-SUPPORTING INFORMATION-

Scalable synthesis of salt-free quaternary ammonium carboxylate catanionic surfactants

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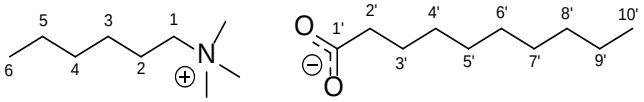
GENERAL INFORMATION

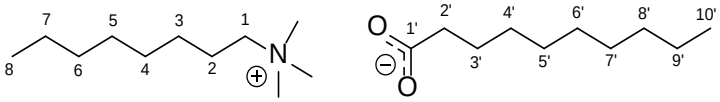
IR spectra were obtained with a Perkin–Elmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support. High resolution mass spectra (HRMS) were recorded on Agilent 6224 time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an HPLC instrument. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance III 500 MHz NMR (500 MHz, and 126 MHz) instrument at 296 K in DMSO-d_6 using TMS as an internal standard. Proton and carbon spectra were referenced to the residual chloroform shifts of 7.26 ppm and 77.16 ppm, respectively.[1] Assignments of proton, carbon and nitrogen resonances were performed by 2D NMR techniques (^{1}H–^{1}H *gs*-COSY, ^{1}H–^{13}C *gs*-HSQC, ^{1}H–^{13}C *gs*-HMBC and ^{1}H–^{15}N *gs*-HMBC). Carbon resonances without labels belong to the chain carbons and could not have been differentiated.

CHARACTERIZATION OF COMPOUNDS

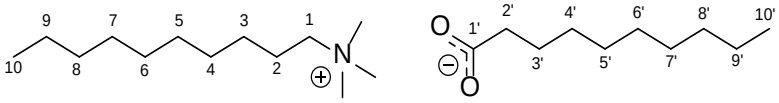


N-hexyl-*N*,*N*,*N*-trimethylammonium decanoate (**5a**)
White solid (11.5 g, 35 %).
IR = 3473, 3393, 3020, 2920, 2852, 1572, 1377, 1055, 963, 643 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.42–3.35 (m, 2H, CH_2-1), 3.32 (s, 9H, NMe_3), 2.14–2.06 (m, 2H, CH_2-2'), 1.75–1.64 (m, 2H, CH_2-2), 1.59–1.48 (m, 2H, CH_2-3'), 1.38–1.15 (m, 18H, CH_2-chain), 0.92–0.78 (m, 6H, CH_3-10' and CH_3-6).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 179.8 (COO), 66.9 (30.21), 53.2 (NMe_3), 39.4 (C-2'), 32.0, 31.4, 30.2, 29.9, 29.8, 29.50 , 27.3, 26.0, 23.2, 22.8, 22.5 , 14.2 (CH_3-6/CH_3-10'), 14.0 (CH_3-6/CH_3-10').
^{15}N NMR (51 MHz, $CDCl_3$) δ = 49.5 (NMe_3).
HRMS (ESI+): calcd. for $C_9H_{22}N^+$ [M^+] 144.1747, found 144.1749.
HRMS (ESI–): calcd. for $C_{10}H_{19}O_2^-$ [M^-] 171.1391, found 171.1389.

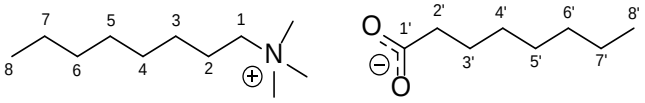
[1] Gottlieb, H. E.; Kotlyar, V.; Nudelman, A., *J. Org. Chem.* **1997**, *62*, 7512–7515.



N-octyl-*N*,*N*,*N*-trimethylammonium decanoate (**5b**)
White solid (14.7 g, 63 %).
IR = 3317, 3119, 3032, 2919, 2851, 1657, 1569, 1380, 972, 756 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.43 – 3.38 (m, 2H, CH_2-1), 3.38 – 3.31 (m, 9H, NMe_3), 2.19 – 2.05 (m, 2H, CH_2-2'), 1.76–1.61 (m, 2H, CH_2-2), 1.60–1.49 (m, 2H, CH_2-3'), 1.41–1.13 (m, 22H, CH_2-chain), 0.89–0.79 (m, 6H, CH_3-8 and CH_3-10).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 179.6 (COO), 66.9 (C-1), 53.2 (NMe_3), 39.2 (C-2'), 32.0 , 31.7, 30.2, 29.8, 29.8, 29.5 , 29.3, 29.1, 27.3 (C-3'), 26.4, 23.2 (C-2), 22.8, 22.7, 14.2 (CH_3-8/CH_3-10'), 14.1 (CH_3-8/CH_3-10').
^{15}N NMR (51 MHz, $CDCl_3$) δ = 49.7 (NMe_3).
HRMS (ESI+): calcd. for $C_{11}H_{26}N^+$ [M^+] 172.2060, found 172.2057.
HRMS (ESI–): calcd. for $C_{10}H_{19}O_2^-$ [M^-] 171.1391, found 171.1386.

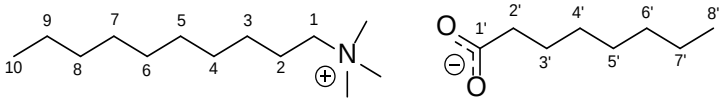


N-decyl-*N*,*N*,*N*-trimethylammonium decanoate (**5c**)
White solid (25.3 g, 72 %).
IR = 3429, 3348, 3195, 3119, 3032, 2916, 2850, 1656, 1566, 1387 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.42–3.35 (m, 2H, CH_2-1), 3.32 (s, 9H, NMe_3), 2.16–2.07 (m, 2H, CH_2-2'), 1.74–1.63 (m, 2H, CH_2-2), 1.54 (p, *J* = 7.2 Hz, 2H, CH_2-3'), 1.38–1.14 (m, 26H, CH_2-chain), 0.91–0.79 (m, 6H, CH_3-10 and , CH_3-10').
^{13}C NMR (126 MHz, $CDCl_3$) δ = 179.6 (COO), 66.9 (C-1), 53.2 (NMe_3), 39.0 (C-2'), 32.0 , 31.9, 30.2, 29.9, 29.8, 29.54 , 29.51, 29.4, 27.2 (C-3'), 26.4, 23.3 (C-2), 22.79, 22.75, 14.22 (CH_3-10/CH_3-10'), 14.19 (CH_3-10/CH_3-10').
^{15}N NMR (51 MHz, $CDCl_3$) δ = 49.5 (NMe_3).
HRMS (ESI+): calcd. for $C_{13}H_{30}N^+$ [M^+] 200.2373, found 172.2373.
HRMS (ESI–): calcd. for $C_{10}H_{19}O_2^-$ [M^-] 171.1391, found 171.1388.

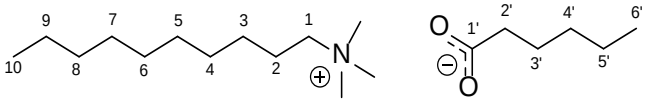


N-octyl-*N*,*N*,*N*-trimethylammonium octanoate (**5d**)
White solid (10.8 g, 28 %).
IR = 3510, 3022, 2919, 2851, 1657, 1573, 1378, 974, 918, 773 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.43–3.36 (m, 2H, CH_2-1), 3.35–3.25 (m, 9H, NMe_3), 2.16–2.05 (m, 2H, CH_2-2'), 1.74–1.61 (m, 2H, CH_2-2), 1.59–1.46 (m, 2H, CH_2-3'), 1.35–1.12 (m, 14H, CH_2-chain), 0.89–0.75 (m, 6H, CH_3-8 and CH_3-8').
^{13}C NMR (126 MHz, $CDCl_3$) δ = 179.5 (COO), 66.8 (C-1), 53.1 (NMe_3), 39.1 (C-2'), 32.0 , 31.7, 30.1, 29.5, 29.3, 29.1 , 27.2 (C-3'), 26.3, 23.2 (C-2), 22.8, 22.6, 14.2(CH_3-8/CH_3-8'), 14.1(CH_3-8/CH_3-8').
^{15}N NMR (51 MHz, $CDCl_3$) δ = 49.4 (NMe_3).

