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Design and Synthesis of 2-Acylbenzothiazoles via In Situ Cross-Trapping Strategy from Benzothiazoles with Aryl Ketones

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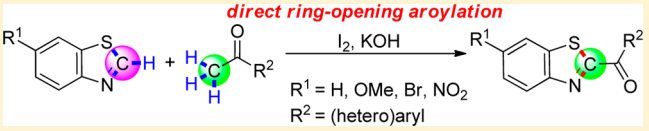
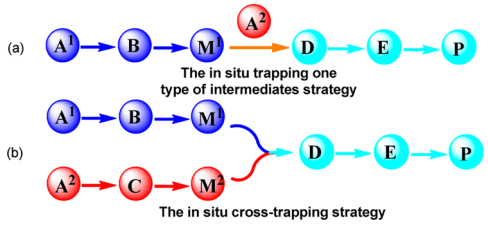
Supporting Information

ABSTRACT: An I_2/KOH synergistically promoted direct ring-opening aroylation of benzothiazoles with aryl ketones has been discovered. Aryl ketones were seen to act as carbonyl sources to construct 2-acylbenzothiazoles. This reaction could provide an example for the convergent integration of self-labor domino sequences based on an in situ cross-trapping strategy.



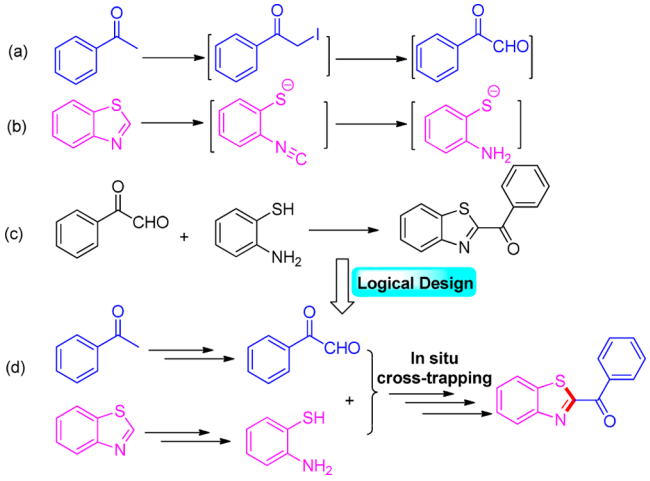
The development of synthetic strategies for the effective synthesis of complex products from simple substrates is an ongoing interest in organic chemistry. Accordingly, the in situ trapping of unstable intermediates via domino reactions has already been successfully developed.[1] Recently, we reported an efficient strategy for the in situ trapping of metastable α-ketoaldehyde intermediates, providing a new method for direct synthesis of pharmacologically interesting heterocycles.[2] Inspired by the in situ trapping of one type of intermediates (Scheme 1a), we envisioned that substrates could be concurrently involved in two or more different domino sequences, with the in situ trapping of respectively generated intermediates converging on the desired product (Scheme 1b). This could provide a more efficient tool for constructing complex molecules from diverse simple substrates. To demonstrate the power and potential of the in situ cross-trapping strategy, we herein present a convenient and efficient method for the direct aroylation of benzothiazoles with aryl ketones.

Scheme 1. In Situ Trapping Strategies



In our previous studies,[2] methyl ketones were seen to be transformed in situ to α-ketoaldehydes via a domino iodination–Kornblum oxidation reaction (Scheme 2a). According to previous literatures, benzothiazole could be converted to 2-aminobenzenethiol via a domino deprotonation–hydroxyzation reaction,[3] which allowed a further reaction with α-ketoaldehyde to afford 2-acylbenzothiazoles[4] (Scheme 2b and c). We therefore suppose that the in situ generated metastable α-ketoaldehyde intermediate could cross-trap another in situ formed 2-aminobenzenethiol via condensation, Michael addition, and oxidative dehydrogenation sequences to construct 2-acylbenzothiazole (Scheme 2d).

