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C–C Coupling Reactions | *Very Important Paper* |

Suzuki–Miyaura Coupling of Verdazyl Radicals

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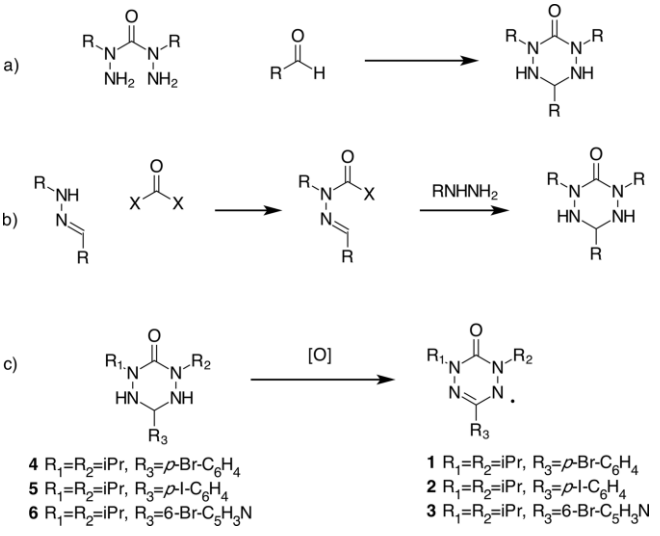
Abstract: Halogenated 3-aryl-1,5-diisopropyl verdazyl radicals have been shown to undergo Suzuki–Miyaura coupling reactions with a variety of boronic acids to give biaryl-substituted verdazyl derivatives in acceptable to good yields (50–90 %). The successful coupling depends on the halo substituent and the boronic acid, but most boronic acids could be coupled with the iodophenyl verdazyl radical under either ligandless conditions or in the presence of triphenylphosphine. The successful palladium-catalyzed coupling reaction facilitates the incorporation of verdazyl moieties into conjugated systems and can be used to modify the properties of organic materials. The new radicals were characterized by UV/Vis, ESR, and HRMS analysis and, particularly, by electron impact mass spectrometry, which generated the distinctive verdazyl fragmentation pattern.

Introduction

Stable free radicals, although often considered relatively uncommon species, have increasingly important applications as spin probes,[1] fluorescence quenchers,[2] spin relaxation agents, and components of new materials such as liquid crystals[3] and organic conductors.[4] There are relatively few classes of stable organic radicals, the most prominent of which possibly being nitroxides and nitronyl nitroxides. Others include thiadiazolyl, benzotriazinyl (the Blatter radicals), and verdazyl radicals. For materials applications, the latter two types are in some ways the most interesting because of the availability of multiple substitution sites. These could potentially be used to fine-tune the structure and properties of the resulting materials, provided that the functionality can be easily modified through standard synthetic methods. Most current methods for the synthesis of 6-oxoverdazyl radicals involve either the condensation reaction of an aldehyde with a carbonobis(hydrazide) to form a tetrazane (Scheme 1a)[5] or the stepwise assembly of a tetrazane ring from an aldehyde, substituted hydrazines, and phosgene or triphosgene (Scheme 1b).[3c,6] In either case, the resulting tetrazane is oxidized with organic or inorganic oxidants to give the verdazyl free radical (Scheme 1c).

Yields are relatively high for both pathways, but each requires at least two steps from the starting aldehyde, and the formation of the free radical is typically the final step of the synthesis. Synthetic methods that directly modify an existing verdazyl ring would have significant advantages over existing technology, as such an approach would facilitate access to a variety of side chain groups (e.g., nucleophilic or easily oxidized groups) that are otherwise incompatible with the verdazyl synthesis. Because facile oxidation is a hallmark of many organic conductors, the direct modification of a verdazyl ring may provide a more convenient method to prepare radical-substituted organic conductors. Such reactions may also facilitate the use of verdazyl radicals as labels and the rapid synthesis of diverse verdazyl libraries. Some work has already been done in this area. Notably, nitroaryl verdazyl radicals have been reduced to give the corresponding amines, which were subsequently acylated.[7] Similarly, ester-substituted verdazyl radicals have been deprotected, and the resulting phenoxides have been acylated without destroying the radical.[7] The alkylations of verdazyl species that have a phenoxide group at the 3-position[8] have been successful, but the alkylations of those that have a phenoxide at the 1- and 5-positions have not.[7]



Scheme 1. Synthesis of verdazyl radicals. (a) Synthesis of oxotetrazanes from carbonobis(hydrazide)s and aldehydes. (b) Synthesis of oxotetrazanes from hydrazones and hydrazines. (c) Oxidation of tetrazanes to 6-oxoverdazyls. Oxidants include *p*-benzoquinone, PbO_2, tetraphenylhydrazine, $NaIO_4$, $K_3Fe(CN)_6$.

