

Influence of ion size on the stability of the smectic phase of ionic liquid crystals

Wudi Cao,^{a,b} Beeran Senthilkumar,^c Valerio Causin,^d Vincent P. Swamy,^{*c} Yanting Wang,^{*a,b} and Giacomo Saielli^{*d,e}

Synthetic procedures	p. 2
Spectral data	p. 5
NMR spectra	p. 10

^a CAS Key Laboratory of Theoretical Physics, Institute of Theoretical Physics, Chinese Academy of Sciences, 55 East Zhongguancun Road, P. O. Box 2735, Beijing 100190, China. Email: wangyt@itp.ac.cn

^b School of Physical Sciences, University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China.

^c Organic Chemistry Division, CSIR-National Chemical Laboratory, Dr Homi Bhabha Road, Pune 411008, India. E-mail: vp.swamy@ncl.res.in; Fax: +91 20 2590 2629; Tel: +91 20 2590 2313.

^d Department of Chemical Sciences, University of Padova, Via Marzolo, 1 – 35131, Padova, Italy.

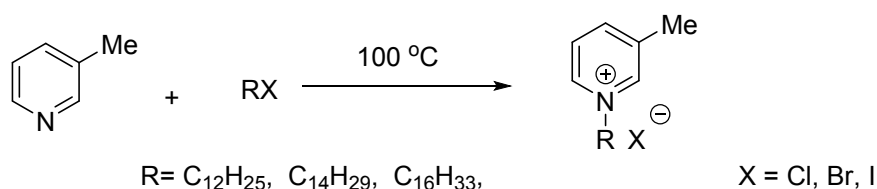
^e CNR Institute on Membrane Technology, Unit of Padova, Via Marzolo, 1 – 35131, Padova, Italy. Email: giacomo.saielli@unipd.it; giacomo.saielli@cnr.it

General information: All reagents were purchased from commercial sources (Sigma-Aldrich, Merck and Lancaster) and were used without further purification. Solvents used as reaction media were purchased from local sources and were used after distillation. Reactions were monitored using commercially available, pre-coated thin-layer chromatography (TLC) plates (Merck, silica gel 60 F₂₅₄, 0.25 mm) and compounds were visualized under ultraviolet light (254 nm) and by staining with *p*-anisaldehyde or iodine. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance 200 and 400 instrument operating at 200 MHz (¹H), 400 MHz (¹H) and 400 MHz (¹³C). Chemical shifts (δ) are quoted in ppm and referenced to internal TMS (δ 0.00 for ¹H NMR), DMSO-d₆ (δ 2.50 for ¹H NMR & 39.5 for ¹³C NMR) or CDCl₃ (δ 77.0 for ¹³C NMR); coupling constants (*J*) are quoted in Hz. Melting points were determined on a Buchi instrument and were uncorrected.

Experimental Section

Synthesis of 1-alkyl-3-methylpyridinium halides:

[C_{*n*}mPy]X (*n* = 12, 14, 16; X = Cl, Br, I), 1-dodecyl-3-methylpyridinium halide, 1-tetradecyl-3-methylpyridinium halide, and 1-hexadecyl-3-methylpyridinium halide were synthesised as shown in Scheme 1.



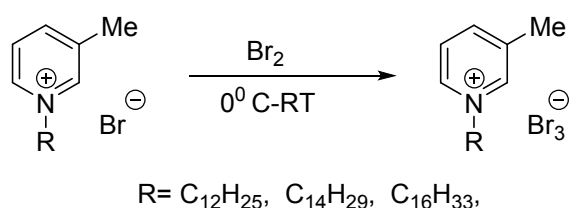
Scheme 1

[C_{*n*}mPy]X were synthesized by the reaction of 0.1 mole equivalents of 3-methylpyridine with an excess of the appropriate haloalkane (1.1 mole equivalents) at 100 °C for 24 hours. The excess haloalkane allows for the reaction to be stirred without additional solvents. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was evaporated under rotavapor to remove traces of starting material to obtain brownish viscous oil. To this was added 50 ml x 3 pet ether, stirred at room temperature for 1h and decanted to obtain ionic

liquid. This was further purified by adding 50 ml x 3 pet ether + ethyl acetate (1:0.5/1:1), stirred at room temperature for 1h and decanted to obtain pure ionic liquid.

Synthesis of ionic liquid 1-alkyl-3-methylpyridinium tribromide

[C_nmPy]Br₃ (*n* = 12, 14 & 16), 1-dodecyl-3-methylpyridinium tribromide, 1-tetradecyl-3-methylpyridinium tribromide, and 1-hexadecyl-3-methylpyridinium tribromide were synthesized as shown in Scheme 2.

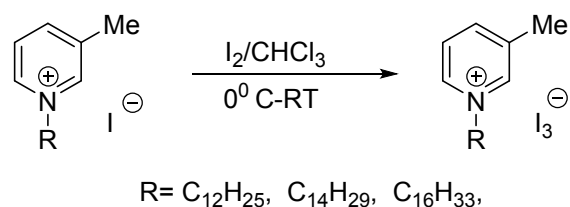


Scheme 2

In a fume cupboard, molecular bromine (0.038 mol) was added drop wise over 15 min to the corresponding 1-alkyl-3-methylpyridinium bromide [C_nmPy]Br (0.045 mol) with stirring and cooling in a ice bath. After removal of ice bath, the reaction was continued under stirring at room temperature for 2h. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was evaporated under reduced pressure over 5 h at 60 °C on rotavapor to afford a deep red liquid in quantitative yields (95-98%).

Synthesis of ionic liquid 1-alkyl-3-methylpyridinium triiodide

[C_nmPy]I₃ (*n* = 12, 14, 16), 1-dodecyl-3-methylpyridinium triiodide, 1-tetradecyl-3-methylpyridinium triiodide, and 1-hexadecyl-3-methylpyridinium triiodide were synthesized as shown in Scheme 3.

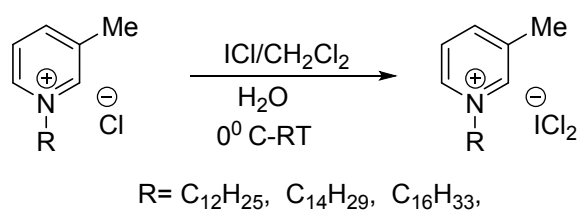


Scheme 3

Molecular iodine (0.072 mol) was added drop wise over 15 min to the corresponding 1-alkyl-3-methylpyridinium iodide [C_nmPy]I (0.036 mol), dissolved in 50ml

chloroform, with stirring and cooling in a ice bath. The reaction was continued for 2h in an ice bath and then left to attain room temperature and continued at room temperature for additional 10h. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was evaporated under reduced pressure over 5 h at 60 °C on rotavapor to afford a deep red liquid. This was further purified by giving wash with pet ether, followed by (50ml x 3) pet ether + ethyl acetate (90:10) mixture to afford red oil in quantitative yields (95-98%).

Synthesis of ionic liquid 1-alkyl-3-methylpyridinium dichloroiodate



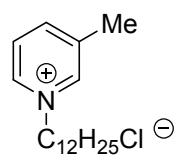
Scheme 4

[C_nmPy]X (*n* = 12, 14, 16; X = ICl₂), 1-dodecyl-3-methylpyridinium dichloroiodate, 1-tetradecyl-3-methylpyridinium dichloroiodate, and 1-hexadecyl-3-methylpyridinium dichloroiodate were synthesized as shown in Scheme 4.

A black solution of ICl (19.39 mmol) in dichloromethane (35 ml), was added drop wise to an ice cold solution of 1-alkyl-3-methylpyridinium chloride (16.16 mmol) in water (16 ml) under stirring and then left to attain room temperature. After the reaction mixture was stirred for 1 hour at room temperature, the dichloromethane layer was separated and dried with sodium sulphate and then evaporated under vacuum to afford dark reddish brown ionic liquid 1-alkyl-3-methylpyridinium dichloroiodate in quantitative yields (95-98%). This ionic liquid was stable and stored in dark at 10 °C (in refrigerator) for several months without any change in color, loss of reactivity and degradation (checked by ¹H NMR).

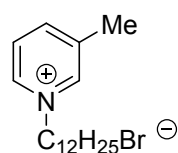
The NMR (¹H and ¹³C) data of compounds(a–p) are given as:

1. **1-dodecyl-3-methylpyridinium chloride¹ (a)**: Dark red viscous semi-solid.



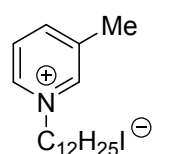
¹H NMR (200 MHz, CDCl₃ δ/ppm): 0.82 (t, 3H, J=6.19 Hz), 1.21 (m, 19H), 2.03 (m, 3H), 2.62 (s, 3H), 4.89 (t, 2H, J=5.56 Hz), 8.01 (s, 1H), 8.23 (d, 1H, J=7.7 Hz), 9.20 (s, 2H). ¹³C NMR (125 MHz, CDCl₃, δ/ppm): 14.01, 18.62, 22.55, 26.01, 29.03, 29.20, 29.28, 29.43, 29.48, 31.77, 31.80, 61.82, 127.86, 139.45, 142.32, 144.27, 145.59.

2. **1-dodecyl-3-methylpyridinium bromide² (b)**: Dark red viscous semi-solid.



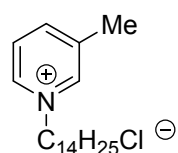
¹H NMR (200 MHz, CDCl₃ δ/ppm): 0.82 (t, 3H, 5.75 Hz), 1.22 (s, 18H), 2.16-1.96 (m, 2H), 2.64 (s, 3H), 4.96 (t, 2H, 6.48 Hz), 7.96 (t, 1H, 7.71 Hz), 8.22 (d, 1H, 7.96 Hz), 9.19 (d, 1H, 5.83 Hz), 9.33 (s, 1H). ¹³C NMR (125 MHz, CDCl₃, δ/ppm): 14.01, 18.63, 22.55, 25.98, 28.97, 29.20, 29.25, 29.40, 29.46, 31.77, 31.85, 61.79, 127.77, 139.52, 142.18, 144.38, 145.52.

3. **1-dodecyl-3-methylpyridinium iodide³ (c)**: Dark red liquid. **(Give integration in NMR)**



¹H NMR (200 MHz, CDCl₃, δ/ppm): 0.82 (t, 3H, 5.75 Hz), 1.22 (m, 18H), 2.16-1.96 (sextet, 2H), 2.64 (s, 3H), 4.82 (t, 2H, 6.4 Hz), 7.96 (t, 1H, 7.71s Hz), 8.26 (d, 1H, 7.96 Hz), 9.08 (d, 1H, 5.83 Hz), 9.28 (s, 1H). ¹³C NMR (125 MHz, CDCl₃, δ/ppm): 13.98, 18.67, 22.52, 25.90, 28.92, 29.17, 29.21, 29.37, 29.43, 31.71, 31.73, 61.77, 127.83, 139.57, 141.83, 144.15, 145.83.

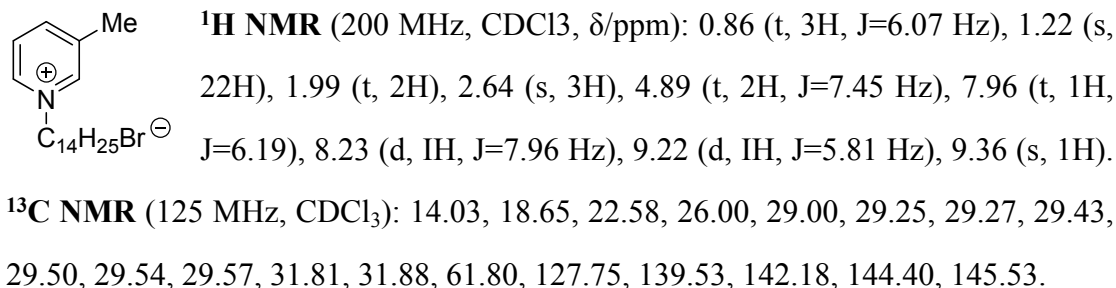
4. **1-tetradecyl-3-methylpyridinium chloride⁴ (d)**: Orange semi-solid.



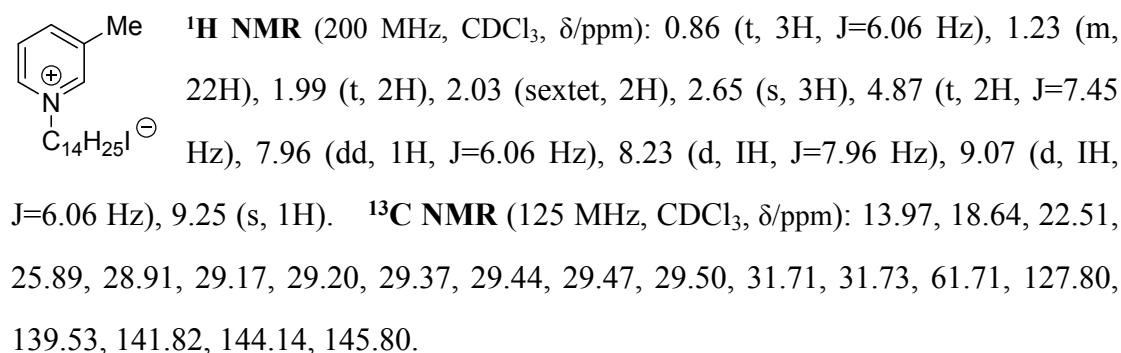
¹H NMR (200 MHz, CDCl₃, δ/ppm): 0.82 (t, 3H, J=6.06 Hz), 1.22 (s, 18H), 2.16-1.96 (sextet, 2H), 2.29 (2H), 2.62 (s, 3H), 4.90 (t, 2H, J=7.33 Hz), 7.96 (t, 1H, J=6.07 Hz), 8.24 (d, 1H, J=7.83 Hz), 9.30 (d, 1H, J=5.69 Hz), 9.40 (s, 1H). ¹³C NMR (125 MHz, CDCl₃, δ/ppm): 145.29, 144.58, 142.39, 139.43, 127.74, 61.67, 31.88, 31.72, 29.49, 29.45, 29.42, 29.36, 29.20, 29.17,

28.95, 25.96, 22.49, 18.56, 13.95.

