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Rhodium(III)-catalyzed C–H functionalization of C-alkenyl azoles with sulfoxonium ylides for the synthesis of bridgehead *N*-fused [5,6]-bicyclic heterocycles

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ABSTRACT

The synthesis of bridgehead *N*-fused [5,6]-bicyclic heterocycles via rhodium(III)-catalyzed C–H functionalization of C-alkenyl azoles with sulfoxonium ylides is disclosed. Reactions proceeded in good to high yields for a range of aryl, heteroaryl and alkyl sulfoxonium ylides. In addition, 2-alkenyl imidazoles with different substitution patterns as well as C-alkenyl triazoles were effective inputs. The reaction could also be performed under straightforward bench top conditions.

1. Introduction

The [5,6]-bicyclic nitrogen heterocycle class is exemplified by the purine motif and is heavily represented in U.S. FDA approved drugs.[1] In recent years the sub-class of [5,6]-bicyclic heterocycles with a ring junction nitrogen have increasingly been investigated and have resulted in a number of approved drugs[2] as well as candidates in clinical trials.[3] Transition-metal-catalyzed C–H functionalization can provide an efficient approach for the convergent synthesis of nitrogen heterocycles from readily available starting materials.[4] Nevertheless, only a few approaches have been reported for the preparation of fused bicyclic heterocycles with ring-junction nitrogens. The most extensive related research has focused on C–H functionalization of C-aryl azoles for the synthesis of tricyclic and higher order aza-fused heterocycles.[5–13] Dong and co-workers reported the first examples of C–H functionalization for the preparation of ring-junction nitrogen [5,6]-bicyclic heterocycles by annulation of *N*-alkenyl imidazoles with internal alkynes.[14] More recently, we reported the C–H functionalization of C-alkenyl azoles with various electrophiles, including internal alkynes and diazoketones, for the synthesis of bridgehead *N*-fused bicyclic heterocycles (Scheme 1A).[15] While a variety of different products were obtained with high regioselectivity, in all cases, the methods required placement of carbon substituents at both the R^3 and R^4 positions.

Sulfoxonium ylides have been introduced as convenient carbene precursors[16] that are a safer alternative to analogous diazo compounds.[17] Recently these reagents have been shown to be particularly effective for the Rh(III)-catalyzed acylmethylation of arenes with the carbonyl functionality in the product available for further elaboration.[18,19] Herein, we report Rh(III)-catalyzed coupling of C-alkenyl azoles with sulfoxonium ylides with in situ cyclodehydration to give differently substituted bridgehead N-fused [5,6]-bicyclic heterocycles with complete regioselectivity (Scheme 1B).

2. Results and discussion

Preformed catalyst $[Cp^*Rh(MeCN)_3](SbF_6)_2$ in toluene at 120 °C provided effective conditions for annulation of C-alkenyl imidazole **1a** with sulfoxonium ylide **2a** (entry 1, Table 1). Lowering the temperature to 100 °C resulted in a slightly lower yield (entry 2). The optimal conditions were similarly effective for the electron rich sulfoxonium ylide **2b** (entry 3). When the stoichiometry of sulfoxonium ylide **2b** was reduced from 2.0 to 1.5 equiv, only a slight

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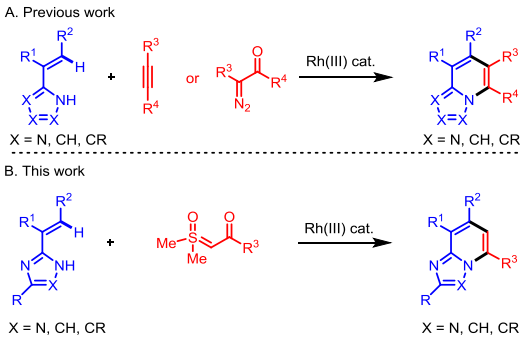
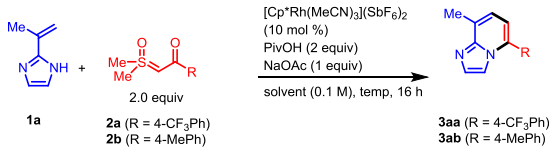


Scheme 1. Rh(III)-catalyzed synthesis of fused [5,6]-bicyclic heterocycles from C-alkenyl azoles.

Table 1
C–H functionalization of **1a** and **2**.[a]



Entry	Ylide	Solvent	Temp (°C)	Variation	Yield %[b]
1	**2a**	toluene	120	none	73 (71)[c]
2	**2a**	toluene	100	none	61
3	**2b**	toluene	120	none	68 (69)[c]
4	**2b**	toluene	120	**2** (1.5 equiv)	67
5	**2b**	toluene	120	no NaOAc	29
6	**2b**	toluene	120	no PivOH	33
7	**2b**	toluene	120	No Rh	0
8	**2b**	toluene	120	$[Cp^*RhCl_2]_2$[d]	65
9	**2b**	toluene	120	$[Cp^*RhCl_2]_2$[e]	45
10	**2b**	toluene	120	0.2 M	45
11	**2b**	dioxane	120	none	45
12	**2b**	DCE	120	none	53
13	**2b**	MeCN	120	none	50
14	**2b**	xylenes	120	bench-top	65

[a] Conditions: **1a** (0.10 mmol), **2** (0.20 mmol), 0.1 M, 16 h.
[b] Yield determined by ^{1}H NMR relative to 1,3,5-trimethoxybenzene as external standard.
[c] Isolated yield of a 0.30 mmol scale (see Fig. 1).
[d] $[Cp^*RhCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %).
[e] $[Cp^*RhCl_2]_2$ (5 mol %) only.

reduction in yield was observed (entry 4). The importance of both PivOH and NaOAc were documented by the lower yields that were obtained in the absence of these additives (entries 5 and 6, respectively). As expected, the Rh(III) catalyst was essential to the reaction (entry 7). While the cationic Rh(III) catalyst could be prepared in situ without any effect on the reaction yield (entry 8), when the chlorides were not abstracted from $[Cp^*RhCl_2]_2$, a lower yield was observed (entry 9). Doubling the concentration also resulted in a lower yield (entry 10). The reaction was dependent on solvent with dioxane, DCE and acetonitrile all resulting in lower yields (entries 11–13). The optimal reaction temperature of 120 °C required that a pressurized reaction vessel be used when toluene was used as the reaction solvent. Therefore, xylenes, with a boiling point higher than 120 °C was evaluated, with bench-top set up, and provided a comparable reaction yield (entry 14).

