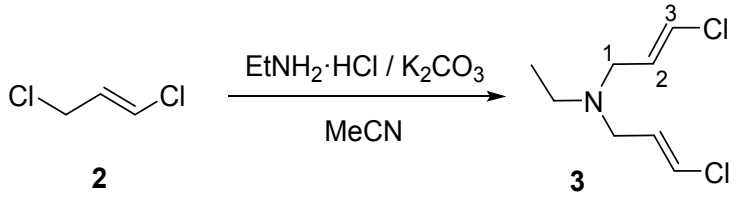
# SUPPLEMENTARY INFORMATION

## 1. Synthesis of Alverine (1)

The synthesis of alverine (1) was carried out according to the procedure previously described by Shakhmaev et al.[1]

### 1a. Synthesis of (2*E*)-3-chloro-*N*-[(2*E*)-3-chloroprop-2-en-1-yl]-*N*-ethylprop-2-en-1-amine (3)




**2** **3**

(*E*)-1,3-dichloropropene (**2**) (0.46 mL, 4.5 mmol), $K_2CO_3$ (1.050 g, 7.5 mmol) and $EtNH_2 \cdot HCl$ (0.193 g, 2.3 mmol) were dissolved in anhydrous MeCN (5.6 mL). The reaction mixture was allowed to stir at 100 °C for 16 h until the end of the reaction, as indicated by t.l.c. ($CH_2Cl_2$/MeOH 5%). The suspension was cooled down to room temperature, filtered and the solvent was removed under reduced pressure. The product was isolated by distillation by heating under high vacuum (2 x 10-1Pa) to obtain (2*E*)-3-chloro-*N*-[(2*E*)-3-chloroprop-2-en-1-yl]-*N*-ethylprop-2-en-1-amine (**3**) as a yellowish liquid (0.40 g, 90%).

**NMR-$^1$H (400 MHz, $\delta_H$, $CDCl_3$):** δ= 6.16 (d, $J_{H-H}$=13.3 Hz, 2H, H-3), 5.98 (m, 2H, H-2), 3.14 (d, $J_{H-H}$=6.8 Hz, 4H, H-1), 2.56 (q, $J_{H-H}$=7.0 Hz , 2H, $CH_3C\underline{H}_2N$), 1.13 (t, $J_{H-H}$= 7.1 Hz, 3H, $C\underline{H}_3CH_2N$).

**NMR-$^{13}$C (100.6 MHz, $\delta_C$, $CDCl_3$):** δ= 130.5 (C-2), 120.0 (C-3), 52.8 (C-1), 46.9 ($CH_3\underline{C}H_2N$), 12.0 ($\underline{C}H_3CH_2N$).

