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Iron-catalyzed *N*-alkylation using π-activated ethers as electrophiles†

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A new method for the synthesis of diverse *N*-alkylation compounds was developed *via* an iron-catalyzed etheric C_{sp^3}–O cleavage with the C–N bond formation in the reaction of π-activated ethers with various nitrogen-based nucleophiles. In addition, the mechanism of this reaction was investigated.

Introduction

The direct functionalization of etheric carbon–oxygen bonds is an attractive strategy for construction of carbon–carbon and carbon–heteroatom bonds in organic synthesis,[1] since ethers are stable and readily available building blocks in the natural and synthetic world, and they have many apparent advantages from environmental and economical viewpoints compared with the corresponding halides. In the past decade, considerable achievements have been made for the transition-metal catalytic activation of etheric C_{sp^2}–O bonds in C–C and C–N bond formation reactions,[2] such as using aryl ethers instead of aryl halides in Suzuki and Kumada couplings. However, compared to the C_{sp^2}–O bond activation, far fewer methods exist for the etheric C_{sp^3}–O bond cleavage due to its high bond dissociation energy and difficulty in differentiating two different C_{sp^3}–O bonds in unactivated ethers.[1,3] Most reported examples of C_{sp^3}–O cleavage are with strained cyclic ethers,[3e,f] alkyl C–O bonds with good leaving groups such as OTs and OMs,[4] or relatively reactive C_{sp^3}–O bonds of allylic or benzylic acetates and alcohols.[5,6]

In 2008, Shi and co-workers reported the first example of Ni-catalyzed selective activation of benzylic C_{sp^3}–O etheric bonds in C–C bond formations.[3a] However, up to now, only a few examples of conversion of benzylic or allylic C_{sp^3}–O etheric bonds to C–N bonds have been disclosed.[7] Among them, the reaction of allylic or benzylic ethers with chlorosulfonyl isocyanate (CSI) was found to be a particularly useful methodology and has been applied to the total synthesis of biologically active alkaloids.[7g,h] Given the importance of nitrogen-containing compounds in organic synthesis,[8] further exploration of new methods for this transformation is highly desirable. As one of our continuous interests in nitrogen-containing compound synthesis,[9] herein we report a practical method for the synthesis of diverse *N*-alkylation compounds *via* an iron-catalyzed etheric C_{sp^3}–O cleavage strategy, which serves as a supplement to those existing methodologies.[5–7,10]

Results and discussion

Initial examinations were carried out on the reactions of benzyl methyl ether (**1a**) and (1-methoxyethyl)benzene (**1b**) with *p*-toluenesulfonamide (**2a**) in various solvents. $FeCl_3$ was chosen as the catalyst because iron is an abundant, economical, and environmentally friendly metal on earth and shows increasing and promising catalytic abilities for the C–C and C–N bond formations.[11] The results are summarized in Table 1. To our delight, primary and secondary benzylic methyl ethers **1a** and **1b** can both serve as electrophiles in this *N*-alkylation reaction. For primary ether **1a**, a relatively high reaction temperature was required (80 °C, Table 1, entries 1 and 17). Encouraged by these initial results, further investigation of the solvent effect indicates that the nature of the reaction media significantly affects the reaction (Table 1, entries 4–11). DCE and DCM were found to be the more suitable solvents for the transformation of primary benzylic ether **1a** and secondary benzylic ether **1b**, respectively (Table 1, entries 2 and 18). With respect to the catalyst loading, 20 mol % of $FeCl_3$ was found to be optimal (Table 1, entries 1–3 and 17–19). Under the optimized reaction conditions, the desired amidation products **3a** and **3b** could be isolated in 61% and 75% yields, respectively (Table 1, entries 2 and 18). Note that the reaction time and temperature are crucial to this transformation due to the instability of the products under the reaction conditions.[12] Recently, the iron-catalyzed cleavage of the C–N bond of benzylic sulfonamides has emerged as a useful strategy in C–C bond formation reactions.[13] Other iron and copper salts, such as $FeCl_2$, $Fe(acac)_3$, and CuI, proved to be ineffective for this reaction (Table 1, entries 12–14). Replacing

