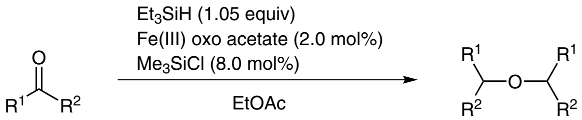
Synthesis of Ethers from Carbonyl Compounds by Reductive Etherification Catalyzed by Iron(III) and Silyl Chloride

Risto Savela
Reko Leino*

Laboratory of Organic Chemistry, Åbo Akademi University,
20500 Åbo, Finland
reko.leino@abo.fi



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Abstract A simple iron- and silyl chloride catalyzed method for the preparation of symmetrical and nonsymmetrical ethers is presented. Various aldehydes and ketones were reductively etherified by using triethylsilane as a reducing agent in the presence of 2 mol% of iron(III) oxo acetate and 8 mol% of chloro(trimethyl)silane. The reactions can be carried out at ambient temperatures and pressures with ethyl acetate as the solvent.

Key words iron, catalysis, silicon, reductions, ethers, aldehydes, ketones

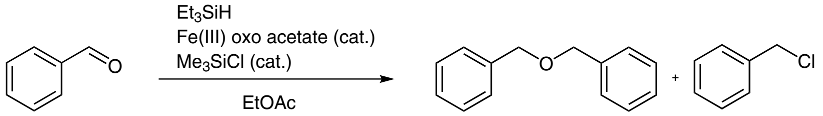
The formation of C–O bonds is one of the oldest known transformations in synthetic organic chemistry, the first method dating back to 1850.[1] In the Williamson ether synthesis, an alkoxide is used to attack an alkyl halide. Some years later, Wurtz developed a synthesis of dimethyl ether from methyl iodide and silver oxide.[2] Although it remains one of the most widely used methods for preparing ethers, the Williamson synthesis lacks generality, as it is only applicable to primary halides. With secondary halides, elimination and isomerization of the starting materials begin to compete, leading to mixtures of products.

In the 1970s, in a series of papers, Doyle and co-workers described acid-catalyzed etherifications of aldehydes in the presence of silanes.[3] However, the reported method has the disadvantages of requiring a large excess of the silane and the presence of an acid such as concentrated sulfuric acid or trifluoroacetic acid. Later, Noyori reported the use of trimethylsilyl triflate as a catalyst for the synthesis of ethers from acetals or ketones, with trialkylsilanes acting as the reducing agents.[4] Subsequently, Mukaiyama and co-workers reported the use of trityl perchlorate as a catalyst for similar reactions.[5]

These new methods circumvented the earlier problems, at least to some degree, providing the isolated ethers in acceptable to good yields. The application of trimethylsilyl triflate as a catalyst for ether synthesis was improved by Olah and co-workers, who also extended the reaction to the use of trimethylsilyl iodide as a separate catalyst.[6] Several other methods that use silanes or other compounds as reagents and/or catalysts in the syntheses of ethers have been reported in recent decades. Among the catalysts that have been used are boron trifluoride etherate,[7] trimethylsilyl triflate, trimethylsilyl iodide,[8] bismuth(III) chloride, bismuth(III) bromide,[9] indium(III) bromide,[10] triflic acid, triflic anhydride,[11] solid acids or bases,[12] molecular iodine,[13] copper(II) triflate,[14] antimony(III) iodide,[15] and zinc(II) triflate.[16]

Iron-catalyzed reactions have been widely investigated in recent years.[17] In particular, the use of organosilanes as reducing agents in combination with iron catalysts has generated significant attention.[18] Of particular interest have been various reduction reactions of carbonyl compounds to alcohols;[19] reductions of amides, imines, and cyano compounds;[20] and, recently, the reduction of sulfoxides to sulfides.[21] Iron-catalyzed benzylations,[21,22] one-pot reduction/chlorination reactions of benzylic carbonyl compounds,[23] and transformations of alcohols to azides have also been reported.[24] Two iron-catalyzed methods that use organosilanes as reducing agents for synthesis of ethers have recently emerged; these involve either reductive etherifications of ketones, aldehydes, or alcohols,[25] or the reduction of the carbonyl groups of esters.[26]

In our previous and ongoing work on iron-catalyzed benzylation[27] and chlorination[28] of benzylic carbonyl compounds, we frequently observed the formation of dibenzyl ether derivatives as side products. As a result, we became interested in investigating the potential extension of such transformations to the synthesis of ethers. Here, we de-



1

1a
undesired
byproduct

Scheme 1 Synthesis of dibenzyl ether

scribe a condensation-type etherification of carbonyl compounds in the presence of iron-based precatalysts in ethyl acetate. In related transformations, previously reported by Oriyama and co-workers, less-benign nitromethane was used as the solvent.[25]

In the present work, we made use of atmospherically oxidized iron(II) acetate, which we refer to as ‘iron(III) oxo acetate’. This known precatalyst is probably a trinuclear iron complex with a central oxygen atom bridging three iron(III) molecules. Such trinuclear metal acetate complexes have been used previously, and although various structural features have been proposed, no definite proof has been presented of the exact structure of this particular complex. A tentative structure is, however, shown in Figure 1.[29]

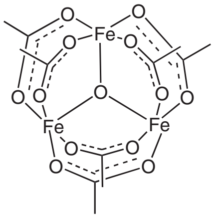


Figure 1 Tentative structure of iron(III) oxo acetate

In addition to iron(III) oxo acetate, we used chloro(trimethyl)silane as a co-catalyst and triethylsilane as the hydride source in ethyl acetate solution (Scheme 1).

First, we optimized the loadings of the iron(III) oxo acetate and chloro(trimethyl)silane catalysts to provide a satisfactory selectivity between the desired dibenzyl ether (**1**) and the undesired byproduct benzyl chloride (**1a**) with practical reaction times and conditions. The use of a significant excess of chloro(trimethyl)silane resulted in the formation of small amounts of benzyl chloride, whereas the use of less than 0.1 equivalents of chloro(trimethyl)silane suppressed the formation of the byproduct. Our complete results are listed in Table 1.

The presence of both precatalysts, iron(III) oxo acetate and chloro(trimethyl)silane, was necessary for the reaction to proceed. In the absence of either of these compounds, no ether formation was observed. The rate of the reaction was influenced to a greater degree by the loading of chloro(trimethyl)silane than by that of iron(III) oxo acetate.

Table 1 The Effects of Iron(III) Species and Chloro(trimethyl)silane as Catalysts on the Reaction Time and Selectivity in the Synthesis of Dibenzyl Ether[a]

Fe(III) oxo acetate (mol%)	Me_3SiCl (equiv)	Time (h)	Selectivity **1**/**1a**	Conv. (%)[b]
4.0	1.0	1	95:5	>99
4.0	0.5	1	95:5	>99
4.0	0.25	1	95:5	>99
4.0	0.08	1	100:0	>99
4.0	0.04	24	100:0	66[c]
2.0	0.08	1	100:0	>99
2.0	0.04	6	100:0	>99
1.0	0.04	3	100:0	>99
1.0	0.02	6	100:0	51
0.0	0.08	6	–	–
2.0	0.04	6	–	–

[a] Reactions conditions: PhCHO (2 mmol), Et_3SiH (2.1 mmol), EtOAc (1 mL), r.t.
[b] Determined by GC (FID).
[c] The catalyst dissolved very slowly under these conditions.

