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Direct Substitution of Hydroxy Group of π-Activated Alcohols with Electron-Deficient Amines Using Re_2O_7 Catalyst

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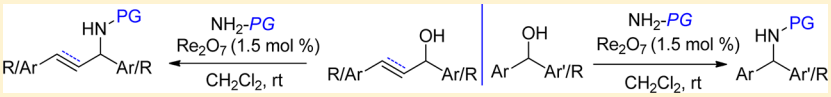
Supporting Information



ABSTRACT: The first example of simple Re_2O_7-catalyzed direct dehydrative coupling between allylic alcohols with electron-deficient amines has been achieved under mild and open flask conditions. The protocol has also been successfully applied to benzylic and propargylic alcohols. The mechanistic proof for the S_N1-type process has also been provided.

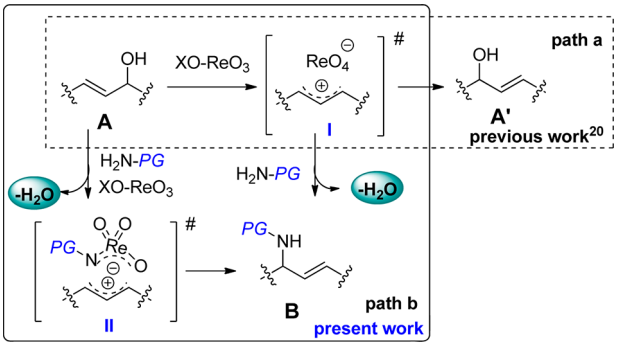
INTRODUCTION

The direct catalytic amination of *underivatized* π-activated alcohols, producing water as the only byproduct, is a very powerful strategy for the synthesis of various π-activated amines. In recent years, therefore, there have been continuous efforts to develop such reaction protocols using novel catalytic systems with improved efficiency.[1] The use of alcohol is limited by its leaving group ability despite the atom-economical and ecological advantage of this strategy.[2] For example, for the synthesis of allylic amines via π-allyl Pd complexes, which have been widely used,[3] very few reports exist wherein an allylic alcohol is indeed used as a substrate[4,5] compared to activated derivatives of allyl alcohols (esters, carbonates, carbamates, phosphates, halides, etc.)[6] or allylic alcohols with activators.[7] However, such palladium-catalyzed reactions are limited to electron-rich amines as nucleophiles; electron-deficient nitrogen nucleophiles did not undergo any reaction due to their low nucleophilicity. However, the higher nucleophilicity of the monoalkylated product in comparison to that of the starting amine results in further alkylation at the nitrogen center, which becomes a limiting factor in such a synthetic strategy.

On the other hand, the protocols with electron-deficient nitrogen nucleophiles have been developed using various Lewis acids[8−17] or Brønsted acids.[18,19] However, besides the advantages, most of these catalysts are *not broadly applicable to all classes* (namely, allyl, benzyl, and propargyl) *of π-activated alcohols*. Additionally, in many cases, the reaction using such acids is *restricted to aromatic amines only*, or *disubstituted amines are used* to avoid overalkylation. Therefore, a milder catalyst with high oxophilicity as well as applicability to all classes of π-activated alcohols toward simple monoprotected amines is highly desirable.

Recently, the metal-oxo complexes display high catalytic activity for allyl alcohol transposition, and oxo-rhenium(VII) catalysts have been shown to be superior in terms of reactivity and chemoselectivity, with no competitive oxidation (path a, Scheme 1).[20] Unfortunately, these oxo-rhenium catalysts have never been utilized for allylic amination reactions.[21] In continuation of our research directed toward the development

Scheme 1. Oxo-Re Catalysis[a]



[a]Path a: allylic transposition of allyl alcohol. Path b: working hypothesis of allylic amination of allyl alcohol.

of atom-economic reactions catalyzed by oxo-rhenium catalysts[22] because of their mild, moisture/air-tolerant nature,[23] we, *for the first time*, initiated a study of oxo-rhenium-catalyzed direct substitution of allylic alcohols toward various electron-deficient amines. Hypothetically, there could be a possibility of the reaction proceeding via an intramolecular aza-Cope rearrangement of in situ formed aza-/oxa-rhennate intermediate (**II**), which might enhance the rate of the reaction (path b, Scheme 1).[24,25]

RESULTS AND DISCUSSION

Table 1 summarizes the results of the catalyst screening of the allylic amination reaction of the diphenyl allylic alcohol (**1a**) with Cbz-NH_2 (**2a**) as the model substrate. As shown in entry 1, using MTO as catalyst, the desired product was given in low yield and ether (**III**) was obtained as the major product.