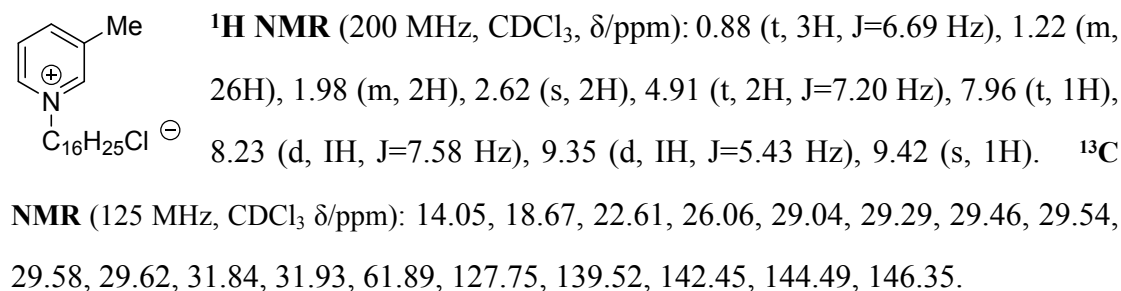
5. 1-tetradecyl-3-methylpyridinium bromide² (e): White solid, M.P. 78-79 °C.



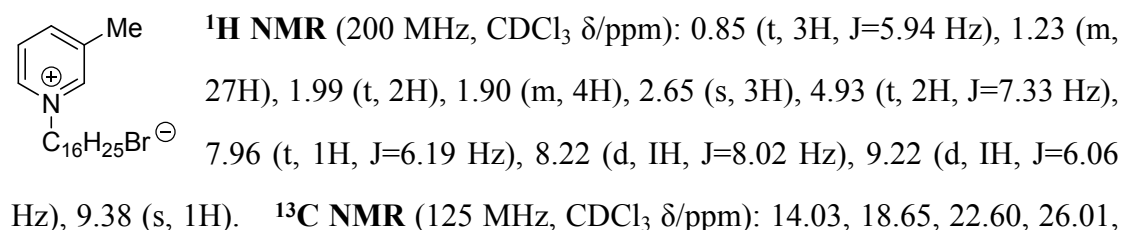
6. 1-tetradecyl-3-methylpyridinium iodide (f): Dark brown solid, M.P. 44-45 °C.



7. 1-hexadecyl-3-methylpyridinium chloride⁴ (g): White creamish solid, M.P. 68-69 °C.

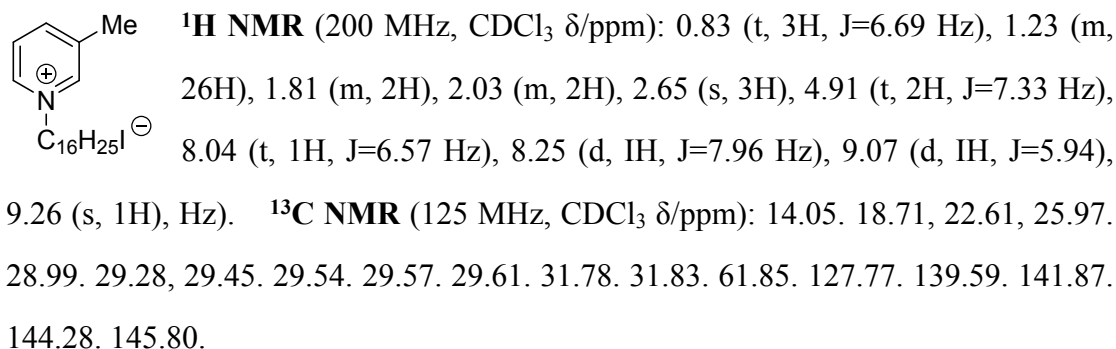


8. 1-hexadecyl-3-methylpyridinium bromide⁵ (h): White solid, M.P. 49-50 °C.

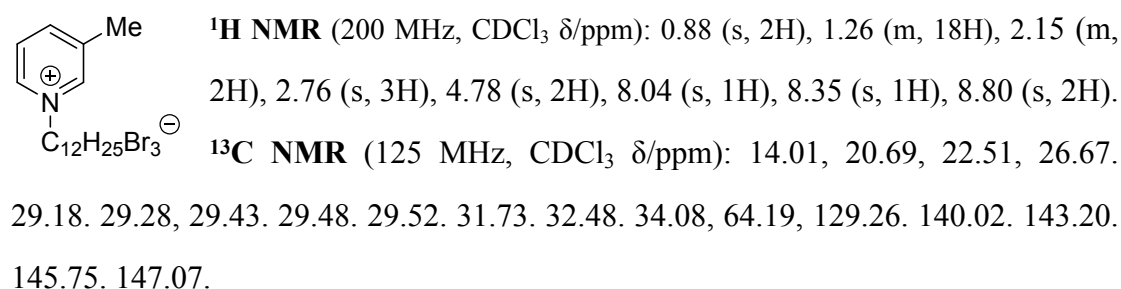


29.01, 29.27, 29.44, 29.52, 29.57, 29.60, 31.83, 31.88, 61.83, 127.73, 139.54, 142.19, 144.42, 145.52,

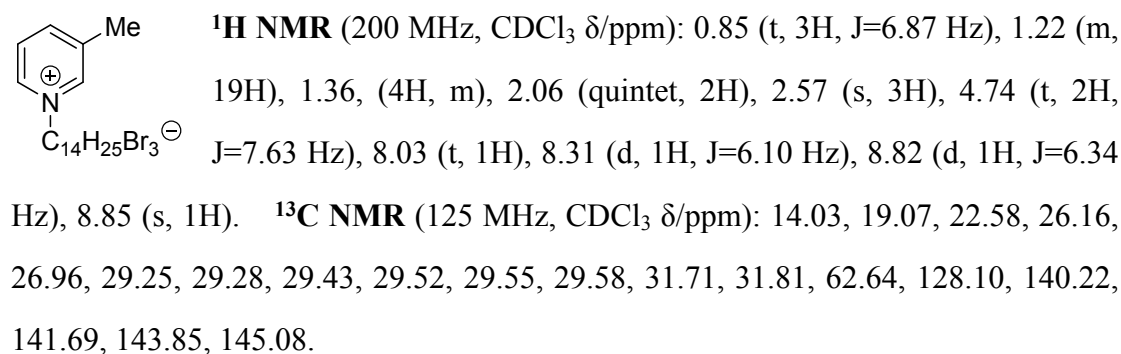
9. 1-hexadecyl-3-methylpyridinium iodide⁶ (i): Pale yellow solid, M.P. 58-59 °C.



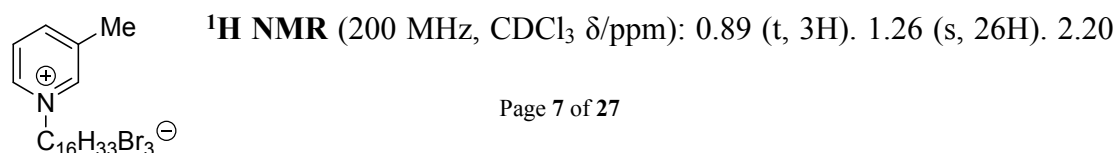
10. 1-dodecyl-3-methylpyridinium tribromide (j): Dark red liquid.



11. 1-tetradecyl-3-methylpyridinium tribromide (k): Red semi-solid.

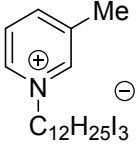


12. 1-hexadecyl-3-methylpyridinium tribromide (k): White solid, M.P. 58-59 °C.

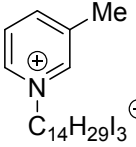


(s, 2H), 2.79 (s, 3H). 4.83 (s, 2H). 8.04 (s, 1H). 8.36 (s, 1H), 8.89 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 δ/ppm): 14.03.18.65, 22.60, 26.01. 29.01. 29.27, 29.44. 29.52. 29.57. 29.60, 31.83. 31.88, 61.83, 127.73. 139.54. 142.19. 144.42. 145.52.

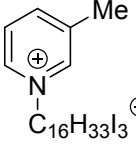
13. 1-dodecyl-3-methylpyridinium triiodide (l): Dark red liquid.

 ^1H NMR (200 MHz, CDCl_3 δ/ppm): 0.87 (t, 3H, $J=6.19$), 1.25 (s, 18H), 2.15 (sextet, 2H), 2.72 (s, 3H), 4.73 (t, 2H, $J=7.58$), 8.09 (t, 1H, $J=6.82$), 8.39 (d, 1H, $J=8.21$), 8.57 (s, 1H), 8.64 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3 δ/ppm): 14.14, 19.68, 22.66, 26.34, 29.01, 29.32, 29.49, 29.58, 31.68, 31.70, 31.87, 63.32, 128.53, 140.69, 141.63, 143.88, 146.60.

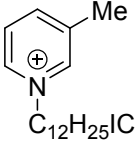
14. 1-tetradecyl-3-methylpyridinium triiodide (m): Dark red liquid.

 ^1H NMR (200 MHz, CDCl_3 δ/ppm): 0.84 (t, 3H, $J=6.57$), 1.25 (s, 22H), 2.17 (m, 2H), 2.72 (s, 3H), 4.74 (t, 2H, $J=7.71$), 8.09 (t, 1H, $J=6.57$), 8.39 (d, 1H, $J=7.63$), 8.67 (d, 2H). ^{13}C NMR (125 MHz, CDCl_3 δ/ppm): 14.12, 19.72, 22.64, 26.36, 29.02, 29.32, 29.36, 29.51, 29.61, 29.65, 31.71, 31.86, 63.28, 128.57, 140.66, 141.63, 143.87, 146.64.

15. 1-hexadecyl-3-methylpyridinium triiodide (m): Dark brown solid, M.P. 40-41 $^\circ\text{C}$.

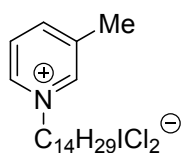
 ^1H NMR (200 MHz, CDCl_3 δ/ppm): 0.87 (s, 3H), 1.25 (s, 26H), 2.12 (s, 3H), 2.73 (s, 3H), 4.64 (t, 3H), 8.03 (t, H), 8.39 (d, 1H), 8.86 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 δ/ppm): 14.11, 19.64, 22.66, 26.35, 29.01, 29.34, 29.51, 29.60, 29.65, 29.68, 31.68, 31.89, 63.34, 128.52, 140.71, 141.62, 143.88, 146.58,

16. 1-dodecyl-3-methylpyridinium dichloroiodate (n): Dark red liquid.

 ^1H NMR (200 MHz, CDCl_3 δ/ppm): 0.87 (t, 3H), 1.26 (s, 18H), 2.17-2.04 (m, 2H), 2.74 (s, 3H), 4.67 (s, 2H), 8.06 (s, 1H), 8.38 (s, 1H), 8.65 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 , δ/ppm): 14.07,

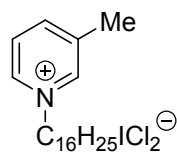
19.51, 22.61, 26.34, 29.00, 29.25, 29.31, 29.45, 29.53, 31.82, 31.90, 63.35, 128.51, 140.65, 141.78, 144.27, 146.51.

17. 1-tetradecyl-3-methylpyridinium dichloroiodate (o): Dark red liquid.



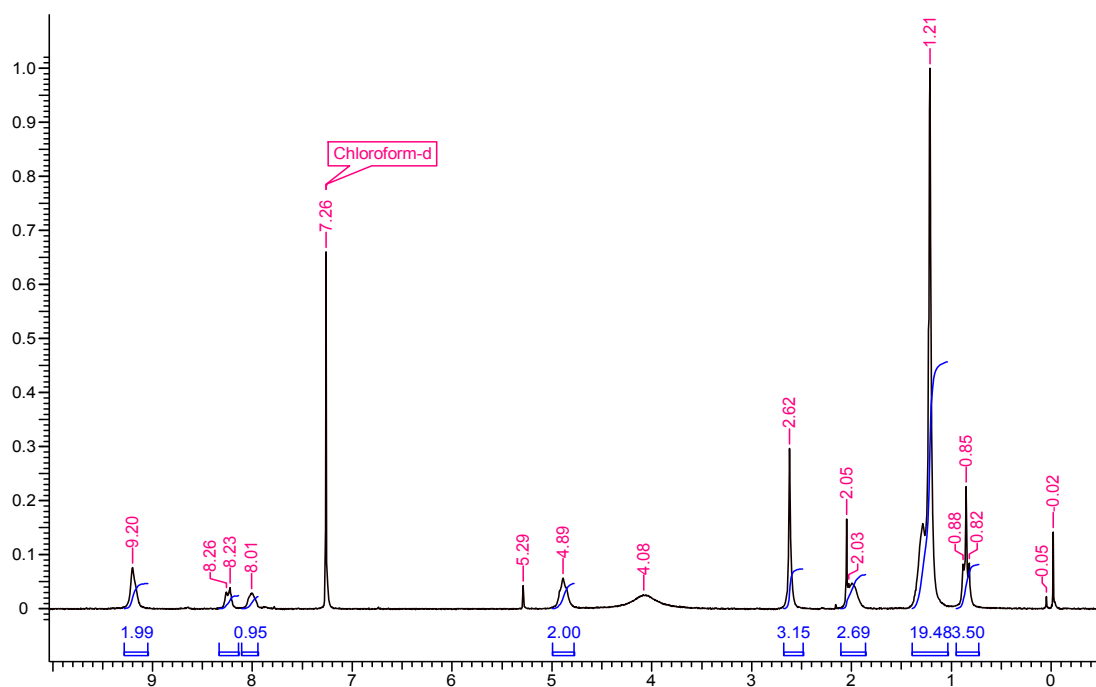
¹H NMR (200 MHz, CDCl₃ δ/ppm): 0.87 (t, 3H, J=6.06 Hz), 1.25 (m, 24H), 2.09 (t, 2H), 2.72 (s, 3H), 4.67 (t, 2H, J=7.20 Hz), 8.04 (t, J=6.32 Hz, 1H), 8.34 (d, 1H, J=7.83 Hz), 8.70 (t, 2H). **¹³C NMR** (125 MHz, CDCl₃, δ/ppm): 14.04, 19.19, 22.58, 26.23, 28.95, 29.25, 29.28, 29.43, 29.55, 29.58, 31.74, 31.81, 62.89, 128.26, 140.55, 141.49, 143.90, 146.31.

15. 1-hexadecyl-3-methylpyridinium dichloroiodate (p): Pale yellow solid, M.P. 58-59 °C.

