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Ligand-free, Quinoline *N*-assisted Copper-catalyzed Nitrene Transfer Reaction to Synthesize 8-quinolylsulfimides

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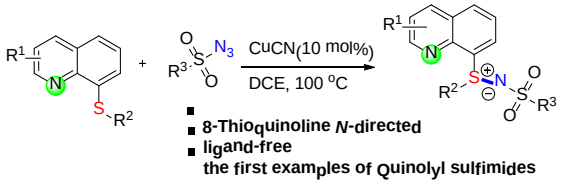


ABSTRACT: An efficient copper-catalyzed, quinolyl *N*-directed nitrene transfer reaction to 8-quinolylsulfides was described. A variety of 8-quinolylsulfimides with different functional groups were synthesized in moderate to high yields. The obtained 8-quinolylsulfimides were proved to be a promising novel type of bidentate ligands in Pd(II)-catalyzed allylic alkylation.

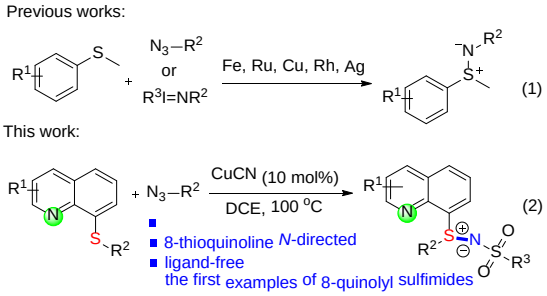
INTRODUCTION

Sulfilimines[1] (or sulfimides), which are the mono-nitrogen equivalent of sulfoxides[2], have been widely used as reagents in organic synthesis or chiral auxiliaries in asymmetric catalysis. For example, the chiral S-N bond of a sulfimide can serve as a chiral auxiliary in the preparation of optically active epoxides[3] through methylene transfer reactions. [2,3]-sigmatropic rearrangement of chiral allylic sulfimide provided an efficient route to enantioenriched allylic sulfenamides.[4] By taking full advantage of Pummerer (ene) reaction of this 1,2-diplolar functionality, a series of fascinating transformations to synthesize aza-heterocycles, natural products or drug molecules have been carried out by Padwa *et al.*[5] Studies also indicated that they have not only been explored as ligands in transition metal catalysis[6], but also have been used as cationic reagents in electrochemical reactions.[7] In addition to its great role in organic synthesis, the molecules that comprise this structural unit themselves possess interesting bioactivities.[8] Furthermore, oxidation of this simple functionality provides another important kind of sulfur-containing compouds, the highly heteroatomized sulfoximines[9], which have exhibited significant biological activities in crop protection[10] and medicinal chemistry[8a, 11]. As their sulfur(IV) precursors (sulfilimines), the sulfoximines have been frequenly used as ligands in metal catalysis,[12] or reagents[13] in organic synthesis as well. However, compared with sulfoxides and sulfoximines, the sulfimides are still a relatively poorly studied class of sulfur ylides. Preparation of the ones that consist of specific substitution patterns and application of them as ligands in transition-metal catalyzed reaction are especially highly desired.

Due to the significant role that the sulfimides play in organic synthesis and life science, preparation of this type of 1,2-dipolar compounds especially the asymmetric catalytic variant have drawed a great of interests in the past few decades.[14] The straightforward amination of thioethers with electrophilic nitrogen reagents is the oldest and most widely reported method to prepare sulfimides, among which transition-metal promoted sulfimidations are very efficient conversions as they can not only conducted the transformations in relatively mild reaction conditions, but also provide possible approaches to enantiomer enriched products with the assistance of proper chiral ligands. Various metal catalyzed procedures, such as Cu,[4d, 4e] Mn,[15] Ru,[16] Rh[17] Ag[18] and Fe[4a, 19], were presumably proceeding via the formation of metal nitrene species[20] with the use of iminoiodinanes, azides *etc.* as the imidating agents. In recently years, breakthrough in preparation of

optically active sulfimides via novel means has also been made (Scheme 1). For example, the group of Lebel delineated a Rh-catalyzed stereoselective amination of thioethers with the use of chiral *N*-mesyloxycarbamate as the nitrogen source in 2014.[21] Arnold *et al.* disclosed an enzyme-catalyzed amination of aromatic thioethers at the same year.[22] Despite great progress has been made in this field, the preparation of simple 8-quinolyl sulfides have never been covered in any imidation reactions before. The fact that the lewis basic nitrogen atom is probably poisonous to the metal catalyst and would devitalize the corresponding catalytic activity might be the main reason for this absence. As quinolyl nitrogen atom have frequently served as directing group in numerous metal catalyzed C-H bond functionalizations,[23] encouraged by these delighting reaserch works, we put forword a similar 8-quinolyl nitrogen assisted straightforward synthetic strategy to prepare the target 8-quinolylsulfimides. Herein, we describe the first synthesis of 8-quinolylsulfimides with a variety of functional groups via Cu(I)-catalyzed, ligand-free nitrene transfer reaction to 8-quinolylsulfides and the application as a novel type of bidentate ligand in Pd(II)-catalyzed allylic alkylation.

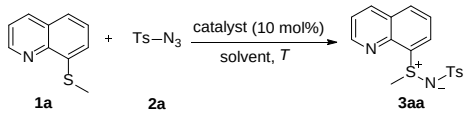
Scheme 1. Metal-catalyzed Nitrene Transfer Reaction to Sulfilimine



RESULTS AND DISCUSSION

Initially, in order to verify the feasibility of the ligand-free nitrene transfer process for the preparation of 8-quinolyl alkyl sulfimide, 8-(methylthio)quinoline (**1a**) and 4-methylbenzenesulfonyl azide (TsN_3, **2a**) were chosen as the templet substrates for investigation. When we employed 10 mol% CuBr as the catalyst, and conducted the reaction in toluene at 80 °C under argon atmosphere in a sealed reaction tube, the expected 8-quinolyl alkyl sulfimide **3aa** was produced in 23% yield (Table 1, entry 1). Encouraged by this preliminary result, a series of Cu(I) catalysts were subsequently tested (Table 1, entries 2-4), and the outcome indicated that CuCN was slightly superior to CuI and CuCl. Replacement of CuBr with other metal catalysts, such as $Pd(OAc)_2$, $[Rh_2(OAc)_4]$, $[RuCl_2(p\text{-Cym})]_2$, $FeSO_4$ and $Fe(acac)_3$ (Table 1,entries 5-9), or with the absence of CuBr (Table 1,entry 10), the same reaction to form 8-quinolyl alkyl sulfimide **3aa** could not occur. Thus, CuCN was chosen as the catalyst for solvent screening (Table 1, entries 11-18). We found that changes in the solvent have a significant effect on the reaction yield. Among the solvents tested, DCE appeared to be the most suitable reaction media, giving the target product in 66% yield (Table 1, entry 18). Gratifyingly, the reaction yield could be further improved to 87% by elevating the reaction temperature from 80 °C to 100 °C (Table 1, entry19). However, excessive higher reaction temperature did no help to the reaction, as a futher increase from 100 °C to 120 °C led no further increase of yield (Table 1,entry 20).

