

SUPPLEMENTARY MATERIAL

Solvent-free, microwave assisted conversion of tosylates into iodides.

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1. General procedures

¹H NMR spectra were determined at 300 MHz with a Bruker Avance DPX300 spectrometer or at 400 MHz with a Bruker Avance DRX400 spectrometer (Bruker BioSpin Corp., Billerica, Massachusetts, USA). The chemical shifts (δ , ppm) were referenced to the residual CHCl₃ signal (δ = 7.26 ppm). Each resonance was quoted with chemical shifts measured in parts per million (ppm), multiplicities, coupling constants (J Hz), number of protons, and structural assignments. Multiplicities were denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or b (broad).

¹³C NMR spectra were recorded on 100 MHz with a Bruker Avance DRX400 spectrometer (Bruker BioSpin Corp., Billerica, Massachusetts, USA) in CDCl₃, referenced with the residual CHCl₃ signal (δ 77.16 ppm). Each resonance was quoted with chemical shifts measured in parts per million (ppm) and structural assignment.

Accurate mass determinations were made on an Agilent G1969A LC-TOF system (Agilent Technologies, Santa Clara, California, USA) with reference and mass

correction at 4000 V capillary voltage for electrospray ionisation.

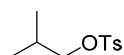
Optical Rotations were measured on a PolAAR 2001 automatic polarimeter (Optical Activity Ltd., Huntingdon, Cambridgeshire, UK) with 1 dm cell in CHCl₃, at a wavelength of 589 nm (sodium D line) at r.t., and were assigned as [α]_D, temperature, concentration *c* (g/100 mL) and solvent.

Analytical TLC was performed on Merck Silica Gel 60 F₂₅₄, and visualised under a 254 nm UV lamp and/or stained using an alkaline KMnO₄ solution. Flash chromatography was performed using Silica Gel 60 (230-400 mesh, no. 9385) from Merck or SiliaFlash[®] P60 (230-400 mesh) from Silicycle.

2. Preparation of tosylates from alcohols

To a solution of alcohol in CH₂Cl₂ (0.1 M) was added TsCl (1.5 eq.), pyridine (3 eq.) and DMAP (0.1 eq.). The reaction was stirred at r.t. for 24 h. Following this, the reaction mixture was washed by HCl solution (1 M) and aqueous NaHCO₃, dried over Na₂SO₄, filtered, and the solvent removed *in vacuo*. The products for primary alcohols were pure enough for the next step without further purification. The tosylate product for secondary alcohol was purified by flash chromatography.

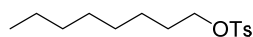
2.1. *i*-Butyl *p*-toluenesulfonate (**1a**)



Tosylate **1a** was prepared as a colourless liquid according to the above general procedure after stirring at r.t. for 24 h in 98 % yield. The ¹H NMR data were in agreement with literature values.²

¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 2 H, ArH), 7.34 (d, *J* = 7.9 Hz, 2 H, ArH), 3.79 (d, *J* = 6.5 Hz, 2 H, CH₂), 2.44 (s, 3 H, CH₃ for Ts), 2.04 – 1.85 (m, 1 H, CH), 0.89 (d, *J* = 6.8 Hz, 6 H, 2 \times CH₃).

2.2. Octyl *p*-toluenesulfonate (**1b**)

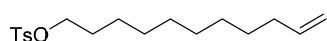


Tosylate **1b** was prepared as a colourless liquid according to the above general

procedure after stirring at r.t. for 12 h in 95 % yield. The ^1H NMR data were in agreement with literature values.³

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 2 H, ArH), 7.34 (d, $J = 8.0$ Hz, 2 H, ArH), 4.02 (t, $J = 6.5$ Hz, 2 H, CH_2OTs), 2.45 (s, 3 H, CH_3 for Ts), 1.69-1.56 (m, 2 H, CH_2), 1.37-1.13 (m, 10 H, $5 \times \text{CH}_2$), 0.87 (t, $J = 7.0$ Hz, 3 H, CH_3).

