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# *N*-{3-Isopropoxy-4-methoxy-2-[(*E*)-1-propenyl]benzyl}(phenyl)methanesulfonamide

**Willem A. L. van Otterlo,* Jenny-Lee Panayides and Manuel A. Fernandes**

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits, 2050 Johannesburg, South Africa

Correspondence e-mail:
willem@aurum.chem.wits.ac.za

**Key indicators**

Single-crystal X-ray study
*T* = 173 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.048
*wR* factor = 0.135
Data-to-parameter ratio = 18.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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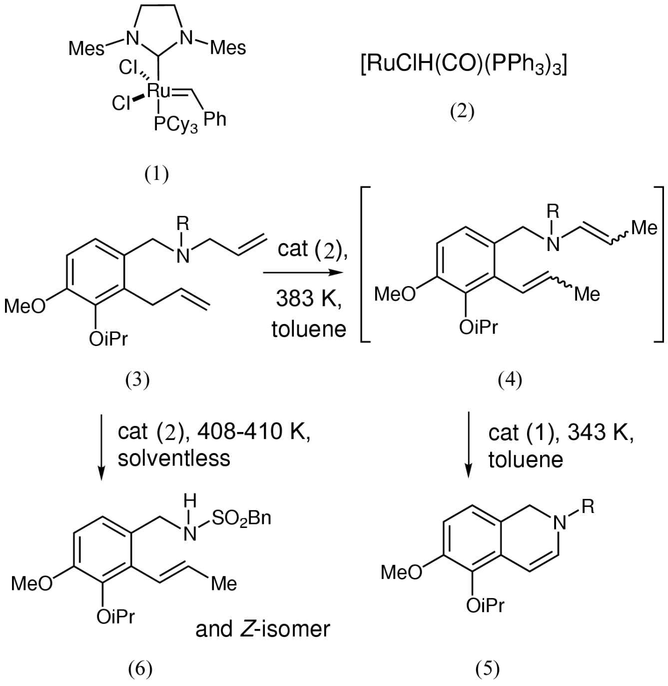
The crystal structure of the title compound, $C_{21}H_{27}NO_4S$, confirms the presence of a monoalkylated sulfonamide group and that the propenyl group of the synthetic precursor has isomerized into the more thermodynamically favoured styrene. Analysis of the structure reveals that it is held together by a network of N—H···O, C—H···O=S and π–π interactions.

## Comment

The synthesis of benzo-fused heterocycles using ring-closing metathesis (RCM) with ruthenium catalysts like (1) (see scheme) is fairly well developed (Deiters & Martin, 2004, and references therein) and includes examples from our own research group (van Otterlo, Ngidi *et al.*, 2003; van Otterlo *et al.*, 2004).



The use of a sequential isomerization/RCM strategy to afford this class of compounds has seen little investigation (Schmidt, 2004). Our research group has recently been investigating the isomerization of Ar-, O- and N-allyl groups using the ruthenium catalyst $[RuClH(CO)(PPh_3)_3]$, (2), followed by RCM (van Otterlo, Pathak & de Koning, 2003; van Otterlo, Ngidi & de Koning, 2003). For example, we have been successful in synthesizing dihydroisoquinolines, such as (5) (*R* = Ts), from the bis-allyl compound (3) (*R* = Ts) *via* intermediate (4) (*R* = Ts) (van Otterlo, Pathak & de Koning,

