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An internal oxidant-directing strategy enabling transition metal-free C–S bond ligation

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ABSTRACT

Organic sulfur compounds have broad applications in biology, medicine and material sciences and intensive efforts have been devoted to developing mild and general C–S bond-forming methods. However, a mild, transition-metal-free, direct C–H bond functionalization method remains elusive. Here, we report the use of an internal oxidant-directing strategy to achieve this goal. The cascade reactions described here show excellent chemoselectivity and a wide substrate scope for both oxyamines and sulfenylation reagents. This study enlarges the synthesis toolbox for preparing structurally diverse sulfilimines under mild conditions.

1. Introduction

Organic sulfur compounds play important roles in material, biological, and pharmaceutical sciences [1–6]. In materials science, the presence of sulfur components is an important determinant of physical, electronic, and surface properties [1]. In biology, sulfur bonding helps maintain the strength and shape of proteins and mediates electron transfer reactions [7]. Traditional methods for construction of a C–S bond involve thiol coupling with organic halides or thiol addition to unsaturated C–C bonds [8]. However, such classic methods suffer from significant limitations, such as the use of malodorous sulfur sources, highly pre-functionalized precursors and the formation of undesired toxic by-products.

In parallel with the development of modern C–C and C–N coupling reactions, a number of highly efficient coupling methods have been developed in recent decades to produce a C–S bond from a C–H bond [9]. Two major strategies among these methods are transition-metal-catalyzed C–H bond functional-ization and oxidative C–S bond coupling (Schemes 1a and 1b). In the first strategy, various transition metal complexes were used to selectively functionalize a C–H bond, enabling the subsequent C–S bond formation. In the latter strategy, the C–S bond formation was realized under oxidative, transition metal-free conditions either through a radical process or by forming an active organosulfur intermediate. However, many reported reactions suffered from requirement of a high reaction temperature, poor substrate scope, or low selectivity. Recently, pivotal progress has been made in C–H sulfenylation of arenes under metal-free conditions [10–13], but a mild, transition metal-free method of direct C–H bond functionalization still remains elusive.

The sulfilimine bond (S=N) is a useful functional group and can undergo unique rearrangements in the synthesis of natural products or pharmacological agents [14–21]. However, the synthesis of sulfilimines traditionally involves oxidative imination of thioethers [22–28], and this requires the preparation of thioethers and the use of elaborate imidation reagents, which in turn limit the scope of synthetic sulfilimines.

Based on our continuing effort in O–N bond-directed synthesis of *o*-functionalized phenols [29–31] and our previous metal-free

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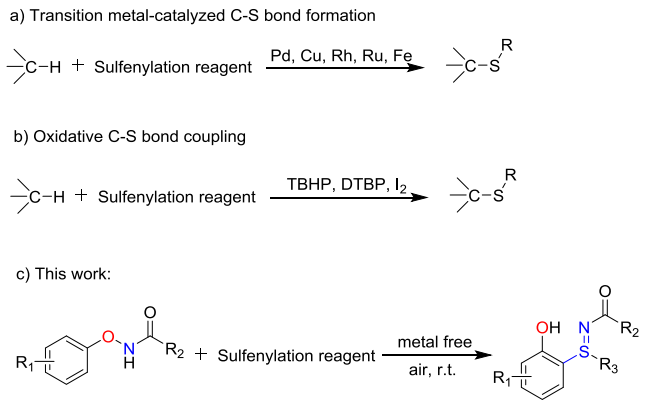


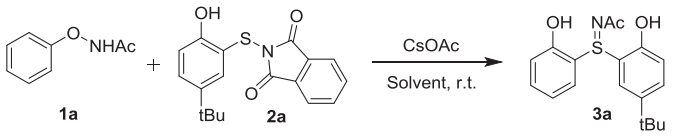
Scheme 1. C–S bond forming strategies. a) Transition metal-catalyzed C–S bond formation. b) Oxidative C–S bond coupling. c) An internal oxidant-directing strategy.

coupling method to synthesize sulfilimines [32], we sought to further extend the synthesis toolbox. Accordingly, we developed more sulfenylation reagents for synthesis of structurally diverse sulfilimines under mild conditions (Scheme 1c).

2. Results and discussion

To begin this study, we studied the reaction of *N*-phenoxyacetamide (**1a**) with 2-((5-(*t*-butyl)-2-hydroxyphenyl)-thio)isoindoline-1,3-dione (**2a**) (Table 1). Under the standard conditions described in our previous reports [32], CsOAc (0.5 equiv) was used in MeOH at room temperature for 3 h to examine the coupling reaction. The reaction proceeded smoothly and furnished a phenolic sulfilimine product (**3a**) in 78% yield (Table 1, entry 1). We examined different bases, but failed to obtain a higher yield. Then we turned our attention to evaluation of the effect of solvent and screened a variety of solvents. The reaction in THF delivered a yield of 48% but Et_2O proved to be the most effective solvent, affording the product in 90% yield (Table 1, entry 4), suggesting that the solvent plays a key role in this reaction.

Table 1
Optimization of reaction conditions.



