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Substituent effects on the reactivity of 2-aminobenzonitriles with carbon dioxide in ionic liquids

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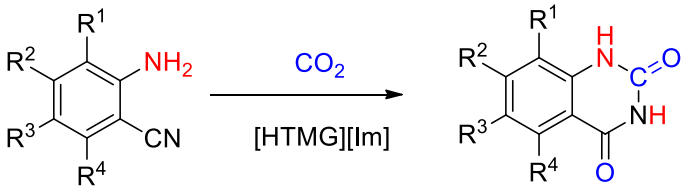
Abstract

In this study, we systematically investigate the substituent effects on the reactivity of 2-aminobenzonitrile with CO_2 in ionic liquids, focusing on synthesizing structurally diverse quinazoline-2,4(1*H*,3*H*)-dione derivatives. Para-substituent effects are dominated by electronic factors, with strong electron-withdrawing groups reducing yields. Ortho-substituents at the amino group partially hinder CO_2 activation. An unexpected benzimidazole derivative was identified from 2, 3-diaminobenzonitrile. Substituents at the 6-position drastically impact yields due to steric hindrance. These findings offer guidelines for optimizing CO_2 utilization in synthesizing quinazoline-2, 4(1*H*, 3*H*)-diones.



Substituent effects:
R^1: Steric hindrance (moderate yield impact)
R^2/R^3: Electronic effect (moderate yield impact)
R^4: Steric hindrance (major yield impact)

Keywords: Quinazoline-2,4(1*H*,3*H*)-dione; Carbon dioxide; Ionic liquid; 2-aminobenzonitrile; Substituent effects

Introduction

The efficient utilization of carbon dioxide (CO_2) as a resource is of great significance for achieving carbon neutrality and promoting sustainable green development. As a promising C1 synthon, CO_2 has attracted widespread attention in organic synthesis.[1-3] However, due to its inherent thermodynamic stability and kinetic inertness, the development of effective strategies for activating and converting CO_2 remains crucial. Ionic liquids (ILs) exhibit unique advantages in CO_2 capture and utilization, owing to their tunable structures, high stability, low vapor pressure, and low melting points. In CO_2 conversion processes, ILs not only function as solvents, but also act as activators through CO_2 absorption, thereby serving dual roles as catalysts or co-catalysts.[4-5] CO_2 conversion in ILs primarily proceeds via three pathways: electrochemical, photochemical, and thermal reactions.[6] Thermal conversion routes include CO_2 hydrogenation and its reactions with oxygen-, nitrogen-, and carbon-based nucleophiles. These reactions enable the synthesis of high-value-added chemicals through the formation of new C-O, C-N, and C-C bonds, yielding products such as cyclic carbonates,[7-8] 4-hydroxyquinolin-2(1*H*)-ones,[9] oxazolidinones,[10-11] ureas,[12] benzimidazolones,[13] N-formamides[14] and quinazoline-2, 4(1*H*, 3*H*)-diones.[15-22]

Quinazoline-2,4(1*H*,3*H*)-diones represent core structural motifs in bioactive molecules with diverse pharmacological activities and are widely used as intermediates in drug synthesis.[23-24] Consequently, developing efficient synthetic methods for these compounds holds significant practical value. Traditional synthesis methods involve reactions of anthranilic acid with urea, potassium cyanate, or chlorosulfonyl agents, or anthranilamide with phosgene.[25] In recent years, methods based on the cyclization of tert-butyl (2-cyanoaryl)carbamates and visible light-induced cascade N-alkylation/amidation reactions of quinazolin-4(3H)-ones have been successively reported.[26-27] However, these approaches suffer from limitations such as harsh reaction conditions (e.g., high temperatures and strong bases), multiple reaction steps, or low yields, which hinder their broader application. In the past decade, ILs have been extensively employed to catalyze the atom-economical synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO_2 and 2-aminobenzonitriles, offering advantages such as high yields, simplified post-processing, and in some cases, recyclability of the IL catalysts.[28-31] Nevertheless, existing studies have predominantly focused on IL design, while substrate exploration in reported works has been limited to a few para-substituted derivatives without systematic investigation of substituent effects. Building upon these foundations, our work systematically explores the influence of substituents on the benzene ring of 2-aminobenzonitriles, enabling the synthesis of structurally diverse quinazoline-2,4(1*H*,3*H*)-dione derivatives.