Table 1. Optimization of the Reaction Parameters [a]



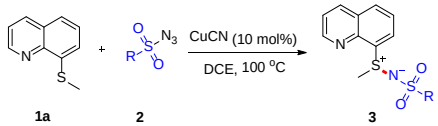
1a 2a 3aa

Entry	Catalyst (mol%)	Solv.[b]	*T* (°C)	Yield (%)[c]
1	CuBr	toluene	80	23
2	CuI	toluene	80	27
3	CuCl	toluene	80	20
4	CuCN	toluene	80	33
5	$Pd(OAc)_2$	toluene	80	0
6	$[Rh_2(OAc)_4]$	toluene	80	0
7	$[RuCl_2(p\text{-Cym})]_2$	toluene	80	0
8	$FeSO_4$	toluene	80	0
9	$Fe(acac)_3$	toluene	80	0
10	-	toluene	80	0
11	CuCN	1,4-dioxane	80	44
12	CuCN	MeOH	80	21
13	CuCN	THF	80	32
14	CuCN	$CHCl_3$	80	54
15	CuCN	DMSO	80	25
16	CuCN	CH_3CN	80	36
17	CuCN	EA	80	17
18	CuCN	DCE	80	66
19	CuCN	DCE	100	87
20	CuCN	DCE	120	85

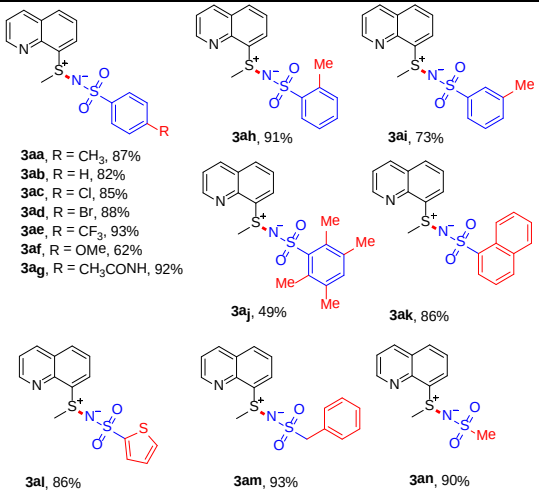
[a]Unless otherwise noted, all the reactions were performed with 8-(methylthio)quinoline (**1a**) (0.20 mmol) and 4-methylbenzenesulfonyl azide (**2a**) (0.24 mmol) with metal catalysts (10 mol%) in solvent (1.0 mL) at the setting temperature for 12 h under Ar in a sealed reaction tube. [b]THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, EA = ethyl acetate , DCE = 1,2-dichloroethane. [c] Isolated yield.

With the optimized reaction conditions in hand (Table 1, entry 19), various sulfonyl azides were explored to investigate the generality of this Cu(I)-catalyzed nitrene transfer reaction, and the results are summarized in Scheme 2. The substrate scope of sulfonyl azides is quite general, benzenesulfonyl azide (**2b**) and various *para*-substituted benzenesulfonyl azides bearing both electron-withdrawing and electron-donating groups could smoothly react with the 8-(methylthio)quinoline (**1a**), providing the expected sulfimides in moderate to good yield (**3ac**-**3ag**, 62-93%). *Ortho*- and *meta*-methyl substituted benzenesulfonyl azide also worked well in this reaction to furnish the corresponding sulfimide **3ah** and **3ai** in 91% and 73% yield respectively. However, the steric congested 2,3,5,6-tetramethyl benzenesulfonyl azide (**2j**) seemed a reluctant reactant in the reaction as only 49% yield could be obtained. In addition, naphthylsulfonyl azide (**2k**), 2-thiophenesulfonyl azide (**2l**), phenylmethanesulfonyl azide (**2m**) and methanesulfonyl azide (**2n**) were compatible in the reaction as well, producing the corresponding sulfimidation products **3ak**-**3an** in 86-93% yields. Except sulfonyl azides, other types of organic azides, such as benzyl, aryl and Boc azide, have also been examined as the nitrogen source, but unfortunately no targeted imidated product formed.

Scheme2. Substrate Scope for the Sulfonyl Azide[a, b]

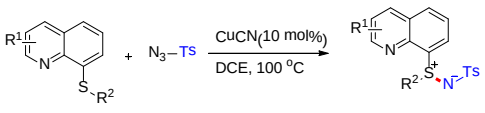


1a 2 3

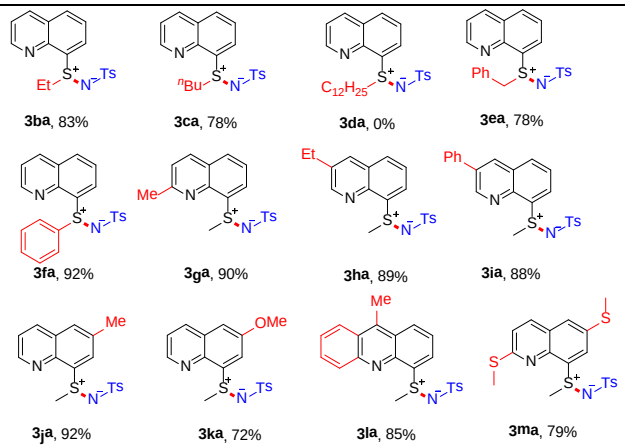


[a]Unless otherwise noted, all the reactions were performed with 8-(methylthio)quinoline (**1a**) (0.20 mmol) and sulfonyl azide (**2**) (0.24 mmol) with CuCN (10 mol%) in DCE (1.0 mL) at the 100℃ for 12 h under Ar in a sealed reaction tube. [b]Isolated yield.

Scheme 3. Substrate Scope for the Sulfides [a, b]



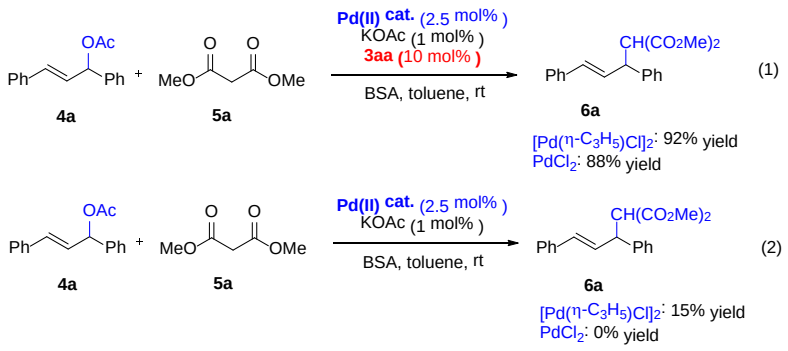
1 2a 3



[a]Unless otherwise noted, all the reactions were performed with sulfide (**1**) (0.20 mmol) and sulfonyl azide (**2a**) (0.24 mmol) with CuCN (10 mol%) in DCE (1.0 mL) at the 100℃ for 12 h under Ar in a sealed reaction tube. [b]Isolated yield.

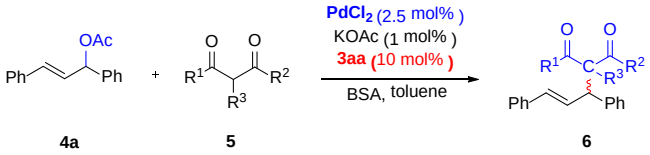
The scope of sulfides was also evaluated, and the results are exhibited in Scheme 3. 8-Quinolyl sulfide with short chain alkyl, such as ethyl (**1b**) and butyl (**1c**) could smoothly reacted with the 4-methylbenzenesulfonyl azide **2a**, furnishing the targeted sulfimidation product **3ba** and **3ca** in 83% and 78% yield respectively. However, variation of the alkyl substitution of the alkyl 8-quinolyl sulfide from short chain to longer one, such as dodecyl (**1d**), the same sulfimidation reaction could not be obseved. In addition to alkyl group, benzyl 8-quinolyl sulfide (**1e**) and phenyl 8-quinolyl sulfide (**1f**) were tolerated in this sulfimidation reaction, giving the corresponding sulfilimine in high or moderate yield. Next, various substituted 8-quinolyl methyl sulfide were tested. As revealed by the results of the reations of 2-methyl (**1g**), 3-ethyl (**1h**), 3-phenyl (**1i**), 6-methyl (**1j**), 6-methoxyl (**1k**) substituted 8-quinolyl methyl sulfide, various substitution patterns were compatible in the reaction, leading to the corresponding sulfimides in moderate to high yield. Except 8-quinolyl, similar 9-methyl-4-(methylthio)acridine (**1l**) was also applicable, affording the corresponding sulfimide **3la** in 85% yield. Noteworthy, for the multi methyl-thio-substituted substrate, such as 2,6,8-tris(methylthio)quinoline (**1m**), chemoselective sulfimidation occured only at the 8-position, providing the mono-sulimide **3ma** in 79% yield.

