Flavonoids, 42.[1] Anomalous Intramolecular Conjugate Addition: Synthesis of 2-Amino-2-benzyl-3(2*H*)-benzofuranone and Related Compounds

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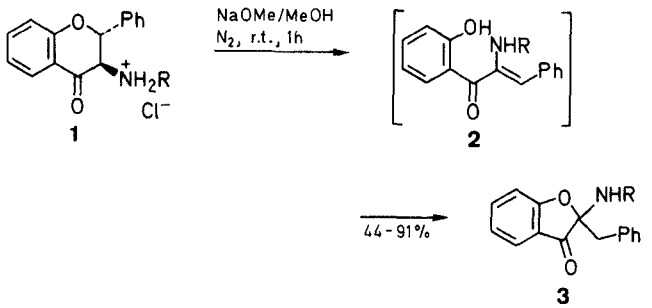
An easy and convenient preparation of 2-amino-2-benzyl-3(2*H*)-benzofuranone and related compounds is described. The method utilizes the anomalous intramolecular conjugate addition of intermediate 2-amino-1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-ones. 2-Benzyl-2-triphenylphosphoranylideneamino-3(2*H*)-benzofuranones by an analogous method are extremely unreactive and have limited synthetic applicability.

Intramolecular conjugate addition of 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one derivatives leading to 2-phenyl-2,3-dihydro-4*H*-benzopyran-4-ones (flavanones), is a well-known reaction.[2-4] However, in a few cases an anomalous ring closure has been reported. Condensation of (2-hydroxyphenyl)-1-propanone with pyridinecarbaldehydes[5] or ring contraction of *trans*-3-hydroxy-2-phenyl-2,3-dihydro-4*H*-benzopyran-4-ones[6-8] in strongly basic medium afforded 2-substituted 2-benzyl-3(2*H*)-benzofuranones. These reactions are considered to take place via 2-substituted 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one derivatives. Our previous observation on the ring opening and recyclization of *trans*-3-dialkylamino-2-phenyl-2,3-dihydro-4*H*-benzopyran-4-ones into 2-benzyl-2-dialkylamino-3(2*H*)-benzofuranones[9] prompted us to examine the extension of this transformation to the synthesis of various 2-amino-2-benzyl-3(2*H*)-benzofuranone derivatives. These compounds, with the exception of the above mentioned 2-dialkylamino-2-benzyl-3(2*H*)-benzofuranones, are hitherto unknown.

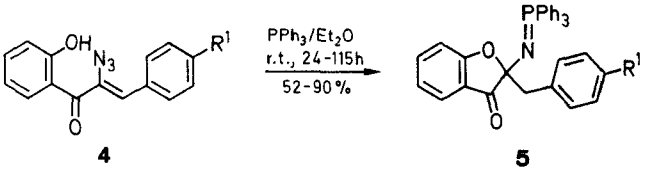
Treatment of 3-ammonio- and -alkylammonio-2-phenyl-2,3-dihydro-4*H*-benzopyran-4-one chlorides **1a–h** with sodium methoxide gave the corresponding 2-amino- and -alkylamino-2-benzyl-3(2*H*)-benzofuranones **3a–h** via 2-amino- and 2-alkylamino-1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-ones **2** in moderate to good yield. The reaction must be carried out under an inert atmosphere, otherwise the concurrent base-induced dehydrogenation leading to 3-amino-2-phenyl-4*H*-benzopyran-4-ones[10-12] lowers the yield of **3** considerably. The reaction is completed within 1 hour at room temperature and is not influenced by the nature of the alkyl or alkyl group.



