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Lewis acids catalyzed ring-opening reactions of methylenecyclopropanes and epoxides in supercritical carbon dioxide or modified supercritical carbon dioxide with perfluorocarbon

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Abstract

The reactions of methylenecyclopropanes (MCPs) and epoxides with alcohols and aromatic amines can be carried out in supercritical carbon dioxide ($scCO_2$) or modified $scCO_2$ with perfluorocarbon which offer a way to synthesize various alcohols, amino-alcohols, homoallylic ethers, and amines under an environmentally benign condition.

Keywords: Epoxides; Methylenecyclopropanes (MCPs); Supercritical carbon dioxide; Lewis acid; Perfluorocarbon

1. Introduction

In the past decade, researchers have focused on using liquid or supercritical carbon dioxide ($scCO_2$) as ideal solvent alternatives [1], which have become one of the most important parts in green chemistry. Several of the advantages include that CO_2 is inexpensive, nonflammable, environmentally benign and readily separated from products [2]. Meanwhile, CO_2 is not strongly Lewis acidic or basic and chemically inert to most conditions [3]. Although CO_2 has been considered as a greenhouse gas, the process using CO_2 do not add directly to the greenhouse effect but rather aid in the reduction of emitted CO_2 [4]. Above the critical temperature and pressure, ($T_c = 31\ ^\circ C$, $P_c = 7.4$ MPa) CO_2 has gas-like viscosity and liquid-like density. These moderate critical conditions allow for safe commercial and laboratory operating conditions. For example, in 1994 Noyori and coworkers [5], reported one of the first synthetically useful homogeneous catalytic hydrogenation catalyzed by Ru(II) catalyst involving $scCO_2$ as both solvent and substrate. Tanko and Blackert [3], Tanko and co-workers [6], Beckman and co-workers [7] reported radical reactions in $scCO_2$. Besides, a number of applications, such as oxidation [8], hydroformylation [9], Diels-Alder cycloaddition [10], Mukaiyama aldol reaction [11] and various metal-catalyzed reactions [12] were carried out in $scCO_2$. CO_2, however, is a non-polar molecule and therefore the solubility of polar molecules is much lower than for non-polar molecules. For this reason, the key factor of the metal catalyzed reaction in $scCO_2$ is to find ways to enhance the solubility of metal catalyst and substrate. Of special interest, is the greater solubility of organic fluorocarbons in $scCO_2$, compared to the corresponding hydrocarbons. Hence, the metal-attached phosphine ligands containing perfluorinated side chains or the reactants of perfluorinated side chains as CO_2-philic surfactants are widely investigated to increase the solubility in $scCO_2$ [11,13].

Methylenecyclopropanes (MCPs) and epoxides can react with many nucleophilies via a ring-opening reaction in conventional organic solvents, such as 1,2-dichloroethane (DCE), dichloromethane (DCM), CH_3CN, THF or toluene in the presence of various metal catalysts [14]. But to the best of our knowledge, many organic solvents are environmentally hazardous materials. Herein, we wish to report the ring-opening reactions of MCPs and epoxides with aromatic amines and alcohols catalyzed by Lewis acids in the presence of perfluorinated compounds in $scCO_2$, which offer a way to produce various alcohols, amino-alcohols, homoallylic amines and ethers under an environmentally benign condition.

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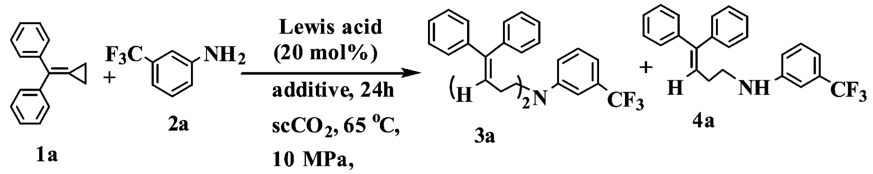


Scheme 1.

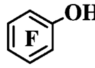
2. Results and discussion

First of all, we used diphenylmethylenecyclopropane **1a** and 3-(trifluoromethyl)aniline **2a** as the substrates to examine the reaction product in the presence of various Lewis acids in $scCO_2$. It was found that the reaction can proceed in the presence of Lewis acid $Yb(C_8F_{17}SO_3)_3$, but unfortunately, the yield was very low, if without any additive (Scheme 1, Table 1, entry 1). Then we used $Sn(OTf)_2$ instead of $Yb(C_8F_{17}SO_3)_3$ as the catalyst. However, the yields of **3a** and **4a** are still low (Table 1, entry 2). This may be due to the low solubility of reactants and catalysts in $scCO_2$. Based on the consideration that perfluorinated surfactants may increase the solubility of catalyst and substrate in $scCO_2$, we added pentafluorophenol **F1** to the reaction system. As results, we found that the yields of **3a** and **4a** were dramatically increased (Table 1, entries 3 and 4). Lewis acid $Sn(OTf)_2$ is more effective than $Yb(C_8F_{17}SO_3)_3$ under the same conditions. In addition, instead of pentafluorophenol **F1**, using perfluorotoluene **F2** as an additive in this reaction gave two products **3a** and **4a** in higher yields (Table 1, entry 5). The effect of perfluorodecalin (*cis*- and *trans*-mixture) **F3** on this reaction was also examined, but it is less effective than perfluorotoluene **F2** (Table 1, entry 6). Using $Yb(OTf)_3$ as the catalyst also gave lower yields than that of $Sn(OTf)_2$ (Table 1, entry 7). Through the high pressure glass window placed in $scCO_2$ reaction vessel, we confirmed that the fluorocabons can make reactants and catalyst to be completely dissolved in $scCO_2$ to form homogeneous system.[1] Accordingly, monoalkylated product **4** and dialkylated product **3** were produced in good yields.