Entry	Solvent	time	Additive (eq.)	Yield (%)[b]
1	MeOH	3 h	CsOAc (0.5)	78
2	DCM	3 h	CsOAc (0.5)	80
3	$CHCl_3$	3 h	CsOAc (0.5)	78
4	Et_2O	3 h	CsOAc (0.5)	90
5	CH_3CN	3 h	CsOAc (0.5)	76
6	THF	3 h	CsOAc (0.5)	48
7	dioxane	3 h	CsOAc (0.5)	64
8	$PhCH_3$	3 h	CsOAc (0.5)	76
9	Benzene	3 h	CsOAc (0.5)	76
10	Et_2O	3 h	CsOAc (0.5)	88[a]
11	Acetone	3 h	CsOAc (0.5)	80
12	t-AmOH	3 h	CsOAc (0.5)	68
13	TFE	3 h	CsOAc (0.5)	62
14	$PhCF_3$	3 h	CsOAc (0.5)	80
15	Et_2O	8 h	CsOAc (0.5)	90

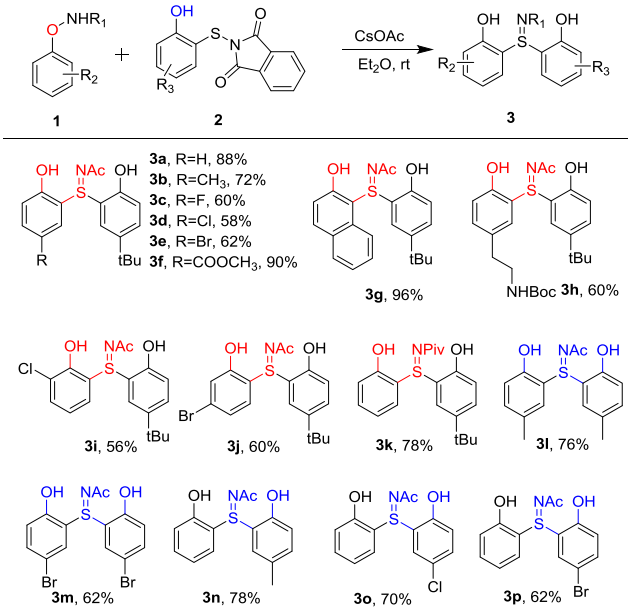
[a] Yields of isolated products.
[b] Crude yield, as determined by ^1H NMR spectroscopy with 1,4-dimethoxy-benzene as an internal standard.

With the optimum conditions in hand, a series of oxyamide substrates and *o*-phenolic sulfenylation reagents were tested in this cascade reaction (Table 2). *N*-Phenoxyacetamide with either electron-rich or electron-deficient substituents reacted smoothly. The reaction was compatible with a variety of functional groups such as fluoro, chloro, bromo, ester and amide. The naphthyl substrate afforded high regioselectivity and excellent yield, and functionalized only the *ortho* C–H at C-1 (**3g**). The *m*-substituted *N*-phenoxyacetamide reacted at only the less hindered *o*-position. The high degree of regiospecificity manifested in **3j** suggests that the steric effect is important. Replacing the acetyl group of substrate **1** with the more bulky pivaloyl moiety also affords the sulfilimine product (**3k**) in good yield. Symmetrical diphenolic sulfilimines (**3l**, **3m**) can be obtained by controlling the substituents R_2 and R_3. In addition, a series of *o*-phenolic sulfenylation reagents were shown to reacted with *N*-phenoxy- acetamide to afford products **3n**–**3p** in 62–78% yield.

To extend the diversity of sulfilimines, we tested a series of modified styrene sulfenylation reagents. Thus the product **5a** was isolated in high yield when the solvent Et_2O was changed to benzene (Table S1). The structure of **5a** was confirmed by NMR spectroscopy, HR mass specrometry, and X-ray crystallography (Fig. S1 in Supplementary Data). As shown in Table 3, various aryoxyamides and sulfenylation reagents (**4**) with different substituents including electron-neutral, electron-donating and electron-withdrawing groups were well tolerated, providing the desired products in high yields and with good to excellent Z/E ratios.

In general, *o*-phenolic sulfenylation reagents (**2**) and modified styrene sulfenylation reagents (**4**) are usually prepared by the reaction of *N*-(chlorosulfenyl)phthalimide with phenols or styrene, respectively. If the modified sulfenylation reagents can be produced *in situ*, a more practical and attractive one-pot protocol could be developed. In fact, it was found that treatment of a mixture of *N*-

Table 2
Substrate scope of aryloxyamides and *ortho*-phenolic sulfenylation reagents.[a]



[a] Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol) and CsOAc (0.5 equiv) in Et_2O (2 mL) at rt for 3 h. Yields of isolated products are given.

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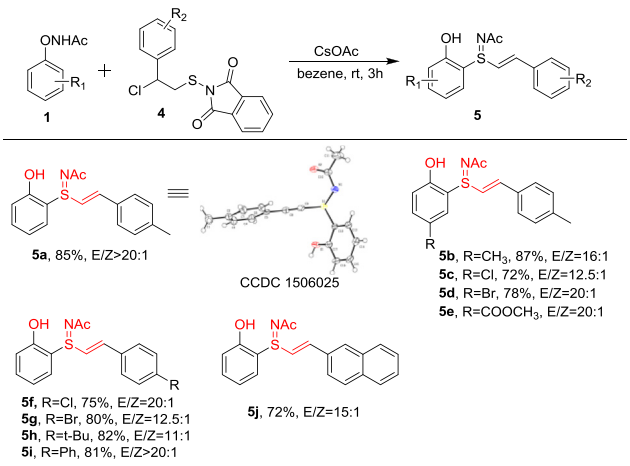
Table 3
Substrate scope of aryloxyamides and modified styrene sulfenylation reagents **4**.[a]

