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Synthesis of Pyrazines from Rhodium-Catalyzed Reaction of 2*H*-Azirines with *N*-Sulfonyl 1,2,3-Triazoles

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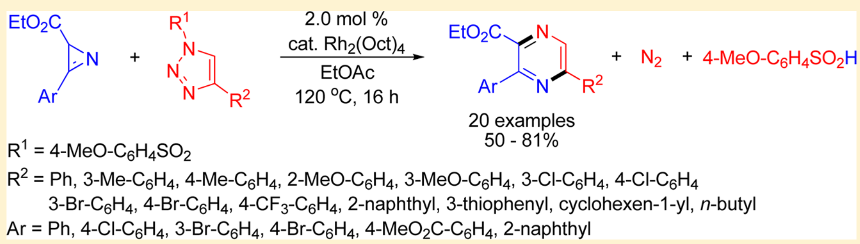
Supporting Information



ABSTRACT: An efficient synthetic route to a wide range of trisubstituted pyrazines is developed from Rh-catalyzed reaction of 2*H*-azirines with *N*-sulfonyl-1,2,3-triazoles through the elimination of nitrogen molecule and arylsulfinic acid. The present reaction proceeds through formation of *in situ* generated dihydropyrazines.

■ INTRODUCTION

Development of a new synthetic method for azaheterocyclic compounds is highly significant in the investigation for new medicines, active pharmaceutical ingredients (API), and fine chemicals.[1] In particular, pyrazine is one of the most representative privileged azaheterocyclic scaffolds, which show cytostatic, antifungal, and antitumor properties and are broadly present in flavorings and alarm pheromones (Figure 1).[2]

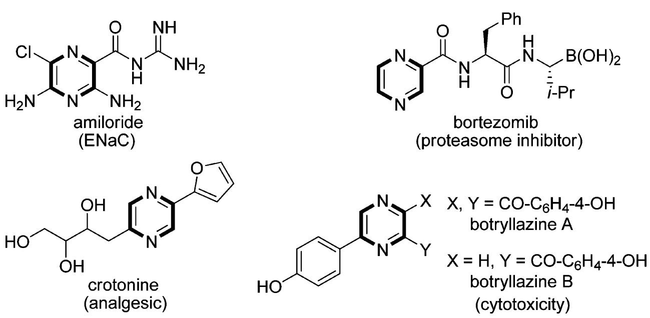
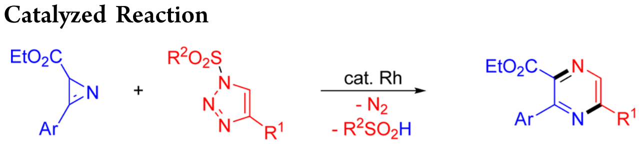


Figure 1. Bioactive compounds containing pyrazine moieties.

Accordingly, access to pyrazines from easily available starting materials is highly required. In general, the preparation of novel pyrazine scaffolds can be achieved by *de novo* synthesis from suitable starting materials. To date, some of the most usual *de novo* synthetic approaches described in the literature contain condensation of α-oximido carbonyl compounds with allylamines,[3] 1,4-addition of 1,2-diamines to 1,2-diaza-1,3-butadienes,[4] reductive condensation of α-nitro ketones with α-amino ketones using electron transfer reagent,[5] N−H insertion of Boc-amino acid amides followed by acid-promoted cyclodehydration,[6] opening of epoxides with 1,2-amino alcohols and Swern oxidation,[7] Ru-catalyzed dehydrogenative coupling of β-amino alcohols,[8] and opening of 2*H*-azirines and dimerization.[9] In addition, a wide range of pyrazines can be prepared by functionalization of a preformed pyrazine nucleus or cyclohexane derivatives having two nitrogen atoms at 1,4-position.[10] However, some of these synthetic methods are restricted by their low yields, rigorous conditions, difficulties of preparing unsymmetrical substituted pyrazines, or lack of substrate variation.

Over the last three years, the synthetic application of imino carbenes derived from *N*-sulfonyl-1,2,3-triazoles has been a very active area of research.[11] In this regard, we have intensively explored the utility of *N*-sulfonyl-1,2,3-triazoles as modular building blocks for the preparation of a wide range of aza- and carbo-heterocyclic compounds[12] and C−H bond insertion of azulene.[13] In continuing studies, we envisaged that the Rh-catalyzed reaction of 2*H*-azirines with *N*-sulfonyl-1,2,3-triazoles would allow the formation of pyrazines. Herein we report an efficient method for the synthesis of a plethora of trisubstituted pyrazines from Rh-catalyzed reaction of 2*H*-azirines with *N*-sulfonyl-1,2,3-triazoles through the elimination of nitrogen molecule and arylsulfinic acid (Scheme 1).[14]

Scheme 1. Synthesis of Pyrazines through Rhodium-Catalyzed Reaction



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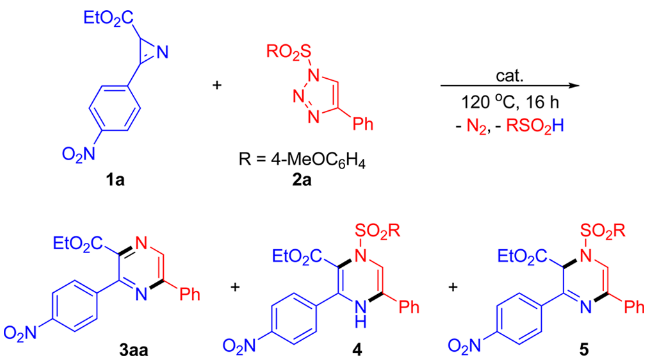
■ RESULTS AND DISCUSSION

First, we commenced our studies with a variety of *N*-sulfonyl-4-phenyl-1,2,3-triazoles (**2**) generated from Cu-catalyzed [3 + 2] cycloaddition of phenylacetylenes with sulfonyl azides.[15] 4-Methoxyphenylsulfonyl azide was the best 1,3-dipolar reagent among several sulfonyl azides screened (methane-, isopropane-, *n*-butane-, 4-trifluoromethylbenzene-, 4-methylbenzene-, and 4-methoxybenzene-sulfonyl azide). Next, Rh-catalyzed reaction of *N*-4-methoxybenzenesulfonyl-4-phenyl-1,2,3-triazole (**2a**) with ethyl 3-(4-nitrophenyl)-2*H*-azirine-2-carboxylate (**1a**)[16] was investigated (Table 1). Ethyl acetate was the best solvent

Table 1. Reaction Optimization[a]



