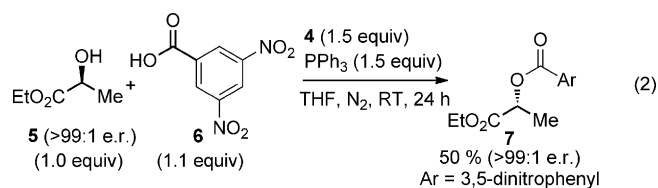
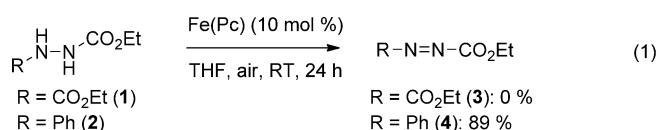


Recyclable Mitsunobu Reagents: Catalytic Mitsunobu Reactions with an Iron Catalyst and Atmospheric Oxygen**

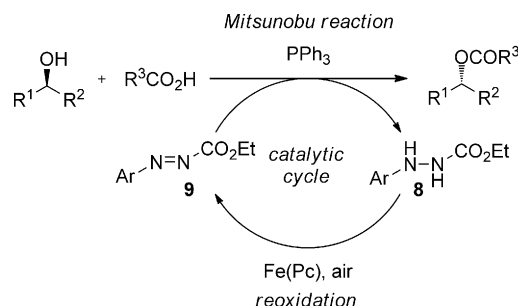
Daisuke Hirose, Tsuyoshi Taniguchi,* and Hiroyuki Ishibashi

In 1967, Mitsunobu and co-workers reported that a combination of diethyl azodicarboxylates (DEAD; **3**) and triphenylphosphine causes condensation reactions between alcohols and acids (phosphoric acids or carboxylic acids) to give the corresponding esters.^[1] Notably, when chiral secondary alcohols are used in this reaction, ester products are provided with inversion of the stereochemistry.^[2] Moreover, various nucleophiles, such as phenols, sulfonyl amines, azide, thiols, and activated methylenes, can be used instead of carboxylic acids, although the reactivity depends on the acidity of nucleophiles.^[2] Owing to these characteristic and mild reaction conditions, the Mitsunobu reaction has been established as one of the most useful tasks in synthetic chemistry. However, there are significant problems with using DEAD, including high toxicity, explosion risk, and difficulty in removal of the resultant hydrazine waste (diethyl 1,2-hydrazinedicarboxylate) after the reaction. Because of these drawbacks, and the problem of phosphine reagent waste, synthetic chemists in fields of process chemistry or manufacturing hesitate to use the Mitsunobu reaction. Therefore, several substituted reagents and modified methods to avoid these problems have been reported.^[2,3] In this regard, obviously, reducing azo reagents to a catalytic amount with the aid of safe and inexpensive stoichiometric oxidants is a significant improvement in the Mitsunobu reaction.^[4] In 2006, Toy and co-workers succeeded in reducing the amount of DEAD to a catalytic amount (10 mol %) using iodobenzene diacetate [PhI(OAc)₂] as a reoxidizer.^[5] This is the only example of a catalytic (in azo reagents) Mitsunobu reaction to date.^[6]

Recently, we reported the generation and reactions of alkoxy carbonyl radicals with Fe^{II}(Pc)-catalyzed (Pc = phthalocyanine) aerobic oxidation of carbazates (RCO₂NHNH₂).^[7] Inspired by this result, we conceived the iron-catalyzed aerobic reoxidation of diethyl 1,2-hydrazinedicarboxylate (**1**) to DEAD (**3**). Unfortunately, however, exposure of hydrazine **1** to air in the presence of a catalytic amount of Fe(Pc) gave no product [Equation (1)].^[8] This is not a surprising result, as nitrogen atoms masked by electron-drawing ethyl carbonates, unlike alkyl or aryl hydrazines, are unreactive under normal aerobic oxidation conditions.^[9] Next, we turned to the reaction of ethyl 2-phenylhydrazinecarboxylate (**2**), as we expected that a nitrogen atom adjoining a phenyl group would be easily oxidized owing to stabilization of the intermediary radical or cation by delocalization on the aromatic ring.^[10,11] Indeed, **2** was readily oxidized to the corresponding ethyl 2-phenylazocarboxylate (**4**) under the iron-catalyzed aerobic conditions. To our delight, the Mitsunobu reaction between (–)-(*S*)-ethyl lactate (**5**) and 3,5-dinitrobenzoic acid (**6**) proceeded in the presence of **4** and triphenylphosphine to afford the corresponding ester product with inversion of the stereochemistry [Equation (2)].