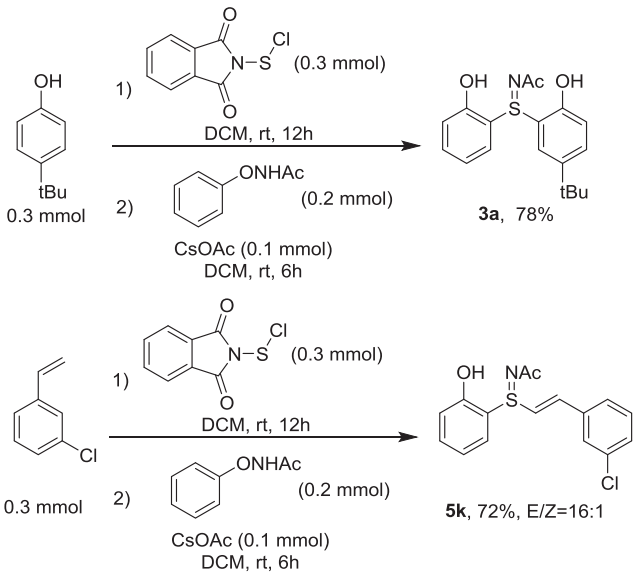


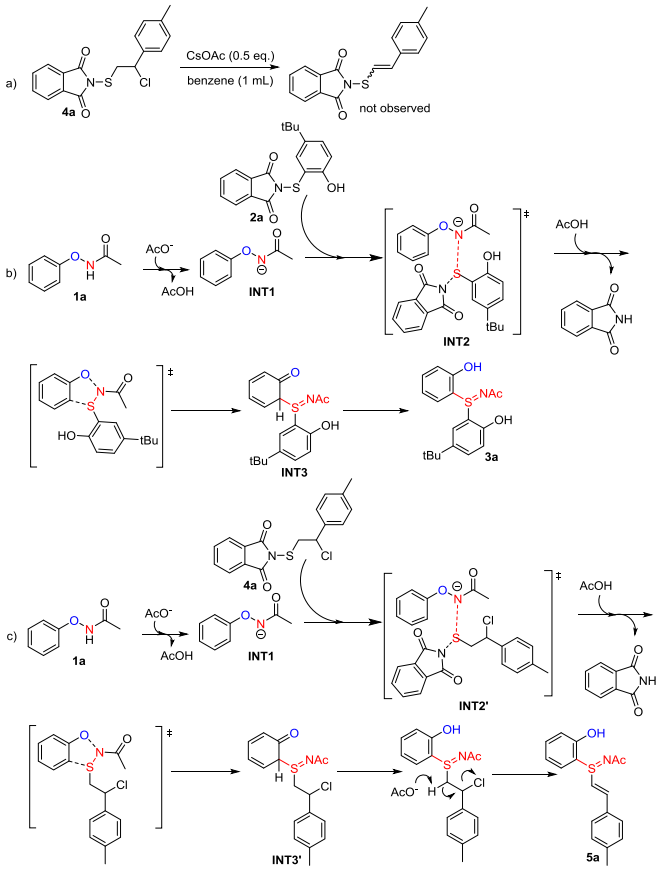
[a] Reaction conditions: **1** (0.2 mmol), **4** (0.24 mmol) and CsOAc (0.5 equiv) in benzene (2 mL) at room temperature for 3 h. Yields of isolated products are given. The E/Z ratio was determined by ^{1}H NMR.

(chlorosulfenyl)phthalimide with 4-*t*-butyl-phenol or 3-chlorostyrene in CH_2Cl_2 at room temperature for 12 h, and subsequent addition of *N*-phenoxyacetamide and CsOAc, after 6 h led to the formation of the corresponding sulfilimines (**3a**, **5k**) in 78% and 72% yields, respectively (Table 4).

To further probe the reaction mechanism, the mixture of thiophthalimide **4a**/CsOAc/toluene in the absence of *N*-phenoxyacetamide was conducted and the corresponding elimination product was not observed (scheme 2a). On the basis of these results and our earlier work [32], a mechanism for the convenient synthesis of *o*-phenolic sulfilimines is proposed and is shown in Scheme 2. In the presence of a weak base such as CsOAc [33], an intermediate (**INT1**) is generated from *N*-phenoxyacetamide (**1a**), and then attacks the sulfur of the sulfenylation reagent (**2a or 4a**) to form the intermediate (**INT2 or INT2'**). The reaction then proceeds

Table 4
One-pot protocol of *N*-phenoxyacetamide **1** reacted with phenols or styrene.





Scheme 2. Proposed reaction pathway for the cascade reaction.

through an intramolecular [2,3] sigmatropic rearrangement followed by aromatization to afford the product (**3a**). In Scheme 2c, the β-H elimination in the presence of $^-$OAc occurred to afford the product **5a**.

3. Conclusion

In conclusion, a strategy for the synthesis of diverse phenolic sulfilimines using different sulfenylation reagents under mild conditions has been developed. Various oxyamides and sulfenylation reagents are well tolerated and afford phenolic sulfilimines in moderate to excellent isolated yields (56–96%). Symmetrical diphenolic sulfilimines can be obtained by controlling the substituent groups of both substrates, and a convenient and efficient one-pot reaction for the synthesis of sulfilimines has been developed. Research into the applications of oxyamides to other types of cascade reactions and the development of other new approaches to the synthesis of sulfilimines is currently in progress in our laboratory.

4. Experimental section

4.1. General information

Commercially available chemicals were obtained from Sigma-Aldrich, Alfa Aesar, TCI and Aladdin and used as received unless otherwise stated. Reactions were monitored with analytical thin-layer chromatography (TLC) on silica. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker nuclear resonance (300 MHz, 400 MHz and 500 MHz) spectrometers unless otherwise specified,

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respectively. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm). HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at Peking University, Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

4.2. General procedure for C–S bond coupling reaction (Tables 2 and 3)

N-phenoxyacetamide (**1**) (0.2 mmol), sulfenylation reagent (0.24 mmol), and CsOAc (0.10 mol) were weighed into a 25 mL pressure tube, to which was added Et_2O or benzene (2 mL). The reaction vessel was stirred at room temperature for 3 h. Then the mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to afford the corresponding product.

4.2.1. (Z)-N-((5-(tert-butyl)-2-hydroxyphenyl)(2-hydroxyphenyl)-λ4-sulfanylidene)acetamide (**3a**)

White solid, yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.50 (s, 2H), 7.48–7.39 (m, 2H), 7.18 (dd, J = 8.1, 1.5 Hz, 1H), 7.14 (d, J = 2.3 Hz, 1H), 7.07 (dd, J = 8.3, 1.0 Hz, 1H), 7.00 (d, J = 8.7 Hz, 1H), 6.93–6.87 (m, 1H), 2.17 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.5, 159.3, 157.1, 144.1, 134.7, 132.2, 128.9, 125.3, 120.9, 120.2, 119.9, 116.4, 114.2, 34.3, 31.1, 23.9. HRMS (ESI) calculated for $C_{18}H_{28}NO_2S$ $[M-H]^-$: 330.1164; Found: 330.1165.

