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Sulfonylative alkoxyhydroxylation of 2-arylpropenes

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ABSTRACT

One-pot three-step sulfonylative alkoxyhydroxylation of 2-arylpropenes **1** affords oxygenated sulfonylcumenes **4** in moderate yields via a sequential route: (i) NBS-mediated allylic bromination of 2-arylpropenes **1** in CH_2Cl_2, (ii) sodium sulfinates **2**-promoted nucleophilic substitution of the resulting styryl bromides in a co-solvent of alcohol and water, and (iii) V_2O_5/H_2O_2 mediated alkoxyhydroxylation of corresponding styryl sulfones **3** in alcohol. The synthetic route provides a highly effective protocol for the 1,2,3-tricarbofunctionalization of 2-arylpropenes **1** via two carbon-oxygen and one carbon-sulfur bond formations.

1. Introduction

During the past decade, much attention has been paid to the vicinal difunctionalization of olefinic arms on styrene (vinylarene) via transition-metal,[1] non-metallic peroxide[2] or iodoarene-containing oxidant,[3] and organocatalyst[4] promoted carbon-heteroatom or carbon-carbon formations. Based on recent reports, transition-metal ions such as Ni(II),[1a] Pd(II)/Cu(II),[1b] or Pd(II)[1c] promoting one-step 1,2-dicarbofunctionalization of substituted styrenes with substituted stannanes, boronic acids, or triflates, have been major pathways (Scheme 1). Among these routes, we find that selenium-based compounds (selenocysteine[2a] or SeO_2[2b-c]) containing H_2O_2 mediated direct dihydroxylation or alkoxyhydroxylation of double bonds on styrene synthons provide some facile accesses to substituted vicinal diols or alkoxyalcohols.

Oxidative functionalization of styrene derivatives has great relevance in organic fields. Despite remarkable advances in the functionalization of alkenes, new transition metal promoted synthetic designs of sulfone-based building blocks still represent a continuing demand in the organic field, especially those that allow one-pot regioselective well-defined operations. Compared with commercially available substituted styrenes, few reports have been documented for synthetic application of α-methylstyrene (2-arylpropene, cumene).[5] Notably, no reports for one-pot 1,2,3-tricarbofunctionalization of the propenyl group on 2-arylpropenes have been presented. In our ongoing research in the applications of sodium sulfinates,[6] we turn the synthetic aim to the 1,2,3-tricarbofunctionalization from 2-arylpropenes to oxygenated sulfonylcumenes via three regioselective bond formations of 2 carbon-oxygen (C-O) and 1 carbon-sulfur (C-S).

In Scheme 2, we describe a facile one-pot synthetic route of oxygenated sulfonylcumenes **4**, including (i) NBS-mediated allylic bromination of 2-arylpropenes **1** in CH_2Cl_2, (ii) sodium sulfinates (**2**, YSO_2Na)-promoted nucleophilic substitution of the resulting styryl bromides in a co-solvent of alcohol and water, and (iii) V_2O_5/H_2O_2 mediated alkoxyhydroxylation of the corresponding styryl sulfones **3** in alcohol.[7] According to a report from Desbordes and Euvrard (Rhone-Poulenc Agrochimie company),[8] a series of dihydroxyl sulfonylcumenes performed highly effective herbicidal activity.

2. Results and discussion

To initiate our work, allylic bromination of model substrate **1a** (1.0 mmol) with NBS (1.05 equiv) in CH_2Cl_2 (5 mL) at reflux for 2 h followed by nucleophilic substitution of the resulting allylic bromide with $TolSO_2Na$ (**2a**, 1.07 equiv) in MeOH (10 mL) at reflux for 2 h provided **3a** in a nearly quantitative yield. By the one-pot two-step transformation from **1a** to **3a**, the sulfonyl group was efficiently installed into the α-methyl position of **1a** via a C-S bond formation. Without further purification, **4a** produced an 82% yield with the addition of V_2O_5 (0.3 equiv) and H_2O_2 (35%, 0.5 mL) to the resulting reaction mixture at reflux for 2 h via two C-C bond formations.[9] The one-pot three-step regioselective process showed sulfonylative methoxyhydroxylation (Table 1, entry 1). With the results in mind, different metal oxides (e.g. $MeReO_3$, MoO_5)[10,11] and

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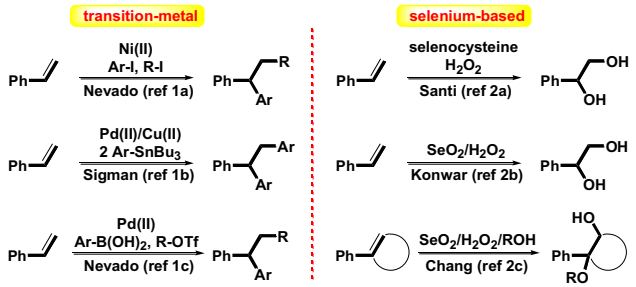
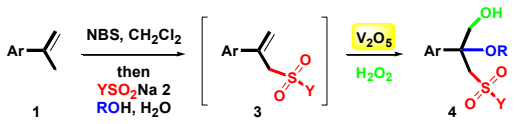
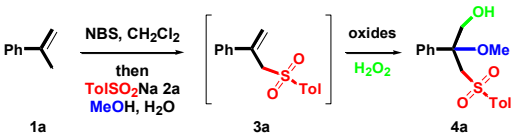


Scheme 1. Difunctionalization of olefin motif on styrenes.