Among different oxo-rhenium(V) catalysts, (entries 2−4, Table 1), $ReCl_3O(SMe_2)(OPPh_3)$ showed moderate reactivity (60% conversion only). Interestingly, the best catalytic activity

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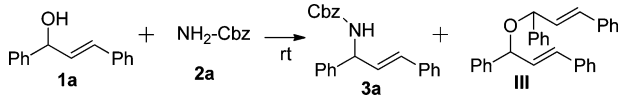
Table 1. Optimization of the Reaction Conditions



	catalyst (1.5 mol %)	solvent	min	3a [%][a]
1	$MeReO_3$ (MTO)	CH_2Cl_2	15	18
2	$ReCl_3O(PPh_3)_2$	CH_2Cl_2	15	0
3	$ReIO_3(PPh_3)_2$	CH_2Cl_2	15	6
4	$ReCl_3O(SMe_2)(OPPh_3)$	CH_2Cl_2	15	61
5	Re_2O_7	CH_2Cl_2	10	100 (99)[b]

[a]Conversion was determined by ^1H NMR spectroscopy of the reaction mixture using *p*-anisaldehyde as internal standard. [b]In parentheses, the yield of the isolated product after column chromatography.

was shown by using 1.5 mol % Re_2O_7 at room temperature in CH_2Cl_2; an almost quantitative yield of the corresponding allylamine (**3a**) was obtained with excellent chemoselectivity within 10 min. However, the reaction took place in a less-effective manner, using solvents, such as THF (74%), Et_2O (48%), toluene (36%), and MeOH (0%).

To broaden the scope of amines used, we carried out the reaction of the same alcohol with several protected amines (summarized in Table 2) under the optimized conditions as mentioned above. As shown in entries 1−7, a variety of primary amines protected with sensitive carbamates, such as Cbz-, Boc-, and EtOCO-, primary amides (Ac-, Bz-), and tosylate (Ts-, pNosyl-) participate in the reaction to provide excellent yields of the corresonding amines (**3a**−**3g**, respectively). As shown in entries 8−10, cyclic amides also reacted smoothly (**3h**−**3j**, respectively). Nevertheless, the aromatic amine (**2k**) also provided the allylamine (**3k**). However, benzoylhydrazine (**2l**) remained unreactive under similar reaction conditions (entry 12).

The scope of the reaction with respect to the alcohol substrate is summarized in Table 3. For example, nonbenzylic acyclic allylic alcohols (**1b** and **1c**, entries 1 and 2) were successful in reaction with protected amine (**2a**). Interestingly, the reaction of **1b** afforded the linear amine (**4a**), whereas **1c** provided a more substituted allyl amine (**4b**), in a highly regioselective manner in both the cases (Table 3, entries 1 and 2). The regioselective formation of **4b** probably resulted from the most stabilized allyl-cation intermediates (e.g., intermediate like **I** or **II** in Scheme 1), which indirectly supports the S_N1-like reaction pathway. Nonbenzylic cyclic alcohols (entries 3−6) also worked efficiently under these conditions.

Next, we applied the present protocol for propargylic alcohols (Table 3, **1g**−**1j**) with the above-mentioned amines (entries 7−12). Although the reaction time was longer than the allylation reaction, notably, only propargylic products were observed with high regioselectivity, without any interference from the allenic product.[26]

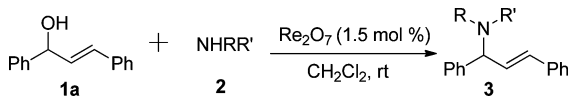
Finally, N-benzylation of various amides was also examined from benzyl alcohols in the presence of the Re_2O_7 catalyst, as summarized in Table 4. For example, Cbz-NH_2 (**2a**) and Ts-NH_2 (**2f**) with diphenyl alcohol (**5a**) proceeded smoothly to afford the corresponding desired products in high yield (entries 1 and 2, respectively). The cyclic amide (**2h**) also worked well, except it required a longer reaction time (entry 3). Other diaryl alcohols (**5b**−**5e**) underwent conversion to provide the desired products (entries 4−7).

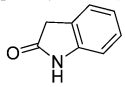
To gain further insight into the mechanism of this Re_2O_7 catalysis, we performed the following reactions. An optically active alcohol **1c-crl** with 50% ee was treated with **2a** under the specified reaction conditions, and the racemic product **4b** was obtained (see Scheme 2). This result also suggested that the substitution probably proceeded through an S_N1-like mechanism.

CONCLUSIONS

In conclusion, the ligand- and additive-free simple oxo-rhenium catalyst (1.5 mol % Re_2O_7) has been utilized, *for the first time*, for the direct substitution of allylic alcohols under mild and open flask conditions. Also, other π-activated alcohols, namely, benzylic and propargylic alcohols, worked smoothly under

Table 2. Allylic Amination Reaction[a,b]



z	NHRR', **2**	min	**3**	[%][a]
1	Cbz-NH_2 (**2a**)	10	**3a**	99
2	Boc-NH_2 (**2b**)	15	**3b**	99
3	EtOCO-NH_2 (**2c**)	60	**3c**	99
4	Ac-NH_2 (**2d**)	4h[b]	**3d**	95
5	Bz-NH_2 (**2e**)	60	**3e**	97
6	Ts-NH_2 (**2f**)	10	**3f**	95
7	*p*Nosyl-NH_2 (**2g**)	60	**3g**	93
8	 (**2h**)	10	**3h**	99
9	 (**2i**)	20h	**3i**	99
10	 (**2j**)	30	**3j**	99
11	*p*-NO_2-$C_6H_4NH_2$ (**2k**)	6h[b]	**3k**	98
12	PhCO-$NHNH_2$ (**2l**)	12	-	0

[a]Isolated yield after column chromatography. [b]The reaction was carried out at 45 °C.

