2959 (m), 1716 (s), 1599 (m), 1483 (m), 1469 (s), 1310 (s), 1263 (s), 1125 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.02 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 4.30 (q, J = 7.5 Hz, 2H), 4.00–3.40 (br s, 4H), 3.73 (s, 4H), 1.98 (br s, 4H), 1.33 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 168.8, 151.9, 136.8, 135.1, 125.8, 118.3, 72.2, 60.6, 48.2, 46.3, 31.8, 23.72, 23.70, 21.9, 14.3 ppm; MS (70 eV, EI): *m*/*z* (%): 359 (4) $[M]^+$, 314 (3), 289 (14), 261 (49), 233 (100), 217 (8), 147 (9), 131 (19), 69 (12); HRMS (EI): *m*/*z* calcd for $C_{18}H_{26}BN_3O_4$: 359.2016; found: 359.2022.

7c: Prepared according to TP1 from 2-cyano-4-iodoaniline[13] (4.4 g, 18.1 mmol), concentrated HCl (7.2 mL), $NaNO_2$ (1.3 g, 19 mmol), pyrrolidine (2.6 g, 36.2 mmol), and K_2CO_3 (12.5 g, 90.5 mmol). Reaction conditions: 0 °C, 0.5 h; 25 °C, 0.5 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 2:1) yielded 1-(2-cyano-4-iodophenylazo)pyrrolidine (**7c**; 5.5 g, 93%) as a pale-brown solid. M.p.: 143.7–144.9 °C; IR (KBr): $\tilde{\nu}$ = 3064 (w), 2970 (w), 2871 (w), 2222 (m), 1410 (s), 1380 (s), 1312 (s), 1274 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.84 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 3.60–4.04 (m, 4H), 2.03 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.5, 141.8, 140.9, 118.9, 116.4, 109.0, 86.6, 51.4, 47.3, 23.9, 23.3 ppm; MS (70 eV, EI): *m*/*z* (%): 326 (17) $[M]^+$, 256 (84), 228 (100), 207 (9), 126 (10), 101 (61), 70 (21); HRMS (EI): *m*/*z* calcd for $C_{11}H_{11}IN_4$: 326.0028; found: 326.0055.

9c: Prepared according to TP2 from **7c** (326 mg, 1 mmol), *i*PrMgCl (0.55 mL, 1.1 equiv, 2.0 M in THF), $B(OiPr)_3$ (0.28 mL, 1.2 mmol), and neopentylglycol (130 mg, 1.25 mmol). Reaction conditions: −40 °C, 0.5 h; 25 °C, 2 h; 25 °C, 12 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:2) yielded 5-(5,5-dimethyl[1,3,2]dioxaborinan-2-yl)-2-(pyrrolidin-1-ylazo)benzonitrile (**9c**; 259 mg, 83%) as a yellow solid. M.p.: 139.7–141.3 °C; IR (KBr): $\tilde{\nu}$ = 2964 (m), 2877 (w), 2222 (m), 1597 (m), 1558 (w), 1480 (m), 1406 (s), 1376 (m), 1312 (s), 1270 (s), 1127 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.01 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 4.04–3.66 (m, 4H), 3.73 (s, 4H), 2.12–1.92 (m, 4H), 1.00 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 155.3, 139.1, 138.3, 118.3, 116.2, 106.7, 72.3, 51.3, 47.1, 31.9, 23.9, 23.4, 21.8 ppm; MS (70 eV, EI): *m*/*z* (%): 312 (15) $[M]^+$, 242 (42), 214 (99), 172 (45), 158 (9), 146 (30), 128 (20), 102 (12), 69 (100), 56 (13); HRMS (EI): *m*/*z* calcd for $C_{16}H_{21}BN_4O_2$: 312.1758; found: 312.1745.

9d: Prepared according to TP2 from 1-(2,6-dibromophenylazo)pyrrolidine[12] (**7d**; 333 mg, 1 mmol), *i*PrMgCl (0.55 mL, 1.1 equiv, 2.0 M in THF), $B(OiPr)_3$ (0.28 mL, 1.2 mmol), and neopentylglycol (130 mg, 1.25 mmol). Reaction conditions: −40 to −15 °C, 5 h; 25 °C, 2 h; 25 °C, 12 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded (2-bromo-6-(5,5-dimethyl-[1,3,2]dioxaborinan-2-yl)phenyl)pyrrolidin-1-yldiazene (**9d**; 201 mg, 55%) as a brown solid. M.p.: 103.5–104.2 °C; IR (KBr): $\tilde{\nu}$ = 3048 (w), 2962 (w), 2931 (w), 2872 (w), 1476 (m), 1424 (m), 1396 (s), 1359 (m), 1314 (s), 1244 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.53 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz,

1H), 6.95 (t, $J=7.6$ Hz, 1H), 3.80 (br s, 4H), 3.66 (s, 4H), 2.01 (br s, 4H), 1.03 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=151.4$, 133.5, 131.4, 125.8, 119.0, 72.5, 51.3, 47.1, 31.7, 23.8, 22.0 ppm; MS (70 eV, EI): m/z (%): 365 (5) $[M]^+$, 295 (26), 267 (22), 225 (22), 199 (19), 183 (17), 146 (15), 69 (100), 41 (27); HRMS (EI): m/z calcd for $C_{15}H_{21}BBrN_3O_2$: 365.0910; found: 365.0899.

9e: Prepared according to TP2 from 1-(4-cyano-2-iodophenylazo)pyrrolidine[12] (**7e**) (326 mg, 1 mmol), *i*PrMgCl (0.55 mL, 1.1 equiv, 2.0 M in THF), $B(OiPr)_3$ (0.28 mL, 1.2 mmol), and neopentylglycol (130 mg, 1.25 mmol). Reaction conditions: −40 °C, 0.7 h; 25 °C, 2 h; 25 °C, 12 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:3) yielded 3-(5,5-dimethyl[1,3,2]dioxaborinan-2-yl)-4-(pyrrolidin-1-ylazo)-benzonitrile (**9e**; 203 mg, 65%) as a brown solid. M.p.: 146.2–148.1 °C; IR (KBr): $\tilde{\nu}=2950$ (m), 2833 (w), 2225 (m), 1600 (m), 1550 (w), 1425 (s), 1366 (m), 1305 (s), 1115 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=$ 7.67 (s, 1H), 7.46 (d, $J=8.4$ Hz, 1H), 7.36 (d, $J=8.4$ Hz, 1H), 4.10–3.55 (m, 8H), 1.97 (br s, 4H), 0.99 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=158.1$, 137.1, 133.8, 133.4, 120.2, 107.7, 73.0, 51.9, 47.3, 32.2, 24.3, 24.0, 22.3 ppm; MS (70 eV, EI): m/z (%): 312 (17) $[M]^+$, 242 (40), 214 (96), 172 (43), 146 (30), 128 (25), 102 (11), 69 (100); HRMS (EI): m/z calcd for $C_{16}H_{21}BN_4O_2$: 312.1758; found: 312.1750.