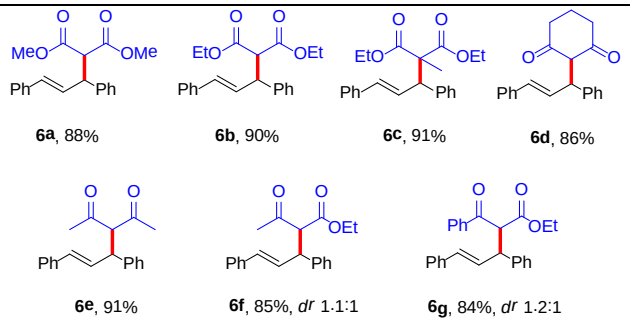
Scheme 4. Synthetic Application of the 8-Quinolyl Sulfimide



In view of synthetic application of the produced 8-quinolyl sulfimides, we envisaged that this type of compounds could function as a novel type of bidentate ligands in the Pd(II)-catalyzed allylic substitution. The result of the reaction of 1,3-diphenyl-3-acetoxy-1-propene (**a**) with dimethyl malonate in the presence of a catalytic amount of Pd(II) catalyst showed that the allylated product **6a** was obtained in good or high yield when the sulfimide **3aa** was employed as the ligand (Scheme 4, Equ (1)). However, with the absence of the sulfimide **3aa**, the yield for $[Pd(\eta\text{-}C_3H_5)Cl]_2$-catalyzed allylic substitution dramatically decreased from 92% to 15%. In ligand-free conditions, the same allylic substitution even did not occur when $PdCl_2$ was used as catalyst (Scheme 4, Equ (2)). Furthermore, the reaction of allylic acetate **4** with a wide range of 1, 3-dicarbonyl compounds was investigated to examine the generality of the palladium-**3aa** catalyzed allylic substitution. As shown in Scheme 5, except dimethyl malonate **5a**, diethyl malonate **5b**, methy-substituted diethyl malonate **5c**, 1, 3-diketone (including cyclic 1,3-cyclohexanedione **5d** and acyclic acetylacetone **5e**), ethyl acetoacetate **5f** and ethyl benzoylacetate **5g** were all compatible in the catalytic system, evolving corresponding alkylated products **6** in good to high yields (84-91%).

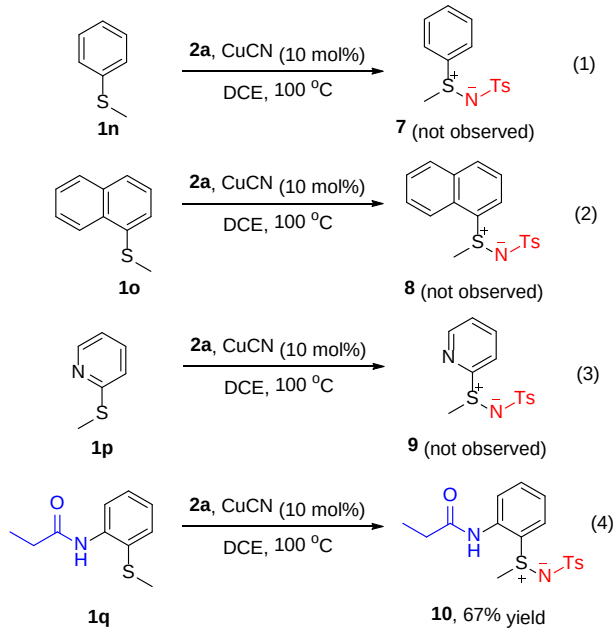
Scheme 5. Substrate Scope of the 1, 3-Dicarbonyl Compounds for the Pd(II)-3aa Catalyzed Allylic Alkylation [a,b]





[a]Unless otherwise noted, all the reactions were performed with 1,3-diphenyl-3-acetoxy-1-propene (**4a**) (0.10 mmol) , 1,3-dicarbonyl compound (**5**) and N,O-Bis(trimethylsilyl)acetamide (0.44 mL, 1.8 mmol) with $PdCl_2$ (2.5 mol%) in toluene (1.0 mL) at the room temperature for 12 h under N_2 in a reaction tube. [b]Isolated yield.

Scheme 6. Controlled Experiments

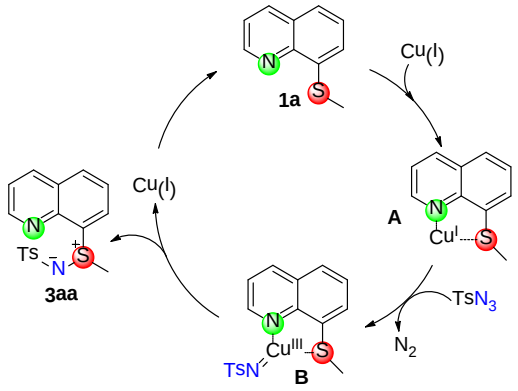


In order to shed some light on the mechanism of the present sulfimidation reaction, several controlled experiments were conducted. The reaction of methyl(phenyl)sulfane (**1n**) and methyl(naphthalen-1-yl)sulfane (**1o**) with 4-methylbenzenesulfonyl azide (**2a**) was performed under the standard conditions, respectively, and no sulfimidation products were produced (Scheme 6, Equ (1) and (2)). These results obviously implied that the quinoline nitrogen played a key role in the chelation-directed sulfimidation process. Moreover, 2-(methylthio)pyridine (**1p**) which could hardly chelate with the copper catalyst was identified still inert in this reaction (Scheme 6, Equ (3)).

Subsequently, a sulfide substrate *N*-(2-(methylthio)phenyl)propionamide (**1q**) which could similarly chelate with the copper catalyst was exposed to the ligand-free catalytic system, and to our delight, the corresponding sulfimidation product **10** was obtained in 67% yield.

On the basis of the results of the above controlled experiment, a plausible mechanism for this ligand-free nitrene-transfer reaction was proposed as below (Scheme 7). Firstly, chelation of the Cu(I) salt with the 8-quinolyl sulfide generated a Cu(I)-quinoline complex **A**; subsequently, Cu(I)-promoted decomposition of sulfonyl azide accompanied by the extrusion of N_2 gas resulted in the formation of the Cu-nitrene intermediate **B**; finally, nitrene transfer to the sulfide with concurrently release of the Cu(I) catalyst delivered 8-quinolylsulfimide.

Scheme 7. Possible Mechanism for the Cu(I)-Catalyzed Nitrene Transfer Reaction



CONCLUSION

In summary, we disclosed herein the first efficient synthesis of a variety of 8-quinolylsulfimides with different functional groups from readily accessible sulfonyl azides and 8-quinolyl thioethers via Cu(I)-catalyzed nitrene transfer reaction. This synthetic method is featured by environmentally friendly as not only ligand-free cheap metal catalysis was adoptted, but also the nonhazardous nitrogen gas was the only by-product. Quinolyl nitrogen atom played a crucial role in the catalytic process probably though chelating with the Cu(I) catalyst to assist the nitrene transformation. The obtained 8-quinolylsulfimides proved to be a promising novel type of bidentate ligands in Pd(II)-catalyzed allylic alkylation. Further studies on the enantioselective synthesis of 8-quinolylsulfimides and applications of this nascent type of compounds in organic synthesis and transition-metal catalysis are currently in progress in our laboratory.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or Strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (200-300 mesh). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance III HD 400 fourier Transform spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for $^{13}C\{^{1}H\}$ NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. Crystal data were collected on a Bruker D8 Advance employing

graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293(2) K and operating in the φ-ω scan mode. The structure was solved by direct methods SHELXS-97. The starting materials The starting materials *8-(Thio)quinoline Substrates (**1a-1m, 1p**),* [24] *sulfonyl azides*[25] and *(rac)-(E)-1,3-Diphenyl allyl acetate (**4a**)* [26]were prepared according to the previously reported procedures.

*Typical Procedure for the Preparation of the 8-(Thio)quinoline Substrates (**1a-1m, 1p**).* All of the substrates (***1a-1m, 1p***) were prepared according to the previously reported procedures.[24] To a solution of 1.12 g (20 mmol) KOH in anhydrous DMSO (20 mL) were added 50 mmol of R^2SNa and 10 mmol of 8-bromoquinoline derivatives. The resulting mixture was stirred under inert atmosphere (N_2) for 5 h at RT and overnight at 80 °C. Water (50 mL) was then added, and the reaction products were extracted by Et_2O (50 mL). The organic solution was dried over $MgSO_4$ (6 h), filtered, and dried under vacuum. The purification of the crude product was achieved by flash chromatography through a silica column with ethyl acetate/petroleum as eluent.

*8-(Methylthio)quinoline(**1a**).*[27] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a white solid. 1.61g, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.41 – 7.35 (m, 2H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.1, 145.4, 139.9, 136.3, 128.1, 126.6, 123.5, 122.8, 121.6, 14.2. MS (ESI): m/z= 175.1 $[M]^+$.

