Copper-catalysed selective 3-sulfonylation of indoles: a mild synthesis of indolyl sulfones

Yi Du and Yunyun Liu*

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P.R. China

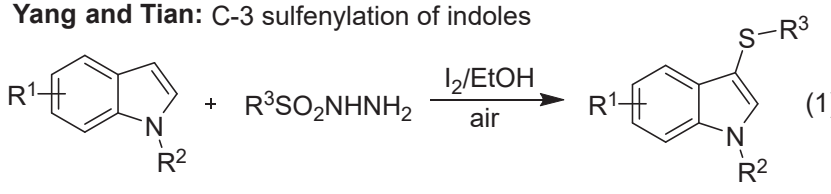
The selective C3-sulfonylation of some 4-, 5- and 6-substituted indoles using sodium arenesulfinates as reaction partners has been realised under mild conditions using catalytic CuI/1,10-phenanthroline at 70 °C. The reaction had a satisfactory application scope and proceeded in fair to excellent yields.

Keywords: copper catalysis, indole, sulfinate, selective, C–H sulfonylation

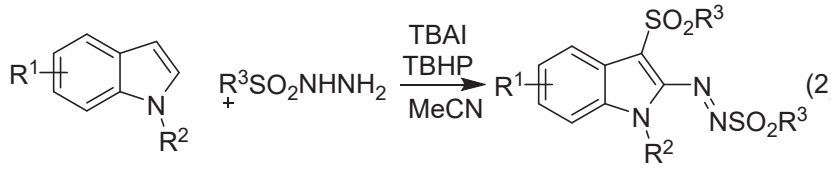
Owing to their rich biological and medicinal profiles, indole derivatives have attracted extensive research interest from the chemical community and many related disciplines.[1–3] Thus, research on synthetic methods towards indole-based molecules occupies a central position in modern organic synthesis.[4–7] Among the numerous strategies for indole synthesis, the most facile is the direct elaboration of indoles because of the high and versatile reactivity of simple indoles.[8–11] During recent years, the synthesis of sulfur-containing indole derivatives such as sulfenylated and sulfonylated indoles and other sulfur-containing indole derivatives has received notable attention and advances because of the inherent potential of these compounds in the discovery of new lead compounds.[12–18]

Among the reaction partners used for the C–S bond elaboration of indoles, the sulfonic acid derivatives such as sulfonohydrazides, sulfonyl chlorides and sulfinate salts have been found to be highly efficient and versatile in providing different types of products. Depending on the catalytic conditions and reaction partners, the selective synthesis of various sulfenylated or sulfonylated indoles by the functionalisation at either the C-2 or C-3 position has been achieved. For example, by employing sulfonohydrazides to react with indoles, Yang and Tian observed the selective formation of 3-sulfenylated indoles in the presence of molecular iodine (Eqn 1 in Scheme 1).[19] On the other hand, Tu and co-workers discovered that the reactions of indoles with sulfonohydrazides provided 3-sulfonyl-2-diazosulfonylindoles in the oxidative system of tetrabutylammonium iodide (TBAI)/*tert*-butyl hydroperoxide (TBHP) (Eqn 2 in Scheme 1).[20] In their investigation on the sulfinate-based synthesis, Deng and co-workers found that the reactions of sodium sulfinates and indoles yield sulfenylated indoles when molecular iodine is employed as the catalyst.[21] Interestingly, the reactions of identical starting materials have been discovered to provide 2-sulfonylated products selectively

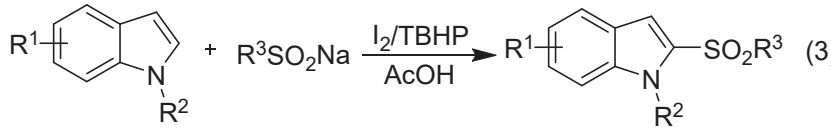
Yang and Tian: C-3 sulfenylation of indoles



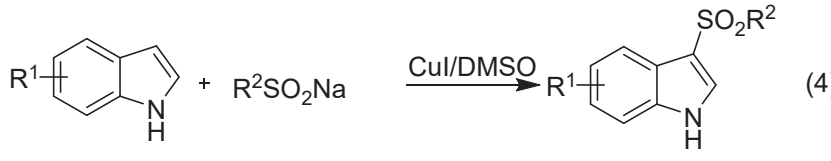
Tu and co-workers: C-3 and C-2 difunctionalisation of indoles



