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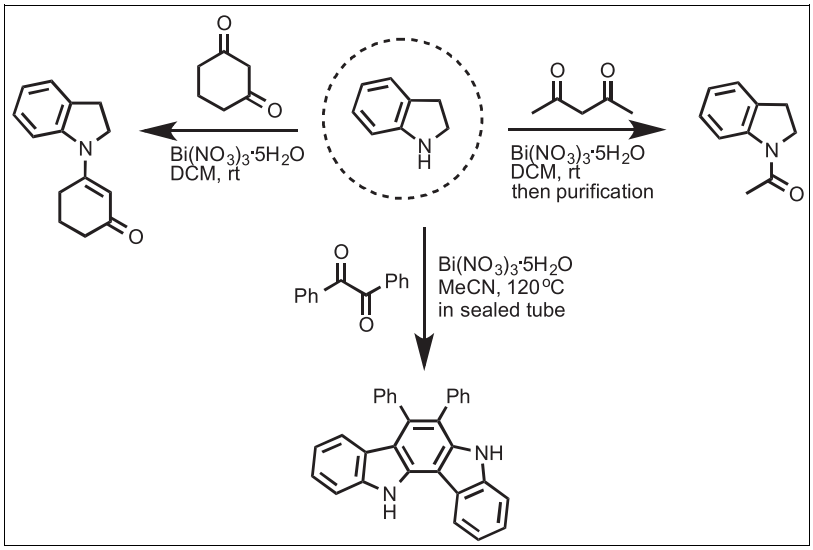

Bismuth nitrate catalyzed condensation reactions of indoline with 1,2- and 1,3-diketones were investigated and were reported to proceed via different reaction pathways with the involvement of one or two of the carbonyl groups. While the reaction of indoline with cyclohexane-1,3-dione (**4**) gave solely condensation product, the reaction between the acetylacetone (**5**) and indoline provided *N*-acetyl indoline as single products on retro-aldol process. In contrast to 1,3-diketones, the reaction with benzil (**17**) was performed under difficult conditions and proceeded to give secondary products.

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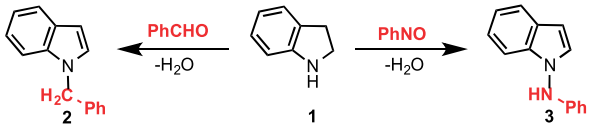
INTRODUCTION

Indole moiety is found in many natural products, fine chemicals, and pharmaceuticals. *N*-Alkyl indoles represent a particularly interesting class and are also known to possess a wide spectrum of biological activities in numerous natural products and pharmaceutical compounds [1–3]. However, in contrast to the much more developed C-2 and especially C-3 functionalization, the development of new methods for functionalization at the *N*-position of indoles is still highly desirable. Recently, a redox amination is a powerful strategy developed for the synthesis of *N*-alkylation of indoles, pyrroles and *N*-heterocycles by N–C bond formation [4]. Previous studies have been reported to generate *N*-alkyl indoles over the redox amination process from indolines with aryl or non-enolizable aldehydes by Tunge, Pan, and Siedel groups (Scheme 1) [5–9]. But the reactions used salicylaldehyde as the substrate gave *N*-alkyl indolines over the reductive amination process with intermolecular hydride transfer from indoline instead of the usual redox amination reaction [6]. In a recent article, Tunge *et al.* synthesized *N*-aryl-1-aminoindoles from indolines with different nitrosobenzenes via intermolecular redox amination (Scheme 1) [10]. Recently, we also investigated the redox amination potential of both enolizable cyclic and acyclic ketones and benzylic ketones with indoline [11,12]. Our results showed that the formation of *N*-alkyl substituted indole/indoline derivatives over competitive redox and reductive amination processes depending on the reaction condition and ketones. In the continuation of our research interest on redox amination of indoline, we next turned attention toward the effect of the second carbonyl group and here in report the reactions of some 1,2- and 1,3-diketones with indoline.

