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Iodine-mediated synthesis of indole-fused benzothiazepinones through intramolecular C2-amidation of amide-tethered C3-sulfenylindoles

Gargi Singh, Mariyaraj Arockiaraj and Venkatachalam Rajeshkumar *

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A transition-metal-free, iodine-mediated strategy has been developed for the synthesis of biologically significant indole-fused benzothiazepinones. This method involves an initial electrophilic C3 iodination of indole, followed by intramolecular C2 amidation of readily accessible amide-tethered C3-sulfenylindoles to afford indole-fused benzothiazepinones in good yields. The protocol exhibits broad substrate compatibility, high functional group tolerance, and scalability. Additionally, the synthetic versatility of the resulting indole-fused benzothiazepinones was demonstrated through their transformation into the corresponding sulfoxides and sulfones.

Introduction

Indole-fused heterocycles are crucial structural motifs found in many natural products and pharmaceuticals.[1,2] These indole-based annulated heterocycles exhibit a broad spectrum of biological activities, including antimicrobial,[3] anticancer,[4] antihypertensive,[5] antiviral,[2d] and anti-inflammatory properties.[6] Notably, azepinoindole alkaloids, such as paullones, are renowned natural products with significant antitumor activity.[7] Furthermore, ibogaine and its derivatives are therapeutically utilized for the treatment of neurological and psychiatric disorders.[8] In this context, thiazepine and its derivatives serve as crucial structural motifs in a wide range of medicinally significant compounds with diverse pharmacological activities. These heterocyclic frameworks contribute to the development of antitumor, antimicrobial, anti-inflammatory, and CNS-active agents, among others.[9] This scaffold is also present in the structures of several commercially available drugs, including diltiazem, a marketed medicine used to treat hypertension, also a common calcium channel blocker,[10] and thiazesim, an antidepressant drug.[11] Several dibenzothiazepines, such as metiapine and clotiapine, are potential antipsychotic drugs used to treat schizophrenia and schizoaffective disorders.[12] Additionally, temocapril is an angiotensin-converting enzyme (ACE) inhibitor primarily used for the treatment of hypertension and heart failure[13] (Fig. 1). Various synthetic methodologies have been developed to construct indole-fused benzoazepines. For example, substituted paullones have been synthesized through a one-pot Suzuki–Miyaura cross-coupling of *o*-aminoarylboronic acid and C2-iodoindoleacetic acid, followed by intramolecular amide formation to yield the 7,12-dihydroindolo[3,2-*d*][1]benzazepine-6(5*H*)-one scaffold (Scheme 1a).[14] Jia and coworkers reported the synthesis of benzazepinoindoles by Pd-catalyzed C(sp^2)–H imidoylative cyclization of 3-(2-isocyanobenzyl)-1*H*-indoles (Scheme 1b).[15]

Recently, the synthesis of azepinoindole and oxepinoindole skeletons was reported using a mild acid-catalyzed cyclization of dearomatized phenols with tryptamines or tryptophols (Scheme 1c).[16] More recently, a trifluoroacetic acid-mediated direct assembly of azepino[4,5-*b*]indoles was achieved *via* C–H functionalization and annulation of 2-alkyl tryptamines with aldehydes (Scheme 1d).[17] Despite significant progress in the synthesis of azepinoindoles,[18] a protocol for the synthesis of indole-fused benzothiazepines has yet to be developed. In our

