Tetrahedron 68 (2012) 7380–7385

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of asymmetric 3,5-diaryl-4*H*-1,2,6-thiadiazin-4-ones via Suzuki–Miyaura and Stille coupling reactions

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ARTICLE INFO

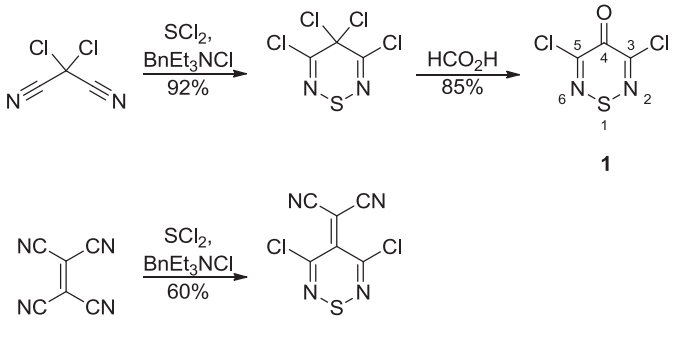
Article history:
Received 21 March 2012
Received in revised form 12 June 2012
Accepted 20 June 2012
Available online 28 June 2012

ABSTRACT

Asymmetric 3,5-diaryl substituted 4*H*-1,2,6-thiadiazin-4-ones can be prepared from 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) via a multi-step protocol: selective nucleophilic mono-chloro substitution gives either the mono-methoxy or benzyloxy substituted mono-chlorothiadiazinones that can be phenylated via Suzuki–Miyaura coupling. Subsequent BBr_3 mediated dealkylation gives 3-hydroxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) that can be activated by a modified Finkelstein halodehydroxylation via the triflate, enabling further arylation reactions using Suzuki–Miyaura or Stille coupling chemistry.

1. Introduction

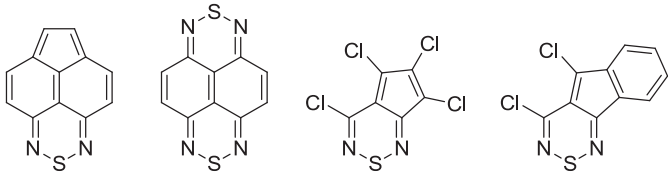
Various oxidized 1,2,6-thiadiazines such as the sulfoxides and, more importantly, sulfones have received considerable attention in various areas of applied chemistry including the pharmaceutical,[1] agrochemical[2] and materials[3] sectors. 1,2,6-Thiadiazines that are not oxidized at sulfur are rare.[4,5] Two notable exceptions, 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) and its dicyanomethylene analogue **2**, are potentially useful thiadiazine building blocks.[6–14] The former can be readily prepared from dichloromalononitrile and SCl_2, followed by hydrolysis with formic acid, in good overall yield (78%),[6] while the latter from tetracyanoethylene (TCNE) and SCl_2 (Scheme 1).[7,8]



1 **2**

Scheme 1.

While many 5-substituted derivatives of 3-chloro-4*H*-1,2,6-thiadiazin-4-ones have high fungicidal activity,[15–18] this application has not prompted extensive synthetic studies. Indeed the chemistry of the dichlorothiadiazines **1** and **2** remains limited. The chlorines in **1** and **2** can be successively displaced by a range of nucleophiles, the second compound requiring more harsh conditions.[6,10,11] Furthermore, both dichlorothiadiazines **1** and **2** react with bisnucleophiles to undergo nucleophilic substitution of the chlorine and subsequent cyclocondensation reactions at C-4 to give fused 4*H*-1,2,6-thiadiazines.[10] Interestingly, fused 4*H*-1,2,6-thiadiazines are of interest: acenaphtho[5,6-*cd*][1,2,6]thiadiazine (**3**)[19,20] and naphtho[1,8-*cd*:4,5-*c′d′*]bis([1,2,6]thiadiazine) (**4**),[21] are examples of 'extreme quinoids', that have ambiguous aromatic character and cyclopenta[1,2,6]thiadiazines **5** and **6**,[22,23] display unusual liquid crystalline properties or behave as near infra-red dyes (Scheme 2).



3 **4** **5** **6**

Scheme 2.

Recently, we demonstrated that 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) undergoes both Suzuki–Miyaura and Stille coupling chemistry to afford symmetrical 3,5-diaryl or heteroaryl substituted analogues.[12] The successful preparation of asymmetrical

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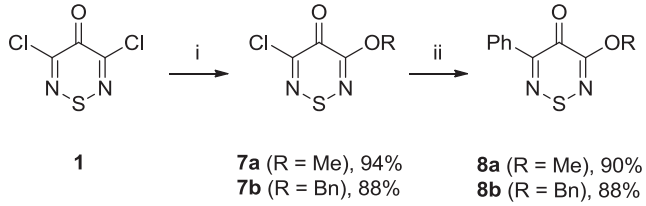
http://dx.doi.org/10.1016/j.tet.2012.06.079

diaryl substituted analogues was also achieved via Stille coupling reactions of non-symmetrical 3,5-dihalo(pseudohalo)-1,2,6-thiadiazin-4-ones.[13] Nevertheless, attempts to selectively prepare asymmetric diaryl analogues starting from 3,5-dihalo(pseudohalo)-1,2,6-thiadiazin-4-ones using the Suzuki–Miyaura reaction gave, in all cases, a mixture of mono and bi-arylated systems.[13]

We now report a successful protecting group strategy that takes advantage of the facile reaction of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) with alkoxides that can selectively afford in high yields the mono-chloro displaced 3-alkoxy-5-chloro-4*H*-1,2,6-thiadiazin-4-one. Subsequent arylation, followed by dealkylation and halo-dehydroxylation affords 3-aryl-5-halo-4*H*-1,2,6-thiadiazin-4-ones that can undergo a final Suzuki or Stille coupling to give asymmetric diarylthiadiazines.

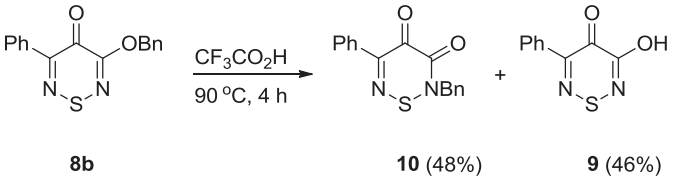
2. Results and discussion

The selective introduction of an alkoxy group is readily achieved since on mono-chloride substitution the new alkoxy substituent mesomerically releases electron density into the thiadiazine ring, making the ring less electron-deficient and subsequently, less reactive towards nucleophilic substitution.[6,9] The 5-methoxy and 5-benzyloxy thiadiazinones **7a** and **7b** were, therefore, readily prepared from 3,5-dichloro-1,2,6-thiadiazin-4-one (**1**) after treatment with 1 equiv of either sodium methoxide and sodium benzyloxide, respectively (Scheme 3). Both compounds **7a** and **7b**, undergo Suzuki–Miyaura coupling with phenylboronic acid to give 3-methoxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**8a**) and 3-benzyloxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**8b**) in 90 and 88% yields, respectively (Scheme 3).

