Electronic Supplementary Material (ESI) for RSC Advances.

Application of novel multi-cationic ionic liquids in microwave assisted 2-amino-4*H*-chromene synthesis

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Supporting Information

Experimental

General Remarks

^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) spectrometer using D_2O and MSO-d_6 as solvent and tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a PerkinElmer FTIR spectrometer. The samples were examined as KBr discs~5% w/w. Melting points were determined with a DBK melting point apparatus and are uncorrected. All the chemicals were obtained from Spectrochem, Sigma Aldrich and were used without further purification. The compounds Ia, IIa and IIIa were prepared following the literature procedure.[1] Microwave irradiation was made using a Samsung domestic Microwave oven with adjustable 0-300 W output power.

Typical procedure for synthesis of bromide salts (**Ib**, **IIb** and **IIIb**):

A solution of 1-methyl imidazole (30 mmol) in MeCN (10mL) was added dropwise to

slurry of mono (bromomethyl) mesitylene (30 mmol) or bis (bromomethyl) mesitylene (15 mmol) or tris (bromomethyl) mesitylene (10 mmol) in MeCN (20 mL). The reaction mixture was stirred at room temperature for 24 h. A white precipitate formed was filtered, washed with MeCN (3×10 mL) and dried in vacuum to afford **Ib, IIb** and **IIIb** as white solids.

Typical procedure for synthesis of hydroxide salts Ic, **IIc** and **IIIc.**

Aqueous solution of hydroxide salts **(Ic**, **IIc** and **IIIc)** were prepared from corresponding bromide salts (**Ib, IIb** and **IIIb)** by anion metathesis reaction over anion exchange resin AMBERLYST A26 OH. In typical experiment corresponding bromide salts (25 g, Ib, IIb and IIIb) were dissolved in deionized water (200 mL) and passed over anion exchange resin (250 g) slowly. The absence of any bromide ions in aqueous ILs solution was tested by $AgNO_3$ test. The amount of hydroxide ILs in aqueous solution was determined by titrating the aqueous ILs solution with standard HCl (0.1 N) conductometrically.

Typical procedure for synthesis of acetate (Id, IId and **IIId) and methane sulfonate salts** (**Ie, IIe** and **IIIe).**

To an aqueous solution of hydroxide salts **Ic, IIc** and **IIIc** were added a equimolar amount of acetic acid /methane sulphonic acid in water. The reaction mixture was stirred at room temperature for 12 hrs. The solvent was removed on a rotary evaporator and the resultant oily compound was dried in vacuum at 80°C affording the corresponding ILs.

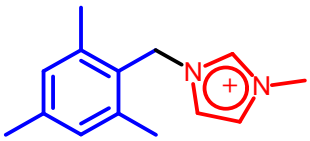
Typical procedure for synthesis of 2-amino-4*H*-chromene.

A mixture of an aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), α/β-Naphthol (1 mmol) and 20 mol % IL was irradiated in microwave oven under solvent-free condition for appropriate time. After completion of the reaction (as monitored by TLC)

water was added and the solid product obtained was filtered, washed with water and recrystallized from hot ethanol.

Spectral of Compounds:

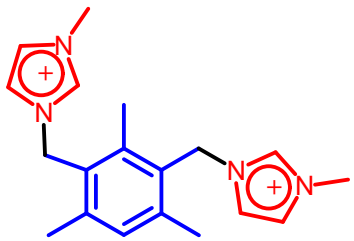
3[(2, 4, 6-trimethyl-1-phenylene) mono (methylene)] mono (1-methyl-1*H*-imidazol-3-ium) monobromide (Ib);



Br^-

Yield- 95 %; IR (KBr): υ = 3480, 3407, 3135, 3098, 3060, 2968 2868, 1612, 1569, 1463, 1274, 1159, 1094, 1028, 871, 842, 798, 765 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 2.05 (s, 6H), 2.08 (s, 3H), 3.64 (3H), 5.17 (s, 2H), 6.84 (s, 2H), 7.13(d, 1H), 7.24(d, 1H), 8.23 (s, 1H); ^{13}C NMR (75MHz, D_2O): 18.5, 20.0, 35.8, 47.1, 121.8, 123.6, 125.8, 129.3, 135.3, 138.6, 140.1

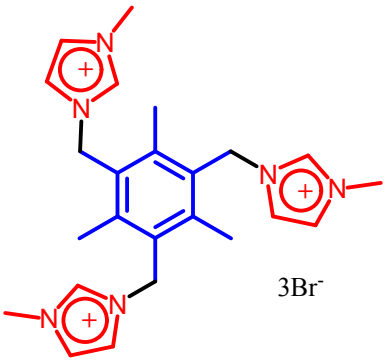
3, 3′[(2, 4, 6-trimethyl-1, 3-phenylene) bis (methylene)] bis(1-methyl-1*H*-imidazol-3-ium) dibromide (IIb);



$2Br^-$

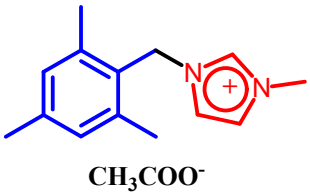
Yield- 96 %; IR (KBr): υ= 3438, 3350, 3140, 3073, 2952, 2887, 1601, 1567, 1454, 1333, 1157, 1019, 883, 811, 749, 614 cm^{-1}; ^1H NMR(300MHz, D_2O):δ 2.02 (s, 3H), 2.15 (s, 6H), 3.64 (s, 6H), 5.30 (s, 4H), 7.08 (s, 1H), 7.18 (s, 2H), 7.25 (d, 1H), 7.26 (d, 1H), 8.25 (s, 1H); ^{13}C NMR (75MHz, D_2O):16.4, 18.8, 35.7, 47.5, 121.8, 123.7, 127.6, 131.2, 135.3, 139.0, 140.7

3, 3′,3′′[(2, 4, 6-trimethyl-1,3,5-phenylene) tris (methylene)] tris (1-methyl-1*H*-imidazol-3-ium) tribromide (IIIb);



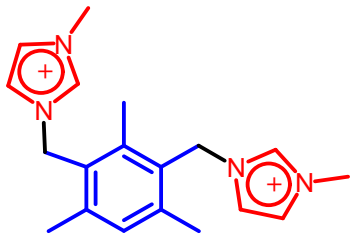
Yield- 95 %; (KBr): υ= 3435, 3144, 3078, 1630, 1570, 1489, 1333, 1158, 830, 762, 619 cm^{-1}; ^{1}H NMR (300 MHz, D_2O): δ 2.22 (s, 9H), 3.73 (s, 9H), 5.48 (s, 6H), 7.27 (d, 3H), 7.29 (d, 3H), 8.34 (s, 3H); ^{13}C NMR (75MHz, D_2O): 15.2, 15.6, 35.9, 48.0, 121.8, 124.0, 129.0 135.4, 140.6, 141.6.

3[(2, 4, 6-trimethyl-1-phenylene) mono (methylene)] mono (1-methyl-1*H*-imidazol-3-ium) monoacetate (Id)



Yield 97 %; IR (thin film): υ = 3479, 3411, 3140, 3094, 1571, 1408, 1160, 1017, 839, 763, 663 cm^{-1}; ^{1}H NMR (300 MHz, D_2O): δ 1.72 (s, 3H), 2.10 (s, 9H), 3.62 (s, 3H), 5.19 (s, 2H), 6.88 (s, 2H), 7.15 (d, 1H), 7.23 (d, 1H), 8.19 (s, 1H); ^{13}C NMR (75MHz, D_2O):18.3, 19.9, 23.0, 35.5, 47.0, 121.8, 123.6, 125.7, 129.2, 135.2, 138 .6, 140.2, 181.1.

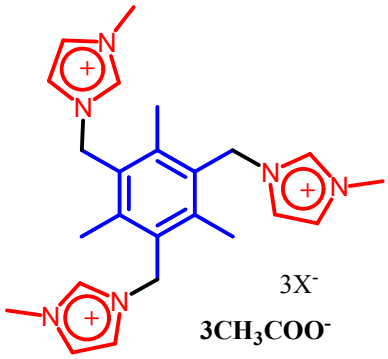
3, 3′[(2, 4, 6-trimethyl-1, 3-phenylene) bis (methylene)] bis (1-methyl-1*H*-imidazol-3-ium) diacetate (IId)



$2CH_3COO^-$

Yield96 %;IR (thinfilm):υ= 3438, 3354, 3147, 3075, 1649, 1573, 1408, 1158, 1018, 805, 702, 614 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 1.64 (s, 6H), 1.19 (s, 3H), 2.11(s, 6H), 3.64 (s, 6H), 5.38 (s, 4H), 7.03 (s, 1H), 7.24 (d, 2H), 7.26 (d, 2H), 8.33 (s, 2H); ^{13}C NMR (75MHz, D_2O):14.5, 18.3, 23.1, 35.6, 47.4, 121.7, 123.7, 127.6, 131.3, 135.3, 138.9, 140.7, 180.8.

3, 3′, 3′′[(2, 4, 6-trimethyl-1,3,5-phenylene) tris (methylene)] tris(1-methyl-1*H*-imidazol-3-ium) triacetate (IIId)

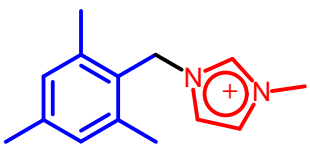


$3X^-$

$3CH_3COO^-$

Yield 96 %; IR (thin film): υ = 3444, 3354, 3151, 3101, 1642, 1574, 1410, 1336, 1160, 1019, 843, 763, 621 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 1.68 (s, 9H), 2.13 (s, 9H), 3.65 (s, 9H), 5.39 (s, 6H), 7.17 (d, 3H), 7.28 (d, 3H), 8.32 (s, 3H); ^{13}C NMR (75MHz, D_2O):15.4, 23.1, 35.7, 47.8, 121.6, 123.8, 128.9, 135.5, 141.5, 181.1.

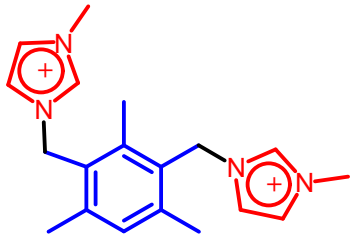
3,[(2, 4, 6-trimethyl-1-phenylene) mono (methylene)] mono (1-methyl-1*H*-imidazol-3-ium) mono methane sulphonate (Ie)



$CH_3SO_3^-$

Yield 96 %; IR (thinfilm):υ = 3482, 3136, 3095, 3061, 3014, 2968, 1613, 1570, 1463, 1194, 1058, 785,700 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 2.00 (s, 9H), 2.56 (s, 3H), 3.63 (s, 3H), 5.11 (s, 2H), 6.75 (s, 2H), 7.05 (d, 1H), 7.21 (d, 1H), 8.22 (s, 1H); ^{13}C NMR (75MHz, D_2O):18.9, 20.0, 35.6, 38.4, 47.0, 121.7, 123.7, 125.8, 129.3, 135.3, 138.5, 139.9.

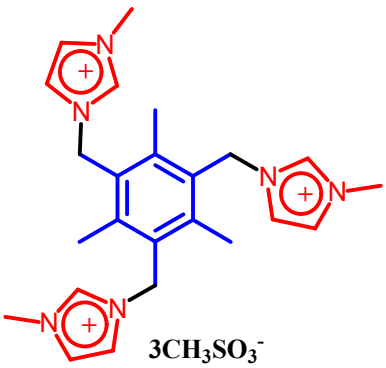
3, 3′[(2, 4, 6-trimethyl-1, 3-phenylene) bis (methylene)] bis(1-methyl-1*H*-imidazol-3-ium) di methanesulphonate (IIe)



$2CH_3SO_3^-$

Yield 97 %; IR (thinfilm) :υ= 3420, 3140, 3079, 3014, 2979, 1615, 1571, 1460, 1330, 1194, 1058, 785, 616 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 2.05 (s, 3H), 2.17 (s, 6H), 3.05 (s, 6H), 3.67 (s, 6H), 5.31 (s, 4H), 7.08 (s, 1H), 7.20 (d, 2H), 7.29 (d, 2H), 8.29 (s, 2H), ; ^{13}C NMR (75MHz, D_2O):14.6, 18.9, 35.7, 44.0, 47.5, 121.7, 123.8, 127.7, 131.3, 135.3, 139.0,140.7.