4.2.2. (Z)-N-((5-(tert-butyl)-2-hydroxyphenyl)(2-hydroxy-5-methylphenyl)-4-sulfanylidene)acetamide (**3b**)

White solid, yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, 2H), 7.46 (dd, J = 8.7, 1.4 Hz, 1H), 7.23 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 1.6 Hz, 1H), 7.00 (t, J = 8.1 Hz, 2H), 6.95 (s, 1H), 2.20 (s, 3H), 2.15 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.4, 157.2, 157.0, 144.1, 135.7, 132.2, 130.6, 128.6, 125.4, 120.1, 120.0, 115.3, 114.9, 34.3, 31.1, 23.8, 20.4. HRMS (ESI) calculated for $C_{19}H_{22}NO_3S$ $[M-H]^-$:344.1320; Found: 344.1327.

4.2.3. (E)-N-((5-(tert-butyl)-2-hydroxyphenyl)(5-fluoro-2-hydroxyphenyl)-4-sulfanylidene)acetamide (**3c**)

White solid, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 2H), 7.48 (dd, J = 8.8, 2.4 Hz, 1H), 7.22 (d, J = 2.3 Hz, 1H), 7.10 (ddd, J = 9.1, 7.7, 3.0 Hz, 1H), 7.02–6.96 (m, 2H), 6.92 (dd, J = 7.7, 3.0 Hz, 1H), 2.18 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.7, 157.4, 157.3, 154.9, 144.2, 132.5, 125.4, 122.1, 121.8, 121.34, 121.26, 120.0, 118.7, 118.6, 114.3, 114.1, 112.2, 34.3, 31.1, 23.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.99. HRMS (ESI) calculated for $C_{18}H_{19}FNO_3S$ $[M-H]^-$:348.1070; Found: 348.1073.

4.2.4. (E)-N-((5-(tert-butyl)-2-hydroxyphenyl)(5-chloro-2-hydroxyphenyl)-4-sulfanylidene)acetamide (**3d**)

White solid, yield: 58%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.39 (s, 2H), 7.46 (dd, J = 8.7, 2.2 Hz, 1H), 7.31–7.27 (m, 1H), 7.24 (d, J = 2.3 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 6.93 (d, J = 8.7 Hz, 1H), 2.20 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.6, 157.5, 157.2, 144.2, 134.5, 132.4, 127.5, 125.5, 125.2, 121.3, 120.0, 118.7, 113.1, 34.3, 31.1, 23.9. HRMS (ESI) calculated for $C_{18}H_{19}ClNO_3S$ $[M-H]^-$:364.0774; Found: 364.0779.

4.2.5. (E)-N-((5-bromo-2-hydroxyphenyl)(5-(tert-butyl)-2-hydroxyphenyl)-4-sulfanylidene)acetamide (**3e**)

White solid, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 2H), 7.51–7.42 (m, 2H), 7.29 (d, J = 2.1 Hz, 1H), 7.20 (d, J = 2.1 Hz, 1H), 6.99 (d, J = 8.7 Hz, 1H), 6.90 (d, J = 8.8 Hz, 1H), 2.19 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.6, 158.0, 157.2, 144.3, 137.4, 132.6, 130.4, 125.3, 121.8, 120.1, 119.0, 113.0, 112.2, 34.4, 31.1, 23.9. HRMS (ESI) calculated for $C_{18}H_{19}BrNO_3S$ $[M-H]^-$:408.0269; Found: 408.0271.

4.2.6. Methyl(E)-3-(N-acetyl-S-(5-(tert-butyl)-2-hydroxyphenyl)sulfinimidoyl)-4-hydroxybenzoate (**3f**)

White solid, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 2H), 8.05 (d, J = 2.0 Hz, 1H), 7.99 (dd, J = 8.7, 1.9 Hz, 1H), 7.38 (dd, J = 8.7, 2.3 Hz, 1H), 7.25 (d, J = 2.3 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 6.90 (d, J = 8.7 Hz, 1H), 3.84 (s, 3H), 2.22 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.3, 165.4, 163.0, 156.5, 144.0, 135.5, 132.3, 130.7, 124.7, 122.6, 119.6, 119.5, 115.9, 115.1, 52.3, 34.3, 31.1, 24.1. HRMS (ESI) calculated for $C_{20}H_{22}NO_5S$ $[M-H]^-$:388.1219; Found: 388.1226.

4.2.7. (E)-N-((5-(tert-butyl)-2-hydroxyphenyl)(2-hydroxynaphthalen-1-yl)-4-sulfanylidene)acetamide (**3g**)

White solid, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.24 (s, 2H), 8.00 (d, J = 9.0 Hz, 1H), 7.77 (dd, J = 15.9, 8.2 Hz, 2H), 7.48–7.42 (m, 1H), 7.40 (dd, J = 8.6, 2.4 Hz, 1H), 7.38–7.33 (m, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.05 (d, J = 8.6 Hz, 1H), 6.98 (d, J = 2.3 Hz, 1H), 2.19 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.3, 163.2, 155.5, 144.6, 135.8, 132.6, 131.1, 128.9, 128.8, 128.3, 124.4, 124.0, 121.4, 120.8, 120.2, 34.2, 30.9, 23.9. HRMS (ESI) calculated for $C_{22}H_{22}NO_3S$ $[M-H]^-$:380.1320; Found: 380.1327.

