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Electrochemical Oxidative Cross-Coupling Reaction to Access Unsymmetrical Thiosulfonates and Selenosulfonates

Xiaofeng Zhang,[a] Ting Cui,[a] Yanghao Zhang,[a] Weijin Gu,[a] Ping Liu,[a,*] and Peipei Sun[a,*]

[a] College of Chemistry and Materials Science, Jiangsu Provincial Key Laboratory of Material Cycle Processes and Pollution Control, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Nanjing Normal University, Nanjing 210023, People's Republic of China.
E-mail: sunpeipei@njnu.edu.cn; pingliu@njnu.edu.cn

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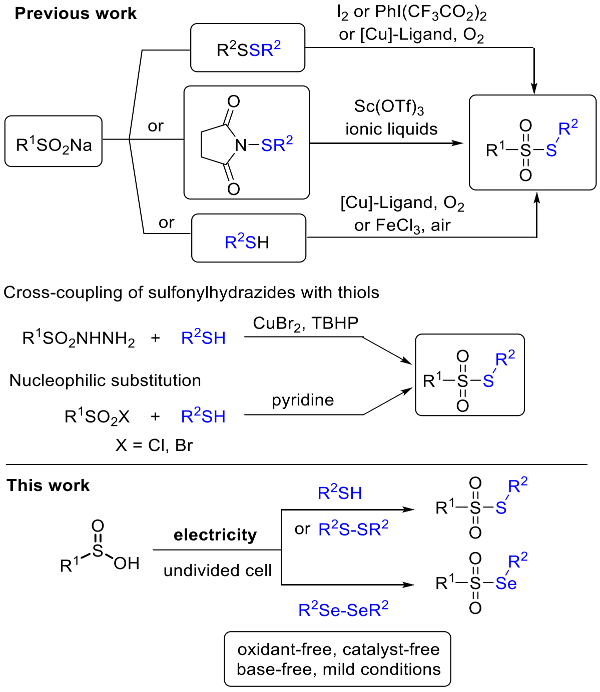
Abstract. The electrochemical oxidative cross-dehydrogenative coupling of arylsulfinic acids with thiophenols was achieved via a radical process. A wide range of arylsulfinic acids and substituted thiophenols were found to be tolerated, providing unsymmetrical thiosulfonates in good to excellent yields. This electrochemical method can also be used for the reaction of arylsulfinic acids with disulfides or diselenides to obtain thiosulfonates or selenosulfonates.

Keywords: Electrochemistry; oxidative cross-coupling; arylsulfinic acids; thiosulfonates; selenosulfonates

Organosulfur compounds are widely present in natural products, and are used in pharmaceuticals, as well as in organic synthesis.[1] Thiosulfonates ($R^1SO_2SR^2$), which are structurally similar to the antibacterial agent allicin (diallyl thiosulfinate), show diverse biological properties such as antimicrobial,[2] antifungal[3] and anticancer activities,[4] as well as use as cysteine scanning reagents.[5] Some thiosulfonates have been exploited for linkage or functionalization of polymers.[6] Furthermore, during recent years, some thiosulfonates have been employed as versatile synthetic precursors for the introduction of R^1SO_2-[7] and R^2S-[8] groups into organic molecules via a diverse range of chemical transformations.

Because of the aforementioned applications, substantial efforts have been devoted to develop new strategies for the synthesis of thiosulfonates. The direct oxidation of disulfides or thiosulfinates to construct thiosulfonates had been used in early works, but these methods require substrates bearing an S–S bond.[9] Symmetrical thiosulfonates can be obtained through intermolecular S–S bond construction in which two identically substituted sulfur-containing compounds are used as substrates. Examples include the oxidation dimerization of thiols,[10] the decomposition of sulfonyl hydrazides[11] or the reduction of sulfonyl chlorides.[12] Unsymmetrical thiosulfonates can be generated through the cross-coupling of two differently substituted sulfur precursors. Examples include the coupling of sodium sulfonates with disulfide,[13] thiols,[14] or *N*-(organothio)succinimides[15] and the reaction of sulfonylhydrazides with thiols.[16] An alternative method is nucleophilic substitution which occurs by addition of thiols to sulfonyl halides, followed by elimination of hydrogen halide.[17] Despite considerable advances, these methods often require the use of stoichiometric amounts of oxidants ($NaIO_4$, $PhI(CF_3CO_2)_2$, I_2, N_2O_4, CAN, $ZnCr_2O_7$ or Oxone), reducing agents (Zn, Sm, $^nBu_4NI$), or toxic organic base (pyridine), resulting in the generation of undesired waste. Thus, the development of convenient and green methods to prepare thiosulfonates is highly desirable.

