Intramolecular [4 + 2] Cycloaddition Reactions of Ketenimines: A New Synthesis of Benz[*b*]acridines

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Abstract: *N*-[2-(2-Propenyl)phenyl]-*C*,*C*-diphenyl ketenimines undergo a thermally induced intramolecular [4 + 2] cycloaddition to give 5,11,11a,12-tetrahydrobenz[*b*]acridines, which are converted into the fully aromatic benz[*b*]acridines by oxidation with Pd/C in refluxing *ortho*-xylene.

Key words: azides, acridines, cycloadditions, polycycles, ketenimines, phosphazenes

Ketenimines have been extensively used in organic synthesis as substrates for the construction of isolated or fused six-membered heterocycles via inter or intramolecular [4 + 2] cycloaddition reactions,[1] where the ketenimines are able to play different roles. First, these heterocumulenes can serve as the 2π-electron components by using either their C=N or C=C bonds. Secondly, ketenimines may act in [4 + 2] cycloadditions as 2-azadienes, reacting across the dienic system formed by their C=N bond and a conjugated C=C bond from a substituent on the nitrogen atom [*N*-vinyl (or aryl) ketenimines], or as an all-carbon diene, using their cumulative C=C bond and a conjugated C=C bond on the sp^2 carbon terminus [*C*-vinyl (or aryl) ketenimines]. We have applied this methodology to the synthesis of benzo[*de*][1,6]naphthyridines[2] and pyrido[2,3,4-*de*]quinazolines[2] (ketenimine as 2-azadiene), 11-aryl-6-phenyl-6,11-dihydrobenzimidazo[1,2-*b*]isoquinolines[3] (ketenimine as an all-carbon diene) and 3-aryl-3,4-dihydropyrido[1,2-*a*]benzimidazoles[4] (ketenimine as 2π-electron component via its C=C bond).

As a further application we report herein a new general synthesis of the benz[*b*]acridine ring system,[5] based on an intramolecular [4 + 2] cycloaddition reaction on *N*-[2-(2-propenyl)phenyl]-*C*,*C*-diphenyl ketenimines, in which the ketenimine function acts as an all-carbon diene and the C=C bond of the allyl side-chain plays the role of the dienophile.

Staudinger reaction[6] of 2-allyl-1-azidobenzene[7] (**1**) with triphenylphosphane, in toluene solution at room temperature, yielded the corresponding triphenylphosphazene **2**. The transformation **1**→**2** was completed in less than 1 hour, as followed by IR (disappearance of the azide vibration near 2100 cm^{-1}) and ^{31}P NMR.[8] The reaction of triphenylphosphazene **2** in the same reaction flask with one equivalent of diphenylketene led to *N*-(2-allylphenyl)-*C*,*C*-diphenylketenimine (**3**), which was used in the next step without purification due to the hydrolytic sensitivity of the ketenimine function. Nevertheless, its formation was established by IR spectroscopy: the reaction mixture showed a strong absortion around 2000 cm^{-1} attributable to the N=C=C grouping. When compound **3** was heated at 130 °C for 16 hours (toluene solution, sealed tube), 6-phenyl-5,11,11a,12-tetrahydrobenz[*b*]acridine (**5**) was obtained in a 39% yield, after purification by column chromatography (Scheme 1).

Compound **5** was characterized by its analytical and spectroscopic data. In this respect, its ^1H and ^{13}C NMR spectra indicated that the original allyl side-chain now appears as a three sp^3-carbon chain, with one central methine group flanked by two methylenes. In the ^1H NMR the four methylene protons were observed as a multiplet at δ = 2.73–3.10, and the H-C11a proton also appears as a multiplet at δ = 3.25–3.45. The ^{13}C NMR spectrum shows the signals due to the two methylene carbon atoms, C11 and C12, at δ = 33.1 and 36.1, and the methine carbon C11a at δ = 34.6.

We believe that the conversion **3**→**5** involves an intramolecular [4 + 2] cycloaddition, in which the ketenimine fragment acts as an all-carbon diene, followed by H shift. The 5,11,11a,12-tetrahydrobenz[*b*]acridine **5** was oxidized in refluxing *ortho*-xylene in the presence of Pd/C to give the fully aromatic compound **6** in almost quantitative yield (Scheme 1). However, this method could not be applied to the preparation of 6-alkyl substituted analogues of **6**, as the thermal treatment of *C*-alkyl-*C*-phenyl ketenimines (prepared from **2** and alkyl phenyl ketenes) yielded only intractable mixtures.