7f: Prepared according to TP1 from 3-iodoaniline (3.9 g, 18.1 mmol), concentrated HCl (7.2 mL), $NaNO_2$ (1.3 g, 19 mmol), pyrrolidine (2.6 g, 36.2 mmol), and K_2CO_3 (12.5 g, 90.5 mmol). Reaction conditions: 0 °C, 0.5 h; 25 °C, 0.5 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 2:1) yielded 1-(3-iodophenylazo)pyrrolidine (**7f**; 5.2 g, 95%) as a brown solid. M.p.: 45.8–46.9 °C; IR (KBr): $\tilde{\nu}=3058$ (w), 2961 (w), 2874 (w), 1580 (m), 1554 (m), 1393 (s), 1309 (s), 1152 (w), 986 cm^{-1} (w); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=7.77$ (s, 1H), 7.41 (d, $J=7.4$ Hz, 1H), 7.33 (d, $J=7.4$ Hz, 1H), 7.01 (t, $J=7.4$ Hz, 1H), 3.76 (br s, 4H), 2.06–1.94 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=152.7$, 133.7, 130.3, 128.8, 120.3, 94.5, 51.2, 46.5, 23.8 ppm; MS (70 eV, EI): m/z (%): 301 (15) $[M]^+$, 231 (65), 203 (100), 76 (12); HRMS (EI): m/z calcd for $C_{10}H_{12}IN_3$: 301.0076; found: 301.0093.

9f: Prepared according to TP2 from **7f** (1.51 g, 5 mmol), *i*PrMgCl (2.8 mL, 1.1 equiv, 2.0 M in THF), $B(OiPr)_3$ (1.4 mL, 6 mmol), and neopentylglycol (650 mg, 6.25 mmol). Reaction conditions: −30 °C, 1 h; 25 °C, 2 h; 25 °C, 12 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded (3-(5,5-dimethyl[1,3,2]dioxaborinan-2-yl)phenyl)pyrrolidin-1-yldiazene (**9f**; 1.23 g, 86%) as a brown solid. M.p.: 145.9–147.6 °C; IR (KBr): $\tilde{\nu}=2953$ (w), 2874 (w), 1479 (m), 1396 (m), 1293 (s), 1121 (s), 918 cm^{-1} (w); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta=7.83$ (s, 1H), 7.75 (d, $J=7.5$ Hz, 1H), 7.45 (d, $J=7.5$ Hz, 1H), 7.30 (t, $J=7.5$ Hz, 1H), 3.90–3.60 (m, 4H), 3.75 (s, 4H), 2.01–1.95 (m, 4H), 1.00 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=150.7$, 130.6, 128.1, 125.6, 122.9, 72.2, 50.1, 47.0, 31.8, 23.8, 21.9 ppm; MS (70 eV, EI): m/z (%): 287 (14) $[M]^+$, 258 (11), 217 (11), 203 (7), 189 (100), 147 (21), 133 (13), 121 (46), 103 (27); HRMS (EI): m/z calcd for $C_{15}H_{22}BN_3O_2$: 287.1805; found: 287.1813.

10a: Prepared according to TP3 from **9a** (287 mg, 1 mmol), 4-bromobenzaldehyde (222 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100 °C, 5 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 3:2) yielded 4′-(pyrrolidin-1-ylazo)biphenyl-4-carbaldehyde (**10a**; 223 mg, 80%) as a yellow solid. M.p.: 144.5–145.5 °C; IR (KBr): $\tilde{\nu}=2958$ (w), 2881 (w), 2808 (w), 2728 (w), 1694 (vs), 1592 (vs), 1487 (m), 1386 (s), 1153 (m), 818 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=10.01$ (s, 1H), 7.90 (d, $J=8.5$ Hz, 2H), 7.74 (d, $J=8.3$ Hz, 2H), 7.60 (d, $J=8.3$ Hz, 2H), 7.49 (d, $J=8.5$ Hz, 2H), 3.80 (br s, 4H), 2.08–1.96 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=191.9$, 151.7, 147.0, 135.9, 134.7, 130.2, 127.8, 127.1, 120.9, 71.7, 23.8 ppm; MS (70 eV, EI): m/z (%): 279 (18) $[M]^+$, 209 (30), 181 (95), 152 (100), 127 (10); HRMS (EI): m/z calcd for $C_{17}H_{17}N_3O$: 279.1372; found: 279.1381.

10b: Prepared according to TP3 from **9a** (287 mg, 1 mmol), 5-bromo-2-chloropyridine (230 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100 °C, 6 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 3:2) yielded (4-(6-chloropyridin-3-yl)phenyl)pyrrolidin-1-yldiazene (**10b**; 201 mg, 70%) as a yellow solid. M.p.: 157.0–159.5 °C; IR (KBr): $\tilde{\nu}=3032$ (w), 2972 (w), 2866 (w), 1601 (w), 1447 (m), 1399 (s), 1316 (s), 1222 (m), 1101 (s), 998 cm^{-1} (m); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta=8.59$ (d, $J=2.6$ Hz, 1H), 7.81 (dd, $J=8.4$, 2.6 Hz, 1H), 7.49 (s, 4H), 7.34 (d, $J=8.4$ Hz, 1H), 3.80 (br s, 4H), 2.02 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=151.7$, 149.7, 147.6, 136.7, 135.5, 132.8, 127.4, 124.1, 121.1, 51.0, 46.3, 23.8 ppm; MS (70 eV, EI): m/z (%): 286 (23) $[M]^+$, 216 (31), 188 (100), 153 (40), 126 (11); HRMS (EI): m/z calcd for $C_{15}H_{15}ClN_4$: 286.0985; found: 286.0987.

