Tetrahedron Letters 53 (2012) 6361–6366

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Ferrocene tagged functional polymer: a robust solid-phase reagent for O-demethylation

Rajanikant Kurane [a], Vipul Gaikwad [a], Jagannath Jadhav [a], Rajashri Salunkhe [a], Gajanan Rashinkar [a,*]

[a] *Department of Chemistry, Shivaji University, Kolhapur 416004, Maharashtra, India*

ARTICLE INFO

Article history:
Received 2 August 2012
Revised 5 September 2012
Accepted 6 September 2012
Available online 21 September 2012

Keywords:
Functional polymer
Ferrocene
O-demethylation
Merrifield resin
Reusability

ABSTRACT

Ferrocene tagged functional polymer was synthesized by exploiting the propensity of the Merrifield resin to undergo quaternization with *N*-ferrocenylmethyl benzimidazole followed by subsequent anion metathesis reaction. The synthesized polymer when employed as a solid-phase reagent for O-demethylation of aryl methyl ethers, showed TON in the range of 7373–8930 and TOF in the range of 279–494 h^{-1}.

Development of new solid-phase reagents is a subject of immense interest in the context of generating libraries of molecules for the discovery of biologically active leads and also for the optimization of drug candidates.[1] A number of tangible benefits arise from the use of solid-phase reagents, chief of which are the ease of purification process after the reaction as well as facilitating significant advances in selectivity, recycling reproducibility, and activity.[2] At the same time, they can add economic value via more efficient consumption of energy, through the use of milder conditions and achieving greater atom-economy containing fewer steps.[3] As a consequence of the need for robust solid-phase reagents, the development of functional polymers based on Merrifield resin has gained considerable momentum in recent years since they provide significant stability to mechanical, chemical, and thermal demands under diverse operating conditions.[4] Since the turn of the century, there has been a constant drive to develop new and improved strategies for organic synthesis using functional polymers based on Merrifield resin backbone.[5]

The protection of functional groups and their regeneration is an important area of research in organic synthesis.[6] In this context, O-demethylation constitutes an important method in the light of its importance for protection of hydroxyl groups from phenols and its involvement in the manufacture of a number of pharmaceuticals, drugs, and other fine chemicals.[7] It is a nearly ubiquitous process in the synthesis of multifunctional heterocyclic compounds where aryl methyl ethers are used as protected phenols.[8] The methoxy unit, being stable to a vast array of reaction conditions, is particularly well utilized for protection of phenols which makes O-demethylation difficult under normal milder conditions.[9] A variety of reagents such as aluminum chloride,[10] boron tribromide,[11] cerium chloride,[12] alkaline thiolate,[13] L-selectride,[14] iodocyclohexane,[15] [Bmim]Br,[16] pyridine hydrochloride,[17] protic acids in ionic liquids,[18] 2-(diethylamino)ethanethiol,[19] sodium bis(trimethylsilyl)amide and lithium diisopropylamide,[20] chloroaluminate ionic liquids,[8] $SiCl_4/LiI/BF_3$,[21] 1-decanethiol,[22] lithium thioethoxide,[23] etc have been developed for O-demethylation. However, despite numerous and significant methods available to perform this transformation, a mild protocol for O-demethylation using a highly robust heterogeneous catalyst still represents a considerable synthetic challenge.