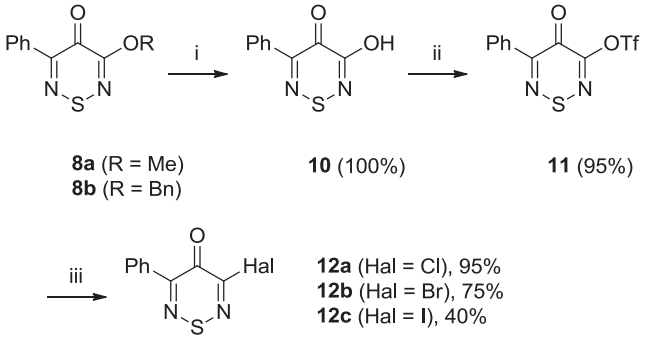


Scheme 3. Reagents and conditions: (i) R=Me, Na (1 equiv), MeOH, 0 °C, 15 min, 94%, R=Bn, BnOH (1.5 equiv), NaH (2 equiv), THF, rt, 8 h, 88%; (ii) $PhB(OH)_2$, $Pd(OAc)_2$ (5 mol %) Na_2CO_3 (1.5 equiv), dioxane/H_2O (5:3), 1.5 h, 20–100 °C, R=Me, 90%, R=Bn, 88%.

Initial attempts to debenzylate the 3-benzyloxy compound **7b** to access the desired 3-hydroxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) included a variety of conditions: (i) reductive cleavage using Pd/C and H_2, (ii) DIBAL and (iii) oxidative cleavage using DDQ or Br_2. All these attempts failed, affording mainly unreacted starting material. Treatment with protic or Lewis acids, however, did give some product. Interestingly, treating the benzyloxythiadiazinone **8b** in neat TFA at 90 °C gave a moderate yield (46%) of the desired hydroxythiadiazinone **9** together with a second product **10**, which was isolated as yellow needles, mp 126–129 °C (from cyclohexane). Microanalysis of this compound and mass spectrometry (*m*/*z* 296) indicated the unknown product was an isomer of the benzyloxythiadiazinone **8b**. ^1H and ^{13}C NMR spectroscopic analysis indicated 10 aromatic protons confirming the presence of both the phenyl rings but more interestingly the signals for the benzylic methylene CH_2 had shifted from δ_H 5.39 and δ_C 60.1 ppm in the starting benzyloxythiadiazinone **8b** to δ_H 5.01 and δ_C 49.4 ppm in the new product, tentatively indicating that they were now bound to a less electronegative heteroatom. The above data suggested that the benzyl group had undergone an O to N migration to give *N*-benzyl-5-phenyl-1,2,6-thiadiazin-3,4-dione (**10**) (48%).



Benzyl groups are known to undergo O to N migration in acidic medium,[24] but the reverse is not known. Not surprisingly, treating *N*-benzyl-5-phenyl-1,2,6-thiadiazin-3,4-dione (**10**) in neat trifluoroacetic acid (TFA) at ca. 90 °C for 24 h gave only recovered starting material indicating that cleavage or migration (N to O) of the *N*-benzyl group under these conditions did not occur. As such, the protic acid-mediated deprotection of the benzyloxy group had limitations. Fortunately, the use of BBr_3 in DCM at ca. 0 °C for 10 min gave the desired hydroxythiadiazinone **9** in high yield (94%). The use of BBr_3 in DCM at ca. 20 °C for 10 min also demethylated the methoxy compound **8a** smoothly to afford the hydroxythiadiazinone **10** in quantitative yield (Scheme 4).



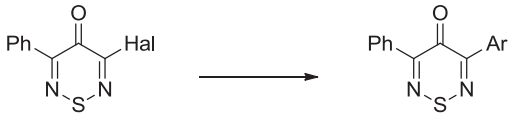
Scheme 4. Reagents and conditions: (i) R=Me or Bn, BBr_3 (1.2 equiv), DCM, rt, 10 min, 100%; (ii) Tf_2O (2 equiv), Et_3N (1.1 equiv), DCM, 0–10 °C, 30 min, 95%; (iii) Hal=Cl, $BnEt_3NCl$ (1.2 equiv), acetone, 20–56 °C, 95%; Hal=Br, Et_4NBr (1.2 equiv), acetone, 20–56 °C, 75%; Hal=I, KI (1.2 equiv), acetone, 20–56 °C, 6 h, 40%.

Having the hydroxythiadiazinone **10** in high yield, we attempted the direct synthesis of the chloro or the bromo analogues **12a** and **12b**. Treating the hydroxythiadiazinone **10** with either $POCl_3$, $SOCl_2$, $POBr_3$ or $SOBr_2$ at room temperature led to mainly recovered starting material, while on heating, traces of the desired products could be detected but mainly ring-opening and decomposition were observed. Nevertheless, the synthesis of the halo derivatives could be achieved via a modified Finkelstein reaction,[13] which first required the synthesis of the triflate and then subsequent conversion to the halogen. As such, treatment of the hydroxythiadiazinone **10** with trifluoromethanesulfonic anhydride in the presence of triethylamine gave the 3-phenyl-5-triflate thiadiazinone **11** in 95% yield, which after treatment with tetralkylammonium halides or KI afforded in high yields the 3-halo-5-phenylthiadiazinones **12a** (Hal=Cl), **12b** (Hal=Br) and **12c** (Hal=I) (Scheme 4).

2.1. Suzuki–Miyaura and Stille reactions

A preliminary study of the Suzuki–Miyaura reaction included our previously optimized Suzuki conditions for the reaction of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**): $RB(OH)_2$ (2.2 equiv), $Pd(OAc)_2$ (5 mol %), Na_2CO_3 (2 equiv) in dioxane/H_2O (0.5:0.3 mL) at ca. 100 °C.[12] Using this protocol the triflate **11** suffered hydrolysis to give back the hydroxythiadiazine **10**; fortunately both the chloro and bromo analogues **12a** and **12b** successfully afforded the desired diaryl products **13** in good yields (Table 1).