1 2 3

1–3	R	1–3	R
a	H	e	*t*-Bu
b	*i*-Pr	f	*c*-C_6H_{11}
c	*i*-Bu	g	$PhCH_2$
d	*s*-Bu	h	$PhCH_2CH_2$

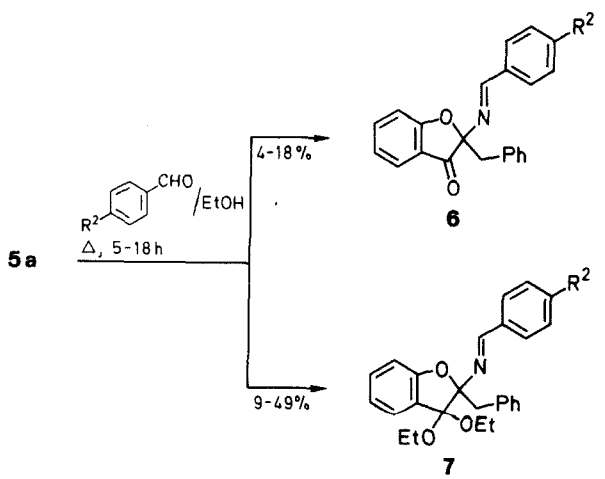
The generality of this ring contraction urged us to reanalyze the structure of the cyclization product of 1-(2-hydroxyphenyl)-2-phenyl-2-triphenylphosphoranylidene amino-2-propen-1-ones formed in the reaction of 2-azido-1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-ones **(4a)** and triphenylhosphine.[13] Detailed spectral investigations verified the error of the previous assignation[13] and clearly indicated the 2-benzyl-2-triphenylphosphoranylideneamino-3(2*H*)-benzofuranone **(5a)** structure. Substituted derivatives **5b,c** were also synthesized. During the preparation of these latter compounds precipitation of phosphazide adducts[14,15] from the ethereal reaction mixture was observed. Recrystallization of the phosphazides from ethanol resulted in the immediate formation of **5b,c** with loss of nitrogen.



4 5

4, 5	R^1	6, 7	R^2
a	H	a	H
b	OMe	b	OMe
c	Cl	c	NO_2

Iminophosphoranes are useful intermediates in the synthesis of various nitrogen-containing derivatives,[15] but **5a** was highly unreactive towards electrophilic reagents. The only reaction found the formation of Schiff bases **6a–c** and their acetals **7a–c** in poor yield when iminophosphorane **5a** was heated with aromatic aldehydes in ethanolic solution. Attempts to obtain **6** by acidic hydrolysis of the acetal function failed due to simultaneous cleavage of the C=N bond.



6 7

Table 1. 3-Alkylammonio-2-phenyl-2,3-dihydro-4*H*-benzopyran-4-one Chlorides **1** Prepared