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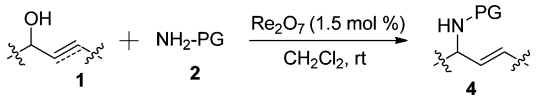
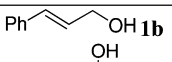
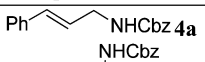
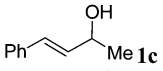
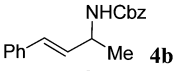
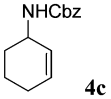
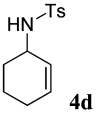
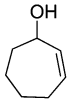
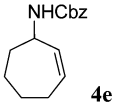
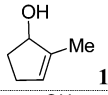
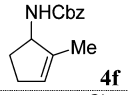
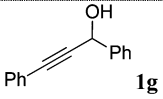
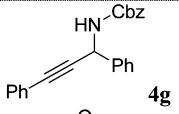
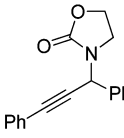
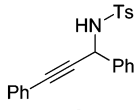
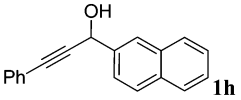
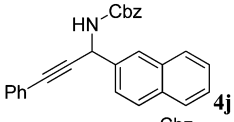
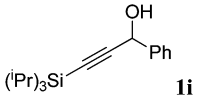
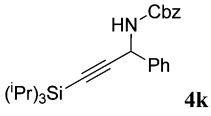
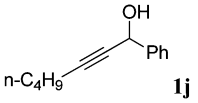
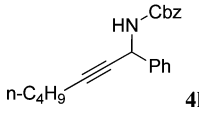
Table 3. Amination of Allylic and Propargylic Alcohols[a,b,c]



1 2 4

	alcohol, **1**	**2**, [h]	product, **4**	[%][a]
1	 **1b**	**2a**, 4[b]	 **4a**	61
2	 **1c**	**2a**, 3	 **4b**	99[c]
3	 **1d**	**2a**, 6	 **4c**	76
4		**2f**, 4	 **4d**	89
5	 **1e**	**2a**, 6	 **4e**	61
6	 **1f**	**2a**, 6	 **4f**	72
7	 **1g**	**2a**, 24	 **4g**	68
8	**1g**	**2j**, 24	 **4h**	83
9	**1g**	**2f**,12[b]	 **4i**	77
10	 **1h**	**2a**, 15	 **4j**	74
11	 **1i**	**2a**, 6	 **4k**	91
12	 **1j**	**2a**, 12	 **4l**	62

[a]Isolated yield after column chromatography. [b]The reaction was carried out at 45 °C. [c]Only regioisomer observed.

these conditions. Excellent chemoselective formation of only the monoalkylated product was observed. Finally, the proof for the S_N1-type process has also been developed.

EXPERIMENTAL SECTION

General Experimental Methods. All reagents and solvents were used as supplied commercially. Commercial Re_2O_7, ranging in color from yellow to brown-black, was stored in a desiccator over $CaCl_2$. Reactions were conducted in an open atmosphere. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates. Visualization was accomplished with UV light (254 nm) and exposure to either phosphomolybdic acid (PMA)-$CeSO_4$/10% H_2SO_4, anisaldehyde, or $KMnO_4$ solution, followed by heating. Melting points are uncorrected. ^{1}H NMR spectra were acquired on either a 400 or a 500 MHz MNR spectrometer, and chemical shifts are reported relative to the residual solvent peak. ^{13}C NMR spectra were acquired on either a 100 or a 125 MHz NMR spectrometer, and chemical shifts are reported in parts per million relative to the residual solvent peak. Unless noted, NMR spectra were acquired in $CDCl_3$; individual peaks are reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants in hertz (Hz). All IR spectra were obtained as neat films, and selected absorbances are reported in cm^{-1}. Low-resolution and high-resolution mass spectrometry data were acquired using a Q-TOF analyzer in CH_3CN/H_2O as solvent (unless otherwise noted).

Standard Procedure of Amination Reaction from π-Activated Alcohol and Amines. To a stirred solution of alcohol (0.5 mmol) and amine (0.6 mmol, 1.2 equiv) in CH_2Cl_2 (2 mL) was added Re_2O_7 (0.0075 mmol, 1.5 mol %), and the solution was stirred

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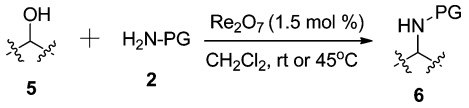
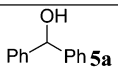
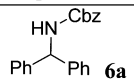
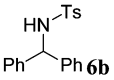
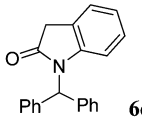
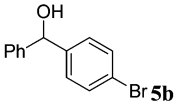
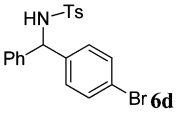
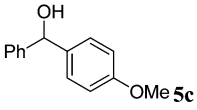
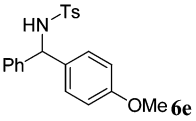
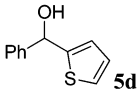
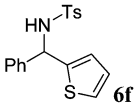
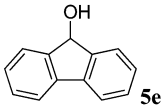
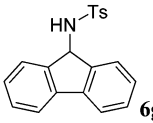
Table 4. Benzylation of Amine[a,b]

