Synthesis and Characterization of Novel Pyridines and 3,3′-Bridged Bipyridines Using 1,*x*-Cyclohexanediones☆

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A one-pot reaction using 1,*x*-cyclohexanediones, a Mannich base (or its hydrochloride), and ammonium acetate delivers novel pyridines or 3,3′-bridged bipyridine compounds **8**, **16**, **18**, **20**, and **22**. This strategy offers a great flexibility in the design of new building blocks, e.g. in supramolecular chemistry and underlines the efficiency of domino reactions.

The rapidly growing importance of the two research areas − supramolecular chemistry and domino reactions − has been documented in an increasing number of publications during the last few years[1][2][3][4][5][6][7][8][9][10][11]. In particular, pyridine or bipyridine building blocks play an important role in supramolecular chemistry. These fragments are constituents of coordination arrays (racks, ladders, grids)[4][12], molecular wires[13][14][15], helicates[16−22], and electroswitching devices[23−33].

Domino reactions offer many important advantages over traditional syntheses[10]. They will presumably be the key to more efficiency in preparative chemistry: In general, several bonds are formed in one sequence without the need to isolate and purify the intermediates, to add reagents or to change the reaction conditions. This type of reaction allows the minimization of waste, and in comparison to stepwise reactions the amount of solvents, reagents, adsorbents, and energy will be dramatically decreased.

We recently reported[34][35] the synthesis of polycyclic pyridines, bipyridines, and oligopyridines by different and efficient domino reactions. In this paper, the preparation of novel polycyclic heterocycles is described. The products may become interesting in applications with regard to supramolecular chemistry.

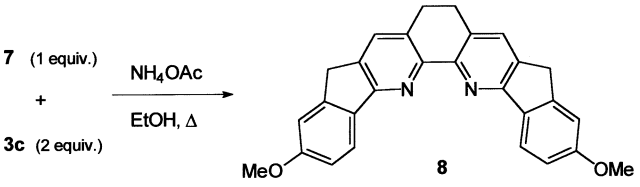
Results and Discussion

As reported[34], the reaction of one equivalent of a β-amino ketone hydrochloride and one equivalent of a ketone in the presence of ammonium acetate may lead to the formation of pyridines or bipyridines. In order to determine the scope of this strategy, we started to use polyfunctional starting materials (1,*x*-cyclohexanediones) rather than simple carbonyl compounds. The following examples will show, that 1,2-, 1,3- and 1,4-cyclohexanediones can serve as components of matrices that determine the specific geometry in the product structures.

Pyridines Derived from 1,2-Cyclohexanedione

1,2-Cyclohexanedione (**7**) is best suited for the preparation of symmetrical products. The reaction of **7** with two equiv. of the Mannich base **3c** yielded the bipyridine **8** in 12% (Scheme 1). Probably, the main reason for the low yield is the tendency of 1,2-cyclohexanedione (**7**) to form polymeric by-products. So far, all attempts to increase the yield (variation of the temperature, the solvent, or the reaction time) have failed. A solution to this problem might be the monoketalization[36] of **7** or the preparation of a bisaminomethylated 1,2-cyclohexanedione.

Scheme 1. Synthesis of the symmetrical bipyridine **8** from 1,2-cyclohexanedione (**7**)



Pyridines Derived from 1,3-Cyclohexanedione

The reaction of diisopropyl(4-oxochroman-3-ylmethyl)-ammonium chloride (**3d**; R = *i*Pr, resulting from the aminomethylation of 4-chromanone) and 1,3-cyclohexanedione (**1**) led to the formation of two crystalline products. Product **13** was insoluble and could be filtered off from the reaction solution after cooling to room temperature. After chromatography of the remaining crude product the pyridine **14** was obtained. Structural assignment took place by ^{1}H-and ^{13}C-NMR spectroscopy.

The postulated mechanism (Scheme 2) gives an explanation for this observation. Following the thermally induced amine elimination, the Michael addition should form the intermediate **23**. In one case we were able to isolate such an intermediate **12** in 33% yield. Path A is already known

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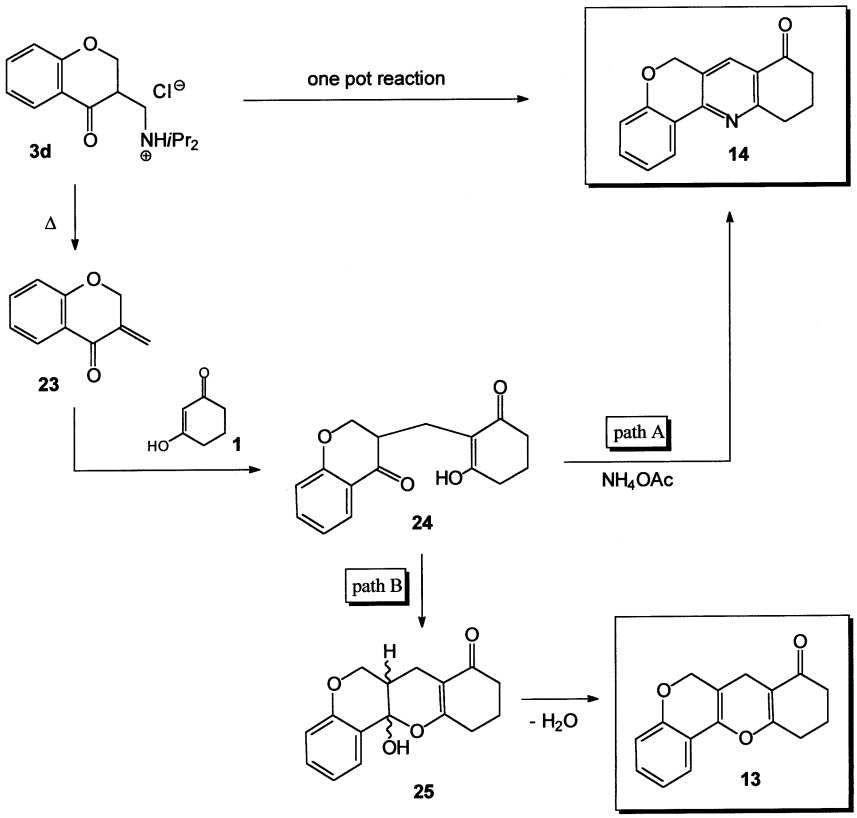
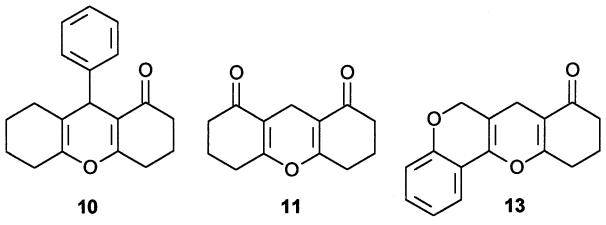
Scheme 2. Mechanistic considerations on the formation of the heterocycles **13** and **14**



