Supporting Information

A Facile Route to Hydrophilic Ionic Liquids

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Contents

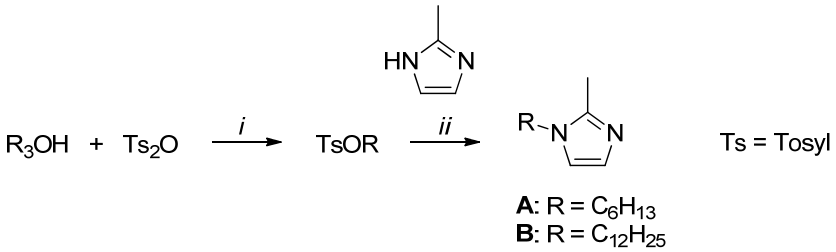
1.1 Instrumental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-500 (500 MHz), Varian VXR-400 (400 MHz) and a Bruker AC-300 (300 MHz) spectrometer. Spectra were recorded in $CDCl_3$, CD_3OD or DMSO-d_6. Chemical shifts are reported in ppm referenced against the residual solvent signal (CHD_2OD at 3.31 ppm and DMSO-d_5 at 2.5 ppm) at or internal references for $CDCl_3$ (TMS, 0.0 ppm). HRMS (ESI) mass measurements were performed on a JEOL Accu TOF-CS instrument in the positive mode using acetonitrile as solvent. Measurements in negative mode were carried out, however due to the nature of the counter-ions, only for compound **6g** a signal was observed.

1.2 Synthetic procedure of ionic presursors 1-3

1.2.1 Synthesis of ionic precursors for 2a and 3a (Scheme S1)

Scheme S1: Synthesis of 1-alkyl-2-methylimidazole precursors.



Key: (*i*) Pyridine, DCM, 0°C, overnight; (*ii*) ethanol, DMF, Cs_2CO_3, reflux, over night

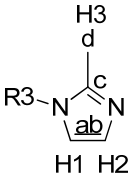
General procedure for the synthesis of A and B: A mixture of p-toluensulfonic anhydride (20 mmol), pyridine (50mmol) and the alcohol (40mmol) was stirred in DCM (50 mL) at 0 °C and slowly heated to room temperature. After one night reaction, the DCM solution was precipitated in 200 mL pentane and filtered to remove the solids. The crude reaction mixture was reprecipitated twice and purified on a silica column using (eluent: diethyl ether/pentane (1:9). The resulting product contains traces of the p-toluenesulfonic anhydride. Yield: hexyl tosylate 95%; dodecyl tosylate 91%. The appropriate alkyl tosylate (20 mmol), 2-methylimidazol (60 mmol), Cs_2CO_3 (60 mmol) and DMF (2 mL) were refluxed in ethanol (50 mL). After one night reaction the crude mixture was filtered, the solvent was evaporated and the crude product was purified by a silica column (eluent: methanol/chloroform (1:9). Yield: 33% compound **A**, 21% compound **B**.

Characterization:

A

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 6.92 (d, 1 H, *J* = 1.51 Hz, H_1), 6.82 (d, 1 H, *J* = 1.51 Hz, H_2), 3.83 (t, 2 H, *J* = 7.29 Hz, H_4), 2,39 (s, 3 H, H_3), 1,77-1.67 (m, 2 H, H_5), 1,36-1.29 (m, 6 H, $H_{6, 7, 8}$), 0.91 (t, 3 H, J= 6.51 Hz, H_9).

Figure S1: NMR assignment



A: R3 = $CH_2CH_2CH_2CH_2CH_2CH_3$
H4 H5 H6 H7 H8 H9
e f g h i j

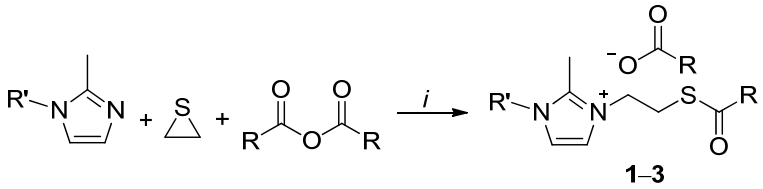
B: R3 = $CH_2CH_2(CH_2)_7CH_2CH_2CH_3$
H10 H11 H12 H13 H14 H15
k l m-s t u v

B

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 6.90 (d, 1 H, *J* = 1.33 Hz, H_1), 6.80 (d, 1 H, *J* = 1.33 Hz, H_2), 3.80 (t, 2 H, *J* = 7.21 Hz, H_{10}), 2.37 (s, 3 H, H_3), 1.72 (dd, 2 H, *J* = 7.29, 14.36 Hz, H_{11}), 1.34-1.23 (m, 18 H, H_{12-14}), 0.88 (t, 3 H, *J* = 6.89 Hz, H_{15}).