Results and Discussion

Initially, we evaluated the reaction of 2,5-diaminobenzonitrile with CO_2 using several literature-reported and easily synthesized ionic liquids (Figure 1). As shown in Table 1, [HTMG][Im] demonstrated the best performance. While literature methods typically require organic solvents for synthesizing such ionic liquids, followed by time-consuming solvent removal, we found that simply stirring tetramethylguanidine and imidazole at room temperature for 4 hours directly yielded [HTMG][Im]. NMR analysis confirmed its structure, with no significant difference in reactivity compared to conventional methods. We subsequently conducted a detailed investigation into the substituent effects on the benzene ring, with the results summarized in Table 2.

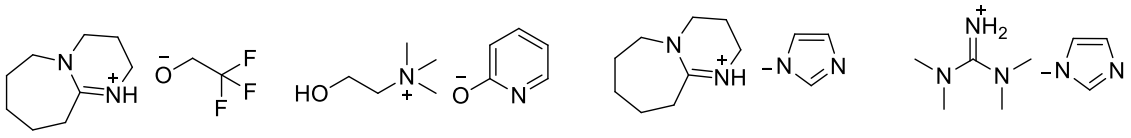
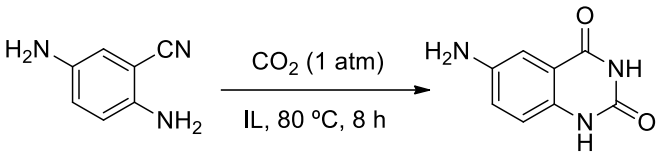


Figure 1. The ionic liquids used in this study.

Table 1. Condition Optimization



Entry	ILs (3.0 equiv.)	Yield(%)[a]
1	[HDBU][TFE]	90
2	[Ch][2-OP]	93
3	[HDBU][Im]	92
4	[HTMG][Im]	95(96[b])

[a] Isolated yield. [b] Using [HTMG][Im] synthesized via a solvent-free method.