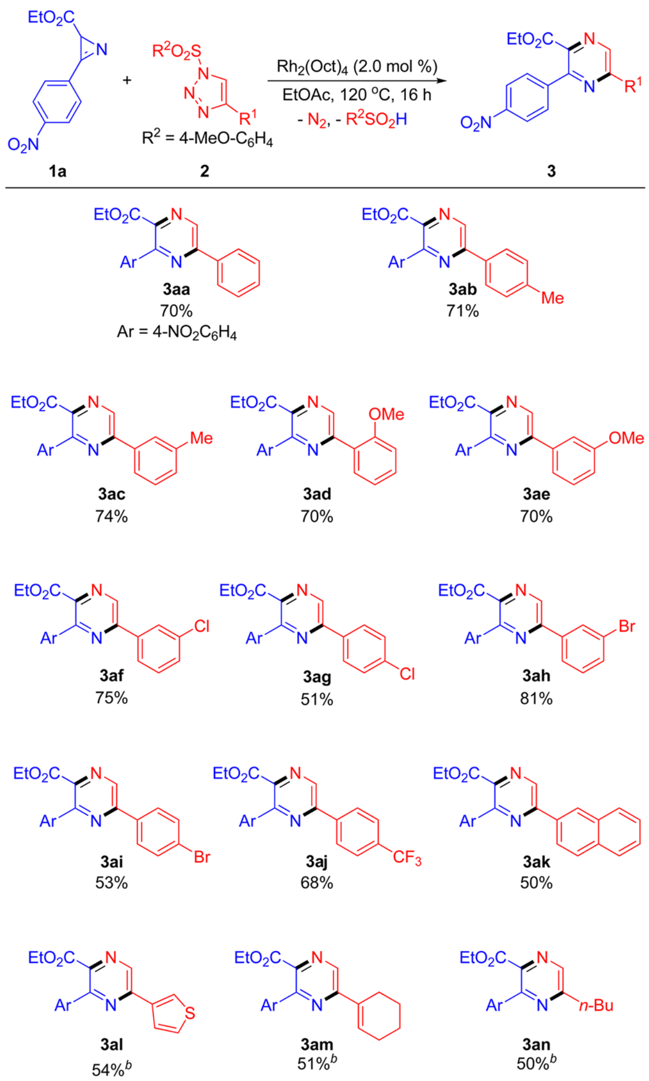
entry	cat. (2.0 mol %)	solvent	temp (°C)	yield (%)[b] 3aa	4	5
1	$Rh_2(OAc)_4$	DCE	120	56	16	-
2	$Rh_2(OAc)_4$	$CHCl_3$	120	53	17	-
3	$Rh_2(OAc)_4$	toluene	120	55	-	-
4	$Rh_2(OAc)_4$	PhCl	120	53	-	-
5	$Rh_2(OAc)_4$	*n*-hexane	120	52	-	-
6	$Rh_2(OAc)_4$	cyclohexane	120	66	-	-
7	$Rh_2(OAc)_4$	EtOAc	120	72	-	-
8	$Rh_2(OAc)_4$	EtOAc	100	15	14	53
9	$Rh_2(OAc)_4$	EtOAc	80	5	15	56
10	$Rh_2(OAc)_4$	EtOAc	120	73 (70)[c]	-	-
11	$Rh_2(S\text{-DOSP})_4$	EtOAc	120	66	12	-
12	$Rh_2(esp)_2$	EtOAc	120	64	12	-
13	-	EtOAc	120	-	-	-

[a]Reactions were carried out with **1a** (0.2 mmol) and **2a** (1.5 equiv) in solvent (1.0 mL, 0.2 M) at 120 °C for 16 h. [b]NMR yield using CH_2Br_2 as an internal standard. [c]Isolated yield of **3aa**.

among several reaction media examined (dichloroethane, chloroform, toluene, chlorobenzene, *n*-hexane, cyclohexane, and ethyl acetate). A number of rhodium(II) catalysts were tested to reveal that $Rh_2(Oct)_4$ (2.0 mol %) was the catalyst of choice. The best result was obtained from a reaction of **1a** (1.0 equiv, 0.2 mmol) with **2a** (1.5 equiv) using $Rh_2(Oct)_4$ (2.0 mol %) in ethyl acetate at 120 °C for 16 h, producing ethyl 3-(4-nitrophenyl)-5-phenylpyrazine-2-carboxylate (**3aa**) in 70% isolated yield (entry 10). When the present reaction was conducted with $Rh_2(OAc)_4$ (2.0 mol %) at or below 100 °C, dihydropyrazines **4** and **5** were produced (entries 8 and 9). These results indicate that pyrazine **3aa** is produced through elimination of arylsulfinic acid from dihydropyrazines **4** and **5**. In addition, the present reaction did not proceed under thermal conditions without using Rh catalyst (entry 13). Optimization of the stoichiometric ratio between starting materials **1a** and **2a** is described in the Supporting Information.

On the basis of the optimal reaction conditions, we next explored the substrate scope as well as the functional group compatibility in the reaction with ethyl 3-(4-nitrophenyl)-2*H*-azirine-2-carboxylate (**1a**) (Scheme 2). Electronic variation of

Scheme 2. Rh-Catalyzed Synthesis of Pyrazines Using Various Triazoles[a]



[a]Reactions were carried out with **1a** (0.2 mmol) and **2** (1.5 equiv) in solvent (1.0 mL, 0.2 M) at 120 °C for 16 h. [b]**2** (2.0 equiv) was used.

substituents at the aryl ring of *N*-sulfonyl triazoles (**2**) did not affect the reaction efficiency. For example, *N*-4-methoxybenzenesulfonyl-4-aryl-1,2,3-triazoles (**2**) having electron-donating 3-methyl, 4-methyl, 2-methoxy, and 3-methoxy groups on the phenyl ring underwent the Rh-catalyzed reactions, affording the desired pyrazines (**3ab**, **3ac**, **3ad**, and **3ae**) in good yields ranging from 70% to 74%. The structure of **3ab** was unambiguously determined by X-ray crystallography (see the Supporting Information).[17] In addition, the reactions of substrates with electron-withdrawing 3-chloro, 4-chloro, 3-bromo, and 4-bromo groups on the phenyl ring provided the cyclization products (**3af**, **3ag**, **3ah**, and **3ai**) in moderate to good yields ranging from 51% to 81%. The tolerance of chloro