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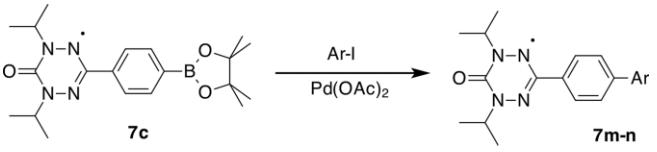
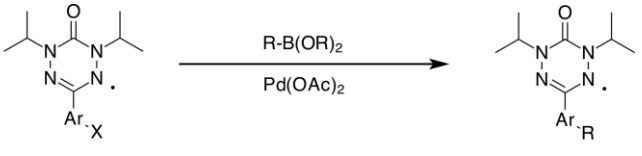
We are particularly interested in the development of verdazyl-containing conducting materials, in which the verdazyl spin interacts with the conducting "backbone". Previous results show that verdazyls interact ferromagnetically with the spins at the 3-position,[9] and, thus, the introduction of further conjugated substituents at this position may be a useful way to synthesize new organic conductors and spintronic materials. Palladium-catalyzed coupling reactions are particularly useful in this regard, as they use mild reaction conditions and are tolerant of numerous functional groups. There are few existing reports, however, of palladium-catalyzed coupling reactions of free radicals. Kalai,[10] Keddie,[11] and Fairfull-Smith[2f] studied palladium-catalyzed reactions of nonconjugated nitroxides. Stroh et al. reported the successful, albeit relatively poor yielding (approximately 40 %), Suzuki coupling reaction of nitronyl nitroxides.[12] More recently the palladium-catalyzed coupling reaction between a nitronyl nitroxide-gold species and various aryl halides was more successful. The palladium-catalyzed coupling of benzotriazinyls afforded products in much better yields (80–90 %),[13] but the Suzuki coupling of 6-oxoverdazyls that have a halophenyl substituent at the 1-position of the verdazyl group failed.[7] There have been no reports, however, of Pd-catalyzed coupling reactions that involve a 3-substituted verdazyl group. We report herein the successful Suzuki–Miyaura coupling of 3-(haloaryl)-substituted verdazyl radicals with boronic acids. We also report the synthesis of a verdazyl boronate ester and its subsequent coupling reactions to two aryl iodides. Together these reactions touch on the scope and limitations of the Suzuki–Miyaura reaction and the development of new verdazyl radical substituted materials.

Results and Discussion

Our studies used verdazyl radicals **1**–**3**, which feature halogenated aryl groups at the 3-position. These compounds were synthesized by condensation reactions of the corresponding aldehyde and 2,4-diisopropylcarbonobis(hydrazide) bis(hydrochloride) to give oxotetrazanes **4**–**6**. The subsequent oxidation with benzoquinone in toluene gave **1**–**3** in good yields,[5b] which were employed in Suzuki–Miyaura coupling reactions with a variety of different boronic acids and esters. Two different reaction conditions were utilized (Scheme 2), that is, under standard conditions with toluene as the solvent, potassium carbonate as the base, and palladium acetate/triphenylphosphine as the catalyst or under ligandless conditions, reported by Goodson et al.,[14] that use acetone as the solvent and no phosphorus ligand. Reactions that failed with *p*-bromophenyl-substituted verdazyl **1** were also attempted with *p*-iodophenyl-substituted verdazyl **2**, which was expected to be more reactive. Verdazyl **3** features an additional coordinating pyridine group, which may act as a ligand to possibly help or hinder the reaction. One product, verdazyl boronate ester **7c**, was used as a substrate for further coupling with aryl halides (Scheme 3). The reactions that employed standard conditions are found in



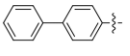
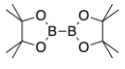
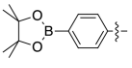
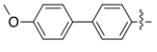
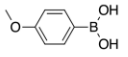
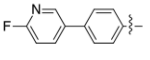
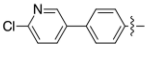
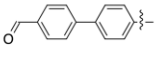
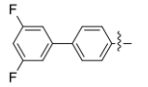
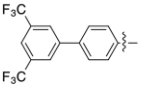
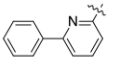
Scheme 3. Coupling of verdazyl boronate ester **7c**.



1. Ar=p-C_6H_4, X=Br
2. Ar=p-C_6H_4, X=I
3. Ar=2,6-C_5H_3N, X=Br

Scheme 2. Coupling of verdazyl aryl halides with boronic acids.

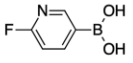
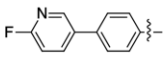
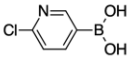
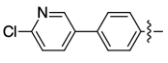
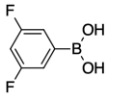
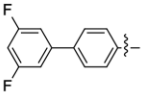
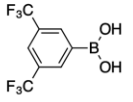
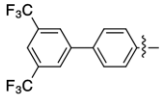
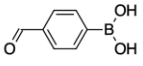
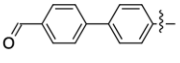
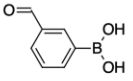
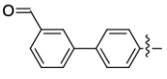
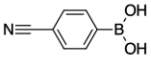
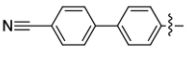
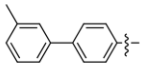
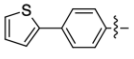
Table 1. Suzuki–Miyaura coupling reactions of verdazyls **1**–**3** under standard conditions.

Entry	Halide	Boronic acid	Ar-R	Product	Reaction time [h][a]	Yield [%]
1	**1**			**7a**	48	78
2	**1**			**7b**	36	50[b]
3	**1**			**7c**	75	84
4	**1**			**7d**	60	75
5	**1**			**7e**	72	75
6	**1**			**7f**	72	80
7	**1**			**7g**	72	14
8	**2**			**7h**	72	57
9	**2**			**7i**	72	41
10	**3**			**7j**	72	97

[a] Reagents and conditions: toluene/N_2, $Pd(OAc)_2$ (5 mol-%), Ph_3P (15 mol-%), K_2CO_3 (2 equiv.), 80 °C. [b] Yield determined by GC analysis, and the remaining material was unreacted verdazyl **1**.

Table 1, and those carried out under ligandless conditions are reported in Table 2.

Table 2. Suzuki–Miyaura coupling reactions of verdazyl radicals **2** and **7c** under ligandless conditions.

