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Hydroarylation of acetylenes, acrylates, and isocyanates with heteroaromatic compounds under rhenium catalysis

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ABSTRACT

With the aid of a directing group, an imine moiety, heteroaromatic compounds add to acetylenes in the presence of a catalytic amount of $[ReBr(CO)_3(THF)]_2$ at the adjacent position of the directing group regioselectively to give hydroarylation of the acetylenes in good to excellent yields. Similarly, heteroaromatic compounds react with acrylates and isocyanates to give the corresponding hydroarylation products under rhenium catalysis.

1. Introduction

Heteroaromatic compounds are important because many functional materials and bioactive compounds contain heteroaromatic skeletons as core structures.[1] Various methods for functionalization of heteroaromatic compounds have been developed, with electrophilic, nucleophilic, and radical attack of substrates to heteroaromatic compounds being well known examples.[2] In addition, transition metal-catalyzed hydroarylation has a great potential to obtain functionalized heteroaromatic compounds efficiently and thus several trials have been investigated.[3] For example, palladium-catalyzed arylation of acrylates with furans[4] and cationic zirconium-catalyzed arylation of propene using α-picoline have been reported.[5] Recently, by using a directing group on heteroaromatic rings, the functionalization can be achieved in high yields and selectivities under ruthenium or rhodium catalysis: hydroarylation of olefins,[6] acetylenes,[7] and isocyanates[8] with heteroaromatic compounds. We have also reported on rhenium-catalyzed hydroarylation of isocyanates by reactions with heteroaromatic compounds.[9] Intramolecular arylation of an olefin moiety with heteroaromatic compounds has also been reported.[10] Since the direct hydroarylation of unsaturated molecules is atom economic and the starting materials are available easily, this method is an efficient and powerful tool to functionalize heteroaromatic compounds. We report herein the hydroarylation of acetylenes, acrylates, and isocyanates by treatment with heteroaromatic compounds using a rhenium complex as a catalyst.[11]

2. Results and discussion

2.1. Hydroarylation of acetylenes

Treatment of a furan derivative bearing an imino group at the 3-position, **1a**, with diphenyl acetylene (**2a**) gave an alkenylated furan. During column chromatography, hydrolysis resulted in the formation of the corresponding furyl aldehyde **4a** in 89% yield (Table 1, entry 1).[12–14] The reaction did not proceed in the presence of catalysts such as $Re_2(CO)_{10}$, $MnBr(CO)_5$, $Mn_2(CO)_{10}$, $RhCl(PPh_3)_3$, $Ir_4(CO)_{12}$, $SnCl_4$, and $ZnCl_2$. Only a trace amount of **4a** was formed with a catalytic amount of $Ru_3(CO)_{12}$ and $RuH_2(CO)(PPh_3)_3$. Acetylenes possessing alkyl groups, **2b** and **2c**, also provided the corresponding alkenyl furans **4b** and **4c** in good yields and selectivities (Table 1, entries 2 and 3). The mixture of alkenyl furans **4d** and **3a** was produced by the reaction of imino furan **1a** with acetylene having an ester group, **2d** (Table 1, entry 4). Although the yield of **3a** was low, the alkenylation reaction occurred not only at the 2-position but also at the 4-position of the furan ring.[15,16] Terminal acetylenes such as ethynylbenzene and 1-dodecyne did not react with **1a** under the same conditions.

The hydroarylation reaction also proceeded with an imino indole. For example, treatment of 3-imino indole **5a** with acetylene **2a** in the presence of a catalytic amount of $[ReBr(CO)_3(THF)]_2$ gave 2-alkenylated indole **6a** in 72% yield regioselectively. In the case of 2-imino indole **5b**, the reaction proceeded to give 3-alkenylated product **6b** in 26% yield (Scheme 1).

The proposed mechanism is described as follows (Scheme 2):[17] (1) oxidative addition of a C–H bond of an aldimine to a rhenium center (C–H bond activation); (2) insertion of an acetylene into a rhenium–carbon bond;[18] (3) reductive elimination, which regenerates the rhenium catalyst.

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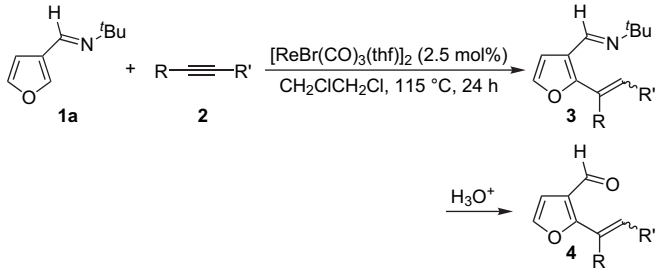
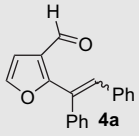
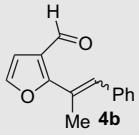
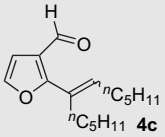
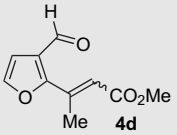
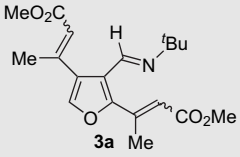
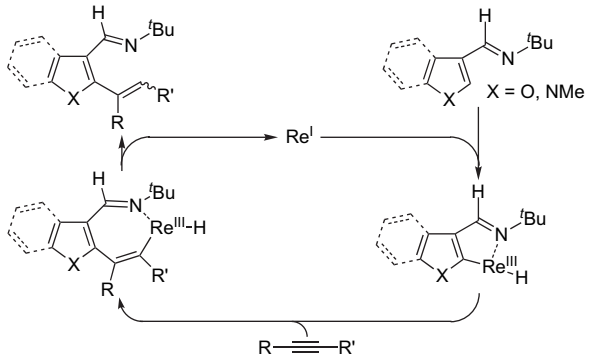
Table 1
Reactions between aldimine **1a** and acetylenes **2**[a]



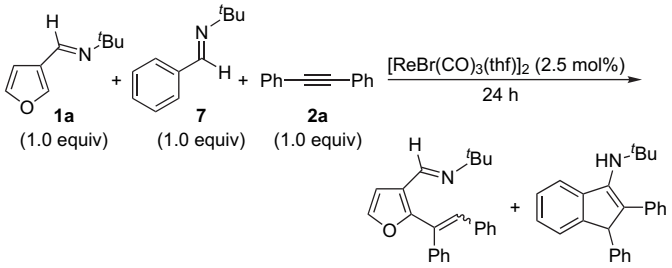
Entry	Acetylene	Product	Yield/%[b]
1[c]	Ph—≡—Ph **2a**	 **4a**	89 [89:11]
2	Ph—≡—Me **2b**	 **4b**	73 [>99:<1]
3	$^{n}C_5H_{11}$—≡—$^{n}C_5H_{11}$ **2c**	 **4c**	80 [95:5]
4	Me—≡—CO_2Me **2d**	 **4d**	66 [>99:<1]
		 **3a**	9 [>99:<1]

[a] Compounds **1a** (1.0 equiv) and **2** (1.0 equiv).
[b] The ratios of *E* and *Z* isomers are given in square brackets. However, the stereochemistry could not be determined.
[c] Temperature: 100 °C.