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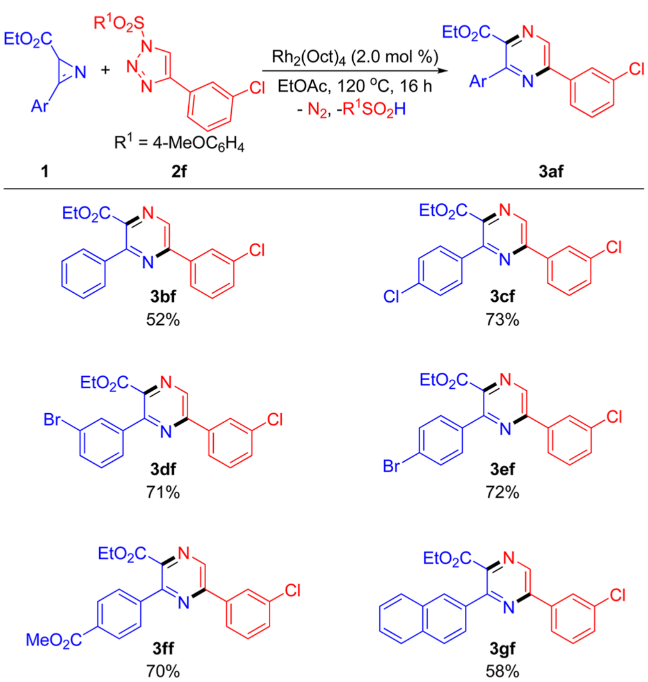
and bromo groups is especially meaningful, as further transformations of functional group are feasible. When a substrate having electron-withdrawing trifluoromethyl group was subjected to the Rh-catalyzed reaction, the product was formed in 68% yield. Substrate (**2k**) having 2-naphthyl group was also readily employed in the cyclization process. It was noteworthy that triazole bearing 3-thiophenyl group was also successfully applied to the current Rh-catalyzed reaction conditions, producing **3al** in 54% yield. When cyclohexenyl-substituted triazole (**2m**) was reacted with **1a** in the presence of the rhodium catalyst, the desired pyrazine **3am** was obtained in 51% yield. Triazole (**2n**) having a *n*-butyl group at 4-position turned out to be compatible with the optimal reaction conditions, delivering the desired pyrazine **3an** in 50% yield without *β*-hydride elimination.

With the success of the above reactions, we next investigated the effects of a number of substituents of ethyl 3-(4-aryl)-2*H*-azirine-2-carboxylate on cyclization (Scheme 3). Treatment of triazole **2f** with ethyl 3-(4-phenyl)-2*H*-azirine-2-carboxylate (**1b**) afforded ethyl 5-(3-chlorophenyl)-3-phenylpyrazine-2-carboxylate (**3bf**) in 52% yield. Electronic modification of substituents on the aryl ring of 2*H*-azirine **1** did not largely influence efficiency of the reaction. For instance, ethyl 3-(4-chlorophenyl)-2*H*-azirine-2-carboxylate (**1c**) was converted to the desired pyrazine **3cf** in 73% yield. In addition, electron-withdrawing 3- and 4-bromo groups on the aryl ring afforded the cyclization products (**3df** and **3ef**) in good yields. 2*H*-Azirine (**1f**) having 4-methoxycarbonyl group on the aryl ring worked equally well in the reaction with triazole **2f** to produce the corresponding pyrazine **3ff** in 70% yield. When the 2*H*-azirine (**1g**) bearing 2-naphthyl group was subjected to triazole **2f** under the optimal conditions, Rh-catalyzed reaction smoothly took place to afford trisubstituted pyrazine **3gf** in 58% yield. Unfortunately, 2*H*-azirines having electron-donating substituents such as methyl and methoxy groups on the aryl ring failed to prepare.

Scheme 3. Rh-Catalyzed Synthesis of Pyrazines Using Various 2*H*-Azirines[a]



[a]Reactions were carried out with **1a** (0.2 mmol) and **2** (1.5 equiv) in solvent (1.0 mL, 0.2 M) at 120 °C for 16 h. [b]**2** (2.0 equiv) was used.

A proposed reaction pathway for the formation of pyrazine (**3**) from *N*-sulfonyl-1,2,3-triazole **2** and 2*H*-azirine **1** is shown in Scheme 4. First, a ring−chain tautomerization of triazole **2** followed by treatment of a rhodium catalyst provides *α*-imino rhodium carbenoid **B** along with evolution of nitrogen molecule. Addition of 2*H*-azirine **1** to the carbene center of **B** produces the rhodium-bound zwitterionic intermediate **C**. Then, a ring-opening reaction through the release of an electron pair from anionic rhodium of **C** provides dihydropyrazine **5** (**pathway b**). Finally, elimination of arylsulfinic acid from **5** produces pyrazine **3**. 6*π*-Electrocyclization (**pathway a**) of 1,4-diazatriene **D** might be involved to the formation of dihydropyrazine **5**. Because regioisomeric pyrazine **H** and pyrazine **J** are not observed from this reaction, an intramolecular hydrogen transfer (**pathway d**) and dimerization of nitrile ylide dipole (**pathway c**) can be ruled out.[14,18] In fact, this postulation is supported by X-ray structure of pyrazine **3ab**. In addition, *tert*-butyl 3-methyl-2*H*-azirine-2-carboxylate was not reacted with triazole, indicating that steric as well as electronic effects of substrate might be important for the formation of pyrazine.

■ CONCLUSION

In summary, we have developed an efficient synthetic method for a range of trisubstituted pyrazines from Rh-catalyzed reaction of 2*H*-azirines with *N*-sulfonyl-1,2,3-triazoles through the elimination of nitrogen molecule and arylsulfinic acid. The present reaction proceeds through formation of *in situ* generated dihydropyrazines.

■ EXPERIMENTAL SECTION

General. Reactions were carried out in oven-dried glassware under air atmosphere. $Rh_2(Oct)_4$, $Rh_2(OAc)_4$, $Rh_2(esp)_2$, $Rh_2(S\text{-}DOSP)_4$ were purchased and used as received. Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel precoated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230−400 mesh). ^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (100 MHz), and ^{19}F NMR (377 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (*δ*) are reported in parts per million relative to the residual signals of this solvent [*δ* 7.26 for ^{1}H (chloroform-*d*), *δ* 2.05 for ^{1}H (acetone-d_6), *δ* 77.2 for $^{13}C\{^{1}H\}$ (chloroform-*d*), and *δ* 29.84, 206.26 for $^{13}C\{^{1}H\}$ (acetone-d_6)]. Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector−electric sector double focusing mass analyzer). Melting points were determined in open capillary tube.

Starting Materials of 2*H*-Azirines (1) and *N*-Sulfonyl-1,2,3-triazoles (2).[12b,16c] *Ethyl 3-(4-Nitrophenyl)-2H-azirine-2-carboxylate (1a).* Yellow solid, melting point: 84−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.44 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 4.30−4.18 (m, 2H), 2.97 (s, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) *δ* 170.1, 158.6, 131.3, 130.4, 1280, 124.5, 61.7, 30.5, 14.2; IR (film) 2984, 1727, 1528, 1465, 1346, 1316, 1202, 752, 685 cm^{-1}; HRMS (FAB) $[M + H]^+$ *m*/*z* calcd. for $C_{11}H_{11}N_2O_4$, 235.0719; found, 235.0717.

