Preparation of β-aminoketone by 2,3-dichloro-5,6-dicyanobenzoquinone catalysed three-component Mannich reaction

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2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) was used as an efficient catalysts for a one-pot, three-component Mannich reaction of cyclohexanone or acetophenone with aromatic aldehydes and aromatic amines under solvent free condition. This protocol has the advantage of high yield, mild reaction conditions, lower catalyst loading and simple work up procedure.

Keywords: DDQ, β-amino ketone, Mannich reaction, catalysis

The development of protocol leading to β-amino/β-acetamido carbonyl compounds has been important in the synthesis of natural products and pharmaceuticals. The Mannich reaction represents one of the most important methods for the preparation of natural products and biologically active nitrogen-containing compounds, including β-amino acids, aldehydes and ketones.[1–4] Three-component Mannich reactions are important in organic synthesis and are used for making intermediates, since several components can be introduced in a single step into a molecule.

The Mannich reaction relies on two- as well as three-component systems, but the preferred route is the use of a one-pot three-component rather than a two-step process. Numerous versions of the Mannich reaction have been developed in the past. Bronsted acids,[5,6] Lewis acids,[7–9] Lewis bases,[10] rare metal salts,[11,12] and other compounds[13–16] have been investigated as catalysts for Mannich-type reaction in the past. However, traditional protocols require somewhat harsh conditions, using toxic organic solvents, long reaction times,[7] the need of a large amount of catalyst,[16] expensive catalyst,[9,11] and sometimes give low yields of the products. The conventional synthetic procedures invariably use organic solvents as media to provide a homogeneous phase. However, the organic solvents used are harmful and do not drive the reactions to total completion. The search for new readily available, green catalysts is still being actively pursued.

DDQ is a well-known oxidant in organic chemistry.[17] For many years, it has been used for the oxidation of allylic alcohol[18] and allylic ethers[19] to α, *β*-unsaturated carbonyl compounds. Recently, DDQ has emerged as an important mediator for the construction of carbon–carbon via a cross-dehydrogenative-coupling (CDC) reaction.[20,21]

In continuation of our studies on developing cheap and environmentally benign methodologies for organic reactions we sought new efficient catalysts for the three-component Mannich reaction. DDQ was an attractive candidate reagent since it is an inexpensive, stable crystalline solid that is easy to handle. We now report the three-component Mannich reaction in the presence of DDQ as catalysts under solvent-free conditions to produce *β*-amino carbonyl compounds.

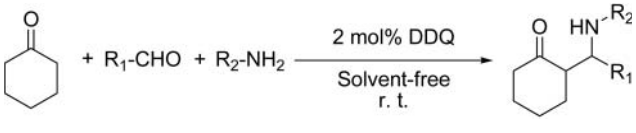
Result and discussion

The Mannich reaction between the substituted aromatic aldehydes, aromatic amines and cyclohexanone to produce *β*-amino carbonyl compounds catalysed by DDQ is shown in Scheme 1.

The initial model reaction of cyclohexanone (1 mmol), phenylamine (1 mmol) and benzaldehyde (1 mmol) in the presence DDQ (0.1 mmol) at room temperature in ethanol smoothly produced a *β*-aminoketone in good yield. Encouraged by this result, we conducted the reaction in different solvents, different amount of DDQ and ratio of starting material in order to optimise the reaction condition. These results shown in Table 1 imply that the reaction solvent (whether polar or non-polar), and the amount DDQ cannot dramatically improve the yields (Table 1 entries 1–5). In the light of the advantage of solvent free reactions, we carried out this reaction under solvent free conditions by increasing the amount of cyclohexanone. Fortunately, the yields improved and the reaction time decreased (Table 1 entries 6–10). Even when the amount of DDQ was decreased to 2 mmol%, the reaction still goes well and the yield of product increased a little compared with the case of 5 mmol% DDQ. This may be caused by the lower solubility of DDQ in cyclohexanone. Furthermore, the reaction temperature was also investigated. However, when the temperature was increased to 40 or 60 °C, a lower yield was obtained. The optimum reaction condition are DDQ 2 mmol%, 1.5/1.0/1.0 of cyclohexanone/phenylamine/benzaldehyde, room temperature.

Other substituted arylamines and benzaldehyde were then subjected to the Mannch reaction using DDQ as catalyst. The results are shown in Table 2.

Table 2 shows that all the reactions gave good to high yields and were finished within 10 minutes. In the case of aromatic aldehydes or amines, a strong electron-withdrawing group is



Scheme 1 DDQ catalysed reaction of cyclohexanone, aromatic amine and aromatic aldehyde for preparation of β-aminoketones.

