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Remote 'Imidazole' Based Ruthenium(II) Para-Cymene Pre-catalyst for Selective Oxidation Reaction of Alkyl Arenes and Alcohols

Manali Dutta,^[a] Kusum K. Bania,^[a] and Sanjay Pratihar*^{[a],[b]}

Dedication ((optional))

Abstract: Herein we disclosed the utilization of remote 'imidazole' based precatalyst [(para-cymene)Rull(L)Cl]+, C-1 where L = 2-(4substituted-phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline) for the selective oxidation of variety of alkyl arenes/heteroarenes and alcohols to their corresponding aldehydes or ketones in presence of tert-butyl hydroperoxide (TBHP). The remote 'imidazole' moiety present in the complex facilitate the activation of oxidant and subsequent generation of active species via the release of paracymene from C-1, which in-turn was less effective without the 'imidazole' moiety. The mechanistic features of C-1 promoted oxidation of alkyl arenes were also assessed from spectroscopic, kinetic, and few other controlled experiments. The substrate scope for C-1 promoted oxidation reaction was performed for the selective oxidation of 27-different alkyl arenes/heteroarenes and 25 different alcohols to their corresponding aldehydes/ketones with moderate to good yields.

Introduction

Selective oxidation of alkyl arenes/heteroarenes to their valuable building blocks such as aldehydes and ketones using transition metal-based catalyst is one of the most challenging reactions [1]. In an early demonstration, Shing et al. first reported that $RuCl_3{\cdot}xH_2O$ (7 mol%) in presence of $NalO_4$ was an effective catalyst for the dihydroxylation of various alkenes in EtOAc/MeCN/H₂O solvent systems under controlled reaction condition [2]. Later on, by adding Brønsted or Lewis acids with lower amount of catalyst loading, Plietker and Niggemann showed an improvement of the existing RuCl₃·xH₂O/NalO₄ system promoted reactions [3]. Waegell also demonstrated the use of ruthenium in C-H bond activation with in-situ generated RuO₄ [4]. These potential high-valent oxidizing intermediates could be generated from the reaction between low valent transition metal complexes and sacrificial oxidant (such as oxygen, ^tBuOOH, (NH₄)₂Ce(NO₃)₆, NaIO₄ etc.) through (i) reductive O₂ activation, (ii) oxo transfer from peroxides, (iii) proton-coupled electron-transfer (PCET) oxidation of a low-valent aqua complex, and (iv) photo-induced homolytic/heterolytic cleavage of the O-X bond [5-6].

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Very recently, it has been found that these intermediates could also be generated under oxidizing environment via the oxidative loss of Cp* from [Ir(Cp*)L] [7-9] and oxidative loss of arenes from the ruthenium-based precatalysts [10-11]. Although these oxidizing intermediates are known for their selective oxidative transformation of variety of organic substrates including alkane, alkene, and alkyne to their useful and functional oxygenated products, but the selectivity and progress of the reaction depends on various factors and could be tuned through the stereoelectronic adjustment of the ligand [12-16]. Towards this, the group of Mayer [17-18], Nam [19-20], Saik [21], Che [22], Fukuzumi [23-25], and others [26-33] have developed variety of ligand-bound well-defined high valent ruthenium-oxo/dioxo intermediates and utilized as potential catalyst for variety of oxidative transformation reaction. In continuation of our goal to develop sustainable catalytic methods for the selective oxidation reaction [11], [34], herein, we disclosed the utilization of remote 'imidazole' based ruthenium(II) η6-p-cymene precatalyst for selective oxidation of alkyl arenes/heteroarenes to their corresponding aldehyde/ketones using tert-butyl hydroperoxide (TBHP) as oxidant.