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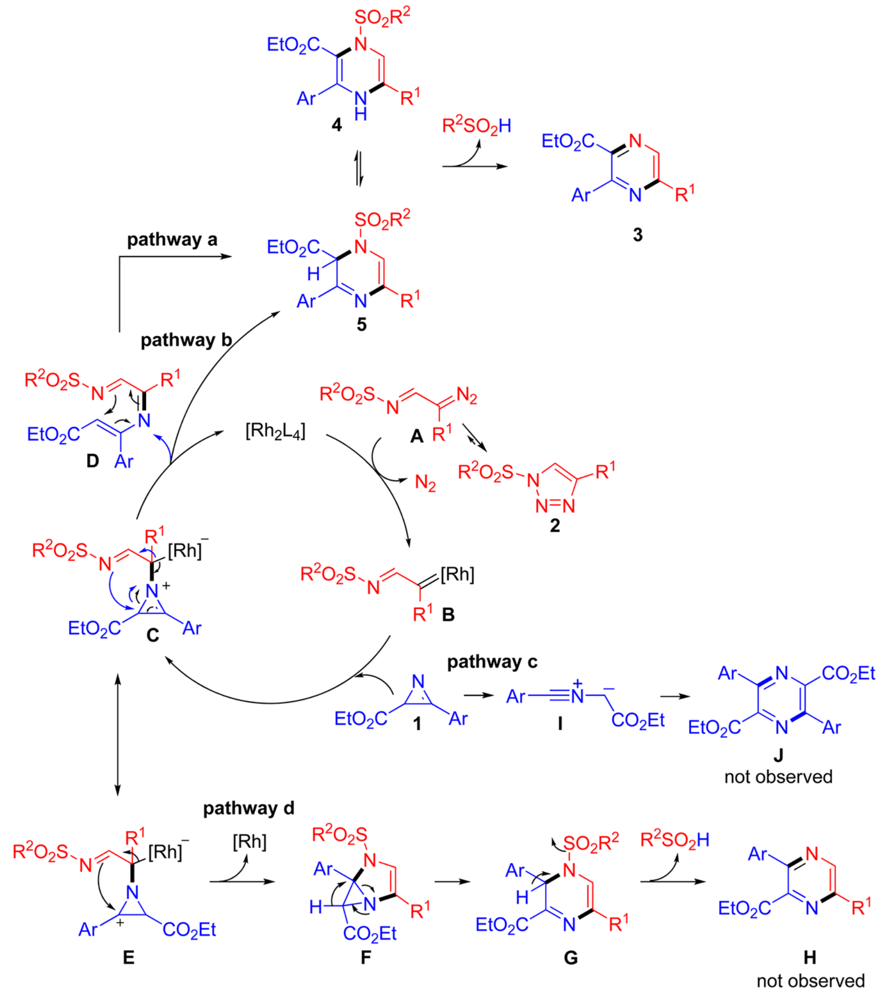
Scheme 4. Proposed Mechanism



*Ethyl 3-Phenyl-2H-azirine-2-carboxylate (**1b**).* Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.67−7.57 (m, 3H), 4.26−4.18 (m, 2H), 2.85 (s, 1H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.7, 158.6, 133.9, 130.4, 129.3, 122.3, 61.3, 29.7, 14.2; IR (film) 2982, 1729, 1579, 1465, 1451, 1334, 1199, 762, 689 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd. for $C_{11}H_{12}NO_2$, 190.0868; found, 190.0868.

*Ethyl 3-(4-Chlorophenyl)-2H-azirine-2-carboxylate (**1c**).* Yellow solid, melting point: 57−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 4.25−4.18 (m, 2H), 2.85 (s, 1H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4, 158.0, 140.4, 131.6, 129.8, 120.8, 61.4, 29.8, 14.2; IR (film) 2982, 1729, 1593, 1199, 835, 554 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd. for $C_{11}H_{11}ClNO_2$, 224.0478; found, 224.0474.

*Ethyl 3-(3-Bromophenyl)-2H-azirine-2-carboxylate (**1d**).* Orange oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, J = 1.6 Hz, 1H), 7.84 (dt, J = 7.7, 1.3 Hz, 1H), 7.77 (dq, J = 8.1, 1.0 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 4.26−4.17 (m, J = 7.1 Hz, 2H), 2.87 (s, 1H), 1.29 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2, 158.1, 136.7, 132.9, 130.9, 128.8, 124.2, 123.2, 61.4, 30.0, 14.2; IR (film) 2981, 1729, 1566, 1472, 1199, 787, 679, 578 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd. for $C_{11}H_{11}BrNO_2$, 267.9973; found, 267.9975.

*Ethyl 3-(4-Bromophenyl)-2H-azirine-2-carboxylate (**1e**).* Orange solid, melting point, 65−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 13.1, 8.8 Hz, 4H), 4.27−4.16 (m, 2H), 2.86 (s, 1H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4, 158.2, 132.8, 131.6, 129.0, 121.3, 61.4, 29.8, 14.2; IR (film) 2981, 1728, 1588, 1481, 1445, 1334, 1199, 831, 702 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd. for $C_{11}H_{11}BrNO_2$, 267.9973; found, 267.9972.

*Ethyl 3-(4-(Methoxycarbonyl)phenyl)-2H-azirine-2-carboxylate (**1f**).* Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H), 4.26−4.20 (m, 2H), 3.98 (s, 3H), 2.90 (s, 1H) 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.3, 165.8, 153.7, 134.8, 130.4, 130.3, 126.1, 61.5, 52.7, 30.1, 14.3; IR (film) 2984, 2954, 1726, 1571, 1335, 1199, 863, 769, 693 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd. for $C_{13}H_{14}NO_4$, 248.0923; found, 248.0920.

*Ethyl 3-(Naphthalen-2-yl)-2H-azirine-2-carboxylate (**1g**).* Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (S, 1H), 8.03−7.92 (m, 4H), 7.69−7.59 (m, 2H), 4.29−4.18 (m, 2H), 2.94 (s, 1H), 1.29 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.8, 158.6, 135.8, 133.0, 132.7, 129.4, 129.17, 129.2, 128.1, 127.4, 124.8, 119.6, 61.4, 29.9, 14.3; IR (film) 2981, 1727, 1596, 1465, 1332, 1191, 863, 820, 750 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd. for $C_{15}H_{14}NO_2$, 240.1025; found, 240.1024.