1.2.2 Synthesis of ionic precursors 1a-d (Scheme S2)

Scheme S2. Synthesis of precursors 1–3.



	anion	Im-substituent
1a	R = CH_3	R' = CH_3
1b	R = CH_2CH_3	R' = CH_3
1c	R = $(CH_2)_3CH_3$	R' = CH_3
1d	R = $C(CH_3)_3$	R' = CH_3
1e	R = CF_3	R' = CH_3
2a	R = CH_3	R' = $(CH_2)_5CH_3$
3a	R = CH_3	R' = $(CH_2)_{11}CH_3$

Key (*i*): General conditions: neat, room temperature, 7−14 days. Further conditions and yields are detailed in **Table S1**.

Table S1. Reaction conditions[a] and yields[b] for the precursor synthesis (see Scheme 2).

Entry	R	R'	Molar reactant ratios			Product	Time / days	Yield / %
			imidazole	thiirane	anhydride			
1	CH_3	CH_3	1	1	5	**1a**	1	10
2	CH_3	CH_3	1	1	5	**1a**	7	58
3[c]	CH_3	CH_3	1	1	5	**1a**	7	0
4[d]	CH_3	CH_3	1	1	5	**1a**	1	35
5[d]	CH_3	CH_3	1	1	5	**1a**	7	38
6	CH_3	CH_3	1	2	5	**1a**	7	64
7	CH_3	CH_3	1	2	5	**1a**	14	81
8	CH_2CH_3	CH_3	1	1	5	**1b**	14	60
9	$(CH_2)_3CH_3$	CH_3	1	1	5	**1c**	14	56
10	$C(CH_3)_3$	CH_3	1	1	5	**1d**	14	30[e]
11	CF_3	CH_3	1	1	5	**1e**	14	n.d.[f]
12	CH_3	$(CH_2)_5CH_3$	1	1	5	**2a**	14	77
13	CH_3	$(CH_2)_{11}CH_3$	1	1	5	**3a**	14	48

[a]Reaction conditions: neat (no solvent) typically 1 mL imidazole scale, room temperature, Ar atmosphere; [b]Yields determined from ^{1}H NMR spectra of the reaction mixture; [c]Addition of 0.5 mL acetic acid; [d]Reaction at *T* = 35 °C; [e]Product precipitated from the reaction mixture as a white solid. [f]n.d. = not determined.

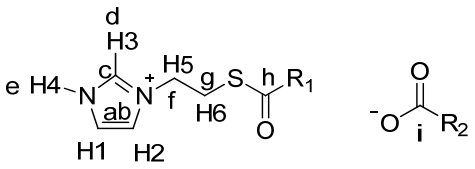
General procedure for the synthesis of 1a-d: A mixture of 1,2-dimethylimidazole (10 mmol), thiirane and the anhydride (50 mmol) were stirred without solvent at the indicated conditions (**Table S1**). The crude product was dissolved in dichloromethane (10 mL) and precipitated in diethyl ether (200 mL). The mixture was centrifuged and the ether layer was removed. The product was reprecipitated twice and subsequently dried in vacuo. Yields are given in **Table S1**.

Characterization:

1a

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.47 (d, 1 H, *J* = 2.1 Hz, H_1), 7.34 (d, 1 H, *J* = 2.0 Hz, H_2), 4.40 (t, 2 H, *J* = 6.9 Hz, H_5), 3.88 (s, 3 H, H_4), 3.28 (t, 2 H, *J* = 6.9 Hz, H_6), 2.78 (s, 3 H, H_3), 2.33 (s, 3 H, H_7), 1.97 (s, 6 H, H_{15}). ^{13}C-NMR, 75 MHz, $CDCl_3$: 195.29 (h), 175.78 (i), 144.58 (c), 122.45 (a), 121.84 (b), 47.90 (f), 35.46 (e), 30.50 (g), 28.23 (j), 22.39 (s), 9.90 (d). HRMS for **$C_9H_{15}N_2OS$**: Calcd: 199.09051. Found: 199.09157.

Figure S2: NMR assignment



	H7	H8	H9	H10	H11	H12	H13	H14	
R_1 =	j	k	l	m	n	o	p	q	r
	CH_3,	CH_2CH_3,		$CH_2CH_2CH_2CH_3$,				$C(CH_3)_3$	
R_2 =	H15	H16	H17	H18	H19	H20	H21	H22	
	s	t	u	v	w	x	y	z	aa