Several examples of the $Sn(OTf)_2$ catalyzed reaction of **1a** with various aromatic amines (we have already known that no reaction occurred using aliphatic amines under the same conditions) [14b] in the presence of perfluorotoluene **F2** in $scCO_2$ at 10 MPa are shown in Table 2. Moreover, in this case the electron-withdrawing groups on the benzene ring of aromatic amine can significantly accelerate the reaction [14b]. While, the reaction of **1a** with aniline **2c** or 4-ethoxylaniline **2d** having an electron-donating group on the benzene ring of aromatic amine is much slower than that of **1a** with 3-fluoroaniline **2b** to give monoalkylated product **4** in trace without any dialkylated product **3** at 65 °C (Scheme 2, Table 2, entries 1, 2 and 3). Thus, we carried out the reaction of **1a** with **2b** at higher temperature (85 °C) in $scCO_2$, the yields were found to be significantly improved (Table 2, entry 4). The reaction of **1a** with 3,5-dichloroaniline **2e** produced only dialkylated product **3e** in high yield with no monoalkylated product **4e**, which was thoroughly transformed to give **3e** at 85 °C (Table 2, entry 5). Even the reaction of **1a** with 2,6-dibromoaniline **2f** which is a more sterically hindered aromatic amine also proceeded smoothly to form dialkylated product **3f** in high yield under the same conditions (Table 2, entry 6).

Besides **1a**, we also examined the reactions of diverse MCPs with **2a** catalyzed by $Sn(OTf)_2$ in the presence of perfluorotoluene **F2** within 24 h at 10 MPa in $scCO_2$. As can be seen from Table 3, both aromatic and aliphatic MCPs can react with **2a** to give the corresponding homoallylic amines. Moreover, the reaction of di(*p*-tolyl)methylenecyclopropane **1b** or di(*p*-methoxyphenyl)methylenecyclopropane **1c** with **2a** even can be completed at lower temperature (60 or 40 °C) giving dialkylated adduct **3i** or **3j** in high yield (Scheme 3, Table 3, entries 1 and 2). Compared with those MCPs having electron-donating groups on the benzene ring, the reaction of **2a** with 2-chlorobenzophenylmethylenecyclopropane **1d**, which has electron-withdrawing groups on the benzene ring, gave **3k** in lower yield even under higher temperature (Table 3, entry 3). Aliphatic MCPs, such as *p*-phenylcyclo-

Table 1
The effects of Lewis acids and additives on the reactions of **1a** with **2a** in $scCO_2$

Entry	Lewis acid	Additive	Yields (%)[a]	
			3a	**4a**
1	$Yb(C_8F_{17}SO_3)_3$	None	–	9
2	$Sn(OTf)_2$	None	13	11
3	$Yb(C_8F_{17}SO_3)_3$	 **(F1)**	23	15
4	$Sn(OTf)_2$	**F1**	27	35
5	$Sn(OTf)_2$	 **(F2)**	56	18
6	$Sn(OTf)_2$	 **(F3)**	20	33
7	$Yb(OTf)_3$	**F2**	58	7

[a] Isolated yield.

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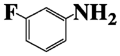
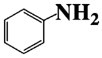
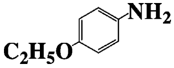
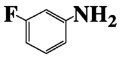
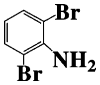
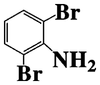
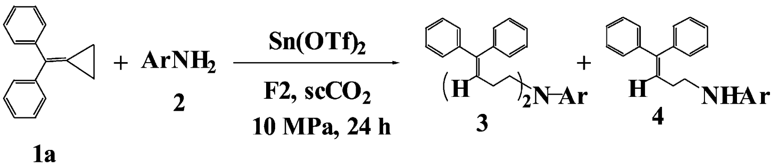
[1] Typical reaction procedure: **1a** (93 mg, 0.45 mmol), **2a** (24 mg, 0.15 mmol), $Sn(OTf)_2$ (13 mg, 20 mol%) and **F2** (40 mg) were placed in the equipment of $scCO_2$. The reaction proceeded at 65 °C, 10 MPa for 24 h. The residue was purified by flash chromatography (SiO_2) using CH_2Cl_2/hexane (1:8) as the eluent to yield **3a** (0.048 g, 56%) as colorless solid and **3b** (0.010 g, 18%) as an oil compound. Their spectroscopic data have been shown in supporting information.

Table 2
The reactions of **1a** with $ArNH_2$ catalyzed by Lewis acid $Sn(OTf)_2$ (20 mol%) in the presence of perfluorotoluene **F2** in $scCO_2$

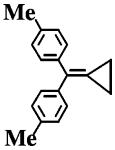
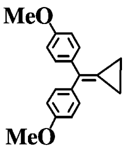
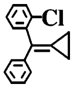
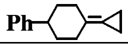
Entry	$ArNH_2$	Temperature (°C)	Yields (%)[a]	
			Compound **3**	Compound **4**
1	 **2b**	65	**3b** (34)	**4b** (16)
2	 **2c**	65	–	Trace
3	 **2d**	65	–	Trace
4	 **2b**	85	**3b** (61)	**4b** (21)
5	 **2e**	85	**3e** (93)	–
6	 **2f**	85	**3f** (81)	–

[a] Isolated yield.



Scheme 2.

Table 3
The reactions of MCPs with **2a** catalyzed by $Sn(OTf)_2$ (20 mol%) in the presence of perfluorotoluene **F2** in $scCO_2$

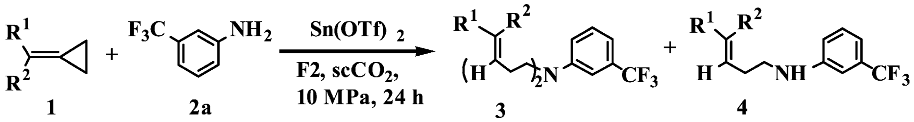
Entry	MCPs	Temperature (°C)	Yields (%)[a]	
			Compound **3**	Compound **4**
1		65	**3b** (34)	**4b** (16)
2		40	–	Trace
3		85	–	Trace
4		85	**3b** (61)	**4b** (21)

[a] Isolated yield.

hexylidenecyclopropane **1e** was also examined, albeit in low yield (Table 3, entry 4).