Results and Discussion

The precatalysts (C-1 to C-5) were synthesized and charecterized by following our earlier reported procedure [11]. Initially, to check the reactivity of the complexes, reaction condition was optimized from the screening of catalyst loading (entry 1-3, Table 1), solvent (entry 8-13, Table 1), temperature (entry 3-5, Table 1), and time (entry 1-7, Table 1) using oxidation of toluene to benzaldehyde as model reaction. To check the effect of oxidizing agents (entry 2-9, Table 1). C-1 promoted model reaction was performed in acetonitrile in presence of various reagents such as: hvdrogen peroxide (H_2O_2) , sodium metaperiodate $(NalO_4)$, *tert*-butyl hydroperoxide (TBHP), oxygen, and ceric ammonium nitrate (CAN). Amongst all, TBHP was found to be effective for the selective oxidation of toluene to benzaldehvde in 84% vield. The precatalysts C-2 and C-3 promoted oxidation of toluene afforded benzaldehyde with 72% and 74%, respectively after 3h (entry 18-19, Table 1). The blank reactions without the catalyst or the oxidant did not produce any desired product even after 6h (entry 5-6, Table 1). To check the effect of acid/base in the reaction. model reaction was performed under optimized reaction condition with addition of acid (trifluoro acetic acid, 1 eqv,) or base (triethyl amine, 1 eqv.). However, the presence of acid with complex C-1 does not show any significant enhancement in its catalytic activity (entry 14, Table 1). On the other hand, the presence of base completely halt the model reaction. To check the effect of imidazole moiety, model reaction was conducted with C-4 (does not contain remote imidazole moiety) and C-5 (stable octahedral

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geometry). C-4 and C-5 promoted model reaction afforded benzaldehyde in 34% and 0% yield, respectively after 6h. The inactivity of C-5 suggests that a vacant coordination site at the Ru(II) center was required for the reaction and also rulled out the possible involvemnet of ligand in the reaction, which encouraged us to look for the reactivity with other Ru(II) complexes. Interestingly, other Ru(II) complexes such as; [Ru(BPy)₃]Cl₂, [Ru(BPy)₂Cl₂], [Ru(n⁶-p-cymene)Cl₂]₂, and [Ru(n⁶-p-cymene)Cl₂]₂ in combination with 2 equivalent AgPF₆ were screened for the model reaction. In all the cases, lower yield of the product was achieved (entry 22-25, Table 1). At the same time, all of the tested metal salts or complexes were also found to be less effective for the reaction (entry 26-33, Table 1). Next, to check the stability of the metal-ligand backbone in C-1 under oxidizing environment, the reactivity of C-1 was compared with other reagent systems. The significantly higher catalytic activity of C-1/TBHP for the oxidation of toluene (84% yield of benzaldehyde) compared with other systems (entry 2. Table 1) such as: RuCl₃/NaIO₄ (known to generate RuO₄, 8% vield of benzaldehvde, entry 32, Table 1) and [Ru(n⁶-p-cymene)Cl₂]/TBHP (20% yield of benzaldehyde, entry 31, Table 1) and [Ru(n⁶-p-cymene)Cl₂]/NalO₄ (6% yield of benzaldehyde, entry 34, Table 1) was observed. The above mentioned comparative reactivity study suggested that complete degradation of ligand backbone in C-1 to form "ligand-free" RuO₄ was unlikely in the present system.



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14	C-1	2	TBHP + TFA	6	MeCN	82
15	C-1	2	TBHP + Et ₃ N	6	MeCN	0
16	C-1	2	TEMPO	12	MeCN	15
17	C-1	1	DPPH	12	MeCN	10
18	C-2	2	твнр	3	MeCN	74
19	C-3	2	ТВНР	3	MeCN	72
20	C-4	2	ТВНР	6	MeCN	34
21	C-5	5	ТВНР	6	MeCN	0
22	[Ru(BPy) ₃]Cl ₂	5	твнр	6	MeCN	0
23	Ru(BPy) ₂ Cl ₂	5	ТВНР	6	MeCN	30
24	[RuCl ₂ (p-Cy)] ₂	5	ТВНР	6	MeCN	15
25	[RuCl ₂ (<i>p</i> -Cy)] ₂ + AgPF ₆	5/5	TBHP	6	MeCN	26
26	CuCl ₂	5	TBHP	6	MeCN	20
27	CuCl	5	TBHP	6	MeCN	21
28	Cu(OAc) ₂	5	ТВНР	6	MeCN	32
29	[Fe(Phen)3]Cl2	5	ТВНР	6	MeCN	0
30	Cu(Phen)Cl ₂	5	ТВНР	6	MeCN	24
31	RuCl ₃	5	ТВНР	6	MeCN	20
32	RuCl₃	5	NalO ₄	6	MeCN- H₂O	08
33	FeCl ₃	5	ТВНР	6	MeCN	12
34	[RuCl ₂ (p-Cy)] ₂	5	NalO ₄	6	MeCN	06

