

# A Metal Free, Microwave Assisted Preparation of *N*-Sulfonyl and *N*-Sulfinyl Imines and Imidates

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This supporting information includes two Tables, 3 Figures (1-3) and 33 pages overall

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## General Methods

Thin-layer chromatography was performed on (0.2 mm) silica-gel aluminum backed plates, which were visualized by exposure to ultraviolet light followed by staining with basic potassium permanganate solution. Silica gel (0.040-0.063 mm) was employed for flash column chromatography. Melting points are uncorrected. A Fourier transform infrared spectrometer was used to record IR spectra. NMR spectra were recorded at 298 K, at the frequency stated and run as a dilute solution in CDCl<sub>3</sub>. Chemical shifts are expressed in ppm downfield with the solvent residual peak (CDCl<sub>3</sub>  $\delta_{\text{H}}$  7.26,  $\delta_{\text{C}}$  77.16) as the internal standard. All coupling constants are reported in Hertz (Hz) and multiplicity of each signal is designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; app, apparent; br, broad or some combinations thereof. Assignments of <sup>13</sup>C spectra were made with the aid of DEPT experiments. Mass spectra were recorded by using ESI techniques. HRMS were recorded on an Orbitrap apparatus (ESI). Molecular sieve was activated at 230 °C under vacuum overnight and stored at room temperature under vacuum.

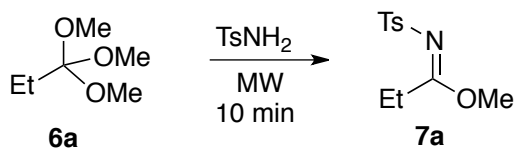
Microwave irradiation experiments were conducted in a CEM Discover S-Class apparatus (single mode technology) under magnetic stirring and internal (optical probe) temperature measurements (and external IR view).

Small scale reactions (1 mmol) were all conducted in a 10 mL sealed CEM microwave reactor and the 30 mmol reaction was conducted in the 35 mL one.

HPLC separation for compound **4a** has been conducted on an Agilent 1260 Infinity Analytical SFC system. HPLC separation for compound **8d** has been conducted on a Waters Delta 600 system.

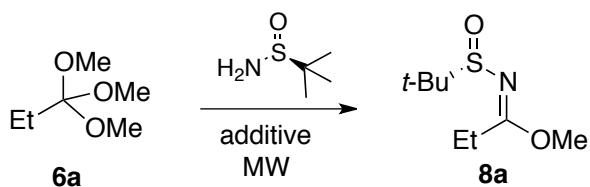
## Table of reaction conditions optimization for imidates synthesis

**Table S1** Optimisation of the conditions for the microwave assisted preparation of *N*-tosylimidates



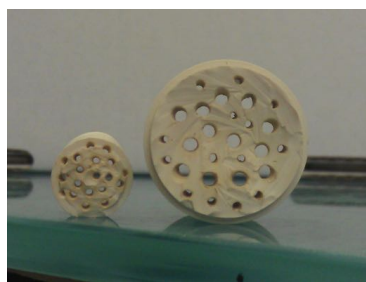
| Entry | T (°C) | Without MS<br>Conv (%) | With MS<br>Conv (%) | yield |
|-------|--------|------------------------|---------------------|-------|
| 1     | 120    | 63                     | 59                  | /     |
| 2     | 140    | 86                     | 87                  | /     |
| 3     | 160    | 97                     | 97                  | /     |
| 4     | 180    | 100                    | /                   | 99    |

**Table S2** Optimisation of the conditions for the microwave assisted preparation of sulfinylimidates



| Entry | T (°C) | t (min) | Solvent       | PPTS | Conv (%) |
|-------|--------|---------|---------------|------|----------|
| 1     | 80     | 30      | <i>i</i> PrOH | 0    | 0        |
| 2     | 80     | 30      | <i>i</i> PrOH | 10%  | 55       |
| 3     | 80     | 30      | -             | 0    | 80       |
| 4     | 80     | 30      | -             | 10%  | 100      |

**Pictures of setting up the microwave tubes with molecular sieves and internal temperature probe**



Septums with holes made with a hot needle



**1.** Reagents in the MW tube, and then septum introduce; the size prevent the septum from falling at the bottom



**2.** Introduction of the temperature probe through the septum; adjustment of the position of septum in the tube



**3.** Addition of the molecular sieves



**4.** Lifting the tube to the top of the MW internal probe adaptor



**5.** Putting the tube with adaptor in the MW machine (here CEM); same principle with an Anton Paar machine

### **Pictures of setting up the microwave tubes with molecular sieves**

The set up is similar to the previous one, but much simpler to set up without the temperature probe. The reagents are charged in the tube, then the leaky septum, the molecular sieves and finally, the tube stopper. Standard introduction in the MW (same for CEM or Anton Paar)



**General procedure for the microwave-assisted synthesis of *N*-Sulfonylimines **2** :** A microwave-tube was charged with 4-methylbenzenesulfonamide (1 eq), dimethylacetal (1.2 eq), and a magnetic stirrer. A leaky septum filled with 4Å MS was placed 3 cm above the top of the tube and the reaction mixture was heated at 180 °C for 20 minutes. The crude imine was then recrystallized (pentane/AcOEt) and a filtration afforded the pure *N*-sulfonylimine.

**Figure S1: Microwave temperature profile for **2a**.** [grey: *internal temperature (control)* ; *red: external temperature*]

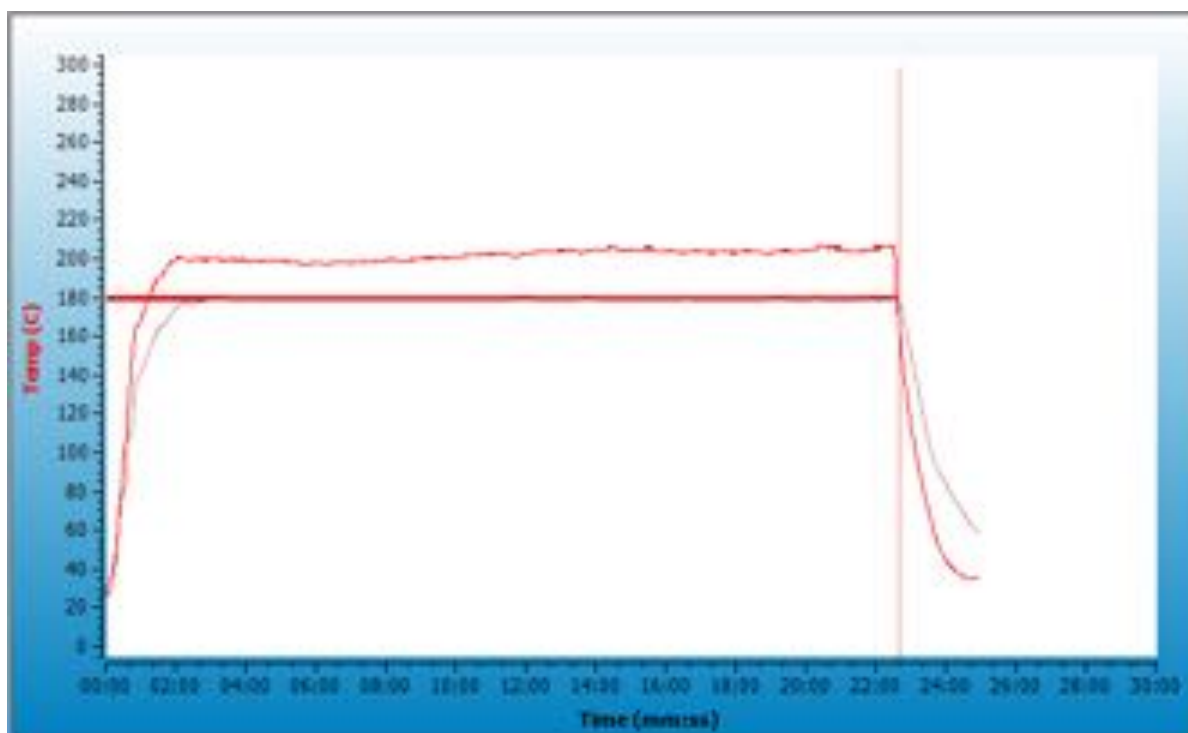
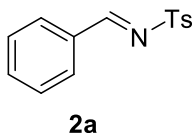