With optimized reaction conditions in hand, the scope for the sulfoxonium ylide input was next explored. A variety of aryl ylides with different electronic properties coupled equally well under the standard conditions to afford products **3aa**–**ad** in good yields

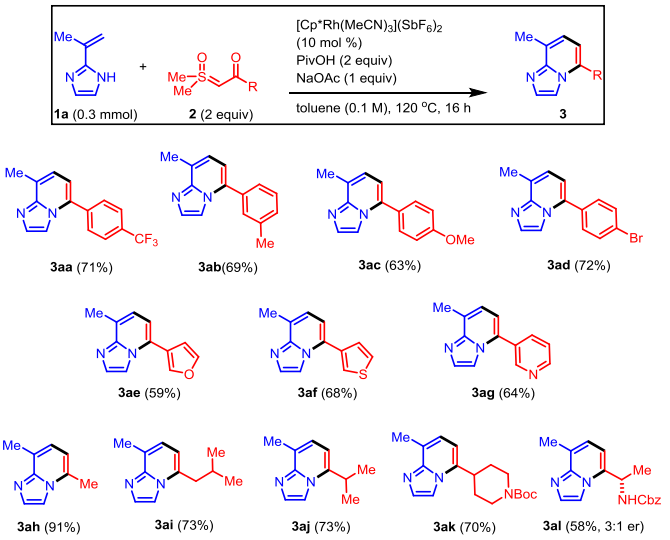


Fig. 1. Sulfoxonium ylide scope in Rh(III)-catalyzed C–H functionalization of C-alkenyl imidazoles.

(63–72%). Both electron rich and deficient heteroaryl ylides were also effective coupling partners as exemplified for products **3ae**–**ag**. A number of alkyl ylides, including methyl (**2h**), β-branched (**2i**), and α-branched (**2j**–**l**) were also effective inputs and provided good to excellent yields of the products **3ah**–**al**. Under the reaction conditions, chiral product **3al** is obtained in reasonable yield though with significant epimerization (3:1 er).[21] Notably, the tertiary *N*-Boc piperidine- and secondary *N*-Cbz-containing adducts, **3ak** and **3al**, respectively, establish that *N*-protected amine functionality can readily be introduced to provide versatile handles for further elaboration.

We next turned our attention to different C-alkenyl azoles (Fig. 2). Imidazoles **1b**–**e** bearing a range of substituents at different sites on the alkene and/or imidazole ring all effectively coupled with both aryl and alkyl ylides (**3ba**–**ek**). Only the unsubstituted C-vinyl imidazole **1f** was found to be ineffective (**3fk**). The C-alkenyl

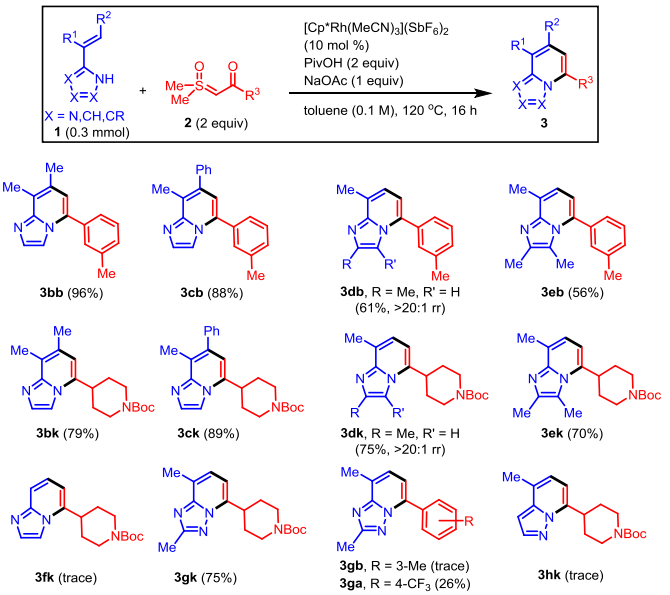


Fig. 2. C-alkenyl azole scope in Rh(III)-catalyzed C–H functionalization with sulfoxonium ylides.

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triazole **1g** coupled with alkyl ylide **2k** to provide **3gk** in good yield. However, when the reaction was performed with aromatic ylide **2b**, only trace amounts of **3gb** was obtained and with no remaining triazole **1g**. The electron deficient aromatic ylide **2a** ($R^3 = 4\text{-}CF_3Ph$) did provide product **3ga**, albeit in only modest yield.[20] In addition, pyrazole **1h** was not an effective coupling partner. Only trace amounts of remaining **1h** and product **3hk** were observed under standard conditions with ylide **2k**.

A mechanism that is consistent with both our previously proposed C-H functionalization of C-alkenyl azoles[15] and the previously proposed C–H functionalization of sulfoxonium ylides[18,19] is depicted in Fig. 3. Concerted metalation-deprotonation provides the five-membered metallocycle **A**. Reaction with sulfoxonium ylide **2** then provides the six-membered metallocycle **B**. Protodemetalation regenerates the Rh(III) catalyst and ketone **C**, which undergoes cyclodehydration to give heteroaromatic, *N*-fused bicyclic product **3**.

