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Reaction Mechanisms

Diversity in Gold-Catalyzed Formal Cycloadditions of Ynamides with Azidoalkenes or 2*H*-Azirines: [3+2] versus [4+3] Cycloadditions

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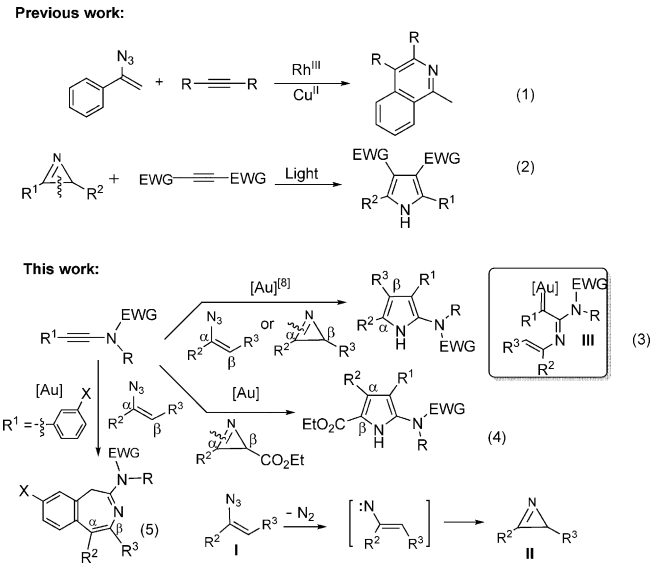
Abstract: Gold-catalyzed cycloadditions of ynamides with azidoalkenes or 2*H*-azirines give [3+2] or [4+3] formal cycloadducts of three classes. Cycloadditions of ynamides with 2*H*-azirine species afford pyrrole products with two regioselectivities when the C_β-substituted 2*H*-azirine is replaced from an alkyl (or hydrogen) with an ester group. For ynamides substituted with an electron-rich phenyl group, their reactions with azidoalkenes proceed through novel [4+3] cycloadditions to deliver 1*H*-benzo[*d*]azepine products instead.

Introduction

Metal-catalyzed cycloadditions are powerful tools to construct carbo- or heterocyclic frameworks.[1] Organic azides are valuable precursors to generate nitrenes in catalytic cycloadditions to access azacyclic compounds.[2] Related azidoalkenes commonly serve as three-atom motifs for several catalytic [3+2] cycloaddition reactions.[3] At elevated temperatures, azidoalkenes (**I**) undergo a loss of N_2 to form stable 2*H*-azirines (**II**).[4,5] Azidoalkenes and 2*H*-azirines, accordingly, are likely to give the same products under thermal activation. Chiba et al. reported rhodium-/copper-catalyzed [4+2] formal cycloadditions of 1-azidostyrene with internal alkynes to form isoquinoline derivatives [Eq (1)].[6] Xiao et al. reported metal-free, light-induced [3+2] formal cycloadditions of 2*H*-azirines with alkynes to yield functionalized pyrrole products through the cleavage of a C–C bond of the 2*H*-azirines [Eq. (2); EWG = electron-withdrawing group).[7] Immediately prior to completion of this work, Huang and co-workers reported gold-catalyzed [3+2] formal cycloadditions of 2*H*-azirines with ynamides to form pyrrole derivatives [Eq. (3)];[8] gold carbenes (**III**) were postulated as reaction intermediates. The work of Huang and co-workers does not reflect the diversity of reactions that can generate products of three types, as depicted in Equations (3)–(5). With the use of azidoalkenes, the reactions produce the same compounds as those described in Huang's work [Eq. (3)], but the reaction regioselectivity is completely different for those 2*H*-azirines with a C_β-substituted ester [Eq. (4)]. Particularly notable are the novel [4+3] formal cycloadditions between azidoalkenes and arenynamides with an electron-rich aryl group [Eq. (5)]. Notably, pyrroles and 1*H*-benzo[*d*]azepines in Equations (4) and (5) involve cleavage of the C_α=N bond of 2*H*-azirine, whereas the pyrrole products in Equation (3) arise from cleavage of the C_β–N bond of 2*H*-azirine. The occurrence of these diverse products enables precise elucidation of the reaction mechanism, which excludes the intermediacy of gold carbenes (**III**) because of improper rationalization of the resulting products in Equations (4) and (5).[9,10]



Results and Discussion

We first examined the reactions of cyclopropyl-substituted ynamide **1a** with 1-azidostyrene **2a** over $LAuCl/AgNTf_2$ (L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) or (tBu)$_2$(o-biphenyl)P) in CH_2Cl_2 or nitromethane at 28 °C, but no desired pyrrole product **3a** formed in a detectable amount. Table 1, entry 1, depicts the reaction conditions with P(tBu)$_2$(o-

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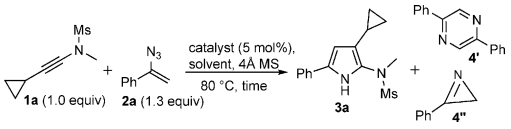
Table 1. Optimized conditions for [3+2] formal cycloadditions.



Entry	Catalyst[a]	Solvent	*t* [h]	Yield [%][c] 1a	3a	4′[d]	4′′[d]
1	$LAuCl/AgNTf_2$[b]	CH_3NO_2	11	–	65	12	–
2	$PPh_3AuCl/AgNTf_2$	CH_3NO_2	11	15	60	11	–
3	$AuCl_3$	CH_3NO_2	10	–	52	33	–
4	$IPrAuCl/AgNTf_2$	CH_3NO_2	12	–	84	5	–
5	$IPrAuCl/AgSbF_6$	CH_3NO_2	12	–	75	5	–
6	$IPrAuCl/AgNTf_2$	DCE[e]	12	–	72	8	–
7	$AgNTf_2$	CH_3NO_2	12	95	–	–	60

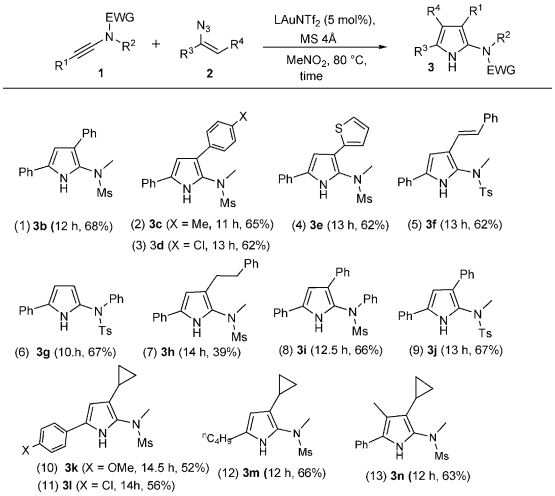
[a] [**1a**] = 0.24 M, 4 Å molecular sieves (4 Å MS; 20 mg). Tf = triflyl, Ms = mesyl. [b] L = P(*t*Bu)$_2$(*o*-biphenyl) or IPr. [c] Product yields are reported after separation on a column of silica gel. [d] The yields of compound **4′** are reported based on starting **2a**. [e] DCE = 1,2-dichloroethane.