Figure S1



**(E)-N-Benzylidene-4-methylbenzenesulfonamide (2a).** 4-methylbenzenesulfonamide (5.14 g, 29.4 mmol) and benzaldehyde dimethylacetal **1a** (5.37 g, 35.3 mmol) afforded 7.24 g (95 %) of imine **2a** as a white solid. m.p. 114-116 °C [litt. 114-116°C]<sup>1</sup>; IR (neat) 3071, 3003, 1595, 1573, 1316, 1154 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 9.03 (s, 1H), 7.93 (d, *J* = 7.3 Hz, 2H), 7.89 (d, *J* = 8.2, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (pseudo t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm) 170.5, 144.9, 135.6, 135.3, 132.8, 131.7, 130.2, 129.5, 128.5, 22.0; MS (ESI) *m/z* 260.1 [M+H]<sup>+</sup>, 282.0 [M+Na]<sup>+</sup>.

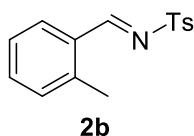
For this example, we have evaluated four different green chemistry metrics:

**E-factor:** (1.07 (remaining acetal) + 1.88 (2 eq of MeOH) + 13 (19 mL of Pentane + 1 mL of AcOEt for recrystallization) / 7.24 (weight of product)= 2.2

**Atom Economy:** 259.32/(152.19+171.22)= 0.8

**Mass efficiency:** 7.24 (5.37+5.14)= 0.688

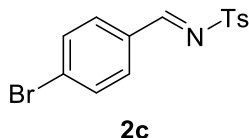
**Eco-Scale:** penalty points (100-95)/2 + 0 (price) + 5 (toxicity of acetal) + 2 (unconventional warming) + 2 (heating < 2h) + 1 (crystallization) = 12.5 (Eco scale of 87.5)



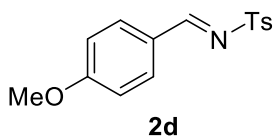
**(E)-4-Methyl-N-(2-methylbenzylidene)benzenesulfonamide (2b).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 2-methylbenzaldehyde dimethylacetal **1b** (200 mg, 1.2 mmol) afforded 242 mg (89%) of imine **2b** as a white solid. m.p. 95-97 °C; IR (neat) 3074, 3034, 1586, 1561, 1318, 1152 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 9.37 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31 (pseudo t, *J* = 8.7 Hz, 1H), 2.61 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

<sup>1</sup> Jin, T.; Feng, G.; Yang, M.; Li, T. *Synth. Commun.* **2004**, *34*, 1277.

:  $\delta$  (ppm) 187.0, 144.8, 142.5, 135.7, 134.9, 131.9, 131.0, 130.7, 130.1, 128.3, 126.9, 22.0, 20.0;  
MS (ESI)  $m/z$  273.1  $[M+H]^+$ , 296.1  $[M+Na]^+$ .



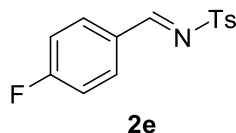
**(E)-N-(4-Bromobenzylidene)-4-methylbenzenesulfonamide (2c).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 4-bromobenzaldehyde dimethylacetal **1c** (277 mg, 1.2 mmol) afforded 332 mg (98 %) of imine **2c** as a white solid. m.p. 195-197 °C [litt. 200-210 °C]<sup>2</sup>; IR (neat) 3064, 3037, 1605, 1586, 1315, 1158  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.98 (s, 1H), 7.88 (d,  $J$  = 8.2 Hz, 2H), 7.78 (d,  $J$  = 8.5 Hz, 2H), 7.64 (d,  $J$  = 8.5 Hz, 2H), 7.35 (d,  $J$  = 8.2 Hz, 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 169.1, 145.14, 135.3, 133.0, 132.7, 131.6, 130.6, 130.2, 128.5, 22.0; MS (ESI)  $m/z$  338.0  $[M+H]^+$ , 359.9  $[M+Na]^+$  ( $^{79}\text{Br}$ ).



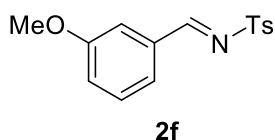
**(E)-N-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide (2d).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 4-methoxybenzaldehyde dimethylacetal **1d** (219 mg, 1.2 mmol) afforded 275 mg (95 %) of imine **2d** as a white solid. m.p. 127-128 °C [litt. 126-127 °C]<sup>1</sup>; IR (neat) 3068, 2940, 1592, 1557, 1315, 1154  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.94 (s, 1H), 7.93-7.83 (m, 4H), 7.33 (d,  $J$  = 8.1 Hz, 2H), 6.97 (d,  $J$  = 8.8 Hz, 1H), 3.88 (s, 3H),

<sup>2</sup> Vaas, A.; Dudas, J.; Rajender, S. V. *Tetrahedron Lett.* **1999**, 40, 4951.

2.43 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 169.5, 165.6, 144.6, 136.2, 134.1, 130.1, 128.3, 125.6, 115.0, 56.0, 22.0; MS (ESI)  $m/z$  290.1  $[\text{M}+\text{H}]^+$ , 312.1  $[\text{M}+\text{Na}]^+$ .



**(E)-N-(4-Fluorobenzylidene)-4-methylbenzenesulfonamide (2e).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 4-fluorobenzaldehyde dimethylacetal **1e** (204 mg, 1.2 mmol) afforded 260 mg (93 %) of imine **2e** as a white solid. m.p. 116-117 °C; IR (neat) 3116, 3090, 1581, 1318, 1149  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 9.00 (s, 1H), 8.00-7.91 (m, 2H), 7.88 (d,  $J$  = 8.24 Hz, 1H), 7.33 (dd,  $J$  = 15.90, 5.54 Hz, 2H), 7.22-7.13 (m, 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 168.8, 167.3 (d,  $J_{\text{F-C}}$  = 257 Hz), 145.0, 135.5, 134.1 (d,  $J_{\text{F-C}}$  = 10 Hz), 130.2, 129.2 (d,  $J_{\text{F-C}}$  = 3 Hz), 128.5, 117.4 (d,  $J_{\text{F-C}}$  = 22 Hz), 22.0; MS (ESI)  $m/z$  278.1  $[\text{M}+\text{H}]^+$ , 300.0  $[\text{M}+\text{Na}]^+$ .