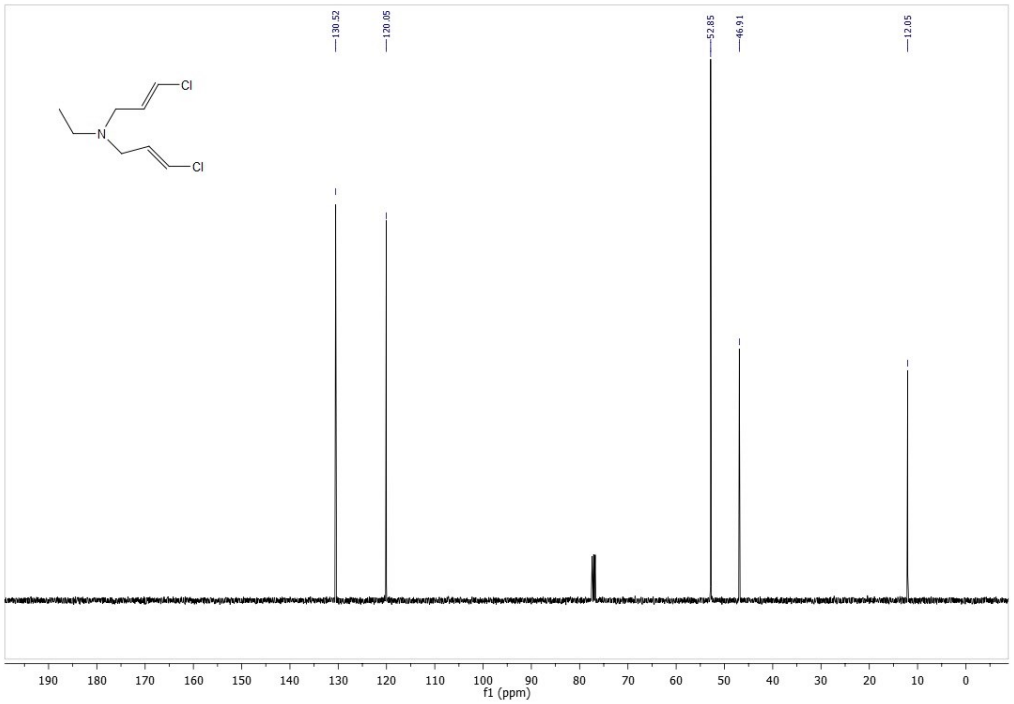



**Figure S1.** NMR-$^{13}$C of (2*E*)-3-chloro-*N*-[(2*E*)-3-chloroprop-2-en-1-yl]*N*-ethylprop-2-en-1-amine (**3**)

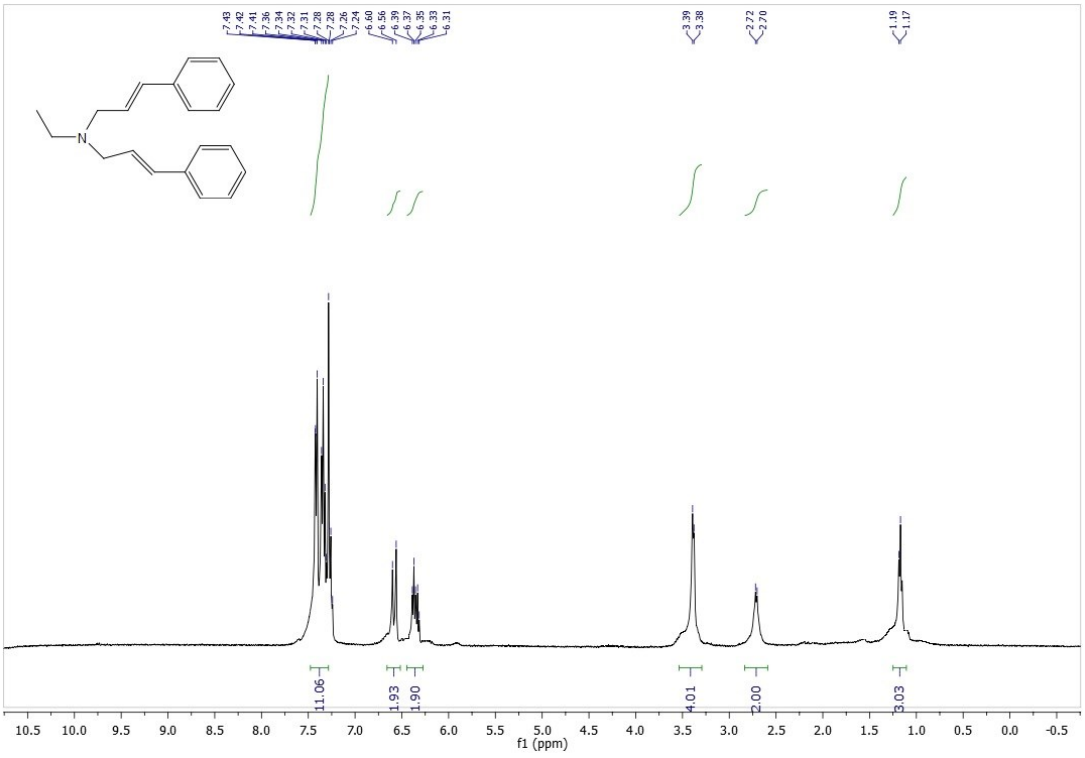
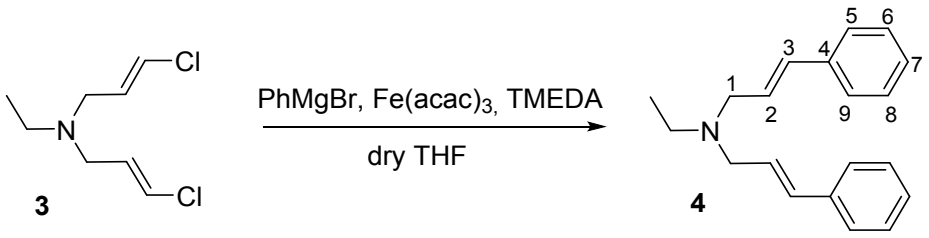



**Figure S2.** NMR-$^{1}$H of (2*E*)-*N*-ethyl-3-phenyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]prop-2-en-1-amine (**4**)

**1b. Synthesis of (2*E*)-*N*-ethyl-3-phenyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]-prop-2-en-1-amine (4)**




$Fe(acac)_3$ (0.012 g, 0.03 mmol) was dissolved in dry THF (1 mL) and added to a solution of **3** (0.306 g, 1.55 mmol) at 0 °C and in an inert atmosphere. Next was added TMEDA (0.03 mL, 0.15 mmol) and PhMgBr (2 mL, 3.2 mmol). The mixture was stirred at room temperature for 2 h until the end of the reaction, as indicated by t.l.c. (Hex/AcOEt 2:1). Water was then added (2mL) and the crude was extracted with AcOEt (3 x 7 mL). The organic phases were collected and washed with saturated aqueous solution of NaCl, dried with anhydrous $Na_2SO_4$ and concentrated via rotary evaporation. Finally, the product was isolated by column chromatography using as eluent Hex/AcOEt (2:1) obtaining a yellow liquid (**4**, 0.24 g, 55%).

**RMN-$^1$H (400 MHz, $\delta_H$, $CDCl_3$):** δ= 7.43-7.26 (m, 10H, H-Ar), 6.58 (d, $J_{H-H}$=15.8 Hz, 2H, H-3), 6.35 (m, 2H, H-2), 3.38 (d, $J_{H-H}$=6.8 Hz, 4H, H-1), 2.71 (m, 2H, $CH_3C\underline{H}_2N$), 1.17 (t, $J_{H-H}$=7.1 Hz, 3H, $C\underline{H}_3CH_2N$).

**RMN-$^{13}$C (100.6 MHz, $\delta_C$, $CDCl_3$):** δ= 137.0 (C-4), 133.1 (C-3), 128.6 (C-5,6,8,9), 127.5 (C-2), 126.3 (C-7), 55.7 (C-1), 47.2 ($CH_3\underline{C}H_2N$), 11.7 ($\underline{C}H_3CH_2N$).

**Figure S3.** NMR-$^{1}$H of (2*E*)-*N*-ethyl-3-phenyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]prop-2-en-1-amine (**4**)