As **4** turned out to work as a Mitsunobu reagent, we proposed a catalytic system that consists of iron-catalyzed aerobic reoxidation of 2-arylhydrazinecarboxylate **8**, as shown in Scheme 1. 2-Arylazocarboxylate **9** promotes Mitsunobu reactions in the presence of alcohols, carboxylic acids, and triphenylphosphine to give ester products and **8**. As **8** could be reoxidized to its azo form (**9**) by in situ iron-catalyzed aerobic oxidation, **8** or **9** should work as a catalyst for the Mitsunobu reaction with the aid of an iron catalyst and air (oxygen) as a terminal oxidizer.^[12] However, when



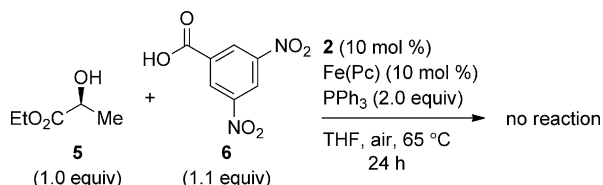
Scheme 1. Concept for a catalytic Mitsunobu reaction.

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a mixture of alcohol **5**, carboxylic acid **6**, and triphenylphosphine in tetrahydrofuran (0.5 M) was heated with catalytic amounts (10 mol %) of Fe(Pc) and hydrazine **2** under air, the desired ester product was not obtained at all (Scheme 2).



Scheme 2. An unsuccessful reaction.

Therefore, we decided to implement a reaction condition screen (solvents, additives, concentration, and temperature; see the Supporting Information). Fortunately, after several preliminary experiments, we found that the addition of molecular sieves (MS) triggered the reaction. A reaction in the presence of activated 5 Å MS (470 mg mmol⁻¹) gave product **7** in 17% yield, although with incomplete inversion of stereochemistry (Table 1, entry 1).^[13]

Encouraged by this result, we decided to seek effective hydrazine catalysts. First, the electronic effects of the functional groups of ethyl 2-arylhydrazinecarboxylate **8a–e** were tested (Table 1, entries 2–6). It was revealed that hydrazine catalysts with electron-withdrawing groups, such as halogens (chloro and bromo) and a nitro group, gave the inversion product **7** in a relatively high enantiomeric ratio, but the yield was still low (entries 3–5). In contrast to these results, hydrazine **8e**, which has an electron-donating *p*-methoxy group, did not improve the result (entry 6). Electron-deficient aromatic rings seemed to be important for obtaining the inversion product **7**. On the other hand, hydrazine **8a**, with an electron-withdrawing fluorine substituent at the *para* position, did not improve the result (entry 2). However, *m*-fluorophenylhydrazine derivative **8f** gave inversion product **7** in high selectivity (entry 7). The result for **8a** is probably due to an electron donation through the conjugated system, rather than an inductive effect. Interestingly, both *m*-chlorophenylhydrazine **8g** and *m*-bromophenylhydrazine **8h** provided inversion product **7** in better yield, and with high selectivity (entries 8 and 9). The tuning of catalysts using chlorine or bromine atoms seemed to be promising for obtaining better results. Incidentally, *o*-halophenylhydrazine catalysts **8i** and **8j** did not perform well, probably for steric reasons (entries 10 and 11). Next, we tested the catalytic activity of arylhydrazine derivatives bearing two chlorine atoms. The 3,5-dichlorophenylhydrazine catalyst **8k** afforded almost the same result as **8g** (entry 12), whereas 3,4-dichlorophenylhydrazine catalyst **8l** provided inversion product **7** in the highest yield (79%) with almost perfect selectivity (e.r., 98:2; entry 13). Although we have tested further combinations of other halogens and positions, no catalyst superior to **8l** was found. Replacement of the ethoxy group of **8l** with a cyclohexylamino group caused the disappearance of catalytic activity (catalyst **8m**; entry 14).