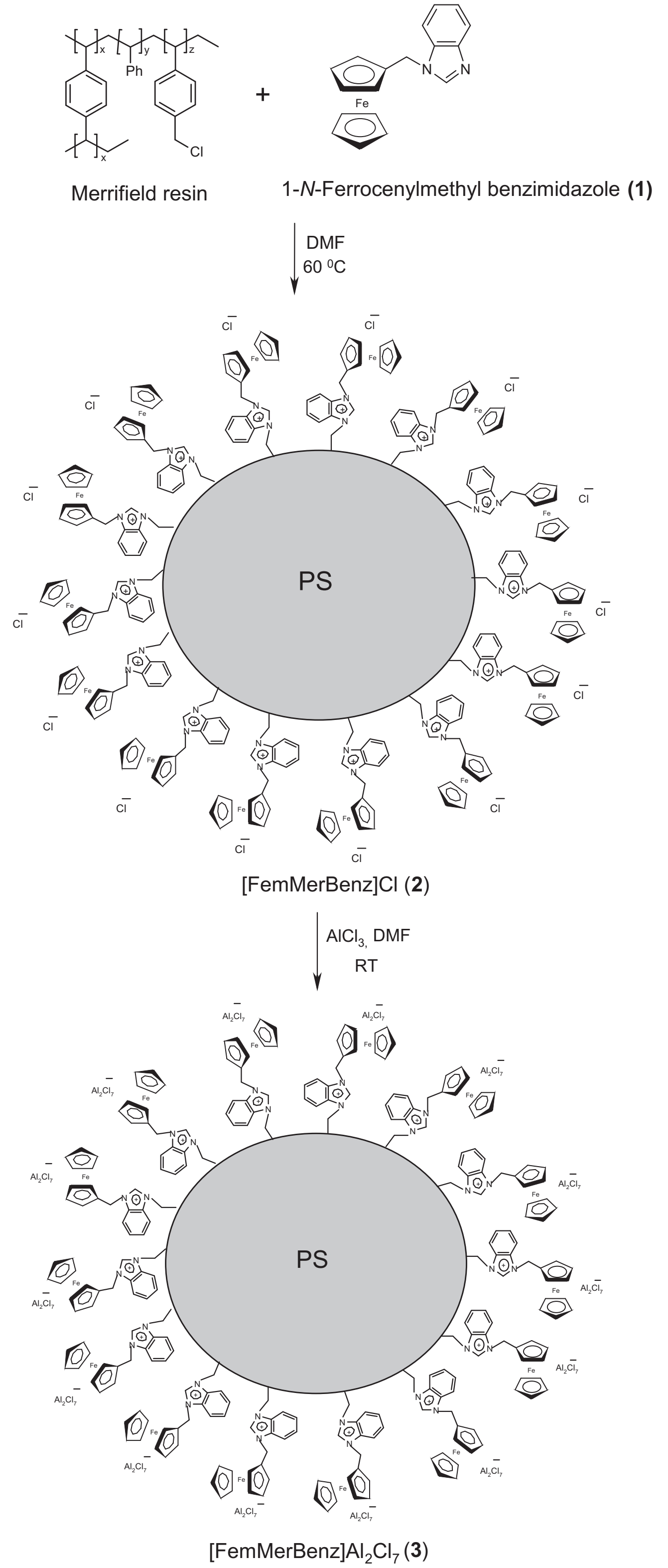
As a continuation of our on-going investigations related to heterogeneous catalysis,[24] we report herein a solid-phase O-demethylation of aryl methyl ethers using ferrocene tagged functional polymer.

In the synthesis of ferrocene tagged functional polymer (Scheme 1),[25] Merrifield resin was quaternized with 1-*N*-ferrocenylmethyl benzimidazole (**1**) to give [FemMerBenz]Cl (**2**). The resulting compound when treated with excess of $AlCl_3$ underwent anion metathesis reaction to afford the desired ferrocene tagged functional polymer, acronymed as [FemMerBenz]Al_2Cl_7 (**3**). The FT-IR and FT-Raman spectroscopy were performed to monitor the progress of the reactions involved in the synthesis of **3**. The reaction of **1** with Merrifield resin was supervised by using FT-Raman spectroscopy. The negative going bands at 640 cm^{-1} (C–Cl stretching band) and 1267 cm^{-1} (wagging bands of CH_2–Cl) almost

---

[*] Corresponding author. Tel.: +91 231 260 9169; fax: +91 231 2692333.
E-mail addresses: gsrchemsuk@yahoo.co.in, gsr_chem@unishivaji.ac.in (G. Rashinkar).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.09.021



Scheme 1. Synthesis of ferrocene tagged functional polymer, [FemMerBenz]Al_2Cl_7.