3, 3′, 3′′[(2, 4, 6-trimethyl-1,3,5-phenylene) tris (methylene)] tris(1-methyl-1*H*-imidazol-3-ium) tri methane sulphonate (IIIe)



$3CH_3SO_3^-$

Yield 96 %; IR (thin film): υ = 3452, 3155, 3103, 2933, 1634, 1574, 1455, 1333, 1193, 1058, 784, 621 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 2.12(s, 9H), 2.57 (s, 9H), 3.65 (s, 9H),

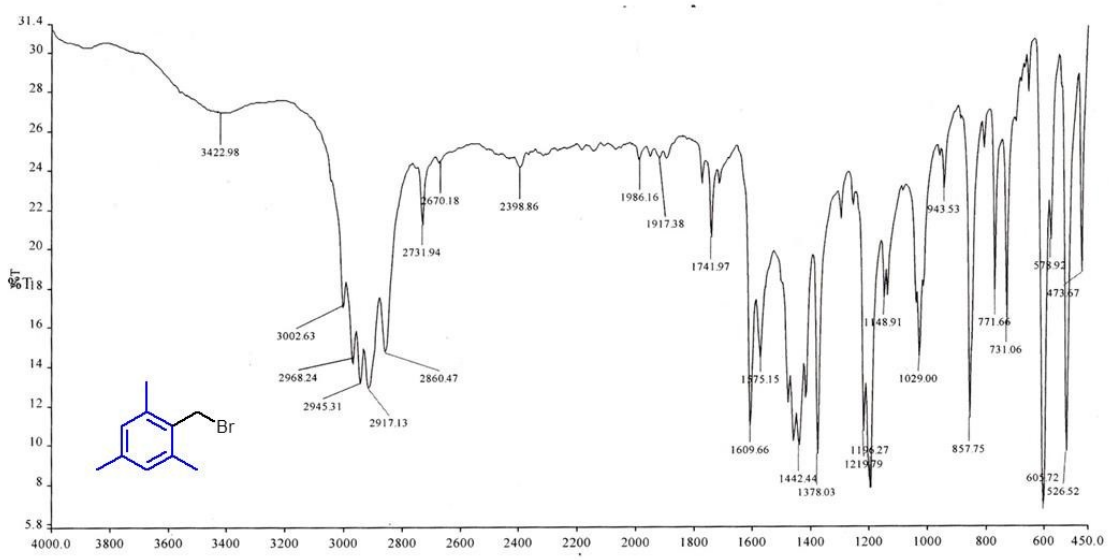
5.38 (s, 6H), 7.19 (d, 3H), 7.27 (d, 3H), 8.30 (s, 3H); ^{13}C NMR(75MHz, D_2O):15.5, 35.7, 38.3, 47.9, 121.7, 123.9, 128.9, 135.3, 141.5.

2-amino-4-(2-chlorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromene-3-carbonitrile (Table 2, entry 1): IR (KBr) ν = 3479, 3327, 3192, 3056, 2199, 1661, 1407, 1185, 1102, 1049, 751 cm^{-1} ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.30 (s, 1H), 6.90 (d, 1H, *J=8.4*), 7.15-7.16 (m, 5H), 7.35 (d, 1H, *J= 6.9*), 7.47-7.56 (m, 3H), 7.77 (d, 1H, *J = 7.5*), 8.14 (d, 1H, *J=8.1*) 13C NMR (75 MHz, DMSO-d_6): δ 55.29, 117.01, 120.62, 121.18, 123.09, 124.54, 125.88, 127.21, 127.36, 128.14, 128.40, 129.32, 130.26, 131.66, 132.45, 133.27, 142.63, 143.43, 160.82.

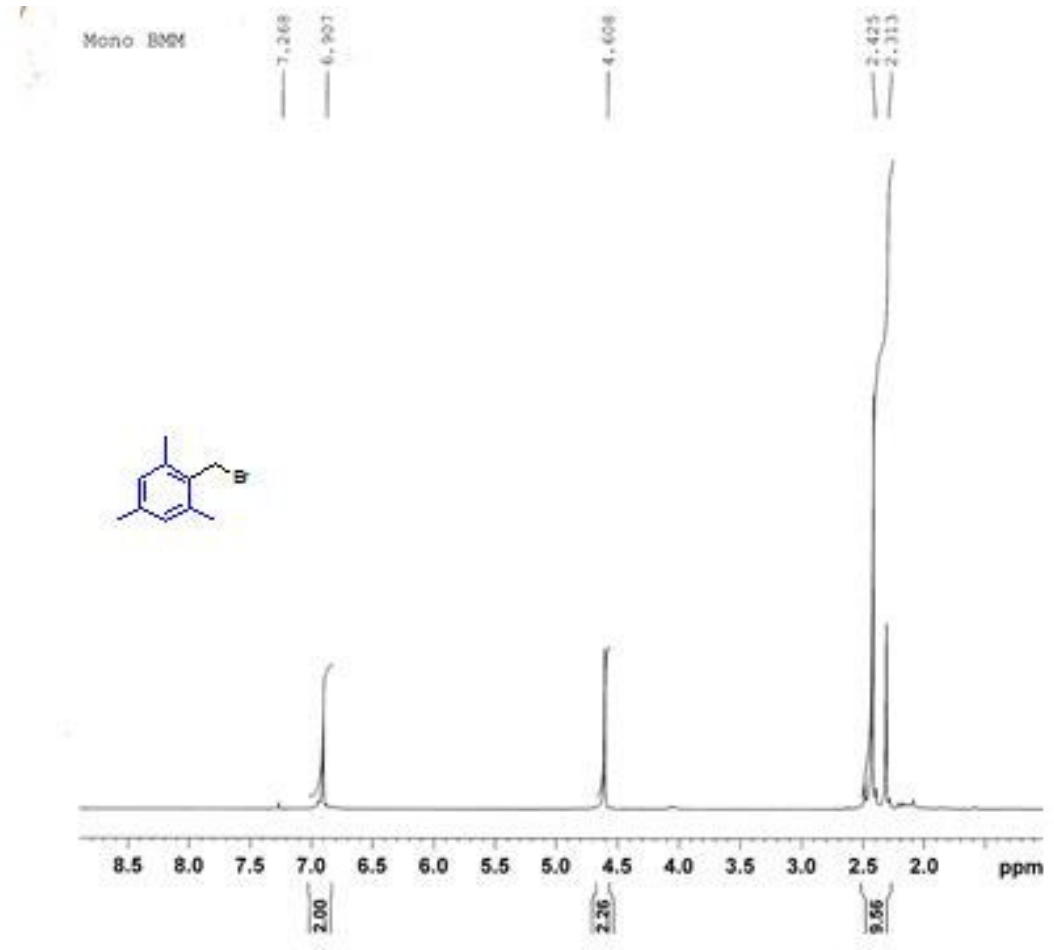
References:

1. A. D. Van der Made and H. Van der Made, *J. Org. Chem*. 1993, ***58***, 1262-1263.

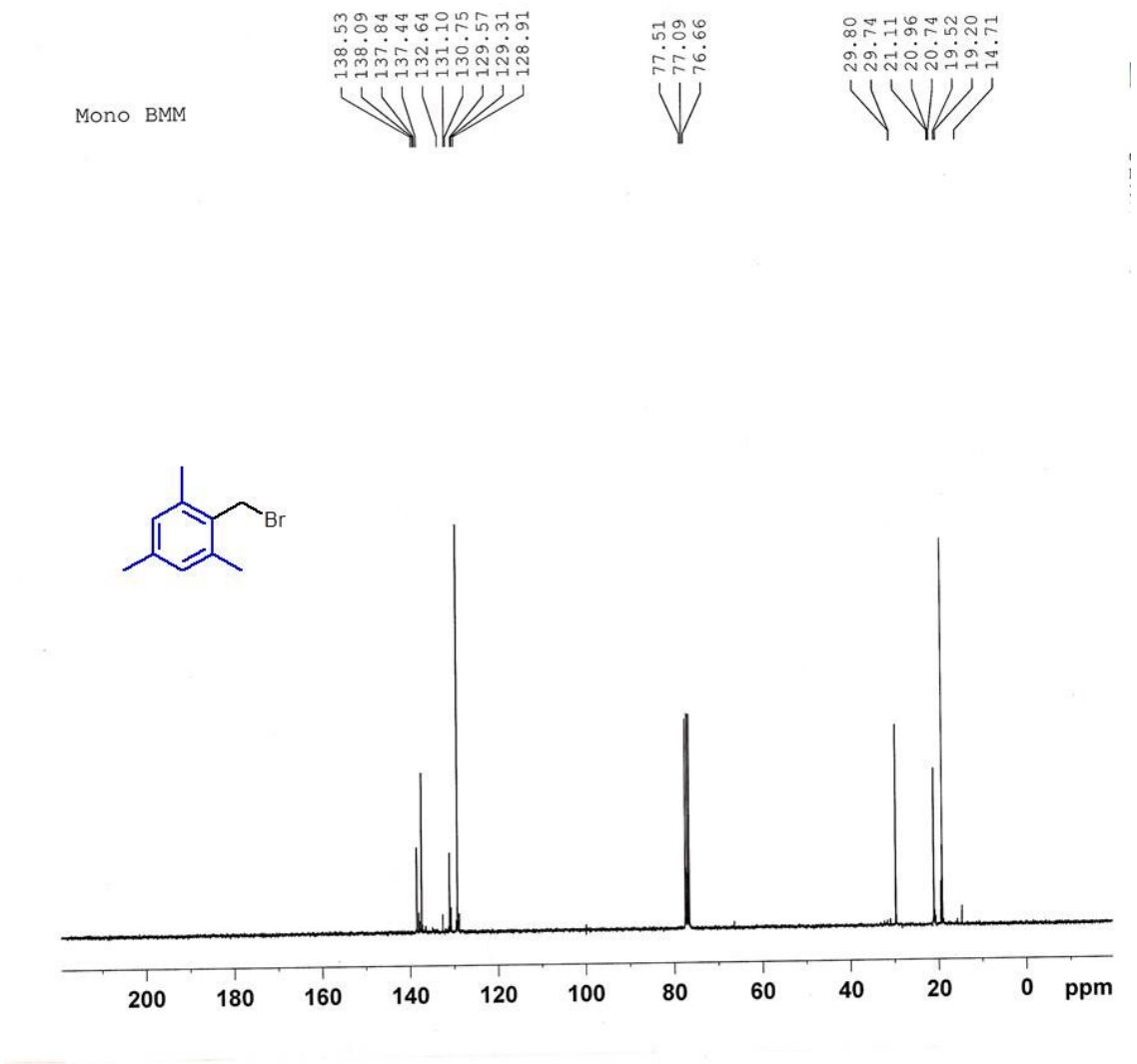
IR and NMR Spectra of compounds:



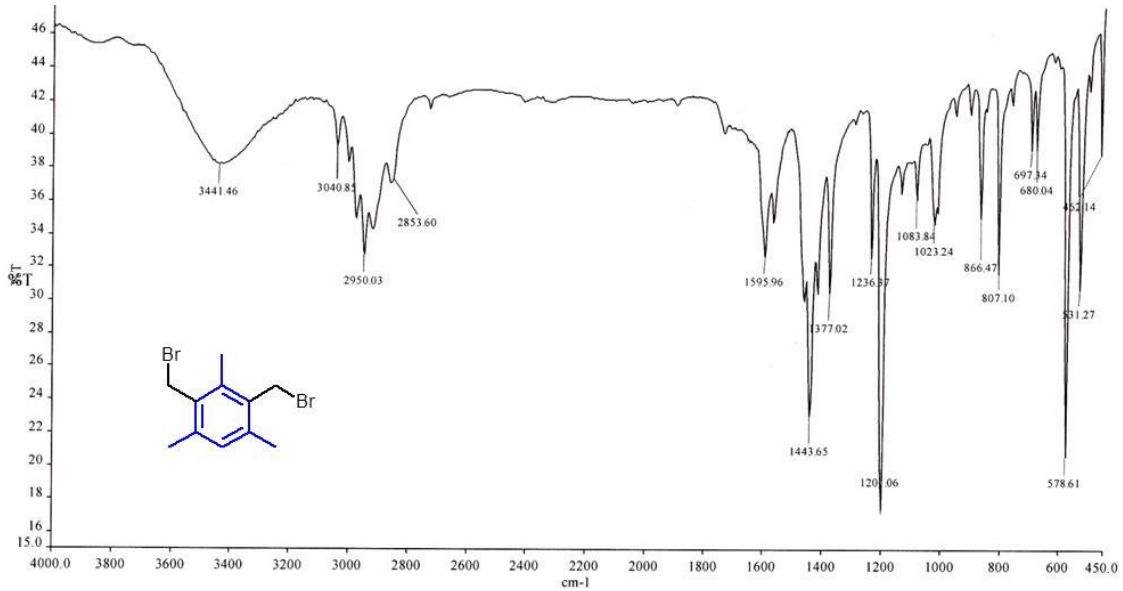
Spectra 1. IR spectrum of compound **Ia**