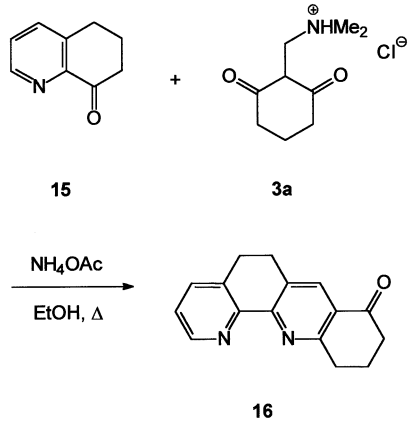
and leads to the formation of the expected pyridine derivative[34][35]. This conversion can be compared with the corresponding Hantzsch cyclization. In the other case the intermediate **25** with a hemiacetal or an enol ether structure is formed. Elimination of water leads to the formation of the heterocyclic compound **7**. We were able to prepare the compounds **10** [45%, from **1** and 2-(morpholin-4-yl-phenylmethyl)cyclohexanone (**9**)] and **11** (61%, from **1** and the β-amino ketone hydrochloride **3a**) in the same way.

Figure 1. 4*H*-Pyrans derived from 1,3-cyclohexanedione



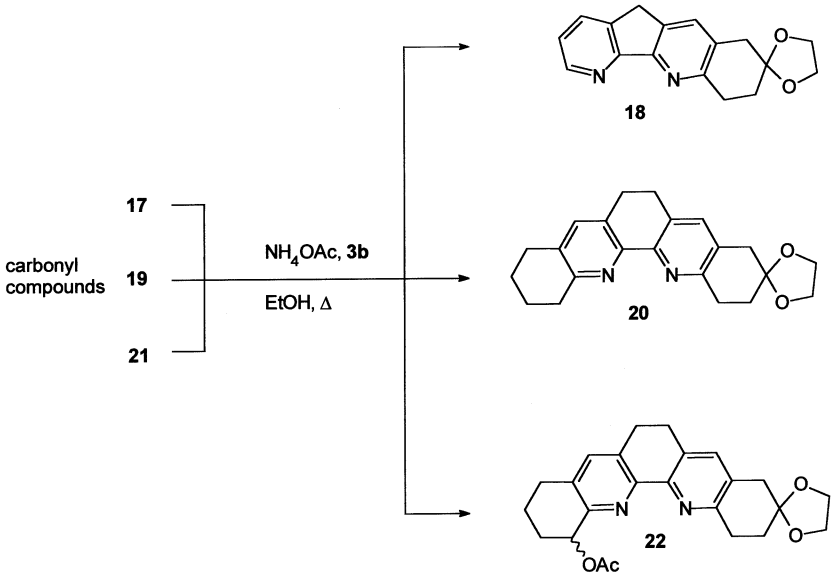
In order to prepare the bipyridine **16** and to avoid the formation of compounds like **10**, **11**, and **13**, the aminomethylated 1,3-cyclohexanedione **3a** is synthesized. The conversion of this Mannich base and 6,7-dihydro-5*H*-quinolin-8-one (**15**) leads to the expected bipyridine **16** (see Scheme 3) in an extremely high yield (75%)[34]. Whether this Mannich base can be used without limitations in our domino reaction is still under investigation.

Scheme 3. Synthesis of the bipyridine **16** from Mannich salt **3a** and ketone **15**



One exception we already know is the reaction of 4-chromanone (**6**) and **3d.** In this case we expected the formation of pyridine, but the isolation of such a product failed. Further investigations with meldrum acid and also the aminomethylated meldrum acid as a 1,3-dicarbonyl compound were made. In a few cases we were able to isolate crystalline products, but so far the constitution of these compounds is uncertain.

Scheme 4. Syntheses of the bipyridines **18**, **20**, and **22** from 1,4-cyclohexanedione



Pyridines Derived from 1,4-Cyclohexanedione

The use of 1,4-cyclohexanedione led to the formation of rodlike oligopyridines. To avoid side reactions (cf. 1,2-cyclohexanedione, **7**), we used the monoketalized derivative **4**, which is commercially available. The corresponding β-amino ketone hydrochloride **3b** was synthesized in high yield. Some of the resulting bipyridines from **3b** are shown in Scheme 4.