Scheme 2. Logical Design and Synthesis of 2-Acylbenzothiazoles



2-Acylbenzothiazoles have attracted much attention due to their diverse biological activities[5] and have also been used to study the regioselectivity in Grignard reagent reactions.[6] However, only a few procedures have been developed to access 2-acylbenzothiazoles due to the difficulty in introducing an acyl group at the 2-position of benzothiazoles.[7] Therefore, the development of a direct aroylation of benzothiazoles protocol to access 2-acylbenzothiazoles derivatives has aroused great interest.[8] Meanwhile, direct aroylation of the aromatic rings remains an important transformation in organic synthesis. They are usually synthesized by the classical Friedel–Crafts

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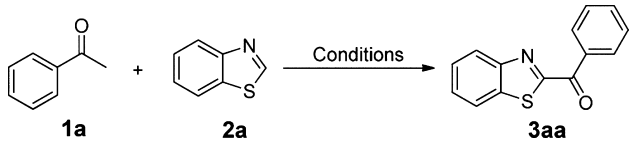
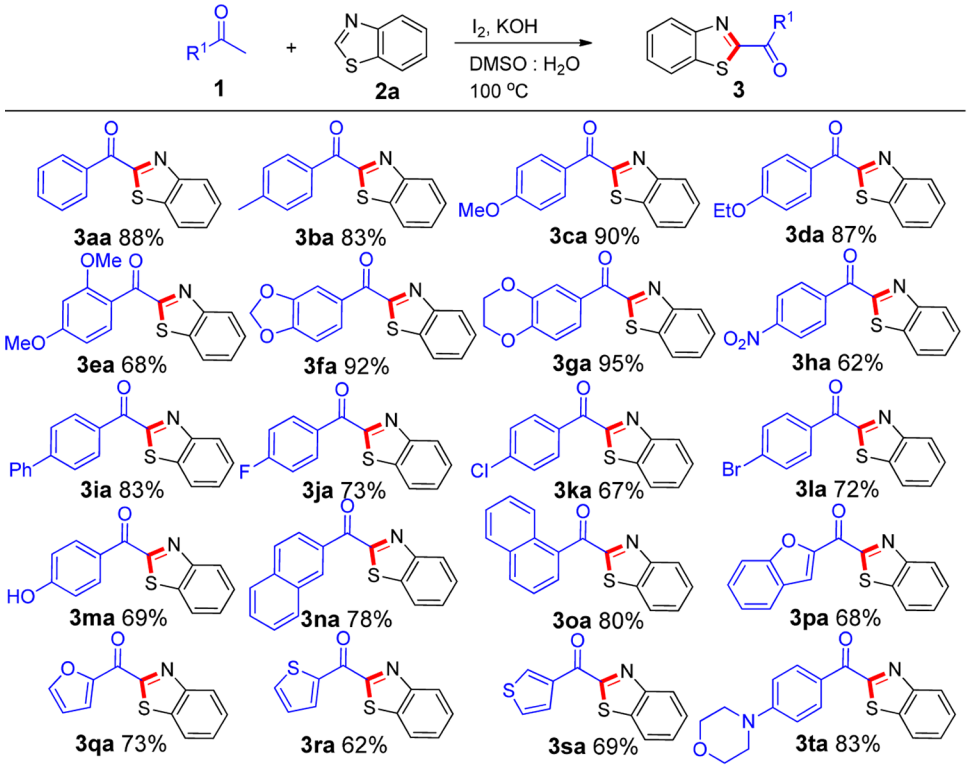
Table 1. Optimization of the Reaction Conditions[a]



entry	I_2 (equiv)	base	solvent	temp (°C)	yield[b] (%)
1	1.5	$K_2S_2O_8$	DMSO	100	8
2	1.5	$K_2S_2O_8$	DMSO/H_2O(1:1)	100	47
3	1.5	$K_2S_2O_8$	DMSO/H_2O(2:1)	100	69
4	1.5	$K_2S_2O_8$	DMSO/H_2O(3:1)	100	83
5	1.5	$K_2S_2O_8$	H_2O	100	0
6	1.5	$K_3PO_4{\cdot}3H_2O$	DMSO/H_2O(3:1)	100	52
7	1.5	K_2CO_3	DMSO/H_2O(3:1)	100	28
8	1.5	*t*-BuOK	DMSO/H_2O(3:1)	100	85
9	**1.5**	**KOH**	**DMSO/H_2O(3:1)**	**100**	**88**
10	1.5	Cs_2CO_3	DMSO/H_2O(3:1)	100	12
11	1.5	NaOH	DMSO/H_2O(3:1)	100	50
12	1.5	$LiOH{\cdot}H_2O$	DMSO/H_2O(3:1)	100	48
13	1.5	$NaHCO_3$	DMSO/H_2O(3:1)	100	0
14	1.5		DMSO/H_2O(3:1)	100	0
15	1.2	KOH	DMSO/H_2O(3:1)	100	81
16	1.0	KOH	DMSO/H_2O(3:1)	100	48
17		KOH	DMSO/H_2O(3:1)	100	0
18[c]	1.5	KOH	DMSO/H_2O(3:1)	100	75
19[d]	1.5	KOH	DMSO/H_2O(3:1)	100	72
20	1.5	KOH	DMSO/H_2O(3:1)	80	15
21	1.5	KOH	DMSO/H_2O(3:1)	90	77
22	1.5	KOH	DMSO/H_2O(3:1)	110	85