4.2.8. Tert-butyl(Z)-(3-(N-acetyl-S-(5-(tert-butyl)-2-hydroxyphenyl)sulfinimidoyl)-4-hydroxyphenethyl)carbamate (**3h**)

White solid, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 2H), 7.46 (dd, J = 8.7, 2.3 Hz, 1H), 7.29 (s, 1H), 7.13 (s, 1H), 7.03 (dd, J = 10.8, 8.8 Hz, 3H), 4.53 (s, 1H), 3.25 (d, J = 6.2 Hz, 2H), 2.67 (t, J = 6.9 Hz, 2H), 2.17 (s, 3H), 1.42 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.4, 158.2, 156.8, 155.8, 144.1, 139.1, 135.2, 132.2, 131.7, 128.6, 125.1, 120.4, 119.9, 115.3, 79.4, 41.6, 35.1, 34.3, 31.1, 28.4, 23.9. HRMS (ESI) calculated for $C_{25}H_{33}N_2O_5S$ $[M-H]^-$:473.2110; Found: 473.2114.

4.2.9. (E)-N-((5-(tert-butyl)-2-hydroxyphenyl)(3-chloro-2-hydroxyphenyl)-4-sulfanylidene)acetamide (**3i**)

White solid, yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (s, 2H), 7.50 (dd, J = 8.6, 2.2 Hz, 1H), 7.18 (d, J = 2.2 Hz, 1H), 7.12–7.05 (m, 2H), 7.03 (d, J = 8.7 Hz, 1H), 6.88 (dd, J = 8.6, 1.4 Hz, 1H), 2.19 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.6, 159.7, 157.4, 144.3, 140.7, 132.5, 129.6, 125.4, 121.4, 120.4, 120.1, 116.2, 112.7, 34.4, 31.1, 23.8. HRMS (ESI) calculated for $C_{18}H_{19}ClNO_3S$ $[M-H]^-$:364.0774; Found: 364.0780.

4.2.10. (Z)-N-((4-bromo-2-hydroxyphenyl)(5-(tert-butyl)-2-hydroxyphenyl)-4-sulfanylidene)acetamide (**3j**)

White solid, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 7.46 (d, J = 7.0 Hz, 1H), 7.23 (d, J = 1.9 Hz, 1H), 7.16 (s, 1H), 7.06 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 2.19 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.6, 159.3, 157.2, 144.2, 132.4, 129.3, 128.8, 125.3, 124.2, 123.2, 119.9, 116.9, 112.8, 34.4, 31.2, 24.0. HRMS (ESI) calculated for $C_{18}H_{19}BrNO_3S$ $[M-H]^-$:408.0269; Found: 408.0276.

4.2.11. (Z)-N-((5-(tert-butyl)-2-hydroxyphenyl)(2-hydroxyphenyl)-4-sulfanylidene)pivalamide (**3k**)

White solid, yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 2H), 7.33 (dtd, J = 9.5, 8.4, 1.5 Hz, 3H), 7.27–7.24 (m, 1H), 6.98 (dd, J = 8.3, 1.0 Hz, 1H), 6.90–6.84 (m, 1H), 6.81 (d, J = 8.7 Hz, 1H), 1.29 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 159.3, 156.7, 143.5,

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134.3, 131.7, 128.8, 124.4, 120.5, 119.9, 119.1, 116.6, 114.9, 40.4, 34.3, 31.2, 28.3. HRMS (ESI) calculated for $C_{21}H_{26}NO_3S$ $[M-H]^-$:372.1633; Found: 372.1637.

*4.2.12. N-(bis(2-hydroxy-5-methylphenyl)-4-sulfanylidene) acetamide (**3l**)*

White solid, yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 2H), 7.29–7.27 (m, 2H), 7.03 (d, J = 8.5 Hz, 2H), 6.92 (s, 2H), 2.23 (s, 6H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.5, 157.3, 135.8, 130.7, 128.7, 120.4, 115.1, 23.8, 20.4. HRMS (ESI) calculated for $C_{16}H_{16}NO_3S$ $[M-H]^-$:302.0851; Found: 302.0858.

*4.2.13. N-(bis(5-bromo-2-hydroxyphenyl)-4-sulfanylidene) acetamide (**3m**)*

White solid, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 2H), 7.50 (dd, J = 8.8, 2.3 Hz, 2H), 7.38 (d, J = 2.3 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.8, 158.1, 137.8, 130.4, 122.0, 117.0, 112.4, 24.0. HRMS (ESI) calculated for $C_{14}H_{10}Br_2NO_3S$ $[M-H]^-$:429.8748; Found: 429.8753.

*4.2.14. (Z)-N-((2-hydroxy-5-methylphenyl)(2-hydroxyphenyl)-λ4-sulfanylidene)acetamide (**3n**)*

White solid, yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 2H), 7.44–7.38 (m, 1H), 7.23 (dd, J = 8.4, 1.7 Hz, 1H), 7.16 (dd, J = 8.1, 1.5 Hz, 1H), 7.06 (dd, J = 8.3, 1.0 Hz, 1H), 6.97 (d, J = 8.5 Hz, 2H), 6.92–6.86 (m, 1H), 2.21 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.5, 159.2, 157.3, 135.7, 134.7, 130.6, 128.9, 128.6, 120.9, 120.4, 120.2, 116.4, 114.6, 23.9, 20.4. HRMS (ESI) calculated for $C_{15}H_{14}NO_3S$ $[M-H]^-$:288.0694; Found: 288.0701.

*4.2.15. (Z)-N-((5-chloro-2-hydroxyphenyl)(2-hydroxyphenyl)-λ4-sulfanylidene)acetamide (**3o**)*

White solid, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (s, 2H), 7.43–7.33 (m, 2H), 7.31–7.24 (m, 2H), 6.99 (d, J = 8.2 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.6, 159.1, 157.2, 134.8, 134.4, 128.6, 127.1, 125.4, 121.0, 120.8, 120.0, 118.1, 114.7, 24.2. HRMS (ESI) calculated for $C_{14}H_{11}ClNO_3S$ $[M-H]^-$:308.0148; Found: 308.0153.