All experiments with β-amino ketone hydrochloride **3b** led to the expected products **18**, **20**, and **22** in good yields. All doubts, that the ketal might be opened under the reaction conditions, turned out to be unfounded. Especially, bipyridine structures like **22** are promising with regard to further investigations. In principle, the different O-protecting groups allow a consecutive deprotection and the independent design of both parts of the molecule.

Further constructions of building blocks for supramolecular arrangements (new types of grids, racks, and ladder structures) and also for applications in homogeneous catalysis are in progress. In order to prove the complexation properties of these compounds, one typical example is described[40].

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Experimental Section

General: Melting points are uncorrected. − ^{1}H and ^{13}C NMR: Bruker ARX 200. Chemical shifts are reported in ppm (δ values) relative to Me_4Si. − IR: Nicolet P510. − MS: Varian MAT 311 A. − EtOH was distilled from sodium, Et_2O from $LiAlH_4$, and CH_2Cl_2 from P_4O_{10} directly before use. The β-amino ketone hydrochlorides and the pyridine derivatives were prepared according the methods described in previous papers[34][39].

Preparation of the β-Amino Ketone Hydrochlorides **3a−d**: The β-amino ketone hydrochlorides were synthesized according to the method described by Tietze and Kinast[39] (see Table 1).

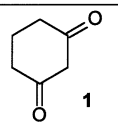
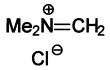
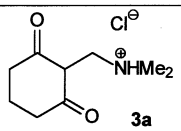
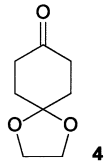
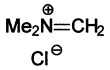
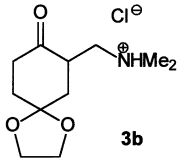
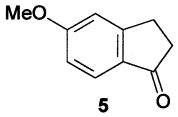
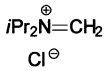
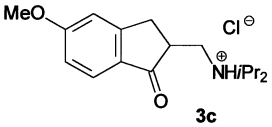
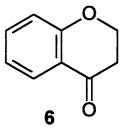
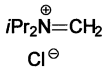
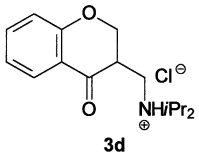
General Procedure for the Preparation of Pyridine Derivatives **8**, **14**, **16**, **18**, **20**, **22**: A suspension of 5 mmol of the appropriate carbonyl compound, 5−6 mmol of the β-amino ketone hydrochloride **3** (or of the Mannich base **9**) and 16 mmol of ammonium acetate (anhydrous) in 25−30 ml of absolute ethanol were refluxed for 3−4 h under argon. After cooling to room temp., the ethanol was removed in vacuo. The oily raw product was dissolved in a mixture of 35−40 ml of CH_2Cl_2, 15−20 ml of H_2O and 5 ml of 25% ammonia solution. The organic layer was separated and the residual aqueous layer was extracted three times with 15 ml of CH_2Cl_2. The combined organic layers were washed with H_2O up to a pH = 7 and dried with Na_2SO_4. After removal of the solvent, the brown oily residue was purified by chromatography on silica gel (50−60 g) eluted by solvent gradient.

The exact initial weight and possible variations are mentioned in the experimental part of the concerning compound.

(1,3-Dioxocyclohex-2-ylmethyl)dimethylammonium Chloride [(2-Hydroxy-6-oxocyclohex-1-enylmethyl)dimethylammonium Chloride] (**3a**): **3a** was synthesized from 1.93 g (17.2 mmol) of 1,3-cyclohexanedione (**1**) and 1.61 g (17.2 mmol) of *N,N*-dimethylmethyleneiminium chloride (**2a**). Yield: 2.55 g of a white powder (72%), m.p. 134.7°C. − IR (KBr): $\tilde{\nu}$ = 3085 cm^{-1} (m), 2944 (s), 2892 (s), 2826 (m), 1624 (vs), 1482 (m), 1414 (s), 1399 (s), 1357 (s), 1335 (s), 1296 (s), 1269 (m), 1159 (s), 1148 (s), 1053 (m), 1013 (m), 933 (m), 729 (m). − ^{1}H NMR [200 MHz, $CDCl_3/CD_3OD$ (5:1)]: δ = 3.85 (s, 2 H, CH_2), 2.69 [s, 6 H, $N(CH_3)_2$], 2.49 (t, ^3J = 6.32 Hz, 4 H, 2 CH_2), 1.92 (m_c, 2 H, CH_2). − $C_9H_{16}ClNO_2$ (205.68): calcd. C 52.55, H 7.78, N 6.81; found C 52.70, H 7.71, N 7.00.

Dimethyl(8-oxo-1,4-dioxaspiro[4.5]dec-7-ylmethyl)ammonium Chloride (**3b**): **3b** was prepared from 2.0 g (12.8 mmol) of 1,4-cyclohexanedione monoethylene ketal (**4**) and 1.2 g (12.8 mmol) of *N,N*-dimethylmethyleneiminium chloride (**2a**). Yield: 3.1 g of a white powder (97%), m.p. 126.5°C. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (m), 2983 (s), 2959 (s), 2880 (s), 2814 (m), 1716 (vs), 1475 (s), 1437 (m), 1398 (m), 1356 (s), 1230 (m), 1168 (s), 1144 (s), 1122 (s), 1055 (vs), 951 (s), 938 (s), 851 (m), 813 (m), 741 (m), 698 (m), 486 (m), 428 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.75 (br. s, 1 H, NH), 4.21−3.87 (m, 4 H, 2 CH_2), 3.56 (m_c, 1 H), 3.26 (m_c, 1 H), 2.81 (s, 3 H, CH_3), 2.73 (s, 3 H, CH_3), 2.66−2.32 (m, 4 H, 2 CH_2), 1.97

