Functionalization of the Benzo[*c*][1,2,5]thiadiazole Scaffold via Mg-, Zn- and Mn-Intermediates

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Abstract: The metalation of all positions of the benzo[*c*][1,2,5]thiadiazole scaffold using LiCl-solubilized TMP-bases is demonstrated on various substrates. Thus, unsymmetrically substituted benzothiadiazole derivatives and a new fused thiadiazoloindazole have been prepared.

Key words: organometallic reagents, metalation, bicyclic compounds, heterocycles, benzo[*c*][1,2,5]thiadiazole

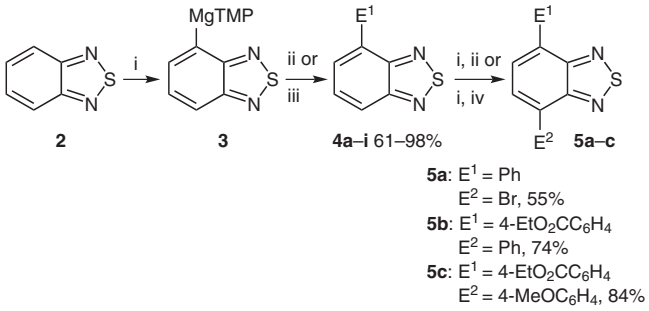
Condensed heterocycles gain importance due to their synthetic applications in biological and material science. Their functionalization is therefore an active research field.[1] The benzothiadiazole scaffold is part of many important compounds such as the muscle relaxant tizanidine, which is used for the treatment of chronical migraine and as antispastic agent.[2] Moreover, it is a suitable building block for semiconducting polymers and copolymers[3] as well as for printable organic semiconductors,[4] which find application as organic thin film transistors (OTFT), organic photovoltaic cells (OPV), light-emitting diodes (LED), or as fluorescent probes for bioimaging.[5] Despite their versatile use, only few methods for the functionalization of this heterocycle have been reported.[6,7] 4,7-Dibromobenzo[*c*][1,2,5]thiadiazole (**1**, Scheme 3)[7] has been used in cross-coupling reactions to provide the corresponding polymers.[8] The synthesis of unsymmetrically functionalized benzo[*c*][1,2,5]thiadiazoles has also been published.[7,9]

Herein, we wish to report a new pathway for the direct access to unsymmetrically substituted benzo[*c*][1,2,5]thiadiazole derivatives via organometallic intermediates. Benzo[*c*][1,2,5]thiadiazole (**2**)[10] was readily magnesiated at position 4 with $TMP_2Mg{\cdot}2LiCl$[11] at –40 °C to give reagent **3** within 14 hours (Scheme 1). After transmetalation with $ZnCl_2$, the intermediate underwent Pd-mediated Negishi cross-coupling reactions[12] with various aryl halides and iodothiophenes providing the fluorescent compounds **4a**–**h** in 61–98% yields (Table 1, entries 1–8). Iodination of **3** gave the corresponding 4-halogenated compound **4i** in 85% yield (entry 9).

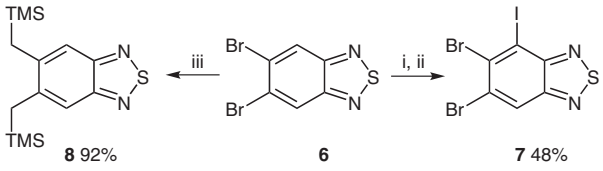
Also, a second metalation at position 7 was achieved with $TMP_2Mg{\cdot}2LiCl$ (Scheme 1). The organometallic reagent derived from **4c** reacted with 1,2-dibromo-1,1,2,2-tetrachloroethane to give the 7-brominated compound (**5a**) in 55% yield. Deprotonation of precursor **4d** and subsequent transmetalation with $ZnCl_2$ followed by Negishi cross-coupling reactions[12] with aryl iodides provided the 4,7-bis-aryl compounds **5b**,**c** in 74 and 84% yield, respectively. Interestingly, all compounds which bear a phenol subunit (**4e**,**f**, **5c**) display a large Stokes shift of 122 to 123 nm.

5,6-Dibromobenzo[*c*][1,2,5]thiadiazole (**6**)[13] was magnesiated with TMPMgCl·LiCl[14] at –20 °C within 10 minutes followed by an iodolysis to provide compound **7** in 48% yield (Scheme 2). Alternatively, a Pd-catalyzed cross-coupling of **6** with trimethylsilylmethylzinc chloride[15] proceeded almost quantitatively to give the benzothiadiazole derivative **8** in 92% yield.

Metalation at position 4 of the benzothiadiazole scaffold could also be achieved by an oxidative magnesium insertion[16] when 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**1**)[7] was used as substrate (Scheme 3). After in situ transmetalation with $ZnCl_2$ and a cross-coupling reaction with



Scheme 1 Successive deprotonation and functionalization at positions 4 and 7. *Reagents and conditions*: (i) $TMP_2Mg{\cdot}2LiCl$ (1.5 equiv), THF, –40 °C, 14 h; (ii) $ZnCl_2$ (1.6 equiv), E^1I or E^2I (1.8 equiv), $Pd(dba)_2$ (4 mol%), P(*o*-furyl)$_3$ (8 mol%), 25 °C; (iii) I_2 (3.0 equiv), –40 to 25 °C in 3 h; (iv) $(BrCl_2C)_2$ (2.5 equiv), –40 °C, 5 h.