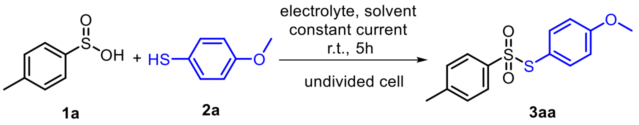


Scheme 1. Synthesis of unsymmetrical thiosulfonates.

Organic electrosynthesis has been recognized as an eco-friendly synthetic tool since it can avoid the use of some dangerous oxidants, reducing agents, or toxic bases, thus reducing waste and pollution.[18] Electrochemical oxidative cross-dehydrogenative coupling (CDC) is one of the most attractive fields of organic electrosynthesis, as it removes the requirement for prefunctionalization of starting materials and oxidants to mediate the transformation.[19] In 2017, Lei and co-workers described an electrochemical oxidative CDC of electron-rich arenes and thiols to form C–S bonds.[20a] Furthermore, the same group later reported an electrochemical oxidative CDC method to access unsymmetrical disulfides and to construct S–S bonds using two different thiol precursors.[20b] Encouraged by these excellent achievements, we postulated that electrochemical oxidative CDC would be amenable to the formation of unsymmetrical thiosulfonates (Scheme 1). Most recently, electrochemical sulfonylation of thiols with sulfonyl hydrazides to give unsymmetrical thiosulfonates was developed by Tang, Pan, Chen and co-workers during the course of our research.[21] Herein, we present our preliminary efforts on the electrochemical oxidative CDC of sulfinic acids with thiols, disulfides, and diselenides, leading to diverse thiosulfonate and selenosulfonate products.

We started our investigation by choosing 4-methylbenzenesulfinic acid (**1a**) and 4-methoxybenzenethiol (**2a**) as model substrates for optimization studies (Table 1). Gratifyingly, utilizing a platinum anode and cathode, $LiClO_4$ (0.3 M) as the electrolyte and CH_3CN as the solvent, the product *S*-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**3aa**) was obtained in 86% yield under air after 5 hours (entry 1). A comparable yield (85%) was obtained under Ar atmosphere (entry 2). Using a graphite plate to replace the platinum plate anode or cathode led to reduced yields (entries 3 and 4). When ammonium salts (^{n}Bu$_4$NBF$_4$, ^{n}Bu$_4$NPF$_6$) were employed as the supporting electrolyte instead of $LiClO_4$, slightly decreased yields were obtained (entries 5 and 6). Solvent also played a very important role in this transformation. DMF and 1,2-dichloroethane (DCE) showed less efficiency compared with CH_3CN (entries 7 and 8). Both EtOH and THF were not suitable for this coupling process (entries 9 and 10). When CH_3CN and DCE (9:1) was used instead of CH_3CN, the yield of **3aa** remained unchanged (entry 11). Both higher and lower current densities resulted in decreased yields, even though the electrical energy input was the same (entries 12−14). Cutting down the quantity of electrolyte $LiClO_4$ to 0.2 M led to a lower yield of 79% (entry 15). Finally, no product **3aa** was observed in the absence of electric current (entry 16).

Table 1. Optimization of the cross-coupling reaction conditions.[a]