Table 1. Synthesis of the β-amino ketone hydrochlorides **3a–d**

No	Starting materials		Product	Yield [%]
1	 **1**	 **2a**	 **3a**	72
2	 **4**	 **2a**	 **3b**	97
3	 **5**	 **2b**	 **3c**	92
4	 **6**	 **2b**	 **3d**	99

(m_c, 2 H, CH_2), 1.71 (t, ^3J = 13.20 Hz, 1 H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.5 (s, C=O), 106.6 (s), 65.3 (t), 65.1 (t), 57.0 (t), 45.4 (d), 43.4 (q), 42.8 (q), 39.9 (t), 38.4 (t), 35.1 (t). – $C_{11}H_{20}ClNO_3$ (249.73): calcd. C 52.90, H 8.01, N 5.61; found C 52.79, H 8.19, N 5.83.

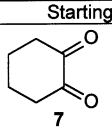
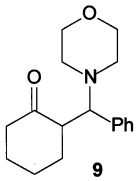
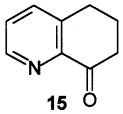
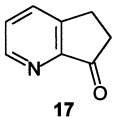
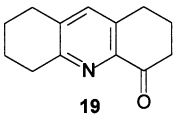
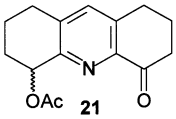
Diisopropyl(5-methoxy-1-oxoindan-2-ylmethyl)ammonium Chloride (**3c**): **3c** was synthesized from 4.0 g (24.7 mmol) of 5-methoxyindan-1-one (**5**) and 3.74 g (25.0 mmol) of *N,N*-diisopropylmethyleneiminium chloride (**2b**). Yield: 7.0 g of a white powder (92%), m.p. 157.8°C. – IR (KBr): $\tilde{\nu}$ = 3085 cm^{-1} (w), 2990 (m), 2585 (m), 2444 (s), 1696 (vs), 1493 (vs), 1437 (s), 1393 (m), 1337 (m), 1300 (s), 1283 (s), 1229 (m), 1181 (m), 1136 (m), 1034 (s), 858 (m), 776 (m), 763 (m). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.48 (br s, 1 H, NH), 7.30 (d, ^3J = 8.35 Hz, 1 H), 7.14 (dd, ^3J = 8.35 Hz, ^4J = 2.43 Hz, 1 H), 7.07 (d, ^4J = 2.43 Hz, 1 H), 4.07–3.95 (m, 1 H), 3.76 (s, 3 H, OCH_3), 3.61 (m_c, 4 H, 2 CH_2), 3.06–2.81 (m, 2 H, 2 CH), 1.56 (m_c, 9 H, 3 CH_3), 1.32 (t, ^3J = 6.50 Hz, 3 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 204.1 (s, C=O), 159.9 (s), 146.5 (s), 136.5 (s), 127.7 (d), 125.1 (d), 105.6 (d), 57.9 (d), 56.0 (q, CH_3O), 54.2 (d), 49.6 (t), 47.2 (d), 34.6 (t), 19.6 (q), 19.1 (q), 18.0 (q), 16.2 (q). – $C_{17}H_{26}ClNO_2$ (311.85): calcd. C 65.48, H 8.40, N 4.49; found C 65.71, H 8.53, N 4.60.

Diisopropyl(4-oxochroman-3-ylmethyl)ammonium Chloride (**3d**): **3d** was prepared from 3.0 g (20.25 mmol) of 4-chromanone (**6**) and 3.0 g (20.0 mmol) of *N,N*-diisopropylmethyleneiminium chloride (**2b**). Yield: 5.9 g (99%), m.p. 210.4°C. – IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (w), 3039 (w), 2991 (s), 2939 (m), 2748 (m), 2544 (s), 2496 (s), 2399 (s), 1679 (vs), 1607 (vs), 1482 (s), 1470 (vs), 1454 (s), 1402 (m), 1337 (s), 1305 (vs), 1221 (m), 1152 (s), 1116 (m), 1040 (m), 927 (s), 778 (s), 758 (s), 674 (m), 605 (m), 577 (m). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.75 (br. s, 1 H, NH), 7.83 (dd, ^3J = 7.86 Hz, ^4J = 1.63 Hz, 1 H), 7.49 (m_c, 1 H), 7.00 (m_c, 2 H), 5.18 (dd, ^3J = 11.33 Hz, ^4J = 4.96 Hz, 1 H), 4.50 (m_c, 1 H), 3.90–3.48 (m, 4 H), 2.95 (m_c, 1 H), 1.59 (AB system, J_{AB} = 6.60 Hz, 9 H), 1.36 (AB system, J_{AB} = 6,60 Hz, 3 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.3 (s, C=O), 162.3 (s), 137.2 (d), 127.7 (d), 122.1 (d), 120.3 (s), 118.7 (d), 69.9 (t), 57.9 (d), 54.4 (d), 44.0 (t), 43.8 (d), 19.5 (q), 18.8 (q), 18.0 (q), 16.5 (q).