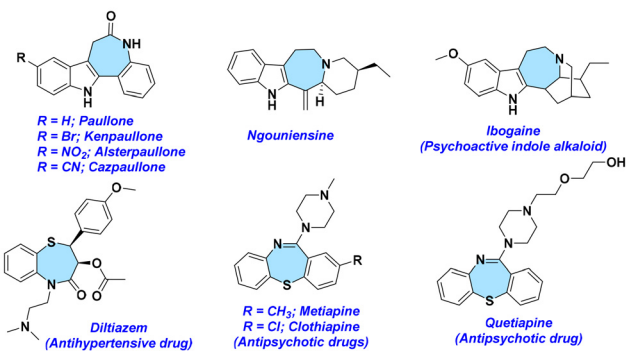
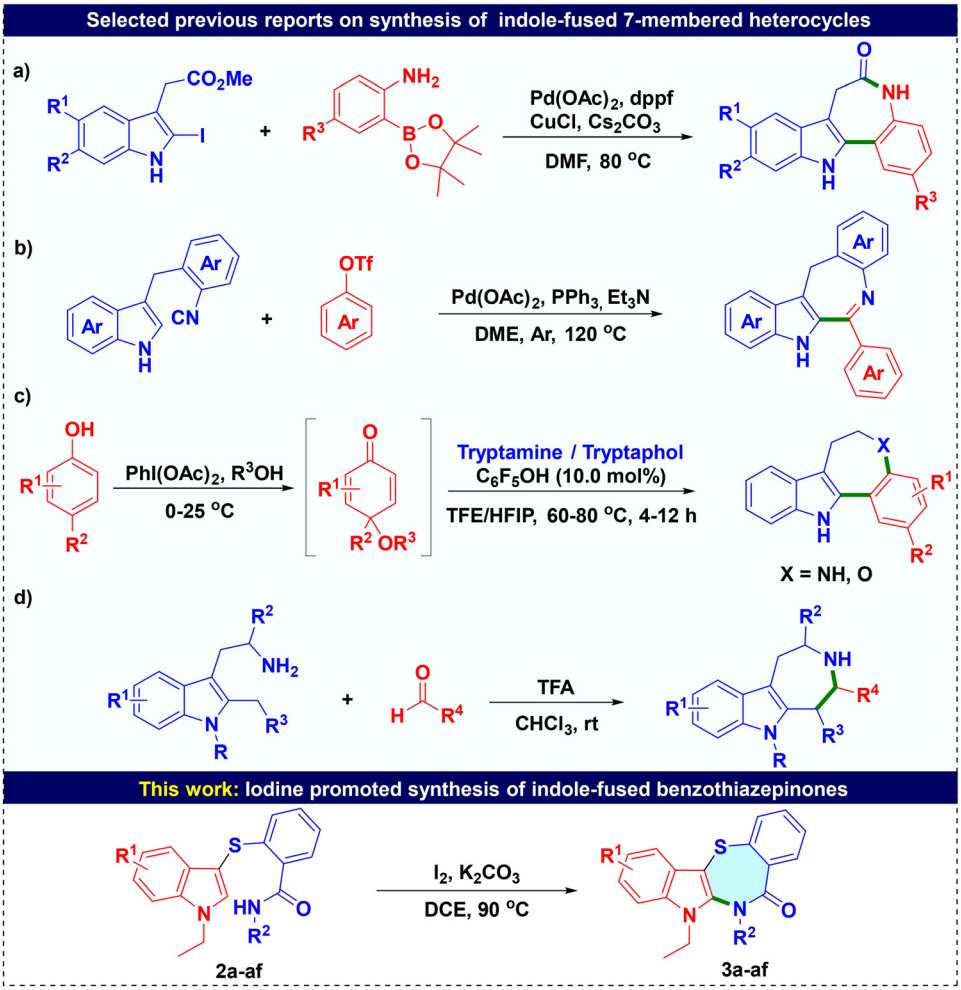


Fig. 1 Representative bioactive motifs containing azepinoindoles and thiazepine framework.

Organic Synthesis & Catalysis Lab, Department of Chemistry, National Institute of Technology Warangal, Hanumakonda - 506004, Telangana, India.
E-mail: rajeshv@nitw.ac.in



Scheme 1 Reported methods for the synthesis of azepinoindoles.

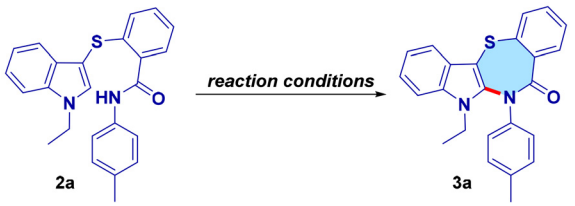
initial attempts to synthesize indole-fused benzothiazepines using 2-(1*H*-indol-3-ylsulfanyl)-phenylamines and aryl methyl ketones, the reaction unexpectedly yielded benzo-β-carbolines through a desulfurative cyclization pathway.[19]

With the continuation of our effort, here we report a successful approach to the synthesis of seven membered indole-fused benzothiazepinones through iodine mediated an intramolecular C2 amidation of amide-tethered C3 sulfenylindoles (Scheme 1).