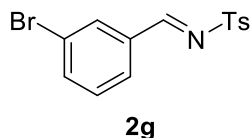


**(E)-N-(3-Methoxybenzylidene)-4-methylbenzenesulfonamide (2f).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 3-methoxybenzaldehyde dimethylacetal **1f** (219 mg, 1.2 mmol) afforded 269 mg (93%) of imine **2f** as a white solid. m.p. 73-74 °C [litt. 78-79 °C]<sup>3</sup>; IR (neat) 3070, 3004, 1595, 1574, 1319, 1153  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.99 (s, 1H), 7.89 (d,  $J$  = 8.3 Hz, 2H), 7.49-7.32 (m, 5H), 7.22-7.16 (m, 1H), 3.84 (s, 3H), 2.44 (s, 3H);

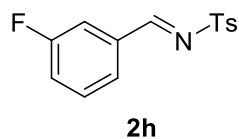
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<sup>3</sup> Ruano, J. L. G.; Allemen, J.; Cid, M. B.; Parra, A. *Org. Lett.* **2005**, 7, 179

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 170.4, 160.4, 145.0, 135.4, 134.0, 130.4, 130.1, 128.4, 125.6, 122.5, 113.6, 55.8, 22.0; MS (ESI)  $m/z$  290.1  $[\text{M}+\text{H}]^+$ , 312.1  $[\text{M}+\text{Na}]^+$ .

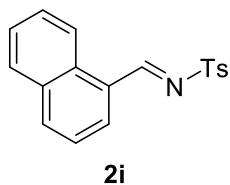


**(E)-N-(3-Bromobenzylidene)-4-methylbenzenesulfonamide (2g).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 3-bromobenzaldehyde dimethylacetal **1g** (277 mg, 1.2 mmol) afforded 315 mg (93 %) of imine **2g** as a white solid. m.p. 94-95 °C; IR (neat) 3059, 1607, 1557, 1319, 1159  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.96 (s, 1H), 8.09 (s, 1H), 7.89 (d,  $J = 8.3$  Hz, 2H), 7.82 (d,  $J = 7.9$  Hz, 1H), 7.72 (d,  $J = 7.9$  Hz, 1H), 7.40-7.33 (m, 3H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 168.8, 145.3, 137.9, 135.1, 134.6, 133.6, 131.0, 130.5, 130.2, 128.6, 123.7, 22.0; MS (ESI)  $m/z$  338.0  $[\text{M}+\text{H}]^+$ , 359.9  $[\text{M}+\text{Na}]^+$  ( $^{79}\text{Br}$ ).

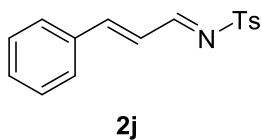


**(E)-N-(3-Fluorobenzylidene)-4-methylbenzenesulfonamide (2h).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 3-fluorobenzaldehyde dimethylacetal **1h** (204 mg, 1.2 mmol) afforded 249 mg (90 %) of imine **2h** as a white solid. m.p. 100-102 °C; IR (neat) 3088, 1608, 1573, 1319, 1157  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 9.00 (s, 1H), 7.89 (d,  $J = 8.1$  Hz, 2H), 7.67 (pseudo t,  $J = 7.9$  Hz, 2H), 7.52-7.44 (m, 1H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.34-7.27 (m, 1H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 169.0 (d,  $J_{\text{F-C}} = 3$  Hz), 163.2 (d,  $J_{\text{F-C}} = 248$  Hz), 145.2, 135.2, 134.9 (d,  $J_{\text{F-C}} = 8$  Hz), 131.2 (d,  $J_{\text{F-C}} = 8$  Hz), 130.2, 128.5, 128.1

(d,  $J_{F-C} = 3$  Hz), 122.2 (d,  $J_{F-C} = 22$  Hz), 116.9 (d,  $J_{F-C} = 22$  Hz), 22.0; MS (ESI)  $m/z$  278.1 [M+H]<sup>+</sup>, 300.0 [M+Na]<sup>+</sup>.



**(E)-4-Methyl-N-(naphthalen-1-ylmethylene)benzenesulfonamide (2i).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 1-naphthaldehyde dimethylacetal **1i** (243 mg, 1.2 mmol) afforded 257 mg (83 %) of imine **2i** as a white solid. m.p. 137-138 °C; IR (neat) 3065, 3034, 1586, 1315, 1118 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) : δ (ppm) 9.59 (s, 1H), 8.97 (d,  $J = 8.6$  Hz, 1H), 8.11 (d,  $J = 7.5$  Hz, 1H), 8.07 (d,  $J = 8.2$  Hz, 1H), 7.96 (d,  $J = 8.2$  Hz, 2H), 7.89 (d,  $J = 8.1$  Hz, 1H), 7.65 (t,  $J = 7.5$  Hz, 1H), 7.60-7.50 (m, 2H), 7.34 (d,  $J = 8.1$  Hz, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) : δ (ppm) 170.1, 144.8, 136.4, 135.7, 135.4, 134.0, 132.0, 130.1, 129.3, 129.2, 128.3, 127.8, 127.2, 125.4, 124.5, 21.9; MS (ESI)  $m/z$  310.1 [M+H]<sup>+</sup>, 332.0 [M+Na]<sup>+</sup>.



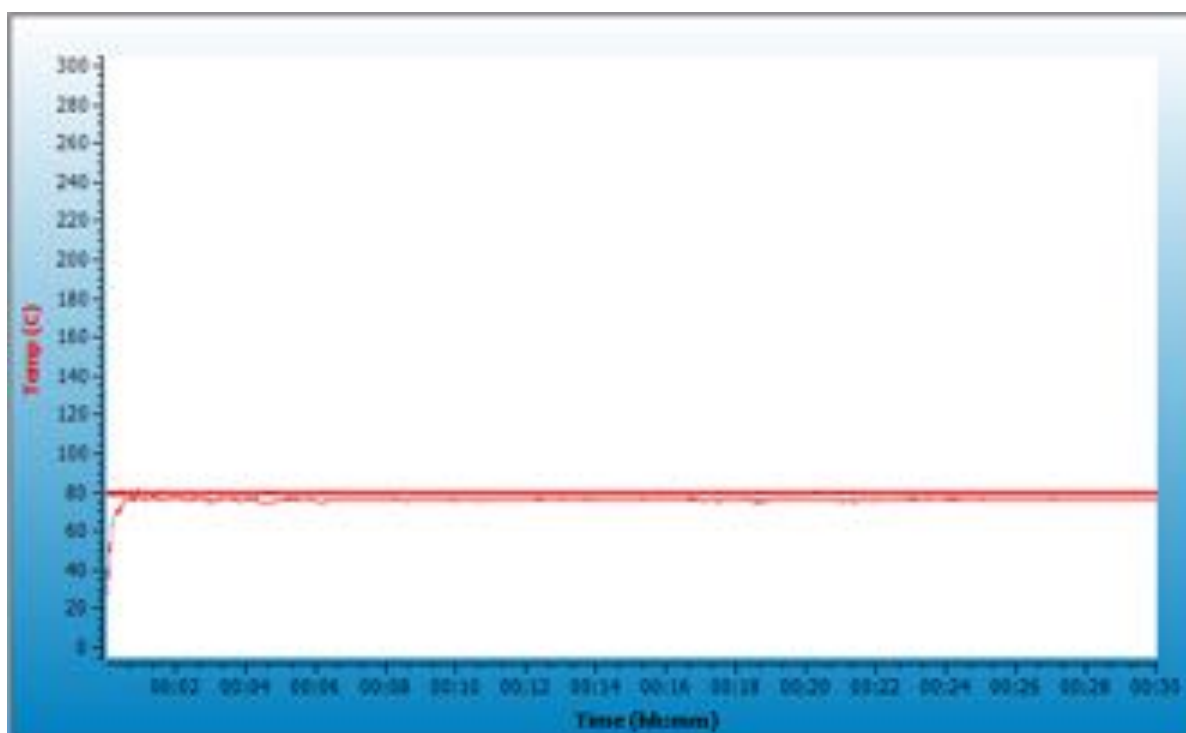
**4-Methyl-N-((1E,2E)-3-phenylallylidene)benzenesulfonamide (2j).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and cinnamaldehyde dimethylacetal **1j** (214 mg, 1.2 mmol) afforded 274 mg (96 %) of imine **2j** as a yellow pale solid. m.p. 115-117 °C [litt. 110 °C]<sup>1</sup>; IR (neat) 3046, 2923, 1578, 1508, 1312, 1150, cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 8.78 (d,  $J = 9.4$  Hz, 1H), 7.86 (d,  $J = 8.2$  Hz, 2H), 7.58-7.53 (m, 2H), 7.52-7.39 (m, 4H), 7.34 (d,  $J = 8.2$  Hz, 2H), 6.99 (dd,  $J = 15.8, 9.4$  Hz, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm)