Bipyridine **8**: **8** was synthesized from 0.17 g (1.5 mmol) of 1,2-cyclohexanedione (**7**), 0.94 g (3.0 mmol) of β-amino ketone hydrochloride **3c**, and 500 mg (6.5 mmol) of NH_4OAc. Yield: 73 mg of yellow crystals [12%, after chromatography on SiO_2, CH_2Cl_2/petroleum ether (1:1), CH_2Cl_2, CH_2Cl_2/acetone (10:1)], m.p. 244.9°C. – IR (KBr): $\tilde{\nu}$ = 3035 cm^{-1} (w), 2995 (w), 2931 (m), 2886 (w), 2834 (w), 1613 (s), 1548 (s), 1486 (vs), 1474 (s), 1436 (s), 1383 (s), 1281 (s), 1274 (s), 1254 (s), 1225 (m), 1187 (m), 1170 (m), 814 (m), 729 (s). – ^{1}H NMR (200 MHz, $CDCl_3$, T = 310 K): δ = 8.02 (d, ^4J = 2.40 Hz, 2 H), 7.74 (s, 2 H), 7.48 (d, ^3J = 8.27 Hz, 2 H), 7.04 (dd, ^3J = 8.26 Hz, ^4J = 2.47 Hz, 2 H), 4.02 (s, 6 H, 2 CH_3O), 3.88 (s, 4 H, 2 CH_2), 3.12 (s, 4 H, 2 CH_2). – ^{13}C NMR (50 MHz, $CDCl_3$, T = 310 K): δ = 160.6 (2 s), 159.9 (2 s), 151.5 (2 s), 142.9 (2 s), 138.4 (2 s), 136.2 (2 s), 132.7 (2 d), 132.5 (2 s), 125.8 (2 d), 117.1 (2 d), 106.1 (2 d), 56.3 (2 q), 34.1 (2 t), 29.1 (2 t). – MS (70 eV); *m/z* (%): 418 (9, [M^+]), 343 (20), 329 (56), 315 (100), 300 (49), 284 (15), 256 (11), 240 (17), 189 (14), 176 (48), 175 (34), 174 (55), 173 (15), 158 (18), 115 (19), 77 (22). – $C_{28}H_{22}N_2O_2$ (418.49): calcd. C 80.36, H 5.30, N 6.69; found C 80.12, H 5.03, N 6.77.

9-Phenyl-2,3,4,5,6,7,8,9-octahydroxanthen-1-one (**10**): **10** was prepared from 376 mg (3.35 mmol) of 1,3-cyclohexanedione (**1**), 919 mg (3.36 mmol) of 2-[morpholin-4-yl(phenyl)methyl]cyclohexanone (**9**)[37], and 770 mg (10.0 mmol) of NH_4OAc. Yield: 426 mg of a yellow powder (45%), m.p. 264.3°C. – IR (KBr): $\tilde{\nu}$ = 3233 cm^{-1} (m), 3171 (w), 2945 (w), 2923 (m), 1585 (s), 1494 (vs), 1388 (s), 1279 (m), 1270 (m), 1194 (s), 1131 (m), 696 (m). – ^{1}H NMR (200 MHz, $CDCl_3$, T = 293 K): δ = 7.30–7.04 (m, 5 H, ArH), 2.39 (m_c, 2 H), 2.25 (m_c, 2 H), 1.98–1.79 (m, 4 H), 1.72–1.52 (m, 5 H). – ^{13}C NMR (50 MHz, $CDCl_3$/CD_3OD (5:2), T = 315 K): δ = 196.9 (s, C=O), 154.4 (s), 147.5 (s), 128.2 (2 d), 128.1 (2 d),

Table 2. Polycyclic heterocycles obtained by domino reactions using 1,*x*-cyclohexanediones

No.	Starting materials		Product	Yield [%]
1	 **7**	**3c**	**8**	12
2	**1**	 **9**	**10**	45
3	**1**	**3a**	**11 / 12**	61 / 33
4	**1**	**3d**	**13 / 14**	18 / 40
5	 **15**	**3a**	**16**	75
6	 **17**	**3b**	**18**	36
7	 **19**	**3b**	**20**	57
8	 **21**	**3b**	**22**	36

127.1 (s), 126.0 (d), 114.2 (s), 109.0 (s), 42.6 (d), 37.1 (t), 27.8 (t), 27.4 (t), 26.2 (t), 23.1 (t), 22.7 (t), 21.5 (t). − $C_{19}H_{20}O_2$ (280.36): calcd. C 81.39, H 7.13; found C 81.62, H 7.21.

3,4,5,6,7,9-Hexahydro-2H-xanthene-1,8-dione (**11**): **11** was prepared from 327 mg (2.92 mmol) of 1,3-cyclohexanedione (**1**), 600 mg (2.92 mmol) of β-amino ketone hydrochloride **3a**, and 770 mg (10.0 mmol) of NH_4OAc. Yield: 391 mg of yellow powder (61%, filtered from the reaction solution), m.p. 267.9°C. Additionally, 225 mg of pale yellow crystals (33%, after chromatography on SiO_2, CH_2Cl_2) was isolated and indicated as the by-product **12**. − IR (KBr): $\tilde{\nu}$ = 3277 cm^{-1} (vs), 3247 (vs), 3213 (vs), 3098 (m), 3072 (m), 2948 (s), 2880 (m), 2841 (m), 1659 (s), 1634 (vs), 1599 (vs), 1497 (vs), 1390 (vs), 1322 (m), 1249 (vs), 1181 (vs), 1138 (vs), 963 (m), 857 (m), 724 (m), 707 (m), 532 (m). − ^{1}H NMR (200 MHz, [D$_6$]DMSO, *T* = 323 K): δ = 2.86 (s, 2 H), 2.38 (t, ^3J = 6.03 Hz, 4 H), 2.26 (t, ^3J = 6.45 Hz, 4 H), 1.90 (m_c, 4 H). − ^{13}C NMR (50 MHz, [D$_6$]DMSO, *T* = 323 K): δ = 195.9 (2 s, C=O), 152.8 (2 s), 109.4 (2 s), 37.3 (2 t), 27.1 (2 t), 21.8 (2 t), 19.5 (t). − MS (eV); *m/z* (%): 218 (10) [M^+], 217 (74), 216 (100), 215 (38), 200 (22), 187 (64), 174 (6), 161 (14), 131 (14), 117 (6), 104 (11), 91 (7), 77 (12), 63 (12), 51 (8), 44 (33). − $C_{13}H_{14}O_3$ (218.25): calcd. C 71.54, H 6.47; found C 71.64, H 6.63.