Deng and co-workers: C-2 sulfonylation of indoles



This work: C-3 sulfonylation of indoles



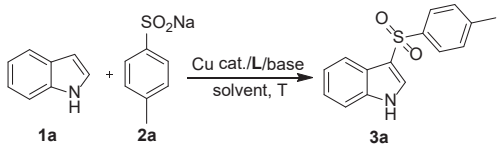
Scheme 1 Sulfenylation and sulfonylation of indole C–H bonds.

* Correspondent. E-mail: chemliuyunyun@jxnu.edu.cn

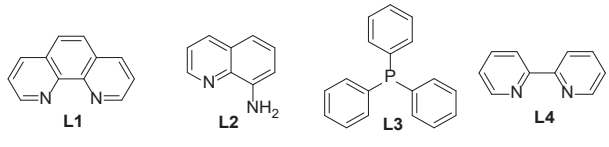
when the modified reaction conditions of I_2/TBHP in AcOH are employed (Eqn 3 in Scheme 1).[22] While elegant results on the synthesis of these sulfenylated and sulfonylated indoles have been achieved, selective synthetic approaches towards 3-sulfonylated indoles by corresponding C–H functionalisation of indoles remain scarce.[23–24] During our preparation of the manuscript, Zhang and co-workers reported the copper-catalysed C-3 sulfonylation of indoles employing sulfinates as the sulfonyl source and closely related to our work.[25] Based on our longstanding interest in copper-catalysed coupling chemistry, we report here our work on copper/iodide-catalysed selective C-3 sulfonylation of indoles by using sulfinates as reaction partners.

To start the investigation, the model reaction of indole **1a** and sulfinate **2a** was selected and the primary comparison experiments conducted in the presence of CuBr and 1,10-phenanthroline (1,10-phen)/K_2CO_3 showed that employment of excess sulfinate **2a** was positive to the result (Table 1, entries 1–2). The subsequent experiments employing different copper catalysts disclosed the fact the CuI was the best catalyst (Table 1, entries 3–6). Reducing the amount of CuI load resulted in slight loss of product yield (Table 1, entry 7).

Table 1 Optimisation of reaction conditions[a]



Entry	Catalyst	Ligand (**L**)	Base	Solvent	Yield[b]/%
1	CuBr	**L1**	K_2CO_3	DMSO	60
2[c]	CuBr	**L1**	K_2CO_3	DMSO	46
3	–	**L1**	K_2CO_3	DMSO	Nr
4	CuCl	**L1**	K_2CO_3	DMSO	52
5	CuI	**L1**	K_2CO_3	DMSO	83
6	$CuBr_2$	**L1**	K_2CO_3	DMSO	53
7[d]	CuI	**L1**	K_2CO_3	DMSO	74
8	CuI	**L2**	K_2CO_3	DMSO	52
9	CuI	**L3**	K_2CO_3	DMSO	Trace
10	CuI	**L4**	K_2CO_3	DMSO	43
11	CuI	–	K_2CO_3	DMSO	Nr
12	CuI	**L1**	Cs_2CO_3	DMSO	36
13	CuI	**L1**	KOH	DMSO	Trace
14	CuI	**L1**	EtONa	DMSO	34
15	CuI	**L1**	K_2CO_3	DMF	Trace
16	CuI	**L1**	K_2CO_3	Dioxane	Trace
17	CuI	**L1**	K_2CO_3	Toluene	Nr
18	CuI	**L1**	K_2CO_3	EtOH	45
19[e]	CuI	**L1**	K_2CO_3	DMSO	85
20[f]	CuI	**L1**	K_2CO_3	DSMO	65



[a]General conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), catalyst (20 mol%), ligand (20 mol%), base (0.6 mmol), solvent (2 mL), stirred at 80 °C or reflux for 6 h.
[b]Isolated yield based on **1a**. Nr = no reaction.
[c]**2a** (0.45 mmol).
[d]CuI in 15 mol% loading.
[e]Reaction at 70 °C.
[f]Reaction at 60 °C.