biphenyl)AuCl/$AgNTf_2$ in $MeNO_2$ at 80 °C (11 h); desired cycloadduct **3a** and 2,5-diphenylpyrazine **4′**[11] were obtained in 65 and 12% yield, respectively. Compound **4′** arose from a dehydrogenative dimerization of species **2a** under the reaction conditions. The use of $PPh_3AuCl/AgNTf_2$ and $AuCl_3$ afforded the desired cycloadduct **3a** in diminished yields, that is, 60 and 52%, respectively (Table 1, entries 2 and 3). To our delight, the use of $IPrAuCl/AgNTf_2$ in hot nitromethane increased the yield of desired **3a** to 84% (Table 1, entry 4). Changing the silver source to $IPrAuCl/AgSbF_6$ slightly decreased the yield of cycloadduct **3a** to 75% (Table 1, entry 5). Commonly used DCE appeared to be less efficient than nitromethane, giving **3a** in 72% yield (Table 1, entry 6). $AgNTf_2$ alone was catalytically inactive, instead 1-azidostyrene **2a** was transformed into 2*H*-azirine **4′′**, whereas ynamide **1a** remained intact (Table 1, entry 7).

We expanded the scope of the reaction by using diverse ynamides **1** with various azidoalkenes **2** to access pyrrole compounds **3** (Table 2). The reactions of phenyl-substituted ynamides **1b–d** (X = H, Me, and Cl) with (1-azidovinyl)benzene (**2a**) and $IPrAuCl/AgNTf_2$ (5 mol%) in hot nitromethane (80 °C, 11–13 h) gave desired cycloadducts **3b–d** in 62–68% yield (Table 2, entries 1–3). The reaction was extended to thienyl-substituted ynamide **1e** to afford desired **3e** in 62% yield (Table 2, entry 4). The reaction was compatible with 2-en-1-ynamide **1f**, yielding pyrrole derivative **3f** in 62% (Table 2, entry 5). For unsubstituted and alkyl-substituted ynamides **1g** and **1h**, their gold-catalyzed cycloadditions with **2a** produced desired products **3g** and **3h** in 67 and 39% yield, respectively (Table 2, entries 6 and 7). Such [3+2] formal cycloadditions were extended to ynamides **1i** and **1j**, with different sulfonamides, giving desired **3i** and **3j** in 66 and 67% yield, respectively (Table 2, entries 8 and 9). The results in Table 2, entries 10 and 11, show the compatibility of this reaction with various vinylazides **2b** and **2c**, which have different 4-phenyl substituents (4-XC_6H_4, X = OMe and Cl), giving expected pyrrole products **3k** and **3l** in 52 and 56% yield, respectively. For *n*-butyl-substituted vinyl azide **2d**, its reaction with 2-cyclopropyl-1-ynamide **1a** afforded pyrrole species **3m** in 66% yield (Table 2, entry 12). We also tested the reaction on 1,2-disubstituted azidovinyl species **2e**, resulting in pyrrole species **3n** in 63% yield (Table 2, entry 13). Among these products, we performed XRD on representative species **3c** to elucidate its structure.[12]

We tested the reaction on (*E*)-ethyl 3-azidobut-2-enoate (**5a**), which gave products in a complicated mixture in hot DCE or $MeNO_2$ for either $IPrAuCl/AgNTf_2$ or $PPh_3AuCl/AgNTf_2$ [Eq. (6)] because azide species **5a** did not convert into 2*H*-azirine **5a′** at elevated temperatures. In contrast, the use of 2*H*-azirine **5a′** with these two catalysts enabled the efficient production of cycloadducts **6a** in 82 and 90% yield with $IPrAuCl/AgNTf_2$ or $PPh_3AuCl/AgNTf_2$, respectively [Eq. (7)]. Herein, the regioselectivity of this cycloaddition involves cleavage of the C_α=N bond of 2*H*-azirine, which is distinct from those instances in Table 2 and Equation (3), which involve the cleavage of a single C_β–N bond.

Table 2. Scope of [3+2] formal cycloadditions.



[a] L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, [**1**] = 0.24 M, 4 Å MS (20 mg). [b] Product yields are reported after separation on a column of silica gel.

The results in Table 3 show the substrate scope of the reaction. Herein, ynamides **1** were treated with ethyl 2*H*-azirine-2-carboxylates **5** (1.2 equiv) and $AuClPPh_3/AgNTf_2$ (5 mol%) in DCE (28 °C) for 3–11 h, producing cycloadducts **6b–i** in reasonable yields (74–86%). We first tested the reactions on phenyl-substituted ynamides **1b**, **1k**, and **1l** (X = H, OMe, and CF_3), affording desired **6b–d** in 75–86% yield. These cyclo-

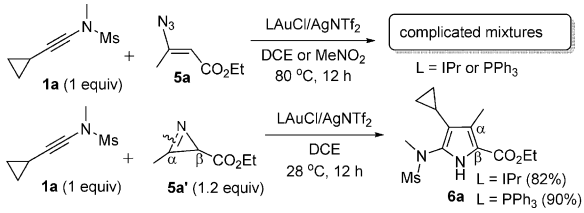
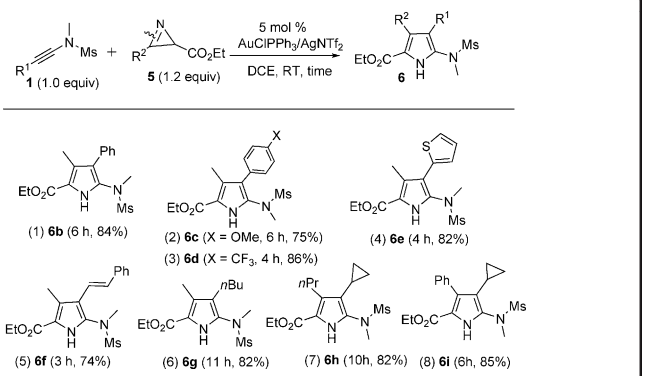


Table 3. Distinct regioselectivity of ethyl 2*H*-azirine-2-carboxylates.