Methylenebis(1,3-cyclohexanedione) (**12**; 1,5-diketone by-product, see above): Yield: 225 mg of pale yellow crystals (33%, after chromatography on SiO_2, CH_2Cl_2), m.p. 139.8°C. − IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (m), 3228 (m), 3113 (s), 2937 (s), 1676 (s), 1585 (vs), 1493 (s), 1406 (vs), 1261 (s), 1184 (s), 1109 (s), 1018 (s), 918 (s). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.48 (br. s, 1 H, OH exchange with D_2O), 4.97 (br. s, 1 H, OH exchange with D_2O), 3.23 (s, 2 H), 2.42 (m_c, 8 H), 1.97 (m_c, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 201.3 (s), 197.6 (s), 179.5 (s), 168.1 (s), 114.9 (s), 109.3 (s), 36.7 (t), 35.2 (t), 30.2 (t), 30.1 (t), 21.4 (t), 21.2 (t), 17.4 (t). − $C_{13}H_{16}O_4$ (236.26): calcd. C 66.08, H 6.77; found C 66.30, H 6.59.

7,9,10,11-Tetrahydro-6H-chromeno[4,3-b]chromen-8-one (**13**): **13** was prepared from 376 mg (3.35 mmol) of 1,3-cyclohexanedione (**1**), 1.0 g (3.36 mmol) of β-amino ketone hydrochloride **3d**, and 770 mg (10.0 mmol) of NH_4OAc. Yield: 152 mg, (18%) of yellow crystals (from the reaction solution), m.p. 175.7°C. − IR (KBr): $\tilde{\nu}$ = 3305 cm^{-1} (m), 2943 (m), 1686 (s), 1585 (vs), 1508 (s), 1499 (vs), 1421 (m), 1350 (m), 1232 (s), 1201 (s), 1028 (m), 758 (s). − ^{1}H NMR [200 MHz, $CDCl_3$/CD_3OD (5/1)]: δ = 7.10 (m_c, 2 H), 6.96−6.76 (m, 2 H), 4.58 (s, 2 H), 2.93 (s, 2 H), 2.41 (m_c, 4 H), 1.96 (m_c, 2 H). − ^{13}C NMR [50 MHz, $CDCl_3$/CD_3OD (5:1)]: δ = 201.3 (s, C=O), 159.7 (s), 158.1 (s), 133.3 (d), 125.3 (d), 123.5 (d), 121.7 (s), 120.6 (d), 120.5 (s), 111.7 (s), 108.9 (s), 72.3 (t), 40.7 (t), 32.0 (t), 26.8 (t), 25.6 (t). − $C_{16}H_{14}O_3$ (254.28): calcd. C 75.57, H 5.51; found C 75.48, H 5.55.

6,9,10,11-Tetrahydrochromeno[4,3-b]quinolin-8-one (**14**): **14** was prepared from 376 mg (3.35 mmol) of 1,3-cyclohexanedione (**1**), 1.0 g (3.36 mmol) of β-amino ketone hydrochloride **3d**, and 770 mg (10.0 mmol) of NH_4OAc. Yield: 338 mg of light brown crystals [40%, after chromatography on silica gel, petroleum ether/CH_2Cl_2 (1:1), CH_2Cl_2, CH_2Cl_2/acetone (10:1), CH_2Cl_2/MeOH (4:1)], m.p. 146.2−147.2°C. − IR (KBr): $\tilde{\nu}$ = 3063 cm^{-1} (w), 2959 (w), 2886 (w), 2838 (w), 1681 (vs), 1595 (vs), 1582 (s), 1467 (s), 1419 (s), 1349 (m), 1340 (m), 1228 (s), 1199 (m), 1038 (m), 759 (s). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.16 (dd, ^3J = 7.77 Hz, ^4J = 1.64 Hz, 1 H), 7.89 (s, 1 H), 7.27 (m_c, 1 H), 7.01 (m_c, 1 H), 6.87 (dd, ^3J = 8.14 Hz, ^4J = 0.91 Hz, 1 H), 5.12 (s, 2 H), 3.07 (t, ^3J = 6.16 Hz, 2 H), 2.60 (m_c, 2 H), 2.10 (m_c, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.0 (s, C=O), 164.2 (s), 157.7 (s), 152.4 (s), 133.1 (d), 131.2 (d), 127.2 (s), 126.1 (d), 124.9 (s), 122.9 (d), 122.8 (s), 117.7 (d), 68.0 (t), 38.9 (t), 33.1 (t), 22.3 (t). − MS (70 eV); *m/z* (%): 251 (100) [M^+], 250 (93), 223 (17), 194 (17), 156 (10), 139 (6), 77 (8), 63 (7), 44 (45), 40 (43). − $C_{16}H_{13}NO_2$ (251.28): calcd. C 76.48, H 5.21, N 5.57; found C 76.40, H 5.11, N 5.44.

