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$FeCl_3$/NaI-Catalyzed Allylic C−H Oxidation of Arylalkenes with a Catalytic Amount of Disulfide under Air

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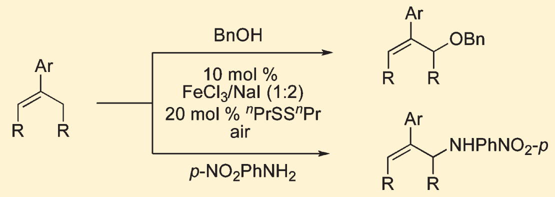
S *Supporting Information*

ABSTRACT: This paper describes a $FeCl_3$/NaI-catalyzed formal allylic C−H oxidation of arylalkenes using a catalytic amount of disulfide with BnOH and 4-nitroaniline as nucleophiles and air as oxidant to form the corresponding allyl ethers and amines. A possible reaction mechanism has been proposed.



Allylic C−H oxidation provides an important approach to functionalize olefins. While various systems have been developed,[1−6] there are still challenges, and new processes need to be explored. Recently, we reported a mild acid-catalyzed formal allylic C−H oxidation of aryl cycloalkenes with *N*-propylthiosuccinimide in the presence of various nucleophiles, providing allyl ethers, esters, and sulfonamides (Scheme 1).[7] However, this process requires 2.2 equiv of *N*-propylthiosuccinimide and generates a substantial amount of succinimide and disulfide as byproduct, which prompted us to develop a new process requiring only a catalytic amount of sulfur reagent. Along this line, we have been investigating the possibility of replacing *N*-propylthiosuccinimide with a disulfide to mediate the allylic C−H oxidation process while the disulfide can be regenerated in situ by an oxidant.[8,9] During our studies, we found that the allylic C−H oxidation can be achieved using a catalytic amount of disulfide and $FeCl_3$/NaI with air as oxidant (Scheme 2). Herein we report our studies on this subject.

Initial studies were carried out with 1-phenylcyclohexene as substrate and BnOH as nucleophile. After some screenings, it was found that the allyl ether product was formed in the presence of a catalytic amount of disulfide with $FeCl_3$/NaI as catalyst and air as oxidant (Table 1).[10,11] Among the disulfides studied, ^{n}PrSS^{n}Pr appears to be more effective, giving the allyl benzyl ether in 79% yield (Table 1, entry 1). Other Fe species such as $FeCl_3 \cdot 6H_2O$, FeF_3, $FeBr_3$, and $FeCl_2$ can also catalyze this reaction, giving the product in 45−73% yield (Table 1, entries 6−9), but no reaction was observed with $Fe(acac)_3$ (Table 1, entry 10). Studies showed that both $FeCl_3$ and iodide sources are required for the reaction (Table 1, entries 11, 12) with NaI being the most effective cocatalyst (Table 1, entries 1, 13−15). Further studies showed that other alcohols can also be employed to form the corresponding allyl ethers in moderate yields (Table 1, entries 16−19). Among various nitrogen nucleophiles examined, 4-nitroaniline was found to be effective, giving the corresponding allyl amine in 86% yield (Table 1, entry 20).

The substrate scope was subsequently examined with BnOH and 4-nitroaniline as nucleophiles. As shown in Table 2, various substituted 1-phenylcyclohexenes (**1a**−**e**), 1-naphthylcyclohexene (**1f**), 1-(3-thiophene-yl)cyclohexene (**1g**), 1-phenylcycloheptene (**1h**), and 1-phenylcyclopentene (**1i**) were found to be suitable substrates for the reaction, producing the corresponding allyl ethers and amines in 50−86% yields (Table 2, entries 1−9). The oxidation reaction can also be extended to acyclic olefins (Table 2, entries 10−12). The oxidation appears to be highly stereoselective, giving the corresponding allyl ethers and amines with high *E*/*Z* ratio regardless of the geometry of olefin substrates.

When the reaction was monitored by ^{1}H NMR, compounds **6a** and **7a** were detected along with allyl ether **4a** during the reaction process (Scheme 3). When preformed compound **6a** was treated with $FeCl_3$ (10 mol %), NaI (20 mol %), and ^{n}PrSS^{n}Pr (20 mol %) in $CHCl_3$ at 60 °C for 18 h, allyl ether **4a** was formed with a small amount of allyl sulfide **7a** (Scheme 4). When preformed compound **7a** was subjected to the reaction conditions, it was readily converted to allyl ether **4a** (Scheme 5). These results indicate that compounds **6a** and **7a** are likely to be the intermediates involved in the reaction pathway. Control studies showed that the transformations described in Scheme 4 and 5 require $FeCl_3$ and are facilitated by NaI. No reaction occurred without $FeCl_3$. In the absence of NaI, the reaction proceeded at a slower rate with more byproduct.