*8-(Ethylthio)quinoline(**1b**).*[28] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a white solid. 1.72 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.46 – 7.37 (m, 3H), 3.08 (d, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.17, 145.5, 138.8, 136.4, 128.3, 126.6, 123.9, 123.7, 121.6, 25.0, 13.4. MS (ESI): m/z= 189.1 $[M]^+$.

*8-(Butylthio)quinoline(**1c**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a colorless oil. 1.78 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 4.4 Hz, 1H), 7.45 (d, *J* = 3.7 Hz, 2H), 7.41 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.06 (t, *J* = 7.3 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.57 (dd, *J* = 14.7, 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.2, 145.6, 139.1, 136.4, 128.3, 126.6, 123.8, 123.6, 121.6, 30.6, 30.4, 22.3, 13.7. HR-MS (ESI) calcd for $[M+H]^+$: $C_{13}H_{16}NS$: 218.0998, found: 218.0997; IR (KBr): 2924, 2860, 1599, 1524, 1462, 1170, 810, 751 cm^{-1}.

*8-(Dodecylthio)quinoline(**1d**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a colorless oil. 2.63 g, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.1 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.46 (d, *J* = 4.9 Hz, 2H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.06 (t, *J* = 7.3 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.58 – 1.49 (m, 2H), 1.26 (s, 16H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.2, 145.6, 139.2, 136.3, 128.3, 126.6, 123.8, 123.6, 121.6, 31.9, 31.0, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 28.4, 22.7, 14.1. HR-MS (ESI) calcd for $[M+H]^+$: $C_{21}H_{32}NS$: 330.2250, found: 330.2251; IR (KBr): 3031, 2923, 2861, 1600, 1519, 14612, 1284, 816, 751 cm^{-1}.

*8-(Benzylthio)quinoline(**1e**).*[29] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a colorless oil. 2.36 g, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 – 8.90 (m, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.38 (m, 5H), 7.31 – 7.22 (m, 3H), 4.30 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.3, 145.6, 138.4, 136.7, 136.4, 129.0, 128.5, 128.3, 127.2, 126.6, 124.9, 124.3, 121.6, 36.2. MS (ESI): m/z= 251.1 $[M]^+$.

*8-(Phenylthio)quinoline(**1f**).*[30] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a colorless oil. 2.08 g, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.44 (dd, *J* = 7.7, 3.0 Hz, 4H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.06 – 6.99 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.4, 144.8, 140.1, 136.3, 135.6, 132.0, 129.7, 128.9, 128.3, 126.7, 125.5, 124.4, 121.8. MS (ESI): m/z= 237.1 $[M]^+$.

*2-Methyl-8-(methylthio)quinoline(**1g**).*[24] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a white solid. 1.78 g, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 2.75 (s, 3H), 2.53 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.1, 144.9, 139.1, 136.2, 126.1, 125.7, 123.2, 122.6, 122.5, 25.4, 14.2. MS (ESI): m/z= 189.1 $[M]^+$.

*3-Ethyl-8-(methylthio)quinoline(**1h**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a white solid. mp 113-115℃. 1.84 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.86 (s, 1H), 7.51 – 7.41 (m, 2H), 7.30 (d, *J* = 7.1 Hz, 1H), 2.81 (q, *J* = 7.6 Hz, 2H), 2.55 (s, 3H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.5, 143.9, 139.6, 137.3, 133.7, 128.0, 126.6, 123.1, 121.9, 26.2, 15.2, 14.2. HR-MS (ESI) calcd for $[M+H]^+$: $C_{12}H_{14}NS$: 204.0842, found: 204.0841; IR (KBr): 2923, 2860, 1601, 1525, 1462, 1288, 814, 750 cm^{-1}.

*8-(Methylthio)-3-phenylquinoline(**1i**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a white solid. mp 137-139℃. 2.19 g, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.28 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 5.9 Hz, 3H), 7.44 (dd, *J* = 21.0, 7.3 Hz, 2H), 2.62 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.5, 139.9, 137.7, 134.4, 133.5, 129.2, 128.2, 127.9, 127.4, 127.1, 123.7, 122.8, 116.7, 14.3. HR-MS (ESI) calcd for $[M+H]^+$: $C_{16}H_{14}NS$: 252.0842, found: 252.0844; IR (KBr): 3032, 2928, 2861, 1524, 1463, 1189, 820 cm^{-1}.

*6-Methyl-8-(methylthio)quinoline(**1j**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a white solid. mp 104-106℃. 1.75 g, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.0 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.30 (s, 1H), 7.21 (s, 1H), 2.56 (s, 3H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.3, 144.1, 139.4, 136.5, 135.6, 128.2, 125.1, 122.6, 121.6, 21.9, 14.3. HR-MS (ESI) calcd for $[M+H]^+$: $C_{11}H_{12}NS$: 190.0685, found: 190.0683; IR (KBr): 3030, 2926, 2864, 1599, 1462, 1189, 749 cm^{-1}.

*6-Methoxy-8-(methylthio)quinoline(**1k**).* [30] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) affords the title compound as a white solid. 1.74 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 – 8.71 (m, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.01 (s, 1H), 6.76 (s, 1H), 3.89 (s, 3H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.9, 146.6, 141.8, 135.0, 129.0, 121.9, 115.6, 100.7, 55.4, 14.2. MS (ESI): m/z= 205.1 $[M]^+$.

*9-Methyl-4-(methylthio)acridine (**1l**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid. mp 136-138℃. 2.09 g, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.59 – 7.54 (m, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 1H), 3.11 (s, 3H), 2.61 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 145.8, 142.3, 141.0, 130.8, 129.4, 125.9, 125.7, 125.2, 124.2, 122.1, 120.0, 14.4, 13.9. HR-MS (ESI) calcd for $[M+H]^+$: $C_{15}H_{14}NS$: 240.0842, found: 240.0846; IR (KBr): 2929, 2860, 1603, 1522, 1463, 1289, 814, 749 cm^{-1}.

*2,6,8-Tris(methylthio)quinoline(**1m**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) affords the title compound as a white solid. mp 164-166℃. 1.77 g, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.22 (s, 1H), 2.61 (d, *J* = 3.7 Hz, 6H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.9, 145.0, 143.7, 142.7, 134.0, 129.9, 123.3, 122.9, 118.3, 18.6, 15.8, 14.2. HR-MS (ESI) calcd for $[M+H]^+$: $C_{12}H_{14}NS_3$: 268.0283, found: 268.0286; IR (KBr): 3032, 2928, 2861, 1603, 1515, 1462, 1189, 810, 720 cm^{-1}.

*Methyl(naphthalen-1-yl)sulfane(**1p**).*[31] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a colorless oil. 1.55 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.48 (dtd, *J* = 13.3, 6.8, 5.5 Hz, 2H), 7.39 – 7.30 (m, 2H), 2.50 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.9, 133.7, 131.7, 128.6, 126.3, 126.2, 125.8, 125.8, 124.4, 123.5, 16.2. MS (ESI): m/z= 174.1 $[M]^+$.

*Procedure for the preparation of N-(2-(methylthio)phenyl)propionamide (**1q**).*[32] 2-Methylthioaniline (3.0 g, 21.5 mmol) and Et_3N (3.1 mL, 22.2 mmol) were dissolved in dichloromethane (20 mL) followed by dropwise addition of propionic acid anhydride (2.8 mL, 21.5 mmol). The resulting mixture was stirred overnight. The reaction mixture was diluted with dichloromethane and washed twice with 1M HCl, once with saturated aqueous $NaHCO_3$, and once with water. Organic layer was dried over $MgSO_4$. Evaporation of solvent gave 4.11 g (99% yield) of white crystals 2-Methylthio-N-propionylaniline(**1q**).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 2.47 (q, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.1, 138.4, 132.9, 128.9, 125.1, 124.2, 120.6, 31.1, 18.9, 9.7.

General Procedure for the Preparation of Sulfonyl Azides.[25] To a solution of sodium azide (1.95 g, 30.0 mmol) in water (10 mL) was added dropwise over 1 h a solution of sulfonyl chloride (20.0 mmol) in acetone (20 mL) at 0 °C. The reaction mixture was warmed up to

room temperature and stirred for 12 h. Acetone was removed under reduced pressure and the reaction mixture was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over $MgSO_4$ and solvent was removed under reduced pressure. Crude product was used without further purification.

