Supporting Information

Coordinating chiral ionic liquids

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2. Crystal structure determination of 1-methyl-3-[[[dimethyl[(1*R*,2*S*)-2-hydroxy-1-methyl-2-phenyl]ethyl]ammonio]methyl]pyridinium diiodide 35

Crystals of **35** suitable for X-ray structure determination were obtained from H_2O/EtOH. X-ray diffraction data were collected at T = 100(2) K on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo-Kα radiation, λ = 0.71073 Å, using 0.3° ω-scan frames covering a 3/4-sphere of the reciprocal space. After data integration with program SAINT (Bruker AXS), corrections for absorption and λ/2-effects were applied with program SADABS (Bruker AXS). The structure was solved with direct methods and was then refined on F^2 with the program package SHELX97 (G.M. Sheldrick, *Acta Cryst.* (2008). A**64**, 112-122). The non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions riding on their carrier atoms with U_{iso} = 1.2 or 1.5 (for Me) × U_{eq}(C,N,O) . The absolute structure of the compound could be unambiguously determined with the help of the Flack absolute structure parameter (FAS = -0.018(15)). Crystallographic data are given in Table S1. Atomic coordinates and thermal parameters are reported in Tables S2 to S4, and geometric data in Table S5. A CIF has been deposited at The Cambridge Crystallographic Data Centre (CCDC 667736). Figures S1, S2, and S3 show details of the crystal structure.

Fig. S1. Thermal ellipsoid diagram (50% ellipsoids) of the molecular structure of the diiodide salt **35**.

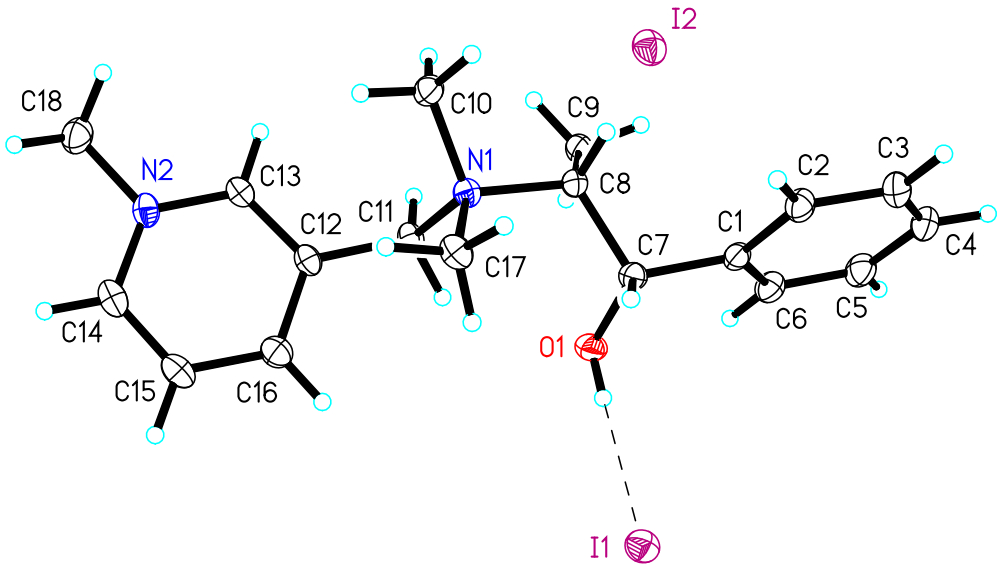
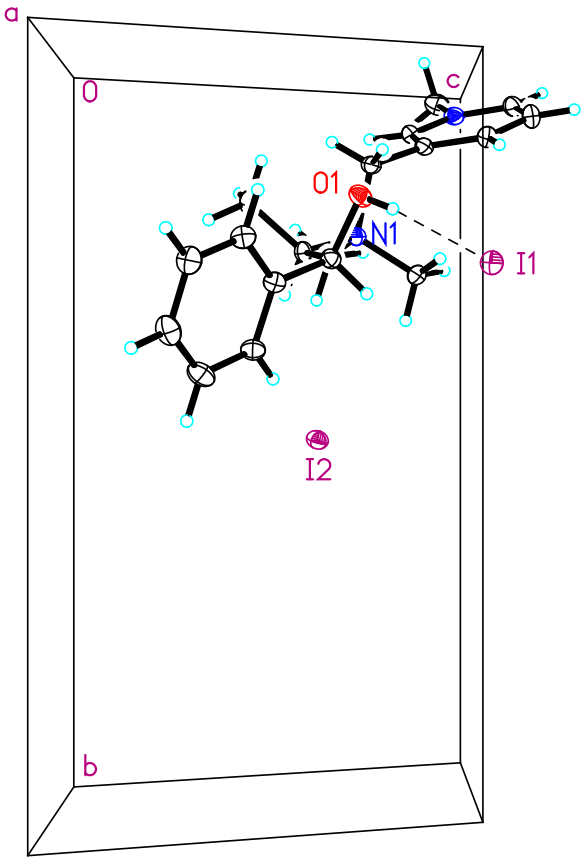


Fig. S2. Asymmetric unit of the diiodide salt **35** in perspective views along a- and b-axis of the unit cell.



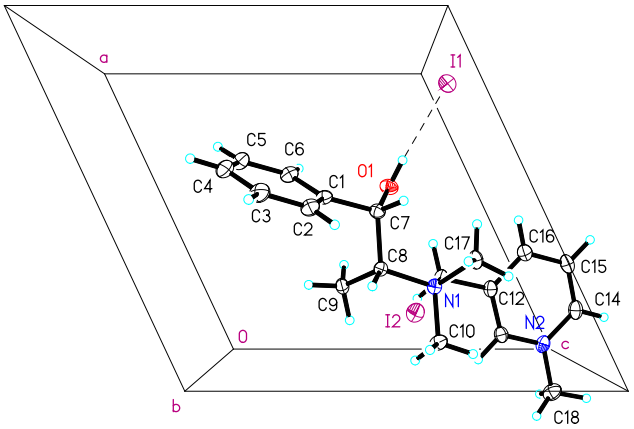


Fig. S3. Packing diagrams of diiodide salt **35** in views along a- and b-axis of the unit cell.

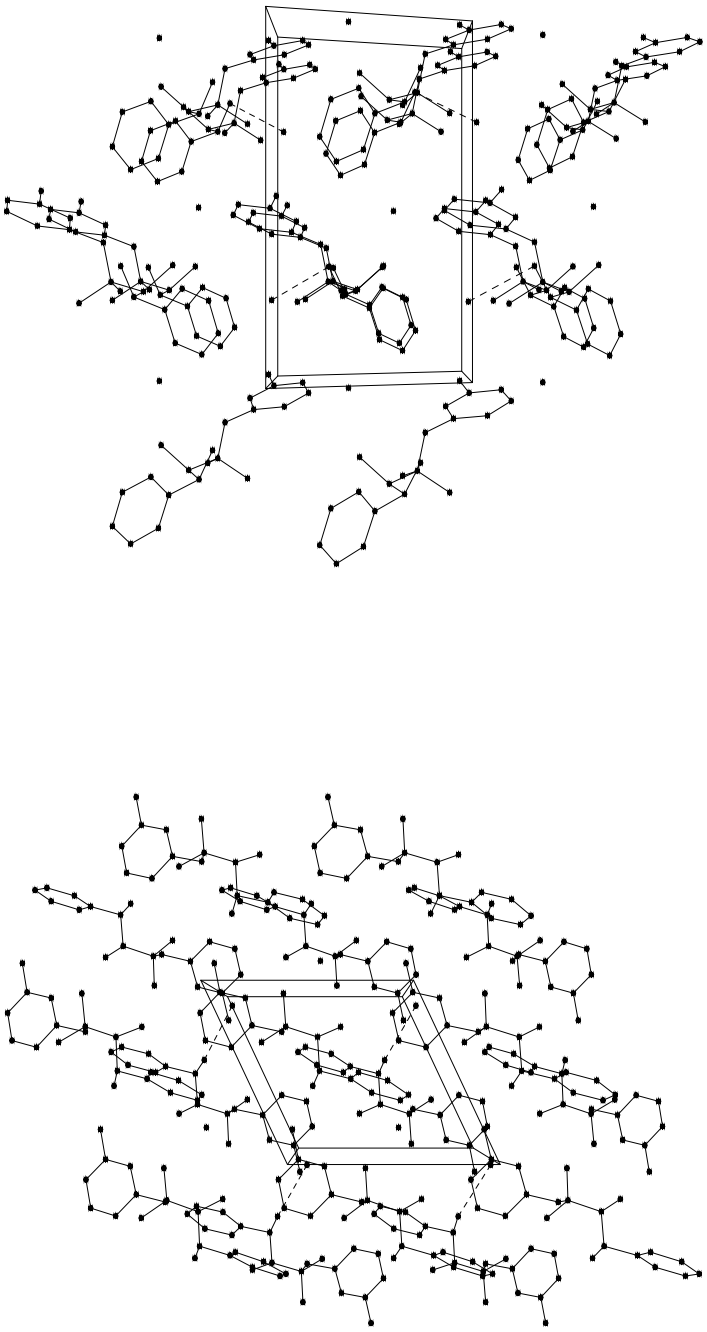


Table S1. Crystal data and structure refinement diiodide salt **35**

Identification code	1294m
Empirical formula	C18 H26 I2 N2 O
Formula weight	540.21
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 8.6242(6) Å α = 90 deg. b = 14.6111(10) Å β = 115.147(1) deg. c = 9.0040(6) Å γ = 90 deg.
Volume	1027.05(12) $Å^3$
Z, Calculated density	2, 1.747 Mg/m^3
Absorption coefficient	3.068 mm^{-1}
F(000)	524
Crystal size	0.30 x 0.13 x 0.12 mm
Diffractometer	Bruker SMART CCD diffractometer (sealed X-ray tube, Mo Kα radiation, graphite monochromator, Bruker Kryo-flex cooling unit)
Scan type / width / speed	ω-scans / Δω = 0.3° / 6 sec. per frame ¾-sphere data collection
Theta range for data collection	2.50 to 30.00 deg.
Index ranges	-12 ≤ h ≤ 11, -20 ≤ k ≤ 20, -12 ≤ l ≤ 12
Reflections collected / unique	12666 / 5686 [R(int) = 0.0169]
Completeness to theta = 30.00	99.8%
Absorption correction	Multi-scan (program SADABS)
Max. and min. transmission	0.69 and 0.44
Structure solution	Direct methods (program SHELXS97)
Refinement method	Full-matrix least-squares on F^2 (SHELXL97)
Data / restraints / parameters	5686 / 55 / 215
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0209, wR2 = 0.0523
R indices (all data)	R1 = 0.0211, wR2 = 0.0524
Absolute structure parameter	-0.018(15)
Largest diff. peak and hole	1.00 and -0.43 $eÅ^{-3}$

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{½}$

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for diiodide salt **35.** U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
I(1)	9187(1)	2756(1)	10267(1)	22(1)
I(2)	1687(1)	5112(1)	6153(1)	19(1)
O(1)	5785(2)	1788(1)	7213(2)	21(1)

N(1)	2366(3)	2210(1)	7156(2)	16(1)
N(2)	206(3)	276(1)	9816(2)	18(1)
C(1)	5369(3)	2970(2)	5135(3)	17(1)
C(2)	4994(3)	3875(2)	4613(3)	20(1)
C(3)	5450(3)	4212(2)	3408(3)	25(1)
C(4)	6255(3)	3650(2)	2702(3)	26(1)
C(5)	6591(3)	2742(2)	3194(3)	24(1)
C(6)	6165(3)	2405(2)	4416(3)	21(1)
C(7)	4915(3)	2619(2)	6496(3)	17(1)
C(8)	2975(3)	2469(2)	5808(3)	16(1)
C(9)	2360(3)	1771(2)	4421(3)	19(1)
C(10)	483(3)	2443(2)	6490(3)	20(1)
C(11)	2620(3)	1191(2)	7529(3)	17(1)
C(12)	2225(3)	871(2)	8920(3)	17(1)
C(13)	581(3)	605(2)	8616(3)	18(1)
C(14)	1435(3)	167(2)	11361(3)	22(1)
C(15)	3101(3)	411(2)	11728(3)	24(1)
C(16)	3510(3)	766(2)	10516(3)	20(1)
C(17)	3287(3)	2765(2)	8689(3)	19(1)
C(18)	-1566(3)	-2(2)	9432(3)	25(1)

Table S3. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) of diiodide salt **35.**

	x	*y*	*z*	U_{eq}
H(1O)	6690(30)	1980(30)	7980(30)	31
H(2)	4430	4261	5078	24
H(3)	5210	4831	3065	30
H(4)	6573	3885	1887	31
H(5)	7113	2351	2695	29
H(6)	6417	1787	4764	25
H(7)	5247	3096	7374	20
H(8)	2419	3065	5326	19
H(9A)	2421	2039	3449	28
H(9B)	1173	1600	4158	28
H(9C)	3089	1226	4762	28
H(10A)	88	2356	7353	30
H(10B)	-168	2042	5560	30
H(10C)	309	3083	6127	30
H(11A)	1884	849	6528	21
H(11B)	3825	1034	7790	21
H(13)	-302	657	7536	21
H(14)	1150	-77	12191	27
H(15)	3967	337	12811	29
H(16)	4657	937	10764	24
H(17A)	2731	2677	9428	29
H(17B)	3247	3414	8401	29

H(17C)	4483	2564	9237	29
H(18A)	-2365	387	8553	38
H(18B)	-1777	66	10413	38
H(18C)	-1733	-642	9075	38

Hydrogen atoms inserted in idealized positions and refined riding with the atoms to which they were bonded. All H atoms had $U_{iso} = U_{eq}$ x 1.2 (x 1.5 for CH_3) of their carrier atoms.