Scheme 2 Functionalization of 5,6-dibromobenzo[*c*][1,2,5]thiadiazole (**6**). *Reagents and conditions*: (i) TMPMgCl·LiCl (1.1 equiv), THF, –20 °C, 10 min; (ii) I_2 (2.0 equiv), to 25 °C in 5 h; (iii) $TMSCH_2ZnCl{\cdot}MgCl_2$ (4.0 equiv), $Pd(OAc)_2$ (2 mol%), SPhos (4 mol%), THF, 25 °C, 30 min.

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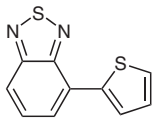
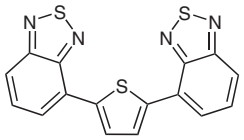
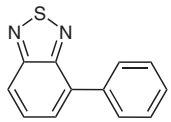
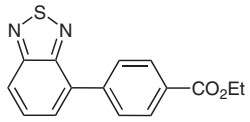
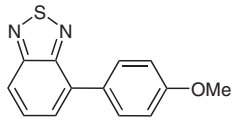
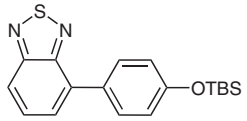
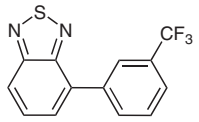
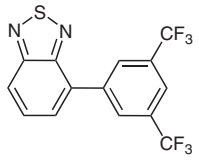
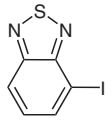
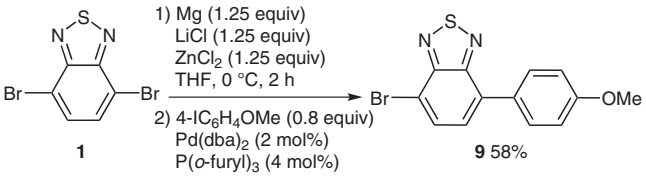
Table 1 Functionalization of Benzo[*c*][1,2,5]thiadiazole (**2**) via the Magnesiated Intermediate **3**

Entry	Electrophile	Time (h)	Product	Yield (%)[a]
1	2-iodothiophene	5	 **4a**	61[b]
2	2,5-diiodothiophene	24	 **4b**	98[b,c]
3	PhI	3	 **4c**	83[b]
4	4-$IC_6H_4CO_2Et$	24	 **4d**	72[b]
5	4-IC_6H_4OMe	7	 **4e**	74[b]
6	4-IC_6H_4OTBS	7	 **4f**	82[b]
7	3-$IC_6H_4CF_3$	24	 **4g**	63[b]
8	3,5-$(F_3C)_2C_6H_3Br$	24	 **4h**	61[b]
9	I_2	3	 **4i**	85[d]

[a] Isolated, analytically pure product.
[b] Obtained by Pd-catalyzed cross-coupling reaction with $Pd(dba)_2$ (2 mol%) and P(*o*-furyl)$_3$ (4 mol%) as catalyst and ligand, respectively.
[c] Obtained by cross-coupling reaction with 0.4 equiv of the electrophile.
[d] Obtained by reaction with I_2 (3.0 equiv).



Scheme 3 Functionalization of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**1**) via magnesium insertion

4-iodoanisole, the 4,7-bis-substituted compound **9** was obtained in 58% yield.

Deprotonation of **1** at position 5 was achieved with $TMP_2Mn{\cdot}2MgCl_2{\cdot}4LiCl$.[9c] The resulting organomanganese reagent reacted with 1,2-dibromo-1,1,2,2-tetrachloroethane to give the 4,5,7-tribromo compound **10** in 70% yield. This 4,5,7-tribromobenzo[*c*][1,2,5]thiadiazole was readily metalated with $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (1.0 equiv, 25 °C, 3 h) and a Cu-catalyzed acylation reaction[17] with 3-chlorobenzoyl chloride furnished the tetrasubstituted benzothiadiazole derivative **12** in 46% yield. The ketone **11** was synthesized according to a reported method,[9c] and further reaction with hydrazine gave the fused thiadiazoloindazole **13** in 65% yield (Scheme 4).

In conclusion, we have prepared a range of new substituted benzo[*c*][1,2,5]thiadiazoles using magnesium, zinc, and manganese intermediates. Further applications of these polyfunctional N-heterocycles are currently studied in our laboratories.

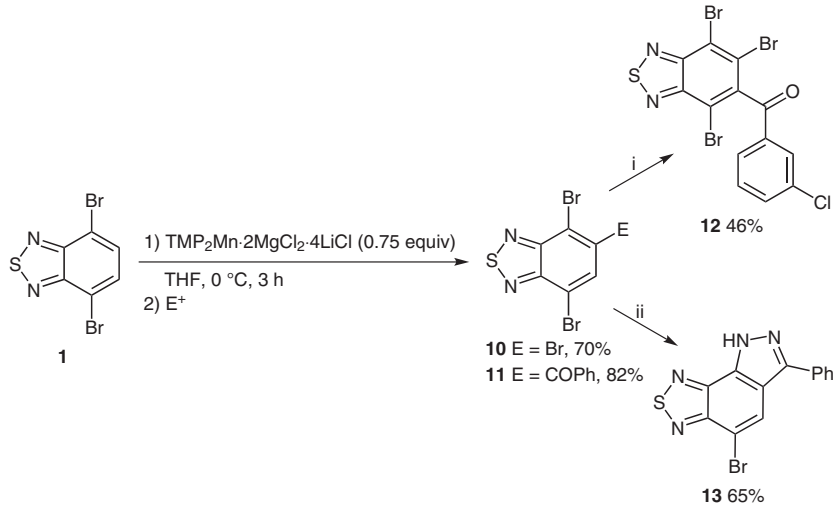
Melting points (Mp) were measured on a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded of solutions in $CDCl_3$ on Varian Mercury 200, Bruker AXR 300, Varian VXR 400S and Bruker AMX 600. Chemical shifts are reported as δ values in ppm relative to the residual solvent peak of $CHCl_3$ (δ_H: 7.25, δ_C: 77.0). UV/Vis spectra were recorded on Varian Cary 5000 and Bruins Omega 20, fluorescence spectra on Varian Cary Eclispe. IR-spectra were recorded on a Perkin-Elmer Spectrum BX-59343 instrument from 4500 to 65 cm^{-1}. For detection, a Smiths detection DuraSamplIR II Diamond ATR sensor was used. Low-resolution mass spectra were recorded using a GC/MS-combination from Hewlett-Packard HP 6890/ MSD 5973. High-resolution mass spectra were recorded on a Finnigan-MAT 95Q instrument (electron impact ionization, 70 eV). Flash column chromatographic purifications were carried out using silica gel 60 (0.040–0.063 mesh) from Merck.