*4.2.16. (Z)-N-((5-bromo-2-hydroxyphenyl)(2-hydroxyphenyl)-λ4-sulfanylidene)acetamide (**3p**)*

White solid, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (s, 2H), 7.45 (dd, J = 11.3, 4.5 Hz, 2H), 7.30 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.0, 159.4, 158.1, 137.5, 135.0, 130.4, 128.9, 121.9, 121.0, 120.5, 118.2, 114.5, 112.2, 24.0. HRMS (ESI) calculated for $C_{14}H_{11}BrNO_3S$ $[M-H]^-$:351.9643; Found: 351.9648.

*4.2.17. N-((E)-(2-hydroxyphenyl)((E)-4-methylstyryl)-4-sulfanylidene)acetamide (**5a**)*

White solid, yield: 85%, E/Z > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.32 (m, 5H), 7.18 (d, J = 8.0 Hz, 2H), 7.04 (dd, J = 8.4, 1.0 Hz, 1H), 6.97–6.91 (m, 1H), 6.76 (d, J = 15.3 Hz, 1H), 2.37 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 160.2, 142.8, 141.5, 134.3, 130.2, 129.7, 128.9, 128.1, 120.3, 120.2, 119.6, 114.9, 24.4, 21.5. HRMS (ESI) calculated for $C_{17}H_{16}NO_2S$ $[M-H]^-$:298.0902; Found: 298.0909.

*4.2.18. N-((E)-(2-hydroxy-5-methylphenyl)((E)-4-methylstyryl)-λ4-sulfanylidene)acetamide (**5b**)*

White solid, yield: 87%, E/Z = 16:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.38 (d, J = 15.2 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.17 (dd, J = 13.9, 8.2 Hz, 4H), 6.92 (d, J = 8.1 Hz, 1H), 6.78 (d, J = 15.3 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 142.8, 141.4, 135.1, 130.3, 130.0, 129.7, 129.6, 128.3, 128.1, 127.1, 119.7, 119.3, 24.4, 21.5, 20.3. HRMS (ESI) calculated for $C_{18}H_{18}NO_2S$ $[M-H]^-$:312.1058; Found: 312.1063.

*4.2.19. N-((E)-(5-chloro-2-hydroxyphenyl)((E)-4-methylstyryl)-λ4-sulfanylidene)acetamide (**5c**)*

White solid, yield: 72%, E/Z = 12.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 15.4 Hz, 1H), 7.35 (t, J = 5.6 Hz, 3H), 7.32 (dd, J = 8.8, 2.5 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 15.3 Hz, 1H), 2.37 (d, J = 6.4 Hz, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.1, 158.3, 143.5, 141.7, 134.0, 130.1, 129.8, 128.2, 127.4, 124.9, 121.2, 118.7, 117.0, 24.4, 21.5. HRMS (ESI) calculated for $C_{17}H_{15}ClNO_2S$ [M – H]–:332.0512; Found: 332.0516.

*4.2.20. N-((E)-(5-bromo-2-hydroxyphenyl)((E)-4-methylstyryl)-λ4-sulfanylidene)acetamide (**5d**)*

White solid, yield: 78%, E/Z = 20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 2.4 Hz, 1H), 7.45–7.37 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.8 Hz, 1H), 6.67 (d, J = 15.3 Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1, 158.5, 143.3, 141.6, 136.7, 130.1, 130.0, 129.7, 128.2, 121.4, 118.7, 117.9, 111.5, 24.4, 21.5. HRMS (ESI) calculated for $C_{17}H_{15}BrNO_2S$ [M – H]–: 376.0007; Found: 376.0011.

*4.2.21. Methyl 3-((E)-N-acetyl-S-((E)-4-methylstyryl) sulfinimidoyl)-4-hydroxybenzoate (**5e**)*

White solid, yield: 92%, E/Z = 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.3, 1.6 Hz, 2H), 7.45 (d, J = 15.4 Hz, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.04 (dd, J = 7.9, 1.2 Hz, 1H), 6.73 (d, J = 15.3 Hz, 1H), 3.89 (s, 3H), 2.37 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.4, 165.4, 164.4, 143.7, 141.8, 135.3, 131.2, 130.0, 129.8, 128.3, 122.2, 120.2, 119.4, 114.5, 52.2, 24.3, 21.5. HRMS (ESI) calculated for $C_{19}H_{20}NO_4S$ $[M+H]^+$: 358.1113; Found: 358.1109.

*4.2.22. N-((E)-((E)-4-chlorostyryl)(2-hydroxyphenyl)-4-sulfanylidene)acetamide (**5f**)*

White solid, yield: 75%, E/Z = 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.40–7.29 (m, 7H), 7.00 (d, J = 8.2 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 15.4 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3, 159.4, 141.3, 136.9, 134.5, 131.4, 131.2, 129.34, 129.27, 129.1, 128.6, 128.4, 120.8, 120.5, 119.7, 24.3; HRMS (ESI) calculated for $C_{16}H_{13}ClNO_2S$ $[M-H]^-$:318.0356; Found: 318.0369.

*4.2.23. N-((E)-((E)-4-bromostyryl)(2-hydroxyphenyl)-4-sulfanylidene)acetamide (**5g**)*

White solid, yield: 80%, E/Z = 12.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.44–7.35 (m, 2H), 7.33–7.27 (m, 3H), 7.01 (dd, J = 8.3, 1.0 Hz, 1H), 6.95 (td, J = 8.0, 1.2 Hz, 1H), 6.78 (d, J = 15.3 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0, 160.0, 140.9, 134.4, 132.2, 131.9, 129.5, 128.6, 125.2, 121.7, 120.3, 120.1, 114.5, 24.4; HRMS (ESI) calculated for $C_{16}H_{13}BrNO_2S$ $[M-H]^-$: 361.9850; Found: 361.9854.