1b

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.64 (d, 1 H, *J* = 2.0 Hz, H_1), 7.55 (d, 1 H, *J* = 2.0 Hz, H_2), 4.41 (t, 2 H, *J* = 6.9 Hz, H_5), 3.91 (s, 3 H, H_4), 3.29 (t, 2 H, *J* = 6.9 Hz, H_6), 2.78 (s, 3 H, H_3), 2.57 (q, 2 H, *J* = 7.5 Hz, H_8), 2.23 (q, 4 H, *J* = 7.6 Hz, H_{16}), 1.14 (t, 3 H, *J* = 7.5 Hz, H_9), 1.06 (t, 6 H, *J* = 7.6 Hz, H_{17}). ^{13}C-NMR, 75 MHz, $CDCl_3$: 199.47 (h), 178.80 (i), 144.10 (c), 122.46 (a), 121.80 (b), 47.56 (f), 37.07 (k), 35.15 (e), 29.95 (g), 29.25 (t), 9.95 (d), 9.55 (l), 9.19 (u). HRMS for **$C_{10}H_{17}N_2OS$**: Calcd: 213.10616. Found: 213.10746.

1c

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.61 (d, 1 H, J=2.1 Hz, H_1), 7.52 (d, 1 H, J=2.1 Hz, H_2), 4.31 (t, 2 H, J=6.9 Hz, H_5), 3.28 (t ,2 H, J=6.9 Hz, H_6), 3.26 (s, 3 H, H_4), 2.77 (s, 3 H, H_3), 2.54 (t, 2 H, J=7.4 Hz, H_{10}), 2.21 (t, 4 H, J=7.9 Hz, H_{18}), 1.61-1.57 (m, 2 H, H_{11}), 1.58-1.52 (m, 4 H, H_{19}), 1.37-1.31 (m, 2 H, H_{12}), 1.35-1.29 (m, 4 H, H_{20}), 0.91 (t, 3 H, J=7.4 Hz, H_{13}), 0.89 (t, 6 H, J=7.5 Hz, H_{21}). ^{13}C-NMR, 75 MHz, $CDCl_3$, δ ppm: 198.94 (h), 178.30 (i), 144.29 (c), 122.63 (a), 121.97 (b), 47.74 (f), 43.58 (m), 36.18 (e), 36.16 (v), 28.03 (g), 28.00 (n), 27.33 (w), 22.52 (o), 21.89 (x), 13.84 (p), 13.71 (y), 9.75 (d). HRMS for **$C_{12}H_{21}N_2OS$**: Calcd: 241.13746. Found: 241.13846.

1d

^{1}H-NMR, 400 MHz, CD_3OD, δ ppm: 7.48 (d, 1 H, *J* = 2.1 Hz, H_1), 7.44 (d, 1 H, *J* = 2.1 Hz, H_2), 4.39 (t, 2 H, *J* = 6.9 Hz, H_5), 3.80 (s, 3 H, H_4), 3.28 (t, 2 H, *J* = 6.9 Hz, H_6), 2.71 (s, 3 H, H_3), 1.18 (s, 9 H, H_{14}), 1.14 (s, 18 H, H_{22}). ^{13}C-NMR, 75 MHz, $CDCl_3$: 205.57 (h), 180.18 (i), 145.25 (c), 122.48 (a), 122.00 (b), 47.23 (f), 46.35 (q), 38.43 (z), 35.19 (e), 28.28 (g), 27.62 (r),), 27.21 (aa), 9.55 (d). HRMS for **$C_{12}H_{21}N_2OS$**: Calcd: 241.13746. Found: 241.13756.

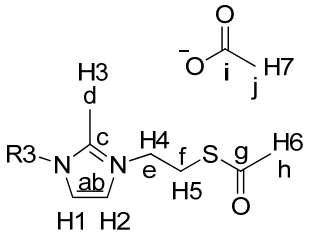
General procedure for the synthesis of 2a and 3a: A mixture of imidazole **A** or **B** (10 mmol), thiirane (10 mmol) and acetic anhydride (50 mmol) was stirred for 14 days at 25 ^{0}C. The crude product was dissolved in dichloromethane (10 mL) and precipitated in diethyl ether (200 mL). The mixture was centrifuged and the ether layer was removed. The product was reprecipitated twice and subsequently dried in vacuo. Yields: **2a** 77% of a brown liquid, **3a** 48% of a yellow liquid.

Characterization

2a

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.70 (d, 1 H, *J* = 2.1 Hz, H_1), 7.28 (d, 1 H, *J* = 2.0 Hz, H_2), 4.48 (t, 2 H, *J* = 6.64 Hz, H_4), 4.09 (t, 2 H, *J* = 6.64 Hz, H_8), 3.30 (t, 2 H, *J* = 6.64 Hz, H_5), 2,77 (s, 3 H, H_3), 2.29 (s, 3 H, H_6), 1.96 (s, 3 H, H_7), 1.80 (dd, 2 H, *J* = 5.48, 8.88 Hz, H_9), 1.32 (m, 6 H, $H_{10, 11, 12}$), 0.89 (t, 3 H, *J* = 6.9 Hz, H_{13}). ^{13}C-NMR, 75 MHz, $CDCl_3$: 195.23 (g), 176.66 (i), 143.76 (c), 122.50 (a), 120.85 (b), 48.40 (e), 47.68 (k), 31.04 (n), 30.17 (f), 29.39 (l), 28.18 (h), 25.73 (m), 23.16 (o), 22.26 (j), 13.79 (p), 9.60 (d). HRMS for **$C_{14}H_{25}N_2OS$**: Calcd: 269.17213. Found: 269.17069