When deuterium-labeled 1-phenylcyclohexene (**1l**:**1m** = 80:20) was subjected to the reaction conditions, compounds **8** and **9** were obtained as a 1:1 mixture with the remaining **1l** and **1m** being 70:30 (Scheme 6). Since compound **1l** could slowly convert to **1m** under the reaction conditions, the reaction was

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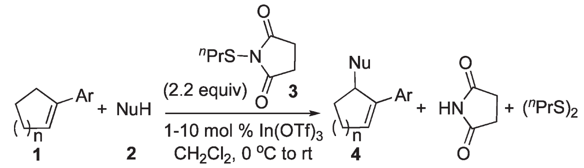
Scheme 1



Scheme 2

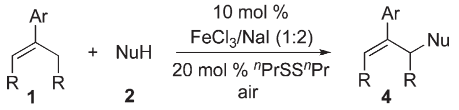
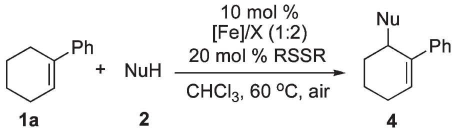


Table 1. Studies on Reaction Conditions and Nucleophiles[a]



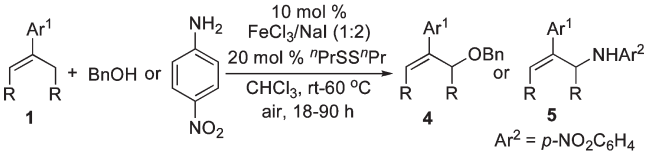
entry	NuH	catalyst	RSSR	time (h)	yield (%)
1	**BnOH**	**FeCl$_3$/NaI**	**^{n}PrSS^{n}Pr**	**18**	**79**
2	BnOH	FeCl$_3$/NaI	PhSSPh	18	69
3	BnOH	FeCl$_3$/NaI	BnSSBn	18	50
4	BnOH	FeCl$_3$/NaI	PhSeSePh	18	38
5	BnOH	FeCl$_3$/NaI		18	14
6	BnOH	FeCl$_3$•6H$_2$O/NaI	^{n}PrSS^{n}Pr	18	73
7	BnOH	FeF$_3$/NaI	^{n}PrSS^{n}Pr	18	45
8	BnOH	FeBr$_3$/NaI	^{n}PrSS^{n}Pr	18	72
9	BnOH	FeCl$_2$/NaI	^{n}PrSS^{n}Pr	18	68
10	BnOH	Fe(acac)$_3$/NaI	^{n}PrSS^{n}Pr	18	NR
11	BnOH	FeCl$_3$	^{n}PrSS^{n}Pr	18	trace
12	BnOH	NaI	^{n}PrSS^{n}Pr	18	NR
13	BnOH	FeCl$_3$/KI	^{n}PrSS^{n}Pr	18	54
14[b]	BnOH	FeCl$_3$/I$_2$	^{n}PrSS^{n}Pr	18	43
15	BnOH	FeCl$_3$/NIS	^{n}PrSS^{n}Pr	18	49
16	MeOH	FeCl$_3$/NaI	^{n}PrSS^{n}Pr	35	43
17	*i*-PrOH	FeCl$_3$/NaI	^{n}PrSS^{n}Pr	23	53
18	*n*-BuOH	FeCl$_3$/NaI	^{n}PrSS^{n}Pr	26	62
19	Cl(CH$_2$)$_3$OH	FeCl$_3$/NaI	^{n}PrSS^{n}Pr	18	71
20	4-nitroaniline	FeCl$_3$/NaI	^{n}PrSS^{n}Pr	18	86

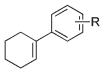
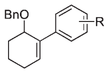
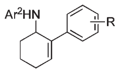
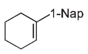
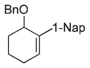
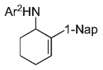
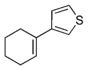
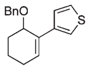
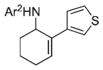
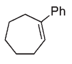
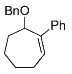
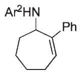
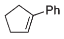
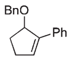
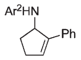
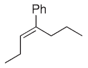
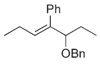
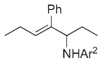
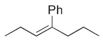
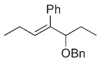
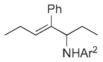
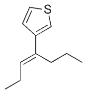
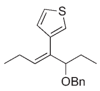
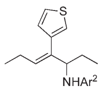
[a] The reaction was carried out with **1a** (0.5 mmol), NuH (1.0 mmol), FeCl$_3$ (10 mol %), X (20 mol %), and RSSR (20 mol %) in CHCl$_3$ (0.5 mL) at 60 °C under air unless otherwise stated. [b] 10 mol % of I$_2$ was used.

stopped with partial conversion so that the ratio of the remaining **1l** and **1m** could be determined.

While a precise understanding of the reaction mechanism for the FeCl$_3$/NaI-catalyzed allylic C–H oxidation awaits further studies, a plausible catalytic pathway is proposed in Scheme 7.[7] The disulfide initially reacts with the olefin to generate thiiranium ion **10** with the assistance of FeCl$_3$/NaI.[8,9c] Thiiranium ion **10** is subsequently converted to allyl sulfide **12** directly or via compound

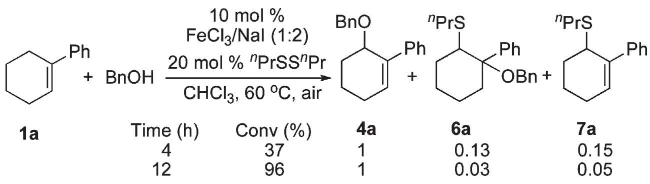
Table 2. Allylic Oxidation of Arylalkenes[a]