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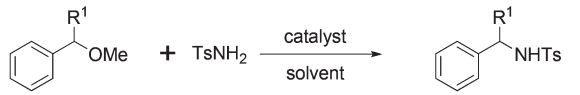
Table 1 Optimization of reaction conditions[a]



1a R^1=H, **1b** R^1=CH_3 **2a** **3a** R^1=H, **3b** R^1=CH_3

Entry	R^1	Catalyst (mol%)	Solvent	T (°C)/t (h)	Yield[b] (%)
1	H	$FeCl_3$ (15)	DCE	90/6	45
2	**H**	**$FeCl_3$ (20)**	**DCE**	**90/1**	**61**
3	H	$FeCl_3$ (30)	DCE	90/0.5	42
4	H	$FeCl_3$ (20)	DCM	40/24	9
5	H	$FeCl_3$ (20)	CH_3NO_2	75/0.5	41
6	H	$FeCl_3$ (20)	DMF	90/1.5	0
7	H	$FeCl_3$ (20)	Toluene	90/9	0
8	H	$FeCl_3$ (20)	THF	65/6	Trace
9	H	$FeCl_3$ (20)	EtOAc	65/5	Trace
10	H	$FeCl_3$ (20)	Dioxane	90/7	0
11	H	$FeCl_3$ (20)	None	90/1.5	47
12	H	$FeCl_2$ (20)	DCE	90/6.5	0
13	H	$Fe(acac)_3$ (20)	DCE	90/2	Mess
14	H	CuI (10)	DCE	90/2	0
15	H	None	DCE	90/3	0
16	Me	$FeCl_3$ (20)	DCE	90/1	18
17	Me	$FeCl_3$ (10)	DCM	rt/6	49
18	**Me**	**$FeCl_3$ (20)**	**DCM**	rt/1	**75**
19	Me	$FeCl_3$ (30)	DCM	rt/1	55
20[c]	Me	$FeCl_3$ (20)	DCM	rt/6	60
21	Me	$FeCl_3{\cdot}6H_2O$ (20)	DCM	rt/6	21
22	Me	$FeCl_3$ (20)/TMEDA (20)	DCM	rt/11	2
23	Me	$FeCl_3$ (20)/K_2CO_3 (20)	DCM	rt/6	36
24[c]	Me	TfOH (20)	DCM	rt/2	48

[a] Reaction conditions: benzylic ether (0.35 mmol), $TsNH_2$ (0.46 mmol), solvent (4 mL), under argon. [b] Isolated yield. [c] In air.