Reaction Condition: Toluene (1 mmol), TBHP (200 μ L), Catalyst (2-5 mol%), MeCN (5 mL), ^aThe yields were calculated based on gas chromatography (GC) analysis using *ortho*-xylene as external standard. ^bReaction conducted at 45 °C.

Mechanistic studies for C-1 promoted oxidation of toluene to benzaldehyde

Next, to check the effect of remote "imidazole" in C-1, ¹H NMR titration was conducted with time for C-1 in CD₃CN in presence of TBHP at 60 °C. The ¹H NMR spectrum of C-1 showed the presence of ruthenium coordinated *para*-cymene, which gradually release from C-1 during the generation of intermediate as was evident from the regular appaearance of the peak due to free *para*-cymene (Figure 1c). On the other hand, the ¹H NMR monitoring of C-1 in CD₃CN in presence of substrate (toluene) showed subsequent oxidation of toluene to benzaldehyde (Figure S44). Next to check the invovement of *para*-cymene in the rate determining step, C-1 promoted oxidation of toluene to benzaldehyde was conducted in MeCN in presence of different added arenes such as 1,3 dimethoxy benzene, para-cymene, toluene, and 4-fluoro benzene (Figure 2).

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However, we did not observe any change in the conversion of benzaldehyde in presence of added arenes, which suggested that the release of *para*-cymene from the precatalyst is not involved in the rate determining step (Figure 2c). The complex **C-1** showed an intense absorption MLCT band centered at 405 nm in acetonitrile. The reaction of **C-1** with TBHP in acetonitrile at 60 °C produced a colour change (light yellow to green) along with the generation of two new band centered at 580 nm and 704 nm due the high valent ruthenium-oxo species [24], [35-39] in the solution (Figure 1a).



Figure 1. Monitoring of UV-visible spectra with time for the reaction between C-1 with *tert*-butyl hydroperoxide (TBHP) in MeCN at 60 °C (a), FT-IR spectra of the intermediate obtained after the reaction between C-1 and tertbutyl hydroperoxide in MeCN at 60 °C (b), ¹H NMR monitoring of C-1 in presence of TBHP at 60 °C in CD₃CN (c).



 $K_H/K_D = 0.86$ (Toluene/Toluene-d_a); Hamett substituent constant (p) = 0.26

Figure 2. Hammet plot for the C-1 promoted oxidation of four different *para*substituted toluenes to their corresponding aldehydes (a), C-1 promoted oxidation of toluene in presence of different added arenes (b), and plausible mechanism for C-1 promoted oxidation of toluene to benzaldehyde (C).

The FT-IR spectra of the reaction mixture (after the reaction of **C**-1 and TBHP in MeCN at 60 °C) suggest an intense band at 840