Commercially available starting materials with a purity of >97% were used without further purification. Solvents were distillated and dried before use.

Starting materials **1**, **2**, **6**, and **11** were prepared according to reported methods.

4-(Thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (4a); Typical Procedure

In a dry Schlenk tube under an argon atmosphere $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol) was added dropwise to a solution of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol) in THF (1 mL) at –40 °C. After stirring at this temperature for 14 h, a solution of $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol) was added dropwise and the reaction mixture was warmed up to 25 °C. The resulting solution was treated with $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and 2-iodo-



Scheme 4 Functionalization of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**1**). *Reagents and conditions*: (i) $TMP_2Zn·2MgCl_2·2LiCl$ (1.0 equiv), THF, 25 °C, 3 h; CuCN·2LiCl (50 mol%), 3-chlorobenzoyl chloride (1.5 equiv), –15 °C, 3 h; (ii) $N_2H_4·H_2O$ (10.0 equiv), EtOH–$CHCl_3$ (1:1), 60 °C, 10 h.

thiophene (380 mg, 1.8 mmol). After stirring the reaction mixture at 25 °C for 5 h, sat. aq NH_4Cl (10 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane–Et_3N, 100:1), providing the compound **4a** (135 mg, 63%) as a yellow solid; mp 53–54 °C.

IR (ATR): 3071 (w), 2923 (w), 2852 (w), 2752 (w), 1952 (w), 1731 (w), 1591 (w), 1542 (m), 1485 (m), 1428 (w), 1209 (w), 1044 (w), 1036 (w), 851 (m), 841 (m), 820 (m), 802 (s), 751 (s), 707 (m), 684 cm^{-1} (vs).

^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 3.8, 1.1 Hz, 1 H), 7.90 (dd, *J* = 8.8, 1.1 Hz, 1 H), 7.82 (dd, *J* = 7.2, 1.1 Hz, 1 H), 7.59 (dd, *J* = 8.8, 1.1 Hz, 1 H), 7.44 (dd, *J* = 5.1, 1.1 Hz, 1 H), 7.19 (dd, *J* = 5.1, 3.8 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 152.4, 139.5, 129.8, 128.2, 128.0, 127.9, 127.0, 125.7, 120.3.

MS: *m*/*z* (%) = 220 (9), 219 (13), 218 (M^+, 100), 217 (10), 185 (5), 174 (9), 173 (10), 109 (5), 87 (5).

HRMS: *m*/*z* calcd for $C_{10}H_6N_2S_2$: 217.9972; found: 217.9964.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 390 (1.0), 308 (1.7), 279 nm (2.5). Fluorescence ($CHCl_3$): λ_{max} = 492 nm.

2,5-Bis(benzo[*c*][1,2,5]thiadiazol-4-yl)thiophene (4b)

Obtained by the reaction of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol), $TMP_2Mg·2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and 2,5-diiodothiophene (134 mg, 0.4 mmol) as described above, after purification by flash chromatography (pentane–Et_2O–Et_3N, 15:1:0.01) as an orange solid; yield: 140 mg (98%); mp 188–189 °C.

IR (ATR): 2923 (w), 2854 (w), 1651 (w), 1532 (w), 1475 (w), 1363 (w), 1317 (w), 1041 (m), 981 (w), 916 (w), 880 (m), 862 (m), 831 (m), 794 (vs), 752 (m), 739 (s), 694 (m), 632 (w), 620 cm^{-1} (w).

^1H NMR (400 MHz, DMSO-d_6): δ = 8.25 (s, 2 H), 8.18 (dd, *J* = 7.1, 0.9 Hz, 2 H), 8.05 (dd, *J* = 8.7, 0.9 Hz, 2 H), 7.79 (dd, *J* = 8.7, 7.1 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.4, 151.7, 140.5, 130.7, 128.7, 126.7, 126.1, 120.8.

MS: *m*/*z* (%) = 353 (19), 352 (22), 351 (M^+, 100), 179 (13), 165 (12), 97 (13), 83 (15), 81 (11), 71 (16), 70 (14), 69 (29), 57 (26), 44 (37).

HRMS: *m*/*z* calcd for $C_{16}H_8N_4S_3$: 351.9911; found: 351.9923.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 434 (1.0), 308 nm (1.8). Fluorescence ($CHCl_3$): λ_{max} = 532 nm.

4-Phenylbenzo[*c*][1,2,5]thiadiazole (4c)

Obtained by the reaction of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol), $TMP_2Mg·2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and iodobenzene (367 mg, 1.8 mmol) as described above, after purification by flash chromatography (pentane–Et_2O, 15:1) as a yellow solid; yield: 177 mg (83%); mp 70–71 °C.