Lastly, the reaction was optimized to enhance its practicality for straightforward bench-top set up as demonstrated at a larger 2 mmol scale for aryl sulfoxonium ylide **2b** and alkyl sulfoxonium ylide **2k** (Scheme 2). Notably, xylenes, which boil above the reaction temperature of 120 °C, were used without drying or purification. Moreover, the catalyst loading was lowered to 5 mol % without any reduction in reaction yields.

3. Conclusions

In summary, we have developed a method for the synthesis of ring-junction nitrogen fused bicyclic heterocycles by Rh(III)-catalyzed annulation of C-alkenyl azoles with sulfoxonium ylides. The reaction proceeds in good to high yields and with complete regioselectivity for a range of aryl, heteroaryl and alkyl sulfoxonium ylides. Moreover, the reaction is applicable to straightforward bench-top set up with xylenes as solvent without drying or purification.

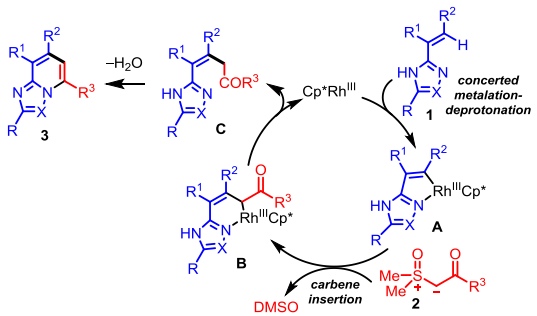
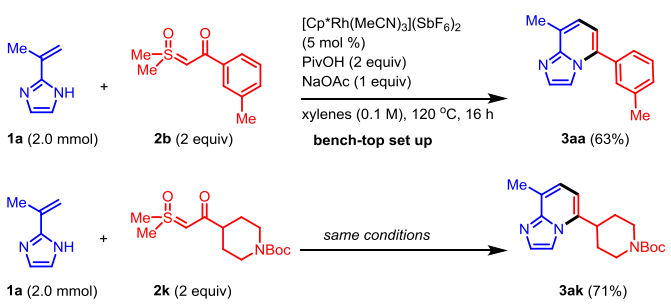


Fig. 3. Proposed catalytic cycle.



Scheme 2. Bench-top reaction set up on 2 mmol scale.

4. Experimental section

4.1. General

Unless otherwise noted, all commercially available reagents were purchased and used as received. Solvents including toluene, 1,4-dioxane, 1,2-dichloroethane (DCE), and acetonitrile (MeCN) were deoxygenated by sparging with argon and stored over activated 3 Å molecular sieves in a nitrogen filled glove box. Xylenes (mixtures of isomers, not anhydrous) was purchased and used as received. Commercial $AgSbF_6$ was stored in a nitrogen filled glove box. ^{1}H-, ^{13}C-, and ^{19}F NMR spectra were recorded on 400 MHz, 500 MHz or 600 MHz spectrometers. The chemical shift [δ (ppm)], coupling constants [J (Hz)], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, m = multiplet, br = broad), and integration are reported. Chemical shifts for ^{1}H and ^{13}C NMR are reported relative to residual undeuterated solvent in CDCl3 (7.26 ppm for 1H NMR and 77.16 ppm for 13C NMR) and (CD3)2CO (2.05 ppm for 1H NMR and 29.84 ppm for 13C NMR). Flash chromatography was carried out with SiliaFlash® P60 (particle size 40–63 μm, 230–400 mesh). Partial data are provided for IR spectra. Melting points are reported uncorrected. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) on a time of flight (TOF) mass spectrometer. Enantiomeric ratios were determined using an Agilent 1100 series HPLC equipped with Chiralpak-IB or Chiralcel-OD-H columns and a multiwavelength detector.

4.2. Preparation of catalysts and reactants

$[Cp^*Rh(MeCN)_3(SbF_6)_2]$ was synthesized according to literature procedures.[18b] All C-alkenyl substrates were synthesized according to literature procedures.[15] Sulfoxonium ylides **2a**–**f, 2h, 2i,** and **2k** were synthesized according to literature procedures.[18,22] Ylides **2g** and **2i** were prepared from the corresponding acid chlorides via literature procedures[18b] with slight modification. Ylide **2l** was prepared according to a literature procedure for a related compound.[23]

4.2.1. 2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-(pyridin-3-yl)ethan-1-one (*2g*)

Ylide **2g** from the corresponding acid chlorides via literature procedures[18b] with slight modification. The mixture of trimethylsulfoxonium iodide (5.94 g, 27.0 mmol, 3 equiv) and potassium *tert*-butoxide (3.03 g, 27.0 mmol, 3 equiv) in THF (55 mL) was refluxed (67 °C) for 2 h under nitrogen. After cooling to room temp then 0 °C, to the above mixture was added a solution of nicotinoyl chloride (prepared in situ by stirring a mixture of nicotinoyl chloride hydrochloride (1.60 g, 9.00 mmol, 1 equiv) and triethylamine (1.26 mL, 9.00 mmol, 1 equiv) in THF (10 mL) for 1 h at room temp). The resulting mixture was slowly warmed to room temp and stirred overnight, filtered through a plug of celite, and concentrated under reduced pressure. Purification by silica gel column chromatography (10–50% MeOH/DCM) afforded **2g** (851 mg, 48%) as a white solid. mp 120–122 °C. FTIR (neat): 3093, 2989, 1581, 1534, 1390, 1169, 1089, 1024, 991, 949, 897, 839, 727, 511 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 2.2, 0.9 Hz, 1H), 8.58 (dd, J = 4.8, 1.7 Hz, 1H), 8.02 (dt, J = 7.9, 2.0 Hz, 1H), 7.27 (ddd, J = 7.9, 4.8, 0.9 Hz, 1H), 4.98 (s, 1H), 3.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 151.3, 148.2, 134.2, 134.0, 123.2, 69.5, 42.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_9H_{12}NO_2S^+$, 198.0583; found 198.0578.

