Iminophosphorane-Mediated Annulation of 1,3,5-Triazine to Benzimidazole: Synthesis of 1,3,5-Triazino[1,2-*a*]benzimidazoles

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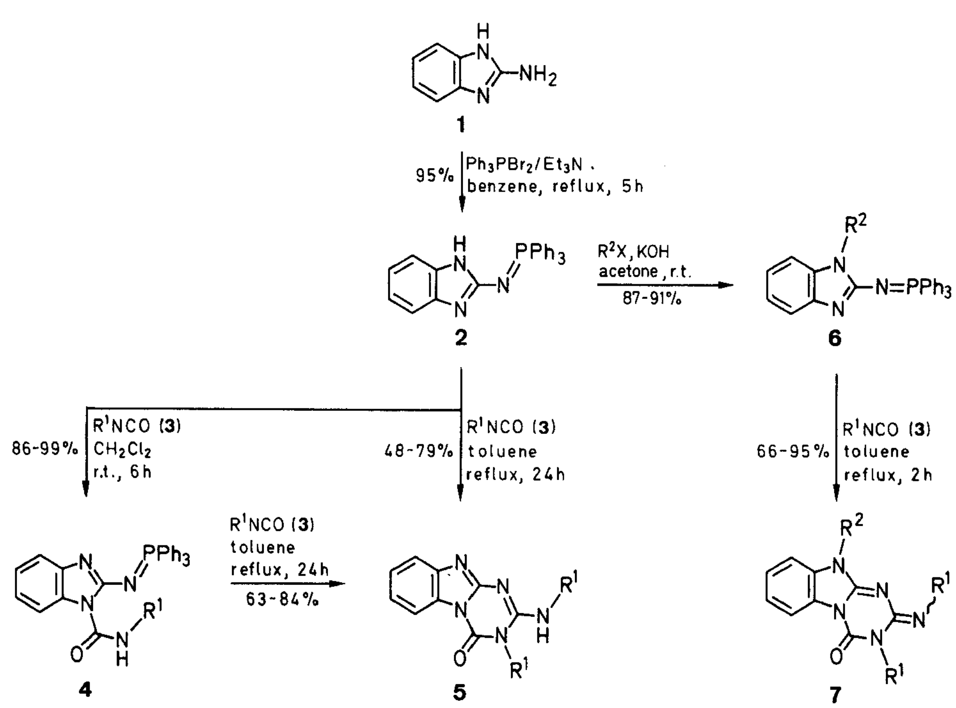
A number of 1,3,5-triazino[1,2-a]benzimidazoles **5** and **7** have been prepared by aza-Wittig-type reaction of 2-(triphenylphosphoranylideneamino)benzimidazoles **2** and **6**, which were derived from 2-aminobenzimidazoles, with isocyanates under neutral conditions.

The imidazole ring plays an essential role in several biological processes. Accordingly a massive research effort has been expended on the chemistry of this ring, and also on condensed derivatives.[1] As part of an investigation on the iminophosphorane-mediated synthesis of fused heterocycles, in particular heterocycles containing the imidazo moiety, we recently reported the synthesis of imidazo[1,2-*b*][1,2,4]triazoles,[2] imidazo[2,1-*b*]-1,3,4-thiadiazoles,[3] imidazo[5,1-*f*][1,2,4] triazines,[4] imidazo[1,5-*a*]benzimidazoles,[5] benzimidazo[1,2-*c*]quinazolines,[6] imidazo[1,5-*d*][1,3,4]thiadiazines, and imidazo[1,5-*d*][1,3,4]oxadiazines.[7] We now describe a new general method for the preparation of some derivatives of the 1,3,5-triazino[1,2-*a*]benzimidazole ring. The methods hitherto reported for the preparation of some representative derivatives of the 1,3,5-triazino[1,2-*a*]benzimidazole ring either use 2-aminobenzimidazoles as starting material, e.g., reaction with iso(thio)cyanate,[8] *N*-cyanoacetimidate,[9,10] and cyanoguanidine[11] or start from 2-guanidinobenzimidazoles e.g. reaction with benzoyl isothiocyanate,[12] diethyl azodicarboxylate,[13] carbon disulfide,[14] and orthoesters.[9,14]

Our approach to 1,3,5-triazino[1,2-*a*]benzimidazoles **5** and **7** is based on the ready synthesis and subsequent aza-Wittig-type reaction of iminophosphorane **2**, derived from 2-aminobenzimidazoles **1**, with isocyanates.



4, 5	R^1	7	R^1	R^2
a	Me	a	Me	Me
b	Et	b	Me	$CH_2=CHCH_2$
c	Bn	c	Ph	$CH_2=CHCH_2$
d	Ph	d	$4\text{-}MeC_6H_4$	$CH_2=CHCH_2$
e	$4\text{-}MeC_6H_4$	e	$PhCH=CH$	$CH_2=CHCH_2$
f	$4\text{-}ClC_6H_4$	f	$4\text{-}ClC_6H_4CH=CH$	$CH_2=CHCH_2$
g	$4\text{-}FC_6H_4$	g	$4\text{-}MeOC_6H_4CH=CH$	$CH_2=CHCH_2$
h	$4\text{-}MeOC_6H_4$			

The key intermediate **2** is easily prepared in 95% yield from 2-aminobenzimidazole **1** and dibromotriphenylphosphorane in the presence of triethylamine. In the ^{13}C NMR spectrum the carbon atom at position 2 of the benzimidazole ring appears at $\delta = 156.97$ ($^2J_{P-C} = 1.2$ Hz) coupled with the phosphorous atom. The EI-mass spectrum shows the expected molecular ion peak and the fragmentation pattern is in accord with the proposed structure. The reaction of iminophosphorane **2** with alkyl and aryl isocyanates **3** in dry dichloromethane at room temperature leads to iminophosphoranes **4** in excellent yields. When iminophosphoranes **4** are treated with isocyanates in dry toluene at reflux temperature the corresponding 1,3,5-triazino[1,2-*a*]benzimidazoles **5** are

