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From Triazoles to Imidazolines through the Sequential N−H Insertion of α-Imino Rhodium−Carbenes into β-Enamino Esters/Enamine−Imine Tautomerization/Conjugate Addition Cascade

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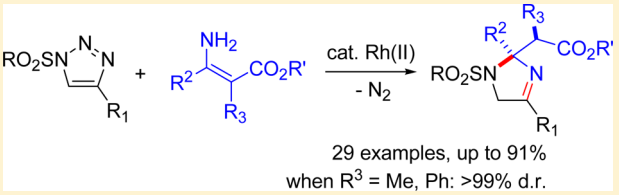
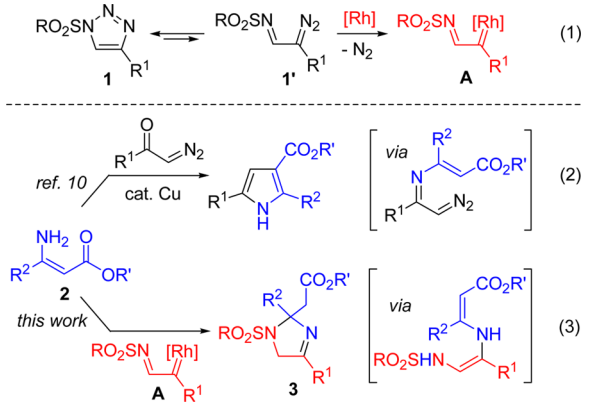
Supporting Information

ABSTRACT: A rhodium(II)-catalyzed denitrogenative coupling of *N*-sulfonyl-1,2,3-triazoles with ambiphilic β-enamino esters affords 2,5-dihydro-1*H*-imidazoles (3-imidazolines) with broad functional group tolerance. Mechanistic studies using a deuterium-labeled triazole suggest that the reaction proceeds in a cascade through the N−H insertion of an α-imino rhodium−carbene, followed by enamine−imine tautomerization and conjugate addition. Moreover, the reaction proceeds with high diastereoselectivity for α-substituted β-enamino esters (R^3 = Me, Ph) to give a single diastereomer.



Diazo compounds are ambiphilic (ambivalent) reagents that are widely used in organic synthesis.[1] While the diazo carbon is the preferred site of attack by electrophiles, the polarity of the carbon is reversed when the diazo compounds are converted to metal−carbene complexes. This reactivity umpolung greatly expands the synthetic utility of diazo compounds.[2] In particular, the diverse reactivity of rhodium carbene complexes **A** derived in situ from diazo imines **1′**, which are formed by ring-chain tautomerization of *N*-sulfonyl-1,2,3-triazoles **1**, has recently gained considerable attention (eq 1).[3] The electrophilic nature of the carbene carbon, when



combined with the nucleophilic character of the nitrogen atom of the α-imino group, enables a palette of reactivity with nitriles,[4a] alkynes,[4b,c] allenes,[4d] isocynates,[4e] α,β-unsaturated aldehydes,[4f] furans,[4g] indoles,[4h] and aromatic hydrocarbons (intramolecularly)[4i] to provide various nitrogen heterocycles.[4] The carbene complex **A** also inserts into the O−H bond of H_2O, alcohols, and carboxylic acids, and the N−H bond of primary and secondary amides, and carbamates.[5] More recently, our group[6a] and others (Murakami[6b] and Yoo[6c] groups) independently reported the stereoselective insertion of **A** into the C═O bond of *N*,*N*-disubstituted amides to afford *cis*-diamino enones.

β-Enamino esters also possess an ambivalent character that combines a nucleophilic enamine with an electrophilic α,β-unsaturated ester (Michael acceptor), and have been employed as useful reagents in the synthesis of various heterocycles.[7] Given our continuing interest for β-enamino ester derivatives,[8] we envisioned that the ambiphilic β-enamino esters would be promising partners to couple with the putative α-imino rhodium−carbene **A**.[9] With the exception of a recent report by Reddy and co-workers claiming that β-enamino esters could react with α-diazo ketones to form α-diazo imine intermediates on the route to pyrroles (eq 2),[10] the reactions of β-enamino esters with metal−carbenes have no precedents to the best of our knowledge. Herein, we report a sequential N−H insertion of α-imino rhodium−carbene **A** into β-enamino esters, followed by enamine−imine tautomerization and conjugate addition of the resulting bis-enamide, which provides an efficient catalytic method for the transformation of *N*-sulfonyl-1,2,3-triazoles **1** to 2,5-dihydro-1*H*-imidazoles (3-imidazolines) **3** (eq 3). Whereas many synthetic efforts have been directed toward the preparation of 2- and 4-imidazolines,[11] reports on the synthesis of 3-imidazolines remain rare.[12]

Our investigations started with the reaction of the triazole **1a** (R = Tolyl, R^1 = Ph) with 1.1 equiv of enamino ester **2a** (R_2 = Ph, R′ = Et) in toluene in the presence of 2.5 mol % $Rh_2(OAc)_2$, which gave the corresponding imidazole **3aa** in 76% yield (entry 1, Table 1). When the reaction was conducted either in the absence of $Rh_2(OAc)_4$ or with $Cu(OAc)_2$ in place of the rhodium catalyst, the reaction was not clean, and no

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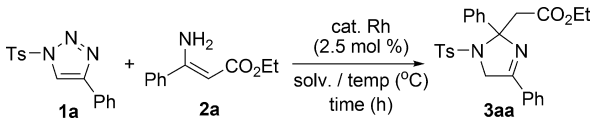
Table 1. Optimization of the Reaction Conditions[a]



entry	Rh(II)	solvent	T (°C)/h	yield (%)[b]
1	$Rh_2(OAc)_4$	toluene	100/4	76
2	Rh_2(S-DOSP)$_4$	toluene	100/4	68
3	$Rh_2(^tBuCO_2)_4$	toluene	100/4	78
4	Rh_2(TPA)$_4$	toluene	100/4	44
5	Rh_2(S-NTTL)$_4$	toluene	100/4	63
6	$Rh_2(Oct)_4$	toluene	100/4	83
7	$Rh_2(Oct)_4$	toluene	100/2	87
8[c]	$Rh_2(Oct)_4$	toluene	100/4	78
9	$Rh_2(Oct)_4$	toluene	80/4	64
10	$Rh_2(Oct)_4$	PhCl	100/4	78
11	$Rh_2(Oct)_4$	$ClCH_2CH_2Cl$	100/4	80
12	$Rh_2(Oct)_4$	cyclohexane	100/4	82
13	$Rh_2(Oct)_4$	$CHCl_3$	100/4	52