The entries respectively employing some different ligands and bases suggested that 1,10-phen and K_2CO_3 were most favoured in the reaction (Table 1, entries 8–14). In addition, the reactions performed in different solvents proved that DMSO was the most suitable medium (Table 1, entries 15–18). Finally, the variation in the reaction temperature to 70 °C provided enhanced results in terms of product yield (Table 1, entries 19–20).

Based on the optimised reaction conditions, we then conducted an extended investigation on this approach by synthesising different sulfonylated indoles. According to the results (Table 2), the present synthetic method tolerated a variety of different functional groups in both components, including both electron-donating and electron-withdrawing groups. The property of the substituent did not exhibit evident impact on the reaction results. However, employing aliphatic sulfinates such as sodium methanesulfinate turned out to be ineffective and in addition, employment of *N*-substituted indoles was not possible. No target products were observed in either of these reactions.

On the basis of the acceptable application scope, the potential application of the reaction was further examined by performing the model reaction at 10 times larger scale (using 3 mmol of **1a**). It was found that a good yield (76%) of target product **3a** could be obtained (Eqn 5), demonstrating the present reaction as a practical synthetic protocol.

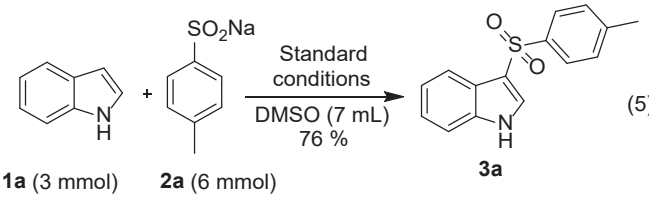
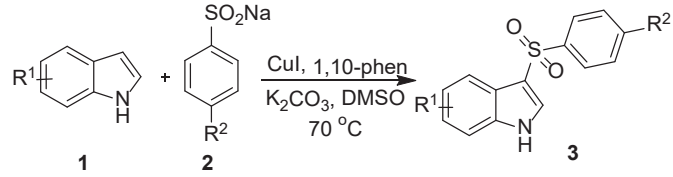


Table 2 Scope for the selective C–H sulfonylation of indoles[a]



Entry	R^1	R^2	Product	Yield[b]/%
1	H	CH_3	**3a**	83
2	5-Br	CH_3	**3b**	75
3	6-Br	CH_3	**3c**	80
4	5-OCH_3	CH_3	**3d**	69
5	4-CHO	CH_3	**3e**	58
6	5-CN	CH_3	**3f**	66
7	5-$COOCH_3$	CH_3	**3g**	68
8	H	H	**3h**	60
9	5-Br	H	**3i**	82
10	6-Br	H	**3j**	74
11	5-CN	H	**3k**	58
12	5-OCH_3	H	**3l**	67
13	H	OCH_3	**3m**	87
14	5-Br	OCH_3	**3n**	76
15	5-$COOCH_3$	NO_2	**3o**	74
16	4-CHO	NO_2	**3p**	66
17	6-Br	Cl	**3q**	59

[a]General conditions: **1** (0.3 mmol), **2** (0.6 mmol), CuI (20 mol%), 1,10-phen (20 mol%), K_2CO_3 (0.6 mmol), DMSO (2 mL), stirred at 70 °C for 6 h.
[b]Isolated yield based on **1**.

Conclusion

In conclusion, by employing the strategy of copper(I) iodide catalysis, we have developed an effective method for the synthesis of indolyl-3-sulfones by selective C-3 sulfonylation. The mild reaction conditions, short reaction time and high efficiency in both conventional laboratory scale and gram scale reactions have proved the usefulness of the present method in the practical synthesis of these important indole derivatives.

Experimental

All chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. All reactions were performed under an air atmosphere. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz instrument using $CDCl_3$ or DMSO-d_6 as solvent. The frequencies for ^{1}H NMR and ^{13}C NMR measurements were 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm using TMS as internal standard. HRMS results were obtained on a micrOTOF-QII Q-TOF mass spectrometer (ESI model).