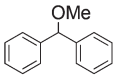
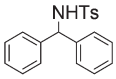
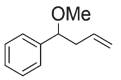
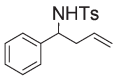
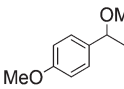
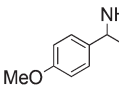
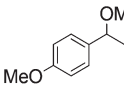
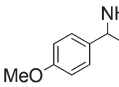
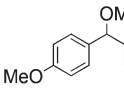
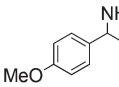
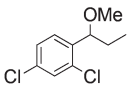
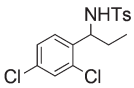
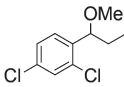
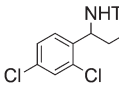
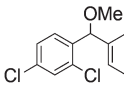
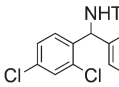
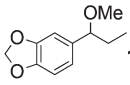
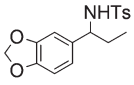
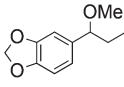
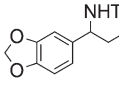
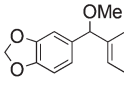
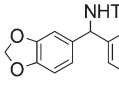
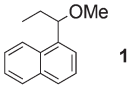
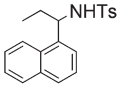
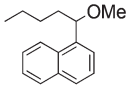
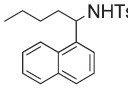
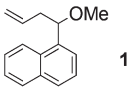
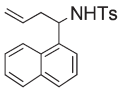
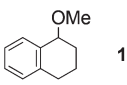
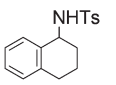
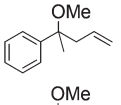
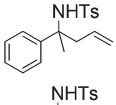
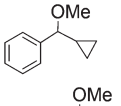
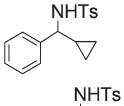
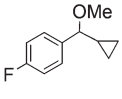
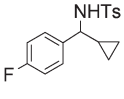
$FeCl_3$ with $FeCl_3{\cdot}6H_2O$, the reaction proceeded in lower yield (21%, Table 1, entry 21). No desired products were formed in the absence of catalyst (Table 1, entry 15). Optimization also revealed that the present reaction is more favored under an argon atmosphere than in air (Table 1, entries 18 and 20). In order to further improve the yield of this transformation, the additives of K_2CO_3 and TMEDA were added to the optimized reaction conditions separately, since it has been reported that some basic and ligand additives can affect the yields of the iron-catalyzed reactions.[11,14] Unfortunately, no favorable effect on the yields was observed (Table 1, entries 22 and 23). In addition, several Brønsted acids were also examined as catalysts for the reaction between **1b** and **2a** in DCM at room temperature. It was found that only triflic acid (Table 1, entry 24) exhibited catalytic activity in this transformation and a lower yield of **3b** was obtained.[15]

With the optimized reaction conditions in hand (Table 1, entries 2 and 18), the generality of this *N*-alkylation reaction was investigated on a series of secondary and tertiary benzylic methyl ethers (Table 2).[16] Functional groups, such as aromatic chloro or methoxy groups, C=C double bond, cyclopropyl and acetal, can tolerate the reaction conditions. In general, the reaction proceeds efficiently for both electron-rich and -poor benzylic methyl ethers within a very short period of time at room temperature, and the yields are relatively consistent with the electronic and steric properties of benzylic ethers and the stability of the corresponding products.[12,13] For example, with the more sterically hindered tertiary benzylic methyl ether **1r** (Table 2, entry 16) as the reactant, the alkylation took place at longer reaction time and the product **3r** was obtained in lower yield. With respect to the electronic effect, the substituents on the phenyl ring of benzylic ethers had an obvious influence on the product yields (Table 2, entries 3 and 6). Overall, the reaction was facilitated with electron-rich benzylic methyl ethers which bear an electron-donating group on the phenyl ring (Table 2, entries 3, 9, and 10). The relatively lower yields of **3g** and **3m** are presumably due to their lower stability under the iron catalytic conditions (Table 2, entries 5 and 11).

Further investigation of the generality and efficiency of this reaction was also conducted by using non-π-activated ethers, allylic methyl ethers, *p*-toluenesulfonamide, aniline, benzamide, 4-nitroaniline and trimethylsilyl azide as substrates (Table 3). Various allylic methyl ethers can react smoothly with *p*-toluenesulfonamide, 4-nitroaniline and trimethylsilyl azide[17] under the optimized conditions, giving the corresponding products in moderate to good yields. Interestingly, for the allylic methyl ether **1v**, only the thermodynamically favored isomeric product **3v** was obtained (Table 3, entry 2). Similarly, the catalytic system was also effective for the reaction of secondary benzylic methyl ethers **1n** and **1j** with 4-nitroaniline (**2b**) and trimethylsilyl azide (**2e**), affording aniline-based product **3nb** and azide product **3je** in 85% and 87% yields respectively (Table 3, entries 7 and 11). However, to our disappointment, non-π-activated ethers, such as 2-phenylethyl methyl ether **1u**, could not undergo this transformation even under harsh reaction conditions (Table 3, entry 1).[18] Examination also revealed that aniline (**2c**) and benzamide (**2d**) were not suitable nucleophiles for this transformation (Table 3, entries 8, 9 and 10). Based on the above results, we can conclude that (1) the π-activated ethers, such as allylic methyl ethers and primary, secondary and tertiary benzylic methyl ethers, can serve as electrophiles in this *N*-alkylation, (2) the benzylic methyl ethers are more reactive than the allylic methyl ethers, and (3) amines with higher nitrogen basicity lead to lower reactivity in this iron-catalyzed reaction.