Next we applied this synthetic methodology to the preparation of a series of 6-phenylbenz[*b*]acridines substituted at C11. Thus, the Wittig reaction of 2-azidophenylacetaldehyde[7] **7** with several benzyltriphenylphosphonium bromides **8** in the presence of potassium carbonate and dibenzo-18-crown-6, in dichloromethane at room temperature, provided 1-aryl-3-(2-azidophenyl)propenes **9** in moderate to good yields (Table 1). Azides **9** were converted into the corresponding ketenimines **10** by sequential treatment with triphenylphosphane and diphenylketene. When compounds **10** were heated at 130 °C for 16 hours, in toluene solution in a sealed tube, and the crude material resulting from this thermal treatment[9] subsequently heated in refluxing *ortho*-xylene in the presence

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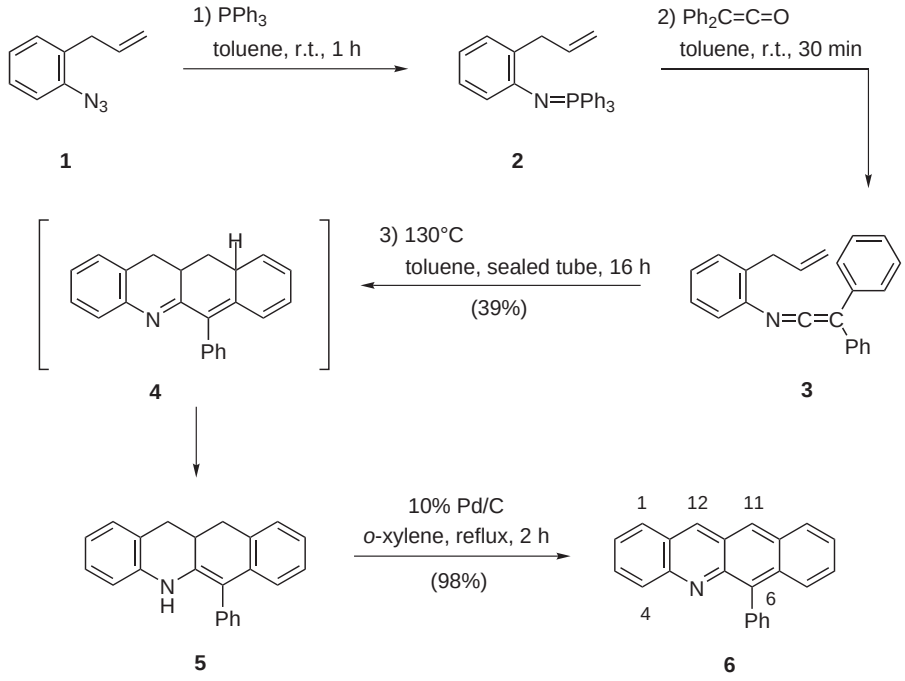
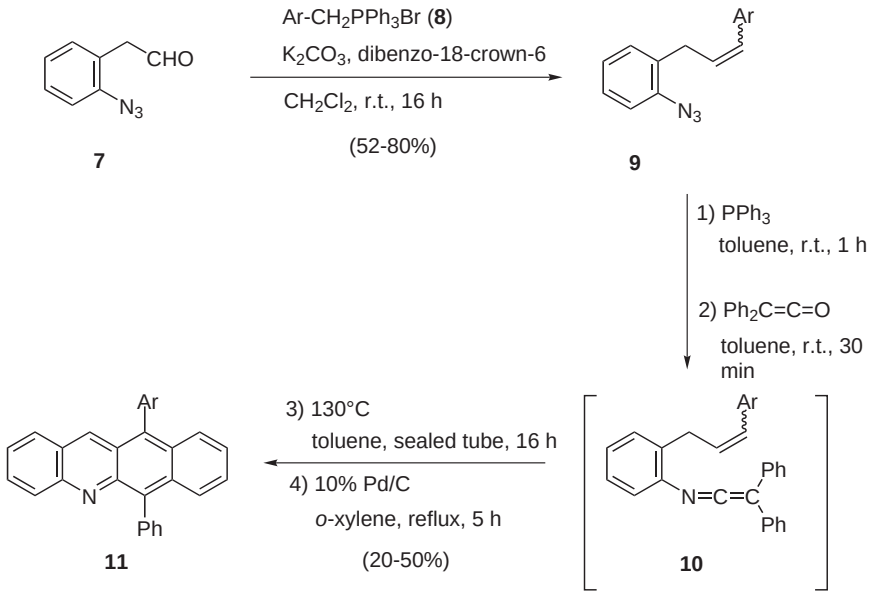


Scheme 1

of Pd/C the 11-aryl-6-phenylbenz[*b*]acridines **11** were isolated and purified by column chromatography (Scheme 2). Compounds **11** were obtained in acceptable global yields (20–50%) for the conversion **9**→**11**, four reaction steps in a one-pot process (Table 1).

The hexacyclic 9-phenyl-15*H*-benzo[*i*]quino[4,3,2-*kl*]acridine (**12**) accompanied compound **11d** in the mixture resulting from the thermal treatment and subsequent oxidation of ketenimine **10d** (Ar = 2-O_2N-C_6H_4). In fact, **12** was the major reaction product (36% yield vs. 20% yield of **11d**). To the best of our knowledge, compound **12** is representative of a new heterocyclic system. Its structure was unambiguously deduced from its spectroscopic and analytical data. The absence of a low-field signal corresponding to the H–C12 proton of the benz[*b*]acridines **11** in the ^{1}H NMR spectrum of **12** is particularly significant for assigning its structure.