*Procedure for the preparation of (rac)-(E)-1,3-Diphenyl allyl acetate(**4a**).*[26] In an oven dried, one neck, 50 mL round bottom flask equipped with a magnetic stir bar and septum, was placed (*rac*)-(*E*)-1,3-diphenyl allyl alcohol (1.0 g, 4.76 mmol) followed by dichloromethane (10 mL) and triethylamine (1.33 mL, 9.52 mmol) via syringe, under argon. The flask was placed into an ice-water bath and acetic anhydride (0.90 mL, 9.52 mmol) was slowly added via syringe. The reaction was allowed to stir overnight at room temperature, when TLC showed no remaining alcohol. The organic layer was extracted with saturated $NaHCO_3$ (1 x 10 mL), water (1 x 10 mL), brine (1 x 10 mL), dried (Na_2SO_4) and concentrated to yield a dark yellow oil that was purified by flash chromatography to yield *(rac)*-(*E*)-1,3-diphenyl allyl acetate (**4a**) (1.03 g, 4.25 mmol, 90%) as a clear oil. (*rac*)-(*E*)-1,3-Diphenyl allyl acetate (**4a**), 1.03 g, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 6H), 7.37 (ddd, *J* = 9.6, 6.8, 1.5 Hz, 3H), 7.32 – 7.28 (m, 1H), 6.70 (d, *J* = 15.8 Hz, 1H), 6.51 (d, *J* = 6.7 Hz, 1H), 6.47 – 6.38 (m, 1H), 2.19 (d, *J* = 2.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 139.3, 136.2, 132.6, 128.7, 128.6, 128.2, 128.1, 127.5, 127.1, 126.7, 76.2, 21.4.

*Typical Procedure for the Quinoline N-assisted Cu(I)-Catalyzed Nitrene Transfer Reactions (**3aa**-**3ma**).* All of the products (**3aa**-**3ma**) were obtained according to the following procedure. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 8-(thio)quinoline (0.20 mmol), azide (0.24 mmol), CuCN (1.8 mg, 0.01 mmol, 10 mol %) and 1, 2-dichloroethane (1.0 mL) under Ar atmosphere conditions. The reaction mixture was stirred at 100 ^{o}C for 12 h, filtered through a pad of celite and then washed with ethyl acetate (10 mL × 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate/petroleum as the eluent to give the desired products. All of the yields are isolated yield.

*S-Methyl S-(quinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3aa**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 112-114℃. 59.8 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.53 (dd, *J* = 7.4, 0.8 Hz, 1H), 8.27 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.04 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.6, 143.8, 141.6, 141.6, 136.6, 133.9, 131.6, 129.3, 128.5, 128.5, 126.9, 126.4, 122.6, 38.6, 21.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{17}N_2O_2S_2$: 345.0726, found: 345.0732; IR (KBr): 3028, 2927, 1598, 1484, 1250, 1197, 1163, 809, 780, 756, 731, 672, 664 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(benzenesulfonyl)sulfimide (**3ab**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 108-110℃. 54.1 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 3.9 Hz, 1H), 8.50 (d, *J* = 7.4 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.99 (t, *J* = 8.9 Hz, 3H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 8.1, 4.1 Hz, 1H), 7.43 (d, *J* = 6.4 Hz, 3H), 3.05 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.6, 144.4, 143.7, 136.6, 133.8, 131.7, 131.2, 128.7, 128.5, 128.4, 126.9, 126.3, 122.6, 38.6. HR-MS (ESI) calcd for $[M+H]^+$: $C_{16}H_{15}N_2O_2S_2$: 331.0569, found: 331.0571; IR (KBr): 3012, 2926, 1590, 1572, 1483, 1285, 1260, 1193, 758, 698 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(4-chlorobenzenesulfonyl) sulfimide (**3ac**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 137-139℃. 62.1 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 1.6 Hz, 1H), 8.50 (d, *J* = 7.4 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 3.07 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.7, 143.7, 143.0, 137.4, 136.6, 133.6, 131.8, 128.9, 128.6, 128.3, 127.9, 126.9, 122.7, 38.7. HR-MS (ESI) calcd for $[M+H]^+$: $C_{16}H_{14}ClN_2O_2S_2$: 365.0180, found: 365.0183; IR (KBr): 3023, 2940, 1601, 1485, 1455, 1402, 1275,1232, 1163, 1094, 1074, 1033, 830, 794, 714, 641 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(4-bromobenzenesulfonyl) sulfimide (**3ad**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 142-143℃.72.0 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.1 Hz, 1H), 8.50 (d, *J* = 7.4 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 3H), 3.07 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.7, 143.8, 143.5, 136.6, 133.6, 131.9,