Table 1: Screening of hydrazine catalysts.

Entry	Catalyst	Yield [%] ^[a]	e.r.
1		17	11:89
2	8a , X = F	20	11:89
3	8b , X = Cl	37	80:20
4	8c , X = Br	36	82:18
5	8d , X = NO ₂	30	87:13
6	8e , X = OMe	19	8:92
7		25	94:6
8	8g , X = Cl	53	94:6
9	8h , X = Br	48	92:8
10		28	60:40
11	8j , X = Cl	23	85:15
12		57	93:7
13		79	98:2
14		34	4:96

[a] Yield of isolated product.

The effects of minor changes from the optimized reaction conditions are shown in Table 2. A significant drop in reactivity was observed by replacing Fe(Pc) with other catalysts such as tetraphenylporphyrin iron(III) chloride, cobalt(II) phthalocyanine, copper(II) phthalocyanine, or Manganese(II) phthalocyanine (Table 2, entries 2–5). When the amount of Fe(Pc) was reduced to half, the yield of **7** somewhat decreased, and reducing the amounts of both Fe(Pc) and **8l** caused a further decline in the yield (entry 6). When THF was substituted for a safer solvent, cyclopentyl methyl ether (CPME),^[14] lower yields and inversion ratios were obtained (entry 7). Fortunately, reaction at a higher temperature (90 °C) in CPME gave almost the same result as that obtained with the standard conditions, and with shorter reaction time (12 h; entry 7). As a notable result, we found that this catalytic reaction proceeded at room temperature,

Table 2: Effects of changing reaction conditions.

Entry	Conditions	Yield [%] ^[a]	e.r.
1	standard conditions	79	98:2
2	Fe(Pc)→FeCl(TPP)	20	92:8
3	Fe(Pc)→Co(Pc)	4	—
4	Fe(Pc)→Cu(Pc)	2	—
5	Fe(Pc)→Mn(Pc)	2	—
6	Fe(Pc) 10 mol %→5 mol %	63 (49) ^[b]	99:1 (98:2) ^[b]
7	THF→CPME	53 (80) ^[c]	89:11 (97:3) ^[c]
8 ^[d]	at room temperature	60	98:2
9	under O ₂ atmosphere	64	98:2
10	without 81	40	1:99 ^[e]
11	without 5 Å MS	n.r.	—
12 ^[f]	scale up	84	95:5

[a] Yield of isolated product. [b] With 5 mol % of both Fe(Pc) and **81**. [c] 90 °C, 12 h. [d] 48 h. [e] 1:99 or greater. [f] 60 h, **5** (10 mmol) was used. CPME=cyclopentyl methyl ether, n.r.=no reaction, TPP=tetraphenylporphyrin.

though the reaction was somewhat sluggish (entry 8). The use of pure oxygen gas instead of air did not improve the result (entry 9). Reaction in the absence of catalyst **81** gave no inversion product **7**, but rather gave the corresponding retention product (entry 10).^[13] As described above (Scheme 2), 5 Å MS seem to be essential in this reaction (entry 11). Although an exact explanation for this effect is difficult, 5 Å MS might remove water or hydroperoxide generated by oxidation of the hydrazine catalyst with oxygen. A scaled-up reaction (10 mmol of **5**) was somewhat slow, but gave inversion product **7** in almost the same yield, but slightly lower enantiomeric ratio, than that of the small-scale reaction (entry 12).

