Novel C–S Bond Formation Through α',β-Elimination of *tert*-Butyl Sulfoxonium Ylides: A Facile Approach to Chiral Sulfoxides

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Abstract: Chiral sulfoxides were prepared in excellent enantioselectivity through α',β-elimination of the *tert*-butyl substituted sulfoxonium ylide intermediates in situ generated from diazoacetates and (*R*)-*N*-*tert*-butylsulfinyl aldimines in the presence of a copper(I) catalyst.

Key words: chiral sulfoxides, sulfoxonium ylide, α',β-elimination

Ylides as reactive intermediates have been known to undergo synthetically useful transformations.[1] The reaction of carbenes or carbenoids with sulfur compounds represents a useful approach to generate sulfonium ylides. As useful intermediates in synthetic chemistry, the sulfonium ylides have been used in many reactions, such as 1,2-Stevens,[2] 2,3-sigmatropic rearrangements,[3] and Corey–Chaykovsky reaction.[4]

α',β-Elimination reaction of a sulfonium ylide derived from di-*tert*-butyl or diethyl sulfide and ethyl diazoacetate was reported to give corresponding ethyl *tert*-butyl- or ethylthioacetate.[5] In contrast, the reaction of carbenes with sulfoxides to generate sulfoxonium ylides and subsequential transformations[6,7–11] was scarcely reported despite the potential usefulness in constructing sulfur-containing molecules. Due to a competing attack of the carbene on oxygen of the sulfoxide resulting in deoxygenation of the sulfoxide, the reaction in generating the desired sulfoxonium ylides was complicated.[7,10] Nevertheless, a number of stable alkyl sulfoxonium ylides were isolated in high yields through copper(I)- or rhodium(II)-catalyzed diazo decomposition of diazoacetates in the presence of alkyl sulfoxides.[8,9–11] For example, Ando has reported that the $CuSO_4$-catalyzed decomposition of ethyl diazoacetate in the presence of dimethyl or diphenyl sulfoxide gave the corresponding sulfoxonium ylides.[9] Similarly the copper cyanide catalyzed decomposition of various ethyl aryl diazoacetates in the presence of dimethyl sulfoxide was found to give good yields of sulfoxonium ylides.[10] Moody has reported that the cyclic sulfoxonium ylides were formed in the intramolecular interception of rhodium carbenoids by sulfoxides.[11]

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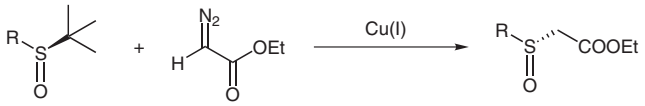
In this communication, we describe a novel reaction of copper(I)-catalyzed diazo decomposition of diazocarbonyl compounds in the presence of *tert*-butyl sulfoxides. *tert*-Butyl sulfoxonium ylides from the reaction were found to be unstable, and underwent subsequential α',β-elimination to give α-sulfinyl acetate derivatives with inversion of absolute configuration of the sulfoxides (Scheme 1).



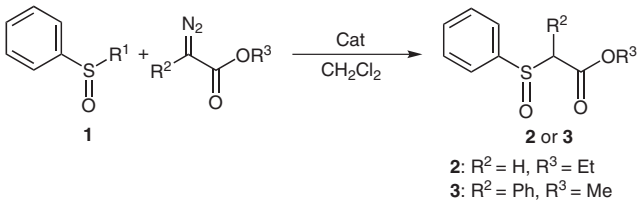
Scheme 1 Copper-catalyzed reaction of ethyl diazoacetate with *tert*-butyl sulfoxides

As important building blocks in organic synthesis, α-sulfinyl acetates have been used to synthesize β-amino acid and β-hydroxy acid derivatives exhibiting powerful antibacterial properties.[12] The α-sulfinyl acetates have been also reported as key constituents for many naturally occurring peptides, terpenes, alkaloids, macrolide and β-lactam antibiotics.[13]

Our initial study began with the copper(I)-catalyzed reaction of ethyl diazoacetate with racemic alkyl phenyl sulfoxides. No rearrangement products **2** were observed with the use of methyl, ethyl, or benzyl phenyl sulfoxide as starting materials (Table 1, entries 1–3). For example, the reaction with ethyl phenyl sulfoxide gave corresponding stable sulfoxonium ylide in 40% yield (Table 1, entry 2).