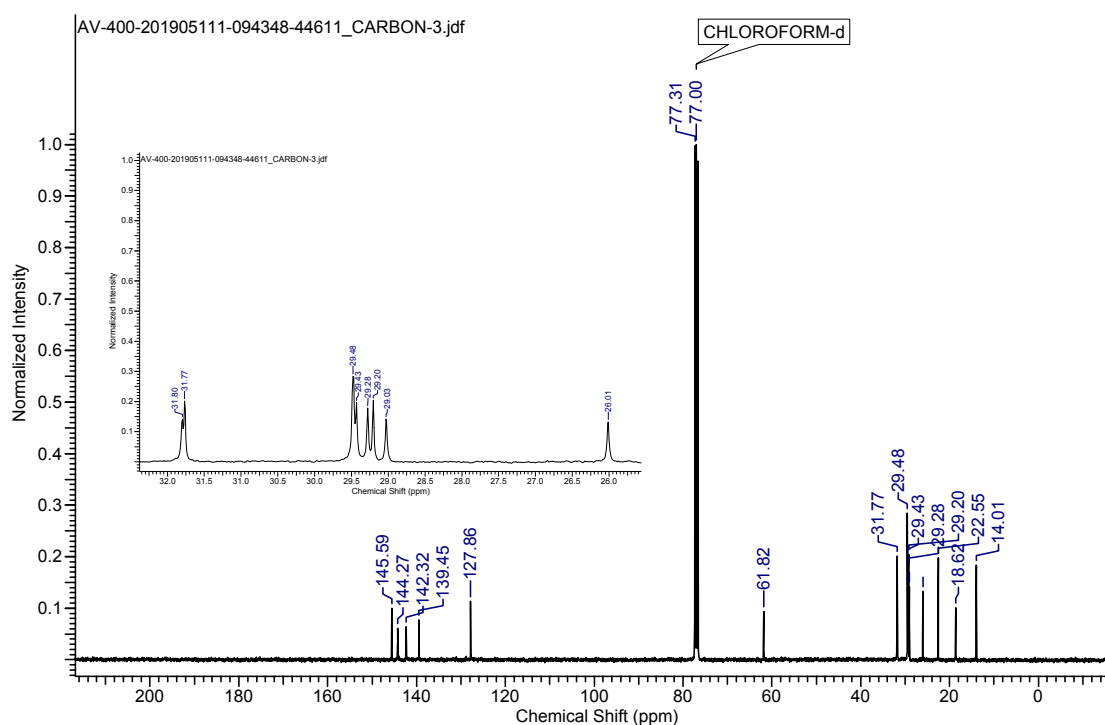


¹H NMR (200 MHz, CDCl₃ δ/ppm): 0.83 (t, 3H, J=6.87 Hz), 1.19 (m, 24 H), 1.99 (quintet, 2H), 2.20 (m, 3H), 2.62 (s, 3H), 4.88 (t, 2H, J=7.33 Hz), 8.01 (dd, J=7.78 Hz, 1H), 8.23 (d, 1H, J=8.24 Hz), 9.19 (d, 1H, J=5.95 Hz), 9.34 (s, 1H). **¹³C NMR** (125 MHz, CDCl₃, δ/ppm): 14.05, 20.03, 22.60, 26.54, 29.12, 29.27, 29.37, 29.50, 29.57, 29.62, 31.83, 32.23, 64.13, 128.84, 140.67, 142.51, 145.12, 146.69.

1. 1-Dodecyl-3-methylpyridinium chloride (a)

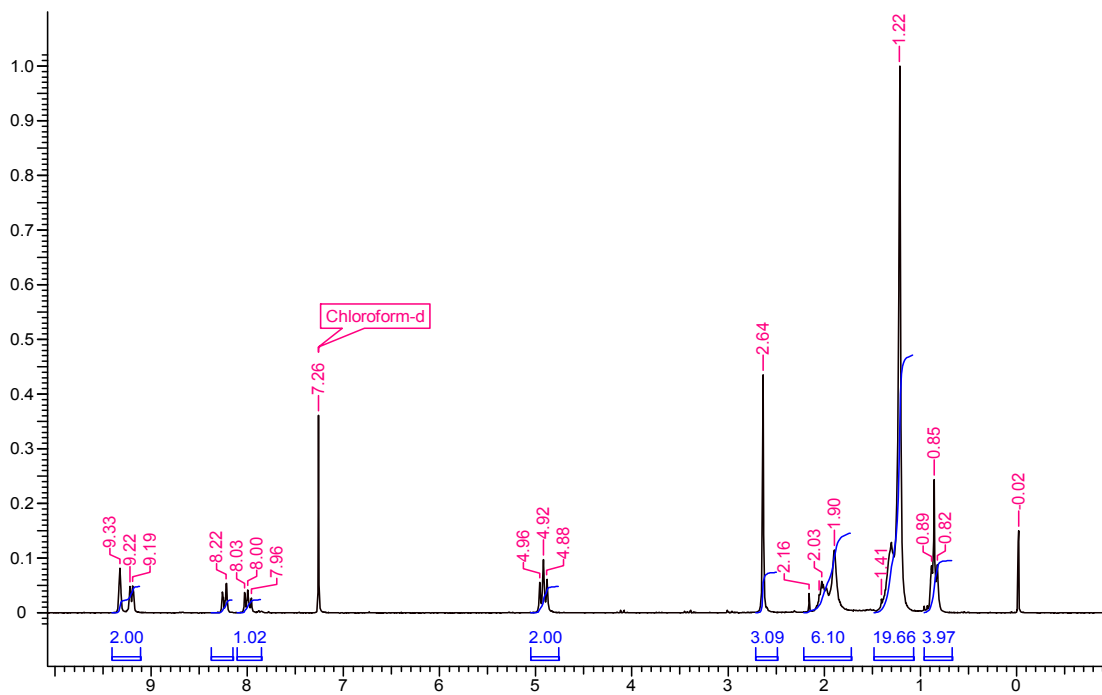


¹H NMR of 1-dodecyl-3-methylpyridinium chloride

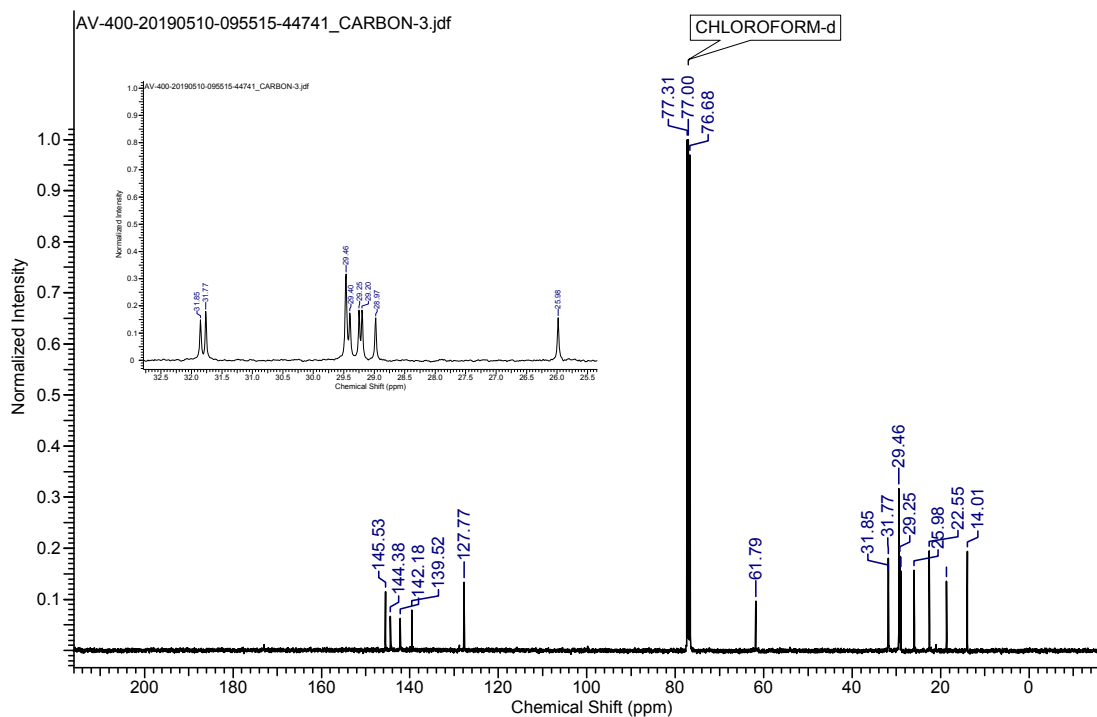


¹³C NMR of 1-dodecyl-3-methylpyridinium chloride

2. 1-dodecyl-3-methylpyridinium bromide (b)

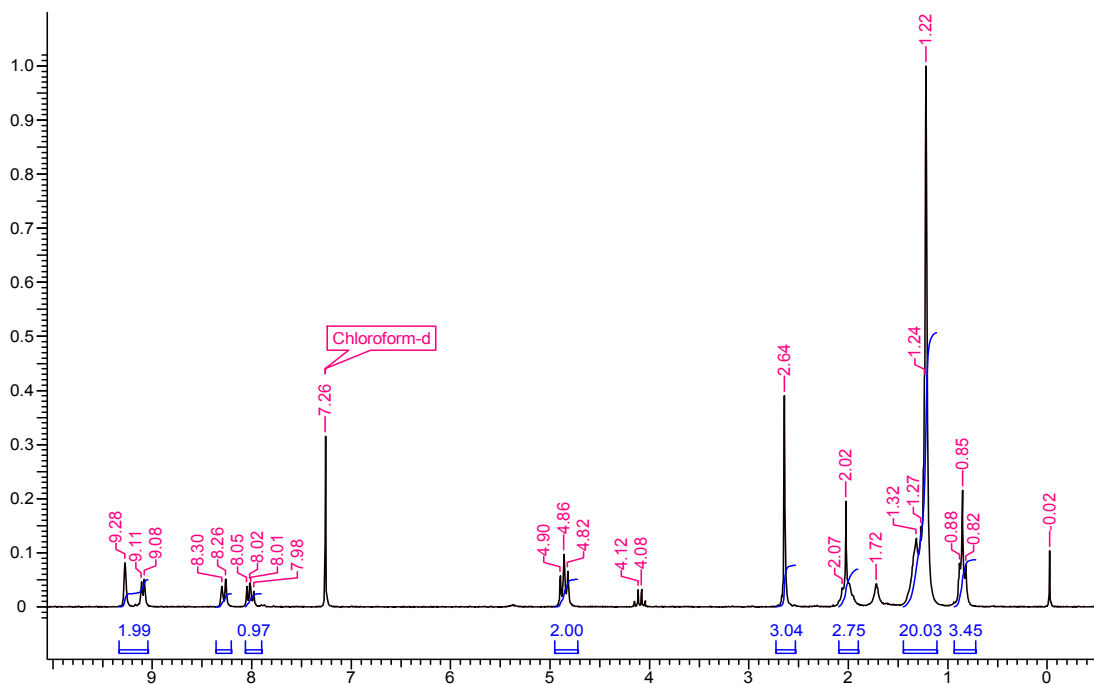


¹H NMR of 1-dodecyl-3-methylpyridinium bromide

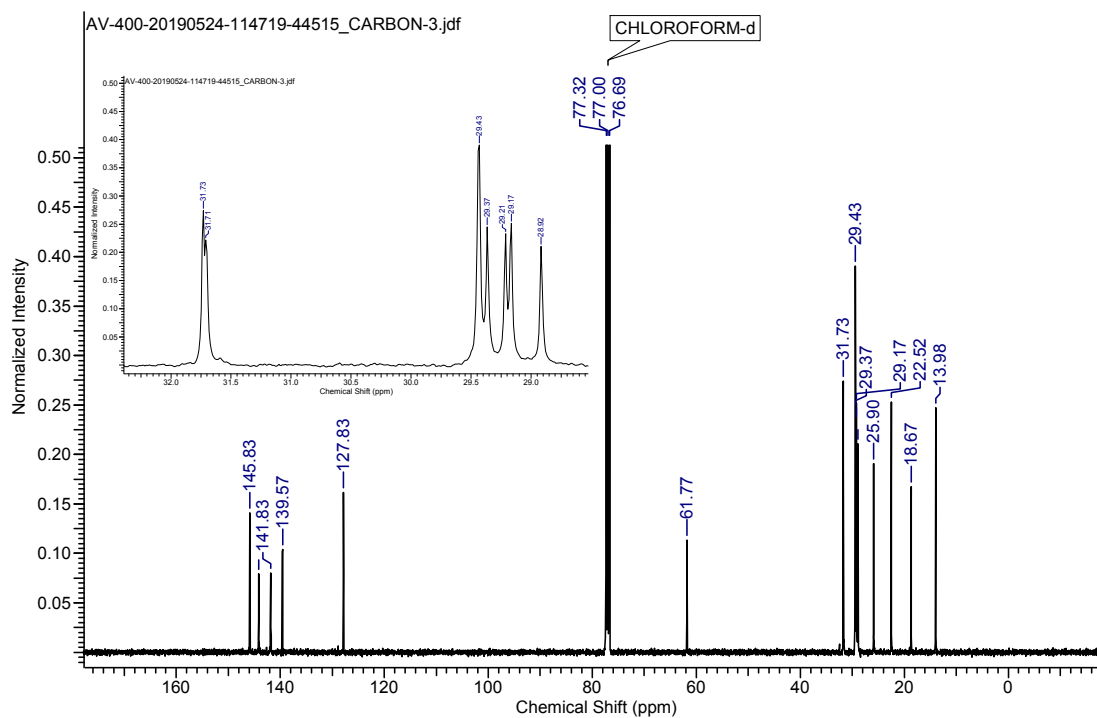


¹³C NMR of 1-dodecyl-3-methylpyridinium bromide

3. 1-dodecyl-3-methylpyridinium iodide (c)