On the basis of the optimization studies, we selected a combination of 2.0 mol% of iron(III) oxo acetate and 8.0 mol% of chloro(trimethyl)silane as the preferred general catalyst for further studies on the scope of the reaction. Our initial investigations on the general substrate scope were conducted on a 2 mmol scale by reacting aryl aldehydes to form symmetrical ethers in short reaction times and good to excellent yields (Table 2, entries 1–15). In two cases, the reaction was scaled up to 10 mmol scale (entries 7 and 11), and, in one case, it was scaled up to a 100 mmol scale (entry 6). In an attempt to introduce hydroxy substituents onto the aromatic ring, we examined the reactions of *para*- and *ortho*-hydroxy-substituted benzaldehydes. Although full conversions of the starting materials were attained, the desired reactivity was hampered, apparently, by activation of the benzylic position, resulting in oligomerization, and only in one case, that of the *meta*-substituted aldehyde, was the desired product formed in a good yield (entry 11). However, by protecting the hydroxy group as its acetyl derivative, the *para*-product could also be obtained (Entry 12). When cyano-, methoxy- or acetamido-substituted benzaldehyde derivatives were used, only the starting material was observed, even after prolonged reaction times. We also briefly examined the etherification of some nonbenzylic ketones and aldehydes (entries 16–19). Whereas no reactivity was observed with iron(III) oxo acetate as the catalyst, good yields of the desired ethers were obtained on switching to iron(III) chloride. Citronellal was also investigated as a starting material, but in this case, the reaction gave significant amounts of pulegol isomers and a nonseparable mixture of ethers.

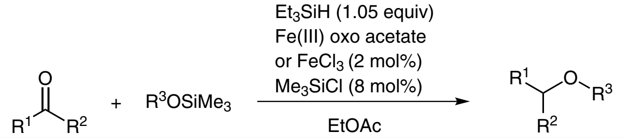
Table 2 Etherification of Aldehydes and Ketones[a]

Entry	Substrate	Time	Product		Yield[b] (%)
1[30]	PhCHO	1 h	**1**	Bn_2O	93
2[31]	4-TolCHO	1 h	**2**	$(4\text{-TolCH}_2)_2O$	76
3[32]	2-TolCHO	1 h	**3**	$(2\text{-TolCH}_2)_2O$	92
4[33]	4-*t*-BuC_6H_4CHO	1 h	**4**	$(4\text{-}t\text{-BuC}_6H_4CH_2)_2O$	98
5[16]	4-ClC_6H_4CHO	1 h	**5**	$(4\text{-ClC}_6H_4CH_2)_2O$	64
6	2-ClC_6H_4CHO	2 h	**6**	$(2\text{-ClC}_6H_4CH_2)_2O$	75[c]
7	$2,4\text{-Cl}_2C_6H_3CHO$	2 h	**7**	$(2,4\text{-Cl}_2C_6H_3CH_2)_2O$	75[d]
8[34]	4-FC_6H_4CHO	3 h	**8**	$(4\text{-FC}_6H_4CH_2)_2O$	97
9[35]	$4\text{-F}_3CC_6H_4CHO$	3 h	**9**	$(4\text{-F}_3CC_6H_4CH_2)_2O$	96
10[36]	4-BrC_6H_4CHO	1.5 h	**10**	$(4\text{-BrC}_6H_4CH_2)_2O$	73
11	3-HOC_6H_4CHO	1 h	**11**	$(3\text{-HOC}_6H_4CH_2)_2O$	77
12[37]	4-AcOC_6H_4CHO	2 h	**12**	$(4\text{-AcOC}_6H_4CH_2)_2O$	68
13[38]	$2\text{-O}_2NC_6H_4CHO$	2 h	**13**	$(2\text{-O}_2NC_6H_4CH_2)_2O$	63[d]
14[39]	$4\text{-MeO}_2CC_6H_4CHO$	1 h	**14**	$(4\text{-MeO}_2CC_6H_4CH_2)_2O$	79
15	4-PhC_6H_4CHO	1 h	**15**	$(4\text{-PhC}_6H_4CH_2)_2O$	89
16[e,40]	cyclohexanone	5 h	**16**	Cy_2O	84
17[e,11c]	CyCHO	15 min	**17**	$(CyCH_2)_2O$	83
18[e,11c]	$Me(CH_2)_4CHO$	1 h	**18**	$[Me(CH_2)_5]_2O$	94
19[e]	CyCOMe	3 h	**19**	$[CyCH(Me)]_2O$	64

[a] Reaction conditions: carbonyl compound (2 mmol), Et_3SiH (2.1 mmol), Fe(III) oxo acetate (2.0 mol%), Me_3SiCl (8 mol%), EtOAc (1 mL), r.t.
[b] Isolated yield.
[c] Reaction carried out on a 100 mmol scale
[d] Reaction carried out on a 10 mmol scale.
[e] $FeCl_3$ was used instead of Fe(III) oxo acetate.

When acetophenone derivatives were used as starting materials, they gave only traces of the corresponding ethers with concomitant formation of small amounts of the corresponding halogenated products, formed through consumption of the chloro(trimethyl)silane catalyst. 1-Phenylbutane-1,3-dione and 1,3-diphenylacetone similarly showed no reactivity, whereas benzophenone only underwent a slow Clemmens-type reduction. Finally, α,β-unsaturated ketones and aldehydes were also tested as starting materials, but no reactions were observed by GC monitoring.

Next, we examined the preparation of nonsymmetrical ethers by using trimethylsilylated alcohols in combination with aldehyde derivatives (Scheme 2).



Scheme 2 Synthesis of unsymmetrical ethers

The results are collected in Table 3. Whereas good yields were observed in all reactions within one hour at room temperature, small amounts of the corresponding symmetrical ethers were produced when aliphatic ketones or aldehydes were used in combination with (benzyloxy)(trimethyl)silane (entries 6 and 7). This issue could, however, be resolved by reversing the roles of the reagents (entries 8–11). The reaction of hexanal with cyclohexyloxy(trimethyl)silane resulted in the formation of various side products that could not be separated from the desired product. This again could be resolved by treating the primary trimethylsilylated alcohol with the corresponding ketone (entries 12 and 13). When (–)-menthyl trimethylsilyl ether was treated with benzaldehyde or biphenyl-4-carboxaldehyde, the desired ether products were formed within 30 minutes, with retention of configuration at all stereocenters (entries 14 and 15). As in the case of trimethylsilylated alcohols, the use of acetophenones led to mixtures of the desired nonsymmetrical ether and small amounts of the undesired symmetrical ether, as well as to reductive halogenation of the acetophenone. Full conversions of the starting material could only be attained by increasing the amount of chloro(trimethyl)silane, which in turn shifted the reaction towards reductive halogenation of the acetophenone.

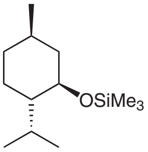
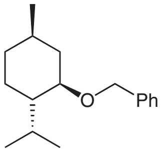
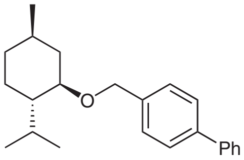
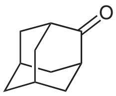
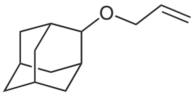
Finally, whereas the approach using α,β-unsaturated aldehydes and ketones for the preparation of symmetrical ethers failed, the reaction of (allyloxy)(trimethyl)silane in combination with benzylic aldehydes or adamantan-2-one gave the desired ethers in good yields (entries 16–18), although concomitant isomerization of the allylic double bond to a vinylic double bond was observed to a minor degree.