disappeared while the peaks at 455 cm^{-1} (Fe–Cp stretching band), 1258 cm^{-1}, 1335 cm^{-1}, 1408 cm^{-1}, and 1460 cm^{-1} (ring stretching modes of benzimidazolium ring), 3135 cm^{-1} and 3186 cm^{-1} (C–H stretching of Cp rings) increased in intensity after 72 h reflecting the substantial grafting of **1** in the matrix of Merrifield resin. Anion metathesis reaction was monitored using FT-IR spectroscopy. Appearance of peaks at 308 cm^{-1}, 333 cm^{-1}, 384 cm^{-1}, 437 cm^{-1}, and 543 cm^{-1} which are characteristic peaks of $Al_2Cl_7^-$ confirmed the formation of **3**.[26] The Al loading of the ferrocene tagged functional polymer as determined by EDAX was found to be 0.048 mmol of aluminum g^{-1}.

Scanning electron micrographs (SEM) at various stages of preparation of **3** were recorded to understand the morphological changes occurring on the surface of Merrifield resin. Scanning was done across the length of polymer beads. Comparison of images taken at a magnification of $\sim 5 \times 10^2$ indicates that the spherical beads of Merrifield resin with smooth surface (Fig. 1a) were altered upon functionalization. The resin beads in **3** were not spherical like the original Merrifield resin beads (Fig. 1). In fact the bead degradation observed (Fig. 1b) was plausibly due to the stress generated during the surface confinement of the Merrifield resin with **1** and the subsequent anion metathesis reaction.[27]

Thermogravimetric analysis revealed that the Merrifield resin as well as **3** degraded in two stages (Fig 2). The former began to decompose at 258 °C and lost almost all of its mass at 757 °C while the latter which contained about 15% evaporable moieties such as physisorbed water and volatile solvents occluded during handling, started to decompose at 239 °C and lost most of its mass at 615 °C. The profiles of thermogram manifested that **3** was comparatively less stable than the Merrifield resin.

Our next task was to assess the catalytic activity of **3** in the O-demethylation reactions.[28] Initial studies started with the reaction of *p*-methoxy acetophenone (**1a**) using 200 mg of catalyst (0.96 mol %) in DMF under reflux condition (Table 1, entry 8). The reaction was completed in 24 h as confirmed by TLC. The reaction mixture was poured into water and extracted with ethyl acetate. The corresponding O-demethylation product was obtained in 78% yield. A parallel experiment was also carried out to confirm that no product was obtained in the absence of **3**.

We also investigated the influence of solvent on the outcome of the aforementioned O-demethylation reaction catalyzed by ferrocene tagged functional polymer (Table 1). DMF was found to be the most effective solvent. Employing THF as the solvent significantly decreased the yield of product. On the other hand, when dichloromethane, methanol, ethanol, and DMSO were used as a solvent, no reaction occurred even after prolonged reaction time.

Next, we investigated the effect of catalyst loading on the O-demethylation of **1a** (Table 1). The use of 100 mg catalyst (0.48 mol %) afforded the anticipated product in 51% after 24 h. When increased to 200 mg (0.96 mol %), the product yield was improved to 78% after 24 h under same reaction conditions. We then used 300 mg of catalyst (1.44 mol %), to catalyze the reaction, but no significant change in the yield and reaction time was observed. Thus, 200 mg of catalyst (0.96 mol %) loading was selected as the optimum concentration for further studies.

With optimization conditions in hand, we evaluated the scope of O-demethylation of structurally diverse aryl methyl ethers in the presence of **3** (Scheme 2) and the results are summarized in Table 2. A variety of aryl methyl ethers bearing electron-withdrawing as well as electron-donating substituents reacted efficiently affording products with high TON and TOF.[29] The protocol furnished excellent results with both heteroaromatic methyl ethers and methyl ethers of tetralones. It is worthy of note that compounds with relatively acidic protons could be O-demethylated in better yields. Surprisingly, selective O-demethylation was observed when 3,4,5-trimethoxy benzaldehyde was reacted with functional polymer giving 4-hydroxy-3,5-dimethoxy benzaldehyde. This selectivity can be rationalized on the fact that once the first deprotection has taken place, the ring becomes more electron-rich and additional demethylation is disfavored.[19]

When a functional polymer that mimics **3** but without ferrocene tag ([MeMerBenz]Al_2Cl_7)[30] was used as a catalyst, the