131.82, 128.6, 128.4, 128.0, 126.9, 125.8, 122.7, 38.7. HR-MS (ESI) calcd for $[M+H]^+$: $C_{16}H_{14}BrN_2O_2S_2$: 408.9675, found: 408.9675; IR (KBr): 3022, 2980, 1501, 1460, 1270, 1179, 1153, 831, 810, 725, 691, 638 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(4-trifluoromethylbenzenesulfonyl) sulfimide (**3ae**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 132-134℃. 74.0 mg, 93% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.94 – 8.88 (m, 1H), 8.48 (d, *J* = 7.4 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.71 (dd, *J* = 14.2, 7.9 Hz, 3H), 7.57 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.09 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.8, 147.981, 143.7, 136.7, 133.4, 132.9(d, J = 32.0 Hz), 131.9, 128.6, 128.2, 126.8, 125.8(q, J = 3.0 Hz) , 123.5(d, J = 271.0 Hz) 122.8, 38.7. HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{14}F_3N_2O_2S_2$: 399.0443, found: 399.0439; IR (KBr):2923, 2853, 1612, 1513, 1281, 1157, 1108, 844, 804, 741, 710, 618 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(4-methoxybenzenesulfonyl)sulfimide (**3af**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, v/v) affords the title compound as a white solid. m.p. 145-147℃. 44.6 mg, 62% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.0 Hz, 1H), 8.54 (d, *J* = 7.4 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 3H), 3.04 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ161.8, 150.6, 143.8, 136.6, 136.5, 134.0, 131.6, 128.5, 128.5, 128.3, 126.9, 122.6, 113.8, 55.5, 38.6. HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{17}N_2O_3S_2$: 361.0675, found: 361.0673; IR (KBr): 2981, 2935, 1502, 1463, 1271, 1231, 1179, 1104, 1069, 832, 810, 724, 690 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(4-acetamidobenzenesulfonyl) sulfimide (**3ag**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, v/v) affords the title compound as a white solid. m.p. 125-127℃. 71.4 mg, 92% yield. ^1H NMR (400 MHz, DMSO) δ 10.19 (s, 1H), 9.02 – 8.95 (m, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 7.4 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.71 (dt, *J* = 15.8, 8.5 Hz, 5H), 3.05 (s, 3H), 2.07 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO) δ 168.7, 151.3, 142.9, 141.7, 138.4, 136.9, 133.6, 132.0, 128.2, 127.6, 126.7, 123.0, 118.4, 37.6, 24.0. HR-MS (ESI) calcd for $[M+H]^+$: $C_{18}H_{18}N_3O_3S_2$: 388.0784, found: 388.0787; IR (KBr): 3024, 2982, 2846, 1711, 1494, 1452, 1387, 1151, 1017, 785, 734, 697 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(2-methylbenzene sulfonyl) sulfimide (**3ah**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 106-108℃. 62.6 mg, 91% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 – 8.83 (m, 1H), 8.59 (d, *J* = 7.4 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.02 (dd, *J* = 16.8, 8.0 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 8.1, 4.1 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.24 (dt, *J* = 15.2, 6.9 Hz, 2H), 3.02 (s, 3H), 2.82 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 143.7, 142.1, 136.8, 136.6, 134.1, 132.0, 131.7, 131.4, 128.5, 128.1, 126.9, 125.6, 122.6, 38.4, 20.7. HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{17}N_2O_2S_2$: 345.0726, found: 345.0724; IR (KBr):3313, 3059, 2324, 2099, 1663, 1591, 1539, 1324, 1074, 1021, 961 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(3-methylbenzene sulfonyl) sulfimide (**3ai**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 115-117℃. 50.2 mg, 73% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 – 8.87 (m, 1H), 8.52 (d, *J* = 7.4 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 3.05 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 144.3, 143.7, 138.6, 136.6, 133.9, 132.0, 131.7, 128.6, 128.5, 128.4, 126.8, 126.8, 123.4, 122.6, 38.6, 21.3. HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{17}N_2O_2S_2$: 345.0726, found: 345.0732; IR (KBr): 3022, 2980, 1631, 1445, 1367, 1257, 1213, 1087, 1029, 838, 726, 685 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(2,3,5,6-tetramethylbenzene sulfonyl) sulfimide (**3aj**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 122-124℃. 37.8 mg, 49% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.2 Hz, 1H), 8.65 (d, *J* = 7.4 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.04 (s, 1H), 3.03 (s, 3H), 2.69 (s, 6H), 2.25 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ150.5, 143.9, 142.5, 136.5, 135.2, 134.7, 134.4, 134.3, 131.5, 128.9, 128.5, 127.0, 122.4, 38.4, 20.9, 18.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{20}H_{23}N_2O_2S_2$: 387.1195, found: 387.1197; IR (KBr): 3012, 2927, 1534, 1361, 1256, 1217, 821 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(naphthalen-1-ylsulfonyl) sulfimide (**3ak**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) affords the title compound as a white solid. m.p. 134-136℃. 65.4 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.2 Hz, 1H), 8.55 (d, *J* = 7.4 Hz, 1H), 8.51 (s, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 6.9 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.57 – 7.50 (m, 3H), 3.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.6, 143.7, 141.3, 136.5, 134.3, 133.8, 132.3, 131.7, 129.1, 129.0, 128.5, 128.5, 127.9, 127.7, 127.0, 126.8, 126.7, 122.8, 122.6, 38.6. HR-MS (ESI) calcd for $[M+H]^+$: $C_{20}H_{17}N_2O_2S_2$: 381.0726, found: 381.0722; IR (KBr): 3014, 2920, 1591, 1347, 1263, 1213, 1089, 1034, 973, 822, 727 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(thiophen-2-ylsulfonyl) sulfimide (**3al**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 110-112℃. 57.8 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.1 Hz, 1H), 8.53 (d, *J* = 7.4 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.42 (d, *J* = 4.9 Hz, 1H), 6.97 (t, *J* = 4.3 Hz, 1H), 3.09 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.7, 146.0, 143.7, 136.6, 133.3, 131.8, 129.9, 129.8, 128.5, 128.4, 126.9, 126.8, 122.7, 38.6. HR-MS (ESI) calcd for $[M+H]^+$: $C_{14}H_{13}N_2O_2S_3$: 337.0134, found: 337.0137; IR (KBr): 3013, 2927, 1591, 1252, 1211, 1097, 1028, 831 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(benzylsulfonyl) sulfimide (**3am**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) affords the title compound as a white solid. m.p. 124-126℃. 64.0 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 – 8.80 (m, 1H), 8.47 (d, *J* = 7.4 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.27 (d, *J* = 5.7 Hz, 3H), 4.45 – 4.35 (m, 2H), 2.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.4, 143.5, 136.4, 134.9, 131.5, 131.2, 130.8, 128.4, 128.3, 128.2, 128.1, 126.8, 122.5, 60.7, 38.3. HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{17}N_2O_2S_2$: 345.0726, found: 345.0729; IR (KBr): 2927, 1601, 1507, 1262, 1208, 1156, 1021, 834, 755, 687 cm^{-1}.

*S-Methyl S-(quinolin-8-yl) N-(methylsulfonyl) sulfimide (**3an**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) affords the title compound as a white solid. m.p. 101-103℃. 48.2 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.84 (m, 1H), 8.51 (d, *J* = 7.4 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.09 (s, 3H), 2.98 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.7, 143.8, 136.6, 134.6, 131.7, 128.6, 128.1, 127.0, 122.7, 42.6, 39.1. HR-MS (ESI) calcd for $[M+H]^+$: $C_{11}H_{13}N_2O_2S_2$: 269.0413, found: 269.0411; IR (KBr):2923, 2853, 1593, 1502, 1462, 1325, 1168, 1135, 836, 754, cm^{-1}.

*S-Ethyl S-(quinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ba**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 111-113℃. 59.4 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 2.3 Hz, 1H), 8.50 (d, *J* = 7.3 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.54 (dd, *J* = 7.9, 4.0 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 3.47 (dd, *J* = 13.1, 6.8 Hz, 1H), 3.17 (dd, *J* = 13.1, 6.8 Hz, 1H), 2.36 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.5, 144.1, 141.6, 141.5, 136.5, 132.1, 131.5, 129.4, 129.2, 128.5, 126.8, 126.4, 122.5, 46.0, 21.4, 7.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{18}H_{19}N_2O_2S_2$: 359.0882, found: 359.0883; IR (KBr): 2920, 2834, 1603, 1511, 1246, 1170, 1033, 816, 751 cm^{-1}.

*S-Butyl S-(quinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ca**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) affords the title compound as a white solid. m.p. 104-106℃. 60.2 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 – 8.86 (m, 1H), 8.51 (d, *J* = 7.4 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.46 (dt, *J* = 12.4, 8.1 Hz, 1H), 3.11 – 3.02 (m, 1H), 2.37 (s, 3H), 1.75 – 1.68 (m, 1H), 1.48 – 1.40 (m, 1H), 1.31 (dd, *J* = 12.7, 7.0 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.5, 144.0, 141.6, 141.5, 136.5, 133.0, 131.4, 129.1, 128.9, 128.4, 126.9, 126.4, 122.5, 52.1, 25.0, 21.4, 21.1, 13.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{20}H_{23}N_2O_2S_2$: 387.1195, found: 387.1193; IR (KBr): 3191, 2982, 1529, 1161, 1032, 953, 738, 689 cm^{-1}.

*S-Benzyl S-(quinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ea**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 122-124℃. 65.5 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.44 – 8.34 (m, 1H), 8.30 – 8.19 (m, 1H), 8.03 – 7.92 (m, 1H), 7.68 – 7.51 (m, 4H), 7.21 (d, *J* = 4.9 Hz, 1H), 7.15 –

6.92 (m, 6H), 4.74 (dd, *J* = 12.3, 3.8 Hz, 1H), 4.24 (dd, *J* = 12.4, 4.0 Hz, 1H), 2.32 (d, *J* = 3.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 144.1, 141.3, 141.1, 136.6, 132.4, 131.5, 130.7, 129.5, 129.0, 128.8, 128.7, 128.4, 126.9, 126.2, 122.5, 57.6, 21.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{21}N_2O_2S_2$: 421.1039, found: 421.1044; IR (KBr): 3191, 2954, 2926, 1446, 1170, 1123, 734, 688 cm^{-1}.

*S-Phenyl S-(quinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3fa**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 112-114℃. 74.7 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.70 (dd, *J* = 7.4, 0.8 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.72 (dt, *J* = 7.8, 4.0 Hz, 3H), 7.45 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.35 – 7.25 (m, 3H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.31 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 143.9, 141.7, 141.4, 138.0, 136.2, 134.1, 131.9, 131.7, 129.3, 129.1, 128.7, 128.5, 127.7, 126.8, 126.4, 122.5, 21.3. HR-MS (ESI) calcd for $[M+H]^+$: $C_{22}H_{19}N_2O_2S_2$: 407.0882, found: 407.0878; IR (KBr): 3052, 1603, 1511, 1445, 1151, 1038, 830, 770, 734, 687 cm^{-1}.

*S-Methyl S-(2-methylquinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ga**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 110-112℃. 64.4 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 3.06 (s, 3H), 2.72 (s, 3H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 143.4, 141.8, 141.5, 136.3, 132.9, 131.2, 129.2, 128.1, 126.7, 126.3, 125.9, 123.4, 38.9, 25.3, 21.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{18}H_{19}N_2O_2S_2$: 359.0882, found: 359.0880; IR (KBr): 3193, 1590, 1482, 1243, 1085, 1051, 805, 739, 693 cm^{-1}.