171.2, 154.1, 144.8, 135.8, 134.6, 132.0, 130.2, 129.6, 129.0, 128.3, 125.2, 22.0; MS (ESI)  $m/z$  286.1  $[M+H]^+$ , 308.0  $[M+Na]^+$ .

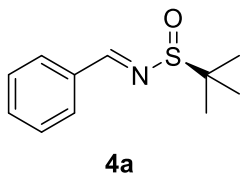
**General procedure for the microwave-assisted synthesis of *N*-*tert*-butanesulfinylimines 4:**

A microwave-tube was charged with *tert*-butanesufinamide, dimethylacetal (1.2 eq), PPTS (10 mol%) and a magnetic stirrer in 1 mL of 2-propanol. The reaction mixture was heated at 80°C for 30 minutes. The crude material was then purified by flash chromatography on silica gel pretreated with 2.5% of triethylamine (eluent ethyl acetate/pentane) to afford the pure *N*-*tert*-butanesulfinylimine.

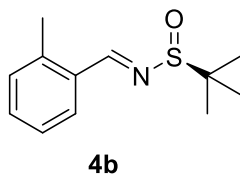
**Figure S2. Microwave temperature profile for 4a.** [grey: internal temperature (control) ; red: external temperature]



**Figure S2**



**(*S,E*)-*N*-Benzylidene-2-methylpropane-2-sulfinamide (4a).** *tert*-butanesulfinamide (1.81 g, 15 mmol) and benzaldehyde dimethylacetal **1a** (2.74 g, 18 mmol) in 2-propanol (only 5 mL for this scale) afforded 2.97 g (95 %) of imine **4a** as a yellow pale oil.  $[\alpha]_D^{20} +117.5$  (*c* 1.0, CHCl<sub>3</sub>) [litt Rs -122]<sup>4</sup>; IR (neat) 2978, 2924, 1605, 1572, 1082, cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 8.55 (s, 1H), 7.82-7.78 (m, 2H), 7.49-7.38 (m, 3H), 1.22 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 126.7, 134.0, 132.4, 129.3, 128.9, 57.7, 22.6; MS (ESI) *m/z* 210,1 [M+H]<sup>+</sup>, 232,0 [M+Na]<sup>+</sup>. HPLC (Daicel chiralpak ID-3, 20% MeOH/supercritical CO<sub>2</sub>, 1.5 mL/min) : *t* = 3.02 (*R<sub>s</sub>*), 3.28 (*S<sub>s</sub>*) ; ee > 99 %.

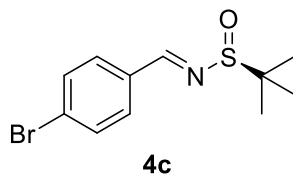


**(*S,E*)-2-Methyl-*N*-(2-methylbenzylidene)propane-2-sulfinamide (4b).** *tert*-butanesulfinamide (121.2 mg, 1 mmol) and 2-méthylbenzaldehyde dimethylacetal **1b** (200 mg, 1.2 mmol) afforded 197 mg (88 %) of imine **4b** as a colourless oil.  $[\alpha]_D^{20} +138.7$  (*c* 1.0, CHCl<sub>3</sub>) [litt +135.2 (*c* 1.15, CHCl<sub>3</sub>)]<sup>5</sup>; IR (neat) 2958, 2924, 1589, 1566, 1080, cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 8.86 (s, 1H), 7.94-7.87 (m, 1H), 7.39 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.33-7.22 (m,

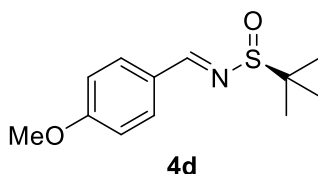
<sup>4</sup> Liu, G.; Cogan, D. A.; Owens, T. D.; Tang, T. P.; Ellman, J. A. *J. Org. Chem.* **1999**, *64*, 1278.

<sup>5</sup> Maji, M. S.; Fröhlich, R.; Studer, A. *Org. Lett.* **2008**, *10*, 1847.

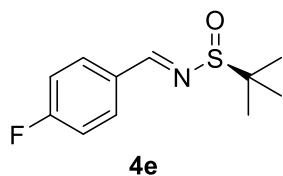
2H), 2.61 (s, 3H), 1.27 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 161.6, 139.4, 132.2, 132.0, 131.4, 129.5, 126.3, 57.4, 22.6, 19.9; MS (ESI)  $m/z$  224.1  $[\text{M}+\text{H}]^+$ , 246.1  $[\text{M}+\text{Na}]^+$ .



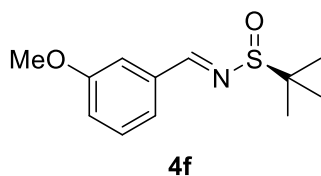
**(*S,E*)-4-Methyl-*N*-(4-bromobenzylidene)propane-2-sulfinamide (4c).** *tert*-butanesulfinamide (121.2 mg, 1 mmol) and 4-bromobenzaldehyde dimethylacetal **1c** (277 mg, 1.2 mmol) afforded 216 mg (75 %) of imine **4c** as a colourless oil.  $[\alpha]_D^{20} +60.4$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (neat) 2959, 2923, 1586, 1561, 1068,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.49 (s, 1H), 7.71-7.62 (m, 2H), 7.60-7.52 (m, 2H), 1.21 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 161.6, 132.9, 132.3, 130.6, 127.2, 27.9, 22.6; MS (ESI)  $m/z$  287.9  $[\text{M}+\text{H}]^+$ , 309.9  $[\text{M}+\text{Na}]^+$  ( $^{79}\text{Br}$ ).