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.33 mmol), Rh(II) (2.5 mol %), solvent (1.5 mL). [b]Isolated yield after silica column chromatography. [c]Reaction in the presence of 1.0 mol % of catalyst. Rh_2(S-DOSP)$_4$: tetrakis[(*S*)-*N*-(*p*-dodecylphenylsulfonyl)prolinato]-dirhodium(II). TPA: triphenylacetate. Rh_2(S-NTTL)$_4$: tetrakis[(*S*)-*N*-(1,8-naphthoyl)-*tert*-leucinate]dirhodium(II).

product could be isolated. Screening of the reaction conditions as shown in Table 1 ultimately led to an optimal protocol in which triazole **1a** is reacted with 1.1 equiv of **2a** in toluene in the presence of 2.5 mol % $Rh_2(Oct)_4$ at 100 °C for 2.0 h to afford **3aa** in 87% yield (entry 7, Table 1). The structure of **3aa** was unambiguously determined by spectroscopic analyses and X-ray crystallography, and is clearly consistent with the imine tautomer (C═N bond length: 1.279 Å; Figure 1).[13] Preference

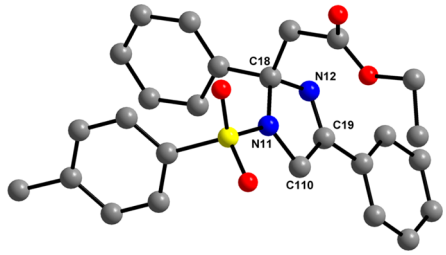
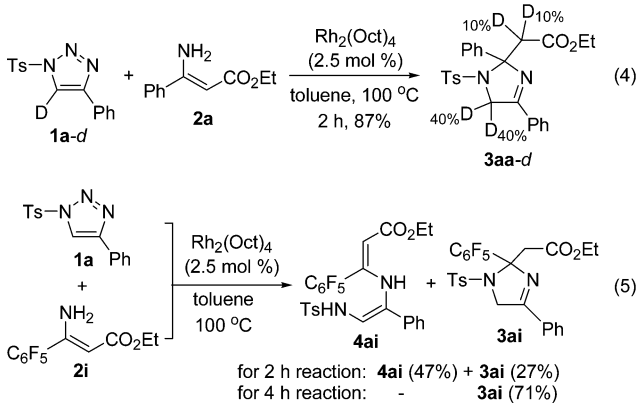


Figure 1. X-ray structure of **3aa**. For clarity, hydrogens and disordered atoms were omitted. Selected bond distances: C18–N12 1.462(5) Å, N12–C19 1.279(6) Å, C19–C110 1.510(6) Å, C110–N11 1.453(5) Å, N11–C18 1.504(5) Å.

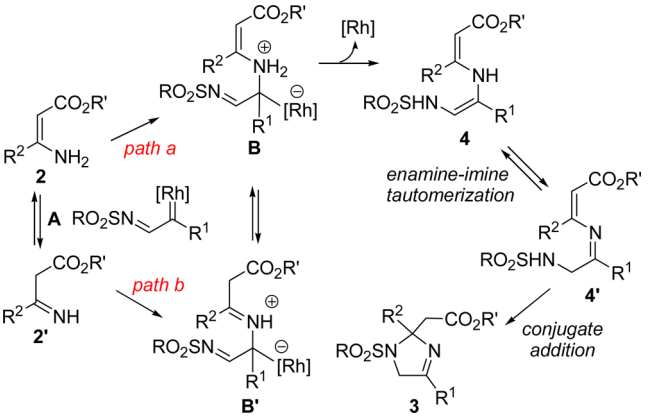
for the imine tautomer is corroborated by DFT calculations, which favor it over the enamine tautomer by ca. 7.3 kcal/mol.[14] In order to get insight into the reaction mechanism, the coupling reaction of deuterium-labeled triazole **1a**-*d*, prepared by the Cu-catalyzed cycloaddition of deuterated phenylacetylene and tosyl azide, with **2a** was carried out and found to result in the scrambling of deuterium at the two methylene groups of **3aa**-*d* (eq 4). Moreover, during the reaction of **1a** with **2i** having a pentafluorophenyl group, we could fortunately detect and isolate the bis-enamine intermediate **4ai** in 47% yield along with **3ai** (27%) when the reaction was carried out for 2 h. Prolonging this reaction to 4 h leads to the



disappearance of intermediate **4ai**, and complete conversion to the corresponding imidazole **3ai** with 71% yield (eq 5).

On the basis of the labeling experiment and intermediacy of bis-enamine **4** implying the enamine–imine tautomerization, two different pathways can be considered for the formation of **3**. One possible route would be the N-nucleophilic addition of enamino ester **2** to the electrophilic carbene carbon, forming enamine ylide **B** to afford bis-enamine **4**. The enamine–imine tautomerization to **4′**, followed by conjugate addition, could afford **3** (path *a* in Scheme 1). Another possibility is that the

Scheme 1. Possible Reaction Pathways of Rhodium–Carbene A with β-Enamino Ester 2



imino ester tautomer **2′** reacted with **A** to generate ketimine ylide **B′** first, then tautomerized to the enamine ylide **B** (path *b* in Scheme 1). Finally, alternate cyclization from the Rh-bound zwitterionic intermediates **B**/**B′** may not entirely be ruled out at present.

Under optimized reaction conditions, we investigated the scope of this reaction with respect to triazole **1** using β-enamino ester **2a** as a coupling partner (Table 2). As previously observed in rhodium(II)-catalyzed couplings of triazoles with DMF,[6a] the reactivity of 4-phenyl substituted triazoles **1b**–**1j** having different substituents on the phenyl ring was not greatly influenced by their electronic properties, but could be affected by sterics. For example, the triazoles having electron-donating methyl (**1b** and **1c**), methoxy groups (**1e**), and electron-withdrawing halogens (**1f**, **1h**, and **1i**) at the *meta*- and *para*-positions afforded the corresponding imidazolines **3** in good yields; the *p*-cyanophenyl substituted triazole **1j** is an exception and gave a slightly lower yield of imidazoline **3ja** (entry 9, Table 2). 4-Phenyltriazoles bearing methyl (**1d**) and fluorine

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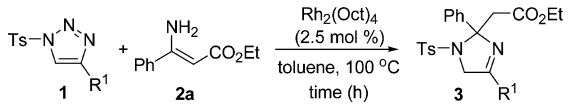
Table 2. Scope with Respect to Triazole 1[a,b]