IR (ATR): 3059 (w), 3029 (w), 1540 (w), 1479 (m), 1448 (m), 893 (m), 852 (m), 829 (m), 812 (m), 753 (vs), 696 (s), 670 (m), 636 (m), 625 (m), 608 (m), 596 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 8.02–7.96 (m, 1 H), 7.93–7.89 (m, 2 H), 7.69–7.64 (m, 2 H), 7.56–7.50 (m, 2 H), 7.47–7.42 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.9, 153.8, 137.6, 134.9, 129.9, 129.5, 128.9, 128.7, 128.0, 120.8.

MS: *m*/*z* (%) = 213 (14), 212 (M^+, 100), 211 (74), 166 (10), 152 (7), 140 (8), 106 (8).

HRMS: *m*/*z* calcd for $C_{12}H_8N_2S$: 212.0408; found: 212.0409.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 351 (1.0), 315 (1.8), 307 nm (1.8). Fluorescence ($CHCl_3$): λ_{max} = 449 nm.

Ethyl 4-(Benzo[*c*][1,2,5]thiadiazol-4-yl)benzoate (4d)

Obtained by the reaction of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol), $TMP_2Mg·2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and ethyl 4-iodobenzoate (497 mg, 1.8 mmol) as described above, after purification by flash chromatography (pentane–Et_2O–Et_3N, 15:1:0.01) as a yellow solid; yield: 205 mg (72%); mp 120–123 °C.

IR (ATR): 3064 (w), 2989 (w), 1715 (s), 1609 (w), 1480 (w), 1361 (w), 1284 (m), 1271 (s), 1181 (m), 1124 (m), 1098 (m), 1022 (m), 891 (m), 852 (m), 828 (s), 812 (m), 761 (vs), 695 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21–8.17 (m, 2 H), 8.04–8.00 (m, 3 H), 7.74–7.66 (m, 2 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 1.42 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 155.8, 153.5, 141.9, 133.7, 130.5, 130.0, 129.7, 129.4, 128.4, 121.6, 61.3, 14.6.

MS: *m*/*z* (%) = 284 (M^+, 36), 256 (13), 239 (46), 231 (12), 211 (20), 181 (21), 169 (22), 131 (31), 119 (28), 69 (100).

HRMS: *m*/*z* calcd for $C_{15}H_{12}N_2O_2S$: 284.0619; found: 284.0605.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 348 (1.0), 316 (1.7), 308 (1.7), 271 nm (2.2). Fluorescence ($CHCl_3$): λ_{max} = 438 nm.

4-(4-Methoxyphenyl)benzo[*c*][1,2,5]thiadiazole (4e)

Obtained by the reaction of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol), $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and 4-iodoanisole (421 mg, 1.8 mmol) as described above, after purification by flash chromatography (pentane–Et_2O, 25:1) as a yellow solid; yield: 178 mg (74%); mp 126–127 °C.

IR (ATR): 1601 (w), 1568 (w), 1510 (m), 1479 (m), 1452 (w), 1440 (w), 1277 (m), 1245 (m), 1177 (m), 1023 (s), 896 (m), 856 (m), 833 (m), 804 (vs), 753 (s), 720 (m), 644 (w), 588 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97–7.86 (m, 3 H), 7.67–7.61 (m, 2 H), 7.09–7.04 (m, 2 H), 3.88 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 155.9, 154.9, 134.4, 130.7, 130.1, 130.0, 127.1, 120.1, 114.3, 55.6.

MS: *m*/z (%) = 243 (14), 242 (M^+, 100), 228 (6), 227 (38), 199 (26), 153 (9).

HRMS: *m*/*z* calcd for $C_{13}H_{10}N_2OS$: 242.0514; found: 242.0514.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 373 (1.0), 316 (2.3), 308 (1.9), 303 nm (1.8). Fluorescence ($CHCl_3$): λ_{max} = 495 nm.

4-{4-[(*tert*-Butyldimethylsilyl)oxy]phenyl}benzo[*c*][1,2,5]thiadiazole (4f)

Obtained by the reaction of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol), $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and *tert*-butyl(4-iodophenoxy)dimethylsilane (602 mg, 1.8 mmol) as described above, after purification by flash chromatography (pentane–Et_2O–Et_3N, 50:1:0.01) as a pale yellow solid; yield: 280 mg (82%); mp 75–76 °C.

IR (ATR): 2953 (w), 2928 (w), 2856 (w), 1603 (m), 1540 (w), 1510 (m), 1483 (m), 1472 (m), 1461 (w), 1280 (s), 1266 (m), 1253 (m), 1176 (m), 1120 (w), 1108 (w), 1105 (w), 919 (s), 833 (s), 803 (vs), 782 (s), 749 (s), 697 (m), 668 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.91 (m, 1 H), 7.86–7.81 (m, 2 H), 7.64–7.62 (m, 2 H), 7.01–6.96 (m, 2 H), 1.02 (s, 9 H), 0.26 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 155.9, 153.8, 134.5, 130.6, 129.9, 129.6, 127.2, 120.4, 120.1, 25.9, 18.5, –4.1.

MS: *m*/*z* (%) = 343 (18), 342 (M^+, 100), 281 (30), 280 (89), 279 (27), 265 (52).

HRMS: *m*/*z* calcd for $C_{18}H_{22}N_2OSSi$: 342.1222; found: 342.1228.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 371 (1.0), 316 (2.2), 308 (1.9), 303 nm (1.8). Fluorescence ($CHCl_3$): λ_{max} = 493 nm.