10c: Prepared according to TP3 from **9a** (287 mg, 1 mmol), 5-acetyl-2-iodothiophene (302 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100 °C, 3 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 2:3) yielded 1-(5-(4-(pyrrolidin-1-ylazo)phenyl)thiophen-2-yl)ethanone (**10c**; 201 mg, 70%) as a yellow solid. M.p.: 171.8–173.8 °C; IR (KBr): $\tilde{\nu}=3002$ (w), 2920 (w), 2844 (w), 1698 (vs), 1582 (s), 1478 (m), 1436 (m), 1398 (m), 1296 (s), 1216 (s), 1034 cm^{-1} (m); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta=7.62$ (d, $J=$ 4.0 Hz, 1H), 7.59 (d, $J=8.4$ Hz, 2H), 7.43 (d, $J=8.4$ Hz, 2H), 7.26 (d, $J=$ 4.0 Hz, 1H), 3.79 (br s, 4H), 2.53 (s, 3H), 2.02 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=190.4$, 153.2, 142.3, 134.7, 133.5, 129.9, 126.8, 123.1, 120.9, 51.0, 47.1, 26.5, 23.7 ppm; MS (70 eV, EI): m/z (%): 299 (40) $[M]^+$, 229 (27), 201 (100), 186 (8), 158 (16), 115 (7); HRMS (EI): m/z calcd for $C_{16}H_{17}N_3OS$: 299.1092; found: 299.1089.

10d: Prepared according to TP3 from **9a** (287 mg, 1 mmol), 2-iodotoluene (262 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100 °C, 4 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded (2′-methylbiphenyl-4-yl)pyrrolidin-1-yldiazene (**10d**; 199 mg, 75%) as a brown solid. M.p.: 60.0–61.8 °C; IR (KBr): $\tilde{\nu}=2962$ (m), 2864 (m), 1600 (w), 1478 (m), 1392 (m), 1316 (m), 1155 (m), 1032 (m), 943 cm^{-1} (w); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta=7.46$ (d, $J=8.4$ Hz, 2H), 7.29 (d, $J=8.4$ Hz, 2H), 7.27–7.21 (m, 4H), 3.82 (br s, 4H), 2.30 (s, 3H), 2.04 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=150.2$, 141.8, 138.7, 135.4, 130.3, 129.8, 129.7, 128.5, 128.4, 127.0, 125.7, 120.0, 71.7, 67.1, 23.8, 21.3, 20.5 ppm; MS (70 eV, EI): m/z (%): 265 (27) $[M]^+$, 195 (33), 167 (100), 152 (44), 115 (5); HRMS (EI): m/z calcd for $C_{17}H_{19}N_3$: 265.1579; found: 265.1575.

10e: Prepared according to TP3 from **9a** (287 mg, 1 mmol), 4-iodoanisole (281 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100 °C, 6 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 4:1) yielded (4′-methoxybiphenyl-4-yl)pyrrolidin-1-yldiazene (**10e**; 171 mg, 61%) as a pale-yellow solid. M.p.: 121.8–124.0 °C; IR (KBr): $\tilde{\nu}=3032$ (w), 2968 (w), 2871 (w), 1605 (m), 1490 (s), 1396 (s), 1319 (s), 1184 (m), 1030 (m), 905 cm^{-1} (w); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta=7.55$–7.49 (m, 4H), 7.45 (d, $J=$ 8.4 Hz, 2H), 6.95 (d, $J=8.8$ Hz, 2H), 3.83 (s, 3H), 3.79 (br s, 4H), 2.01 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=158.8$, 150.2, 137.5, 133.6, 127.8, 127.0, 120.6, 114.1, 67.0, 55.3, 23.8 ppm; MS (70 eV, EI): m/z (%): 281 (38) $[M]^+$, 211 (14), 183 (100), 168 (22), 152 (10), 140 (12); HRMS (EI): m/z calcd for $C_{17}H_{19}N_3O$: 281.1582; found: 281.1503.

10f: Prepared according to TP3 from **9b** (359 mg, 1 mmol), 4-bromoisoquinoline (250 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100 °C, 6 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:4) yielded 5-isoquinolin-4-yl-2-(pyrrolidin-1-ylazo)benzoic acid ethyl ester (**10f**; 318 mg, 85%) as a yellow liquid. IR (KBr): $\tilde{\nu}=2973$ (m), 2870 (m), 1718 (vs), 1620 (m), 1568 (m), 1406 (s), 1312 (m), 1238 (m), 1073 (m), 895 cm^{-1} (m); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta=9.22$ (s, 1H), 8.47 (s, 1H), 8.01 (d, $J=$ 8.4 Hz, 1H), 7.90 (d, $J=8.4$ Hz, 1H), 7.74 (s, 1H), 7.66 (t, $J=8.0$ Hz, 1H), 7.61 (t, $J=8.0$ Hz, 1H), 7.57–7.50 (m, 2H), 4.34 (q, $J=7.1$ Hz, 2H), 3.94 (br s, 2H), 3.72 (br s, 2H), 2.04 (br s, 4H), 1.34 ppm (t, $J=7.1$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=168.3$, 152.0, 149.9, 142.7, 134.2, 133.1, 133.0, 132.4, 130.8, 130.7, 128.4, 127.9, 127.2, 126.6, 124.7, 119.6, 61.0, 51.2, 46.6, 23.3, 20.9, 14.3 ppm; MS (70 eV, EI): m/z (%): 374 (15) $[M]^+$, 304 (30), 277 (68), 248 (100), 232 (38), 220 (13), 204 (32), 177 (12); HRMS (EI): m/z calcd for $C_{22}H_{22}N_4O_2$: 374.1743; found: 374.1759.

10g: Prepared according to TP3 from **9b** (359 mg, 1 mmol), 4-bromoisoquinoline (250 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$

(35 mg, 3 mol%). Reaction conditions: 100°C, 6 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:4) yielded 6-(3-ethoxycarbonyl-4-(pyrrolidin-1-ylazo)phenyl)naphthalene-2-carboxylic acid methyl ester (**10g**; 318 mg, 85%) as a yellow liquid. IR (KBr): $\tilde{\nu}$ = 2955 (w), 2875 (w), 1706 (vs), 1627 (m), 1406 (m), 1311 (m), 1270 (m), 1240 (m), 1209 (s), 1136 (m), 1085 cm^{-1} (s); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 8.59 (s, 1H), 8.05 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 7.2 Hz, 2H), 7.90 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 3.96 (s, 3H), 3.92 (br s, 2H), 3.70 (br s, 2H), 2.02 (br s, 4H), 1.38 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 168.6, 167.2, 149.7, 139.8, 136.5, 135.8, 131.5, 130.7, 130.1, 129.8, 128.3, 128.2, 127.2, 126.9, 126.0, 125.7, 125.1, 119.9, 61.0, 52.2, 51.0, 46.5, 23.9, 23.6, 14.4 ppm; MS (70 eV, EI): *m/z* (%): 431 (15) $[M]^+$, 361 (19), 334 (65), 305 (100), 289 (22), 202 (25), 189 (11), 137 (13); HRMS (EI): *m/z* calcd for $C_{25}H_{25}N_3O_4$: 431.1845; found: 431.1829.