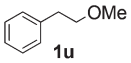
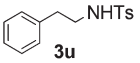
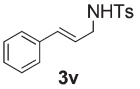
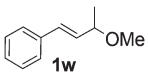
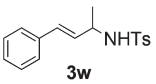
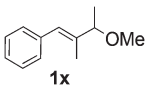
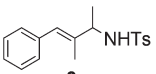
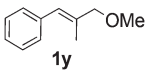
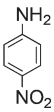
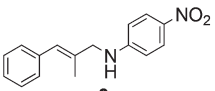
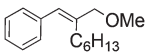
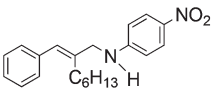
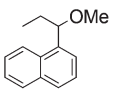
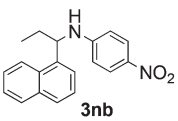
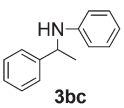
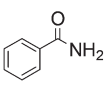
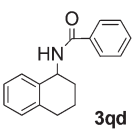
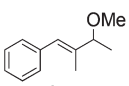
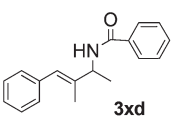
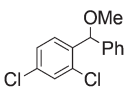
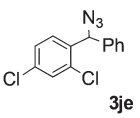
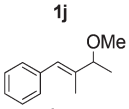
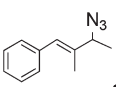
With respect to the reaction mechanism, an elimination–hydroamidation pathway could be ruled out,[12] since both primary benzylic methyl ether and benzhydrylic methyl ethers served as suitable reaction components in this transformation (Table 1, entry 2, and Table 2, entries 1, 5, 8 and 11). The reaction most likely proceeded *via* an S_N1-type substitution process. In order to verify this proposal, (*R*)-(1-methoxyethyl)-benzene ((*R*)-**1b**, >97% ee) was prepared from commercially available (*R*)-1-phenylethanol (>97% ee), and then treated with toluenesulfonamide (**2a**) under the typical reaction conditions (Scheme 1). After 1 h, the product **3b** was isolated in 73% yield in racemic form. This result suggests that a benzylic cation intermediate was generated from (*R*)-**1b** through iron-catalyzed C_{sp^3}–O etheric bond cleavage. Furthermore, considering that the aniline **2c**, which was more nucleophilic than 4-nitroaniline **2b**, could not react as a nucleophile in this reaction

Table 2 Reaction of benzylic ethers with *p*-toluenesulfonamide[a]

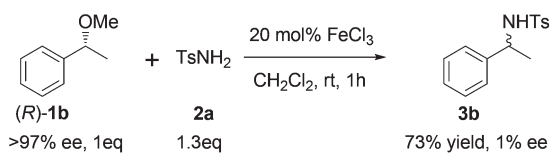
Entry	Ether	Product	T (°C)/t (h)	Yield[b] (%)
1	 **1c**	 **3c**	rt/2	96
2	 **1d**	 **3d**	rt/2	88
3	 **1e**	 **3e**	rt/0.5	90
4	 **1f**	 **3f**	rt/0.2	70
5	 **1g**	 **3g**	rt/1.5	71
6	 **1h**	 **3h**	40/12	52
7	 **1i**	 **3i**	40/12	61
8	 **1j**	 **3j**	40/3	98
9	 **1k**	 **3k**	rt/0.8	81
10	 **1l**	 **3l**	rt/0.8	83
11[c]	 **1m**	 **3m**	rt/1	63
12	 **1n**	 **3n**	rt/1	98
13	 **1o**	 **3o**	rt/1	80
14	 **1p**	 **3p**	rt/1	74
15	 **1q**	 **3q**	rt/0.25	74
16	 **1r**	 **3r**	40/7.5	32
17	 **1s**	 **3s**	rt/0.3	67
18	 **1t**	 **3t**	rt/0.3	62

