Catalytic Oxidation of *N*-Phenylamidrazones to 1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yls: An Improved Synthesis of Blatter's Radical

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Abstract: Blatter's radical, 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1a**, R = H), and several of its C-7 substituted analogues (R = CF_3, Cl, Br, I, Me, OMe) were prepared in good-to-excellent yields through catalytic oxidation of the corresponding amidrazones by using palladium-on-carbon (1.6 mol%) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.1–1.0 equiv) in air. The reaction conditions were suitable for the preparation of Blatter's radical on a one-gram scale in up to 87% yield.

Key words: catalysis, oxidations, ring closure, heterocycles, organic radicals, benzotriazines, DBU

Organic radicals have attracted the interest of many scientists[1] owing to their potential uses as organic magnets[2] and conductors.[3] Recently, several applications of organic radicals have been developed, such as organic batteries,[4] magnetic inks,[5] electrochromic devices,[6] photosensitive devices,[7] and spin probes.[8]

Blatter's radical (**1a**; R = H), which has been described as indefinitely stable[9] or as super-stable,[10] forms semiconducting, pressure-sensitive, charge-transfer complexes with tetracyanoquinodimethane (TCNQ),[11] and was the inspiration behind the charge-separated zwitterionic biscyanine tetraphenylhexaazaanthracene **3** (TPHA).[12] In addition, extensive studies of its magnetic behavior have been reported.[13] Moreover, some 1,2,4-benzotriazines have shown herbicidal behavior (e.g., benzotriazine **2**)[14] or antitumor properties.[15]

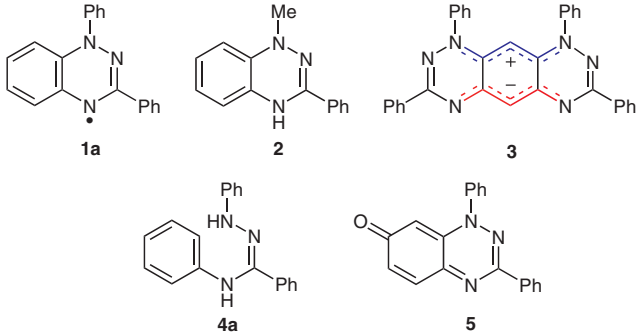

Figure 1

Until now, Blatter's radical (**1a**) was available in only moderate yields by treatment of the *N*-phenylamidrazone **4a** with either a large excess of toxic mercury(II) oxide[16] or an expensive oxidant such as silver(II) oxide.[17] As part of our studies on benzotriazin-4-yl radicals, we required a better method for converting valuable and relatively inaccessible amidrazones into stable radicals. We have therefore developed a mild and high-yielding method using both palladium-on-carbon and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in an atmosphere of air.

Initially, several oxidants were screened as replacements for mercury(II) oxide; 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone, *N*-chlorosuccinimide, potassium peroxymonosulfate (Oxone), cerium(IV) ammonium nitrate, and selenium dioxide were all tested without success. Sodium periodate (10 equiv) gave the desired product in 75% yield, but the reaction was slow (7 days), whereas more powerful oxidants, such manganese dioxide (20 equiv, 8 days) or potassium permanganate (10 equiv, 3 days) gave the over-oxidized benzotriazinone **5** in 68% and 82% yields, respectively. Fortunately, the reaction with a catalytic amount of palladium-on-carbon (1.6 mol%, 1 day) in an oxygen atmosphere gave the radical **1a** rapidly in 65% yield.

Palladium-on-carbon is known to catalyze the aerobic oxidation of alcohols,[18] and studies have suggested that these oxidations are influenced by the pH.[18b,19] We therefore examined the use of palladium-on-carbon in the presence of various organic bases. Under an oxygen atmosphere, treatment of *N*-phenylamidrazone **4a** with palladium-on-carbon and pyridine, 4-(dimethylamino)pyridine (DMAP), triethylamine, or ethyl(diisopropyl)-amine (Hünig's base) (1 equiv) for one day gave the desired product in good yields (67–94%). Surprisingly, with DBU as the base, the reaction reached completion rapidly (~ 4 h) and gave the benzotriazin-4-yl **1a** in 93% yield. With the aim of simplifying the reaction further, the same reactions were performed under atmosphere of air. After one day, pyridine, DMAP, triethylamine, and Hünig's base each gave an incomplete reaction, and the product mixture contained some benzotriazinone **5**, whereas DBU gave the radical **1a** in 95% yield after only three hours. When the reaction was performed under an oxygen-free atmosphere (argon), only a trace of the radical **1a** was detected by thin-layer chromatography (TLC) after one day, suggesting that some oxygen was needed for the conversion to occur. Furthermore, under an air atmosphere in the