Product	Yield[a] (%)	mp (°C)	Molecular Formula[b]	IR (KBr) ν(cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS) δ, J(Hz)
1b[c]	53	172–182 (dec)	$C_{18}H_{20}ClNO_2$ (317.8)	2900–2200 br (NH_2), 1696 (C=O), 1396, 1382, 1328, 1318, 1233, 1015	0.70, 0.83 (2 × d, 6H, CH_3, J = 6), 1.85 (m, 1H, CH), 2.05 (br s, 1H, NH), 3.77 (d, 1H, H-3, J = 12), 5.11 (d, 1H, H-2, J = 12), 6.95 (dd, 1H, H-8, J = 8, 1.5), 7.04 (m, 1H, H-6), 7.30–7.60 (m, 6H, H-7 + C_6H_5), 7.85 (dd, 1H, H-5, J = 8, 2)
1d[c,d]	39	159–163 (dec)	$C_{19}H_{22}ClNO_2$ (331.8)	3000–2300 br (NH_2), 1695 (C=O), 1391, 1325, 1232, 1008	0.54, 0.72 (2 × t, 3H, CH_3, J = 8), 0.64, 0.83 (2 × d, 3H, CH_3, J = 6.5), 1.06, 1.20 (2 × m, 2H, CH_2), 1.54, 1.70 (2 × m, 1H, CH), 1.98 (br s, 1H, NH), 3.82, 3.83 (2 × d, 1H, H-3, J = 12, 11.3), 5.10, 5.12 (2 × d, 1H, H-2, J = 12, 11.3), 7.00 (dd, 1H, H-8, J = 9, 1.5), 7.04 (m, 1H, H-6), 7.40, 7.58 (m, 6H, H-7 + C_6H_5), 7.92 (dd, 1H, H-5, J = 8.5, 2)
1e	27	155–170 (dec)	$C_{19}H_{22}ClNO_2$ (331.8)	2972, 2881, 2800–2200 br (NH_2), 1678 (C=O), 1384, 1365, 1330, 1322, 1286, 1228, 1028, 1004	1.26 (s, 3H, CH_3), 4.89 (d, 1H, H-3, J = 6), 6.36 (s, 1H, H-2), 7.16 (dd, 1H, H-8, J = 7.5, 1.5), 7.27 (m, 1H, H-6), 7.42 (m, 5H, C_6H_5), 7.61 (m, 1H, H-7), 9.2–9.5 (br s, 2H, NH_2)
1h	32	182–184	$C_{23}H_{22}ClNO_2$ (379.9)	2925, 2877, 3100–2300 br (NH_2), 1690 (C=O), 1325, 1307, 1223, 1013	2.56 (m, 2H, CH_2), 2.85 (m, 2H, CH_2), 5.28 (d, 1H, H-3, J = 11.2), 6.18 (d, 1H, H-2, J = 11.2), 6.96 (m, 2H, H-6, 8), 7.24, 7.53, 7.70–7.95 (m, 12H_{arom}), 9.7–9.3 (br s, 2H, NH_2)

[a] After recrystallization.
[b] Satisfactory microanalyses obtained: Cl ±0.29, N ±0.31.
[c] ^{1}H-NMR data refer to the free base, solvent: $CDCl_3$.
[d] The duplication of each ^{1}H-NMR signal is attributed to the incorporation of the new chiral center. Because of the hindered rotation, the enantiomers exist in different conformation. Similar duplication was also observed in ^{13}C-NMR spectrum. Detailed investigations of this phenomenon will be published elsewhere.