RESULTS AND DISCUSSIONS

Our research interest on redox amination with ketones of indoline encouraged us to ascertain the behavior of both 1,2- and 1,3-diketones against the redox amination reactions of indoline. Cyclohexane-1,3-dione (**4**) and acetylacetone (**5**)

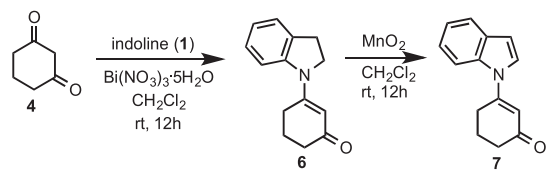
Scheme 1. Examples for redox amination synthesis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].



as 1,3-diketone povided an opportunity to investigate the effect of -carbonyl group on the redox amination of indoline with ketones. The bismuth nitrate-catalyzed reaction of indoline with cyclohexane-1,3-dione (**4**) in CH_2Cl_2 (DCM) gave enamine product **6** in 94% yield, instead of the desired product **11** (Schemes 2 and 3). The introduction of the second carbonyl group into the cyclohexanone ring has a profound effect on the dehydration step in the outcome of the reaction. The second competing product **11**, which is a possible desired indole type-redox amination product, was not observed in the case of cyclohexane-1,3-dione (**4**). In this case, the presence of the second carbonyl group plays a crucial role in the formation of conjugated enone **6**, which is formed via a 1,2-addition of indoline with cyclic-1,3-diketone, followed by dehydration through two mechanisms (Scheme 3). Probably, no aromatization was observed, because of the conjugated structure of the resulting cyclohexenone. Furthermore, 3-(indolin-1-*yl*)cyclohex-2-enone (**6**) was easily aromatized with MnO_2 to afford the 3-(1*H*-indol-1-*yl*)cyclohex-2-enone (**7**) in 96% yield (Scheme 2).

Under the similar reaction conditions, acetylacetone (**5**) readily underwent enamine formation and retro-aldol type cleavage, probably through a six-membered cyclic mechanism (Scheme 4, 5). When a mixture of indoline and **5** in the presence of bismuth nitrate under solvent-free condition was heated in a sealed glass tube at 120°C for 1 h and the resulting mixture was analyzed by ^{1}H NMR, the formation of the similar products was observed. Then the reaction mixture was subjected to silica gel column chromatography to give only *N*-acetyl indoline **13**. However, this transformation was carried out in the presence of SiO_2 in MeCN:H_2O (9:1). All attempts to obtain the products from the mixture were unsuccessful. Surprisingly, the oxidation of the mixture with MnO_2 or DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) also led to the formation of *N*-acylated indoline instead of the expected mixture of the corresponding indoline products (Scheme 4). Because of the susceptibility of the double bond toward the moisture,

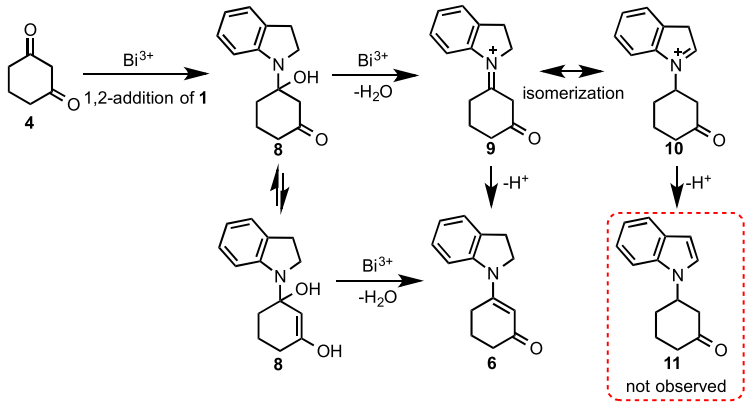
Scheme 2. Synthesis of 6 and 7.



the hydration of the conjugated double bond undergoes carbon-carbon bond cleavage to give *N*-acetyl indoline (**13**) and acetone. It can be hypothesized that MnO_2, DDQ or SiO_2 act as a Lewis acid during the addition of water to the double bond. The ^{1}H NMR spectrum of **13** revealed that *N*-acetyl indoline exists as an 85:15 mixture of the rotamers. Unfortunately, all oxidation attempts of pure *N*-acetyl indoline **13** to prepare *N*-acetyl indole **16** failed. Using manganese dioxide or DDQ in CH_2Cl_2 yielded only unreacted starting material. This resistance to chemical oxidation might be the result of the electron-withdrawing character of carbonyl group, causing the five-membered ring to be electron-deficient (Scheme 5).