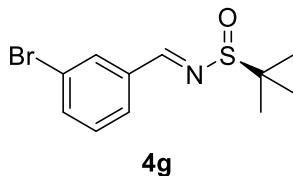
**(*S,E*)-4-Methyl-*N*-(4-methoxybenzylidene)propane-2-sulfinamide (4d).** *tert*-butanesulfinamide (121.2 mg, 1 mmol) and 4-methoxybenzaldehyde dimethylacetal **1d** (219 mg, 1.2 mmol) afforded 213 mg (89 %) of imine **4d** as a white solid. m.p. 90-92 °C [litt. 91-93 °C]<sup>4</sup>;  $[\alpha]_D^{20} +66.8$  ( $c$  1.0,  $\text{CHCl}_3$ ) [litt  $R_s$  -70,2]<sup>4</sup>; IR (neat) 2981, 2958, 1589, 1568, 1078  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.42 (s, 1H), 7.74-7.68 (m, 2H), 6.92-6.84 (m, 2H), 3.76 (s, 3H), 1.16 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 163.3, 161.9, 131.5, 127.5, 114.6, 57.7, 55.7, 22.8; MS (ESI)  $m/z$  240.1  $[\text{M}+\text{H}]^+$ , 262.0  $[\text{M}+\text{Na}]^+$ .



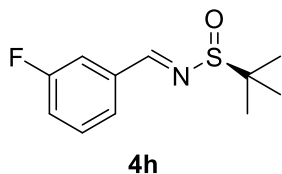
**(*S,E*)-4-Methyl-*N*-(4-fluorobenzylidene)propane-2-sulfinamide (4e).** *tert*-butanesulfinamide (121.2 mg, 1 mmol) and 4-fluorobenzaldehyde dimethylacetal **1e** (204 mg, 1.2 mmol) afforded 213 mg (83 %) of imine **4e** as a colourless oil.  $[\alpha]_D^{20} +113.1$  (*c* 1.0,  $\text{CHCl}_3$ ); IR (neat) 2983, 2961, 1600, 1580, 1078,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.48 (s, 1H), 7.83-7.74 (m, 2H), 7.14-7.03 (m, 2H), 1.18 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 165.2 (d,  $J_{\text{F-C}} = 253$  Hz), 161.3, 131.5 (d,  $J_{\text{F-C}} = 9$  Hz), 130.5 (d,  $J_{\text{F-C}} = 3$  Hz), 116.1 (d,  $J_{\text{F-C}} = 22$  Hz), 57.7, 22.5; MS (ESI)  $m/z$  228.1  $[\text{M}+\text{H}]^+$ , 250.1  $[\text{M}+\text{Na}]^+$ . HRMS (ESI)  $m/z$  Calcd for  $\text{C}_{11}\text{H}_{15}\text{FNOS}$   $[\text{M}+\text{H}]^+$  : 228.0853; found: 228.0853.



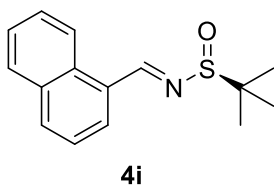
**(*S,E*)-4-Methyl-*N*-(3-methoxybenzylidene)propane-2-sulfinamide (4f).** *tert*-butanesulfinamide (121.2 mg, 1 mmol) and 3-methoxybenzaldehyde dimethylacetal **1f** (219 mg, 1.2 mmol) afforded 213 mg (89 %) of imine **4f** as a colourless oil.  $[\alpha]_D^{20} +65.0$  (*c* 1.0,  $\text{CHCl}_3$ ); IR (neat) 2984, 2959, 1607, 1576, 1078,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.49 (s, 1H), 7.39-7.27 (m, 3H), 7.02-6.97 (m, 1H), 3.78 (s, 3H), 1.20 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 162.6, 160.0, 135.3, 130.0, 122.5, 118.7, 113.2, 57.7, 55.3, 22.6; MS (ESI)  $m/z$  240.1  $[\text{M}+\text{H}]^+$ , 262.0  $[\text{M}+\text{Na}]^+$ . HRMS (ESI)  $m/z$  Calcd for  $\text{C}_{12}\text{H}_{18}\text{NO}_2\text{S}$   $[\text{M}+\text{H}]^+$  : 240.1053; found: 240.1054.



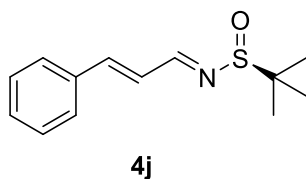
**(*S,E*)-4-Methyl-*N*-(3-bromobenzylidene)propane-2-sulfonamide (4g).** *tert*-butanesulfonamide (121.2 mg, 1 mmol) and 3-bromobenzaldehyde dimethylacetal **1g** (277 mg, 1.2 mmol) afforded 110 mg (38 %) of imine **4g** as a colourless oil.  $[\alpha]_D^{20} +59.5$  (*c* 1.0, CHCl<sub>3</sub>); IR (neat) 2958, 2925, 1597, 1561, 1081, cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 8.50 (s, 1H), 7.99 (t, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.63-7.59 (m, 1H), 7.33 (pseudo t, *J* = 7.7 Hz, 1H), 1.25 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 161.4, 135.9, 135.2, 131.6, 130.5, 128.4, 123.2, 58.0, 22.6; MS (ESI) *m/z* 287.9 [M+H]<sup>+</sup>, 309.9 [M+Na]<sup>+</sup> (<sup>79</sup>Br). HRMS (ESI) *m/z* Calcd for C<sub>11</sub>H<sub>15</sub>BrNOS [M+H]<sup>+</sup> : 288.0052; found: 288.0050.



**(*S,E*)-4-Methyl-*N*-(3-fluorobenzylidene)propane-2-sulfonamide (4h).** *tert*-butanesulfonamide (121.2 mg, 1 mmol) and 3-fluorobenzaldehyde dimethylacetal **1h** (204 mg, 1.2 mmol) afforded 91 mg (40 %) of imine **4h** as a colourless oil.  $[\alpha]_D^{20} +96.8$  (*c* 1.0, CHCl<sub>3</sub>); IR (neat) 2996, 2927, 1605, 1578, 1084, cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 8.47 (s, 1H), 7.52-7.48 (m, 2H), 7.40-7.33 (m, 1H), 7.16-7.08 (m, 1H), 1.19 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 163.1 (d, *J*<sub>F-C</sub> = 246 Hz), 161.6, (d, *J*<sub>F-C</sub> = 3 Hz), 136.2 (d, *J*<sub>F-C</sub> = 7 Hz), 130.7 (d, *J*<sub>F-C</sub> = 8 Hz), 125.8 (d, *J*<sub>F-C</sub> = 3 Hz), 119.5 (d, *J*<sub>F-C</sub> = 22 Hz), 115.1 (d, *J*<sub>F-C</sub> = 22 Hz), 58.0, 22.7; MS (ESI) *m/z* 228.1 [M+H]<sup>+</sup>. HRMS (ESI) *m/z* Calcd for C<sub>11</sub>H<sub>15</sub>FNOS [M+H]<sup>+</sup> : 228.0853; found: 228.0853.