Table 2. 2-Benzyl-3(2*H*)-benzofuranones **3**, **5**, **6**, **7** Prepared

Product	Yield[a] (%)	mp (°C)	Molecular Formula[b]	IR (KBr) ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
3a	91	108–110	$C_{15}H_{13}NO_2$ (239.4)	3362, 3292 (NH_2), 1712 (C=O), 1319, 1297, 1258, 955	2.05 (br s, 2H, NH_2), 3.11 (AB, 2H, CH_2, J = 13.7), 7.00 (m, 1H, H-5), 7.03 (dd, 1H, H-7, J = 6, 1.5), 7.32 (m, 5H, C_6H_5), 7.58 (m, 1H, H-6), 7.63 (dd, 1H, H-4, J = 8.2)
3b	75	98–99.5	$C_{18}H_{19}NO_2$ (281.4)	3327 (NH), 2984, 1709 (C=O), 1386, 1368, 1324, 1306, 1177, 951	0.90, 0.97 (2 × d, 6H, CH_3), 1.90 (br s, 1H, NH), 2.80 (m, 1H, CH), 3.06 (s, 2H, CH_2), 6.89 (m, 1H, H-5), 6.94 (dd, 1H, H-7, J = 6.2), 7.20 (m, 5H, C_6H_5), 7.46 (m, 1H, H-6), 7.52 (dd, 1H, H-4, J = 8.2)
3c	44	75.5–77	$C_{19}H_{21}NO_2$ (295.4)	3317 (NH), 2968, 2954, 1708 (C=O), 1388, 1370, 1321, 1177, 954	0.78, 0.84 (2 × d, 6H, CH_3), 1.57 (m, 1H, CH), 1.88 (br s, 1H, NH), 2.09, 2.33 (ABM, 2H, CH_2), 3.07 (AB, 2H, CH_2, J = 13.8), 6.98 (m, 1H, H-5), 7.01 (dd, 1H, H-7, J = 6.5, 2), 7.26 (m, 5H, C_6H_5), 7.55 (m, 1H, H-6), 7.60 (dd, 1H, H-4, J = 8, 1.5)
3d	74	57–58	$C_{19}H_{21}NO_2$ (295.4)	3323 (NH), 2963, 2919, 2875, 1705 (C=O), 1322, 1306, 1268, 1180, 958	0.67, 0.81 (ABM$_3$, 6H, CH_3), 0.91 (d, 3H, CH_3, J = 5.5), 1.25 (ABM$_3$, 2H, CH_2), 1.89 (s, 1H, NH), 2.48 (m, 1H, CH), 3.05 (s, 2H, CH_2), 6.96 (m, 1H, H-5), 7.23 (m, 5H, C_6H_5), 7.55 (m, 2H, H-4, 6)
3e	75	123–124	$C_{19}H_{21}NO_2$ (295.4)	3337 (NH), 2970, 2917, 2864, 1715 (C=O), 1390, 1366, 1321, 1303, 1241, 1186, 968	1.01 (s, 9H, CH_3), 2.00 (s, 1H, NH), 3.03 (s, 2H, CH_2), 6.95 (m, 1H, H-5), 7.02 (dd, 1H, H-7, J = 5, 1.5), 7.28 (m, 5H, C_6H_5), 7.60 (m, 2H, H-4, 6)
3f	81	83.5–85	$C_{21}H_{23}NO_2$ (321.4)	3317 (NH), 2928, 2852, 1709 (C=O), 1319, 1300, 1265, 1176, 956	1.02 (m, 4H, CH_2), 1.55 (m, 6H, CH_2), 1.88 (br s, 1H, NH), 2.40 (m, 1H, CH), 3.08 (s, 2H, CH_2), 6.93 (m, 1H, H-5), 6.97 (dd, 1H, H-7, J = 6, 2), 7.30 (m, 5H, C_6H_5), 7.58 (m, 2H, H-4, 6)

Table 2. (continued)