Entry	Aryl halide	Boronic acid	R-Ar	Product	Yield[a] %
1	**2**			**7e**	45
2	**2**			**7f**	60
3	**2**			**7h**	98
4	**2**			**7i**	61
5	**2**			**7g**	73
6	**2**			**7k**	88
7	**2**			**7l**	86
8		**7c**		**7m**	40
9		**7c**		**7n**	40

[a] Reagents and conditions: acetone/H_2O (1:1), K_2CO_3 (2 equiv.), $Pd(OAc)_2$ (1 mol-%), at reflux for 2 h under N_2.

The progress of all of reactions was monitored by TLC or GC analysis, and the products of successful reactions were purified by recrystallization and/or chromatography (with the exception of the product from methylboronic acid). New species were characterized by GC–MS, HRMS, ESR, IR and UV/Vis spectroscopy. The ESR spectra of all of the verdazyl radicals were indistinguishable from the other diisopropyl-substituted aryl verdazyls.[5b,8] For example, the ESR spectrum and simulated spectrum of radical **7n** are shown in Figure 1. The UV/Vis spectra of all of the radicals showed prominent bands in the visible range at 420 and at approximately 505 nm, which are typical for these structures.[5b,8] The mass spectrometry data, in particular, showed a reproducible fragmentation pattern that we have observed from other diisopropyl verdazyl radicals. Notably, there were prominent fragment ions at [M – 42], [M – 84], presumably from the successive loss of the isopropyl groups through McLafferty-type fragmentations, and [M – 155].[5b,8]

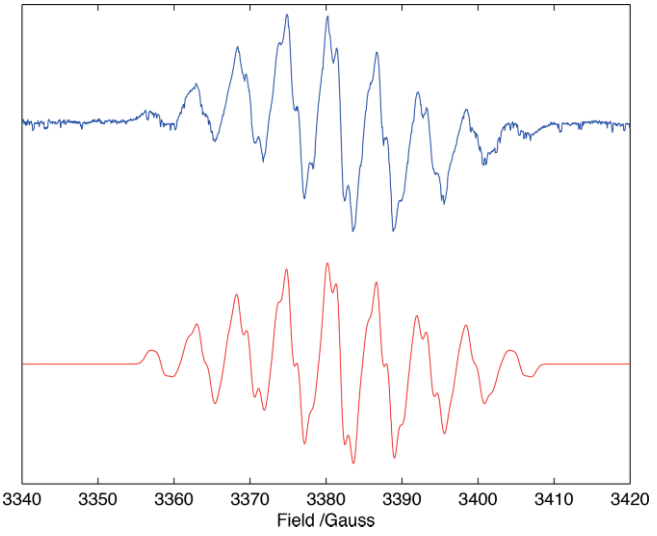
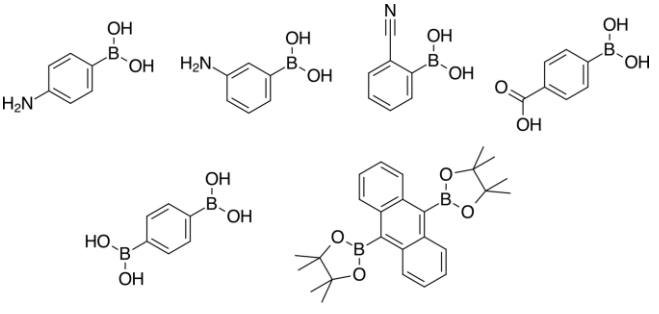


Figure 1. Experimental EPR spectrum (top) and spectral simulation (bottom) of radical **7n**. Simulation parameters: g = 2.0058, a_H = 1.1 G, a_N = 5.16 G, a_N = 6.66 G, linewidth: 1.5 G.

There are several notable observations as a result of this data. First, a few of the boronic acids did not proceed in the reaction under either of the investigated conditions (Scheme 4). These include 4- and 3-aminophenyl boronic acids, 2-cyanophenyl boronic acid, 4-carboxyphenylboronic acid, benzene 1,4-bis(boronic acid), and anthracene-9,10-bis(pinacolylboronate). We believe that steric factors are one explanation for this, as one reaction with the less hindered 4-cyanophenyl boronic acid was successful. The failure of the amino and carboxy boronic acids may be the result of the competing coordination of the functional group to the metal center. The reasons for failure of the benzene bis(boronic acid) and the anthracene bis(boronate) are less clear but may be the result of their limited solubility under the reaction conditions. For all these unsuccessful reactions, the starting verdazyl radical was recovered unchanged, and the boronic acid was typically phenylated in the presence of triphenylphosphine.



Scheme 4. Boronic acids/esters that failed to react under any of the reaction conditions that were employed.

Of the two reaction conditions, the ligandless method seemed to give consistent results with a larger number of boronic acids, provided that the iodophenyl verdazyl **2** was used as the aryl halide. Under these conditions, the reaction

times were short (i.e., 2 h) and the workup was straightforward, although the yields were not necessarily any better. However, using bromophenyl verdazyl **1** as the substrate under the ligandless conditions produced no detectable levels of product within the same reaction time. Both the bromides and iodides provided products under the standard conditions, but the reaction times were typically long (up to 72 h). In several cases, a competitive C–P bond cleavage followed by phenylation of the boronic acid resulted in a much reduced or zero percent yield of the intended Suzuki product. Other byproducts observed by GC–MS included those from the homocoupling of the boronic acid and a small amount of product resulting from the hydrodehalogenation of the verdazyl radical. In some cases, these reactions were minimized by using the iodophenyl rather than the bromophenyl verdazyl radical, which suggests that a slow oxidative addition step allowed for the competition of the C–P bond cleavage. Using verdazyl **7c** as the boronic acid component was successful in the reactions with aryl iodides but not with aryl bromides. The phenylation of the boronic acid from triphenylphosphine was also a problem that was prevented by using the ligandless conditions.