Figure S3: NMR assignment



H8 H9 H10 H11 H12 H13

2a: R3 = $CH_2CH_2CH_2CH_2CH_2CH_3$

k l m n o p

H16–

H14 H15 H22 H23 H24 H25

3a: R3 = $CH_2CH_2(CH_2)_7CH_2CH_2CH_3$

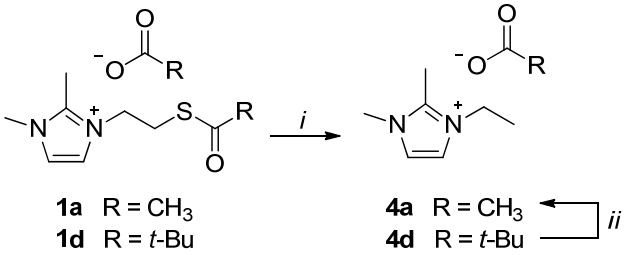
q r s-y z aa ab

3a

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.47 (d, 1 H, *J* = 2.1 Hz, H_1), 7.23 (d, 1 H, *J* = 2.17Hz, H_2), 4.30 (t, 2 H, *J* = 6.64 Hz, H_4), 3.98 (t, 2 H, *J* = 6.64 Hz, H_{14}), 3.16 (t, 2 H, *J* = 6.64 Hz, H_5), 2.63 (s, 3 H, H_3), 2.16 (s,3 H, H_6), 1.83 (s, 6 H, H_7), 1,66 (t, 2 H, *J* = 4.51 Hz, H_{15}), 1.16 (m, 18 H, $H_{16\text{-}24}$), 0.74 (t, 3 H, *J* = 6.88 Hz, H_{25}). ^{13}C-NMR, 75 MHz, $CDCl_3$: 195.02 (g), 175.52 (i), 143.65 (c), 122.51 (a), 120.88 (b), 48.53 (e), 47.73 (q), 31.66 (z), 30.20 (f), 29.45(r), 29.23-28.92 (t-y), 28.10 (h), 26.10 (s), 22.62 (aa), 22.45 (j), 13.90 (ab), 9.66 (d). HRMS for **$C_{20}H_{37}N_2OS$**: Calcd: 353.26266. Found: 353.26360.

1.3 Hydrogenolysis: Synthesis of ILs 4d and 4a (Scheme S3)

Scheme S3. Thioester hydrogenolysis towards conventional with carboxylate counter ions.



Key: (*i*) H_2, RCO_2H-activated Raney Ni, EtO H, room temperature, 1–16 h,; (*ii*) AcOH (excess) and precipitation.

Synthesis of 1,2-dimethyl-3-ethyl-imidazolium pivalate (4d): Prior to hydrogenolysis, the Raney nickel catalyst was treated: 1 gram of the catalyst was stirred for 15 min in a 0.1 M aqueous pivalic acid solution (100 mL). The catalyst was filtered off and washed with MilliQ water (100 mL, 5×) and ethanol (200 mL 5×). Compound **1d** (0.5 mmol) was dissolved in ethanol (50 mL) and a large excess of treated Raney nickel catalyst was added. The reaction mixture was stirred overnight under hydrogen atmosphere. The catalyst was filtered off, washed with ethanol (20 mL, 3×) and the filtrate was evaporated to dryness. The crude product was dissolved in methanol (10 mL) and precipitated in diethyl ether (200 mL). The product was reprecipitated twice and subsequently dried in vacuo, yielding **4d** as a white solid in 92% yield.

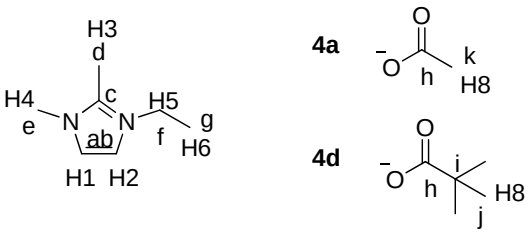
Synthesis of 1,2-dimethyl-3-ethyl-imidazolium acetate (4a): Compound **4d** (0.4 mmol) was dissolved in methanol (10 mL). A large excess of acetic acid (8 mmol) was added. After 10 minutes stirring, the solvent was evaporated. This step was repeated twice. The final compound was dried under vacuum overnight, yielding **4a** in 98% yield as a transparent colorless liquid.