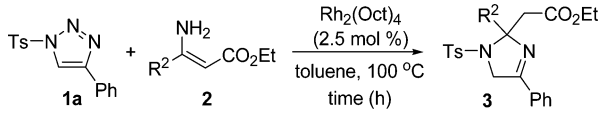
entry	1, R^1	h	3	Yield (%)[b]
1	*p*-$CH_3C_6H_4$ (**1b**)	2.0	**3ba**	80
2	*m*-$CH_3C_6H_4$ (**1c**)	2.0	**3ca**	80
3	*o*-$CH_3C_6H_4$ (**1d**)	2.5	**3da**	54
4	*p*-$CH_3OC_6H_4$ (**1e**)	2.0	**3ea**	82
5	*p*-FC_6H_4 (**1f**)	2.5	**3fa**	87
6	*o*-FC_6H_4 (**1g**)	2.0	**3ga**	56
7	*p*-ClC_6H_4 (**1h**)	2.0	**3ha**	81
8	*p*-BrC_6H_4 (**1i**)	2.0	**3ia**	80
9	*p*-CNC_6H_4 (**1j**)	2.5	**3ja**	58
10	$PhCH_2CH_2$ (**1k**)	4.0	**3ka**	68
11	 (**1l**)	2.0	**3la**	73

[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.33 mmol), $Rh(Oct)_4$ (2.5 mol %), solvent (1.5 mL). [b]Isolated yield after silica column chromatography.

(**1g**) substituents at the *ortho*-position afforded imidazolines **3da** (entry 3, Table 2) and **3ga** (entry 6, Table 2), respectively, in more modest yields. The reaction conditions were also successfully applied to alkyl-substituted triazole **1k** to afford the imidazoline **3ka** in moderate yield (entry 10, Table 1). The cyclohexenyl-substituted triazole **1l** was also successfully transannulated to the corresponding imidazoline **3la** in a yield of 73% (entry 11, Table 2).

The reaction also showed broad substrate scope with respect to β-enamino esters **2** (Table 3). As shown in Table 3, the

Table 3. Scope with Respect to β-Enamino Ester 2[a,b]

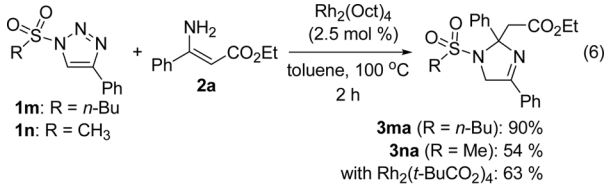


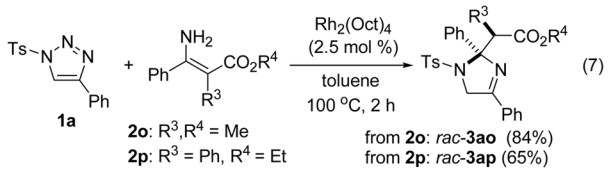
entry	1, R^2	h	3	Yield (%)[b]
1	*p*-$CH_3C_6H_4$ (**2b**)	2.5	**3ab**	83
2	*m*-$CH_3C_6H_4$ (**2c**)	2.5	**3ac**	85
3	*o*-$CH_3C_6H_4$ (**2d**)	1.5	**3ad**	27
4	*p*-$CH_3OC_6H_4$ (**2e**)	2.0	**3ae**	84
5	*p*-BrC_6H_4 (**2f**)	2.0	**3af**	91
6	*p*-FC_6H_4 (**2g**)	2.5	**3ag**	83
7	*p*-$CF_3C_6H_4$ (**2h**)	4.0	**3ah**	83
8	C_6F_5 (**2i**)	4.0	**3ai**	71
9	 (**2j**)	2.0	**3aj**	68
10	$PhCH_2$ (**2k**)	2.0	**3ak**	71
11	$PhCH_2CH_2$ (**2l**)	2.5	**3al**	69
12	$CH_3(CH_2)_2$ (**2m**)	2.0	**3am**	66
13	$(CH_3)_2CHCH_2$ (**2n**)	4.9	**3an**	84

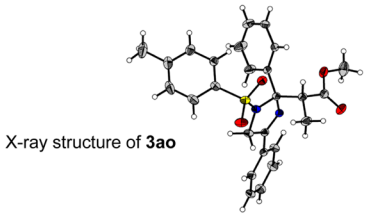
[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.33 mmol), $Rh_2(Oct)_4$ (2.5 mol %), solvent (1.5 mL). [b]Isolated yield after silica column chromatography.

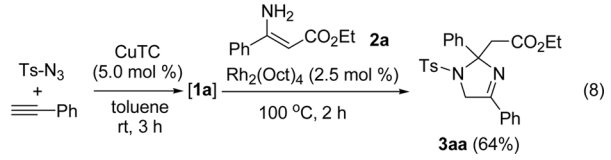
reactions of triazole **1a** with β-phenyl β-enamino esters **2b**–**2i** bearing electron-donating and electron-withdrawing substitutents on the phenyl ring afforded the corresponding imidazolines **3ab**–**3ai** in high yields (entries 1–8, Table 3), except the reaction with sterically congested *ortho*-methyl substituted **2d** that afforded only 27% yield of **3ad** (entry 3, Table 3). Although the corresponding bis-enamine **4ad** was formed in 66% yield as a major product, the yield of **3ad** was not improved further at higher reaction temperatures or upon prolonged reaction times. A heteroaromatic furyl-substituted β-enamino ester **2j** also afforded the corresponding imidazoline **3aj** in good yield (entry 9, Table 3). Alkyl-substituted enamino esters **2k**–**2n** were also tolerated and gave the corresponding imidazolines **3ak**–**3an** in good to excellent yields (entries 10–12, Table 3).

As shown in eq 6, when the *N*-tosyl group of **1** was changed to alkanesulfonyls such as butanesulfonyl triazole **1m**, the









reaction efficiency remained high, providing the corresponding imidazoline **3ma** in 90% yield. However, the methanesulfonyl substituted **3na** was isolated from the reaction in a lower yield of 54%, although its yield was slightly increased (63%) by employing $Rh_2(t\text{-}BuCO_2)_4$ as a catalyst. Under the standard conditions, α-methyl- **2o** and α-phenyl-substituted β-enamino esters **2p** were also successfully incorporated to afford the racemic mixtures of the single diastereomers **3ao** and **3ap**, respectively (eq 7). Formation of a single diastereomer, the structure of which was confirmed by X-ray crystallography for **3ao**,[13] may be ascribed to the protonation under thermodynamic control of the enolates formed after conjugate cyclization of imino enamine **4′**. The reaction can also be carried out in a tandem one-pot fashion starting from a sulfonyl azide and a terminal alkyne. For instance, a solution triazole **1a** was prepared by the cycloaddition of phenylacetylene and *p*-toluenesulfonyl azide at room temperature for 3 h in the presence of 5 mol % of CuTC catalyst. Enamino ester **2a** and the Rh catalyst were added, and the reaction mixture was then stirred at 100 °C for 2 h to afford imidazoline **3aa** in 64% yield based on phenylacetylene (eq 8).

