Selenium catalysed oxidations with aqueous hydrogen peroxide. Part I: epoxidation reactions in homogeneous solution

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Several diselenides were synthesised and tested for catalytic activity in epoxidation reactions with aqueous hydrogen peroxide. Bis[3,5-bis(trifluoromethyl)phenyl] diselenide forms the corresponding 3,5-bis(trifluoromethyl)benzene seleninic acid (L. Syper and J. Mlochowski, *Tetrahedron*, 1987, **43**, 207.) *in situ*, which is a highly reactive and selective catalyst for the epoxidation of olefins in 2,2,2-trifluoroethanol. This is the first selenium compound that effectively (substrate to catalyst molar ratio *s/c* = 200) catalyses the formation of sensitive epoxides in nearly quantitative yields.

Introduction

Olefin epoxidation is a key transformation in organic synthesis both on a laboratory and an industrial scale.[2,3] The method of choice—in fine chemicals production—is usually the Prilezhaev reaction of olefins with stoichiometric amounts of percarboxylic acids, such as peracetic and *m*-chloroperbenzoic acid.[4] Major disadvantages of this method are the relatively high cost of peracids, the need for large amounts of (buffered) organic solvents and the co-production of the corresponding carboxylic acid, which has to be separated from the product. Moreover, increasingly stringent regulation of the transport, storage and handling of peracetic acid are making its use prohibitive. Consequently, effective catalytic methods for epoxidation with aqueous hydrogen peroxide are actively being sought. Aqueous hydrogen peroxide is inexpensive, relatively safe and easy to handle and produces water as the sole co-product.

Several systems have been reported in the literature, based on tungstate,[5,6] methyl rhenium trioxide (MTO),[7] manganese triazacyclononane complexes[8] and the heterogeneous titanium silicalite (a hydrophobic molecular sieve),[9] but the search for effective, stable catalysts with broad scope continues. Organometallic compounds of main group elements, notably arsenic[10] and selenium[11] are also known to catalyse epoxidations. Peroxyseleninic acids were first used as stoichiometric oxidants,[12] but following the discovery, by Sharpless,[13] that *tert*-butyl hydroperoxide can be used in conjunction with catalytic amounts, the method gained interest.[14] Further improvements came with the use of hydrogen peroxide instead of *tert*-BuOOH as the oxidant, heterogenisation[15,16] and functionalisation of the aromatic ring of the selenium catalyst with electron withdrawing nitro-substituents (Fig. 1).[17] However, the reaction conditions (≥5 mol% catalyst, reaction times up to 12 h) and results (selective epoxidation of activated olefins only) left room for improvement.[16,17] This prompted us to study the effect of the nature and position of substituents in the aromatic ring of the selenium catalysts and solvent and base effects to ascertain whether further improvement was possible.

Results

The structures of the diselenides used are depicted in Fig. 2. Under the reaction conditions the diselenides are oxidised by H_2O_2 to give the corresponding aryl seleninic acids (ArSe(O)-OH) which are the true catalysts.[1]

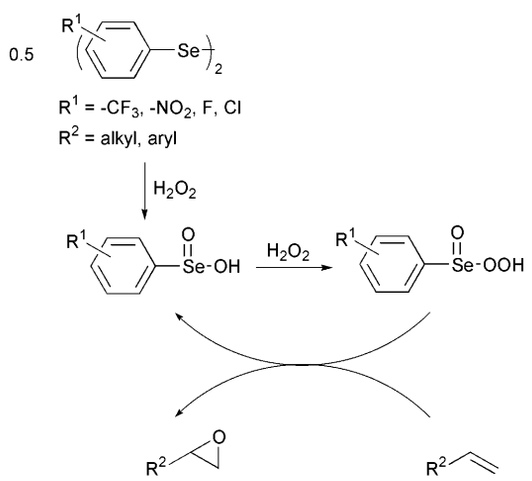

Fig. 1 Catalytic epoxidation with arylseleninic acid–hydrogen peroxide systems.