The formation of the benzo[*i*]quino[4,3,2-*kl*]acridine **12** during the preparation of **11d** can be understood as resulting from the reduction of the nitro group of **11d** to give the 11-aminophenyl derivative **13**, which by means of an intramolecular amination process of the pyridine ring and a



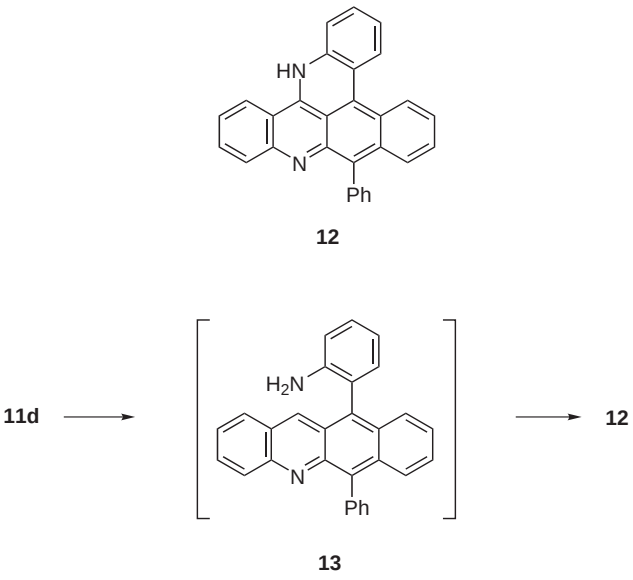
Scheme 2

Table 1 1-Aryl-3-(2-azidophenyl)propenes **9** and 11-Aryl-6-phenylbenz[*b*]acridines **11**

Entry	Ar	Yield of **9** (%)	Yield of **11** (%)[a]
a	2-Br-C_6H_4	74	40
b	4-Br-C_6H_4	55	27
c	4-Me-C_6H_4	52	50
d	2-O_2N-C_6H_4	71	20
e	4-O_2N-C_6H_4	80	33
f	4-MeO-C_6H_4	35	36

[a] Global yields of the conversion **9**→**11**

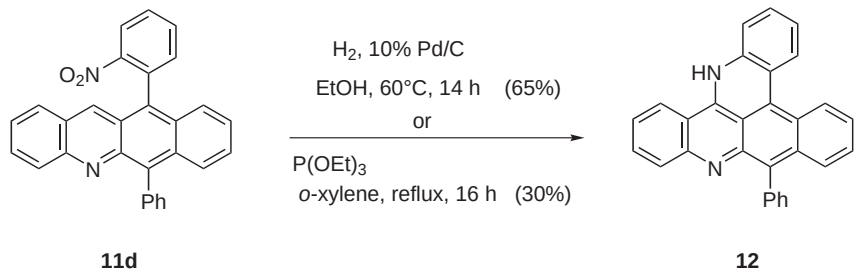
further oxidation step should lead to **12** (Scheme 3). This assumption was eventually confirmed: when the benz[*b*]acridine **11d** was kept under H_2 atmosphere in the presence of Pd/C compound **12** was obtained in 65% yield as the only reaction product (Scheme 4). The presumed conversion of **13** into **12** is not widely precedented and we are currently investigating its occurrence in other benzo-fused pyridines.



Scheme 3

Alternatively when a solution of the 11-(2-nitrophenyl)benz[*b*]acridine **11d** in a mixture of triethylphosphite and *ortho*-xylene was heated at reflux temperature for 16 hours a 30% yield of compound **12** was obtained, as expected for a nitrene insertion[10] into the 4-pyridyl C–H bond (Scheme 4).

In conclusion we have developed a general approach to the tetracyclic benz[*b*]acridine core, based on a new intramolecular [4 + 2] cycloaddition in *C,C*-diphenylketenimines, which in turn are easily accessible from adequately substituted azidobenzenes. From these compounds, four consecutive reaction steps are carried out in one-pot, and the final products are obtained in acceptable yields.



Scheme 4

All mps were determined on a Kofler hot-plate mp apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC-200 or a Varian Unity 300 spectrometer, using $SiMe_4$ as the internal standard. Mass spectra were recorded on a Hewlett–Packard 5993C spectrometer. Microanalyses were performed on a Carlo Erba EA-1108 instrument. 2-Allyl-1-azidobenzene[7] (**1**), 2-azidophenylacetaldehyde[7] (**7**) and diphenylketene[11] were prepared according to literature procedures. Benzyltriphenylphosphonium bromides **8** were prepared from the corresponding commercially available benzylbromides following the procedure described by Le Corre for the preparation of 2-nitrobenzyltriphenylphosphonium bromide.[12]

6-Phenyl-5,11,11a,12-tetrahydrobenz[*b*]acridine (5)

To a solution of 2-allyl-1-azidobenzene (**1**) (0.45 g, 2.8 mmol) in anhyd toluene (15 mL) Ph_3P (0.74 g, 2.8 mmol) was added. The reaction mixture was stirred at r.t. under N_2 for 1 h. Then, a solution of diphenylketene (0.54 g, 2.8 mmol) in anhyd toluene (2 mL) was added to the mixture, and the stirring continued for 30 min. The resulting toluene solution was heated at 130 °C in a sealed tube for 16 h. After removing the solvent under reduced pressure the residue was purified by column chromatography (silica gel; hexane–Et_2O, 9:1) to give **5**.