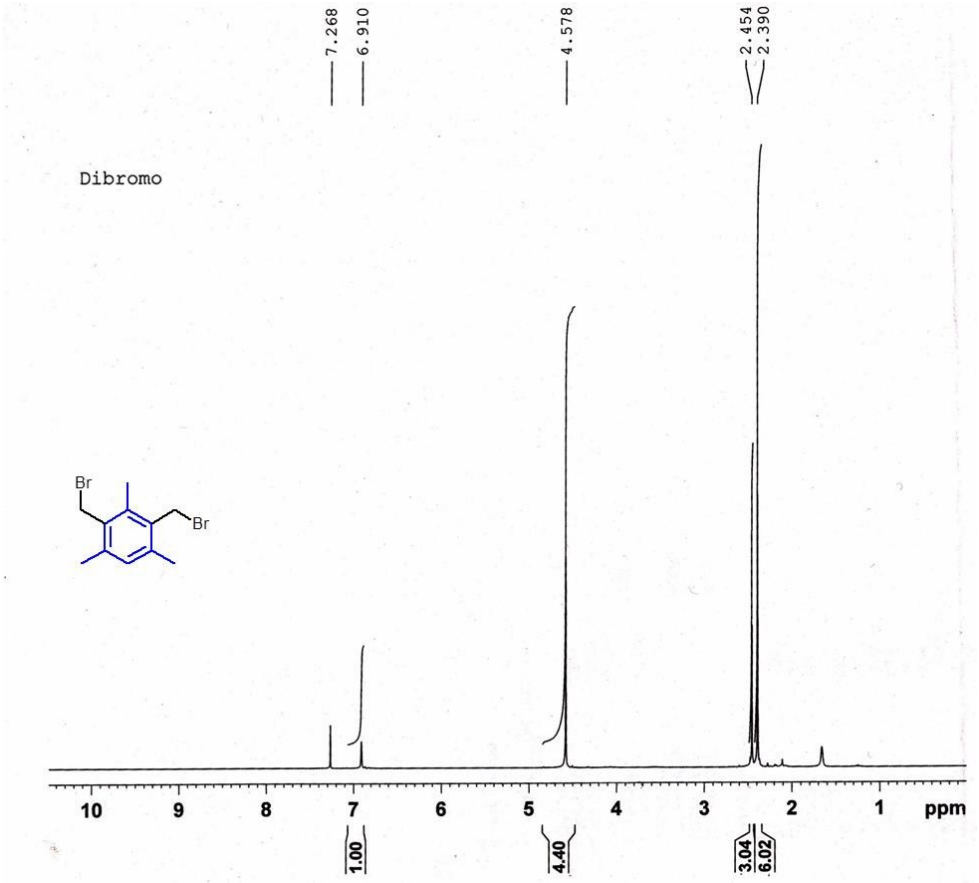
Spectra 2. ^{1}H NMR spectrum of compound **Ia**



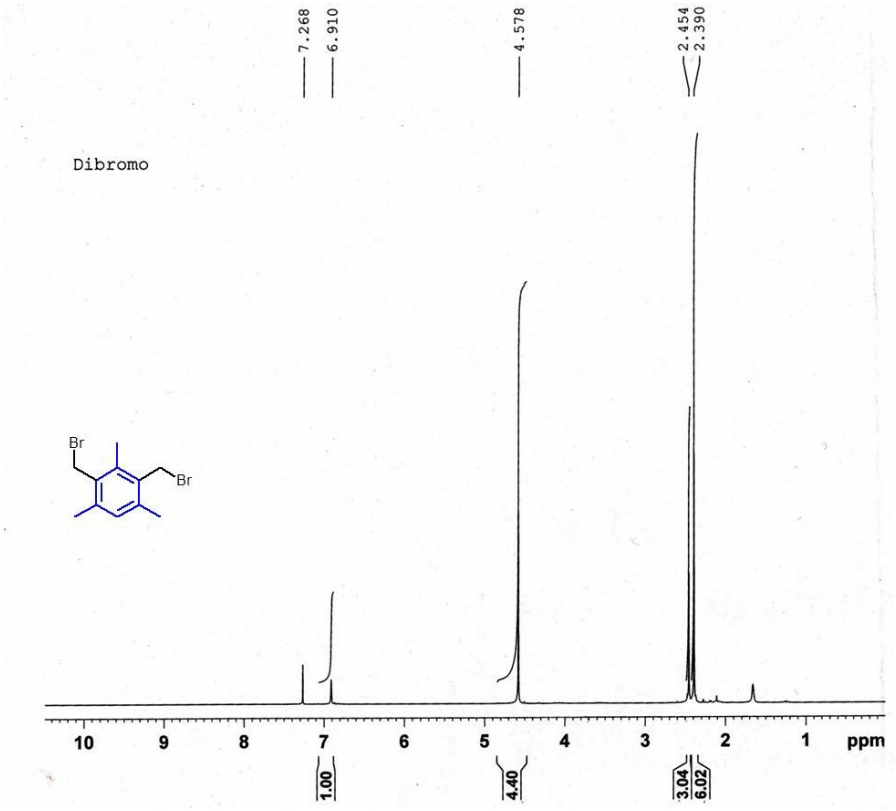
Spectra 3. ^{13}C NMR spectrum of compound **Ia**



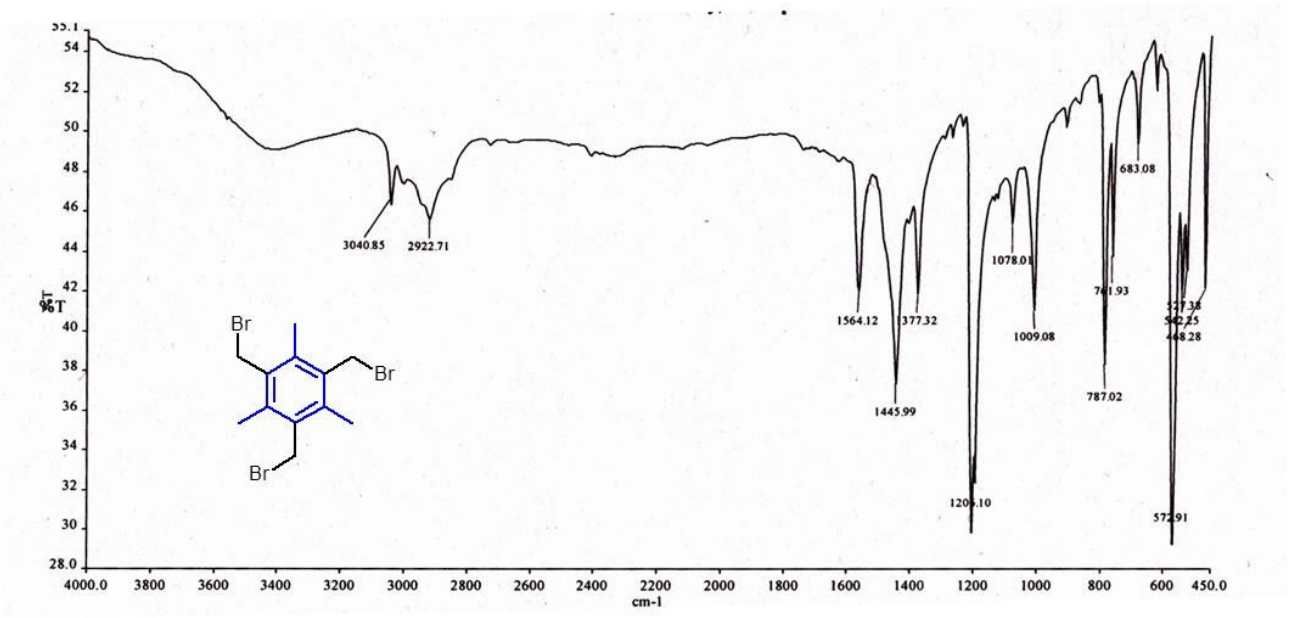
Spectra 4. IR spectrum of compound **IIa**



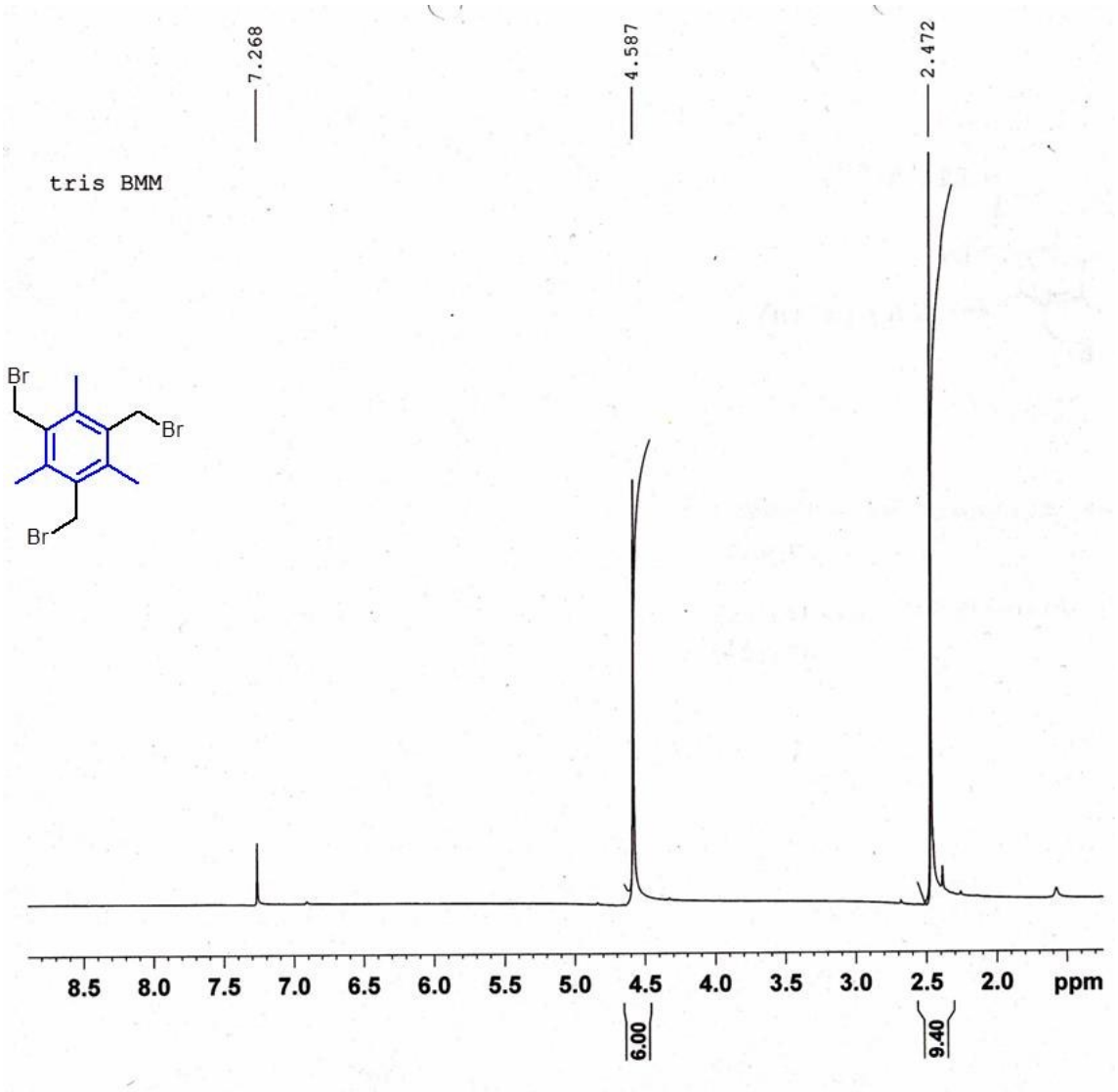
Spectra 5. [1]H NMR spectrum of compound **IIa**



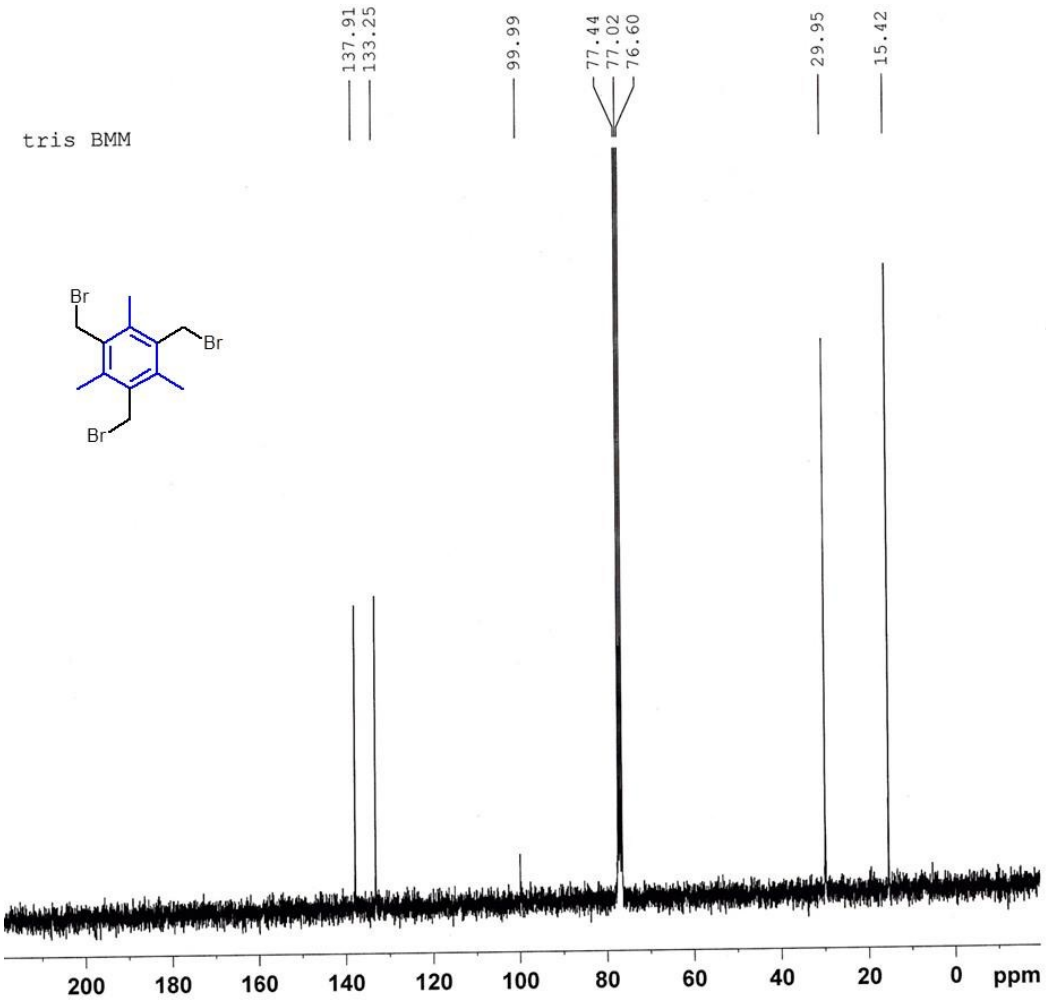
Spectra 6. [13]C NMR spectrum of compound **IIa**