To compare the reactivities of heteroaromatic and aromatic compounds, the reaction of imino furan **1a** and aromatic imino benzene **7** with **2a** was conducted in 1,2-dichloroethane or toluene (Scheme 3). As a result, alkenyl furan **3a** was obtained selectively under both reaction conditions.



Scheme 2.



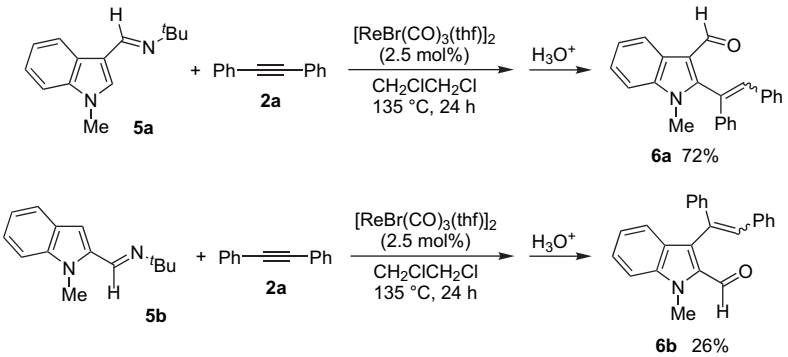
Solvent	Temp	**3a**	**8**
CH_2ClCH_2Cl	100 °C	78%	0%
toluene	115 °C	74%	4%

Scheme 3.

The reaction between furan having an imino group at the 2-position, **1b**, and acetylene **2a** did not proceed at all. 3-Imino furan with a substituent at the 2-position, **1c**, and with substituents at the 2- and 5-position, **1d**, did not give the alkenylated products **3g** and **3h**. (Scheme 4).

From the results of these experiments, the order of reactivities for hydroarylation is as follows: the 3-position of the furyl group ≪phenyl group<the 2-position of the furyl group (Fig. 1).

When the 2-position was blocked with a methyl group, the 4-position of an imino thiophene could be functionalized.[17] For example, the hydroarylation of **2a** with thiophene **9a** at the 4-position was accomplished in the presence of a catalytic amount of $[ReBr(CO)_3(THF)]_2$ (Scheme 5). Other thiophenes, such as 2-imino, 3-imino, and 2-methyl-3-imino thiophenes or imino pyrroles, gave complex mixtures.



Scheme 1.

2.2. Hydroarylation of acrylates

Ethyl acrylate (**11a**) also reacted with a heteroaromatic aldimine **9c** by a catalytic amount of $[ReBr(CO)_3(THF)]_2$ to give the corresponding adduct. After hydrolysis, **12a** was obtained in 15% yield (Scheme 6). In this case, the yield was improved with an $Re_2(CO)_{10}$ catalyst. In contrast to the reaction with **9c**, reactions with imino furans **1a** and **1d** or imino indoles **5a** and **5b** provided complex mixtures.

Treatment of 2-imino thiophene **9d** with **11a** in the presence of a catalytic amount of $Re_2(CO)_{10}$ gave the expected adduct **12b** in 25% yield (Table 2, entry 1). In the case of substituted imino thiophene **9b**, which was protected by methyl groups at both 2- and 6-position, the reaction proceeded almost quantitatively to give **12c** and **13** in 48% and 50% yields, respectively (Table 2, entry 2). The formation of **13** indicates that the intramolecular nucleophilic attack occurred prior to the reductive elimination leading to β-lactum. Imino pyrrole **14** reacted with **12a** but resulted in a low yield (Table 2, entry 3).

Other α,β-unsaturated carbonyl compounds, such as vinyl ketone **11b**, reacted with **9c** to give the corresponding alkylated products **12e** (Scheme 7). However, acrylamide and styrene gave complex mixtures.

2.3. Hydroarylation of isocyanates

Compared with the functionalization of heteroaromatic compounds with non-polar unsaturated molecules, such as olefins and acetylenes, the use of polar unsaturated molecules is still rare. We have recently succeeded in the insertion of polar unsaturated molecules using a rhenium catalyst.[11b,d] By using the rhenium catalyst, $[ReBr(CO)_3(THF)]_2$, hydroarylation of isocyanates with heteroaromatic compounds also occurred.

Treatment of a thiophene bearing an aldimine moiety, **9c**, with phenyl isocyanate (**15a**) in the presence of a catalytic amount of $[ReBr(CO)_3(THF)]_2$ in 1,2-dichloroethane at 90 °C for 24 h promoted the hydroarylation of **15a** selectively at the 2-position of the thiophene ring. After hydrolysis, amide thiophene **16a** was obtained in 92% yield (Table 3, entry 1).[10,11] The 3-position of thiophene ring could also be functionalized using 2-imino thiophene **9d** and the corresponding amidated product **16b** was formed in 77% yield (Table 3, entry 2). When 2-methyl-substituted thiophene **9a** or 2,5-dimethyl-substituted thiophene **9b** was employed, hydroarylation occurred at the 4-position selectively (Table 3, entries 3 and 4). During column chromatography, intramolecular cyclization occurred to give the cyclic product **17a** in 57% yield (Table 3, entry 4). The reactions of 3-imino furan **1a** and 2-imino furan **1b** with isocyanate **15a** gave furan-2-carboxamide **18a** and furan-3-carboxamide **18b** in 63% and 36% yields, respectively (Table 3, entries 5 and 6). When the 2-position was blocked with a methyl group, the reaction proceeded at the 4-position (Table 3, entry 7). Imino pyrrole **14** and indoles **5a** and **5b** afforded the corresponding carboxamides **19**, **20a**, and **20b** in high yields (Table 3, entries 8–10).

Aryl isocyanates with an electron-withdrawing or electron-donating group, **15b** and **15c**, provided thiophene-2-carboxamides **16d** and **16e** in 72% and 81% yields, respectively (Table 4, entries 1 and 2). On the other hand, the yield of amide decreased when using an isocyanate bearing a substituent at the *ortho*-position (Table 4, entry 3). Thiophene-2-carboxamides **16g** and **16h** were also produced with primary and secondary alkyl isocyanates **15e** and **15f** (Table 4, entries 4 and 5). In entry 4, cyclic compound **17b** was also formed in 19% yield. Although hydroarylation of alkyl isocyanates by treatment with aromatic imines did not proceed,[11b] hydroarylation of alkyl isocyanates with heteroaromatic compounds occurred.

