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A mild and practical procedure for synthesis of substituted 2-aminobenzophenones

Er-Qian Ma · Ping Wang · Pei-He Li · Li-Ping Mo

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Abstract A convenient three-step procedure has been developed for synthesis of substituted 2-aminobenzophenones from substituted anilines. The anilines are first protected as acetanilides, by reaction with acetic anhydride. These are then benzoylated with (trichloromethyl)benzene in the presence of aluminium-generated 2-acetamidobenzophenone. Finally, removal of the acetyl group from the amino group provides the substituted 2-aminobenzophenones in moderate to good yields.

Keywords 2-Aminobenzophenones · Anilines · (Trichloromethyl)benzene

Introduction

2-Aminobenzophenones are valuable synthons in a variety of organic reactions for synthesis of important heterocyclic compounds, for example quinolines [1–4], tetrahydroquinolines [5], quinazolines [6], 1,2-dihydroquinazolines [7, 8], 2,3-disubstituted indoles [9], 3,3-dimethyl-9-phenyl-3,4-dihydroacridin-1(2*H*)-one [10], dibenzodiazepines [11], and benzodiazepin-2-one [12]. They are also used as starting materials for preparation of the antidepressant drug tampramine [13] and tetradentate Schiff-base ligands [14]. Their synthesis is difficult because they have both amino and carbonyl active groups in the position *ortho* to the benzene ring. Synthetic strategies reported for preparation of substituted 2-aminobenzophenones include:

E.-Q. Ma · P.-H. Li · L.-P. Mo (✉)
College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China
e-mail: moliping@126.com

P. Wang
Department of Chemical and Environmental Engineering, Hebei Chemical and Pharmaceutical Vocational Technology College, Shijiazhuang 050026, China

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(a) one-pot reaction of aryl bromides, anthranilic acid *N*-methoxy-*N*-methylamide, and *n*-butyllithium [15];
(b) protection of *o*-aminobenzoic acid by tosylation, then Friedel–Crafts reaction, and, finally, hydrolysis by use of concentrated H_2SO_4 [16];
(c) palladium(II) bipyridine-catalyzed addition of phenylboronic acid to 2-aminobenzonitrile [17];
(d) carbonylative Suzuki–Miyaura coupling of 2-iodoaniline with phenylboronic acid [18];
(e) Pd-catalyzed arylation/oxidation of benzylic C–H bonds leading to diaryl ketones and subsequent cleavage of the amide by hydrolysis under basic conditions [19];
(f) nucleophilic addition of aryl Grignard reagents to 2-aminobenzonitrile and subsequent hydrolysis [20];
(g) reduction of 2-azidobenzophenone by use of $FeSO_4{\cdot}7H_2O/NH_3$ [21];
(h) catalytic hydrogenation of 2-nitrobenzophenone [22]; and
(i) Pd-catalyzed addition of arylsulfinates to 2-aminobenzonitriles [23].

However, some of these methods have such disadvantages as limited substrate scope, complex manipulations, inaccessible starting materials, or use of expensive catalysts and ligands. Because of their extensive application, it is very desirable to develop a practical and convenient approach for synthesis of substituted 2-aminobenzophenones.

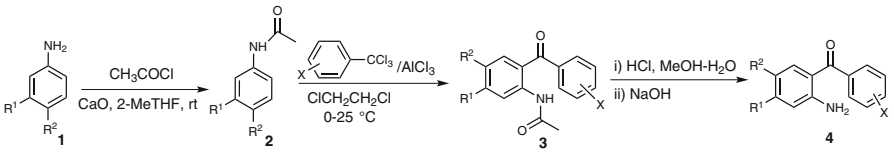
As part of our continuing interest in developing novel synthetic methods [24–33], we describe herein a convenient three-step procedure for synthesis of substituted 2-aminobenzophenones starting from substituted anilines (Scheme 1).

Experimental

Melting points were determined on an X-4 apparatus and are uncorrected. IR spectra were acquired by use of a Bruker-Tensor 27 spectrometer. NMR spectra were acquired by use of a Bruker DRX-500 spectrometer at 500 MHz (^{1}H) and 125 MHz (^{13}C) with $CDCl_3$ as solvent and TMS as internal standard. Mass spectra (MS) were acquired by use of a ThermoFinnigan LCQ Advantage instrument with an ESI source (4.5 keV).