Results and discussion

We started our investigation by choosing 2-((1-ethyl-1*H*-indol-3-yl)thio)-*N*-(*p*-tolyl)benzamide **2a** as a model substrate to synthesize a indole-fused benzothiazepinone 5-ethyl-6-(*p*-tolyl)-5,6-dihydro-7*H*-benzo[6,7][1,4]thiazepino[3,2-*b*]indol-7-one **3a**. As depicted in Table 1, the initial reaction was conducted using the substrate **2a** (100 mg, 0.268 mmol) in the presence of I_2 (1.5 equiv.) and K_2CO_3 (3.0 equiv.) in DCE solvent at room temperature and the desired product **3a** was isolated in 75% yield (Table 1, entry 1). Gratifyingly, when the reaction was conducted at 60 °C, the yield was improved to 78% (entry 2). Next, when we increased the reaction temperature to 80 °C, the product **3a** was obtained in 80% yield (entry 3). Further increasing the temperature to 90 °C yielded the desired product **3a** in 84% (entry 4). However, increasing the temperature to 100 °C resulted in a reduced yield of 76% (entry 5). Thus, the reaction temperature was set at 90 °C for further optimization of the reaction conditions. Next, we examined the effect of iodine loading on the reaction. Reducing the iodine amount significantly lowered the reaction yield (entries 6 and 7) and prolonged the reaction time. The reaction was further tested with various bases such as Cs_2CO_3, Na_2CO_3 and $NaHCO_3$ using 1.5 equivalents of I_2. However, these