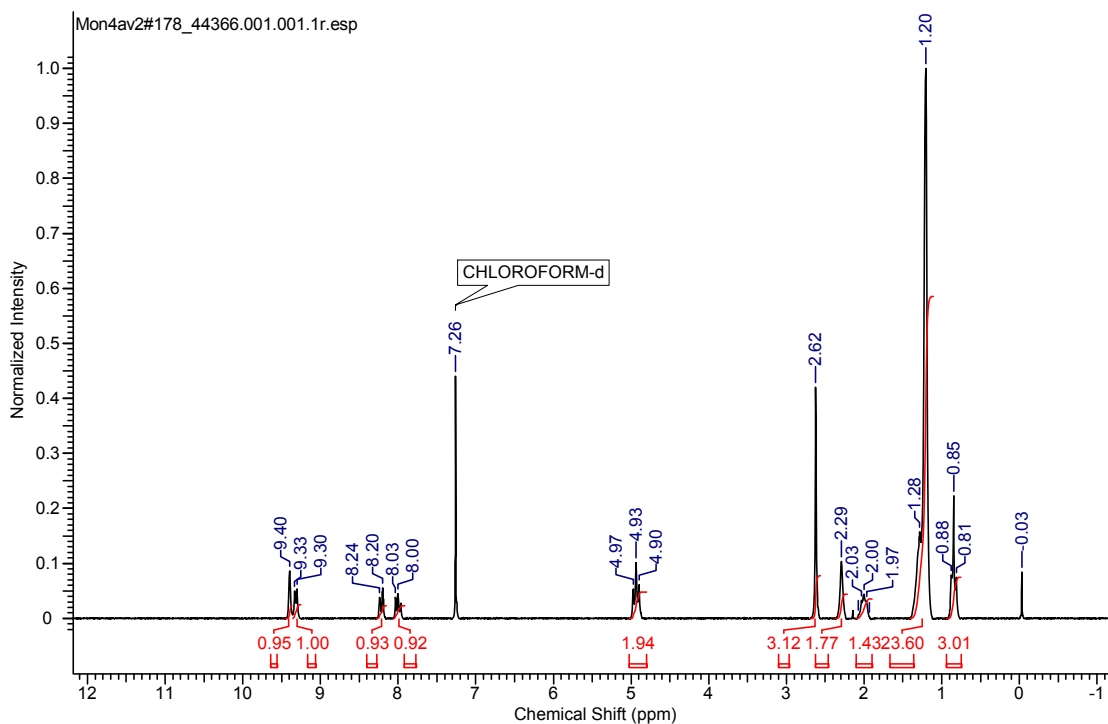


¹H NMR of 1-dodecyl-3-methylpyridinium iodide

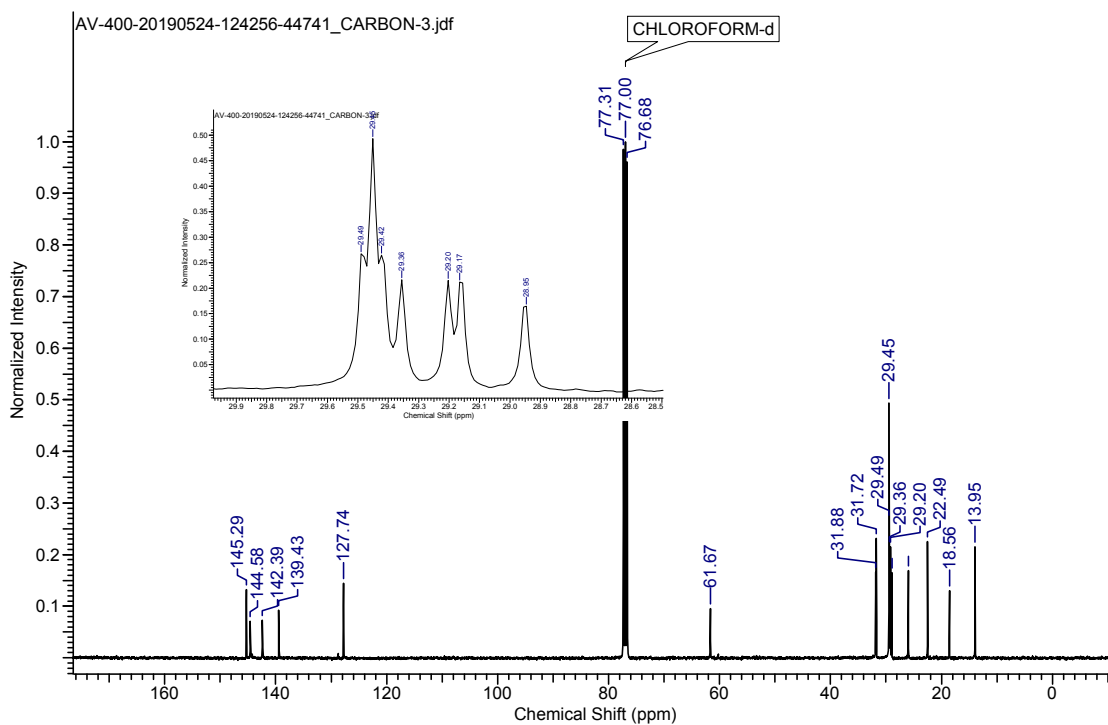


¹³C NMR of 1-dodecyl-3-methylpyridinium iodide

4. 1-tetradecyl-3-methylpyridinium chloride (d)

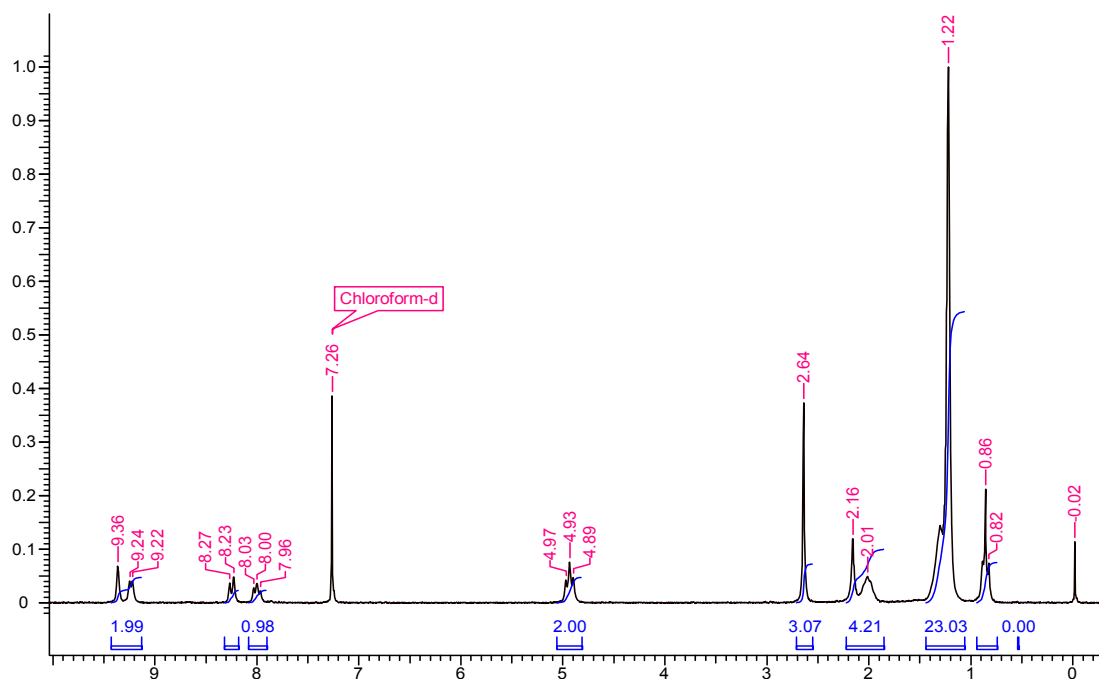


¹H NMR of 1-tetradecyl-3-methylpyridinium chloride

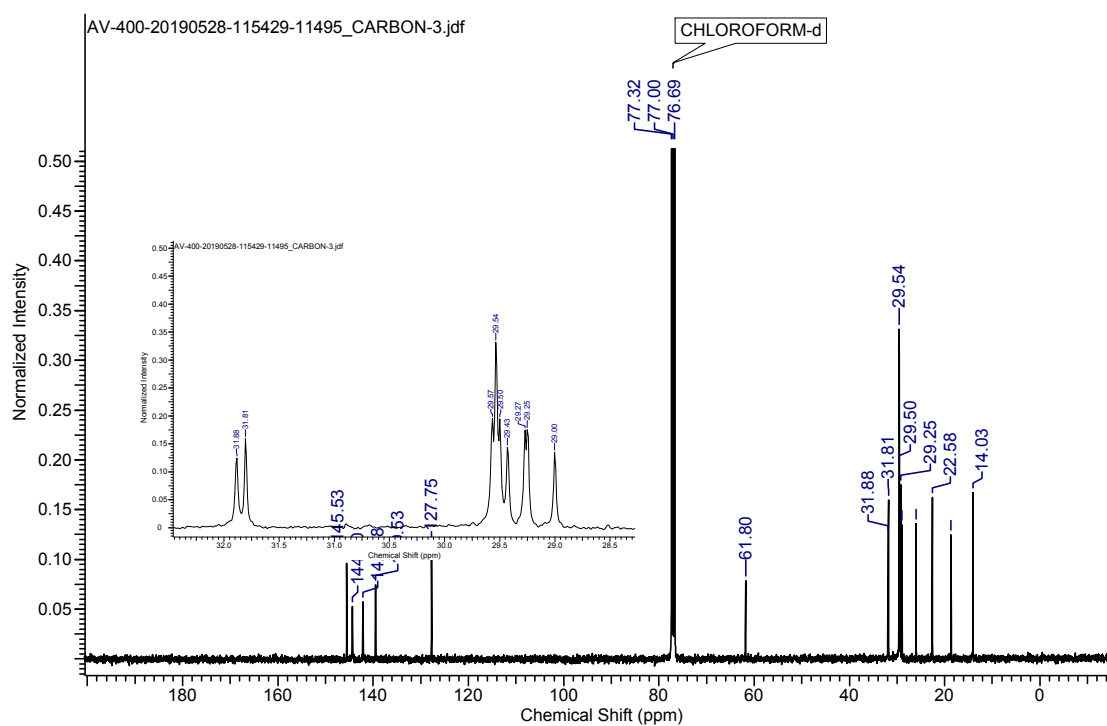


¹³C NMR of 1-tetradecyl-3-methylpyridinium chloride

5. 1-tetradecyl-3-methylpyridinium bromide (e)

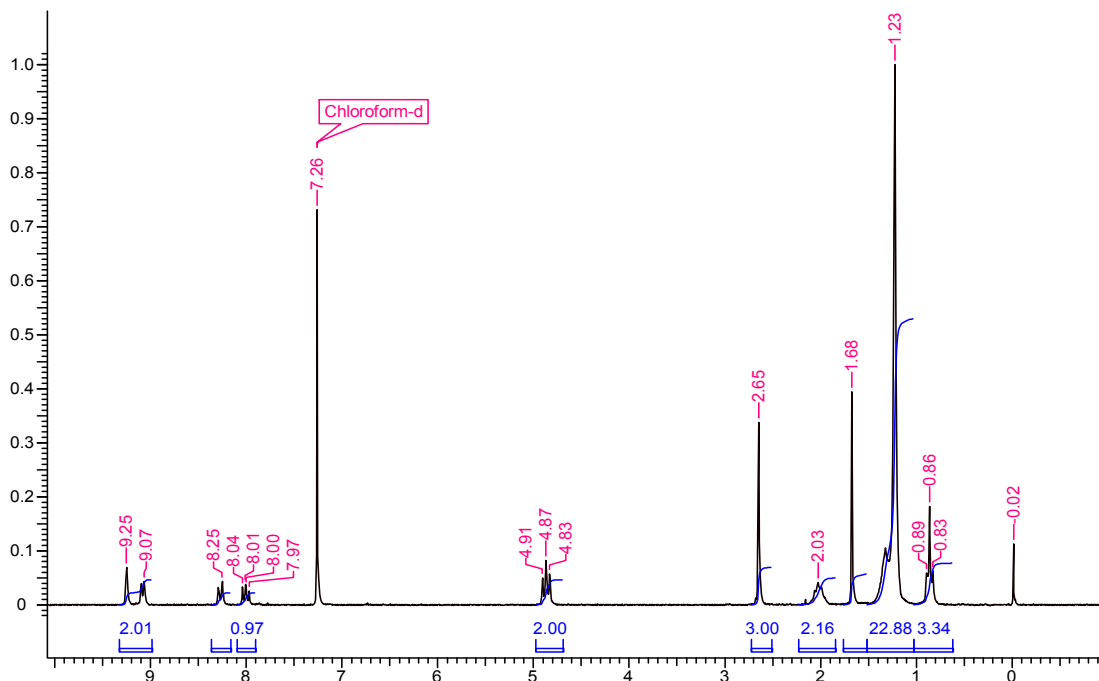


¹H NMR of 1-tetradecyl-3-methylpyridinium bromide

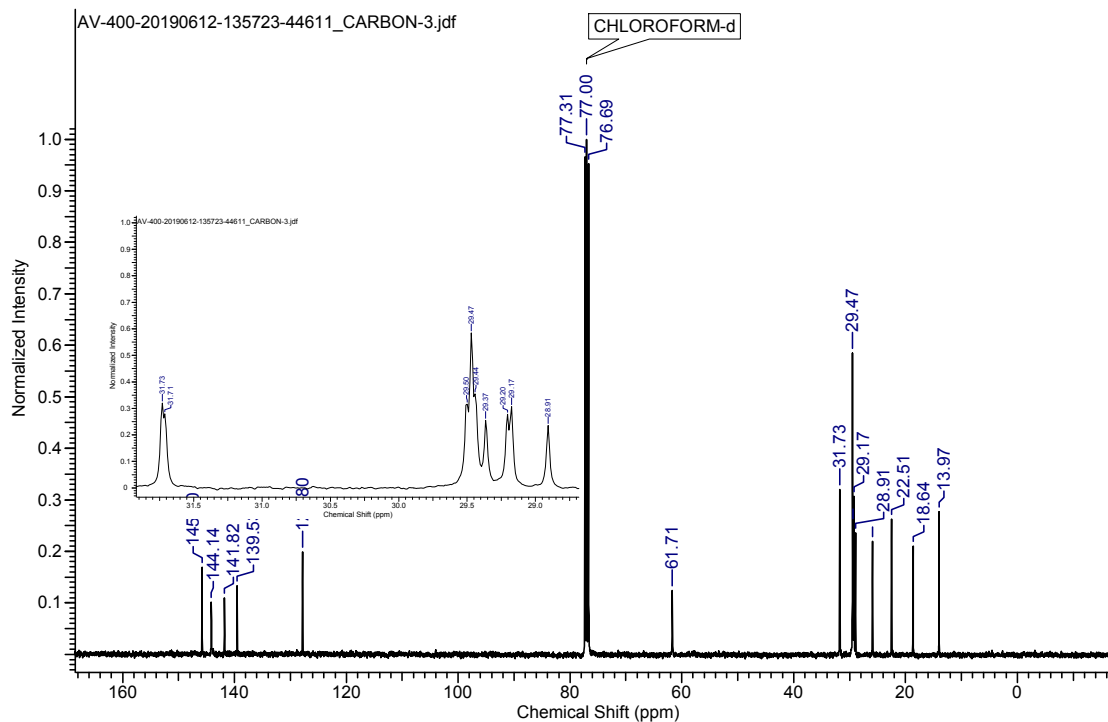


¹³C NMR of 1-tetradecyl-3-methylpyridinium bromide

6. 1-tetradecyl-3-methylpyridinium iodide (f)