Table 1 Model reaction for effect of catalyst quantity and solvent

Entry	DDQ/mol%	Solvent/mL	Time	Yield/%[a]
1	10	Toluene/10	8h	40
2	10	CH_2Cl_2/10	8h	53
3	10	CH_3CN/10	8h	65
4	10	EtOH/10	8h	73
5	15	EtOH/10	8h	72
6	10[b]	—	45min	82
7	5[b]	—	32min	85
8	2[b]	—	35min	90
9	2[c]	—	50min	84
10	1[b]	—	60min	85

[a]Isolated yield. [b]1.5 mmol cyclohexanone. [c]3 mmol cyclohexanone.

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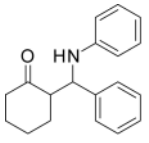
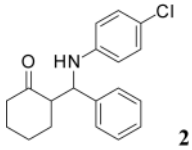
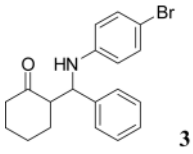
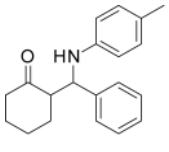
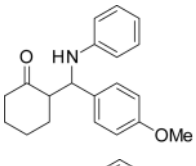
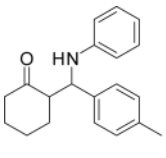
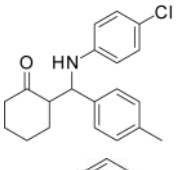
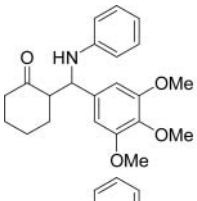
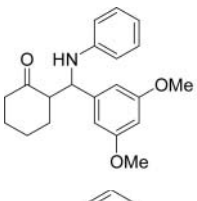
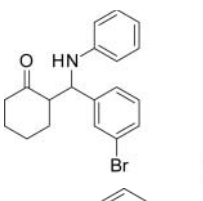
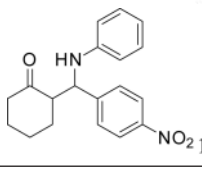
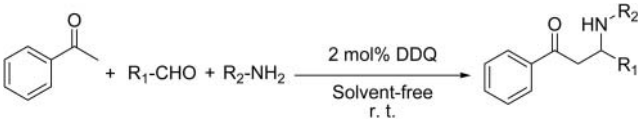
Table 2 DDQ catalysed reaction of cyclohexanone, aromatic amine and aromatic aldehyde for preparation β-aminoketones

Entry	R_1	R_2	Product[a]	Reaction time/min	Anti/syn[b]	Yield/%[c]
1	Phenyl	Phenyl	 **1**	35	59:41	90
2	Phenyl	4-Chlorophenyl	 **2**	45	53:47	85
3	Phenyl	4-Bromophenyl	 **3**	60	64:36	75
4	Phenyl	4-Methylphenyl	 **4**	60	78:21	82
5	4-Methoxyphenyl	Phenyl	 **5**	45	65:35	70
6	4-Methylphenyl	Phenyl	 **6**	60	74:26	80
7	4-Methylphenyl	4-Chlorophenyl	 **7**	40	50:50	92
8	3,4,5-Trimethoxyphenyl	Phenyl	 **8**	70	66:34	82
9	3,5-Dimethoxyphenyl	Phenyl	 **9**	65	64:36	88
10	3-Bromophenyl	Phenyl	 **10**	80	50:50	80
11	4-Nitrophenyl	Phenyl	 **11**	300	0	0

[a]All products were characterised by m.p., IR, and ^{1}H NMR, product **8** and **9** also by ^{13}C NMR and elemental analysis.
[b]The ratio of anti/syn isomer were measured by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.
[c]Isolated yields.



Scheme 2 DDQ catalysed reaction of acetophenone, aromatic amine and aromatic aldehyde for preparation of β-aminoketones.

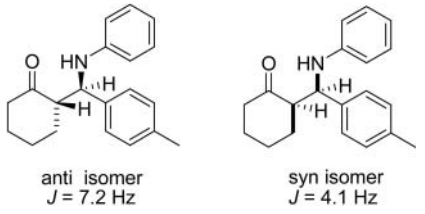


Fig. 1 The structures of *syn*- and *anti*- isomer of product **6**.

detrimental to the reaction even unworkable (Table 2 entry 11). Acetophenone can be used instead of cyclohexanone in the above reaction as shown in Scheme 2. This resulted in a slight decrease in yield and an increase in reaction time (Table 3) compared with the case of cyclohexanone.