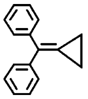
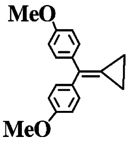
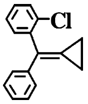
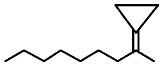
From Tables 2 and 3, we can conclude that MCPs having electron-donating groups or aromatic amines having electron-withdrawing groups on the benzene ring should be used as substrates in the reactions of MCPs with aromatic amines to give the corresponding homoallylic amines in high yields in modified $scCO_2$ with perfluorocarbon.

In addition to aromatic amines as nucleophiles, alcohols, such as ethanol, isopropanol and *tert*-butanol can also act as nucleophiles to give homoallyic ethers **5** in high yields. It can be seen from Table 4, all reactions proceeded very well without any perfluorocarbon as additive. This is because alcohol itself can modify $scCO_2$ fluid to solvate Lewis acids. In this case, even for (*o*-chlorophenyl)phenylmethylenecyclopropane **1d** and methylheptylmethylenecyclopropane **1f** which were less reactive or inactive in the reaction of aromatic amines with MCPs, the conversion of the reaction was approximately 100% to give the corresponding homoallylic ethers **5** in very high yields (Scheme 4, Table 4, entries 5 and 6).



Scheme 3.

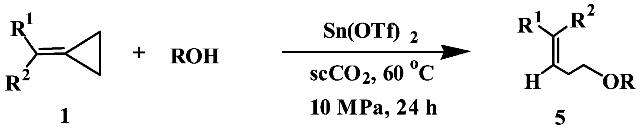
Table 4
The reactions of MCPs with various ROH catalyzed by $Sn(OTf)_2$ (5 mol%) in $scCO_2$

Entry	MCPs **1**	ROH	Compound **5** (yield, %)[a]
1	 **1a**	EtOH	**5a** (95)
2		*i*-PrOH	**5b** (99)
3		*i*-BuOH	**5c** (93)
4	 **1c**	EtOH	**5d** (96)
5	 **1d**	EtOH	**5e** (*E*/*Z* = 5.6:1) (90)
6	 **1f**	EtOH	**5f** (*E*/*Z* = 3.2:1) (96)

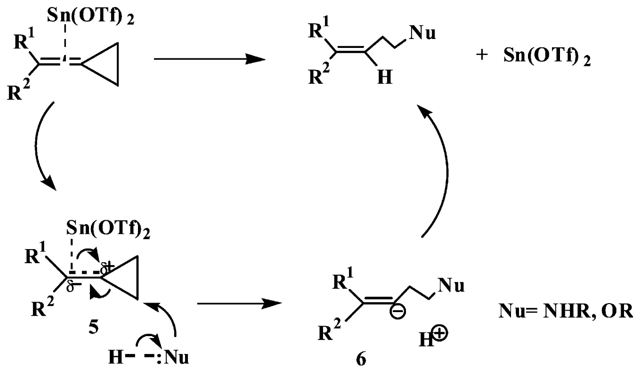
[a] The products were isolated and the starting MCPs disappeared.

A plausible mechanism for the ring-opening reactions of MCPs with HNu is shown in Scheme 5. The MCPs first coordinate with Lewis acid before the subsequent nucleophilic attack of HNu to affords the adduct **6**. The final product is formed after proton-transfer.

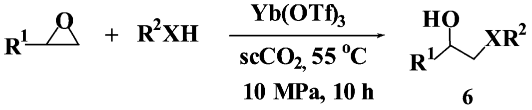
For epoxides, we found that the ring-opening reactions with aromatic amine or alcohol can be carried out in the presence of a Lewis acid $Yb(OTf)_3$ without perfluorocarbon under the same conditions (Scheme 6). This is because epoxides are more reactive than MCPs **1** and polar epoxide itself can modify the physical property of $scCO_2$ to dissolve Lewis acid $Yb(OTf)_3$ very well. Thus, the ring-opening reactions of epoxides with nucleophiles take place more easily in a homogeneous phase. This phenomenon can be confirmed through a high-pressure glass window placed in $scCO_2$ apparatus. The results were summarized in Table 5.



Scheme 4.



Scheme 5.



Scheme 6.

In conclusion, $scCO_2$ is rapidly emerging as an ideal medium for carrying out a diverse range of synthetic reactions in the replacement of conventional organic solvents. Herein, we have disclosed the reactions of MCPs with $ArNH_2$ and alcohol catalyzed by Lewis acid in the presence of perfluorotoluene in $scCO_2$ to give various homoallylic amines and ethers which are an important class of compounds for its utilities as synthetic intermediates in good yields. In addition, the ring-opening reactions of epoxides have been also investigated. The corresponding aminoalcohols can be obtained in good yields under an environmentally benign condition. Our success is helpful to broaden the reactions in $scCO_2$ catalyzed by Lewis acids. Further investigations to develop this reaction of MCPs or epoxides with other nucleophiles in $scCO_2$ or modified $scCO_2$ are now in progress.

3. Experimental section

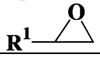
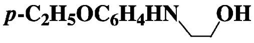
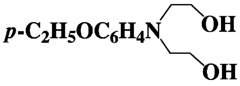
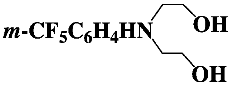
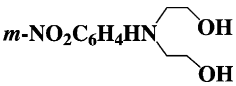
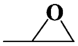
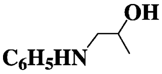
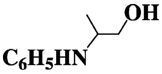
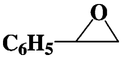
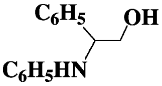
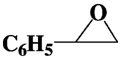
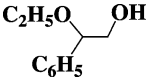
3.1. General methods

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA^+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. The starting materials **1a–e** were prepared according to the literature [15].