We were gratified to find that the α',β-elimination product **2a** was isolated in 28% yield with *tert*-butyl phenyl sulfoxide catalyzed by $CuPF_6(MeCN)_4$ (Table 1, entry 4). Other Cu(I) complexes including $Cu(acac)_2$, CuI, CuOAc, and CuOTf were also tested in order to improve the reaction yield (Table 1, entries 5–8). Among the catalysts, only CuOTf was found to be effective and gave 25% yield of **2a** (Table 1, entry 8). It was found that $Rh_2(OAc)_4$ was also an effective catalyst to give the desired product in 43% yield (Table 1, entry 9).[14] The reaction was extended to other diazo compounds by using $Rh_2(OAc)_4$ catalyst. When methyl phenyl diazoacetate was employed, the corresponding product **3** was obtained in 21% yield (Table 1, entry 10).[14] The reaction failed to give the desired product with the use of dimethyl diazomalonate (Table 1 entry 11).

Table 1 Reaction of Diazocarbonyl Compounds with Alkyl Phenyl Sulfoxides



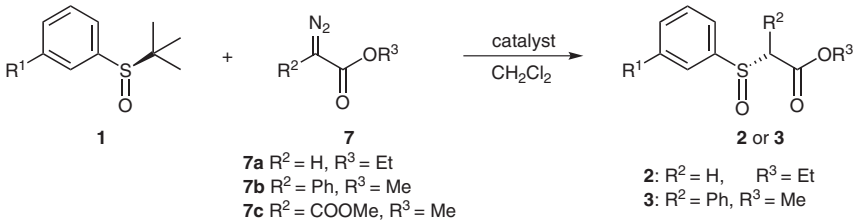
Entry	R^1	R^2	R^3	Catalyst	Yield (%)[a]
1	Me	H	Et	$CuPF_6(MeCN)_4$	–
2	Et	H	Et	$CuPF_6(MeCN)_4$	–
3	Bn	H	Et	$CuPF_6(MeCN)_4$	–
4	*t*-Bu	H	Et	$CuPF_6(MeCN)_4$	28 (±**2a**)
5	*t*-Bu	H	Et	CuI	trace
6	*t*-Bu	H	Et	$Cu(acac)_2$	trace
7	*t*-Bu	H	Et	CuOAc	trace
8	*t*-Bu	H	Et	CuOTf	25 (±**2a**)
9	*t*-Bu	H	Et	$Rh_2(OAc)_4$	43 (±**2a**)
10	*t*-Bu	Ph	Me	$Rh_2(OAc)_4$	21 (±**3**)
11	*t*-Bu	COOMe	Me	$Rh_2(OAc)_4$	–

[a] Isolated yield after column chromatography.

We next turned our attention towards the reaction by using optically active *tert*-butyl phenyl sulfoxide. We were very interested to see whether we can maintain the optical purity at the chiral sulfur center after the reaction. This would provide us useful information regarding the reaction mechanism. As shown in Table 2, the reaction of (*R*)-*tert*-butyl phenyl sulfoxide [(*R*)-**1a**] with ethyl diazoacetate catalyzed by $Rh_2(OAc)_4$ gave optically active α-sulfinyl acetates **2a** in moderate yield (Table 2, entry 1).[14] The absolute configuration of (*S*)-ethyl 2-(phenylsulfinyl)acetate (**2a**)[15] was confirmed by comparison of the optical rotation with literature values.[13g] A similar result was obtained with sulfoxide (*R*)-**1b** bearing an electron-donating 3-MeO substituent (Table 2, entry 2).[16] Extension of diazo compound to methyl phenyl diazoacetate afforded corresponding product **3** in 77:23 dr with 97.5% ee for the major diastereomer, but in lower yield (Table 2, entry 3).[17] Again, no desired product was observed for dimethyl diazomalonate catalyzed by $Rh_2(OAc)_4$ or $CuPF_6(MeCN)_4$ (Table 2, entries 4 and 5).