*4.2.24. N-((E)-((E)-4-(tert-butyl)styryl)(2-hydroxyphenyl)-4-sulfanylidene)acetamide (**5h**)*

White solid, yield: 82%, E/Z = 11:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.33 (m, 7H), 6.97 (d, J = 7.9 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 15.3 Hz, 1H), 2.17 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8, 159.7, 154.4, 142.4, 134.1, 130.2, 128.4, 127.9, 125.9, 120.2, 119.81, 119.75, 115.5, 34.9, 31.1, 24.4; HRMS (ESI) calculated for $C_{20}H_{22}NO_2S$ $[M-H]^-$: 340.1371; Found: 340.1377.

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*4.2.25. N-((E)-((E)-2-([1,1′-biphenyl]-4-yl)vinyl)(2-hydroxyphenyl)-4-sulfanylidene)acetamide (**5i**)*

White solid, yield: 81%, E/Z > 20:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.58 (m, 4H), 7.53 (d, J = 8.3 Hz, 2H), 7.50–7.47 (m, 1H), 7.45 (ddd, J = 7.8, 4.0, 1.8 Hz, 3H), 7.42–7.38 (m, 2H), 7.07 (dd, J = 8.4, 1.0 Hz, 1H), 6.99–6.94 (m, 1H), 6.86 (dd, J = 12.2, 8.3 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 160.3, 143.6, 142.2, 139.8, 134.4, 131.9, 130.5, 128.9, 128.6, 128.0, 127.6, 127.1, 120.7, 120.4, 120.3, 114.7, 24.4; HRMS (ESI) calculated for $C_{22}H_{18}NO_2S$ $[M-H]^-$: 360.1058; Found: 360.1062.

*4.2.26. N-((E)-(2-hydroxyphenyl)((E)-2-(naphthalen-2-yl)vinyl)-λ4-sulfanylidene)acetamide (**5j**)*

White solid, yield: 72%, E/Z = 15:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.83–7.73 (m, 4H), 7.59–7.47 (m, 5H), 7.43–7.36 (m, 1H), 7.16–7.04 (m, 2H), 6.95 (t, J = 7.6 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 159.3, 143.7, 134.7, 134.4, 133.0, 130.4, 130.2, 128.9, 128.68, 128.66, 127.81, 127.77, 127.0, 123.2, 120.5, 119.6, 119.3, 114.9, 24.2. HRMS (ESI) calculated for $C_{20}H_{16}NO_2S$ $[M-H]^-$: 334.0902; Found: 334.0910.

*4.2.27. N-((E)-((E)-3-chlorostyryl)(2-hydroxyphenyl)-l4-sulfanylidene)acetamide (**5k**)*

White solid, yield: 72%, E/Z = 15:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.4, 1.5 Hz, 2H), 7.40 (dd, J = 5.1, 1.6 Hz, 1H), 7.38–7.33 (m, 2H), 7.33–7.29 (m, 2H), 7.04–7.00 (m, 1H), 6.98–6.93 (m, 1H), 6.80 (d, J = 15.3 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0, 160.0, 140.4, 135.0, 134.7, 134.5, 130.6, 130.2, 128.7, 127.8, 126.3, 122.5, 120.4, 120.1, 114.4, 24.4; HRMS (ESI) calculated for $C_{16}H_{13}ClNO_2S$ $[M-H]^-$: 318.0356; Found: 318.0360.

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Appendix A. Supplementary data