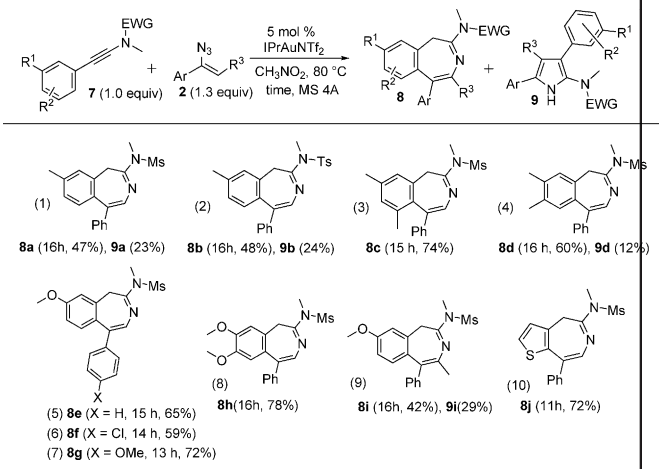


[a] [**1**] = 0.23 M, 4 Å MS (20 mg). [b] Product yields are reported after separation on a column of silica gel.

additions were applicable to thienyl-substituted ynamide **1e**, which yielded pyrrole derivative **6e** in 82% (Table 3, entry 4). These cycloadditions proceeded well with alkenyl- and alkyl-substituted ynamides **1f** and **1m**; the corresponding products **6f** and **6g** were obtained in 74 and 82% yield, respectively (Table 3, entries 5 and 6). The results in Table 3, entries 7 and 8, show the compatibility of such cycloadditions with ethyl 2*H*-azirine-2-carboxylates **5b** and **5c**, which gave the corresponding products **6h** and **6i** in satisfactory yields (Table 3, entries 7 and 8). XRD of cycloadduct **6b** was undertaken to verify its proposed structure.[12]

Surprisingly, new [4+3] formal cycloadditions occur with those ynamides with R^1 = Me or OMe at their *meta*-phenyl positions, as exemplified by species **7a–f** (Table 4); the conditions are the same as those outlined in Table 2. We tested the catalytic reactions of **2a** with arenynamides **7a** and **7b** (R^1 = Me), which contained two distinct sulfonamides, yielding 1*H*-benzo[d]azepine derivatives **8a** and **8b** in 47 and 48%, respectively; competing pyrrole species **9a** and **9b** were produced in 23 and 24% yield, respectively. The [4+3] formal cycloadducts **8c** and **8d** were produced in satisfactory yields (74 and 60%, respectively) from **2a** and arenynamides **7c** and **7d**, which contained 3,5- and 3,4-dimethylphenyl groups (Table 4, entries 3 and 4). Such cycloaddition reactions were compatible with various 1-azidostyrenes **2a–c** (Ar = 4-XC_6H_4; X = H, Cl, and OMe) that reacted with arenynamide **7e** (R^1 = OMe) to form [4+3] formal cycloadducts **8e–g** in 59–72% yields (Table 4, entries 5–7). This [4+3] cycloaddition can be extended to arenynamide **7f**, which contains a 3,4-dimethoxyphenyl group, giving the expected cycloadduct **8h** in 78% yield (Table 4, entry 8). The formal cycloaddition of **7e** with **2e** afforded the corresponding

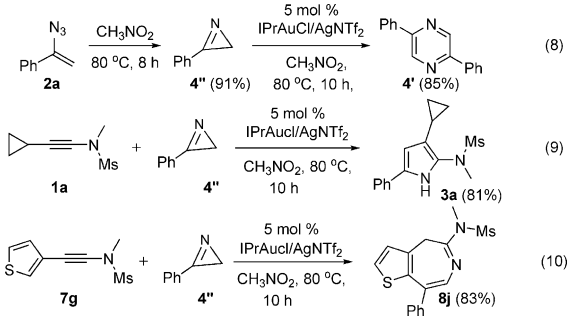
Table 4. Scope of gold-catalyzed [4+3] formal cycloadditions.



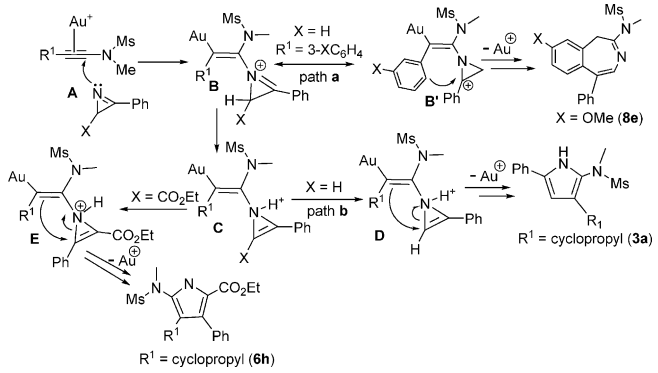
[a] [**7**] = 0.24 M, 4 Å MS (20 mg). [b] Product yields are reported after separation on a column of silica gel.

cycloadduct **8i** in 42% yield, together with pyrrole species **9i** in 29% yield (Table 4, entry 9). For 3-thienyl-substituted ynamide **7g**, its reaction with **2a** gave [4+3] cycloadduct **8j** efficiently (72%; Table 4, entry 10). Among these [4+3] cycloadducts, we undertook XRD analysis of compounds **8a** and **8j** to confirm their 3*H*-azepine frameworks.[12]

We conducted experiments to confirm that 2*H*-azirine **4″** was produced in 91% yield by heating **2a** in hot nitromethane (80 °C, 8 h); species **4″** thereby underwent dimerization to form 2,5-diphenylpyrazine **4′** selectively [Eq. (8)].[11] We observed such a pyrazine derivative **4′** during catalyst screening experiments (see Table 1). Particularly notable was the use of 2*H*-azirine **4″**, which reacted with cyclopropyl- and 3-thienyl-substituted ynamides **1a** and **7g** to yield desired [3+2] and [4+3] cycloadducts **3a** and **8j** selectively [Eqs. (9) and (10)]. We postulate that these cycloadditions might proceed through an initial transformation of **2a** into **4″**, which is an active intermediate in this catalytic system.