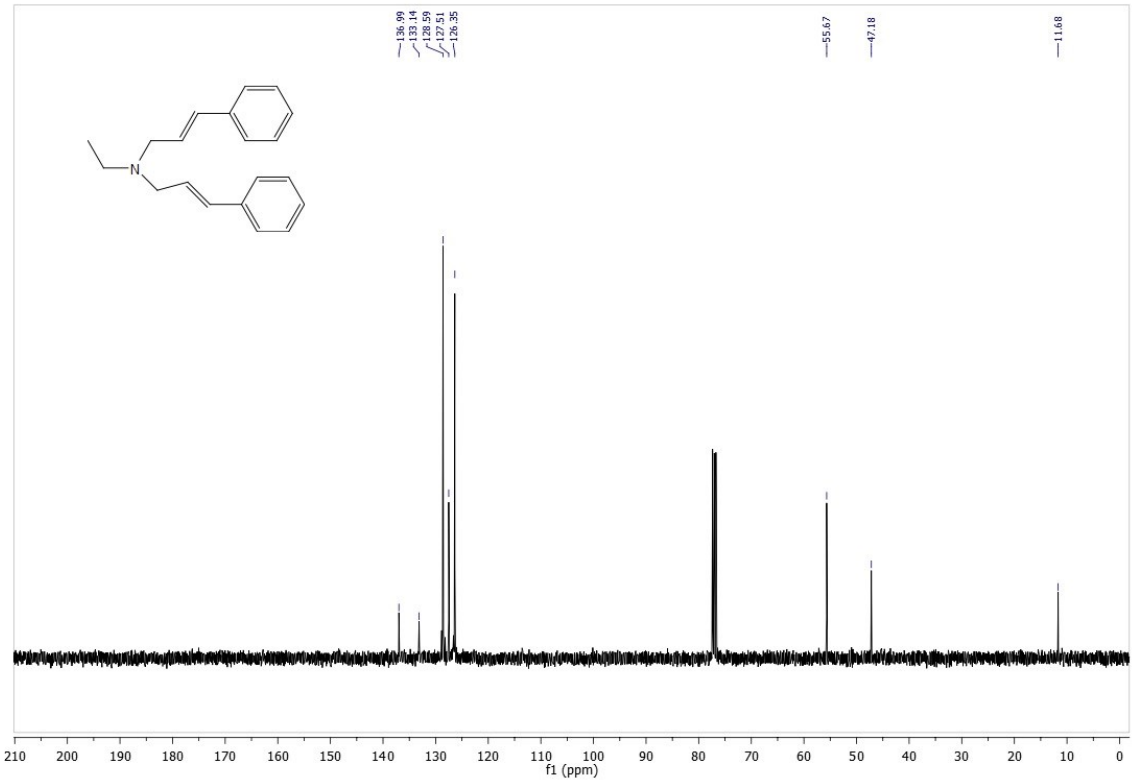
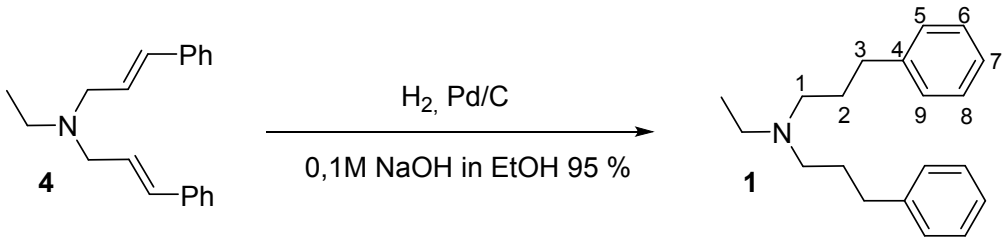



**Figure S4.** NMR-$^{13}$C of (2*E*)-*N*-ethyl-3-phenyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]prop-2-en-1-amine (**4**)

**1c. Synthesis of Alverine (*N*-ethyl-3-phenyl-*N*-(3-phenylpropyl)-propan-1-amine, 1)**




A solution of NaOH 0.1M in EtOH 95% (1.8 mL) was added to Pd/C 10% (5 mg) and **4** (0.1 g, 0.36 mmol). This suspension was stirred under an atmosphere of $H_2$ for 5 h until the end of the reaction, as indicated by t.l.c. (Hex/AcOEt 2:1). The mixture was filtered, concentrated and purified by column chromatography using as eluent Hex/AcOEt (9:1). The product was isolated as a yellow liquid (**1**, 0.124 g, 72%).

**RMN-$^1$H (400 MHz, $\delta_H$, $CDCl_3$):** δ= 7.34-7.21 (m, 10H, PhH), 2.67 (t, $J_{H-H}$=7.6 Hz, 4H, H-3), 2.61-2.50 (m, 6H, $CH_3C\underline{H}_2N$, H-1), 1.82 (m, 4H, H-2), 1.05 (t, $J_{H-H}$=7.1 Hz, 3H, $C\underline{H}_3CH_2N$).

**RMN-$^{13}$C (100.6 MHz, $\delta_C$, $CDCl_3$):** δ= 142.4 (C-4), 128.4 (C-6,8), 128.3 (C-5,9), 125.7 (C-7), 53.0 (C-1), 47.5 ($CH_3\underline{C}H_2N$), 33.8 (C-3), 28.8 (C-2), 11.7 ($\underline{C}H_3CH_2N$).