With the optimized conditions in hand, we investigated the reactions of several alcohols and nucleophiles (Table 3). In addition to carboxylic acids, such as benzoic acid and 4-nitrobenzoic acid, phenol, *N*-hydroxyphthalimide, phthalimide, and *N*-benzyl-2-nitrobenzenesulfonylamide^[15] reacted with 3-phenylpropanol (**10**) under the catalytic Mitsunobu conditions to provide the corresponding substituted products **11–16** (Table 3, entries 1–6).^[2] As with reactions of (–)-(*S*)-ethyl lactate (**5**) with carboxylic acids to give inversion products **7** and **17** (entries 7 and 8), other secondary alcohols such as (+)-(*R*)-3-butyn-2-ol (**18**), (+)-(*R*)-1-phenyl-1-ethanol (**20**), (+)-(*S*)-2-octanol (**22**), (±)-(*1R**,*5R**)-3,3,5-trimethylcyclohexa-1-ol (**24**), and dihydrocholesterol (**26**) underwent inversion of stereochemistry to give the corresponding esters **19**, **21**, **23**, **25**, and **27**, respectively, with high enantiomeric or diastereomeric purities (entries 9–13). On the other hand, when sterically hindered (–)-menthol (**28**) was used as a substrate, the yield and ratio of inversion product **29** were low (entry 14).^[13] Although sensitivity to steric factors is one of the problems with the original Mitsunobu reaction, the use of highly acidic carboxylic acids such as 4-nitrobenzoic acid

usually improves the results in stoichiometric reactions.^[16] Therefore, moderate reactivity is a limitation in this catalytic method at present, and further improvement is a future subject.

We would like to emphasize the advantageous characteristics of hydrazine catalyst **81**. It was easily prepared in one step (ethoxycarbonylation) from commercially available 3,4-dichlorophenylhydrazine hydrochloride (see the Supporting Information). A highly pure material was obtained by recrystallization, and the crystalline solid was stable under ambient conditions for more than one month. After the reaction, we were able to almost completely recover hydrazine catalyst **81** in its azo form (96 % yield), along with the product, by silica gel chromatography.

In conclusion, we have developed a new catalytic method for the Mitsunobu reaction. The most significant feature is that ethyl 2-(3,4-dichlorophenyl)hydrazinecarboxylate (**81**) can work as a good catalyst in air, which is an ideal terminal oxidizer. Iron phthalocyanine, which complements this catalytic system, is inexpensive and nontoxic, and is often used as a pigment in food and clothing.^[17] Although the current reaction may not be perfect from the viewpoints of yield and reaction conditions, this catalytic concept is innovative and has significant potential. The combination of this concept with modified phosphine reagents^[2,6] has not yet been tested, but we anticipate that it has promise for achieving a practical Mitsunobu reaction. In short, the present reaction illustrates one of the ideal catalytic concepts for improving an important synthetic method.^[18] Further studies to improve on this catalytic reaction are currently in progress.