Scheme 2. Trifunctionalization of olefin motif on styrenes.

Table 1
Reaction Conditions.[a]



Entry	Oxides (equiv)	Temp (°C)	Time (h)	**4a** (%)[b]
1	V_2O_5 (0.3)	65	2	82
2	$MeReO_3$ (0.3)	65	2	-[c-d]
3	TeO_2 (0.3)	65	2	-[c-d]
4	MoO_5 (0.3)	65	2	10[d]
5	SeO_2 (0.3)	65	2	61
6	V_2O_5 (0)	65	2	-[c-d]
7	V_2O_5 (0.1)	65	2	48
8	V_2O_5 (1.0)	65	2	81
9	V_2O_5 (0.3)	25	2	<10[d]
10	V_2O_5 (0.3)	65	10	75

[a] Reactions were run on a 1.0 mmol scale with **1a**, NBS (187 mg, 1.05 equiv), CH_2Cl_2 (5 mL), reflux, 2 h; $TolSO_2Na$ (**2a**, 190 mg, 1.07 equiv), MeOH (10 mL), reflux, 2 h; oxides, H_2O_2 (35% in H_2O, 0.5 mL).
[b] Isolated yields.
[c] No reaction.
[d] **3a** was recovered as the major product.

non-metal oxides (e.g. SeO_2, TeO_2)[2b-c,–12] were also examined for the one-pot process. When the resulting **3a** was treated with $MeReO_3$, TeO_2, MoO_5, or SeO_2 or at a reflux for 2 h, no isolation of **3a** was observed (for entries 2–3); and **4a** was isolated in low (for entry 4, 10%) and moderate yields (for entry 5, 61%), respectively. By increasing or decreasing the amounts of V_2O_5 (0, 0.1 or 1.0 equiv), the yield of **4a** was poorer than for the 1.1 equiv (entries 6–8, 0%, 48% or 81%). Therefore, V_2O_5 (0.3 equiv) was chosen as the oxidant for scanning the reaction conditions. When the reaction temperature was decreased (65 → 25, entry 9), only <10% yield of **4a** was obtained. Next, by elongating the reaction time (2 → 10 h), the yield of **4a** was slightly decreased to 75% (entry 10). On the basis of a higher yield and activity, we believe that V_2O_5 could be an optimal oxidant for the formation of **4a**.

The structural framework and relative regiochemistry of **4a** were determined from ^{1}H NMR and *J* coupling analysis. In the ^{1}H NMR spectrum, the equatorial proton showed a doublet with a coupling constant of 12.0 Hz at δ 4.36 ppm and 12.0 Hz at δ 4.29 ppm, which indicates that one methylene group (for the sulfonyl arm) and the other methylene group (for the hydroxyl arm) is doublet with a coupling constant 15.2 Hz at δ 3.75 ppm and 15.2 Hz at δ 3.73 ppm. The structure of **4a** with *three arms* (one hydroxyl, one methoxy, and one sulfonyl group) was determined by single-crystal X-ray analysis (see Fig. 1).[13] To our best knowledge, there is currently no experimental report on V_2O_5/H_2O_2-mediated methoxyhydroxylation. On the basis of experimental results, a possible reaction mechanism is shown in Scheme 3. The mechanism should be initiated to form NBS-mediated bromination of **1a**. By the involvement of **2a**, **3a** is yielded. In the presence of MeOH (2 equiv), V_2O_5 forms methyl peroxyvanadate (2 equiv) under the H_2O_2 mediated oxidation condition. After the coordination of **3a** with the corresponding peroxy species, intermediate **A** with a six-membered ring conformation is provided. Then, by the removal of *in situ* generated VO_2, **3a** is produced. Finally, V_2O_5 is recovered via the complexation of VO_2 and H_2O_2.

According to the above reaction conditions, we explored the substrate scope, and the results are shown in Table 2. To adjust the Ar group of **2a**-**f**, a Y group of **3a**-**m** and an R group of alcohols, **4a**-**v** (Ar = Ph, 4-$NO_2C_6H_4$, 3-FC_6H_4, 4-$CF_3C_6H_4$, 4-ClC_6H_4, 3,4-$Cl_2C_6H_3$; Y = Tol, Ph, Me, *n*Bu, 4-FC_6H_4, 4-$MeOC_6H_4$, 3-MeC_6H_4, 4-EtC_6H_4, 4-*i*PrC_6H_4, 4-*n*BuC_6H_4, 4-*t*BuC_6H_4, 4-BrC_6H_4, 4-ClC_6H_4,; R = Me, Et, *n*Bu, *i*Pr, *t*Bu) were provided in a range of 5%–86% yields, as shown in entries 1–22. For the uses of Ar and Y substituents, the phenyl ring with an electron-donating group, electron-neutral group, and electron-withdrawing group (besides entry 14, Ar = 4-nitrophenyl group) were well tolerated. For the R group, the primary and secondary alphabetic substituents performed well.