Table 1
Suzuki reaction of 3-halo-5-phenyl-4*H*-1,2,6-thiadiazin-4-ones **12a** (Hal=Cl) and **12b** (Hal=Br) (0.22 mmol) with $RB(OH)_2$ (1 equiv), $Pd(OAc)_2$ (5 mol %) and Na_2CO_3 (1.5 equiv) in dioxane/H_2O (0.5:0.3 mL) at ca. 100 °C



12a (Hal = Cl)
12b (Hal = Br)

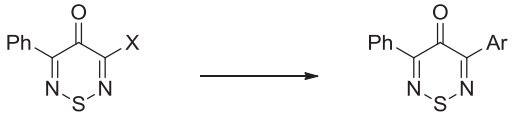
13a-d

Hal	Ar	Time (h)	Yields (%)
Br	2-$MeOC_6H_4$	5.0	**13a** (79)
Cl	2-$MeOC_6H_4$	6.0	**13a** (78)
Br	4-$MeOC_6H_4$	5.5	**13b** (91)
Cl	4-$MeOC_6H_4$	6.3	**13b** (81)
Br	3-$O_2NC_6H_4$	3.5	**13c** (83)
Cl	3-$O_2NC_6H_4$	3.6	**13c** (78)
Br	4-ClC_6H_4	3.5	**13d** (77)
Cl	4-ClC_6H_4	4.0	**13d** (80)

The reactions with arylboronic acid supporting electron-donating substituents (2 and 4-MeO) gave marginally longer reaction times compared to those with electron-withdrawing substituents (Cl and NO_2). Furthermore, no significant difference could be ascertained between the reactivity of the bromo or chlorothiadiazinones.

In light of the successful preparation of asymmetrically substituted diaryl analogues using the Suzuki–Miyaura protocol we then examined the reactivity of the newly synthesized triflate and halo thiadiazinones **11**, **12a**, **12b** and **12c** towards our typical Stille coupling conditions: stannyl reagent (1 equiv) and $Pd(Ph_3P)_2Cl_2$ (5 mol %) in MeCN at ca. 82 °C.[12] Initial studies using 2-(tributyltin)thiophene led to moderate to high yields of 3-phenyl-5-(thien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**13e**) (**12a**, Cl=99%, t_R=4 h; **12b**, Br=89%, t_R=3.5 h; **12c**, I=80%, t_R=1.5; **11**, OTf=92%, t_R=0.5 h) (see Table 2).

Table 2
Stille reactions of 3-halo and 3-triflate 5-phenyl-4*H*-1,2,6-thiadiazin-4-ones **12** and **11** (0.22 mmol) with $ArSnBu_3$ (1 equiv) and $Pd(Ph_3P)_2Cl_2$ (5 mol %) in MeCN at ca. 82 °C



11, 12a-c

13e-g

11, **12a–c**	Ar	Time (h)	Yields (%)
12a (X=Cl)	Thien-2-yl	4.0	**13e** (99)
12b (X=Br)	Thien-2-yl	3.5	**13e** (89)
12c (X=I)	Thien-2-yl	1.5	**13e** (80)
11 (X=OTf)	Thien-2-yl	0.5	**13e** (92)
12a (X=Cl)	*N*-Me-pyrrol-2-yl	3.5	**13f** (77)
12b (X=Br)	*N*-Me-pyrrol-2-yl	3.0	**13f** (86)
11 (X=OTf)	*N*-Me-pyrrol-2-yl	0.8	**13f** (88)
12a (X=Cl)	Fur-2-yl	3.8	**13g** (100)
12b (X=Br)	Fur-2-yl	3.6	**13g** (88)
11 (X=OTf)	Fur-2-yl	0.7	**13g** (94)

Worthy of note was the fast reaction times observed with triflate **11**. Furthermore, the iodothiadiazinone **12c**, while it gave relatively fast reaction times (1.5 h) gave the lowest yield of the desired product **13e** (80%). Owing to the low-yielding preparation of the iodothiadiazinone **12c** (40%, see Scheme 4) in comparison with the chloro and bromo analogues **12a** and **12b**, it was not chosen for further derivatisation. This difference in reactivity (OTf>I>Br>Cl) was similar to our previous observations,[13] and in general was maintained when the more electron rich or electron-deficient stannyl reagents 1-methyl-2-(tributyltin)pyrrole or 2-(tributyltin) furan, respectively, were used (Table 2). In general, the highest yields were obtained with the chlorothiadiazine **12a**, while significantly shorter reaction times were obtained with the triflate **11**.

3. Conclusions

A multi-step protocol for the Suzuki–Miyaura mediated asymmetric 3,5-diarylation of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one has been developed. The protocol takes advantage of the facile and mono selective introduction of a methoxy or benzyloxy substituent that after subsequent arylation can be dealkylated in high yield to give the arylhydroxythiadiazinone. Conversion of the arylhydroxythiadiazinone into a range of 3-halo/pseudohalo 5-aryl-4*H*-1,2,6-thiadiazin-4-ones was achieved via a modified Finkelstein reaction. These can undergo a second arylation using either Suzuki–Miyaura or Stille coupling reactions to afford the target compounds in high yield.

4. Experimental

4.1. General procedures

Reactions were protected by $CaCl_2$ drying tubes. Anhydrous Na_2SO_4 was used for drying organic extracts and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm).[25] Melting points were determined using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus. Decomposition points (decomp.) and mp >250 °C were determined using a TA Instruments DSC Q1000 with samples hermetically sealed in aluminium pans under an argon atmosphere; using heating rates of 5 °C/min. Solvents used for recrystallization are indicated after the melting point. A CEM Discover Microwave Reactor was used for microwave experiments. UV spectra were obtained using a Perkin–Elmer Lambda-25 UV/vis spectrophotometer and inflections are identified by the abbreviation 'inf'. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with Pike *Miracle* Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w, respectively. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 machine (at 500 and 125 MHz, respectively). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low-resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GC–MS with direct inlet probe. Microanalysis was performed at London Metropolitan University on a Perkin–Elmer 2400 Series II CHN Analyzer. 3,5-Dichloro-4*H*-1,2,6-thiadiazn-4-one (**1**) was prepared according to literature procedures.[6]

4.2. 3-Chloro-5-methoxy-4*H*-1,2,6-thiadiazin-4-one (7a)

To a flask containing dry MeOH (8 mL) under argon at 0 °C, was added sodium (128.8 mg, 5.6 mmol). To the resulting solution, 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) (1.00 g, 5.6 mmol) was added and the mixture left at this temperature until no starting material remained (TLC). The mixture was then adsorbed onto silica and chromatography (hexane/DCM, 1:1) gave the title compound **7a**

(940 mg, 94%) as yellow needles, mp 68–69 °C (from cyclohexane), (lit.,[6] 74–75 °C), R_f 0.26 (hexane/DCM, 1:1); λ_{max} (DCM)/nm 278 (log ε 3.0), 344 (3.33); ν_{max}/cm^{-1} 2997w, 2938w, 2845w, 1649s (C=O), 1520m, 1456w, 1447w, 1331m, 1233w, 1211m, 1182w, 991s, 955m, 854m, 804m; δ_H (500 MHz; $CDCl_3$) 4.01 (3H, s, OC*H*$_3$); δ_C (125 MHz; $CDCl_3$) 157.7 (s), 156.4 (s), 147.7 (s), 55.4 (q, OC*H*$_3$); *m*/*z* (EI) 180 (M^++2, 35%), 178 (M^+, 92), 150 (27), 148 (72), 123 (10), 121 (28), 112 (47), 95 (36), 93 (100), 89 (51), 86 (13), 74 (58), 61 (20), 58 (35), 54 (40).