*1-((4-Methoxyphenyl)sulfonyl)-4-phenyl-1H-1,2,3-triazole (**2a**).* White solid, melting point, 145−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.09 (d, J = 9.1 Hz, 2H), 7.84−7.82 (m, 2H), 7.46−7.41 (m, 2H), 7.39−7.35 (m, 1H), 7.04 (d, J = 9.1 Hz, 2H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 147.3, 131.2, 129.1, 129.0, 128.9, 126.9, 126.1, 118.8, 115.1, 56.0; IR (film) 3090, 1590, 1268, 1166, 839, 768, 674 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{13}N_3O_3S$, 315.0678; found, 315.0676.

*1-((4-Methoxyphenyl)sulfonyl)-4-(p-tolyl)-1H-1,2,3-triazole (**2b**).* White solid, melting point, 152−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.08 (d, J = 9.1 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.04 (d, J = 9.1 Hz, 2H), 3.89 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 147.4, 139.1, 131.2, 129.7, 127.1, 126.1, 126.0, 118.4, 115.1, 56.0, 21.4; IR (film)

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3050, 1590, 1263, 1169, 1002, 980, 820, 770, 675 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{15}N_3O_3S$, 329.0834; found, 329.0833.

1-((4-Methoxyphenyl)sulfonyl)-4-(m-tolyl)-1H-1,2,3-triazole (**2c**). White solid, melting point, 85−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.08 (d, J = 9.1 Hz, 2H), 7.67 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.04 (d, J = 9.1 Hz, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 147.4, 138.8, 131.2, 129.8, 128.9, 128.8, 127.0, 126.7, 123.2, 118.8, 115.1, 56.0, 21.4; IR (film) 2916, 1592, 1268, 1197, 1166, 1091, 1006, 836, 785, 680 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{15}N_3O_3S$, 329.0834; found, 329.0835.

4-(2-Methoxyphenyl)-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2d**). White solid, melting point, 110−115 °;, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.32 (dd, J = 7.8, J = 1.7 Hz, 1H), 8.09 (d, J = 9.0 Hz, 2H), 7.34 (td, J = 7.8, J = 1.7 Hz, 1H), 7.09−7.00 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 156.0, 142.7, 131.1, 130.0, 128.0, 127.4, 122.0, 121.0, 117.8, 115.0, 110.8, 56.0, 55.5; IR (film): 3076, 1592, 1267, 1022, 835, 755, 678 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{15}N_3O_4S$, 345.0783; found, 345.0785.

4-(3-Methoxyphenyl)-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2e**). White solid, melting point, 76−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.09 (d, J = 9.0 Hz, 2H), 7.42−7.31 (m, 3H), 7.04 (d, J = 9.0 Hz, 2H), 6.92 (dt, J = 7.4, 2.2 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 160.1, 147.2, 131.2, 130.2, 130.1, 126.9, 119.0, 118.4, 115.1, 111.1, 77.3, 56.0, 55.4; IR (film) 2943, 1592, 1269, 1044, 1024, 835, 783, 678 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{15}N_3O_4S$, 345.0783; found, 345.0786.

4-(3-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2f**). White solid, melting point, 132−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.09 (d, J = 9.1 Hz, 2H), 7.84−7.83 (m, 1H), 7.71 (dt, J = 7.0, 1.7, Hz, 1H), 7.39−7.33 (m, 2H), 7.05 (d, J = 9.1 Hz, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.5, 146.0, 135.0, 131.3, 130.8, 130.3, 129.1, 126.8, 126.1, 124.1, 119.3, 115.2, 56.0; IR (film) 3143, 1292, 1269, 1022, 963, 767, 676, 586 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{12}ClN_3O_3S$, 349.0288; found, 349.0286.

4-(4-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2g**). White solid, melting point, 129−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.09 (d, J = 9.1 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 9.1 Hz, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.5, 146.2, 134.9, 131.3, 129.3, 127.5, 127.3, 126.8, 118.9, 115.2, 56.0; IR (film) 3095, 1591, 1267, 1022, 836, 781, 679, 591 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{12}ClN_3O_3S$, 349.0288; found, 349.0284.

4-(3-Bromophenyl)-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2h**). White solid, melting point, 103−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.09 (d, J = 9.1 Hz, 2H), 7.99 (t, J = 1.7 Hz, 1H), 7.78−7.75 (m, 1H), 7.50 (ddd, J = 8.0, 1.9, 1.0 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.05 (d, J = 9.1 Hz, 2H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 145.9, 132.1, 131.4, 131.1, 130.7, 129.1, 126.8, 124.7, 123.2, 119.4, 115.3, 56.1; IR (film) 2944, 1592, 1269, 1024, 835, 784, 676, 589 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{12}BrN_3O_3S$, 392.9783; found, 392.9783.

4-(4-Bromophenyl)-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2i**). White solid, melting point, 155−160 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.07 (s, 1H), 8.15 (d, J = 9.0 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 9.0 Hz, 2H), 3.96 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 166.6, 146.9, 132.9, 132.0, 129.5, 128.6, 127.7, 123.2, 121.4, 116.3, 56.6; IR (film) 2976, 1591, 1267, 1197, 1019, 837, 786, 679, 593 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{12}BrN_3O_3S$, 392.9783; found, 392.9784.

1-((4-Methoxyphenyl)sulfonyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2j**). White solid, melting point, 133−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.10 (d, J = 9.1 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 9.1 Hz, 2H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 145.8, 131.4, 130.9 (q, J = 32.5 Hz), 126.2, 126.02, 126.01 (q, J = 4.2 Hz), 125.98, 123.9 (q, J = 272.2 Hz), 119.7, 115.2, 56.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.73; IR (film) 3106, 1596, 1394, 1326, 1270, 1164, 1024, 838, 829, 679 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{12}F_3N_3O_3S$, 383.0551; found, 383.0549.

1-((4-Methoxyphenyl)sulfonyl)-4-(naphthalen-2-yl)-1H-1,2,3-triazole (**2k**). White solid, melting point, 130−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.37 (s, 1H), 8.11 (d, J = 9.1 Hz, 2H), 7.92−7.84 (m, 4H), 7.54−7.49 (m, 2H), 7.05 (d, J = 9.1 Hz, 2H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 147.3, 133.5, 133.4, 131.3, 128.8, 128.3, 127.8, 127.0, 126.7, 126.67, 126.2, 125.3, 123.6, 125.3, 123.6, 119.1, 115.1, 56.0; IR (film) 3144, 1592, 1268, 1019, 804, 751, 676 cm^{-1}; HRMS (EI) m/z calcd. for $C_{19}H_{15}N_3O_3S$, 365.0834; found, 365.0832.