Especially, when reaction of **2b** (Ar = 4-$NO_2C_6H_4$) and **3a** was treated with the optimal combination, only trace amounts of **4n** (5%) was observed and **4n-1** was isolated in a 34% yield (entry 14). From the results, we believed that the key nitro group promoted the removal of methoxy group of **4n** to generate the stable tertiary carbocation such that the epoxide ring was formed by an intramolecular annulation of primary hydroxyl group. However, with the use of *t*BuOH as the solvent (entry 22), only diol **4v-1** was isolated in a 74% yield via the introduction of H_2O. During the process, only water was involved into tertiary carbon center and no *t*-butyl substituent was installed due to the bulky steric hindrance of *t*-Bu group. When the reaction of **2a** (Ar = Ph) was treated with **3n** (Y = CF_3) in MeOH, complex products was detected under the optimal condition (entry 23). Furthermore, when Ar was a 2-furyl

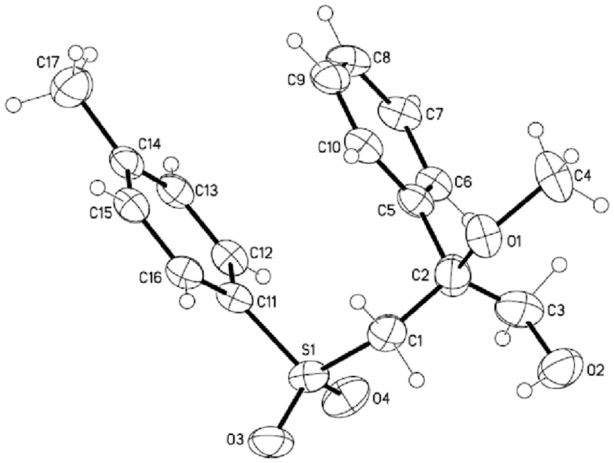


Fig. 1. X-ray structure of **4a**.

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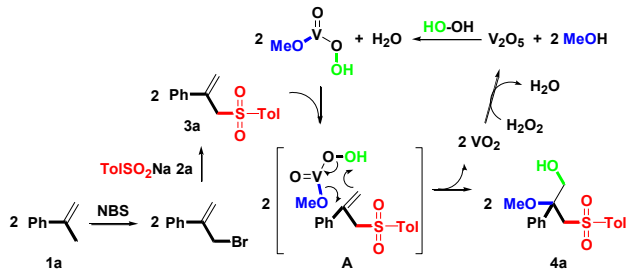
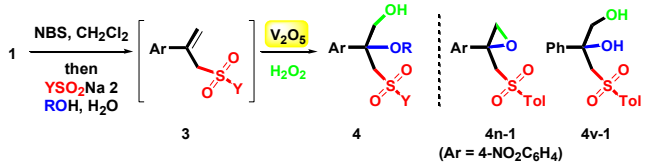


Scheme 3. Possible Mechanism.

Table 2
Synthesis of **4**.[a]



Entry	**1**, Ar =	**2**, Y =	ROH	**4** (%)[b]
1	**2a**, Ph	**3a**, Tol	MeOH	**4a**, 82
2	**2a**, Ph	**3b**, Ph	MeOH	**4b**, 80
3	**2a**, Ph	**3c**, Me	MeOH	**4c**, 70
4	**2a**, Ph	**3d**, *n*Bu	MeOH	**4d**, 70
5	**2a**, Ph	**3e**, 4-FC_6H_4	MeOH	**4e**, 83
6	**2a**, Ph	**3f**, 4-$MeOC_6H_4$	MeOH	**4f**, 80
7	**2a**, Ph	**3g**, 3-MeC_6H_4	MeOH	**4g**, 82
8	**2a**, Ph	**3h**, 4-EtC_6H_4	MeOH	**4h**, 78
9	**2a**, Ph	**3i**, 4-*i*PrC_6H_4	MeOH	**4i**, 80
10	**2a**, Ph	**3j**, 4-*n*BuC_6H_4	MeOH	**4j**, 84
11	**2a**, Ph	**3k**, 4-*t*BuC_6H_4	MeOH	**4k**, 86
12	**2a**, Ph	**3l**, 4-BrC_6H_4	MeOH	**4l**, 80
13	**2a**, Ph	**3m**, 4-ClC_6H_4	MeOH	**4m**, 81
14	**2b**, 4-$NO_2C_6H_4$	**3a**, Tol	MeOH	**4n**, 5[c]
15	**2c**, 3-FC_6H_4	**3a**, Tol	MeOH	**4o**, 62
16	**2d**, 4-$CF_3C_6H_4$	**3a**, Tol	MeOH	**4p**, 60
17	**2e**, 4-ClC_6H_4	**3a**, Tol	MeOH	**4q**, 78
18	**2f**, 3,4-$Cl_2C_6H_3$	**3a**, Tol	MeOH	**4r**, 72
19	**2a**, Ph	**3a**, Tol	EtOH	**4s**, 80
20	**2a**, Ph	**3a**, Ph	*n*BuOH	**4t**, 72
21	**2a**, Ph	**3a**, Ph	*i*PrOH	**4u**, 58
22	**2a**, Ph	**3a**, Ph	*t*BuOH	**4v**, -[d]
23	**2a**, Ph	**3n**, CF_3	MeOH	**4w**, -[e]
24	**2g**, 2-furyl	**3a**, Tol	MeOH	**4x**, -[e]
25	**2h**, 4-$MeOC_6H_4$	**3a**, Tol	MeOH	**4y**, -[e]
26	**2i**, 4-MeC_6H_4	**3a**, Tol	MeOH	**4z**, -[e]