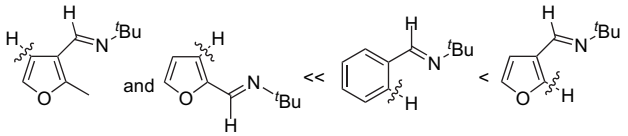
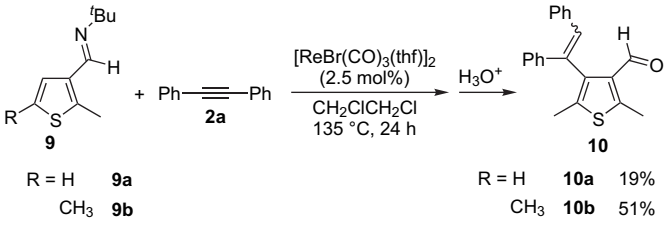
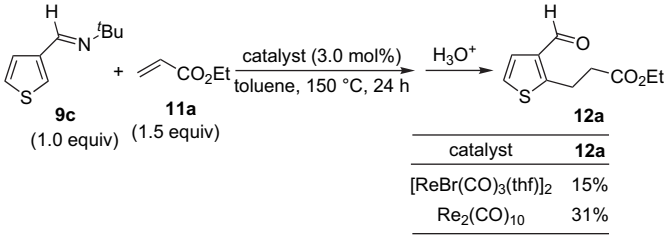


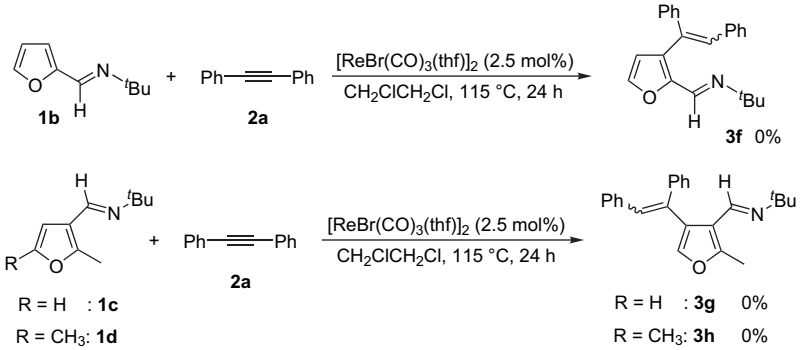
Figure 1. Order of the reactivities between furyl and phenyl groups.



Scheme 5.

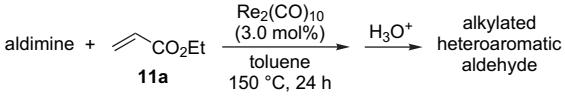


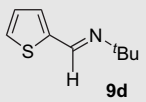
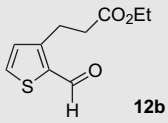
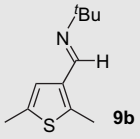
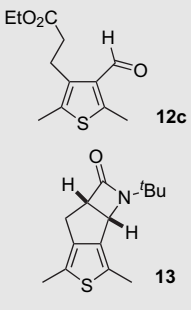
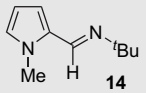
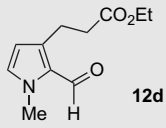
Scheme 6.



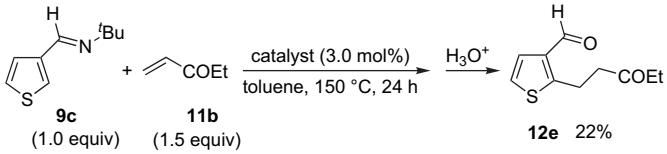
Scheme 4.

Table 2
Reactions between heteroaromatic aldimines and ethyl acrylate **12a**[a]



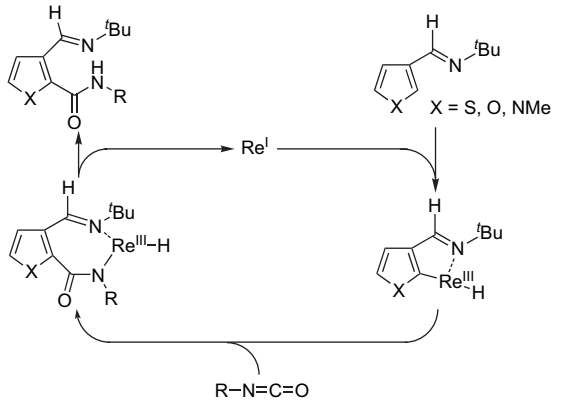
Entry	Aldimine	Product	Yield/%
1	 **9d**	 **12b**	25
2	 **9b**	 **12c** / **13**	48 / 50
3	 **14**	 **12d**	12

[a] Compound **12a** (1.5 equiv).



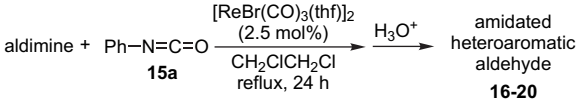
Scheme 7.

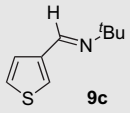
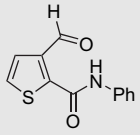
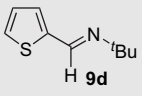
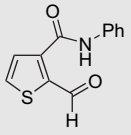
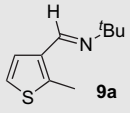
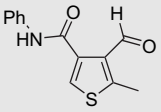
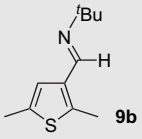
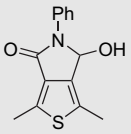
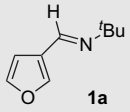
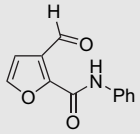
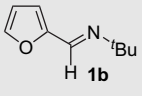
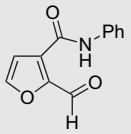
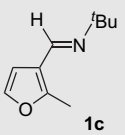
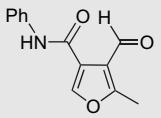
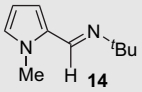
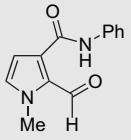
The proposed mechanism for the generation of amidated heteroaromatic aldimines is described as follows (Scheme 8):[17] (1) oxidative addition of a C–H bond of an aldimine to a rhenium center (C–H bond activation); (2) insertion of an isocyanate into a rhenium–carbon bond;[18] (3) reductive elimination. As a result, an



Scheme 8.

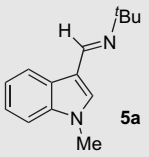
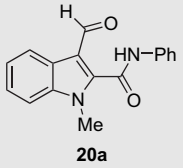
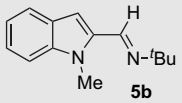
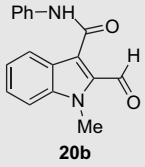
Table 3
Reactions between heteroaromatic aldimines and phenyl isocyanate **15a**[a]



Entry	Aldimine	Product	Yield/%
1	 **9c**	 **16a**	92
2	 **9d**	 **16b**	77
3	 **9a**	 **16c**	38
4	 **9b**	 **17a**	57
5[b]	 **1a**	 **18a**	63
6	 **1b**	 **18b**	36
7	 **1c**	 **18c**	38
8	 **14**	 **19**	80

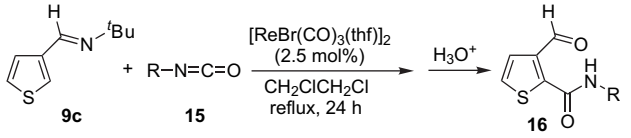
(*continued on next page*)

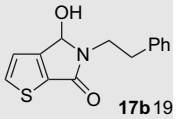
Table 3 (*continued*)

Entry	Aldimine	Product	Yield/%
9[b]	 **5a**	 **20a**	92
10[b]	 **5b**	 **20b**	72

[a] Compound **15a** (1.0 equiv).
[b] Temperature: 135 °C.