Table 1. Iminophosphoranes **4**, 1,3,5-Triazino[1,2-*a*]benzimidazoles **5** and **7** Prepared

Product	Yield[a] (%)	mp (°C)[b]	Molecular Formula[c]	MS (70 eV)[d] *m*/*z* (%)
4a	96	170–171	$C_{27}H_{23}N_4OP$ (450.5)	450 (M^+, 1), 393 (29), 238 (27), 183 (100), 157 (15), 152 (17), 132 (11), 108 (25), 77 (36), 57 (43)
4b	80	198–199	$C_{28}H_{25}N_4OP$ (464.5)	464 (M^+, 1), 393 (2), 238 (4), 183 (42), 157 (4), 152 (10), 133 (5), 108 (12), 77 (31), 71 (49)
4c	88	181–183	$C_{33}H_{27}N_4OP$ (526.6)	393 (M^+-R^1NCO, 41), 238 (26), 183 (100), 157 (15), 152 (22), 133 (52), 132 (25), 108 (26), 91 (59), 77 (67)
4d	91	180–181	$C_{32}H_{25}N_4OP$ (512.5)	393 (M^+-R^1NCO, 48), 238 (22), 183 (100), 157 (13), 152 (25), 132 (9), 119 (25), 108 (26), 77 (93)
4e	99	190–191	$C_{33}H_{27}N_4OP$ (526.6)	393 (M^+-R^1NCO, 33), 238 (19), 183 (91), 133 (100), 132 (57), 108 (19), 104 (39), 91 (18), 77 (60)
4f	92	205–206	$C_{32}H_{24}ClN_4OP$ (547.0)	393 (M^+-R^1NCO, 72), 392 (100), 238 (6), 183 (5), 153 (20), 127 (10), 125 (12), 90 (4)
4g	92	173–174	$C_{32}H_{24}FN_4OP$ (530.5)	393 (M^+-R^1NCO, 63), 392 (90), 277 (100), 238 (14), 183 (64), 152 (17), 137 (10), 108 (8), 77 (39)
4h	86	173–175	$C_{33}H_{27}N_4O_2P$ (542.6)	393 (M^+-R^1NCO, 16), 277 (78), 238 (13), 183 (40), 152 (9), 149 (100), 108 (11), 77 (13)
5a	57	338–339	$C_{11}H_{11}N_5O$ (229.2)	229 (M^+, 71), 172 (24), 159 (22), 118 (14), 104 (8), 90 (32), 71 (100)
5b	48	241–242	$C_{13}H_{15}N_5O$ (257.3)	257 (M^+, 94), 229 (31), 186 (100), 159 (70), 158 (65), 133 (53), 104 (33), 97 (85), 90 (83), 71 (37)
5c	62	227–229	$C_{23}H_{19}N_5O$ (381.4)	381 (M^+, 100), 372 (9), 291 (21), 290 (83), 248 (7), 241 (6), 222 (6), 132 (6), 91 (56)
5d	52	270–271	$C_{21}H_{15}N_5O$ (353.4)	353 (M^+, 49), 234 (11), 195 (33), 158 (5), 119 (6), 104 (11), 92 (34), 90 (25), 77 (100)
5e	58	277–278	$C_{23}H_{19}N_5O$ (381.4)	381 (M^+, 100), 248 (24), 223 (28), 190 (13), 159 (19), 158 (6), 133 (7), 106 (65), 91 (87), 90 (31), 77 (38)
5f	51	261–263	$C_{21}H_{13}Cl_2N_5O$ (422.3)	423 ($M^+ + 2$, 10), 421 (M^+, 15), 268 (14), 263 (10), 158 (9), 153 (95), 126 (90), 111 (62), 104 (19), 90 (100)
5g	72	273–274	$C_{21}H_{13}F_2N_5O$ (389.4)	389 (M^+, 100), 252 (16), 231 (21), 158 (5), 137 (8), 110 (85), 107 (17), 95 (70), 90 (41)
5h	79	184–185	$C_{23}H_{19}N_5O_3$ (413.4)	413 (M^+, 30), 264 (17), 255 (12), 249 (20), 158 (10), 149 (43), 122 (100), 104 (15), 99 (33)
7a	80	246–247	$C_{12}H_{13}N_5O$ (243.3)	243 (M^+, 42), 214 (43), 186 (100), 171 (10), 158 (10), 131 (6), 118 (12), 90 (11), 57 (4)
7b	70	145–147	$C_{14}H_{15}N_5O$ (269.3)	269 (M^+, 48), 240 (28), 228 (19), 212 (100), 199 (11), 171 (44), 157 (44), 129 (5), 90 (26)
7c	75	209–211	$C_{24}H_{19}N_5O$ (393.4)	393 (M^+, 56), 392 (100), 352 (9), 274 (22), 233 (48), 170 (33), 157 (6), 119 (10), 91 (16), 90 (29), 77 (56)
7d	66	214–215	$C_{26}H_{23}N_5O$ (421.5)	421 (M^+, 67), 420 (100), 380 (12), 288 (55), 247 (41), 170 (44), 157 (51), 133 (10), 91 (38), 90 (16)
7e	95	213–214	$C_{28}H_{23}N_5O$ (445.5)	445 (M^+, 13), 368 (22), 299 (19), 259 (16), 183 (13), 145 (25), 129 (36), 117 (40), 103 (68), 90 (73), 77 (100)
7f	86	242–244	$C_{28}H_{21}Cl_2N_5O$ (514.4)	515 ($M^+ + 2$, 6), 513 (M^+, 9), 402 (23), 334 (8), 293 (11), 265 (59), 225 (80), 198 (52), 183 (14), 179 (100), 157 (67), 151 (47), 137 (20), 90 (33)
7g	86	216–218	$C_{30}H_{27}N_5O_3$ (505.6)	505 (M^+, 4), 330 (4), 305 (16), 240 (57), 198 (45), 183 (10), 175 (100), 158 (36), 157 (25), 132 (70), 90 (16)

[a] Yield of isolated pure product.
[b] Uncorrected.
[c] Satisfactory microanalyses: C ±0.28, H ±0.27, N ±0.29.
[d] Recorded on a Hewlett-Packard 5993 C instrument.

isolated in fair yields (Table 1). Compounds **5** can also be prepared from **2** by reaction with two moles of isocyanate **3** in dry toluene at reflux temperature (48–79%). The conversion **2** → **5** involves initial formation of **4** followed by an aza-Wittig-type reaction between the iminophosphorane moiety and the isocyanate to give a carbodiimide as highly reactive intermediate which undergoes cyclization by nucleophilic attack of the adjacent carbamoyl group to give **5**. Although, reaction of carbodiimides with compounds containing an amino group have been reported,[15] to our knowledge this is the first reported example of a triazine annulation based on the reaction of carbodiimides with carbamoyl groups.