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) diiodide salt of diiodide salt **35.**
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	22(1)	21(1)	20(1)	0(1)	7(1)	0(1)
I(2)	22(1)	16(1)	22(1)	2(1)	11(1)	3(1)
O(1)	18(1)	20(1)	21(1)	5(1)	5(1)	3(1)
N(1)	17(1)	14(1)	16(1)	0(1)	8(1)	0(1)
N(2)	24(1)	15(1)	20(1)	1(1)	13(1)	-1(1)
C(1)	14(1)	17(1)	20(1)	1(1)	7(1)	-1(1)
C(2)	20(1)	17(1)	25(1)	0(1)	11(1)	-2(1)
C(3)	24(1)	23(1)	30(1)	8(1)	13(1)	-1(1)
C(4)	21(1)	34(1)	25(1)	5(1)	13(1)	-3(1)
C(5)	21(1)	30(1)	25(1)	-1(1)	13(1)	0(1)
C(6)	19(1)	20(1)	25(1)	-1(1)	11(1)	0(1)
C(7)	16(1)	16(1)	17(1)	1(1)	6(1)	0(1)
C(8)	15(1)	19(1)	15(1)	1(1)	7(1)	-1(1)
C(9)	19(1)	24(1)	13(1)	-1(1)	7(1)	-3(1)
C(10)	18(1)	20(1)	25(1)	4(1)	11(1)	2(1)
C(11)	23(1)	14(1)	18(1)	1(1)	12(1)	2(1)
C(12)	22(1)	14(1)	16(1)	1(1)	9(1)	1(1)
C(13)	21(1)	16(1)	15(1)	2(1)	7(1)	1(1)
C(14)	31(1)	20(1)	19(1)	3(1)	13(1)	1(1)
C(15)	29(1)	26(1)	15(1)	2(1)	7(1)	1(1)
C(16)	22(1)	21(1)	18(1)	-1(1)	8(1)	1(1)
C(17)	25(1)	17(1)	16(1)	-2(1)	9(1)	1(1)
C(18)	24(1)	23(1)	32(1)	4(1)	16(1)	0(1)

Table 5. Bond lengths [Å] and angles [deg] of diiodide salt **35.**

Bond distances		Bond angles	
O(1)-C(7)	1.429(3)	C(17)-N(1)-C(10)	107.56(18)
O(1)-H(1O)	0.84000(12)	C(17)-N(1)-C(11)	110.74(18)
N(1)-C(17)	1.503(3)	C(10)-N(1)-C(11)	109.72(19)
N(1)-C(10)	1.512(3)	C(17)-N(1)-C(8)	111.29(18)
N(1)-C(11)	1.522(3)	C(10)-N(1)-C(8)	107.28(17)
N(1)-C(8)	1.560(3)	C(11)-N(1)-C(8)	110.15(17)
N(2)-C(13)	1.342(3)	C(13)-N(2)-C(14)	121.2(2)
N(2)-C(14)	1.353(3)	C(13)-N(2)-C(18)	119.4(2)
N(2)-C(18)	1.473(3)	C(14)-N(2)-C(18)	119.3(2)
C(1)-C(2)	1.396(3)	C(2)-C(1)-C(6)	119.6(2)
C(1)-C(6)	1.396(3)	C(2)-C(1)-C(7)	119.2(2)
C(1)-C(7)	1.525(3)	C(6)-C(1)-C(7)	121.2(2)
C(2)-C(3)	1.391(3)	C(3)-C(2)-C(1)	119.8(2)
C(2)-H(2)	0.9500	C(3)-C(2)-H(2)	120.1
C(3)-C(4)	1.392(4)	C(1)-C(2)-H(2)	120.1
C(3)-H(3)	0.95	C(4)-C(3)-C(2)	120.6(3)
C(4)-C(5)	1.389(4)	C(4)-C(3)-H(3)	119.7
C(4)-H(4)	0.95	C(2)-C(3)-H(3)	119.7
C(5)-C(6)	1.390(3)	C(5)-C(4)-C(3)	119.7(2)
C(5)-H(5)	0.95	C(5)-C(4)-H(4)	120.2
C(6)-H(6)	0.95	C(3)-C(4)-H(4)	120.2
C(7)-C(8)	1.533(3)	C(4)-C(5)-C(6)	120.1(3)
C(7)-H(7)	1.00	C(4)-C(5)-H(5)	120.0
C(8)-C(9)	1.522(3)	C(6)-C(5)-H(5)	120.0
C(8)-H(8)	1.00	C(5)-C(6)-C(1)	120.3(3)
C(9)-H(9A)	0.98	C(5)-C(6)-H(6)	119.8
C(9)-H(9B)	0.98	C(1)-C(6)-H(6)	119.8
C(9)-H(9C)	0.98	O(1)-C(7)-C(1)	112.61(18)
C(10)-H(10A)	0.98	O(1)-C(7)-C(8)	109.51(19)
C(10)-H(10B)	0.98	C(1)-C(7)-C(8)	109.41(17)
C(10)-H(10C)	0.98	O(1)-C(7)-H(7)	108.4
C(11)-C(12)	1.505(3)	C(1)-C(7)-H(7)	108.4
C(11)-H(11A)	0.99	C(8)-C(7)-H(7)	108.4
C(11)-H(11B)	0.99	C(9)-C(8)-C(7)	111.54(19)
C(12)-C(13)	1.380(3)	C(9)-C(8)-N(1)	111.19(19)
C(12)-C(16)	1.402(3)	C(7)-C(8)-N(1)	113.00(17)
C(13)-H(13)	0.95	C(9)-C(8)-H(8)	106.9
C(14)-C(15)	1.377(4)	C(7)-C(8)-H(8)	106.9
C(14)-H(14)	0.95	N(1)-C(8)-H(8)	106.9
C(15)-C(16)	1.382(3)	C(8)-C(9)-H(9A)	109.5
C(15)-H(15)	0.95	C(8)-C(9)-H(9B)	109.5
C(16)-H(16)	0.95	H(9A)-C(9)-H(9B)	109.5
C(17)-H(17A)	0.98	C(8)-C(9)-H(9C)	109.5
C(17)-H(17B)	0.98	H(9A)-C(9)-H(9C)	109.5
C(17)-H(17C)	0.98	H(9B)-C(9)-H(9C)	109.5
C(18)-H(18A)	0.98	N(1)-C(10)-H(10A)	109.5
C(18)-H(18B)	0.98	N(1)-C(10)-H(10B)	109.5
C(18)-H(18C)	0.98	H(10A)-C(10)-H(10B)	109.5
		N(1)-C(10)-H(10C)	109.5
		H(10A)-C(10)-H(10C)	109.5
		H(10B)-C(10)-H(10C)	109.5

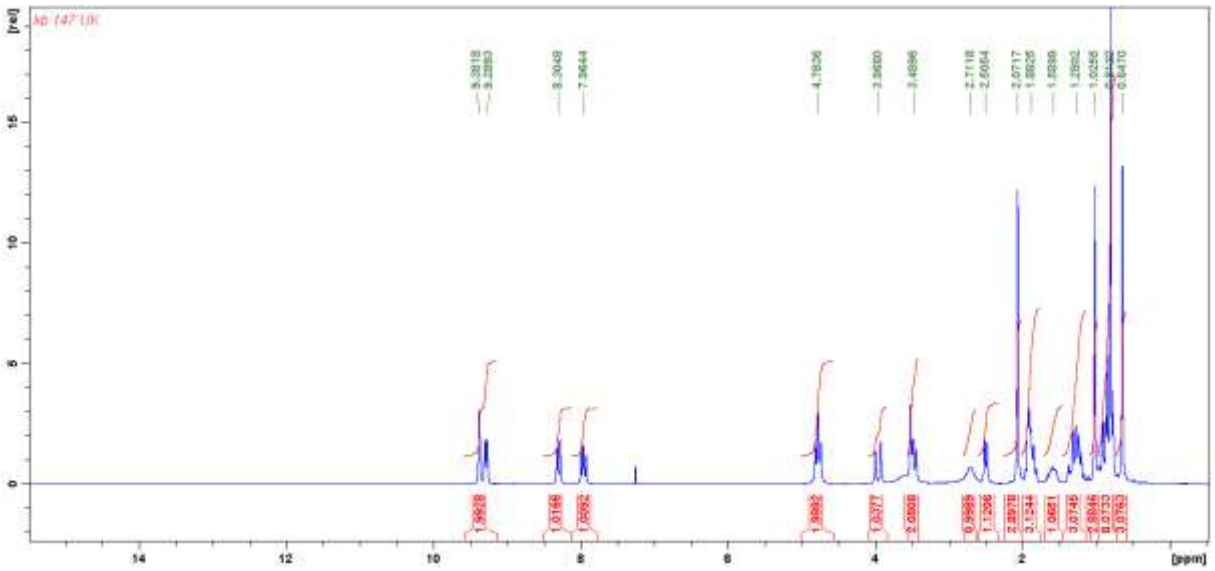
C(12)-C(11)-N(1)	115.21(18)	Torsion angles	
C(12)-C(11)-H(11A)	108.5		
N(1)-C(11)-H(11A)	108.5	C6-C1-C2-C3	-1.4(4)
C(12)-C(11)-H(11B)	108.5	C7-C1-C2-C3	178.0(2)
N(1)-C(11)-H(11B)	108.5	C1-C2-C3-C4	0.9(4)
H(11A)-C(11)-H(11B)	107.5	C2-C3-C4-C5	0.6(4)
C(13)-C(12)-C(16)	118.0(2)	C3-C4-C5-C6	-1.7(4)
C(13)-C(12)-C(11)	119.9(2)	C4-C5-C6-C1	1.2(4)
C(16)-C(12)-C(11)	121.8(2)	C2-C1-C6-C5	0.3(3)
N(2)-C(13)-C(12)	121.3(2)	C7-C1-C6-C5	-179.0(2)
N(2)-C(13)-H(13)	119.3	C2-C1-C7-O1	-163.4(2)
C(12)-C(13)-H(13)	119.3	C6-C1-C7-O1	16.0(3)
N(2)-C(14)-C(15)	119.8(2)	C2-C1-C7-C8	74.6(3)
N(2)-C(14)-H(14)	120.1	C6-C1-C7-C8	-106.1(2)
C(15)-C(14)-H(14)	120.1	O1-C7-C8-C9	-63.8(2)
C(14)-C(15)-C(16)	119.9(2)	C1-C7-C8-C9	60.1(3)
C(14)-C(15)-H(15)	120.1	O1-C7-C8-N1	62.3(2)
C(16)-C(15)-H(15)	120.1	C1-C7-C8-N1	-173.78(19)
C(15)-C(16)-C(12)	119.7(2)	C17-N1-C8-C9	167.10(19)
C(15)-C(16)-H(16)	120.2	C10-N1-C8-C9	-75.5(3)
C(12)-C(16)-H(16)	120.2	C11-N1-C8-C9	43.9(2)
N(1)-C(17)-H(17A)	109.5	C17-N1-C8-C7	40.8(3)
N(1)-C(17)-H(17B)	109.5	C10-N1-C8-C7	158.18(19)
H(17A)-C(17)-H(17B)	109.5	C11-N1-C8-C7	-82.4(2)
N(1)-C(17)-H(17C)	109.5	C17-N1-C11-C12	51.3(3)
H(17A)-C(17)-H(17C)	109.5	C10-N1-C11-C12	-67.3(2)
H(17B)-C(17)-H(17C)	109.5	C8-N1-C11-C12	174.83(19)
N(2)-C(18)-H(18A)	109.5	N1-C11-C12-C13	88.5(3)
N(2)-C(18)-H(18B)	109.5	N1-C11-C12-C16	-96.4(3)
H(18A)-C(18)-H(18B)	109.5	C14-N2-C13-C12	-1.9(4)
N(2)-C(18)-H(18C)	109.5	C18-N2-C13-C12	-179.8(2)
H(18A)-C(18)-H(18C)	109.5	C16-C12-C13-N2	1.6(4)
H(18B)-C(18)-H(18C)	109.5	C11-C12-C13-N2	176.8(2)
		C13-N2-C14-C15	1.1(4)
		C18-N2-C14-C15	179.0(2)
		N2-C14-C15-C16	0.0(4)
		C14-C15-C16-C12	-0.2(4)
		C13-C12-C16-C15	-0.5(4)
		C11-C12-C16-C15	-175.7(2)

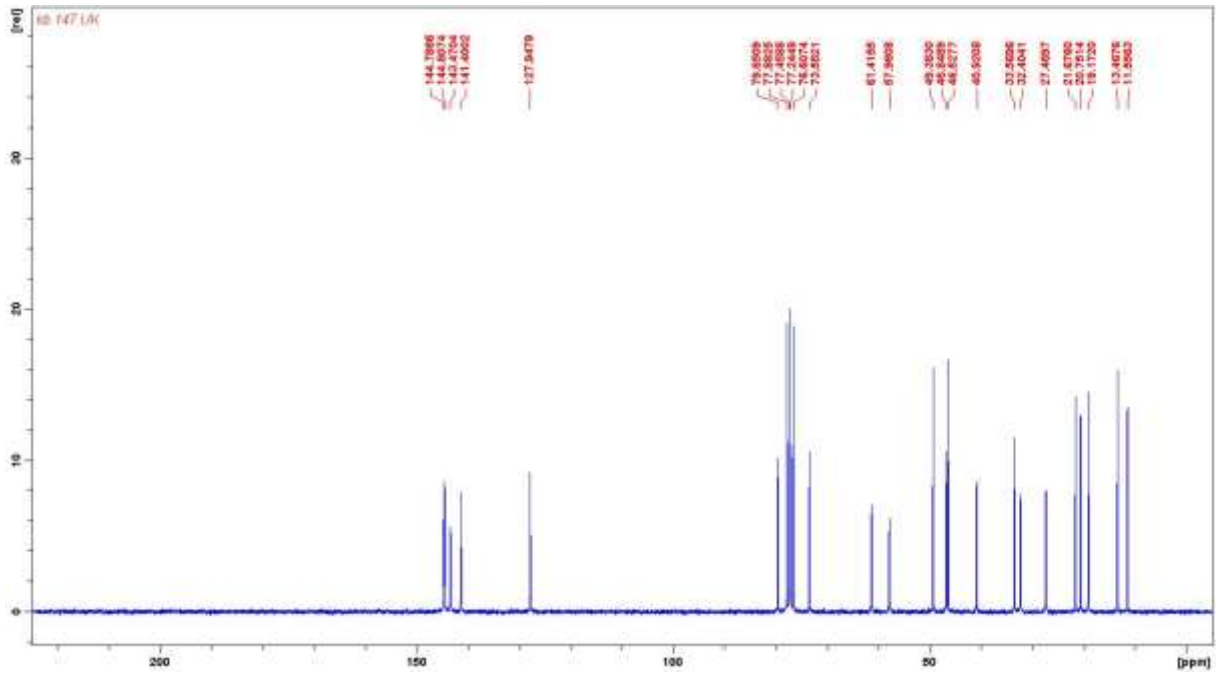
Hydrogen-bond [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...I(1)	0.84	2.529(5)	3.3639(18)	173(4)