HRMS (ESI+): calcd. for $C_{11}H_{26}N^+$ [M^+] 172.2060, found 172.2054.
HRMS (ESI–): calcd. for $C_8H_{15}O_2^-$ [M^-] 143.1078, found 143.1076.



N-decyl-*N*,*N*,*N*-trimethylammonium octanoate (**5e**)
White solid (16.7 g, 54 %).
IR = 3464, 3385, 3021, 2919, 2851, 1572, 1380, 915, 772, 722 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.45–3.39 (m, 2H, CH_2-1), 3.40–3.35 (m, 9H, NMe_3), 2.23–2.11 (m, 2H, CH_2-2'), 1.79–1.67 (m, 2H, CH_2-2), 1.65–1.53 (m, 2H, CH_2-3), 1.42–1.18 (m, 22H, CH_2-chain), 0.93–0.81 (m, 6H, , CH_3-10 and , CH_3-8').
^{13}C NMR (126 MHz, $CDCl_3$) δ = 180.0 (COO), 67.1 (C-1), 53.4 (NMe_3), 39.3 (C-2'), 32.1 , 32.0, 30.2, 29.6, 29.53, 29.49 , 29.36, 29.34, 27.3 (C-3'), 26.4, 23.3 (C-2'), 22.9, 22.8, 14.3 (CH_3-10/CH_3-8'), 14.2(CH_3-10/CH_3-8').
^{15}N NMR (51 MHz, $CDCl_3$) δ = 49.7 (NMe_3).
HRMS (ESI+): calcd. for $C_{13}H_{30}N^+$ [M^+] 200.2373, found 172.2375.
HRMS (ESI–): calcd. for $C_8H_{15}O_2^-$ [M^-] 143.1078, found 143.1073.



N-decyl-*N*,*N*,*N*-trimethylammonium hexanoate (**5f**)
White solid (2.2 g, 13 %).
IR = 3359, 3021, 2922, 2854, 1572, 1377, 973, 918, 766, 644 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.45–3.37 (m, 2H, CH_2-1), 3.38–3.30 (m, 9H, NMe_3), 2.21–2.03 (m, 2H, CH_2-2'), 1.76–1.61 (m, 2H , CH_2-2), 1.61–1.50 (m, 2H, CH_2-3'), 1.38–1.15 (m, 18H, CH_2-chain), 0.92–0.78 (m, 6H, CH_2-8 and CH_2-).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 179.6 (COO), 66.9 (C-1), 53.2 (NMe_3), 39.2 (C-2'), 32.4 , 31.9, 29.50, 29.46, 29.3, 26.9 (3'), 26.4, 23.3 (C-2), 22.8, 22.7, 14.3(CH_3-10/CH_3-6'), 14.2(CH_3-10/CH_3-6').
^{15}N NMR (51 MHz, $CDCl_3$) δ = 49.8 (NMe_3).
HRMS (ESI+): calcd. for $C_{13}H_{30}N^+$ [M^+] 200.2373, found 200.2370.
HRMS (ESI–): calcd. for $C_{10}H_{19}O_2^-$ [M^-] 171.1391, found 171.1386.

THERMOGRAVIMETRIC ANALYSIS (TG) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Thermogravimetric (TG) measurements were performed on a Mettler Toledo TGA/DSC1 Instrument in the temperature range from 25 to 400 °C under dynamic air flow (100 cm^3 min^{-1}) with a heating rate of 5 K min^{-1}. Approximately 3-5 mg of sample was weighed into a 150 µL platinum crucible and the baseline was subtracted. Differential scanning calorimetry (DSC) measurements were performed separately on a Mettler Toledo DSC 1 Instrument in 40 µL aluminium crucibles under the same conditions.

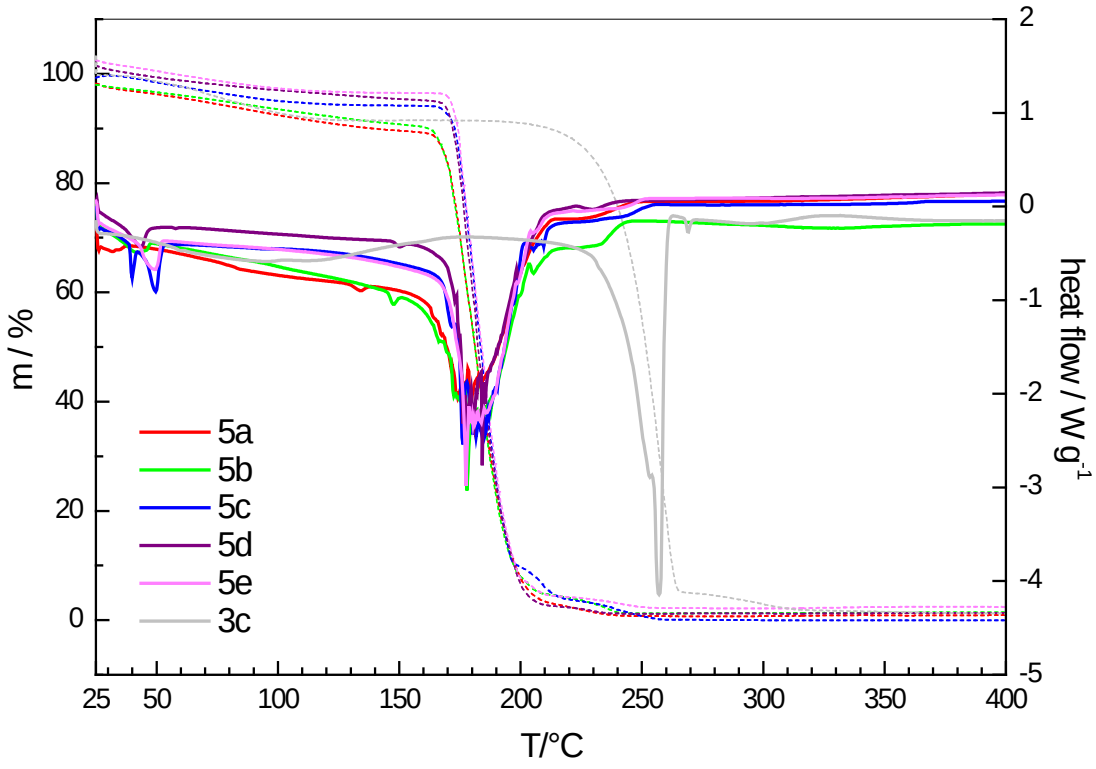


Figure S1. TG (dashed lines) and DSC (solid lines) curves in the temperature range between 25 and 400 °C for synthesized compounds according to procedure A.