Synthesis of sulfonylated indoles **3***; general procedure*

Indole **1** (0.3 mmol), sodium sulfinate **2** (0.6 mmol), CuI (0.06 mmol), 1,10-phenanthroline (0.06 mmol), K_2CO_3 (0.6 mmol) and DMSO (2 mL) were added to a 25 mL round bottom flask equipped with a condenser and stirring bar. The mixture was stirred at 70 °C for 6 h. Upon completion (TLC), the mixture was allowed to cool to room temperature and water (10 mL) was added. The resulting suspension was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over Na_2SO_4. After filtration, the acquired solution was collected and the solvent was removed under reduced pressure at *ca.* 50 °C. The residue was subjected to silica gel column chromatography to give pure products by using mixed petroleum ether (60–90 °C) and ethyl acetate (v/v = 2:1) as eluent.

*3-Tosyl-1*H*-indole* (**3a**):[26] Yellow solid; m.p. 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.89 (d, 3 H, *J* = 7.6 Hz), 7.82 (s, 1 H), 7.38–7.37 (m, 1H), 7.22 (t, 4H, *J* = 6.8 Hz), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 140.3, 136.4, 130.0, 129.6, 126.6, 123.8, 123.4, 122.3, 119.2, 116.6, 112.3, 21.3; HRMS (ESI) calcd for $C_{15}H_{14}NO_2S^+$: [M + H]$^+$: 272.0740; found: 272.0743.

*5-Bromo-3-tosyl-1*H*-indole* (**3b**): Brown solid; m.p. 205–206 °C (lit.[25] 193–196 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.46 (s, 1H), 8.26 (s, 1H), 7.90 (s, 1H), 7.86 (d, 2 H, *J* = 8.0 Hz), 7.49 (d, 2H, *J* = 8.0 Hz), 7.38–7.32 (m, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.2, 140.3, 135.1, 132.7, 129.8, 126.2, 125.8, 124.8, 120.6, 114.9, 114.7, 114.4, 20.8; HRMS (ESI) calcd for $C_{15}H_{13}{}^{79}BrNO_2S^+$: [M + H]$^+$: 394.9845; found: 349.9844.

*6-Bromo-3-tosyl-1*H*-indole* (**3c**): Yellow solid; m.p. 202–203 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.39 (s, 1H), 8.24 (s, 1H), 7.88 (d, 2H, *J* = 8.0 Hz), 7.75 (d, 2H, *J* = 8.0 Hz), 7.36 (t, 3H, *J* = 8.0 Hz), 2.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.7, 140.8, 137.7, 132.7, 130.2, 126.7, 125.2, 122.6, 120.8, 116.3, 115.9, 21.3; HRMS (ESI) calcd for $C_{15}H_{13}{}^{79}BrNO_2S^+$: [M + H]$^+$: 394.9845; found: 349.9846.

*5-Methoxy-3-tosyl-1*H*-indole* (**3d**):[24] Black solid; m.p. 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, 1H), 7.87 (d, 2H, *J* = 8.0 Hz), 7.77 (s, 1H), 7.31–7.23 (m, 4H), 6.87 (d, 1H, *J* = 8.0 Hz), 3.82 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 143.4, 140.3, 131.2 130.0, 129.6, 126.5, 124.2, 114.2, 113.1, 100.8, 55.7, 21.4.

*3-Tosyl-1*H*-indole-4-carbaldehyde* (**3e**). White solid; m.p. 203–204 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.90 (s, 1H), 10.74 (s, 1H), 8.54 (s, 1H), 7.92 (d, 1H, *J* = 8.0 Hz), 7.74 (t, 3H, *J* = 8.0 Hz), 7.46–7.38 (m, 3H), 2.34 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.0, 143.5, 139.4, 138.6, 136.9, 129.9, 127.5, 126.2, 123.1, 121.9, 121.3, 119.3, 114.4, 20.8; HRMS (ESI) calcd for $C_{16}H_{14}NO_3S^+$: [M + H]$^+$: 300.0689; found: 300.0688.

*3-Tosyl-1*H*-indole-5-carbonitrile* (**3f**): Brown solid; m.p. 166–167 °C (lit.[25] 183–185 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.80 (s, 1H), 8.44 (s, 1H), 8.27 (s, 1H), 7.97 (d, 2H, *J* = 8.0 Hz), 7.72 (d, 1H), 7.65 (d, 1H, *J* = 8.0 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 2.33 (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 143.5, 139.9, 138.1, 134.0, 129.8, 126.4, 126.0, 123.7, 122.8, 119.6, 116.2, 114.4, 104.2, 20.8; HRMS (ESI) calcd for $C_{16}H_{13}N_2O_2S^+$: [M + H]$^+$: 297.0692; found: 297.0692.