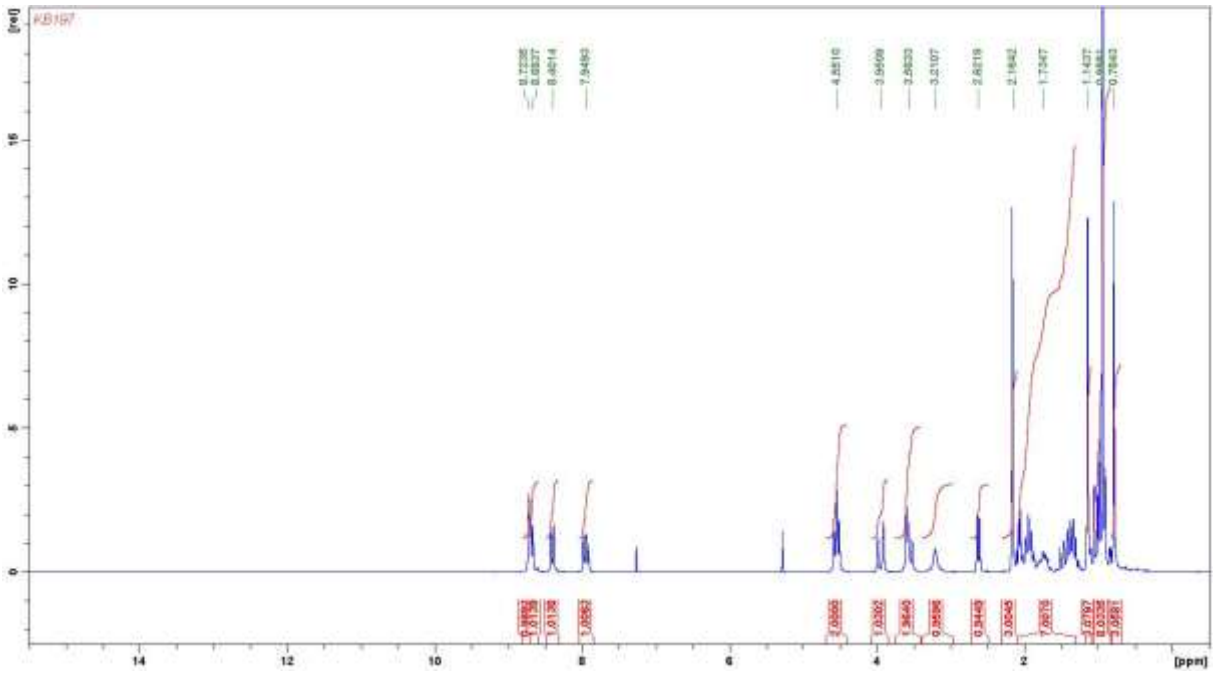
2. NMR spectra of novel compounds

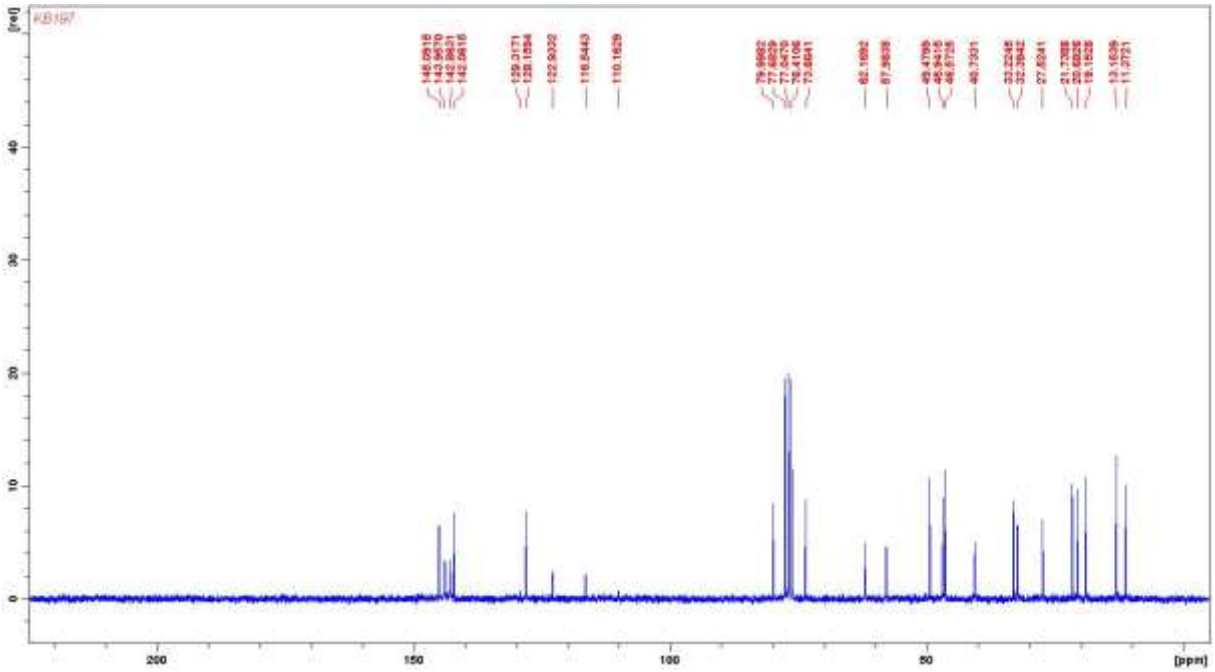
2.1. 1-Butyl-3-[[[[(1*S*,2-exo,3-exo)-3-hydroxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]methyl]amino]methyl]pyridinium bromide 4



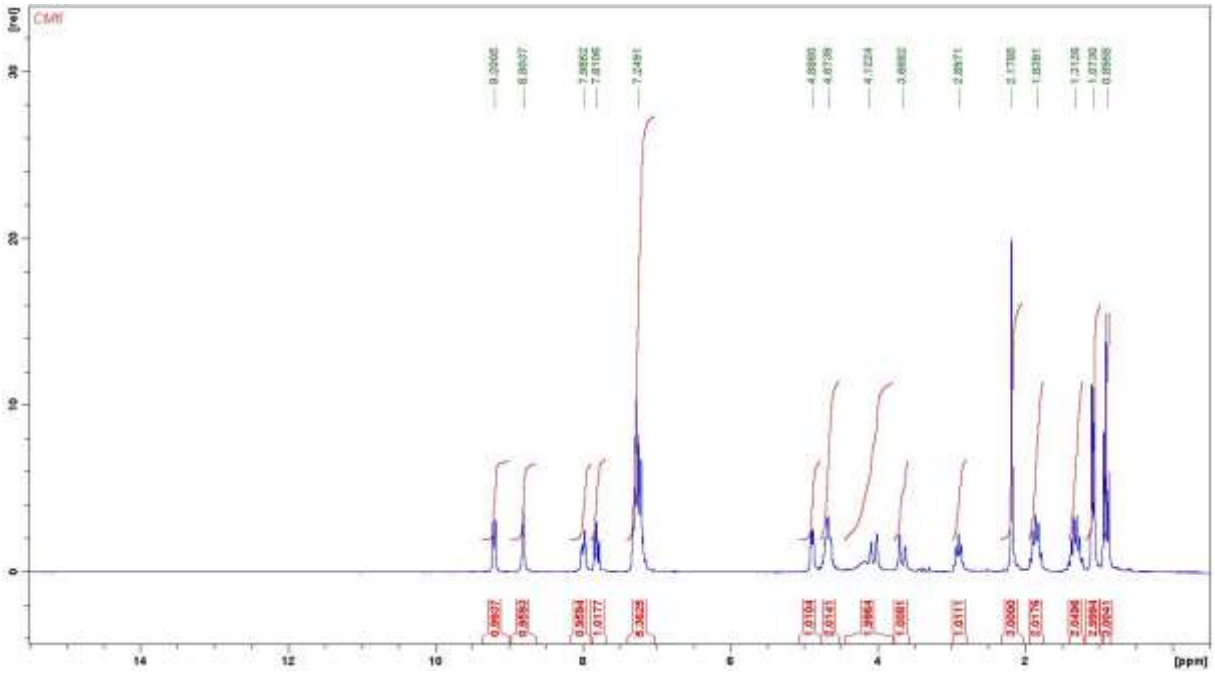


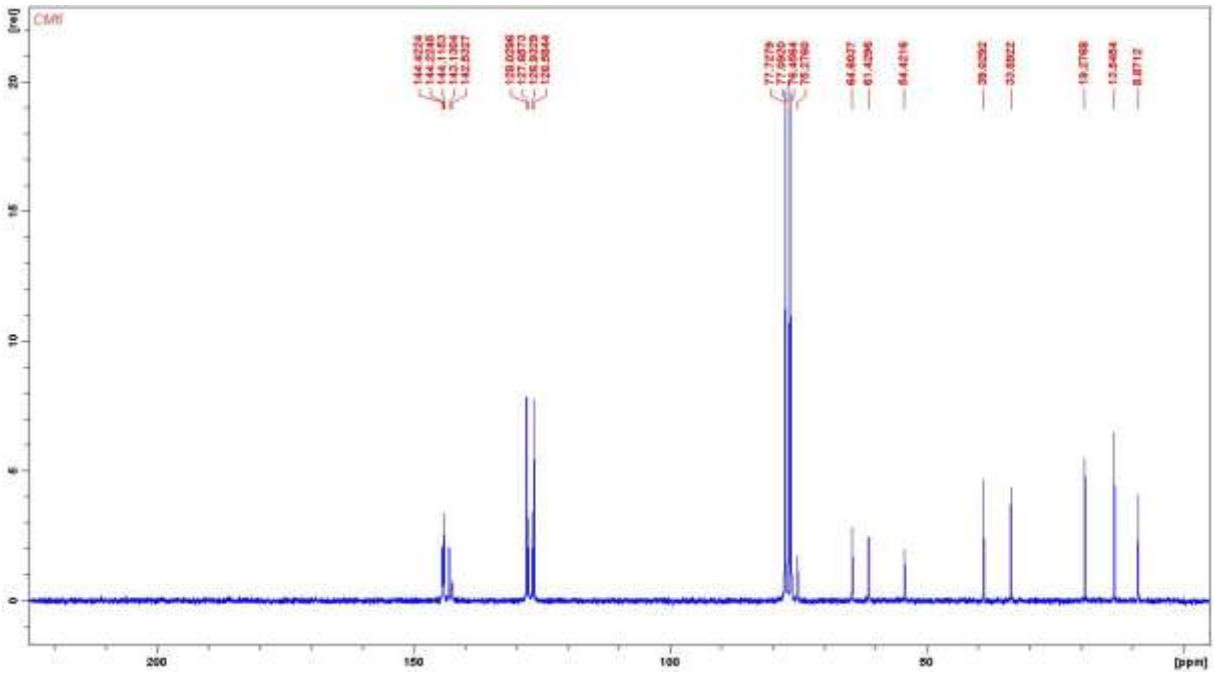
2.2. 1-Butyl-3-[[[[(1*S*,2-*exo*,3-*exo*)-3-hydroxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]methyl]amino]methyl]pyridinium bis(trifluoromethanesulfonyl)imide 5



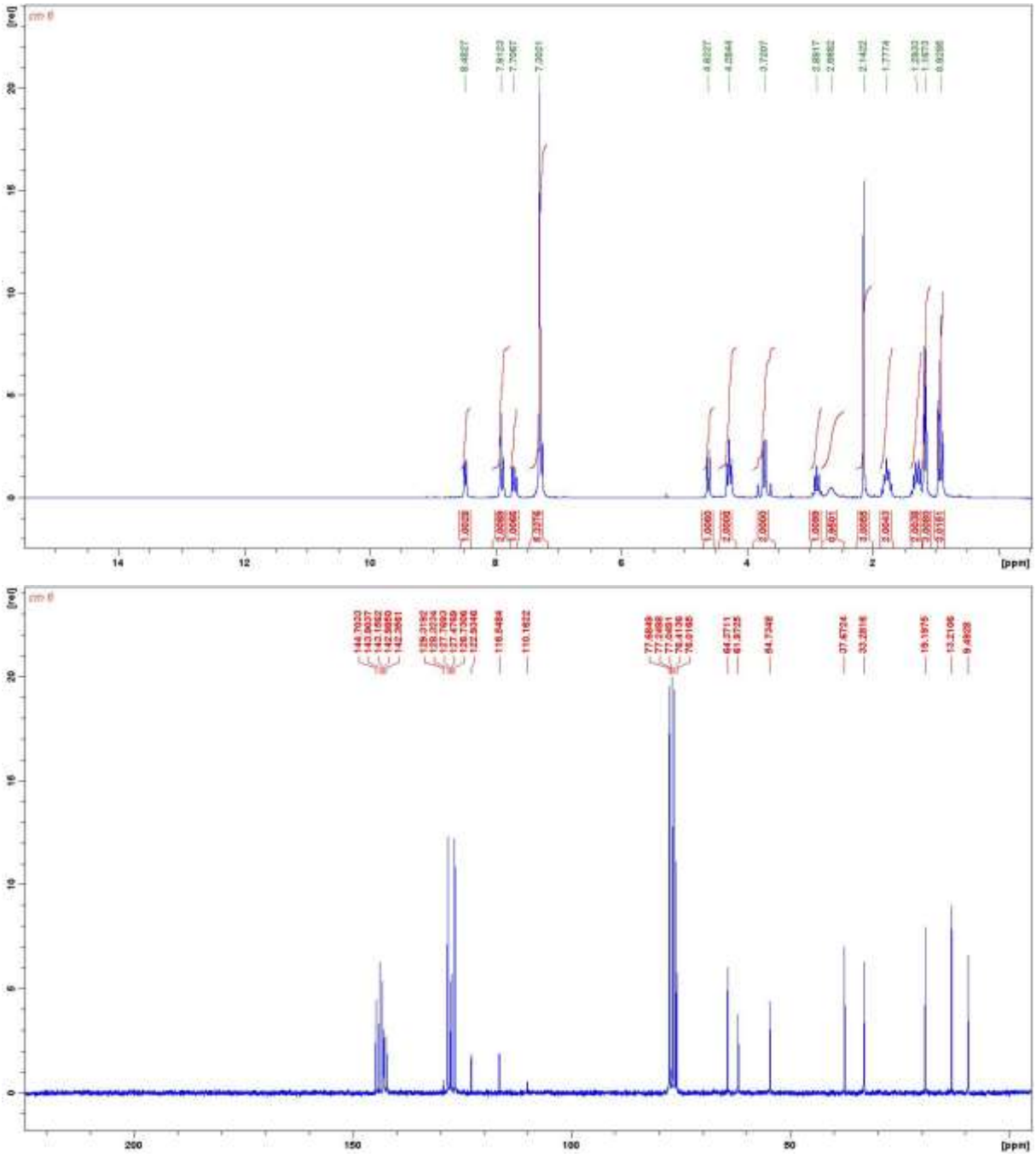


2.3. 1-Butyl-3-[[[(1*R*,2*S*)-2-hydroxy-1-methyl-2-phenylethyl]methylamino]methyl]pyridinium bromide 8

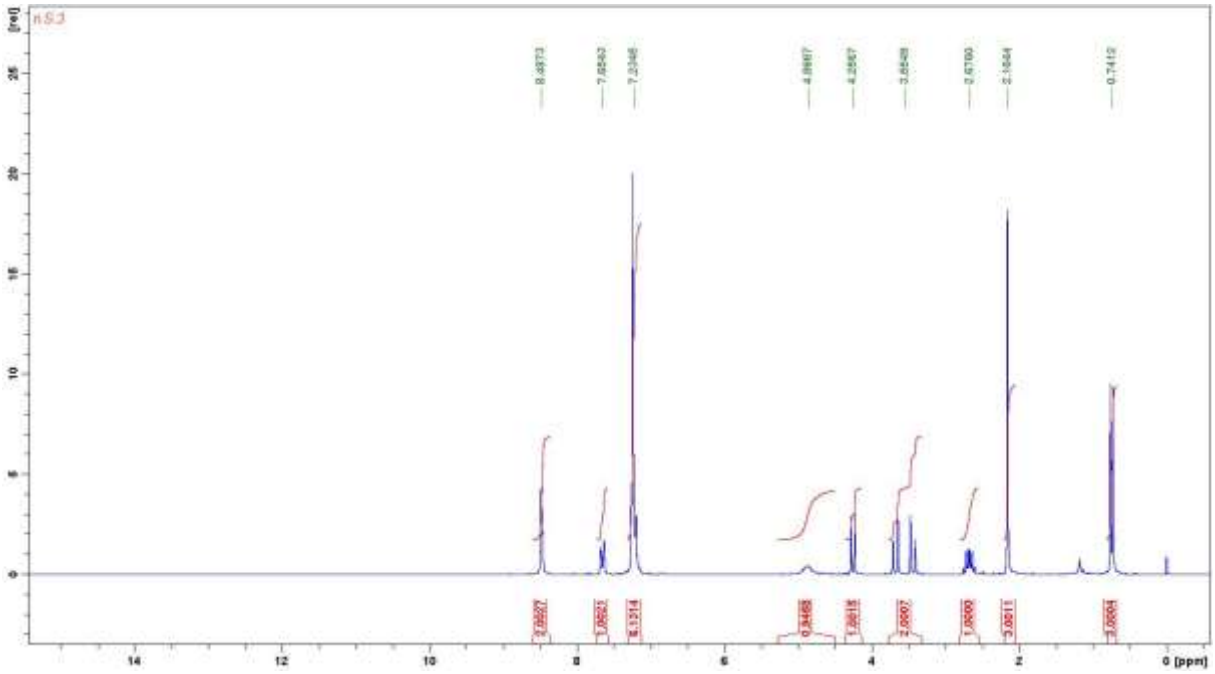


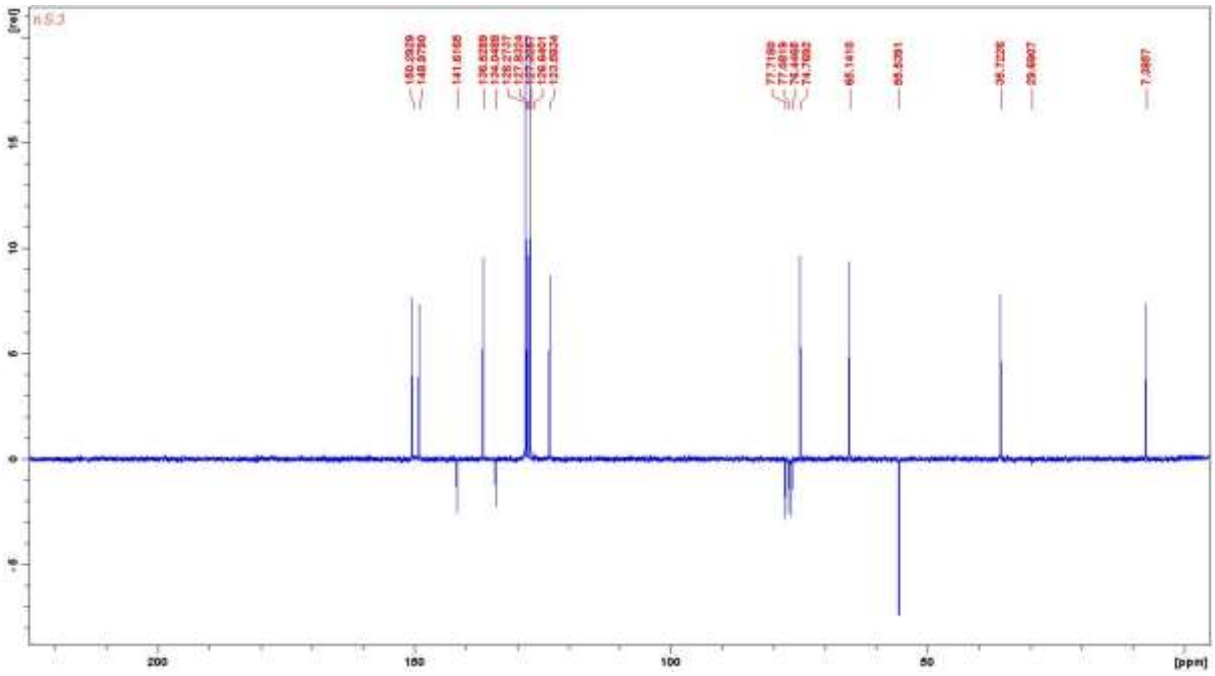


2.4. 1-Butyl-3-[[[(1*R*,2*S*)-2-hydroxy-1-methyl-2-phenylethyl]methylamino]methyl]pyridinium bis(trifluoromethanesulfonyl)imide 9