Baba and co-workers have suggested a tentative mechanism for the Lewis acid catalyzed derivatization of carbonyl compounds in combination with silyl halides.[51,52] A similar mechanistic interpretation was included in our preceding work on the arylation of aromatic carbonyl compounds[27] and the halogenation of carbonyl compounds.[28] In accordance with previously postulated reaction mechanisms for similar reactions,[5,6,11c,53] the present reaction probably proceeds through initial activation of either the trimethylsilyl chloride or the iron(III) species in question, followed by coordination of the carbonyl group to either an iron or a silicon species. The use of trimethylsilyl iodide or trimethylsilyl triflate as the catalyst[4,11] supports coordination to a silicon species with subsequent silylium ion-type catalysis.[54] The complex formed might undergo hydrosilylation and subsequent S_N2-type addition of the second carbonyl compound with transfer of a siloxy moiety to the attacking carbonyl carbon. The existence of an S_N2-type reaction is also supported by the full retention of the stereocenters in products **32** and **33**. The acetal that is formed is subsequently reduced to the desired ether. A tentative catalytic cycle is shown in Scheme 3.

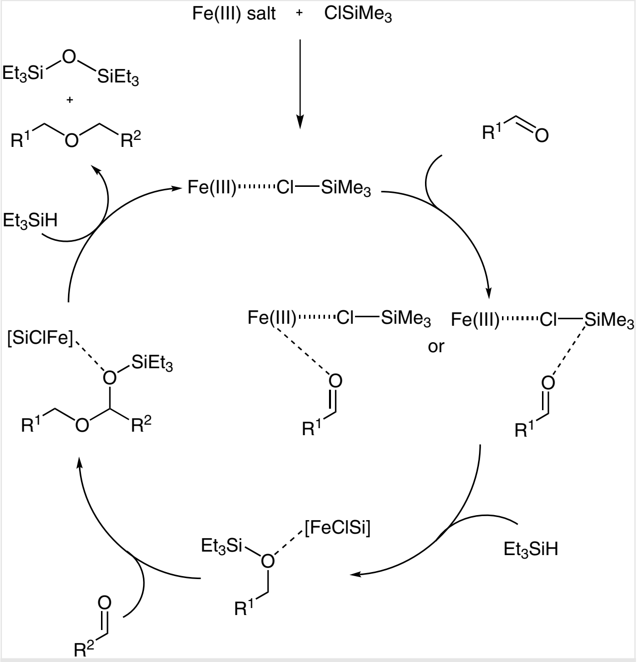
To conclude, we have developed a robust method for the production of symmetrical and unsymmetrical ethers under mild conditions in a benign solvent. This method might prove applicable to syntheses of important building blocks for pharmaceuticals or, for example, to methods for the introduction of benzyl ether protecting groups.

All chemicals were purchased from commercial sources and used without further purification unless otherwise mentioned. $FeCl_3$ was obtained from Sigma Aldrich (97% purity). Similar reactivities were observed in selected test reactions using higher grade $FeCl_3$ (99.99%, Sigma Aldrich). Test reactions under similar conditions using palladi-

Table 3 Ethers from Trimethylsilylated Alcohols[a]

Entry	Reactants		Time(h)	Product		Yield[c] (%)
1[25a]	$BnOSiMe_3$	$4\text{-}BrC_6H_4CHO$	1	**20**	$4\text{-}BrC_6H_4CH_2OBn$	79
2[c,41]		$4\text{-}F_3CC_6H_4CHO$	1	**21**	$4\text{-}F_3CC_6H_4CH_2OBn$	89
3[c,42]		$2\text{-}O_2NC_6H_4CHO$	1	**22**	$2\text{-}O_2NC_6H_4CH_2OBn$	77
4[43]		4-TolCHO	1	**23**	4-TolCH_2OBn	89
5[44]		$3\text{-}HOC_6H_4CHO$	1	**24**	$3\text{-}HOC_6H_4CH_2OBn$	83
6[45]		$Me(CH_2)_4CHO$	1[d]	**25**	$Me(CH_2)_5OBn$	78
7[46]		cyclohexanone	1[d]	**26**	CyOBn	85
8[45]	$CyOSiMe_3$	PhCHO	0.5[d]		CyOBn	87
9[45]		4-TolCHO	0.5[d]	**27**	4-TolCH_2OCy	80
10[45]		$4\text{-}MeO_2CC_6H_4CHO$	0.5[d]	**28**	$4\text{-}MeO_2CC_6H_4CH_2OCy$	80
11[47]		$4\text{-}PhC_6H_4CHO$	0.5[d]	**29**	$4\text{-}PhC_6H_4CH_2OCy$	85
12[6]	$Me(CH_2)_7OSiMe_3$	cyclohexanone	0.5[d]	**30**	$Me(CH_2)_7OCy$	90
13[48]		i-BuCOMe	0.5[d]	**31**	$i\text{-}BuCH(Me)O(CH_2)_7Me$	77
14[45]		PhCHO	0.5[d]	**32**		88
15[47]		$4\text{-}PhC_6H_4CHO$	0.5[d]	**33**		76
16[49]	$AllOSiMe_3$	PhCHO	0.5[d]	**34**	BnOAll	80
17[34]		$4\text{-}FC_6H_4CHO$	0.5[d]	**35**	$4\text{-}FC_6H_4CH_2OAll$	92
18[50]			0.5[d]	**36**		72

[a] Reaction conditions: trimethylsilyl ether (1.0 mmol), carbonyl compound (1.0 mmol), Et_3SiH (1.05 mmol), Fe(III) oxo acetate (2.0 mol%), Me_3SiCl [0.08 equiv (from 2 mmol)].
[b] Isolated yield.
[c] Reaction performed on a 5 mmol scale.
[d] $FeCl_3$ was used instead of Fe(III) oxo acetate.



Scheme 3 Tentative catalytic cycle for the reductive etherification reaction

um black, $PdCl_2$, $CuCl_2$, or NiI_2 as the catalyst did not result in any detectable formation of ether products. NMR spectra were recorded by using 600 MHz and 500 MHz Bruker spectrometers. The 600 MHz spectrometer was equipped with a BBI-5mm-Zgrad-ATM probe or a BBO-5mm-Zgrad probe at 298 K and was operated at 600.13 MHz for ^1H and 150.92 for ^{13}C. The 500 MHz spectrometer was equipped with a BBI-5mm-Zgrad-ATM probe or a BBO-5mm-Zgrad probe at 298 K and was operated at 500.13 MHz for ^1H and 125.76 for ^{13}C. The NMR spectra were calibrated to the solvent peak.

The product distribution and the purity were monitored by GC/FID using an Agilent GC chromatograph equipped with an HP-1 column (30 μm × 320 mm × 0.25 μm) with H_2 as carrier gas. The chromatograph was operated with the following temperature program: injector 220 °C, oven T_{initial} = 50 °C (2 min), rate 10 °C/min, T_{final} = 300 °C, hold 2 min. Trimethylsilylation reactions of BnOH, CyOH, (–)-menthol, and octan-1-ol were carried out as described previously.[55] For product **19**, the dr was verified by GC/FID. For products **32** and **33**, the dr and er were verified by GC/FID in combination with information on the coupling constants from the ^1H NMR and reference spectra.