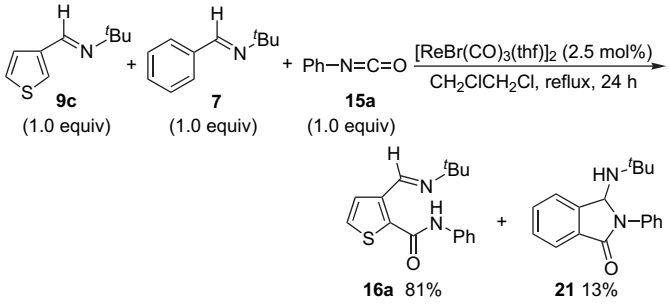
Table 4
Reaction of thiophenyl aldimine **9b** with several isocyanates **16**[a]



Entry	R		Yield/%	
1	$(p\text{-}CF_3)C_6H_4$ (**15b**)	**16d**	72	
2	$(p\text{-}MeO)C_6H_4$ (**15c**)	**16e**	81	
3	$(o\text{-}MeO)C_6H_4$ (**15d**)	**16f**	61	
4	$PhCH_2CH_2$ (**15e**)	**16g**	64	 **17b** 19
5[b]	 **(15f)**	**16h**	70	

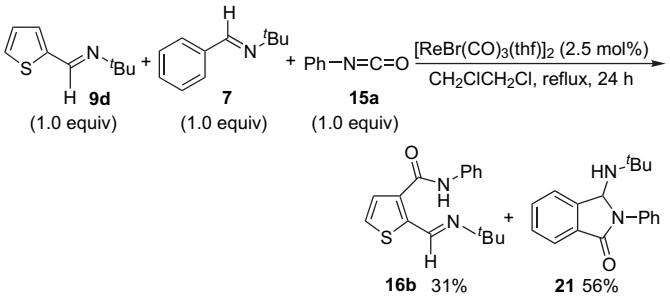
[a] Compounds **9b** (1.0 equiv) and **15** (1.0 equiv).
[b] Temperature: 135 °C.

amide derivative is formed and the rhenium catalyst is regenerated.



Scheme 9.

To compare the reactivities of heteroaromatic and aromatic compounds, the following reactions were conducted (Schemes 9 and 10). Treatment of thiophenyl aldimine **9c** and aromatic



Scheme 10.

aldimine **7** with phenyl isocyanate **15a** in the presence of a catalytic amount of $[ReBr(CO)_3(THF)]_2$ promoted hydroarylation of **15a**, and the corresponding thiophene derivative **16a** and phthalimidine derivative **21** were formed in 81% and 13% yields, respectively (Scheme 9). On the other hand, thiophenyl aldimine **9d** showed low reactivity compared with aromatic aldimine **7** (Scheme 10). The difference in the reactivities between **9c**, **9d**, and **7** must reflect the electron density at the 2-positions of the thiophene or the phenyl ring. From the results of these experiments, the order of reactivities of C–H bonds is as follows: the 3-position of thiophenyl group<phenyl group<the 2-position of thiophenyl group (Fig. 2).

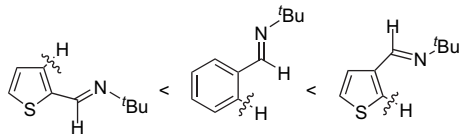


Figure 2. Order of the reactivities between thiophenyl and phenyl groups.

3. Conclusion

We have succeeded in hydroarylation of acetylenes, acrylates, and isocyanates with heteroaromatic compounds regioselectively using a rhenium complex, $[ReBr(CO)_3(THF)]_2$, as a catalyst. In these reactions, both 2- and 3-position of heteroaromatic compounds could be functionalized selectively. In addition, hydroarylation of an acetylene, acrylate, and isocyanate proceeded even at the 4-position of heteroaromatic compounds where it is usually difficult to be functionalized. We hope that these reactions can become powerful tools to functionalize heteroaromatic compounds and contribute to the development of transformations via hydroarylation of heteroaromatic compounds.

4. Experimental

4.1. General

All reactions were carried out in a dry and degassed solvent under an argon atmosphere. 1,2-Dichloroethane and toluene were purchased from Wako Pure Chemical Industries and dried and degassed before use. $[ReBr(CO)_3(THF)]_2$ was prepared by heating a THF solution of $ReBr(CO)_5$ at reflux temperature for 16 h and was recrystalized from THF/hexane. Imines were prepared by condensation of the corresponding aldehydes with the corresponding amines in the presence of molecular sieves (4 Å) in hexane at 50 °C for 10 h, and were used after distillation. Aldehydes, acetylenes, acrylates, and isocyanates were purchased from Wako Pure

Chemical Industries, Tokyo Kasei Kogyo Co., and Aldrich Co., and used as-received. Silica gel (60N, spherical neutral) was purchased from Kanto Chemical Co.

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm. IR spectra were recorded on Nicolet Protégé 460.

4.2. General procedure for the reaction of heteroaromatic aldimines with acetylenes

A mixture of a heteroaromatic aldimine (0.25 mmol), an acetylene (0.25 mmol), and $[ReBr(CO)_3(THF)]_2$ (5.3 mg, 6.3 μmol) in 1,2-dichloroethane (0.50 mL) was heated for 24 h in sealed test tube. The products were isolated by silica gel column chromatography (AcOEt/hexane=100:1).

4.3. General procedure for the reaction of heteroaromatic aldimines with acrylates

A mixture of a heteroaromatic aldimine (0.25 mmol), ethyl acrylate (0.25 mmol), and $Re_2(CO)_{10}$ (4.9 mg, 7.5 μmol) in toluene (0.50 mL) was heated for 24 h in sealed test tube. The products were isolated by silica gel column chromatography (AcOEt/hexane=20:1).

4.4. General procedure for the reaction of heteroaromatic aldimines with isocyanates

A mixture of a heteroaromatic aldimine (0.25 mmol), an isocyanate (0.25 mmol), and $[ReBr(CO)_3(THF)]_2$ (5.3 mg, 6.3 μmol) in 1,2-dichloroethane (0.50 mL) was heated for 24 h in sealed test tube. The products were isolated by silica gel column chromatography (AcOEt/hexane=10:1).