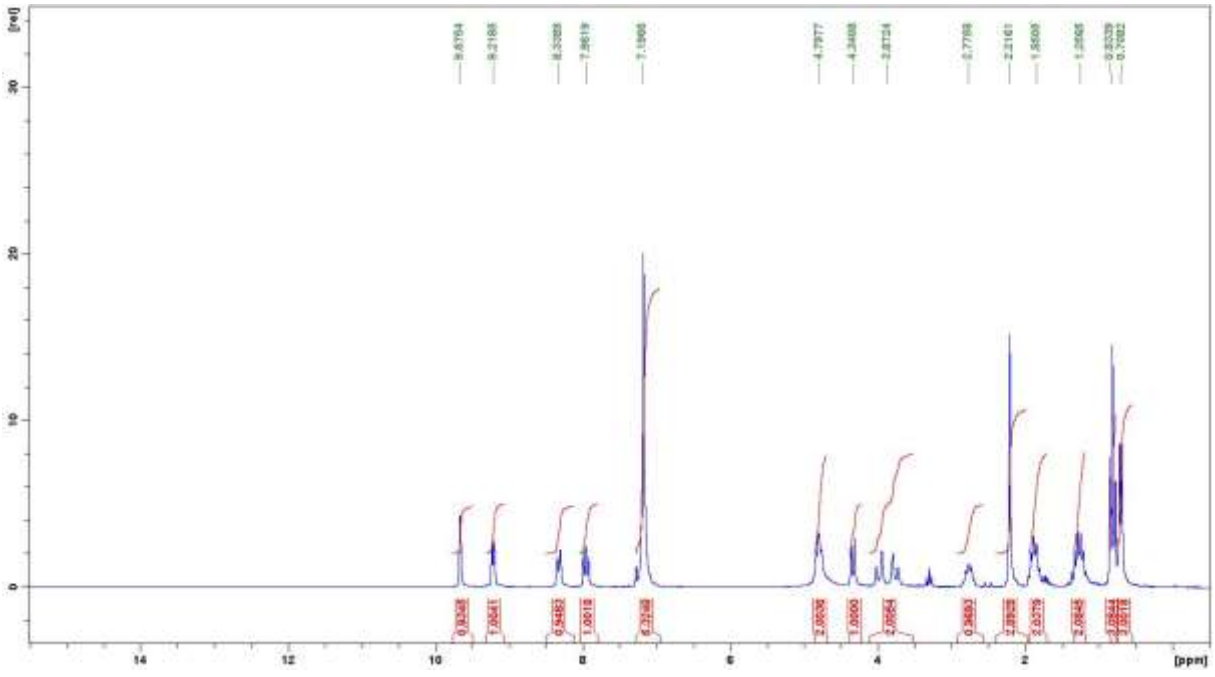


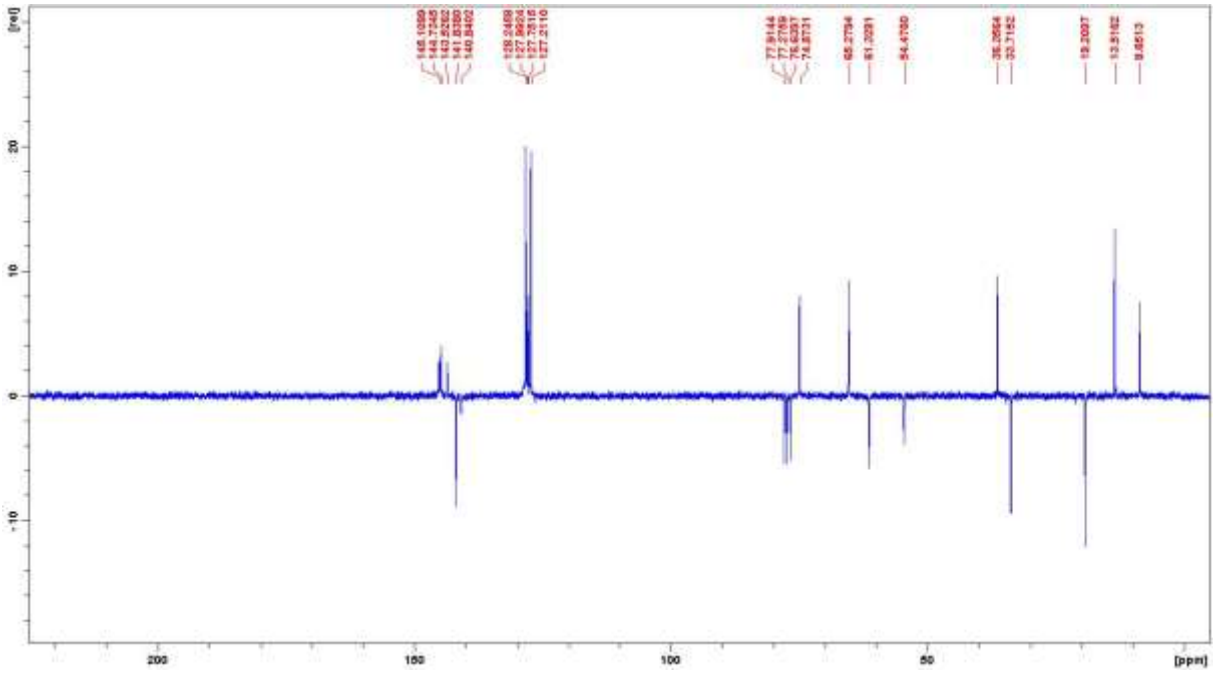
2.5. (1*S*,2*S*)-2-[Methyl(pyridin-3-ylmethyl)amino]-1-phenylpropan-1-ol 11



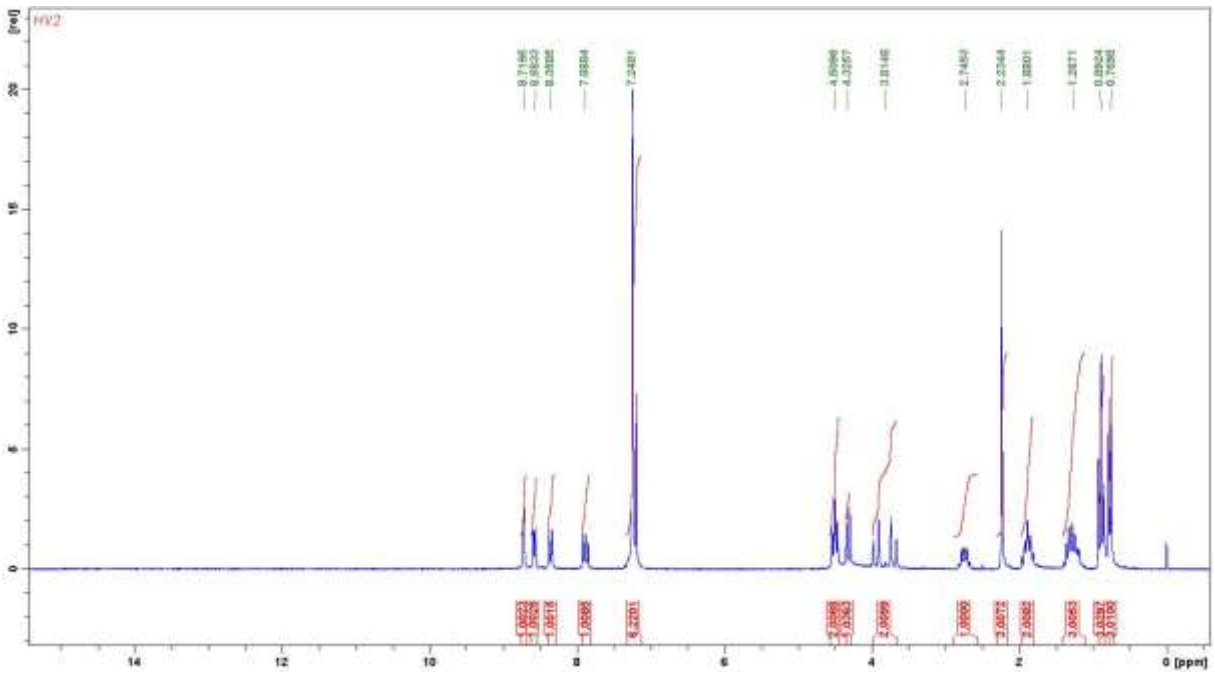


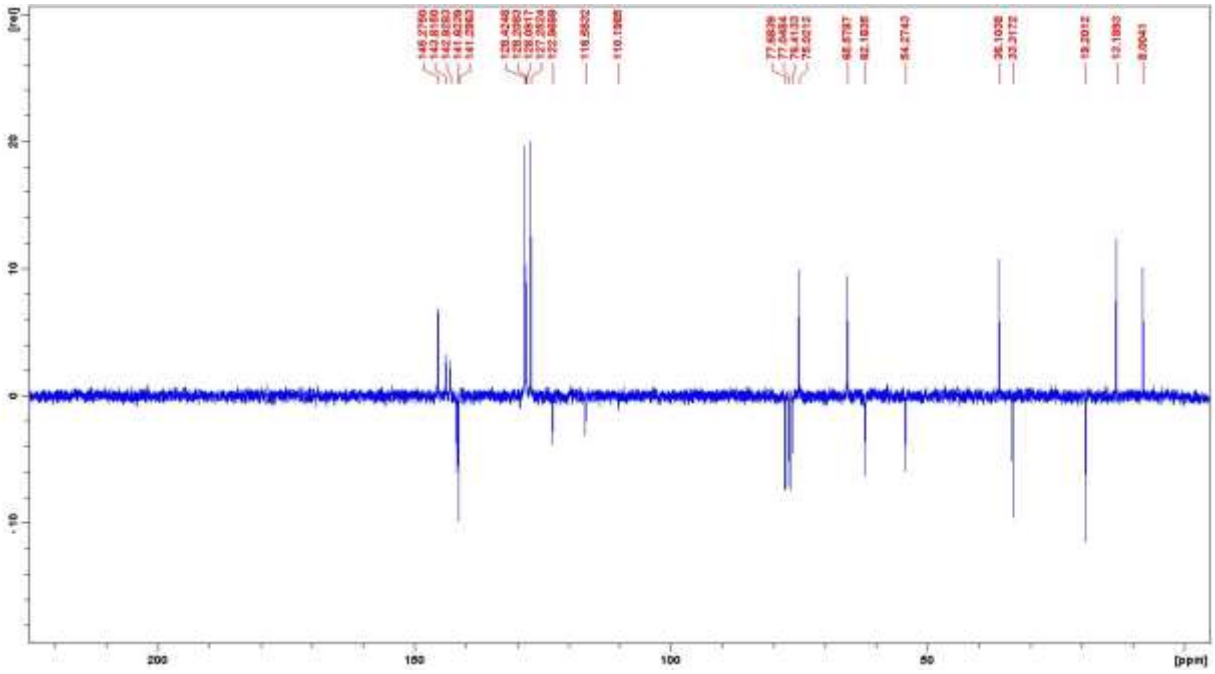
2.6. 1-Butyl-3-[[[(1*S*,2*S*)-1-hydroxy-1-phenylprop-2-yl]methylamino]methyl]pyridinium bromide 12