The structure of compounds **5** was determined by microanalyses and spectral data. The IR spectra show absorption bands in the region $\nu = 3420-3185\ cm^{-1}$ due to the amino group, and in the regio $\nu = 1746-1723\ cm^{-1}$ attributable to the carbonyl group. The ^1H NMR spectra suggest the presence of an exocyclic amino group at position 2, e.g., for compound **5a** a methyl group appears as a doublet at $\delta = 2.90$ ($J = 3.3$ Hz) and the NH group as a quadruplet at $\delta = 7.82$ ($J = 3.3$ Hz). Salient features of the ^1H and ^{13}C NMR spectra are given in Table 2. The EI-mass spectra show the expected molecular ion peaks.

Compound **2** undergoes *N*-alkylation on the endocyclic nitrogen atom to give **6** in excellent yields. Iminophosphoranes **6** react with several isocyanates in dry toluene at reflux temperature for 2 h to give the corresponding 1,3,5-triazino[1,2-*a*]benzimidazoles **7** in good to excellent yields (Table 1). We believe that the conversion **6** to **7** involves formation of an intermediate type **10**; reaction of iminophosphorane **6** with one mole of isocyanate involving either the endocyclic nitrogen atom or the iminophosphorane moiety leads to the intermediates **8** or **9**, respectively, whose reaction with a second mole of isocyanate leads to the intermediate **10**. Finally, intramolecular nucleophilic attack of the carbamoyl group on the central carbon atom of the carbodiimide affords **7**. The structure **7** is corroborated by microanalyses and spectral data. Salient features of the EI-mass, IR, ^1H and ^{13}C NMR spectra are given in Tables 1 and 2.

Table 2. Spectral Data of Iminophosphoranes **4**, and 1,3,5-Triazino[1,2-*a*]benzimidazoles **5**, and **7**