Iron(III) Oxo Acetate Catalyst

The oxidized Fe(III) oxo acetate catalyst used in the reactions was reproducibly prepared from $Fe(OAc)_2$ (Sigma Aldrich; 99.99% purity) by solid-state oxidization under ambient conditions over a prolonged period of time or at 110 °C for 24 or 72 h. The prepared catalysts were characterized by IR spectroscopy, elemental analysis, Mössbauer spectroscopy, and inductively coupled plasma (ICP) techniques to verify and determine their iron(III) contents. (For details, see Supporting Information.) The iron(III) oxo acetate samples used in this work were prepared at r.t. or at 110 °C for 24 h, and had iron contents of 31.25% and 34.64%, respectively (ICP).

Optimization of the Reaction of Benzaldehyde (1) with Triethylsilane

The desired amount of iron(III) oxo acetate (iron content 31.25%) was suspended in EtOAc (1.0 mL) and the corresponding amount of Me_3SiCl was added, resulting in dissolution of the iron salt. PhCHO (0.2 mL, 2.0 mmol) and Et_3SiH (0.34 mL, 2.1 mmol) were added sequentially, and the resulting solution was stirred for up to 6 h at r.t. while the reaction was monitored hourly by GC/FID.

Preparation of Catalyst Stock Solution

Iron (III) oxo acetate (oxidized at r.t.: 70 mg, 0.3 mmol; oxidized at 110 °C for 24 h: 64.5 mg, 0.3 mmol) or $FeCl_3$ (45 mg, 0.3 mmol) was suspended in EtOAc (~5 ml) in a 10 mL volumetric flask, and Me_3SiCl (0.2 mL, 1.6 mmol) was added. When the iron salt had dissolved, EtOAc was added to adjust the total volume to 10 mL.

Reductive Etherification; General Method

The appropriate reactant (2 mmol) and Et_3SiH (0.34 mL, 2.1 mmol) were successively added to the stock solution of catalysts (1.0 mL), and the mixture was stirred at r.t. until full conversion was attained. The mixture was then diluted with EtOAc (10 mL) and washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phase was washed with EtOAc (3 mL), and then the organic phases were combined, dried (Na_2SO_4), and evaporated to dryness. The resulting crude product was purified by flash chromatography or by crystallization.

Dibenzyl Ether (1)

Prepared according to the general method with a reaction time of 1 h and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a colorless liquid; yield: 185 mg (93%); R_f = 0.67 (EtOAc–hexane, 1:4); purity: >99%.

^1H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.41–7.36 (m, 8 H), 7.33–7.30 (m, 2 H), 4.58 (s, 4 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 139.0, 128.7, 128.1, 127.9, 72.6.

Bis(4-methylbenzyl) Ether (2)

Prepared according to the general method with a reaction time of 1 h and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a white solid that was crystallized (hexane) to provide white crystals; yield: 171 mg (76%); mp 62 °C (lit.[17] 61–62 °C); R_f = 0.67 (EtOAc–hexane, 1:4); purity: >99%.

^1H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.25 (d, J = 8.0 Hz, 4 H), 7.17 (d, J = 8.0 Hz, 4 H), 4.50 (s, 4 H), 2.35 (s, 6 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 137.7, 136.0, 129.3, 128.2, 72.3, 21.3.

Bis(2-methylbenzyl) Ether (3)

Prepared according to the general method with a reaction time of 1 h and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a white solid that was crystallized (hexane) to provide white needles; yield: 208 mg (92%); mp 50–51 °C (lit.[56] 51–52 °C); R_f = 0.7 (EtOAc–hexane, 1:4); purity: >99%.

^1H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.38–7.36 (m, 2 H), 7.23–7.18 (m, 6 H), 4.58 (s, 4 H), 2.34 (s, 6 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 137.1, 136.9, 130.5, 128.9, 128.1, 126.1, 71.1, 18.9.

Bis(4-*tert*-butylbenzyl) Ether (4)

Prepared according to the general method with a reaction time of 1 h and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a colorless liquid; yield: 303 mg (98%); R_f = 0.8 (EtOAc–hexane, 1:4); purity: 99%.

^{1}H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.39 (ddd, *J* = 2.1, 8.5 Hz, 4 H), 7.30 (ddd, *J* = 2.1, 8.5 Hz, 4 H), 4.52 (s, 4 H), 1.33 (s, 18 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 151.0, 136.1, 127.9, 125.6, 72.3, 34.8, 31.5.

Bis(4-chlorobenzyl) Ether (5)

Prepared according to the general method with a reaction time of 1 h and workup in EtOAc. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a white solid; yield: 172 mg (64%); R_f = 0.45 (EtOAc–hexane, 1:4); purity: 99%.

^{1}H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.35–7.30 (m, 8 H), 4.52 (s, 4 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 137.4, 133.6, 129.5, 128.8, 71.8.

Bis(2-chlorobenzyl) Ether (6)

2-Chlorobenzaldehyde (14.1 g, 100 mmol) and Fe(III) oxo acetate (0.45 g, 2 mmol) were dissolved in EtOAc (100 mL). Me_3SiCl (1 mL, 8 mmol) was added, and the mixture was stirred at r.t. until the Fe(III) oxo acetate dissolved (~5 min). Et_3SiH (17 mL, 105 mmol) was then added, resulting in spontaneous refluxing for ~5 min. The solution was stirred for 1 h at r.t., EtOAc (50 mL) was added, and the mixture was washed with sat. aq $NaHCO_3$ (2 × 30 mL). The aqueous phases were combined and washed with EtOAc (30 mL), and the organic phases were then combined and dried (Na_2SO_4). The crude product was purified by crystallization (EtOH, –18 °C) to give white crystals; yield: 10.0 g (75%); mp 48–49 °C (lit.[57] 48–49 °C); purity: 98%.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.58–7.56 (m, 2 H), 7.38 (dd, *J* = 1.5, 7.6 Hz, 2 H), 7.31 (ddd, *J* = 1.5, 7.6 Hz, 2 H), 7.26 (ddd, *J* = 1.8, 7.6 Hz, 2 H), 4.74 (s, 4 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 136.4, 133.2, 129.6, 129.5, 129.2, 70.2.

Anal. Calcd for $C_{14}H_{12}Cl_2O$: C, 62.94%; H, 4.53%. Found: C, 62.98%; H, 4.53%.

Bis(3,4-dichlorobenzyl) Ether (7)

3,4-Dichlorobenzaldehyde (1.75 g, 10 mmol) was dissolved in the catalyst stock solution (5 mL). Et_3SiH (1.7 mL, 10.5 mmol) was added, and the mixture was stirred at r.t. for 2 h. EtOAc (30 mL) was then added and the resulting solution was washed with sat. aq $NaHCO_3$ (2 × 10 mL). The aqueous phases were combined and washed with EtOAc (10 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a white solid that was crystallized (hexane) to provide white needles; yield: 1.26 g (75%); mp 61 °C; R_f = 0.52 (EtOAc–hexane, 1:4); purity: > 99%.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): 7.47 (d, *J* = 2.0 Hz, 2 H), 7.44 (d, *J* = 8.2 Hz, 2 H) 7.22–7.20 (m, 2 H), 4.51 (s, 4 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): 139.0, 132.7, 131.8, 130.8, 129.8, 127.3, 71.4.

Anal. Calcd for $C_{14}H_{10}Cl_4O$: C, 50.04%; H, 3.00%. Found: C, 50.07%; H, 2.99%.