3.1.1. General procedure for the reactions of MCP *1a* with $ArNH_2$ *2a* in the presence of various additives

MCP **1a** (93 mg, 0.45 mmol), $ArNH_2$ **2a** (24 mg, 0.15 mmol), $Sn(OTf)_2$ (13 mg, 20 mol%) and corresponding additive (40 mg) were placed in the equipment of $scCO_2$. The reaction was performed at 65 °C, 10 MPa for 24 h. Purification was carried out by passing through a silica gel column (hexane/CH_2Cl_2 as an eluent) to afford the products **3a** and **4a**.

Table 5
The reactions of epoxide with various aromatic amines or ethanol catalyzed by $Yb(OTf)_3$ (5 mol%) in $scCO_2$

Entry	Epoxide 	R^2XH	Compound **6**	Yields (%)[a]
1		p-$C_2H_5OC_6H_4NH_2$	 **6a**	27
			 **6b**	58
2		m-$CF_3C_6H_4NH_2$	 **6c**	38
			 **6d**	51
3		m-$NO_2C_6H_4NH_2$	 **6e**	26
			 **6f**	33
4		$C_6H_5NH_2$	 **6g**	32
			 **6h**	8
5		$C_6H_5NH_2$	 **6i**	75
6		C_2H_5OH	 **6j**	95

[a] Isolated yield.

3.1.2. *General procedure for the reactions of MCP **1a** with $ArNH_2$ **2a–d** in the presence of perfluorotoluene **F2***

MCP **1a** (93 mg, 0.45 mmol), the corresponding $ArNH_2$ **2** (0.15 mmol), $Sn(OTf)_2$ (13 mg, 20 mol%) and perfluorotoluene **F2** (40 mg) were placed in the equipment of $scCO_2$. The reaction was performed at 65 °C, 10 MPa for 24 h. Purification was carried out by passing through a silica gel column (hexane/CH_2Cl_2 as an eluent) to afford the products **3** and **4**.

3.1.3. *General procedure for the reactions of MCP **1a** with $ArNH_2$ **2e–f** in the presence of perfluorotoluene **F2***

MCP **1a** (93 mg, 0.45 mmol), the corresponding $ArNH_2$ **2** (0.15 mmol), $Sn(OTf)_2$ (13 mg, 20 mol%) and perfluorotoluene **F2** (40 mg) were placed in the equipment of $scCO_2$. The reaction was performed at 85 °C, 10 MPa for 24 h. Purification was carried out by passing through a silica gel column (hexane/CH_2Cl_2 as an eluent) to afford the product **3**.

3.1.4. *Procedure for the reactions of MCPs **1b,1c,1d,1e** with $ArNH_2$ **2a** in the presence of perfluorotoluene **F2***

MCPs **1b–e**, respectively (0.45 mmol), $ArNH_2$ **2a** (0.15 mmol), $Sn(OTf)_2$ (13 mg, 20 mol%) and perfluorotoluene **F2** (40 mg) were placed in the equipment of $scCO_2$. The reaction was performed at 65, 40, 85, 85 °C, respectively, 10 MPa for 24 h. Purification was carried out by passing through a silica gel column (hexane/CH_2Cl_2 as an eluent) to afford the products **3** and **4**.

*3.1.4.1. [N,N-di-(1,1-diphenyl-1-butenyl)-3-(trifluoromethyl)]aniline (**3a**).* **3a** was obtained as colorless solid, yield 56%. mp 118–120 °C, IR (neat): ν 3052, 3028, 2925, 2883, 1609, 1495, 1454, 1322, 1120, 850, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.30–2.38 (m, 4H, CH_2), 3.29 (t, 4H, $J = 7.6$ Hz, CH_2), 6.05 (t, 2H, $J = 7.5$ Hz, =CH), 6.40–6.43 (m, 1H, Ar), 6.69 (s, 1H, Ar), 6.81 (d, 1H, $J = 8.0$ Hz, Ar), 7.07–7.39 (m, 21H, Ar); MS (EI) m/z: 573 (M^+, 0.3), 380 (54), 167 (100), 129 (61), 91 (53); Anal. Calcd. for $C_{39}H_{34}F_3N$ (%): C, 81.68; H, 5.93; N, 2.44. Found: C, 81.72; H, 6.09; N, 2.41.

*3.1.4.2. 1-(1,1-Diphenyl-1-butenylamino)-3-(trifluoromethyl)benzene (**4a**).* **4a** was obtained as a colorless oil, yield 18%. IR (neat): ν 3421, 3054, 2986, 1614, 1495, 1449, 1421, 1265 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.43–2.50 (m, 2H, CH_2), 3.24 (t, 2H, $J = 6.8$ Hz, CH_2), 3.81 (s, 1H, NH), 6.12 (t, 1H, $J = 7.5$ Hz, =CH), 6.64–6.67 (m, 1H, Ar), 6.74 (s, 1H, Ar), 6.90–6.92 (d, 1H, $J = 7.5$ Hz, Ar), 7.10–7.41 (m, 11H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.810, 43.886, 109.788, 111.494, 113.878, 123.749 (q, $J = 271.4$ Hz), 125.802, 127.274, 127.392, 127.452, 128.366, 128.584, 129.796, 129.942, 130.059 (q, $J = 31.6$ Hz), 139.868, 143.543, 145.976, 149.833; MS (EI) *m/z*: 367 (M^+, 1.75), 174 (100), 145 (9.25), 91 (6.68), 77 (3.25); HRMS (EI) Calcd. for $C_{23}H_{20}F_3N$ 367.1548, Found: 367.1526.