Compound	IR (Nujol)[a] ν (cm^{-1})	^{1}H NMR (200 MHz, solvent)[b] δ, J (Hz)	^{13}C NMR (50 MHz, solvent)[b] δ, J (Hz)
4a	3185, 1715, 1532, 1456, 1437, 1331, 1115, 984, 872, 731	2.96 (d, 3H, $J = 4.3$, CH_3), 6.96 (m, 3H), 7.65 (m, 9H), 7.82 (m, 6H, 6 × H_o), 8.00 (d, 1H, $J = 6.6$, H-7), 10.00 (q, 1H, $J = 4.3$, NH)	26.14 (CH_3), 113.75 (C-7), 115.25 (C-4), 119.79 (C-6), 122.23 (C-5), 126.87 ($^{1}J_{P-C} = 102.5$, C_i), 129.07 ($^{3}J_{P-C} = 12.4$, C_m), 132.39 (C-7a), 132.64 ($^{2}J_{P-C} = 10.4$, C_o), 132.88 ($^{4}J_{P-C} = 2.8$, C_p), 141.46 (C-3a), 152.81 (C=O), 154.60 (C-2)
4b	3186, 1705, 1532, 1456, 1441, 1329, 1113, 1017, 876, 725	1.21 (t, 3H, $J = 7.3$, CH_3), 3.48 (m, 2H, CH_2), 7.00 (m, 2H), 7.17 (m, 1H, H-4), 7.51 (m, 9H), 7.79 (m, 6H, 6 × H_o), 8.19 (m, 1H, H-7), 10.09 (t, 1H, $J = 4.1$, NH)	14.86 (CH_3), 34.62 (CH_2), 114.47 (C-7), 115.61 (C-4), 120.06 (C-6), 122.16 (C-5), 127.62 ($^{1}J_{P-C} = 102.7$, C_i), 128.72 ($^{3}J_{P-C} = 12.6$, C_m), 132.61 ($^{4}J_{P-C} = 2.8$, C_p), 132.98 ($^{2}J_{P-C} = 10.3$, C_o), 141.97 (C-3a), 153.24 (C=O), 154.72 ($^{2}J_{P-C} = 1.0$, C-2). The carbon atom C-7a is not observed
4c	3183, 1699, 1534, 1456, 1440, 1331, 1115, 725	4.63 (d, 2H, $J = 5.6$, CH_2), 6.99 (m, 3H), 7.51 (m, 20H), 8.04 (m, 1H, H-7), 10.53 (t, 1H, $J = 4.3$, NH)	43.16 (CH_2), 113.92 (C-7), 115.38 (C-4), 119.85 (C-6), 122.37 (C-5), 127.18, 127.50, 126.70 ($^{1}J_{P-C} = 102.4$, C_i), 128.54, 128.96 ($^{3}J_{P-C} = 12.5$, C_m), 132.57 ($^{2}J_{P-C} = 10.5$, C_o), 132.84 ($^{4}J_{P-C} = 2.1$, C_p), 138.78 (q), 141.68 (C-3a), 152.37 (C=O), 154.56 ($^{2}J_{P-C} = 2.2$, C-2). The carbon atom C-7a is not observed
4d	3360, 1705, 1534, 1458, 1439, 1186, 1113, 748	7.06 (m, 4H), 7.31 (t, 2H, $J = 7.7$), 7.45 (d, 2H, $J = 7.9$), 7.65 (m, 9H), 7.86 (m, 6H, 6 × H_o), 8.09 (m, 1H, H-7), 12.47 (s, 1H, NH)	114.17 (C-7), 115.59 (C-4), 119.42, 120.13 (C-6), 122.72 (C-5), 123.48, 126.48 ($^{1}J_{P-C} = 102.4$, C_i), 128.87, 129.09 ($^{3}J_{P-C} = 12.6$, C_m), 132.42 (C-7a), 132.82 ($^{2}J_{P-C} = 10.4$, C_o), 133.08 ($^{4}J_{P-C} = 2.1$, C_p), 137.74 (q), 141.69 (C-3a), 149.60 (C=O), 154.34 ($^{2}J_{P-C} = 1.3$, C-2)
4e	3250, 1701, 1539, 1456, 1439, 1339, 1186, 1115, 748	2.29 (s, 3H, CH_3), 7.11 (m, 4H), 7.20 (m, 1H, H_4), 7.32 (d, 2H, $J = 8.4$), 7.54 (m, 9H), 7.83 (m, 6H, 6 × H_o), 8.25 (m, 1H, H-7), 12.43 (s, 1H, NH)	20.79 (CH_3), 114.82 (C-7), 115.87 (C-4), 119.71, 120.45 (C-6), 122.63 (C-5), 127.31 ($^{1}J_{P-C} = 103.0$, C_i), 128.88 ($^{3}J_{P-C} = 12.5$, C_m), 129.08 (q), 129.29, 132.81 ($^{4}J_{P-C} = 2.4$, C_p), 132.93 ($^{4}J_{P-C} = 1.5$, C-7a), 133.15 ($^{2}J_{P-C} = 10.1$, C_o), 135.69 (q), 141.94 (C-3a), 150.51 (C=O), 154.37 ($^{2}J_{P-C} = 2.2$, C-2)
4f	3254, 1699, 1537, 1458, 1439, 1337, 1186, 1115, 748	7.08 (m, 2H), 7.19 (m, 3H), 7.35 (d, 2H, $J = 8.9$), 7.55 (m, 9H), 7.84 (m, 6H, 6 × H_o), 8.24 (m, 1H, H-7), 12.63 (s, 1H, NH)	114.75 (C-7), 116.04 (C-4), 120.59, 120.77 (C-6), 122.84 (C-5), 127.18 ($^{1}J_{P-C} = 103.0$, C_i), 128.06 (q), 128.73, 128.95 ($^{3}J_{P-C} = 12.8$, C_m), 132.79 (C-7a), 132.92 ($^{4}J_{P-C} = 2.8$, C_p), 133.15 ($^{2}J_{P-C} = 10.5$, C_o), 136.99 (q), 142.00 (C-3a), 154.41 (C=O), 154.23 ($^{2}J_{P-C} = 1.4$, C-2)
4g	3255, 1699, 1534, 1460, 1437, 1337, 1186, 1111, 748	6.95 (t, 2H, $J = 8.7$), 7.08 (m, 2H), 7.22 (m, 1H, H-4), 7.37 (q, 2H, $J = 9.0, 4.8$), 7.58 (m, 9H), 7.84 (m, 6H, 6 × H_o), 8.22 (m, 1H, H-7), 12.53 (s, 1H, NH)	114.81 (C-7), 115.40 ($^{2}J_{F-C} = 22.2$), 116.03 (C-4), 120.60 (C-6), 121.26 ($^{3}J_{F-C} = 7.7$), 122.82 (C-5), 127.30 ($^{1}J_{P-C} = 103.0$, C_i), 128.98 ($^{3}J_{P-C} = 12.8$, C_m), 132.94 ($^{4}J_{P-C} = 2.8$, C_p), 133.19 ($^{2}J_{P-C} = 10.3$, C_o), 134.40 ($^{4}J_{F-C} = 2.8$, q), 142.02 (C-3a), 150.63 (C=O), 154.33 ($^{2}J_{P-C} = 2.2$, C-2), 158.87 ($^{1}J_{F-C} = 242.5$, q). The carbon atom C-7a is not observed
4h	3257, 1699, 1532, 1456, 1441, 1333, 1237, 1184, 1113, 1038, 831, 750	3.76 (s, 3H, CH_3O), 6.81 (d, 2H, $J = 8.9$), 7.06 (m, 2H), 7.22 (m, 1H, H-4), 7.36 (d, 2H, $J = 9.0$), 7.54 (m, 9H), 7.83 (m, 6H, 6 × H_o), 8.24 (m, 1H, H-7), 12.38 (s, 1H, NH)	51.41 (CH_3O), 114.00, 114.75 (C-7), 115.85 (C-4), 120.41 (C-6), 122.59 (C-5), 127.29 ($^{1}J_{P-C} = 103.0$, C_i), 128.87 ($^{3}J_{P-C} = 12.6$, C_m), 131.38 (q), 132.80 ($^{4}J_{P-C} = 2.8$, C_p), 132.90 ($^{4}J_{P-C} = 1.5$, C-7a), 133.11 ($^{2}J_{P-C} = 10.4$, C_o), 141.92 (C-3a), 150.61 (C=O), 153.34 ($^{2}J_{P-C} = 1.7$, C-2), 155.75 (q)
5a	3237, 1730, 1631, 1597, 1456, 1385, 1246, 756	2.90 (d, 3H, $J = 3.3$, $\underline{C}H_3$–NH), 3.37 (s, 3H, CH_3–N), 7.16 (t, 1H, $J = 7.5$, H-7), 7.27 (t, 1H, $J = 7.6$, H-8), 7.45 (d, 1H, $J = 7.8$, H-9), 7.82 (q, 1H, $J = 3.4$, NH), 7.94 (d, 1H, $J = 7.7$, H-6)	28.81 (2 × CH_3), 113.15 (C-6), 116.84 (C-9), 120.99 (C-7), 124.63 (C-8), 128.27 (C-5a), 143.07 (C-9a), 146.46 (C-4), 151.63 (C-2), 153.20 (C-10a)
5b	3185, 1723, 1632, 1599, 1580, 1458, 1246, 766	1.20 (t, 6H, $J = 7.1$, 2 × CH_3), 3.44 (m, 2H, CH_2), 4.03 (q, 2H, $J = 7.0$, CH_2), 7.12 (t, 1H, $J = 7.5$, H-7), 7.24 (t, 1H, $J = 7.5$, H-8), 7.42 (d, 1H, $J = 7.8$, H-9), 7.83 (t, 1H, $J = 5.2$, NH), 7.93 (d, 1H, $J = 7.7$, H-6)	12.67 (CH_3), 14.18 (CH_3), 36.49 (CH_2), 36.64 (CH_2), 113.05 (C-6), 116.88 (C-9), 120.64 (C-7), 124.38 (C-8), 128.38 (C-5a), 143.65 (C-9a), 146.24 (C-4), 151.34 (C-2), 151.60 (C-10a)
5c	3200, 1738, 1636, 1578, 1456, 1404, 1235, 764	4.47 (d, 2H, $J = 5.1$, CH_2), 5.31 (s, 2H, CH_2), 6.85 (m, 2H), 6.98 (m, 4H), 7.25 (m, 8H), 8.01 (d, 1H, $J = 7.3$, H-6)	45.06 (CH_2), 45.77 (CH_2), 114.09 (C-6), 116.68 (C-9), 122.53 (C-7), 125.64 (C-8), 126.90, 127.14, 127.14, 128.04 (C-5a), 128.20, 128.20, 128.94, 133.99 (C_i), 137.13 (C_i'), 140.76 (C-9a), 146.41 (C-4), 151.16 (C-2), 151.42 (C-10a)
5d	3407, 1732, 1634, 1591, 1555, 1454, 1377, 748	6.42 (s, 1H, NH), 7.10 (t, 1H, $J = 7.2$, H-7), 7.32 (m, 4H), 7.50 (m, 4H), 7.67 (m, 4H), 8.02 (d, 1H, $J = 7.8$, H-6)	114.00 (C-6), 118.70 (C-9), 121.60 (C_o), 122.73 (C-7), 125.37 (C-8), 125.54 (C_p), 128.88 (C-5a), 128.98 (C_m), 129.32 (C_o'), 131.14 (C_m'), 131.19 (C_p'), 132.3 (C_i'), 136.19 (C_i), 143.59 (C-9a), 145.99 (C-4), 148.88 (C-2), 150.36 (C-10a)
5e	3412, 1740, 1644, 1615, 1559, 1512, 1454, 1370, 1273, 802, 760	2.22 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 6.57 (s, 1H, NH), 6.98 (d, 2H, $J = 8.3$, H_o'), 7.20 (t, 1H, $J = 7.6$, H-7), 7.36 (m, 7H), 7.60 (d, 1H, $J = 7.8$, H-9), 7.97 (d, 1H, $J = 7.7$, H-6)	20.68 (CH_3), 21.19 (CH_3'), 113.80 (C-6), 118.36 (C-9), 121.36 (C_o), 122.32 (C-7), 125.25 (C-8), 128.74 (C-5a), 128.82 (C_m), 129.23 (C_o'), 129.37 (C_i'), 131.49 (C_m'), 133.61 (C_i), 134.88 (C_p), 141.39 (C_p'), 143.47 (C-9a), 145.96 (C-4), 149.01 (C-2), 150.41 (C-10a)