In summary, we have found that a rhodium(II)-catalyzed denitrogenative coupling of *N*-sulfonyl-1,2,3-triazoles with ambiphilic β-enamino esters affords 2,5-dihydro-1*H*-imidazoles.

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Mechanistic investigations support the intermediacy of a bis-enamine formed by insertion of the Rh(II) carbene into the N−H bond of the enamino ester, which then tautomerizes and cyclizes in a conjugate addition to give the five-membered N-heterocycles. When α-substituted enamino esters were employed, the reactions were found to proceed with complete diastereoselectivity (>99% d.r.). The reaction can also be carried out in a tandem one-pot fashion starting from a sulfonyl azide and a terminal alkyne, avoiding isolation of triazole to minimize generation of waste.

EXPERIMENTAL SECTION

All reactions were performed under an argon atmosphere using standard Schelenk techniques. Reaction flasks were flame-dried under a stream of argon. Anhydrous solvents and other purchased reagents were used without further purification. Anhydrous solvent was transferred by an oven-dried syringe. $Rh_2(^tBuCO_2)_4$ and Rh_2(S-NTTL)$_4$ were synthesized according to the reported procedures.[15] *N*-Sulfonylated-1,2,3-triazoles (**1a**−**1k**)[16] and β-enamino esters (**2a**−**2o**)[17] were prepared according to the literature procedures. The NMR spectra were recorded at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 282 MHz for ^{19}F. HRMS data were obtained by electron ionization and fast atom bombardment with a magnetic sector-electronic sector double focusing mass analyzer.

General Procedure for the Synthesis of 2,5-Dihydro-1*H*-imidazoles (3-Imidazolines). Triazole **1** (0.3 mmol), β-enamino ester **2** (0.33 mmol), and $Rh_2(Oct)_4$ (2.5 mol %, 5.8 mg, 7.59×10^{-3} mmol) catalyst, and toluene (1.5 mL) were successively added into a flame-dried vial reactor. The mixure was then heated at 100 °C for 2 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica chromatography to afford the corresponding 2,5-dihydro-1*H*-imidazoles **3**.

*Ethyl {1-[(4-Methylphenyl)sulfonyl]-2,4-diphenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3aa**).* Yield: 87% (121 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 115−117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.1 Hz, 3H), 2.31 (s, 3H), 3.56 (d, *J* = 16.0 Hz, 1H), 3.98−4.10 (m, 2H), 4.16 (d, *J* = 16.0 Hz, 1H), 4.63 (d, *J* = 14.1 Hz, 1H), 5.01 (d, *J* = 14.1 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.15−7.33 (m, 5H), 7.39−7.55 (m, 3H), 7.80 (d, *J* = 6.9 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.5, 41.8, 57.2, 60.5, 95.3, 126.7, 126.8, 127.8, 128.3, 128.5, 128.9, 129.1, 131.1, 132.0, 136.6, 139.4, 142.8, 166.5, 169.4 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{26}H_{27}N_2O_4S$: 463.1692; Found 463.1693.

*Ethyl {4-(4-Methylphenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ba**).* Yield: 80% (114 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 104−105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.1 Hz, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 3.55 (d, *J* = 15.9 Hz, 1H), 3.99−4.10 (m, 2H), 4.15 (d, *J* = 15.9 Hz, 1H), 4.60 (d, *J* = 14.1 Hz, 1H), 4.98 (d, *J* = 14.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.18−7.32 (m, 7H), 7.68 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.4, 21.6, 41.8, 57.1, 60.4, 95.2, 126.7(126.67), 126.7(126.70), 127.8, 128.2, 128.3, 128.4, 129.0, 129.5, 136.6, 139.5, 142.5, 142.7, 166.3, 169.4 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{27}H_{29}N_2O_4S$ 477.1848; Found 477.1850.

*Ethyl {4-(3-Methylphenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ca**).* Yield: 80% (114 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 143−144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.1 Hz, 3H), 2.28 (s, 3H), 2.35 (s, 3H), 3.56 (d, *J* = 16.0 Hz, 1H), 4.00−4.11 (m, 2H), 4.17 (d, *J* = 16.0 Hz, 1H), 4.63 (d, *J* = 14.1 Hz, 1H), 5.01 (d, *J* = 14.1 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.18−7.34 (m, 7H), 7.55 (d, *J* = 5.8 Hz, 1H), 7.66 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.2, 21.4, 41.7, 57.2, 60.3, 95.1, 125.0, 126.6(126.59), 126.6(126.64), 128.2(128.15), 128.2(128.21), 128.4, 128.7, 129.0, 130.9, 132.7, 136.5, 138.6, 139.3, 142.7, 166.6, 169.3 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{27}H_{29}N_2O_4S$ 477.1848; Found 477.1851.

*Ethyl {4-(2-Methylphenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3da**).* Yield: 54% (77 mg); Eluents: *n*-hexane/EtOAc = 6/1; pale yellow solid; mp: 132−134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (t, *J* = 7.1 Hz, 3H), 2.30 (s, 3H), 2.53 (s, 3H), 3.58 (d, *J* = 15.9 Hz, 1H), 4.02−4.10 (m, 3H), 4.62 (d, *J* = 14.1 Hz, 1H), 4.97 (d, *J* = 14.1 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.22−7.38 (m, 8H), 7.41−7.49 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.5, 22.3, 41.9, 58.9, 60.5, 95.8, 126.0, 126.7, 126.8, 128.3, 128.4, 129.1, 129.4, 130.2, 130.7, 132.0, 136.6, 139.1, 139.7, 142.8, 167.6, 169.5 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{27}H_{29}N_2O_4S$ 477.1848; Found 477.1851.