*3.1.4.3. [N,N-di-(1,1-diphenyl-1-butenyl)-3-fluoro]aniline (**3b**).* **3b** was obtained as colorless oil, yield 61%. IR (neat): ν 3079, 3055, 3022, 2969, 2885, 1618, 1598, 1576, 1497, 1443, 1265, 1154, 822 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28–2.36 (m, 4H, CH_2), 3.22 (t, 4H, $J = 7.4$ Hz, CH_2), 6.06 (t, 2H, $J = 7.8$ Hz, =CH), 6.08–6.14 (m, 2H, Ar), 6.24–6.30 (m, 1H, Ar); 6.91–6.99 (m, 1H, Ar), 7.12–7.37 (m, 20H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.882, 51.059, 98.985 (d, $J = 25.2$ Hz), 102.397 (d, $J = 20.4$ Hz), 107.058, 125.758, 127.443, 127.504, 127.562, 128.531, 128.727, 130.039, 130.503 (d, $J = 10.2$ Hz), 140.056, 142.484, 144.348, 149.541 (d, $J = 9.0$ Hz), 164.619 (d, $J = 240.2$ Hz); MS (EI) *m/z*: 523 (M^+, 1.98), 330 (61.92), 167 (100), 129 (71.14), 91 (73.30); HRMS (EI) Calcd. for $C_{23}H_{21}FN$: 330.1658, Found: 330.1707 ($[M - 193.1017]^+$).

*3.1.4.4. 1-(1,1-Diphenyl-1-butenylamino)-3-fluorobenzene (**4b**).* **4b** was obtained as colorless oil, yield 16%, IR (neat): ν 3057, 2960, 2929, 1713, 1621, 1591, 1511, 1497, 1442, 1266 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40–2.47 (m, 2H, CH_2), 3.20 (t, 2H, $J = 7.1$ Hz, CH_2), 3.78 (s, 1H, NH), 6.11 (t, 1H, $J = 7.5$ Hz, =CH), 6.20–6.25 (m, 1H, Ar), 6.21–6.31 (m, 1H, Ar), 6.32–6.39 (m, 1H, Ar), 7.05–7.07 (m, 1H, Ar), 7.16–7.38 (m, 10H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.538, 43.952, 100.558 (d, $J = 22.7$ Hz), 105.099 (d, $J = 21.6$ Hz), 108.337, 125.744, 125.955, 127.390, 127.435, 128.381, 128.589, 129.962, 130.565 (d, $J = 9.2$ Hz), 140.169, 142.581, 144.197, 149.167 (d, $J = 9.5$ Hz), 160.484 (d, $J = 248.6$ Hz). MS (EI) *m/z*: 317 (M^+, 7.60), 124 (100), 91 (4.10), 77 (2.35); HRMS (EI) Calcd. for $C_{22}H_{20}FN$: 317.1580, Found: 317.1593.

*3.1.4.5. [N,N-di-(1,1-diphenyl-1-butenyl)-3,5-(dichloro)]-aniline (**3e**).* **3e** was obtained as colorless oil, yield 93%. IR (neat): ν 3080, 3053, 3024, 2985, 1738, 1626, 1587, 1551, 1492, 743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27–2.34 (m, 4H, CH_2), 3.20 (t, 4H, $J = 7.3$ Hz, CH_2), 6.01 (t, 2H, $J = 7.7$ Hz, =CH), 6.31 (s, 2H, Ar), 6.57 (s, 1H, Ar), 7.09–7.37 (m, 20H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.341, 50.462, 109.854, 115.384, 124.801, 127.077, 127.118, 127.188, 128.127, 128.357, 129.465, 135.424, 139.442, 141.935, 144.148, 148.073; MS (EI) *m/z*: 573 (M^+, 2.75), 380 (54.45), 167 (100), 129 (48.45), 91 (34.76); HRMS (EI) Calcd. for $C_{23}H_{20}Cl_2N$: 380.0973, Found: 380.1003 ($[M - 193.1017]^+$).

*3.1.4.6. [N,N-di-(1,1-diphenyl-1-butenyl)-2,6-(dibromo)]aniline (**3f**).* **3f** was obtained as colorless oil, yield 81%, IR (neat): ν 3054, 2986, 1738, 1601, 1494, 1443, 1424 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24–2.32 (m, 4H, CH_2), 3.23 (t, 4H, $J = 7.4$ Hz, CH_2), 6.11 (t, 2H, $J = 7.5$ Hz, =CH), 6.79 (t, 1H, $J = 8.3$ Hz, Ar), 7.09–7.47 (m, 22H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.760, 53.063, 126.794, 126.862, 127.135, 127.184, 127.287, 127.381, 128.012, 128.068, 129.788, 133.065, 139.934, 142.509, 142.599, 146.770; MS (EI) *m/z*: 663 (M^+, 0.78), 470 (51.58), 167 (67.24), 129 (100), 91 (87.64), 77 (9.95); HRMS (EI) Calcd. for $C_{23}H_{20}Br_2N$: 467.9962, Found: 467.9944 ($[M - 193.1017]^+$).

*3.1.4.7. [N,N-di-(1,1-di-p-tolyl-1-butenyl)-3-(trifluoromethyl)]aniline (**3i**).* **3i** was obtained as colorless oil, yield 85%; IR (neat): ν 3023, 2922, 2851, 1609, 1584, 1508, 1454, 1322 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 6H, CH_3), 2.28 (s, 6H, CH_3) 2.29–2.37 (m, 4H, CH_2), 3.26 (t, 4H, $J = 7.4$ Hz, CH_2), 5.99 (t, 2H, $J = 7.8$ Hz, =CH), 6.38–6.41 (m, 1H, Ar), 6.69 (s, 1H, Ar), 6.80 (d, 1H, $J = 7.8$ Hz, Ar), 6.99–7.12 (m, 17H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.498, 21.655, 27.846, 51.118, 108.289, 112.334, 115.080, 124.582, 127.034 (q, $J = 271.7$ Hz), 127.472, 129.309, 129.461, 129.922, 129.974, 131.844 (q, $J = 31.4$ Hz), 137.109, 137.251, 137.286, 140.005, 144.348, 148.013; MS (EI) *m/z*: 629 (M^+, 0.26), 408 (12.86), 195 (100), 143 (39.03), 105 (35.57), 91 (4.71); HRMS (EI) Calcd. for $C_{26}H_{25}F_3N$: 408.1939, Found: 408.1942 ($[M - 193.1017]^+$).