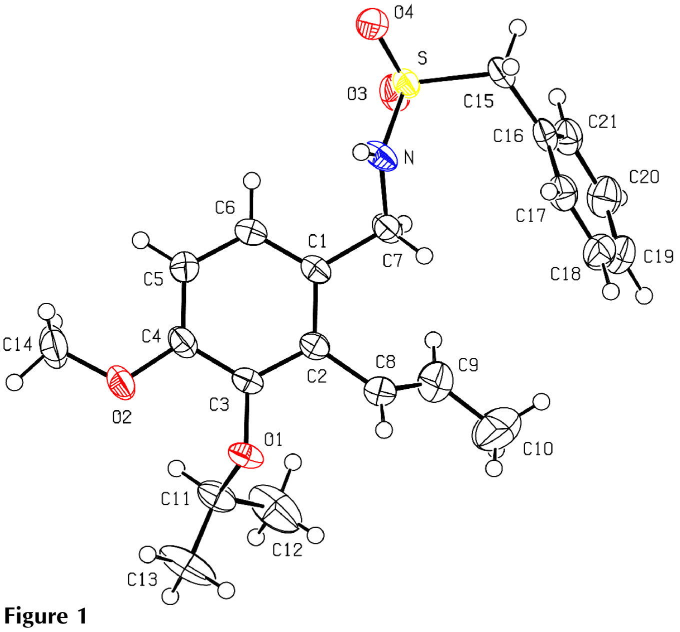


**Figure 1**
A view of (6) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

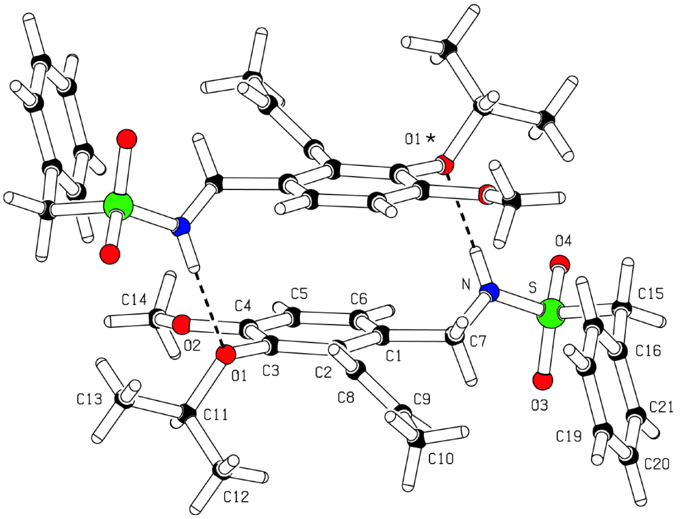


**Figure 2**
Part of the structure of (6), showing the $R_2^2(14)$ motif in which two molecules of (6) are N—H$\cdots$O hydrogen bonded to each other forming a dimer. This is futher reinforced by the $\pi$–$\pi$ interaction between the aromatic rings. The O atom with an asterisk (*) is in the symmetry position $(-x, -y, 1-z)$.

2003). In a related study with a different protecting group on nitrogen using (3) ($R$ = $SO_2Bn$), we tried to optimize the yield of dihydroisoquinoline (5) ($R$ = $SO_2Bn$) in a one-pot two-step isomerization/RCM reaction. For the first step, we thus subjected substrate (3) ($R$ = $SO_2Bn$) to a range of isomerization conditions. These included the heating of (3) ($R$ = $SO_2Bn$) in the absence of solvent with a catalytic amount of [$RuClH(CO)(PPh_3)_3$] (2) (Krompiec *et al.*, 2000, 2002) at high temperature (408–410 K). Chromatography of the resultant mixture afforded compound (6) in which the catalyst had evidently mediated an *N*-deallylation reaction, as well as the isomerization of the aryl–allyl group (4:1 ratio of *E*/*Z* isomers). Confirmation of the structure of (6) was obtained using a single-crystal grown directly from the oil (Fig. 1) which gave the structure of the E isomer. It is of interest to note that a mixture of DIBAL/$Ni^{II}$ (Taniguchi & Ogasawara, 1998) and $Li/C_{10}H_8$ (Alonso *et al.*, 1997) has been used before for *N*-sulfonamide allyl cleavage. However, to the best of our knowledge, this is the first example using a ruthenium-based catalyst for the removal of this particular functional group.

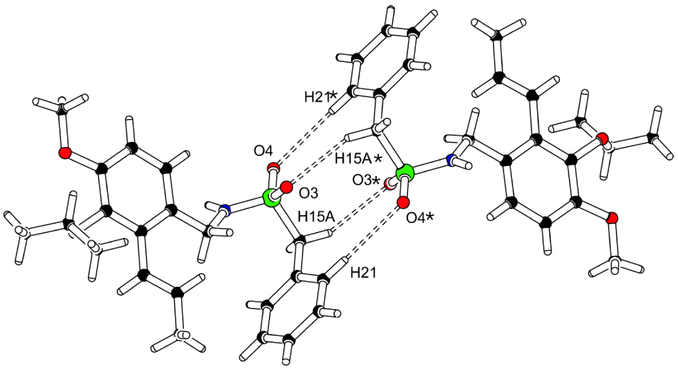


**Figure 3**
Weak C—H$\cdots$O═S interactions between centrosymmetrically related molecules in the structure of (6). The molecule with the asterisk (*) is in the symmetry position $(1-x, -y, 2-z)$.

In the crystal structure of (6), centrosymmetrically related molecules are bound by N—H$\cdots$O hydrogen bonds to form hydrogen bonded dimers (Table 1 and Fig. 2). In addition, this hydrogen-bonded dimer pair is further reinforced by a $\pi$–$\pi$ interaction between the aromatic rings of each molecule (Fig. 2). The two rings are strictly parallel, with an interplanar spacing of 3.572 (2) Å and a centroid separation of 4.058 (2) Å. Each of these molecules is in turn hydrogen bonded *via* two weak C—H$\cdots$O═S interactions to a third centrosymmetrically related molecule (Table 1 and Fig. 3). The combination of N—H$\cdots$O hydrogen bonding and the C—H$\cdots$O═S interactions produces a chain of rings parallel to $[10\bar{1}]$. Finally, a weak C—H$\cdots$O═S interaction between C13—H13*B* and O4$(-x, y-\frac{1}{2}, \frac{3}{2}-z)$ links these chains to each other (Table 1).