Yield: 0.34 g, 39%; colourless prisms; mp 158–160°C (Et_2O).

IR (Nujol): 3392, 1634, 1610, 1595, 1303, 1165, 761, 725, 703 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.73–3.10 (m, 4 H), 3.25–3.45 (m, 1 H), 5.95 (s, 1 H), 6.31 (d, 1 H, *J* = 7.7 Hz), 6.44 (d, 1 H, *J* = 7.2 Hz), 6.68 (t, 1 H, *J* = 7.3 Hz), 6.85–7.07 (m, 5 H), 7.28–7.55 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 33.1, 34.6, 36.1, 109.2 (s), 113.3, 119.5, 122.1 (s), 122.7, 123.5, 126.7, 126.8, 127.5, 128.1, 129.7, 131.4, 137.0 (s), 138.1 (s), 138.2 (s), 139.5 (s).

MS (EI): *m*/*z* (%) = 309 (M^+, 100).

Anal. Calcd for $C_{23}H_{19}N$ (309.40): C, 89.28; H, 6.19; N, 4.53. Found: C, 89.23; H, 6.20; N, 4.57.

6-Phenylbenz[*b*]acridine (6)
To a solution of **5** (50 mg, 0.16 mmol) in anhyd *ortho*-xylene (4 mL), Pd/C (32 mg) was added. The mixture was stirred at reflux temperature for 2 h. Then the hot solution was filtered through a short path of Celite, which afterward was washed with toluene (3 × 5 mL). The solvent was removed under reduced pressure and the residue purified by column chromatography (silica gel; hexane–Et_2O, 7:3) to give **6**.

Yield: 48 mg (98%); red needles; mp 209–211°C (Et_2O).

IR (Nujol): 1629, 1616, 1588, 1519, 1077, 915, 806, 759, 690 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.29–7.45 (m, 3 H), 7.53–7.65 (m, 6 H), 7.90 (t, 2 H, *J* = 9.1 Hz), 8.00–8.02 (m, 2 H), 8.65 (s, 1 H), 8.96 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 125.0 (s), 125.2, 125.4, 125.9 (s), 126.0, 127.0, 127.1, 127.2, 127.8, 127.9, 128.5, 130.0, 130.6, 131.3 (s), 132.1, 132.6 (s), 136.2, 137.6 (s), 138.2 (s), 143.9 (s), 150.1 (s).

MS (EI): *m*/*z* (%) = 305 (M^+, 82), 304 (100).

Anal. Calcd for $C_{23}H_{15}N$ (305.37): C, 90.56; H, 4.95; N, 4.59. Found: C, 90.31; H, 5.03; N, 4.66.

1-Aryl-3-(2-azidophenyl)propenes 9; General Procedure
To a solution of the corresponding benzyltriphenylphosphonium bromide **8** (3.85 mmol) in anhyd CH_2Cl_2 (25 mL) was added a solution of 2-azidophenylacetaldehyde (**7**) (0.8 g, 5 mmol) in the same solvent (5 mL). Then anhyd K_2CO_3 (0.7 g, 5 mmol) and a catalytic amount of dibenzo-18-crown-6 were added. The reaction mixture was stirred at r.t. for 16 h. After separation of the KBr by filtration, the solvent was removed under reduced pressure and the crude product was purified by column chromatography to give compounds **9** as colourless oils.

3-(2-Azidophenyl)-1-(2-bromophenyl)propene (9a)
Silica gel; hexane–Et_2O, 9:1.

Yield: 0.85 g (74%); ratio *Z*:*E* = 2:1.

IR (neat): 2122, 1646, 1581, 1487, 1465, 1449, 1436, 1286, 1046, 966 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.44 (d, 2 H_Z, *J* = 7.4 Hz), 3.52 (d, 2 H_E, *J* = 6.8 Hz), 5.87 (dt, 1 H_Z, *J* = 11.2, 7.4 Hz), 6.22 (dt, 1 H_E, *J* = 15.9, 6.8 Hz), 6.60 (d, 1 H_Z, *J* = 11.2 Hz), 6.77 (d, 1 H_E, *J* = 15.9 Hz), 7.00–7.32 (m, 14 $H_{Z,E}$), 7.48 (t, 1 H_Z, *J* = 7.8 Hz), 7.59 (d, 1 H_Z, *J* = 7.8 Hz).

^{13}C NMR ($CDCl_3$): δ = 29.8, 34.6, 118.1, 118.2, 123.4 (s), 124.1 (s), 124.9, 127.0, 127.4, 127.7, 127.9, 128.5, 128.6, 130.0, 130.1, 130.2, 130.5, 130.6, 130.7, 131.1, 131.6 (s), 132.6, 132.9, 137.3 (s), 138.0 (s).

MS (EI): *m*/*z* (%) = 287 [(M^+ + 2) – N_2, 90], 285 (M^+ – N_2, 91), 204 (100).