The β-aminoketones prepared by the reaction of cyclohexanone, aromatic amine and aromatic aldehyde catalysed by DDQ as shown in Scheme 1, are mixtures of *syn*- and *anti*- isomer. The ratios of *syn*- and *anti*- isomer was measured by ^{1}H NMR spectroscopic analysis of the product, and are indicated in Table 1. The representive structures of *syn*- and *anti*- isomer of product **6** were shown in Fig. 1.

In conclusion, we have demonstrated an efficient and simple alternative for the preparation of *β*-amino carbonyl compounds *via* the DDQ catalysed three-component Mannich reaction in solvent-free conditions. Prominent among the advantages of this new method are high yield, mild reaction conditions, lower catalyst loading and a simple work-up procedure.

Experimental

Starting materials were obtained from commercial suppliers used without further purification. Melting point was determined with X-5 apparatus in open glass capillaries and was uncorrected. IR spectra were recorded on Equinx 55 FT-IR spectrometer using KBr pellets. NMR spectral data were collected on an Avance 300 MHz with TMS as an internal standard.

General experimental procedure

DDQ (0.04 mmol, 0.0091 g) was added to the aromatic aldehyde (2 mmol), aromatic amine (2 mmol) and ketone (3 mmol) in a 50 mL round flask and the contents were stirred at room temperature for the fixed period. After completion of the reaction (monitored by TLC, the time indicated in Table 2). The reaction mixture was added aqueous saturated sodium bicarbonate 20 mL and extracted with ethyl acetate (2×20 mL). The organic phase was separated, dried, and purified by chromatography on silica gel for analysis.

The new products (**8**) and (**9**) were characterised by the melting point, IR, ^{1}H/^{13}C NMR and elemental analysis. The structure of known product was confirmed by the melting point, IR and ^{1}H NMR. The data of the products were consistent with that of the expected structure or identical with those described in the literature

2-(Phenyl(phenylamino)methyl)cyclohexanone (**1**): White solid, m.p. 118–120 °C [lit.[22]:115–116 °C]. IR (KBr): υ 3381 (NH), 1698 (C=O), 1600 (C=C) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.58–2.00 (*m*, 6H), 2.29–2.43 (*m*, 2H), 2.75–2.77 (*m*, 1H), 4.61 (*d*, *anti*, *J* = 7.0 Hz, 0.59H), 4.80 (*d*, *syn*, *J* = 4.0 Hz, 0.41H), 6.52–6.62 (*m*, 3H, ArH), 7.05–7.38 (*m*, 7H, ArH)

2-((4-Chlorophenylamino)(phenyl)methyl)cyclohexanone (**2**): Whi te solid, m.p. 114–115 °C. [lit.[23]]. IR(KBr): υ 3411, 3386 (NH), 1700 (C=O), 1600 (C=C) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.58–2.03 (*m*, 6H), 2.29–2.44 (*m*, 2H), 2.75–2.77 (*m*, 1H), 4.53 (*d*, *anti*, *J* = 6.9Hz, 0.5H), 4.73 (*d*, *syn*, *J* = 3.8Hz, 0.5H), 6.45 (*d*, *J* = 8.3Hz, 2H), 6.97–7.01 (*m*, 2H, ArH), 7.21–7.32 (*m*, 5H, ArH).

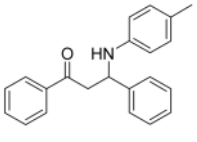
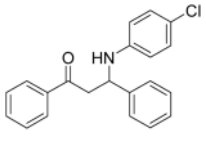
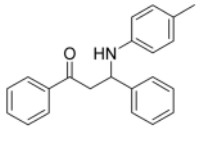
2-((4-Bromophenylamino)(phenyl)methyl)cyclohexanone (**3**): Whit e solid, m.p. 122–124 °C. [lit.[24]]. IR(KBr): υ 3397 (NH), 1697 (C=O), 1592 (C=C) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.57–2.00 (*m*, 6H), 2.32–2.44 (*m*, 2H), 2.75–2.76 (*m*, 1H), 4.53 (*d*, *anti*, *J* = 6.51Hz, 0.64H), 4.72 (*d*, *syn*, *J* = 3.8Hz, 0.36H), 6.41 (*d*, *J* = 8.1Hz, 2H, ArH), 7.11–7.32 (*m*, 7H, ArH).