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol), base (1.0 mmol), solvent (4 mL). [b]Isolated yields. [c]**2a** (1.2 mmol). [d]**2a** (1.0 mmol).

Scheme 3. Scope of Methyl Ketones[a]



[a]Reaction conditions: **1** (1.0 mmol), **2a** (1.5 mmol), I_2 (1.5 mmol), and KOH (1.0 mmol) in DMSO/H_2O = 3:1 mL at 100 °C. Isolated yield.

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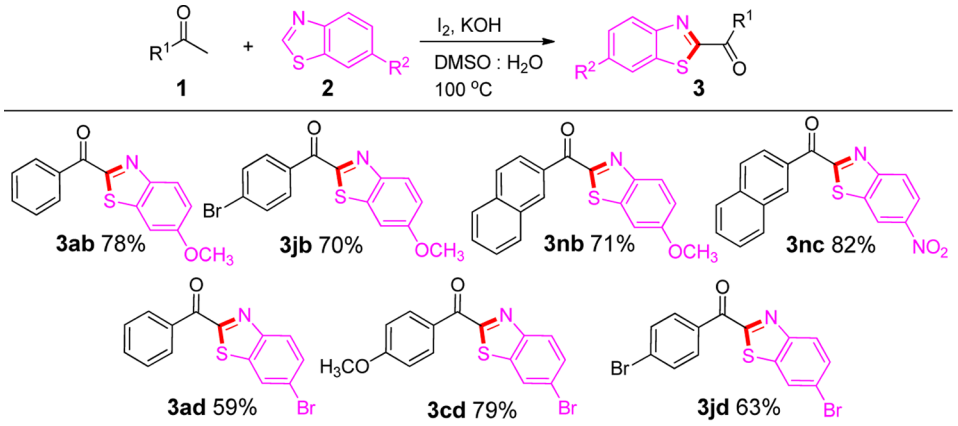
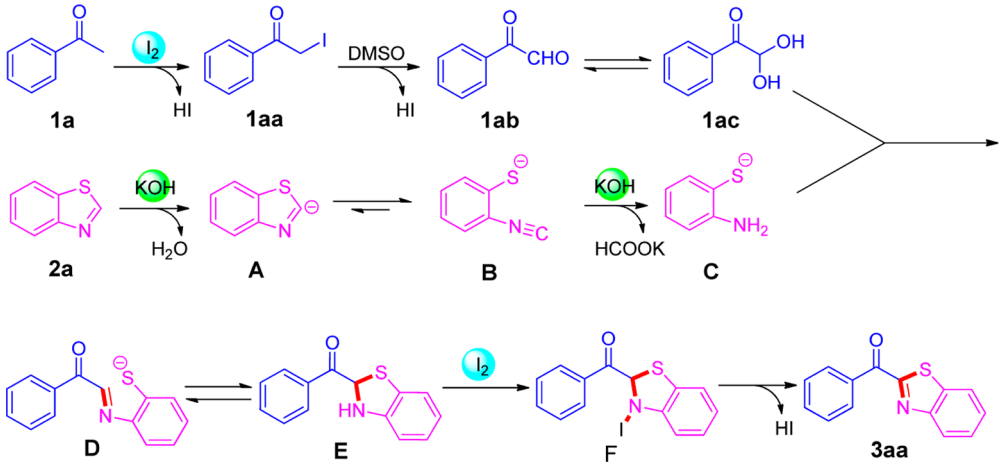
Scheme 4. Scope of Methyl Ketones and Benzothiazoles[a]



[a]Isolated yield

Scheme 5. Possible Mechanism



acylation.[9] Alternatively, the direct aroylation of aryl C−H bonds with carbonyl sources, such as carbon monoxide,[10] aldehydes,[11] alcohols,[12] α-ketone acids,[13] α-diketones,[14] and alkylbenzene,[15] could potentially complement Friedel−Crafts acylation. However, heteroaryl compounds have proven to be much less applicable to these methods.[8,16] In this paper, an I_2/KOH synergistically promoted aroylation of benzothiazoles with aryl ketones is described.