[a] Reaction conditions: benzylic ether (0.35 mmol), $TsNH_2$ (0.46 mmol), DCM (4 mL), $FeCl_3$ (20 mol%), under argon. [b] Isolated yield. [c] 10 mol% $FeCl_3$.

Table 3 Reaction of *p*-toluenesulfonamide, aniline, 4-nitroaniline, benzamide and trimethylsilyl azide with various ethers[a]

Entry	Ether	Amine	Product	*T* (°C)/*t* (h)	Yield[b] (%)
1	 **1u**	$TsNH_2$ **2a**	 **3u**	40/8	n.r.
2[c]	 **1v**	**2a**	 **3v**	40/15	55
3	 **1w**	**2a**	 **3w**	rt/1	61
4	 **1x**	**2a**	 **3x**	rt/1	63
5	 **1y**	 **2b**	 **3y**	rt/1	71
6	 **1z**	**2b**	 **3z**	rt/22	47
7	 **1n**	**2b**	 **3nb**	rt/8	85
8	 **1b**	 **2c**	 **3bc**	40/8	n.r.
9	 **1q**	 **2d**	 **3qd**	40/4	Trace
10	 **1x**	**2d**	 **3xd**	40/8	Trace
11	 **1j**	$TMSN_3$ **2e**	 **3je**	rt/3	87
12	 **1x**	**2e**	 **3xe**	rt/2.5	82

[a] Reaction conditions: benzylic ether (0.35 mmol), $TsNH_2$ (0.46 mmol), DCM (4 mL), $FeCl_3$ (20 mol%), under argon. [b] Isolated yield. [c] In dioxane.

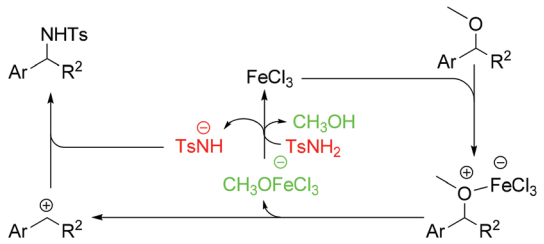


Scheme 1 *N*-Alkylation of **2a** with (*R*)-**1b**.

(Table 3, entries 7 and 8), we assume that an amino anion, rather than amine itself, acts as a nucleophile in this iron-catalyzed *N*-alkylation reaction. In light of the above results, a mechanism for this reaction was proposed in Scheme 2.

Conclusions

In summary, we have developed a new iron-catalyzed *N*-alkylation reaction using π-activated benzylic and allylic ethers as electrophiles, which provides an alternative method for the synthesis of nitrogen-containing compounds. In addition, the



Scheme 2 Proposed mechanism.

reaction pathway was also proposed based on the preliminary mechanistic study and experimental results. Further exploration of the oxygen-containing compounds as electrophiles in organic synthesis is in progress in our laboratory.

Experimental

General

Reactions were monitored by analytical TLC using ultraviolet light and phosphomolybdic acid for visualization. All organic solvents were dried and freshly distilled before use. Purification of products was accomplished by flash chromatography on silica gel (200–300 mesh) and the purified compounds show a single spot by analytical TLC. NMR spectra were recorded on Bruker Avance-III 400 and Varian Mercury 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) nuclear magnetic resonance spectrometers. $CDCl_3$ was used as the solvent with TMS as an internal standard. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz) respectively. HRMS (ESI) analysis was measured on a Bruker APEX II (ESI) mass spectrometer. Melting points were measured on a micro melting apparatus and uncorrected.