*4.4.1. 3-[3-(tert-Butylimino methyl)-4-(2-methoxycarbonyl-1-methylvinyl)-furan-2-yl] but-2-enoic acid methyl ester (**3a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.42 (s, 3H), 2.49 (d, J=0.9 Hz, 3H), 3.37 (s, 3H), 3.74 (s, 3H), 6.00 (s, 1H), 6.39 (s, 1H), 7.50 (s, 1H), 8.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 19.3, 29.2, 51.1, 51,3, 58.5, 117.8, 122.1, 130.2, 141.2, 143.4, 147.5, 149.0, 166.9; IR (Nujol, ν/cm^{-1}) 1724, 1624, 1463, 1377, 1173, 1037, 877, 722; HRMS (ESI) calcd for $C_{19}H_{25}NO_5Na$ ($[M+Na]^+$): 370.1631, found: 370.1599.

*4.4.2. 2-(1,2-Diphenylvinyl) furan-3-carbaldehyde (**4a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J=1.8 Hz, 1H), 7.07–7.05 (m, 2H), 7.15–7.18 (m, 2H), 7.32–7.36 (m, 3H), 7.39–7.43 (m, 4H), 8.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.7, 124.6, 124.6, 128.1, 128.2, 128.9, 129.6, 129.8, 129.9, 130.0, 130.3, 132.8, 135.3, 137.0, 142.3, 186.2; IR (Nujol, ν/cm^{-1}) 1660, 1595, 1558, 1457, 1418, 1390, 1262, 1169, 1122, 1079, 1027, 922, 879, 760, 717, 697. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.42. Found: C, 83.26; H, 5.42.

*4.4.3. 2-(1-Methyl-2-phenylvinyl) furan-3-carbaldehyde (**4b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (d, J=1.2 Hz, 3H), 6.85 (d, J=2.1 Hz, 1H), 7.07 (d, J=1.2 Hz, 1H), 7.03–7.36 (m, 1H), 7.38–7.42 (s, 5H), 10.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 109.2, 123.4, 126.1, 127.9, 128.4, 129.4, 134.7, 136.0, 141.9, 164.7, 185.58; IR (Nujol, ν/cm^{-1}) 1733, 1675, 1568, 1455, 1378, 1140, 889, 751, 701; HRMS (ESI) calcd for $C_{14}H_{12}O_2Na$ ($[M+Na]^+$): 235.0735, found: 235.0794.

*4.4.4. 2-(6-Dodec-6-enyl) furan-3-carbaldehyde (**4c**)*

The isomers could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.9 Hz), 0.91 (t, J=6.9 Hz), 1.21–1.45 (m), 1.47–1.62 (m), 2.03 (q, J=7.5 Hz), 2.27 (q, J=7.5 Hz), 2.39 (t, J=7.5 Hz), 2.49 (t, J=7.6 Hz), 5.86 (t, J=7.5 Hz), 5.92 (t, J=7.5 Hz), 6.75–6.77 (m), 7.32 (d, J=2.1 Hz), 7.41 (s), 9.74 (s), 9.87 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.4, 22.5, 28.1, 28.6, 29.1, 29.2, 29.6, 31.2, 31.2, 31.6, 36.9, 107.3, 108.3, 123.2, 128.8, 129.8, 136.8, 138.6, 141.5, 142.9, 166.4, 185.91; IR (Nujol, ν/cm^{-1}) 1682, 1635, 1570, 1457, 1417, 1270, 1125, 756, 711; HRMS (ESI) calcd for $C_{17}H_{26}O_2Na$ ($[M+Na]^+$): 285.1830, found: 285.1872.

*4.4.5. 3-(3-Formylfuran-2-yl) but-2-enoic acid methyl ester (**4d**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (d, J=1.2 Hz, 3H), 3.79 (s, 3H), 6.39 (d, J=1.2 Hz, 1H), 6.88 (d, J=1.7 Hz, 1H), 7.45 (d, J=1.7 Hz, 1H), 10.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 51.6, 110.2, 121.3, 125.6, 142.1, 143.4, 160.4, 166.2, 184.9; IR (Nujol, ν/cm^{-1}) 1709, 1659, 1619, 1556, 1457, 1415, 1376, 1261, 1179, 888, 789, 727; HRMS (ESI) calcd for $C_{10}H_{10}O_4Na$ ($[M+Na]^+$): 217.0477, found: 217.0524.

*4.4.6. 2-(1,2-Diphenylvinyl)-1-methyl-1H-indole-3-carbaldehyde (**6a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (s, 3H), 6.93–6.96 (m, 2H), 7.12–7.17 (m, 3H), 7.31–7.36 (m, 5H), 7.37–7.39 (m, 3H), 7.54 (s, 1H), 8.38–8.41 (m 1H), 9.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 109.0, 114.9, 122.2, 122.5, 123.2, 123.8, 125.3, 126.3, 128.3, 128.5, 128.8, 128.9, 129.7, 135.2, 135.4, 137.6, 140.4, 149.1, 185.9; IR (Nujol, ν/cm^{-1}) 1649, 1658, 1464, 1382, 759, 692; HRMS (ESI) calcd for $C_{24}H_{19}NONa$ ($[M+Na]^+$): 360.1364, found: 360.1437.

*4.4.7. 3-(1,2-Diphenyl-vinyl)-1-methyl-1H-indole-2-carbaldehyde (**6b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (s, 3H), 6.93–6.96 (m, 2H), 7.12–7.17 (m, 3H), 7.31–7.36 (m, 5H), 7.37–7.39 (m, 3H), 7.54 (s, 1H), 8.38–8.41 (m 1H), 9.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 109.0, 114.9, 122.2, 122.5, 123.2, 123.8, 125.3, 126.3, 128.3, 128.5, 128.8, 128.9, 129.7, 135.2, 135.4, 137.6, 140.4, 149.1, 185.9; IR (Nujol, ν/cm^{-1}) 1663, 1466, 1384, 1345, 748, 696; HRMS (ESI) calcd for $C_{24}H_{19}NONa$ ($[M+Na]^+$): 360.1364, found: 360.1437.

*4.4.8. N-tert-Butyl-2,3-diphenyl-3H-inden-1-amine (**8**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (s, 9H), 4.87 (s, 1H), 7.04 (d, J=7.6 Hz, 2H), 7.09–7.17 (m, 6H), 7.22 (t, J=7.7 Hz, 2H), 7.28–7.31 (m, 1H), 7.34 (d, J=8.4 Hz, 2H), 7.48 (d, J=6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.0, 54.9, 56.7, 119.9, 123.8, 125.4, 126.4, 126.5, 128.1, 128.2, 128.3, 128.5, 128.9, 136.7, 137.0, 140.4, 143.2, 144.3, 147.4; IR (Nujol, ν/cm^{-1}) 3061, 3022, 1951, 1653, 1601, 1493, 1430, 1389, 1378, 1284, 1218, 1199, 1121, 1095, 1071, 1026, 938, 918, 815, 783, 759, 736, 696, 675, 666, 651, 621. Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.57; H, 7.41; N, 4.03.