*3.1.4.8. [N,N-di-(1,1-di-p-methoxyphenyl-1-butenyl)-3-(trifluoromethyl)]aniline (**3j**).* **3j** was obtained as colorless oil, yield 74%. IR (neat): ν 2956, 2934, 2836, 1646, 1606, 1515, 1462, 1200, 1120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.31–2.38 (m, 4H, CH_2), 3.29 (t, 4H, $J = 7.4$ Hz, CH_2), 3.76 (s, 6H, OCH_3), 3.79 (s, 6H, OCH_3), 5.93 (t, 2H, $J = 7.8$ Hz, =CH), 6.43–6.46 (m, 1H, Ar), 6.71 (s, 1H, Ar), 6.78–6.88 (m, 9H, Ar), 7.01–7.16 (m, 9H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.342, 50.587, 55.163, 55.351, 107.585, 111.559, 113.377, 113.552, 114.420, 123.269, 124.469 (q, $J = 271.5$ Hz), 128.157, 130.659, 131.238 (q, $J = 31.6$ Hz), 132.028, 132.180, 135.126, 142.950, 147.596, 158.528, 158.759; MS (EI) *m/z*: 244 (M^+, 1.85), 440 (10.31), 227 (100), 167 (30.58), 129 (29.26), 91 (27.20); HRMS (EI) Calcd. for $C_{26}H_{25}F_3NO_2$: 440.1837, Found: 440.1850 ($[M - 193.1017]^+$).

*3.1.4.9. [N,N-di-(1-o-chlorophenyl-1-phenyl-1-butenyl)-3-(trifluoromethyl)]aniline (**3k**).* **3k** was obtained as colorless oil, yield 21%. IR (neat): ν 3062, 2917, 2865, 1623, 1599, 1499 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20–2.25 (m, 4H, CH_2), 3.32 (t, 4H, $J = 7.5$ Hz, CH_2), 6.23 (t, 2H, $J = 7.7$ Hz, =CH), 6.42–6.79 (m, 4H, Ar), 7.05–7.44 (m, 18H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.393, 43.433, 106.291, 108.890, 111.199, 116.960, 125.111 (q, $J = 270.8$ Hz), 126.404, 126.453, 127.661, 128.537, 128.845, 129.933, 131.370, 131.594, 131.869 (q, $J = 31.5$ Hz), 133.601, 140.068, 141.709, 142.518, 148.212; MS (EI) *m/z*: 641 (M^+, 2.05), 414 (100), 145 (10.81), 91 (7.09), 77 (2.76); HRMS (EI) Calcd. for $C_{39}H_{32}F_3NCl_2$: 641.1864, Found: 641.1878.

*3.1.4.10. 1-(p-Phenylcyclohexylidene-n-propylamino)-3-(trifluoromethyl)benzene (**4l**).* **4l** was obtained as a colorless oil, yield 36%. IR (neat): ν 3415, 3060, 2926, 1615, 1599, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21–2.40 (m, 9H, CH_2, CH), 2.67–2.75 (m, 2H, CH_2), 3.14–3.20 (m, 2H, CH_2), 3.87 (s, 1H, NH), 5.19 (t, 1H, $J = 7.4$ Hz, =CH), 6.72–6.94 (m, 3H, Ar), 7.17–7.33 (m, 6H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.898, 28.476, 35.080, 35.771, 36.848, 43.817, 44.584, 109.112, 113.832, 116.119, 118.153, 125.236 (q, $J = 273.9$ Hz), 125.979, 126.817, 128.300, 129.545, 131.456 (q, $J = 31.5$ Hz), 141.534, 146.692, 148.027; MS (EI) *m/z*: 359 (M^+, 2.01), 174 (100), 145 (6.23), 91 (9.18), 77 (3.82); HRMS (EI) Calcd. for $C_{22}H_{24}F_3N$ 359.1861, Found: 359.1909.

*3.1.5. General procedure for the reactions of MCPs **1** with alcohols in scCO$_2$*

The reaction was carried out in the same manner as that described earlier. For the known compounds, their structures have been checked by the ^{1}H NMR spectroscopic data with those reported previously.

*3.1.5.1. 4,4-Diphenyl-but-3-enyl ethyl ether (**5a**).* **5a** was obtained as colorless oil, yield 95%. IR (neat): ν 3023, 2973, 2861, 1598, 1493, 1443, 1110 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, $J = 6.8$ Hz, 3H), 2.40 (q, $J = 7.3$ Hz, 2H), 3.42–3.50 (m, 4H), 6.12 (t, $J = 7.3$ Hz, 1H), 7.19–7.38 (m, 10H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.26, 30.52, 66.16, 70.30, 125.84, 126.98, 127.00, 127.27, 128.05, 128.23, 129.89, 139.95, 142.58, 143.16; MS (EI) *m/z*: 252 (M^+), 208, 193, 178, 115, 91; HRMS (EI) Calcd. for $C_{18}H_{20}O$: 252.1514, Found: 252.1489.