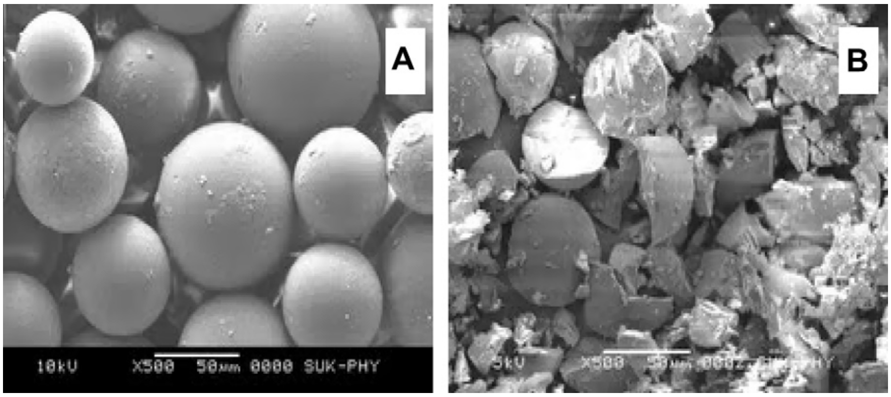


Figure 1. Scanning electron micrographs of (A) Merrifield resin and (B) [FemMerBenz]Al_2Cl_7.

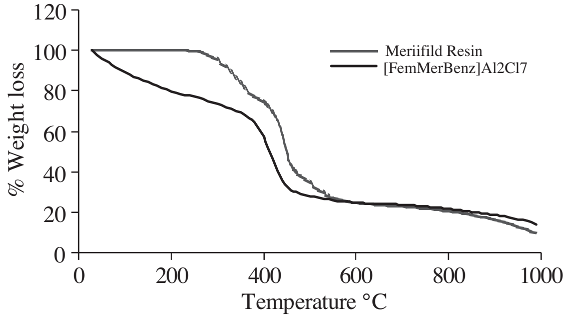
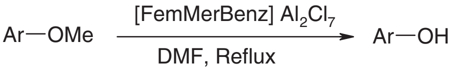


Figure 2. TGA curves of Merrifield resin and [FemMerBenz]Al_2Cl_7.



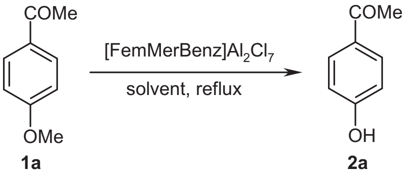
Scheme 2. O-demethylation using [FemMerBenz]Al_2Cl_7.

efficiency of O-demethylation was low and the isolated yield of the product was only 51%. We have also synthesized and studied the catalytic activity of the corresponding functional polymer possessing bulky benzyl group instead of ferrocene tag which is acronymed as [BnMerBenz]Al_2Cl_7.[30] Although [BnMerBenz]Al_2Cl_7 showed an increase in catalytic activity as compared to [MeMerBenz]Al_2Cl_7 (ca. 59%), it was still lower as compared to **3**. It is reasonable to assume that the significantly improved catalytic activity of **3** may stem from ferrocene tag that enhances micropolarity; a key factor that ascertains the catalytic properties of heterogeneous catalysts.[31] The presence of ferrocene results in unsymmetrical charge distribution on the benzimidazole ring resulting in the significant enhancement of overall polarity of **3**.

A tentative mechanistic rationale for the O-demethylation using functional polymer is presented in Scheme 3. Initially, aluminum coordinates to oxygen atom of methoxy functionality. This phenomenon activates the C–O bond between oxygen and methyl group. This process is followed by an attack of chloride anion to methyl carbon atom with a subsequent loss of methyl chloride.