Solvent effects

The choice of solvent for epoxidation reactions with hydrogen peroxide is limited. A solvent should preferably be polar, non-coordinating, non-basic and inert under the oxidising conditions. This leaves only a few possibilities *e.g.* chlorinated hydrocarbons, 2,2,2-trifluoroethanol[18] and sulfolane (1,1-dioxothiole). A water-immiscible solvent is often preferred, to minimise hydrolysis of the epoxides,[6] but with aqueous hydrogen peroxide this can cause problems with mass transfer.[5,19] Chlorinated hydrocarbons are less interesting because of environmental issues associated with their use.[20]

In an initial solvent screening (Table 1) the epoxidation of cyclohexene in the presence of 0.5 mol% of bis[3,5-bis(trifluoromethyl)phenyl] diselenide (**1**) was studied since this olefin gives information regarding reactivity and selectivity. The best results were obtained in 2,2,2-trifluoroethanol, dichloromethane and sulfolane. The advantage of 2,2,2-trifluoroethanol as a solvent in epoxidations has been known for some time.[21] It combines the prerequisites of a good solvent (polar, non-basic, non-coordinating, non-oxidisable) with a very high rate of epoxidation compared to the rate of solvolysis. Consequently, the complete miscibility with aqueous hydrogen peroxide, which eliminates mass transfer limitations, does not pose a threat to

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Table 1 Solvent screening for cyclohexene epoxidation **1** [a]

Solvent	TOF_0 [b]	Yield (%) [c]	Selectivity (%) [d]
2,2,2-Trifluoroethanol	250	88	90
Dichloromethane	40	35	90
1,2-Dichloroethane	34	21	68
Nitromethane	27	19	69
Sulfolane [e]	21	14	95
α,α,α-Trifluorotoluene	12	7	49

[a] Conditions: 0.5 mol% **1**, 2 mmol cyclohexene, 4 mmol 60% H_2O_2, 1 M solutions, $T = 20$ °C, $t = 1$ h. [b] TOF_0 = initial rate in mmol product (mmol catalyst)$^{-1}$ h^{-1}. [c] GC-yield on epoxide. [d] Selectivity = mmol epoxide (mmol converted olefin)$^{-1}$. [e] Reaction carried out at 30 °C (mp sulfolane = 27 °C).

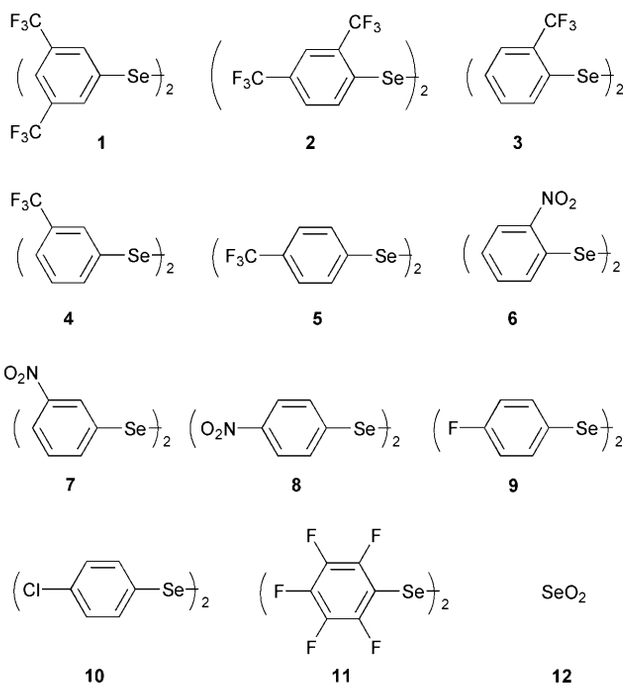


Fig. 2 Selenium compounds tested for catalytic activity.

the product.[22] Since 2,2,2-trifluoroethanol was by far superior to other solvents further reactions were carried out in this medium.

Base effects

Generally speaking, epoxidation reactions that remain selective in the course of time also maintain a high reaction rate because it is often the side-products (*vic*-diols) that inhibit catalytic activity.[23] Therefore, sensitive epoxides (*e.g.* 1,2-epoxycyclohexane) are best prepared in the presence of mild bases which neutralise the acidic H_2O_2 solution from pH ~ 2.5 to 4.5–5.[24] Tertiary amines, for example, are known to accelerate epoxidation with MTO[6] and other systems.[25] For epoxidations with hydrogen peroxide it is important to add a weakly nucleophilic base with a pK_a ~ 2–7.5 (in water), which is stable towards hydrogen peroxide[26] (Table 2).