We initiated the present study with acetophenone (**1a**) and benzothiazole (**2a**) as model substrates. It was found that the reaction led to the desired product 2-acylbenzothiazole (**3aa**) in a very low yield of 8% (Table 1, entry 1). To our surprise, the reaction could perform in moderate yield in the presence of H_2O (Table 1, entry 2). When the ratio of DMSO to H_2O was changed from 1:1 to 3:1, the yield increased to 83% (Table 1, entry 4). Other bases were also tested, which demonstrated that KOH was the best choice (Table 1, entries 6−13). However, aroylation of benzoxazole was not observed in the absence of either base or iodine, indicating that an I_2/KOH combination is crucial for the reaction (Table 1, entries 14 and 17).

After achieving the optimized reaction conditions, the scope of aryl methyl ketones was explored (Scheme 3). Aryl methyl ketones bearing electron-neutral (4-H, 4-Me), electron-rich (4-OMe, 4-OEt, 2,4-OMe_2, 3,4-OCH_2O, 3,4-OCH_2CH_2O), and electron-deficient (4-NO_2, 4-Ph) groups all participated in this reaction smoothly to afford the expected 2-acylbenzothiazoles in moderate to excellent yields (62−95%; **3aa**−**3ia**). Much to our satisfaction, the conditions were mild enough to be compatible with halogenated (4-F, 4-Cl, 4-Br) and hydroxylated substrates (67−73%; **3ja**−**3ma**). Notably, 2-naphthyl methyl ketone and 1-naphthyl methyl ketone also gave their corresponding products **3na** and **3oa** in 78% and 80% yields, respectively. Furthermore, heteroaryl ketones, including benzofuryl, furanyl, thienyl, and morpholinyl, were also found to be adept in efficiently furnishing the desired products in moderate to excellent yields (62−83%; **3pa**−**3ta**).

Subsequently, the scope was also extended to some substituted benzothiazoles (Scheme 4). To our delight, benzothiazoles with electron-rich and electron-deficient substituents at the phenyl ring worked well under the optimized reaction conditions, affording the corresponding products **3ab**−**3nc** in 70−82% yields. On the other hand, 6-bromobenzothiazole (**2d**) was also tolerant to the reaction. The corresponding products **3ad**−**3jd** were thus obtained in 59−79% yields. Unfortunately, benzoxazole and benzimidazole could not be applied to this transformation.[17]

On the basis of the control experiments (Supporting Information, Figure S1), a plausible mechanism for the reaction was proposed (Scheme 5). Initially, **1a** was converted to α-iodo acetophenone in the presence of I_2. Subsequently, further oxidation of **1aa** by DMSO took place to **1ab** and **1ac**. At the same time, the ring-opened intermediate **B** was generated by

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deprotonation of **2a** under the assistance of KOH. The intermediate **C** that was formed through hydroxyzation of **B**[3,18] in situ trapped **1ab** to give intermediate **D**. Finally, **D** via Michael addition and oxidative dehydrogenation sequences to furnished the desired product **3aa** in the presence of iodide.[4a]

In summary, we have developed an I_2/KOH synergistically promoted aroylation of benzothiazoles using aryl ketones as carbonyl sources. The protocol could provide an efficient method to synthesize 2-acylbenzathiazoles through an in situ cross-trapping strategy. This method could complement the existing methods of aroylation of aromatic rings.

EXPERIMENTAL SECTION

General Information. IR spectra were recorded as KBr pellets with absorption in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. HRMS were obtained on a 7.0T FTMS equipped with ESI or APCI.

General Procedure for the Synthesis of 3 (3aa as Example). A mixture of acetophenone **1a** (1.0 mmol), benzothiazole **2a** (1.5 mmol), I_2 (1.5 mmol), and KOH (1.0 mmol) in DMSO/H_2O = 3:1 mL was stirred at 100 °C. After disappearance of the reactant (monitored by TLC), 50 mL of water was added to the mixture, which was then extracted with EtOAc 3 times. The extract was washed with $Na_2S_2O_3$ solution, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by column chromatography to afford **3aa**.