*Ethyl {4-(4-Methoxyphenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ea**).* Yield: 82% (121 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 141−143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.1 Hz, 3H), 2.31 (s, 3H), 3.54 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 3.98−4.10 (m, 2H), 4.14 (d, *J* = 15.9 Hz, 1H), 4.59 (d, *J* = 13.9 Hz, 1H), 4.96 (d, *J* = 14.0 Hz, 1H), 6.88−6.95 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.16−7.31 (m, 5H), 7.74 (d, *J* = 8.9 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.4, 41.9, 55.5, 57.0, 60.4, 95.1, 114.2, 123.7, 126.7, 128.2, 128.4, 129.1, 129.6, 136.6, 139.6, 142.7, 162.6, 165.6, 169.4 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{27}H_{29}N_2O_5S$ 493.1797; Found 493.1796.

*Ethyl {4-(4-Fluorophenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3fa**).* Yield: 87% (125 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 140−142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.1 Hz, 3H), 2.30 (s, 3H), 3.55 (d, *J* = 16.1 Hz, 1H), 3.99−4.11 (m, 2H), 4.16 (d, *J* = 16.1 Hz, 1H), 4.62 (d, *J* = 14.1 Hz, 1H), 4.99 (d, *J* = 14.1 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 7.05−7.16 (m, 4H), 7.18−7.32 (m, 5H), 7.80 (dd, *J* = 8.7, 5.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.4, 41.5, 57.1, 60.4, 95.2, 115.8, 116.1, 126.6, 126.7, 127.4 (d, *J* = 3.8 Hz) 128.3, 128.5, 129.1, 130.0, 130.1, 136.4, 139.3, 142.8, 164.9 (d, *J* = 251.3 Hz), 165.2, 169.3 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{26}H_{26}FN_2O_4S$ 481.1597; Found 481.1598.

*Ethyl {4-(2-Fluorophenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ga**).* Yield: 52% (77 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 116−118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, *J* = 7.1 Hz, 3H), 2.30 (s, 3H), 3.56 (d, *J* = 15.9 Hz, 1H), 4.00−4.26 (m, 3H), 4.68 (dd, *J* = 15.4, 3.0 Hz, 1H), 5.00 (dd, *J* = 15.4, 2.7 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.11−7.32 (m, 7H), 7.40−7.51 (m, 1H), 8.00−8.15 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.5, 41.8, 59.2 (d, *J* = 12.8 Hz), 93.8, 116.4 (d, *J* = 21.9 Hz), 119.1 (d, *J* = 12.8 Hz), 124.8 (d, *J* = 3.0 Hz), 126.8 (d, *J* = 7.6 Hz), 128.4, 128.5, 129.1, 130.2 (d, *J* = 3.0 Hz), 133.8 (d, *J* = 8.3 Hz), 136.6, 139.3, 142.8, 161.9 (d, *J* = 253.7 Hz), 163.3 (d, *J* = 3.0 Hz), 169.4 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{26}H_{26}FN_2O_4S$ 481.1597; Found 481.1600

*Ethyl {4-(4-Chlorophenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ha**).* Yield: 81% (121 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 127−129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.1 Hz, 3H), 2.29 (s, 3H), 3.54 (d, *J* = 16.1 Hz, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 4.15 (d, *J* = 16.1 Hz, 1H), 4.61 (d, *J* = 14.2 Hz, 1H), 4.98 (d, *J* = 14.1 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.15−7.32 (m, 5H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.4, 41.6, 57.1, 60.5, 95.3, 126.6, 126.7, 128.3, 129.1, 129.5, 136.5, 138.1, 139.2, 142.9, 165.4, 169.4 ppm. HRMS (FAB) *m*/*z*: [M + H]$^+$ Calcd for $C_{26}H_{26}ClN_2O_4S$ 497.1302; Found 497.1304.

*Ethyl {4-(4-Bromophenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ia**).* Yield: 80% (130 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 133−135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (t, *J* = 7.1 Hz, 3H), 2.23 (s, 3H), 3.54 (d, *J* = 16.1 Hz, 1H), 4.03(q, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 16.1 Hz, 1H), 4.61 (d, *J* = 14.2 Hz, 1H), 4.98 (d, *J* = 14.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.13−7.35 (m, 5H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.5, 41.5, 60.5, 95.4, 126.6, 126.8, 128.4, 128.6, 129.2,

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129.3, 130.0, 132.1, 136.5, 139.2, 142.9, 165.6, 169.4 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}{}^{79}BrN_2O_4S$ 541.0797; Found 541.0794, Calcd for $C_{26}H_{26}{}^{81}BrN_2O_4S$ 543.0776; Found 543.0740.

*Ethyl {4-(4-Cyanophenyl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ja**).* Yield: 58% (85 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 148−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, J = 7.1 Hz, 3H), 2.32 (s, 3H), 3.55 (d, J = 16.4 Hz, 1H), 4.04 (q, J = 7.1 Hz, 2H), 4.16 (d, J = 16.4 Hz, 1H), 4.65 (d, J = 14.3 Hz, 1H), 5.02 (d, J = 14.3 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 7.15−7.36 (m, 5H), 7.72 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.5, 41.2, 57.2, 60.5, 95.5, 115.2, 118.1, 126.5, 126.8, 128.4(128.38), 128.4(128.43), 128.7, 129.2, 132.6, 134.9, 136.4, 139.0, 143.1, 165.2, 169.3 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{27}H_{26}N_3O_4S$ 488.1644; Found 488.1643.

*Ethyl {1-[(4-Methylphenyl)sulfonyl]-4-(2-phenylethyl)-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ka**).* Yield: 68% (100 mg); Eluents: *n*-hexane/EtOAc = 4/1; yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, J = 7.1 Hz, 3H), 2.32 (s, 3H), 2.68−2.87 (m, 2H), 2.88−3.09 (m, 2H), 3.43 (d, J = 16.2, 1H), 3.96−4.18 (m, 4H), 4.49 (d, J = 14.5 Hz, 1H), 6.93−6.99 (m, 5H), 7.09−7.31 (m, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.4, 31.8, 33.1, 41.3, 59.1, 60.3, 94.7, 126.4, 126.5, 126.6, 128.1, 128.3, 128.4, 128.6, 129.0, 136.5, 139.0, 140.3, 142.6, 169.4, 171.3 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{28}H_{31}N_2O_4S$ 491.2005; Found 491.2006.

