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Visible Light-Promoted Formation of C–B and C–S Bonds under Metal- and Photocatalyst-Free Conditions

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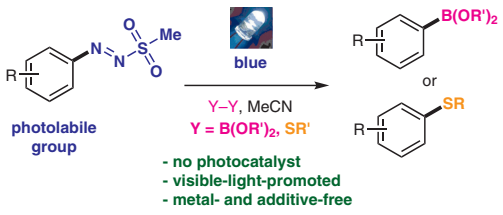

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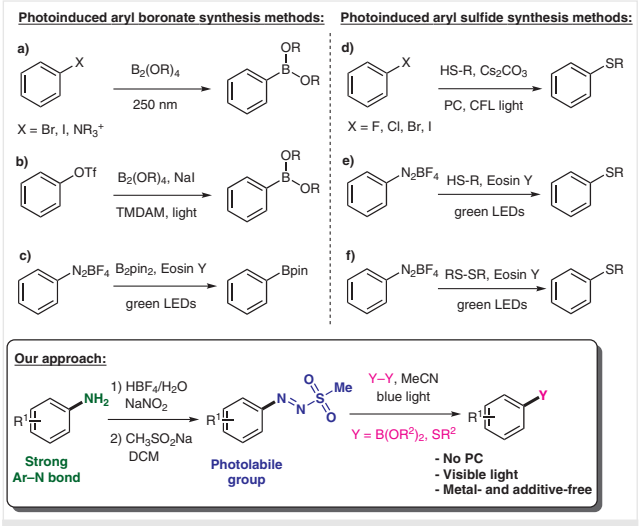
Abstract A green, efficient, photoinduced synthesis of arylboronic esters and aryl sulfides has been developed. Bench stable arylazo sulfones were used as radical precursors for a photocatalyst- and additive-free carbon–heteroatom bond formation under visible light. The protocols are applicable to a wide range of substrates, providing products in good yields.

Key words arylazo sulfones, aryl radicals, arylboronic esters, aryl sulfides

The development of mild and sustainable protocols for carbon–heteroatom bond formation has received an impressive attention in recent years. Indeed, aryl boronates and aryl sulfides play a key role in organic synthesis,[1] catalysis,[2] material science,[3] and especially medicinal chemistry.[4] Many natural products, drugs, and crop-protection substances bear sulfur-containing functional groups.[5] In addition, since the introduction of Bortezomib in 2003 by the FDA (US Federal Drug Administration)[6] for treating multiple myeloma, an increasing interest in boronic acids as drug candidates has developed.[7]

Classical methods for the generation of carbon–heteroatom bonds involve thermal reactions with organometal derivatives,[8] the use of transition-metal catalysts in combination with expensive often air-sensitive ligands, strong bases, and additives in excess amounts.[9] In order to reduce costs and contaminations with heavy metals, the development of more efficient and environmentally friendly alternative routes is highly desirable.

Several metal-free photoinduced borylation protocols of haloarenes,[10] quaternary arylammonium salts, aryl triflates,[11] and carboxylic acids[12] as substrates have been published recently (Scheme 1, a–c). Such methods feature the advantage of avoiding the use of late transition metals. Nevertheless, they still suffer from several drawbacks, like the need of ultraviolet light irradiation and additives such as NaI, *N*,*N*,*N*′,*N*′-tetramethyldiaminomethane (TMDAM), or Cs_2CO_3 in stochiometric amounts. An alternative for the preparation of arylboronic esters and aryl sulfides under photochemical conditions, takes advantage of aryl halides and aryldiazonium salts (Scheme 1, d–f),[13] which are widely used as aryl radical sources in photochemistry. The activation of aryldiazonium salts under visible light requires a photocatalyst (PC), since the aryl radical can only be formed by single-electron transfer (SET) from the excited state of the photocatalyst to the diazonium salt.



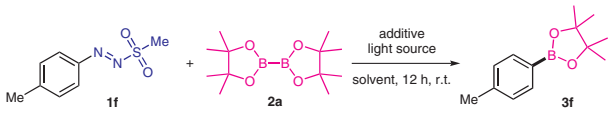
Scheme 1 Representative methods for the synthesis of arylboronic esters and aryl sulfides

Recently published protocols revealed that arylazo sulfones can be successfully used in the metal-free arylation of heterocycles and unactivated arenes without the need of additives.[14] Herein, we report the application of arylazo sulfones in the photocatalyst-, metal- and additive-free, visible-light-driven synthesis of aryl sulfides and aryl boronates.[15]

The present protocol is a sustainable approach that exploit bench stable arylazo sulfones, easily prepared from anilines, and allow the wavelength selective generation of aryl radicals and aryl cations.[14,15]

At the beginning of our studies, several reaction conditions were evaluated in order to determine the ideal setup for the photocatalyst-free borylation of arylazo sulfones (Table 1). Initially, a solution of arylazo sulfone **1f**, bis(pinacolato)diboron [$B(pin)_2$, **2a**], with NaI and TMDAM as additives in acetonitrile was stirred at room temperature. No product formation was observed neither in the absence of light (Table 1, entry 1) nor when exposing the solution to daylight (entry 2). Only traces of the aryl-B(pin) **3f** were obtained using 12 W LEDs for 12 hours (entry 3). However, **3f** was isolated in 59% yield using high power 24 W blue LEDs (entry 4). Also, the H150 blue Kessil lamp (34 W) was tested for irradiation, increasing the yield up to 79% (entry 6). Reactions without NaI and TMDAM showed that there is no need for additives to form the aryl boronate **3f** in 56% yield, when using high power blue LEDs (entry 5). The yield was further improved to 78% by using a blue 34 W Kessil lamp (entry 7). Other polar solvents like methanol and an acetonitrile/water mixture (9:1) gave no improvement on the yield (entries 8 and 9). The best results were obtained in acetonitrile using 34 W blue light lamp for irradiation (entry 7).