Representative procedure for synthesis of acetanilides

CaO (0.2 mol) was added to a solution of a substituted aniline (0.1 mol) in 2-methyltetrahydrofuran (2-MeTHF, 270 mL) and the resulting suspension was stirred at room temperature (rt) for 5 min. A solution of acetyl chloride (0.11 mol) in 2-MeTHF (100 mL) was then added dropwise over 10 min. The mixture was stirred at rt and the progress of the reaction was monitored by TLC. On completion, the reaction mixture was filtered and the filtrate was washed with aqueous saturated $NaHCO_3$. The two resulting phases were separated and the organic phase (2-



Scheme 1 Synthesis of 2-aminobenzophenones from substituted anilines

MeTHF) was dried over anhydrous $MgSO_4$, filtered, and dried in vacuo to afford the acetanilide.

Representative procedure for synthesis of 2-acetamidobenzophenones

(Trichloromethyl)benzene (0.11 mol) was added dropwise over 15 min, with efficient stirring, to a cooled solution (0–5 °C) of anhydrous $AlCl_3$ (0.3 mol) in 1,2-dichloroethane (100 mL). Acetanilide, prepared as described above, was added over 15 min and the reaction mixture was stirred at rt for an appropriate time. On completion (monitored by TLC), the mixture was poured into crushed ice (500 g) and the resulting mixture was stirred at 70 °C for 0.5 h. After cooling, the organic layer was separated, washed with distilled water, and dried over anhydrous Na_2SO_4. The 2-acetamidobenzophenone was obtained after removal of the solvent under reduced pressure.

Representative procedure for synthesis of substituted 2-aminobenzophenones

The 2-acetamidobenzophenone obtained as described above was heated under reflux with 100 mL MeOH–HCl (MeOH:6 mol/L HCl = 1:1) in a round-bottomed flask for 2 h. The hot mixture was poured into a beaker and cooled. The hydrochloride of the 2-aminobenzophenone was isolated by suction filtration, washed with chilled alcohol, then suspended in 800 mL water in a beaker with a mechanical stirrer. The pH was adjusted to 8.0 by addition of a solution of 2 mol/L sodium hydroxide. The mixture was extracted with ethyl acetate, and the extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by recrystallization or by column chromatography on silica gel with petroleum ether–ethyl acetate as eluent.

*(2-Amino-4-methylphenyl)(phenyl)methanone (**4a**)*

Yellow-red crystals; IR (KBr): 3454, 3330, 3066, 2918, 2320, 1959, 1627, 1573, 1541, 1446, 1379, 1319, 1245, 1178, 966, 900, 867, 790, 752, 696, 613, 570, 447 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, $J = 7.0$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.2$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 1H), 6.55 (s, 1H), 6.42 (d, $J = 8.0$ Hz, 1H), 6.11 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 21.8, 115.8, 116.9, 117.3, 128.2, 129.1, 130.9, 134.7, 140.6, 145.4, 151.7, 198.6; ESI–MS: $m/z = 212$ $(M + 1)^+$.