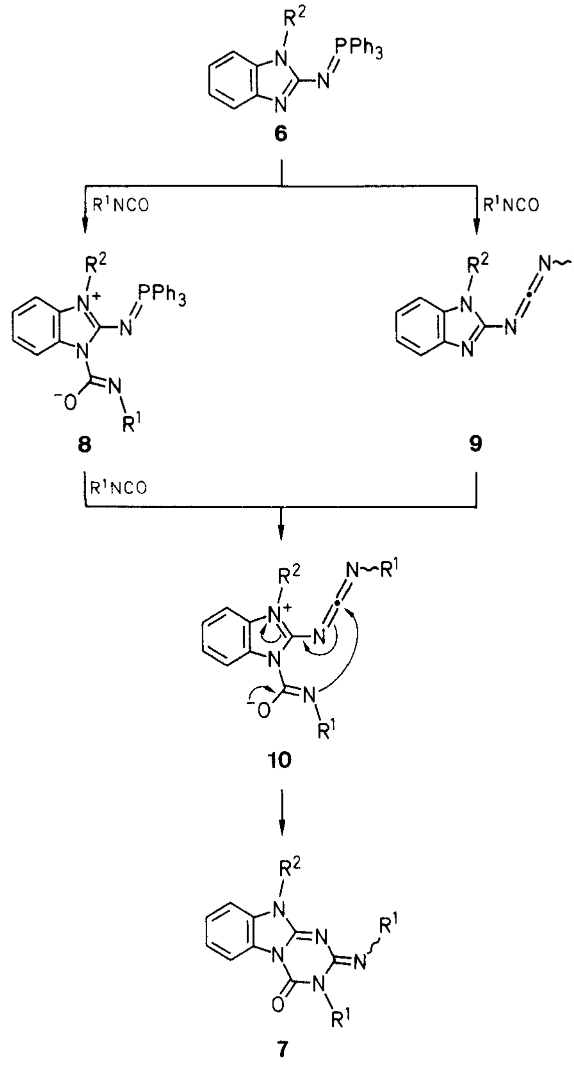
Table 2. (continued)