Table 1 Reaction Optimization for the Photocatalyst-Free Aryl Borylation[a]



Entry	Additive	Light source	Yield (%)
1	NaI/TMDAM	in the dark	–
2	NaI/TMDAM	daylight	–
3	NaI/TMDAM	blue LEDs 12 W	traces
4	NaI/TMDAM	blue LEDs 24 W	59
5	–	blue LEDs 24 W	56
6	NaI/TMDAM	Kessil lamp 34 W	79
7	**–**	**Kessil lamp 34 W**	**78**
8[b]	–	Kessil lamp 34 W	59
9[c,d]	–	Kessil lamp 34 W	61

[a] Reaction conditions: **1f** (0.1 mmol), **2a** (0.2 mmol), NaI (50 mol%), TMDAM (1 equiv), MeCN, r.t., 12 h, yield after purification by column chromatography.
[b] Reaction was carried out in MeOH.
[c] Reaction was carried out in $MeCN/H_2O$ (9:1).
[d] Yield, determined via ^1H NMR spectroscopy using dimethyl sulfone as internal standard.

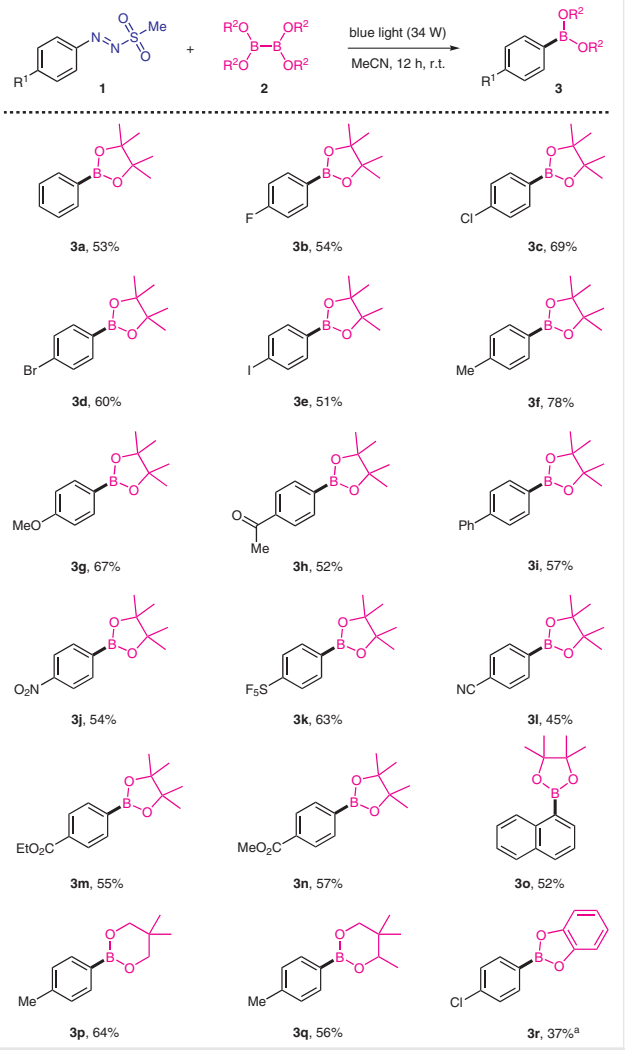
Based on the optimised conditions, the substrate scope was examined using different arylazo sulfones and borylating agents (Scheme 2). We were pleased to see that the photoinduced aryl borylation tolerates the presence of halides (**3b–e**), electron-donating (**3f–g**), and electron-withdrawing substituents (**3h–o**) on the aromatic moiety of the arylazo sulfones. In all cases, moderate to good yields were achieved (up to 78%). In addition, substrates containing potentially light-reactive substituents such as aryl ketone (**3h**) and biaryl (**3i**) were also appropriate radical precursors to give the resulting product under the described reaction conditions. Gratifyingly, arylazo sulfones bearing a bromide and iodide as substituent underwent also borylation (**3d** and **3e**), without cleavage of the carbon–halogen bond.

Next, different borylating agents were studied. The results showed that compared to B_2pin_2 (**2a**), bis(neopentyl glycolato)diboron (**2b**), and bis(hexylene glycolato)diboron (**2c**) gave slightly lower yields for the respective products **3p** (64%) and **3q** (56%). The borylation of 4-chlorophenylazo sulfone using bis(catecholato)diboron (**2d**) was also feasible.

We thus extended our investigation to the synthesis of thioethers, the visible light-mediated thiolation of arylazo sulfones was approached in the presence of disulfides as the thiolating reagent (Scheme 3). The scope was evaluated by employing various arylazo sulfones bearing halides, cyano, nitro, pentafluorosulfide, and keto groups (**5a–j**). The products were obtained in moderate to good yields. Additionally, different *ortho*- and *meta*-substituents were tolerated (**5k–m**). Diethyl sulfide (**4b**) and diphenyl sulfide (**4c**) were also successful in the photocatalyst-free thioether synthesis leading to **5n** and **5o** in 50% and 46% yield, respectively.

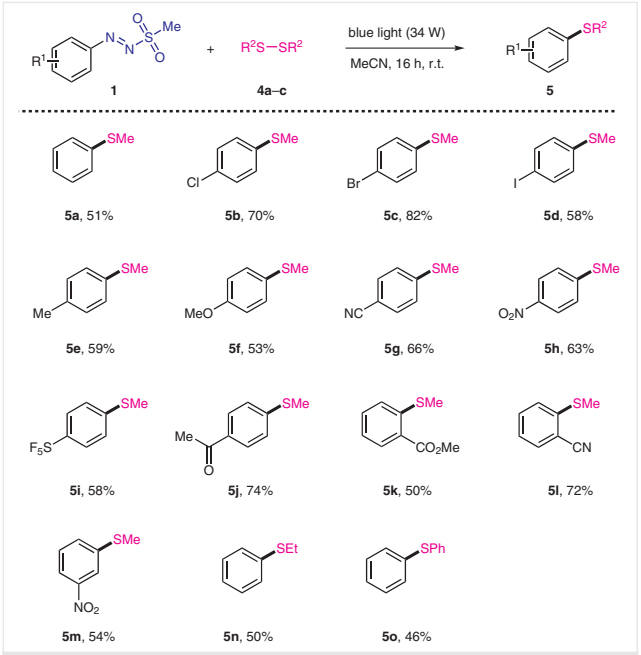
The proposed mechanism for the synthesis of aryl sulfides and boronates is depicted in Scheme 4. Irradiation of **1** with blue light (λ = 420 nm) leads to the excited $^1n\pi^*$-state **1*** (path a). Subsequent homolytic cleavage of the S–N bond (path b) affords the aryl radical **6** and methanesulfonyl radical **7**.[14] Such radicals are trapped by the diboron/disulfide (Y–Y) reagent **2** to give products **3** or **5** and the boron/sulfide radical (Y•) **8** (path c and f). The combination between aryl and X-radicals to form **3** or **5** is also possible (path d). Hydrogen atom abstraction by the generated radicals from the solvent to give arenes **9** and sulfinic acid (**10**) could also take place as a secondary path (path g). Finally, the recombination of the aryl **6** and methanesulfonyl radical **7** leads to a second possible by-product sulfone **12** (path e, see SI).