4-(3-(Trifluoromethyl)phenyl)benzo[*c*][1,2,5]thiadiazole (4g)

Obtained by the reaction of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol), $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and 1-iodo-3-(trifluoromethyl)benzene (490 mg, 1.8 mmol) as described above, after purification by flash chromatography (pentane–Et_2O–Et_3N, 15:1:0.01) as a yellow solid; yield: 175 mg (63%); mp 50–51 °C.

IR (ATR): 1542 (w), 1484 (w), 1441 (w), 1397 (w), 1336 (s), 1314 (m), 1291 (m), 1262 (m), 1172 (m), 1179 (m), 1161 (m), 1106 (vs), 1092 (s), 1072 (s), 964 (m), 896 (m), 832 (m), 797 (s), 752 (s), 732 (m), 700 (s), 667 (m), 654 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20–8.17 (br, 1 H), 8.16–8.12 (br, 1 H), 8.07–8.01 (m, 1 H), 7.74–7.61 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 153.4, 138.3, 133.2, 132.8, 131.3 (q, $^2J_{C,F}$ = 32 Hz), 129.7, 129.3, 128.3, 126.3 (q, $^3J_{C,F}$ = 4 Hz), 125.3 (q, $^3J_{C,F}$ = 4 Hz), 124.4 (q, $^1J_{C,F}$ = 272 Hz), 121.6.

MS: *m*/*z* (%) = 282 (6), 281 (16), 280 (M^+, 100), 279 (31), 261 (8), 260 (13), 234 (7), 212 (6), 211 (43).

HRMS: *m*/*z* calcd for $C_{13}H_7F_3N_2S$: 280.0282; found: 280.0267.

UV/Vis ($CHCl_3$): λ_{ax} (ε_{rel}) = 343 (1.0), 315 (2.5), 307 nm (2.2). Fluorescence ($CHCl_3$, nm): λ_{max} = 435 nm.

4-[3,5-Bis(trifluoromethyl)phenyl]benzo[*c*][1,2,5]thiadiazole (4h)

Obtained by the reaction of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol), $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol) and 1-bromo-3,5-bis(trifluoromethyl)benzene (527 mg, 1.8 mmol) as described above, after purification by flash chromatography (pentane–Et_3N, 100:1) as a yellow solid ; yield: 210 mg (61%); mp 73–75 °C.

IR (ATR): 3083 (w), 1622 (w), 1544 (w), 1463 (w), 1381 (m), 1352 (w), 1316 (w), 1276 (s), 1183 (m), 1165 (s), 1117 (vs), 1108 (s), 984 (m), 892 (s), 832 (m), 811 (m), 796 (m), 753 (s), 700 (m), 684 (s), 592 cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45–8.41 (br, 2 H), 8.10 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.97–7.93 (s, 1 H), 7.78 (dd, *J* = 7.1, 1.6 Hz, 1 H), 7.73 (dd, *J* = 8.4, 7.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7, 153.0, 139.4, 132.2 (q, $^2J_{C,F}$ = 32 Hz), 129.6, 129.5 (q, $^3J_{C,F}$ = 4 Hz), 128.7, 123.6 (q, $^1J_{C,F}$ = 273 Hz), 122.6, 122.2 (sept, $^3J_{C,F}$ = 4 Hz).

MS: *m*/*z* (%) = 349 (14), 348 (M^+, 100), 347 (21), 329 (16), 328 (22), 327 (5), 302 (10), 280 (5), 279 (40), 163 (5).

HRMS: *m*/*z* calcd for $C_{14}H_6F_6N_2S$: 348.0156; found: 348.0158.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 337 (1.0), 315 (2.4), 308 nm (2.1). Fluorescence ($CHCl_3$): λ_{max} = 417 nm.

4-Iodobenzo[*c*][1,2,5]thiadiazole (4i)

In a dry Schlenk tube under an argon atmosphere, $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol) was added dropwise to a solution of benzo[*c*][1,2,5]thiadiazole (**2**; 136 mg, 1.0 mmol) in THF (1 mL) at –40 °C. After stirring at this temperature for 14 h, a solution of I_2 (3 mL, 1.0 M in THF, 3.0 mmol) was added dropwise and the reaction mixture was warmed up to 25 °C within 3 h. Sat. aq NH_4Cl (10 mL) and sat. aq $Na_2S_2O_3$ (3 mL) were added, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane) and the compound **4i** was obtained as a yellow solid; yield: 220 mg (85%).

^{1}H NMR corresponded to that of the commercially available compound from Maybridge.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (dd, *J* = 7.1, 0.9 Hz, 1 H), 7.97 (dd, *J* = 8.7, 1.0 Hz, 1 H), 7.34 (dd, *J* = 8.8, 7.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7, 152.9, 139.0, 130.5, 121.7, 87.2.

HRMS: *m*/*z* calcd for $C_6H_3IN_2S$: 261.9062; found: 261.9069.

4-Bromo-7-phenylbenzo[*c*][1,2,5]thiadiazole (5a)

In a dry Schlenk tube under an argon atmosphere $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol) was added dropwise to a solution of 4-phenylbenzo[*c*][1,2,5]thiadiazole (**4c**; 212 mg, 1.0 mmol) in THF (2 mL) at –40 °C. After stirring at this temperature for 14 h, $(BrCl_2C)_2$ (2.5 mL, 1.0 M in THF, 2.5 mmol) was added dropwise and the reaction mixture was stirred at –40 °C for 5 h. Sat. aq NH_4Cl (10 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane– Et_3N, 100:1), providing the compound **5a** (160 mg, 55%) as a beige solid; mp 84–85 °C.