attempts resulted in the poor yields (entries 8–10). Moreover, the reaction did not proceed when bases such as NaOAc, DABCO, DBU, DIPEA, and Et_3N were used (entries 11–15). After evaluating various bases, we next investigated the effect of different solvents to present reaction. The product yield was significantly

Table 1 Optimization of the reaction conditions[a,b]



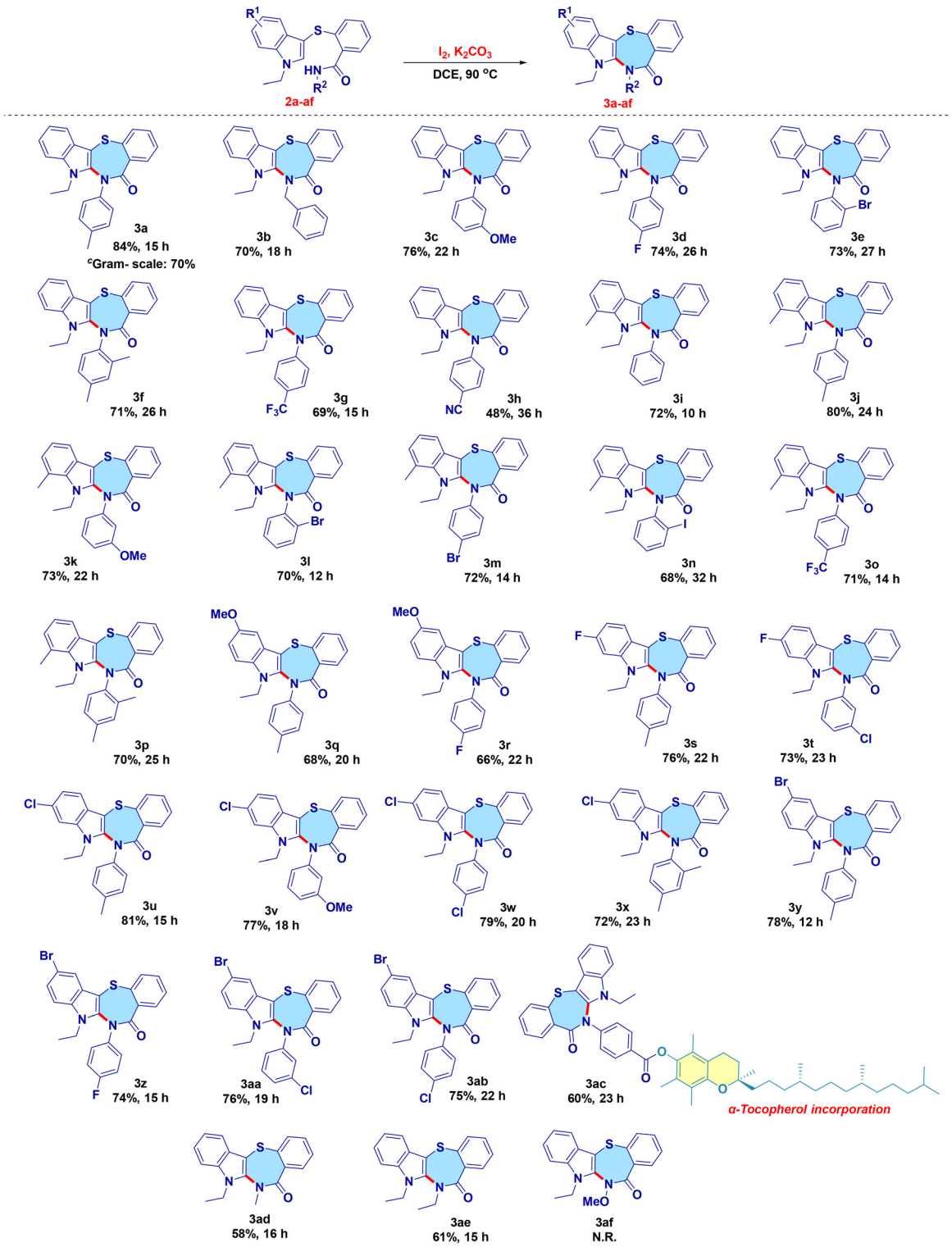
Entry	Reagent	Base (3 equiv.)	Solvent	Temp (°C)	Time (h)	Yield 3a [b] (%)
1	I_2 (1.5 eq.)	K_2CO_3	DCE	rt	30	75
2	I_2 (1.5 eq.)	K_2CO_3	DCE	60	26	78
3	I_2 (1.5 eq.)	K_2CO_3	DCE	80	20	80
4	I_2 (1.5 eq.)	K_2CO_3	DCE	90	15	84
5	I_2 (1.5 eq.)	K_2CO_3	DCE	100	15	76
6	I_2 (1.2 eq.)	K_2CO_3	DCE	90	20	80
7	I_2 (1.0 eq.)	K_2CO_3	DCE	90	23	79
8	I_2 (1.5 eq.)	Cs_2CO_3	DCE	90	24	24
9	I_2 (1.5 eq.)	Na_2CO_3	DCE	90	24	20
10	I_2 (1.5 eq.)	$NaHCO_3$	DCE	90	24	19
11	I_2 (1.5 eq.)	NaOAc	DCE	90	24	NR
12	I_2 (1.5 eq.)	DABCO	DCE	90	24	NR
13	I_2 (1.5 eq.)	DBU	DCE	90	24	NR
14	I_2 (1.5 eq.)	DIPEA	DCE	90	24	NR
15	I_2 (1.5 eq.)	Et_3N	DCE	90	24	NR
16	I_2 (1.5 eq.)	K_2CO_3	CH_3CN	90	24	25
17	I_2 (1.5 eq.)	K_2CO_3	Dioxane	90	24	22
18	I_2 (1.5 eq.)	K_2CO_3	THF	90	24	NR
19	I_2 (1.5 eq.)	K_2CO_3	DMF	90	24	NR
20	I_2 (1.5 eq.)	K_2CO_3	DMSO	90	24	NR
21	NIS (1.5 eq.)	K_2CO_3	DCE	90	24	30
22	NBS (1.5 eq.)	K_2CO_3	DCE	90	24	Trace
23	I_2 (1.5 eq.)	—	DCE	90	24	NR
24	—	K_2CO_3	DCE	90	24	NR