We next extended the reaction to optically active (*R*)-*N*-*tert*-butylsulfinyl aldimines **4**, because these chiral substrates are easier to obtain from the condensation of corresponding aldehydes with commercially available (*R*)-*tert*-butylsulfinyl amide. A number of (*R*)-*N*-*tert*-butylsulfinyl aldimines **4** were examined.[18] Unfortunately, $Rh_2(OAc)_4$ catalyst failed to give the desired product **5** or **6** in this case. $CuPF_6(MeCN)_4$ was identified to be the best catalyst of choice and gave optically active α-sulfinyl acetates in moderate yield with inversion of the absolute configuration (Table 3, entries 1–7). The reaction tolerated the sulfoxide substrate with a good range of substitutions on the aromatic ring except the substrate bearing *o*-substitution on the phenyl ring. This is probably due to steric effect of the *ortho*-substitution resulting in difficult formation of corresponding sulfoxonium ylide intermediate (Table 3, entries 8, 9). When methyl phenyl diazoacetate was em-

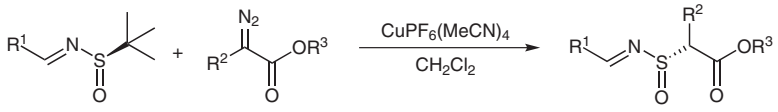
Table 2 The Reaction of Diazocarbonyl Compounds with Enantiopure *tert*-Butyl Phenyl Sulfoxides[a]



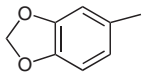
Entry	R^1	7	Catalyst	Yield (%)[b]	ee (%)[c]
1	H (**1a**)	**7a**	$Rh_2(OAc)_4$	43 (**2a**)[e]	90
2	MeO (**1b**)	**7a**	$Rh_2(OAc)_4$	40 (**2b**)	99
3[d]	H (**1a**)	**7b**	$Rh_2(OAc)_4$	21 (**3**)	97.5
4	H (**1a**)	**7c**	$Rh_2(OAc)_4$	n.r.	
5	H (**1a**)	**7c**	$CuPF_6(MeCN)_4$	n.r.	

[a] Reactions were performed on a 0.2 mmol scale (**1**/diazo = 1:3) in the presence of a catalyst (3 mol%) at 40 °C in CH_2Cl_2 (3.0 mL) under an inert atmosphere.
[b] Isolated yield after column chromatography purification.
[c] The ee values were determined by HPLC on a chiral stationary phase.
[d] Diastereomeric ratio (*R*,*S*)-**3**[17]/(*S*,*S*)-**3** = 77:23, as determined by ^1H NMR analysis of the crude reaction mixture.
[e] The absolute configuration of (*S*)-ethyl 2-(phenylsulfinyl)acetate **2a** was confirmed by comparison of its optical rotation with that reported in literature.[13g]

Table 3 Copper-Catalyzed Reaction of Diazocarbonyl Compounds with the Optically Active *N*-*tert*-Butylsulfinyl Aldimines[a]



5: R^2 = H, R^3 = Et
6: R^2 = Ph, R^3 = Me

Entry	R^1	R^2	R^3	Yield (%)[b]	ee (%)[c]
1	Ph (**4a**)	H	Et	55 (**5a**)	98
2	4-$MeOC_6H_4$ (**4b**)	H	Et	51 (**5b**)	97.7
3[f]	4-$O_2NC_6H_4$ (**4c**)	H	Et	42 (**5c**)	100.0
4	4-ClC_6H_4 (**4d**)	H	Et	47 (**5d**)	99.8
5	4-BrC_6H_4 (**4e**)	H	Et	40 (**5e**)	98
6[f]	4-Cl-3-$O_2NC_6H_3$ (**4g**)	H	Et	45 (**5f**)	99.8
7	 (**4i**)	H	Et	43 (**5g**)	99.2
8	2,4-$O_2NC_6H_3$ (**4h**)	H	Et	n.r.	
9	2,4-$MeOC_6H_3$ (**4f**)	H	Et	n.r.	
10[f]	4-$O_2NC_6H_4$ (**4c**)	Ph	Me	53 (**6a**)[d]	99/99
11[f]	4-$O_2NC_6H_4$ (**4c**)	4-BrC_6H_4	Me	50 (**6b**)[e]	98/99