The successful recovery and reuse of catalyst is an essential aspect of green chemistry and is one of the important factors in determining its potential value for large-scale operation and industrial point of view. To check the possibility of the catalyst recycling,

Table 1
Optimization studies of O-demethylation reaction[a,b]



Entry	Amount of catalyst (mg)	Solvent	Yield[c] (%)	TON[d]	TOF[e] (h^{-1})
1	200	Dichloromethane	NR	—	—
2	200	MeOH	NR	—	—
3	200	EtOH	NR	—	—
4	200	DMSO	NR	—	—
5	200	THF	61	6334	263
6	50	DMF	24	2492	103
7	100	DMF	51	5296	220
8	200	DMF	78	8100	337
9	300	DMF	79	8203	341
10	Nil	DMF	NR	—	—

[a] All products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry.
[b] Reaction time of 24 h.
[c] Isolated yields after chromatography.
[d] % Conversion per mol of catalyst.
[e] TON per hour.

Table 2
O-demethylation of aryl methyl ethers using [FemMerBenz]Al_2Cl_7[a]

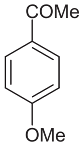
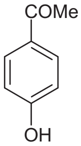
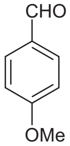
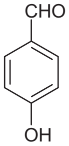
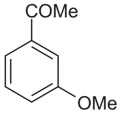
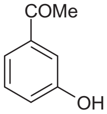
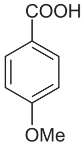
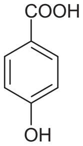
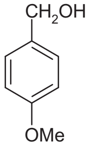
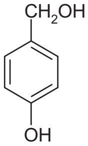
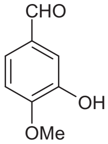
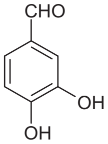
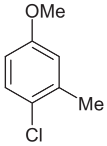
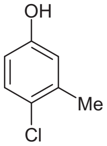
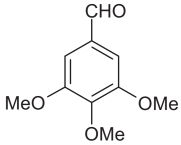
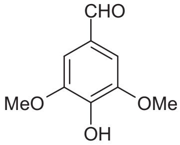
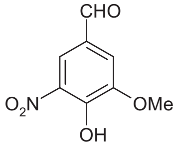
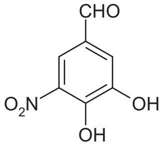
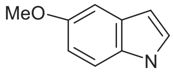
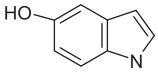
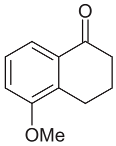
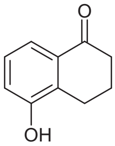
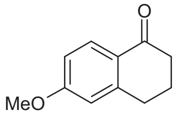
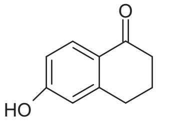
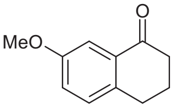
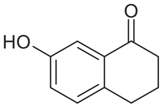
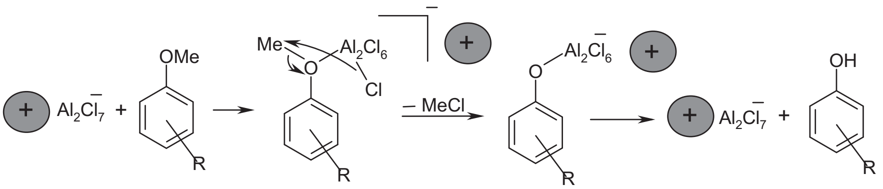
Entry	Aryl methyl ether **1**	Product **2**	Yield[b] (%)	TON	TOF (h^{-1})
a			78	8100	337
b			86	8930	425
c			76	7892	438
d			73	7580	291
e			79	8203	292
f			81	8411	336
g			80	8307	361
h			78	8100	279
i			73	7580	344
j			71	7373	320
k			82	8515	437
l			79	8203	410

Table 2 (*continued*)

Entry	Aryl methyl ether **1**	Product **2**	Yield[b] (%)	TON	TOF (h^{-1})
m			81	8411	494

[a] All products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry.
[b] Isolated yields after chromatography.



Scheme 3. A plausible mechanism for O-demethylation using [FemMerBenz]Al_2Cl_7.