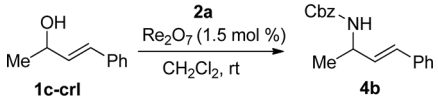


5 2 6

	alcohols, 5	2, [h]	product, 6	[%][a]
1	 **5a**	**2a**, 8	 **6a**	99
2	**5a**	**2f**, 4	 **6b**	97
3	**5a**	**2h**, 20[b]	 **6c**	88
4	 **5b**	**2f**, 4	 **6d**	89
5	 **5c**	**2f**, 1	 **6e**	92
6	 **5d**	**2f**, 3	 **6f**	86
7	 **5e**	**2f**, 8	 **6g**	91

[a]Isolated yield after column chromatography. [b]The reaction was carried out at 45 °C.

Scheme 2. Amination of Chiral Allyl Alcohol



1c-crI 50% ee → **4b** 0% ee

at rt or at 45 °C, as mentioned in Table 2, 3, or 4. After the completion of the reaction, 1 mL of a saturated solution of NH_4Cl was added and the solution was extracted with EtOAc (3 × 10 mL). The combined organic extract was dried over anhydrous sodium sulfate, and then the crude reaction mixture was purified by column chromatography on silica gel.

*(E)-Benzyl (1,3-Diphenylallyl)carbamate (**3a**):*[12b] 0.169 g, 99% yield; R_f = 0.24 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 111−113 °C; IR (neat) 3325, 3028, 1693, 1492, 1450, 1257, 1234, 1026, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.50−7.20 (15H), 6.59 (d, *J* = 16 Hz, 1H), 6.36 (dd, *J* = 6, 16 Hz, 1H), 5.57 (s,1H), 5.40−5.00 (3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.5, 140.9, 136.3, 131.2,129.1, 128.8,128.6, 128.5, 128.2, 127.8, 127.7, 127.0, 126.5, 67.0, 56.8; HRMS (ESI, *m*/*z*) $[M + Na]^+$ calculated for $C_{23}H_{21}NNaO_2$, 366.1465; found, 366.1465.

*(E)-tert-Butyl (1,3-Diphenylallyl)carbamate (**3b**):*[14] 0.153 g, 99% yield; R_f = 0.24 (5:95 = EtOAc/*n*-hexane); colorless solid; mp 109−111 °C; IR (neat) 3344, 3028, 2974, 1693, 1492, 1365, 1165, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.50−7.20 (10H), 6.57 (dd, *J* = 1.2, 16 Hz, 1H), 6.35 (dd, *J* = 6, 16 Hz, 1H), 5.49 (s, 1H), 5.09 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.0, 141.3, 136.5, 130.9, 129.6, 128.7, 128.5, 127.7, 127.5, 127.0, 126.5, 79.8, 56.4, 28.4; HRMS (ESI, *m*/*z*) $[M + Na]^+$ calculated for $C_{20}H_{23}NNaO_2$, 332.1626; found, 332.1637.

*(E)-Ethyl (1,3-Diphenylallyl)carbamate (**3c**):* 0.140 g, 99% yield; R_f = 0.3 (15:85 = EtOAc/*n*-hexane); colorless solid; mp 104−106 °C; IR (neat) 3317, 3028, 2978, 1725, 1527, 1496, 1246, 1037, 968 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.55−7.15 (10H), 6.59 (dd, *J* = 1.2 and 16 Hz, 1H), 6.36 (dd, *J* = 6 and 16 Hz, 1H), 5.55 and 5.19 (two s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.8, 141.1, 136.4, 131.1, 129.3, 128.8, 128.5, 127.8, 127.7, 127.0, 126.5, 61.1, 56.6, 14.6; HRMS (ESI, *m*/*z*) $[M + Na]^+$ calculated for $C_{18}H_{19}NNaO_2$, 304.1313; found, 304.1314.

*(E)-N-(1,3-Diphenylallyl)acetamide (**3d**):* 0.119 g, 95% yield; R_f = 0.27 (30:70 = EtOAc/*n*-hexane); colorless solid; mp 136−138 °C; IR (neat) 3275, 3059, 2924, 1647, 1539, 1492, 1300, 968 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.48−7.28 (10H), 6.55 (dd, *J* = 1.32 and 16 Hz, 1H), 6.36 (dd, *J* = 6 and 16 Hz, 1H), 6.08 (d, *J* = 8 Hz, 1H), 5.88−5.80 (1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 169.1, 140.8, 136.4, 131.3, 128.9, 128.8, 128.5, 127.8, 127.7, 127.2, 126.5, 54.8, 23.4; HRMS (ESI, *m*/*z*) $[M + Na]^+$ calculated for $C_{17}H_{17}NNaO$, 274.1208; found, 274.1208.