*Methyl 3-tosyl-1*H*-indole-5-carboxylate* (**3g**): Yellow solid, m.p. 205–206 °C (lit. [25] 198–200 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.67 (s, 1H), 8.51 (s, 1H), 8.40 (s, 1H), 7.91–7.88 (m, 3H), 7.65 (d, 1H, *J* = 8 Hz), 7.38 (d, 2H, *J* = 8.0 Hz), 3.91 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 166.5, 143.3, 140.3, 138.9, 133.5, 129.8, 126.1, 123.9, 123.2, 122.7, 120.7, 116.1, 113.0, 52.0, 20.8.

*3-(Phenylsulfonyl)-1*H*-indole* (**3h**): White solid; m.p. 143–144 °C (lit.[26] 149–150 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.33 (s, 1H), 8.24 (d, 1H, *J* = 4.0 Hz), 8.00 (d, 2H, *J* = 4.0 Hz), 7.81 (d, 1H, *J* = 4.0 Hz), 7.57–7.51 (m, 4H), 7.27–7.20 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.4, 136.3, 132.6, 131.6, 129.3, 126.1, 123.1, 123.0, 121.7, 118.5, 114.5, 112.8; HRMS (ESI) calcd for $C_{14}H_{12}NO_2S^+$: [M + H]$^+$: 258.0583; found: 258.0584.

*5-Bromo-3-(phenylsulfonyl)-1*H*-indole* (**3i**):[27] White solid; m.p. 179–180 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.50 (s, 1H), 8.29 (s, 1H), 8.00–7.97 (m, 2H), 7.92 (d, 2H, *J* = 8.0 Hz), 7.58–7.55 (m, 3H), 7.49 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, DMSO): δ 143.64, 135.6, 133.5, 133.3, 129.9, 126.6, 126.4, 125.3, 121.1, 115.5, 115.0, 114.7.

*6-Bromo-3-(phenylsulfonyl)-1*H*-indole* (**3j**):[27] Yellow solid; m.p. 241–242 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.42 (s, 1H), 8.26 (s, 1H), 8.01–7.99 (m, 2H), 7.77–7.73 (m, 2H), 7.62–7.57 (m, 3H), 7.39–7.36 (m, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 143.6, 137.5, 133.3, 133.1, 129.8, 126.6, 125.3, 122.6, 120.8, 116.4, 116.0, 115.5.

*3-(Phenylsulfonyl)-1*H*-indole-5-carbonitrile* (**3k**): White solid; m.p. 242–243 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.77 (s, 1H), 8.43 (s, 1H), 8.24 (s, 1H), 8.05 (d, 2H, *J* = 8.0 Hz), 7.68 (d, 2H, *J* = 8.0 Hz), 7.63–7.55 (m, 4H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 143.2, 138.7, 134.8, 133.5, 130.0, 126.9, 126.5, 124.2, 123.3, 120.1, 116.3, 114.9, 104.8; HRMS (ESI) calcd for $C_{15}H_{11}N_2O_2S^+$: [M + H]$^+$: 283.0536; found: 283.0538.

*5-Methoxy-3-(phenylsulfonyl)-1*H*-indole* (**3l**): Black solid; m.p. 152–153 °C (lit.[28] 91 °C, there are no other literature values); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 7.98 (d, 2H, *J* = 4.0 Hz), 7.78 (d, 1H), 7.49–7.44 (m, 3H), 7.31 (s, 1H), 7.26 (t, 1H, 8.0 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 3.81 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 155.5, 142.6, 132.1, 130.6, 129.7, 128.5, 126.0, 123.7, 113.9, 112.6, 100.2, 55.3.