In summary, we have developed an efficient, green, photoinduced aryl borylation and aryl thioether formation protocol with arylazo sulfones as aryl radical precursors.

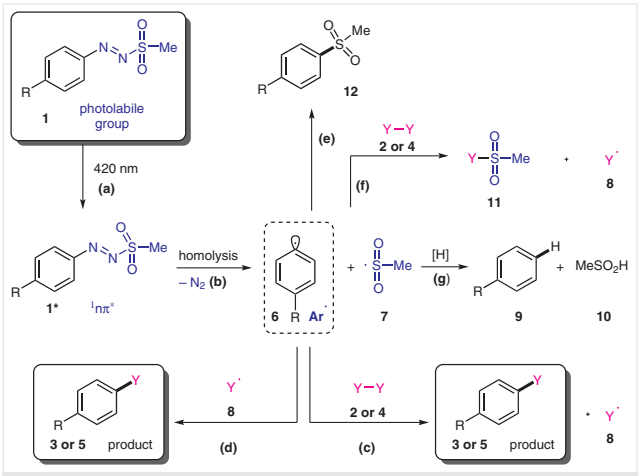


Scheme 2 Substrate scope of the photoinduced aryl borylation. *Reagents and conditions*: **1** (0.1 mmol), **2** (0.2 mmol), MeCN, r.t., H150 Kessil lamp (blue light 34 W), 12 h; yields after purification by column chromatography. [a] Yield determined via ^{1}H NMR using dimethyl sulfone as internal standard, confirmed by MS (EI): m/z = 230 (87).

These stable and easy to handle aryldiazonium salt derivatives show a high photoreactivity under blue light irradiation. The scope of the borylation reaction includes both, different aryl derivatives and different diboron esters, providing products in moderate to good yields. In addition, this simple approach could also be transferred to the aryl sulfide synthesis with disulfides.



Scheme 3 Substrate scope of the photoinduced synthesis of aryl sulfides. *Reagents and conditions*: **1** (0.2 mmol), **4** (0.4 mmol), MeCN, r.t., H150 Kessil lamp (blue light 34 W), 12 h. Yields after purification by column chromatography.



Scheme 4 Proposed mechanism for the PC-free photoinduced borylation and aryl sulfide formation via arylazo sulfones as stable radical precursors

Unless otherwise noted, all reagents were obtained from commercial suppliers. Organic solvents were purified from by solvent purification system MBraun SPS-5 and stored over molecular sieves under argon. Diazonium salts were synthesised by following a known procedure[16] and purified by recrystallisation from acetone/Et_2O. For irradiation of the reaction mixtures, different light sources were used: a) blue LED stripes (12W, 24 W) and b) H150 Kessil lamp (34 W, λ = 420 nm). The reaction was cooled using a small ventilator, placed at 3 cm from the reaction vessels. A shield covered with aluminum foil was placed in front of the reaction setup to protect eyes from light irradiation. Solvents for chromatography were technical grade and distilled prior to use. TLC was carried out on Merck aluminum support plates Silica gel 60 F_{254}. Visualisation was achieved under a UV mineral light or stained using cer-molybdato phosphoric acid (CAM). Column chromatography was performed using silica gel Merck 60 (0.2–0.063 mm). ^{1}H NMR spectra were recorded on Varian 400 MHz and 600 MHz

spectrometers at 400 and 600 MHz. ^{13}C NMR spectra were similarly recorded at 100 or 150 MHz, using a broadband decoupled mode. ^{11}B NMR spectra were measured at 128 MHz and ^{19}F NMR measurements were performed at 376 MHz on Varian 400 MHz and Mercury 300 MHz spectrometers, respectively. NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton signals in $CDCl_3$ (δ = 7.26, 77.16 ppm). Coupling constants (*J*) are reported in hertz (Hz) and refer to apparent multiplicities. Standard abbreviations are used for the multiplicities. Mass spectra (EI-MS, 70 eV) were conducted on a Finnigan SSQ 7000 spectrometer. HRMS were recorded on a Thermo Scientific TQ Orbitrap XI spectrometer. IR spectra were recorded on an Jasco FT/IR-420 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}).

Synthesis of Arylazosulfones 1;[14a] General Procedure

To a cooled (0 °C) suspension of the appropriative diazonium salt (1.00 equiv, 0.30 M) in anhyd CH_2Cl_2 was added $MeSO_2Na$ (1.00 equiv) in one portion. The temperature was allowed to rise to r.t. overnight. The resulting mixture was filtered, and the obtained solution evaporated. The crude solid was purified by either dissolving in cold CH_2Cl_2 and precipitation by adding *n*-hexane or column chromatography.

1-(Methylsulfonyl)-2-(phenyl)diazene (1a)

Reaction of benzenediazonium tetrafluoroborate (300 mg, 1.56 mmol) and $MeSO_2Na$ (160 mg, 1.56 mmol, 1.00 equiv) in CH_2Cl_2 (5.00 mL, 0.3 M) gave **1a** (185 mg, $9.93 \cdot 10^{-1}$ mmol, 65%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 8.4, 1.1 Hz, 2 H), 7.70–7.65 (m, 1 H), 7.58 (t, *J* = 7.6 Hz, 2 H), 3.23 (d, *J* = 3.3 Hz, 3 H).

The NMR data were in accordance with the literature.[14a]

1-(Methylsulfonyl)-2-(4-fluorophenyl)diazene (1b)

Reaction of 4-fluorobenzenediazonium tetrafluoroborate (300 mg, 1.43 mmol) and $MeSO_2Na$ (146 mg, 1.43 mmol, 1.00 equiv) in CH_2Cl_2 (5.00 mL, 0.30 M) gave **1b** (197 mg, $9.76 \cdot 10^{-1}$ mmol, 68%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid; mp 66.7–67.0 °C (dec.).