10,11-Dihydro-9H-benzo[b][1,10]phenanthrolin-8-one (**16**): **16** was synthesized from 0.60 g (4.1 mmol) of compound **15**, 0.85 g (4.2 mmol) of β-amino ketone hydrochloride **3a**, and 770 mg (10.0 mmol) of NH_4OAc. Yield: 510 mg of a yellow fine powder [75%, after chromatography on SiO_2, CH_2Cl_2/petroleum ether (1:1), CH_2Cl_2, CH_2Cl_2/acetone (3:1), CH_2Cl_2/MeOH (4:1)], m.p. 192.6°C. − IR (KBr): $\tilde{\nu}$ = 3039 cm^{-1} (w), 2949 (m), 2878 (w), 1671 (vs), 1595 (vs), 1454 (m), 1438 (m), 1421 (s), 1347 (s), 1224 (s), 1197 (m), 1160 (m), 1092 (m), 907 (m), 760 (s). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.77 (dd, ^3J = 4.72 Hz, ^4J = 1.62 Hz, 1 H), 8.18 (s, 1 H), 7.62 (dd, ^3J = 7.64 Hz, ^4J = 1.59 Hz, 1 H), 7.30 (m_c, 1 H), 3.34 (t, ^3J = 6.16 Hz, 2 H, CH_2), 3.04 (s, 4 H, 2 CH_2), 2.73 (m_c, 2 H, CH_2), 2.19 (m_c, 2 H, CH_2). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.6 (s, C=O), 163.3 (s), 155.1 (s), 151.1 (s), 149.6 (d), 136.7 (d), 135.6 (s), 135.0 (d), 132.7 (s), 128.0 (s), 124.8 (d), 39.0 (t), 33.0 (t), 27.7 (t), 27.3 (t), 22.4 (t). − MS (70 eV), *m/z* (%): 251 (30), 250

(100) [M^+], 222 (79), 194 (27), 166 (7), 97 (9), 72 (20). – $C_{15}H_{14}N_2O$ (250.30): C 76.78, H 5.64, N 11.19; found C 76.92, H 5.77, N 10.97.

Bipyridine **18**: **18** was synthesized from 500 mg (3.76 mmol) of 5,6-dihydro-[1]pyrindin-7-one (**17**), 962 mg (3.85 mmol) of β-amino ketone hydrochloride **3b**, and 770 mg (10.0 mmol) of NH_4OAc. Yield: 378 mg of violet crystals [36%, after chromatography on SiO_2, petroleum ether/CH_2Cl_2 (1:1), CH_2Cl_2, CH_2Cl_2/acetone (3:1)] m.p. > 97.2°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3047 cm^{-1} (w), 2943 (m), 2882 (m), 1720 (w), 1627 (m), 1559 (m), 1406 (s), 1269 (m), 1164 (m), 1108 (vs), 1060 (vs), 947 (s), 843 (m), 802 (s), 790 (m). – ^1H NMR (200 MHz, $CDCl_3$): δ = 8.72 (dd, ^3J = 4.83 Hz, ^4J = 0.73 Hz, 1 H), 7.86 (dd, ^3J = 7.61 Hz, ^4J = 0.73 Hz, 1 H), 7.57 (s, 1 H), 7.28 (dd, ^3J = 7.61 Hz, ^4J = 4.83 Hz, 1 H), 4.09 [s, 4 H, $O(CH_2)_2O$], 3.82 (s, 2 H), 3.37 (t, ^3J = 6.94 Hz, 2 H), 3.13 (s, 2 H), 2.14 (t, ^3J = 6.94 Hz, 2 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.3 (s), 157.2 (s), 156.4 (s), 149.6 (d), 137.8 (s), 135.4 (s), 134.2 (d), 133.2 (d), 129.2 (s), 122.6 (d), 108.1 (s), 65.1 (2 t), 39.6 (t), 32.2 (t), 32.1 (t), 31.5 (t). – $C_{17}H_{16}N_2O_2$ (280.32): calcd. C 72.83, H 5.71, N 9.99; found C 72.89, H 5.76, N 10.12.

Bipyridine **20**: **20** was synthesized from 165 mg (0.82 mmol) of 2,3,5,6,7,8-hexahydro-3*H*-acridin-4-one (**19**), 250 mg (1.0 mmol) of the β-amino ketone hydrochloride **3b**, and 385 mg (5.0 mmol) of NH_4OAc. Yield: 162 mg of a yellow oil, which slowly crystallizes after several weeks [57%, after chromatography on SiO_2, petroleum ether/CH_2Cl_2 (1:1), CH_2Cl_2, CH_2Cl_2/MeOH (4:1)]. – IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} (w), 2963 (m), 2890 (m), 1627 (m), 1562 (m), 1406 (s), 1289 (m), 1165 (s), 1128 (vs), 1068 (vs), 967 (s), 843 (m), 800 (s), 793 (s). – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.18 (s, 2 H), 4.01 (s, 4 H), 3.28 (t, ^3J = 6.74 Hz, 2 H), 3.07 (t, ^3J = 5.80 Hz, 2 H), 2.99 (s, 2 H), 2.82 (s 4 H), 2.75 (t, ^3J = 5.80 Hz, 2 H), 2.03 (t, ^3J = 6.74 Hz, 2 H), 1.83 (m_c, 4 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 156.9 (s), 153.4 (s), 150.2 (s), 149.4 (s), 136.9 (d), 136.7 (d), 132.5 (s), 131.6 (s), 131.4 (s), 129.5 (s), 108.1 (s), 65.0 (2 t), 38.9 (t), 33.1 (t), 32.2 (t), 31.4 (t), 29.1 (t), 27.8 (t), 27.7 (t), 23.6 (t), 23.2 (t). – $C_{22}H_{24}N_2O_2$ (348.44): calcd. C 75.83, H 6.89, N 8.04; found C 75.88, H 6.82, N 8.12.