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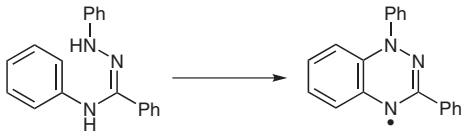
presence of palladium-on-carbon (1.6 mol%), the number of equivalents of DBU required could be reduced to only 0.1 without significantly increasing the reaction time (6 h) or affecting the yield (98%). With these improved conditions, Blatter's radical (**1a**) could be prepared on a one-gram scale in 87% yield, although with an increased reaction time (18.5 h). At the same scale (1 g), the reaction time could be reduced (6 h) by bubbling dry air into the reaction mixture, confirming the need for aerobic conditions (Table 1).

Table 1 Preparation of 1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1a**) from *N*-Phenylamidrazone **4a**



Pd/C (mol%)	DBU (equiv)	Atmosphere	Time (h)	Yield of **1a** (%)
1.6	0	O_2	24	65
1.6	0	air	24	trace
1.6	0.1	O_2	6	87
1.6	0.1	air	6	98
1.6	0.1	air	18.5	87[b]
1.6	0.1	air	6	82[b,c]
1.6	1	O_2	4	93
1.6	1	air	3	95
1.6	1	argon	24	trace
0	1	O_2	26	79
0	1	air	22	91
0	0.1	O_2	24	–[d]
0	0.1	air	24	–[d]

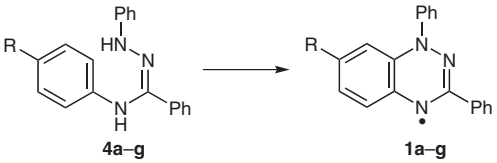
[a] Reaction conditions: **4a** (0.174 mmol), CH_2Cl_2 (1 mL), r.t.
[b] Reaction conditions: **4a** (1 g, 3.48 mmol) in CH_2Cl_2 (20 mL), r.t.
[c] Dry air was bubbled into the mixture.
[d] Incomplete reaction.

In the absence of palladium-on-carbon, treatment of the amidrazone **4a** with DBU (1 equiv) for one day gave the desired radical **1a** in 91% yield. Under analogous conditions with replacement of DBU by pyridine, DMAP, triethylamine, or Hünig's base gave only traces of the radical (by TLC). An attempt to use DBU in a catalytic amount (10 mol%) under an atmosphere of either air or oxygen led to an incomplete reaction after one day; longer reaction times led to increasingly complex reaction mixtures (by TLC). The presence of DBU was therefore shown to be critical, but its role is not clear. Rapid reactions required both DBU and palladium-on-carbon. DBU is a strong base,[20] but it can also act as a soft nucleophile.[21]

Furthermore, the formation of TPHA **3** from the corresponding bisamidrazone was achieved by using an excess of DBU (2.8 equiv, 14 d; 40%).[12]

Several electron-rich and electron-deficient amidrazones **4b–g** (0.5 mmol) were treated with DBU with and without palladium-on-carbon to compare the improved palladium-catalyzed oxidative cyclization with the transition-metal-free oxidative route to the corresponding 7-substituted 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yls **1b–g** (Table 2).

Table 2 Synthesis of Various 1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yls **1a–g** from *N*-Phenylamidrazones **4a–g**[a]



R	DBU (equiv)	Pd/C (mol%)	Time (h)	Product	Yield (%)
H	0.1	1.6	7	**1a**	85
H	1	0	26	**1a**	77
CF_3	0.1	1.6	6.5	**1b**	80[b]
CF_3	1	0	23	**1b**	74[b]
Cl	1	1.6	8	**1c**	82
Cl	1	0	23	**1c**	62[b]
Br	0.1	1.6	9	**1d**	94
Br	1	0	22	**1d**	70[b]
I	1	1.6	6	**1e**	81
I	1	0	23	**1e**	62[b]
Me	1	1.6	7	**1f**	70
Me	1	0	24	**1f**	56
OMe	1	1.6	4	**1g**	72
OMe	1	0	24	**1g**	58[b]

[a] Reaction conditions: **4a–g** (0.5 mmol), CH_2Cl_2 (3 mL), DBU, Pd/C (1.6 mol% or 0 mol%), r.t., air.
[b] With 4 Å molecular sieves.