2-(Phenyl(p-tolylamino)methyl)cyclohexanone (**4**): White solid, m. p. 102–103 °C. [lit.[25]:105–108 °C]. IR(KBr): υ 3382 (NH), 1696 (C=O), 1616 (C=C) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.42–2.03 (*m*, 6H), 2.15 (*s*, 3H, $-CH_3$), 2.29–2.45 (*m*, 2H), 2.72–2.74 (*m*, 1H), 4.59 (*d*, *anti*, *J* = 7.41Hz, 0.78H), 4.76 (*d*, *syn*, *J* = 3.93Hz, 0.21H), 6.46 (d, *J* = 7.47Hz, 2H, ArH), 6.86 (*d*, *J* = 7.74Hz, 2H, ArH), 7.17–7.37 (*m*, 5H, ArH).

2-((4-Methoxyphenyl)(phenylamino)methyl)cyclohexanone (**5**): White solid, m.p.104–106 °C, [lit.[26]]. IR(KBr): υ 3410 (NH), 1693 (C=O), 1605 (C=C) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.61–2.04 (*m*, 6H), 2.24–2.46 (*m*, 2H), 2.70–2.77 (*m*, 1H), 3.76 (*s*, 3H, $-OCH_3$), 4.58 (*d*, *anti*, *J* = 6.39Hz, 0.65H), 4.71 (*d*, *syn*, *J* = 3.42Hz, 0.35H), 6.52–6.65 (*m*, 3H, ArH), 6.82–6.84 (*m*, 2H, ArH), 7.03–7.08 (*m*, 2H, ArH), 7.25–7.30 (*m*, 2H, ArH).

2-((Phenylamino)(p-tolyl)methyl)cyclohexanone (**6**): White solid, m.p. 113–115 °C. [lit.[27]]. IR(KBr): υ 3387 (NH), 1700 (C=O), 1601 (C=C) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): δ 1.55–2.05 (*m*, 6H), 2.29 (*s*, 3H, $-CH_3$), 2.32–2.46 (*m*, 2H), 4.58 (*d*, *anti*, *J* = 7.2Hz, 0.74H),

Table 3 DDQ catalysed reaction of acetophenone, aromatic amine and aromatic aldehyde for preparation β-aminoketones

Entry	R_1	R_2	Product [a]	Reaction time /h	Yield /% [b]
1	Phenyl	4-Methylphenyl	 **12**	8	80
2	Phenyl	4-Chlorophenyl	 **13**	8	75
3	Phenyl	4-Methylphenyl	 **14**	8	70

[a]All products were characterised by m.p., IR and ^{1}H NMR.
[b]Isolated yields.

4.75 (*d*, *syn*, *J* = 4.1Hz, 0.26H), 6.54–6.66 (*m*, 2H, ArH), 7.03–7.11 (*m*, 4H, ArH), 7.21–7.25 (*m*, 3H, ArH).

2-((4-Chlorophenylamino)(p-tolyl)methyl)cyclohexanone (**7**): Whit e solid, m.p. 102–103 °C. [lit.[28]:105–106 °C]. IR (KBr): υ 3409 (NH), 1698 (C=O), 1599 (C=C) cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 1.58–2.03 (*m*, 6H), 2.29 (*s*, 3H, $–CH_3$), 2.33–2.41 (*m*, 2H), 2.70–2.73 (*m*, 1H), 4.50 (*d*, *anti*, *J* = 7.02Hz, 0.5H), 4.69 (*d*, *syn*, *J* = 3.75Hz, 0.5H), 6.43–6.47 (*m*, 2H, ArH), 6.97–7.01 (*m*, 2H, ArH), 7.08–7.11 (*m*, 2H, ArH), 7.18–7.25 (*m*, 2H, ArH).

2-((Phenylamino)(3,4,5-trimethoxyphenyl)methyl)cyclohexanone (**8**): White solid, m.p. 151–153 °C. IR(KBr): υ 3334 (NH), 2931, 2833, 1702 (C=O), 1596 (C=C) cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 1.63–1.91 (*m*, 6H), 2.34–2.41 (*m*, 2H), 2.71–2.73 (*m*, 1H), 3.80–3.83 (*s*, 9H, $–OCH_3$), 4.51 (*d*, *anti*, *J* = 6.91, 0.66H), 4.70 (*d*, *syn*, *J* = 3.48, 0.34H), 6.55–6.68 (*m*, 5H, ArH), 7.06–7.11 (*m*, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.7, 24.9, 27.0, 27.8, 28.7, 31.4, 41.9, 42.4, 56.2, 56.6, 57.5, 57.8, 58.7, 60.8, 104.4, 104.5, 113.9, 114.2, 117.8, 129.0, 129.1, 134.4, 147.2, 147.6, 153.2, 153.3, 211.3, 212.8. Anal. Calcd for $C_{22}H_{27}NO_4$ (369.45) C, 71.52; H, 7.37; N, 3.79. Found: C, 71.64; H, 7.42; N, 3.72%.

