**Ammonium Chloride-Catalyzed One-Pot Synthesis of 4(3*H*)-Quinazolinones Under Solvent-free
Conditions**

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I. Synthesis and NMR spectral data of 2-amino-3-bromobenzoic acid methyl ester

N-Bromosuccinimide (NBS, 1.960 g, 11.0 mmol) was added portionwise to a stirred solution of 2-aminobenzoic acid ester (1.511 g, 10.0 mmol) dissolved in acetic acid (16 ml) and the reaction mixture was stirred overnight at room temperature. The mixture was added with H₂O and extracted with EtOAc (3×20 mL). The combined organic extract was washed with brine, dried over MgSO₄, and the solvent was evaporated. The residue was purified by column chromatography (petroleum ether/CHCl₃ = 2:1) to give the pure product.

Yellow solid. Yield: 69%. ¹H NMR (500 MHz, CDCl₃) δ = 7.96 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 5.75 (s, 2H), 3.87 (s, 3H). ¹³C NMR (CDCl₃) δ = 167.6, 149.4, 136.9, 133.5, 118.5, 112.2, 107.5, 51.9.

II. NMR Spectrum of 2-amino-3-bromobenzoic acid methyl ester

1. The ^1H NMR spectrum in CDCl_3

2. The ^{13}C NMR spectrum in CDCl_3

III. Typical procedure for the NH₄Cl-catalyzed synthesis of 4(3*H*)-quinazolinones under solvent-free conditions

A mixture of 2-amino-benzoic acid esters (1.0 mmol), aromatic amines (1.2 mmol), ortho esters (1.5 mmol) and NH₄Cl (0.021 g, 0.4 mmol) was heated with stirring at 100°C for 2 h. After cooling, H₂O was added and the product was extracted with EtOAc. The organic layer was dried (MgSO₄) and evaporated, the residue recrystallized from EtOH-hexane to afford the pure product.

IV. NMR spectral data of 4(3*H*)-quinazolinones

1. 3-Phenyl-4(3*H*)-quinazolinone (**4a**)[1-4]

White solid. ¹H NMR (DMSO) δ = 8.35 (s, 1H), 8.21 (dd, J = 8.0, 1.2 Hz, 1H), 7.91-7.86 (m, 1H), 7.77-7.73 (m, 1H), 7.63-7.49 (m, 6H). ¹³C NMR (CDCl₃) δ = 8.38 (dd, J = 8.0, 1.3 Hz, 1H), 8.13 (s, 1H), 7.85-7.74 (m, 2H), 7.60-7.52 (m, 3H), 7.52-7.47 (m, 1H), 7.46-7.40 (m, 2H).

2. 3-(4-Methylphenyl)-4(3*H*)-quinazolinone (**4b**)[1,3,4]

White solid. ¹H NMR (CDCl₃) δ = 8.37 (d, J = 7.9 Hz, 1H), 8.12 (s, 1H), 7.79 (dt, J = 15.0, 7.3 Hz, 2H), 7.55 (t, J = 7.0 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H).

3. 3-(1-naphthyl)-4(3*H*)-quinazolinone (**4c**)[3]

White solid. ¹H NMR (CDCl₃) δ = 8.42 (d, J = 7.8 Hz, 1H), 8.11 (s, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.89-7.82 (m, 2H), 7.66-7.49 (m, 6H). ¹³C NMR (CDCl₃) δ = 161.2, 148.3, 147.0, 134.8, 134.5, 134.2, 130.4, 129.9, 128.7, 127.9, 127.8, 127.4, 127.1, 126.1, 125.6, 122.5, 122.1.

4. 3-(2-Methylphenyl)-4(3*H*)-quinazolinone (**4d**)[1,3]

White solid. ¹H NMR (CDCl₃) δ = 8.39 (d, J = 7.8 Hz, 1H), 8.01 (s, 1H), 7.85-7.79 (m, 2H), 7.60-7.55 (m, 1H), 7.44-7.37 (m, 3H), 7.27 (s, 1H), 2.22 (s, 3H).

5. 3-(4-Methoxyphenyl)-4(3*H*)-quinazolinone (**4i**)[1]

White solid. ¹H NMR (CDCl₃) δ = 8.37 (d, J = 8.0 Hz, 1H), 7.82-7.75 (m, 2H), 7.56-7.53 (m, 1H), 7.34 (d, J = 8.9 Hz, 2H), 7.05 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H).