General procedure for iron-catalyzed *N*-alkylation

To a stirred solution of (1-methoxyethyl)benzene **1b** (47.7 mg, 0.35 mmol, 1 equiv.) in 4 mL anhydrous CH_2Cl_2 under argon was added *p*-toluenesulfonamide **2a** (77.9 mg, 0.455 mmol) and $FeCl_3$ (11.4 mg, 0.07 mmol, 20 mol%) successively at room temperature. After stirring at room temperature for 1 h (monitored by TLC), the reaction was quenched by addition of H_2O (3 mL) and then extracted with ethyl acetate (3 × 3 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 6 : 1) to afford the corresponding amidation product **3b**.

Characterization data for all new compounds

***N*-(1-(2,4-Dichlorophenyl)propyl)-4-methylbenzenesulfonamide (3h).** White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, J = 8.2, 1.5 Hz, 2H), 7.16–6.99 (m, 5H), 5.82–5.66 (m, 1H), 4.67–4.60 (m, 1H), 2.37 (s, 3H), 1.74–1.68 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.32, 136.99, 133.27, 132.94, 129.24, 129.07, 127.11, 126.96, 56.03, 29.42, 21.37, 10.19. HRMS (ESI): $(M + NH_4)^+$ $C_{16}H_{21}Cl_2N_2O_2S$, Calcd 375.0701, found 375.0695. m.p. 153–154 °C.

***N*-(1-(2,4-Dichlorophenyl)but-3-enyl)-4-methylbenzenesulfonamide (3i).** White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.56 (m, 2H), 7.24–7.12 (m, 4H), 7.06 (dd, J = 8.4, 2.1 Hz, 1H), 5.52–5.39 (m, 1H), 5.17–5.04 (m, 3H), 4.74 (dd, J = 13.8, 6.1 Hz, 1H), 2.45–2.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.51, 136.53, 133.46, 132.66, 132.27, 129.33, 129.12, 127.07, 119.77, 53.51, 40.09, 21.41. HRMS (ESI): $(M + Na)^+$ $C_{17}H_{17}Cl_2NNaO_2S$, Calcd 392.0255, found 392.0249. m.p. 132–133 °C.

***N*-(1-(Benzo[*d*][1,3]dioxol-5-yl)propyl)-4-methylbenzenesulfonamide (3k).** White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.62–6.41 (m, 3H), 5.85 (d, J = 7.3 Hz, 2H), 5.43 (d, J = 6.5 Hz, 1H), 4.08 (q, J = 7.1 Hz, 1H), 2.36 (s, 3H), 1.77 (dt, J = 14.1, 7.1 Hz, 1H), 1.68–1.59 (m, 1H), 0.76 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.45, 146.58, 142.75, 137.71, 134.64, 129.11, 127.01, 120.28, 107.79, 106.80, 100.85, 59.68, 30.42, 21.37, 10.44. m.p. 91–92 °C.

***N*-(1-(Benzo[*d*][1,3]dioxol-5-yl)pentyl)-4-methylbenzenesulfonamide (3l).** White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.54 (dd, J = 37.6, 7.9 Hz, 2H), 6.44 (s, 1H), 5.87 (d, J = 7.5 Hz, 2H), 4.93 (s, 1H), 4.16 (t, J = 7.2 Hz, 1H), 2.37 (s, 3H), 1.77–1.68 (m, 1H), 1.61 (dd, J = 7.5, 5.5 Hz, 1H), 1.22 (dt, J = 33.3, 14.5 Hz, 4H), 1.06 (dd, J = 12.1, 7.0 Hz, 1H), 0.80 (dd, J = 13.7, 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.52, 146.63, 142.81, 137.69, 134.89, 129.12, 127.04, 120.18, 107.85, 106.70, 100.89, 58.13, 37.17, 27.92, 22.12, 21.37, 13.77. HRMS (ESI): $(M + Na)^+$ $C_{19}H_{23}NNaO_4S$, Calcd 384.1245, found 384.1240. m.p. 97–98 °C.