Product	Yield[a] (%)	mp (°C)	Molecular Formula[b]	IR (KBr) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
3g	52	126–127	$C_{22}H_{19}NO_2$ (329.4)	3322 (NH), 3061, 2837, 1707 (C=O), 1322, 1305, 1178, 959	2.28 (ABM, 1H, NH), 3.15 (AB, 2H, CH_2, $J = 13.3$), 3.57, 3.69 (ABM, 2H, CH_2N), 6.99 (m, 1H, H-5), 7.05 (dd, 1H, H-7, $J = 7$, 1.5), 7.23 (m, 10H, $2 \times C_6H_5$), 7.56 (m, 2H, H-4, 6)
3h	72	84–85	$C_{23}H_{21}NO_2$ (343.4)	3313 (NH), 3082, 3060, 2938, 2927, 2915, 2860 br, 1708 (C=O), 1320, 1301, 1267, 1177, 955	2.45 (br s, 1H, NH), 2.61 (m, 2H, CH_2), 2.76 (m, 2H, CH_2N), 3.06 (AB, 2H, CH_2, $J = 14$), 7.00 (m, 2H, H-5, 7), 7.20 (m, 10H, $2 \times C_6H_5$), 7.57 (m, 2H, H-4, 6)
5a[c,d]	90	148–150	$C_{33}H_{26}NO_2P$ (499.6)	1704 (C=O), 1437, 1110 (Ar–P), 1345 (N=P), 1295, 1265, 1194, 948	3.17, 3.31 (AB, 2H, CH_2, $J = 13.2$, $^4J_{PH} = 3.9$)[e], 6.50–8.10 (m, $23H_{arom}$)
5b	65	124–126	$C_{34}H_{27}NO_3P$ (529.6)	2836 (OCH_3), 1715 (C=O), 1438, 1109 (Ar–P), 1326 (N=P), 1291, 1266, 1181, 952 br, 1248, 1031	3.13, 3.25 (AB, 2H, CH_2, $J = 13.8$, $^4J_{PH} = 3.7$)[e], 3.74 (s, 3H, OCH_3), 6.50–8.15 (m, $23H_{arom}$)
5c	52	137–139	$C_{33}H_{25}ClNO_2P$ (534.0)	3055 (CH), 1708 (C=O), 1436 (Ar–P), 1334 (N=P), 1303, 1287, 1275, 1272, 959, 1087	3.01, 3.11 (AB, 2H, CH_2, $J = 13.2$, $^4J_{PH} = 3.9$)[e], 6.60–8.15 (m, $23H_{arom}$)
6a[f]	4	135–137	$C_{22}H_{17}NO_2$ (327.4)	2932 (CH_2), 1731 (C=O), 1630 (C=N), 1330, 1302, 1150, 1006	3.44 (s, 2H, CH_2), 6.94 (m, 1H, H-5), 7.10–7.50 (m, 11H, H-7 + $2 \times C_6H_5$), 7.75 (m, 2H, H-4, 6), 8.38 (s, 1H, N=CH)
6b[g]	5	149–151	$C_{23}H_{19}NO_3$ (357.4)	2835 (OCH_3), 1728 (C=O), 1632 (C=N), 1323, 1314, 1296, 1173, 993, 1250, 1031	3.37, 3.46 (AB, 2H, CH_2, $J = 13.7$), 3.81 (s, 3H, OCH_3), 6.90 (d, 2H, H-3″, 5″ $J = 9$), 7.00 (m, 1H, H-5), 7.30–7.45 (m, 6H, H-7 + C_6H_5), 7.58 (m, 2H, H-4, 6), 7.73 (d, 2H, H-2″, 6″, $J = 9$), 8.29 (s, 1H, N=CH)
6c	18	169–171	$C_{22}H_{16}N_2O_4$ (372.4)	1720 (C=O), 1636 w (C=N), 1518, 1338 (NO_2), 1289, 1208, 1007	3.41, 3.52 (AB, 2H, CH_2, $J = 13.6$), 7.06 (m, 1H, H-5), 7.20 (m, 6H, H-7 + C_6H_5), 7.65 (m, 2H, H-4, 6), 7.96 (d, 2H, H-2″, 6″, $J = 9.5$), 8.26 (d, 2H, H-3″, 5″, $J = 9.5$), 8.41 (s, 1H, N=CH)
7a	17	106–107	$C_{26}H_{27}NO_3$ (401.5)	2985, 2890 (CH_3), 2944 (CH_2), 1647 (C=O), 1250, 1208, 1087, 1060, 996	1.14, 1.31 ($2 \times$ t, $2 \times 3H$, CH_3, $J = 7$), 3.39, 3.50 (AB, 2H, CH_2, $J = 13.3$), 3.62, 3.97 ($2 \times$ m, $2 \times 2H$, CH_2CH_3), 6.96 (m, 2H, H-5, 7), 7.16 (m, 5H, C_6H_5), 7.34 (m, 5H, C_6H_5), 7.64 (m, 2H, H-4, 6), 7.96 (s, 1H, N=CH)
7b[h]	49	oil	$C_{27}H_{29}NO_4$ (431.5)	2973, 2892 (CH_3), 2927 (CH_2), 2835 (OCH_3), 1649 (C=O), 1250, 1207, 1086, 1060, 990, 1165, 1031	1.14, 1.31 ($2 \times$ t, $2 \times 3H$, CH_3), 3.39, 3.49 (AB, 2H, CH_2, $J = 13.5$), 3.61, 3.95 ($2 \times$ m, $2 \times 2H$, CH_2CH_3), 3.78 (s, 3H, OCH_3), 6.82 (d, 2H, H-3″, 5″, $J = 9$), 6.99 (m, 2H, H-5, 7), 7.15 (m, 5H, C_6H_5), 7.55 (m, 2H, H-4, 6), 7.66 (d, 2H, H-2″, 6″, $J = 9$), 7.92 (s, 1H, N=CH)
7c	9	140–155 (dec)	$C_{26}H_{26}N_2O_5$ (446.5)	2980 (CH_3), 1648 (C=N), 1520, 1344 (NO_2), 1251, 1240, 1208, 1082, 1057, 1013, 997	1.14, 1.30 ($2 \times$ t, $2 \times 3H$, CH_3), 3.40, 3.50 (AB, 2H, CH_2, $J = 13.5$), 3.64, 3.97 ($2 \times$ m, $2 \times 2H$, CH_2CH_3), 6.94 (m, 2H, H-5, 7), 7.15 (m, 5H, C_6H_5), 7.28 (m, 1H, H-6), 7.37 (dd, 1H, H-4, $J = 8$, 2), 7.78 (d, 2H, H-2″, 6″, $J = 9.5$), 8.02 (s, 1H, N=CH), 8.20 (d, 2H, H-3″, 5″, $J = 9.5$)