10h: Prepared according to TP3 from **9b** (359 mg, 1 mmol), 1-bromomesitylene (239 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 7 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 3:2) yielded 2′,4′,6′-trimethyl-4-(pyrrolidin-1-ylazo)biphenyl-3-carboxylic acid ethyl ester (**10h**; 263 mg, 72%) as a pale-yellow solid. IR (KBr): $\tilde{\nu}$ = 2977 (w), 2919 (w), 2873 (w), 1692 (vs), 1603 (m), 1472 (m), 1399 (s), 1235 (s), 1089 (s), 1017 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.53–7.45 (m, 2H), 7.23 (d, J = 8.8 Hz, 1H), 6.98 (s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 3.86 (br s, 4H), 2.37 (s, 3H), 2.12–2.00 (m, 10H), 1.39 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 168.3, 149.0, 137.3, 136.6, 136.1, 132.5, 130.3, 128.0, 126.6, 124.5, 119.5, 60.7, 50.8, 46.6, 23.7, 20.9, 20.7, 14.3 ppm; MS (70 eV, EI): *m/z* (%): 365 (36) $[M]^+$, 295 (20), 267 (64), 239 (100), 164 (8); HRMS (EI): *m/z* calcd for $C_{22}H_{27}N_3O_2$: 365.2103; found: 365.2130.

10i: Prepared according to TP3 from **9c** (312 mg, 1 mmol), 1-bromo-4-ethynylbenzene (217 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 5 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded 4′-ethynyl-4-(pyrrolidin-1-ylazo)biphenyl-3-carbonitrile (**10i**; 165 mg, 55%) as a yellow solid. M.p.: 145.9–148.0°C; IR (KBr): $\tilde{\nu}$ = 3258 (m), 3038 (w), 2969 (w), 2876 (w), 2214 (m), 1601 (w), 1479 (m), 1383 (s), 1309 (m), 1256 (m), 1162 (m), 1102 (m), 907 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 7.78 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 4.02–3.92 (m, 2H), 3.82–3.70 (m, 2H), 3.13 (s, 1H), 2.12–1.98 ppm (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 153.1, 139.2, 136.4, 132.7, 131.6, 131.2, 126.5, 121.4, 117.9, 117.7, 107.7, 83.3, 78.2, 51.4, 47.2, 23.9, 23.4 ppm; MS (70 eV, EI): *m/z* (%): 300 (19) $[M]^+$, 230 (23), 202 (100), 175 (32), 150 (8); HRMS (EI): *m/z* calcd for $C_{19}H_{14}N_4$: 301.1453 $[M+H]^+$; found: 301.1445.

10j: Prepared according to TP3 from **9c** (312 mg, 1 mmol), 4-iodonitrobenzene (299 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 3 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded 4′-nitro-4-(pyrrolidin-1-ylazo)biphenyl-3-carbonitrile (**10j**; 231 mg, 72%) as an orange solid. M.p.: 149.1–151.4°C; IR (KBr): $\tilde{\nu}$ = 3096 (w), 2978 (w), 2872 (w), 2224 (m), 1593 (s), 1511 (s), 1478 (m), 1383 (m), 1338 (m), 1268 (m), 1106 (m), 1030 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 8.28 (d, J = 8.8 Hz, 2H), 7.83 (s, 1H), 7.72–7.67 (m, 3H), 7.64 (d, J = 8.8 Hz, 1H), 4.02–3.96 (m, 2H), 3.81–3.75 (m, 2H), 2.13–2.01 ppm (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 154.1, 145.3, 141.1, 134.7, 131.8, 131.7, 127.3, 124.3, 118.0, 117.6, 107.6, 51.6, 47.4, 23.9, 23.4 ppm; MS (70 eV, EI): *m/z* (%): 321 (17) $[M]^+$, 251 (41), 223 (63), 206 (27), 193 (15), 177 (100), 164 (10), 150 (20); HRMS (EI): *m/z* calcd for $C_{17}H_{15}N_5O_2$: 321.1226; found: 321.1231.

10k: Prepared according to TP3 from **9c** (312 mg, 1 mmol), 2-bromo-1,3,5-triisopropylbenzene (340 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 8 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 7:3) yielded 2′,4′,6′-triisopropyl-4-(pyrrolidin-1-ylazo)biphenyl-3-carbonitrile (**10k**; 210 mg, 52%) as a pale-yellow solid. M.p.: 75.0–77.0°C; IR (KBr): $\tilde{\nu}$ = 2958 (s), 2868 (m), 2224 (m), 1606 (w), 1569 (w), 1410 (s), 1312 (s), 1271 (m), 1105 (m), 970 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 7.56 (d, J = 8.4 Hz, 1H), 7.39 (s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.03 (s, 2H), 4.00–3.94 (m, 2H), 3.81–3.75 (m, 2H), 2.91 (sept, J = 7.1 Hz, 1H), 2.56 (sept, J = 7.1 Hz, 2H), 2.12–2.00 (m, 4H), 1.28 (d, J = 7.1 Hz, 6H), 1.07 (d, J = 7.1 Hz, 6H), 1.04 ppm (d, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 152.4, 148.5, 146.6, 137.6, 134.9, 134.8, 133.8, 120.7, 118.2, 117.0, 106.9, 51.4, 47.1, 34.3, 30.3, 24.1, 24.0, 23.9, 23.5 ppm; MS (70 eV, EI): *m/z* (%): 402 (34) $[M]^+$, 232 (18), 304 (100), 289 (11), 274 (8), 262 (16), 246 (21), 227 (79), 204 (20), 190 (11); HRMS (EI): *m/z* calcd for $C_{26}H_{35}N_4$: 403.2862 $[M+H]^+$; found: 403.2850.