*(E)-N-(1,3-Diphenylallyl)benzamide (**3e**):*[12b] 0.150 g, 97% yield; R_f = 0.20 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 163−165 °C; IR (neat) 3348, 3032, 1631, 1516, 1485, 1361, 1311, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.94−7.78 (2H), 7.62−7.18 (13H), 6.75−6.55 (2H), 6.47 (dd, *J* = 6, 16 Hz, 1H), 6.05 (t, *J* = 7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.5, 140.8, 136.4, 134.3, 131.7, 131.6, 128.9, 128.7, 128.6, 128.5, 127.9, 128.8, 127.2, 127.0, 126.6, 55.2; HRMS (ESI, *m*/*z*) $[M + H]^+$ calculated for $C_{22}H_{20}NO$, 314.1545; found, 314.1564.

*(E)-N-(1,3-Diphenylallyl)-4-methylbenzenesulfonamide (**3f**):*[12b] 0.172 g, 95% yield; R_f = 0.18 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 119−121 °C; IR (neat) 3275, 3028, 1597, 1492, 1450, 1323, 1157, 1091, 968 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.75−7.63 (2H), 7.40−7.05 (12H), 6.37 (d, *J* = 16 Hz, 1H), 6.10 (dd, *J* = 6.8, 16 Hz, 1H), 5.25−5.09 (2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

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143.2, 139.6, 137.7, 136.0, 132.1, 129.4, 128.7, 128.4, 128.2, 127.9, 127.8, 127.3, 127.0, 126.5, 59.7, 21.4; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{22}H_{21}NNaO_2S$, 386.1191; found, 386.1199.

(E)-N-(1,3-Diphenylallyl)-4-nitrobenzenesulfonamide (**3g**): 0.175 g, 93% yield; R_f = 0.24 (30:70 = EtOAc/*n*-hexane); colorless solid; mp 156 °C; IR (neat) 3279, 3028, 2914, 1606, 1528, 1347, 1311, 1160, 1090, 1027, 971, 853, 736, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.12 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.80 Hz, 2H), 7.28−7.19 (m, 10H), 6.45 (d, J = 15.92 Hz, 1H), 6.14 (dd, J = 6.90 and 9.04 Hz, 1H), 5.39 (s, 1H), 5.27 (d, J = 6.67 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.6, 146.6, 138.6, 135.4, 133.0, 128.9, 128.6, 128.4, 128.3, 127.3, 127.1, 126.4, 123.9, 60.2; HRMS (ESI, m/z) $[M - H]^+$ calculated for $C_{21}H_{17}N_2O_4S$, 393.0908; found, 393.0918.

(E)-1-(1,3-Diphenylallyl)indolin-2-one (**3h**): 0.161 g, 99% yield; R_f = 0.15 (20:80 = EtOAc/*n*-hexane); light brown liquid; IR (neat) 3055, 3028, 1712, 1612, 1450, 1338, 1199, 968 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.54−7.22 (12H), 7.19−6.93 (2H), 6.90−6.73 (2H), 6.66 (d, J = 7.6 Hz, 1H), 6.52 (d, J = 6.4 Hz, 1H), 3.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 174.9, 143.0, 137.8, 136.2, 135.0, 128.7, 128.6, 128.1, 127.6, 127.4, 127.1, 126.7, 124.6, 124.5, 124.3, 122.1, 111.2, 56.0, 35.8; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{23}H_{20}NO$, 326.1545; found, 326.1544.

(E)-1-(1,3-Diphenylallyl)pyrrolidin-2-one (**3i**): 0.137 g, 99% yield; R_f = 0.15 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 63−65 °C; IR (neat) 3028, 1681, 1492, 1415, 1265, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.55−7.20 (10H), 6.65 (d, J = 16 Hz, 1H), 6.48 (dd, J = 6.4, 15.6 Hz, 1H), 6.12 (d, J = 6.8 Hz, 1H), 3.52−3.40 (1H), 3.23−3.09 (1H), 2.70−2.40 (2H), 2.20−1.90 (2H); ^{13}C NMR (100 MHz, $CDCl_3$) 174.7, 138.7, 136.4, 133.4, 128.7, 128.6, 127.9, 127.8, 127.7, 126.5, 125.4, 56.2, 43.4, 31.2, 18.1; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{19}H_{20}NO$, 278.1545; found, 278.1547.

(E)-3-(1,3-Diphenylallyl)oxazolidin-2-one (**3j**):[12b] 0.138 g, 99% yield; R_f = 0.23 (20:85 = EtOAc/*n*-hexane); colorless liquid; IR (neat) 3029, 1732, 1494, 1417, 1250, 974 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.50−7.26 (10H), 6.71 (d, J = 16 Hz, 1H), 6.49 (dd, J = 6.4, 16 Hz, 1H), 5.84 (d, J = 6.4 Hz, 1H), 4.45−4.25 (2H), 3.68−3.57 (1H), 3.37−3.25 (1H); ^{13}C NMR (100 MHz, $CDCl_3$) 158.2, 138.0, 136.2, 133.8, 128.9, 128.7, 128.17, 128.17, 127.8, 126.6, 124.8, 62.1, 58.4, 41.0; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{18}H_{17}NaNO_2$, 302.1157; found, 302.1149.