*4.4.9. 4-(1,2-Diphenylvinyl)-2-methylthiophene-3-carbaldehyde (**10a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 6.74 (s, 1H), 6.93 (s, 1H), 7.10–7.11 (m, 2H), 7.15–7.20 (m, 5H), 7.22–726 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 120.9, 127.2, 127.8, 128.0, 128.6, 129.4, 129.7, 131.2, 133.6, 136.2, 136.5, 139.8, 151.5, 187.2; IR (Nujol, ν/cm^{-1}) 1674, 1598, 1506, 1458, 1376, 704; HRMS (ESI) calcd for $C_{20}H_{16}NOSNa$ ($[M+Na]^+$): 327.0802, found: 327.0861.

*4.4.10. 4-(1,2-Diphenylvinyl)-2,5-dimethylthiophene-3-carbaldehyde (**10b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.70 (s, 3H), 6.61(s, 1H), 7.12–7.21 (m, 10H), 9.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 15.5, 127.2, 127.6, 128.1, 128.4, 129.3, 129.5, 132.7, 132.8, 134.4, 135.1, 136.6, 139.4, 142.2, 148.2, 187.5; IR (Nujol, ν/cm^{-1}) 1678.92, 1463.11,

1416.03, 1376.92, 742.05, 705.57, 649.55; HRMS (ESI) calcd for $C_{21}H_{18}OSNa$ ([M+Na]$^+$): 341.0976, found: 341.0934.

*4.4.11. 3-(3-Formylthiophen-2-yl) propionic acid ethyl ester (**12a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J=7.2 Hz, 3H), 2.74 (t, J=7.2 Hz, 2H), 3.51 (t, J=7.2 Hz, 2H), 4.14 (q, J=7.2 Hz, 2H), 7.13 (d, J=5.4 Hz, 1H), 7.39 (d, J=5.4 Hz, 1H), 10.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.4, 35.8, 60.8, 123.4, 128.0, 137.0, 171.7, 184.6, 185.6; IR (Nujol, ν/cm^{-1}) 2980, 1732, 1681, 1520, 1446, 1374, 1234, 1181, 1043, 725; HRMS (ESI) calcd for $C_{10}H_{12}O_3SNa$ ([M+Na]$^+$): 235.0405, found: 235.0429.

*4.4.12. 3-(2-Formyl-thiophen-3-yl) propionic acid ethyl ester (**12b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J=7.2 Hz, 3H), 2.75 (t, J=7.5 Hz, 2H), 3.30 (t, J=7.5 Hz, 2H), 4.12 (q, J=7.2 Hz, 2H), 7.05 (d, J=4.5 Hz, 1H), 7.66 (d, J=4.5 Hz, 1H), 10.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 23.6, 35.1, 60.7, 130.5, 134.6, 138.1, 149.5, 172.0, 182.2; IR (Nujol, ν/cm^{-1}) 1731, 1660, 1427, 1393, 1373, 1241, 1190, 1096, 1041, 752; HRMS (ESI) calcd for $C_{10}H_{12}O_3SNa$ ([M+Na]$^+$): 235.0405, found: 235.0385.

*4.4.13. 3-(4-Formyl-2,5-dimethylthiophen-3-yl) propionic acid ethyl ester (**12c**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J=7.2 Hz, 3H), 2.31 (s, 3H), 2.51 (t, J=7.7 Hz, 2H), 2.69 (s, 3H), 3.06 (t, J=7.7 Hz, 2H), 4.09 (q, J=7.2 Hz, 2H), 10.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.3, 13.6, 22.3, 34.5, 60.3, 131.2, 134.5, 135.9, 151.4, 173.1, 185.2; IR (Nujol, ν/cm^{-1}) 1734, 1675, 1558, 1457, 1375, 1297, 125, 1172, 1101, 1037; HRMS (ESI) calcd for $C_{12}H_{16}O_3SNa$ ([M+Na]$^+$): 263.0718, found: 263.0682.

*4.4.14. 3-(2-Formyl-1-methyl-1H-pyrrol-3-yl) propionic acid ethyl ester (**12d**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J=7.1 Hz, 3H), 2.62 (t, J=7.8 Hz, 2H), 3.08 (t, J=7.8 Hz, 2H), 3.90 (s, 3H), 4.13 (q, J=7.1 Hz, 2H), 6.03 (d, J=2.4 Hz, 1H), 6.75 (d, J=2.4 Hz, 1H), 9.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 20.9, 35.8, 36.9, 60.5, 109.2, 127.7, 131.1, 137.3, 172.6, 178.2; IR (Nujol, ν/cm^{-1}) 1734, 1657, 1507, 1461, 1376, 1184; HRMS (ESI) calcd for $C_{11}H_{15}NO_3Na$ ([M+Na]$^+$): 232.0950; found: 232.0908.

*4.4.15. 3-(3-Oxo-pentyl) thiophene-2-carbaldehyde (**12e**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J=7.3 Hz, 3H), 2.44 (q, J=7.3 Hz, 2H), 2.85 (t, J=7.4 Hz, 2H), 3.46 (t, J=7.4 Hz, 2H), 7.11 (d, J=5.3 Hz, 1H), 7.38 (d, J=5.3 Hz, 1H), 10.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.7, 22.1, 36.0, 43.4, 123.2, 128.0, 136.7, 155.3, 184.7, 209.1; IR (Nujol, ν/cm^{-1}) 1714, 1676, 1519, 1457, 1411, 1387, 1234, 1114, 730; HRMS (ESI) calcd for $C_{10}H_{12}O_2SNa$ ([M+Na]$^+$): 219.0546, found: 219.0444.

*4.4.16. 2-tert-Butyl-3,5-dimethyl-2,2a,6,6a-tetrahydro-4-thia-2-azacyclobuta[a]pentalen-1-one (**13**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.21 (s, 3H), 2.40 (s, 3H), 2.53 (ddd, J=1.2, 10.2, 16.8 Hz, 1H), 2.92 (dd, J=1.2, 16.8 Hz, 1H), 4.05 (ddd, J=2.4, 4.2, 10.2 Hz, 1H), 4.57 (d, J=4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 14.7, 24.5, 28.3, 53.3, 53.7, 58.7, 126.9, 129.7, 140.3, 145.1, 169.9; IR (Nujol, ν/cm^{-1}) 1716, 1458, 1376, 1294, 1260, 1229, 1192, 1129, 1084, 1013, 843, 729; HRMS (ESI) calcd for $C_{14}H_{19}NOSNa$ ([M+Na]$^+$): 272.1085, found: 272.1082.