Compound	IR (Nujol)[a] ν (cm^{-1})	^1H NMR (200 MHz, solvent)[b] δ, J (Hz)	^{13}C NMR (50 MHz, solvent)[b] δ, J (Hz)
5f	3266, 1738, 1626, 1580, 1554, 1375, 1090, 768	6.50 (br s, 1 H, NH), 7.3 (m, 8 H), 7.64 (m, 3 H), 8.02 (d, 1 H, J = 7.7, H_6)	114.06 (C-6), 118.62 (C-9), 123.03 (C_o), 123.14 (C-7), 125.83 (C-8), 128.62 (C-5a), 129.07 (C_m), 130.53 (C'_i), 130.72 (C'_o), 130.85 (C_p), 131.46 (C'_m), 134.66 (C_i), 137.66 (C'_p), 142.94 (C-9a), 145.61 (C-4), 148.55 (C-2), 149.84 (C-10a)
5g	3314, 1746, 1628, 1578, 1507, 1456, 1375, 1238, 1157, 756	6.36 (s, 1 H, NH), 7.00 (t, 2 H, J = 8.6), 7.40 (m, 8 H), 7.65 (d, 1 H, J = 7.7, H-9), 8.01 (d, 1 H, J = 7.5, H-6)	113.98 (C-6), 115.82 ($^2J_{F-C}$ = 22.8, C_m), 118.38 ($^2J_{F-C}$ = 23.2, C'_m), 118.76 (C-9), 122.94 (C-7), 123.94 (C_o, $^3J_{F-C}$ = 8.3), 125.69 (C-8), 128.02 ($^4J_{F-C}$ = 3.8, C'_i), 128.79 (C-5a), 131.46 ($^3J_{F-C}$ = 9.1, C'_o), 131.94 (C_i, $^4J_{F-C}$ = 3.0), 143.48 (C-9a), 145.94 (C-4), 149.00 (C-2), 150.09 (C-10a), 160.19 ($^1J_{F-C}$ = 246.2, C_p), 141.39 ($^1J_{F-C}$ = 253.3, C'_p)
5h	3420, 1744, 1634, 1551, 1454, 1370, 752	3.72 (s, 3 H, CH_3O), 3.82 (s, 3 H, CH_3O), 6.70 (s, 1 H, NH), 6.77 (d, 2 H, J = 9.0), 7.06 (d, 2 H, J = 8.8), 7.22 (t, 1 H, J = 7.5, H-7), 7.37 (m, 5 H), 7.58 (d, 1 H, J = 7.8, H-9), 8.01 (d, 1 H, J = 7.7, H-6)	55.38 (CH_3O), 55.60 (CH'_3O), 55.60 (CH'_3O), 113.82 (C-6), 113.98 (C_m), 116.05 (C'_m), 118.35 (C-9), 122.36 (C-7), 123.80 (C_o), 124.26 (C'_i), 125.32 (C-8), 128.79 (C-5a), 129.12 (C_i), 130.38 (C'_o), 143.51 (C-9a), 146.25 (C-4), 149.77 (C-2), 150.61 (C-10a), 157.20 (C_p), 161.13 (C'_p)
7a	1715, 1665, 1634, 1456, 1400, 1294, 758	3.16 (s, 3 H, CH_3), 3.37 (s, 3 H, CH_3), 3.53 (s, 3 H, CH_3–N-10), 7.07 (d, 1 H, J = 7.9, H-9), 7.19 (t, 1 H, J = 7.4, H-7), 7.28 (t, 1 H, J = 7.4, H-8), 7.99 (d, 1 H, J = 7.4, H-6)	27.56 (CH_3N-10), 28.93 (CH_3N-3), 34.94 (CH_3–N=C), 108.14 (C-9), 113.91 (C-6), 123.05 (C-7), 125.05 (C-8), 125.56 (C-5a), 131.75 (C-9a), 147.16 (q), 148.03 (q), 149.20 (q)
7b	1721, 1661, 1626, 1614, 1446, 1427, 1397, 750	3.15 (s, 3 H, CH_3), 3.38 (s, 3 H, CH_3), 4.63 (d, 2 H, J = 5.5, $-C\underline{H}_2-N$), 5.31 (m, 2 H, $C\underline{H}_2=C$), 5.93 (m, 1 H, $C\underline{H}=$), 7.08 (dd, 1 H, J = 8.0, 1.6, H-9), 7.23 (m, 2 H), 8.01 (dd, 1 H, J = 7.9, 1.5, H-6)	28.88 (CH'_3), 34.91 (CH_3), 43.89 ($-\underline{C}H_2-N$), 108.93 (C-9), 113.92 (C-6), 118.91 ($\underline{C}H_2=C$), 122.97 (C-7), 124.90 (C-8), 125.62 (C-5a), 130.25 ($-\underline{C}H=$), 130.96 (C-9a), 147.13 (q), 147.60 (q), 149.13 (q)
7c	1740, 1663, 1628, 1591, 1447, 1424, 1381, 745	4.51 (d, 2 H, J = 5.7, $-C\underline{H}_2-N$), 5.28 (m, 2 H, $C\underline{H}_2=C$), 5.86 (m, 1 H, $-C\underline{H}=$), 7.11 (m, 8 H), 7.46 (m, 5 H), 8.04 (dd, 1 H, J = 8.0, 1.5, H-6)	44.27 ($-\underline{C}H_2-N$), 109.34 (C-9), 114.35 (C-6), 119.54 ($\underline{C}H_2=C$), 122.18 (C_p), 123.28 (C_o), 123.48 (C-7), 125.42 (C-8), 125.83 (C-5a), 127.97 (C_m), 128.26 (C'_p), 128.89 (C'_o), 129.24 (C'_m), 130.18 ($-\underline{C}H=$), 131.16 (C-9a), 136.42 (CH'_i), 147.16 (q), 148.04 (q), 148.36 (q), 148.40 (C_i)
7d	1727, 1654, 1631, 1597, 1444, 1421, 1169, 929, 756	2.26 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 4.51 (d, 2 H, J = 5.7, $-\underline{C}H_2-N$), 5.28 (m, 2 H, $C\underline{H}_2=C$), 5.86 (m, 1 H, $-C\underline{H}-$), 6.96 (m, 4 H), 7.09 (dd, 1 H, J = 7.8, 1.4, H-9), 7.26 (m, 6 H), 8.01 (dd, 1 H, J = 7.9, 1.5, H-6)	20.83 (CH_3), 21.22 (CH'_3), 44.20 ($-\underline{C}H_2-N$), 109.25 (C-9), 114.26 (C-6), 119.39 ($\underline{C}H_2=C$), 123.13 (C_o), 123.33 (C-7), 125.28 (C-8), 125.83 (C-5a), 128.50 (C'_o), 128.50 (C_m), 129.94 (C'_m), 130.29 ($-\underline{C}H=$), 131.15 (C-9a), 131.29 (C_p), 133.74 (C'_i), 137.92 (C'_p), 145.67 (C_i), 147.24 (q), 147.90 (q), 148.21 (C-10a)
7e	1730, 1651, 1599, 1563, 1447, 1379, 957, 748	4.72 (d, 2 H, J = 5.5, $-C\underline{H}_2-N$), 5.36 (m, 2 H, $C\underline{H}_2=C$), 5.97 (m, 1 H, $-C\underline{H}=$), 6.57 (d, 1 H, J = 13.7), 7.14 (m, 2 H), 7.41 (m, 13 H), 8.13 (m, 1 H), 8.16 (d, 1 H, J = 14.0)	44.39 ($-\underline{C}H_2-N$), 109.57 (C-9), 114.65 (C-6), 119.46 ($\underline{C}H_2=C$), 122.04, 123.34 (C-7), 123.69, 125.65 (C-8), 125.80 (C-5a), 126.00, 126.66, 127.61, 128.40, 128.54, 130.20 ($-\underline{C}H=$), 131.15 (C-9a), 134.18, 136.02 (q), 138.34 (q), 146.01 (q), 146.94 (q), 148.65 (C-10a)
7f	1716, 1659, 1566, 1551, 1491, 1445, 754	4.72 (d, 2 H, J = 5.7, $-C\underline{H}_2-N$), 5.37 (m, 2 H, $C\underline{H}_2=C$), 5.97 (m, 1 H, $-C\underline{H}=$), 6.48 (d, 1 H, J = 13.7), 7.34 (m, 13 H), 8.10 (d, 1 H, J = 13.7), 8.11 (dd, 1 H, J = 8.0, 1.8, H-6)	44.43 ($-\underline{C}H_2-N$), 109.65 (C-9), 114.65 (C-6), 119.55 ($\underline{C}H_2=C$), 122.01, 122.45, 123.81 (C-7), 125.17, 125.68 (C-5a), 125.77, 126.93, 127.76, 128.51, 128.72, 130.12 ($-\underline{C}H=$), 131.07 (C-9a), 131.34 (q), 133.24 (q), 134.56, 136.76 (q), 145.84 (q), 146.88 (q), 148.77 (C-10a). One quaternary carbon atom is not observed
7g	1723, 1659, 1609, 1564, 1512, 1443, 1252, 1036, 762	3.78 (s, 3 H, CH_3O), 3.81 (s, 3 H, CH_3O), 4.69 (d, 2 H, J = 5.6, $-C\underline{H}_2-N$), 5.34 (m, 2 H, $C\underline{H}_2=C$), 5.96 (m, 1 H, $-C\underline{H}=$), 6.52 (d, 1 H, J = 13.7), 6.83 (m, 4 H), 7.12 (dd, 1 H, J = 7.9, 1.9, H-9), 7.26 (m, 4 H), 7.35 (d, 2 H, J = 8.7), 7.42 (d, 2 H, J = 8.7), 8.03 (d, 1 H, J = 13.7), 8.10 (dd, 1 H, J = 8.0, 1.8, H-6)	44.31 ($-\underline{C}H_2-N$), 55.22 (2 × CH_3O), 109.44 (C-9), 113.90, 113.94, 114.51 (C-6), 119.33 ($\underline{C}H_2=C$), 120.25, 122.81, 123.50 (C-7), 125.46 (C-8), 125.80 (C-5a), 126.41, 126.90, 127.81, 128.61 (q), 130.28 ($-\underline{C}H=$), 131.08 (q), 131.15 (C-9a), 132.49, 146.05 (q), 146.81 (q), 148.13 (C-10a), 158.11 (q), 159.26 (q)