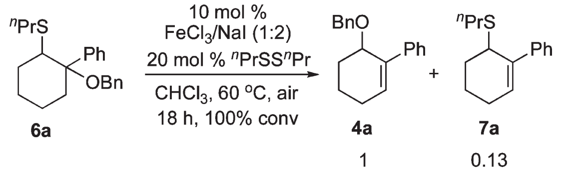
Entry	Substrate	4, Yield (%)[b]	5, Yield (%)[b]
			
1	**1a**, R = H	**4a**, 79	**5a**, 86
2[c]	**1b**, R = *o*-OMe	**4b**, 67	**5b**, 64
3	**1c**, R = *m*-OMe	**4c**, 57	**5c**, 70
4[c]	**1d**, R = *p*-OMe	**4d**, 77	**5d**, 71
5	**1e**, R = *p*-Br	**4e**, 76	**5e**, 81
6	 **1f**	 **4f**, 75	 **5f**, 73
7[c]	 **1g**	 **4g**, 66	 **5g**, 58
8	 **1h**	 **4h**, 62	 **5h**, 82
9[d]	 **1i**	 **4i**, 60	 **5i**, 50
10	 **1j** *E*/*Z* = 5/1	 **4j**, 64 *E*/*Z* = 95/5	 **5j**, 49 *E*/*Z* > 98/2
11	 **1j’** E/Z = 1/12	 **4j**, 60 *E*/*Z* = 95/5	 **5j**, 61 *E*/*Z* > 98/2
12	 **1k** *E*/*Z* = 10/1	 **4k**, 70 *E*/*Z* = 95/5	 **5k**, 52 *E*/*Z* > 98/2

[a] The reactions were carried out with **1** (0.5 mmol), BnOH or *p*-NO$_2$C$_6$H$_4$NH$_2$ (1.0 mmol), FeCl$_3$ (10 mol %), NaI (20 mol %), and ^{n}PrSS^{n}Pr (20 mol %) in CHCl$_3$ (0.5 mL) at 60 °C under air unless otherwise stated. [b] *E*/*Z* ratios were determined by the ^{1}H NMR analysis of the crude reaction mixture. [c] At 40 °C. [d] At rt.

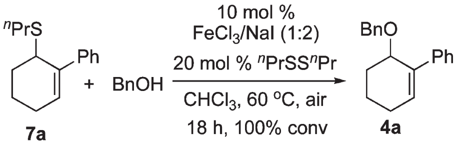
Scheme 3



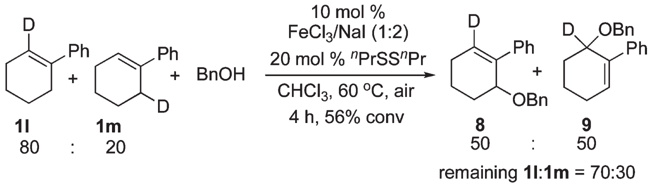
Scheme 4



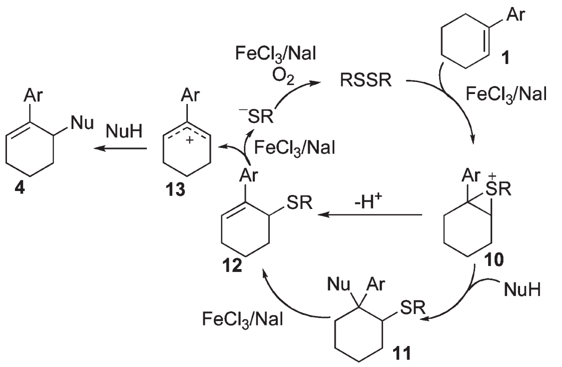
Scheme 5



Scheme 6



Scheme 7. Proposed Catalytic Pathway



11 under the reaction conditions. Allyl cation **13** is then generated from allyl sulfide **12** by FeCl$_3$/NaI and reacts with the nucleophile to give product **4**. The disulfide is finally regenerated by oxidation of the thiolate with FeCl$_3$/NaI and air.[12] FeCl$_3$/NaI plays multiple roles in the catalytic cycle. It promotes the addition of disulfide to the olefin, the formation of allyl sulfide and allyl cation, and the regeneration of disulfide.[9c]

In summary, we have developed a FeCl$_3$/NaI-catalyzed formal allylic C−H oxidation of arylalkenes using a catalytic amount of disulfide with air as oxidant. Various arylalkenes can be oxidized to form allyl ethers and amines with BnOH and 4-nitroaniline as nucleophiles. In the case of acyclic alkenes, the reaction is highly stereoslective, giving the product with a high E/Z ratio. FeCl$_3$/NaI plays a crucial role in the catalytic cycle. The Fe(III) species acts as both Lewis acid and oxidant. The current process provides a new entry to the allylic C−H oxidation.