Experimental Section

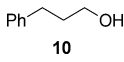
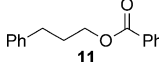
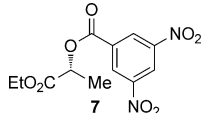
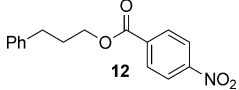
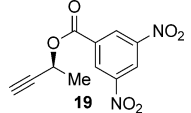
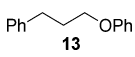
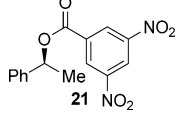
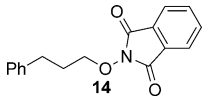
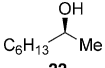
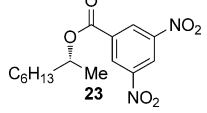
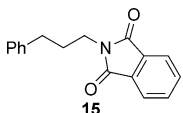
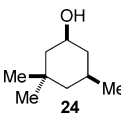
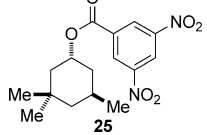
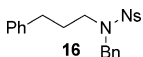
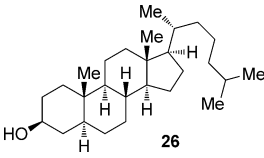
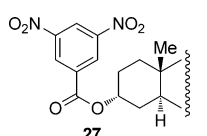
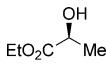
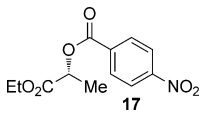
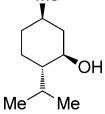
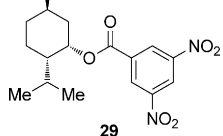
Typical procedure for catalytic Mitsunobu reactions: A mixture of (–)-(*S*)-ethyl lactate (**5**; 100 mg, 0.850 mmol), 3,5-dinitrobenzoic acid (**6**; 198 mg, 0.935 mmol), triphenylphosphine (446 mg, 1.70 mmol), hydrazine **81** (21.2 mg, 0.0850 mmol), iron phthalocyanine (48.3 mg, 0.0850 mmol) and activated 5 Å MS (400 mg) in THF (1.7 mL) was heated at 65 °C under air (balloon). After the reaction mixture was cooled to room temperature and filtered, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexane/EtOAc, 6:1). Ethyl 2-(3,4-dichlorophenyl)azocarboxylate (20.1 mg, 0.0813 mmol, 96 %) was recovered from the first fraction as a red solid (see the Supporting Information for spectroscopic data). The second fraction gave (*R*)-**7**^[5b] (209 mg, 0.668 mmol, 79 %, 98:2 e.r.) as a white solid; mp 98–99 °C; ¹H NMR (600 MHz, CDCl₃): δ = 9.254–9.247 (m, 1H), 9.20 (d, *J* = 2.1 Hz, 2H), 5.42 (q, *J* = 6.9 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.73 (d, *J* = 6.9 Hz, 3H), 1.32 ppm (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 169.6, 161.9, 148.7, 133.2, 129.6, 122.6, 70.8, 61.9, 16.9, 14.1 ppm. The enantiomeric ratio was determined by HPLC analysis with a chiral stationary phase. Chiral HPLC: Daicel-Chiralpak OJ-H 46 × 150 mm, 254 nm UV detector, room temperature eluent: (*n*-hexane/*i*PrOH) 1:5, flow rate: 0.5 mL min^{–1}, retention time (min) 17.0 (*S* isomer), 20.2 (*R* isomer). [α]_D²² = –8.1 (*c* = 1.00, CHCl₃) [(*S*)-1-ethoxycarbonyl ethyl 3,5-dinitrobenzoate (> 99:1 er): [α]_D²² = +8.8 (*c* = 1.00, CHCl₃)].

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Table 3: Catalytic Mitsunobu reaction scope.^[a]

Entry	Alcohol	Product	Yield [%] ^[b] (selectivity)	Entry	Alcohol	Product	Yield [%] ^[b] (selectivity)
1			71	8	5 (>99:1 e.r.)		79 (98:2 e.r.)
2	10		92	9			91 (97:3 e.r.)
3	10		55	10			73 (93:7 e.r.)
4	10		64	11			70 (94:6 e.r.)
5	10		65	12			57 (92:8 d.r.)
6	10		51	13			67 (97:3 d.r.)
7			50 (97:3 e.r.)	14			28 (25:75 d.r.)

[a] Reaction conditions: Alcohol (0.734–0.850 mmol), nucleophile (1.1 equiv), **81** (10 mol %), Fe(Pc) (10 mol %), PPh₃ (2 equiv), 5 Å MS (345–400 mg) in THF (0.50 M) at 65 °C under air for 12–48 h. [b] Yield of isolated product. Bn = benzyl, Ns = 2-nitrobenzenesulfonyl.