Similarly, the reaction of indoline with benzil (**17**) as 1,2-diketone was also investigated under the similar reaction conditions. But no reaction was observed after 2 days at room temperature. When benzil (**17**) was subjected to bismuth nitrate-catalyzed redox amination in either acetonitrile or excess indoline as solvent-free in a sealed tube at 120°C, a mixture of three unexpected separable product (**18–20**) apart from indole (**21**) was obtained (Scheme 6). We assume that all of products except for indole are secondary products, which are formed after secondary reactions of **17** under the given reaction conditions. The mechanism for the formation of minor product **18** is shown in Scheme 7. The first part of the mechanism is the formation of reductive amination product **23** and indole by a hydride transfer from indoline to iminium ion **22** resulting from condensation of indoline and benzil. Later, the cyclization of *N*-alkyl indoline **23** to 4,5-diphenyl-1,2-dihydropyrrolo[3,2,1-*hi*]indole (**18**) involves an internal Friedel-Crafts alkylation followed by dehydration in the presence of bismuth nitrate. For the unexpected formation of the other products in the $Bi(NO_3)_3{\cdot}5H_2O$-catalyzed reaction of **1** and **17**, we assume that indole occurring during reductive alkylation processes play an important role. The condensation of indole with benzil probably goes through two different channels, leading to C3-alkylation **20** and indolocarbazol **19**, via the intermediate **25**, as shown in Scheme 7. The surprising intermediate **25**, which can be trapped by various nucleophiles, that is present in the reaction mixture. The formation of C3-alkylation product **20** can be easily envisioned with the intramolecular hydride transfer from indoline to the intermediate **25**. The trapping of **25** by indole gives indolocarbazole **19** by a stepwise process involving intermolecular Friedel-Crafts alkylation and dehydration to provide the aromatization. We assumed that the driving force for the reaction is the formation of azafulvenium ion **25**, which can be more stabilized by the carbonyl group than iminum ion **22**. The 6,7-diphenyl-5,12-dihydroindolo[3,2-*a*]carbazole (**19**) was also synthesized by an independent experiment from the reaction of indole with benzil under same conditions in 71% yield

Scheme 3. Proposed mechanism for formation of 6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].



(Scheme 6). One-pot method for the synthesis of dihydroindolo[3,2-*a*]carbazole **19** in 62% yield by the *para*-toluenesulfonic acid catalyzed condensation of indole with benzil was previously described by Nair *et al.* [13]

Actually, we examined the reactions of indoline (**1**) with 1,2-diketones such as 2,3-butanedione (**28**), acenaphthenequinone (**29**), and isatin (1*H*-indole-2,3-dione) (**30**) apart from benzil (**17**) under similar conditions (Fig. 1). But we have not received positive results from these diketones. The reaction of diketones **28** and **29** gave no isolable product, whereas no reaction was observed with **30**.

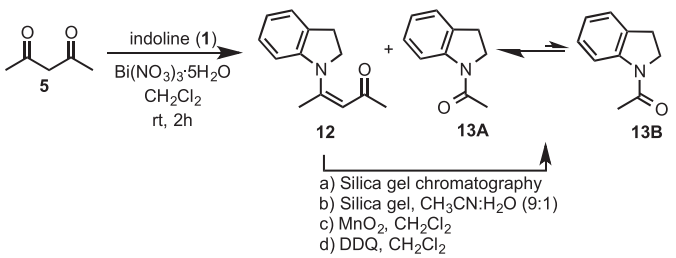
CONCLUSION

Finally, the redox amination potentials of indoline with 1,2- and 1,3-diketones in the presence of bismuth nitrate catalyst were investigated, and these ketones exhibited the different behaviors from both enolizable cyclic and acyclic and benzylic monoketones. Cyclohexane-1,3-dione (**4**) gave primarily enamine condensation product **6**, whereas acetylacetone (**5**) underwent an inseparable mixture of enamine and retro-aldol-type cleavage products. The enamine type product is sensitive to acid-induced retro-aldol type cleavage to yield *N*-acetyl indoline as a single product. The reaction of indoline with 1,2-diketone **7** provided a separable mixture of unexpected secondary products.