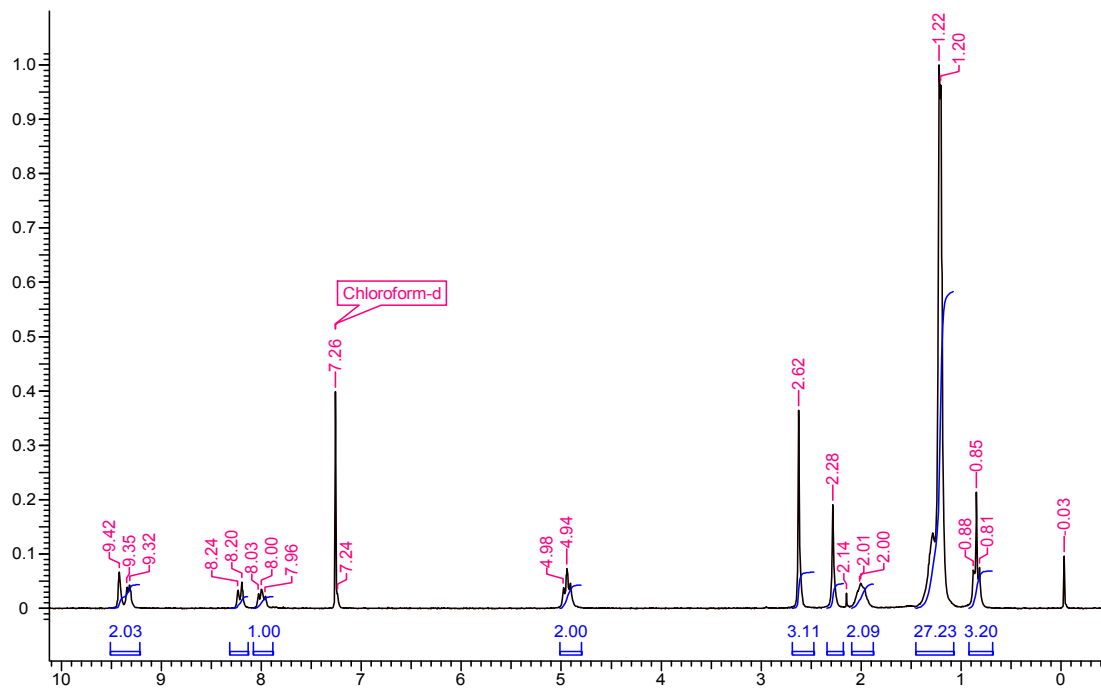


¹H NMR of 1-tetradecyl-3-methylpyridinium iodide

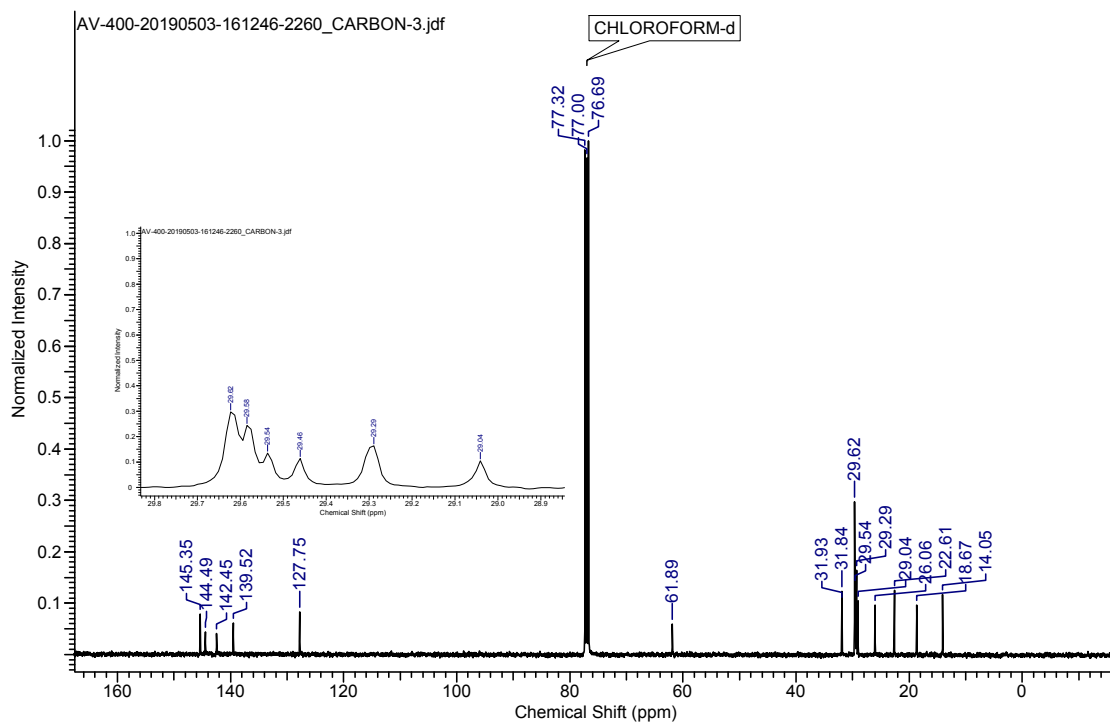


¹³C NMR of 1-tetradecyl-3-methylpyridinium iodide

7. 1-hexadecyl-3-methylpyridinium chloride (g)

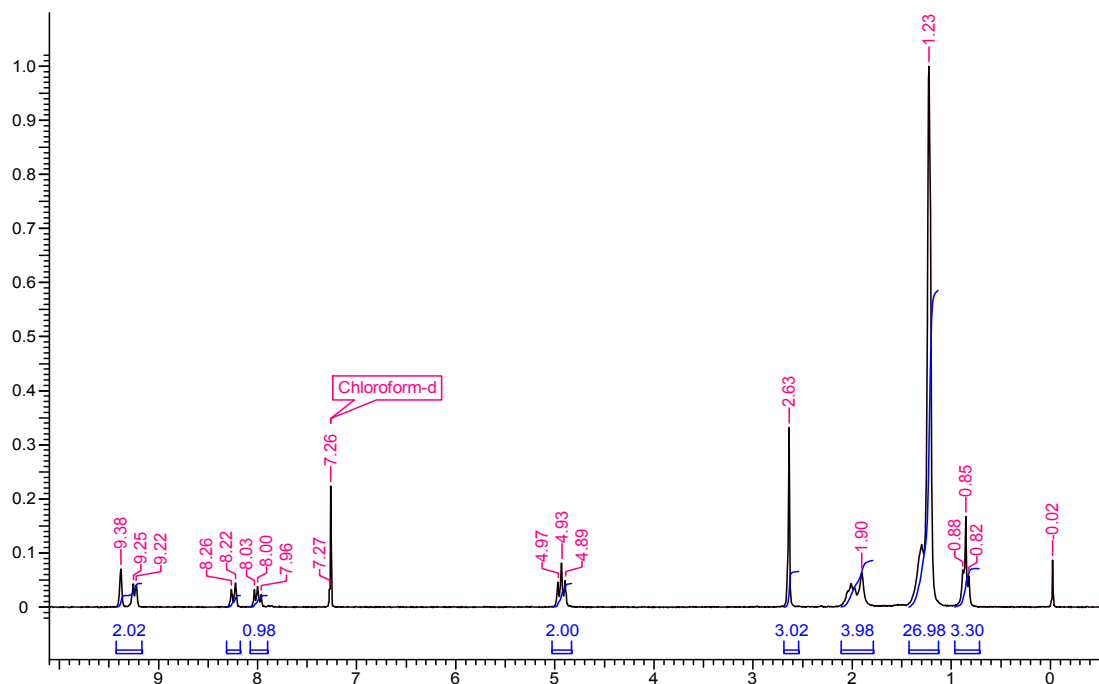


¹H NMR of 1-hexadecyl-3-methylpyridinium chloride

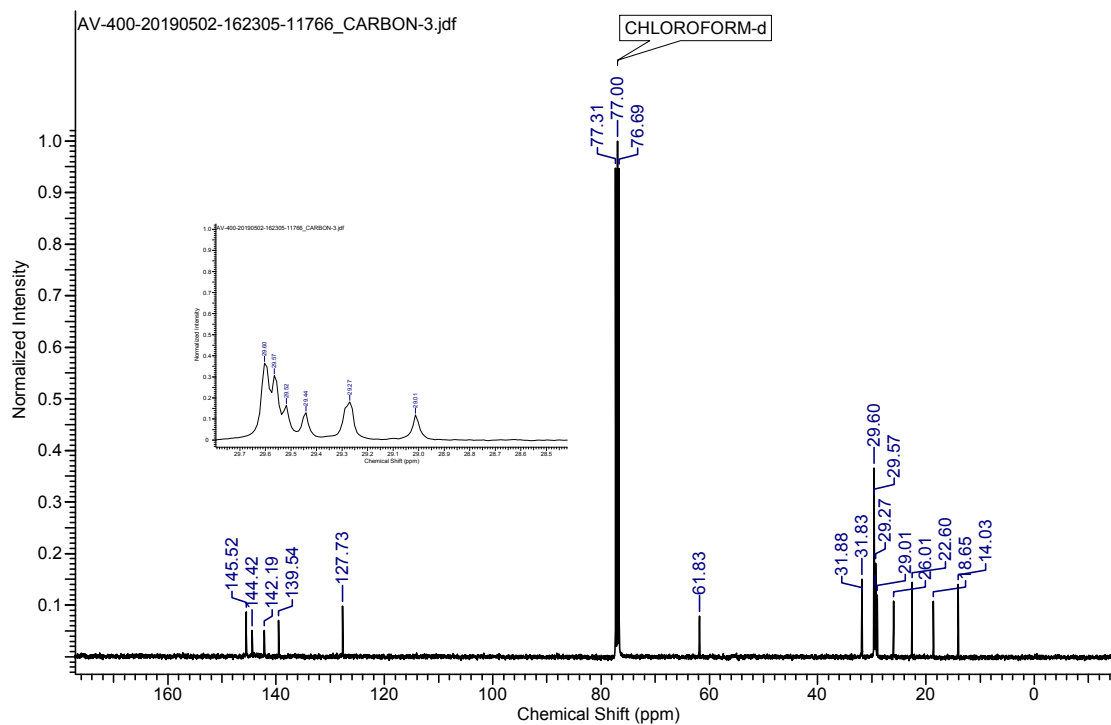


¹³C NMR of 1-hexadecyl-3-methylpyridinium chloride

8. 1-hexadecyl-3-methylpyridinium bromide (h)

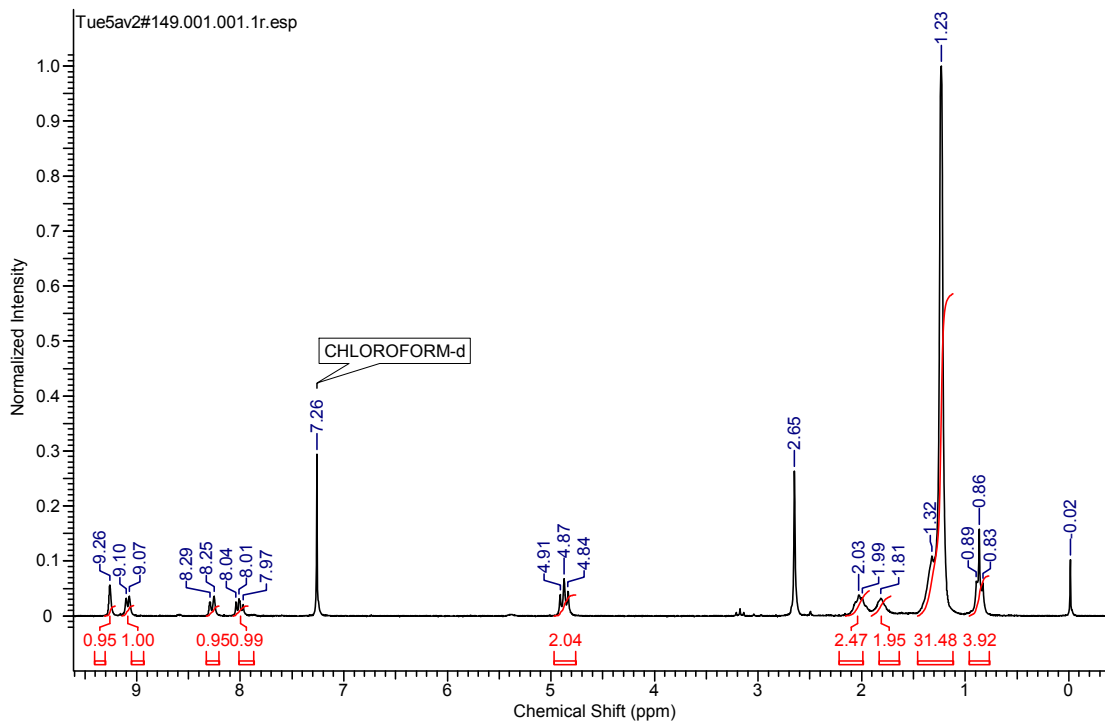


¹H NMR of 1-hexadecyl-3-methylpyridinium bromide

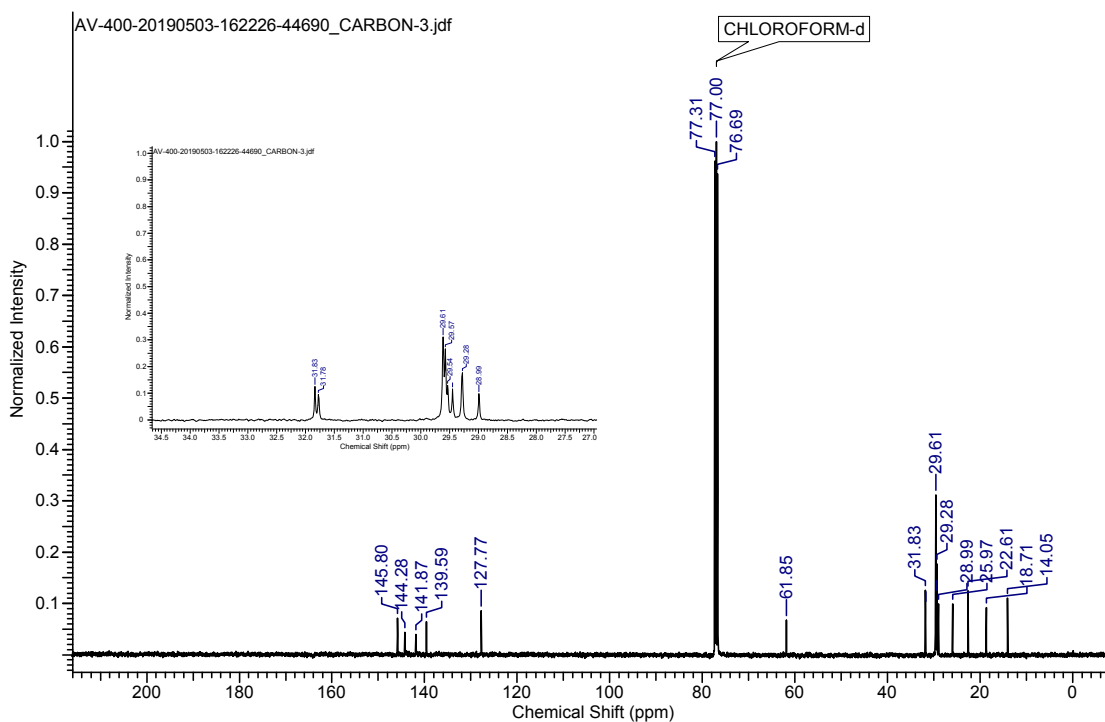


¹³C NMR of 1-hexadecyl-3-methylpyridinium bromide

9. 1-hexadecyl-3-methylpyridinium iodide (i)