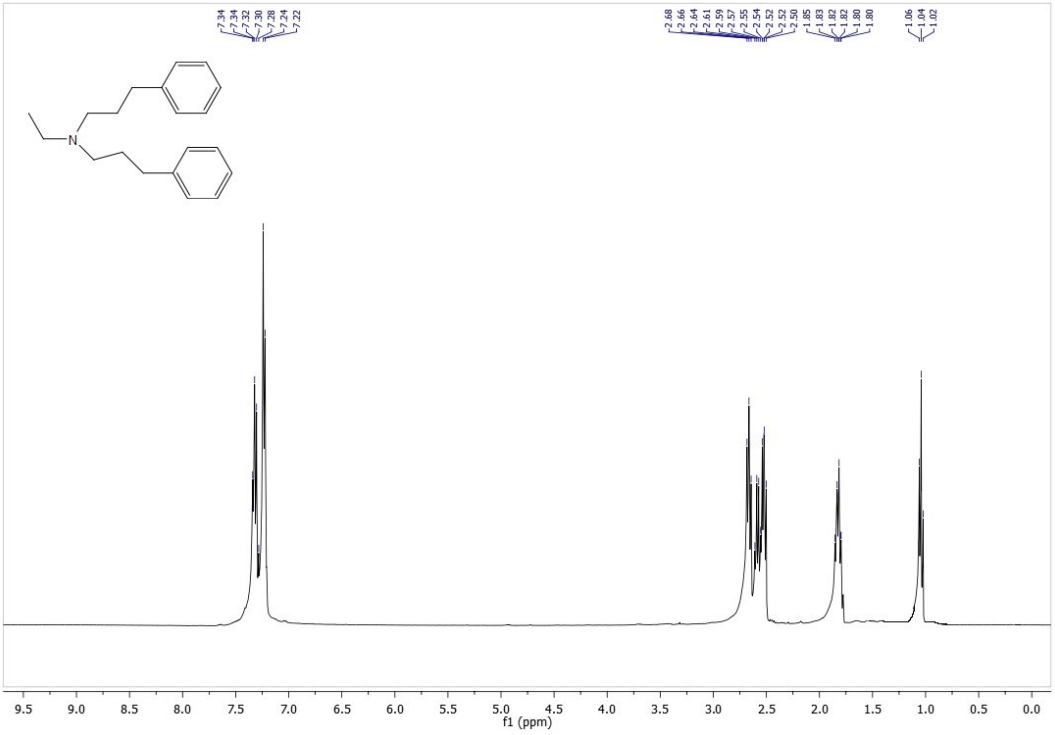



**Figure S5.** NMR-$^1$H of alverine (**1**)

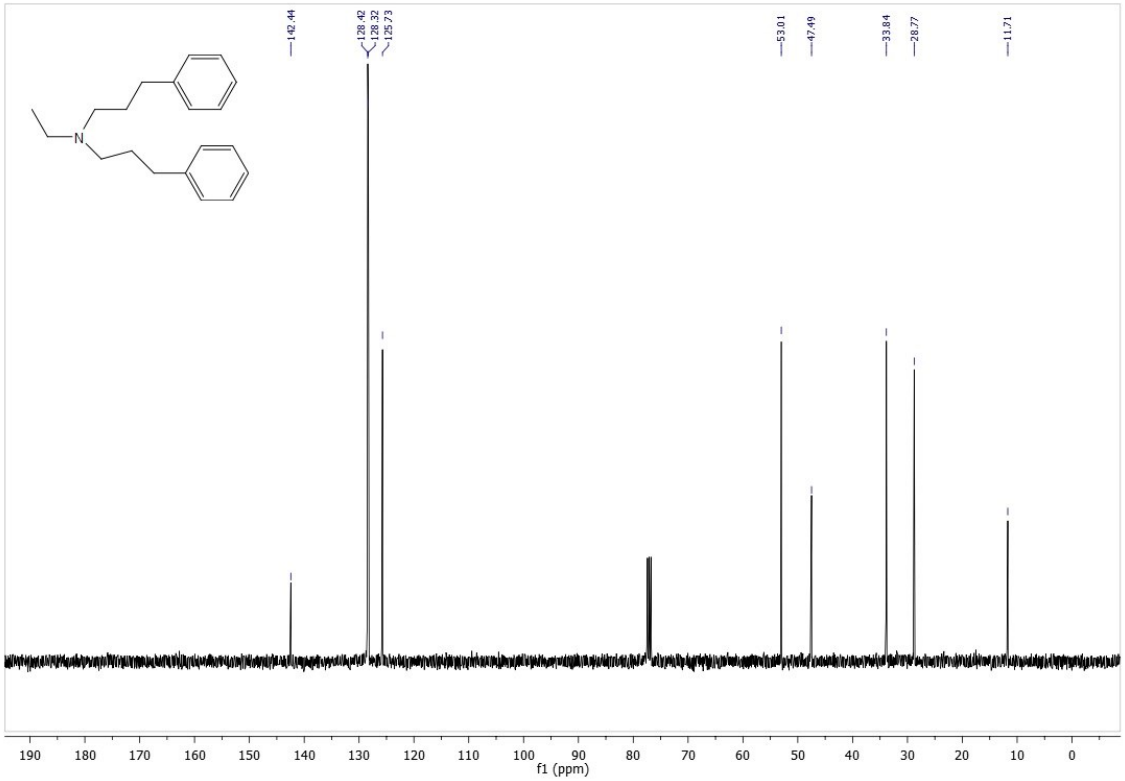
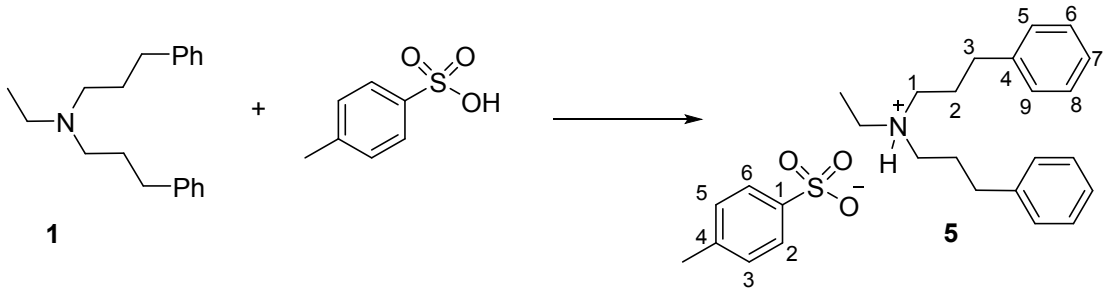



**Figure S6.** NMR-$^{13}$C of alverine (**1**)

## 2. Synthesis of Alverine-based ILs

**General procedure**: Alverine (**1**) and an equivalent amount of the corresponding acid (p-toluensulfonic acid, salycilic acid and benzoic acid) were allowed to stir at 100 °C for 2 h.

### 2a. Synthesis of alverinium tosylate [ALV][TOS] (5)




The general procedure using *p*-toluensulfonic acid (0.072 g, 0.37 mmol) was applied. The product was obtained as a solid (**5**, 0.168 g, 99%); mp 65-66 °C (from MeOH)

**RMN-$^1$H (400 MHz, $\delta_H$, $CDCl_3$):** δ= 7.80 (d, $J_{H-H}$=8.1 Hz, 2H, H-2 TOS, H-6 TOS), 7.32-7.16 (m, 12H, H-Ar), 5.03 (s, 1H, N<u>H</u>), 2.81 (m, 2H, $CH_3C\underline{H_2}N$), 2.71 (t, $J_{H-H}$=8.0 Hz, 4H, H-1 ALV), 2.65 (t, $J_{H-H}$=7.5 Hz, 4H, H-3 ALV), 2.38 (s, 3H, $CH_3$ TOS), 1.90 (m, 4H, H-2 ALV), 1.11 (t, $J_{H-H}$=7.2 Hz, 3H, $C\underline{H_3}CH_2N$).