[a] After recrystallization.
[b] Satisfactory microanalyses obtained: C ±0.31, H ±0.25, N ±0.29, Cl ±0.12, P ±0.11.
[c] ^{13}C-NMR ($CDCl_3$/TMS): $\delta = 46.34$ (C_α, $^3J_{P-C} = 17.1$), 103.63 (C-2, $^2J_{P-C} = 5$), 112.49 (C-7), 120.90 (C-3a), 123.92 (C-5), 126.00 (C-4), 130.80 (C-1′), 136.09 (C-1″), 136.86 (C-6), 169.66 (C-7a), 181.38 (C-3), not assigned signals: 119.57, 127.24, 127.83, 127.84, 128.28, 128.71, 131.10, 132.56, 133.38, 135.15.
[d] MS (EI, 70 eV): m/z (%) = 499 (10), 497 (27), 470 (3), 408 (78), 378 (6), 304 (17), 288 (12), 277 (90), 262 (100), 222 (23), 201 (18), 185 (26), 183 (42), 165 (13), 121 (11), 108 (26), 91 (21), 77 (15).
[e] The upfield part of the AB signal is split due to long-range carbon phosphorus coupling.
[f] MS (EI, 70 eV): m/z (%) = 327 (17), 236 (50), 207 (24), 206 (16), 181 (8), 167 (21.5), 130 (6), 121 (8), 120 (5.5), 116 (15.5), 91 (100), 89 (18).
[g] MS (EI, 70 eV): m/z (%) = 357 (8.5), 266 (100), 237 (13), 236 (12.5), 197 (23), 146 (35.5), 135 (16), 121 (80), 120 (13.5), 91 (44), 77 (17).
[h] MS (EI, 70 eV): m/z (%) = 431 (7.5), 402 (13.5), 386 (26.5), 357 (4), 314 (6), 284 (63), 237 (18), 222 (20), 195 (86), 167 (55), 148 (15), 146 (14), 139 (33), 121 (100), 120 (28.5), 105 (27), 91 (78.5), 77 (16.5).

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra (KBr) were recorded on Unicam SP 800 and Perkin-Elmer 283 spectrophotometers. ^{1}H-NMR and proton decoupled ^{13}C-NMR spectra were measured on a Bruker WP 200 SY instrument at 200 and 50.3 MHz, respectively. ^{13}C-NMR assignations were confirmed by *J*-modulated spin-echo technique.[16] Mass spectra were obtained using a VG 7035 GC-MS-DS system with EI mode. The starting ammonium salts **1a** and **1c,f,g** were synthesized according to procedures in Refs. 17 and 10, respectively. Hitherto unknown 3-alkylammonio-2-phenyl-2,3-dihydro-4*H*-benzopyran-4-one chlorides **1b,d,e,h** were prepared according to procedure in Ref. 10 and their data are given in Table 1.