At this point, it has been well-established that the standard Suzuki-type coupling reactions occur through an oxidative addition/transmetallation/reductive elimination pathway at the Pd center, which is stabilized by several phosphine ligands.[15] The ligandless coupling reactions are presumed to follow a similar path, although many are heterogeneous systems and have been less studied.[16] In the standard homogeneous systems, substrates that can coordinate to the catalytic metal center can slow down or halt the catalytic cycle, but the effect is more subtle in the ligandless systems, which reflects a balance between interfering with the catalytic cycle and stablizing the catalytic Pd nanoparticles.[16b] Verdazyl radicals are weak sigma donor ligands but have significant pi acceptor capability and can show non-innocent behavior. Hicks has reported several recent studies on verdazyl palladium species, in particular, palladium(0) species that reduce verdazyl radicals upon coordination to give Pd^{II} complexes of leucoverdazyls.[17] This latter observation may provide some insight as to why many of these reactions were successful, whereas those of Kaszynski failed. Kaszynski's reactions were attempted with a halophenyl substituent at the 1-position of the verdazyl radical. At this position, the spin is partially delocalized onto the phenyl ring (Figure 2), which allows it to interact with the Pd center of the intermediate after the oxidative addition to the aryl halogen bond. Such an interaction may interfere with the redox cycle required for catalysis. In the current study, the node at the 3-position of the singly occupied molecular orbital (SOMO) of the verdazyl radical (Figure 2) precludes such an interaction during the catalytic cycle, although the reversible coordination of the verdazyl nitrogen atom to Pd may reduce the amount of available catalyst.

The long reaction times of the Suzuki coupling reactions under standard conditions (Table 1) are consistent with this idea. Somewhat surprising, however, is that the reaction of the chelating verdazyl **3** (Table 1, Entry 10) was not significantly slower than any of the other bromophenyl verdazyls. It is more surprising that the reaction proceeds far more rapidly without any phosphine to coordinate to the Pd center. However, such apparently contradictory observations have been made before.[16b] It is believed that in such reactions, the substrate also helps to stabilize the palladium nanoparticles through coordination.

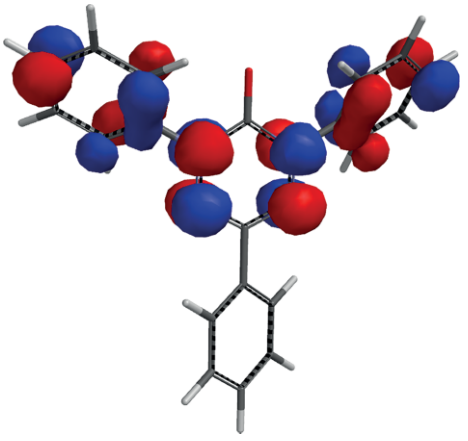


Figure 2. SOMO of the 1,3,5-triphenyl-6-oxoverdazyl (calculated by the semi-empirical AM1 method), which shows the node at the 3-position and the delocalization of the SOMO onto the phenyl groups at the 1- and 5-positions.

Apart from the role of the verdazyl-palladium coordination, the successful palladium-catalyzed coupling of verdazyl radicals to other conjugated species provides new pathways to introduce free radical substituents into organic molecules. This is particularly important for the design of organic materials, as many conducting materials are susceptible to the oxidation conditions that are used in prior syntheses of verdazyls. The synthesis of a verdazyl-substituted thiophene, in particular, suggests the synthetic possibility of verdazyl-substituted oligothiophenes, which can act as components of new organic conductors. We anticipate further use of these coupling reactions to synthesize verdazyl-modified materials and other new organic and organometallic ligands.

Conclusions

Verdazyl radicals that are substituted with a halogenated aryl group at the 3-position can undergo Suzuki–Miyaura-type coupling reactions with boronic acids and esters to give products in modest to excellent yields. The reaction occurs under both standard and ligandless conditions, though the latter proceeds in far shorter reaction times and with a greater variety of substrates. These reactions may be useful for the incorporation of verdazyl-type radicals into functional organic materials.

Experimental Section

General Methods: Verdazyl radicals **1**–**3** were synthesized from the corresponding tetrazanes **4**–**6** by following previously described methods.[5b] All verdazyl radicals were isolated as red-orange crystalline solids. GC–MS was perfomed on a phenylmethyl siloxane column (30 m) under the two different conditions: (A) starting oven temperature at 50 °C, 2 min hold, ramp to 300 °C at 20 °C min^{-1}

and (B) starting oven temperature at 150 °C, 2 min hold, ramp to 300 °C at 20 °C min^{-1}. The NMR spectroscopic data were recorded at 300 MHz with the residual solvent signal ($CHCl_3$ at δ = 7.25 ppm for ^1H NMR) and the solvent signal ($CHCl_3$ at δ = 77.0 ppm for ^{13}C NMR) as references. IR spectra were recorded by using attenuated total reflectance (ATR). ESR spectra were recorded in degassed toluene at room temperature on an X-band instrument.