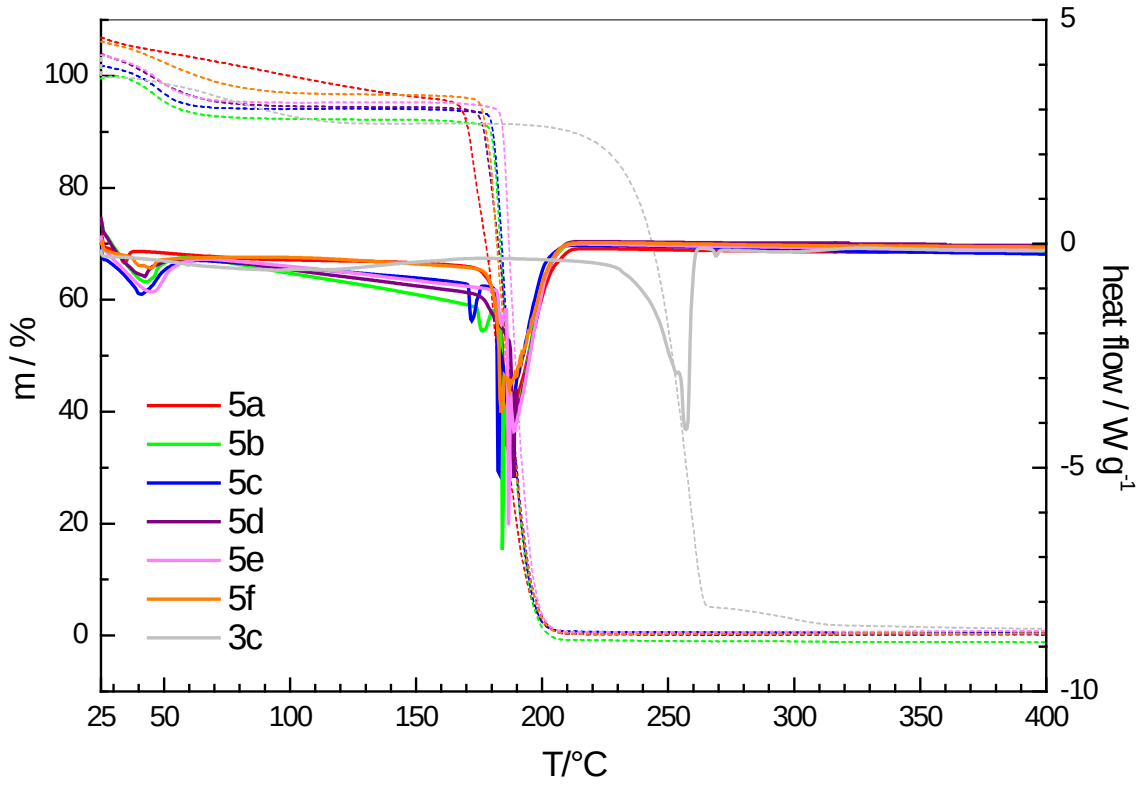


Figure S2. TG (dashed lines) and DSC (solid lines) curves in the temperature range between 25 and 400 °C for synthesized compounds according to procedure B.

IR SPECTRA

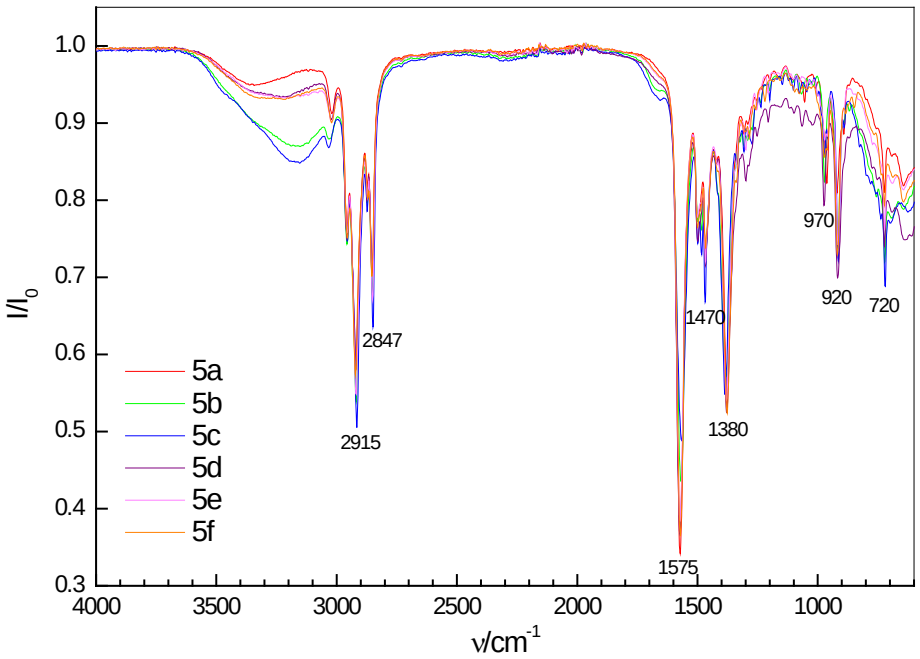
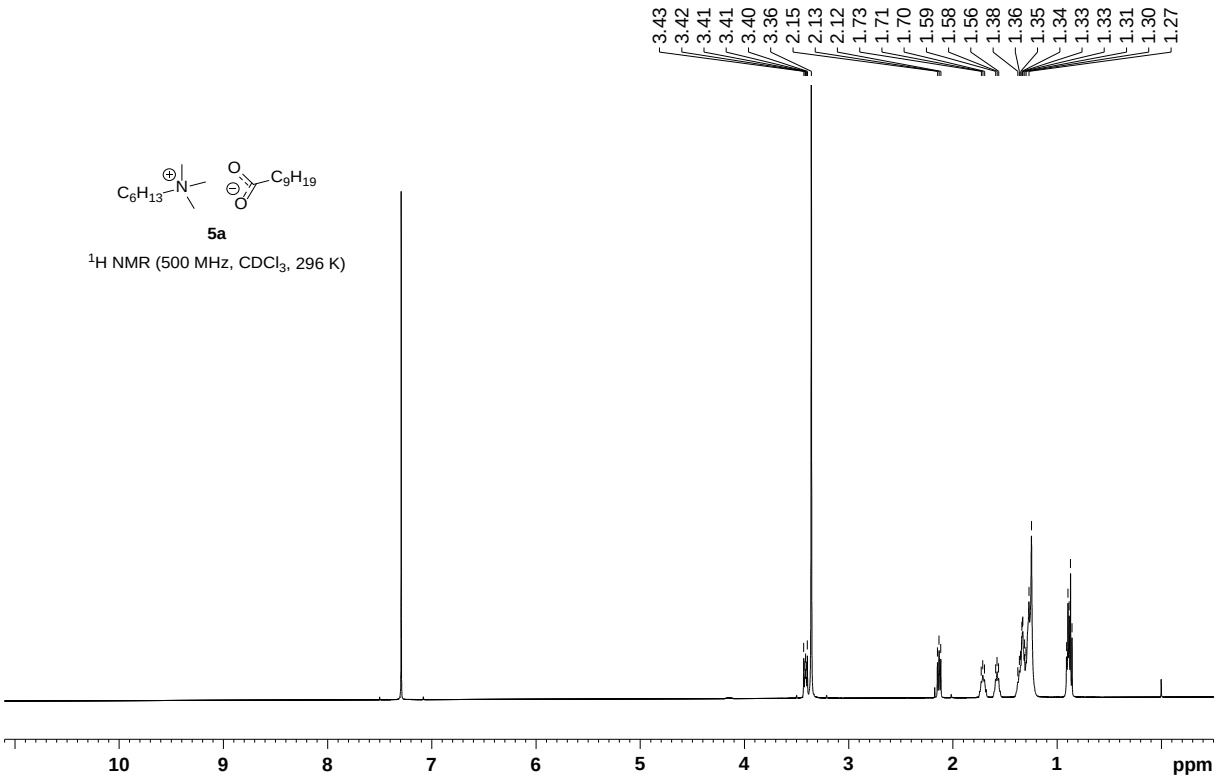