In all cases, the palladium-catalyzed oxidative cyclizations came to completion faster (4–9 h) than did the transition-metal-free cyclizations (22–26 h). Nevertheless, in several of the palladium-catalyzed examples (R = Cl, I, Me, OMe), it was noteworthy that with catalytic amounts of DBU, the reaction failed to reach completion; when prolonged reaction times were used, complex mixtures containing the over-oxidized benzotriazinone **5** (as observed by TLC) were obtained. In these cases (R = Cl, I, Me, OMe), the problem was solved by the use of one equivalent of DBU. In the case of amidrazone **4b**, some *N*-[4-(trifluoromethyl)phenyl]benzamide was observed by

TLC; amidrazones can hydrolyze under basic conditions to afford benzanilides;[22] in this case, the introduction of molecular sieves (4 Å) to the reaction mixture permitted the use of a catalytic amount of DBU.

The precise mechanism of the DBU/palladium/oxygen reaction is beyond the scope of the present study and, in mechanistic terms, it is not clear why this reaction proceeds so rapidly. DBU can deprotonate the *N*-phenylamidrazones to afford anions that, owing to their energetically raised HOMOs, are more susceptible to oxidation. Dioxygen present in the air can act as the oxidant, and it is noteworthy that under a dioxygen-depleted atmosphere of argon, only traces of radicals were observed. Furthermore, palladium is well known to abstract hydrogen atoms and it can coordinate with nitrogen lone pairs, thereby assisting the reaction through resonance stabilization of an intermediate species.[23] Finally, amine ligands can stabilize active palladium species, thereby preventing aggregation and deactivation of the catalyst.[24] Nevertheless, predicting the order and number of mechanistic events on the basis of the current study would be highly speculative, and a deeper mechanistic understanding will require additional studies.

In summary, we have developed an improved preparation of Blatter's radical (**1a**) and related analogues from the corresponding amidrazones by using DBU and, optionally, palladium-on-carbon. The solid-state properties of the new benzotriazin-4-yl radicals will be reported in the near future.

Solvents CH_2Cl_2 and benzene were freshly distilled from CaH_2 under argon. Reactions were protected by means of $CaCl_2$ drying tubes. Anhyd $MgSO_4$ 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 aluminum-backed TLC plates (Merck Kieselgel 60 F_{254}). The plates were visualized under UV radiation at 254 and 365 nm. The technique of dry flash chromatography (Merck silica gel 60; <0.063 mm) was used throughout for all non-TLC-scale chromatographic separations. Melting points were determined by using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage microscope apparatus. Solvents used for recrystallization are indicated after the melting points. UV spectra were recorded by using a Perkin-Elmer Lambda-25 UV/vis spectrophotometer, and inflection points 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 shown as s, m, and w, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 machine at 300 and 75 MHz, respectively. *C*H and *C*H_2 assignments were supported by ^{13}C NMR DEPT 90 and DEPT 135 experiments. Deuterated solvents were used to achieve a homonuclear lock, and the signals are referenced to the deuterated solvent peaks. Low-resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GCMS with a direct inlet probe. EPR measurements were carried out on a Bruker EMX spectrometer by using an X-Band (9.8 GHz) microwave bridge at 290 K. *N*′-Phenylbenzohydrazonoyl chloride,[25] *N*,*N*′-diphenylbenzenecarbohydrazonamide (**4a**), *N*-(4-methylphenyl)-*N*′-phenylbenzenecarbohydrazonamide (**4f**),[26] *N*-(4-chlorophenyl)-*N*′-phenylbenzenecarbohydrazonamide (**4c**),[27] *N*-(4-bromophenyl)-*N*′-phenylbenzenecarbohydrazonamide (**4d**),[28] and *N*-(methoxyphenyl)-*N*′-phenylbenzenecarbohydrazonamide (**4g**),[16] were prepared according to literature procedures.

1,3-Diphenyl-1,2,4-benzotriazin-7(1*H*)-one (5)

$KMnO_4$ (275 mg, 1.74 mmol) was added to a stirred soln of amidrazone **4a** (50 mg, 0.174 mmol) in benzene (2 mL), and the mixture was refluxed for 3 d until the starting material was consumed and a polar purple compound was detected [TLC; *t*-BuOMe–hexane (1:4)]. The solvent was evaporated under reduced pressure and the residue was purified by dry flash chromatography (EtOAc) to give purple crystals; yield: 42.9 mg (82%); mp 215–218 °C (benzene) (Lit.[7] 216–217.5 °C).