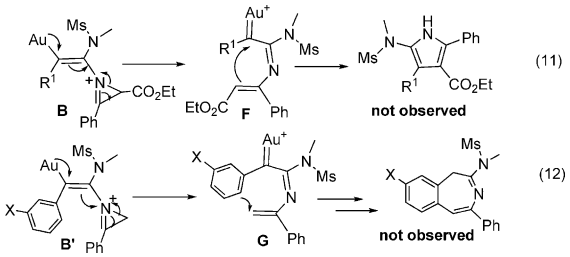
We postulate the reaction mechanism in Scheme 1 to rationalize the resulting three types of cycloadducts. These products begin with the addition of 2*H*-aziridines on gold π-alkyne **A** to yield common intermediates **B**. Because the 2*H*-aziridine ring of species **B** also has an iminium character, we accordingly



Scheme 1. Proposed mechanisms for diverse products.

postulate phenyl attack of those ynamides with an electron-rich group ($R^1 = 3\text{-}XC_6H_4$) at their azirine rings, ultimately giving desired product **8e** (X = OMe). For other ynamides and 2*H*-aziridines (X = H, CO_2Et), their corresponding intermediates **B** undergo a 1,2-hydrogen shift to form new intermediates **C**. In the case of 2*H*-aziridines with X = H, species **D** undergoes intramolecular cyclization through alkene attack at the less hindered *C*H= carbon of the aziridine ring, yielding pyrrole product **3a**. For 2*H*-aziridines with an ester moiety, the corresponding intermediate **E** prefers a Michael-type reaction, in which the =*C*HPh carbon is attacked by this tethered alkene, further yielding pyrrole products **6h**.

Our mechanism opposes the intermediacy of gold carbenes that are postulated by Huang et al.[8] because they cannot rationalize products **6h** and **8e**. As depicted in Equation (11), gold-driven ring opening of an azirinium ring of species **B** is expected to give gold carbene **F**, which undergoes an aza-Nazarov cyclization[13] to give pyrrole products with different structures from our resulting product **6h** (R^1 = cyclopropyl). Similarly, although the electron-rich benzene group of gold carbenes **G** can attack at the *C*H_2=CPh carbon, the resulting seven-membered product is expected to have a structure distinct from our observed product **8e** [X = OMe; Eq. (12)]. Accordingly, the intermediacy of gold carbenes is unlikely to occur here.



(11)

(12)

Conclusion

Diverse chemoselectivity of gold-catalyzed cycloadditions of ynamides with azidoalkenes or 2*H*-azirines was described. Our control experiments indicated that the initial azidoalkenes were thermally converted into 2*H*-azirines to activate the reactions. Formal cycloadditions of ynamides with 2*H*-aziridines afforded [3+2] pyrrole products with two distinct regioselectivities, depending on the substituents of the 2*H*-azirines. For ynamides substituted with an electron-rich phenyl group, their reactions with azidoalkenes proceeded through novel [4+3] cycloadditions[14] to deliver 1*H*-beno[*d*]azepine products instead. The presence of such diverse cycloadducts provides precise information on the mechanism of cycloaddition; thus excluding gold carbenes as reaction intermediates.

Experimental Section

General

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware by using standard syringe, cannula, and septa apparatus. THF and hexane were dried with sodium benzophenone and distilled before use. CH_2Cl_2, DCE, and toluene were dried over CaH_2 and distilled before use. Nitromethane was dried over activated 4 Å MS. Et_3N and CH_3NO_2 were stored over 4 Å MS prior to use. Reagents were purchased from commercial sources and used without purification, unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on Varian 400 MHz, Varian 500 MHz, Bruker 400 MHz, and Bruker 600 MHz spectrometers by using $CDCl_3$, CD_2Cl_2, and C_6D_6 as internal standards.

Standard procedure for synthesis of 3a

A solution of **1a** (100 mg, 0.58 mmol) and **2a** (109 mg, 0.75 mmol) in nitromethane (1.5 mL) at 28 °C was added to a solution of [1,3-bis(diisopropylphenyl)imidazol-2-ylidene]AuCl (17.9 mg, 0.03 mmol), silver bis(trifluoromethanesulfonyl)imide (11.2 mg, 0.03 mmol), and powdered 4 Å MS (20 mg) in nitromethane (0.5 mL). The resulting solution was stirred at 80 °C for 12 h before it was filtered through a short Celite pad, concentrated, and eluted through a column of silica gel (10% ethyl acetate/hexane, $R_f = 0.3$ in 25% ethyl acetate/hexane system) to afford compound **3a** (141 mg, 0.48 mmol, 84%) as a pale yellow solid.

Standard procedure for synthesis of 6a

A solution of **1a** (100 mg, 0.58 mmol) and **5a′** (88 mg, 0.69 mmol) in DCE (2.0 mL) at 28 °C was added to a solution of PPh_3AuCl (14.3 mg, 5 mol%), silver bis(trifluoromethanesulfonyl)imide (11.2 mg, 5 mol%), and powdered 4 Å MS (20 mg) in DCE (0.5 mL). The resulting solution was stirred at RT for 8 h before it was filtered through a short Celite pad, concentrated, and eluted through a column of silica gel (20% ethyl acetate/hexane system) to afford compound **6a** (156 mg, 0.52 mmol, 90%) as a white solid.

Standard procedure for synthesis of 8a

A solution of **7a** (100 mg, 0.45 mmol) and **2a** (85 mg, 0.58 mmol) in nitromethane (1.5 mL) at 28 °C was added to a solution of [1,3-bis(diisopropylphenyl)imidazol-2-ylidene]AuCl (13.9 mg, 5 mol%), silver bis(trifluoromethanesulfonyl)imide (8.7 mg, 5 mol%), and powdered 4 Å MS (20 mg) in nitromethane (0.5 mL). The resulting solution was stirred at 80 °C for 16 h before it was filtered through a short Celite pad, concentrated, and eluted through a column of silica gel (8% ethyl acetate/hexane, $R_f = 0.3$ in 20% ethyl acetate/hexane system) to afford compound **8a** (72 mg, 0.21 mmol, 47%) as a white solid and **9a** (35 mg, 0.10 mmol, 23%) as a colorless viscous liquid.

Compound 3a: Pale yellow solid (141 mg, 84%); m.p. 195–196 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 7.39–7.38 (m, 2H), 7.32–7.29 (m, 2H), 7.19–7.17 (m, 1H), 6.97 (d, J = 3.0 Hz, 1H), 3.38 (s, 3H), 3.02 (s, 3H), 1.65–1.61 (m, 1H), 0.91–0.88 (m, 2H), 0.66–0.63 ppm (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 131.9, 130.0, 128.8, 126.6, 125.2, 123.8, 122.6, 101.9, 38.4, 37.6, 7.7, 6.8 ppm; HRMS: *m/z* calcd for $C_{15}H_{18}N_2O_2S$: 290.1089; found: 290.1100.