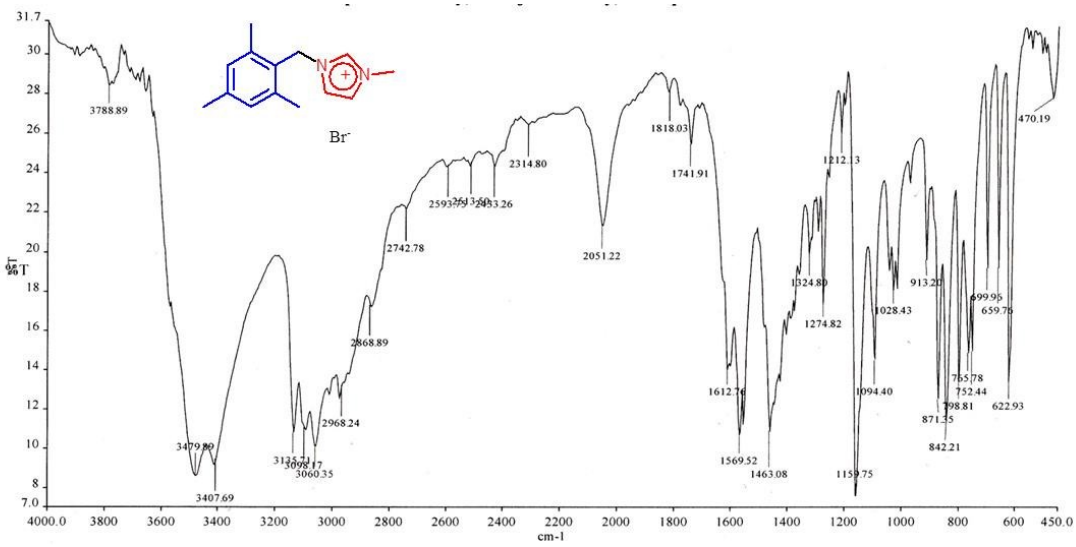
Spectra 7. IR spectrum of compound **IIIa**



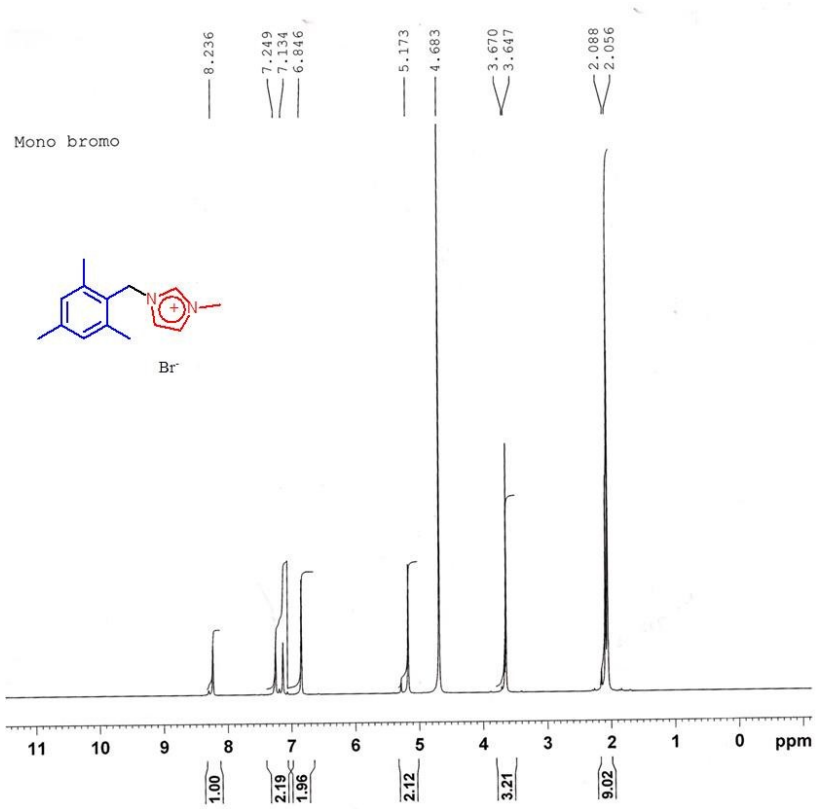
Spectra 8. ^{1}H NMR spectrum of compound **IIIa**



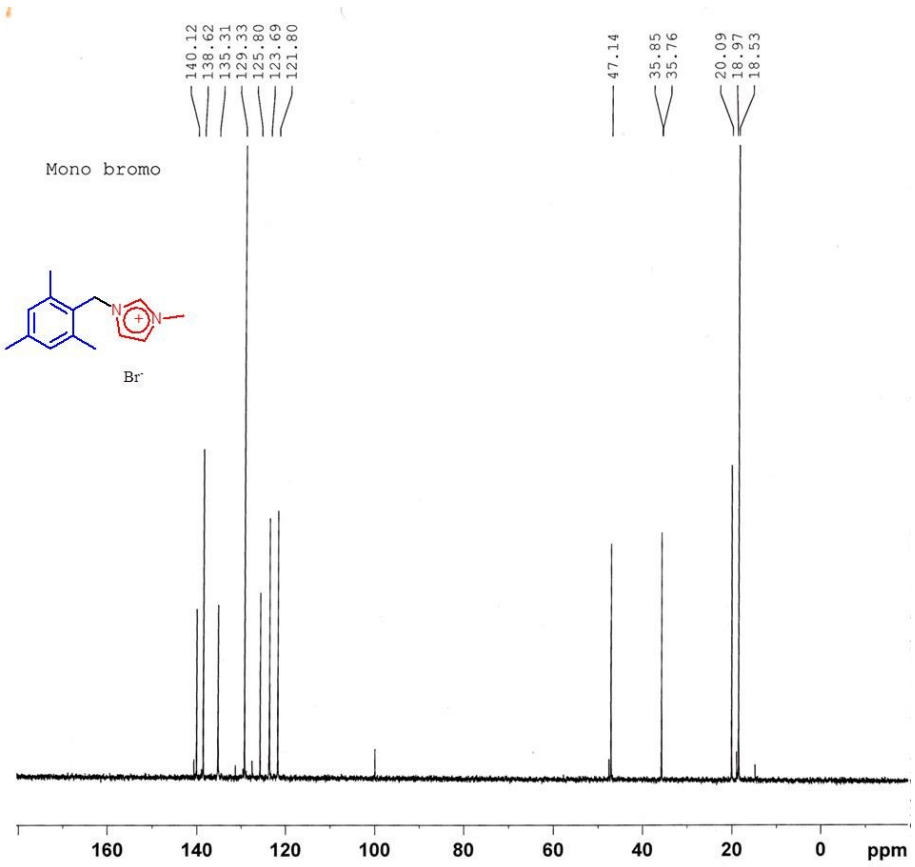
Spectra 9. ^{13}C NMR spectrum of compound **IIIa**



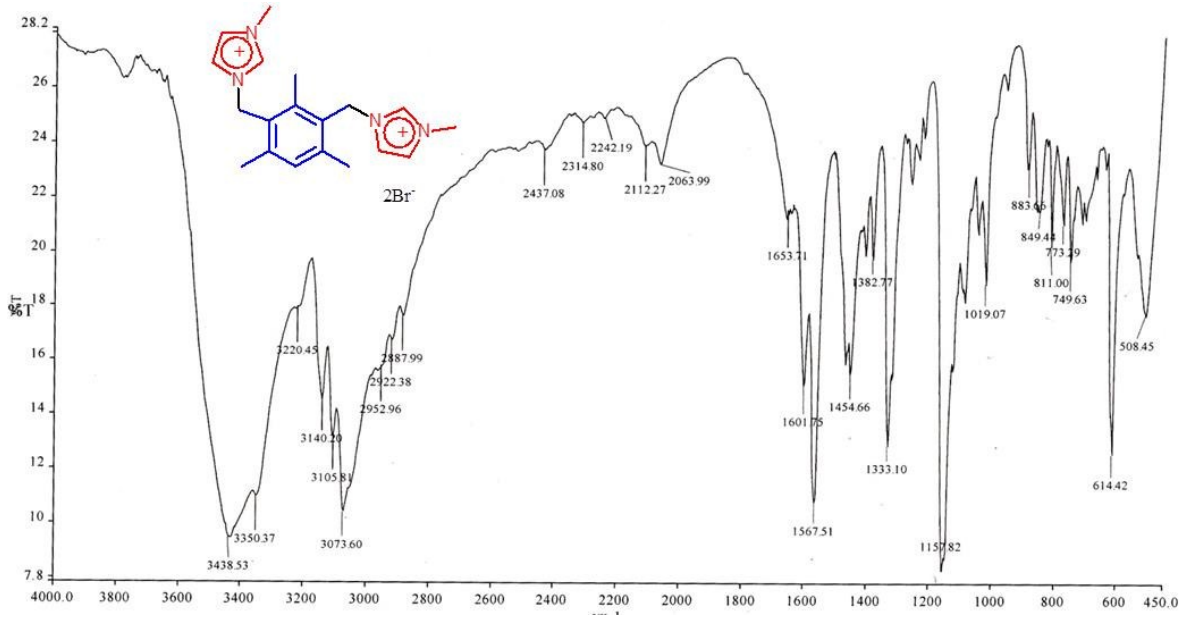
Spectra 10. IR spectrum of compound **Ib**



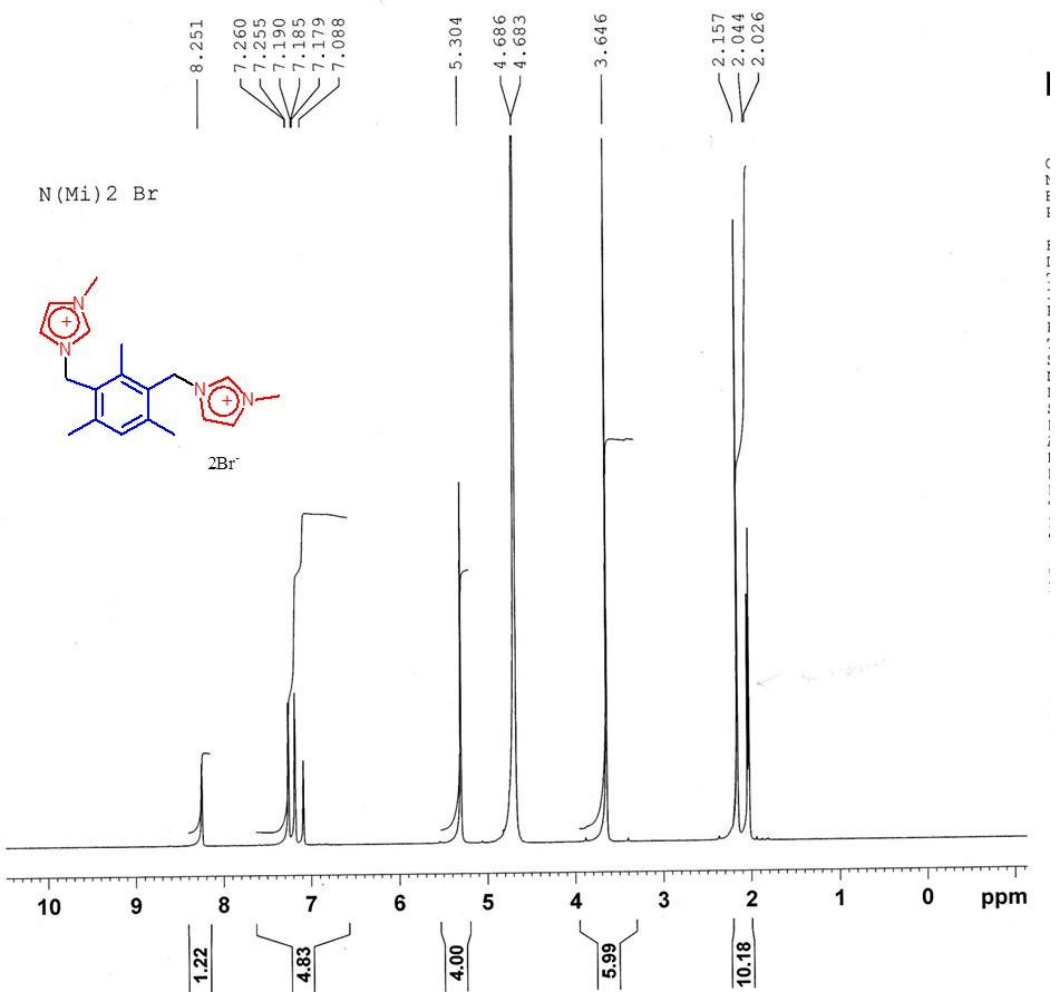
Spectra 11. [1]H NMR spectrum of compound **Ib**