[a] Reaction conditions: all the reactions were performed using **2a** (100 mg, 0.268 mmol) in 2 mL of DCE solvent with different conditions mentioned in the table. [b] Isolated yields are reported.

lower when the reaction was carried out in other solvents such as CH_3CN and 1,4-dioxane (entries 16 and 17). Moreover, no reaction occurred when THF, DMF, or DMSO were used as solvents (entries 18–20). Next, reagents like NIS and NBS were also evaluated for the present reaction but ineffective to produce the desired outcome (entries 21 and 22). Furthermore, the reaction did not proceed in the absence of either a base or iodine (entries 23 and 24). After systematic investigations, the optimized reaction conditions were identified as entry 4, where the reaction was performed with 1.5 equivalent of iodine, along with 3.0 equivalents of K_2CO_3 in 2 mL of DCE at 90 °C.

With the optimized reaction conditions in hand, we next explored the substrate scope of this protocol to synthesize a variety of indole-fused benzothiazepinones, as shown in Table 2. All the reactions proceeded well to synthesize the library of substrates **3a–z** in good yields. Initially, we investigated the unsubstituted indole ring with different substituents at the R_2 position under the optimized reaction conditions. The benzyl group was tested, resulting in the formation of the desired cyclized product **3b** in 70% yield. Then, the incorporation of electron-donating methoxy group resulted in yielding the product **3c** in 76% yield. Subsequently, we investigated the influence of fluoro and bromo substituents on the reaction and observed that the cyclized products **3d–e** were obtained in excellent yields of 74 and 73% respectively. The substrate **2f**, featuring a 2,4-dimethylphenyl group on the amide nitrogen, underwent annulation under the optimized reaction conditions, leading to the formation of the desired cyclized product **3f** in 71% yield. Further, we examined the substrates containing electron-withdrawing $-CF_3$ and –CN groups at the *para* position of the aryl ring attached to the nitrogen of the amide group. The reactions proceeded smoothly to give the corresponding products **3g** and **3h** 48–69% yield. Next, we examined indole substrates bearing electron-donating groups, such as methyl ($-CH_3$) and methoxy (–OMe), to the reaction. The 7-methylindole substrate **2i**, featuring a phenyl group on the amide nitrogen, was well-tolerated under the optimized conditions, affording the cyclized product **3i** in 72% yield. Similarly, substrates bearing *p*-tolyl and 3-methoxyphenyl groups underwent smooth cyclization, producing the corresponding products **3j** and **3k** in 80 and 73% yields, respectively. The substrates featuring halogen substitutions (*o*-Br, *p*-Br, and *o*-I) on the phenyl ring attached to the amide nitrogen underwent cyclization, affording the desired products **3l–n** in the range of 68–72% yields. In addition, the presence of an electron-withdrawing $-CF_3$ group was tested, and to our delight, the corresponding product **3o** was obtained in 71% yield. Furthermore, the presence of a 2,4-dimethylphenyl group on the amide nitrogen led to the formation of the corresponding cyclized product **3p** in 70% yield. Next, substitution of the C5 position of indole with an –OMe group, along with *p*-tolyl or 4-fluorophenyl on the amide nitrogen, successfully led to the formation of cyclized products **3q** and **3r** in 66–68% yields. Further exploration of the substrate scope revealed that halogen substitutions on the indole ring was well-tolerated, facilitating the efficient synthesis of indole-fused benzothiazepinones. The 6-fluoroindole substrates **2s–t**, bearing *p*-Me and *m*-Cl phenyl groups on the amide, underwent cyclization smoothly to afford the respective products **3s** and **3t** in 73–76% yield. Next, chloro-substituted indole substrates were subjected to the standard conditions, delivering the desired cyclized products **3u–x** in good yields ranging from 72–81%. Similarly, bromo-substituted indole substrates exhibited excellent compatibility with various substitutions on amide such as *p*-Me, *p*-F, *m*-Cl, and *p*-Cl phenyl, yielding the corresponding products **3y–ab** in 74–78% yields. Furthermore, the successful incorporation of an α-tocopherol moiety into the substrate led to the efficient synthesis of the cyclized product **3ac**, which was obtained in 60% yield. This demonstrates the broad applicability of the reaction conditions in accommodating biologically relevant functional groups. Similarly, alkyl groups were well tolerated in the substrate scope, including methyl and ethyl substituents at the amide nitrogen, which afforded the desired products **3ad–3ae** in 58–61% yield. However, the product **3af** was not obtained when a methoxy group was present on the amide nitrogen. Further, the exact structure of compound **3a** was unambiguously con-

Table 2 Substrate scope for the synthesis of indole-fused be nzothiazepinones[a,b]



[a] Reaction conditions: all the reactions were performed using substrates **2a–af** (100 mg, 1.0 equiv.) in the presence of I_2 (1.5 equiv.) and K_2CO_3 (3.0 equiv.) in 2 mL of 1,2-dichloroethane solvent at 90 °C. [b] Isolated yields are reported. [c] Yield of gram-scale reaction of substrate **2a** (1.0 g, 2.68 mmol) under optimized reaction conditions.

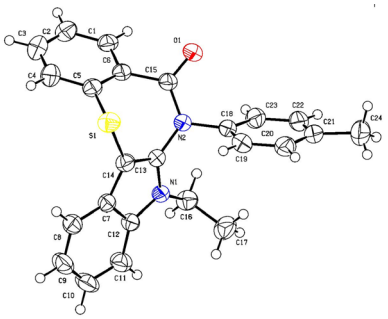
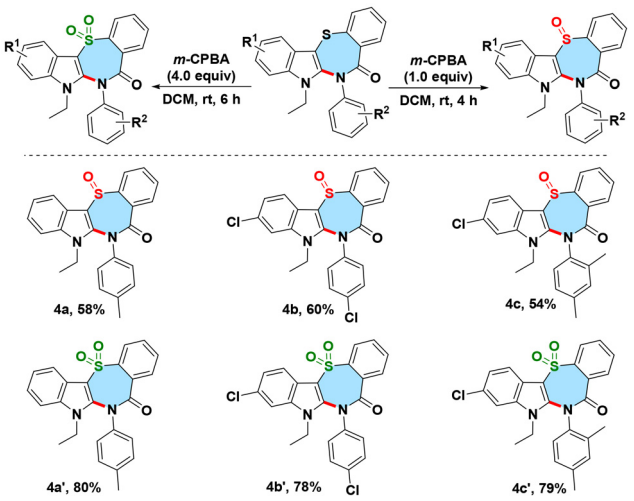