4.3. 3-(Benzyloxy)-5-chloro-4*H*-1,2,6-thiadiazin-4-one (7b)

To a stirred solution of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) (1.00 g, 5.6 mmol) in THF (8 mL) at ca. 20 °C, was added NaH (268.8 mg, 11.2 mmol) and BnOH (0.87 mL, 8.4 mmol) and the reaction mixture was stirred at rt until no starting material remained (TLC). The reaction mixture was diluted with DCM, adsorbed onto silica and chromatographed (1:1, hexane/DCM) to give the title compound **7b** (1.25 g, 88%) as pale yellow plates, mp 141–142 °C (from cyclohexane), R_f 0.38 (hexane/DCM, 1:1); (found: C, 47.20; H, 2.72; N, 10.99. $C_{10}H_7ClN_2O_2S$ requires C, 47.16; H, 2.77; N, 11.00%); λ_{max} (DCM)/nm 278 (log ε 3.06), 343 (3.29); ν_{max}/cm^{-1} 3271w (Ar CH), 2835w, 1645s (C=O), 1522m, 1499w, 1454w, 1389w, 1319s, 1250w, 1219w, 1194m, 958s, 922m, 853w, 841w, 816m, 756m, 725m, 704m; δ_H (500 MHz; $CDCl_3$) 7.45–7.43 (2H, m, Ph *H*), 7.39–7.35 (3H, m, Ph *H*), 5.38 (2H, s, OC*H*$_2$); δ_C (125 MHz; $CDCl_3$) 157.6 (s), 155.5 (s), 147.8 (s), 134.1 (s), 128.8 (d), 128.7 (d), 128.6 (d), 70.0 (t, OCH$_2$); *m*/*z* (EI) 254 (M^+, 3%), 165 (3), 105 (5), 92 (8), 91 (100), 77 (2), 65 (12), 51 (3).

4.4. 3-Methoxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (8a)

To a stirred solution of 3-chloro-5-methoxy-4*H*-1,2,6-thiadiazin-4-one (**7a**) (1.00 g, 5.6 mmol) in dioxane/H_2O (5:3, 8 mL) at ca. 20 °C, was added $PhB(OH)_2$ (819 mg, 6.7 mmol), Na_2CO_3 (890 mg, 8.4 mmol) and $Pd(OAc)_2$ (62.8 mg, 0.28 mmol, 5 mol%). The reaction mixture was then heated at ca. 100 °C until no starting material remained (TLC). On cooling to ca. 20 °C the reaction mixture was then diluted with DCM (20 mL) and extracted (H_2O). The organic extracts were combined, dried (Na_2SO_4), filtered and adsorbed onto silica. Chromatography (hexane/DCM, 1:1) gave the title compound **8a** (1.11 g, 90%) as yellow needles, mp 73–75 °C (from pentane), R_f 0.26 (hexane/DCM, 1:1); (found: C, 54.63; H, 3.76; N, 12.64. $C_{10}H_8N_2O_2S$ requires C, 54.53; H, 3.66; N, 12.72%); λ_{max} (DCM)/nm 235 (log ε 3.55), 270 (2.21); ν_{max}/cm^{-1} 3046w (Ar CH), 2949w, 2936w, 2859w, 1644m (C=O), 1629s, 1600w, 1531m, 1453w, 1438w, 1348s, 1335m, 1314w, 1283m, 1197w, 1159w, 1139s, 1073w, 1004w, 990s, 965w, 951w, 914w, 861w, 821m, 801w, 746s; δ_H (500 MHz; $CDCl_3$) 8.13–8.11 (2H, m, Ph *H*), 7.45 (3H, br s, Ph *H*), 4.00 (3H, s, OC*H*$_3$); δ_C (125 MHz; $CDCl_3$) 161.3 (s), 158.7 (s), 157.5 (s), 134.3 (s), 130.6 (d), 128.6 (d), 128.2 (d), 54.7 (q, OCH$_3$); *m*/*z* (EI) 206 (M^+, 47%), 169 (4), 135 (13), 111 (5), 104 (80), 97 (8), 85 (9), 81 (5), 77 (32), 75 (45), 71 (12), 69 (13), 64 (13), 57 (20), 51 (17).

4.5. 3-(Benzyloxy)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (8b)

Similar treatment of 3-(benzyloxy)-5-chloro-4*H*-1,2,6-thiadiazin-4-one (**7b**) (1.40 g, 5.6 mmol) with $PhB(OH)_2$ (819 mg, 6.7 mmol), Na_2CO_3 (890 mg, 8.4 mmol) and $Pd(OAc)_2$ (62.8 mg, 0.28 mmol) gave the title compound **8b** (1.46 g, 88%) as yellow needles, mp 126–128 °C (from cyclohexane), R_f 0.38 (hexane/DCM, 1:1); (found: C, 65.00; H, 4.08; N, 9.61. $C_{16}H_{12}N_2O_2S$ requires C, 64.85; H, 4.08; N, 9.45%); λ_{max} (DCM)/nm 230 (log ε 3.06), 238 inf (2.80), 306 (3.23), 354 (3.28); ν_{max}/cm^{-1} 3061w, 3030w and 3001w (Ar CH), 2955w, 1632s and 1622s (C=O), 1601w, 1585w, 1526s, 1497w, 1489w, 1454w, 1427w, 1383m, 1331s, 1306s, 1267s, 1244w, 1210w, 1125s, 1082w, 1076w, 1030w, 1015w, 999w, 965s, 943m, 908w, 885w, 827w, 814w, 802w; δ_H (500 MHz; $CDCl_3$) 8.14–8.12 (2H, m, Ph *H*), 7.50–7.35 (8H, m, Ph *H*), 5.39 (2H, s, OC*H*$_2$); δ_C (125 MHz; $CDCl_3$) 161.3 (s), 157.8 (s), 157.7 (s), 134.9 (s), 134.4 (s), 130.6 (d), 128.7 (d), 128.6 (d), 128.5 (d), 128.4 (d), 128.2 (d), 69.1 (t, OCH$_2$); *m*/*z* (EI) 296 (M^+, 4%), 268 (2), 165 (2), 135 (6), 107 (4), 105 (9), 103 (17), 91 (100), 76 (9), 74 (5), 65 (12), 51 (6).