*4.4.17. 3-Formylthiophene-2-carboxylic acid phenylamide (**16a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J=7.5 Hz, 1H), 7.37 (t, J=7.5 Hz, 2H), 7.58 (s, 2H), 7.79 (d, J=7.5 Hz, 2H), 9.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.4, 124.6, 129.0, 130.1, 134.4, 135.2, 137.9, 149.3, 157.8, 187.4; IR (Nujol, ν/cm^{-1}) 1671, 1646, 1624, 1559, 1540, 1404, 1322, 1273, 1245, 1189, 1120, 1013, 691. Anal. Calcd for $C_{12}H_9N_2S$: C, 62.32; H, 3.92; N, 6.06. Found: C, 62.04; H, 4.03; N, 6.09.

*4.4.18. 2-Formylthiophene-3-carboxylic acid phenylamide (**16b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J=7.5 Hz, 1H), 7.39 (t, J=7.8 Hz, 2H), 7.78 (d, J=7.8 Hz, 2H), 7.85 (d, J=4.8 Hz, 1H), 7.94 (d, J=4.8 Hz, 1H), 9.99 (s, 1H), 10.87 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.3, 120.4, 124.7, 129.1, 134.2, 135.0, 137.9, 142.1, 174.8, 183.8; IR (Nujol, ν/cm^{-1}) 3328, 3097, 1659, 1598, 1539, 1514, 1443, 1419, 1316, 1260, 1205, 906, 772; HRMS (ESI) calcd for $C_{12}H_9NO_2SNa$ ([M+Na]$^+$): 254.0252, found: 254.0203.

*4.4.19. 4-Formyl-5-methylthiophene-3-carboxylic acid phenylamide (**16c**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (s, 3H), 7.13 (t, J=7.8 Hz, 1H), 7.37 (t, J=7.8 Hz, 2H), 7.79 (d, J=7.8 Hz, 2H), 8.21 (s, 1H), 11.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 120.4, 124.2, 128.9, 131.8, 132.0, 137.8, 138.5, 159.2, 160.1, 186.6; IR (Nujol, ν/cm^{-1}) 1653, 1559, 1456, 1377, 1193, 763; HRMS (ESI) calcd for $C_{13}H_{11}NO_2SNa$ ([M+Na]$^+$): 268.0408, found: 268.0379.

*4.4.20. 3-Formylthiophene-2-carboxylic acid (4-trifluoro-methylphenyl) amide (**16d**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.67 (m, 4H), 7.92 (d, J=8.4 Hz, 2H), 9.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.1, 126.2, 126.3, 126.3, 130.8, 134.8, 135.2, 141.0, 148.6, 158.1, 187.7; IR (Nujol, ν/cm^{-1}) 1675, 1619, 1602, 1554, 1504, 1430, 1412, 1319, 1254, 1158, 1122, 1106, 1073, 1008, 846. Anal. Calcd for $C_{13}H_8F_3NS$: C, 52.17; H, 2.69; N, 4.68. Found: C, 52.00; H, 2.95; N, 4.57.

*4.4.21. 3-Formylthiophene-2-carboxylic acid (4-methoxyphenyl) amide (**16e**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.91 (d, J=9.0 Hz, 2H), 7.58–7.61 (m, 2H), 7.73 (d, J=9.0 Hz, 2H), 9.95 (s, 1H), 11.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 114.1, 121.8, 129.8, 131.0, 134.4, 135.0, 149.6, 156.5, 157.4, 187.4; IR (Nujol, ν/cm^{-1}) 1875, 1674, 1644, 1565, 1504, 1402, 1278, 1241, 1193, 1170, 1124, 1111, 1029, 857, 828, 800, 714; HRMS (ESI) calcd for $C_{13}H_{11}NO_3SNa$ ([M+Na]$^+$): 284.0357, found: 284.0303.

*4.4.22. 3-Formylthiophene-2-carboxylic acid (2-methoxyphenyl) amide (**16f**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 6.94 (d, J=8.1 Hz, 1H), 7.00 (t, J=7.8 Hz, 1H), 7.12 (t, J=7.8 Hz, 1H), 7.55 (d, J=5.4 Hz, 1H), 7.59 (d, J=5.4 Hz, 1H), 8.47 (d, J=8.1 Hz, 1H), 10.06 (s, 1H), 11.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 110.4, 120.9, 121.4, 124.8, 127.3, 129.6, 133.1, 136.5, 148.2, 149.3, 158.1, 186.5; IR (Nujol, ν/cm^{-1}) 3120, 3086, 2769, 1683, 1633, 1603, 1542, 1508, 1427, 1402, 1332, 1266, 1224, 1193, 1179, 1164, 1129, 1030, 931, 822, 802, 771, 746; HRMS (ESI) calcd for $C_{13}H_{11}NO_3SNa$ ([M+Na]$^+$): 284.0357, found: 284.0331.

*4.4.23. 3-Formylthiophene-2-carboxylic acid phenethylamide (**16g**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (t, J=7.5 Hz, 2H), 3.69–3.74 (m, 2H), 7.21–7.34 (m, 5H), 7.51 (d, J=5.1 Hz, 1H), 7.54 (d, J=5.1 Hz, 1H), 9.69 (br, 1H), 9.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.4, 41.4, 126.4, 128.5, 128.7, 129.3, 133.6, 135.8, 138.8, 148.0, 160.0, 186.8; IR (Nujol, ν/cm^{-1}) 3254, 3117, 1674, 1615, 1556, 1515, 1307, 1225, 1195, 819. Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40. Found: C, 65.11; H, 5.26; N, 5.41.

*4.4.24. 3-Formylthiophene-2-carboxylic acid cyclohexyl-amide (**16h**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26–2.01 (m, 10H), 3.96 (br, 1H), 7.52 (d, J=5.4 Hz, 1H), 7.56 (d, J=5.1 Hz, 1H), 9.61 (br, 1H), 9.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 25.6, 31.5, 32.6, 48.7, 129.0, 133.7, 135.6, 138.9, 186.9; IR (Nujol, ν/cm^{-1}) 3285, 3083, 1678, 1619, 1544, 1514, 1348, 1322, 1257, 1241, 1229, 1151, 1137, 1096, 924, 824, 792. Anal. Calcd for $C_{12}H_{15}N_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.43; H, 6.46; N, 5.68.

*4.4.25. 6-Hydroxy-1,3-dimethyl-5-phenyl-5,6-dihydrothieno [3,4-c]pyrrol-4-one (**17a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.45 (s, 3H), 3.98 (d, J=11.7 Hz, 1H), 6.12 (d, J=11.4 Hz, 1H), 7.15 (t, J=8.1 Hz, 1H), 7.31 (t, J=8.4 Hz, 2H), 7.61 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 12.5, 79.4, 121.2, 124.9, 128.8, 131.1, 131.4, 137.8, 138.7, 139.5, 162.9; IR (Nujol, ν/cm^{-1}) 3316, 1668, 1597, 1560, 1497, 1261, 1160, 1094, 1042, 938, 896, 802, 783, 762, 696, 683; HRMS (ESI) calcd for $C_{14}H_{13}NO_2SNa$ ([M+Na]$^+$): 282.0565, found: 282.0531.