Benzo[d]thiazol-2-yl(phenyl)methanone (**3aa**).[4c] Yellow solid; 210.3 mg (yield 88%); mp 97−99 °C; IR (KBr) 1667, 1596, 1485, 1272 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.56 (d, J = 7.8 Hz, 2H), 8.24 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.60−7.53 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 185.3, 167.1, 153.8, 136.9, 134.9, 133.9, 131.2, 128.5, 127.6, 126.9, 125.7, 122.1; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{14}H_{10}NOS$ 240.0478, found 240.0473.

Benzo[d]thiazol-2-yl(p-tolyl)methanone (**3ba**).[4c] Yellow solid; 210 mg (yield 83%); mp 95−97 °C; IR (KBr) 1640, 1604, 1482, 1290 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.47 (d, J = 7.8 Hz, 2H), 8.23 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.59−7.51 (m, 2H), 7.35 (d, J = 7.8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 184.9, 167.4, 153.8, 145.0, 136.9, 132.3, 131.4, 129.2, 127.4, 126.8, 125.6, 122.1, 21.8; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}NOS$ 254.0634, found 254.0630.

Benzo[d]thiazol-2-yl(4-methoxyphenyl)methanone (**3ca**).[7a] White solid; 242.1 mg (yield 90%); mp 118−121 °C; IR (KBr) 1628, 1602, 1492, 1302 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.64 (d, J = 9.0 Hz, 2H), 8.22 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.59−7.50 (m, 2H), 7.03 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 183.3, 167.8, 164.3, 153.8, 136.8, 133.8, 127.7, 127.3, 126.7, 125.5, 122.1, 113.8, 55.5; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}NO_2S$ 270.0583, found 270.0581.

Benzo[d]thiazol-2-yl(4-ethoxyphenyl)methanone (**3da**). Yellow solid; 246.2 mg (yield 87%); mp 112−115 °C; IR (KBr) 1631, 1604, 1493, 1298 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.64 (d, J = 9.0 Hz, 2H), 8.24 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.60−7.51 (m, 2H), 7.03 (d, J = 9.0 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 1.48 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 183.2, 167.9, 163.8, 153.8, 136.8, 133.8, 127.5, 127.3, 126.7, 125.5, 122.0, 114.2, 63.80, 14.61; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{16}H_{14}NO_2S$ 284.0740, found 284.0742.

Benzo[d]thiazol-2-yl(2,4-dimethoxyphenyl)methanone (**3ea**).[4a] Yellow solid; 203.3 mg (yield 68%); mp 122−125 °C; IR (KBr) 1646, 1604, 1458, 1271 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.15 (d, J = 7.8 Hz, 1H), 8.01−7.96 (m, 2H), 7.55−7.47 (m, 2H), 6.62−6.58 (m, 1H), 6.56−6.54 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 185.5, 168.3, 164.7, 161.3, 153.5, 136.9, 134.3, 127.1, 126.6, 125.3, 122.1, 118.5, 104.6, 99.1, 55.8, 55.5; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{16}H_{14}NO_3S$ 300.0689, found 300.0685.

Benzo[d][1,3]dioxol-5-yl(benzo[d]thiazol-2-yl)methanone (**3fa**). Yellow solid; 260.4 mg (yield 92%); mp 134−138 °C; IR (KBr) 1626, 1596, 1486, 1273 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.43−8.38 (m, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.06 (br, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.61−7.52 (m, 2H), 6.97 (d, J = 8.4 Hz, 1H), 6.10 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 182.9, 167.6, 153.8, 152.7, 148.0, 136.9, 129.3, 128.7, 127.4, 126.8, 125.6, 122.1, 110.7, 108.2, 102.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{10}NO_3S$ 284.0376, found 284.0381.