Table 1 Synthesis of 2-aminobenzophenones from substituted anilines

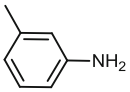
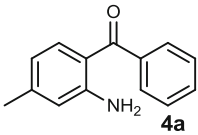
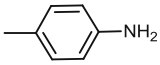
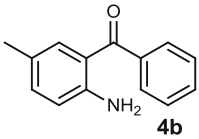
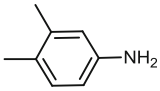
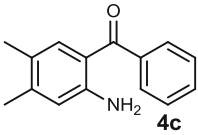
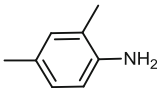
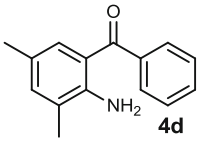
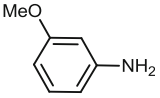
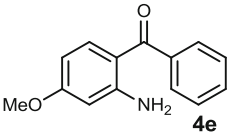
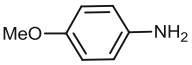
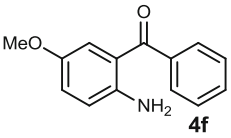
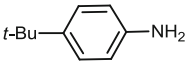
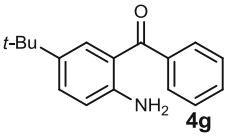
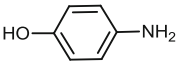
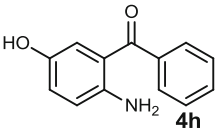
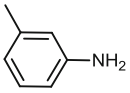
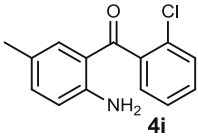
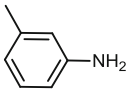
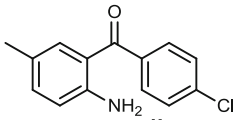
Entry	Amine	Product	Yield (%)	mp (°C)
1		 **4a**	48	66–67 (67–68) [23]
2		 **4b**	68	65–66 (64–66) [37]
3		 **4c**	81	91–92
4		 **4d**	75	69–70 (68–70) [38]
5		 **4e**	45	109–111 (106–108) [37]
6		 **4f**	66	49–50 (51–52) [37]
7		 **4g**	82	45–46
8		 **4h**	60	129–130 (127–128) [37]
9		 **4i**	69	105–106 (106–107) [37]

Table 1 continued

Entry	Amine	Product	Yield (%)	mp (°C)
10		 **4j**	70	96–97 (95–97) [37]

*(2-Amino-5-methylphenyl)(phenyl)methanone (**4b**)*

Yellow solid; IR (KBr): 3473, 3350, 3057, 3022, 2920, 2858, 2736, 1907, 1633, 1579, 1558, 1485, 1444, 1301, 1249, 1163, 1136, 954, 821, 750, 702, 655, 532 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm 7.64 (d, $J = 7.0$ Hz, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 2H), 7.23 (s, 1H), 7.13 (dd, $J = 8.5$, 1.5 Hz, 1H), 6.67 (d, $J = 8.5$ Hz, 1H), 5.91 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 20.4, 117.3, 118.2, 124.5, 128.2, 129.2, 131.1, 134.1, 135.5, 140.3, 149.0, 199.1; ESI–MS: $m/z = 212$ $(M + 1)^+$.

*(2-Amino-4,5-dimethylphenyl)(phenyl)methanone (**4c**)*

Yellow crystals; IR (KBr): 3438, 3327, 3195, 3020, 2943, 2856, 2343, 1631, 1593, 1533, 1490, 1442, 1361, 1317, 1257, 1176, 1097, 1024, 925, 896, 866, 758, 698, 605, 472 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHZ) δ ppm 7.62 (d, $J = 7.0$ Hz, 2H), 7.51 (t, $J = 7.0$ Hz, 1H), 7.45 (t, 2H, $J = 7.5$ Hz), 7.18 (s, 1H), 6.56 (s, 1H), 5.94 (s, 2H), 2.22 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 18.8, 20.3, 116.3, 118.1, 123.8, 128.1, 129.1, 130.8, 134.7, 140.6, 144.5, 149.7, 198.6; Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.23; H, 6.48; N, 6.01; ESI–MS: $m/z = 226$ $(M + 1)^+$.

*(2-Amino-3,5-dimethylphenyl)(phenyl)methanone (**4d**)*

Yellow flaky crystals; IR (KBr): 3454, 3373, 3244, 2970, 2927, 2322, 1635, 1608, 1577, 1504, 1456, 1377, 1317, 1299, 1257, 1172, 916, 887, 825, 738, 678, 592 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm 7.80 (d, $J = 7.0$ Hz, 2H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 6.97 (s, 1H), 6.65 (s, 1H), 3.55 (s, 2H), 2.20 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 17.3, 19.1, 115.4, 125.2, 126.2, 128.4, 130.1, 132.9, 133.1, 136.8, 138.2, 142.2, 198.9; ESI–MS: $m/z = 226$ $(M + 1)^+$.