- [1] a) O. Mitsunobu, M. Yamada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 935–939; b) O. Mitsunobu, M. T. Yamada, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380–2382.
- [2] For reviews, see: a) O. Mitsunobu, *Synlett* **1981**, 1–28; b) D. L. Hughes, *Org. React.* **1992**, *42*, 335–656; c) T. Y. S. But, P. H. Toy, *Chem. Asian J.* **2007**, *2*, 1340–1355; d) K. C. Kumara Swamy, N. N. Bhuvan Kumar, E. Balaraman, K. V. P. Pavan Kumar, *Chem. Rev.* **2009**, *109*, 2551–2651.
- [3] For reviews on the modification of Mitsunobu reactions, see: a) R. Dembinski, *Eur. J. Org. Chem.* **2004**, 2763–2772; b) S. Dandapani, D. P. Curran, *Chem. Eur. J.* **2004**, *10*, 3130–3138; see also Refs [2c] and [2d]. For a recent example of modification, see: c) M. Figlus, N. Wellaway, A. W. J. Cooper, S. L. Solis, R. C. Hartley, *ACS Comb. Sci.* **2011**, *13*, 280–285.
- [4] D. J. C. Constable, P. J. Dunn, J. D. Hayler, G. R. Humphrey, J. L. Leazer, Jr., R. J. Linderman, K. Lorenz, J. Manley, B. A. Pearlman, A. Wells, A. Zaks, T. Y. Zhang, *Green Chem.* **2007**, *9*, 411–420.
- [5] a) T. Y. S. But, P. H. Toy, *J. Am. Chem. Soc.* **2006**, *128*, 9636–9637; b) T. Y. S. But, J. Lu, P. H. Toy, *Synlett* **2010**, 1115–1117.

- [6] The possibility of conducting a Mitsunobu reaction using a catalytic amount of a phosphine reagent has been reported in a patent: a) C. J. O'Brien, PCT Int. Appl. WO2010/118042A2, **2010**. For related reports, see: b) C. J. O'Brien, J. L. Tellez, Z. S. Nixon, L. J. Kang, A. L. Carter, S. R. Kunkel, K. C. Przeworski, G. A. Chass, *Angew. Chem.* **2009**, *121*, 6968–6971; *Angew. Chem. Int. Ed.* **2009**, *48*, 6836–6839.
- [7] T. Taniguchi, Y. Sugiura, H. Zaimoku, H. Ishibashi, *Angew. Chem.* **2010**, *122*, 10352–10355; *Angew. Chem. Int. Ed.* **2010**, *49*, 10154–10157.
- [8] The preparation of *N,N,N',N'*-tetramethylazodicarboxamide (TMAD) by palladium-catalyzed aerobic oxidation of the corresponding hydrazine has been reported in a patent: T. Tsunoda, K. Nishii, Japan Patent Kokai P2008–214301A, **2008**.
- [9] For examples of aerobic oxidation of hydrazine compounds, see: a) S. G. Cohen, R. Zand, C. Steel, *J. Am. Chem. Soc.* **1961**, *83*, 2895–2900; b) S. F. Wang, L. Mathew, J. Warkentin, *J. Am. Chem. Soc.* **1988**, *110*, 7235–7236; c) L. Coyne, R. Mariner, A. Rice, *Langmuir* **1991**, *7*, 1660–1674; d) B. C. Gilbert, P. Ionita, J. R. L. Smith, J. Oakes, N. Ouwerkerk, *ARKIVOC* **2006**, *iii*, 127–147; e) T. Taniguchi, H. Zaimoku, H. Ishibashi, *Chem. Eur. J.* **2011**, *17*, 4307–4312.