**(*S,E*)-2-Methyl-*N*-(naphthalen-1-ylmethylene)propane-2-sulfinamide (4i).** *tert*-butanesulfinamide (121.2 mg, 1 mmol) and 1-naphthaldehyde dimethylacetal **1i** (243 mg, 1.2 mmol) afforded 215 mg (83 %) of imine **4i** yellow oil.  $[\alpha]_D^{20} +10.0$  (*c* 1.0, CHCl<sub>3</sub>) [litt Rs -4,5 (*c* 1.0, CHCl<sub>3</sub>)]<sup>6</sup>; IR (neat) 2977, 2959, 1596, 1581, 1078, cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 9.12 (s, 1H), 8.97 (d, *J* = 8.6 Hz, 1H), 7.97 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.58 (ddd, *J* = 8.6, 6.9, 1.3 Hz, 1H), 7.49 (dt, *J* = 8.0, 4.2 Hz, 2H), 1.28 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 162.3, 133.7, 133.2, 131.8, 131.1, 129.2, 128.7, 127.9, 126.4, 125.1, 124.2, 57.5, 22.5; MS (ESI) *m/z* 260.1 [M+H]<sup>+</sup>, 282.0 [M+Na]<sup>+</sup>.



**(*S*)-2-Methyl-*N*-((1*E*,2*E*)-3-phenylallylidene)propane-2-sulfinamide (4j).** *tert*-butanesulfinamide (121.2 mg, 1 mmol) and cinnamaldehyde dimethylacetal **1j** (214 mg, 1.2 mmol) afforded 209 mg (89 %) of imine **4j** as a brown solid. m.p. 58-60 °C;  $[\alpha]_D^{20} +287.1$  (*c* 1.0, CHCl<sub>3</sub>) [litt +329 (*c* 1.1, CHCl<sub>3</sub>)]; IR (neat) 2960, 2924, 1579, 1568, 1072., cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) 8.37 (d, *J* = 9.2 Hz, 1H), 7.56-7.47 (m, 2H), 7.42-7.33 (m, 3H), 7.22 (d, *J* = 15.9 Hz, 1H), 7.07 (dd, *J* = 15.9, 9.2 Hz, 1H), 1.23 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) :  $\delta$

<sup>6</sup> Collados, J. F.; Toledano, E.; Guijarro, D.; Yus, M. *J. Org. Chem.* **2012**, 77, 5744.

(ppm) 164.1, 146.7, 135.4, 130.6, 129.3, 128.3, 125.9, 57.9, 22.8; MS (ESI)  $m/z$  236.1  $[M+H]^+$ , 258.0  $[M+Na]^+$ .

**General procedure for the microwave-assisted synthesis of *N*-Sulfonylimidates 7:** A microwave-tube was charged with 4-methylbenzenesulfonamide, trimethylorthoester (1.2 eq), and a magnetic stirrer. A leaky septum filled with 4Å MS was 3 cm above the top of the tube and the reaction mixture was heated at 180°C for 10-30 minutes. The crude material was then purified by flash chromatography on silica gel (eluent ether/pentane) to afford the pure *N*-sulfonylimidate.

**Figure S3. Microwave temperature profile for 7f.** [*grey: internal temperature (control)* ; *red: external temperature*]

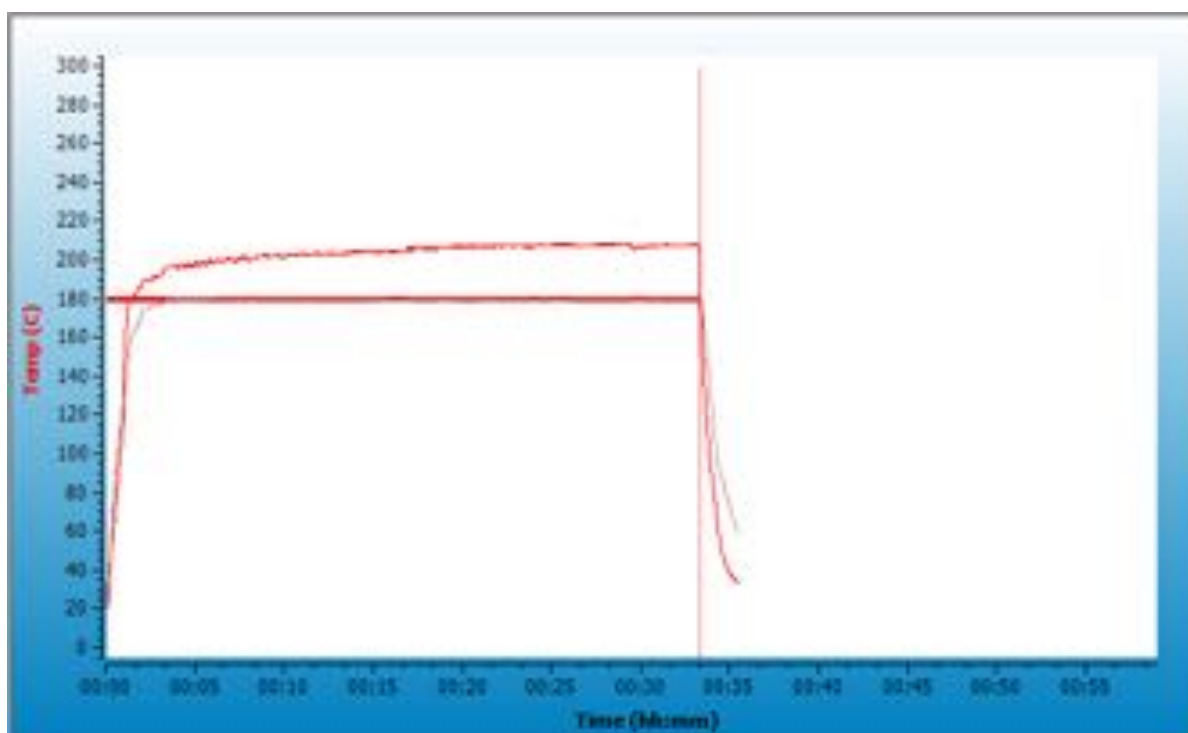
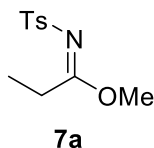
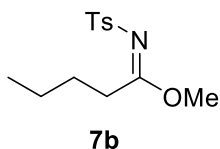


Figure S3



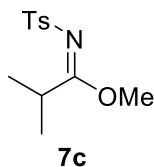
**Methyl (*E*)-*N*-tosylpropionimide (7a).** 4-methylbenzenesulfonamide (5.14 g, 30 mmol) and 1,1,1-trimethoxypropane **6a** (4.61 g, 33 mmol) afforded 6.87 g (95%) of imidate **7a** as a white solid. m.p. 42-44 °C [litt. 46 °C]<sup>7</sup>; IR (neat) 3093, 2952, 1596, 1328, 1148 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 7.84 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.74 (s, 3H), 2.94 (q, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm) 177.8, 143.5, 139.6, 129.7, 127.0, 55.7, 27.8, 21.9, 10.4; MS (ESI) *m/z* 242.1 [M+H]<sup>+</sup>, 264.1 [M+Na]<sup>+</sup>.



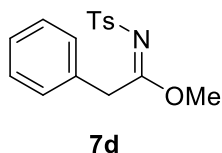
**Methyl (*E*)-*N*-tosylpentanimide (7b).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 1,1,1-trimethoxypentane **6b** (195 mg, 1.2 mmol) afforded 264 mg (98 %) of imidate **7b** as a colourless oil. IR (neat) 3028, 2957, 1597, 1302, 1152 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 7.84 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.73 (s, 3H), 2.94-2.85 (t, *J* = 7.8 Hz, 2H), 2.43 (s, 3H), 1.68 (tt, *J* = 7.8, 6.7 Hz, 2H), 1.31-1.48 (td, *J* = 7.4, 6.7 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm) 177.2, 143.4, 139.7, 129.7, 127.0, 55.6, 33.9, 28.4, 22.8, 21.9, 14.0; MS (ESI) *m/z* 270.1 [M+H]<sup>+</sup>, 292.1 [M+Na]<sup>+</sup>.