■ EXPERIMENTAL SECTION

General Methods. All commercially available reagents were used without further purification. All dry solvents were freshly distilled under nitrogen from appropriate drying agents before use. Toluene, tetrahydrofuran, and ethyl ether were distilled from sodium benzophenone. CH$_2$Cl$_2$, 1,2-DCE and MeCN were distilled from CaH$_2$. CHCl$_3$ was distilled from P$_2$O$_5$. Column chromatography was performed on silica gel (200−300 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer, and ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on an FT-IR spectrometer. Melting points were uncorrected. 1-Phenylcyclohexene (**1a**) was purchased from a commercial supplier. Cycloalkenes **1b**−**f**,**h**,**i**, and acyclic alkene **1j** (E/Z = 5/1) were prepared from the corresponding alkanones by the addition of appropriate Grignard reagents and subsequent dehydration with HCO$_2$H, CF$_3$CO$_2$H, or p-TsOH. Alkenes **1g** and **1k** (E/Z = 10/1) were prepared according to the reported procedure.[13] Acyclic alkene **1j**′ (E/Z = 1/12) was prepared by Wittig reaction of 1-phenylbutan-1-one and propyltriphenylphosphonium bromide.

Representative Procedure for Allylic C−H Oxidation (Table 2, Entry 1). **4a**: To a Schlenk tube charged with condenser were added FeCl$_3$ (0.0081 g, 0.050 mmol), NaI (0.015 g, 0.10 mmol), CHCl$_3$ (0.5 mL), BnOH (0.108 g, 1.0 mmol), 1-phenylcyclohexene (0.079 g, 0.50 mmol), and ^{n}PrSS^{n}Pr (0.015 g, 0.10 mmol). The resulting mixture was stirred at 60 °C for 18 h under air, quenched with 10% aqueous Na$_2$S$_2$O$_3$ (5 mL), extracted with CH$_2$Cl$_2$ (3 × 10 mL), washed with brine (10 mL), dried over MgSO$_4$, filtered, concentrated, and purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 200/1) to give allyl ether **4a** as a pale yellow oil (0.104 g, 79%). [Reaction time: **4a**, **4c** (18 h); **4d**, **4f** (24 h); **4b** (26 h); **4g**, **4h** (30 h); **4i** (43 h); **4e**, **4k** (48 h); **4j** (90 h).]

5a: To a Schlenk tube charged with condenser were added FeCl$_3$ (0.0081 g, 0.050 mmol), NaI (0.015 g, 0.10 mmol), 4-nitroaniline (0.138 g, 1.0 mmol), CHCl$_3$ (0.5 mL), 1-phenylcyclohexene (0.079 g, 0.50 mmol), and ^{n}PrSS^{n}Pr (0.015 g, 0.10 mmol). The resulting mixture was stirred at 60 °C for 18 h under air, quenched with 10% aqueous Na$_2$S$_2$O$_3$ (5 mL), extracted with CH$_2$Cl$_2$ (3 × 10 mL), washed with brine (10 mL), dried over MgSO$_4$, filtered, concentrated, and purified by flash chromatography (silica gel, petroleum ether/ethyl acetate =10/1) to give allyl amine **5a** as yellow solid (0.127 g, 86%). [Reaction time: **5a** (18 h); **5c**, **5d**, **5f**, **5 h** (24 h); **5b**, **5g** (30 h); **5e**, **5i**, **5k** (48 h); **5j** (90 h).]

*6-Benzyloxy-1-phenylcyclohexene (**4a**)*:[7] pale yellow oil; IR (film) 1494, 1453, 1067 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38−7.32 (m, 2H), 7.30−7.14 (m, 8H), 6.17 (dd, J = 4.4, 3.6 Hz, 1H), 4.58 (d, J = 11.6 Hz, 1H), 4.46 (d, J = 11.6 Hz, 1H), 4.42−4.37 (m, 1H), 2.33−2.23 (m, 1H), 2.22−2.08 (m, 2H), 1.94−1.81 (m, 1H), 1.71−1.59 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.5, 138.8, 137.8, 129.8, 128.3, 128.2, 128.0, 127.5, 126.8, 126.2, 72.6, 70.7, 27.3, 26.2, 17.3.

*6-(4-Nitrophenylamino)-1-phenylcyclohexene (**5a**)*: yellow solid; mp 148−150 °C; IR (film) 3373, 1599, 1313, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 9.2 Hz, 2H), 7.38−7.20 (m, 5H), 6.54 (d, J = 9.2 Hz, 2H), 6.40 (dd, J = 4.4, 3.6 Hz, 1H), 4.63−4.50 (m, 2H), 2.40−2.18 (m, 2H), 2.16−2.07 (m, 1H), 1.85−1.60 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.3, 139.6, 138.1, 136.0, 130.2, 128.8, 127.6, 126.8, 125.5, 111.4, 48.3, 27.9, 26.0, 17.4. Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.35; H, 6.21; N, 9.48.

6-Benzyloxy-1-(2-methoxyphenyl)cyclohexene (**4b**):[7] white solid; mp 46−47 °C; IR (film) 1597, 1489, 1453, 1243, 1066 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26−7.18 (m, 2H), 7.16−7.11 (m, 3H), 6.97−6.89 (m, 3H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.86 (dd, *J* = 3.6, 3.2 Hz, 1H), 4.52−4.47 (m, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.62 (s, 3H), 2.27−2.09 (m, 2H), 2.02−1.92 (m, 1H), 1.92−1.77 (m, 2H), 1.71−1.60 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.9, 139.4, 138.8, 131.7, 131.2, 130.5, 128.1, 127.7, 127.1, 120.8, 110.5, 72.9, 70.8, 55.3, 28.0, 26.0, 18.3.