IR (ATR): 3063w (Ar CH), 2923s, 2849m, 1612m (C=O), 1590s, 1538s, 1456m, 1386m, 1309m, 1234m, 1190m, 1101m, 1067w, 973m, 908w, 853m, 816m, 774m, 749m, 692m, 668m, 608m cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32–8.24 (m, 2 H), 7.73 (d, 1 H, *J* = 9.7 Hz, H-5), 7.67–7.56 (m, 5 H), 7.55–7.45 (m, 3 H), 7.33 (dd, 1 H, *J* = 9.7, 2.1 Hz, H-6), 6.12 (d, 1 H, *J* = 2.1 Hz, H-8).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.4 (Ar *C*=O, C-7), 155.3 (Ar *C*), 151.3 (Ar *C*), 142.8 (Ar *C*), 141.4 (Ar *C*), 136.9 (Ar *C*), 134.2 (Ar *C*), 132.6 (Ar *C*H), 131.0 (Ar *C*H), 130.6 (Ar *C*H), 130.5 (Ar *C*H), 129.2 (Ar *C*H), 127.1 (Ar *C*H), 126.0 (Ar *C*H), 98.2 (Ar *C*H, C-8).

MS (EI, 70 eV): *m/z* (%) = 300 (27) [M$^+$ + 1], 299 (100) [M$^+$], 282 (6), 271 (60), 168 (38), 139 (10), 104 (4), 103 (5), 89 (6), 77 (67), 63 (27), 51 (21).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 231 (4.32), 299 (4.61), 544 (3.82).

***N*′-Phenyl-*N*-[4-(trifluoromethyl)phenyl]benzenecarbohydrazonamide (4b); Typical Procedure**

$F_3CC_6H_4NH_2$ (0.52 mL, 4.22 mmol) was added to a stirred soln of PhNHN=CClPh (0.972 g, 4.22 mmol) in dry benzene (2.5 mL), and the mixture was refluxed for 8 h until TLC (*t*-BuOMe–hexane 1:4) showed the presence of a new more polar compound and the absence of the starting material. The mixture was then concentrated under reduced pressure, and the residue was purified by dry flash chromatography [*t*-BuOMe–hexane (1:9)] to give colorless crystals; yield: 520 mg (35%); mp 127–130 °C (*t*-BuOMe–hexane 1:9).

IR (ATR): 3333w (Ar NH), 1653w, 1643m, 1616m, 1601s, 1582w, 1559w, 1527m, 1505m, 1491m, 1445w, 1433w, 1404w, 1331s, 1318s, 1296w, 1246s, 1185m, 1167m, 1155m, 1110s, 1069s, 1024w, 827s, 771m, 753s, 718w cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (br s, 1 H, N*H*), 7.71–7.67 (m, 2 H) 7.46 (d, *J* = 8.4 Hz, 2 H), 7.38–7.36 (m, 3 H), 7.31–7.26 (m, 2 H), 7.14 (d, *J* = 7.8 Hz, 2 H), 6.91 (t, *J* = 7.2 Hz, 1 H), 6.74 (d, *J* = 8.4 Hz, 2 H).

MS (EI, 70 eV): *m/z* (%) = 356 (10) [M$^+$ + 1], 355 (42) [M$^+$], 249 (4), 248 (22), 195 (6), 194 (42), 167 (4), 145 (10), 104 (12), 91 (100), 77 ($C_6H_5^+$, 23), 65 (26), 51 (9).

Anal. Calcd for $C_{20}H_{16}F_3N_3$: C, 67.60; H, 4.54; N, 11.82. Found: C, 67.58; H, 4.57; N, 11.83.

***N*-(4-Iodophenyl)-*N*′-phenylbenzenecarbohydrazonamide (4e)**

Colorless crystals; yield: 840 mg (47%); mp 161–165 °C (cyclohexane).