Entry	Anode/ Cathode	Electrolyte	Solvent	J (mA/cm^2)	Yield (%)[b]
1	**Pt/Pt**	**$LiClO_4$**	**CH_3CN**	**5**	**86**
2[c]	Pt/Pt	$LiClO_4$	CH_3CN	5	85
3	C/Pt	$LiClO_4$	CH_3CN	5	68
4	Pt/C	$LiClO_4$	CH_3CN	5	60
5	Pt/Pt	^{n}Bu$_4$NBF$_4$	CH_3CN	5	72
6	Pt/Pt	^{n}Bu$_4$NPF$_6$	CH_3CN	5	81
7	Pt/Pt	$LiClO_4$	DMF	5	35
8	Pt/Pt	$LiClO_4$	DCE	5	47
9	Pt/Pt	$LiClO_4$	EtOH	5	0
10	Pt/Pt	$LiClO_4$	THF	5	0
11	Pt/Pt	$LiClO_4$	CH_3CN:DCE (9:1)	5	85
12[d]	Pt/Pt	$LiClO_4$	CH_3CN	10	63
13[e]	Pt/Pt	$LiClO_4$	CH_3CN	7.5	75
14[f]	Pt/Pt	$LiClO_4$	CH_3CN	2.5	76
15[g]	Pt/Pt	$LiClO_4$	CH_3CN	5	79
16	Pt/Pt	$LiClO_4$	CH_3CN	0	0

[a] Reaction conditions: platinum plate anode (10 mm × 10 mm), platinum plate cathode (10 mm × 10 mm), constant current (5.0 mA), supporting electrolyte (0.3 M), **1a** (0.6 mmol), **2a** (0.4 mmol), solvent (10 mL), air, r.t., 5 h, undivided cell.

[b] Isolated yield based on **2a**.

[c] Under Ar.

[d] Reaction time: 2.5h.

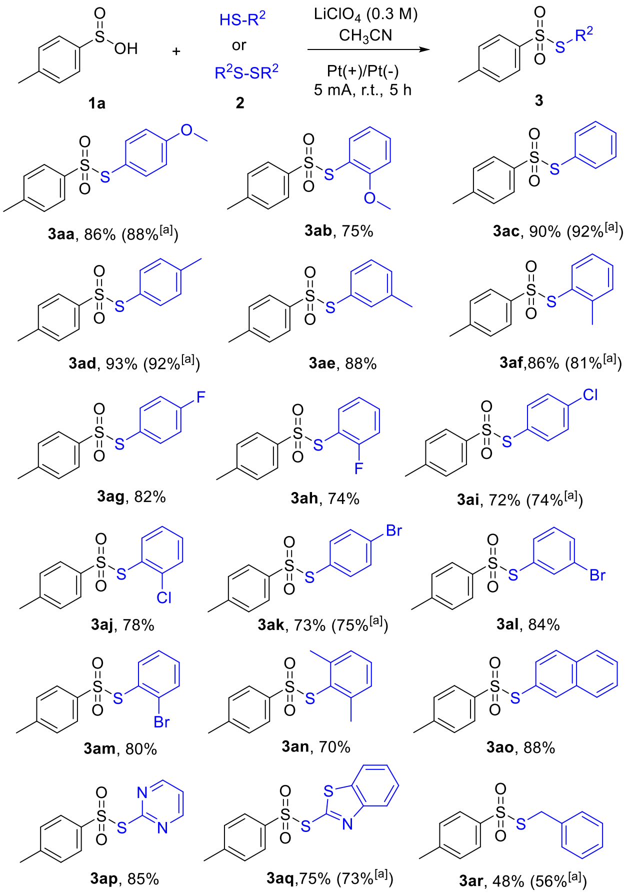
[e] Reaction time: 3.3h.

[f] Reaction time: 10h.

[g] $LiClO_4$ (0.2 M).