6-(4-Nitrophenylamino)-1-(2-methoxyphenyl)cyclohexene (**5b**). yellow solid; mp 124−126 °C; IR (film) 3378, 1598, 1310, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 9.2 Hz, 2H), 7.24−7.18 (m, 1H), 7.13−7.08 (m, 1H), 6.89 (t, *J* = 3.2 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 9.2 Hz, 2H), 5.93 (dd, *J* = 3.6, 3.2 Hz, 1H), 4.74 (d, *J* = 7.6 Hz, 1H), 4.65−4.58 (m, 1H), 3.74 (s, 3H), 2.30−2.15 (m, 2H), 2.05−1.94 (m, 1H), 1.92−1.83 (m, 1H), 1.85−1.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.8, 153.1, 137.5, 137.0, 131.4, 130.7, 130.6, 128.9, 126.6, 121.0, 111.2, 110.8, 55.6, 50.8, 28.9, 25.7, 18.7. Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.21; H, 6.37; N, 8.34.

6-Benzyloxy-1-(3-methoxyphenyl)cyclohexene (**4c**):[7] pale yellow oil; IR (film) 1598, 1453, 1285, 1051 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28−7.17 (m, 6H), 6.96−6.92 (m, 2H), 6.80−6.76 (m, 1H), 6.18 (dd, *J* = 4.4, 3.2 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.40−4.36 (m, 1H), 3.75 (s, 3H), 2.34−2.24 (m, 1H), 2.23−2.08 (m, 2H), 1.95−1.82 (m, 1H), 1.71−1.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.7, 143.3, 138.9, 137.9, 130.2, 129.2, 128.4, 128.0, 127.5, 118.8, 112.6, 111.8, 72.8, 70.9, 55.3, 27.4, 26.2, 17.3.

6-(4-Nitrophenylamino)-1-(3-methoxyphenyl)cyclohexene (**5c**): yellow solid; mp 98−101 °C; IR (film) 3372, 1598, 1306, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, *J* = 9.2 Hz, 2H), 7.23−7.17 (m, 1H), 6.97−6.92 (m, 1H), 6.90−6.88 (m, 1H), 6.82−6.76 (m, 1H), 6.55 (d, *J* = 9.2 Hz, 2H), 6.40 (dd, *J* = 4.4, 3.6 Hz, 1H), 4.59−4.52 (m, 2H), 3.73 (s, 3H), 2.39−2.18 (m, 2H), 2.14−2.04 (m, 1H), 1.84−1.60 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.0, 152.3, 141.3, 138.2, 136.0, 130.5, 129.8, 126.8, 118.0, 112.8, 111.7, 111.4, 55.4, 48.5, 28.0, 26.0, 17.4. Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.61; H, 6.38; N, 8.24.

6-Benzyloxy-1-(4-methoxyphenyl)cyclohexene (**4d**):[7] pale yellow oil; IR (film) 1607, 1511, 1453, 1248, 1038 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32−7.18 (m, 7H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.10 (dd, *J* = 4.4, 3.6 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.39−4.34 (m, 1H), 3.80 (s, 3H), 2.32−2.09 (m, 3H), 1.93−1.80 (m, 1H), 1.70−1.59 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.7, 138.9, 137.2, 134.2, 128.5, 128.4, 128.1, 127.5, 127.2, 113.7, 72.7, 70.7, 55.4, 27.3, 26.2, 17.4.

6-(4-Nitrophenylamino)-1-(4-methoxyphenyl)cyclohexene (**5d**): yellow solid; mp 103−106 °C; IR (film) 3371, 1598, 1304, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, *J* = 9.2 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 9.2 Hz, 2H), 6.30 (dd, *J* = 4.4, 3.6 Hz, 1H), 4.56−4.51 (m, 2H), 3.77 (s, 3H), 2.37−2.17 (m, 2H), 2.14−2.06 (m, 1H), 1.83−1.59 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.2, 152.4, 138.1, 135.4, 132.1, 128.4, 126.8, 126.6, 114.2, 111.4, 55.5, 48.4, 27.9, 26.0, 17.4. Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.41; H, 6.14; N, 8.30.

6-Benzyloxy-1-(4-bromophenyl)cyclohexene (**4e**):[7] white solid; mp 47−48 °C; IR (film) 1453, 1142, 1071 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39−7.35 (m, 2H), 7.30−7.17 (m, 7H), 6.17 (dd, *J* = 4.4, 3.2 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.35−4.31 (m, 1H), 2.34−2.08 (m, 3H), 1.93−1.80 (m, 1H), 1.71−1.61 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.5, 138.6, 137.0, 131.3, 130.6, 128.5, 128.2, 127.9, 127.7, 120.7, 72.4, 70.7, 27.2, 26.3, 17.3.

6-(4-Nitrophenylamino)-1-(4-bromophenyl)cyclohexene (**5e**): yellow solid; mp 130−133 °C; IR (film) 3372, 1598, 1313, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, *J* = 9.2 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 9.2 Hz, 2H), 6.39 (dd, *J* = 4.4, 3.2 Hz, 1H), 4.56−4.47 (m, 2H), 2.38−2.17 (m, 2H), 2.14−2.06 (m, 1H), 1.84−1.60 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.1, 138.6, 138.3, 135.2, 131.9, 130.9, 127.2, 126.8, 121.5, 111.4, 48.2, 27.8, 26.0, 17.3. Anal. Calcd for $C_{18}H_{17}BrN_2O_2$: C, 57.92; H, 4.59; N, 7.51. Found: C, 57.75; H, 4.67; N, 7.13.