Compound 3b: Pale yellow solid (106 mg, 68%); m.p. 178–179 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.89 (s, 1H), 7.52–7.51 (m, 2H), 7.48–7.47 (m, 2H), 7.40–7.38 (m, 2H), 7.37–7.34 (m, 2H), 7.28–7.22 (m, 2H), 6.61 (d, J = 3.1 Hz, 1H), 3.34 (s, 3H), 2.74 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 134.4, 131.6, 130.9, 128.9, 128.7, 127.0, 126.9, 126.7, 124.0, 121.4, 105.2, 38.8, 38.6 ppm (one aromatic quaternary carbon merged); HRMS: *m/z* calcd for $C_{18}H_{18}N_2O_2S$: 326.1089; found: 326.1090.

Compound 3c: White solid (99 mg, 65%); m.p. 186–187 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.75 (s, 1H), 7.48–7.47 (m, 2H), 7.41–7.40 (m, 2H), 7.37–7.35 (m, 2H), 7.25–7.23 (m, 1H), 7.22–7.19 (m, 2H), 6.59 (d, J = 3.1 Hz, 1H), 3.33 (s, 3H), 2.75 (s, 3H), 2.36 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 136.4, 131.7, 131.4, 130.8, 129.4, 128.9, 127.0, 126.9, 124.0, 123.9, 121.4, 105.3, 38.7, 38.6, 21.1 ppm; HRMS: *m/z* calcd for $C_{19}H_{20}N_2O_2S$: 340.1245; found: 340.1251.

Compound 3d: Pale yellow solid (91.8 mg, 62%); m.p. 203–204 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.88 (s, 1H), 7.47–7.44 (m, 4H), 7.37–7.35 (m, 4H), 7.26–7.23 (m, 1H), 6.57 (d, J = 3.1 Hz, 1H), 3.33 (s, 3H), 2.77 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 132.8, 132.4, 131.4, 131.2, 128.9, 128.1, 127.2, 124.1, 124.0, 120.2, 104.9, 38.9, 38.5 ppm (two aromatic CH merged); HRMS: *m/z* calcd for $C_{18}H_{17}ClN_2O_2S$: 360.0699; found: 360.0695.

Compound 3e: Pale yellow solid (95.7 mg, 62%); m.p. 155–156 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.04 (s, 1H), 7.48–7.46 (m, 2H), 7.36–7.33 (m, 2H), 7.25–7.21 (m, 2H), 7.17–7.16 (dd, J = 1.1, 3.5 Hz, 1H), 7.06–7.05 (m, 1H), 6.61 (d, J = 3.1 Hz, 1H), 3.36 (s, 3H), 2.91 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 135.9, 131.4, 131.2, 128.8, 127.3, 127.1, 124.1, 123.6, 123.5, 123.3, 115.7, 104.5, 39.0, 38.3 ppm; HRMS: *m/z* calcd for $C_{16}H_{16}N_2O_2S_2$: 332.0653; found: 332.0650.

Compound 3f: Pale yellow solid (85.3 mg, 62%); m.p. 196–197 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.50–7.48 (m, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.25–7.22 (m, 5H), 7.16–7.14 (m, 1H), 7.01–7.00 (m, 2H), 6.59 (d, J = 2.9 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 5.78 (d, J = 16.1 Hz, 1H), 3.34 (s, 3H), 2.20 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.3, 137.5, 134.6, 131.6, 131.0, 129.7, 128.9, 128.4, 127.8, 126.9, 126.8, 126.7, 125.9, 125.7, 123.9, 119.1, 118.7, 102.0, 39.6, 21.3 ppm; HRMS: *m/z* calcd for $C_{26}H_{24}N_2O_2S$: 428.1558; found: 428.1555.

Compound 3g: Pale yellow solid (96 mg, 67%); m.p. 182–183 °C; ^{1}H NMR (600 MHz, C_3D_6O): δ = 10.52 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.47–7.45 (m, 2H), 7.41–7.40 (m, 2H), 7.36–7.34 (m, 4H), 7.28–7.25 (m, 3H), 7.12–7.10 (m, 2H), 6.25–6.24 (m, 1H), 2.45 ppm (s, 3H); ^{13}C NMR (150 MHz, C_3D_6O): δ = 144.9, 142.4, 137.4, 136.7, 130.3, 129.9, 129.8, 129.3, 128.9, 128.5, 128.1, 126.1, 125.4, 124.9, 114.2, 104.5, 21.5 ppm; HRMS: *m/z* calcd for $C_{23}H_{20}N_2O_2S$: 388.1245; found: 388.1247.

Compound 3h: Colorless viscous oil (58.3 mg, 39%); ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.42 (s, 1H), 7.48–7.46 (m, 2H), 7.39–7.36 (m, 2H), 7.27–7.17 (m, 6H), 6.42 (d, J = 3.0 Hz, 1H), 3.10 (s, 3H), 2.95 (t, J = 7.5 Hz, 2H), 2.83 (s, 3H), 2.74 ppm (t, J = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 142.5, 132.5, 130.5, 129.3, 128.9, 128.8, 127.0, 126.4, 125.6, 124.1, 120.9, 106.1, 38.8, 38.0, 37.1, 28.1 ppm; HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_2S$: 354.1402; found: 354.1404.

Compound 3i: White solid (94.5 mg, 66%); m.p. 152–153 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.98 (s, 1H), 7.54–7.52 (m, 2H), 7.39–7.16 (m, 13H), 6.66 (d, J = 3.1 Hz, 1H), 2.89 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.6, 134.1, 131.6, 131.5, 129.4, 128.9, 128.5, 127.4, 127.1, 126.8, 125.8, 124.1, 123.4, 123.1, 122.3, 105.9, 40.6 ppm; HRMS: *m/z* calcd for $C_{23}H_{20}N_2O_2S$: 388.1245; found: 388.1250.

Compound 3j: Pale yellow solid (77.6 mg, 67%); m.p. 157–158 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.25–7.24 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.11–7.07 (m, 3H), 6.82–6.81 (m, 2H), 6.50 (d, J = 3.2 Hz, 1H), 3.16 (s, 3H), 2.38 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.0, 134.9, 134.3, 131.8, 129.8, 129.6, 128.9, 128.0, 127.6, 127.2, 126.8, 126.2, 124.3, 123.8, 120.9, 105.6, 38.3, 21.5 ppm; HRMS: *m/z* calcd for $C_{24}H_{22}N_2O_2S$: 402.1402; found: 402.1410.