Characterization

4d

^{1}H-NMR, 400 MHz, CD_3OD, δ ppm: 7.51 (d, 1 H, *J* = 2.1 Hz, H_1), 7.45 (d, 1 H, *J* = 2.1 Hz, H_2), 4.17 (q, 2 H, *J* = 7.3 Hz, H_5), 3.79 (s, 3 H, H_4), 2.59 (s, 3 H, H_3), 1.43 (t, 3 H, *J* = 7.3 Hz, H_6), 1.15 (s, 9 H, H_7). ^{13}C-NMR, 75 MHz, methanol-d_4: 186.13 (h), 144.16 (c), 122.17 (a), 120.03 (b), 43.06 (i), 39.43 (f), 33.78 (e), 27.47 (j), 13.67 (g), 7.87 (d). HRMS for **$C_7H_{13}N_2$**: Calcd: 125.10787. Found: 125.10985.

Figure S4: NMR assignment

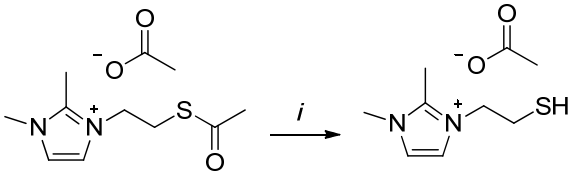


4a

^{1}H-NMR, 400 MHz, CD_3OD, δ ppm: 7.50 (d, 1 H, *J* = 2.1 Hz, H_1), 7.44 (d, 1 H, *J* = 2.1 Hz, H_2), 4.16 (q, 2 H, *J* =7.3 Hz, H_5), 3.79 (s, 3 H, H_4), 2.59 (s, 3 H, H_3), 1,9 (s, 3 H, H8), 1.43 (t, 3 H, *J* = 7.3Hz, H_6), ^{13}C-NMR, 75 MHz, metanol-d_4: 176.40 (h), 144.13 (c), 122.16 (a), 120.02 (b), 43.06 (f), 33.92 (e), 23.86 (k), 13.54 (g), 7.92 (d). HRMS for **$C_7H_{13}N_2$**: Calcd: 125.10787. Found: 125.10942.

1.4 Ammonolysis: Synthesis of TSIL 5a (Scheme S4)

Scheme S4. Precursor hydrolysis.



1a **5a**

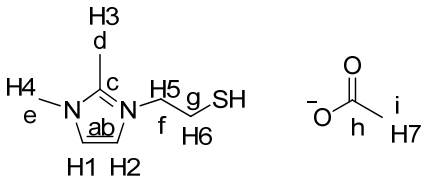
Key: (*i*) aq. NH_3, room temperature, 30 min, quantitative.

Synthesis of 1,2-dimethyl-3-ethyl-imidazolium pivalate (5a): Compound **1a** (10 mmol) was dissolved in a 2M ammonia (100 mL) and stirred in an inert atmosphere. After 30 minutes the solution was evaporated to dryness. Additional water was removed by the addition and evaporation of toluene (200 mL, 3×) and the product was subsequently dried in vacuo to yield a brown liquid in a >98 % conversion.

5a

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.49 (d, 1 H, *J* = 2.1Hz, H_1), 7.46 (d, 1 H, *J* = 2.1Hz, H_2), 4.45 (t, 2 H, *J* = 6.5 Hz, H_5), 3.78 (s, 3 H, H_4), 3.15 (t, 2 H, *J* = 6.5 Hz, H_6), 2.60 (s, 3 H, H_3), 1.85 (s, 6 H, H_8). ^{13}C-NMR, 75 MHz, DMSO-d_6: 176.70 (h), 144.93 (c), 122.39 (a), 121.09 (b), 49,98 (f), 35.71 (e), 34.04 (g), 21.35 (i), 8.38 (d). HRMS for **$C_7H_{13}N_2S$**: Calcd: 157.07994. Found: 157.08164.