IR (KBr, neat): 3025, 2942, 1587, 1492, 1332, 1227, 1137, 954, 892, 851 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (ddd, *J* = 8.2, 5.1, 2.6 Hz, 2 H), 7.31–7.19 (m, 2 H), 3.20 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 145.5, 127.2, 116.9, 34.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –101.0.

MS (EI): *m*/*z* (%) = 123 (27), 95 (100).

1-(Methylsulfonyl)-2-(4-Chlorophenyl)diazene (1c)

Reaction of 4-chlorobenzenediazonium tetrafluoroborate (1.20 g, 5.30 mmol) and $MeSO_2Na$ (541 mg, 5.30 mmol, 1.00 equiv) in CH_2Cl_2 (17.5 mL, 0.30 M) gave **1c** (584 mg, 2.67 mmol, 51%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.6 Hz, 2 H), 7.56 (d, *J* = 8.6 Hz, 2 H), 3.22 (s, 3 H).

The NMR data were in accordance with the literature.[14a]

1-(Methylsulfonyl)-2-(4-Bromophenyl)diazene (1d)

Reaction of 4-bromobenzenediazonium tetrafluoroborate (1.00 g, 3.69 mmol) and $MeSO_2Na$ (377 mg, 3.69 mmol, 1.00 equiv) in CH_2Cl_2 (12.3 mL, 0.30 M) gave **1d** (533 mg, 2.03 mmol, 55%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.7 Hz, 2 H), 7.73 (d, *J* = 8.7 Hz, 2 H), 3.22 (s, 3 H).

The NMR data were in accordance with the literature.[14b]

1-(Methylsulfonyl)-2-(4-Iodophenyl)diazene (1e)

Reaction of 4-iodobenzenediazonium tetrafluoroborate (497 mg, 1.56 mmol) and $MeSO_2Na$ (160 mg, 1.56 mmol, 1.00 equiv) in CH_2Cl_2 (5.20 mL, 0.30 M) gave **1e** (212 mg, $6.85 \cdot 10^{-1}$ mmol, 44%) after recrystallisation from cold CH_2Cl_2/*n*-hexane) as an orange solid; mp 132.0–132.4 °C (dec.).

IR (KBr, neat): 3037, 2928, 2074, 1474, 1316, 1139, 952, 887, 830 cm^{-1}.

^1H NMR (600·MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.6 Hz, 2 H), 7.65 (d, *J* = 8.6 Hz, 2 H), 3.22 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.2, 139.2, 125.6, 103.6, 34.8.

MS (EI): *m*/*z* (%) = 76 (75), 203 (100), 231 (47).

1-(Methylsulfonyl)-2-(4-Methylphenyl)diazene (1f)

Reaction of 4-methylbenzenediazonium tetrafluoroborate (225 mg, 1.09 mmol) and $MeSO_2Na$ (112 mg, 1.09 mmol, 1.00 equiv) in CH_2Cl_2 (3.60 mL, 0.30 M) gave **1f** (75.4 mg, $3.80 \cdot 10^{-1}$ mmol, 35%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid; mp 100.2–100.9 °C (dec.).

IR (KBr, neat): 3043, 2937, 3390, 2073, 1324, 1146, 948, 893, 826 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.2 Hz, 2 H), 3.21 (s, 3 H), 2.48 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.9, 130.3, 124.7, 34.7, 21.9.

MS (EI): *m*/*z* (%) = 65 (39), 91 (100), 119 (27).

1-(Methylsulfonyl)-2-(4-Methoxyphenyl)diazene (1g)

Reaction of 4-methoxybenzenediazonium tetrafluoroborate (225 mg, 1.01 mmol) and $MeSO_2Na$ (103 mg, 1.01 mmol, 1.00 equiv) in CH_2Cl_2 (3.40 mL, 0.30 M) gave **1g** (143 mg, $6.67 \cdot 10^{-1}$ mmol, 66%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 9.0 Hz, 2 H), 7.04 (d, *J* = 9.0 Hz, 2 H), 3.94 (s, 3 H), 3.19 (s, 3 H).

The NMR data were in accordance with the literature.[14a]

1-(Methylsulfonyl)-2-(4-Acetylphenyl)diazene (1h)

Reaction of 4-acetylbenzenediazonium tetrafluoroborate (1.00 g, 4.27 mmol) and $MeSO_2Na$ (437 mg, 4.27 mmol, 1.00 equiv) in CH_2Cl_2 (14.0 mL, 0.30 M) gave **1h** (840 mg, 3.71 mmol, 87%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.5 Hz, 2 H), 8.03 (d, *J* = 8.5 Hz, 2 H), 3.26 (s, 3 H), 2.69 (s, 3 H).

The NMR data were in accordance with the literature.[14a]

1-(Methylsulfonyl)-2-(1,1′biphenyl)diazene (1i)

Reaction of 1,1′-biphenyldiazonium tetrafluoroborate (338 mg, 1.43 mmol) and $MeSO_2Na$ (146 mg, 1.43 mmol, 1.00 equiv) in CH_2Cl_2 (5.00 mL, 0.30 M) gave **1i** (223 mg, $8.58{\cdot}10^{-1}$ mmol, 60%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as an orange solid; mp 115.5–115.9 °C (dec.).

IR (KBr, neat): 3038, 2932, 2263, 2062, 1482, 1328, 1142, 953, 889, 848, 767, 690 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.5 Hz, 2 H), 7.81 (d, *J* = 8.5 Hz, 2 H), 7.67 (d, *J* = 7.5 Hz, 2 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 7.45 (t, *J* = 7.3 Hz, 1 H), 3.24 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.8, 148.0, 139.0, 129.1, 128.8, 128.2, 127.3, 125.2, 34.8.

MS (EI): *m*/*z* (%) = 181 (22), 153 (100).