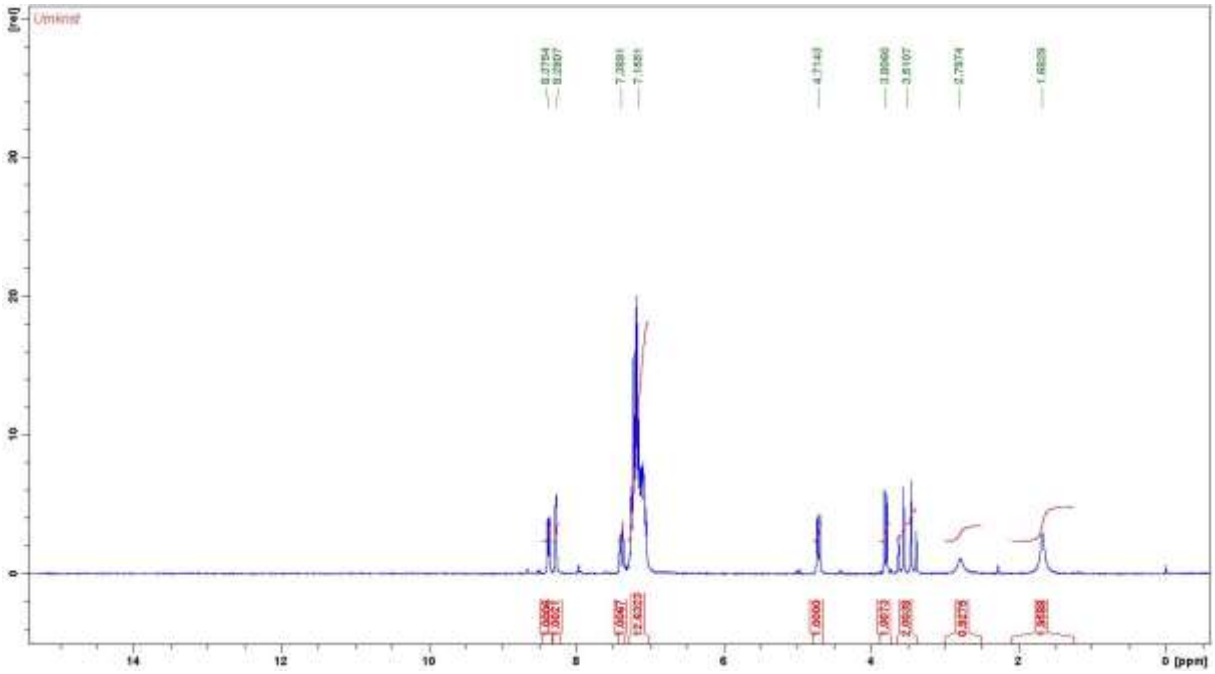


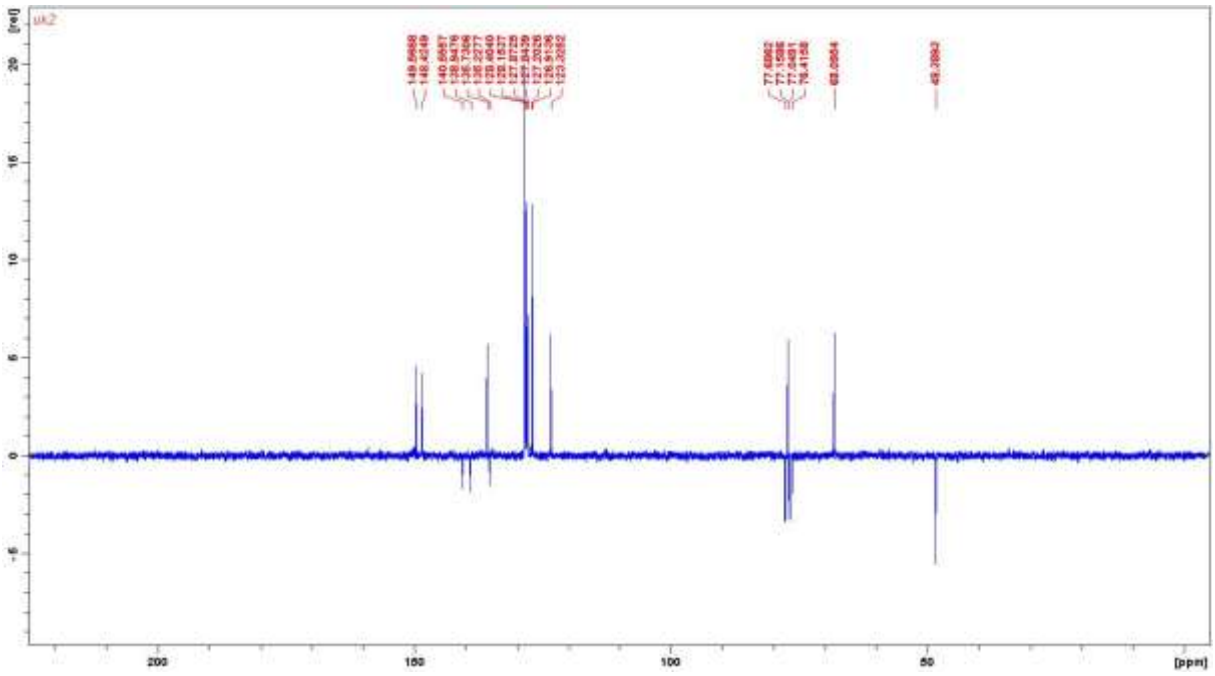
2.7. 1-Butyl-3-[[[(1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl]methylamino]methyl]pyridinium bis(trifluoromethanesulfonyl)imide 13



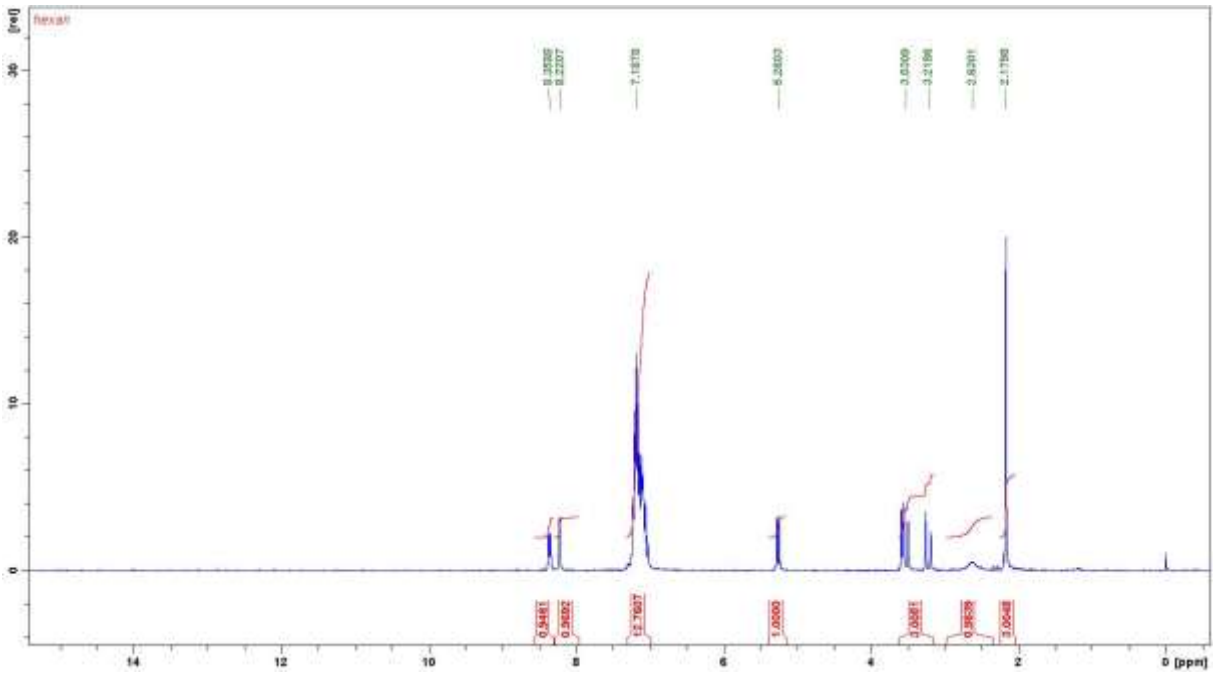


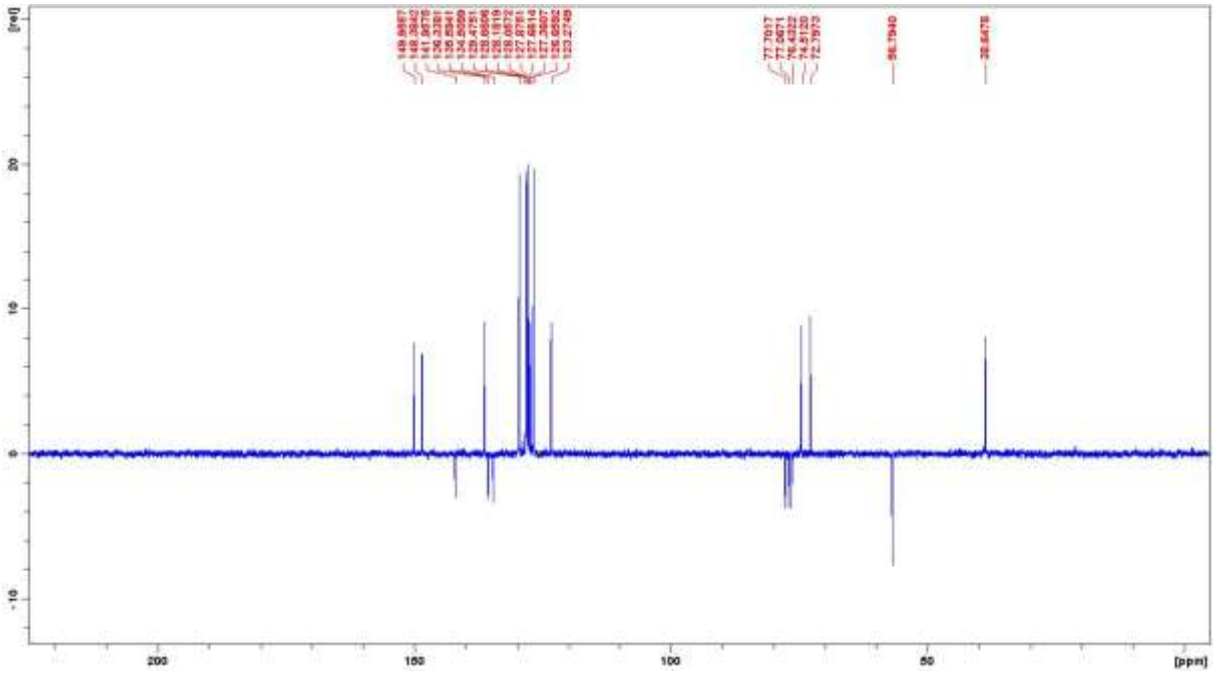
2.8. (1*S*,2*R*)-1,2-Diphenyl-2-[(pyridin-3-ylmethyl)amino]ethanol 15



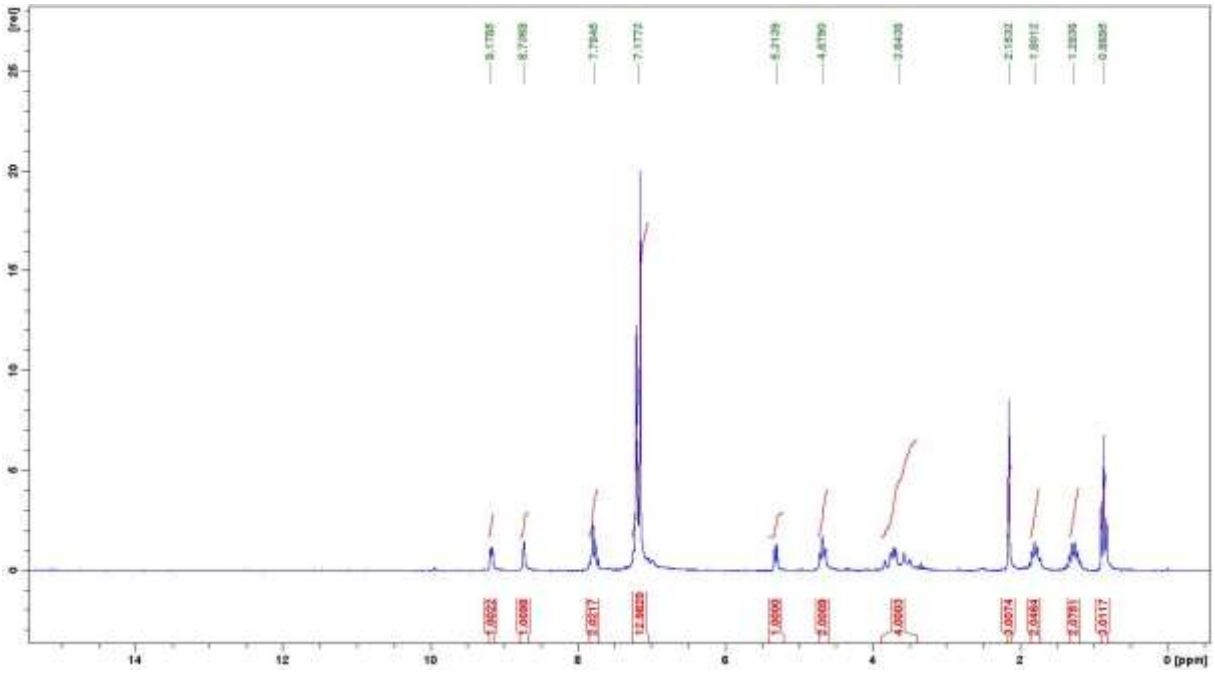


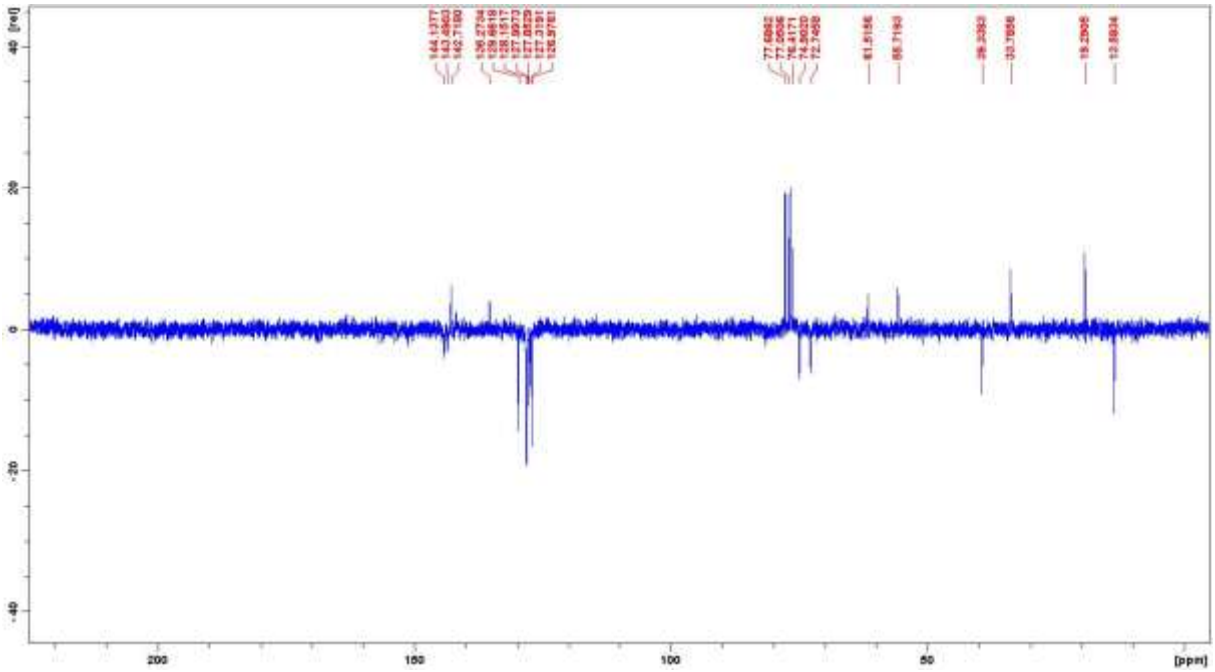
2.9. (1*S*,2*R*)-2-[Methyl(pyridin-3-ylmethyl)amino]-1,2-diphenylethanol 16