3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-6-phenylpyridazine (**3ga**).[4a] Yellow solid; 282.2 (yield 95%); mp 140−142 °C; IR (KBr) 1629, 1593, 1494, 1302 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.27−8.21 (m, 2H), 8.18 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.60−7.49 (m, 2H), 7.01 (d, J = 8.4 Hz, 1H), 4.36 (s, 2H), 4.32 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 183.2, 167.6, 153.8, 149.1, 143.2, 136.8, 128.3, 127.4, 126.8, 125.7, 125.6, 122.1, 120.9, 117.3, 64.8, 64.0; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{16}H_{12}NO_3S$ 298.0532, found 298.0531.

Benzo[d]thiazol-2-yl(4-nitrophenyl)methanone (**3ha**).[7a] Yellow solid; 176.1 mg (yield 62%); mp 174−277 °C; IR (KBr) 1643, 1597, 1482, 1293 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.74 (d, J = 9.0 Hz, 2H), 8.40 (d, J = 9.0 Hz, 2H), 8.26 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.65−7.58 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 183.8, 165.8, 153.7, 150.5, 139.7, 137.2, 132.3, 128.3, 127.3, 125.9, 123.5, 122.3; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{14}H_9N_2O_3S$ 285.0328, found 285.0328.

[1,1′-Biphenyl]-4-yl(benzo[d]thiazol-2-yl)methanone (**3ia**).[4a] Yellow solid; 261.4 mg (yield 83%); mp 104−107 °C; IR (KBr) 1636, 1600, 1484, 1294 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.64 (d, J = 7.8 Hz, 2H), 8.25 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 7.60−7.51 (m, 2H), 7.50−7.44 (m, 2H), 7.42−7.39 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 184.7, 167.2, 153.8, 146.5, 139.8, 136.9, 133.6, 131.8, 128.9, 128.3, 127.6, 127.3, 127.1, 126.9, 125.7, 122.1; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{20}H_{14}NOS$ 316.0791, found 316.0790.

Benzo[d]thiazol-2-yl(4-fluorophenyl)methanone (**3ja**).[4b] Yellow solid; 187.6 mg (yield 73%); mp 100−102 °C; IR (KBr) 1641, 1594, 1485, 1292 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.69−8.64 (m, 2H), 8.23 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.61−7.52 (m, 2H), 7.25−7.21 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 183.5, 167.2, 167.0, 165.5, 153.8, 136.9, 134.2, 134.1, 131.2, 127.7, 127.0, 125.6, 122.1, 115.8, 115.6; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{14}H_9FNOS$ 258.0383, found 258.0385.

Benzo[d]thiazol-2-yl(4-chlorophenyl)methanone (**3ka**).[4c] White solid; 182.9 mg (yield 67%); mp 99−102 °C; IR (KBr) 1639, 1586, 1480, 1293 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.56 (d, J = 8.4 Hz, 2H), 8.24 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.63−7.52 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 184.0, 166.8, 153.8, 140.6, 137.0, 133.2, 132.7, 128.9, 127.8, 127.0, 125.7, 122.2; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{14}H_9ClNOS$ 274.0088, found 274.00863.

Benzo[d]thiazol-2-yl(4-bromophenyl)methanone (**3la**).[4c] Yellow solid; 228.2 mg (yield 72%); mp 121−123 °C; IR (KBr) 1641, 1581, 1477, 1291 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.46 (d, J = 8.4 Hz, 2H), 8.22 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.60−7.52 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 184.1, 166.7, 153.7, 137.0, 133.6, 132.7, 131.8, 129.5, 127.8, 127.0, 125.7, 122.2; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{14}H_9BrNOS$ 317.9583, found 317.9581.

Benzo[d]thiazol-2-yl(4-hydroxyphenyl)methanone (**3ma**).[4a] Yellow solid; 176 mg (yield 69%); mp 179−182 °C; IR (KBr) 1628, 1597, 1487, 1239 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ (ppm) 10.77, (s, 1H), 8.48 (d, J = 9.0 Hz, 2H), 8.27−8.20 (m, 2H), 7.66−7.58 (m, 2H), 6.98 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 182.2, 167.8, 163.5, 153.3, 136.0, 133.8, 127.7, 127.2, 125.5, 125.1, 122.7, 115.6; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{14}H_{10}NO_2S$ 256.0427, found 256.0423.

Benzo[d]thiazol-2-yl(naphthalen-2-yl)methanone (**3na**).[4a] Yellow solid; 225.4 mg (yield 78%); mp 164−166 °C; IR (KBr) 1632, 1618, 1485, 1291 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.34

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(s, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.66−7.54 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 185.1, 167.3, 153.9, 137.0, 135.9, 134.3, 132.4, 132.1, 130.2, 129.0, 128.3, 127.8, 127.6, 126.9, 126.7, 125.8, 125.7, 122.2; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{18}H_{12}NOS$ 290.0634, found 290.0633.