General Procedure for the Suzuki–Miyaura Coupling Reaction of Verdazyl Halides under Standard Reaction Conditions: Under nitrogen, a sample of one of the verdazyls **1**–**3** was added to a three-neck round bottomed flask that contained toluene (50 mL), the organoboronic acid or ester (2 mol equiv.), and potassium carbonate (1.5 mol equiv.). The solution was degassed with nitrogen at room temperature for 10 min. To this solution was added triphenylphosphine (0.40 mol equiv.), and the resulting mixture was stirred until everything was completely dissolved. The reaction flask was degassed again for 5 min. Then palladium(II) acetate (0.1 mol equiv.) was quickly added to the solution as a positive flow of nitrogen gas was passed into the reaction flask. The reaction flask was degassed for an additional 10 min and then heated in an oil bath at 80 °C for the duration of the reaction. The progress of the coupling reactions were monitored by either GC–MS or TLC. Once the reaction reached completion, the solution was filtered, and the filtrate was evaporated. The resulting residue was purified by chromatography on a silica gel column (dichloromethane/ethyl acetate) to give the products as orange-red crystalline solids.

General Procedure for the Suzuki–Miyaura Coupling of Verdazyl Halides and Boronates under Ligandless Reaction Conditions: The boronic acid or boronate ester (38 mg, 0.1 mmol) was combined with the aryl iodide (0.1 mmol) and potassium carbonate (0.25 mmol) in water (0.5 mL) and the palladium acetate (1 mg) in acetone (1 mL). The mixture was purged with nitrogen for 5 min and then heated at reflux for 2 h. At this time, GC–MS indicated that no boronate/boronic acid remained. After the cooling and evaporation of the solvent, the mixture was triturated with hexane, and the hexane was evaporated to give the crude products as orange-red crystalline solids. These solids were purified by recrystallization and/or chromatography on a silica gel column.

3-(4′-Bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (1): By using the previously reported reaction conditions, 6-(4′-bromophenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (**4**, 1.501 g, 4.41 mmol) gave 3-(4′-bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 1.402 g, 94 % yield); m.p. 89–90 °C. GC–MS (B): t_R = 8.38 min, >99 % pure by integration, *m/z* (%) = 337 (38), 296 (30), 253 (100), 182 (45), 102 (48). HRMS: calcd. for $C_{14}H_{19}{}^{79}BrN_4O$ $[M]^+$ 337.0664; found 337.0667. IR (ATR): $\tilde{\nu}$ = 1680 (C=O), 3000 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 415 [3.3], 495 [2.8] nm.

3-(4′-Iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (2): By using the previously reported reaction conditions, 6-(4′-iodophenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (**5**, 1.900 g, 4.90 mmol) gave 3-(4′-iodophenyl)-1,5-diisopropyl--6-oxoverdazyl (**2**, 1.537 g, 82 % yield); m.p. 87–91 °C. GC–MS (B): t_R = 8.96 min, >99 % pure by integration, *m/z* (%) = 385 (48), 343 (35), 301 (100), 230(40), 102 (48). HRMS: calcd. for $C_{14}H_{19}IN_4O$ $[M]^+$ 385.0525; found 385.0517. IR (ATR): $\tilde{\nu}$ = 1656 (C=O), 2975 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 416 [3.4], 502 [2.8] nm.

3-(6′-Bromopyridyl)-1,5-diisopropyl-6-oxoverdazyl (3): By using the previously reported reaction conditions, 6-(6′-bromo-2-pyridyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (**6**, 3.44 g, 9.27 mmol) gave 3-(6′-bromopyridyl)-1,5-diisopropyl-6-oxoverdazyl (**3**, 3.133 g, 92 % yield); m.p. 99–100 °C. GC–MS (A): t_R = 8.21 min, 96 % pure by integration *m/z* (%) = 338 (42), 296 (55), 254 (85), 183 (84), 103 (100). HRMS: calcd. for $C_{13}H_{18}{}^{79}BrN_5O$ $[M + H]^+$ 339.0695; found 339.0680 IR (ATR): $\tilde{\nu}$ = 1662 (C=O), 2980 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 409 [3.5], 462 [2.7] nm.

6-(4′-Bromophenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (4): By using the previously reported reaction conditions, 4-bromobenzaldehyde (1.218 g, 6.58 mmol) gave 6-(4′-bromophenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (**4**, 1.621 g, 94 % yield) as a white crystalline solid; m.p. 224–226 °C. GC–MS (A): t_R = 14.82 min, *m/z* = 340. HRMS: calcd. for $C_{14}H_{23}{}^{79}BrN_4O$ $[M + H]^+$ 341.0977; found 341.0659. IR (ATR): $\tilde{\nu}$ = 1628 (C=O), 2993, 3043 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.50 (m, 4 H), 4.97 (septet, $^3J_{H,H}$ = 6.6 Hz, 2 H), 4.57 (t, $^3J_{H,H}$ = 12 Hz, 1 H), 3.73 (d, $^3J_{H,H}$ = 12 Hz, 2 H), 1.14 (d, $^3J_{H,H}$ = 6.56 Hz, 6 H), 1.12 (d, $^3J_{H,H}$ = 6.56 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 19.0 (CH_3), 19.7 (CH_3), 48.9 (isopropyl CH), 71.1 (CH), 123.7, 128.6 (CH), 132.1 (CH), 133.1, 153.3 (C=O) ppm.