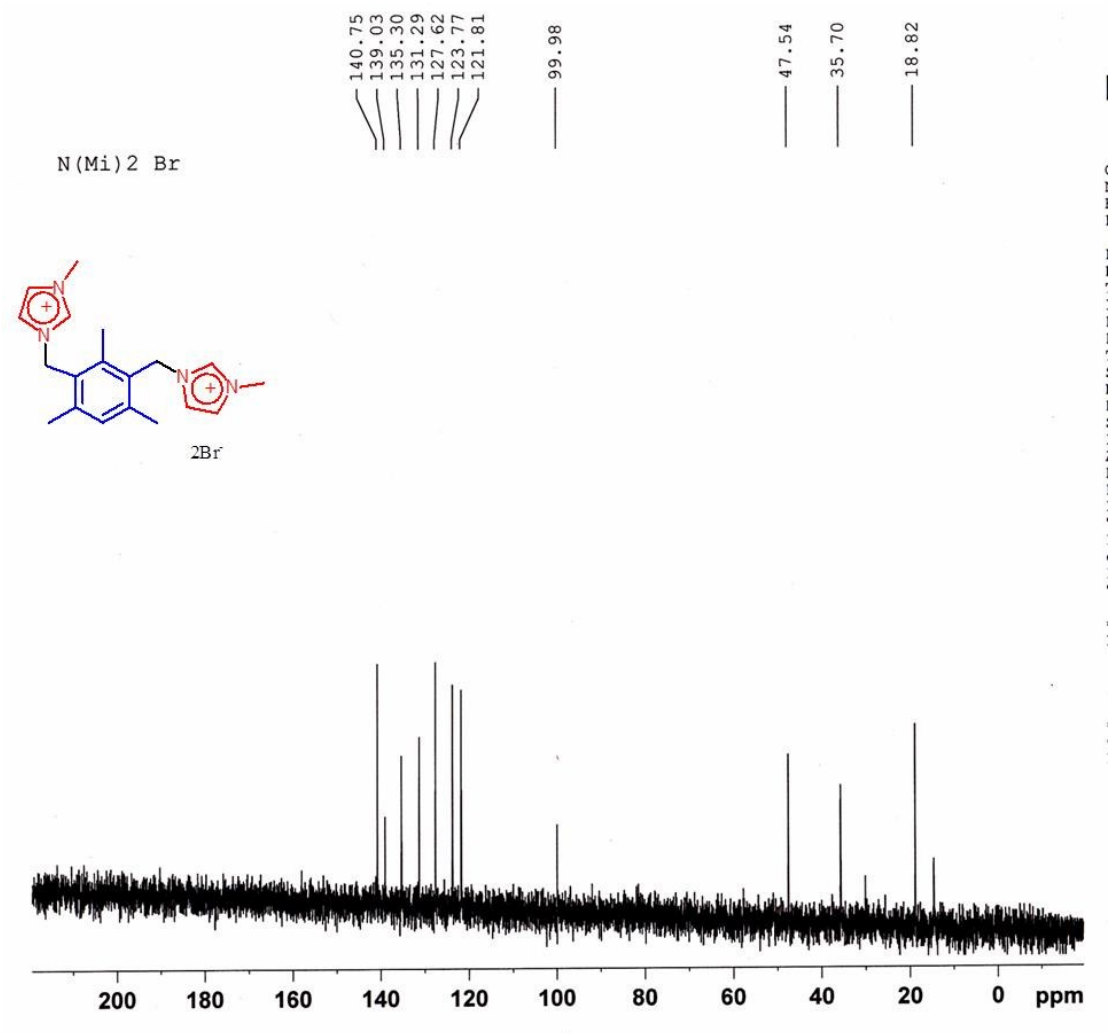
Spectra 12. [13]C NMR spectrum of compound **Ib**



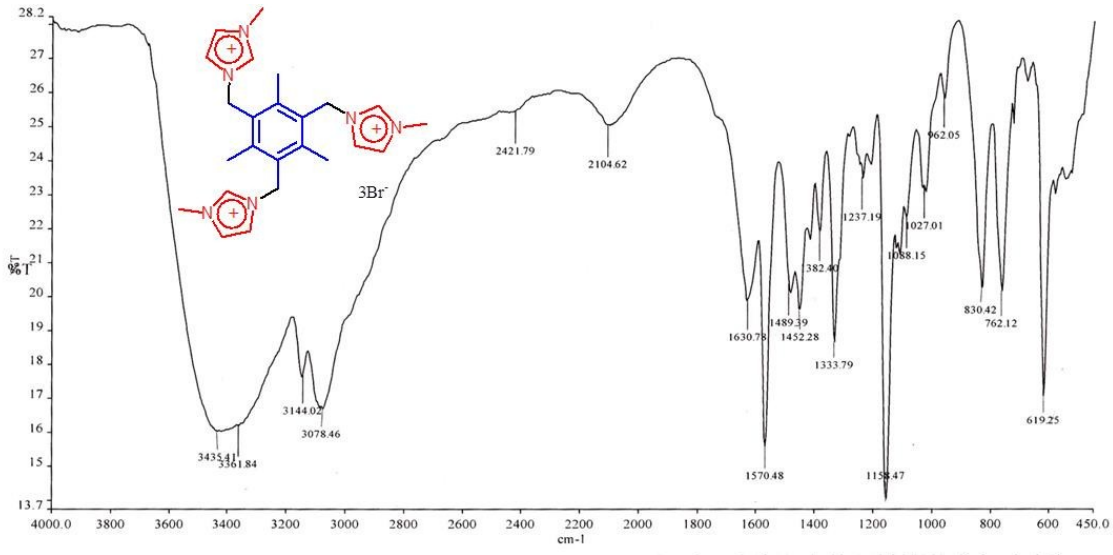
Spectra 13. IR spectrum of compound **IIb**



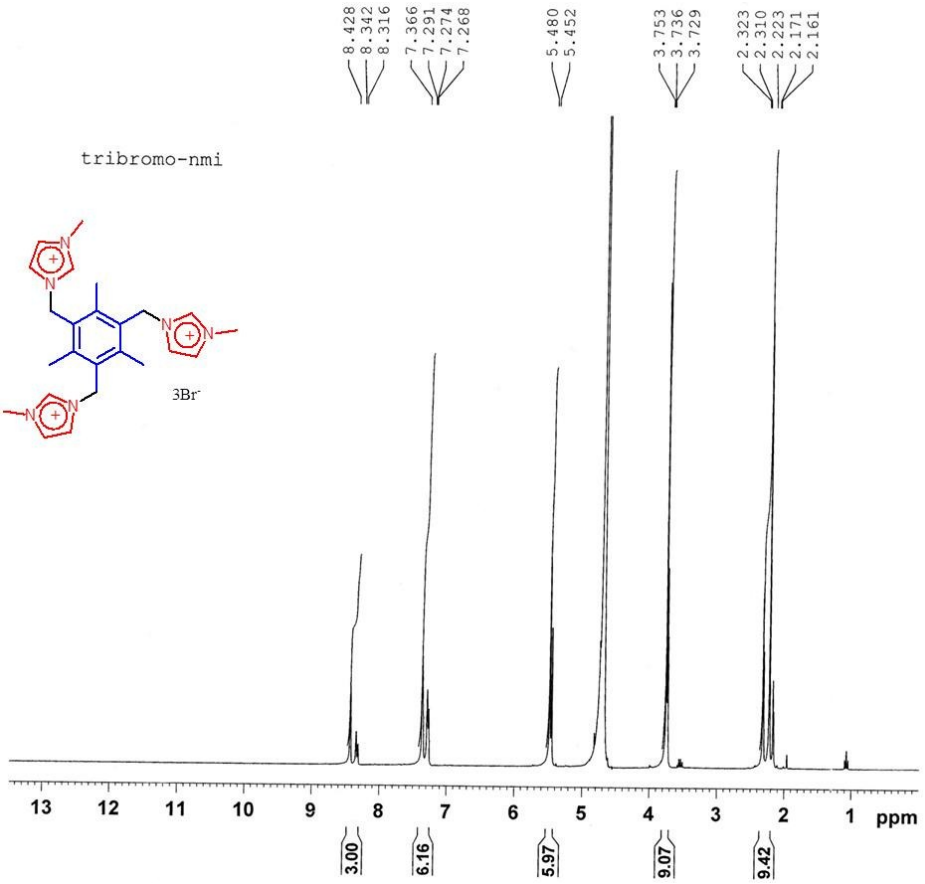
Spectra 14. [1]H NMR spectrum of compound **IIb**



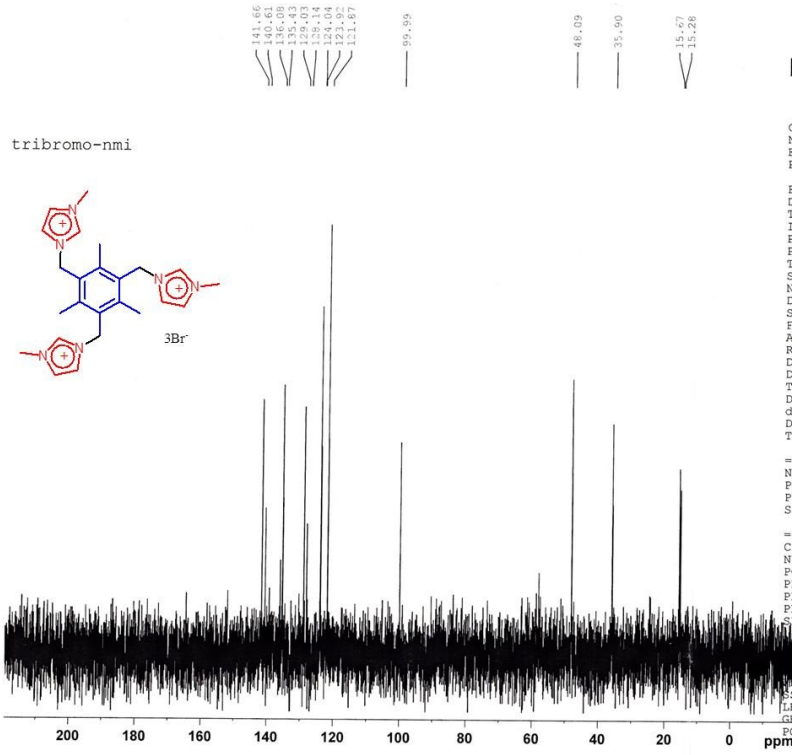
Spectra 15. ^{13}C NMR spectrum of compound **IIb**



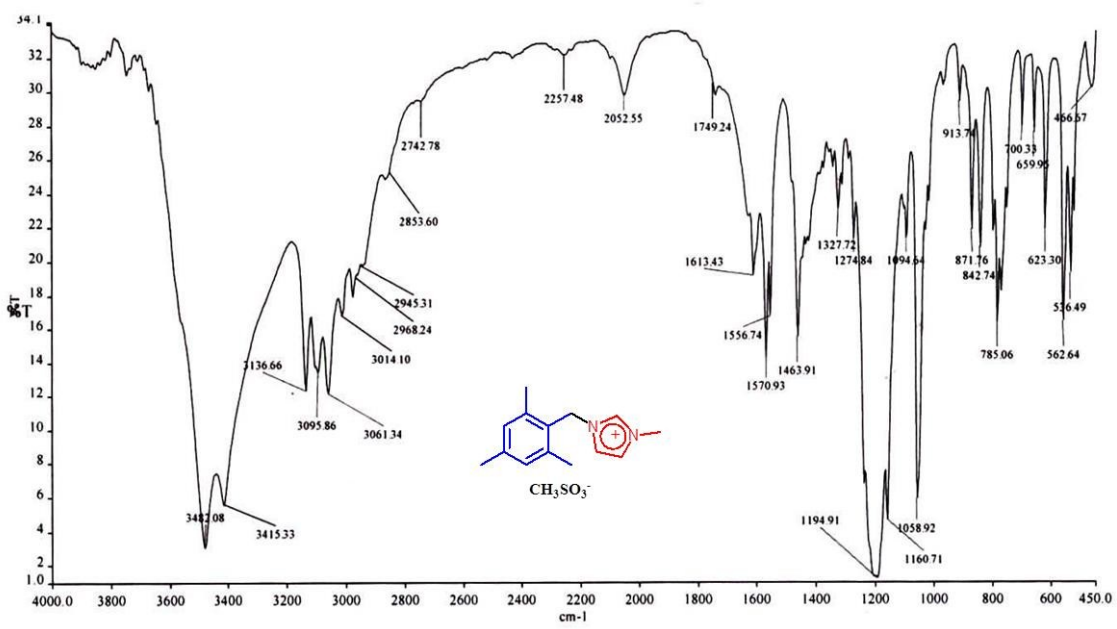
Spectra 16. IR spectrum of compound **IIIb**