6-Benzyloxy-1-(1-naphthyl)cyclohexene (**4f**):[7] pale yellow oil; IR (film) 1453, 1066 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.90−7.86 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.50−7.43 (m, 3H), 7.40−7.37 (m, 1H), 7.15−7.05 (m, 3H), 6.90−6.85 (m, 2H), 5.95 (t, *J* = 3.6 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.27−4.22 (m, 1H), 4.16 (d, *J* = 12.0 Hz, 1H), 2.42−2.32 (m, 1H), 2.30−2.13 (m, 2H), 2.08−1.87 (m, 2H), 1.83−1.73 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.8, 138.9, 138.2, 133.9, 132.4, 131.8, 128.3, 128.1, 127.6, 127.2, 127.1, 126.4, 126.2, 125.7, 125.6, 125.4, 75.1, 71.5, 28.4, 25.9, 18.0.

6-(4-Nitrophenylamino)-1-(1-naphthyl)cyclohexene (**5f**): yellow solid; mp 167−171 °C; IR (film) 3372, 1598, 1306, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97−7.93 (m, 1H), 7.88−7.80 (m, 3H), 7.74−7.70 (m, 1H), 7.54−7.44 (m, 2H), 7.38−7.33 (m, 1H), 7.28−7.24 (m, 1H), 6.26 (d, *J* = 9.2 Hz, 2H), 6.04 (t, *J* = 3.6 Hz, 1H), 4.54−4.43 (m, 2H), 2.43−2.25 (m, 2H), 2.12−2.02 (m, 2H), 1.90−1.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.5, 139.4, 137.8, 136.8, 134.0, 133.0, 132.1, 128.9, 127.9, 126.3, 126.04, 125.98, 125.4, 125.0, 111.4, 51.5, 28.6, 25.6, 18.0; HRMS calcd for $C_{22}H_{20}N_2O_2$ (M$^+$) 344.1525, found 344.1529.

6-Benzyloxy-1-(3-thiophene-yl)cyclohexene (**4g**):[7] yellow oil; IR (film) 1453, 1349, 1068 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35−7.23 (m, 5H), 7.22−7.18 (m, 1H), 7.17−7.14 (m, 1H), 7.08−7.05 (m, 1H), 6.28 (dd, *J* = 4.8, 3.2 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.35−4.31 (m, 1H), 2.33−2.09 (m, 3H), 1.94−1.80 (m, 1H), 1.69−1.57 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.5, 138.7, 132.8, 128.7, 128.4, 128.1, 127.6, 125.8, 124.9, 119.2, 73.0, 70.6, 26.8, 26.0, 17.2.

6-(4-Nitrophenylamino)-1-(3-thiophene-yl)cyclohexene (**5g**): yellow solid; mp 164−166 °C; IR (film) 3381, 1599, 1307, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, *J* = 9.2 Hz, 2H), 7.28−7.24 (m, 1H), 7.20−7.17 (m, 1H), 7.05−7.02 (m, 1H), 6.58 (d, *J* = 9.2 Hz, 2H), 6.44 (dd, *J* = 4.4, 3.2 Hz, 1H), 4.64 (d, *J* = 6.8 Hz, 1H), 4.51−4.44 (m, 1H), 2.38−2.17 (m, 2H), 2.15−2.06 (m, 1H), 1.80−1.60 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.3, 141.3, 138.2, 131.4, 128.9, 126.9, 126.1, 125.0, 119.3, 111.3, 49.0, 27.7, 25.7, 17.3. Anal. Calcd for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33. Found: C, 63.93; H, 5.47; N, 9.14.

7-Benzyloxy-1-phenylcycloheptene (**4h**):[7] pale yellow oil; IR (film) 1492, 1444, 1089 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35−7.20 (m, 10H), 6.17 (dd, *J* = 7.6, 6.0 Hz, 1H), 4.52−4.45 (m, 2H), 4.39 (d, *J* = 11.6 Hz, 1H), 2.66−2.56 (m, 1H), 2.25−2.10 (m, 3H), 1.85−1.70 (m, 3H), 1.60−1.48 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.8, 144.0, 139.1, 133.8, 128.4, 128.2, 127.8, 127.4, 126.6, 126.5, 79.3, 70.6, 31.4, 27.8, 27.1, 26.0.

7-(4-Nitrophenylamino)-1-phenylcycloheptene (**5h**): yellow solid; mp 106−107 °C; IR (film) 3384, 1599, 1305, 1111 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 9.2 Hz, 2H), 7.30−7.18 (m, 5H), 6.48 (d, *J* = 9.2 Hz, 2H), 6.13 (t, *J* = 6.8 Hz, 1H), 4.75−4.63 (m, 2H), 2.45−2.37 (m, 2H), 2.23−2.13 (m, 1H), 1.97−1.80 (m, 3H), 1.80−1.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.3, 144.7, 142.9, 138.2, 133.2, 128.6, 127.3, 126.7, 126.4, 111.5, 56.0, 30.6, 28.1, 26.9, 26.0; HRMS calcd for $C_{19}H_{20}N_2O_2$ (M$^+$) 308.1525, found 308.1528.