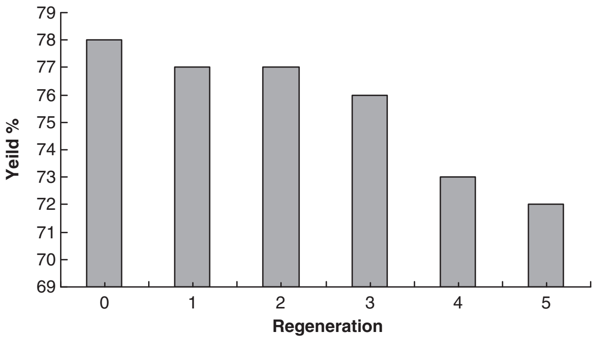


Figure 3. Reusability of [FemMerBenz]Al_2Cl_7 in O-demethylation reaction.

the O-demethylation of *p*-methoxy acetophenone was carried out in the presence of **3**. After the reaction, the catalyst was separated by simple filtration, washed with DMF, and dried in vacuum before being reused in subsequent runs. The catalyst could be reused at least five times without noticeable decrease in the catalytic activity (Fig. 3). The FT-IR and FT-Raman spectra of reused catalyst were indistinguishable from those of the fresh catalyst, which revealed that the main characteristics of the catalyst were preserved during recycling and reuse.

In conclusion, we have developed a simple and efficient methodology for the O-demethylation of aryl methyl ethers using ferrocene tagged functional polymer, which served as an excellent recyclable and reusable heterogeneous catalyst. The operational simplicity, application of stable catalyst, excellent TON, and TOF are the unique features of the presented protocol.

Acknowledgments

Authors G.S.R., R.S.S., and R.M.K. thank UGC, New Delhi for financial assistance [F. No. 40-96/2011 (SR)] and for the research fellowship, respectively.