(E)-N-(1,3-Diphenylallyl)-4-nitroaniline (**3k**):[18c] 0.140 g, 98% yield; R_f = 0.3 (15:85 = EtOAc/*n*-hexane); yellow solid; mp 135−137 °C; IR (neat) 3390, 3375, 1600, 1500, 1275, 1111, 968 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.15−8.03 (2H), 7.55−7.15 (10H), 6.70−6.55 (3H), 6.41 (dd, J = 6, 16 Hz, 1H), 5.23 (d, J = 6 Hz, 1H), 4.93 (b s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.1, 140.3, 138.5, 136.0, 132.3, 129.2, 128.7, 128.6, 128.2, 128.1, 127.1, 126.6, 126.2, 112.1, 60.0; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{21}H_{18}NaN_2O_2$, 353.1266; found, 353.1278.

(E)-Benzyl 4-Phenylbut-3-enoate (**4a**): 0.080 g, 61% yield; R_f = 0.25 (10:90 = EtOAc/*n*-hexane); colorless oil; IR (neat) 3414, 3332, 3028, 2924, 1725, 1516, 1246, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.55−7.20 (10H), 6.54 (d, J = 15.6 Hz, 1H), 6.35−6.05 (1H), 5.17 (s, 2H), 4.92 (b s, 1H), 4.02 (2H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.2, 136.5, 131.8, 129.2, 128.6, 128.5, 128.3, 128.1, 127.7, 127.0, 126.4, 126.0, 125.7, 66.8, 43.2; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{18}NO_2$, 268.1332; found, 268.1320.

(E)-Benzyl (4-Phenylbut-3-en-2-yl)carbamate (**4b**): 0.139 g, 99% yield; R_f = 0.2 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 66−68 °C; IR (neat) 3321, 3028, 1697, 1527, 1450, 1234, 1049, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.60−7.15 (10H), 6.54 (d, J = 16 Hz, 1H), 6.18 (dd, J = 6, 16 Hz, 1H), 5.15 (s, 2H), 4.83 (b s, 1H), 4.51 (b s, 1H), 1.36 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.6, 136.6, 136.5, 131.1, 129.6, 128.6, 128.5, 128.1, 127.6, 126.4, 66.7, 48.4, 21.1; HRMS (ESI, m/z) $[M + 2H]^+$ calculated for $C_{18}H_{20}NO_2$, 282.1494; found, 282.1493.

Benzyl Cyclohex-2-en-1-ylcarbamate (**4c**):[14] 0.088 g, 76% yield; R_f = 0.26 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 83−85 °C; IR (neat) 3313, 2916, 181, 1539, 1315, 1257, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.50−7.30 (5H), 5.92−5.80 (1H), 5.68−5.55 (1H), 5.12 (1H), 4.78 (1H), 4.25 (1H), 2.10−1.85 (3H), 1.75−1.50 (3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.6, 136.6, 130.8, 128.5, 128.4, 128.1, 128.0, 127.7, 66.5, 46.3, 29.7, 24.7, 19.5; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{14}H_{18}NO_2$, 232.1338; found, 232.1359.

N-(Cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (**4d**):[14] 0.112 g, 89% yield; R_f = 0.23 (5:95 = EtOAc/*n*-hexane); colorless solid; mp 98−100 °C; IR (neat) 3282, 2927, 1597, 1427, 1327, 1157, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.79 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 5.76 (d, J = 10 Hz, 1H), 5.36 (d, J = 9.8 Hz, 1H), 4.66 (d, J = 8.4 Hz, 1H), 3.82 (s, 1H), 2.44 (s, 3H), 2.10−1.45 (6H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.2, 138.3, 131.5, 129.6, 127.06, 127.00, 48.9, 30.2, 24.4, 21.5, 19.3; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{13}H_{17}NNaO_2S$, 274.0878; found, 274.0881.

Benzyl Cyclohept-2-en-1-ylcarbamate (**4e**): 0.075 g, 61% yield; R_f = 0.29 (5:95 = EtOAc/*n*-hexane); colorless solid; mp 83−85 °C; IR (neat) 3422, 3314, 2916, 1685, 1541, 1400, 1254, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.46−7.30 (5H), 5.95−5.70 (1H), 5.65−5.50 (1H), 5.12 (s, 2H), 4.90 (s, 1H), 4.28 (s, 1H), 2.30−1.80 (4H), 1.78−1.32 (4H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.5, 136.6, 134.9, 132.1, 128.5, 128.2, 128.1, 66.6, 52.2, 34.2, 28.4, 27.5, 26.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{15}H_{20}NO_2$, 246.1494; found, 246.1486.

Benzyl (2-Methylcyclopent-2-en-1-yl)carbamate (**4f**): 0.083 g, 72% yield; R_f = 0.29 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 50−52 °C; IR (neat) 3325, 2935, 1693, 1519, 1234, 1060, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.44−7.28 (5H), 5.60−5.00 (3H), 4.85−4.40 (2H), 2.50−2.05 (3H), 1.85−1.50 (4H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.1, 144.9, 139.7, 136.7, 136.6, 128.52, 128.50, 128.1, 128.0, 125.0, 66.5, 59.8, 35.2, 32.3, 29.8, 16.6, 13.7; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{14}H_{17}NNaO_2$, 254.1157; found, 254.1165.