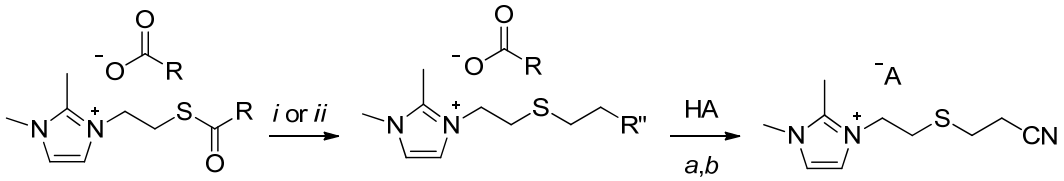
Figure S5: NMR assignment



5a

1.5 Michael addition procedure and ion exchange: synthesis of thioethers 6-8 (Scheme S5)

Scheme S5



1a R = CH_3
1d R = *t*-Bu

6a,d R'' = CN
7a R'' = CO_2CH_3
8a R'' = COEt

6b A^- = $CH_3CH_2CO_2^-$
6c A^- = $CH_3(CH_2)_2CO_2^-$
6e A^- = $CHF_2CO_2^-$
6f A^- = $CF_3CO_2^-$
6g A^- = BF_4^-

Key: (*i*) NEt_3, aq. MeO H, Michael acceptor (acrylonitrile, ethyl acrylate or penten-3-one), room temperature, 5 days; (*ii*) NEt_3, EtOH/H_2O (4:1), acrylonitrile, reflux, 5 d; (a) HA (excess), MeO H, room temperature, 5 min; (b) evaporation of the volatiles (and optionally a precipitation procedure).

General procedure for the synthesis of compound 6a, 6b, 6c, 6e, 6f and 6g (route *i*): A mixture of **1a** (1 mmol) triethylamine (10 mmol) and acrylonitrile (5 mmol) in ethanol (100 mL) was stirred for 5 days at room temperature and afterwards dried in vacuo. Analogous to **1a**, the crude product was dissolved in dichloromethane (10 mL) and precipitated in diethyl ether (200 mL) three times. The final product was dried in vacuo at 50 °C to yield a brown liquid in 90% yield. **Ion exchange (route *a* and *b*):** To a stirred solution of **5a** (10 mmol) in methanol (10 mL), an excess of the corresponded acid was added and stirred for 10 minutes. After addition, the reaction mixture was dried in vacuo to remove the acetic acid. This step was repeated 2 times. The crude product was precipitated three times from dichloromethane (10 mL) into diethyl ether (200 mL), and extensively dried in vacuo at 35 °C to yield a brown liquid in ~90% yield (**6b**: 92%; **6c**: 86%; **6e**: 97%; **6f**: 87% and **6g**: 92%).
Synthesis of compound 6d (route *ii*): A mixture of **1d** (1 mmol) triethylamine (10 mmol) and acrylonitrile (5 mmol) in a mixture ethanol/H_2O (8:2) (100 mL) was stirred under reflux for 7 and afterwards and dried in vacuo. The crude product was dissolved in dichloromethane (10 mL) and precipitated in diethyl ether (200 mL). The product was reprecipitated twice. The final product was dried in vacuo at 50 °C to yield a slightly yellow liquid in 87% yield.

Characterization:

6a

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.92 (d, 1 H, *J* = 2.1 Hz, H_1), 7.44 (d, 1 H, *J* = 2.1 Hz, H_2), 4.49 (t, 2 H, *J* = 6.5 Hz, H_5), 3.86 (s, 3 H, H_4), 3.17 (t, 2 H, J= 6.5 Hz, H_6), 2.84 (t, 2 H, *J* = 6.4 Hz, H_7), 2.72 (t, 2 H, *J* = 6.5 Hz, H_8), 2.63 (s, 3 H, H_3), 1.94 (s, 6 H, H_9). ^{13}C-NMR, 77 MHz, $CDCl_3$, δ ppm: 176.15 (k), 144.42 (c), 122.70 (a), 122.29 (b), 118.77 (j), 48.10 (f), 35.45 (e), 31.62 (g), 27.79 (h), 23.60 (l), 18.99 (i), 10.23 (d). HRMS for **$C_{10}H_{16}N_3S$**: Calcd: 210.10649. Found: 210.10688.

6b

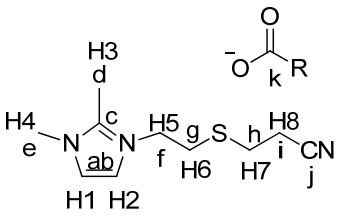
^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 8.25 (d, 1 H, *J* = 2.1 Hz, H_1), 7.29 (d, 1 H, *J* = 2.0 Hz, H_2), 4.57 (t, 2 H, *J* = 6.3 Hz, H_5), 3.86 (s, 3 H, H_4), 3.10 (t, 2 H, *J* = 6.3 Hz, H_6), 2.88-2.80 (m, 2 H, H_7), 2.80-2.71 (m, 2 H, H_8), 2.68 (s, 3 H, H_3), 2.24 (q, 2 H, *J* = 7.6 Hz, H_{10}), 1.09 (t, 3 H, *J* = 7.6 Hz, H_{11}). ^{13}C-NMR, 75 MHz, $CDCl_3$,

δ ppm: 178.83 (k), 145.38 (c), 122.96 (a), 121.40 (b), 120.76 (j), 47.73 (f), 35.21 (e), 31.65 (g), 31.25 (m), 27.37 (h), 18.85 (i), 10.72 (n), 9.67 (d). HRMS for **$C_{10}H_{16}N_3S$**: Calcd: 210.10649. Found: 210.10685.