2.3. Undec-10-en-1-yl *p*-toluenesulfonate (1c)

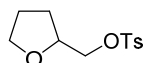


Tosylate **1c** was prepared as a colourless liquid according to the above general procedure after stirring at r.t. for 12 h in 95 % yield. The NMR data were in agreement with literature values.⁴

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 2 H, ArH), 7.39-7.29 (m, 2 H, ArH), 5.86-5.74 (m, 1 H, $\text{CH}=\text{CH}_2$), 5.04-4.87 (m, 2 H, $\text{CH}=\text{CH}_2$), 4.02 (t, $J = 6.5$ Hz, 2 H, CH_2OTs), 2.44 (s, 3 H, CH_3 of Ts), 2.09-1.96 (m, 2 H, $\text{CH}-\text{CH}_2$), 1.70-1.56 (m, 2 H, CH_2), 1.41-1.15 (m, 12 H, $6 \times \text{CH}_2$).

^{13}C NMR (100 MHz, CDCl_3) δ 144.73(ArC), 139.27($\text{CH}=\text{CH}_2$), 133.45(ArC), 129.92(ArC), 128.01(ArC), 114.28($\text{CH}=\text{CH}_2$), 70.81(CH_2OTs), 33.89($\text{CH}-\text{CH}_2$); 29.43, 29.16, 29.02, 28.94 and 25.44(CH_2), 21.74 (CH_3 of Ts).

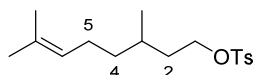
2.4. Tetrahydrofuran-2-ylmethyl *p*-toluenesulfonate (1d)



Tosylate **1d** was prepared as a colourless liquid according to the above general procedure after stirring at r.t. for 24 h in 93 % yield. The ^1H NMR data were in agreement with literature values.⁵

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.3$ Hz, 2 H, ArH), 7.34 (d, $J = 8.0$ Hz, 2 H, ArH), 4.13-4.04 (m, 1 H, CH_2OTs), 4.04-3.94 (m, 2 H, CH_2OTs and CH), 3.83-3.68 (m, 2 H, CH_2O), 2.45 (s, 3 H, CH_3), 2.03-1.92 (m, 1 H, CH_2CH), 1.91-1.82 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.72-1.61 (m, 1 H, CH_2CH).

2.5. 3,7-Dimethyloct-6-en-1-yl *p*-toluenesulfonate (Citronellyl tosylate) (1e)

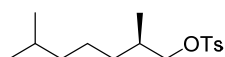


Tosylate **1e** was prepared as a colourless liquid according to the above general procedure after stirring at r.t. for 24 h in 93 % yield. The NMR data were in agreement with literature values.⁶

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2 H, ArH), 7.34 (d, *J* = 8.0 Hz, 2 H, ArH), 5.06-4.99 (m, 1 H, C=CH), 4.13-4.00 (m, 2 H, CH₂OTs), 2.45 (s, 3 H, CH₃ for Ts), 2.04-1.04 (m, 7 H, CH and 3 × CH₂), 1.67 and 1.57 (2 s, 6 H, 2 × CCH₃), 0.82 (d, *J* = 6.5 Hz, 3 H, CHCH₃).

¹³C NMR (100 MHz, CDCl₃) δ 144.76 (ArC), 133.44 (ArC), 131.61 (CCH₃), 129.94 (ArC), 128.02 (ArC), 124.46 (C=CH), 69.19 (CH₂OTs), 36.85 (C2), 35.81 (C4), 29.03 (CH), 25.82 (CCH₃), 25.40 (C5), 21.76 (CH₃ of Ts), 19.19 (CHCH₃), 17.76 (CCH₃).

2.6. (R)-2,6-Dimethylheptyl 4-methylbenzenesulfonate (1f)



Tosylate **1f** was prepared as a colourless liquid according to the above general procedure after stirring at r.t. for 24 h in 95 % yield.