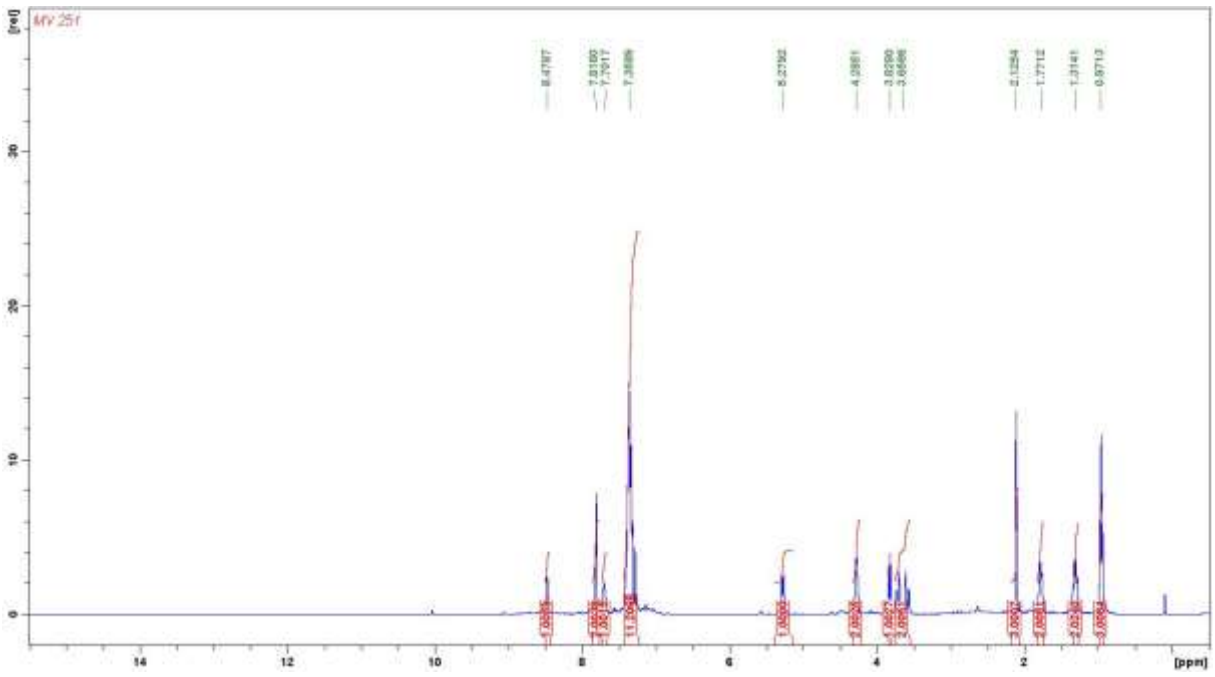


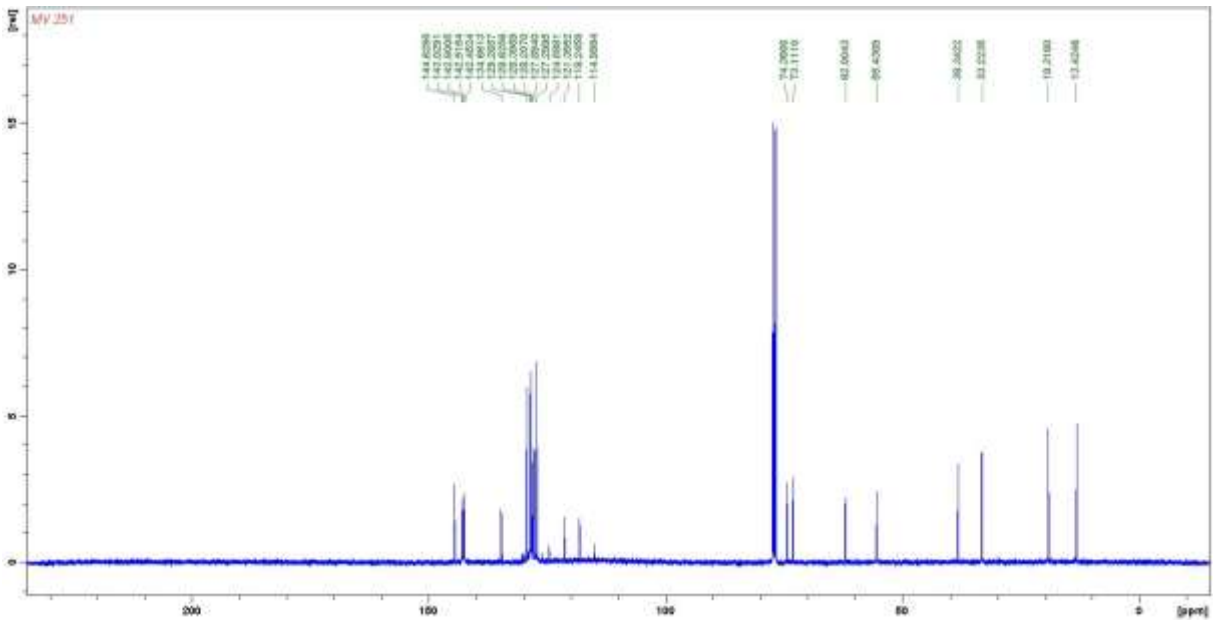
2.10. 1-Butyl-3-[[[(1*R*,2*S*)-2-hydroxy-1,2-diphenylethyl]methyl-amino]methyl]pyridinium bromide 17



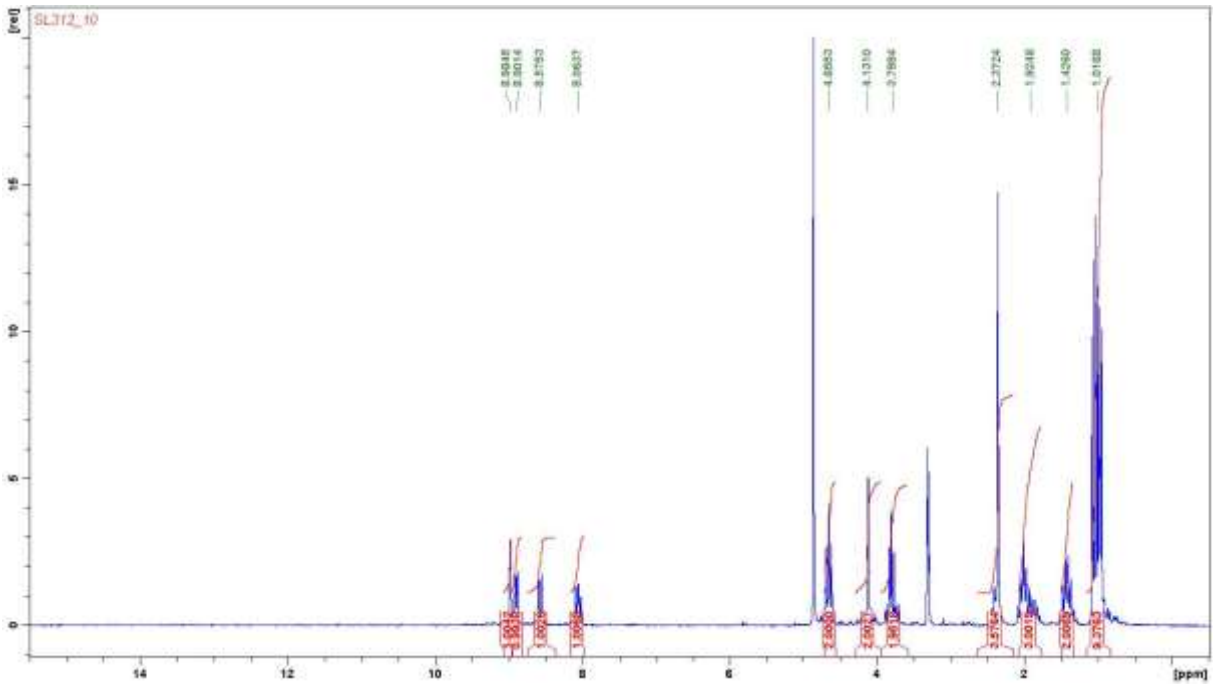


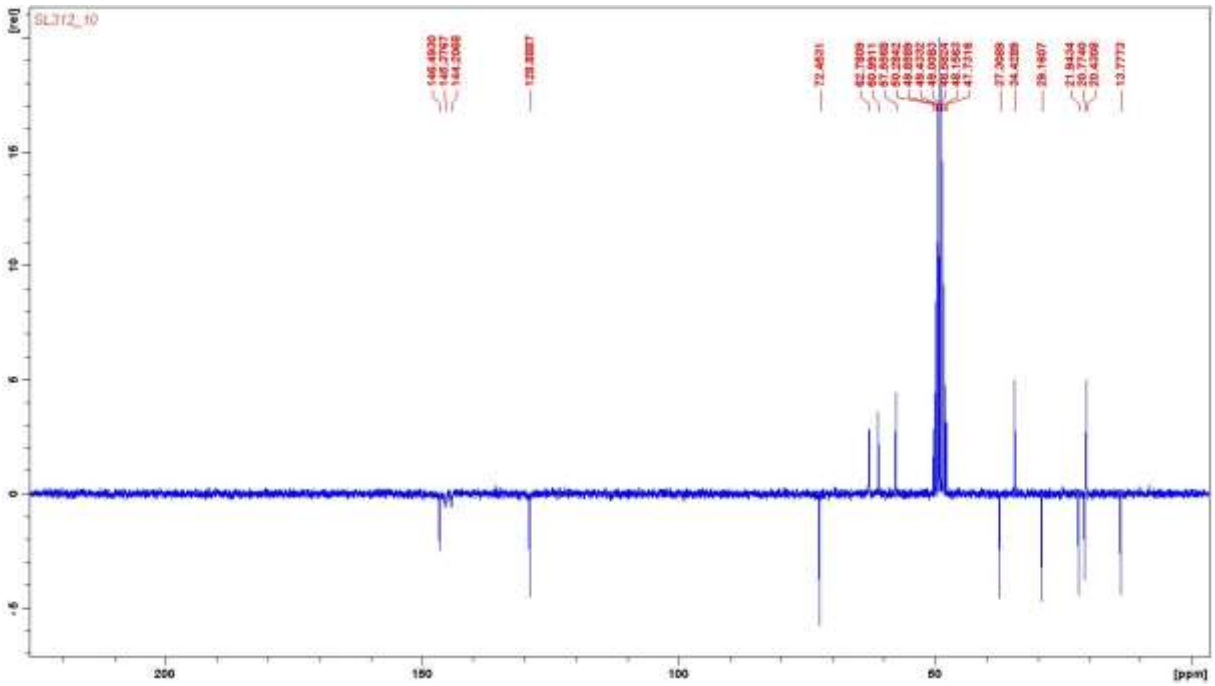
2.11. 1-Butyl-3-[[[(1*R*,2S)-2-hydroxy-1,2-diphenylethyl]-methylamino]methyl]pyridinium bis(trifluoromethanesulfonyl)imide 18



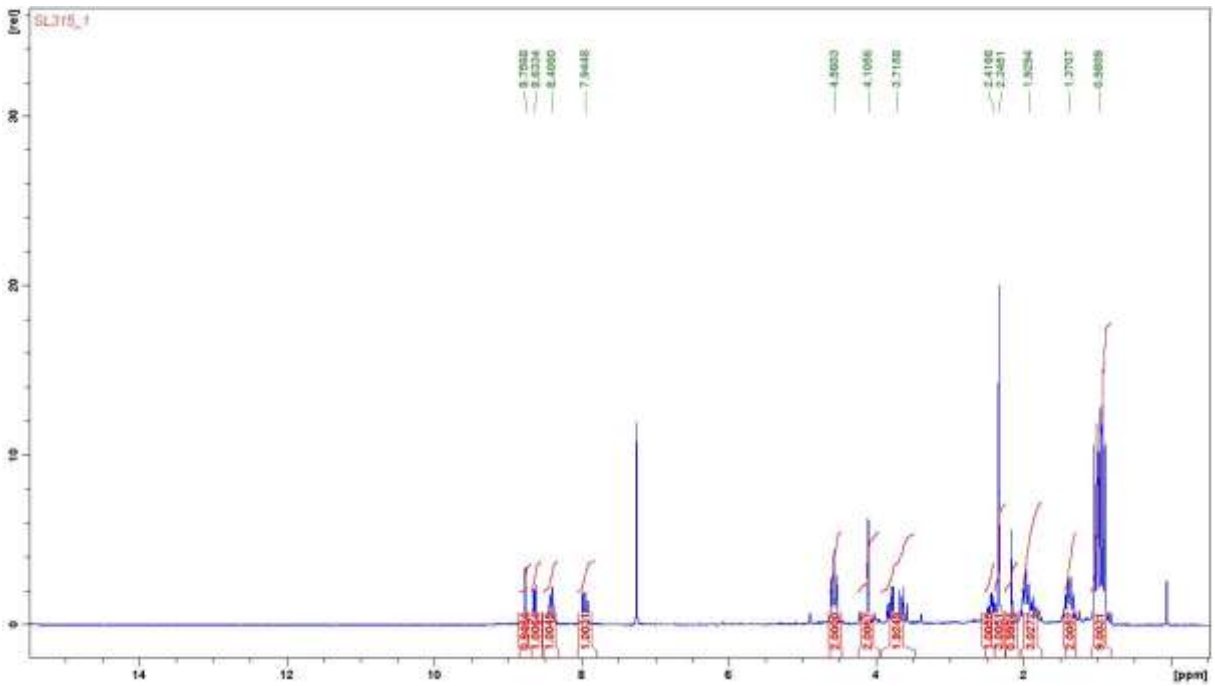


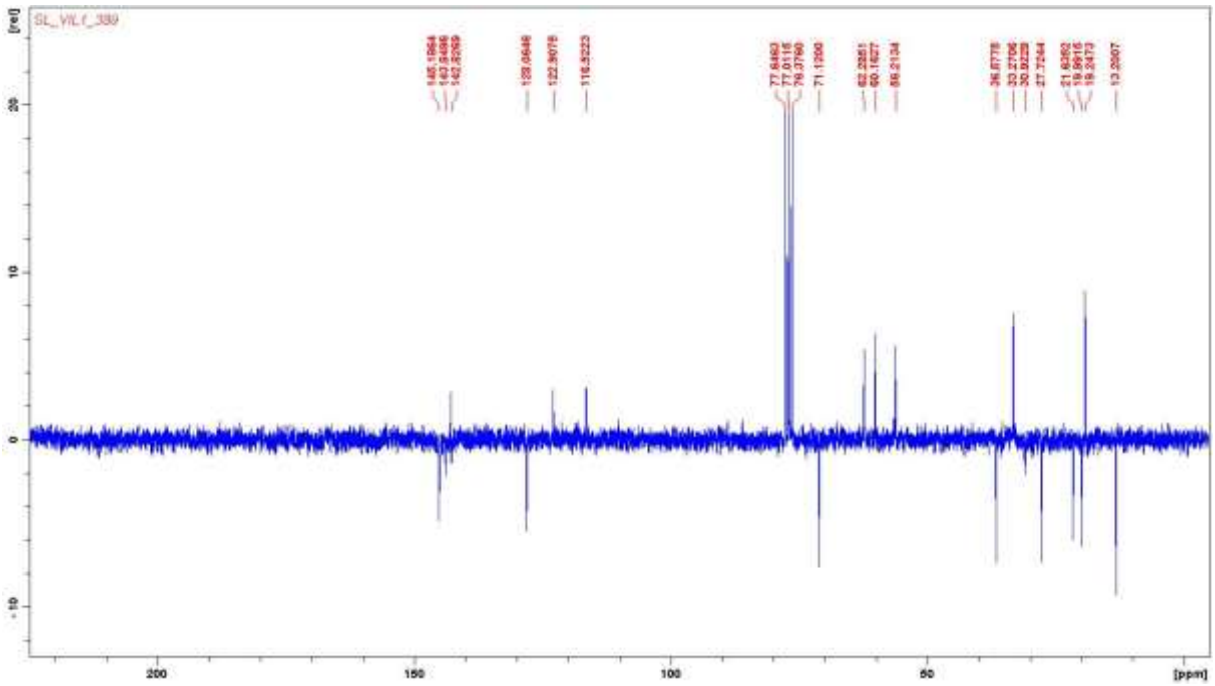
2.12. 1-Butyl-3-[[[(1*S*)-1-(hydroxymethyl)-2-methylpropyl]methylamino]methyl]pyridinium bromide 21