6-(4′-Iodophenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (5): By using the previously reported reaction conditions, 4-iodobenzaldehyde (1.89 g, 8.13 mmol) gave 6-(4′-iodophenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (**5**, 2.105 g, 90 % yield) as a white crystalline solid; m.p. 175–182 °C. GC–MS (A): t_R = 14.82 min, *m/z* = 388. HRMS: calcd. for $C_{14}H_{23}IN_4O$ $[M + H]^+$ 389.0838; found 389.0838. IR (ATR): $\tilde{\nu}$ = 1574 (C=O), 3209 (NH), 2976 (CH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, $^3J_{H,H}$ = 8 Hz, 2 H), 7.34 (d, $^3J_{H,H}$ = 8 Hz, 2 H), 4.61 (septet, $^3J_{H,H}$ = 6.6 Hz, 2 H), 4.52 (t, $^3J_{H,H}$ = 12 Hz, 1 H), 3.86 (d, $^3J_{H,H}$ = 12 Hz, 2 H), 1.11 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H), 1.09 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 18.7(CH_3), 19.8 (CH_3), 48.0 (isopropyl CH), 71.0 (CH), 95.0, 128.4 (CH), 135.4, 137.9 (CH), 154.5 (C=O) ppm.

6-(6′-Bromo-2-pyridyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (6): By using the previously reported reaction conditions, 6-bromopyridine-2-carboxaldehyde (0.738 g, 3.97 mmol) gave 6-(6′-bromo-2-pyridyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (**6**, 1.104 g, 83 % yield) as a white crystalline solid; m.p. 227 °C (dec). GC–MS (A): t_R = 15.72 min, *m/z* = 341. HRMS: calcd. for $C_{13}H_{21}{}^{79}BrN_5O$ $[M + H]^+$ 342.0929; found 342.0930. IR (ATR): $\tilde{\nu}$ = 1577 (C=O), 3240 (NH) cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.79 (t, $^3J_{H,H}$ = 7.71 Hz, 1 H), 7.34 (dd, $^3J_{H,H}$ = 7.33 Hz, 2 H), 5.06 (d, $^3J_{H,H}$ = 11.32 Hz, 1 H), 4.44(m, 3 H), 0.99 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H), 0.97 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 18.6 (CH_3), 19.7 (CH_3), 47.9 (isopropyl CH), 71.2 (CH), 122.7 (CH), 129.0 (CH), 139.7 (CH), 142.5, 153.6, 157.1 (C=O) ppm.

3-Biphenyl-1,5-diisopropyl-6-oxoverdazyl (7a): 3-(4′-Bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 0.0285 g, 0.0843 mmol) coupled with phenylboronic acid (2 mol equiv.) gave 3-biphenyl-1,5-diisopropyl-6-oxoverdazyl (**7a**, 0.0221 g, 78 % yield). GC–MS (B): t_R = 10.67 min, 96 % pure by integration, *m/z* (%) = 335 (60), 293 (20), 252 (40), 251 (100), 180 (80), 179 (75). IR (ATR): $\tilde{\nu}$ = 1675 (C=O), 2975 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} = 420, 504 nm. This data matches the previously reported parameters for this verdazyl radical.[5b]

1,5-Diisopropyl-3-(4′-methylphenyl)-6-oxoverdazyl (7b): Under the standard conditions, 3-(4′-bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 0.0285 g, 0.0843 mmol) coupled with methylboronic acid (2 mol equiv.) gave an approximately 50:50 mixture of 1,5-diisopropyl-3-(4′-methylphenyl)-6-oxoverdazyl (**7b**, identified by GC–MS analysis) and the starting material. The separation of the product from the starting material by column chromatography

proved extremely challenging. GC–MS (A): t_R = 12.422 min, *m/z* (%) = 273 (41), 231(20), 189 (100), 118 (75). Similar results were obtained by using 1,5-diisopropyl-3-(4′-iodophenyl)-6-oxoverdazyl (**2**) as the aryl halide component. No further attempts were made to separate the product mixture as verdazyl **7b** was more conveniently synthesized from *p*-tolualdehyde.

1,5-Diisopropyl-3-[4′-(4′′,4′′,5′′,5′′-tetramethyl-1′′,3′′-dioxaborolane)phenyl]-6-oxoverdazyl (7c): Under the standard conditions, 3-(4′-bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 0.0285 g, 0.0843 mmol) coupled with bis(pinacolato)diboron (2 mol equiv.) gave 1,5-diisopropyl-3-[4′-(4′′,4′′,5′′,5′′-tetramethyl-1′′,3′′-dioxaborolane)phenyl]-6-oxoverdazyl (**7c**, 0.0274 g, 84 % yield); m.p. 161–162 °C. GC–MS (B): t_R = 10.38 min, 96 % pure by integration, *m/z* (%) = 385 (67), 343 (25), 301 (100), 230 (35). HRMS: calcd. for $C_{25}H_{30}BN_4O_3$ $[M]^+$ 385.2411; found 385.2421. IR (ATR): $\tilde{\nu}$ = 1687 (C=O), 2993 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 417 [3.3], 473 [2.7] nm.

1,5-Diisopropyl-3-[4′-(4′′-methoxybiphenyl)]-6-oxoverdazyl (7d): Under the standard conditions, 3-(4′-bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 0.0285 g, 0.0843 mmol) coupled with 4-methoxyphenylboronic acid gave 1,5-diisopropyl-3-[4′-(4′′-methoxybiphenyl)]-6-oxoverdazyl (**7d**, 0.0231 g, 75 % yield); m.p. 127–130 °C. GC–MS (B): t_R = 12.56 min, 97 % pure by integration, *m/z* (%) = 365 (55), 323 (23), 281 (100), 210 (70). HRMS: calcd. for $C_{21}H_{25}N_4O_2$ $[M]^+$ 365.1977; found 365.1923. IR (ATR): $\tilde{\nu}$ = 1675 (C=O), 2965 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 421 [3.3], 501 [2.9] nm.