1-(Methylsulfonyl)-2-(4-nitrophenyl)diazene (1j)

Reaction of 4-nitrobenzenediazonium tetrafluoroborate (304 mg, 1.28 mmol) and $MeSO_2Na$ (131 mg, 1.28 mmol, 1.00 equiv) in CH_2Cl_2 (4.30 mL, 0.30 M) gave **1j** (215 mg, $9.38{\cdot}10^{-1}$ mmol, 71%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 9.0 Hz, 2 H), 8.12 (d, *J* = 8.9 Hz, 2 H), 3.28 (s, 3 H).

The NMR data were in accordance with the literature.[14b]

1-(Methylsulfonyl)-2-[4-pentafluorosulfanyl)phenyl]diazene (1k)

Reaction of 4-(pentafluorosulfanyl)benzenediazonium tetrafluoroborate (497 mg, 1.56 mmol) and $MeSO_2Na$ (160 mg, 1.56 mmol, 1.00 equiv) in CH_2Cl_2 (5.30 mL, 0.30 M) gave **1k** (281 mg, $9.06{\cdot}10^{-1}$ mmol, 58%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as an orange solid; mp 100.4–100.9 °C (dec.).

IR (KBr, neat): 3019, 2934, 1323, 1142, 963, 825 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.07–7.92 (m, 4 H), 3.24 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.8, 127.7, 124.4, 34.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = 83.35–79.34 (m), 62.52 (d, *J* = 150.5 Hz).

MS (EI): *m*/*z* (%) = 231 (35), 203 (100), 95 (69), 75 (61).

1-(Methylsulfonyl)-2-(4-cyanophenyl)diazene (1l)

Reaction of 4-cyanobenzenediazonium tetrafluoroborate (278 mg, 1.28 mmol) and $MeSO_2Na$ (131 mg, 1.28 mmol, 1.00 equiv) in CH_2Cl_2 (4.30 mL, 0.30 M) gave **1l** (230 mg, 1.10 mmol, 86%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.5 Hz, 2 H), 7.90 (d, *J* = 8.6 Hz, 2 H), 3.26 (s, 3 H).

The NMR data were in accordance with the literature.[14b]

1-(Methylsulfonyl)-2-(4-ethoxycarbonylphenyl)diazene (1m)

Reaction of 4-ethoxycarbonylbenzediazonium tetrafluoroborate (431 mg, 1.56 mmol) and $MeSO_2Na$ (160 mg, 1.56 mmol, 1.00 equiv) in CH_2Cl_2 (5.30 mL, 0.30 M) gave **1m** (265 mg, 1.03 mmol, 66%) after column chromatography on silica gel (eluent: 3:1 pentane/EtOAc), followed by recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid; mp 104.6–105.0 °C (dec.).

IR (KBr, neat): 3016, 2988, 2935, 2901, 1717, 1334, 1272, 1148, 1102, 1015, 960, 895, 867, 770 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.5 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 4.43 (q, *J* = 7.1 Hz, 2 H), 3.25 (s, 3 H), 1.43 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.1, 151.1, 130.9, 124.2, 61.8, 34.8, 14.2.

MS (EI): *m*/*z* (%) = 177 (100), 149 (11).

1-(Methylsulfonyl)-2-(4-methoxycarbonylphenyl)diazene (1n)

Reaction of 4-methoxycarbonylbenzediazonium tetrafluoroborate (391 mg, 1.56 mmol) and $MeSO_2Na$ (160 mg, 1.56 mmol, 1.00 equiv) in CH_2Cl_2 (5.30 mL, 0.30 M) gave **1n** (293 mg, 1.21 mmol, 78%) after column chromatography on silica gel (eluent: 3:1 pentane/EtOAc), followed by recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid; mp 113.0–113.5 °C (dec.).

IR (KBr, neat): 3016, 2935, 1713, 1435, 1331, 1282, 1155, 1105, 897, 865, 773, 689 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.5 Hz, 2 H), 8.00 (d, *J* = 8.5 Hz, 2 H), 3.98 (s, 3 H), 3.25 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.6, 151.2, 135.5, 130.9, 124.2, 52.7, 34.8.

MS (EI): *m*/*z* (%) = 163 (90), 135 (100), 103 (37).

1-(Methylsulfonyl)-2-(α-naphthalene)diazene (1o)

Reaction of α-naphthalenediazonium tetrafluoroborate (315 mg, 1.30 mmol) and $MeSO_2Na$ (133 mg, 1.30 mmol, 1.00 equiv) in CH_2Cl_2 (4.30 mL, 0.30 M) gave **1o** (286 mg, 1.22 mmol, 91%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as an orange solid; mp 133.1–133.5 °C (dec.).

IR (KBr, neat): 3042, 2936, 2074, 1326, 1147, 1087, 1147, 955, 981, 851, 806, 763 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 8.4 Hz, 1 H), 8.18 (t, *J* = 14.9 Hz, 1 H), 8.03–7.95 (m, 2 H), 7.73 (dd, *J* = 18.1, 10.4 Hz, 1 H), 7.64 (dt, *J* = 22.0, 7.9 Hz, 2 H), 3.34 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.9, 136.3, 134.3, 131.4, 128.6, 128.4, 127.3, 125.3, 122.5, 115.1, 35.1.

MS (EI): *m*/*z* (%) = 155 (100), 143 (76), 127 (28).

1-(Methylsulfonyl)-2-(2-Cyanophenyl)diazene (1p)

Reaction of 2-cyanobenzenediazonium tetrafluoroborate (100 mg $4.61{\cdot}10^{-1}$ mmol) and $MeSO_2Na$ (46.7 mg, $4.61{\cdot}10^{-1}$ mmol, 1.00 equiv) in CH_2Cl_2 (1.50 mL, 0.30 M) gave **1p** (38.0 mg, $1.82{\cdot}10^{-1}$ mmol, 40%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid; mp 112.1–112.7 °C (dec.).

IR (KBr, neat): 3455, 3149, 3098, 3036, 3010, 2926, 2852, 2633, 2491, 2339, 2231, 2089, 1989, 1870, 1440, 1647, 1550, 1485, 1421, 1334, 1273, 1209, 1151, 1039, 956, 887, 810, 773, 746, 694 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.99–7.88 (m, 2 H), 7.85–7.78 (m, 2 H), 3.29 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.1, 135.1, 134.1, 133.9, 117.2, 116.0, 115.2, 34.6.