*Benzo[d]thiazol-2-yl(naphthalen-1-yl)methanone (**3oa**).*[4a] Yellow solid; 231.2 mg (yield 80%); mp 141−143 °C; IR (KBr) 1653, 1593, 1481, 1254 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.52 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 7.2 Hz, 1H), 8.20−8.17 (m, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.05−8.02 (m, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.63−7.52 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 188.3, 168.0, 153.7, 137.3, 133.9, 133.6, 132.2, 131.9, 131.1, 128.6, 128.0, 127.7, 127.0, 126.6, 125.8, 125.4, 124.3, 122.2; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{18}H_{12}NOS$ 290.0634, found 290.0633.

*Benzo[d]thiazol-2-yl(benzofuran-2-yl)methanone (**3pa**).*[4a] Yellow solid; 189.7 mg (yield 68%); mp 123−125 °C; IR (KBr) 1637, 1542, 1488, 1215 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.76 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.56−7.50 (m, 2H), 7.44 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.8, 165.8, 156.3, 153.7, 149.6, 136.9, 129.2, 127.7, 127.3, 127.1, 125.5, 124.1, 124.0, 122.2, 121.0, 112.6; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{16}H_{10}NO_2S$ 280.0427, found 280.0425.

*Benzo[d]thiazol-2-yl(furan-2-yl)methanone (**3qa**).*[4a] Yellow solid; 167.2 mg (yield 73%); mp 149−151 °C; IR (KBr) 1640, 1554, 1493, 1230 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.38 (d, J = 3.6 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.84 (s, 1H), 7.62−7.53 (m, 2H), 7.68−7.67 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 172.0, 166.0, 153.7, 149.8, 148.9, 136.8, 127.5, 127.0, 125.5, 125.0, 122.2, 112.9; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{12}H_8NO_2S$ 230.0270, found 230.0265.

*Benzo[d]thiazol-2-yl(thiophen-2-yl)methanone (**3ra**).*[4a] Yellow solid; 151.9 mg (yield 62%); mp 104−106 °C; IR (KBr) 1618, 1459, 1409, 1227 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.76 (d, J = 3.0 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 4.2 Hz, 1H), 7.61−7.50 (m, 2H), 7.26 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 176.9, 166.5, 153.6, 139.6, 137.4, 136.9, 136.8, 128.5, 127.5, 126.9, 125.5, 122.2; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{12}H_8NOS_2$ 246.0042, found 246.0038.

*Benzo[d]thiazol-2-yl(thiophen-3-yl)methanone (**3sa**).*[4a] Yellow solid; 169 mg (yield 69%); mp 100−102 °C; IR (KBr) 1630, 1511, 1491, 1269 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.30 (s, 1H), 8.23 (d, J = 7.8 Hz,1H), 8.03−7.97 (m, 2H), 7.62−7.51 (m, 2H), 7.42−7.38 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 178.3, 167.5, 153.8, 138.4, 138.0, 136.9, 128.8, 127.5, 126.9, 125.8, 125.5, 122.2; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{12}H_8NOS_2$ 246.0042, found 246.0037.

*Benzo[d]thiazol-2-yl(4-morpholinophenyl)methanone (**3ta**).*[4a] Yellow solid; 268.9 mg (yield 83%); mp 150−152 °C; IR (KBr) 1603, 1490, 1437, 1244 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.61 (d, J = 9.0 Hz, 2H), 8.22 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.58−7.49 (m, 2H), 6.95 (d, J = 8.4 Hz, 2H), 3.87 (t, J = 9.6 Hz, 4H), 3.39 (t, J = 9.0 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 182.6, 168.5, 154.7, 153.9, 136.7, 133.6, 127.1, 126.6, 125.3, 125.0, 122.1, 113.0, 66.5, 47.1; HRMS (APCI) m/z [M + H]$^+$ calcd for $C_{18}H_{17}N_2O_2S$ 325.1005, found 325.1003.