[a] Reactions were performed on a 0.2 mmol scale (**4**/diazo = 1:3) in the presence of $CuPF_6(MeCN)_4$ (3 mol%) at 40 °C in CH_2Cl_2 (3.0 mL) under an inert atmosphere.
[b] Isolated yield after column chromatography purification.
[c] The ee values were determined by HPLC on a chiral stationary phase.
[d] Diastereomeric ratio (*R*,*R*)-**6a**/(*S*,*R*)-**6a** = 44:56, as determined by ^1H NMR analysis of the crude reaction mixture.
[e] Diastereomeric ratio (*R*,*R*)-**6b**/(*S*,*R*)-**6b** = 60:40, as determined by ^1H NMR analysis of the crude reaction mixture.
[f] (*S*)-*N*-*tert*-Butylsulfinyl aldimines were used.

ployed, the reaction also afforded corresponding products with 98–99% ee and moderate dr (Table 3, entries 10, 11). The structure of (*R*,*R*)-**6a** was conformed by single-crystal X-ray structural analysis (Figure 1).[20]

The CD spectra of compounds (*S*)-**4c** and (*R*)-**5c**[19] were recorded in order to get information regarding to the absolute configuration of the product. As shown in Figure 2, the CD curve of (*R*)-**5c** showed the opposite trend against the starting material (*S*)-**4c**, indicating that the product has the opposite absolute configuration at the sulfur atom. The reaction mechanism is proposed as following: carbene formed by the copper-catalyzed decomposition of diazoacetate can easily attack on a long-pair electron of the sulfur atom to give sulfoxonium ylide. The ylide carrying a large *tert*-butyl group is unstable, and prefers to undergo α′,β-elimination to afford α-sulfinyl acetate. The α′,β-elimination of the sulfoxonium ylide intermediate is probably through a five-membered cyclic transition state and resulting in inversion of the stereochemistry in the product (Scheme 2).

In summary, we report here the first example of elimination of *tert*-butyl sulfoxonium ylide in situ generated from diazocarbonyl compounds and *tert*-butyl sulfoxides. The reaction affords α-sulfinyl acetate with inversion of absolute configuration. Optically active α-sulfinyl acetate can be made from chiral *tert*-butyl sulfoxides in moderate yield. This reaction provides an easy entry for the preparation of chiral sulfoxides and should be applicable in asymmetric synthesis through additional transformations.