cm⁻¹ (Figure 1)assigned to the corresponding vasvRu^{IV}=O stretch [6], [40]. Next, to identify the intermediate, C-1 was reacted with TBHP (C-1 : TBHP = 1:3) in acetonitrile at 60 °C for 1.5 h. Mass spectral analysis of the corresponding reaction mixture showed peaks at m/z = 531.03 due [(L)Ru(CH₃CN)₂=O-H]+ and m/z = 566.01 due to [(L)RuCl(CH₃CN)₂=O]⁺ apart from its parent complex $[n^6-p$ -cymene (L)Ru(Cl)]⁺ at m/z = 601.05 (Figure S9). The presence of above mentioned fragments in ESI-MS study further suggested the generation of high valent (L)Ru^{IV}=O from C-1 under the oxidizing environment through the release of paracymene. Further, to understand the mechanism, kinetic orders of dependency for precatalyst, TBHP, and substrate were determined with model reaction by using initial rate methods under optimized reaction condition (details supplied in the ESI). The observed rate kinetics data showed first order rate dependency with respect to precatalyst, TBHP, and substrate. (Please see Figure S10 to S-12 in ESI). Next, initial rate kinetics for C-1 promoted oxidation of four different para-substituted toluene (p-Y-C₆H₄CH₃; Y=OH, H, Br, NO₂) to their corresponding benzaldehyde was monitored and showed the order as Y=NO₂>Br>H>OH. The small positive Hammett reaction constant (p=0.26) in case of C-1 indicates the generation of a negligible negative charge at the transition state (TS) and consistent with the addition of TBHP radical to the benzyl radical (Figure 2). Next, we employed competition kinetic isotope effect (KIE) experiments to get an idea about rate determining step of the reaction. An inverse secondary intermolecular $k_{\rm H}/k_{\rm D} = 0.86 \pm 0.03$ for toluene to benzaldehyde was measured, which proposed rehybridization of the C-H bond from sp² to sp³ in the product determining transition state. Further to confirm the involvement of radical, C-1 promoted oxidation of toluene to benzaldehyde was performed in presence radical scavenger such of as; (2.2.6.6 tetramethylpiperidin-1-yl)oxyl (TEMPO), 2,2-diphenyl-1picrylhydrazyl (DPPH) (entry 16-17, Table 1). In both the cases, a substantial decrease in the yield of benzaldehyde was observed, which justifies the involvement of radical species during the reaction. Further, to check the life time and stability of the intermediate under oxidizing environment, solid (sticky) intermediate was isolated after the reaction of C-1 with TBHP (C-1 : TBHP = 1 : 10) in MeCN for 1.5 h. The model reaction was conducted with isolated intermediates (20 mol%). However, the model reaction produced only 48% of benzaldehyde with isolated intermediates. Based on the above-mentioned preliminary experimental results and arguments, plausible mechanism have been suggested for the present C-1 promoted C-H oxidation reaction (Figure 2c). However, a detailed examination would be further required to consider or nullify other possibilities [40].

Substrate scope for C-1 promoted oxidation of alkyl arenes/heteroarenes

Next, the substrate scope of **C-1** promoted oxidation reaction for variety of aryl/heteroaryl alkanes is illustrated in Scheme 1 [41]. The oxidation of toluene derivatives attached with electron-withdrawing groups at *para-/ortho*-position were effective and produced their corresponding aldehyde selectively with very good to excellent yield. **C-1** promoted oxidation of 4-methoxy tolune produced the corresponding 4-methoxy benzaldehyde in 74% yield after 3h. The similar oxidation for 2-hydroxy or 4-hydroxy toluene produced their corresponding benzaldehyde in 65% and 62% yield, respectively. Further, **C-1** promoted oxidation reaction is found to have excellent functional group tolerance and

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produced their corresponding aldehyde in presence of functional group such as; -NO₂, -Cl, Br, -I, -OH, -OMe, -CHO, -CO₂H, and CO₂Me (Scheme 1). However, reaction failed to produce any such aldehyde in case of 4-methyl aniline, 2,6-dimethyl pyridine, 2amino,-6-methyl pyridine. Next, the oxidation reaction was tested with alkyl-hetero-arenes such as; 2-methyl thiophene, 2-methyl furan, and 3-methyl pyridine and observed their corresponding aldehyde in 71% (2I), 70% (2m), and 65% (2n), respectively. Notably, reaction proceeds smoothly in case of para-xylene and meta-xylene afforded corresponding terephthalaldehyde (20) and isophthalaldehyde (2r) in 74% and 62% yield, respectively (Scheme 1). However, similar type of oxidation failed in case of ortho-xylene and 2,6-lutidine. Next, the methodology was also found to be successful for the oxidation of alkyl benzene such as; ethyl benzene, n-propyl benzene, n-butyl benzene and afforded the corresponding ketones selectively in 80% (2w), 70% (2x), and 72% (2y) yields, respectively. Similarly, the oxidation of other substrate such as: diphenvlmethane, and 4-bromo acetophenone were found to proceed smoothly and produced their corresponding oxygenated products in 82% (2u) and 74% (2v) vield. Next, to compare the reactivity between different alkyl benzenes, initial rate kinetics were performed (Figure 3) for C-1 promoted oxidation of eight different substrates under optimized reaction condition and suggested the following order as 1a > 1b > 1c > 1d > 1e > 1f > 1g>1h (Table 2).