[a] Recorded on a Nicolet FT 5 DX spectrophotometer.

[b] Recorded on a Bruker AC-E 200 spectrometer; solvent: $CDCl_3$ for **4b**, **4d-h**, **5c–h**, **7** and DMSO-d_6 **4a**, **4c**, **5a**, **5b**.

The above method demonstrates that the reaction of iminophosphorane derived from 2-aminobenzimidazole with isocyanates affords a new and general enty to variety of 1,3,5-triazino[1,2-*a*]benzimidazoles with variable substituents at the triazine ring. Due to the easy access of the starting materials, the good yields in the iminophos-



phorane preparation as well as in the cyclization step, and due to the simplicity of the experimental one pot procedure this synthetic approach compares favorably with other methods.

2-(Triphenylphosphoranylideneamino)benzimidazole (2):

A solution of Br_2 (1.20 g, 7.5 mmol) in dry benzene (15 mL) was added dropwise to a stirred solution of Ph_3P (1.97 g, 7.5 mmol) in the same solvent (25 mL) at 0 °C under N_2. The mixture was stirred for 1 h and then allowed to stand at r. t. for 30 min. A solution of 2-aminobenzimidazole (**1**; 1 g, 7.5 mmol) and Et_3N (1.52 g, 15 mmol) in dry benzene (20 mL) was added and the mixture was heated to reflux for 5 h, whereupon a solid ($Et_3N \cdot BrH$) precipitated, which was separated by suction filtration from the warm solution. The filtrate was concentrated to dryness to afford the crude product **2**, which was triturated with hexane (30 mL), isolated by suction filtration, and recrystallized from benzene; yield: 2.81 g (95 %); mp 175–177 °C.

$C_{25}H_{20}N_3P$	calc.	C 76.32	H 5.12	N 10.68
(393.4)	found	76.49	5.34	10.49

EI-MS (70 eV): m/z (%) = 393 (M^+, 70), 392 (82), 328 (24), 183 (100).

IR (Nujol): ν = 3183, 1622, 1439, 1117, 721 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 6.90 (m, 4 H), 7.51 (m, 9 H), 7.94 (m, 6 × H_o), 8.57 (br s, 1 H, NH).