Anal. Calcd for $C_{15}H_{12}BrN_3$ (314.18): C, 57.34; H, 3.85; N, 13.37. Found: C, 57.19; H, 3.89; N, 13.25.

3-(2-Azidophenyl)-1-(4-bromophenyl)propene (9b)
Silica gel; hexane–Et_2O, 9:1.

Yield: 0.66 g (55%); ratio *Z*:*E* = 2:1.

IR (neat): 2120, 1644, 1582, 1560, 1486, 1470, 1451, 1283, 1147, 1025, 970 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.44 (d, 2 H_Z, *J* = 7.4 Hz), 3.52 (d, 2 H_E, *J* = 6.8 Hz), 5.88 (dt, 1 H_Z, *J* = 11.3, 7.4 Hz), 6.23 (dt, 1 H_E, *J* = 15.7, 6.8 Hz), 6.60 (d, 1 H_Z, *J* = 11.3 Hz), 6.77 (d, 1 H_E, *J* = 15.7 Hz), 6.99–7.33 (m, 14 $H_{Z,E}$), 7.49 (td, 1 H_Z, *J* = 7.4, 1.4 Hz), 7.59 (d, 1 H_Z, *J* = 7.8 Hz).

^{13}C NMR ($CDCl_3$): δ = 29.8, 34.6, 118.1, 118.2, 123.4 (s), 124.1 (s), 124.9, 127.0, 127.4, 127.7, 127.9, 128.5, 128.6, 130.0, 130.3, 130.5, 130.6, 130.7, 131.2, 131.6 (s), 132.7, 132.9, 137.3 (s), 138.0 (s).

MS (EI): *m*/*z* (%) = 287 [(M^+ + 2) – N_2, 59], 285 (M^+ – N_2, 64), 204 (100).

Anal. Calcd for $C_{15}H_{12}BrN_3$ (314.18): C, 57.34; H, 3.85; N, 13.37. Found: C, 57.27; H, 3.80; N, 13.30.

3-(2-Azidophenyl)-1-(4-methylphenyl)propene (9c)
Silica gel; hexane–Et_2O, 4:1.

Yield: 0.5 g (52%); ratio *Z*:*E* = 10:3.

IR (neat): 2122, 1598, 1584, 1513, 1487, 1450, 1284, 1162, 1148, 1087, 968 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.30 (s, 3 H_E), 2.34 (s, 3 H_Z), 3.46 (d, 2 H_E, *J* = 6.0 Hz), 3.60 (dd, 2 H_Z, *J* = 7.4, 2.0 Hz), 5.71 (dt, 1 H_Z, *J* = 11.6, 7.4 Hz), 6.23 (dt, 1 H_E, *J* = 17.5, 6.0 Hz), 6.39 (d, 1 H_E, *J* = 17.5 Hz), 6.53 (d, 1 H_Z, *J* = 11.6 Hz), 7.05–7.24 (m, 16 $H_{Z,E}$).

^{13}C NMR ($CDCl_3$): δ = 21.0, 21.1, 29.9, 30.0, 118.1, 118.2, 124.4, 126.0, 127.0, 127.5, 127.6, 128.7, 128.9, 129.2, 130.0, 130.2, 130.5, 131.2, 131.8 (s), 132.3 (s), 134.4 (s), 134.6 (s), 136.5 (s), 136.8 (s), 138.0 (s).

MS (EI): *m*/*z* (%) = 222 (27), 221 (M^+ – N_2, 81), 220 (100).

Anal. Calcd for $C_{16}H_{15}N_3$ (249.31): C, 77.08; H, 6.06; N, 16.85. Found: 76.90; H, 5.98; N, 16.95.

3-(2-Azidophenyl)-1-(2-nitrophenyl)propene (9d)
Silica gel; hexane–Et_2O, 7:3.

Yield: 0.77 g (71%); ratio *Z*:*E* = 10:3.

IR (neat): 2122, 1644, 1608, 1582, 1522, 1489, 1450, 1344, 1283, 1150, 1086, 964 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.35 (d, 2 H_Z, *J* = 7.5 Hz), 3.54 (d, 2 H_E, *J* = 6.7 Hz), 5.93 (dt, 1 H_Z, *J* = 11.3, 7.5 Hz), 6.30 (dt, 1 H_E, *J* = 15.5, 6.7 Hz), 6.86 (d, 1 H_Z, *J* = 11.3 Hz), 7.02–7.63 (m, 15 $H_{Z,E}$), 7.88 (d, 1 H_E, *J* = 8.0 Hz), 8.04 (d, 1 H_Z, *J* = 8.0 Hz).

^{13}C NMR ($CDCl_3$): δ = 29.9, 34.7, 118.1, 118.3, 124.5, 124.6, 124.9, 126.5, 126.9, 127.7, 127.8, 128.0, 128.6, 129.9, 130.7, 131.1, 131.8, 132.6 (s), 132.8, 132.9, 133.0 (s), 133.7, 148.3 (s).

MS (EI): *m*/*z* (%) = 252 (M^+ – N_2, 30), 117 (100).

Anal. Calcd for $C_{15}H_{12}N_4O_2$ (280.28): C, 64.28; H, 4.32; N, 19.99. Found: C, 64.13; H, 4.41; N, 20.08.