Bis(4-fluorobenzyl) Ether (8)

Prepared according to the general method with a reaction time of 3 h and workup in EtOAc. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a colorless liquid; yield: 227 mg (97%); R_f = 0.67 (EtOAc–hexane, 1:4); purity: >99%.

^{1}H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.35 (m, 4 H), 7.06 (tt, *J* = 2.5, 9.1 Hz, 4 H), 4.51 (s, 4 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 162.7 (d, $J_{C,F}$ = 245 Hz), 134.8 (d, $J_{C,F}$ = 3 Hz), 129.9 (d, $J_{C,F}$ = 9 Hz), 115.5 (d, $J_{C,F}$ = 22 Hz), 71.8.

Bis[4-(trifluoromethyl)benzyl] Ether (9)

Prepared according to the general method with a reaction time of 3 h and workup in EtOAc. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a colorless liquid; yield: 320 mg (96%); R_f = 0.67 (EtOAc–hexane, 1:4); purity: 99%.

^{1}H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.64 (d, *J* = 8.0 Hz, 4 H), 7.52 (d, *J* = 8.0 Hz, 4 H), 4.66 (s, 4 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 143.0, 130.0 (q, $J_{C,F}$ = 32 Hz), 128.1, 125.7 (q, $J_{C,F}$ = 4 Hz), 124.8 (q, $J_{C,F}$ = 272 Hz), 72.1.

Bis(4-bromobenzyl) Ether (10)

Prepared according to the general method with a reaction time of 1.5 h and workup in EtOAc. The crude product was purified by crystallization from hexane to give white needles; yield: 259 mg (73%); mp 84 °C (lit.[58] 84.5–85.5 °C); purity: 98%.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.49 (td, *J* = 2.2, 8.7 Hz, 4 H), 7.25 (d, *J* = 8.7 Hz, 4 H), 4.50 (s, 4 H).

^{13}C NMR (125.75 MHz, CD_2Cl_2, 25 °C): δ = 137.8, 131.8, 129.8, 121.7, 71.8.

4,4′-[Oxydi(methylene)]diphenol (11)

Prepared according to the general method with a reaction time of 1 h and workup in EtOAc. The crude product was purified by flash chromatography (silica gel, gradient 20–80% hexane–EtOAc) to give a thick colorless liquid containing a small amount of residual EtOAc as an impurity that could not be removed; yield: 176 mg (77%);[59] R_f = 0.63 (EtOAc–hexane, 1:1).

^{1}H NMR (600.13 MHz, CD_2Cl_2, 25 °C): δ = 7.19 (t, *J* = 7.8 Hz, 2 H), 6.89 (m, 2 H), 6.84 (m, 2 H), 6.74 (m, 2 H), 5.81 (br s, 2 H), 4.50 (s, 4 H).

^{13}C NMR (150.92 MHz, CD_2Cl_2, 25 °C): δ = 156.3, 140.2, 130.0, 120.4, 115.1, 115.0, 72.2.

Oxybis(methylene-4,1-phenylene) Diacetate (12)

Prepared according to the general method with a reaction time of 2 h and workup in CH_2Cl_2. The crude product was purified by flash chromatography (silica gel, gradient 0–80% hexane–EtOAc) to give a white solid; yield: 214 mg (68%); mp 109–110 °C (Lit.[37] 113–114 °C); R_f = 0.19 (EtOAc–hexane, 1:4); purity >99%.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): 7.40–7.37 (m, 4 H), 7.07 (td, *J* = 2.4, 9.0 Hz, 4 H), 4.56 (s, 4 H), 2.28 (s, 6 H).

^{13}C NMR (125.76 MHz, CD$_2$Cl$_2$, 25 °C): 169.8, 150.6, 136.5, 129.0, 122.0, 71.9, 21.3.

Bis(2-nitrobenzyl) Ether (13)

2-Nitrobenzaldehyde (1.5 g, 10 mmol) was dissolved in the stock catalyst solution (5 mL). Et$_3$SiH (1.7 mL, 10.5 mmol) was added, and the mixture was stirred for 2 h. The solution was filtered and the filtrate was discarded. The off-white solid residue was crystallized (EtOAc) to give white crystals; yield: 0.9 g (63%); mp 160 °C (lit.[38] 160.5–161 °C); purity: >99%.

^{1}H NMR (600.13 MHz, DMSO, 25 °C): δ = 8.08 (d, J = 7.9 Hz, 2 H), 7.81–7.78 (m, 4 H), 7.62–7.57 (m, 2 H), 4.96 (s, 4 H).

^{13}C NMR (150.92 MHz, DMSO, 25 °C): δ = 147.3, 134.0, 133.7, 128.81, 128.76, 124.6, 68.8.

Dimethyl 4,4′-[Oxydi(methylene)]dibenzoate (14)

Prepared according to the general method with a reaction time of 1 h and workup in CH$_2$Cl$_2$. The crude product was purified by trituration in hexane for 2 h to give a white powder; yield: 79% (249 mg); mp 108–110 °C; purity: 98%.

^{1}H NMR (500.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 8.01 (d, J = 8.5 Hz, 4 H), 7.46 (d, J = 8.5 Hz, 4 H), 5.32 (s, 4 H), 3.89 (s, 6 H).

^{13}C NMR (125.75 MHz, CD$_2$Cl$_2$, 25 °C): δ = 167.1, 143.9, 129.9, 127.7, 72.2, 52.3.

Bis(4-biphenylmethyl) Ether (15)

Prepared according to the general method with a reaction time of 1 h and workup in EtOAc. After 45 min, EtOAc (1 mL) was added and the mixture was stirred for additional 15 min. The crude product was purified by crystallization (EtOH) to give white crystals; yield: 312 mg (89%); mp 87 °C (lit.[60] 87–89 °C); purity: >99%.

^{1}H NMR (600.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.64–7.62 (m, 8 H), 7.49–7.44 (m, 8 H), 7.36 (tt, J = 1.3, 7.5 Hz, 2 H), 4.64 (s, 4 H).

^{13}C NMR (150.92 MHz, CD$_2$Cl$_2$, 25 °C): δ = 141.2, 140.8, 138.1, 129.2, 128.6, 127.7, 127.41, 127.38, 72.3.

Anal. Calcd for $C_{26}H_{22}O$: C, 89.1%; H, 6.3%. Found: C, 89.2%; H, 6.3%.

Dicyclohexyl Ether (16)

Prepared according to the general method with FeCl$_3$ as the catalyst, a reaction time of 5 h, and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a colorless liquid; yield: 182 mg (84%); R_f = 0.77 (EtOAc–hexane, 1:4); purity: 95%.

^{1}H NMR (600.13 MHz, CDCl$_3$, 25 °C): δ = 3.33–3.28 (m, 2 H), 1.87–1.83 (m, 4 H), 1.75–1.70 (m, 4 H), 1.54–1.51 (m, 2 H), 1.27–1.11 (m, 10 H).

^{13}C NMR (150.92 MHz, CDCl$_3$, 25 °C): δ = 74.8, 33.5, 26.0, 24.7.

Bis(cyclohexylmethyl) Ether (17)

Prepared according to the general method with FeCl$_3$ as the catalyst, a reaction time of 15 min, and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a colorless liquid; yield: 178 mg (83%); R_f = 0.84 (EtOAc–hexane, 1:4); purity: 93%.