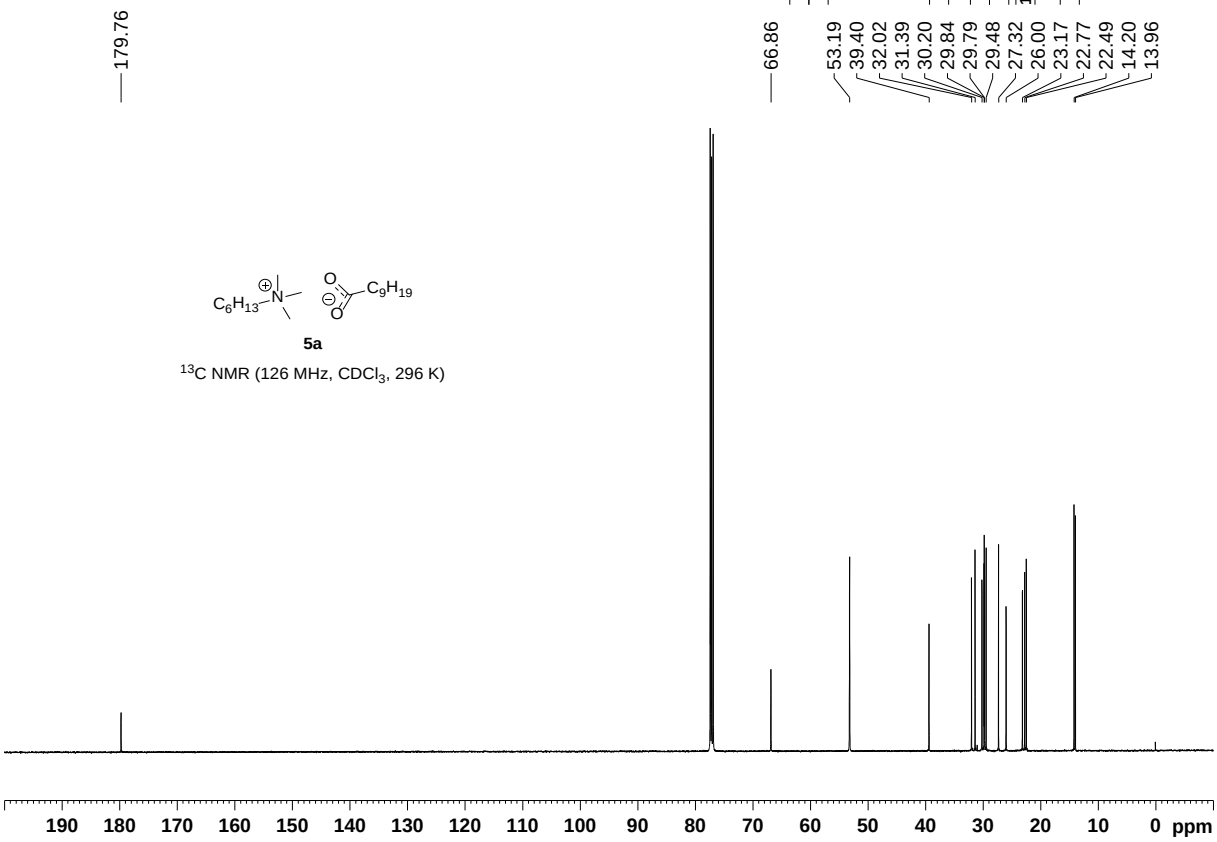
Figure S3. IR spectra of synthesized compounds according to procedure B.

COPIES OF NMR SPECTRA



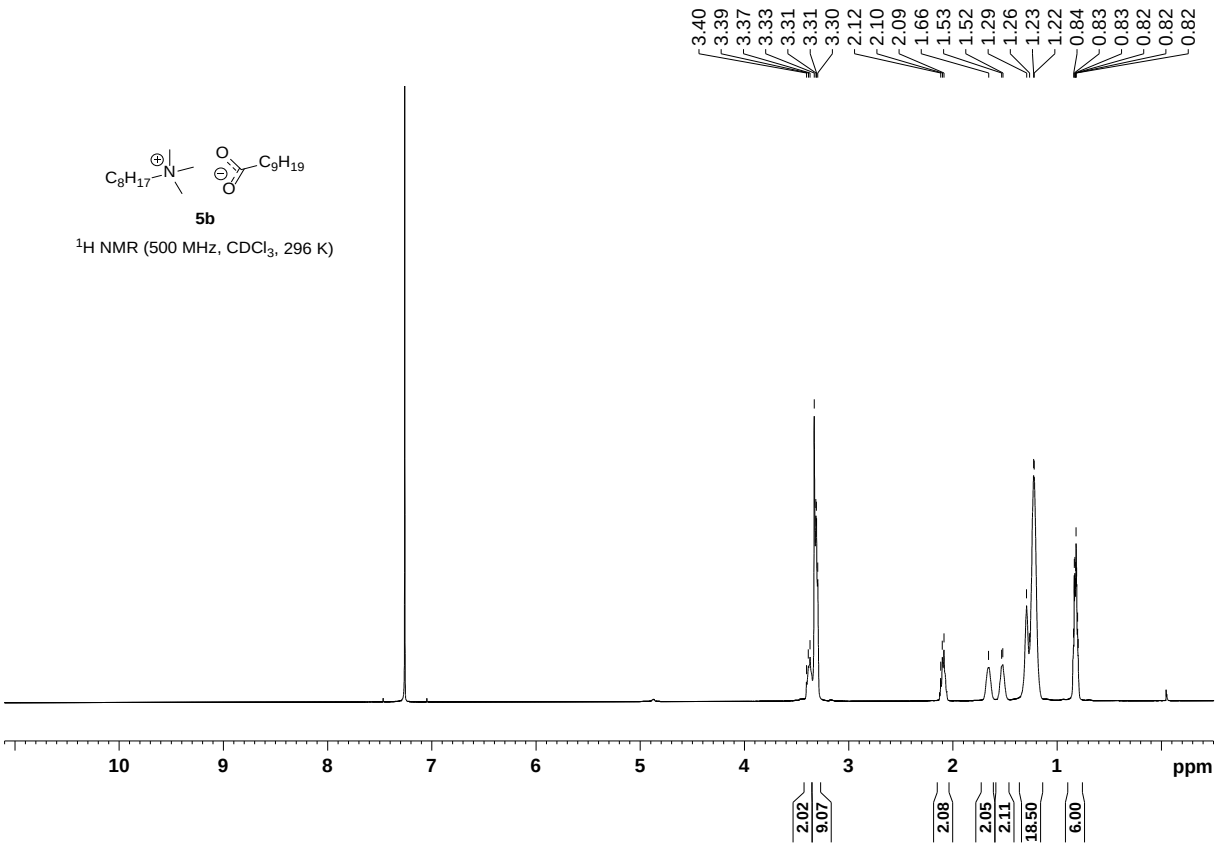
5a

^{1}H NMR (500 MHz, $CDCl_3$, 296 K)