- [10] G. Gaviraghi, M. Pinza, G. Pifferi, *Synthesis* **1981**, 608–610.
- [11] Y. Zhao, F. G. Bordwell, J.-P. Cheng, D. Wang, *J. Am. Chem. Soc.* **1997**, *119*, 9125–9129.
- [12] For reviews on catalytic reactions using molecular oxygen, see: a) S. S. Stahl, *Angew. Chem.* **2004**, *116*, 3480–3501; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400–3420; b) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329–2364; c) M. S. Sigman, D. R. Jensen, *Acc. Chem. Res.* **2006**, *39*, 221–229; d) J. Piera, J.-E. Bäckvall, *Angew. Chem.* **2008**, *120*, 3558–3576; *Angew. Chem. Int. Ed.* **2008**, *47*, 3506–3523; e) K. M. Gligorich, M. S. Sigman, *Chem. Commun.* **2009**, 3854–3867; f) A. N. Campbell, S. S. Stahl, *Acc. Chem. Res.* **2012**, *45*, 851–863.
- [13] We have reported condensation reactions between alcohols and carboxylic acids using triphenylphosphine and atmospheric oxygen in the presence of a catalytic amount of Fe(Pc). The stereochemistry of esters obtained from chiral secondary alcohols was absolutely retained in this reaction, see: T. Taniguchi, D. Hirose, H. Ishibashi, *ACS Catal.* **2011**, *1*, 1469–1474. This esterification could compete with the present catalytic Mitsunobu reaction and decrease inversion products in some cases.
- [14] Although we never detected peroxides from THF in the present reaction, attention should be given to the possibility of an explosion when a combination of THF and air is used. CPME is a good substitute for THF because the corresponding peroxide is hardly formed under air, see: K. Watanabe, N. Yamagiwa, Y. Torisawa, *Org. Process Res. Dev.* **2007**, *11*, 251–258.
- [15] T. Fukuyama, C.-K. Jow, M. Cheung, *Tetrahedron Lett.* **1995**, *36*, 6373–6374.
- [16] S. F. Martin, J. A. Dodge, *Tetrahedron Lett.* **1991**, *32*, 3017–3020.
- [17] For recent examples of Fe(Pc)-catalyzed reactions, see: a) A. A. Kuznetsova, L. I. Solovyeva, O. L. Kaliya, E. A. Lukyanets, D. G. Knorre, O. S. Fedorova, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 4335–4338; b) H. M. Nue, M. S. Yusubov, V. V. Zhdankin, V. N. Nemykin, *Adv. Synth. Catal.* **2009**, *351*, 3168–3174; c) T. Taniguchi, N. Goto, A. Nishibata, H. Ishibashi, *Org. Lett.* **2010**, *12*, 112–115; for additions and corrections, see: T. Taniguchi, N. Goto, A. Nishibata, H. Ishibashi, *Org. Lett.* **2010**, *12*, 5084; d) L. X. Alvarez, E. V. Kudrik, A. B. Sorokin, *Chem. Eur. J.* **2011**, *17*, 9298–9301; e) S. M. Paradine, M. C. White, *J. Am. Chem. Soc.* **2012**, *134*, 2036–2039; f) E. K. Leggans, T. J. Barker, K. K. Duncan, D. L. Boger, *Org. Lett.* **2012**, *14*, 1428–1431.
- [18] Markó and co-workers have reported the copper-catalyzed aerobic oxidation of alcohols using a catalytic amount of di-*tert*-butyl 1,2-hydrazinedicarboxylate; see: a) I. E. Markó, P. R. Giles, M. Tsukazaki, S. M. Brown, C. J. Urch, *Science* **1996**, *274*, 2044–2046. Modification: b) T. Nishii, T. Ouchi, A. Matsuda, Y. Matsubara, Y. Haraguchi, T. Kawano, H. Kaku, M. Horikawa, T. Tsunoda, *Tetrahedron Lett.* **2012**, *53*, 5880–5882, and references therein.