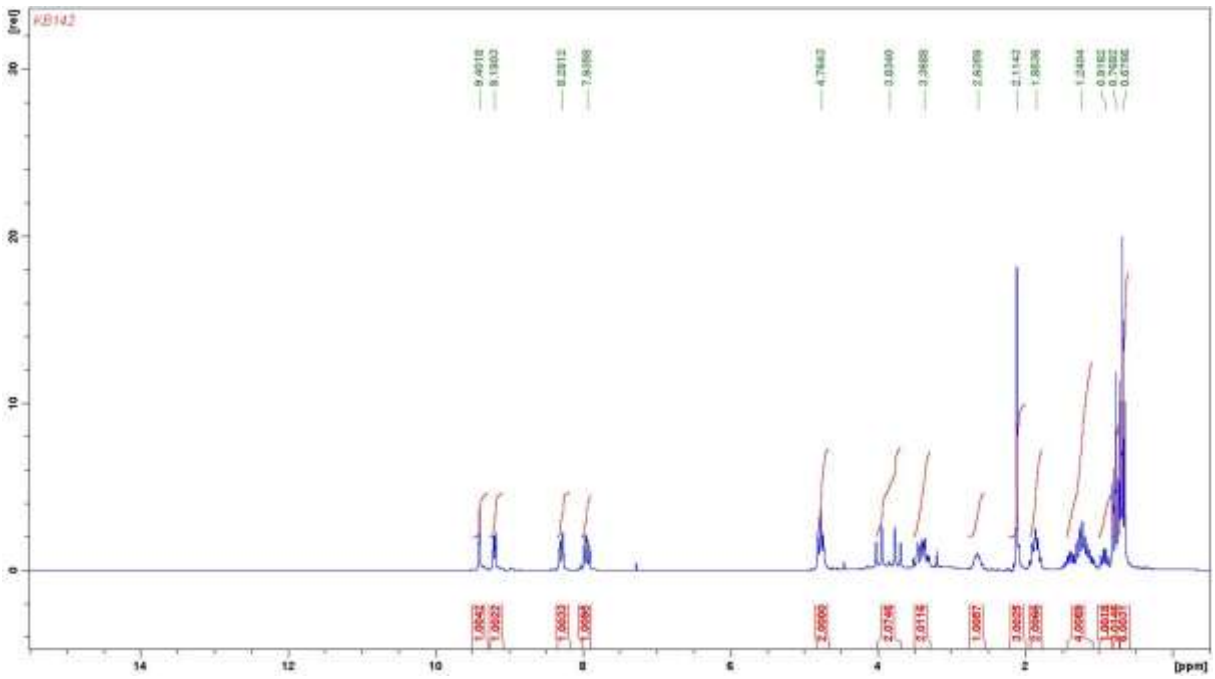


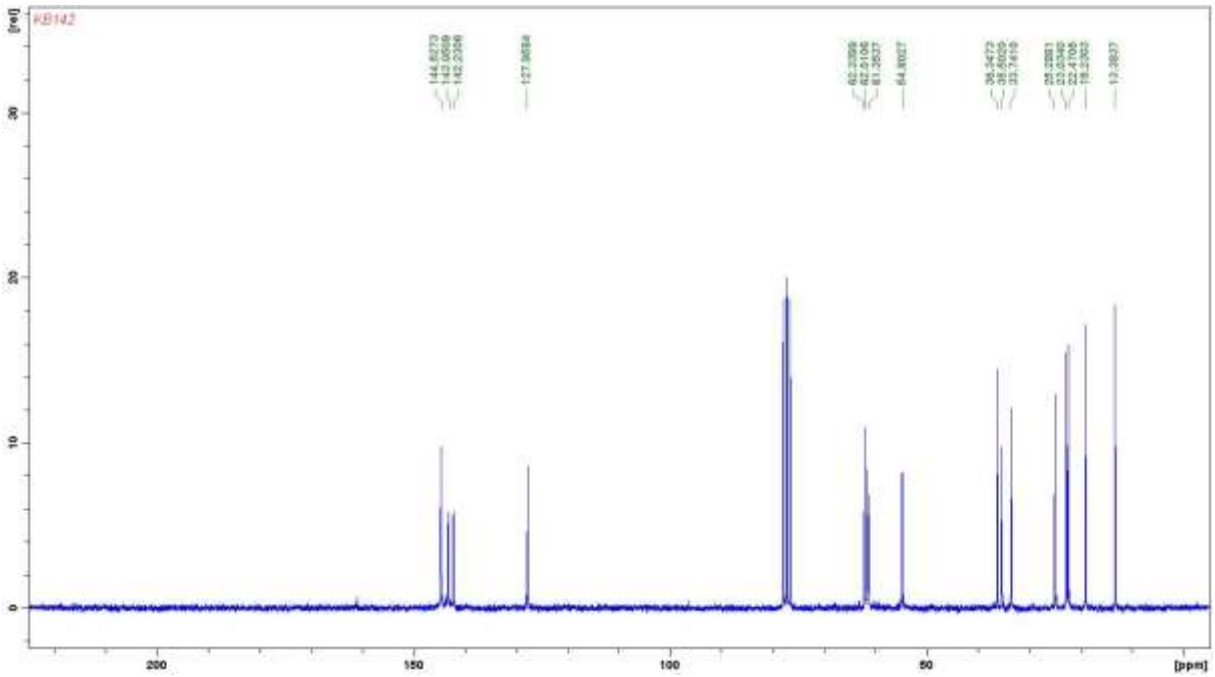
2.13. 1-Butyl-3-[[[(1*S*)-1-(hydroxymethyl)-2-methyl-propyl]methyl-amino]methyl]pyridinium bis (trifluoromethanesulfonyl)imide 22



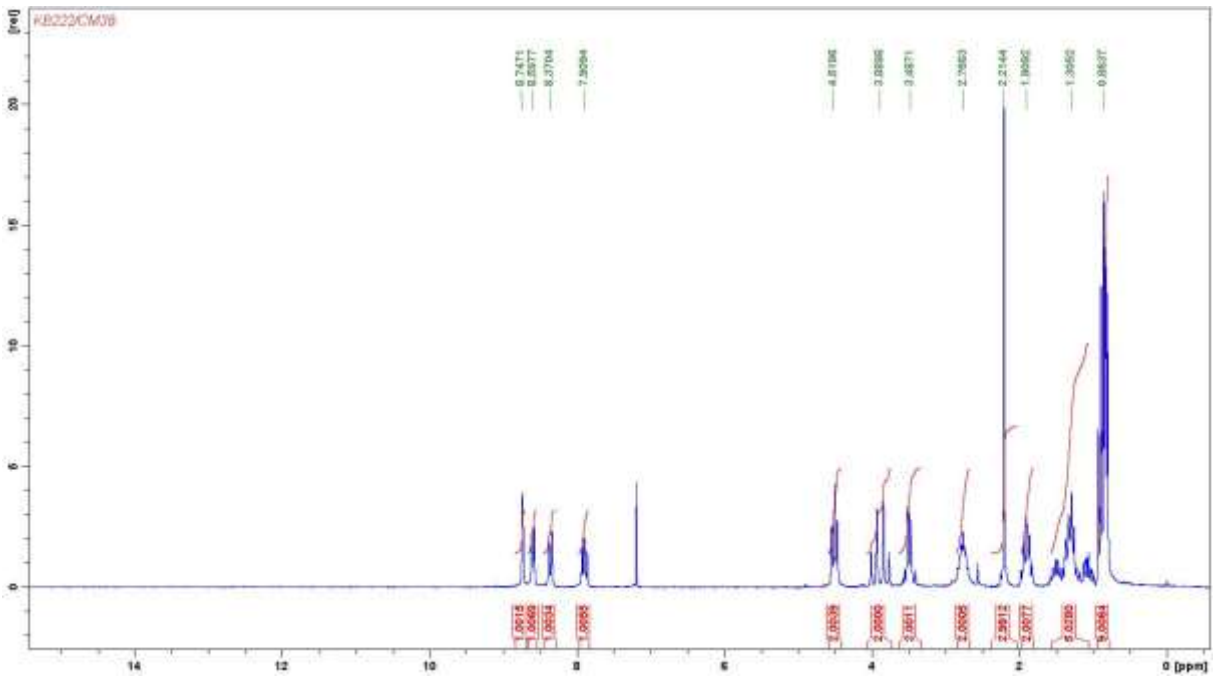


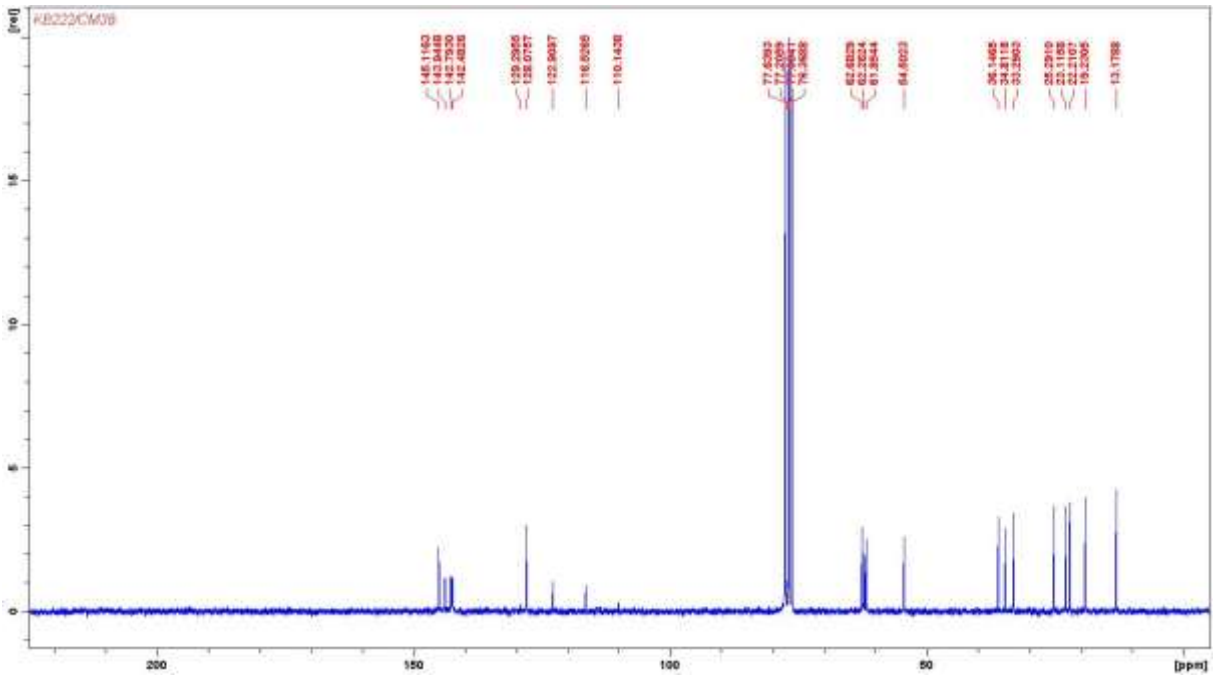
2.14. 1-Butyl-3-[[[(1*S*)-1-(hydroxymethyl)-3-methyl-butyl]methylamino]methyl]pyridinium bromide 25



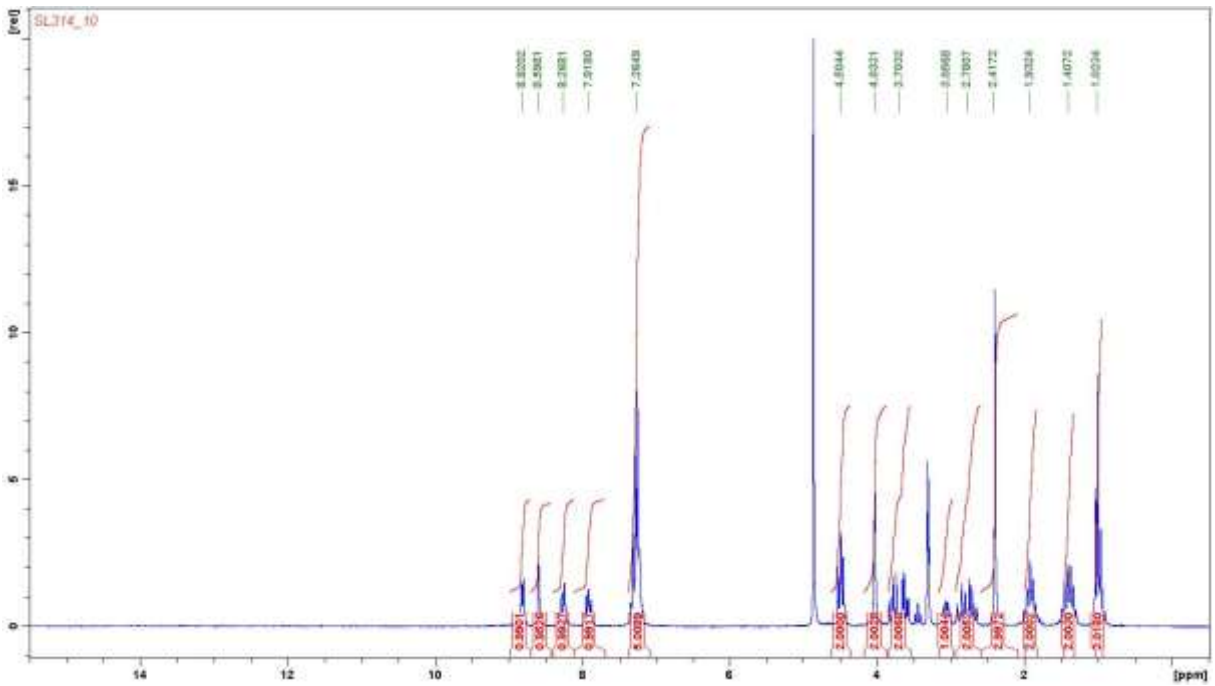


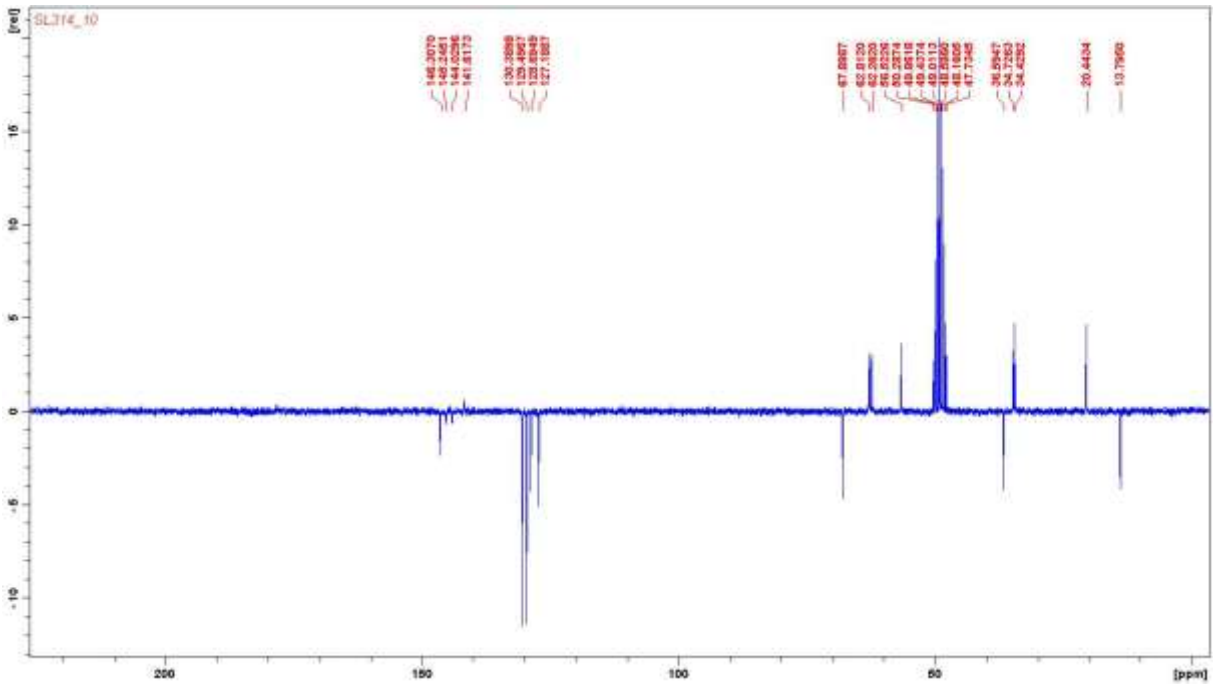
2.15. 1-Butyl-3-[[[(1*S*)-1-(hydroxymethyl)-3-methylbutyl]methylamino]methyl]pyridinium bis(trifluoromethanesulfonyl)imide 26