*3-[(4-Methoxyphenyl)sulfonyl]-1*H*-indole* (**3m**): Brown solid; m.p. 144–145 °C (lit.[26] 157–159 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.23 (s, 1H), 8.15 (s, 1H), 7.91 (d, 2H, *J* = 8.0 Hz), 7.77 (d, 1H, *J* = 8.0 Hz), 7.50 (d, 1H, *J* = 8.0 Hz), 7.24–7.19 (m, 2H), 7.06 (d, 2H, *J* = 8.0 Hz), 3.78 (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 162.8, 136.8, 135.5, 131.4, 128.9, 123.5, 123.4, 122.1, 119.0, 115.9, 114.9, 113.2, 56.0.

*5-Bromo-3-[(4-methoxyphenyl)sulfonyl]-1*H*-indole* (**3n**): Yellow solid; m.p. 212–213 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.45 (s, 1H), 8.23 (s, 1H), 7.91 (d, 3H, *J* = 8.0 Hz), 7.49 (d, 1H, *J* = 8.0 Hz), 7.37 (d, 1H, *J* = 8.0 Hz), 7.06 (d, 2H, *J* = 8.0 Hz), 3.76 (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 162.4, 135.1, 134.7, 132.4, 128.4, 125.8, 124.6, 120.5, 115.1, 114.9, 114.5, 114.3, 55.5; HRMS (ESI) calcd for $C_{15}H_{13}{}^{79}BrNO_3S^+$: [M + H]$^+$: 365.9794; found: 365.9785.

*Methyl 3-[(4-nitrophenyl)sulfonyl]-1*H*-indole-5-carboxylate* (**3o**); Yellow solid; m.p. 248–249 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.90 (s, 1H), 8.56 (s, 1H), 8.52 (s, 1H), 8.41 (d, 2H, *J* = 8.0 Hz), 8.26 (d, 2H, *J* = 8.0 Hz), 7.93 (d, 1H, *J* = 8.0 Hz), 7.69 (d, 1H, *J* = 8.0 Hz), 3.92 (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 166.4, 149.7, 148.2, 139.0, 135.0, 127.6, 124.8, 124.2, 123.6, 122.8, 120.4, 114.0, 113.3, 52.0; HRMS (ESI) calcd for $C_{16}H_{13}N_2O_6S^+$: [M + H]$^+$: 361.0489; found: 361.0483.

*3-[(4-Nitrophenyl)sulfonyl]-1*H*-indole-4-carbaldehyde* (**3p**): White solid; m.p. 234–235 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.1 (s, 1H), 10.6 (s, 1H), 8.7 (s, 1H), 8.40 (d, 2H, *J* = 8.0 Hz), 8.16 (d, 2H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 8.0 Hz), 7.77 (d, 1H, *J* = 8.0 Hz), 7.49 (t, 1H, *J* = 8.0 Hz); ^{3}C NMR (400 MHz, DMSO-d_6): δ 191.4, 149.7, 147.9, 138.7, 138.2, 127.7, 127.7, 124.8, 123.4, 122.7, 121.5, 119.5, 112.5;

HRMS (ESI) calcd for $C_{15}H_{11}N_2O_5S^+$: $[M + H]^+$: 331.0383; found: 331.0395.

6-Bromo-3-[(4-chlorophenyl)sulfonyl]-1H-indole (**3q**): Yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.46 (s, 1H), 8.26 (s, 1H), 7.98 (d, 2H, J = 8.0 Hz), 7.72 (t, 2H), 7.64 (d, 2H, J = 8.0 Hz), 7.38–7.36 (m, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 142.4, 138.3, 137.7, 133.4, 130.0, 128.6, 125.6, 122.5, 120.7, 116.4, 116.0, 114.8; HRMS (ESI) calcd for $C_{14}H_{10}{}^{79}Br^{35}ClNO_2S^+$: $[M + H]^+$: 369.9299; found: 369.9349.

Financial support from the National Natural Science Foundation of China (21562024) and the Natural Science Foundation of Jiangxi Province (20142BAB213007) is gratefully acknowledged.