References and notes

1. (a) Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *9*, 135–144; (b) Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. *J. Chem. Soc., Perkin Trans.* **2000**, *1*, 3815–4195; (c) Gordon, E. M.; Dower, W. J.; Barrett, R. W.; Fodor, S. P. A.; Gallop, M. A. *J. Med. Chem.* **1994**, *37*, 1233–1251; (d) Fruchtel, J. S.; Jung, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 17–42; (e) Hermkens, P. H. H.; Ottenheijm, H. C. J.; Rees, D. *Tetrahedron* **1996**, *52*, 4527–4554; (f) Terrett, N. K.; Gardner, M.; Gordon, D. W.; Kobylecki, R. J.; Steele, J. *Tetrahedron* **1995**, *51*, 8135–8173; (g) Thompson, L.; Ellman, J. A *Chem. Rev.* **1996**, *96*, 555–600.
2. Smith, K. *Solid Supports and Catalysts in Organic Synthesis*; PTR Prentice Hall: New York, 1992.
3. Barbaro, P.; Liguori, F. *Chem. Rev.* **2009**, *109*, 515–529.
4. Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149–2154.
5. For selected examples see: (a) Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815–838; (b) Buchmeiser, M. R. *Chem. Rev.* **2009**, *109*, 303–321; (c) Cai, J.; Wathey, B. *Tetrahedron Lett.* **2001**, *42*, 1383–1385; (d) Török, B.; Bucsi, I.; Suryaprakash, G. K.; Olah, G. A. *Chem. Commun.* **2002**, 2882–2883; (e) Reddy, C. R. V.; Verkade, J. G. *J. Org. Chem.* **2007**, *72*, 3093–3096; (f) Dyer, P. W.; Handa, S.; Reeve, T. B.; Suhard, S. *Tetrahedron Lett.* **2005**, *46*, 4753–4756; (g) Yang, J.; Li, P.; Wang, L. *Tetrahedron* **2011**, *67*, 5543–5549; (h) Schweizer, S.; Becht, J.-M.; Drian, C. L. *Tetrahedron* **2010**, *66*, 765–772.
6. (a) Ley, S. V.; Baeschlin, D. K.; Dixon, D. J.; Foster, A. C.; Ince, S. J.; Priepke, H. W. M.; Reynolds, D. J. *Chem. Rev.* **2001**, *101*, 53–80; (b) Sureshan, K. M.; Shashidhar, M. S.; Praveen, T.; Das, T. *Chem. Rev.* **2003**, *103*, 4477–4504; (c) Sartori, G.; Bigi, F.; Bosica, G.; Maggi, R.; Righi, P. *Chem. Rev.* **2004**, *104*, 199–250; (d) Isidro-Llobet, A.; Alvarez, M.; Albericio, F. *Chem. Rev.* **2009**, *109*, 2455–2504; (e) Ramesh, R.; Chandrasekaran, S. *Organic Lett.* **2005**, *7*, 4947–4950.
7. (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, 1999. pp. 246–276; (b) Fang, Z.; Zhou, G.-C.; Zheng, S. L.; He, G. L.; Li, J.-L.; He, L.; Bei, D. *J. Mol. Catal. A: Chem.* **2007**, *274*, 16–23.
8. Kemperman, G. J.; Roeters, T. A.; Hilberink, P. W. *Eur. J. Org. Chem.* **2003**, 1681–1686.
9. Li, G.; Patel, D.; Hruby, H. J. *Tetrahedron Lett.* **1993**, *34*, 5393–5396.
10. Parker, K. A.; Petraitis, J. J. *Tetrahedron Lett.* **1981**, *22*, 397–400.
11. Miller, J. M.; So, K. H.; Clark, J. H. *Can. J. Chem.* **1979**, *57*, 1887–1889.
12. Yadav, J. S.; Reddy, B. V. S.; Madan, C.; Hashim, S. R. *Chem. Lett.* **2000**, *29*, 738–739.
13. Dodge, J. A.; Stocksdale, M. G.; Fahey, K. J.; Jones, C. D. *J. Org. Chem.* **1995**, *60*, 739–741.
14. Coop, A.; Janetka, J. W.; Lewis, J. W.; Rice, K. C. *J. Org. Chem.* **1998**, *63*, 4392–4396.
15. Zuo, L.; Yao, S.; Wang, W.; Duan, W. *Tetrahedron Lett.* **2008**, *49*, 4054–4056.
16. Park, J.; Chae, J. *Synlett* **2010**, 1651–1656.
17. Kulkarni, P. P.; Kadam, A. J.; Mane, R. B.; Desai, U. V.; Wadgaonkar, P. P. *J. Chem. Res. (S)* **1999**, 394–395.
18. Boovanahalli, S. K.; Kim, D. W.; Chi, D. Y. *J. Org. Chem.* **2004**, *69*, 3340–3344.
19. Magano, J.; Chen, M. H.; Clark, J. D.; Nussbaumer, T. *J. Org. Chem.* **2006**, *71*, 7103–7105.
20. Hwu, J. R.; Wong, F. F.; Huang, J. J.; Tsay, S. C. *J. Org. Chem.* **1997**, *62*, 4097–4104.
21. Zewge, D.; King, A.; Weissman, S.; Tschaen, D. *Tetrahedron Lett.* **2004**, *19*, 3729–3732.
22. Kale, B.; Shinde, A.; Sonar, S.; Shingate, B.; Kumar, S.; Ghosh, S.; Venugopal, S.; Shingare, M. *Tetrahedron Lett.* **2010**, *51*, 3075–3078.
23. Cvengroš, J.; Neufeind, S.; Becker, A.; Schmalz, H.-G. *Synlett* **2008**, 1993–1998.
24. (a) Rashinkar, G.; Salunkhe, R. *J. Mol. Catal. A: Chem.* **2010**, *316*, 146–152; (b) Rashinkar, G.; Kamble, S.; Kumbhar, A.; Salunkhe, R. *Catal. Commun.* **2011**, *11*, 1442–1447.
25. *Preparation of [FemMerBenz]Cl (**2**):* A mixture of Merrifield resin (3.0 g) and 1-*N*-ferrocenylmethyl benzimidazole (3.16 g, 10 mmol) in 25 mL of DMF was heated at 80 °C in an oil bath. After 72 h, the polymer was filtered, washed with DMF (3 × 50 mL), MeOH (3 × 50 mL), CH_2Cl_2 (3 × 50 mL), and dried under vacuum at 50 °C for 24 h to afford [FemMerBenz]Cl (**2**). IR (neat, thin film):