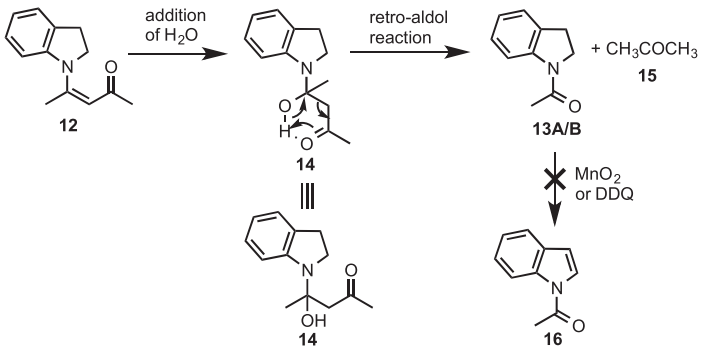
EXPERIMENTAL

3-(Indolin-1-*yl*)cyclohex-2-en-1-one (6): A mixture of indoline (**1**; 500 mg, 4.2 mmol) in CH_2Cl_2 (10 mL), cyclohexane-1,3-dione (**4**; 471 mg, 4.2 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol) was stirred magnetically at rt for 12 h. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with EtOAc (30 mL) and washed with water (3 × 50 mL), and organic phase was dried over Na_2SO_4. 3-(Indolin-1-*yl*)cyclohex-2-en-1-one (**6**; 845 mg, 94%, orange solid, mp = 81-82 °C (hexane), eluent: EtOAc/hexane (20%), Rf = 0.17 (254 nm)) was purified on a silica gel column chromatograph with EtOAc/hexane. 3-(Indolin-1-*yl*)cyclohex-2-en-1-one (**6**) [14]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 7.2 Hz, =CH, 1H), 7.17-7.12 (m, =CH, 2H), 6.95 (t, J = 7.2 Hz, =CH, 1H), 5.44 (s, =CH, 1H), 3.91 (t, J = 8.3 Hz, CH_2, 2H), 3.14 (t, J = 8.3 Hz, CH_2, 2H), 2.87 (t, J = 6.3 Hz, CH_2, 2H), 2.41 (t, J = 6.3 Hz, CH_2, 2H), 2.10 (p, J = 6.3 Hz, CH_2, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 161.0, 143.6, 133.6, 127.3, 125.7, 122.6, 114.4, 103.7, 51.2, 36.2, 28.8, 27.7, 23.1. IR (KBr, cm^{-1}) 2947, 1624, 1483, 1436, 1410, 1353, 1265, 1190, 750. *Anal.* Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57, found: C, 78.82; H, 7.08; N, 6.53.

Scheme 4. Reaction of indoline (1; 1 equiv.) with acetylacetone (5; 1 equiv.).



Scheme 5. Formation mechanism for 13A/B.



3-(1*H*-Indol-1-*yl*)cyclohex-2-en-1-one (7): To a solution of of 3-(indolin-1-*yl*)cyclohex-2-en-1-one (**6**; 500 mg, 2.3 mmol) in CH_2Cl_2 (10 mL) was added the active MnO_2 (2.0 g, 23.0 mmol). The mixture was stirred at rt for 12 h. The reaction was monitored by TLC. After filtration, the mixture was evaporated under reduced pressure, and the compound **7** was purified by silica gel column chromatography with EtOAc/hexane. 3-(1*H*-Indol-1-*yl*)cyclohex-2-en-1-one (**7**) was obtained as red viscous liquid (475 mg, 96%, eluent: 20% EtOAc/hexane, Rf = 0.14 (254 nm)). 3-(1*H*-Indol-1-*yl*)cyclohex-2-en-1-one (**7**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, =CH, 1H), 7.63 (d, J = 8.0 Hz, =CH, 1H), 7.33 (d, J = 2.8 Hz, =CH, 1H), 7.31-7.20 (m, =CH, 2H), 6.72 (d, J = 2.8 Hz, =CH, 1H), 6.41 (s, =CH, 1H), 2.97 (t, J = 6.1, CH_2, 2H), 2.55 (t, J = 6.1, CH_2, 2H), 2.25 (p, J = 6.1 Hz, CH_2, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 156.3, 135.2, 131.0, 125.2, 123.7, 122.2, 121.7, 115.6, 113.4, 107.3, 36.8, 29.1, 22.3. IR (KBr, cm^{-1}) 2950, 1658, 1598, 1454, 1184, 1128, 744. *Anal*. Calcd. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63, found: C, 79.62; H, 6.24; N, 6.61.