C-1 (2 mol%) TBHP, 60 ℃ MeCN R сно сно сно сно O₂N но MeO 2d, 3h, 84 (70)% 2a, 1h, 92 (81)%^a 2c, 3h, 74 (65)% 2e, 2h, 78% 2b, 1h, 95% O₂N сно сно 2j, 2h, 82 (62)% 2f, 2h, 82% **2g,** 3h, 74 (62)% **2h**, 2h, (74)% 2i, 1h, 85 (70)% сно сно сно 2k. 2h. 82% **21**. 3h 71% 2m. 2.5 h. 70% 2n. 2h. 65% 20, 4h, (74)% Failed/Low vielding Reaction CH СН СН H₃C NH. H₂N H₂C сн H₂N сно OHC' онс HO₂0 2t, 4h, (62)% 2r, 3h, (62)% 2s, 4h, (78)% 2p, 4h, (74)% **2q,** 1h, 82% 2u, 2h, 82(70)% 2v, 2h, (74)% 2w, 2h, 80% 2x, 2.5h, 70% 2y, 2.5h, 72% 3a, 6h, 70 (61)% 3b, 7h, 72 (63)%

Scheme 1. Substrate scope of C-1 promoted oxidation of alkyl arenes/heteroarenes.

The observed reactivity trends also suggested the higher oxidation tendency of secondary C-H bond as compared to primary C-H bond (Table 2). Gratifyingly, **C-1** promoted selective oxidation 2-benzylisoindolin-1-one afforded 2-benzylisoindoline-1,3-dione (**3a**) in 70% after 6h without hampering the benzyl moiety of the substrate. Whereas 2-(3,5-dimethylphenyl)isoindolin-1-one could also be succesfully converted to 2-(3,5-dimethylphenyl)isoindoline-1,3-dione (**3b**) in 72% yield, without oxidizing the other alkyl substituent attached at the aromatic moiety of the substrate (Scheme 1).



Figure 3. UV-Vis monitoring of intermediate of C-1 in presence of substarte.

Table 2. C-1 promoted oxidation of eight different substrate to their corresponding aldehyde/ketone and their reactivity order.					
Substrate	Rate (k ×10 min ⁻¹)				
Diphenyl methane (1a)	3.25				
Cumene (1b)	1.75				
Ethyl benzene (1c)	1.03				
4-nitro tolene (1d)	0.32				
4-bromo toluene (1e)	0.27				
4-iodo toluene (1f)	0.23				
Toluene (1g)	0.18				
4-hydroxy toluene (1h)	0.17				

Substrate Scope for C-1 promoted oxidation of alcohols

During the course of our study, we realized that C-1/TBHP reagent would be useful for the oxidation of alcohols to their corresponding aldehyde or ketone. Thus, oxidation of variety of primary and secondary benzyl alcohols were attempted and illustrated in Scheme 2 [41]. Under optimized reaction condition, very good to excellent yield were achieved for variety of primary benzyl alcohols attaching with electron donating/withdrawing

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substituent at ortho-/meta-/para- position. Whereas, the oxidation of pyridin-2-ylmethanol produced the corresponding aldehyde in 40% yield. However, the oxidation of corresponding pyridin-4ylmethanol or thiophen-2-ylmethanol or furan-2-ylmethanol were effective under similar reaction condition and produced their corresponding aldehyde 4i, 4h, and 4f in 75, 68, and 70% yield, respectively. The methodology was also effective for n-octanol to produce the corresponding octanal selectively in 72% yield. Furthermore, oxidation of cinamyl alcohol was also found to be selective and afforded cinamaldehyde in 68% yield. The methodology is not only limited for the oxidation of primary alcohols, but it could be extended for the oxidation of secondary alcohols to corresponding ketones. Thus, varieties of secondary alcohols were screened under optimized reaction condition (Scheme 2). Gratifyingly, selective oxidations of these alcohols were found to be useful to produce their corresponding ketones in good to excellent yield. It is noteworthy to mention that the methodology was also effective for the selective oxidation of alcohols to corresponding ketones for eight different (E)-1.3-diaryl-prop-2-en-1-ol derivatives with good to excellent yield. Interestingly, double bond in these compounds was found to be intact after the oxidation.