[a] Reactions were run on a 1.0 mmol scale with **1a**, NBS (187 mg, 1.05 equiv), CH_2Cl_2 (5 mL), reflux, 2 h; YSO_2Na (**2**, 1.07 equiv), ROH (10 mL), reflux, 2 h; V_2O_5 (60 mg, 0.3 equiv), H_2O_2 (35% in H_2O, 0.5 mL).
[b] Isolated yields.
[c] 34% of **4n-1** was isolated.
[d] 74% of **4v-1** was isolated.
[e] Complex products were isolated.

(for **2g**, a heterocyclic ring), 4-methoxyphenyl (for **2h**, an electron-donating group) or 4-methylphenyl substituent (for **2i**, a benzylic position), complex mixture were still observed in entries 24–26. From the results, we found that 2-furyl, 4-$MeOC_6H_4$ and 4-MeC_6H_4 groups could be affected in the first bromination step. The reasonable explanation should be NBS triggered **2g**-**i** to produce inseparated bromoarenes (e.g., bromofurans, oxygenated bromobenzenes, or benzylic bromides) in converting into complex mixture. Moreover, when 1.18 g of **1a** (10.0 mmol) was treated with the combination, 2.33 g of **4a** was isolated in a 73% yield. This route can be enlarged to gram scale.

3. Conclusion

In summary, we have developed a one-pot three-step synthesis of oxygenated **4** via a sequential route: (i) NBS-mediated allylic bromination of **1** in CH_2Cl_2, (ii) sodium sulfinate-promoted nucleophilic substitution of the resulting styryl bromides in a co-solvent of alcohol and water, and (iii) V_2O_5/H_2O_2 mediated alkoxyhydroxylation of **3** in alcohol. The synthetic route provides a highly effective protocol for the 1,2,3-tricarbofunctionalization of 2-arylpropenes **1** via two carbon-oxygen and one carbon-sulfur bond formations. The plausible mechanism has been discussed and proposed.

4. Experimental section

4.1. General

All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. Infrared spectra were recorded with a Perkin–Elmer 100 series FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

4.1.1. 1-Methyl-4-(2-phenylallylsulfonyl)benzene (*3a*)

NBS (*N*-bromosuccinimide, 187 mg, 1.05 mmol) was added to a solution of 2-phenylpropene (**1a**, 118 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) at rt. The reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and a solution of sodium toluenesulfinates **2** (**2a**, $TolSO_2Na$, 190 mg, 1.07 mmol) in MeOH (10 mL) at rt. Then, the reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **3a**. Yield = ~100% (270 mg); Colorless solid; mp = 96–97 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3102, 3023, 2985, 1503, 1123, 956, 783 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{16}H_{17}O_2S$ 273.0949, found 273.0948; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.4 Hz, 2H), 7.28–7.20 (m, 7H), 5.59 (s, 1H), 5.21 (s, 1H), 4.25 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.56, 138.84, 136.57, 135.42, 129.46 (2x), 128.64 (2x), 128.32 (2x), 127.89, 126.20 (2x), 121.70, 62.12, 21.54.

*A representative synthetic procedure of skeleton **4** is as follows:* NBS (*N*-bromosuccinimide, 187 mg, 1.05 mmol) was added to a solution of 2-phenylpropene (**1a**, 118 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) at rt. The reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and a solution of sodium toluenesulfinates (**2a**, $TolSO_2Na$, 190 mg, 1.07 mmol) in alcohols (10 mL) at rt. The reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C. Without further purification, V_2O_5 (60 mg, 0.3 mmol) and H_2O_2 (35% in H_2O, 0.5 mL) were added to the resulting mixture at rt. Then, the reaction mixture was stirred at reflux for 2 h. The residue was diluted with water (10 mL) and the

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mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **4**.