As shown in Table 2 the addition of bases with pK_a ranging from 2.5 to 7.2 resulted in a substantial improvement in rate and selectivity of cyclohexene epoxidation. With 0.5% of **1** (1 mol% active $ArSe(O)O_2H$) and 0.2% of base the conversion of cyclohexene was already *ca.* 90% after 15 minutes. This necessitated a reduction of the amount of catalyst to 0.25 mol% (0.5 mol% active $ArSe(O)O_2H$) to follow the reaction more accurately. The optimum amount of base was found to be 0.1 to 0.3 mol%. Below these values the selectivity decreased and above these values the reactivity decreased significantly in all three cases. At the optimum concentration all three bases improve the

Table 2 Effect of base on cyclohexene epoxidation with **1** [a]

Base	pK_a	TOF_0 [b]	Yield (%) [c]	Selectivity (%) [d]	Diol formation (%)
None	—	300	80	85	~3
Pyrazole	2.5	350	75	96	~3
NaOAc	4.77	420	98	99	<1
Na_2HPO_4	7.21	470	82	91	0

[a] Conditions: 0.25 mol% **1**, 2 mmol cyclohexene, 0.2 mol% base, 4 mmol 60% H_2O_2, 1 M solutions, $T = 20$ °C, $t = 1$ h; pK_a denotes the pK_a of the conjugated acid. [b] TOF_0 = initial rate in mmol product (mmol catalyst)$^{-1}$ h^{-1}. [c] GC-yield on epoxide. [d] Selectivity = mmol epoxide (mmol converted olefin)$^{-1}$.

Table 3 Initial catalyst screening for epoxidation of cyclohexene in 2,2,2-trifluoroethanol [a]

Catalyst	TOF_0 [b]	Yield (%) [c]	Selectivity (%) [d]
1	250	88	90
2	140	80	90
3	120	73	94
4	190	78	88
5	150	68	79
6	200	80	80
7	260	73	81
8	160	27	25
9	150	73	95
10	130	57	70
11	4	2	7
12	320	8	8.4

[a] Conditions: 1 mol% catalyst (based on active $ArSe(O)O_2H$), 2 mmol cyclohexene, 4 mmol 60% H_2O_2, 2 ml CF_3CH_2OH, $T = 20$ °C, $t = 1$ h. [b] TOF_0 = initial rate in mmol product (mmol catalyst)$^{-1}$ h^{-1}. [c] GC-yield on epoxide. [d] Selectivity = mmol epoxide (mmol converted olefin)$^{-1}$.

reaction, but significant cyclohexane-1,2-diol formation was observed when pyrazole was used as a base, which probably explains why the reaction slowed down. The low pK_a of pyrazole may not be sufficient to scavenge all acids present, preventing diol formation and addition of larger amounts of base would inhibit the reaction too drastically. On the other hand, addition of Na_2HPO_4 gives good reactivity but induces formation of a large number of side-products, which leaves NaOAc as the optimum base for cyclohexene epoxidation in 2,2,2-trifluoroethanol. Table 2 also shows that probably only Brønsted basicity is involved since the bases are not expected to coordinate to the metal centre as in epoxidation reactions with *e.g.* MTO.[27]

Substituent effects

Earlier reports show that the presence of nitro-groups in areneseleninic acids—preferably at the *ortho*-position—improves catalysis.[17] A second nitro-group—placed at the *para*-position—did not improve results further, which might imply an optimum in electronegativity of the aryl ring. Therefore, we tested a fairly extensive range of selenium compounds (Fig. 2, Tables 3 and 4).

Tables 3 and 4 show a general trend that both reactivity and selectivity of the selenium catalysts increase through the addition of acetate. Under optimised conditions, most diaryl diselenides show selectivities of (95 ± 4)% with bis[2,4-bis(trifluoromethyl)phenyl] diselenide (**2**) and bis(4-nitrophenyl) diselenide (**8**) being negative exceptions. For most diaryl diselenides the initial turnover rate is roughly (400 ± 20) h^{-1}, while the bis(2-nitrophenyl) diselenide (**6**) and **8** react more slowly (300 h^{-1}) and show a larger tendency to destroy the more sensitive epoxides, such as 1,2-epoxycyclohexane.[17] The bis(nitrophenyl) diselenides **6** and **8** both give rise to cyclohexane-

Table 4 Catalyst screening for epoxidation of cyclohexene under optimised conditions[a]