*4.4.26. 4-Hydroxy-5-phenethyl-4,5-dihydrothieno[2,3-c]-pyrrol-6-one (**17b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (t, J=7.5 Hz, 1H), 3.65 (m, 1H), 3.86 (m, 1H), 7.09–7.17 (m, 6H), 7.22 (t, J=7.7 Hz, 2H), 7.09 (d, J=4.8 Hz 1H), 7.21–7.29 (m 5H), 7.61 (d, J=4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.0, 41.8, 80.2, 121.2, 126.5, 128.6, 128.8, 128.9, 129.3, 135.3, 139.0, 154.0; IR (Nujol, ν/cm^{-1}) 3193, 1657, 1462, 1377, 1291.38, 1280.30, 1114.65, 747.58, 697.16; HRMS (ESI) calcd for $C_{14}H_{13}NO_2SNa$ ([M+Na]$^+$): 282.0565, found: 282.0592.

*4.4.27. 3-Formylfuran-2-carboxylic acid phenylamide (**18a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J=1.8 Hz, 1H), 7.20 (t, J=7.5 Hz, 1H), 7.40 (t, J=7.5 Hz, 2H), 7.58 (d, J=1.8 Hz, 1H), 7.72 (d, J=7.5 Hz, 2H), 9.43 (br, 1H), 10.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.6, 120.3, 125.1, 127.7, 129.2, 136.9, 144.2, 149.7, 154.8, 187.6; IR (Nujol, ν/cm^{-1}) 3274, 3138, 3119, 1684, 1655, 1607, 1597, 1545, 1499, 1444, 1419, 1326, 1262, 1232, 1181, 786, 693; HRMS (ESI) calcd for $C_{12}H_9NO_3Na$ ([M+Na]$^+$): 238.0480, found: 238.0416.

*4.4.28. 2-Formylfuran-3-carboxylic acid phenylamide (**18b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J=7.5 Hz, 1H), 7.32 (s, 1H), 7.39 (t, J=7.5 Hz, 2H), 7.76 (s, 1H), 7.80 (d, J=7.8 Hz, 2H), 9.92 (s, 1H), 11.37 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.5, 120.2, 120.3, 124.6, 129.1, 138.0, 148.0, 148.2, 157.5, 182.4; IR (Nujol, ν/cm^{-1}) 3193, 3117, 3038, 1676, 1624, 1612, 1600, 1563, 1496, 1420, 1328, 1257, 1212, 1177, 1163, 1151, 1093, 908, 802, 755, 692, 599; HRMS (ESI) calcd for $C_{12}H_9NO_3Na$ ([M+Na]$^+$): 238.0480, found: 238.0482.

*4.4.29. 4-Formyl-5-methyl-furan-3-carboxylic acid phenylamide (**18c**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H), 7.12 (t, J=7.5 Hz, 1H), 7.36 (t, J=7.5 Hz, 2H), 7.78 (d, J=7.5 Hz, 2H), 7.22 (s, 1H), 11.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 111.85, 120.0, 124.2, 128.9, 138.4, 149.5, 158.9, 168.2, 186.6; IR (Nujol, ν/cm^{-1}) 1663, 1628, 1599, 1563, 1462, 1403, 1377, 1338, 760; HRMS (ESI) calcd for $C_{13}H_{11}NO_3Na$ ([M+Na]$^+$): 252.0637, found: 252.0668.

*4.4.30. 2-Formyl-1-methyl-1H-pyrrole-3-carboxylic acid phenylamide (**19**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 6.83 (d, J=2.4 Hz, 1H), 6.88 (d, J=2.4 Hz, 1H), 7.10 (t, J=7.4 Hz, 1H), 7.34 (t, J=7.6 Hz, 2H), 7.75 (d, J=7.7 Hz, 2H), 9.99 (s, 1H), 10.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.3, 113.3, 120.1, 123.9, 128.5, 128.8, 129.7, 130.4, 138.5, 160.5, 180.7; IR (Nujol, ν/cm^{-1}) 3293, 1676, 1610, 1593, 1560, 1522, 1490, 1315, 1254, 1188; HRMS (ESI) calcd for $C_{13}H_{12}N_2O_2Na$ ([M+Na]$^+$): 251.0797, found: 251.0820.

*4.4.31. 3-Formyl-1-methyl-1H-indole-2-carboxylic acid phenylamide (**20a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (s, 3H), 7.17 (t, J=7.4 Hz, 1H), 7.37–7.50 (m, 5H), 7.88 (d, J=8.3 Hz, 2H), 8.04 (d, J=7.8 Hz, 1H), 10.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.3, 111.1, 113.7, 118.9, 120.7, 123.9, 124.7, 125.4, 127.2, 129.0, 136.6, 137.6, 138.2, 158.2, 185.6; IR (Nujol, ν/cm^{-1}) 3280, 1674, 1635, 1597, 1538, 1498, 1129, 784, 694; HRMS (ESI) calcd for $C_{17}H_{14}N_2O_2Na$ ([M+Na]$^+$): 301.0953, found: 301.0881.

*4.4.32. 3-Formyl-1-methyl-1H-indole-2-carboxylic acid phenylamide (**20b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (s, 3H), 7.18 (t, J=7.3 Hz, 1H), 7.29–7.34 (m, 1H), 7.40 (t, J=7.2 Hz, 2H), 7.44–7.51 (m, 2H), 7.72 (d, J=7.7 Hz, 1H), 8.19 (d, J=8.2 Hz, 1H), 9.00 (s, 1H), 10.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.9, 110.9, 120.1, 120.7, 122.4, 123.1, 124.5, 124.7, 127.3, 129.1, 133.6, 138.0, 138.6, 161.8, 184.7; IR (Nujol, ν/cm^{-1}) 1673, 1656, 1532, 1462, 1377, 1312, 746; HRMS (ESI) calcd for $C_{17}H_{13}N_2O_2Na$ ([M+Na]$^+$): 301.0953, found: 301.1014.

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12. Investigation of solvents: dioxane, 34%; THF, 45%; hexane, 67%; 1,2-dichloroethane, 76%; toluene, 76%.
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14. Investigation of reaction time: 1 h, 19%; 3 h, 47%; 8 h, 52%; 24 h, 76%.
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17. Another possible mechanism is an electrophilic pathway (Friedel–Crafts type mechanism). In this pathway, a heteroaryl-rhenium complex and H^+ are formed as intermediates. When we examined the rhenium-catalyzed amidation in the presence of tributylamine as a Lewis base, the reaction proceeded without decreasing the yield. Thus, we are tempted to assume that this reaction proceeds via C–H bond activation.
18. Insertion of unsaturated molecules into an Re–H bond followed by reductive elimination can also give the same product; however, we have observed that the insertion into an Re–C bond occurs faster. See Ref. 11.