Benzyl (1,3-Diphenylprop-2-yn-1-yl)carbamate (**4g**):[16a] 0.115 g, 68% yield; R_f = 0.34 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 88−90 °C; IR (neat) 3305, 3032, 1689, 1531, 1253, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.75−7.25 (15H), 5.99 (d, J = 8 Hz, 1H), 5.59 (d, J = 7.2 Hz, 1H), 5.29−5.09 (2H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.4, 139.0, 136.2, 131.8, 128.7, 128.6, 128.5, 128.3, 128.2, 127.0, 122.4, 86.9, 85.1, 67.2, 47.4; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{23}H_{19}NNaO_2$, 364.1308; found, 364.1302.

3-(1,3-Diphenylprop-2-yn-1-yl)oxazolidin-2-one (**4h**): 0.115 g, 83% yield; R_f = 0.2 (10:90 = EtOAc/*n*-hexane); light brown liquid; IR (neat) 3491, 3059, 2916, 1955, 1894, 1743, 1489, 1415, 1246, 1068, 1029, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.67−7.60 (2H), 7.58−7.51 (2H), 7.47−7.30 (6H), 4.48−4.37 (1H), 4.35−4.24 (1H), 3.87−3.75 (1H), 3.32−3.20 (1H); ^{13}C NMR (100 MHz, $CDCl_3$) 157.8, 136.0, 131.9, 128.5, 127.4, 122.0, 87.4, 83.4, 62.2, 49.8, 40.4; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{16}NO_2$, 278.1181; found, 278.1186.

N-(1,3-Diphenylprop-2-yn-1-yl)-4-methylbenzenesulfonamide (**4i**):[12b] 0.138 g, 77% yield; R_f = 0.2 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 182−184 °C; IR (neat) 3267, 1593, 1489, 1427, 1323, 1153, 1049, 813 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.84 (d, J = 8 Hz, 2H), 7.58 (d, J = 8 Hz, 2H), 7.45−7.20 (8H), 7.14 (d, J = 7.6 Hz, 2H), 5.58 (d, J = 9.2 Hz, 1H), 4.96 (d, J = 9.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.5, 137.4, 131.5, 129.5, 128.7, 128.6, 128.5, 128.1, 127.5, 127.3, 121.9, 86.7, 85.4, 49.8, 21.4; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{22}H_{19}NaNO_2S$, 384.1034; found, 384.1078.

Benzyl (1-(Naphthalen-2-yl)-3-phenylprop-2-yn-1yl)carbamate (**4j**): 0.145 g, 74% yield; R_f = 0.32 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 160−165 °C; IR (neat) 3309, 2918, 1684, 1653, 1506, 1322, 1226, 1045, 972, 814, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.06 (s, 1H), 7.95−7.82 (3H), 7.67 (d, J = 8.4 Hz, 1H), 7.58−7.47 (4H), 7.45−7.32 (7H), 6.14 (d, J = 8.0 Hz, 1H), 5.45 (d, J = 7.6 Hz, 1H), 5.29−5.11 (2H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.4, 136.1, 133.2, 133.1, 131.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.6, 126.4, 126.3, 125.8, 124.8, 122.4, 86.9, 85.4, 67.2, 47.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{27}H_{22}NO_2$, 392.1651; found, 392.1640.

Benzyl (1-Phenyl-3-(triisopropylsilyl)prop-2-yn-1-yl)carbamate (**4k**): 0.189 g, 91% yield; R_f = 0.31 (10:90 = EtOAc/*n*-hexane); colorless oil; IR (neat) 3318, 2943, 2866, 1715, 1699, 1496, 1456,

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1307, 1232, 1041, 917, 883, 750, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.65−7.45 (2H), 7.40−7.27 (8H), 5.75 (d, J = 8 Hz, 1H), 5.32−5.00 (3H), 1.30−0.80 (21H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.3, 139.1, 136.2, 128.6, 128.5, 128.2, 128.1, 128.0, 127.0, 104.9, 86.5, 67.1, 47.6, 18.6, 11.1; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{26}H_{35}NaNO_2Si$, 444.2335; found, 444.2331.

*Benzyl (1-Phenylpent-2-yn-1-yl)carbamate (**4l**):* 0.101 g, 62% yield; R_f = 0.26 (05:95 = EtOAc/*n*-hexane); colorless oil; IR (neat) 3324, 2958, 2931, 1715, 1496, 1455, 1309, 1231, 1115, 1027, 915, 752, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.65−7.15 (10H), 5.70 (s, 1H), 5.38−5.00 (3H), 2.27 (t, J = 6.8 Hz, 2H), 1.70−1.10 (4H), 0.94 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.4, 139.7, 136.2, 128.6, 128.5, 128.1, 127.9, 126.9, 85.9, 77.8, 67.0, 47.1, 30.6, 29.7, 21.9, 18.4, 13.5; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{21}H_{24}NO_2$, 322.1807; found, 322.1811.