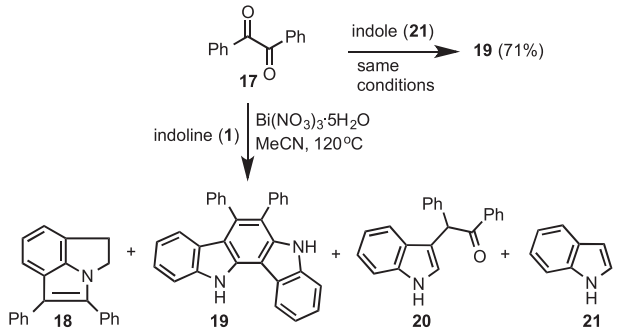
1-(Indolin-1-*yl*)ethan-1-one (13A/B): Procedure A: A mixture of indoline (**1**; 500 mg, 4.2 mmol), acetylacetone (**5**; 420 mg, 4.2 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol) in CH_2Cl_2 (10 mL) was stirred magnetically at rt for 2 h. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with EtOAc (30 mL) and washed with water (3 × 30 mL), and organic phase was dried over Na_2SO_4. The crude product (907 mg) was eluted on silica gel (25 g) with EtOAc/hexane. 1-(Indolin-1-*yl*)ethan-1-one (**13A/B**; ratio of rotamers: 85:15, 640 mg, 94%, white solid, mp = 99-100 °C (hexane), eluent: EtOAc/hexane (15%), = 0.35 (254 nm)). 1-(Indolin-1-*yl*)ethan-1-one **(13A/B)** [15–17]**:** ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ 8.20 (d, J = 7.7 Hz, =CH, 1H), 7.24-7.09 (m, =CH, 2H), 6.99 (t, J = 7.7 Hz, =CH, 1H), 4.15-4.08 (m, CH_2, 0.3H), 3.99 (t, J = 8.4 Hz, 1.7H), 3.15 (t, J = 8.4 Hz, 1.7H), 3.08-3.01 (m, CH_2, 0.3H), 2.42 (s, CH_3, 0.4H), 2.19 (s, CH_3, 2.6H).^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 168.9, 143.1, 131.3, 127.7, 127.5, 126.1, 124.8, 123.8, 123.3, 117.1, 114.3, 49.0, 48.2, 28.2, 27.0, 24.8, 24.4. IR (KBr, cm^{-1}): 2964, 2948, 1652, 1598, 1483, 1463, 1403, 1341, 1321, 1295, 1032, 885, 805, 762, 745. *Anal*. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69, found: C, 74.47; H, 6.84; N, 8.73.

1-(Indolin-1-*yl*)ethan-1-one (13A/B): Procedure B: To a solution of (162 mg) of (*Z* or *E*)-4-(indolin-1-*yl*) pent-3-en-2-one (**12**) and 1-(indolin-1-*yl*)ethan-1-one (**13A/B**) in 20 mL MeCN:H_2O (9:1) was added 50 mg of column chromatography silica gel. After stirring for 12 h at rt, the mixture was diluted with EtOAc (30 mL) and washed with water (3 × 30 mL), and organic phase was dried over Na_2SO_4. The crude product (150 mg) was eluted on silica gel (25 g) with EtOAc/hexane (2:8) to give 1-(indolin-1-*yl*)ethan-1-one (**13A/B**; 130 mg, 96%).