^{1}H NMR (600.13 MHz, CDCl$_3$, 25 °C): δ = 3.17 (d, J = 6.7 Hz, 4 H), 1.76–1.63 (m, 10 H), 1.60–1.53 (m, 2 H), 1.23 (tq, J = 3.2, 12.3 Hz, 4 H), 1.15 (tq, J = 3.2, 12.3 Hz, 2 H), 0.90 (dq, J = 3.2, 12.3 Hz, 4 H).

^{13}C NMR (150.92 MHz, CDCl$_3$, 25 °C): 77.2, 38.2, 30.3, 26.9, 26.1.

Dihexyl Ether (18)

Prepared according to the general method with FeCl$_3$ as the catalyst, a reaction time of 1 h, and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc) to give a colorless liquid; yield: 174 mg (94%); R_f = 0.86 (EtOAc–hexane, 1:4); purity: 97%.

^{1}H NMR (600.13 MHz, CDCl$_3$, 25 °C): δ = 3.38 (t, J = 6.8 Hz, 4 H), 1.58–1.53 (m, 4 H), 1.35–1.24 (m, 12 H), 0.88 (t, J = 7.1 Hz, 6 H).

^{13}C NMR (150.92 MHz, CDCl$_3$, 25 °C): δ = 71.1, 31.9, 29.9, 26.0, 22.8, 14.2.

Bis(1-cyclohexylethyl) Ether (19)

Prepared according to the general method with FeCl$_3$ as the catalyst, a reaction time of 3 h, and workup in hexane. The crude product was purified by flash chromatography (silica gel, gradient 0–35% hexane–EtOAc), resulting in partial separation of the diastereomers as colorless liquids.

Fraction 1

Yield: 65 mg (27%); R_f = 0.91 (EtOAc–hexane, 1:9); purity: 98%; dr 100:0.

^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): δ = 3.11 (quint, J = 6.2 Hz, 2 H), 1.89–1.84 (m, 2 H), 1.74–1.61 (m, 8 H), 1.33–1.08 (m, 8 H), 1.02 (d, J = 6.2 Hz, 6 H), 1.01–0.87 (m, 4 H).

^{13}C NMR (125.75 MHz, CDCl$_3$, 25 °C): δ = 76.5, 43.1, 28.7, 28.1, 26.0, 25.7, 25.6, 16.2.

Fraction 2

Yield: 88 mg (37%); R_f = 0.87 (EtOAc–hexane, 1:9); purity: >99%; dr: 10:90.

^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): δ (major diastereomer) = 3.15 (quint, J = 6.2 Hz, 2 H), 1.85–1.79, (m, 2 H), 1.76–1.62 (m, 8 H), 1.38–1.31 (m, 2 H), 1.27–1.10 (m, 6 H), 1.05 (d, J = 6.2 Hz, 6 H), 1.00–0.90 (m, 4 H).

^{13}C NMR (125.75 MHz, CDCl$_3$, 25 °C): δ (major diastereomer) = 78.1, 43.7, 29.6, 28.6, 26.9, 26.61, 26.57, 17.9.

Benzyl 4-Bromobenzyl Ether (20)

BnOSiMe$_3$ (0.18 g, 1 mmol), 4-bromobenzaldehyde (0.19 g, 1 mmol), and Et$_3$SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution (1 mL) was added, and the mixture was stirred for 1 h. EtOAc (10 mL) was added and the mixture was washed with sat. aq NaHCO$_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 219 mg (79%); R_f = 0.68 (EtOAc–hexane, 1:4); purity: 98%.

^{1}H NMR (500.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.50 (ddd, J = 2.2, 8.8 Hz, 2 H), 7.38–7.35 (m, 4 H), 7.34–7.25 (m, 3 H), 4.56 (s, 2 H), 4.52 (s, 2 H).

^{13}C NMR (125.75 MHz, CD$_2$Cl$_2$, 25 °C): δ = 138.7, 138.1, 131.8, 129.7, 128.7, 128.1, 128.0, 121.6, 72.6, 71.7.

Benzyl 4-(Trifluoromethyl)benzyl Ether (21)

BnOSiMe$_3$ (0.9 g, 5 mmol), 4-(trifluoromethyl)benzaldehyde (0.68 mL, 5 mmol), and Et$_3$SiH (0.84 mL, 5.25 mmol) were mixed together, the stock catalyst solution (5 mL) was added, and the mixture was stirred for 1 h. EtOAc (20 mL) was then added and the solution was washed with sat. aq NaHCO$_3$ (2 × 8 mL). The aqueous phases were combined and washed with EtOAc (8 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 1.18 g (89%); R_f = 0.75 (EtOAc–hexane, 1:4); purity: 97%.

^{1}H NMR (600.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.64 (d, J = 8.1 Hz, 2 H), 7.52 (d, J = 8.1 Hz, 2 H), 7.41–737 (m, 4 H), 7.34–7.31 (m, 1 H), 4.64 (s, 2 H), 4.60 (s, 2 H).

^{13}C NMR (150.92 MHz, CD$_2$Cl$_2$, 25 °C): δ = 143.4, 138.6, 129.8 (q, $J_{C,F}$ = 32 Hz), 128.8, 128.2, 128.1, 128.0, 125.6 (q, $J_{C,F}$ = 4 Hz), 124.8 (q, $J_{C,F}$ = 272 Hz), 73.0, 71.7.

Benzyl 2-Nitrobenzyl Ether (22)

BnOSiMe$_3$ (0.9 g, 5 mmol), 2-nitrobenzaldehyde (0.76 g, 5 mmol), and Et$_3$SiH (0.84 mL, 5.25 mmol) were mixed, the stock catalyst solution (5 mL) was added, and the mixture was stirred for 1 h. EtOAc (20 mL) was then added and the mixture was washed with sat. aq NaHCO$_3$ (2 × 8 mL). The aqueous phases were combined and washed with EtOAc (8 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–50% EtOAc–hexane) to give a white to pale-yellow solid that was crystallized (hexane) to provide white needles; yield: 0.94 g (77%); mp 58–59 °C (lit.[61] 64–66 °C); R_f = 0.49 (EtOAc–hexane, 1:4); purity: 97%.

^{1}H NMR (600.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 8.05 (dd, J = 1.3, 8.1 Hz, 1 H), 7.87–7.85 (m, 1 H), 7.67–7.66 (m, 1 H), 7.48–7.45 (m, 1 H), 7.41–7.36 (m, 4 H), 7.33–7.30 (m, 1 H), 4.94 (s, 2 H), 4.66 (s, 2 H).

^{13}C NMR (150.92 MHz, CD$_2$Cl$_2$, 25 °C): δ = 147.8, 138.4, 135.4, 134.0, 129.2, 128.8, 128.4, 128.15, 128.09, 124.9, 73.5, 69.3.

Benzyl 4-Methylbenzyl Ether (23)

BnOSiMe$_3$ (0.18 g, 1 mmol), 4-methylbenzaldehyde (0.14 g, 1 mmol), and Et$_3$SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution (1 mL) was added, and the mixture was stirred for 1 h. EtOAc (10 mL) was then added and the solution was washed with sat. aq NaHCO$_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 186 mg (89%); R_f = 0.76 (EtOAc–hexane, 1:4); purity: 95%.

^{1}H NMR (600.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.39–7.35 (m, 4 H), 7.32–7.29 (m, 1 H), 7.28–7.25 (m, 2 H), 7.19–7.17 (m, 2 H), 4.56 (s, 2 H), 4.52 (s, 2 H), 2.36 (s, 3 H).