4.2.2. 1-(Dimethyl(oxo)-λ^6-sulfaneylidene)-4-methylpentan-2-one (*2i*)

Ylide **2i** was prepared following the procedures for the

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preparation of sulfoxonium ylide **2g** but with isovaleraldehyde (0.970 mL, 9.00 mmol, 1 equiv). After purification by silica gel column chromatography (0–10% MeOH/DCM), **2i** (1.11 g, 70%) was obtained as a white solid. mp 108.5–110 °C. FTIR (neat): 3014, 2954, 2924, 2868, 1548, 1388, 1326, 1165, 1032, 998, 853, 760, 542, 448 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 1H), 3.34 (s, 6H), 2.05–1.95 (m, 3H), 0.88 (d, $J = 6.3$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 69.5, 50.2, 42.2, 26.2, 22.3. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_8H_{17}O_2S^+$, 177.0944; found 177.0945.

4.2.3. Benzyl (S)-(4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-oxobutan-2-yl)carbamate (**2l**)

Ylide **2l** was prepared according to a literature procedure for a related compound.[23] To a flame-dried 100-mL 3-necked round bottom flask was added trimethylsulfoxonium iodide (3.52 g, 3.20 equiv, 15.0 mmol). The flask was connected to a flame-dried refluxed condenser, degassed, and filled with nitrogen. To the flask were added THF (15 mL) and potassium *tert*-butoxide (15.0 mL, 15.0 mmol, 1.00 M in THF, 3.00 equiv) sequentially. The reaction mixture was refluxed at 68 °C for 2 h then slowly cooled to 0 °C. To the resulting mixture was added a solution of (4-nitrophenyl) (2*S*)-2-(benzyloxycarbonylamino)propanoate in THF (10 mL) dropwise over 15 min. After a stirring for one hour at 0 °C, the reaction was quenched by slow addition of water (5 mL), and the resulting mixture was stirred for another 15 min at 0 °C. The reaction mixture was slowly warmed to room temp and filtered through a pad of celite and washed with diethyl ether (10 mL). The filtrate was rinsed to a separatory funnel with water (20 mL) and extracted with EtOAc (2 × 20 mL). The combined organic layers were sequentially washed with water (10 mL), brine (2 × 10 mL), dried (anhyd. Na_2SO_4), and concentrated under reduced pressure to afford the crude **2l** as a light yellow solid (1.02 g). The crude **2l** was then recrystallized with EtOAc:hexanes (1:10, ca. 55 mL; *note: do not use heat to dissolve the crude in EtOAc*) in a freezer for 2 h and filtered to afford the title compound **2l** as a light yellow solid (673 mg, 45% yield). ^1H and ^{13}C NMR spectra matched with reported literature.[22] Sulfoxonium ylide **2l** was converted to the corresponding α-chloroketone by a literature procedure, LiCl and methanesulfonic acid,[24] to confirm the enantiomeric purity; chiral HPLC analysis (Chiralpak-IB, 90:10 hexanes:isopropanol, flow rate = 1.0 mL/min) showed peaks at 15.7 min (2.0% (*R*)) and 17.9 min (98.0% (*S*)).

4.3. General procedures for C–H functionalization of C-alkenyl azoles with sulfoxonium ylides (0.3 mmol scale)

To a flame-dried 2–5 mL Biotage microwave reaction vial in a glove box was added alkenyl azole (0.3 mmol, 1 equiv), sulfoxonium ylide (0.600 mmol, 2 equiv), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10 mol %, 0.030 mmol, 25.0 mg), PivOH (0.600 mmol, 2 equiv, 61.2 mg), NaOAc (0.300 mmol, 1 equiv, 24.6 mg), and toluene (0.1 M, 3.0 mL). The vial was capped with a Teflon-lined cap, removed from the glove box, and the mixture was stirred at 120 °C for 16 h. The resultant mixture was then cooled to room temp, filtered through a pad of celite, washed thoroughly with acetone, and concentrated under reduced pressure. The product was purified by silica gel column chromatography.

4.3.1. 8-Methyl-5-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (**3aa**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 159 mg of sulfoxonium ylide **2a**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3aa** (59 mg, 71%) as a tan solid. mp 92.5–94.0 °C. FTIR (neat) 2920, 1323, 1173, 1101, 1060, 1015, 830, 704 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.92 (apparent s, 4H), 7.76 (d, $J = 1.3$ Hz, 1H), 7.57 (d, $J = 1.3$ Hz, 1H), 7.13 (dd, $J = 7.0$, 1.1 Hz, 1H), 6.83 (d, $J = 7.0$ Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 146.1, 138.6, 134.7, 133.0, 130.6 (q, $J = 32.4$ Hz), 129.1, 127.0, 126.1 (q, $J = 3.8$ Hz), 125.5, 123.0, 113.1, 111.1, 16.2. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −62.3. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{15}H_{12}F_3N_2^+$, 277.0947; found 277.0944.

4.3.2. 8-Methyl-5-(m-tolyl)imidazo[1,2-a]pyridine (**3ab**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 126 mg of sulfoxonium ylide **2b**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3ab** (46 mg, 69%) as a yellow oil. FTIR (neat) 2920, 1511, 1483, 1330, 1302, 1273, 1247, 1146, 1097, 818, 787, 726, 699 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, $J = 1.3$ Hz, 1H), 7.59 (d, $J = 1.3$ Hz, 1H), 7.40–7.35 (m, 3H), 7.30–7.25 (m, 1H), 7.01 (dd, $J = 7.0$, 1.2 Hz, 1H), 6.62 (d, $J = 6.9$ Hz, 1H), 2.63 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 138.9, 136.4, 134.6, 132.4, 130.1, 128.9, 128.9, 126.0, 125.3, 123.6, 112.5, 111.4, 21.4, 17.1. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{15}H_{15}N_2^+$, 223.1230; found 223.1232.