**RMN-$^{13}$C (100.6 MHz, $\delta_C$, $CDCl_3$):** 142.4 (C-1 TOS, C-4 TOS), 139.9 (C-4 ALV), 129.0 (C-3 TOS, C-5 TOS), 128.6 (C-6 ALV,C-8 ALV), 128.5 (C-5 ALV, C-9 ALV, C-2 TOS,C-6 TOS), 125.9 (C-7 ALV), 53.0 (C-1 ALV), 47.6 ($CH_3\underline{C}H_2N$), 33.9 (C-3 ALV), 28.7 ($\underline{C}H_3$ TOS), 21.5 (C-2 ALV), 11.7 ($\underline{C}H_3CH_2N$).

**HRMS (ESI) *m/z* (%):** calcd for $[C_{20}H_{28}N]^+$: 282.2219 $[M]^+$; found 282.2216 (100); calcd for $[C_{14}H_{15}O_6S_2]^-$: 343.0316 $[M]^-$; found: 343.0316 (100).

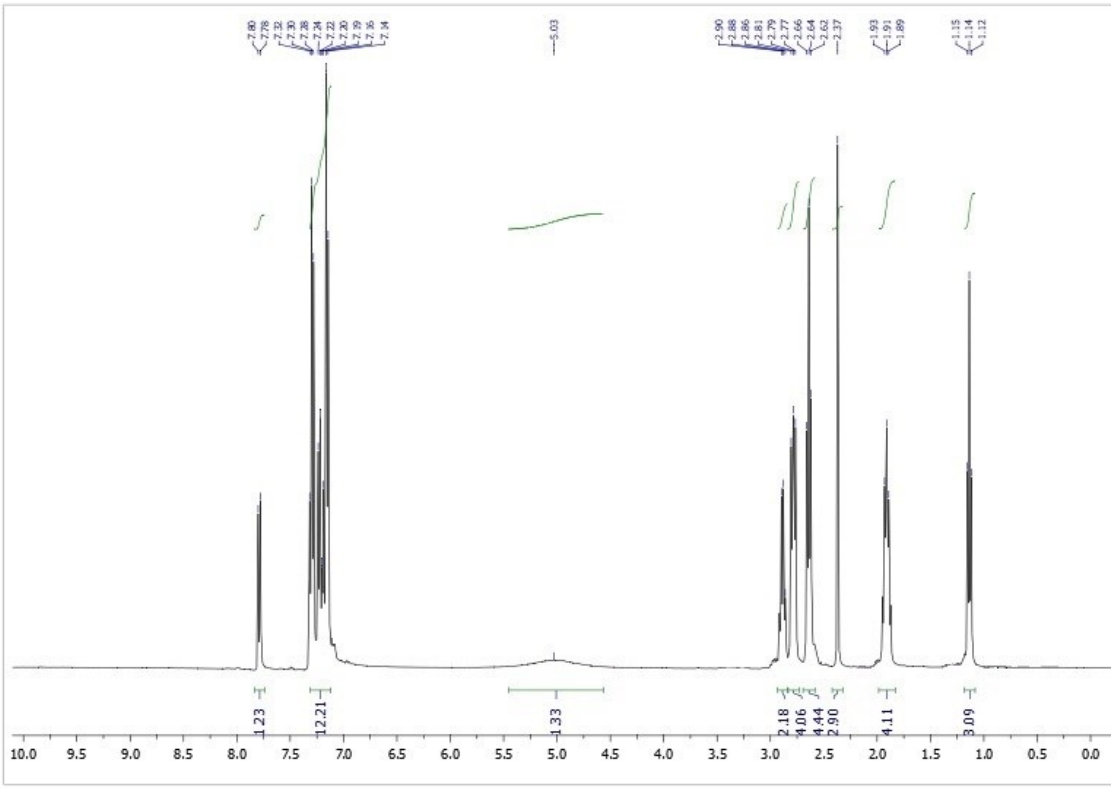



**Figure S7.** NMR-$^1$H of alverinium tosylate [ALV][TOS] (**5**)

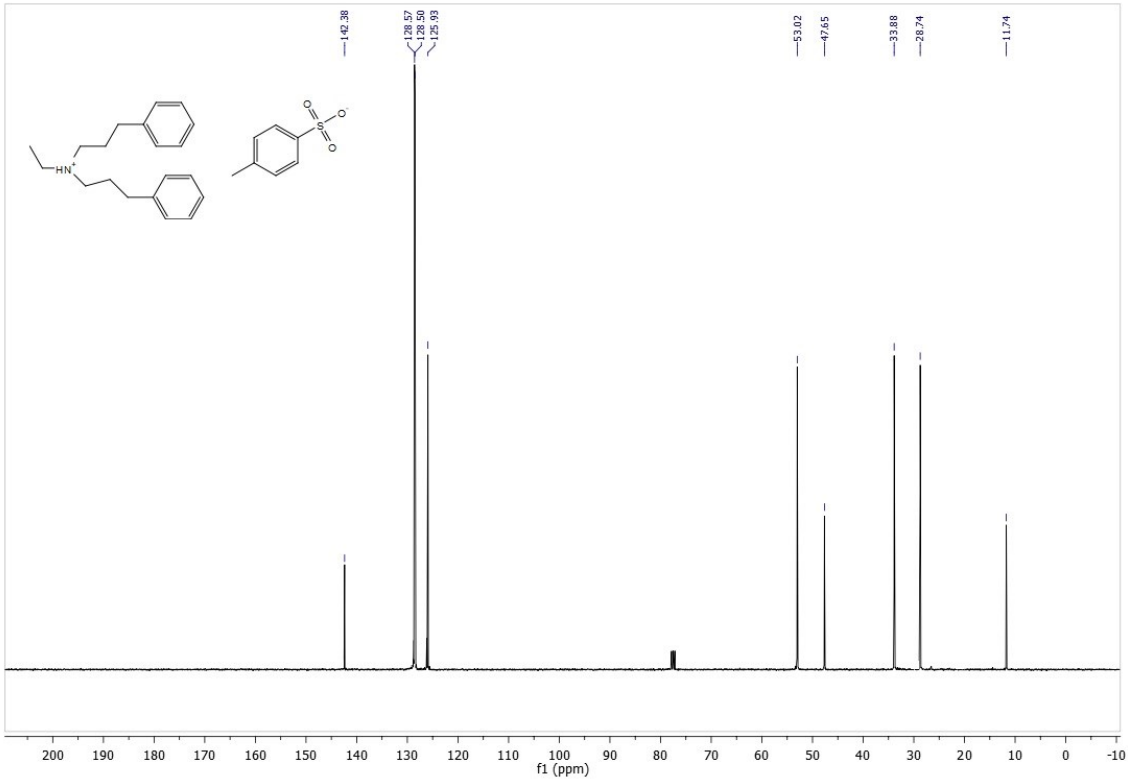
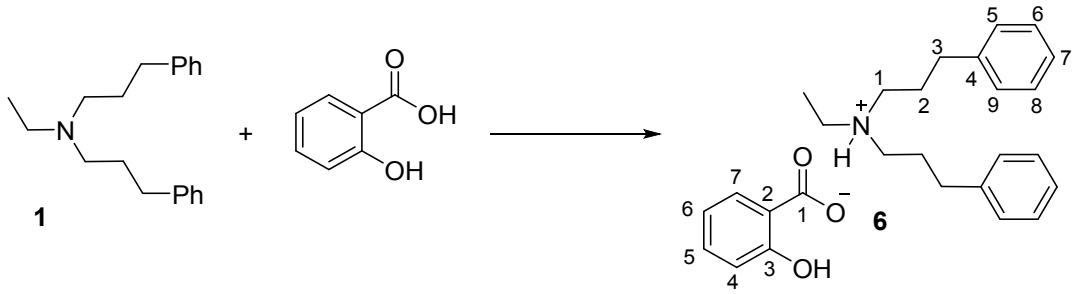