5-Benzyloxy-1-phenylcyclopentene (**4i**):[7] yellow oil; IR (film) 1496, 1452, 1142, 1068 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52−7.48

(m, 2H), 7.33–7.20 (m, 8H), 6.38 (t, J = 2.4 Hz, 1H), 5.10–5.05 (m, 1H), 4.57 (d, J = 11.6 Hz, 1H), 4.49 (d, J = 11.6 Hz, 1H), 2.73–2.63 (m, 1H), 2.49–2.39 (m, 1H), 2.30–2.18 (m, 1H), 2.17–2.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 138.8, 135.5, 131.3, 128.5, 128.2, 127.7, 127.3, 126.4, 83.9, 69.8, 31.2, 29.9.

5-(4-Nitrophenylamino)-1-phenylcyclopentene (***5i***): yellow solid; mp 127–128 °C; IR (film) 3361, 1599, 1306, 1111 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.8 Hz, 2H), 7.45–7.40 (m, 2H), 7.35–7.29 (m, 2H), 7.29–7.23 (m, 1H), 6.56 (d, J = 8.8 Hz, 2H), 6.49–6.45 (m, 1H), 5.02–4.96 (m, 1H), 4.57 (d, J = 6.8 Hz, 1H), 2.74–2.63 (m, 1H), 2.62–2.52 (m, 1H), 2.51–2.40 (m, 1H), 2.05–1.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 141.8, 138.2, 134.1, 131.4, 129.0, 128.0, 126.7, 126.2, 111.6, 59.1, 31.7, 31.2. Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; Found: C, 72.78; H, 5.83; N, 9.90.

(E)-5-Benzyloxy-4-phenyl-3-heptene (***4j***): pale yellow oil; IR (film) 1454, 1308, 1067 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.20 (m, 8H), 7.17 (d, J = 7.6 Hz, 2H), 5.66 (dd, J = 7.6, 7.2 Hz, 1H), 4.77 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 3.80 (t, J = 6.4 Hz, 1H), 2.06–1.93 (m, 2H), 1.50–1.40 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H), 0.86 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 139.0, 138.7, 133.5, 129.4, 128.5, 128.1, 128.0, 127.6, 126.9, 86.0, 70.1, 27.5, 22.2, 14.8, 10.5; HRMS calcd for $C_{20}H_{24}O$ (M^+) 280.1827, found 280.1831.

(E)-5-(4-Nitrophenylamino)-4-phenyl-3-heptene (***5j***): yellow solid; mp 80–82 °C; IR (film) 3373, 1600, 1307, 1112 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 9.2 Hz, 2H), 7.36–7.27 (m, 3H), 6.98 (d, J = 7.2 Hz, 2H), 6.60 (d, J = 9.2 Hz, 2H), 5.69 (dd, J = 7.6, 7.2 Hz, 1H), 4.38 (d, J = 7.6 Hz, 1H), 3.98 (q, J = 7.2 Hz, 1H), 1.92–1.78 (m, 2H), 1.70–1.47 (m, 2H), 1.04 (t, J = 7.6 Hz, 3H), 0.90 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 138.5, 138.0, 137.9, 133.2, 129.2, 128.3, 127.3, 126.5, 112.0, 61.9, 27.4, 22.2, 14.6, 10.9; HRMS calcd for $C_{19}H_{22}N_2O_2$ (M^+) 310.1681, found 310.1685.

(E)-5-Benzyloxy-4-(3-thiophene-yl)-3-heptene (***4k***): yellow oil; IR (film) 1454, 1377, 1067 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.20 (m, 6H), 7.13–7.10 (m, 1H), 7.04–6.99 (m, 1H), 5.66 (t, J = 7.2 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 3.77 (t, J = 6.8 Hz, 1H), 2.19–2.08 (m, 2H), 1.62–1.35 (m, 2H), 1.01 (t, J = 7.6 Hz, 3H), 0.83 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.9, 134.9, 134.0, 129.1, 128.6, 128.0, 127.6, 124.5, 122.8, 86.3, 69.9, 27.4, 22.5, 14.8, 10.5; HRMS (ESI) calcd for $C_{18}H_{22}OS$ (M + Na) 309.1284, found 309.1284.

(E)-5-(4-Nitrophenylamino)-4-(3-thiophene-yl)-3-heptene (***5k***): yellow oil; IR (film) 3373, 1600, 1308, 1112 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.31–7.27 (m, 1H), 6.90–6.87 (m, 1H), 6.80–6.76 (m, 1H), 6.57 (d, J = 7.6 Hz, 2H), 5.71 (t, J = 7.2 Hz, 1H), 4.48 (d, J = 7.2 Hz, 1H), 3.94 (q, J = 7.2 Hz, 1H), 1.98–1.88 (m, 2H), 1.66–1.52 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 138.2, 137.4, 134.5, 133.8, 128.7, 126.5, 125.4, 122.8, 112.1, 61.8, 27.7, 22.4, 14.6, 11.0; HRMS (ESI) calcd for $C_{17}H_{20}N_2O_2S$ (M + Na) 339.1138, found 339.1140.