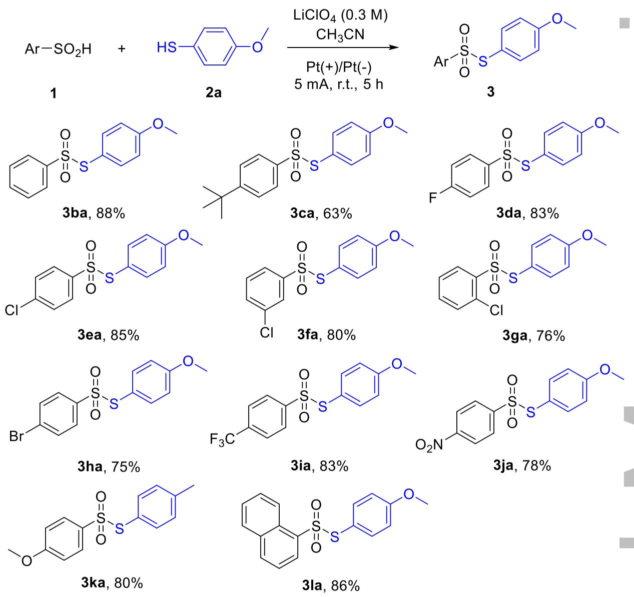
With the optimal reaction conditions in hand, the scopes of thiophenols were firstly investigated in our method (Scheme 2). Thiophenols bearing electron-donating groups (MeO, Me) at the *para*- or *meta*-position of benzene ring gave excellent yields through this electrochemical oxidative CDC reaction (**3aa**, **3ad**−**3ae**). Unsubstituted benzenethiol also provided the desired product **3ac** in 90% yield. Slightly decreased yields were obtained when the substituent groups are at the *ortho*-position probably due to steric hindrance (**3ab**, **3af**). Thiophenols possessing electron-withdrawing halogen groups (F, Cl, Br) afforded the cross-coupling products in good yields (72−84%) regardless of these substituents at the *para*-, *meta*- or *ortho*-position (**3ag**−**3am**). Thiol **3** bearing two substituents such as 2,6-dimethylbenzenethiol readily provided the desired product **3an** in satisfactory yield. 2-Naphthalenethiol was also efficient and furnished the product **3ao** in

88% yield. Notably, heterocyclic thiophenols such as pyrimidine-2-thiol and 2-mercaptobenzothiazole exhibited good reactivity and gave the corresponding thiosulfonates **3ap** and **3aq** in 85% and 75%, respectively. Finally, benzyl mercaptan was also successful and gave the product **3ar** in moderate yield (48%), demonstrating compatibility of our method with alkylthiols as well as thiophenol derivatives. It should be pointed out that similar results could be obtained when we used stable disulfides instead of thiols, and some representative results of the cross-coupling of 4-methylbenzenesulfinic acid with disulfides were listed in parentheses.



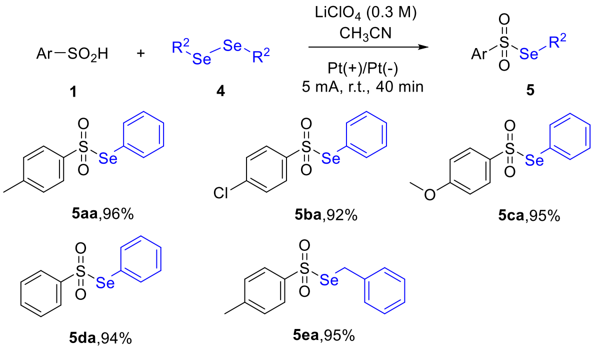
Scheme 2. Reaction scope of thiophenols **2**. Reaction conditions: platinum plate anode (10 mm × 10 mm), platinum plate cathode (10 mm × 10 mm), constant current (5.0 mA), $LiClO_4$ (0.3 M), **1a** (0.6 mmol), **2** (0.4 mmol), CH_3CN (10 mL), under air, r.t., 5 h, undivided cell. [a] 0.2 mmol corresponding disulfides instead of 0.4 mmol thiophenols.

Next, our attention turned to the applicability of other sulfinic acids in this electrochemical cross-coupling reaction (Scheme 3). Benzenesulfinic acid smoothly reacted with 4-methoxybenzenethiol to form the product **3ba** in 88% yield. Bulky substituents such as *tert*-butyl at the *para*-position of benzene ring proved compatible under the standard conditions, although lower reactivity was observed (**3ca**). When a series of arylsulfinic acids with electron-withdrawing groups such as F, Cl, Br, CF_3 and NO_2 groups were used, the desired products **3da**−**3ja** were obtained in 75%−85% yields. This electrosynthetic method could also be applied to access *S*-(*p*-tolyl) 4-methoxybenzenesulfonothioate (**3ka)** by using 4-methoxybenzenesulfinic acid as a starting material. Furthermore, naphthalene-1-sulfinic acid were found to be viable coupling partners with 4-methoxybenzenethiol and product **3la** was obtained in 86% yield.