**Figure S8.** NMR-$^{13}$C of alverinium tosylate [ALV][TOS] (**5**)

**2b. Synthesis of alverinium salicylate [ALV][SAL] (6)**




General procedure was applied using salycilic acid (0.050 g, 0.37 mmol) to obtain a yellow liquid (**6**, 0.119 g, 99%).

**RMN-$^1$H (400 MHz, $\delta_H$, $CDCl_3$):** δ= 7.93 (d, $J_{H-H}$=7.9 Hz, 1H, H-7 SAL), 7.29 (m, 5H, H-6 ALV, H-8 ALV, H-5 SAL), 7.23 (t, $J_{H-H}$=7.1 Hz, 2H, H-7 ALV), 7.16 (d, $J_{H-H}$=7.3 Hz, 4H, H-5 ALV, H-9 ALV), 6.94 (d, $J_{H-H}$=8.1 Hz, 1H, H-4 SAL), 6.84 (t, $J_{H-H}$=7.4 Hz, 1H, H-6 SAL), 3.12 (q, $J_{H-H}$=7.3 Hz, 2H, $CH_3C\underline{H}_2N$), 2.99 (m, 4H, H-1 ALV), 2.69 (t, $J_{H-H}$=7.2 Hz, 4H, H-3 ALV), 2.03 (m, 4H, H-2 ALV), 1.23 (t, $J_{H-H}$=7.2 Hz, 3H, $C\underline{H}_3CH_2N$).

**RMN-$^{13}$C (100.6 MHz, $\delta_C$, $CDCl_3$):** δ= 174.9 (C-1 SAL), 162.1 (C-3 SAL), 140.7 (C-4 ALV), 132.8 (C-5 SAL), 130.8 (C-7 SAL), 128.6 (C-6 ALV, C-8 ALV), 128.4 (C-5 ALV, C-9 ALV), 126.3 (C-7 ALV), 119.1 (C-2 SAL), 117.8 (C-6 SAL), 116.5 (C-4 SAL), 51.3 (C-1 ALV), 46.9 ($CH_3\underline{C}H_2N$), 33.1 (C-3 ALV), 26.0 (C-2 ALV), 9.6 ($\underline{C}H_3CH_2N$).

**HRMS (ESI) *m/z* (%):** calcd for $[C_{20}H_{28}N]^+$: 282.2218 $[M]^+$; found 282.2216 (100); calcd for $[C_7H_5O_3]^-$: 137.0238 $[M]^-$; found 137.0244 (100).