6. 3-(3,4-Dichlorophenyl)-4(3*H*)-quinazolinone (**4j**)[5]

White solid. ^1H NMR (CDCl_3) δ = 8.35 (d, J = 7.8 Hz, 1H), 8.07 (s, 1H), 7.84-7.81 (m, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.59-7.56 (m, 2H), 7.31 (dd, J = 8.5, 2.2 Hz, 1H). ^{13}C NMR (CDCl_3) δ = 160.5, 147.8, 145.1, 136.7, 135.0, 133.8, 131.4, 129.3, 128.1, 127.9, 127.3, 126.5, 122.2.

7. 3-(4-Acetylphenyl)-4(3*H*)-quinazolinone (**4j**)[6]

Yellow solid. ^1H NMR (CDCl_3) δ = 8.38 (d, J = 7.9 Hz, 1H), 8.15 (s, 1H), 8.13 (d, J = 5.2 Hz, 2H), 7.85-7.81 (m, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.59-7.56 (m, 3H), 2.67 (s, 3H). ^{13}C NMR (CDCl_3) δ = 196.8, 160.6, 147.9, 145.3, 141.4, 137.5, 135.0, 129.8, 128.0, 127.9, 127.4, 127.3, 122.4, 26.8. HRMS (EI): calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$ [MH^+] 265.2861, found 265.2856.

8. 3-(4-Nitrophenyl)-4(3*H*)-quinazolinone (**4l**)[1,3]

Yellow solid. ^1H NMR (CDCl_3) δ = 8.46-8.41 (m, 2H), 8.38 (dd, J = 8.0, 1.3 Hz, 1H), 8.13 (s, 1H), 7.87-7.84 (m, 1H), 7.80 (d, J = 7.3 Hz, 1H), 7.70-7.65 (m, 2H), 7.62-7.57 (m, 1H). ^{13}C NMR (CDCl_3) δ = 160.4, 147.8, 147.7, 144.6, 142.8, 135.3, 128.3, 128.1, 128.0, 127.4, 125.1, 122.1.

9. 3-(4-Carboxylphenyl)-4(3*H*)-quinazolinone (**4m**)[7-9]

White solid. ^1H NMR (DMSO) δ = 8.39 (s, 1H), 8.22 (d, J = 7.0 Hz, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.93-7.87 (m, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H). ^{13}C NMR (DMSO) δ = 166.5, 159.8, 147.6, 146.6, 141.1, 134.8, 130.9, 130.1, 127.7, 127.5, 127.3, 126.4, 121.8.

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V. NMR spectrum of 4(3*H*)-quinazolinones

The ^1H NMR spectrum of **4a** in CDCl_3

The ^1H NMR spectrum of **4a** in $\text{DMSO}-d_6$

The ^1H NMR spectrum of **4b** in CDCl_3

The ^1H NMR spectrum of **4c** in CDCl_3

The ^1H NMR spectrum of **4d** in CDCl_3

The ^1H NMR spectrum of **4e** in CDCl_3

The ^{13}C NMR spectrum of **4e** in CDCl_3

The ^1H NMR spectrum of **4f** in CDCl_3

The ^{13}C NMR spectrum of **4f** in CDCl_3

The ^1H NMR spectrum of **4g** in CDCl_3

The ^{13}C NMR spectrum of **4g** in CDCl_3

The ^1H NMR spectrum of **4h** in CDCl_3

The ^{13}C NMR spectrum of **4h** in CDCl_3

The ^1H NMR spectrum of **4i** in CDCl_3

The ^1H NMR spectrum of **4j** in CDCl_3

The ^{13}C NMR spectrum of **4j** in CDCl_3

The ^1H NMR spectrum of **4k** in CDCl_3

The ^{13}C NMR spectrum of **4k** in CDCl_3

The ^1H NMR spectrum of **4l** in CDCl_3

The ^{13}C NMR spectrum of **4l** in CDCl_3

The ^1H NMR spectrum of **4m** in $\text{DMSO}-d_6$

The ^{13}C NMR spectrum of **4m** in $\text{DMSO}-d_6$

The ^1H NMR spectrum of **4n** in CDCl_3

The ^{13}C NMR spectrum of **4n** in CDCl_3

The ^1H NMR spectrum of **4o** in CDCl_3

The ^{13}C NMR spectrum of **4o** in CDCl_3

The ^1H NMR spectrum of **4p** in CDCl_3

The ^{13}C NMR spectrum of **4p** in CDCl_3

The ^1H NMR spectrum of **4q** in CDCl_3

The ^{13}C NMR spectrum of **4q** in CDCl_3