*4.1.2. 2-Methoxy-2-phenyl-3-(toluene-4-sulfonyl)propan-1-ol (**4a**)*

Yield = 82% (262 mg); Colorless solid; mp = 107–109 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3606, 2985, 1521, 1145 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{17}H_{21}O_4S$ 321.1161, found 321.1162; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.33–7.24 (m, 7H), 4.36 (d, J = 12.0 Hz, 1H), 4.29 (d, J = 12.0 Hz, 1H), 3.74 (d, J = 1.6 Hz, 2H), 2.98 (s, 3H), 2.91 (br s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.40, 139.43, 137.64, 129.53 (2x), 128.51 (2x), 128.06, 127.80 (2x), 126.39 (2x), 80.16, 64.39, 61.26, 50.45, 21.48. Single-crystal X-Ray diagram: crystal of compound **4a** was grown by slow diffusion of EtOAc into a solution of compound **4a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group C 2/c, a = 32.603(4) Å, b = 5.7618(6) Å, c = 16.0111(16) Å, V = 3005.1(6) $Å^3$, Z = 8, d_{calcd}= 1.354 g/cm^3, $F(000)$ = 1296, 2θ range 1.250–26.398°, R indices (all data) R1 = 0.0948, w$R2$ = 0.2174.

*4.1.3. 3-Benzenesulfonyl-2-methoxy-2-phenylpropan-1-ol (**4b**)*

Yield = 80% (245 mg); Colorless solid; mp = 93–95 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3611, 2987, 1525, 1144 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{16}H_{19}O_4S$ 307.1004, found 307.1008; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82–7.79 (m, 2H), 7.59–7.55 (m, 1H), 7.48–7.44 (m, 2H), 7.33–7.23 (m, 5H), 4.37 (d, J = 11.6 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 3.80 (d, J = 14.4 Hz, 1H), 3.75 (d, J = 14.4 Hz, 1H), 3.10 (br s, 1H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.54, 139.22, 133.39, 128.93 (2x), 128.55 (2x), 128.18, 127.77 (2x), 126.40 (2x), 80.12, 64.26, 61.20, 50.43.

*4.1.4. 3-Methanesulfonyl-2-methoxy-2-phenylpropan-1-ol (**4c**)*

Yield = 70% (172 mg); Colorless oil; IR ($CHCl_3$): 3613, 2982, 1522, 1141 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{11}H_{17}O_4S$ 245.0848, found 245.0845; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.31 (m, 5H), 4.38 (d, J = 12.0 Hz, 1H), 4.28 (d, J = 12.4 Hz, 1H), 3.58 (d, J = 15.2 Hz, 1H), 3.51 (d, J = 15.2 Hz, 1H), 3.16 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.56, 128.90 (2x), 128.44, 126.25 (2x), 79.40, 63.61, 62.41, 50.87, 43.38.

*4.1.5. 3-(Butane-1-sulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4d**)*

Yield = 70% (200 mg); Colorless oil; IR ($CHCl_3$): 3605, 2982, 1522, 1144 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{14}H_{23}O_4S$ 287.1317, found 287.1312; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.30 (m, 5H), 4.40 (d, J = 12.4 Hz, 1H), 4.27 (d, J = 12.0 Hz, 1H), 3.60 (br s, 1H), 3.54 (d, J = 15.2 Hz, 1H), 3.42 (d, J = 15.2 Hz, 1H), 3.15 (s, 3H), 3.07–2.90 (m, 2H), 1.81–1.73 (m, 2H), 1.45–1.35 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.80, 128.82 (2x), 128.35, 126.21 (2x), 79.48, 63.55, 60.48, 54.92, 50.82, 23.77, 21.53, 13.40.

*4.1.6. 3-(4-Fluorobenzenesulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4e**)*

Yield = 83% (269 mg); Colorless solid; mp = 125–127 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3606, 2979, 1521, 1143 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{16}H_{18}FO_4S$ 325.0910, found 325.0911; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80–7.76 (m, 2H), 7.29–7.24 (m, 5H), 7.13–7.08 (m, 2H), 4.32 (s, 2H), 3.81 (d, J = 14.4 Hz, 1H), 3.75 (d, J = 14.8 Hz, 1H), 2.97 (s, 3H), 2.63 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.47 (d, J = 254.7 Hz), 138.95, 136.60 (d, J = 3.0 Hz), 130.73 (d, J = 9.1 Hz, 2x), 128.58 (2x), 128.24, 126.42 (2x), 116.12 (d, J = 22.8 Hz, 2x), 79.90, 63.88, 61.43, 50.36.