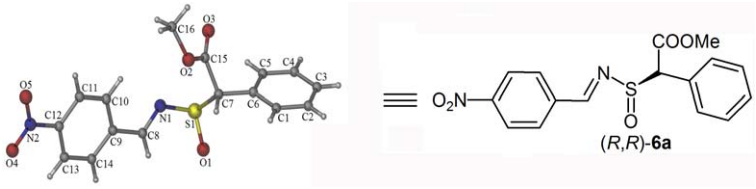


Figure 1 X-ray crystal structure of (*R*,*R*)-**6a**

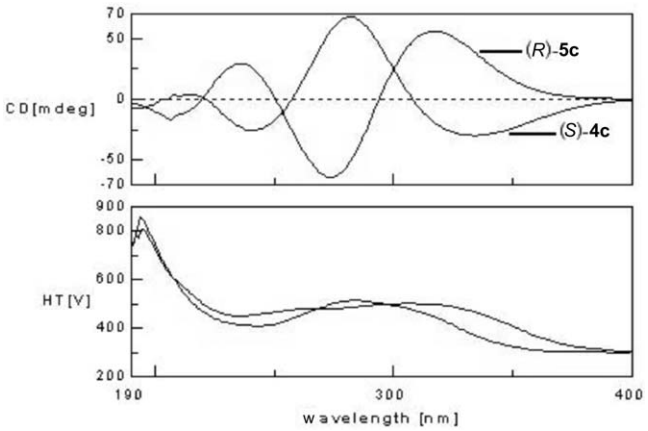
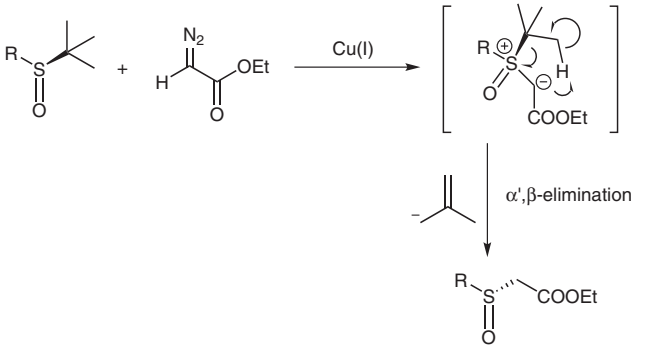


Figure 2 CD spectrum structure of (*S*)-**4c** and (*R*)-**5c**



Scheme 2 Proposed reaction mechanism

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(14) **Typical Procedure for the Synthesis of Compounds 2 and 3**
To a refluxing CH_2Cl_2 (3 mL) solution of $Rh_2(OAc)_4$ (2.6 mg, 3 mol%), (*R*)-(*tert*-butylsulfinyl)benzene [(*R*)-**1a**, 36.4 mg, 0.2 mmol] was added ethyl diazoacetate (68.4 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) over 1 h via a syringe pump. After the addition was completed, the reaction mixture was cooled to r.t. Solvent was removed, and the crude product was purified by a flash column chromatography on silica gel eluting with 20% EtOAc–light PE to give (*S*)-**2a** (18 mg) in 43% yield.

(15) **Analytical Data of (*S*)-Ethyl 2-(Phenylsulfinyl)acetate [(*S*)-2a]**
TLC: R_f = 0.15 (PE–EtOAc, 5:1); $[\alpha]_D^{20}$ –131 (*c* 1, EtOAc);

90% ee, determined by HPLC [Daicel Chiralpak AD-H, flow rate 0.4 mL/min, hexane–2-PrOH = 90:10, 254 nm; t_R(major) = 37.2 min and t_R(minor) = 40.0 min]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.1 Hz, 3 H), 3.68 (d, *J* = 13.6 Hz, 1 H), 3.87 (d, *J* = 13.6 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 7.52–7.70 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.98, 61.70, 62.01, 124.17, 129.36, 131.75, 143.07, 164.68 ppm. HRMS (EI): *m/z* calcd for $C_{10}H_{12}NaO_3S$ [M + Na]$^+$: 235.0405; found: 235.0399.

(16) **Analytical Data of (*S*)-Ethyl 2-(Phenylsulfinyl)acetate [(*S*)-2b]**
TLC: R_f = 0.13 (PE–EtOAc, 5:1); $[\alpha]_D^{20}$ –120 (*c* 1, EtOAc); 99% ee, determined by HPLC [Daicel Chiralpak AD-H, flow rate 0.4 mL/min, hexane–2-PrOH = 90:10, 254 nm, t_R(major) = 42.35 min and t_R(minor) = 45.58 min]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.2 Hz, 3 H), 3.67 (d, *J* = 13.5 Hz, 1 H), 3.85 (d, *J* = 10.8 Hz, 1 H), 3.86 (s, 3 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 7.03–7.20 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.02, 55.60, 61.90, 62.04, 108.41, 116.18, 118.23, 130.31, 144.61, 160.53, 164.73 ppm. HRMS (EI): *m/z* calcd for $C_{11}H_{14}NaO_4S$ [M + Na]$^+$: 265.0510; found: 265.0505.