Compound 3k: White solid (96.2 mg, 52%); m.p. 135–136 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.32–7.31 (m, 2H), 6.87–6.85 (m, 2H), 5.85 (d, J = 3.0 Hz, 1H), 3.79 (s, 3H), 3.36 (s, 3H), 3.01 (s, 3H), 1.61–1.59 (m, 1H merged with water signal from $CDCl_3$), 0.89–0.87 (m, 2H), 0.64–0.62 ppm (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.6, 130.1, 125.2, 124.9, 124.6, 122.5, 114.3, 100.9, 55.3, 38.4, 37.6, 7.7, 6.9 ppm; HRMS: *m/z* calcd for $C_{16}H_{20}N_2O_3S$: 320.1195; found: 320.1197.

Compound 3l: Pale yellow solid (105 mg, 56%); m.p. 170–171 °C; ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.48 (s, 1H), 7.37–7.35 (m, 2H), 7.33–7.31 (m, 2H), 6.02 (d, J = 3.1 Hz, 1H), 3.37 (s, 3H), 3.04 (s, 3H), 1.65–1.56 (m, 1H), 0.93–0.90 (m, 2H), 0.66–0.63 ppm (m, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 132.4, 131.0, 129.4, 128.9, 126.4, 125.3, 123.4, 103.0, 38.7, 38.1, 7.9, 7.1 ppm; HRMS: *m/z* calcd for $C_{15}H_{17}ClN_2O_2S$: 324.0699; found: 324.0693.

Compound 3m: Brown viscous liquid (103 mg, 66%); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 5.36 (d, J = 3.0 Hz, 1H), 3.30 (s, 3H), 2.96 (s, 3H), 2.43 (t, J = 7.7 Hz, 2H), 1.56–1.49 (m, 3H), 1.34–1.30 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H), 0.82–0.80 (m, 2H), 0.55–0.53 ppm (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 131.3, 122.3, 120.8, 101.1, 38.4, 37.4, 31.3, 27.5, 22.4, 13.8, 7.6, 6.8 ppm; HRMS: *m/z* calcd for $C_{13}H_{22}N_2O_2S$: 270.1402; found: 270.1403.

Compound 3n: White solid (110 mg, 63%); m.p. 156–157 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.38–7.35 (m, 4H), 7.24–7.22 (m, 1H), 3.30 (s, 3H), 3.00 (s, 3H), 2.19 (s, 3H), 1.55–1.51 (m, 1H), 0.86–0.83 (m, 2H), 0.63–0.61 ppm (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 132.9, 128.6, 126.8, 126.6, 126.4, 124.8, 119.7, 116.3, 38.6, 38.5, 10.7, 6.1, 5.2 ppm; HRMS: *m/z* calcd for $C_{16}H_{20}N_2O_2S$: 304.1245; found: 304.1246.

Compound 6a: White solid (156 mg, 90%); m.p. 133–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (br s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.18 (s, 3H), 3.01 (s, 3H), 2.36 (s, 3H), 1.84–1.80 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 0.84–0.80 (m, 2H), 0.61–0.57 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 134.2, 122.7, 121.6, 111.5, 59.3,

38.9, 38.5, 14.4, 13.7, 7.4, 6.4 ppm; HRMS: *m/z* calcd for $C_{13}H_{20}N_2O_4S$: 300.1144; found: 300.1140.

Compound 6b: White solid (135 mg, 84%); m.p. 199–203 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.09 (s, 1H), 7.40 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 7.3 Hz, 1H), 7.24 (d, J = 6.5 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.14 (s, 3H), 2.57 (s, 3H), 2.21 (s, 3H), 1.35 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0, 133.3, 129.9, 128.6, 127.5, 127.4, 126.2, 122.5, 117.2, 60.3, 38.9, 38.2, 14.5, 11.0 ppm; HRMS: *m/z* calcd for $C_{16}H_{20}N_2O_4S$: 336.1144; found: 336.1137.

Compound 6c: White solid (115 mg, 75%); m.p. 187–190 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.94 (s, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 3.13 (s, 3H), 2.61 (s, 3H), 2.19 (s, 3H), 1.35 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.9, 159.0, 131.1, 127.4, 126.4, 125.4, 122.1, 117.0, 114.0, 60.2, 55.2, 38.8, 38.3, 14.5, 11.0 ppm; HRMS: *m/z* calcd for $C_{17}H_{22}N_2O_5S$: 366.1249; found: 366.1247.

Compound 6d: White solid (125 mg, 86%); m.p. 204–207 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.26 (br s, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.13 (s, 3H), 2.66 (s, 3H), 2.22 (s, 3H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.9, 137.2, 130.1, 129.6 (q, J(C,F) = 30.0 Hz), 127.5, 125.8, 125.5 (d, J(C,CF_3) = 3.3 Hz), 124.0 (d, J(C,CF_3) = 271.0 Hz), 121.3, 117.7, 60.5, 38.8, 38.6, 14.4, 11.1 ppm; HRMS: *m/z* calcd for $C_{17}H_{19}F_3N_2O_4S$: 404.1018; found: 404.1022.

Compound 6e: White solid (130 mg, 82%); m.p. 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (s, 1H), 7.29 (dd, J = 4.96, 1.2 Hz, 1H), 7.02–6.98 (m, 2H), 4.10 (q, J = 7.1 Hz, 2H), 3.18 (s, 3H), 2.64 (s, 3H), 2.44 (s, 3H), 1.10 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.6, 134.3, 134.2, 128.0, 126.6, 125.3, 124.5, 113.8, 111.2, 59.3, 39.5, 38.0, 13.9, 13.5 ppm; HRMS: *m/z* calcd for $C_{14}H_{18}N_2O_4S_2$: 342.0708; found: 342.0703.

Compound 6f: White solid (114 mg, 74%); m.p. 172–174 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.94 (s, 1H), 7.57 (d, J = 16.7 Hz, 1H), 7.45 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.23 (d, J = 7.0 Hz, 1H), 6.86 (d, J = 16.8 Hz, 1H), 4.30 (q, J = 6.8 Hz, 2H), 3.32 (s, 3H), 2.95 (s, 3H), 2.43 (s, 3H), 1.36 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.3, 137.8, 134.8, 129.7, 128.6, 127.4, 126.0, 122.4, 120.6, 118.4, 110.0, 59.6, 39.3, 38.0, 14.4, 13.9 ppm; HRMS: *m/z* calcd for $C_{18}H_{22}N_2O_4S$: 362.1300; found: 362.1304.