2-Amino-2-benzyl-3(2*H*)-benzofuranones 3; General Procedure:
A solution of NaOMe (540 mg, 10 mmol) in absolute MeOH (10 mL) is added dropwise under N_2 atmosphere to a stirred suspension of **1a–h** (2.5 mmol) in absolute MeOH (25 mL) in 15 min. The stirring is continued at r.t. for 45 min. The solution is poured into water (200 mL) containing HOAc (1 mL) and extracted with Et_2O (3 × 50 mL). The organic layer is washed with 10% $NaHCO_3$ solution (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The solid residue is recrystallized from hexane to give **3** (Table 2).

2-Benzyl-2-triphenylphosphoranylideneamino-3(2*H*)-benzofuranones (5a):
Ph_3P (3.25 g, 12.39 mmol) is added to a solution of **4a**[18] (3.27 g, 12.31 mmol) in Et_2O (75 mL) and allowed to stand at r.t. for 70 h (slight N_2 evolution and precipitation of crystals can be observed). The crystals are filtered and washed with Et_2O (10 mL) to give pure **5a** (5.07 g, 82%). Et_2O (10 mL) is added to the concentrated reaction mixture and the precipitated solid is filtered off to give a further crop of **5a** (487 mg, 8%) which is recrystallized from EtOH; total yield: 5.557 g (90%); mp 148–150°C (Table 2).

2-(4-Methoxybenzyl)-2-triphenylphosphoranylideneamino-3(2*H*)-benzofuranone (5b):
Ph_3P (900 mg, 3.43 mmol) is added to a solution of **4b**[18] (1.01 g, 3.42 mmol) in Et_2O (20 mL) and allowed to stand at r.t. for 115 h (slight N_2 evolution and precipitation of crystals can be observed). The crystals are filtered and washed with Et_2O (4 mL) to give a yellow crystalline powder (354 mg, mp 105–115°C) which is recrystallized from EtOH to afford pure **5b** (209 mg, 12%). The filtrate is evaporated and the resulting orange oil is crystallized from EtOH to give additional **5b** (1.16 g, 64%) (Table 2); total yield: 1.369 g (76%); mp 124–126°C (Table 2).

Note: Microanalyses (N 7.14, P 4.66) of the unstable yellow crystalline powder (mp 105–115°C) incicate a phosphazide structure (calc. for $C_{34}H_{28}N_3OP$ (557.6): N 7.54, P 5.56) contaminated with some **5b**.

2-(4-Chlorobenzyl)-2-(triphenylphosphoranylideneamino-3(2*H*)-benzofuranone (5c):
Ph_3P (890 mg, 3.39 mmol) is added to a solution of **4c**[18] (1.01 g, 3.38 mmol) in Et_2O (20 mL) and allowed to stand at r.t. for 24 h (strong and quick precipitation after 1 min). The solid material is filtered and washed with Et_2O (6 mL) to afford a yellow powder [1.41 g, mp 120–125°jC (dec)] which is recrystallized from EtOH to give pure **5c**; yield: 0.93 g (52%); mp 137–139°C.

2-Arylideneamino-2-benzyl-3(2*H*)-benzofuranones 6 and 2-Arylideneamino-2-benzyl-3-(2*H*)-benzofuranone Diethyl Acetal 7; General Procedure:
A solution of **5a** (750 mg, 1.5 mmol) and the appropriate aromatic aldehyde (2.47 mmol) in absolute EtOH (20 mL) is refluxed until the starting material has disappeared (TLC: silica gel, eluent: benzene) (benzaldehyde: 16 h, 4-methoxybenzaldehyde: 18 h, 4-nitrobenzaldehyde: 5 h). The mixture is poured into water (300 mL) extracted with Et_2O (3 × 50 mL), the ether extract is washed with 10% $NaHCO_3$ solution (50 mL), and dried ($MgSO_4$). The solvent is evaporated and the residue is chromatographed on a silica gel column [Kieselgel 60 (Merck), 70–230 mesh] using benzene as eluent (Table 2).

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