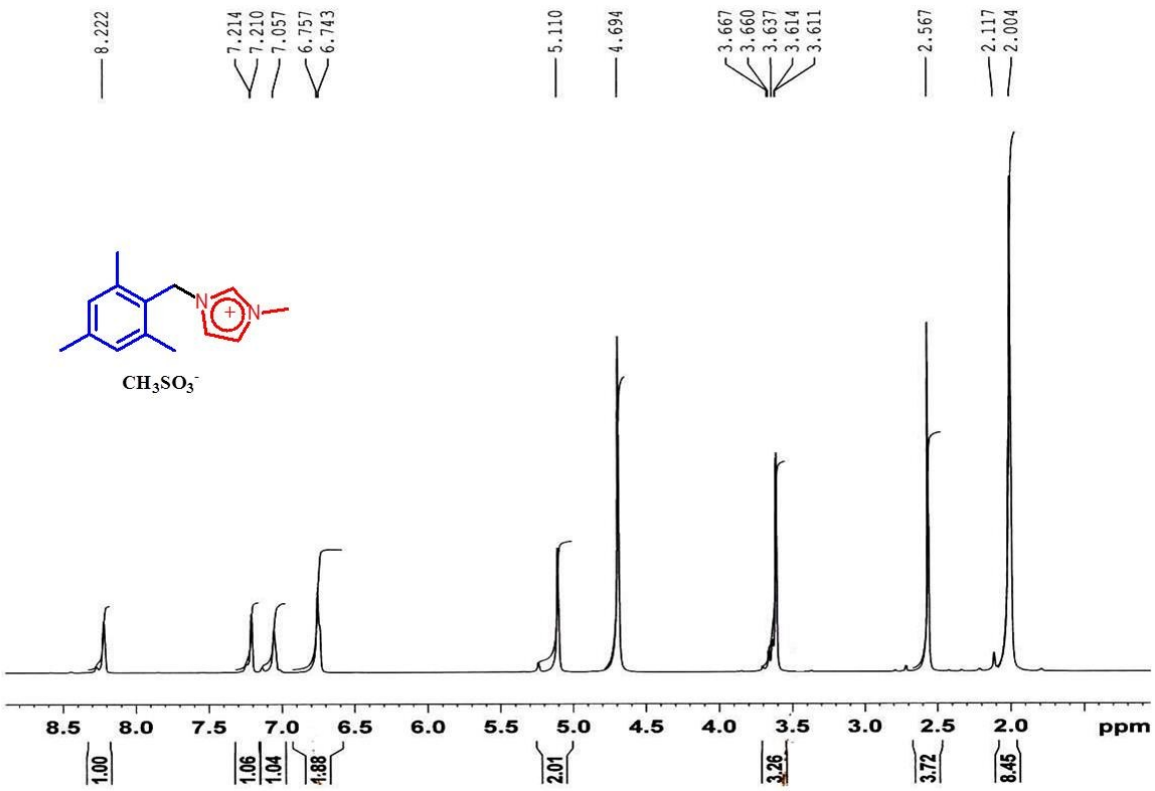
Spectra 17. [1]H NMR spectrum of compound **IIIb**



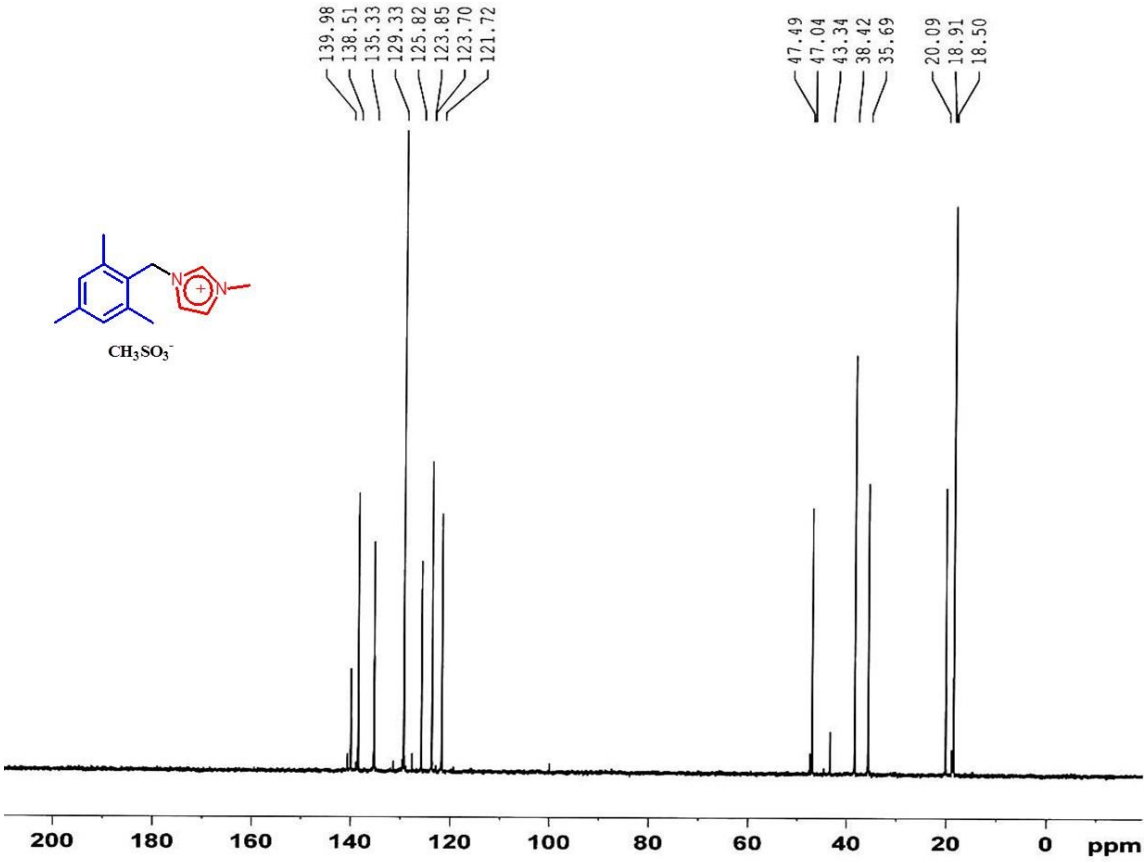
Spectra 18. [13]C NMR spectrum of compound **IIIb**



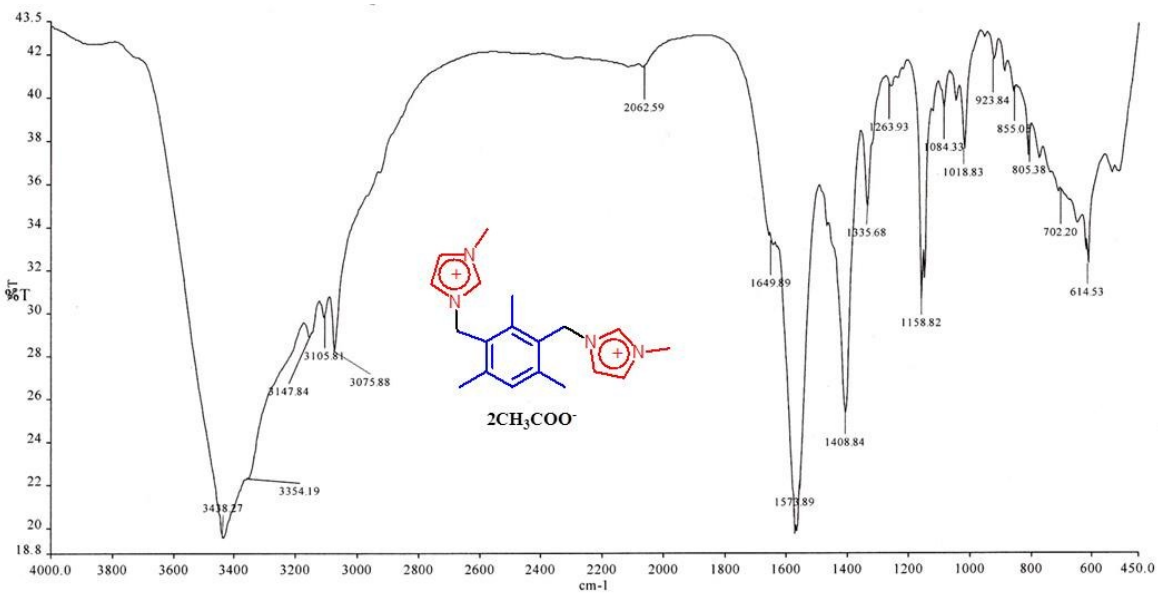
Spectra 19. IR spectrum of compound **Id**



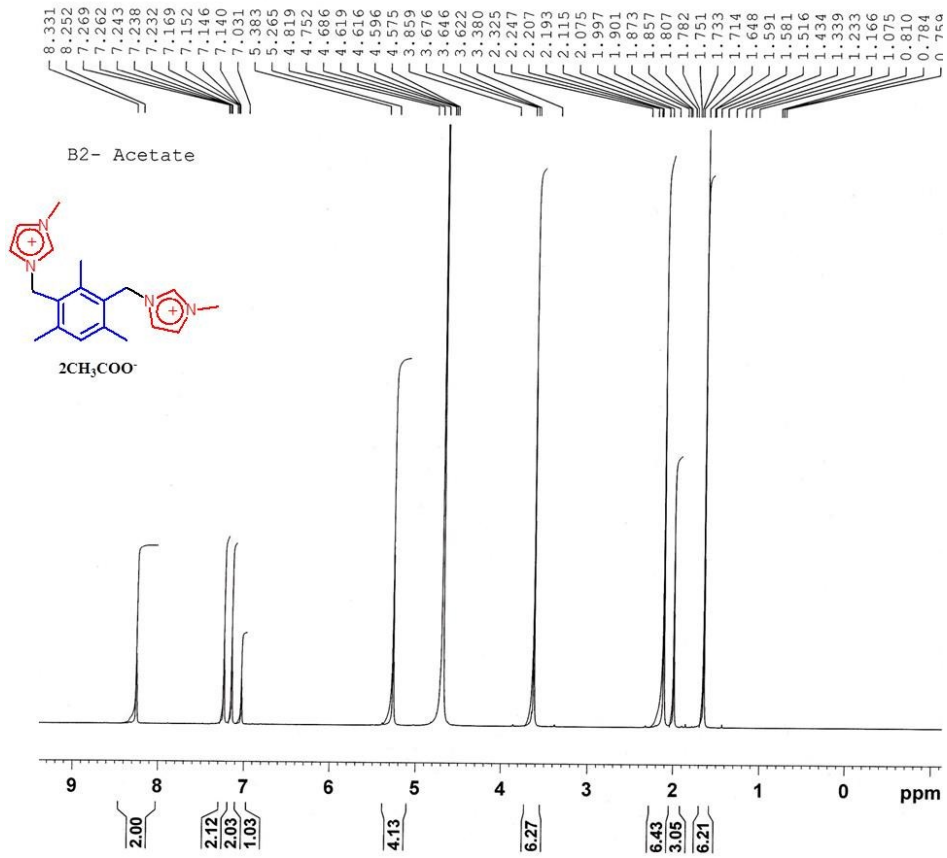
Spectra 20. ^{1}H NMR spectrum of compound **Id**



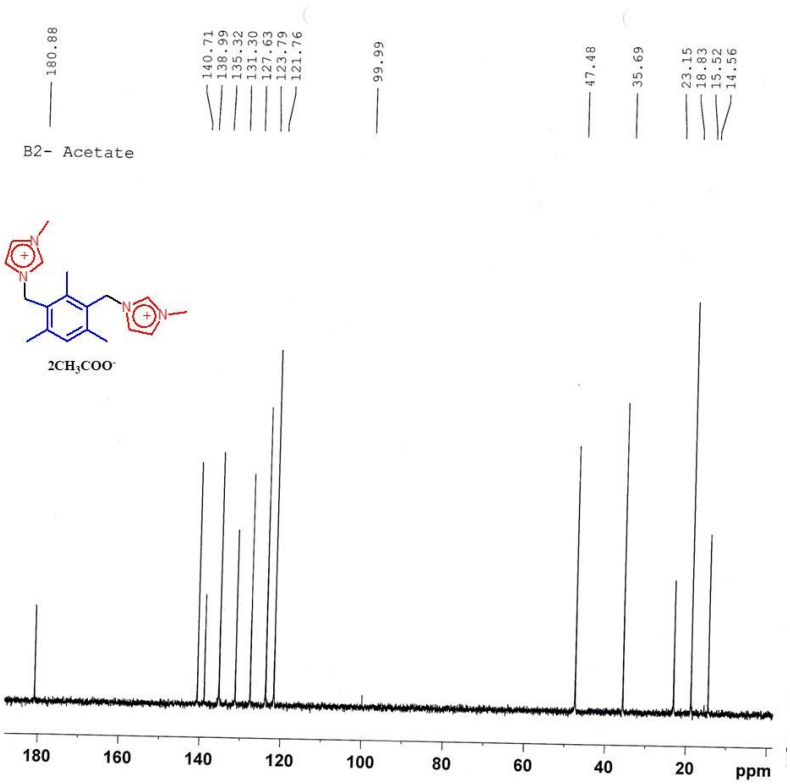
Spectra 21. ^{13c} NMR spectrum of compound **Id**