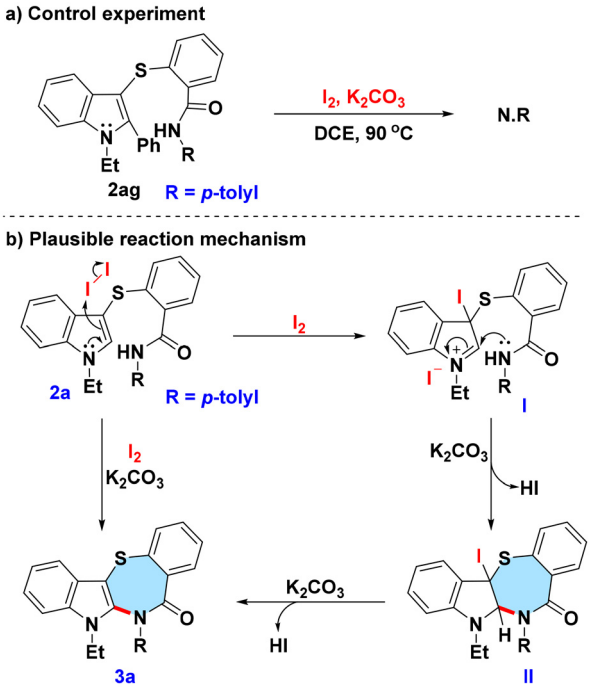
Fig. 2 Single-crystal X-ray structure of **3a** (CCDC 2426072).

firmed through single-crystal X-ray analysis (CCDC 2426072; Fig. 2).

To showcase the potential applicability of this synthetic approach, a reaction was conducted on a gram scale using 2-((1-ethyl-1*H*-indol-3-yl)thio)-*N*-(*p*-tolyl)benzamide **2a** (1.0 g, 2.68 mmol) under the standard reaction conditions. Gratifyingly, the transformation proceeded efficiently, affording **3a** in 70% yield as illustrated in Table 2. Furthermore, we demonstrated the synthetic versatility of indole-fused benzothiazepinones by oxidizing sulfur atom present in the ring[20] using *m*-CPBA under mild conditions. The corresponding sulfoxides and sulfones were obtained using 1 eq. and 4 eq. of *m*-CPBA, respectively, as illustrated in Scheme 2. To gain further insight into the proposed mechanism, a control experiment was conducted using a substrate **2ag** derived from 2-phenylindole. However, when this substrate was subjected to the standard reaction conditions, the corresponding cyclized product was not obtained (Scheme 3a). Based on this observation and prior literature reports,[21] a plausible reaction mechanism is proposed using substrate **2a**, as illustrated in Scheme 3b. Initially, the substrate **2a** undergoes iodination at the C3 position of the indole, leading to the formation of an iminium ion intermediate **I**.



Scheme 2 Synthetic transformation of indole-fused benzothiazepinones to corresponding sulfoxides and sulfones.



Scheme 3 Control experiment and plausible reaction mechanism.

Subsequently, the amide nitrogen undergoes an intramolecular nucleophilic attack at the C2 position of the indole, generating the seven-membered intermediate **II**. This intermediate then undergoes aromatization in the presence of a base, yielding the desired cyclized product, indole-fused benzothiazepinone **3a**.

Conclusions

In conclusion, we have successfully developed a transition-metal-free, iodine-mediated protocol for the synthesis of biologically significant indole-fused benzothiazepinones through intramolecular C2 amidation of readily accessible amide-tethered C3-sulfenylindoles. This transformation proceeds *via* an electrophilic C3 iodination of indole, facilitating intramolecular cyclization to afford the target benzothiazepinones in good yields. The developed protocol is compatible with a broad substrate scope, demonstrating high functional group tolerance and scalability. Furthermore, the synthetic versatility of the obtained indole-fused benzothiazepinones was explored through their transformation into the corresponding sulfoxides and sulfones. Given the structural relevance of benzothiazepinone scaffolds in medicinal chemistry, this approach provides a valuable synthetic tool for the development of bioactive molecules and pharmaceutical intermediates.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI: experimental procedures, characterization data, and copies of the ^{1}H and ^{13}C $\{^{1}H\}$ spectra of all new compounds are included. See DOI: **https://doi.org/10.1039/d5ob00842e**.

CCDC 2426072 contains the supplementary crystallographic data for this paper.[22]

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References

1 (*a*) S. Lepri, F. Buonerba, L. Goracci, I. Velilla, R. Ruzziconi, B. D. Schindler, S. M. Seo, S. Kaatz and G. Cruciani, *J. Med. Chem.*, 2016, **59**, 867–891; (*b*) S. Pathania, R. K. Narang and R. K. Rawal, *Eur. J. Med. Chem.*, 2019, **180**, 486–508; (*c*) M. F. Khan, M. M. Alam, G. Verma, W. Akhtar, M. Akhter and M. Shaquiquzzaman, *Eur. J. Med. Chem.*, 2016, **120**, 170–201; (*d*) K. Laxmikeshav, P. Kumari and N. Shankaraiah, *Med. Res. Rev.*, 2022, **42**, 513–575; (*e*) M. M. Heravi and V. Zadsirjan, *RSC Adv.*, 2020, **10**, 44247–44311; (*f*) Y. P. Zheng, J. X. Li, W. Q. Wu, C. R. Qi and H. F. Jiang, *Org. Process Res. Dev.*, 2024, **28**, 2988–3025.