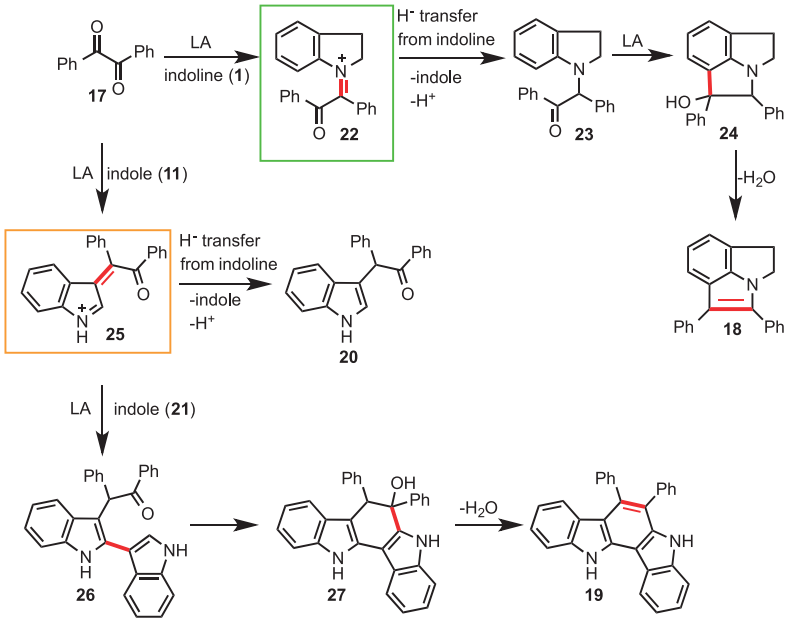
1-(Indolin-1-*yl*)ethan-1-one (13A/B): Procedure C: 1-(Indolin-1-*yl*)ethan-1-one (**13A/B**) was obtained as white solid (120 mg, 87%) from the reaction of a mixture of (**12** and **13A/B**; 159 mg) with MnO_2 (677 mg, 8.0 mmol) in CH_2Cl_2 at rt for 12 h.

1-(Indolin-1-*yl*)ethan-1-one (13A/B): Procedure D: 1-(Indolin-1-*yl*)ethan-1-one (**13A/B**) was obtained as white solid (129 mg 95%) from the reaction of a mixture of (**12** and **13A/B**; 180 mg) with DDQ (190 mg, 0.8 mmol) in CH_2Cl_2 at rt for 12 h.

Scheme 6. Reaction of indoline (1; 1 equiv.) and indole (21) with benzil (17; 1 equiv.).



Scheme 7. Formation mechanism for 18–20. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].



Reaction of indoline (1) (1.0 equiv.) with benzil (17) (1.0 equiv.): To a solution of indoline (**1**; 500 mg, 4.2 mmol) in MeCN (5 mL) was added benzil (**17**; 882 mg, 4.2 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol). Reaction mixture was stirred magnetically in a sealed tube at 120°C for 8 h. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethylacetate (30 mL) and washed with water (2 × 50 mL), and organic phase was dried over Na_2SO_4. The crude product was purified by silica gel column chromatograph and isolated compounds were given according to elution sequence (EtOAc/hexane or hexane) in general.