4.3.3. 5-(4-Methoxyphenyl)-8-methylimidazo[1,2-a]pyridine (**3ac**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 136 mg of sulfoxonium ylide **2c**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3ac** (45 mg, 63%) as a yellow oil. FTIR (neat) 1606, 1495, 1247, 1175, 1146, 1027, 813, 701, 596, 554, 506 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, $J = 14.7$, 1.4 Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 2H), 7.06–6.96 (m, 3H), 6.59 (d, $J = 7.0$ Hz, 1H), 3.85 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 146.5, 136.1, 132.6, 129.6, 127.1, 125.8, 123.5, 114.4, 112.3, 111.2, 55.4, 17.0. HRMS (ESI): *m/z* $(M + H)^+$; calcd for $C_{15}H_{15}N_2O^+$, 239.1179; found 239.1196.

4.3.4. 5-(4-Bromophenyl)-8-methylimidazo[1,2-a]pyridine (**3ad**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 165 mg of sulfoxonium ylide **2d**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3ad** (62 mg, 72%) as a white solid. mp 135–137 °C. FTIR (neat) 2918, 1484, 1196, 1146, 1100, 1074, 1010, 816, 704 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, $J = 8.4$ Hz, 2H), 7.61–7.56 (m, 2H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.02 (d, $J = 6.9$ Hz, 1H), 6.62 (d, $J = 6.9$ Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 135.0, 133.6, 133.0, 132.4, 129.8, 126.8, 123.6, 123.4, 112.8, 111.1, 17.1. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{14}H_{12}BrN_2^+$, 287.0178; found 287.0166.

4.3.5. 5-(Furan-2-yl)-8-methylimidazo[1,2-a]pyridine (**3ae**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 112 mg of sulfoxonium ylide **2e**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3ae** (35 mg, 59%) as a yellow solid. mp 63–65 °C. FTIR (neat) 3099, 1506, 1329, 1203, 1152, 754, 729, 590, 527 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, $J = 1.3$ Hz, 1H), 7.70 (d, $J = 1.3$ Hz, 1H), 7.59 (dd, $J = 1.8$, 0.7 Hz, 1H), 7.10–7.00 (m, 2H), 6.85 (dd, $J = 3.4$, 0.7 Hz, 1H), 6.57 (dd, $J = 3.5$, 1.8 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 145.4, 143.1, 133.1, 126.8, 126.7, 123.1, 122.3, 111.8, 111.2, 109.6, 17.2. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{12}H_{11}N_2O^+$, 199.0866; found 199.0869.

4.3.6. 8-Methyl-5-(thiophen-2-yl)imidazo[1,2-a]pyridine (**3af**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 121 mg of sulfoxonium ylide **2f**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3af** (44 mg, 68%) as a tan solid. mp

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68–70 °C. FTIR (neat) 3103, 2918, 1656, 1494, 1412, 1328, 1274, 1147, 1100, 844, 812, 696, 525, 475 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, $J = 1.4$ Hz, 1H), 7.63 (d, $J = 1.3$ Hz, 1H), 7.46–7.42 (m, 2H), 7.19–7.13 (m, 1H), 6.99 (dd, $J = 7.1, 1.2$ Hz, 1H), 6.80 (d, $J = 7.1$ Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 135.6, 132.9, 129.6, 127.7, 127.3, 127.0, 126.8, 123.2, 113.7, 111.7, 17.1. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{12}H_{11}N_2S^+$, 215.0637; found 215.0642.

4.3.7. 8-Methyl-5-(pyridin-3-yl)imidazo[1,2-a]pyridine (**3ag**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 118 mg of sulfoxonium ylide **2g**. Purification by silica gel column chromatography (10–70% acetone/hexanes) afforded **3ag** (40 mg, 64%) as a light yellow solid. mp 166–167.5 °C. FTIR (neat) 3034, 1511, 1480, 1420, 1304, 1271, 1147, 830, 800, 762, 709, 624, 530 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, $J = 2.4$ Hz, 1H), 8.70 (d, $J = 4.2$ Hz, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.59 (s, 1H), 7.54 (s, 1H), 7.43 (dd, $J = 7.8, 4.9$ Hz, 1H), 7.04 (d, $J = 6.9$ Hz, 1H), 6.66 (d, $J = 6.9$ Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.5, 149.2, 146.4, 135.5, 133.2, 132.7, 130.7, 127.4, 123.7, 123.3, 113.5, 110.8, 17.1. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{13}H_{12}N_3^+$, 210.1026; found 210.1029.

4.3.8. 5,8-Dimethylimidazo[1,2-a]pyridine (**3ah**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 80.5 mg of sulfoxonium ylide **2h**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3ah** (40 mg, 91%) as a yellow oil. FTIR (neat) 3385, 2921, 1635, 1511, 1327, 1281, 1155, 1144, 1101, 809, 695, 524 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, $J = 1.2$ Hz, 1H), 7.42 (d, $J = 1.2$ Hz, 1H), 6.90 (dd, $J = 6.9, 1.2$ Hz, 1H), 6.49 (dd, $J = 6.8, 1.1$ Hz, 1H), 2.57 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.1, 132.8, 132.0, 124.6, 123.4, 111.3, 109.8, 18.5, 16.9. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_9H_{11}N_2^+$, 147.0917; found 147.0916.