MS (EI): *m*/*z* (%) = 102 (100), 130 (53).

Methyl 2-[(Methylsulfonyl)diazenyl]benzoate (1q)

Reaction of 2-methoxycarbonylbenzenediazonium tetrafluoroborate (100 mg, 0.40 mmol) and $MeSO_2Na$ (40.9 mg, 0.40 mmol, 1.00 equiv) in CH_2Cl_2 (1.50 mL, 0.30 M) gave **1q** (60.7 mg, $2.51{\cdot}10^{-1}$ mmol, 63%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid; mp 78.8–79.2 °C (dec.).

IR (KBr, neat): 3436, 3101, 3019, 2940, 2848, 2638, 2281, 2163, 2096, 1719, 1586, 1489, 1441, 1319, 1267, 1199, 1141, 1267, 1199, 1141, 1077, 958, 889, 833, 765, 701 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.99 (dd, *J* = 7.2, 1.8 Hz, 1 H), 7.75–7.64 (m, 2 H), 7.61 (dd, *J* = 7.5, 1.5 Hz, 1 H), 3.94 (s, 3 H), 3.21 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.7, 147.9, 133.5, 132.7, 130.8, 130.4, 117.5, 52.8.

MS (EI): *m*/*z* (%) = 163 (26), 135 (100).

1-(Methylsulfonyl)-2-(3-nitrophenyl)diazene (1r)

Reaction of 3-nitrobenzenediazonium tetrafluoroborate (100 mg, 0.42 mmol) and $MeSO_2Na$ (42.4 mg, 0.42 mmol, 1.00 equiv) in CH_2Cl_2 (1.50 mL, 0.30 M) gave **1r** (38.6 mg, $1.82 \cdot 10^{-1}$ mmol, 40%) after recrystallisation from cold CH_2Cl_2/*n*-hexane as a yellow solid; mp 120.9–121.4 °C (dec.).

IR (KBr, neat): 3086, 3019, 2935, 2875, 2652, 2323, 2165, 2113, 1996, 1969, 1931, 1827, 1755, 1605, 1525, 1330, 1154, 1084, 1002, 957, 918, 869, 817, 790, 728, 667 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.78 (t, *J* = 2.0 Hz, 1 H), 8.53 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1 H), 8.33–8.24 (m, 1 H), 7.83 (t, *J* = 8.1 Hz, 1 H), 3.29 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.2, 130.8, 129.3, 119.4, 35.1.

MS (EI): *m*/*z* (%) = 122 (100), 151 (53).

Photoinduced Arylborylation; General Procedure

A solution of arylazo sulfone **1** (0.10 mmol) and the respective diboron **2** (0.20 mmol, 2.00 equiv) in degassed MeCN (2.00 mL, 0.05 M) was poured into a glass vessel, capped, and exposed to blue light (H150 Kessil lamp, 34 W, 420 nm) at r.t. for 12 h. After the completion of the reaction (detected by TLC), the solvent was removed in vacuo and the crude product was purified via column chromatography on silica gel.

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3a)

Reaction of **1a** (18.4 mg, 0.10 mmol) and bis(pinacolato)diboron (**2a**; 50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3a** (10.8 mg, $5.29 \cdot 10^{-2}$ mmol, 53%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless oil.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.0 Hz, 2 H), 7.46 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 2 H), 1.35 (s, *J* = 4.6 Hz, 12 H).

The NMR data were in accordance with the literature.[10b]

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

Reaction of **1b** (20.2 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3b** (11.9 mg, $5.36 \cdot 10^{-2}$ mmol, 54%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 1.34 (s, 12 H).

The NMR data were in accordance with the literature.[17]

2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

Reaction of **1c** (21.9 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3c** (16.4 mg, $6.88 \cdot 10^{-2}$ mmol, 69%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 1.34 (s, 12 H).

The NMR data were in accordance with the literature.[17]

2-(4-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)

Reaction of **1d** (26.3 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3d** (16.9 mg, $5.97 \cdot 10^{-2}$ mmol, 60%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a white solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.80 (t, *J* = 7.2 Hz, 2 H), 7.05 (t, *J* = 8.8 Hz, 2 H), 1.35 (d, *J* = 8.5 Hz, 12 H).

The NMR data were in accordance with the literature.[17]

2-(4-Iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

Reaction of **1e** (26.3 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3e** (16.9 mg, $5.12 \cdot 10^{-2}$ mmol, 51%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless solid.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 7.9 Hz, 2 H), 1.33 (s, 12 H).

The NMR data were in accordance with the literature.[17]

2-(4-Methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

Reaction of **1f** (19.8 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3f** (17.0 mg, $7.79 \cdot 10^{-2}$ mmol, 78%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless oil.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.8 Hz, 2 H), 7.17 (dd, *J* = 19.6, 6.9 Hz, 2 H), 2.37 (s, 3 H), 1.34 (s, 12 H).

The NMR data were in accordance with the literature.[10b]

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

Reaction of 4-methylphenyl mesylate (**1g**, 21.4 mg, 0.10 mmol) and bis(pinacolato)diboron (**2a**, 50.8 mg, 0.20 mmol, 2.00 equiv) in acetonitrile (2.00 mL, 0.05 M) gave **3g** (15.7 mg, $6.71 \cdot 10^{-2}$ mmol, 67%) after purification via column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless oil.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H), 1.33 (s, 12 H) ppm.

The NMR data were in accordance with the reported literature.[10a]

2-(4-Acetylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)

Reaction of **1h** (22.6 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3h** (12.8 mg, $5.20 \cdot 10^{-2}$ mmol, 52%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, 4 H), 2.62 (s, 3 H), 1.36 (s, *J* = 7.3 Hz, 12 H).

The NMR data were in accordance with the literature.[10a]

2-(1,1′-Biphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

Reaction of **1i** (26.0 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3i** (15.9 mg, $5.68 \cdot 10^{-2}$ mmol, 57%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.0 Hz, 2 H), 7.62 (dt, *J* = 11.4, 5.3 Hz, 4 H), 7.45 (t, *J* = 7.7 Hz, 2 H), 7.38–7.34 (m, 1 H), 1.37 (s, 12 H).