Catalyst	TOF_0[b]	Yield (%)[c]	Selectivity (%)[d]
1	420	98	99
2	390	85	86
3	390	73	93
4	470	81	95
5	420	82	98
6	300	83	95
7	360	80	98
8	300	75	80
9	230	64	91
10	220	70	88
11	150	2	7
12	450	21	27
blank	—	1[e]	—

[a] Conditions: 0.5 mol% catalyst (based on active $ArSe(O)O_2H$), 2 mmol cyclohexene, 0.2 mol% NaOAc, 4 mmol 60% H_2O_2, 2 ml CF_3CH_2OH, $T = 20$ °C, $t = 1$ h. [b] TOF_0 = initial rate in mmol product (mmol catalyst)$^{-1}$ h^{-1}. [c] GC-yield on epoxide. [d] Selectivity = mmol epoxide (mmol converted olefin)$^{-1}$. [e] After 16 h.

1,2-diol formation after *ca.* 45 and 15 minutes, respectively, which is only partly solved through the addition of NaOAc. It indeed seems that the strong electron withdrawing properties combined with the resonance effect of the nitro substituent make the seleninic acid too acidic and thus promote hydrolysis of the epoxides, yielding *vic*-diols that in turn react with the catalyst and slow the reaction down. A less likely possibility is that mainly in the cases of **6** and **8** the aryl–selenium bond is cleaved—as was observed by Sharpless and others.[17] The likely product resulting from decomposition—SeO_2—would have had a deleterious effect on the selectivity of the reaction, since in our case SeO_2 is highly reactive, but unselective. However, Sharpless observed similar poor reactivity of **8**, where in that case SeO_2 was not reactive. Also, reaction of cyclohexene with a solution of **1** or **8** in 2,2,2-trifluoroethanol activated 16 hours earlier with H_2O_2 did not give different results to a freshly prepared catalyst solution. Both observations indicate that SeO_2 plays no part in the reaction.

Substitution of the aromatic ring with two trifluoromethyl groups at the *meta*-positions gives by far the best catalyst **1**, which is significantly better than catalysts with only one trifluoromethyl substituent (**3**–**5**), or with two trifluoromethyl substituents placed at *ortho*- and *para*-positions (**2**). In the case of trifluoromethyl substituents there is only an inductive (electron withdrawing) effect, which seems to give the optimum results. Similarly, the *m*-nitro substituent of diselenide **7** can also just show an inductive effect and gives slightly better results than **6** or **8**. Catalysts **9** and **10** are influenced through the electron withdrawing effect of the *p*-fluoro and *p*-chloro substituents, but in these cases the resonance effect is reversed and the catalysts are selective, but considerably less reactive. With the bis(pentafluorophenyl) diselenide **11** poor results were obtained, possibly because the pentafluorophenyl ring is involved in side-reactions.

Epoxidation under optimised conditions

The results of epoxidation of a variety of olefins with the optimised catalyst system are shown in Table 5.

A representative selection of mono-, di- and tri-substituted olefins was studied and the order of reactivity roughly followed that observed with peracids (relative rates in parentheses): $CH_2{=}CH_2$ (1) < $RCH{=}CH_2$ (25) < $ArCH{=}CH_2$ (60) < RCH=CHR and $R_2C{=}CH_2$ (500–600) < $R_2C{=}CHR$ (6000–6500).[3,28] This is consistent with the active oxidant (ArSe(O)OOH) being electrophilic in nature and the oxygen transfer to the olefin being the rate-limiting step. The α-olefins react slowly as expected, but with increased amounts of catalyst (~5 mol%) complete conversion can be reached in *ca.* 4 hours. Allylic alcohols such as 3-methylpent-2-en-1-ol are selectively oxidised, albeit at a relatively low rate, again due to the decreased electron density at the double bond. Furthermore, the alcohol functionality can be protected with methyl, acetyl or trimethylsilyl groups (*cf.* citronellol† in Table 5) which are not affected during epoxidation.

Conclusions

3,5-Bis(trifluoromethyl)benzeneseleninic acid is an effective catalyst for epoxidation of olefins. Electron withdrawing substituents on the benzene ring, preferably with inductive properties only, give the best results in epoxidations. The best solvent for epoxidations is 2,2,2-trifluoroethanol. Addition of sodium acetate improves results allowing effective formation of more delicate epoxides with organoselenium catalysts for the first time.