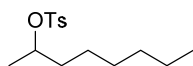
¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2 H, ArH), 7.34 (d, *J* = 8.0 Hz, 2 H, ArH), 3.88 (dd, *J* = 9.3, 5.7 Hz, 1 H, CH₂OTs), 3.81 (dd, *J* = 9.3, 6.5 Hz, 1 H, CH₂OTs), 2.44 (s, 3 H, CH₃ for Ts), 1.83-1.70 (m, 1 H, CH), 1.53-1.41 (m, 1 H, CH(CH₃)₂), 1.34-1.01 (m, 6 H, 3 × CH₂), 0.88 (d, *J* = 6.7 Hz, 3 H, CHCH₃), 0.83 (d, *J* = 6.6 Hz, 6 H, CH(CH₃)₂).

¹³C NMR (100 MHz, CDCl₃) δ 144.72 (ArC), 133.39 (ArC), 129.92 (ArC), 128.04 (ArC), 75.28 (CH₂O), 39.09 (CH₂), 33.02 (CH₂), 32.95 (CH), 27.98 (CH), 24.44 (CH₂), 22.73 (CH₃), 22.65 (CH₃), 21.76 (CH₃), 16.59 (CH₃).

HRMS calculated for C₁₆H₂₆SO₃Na⁺ *m/z* = 321.1495, found 321.1498.

Specific Rotation [α]_D²² -3.7 ° (*c* 1.2, CHCl₃).

2.7. Octan-2-yl 4-methylbenzenesulfonate (**1g**)



Tosylate **1g** was prepared as a colourless liquid according to the above general procedure after stirring at r.t. for 48 h in 90 % yield after flash chromatography purification (hexane/Et₂O 4:1). The ¹H NMR data were in agreement with literature values.⁷

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2 H, ArH), 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 4.60 (dq, *J* = 12.5, 6.3 Hz, 1 H, CH), 2.44 (s, 3 H, CH₃ of Ts), 1.65-1.54 (m, 1 H, CH₂), 1.52-1.41 (m, 1 H, CH₂), 1.26 (d, *J* = 6.3 Hz, 3 H, CHCH₃), 1.24-1.10 (m, 8 H, 4 × CH₂), 0.85 (t, *J* = 7.0 Hz, 3 H, CH₃).

3. Conversion of tosylates to iodides under microwave irradiation

General procedure for conversion tosylates to iodides under microwave irradiation: NaI (3 eq.) was added to neat primary tosylate in a 10 mL microwave vial, which was sealed and heated under microwave irradiation in a CEM DiscoverTM microwave reactor, and subject to 100-150 W irradiations for 0.5-2 h. Following reaction, CH₂Cl₂ was added to the mixture, and the pale yellow solid (remaining NaI and sodium *p*-toluenesulfonate) was removed by filtration. The solvent was removed *in vacuo* yielding the crude product, providing, for primary iodides, pure products in most cases, according to ¹H NMR spectroscopy. In some circumstances, trace amounts of tosylates were detectable in the product, and were removed by purification through Pasteur pipette column.

3.1. *i*-BuI (**2a**)



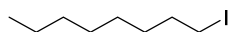
Iodide **2a** was prepared from tosylates **1a** (92 mg, 0.4 mmol) according to the above general procedure by microwave irradiation subject to 100 W for 30 min, with the maximum temperature set as 120 °C and the maximum pressure set as 30 PSI. The crude product was obtained as colourless liquid, and ¹H NMR of the product showed >99% in purity.

¹H NMR (400 MHz, CDCl₃) δ 3.14 (d, *J* = 5.9 Hz, 2 H, CH₂I), 1.78-1.65 (m, 1 H, CH),

1.01 (d, $J = 6.6$ Hz, 6 H, $2 \times \text{CH}_3$).