IR (ATR): 3052 (w), 3031 (w), 1568 (w), 1524 (w), 1475 (m), 1447 (m), 1326 (w), 1188 (w), 1144 (w), 1073 (w), 932 (m), 884 (m), 848 (m), 835 (m), 753 (s), 692 (vs), 669 (m), 632 (m), 615 (m), 609 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.85 (m, 3 H), 7.58–7.43 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1, 153.4, 136.9, 134.3, 132.5, 129.4, 129.0, 128.5, 113.4.

MS: *m*/*z* (%) = 292 (90), 291 (39), 290 (M^+, 100), 289 (21), 278 (20), 212 (18), 211 (85), 210 (21), 179 (16), 178 (17), 140 (22), 106 (29).

HRMS: *m*/*z* calcd for $C_{12}H_7BrN_2S$: 289.9513; found: 289.9505.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 370 (1.0), 316 (1.8), 308 (1.5), 303 nm (1.5). Fluorescence ($CHCl_3$): λ_{max} = 470 nm.

Ethyl 4-(7-Phenylbenzo[*c*][1,2,5]thiadiazol-4-yl)benzoate (5b)

In a dry Schlenk tube under an argon atmosphere $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol) was added dropwise to a solution of ethyl 4-(benzo[*c*][1,2,5]thiadiazol-4-yl)benzoate (**4d**; 284 mg, 1.0 mmol) in THF (5 mL) at –40 °C. After stirring at this temperature for 14 h, $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol) was added dropwise and the reaction mixture was warmed up to 25 °C. The resulting solution was treated with $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and iodobenzene (370 mg, 1.8 mmol). After stirring the reaction mixture at 25 °C for 7 h, sat. aq NH_4Cl (10 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane–Et_2O–Et_3N, 100:1:0.01), providing the compound **5b** (270 mg, 74%) as a yellow solid; mp 139–142 °C.

IR (ATR): 2972 (w), 1700 (s), 1607 (m), 1552 (w), 1472 (w), 1451 (w), 1411 (w), 1368 (w), 1277 (s), 1181 (m), 1128 (m), 1104 (m), 1080 (w), 1017 (m), 973 (w), 932 (w), 890 (m), 846 (s), 772 (s), 764 (vs), 696 (s), 616 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23–8.19 (m, 2 H), 8.07–8.03 (m, 2 H), 7.97–7.93 (m, 2 H), 7.84 (d, *J* = 7.3 Hz, 1 H), 7.79 (d, *J* = 7.3 Hz, 1 H), 7.58–7.52 (m, 2 H), 7.49–7.44 (m, 1 H), 4.43 (q, *J* = 7.1 Hz, 2 H), 1.43 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 154.4, 154.1, 141.9, 137.5, 134.5, 132.4, 130.4, 131.1, 129.5, 129.4, 128.9, 128.9, 128.8, 128.2, 61.3, 14.6.

MS: *m*/*z* (%) = 362 (7), 361 (21), 360 (M^+, 100), 332 (14), 316 (10), 315 (46), 288 (4), 287 (16), 286 (6), 255 (9), 254 (4), 157 (6).

HRMS: *m*/*z* calcd for $C_{21}H_{16}N_2O_2S$: 360.0932; found: 360.0925.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 379 (1.0), 318 (1.1), 286 nm (2.2). Fluorescence ($CHCl_3$): λ_{max} = 481 nm.

Ethyl 4-[7-(4-Methoxyphenyl)benzo[*c*][1,2,5]thiadiazol-4-yl]benzoate (5c)

Obtained by the reaction of ethyl 4-(benzo[*c*][1,2,5]thiadiazol-4-yl)benzoate (**4d**; 284 mg, 1.0 mmol), $TMP_2Mg{\cdot}2LiCl$ (2.3 mL, 0.6 M in THF, 1.5 mmol), $ZnCl_2$ (1.6 mL, 1.0 M in THF, 1.6 mmol), $Pd(dba)_2$ (12 mg, 2 mol%, 0.02 mmol), P(*o*-furyl)$_3$ (9 mg, 4 mol%, 0.04 mmol), and 4-iodoanisole (421 mg, 1.8 mmol) as described above, after purification by flash chromatography (pentane–Et_2O, gradient: 5:1, 3:1, 1:1) as an orange solid; yield: 325 mg (84%); mp 149 °C (dec.).

IR (ATR): 3039 (w), 2980 (w), 1868 (w), 1708 (s), 1607 (m), 1572 (w), 1552 (w), 1504 (m), 1483 (m), 1285 (s), 1255 (s), 1174 (m), 1129 (m), 1106 (s), 1022 (s), 884 (m), 848 (m), 816 (vs), 766 (s), 699 (s), 590 cm^{-1} (m).

^{1}H NMR (400 MHz, toluene-d_8): δ = 8.05–8.02 (m, 2 H), 7.71–7.68 (m, 4 H), 7.11 (d, *J* = 7.3 Hz, 1 H), 7.08 (d, *J* = 7.3 Hz, 1 H), 6.69–6.65 (m, 2 H), 3.93 (q, *J* = 7.0 Hz, 2 H), 3.14 (s, 3 H), 0.86 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, toluene-d_8): δ = 165.6, 160.2, 154.1, 153.9, 141.6, 133.6, 131.0, 130.6, 130.2, 129.7, 129.6, 129.1, 128.2, 126.5, 113.9, 60.4, 54.4, 14.0.

MS: *m*/*z* (%) = 392 (7), 391 (22), 390 (M^+, 100), 375 (6), 362 (10), 347 (7), 345 (11), 274 (6), 172 (7), 137 (5).

HRMS: *m*/*z* calcd for $C_{22}H_{18}N_2O_3S$: 390.1038; found: 390.1039.