3-(2-Azidophenyl)-1-(4-nitrophenyl)propene (9e)
Silica gel; hexane–Et_2O, 7:3.

Yield: 0.86 g (80%).

IR (neat): 2122, 1645, 1597, 1512, 1489, 1450, 1339, 1281, 1180, 1111, 1091 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.58 (dd, 2 H, *J* = 7.4, 1.3 Hz), 5.97 (dt, 1 H, *J* = 11.6, 7.4 Hz), 6.60 (d, 1 H, *J* = 11.6 Hz), 7.05–7.35 (m, 4 H), 7.44 (d, 2 H, *J* = 8.6 Hz), 8.20 (d, 2 H, *J* = 8.6 Hz).

^{13}C NMR ($CDCl_3$): δ = 30.2, 34.7, 118.1, 118.3, 123.6, 123.9, 125.0, 126.6, 128.0, 128.1, 128.4, 129.3, 129.4, 129.9, 130.7, 131.0 (s), 133.5, 138.1 (s), 143.9 (s).

MS (EI): *m*/*z* (%) = 252 (M^+ – N_2, 99), 204 (100).

Anal. Calcd for $C_{15}H_{12}N_4O_2$ (280.28): C, 64.28; H, 4.32; N, 19.99. Found: C, 64.39; H, 4.24; N, 19.93.

3-(2-Azidophenyl)-1-(4-methoxyphenyl)propene (9f)
Silica gel; hexane–Et_2O, 4:1.

Yield: 0.36 g (35%); ratio *Z*:*E* = 3:1.

IR (neat): 2125, 1646, 1607, 1583, 1509, 1490, 1465, 1453, 1288, 1253, 1177, 1087, 1038, 967 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.46 (d, 2 H_E, *J* = 6.6 Hz), 3.59 (dd, 2 H_Z, *J* = 7.2, 1.8 Hz), 3.77 (s, 3 H_E), 3.80 (s, 3 H_Z), 5.67 (dt, 1 H_Z, *J* = 11.4, 7.2 Hz), 6.15 (dt, 1 H_E, *J* = 15.9, 6.6 Hz), 6.35 (d, 1 H_E, *J* = 15.9 Hz), 6.51 (d, 1 H_Z, *J* = 11.4 Hz), 6.81 (d, 2 H_E, *J* = 8.7 Hz), 6.87 (d, 2 H_Z, *J* = 7.8 Hz), 7.04–7.28 (m, 12 $H_{Z,E}$).

^{13}C NMR ($CDCl_3$): δ = 29.8, 30.0, 55.3, 113.8, 114.0, 118.1, 124.9, 125.9, 127.3, 127.6, 127.7, 128.2, 129.9, 130.0, 130.6, 130.7, 132.7 (s), 138.1 (s), 158.6 (s).

MS (EI): *m*/*z* (%) = 237 ($M^+ - N_2$, 99), 236 (100).

Anal. Calcd for $C_{16}H_{15}N_3O$ (265.31): C, 72.43; H, 5.70; N, 15.84. Found: C, 72.55; H, 5.76; N, 15.72.

11-Aryl-6-phenylbenz[*b*]acridines 11; General Procedure
To a solution of the corresponding 1-aryl-3-(2-azidophenyl)propene **9** (1 mmol) in anhyd toluene (20 mL), Ph_3P (0.26 g, 1 mmol) was added. The reaction mixture was stirred at r.t. under N_2 for 1 h. Then a solution of diphenylketene (0.19 g, 1 mmol) in anhyd toluene (2 mL) was added, and the mixture stirred at r.t. for 30 min. The resulting toluene solution was heated at 130 °C in a sealed tube for 16 h. The toluene was removed under reduced pressure, the residue dissolved in anhyd *ortho*-xylene (4 mL) and after addition of Pd/C (0.2 g) the mixture was stirred at reflux temperature for 5 h. Then the hot solution was filtered through a short path of Celite, which afterward was washed with toluene (3 × 5 mL). From the combined solution, the solvent was removed under reduced pressure and the residue purified by column chromatography.

11-(2-Bromophenyl)-6-phenylbenz[*b*]acridine (11a)
Silica gel; hexane–Et_2O, 4:1.

Yield: 0.19 g (40%); red prisms; mp 200–202 °C (Et_2O).

IR (Nujol): 1632, 1600, 1574, 1525, 1131, 1073, 1031, 960, 904, 853, 811, 769, 746, 702 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.30–7.36 (m, 3 H), 7.45–7.50 (m, 2 H), 7.52–7.65 (m, 7 H), 7.68–7.70 (m, 1 H), 7.78 (d, 1 H, *J* = 8.4 Hz), 7.91 (d, 1 H, *J* = 8.4 Hz), 7.95 (dd, 1 H, *J* = 6.6, 3.0 Hz), 8.02 (d, 1 H, *J* = 8.7 Hz), 8.47 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 123.9 (s), 125.5, 125.8, 125.9, 126.0 (s), 126.4, 127.2, 127.6, 127.7, 127.8, 128.4, 129.4 (s), 129.9, 130.1, 130.6, 132.2, 132.4, 132.5 (s), 133.3, 134.6, 136.2 (s), 138.5 (s), 138.6 (s), 139.2 (s), 143.7 (s), 149.9 (s).