The ^1H NMR data were in agreement with literature values.²

3.2. *n*-C₈H₁₇I (**2b**)



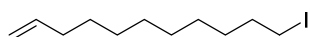
Iodide **2b** was prepared from tosylates **1b** (85 mg, 0.3 mmol) according to the above general procedure by microwave irradiation subject to 120 W for 45 min, with the maximum temperature set as 120 °C and the maximum pressure set as 30 PSI. The crude product was obtained as colourless liquid. The crude product was purified to remove <2% of the starting material by a Pasteur pipette column eluting with hexane, and the yield for the purified iodide **2b** was 95%.

^1H NMR (400 MHz, CDCl₃) δ 3.19 (t, $J = 7.1$ Hz, 2 H, CH_2I), 1.88 – 1.75 (m, 2 H, $\text{CH}_2\text{CH}_2\text{I}$), 1.45-1.23 (m, 10 H, $5 \times \text{CH}_2$), 0.88 (t, $J = 6.9$ Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, CDCl₃) δ 33.74 (CH_2), 31.91 (CH_2), 30.67 (CH_2), 29.24 (CH_2), 28.66 (CH_2), 22.77 (CH_2CH_3), 14.22 (CH_3), 7.45 (CH_2I).

The NMR data were in agreement with literature values.⁸

3.3. Undec-10-en-1-yl iodide (**2c**)



Iodide **2c** was prepared from tosylates **1c** (65 mg, 0.2 mmol) according to the above general procedure by microwave irradiation subject to 150 W for 30 min, with the maximum temperature set as 140 °C and the maximum pressure set as 30 PSI. The crude product was obtained as colourless liquid. The crude product was purified to remove <2% of the starting material by a Pasteur pipette column eluting with hexane, and the yield for the purified iodide **2c** was 95%.

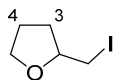
^1H NMR (400 MHz, CDCl₃) δ 5.92 – 5.73 (m, 1 H, $\text{CH}=\text{CH}_2$), 5.14 – 4.88 (m, 2 H, $\text{CH}=\text{CH}_2$), 3.19 (t, $J = 7.1$ Hz, 2 H, CH_2I), 2.10-1.96 (m, 2 H, $\text{CH}-\text{CH}_2$), 1.97 – 1.73 (m, 2 H, $\text{CH}_2\text{CH}_2\text{I}$), 1.58 – 1.14 (m, 12 H, $6 \times \text{CH}_2$).

^{13}C NMR (100 MHz, CDCl₃) δ 139.34 ($\text{CH}_2=\text{CH}$), 114.29 ($\text{CH}_2=\text{CH}$), 33.94 (CH_2), 33.72 (CH_2), 30.65 (CH_2), 29.52 (CH_2), 29.50 (CH_2), 29.22 (CH_2), 29.06 (CH_2), 28.67

(CH₂), 7.43 (CH₂I).

The NMR were in agreement with literature values.⁹

3.4. Tetrahydrofuran-2-ylmethyl iodide (**2d**)



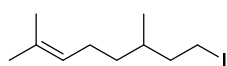
Iodide **2d** was prepared from tosylates **1d** (50 mg, 0.2 mmol) according to the above general procedure by microwave irradiation subject to 100 W for 90 min, with the maximum temperature set as 115 °C and the maximum pressure set as 30 PSI. The crude product was obtained as colourless liquid. The crude product was purified to remove <3% of the starting material by a Pasteur pipette column eluting with hexane, and the yield for the purified iodide **2d** was 94%.

¹H NMR (400 MHz, CDCl₃) δ 4.05 – 3.91 (m, 2 H, CH₂O), 3.88-3.76 (m, 1 H, CH), 3.30 – 3.15 (m, 2 H, CH₂I), 2.18-2.06 (m, 1 H, H3a), 2.04-1.83 (m, 2 H, H4), 1.74-1.61 (m, 1 H, H3b).