*Ethyl {4-(Cyclohex-1-en-1-yl)-1-[(4-methylphenyl)sulfonyl]-2-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3la**).* Yield: 73% (125 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 54−56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J = 7.1 Hz, 3H), 1.48−1.60 (m, 4H), 2.10−2.20 (m, 2H), 2.20−2.32 (m, 5H), 3.40 (d, J = 15.8 Hz, 1H), 3.96−4.08 (m, 3H), 4.28 (d, J = 13.5 Hz, 1H), 4.63 (d, J = 13.5 Hz, 1H), 6.22 (brs, 1H), 6.86−6.98 (m, 4H), 7.05−7.24 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.3, 21.7, 21.8, 24.3, 26.0, 41.7, 56.2, 60.2, 94.8, 126.6(126.57), 126.6(126.61), 128.1, 128.2, 128.9, 132.4, 136.5, 137.6, 139.5, 142.5, 167.5, 169.4 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{26}H_{31}N_2O_4S$ 467.2005; Found 467.2006.

*Ethyl [1-(Butylsulfonyl)-2,4-diphenyl-2,5-dihydro-1H-imidazol-2-yl]acetate (**3ma**).* Yield: 90% (116 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 102−104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (t, J = 7.3 Hz, 3H), 1.05−1.23 (m, 5H), 1.35−1.58 (m, 2H), 2.04−2.46 (m, 2H), 3.48 (d, J = 15.9, 1H), 3.98−4.13 (m, 3H), 4.79 (d, J = 14.5 Hz, 1H), 5.07 (d, J = 14.5 Hz, 1H), 7.31−7.60 (m, 8H), 7.80−7.91 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 14.2, 21.5, 24.9, 41.7, 52.4, 58.1, 60.4, 94.3, 126.4, 127.8, 128.6, 129.0, 131.0, 132.1, 139.8, 167.2, 169.5 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{23}H_{29}N_2O_4S$ 429.1848; Found 429.1849.

*Ethyl [1-(Methylsulfonyl)-2,4-diphenyl-2,5-dihydro-1H-imidazol-2-yl]acetate (**3na**).* Yield: 54% (63 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 116−118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J = 7.1 Hz, 3H), 2.21 (s, 3H), 3.51 (d, J = 15.9, 1H), 3.95−4.14 (m, 3H), 4.73 (d, J = 14.4 Hz, 1H), 5.00 (d, J = 14.4 Hz, 1H), 7.32−7.58 (m, 8H), 7.86 (d, J = 7.0 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 38.3, 41.8, 57.2, 60.4, 94.7, 126.5, 127.8, 128.7, 128.9, 129.0, 130.9, 132.1, 140.0, 166.8, 169.4 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_4S$ 387.1379; Found 387.1380.

*Ethyl {2-(4-Methylphenyl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ab**).* Yield: 83% (119 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 130−132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, J = 7.1 Hz, 3H), 2.31 (d, J = 5.1 Hz, 6H), 3.54 (d, J = 16.0 Hz, 1H), 3.94−4.09 (m, 2H), 4.13 (d, J = 16.0 Hz, 1H), 4.66 (d, J = 14.2 Hz, 1H), 5.00 (d, J = 14.2 Hz, 1H), 6.94−7.02 (m, 4H), 7.03−7.15 (m, 4H), 7.37−7.50 (m, 3H), 7.75−7.84 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.1, 21.4, 41.6, 57.2, 60.3, 95.0, 126.5, 126.7, 127.7, 128.8(128.76), 128.8(128.78), 128.9, 131.1, 131.8, 136.4, 136.6, 138.2, 142.6, 166.1, 169.4 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{27}H_{29}N_2O_4S$ 477.1848; Found 477.1850.

*Ethyl {2-(3-Methylphenyl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ac**).* Yield: 85% (121 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 128−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, J = 7.1 Hz, 3H), 2.13 (s, 3H), 2.31 (s, 3H), 3.55 (d, J = 16.0 Hz, 1H), 4.01−4.19 (m, 3H), 4.66 (d, J = 14.2 Hz, 1H), 5.04 (d, J = 14.1 Hz, 1H), 6.74 (s, 1H), 6.98 (d, J = 8.3 Hz, 2H), 7.04−7.20 (m, 5H), 7.40−7.54 (m, 3H), 7.78−7.88 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.3(21.29), 21.3(21.30), 41.7, 57.3, 60.3, 95.0, 123.5, 126.6, 127.4, 127.7, 128.1, 128.8, 128.9, 129.1, 131.0, 131.9, 136.5, 137.8, 138.9, 142.6, 166.2, 169.3 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{27}H_{29}N_2O_4S$ 477.1848; Found 477.1850.

*Ethyl {2-(2-Methylphenyl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ad**).* Yield: 27% (39 mg); Eluents: *n*-hexane/EtOAc = 6/1; pale yellow solid; mp: 124−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, J = 7.1 Hz, 3H), 1.54 (s, 3H), 2.33 (s, 3H), 3.60 (d, J = 15.1 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 4.15 (d, J = 15.2 Hz, 1H), 4.62 (d, J = 14.2 Hz, 1H), 5.14 (d, J = 14.3 Hz, 1H), 6.8 (d, J = 7.3 Hz, 1H), 7.01 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 7.20−7.27 (m, 1H), 7.28−7.35 (m, 1H), 7.40−7.52 (m, 3H), 7.67 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 6.9 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 20.4, 21.6, 43.9, 58.2, 60.5, 95.7, 126.0, 126.7, 127.8, 127.9, 128.6, 129.0, 129.1, 131.1, 132.1, 133.1, 136.5, 136.7, 138.1, 142.9, 167.8, 169.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{27}H_{29}N_2O_4S$ 477.1848; Found 477.1850.

*Ethyl {2-(4-Methoxyphenyl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ae**).* Yield: 84% (124 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 141−143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, J = 7.1 Hz, 3H), 2.32 (s, 3H), 3.53 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H), 3.98−4.18 (m, 3H) 4.63 (d, J = 14.2 Hz, 1H), 4.99 (d, J = 14.2 Hz, 1H), 6.72 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 7.04−7.18 (m, 4H), 7.35−7.55 (m, 3H), 7.74−7.83 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.4, 41.9, 55.3, 57.1, 60.3, 95.0, 113.4, 126.7, 127.7, 127.9, 128.8, 129.0, 131.0, 131.5, 131.9, 136.6, 142.7, 159.6, 166.1, 169.4 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{27}H_{29}N_2O_5S$ 493.1797; Found 493.1798.