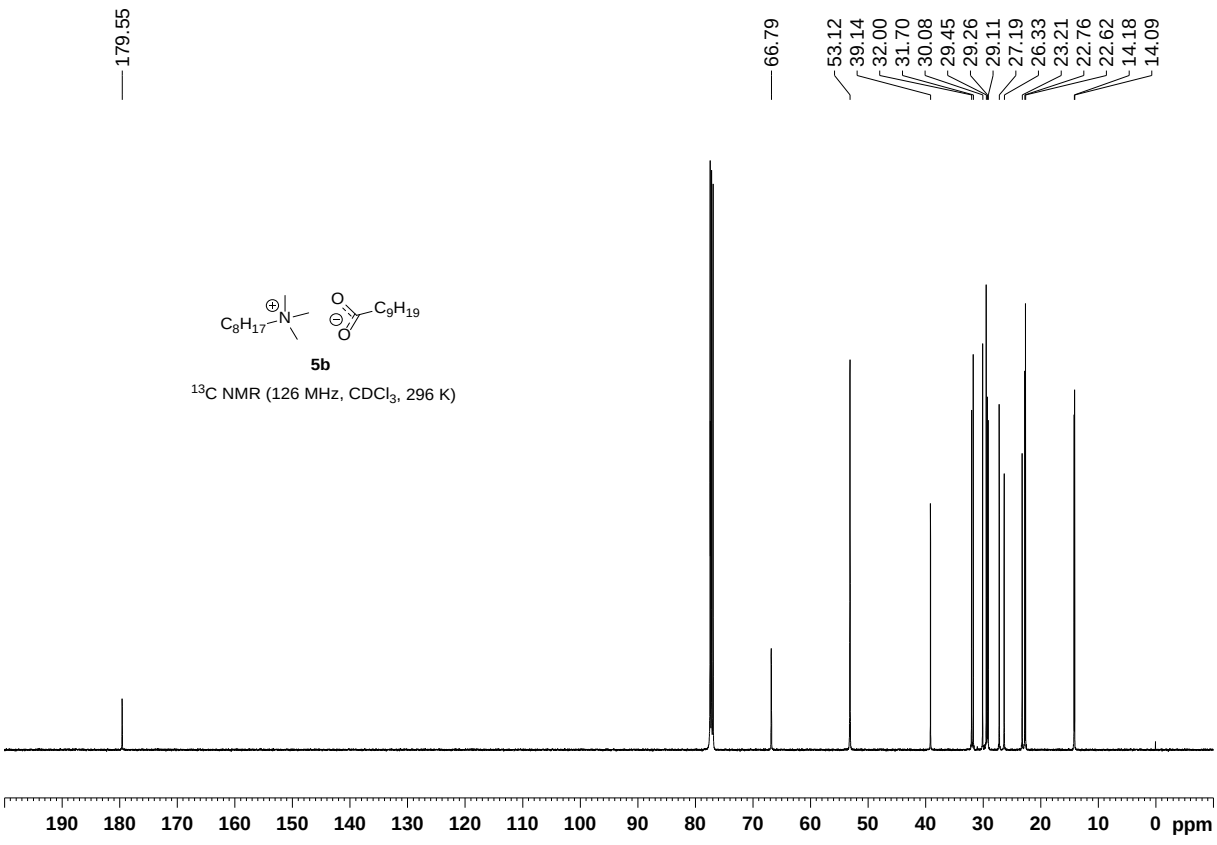
5a

^{13}C NMR (126 MHz, $CDCl_3$, 296 K)



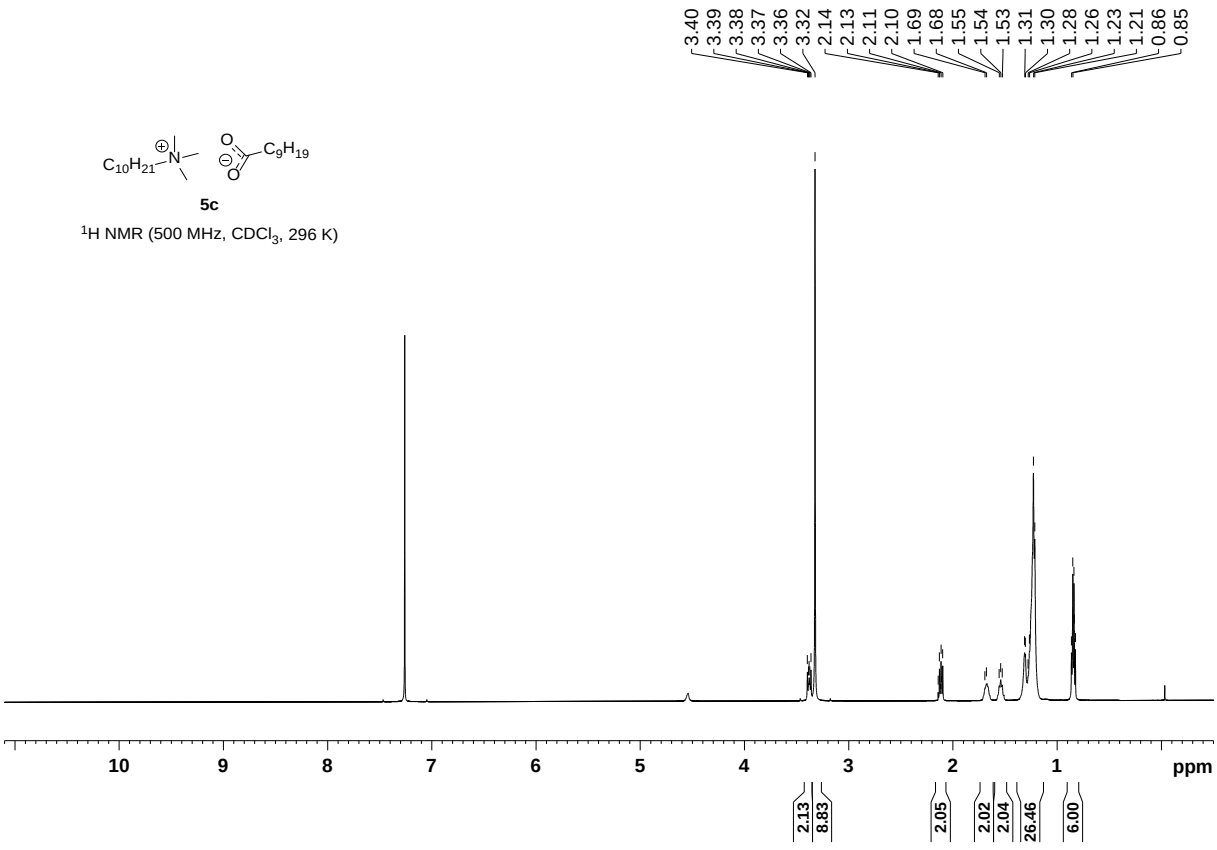
5b

^{1}H NMR (500 MHz, $CDCl_3$, 296 K)