υ = 2922, 2849, 1613, 1384, 1248, 1175, 1016, 810, 744, 690, 616 cm^{-1}; Raman: υ = 3186, 3135, 1460, 1408, 1335, 1258, 770, 620, 459 cm^{-1}; Elemental analysis observed: C, 70.82; H, 5.81; N, 3.97. Loading: 1.41 mmol functional group g^{-1} resin. Preparation of [FemMerBenz]Al_2Cl_7 (**3**): A suspension of [FemMerBenz]Cl (3.0 g) in DMF (25 mL) was stirred under a stream of nitrogen gas while being cooled in an ice bath. Aluminum chloride (3.7 g, 0.02 mol) was added in small portions to the stirred suspension. After all the aluminum chloride had been added, the system was heated at 70 °C for 72 h. Afterward the polymer was filtered and washed with DMF, MeOH (3 × 20 mL), MeOH:H_2O (1:1) (3 × 20 mL), H_2O (3 × 20 mL), and MeOH (3 × 20 mL), and dried under vacuum at 50 °C for 48 h to afford [FemMerBenz]Al_2Cl_7 (**3**). IR (neat, thin film): υ = 2922, 1658, 1386, 1252, 1183, 1015, 805, 748, 656, 543, 437, 384, 333, 308 cm^{-1}; Raman: υ = 3135, 1478, 1408, 1327, 1251, 778, 625, 468 cm^{-1}; Loading: 0.048 mmol of aluminum g^{-1} resin.

26. Hvistendahl, J.; Klaeboe, P.; Rytter, E.; Øye, H. A. *Inorg. Chem.* **1984**, *23*, 706–715.
27. Sanclimens, G.; Crespo, L.; Pons, M.; Giralt, E.; Albericio, F.; Royo, M. *Tetrahedron Lett.* **2003**, *44*, 1751–1754.
28. *Typical procedure for O-demethylation:* A mixture of aryl methyl ether (1 mmol) and [FemMerBenz]Al_2Cl_7 (200 mg, 0.96 mol %) in DMF (5 mL) was refluxed in an oil bath. After completion of the reaction as monitored by the TLC, the reaction mixture was cooled and filtered. The filtrate was poured into water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of the solvent followed by column chromatography over silica gel using ethyl acetate/ petroleum ether (1:4 *v*/*v*) afforded pure *O*-demethylated product, which was characterized by spectral methods. Spectral data for *p*-hydroxy acetophenone (Table 1, entry 1): IR (neat, thin film): υ = 3303, 1663, 2922, 1436, 1358, 1275, 1161, 1112, 848, 671, 567 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (s, 3H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 115.3, 129.8, 131.0, 160.67, 196.8; MS(EI): *m*/*z* 136 (M^+).
29. Based on the EDAX analysis of Al, the amount of Al in **3** was found to be 0.26%. This corresponds to 0.52 mg of Al in 200 mg quantity of **3** which is equivalent to 0.0096 mmol of $Al_2Cl_7^-$, which is an active site for catalysis. TON which is equal to % conversion per mmol of active catalyst was calculated to be 8100 for the O-demethylation of *p*-methoxyacetophenone which yielded *p*-hydroxyacetophenone in 78% yield.
30. [MeMerBenz] Al_2Cl_7 and [BnMerBenz]Al_2Cl_7 were synthesized by using the similar procedure depicted in Scheme 1. Data for [MeMerBenz]Al_2Cl_7. IR (neat, thin film): υ = 2927, 1614, 1371, 1183, 1017, 876, 749, 699, 529, 364, 337, 307 cm^{-1}; Raman: υ = 3057, 1450, 1350, 1189, 776, 641 cm^{-1}; Loading: 0.084 mmol of aluminum g^{-1} resin. Data for [BnMerBenz]Al_2Cl_7: IR (neat, thin film): υ = 3023, 2920, 1613, 1558, 1451, 1372, 1276, 1185, 1016, 816, 749, 702, 547, 357, 337, 305 cm^{-1}; Raman: υ = 3056, 1613, 1583, 1452, 1431, 1348, 1187, 1032, 1003, 818, 774, 642 cm^{-1}; Loading: 0.035 mmol of aluminum g^{-1} resin.
31. Burguete, M. I.; Galindo, F.; García-Verdugo, E.; Karbass, N.; Luis, S. V. *Chem. Commun.* **2007**, 3086–3088. and references therein.