MS (EI): *m*/*z* (%) = 461 (M^+ + 2, 34), 459 (M^+, 37), 378 (100).

Anal. Calcd for $C_{29}H_{18}BrN$ (460.36): C, 75.66; H, 3.94; N, 3.04. Found: C, 75.70; H, 3.88; N, 2.98.

11-(4-Bromophenyl)-6-phenylbenz[*b*]acridine (11b)
Silica gel; hexane–Et_2O, 4:1.

Yield: 0.13 g (27%); red prisms; mp 205 °C (Et_2O).

IR (Nujol): 1624, 1595, 1576, 1522, 1126, 1072, 1025, 911, 899, 850, 810, 769, 742, 701 cm^{-1}.

^1H NMR ($CDCl_3$ + TFA): δ = 7.47 (d, 2 H, *J* = 8.4 Hz), 7.54–7.80 (m, 9 H), 7.89–7.93 (m, 3 H), 8.17 (d, 2 H, *J* = 7.4 Hz), 8.27 (d, 1 H, *J* = 9.2 Hz), 9.54 (s, 1 H).

^{13}C NMR ($CDCl_3$ + TFA): δ = 120.6, 123.3 (s), 124.4 (s), 125.0 (s), 126.9, 127.7, 127.8, 128.2, 129.3 (s), 129.5 (s), 130.1, 130.3, 130.7, 130.8 (s), 131.5, 132.5 (s), 132.7, 132.9, 133.8 (s), 137.5 (s), 140.3, 141.0 (s), 142.2 (s), 150.3.

MS (EI): *m*/*z* (%) = 461 (M^+ + 2, 31), 459 (M^+, 35), 189 (100).

Anal. Calcd for $C_{29}H_{18}BrN$ (460.36): C, 75.66; H, 3.94; N, 3.04. Found: C, 75.56; H, 3.83; N, 3.11.

6-Phenyl-11-(4-methylphenyl)benz[*b*]acridine (11c)
Silica gel; hexane–EtOAc, 9:1.

Yield: 0.2 g (50%); red prisms; mp 227–228 °C (Et_2O).

IR (Nujol): 1626, 1599, 1578, 1515, 1504, 1118, 1125, 1010, 965, 949, 842, 760, 749, 737, 698 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.55 (s, 3 H), 7.26–7.32 (m, 3 H), 7.39–7.45 (m, 4 H), 7.53–7.65 (m, 6 H), 7.73–7.78 (m, 2 H), 7.90–7.93 (m, 1 H), 8.00 (d, 1 H, *J* = 9.0 Hz), 8.69 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 21.5, 124.6 (s), 125.1, 125.2, 125.8, 127.1, 127.2, 127.4, 127.8, 128.4, 129.4, 129.6 (s), 130.1, 130.5, 131.5, 132.3, 132.5 (s), 135.2 (s), 135.6, 137.5 (s), 137.7 (s), 138.0 (s), 138.8 (s), 143.6 (s), 149.8 (s).

MS (EI): *m*/*z* (%) = 395 (M^+, 100).

Anal. Calcd for $C_{30}H_{21}N$ (395.49): C, 91.11; H, 5.35; N, 3.54. Found: C, 91.02; H, 5.25; N, 3.48.

6-Phenyl-11-(2-nitrophenyl)benz[*b*]acridine (11d)
Silica gel; hexane–Et_2O, 4:1.

Yield: 85 mg (20%); orange prisms; mp 214 °C (Et_2O).

IR (Nujol): 1627, 1607, 1523, 1349, 1161, 1070, 1037, 962, 851, 767, 741, 705, 663 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.24–7.46 (m, 4 H), 7.56–7.95 (m, 11 H), 8.03 (d, 1 H, *J* = 8.8 Hz), 8.34 (dd, 1 H, *J* = 7.6, 1.4 Hz), 8.42 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 124.0 (s), 124.9, 125.6, 125.7, 125.8, 125.9 (s), 126.2, 127.3, 127.7 (s), 127.8, 127.9, 128.2, 129.2 (s), 129.7, 130.3, 130.5, 132.1, 132.3 (s), 132.4, 133.4, 134.3, 138.4 (s), 138.7 (s), 143.4 (s), 149.8 (s), 150.4 (s).

MS (EI): *m*/*z* (%) = 426 (M^+, 72), 378 (100).

Anal. Calcd for $C_{29}H_{18}N_2O_2$ (426.47): C, 81.67; H, 4.25; N, 6.57. Found: C, 81.68; H, 4.13; N, 6.51.

6-Phenyl-11-(4-nitrophenyl)benz[*b*]acridine (11e)
Silica gel; hexane–Et_2O, 9:1.

Yield: 0.14 g (33%) red prisms; mp 335–337 °C (Et_2O).

IR (Nujol): 1591, 1513, 1346, 1108, 1037, 968, 918, 853, 825, 764, 742, 699 cm^{-1}.