Compound 6g: Colorless viscous liquid (137 mg, 82%); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.77 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.24 (s, 3H), 2.93 (s, 3H), 2.36 (t, J = 7.8 Hz, 2H), 2.25 (s, 3H), 1.47–1.42 (m, 2H), 1.37–1.31 (m, 5H), 0.92 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0, 127.1, 126.5, 121.5, 117.3, 60.1, 38.5, 38.0, 32.3, 23.7, 22.9, 14.5, 13.8, 10.7 ppm; HRMS: *m/z* calcd for $C_{14}H_{24}N_2O_4S$: 316.1457; found: 316.1460.

Compound 6h: Colorless viscous liquid (155 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.21 (s, 3H), 2.98 (s, 3H), 2.78 (t, J = 7.6 Hz, 2H), 1.87–1.80 (m, 1H), 1.65–1.55 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H), 0.86–0.81 (m, 2H), 0.62–0.59 ppm (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.2, 138.3, 122.9, 121.3, 111.2, 59.3, 38.7, 38.5, 29.7, 22.5, 14.4, 13.8, 7.4, 6.4 ppm; HRMS: *m/z* calcd for $C_{15}H_{24}N_2O_4S$: 328.1457; found: 328.1457.

Compound 6i: White solid (178 mg, 85%); m.p. 180–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 7.39 (q, J = 7.8 Hz, 2H), 7.32 (d, J = 7.1 Hz, 3H), 4.15 (q, J = 7.1 Hz, 2H), 3.24 (s, 3H), 2.98 (s, 3H), 1.89–1.82 (m, 1H), 1.14 (t, J = 7.1 Hz, 3H), 0.88–0.84 (m, 2H), 0.66–0.62 ppm (q, J = 5.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.2, 134.5, 131.8, 128.7, 128.2, 128.0, 125.2, 121.9, 112.5, 59.7, 38.7, 38.5, 13.9, 7.1, 6.3 ppm; HRMS: *m/z* calcd for $C_{18}H_{22}N_2O_4S$: 362.1300; found: 362.1300.

Compound 8a: Pale yellow solid (71.7 mg, 47%); m.p. 161–163 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.38–7.34 (m, 5H), 7.27 (s, 1H), 7.19 (s, 1H), 7.06 (s, 2H), 4.63 (d, J = 12.7 Hz, 1H), 3.22 (s, 3H), 3.11 (s, 3H), 2.79 (d, J = 12.7 Hz, 1H), 2.38 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 147.9, 140.9, 139.6, 133.6, 132.9, 131.8, 131.1, 129.5, 128.9, 128.3, 127.9, 127.7, 127.3, 39.4, 37.9, 35.8, 21.3 ppm; HRMS: *m/z* calcd for $C_{19}H_{20}N_2O_2S$: 340.1245; found: 340.1250.

Compound 9a: Colorless viscous liquid (35 mg, 23%); ^{1}H NMR (600 MHz, CDCl3): δ = 8.67 (s, 1H), 7.49–7.48 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.32–7.30 (m, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.25–7.22 (m, 1H), 7.08 (d, J = 7.4 Hz, 1H), 6.60 (d, J = 3.1 Hz, 1H), 3.34 (s, 3H), 2.74 (s, 3H), 2.38 ppm (s, 3H); ^{13}C NMR (150 MHz, CDCl3): δ = 138.3, 134.3, 131.7, 130.8, 128.9, 128.6, 127.9, 127.5, 126.9, 124.1, 124.0, 121.5, 105.4, 38.8, 38.6, 21.6 ppm (one aromatic quaternary carbon merged); HRMS: *m/z* calcd for $C_{19}H_{20}N_2O_2S$: 340.1245; found: 340.1248.

Compound 8b: Pale yellow solid (67 mg, 48%); m.p. 164–165 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.67 (d, J = 8.3 Hz, 2H), 7.35–7.31 (m, 7H), 7.18 (s, 1H), 7.00 (s, 2H), 6.67 (s, 1H), 4.79 (d, J = 12.7 Hz, 1H), 3.09 (s, 3H), 2.72 (d, J = 12.7 Hz, 1H), 2.44 (s, 3H), 2.29 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 148.4, 144.6, 140.9, 139.3, 134.8, 133.6, 132.9, 131.8, 130.5, 129.9, 129.4, 128.5, 128.2, 128.1, 127.5, 127.2, 127.1, 38.5, 36.5, 21.7, 21.2; HRMS: *m/z* calcd for $C_{25}H_{24}N_2O_2S$: 416.1558; found: 416.1553.

Compound 9b: Pale yellow viscous liquid (33 mg, 24%); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.26–7.24 (m, 3H), 7.00 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.50 (d, J = 3.2 Hz, 1H), 6.30 (s, 1H),3.34 (s, 3H), 2.74 ppm (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.1, 137.4, 133.9, 131.4, 129.8, 129.3, 128.8, 127.9, 127.6, 127.3, 126.8, 126.6, 124.2, 123.8, 123.6, 120.0, 105.5, 37.9, 21.6, 21.3 ppm (one aromatic quaternary carbon merged); HRMS: *m/z* calcd for $C_{25}H_{24}N_2O_2S$: 416.1558; found: 416.1551.

Compound 8c: Pale yellow solid (84 mg, 74%); m.p. 192–194 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.24 (s, 1H), 7.21–7.19 (m, 2H), 7.16–7.13 (m, 3H), 6.96 (s, 1H), 6.81 (s, 1H), 4.43 (d, J = 12.7 Hz, 1H), 3.12 (s, 3H), 3.92 (s, 3H), 2.85 (d, J = 12.7 Hz, 1H), 2.25 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 151.5, 142.4, 138.7, 137.3, 136.7, 136.0, 131.6, 131.4, 131.3, 128.5, 127.5, 126.7, 125.7, 39.5, 38.1, 35.5, 22.5, 20.9 ppm; HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_2S$: 354.1402; found: 354.1404.

Compound 8d: Colorless viscous liquid (89.6 mg, 60%); ^{1}H NMR (600 MHz, CD_2Cl_2 at −50 °C): δ = 7.37–7.36 (m, 4H), 7.34–7.31 (m, 1H), 7.23 (s, 1H), 7.13 (s, 1H), 6.90 (s, 1H), 4.46 (d, J = 12.7 Hz, 1H), 3.23 (s, 3H), 3.16 (s, 3H), 2.72 (d, J = 12.7 Hz, 1H), 2.27 (s, 3H), 2.12 ppm (s, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2 at −50 °C): δ = 147.6, 141.0, 138.6, 135.3, 133.6, 133.0, 130.5, 129.5, 129.4, 129.2, 128.2,

128.1, 127.1, 39.9, 37.2, 35.3, 19.6, 19.5 ppm; HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_2S$: 354.1402; found: 354.1403.