*(6-Methoxybenzo[d]thiazol-2-yl)(phenyl)methanone (**3ab**).*[7d] Yellow solid; 209.8 mg (yield 78%); mp 170−173 °C; IR (KBr) 1637, 1608, 1495, 1258 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.53 (d, J = 7.2 Hz, 2H), 8.10 (d, J = 9.0 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.58−7.53 (m, 2H), 7.41 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.1, 164.7, 159.7, 148.5, 139.0, 135.1, 133.6, 131.1, 128.4, 126.4, 117.6, 103.3, 55.80; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}NO_2S$ 270.0583, found 270.0586.

*(4-Bromophenyl)(6-methoxybenzo[d]thiazol-2-yl)methanone (**3jb**).* Yellow solid; 242.9 mg (yield 70%); mp 197−199 °C; IR (KBr) 1636, 1604, 1495, 1257 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.44 (d, J = 6.6 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 6.6 Hz, 2H), 7.40 (s, 1H), 7.19 (d, J = 7.8 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.0, 159.9, 148.4, 139.2, 133.8, 133.0, 132.6, 131.7, 129.2, 126.5, 117.8, 109.9, 55.9; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{11}BrNO_2S$ 347.9688, found 347.9694.

*(6-Methoxybenzo[d]thiazol-2-yl)(naphthalen-2-yl)methanone (**3nb**).* Yellow solid; 226.5 mg (yield 71%); mp 179−182 °C; IR (KBr) 1615, 1602, 1490, 1255 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.31 (s, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 9.0 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.66−7.55 (m, 2H), 7.43 (s, 1H), 7.20 (d, J = 9.0 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.8, 164.7, 159.7, 148.5, 139.1, 135.8, 134.0, 132.4(3), 132.3(7), 130.2, 128.9, 128.2, 127.7, 126.6, 126.5, 125.8, 117.6, 103.4, 55.8; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{19}H_{14}NO_2S$ 320.0740, found 320.0742.

*Naphthalen-2-yl(6-nitrobenzo[d]thiazol-2-yl)methanone (**3nc**).* Yellow solid; 273.9 mg (yield 82%); mp 192−195 °C; IR (KBr) 1700, 1646, 1342, 1233 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.34 (s, 1H), 8.91 (s, 1H), 8.47−8.33 (m, 3H), 8.06 (d, J = 7.2 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 6.6 Hz, 1H), 7.70−7.63 (m, 1H), 7.62−7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 183.8, 172.7, 157.1, 146.4, 137.0, 136.1, 134.7, 132.3, 131.3, 130.3, 129.5, 128.6, 127.8, 127.0, 126.1, 125.5, 121.9, 118.7; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{18}H_{11}N_2O_3S$ 335.0485, found 335.0485.

*(6-Bromobenzo[d]thiazol-2-yl)(phenyl)methanone (**3ad**).*[7d] Yellow solid; 187 mg (yield 59%); mp 117−120 °C; IR (KBr) 1641, 1491, 1478, 1266 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.54 (d, J = 7.8 Hz, 2H), 8.15 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.71−7.64 (m, 2H), 7.59−7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.9, 167.6, 152.6, 138.5, 134.7, 134.1, 131.2, 130.6, 128.5, 126.7, 124.7, 121.9; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_9BrNOS$ 317.9583, found 317.9586.

*(6-Bromobenzo[d]thiazol-2-yl)(4-methoxyphenyl)methanone (**3cd**).* Yellow solid; 274.1 mg (yield 79%); mp 162−165 °C; IR (KBr) 1636, 1601, 1487, 1262 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.64 (d, J = 7.8 Hz, 2H), 8.16 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 7.8 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.9, 164.5, 152.7, 138.4, 133.8, 132.4, 130.5, 127.5, 126.6, 124.7, 121.6, 113.9, 55.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{11}BrNO_2S$ 347.9688, found 347.9696.

*(6-Bromobenzo[d]thiazol-2-yl)(4-bromophenyl)methanone (**3jd**).* Yellow solid; 248.2 mg (yield 63%); mp 129−133 °C; IR (KBr) 1643, 1584, 1477, 1265 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.46 (d, J = 8.4 Hz, 2H), 8.16 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.73−7.67 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 183.7, 167.2, 152.5, 138.5, 133.3, 132.7, 131.9, 130.7, 129.7, 126.7, 124.7, 122.1; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_8Br_2NOS$ 395.8688, found 395.8681.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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