4,5-Diphenyl-1,2-dihydropyrrolo[3,2,1-*hi*]indole (18) [18]. 52 mg, 4%, white solid (mp = 211-212°C, hexane), eluent: EtOAc/hexane (15%), Rf = 0.82, (254 nm). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.9 Hz, =CH, 1H), 7.46-7.43 (m, =CH, 3H), 7.37-7.29 (m, =CH, 6H), 7.20 (ddd, *J* = 8.3, 2.2, 1.0 Hz, =CH, 1H), 7.09-7.05 (m, =CH, 1H), 6.98 (d, *J* = 6.7 Hz, =CH, 1H), 4.57 (t, *J* = 7.0 Hz, CH_2, 2H), 3.81 (t, *J* = 7.0 Hz, CH_2, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 136.7, 135.5, 133.0, 129.4, 129.3, 128.8, 128.6, 127.7, 125.7, 124.9, 122.7, 120.3, 118.0, 117.4, 115.9, 50.1, 33.8. IR (KBr, cm^{-1}): 3054, 2952, 2919, 2846, 1650, 1599, 1569, 1503, 1446, 1435, 1393, 1138, 1077, 1021, 915. *Anal*. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74, found: C, 89.55; H, 5.74; N, 4.73. 6,7-Diphenyl-5,12-dihydroindolo[3,2-*a*]carbazole **(19)** [13]**.** 552 mg, 40%, pale yellow solid (mp = 325-326°C; hexane), eluent: EtOAc/hexane (15%), Rf = 0.52 (254 nm). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.85 (bs, NH, 1H), 10.73 (bs, NH, 1H), 8.70 (d, *J* = 7.5 Hz, =CH, 1H), 7.60 (d, *J* = 7.7 Hz, =CH, 1H), 7.57 (d, *J* = 8.1 Hz, =CH, 1H), 7.39-7.19 (m, =CH, 13H), 6.79 (ddd, *J* = 8.1, 7.2, 1.0 Hz, =CH, 1H), 6.52 (d, *J* = 7.9 Hz, =CH, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.7, 140.4, 140.0, 138.5, 138.1, 133.9, 133.5, 131.8, 131.0, 128.8, 128.6, 127.5, 127.1, 124.8, 124.3, 123.8, 122.1, 121.7, 120.8, 119.5, 119.1, 117.9, 114.2, 112.2, 111.6, 106.2. IR (KBr, cm^{-1}): 3451, 3400, 3055, 3022, 1947, 1908, 1709, 1638, 1611, 1599, 1567, 1509, 1488, 1462, 1437, 1390, 1372, 1326, 1311, 1269, 1255, 1153, 1134, 1084, 1069, 1022, 1000, 961, 916, 868, 843, 820. *Anal*. Calcd. for $C_{30}H_{20}N_2$: C, 88.21; H, 4.93; N, 6.86, found: C, 88.35; H, 5.04; N, 6.79. 2-(1*H*-Indol-3-*yl*)-1,2-diphenylethan-1-one **(20)** [19]**.** 315 mg, 23%, brown viscous liquid, eluent: EtOAc/hexane (15%), Rf = 0.26 (254 nm). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (bs, NH, 1H), 8.10 (d, *J* = 7.4 Hz, =CH, 2H), 7.55-7.52 (m, =CH, 2H), 7.45-7.39 (m, =CH, 2H), 7.35-7.31 (m, =CH, 2H), 7.27 (t, *J* = 7.5 Hz, =CH, 2H), 7.20 (t, *J* = 7.5 Hz, =CH, 2H), 7.12 (t, *J* = 7.5 Hz, =CH, 2H), 6.90 (d, *J* = 2.8 Hz, =CH, 1H), 6.32 (s, =CH, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 139.2, 137.1, 136.7, 133.3, 129.3, 129.2, 128.9, 128.8, 127.4, 126.8, 124.2, 122.6, 120.0, 119.0, 114.4, 111.7, 51.0. IR (KBr, cm^{-1}): 3410, 3059,

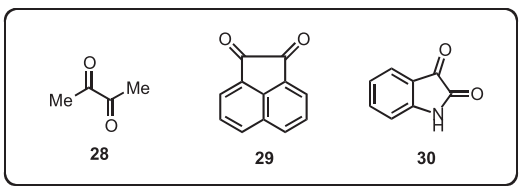


Figure 1. Examined other 1,2-diketones **28–30**.

2920, 1811, 1768, 1681, 1619, 1596, 1579, 1495, 1457, 1448, 1420, 1339, 1287, 1265, 1221, 1126, 1098, 1054, 1030, 1001, 931, 858, 801. Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50, found: C, 84.72; H, 5.55; N, 4.48. **Indole (21):** 238 mg (17%), eluent: 20% EtOAc/hexane, Rf = 0.26 (254 nm).