IR (ATR): 3331w and 3316w (ArNH), 1643m, 1597m, 1583m, 1506m, 1487s, 1444w, 1434w, 1391w, 1346m, 1306m, 1301m, 1287w, 1253m, 1242m, 1180w, 1140m, 1061m, 1026w, 999w, 921w, 885w, 810s, 768m, 755s, 703s cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 3 H), 7.49 (d, *J* = 8.6 Hz, 2 H), 7.37–7.35 (m, 3 H), 7.30–7.25 (m, 2 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 6.89 (t, *J* = 7.2 Hz, 1 H), 6.47 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7 (Ar C), 141.1 (Ar C), 138.1 (Ar CH), 134.2 (Ar C), 129.2 (Ar CH), 129.0 (Ar CH), 128.6 (Ar CH), 126.4 (Ar CH), 120.4 (Ar CH), 118.2 (Ar CH), 113.3 (Ar CH), 82.8 (C-I).

MS (EI, 70 eV): *m/z* (%) = 414 (13) [M$^+$ + 1], 413 (71) [M$^+$], 307 (4), 306 (28), 195 (12), 194 (72), 193 (7), 179 (9), 104 (9), 91 (100), 77 (20) [$C_6H_5^+$], 76 (17), 65 (25), 64 (12), 51 (9).

Anal. Calcd for $C_{19}H_{16}IN_3$: C, 55.22; H, 3.90; N, 10.17. Found: C, 55.27; H, 3.89; N, 10.19.

1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (1a): Typical Procedure

DBU (7.5 μL, 0.05 mmol) and 5% Pd/C (17 mg, 1.6 mol%) were added to a stirred soln of amidrazone **4a** (143.5 mg, 0.5 mmol) in dry CH_2Cl_2 (1 mL). The mixture was stirred at r.t. for 7 h until TLC [*t*-BuOMe–hexane (1:4)] showed the absence of the starting material and the presence of a new fast-running brown compound. The solvent was evaporated under reduced pressure, and the residue was purified dry flash chromatography [*t*-BuOMe–hexane (1:9)] to give needle-shaped black crystals; yield: 121 mg (85%); mp 109–110 °C (EtOH), (Lit.[9] 113–115 °C); *g* = 2.0033.

IR (ATR): 3061w, 3003w, 1585w, 1481s, 1450m, 1395s, 1317w, 1252w, 1206w, 1175w, 1082w, 1065w, 1024w, 984w, 916w, 880w, 841w, 785m, 750s cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 285 (44) [M$^+$ + 1], 284 (100) [M$^+$], 181 (16), 180 (15), 179 (21), 178 (14), 152 (12), 77 (58), 76 (22), 51 (30), 50 (15).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 271 (3.63), 322 (2.93), 372 (2.82), 429 (2.56), 494 (2.17).

1,3-Diphenyl-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (1b)

Brown needles; yield: 141 mg (80%); mp 149–153 °C (cyclohexane); *g* = 2.0036.

IR (ATR): 1593w, 1506w, 1489m, 1452w, 1422m, 1395m, 1356m, 1337w, 1314m, 1281w, 1261m, 1248w, 1204w, 1150m, 1117s, 1063m, 1024w, 905m, 870m, 841m, 793w, 781m, 768m cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 353 (M$^+$ + 1, 33%), 352 (M$^+$, 100), 249 (6), 247 (6), 226 (4), 180 (6), 103 (5), 77 ($C_6H_5^+$, 26), 51 (10).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 259 inf (4.04), 273 (4.21), 284 inf (4.03), 323 (3.55), 373 (3.40), 431 (3.17), 495 (2.84).

Anal. Calcd for $C_{20}H_{13}F_3N_3$: C, 68.18; H, 3.72; N, 11.93. Found: C, 68.27; H, 3.63; N, 11.89.

7-Chloro-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (1c)

Brown crystals; yield: 130 mg (82%); mp 149–152 °C (cyclohexane); *g* = 2.0030.

IR (ATR): 3069w, 2924w, 1614w, 1591w, 1474s, 1449w, 1394m, 1356w, 1317w, 1294w, 1265w, 1242w, 1192w, 1150w, 1092w, 1082w, 1024w, 897m, 846w, 829m, 779m cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 321 (11) [M$^+$ + 3], 320 (35) [M$^+$ + 2], 319 (34) [M$^+$ + 1], 318 (100) [M$^+$], 283 (6) [M$^+$ – Cl], 282 (6), 215 (10), 214 (5), 213 (9), 180 (12), 179 (11), 178 (15), 77 (49), 76 (11), 75 (15), 51 (23), 50 (6).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 275 (3.55), 322 (2.81), 374 (2.72), 436 (2.48), 480 inf (2.05).