*4.1.7. 2-Methoxy-3-(4-methoxybenzenesulfonyl)-2-phenylpropan-1-ol (**4f**)*

Yield = 80% (269 mg); Colorless oil; IR ($CHCl_3$): 3608, 2980, 1522, 1151 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{17}H_{21}O_5S$ 337.1110, found 337.1108; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 9.2 Hz, 2H), 7.33–7.24 (m, 5H), 6.91 (d, J = 9.2 Hz, 2H), 4.35 (d, J = 12.0 Hz, 1H), 4.30 (d, J = 12.0 Hz, 1H), 3.85 (s, 3H), 3.73 (d, J = 2.0 Hz, 2H), 2.98 (s, 3H), 2.82 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.52, 139.48, 132.08, 130.04 (2x), 128.56 (2x), 128.13, 126.39 (2x), 114.14 (2x), 80.15, 64.43, 61.49, 55.62, 50.47.

*4.1.8. 2-Methoxy-2-phenyl-3-(toluene-3-sulfonyl)propan-1-ol (**4g**)*

Yield = 82% (262 mg); Colorless solid; mp = 106–108 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3611, 2984, 1525, 1149 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{17}H_{21}O_4S$ 321.1161, found 321.1162; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62–7.60 (m, 1H), 7.56 (s, 1H), 7.36 (s, 1H), 7.34–7.24 (m, 6H), 4.37 (d, J = 12.0 Hz, 1H), 4.33 (d, J = 11.8 Hz, 1H), 3.78 (d, J = 14.4 Hz, 1H), 3.72 (d, J = 14.4 Hz, 1H), 3.00 (s, 3H), 2.61 (br s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.36, 139.24, 139.18, 134.21, 128.84, 128.49 (2x), 128.17, 128.08, 126.44 (2x), 124.85, 80.15, 64.20, 61.25, 50.46, 21.17.

*4.1.9. 3-(4-Ethylbenzenesulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4h**)*

Yield = 78% (261 mg); Colorless solid; mp = 100–102 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3612, 2984, 1524, 1143 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{18}H_{23}O_4S$ 335.1317, found 335.1321; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.31–7.22 (m, 7H), 4.34 (d, J = 11.6 Hz, 1H), 4.30 (d, J = 12.0 Hz, 1H), 3.78 (d, J = 14.4 Hz, 1H), 3.73 (d, J = 14.8 Hz, 1H), 2.97 (s, 3H), 2.82 (br s, 1H), 2.68 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.42, 139.24, 137.70, 128.43 (2x), 128.35 (2x), 128.02, 127.83 (2x), 126.37 (2x), 80.06, 64.17, 61.06, 50.36, 28.70, 15.02.

*4.1.10. 3-(4-Isopropylbenzenesulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4i**)*

Yield = 80% (278 mg); Colorless solid; mp = 107–109 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3608, 2984, 1523, 1147 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{19}H_{25}O_4S$ 349.1474, found 349.1480; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.31–7.20 (m, 7H), 4.35 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 3.79 (d, J = 14.4 Hz, 1H), 3.73 (d, J = 14.4 Hz, 1H), 2.99–2.90 (m, 1H), 2.98 (s, 3H), 2.62 (br s, 1H), 1.23 (d, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.96, 139.18, 137.71, 128.44 (2x), 128.05, 127.85 (2x), 126.99 (2x), 126.39 (2x), 80.04, 64.09, 61.06, 50.36, 34.06, 23.49, 23.46.

*4.1.11. 3-(4-Butylbenzenesulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4j**)*

Yield = 84% (304 mg); Colorless solid; mp = 90–92 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3611, 2988, 1526, 1139 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{20}H_{27}O_4S$ 363.1630, found 363.1633; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.28–7.19 (m, 7H), 4.31 (d, J = 12.0 Hz, 1H), 4.29 (d, J = 12.0 Hz, 1H), 3.74 (d, J = 14.4 Hz, 1H), 3.69 (d, J = 14.4 Hz, 1H), 2.93 (s, 3H), 2.82 (br s, 1H), 2.61 (t, J = 8.0 Hz, 2H), 1.58–1.50 (m, 2H), 1.33–1.26 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.19, 139.30, 137.70, 128.89 (2x), 128.45 (2x), 128.04, 127.77 (2x), 126.39 (2x), 80.09, 64.24, 61.10, 50.37, 35.40, 33.01, 22.06, 13.70.

*4.1.12. 3-(4-tert-Butylbenzenesulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4k**)*

Yield = 86% (311 mg); Colorless solid; mp = 115–117 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3615, 2985,

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1529, 1143 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{20}H_{27}O_4S$ 363.1630, found 363.1635; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.32–7.23 (m, 5H), 4.37 (d, J = 12.4 Hz, 1H), 4.34 (d, J = 12.0 Hz, 1H), 3.78 (d, J = 14.8 Hz, 1H), 3.72 (d, J = 14.8 Hz, 1H), 2.99 (s, 3H), 2.61 (br s, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.32, 139.29, 137.42, 128.52 (2x), 128.14, 127.62 (2x), 126.46 (2x), 125.96 (2x), 80.15, 64.20, 61.27, 50.44, 35.12, 30.96 (3x).