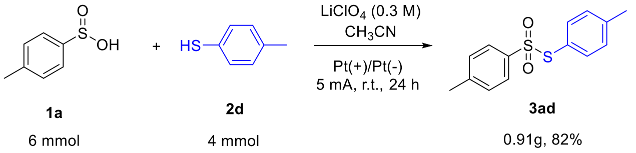
Scheme 3. Reaction scope of arylsulfinic acids **1**. Reaction conditions: platinum plate anode (10 mm × 10 mm), platinum plate cathode (10 mm × 10 mm), constant current (5.0 mA), $LiClO_4$ (0.3 M), **1** (0.6 mmol), **2a** (0.4 mmol), CH_3CN (10 mL), under air, r.t., 5 h, undivided cell.

In addition, our methodology could be extended to the synthesis of selenosulfonates using diselenides as the precursor (Scheme 4). Because of the high reactivity of diselenides, the transformation was complete in 40 minutes compared with 5 h reaction time with disulfides. Benzenesulfinic acid or its derivatives with electron-donating or electron-withdrawing groups all afforded the desired products in excellent yields (**5aa**−**5da**). To our delight, the reaction of 1,2-dibenzyldiselane gave the selenosulfonate **5ea** in 95% yield compared with a moderate yield of 48% from 1,2-dibenzyldisulfane (**3ar**).



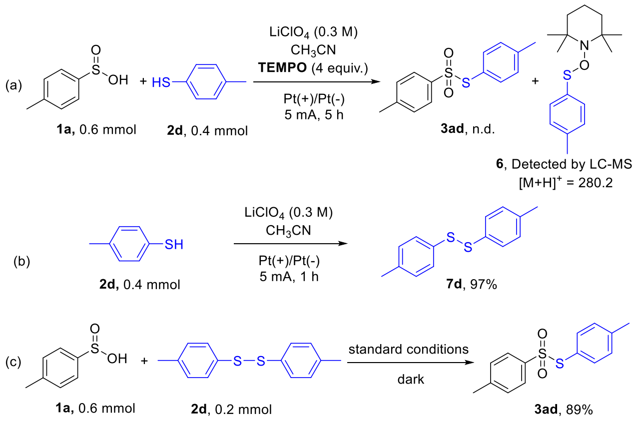
Scheme 4. Reaction scope of arylsulfinic acids **1** with diselenides. Reaction conditions: platinum plate anode (10 mm ×10 mm), platinum plate cathode (10 mm × 10 mm), constant current (5.0 mA), $LiClO_4$ (0.3 M), **1** (0.6 mmol), **4** (0.2 mmol), CH_3CN (10 mL), under air, r.t., 40 min, undivided cell.

To display the practicality and scalability of our method, the electrochemical oxidative cross-coupling reaction was scaled 10-fold and performed on a gram scale (Scheme 5). Using 6 mmol **1a** and 4 mmol **2d** by prolonging the reaction time, the product **3ad** could be obtained in 82% yield, only slightly decreased compared with small scale (92%).



Scheme 5. Gram-scale reaction.

In order to gain insight into the mechanism, we conducted several control experiments (Scheme 6). When 4 equiv. radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction under the optimal conditions, the cross-coupling reaction was obviously suppressed and adduct **6** generated by the addition of sulfur-containing radical and TEMPO was detected by LC-MS (Scheme 6a). This indicated that the crucial intermediate of this electrosynthesis probably was likely a sulfur-centered radical. Under the standard conditions, 4-methylbenzenethiol (**2d**) underwent dimerization to form disulfide **7d** in the absence of sulfinic acid (Scheme 6b). In addition, no obvious change was found if the reaction was performed in the dark using disulfide as the reaction partner (Scheme 6c).



Scheme 6. Control experiments for mechanistic studies.

Cyclic voltammetry (CV) experiments were carried out to detect the oxidation potential of some reactants involving the coupling process. As shown in Figure 1, 4-methylbenzenethiol (**2d**) gave an oxidation peak at 0.05 V, and the oxidation peak of 4-methylbenzenesulfinic acid (**1a**) was observed at 1.80 V. This result demonstrated that the oxidation of **2d** was much easier than **1a**.