*3.1.5.2. 4,4-Diphenyl-but-3-enyl iso-propyl ether (**5b**).* **5b** was obtained as colorless oil, yield 99%. IR (neat): ν 2970, 2857, 1493, 1443, 1366, 1128 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, $J = 6.1$ Hz, 6H), 2.35–2.42 (m, 2H), 3.48 (t, $J = 6.7$ Hz, 2H), 3.57 (q, $J = 6.1$ Hz, 1H), 6.12 (t, $J = 7.3$ Hz, 1H), 7.18–7.38 (m, 10H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.77, 30.93, 67.78, 71.40, 126.09, 126.93, 126.97, 127.28, 128.07, 128.18, 128.21, 129.90, 129.92, 129.93, 140.06, 142.70, 143.10; MS (EI) *m/z*: 266 (M^+), 208, 193, 180, 165, 130, 115; HRMS (EI) Calcd. for $C_{19}H_{22}O$: 266.1671, Found: 266.1628.

*3.1.5.3. 4,4-Diphenyl-but-3-enyl tert-butyl ether (**5c**).* **5c** was obtained as colorless oil, yield 93%. IR (neat): ν 2970, 2856, 1490, 1441, 1366, 1126 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 9H), 2.32–2.39 (m, 2H), 3.41 (t, $J = 6.7$ Hz, 2H), 6.12 (t, $J = 7.3$ Hz, 1H), 7.18–7.36 (m, 10H, Ar); MS (EI) *m/z*: 280 (M^+), 251, 226, 194, 179, 165; HRMS (EI) Calcd. for $C_{20}H_{24}O$: 280.1827, Found: 280.1870.

*3.1.5.4. 4,4-Di-(4-methoxyphenyl)-but-3-enyl ethyl ether (**5d**).* **5d** was obtained as colorless oil, yield 96%. IR (neat): ν 2912, 2864, 1606, 1574, 1463, 1287, 1173 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, $J = 6.6$ Hz, 3H, CH_3), 2.40–2.48 (m, 2H), 3.45–3.52 (m, 4H), 3.78 (s, 3H), 3.83 (s, 3H), 6.00 (t, $J = 7.5$ Hz, 1H), 6.79–6.82 (m, 2H, Ar), 6.89–6.92 (m, 2H, Ar), 7.12–7.19 (m, 4H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.24, 30.53, 55.19, 55.22, 60.09, 70.45, 113.38, 113.51, 123.79, 128.40, 130.98, 132.48, 135.70, 142.19, 158.52, 158.72; MS (EI) *m/z*: 312, 253, 242, 211, 145.

*3.1.5.5. 1-Chloro-2-(4-ethoxy-phenyl-but-1-enyl)-benzene (**5e**).* **5e** was obtained as colorless oil, yield 90%, E:Z = 5.6:1. E–**5e**: IR (neat): ν 2974, 2863, 1494, 1414, 1375, 1353 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, $J = 6.8$ Hz, 3H, CH_3), 2.24–2.28 (m, 2H), 3.50–3.56 (m, 4H), 6.31 (t, $J = 7.3$ Hz, 1H), 7.15–7.45 (m, 9H, Ar); MS (EI) *m/z*: 286 (M^+), 243, 228, 214, 192, 179; HRMS (EI) Calcd. for $C_{18}H_{19}ClO$: 286.1124, Found: 286.1079. Z-**5e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, $J = 6.6$ Hz, 3H), 2.58–2.63 (m, 2H), 3.50–3.56 (m, 4H), 5.81 (t, $J = 7.3$ Hz, 1H), 7.15–7.45 (m, 9H).

*3.1.5.6. 1-Ethoxy-4-methyl-undec-3-ene (**5f**).* **5f** was obtained as colorless oil, yield 96%, E:Z = 3.2:1. IR (neat): ν 2959, 2855, 1376, 1111 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, $J = 6.9$ Hz, 3H, CH_3), 1.14–1.21 (m, 13H), 1.58 (s, 3H), 1.92–2.02 (m, 2H), 2.24–2.31 (m, 2H), 3.34–3.50 (m, 4H), 5.10 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.32, 15.44, 16.19, 22.89, 28.00, 29.20, 30.03, 32.07, 39.91, 66.26, 70.66, 119.99, 137.72; MS (EI) *m/z*: 212 (M^+), 184, 166, 138, 95, 59; HRMS (EI) Calcd. for $C_{14}H_{28}O$: 212.2140, Found: 212.2143.

3.1.6. General procedure for the reactions of epoxides with alcohols in scCO$_2$

The reaction was carried out in the same manner as that described above using Yb(OTf)$_3$ as a Lewis acid but without perfluorotoluene **F2**.

*3.1.6.1. 2-(4-Ethoxyphenylamino)ethanol (**6a**).* 2-(4-Ethoxyphenylamino)ethanol (**6a**): a colorless oil (27%). IR (neat): ν 3350 (broad), 2978, 2926, 2875, 1504, 1455, 821 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (t, $J = 6.9$ Hz, 3H, CH_3), 2.76 (br. s, 1H, OH), 3.24 (t, $J = 5.1$ Hz, 2H, CH_2), 3.80 (t, $J = 5.1$ Hz, 2H, CH_2), 3.81 (s, 1H, NH), 3.97 (q, $J = 6.9$ Hz, 2H, CH_2), 6.62 (d, $J = 9.0$ Hz, 2H, Ar), 6.79 (d, $J = 9.0$ Hz, 2H, Ar); MS (EI) *m/z*: 181 (M^+), 150, 122, 91; HRMS (EI) Calcd. for $C_{10}H_{15}NO_2$ ($M^+ - H_2O$): 163.0997, Found: 163.1018.

*3.1.6.2. N,N-bis(2-hydroxyethyl)-p-phenetidin (**6b**).* *N*,*N*-bis(2-hydroxyethyl)-*p*-phenetidin (**6b**): a colorless oil (58%). This is an known compound [16]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (t, $J = 6.9$ Hz, 3H, CH_3), 3.39 (t, $J = 4.8$ Hz, 4H, CH_2), 3.71 (t, $J = 4.8$ Hz, 4H, CH_2), 3.96 (q, $J = 6.9$ Hz, 2H, CH_2), 4.22 (br. s, 2H, OH), 6.68 (d, $J = 9.0$ Hz, 2H, Ar), 6.82 (d, $J = 9.0$ Hz, 2H, Ar); MS (EI) *m/z*: 225 (M^+), 194, 163, 150, 122.