^{13}C NMR ($CDCl_3$/TMS): δ = 111.56 (C-4 = C-7), 119.19 (C-5 = C-6), 128.64 ($^3J_{P-C}$ = 12.3 Hz, C_m), 128.68 ($^1J_{P-C}$ = 101.9 Hz, C_i), 132.19 ($^4J_{P-C}$ = 2.7 Hz, C_p), 133.03 ($^2J_{P-C}$ = 10.1 Hz, C_o), 138.28 (C-3a = C-7a), 156.97 ($^2J_{P-C}$ = 1.2 Hz, C-2).

^{31}P NMR ($CDCl_3/H_3PO_4$, ext): δ = 16.92.

1-Carbamoyl-2-(triphenylphosphoranylideneamino)benzimidazoles (4); General Procedure:

To a solution of iminophosphorane **2** (0.5 g, 1.3 mmol) in dry CH_2Cl_2 (15 mL), the appropriate isocyanate **3** (1.3 mmol) was added and the mixture was stirred at r. t. for 6 h. The solvent was removed under reduced pressure and the residual material was purified by chromatography on a silica gel column (40 cm × 3.5 cm; 70–230 mesh) using EtOAc/hexane (2:1) as eluent, and finally recrystallized from CH_2Cl_2/hexane (1:1) to give **4** as crystalline solids (Table 1).

2-Alkyl(aryl)amino-3-alkyl(aryl)-4-oxo-3,4-dihydro-1*H*-1,3,5-triazino[1,2-*a*]benzimidazoles (5): General Procedure:

To a solution of iminophosphorane **2** (0.5 g, 1.3 mmol) in dry toluene (15 mL) the appropriate isocyanate (2.6 mmol) was added. The mixture was stirred at reflux temperature for 24 h. After cooling, the solvent was removed under reduced pressure and the residual material was slurried with cold EtOH (2 × 15 mL) and the separated solid was collected by filtration and recrystallized from EtOH to give **5** as white crystals (Table 1).

When solutions of **4** in dry toluene were treated with equimolecular amounts of the appropriate isocyanate **3** at reflux temperature for 24 h, compounds **5** are obtained in 63–84 % yields.

1-Alkyl-2-(triphenylphosphoranylideneamino)benzimidazoles (6):

These compounds were prepared according to the method reported[16] for the *N*-alkylation of benzimidazoles. For compound **6a** (R^2 = Me) dimethyl sulfate was used as alkylating agent.

6a (R^2 = Me): yield: 87 %; mp 155–157 °C.

$C_{26}H_{22}N_3P$	calc.	C 76.64	H 5.44	N 10.31
(407.4)	found	76.39	5.62	10.18

EI-MS (70 eV): m/z (%) = 407 (M^+, 25), 183 (100).

IR (Nujol): ν = 1616, 1524, 1115, 741, 719 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 3.68 (s, 3 H, CH_3), 6.96 (m, 3 H), 7.53 (m, 10 H), 7.85 (m, 6 H, 6 × H_o).

^{13}C NMR ($CDCl_3$/TMS): δ = 28.50 (CH_3N), 106.45 (C-7), 115.45 (C-4), 117.90 (C-6), 119.69 (C-5), 128.39 ($^3J_{P-C}$ = 12.4 Hz, C_m), 129.41 ($^1J_{P-C}$ = 102.1 Hz, C_i), 131.89 ($^4J_{P-C}$ = 2.7 Hz, C_p), 132.90 ($^2J_{P-C}$ = 10.1 Hz, C_o), 135.36 ($^4J_{P-C}$ = 1.8 Hz, C-7a), 143.00 (C-3a), 157.52 ($^2J_{P-C}$ = 3.9 Hz, C-2).

^{31}P NMR ($CDCl_3/H_3PO_4$, ext): δ = 15.38.

6b (R^2 = $CH_2{=}CH{-}CH_2$); yield: 91 %; mp 175–176 °C.

$C_{28}H_{24}N_3P$	calc.	C 77.58	H 5.58	N 9.69
(433.5)	found	77.79	5.36	9.46

EI-MS (70 eV): m/z (%) = 433 (M^+, 62), 183 (100).

IR (Nujol): ν = 1613, 1518, 1256, 1115, 741, 719 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 4.84 (d, 2 H, J = 5.3 Hz), 5.14 (m, 2 H), 6.01 (td, 1 H, J = 17.3, 10.0, 5.3 Hz), 6.94 (m, 3 H), 7.29 (m, 1 H), 7.45 (m, 9 H), 7.85 (m, 6 H, 6 × H_o).

^{13}C NMR ($CDCl_3$/TMS): δ = 44.93 ($CH_2{-}N$), 107.26 (C-7), 115.70 (C-4), 116.23 ($\underline{C}H_2{=}C$), 118.14 (C-6), 119.96 (C-5), 128.55 ($^3J_{P-C}$ = 12.4 Hz, C_m), 129.59 ($^2J_{P-C}$ = 102.2 Hz, C_i), 132.04 ($^4J_{P-C}$ = 2.9 Hz, C_p), 133.06 ($^2J_{P-C}$ = 10.1 Hz, C_o), 133.91 ($-\underline{C}H{=}C$), 134.66 ($^4J_{P-C}$ = 1.5 Hz, C-7a), 143.18 (C-3a), 157.11 ($^2J_{P-C}$ = 4.3 Hz, C-2).

^{31}P NMR ($CDCl_3/H_3PO_4$, ext): δ = 15.08.

2-Alkyl(aryl)imino-3-alkyl(aryl)-10-alkyl-4-oxo-2,3,4,10-tetrahydro-1,3,5-triazino[1,2-*a*]benzimidazoles (7); General Procedure:

To a solution of iminophosphorane **6** (1 mmol) in dry toluene (10 mL), the appropriate isocyanate (2 mmol) was added. The resultant mixture was stirred at reflux for 2 h. After cooling, the solution was concentrated to dryness and the residual material was recrystallized from $CHCl_3$/hexane (1:1) to give **7** as crystalline solids (Table 1).

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