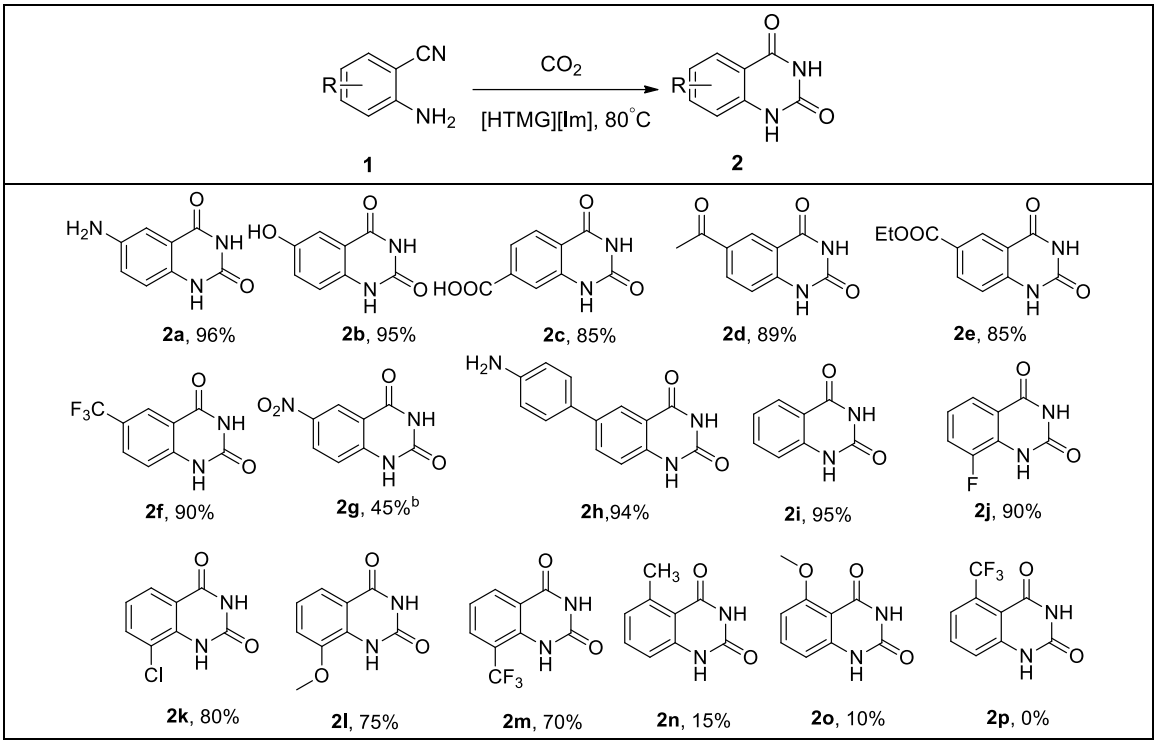
Functional groups with active hydrogens (**2a-c** and **2h**) directly generated corresponding quinazolinones without protection. Moderate electron-withdrawing groups (**2d-f**) provided satisfactory yields. For nitro-substituted substrates (**2g**), the yield was significantly reduced. The decreased yield is hypothesized to result from the strong electron-withdrawing nature of the nitro group, which diminishes the nucleophilicity of the amino group toward carbon dioxide. These results demonstrate that electronic effects, with negligible steric contributions, dominate the substituent effects of para-substituted groups. Strong electron-withdrawing groups induce a significant reduction in yield, while moderate-strength electron-withdrawing groups exhibit minimal impact on the reaction efficiency. Notably, substituents containing active hydrogen exert no detectable influence on the reaction outcome.

Increasing steric bulk at the amino group's ortho-position gradually reduced yields (**2i-f**), though even the most hindered trifluoromethyl group still gave 70% yield (**2f**). This implies that ortho-substituents partially hinder CO_2 activation by ionic liquids but do not completely block the reaction.

Reaction of 2, 3-diaminobenzonitrile (**3**) with CO_2 unexpectedly yielded a gray solid identified as 2-oxo-2, 3-dihydro-1*H*-benzo[d]imidazole-4-carboxamide (**8**) via ^{1}H NMR, ^{13}C NMR and heteronuclear multiple bond correlation (HMBC) analysis (Figure 2 and Figure 3). In the HMBC spectra, the cross-peak between H-1 (δ_H=10.12) and C-2/C-7, H-2 (δ_H=10.80) and C-1/C-7, H-4 (δ_H=7.42) and C-2/C-6/C-8, H-5 (δ_H=6.97) and C-1/C-3, as well as H-6 (δ_H=7.05) and C-2/C-4 collectively confirm the planar structure of compound **8** shown in Figure 3. The two labile hydrogens of the benzamide group exhibit significantly different chemical shifts at 7.98 and 7.40, suggesting that the compound **8** may exist in tautomeric form **7** with the involvement of intramolecular hydrogen bonding. This aligns with prior mechanistic studies: the reactive 3-amino group undergoes intramolecular cyclization with a transient isocyanate intermediate (**6**), supporting the literature-proposed pathway.

Substituents at the 6-position (cyanide ortho-position) drastically impacted yields. Following the order H > methyl > methoxy > trifluoromethyl (**2i**, **2n-p**), yields dropped sharply, with no product detected for trifluoromethyl. This correlates with literature mechanisms: steric hindrance at this position disrupts nucleophilic attack by the amino-carboxylate intermediate on the adjacent cyano group.

Table 2. Synthesis of various quinazoline-2,4-(1*H*,3*H*)-diones[a]



[a] Isolated yield.