Experimental

Catalytic reactions

Hydrogen peroxide (60%, 4 mmol, 200 μl) was added to a stirred solution (1000 rpm) of the appropriate amount of catalyst (0.5–1 mol% on active 'Se') in 2 ml of solvent in a closed flask. After the solution had become colourless, dibutyl ether (0.4 mmol, 67 μl) as internal standard and olefin (2 mmol) were added. The reaction temperature was kept at (20 ± 1) °C with a water bath. Samples (~50 μl) were first treated with MnO_2 (10 mg) + $MgSO_4$ in Et_2O (2 ml) and subsequently filtered and analysed with GC. Identities of the epoxides were confirmed by GC–MS and by comparing retention times with those of commercially available epoxides.

Synthesis

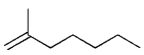
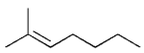
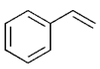
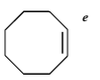
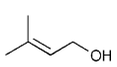
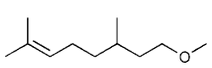
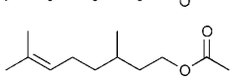
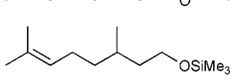
Catalysts **1** to **5**, **8** and **10** were synthesised from the corresponding arylmagnesium bromides and metallic selenium according to the method of Reich *et al.*[29] Catalyst **7** was prepared *via* nitration of diphenyl diselenide[30] to the 3-nitrophenylseleninic acid[31] and subsequent reduction with hydrazine dihydrogen sulfate.[31] Catalyst **8** was synthesised from *p*-nitroaniline *via* diazotation to the *p*-nitrophenyl selenocyanate and treatment with sodium methanolate.[32] The methyl,[33] trimethylsilyl[34] and acetate[35] derivatives of citronellol were synthesised according to known literature procedures.

Bis[3,5-bis(trifluoromethyl)phenyl] diselenide 1. Diselenide **1** was crystallised from *n*-pentane to give dark yellow transparent plates (2.3 g, 3.9 mmol, 79%), purity = 99.9% (GC).[36] Mp = 65 °C (*n*-pentane); δ_H(400 MHz; $CDCl_3$; Me_4Si) 8.03 (4 H, s, H2 + H2′ + H6 + H6′), 7.79 (2 H, s, H4 + H4′); δ_C(100 MHz; $CDCl_3$; Me_4Si) 132.7 (4 C, q, J_{CF} 33.6, C3 + C3′ + C5 + C5′), 132.3 (C1 + C1′), 131.6 (C2 + C2′ + C6 + C6′), 122.7 (4 C, J_{CF} 273.1, 4 × CF_3), 122.3 (C4 + C4′); *m/z* (EI) 586.861 (M^+ with Se_2 pattern, 80%), 567 (22, M − F), 293 (100, M − 3,5-$(CF_3)_2C_6H_3Se$), 291 (66), 273 (40), 213 (41), 163 (25).

Bis[2,4-bis(trifluoromethyl)phenyl] diselenide 2. Diselenide **2** was purified over silica, $R_f = 0.57$ (petroleum ether–EtOAc 95:5) to give light yellow plates (1.6 g, 2.8 mmol, 81%), purity = 99.9% (GC). Mp = 74–76 °C (*n*-pentane); δ_H(400 MHz; $CDCl_3$; Me_4Si) 8.02 (2 H, d, *J* 8.4, H6 + H6′), 7.87 (2 H, s, H3 + H3′), 7.68 (2 H, d, *J* 8.4, H5 + H5′); δ_C(100 MHz; $CDCl_3$; Me_4Si) 133.7 (C6 + C6′), 133.0 (C1 + C1′), 130.5 + 130.4 (4 C, 2q, J_{CF} 34.0 and 32.2, C2 + C2′ + C4 + C4′), 129.4 (C5 + C5′), 123.9 (C3 + C3′), 123.2 (4 C, q, J_{CF} 274.1, *o*-CF_3 + *o*-CF_3′ + *p*-CF_3 + *p*-CF_3′); *m/z* 586.861 (M^+ with Se_2

† The IUPAC name for citronellol is 3,7-dimethyloct-6-enol.