Scheme 2. Substrate scope of C-1 promoted oxidation of alcohols.

Conclusion

In summary, we demonstrated the remote 'imidazole' based precatalysts [(η^6 -*p*-cymene)Ru^{II}(L)CI]⁺, **C-1** where L = 2-(4-substituted-phenyI)-1H-imidazo[4,5-f][1,10] phenanthroline) for the selective oxidation of alkyl arenes/heteroarenes and alcohols to their corresponding aldehyde or ketones. The remote

'imidazole' moiety present in the complex not only facilitates the activation of oxidant and subsequent generation of active species *via* release of para-cymene from the precatalyst but also stabilizes the active species for the selective oxidation reaction, which in turn was not effective without the 'imidazole' moiety. The mechanistic evidences based on spectroscopic, kinetic and few other controlled experiments suggested that rate determining step (rds) of **C-1** promoted oxidation of toluene involve the addition of TBHP radical to the benzyl radical. The pre-catalyst **C-1** showed promising catalytic activity and good selectivity for the oxidation of variety of substrates such as alkyl arenes/heteroarenes and alcohols to their corresponding aldehydes/ketones.

Experimental Section

Experimental Details: For the synthesis of complexes, reactions were performed under dry oxygen free argon atmosphere using standard vacuum lines and Schlenk techniques. The solvents used for the synthesis of complexes were dried and distilled by standard methods and previously deoxygenated in the vacuum line. 1H (400/600 MHz) and ¹³C NMR (100/150 MHz) spectra were recorded on 400/600 MHz spectrometers at 298 K. Electron spray lonization mass spectra (ESI-MS) were recorded on ESI-Q-TOF mass spectrophotometer.

General procedure for C-1 promoted oxidation of alkylarenes or alcohols to aldehydes

In a Schlenk tube, substrate (alkyl arenes/alcohols, 1 mmol), catalyst (2 mol%) and TBHP (2.1 mmol) was taken in 5 mL acetonitrile. The reaction mixture was stirred at 60 °C for the required time. The initial yellow/orange colour of the solution turned yellowish green, which finally turned into deep green. After the completion of the reaction (*via* TLC monitoring), water was added to the reaction mixture and the product was extracted with ethyl acetate (50 mL × 3), washed with brine solution (50 mL × 2) and dried over anhydrous Na₂SO₄. The yield of the reaction was calculated from gas chromatography (GC) analysis using *ortho*-xylene as external standard and ¹H NMR analysis using diphenyl methane as external standard. Some of the isolated products were characterized via ¹H/¹³C NMR analysis.

Acknowledgements ((optional))

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- [40] Based on few experimental evidences, although we are considering the active species as (L)Ru^{IV}=O, but the involvement of other active species such as; (L)Ru^{III}=O, (L)Ru^{III}=OH, (L)Ru^V=O, and (L)Ru^{VI}(O₂) cannot be ruled out from the reaction mixture.
- [41] Yields are calculated from ¹H NMR/GC/GC-MS analysis and those represented in the parenthesis are isolated yield.

FULL PAPER

Entry for the Table of Contents

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R = CI, H, OMe R = CI, H, OMe $Alkyl Arenes \longrightarrow Aldehydes Ketones$ $Alcohols \longrightarrow Ketones$ $Active Catalyst \\
Refease of para Cyment$

The present work disclosed the dual role of remote 'imidazole' attached with the precatalyst $[(\eta^6-p-cymene)Ru^{II}(L)CI]^+$ (L = 2-(4-substituted-phenyI)-1H-imidazo[4,5-f][1,10] phenanthroline) for the activation of oxidant (*tert*-butyI hydroperoxide, TBHP) and generation of active catalyst *via* the release of *para*-cymene for the selective oxidation of 27-different alkyI arenes/heteroarenes and 25 different alcohols to their corresponding aldehydes/ketones with moderate to good yields.

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