10l: Prepared according to TP3 from **9d** (366 mg, 1 mmol), methyl-2-iodobenzoate (314 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 2 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 3:1) yielded 3′-bromo-2′-(pyrrolidin-1-ylazo)biphenyl-2-carboxylic acid methyl ester (**10l**; 210 mg, 54%) as a yellow solid. M.p.: 75.6–77.4°C; IR (KBr): $\tilde{\nu}$ = 3064 (w), 2950 (w), 2864 (w), 1708 (vs), 1599 (m), 1406 (s), 1286 (s), 1122 (s), 1048 (m), 966 (w) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 7.80 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.02 (t, J = 7.9 Hz, 1H), 3.58 (s, 3H), 3.38 (br s, 4H), 1.84 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 168.0, 147.2, 141.0, 136.4, 132.2, 131.5, 131.4, 131.2, 129.3, 129.0, 126.6, 125.3, 117.1, 51.8, 50.7, 45.9, 23.6 ppm; MS (70 eV, EI): *m/z* (%): 387 (10) $[M]^+$, 317 (35), 289 (100), 274 (53), 210 (67), 167 (21), 139 (36); HRMS (EI): *m/z* calcd for $C_{18}H_{18}BrN_3O_2$: 387.0582; found: 387.0568.

10m: Prepared according to TP3 from **9d** (366 mg, 1 mmol), 1-(5-iodofuran-2-yl)propan-1-one (300 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 3 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded 1-(5-(3-bromo-2-(pyrrolidin-1-ylazo)phenyl)thiophen-2-yl)propan-1-one (**10m**; 173 mg, 46%) as a pale-yellow solid. M.p.: 65.6–67.9°C; IR (KBr): $\tilde{\nu}$ = 3110 (w), 2932 (w), 2871 (w), 1675 (vs), 1550 (m), 1506 (m), 1411 (s), 1311 (m), 1244 (m), 1018 (m), 984 (m) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 7.81 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.15 (d, J = 3.7 Hz, 1H), 7.07 (t, J = 7.9 Hz, 1H), 6.51 (d, J = 3.7 Hz, 1H), 3.95–3.65 (m, 4H), 2.85 (q, J = 7.5 Hz, 2H), 2.15–1.95 (m, 4H), 1.20 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 190.0, 154.7, 151.2, 147.8, 133.7, 126.8, 126.0, 124.7, 118.1, 117.8, 112.6, 51.2, 46.7, 31.6, 24.1, 23.8, 8.2 ppm; MS (70 eV, EI): *m/z* (%): 375 (5) $[M]^+$, 307 (42), 279 (37), 250 (11), 221 (22), 170 (100), 142 (34), 113 (26), 70 (21); HRMS (EI): *m/z* calcd for $C_{17}H_{18}BrN_3O_2$: 375.0582; found: 375.0597.

10n: Prepared according to TP3 from **9e** (312 mg, 1 mmol), 4-bromobenzonitrile (218 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 6 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:1) yielded 6-(pyrrolidin-1-ylazo)biphenyl-3,4′-dicarbonitrile (**10n**; 250 mg, 83%) as a pale-yellow solid. M.p.: 174.4–176.6°C; IR (KBr): $\tilde{\nu}$ = 3069 (w), 2970 (w), 2874 (w), 2218 (s), 1667 (w), 1605 (m), 1480 (m), 1378 (s), 1315 (s), 1127 (m), 970 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 7.65 (d, J = 8.4 Hz, 2H), 7.62–7.54 (m, 5H), 3.93 (br s, 2H), 3.43 (br s, 2H), 2.03–1.97 ppm (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 151.5, 143.3, 134.7, 134.1, 132.6, 131.4, 130.8, 119.1, 118.9, 117.9, 110.9, 108.0, 51.4, 47.1, 23.9, 23.3 ppm; MS (70 eV, EI): *m/z* (%): 301 (10) $[M]^+$, 231 (22), 203 (100), 176 (21); HRMS (EI): *m/z* calcd for $C_{18}H_{15}N_5$: 301.1327; found: 301.1341.

10o: Prepared according to TP3 from **9e** (312 mg, 1 mmol), 2-bromo-3-pyridinecarbaldehyde (223 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and [Pd(PPh_3)$_4$] (35 mg, 3 mol%). Reaction conditions: 100°C, 5 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 1:4) yielded 3-(3-formylpyridin-2-yl)-4-(pyrrolidin-1-ylazo)benzonitrile (**10o**; 229 mg, 75%) as a brown solid. M.p.: 164.3–166.0°C; IR (KBr): $\tilde{\nu}$ = 3051 (w), 2973 (w), 2879 (w), 2769 (w), 2220 (s), 1693 (vs), 1577 (s), 1399 (s), 1363 (m), 1311 (m), 1130 (m), 977 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ = 9.72 (s, 1H), 8.84 (d, J = 4.9 Hz, 1H), 8.21 (d, J = 7.5 Hz, 1H), 7.99 (s, 1H), 7.67–7.60 (m, 2H), 7.41 (dd, J = 7.5, 4.9 Hz, 1H), 3.88 (br s, 2H), 3.21 (br s, 2H), 1.95 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 190.7, 157.8, 153.2, 151.6, 135.4, 133.8, 133.6, 132.1, 130.8, 122.8, 119.0, 117.0, 108.4, 51.6, 47.5, 23.8, 23.3 ppm; MS (70 eV, EI): *m/z* (%): 306 (2) $[M+H]^+$, 248 (4), 235 (6), 222 (11), 207 (100), 179 (5), 152

(18); HRMS (EI): *m/z* calcd for $C_{17}H_{16}N_5O$: 306.1355 $[M+H]^+$; found: 306.1350

10p: Prepared according to TP3 from **9e** (312 mg, 1 mmol), 4-iodoanisole (281 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100°C, 6 h. Purification by flash chromatography (*n*-pentane/diethyl ether=3:2) yielded 4′-methoxy-6-(pyrrolidin-1-ylazo)biphenyl-3-carbonitrile (**10p**; 263 mg, 86%) as a yellow solid. M.p.: 120.3–122.2°C; IR (KBr): $\tilde{\nu}$=2948 (w), 2879 (w), 2830 (w), 2215 (s), 1595 (m), 1513 (m), 1479 (m), 1383 (s), 1243 (s), 1173 (s), 1030 cm^{-1} (m); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ=7.60 (s, 1H), 7.51 (d, J=8.4 Hz, 1H), 7.48 (d, J=8.4 Hz, 1H), 7.43 (d, J=8.6 Hz, 2H), 6.90 (d, J=8.6 Hz, 2H), 3.92 (br s, 2H), 3.83 (s, 3H), 3.49 (br s, 2H), 2.00–1.95 ppm (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ=158.9, 151.5, 136.3, 134.2, 131.3, 131.0, 130.5, 119.6, 117.9, 113.0, 107.7, 55.2, 51.1, 46.9, 23.9, 23.3 ppm; MS (70 eV, EI): *m/z* (%): 306 (22) $[M]^+$, 236 (11), 208 (100), 193 (32), 177 (6), 165 (19); HRMS (EI): *m/z* calcd for $C_{18}H_{18}N_4O$: 306.1481; found: 306.1483.