Compound 9d: Colorless viscous liquid (18 mg, 12%); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 7.49–7.48 (m, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.28–7.23 (m, 3H, merged with $CDCl_3$ solvent signal), 7.13 (d, J = 7.8 Hz, 1H), 6.60 (d, J = 3.0 Hz, 1H), 3.33 (s, 3H), 2.76 (s, 3H), 2.29 (s, 3H), 2.27 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 136.8, 135.1, 131.8, 131.7, 130.6, 129.9, 128.9, 128.4, 126.9, 124.3, 123.9, 121.4, 105.4, 38.7, 38.6, 19.9, 19.4 ppm (one aromatic quaternary carbon merged); HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_2S$: 354.1402; found: 354.1402.

Compound 8e: White solid (97 mg, 65%); m.p. 131–132 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.37–7.34 (m, 5H), 7.22 (s, 1H), 7.08 (d, J = 8.8 Hz, 1H), 6.88 (d, J = 2.3 Hz, 1H), 6.80 (dd, J = 8.8, 2.3 Hz, 1H), 4.64 (d, J = 12.6 Hz, 1H), 3.83 (s, 3H), 3.21 (s, 3H), 3.07 (s, 3H), 2.81 ppm (d, J = 12.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 160.5, 147.6, 140.9, 133.1, 132.6, 130.9, 130.4, 129.5, 128.7, 128.3, 127.3, 113.6, 111.0, 55.4, 38.9, 38.4, 35.9 ppm; HRMS: *m/z* calcd for $C_{19}H_{20}N_2O_3S$: 356.1195; found: 356.1191.

Compound 8f: Pale yellow solid (96 mg, 59%); m.p. 167–168 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.33–7.28 (m, 4H), 7.18 (s, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 6.80 (dd, J = 2.6, 8.8, Hz, 1H), 4.64 (d, J = 12.6 Hz, 1H), 3.83 (s, 3H), 3.21 (s, 3H), 3.08 (s, 3H), 2.78 ppm (d, J = 12.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 160.6, 147.7, 139.4, 133.2, 133.0, 132.7, 130.7, 130.2, 129.8, 128.4, 128.3, 113.7, 111.2, 55.4, 39.1, 38.3, 35.8 ppm; HRMS: *m/z* calcd for $C_{19}H_{19}ClN_2O_3S$: 390.0805; found: 390.0806.

Compound 8g: White solid (116 mg, 72%); m.p. 171–172 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.29 (d, J = 8.5 Hz, 2H), 7.18 (s, 1H), 7.08 (d, J = 8.8 Hz, 1H), 6.91–6.88 (m, 3H), 6.81–6.79 (dd, J = 2.6, 8.8, Hz, 1H), 4.63 (d, J = 12.6 Hz, 1H), 3.83 (s, 6H), 3.19 (s, 3H), 3.04 (s, 3H), 2.79 ppm (d, J = 12.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 160.6, 158.8, 147.4, 133.5, 133.1, 131.9, 130.6, 130.5, 128.9, 113.6, 113.5, 111.2, 55.4, 55.3, 38.9, 38.5, 35.9 ppm (one aromatic quaternary carbon merged); HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_4S$: 386.1300; found: 386.1299.

Compound 8h: White solid (112 mg, 78%); m.p. 178–180 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.42–7.37 (m, 5H), 7.27 (s, 1H), 6.89 (s, 1H), 6.62 (s, 1H), 4.66 (d, J = 12.7 Hz, 1H), 3.96 (s, 3H), 3.67 (s, 3H), 3.22 (s, 3H), 3.06 (s, 3H), 2.73 ppm (d, J = 12.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 149.9, 147.3, 147.1, 140.6, 133.0, 130.9, 129.3, 128.3, 128.1, 127.4, 124.4, 110.0, 109.1, 55.9, 55.7, 38.6, 37.7, 35.9 ppm; HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_4S$: 386.1300; found: 386.1294.

Compound 8i: Colorless viscous liquid (65 mg, 42%); ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.36 (t, J = 7.5 Hz, 2H), 7.30–7.29 (m, 1H), 7.22 (s, 2H), 6.84 (d, J = 2.6 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H), 6.69–6.67 (dd, J = 2.7, 8.8 Hz, 1H),), 4.55 (d, J = 12.4 Hz 1H), 3.78 (s, 3H), 3.17 (s, 3H), 2.99 (s, 3H), 2.89 (d, J = 12.7 Hz, 1H), 2.00 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 159.7, 146.3, 142.1, 140.1, 132.8, 131.2, 130.9, 130.4, 128.2, 126.7, 126.2, 113.4, 111.2, 55.4, 38.7, 38.5, 35.9, 22.5 ppm; HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_3S$: 370.1351; found: 370.1350.

Compound 9i: Colorless viscous liquid (45 mg, 29%); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.44–7.43 (m, 2H), 7.41–7.38 (m, 2H), 7.32 (t, J = 7.9 Hz, 1H), 7.27–7.25 (m, 1H), 6.92–6.89 (m, 1H), 6.88–6.85 (m, 2H), 3.82 (s, 3H), 3.42 (s, 3H), 2.59 (s, 3H), 2.12 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.6, 135.9, 132.7, 129.5, 128.7, 127.1, 126.8, 126.7, 124.1, 122.3, 115.7, 114.7, 112.2, 55.2, 39.5, 38.1, 11.2 ppm (one aromatic quaternary carbon merged); HRMS: *m/z* calcd for $C_{20}H_{22}N_2O_3S$: 370.1351; found: 370.1354.

Compound 8j: Pale yellow solid (111 mg, 72%); m.p. 176–177 °C; ^{1}H NMR (600 MHz, $CDCl_3$ at −50 °C): δ = 7.59–7.58 (m, 2H), 7.46 (d, J = 5.1 Hz, 1H), 7.43–7.39 (m, 3H), 7.24 (s, 1H), 6.97 (d, J = 5.1 Hz, 1H), 4.88 (d, J = 13.2 Hz, 1H), 3.21 (s, 3H), 3.09 (s, 3H), 2.49 ppm (d, J = 13.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$ at −50 °C): δ = 142.7, 139.7, 137.6, 131.7, 128.9, 128.6, 128.4, 128.2, 128.1, 126.2, 124.6, 39.0, 36.1, 33.9 ppm; HRMS: *m/z* calcd for $C_{16}H_{16}N_2O_2S_2$: 332.0653; found: 332.0656.

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