4.3.9. 5-Isobutyl-8-methylimidazo[1,2-a]pyridine (**3ai**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 106 mg of sulfoxonium ylide **2i**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3ai** (41 mg, 73%) as a yellow oil. FTIR (neat) 2956, 1509, 1465, 1328, 1277, 1259, 1153, 832, 803, 695, 523 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.47 (s, 1H), 6.90 (dd, $J = 6.9, 1.2$ Hz, 1H), 6.45 (d, $J = 6.9$ Hz, 1H), 2.68 (d, $J = 7.2$ Hz, 2H), 2.55 (s, 3H), 2.15–2.05 (m, 1H), 0.95 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 135.2, 132.5, 124.6, 123.4, 111.6, 110.0, 41.6, 25.1, 22.6, 16.9. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{12}H_{17}N_2^+$, 189.1386; found 189.1389.

4.3.10. 5-Isopropyl-8-methylimidazo[1,2-a]pyridine (**3aj**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 97.3 mg of sulfoxonium ylide **2j**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3aj** (38 mg, 73%) as a yellow solid. mp 71–73 °C. FTIR (neat) 3092, 2967, 1710, 1631, 1509, 1328, 1274, 1247, 1147, 822, 814, 746, 532 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, $J = 1.4$ Hz, 1H), 7.55 (d, $J = 1.4$ Hz, 1H), 6.95 (dd, $J = 7.0, 1.3$ Hz, 1H), 6.53 (d, $J = 7.1$ Hz, 1H), 3.16 (heptet, $J = 6.8$ Hz, 1H), 2.57 (s, 3H), 1.35 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.2, 141.9, 132.6, 124.6, 123.5, 109.8, 107.2, 29.9, 20.2, 16.9. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{11}H_{15}N_2^+$, 175.1230; found 175.1233.

4.3.11. tert-Butyl 4-(8-methylimidazo[1,2-a]pyridin-5-yl) piperidine-1-carboxylate (**3ak**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 182 mg of sulfoxonium ylide **2k**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3ak** (66 mg, 70%) as a yellow foamy solid. mp 48–50 °C (after trituration with pentane). FTIR (neat) 2924, 1684, 1421, 1364, 1275, 1231, 1158, 1125, 1030, 979, 870, 817, 695, 531 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.92 (d, $J = 1.3$ Hz, 1H), 7.59 (s, 1H), 7.00 (dd, $J = 7.1, 1.3$ Hz, 1H), 6.60 (d, $J = 7.1$ Hz, 1H), 4.35–4.15 (m, 2H), 3.20 (tt, $J = 11.9, 3.3$ Hz, 1H), 3.10–2.85 (m, 2H), 2.50 (s, 3H), 2.10–2.00 (m, 2H), 1.57 (qd, $J = 12.5, 4.2$ Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 154.1, 146.0, 139.8, 132.7, 124.7, 123.0, 110.1, 107.6, 78.6, 43.6, 37.9, 29.7, 27.7, 16.0. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{18}H_{26}N_3O_2^+$, 316.2020; found 316.2022.

4.3.12. Benzyl (S)-(1-(8-methylimidazo[1,2-a]pyridin-5-yl)ethyl) carbamate (**3al**)

The reaction was performed according to the general procedure employing 32.5 mg of alkenyl azole **1a** and 178 mg of sulfoxonium ylide **2l**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3al** (54 mg, 58%) as a tan solid. mp 141–143 °C. Chiral HPLC analysis (Chiralcel-OD-H, 90:10 hexanes:isopropanol, flow rate = 1.0 mL/min) showed peaks at 38.0 min (23.3% (*R*)) and 45.5 min (76.6% (*S*)). FTIR (neat) 1698, 1553, 1247, 1050, 822, 739, 699 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.58 (s, 1H), 7.32–7.23 (m, 5H), 6.89 (dd, $J = 7.0, 1.3$ Hz, 1H), 6.64 (d, $J = 7.0$ Hz, 1H), 5.39 (d, $J = 9.0$ Hz, 1H), 5.18 (p, $J = 7.2$ Hz, 1H), 5.10 (s, 2H), 2.53 (s, 3H), 1.60 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.9, 146.1, 136.1, 135.9, 133.1, 128.5, 128.2, 128.0, 126.7, 122.6, 110.9, 108.7, 67.1, 46.7, 18.9, 16.9. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{18}H_{20}N_3O_2^+$, 310.1550; found 310.1551.

4.3.13. 7,8-Dimethyl-5-(m-tolyl)imidazo[1,2-a]pyridine (**3bb**)

The reaction was performed according to the general procedure employing 36.7 mg of alkenyl azole **1b** and 126 mg of sulfoxonium ylide **2b**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3bb** (68 mg, 96%) as a yellow oil. FTIR (neat) 2920, 1507, 1483, 1298, 1153, 1091, 856, 788, 728, 698 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, $J = 1.3$ Hz, 1H), 7.53 (d, $J = 1.3$ Hz, 1H), 7.40–7.35 (m, 3H), 7.30–7.25 (m, 1H), 6.55 (s, 1H), 2.57 (s, 3H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.0, 138.8, 135.1, 134.6, 132.5, 131.6, 130.0, 128.9, 128.9, 125.3, 122.7, 116.2, 110.8, 21.4, 18.6, 13.2. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{16}H_{17}N_2^+$, 237.1386; found 237.1385.

4.3.14. 8-Methyl-7-phenyl-5-(m-tolyl)imidazo[1,2-a]pyridine (**3cb**)

The reaction was performed according to the general procedure employing 55.3 mg of alkenyl azole **1c** and 126 mg of sulfoxonium ylide **2b**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3cb** (79 mg, 88%) as a yellow oil. FTIR (neat) 2922, 1506, 1481, 1300, 1141, 771, 728, 699, 522 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, $J = 1.2$ Hz, 1H), 7.65 (d, $J = 1.2$ Hz, 1H), 7.45–7.35 (m, 8H), 7.31–7.27 (m, 1H), 6.75 (s, 1H), 2.63 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 139.7, 138.9, 136.5, 135.5, 134.4, 133.2, 130.2, 129.3, 128.9, 128.3, 127.4, 125.3, 122.6, 115.4, 111.2, 21.5, 14.6. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{21}H_{19}N_2^+$, 299.1543; found 299.1541.