*(2-Amino-4-methoxyphenyl)(phenyl)methanone (**4e**)*

Colorless crystals; IR (KBr): 3475, 3344, 3014, 2343, 1612, 1537, 1444, 1371, 1226, 1124, 900, 856, 700, 607, 590, 536 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm 7.58 (d, $J = 6.5$ Hz, 2H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.2$ Hz, 2H), 7.39 (d, $J = 9.5$ Hz, 1H), 6.35 (s, 2H), 6.18 (d, $J = 7.5$ Hz, 1H), 6.16 (s, 1H), 3.82 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 55.3, 99.3, 104.1, 112.3, 128.1, 128.8, 130.5, 137.0, 140.7, 153.8, 164.5, 197.8; ESI–MS: $m/z = 228$ $(M + 1)^+$.

*(2-Amino-5-methoxyphenyl)(phenyl)methanone (**4f**)*

Orange crystals; IR (KBr): 2968, 2900, 1662, 1558, 1496, 1448, 1404, 1319, 1232, 1178, 1026, 856, 813, 700, 644, 545 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.82 (d, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 6.79–6.84 (m, 2H), 6.71 (d, $J = 2.5$ Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 56.3, 113.4, 116.0, 118.5, 128.3, 129.4, 129.8, 133.0, 137.7, 140.6, 150.0, 196.8; ESI–MS: $m/z = 228$ $(M + 1)^+$.

*(2-Amino-5-(tert-butyl)phenyl)(phenyl)methanone (**4g**)*

Yellow solid; IR (KBr): 3473, 3350, 2960, 1633, 1577, 1548, 1485, 1363, 1305, 1245, 1172, 956, 860, 825, 761, 711, 653, 590 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.66 (d, $J = 7.0$ Hz, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.45–7.48 (m, 3H), 7.36 (dd, $J = 8.5$, 2.5 Hz, 1H), 6.71 (d, $J = 8.5$ Hz, 1H), 5.92 (s, 2H), 1.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 31.4, 33.8, 117.2, 117.7, 128.1, 129.4, 130.6, 131.2, 132.0, 137.9, 140.4, 149.1, 199.1; Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.41; H, 7.75; N, 5.30; ESI–MS: $m/z = 254$ $(M + 1)^+$.

*(2-Amino-5-hydroxyphenyl)(phenyl)methanone (**4h**)*

Pale yellow powder; IR (KBr): 3741, 3448, 3357, 3251, 2358, 2327, 1647, 1558, 1515, 1336, 1294, 1228, 935, 835, 698, 621, 462 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHZ) δ ppm 12.83 (s, 1H), 7.61 (d, $J = 7.0$ Hz, 2H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.37 (d, $J = 9.0$ Hz, 1H), 6.21 (d, $J = 2.5$ Hz, 1H), 6.10 (dd, $J = 9.0$, 2.5 Hz, 1H), 4.29 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 100.7, 106.5, 111.1, 128.2, 128.7, 131.0, 136.0, 138.7, 154.4, 166.4, 199.1; ESI–MS: $m/z = 214$ $(M + 1)^+$.

*(2-Amino-5-methylphenyl)(2-chlorophenyl)methanone (**4i**)*

Yellow solid; IR (KBr): 3454, 3330, 3271, 1660, 1611, 1498, 1454, 1317, 1233, 1055, 964, 914, 825, 528, 446 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.42–7.39 (m, 3H), 7.34–7.31 (m, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.76 (dd, $J = 8.0$, 2.5 Hz, 1H), 6.65 (d, $J = 2.5$ Hz, 1H), 3.58 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 20.1, 117.7, 119.0, 126.7, 129.1, 130.0, 130.3, 131.4, 131.9, 132.6, 137.6, 139.7, 144.0, 197.4; ESI–MS: $m/z = 246$ $(M + 1)^+$.

*(2-Amino-5-methylphenyl)(4-chlorophenyl)methanone (**4j**)*

Yellow solid; IR (KBr): 3458, 3333, 2922, 2359, 1662, 1583, 1454, 1319, 1240, 1085, 846 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.75 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 1H), 6.74 (dd, $J = 8.5$, 2.5 Hz, 1H), 6.61

(d, $J = 2.5$ Hz, 1H), 3.64 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 18.9, 114.7, 117.3, 126.1, 128.8, 131.5, 131.9, 136.0, 138.9, 139.6, 143.8, 197.6; ESI–MS: $m/z = 246$ $(M + 1)^+$.