4.6. 2-Benzyl-5-phenyl-2*H*-1,2,6-thiadiazine-3,4-dione (10) and 3-hydroxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (9) (using TFA)

A stirred solution of 3-(benzyloxy)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**8b**) (1.00 g, 3.4 mmol) in TFA (4 mL) was heated at ca. 90 °C until no starting material remained (TLC). The reaction mixture allowed to cool to ca. 20 °C, diluted with H_2O (10 mL) and then extracted (DCM, 3×20 mL). The organic extracts were combined, dried (Na_2SO_4), filtered and adsorbed onto silica. Chromatography (hexane/DCM, 1:4) gave the title compound **10** (484 mg, 48%) as yellow needles, mp 126–129 °C (from cyclohexane), R_f 0.23 (hexane/DCM, 1:4); (found: C, 65.02; H, 4.07; N, 9.56. $C_{16}H_{12}N_2O_2S$ requires C, 64.85; H, 4.08; N, 9.45%); λ_{max} (DCM)/nm 229 (log ε 3.15), 279 inf (2.83), 304 (3.07), 391 (3.15); ν_{max}/cm^{-1} 3030w (Ar CH), 1650s and 1649s (C=O), 1491w, 1477w, 1456w, 1435m, 1362w, 1331m, 1312m, 1288w, 1207w, 1159w, 1128w, 1078w, 1036m, 999w, 978w, 934w, 905m, 876w, 847w, 826m, 800w, 760s; δ_H (500 MHz; $CDCl_3$) 7.96–7.94 (2H, m, Ph *H*), 7.47–7.40 (8H, m, Ph *H*), 5.01 (2H, s, NC*H*$_2$); δ_C (125 MHz; $CDCl_3$) 170.5 (s), 158.3 (s), 150.0 (s), 133.9 (s), 133.3 (s), 130.4 (d), 129.3 (d), 129.22 (d), 129.19 (d), 128.4 (d), 128.3 (d), 49.4 (t, OCH$_2$); *m*/*z* (EI) 296 (M^+, 5%), 149 (2), 135 (17), 107 (5), 105 (10), 103 (10), 91 (100), 77 (13), 65 (10), 51 (8). Further elution (*t*-BuOMe/EtOH, 9:1) gave 3-hydroxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) (322 mg, 46%) as yellow plates, mp 120–122 °C (from cyclohexane/DCM), R_f 0.28 (*t*-BuOMe/EtOH, 9:1); (found: C, 52.48; H, 2.91; N, 13.57. $C_9H_6N_2O_2S$ requires C, 52.42; H, 2.93; N, 13.58%); λ_{max} (DCM)/nm 230 (log ε 3.01), 241 (2.80), 307 (3.13), 323 inf (3.04), 361 (3.16); ν_{max}/cm^{-1} 3248br w (OH), 1612s and 1601s (C=O), 1537w, 1491w, 1458w, 1422w, 1379s, 1323w, 1294s, 1223m, 1183m, 1142m, 1076w, 1034w, 947m, 928w, 891w, 835s, 802w, 760w; δ_H (500 MHz; $CDCl_3$) OH peak missing 8.23–8.21 (2H, m, Ph *H*), 7.49–7.48 (3H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 160.7 (s), 160.0 (s), 154.9 (s), 133.8 (s), 131.0 (d), 128.5 (d), 128.4 (d); *m*/*z* (EI) 206 (M^+, 56%), 135 (14), 121 (3), 104 (100), 91 (4), 77 (36), 75 (55), 63 (4), 51 (17).

4.7. 3-Hydroxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (9) (using BBr_3)

To a stirred solution of 3-methoxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**8a**) (1.00 g, 4.5 mmol) [or 3-benzyloxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**8b**) (1.30 g, 4.5 mmol)] in DCM (4 mL) at ca. 0 °C, was added BBr_3 (512 μL, 5.4 mmol) and the mixture was kept at this temperature until no starting material remained (TLC). The reaction mixture was then extracted (H_2O) and the organic extracts were combined, dried (Na_2SO_4) and filtered to afford the title compound **9** (928 mg, 100%) as yellow plates, mp 120–122 °C (from cyclohexane/DCM), R_f 0.28 (*t*-BuOMe/EtOH, 9:1) identical to that described above.

4.8. 3-Phenyl-5-trifluoromethanesulfonoxy-4*H*-1,2,6-thiadiazin-4-one (11)

To a stirred mixture of 3-hydroxy-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) (1.00 g, 4.8 mmol) in DCM (4 mL) at ca. 0 °C was added Et_3N (736 μL, 5.3 mmol) and then Tf_2O (1.60 mL, 9.6 mmol) and the reaction left to warm to ca. 10 °C until no starting material remained (TLC). The reaction mixture was then diluted (DCM) and extracted (H_2O). The organic layer was dried (Na_2SO_4), filtered and

adsorbed onto silica. Chromatography (hexane/DCM, 7:3) gave the title compound **11** (1.54 g, 95%) as yellow plates, mp 59–61 °C (from cyclohexane), R_f 0.41 (hexane/DCM, 7:3); (found: C, 35.60; H, 1.48; N, 8.25. $C_{10}H_5F_3N_2O_4S_2$ requires C, 35.50; H, 1.49; N, 8.28%); λ_{max} (DCM)/nm 231 (log ε 2.89), 258 (2.86), 328 (3.29); ν_{max}/cm^{-1} 3073w (Ar CH), 1730w, 1686w, 1645m (C=O), 1427m, 1331w, 1285w, 1244m, 1227s, 1204m, 1175m, 1125m, 1086w, 1070w, 1030m, 999w, 945w, 935w, 845m; δ_H (500 MHz; $CDCl_3$) 8.23 (2H, dd, *J* 8.5, 1.5, Ph *H*), 7.56 (1H, ddd, *J* 7.0, 1.5, 1.5, Ph *H*), 7.50 (2H, dd, *J* 8.5, 7.0, Ph *H*); δ_C (125 MHz; $CDCl_3$) 163.2 (s), 159.6 (s), 149.1 (s), 132.8 (s), 132.5 (d), 129.2 (d), 128.6 (d), 118.4 (q, $^1J_{CF}$ 318.8, *C*F$_3$); *m*/*z* (EI) 338 (M$^+$, 64%), 269 (2), 205 (5), 177 (29), 149 (13), 143 (45), 134 (49), 115 (18), 103 (40), 91 (5), 77 (22), 69 (100), 51 (15).