Bipyridine **22**: **22** was prepared from 500 mg (1.93 mmol) of 4-acetoxy-1,2,3,4,7,8-hexahydro-6*H*-acridin-5-one (**21**), 500 mg (2.0 mmol) of the β-amino ketone hydrochloride **3b**, and 770 mg (10.0 mmol) of NH_4OAc. Yield: 281 mg of a yellow powder [36%, after chromatography on SiO_2, petroleum ether/CH_2Cl_2 (1:1), CH_2Cl_2, CH_2Cl_2/MeOH (4:1)], m.p. 104.7°C. – IR (KBr): $\tilde{\nu}$ = 3033 cm^{-1} (w), 2939 (s), 1734 (s), 1589 (m), 1551 (w), 1448 (m), 1369 (m), 1238 (vs), 1109 (m), 1061 (s), 1028 (m), 949 (m). – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.31 (s, 1 H), 7.21 (s, 1 H), 6.10 (t, ^3J = 3.30 Hz, 1 H), 4.03 (s, 4 H), 3.28 (m_c, 2 H), 3.01 (s, 2 H), 2.87 (s, 4 H), 2.81 (m_c, 2 H), 2.26 (m_c, 2 H), 2.11 (s, 3 H, CH_3COO), 2.05 (m_c, 2 H), 1.83 (m_c, 2 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.0 (s, C=O), 155.5 (s), 152.4 (s), 150.5 (s), 149.8 (s), 137.1 (d), 137.0 (d), 134.1 (s), 133.9 (s), 131.7 (s), 130.0 (s), 108.0 (s), 72.3 (d), 65.0 (2 t), 39.0 (t), 32.1 (t), 31.3 (t), 29.0 (t), 28.5 (t), 28.0 (t), 27.6 (t), 22.1 (q), 18.3 (t). – $C_{24}H_{26}N_2O_4$ (406.48): calcd. C 70.91, H 6.40, N 6.89; found C 70.94, H 6.47, N 7.11

☆ Dedicated to Professor *Eckehard V. Dehmlow* on the occasion of his 65th birthday.

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[40] [40a] In order to prove the complexation properties of these compounds, one typical example is given. Ruthenium complex: $[Ru(bipy)_2L][PF_6]_2$ (**26**: L = bipyrine **20**) was synthesized from 76 mg (0.16 mmol) of $Ru(bipy)_2Cl_2$ and 53 mg (0.15 mmol) of the bipyridine **20**, which were refluxed in $EtOH/H_2O$ (4/1 ml) for 48 h. After cooling to room temp., 60 mg (0.37 mmol) of NH_4PF_6 in 1 ml of H_2O was added and the mixture was allowed to stand at −20°C for 12 h. The dark red precipitate was filtered and dried in vacuo at 80°C (70 mg). The red solution obtained after filtration was chromatographed on Al_2O_3 (basic, act. III), using an elution gradient [CH_2Cl_2, CH_2Cl_2/MeOH (10/1), CH_2Cl_2/MeOH (5/1)]; 80 mg of complex **26** was isolated. Yield: 150 mg of a dark red powder (95% after chromatography and filtration), m.p. > 223°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3079 (w), 3054 (w), 2940 (m), 1466 (m) 1447 (s), 1413 (m), 840 (vs), 764 (s), 557 (s). − ^{1}H NMR (200 MHz, CD_3CN): δ = 8.55 (m_c, 2 H), 8.44 (m_c, 2 H), 8.15 (m_c, 2 H), 7.99 (m_c, 4 H), 7.65 (m_c, 2 H), 7.57 (m_c, 4 H), 7.27 (m_c, 2 H), 4.01−3.74 (m, 4 H), 3.09−2.68 (m, 8 H), 2.43−2.13 (m, 2 H), 1.69−1.27 (m, 8 H). − ^{13}C NMR (50 MHz, CD_3CN): δ = 162.69 (s), 161.16 (s), 158.17 (s), 158.02 (s), 157.85 (d), 154.57 (s), 153.80 (s), 153.48 (d), 153.40 (d), 152.34 (d), 152.23 (d), 139.23 (d), 138.10 (2 d), 138.01 (2 d), 136.88 (d), 134.61 (s), 134.45 (s), 127.78 (d), 127.64 (d), 127.60 (d), 124.86 (d), 124.68 (d), 124.63 (d), 124.57 (d), 106.26 (s), 64.69 (t), 64.54 (t), 38.67 (t), 32.48 (t), 31.38 (t), 30.79 (t), 28.95 (t), 26.37 (t), 26.36 (t), 22.78 (t), 20.94 (t). [40b] Recently, we described the formation of some similar ruthenium complexes: N. Risch, R. Keuper, *J. Prakt. Chem./Chem.-Ztg.* **1998**, *340*, 424−429. We prefer the synthesis of ruthenium complexes instead of copper(I) complexes (simple handling, high yields, easy characterization by NMR spectroscopy): N. Risch, R. Keuper, *Z. Naturforsch.* **1995**, *50b*, 1115−1120.

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