^{13}C NMR (150.92 MHz, CD$_2$Cl$_2$, 25 °C): δ = 139.1, 137.7, 135.9, 129.4, 128.7, 128.2, 128.1, 127.9, 72.5, 72.4, 21.3.

3-[(Benzyloxy)methyl]phenol (24)

BnOSiMe$_3$ (0.18 g, 1.0 mmol), 3-hydroxybenzaldehyde (0.12 g, 1.0 mmol), and Et$_3$SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution (1 mL) was added, and the mixture was stirred for 1 h. EtOAc (10 mL) was then added and the mixture was washed with sat. aq NaHCO$_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–80% EtOAc–hexane) to give a colorless oil; yield: 178 mg (83%); R_f = 0.21 (EtOAc–hexane, 1:4); purity: >99%.

^{1}H NMR (500.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.39–7.29 (m, 5 H), 7.21 (t, J = 7.9 Hz, 1 H), 6.92–6.90 (m, 1 H), 6.85–6.84 (m, 1 H), 6.75–6.73 (m, 1 H), 5.38 (br s, 1 H), 4.56 (s, 2 H), 4.52 (s, 2 H).

^{13}C NMR (125.76 MHz, CD$_2$Cl$_2$, 25 °C): δ = 156.3, 140.7, 138.7, 129.9, 128.7, 128.2, 128.0, 120.2, 114.85, 114.82, 72.5, 72.2.

Benzyl Hexyl Ether (25)

BnOSiMe$_3$ (0.21 g, 1.15 mmol), hexanal (0.12 ml, 1 mmol), and Et$_3$SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from FeCl$_3$ (1 mL) was added, and the mixture was stirred for 1 h. EtOAc (10 mL) was added, and the mixture was washed with sat. aq NaHCO$_3$ (3 mL). The aqueous phases were combined and washed with EtOAc (2 × 3 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 150 mg (78%); R_f = 0.8 (EtOAc–hexane, 1:4); purity: 94%.

^{1}H NMR (600.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.38–7.33 (m, 4 H), 7.30–7.26 (m, 1 H), 4.48 (s, 2 H), 3.47 (t, J = 6.6 Hz, 2 H), 1.63–1.58 (m, 2 H) 1.40–1.27 (m, 6 H), 0.91 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (150.92 MHz, CD$_2$Cl$_2$, 25 °C): δ = 139.5, 128.6, 127.9, 127.7, 73.1, 71.0, 32.2, 30.2, 26.3, 23.1, 14.3.

Benzyl Cyclohexyl Ether (26)

BnOSiMe$_3$ (0.21 g, 1.15 mmol), cyclohexanone (0.1 ml, 1 mmol), and Et$_3$SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from FeCl$_3$ (1 mL) was added, and the mixture was stirred for 1 h. EtOAc (10 mL) was added, and the mixture was washed with sat. aq NaHCO$_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 162 mg (85%); R_f = 0.68 (EtOAc–hexane, 1:4); purity: 93%.

Alternatively, CyOSiMe$_3$ (0.17 g, 1.0 mmol), PhCHO (0.1 mL, 1.0 mmol), and Et$_3$SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from FeCl$_3$ (1 mL) was added, and the mixture was stirred for 30 min. EtOAc (10 mL) was added, and the mixture was washed with sat. aq NaHCO$_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 166 mg (87%); R_f = 0.68 (EtOAc–hexane, 1:4); purity: >99%.

^{1}H NMR (600.13 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.36–7.32 (m, 4 H), 7.29–7.25 (m, 1 H), 4.52 (s, 2 H), 3.39–3.35 (m, 1 H), 1.95–1.93 (br m, 2 H), 1.78–1.71 (m, 2 H), 1.55–1.53 (m, 1 H), 1.39–1.17 (m, 5 H).

^{13}C NMR (150.92 MHz, CD$_2$Cl$_2$, 25 °C): δ = 140.1, 128.6, 127.8, 127.6, 69.9, 32.6, 26.3, 24.5.

Cyclohexyl 4-Methylbenzyl Ether (27)

CyOSiMe$_3$ (0.17 g, 1.0 mmol), 4-methylbenzaldehyde (0.12 mL, 1.0 mmol), and Et$_3$SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from FeCl$_3$ (1 mL) was added, and the mixture was stirred for 30 min. EtOAc (10 mL) was added, and the mixture was washed with sat. aq NaHCO$_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na$_2$SO$_4$). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 164 mg (80%); R_f = 0.77 (EtOAc–hexane, 1:4); purity: >99%.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.23 (d, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 7.8 Hz, 2 H), 4.48 (s, 2 H), 3.38–3.32 (m, 1 H), 2.34 (s, 3 H), 1.95–1.92 (m, 2 H), 1.78–1.73 (m, 2 H), 1.56–1.52 (m, 1 H), 1.39–1.22 (m, 5 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 137.3, 137.0, 129.2, 127.9, 77.2, 69.8, 32.7, 26.3, 24.5, 21.3.

Methyl 4-[(Cyclohexyloxy)methyl]benzoate (28)

$CyOSiMe_3$ (0.17 g, 1.0 mmol), methyl 4-formylbenzoate (0.16 g, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. EtOAc (10 mL) was added, and the mixture was washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–60% EtOAc–hexane) to give a colorless oil; yield: 198 mg (80%); R_f = 0.67 (EtOAc–hexane, 1:4); purity: >99%.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.98 (ddd, *J* = 1.9, 8.4 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 4.58 (s, 2 H), 3.88 (s, 3 H), 3.39–3.34 (m, 1 H), 1.95–1.93 (br m, 2 H), 1.78–1.73 (m, 2 H), 1.56–1.51 (m, 1 H), 1.40–1.20 (m, 5 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 167.2, 145.5, 129.8, 129.5, 127.4, 77.7, 69.4, 52.3, 32.6, 26.2, 24.4.

Biphenyl-4-ylmethyl Cyclohexyl Ether (29)

$CyOSiMe_3$ (0.17 g, 1.0 mmol), biphenyl-4-carboxaldehyde (0.18 g, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. EtOAc (10 mL) was added, and the mixture was washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 225 mg (85%); R_f = 0.61 (EtOAc–hexane, 1:4); purity: >99%.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.64–7.58 (m, 4 H), 7.47–7.42 (m, 4 H), 7.36 (tt, *J* = 1.5, 7.3 Hz, 1 H), 4.58 (s, 2 H), 3.43–3.38 (m, 1 H), 1.99–1.96 (m, 2 H), 1.81–1.75 (m, 2 H), 1.58–1.53 (m, 1 H), 1.43–1.23 (m, 5 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 141.3, 140.4, 139.2, 129.2, 128.3, 127.6, 127.4, 127.3, 77.4, 69.7, 32.7, 26.3, 24.5.

Cyclohexyl Octyl Ether (30)

Octyloxy(trimethyl)silane (0.20 g, 1.0 mmol), cyclohexanone (0.12 mL, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. EtOAc (10 mL) was added, and the mixture was washed with sat. aq $NaHCO_3$ (3 mL). The aqueous phases were combined and washed with EtOAc (2 × 3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 191 mg (90%); R_f = 0.81 (EtOAc–hexane, 1:4); purity: 99%.

^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 3.42 (t, *J* = 6.8 Hz, 2 H), 3.21–3.16 (m, 1 H), 1.92–1.88 (br m, 2 H), 1.74–1.70 (br m, 2 H), 1.59–1.50 (m, 3 H), 1.33–1.16 (m, 15 H), 0.87 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): δ = 77.6, 68.1, 32.5, 32.0, 30.4, 29.6, 29.4, 26.4, 26.0 24.4, 22.8, 14.2.