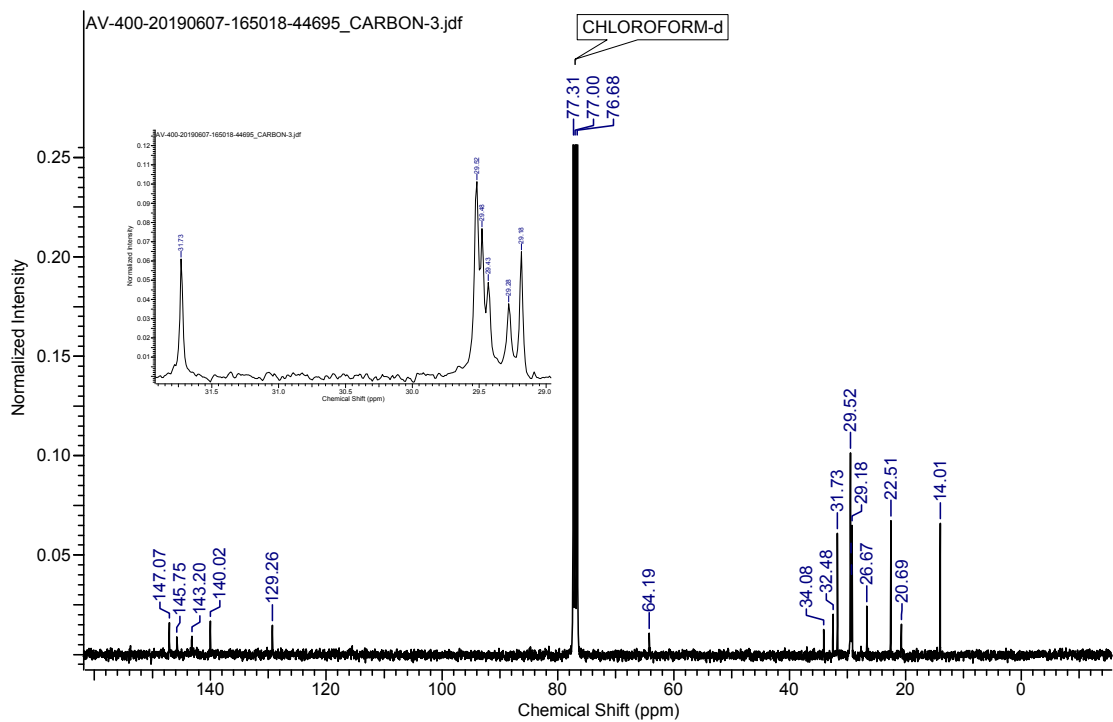
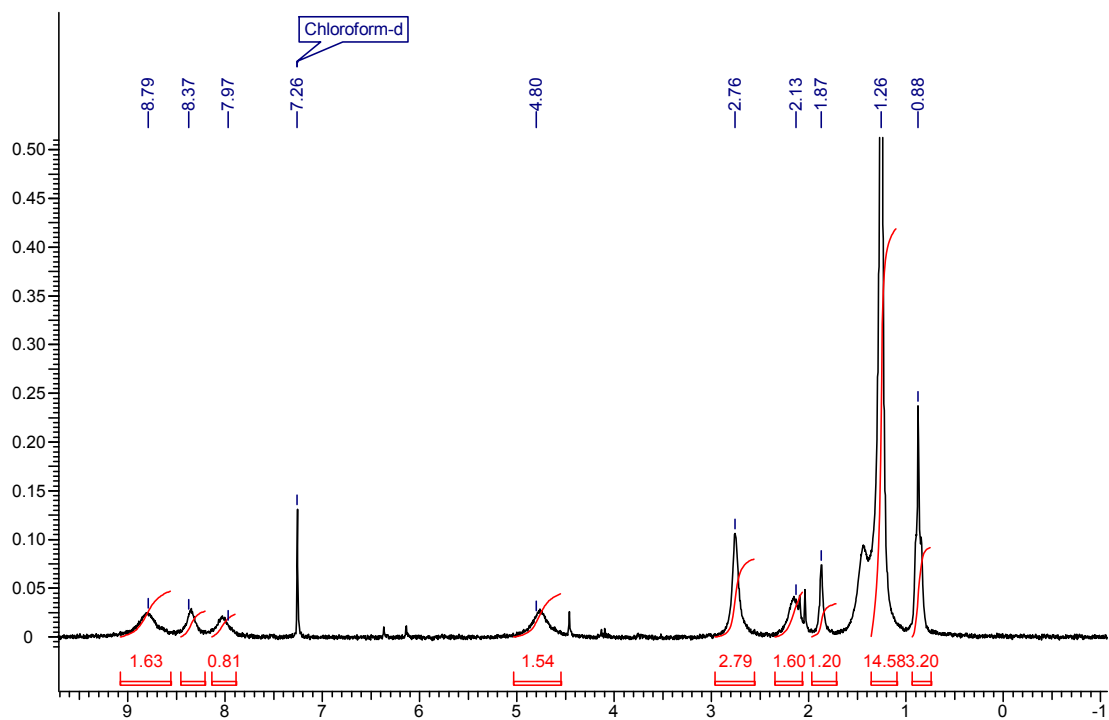


¹H NMR of 1-hexadecyl-3-methylpyridinium iodide

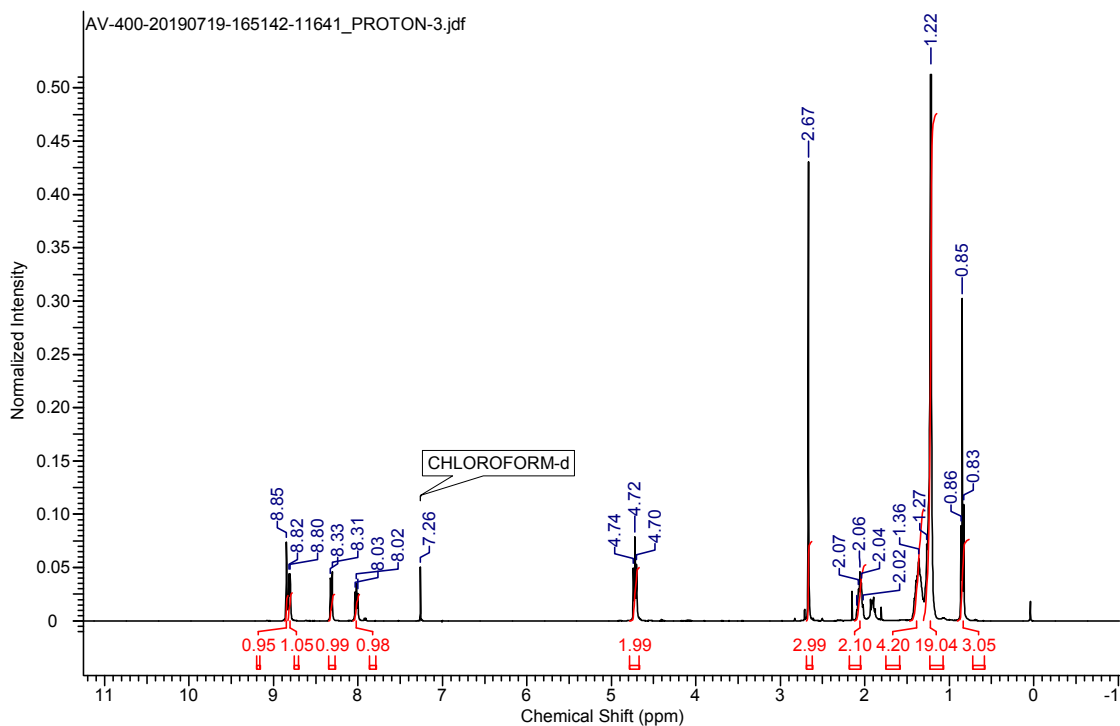


¹³C NMR of 1-hexadecyl-3-methylpyridinium iodide

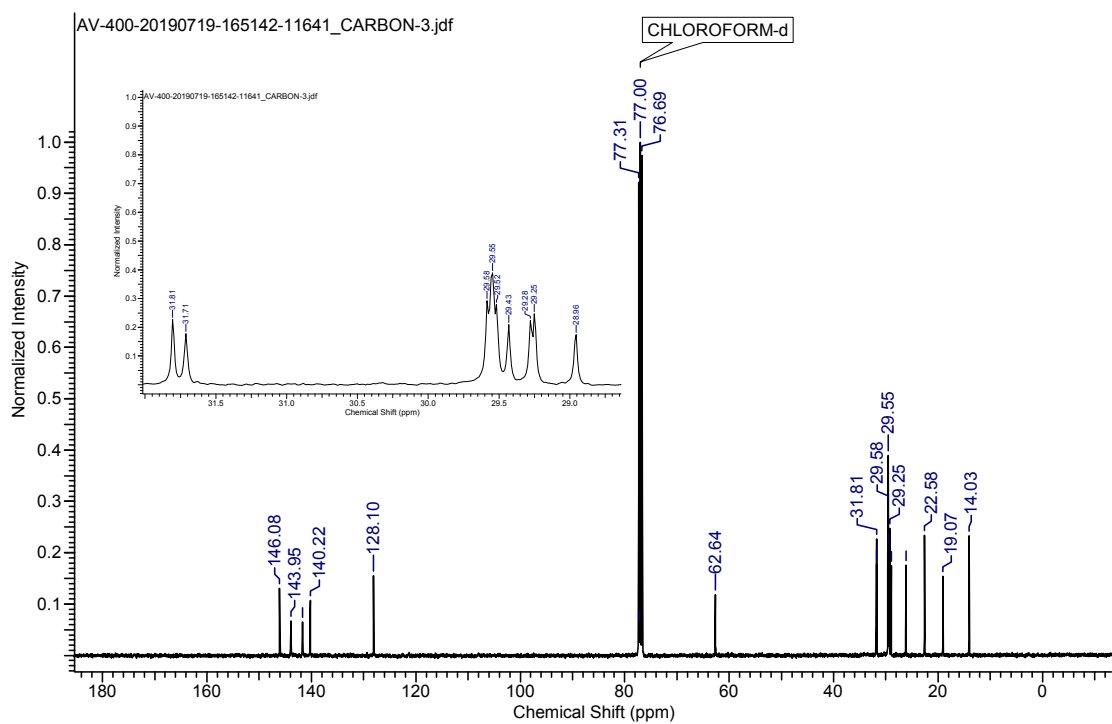
10. 1-dodecyl-3-methylpyridinium tribromide (j)



11. 1-tetradecyl-3-methylpyridinium tribromide (k)

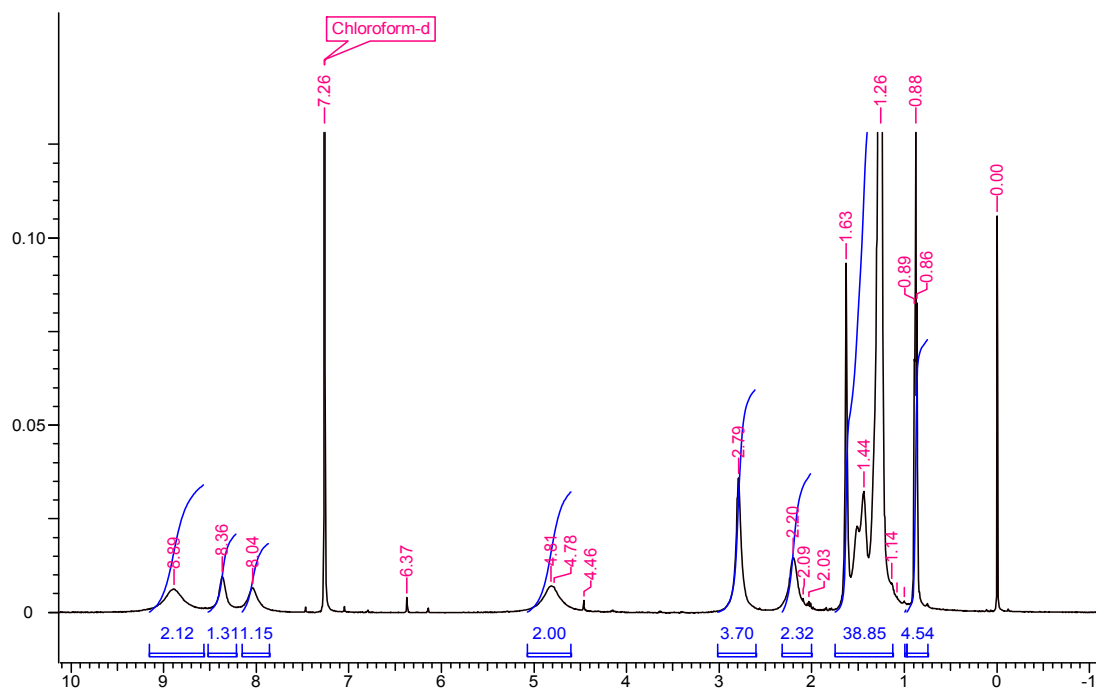


¹H NMR of 1-tetradecyl-3-methylpyridinium tribromide

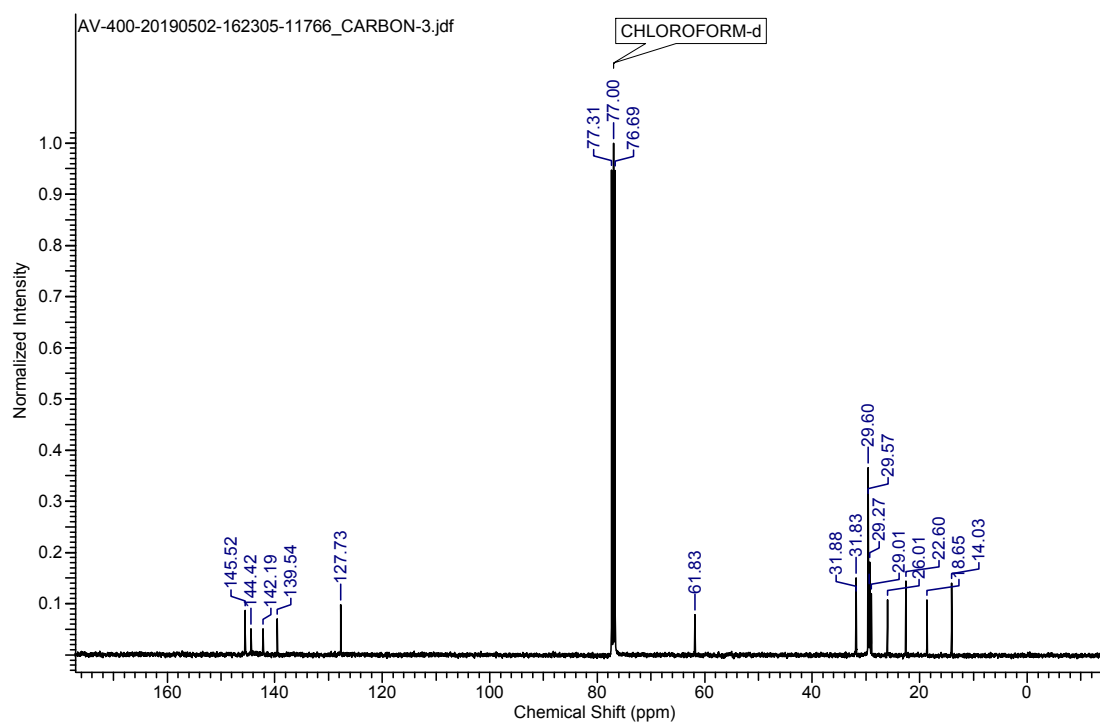


¹³C NMR of 1-tetradecyl-3-methylpyridinium tribromide

12. 1-hexadecyl-3-methylpyridinium tribromide (k)