4.9. 3-Chloro-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (12a)

To a stirred solution of 3-phenyl-5-trifluoromethanesulfonoxy-4*H*-1,2,6-thiadiazin-4-one (**11**) (1.00 g, 3.0 mmol) in acetone (4 mL) at ca. 20 °C, was added $BnEt_3NCl$ (820 mg, 3.6 mmol) and the mixture was heated at reflux until no starting material remained (TLC). On cooling to ca. 20 °C the reaction mixture was adsorbed onto silica and chromatographed (hexane/DCM, 7:3) to give the title compound **12a** (640 mg, 95%) as yellow plates, mp 117–118 °C (from cyclohexane/DCM), R_f 0.28 (hexane/DCM, 7:3); (found: C, 48.21; H, 2.20; N, 12.56. $C_9H_5ClN_2OS$ requires C, 48.11; H, 2.24; N, 12.47%); λ_{max} (DCM)/nm 233 (log ε 2.87), 252 (2.80), 335 (3.29); ν_{max}/cm^{-1} 3055w (Ar CH), 1730w, 1655s (C=O), 1638w, 1624s, 1614m, 1601w, 1524w, 1489m, 1443w, 1354w, 1333w, 1321w, 1285w, 1269w, 1254w, 1225w, 1179w, 1144w, 1101w, 1076w, 1043m, 914w, 874w, 849w, 797w, 766w; δ_H (500 MHz; $CDCl_3$) 8.16 (2H, d, *J* 7.5, Ph *H*), 7.54–7.46 (3H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 160.8 (s), 158.0 (s), 153.1 (s), 133.5 (s), 131.8 (d), 129.2 (d), 128.4 (d); *m*/*z* (EI) 226 (M$^+$+2, 26%), 224 (M$^+$, 62), 163 (3), 135 (47), 123 (17), 121 (45), 108 (6), 103 (53), 95 (40), 93 (100), 76 (43), 63 (8), 58 (13), 51 (31).

4.10. 3-Bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (12b)

To a stirred solution of 3-phenyl-5-trifluoromethanesulfonoxy-4*H*-1,2,6-thiadiazin-4-one (**11**) (1.00 g, 3.0 mmol) in acetone (4 mL) at ca. 20 °C, was added Et_4NBr (757 mg, 3.6 mmol) and the mixture was heated at reflux until no starting material remained (TLC). On cooling to ca. 20 °C the reaction mixture was adsorbed onto silica and chromatographed (hexane/DCM, 7:3) to give the title compound **12b** (606 mg, 75%) as yellow plates, mp 117–118 °C (from cyclohexane/DCM), R_f 0.28 (hexane/DCM, 7:3); (found: C, 40.24; H, 1.92; N, 10.39. $C_9H_5BrN_2OS$ requires C, 40.17; H, 1.87; N, 10.41%); λ_{max} (DCM)/nm 232 (log ε 2.93), 250 (2.80), 334 (3.27); ν_{max}/cm^{-1} 3063w (Ar CH), 1751w, 1695w, 1633s (C=O), 1601w, 1558w, 1541w, 1506w, 1479w, 1435w, 1344w, 1323w, 1296m, 1240w, 1188w, 1167m, 1101w, 1076w, 1034w, 1003m, 991m, 872w, 851w, 839w, 824w, 795m; δ_H (500 MHz; $CDCl_3$) 8.16 (2H, dd, *J* 8.5, 1.5, Ph *H*), 7.54–7.51 (1H, m, Ph *H*), 7.49–7.45 (2H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 160.6 (s), 156.4 (s), 147.7 (s), 133.5 (s), 131.8 (d), 129.2 (d), 128.4 (d); *m*/*z* (EI) 270 (M$^+$+2, 78%), 268 (M$^+$, 80), 167 (78), 165 (80), 139 (82), 137 (88), 135 (100), 108 (14), 103 (100), 91 (17), 86 (20), 76 (75), 63 (14), 58 (21), 51 (46).

4.11. 3-Iodo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (12c)

To a stirred solution of 3-phenyl-5-trifluoromethanesulfonoxy-4*H*-1,2,6-thiadiazin-4-one (**11**) (1.00 g, 3.0 mmol) in acetone (4 mL) at ca. 20 °C, was added KI (598 mg, 3.6 mmol) and the mixture was heated at reflux until no starting material remained (TLC). On cooling to ca. 20 °C the reaction mixture was adsorbed onto silica and chromatographed (hexane/DCM, 7:3) to give the title compound **12c** (379 mg, 40%) as yellow plates, mp 98–101 °C (from cyclohexane/DCM), R_f 0.33 (hexane/DCM, 7:3); (found: C, 34.25; H, 1.63; N, 8.91. $C_9H_5IN_2OS$ requires C, 34.19; H, 1.59; N, 8.86%); λ_{max} (DCM)/nm 233 (log ε 2.83), 247 inf (2.71), 261 inf (2.65), 341 (2.95); ν_{max}/cm^{-1} 3069w (Ar CH), 1630s (C=O), 1591w, 1483w, 1464w, 1433m, 1321w, 1292m, 1258w, 1221w, 1188w, 1161m, 1134w, 1101w, 1074w, 1032w, 999w, 984w, 935w, 874w, 849w, 822w, 793m; δ_H (500 MHz; $CDCl_3$) 8.17–8.15 (2H, m, Ph *H*), 7.52–7.45 (3H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 160.4 (s), 153.0 (s), 133.9 (s), 133.5 (s), 131.9 (d), 129.2 (d), 128.4 (d); *m*/*z* (EI) 316 (M$^+$, 100%), 213 (22), 189 (35), 185 (33), 162 (26), 135 (38), 127 (10), 103 (54), 86 (54), 76 (31), 63 (6), 58 (6), 51 (22).

4.12. 3-(2-Methoxyphenyl)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (13a); (typical procedure)

To a stirred solution of 3-bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**12b**) (50.0 mg, 0.19 mmol) in dioxane/H_2O (0.5:0.3 mL) at ca. 20 °C, was added 2-methoxyphenylboronic acid (28.9 mg, 0.19 mmol), Na_2CO_3 (30.0 mg, 0.29 mmol) and $Pd(OAc)_2$ (2.1 mg, 9.5×10^{-3} mmol) and the mixture was heated at reflux until no starting material remained (TLC). On cooling to ca. 20 °C the reaction mixture was diluted (DCM), extracted (H_2O) and the organic extracts were combined, dried (Na_2SO_4), filtered and adsorbed onto silica. Chromatography (hexane/DCM, 1:1) gave the title compound **13a** (44 mg, 79%) as yellow plates, mp 71–73 °C (from cyclohexane), R_f 0.39 (hexane/DCM, 1:1); (found: C, 64.77; H, 4.04; N, 9.37. $C_{16}H_{12}N_2O_2S$ requires C, 64.85; H, 4.08; N, 9.45%); λ_{max} (DCM)/nm 235 (log ε 3.16), 339 (3.35); ν_{max}/cm^{-1} 3019w (Ar CH), 2959w, 2924w, 2851w, 1638w, 1616m, 1595m, 1584w, 1499w, 1481w, 1462m, 1435m, 1350m, 1288w, 1261m, 1250w, 1238w, 1182w, 1167w, 1115m, 1076w, 1049w, 1024m, 920w, 864w, 851w, 816w, 800w, 768s; δ_H (500 MHz; $CDCl_3$) 8.19 (2H, dd, *J* 8.0, 1.5, Ph *H*), 7.49–7.45 (5H, m, Ph *H*), 7.08 (1H, dd, *J* 7.5, 7.5, Ph *H*), 7.00 (1H, d, *J* 9.0, Ph *H*), 3.85 (3H, s, OC*H*$_3$); δ_C (125 MHz; $CDCl_3$) 164.9 (s), 163.7 (s), 159.1 (s), 156.8 (s), 134.4 (s), 131.7 (d), 131.1 (d), 130.1 (d), 128.7 (d), 128.3 (d), 125.1 (s), 121.0 (d), 111.3 (d), 55.9 (q, O*C*H$_3$); *m*/*z* (EI) 296 (M$^+$, 31%), 265 (12), 193 (5), 165 (33), 135 (100), 119 (10), 108 (6), 103 (30), 91 (21), 77 (27), 63 (9), 51 (11).