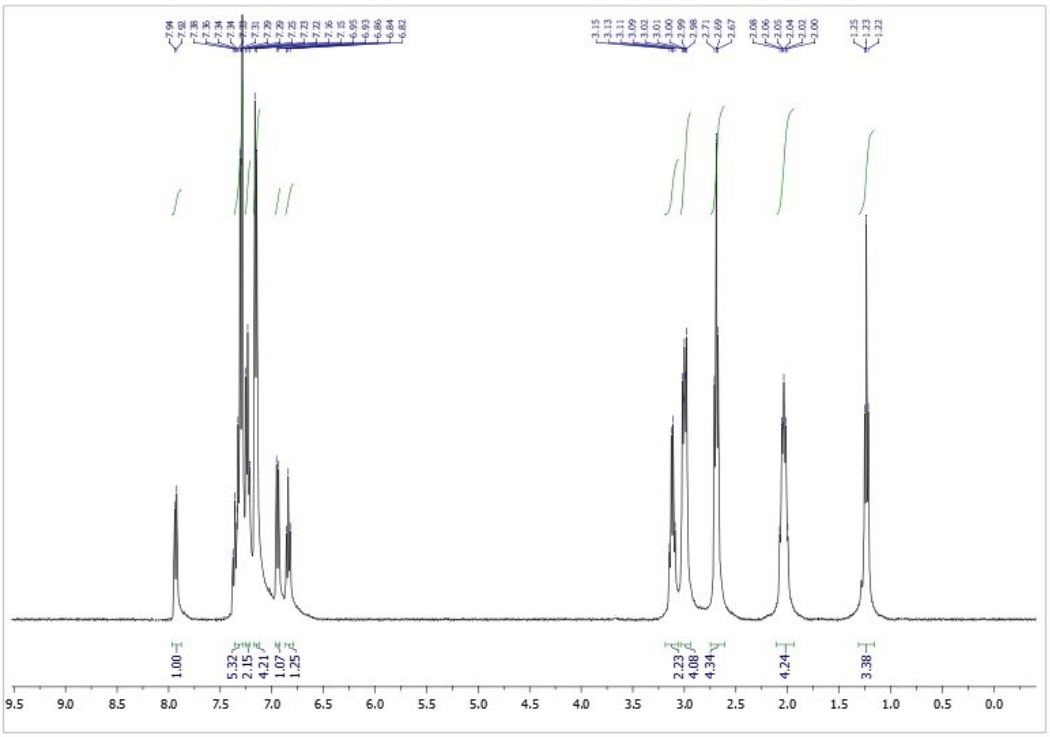


**Figure S9.** NMR-$^1$H of alverinium salicylate [ALV][SAL] (**6**)

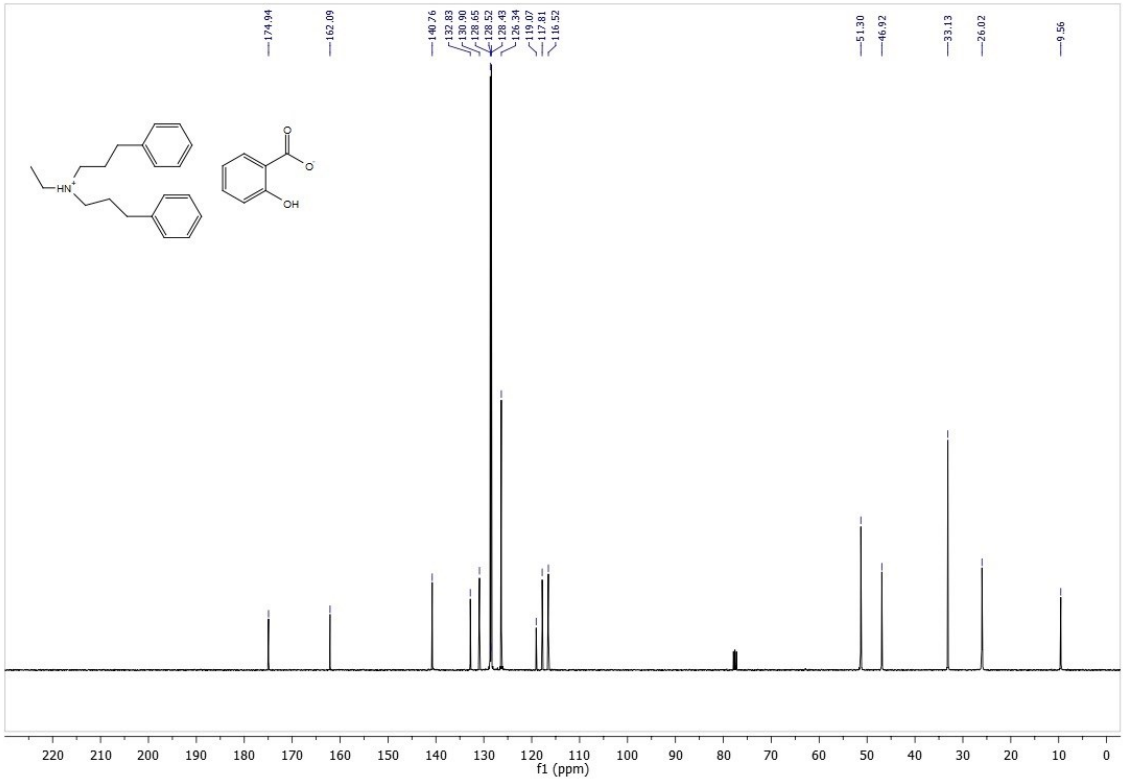
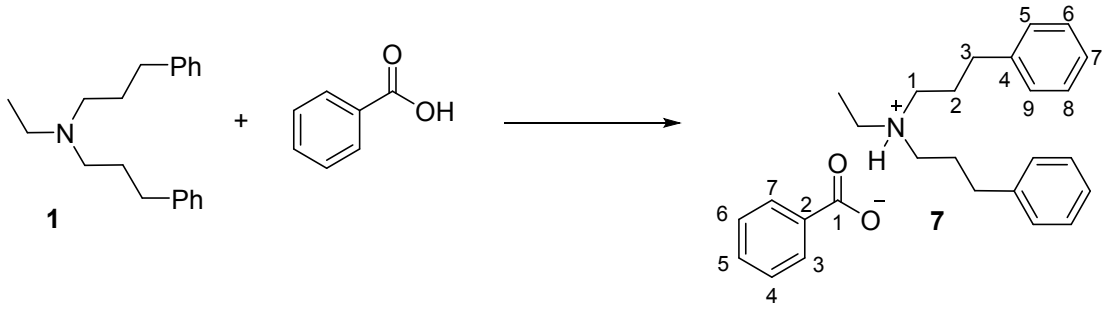


**Figure S10.** NMR-$^{13}$C of alverinium salicylate [ALV][SAL] (**6**)

**2c. Synthesis of alverinium benzoate [ALV][BNZ] (7)**




General procedure was applied using benzoic acid (0.043 g, 0.35 mmol) to obtain an orange liquid (7, 0.106 g, 99%).

**RMN-$^{1}$H (400 MHz, $\delta_H$, $CDCl_3$):** δ= 8.10 (m, 1H, H-5 BNZ), 7.43 (m, 2H, H-3 BNZ, H-7 BNZ), 7.30 (m, 6H, H-Ar), 7.22 (m, 6H, H-Ar), 2.90 (q, $J_{H-H}$=7.2 Hz, 2H, $CH_3CH_2N$), 2.81 (m, 4H, H-1 ALV), 2.67 (t, $J_{H-H}$=7.5 Hz, 4H, H-3 ALV), 1.96 (m, 4H, H-2 ALV), 1.16 (t, $J_{H-H}$=7.2 Hz, 3H, $CH_3CH_2N$).

**RMN-$^{13}$C (100.6 MHz, $\delta_C$, $CDCl_3$):** δ= 172.2 (C-1 BNZ), 140.5 (C-4 ALV), 135.7 (C-2 BNZ), 130.9 (C-3,5,7 BNZ), 129.6 (C-4 BNZ, C-6 BNZ), 128.6 (C-6 ALV, C-8 ALV), 128.3 (C-5 ALV, C-9 ALV), 126.3 (C-7 ALV), 50.6 (C-1 ALV), 46.4 ($CH_3CH_2N$), 33.1 (C-3 ALV), 25.2 (C-2 ALV), 9.0 ($CH_3CH_2N$).