3-[4′-(4′′-Fluoro-3′′-pyridyl)phenyl]-1,5-diisopropyl-6-oxoverdazyl (7e): Under the standard conditions, 3-(4′-bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 0.0285 g, 0.0843 mmol) coupled with 6-fluoropyridyl-3-boronic acid gave 3-[4′-(4′′-fluoro-3′′-pyridyl)phenyl]-1,5-diisopropyl-6-oxoverdazyl (**7e**, 0.0224 g, 75 % yield). Under ligandless conditions, 3-(4′-iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.038 g, 0.1 mmol) was coupled with the same boronic acid to give verdazyl **7e** (0.016 g, 45 % yield); m.p. 102–109 °C. GC–MS (A): t_R = 13.19 min, >99 % pure by integration, *m/z* (%) = 354 (47), 312 (22), 270 (100), 199 (90). HRMS: calcd. for $C_{19}H_{21}FN_5O$ $[M]^+$ 354.1729; found 354.1722. IR (ATR): $\tilde{\nu}$ = 1687 (C=O), 2985 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 416 [3.2], 504 [2.7] nm.

3-[4′-(4′′-Chloro-3′′-pyridyl)phenyl]-1,5-diisopropyl-6-oxoverdazyl (7f): Under the standard conditions, 3-(4′-bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 0.0285 g, 0.0843 mmol) coupled with 6-chloropyridyl-3-boronic acid gave 3-[4′-(4′′-chloro-3′′-pyridyl)phenyl]-1,5-diisopropyl-6-oxoverdazyl (**7f**, 0.0251 g, 80 % yield). Under ligandless conditions, 3-(4′-iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.038 g, 0.1 mmol) was coupled with the same boronic acid to give verdazyl **7f** (0.022 g, 60 % yield); m.p. 143–146 °C. GC–MS (A): t_R = 14.96 min, 95 % pure by integration, *m/z* (%) = 370 (45), 328 (25), 286 (100), 215 (75). HRMS: calcd. for $C_{19}H_{21}ClN_5O$ $[M + H]^+$ 371.1513; found 371.1504. IR (ATR): $\tilde{\nu}$ = 1687 (C=O), 2980 (CH) cm^{-1}. UV/Vis (C_6H_{14}): λ_{max} [log ε/M^{-1} cm^{-1})] = 419 [3.3], 504 [2.8].

3-(4′′-Formylbiphenyl)-1,5-diisopropyl-6-oxoverdazyl (7g): Under the standard conditions 3-(4′-bromophenyl)-1,5-diisopropyl-6-oxoverdazyl (**1**, 0.34 g, 1 mmol) coupled with 4-formylphenylboronic acid gave 3-(4′′-formylbiphenyl)-1,5-diisopropyl-6-oxoverdazyl (**7g**, 0.051 g, 14 % yield). Under the ligandless conditions, 3-(4′-iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.038 g, 0.1 mmol) was coupled with the same boronic acid to give verdazyl **7g** (0.026 g, 73 % yield); m.p. 69–73 °C. UV/Vis (CH_3CN): λ_{max} [log (ε/M^{-1} cm^{-1})] = 420 [3.0], 486 [2.6] nm. IR (ATR): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}. GC–MS (B): t_R = 14.18 min, >99 % pure by integration, *m/z* (%) = 363 (16), 281 (33), 280 (30), 279 (30), 208 (50), 207 (100). HRMS: calcd. for $C_{21}H_{23}N_4O_2$ $[M + H]^+$ 363.1820; found 363.1847.

3-[4′-(3′′,5′′-Difluorobiphenyl)]-1,5-diisopropyl-6-oxoverdazyl (7h): 3-(4′-Iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.022 g, 0.06 mmol) was coupled with 3,5-difluorophenylboronic acid to give 3-[4′-(3′′,5′′-difluorobiphenyl)]-1,5-diisopropyl-6-oxoverdazyl (**7h**, 12 mg, 57 % yield). Under ligandless conditions, 3-(4′-iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.038 g, 0.1 mmol) was coupled with the same boronic acid to give verdazyl **7h** (0.036 g, 98 % yield); m.p. 121–123 °C. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 422 [3.1], 502 [2.7] nm. HRMS: calcd. for $C_{20}H_{21}F_2N_4O$ $[M]^+$ 371.1683; found 371.1683. IR (NaCl): $\tilde{\nu}$ = 1671 (C=O), 2979 (CH) cm^{-1}. GC–MS (B): t_R = 10.22 min, >99 % pure by integration, *m/z* (%) = 371 (48), 329 (20), 287 (100), 216 (75).

1,5-Diisopropyl-3-{4′-[3′′,5′′-bis(trifluoromethyl)biphenyl]}-6-oxoverdazyl (7i): Under the standard conditions, 3-(4′-iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.022 g, 0.06 mmol) was coupled with 3,5-bis(trifluoromethyl)phenylboronic acid to give 1,5-diisopropyl-3-{4′-[3′′,5′′-bis(trifluoromethyl)biphenyl]}-6-oxoverdazyl (**7i**, 11 mg, 41 % yield). Under ligandless conditions, 3-(4′-iodophenyl)-1,5-diisopropyl--6-oxoverdazyl (**2**, 0.038 g, 0.1 mmol) was coupled with the same boronic acid to give verdazyl **7i** (0.029 g, 61 % yield); m.p. 111–113 °C. UV/Vis (C_6H_{14}): λ_{max} [log (ε/M^{-1} cm^{-1})] = 423 [3.1], 502 [2.6] nm. HRMS: calcd. for $C_{22}H_{21}F_6N_4O$ $[M]^+$ 471.1620; found 471.1619. IR (NaCl): $\tilde{\nu}$ = 1679 (C=O), 2961 (CH) cm^{-1}. GC–MS (B): t_R = 9.55 min, 92 % pure by integration, *m/z* (%) = 471 (40), 429 (20), 387 (100), 319 (99).