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References

[1] A.R. Murphy, J.M.J. Fréchet, Organic semiconducting oli-gomers for use in thin film transistors, Chem. Rev. 107 (2007) 1066–1096.
[2] N.S. Li, J.K. Frederiksen, J.A. Piccirilli, Synthesis, proper-ties, and applications of oligonucleotides containing an RNA dinucleotide phosphorothiolate linkage, Acc. Chem. Res. 44 (2011) 1257–1269.
[3] M. Banerjee, A. Poddar, G. Mitra, A. Surolia, T. Owa, B. Bhattacharyya, Sulfonamide drugs binding to the colchicine site of Tubulin: thermodynamic analysis of the Drug–Tubulin interactions by isothermal titration calorimetry, J. Med. Chem. 48 (2004) 547–555.
[4] A. Casini, J.Y. Winum, J.L. Montero, A. Scozzafava, C.T. Supuran, Carbonic anhydrase inhibitors: inhibition of cytosolic isozymes I and II with sulfamide derivatives, Bioorg. Med. Chem. Lett 13 (2003) 837–840.
[5] D.C. Cole, W.J. Lennox, S. Lombardi, J.W. Ellingboe, R.C. Bernotas, G.J. Tawa, H. Mazandarani, D.L. Smith, G. Zhang, J. Coupet, L.E. Schechter, Discovery of 5-arylsulfonamido-3- (pyrrolidin-2-ylmethyl)-1H-indole derivatives as potent, selective 5-HT6 receptor agonists and antagonists, J. Med. Chem. 48 (2004) 353–356.
[6] A. Natarajan, Y. Guo, F. Harbinski, Y.H. Fan, H. Chen, L. Luus, J. Diercks, H. Aktas, M. Chorev, J.A. Halperin, Novel Arylsulfoanilide–Oxindole hybrid as an anticancer agent that inhibits translation initiation, J. Med. Chem. 47 (2004) 4979–4982.
[7] S.S. Mansy, J.A. Cowan, Iron–Sulfur cluster Biosynthesis: toward an understanding of cellular machinery and molecular mechanism, Acc. Chem. Res. 37 (2004) 719–725.
[8] E. Schaumann, Sulfur-mediated rearrangements, Top. Curr. Chem. 274 (2007) 1–34.
[9] C. Shen, P. Zhang, Q. Sun, S. Bai, T.S. Hor, X. Liu, Recent advances in C-S bond formation via C-H bond functionalization and decarboxylation, Chem. Soc. Rev. 44 (2015) 291–314.
[10] T. Miao, P. Li, Y. Zhang, L. Wang, A sulfenylation reaction: direct synthesis of 3-arylsulfinylindoles from arylsulfinic acids and indoles in water, Org. Lett. 17 (2015) 832–835.
[11] T. Hostier, V. Ferey, G. Ricci, D. Gomez Pardo, J. Cossy, TFA-promoted direct C-H sulfenylation at the C2 position of non-protected indoles, Chem. Commun. 51 (2015) 13898–13901.
[12] J.A. Fernandez-Salas, A.P. Pulis, D.J. Procter, Metal-free C-H thioarylation of arenes using sulfoxides: a direct, general diaryl sulfide synthesis, Chem. Commun. 52 (2016) 12364–12367.
[13] D. Chen, Q. Feng, Y. Yang, X.M. Cai, F. Wang, S. Huang, Metal-free O-H/C-H difunctionalization of phenols by o-hydroxyarylsulfonium salts in water, Chem. Sci. 8 (2017) 1601–1606.
[14] A. Armstrong, D.P.G. Emmerson, Enantioselective synthesis of allenamides via sulfimide [2,3]-Sigmatropic rearrangement, Org. Lett. 11 (2009) 1547–1550.
[15] M. Candy, C. Guyon, S. Mersmann, J.R. Chen, C. Bolm, Synthesis of sulfondiimines by *N*-Chlorosuccinimide-Mediated oxidative imination of sulfiliminium salts, Angew. Chem. Int. Ed. 51 (2012) 4440–4443.
[16] D.J. Cram, J. Day, D.R. Rayner, D.M.V. Schriltz, D.J. Duchamp, D.C. Garwood, Stereochemistry of sulfur compounds. I. Stereochemical reaction cycles involving an open chain sulfoxide, sulfimide, and sulfoximide, J. Am. Chem. Soc. 92 (1970) 7369–7384.
[17] T.L. Gilchrist, C.J. Moody, The chemistry of sulfilimines, Chem. Rev. 77 (1977) 409–435.
[18] J.P. Marino, N. Zou, Chemoselective syntheses of γ-butyrolactams using vinyl sulfilimines and dichloroketene, Org. Lett. 7 (2005) 1915–1917.
[19] G.P. Silveira, J.P. Marino, Enantioselective synthesis of dihydro-1H-benzindoles, J. Org. Chem. 78 (2013) 3379–3383.
[20] H. Takada, et al., Catalytic asymmetric sulfimidation, J. Org. Chem. 62 (1997) 6512–6518.
[21] Q. Wang, S. Nara, A. Padwa, A new synthesis of γ-lactams based on the reaction of vinyl sulfilimines with dichloroketene, Org. Lett. 7 (2005) 839–841.
[22] G.Y. Cho, C. Bolm, Silver-catalyzed imination of sulfoxides and sulfides, Org. Lett. 7 (2005) 4983–4985.
[23] F. Collet, R.H. Dodd, P. Dauban, Stereoselective rhodium-catalyzed imination of sulfides, Org. Lett. 10 (2008) 5473–5476.
[24] A.L. Marzinzik, K.B. Sharpless, A simple method for the preparation of *N*-sulfonylsulfilimines from sulfides, J. Org. Chem. 66 (2001) 594–596.
[25] H. Okamura, C. Bolm, Rhodium-catalyzed imination of sulfoxides and Sulfides: efficient preparation of N-unsubstituted sulfoximines and sulfilimines, Org. Lett. 6 (2004) 1305–1307.
[26] H. Takada, K. Ohe, S. Uemura, Catalytic diastereoselective imidation of diaryl sulfides bearing a chiral oxazolinyl moiety with chloramine T trihydrate, Angew. Chem. Int. Ed. 38 (1999) 1288–1289.
[27] C.S. Tomooka, E.M. Carreira, Enantioselective nitrogen transfer to sulfides from nitridomanganese(V) complexes, Helv. Chim. Acta 85 (2002) 3773–3784.
[28] J. Wang, M. Frings, C. Bolm, Enantioselective nitrene transfer to sulfides catalyzed by a chiral iron complex, Angew. Chem. Int. Ed. 52 (2013) 8661–8665.
[29] Y. Chen, D. Wang, P. Duan, R. Ben, L. Dai, X. Shao, M. Hong, J. Zhao, Y. Huang, A multitasking functional group leads to structural diversity using designer C–H activation reaction cascades, Nat. Commun. 5 (2014) 4610.
[30] Q. Wu, Y. Chen, D.Y. Yan, M.Y. Zhang, Y. Lu, W.Y. Sun, J. Zhao, Unified synthesis of mono/bis-arylated phenols via RhIII-catalyzed dehydrogenative coupling, Chem. Sci. 8 (2017) 169–173.
[31] Q. Wu, D.Y. Yan, Y. Chen, T. Wang, F. Xiong, W. Wei, Y. Lu, W.Y. Sun, J. Li, J. Zhao, A redox-neutral catechol synthesis, Nat. Commun. 8 (2017) 14227.
[32] F. Xiong, L. Lu, T.Y. Sun, Q. Wu, D.Y. Yan, Y. Chen, X. Zhang, W. Wei, Y. Lu, W.Y. Sun, J. Li, J. Zhao, A bioinspired and biocompatible *ortho*-sulfiliminyl phenol synthesis, Nat. Commun. 8 (2017) 15912.
[33] G. Liu, Y. Shen, Z. Zhou, X. Lu, Rhodium (III)-catalyzed redox-neutral coupling of *N*-phenoxyacetamides and alkynes with tunable selectivity, Angew. Chem. Int. Ed. 52 (2013) 6033–6037.