2 (*a*) S. Han and M. Movassaghi, *J. Am. Chem. Soc.*, 2011, **133**, 10768–10771; (*b*) J. Dai, W. Dan, U. Schneider and J. Wang, *Eur. J. Med. Chem.*, 2018, **157**, 622–656; (*c*) C. Zheng and S.-L. You, *Nat. Prod. Rep.*, 2019, **36**, 1589–1605; (*d*) M. Z. Zhang, Q. Chen and G. F. Yang, *Eur. J. Med. Chem.*, 2015, **89**, 421–441; (*e*) A. Dorababu, *RSC Med. Chem.*, 2020, **11**, 1335–1353; (*f*) A. Beato, A. Gori, B. Boucherle, M. Peuchmaur and R. Haudecoeur, *J. Med. Chem.*, 2021, **64**, 1392–1422.

3 H. L. Qin, J. Liu, W. Y. Fang, L. Ravindar and K. P. Rakesh, *Eur. J. Med. Chem.*, 2020, **194**, 112245.

4 K. Kaur, H. Verma, P. Gangwar, M. Dhiman and V. Jaitak, *RSC Med. Chem.*, 2024, **15**, 1329–1347.

5 A. V. Danilenko, A. N. Volov, N. A. Volov, Y. B. Platonova and S. V. Savilov, *Bioorg. Med. Chem. Lett.*, 2023, **90**, 129349.

6 L. G. Humber, E. Ferdinandi, C. A. Demerson, S. Ahmed, U. Shah, D. Mobilio, J. Sabatucci, B. D. Lange, F. Labbadia, P. Hughes, J. DeVirgilio, G. Neuman, T. T. Chau and B. M. Weichman, *J. Med. Chem.*, 1988, **31**, 1712–1719.

7 C. Schultz, A. Link, M. Leost, D. W. Zaharevitz, R. Gussio, E. A. Sausville, L. Meijer and C. Kunick, *J. Med. Chem.*, 1999, **42**, 2909–2919.

8 R. B. Kargbo, *ACS Med. Chem. Lett.*, 2022, **13**, 888–890.

9 (*a*) N. Garg, T. Chandra, Archana, A. B. Jain and A. Kumar, *Eur. J. Med. Chem.*, 2010, **45**, 1529–1535; (*b*) T. X. Li, J. Zhang, J. K. Pan, Z. X. Wu, D. Hu and B. Song, *Eur. J. Med. Chem.*, 2017, **125**, 657–662; (*c*) J. B. Bariwal, K. D. Upadhyay, A. T. Manvar, J. C. Trivedi, J. S. Singh, K. S. Jain and A. K. Shah, *Eur. J. Med. Chem.*, 2008, **43**, 2279–2290; (*d*) G. Campiani, S. Butini, C. Fattorusso, B. Catalanotti, S. Gemma, V. Nacci, E. Morelli, A. Cagnotto, I. Mereghetti, T. Mennini, M. Carli, P. Minetti, M. A. Di Cesare, D. Mastroianni, N. Scafetta, B. Galletti, M. A. Stasi, M. Castorina, L. Pacici, M. Vertechy, S. di Serio, O. Ghirardi, O. Tinti and P. Carminati, *J. Med. Chem.*, 2004, **47**, 143–157.

10 (*a*) B. B. Lohray, B. Jayachandran, V. Bhushan, E. Nandanan and T. Ravindranathan, *J. Org. Chem.*, 1995, **60**, 5983–5985; (*b*) E. Carosati, R. Budriesi, P. Ioan, G. Cruciani, F. Fusi, M. Frosini, S. Saponara, F. Gasparrini, A. Ciogli, C. Villani, P. J. Stephens, F. J. Devlin, D. Spinelli and A. Chiarini, *J. Med. Chem.*, 2009, **52**, 6637–6648.

11 (*a*) J. Krapcho, E. R. Spitzmiller and C. F. Turk, *J. Med. Chem.*, 1963, **6**, 544–546; (*b*) J. Krapcho and C. F. Turk, *J. Med. Chem.*, 1966, **9**, 191–195; (*c*) J. Krapcho, C. F. Turk and J. J. Piala, *J. Med. Chem.*, 1968, **11**, 361–364.