[b] The work-up was performed using column chromatography with an eluent of ethyl acetate: petroleum ether = 2:1 (v/v).

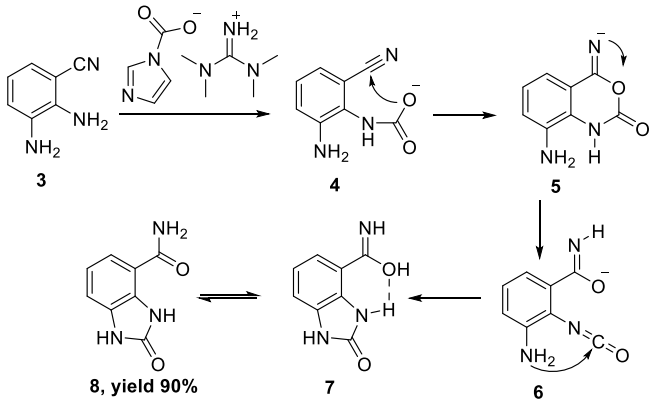


Figure 2. The possible mechanism for the formation of compound **8**.

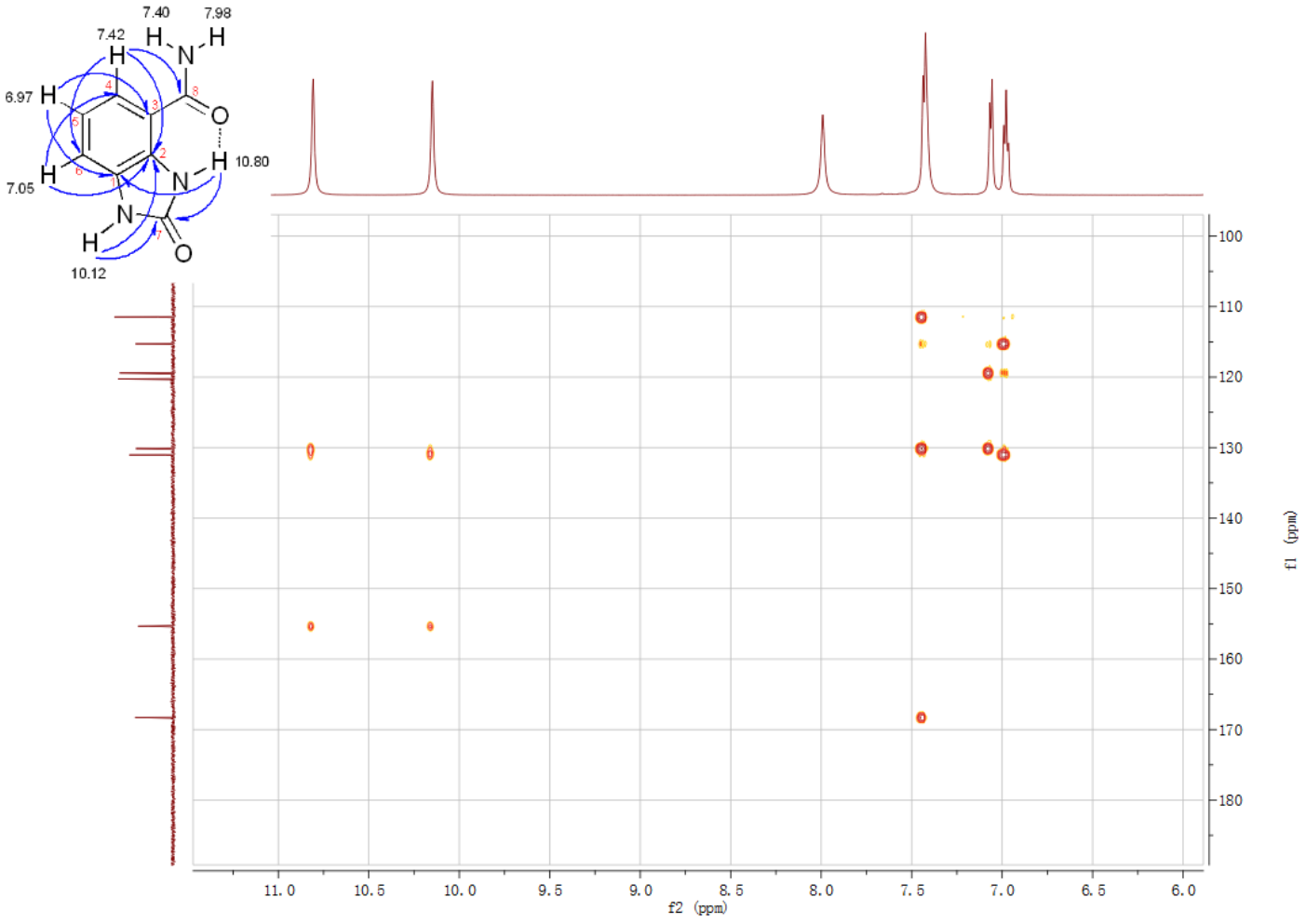


Figure 3. The HMBC analysis of compound **8.**

Conclusions

In summary, this paper studied the substituent effects on the reaction of substituted 2-aminobenzonitriles with CO_2 in the ionic liquid [HTMG][Im]. *Para*-substituent effects are dominated by electronic factors: strong electron-withdrawing groups (e.g., nitro) reduce yields by attenuating amino nucleophilicity, while moderate electron-withdrawing groups and active hydrogen-containing substituents show minimal impact. Notably, substituents with active hydrogen exhibit no discernible influence on product formation. *Ortho*-substituents proximal to the amino group progressively lower yields via steric hindrance, *though* partial reactivity is retained (e.g., 70% yield with trifluoromethyl). An unexpected cyclization of 2,3-diaminobenzonitrile forms a tautomeric benzimidazolone, as corroborated by NMR analysis *and* mechanistic alignment with an isocyanate intermediate. Substituents at the 6-position exhibit drastic steric inhibition, completely eliminating reactivity for groups such as trifluoromethyl. These findings delineate electronic versus steric control across substitution patterns, offering strategic guidelines for optimizing CO_2 utilization during the synthesis of quinazoline-2,4(1*H*,3*H*)-diones.

