Electronic Supplementary Material (ESI) for RSC Advances


# A Simple and Rapid Route to Novel Tetra(-4-thiaalkyl)ammonium Bromides

## Supplemental Information

Characterization of the tetra(4-thiaalkyl)ammonium bromides for $^{1}H$, $^{13}C$ and $^{19}F$ NMR were performed on a JEOL 500 MHz NMR with multi-nuclear capabilities using $CDCl_3$ as the deuterated solvent. Chemical shifts are reported relative to TMS as the internal reference at 0.00 ppm for $^{1}H$ and $^{19}F$ NMR and 77.23 ppm (middle peak, $CDCl_3$) for $^{13}C$ NMR. ESI-MS analyses were performed by flow-injection using HPLC grade acetonitrile on a Thermo Scientific mass spectrometer in positive ion mode.

Tetra(4-thiahexyl)ammonium bromide **(1)**

$^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.40-4.20 (m, 12H), 2.45-2.95 (m, 10H), 1.55-1.80 (m, 10H), 1.05-1.20 (m, 12H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.09, 69.25, 68.43, 68.40, 38.69, 38.65, 38.36, 33.50, 33.31, 30.91, 30.28, 26.73, 22.62, 14.95, 12.93. EI-MS: HRMS calculated $[M + H]^+$ for $C_{20}H_{44}NS_4Br$: 506.7381, found: 337.59.

Tetra(4-thiaheptyl)ammonium bromide **(2)**

$^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.44-4.30 (m, 12H), 2.66-3.00 (m, 10H), 2.46-2.60 (m, 6H), 1.52-1.68 (m, 6H), 1.12-1.24 (m, 9H), 0.94-1.04 (m, 9H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.41, 70.16, 70.09, 69.19, 68.38, 38.79, 38.75, 38.53, 34.85, 34.81, 33.54, 33.45, 33.34, 32.94, 31.19, 30.79, 30.75, 22.96, 13.52, 13.07, 12.65. EI-MS: HRMS calculated $[M + H]^+$ for $C_{24}H_{52}NS_4Br$: 562.8448, found: 330.73.

Tetra(4-thia-5-methylhexyl)ammonium bromide **(3)**

$^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.40-4.28 (m, 12H), 2.68-3.08 (m, 14H), 1.12-1.30 (26H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 71.09, 70.97, 69.70, 69.14, 69.03, 38.92, 38.89, 38.79, 36.01, 35.92, 33.62, 33.44, 33.11, 29.39, 29.09, 29.00, 23.50, 23.47, 12.73, 12.42. EI-MS: HRMS calculated $[M + H]^+$ for $C_{24}H_{52}NS_4Br$: 562.8448, found: 330.73.

Tetra(4-thiaoctyl)ammonium bromide **(4)**

$^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.44-4.30 (m, 12H), 2.50-2.96 (m, 18H), 1.50-1.64 (m, 6H), 1.36-1.48 (m, 6H), 1.14-1.24 (m, 9H), 0.86-0.98 (m, 9H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.18, 69.86, 68.84, 68.13, 38.52, 38.26, 33.31, 33.20, 33.10, 32.68, 32.33, 31.45, 31.08, 30.63, 30.58, 21.79, 13.57, 12.84, 12.42. EI-MS: HRMS calculated $[M + H]^+$ for $C_{28}H_{60}NS_4Br$: 618.9515, found: 358.61.

Tetra(4-thia-5,5-dimethylhexyl)ammonium bromide **(5)**

$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.40-4.34 (m, 8H), 2.60-3.00 (m, 8H), 1.33 (s, 36H), 1.10-1.28 (m, 8H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.65, 70.25, 70.08, 69.14, 68.43, 68.33, 43.22, 43.15, 39.02, 38.91, 33.76, 33.55, 33.02, 31.00 (t-butyl), 27.39, 26.93, 26.82, 13.15, 12.74. EI-MS: HRMS calculated $[M + H]^+$ for $C_{28}H_{60}NS_4Br$: 618.9515, found: 358.65.

Tetra(4-thia-6-methylheptyl)ammonium bromide **(6)**

$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.40-4.26 (m, 11H), 2.64-3.00 (m, 12H), 2.38-2.48 (m, 6H), 1.70-1.86 (m, 3H), 1.12-1.24 (m, 4H), 0.99 (s, 12H), 0.97 (s, 12H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.13, 70.01, 68.79, 68.13, 41.69, 38.58, 38.52, 38.35, 33.25, 33.16, 33.03, 32.67, 31.53, 31.48, 31.10, 28.33, 21.87, 21.82, 12.81, 12.40. EI-MS: HRMS calculated $[M + H]^+$ for $C_{28}H_{60}NS_4Br$: 618.9515, found: 358.62.

Tetra(4-thia-5-methylheptyl)ammonium bromide **(7)**

$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.24-4.12 (m, 12H), 2.45-2.84 (m, 12H), 1.30-1.50 (m, 8H), 0.96-1.20 (m, 16H), 0.78-0.88 (m, 12H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.17, 70.00, 68.82, 68.14, 42.29, 42.23, 38.65, 38.57, 38.49, 38.36, 33.28, 33.16, 33.05, 32.65, 30.81, 29.50, 29.42, 29.08, 28.69, 28.64, 28.57, 20.68, 12.77, 12.37, 11.23, 11.12. EI-MS: HRMS calculated $[M + H]^+$ for $C_{28}H_{60}NS_4Br$: 618.9515, found: 358.63.