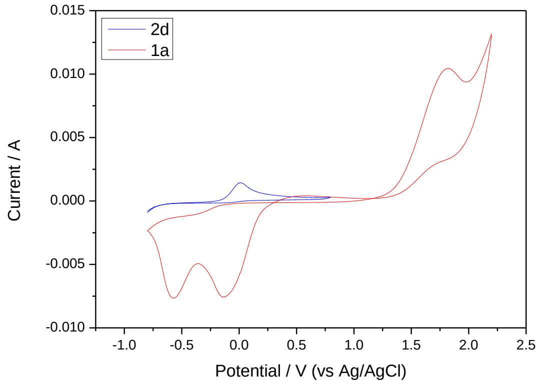
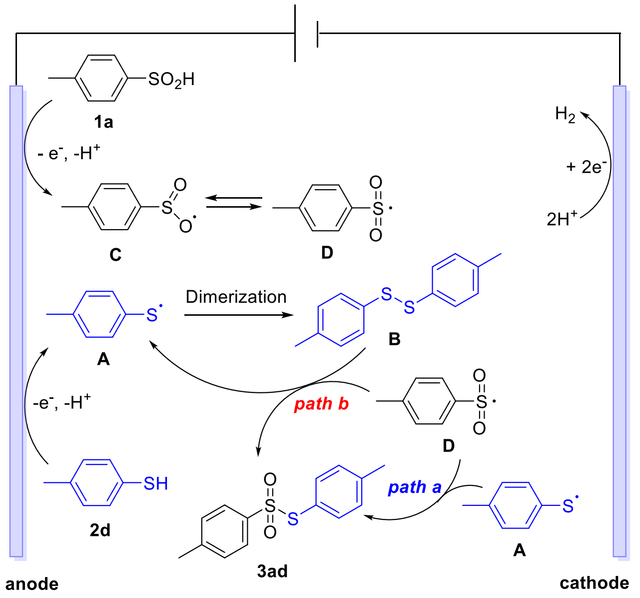


Figure 1. CV scans (scan rate 100 mv·s^{-1}) for **1a** or **2d** in CH_3CN containing $LiClO_4$ (0.3 M) at a platinum-wire electrode under air.

Based on these mechanistic studies and relative literature reports,[20] a plausible mechanism was proposed based on a radical pathway (Scheme 7). Firstly, the anodic oxidation of 4-methylbenzenethiol (**2d**) through single-electron-transfer and deprotonation generated a sulfur radical **A**, which quickly underwent dimerization to form disulfide **B**.[20a] Meanwhile, the similar anodic oxidation of 4-methylbenzenesulfinic acid (**1a**) also led to the generation of radical **C**. The isomerization of radical **C** rapidly took place to produce sulfonyl radical **D** reversibly. Radical **D** was trapped by sulfur radical **A** (*path a*) to afford the desired product **3ad**, or by disulfide **B** (*path b*) to deliver **3ad** and to regenerate radical **A**. Finally, the direct cathodic reduction of protons released hydrogen gas.



Scheme 7. Proposed mechanism.

In summary, we have developed an efficient electrosynthesis of unsymmetrical thiosulfonates and selenosulfonates. Various aryl or heterocyclic thiophenols and arylsulfinic acids were found to be compatible in this electrochemical oxidative cross-dehydrogenative coupling reaction. Additionally, disulfides and diselenides were also practicable under similar conditions. The reaction could be scaled to gram-scale with maintenance of good reaction efficiency. The reactions were operationally simple under oxidant- and catalyst-free conditions. Further transformation through electrochemical oxidative cross-coupling reactions is ongoing in our laboratory.

Experimental Section

In an undivided three-necked flask (25 mL), 4-methylbenzenesulfinic acid (**1a**, 0.6 mmol, 94 mg), 4-methoxybenzenethiol (**2a**, 0.4 mmol, 56 mg), $LiClO_4$ (3 mmol, 319 mg) and CH_3CN (10 mL) were continuously added. The flask was equipped with platinum plate electrodes (1.0×1.0 cm^2) as the cathode and anode. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under air at room temperature for 5 h. After the reaction was completed, the mixture was diluted with water (30 mL) and then extracted by DCM (10 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, concentrated in *vacuo* and the crude product was obtained. The pure product **3aa** was obtained by silica gel chromatography using petroleum ether/ ethyl acetate (30:1) as eluent.

Acknowledgements

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Xiaofeng Zhang, Ting Cui, Yanghao Zhang, Weijin Gu, Ping Liu,* and Peipei Sun*