4-Methyl-*N*-(1-(naphthalen-1-yl)pentyl)benzenesulfonamide (3o). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 5.3 Hz, 1H), 7.78–7.71 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 7.1 Hz, 4H), 7.31–7.20 (m, 2H), 6.84 (d, J = 8.0 Hz, 2H), 5.75 (d, J = 7.1 Hz, 1H), 5.12 (d, J = 6.9 Hz, 1H), 2.20 (s, 3H), 1.88 (dd, J = 14.2, 7.0 Hz, 2H), 1.38–1.29 (m, 1H), 1.23 (dd, J = 13.4, 6.6 Hz, 3H), 0.77 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.60, 137.28, 137.13, 133.63, 130.47, 128.85, 128.71, 127.60, 126.88, 126.05, 125.41, 125.21, 123.91, 122.57, 54.11, 37.24, 28.28, 22.27, 21.27, 13.86. HRMS (ESI): $(M + Na)^+$ $C_{22}H_{25}NNaO_2S$, Calcd 390.1504, found 390.1499. m.p. 131–132 °C.

4-Methyl-*N*-(1-(naphthalen-1-yl)but-3-en-1-yl)benzenesulfonamide (3p). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.6 Hz, 1H), 7.82–7.72 (m, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.51–7.40 (m, 4H), 7.34–7.21 (m, 2H), 6.94 (d, J = 7.9 Hz, 2H), 5.63–5.50 (m, 2H), 5.23 (dd, J = 13.3, 6.6 Hz, 1H), 5.06 (t, J = 14.6 Hz, 2H), 2.62 (t, J = 6.5 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.82, 137.10, 135.90, 133.62, 133.17, 130.17, 128.95, 128.75, 127.75, 126.94, 126.11, 125.40, 125.03, 124.17, 122.36, 119.05, 53.23, 41.17, 21.28. HRMS (ESI): $(M + NH_4)^+$ $C_{21}H_{25}N_2O_2S$, Calcd 369.1637, found 369.1631. m.p. 96–97 °C.

4-Methyl-*N*-(2-phenylpent-4-en-2-yl)benzenesulfonamide (3r). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.2 Hz, 2H), 7.28 (dd, J = 7.7, 1.5 Hz, 2H), 7.21–7.12 (m, 5H), 5.54–5.43 (m, 1H), 5.26 (d, J = 4.0 Hz, 1H), 5.10 (dd, J = 13.3, 6.9 Hz, 2H), 2.69 (dd, J = 13.7, 7.1 Hz, 1H), 2.53 (dd, J = 13.6, 7.4 Hz, 1H), 2.38 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.56, 142.55, 139.86, 132.60, 129.18, 128.00, 126.85, 125.94, 120.00, 60.60, 47.98, 25.59, 21.38. HRMS (ESI): $(M + Na)^+$ $C_{18}H_{21}NNaO_2S$, Calcd 338.1191, found 338.1185. m.p. 83–84 °C.

4-Methyl-*N*-(3-methyl-4-phenylbut-3-en-2-yl)benzenesulfonamide (3x). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.2 Hz, 2H), 7.30–7.15 (m, 5H), 7.01 (d, J = 7.4 Hz, 2H), 6.25 (s, 1H), 5.03 (d, J = 7.2 Hz, 1H), 4.10–4.00 (m, 1H), 2.36 (s, 3H), 1.56 (s, 3H), 1.28 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.09, 137.87, 137.23, 137.00, 129.40, 128.81, 127.91, 127.29, 126.79, 126.46, 57.26, 21.40, 20.71, 13.12. HRMS (ESI): $(M + Na)^+$ $C_{18}H_{21}NNaO_2S$, Calcd 338.1191, found 338.1185. m.p. 101–102 °C.