**HRMS (ESI) *m/z* (%):** calcd for $[C_{20}H_{28}N]^+$: 282.2215 $[M]^+$; found 282.2216 (100); calcd for $[C_7H_5O_2]^-$: 121.0290 $[M]^-$; found 121.0295 (100).

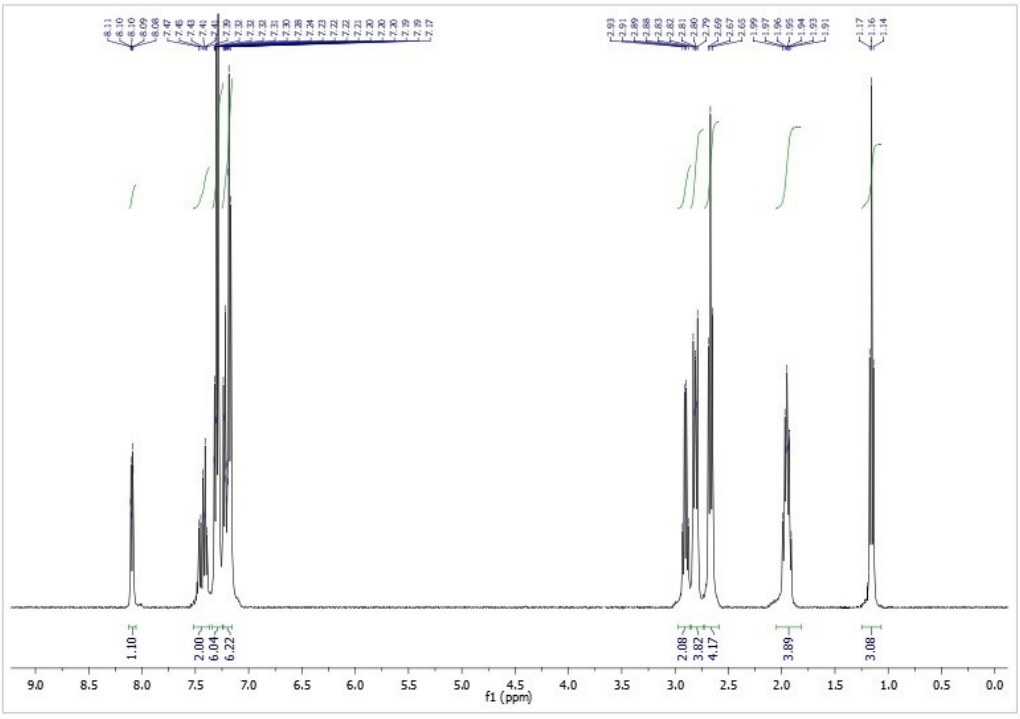



**Figure S11.** NMR-$^{1}$H of alverinium benzoate [ALV][BNZ] (7)

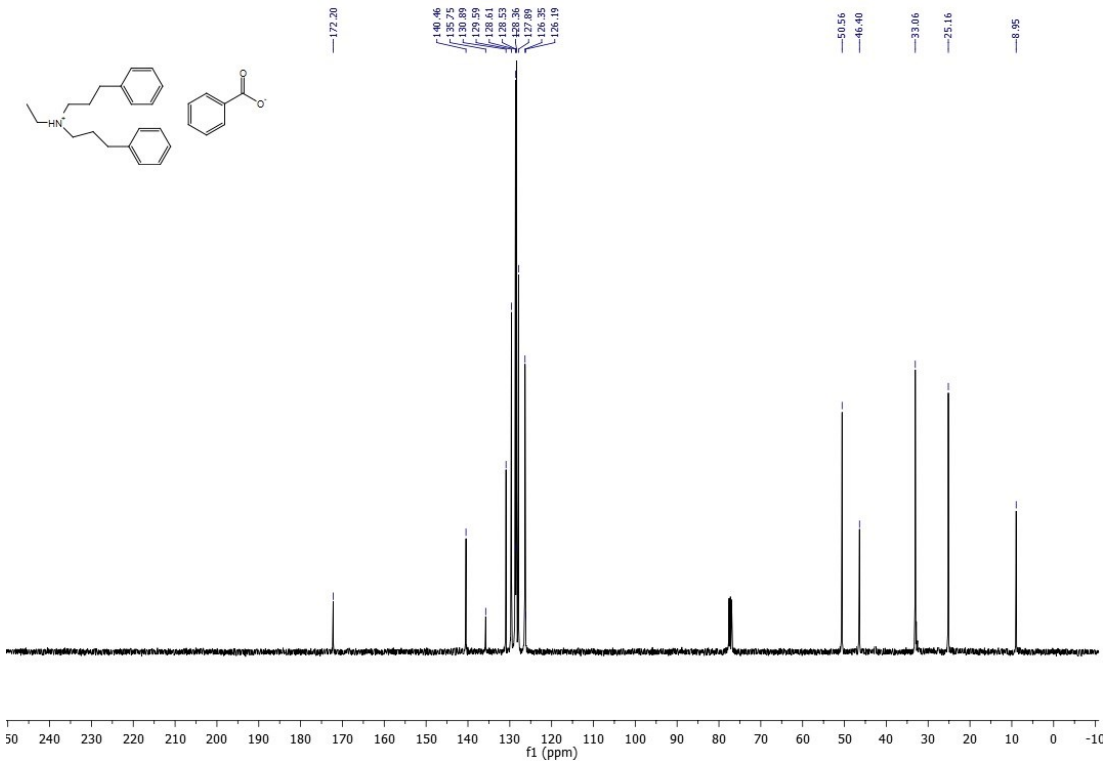



**Figure S12.** NMR-$^{13}$C of alverinium benzoate [ALV][BNZ] (7)

## REFERENCES

1. R. N. Shakhmaev, A. Sh. Sunagatullina and V.V. Zorin, *Russ. J. Org. Chem.*, 2017, **53**, 832–835.