2-((3,5-Dimethoxyphenyl)(phenylamino)methyl)cyclohexanone (**9**) : White solid, m.p.138–140 °C. IR(KBr): υ 3387 (NH), 1698 (C=O), 1600 (C=C), cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 1.58–2.05 (*m*, 6H), 2.29–2.45 (*m*, 2H), 2.71–2.74 (*m*, 1H), 3.75 (*s*, 6H, $–OCH_3$), 4.53 (*d*, *anti*, *J* = 7.35Hz, 0.64H), 4.74 (*d*, *syn*, *J* = 3.75Hz, 0.36H), 6.30 (*s*, 1H, ArH), 6.51–6.66 (*m*, 5H, ArH), 7.04–7.09 (*m*, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.6, 24.8, 27.0, 28.5, 31.2, 41.7, 42.3, 55.3, 56.6, 57.3, 57.4, 58.3, 98.6, 98.8, 105.6, 105.7, 113.8, 114.1, 117.7, 117.8, 128.9, 129.0, 144.4, 144.5, 147.2, 147.6, 160.8, 160.9, 211.1, 212.7. Anal. Calcd for $C_{21}H_{25}NO_3$ (339.43) C, 74.31; H, 7.42; N, 4.13. Found: C, 74.39; H, 7.48; N, 4.16%.

2-((3-Bromophenyl)(phenylamino)methyl)cyclohexanone (**10**): White solid, m.p. 118–120 °C. [lit.[29]]. IR(KBr): υ 3379 (NH), 1702 (C=O), 1600 (C=C) cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 1.54–2.03 (*m*, 6H), 2.30–2.44 (*m*, 2H), 2.71–2.75 (*m*, 1H), 4.55 (*d*, *anti*, *J* = 6.3Hz, 0.5H), 4.73 (*d*, *syn*, *J* = 3.99Hz, 0.5H), 6.51–6.67 (*m*, 3H, ArH), 7.06–7.35 (*m*, 5H, ArH), 7.49 (*s*, 1H, ArH).

1-Phenyl-3-(phenylamino)-3-p-tolylpropan-1-one (**12**): White solid, m.p. 136–138 °C. [lit.[27]: 139–140 °C]. IR(KBr): υ 3387 (NH), 1668(C=O), 1603 (C=C) cm^{-1}. ^1H NMR (300MHz, CDCl3): δ 2.30 (s, 3H, $–CH_3$); 3.36–3.54 (m, 2H, $–CH_2–$); 4.97 (t, *J* = 6.3Hz, 1H, –CH–); 6.56–6.68 (m, 3H, ArH); 7.06–7.58 (m, 9H, ArH); 7.91 (d, *J* = 7.8Hz, 2H, ArH).

3-(4-Chlorophenylamino)-1,3-diphenylpropan-1-one (**13**): White solid, m.p.168–170 °C. [lit.[30]:170–171 °C]. IR(KBr): υ 3371 (NH), 1665 (C=O), 1598 (C=C) cm^{-1}. ^1H NMR (300MHz, CDCl3): δ 3.42–3.48 (m, 2H, $–CH_2–$); 4.92–4.97 (m, 1H, –CH–); 6.49 (d, *J* = 2.7Hz, 2H, ArH); 7.02 (d, 8.7Hz, 2H, ArH); 7.29–7.59 (m, 8H, ArH); 7.89 (d, *J* = 7.5Hz, 2H, ArH).

1,3-Diphenyl-3-(p-tolylamino)propan-1-one (**14**): Solid, m.p. 169–171 °C. [lit.[30]: 167–168 °C]. IR (KBr): υ 3401 (NH), 1679 (C=O), 1620 (C=C) cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 2.17 (s, 3H, $–CH_3$); 3.39–3.54 (m, 2H, $–CH_2–$); 4.97 (t, *J* = 6.1Hz, 1H, –CH); 6.49 (d, *J* = 7.8Hz, 2H, ArH); 6.89 (d, 7.8Hz, 2H, ArH); 7.21–7.57 (m, 8H, ArH); 7.90 (d, *J* = 7.8Hz, 2H, ArH).

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