6c

^{1}H-NMR, 400 MHz, CD_3OD, δ ppm: 7.55 (d, 1 H, *J* = 2.1 Hz, H_1), 7.49 (d, 1 H, *J* = 2.0 Hz, H_2), 4.37(t, 2 H, *J* = 6.3 Hz, H_5), 3.81 (s, 3 H, H_4), 3.07 (t, 2 H, *J* = 6.3 Hz, H_6), 2.86-2.78 (m, 2 H, H_7), 2.78-2.70 (m, 2 H, H_8), 2.65 (s, 3 H, H_3), 2.17 (t, 2 H, *J* = 7.6 Hz, H_{12}), 1,56-1.109 (m, 4 H, H_{13}, H_{14}) 0.91 (t, 3 H, *J* = 7.6 Hz, H_{15}). ^{13}C-NMR, 75 MHz, DMSO-d_6, δ ppm: 178.38 (k), 145.38 (c), 122.96 (a), 121.40 (b), 120.76 (j), 47.73 (f), 35.21 (e), 31.65 (g), 31.25 (o), 27.37 (h), 26.31 (p), 20.29 (q), 18.85 (i), 10.72 (r), 9.67 (d). HRMS for **$C_{10}H_{16}N_3S$**: Calcd: 210.10649. Found: 210.10692.

Figure S5: NMR assignment



H9 H10 H11 H12 H13 H14 H15

R = CH_3, CH_2CH_3, $CH_2CH_2CH_2CH_3$

l m n o p q r

H16 H17

R = $C(CH_3)_3$, CHF_2, CF_3

s t u v

6d

^{1}H-NMR, 400 MHz, DMSO-d_6, δ ppm: 7.58 (d, 1 H, *J* = 2.1 Hz, H_1), 7.50 (d, 1 H, *J* = 2.1 Hz, H_2), 4.38 (t, 2 H, *J* = 6.5 Hz, H_5), 3.82 (s, 3 H, H_4), 3.07 (t, 2 H, *J* = 6.6 Hz, H_6), 2.86-2.78 (m, 2 H, H_7), 2.78-2.72 (m, 2 H, H_8), 2.65 (s, 3 H, H_3), 1.11 (s, 9 H, H_{16}). ^{13}C-NMR, 75 MHz, DMSO-d_6, δ ppm: 180.19 (k), 145.00 (c), 122.67 (a), 121.63 (b), 120.10 (j), 47.14 (f), 35.08 (s), 30.66 (e), 30.01 (g), 26.64 (h), 25.75 (t), 18.42 (i), 9.71 (d). HRMS for **$C_{10}H_{16}N_3S$**: Calcd: 210.10649. Found: 210.10694 .

6e

^{1}H-NMR, 500 MHz, CD_3OD, δ ppm: 7.60 (d, 1 H, *J* = 2.0 Hz, H_1), 7.52 (d, 1 H, *J* = 2.0 Hz, H_2), 5.91 (t, 2 H, J= 54.6 Hz, H_{17}), 4.41 (t, 2 H, *J* =6.5 Hz, H_5), 3.85 (s, 3 H, H_4), 3.11 (t , 2 H, *J* =6.5 Hz, H_6), 2.86 (t, 2 H, *J* = 6.1 Hz, H_7), 2.79 (t, 2 H, *J* = 6.1 Hz, H_8), 2.69 (s, 3 H, H_3).^{13}C-NMR, 75 MHz, CD_3OD, δ ppm: 169.91 (k), 146.55 (c), 128.64 (u), 123.89 (a), 122.57 (b), 120.21 (j), 48.83 (f), 35.66 (e), 32.56 (g), 28.65 (h), 19.43 (i), 10.00 (d), HRMS for **$C_{10}H_{16}N_3S$**: Calcd: 210.10649. Found: 210.10730.

6f

^{1}H-NMR, 500 MHz, CD_3OD, δ ppm: 7.58 (d, 1 H, *J* = 2.1 Hz, H_1), 7.50 (d, 1 H, *J* = 2.1 Hz, H_2), 4.39 (t, 2 H, J= 6.5 Hz, H_5), 3.83 (s, 3 H, H_4), 3.10 (t ,2 H, *J* = 6.6 Hz, H_6),), 2.84 (t, 2 H, *J* = 6.5 Hz, H_7), 2.76 (t, 2 H, *J* = 6.5 Hz, H_8), 2.67 (s, 3 H, H_3). ^{13}C-NMR, 75 MHz, CD_3OD, δ ppm: 162.14 (k), 146.58 (c), 123.91 (a), 122.59 (b), 120.16 (j), 115.78 (v), 48.86 (f), 35.66 (e), 32.61 (g), 28.69 (h), 19.45 (i), 10.00 (d). HRMS for **$C_{10}H_{16}N_3S$**: Calcd: 210.10649. Found: 210.10747.