Anal. Calcd for $C_{19}H_{13}ClN_3$: C, 71.59; H, 4.11; N, 13.18. Found: C, 71.47; H, 4.03; N, 13.12.

7-Bromo-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (1d)

Brown crystals; yield: 171 mg (94%), mp 160–162 °C (Lit.[4] 176–178 °C) (cyclohexane); *g* = 2.0030.

IR (ATR): 3069w, 2926w, 1591w, 1566w, 1476s, 1449m, 1393s, 1317w, 1265w, 1242w, 1196w, 1130w, 1070w, 1061w, 1022w, 926w, 889m, 827m, 777s, 758w, 740w cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 365 (40) [M$^+$ + 2], 364 (100) [M$^+$ + 1], 363 (36) [M$^+$], 362 (97) [M$^+$ – 1], 283 (11) [M$^+$ – Br], 259 (9), 180 (20), 179 (17), 178 (18), 152 (12), 151 (17), 103 (14), 77 (68), 51 (30), 50 (8).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 277 (3.62), 322 (2.87), 376 (2.84), 434 (2.59), 498 (2.08).

Anal. Calcd for $C_{19}H_{13}BrN_3$: C, 62.83; H, 3.61; N, 11.57. Found: C, 62.85; H, 3.60; N, 11.52.

7-Iodo-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (1e)

Brown crystals; yield: 166 mg (81%), mp 149–152 °C (cyclohexane); *g* = 2.0026.

IR (ATR): 1684w, 1653w, 1591w, 1559m, 1539w, 1505w, 1489m, 1477s, 1456m, 1449m, 1392s, 1318m, 1267w, 1246w, 1193w, 1176w, 1069w, 1057w, 1024m, 883s, 828s, 780m, 774s, 739m cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 411 (93) [M$^+$ + 1], 410 (100) [M$^+$], 334 (6), 307 (5), 284 (19), 283 (46) [M$^+$ – I], 282 (23), 205 (7), 180 (14), 179 (15), 178 (12), 152 (10), 127 (5), 104 (11), 103 (13), 77 (44) [$C_6H_5^+$], 51 (27).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 280 (3.37), 323 (2.77), 377 (2.71), 438 (2.37), 481 inf (1.72).

Anal. Calcd for $C_{19}H_{13}IN_3$: C, 55.63; H, 3.19; N, 10.24. Found: C, 55.59; H, 3.07; N, 10.17.

7-Methyl-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (1f)

Brown crystals, yield: 104 mg (70%); mp 160–163 °C (cyclohexane); *g* = 2.0053.

IR (ATR): 3063w, 2920w, 1696w, 1684w, 1653w, 1592m, 1559w, 1539w, 1503m, 1490m, 1459w, 1452m, 1420w, 1394s, 1327m, 1279w, 1257w, 1170m, 1087w, 1067w, 1024m, 1002w, 929w, 917w, 862w, 849w, 844w, 803s, 780s, 759s, 712m cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 299 (68%) [M$^+$ + 1], 298 (100) [M$^+$], 283 (7), 222 (10), 195 (16), 180 (10), 167 (5), 165 (7), 149 (40), 114 (5), 104 (4), 89 (10), 77 (23) [$C_6H_5^+$], 72 (7), 65 (4), 57 (5), 51 (12).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 275 (4.21), 283 inf (4.10), 322 (3.55), 373 (3.35), 433 (2.95), 481 inf (1.58).

Anal. Calcd for $C_{20}H_{16}N_3$: C, 80.51; H, 5.41; N, 14.08. Found: C, 80.50; H, 5.31; N, 13.92.

7-Methoxy-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (1g)

Brown crystals, yield: 113 mg (72%); mp 140–143 °C (Lit.[29] 144–145 °C) (cyclohexane); *g* = 2.0032.

IR (ATR): 3061w, 3011w, 1603w, 1589w, 1578w, 1542w, 1501s, 1487s, 1466w, 1439w, 1418w, 1395m, 1348w, 1315w, 1263w, 1213m, 1163w, 1152w, 1125w, 1099w, 1065w, 1032m, 1003w, 989w, 917w, 851w, 831w, 795w, 773s, 733w, 716m cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 315 (40) [M$^+$ + 1], 314 (100) [M$^+$], 271 (19), 168 (15), 106 (10), 77 (32), 63 (15).

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = (3.15), 277 (3.42), 312 (2.37), 375 (2.45), 417 (2.16), 436 (2.26).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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