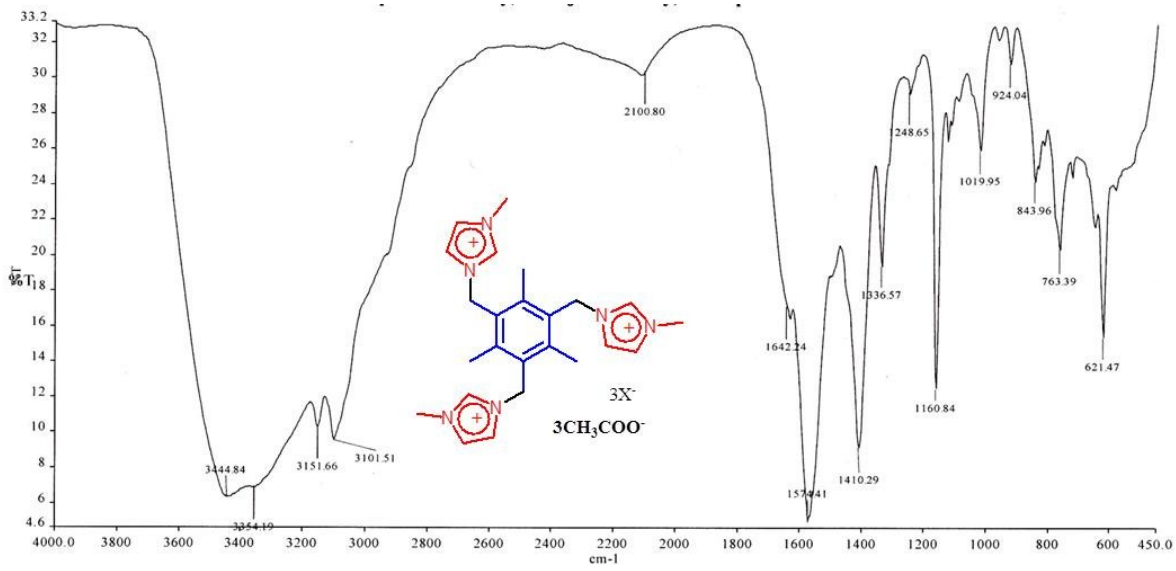
Spectra 22. IR spectrum of compound **IId**



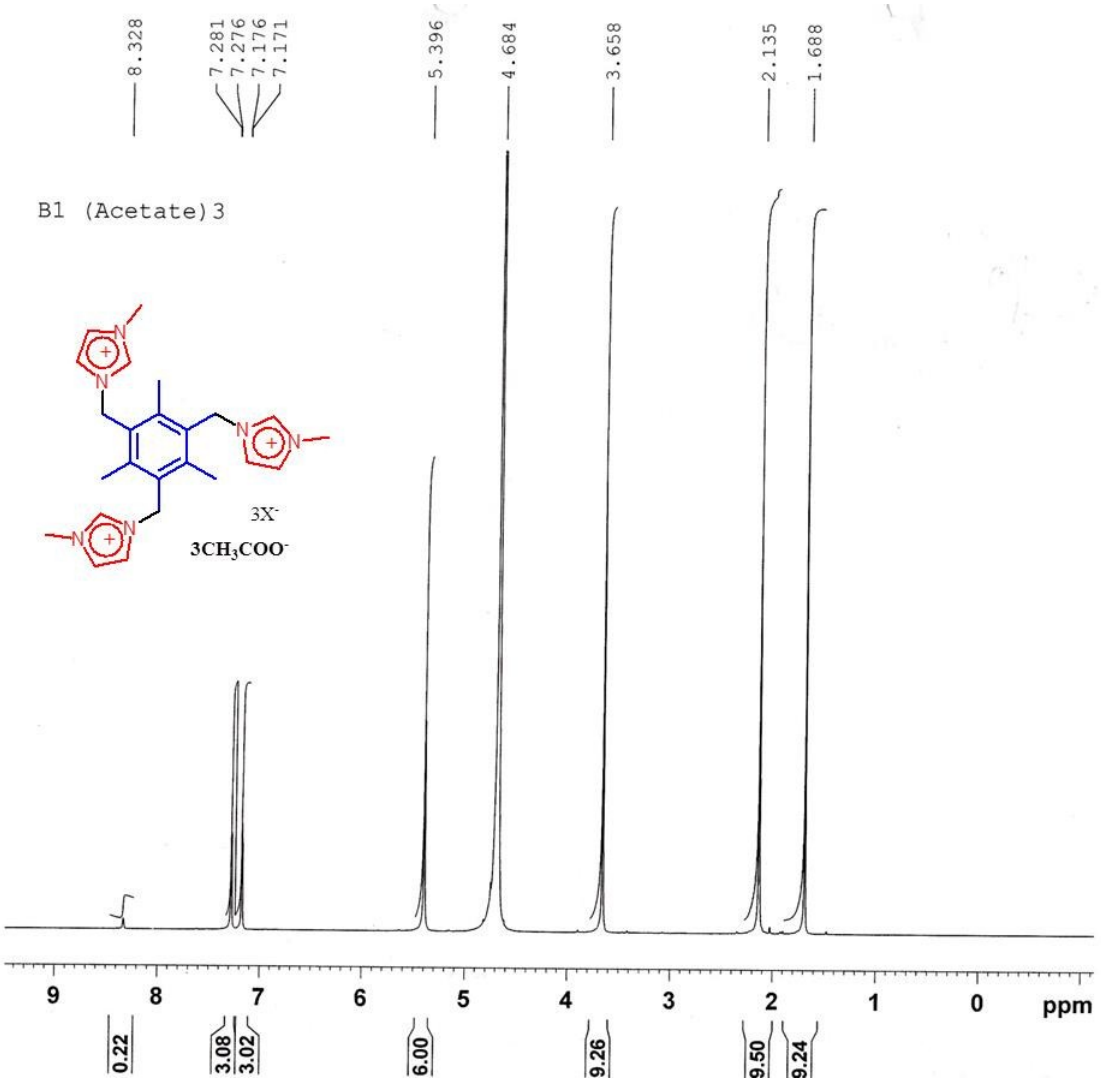
Spectra 23. [1]H NMR spectrum of compound **IId**



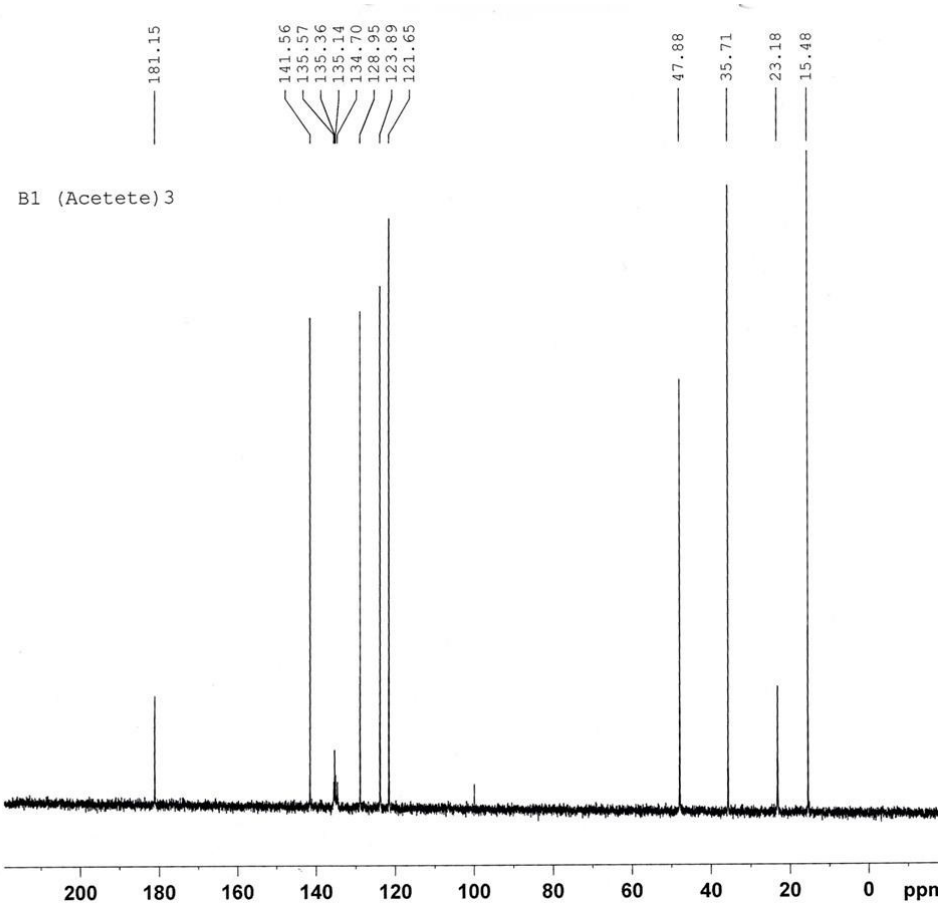
Spectra 24. [13c] NMR spectrum of compound **IId**



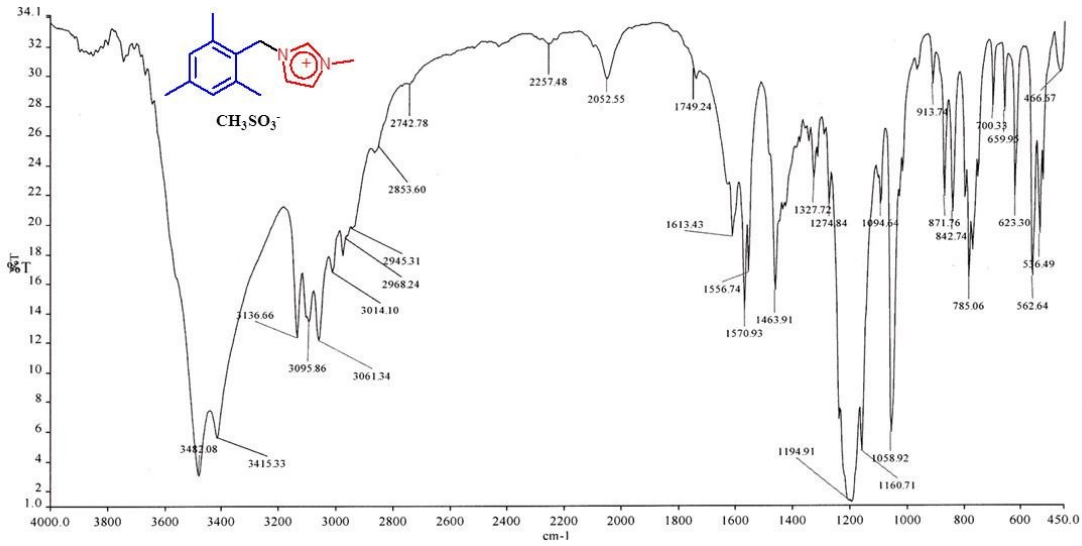
Spectra 25. IR spectrum of compound **IIId**



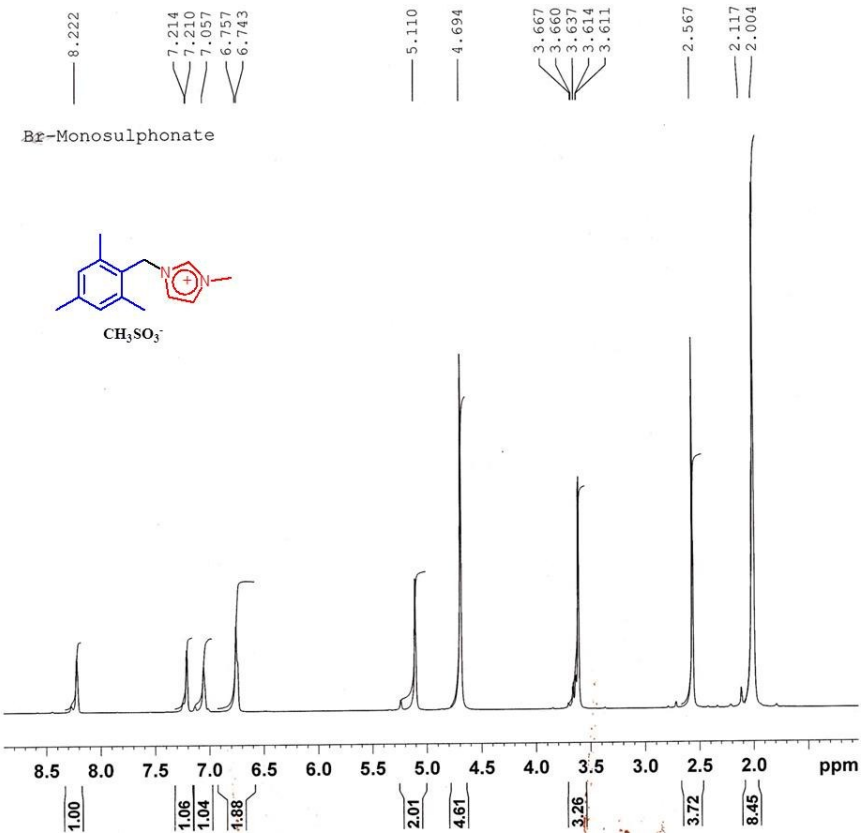
Spectra 26. ^{1}H NMR spectrum of compound **IIId**