*Ethyl {2-(4-Bromophenyl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3af**).* Yield: 91% (147 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 126−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, J = 7.1 Hz, 3H), 2.35 (s, 3H), 3.52 (d, J = 16.0 Hz, 1H), 3.98−4.12 (m, 3H), 4.69 (d, J = 14.3 Hz, 1H), 5.03 (d, J = 14.3 Hz, 1H), 7.01−7.10 (m, 4H), 7.15 (d, J = 8.3 Hz, 2H), 7.27−7.35 (m, 2H), 7.40−7.55 (m, 3H), 7.76−7.84 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.6, 41.6, 57.5, 60.6, 94.7, 122.9, 126.6, 127.9, 128.5, 129.0, 129.3, 130.9, 131.3, 132.2, 136.8, 138.5, 143.2, 167.0, 169.1 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}{}^{79}BrN_2O_4S$ 541.0797; Found 541.0799, Calcd for $C_{26}H_{26}{}^{81}BrN_2O_4S$ 543.0776; Found 543.0781.

*Ethyl {2-(4-Fluorophenyl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ag**).* Yield: 83% (120 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 120−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, J = 7.1 Hz, 3H), 2.33 (s, 3H), 3.54 (d, J = 16.0 Hz, 1H), 3.98−4.16 (m, 3H), 4.66 (d, J = 14.2 Hz, 1H), 5.01 (d, J = 14.2 Hz, 1H), 6.83−6.97 (m, 2H), 7.04 (d, J = 8.2 Hz, 2H), 7.12−7.24 (m, 4H), 7.40−7.55 (m, 3H), 7.75−7.86 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.4, 41.8, 57.2, 60.4, 94.7, 115.0 (d, J = 21.8 Hz), 126.6, 127.8, 128.6 (d, J = 8.3 Hz), 128.9, 129.1, 130.9, 132.1, 135.5 (d, J = 3.8 Hz), 136.7, 143.0, 162.7 (d, J = 246.0 Hz), 166.7, 169.1 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}FN_2O_4S$ 481.1597; Found 481.1598.

*Ethyl {1-[(4-Methylphenyl)sulfonyl]-4-phenyl-2-[4-(trifluoromethyl)phenyl]-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ah**).* Yield: 83% (132 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 153−155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, J = 7.1 Hz, 3H), 2.29 (s, 3H), 3.58 (d, J = 16.0 Hz, 1H), 3.96−4.18 (m, 3H), 4.76 (d, J = 14.3 Hz, 1H), 5.09 (d, J = 14.3 Hz, 1H), 6.98 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.38−7.56 (m, 5H), 7.81 (d, J = 7.1 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.3, 41.5, 57.6, 60.6, 94.4, 123.9 (q, J = 270.0 Hz), 125.1 (q, J = 3.8 Hz), 126.4, 127.2, 127.9, 128.9, 129.2, 130.5 (q, J = 32.3 Hz),

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130.8, 132.3, 136.6, 143.1, 143.2, 167.4, 169.0 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{26}F_3N_2O_4S$ 531.1565; Found 531.1567.

*Ethyl {1-[(4-Methylphenyl)sulfonyl]-2-(pentafluorophenyl)-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ai**).* Yield: 71% (118 mg); Eluents: *n*-hexane/EtOAc = 4/1; yellow solid; mp: 130−132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, J = 7.1 Hz, 3H), 2.39 (s, 3H), 3.70−3.92 (m, 2H) 3.99 (q, J = 7.1 Hz, 2H), 4.81 (d, J = 13.8 Hz, 1H), 4.95 (d, J = 13.9 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.39−7.56 (m, 5H) 7.74 (d, J = 7.1 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.4, 43.4 (t, J = 6.8 Hz),, 57.8 (t, J = 3.0 Hz), 60.6, 93.2, 126.6, 127.9, 129.0, 129.4, 130.5, 132.4, 136.2, 137.8 (dm, J = 256.7 Hz), 144.1, 146.0 (dm, J = 248.4 Hz), 168.5 (t, J = 2.3 Hz), 169.2 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −138.8 (d, J = 14.1 Hz), −153.7 (dt, J = 21.2, 2.8 Hz), −162.2 (td, J = 22.6, 5.6 Hz) ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{22}F_5N_2O_4S$ 553.1220; Found 553.1218.

*Ethyl {2-(Furan-3-yl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3aj**).* Yield: 68% (92 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 132−134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, J = 7.1 Hz, 3H), 2.36 (s, 3H), 3.55 (d, J = 16.3 Hz, 1H), 3.96 (d, J = 16.3 Hz, 1H), 4.01−4.18 (m, 2H), 4.70 (d, J = 14.0 Hz, 1H), 4.96 (d, J = 14.0 Hz, 1H), 6.31 (dd, J = 3.3, 1.8 Hz, 1H), 6.49 (d, J = 3.0 Hz, 1H), 6.99 (d, J = 1.2 Hz, 1H), 7.14 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.37−7.52 (m, 3H), 7.71−7.83 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.5, 41.0, 57.0, 60.5, 90.9, 108.8, 110.3, 126.9, 127.8, 128.8, 129.3, 131.0, 131.9, 136.2, 142.6, 143.0, 151.7, 167.1, 168.6 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}N_2O_5S$ 452.1406; Found 453.1485.

*Ethyl {2-Benzyl-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3ak**).* Yield: 71% (101 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 114−116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.1 Hz, 3H), 2.37 (s, 3H), 3.13 (d, J = 17.3 Hz, 1H), 3.41−3.58 (m, 3H), 3.65 (q, J = 7.1 Hz, 2H), 4.08 (d, J = 13.7 Hz, 1H), 4.47 (d, J = 13.7 Hz, 1H), 7.12−7.30 (m, 5H), 7.31−7.45 (m, 5H), 7.58 (d, J = 7.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 21.5, 41.2, 47.1, 57.1, 60.0, 96.8, 126.7, 127.1, 127.4, 127.7, 128.6, 129.6, 131.2, 131.5, 131.6, 135.2, 137.4, 143.3, 165.5, 168.9 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{29}N_2O_4S$ 477.1848; Found 477.1850.

*Ethyl {1-[(4-Methylphenyl)sulfonyl]-2-(2-phenylethyl)-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3al**).* Yield: 69% (101 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 116−117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, J = 7.1 Hz, 3H), 2.32−2.52 (m, 5H), 2.52−2.73 (m, 2H), 3.08 (d, J = 16.8 Hz, 1H), 3.41 (d, J = 16.8 Hz, 1H), 3.79 (q, J = 7.1 Hz, 2H), 4.71 (s, 2H), 7.09−7.18 (m, 3H), 7.18−7.32 (m, 4H), 7.34−7.53 (m, 3H), 7.68−7.77 (m, 2H), 7.82 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.6, 29.4, 42.3, 42.6, 57.8, 60.2, 97.0, 125.9, 127.2, 127.7, 128.4, 128.6, 128.9, 129.8, 131.3, 131.8, 137.5, 141.4, 143.5, 165.9, 169.2 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{31}N_2O_4S$ 491.2005; Found 491.2007.