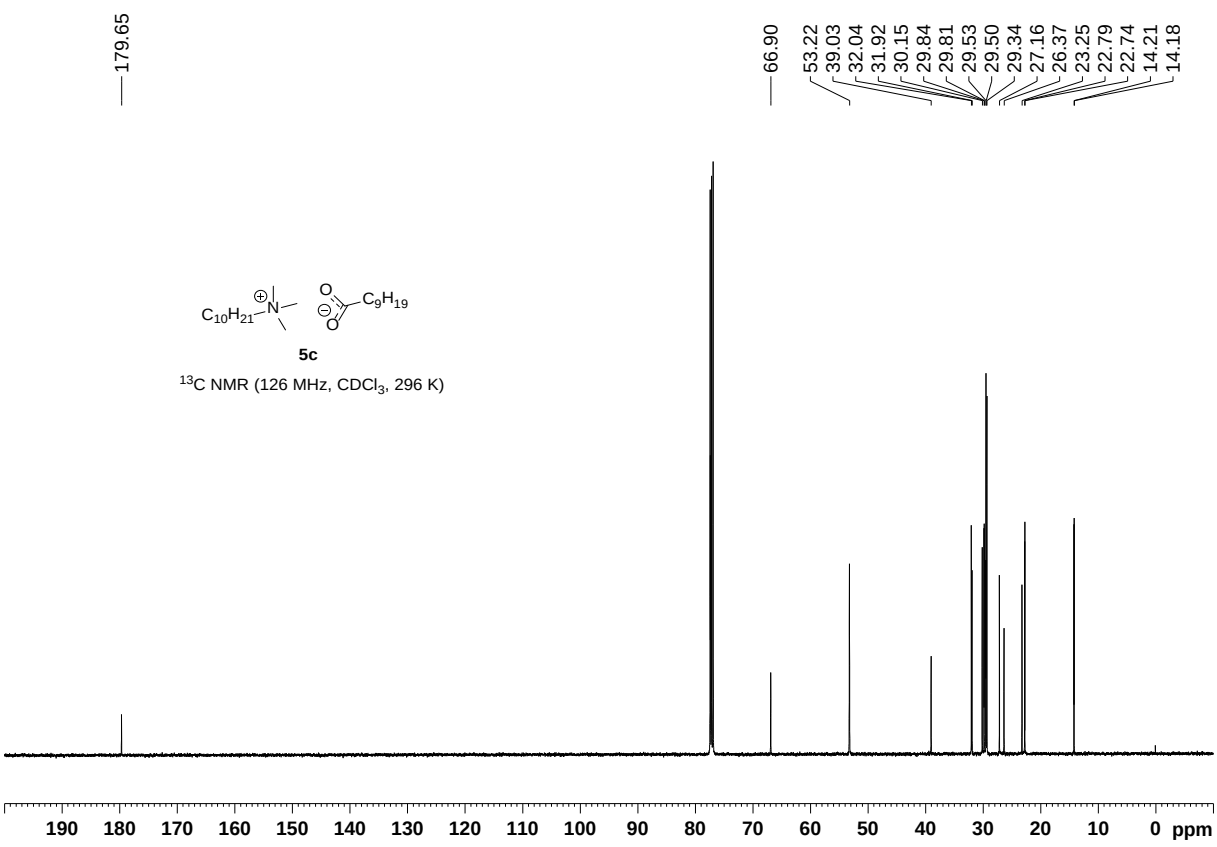
5b

^{13}C NMR (126 MHz, $CDCl_3$, 296 K)



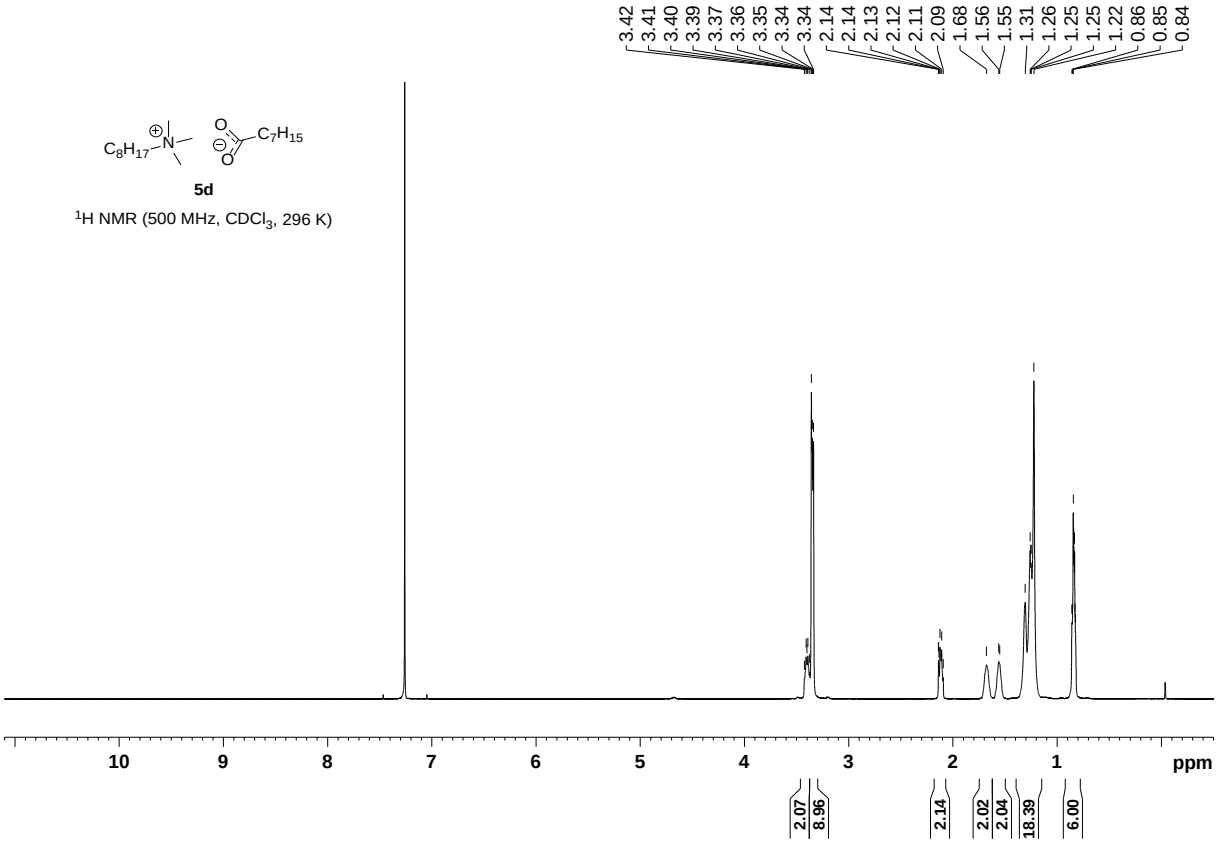
5c

^{1}H NMR (500 MHz, $CDCl_3$, 296 K)