4.1.13. 3-(4-Bromobenzenesulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4l**)

Yield = 80% (307 mg); Colorless solid; mp = 126–128 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3610, 2985, 1530, 1148 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{16}H_{18}BrO_4S$ 385.0109, found 385.0115; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.30–7.25 (m, 5H), 4.32 (br s, 2H), 3.80 (d, J = 14.8 Hz, 1H), 3.74 (d, J = 14.4 Hz, 1H), 2.97 (s, 3H), 2.86 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.46, 138.80, 132.12 (2x), 132.10, 129.38 (2x), 128.59 (2x), 128.24, 126.42 (2x), 79.84, 63.76, 61.36, 50.38.

4.1.14. 3-(4-Chlorobenzenesulfonyl)-2-methoxy-2-phenylpropan-1-ol (**4m**)

Yield = 81% (275 mg); Colorless solid; mp = 122–124 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3605, 2983, 1528, 1152 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{16}H_{18}ClO_4S$ 341.0614, found 341.0618; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.28 (br s, 5H), 4.33 (s, 2H), 3.80 (d, J = 14.8 Hz, 1H), 3.74 (d, J = 14.8 Hz, 1H), 2.98 (s, 3H), 2.80 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.08, 139.01, 138.92, 129.37 (2x), 129.18 (2x), 128.65 (2x), 128.30, 126.44 (2x), 79.92, 63.91, 61.56, 50.43.

4.1.15. 2-(4-Nitrophenyl)-2-(toluene-4-sulfonylmethyl)oxirane (**4n-1**)

Yield = 34% (113 mg); Colorless solid; mp = 114–116 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3113, 3092, 2933, 1512, 1315, 1023, 892 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{16}H_{16}NO_5S$ 334.0749, found 334.0752; ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 3.90 (d, J = 14.8 Hz, 1H), 3.68 (d, J = 14.8 Hz, 1H), 3.28 (d, J = 4.8 Hz, 1H), 2.82 (d, J = 4.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.61, 145.37, 144.41, 136.67, 129.88 (2x), 128.09 (2x), 127.19 (2x), 123.57 (2x), 61.90, 54.93, 54.79, 21.60.

4.1.16. 2-(3-Fluorophenyl)-2-methoxy-3-(toluene-4-sulfonyl) propan-1-ol (**4o**)

Yield = 62% (210 mg); Colorless solid; mp = 90–92 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3628, 2986, 1530, 1149 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{17}H_{20}FO_4S$ 339.1066, found 339.1068; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.29–7.24 (m, 3H), 7.14–7.10 (m, 1H), 7.03 (dt, J = 2.4, 10.4 Hz, 1H), 6.94 (dt, J = 2.4, 8.0 Hz, 1H), 4.34 (d, J = 12.0 Hz, 1H), 4.26 (d, J = 12.0 Hz, 1H), 3.70 (d, J = 1.6 Hz, 2H), 3.00 (s, 3H), 2.70 (br s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.90 (d, J = 244.9 Hz), 144.66, 142.41 (d, J = 6.8 Hz), 137.42, 130.12 (d, J = 7.6 Hz), 129.62 (2x), 127.83 (2x), 122.08 (d, J = 2.3 Hz), 115.08 (d, J = 20.5 Hz), 113.73 (d, J = 22.7 Hz), 79.88, 64.24, 61.18, 50.60, 21.51.

4.1.17. 2-Methoxy-3-(toluene-4-sulfonyl)-2-(4-trifluoromethylphenyl)propan-1-ol (**4p**)

Yield = 60% (233 mg); Colorless solid; mp = 131–133 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3621, 2994, 1537, 1155 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{18}H_{20}F_3O_4S$ 389.1034, found 389.1035; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.36 (s, 2H), 3.77 (d, J = 14.8 Hz, 1H), 3.70 (d, J = 14.4 Hz, 1H), 3.03 (s, 3H), 2.84 (br s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.76, 143.49, 137.25, 130.34 (d, J = 31.9 Hz), 129.68 (2x), 127.80 (2x), 127.08 (d, J = 262.3 Hz), 127.05 (2x), 125.47 (q, J = 3.8 Hz, 2x), 79.84, 63.86, 61.21, 50.64, 21.50.

4.1.18. 2-(4-Chlorophenyl)-2-methoxy-3-(toluene-4-sulfonyl) propan-1-ol (**4q**)

Yield = 78% (276 mg); Colorless solid; mp = 103–105 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3612, 2989, 1535, 1151 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{17}H_{20}ClO_4S$ 355.0771, found 355.0776; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.22 (br s, 4H), 4.29 (s, 2H), 3.75 (d, J = 14.8 Hz, 1H), 3.67 (d, J = 14.4 Hz, 1H), 2.97 (s, 3H), 2.91 (br s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.57, 137.71, 137.30, 134.10, 129.56 (2x), 128.60 (2x), 128.00 (2x), 127.73 (2x), 79.61, 63.67, 61.03, 50.35, 21.50.