UV/Vis ($CHCl_3$): λ_{max} (ε_{rel}) = 398 (1.0), 294 nm (2.2). Fluorescence ($CHCl_3$): λ_{max} = 522 nm.

5,6-Dibromo-4-iodobenzo[*c*][1,2,5]thiadiazole (7)

In a dry Schlenk tube under an argon atmosphere TMPMgCl·LiCl (1.0 mL, 1.1 M in THF, 1.1 mmol) was added dropwise to a solution of 5,6-dibromobenzo[*c*][1,2,5]thiadiazole (**6**; 294 mg, 1.0 mmol) in THF (4 mL) at –20 °C. After stirring at this temperature for 10 min, I_2 (2.0 mL, 1.0 M in THF, 2.0 mmol) was added dropwise and the reaction mixture was slowly warmed up to 25 °C in 5 h. Sat. aq NH_4Cl (10 mL) and sat. aq $Na_2S_2O_3$ (5 mL) were added, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane–Et_2O, 200:1), providing the compound **7** (200 mg, 48%) as a yellow solid; mp 171–172 °C.

IR (ATR): 3066 (vw), 2922 (w), 2852 (vw), 1712 (w), 1560 (w), 1472 (m), 1418 (m), 1368 (w), 1330 (w), 1296 (w), 1244 (w), 1230 (s), 1176 (w), 1160 (w), 1118 (w), 1104 (m), 1096 (m), 964 (w), 952 (m), 908 (m), 876 (m), 856 (vs), 840 (s), 758 (w), 734 (w), 718 (m), 682 (w), 622 cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 150.7, 135.5, 126.2, 124.6, 95.8.

MS: *m*/*z* (%) = 422 (56), 420 (100), 418 (53), 214 (25), 212 (23), 133 (19), 128 (42), 127 (33), 80 (20), 43 (22).

HRMS: *m*/*z* calcd for $C_6HBr_2IN_2S$: 417.7272; found: 417.7274.

5,6-Bis((trimethylsilyl)methyl)benzo[*c*][1,2,5]thiadiazole (8)

In a dry Schlenk tube under an argon atmosphere $TMSCH_2MgCl$ (3.39 mL, 1.18 M in Et_2O, 4.0 mmol) was added dropwise to anhyd $ZnCl_2$ (550 mg, 4.0 mmol) in THF (4 mL) at 0 °C and the mixture was warmed up to 25 °C. 5,6-dibromobenzo[*c*][1,2,5]thiadiazole (**6**; 294 mg, 1.0 mmol), $Pd(OAc)_2$ (5 mg, 2 mol%, 0.02 mmol), and SPhos (16 mg, 4 mol%, 0.04 mmol) were successively added. After

stirring for 30 min, sat aq NH_4Cl (10 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane–Et_2O, 100:1), providing the compound **8** (283 mg, 92%) as a colorless solid; mp 90–91 °C.

IR (ATR): 2954 (w), 2898 (vw), 1492 (w), 1458 (w), 1420 (w), 1400 (w), 1268 (w), 1246 (m), 1160 (w), 1140 (m), 1084 (w), 886 (w), 868 (m), 834 (vs), 820 (s), 778 (m), 758 (w), 712 (w), 694 (m), 664 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 2 H), 2.24 (s, 4 H), 0.04 (s, 18 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 142.7, 117.7, 25.5, –1.4.

MS: *m*/*z* (%) = 308 (11), 295 (6), 294 (11), 291 (43), 74 (9), 73 (100), 45 (17), 43 (12).

HRMS: *m*/*z* calcd for $C_{14}H_{24}N_2SSi_2$: 308.1199; found: 308.1192.

4-Bromo-7-(4-methoxyphenyl)benzo[*c*][1,2,5]thiadiazole (9)

In a dry Schlenk tube under an argon atmosphere LiCl (106 mg, 2.5 mmol), Mg (61 mg, 2.5 mmol), $ZnCl_2$ (2.5 mL, 1.0 M in THF, 2.5 mmol), and THF (5 mL) were successively added. At 0 °C, 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**1**; 588 mg, 2.0 mmol) was added and the reaction mixture stirred for 2 h. The resulting brown solution was canulated to a mixture of $Pd(dba)_2$ (30 mg, 2 mol%, 0.04 mmol), P(*o*-furyl)$_3$ (16 mg, 4 mol%, 0.08 mmol), and 4-iodoanisole (374 mg, 1.6 mmol) in THF (2 mL). After stirring at 25 °C for 5 h, sat. aq NH_4Cl (20 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane–Et_2O, 50:1), providing the compound **9** (300 mg, 58%) as a yellow solid; mp 133–136 °C.

IR (ATR): 3048 (vw), 2990 (vw), 2934 (vw), 2896 (vw), 2836 (vw), 1896 (vw), 1608 (m), 1530 (w), 1508 (m), 1482 (m), 1462 (w), 1454 (w), 1438 (w), 1342 (vw), 1308 (w), 1282 (m), 1272 (w), 1248 (s), 1180 (s), 1152 (w), 1116 (w), 1084 (w), 1030 (s), 972 (vw), 942 (w), 930 (w), 880 (s), 838 (m), 826 (vs), 796 (m), 732 (w), 654 (vw), 628 cm^{-1} (vw).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.84 (m, 3 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.09–7.04 (m, 2 H), 3.90 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 153.9, 153.2, 133.6, 132.3, 130.3, 129.0, 127.4, 114.1, 112.2, 55.4.

MS: *m*/*z* (%) = 323 (16), 322 (100), 321 (15), 320 (98), 307 (35), 305 (35), 279 (20), 277 (21), 198 (26).