1-((4-Methoxyphenyl)sulfonyl)-4-(thiophen-3-yl)-1H-1,2,3-triazole (**2l**). White solid, melting point, 150−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.08−8.05 (m, 2H), 7.76−7.75 (m, 1H), 7.43−7.39 (m, 2H), 7.05−7.02 (m, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 143.4, 131.2, 130.1, 126.9, 126.8, 125.7, 122.7, 118.5, 115.1, 56.0; IR (film) 3098, 1590, 1268, 1006, 837, 785, 676 cm^{-1}; HRMS (EI) m/z calcd. for $C_{13}H_{11}N_3O_3S_2$, 321.0242; found, 321.0242.

4-(Cyclohex-1-en-1-yl)-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2m**). White solid, melting point, 96−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 9.1 Hz 2H), 7.89 (s, 1H), 7.01 (d, J = 9.1 Hz, 2H), 6.67−6.64 (m, 1H), 3.88 (s, 3H), 2.33−2.29 (m, 2H), 2.22−2.17 (m, 2H), 1.78−1.72 (m, 2H), 1.68−1.62 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 148.9, 131.0, 127.5, 127.2, 125.8, 117.3, 115.0, 56.0, 26.2, 25.3, 22.2, 22.0; IR (film) 2931, 2858, 1592, 1268, 1020, 966, 835, 804, 676 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{17}N_3O_3S$, 319.0991; found, 319.0992.

4-Butyl-1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazole (**2n**). White solid, melting point, 75−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 9.1 Hz, 2H), 7.83 (s, 1H), 7.02 (d, J = 9.1 Hz, 2H), 3.89 (s, 3H), 2.71 (t, J = 15.4 Hz, 2H), 1.68−1.60 (m, 2H), 1.39−1.34 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 148.2, 131.0, 127.2, 120.2, 115.0, 55.9, 31.0, 25.1, 22.2, 13.7; IR (film) 2957, 2932, 1593, 1462, 1269, 1013, 835, 715, 676 cm^{-1}; HRMS (EI) m/z calcd. for $C_{13}H_{17}N_3O_3S$, 295.0991; found, 295.0993.

General Procedure for the Preparation of Pyrazines (3). To a screw-top V-vial were added 2*H*-azirine derivatives (**2a**, 0.2 mmol), triazole derivatives (**1a**, 0.3 mmol), and $Rh_2(Oct)_4$ (3.1 mg, 0.004 mmol) in EtOAc (1.0 mL). The resulting mixture was stirred at 120 °C for 16 h. After Celite filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (EtOAc:Hx = 1:5) to yield **3aa** (48.9 mg, 70%) as a white solid.

Ethyl 3-(4-Nitrophenyl)-5-phenylpyrazine-2-carboxylate (**3aa**). Yield 48.9 mg (70%), R_f = 0.26 (EtOAc:Hx = 1:5); White solid, melting point, 137−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.37 (d, J = 8.9 Hz, 2H), 8.16−8.14 (m, 2H), 7.87 (d, J = 8.9 Hz, 2H), 7.58−7.55 (m, 3H), 4.36 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 153.0, 151.3, 148.4, 144.0, 141.8, 139.8, 134.9, 131.1, 129.9, 129.3, 127.5, 123.5, 62.5, 13.9; IR (film) 3059, 2978, 1730, 1520, 1437, 1347, 1138, 1012, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{15}N_3O_4$, 349.1063; found, 349.1060.

Ethyl 3-(4-Nitrophenyl)-5-(p-tolyl)pyrazine-2-carboxylate (**3ab**). Yield 51.6 mg (71%), R_f = 0.2 (EtOAc:Hx = 1:5); white solid, melting point, 131−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.36 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 153.1, 151.4, 148.3, 144.2, 141.7, 141.3, 139.5, 132.1, 130.1, 129.9, 127.4, 123.5, 62.5, 21.5, 13.9; IR (film) 3056, 2982, 1728, 1521, 1443, 1348, 1139, 1014, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{17}N_3O_4$, 363.1219; found, 363.1216.

Ethyl 3-(4-Nitrophenyl)-5-(m-tolyl)pyrazine-2-carboxylate (**3ac**). Yield 53.8 mg (74%), R_f = 0.24 (EtOAc:Hx = 1:5); white solid, melting point, 105−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.37 (d, J = 8.9 Hz, 2H), 7.95−7.92 (m, 2H), 7.87 (d, J = 8.9 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100

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MHz, $CDCl_3$) δ 165.6, 153.2, 151.4, 148.4, 144.1, 141.6, 139.9, 139.2, 134.8, 132.0, 129.9, 129.2, 128.1, 124.7, 123.5, 62.5, 21.6, 13.9; IR (film) 3053, 2982, 1731, 1521, 1443, 1348, 1137, 1014, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{17}N_3O_4$, 363.1219; found, 363.1217.

*Ethyl 5-(2-Methoxyphenyl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3ad**).* Yield 53.2 mg (70%), R_f = 0.14 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 135−140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.35 (d, J = 8.8 Hz, 2H), 7.99 (dd, J = 7.7, 1.8 Hz, 1H), 7.85 (d, J = 8.9 Hz, 2H), 7.50 (ddd, J = 8.3, 7.4, 1.7 Hz, 1H), 7.13 (td, J = 7.5, 0.9 Hz, 1H), 7.07 (d, J = 8.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 157.7, 152.4, 151.3, 148.2, 144.4, 144.3, 140.7, 132.3, 131.5, 129.9, 124.3, 123.5, 121.5, 111.6, 62.4, 55.7, 14.0; IR (film) 3078, 2980, 1731, 1520, 1436, 1347, 1139, 1019, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{17}N_3O_5$, 379.1168; found, 379.1169.

*Ethyl 5-(3-Methoxyphenyl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3ae**).* Yield 53.0 mg (70%), R_f = 0.2 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 155−160 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.36 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.71−7.69 (m, 2H), 7.47 (t, J = 8.2 Hz, 1H), 7.10−7.08 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.5, 160.4, 152.8, 151.3, 148.4, 144.0, 141.9, 139.9, 136.2, 130.4, 129.9, 123.5, 119.8, 116.6, 113.1, 62.5, 55.5, 13.9; IR (film) 3075, 2938, 1728, 1520, 1459, 1348, 1136, 1028, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{17}N_3O_5$, 379.1168; found, 379.1165.

*Ethyl 5-(3-Chlorophenyl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3af**).* Yield 57.5 mg (75%), R_f = 0.23 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 130−135 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.37 (d, J = 8.9 Hz, 2H), 8.16−8.15 (m, 1H), 8.03−8.00 (m, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.54−7.48 (m, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 151.6, 151.4, 148.5, 143.6, 142.5, 139.7, 136.6, 135.5, 131.1, 130.6, 129.9, 127.6, 125.5, 123.6, 62.6, 13.9; IR (film) 3053, 2986, 1731, 1525, 1421, 1349, 1143, 1014, 854 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}ClN_3O_4$, 383.0673; found, 383.0674.