1,5-Diisopropyl-3-[2′-(6′-phenylpyridyl)]-6-oxoverdazyl (7j): Under the standard conditions, 3-(6′-bromopyridyl)-1,5-diisopropyl-6-oxoverdazyl (**3**, 0.34 g, 1 mmol) was coupled with phenylboronic acid to give 1,5-diisopropyl-3-[2′-(6′-phenylpyridyl)]-6-oxoverdazyl (**7j**, 0.33 g, 0.97 mmol, 97 % yield); m.p. 102–104 °C. UV/Vis (CH_3CN): λ_{max} [log (ε/M^{-1} cm^{-1})] = 406 [3.3], 447 [sh, 2.8] nm. IR (ATR): $\tilde{\nu}$ = 1682 (C=O), 2981 (CH) cm^{-1}. GC–MS (B): t_R = 10.41 min, >99 % pure by integration, *m/z* (%) = 337 (55), 294 (30), 252 (39), 181 (100). HRMS: calcd. for $C_{19}H_{23}N_5O$ $[M + H]^+$ 337.1902; found 337.1898.

3-(3′′-Formylbiphenyl)-1,5-diisopropyl-6-oxoverdazyl (7k): Under ligandless conditions 3-(4′-iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.038 g, 0.1 mmol) was coupled with 3-formylphenylboronic acid to give 3-(3′′-formylbiphenyl)-1,5-diisopropyl-6-oxoverdazyl (**7k**, 0.032 mg, 88 % yield); m.p. 140–143 °C. UV/Vis (CH_3CN): λ_{max} [log (ε/M^{-1} cm^{-1})] = 420 [3.0], 486 [2.5] nm. IR (ATR): $\tilde{\nu}$ = 1674 (C=O) cm^{-1}. GC–MS (B): t_R = 12.08 min, >99 % pure by integration, *m/z* (%) = 363 (50), 280 (75), 279 (100), 208 (95). HRMS: calcd. for $C_{21}H_{23}N_4O_2$ $[M + H]^+$ 363.1820; found 363.1816.

3-(4′′-Cyanobiphenyl)-1,5-diisopropyl-6-oxoverdazyl (7l): Under the ligandless conditions, 3-(4′-iodophenyl)-1,5-diisopropyl-6-oxoverdazyl (**2**, 0.038 g, 1 mmol) was coupled with 4-cyanophenylboronic acid to give 3-(4′′-cyanobiphenyl)-1,5-diisopropyl-6-oxoverdazyl (**7l**, 0.031 g, 86 % yield); m.p. 167–169 °C. UV/Vis (CH_3CN): λ_{max} [log (ε/M^{-1} cm^{-1})] = 420 [3.0], 486 [2.7]. IR (ATR): $\tilde{\nu}$ = 1674 (C=O), 2210 (CN) cm^{-1}. GC–MS (B): t_R = 12.28 min, 98 % pure by integration, *m/z* (%) = 360 (42), 317 (20), 277 (55), 276 (100), 205 (80), 204 (75). HRMS: calcd. for $C_{21}H_{22}N_5O$ $[M + H]^+$ 361.1902; found 361.1897.

1,5-Diisopropyl-3-(3′′-methylbiphenyl)-6-oxoverdazyl (7m): Under ligandless conditions, verdazyl boronate **7c** (33 mg) and 3-iodotoluene (18 mg) gave 1,5-diisopropyl-3-(3′′-methylbiphenyl)-6-oxoverdazyl (**7m**, 11 mg, 40 % yield); m.p. 129–131 °C. UV/Vis (CH_3CN): λ_{max} [log (ε/M^{-1} cm^{-1})] = 420 [3.1], 503 [2.7] nm. IR (ATR): $\tilde{\nu}$ = 1666 (C=O) cm^{-1}. GC–MS (B): t_R = 10.33 min, 95 % pure by integration,

m/z (%) = 349 (75), 307 (20), 265 (100), 194 (90). HRMS: calcd. for $C_{21}H_{26}N_4O$ $[M]^+$ 349.2028; found 349.2025.

1,5-Diisopropyl-3-[4′-(2′′-thiophenyl)phenyl]-6-oxoverdazyl (7n): Under ligandless conditions, verdazyl boronate **7c** (33 mg) and 2-iodothiophene (18 mg) gave 1,5-diisopropyl-3-[4′-(2′′-thiophenyl)phenyl]-6-oxoverdazyl (**7n**, 12 mg, 40 % yield); m.p. 122–124 °C. UV/Vis (CH_3CN): λ_{max} [log (ε/M^{-1} cm^{-1})] = 420 [3.1], 505 [2.7] nm. IR (ATR): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}. GC–MS (B): t_R = 9.84 min, 95 % pure by integration, *m/z* (%) = 341 (60) $[M]^+$, 258 (45), 257 (100), 186 (75), 185 (75). HRMS: calcd. for $C_{18}H_{21}N_4OS$ $[M]^+$ 341.1436; found 341.1425.

Supporting Information (see footnote on the first page of this article): The ^1H and ^{13}C NMR spectra of tetrazanes **4**–**6**, GC–MS total ion chromatograms, mass spectra for verdazyls **1**–**3** and **7a**–**7i**, and tables of ESR parameters for verdazyl **1**–**3** and **7a**–**7i**.

Acknowledgments

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Keywords: Radicals · C–C coupling · Nitrogen heterocycles · Palladium · P ligands · Spin labels

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