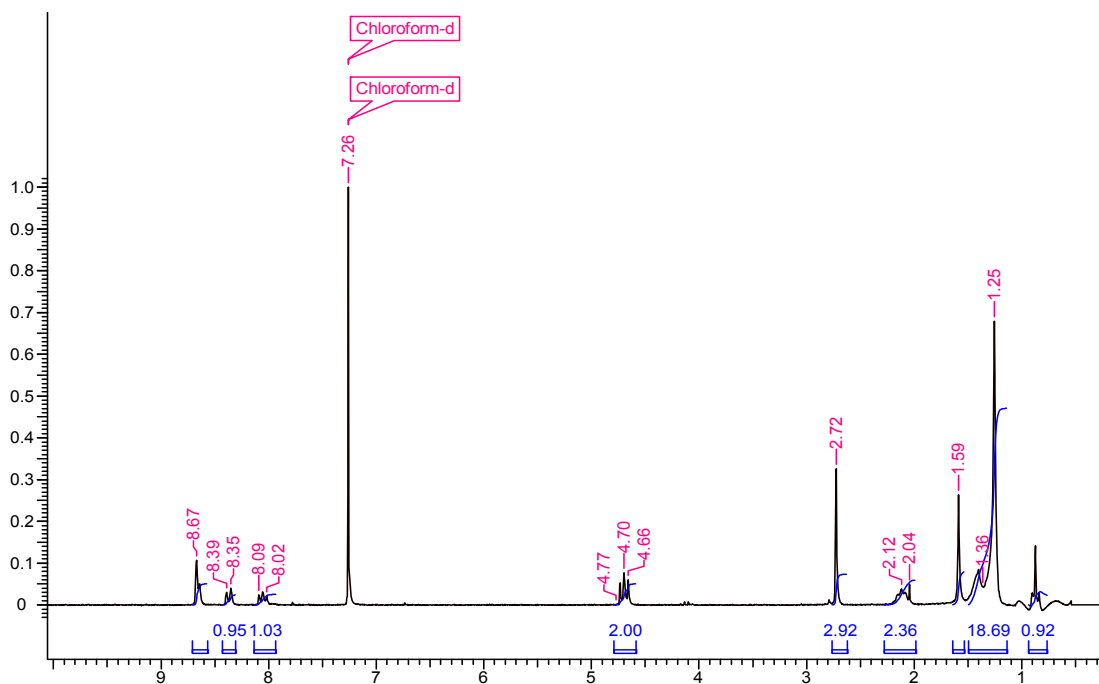


¹H NMR of 1-hexadecyl-3-methylpyridinium tribromide

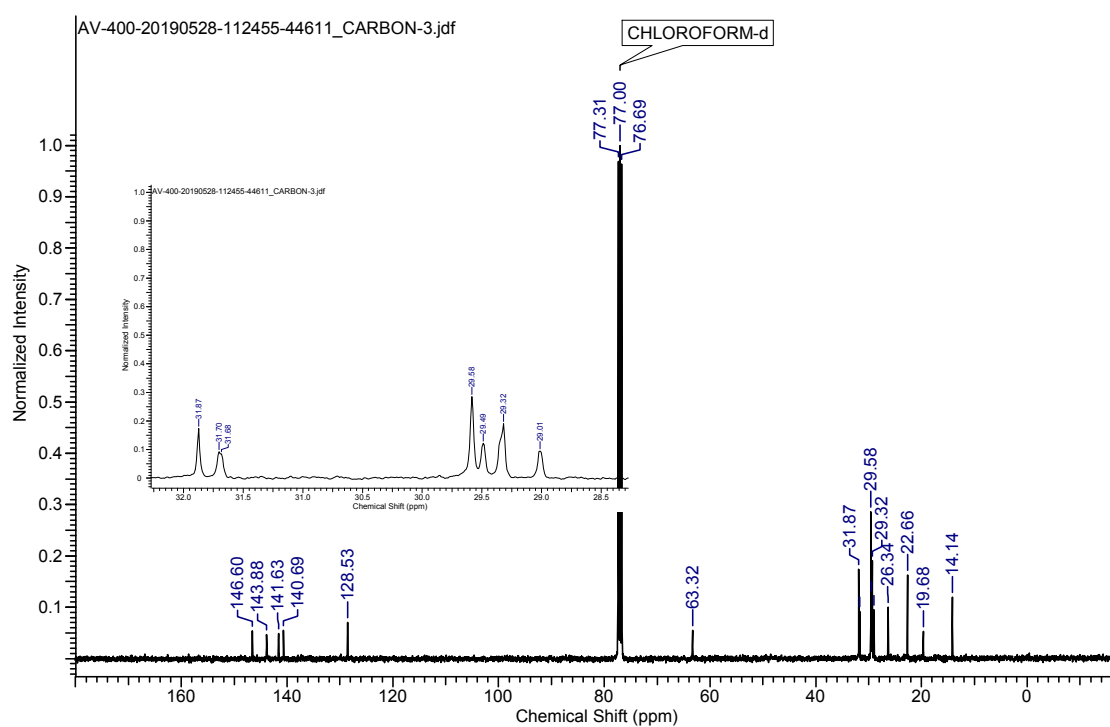


¹³C NMR of 1-hexadecyl-3-methylpyridinium tribromide

13. 1-dodecyl-3-methylpyridinium triiodide (I)

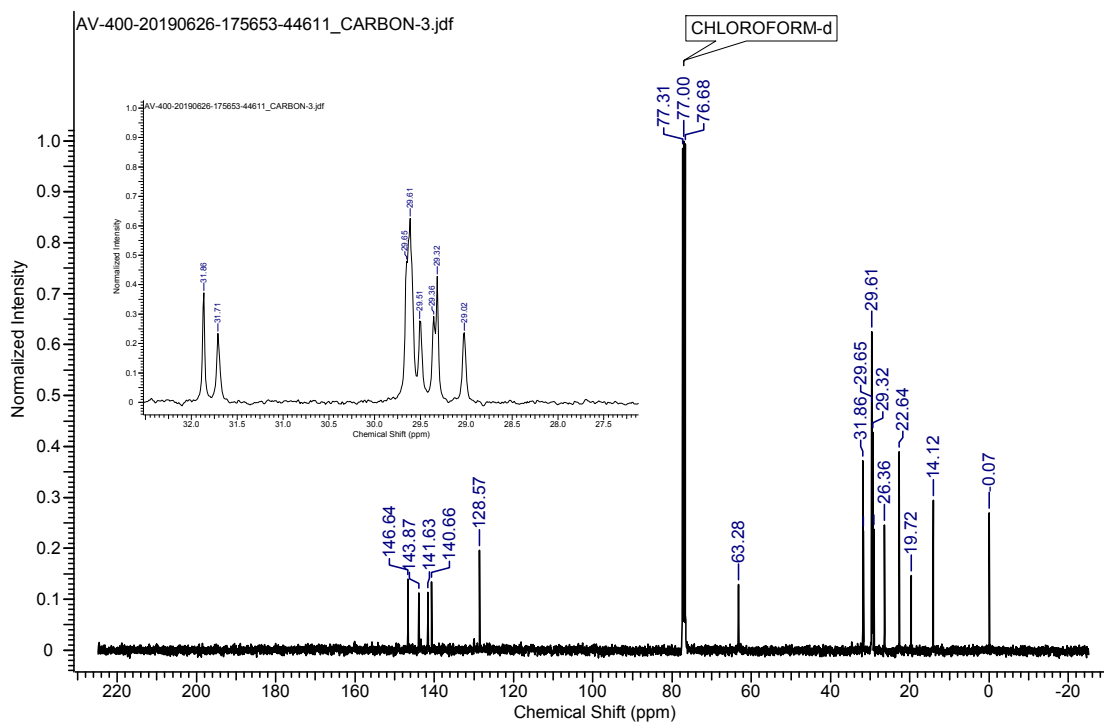
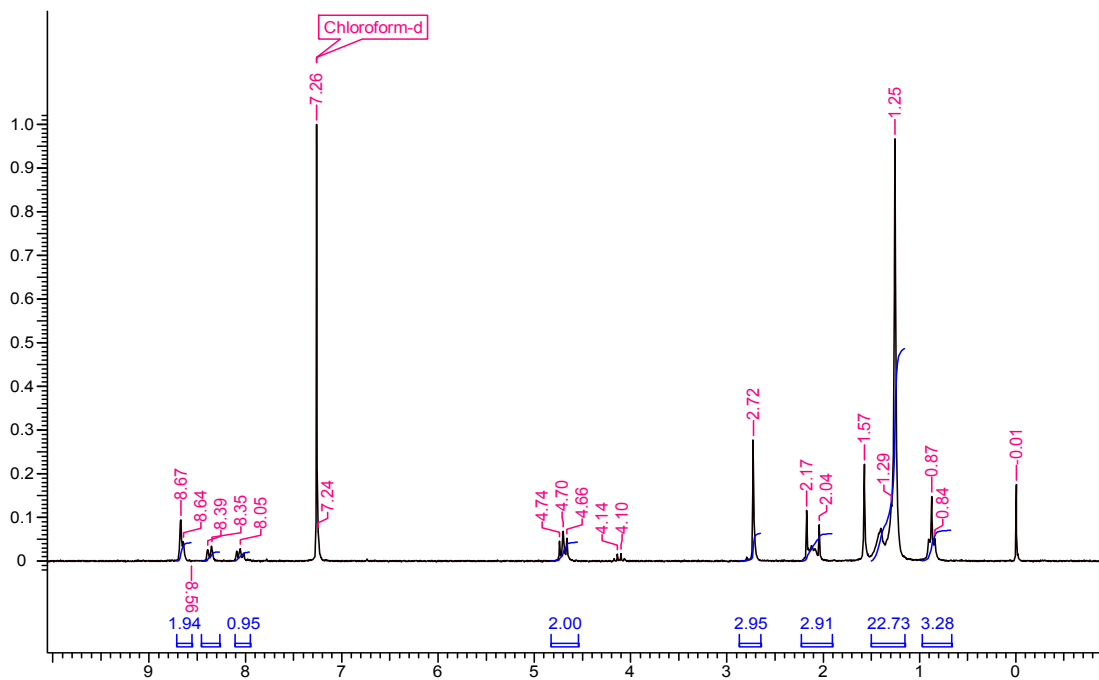


¹H NMR of 1-dodecyl-3-methylpyridinium triiodide



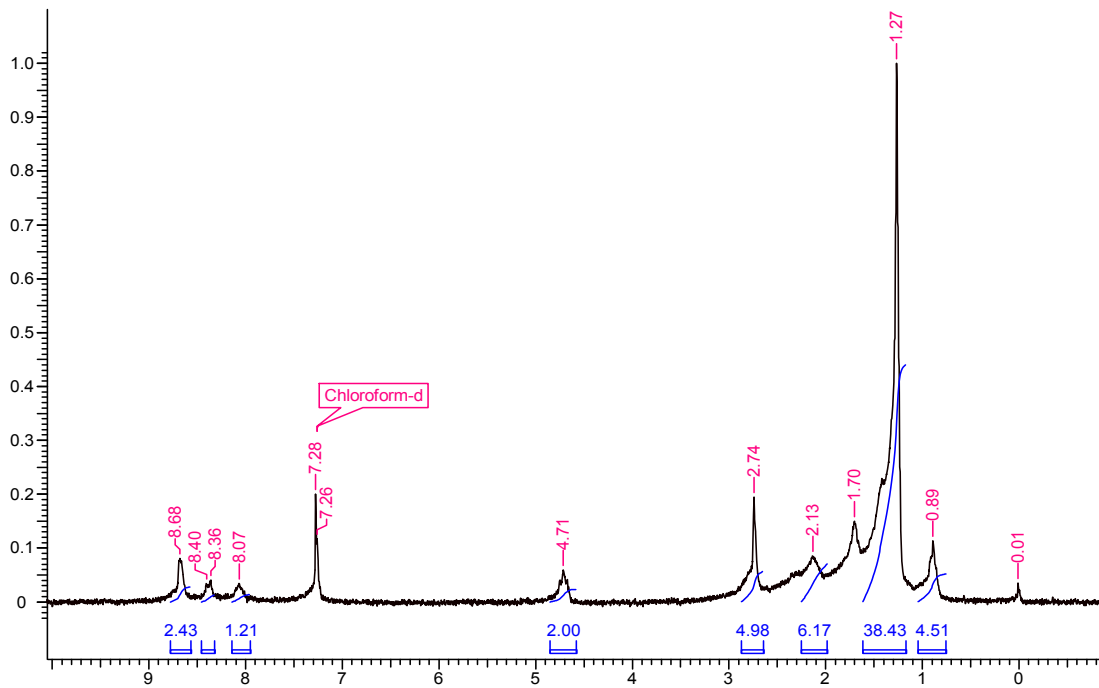
¹³C NMR of 1-dodecyl-3-methylpyridinium triiodide

14. 1-tetradecyl-3-methylpyridinium triiodide (m)