Table 5 Olefin epoxidation in 2,2,2-trifluoroethanol with **1** under optimised conditions[a]

Alkene	TOF_0[b]	Time/h	Yield (%)[c]	Selectivity (%)[d]
 [e]	12	4	25	99
	190	1	74	95
	860	0.5	≥99	≥99
	80	4	12	23
 [e]	600	1	99	≥99
	420	1	98	99
	620	0.5	≥99	≥99
	380	2	74	84
	400	1	99	≥99
	>750	0.5	95	95
	>750	0.5	95	95
	>750	0.5	95	95

[a] Conditions: 0.25 mol% **1**, 2 mmol olefin, 0.2 mol% NaOAc, 4 mmol 60% H_2O_2, 2 ml 2,2,2-trifluoroethanol, T = 20 °C. [b] TOF_0 = initial rate in mmol product (mmol catalyst)$^{-1}$ h^{-1}. [c] Yield on epoxide. [d] Selectivity = mmol epoxide (mmol converted olefin)$^{-1}$. [e] No NaOAc added, since epoxides are stable.

pattern, 79%), 567 (10, M − F), 332 (10), 293 (100, M − 2,4-$(CF_3)_2C_6H_3Se$), 274 (32) 213 (32).

Bis(3-nitrophenyl) diselenide 7. Diselenide **7** was crystallised from methanol to give fine dark-yellow needles (2.5 g, 6.2 mmol, 70% overall), purity = 99.9% (GC). Mp = 82–83 °C (lit.:[31] 81–83 °C); δ_H(400 MHz; $CDCl_3$; Me_4Si) 8.47 (2 H, t, J 1.8, H2 + H2′), 8.12 (2 H, ddd, J 8.2, 2.2 and 1.0, H4 + H4′), 7.92 (2 H, ddd, J 7.9, 1.7 and 1.0, H6 + H6′), 7.48 (2 H, t, J 8.0, H5 + H5′); δ_C(100 MHz; $CDCl_3$; Me_4Si) 148.3 (C3 + C3′), 136.8 (C6 + C6′), 131.8 (C1 + C1′), 130.2 (C5 + C5′), 126.0 (C2 + C2′), 123.0 (C4 + C4′).

Materials

Reagents: 3,5-bis(trifluoromethyl)bromobenzene (99%), 2,4-bis(trifluoromethyl)bromobenzene (98%), *o*-trifluoromethylbromobenzene (99%), *m*-trifluoromethylbromobenzene (99%), *p*-trifluoromethylbromobenzene (99%), bromopentafluorobenzene (99%), KSeCN (99%), bis(2-nitrophenyl) diselenide (97%), bis(4-chlorophenyl) diselenide (98%), 4-bromofluorobenzene (99%), bromobenzene (99%) and hydrazine dihydrogen sulfate (99+%) were purchased from Acros. Cyclohexene (99.5%), cyclooctene (95%), oct-1-ene (97+%), 2-methylhept-2-ene (98%) and pyrazole (98%) were purchased from Fluka. Styrene (99+%), 2-methylhept-1-ene (99%), 1-methylcyclohexene (97%), methylenecyclohexane (98%), 3-methylpent-2-en-1-ol (98%), citronellol (95%) and iodomethane (99%) were purchased from Aldrich. Elemental Se (99+%), Mg (99+%), NaOAc (99+%) and Na_2HPO_4 (99+%) were purchased from Merck. Hydrogen peroxide (60%) was a gift from Solvay Interox.

Solvents: 2,2,2-trifluoroethanol (99+%), α,α,α-trifluorotoluene (99+%), nitromethane (98%), anhydrous THF (99.5+%) and anhydrous Et_2O (99.5+%) were purchased from Fluka. Dichloromethane (99.5+%), 1,2-dichloroethane (99+%) sulfuric acid (96%) and concentrated nitric acid (65%) were purchased from Baker. Fuming nitric acid (100%) was purchased from Merck. Sulfolane (99+%) was purchased from Acros.

All solvents and reagents were used without further purification.

Analysis

Column chromatography was performed with silica gel (particle size 0.063–0.200 mm) from Merck. Melting points were determined with a Buchi 510 Melting Point Apparatus with open capillary. GC measurements were carried out with a Varian Star 3400 equipped with a CP Sil 5-CB column (50 m × 0.53 mm). ^{1}H-NMR and ^{13}C-NMR spectra were carried out on a Varian VXR 400S spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts (δ) relative to tetramethylsilane (TMS). Gas chromatography/mass spectrometry (GC/MS) analyses were performed on a VG 70-SE mass spectrometer equipped with a CP Sil 5-CB column.

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