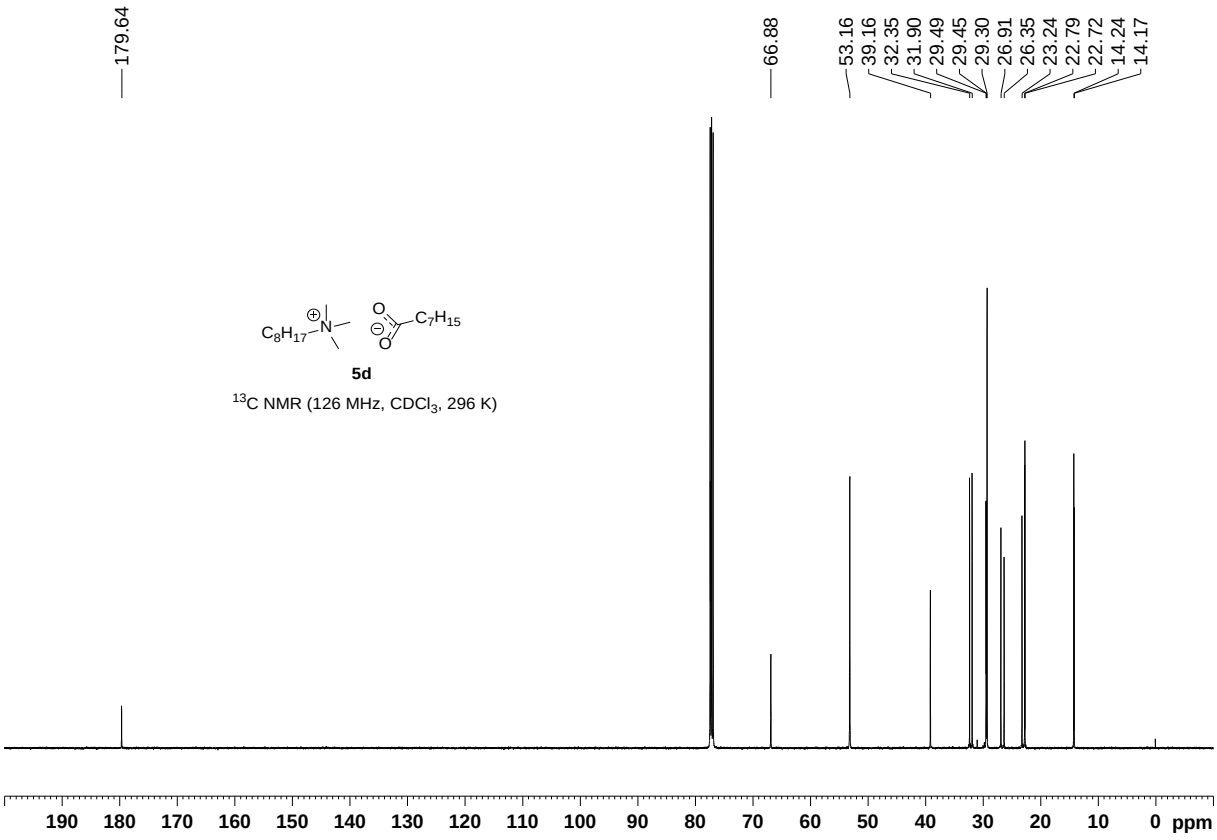
5c

^{13}C NMR (126 MHz, $CDCl_3$, 296 K)



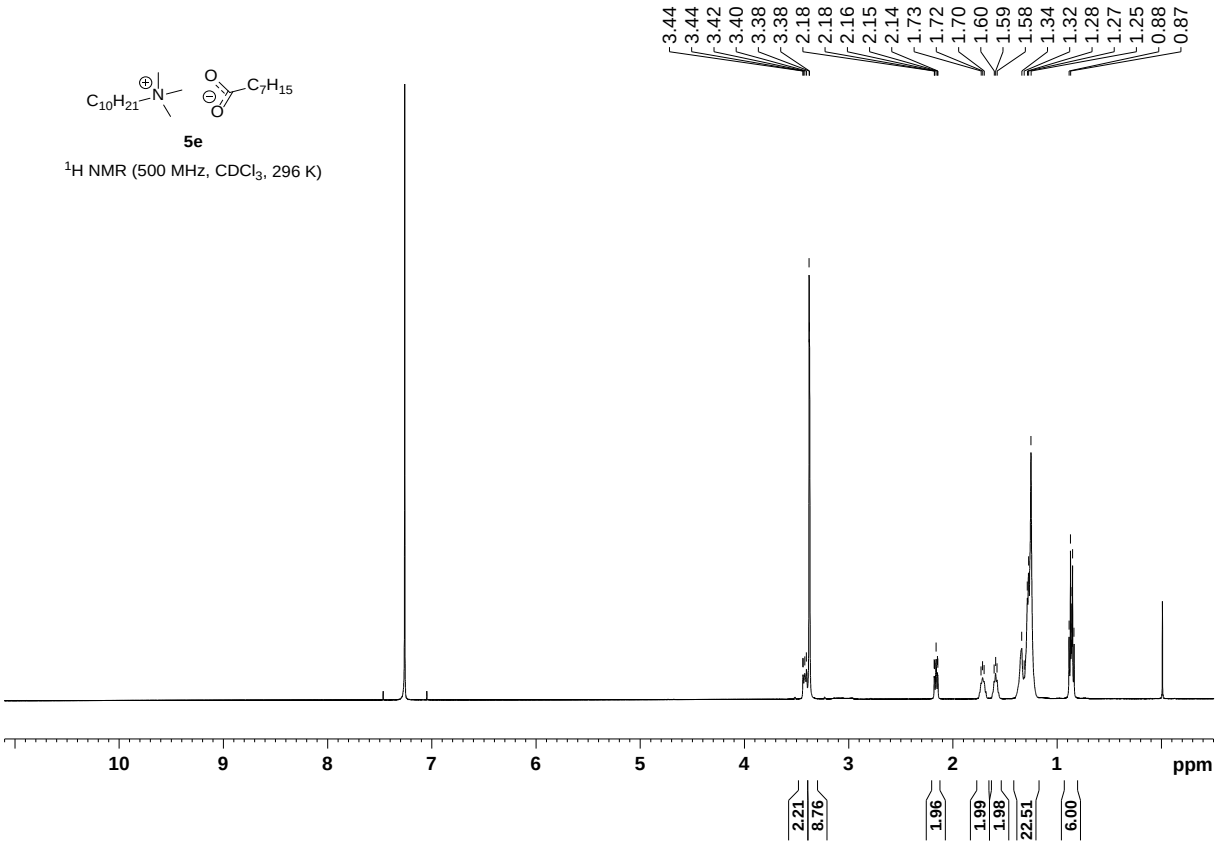
5d

^{1}H NMR (500 MHz, $CDCl_3$, 296 K)



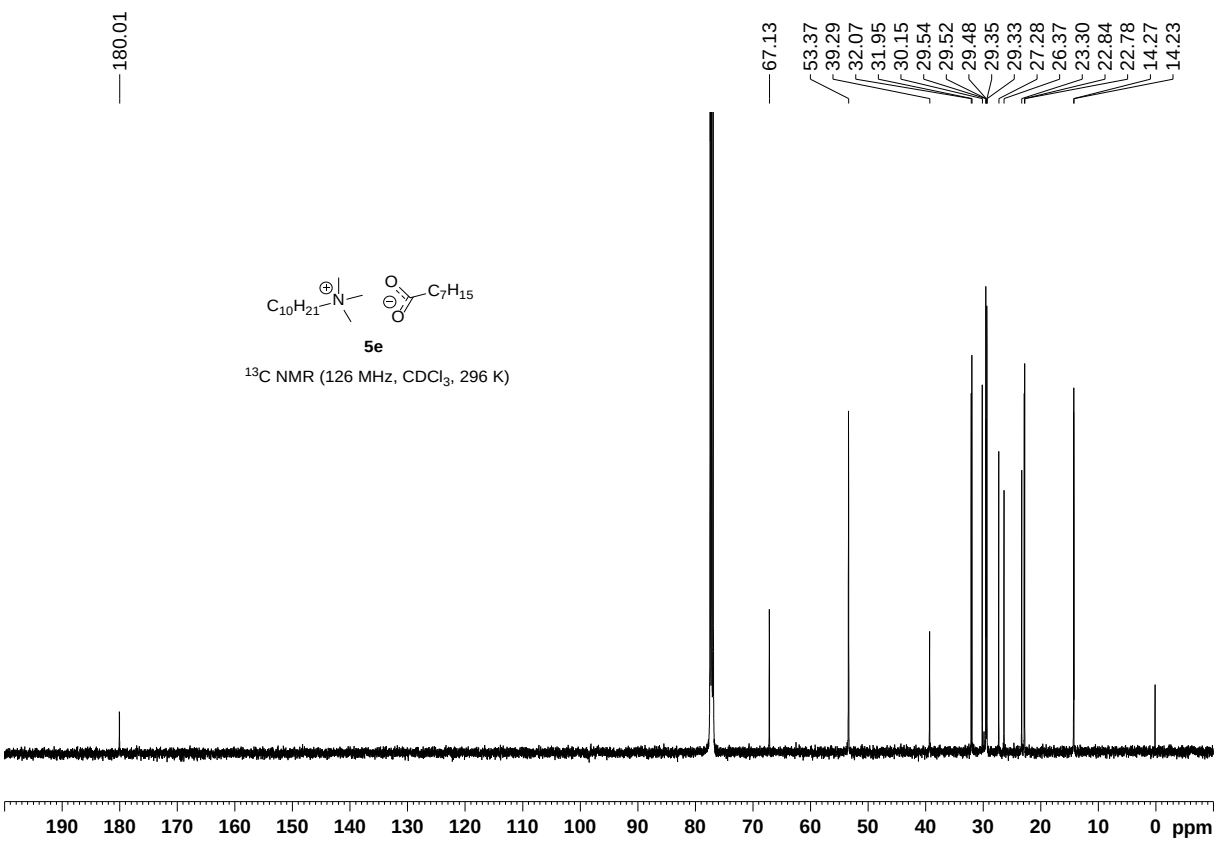
5d

^{13}C NMR (126 MHz, $CDCl_3$, 296 K)