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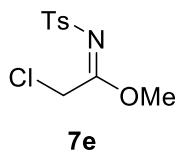
<sup>7</sup> Matsubara, R.; Berthiol, F.; Kobayashi, S. *J. Am. Chem. Soc.* **2008**, *130*, 1804.



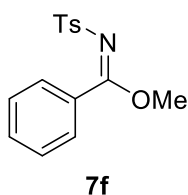
**Methyl (*E*)-*N*-tosylisobutyrimidate (7c).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 1,1,1-trimethoxy-2-methylpropane **6c** (178 mg, 1.2 mmol) afforded 232 mg (91 %) of imidate **7c** as a white solid. m.p. 57-58 °C; IR (neat) 3043, 2981, 1600, 1298, 1148 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 7.84 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.75 (hept, *J* = 6.8 Hz, 1H), 3.72 (s, 3H), 2.43 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm) 180.4, 143.4, 139.8, 129.7, 127.0, 55.7, 33.7, 21.9, 19.8; MS (ESI) *m/z* 256.1 [M+H]<sup>+</sup>, 278.1 [M+Na]<sup>+</sup>.



**Methyl (*E*)-2-phenyl-*N*-tosylacetimidate (7d).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and (2,2,2-trimethoxyethyl)benzene **6d** (235 mg, 1.2 mmol) afforded 297 mg (98 %) of imidate **7d** as a white solid. m.p. 80-82 °C; IR (neat) 3034, 2958, 1592, 1576, 1308, 1147 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 7.84(d, *J* = 8.3, 2H), 7.26-7.37 (m, 7H), 4.25 (s, 2H), 3.71 (s, 3H), 2.43 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm) 174.0, 143.7, 139.4, 133.9, 130.0, 129.7, 129.0, 127.6, 127.1, 56.0, 39.9, 21.9; MS (ESI) *m/z* 304.1 [M+H]<sup>+</sup>, 326.1 [M+Na]<sup>+</sup>.



**Methyl (*E*)-2-chloro-*N*-tosylacetimidate (7e).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and 2-chloro-1,1,1-trimethoxyethane **6e** (186 mg, 1.2 mmol) afforded 241 mg (92 %) of imidate **7e** as a white solid. m.p. 44-45 °C; IR (neat) 3037, 2951, 1615, 1279, 1145 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 7.85 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.69 (s, 2H), 3.83 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm) 168.7, 144.3, 138.3, 129.9, 127.3, 56.8, 38.9, 21.9; MS (ESI) *m/z* 262.0 [M+H]<sup>+</sup>, 284.0 [M+Na]<sup>+</sup>.

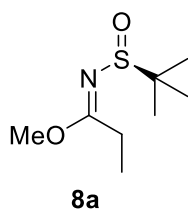
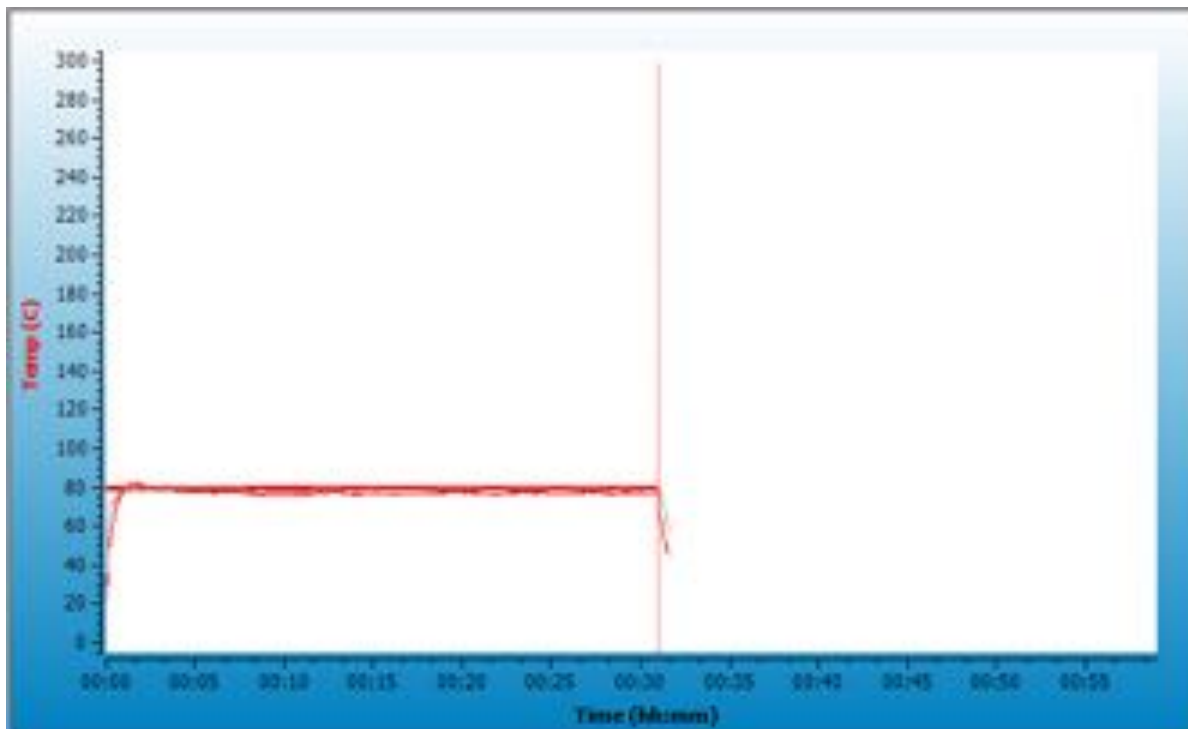


**Methyl (*E*)-*N*-tosylbenzimidate (7f).** 4-methylbenzenesulfonamide (171.2 mg, 1 mmol) and (trimethoxymethyl)benzene **6f** (219 mg, 1.2 mmol) afforded 242 mg (84 %) of imidate **7f** as a white solid. m.p. 113-115 °C; IR (neat) 3069, 2953, 1594, 1569, 1281, 1151 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ (ppm) 7.83-7.79 (m, 2H) 7.81 (d, *J* = 8.3 Hz, 2H), 7.60-7.53 (m, 1H), 7.49-7.42 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ (ppm) 170.5, 143.3, 139.9, 132.8, 131.6, 129.7, 129.6, 128.4, 127.0, 56.4, 21.9; MS (ESI) *m/z* 290.1 [M+H]<sup>+</sup>, 312.1 [M+Na]<sup>+</sup>.

#### General procedure for the microwave-assisted synthesis of *N*-*tert*-butanesulfinylimidates **8**:

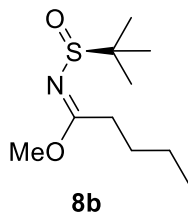
A microwave-tube was charged with *tert*-butanesufinamide, PPTS (10 mol%), trimethyle orthoester (1.1 eq), and a magnetic stirrer. The reaction mixture was heated at 80 °C for 30-60 min. The crude material was then purified by flash chromatography on silica gel (eluent ether/pentane) to afford the pure *N*-*tert*-butanesulfinylimidates.