6g

^{1}H-NMR, 500 MHz, DMSO-d_6, δ ppm: 7.42 (d, 1 H, *J* = 2.1 Hz, H_1), 7.35 (d, 1 H, *J* = 2.1 Hz, H_2), 4.36 (t, 2 H, *J* = 6.5 Hz, H_5), 3.77 (s, 3 H, H_4), 3.08 (t , 2 H, *J* = 6.5 Hz, H_6), 2.83 (t, 2 H, *J* = 6.6 Hz, H_7), 2.79 (t, 2 H, *J* = 6.6 Hz, H_8), 2.62 (s, 3 H, H_3). ^{13}C-NMR, 125 MHz, DMSO-d_6, δ ppm: 145.43 (c), 123.02 (a), 121.46 (b), 120.86 (j), 47.79 (f), 35.27 (e), 31.66 (g), 27.42 (h), 18.89 (i), 9.70 (d). HRMS for **$C_{10}H_{16}N_3S$**: Calcd: 210.10649. Found: 210.10689.

General procedure for the synthesis of compounds 7a and 8a: A mixture of **1a** (1 mmol) triethylamine (10 mmol) and (5 mmol) of ethyl acrylate (for **7a**) or petene-3-one (for **8a**), in ethanol (100 mL) was stirred for 5 days at room temperature and afterwards dried in vacuo. Analogous to **1a**, the crude product was dissolved in dichloromethane (10 mL) and precipitated in diethyl ether (200

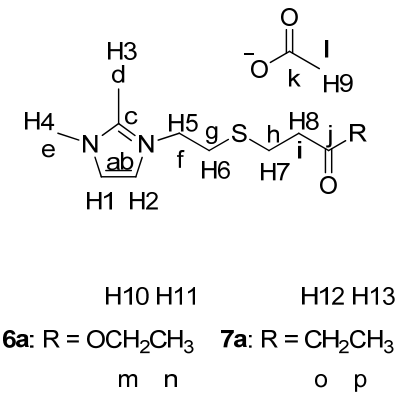
mL) three times. The final product was dried in vacuo at 50 °C. The conversions are quantitative and the isolated yields are given below. The products were obtained as brown liquids.

Characterization:

7a

Yield: 92%. ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.59 (d, 1 H, *J* = 2.1 Hz, H_1), 7.44 (d, 1 H, *J* = 2.1Hz, H_2), 4.33 (t, 2 H, *J* = 6.4 Hz, H_5), 4.01 (q, 2 H, *J* = 7.1 H_{10}), 3.78 (s, 3 H, H_4), 2.90 (t, 2 H, *J* = 6.3 Hz, H_6), 2.64 (dd, 2 H, *J* = 3.41, 10.39 Hz, H_7), 2.46 (t, 2 H, *J* = 6.8 Hz, H_8), 2.61 (s, 3 H, H_3), 1.8 (s, 6 H, H_9), 1.20 (dd,3 H, *J* = (4.7, 9.6) Hz, H_{11}). ^{13}C-NMR, 75 MHz, $CDCl_3$, δ ppm: 176.80 (k), 171.91 (j), 144.34 (c), 122.76 (a), 121.25 (b), 61.3 (m), 47.58 (f), 35.41 (i), 34.45 (e), 31.82 (g), 26.84 (h), 23.45 (l), 14.04 (n), 9.69 (d). HRMS for **$C_{12}H_{21}N_2O_2S$**: Calcd: 257.13237. Found: 257.13188.

Figure S5: NMR assignment



8a

Yield: 89%. ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.51 (d, 1 H, *J* = 2.1 Hz, H_1), 7.37 (d, 1 H, *J* = 2.0 Hz, H_2), 4.23 (t, 2 H, *J* = 6.4 Hz, H_5), 3.71 (s, 3 H, H_4), 2.79 (t, 2 H, *J* = 6.4 Hz, H_6), 2.53 (s, 3 H, H_3), 2.56-2.46 (m, 4 H, H_7 and H_8), 2.24 (q, 2 H, *J* = 7.31 Hz, H_{12}), 1.8(s, 6 H, H_9), 0.82 (t, 3 H, *J* =, H_{13}). ^{13}C-NMR, 75 MHz, $CDCl_3$, δ ppm: 198.17 (j), 176.94 (k), 144.18(c), 122.62 (a), 122.29(b), 47.84(f), 35.45 (o), 34.39 (e), 32.01 (h), 26.95 (i), 23.84 (l), 14.00 (p), 9.91 (d). HRMS for **$C_{12}H_{21}N_2OS$**: Calcd: 241.13746. Found: 241.13843.