10q: Prepared according to TP3 from **9f** (287 mg, 1 mmol), 1-bromomesitylene (239 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100°C, 7 h. Purification by flash chromatography (*n*-pentane/diethyl ether=4:1) yielded pyrrolidin-1-yl(2′,4′,6′-trimethylbiphenyl-3-yl)diazene (**10q**; 182 mg, 62%) as a white solid. M.p.: 113.4–115.0°C; IR (KBr): $\tilde{\nu}$=2948 (w), 2918 (w), 2871 (w), 1600 (w), 1570 (w), 1404 (s), 1314 (m), 1278 (m), 1208 (w), 1142 (w), 1031 (w), 972 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ=7.41–7.35 (m, 2H), 7.25 (s, 1H), 6.94 (s, 2H), 6.92 (d, J=7.1 Hz, 1H), 3.79 (br s, 4H), 2.34 (s, 3H), 2.05 (s, 6H), 2.01 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ=151.5, 141.6, 139.1, 136.3, 135.9, 128.8, 127.9, 126.1, 121.2, 118.6, 51.3, 47.0, 23.8, 21.0, 20.7 ppm; MS (70 eV, EI): *m/z* (%): 293 (22) $[M]^+$, 223 (11), 195 (100), 180 (67), 165 (64), 152 (9); HRMS (EI): *m/z* calcd for $C_{19}H_{23}N_3$: 293.1892; found: 293.1885.

10r: Prepared according to TP3 from **9f** (287 mg, 1 mmol), 4-bromopyrimidine (191 mg, 1.2 mmol), K_3PO_4 (424 mg, 2 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 3 mol%). Reaction conditions: 100°C, 5 h. Purification by flash chromatography (*n*-pentane/diethyl ether=1:4) yielded (3-pyrimidin-5-ylphenyl)pyrrolidin-1-yldiazene (**10r**; 202 mg, 80%) as a pale-yellow solid. M.p.: 84.9–86.5°C; IR (KBr): $\tilde{\nu}$=3051 (w), 2951 (w), 2864 (w), 1606 (w), 1575 (w), 1397 (s), 1333 (s), 1304 (s), 1210 (m), 1110 (w), 898 cm^{-1} (m); ^1H NMR (600 MHz, $CDCl_3$, 25°C): δ=9.16 (s, 1H), 8.95 (s, 2H), 7.60 (s, 1H), 7.47 (d, J=7.7 Hz, 1H), 7.42 (t, J=7.7 Hz, 1H), 7.29 (d, J=7.7 Hz, 1H), 3.90 (br s, 2H), 3.68 (br s, 2H), 2.01 ppm (br s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ=157.3, 154.9, 152.3, 134.7, 134.4, 129.8, 123.3, 120.9, 118.9, 51.0, 46.3, 23.7 ppm; MS (70 eV, EI): *m/z* (%): 253 (18) $[M]^+$, 183 (28), 155 (100), 128 (54), 102 (68), 75 (17); HRMS (EI): *m/z* calcd for $C_{14}H_{15}N_5$: 253.1327; found: 253.1317.

11a: Prepared according to TP4 from **10a** (140 mg, 0.5 mmol), 3-methoxybenzeneboronic acid (152 mg, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0°C, 4 h. Purification by flash chromatography (*n*-pentane/ethyl acetate=1:9) yielded 3″-methoxy[1,1′;4′,1″]terphenyl-4-carbaldehyde (**11a**; 94 mg, 65%) as a white solid. M.p.: 140.5–142.1°C; IR (KBr): $\tilde{\nu}$=3045 (w), 2917 (w), 2844 (w), 2740 (w), 1688 (vs), 1599 (s), 1446 (m), 1307 (m), 1235 (m), 1033 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=10.05 (s, 1H), 7.96 (d, J=7.9 Hz, 2H), 7.79 (d, J=7.9 Hz, 2H), 7.70 (s, 4H), 7.37 (t, J=7.9 Hz, 1H), 7.25–7.14 (m, 2H), 6.92 (d, J=7.9 Hz, 1H), 3.87 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=191.8, 160.0, 146.6, 141.8, 141.2, 138.6, 135.2, 130.3, 129.9, 127.7, 127.6, 127.5, 119.6, 113.0, 112.9, 55.3 ppm; MS (70 eV, EI): *m/z* (%): 288 (100) $[M]^+$, 215 (6), 143 (4); HRMS (EI): *m/z* calcd for $C_{20}H_{16}O_2$: 288.1150; found: 288.1132.

11b: Prepared according to TP4 from **10e** (141 mg, 0.5 mmol), 3-methoxybenzeneboronic acid (152 mg, mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0°C, 3 h. Purification by flash chromatography (*n*-pentane/ethyl acetate=1:9) yielded 4,3″-dimethoxy[1,1′;4′,1″]terphenyl (**11b**; 91 mg, 63%) as a brown solid. M.p.: 136.8–137.3°C; IR (KBr): $\tilde{\nu}$=3002 (w), 2941 (w), 2838 (w), 1602 (m), 1584 (m), 1479 (m), 1282 (m), 1249 (s), 1172 (m), 1028 (s), 872 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.66 (s, 4H), 7.61 (d, J=8.8 Hz, 2H), 7.40 (t, J=7.9 Hz, 1H), 7.26–7.18 (m, 2H), 7.03 (d, J=8.8 Hz, 2H), 6.93 (d, J=7.9 Hz, 1H), 3.90 (s, 3H), 3.89 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=159.9, 159.2, 142.3, 139.9, 139.3, 133.2, 129.7, 128.0, 127.5, 127.0, 119.5, 114.2, 112.7, 112.6, 55.3, 55.2 ppm; MS (70 eV, EI): *m/z* (%): 290 (100) $[M]^+$, 275 (26), 247 (11), 204 (8), 145 (7); HRMS (EI): *m/z* calcd for $C_{20}H_{18}O_2$: 290.1307; found: 290.1297.