**Microwave temperature profile for 8a.** [grey: internal temperature (control) ; red: external temperature]

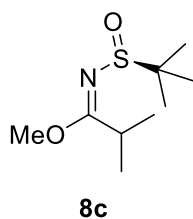


**Methyl (*S,E*)-*N*-(*tert*-butylsulfinyl)propionimide (8a).** *tert*-butanesulfinamide (3.64 g, 30 mmol), PPTS (750 mg, 3 mmol) and 1,1,1-trimethoxypropane **6a** (4.61 g, 33 mmol) afforded 5.31 g (93 %) of imidate **8a** as a colourless oil.  $[\alpha]_D^{20} +125.1$  (*c* 1.0,  $\text{CHCl}_3$ ) [litt *R*<sub>s</sub> -120.3 (*c* 2.9  $\text{CHCl}_3$ )]; IR (neat) 2979, 2947, 1606, 1071,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 3.77 (s, 3H), 2.76-2.62 (m, 2H), 1.21 (s, 9H), 1.20 (t, *J* = 7.3 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) :  $\delta$

(ppm) 178.3, 56.0, 54.4, 26.6, 22.2, 11.1; MS (ESI)  $m/z$  192.1  $[M+H]^+$ . HRMS (ESI)  $m/z$  Calcd for  $C_8H_{18}NO_2S$   $[M+H]^+$  : 192.1053; found: 192.1056.

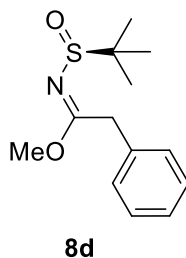


**Methyl (S,E)-N-(tert-butylsulfinyl)pentanimidate (8b).** *tert*-butanesulfinamide (364 mg, 3 mmol), PPTS (75 mg, 0.3 mmol) and 1,1,1-trimethoxypentane **6b** (535 mg, 3.3 mmol) afforded 616 mg (94 %) of imidate **8b** as a colourless oil.  $[\alpha]_D^{20} +81.1$  ( $c$  1.0,  $CHCl_3$ ) [litt -112,3 ( $c$  5.0  $CHCl_3$ )]; IR (neat) 2957, 2866, 1608, 1077,  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ ) :  $\delta$  (ppm) 3.75 (s, 3H), 2.72-2.60 (m, 2H), 1.70-1.55 (m, 2H), 1.41-1.30 (m, 2H), 1.21 (s, 9H), 0.91 (t,  $J$  = 7.4 Hz, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ) :  $\delta$  (ppm) 177.7, 56.0, 54.4, 32.7, 28.8, 22.8, 22.2, 14.0; MS (ESI)  $m/z$  220.1  $[M+H]^+$ , 242.1  $[M+Na]^+$ . HRMS (ESI)  $m/z$  Calcd for  $C_{10}H_{22}NO_2S$   $[M+H]^+$  : 220.1366; found: 220.1368.

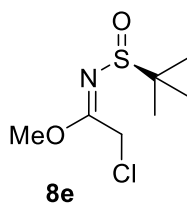


**Methyl (S,E)-N-(tert-butylsulfinyl)isobutyrimidate (8c).** *tert*-butanesulfinamide (364 mg, 3 mmol), PPTS (75 mg, 0.3 mmol) and 1,1,1-trimethoxy-2-methylpropane **6c** (489 mg, 3.3 mmol) afforded 564 mg (92 %) of imidate **8c** as a colourless oil.  $[\alpha]_D^{20} +102.5$  ( $c$  1.0,  $CHCl_3$ ); IR (neat) 2975, 2947, 1602, 1073,  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ ) :  $\delta$  (ppm) 3.76 (s, 3H), 3.42 (sept,  $J$  = 6.8 Hz, 1H), 1.21 (s, 9H), 1.21 (d,  $J$  = 6.8 Hz, 3H), 1.16 (d,  $J$  = 6.8 Hz, 3H);  $^{13}C$  NMR (125

MHz,  $CDCl_3$ ) :  $\delta$  (ppm) 180.9, 55.9, 54.4, 32.4, 22.2, 20.2, 19.8; MS (ESI)  $m/z$  206.1  $[M+H]^+$ , 228.1  $[M+Na]^+$ . HRMS (ESI)  $m/z$  Calcd for  $C_9H_{20}NO_2S$   $[M+H]^+$  : 206.1209; found: 206.1210.



**Methyl (S,E)-N-(tert-butylsulfinyl)-2-phenylacetimidate (8d).** *tert*-butanesulfinamide (364 mg, 3 mmol), PPTS (75 mg, 0.3 mmol) and (2,2,2-trimethoxyethyl)benzene **6d** (648 mg, 3.3 mmol) afforded 742 mg (98 %) of imide **8d** as a colourless oil.  $[\alpha]^{20}_D +142.5$  ( $c$  1.0,  $CHCl_3$ ) [litt Rs -171]<sup>8</sup>; IR (neat) 3029, 2979, 2946, 1611, 1598, 1073,  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ) :  $\delta$  (ppm) 7.35-7.28 (m, 3H), 7.27-7.21 (m, 2H), 4.09 (d,  $J$  = 14.2 Hz, 1H), 3.95 (d,  $J$  = 14.2 Hz, 1H), 3.75 (s, 3H), 1.20 (s, 9H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) :  $\delta$  (ppm) 174.2, 134.8, 129.7, 128.9, 127.4, 56.5, 54.7, 38.9, 22.3; MS (ESI)  $m/z$  254.0  $[M+H]^+$ , 276.0  $[M+Na]^+$ . HPLC (Daicel chiralcel OD-H, 10% *i*PrOH/Hexane, 0.5 mL/min) :  $t$  = 14.31 ( $R_s$ ), 16.64 ( $S_s$ ) ; ee > 99 %.



**Methyl (S,E)-N-(tert-butylsulfinyl)-2-chloroacetimidate (8e).** *tert*-butanesulfinamide (364 mg, 3 mmol), PPTS (75 mg, 0.3 mmol) and 2-chloro-1,1,1-trimethoxyethane **6e** (510 mg, 3.3

<sup>8</sup> Colpaer, F., Mangelinckx S., De Kimpe, N. J. Org. Chem. **2011**, 76, 234.

mmol) afforded 265 mg (40 %) of imidate **8e** as yellow pale oil.  $[\alpha]_D^{20} +263.2$  (*c* 1.0,  $\text{CHCl}_3$ ) [litt  
Rs  $[\alpha]_D^{20} -247.8$  (*c* 1.2,  $\text{CHCl}_3$ )]; IR (neat) 2980, 2948, 1633, 1599, 1075,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500  
MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 4.60 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 3H), 1.24  
(s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) 167.6, 57.4, 55.3, 38.0, 22.4; MS (ESI) *m/z* 212.1  
[*M*+*H*]<sup>+</sup>, 234.0 [*M*+Na]<sup>+</sup>. HRMS (ESI) *m/z* Calcd for  $\text{C}_7\text{H}_{15}\text{NO}_2\text{S}$  [*M*+*H*]<sup>+</sup> : 212.0507; found:  
212.0507.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for **4e**, **4f**, **4g**, **4h**, **8a**, **8b**, **8c**, **8e**, **8f**