HRMS: *m*/*z* calcd for $C_{13}H_9BrN_2OS$: 319.9619; found: 319.9615.

4,5,7-Tribromobenzo[*c*][1,2,5]thiadiazole (10)

In a dry Schlenk tube under an argon atmosphere $TMP_2Mn{\cdot}2MgCl_2{\cdot}4LiCl$ (7.5 mL, 0.5 M in THF, 3.75 mmol) was added dropwise to a solution of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**1**; 1.47 g, 5.0 mmol) in THF (5 mL) at 0 °C. After stirring at this temperature for 3 h, $(BrCl_2C)_2$ (7.5 mL, 1.0 M in THF, 7.5 mmol) was added dropwise and the reaction mixture was slowly warmed up to 25 °C in 5 h. Sat. aq NH_4Cl (20 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane–Et_2O, 100:1), providing the compound **10** (1.3 g, 70%) as a yellow solid; mp 153–154 °C.

IR (ATR): 1736 (vw), 1570 (w), 1540 (vw), 1508 (vw), 1488 (w), 1478 (w), 1452 (w), 1368 (vw), 1302 (w), 1294 (w), 1260 (vw), 1222 (m), 1184 (w), 1138 (w), 1124 (w), 972 (m), 940 (w), 878 (vs), 864 (m), 844 (m), 750 (w), 690 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5, 153.0, 135.9, 127.1, 116.6, 113.7.

MS: *m*/*z* (%) = 376 (32), 374 (100), 372 (97), 370 (30), 295 (15), 293 (29), 291 (14), 216 (18), 214 (19), 58 (24), 43 (67).

HRMS: *m*/*z* calcd for $C_6HBr_3N_2S$: 369.7411; found: 369.7413.

(3-Chlorophenyl)(4,6,7-tribromobenzo[c][1,2,5]thiadiazol-5-yl)methanone (12)

In a dry Schlenk tube under an argon atmosphere $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (2.0 mL, 0.5 M in THF, 1.0 mmol) was added dropwise to a solution of 4,6,7-tribromobenzo[*c*][1,2,5]thiadiazole (**10**; 373 mg, 1.0 mmol) in THF (1 mL). After stirring for 3 h, CuCN·2LiCl (0.5 mL, 1.0 M in THF, 50 mol%, 0.5 mmol) and 3-chlorobenzoyl chloride (263 mg, 1.5 mmol) were successively added at –15 °C, and the reaction mixture stirred for 3 h. Sat. aq NH_4Cl (20 mL) and NH_3 (5 mL) were added, the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude residue was purified by flash chromatography (pentane–Et_2O, 20:1), providing the compound **12** (233 mg, 46%) as a yellow solid; mp 195–198 °C.

IR (ATR): 3096 (w), 3072 (w), 2930 (w), 2872 (w), 1748 (w), 1722 (m), 1680 (s), 1644 (m), 1622 (m), 1588 (m), 1570 (m), 1466 (w), 1448 (m), 1422 (m), 1380 (m), 1370 (m), 1346 (w), 1278 (m), 1264 (vs), 1246 (vs), 1188 (s), 1172 (s), 1132 (s), 1074 (m), 1052 (m), 1000 (w), 968 (w), 942 (w), 908 (m), 884 (s), 846 (w), 810 (m), 788 (m), 758 (s), 738 (vs), 720 (s), 672 (s), 604 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.88 (m, 1 H), 7.74–7.71 (m, 1 H), 7.66–7.63 (m, 1 H), 7.49–7.46 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.7, 153.1, 151.4, 141.8, 135.7, 135.6, 134.7, 130.6, 129.5, 129.4, 128.0, 123.8, 118.8, 111.3.

MS: *m*/*z* (%) = 510 (28), 433 (55), 431 (78), 429 (33), 401 (16), 399 (16), 141 (31), 139 (100), 111 (65), 75 (35).

HRMS: *m*/*z* calcd for $C_{13}H_4Br_3ClN_2OS$: 507.7283; found: 507.7275.

4-Bromo-6-phenyl-8*H*-[1,2,5]thiadiazolo[3,4-*g*]indazole (13)

In a 50 mL round-bottom flask, $N_2H_4{\cdot}H_2O$ (0.5 g, 10.0 mmol) was added dropwise to a solution of (4,7-dibromobenzo[*c*][1,2,5]thiadiazol-5-yl)(phenyl)methanone (**11**; 398 mg, 1.0 mmol) in EtOH–$CHCl_3$ (6 mL each). The reaction mixture was stirred at 60 °C for 10 h, the solvent was evaporated in vacuo and the crude residue was purified by flash chromatography (isohexane–EtOAc, gradient: 5:1, 3:1), providing the compound **13** (214 mg, 65%) as a yellow solid; mp 270–272 °C.

IR (ATR): 3264 (m), 1746 (vw), 1610 (vw), 1516 (vw), 1496 (w), 1446 (w), 1396 (w), 1362 (m), 1338 (w), 1274 (vw), 1246 (w), 1230 (w), 1140 (vw), 1112 (w), 1104 (w), 1074 (w), 978 (w), 888 (m), 870 (vs), 838 (m), 764 (w), 718 (s), 694 (s), 674 (m), 634 cm^{-1} (w).

^1H NMR (400 MHz, DMSO-d_6): δ = 8.47 (m, 1 H), 7.99–7.90 (m, 2 H), 7.63–7.45 (m, 3 H).

MS: *m*/*z* (%) = 333 (16), 332 (100), 331 (20), 330 (92), 329 (5), 218 (9), 164 (5), 77 (15).

HRMS: *m*/z calcd for $C_{13}H_7BrN_4S$: 329.9575; found: 329.9566.

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