*Ethyl {2-Butyl-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3am**).* Yield: 66% (88 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 118−120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (t, J = 7.3 Hz, 3H), 0.98−1.11 (m, 5H), 1.19−1.30 (m, 2H), 2.01−2.15 (m, 1H), 2.19−2.32 (m, 1H), 2.40 (s, 3H), 3.06 (d, J = 16.6 Hz, 1H), 3.40 (d, J = 16.6 Hz, 1H), 3.83 (q, J = 7.1 Hz, 2H), 4.60 (d, J = 13.8 Hz, 1H), 4.70 (d, J = 13.8 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.32−7.49 (m, 3H), 7.65−7.78 (m, 2H), 7.79 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 14.1, 21.5, 22.5, 25.1, 40.1, 43.1, 57.5, 60.1, 97.3, 127.0, 127.5, 128.8, 129.6, 131.3, 131.6, 137.6, 143.3, 165.2, 169.4 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{31}N_2O_4S$ 443.2005; Found 443.2006.

*Ethyl {2-(2-Methylpropyl)-1-[(4-methylphenyl)sulfonyl]-4-phenyl-2,5-dihydro-1H-imidazol-2-yl}acetate (**3an**).* Yield: 84% (111 mg); Eluents: *n*-hexane/EtOAc = 4/1; yellow solid; mp: 68−70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (d, J = 6.6 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H), 1.65−1.80 (m, 1H), 2.05 (dd, J = 14.3, 7.0 Hz, 1H), 2.24 (dd, J = 14.3, 4.3 Hz, 1H), 2.40 (s, 3H), 3.04 (d, J = 16.9 Hz, 1H), 3.35 (d, J = 16.9 Hz, 1H), 3.75 (d, J = 7.1 Hz, 2H), 4.64 (s, 2H), 7.23−7.32 (m, 2H), 7.34−7.48 (m, 3H), 7.68−7.75 (m, 2H) 7.79 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.6, 24.0, 24.2, 24.5, 42.7, 49.3, 57.3, 60.1, 97.7, 127.2, 127.6, 128.8, 129.6, 131.4, 137.5, 143.3, 164.7, 169.3 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{31}N_2O_4S$ 443.2005; Found 443.2007.

*Methyl 2-{1-[(4-Methylphenyl)sulfonyl]-2,4-diphenyl-2,5-dihydro-1H-imidazol-2-yl}propanoate (**3ao**).* Yield: 84% (116 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 124−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (d, J = 7.0 Hz, 2H), 2.27 (s, 3H), 3.59 (s, 3H), 4.44 (d, J = 14.6, 1H), 4.54 (q, J = 7.0 Hz, 1H), 4.83 (d, J = 14.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 7.18−7.36 (m, 5H), 7.42−7.58 (m, 3H), 7.83−7.92 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.6, 21.5, 46.9, 51.8, 56.3, 99.5, 126.8, 127.8, 128.0, 128.5, 128.9, 129.1, 130.8, 132.2, 135.9, 137.8, 142.9, 166.5, 173.0 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{27}N_2O_4S$ 463.1691; Found 463.1690.

*Ethyl Phenyl(2-{1-[(4-methylphenyl)sulfonyl]-2,4-diphenyl-2,5-dihydro-1H-imidazol-2-yl})acetate (**3ap**).* Yield: 65% (105 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 172−174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, J = 7.1 Hz, 3H), 2.24 (s, 3H), 3.60 (d, J = 14.6 Hz, 1H), 3.90−4.05 (m, 1H), 4.09−4.28 (m, 2H), 5.68 (s, 1H), 6.76 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.2 Hz, 2H), 7.15−7.28 (m, 5H), 7.28−7.51 (m, 6H), 7.59−7.70 (m, 2H), 7.70−7.78 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.4, 56.0, 58.9, 60.7, 98.9, 126.4, 127.7(127.65), 127.7(127.74) 128.1(128.05), 128.1(128.10), 128.6, 128.7, 128.9, 130.7, 131.7, 131.9, 133.6, 136.4, 137.4, 142.6, 167.4, 169.9 ppm. HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{31}N_2O_4S$ 539.2005; Found 539.2006.

*Ethyl 3-(2-Methylphenyl)-3-([{2-[(4-methylphenyl)sulfonyl]-amino}-1-phenylethenyl]amino)prop-2-enoate (**4ad**).* Yield: 66% (94 mg); Eluents: *n*-hexane/EtOAc = 4/1; pale yellow solid; mp: 54−56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 3H), 1.94 (s, 3H), 2.44 (s, 3H), 4.21 (q, J = 7.1 Hz, 2H), 4.76 (s, 1H), 6.23 (d, J = 11.0 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.65−6.73 (m, 1H), 6.78−6.90 (m, 3H), 6.93−7.00 (m, 1H), 7.01−7.08 (m, 3H), 7.23 (d, J = 12.3 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 9.69 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 19.4, 21.7, 59.3, 90.6, 117.5, 123.2, 124.9, 125.7, 126.9, 127.3, 128.1, 128.6, 130.0, 130.1, 135.1, 135.3, 137.2, 137.8, 144.2, 162.0, 170.7 ppm. HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{27}H_{28}N_2O_4S$ 476.1770; Found 476.1770.

*Ethyl 3-(2-Pentafluorophenyl)-3-([{2-[(4-methylphenyl)sulfonyl]-amino}-1-phenylethenyl]amino)prop-2-enoate (**4ai**).* Yield: 47% (70 mg); Eluents: *n*-hexane/EtOAc = 6/1; pale yellow solid; mp: 68−70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 2.44 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.88 (s, 1H), 6.38 (s, 1H), 6.95 (t, J = 3.7 Hz, 2H), 7.10−7.18 (m, 3H), 7.34 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 9.57 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.4, 21.6, 60.2, 93.5, 111 (m), 118.3, 121.5, 125.1, 126.8, 127.9, 128.6, 130.1, 136.5, 136.9, 137.2 (dm, J = 241.6 Hz), 143.6 (dm, J = 249.2 Hz), 144.4, 146.6, 169.6 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −139.0 (dm, J = 22.6 Hz), −151.9 (t, J = 21.2 Hz), −161.6 (tm, J = 21.2 Hz) ppm. HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{21}F_5N_2O_4S$ 552.1142; Found 552.1140.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystal data of **3aa** and **3ao**, details for DFT calculations of **3aa** imine and enamine forms, and copies of ^{1}H and ^{13}C NMR spectra for all 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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