*Ethyl 5-(4-Chlorophenyl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3ag**).* Yield 39.1 mg (51%), R_f = 0.23 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 178−183 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.37 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 151.8, 151.4, 148.5, 143.8, 142.1, 139.5, 137.6, 133.3, 129.9, 129.6, 128.7, 123.6, 62.6, 13.9; IR (film) 3058, 2984, 1721, 1519, 1442, 1349, 1140, 1010, 853, 516 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}ClN_3O_4$, 383.0673; found, 383.0675.

*Ethyl 5-(3-Bromophenyl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3ah**).* Yield 69.2 mg (81%), R_f = 0.2 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 150−155 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.38 (d, J = 8.8 Hz, 2H), 8.30 (t, J = 1.8 Hz, 1H), 8.06 (ddd, J = 7.9, 1.5, 1.0 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.68 (ddd, J = 8.0, 1.9, 0.9 Hz, 1H), 7.44 (t, J = 7.9 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 151.5, 151.4, 148.5, 143.6, 142.5, 139.7, 136.8, 134.1, 130.8, 130.5, 129.9, 125.9, 123.6, 62.6, 13.9; IR (film) 3068, 2983, 1731, 1520, 1443, 1348, 1141, 1065, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}BrN_3O_4$, 427.0168; found, 427.0166.

*Ethyl 5-(4-Bromophenyl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3ai**).* Yield 45.3 mg (53%), R_f = 0.2 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 192−197 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.37 (d, J = 8.9 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 151.9, 151.4, 148.5, 143.7, 142.1, 139.4, 133.7, 132.6, 129.9, 128.9, 126.1, 123.6, 62.6, 13.9; IR (film) 3058, 2983, 1720, 1520, 1441, 1348, 1139, 1006, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}BrN_3O_4$, 427.0168; found, 427.0164.

*Ethyl 3-(4-Nitrophenyl)-5-(4-(trifluoromethyl)phenyl)pyrazine-2-carboxylate (**3aj**).* Yield 56.5 mg (68%), R_f = 0.23 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 165−170 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.38 (d, J = 8.9 Hz, 2H), 8.27 (d, J = 8.1 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 151.5, 151.4, 148.5, 143.5, 142.8, 139.9, 138.2, 132.8 (q, J = 32.8 Hz), 129.9, 127.9, 126.2 (q, J = 3.7 Hz), 123.8 (q, J = 272.9 Hz), 123.6, 62.7, 13.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.89; IR (film) 3054, 2987, 1724, 1517, 1446, 1325, 1139, 1112, 1012, 854 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{14}F_3N_3O_4$, 417.0936; found, 417.0936.

*Ethyl 5-(Naphthalen-2-yl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3ak**).* Yield 39.9 mg (50%), R_f = 0.2 (EtOAc:Hx = 1:5); white solid, melting point, 165−170 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.65 (d, J = 1.1 Hz, 1H), 8.39 (d, J = 8.8 Hz, 2H), 8.25 (dd, J = 8.6, 1.8 Hz, 1H), 8.03−8.00 (m, 2H), 7.93−7.89 (m, 3H), 7.62−7.56 (m, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 153.0, 151.5, 148.4, 144.1, 141.6, 140.0, 134.5, 133.3, 132.1, 130.0, 129.2, 129.0, 127.9, 127.88, 127.0, 123.9, 123.6, 62.5, 14.0; IR (film) 3057, 2982, 1730, 1520, 1434, 1348, 1138, 1013, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{17}N_3O_4$, 399.1219; found, 399.1218.

*Ethyl 3-(4-Nitrophenyl)-5-(thiophen-3-yl)pyrazine-2-carboxylate (**3al**).* Yield 38.4 mg (54%), R_f = 0.23 (EtOAc:Hx = 1:5); pale yellow solid, melting point, 171−175 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.36 (d, J = 8.8 Hz, 2H), 8.18 (dd, J = 3.0, 1.2 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.79 (dd, J = 5.1, 1.2 Hz, 1H), 7.50 (dd, J = 5.1, 3.0 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 151.7, 149.2, 148.3, 144.0, 141.1, 139.6, 137.8, 129.9, 127.6, 127.3, 126.0, 123.5, 62.5, 13.9; IR (film) 3073, 2984, 1710, 1521, 1460, 1351, 1140, 1015, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{13}N_3O_4S$, 355.0627; found, 355.0626.

*Ethyl 5-(Cyclohex-1-en-1-yl)-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3am**).* Yield 36 mg (51%), R_f = 0.31 (EtOAc:Hx = 1:5); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.33 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.9 Hz, 2H), 7.03−7.00 (m, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.60−2.57 (m, 2H), 2.37−2.33 (m, 2H), 1.86−1.80 (m, 2H), 1.75−1.69 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 154.4, 150.7, 148.2, 144.4, 140.6, 138.7, 134.5, 134.0, 129.9, 123.4, 62.3, 26.3, 25.2, 22.4, 21.7, 13.9; IR (film) 3051, 2931, 1730, 1520, 1444, 1348, 1135, 1013, 852 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{19}N_3O_4$, 353.1376; found, 353.1373.

*Ethyl 5-Butyl-3-(4-nitrophenyl)pyrazine-2-carboxylate (**3an**).* Yield 32.9 mg (50%), R_f = 0.36 (EtOAc:Hx = 1:5); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.34 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 2.97−2.93 (m, 2H), 1.83−1.75 (m, 2H), 1.49−1.39 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 159.5, 151.2, 148.3, 144.1, 142.6, 141.4, 129.8, 123.5, 62.4, 35.3, 31.3, 22.4, 13.9, 13.8; IR (film) 3046, 2958, 1733, 1521, 1445, 1348, 1129, 1014, 853 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{19}N_3O_4$, 329.1376; found, 329.1377.

*Ethyl 5-(3-Chlorophenyl)-3-phenylpyrazine-2-carboxylate (**3bf**).* Yield 35.2 mg (52%), R_f = 0.14 (EtOAc:Hx = 1:10); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.18−8.17 (m, 1H), 8.03−8.00 (m, 1H), 7.74−7.70 (m, 2H), 7.53−7.45 (m, 5H), 4.32 (q, J = 7.1 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.4, 153.0, 151.1, 142.9, 138.5, 137.3, 137.2, 135.4, 130.6, 130.4, 129.7, 128.8, 128.5, 127.5, 125.4, 62.2, 13.8; IR (film) 3064, 2981, 1732, 1421, 1139, 1064, 1022, 838 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{15}ClN_2O_2$, 338.0822; found, 338.0824.