^1H NMR ($CDCl_3$ + TFA): δ = 7.56–7.85 (m, 12 H), 8.14–8.20 (m, 2 H), 8.32 (d, 1 H, *J* = 9.2 Hz), 8.64 (d, 2 H, *J* = 8.7 Hz), 9.41 (s, 1 H).

^{13}C NMR ($CDCl_3$ + TFA): δ = 119.5, 122.9 (s), 124.6, 125.3 (s), 127.0, 127.3, 128.2, 129.0, 130.2 (s), 130.3, 130.5, 130.8 (s), 131.0, 131.2 (s), 131.4, 132.0, 132.3 (s), 132.7, 137.5 (s), 139.4 (s), 141.0, 141.9 (s), 142.0 (s), 148.9 (s), 150.1.

MS (EI): *m*/*z* (%) = 426 (M^+, 75), 189 (100).

Anal. Calcd for $C_{29}H_{18}N_2O_2$ (426.47): C, 81.67; H, 4.25; N, 6.57. Found: C, 81.53; H, 4.34; N, 6.65.

6-Phenyl-11-(4-methoxyphenyl)benz[*b*]acridine (11f)
Silica gel; hexane–Et_2O, 4:1.

Yield: 0.15 g (36%); red prisms; mp 155–157 °C (Et_2O).

IR (Nujol): 1606, 1574, 1513, 1284, 1247, 1185, 1175, 1104, 913, 839, 818, 766, 745, 702 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.00 (s, 3 H), 7.20 (d, 2 H, *J* = 8.6 Hz), 7.30–7.37 (m, 3 H), 7.47 (d, 2 H, *J* = 8.6 Hz), 7.55–7.67 (m, 6 H), 7.78–

7.81 (m, 2 H), 7.90–7.94 (m, 1 H), 8.02 (d, 1 H, *J* = 8.8 Hz), 8.72 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 55.5, 114.2, 124.8 (s), 125.2, 125.3, 125.8, 127.1, 127.2, 127.4, 127.9, 128.5, 129.9 (s), 130.1, 130.4 (s), 130.5, 132.3, 132.5 (s), 132.7, 135.6, 137.5 (s), 137.8 (s), 138.8 (s), 143.7 (s), 149.8 (s), 160.5 (s).

MS (EI): *m*/*z* (%) = 411 (M^+, 100).

Anal. Calcd for $C_{30}H_{21}NO$ (411.49): C, 87.56; H, 5.14; N, 3.40. Found: 87.58; H, 5.05; N, 3.31.

9-Phenyl-15*H*-benzo[*i*]quino[4,3,2-*kl*]acridine (12)
Yield: 0.14 g (36%); colourless prisms; mp 245 °C (EtOAc–*n*-hexane).

IR (Nujol): 3402, 1617, 1607, 1591, 1567, 1553, 1503, 1235, 1157, 851, 766, 745, 707, 676 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 6.68 (d, 1 H, *J* = 8.1 Hz), 6.99 (s, 1 H), 7.06–7.11 (m, 1 H), 7.30 (ddd, 1 H, *J* = 8.2, 7.0, 1.4 Hz), 7.46–7.49 (m, 5 H), 7.53–7.61 (m, 2 H), 7.65–7.74 (m, 3 H), 8.20 (dd, 1 H, *J* = 8.2, 1.0 Hz), 8.80 (d, 1 H, *J* = 7.2 Hz), 8.86 (d, 1 H, *J* = 8.4 Hz), 8.97–9.00 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 114.8, 116.3 (s), 120.0 (s), 121.2, 123.0, 123.5 (s), 124.0 (s), 124.8, 125.4, 126.0, 127.7, 128.0, 128.5, 128.6, 128.9, 129.5, 130.3, 131.5, 132.7 (s), 133.0 (s), 135.3 (s), 135.6 (s), 139.3 (s), 147.7 (s), 149.7 (s).

MS (EI): *m*/*z* (%) = 394 (M^+, 100).

Anal. Calcd for $C_{29}H_{18}N_2$ (394.47): C, 88.30; H, 4.60; N, 7.10. Found: C, 88.11; H, 4.70; N, 7.18.

9-Phenyl-15*H*-benzo[*i*]quino[4,3,2-*kl*]acridine (12)
Method A
To a solution of **11d** (0.1 g, 0.23 mmol) in EtOH (25 mL) was added Pd/C (10 mg) and the mixture stirred at 60 °C under H_2 atm for 14 h. Then the solution was filtered through a short path of Celite, the solvent removed under reduced pressure, and the crude material purified by column chromatography (silica gel; hexane–Et_2O, 7:3) to give **12**.

Yield: 60 mg (65%).

Method B
A solution of **11d** (64 mg, 0.15 mmol) in a mixture of triethylphosphite (1 mL) and *ortho*-xylene (4.5 mL) was heated at reflux temperature for 16 h. The solvent was removed under reduced pressure and the crude material purified by column chromatography (silica gel, hexane–Et_2O, 7:3) to give **12**.

Yield: 18 mg (30%).

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(8) Compound **2** ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = 1.29.
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