## Experimental

[$RuClH(CO)(PPh_3)_3$] (16.4 mg, 0.017 mmol, 5 mol%) was added to sulfonamide (3) ($R$ = $SO_2Bn$) (0.1478 g, 0.34 mmol) and the reaction mixture was heated at 408–410 K in the absence of solvent for 19 h under $N_2$. During this time the clear oil became a dark brown colour. The reaction mixture was then cooled to room temperature, after which the crude residue was purified by column chromatography (5–15% EtOAc–hexane) to afford (6) as a clear oil containing a mixture of *E*/*Z* isomers (4:1). Cream-coloured needle-like crystals of (6) suitable for X-ray analysis were subsequently grown directly from the oil (0.0754 g, 56% yield, m.p. 400–403 K). Spectroscopic data: found: $M^+$, 389.16542; $C_{21}H_{27}O_4NS$ requires 389.16608; $\delta_H$ (300 MHz, $CDCl_3$), *E* isomer: 1.22 [6H, *d*, $J$ = 6.2 Hz, $OCH(CH_3)_2$], 1.57 (1H, *s*, NH), 1.88 (3H, *dd*, $J$ = 6.5 and 1.3 Hz, H-3′), 3.82 (3H, *s*, $OCH_3$), 4.07–4.20 (4H, *m*, $NCH_2$ and $SO_2CH_2$), 4.31 [1H, *sept*, $J$ = 6.2 Hz, $OCH(CH_3)_2$], 6.01 (1H, *dq*, $J$ = 16.1 and 6.5 Hz, H-2′), 6.32 (1H, *br d*, $J$ = 16.1 Hz, H-1′), 6.76 (1H, *d*, $J$ = 8.5 Hz, H-5), 7.00 (1H, *d*, $J$ = 8.5 Hz, H-6), 7.20–7.26 (2H, *m*, 2 × ArH), 7.32–7.34 (3H, *m*, 3 × ArH);

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signals identified for *Z* isomer: 1.49 (3H, *br d*, *J* = 6.8 Hz, H-3′), 3.84 (3H, *s*, $OCH_3$), 6.26 (1H, *dd*, *J* = 10.9 and 1.3 Hz, H-1′), 6.81 (1H, *d*, *J* = 8.4 Hz, H-5); $\delta_C$ (50 MHz, $CDCl_3$), *E* isomer: 19.2 (C-3′), 22.5 [$OCH(CH_3)_2$], 45.7 ($NHCH_2$), 55.7 ($OCH_3$), 59.4 ($SO_2CH_2$), 75.2 (OCH), 110.3 (C-5), 124.4 (C-1′), 124.7 (C-6), 127.2 (ArC-C), 128.6 (ArC-H), 128.7 (2 × ArC-H), 129.2 (ArC-C), 130.2 (ArC-C), 130.6 (2 × ArC-H), 133.0 (C-2′), 145.3 (ArC-O), 153.1 (ArC-O); $\nu_{max}/cm^{-1}$ (thin film, NaCl plate): 669, 775, 1152, 1331, 1380, 1438, 1481, 1573, 2977, 3019; *m/z* 389 ($M^+$, 11%), 234 (38), 220 (25), 219 (45), 193 (12), 192 (100), 176 (19), 175 (16), 130 (13), 91 (55), 69 (38), 56 (15), 54 (14), 43 (19), 41 (18), 40 (12).

### *Crystal data*

$C_{21}H_{27}NO_4S$
$M_r$ = 389.50
Monoclinic, $P2_1/c$
*a* = 13.659 (2) Å
*b* = 16.160 (2) Å
*c* = 9.5621 (14) Å
$\beta$ = 102.561 (3)°
*V* = 2060.2 (5) $Å^3$
*Z* = 4
$D_x$ = 1.256 Mg $m^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 972 reflections
$\theta$ = 2.5–28.2°
$\mu$ = 0.18 $mm^{-1}$
*T* = 173 (2) K
Prism, colourless
0.48 × 0.32 × 0.27 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: none
12803 measured reflections
4483 independent reflections
3500 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.027
$\theta_{max}$ = 27.0°
*h* = −17 → 16
*k* = −13 → 20
*l* = −12 → 11

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.135$
*S* = 1.04
4483 reflections
249 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 1.1280P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.81 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.34 e $Å^{-3}$

**Table 1**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N—H1···O1$^{i}$ | 0.88 | 2.15 | 2.937 (2) | 148.0 |
| C13—H13*B*···O4$^{ii}$ | 0.98 | 2.46 | 3.396 (4) | 160.0 |
| C15—H15*A*···O3$^{iii}$ | 0.99 | 2.61 | 3.535 (4) | 156.5 |
| C21—H21···O4$^{iii}$ | 0.95 | 2.72 | 3.662 (4) | 171.5 |

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $1-x, -y, 2-z$.

The H atoms were first located in a difference Fourier map, then positioned geometrically and allowed to ride on their respective parent atoms, with C—H or N—H bond lengths of 0.88 (N—H), 0.95 (aromatic C—H), 0.99 ($CH_2$) or 0.98 Å ($CH_3$), and isotropic displacement parameters equal to 1.2 (N—H, C—H and $CH_2$) or 1.5 ($CH_3$) times that of the parent atom.

Data collection: *SMART -NT*(Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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