11c: Prepared according to TP4 from **10h** (183 mg, 0.5 mmol), 3-methoxybenzeneboronic acid (152 mg, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0°C, 5 h. Purification by flash chromatography (*n*-pentane/diethyl ether=7:3) yielded 3-methoxy-2″,4″,6″-trimethyl[1,1′;4′,1″]terphenyl-2′-carboxylic acid ethyl ester (**11c**; 146 mg, 78%) as a pale-yellow liquid. IR (neat): $\tilde{\nu}$=2978 (w), 2834 (w), 1714 (vs), 1600 (m), 1473 (s), 1291 (s), 1232 (vs), 1169 (m), 1138 (m), 1092 (s), 1020 (s), 840 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.59 (s, 1H), 7.41 (d, J=8.0 Hz, 1H), 7.34–7.25 (m, 2H), 6.97–6.84 (m, 5H), 4.10 (q, J=7.1 Hz, 2H), 3.83 (s, 3H), 2.33 (s, 3H), 2.04 (s, 6H), 1.03 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=168.8, 159.3, 142.7, 140.2, 137.0, 136.0, 132.1, 131.4, 131.0, 130.6, 129.6, 129.0, 128.2, 127.2, 121.1, 113.9, 113.0, 61.0, 55.3, 21.0, 20.9, 13.7 ppm; MS (70 eV, EI): *m/z* (%): 374 (100) $[M]^+$, 345 (5), 329 (18), 302 (8), 286 (10), 271 (6), 256 (4), 241 (3), 172 (5); HRMS (EI): *m/z* calcd for $C_{25}H_{26}O_3$: 374.1882; found: 374.1866.

11d: Prepared according to TP4 from **10k** (201 mg, 0.5 mmol), 3-methoxybenzeneboronic acid (152 mg, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0°C, 4.5 h. Purification by flash chromatography (*n*-pentane/diethyl ether=9:1) yielded 2″,4″,6″-triisopropyl-3-methoxy[1,1′;4′,1″]terphenyl-2′-carbonitrile (**11d**; 148 mg, 72%) as a pale-yellow liquid. IR (neat): $\tilde{\nu}$=3057 (w), 2960 (s), 2869 (w), 2224 (m), 1599 (s), 1467 (s), 1224 (s), 1168 (m), 1032 (s), 842 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.55 (d, J=8.0 Hz, 1H), 7.47–7.37 (m, 2H), 7.33 (t, J=8.0 Hz, 1H), 7.20–7.09 (m, 2H), 7.07 (s, 2H), 7.00 (d, J=8.0 Hz, 1H), 3.88 (s, 3H), 2.94 (sept, J=7.1 Hz, 1H), 2.54 (sept, J=7.1 Hz, 2H), 1.30 (d, J=7.1 Hz, 6H), 1.11 (d, J=7.1 Hz, 6H), 1.09 ppm (d, J=7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=159.7, 148.9, 146.5, 143.4, 142.6, 140.9, 139.2, 134.7, 134.4, 129.7, 121.2, 120.8, 119.7, 114.7, 114.2, 112.8, 110.9, 55.4, 34.3, 30.4, 24.2, 24.1, 24.0 ppm; MS (70 eV, EI): *m/z* (%): 411 (100) $[M]^+$, 396 (48), 368 (24), 354 (52), 338 (10), 326 (16), 312 (60), 297 (16), 198 (24); HRMS (EI): *m/z* calcd for $C_{29}H_{33}NO$: 411.2562; found: 411.2543.

11e: Prepared according to TP4 from **10p** (153 mg, 0.5 mmol), 3-methoxybenzeneboronic acid (152 mg, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0°C, 5 h. Purification by flash chromatography (*n*-pentane/diethyl ether=4:1) yielded 3,4″-dimethoxy[1,1′;2′,1″]terphenyl-4′-carbonitrile (**11e**; 113 mg, 72%) as a colorless liquid. IR (neat): $\tilde{\nu}$=2917 (m), 2227 (m), 1736 (m), 1598 (m), 1514 (m), 1474 (m), 1291 (m), 1216 (s), 1176 (m), 1019 (m), 832 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.72 (s, 1H), 7.68 (d, J=7.9 Hz, 1H), 7.54 (d, J=7.9 Hz, 1H), 7.20 (d, J=8.4 Hz, 1H), 7.08 (d, J=8.8 Hz, 2H), 6.88–6.80 (m, 3H), 6.76 (d, J=8.4 Hz, 1H), 6.70 (s, 1H), 3.83 (s, 3H), 3.69 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=159.2, 159.0, 144.8, 141.3, 141.2, 133.9, 131.6, 131.2, 130.6, 130.3, 129.2, 121.9, 118.8, 114.9, 113.7, 113.3, 111.3, 55.2, 55.1 ppm; MS (70 eV, EI): *m/z* (%): 315 (100) $[M]^+$, 300 (4), 284 (20), 252 (5), 240 (15), 227 (10); HRMS (EI): *m/z* calcd for $C_{21}H_{17}NO_2$: 315.1259; found: 315.1244.

11f: Prepared according to TP4 from **10p** (153 mg, 0.5 mmol), 4-formylphenylboronic acid (150 mg, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0°C, 11 h. Purification by flash chromatography (*n*-pentane/ethyl acetate=1:9) yielded 4-formyl-4″-methoxy[1,1′;2′,1″]terphenyl-4′-carbonitrile (**11f**; 102 mg, 65%) as a pale-yellow solid. IR (neat): $\tilde{\nu}$=3054 (w), 2976 (w), 2840 (w), 2742 (w), 2228 (m), 1695 (vs), 1605 (s), 1513 (m), 1480 (m), 1300 (m), 1252 (m), 1207 (m), 1169 (m), 1026 (m), 923 cm^{-1}(w); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ=10.01 (s, 1H), 7.80 (d, J=8.4 Hz, 2H), 7.74 (s, 1H), 7.71 (d, J=7.9 Hz, 1H), 7.53 (d, J=7.9 Hz, 1H), 7.33 (d, J=8.4 Hz, 2H), 7.02 (d, J=8.8 Hz, 2H), 6.80 (d, J=8.8 Hz, 2H), 3.81 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=191.7, 159.2, 146.2, 143.5, 141.5, 135.2, 134.1, 131.1, 130.8, 130.7, 130.5, 130.2, 129.5, 118.5, 113.9, 112.2, 55.2 ppm; MS (70 eV, EI): *m/z* (%): 313 (100) $[M]^+$, 284 (8), 269 (6), 254

(10), 240 (13), 227 (7), 214 (4), 120 (4); HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}NO_2$: 313.1103; found: 313.1083.