***N*-(2-Methyl-3-phenylallyl)-4-nitroaniline (3y).** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 9.2 Hz, 2H), 7.35–7.32 (m, 2H), 7.25–7.21 (m, 3H), 6.60 (d, J = 9.2 Hz, 2H), 6.49 (s, 1H), 4.86 (s, 1H), 3.94 (d, J = 5.8 Hz, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.39, 138.22, 137.09, 133.61, 128.80, 128.22, 126.71, 126.55, 126.39, 111.35, 51.44, 16.20. HRMS (ESI): $(M + H)^+$ $C_{16}H_{17}N_2O_2$, Calcd 269.1290, found 269.1285. m.p. 114–115 °C.

***N*-(2-Benzylideneoctyl)-4-nitroaniline (3z).** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 9.1 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 7.5 Hz, 2H), 6.59 (d, J = 9.1 Hz, 2H), 6.48 (s, 1H), 4.77 (s, 1H), 3.95 (d, J = 5.7 Hz, 2H), 2.31–2.26 (m, 2H), 1.29 (dd, J = 17.0, 7.8 Hz, 8H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.25, 138.10, 128.46, 128.16, 126.57, 126.29, 111.25, 49.14, 31.46, 29.52, 29.34, 28.30, 22.50, 13.96. HRMS (ESI): $(M + H)^+$ $C_{21}H_{27}N_2O_2$, Calcd 339.2073, found 339.2067. m.p. 74–75 °C.

***N*-(1-(Naphthalen-1-yl)propyl)-4-nitroaniline (3nb).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 1H), 7.91 (t, J = 9.4 Hz, 3H), 7.74 (d, J = 8.1 Hz, 1H), 7.60–7.50 (m, 2H), 7.45 (d, J = 7.1 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 6.40 (d, J = 9.0 Hz, 2H), 5.20–5.13 (m, 2H), 2.17–2.05 (m, 1H), 1.95–1.87 (m, 1H), 1.06 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.74, 137.98, 137.16, 134.15, 130.78, 129.41, 128.08, 126.50, 126.29, 125.78, 125.61, 122.80, 122.10, 111.86, 55.36, 30.37, 11.11. HRMS (ESI): $(M + H)^+$ $C_{19}H_{19}N_2O_2$, Calcd 307.1447, found 307.1441.

1-(1-Azido-1-phenylmethyl)-2,4-dichlorobenzene (3je). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 1.8 Hz, 1H), 7.36–7.26 (m, 6H), 6.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.68, 135.95, 134.43, 133.65, 129.62, 129.56, 128.79, 128.42, 127.51, 64.43.

4-Phenyl-3-methyl-3-buten-2-yl azide (3xe). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, J = 7.5 Hz, 2H), 7.30–7.22 (m, 3H), 6.51 (s, 1H), 4.16 (q, J = 6.8 Hz, 1H), 1.89 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.91, 136.73, 129.08, 128.37, 128.19, 127.79, 126.83, 65.47, 18.66, 13.64.

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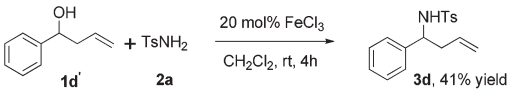
16 A control experiment was also conducted using alcohol **1d′** and *p*-toluenesulfonamide (**2a**) as substrates under the optimized reaction conditions, the desired product **3d** was obtained in 41% yield. This experimental result suggests that ethers are more suitable substrates for this transformation (Table 2, entry 2).



17 With sodium azide as the nucleophile instead of trimethylsilyl azide, the reaction could not occur.

18 Higher catalyst loading (30 mol% $FeCl_3$) and reaction temperature (90 °C) were used in this transformation, but no product was obtained.