Experimental Section

General. All reagents were obtained from various sources and used without further purification. CO_2 was purchased from Hangzhou Jinggong Special Gas Company. ^{1}H NMR and ^{13}C NMR and HMBC studies were performed using a Bruker AVANCE III 500 (500 MHz for protons and 125 MHz for carbons) spectrometer or a Bruker AVANCE III HD 600 (600 MHz for protons and 150 MHz for carbons) with DMSO-d_6 or D_2O as the solvent. According to the reported procedures,[15] the protic ILs were prepared through the neutralization of the corresponding bases and proton donors. The physical data for **2f** and **2i** matched those reported in the literature. [15, 27]

General procedure for synthesizing quinazoline-2,4(1*H*, 3*H*)-dione derivatives. 2-Aminobenzonitrile (1.0 mmol) and [HTMG][Im] (3.0 mmol) were loaded in a 20 mL Schlenk flask equipped with a magnetic stirrer, connecting with a CO_2 balloon. Then, the reaction mixture was stirred at the 80 ℃ for 8 h. After cooling to room temperature, 10 mL of 10% ammonium chloride solution was added into the reactor. The product precipitated from the mixture and was separated by filtration. Then the filter cake was washed with water and a 1:1 (v/v) mixture of petroleum ether and ethyl acetate, respectively, and dried under an infrared lamp for 4 h. The product was further identified by NMR spectra and HR-MS.