1,3-Dimethylbutyl Octyl Ether (31)

Octyloxy(trimethyl)silane (0.20 g, 1.0 mmol), *i*-BuCOMe (0.12 mL, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. Hexane (10 mL) was then added and the mixture was washed with sat. aq $NaHCO_3$ (3 mL). The aqueous phases were combined and washed with EtOAc (2 × 3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 165 mg (77%); R_f = 0.89 (EtOAc–hexane, 1:9); purity: 99%.

^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 3.35–3.47 (m, 1 H), 3.44–3.38 (m, 1 H), 3.31–3.26 (m, 1 H), 1.78–1.70 (m, 1 H), 1.57–1.45 (m, 3 H), 1.36–1.22 (m, 10 H), 1.17–1.10 (m, 4 H), 0.89–0.77 (m, 9 H).

^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): δ = 73.6, 68.6, 46.5, 32.0, 30.4, 29.6, 29.4, 26.4, 24.8, 23.2, 22.8, 22.7, 20.1, 14.2.

Benzyl (–)-Menthyl Ether (32)

(–)-Menthyl trimethylsilyl ether (0.23 g, 1.0 mmol), PhCHO (0.1 mL, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. EtOAc (10 mL) was added, and the mixture was washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 217 mg (88%); R_f = 0.78 (EtOAc–hexane, 1:4); purity: >99%; dr 100:0 (1*R*,2*S*,4*R*/1*S*,2*S*,4*R*).

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.38–7.32 (m, 4 H), 7.29–7.25 (m, 1 H), 4.65 (d, *J* = 11.6 Hz, 1 H), 4.38 (d, *J* = 11.6 Hz, 1 H), 3.19 (ddd, *J* = 4.1, 10.5 Hz, 1 H), 2.34–2.25 (m, 1 H), 2.25–2.20 (m, 1 H), 1.70–1.62 (m, 2 H), 1.44–1.34 (m, 1 H), 1.31–1.25 (m, 1 H), 1.05–0.84 (m, 9 H), 0.75 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 140.0, 128.6, 128.2, 127.6, 79.2, 70.6, 48.9, 40.7 35.0, 32.0, 26.0, 23.7, 22.6, 21.2, 16.3.

Biphenyl-4-ylmethyl (–)-Menthyl Ether (33)

(–)-Menthyl trimethylsilyl ether (0.23 g, 1.0 mmol), biphenyl-4-carboxaldehyde (0.18 g, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. EtOAc (10 mL) was added, and the mixture was washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phases were combined and washed with EtOAc (3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified twice by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane then gradient 0–10% EtOAc–hexane) to give a colorless oil; yield: 245 mg (76%); R_f = 0.69 (EtOAc–hexane, 1:4); purity: >99%; dr 100:0 (1*R*,2*S*,4*R*/1*S*,2*S*,4*R*).

^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.64–7.59 (m, 4 H), 7.48–7.43 (m, 3 H), 7.36 (tt, *J* = 1.3, 7.3 Hz, 1 H), 4.71 (d, *J* = 11.5 Hz, 1 H) 4.43 (d, *J* = 11.5 Hz, 1 H), 3.23 (ddd, *J* = 4.1, 10.5 Hz, 1 H), 2.38–2.29 (m, 1 H), 2.28–2.24 (m, 1 H), 1.72–1.64 (m, 2 H), 1.47–1.36 (m, 1 H), 1.34–1.28 (m, 1 H), 1.08–0.89 (m, 9 H), 0.78 (d, *J* = 8.2 Hz, 3 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 141.3, 140.5, 139.1, 129.2, 128.6, 127.6, 127.4, 127.3, 79.3, 70.3, 48.9, 40.8, 35.1, 32.0, 26.1, 23.8, 22.6, 21.2, 16.4.

Allyl Benzyl Ether (34)

$AllOSiMe_3$ (0.17 mL, 1.0 mmol), PhCHO (0.10 mL, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. Hexane (10 mL) was then added and the mixture was washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phases were combined and washed with hexane (3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 119 mg (80%); R_f = 0.68 (EtOAc–hexane, 1:4); purity: 96%.

^1H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.38–7.34 (m, 4 H), 7.32–7.28 (m, 1 H), 6.01–5.94 (m, 1 H), 5.32 (qd, J = 1.7, 17.2 Hz, 1 H) 5.22–5.19 (m, 1 H), 4.52 (s, 2 H), 4.04 (td, J = 1.5, 5.5 Hz, 2 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 139.1, 135.5, 128.7, 128.0, 127.9, 116.8, 72.5, 71.5.

Allyl 4-Fluorobenzyl Ether (35)

$AllOSiMe_3$ (0.17 mL, 1.0 mmol), 4-FC_6H_4CHO (0.11 mL, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. Hexane (10 mL) was then added and the mixture was washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phases were combined and washed with hexane (3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 152 mg (92%); R_f = 0.63 (EtOAc–hexane, 1:4); purity: 95%.

^1H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 7.33–7.31 (m, 2 H), 7.08–7.03 (m, 2 H), 6.00–5.92 (m, 1 H), 5.30 (qd, J = 1.7, 17.3 Hz, 1 H), 5.21–5.18 (m, 1 H), 4.47 (s, 2 H), 4.02 (td, J = 1.5, 5.6 Hz, 2 H).

^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 162.7 (d, $J_{C,F}$ = 245 Hz), 135.3, 134.9 (d, $J_{C,F}$ = 3 Hz), 129.8 (d, $J_{C,F}$ = 8 Hz), 116.9, 115.4 (d $J_{C,F}$ = 21 Hz), 71.7, 71.5.

2-Adamantyl Allyl Ether (36)

$AllOSiMe_3$ (0.17 mL, 1.0 mmol), adamantan-2-one (0.15 g, 1.0 mmol), and Et_3SiH (0.17 mL, 1.05 mmol) were mixed together, the stock catalyst solution prepared from $FeCl_3$ (1 mL) was added, and the mixture was stirred for 30 min. Hexane (10 mL) was then added and the mixture was washed with sat. aq $NaHCO_3$ (2 × 3 mL). The aqueous phases were combined and washed with hexane (3 mL), and then the organic phases were combined and dried (Na_2SO_4). The crude product was purified by flash chromatography (silica gel, gradient 0–35% EtOAc–hexane) to give a colorless oil; yield: 139 mg (72%); R_f = 0.77 (EtOAc–hexane, 1:9); purity: 96%.

^1H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 5.97–5.92 (m, 1 H), 5.28 (qd, J = 1.7, 17.2 Hz, 1 H), 5.14 (qd, J = 1.7, 10.4 Hz, 1 H), 3.99 (ddd, J = 1.6, 5.4 Hz, 2 H), 3.47 (t, J = 3.2 Hz, 1 H), 2.08–2.01 (br m, 4 H), 1.86–1.77 (br m, 4 H), 1.70 (br s, 2 H), 1.66–1.63 (br m, 2 H), 1.49–1.45 (m, 2 H).

^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): δ = 136.0, 116.0, 81.2, 68.5, 37.7, 36.7, 31.9, 31.7, 27.6.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380155. Included are details on catalyst preparation and characterization and copies of NMR and GC chromatograms of the isolated products.

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