¹³C NMR (100 MHz, CDCl₃) δ 76.84 (CH), 69.08 (CH₂O), 32.05 (CH₂), 26.24 (CH₂), 10.54 (CH₂I).

The NMR were in agreement with literature values.¹⁰

3.5. Citronellyl iodide (**2e**)



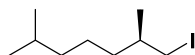
Iodide **2e** was prepared from tosylates **1e** (90 mg, 0.3 mmol) according to the above general procedure by microwave irradiation subject to 120 W for 45 min, with the maximum temperature set as 120 °C and the maximum pressure set as 30 PSI. The crude product was obtained as colourless liquid. The crude product was purified to remove < 2 % of the starting material by a Pasteur pipette column eluting with hexane, and the yield for the purified iodide **2e** was 98%.

¹H NMR (400 MHz, CDCl₃) δ 5.13-5.05 (m, 1 H, C=CH), 3.32-3.08 (m, 2 H, CH₂I), 2.10-1.79 (m, 3 H, CH₂I and CH₂), 1.73 – 1.51 (m, 8 H, 2 × CH₃ and CH₂), 1.41-1.08 (m, 2 H, CH₂CH), 0.89 (d, J = 6.6 Hz, 3 H, CHCH₃).

^{13}C NMR (100 MHz, CDCl_3) δ 124.61 (C=CH), 41.07 (CH_2), 36.47 (CH_2), 33.73 (CHCH_3), 25.86 (CH_3), 25.46 (CH_2), 18.80 (CH_3), 17.83 (CH_3), 5.29 (CH_2I).

The NMR data were in agreement with literature values.¹¹

3.6. (*R*)-1-Iodo-2,6-dimethylheptane (2f)

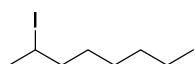


Iodide **2f** was prepared from tosylates **1f** (60 mg, 0.2 mmol) according to the above general procedure by microwave irradiation subject to 110 W for 45 min, with the maximum temperature set as 120 °C and the maximum pressure set as 30 PSI. The crude product was obtained as colourless liquid. The crude product was purified to remove < 3 % of the starting material by a Pasteur pipette column eluting with hexane, and the yield for the purified iodide **2f** was 94 %.

^1H NMR (400 MHz, CDCl_3) δ 3.23 (dd, $J = 9.6, 4.7$ Hz, 1 H, CH_2I), 3.15 (dd, $J = 9.6, 6.1$ Hz, 1 H, CH_2I), 1.61-1.11 (m, 8 H, $2 \times \text{CH}$ and $3 \times \text{CH}_2$), 0.98 (d, $J = 6.5$ Hz, 3 H, CH_3), 0.91-0.83 (m, 6 H, $2 \times \text{CH}_3$).

The ^1H NMR was in agreement with the literature values.¹²

3.7. 2-Iodoctane (2g)



Iodide **2g** was prepared from tosylates **1g** (60 mg, 0.2 mmol) according to the above general procedure by microwave irradiation subject to 100 W for 60 min, with the maximum temperature set as 115 °C and the maximum pressure set as 30 PSI. The crude product was obtained as colourless liquid. The crude product was purified to remove the remaining starting material by a Pasteur pipette column eluting with hexane and Et_2O .

^1H NMR (400 MHz, CDCl_3) δ 4.25-4.04 (m, 1 H, CH), 1.92 (d, $J = 6.8$ Hz, 3 H, CH_3CH), 1.88-1.55 (m, 2 H, CHCH_2), 1.50-1.24 (m, 8 H, $4 \times \text{CH}_2$), 0.87-0.90 (m, 3 H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 43.10 (CH_2CH), 31.81 (CH_2), 30.93 (CH), 29.81 (CH_2), 29.07 (CHCH_3), 28.56 (CH_2), 22.72 (CH_2), 14.19 (CH_2CH_3).

The NMR data were in agreement with literature values.¹³

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