6-Aminoquinazoline-2,4(1*H*,3*H*)-dione(2a). Yellow solid, yield 96%， m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.16 (s, 2H, NH_2), 6.89-6.93 (m, 2H, Ar-H), 7.06 (d, 1H, ^4J = 2.4 Hz, Ar-H), 10.72 (s, 1H, NH), 10.99 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 109.4, 115.4, 116.5, 123.0, 131.8, 144.7, 150.4, 163.5. HR-MS (ESI) *m/z*: Calculated for $C_8H_8N_3O_2$[[M+H]$^+$]: 178.0612, found 178.0596.

6-Hydroxyquinazoline-2,4(1*H*,3*H*)-dione(2b). Brown solid, yield 95%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.03 (d, 1H, J = 9.0 Hz, Ar-H), 7.10 (dd, 1H, ^4J = 2.7 Hz, J = 8.7 Hz, Ar-H), 7.22 (d, 1H, ^4J = 2.4 Hz, Ar-H), 9.60 (s, 1H, OH), 10.89 (s, 1H, NH), 11.15 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 111.2, 115.5, 117.1, 124.2, 134.0, 150.5, 153.1. HR-MS (ESI) *m/z*: Calculated for $C_8H_7N_2O_3$[[M+H]$^+$]: 179.0452, found: 179.0441.

2,4-Dioxo-1,2,3,4-tetrahydroquinazoline-7-carboxylic acid(2c). Colorless solid, yield 85%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.67 (d, 1H, J = 7.8 Hz, Ar-H), 7.75 (s, 1H, Ar-H), 7.98 (d, 1H, J = 7.8 Hz, Ar-H), 11.31 (s, 1H, NH), 11.45 (s, 1H, NH), 13.46 (brs, 1H, COOH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 116.9, 117.8, 122.9, 128.0, 136.9, 141.4, 150.7, 162.8, 166.8. HR-MS (ESI) *m/z*: Calculated for $C_9H_7N_2O_4$[[M+H]$^+$]: 207.0401, found: 207.0402.

6-Acetylquinazoline-2,4(1*H*,3*H*)-dione(2d). Colorless solid, yield 89%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.59 (s, 3H, CH_3), 7.24 (d, 1H, J = 8.4 Hz, Ar-H), 8.17 (dd, 1H, ^4J = 1.8 Hz, J = 8.4 Hz, Ar-H), 8.43 (d, 1H, ^4J = 1.8 Hz, Ar-H), 11.50 (s, 2H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 27.0, 114.5, 116.1, 128.5, 131.5, 134.7, 144.8, 150.7, 162.9, 196.5. HR-MS (ESI) *m/z*: Calculated for $C_{10}H_9N_2O_3$[[M+H]$^+$]: 205.0608, found: 205.0607.

Ethyl 2,4-dioxo-1,2,3,4-tetrahydroquinazoline-6-carboxylate(2e). Colorless solid, yield 85%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 1.33 (t, 3H, J = 7.2 Hz, CH_3), 4.32 (q, 2H, J = 7.2 Hz, CH_2), 7.25 (d, 1H, J = 8.4 Hz, Ar-H), 8.16 (dd, 1H, ^4J = 2.1 Hz, J = 9.0 Hz, Ar-H), 8.43 (d, 1H, ^4J = 1.8 Hz, Ar-H), 11.50 (s, 2H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 14.7, 61.4, 114.8, 116.3, 124.1, 129.1, 135.6, 144.8, 150.7, 162.8, 165.2. HR-MS (ESI) *m/z*: Calculated for $C_{11}H_{11}N_2O_4$[[M+H]$^+$]: 235.0714, found: 235.0723.

6-(Trifluoromethyl)quinazoline-2,4(1*H*,3*H*)-dione(2f). Colorless solid, yield 89%, m. p. >300 ℃ (lit.[27] 293-295℃), ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.35 (d, 1H, J = 8.5 Hz, Ar-H), 7.97 (d, 1H, J = 8.5 Hz, Ar-H), 8.11 (s, 1H, Ar-H), 11.55 (s, 2H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 114.4, 116.6, 122.5 (q, $J_{C\text{-}F}$ = 33.3 Hz), 123.9 (q, $J_{C\text{-}F}$ =

272 Hz), 124.1 (q, J_{C-F} = 4.0 Hz), 131.2 (d, J_{C-F} = 3.0 Hz), 143.8, 150.1, 162.0. HR-MS (ESI) *m/z*: Calculated for $C_9H_4F_3N_2O_2$[M-H]$^-$}: 229.0230, found: 229.0219.