11g: Prepared according to TP4 from **10q** (147 mg, 0.5 mmol), 3-methoxybenzeneboronic acid (152 mg, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0 °C, 4.5 h. Purification by flash chromatography (*n*-pentane/ethyl acetate = 19:1) yielded 3″-methoxy-2,4,6-trimethyl[1,1′;3′,1″]terphenyl (**11g**; 110 mg, 73 %) as a white solid. M.p.: 62.6–64.2 °C; IR (KBr): $\tilde{\nu}$ = 2948 (w), 2917 (w), 1594 (s), 1466 (s), 1326 (m), 1211 (s), 1040 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.59–7.53 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.39 (s, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.16–7.09 (m, 2H), 6.95 (s, 2H), 6.91–6.85 (m, 1H), 3.84 (s, 3H), 2.33 (s, 3H), 2.04 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.0, 142.6, 141.5, 141.0, 138.9, 136.7, 136.0, 129.7, 128.8, 128.4, 128.1, 128.0, 125.3, 119.6, 112.9, 112.7, 55.3, 21.0, 20.8 ppm; MS (70 eV, EI): *m*/*z* (%): 302 (100) $[M]^+$, 287 (13), 272 (7), 257 (4), 194 (3); HRMS (EI): *m*/*z* calcd for $C_{22}H_{22}O$: 302.1671; found: 302.1670.

11h: Prepared according to TP4 from **10q** (147 mg, 0.5 mmol), 4-formylphenylboronic acid (150 mg, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $BF_3{\cdot}OEt_2$ (0.2 mL, 0.75 mmol). Reaction conditions: 0 °C, 12 h. Purification by flash chromatography (*n*-pentane/diethyl ether = 9:1) yielded 2,4,6-trimethyl[1,1′;3′,1″]terphenyl-4″-carbaldehyde (**11h**; 120 mg, 80 %) as a colorless liquid. IR (neat): $\tilde{\nu}$ = 2947 (w), 2916 (w), 2854 (w), 2731 (w), 1699 (vs), 1602 (vs), 1566 (m), 1472 (m), 1377 (m), 1303 (m), 1211 (s), 1167 (s), 1008 (m), 834 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.04 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 2H), 2.33 (s, 3H), 2.04 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 191.9, 147.1, 141.9, 139.7, 138.5, 136.9, 135.9, 135.2, 130.3, 129.5, 129.1, 128.3, 128.2, 127.6, 125.5, 21.0, 20.8 ppm; MS (70 eV, EI): *m*/*z* (%): 300 (100) $[M]^+$, 285 (14), 271 (6), 257 (12), 242 (13), 195 (8), 179 (7), 165 (10), 149 (9); HRMS (EI): *m*/*z* calcd for $C_{22}H_{20}O$: 300.1514; found: 300.1491.

Acknowledgements

We thank the Fonds der Chemischen Industrie for financial support. We thank BASF AG (Ludwigshafen, Germany), Boehringer-Ingelheim (Vienna, Austria), Degussa GmbH (Hanau, Germany), and Chemetall GmbH (Frankfurt, Germany) for the generous gift of chemicals.

[1] a) I. Marek, *Chem. Rev.* **2000**, *100*, 2887; b) I. Marek, *Tetrahedron* **2002**, *58*, 9463.
[2] O. Baron, P. Knochel, *Angew. Chem.* **2005**, *117*, 3193; *Angew. Chem. Int. Ed.* **2005**, *44*, 3133.
[3] C. H. Cho, H. Park, M. A. Park, T. Y. Ryoo, Y. S. Lee, K. Park, *Eur. J. Org. Chem.* **2005**, 3177.
[4] a) P. Bordat, R. Brown, *Chem. Phys. Lett.* **2000**, *331*, 439; b) W. M. F. Fabian, J. M. Kauffman, *J. Lumin.* **1999**, *85*, 137.
[5] a) G. Schiavon, S. Zecchin, G. Zotti, S. Cattarin, *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *213*, 53; b) I. B. Berlman, H. O. Wirth, O. J. Steingraber, *J. Phys. Chem.* **1971**, *75*, 318.
[6] a) R. S. Wright, T. K. Vinod, *Tetrahedron Lett.* **2003**, *44*, 7129; b) B. S. Udayakumar, G. B. Schuster, *J. Org. Chem.* **1992**, *57*, 348.
[7] V. J. Ram, A. Goel, G. K. Patnaik, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 469.
[8] a) A. Krasovskiy, P. Knochel, *Angew. Chem.* **2004**, *116*, 3396; *Angew. Chem. Int. Ed*, **2004**, *43*, 3333; b) F. Kopp, A. Krasovskiy, P. Knochel, *Chem. Commun.* **2004**, 2288; c) H. Ren, A. Krasovskiy, P. Knochel, *Org. Lett.* **2004**, *6*, 4215; see also: d) P. Knochel, W. Dohle, N. Gommermann, F. F. Kneisel, F. Kopp, T. Korn, I. Sapountzis, V. A. Vu, *Angew. Chem.* **2003**, *115*, 4438; *Angew. Chem. Int. Ed.* **2003**, *42*, 4302.
[9] J. Kristensen, M. Lysén, P. Vedsø, M. Begtrup, *Org. Lett.* **2001**, *3*, 1435.
[10] Aryl triazenes are generally quite stable to air, light, and basic conditions. The addition of a Lewis acid, such as $BF_3{\cdot}OEt_2$, would immediately induce the decomposition of a triazene moiety.
[11] T. Saeki, E. C. Son, K. Tamao, *Org. Lett.* **2004**, *6*, 617.
[12] C. Y. Liu, P. Knochel, *Org. Lett.* **2005**, *7*, 2543.
[13] N. V. Harris, C. Smith, K. Bowden, *Synlett* **1990**, 577.

Received: March 23, 2007
Published online: July 6, 2007