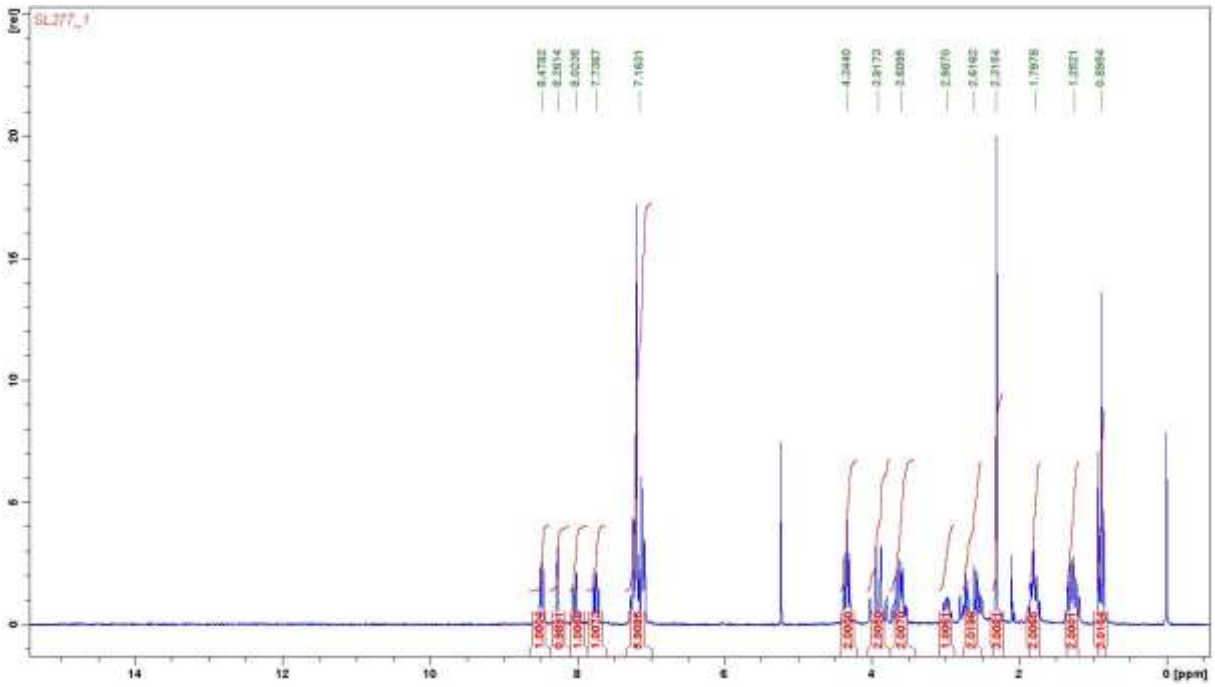


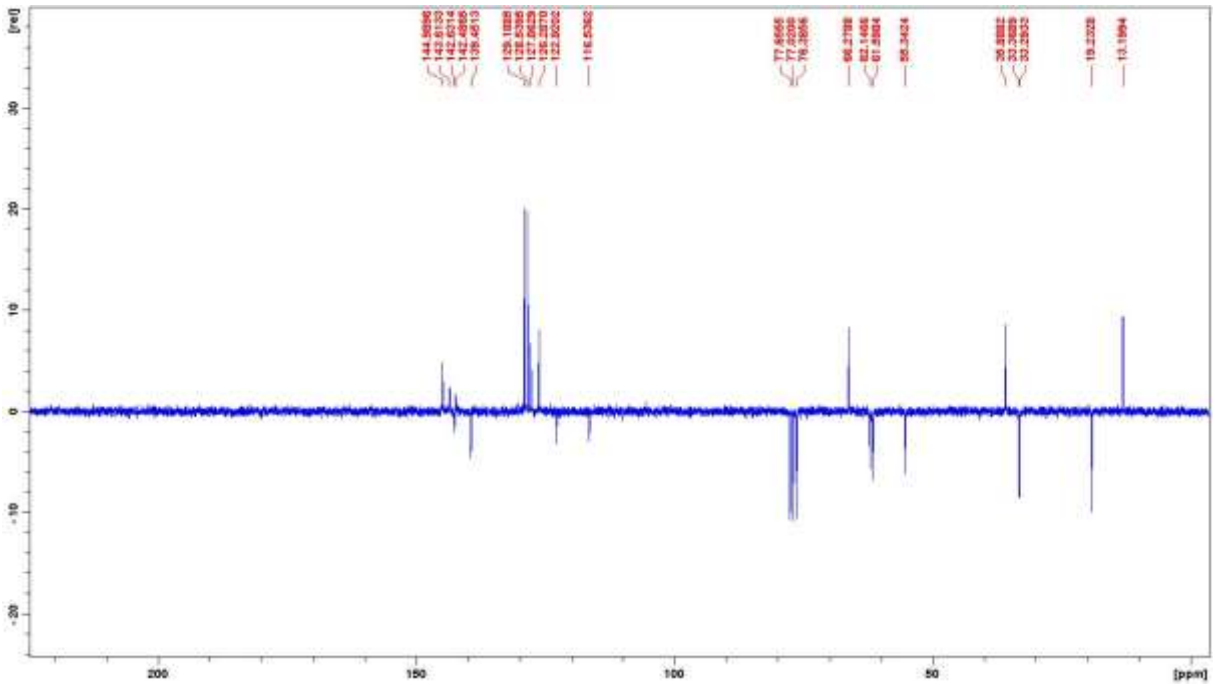
2.16. 1-Butyl-3-[[[(1*S*)-1-(hydroxymethyl)-2-phenylethyl]methylamino]methyl]pyridinium bromide 29



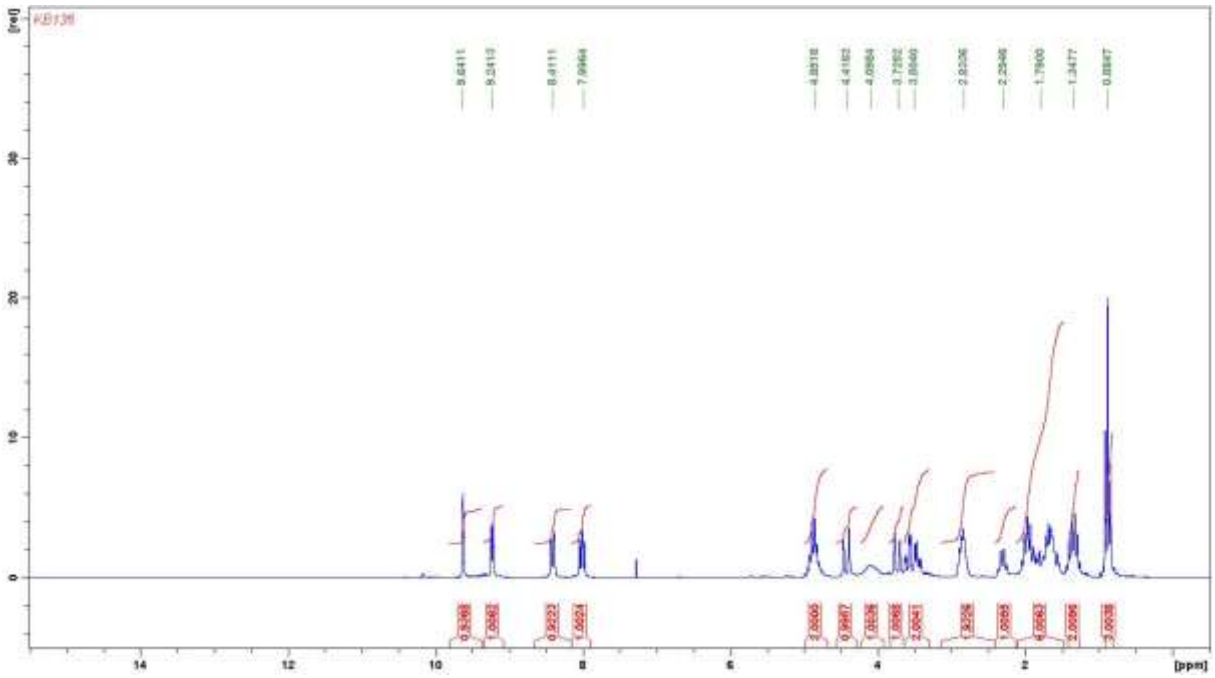


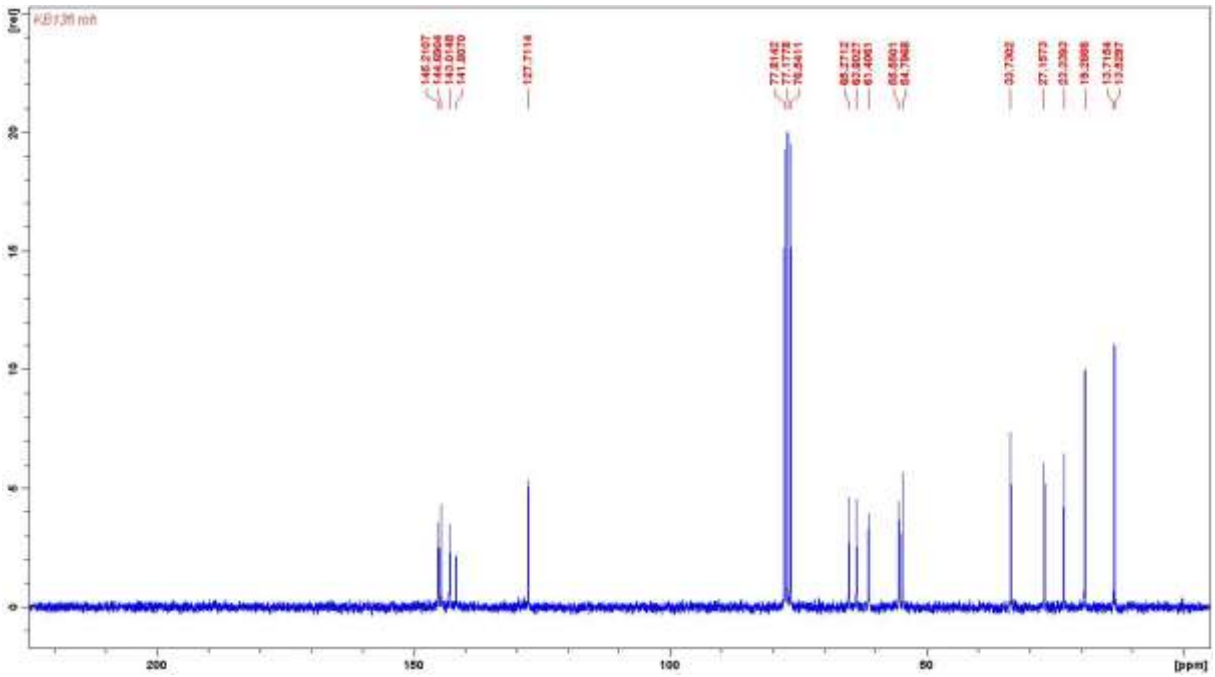
2.17. 1-Butyl-3-[[[(1*S*)-1-(hydroxymethyl)-2-phenylethyl]methylamino]methyl]-pyridinium bis (trifluoromethane sulfonyl)imide 30



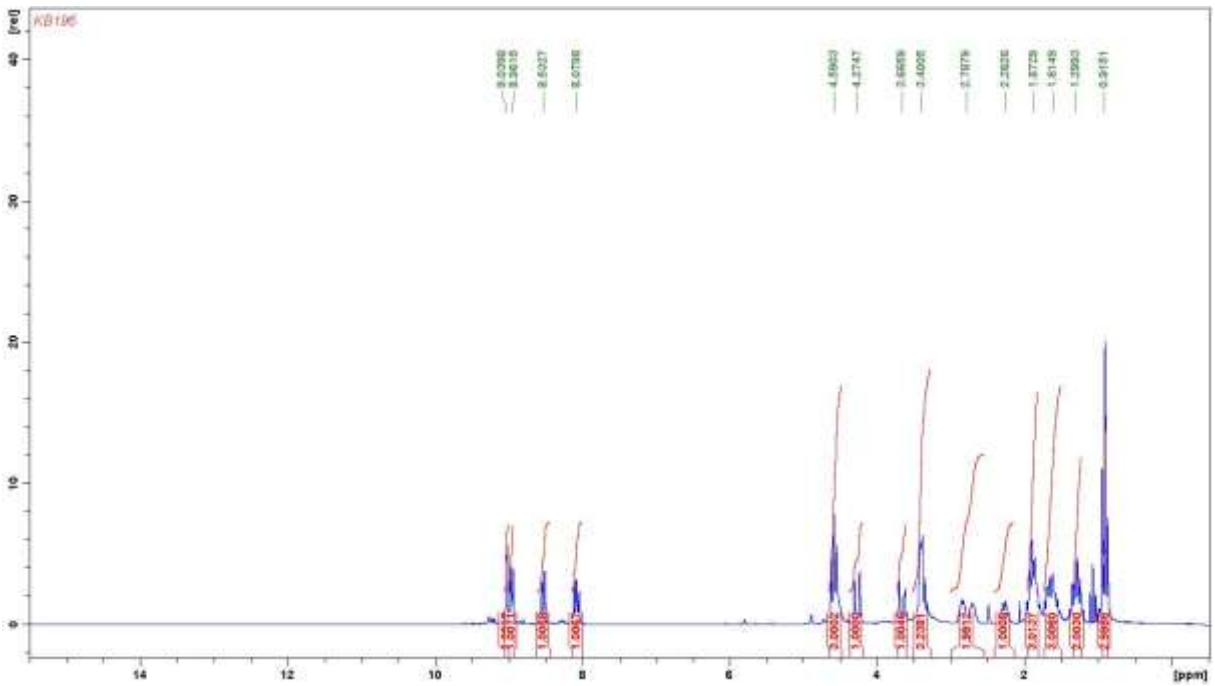


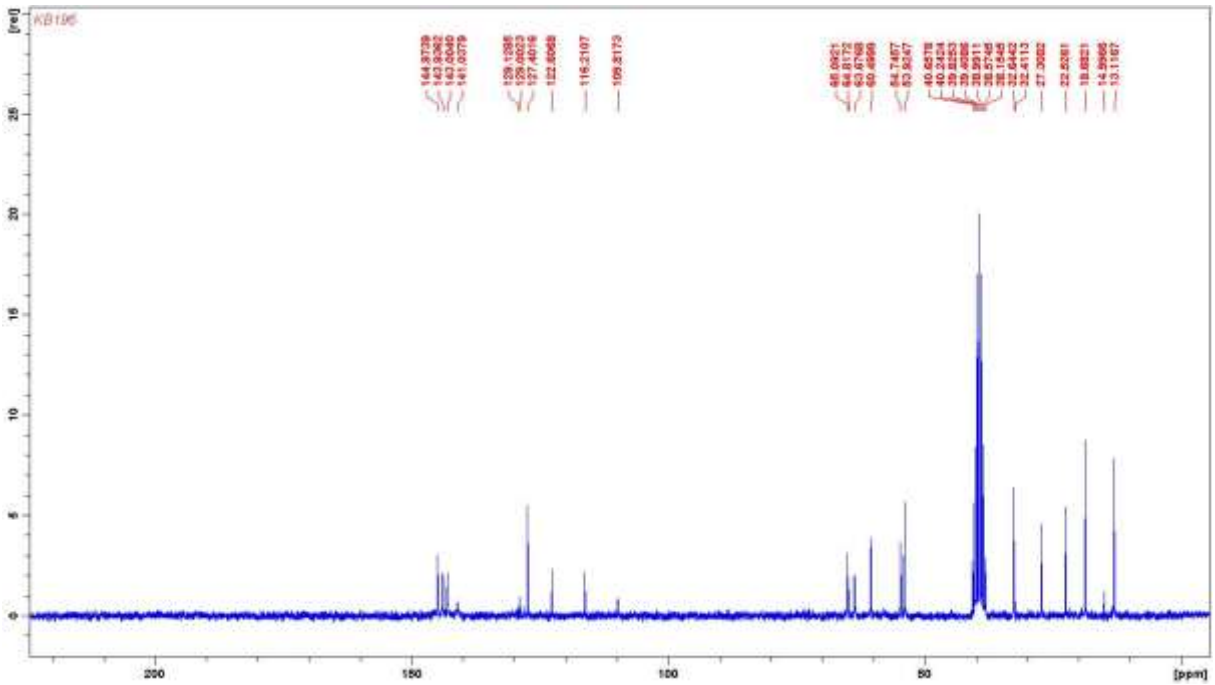
2.18. 1-Butyl-3-[[(2*S*)-2-(hydroxymethyl)pyrrolidin-1-yl]methyl]pyridinium bromide 33





2.19. 1-Butyl-3-[[(2S)-2-(hydroxymethyl)pyrrolidin-1-yl]methyl]pyridinium bis(trifluoromethanesulfonyl)imide 34





2.20. 1-Methyl-3-[[[dimethyl[(1*R*,2*S*)-2-hydroxy-1-methyl-2-phenyl]ethyl]-ammonio]methyl]pyridinium diiodide 35