6-Nitroquinazoline-2,4(1*H*,3*H*)-dione(2g). Yellow solid, yield 45%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.32 (d, 1H, *J* = 9.0 Hz, Ar-H), 8.46 (dd, 1H, ^4J = 2.4 Hz, *J* = 9.0 Hz, Ar-H), 8.59 (d, 1H, ^4J = 2.4 Hz, Ar-H), 11.72 (s, 1H, NH), 11.77 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 115.0, 117.2, 123.6, 130.1, 142.3, 146.1, 150.5, 162.1. ^{13}C NMR (150 MHz, DMSO-d_6) δ 162.1, 150.5, 146.1, 142.3, 130.1, 123.6, 117.2, 115.0. HR-MS (ESI) *m/z*: Calculated for $C_8H_4N_3O_4$[M-H]$^-$}: 206.0207, found: 206.0201.

6-(4-Aminophenyl)quinazoline-2,4(1*H*,3*H*)-dione(2h). Colorless solid, yield 94%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.26 (s, 2H, NH_2), 6.65 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.18 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.36 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.85 (dd, 1H, ^4J = 1.8 Hz, *J* = 8.4 Hz, Ar-H), 7.97 (d, 1H, ^4J = 1.8 Hz, Ar-H), 11.13 (s,1H, NH), 11.27 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 114.8, 115.1, 116.4, 123.0, 126.4, 127.4, 132.8, 135.6, 139.3, 149.0, 150.7, 163.4. HR-MS (ESI) *m/z*: Calculated for $C_{14}H_{12}N_3O_2$[M+H]$^+$}: 254.0925, found: 254.0930.

Quinazoline-2,4(1*H*,3*H*)-dione(2i). Colorless solid, yield 95%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.16-7.19(m, 2H, Ar-H), 7.64 (t, 1H, *J* = 8.1 Hz Ar-H), 7.89 (d, 1H, *J* = 7.8 Hz, Ar-H), 11.14 (s, 1H, NH), 11.28 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 114.8, 115.9, 122.8, 127.4, 135.4, 141.3, 150.8, 163.3.

8-Fluoroquinazoline-2,4(1*H*,3*H*)-dione(2j). Colorless solid, yield 90%, m. p.>250 ℃ (decomposition), ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.15-7.19 (m, 1H, Ar-H), 7.55-7.59 (m, 1H, Ar-H), 7.72 (d, 1H, *J* = 7.5 Hz, Ar-H), 11.29 (s, 1H, NH), 11.44 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 116.7, 120.3 (d, $^2J_{CF}$= 17.5 Hz), 122.2 (d, $^3J_{CF}$= 6.3 Hz), 122.6 (d, $^3J_{CF}$= 2.5 Hz), 129.7 (d, $^2J_{CF}$= 15.0 Hz), 149.9, 149.0 (d, J_{CF}= 245.0 Hz), 162.0 (d, $^4J_{CF}$= 3.8 Hz). HR-MS (ESI) *m/z*: Calculated for $C_8H_6FN_2O_2$ {[M+H]$^+$}: 181.0408, found: 181.0396.

8-Chloroquinazoline-2,4(1*H*,3*H*)-dione(2k). Colorless solid, yield 80%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.20 (t, 1H, *J* = 7.8 Hz, Ar-H), 7.78 (dd, 1H, ^4J = 1.2 Hz, *J* = 7.8 Hz, Ar-H), 7.89 (dd, 1H, ^4J = 1.2 Hz, *J* = 7.8 Hz, Ar-H), 10.68 (s,1H, NH), 11.53 (s,1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 116.9, 119.3, 123.4, 126.6, 135.5, 138.2, 150.4, 162.5. HR-MS (ESI) *m/z*: Calculated for $C_8H_6N_2O_2Cl$[M+H]$^+$}: 197.0113, found: 197.0118.