Electronic Supplementary Information

The ESI (^{1}H and ^{13}C NMR spectra for the products) is available through:
stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

Received 25 April 2016; accepted 5 August 2016
Paper 1604069 doi: 10.3184/174751916X14733526548948
Published online: 23 September 2016

References

1 S. Cacchi and G. Fabrizi, *Chem. Rev.,* 2005, **105**, 2873.
2 G. Zeni and R.C. Larock, *Chem. Rev.*, 2004, **104**, 2285.
3 H. Wu, Y.-P. He and F. Shi, *Synthesis*, 2015, **47**, 1990.
4 G.P. da Silva, A. Ali, R.C. da Silva, H. Jiang and M.W. Paixão, *Chem. Commun. (Cambridge, UK),* 2015, **51**, 15110.
5 M.C. Willis, G.N. Brace and I.P. Holmes, *Angew. Chem., Int. Ed.*, 2005, **44**, 403.
6 X.-L. Lian, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Org. Lett.*, 2014, **16**, 3360.
7 B. Huang, D. Hu, J. Wang, J.-P. Wan and Y. Liu, *Tetrahedron Lett.*, 2015, **56**, 2551.
8 A. Suárez, M. Gohain, M.A. Fernández-Rodríguez and R. Sanz, *J. Org. Chem.*, 2015, **80**, 10421.
9 J. Zhao, P. Li, C. Xia and F. Li, *Chem.- Eur. J.*, 2015, **21**, 16383.
10 A. Taheri, B. Lai, C. Cheng and Y. Gu, *Green Chem.*, 2015, **17**, 812.
11 F. Li, E.H. Elhussin, S. Li, H. Zhou, J. Wu and Y. Tian, *J. Org. Chem.*, 2015, **80**, 10605.
12 X. Huang, R. Goddard and N. Maulide, *Chem. Commun. (Cambridge, UK)*, 2013, **49**, 4292.
13 Y. Liao, Y. Peng, H. Qi, G.-J. Deng, H. Gong and C.-J. Li, *Chem. Commun. (Cambridge, UK)*, 2015, **51**, 1031.
14 P. Sang, Z. Chen, J. Zou and Y. Zhang, *Green Chem.*, 2013, **15**, 2096.
15 W. Ge and Y. Wei, *Green Chem.*, 2012, **14**, 2066.
16 Y. Liu, Y. Zhang, C. Hu, J.-P. Wan and C. Wen, *RSC Adv.*, 2014, **4**, 35528.
17 M. Chen, Z.-T. Huang and Q.-Y. Zheng, *Chem. Commun. (Cambridge, UK)*, 2012, **48**, 11686.
18 T. Hostier, V. Ferey, G. Ricci, D.G. Pardo and J. Cossy, *Chem. Commun. (Cambridge, UK)*, 2015, **51**, 13898.
19 F.-L. Yang and S.-K. Tian, *Angew. Chem., Int. Ed.*, 2013, **52**, 4929.
20 J.-K. Qiu, W.-J. Hao, D.-C. Wang, P. Wei, J. Sun, B. Jiang and S.-J. Tu, *Chem. Commun. (Cambridge, UK)*, 2014, **50**, 14782.
21 F. Xiao, H. Xie, S. Liu and G.-J. Deng, *Adv. Synth. Catal.,* 2014, **356**, 364.
22 F. Xiao, H. Chen, H. Xie, S. Chen, L. Yang and G.-J. Deng, *Org. Lett.*, 2014, **16**, 50.
23 M. Rahman, M. Ghosh, A. Hajra and A. Majee, *J. Sulfur Chem.*, 2013, **34**, 342.
24 J.S. Yadav, B.V.S. Reddy, A.D. Krishna and T. Swamy, *Tetrahedron Lett.*, 2003, **44**, 6055.
25 Y. Yang, W. Li, C. Xia, B. Ying, C. Shen and P. Zhang, *ChemCatChem*, 2016, **8**, 304.
26 G. Tocco, M. Begala, F. Esposito, P. Caboni, V. Cannas and E. Tramontano, T*etrahedron Lett.*, 2013, **54**, 6237.
27 G.D. Heffernan, R.D. Coghlan, E.S. Manas, R.E. McDevitt, Y. Li, P.E. Mahaney, A.J. Robichaud, C. Huselton, P. Alfinito, J.A. Bray, S.A. Cosmi, G.H. Johnston, T. Kenney, E. Koury, R.C. Winneker, D.C. Deecher and E.J. Trybulski, *Bioorg. Med. Chem.,* 2009, **17**, 7802.
28 B.C.G. Söderberg, S.R. Banini, M.R. Turner, A.R. Minter and A.K. Arrington, *Synthesis,* 2008, 903.