4.3.15. 2,8-Dimethyl-5-(m-tolyl)imidazo[1,2-a]pyridine (**3db**)

The reaction was performed according to the general procedure employing 36.7 mg of alkenyl azole **1d** and 126 mg of sulfoxonium ylide **2b**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3db** (43 mg, 61%) as a yellow oil. FTIR (neat) 2922, 1545, 1510, 1482, 1445, 1324, 1246, 1146, 838, 787, 741, 700 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.40–7.35 (m, 4H), 7.30–7.25 (m, 1H), 6.98 (dd, $J = 7.0, 1.1$ Hz, 1H), 6.57 (d, $J = 7.0$ Hz, 1H), 2.62 (s, 3H), 2.43 (s, 3H). 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0, 142.2, 138.8, 135.8, 134.8, 130.0, 128.9, 128.8, 125.3, 125.0, 123.5, 112.0, 108.5, 21.4, 17.2, 14.4. HRMS (ESI): *m/z* $(M + H)^+$ calcd for

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$C_{16}H_{17}N_2^+$, 237.1386; found 237.1389.

4.3.16. 2,3,8-Trimethyl-5-(m-tolyl)imidazo[1,2-a]pyridine (**3eb**)

The reaction was performed according to the general procedure employing 40.9 mg of alkenyl azole **1e** and 126 mg of sulfoxonium ylide **2b**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3eb** (42 mg, 56%) as a yellow oil. FTIR (neat) 2922, 1506, 1482, 1438, 1358, 1249, 1157, 838, 787, 753, 707 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.31–7.24 (m, 2H), 7.18–7.14 (m, 2H), 6.89 (d, $J = 6.9$ Hz, 1H), 6.46 (d, $J = 6.9$ Hz, 1H), 2.61 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 139.8, 137.3, 136.3, 135.3, 130.5, 129.4, 127.5, 127.0, 125.2, 121.8, 117.9, 113.9, 21.4, 17.2, 13.4, 12.4. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{17}H_{19}N_2^+$, 251.1543; found 251.1541.

4.3.17. tert-Butyl 4-(7,8-dimethylimidazo[1,2-a]pyridin-5-yl) piperidine-1-carboxylate (**3bk**)

The reaction was performed according to the general procedure employing 36.7 mg of alkenyl azole **1b** and 182 mg of sulfoxonium ylide **2k**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3bk** (78 mg, 79%) as a tan foamy solid. mp 125–127 °C (after trituration with pentane). FTIR (neat) 2923, 1690, 1424, 1364, 1280, 1231, 1160, 1119, 978, 865, 766, 656, 542 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.82 (d, $J = 1.3$ Hz, 1H), 7.52 (d, $J = 1.3$ Hz, 1H), 6.54 (s, 1H), 4.36–4.14 (m, 2H), 3.15 (tt, $J = 11.9$, 3.2 Hz, 1H), 3.10–2.78 (m, 2H), 2.45 (s, 3H), 2.29 (s, 3H), 2.10–2.00 (m, 2H), 1.58 (qd, $J = 12.5$, 4.2 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 154.1, 146.6, 138.4, 132.6, 130.9, 121.3, 111.1, 109.5, 78.6, 43.6, 37.8, 29.8, 27.7, 17.7, 12.2. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{19}H_{28}N_3O_2^+$, 330.2176; found 330.2179.

4.3.18. tert-Butyl 4-(8-methyl-7-phenylimidazo[1,2-a]pyridin-5-yl) piperidine-1-carboxylate (**3ck**)

The reaction was performed according to the general procedure employing 55.3 mg of alkenyl azole **1c** and 182 mg of sulfoxonium ylide **2k**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3ck** (104.5 mg, 89%) as a tan foamy solid. mp 136–138 °C (after trituration with pentane). FTIR (neat) 2926, 1689, 1423, 1365, 1231, 1163, 872, 772, 703, 542 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.96 (d, $J = 1.3$ Hz, 1H), 7.64 (d, $J = 1.3$ Hz, 1H), 7.47–7.35 (m, 5H), 6.65 (s, 1H), 4.34–4.15 (m, 2H), 3.26 (tt, $J = 11.9$, 3.3 Hz, 1H), 3.10–2.80 (m, 2H), 2.49 (s, 3H), 2.15–2.07 (m, 2H), 1.65 (qd, $J = 12.2$, 3.9 Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 154.1, 146.3, 140.0, 139.0, 135.7, 133.2, 129.3, 128.3, 127.3, 121.1, 110.4, 110.1, 78.6, 43.6, 38.0, 29.7, 27.7, 13.8. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{24}H_{30}N_3O_2^+$, 392.2333; found 392.2336.

4.3.19. tert-Butyl 4-(2,8-dimethylimidazo[1,2-a]pyridin-5-yl) piperidine-1-carboxylate (**3dk**)

The reaction was performed according to the general procedure employing 36.7 mg of alkenyl azole **1d** and 182 mg of sulfoxonium ylide **2k**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3dk** (74 mg, 75%) as a yellow oil. FTIR (neat) 2924, 1685, 1420, 1365, 1230, 1161, 1122, 980, 871, 817, 541 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.67 (s, 1H), 6.95 (dd, $J = 7.3$, 1.3 Hz, 1H), 6.54 (d, $J = 7.1$ Hz, 1H), 4.33–4.10 (m, 2H), 3.12 (tt, $J = 12.0$, 3.3 Hz, 1H), 3.07–2.85 (m, 2H), 2.46 (s, 3H), 2.38 (s, 3H), 2.10–2.01 (m, 2H), 1.55 (qd, $J = 12.1$, 3.9 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 154.1, 145.5, 142.3, 139.2, 123.7, 122.8, 107.2, 107.1, 78.6, 43.8, 38.0, 29.6, 27.7, 16.0, 13.7. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{19}H_{28}N_3O_2^+$, 330.2176; found 330.2178.