*Ethyl 5-(3-chlorophenyl)-3-(4-chlorophenyl)pyrazine-2-carboxylate (**3cf**).* Yield 54.5 mg (73%), R_f = 0.17 (EtOAc:Hx = 1:5); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.15−8.14 (m, 1H), 8.01−7.99 (m, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.52−7.46 (m, 4H), 4.35 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 151.9, 151.2, 142.6, 138.7, 137.0, 136.1, 135.7, 135.4, 130.8, 130.4, 130.2, 128.8, 127.5, 125.4, 62.4, 13.9; IR (film) 3068, 2981, 1733, 1444, 1139, 1067, 1013, 844 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}Cl_2N_2O_2$, 372.0432; found, 372.0431.

*Ethyl 3-(3-Bromophenyl)-5-(3-chlorophenyl)pyrazine-2-carboxylate (**3df**).* Yield 59.1 mg (71%), R_f = 0.37 (EtOAc:Hx = 1:5); yellow

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solid, melting point, 55−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.15−8.14 (m, 1H), 8.01 (dt, J = 6.7, 1.9 Hz, 1H), 7.86 (t, J = 1.8 Hz, 1H), 7.65−7.61 (m, 2H), 7.52−7.46 (m, 2H), 7.37 (t, J = 7.9 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.9, 151.5, 151.3, 142.8, 139.2, 139.0, 137.0, 135.4, 132.7, 131.8, 130.8, 130.5, 130.0, 127.5, 127.4, 125.5, 122.5, 62.4, 13.9; IR (film) 3066, 2980, 1732, 1422, 1141, 1068, 1139, 1012, 841 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}BrClN_2O_2$, 415.9927; found, 415.9926.

*Ethyl 3-(4-Bromophenyl)-5-(3-chlorophenyl)pyrazine-2-carboxylate (**3ef**).* Yield 60.1 mg (72%), R_f = 0.18 (EtOAc:Hx = 1:5); white solid, melting point, 82−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.15−8.14 (m, 1H), 8.01−7.99 (m, 1H), 7.65 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.52−7.46 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 152.0, 151.2, 142.5, 138.8, 137.0, 136.2, 135.4, 131.7, 130.8, 130.44, 130.41, 127.5, 125.4, 124.5, 62.4, 13.9; IR (film) 3067, 2981, 1732, 1443, 1140, 1069, 1034, 1009, 842 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}BrClN_2O_2$, 415.9927; found, 415.9928.

*Ethyl 5-(3-Chlorophenyl)-3-(4-(methoxycarbonyl)phenyl)-pyrazine-2-carboxylate (**3ff**).* Yield 55.6 mg (70%), R_f = 0.29 (EtOAc:Hx = 1:5); white solid, melting point, 142−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.18 (d, J = 8.6 Hz, 2H), 8.16−8.15 (m, 1H), 8.03−8.00 (m, 1H), 7.78 (d, J = 8.6 Hz, 2H), 7.52−7.47 (m, 2H), 4.33 (q, J = 7.2 Hz, 2H), 3.97 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 165.9, 152.2, 151.3, 142.8, 141.6, 139.1, 137.0, 135.5, 131.1, 130.9, 130.5, 129.7, 128.9, 127.6, 125.4, 62.4, 52.4, 13.8; IR (film) 3067, 2983, 1725, 1435, 1279, 1140, 1067, 1016, 862 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{17}ClN_2O_4$, 396.0877; found, 396.0878.

*Ethyl 5-(3-Chlorophenyl)-3-(naphthalen-2-yl)pyrazine-2-carboxylate (**3gf**).* Yield 45.1 mg (58%), R_f = 0.26 (EtOAc:Hx = 1:5); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.22−8.20 (m, 2H), 8.06−8.03 (m, 1H), 7.99−7.91 (m, 3H), 7.83 (dd, J = 8.5, 1.8 Hz, 1H), 7.59−7.53 (m, 2H), 7.52−7.47 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 152.9, 151.2, 143.1, 138.5, 137.3, 135.4, 134.6, 133.8, 133.0, 130.7, 130.4, 128.8, 128.7, 128.3, 127.8, 127.6, 127.2, 126.7, 125.9, 125.5, 62.3, 13.9; IR (film) 3061, 2980, 1731, 1445, 1139, 1068, 1014, 861 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{17}ClN_2O_2$, 388.0979; found, 388.0977.

*Ethyl 3-(4-Nitrophenyl)-5-phenyl-1-tosyl-1,4-dihydropyrazine-2-carboxylate (**4**).* R_f = 0.35 (EtOAc:Hx = 1:2); yellow solid, melting point, 224−227 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 11.13 (s, 1H), 8.26 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 9.0 Hz, 2H), 7.83−7.79 (m, 3H), 7.42 (d, J = 8.3 Hz, 2H), 7.36−7.32 (m, 2H), 7.29−7.25 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 3.92 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 164.6, 148.1, 144.0, 139.0, 137.8, 133.1, 131.9, 131.7, 131.0, 129.8, 129.0, 128.4, 128.2, 128.1, 123.7, 119.5, 113.0, 60.7, 21.4, 14.2; IR (film) 3280, 3064, 2982, 1685, 1516, 1400, 1343, 1256, 1161 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{23}N_3O_6S$, 505.1308; found, 505.1310.

*Ethyl 3-(4-Nitrophenyl)-5-phenyl-1-tosyl-1,2-dihydropyrazine-2-carboxylate (**5**).* R_f = 0.34 (EtOAc:Hx = 1:5); yellow oil; ^{1}H NMR (400 MHz, 400 MHz, $CDCl_3$) δ 8.29 (d, J = 9.0 Hz, 2H), 8.10 (d, J = 9.0 Hz, 2H), 7.76−7.74 (m, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.43−7.39 (m, 2H), 7.37−7.32 (m, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 1.4 Hz, 1H), 6.05 (d, J = 1.4 Hz, 1H), 4.18−3.99 (m, 2H), 2.33 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H) ; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 148.8, 145.1, 145.0, 141.2, 135.5, 135.2, 135.0, 129.9, 128.7, 128.5, 128.3, 126.6, 124.9, 123.7, 111.4, 62.8, 52.8, 21.6, 13.9; IR (film) 3081, 2981, 1733, 1596, 1521, 1346, 1317, 1169 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{23}N_3O_6S$, 505.1308; found, 505.1308.

■ ASSOCIATED CONTENT

Supporting Information

Characterization data, X-ray crystallography data (**3ab**, cif), and ^{1}H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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