4.1.19. 2-(3,4-Dichlorophenyl)-2-methoxy-3-(toluene-4-sulfonyl) propan-1-ol (**4r**)

Yield = 72% (279 mg); Colorless solid; mp = 128–130 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3612, 2985, 1532, 1151 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{17}H_{19}Cl_2O_4S$ 389.0381, found 389.0383; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 2H), 7.33–7.31 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.18–7.11 (m, 2H), 4.28 (d, J = 12.0 Hz, 1H), 4.26 (d, J = 12.0 Hz, 1H), 3.75 (d, J = 14.8 Hz, 1H), 3.65 (d, J = 14.8 Hz, 1H), 3.02 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.81, 139.50, 136.98, 132.76, 132.41, 130.40, 129.59 (2x), 128.87, 127.69 (2x), 126.02, 79.21, 63.30, 60.91, 50.49, 21.54.

4.1.20. 2-Ethoxy-2-phenyl-3-(toluene-4-sulfonyl)propan-1-ol (**4s**)

Yield = 80% (267 mg); Colorless oil; IR ($CHCl_3$): 3603, 2982, 1525, 1147 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{18}H_{23}O_4S$ 335.1317, found 335.1318; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.35–7.25 (m, 7H), 4.35 (d, J = 12.0 Hz, 1H), 4.31 (d, J = 12.0 Hz, 1H), 3.77 (d, J = 14.8 Hz, 1H), 3.73 (d, J = 14.8 Hz, 1H), 3.24–3.17 (m, 1H), 3.10–3.02 (m, 1H), 2.98 (br s, 1H), 2.42 (s, 3H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.35, 140.27, 137.80, 129.49 (2x), 128.53 (2x), 128.02, 127.95 (2x), 126.22 (2x), 79.76, 64.80, 62.10, 57.99, 21.52, 15.08.

4.1.21. 2-n-Butoxy-2-phenyl-3-(toluene-4-sulfonyl)propan-1-ol (**4t**)

Yield = 72% (261 mg); Colorless oil; IR ($CHCl_3$): 3619, 2993, 1530, 1149 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{20}H_{27}O_4S$ 363.1630, found 363.1634; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 2H), 7.31–7.20 (m, 7H), 4.32 (d, J = 12.0 Hz, 1H), 4.28 (d, J = 12.4 Hz, 1H), 3.73 (d, J = 14.4 Hz, 1H), 3.68 (d, J = 14.8 Hz, 1H), 3.10–3.05 (m, 1H), 3.00 (br s, 1H), 2.95–2.90 (m, 1H), 2.38 (s, 3H), 1.26–1.18 (m, 2H), 1.17–1.04 (m, 2H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.29, 140.19, 137.84, 129.49 (2x), 128.49 (2x), 128.01, 127.90 (2x), 126.33 (2x), 79.48, 64.60, 62.31, 62.14, 31.84, 21.50, 19.04, 13.84.

4.1.22. 2-Isopropoxy-2-phenyl-3-(toluene-4-sulfonyl)propan-1-ol (**4u**)

Yield = 58% (202 mg); Colorless solid; mp = 110–112 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3608, 2988, 1528, 1143 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{19}H_{25}O_4S$ 349.1474, found 349.1478; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.40–7.38 (m, 2H), 7.27–7.23 (m, 5H), 4.51–4.47 (m, 1H), 4.36 (d, J = 12.0 Hz, 1H), 3.84 (d, J = 14.8 Hz, 1H), 3.65 (d, J = 14.8 Hz, 1H),

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3.40–3.34 (m, 1H), 3.00 (br s, 1H), 2.41 (s, 3H), 0.97 (d, J = 6.4 Hz, 3H), 0.78 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.20, 139.96, 137.81, 129.43 (2x), 128.21 (2x), 128.18, 127.92 (2x), 127.03 (2x), 80.16, 65.99, 63.71, 63.38, 24.45, 24.12, 21.52.

*4.1.23. 2-Phenyl-3-(toluene-4-sulfonyl)propane-1,2-diol (**4v-1**)*

Yield = 74% (226 mg); Colorless solid; mp = 138–140 °C (recrystallized from hexanes and EtOAc); IR ($CHCl_3$): 3612, 3498, 2976, 1523, 1138, 978 cm^{-1}; HRMS (ESI, M^++1) calcd for $C_{16}H_{19}O_4S$ 307.1004, found 307.1007; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 2H), 7.25–7.23 (m, 2H), 7.18–7.14 (m, 3H), 7.11 (d, J = 8.4 Hz, 2H), 4.91 (s, 1H), 3.95 (d, J = 14.8 Hz, 1H), 3.73 (d, J = 14.8 Hz, 1H), 3.64 (s, 2H), 2.64 (br s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.58, 140.34, 136.92, 129.62, 128.27 (2x), 127.55 (4x), 125.14 (2x), 75.73, 70.40, 61.76, 21.52.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2017.09.047.

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13. CCDC 1539888 (**4a**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).