6-Methoxy-1-phenylcyclohexene (Table 1, entry 16):[7] pale yellow oil; IR (film) 1455, 1071 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.38 (m, 2H), 7.33–7.27 (m, 2H), 7.26–7.21 (m, 1H), 6.19 (dd, J = 4.4, 3.2 Hz, 1H), 4.18–4.14 (m, 1H), 3.34 (s, 3H), 2.33–2.23 (m, 1H), 2.20–2.09 (m, 2H), 1.88–1.74 (m, 1H), 1.67–1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 137.6, 129.7, 128.4, 126.9, 126.0, 74.5, 56.5, 29.5, 26.3, 17.1.

6-Isopropoxy-1-phenylcyclohexene (Table 1, entry 17):[7] pale yellow oil; IR (film) 1599, 1444, 1064 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.48–7.40 (m, 2H), 7.32–7.25 (m, 2H), 7.23–7.18 (m, 1H), 6.09 (dd, J = 4.4, 3.2 Hz, 1H), 4.36–4.29 (m, 1H), 3.68 (septet, J = 6.0 Hz, 1H), 2.32–2.22 (m, 1H), 2.18–2.03 (m, 2H), 1.92–1.78 (m, 1H), 1.67–1.56 (m, 2H), 1.15 (d, J = 6.0 Hz, 3H), 1.03 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.6, 129.9, 128.2, 126.7, 126.6, 71.2, 70.0, 28.6, 26.3, 24.2, 22.4, 17.0.

6-Butoxy-1-phenylcyclohexene (Table 1, entry 18):[7] pale yellow oil; IR (film) 1445, 1091 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.45–7.39 (m, 2H), 7.33–7.27 (m, 2H), 7.24–7.17 (m, 1H), 6.19 (dd, J = 4.4, 3.6 Hz, 1H), 4.23–4.18 (m, 1H), 3.57 (dt, J = 8.8, 6.4 Hz, 1H), 3.37 (dt, J = 8.8, 6.4 Hz, 1H), 2.32–2.22 (m, 1H), 2.19–2.08 (m, 2H), 1.90–1.77 (m, 1H), 1.67–1.47 (m, 4H), 1.35–1.23 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 137.8, 129.5, 128.2, 126.8, 126.0, 73.2, 68.7, 32.5, 27.2, 26.3, 19.6, 17.2, 14.0.

6-(3-Chloropropoxy)-1-phenylcyclohexene (Table 1, entry 19): pale yellow oil; IR (film) 1599, 1444, 1354, 1093 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.43–7.37 (m, 2H), 7.34–7.27 (m, 2H), 7.26–7.19 (m, 1H), 6.21 (dd, J = 4.4, 3.2 Hz, 1H), 4.32–4.26 (m, 1H), 3.76–3.68 (m, 1H), 3.56–3.41 (m, 3H), 2.33–2.22 (m, 1H), 2.20–2.08 (m, 2H), 1.97–1.88 (m, 2H), 1.86–1.73 (m, 1H), 1.70–1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 137.6, 129.6, 128.4, 127.0, 126.0, 73.5, 64.9, 42.3, 33.2, 27.3, 26.3, 17.4. Anal. Calcd for $C_{15}H_{19}ClO$: C, 71.84; H, 7.64. Found: C, 71.81; H, 7.66.

Procedure for Scheme 4. To a Schlenk tube charged with condenser were added $FeCl_3$ (0.0041 g, 0.025 mmol), NaI (0.0075 g, 0.050 mmol), ^{n}PrSS^{n}Pr (0.0075 g, 0.050 mmol), **6a** (0.085 g, 0.25 mmol) (prepared according to the reported procedure[7]), and $CHCl_3$ (0.25 mL). The resulting mixture was stirred at 60 °C under air for 18 h, filtered through a plug of silica with CH_2Cl_2 as eluent, concentrated, and analyzed by ^{1}H NMR.

Procedure for Scheme 5. To a Schlenk tube charged with condenser were added $FeCl_3$ (0.0041 g, 0.025 mmol), NaI (0.0075 g, 0.050 mmol), ^{n}PrSS^{n}Pr (0.0075 g, 0.050 mmol), BnOH (0.054 g, 0.50 mmol), **7a** (0.058 g, 0.25 mmol) (prepared according to the reported procedure[7]), and $CHCl_3$ (0.25 mL). The resulting mixture was stirred at 60 °C under air for 18 h, filtered through a plug of silica with CH_2Cl_2 as eluent, concentrated, and analyzed by ^{1}H NMR.

Procedure for Scheme 6. To a Schlenk tube charged with condenser were added $FeCl_3$ (0.0041 g, 0.025 mmol), NaI (0.0075 g, 0.050 mmol), ^{n}PrSS^{n}Pr (0.0075 g, 0.050 mmol), BnOH (0.054 g, 0.50 mmol), deuterium-labeled 1-phenylcyclohexene (0.0395 g, 0.25 mmol, **1l**:**1m** = 80:20) (prepared according to the reported procedure[7]), and $CHCl_3$ (0.25 mL). The resulting mixture was stirred at 60 °C under air for 4 h, filtered through a plug of silica with CH_2Cl_2 as eluent, concentrated, and analyzed by ^{1}H NMR. The crude product contained 1:1 mixture of **8** and **9** along with unreacted **1l** and **1m** (**1l**/**1m** = 70:30) (56% conversion).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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