Tetra(4-thiadecyl)ammonium bromide **(8)**

$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.40-4.30 (m, 12H), 2.48-3.00 (m, 18H), 1.42-1.62 (m, 6H), 1.10-1.42 (m, 30H), 0.82-0.94 (m, 10H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.17, 70.05, 68.84, 68.17, 38.95, 33.50, 33.10, 31.60, 31.00, 29.71, 28.70, 22.75, 14.24, 13.17. EI-MS: HRMS calculated $[M + H]^+$ for $C_{36}H_{76}NS_4Br$: 731.1649, found: 414.66.

Tetra(4-thiaundecyl)ammonium bromide **(9)**

$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.42-4.30 (m, 12H), 2.44-3.00 (m, 20H), 1.50-1.62 (m, 6H), 1.12-1.44 (m, 36H), 0.82-0.96 (t, 10H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.36, 70.03, 69.04, 68.31, 38.74, 38.50, 33.54, 33.41, 33.32, 32.89, 31.80, 31.28, 30.87, 30.80, 29.64, 28.97. 28.87, 22.67, 14.15, 13.05, 12.64. EI-MS: HRMS calculated $[M + H]^+$ for $C_{40}H_{84}NS_4Br$: 787.2716, found: 442.65.

Tetra(4-thiadodecyl)ammonium bromide **(10)**

$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.40-4.34 (m, 12H), 2.46-3.00 (m, 20H), 1.50-1.65 (m, 6H), 1.12-1.44 (m, 44H), 0.84-0.94 (m, 10H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.30, 69.95, 69.00, 68.26, 38.70, 38.45, 33.48, 33.40, 33.00, 32.97, 29.69, 29.34, 29.00, 22.80, 14.25, 13.13, 12.70. EI-MS: HRMS calculated $[M + H]^+$ for $C_{44}H_{92}NS_4Br$: 843.3783, found: 470.60.

Tetra(4-thiaoctadecyl)ammonium bromide **(11)**

$^{1}$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.40-4.30 (m, 12H), 2.44-3.00 (m, 20H), 1.50-1.80 (m, 9H), 1.12-1.44 (m, 89H), 0.80-0.94 (m, 10H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.57, 70.23, 70.17, 69.28, 68.47, 38.91, 38.87, 38.61, 33.66, 33.54, 33.46, 33.09, 32.09, 31.42, 30.98, 30.93, 29.84, 29.79,

29.73, 29.52, 29.42, 29.02, 22.85, 14.28, 13.12, 12.73, 12.70. EI-MS: HRMS calculated $[M + H]^+$ for $C_{68}H_{140}NS_4Br$: 1180.0184, found: 638.80.

Tetra(4-thiadocosyl)ammonium bromide **(12)**

$^1H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.44-4.34 (m, 8H), 2.48-3.00 (m, 16H), 1.50-1.72 (m, 8H), 1.10-1.45 (m, 128H), 0.82-0.92 (m, 12H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.50, 70.00, 69.50, 39.37, 33.04, 32.10, 29.87, 29.77, 29.68, 29.54, 29.41, 29.04, 28.70, 22.86, 14.29. EI-MS: HRMS calculated $[M + H]^+$ for $C_{84}H_{172}NS_4Br$: 1404.4452, found: 751.00.

Tetra(4-thia-7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro)ammonium bromide **(13)**

$^1H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.65-4.40 (m, 10H), 2.65-3.00 (m, 16H), 2.30-2.50 (m, 6H), 1.10-1.30 (m, 8H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 69.47, 38.33, 31.64, 23.46, 12.84. $^{19}F$ (470 MHz, $CDCl_3$) $\delta_F$ -80.66, -114.05, -114.08, -121.58, -121.83, -122.64, -123.15, -126.04. EI-MS: HRMS calculated $[M + H]^+$ for $C_{52}H_{40}NS_4F_{68}Br$: 2178.9427, found: 1138.70.

Tetra(4-thia-5-phenylpentyl)ammonium bromide **(14)**

$^1H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 8.78 (m, 20H), 3.42-4.10 (m, 14H), 2.45-2.70 (m, 10H), 0.94-1.10 (m, 8H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 138.03, 129.26, 128.88, 128.80, 128.53, 128.35, 127.84, 127.29, 127.09, 126.86, 70.50, 69.79, 68.79, 67.96, 50.75, 43.09, 38.19, 38.12, 36.68, 36.50, 36.40, 33.15, 33.06, 32.99, 32.52, 30.38, 30.19, 29.99, 29.86, 12.72, 12.40, 12.27. EI-MS: HRMS calculated $[M + H]^+$ for $C_{40}H_{52}NS_4Br$: 755.0173, found: 426.55.

Tetra(4-thia-4-cyclohexyl)ammonium bromide **(15)**

$^1H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 3.42-4.30 (m, 11H), 2.60-2.98 (m, 14H), 1.90-2.04 (m, 7H), 1.68-1.80 (m, 5H), 1.56-1.66 (m, 3H), 1.12-1.40 (m, 24H), 0.82-0.94 (m, 4H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 70.31, 69.96, 69.81, 68.99, 68.21, 44.26, 44.20, 38.87, 38.78, 38.49, 33.56, 33.48, 33.29, 33.24, 32.76, 31.49, 29.06, 28.64, 28.58, 25.87, 25.63, 22.57, 14.04, 12.90, 12.48. EI-MS: HRMS calculated $[M + H]^+$ for $C_{36}H_{68}NS_4Br$: 723.1013, found: 410.56.