*S-Methyl S-(3- ethyl quinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ha**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 114-116℃. 66.2 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.42 (d, *J* = 7.3 Hz, 1H), 8.03 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 2H), 3.03 (s, 3H), 2.86 (q, *J* = 7.4 Hz, 2H), 2.35 (s, 3H), 1.35 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.0, 142.1, 141.6, 141.5, 138.5, 133.9, 133.4, 131.3, 129.2, 128.5, 127.3, 126.7, 126.3, 38.6, 26.2, 21.4, 15.0. HR-MS (ESI) calcd for $[M+H]^+$: $C_{19}H_{21}N_2O_2S_2$: 373.1039, found: 373.1038; IR (KBr): 2918, 2834, 1607, 1512, 1447, 1168, 1032, 816, 751 cm^{-1}.

*S-Methyl S-(3-phenylquinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ia**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 158-160℃. 76.4 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.51 (d, *J* = 7.3 Hz, 1H), 8.39 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.71 (dd, *J* = 16.4, 7.9 Hz, 3H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 3.07 (s, 3H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.1, 142.7, 141.6, 141.6, 136.8, 135.5, 133.9, 133.4, 131.7, 129.4, 129.2, 128.8, 128.4, 128.2, 127.5, 127.3, 126.4, 38.7, 21.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{21}N_2O_2S_2$: 421.1039, found: 421.1044; IR (KBr): 3302, 2964, 1447, 1162, 1017, 939, 750, 732, 697 cm^{-1}.

*S-Methyl S-(6-methylquinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ja**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. m.p. 125-127℃. 65.9 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.26 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.73 (s, 1H), 7.49 (dd, *J* = 7.8, 4.1 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.01 (s, 3H), 2.54 (s, 3H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.6, 142.3, 141.7, 141.6, 137.4, 135.8, 133.2, 130.4, 130.2, 129.3, 128.7, 126.4, 122.5, 38.6, 21.6, 21.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{18}H_{19}N_2O_2S_2$: 359.0882, found: 359.0880; IR (KBr): 2965, 2926, 1447, 1170, 1117, 1023, 954, 734, 689 cm^{-1}.

*S-Methyl S-(6-methoxyquinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ka**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, v/v) affords the title compound as a white solid. m.p. 128-130℃. 57.7 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 3.9 Hz, 1H), 8.17 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.45 (dd, *J* = 8.1, 4.1 Hz, 1H), 7.22 (d, *J* = 7.0 Hz, 3H), 3.92 (s, 3H), 3.02 (s, 3H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 147.9, 141.6, 139.5, 135.4, 135.2, 129.9, 129.3, 126.4, 122.7, 120.8, 109.5, 56.1, 38.6, 21.4. HR-MS (ESI) calcd for $[M+H]^+$: $C_{18}H_{19}N_2O_3S_2$: 375.0832, found: 375.0815; IR (KBr): 3065, 3024, 1598, 1509, 1356, 1261, 1083, 749, 691cm^{-1}.

*S-Methyl S-(9-methylacridin-4-yl) N-(p-toluenesulfonyl)sulfimide (**3la**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) affords the title compound as a white solid. m.p. 136-138℃. 69.4 mg, 85% yield. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.57 (d, *J* = 7.1 Hz, 1H), 8.41 (d, *J* = 8.8 Hz, 1H), 8.28 (d, *J* = 8.9 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 7.94 – 7.78 (m, 3H), 7.74 – 7.57 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 4H), 3.16 (s, 6H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.7, 143.9, 143.7, 141.9, 141.5, 134.4, 131.1, 130.0, 129.6, 129.2, 128.4, 126.6, 126.4, 126.1, 125.6, 125.0, 124.6, 39.0, 21.4, 14.1. HR-MS (ESI) calcd for $[M+H]^+$: $C_{22}H_{21}N_2O_2S_2$: 409.1039, found: 409.1036; IR (KBr):2924, 2853, 1591, 1484, 1252, 1158, 1084, 835, 750, 695 cm^{-1}.

*S-Methyl S-(2,6-bis(methylthio)quinolin-8-yl) N-(p-toluenesulfonyl)sulfimide (**3ma**).* Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:2, v/v) affords the title compound as a white solid. m.p. 145-147℃. 68.9 mg, 79% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.6 Hz, 1H), 8.80 (d, *J* = 4.0 Hz, 1H), 8.36 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.59 (dd, *J* = 8.4, 3.9 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 3.10 (s, 3H), 2.60 (s, 3H), 2.38 (d, *J* = 5.5 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.0, 147.0, 141.8, 141.7, 141.5, 135.5, 134.3, 132.1, 130.9, 129.3, 126.3, 123.8, 123.6, 38.4, 21.4, 18.2, 15.6. HR-MS (ESI) calcd for $[M+H]^+$: $C_{19}H_{21}N_2O_2S_4$: 437.0480, found: 437.0477; IR (KBr): 3097, 1500, 1447, 1236, 1090, 1054, 1032, 960, 825, 727, 689 cm^{-1}.

Synthetic Application of This Transformation. *Procedure for the Pd(II)-catalyzed Allylic Substitution.* To a stirring solution of $[Pd_2(\eta_3\text{-}C_3H_5)_2Cl_2]$ or $PdCl_2$ (0.008 mmol) in toluene (1.5 mL) was added the sulfimide ligand (**3aa**) (10.3 mg, 0.03 mmol) under a nitrogen atmosphere. After 30 min, 1,3-diphenyl-3-acetoxy-1-propene (**4a**) (76 mg, 0.30 mmol) was added. The solution was then stirred for 30 min. *N*,*O*-Bis(trimethylsilyl)acetamide (0.44 mL, 1.8 mmol), dimethylmalonate (0.21 mL, 1.8 mmol), and potassium acetate (3.0 mg, 0.03 mmol) were added in that order. The reaction was monitored by TLC. After the solvent was evaporated under reduced pressure, silica gel column chromatography of the residue yielded the pure **6a**.

*Typical Procedure for the $PdCl_2$-Catalyzed Allylic Substitution (**6a-6g**).* All of the products (**6a-6g**) were obtained according to the following procedure. To a stirring solution of $PdCl_2$ (0.008 mmol) in toluene (1.5 mL) was added the sulfimide ligand (**3aa**) (10.3 mg, 0.03 mmol) under a nitrogen atmosphere. After 30 min, 1,3-diphenyl-3-acetoxy-1-propene (**4a**) (76 mg, 0.30 mmol) was added. The solution was then stirred for 30 min. *N*,*O*-Bis(trimethylsilyl)acetamide (0.44 mL, 1.8 mmol), 1, 3-dicarbonyl compounds (1.8 mmol), and potassium acetate (3.0 mg, 0.03 mmol) were added in that order. The reaction was monitored by TLC. Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate/petroleum as the eluent to give the desired products. All of the yields are isolated yield.

*(E)-Dimethyl 2-(1,3-diphenylallyl)malonate (**6a**).*[33] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) affords the title compound as a Colorless oil. In the presence of ligand 3aa, the yields were 92%(89.4 mg) for $[Pd_2(\eta_3\text{-}C_3H_5)_2Cl_2]$ and 88%(85.5 mg) for $PdCl_2$. Without adding the ligand 3aa, the yield was 15%(14.6 mg) for $[Pd_2(\eta_3\text{-}C_3H_5)_2Cl_2]$ and no product was found using $PdCl_2$ as catalyst. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 10H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.37 (dd, *J* = 15.7, 8.6 Hz, 1H), 4.31 (dd, *J* = 10.8, 8.7 Hz, 1H), 4.00 (d, *J* = 10.9 Hz, 1H), 3.74 (s, 3H), 3.55 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.2, 167.8, 140.2, 136.8, 131.9, 129.1, 128.7, 128.5, 127.9, 127.6, 127.2, 126.4, 57.6, 52.6, 52.5, 49.2. MS (ESI): m/z= 324.1 $[M]^+$.

*(E)-Diethyl 2-(1,3-diphenylallyl)malonate (**6b**).*[34] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a Colorless oil. 95.1 mg, 90% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 10H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.34 (dd, *J* = 15.8, 8.5 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.97 (qd, *J* = 7.2, 1.6 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.9, 167.4, 140.3, 136.9, 131.7, 129.4, 128.6, 128.5, 128.0, 127.5, 127.1, 126.4, 61.6, 61.4, 57.8, 49.2, 14.1, 13.8. MS (ESI): m/z= 352.2 $[M]^+$.