The NMR data were in accordance with the literature.[10a]

2-(4-Nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

Reaction of **1j** (22.9 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3j** (13.4 mg, $5.38\cdot10^{-2}$ mmol, 54%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 1.35 (s, 12 H).

The NMR data were in accordance with the literature.[18]

2-[4-Pentafluorosulfanyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)

Reaction of **1k** (31.0 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3k** (20.8 mg, $6.30\cdot10^{-2}$ mmol, 63%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a yellowish solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 1.35 (s, 12 H).

The NMR data were in accordance with the literature.[19]

2-(4-Nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)

Reaction of **1l** (20.9 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3l** (10.3 mg, $4.50\cdot10^{-2}$ mmol, 45%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.9 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 1.35 (s, 12 H).

The NMR data were in accordance with the literature.[10a]

Ethyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3m)

Reaction of **1m** (25.6 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3m** (15.2 mg, $5.50\cdot10^{-2}$ mmol, 55%) after purification via column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2 H), 7.86 (d, *J* = 7.9 Hz, 2 H), 4.38 (q, *J* = 7.1 Hz, 2 H), 1.40 (t, *J* = 7.1 Hz, 3 H), 1.36 (s, 12 H).

The NMR data were in accordance with the literature.[10a]

Methyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3n)

Reaction of **1n** (24.2 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3n** (14.8 mg, $5.68\cdot10^{-2}$ mmol, 57%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (30:1) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.1 Hz, 2 H), 7.87 (d, *J* = 8.1 Hz, 2 H), 3.92 (s, 3 H), 1.35 (s, 12 H).

The NMR data were in accordance with the literature.[17]

2-(Naphthalene-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)

Reaction of **1o** (23.4 mg, 0.10 mmol) and **2a** (50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3o** (13.3 mg, $5.23\cdot10^{-2}$ mmol, 52%) after purification by column chromatography on silica gel with a mixture of toluene/EtOAc (50:1) as a yellowish solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 8.4 Hz, 1 H), 8.76 (d, *J* = 8.4 Hz, 1 H), 8.08 (d, *J* = 6.8 Hz, 1 H), 7.93 (d, *J* = 8.1 Hz, 1 H), 7.83 (d, *J* = 8.1 Hz, 1 H), 7.56–7.50 (m, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 1.43 (s, 12 H).

The NMR data were in accordance with the literature.[9v]

5,5-Dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane (3p)

Reaction of **1f** (19.8 mg, 0.10 mmol) and 5,5,5′,5′-tetramethyl-2,2′-bi(1,3,2-dioxaborinane) (**2b**; 45.1 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3p** (13.1 mg, $5.42\cdot10^{-2}$ mmol, 64%) after purification by column chromatography on silica gel with a mixture of pentane/EtOAc (30:1) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.8 Hz, 2 H), 7.18 (d, *J* = 7.7 Hz, 2 H), 3.76 (s, 4 H), 2.36 (s, 3 H), 1.02 (s, 6 H).

The NMR data were in accordance with the literature.[9k]

4,5,5-Trimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane (3q)

Reaction of **1f** (19.8 mg, 0.10 mmol) and 5,5,5′,5′,6,6′-hexamethyl-2,2′-bi(1,3,2-dioxaborinane) (**2c**; 50.8 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave **3q** (12.1 mg, $5.55\cdot10^{-2}$ mmol, 56%) after purification by column chromatography on silica gel with a mixture of pentane/EtOAc (30:1) as a colourless oil.

IR (KBr, neat): 2970, 2924, 2330, 2095, 1913, 1610, 1374, 1307, 1165, 815 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.7 Hz, 2 H), 7.15 (d, *J* = 7.7 Hz, 2 H), 4.40–4.25 (m, 1 H), 2.35 (s, 3 H), 1.85 (dd, *J* = 13.8, 2.9 Hz, 1 H), 1.66–1.52 (m, 1 H), 1.35 (dd, *J* = 14.2, 6.7 Hz, 9 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.2, 133.7, 128.2, 70.8, 64.8, 46.0, 31.4, 28.16 (s), 23.2, 21.6 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 26.8.

MS (EI): *m*/*z* calcd for $C_{13}H_{19}BO_2$ $[M]^+$: 218.1472; found: 218.1470.

2-(4-Chlorophenyl)benzo[*d*][1,3,2]dioxaborole (3r)

Reaction of **1c** (21.9 mg, 0.10 mmol) and bis(catecholato)diboron (**2d**; 47.6 mg, 0.20 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.05 M) gave the crude product **3r** as a brown solid. Several attempts to purify the product were unsuccessful. For this reason, the yield (35%) was determined by ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.1 Hz, 1 H, product CH_{Ar}), 7.47 (d, *J* = 8.2 Hz, 1 H, product CH_{Ar}), 7.39 (dd, *J* = 5.8, 3.3 Hz, 1 H, product CH_{Ar}), 7.33–7.29 (m, 1 H product CH_{Ar}), 3.00 (s, 6 H internal standard 2 × CH_3).

Product was confirmed by mass spectra.

MS (EI): *m*/*z* (%) = 230 (87).

Photoinduced Synthesis of Aryl Thioethers 5; General Procedure

A solution of arylazo sulfone **1** (0.20 mmol) and the respective disulfide **4** (0.40 mmol, 2.00 equiv) in degassed MeCN (2.00 mL, 0.1 M) was poured into a glass vessel, capped, and exposed to blue light (H150 Kessil lamp, 34 W, 420 nm) at r.t. for 12 h. After the completion

of the reaction (detected by TLC), the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel.

Thioanisole (5a)

Reaction of **1a** (36.8 mg, 0.20 mmol) and dimethyl disulfide (**4a**; 37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5a** (12.8 mg, $10.3 \cdot 10^{-2}$ mmol, 51%) after purification by column chromatography on silica gel with pentane as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.22 (m, 4 H), 7.14 (tt, *J* = 5.6, 1.9 Hz, 1 H), 2.49 (s, 3 H).

The NMR data were in accordance with the literature.[20]

4-Chlorothioanisole (5b)

Reaction of **1c** (43.7 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5b** (21.9 mg, $1.38 \cdot 10^{-1}$ mmol, 69%) after purification by column chromatography on silica gel with pentane as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28–7.21 (m, 2 H), 7.21–7.14 (m, 2 H), 2.46 (s, 3 H).