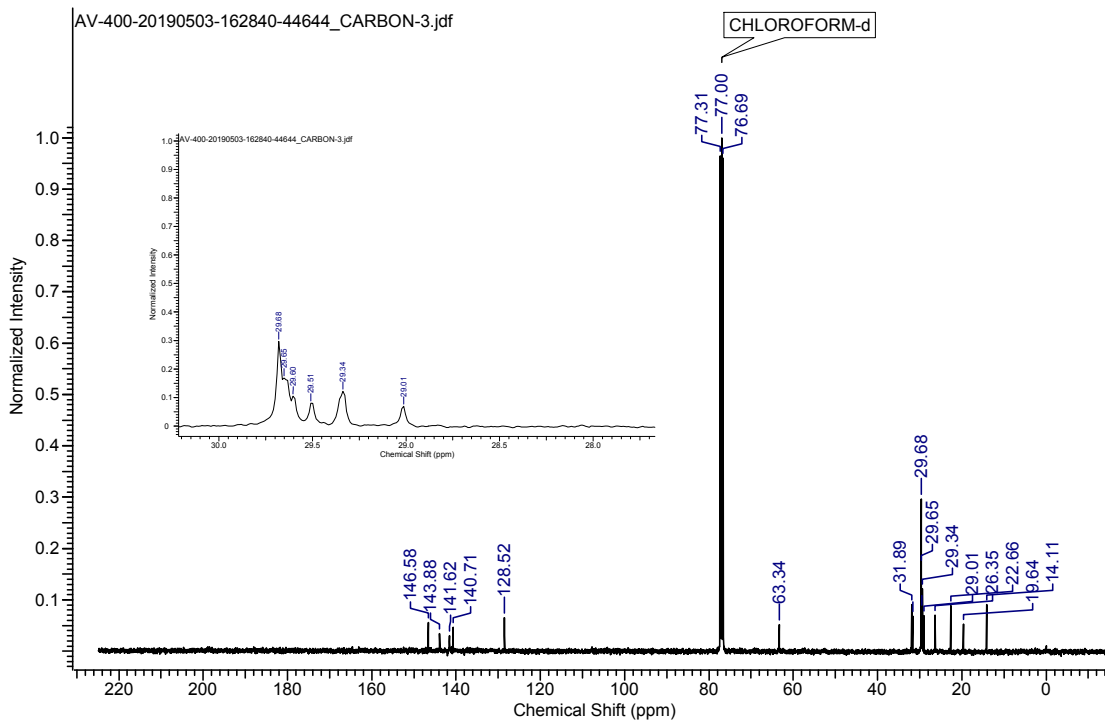


¹³C NMR of 1-tetradecyl-3-methylpyridinium triiodide

15. 1-hexadecyl-3-methylpyridinium triiodide (m)

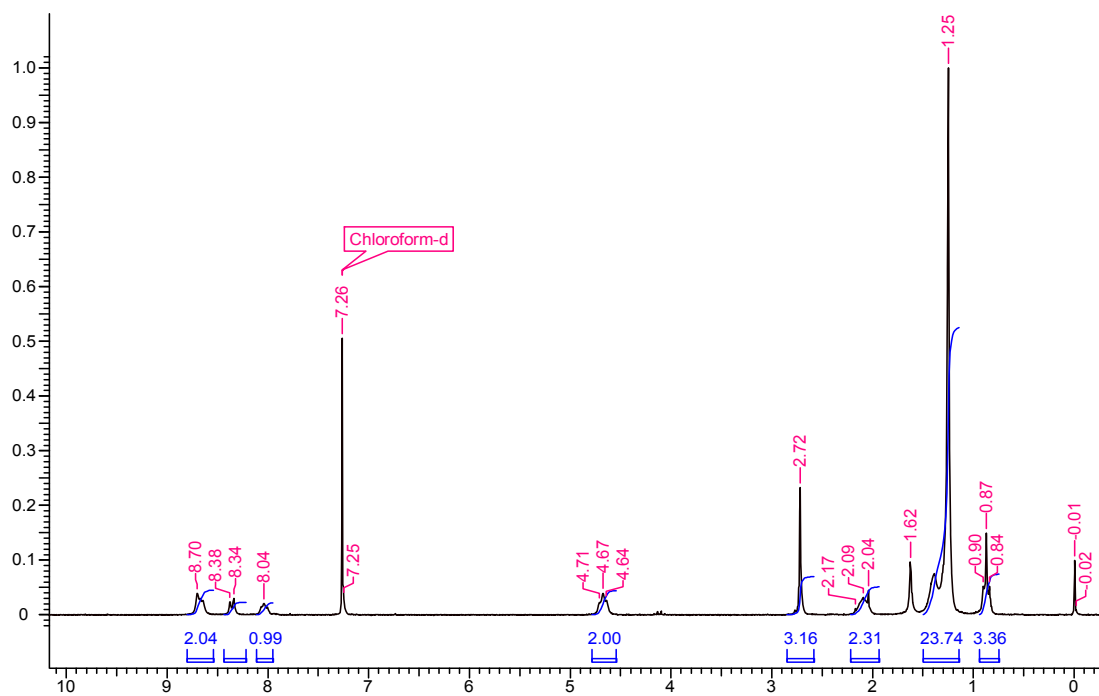


¹H NMR of 1-hexadecyl-3-methylpyridinium triiodide

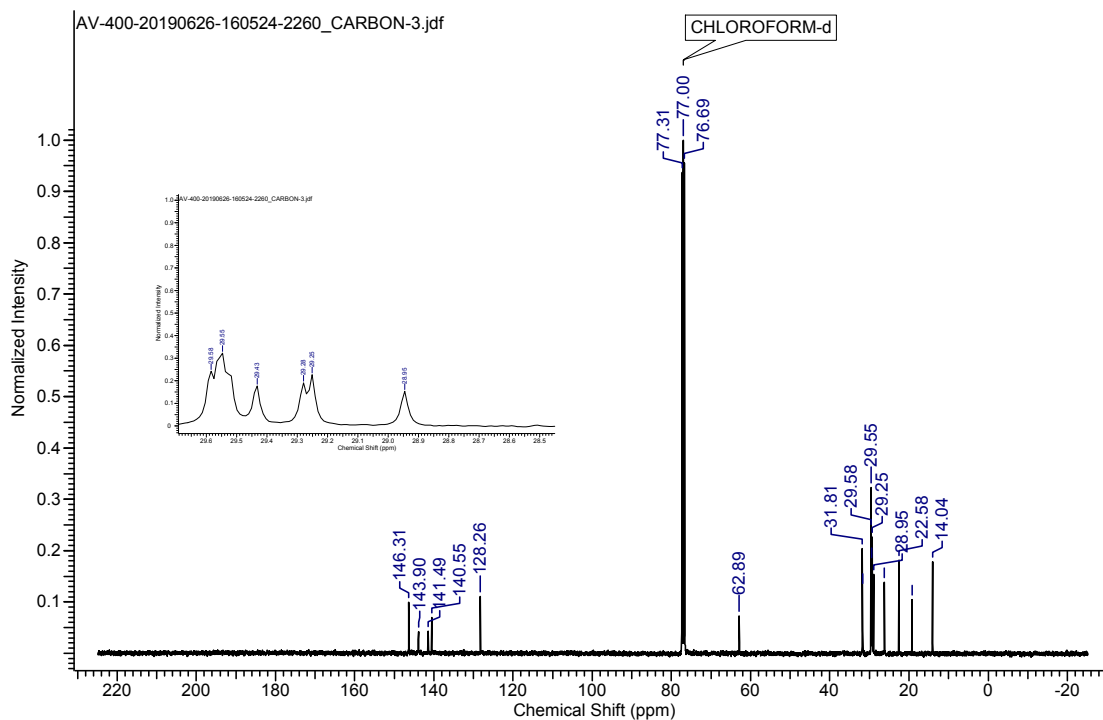


¹³C NMR of 1-hexadecyl-3-methylpyridinium triiodide

17. 1-tetradecyl-3-methylpyridinium dichloroiodate (o)

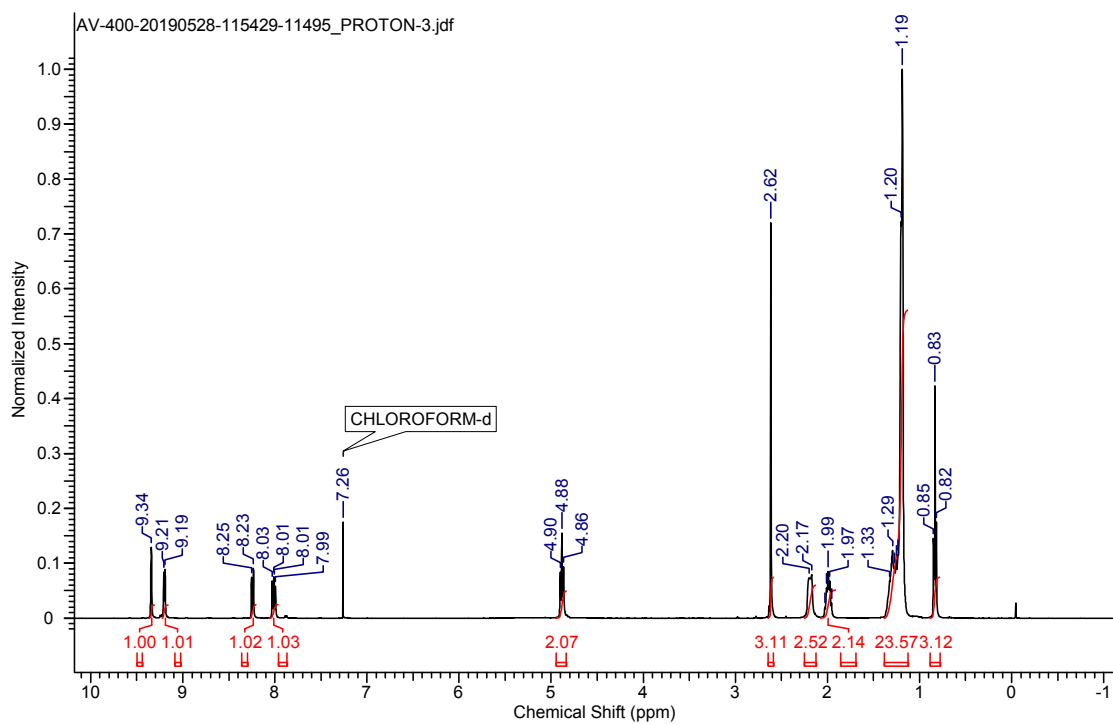


¹H NMR of 1-tetradecyl-3-methylpyridinium dichloroiodate

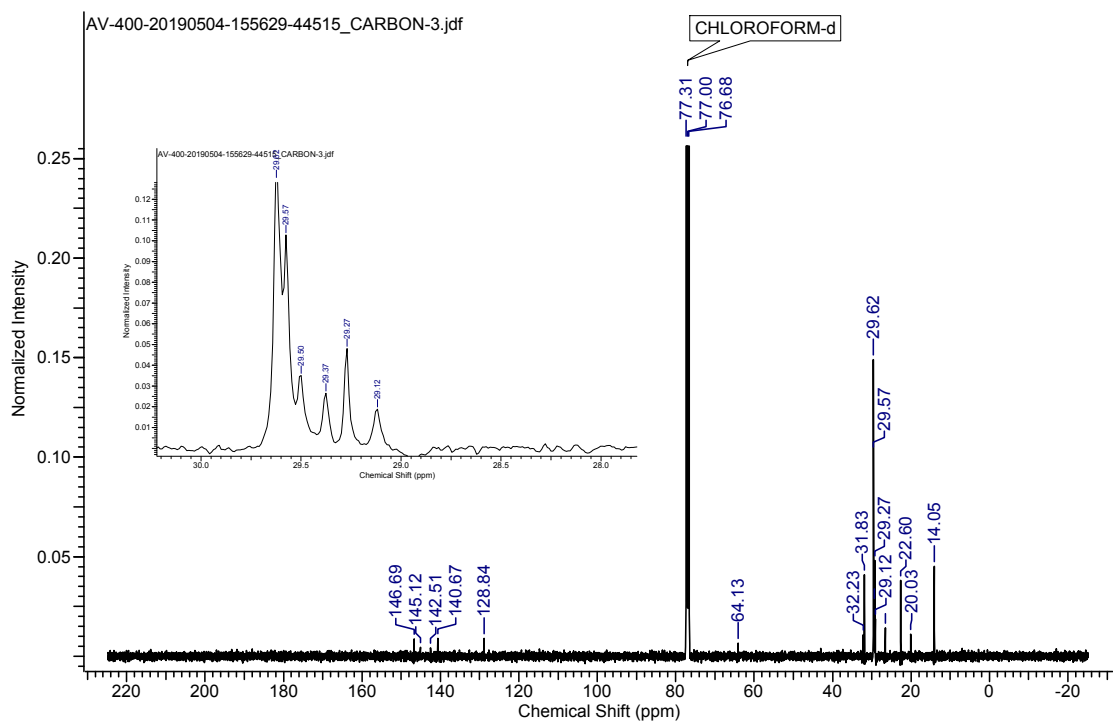


¹³C NMR of 1-tetradecyl-3-methylpyridinium dichloroiodate

15. 1-hexadecyl-3-methylpyridinium dichloroiodate (p)



¹H NMR of 1-hexadecyl-3-methylpyridinium dichloroiodate



¹³C NMR of 1-hexadecyl-3-methylpyridinium dichloroiodate

References:

1. Pereiro, A. B.; Rodriguez, A.; Blesic, M.; Shimizu, K.; Lopes, J.N.C.; Rebelo, L.P.N. *J. Chem. Eng. Data* **2011**, *56*, 4356.
2. Fayyaz, S.; Ali, S.; Khalid, N.; Shah, A.; Ullah, F. *J. Surfactants Deterg.* **2016**, *19*, 841.
3. Dwoskin, L. P.; Sumithran, S. P.; Zhu, J.; Deaciuc, A. G.; Ayers, J. T.; Crooks, P. A. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 1863.
4. Blesic, M.; Lopes, A.; Melo, E.; Petrovski, Z.; Plechkova, N. V.; Lopes, J. N. C.; Seddon K. R.; Rebelo, L. P. N. *J. Phys. Chem. B*, **2008**, *112*, 8645.
5. Sahbaz, Y.; Nguyen, T.-H.; Ford, L.; McEvoy, C. L.; Williams, H. D.; Scammells, P. J.; Porter, C. J. H. *Mol. Pharmaceutics* **2017**, *14*, 3669.
6. Radovici, O.; Barbulescu, E.; Roman, E. *Revistade Chimie* (Bucharest, Romania) **1987**, *38*, 617.