4.13. 3-(4-Methoxyphenyl)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (13b)

Similar treatment of 3-bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**12b**) (50.0 mg, 0.19 mmol) with 4-methoxyphenylboronic acid (28.9 mg, 0.19 mmol) gave the title compound **13b** (51.2 mg, 91%) as yellow needles, mp 84–86 °C (from cyclohexane), R_f 0.31 (hexane/DCM, 1:1); (found: C, 64.93; H, 4.12; N, 9.41. $C_{16}H_{12}N_2O_2S$ requires C, 64.85; H, 4.08; N, 9.45%); λ_{max} (DCM)/nm 243 (log ε 3.13), 365 (3.34), 384 inf (3.16); ν_{max}/cm^{-1} 2922w, 2839w, 1618m, 1603m, 1578w, 1510w, 1468w, 1441w, 1418w, 1348w, 1312w, 1271w, 1254s, 1188m, 1182m, 1152w, 1121w, 1036m, 1013w, 1003w, 864w, 829m, 812w, 797w, 766w; δ_H (500 MHz; $CDCl_3$) 8.25 (2H, d, *J* 9.0, Ph *H*), 8.13 (2H, d, *J* 7.0, Ph *H*), 7.48–7.47 (3H, m, Ph *H*), 6.97 (2H, d, *J* 9.0, Ph *H*), 3.87 (3H, s, OC*H*$_3$); δ_C (125 MHz; $CDCl_3$) 165.5 (s), 162.0 (s), 160.3 (s), 159.9 (s), 134.7 (s), 130.92 (d), 130.89 (d), 128.9 (d), 128.2 (d), 127.2 (d), 113.6 (d), 55.4 (O*C*H$_3$); *m*/*z* (EI) 296 (M$^+$, 56%), 165 (45), 150 (12), 135 (100), 133 (18), 122 (5), 103 (17), 90 (7), 77 (15), 57 (5).

4.14. 3-(3-Nitrophenyl)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (13c)

Similar treatment of 3-bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**12b**) (50.0 mg, 0.19 mmol) with 3-nitrophenylboronic acid (31.7 mg, 0.19 mmol) gave the title compound **13c** (49 mg, 83%) as yellow needles, mp 164–165 °C (from cyclohexane), R_f 0.36 (hexane/DCM, 1:1); (found: C, 57.71; H, 2.77; N, 13.66. $C_{15}H_9N_3O_3S$ requires C, 57.87; H, 2.91; N, 13.50%); λ_{max} (DCM)/nm 237 (log ε 3.35), 267 inf (3.11), 350 (3.39); ν_{max}/cm^{-1} 3078w (Ar CH), 1612s (C=O),

1578w, 1533s, 1490w, 1483w, 1474w, 1445m, 1350s, 1281m, 1271m, 1098w, 1082w, 1072w, 1020w, 1001w, 916w, 903w, 889w, 851w, 835w, 810w, 789w; δ_H (500 MHz; $CDCl_3$) 9.08 (1H, s, Ph *H*), 8.57 (1H, d, *J* 8.0, Ph *H*), 8.34 (1H, dd, *J* 8.2, 1.3, Ph *H*), 8.17 (2H, d, *J* 7.8, Ph *H*), 7.66 (1H, dd, *J* 8.0, 8.0, Ph *H*), 7.53–7.48 (3H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 164.8 (s), 161.6 (s), 158.0 (s), 148.1 (s), 135.7 (s), 134.7 (d), 134.0 (s), 131.6 (d), 129.3 (d), 129.0 (d), 128.4 (d), 125.4 (d), 124.0 (d); *m*/*z* (EI) 311 (M^+, 48%), 180 (100), 135 (75), 108 (5), 103 (19), 90 (16), 77 (17), 63 (7), 51 (8).

4.15. 3-(4-Chlorophenyl)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (13d)

Similar treatment of 3-bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**12b**) (50.0 mg, 0.19 mmol) with 4-chlorophenylboronic acid (29.7 mg, 0.19 mmol) gave the title compound **13d** (44 mg, 77%) as yellow needles, mp 123–126 °C (from cyclohexane), R_f 0.64 (hexane/DCM, 1:1); (found: C, 59.82; H, 3.00; N, 9.27. $C_{15}H_9ClN_2OS$ requires C, 59.90; H, 3.02; N, 9.31%); λ_{max} (DCM)/nm 239 (log ε 3.18), 250 (3.14), 352 (3.36); ν_{max}/cm^{-1} 3044w (Ar CH), 1622s (C=O), 1595m, 1481w, 1441w, 1398m, 1352m, 1279m, 1267m, 1188w, 1156w, 1094s, 1034w, 1018m, 1005w, 997w, 916w, 854w, 826m, 804w, 783s; δ_H (500 MHz; $CDCl_3$) 8.18 (2H, d, *J* 9.0, Ar *H*), 8.14 (2H, dd, *J* 7.8, 1.3, Ph *H*), 7.51–7.46 (3H, m, Ph *H*), 7.44 (2H, d, *J* 8.5, Ar *H*); δ_C (125 MHz; $CDCl_3$) 165.1 (s), 161.0 (s), 159.4 (s), 137.4 (s), 134.4 (s), 132.8 (s), 131.3 (d), 130.4 (d), 128.9 (d), 128.5 (d), 128.3 (d); *m*/*z* (EI) 302 (M^++2, 17%), 300 (M^+, 50), 171 (27), 169 (77), 155 (7), 139 (25), 137 (26), 135 (100), 111 (18), 103 (19), 91 (6), 77 (23), 63 (4), 51 (11).