*(E)-diethyl 2-(1,3-diphenylallyl)-2-methylmalonate (**6c**).*[35] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a Colorless oil. 100.0 mg, 91% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.28 (dt, *J* = 7.4, 3.5 Hz, 4H), 7.24 – 7.16 (m, 2H), 6.70 (dd, *J* = 15.7, 8.9 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 4.29 (d, *J* = 8.9 Hz, 1H), 4.18 (td, *J* = 7.1, 2.2 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2, 170.9, 139.5, 137.4, 132.6, 129.6, 128.9, 128.4, 128.2, 127.3, 127.1, 126.3, 61.4, 61.3, 58.9, 53.7, 18.8, 14.0, 14.0. MS (ESI): m/z= 366.2 $[M]^+$.

*(E)-2-(1,3-diphenylallyl)cyclohexane-1,3-dione (**6d**).*[36] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) affords the title compound as a white solid. 78.5 mg, 86% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.26 (dt, *J* = 7.8, 5.6 Hz, 6H), 7.18 (t, *J* = 7.3 Hz, 2H), 6.80 (dd, *J* = 15.9, 7.8 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 5.18 (d, *J* = 7.7 Hz, 1H),

2.35 (t, *J* = 6.4 Hz, 4H), 1.91 – 1.81 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.7, 137.4, 131.5, 130.8, 128.5, 128.4, 127.8, 127.3, 126.3, 126.2, 117.6, 42.2, 20.6. MS (ESI): m/z= 304.1 $[M]^+$.

*(E)-3-(1,3-diphenylallyl)pentane-2,4-dione (**6e**)*.[37] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a white solid. 79.7 mg, 91% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 10H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.19 (ddd, *J* = 15.8, 5.5, 2.5 Hz, 1H), 4.38 – 4.28 (m, 2H), 2.23 (s, 3H), 1.91 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.8, 202.6, 140.2, 136.6, 131.7, 129.3, 129.1, 128.6, 128.0, 127.7, 127.3, 126.4, 74.5, 49.2, 30.1, 29.8. MS (ESI): m/z= 292.1 $[M]^+$.

*(E)-ethyl 2-acetyl-3,5-diphenylpent-4-enoate (**6f**)*.[37] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) affords the title compound as a Colorless oil. 82.2 mg, 85% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 10H), 6.44 (t, *J* = 15.4 Hz, 1H), 6.27 (ddd, *J* = 20.5, 15.8, 8.3 Hz, 1H), 4.34 – 4.24 (m, 1H), 4.21 – 4.05 (m, 2H), 3.92 (q, *J* = 7.1 Hz, 1H), 2.28 (s, 1.42H), 2.02 (s, 1.54H), 1.19 (t, *J* = 7.1 Hz, 1.56H), 0.96 (t, *J* = 7.1 Hz, 1.43H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.7, 201.4, 168.0, 167.6, 140.4, 140.2, 136.9, 136.7, 131.9, 131.5, 129.6, 129.4, 128.9, 128.7, 128.5, 128.1, 128.0, 127.6, 127.6, 127.2, 127.1, 126.4, 126.4, 65.6, 65.3, 61.6, 61.4, 49.0, 48.8, 30.0, 29.9, 14.2, 13.8. MS (ESI): m/z= 322.2 $[M]^+$.

*(E)-ethyl 2-benzoyl-3,5-diphenylpent-4-enoate (**6g**)*.[38] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) affords the title compound as a Colorless oil. 96.8 mg, 84% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.04 (m, 1.12H), 7.98 – 7.89 (m, 0.92H), 7.52 – 7.08 (m, 13H), 6.58 – 6.19 (m, 2H), 5.03 (dd, *J* = 10.9, 4.8 Hz, 1H), 4.68 – 4.54 (m, 1H), 4.15 – 4.04 (m, 0.88H), 3.90 – 3.78 (m, 1.10H), 1.10 (t, *J* = 7.1 Hz, 1.41H), 0.88 (d, *J* = 7.1 Hz, 1.62H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.2, 192.7, 168.1, 167.6, 141.0, 140.5, 137.0, 137.0, 137.0, 136.7, 133.7, 133.6, 131.9, 131.7, 130.0, 129.9, 128.9, 128.8, 128.7, 128.7, 128.7, 128.6, 128.4, 128.0, 127.6, 127.4, 127.2, 126.9, 126.4, 126.3, 61.8, 61.5, 59.9, 59.7, 49.1, 49.0, 14.2, 13.8. MS (ESI): m/z= 384.2 $[M]^+$.

Control Experiments for the Mechanism Studies. *Procedure for the Cu(I)-Catalyzed nitrene transfer reactions of methyl(phenyl) sulfane (**1n**) with TsN_3 (**2a**)*. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added methyl(phenyl)sulfane (**1o**) (0.2 mmol), 4-methylbenzenesulfonyl azide (**2a**) (0.4 mmol), CuCN (1.8 mg, 0.02 mmol, 10 mol %) and 1, 2-dichloroethane (1.0 mL) under Ar atmosphere conditions. The reaction mixture was stirred at 100 °C for 12 h. The reaction mixture was detected by TLC and no new spot was found.

*Procedure for the Cu(I)-Catalyzed Nitrene Transfer Reactions of 2-(Methylthio)pyridine(**1o**) with TsN_3 (**2a**)*. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added methyl(naphthalen-1-yl)sulfane (**1o**) (0.2 mmol), 4-methylbenzenesulfonyl azide **(2a)** (0.24 mmol), CuCN (1.8 mg, 0.02 mmol, 10 mol %) and 1, 2-dichloroethane (1.0 mL) under Ar atmosphere conditions. The reaction mixture was stirred at 100 °C for 12 h. The reaction mixture was detected by TLC and no new spot was found.

*Procedure for the Cu(I)-Catalyzed Nitrene Transfer Reactions of Methyl(naphthalen-1-yl)sulfane (**1p**) with TsN_3 (**2a**)*. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 2-(methylthio)pyridine (**1p**) (0.2 mmol), 4-methylbenzenesulfonyl azide **(2a)** (0.24 mmol), CuCN (1.8 mg, 0.02 mmol, 10 mol %) and 1, 2-dichloroethane (1.0 mL) under Ar atmosphere conditions. The reaction mixture was stirred at 100 °C for 12 h. The reaction mixture was detected by TLC and no new spot was found.

*Procedure for the Cu(I)-Catalyzed Nitrene Transfer Reactions of N-(2-(methylthio)phenyl)propionamide (**1q**) with TsN_3 (**2a**)*. The products 9 was obtained according to the following procedure. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added *N*-(2-(methylthio)phenyl)propionamide (**1q**, 0.2 mmol), 4-methylbenzenesulfonyl azide **(2a)** (0.24 mmol), CuCN (1.8 mg, 0.02 mmol, 10 mol %) and 1, 2-dichloroethane (1.0 mL) under Ar atmosphere conditions. The reaction mixture was stirred at 100 °C for 12 h, filtered through a pad of celite and then washed with ethyl acetate (10 mL × 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with petroleum / ethyl acetate (1:1, v/v) as the eluent to give the desired products **10**.

*(E)-N-(2-(S-methyl-N-tosylsulfinimidoyl)phenyl)propionamide (**10**)*.White solid. m.p. 114-116℃. 48.7mg, 67% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 9.89 – 9.77 (m, 1H), 7.82 (dd, *J* = 15.0, 7.6 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.65 – 7.60 (m, 1H), 7.46 (ddd, *J* = 8.0, 3.5, 2.1 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.99 (s, 3H), 2.47 – 2.39 (m, 2H), 2.36 (s, 3H), 1.27 – 1.21 (m, 3H). $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$) δ 173.8, 142.1, 140.6, 138.1, 133.7, 129.3, 127.7, 126.0, 125.7, 124.6, 36.1, 30.4, 21.4, 9.6. HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{21}N_2O_3S_2$: 365.0987, found: 365.0989; IR (KBr):2923, 1746, 1590, 1484, 1250, 1158, 1084, 954, 820, 750, 696 cm^{-1}.

ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and $^{13}C\{1H\}$ NMR spectra for all isolated compounds, and the single crystal data of **3ia**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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