*3.1.6.3. 2-(3-Trifluoromethylaniline)ethanol (**6c**).* 2-(3-Trifluoromethylaniline)ethanol (**6c**): a colorless oil (38%). IR (neat): v 3397 (broad), 2932, 2878, 1598, 1497, 1443, 1122, 785 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.34 (t, $J = 5.1$ Hz, 2H, CH_2), 3.88 (t, $J = 5.1$ Hz, 2H, CH_2), 6.78–7.31 (m, 2H, Ar); MS (EI) *m/z*: 205 (M^+), 174, 145, 127; HRMS (EI) Calcd. for $C_9H_{10}F_3NO$ ($M^+ - H_2O$): 187.0609, Found: 187.0615.

*3.1.6.4. N,N-bis(2-hydroxyethyl)-3-trifluoromethylaniline (**6d**).* *N*,*N*-bis(2-hydroxyethyl)-3-trifluoromethylaniline (**6d**): a colorless oil (51%). IR (neat): v 3334 (broad), 2935, 2883, 1586, 1504, 1456, 1121, 782 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (t, $J = 4.8$ Hz, 4H, CH_2), 3.80 (t, $J = 4.8$ Hz, 4H, CH_2), 4.30 (br. s, 2H, OH), 6.79–7.32 (m, 4H, Ar); MS (EI) *m/z*: 249 (M^+), 218, 174, 145, 84; HRMS (EI) Calcd. for $C_{11}H_{14}F_3NO_2$ (M^+): 249.0977, Found: 249.1019.

*3.1.6.5. 2-(3-Nitroaniline)-ethanol (**6e**).* 2-(3-Nitroaniline)-ethanol (**6e**): a colorless oil (26%). IR (neat): v 3407 (broad), 3059, 2935, 2881, 1593, 1529, 1461, 1349, 735 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (br. s, 1H, OH), 3.35 (t, $J = 5.1$ Hz, 2H, CH_2), 3.89 (t, $J = 5.1$ Hz, 2H, CH_2), 4.50 (s, 1H, NH), 6.90–7.55 (m, 4H, Ar); MS (EI) *m/z*: 182 (M^+), 151, 122, 105, 91; HRMS (EI) Calcd. for $C_8H_{10}N_2O_3$ (M^+): 182.0691, Found: 182.0699.

*3.1.6.6. N,N-bis(2-hydroxyethyl)-3-nitroaniline (**6f**).* *N*,*N*-bis(2-hydroxyethyl)-3-nitroaniline (**6f**): a colorless oil (33%). This is an known compound [17]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (t, $J = 4.8$ Hz, 4H, CH_2), 3.83 (t, $J = 4.8$ Hz, 4H, CH_2), 4.38 (br. s, 2H, OH), 6.80–7.52 (m, 4H, Ar); MS (EI) *m/z*: 226 (M^+), 195, 151, 122, 91.

*3.1.6.7. 1-Anilino-propan-2-ol (**6g**).* 1-Anilino-propan-2-ol (**6g**): a colorless oil (32%). This is an known compound [18]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (d, $J = 6.0$ Hz, 3H, CH_3), 2.99 (dd, $J = 12.9$, 8.4 Hz, 1H, CH), 3.23 (dd, $J = 3.3$ Hz, 1H, CH), 3.99–4.05 (m, 1H, CH), 6.66 (d, $J = 7.9$ Hz, 2H, Ar), 6.74 (t, $J = 7.2$ Hz, 1H, Ar), 7.19 (t, $J = 7.9$ Hz, 2H, Ar); MS (EI) *m/z*: 151 (M^+), 106, 91, 77.

*3.1.6.8. 2-Anilino-1-propanol (**6h**).* 2-Anilino-1-propanol (**6h**): a colorless oil (8%). This is an known compound [19]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, $J = 6.6$ Hz, 3H, CH_3), 3.50 (dd, $J = 10.5$, 5.7 Hz, 1H, CH), 3.60–3.67 (m, 1H, CH), 3.72 (dd, $J = 10.5$, 4.2 Hz, 1H, CH), 6.58–6.72 (m, 3H, Ar), 7.15–7.18 (m, 2H, Ar); MS (EI) *m/z*: 151 (M^+), 120, 92, 91.

*3.1.6.9. 2-Phenylamino-2-phenylethanol (**6i**).* 2-Phenylamino-2-phenylethanol (**6i**): a colorless oil (75%). This is an known compound [20]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.72 (dd, $J = 11.0$, 7.2 Hz, 1H, CH), 3.91 (dd, $J = 11.0$, 4.5 Hz, 1H, CH), 4.48 (dd, $J = 6.9$, 4.5 Hz, 1H, CH), 6.54–6.58 (m, 3H, Ar), 7.07–7.12 (m, 2H, Ar), 7.23–7.37 (m, 5H, Ar); MS (EI) *m/z*: 213 (M^+), 180, 135, 121, 91.

*3.1.6.10. 2-Ethoxyl-2-phenylethanol (**6j**).* 2-Ethoxyl-2-phenylethanol (**6j**): a colorless oil (95%). This is an known compound [21]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, $J = 6.9$ Hz, 3H, CH_3), 2.62 (br. s, 1H, OH), 3.38–3.50 (m, 2H, CH, CH), 3.60–3.71 (m, 2H, CH_2), 4.42 (dd, $J = 8.1$, 4.2 Hz, 1H, CH), 7.30–7.38 (m, 5H, Ar); MS (EI) *m/z*: 166 (M^+), 149, 135, 121, 107, 91, 77.

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