Reaction of indoline (1) (5.0 equiv.) with benzil (17) (1.0 equiv.): A mixture of indoline (**1**; 1.5 g, 12.6 mmol), benzil (**17**; 529 mg, 2.5 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol) was stirred magnetically in a sealed tube at 120°C for 2 h under solvent-free condition. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethylacetate (30 mL) and washed with water (2 × 50 mL), and organic phase was dried over Na_2SO_4. The crude product was purified by silica gel column chromatograph, and isolated compounds were given according to elution sequence (EtOAc/Hexane or hexane) in general. 4,5-Diphenyl-1,2-dihydropyrrolo[3,2,1-*hi*]indole **(18).** 48 mg, 4%. 6,7-Diphenyl-5,12-dihydroindolo[3,2-*a*]carbazole **(19):** 632 mg, 56%. 2-(1*H*-Indol-3-*yl*)-1,2-diphenylethan-1-one **(20).** 95 mg (8%), eluent: 15% EtOAc/hexane. Indole **(21).** 282 mg, 25%. Indoline **(1).** 865 mg (7.4 mmol) was recovered.

6,7-Diphenyl-5,12-dihydroindolo[3,2-*a*]carbazole (19): $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol)-catalyzed reaction of indole (**21**; 500 mg, 4.3 mmol) with benzil (**17**; 898 mg, 4.3 mmol) was performed at 120°C for 12 h in MeCN. 6,7-Diphenyl-5,12-dihydroindolo[3,2-*a*]carbazole (**19**; 1.23 g, 71%) was purified on a silica gel column chromatograph with EtOAc/hexane (15%).

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REFERENCES AND NOTES

[1] Mahaney, P. E.; Vu, A. T.; McComas, C. C.; Zhang, P.; Nogle, L. M.; Watts, W. L.; Sarkahian, A.; Leventhal, L.; Sullivan, N. R.; Uveges, A. J.; Trybulski, E. J Bioorg Med Chem 2006, 14, 8455.

[2] Fernandez, L. S.; Buchanan, M. S.; Carroll, A. R.; Feng, Y. J.; Quinn, R. J.; Avery, V. M. Org Lett 2009, 11, 329.

[3] Liu, W. N.; Zhang, X.; Dai, L. X.; You, S. L. Angew Chem Int Ed 2012, 51, 5183.

[4] Pan, S. C. Beilstein J Org Chem 2012, 8, 1374.

[5] Mao, H.; Wang, S.; Yu, P.; Lu, H.; Xu, R.; Pan, Y. J Org Chem 2011, 76, 1167.

[6] Mao, H.; Xu, R.; Wan, J.; Jiang, Z.; Sun, C.; Pan, Y. Chem Eur J 2010, 16, 13352.

[7] Deb, I.; Das, D.; Siedel, D. Org Lett 2011, 13, 812.

[8] Zhang, C.; Siedel, D. J Am Chem Soc 2010, 132, 1798.

[9] Deb, I.; Coiro, D. J.; Siedel, D. Chem Commun 2011, 47, 6473.

[10] Ramakumar, K.; Tunge, J. A. Chem Commun 2014, 50, 13056.

[11] Bayindir, S.; Erdogan, E.; Kilic, H.; Aydin, O.; Saracoglu, N. J Heterocyclic Chem 2015, 52, 1589.

[12] Aydin, O.; Kilic, H.; Bayindir, S.; Erdogan, E.; Saracoglu, N. J Heterocyclic Chem 2015, 52, 1540.

[13] Nair, V.; Nandialath, V.; Abhilash, K. G.; Suresh, E. Org Biomol Chem 2008, 6, 1738.

[14] Bays, D. E.; Coates, I. H. A. W. Oxford and P. C. North, Can. Pat. Appl. 1991, CA 2011107 A1 19910831.

[15] Hou, D. Y.; Wang, D. R.; Chung, M. S.; Hsieh, Y. D.; Gavin, H. H. G. J Org Chem 2007, 72, 9231.

[16] Ana, M.; Stephen, L. B. Org Lett 2008, 10, 2721.

[17] Yamada, K.; Kubo, T.; Tokuyama, H.; Fukuyama, T. Synlett 2002, 2, 231.

[18] Laube, M.; Gassner, C.; Sharma, S. K.; Günther, R.; Pigorsch, A.; König, J.; Köckerling, M.; Wuest, F.; Pietzsch, J.; Kniess, T. J Org Chem 2015, 80, 5611.

[19] Li, Y.; Shi, F. Q.; He, Q. L.; You, S. L. Org Lett 2009, 11, 3182.