12 (*a*) S. K. Bagal, A. D. Brown, P. J. Cox, K. Omoto, R. M. Owen, D. C. Pryde, B. Sidders, S. E. Skerratt, E. B. Stevens, R. I. Storer and N. A. Swain, *J. Med. Chem.*, 2013, **56**, 593–624; (*b*) J. B. Bariwal, K. D. Upadhyay, A. T. Manvar, J. C. Trivedi, J. S. Singh, K. S. Jain and A. K. Shah, *Eur. J. Med. Chem.*, 2008, **43**, 2279–2290.

13 K. Yasunari, K. Maeda, M. Nakamura, T. Watanabe, J. Yoshikawa and A. Asada, *Cardiovasc. Drug Rev.*, 2004, **22**, 189–198.

14 S. Soto, E. Vaz, C. Dell'Aversana, R. Álvarez, L. Altucci and Á. R. de Lera, *Org. Biomol. Chem.*, 2012, **10**, 2101–2112.

15 J. Wang, P. Z. Ren, G. P. Gu, Z. Y. Jiang, B. L. Xiang, S. Tang and A. Q. Jia, *J. Org. Chem.*, 2022, **87**, 9663–9674.

16 R. Mahato, N. Yadav and C. K. Hazra, *Org. Lett.*, 2024, **26**, 3911–3916.

17 K. Xie, Z. Shen, P. Cheng, H. Dong, Z. X. Yu and L. Zu, *Chem. Sci.*, 2024, **15**, 12732–12738.

18 (*a*) W. J. Chiu, T. Y. Chu, I. J. Barve and C. M. Sun, *Org. Lett.*, 2023, **25**, 6246–6250; (*b*) S. Biswas and S. Batra, *Adv. Synth. Catal.*, 2011, **353**, 2861–2867; (*c*) T. U. Thikekar and C.-M. Sun, *Adv. Synth. Catal.*, 2017, **359**, 3388–3396; (*d*) L. Xiao, B. Li, F. Xiao, C. Fu, L. Wei, Y. Dang, X.-Q. Dong and C.-J. Wang, *Chem. Sci.*, 2022, **13**, 4801–4812; (*e*) A. N. Singh Chauhan, G. Mali, G. Dua, P. Samant, A. Kumar and R. D. Erande, *ACS Omega*, 2023, **8**, 27894–27919; (*f*) T. U. Thikekar, M. Selvaraju and C.-M. Sun, *Org. Lett.*, 2016, **18**, 316–319; (*g*) M. Kadagathur, S. Patra, D. K. Sigalapalli, N. Shankaraiah and N. D. Tangellamudi, *Org. Biomol. Chem.*, 2021, **19**, 738–764; (*h*) A. S. K. Hashmi, W. Yang and F. Rominger, *Adv. Synth. Catal.*, 2012, **354**, 1273–1279; (*i*) H. L. Hua, B. S. Zhang, Y. T. He, Y. F. Qiu, J. Y. Hu, Y. C. Yang and Y. M. Liang, *Chem. Commun.*, 2016, **52**, 10396–10399; (*j*) T. Oishi, T. Uchikura and T. Akiyama, *Chem. Commun.*, 2025, **61**, 2576–2579.

19 S. S. Marupalli, M. Arockiaraj and G. Singh, *J. Org. Chem.*, 2023, **88**, 12783–12791.
20 (*a*) V. Rajeshkumar, C. Neelamegam and S. Anandan, *Org. Biomol. Chem.*, 2019, **17**, 982–991; (*b*) M. Arockiaraj and V. Rajeshkumar, *Adv. Synth. Catal.*, 2024, **366**, 2557–2564.
21 (*a*) Y.-X. Li, H.-X. Wang, S. Ali, X.-F. Xia and Y.-M. Liang, *Chem. Commun.*, 2012, **48**, 2343–2345; (*b*) S. Badigenchala, V. Rajeshkumar and G. Sekar, *Org. Biomol. Chem.*, 2016, **14**, 2297–2305; (*c*) S. Badigenchala and G. Sekar, *J. Org. Chem.*, 2017, **82**, 7657–7665; (*d*) H. M. Nelson, S. H. Reisberg, H. P. Shunatona, J. S. Patel and F. D. Toste, *Angew. Chem., Int. Ed.*, 2014, **53**, 5600–5603; (*e*) W. Xie, G. Jiang, H. Liu, J. Hu, X. Pan, H. Zhang, X. Wan, Y. Lai and D. Ma, *Angew. Chem., Int. Ed.*, 2013, **52**, 12924–12927.
22 V. Rajeshkumar, CCDC 2426072: Experimental Crystal Structure Determination, 2025, DOI: **10.5517/ccdc.csd.cc2mfjd0**.