(17) **Analytical Data of (*R*,*S*)-Ethyl 2-(Phenylsulfinyl)acetate [(*R*,*S*)-3]**
TLC: R_f = 0.26 (PE–EtOAc, 5:1); $[\alpha]_D^{20}$ –110 (*c* 1, EtOAc); 97.5% ee, determined by HPLC [Daicel Chiralpak AD-H, flow rate 0.4 mL/min, hexane–2-PrOH = 90:10, 254 nm; t_R(major) = 44.7 min and t_R(minor) = 50.9 min]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 4.55 (s, 1 H), 3.87 (d, *J* = 13.6 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 7.04–7.49 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.70, 78.02, 125.19, 128.50, 128.57, 129.22, 129.37, 129.94, 131.70, 141.18, 168.01 ppm. HRMS (EI): *m/z* calcd for $C_{15}H_{14}NaO_3S$ [M + Na]$^+$: 297.0561; found: 297.0556.

(18) **Typical Procedure for the Synthesis of Compounds 5 and 6**
To a refluxing CH_2Cl_2 (3 mL) solution of $CuPF_6(MeCN)_4$ (2.2 mg, 3 mol%), (*S*)-*N*-(4-nitrobenzylidene)-2-methylpropane-2-sulfinamide (**4c**, 50.8 mg, 0.2 mmol) was added ethyl diazoacetate (68.4 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) over 1 h via a syringe pump. After the addition was completed, the reaction mixture was cooled to r.t. Solvent was removed, and the crude product was purified by a flash column chromatography on silica gel eluting with 20% EtOAc–light PE to give (*R*)-**5c** (24 mg) in 42% yield.

(19) **Analytical Data of (*R*)-*N*-(4-Nitrobenzylidene)-2-ethoxy-2-oxomethanesulfinamide [(*R*)-5c]**
TLC: R_f = 0.12 (PE–EtOAc, 5:1); $[\alpha]_D^{20}$ +84.5 (*c* 1, EtOAc); 100% ee, determined by HPLC [Daicel Chiralpak AS, flow rate 0.6 mL/min, hexane–2-PrOH = 100:30, 254 nm; t_R(major) = 25.72 min and t_R(minor) = 19.09 min]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.1 Hz, 3 H), 3.76 (d, *J* = 13.6 Hz, 1 H), 3.90 (d, *J* = 13.6 Hz, 1 H), 4.31 (q, *J* = 7.1 Hz, 2 H), 8.05 (d, *J* = 8.8 Hz, 2 H), 8.36 (d, *J* = 8.8 Hz, 2 H), 8.76 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.15, 59.98, 62.24, 124.26, 130.39, 132.32, 138.32, 161.13, 164.06 ppm. HRMS (EI): *m/z* calcd $C_{11}H_{12}N_2NaO_5S$ [M + Na]$^+$: 307.0365; found: 307.0359.

(20) **Crystal Structure Data for (*R*,*R*)-*N*-(4-Nitrobenzylidene)-2-ethoxy-2-oxomethane-1-benzylsulfinamide [(*R*,*R*)-6a]**
$C_{16}H_{14}N_2O_5S$, *Mw* = 346.35, light yellow, orthorhombic, *P*2, *a* = 5.70380 (10), *b* = 8.2382 (2), *c* = 34.4784 (8) Å, *α* = 90.00, *β* = 90.00, *γ* = 90.00, *V* = 1620.11 (6) Å^3, *Z* = 4, *T* = 296 (2) K, ρ_{calcd} = 1.420 Mg·m, *F*(000) = 720, λ = 0.71073 Å, μ = 0.229 mm^{-1}, *R*(*F*) = 0.0299 and *wR*(*F*)2 = 0.0792 for 2722 observed reflections, $I > 2\sigma$, 2.36° < θ < 24.99°. CCDC 722774 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax +44 (1223)336033; or deposit@ ccdc.cam.ac.uk].