4.3.20. tert-Butyl 4-(2,3,8-trimethylimidazo[1,2-a]pyridin-5-yl) piperidine-1-carboxylate (**3ek**)

The reaction was performed according to the general procedure employing 40.9 mg of alkenyl azole **1e** and 182 mg of sulfoxonium ylide **2k**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3ek** (72 mg, 70%) as a yellow foamy solid. mp 60–62 °C (after trituration with pentane). FTIR (neat) 2927, 1687, 1421, 1364, 1230, 1160, 1125, 1014, 978, 871, 818, 769, 541 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 6.84 (dd, $J = 7.2$, 1.3 Hz, 1H), 6.53 (d, $J = 7.1$ Hz, 1H), 4.30–4.10 (m, 2H), 3.71 (tt, $J = 11.3$, 2.9 Hz, 1H), 3.05–2.80 (m, 2H), 2.69 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H), 2.02–1.95 (m, 2H), 1.55 (qd, $J = 12.6$, 4.2 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 154.2, 145.5, 141.8, 140.0, 124.1, 121.8, 116.7, 108.2, 78.6, 43.5, 36.3, 32.5, 27.7, 16.2, 12.8, 12.2. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{20}H_{30}N_3O_2^+$, 344.2333; found 344.2340.

4.3.21. 2,8-Dimethyl-5-(4-(trifluoromethyl)phenyl)-[1,2,4]triazolo [1,5-a]pyridine (**3ga**)

The reaction was performed according to the general procedure employing 36.9 mg of alkenyl azole **1g** and 159 mg of sulfoxonium ylide **2a**. Purification by silica gel column chromatography (5–20% acetone/hexanes) afforded **3ga** (23 mg, 26%) as a yellow oil. FTIR (neat) 1619, 1533, 1506, 1478, 1320, 1165, 1112, 1064, 1016, 848, 816 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, $J = 8.1$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.33 (dd, $J = 7.3$, 1.2 Hz, 1H), 6.97 (d, $J = 7.2$ Hz, 1H), 2.65 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.0, 152.2, 136.6, 136.0, 131.4 (q, $J = 32.8$ Hz), 129.3, 128.2, 125.8, 125.5 (q, $J = 3.9$ Hz), 123.8 (q, $J = 272.3$ Hz), 113.7, 17.0, 14.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.9. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{15}H_{13}F_3N_3^+$, 292.1056; found 292.1054.

4.3.22. tert-Butyl 4-(2,8-dimethyl-[1,2,4]triazolo[1,5-a]pyridin-5-yl)piperidine-1-carboxylate (**3gk**)

The reaction was performed according to the general procedure employing 36.9 mg of alkenyl azole **1g** and 182 mg of sulfoxonium ylide **2k**. Purification by silica gel column chromatography (5–20% acetone/hexanes) afforded **3gk** (74 mg, 75%) as a yellow oil. FTIR (neat) 2974, 2927, 1687, 1418, 1365, 1234, 1161, 1124, 873, 730, 546 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, $J = 7.3$, 1.3 Hz, 1H), 6.60 (d, $J = 7.3$ Hz, 1H), 4.40–4.10 (m, 2H), 3.54 (tt, $J = 12.1$, 3.4 Hz, 1H), 2.92 (t, $J = 12.3$ Hz, 2H), 2.59 (s, 3H), 2.54 (s, 3H), 2.15–2.03 (m, 2H), 1.68–1.02 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 154.7, 151.7, 142.4, 128.1, 123.4, 108.8, 79.6, 43.9, 36.9, 29.8, 28.4, 16.7, 14.6. HRMS (ESI): *m/z* $(M + H)^+$ calcd for $C_{18}H_{27}N_4O_2^+$, 331.2129; found 331.2126.

4.4. General procedures for C–H functionalization of C-alkenyl azoles with sulfoxonium ylides (2.0 mmol scale)

On the bench-top, to a flame-dried 50 mL RBF was added alkenyl azole (2.00 mmol, 1 equiv), sulfoxonium ylide (4.00 mmol, 2 equiv), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol %, 0.10 mmol, 83 mg), PivOH (4.00 mmol, 2 equiv, 408 mg), and NaOAc (2.00 mmol, 1 equiv, 164 mg). The flask was connected to a reflux condenser, degassed three times, followed by the addition of xylenes (0.1 M, 20 mL). The resulting mixture was stirred at 120 °C for 16 h. The mixture was then cooled to room temp, filtered through a pad of celite, washed thoroughly with acetone, and concentrated under reduced pressure. The product was purified by silica gel column chromatography.

4.4.1. 8-Methyl-5-(m-tolyl)imidazo[1,2-a]pyridine (**3ab**)

The reaction was performed according to the general procedure employing 216 mg of alkenyl azole **1a** and 841 mg of sulfoxonium ylide **2b**. Purification by silica gel column chromatography (10–30% acetone/hexanes) afforded **3ab** (280 mg, 63%) as a yellow oil. ^1H and ^{13}C NMR spectra matched with **3ab** obtained from smaller scale (0.3 mmol).

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*4.4.2. tert-Butyl 4-(8-methylimidazo[1,2-a]pyridin-5-yl)piperidine-1-carboxylate (**3ak**)*

The reaction was performed according to the general procedure employing 216 mg of alkenyl azole **1a** and 1.21 g of sulfoxonium ylide **2k**. Purification by silica gel column chromatography (10–50% acetone/hexanes) afforded **3ak** (448 mg, 71%) as a yellow foamy solid. ^{1}H and ^{13}C NMR spectra matched with **3ak** obtained from smaller scale (0.3 mmol).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.03.062.

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