The NMR data were in accordance with the literature.[21]

4-Bromothioanisole (5c)

Reaction of **1d** (52.6 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5c** (30.3 mg, $14.9 \cdot 10^{-2}$ mmol, 75%) after purification by column chromatography on silica gel with pentane as a colourless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47–7.34 (m, 2 H), 7.20–7.00 (m, 2 H), 2.47 (s, 3 H).

The NMR data were in accordance with the literature.[22]

4-Iodothioanisole (5d)

Reaction of **1e** (62.0 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5d** (29.0 mg, $11.6 \cdot 10^{-2}$ mmol, 58%) after purification by column chromatography on silica gel with pentane as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56–7.51 (m, 2 H), 6.98–6.93 (m, 2 H), 2.43 (s, 3 H).

The NMR data were in accordance with the literature.[22]

4-Methylthioanisole (5e)

Reaction of **1f** (39.7 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5e** (16.7 mg, $12.1 \cdot 10^{-2}$ mmol, 60%) after purification by column chromatography on silica gel with pentane as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24–7.15 (m, 2 H), 7.12 (d, *J* = 8.1 Hz, 2 H), 2.47 (s, *J* = 4.6 Hz, 3 H), 2.33 (s, 3 H).

The NMR data were in accordance with the literature.[22]

4-Methoxythioanisole (5f)

Reaction of **1g** (42.9 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5f** (16.2 mg, $10.5 \cdot 10^{-2}$ mmol, 53%) after purification by column chromatography on silica gel with pentane as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32–7.21 (m, 2 H), 6.92–6.77 (m, 2 H), 3.79 (s, 3 H), 2.45 (s, 3 H).

The NMR data were in accordance with the literature.[22]

4-(Methylthio)benzonitrile (5g)

Reaction of **1l** (41.8 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5g** (19.3 mg, $13.1 \cdot 10^{-2}$ mmol, 66%) after purification by column chromatography on silica gel with a mixture of pentane/Et_2O (50:1) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58–7.51 (m, 2 H), 7.32–7.20 (m, 2 H), 2.50 (s, 3 H).

The NMR data were in accordance with the literature.[23]

4-Nitrothioanisole (5h)

Reaction of **1j** (45.8 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5h** (21.4 mg, $12.6 \cdot 10^{-2}$ mmol, 63%) after purification by column chromatography on silica gel with a mixture of pentane/Et_2O (90:1) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24–8.04 (m, 2 H), 7.34–7.14 (m, 2 H), 2.54 (s, 3 H).

The NMR data were in accordance with the literature.[22]

Pentafluoro[4-(methylthio)phenyl]sulfane (5i)

Reaction of **1k** (62.1 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5i** (29.1 mg, $11.6 \cdot 10^{-2}$ mmol, 58%) after purification by column chromatography on silica gel with pentane/Et_2O (80:1) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70–7.58 (m, 2 H), 7.29–7.20 (m, 2 H), 2.51 (s, 3 H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = 87.57–81.95 (m), 63.35 (d, *J* = 150.2 Hz).

The NMR data were in accordance with the literature.[24]

4-Acetylthioanisole (5j)

Reaction of **1h** (45.3 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5j** (24.6 mg, $14.8 \cdot 10^{-2}$ mmol, 74%) after purification by column chromatography on silica gel with pentane as a colourless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90–7.83 (m, 2 H), 7.31–7.20 (m, 2 H), 2.56 (s, 3 H), 2.51 (s, 3 H).

The NMR data were in accordance with the literature.[25]

Methyl 2-(Methylthio)benzoate (5k)

Reaction of **1q** (48.5 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5k** (18.3 mg, $10.0 \cdot 10^{-2}$ mmol, 50%) after purification by column chromatography on silica gel with a mixture of pentane/Et_2O (90:1) as a colourless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.50–7.44 (m, 1 H), 7.29–7.27 (m, 1 H), 7.17–7.13 (m, 1 H), 3.93–3.90 (m, 3 H), 2.46 (s, 3 H).

The NMR data were in accordance with the literature.[21]

2-(Methylthio)benzonitrile (5l)

Reaction of **1p** (41.8 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5l** (14.5 mg, $14.5 \cdot 10^{-2}$ mmol, 72%) after purification by column chromatography on silica gel with a mixture of pentane/Et_2O (90:1) as a colourless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.53–7.50 (m, 1 H), 7.32 (d, *J* = 8.1 Hz, 1 H), 7.23–7.20 (m, 1 H), 2.56 (s, 3 H).

The NMR data were in accordance with the literature.[22]

3-Nitrothioanisole (5m)

Reaction of **1s** (33.8 mg, 0.20 mmol) and **4a** (37.7 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5m** (18.2 mg, $10.8 \cdot 10^{-2}$ mmol, 54%) after purification by column chromatography on silica gel with a mixture of pentane/Et_2O as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.05 (t, *J* = 1.9 Hz, 1 H), 7.96 (ddd, *J* = 5.8, 1.9, 0.7 Hz, 1 H), 7.55–7.51 (m, 1 H), 7.43 (t, *J* = 8.0 Hz, 1 H), 2.56 (s, 3 H).

The NMR data were in accordance with the literature.[21]

Ethyl Phenyl Sulfide (5n)

Reaction of **1a** (36.8 mg, 0.20 mmol) and diethyl disulfide (**4b**; 49 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5n** (13.9 mg, $10.1 \cdot 10^{-2}$ mmol, 50%) after purification by column chromatography on silica gel with pentane as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 4 H), 7.22–7.11 (m, 1 H), 2.95 (q, *J* = 7.4 Hz, 2 H), 1.32 (dd, *J* = 9.2, 5.5 Hz, 3 H).

The NMR data were in accordance with the literature.[25]

Diphenyl Sulfide (5o)

Reaction of **1a** (36.8 mg, 0.20 mmol) and diphenyl disulfide (**4c**; 87.3 mg, 0.40 mmol, 2.00 equiv) in MeCN (2.00 mL, 0.1 M) gave **5o** (17.2 mg, $9.23 \cdot 10^{-2}$ mmol, 46%) after purification by column chromatography on silica gel with pentane as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–6.70 (m, 10 H).

The NMR data were in accordance with the literature.[19]

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611648.

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