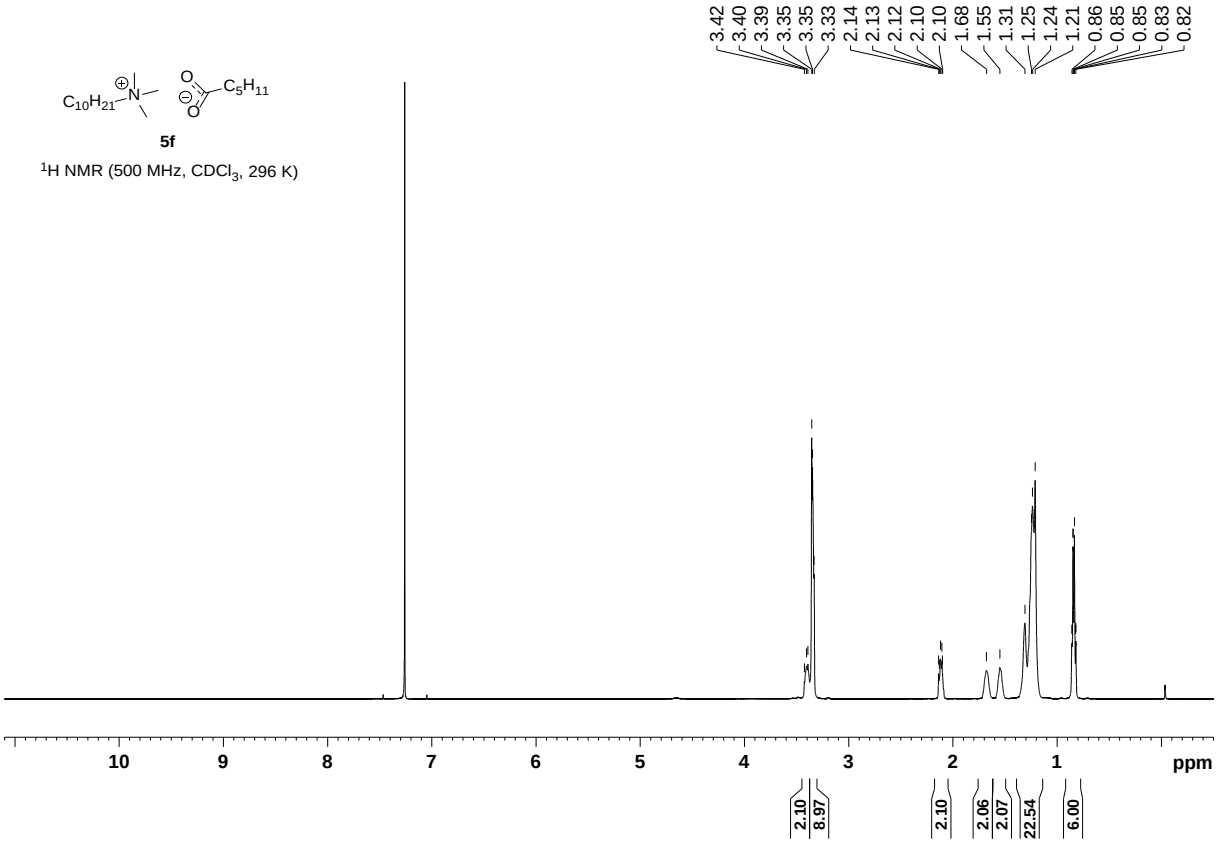
5e

^{1}H NMR (500 MHz, $CDCl_3$, 296 K)



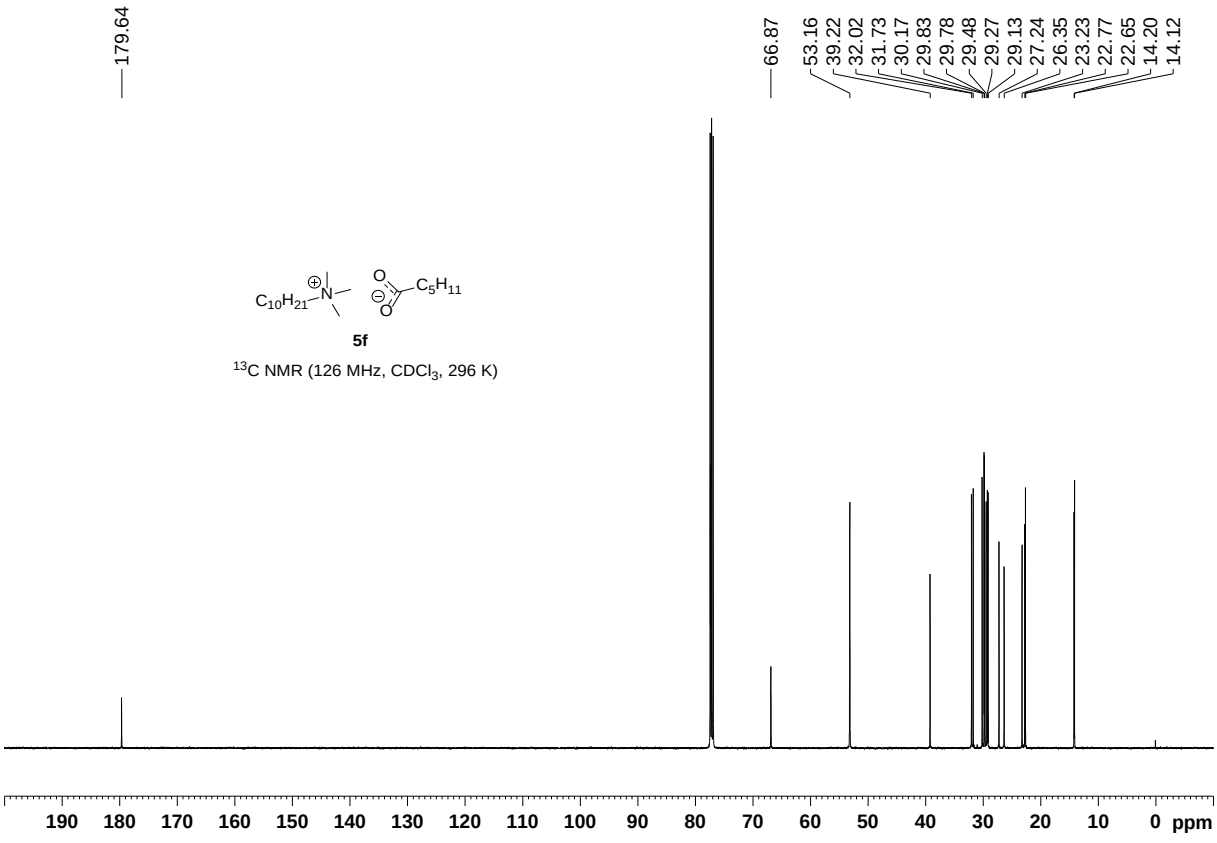
5e

^{13}C NMR (126 MHz, $CDCl_3$, 296 K)



5f

^{1}H NMR (500 MHz, $CDCl_3$, 296 K)



5f

^{13}C NMR (126 MHz, $CDCl_3$, 296 K)