8-Methoxyquinazoline-2,4(1*H*,3*H*)-dione(2l). Colorless solid, yield 75%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.87 (s, 3H, OCH_3), 7.13 (t, 1H, *J* = 8.1 Hz, Ar-H), 7.29 (dd, 1H, ^4J = 1.2 Hz, *J* = 8.4 Hz, Ar-H), 7.47 (dd, 1H, ^4J = 1.2 Hz, *J* = 8.4 Hz, Ar-H), 10.51 (s, 1H, NH), 11.29 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 56.7, 115.5, 115.9, 118.4, 122.7, 131.5, 146.7, 150.5, 163.2. HR-MS (ESI) *m/z*: Calculated for $C_9H_9N_2O_3$[M+H]$^+$}: 193.0608, found: 193.0614.

8-(Trifluoromethyl)quinazoline-2,4(1*H*,3*H*)-dione(2m). Colorless solid, yield 70%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.35 (t, 1H, *J* = 7.8 Hz, Ar-H), 8.01 (d, 1H, *J* = 7.2 Hz, Ar-H), 8.23 (d, 1H, *J* = 7.8 Hz, Ar-H), 10.45 (s, 1H, NH), 11.68 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 115.0 (q, J_{CF}= 133.3 Hz), 117.0, 122.6, 124.5, 132.6, 132.8 (q, $^3J_{CF}$= 22.26 Hz), 138.1, 150.3, 162.1. HR-MS (ESI) *m/z*: Calculated for $C_9H_6F_3N_2O_2$[M+H]$^+$}: 231.0376, found: 231.0386.

5-Methylquinazoline-2,4(1*H*,3*H*)-dione(2n). Colorless solid, yield 15%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.65 (s, 3H, CH_3), 6.94 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.01 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.45 (t, 1H, *J* = 7.8 Hz, Ar-H), 11.00 (s, 1H, NH), 11.05 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 22.5, 113.0, 113.9, 125.6, 134.2, 141.4, 142.6, 150.5, 164.1. HR-MS (ESI) *m/z*: Calculated for $C_9H_9N_2O_2$[M+H]$^+$}: 177.0659, found: 177.0658.

5-Methoxyquinazoline-2,4(1*H*,3*H*)-dione(2o). Yellow solid, yield 10%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.81 (s, 3H, OCH_3), 6.70-6.72 (m, 2H, Ar-H), 7.51 (t, 1H, *J* =8.1 Hz, Ar-H), 10.87 (s, 1H, NH), 10.97 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 56.3, 104.2, 105.4, 107.7, 135.8, 143.6, 150.6, 160.9, 161.3. HR-MS (ESI) *m/z*: Calculated for $C_9H_9N_2O_3$[M+H]$^+$}: 193.0608, found: 193.0591.

2-Oxo-2,3-dihydro-1*H*-benzo[d]imidazole-4-carboxamide(8). Gray solid, yield 90%, m. p.>300 ℃, ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.97 (t, 1H, 1H, *J* = 7.8 Hz, Ar-H), 7.05 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.40 (s, 1H, NH), 7.42 (d,

1H, *J* = 7.8 Hz, Ar-H), 7.98 (s, 1H, NH), 10.12 (s, 1H, NH), 10.80 (s, 1H, NH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 111.5, 115.3, 119.4, 120.3, 130.1, 131.0, 155.3, 168.3. HR-MS (ESI) *m/z*: Calculated for $C_8H_8N_3O_2$\{[M+H]$^+$\}: 178.0617, found: 178.0620.

Acknowledgements

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Supplementary Material

Supplementary information file containing ^{1}H, ^{13}C NMR and HMBC spectra of compounds **2a-2o** and compound **8** is available at the journal website

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