4.16. 3-Phenyl-5-(thien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (13e); (typical procedure)

To a stirred solution of 3-bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**12b**) (50.0 mg, 0.19 mmol) in MeCN (2 mL) at ca. 20 °C, was added 2-(tributyltin)thiophene (60.3 μL, 0.19 mmol) and $Pd(Ph_3P)_2Cl_2$ (6.7 mg, 9.5×10^{-3} mmol) and the reaction was heated at reflux until no starting material remained (TLC). On cooling to ca. 20 °C the reaction mixture was adsorbed onto silica and chromatographed (hexane/DCM, 1:1) to give the title compound **13e** (46 mg, 89%) as yellow needles, mp 104–106 °C (from cyclohexane), R_f 0.66 (hexane/DCM, 1:1); (found: C, 57.34; H, 3.01; N, 10.19. $C_{13}H_8N_2OS_2$ requires C, 57.33; H, 2.96; N, 10.29%); λ_{max} (DCM)/nm 256 (log ε 3.09), 298 (2.80), 380 (3.40), 387 (3.36); ν_{max}/cm^{-1} 3076w (Ar CH), 1622s (C=O), 1595m, 1514w, 1504w, 1454w, 1435m, 1408s, 1375s, 1352w, 1339m, 1263m, 1223w, 1211w, 1182w, 1080w, 1047m, 1032w, 1001m, 866m, 853w, 835w, 802w, 772w, 751m; δ_H (500 MHz; $CDCl_3$) 8.26 (1H, d, *J* 3.5, thienyl *H*), 8.19–8.17 (2H, m, Ph *H*), 7.64 (1H, d, *J* 5.0, thienyl *H*), 7.50–7.48 (3H, m, Ph *H*), 7.19 (1H, dd, *J* 4.5, 4.5, thienyl *H*); δ_C (125 MHz; $CDCl_3$) 163.2 (s), 159.4 (s), 155.5 (s), 136.2 (s), 134.5 (s), 134.4 (d), 133.4 (d), 132.2 (d), 129.0 (d), 128.3 (d), 127.7 (d); *m*/*z* (EI) 272 (M^+, 100%), 141 (79), 135 (86), 109 (18), 103 (17), 91 (6), 77 (20), 71 (8), 58 (7), 51 (7).

4.17. 3-(1-Methyl-1*H*-pyrrol-2-yl)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (13f)

Similar treatment of 3-bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**12b**) (50.0 mg, 0.19 mmol) with 1-methyl-2-(tributyltin)pyrrole (70.3 μL, 0.19 mmol) gave the title compound **13f** (44 mg, 86%) as yellow plates, mp 182–184 °C (from cyclohexane), R_f 0.49 (hexane/DCM, 1:1); (found: C, 62.37; H, 4.15; N, 15.55. $C_{14}H_{11}N_3OS$ requires C, 62.43; H, 4.12; N, 15.60%); λ_{max} (DCM)/nm 252 (log ε 3.24), 380 (3.47), 385 inf (3.43); ν_{max}/cm^{-1} 2957w, 1686w, 1626s (C=O), 1597w, 1524m, 1489s, 1466w, 1416s, 1404m, 1368m, 1342w, 1315w, 1298s, 1269w, 1250w, 1236w, 1225w, 1184w, 1150w, 1096w, 1069s, 1040w, 1026m, 974w, 924w, 894w, 874w, 854w, 818w, 799w, 787w; δ_H (500 MHz; $CDCl_3$) 8.10–8.08 (2H, m, Ph *H*), 7.72 (1H, dd, *J* 4.0, 1.5, pyrrolyl *H*), 7.47–7.46 (3H, m, Ph *H*), 6.88 (1H, s, pyrrolyl *H*), 6.23 (1H, dd, *J* 3.8, 2.8, pyrrolyl *H*), 3.97 (3H, s, NCH_3); δ_C (125 MHz; $CDCl_3$) 163.7 (s), 158.7 (s), 153.7 (s), 135.1 (s), 131.0 (d), 130.5 (d), 128.7 (d), 128.2 (d), 126.4 (s), 120.2 (d), 108.4 (d), 38.6 (q, NCH_3); *m*/*z* (EI) 269 (M^+, 60%), 164 (3), 138 (50), 135 (100), 123 (3), 110 (6), 106 (29), 103 (23), 91 (7), 77 (20), 64 (4), 51 (13).

4.18. 3-(Fur-2-yl)-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (13g)

Similar treatment of 3-bromo-5-phenyl-4*H*-1,2,6-thiadiazin-4-one (**12b**) (50.0 mg, 0.19 mmol) with 2-(tributylstannyl)furan (59.8 μL, 0.19 mmol) gave the title compound **13g** (42.9 mg, 88%) as yellow needles, mp 68–71 °C (from cyclohexane), R_f 0.50 (hexane/DCM, 1:1); (found: C, 60.83; H, 3.26; N, 10.87. $C_{13}H_8N_2O_2S$ requires C, 60.93; H, 3.15; N, 10.93%); λ_{max} (DCM)/nm 242 (log ε 2.97), 293 (2.60), 373 (3.28), 385 inf (3.10); ν_{max}/cm^{-1} 3167w, 3134w and 3109w (Ar CH), 1624s (C=O), 1609w, 1591w, 1560m, 1483s, 1431w, 1389m, 1346m, 1337w, 1273s, 1213w, 1188w, 1173w, 1142w, 1078w, 1036w, 1024s, 1001w, 993w, 926w, 883m, 847s, 806w, 772s, 700s; δ_H (500 MHz; $CDCl_3$) 8.16–8.14 (2H, m, Ph *H*), 7.90 (1H, d, *J* 3.5, furyl *H*), 7.70 (1H, d, *J* 1.5, furyl *H*), 7.49–7.47 (3H, m, Ph *H*), 6.62 (1H, dd, *J* 3.5, 1.5, furyl *H*); δ_C (125 MHz; $CDCl_3$) 162.4 (s), 159.6 (s), 151.1 (s), 147.8 (s), 146.4 (d), 134.5 (s), 131.1 (d), 129.0 (d), 128.3 (d), 120.0 (d), 112.8 (d); *m*/*z* (EI) 256 (M^+, 85%), 135 (46), 125 (100), 103 (16), 93 (11), 77 (19), 70 (10), 64 (7), 51 (10).

Acknowledgements

The authors thank the Cyprus Research Promotion Foundation (grant nos. ΕΝΙΣΧ/0504/08 and ΝΕΚΥΠ/0308/02) for financial support. Furthermore, the authors thank the following organizations in Cyprus for generous donations of chemicals and glassware: the State General Laboratory, the Agricultural Research Institute, the Ministry of Agriculture, MedoChemie Ltd and Biotronics Ltd. Finally, we thank the A. G. Leventis Foundation for helping to establish the NMR facility in the University of Cyprus.

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