*6-Methyl-9-phenyl-1,2,3,4-tetrahydroacridine (**6**)*

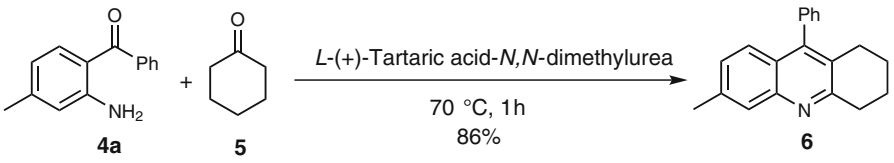
A mixture of (2-amino-4-methylphenyl)(phenyl)methanone (**4a**, 1.0 mmol) and cyclohexanone (1.0 mmol) in 1.5 g L-(+)-tartaric acid–DMU (30:70) was stirred at 70 °C. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to rt and water was added. The solid product which separated out was isolated by filtration, washed with water, and dried to afford product **6** in good purity. Yellow solid; 75–77 °C; IR (KBr): 3412, 3385, 3051, 3024, 2922, 2854, 1728, 1575, 1458, 1352, 1286, 1118, 879, 810, 750, 702, 572 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.80 (s, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.32–7.19 (m, 3H), 7.14 (dd, $J = 8.5$, 1.5 Hz, 1H), 3.18 (t, $J = 6.5$ Hz, 2H), 2.58 (t, $J = 6.5$ Hz, 2H), 2.51 (s, 3H), 1.98–1.93 (m, 2H), 1.80–1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 21.7, 22.9, 23.1, 27.9, 34.2, 124.7, 125.4, 127.4, 127.5, 127.6, 127.7, 128.6, 129.1, 137.3, 138.4, 146.3, 146.5, 158.9; Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.90; H, 6.83; N, 5.07; ESI–MS: $m/z = 274$ $(M + 1)^+$.

Results and discussion

Synthesis was conducted as illustrated in Scheme 1. First, commercially available substituted anilines (**1**) were acetylated with acetyl chloride. The reaction was performed in 2-MeTHF by use of CaO as an innocuous acid scavenger [34]. The corresponding acetanilides (**2**) were obtained in excellent yields without chromatographic purification of the products. 4-Aminophenol underwent acylation exclusively at the aminic site under these conditions.

It is reported that phenyldichlorocarbenium tetrachloroaluminate complex, $[PhCCl_2]^+AlCl_4^-$, derived from (trichloromethyl)benzene and aluminium chloride, is a highly stable, efficient electrophile [35, 36]. Subsequently, the acetanilides (**2**) were benzoylated with (trichloromethyl)benzene in the presence of aluminium in 1,2-dichloroethane. A variety of 3 or 4-substituted acetanilides (**2**) were converted to 2-acetamidobenzophenones (**3**). 3-Substituted acetanilides gave lower yields than 4-substituted acetanilides, because of partial formation of 4-acetamidobenzophenones. Similarly, treatment of substituted (trichloromethyl)benzenes with acetanilides resulted in the corresponding acetamido benzophenones in high yields (Table 1, entries 9, 10). However, a complex mixture of polymeric products was obtained when substrates bearing a free amino group were benzoylated with (trichloromethyl)benzene. The aniline-protection step is, therefore, essential for benzoylation.

Finally, *N*-deacetylation of 2-acetamidobenzophenones was conducted in methanolic HCl, under reflux, to give the desired 2-aminobenzophenones (**4**). The



Scheme 2 Synthesis of quinoline via the Friedländer reaction

general trend with regard to yield seems to follow the pattern of substitution of the anilines. The substrate with a methyl group in the three-position of the aniline gave the lowest yield (Table 1, entry 1), that with 3,4-disubstituted methyl groups gave the highest yield (Table 1, entry 3), and that with a 4-substituted methyl group gave moderate yield (Table 1, entry 2).

The structures of the products were identified from their ^{1}H and ^{13}C NMR spectra and MS. The structure of compound **4a** was also confirmed by Friedländer reaction of **4a** and cyclohexanone (Scheme 2) [1].

In conclusion, we have investigated an innovative and convenient synthetic approach for preparation of substituted 2-aminobenzophenone derivatives, starting from substituted anilines, by use of a three-step sequence. The advantages of this approach include use of readily available anilines, mild reaction conditions, and a simple procedure; a series of substituted 2-aminobenzophenones were obtained in moderate to good yields.

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