*Benzyl Benzhydrylcarbamate (**6a**):*[16a] 0.157 g, 99% yield; R_f = 0.29 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 113−115 °C; IR (neat) 3321, 3028, 1693, 1535, 1492, 1238, 1141, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.50−7.20 (15H), 6.02 (s, 1H), 5.46 (s, 1H), 5.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.6, 141.6, 136.3, 128.7, 128.5, 128.2, 127.5, 127.2, 67.0, 58.9; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{21}H_{20}NO_2$, 318.1489; found, 318.1488.

*N-Benzhydryl-4-methylbenzenesulfonamide (**6b**):*[18c] 0.103 g, 97% yield; R_f = 0.22 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 155−157 °C; IR (neat) 3248, 3028, 1597, 1492, 1450, 1315, 1161, 1091, 1056, 937 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.63−7.55 (2H), 7.35−7.05 (12H), 5.60 (d, J = 7.2 Hz, 1H), 5.32 (d, J = 7.2 Hz, 1H), 2.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.1, 140.5, 137.3, 129.3, 128.5, 127.5, 127.3, 127.2, 61.3, 21.4; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{20}H_{19}NNaO_2S$, 360.1034; found, 360.1049.

*1-Benzhydrylindolin-2-one (**6c**):* 0.130 g, 88% yield; R_f = 0.25 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 154−156 °C; IR (neat) 3059, 2916, 1712, 1612, 1481, 1330, 1234, 1199, 1168 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.50−6.90 (14H), 6.52−6.34 (1H), 3.68 and 3.60 (2H); ^{13}C NMR (100 MHz, $CDCl_3$) 175.2, 143.8, 137.7, 129.3, 128.6, 128.5, 128.3, 127.7, 127.2, 124.5, 124.3, 122.0, 111.9, 58.1, 35.6; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{21}H_{18}NO$, 300.1388; found, 300.1391.

*N-(4-Bromophenyl)(phenyl)methyl)-4-methylbenzene sulfonamide (**6d**):* 0.185 g, 89% yield; R_f = 0.25 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 121−123 °C; IR (neat) 3271, 3059, 2920, 1597, 1489, 1450, 1327, 1161, 1087 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.56 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 7.22 (s, 3H), 7.15 (d, J = 8 Hz, 2H), 7.13−6.98 (4H), 5.53 and 5.43 (two d, J = 7.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.4, 140.0, 139.5, 137.1, 131.5, 129.4, 129.1, 128.7, 127.8, 127.2, 127.1, 121.5, 60.8, 21.5; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{20}H_{18}BrNNaO_2S$, 438.0139; found, 438.0109.

*N-((4-Methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (**6e**):* 0.169 g, 92% yield; R_f = 0.26 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 139−141 °C; IR (neat) 3275, 2927, 1608, 1512, 1454, 1323, 1253, 1157, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.65−7.55 (2H), 7.27−7.09 (7H), 7.06−6.97 (2H), 6.80−6.70 (2H), 5.54 (d, J = 7.2 Hz, 1H), 5.22 (d, J = 7.2 Hz, 1H), 3.77 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 158.9, 143.1, 140.7, 137.4, 132.7, 129.3, 128.4, 127.4, 127.3, 127.2, 113.8, 60.8, 55.2, 21.4; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{21}H_{21}NNaO_3S$, 390.1140; found, 390.1175.

*4-Methyl-N-(phenyl(thiophen-2-yl)methyl)benzene Sulfonamide (**6f**):* 0.147 g, 86% yield; R_f = 0.24 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 121−123 °C; IR (neat) 3259, 2920, 1597, 1492, 1438, 1319, 1161, 1053, 933 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.63−7.53 (2H), 7.30−7.05 (8H), 6.93−6.87 (1H), 6.80 (dd, J = 1.2, 5.2 Hz, 1H), 5.65 (d, J = 7.6 Hz, 1H), 5.37 (d, J = 7.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.2, 141.8, 140.2, 137.4, 129.3, 128.5, 127.6, 127.2, 127.1, 126.6, 126.4, 122.8, 57.5, 21.5; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{18}H_{17}NNaO_2S_2$, 366.0598; found, 366.0587.

*N-(9H-Fluoren-9-yl)-4-methylbenzenesulfonamide (**6g**):* 0.152 g, 91% yield; R_f = 0.24 (10:90 = EtOAc/*n*-hexane); colorless solid; mp 174−176 °C; IR (neat) 3305, 3028, 2920, 1597, 1435, 1327, 1157, 1064, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.20−6.90 (14H), 5.40 (d, J = 9.6 Hz, 1H), 4.82 (d, J = 9.6 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.7, 143.3, 140.0, 138.4, 129.9, 129.8, 128.9, 127.8, 127.3, 125.2, 119.9, 58.3, 21.6; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{20}H_{17}NNaO_2S$, 358.0878; found, 358.0859.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C NMR spectra for compounds **3a−3k**, **4a−4l**, and **6a−6g**. 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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