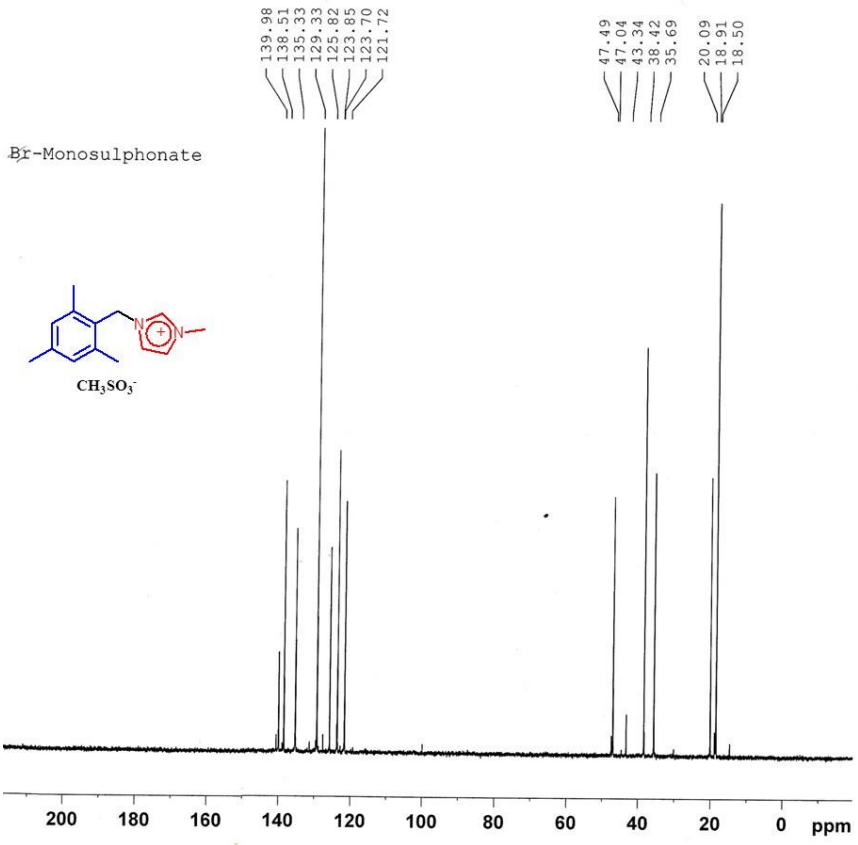
Spectra 27. ^{13}C NMR spectrum of compound **IIId**



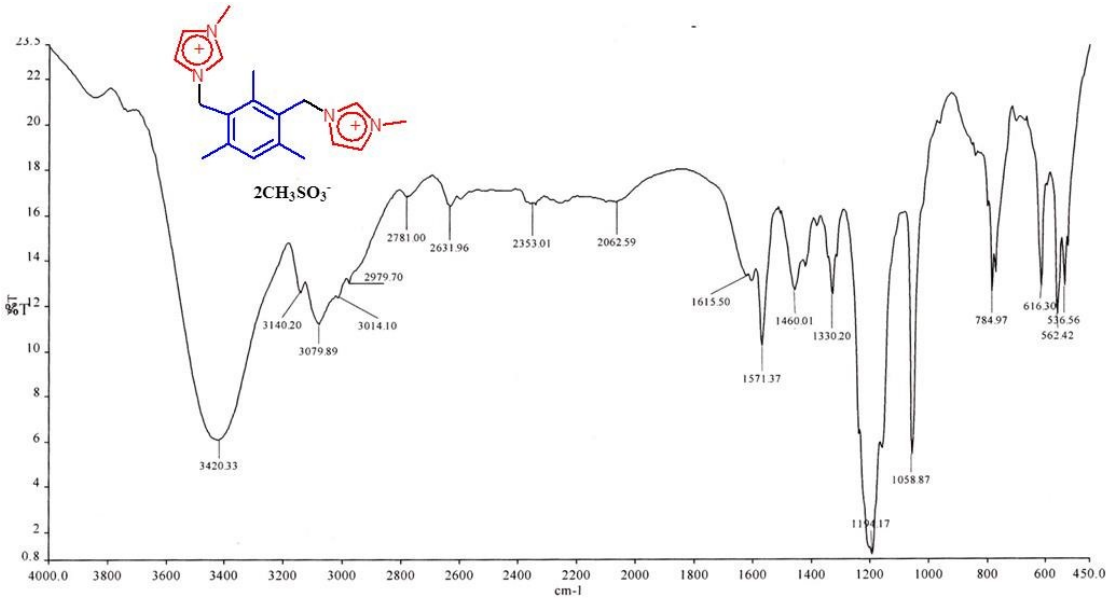
Spectra 28. IR spectrum of compound **Ie**



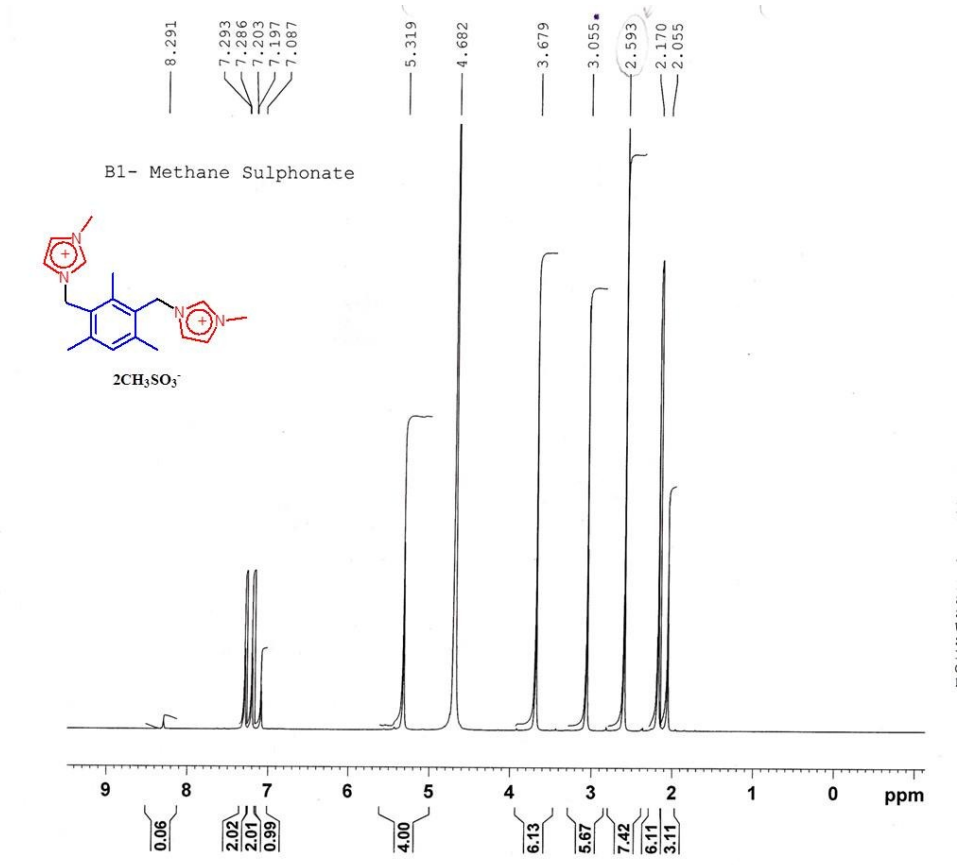
Spectra 29. [1]H NMR spectrum of compound **Ie**



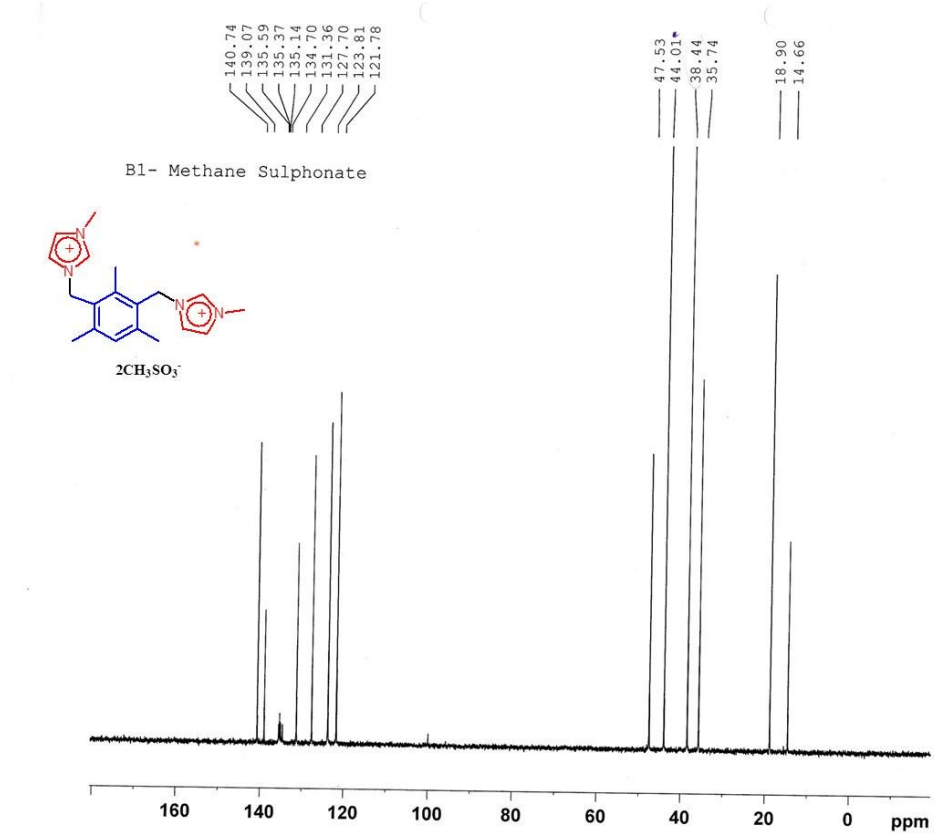
Spectra 30. [13c] NMR spectrum of compound **Ie**



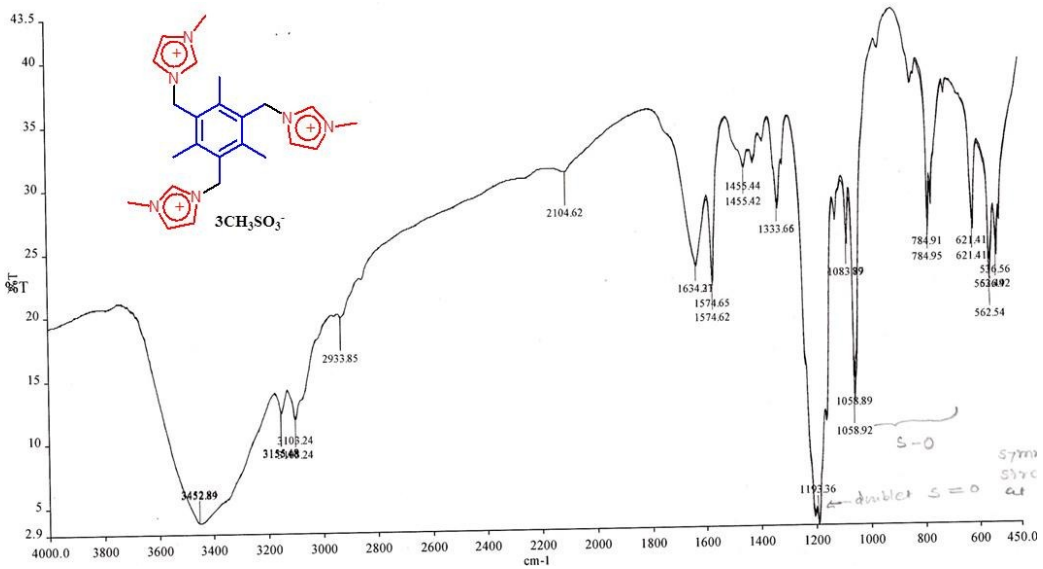
Spectra 31. IR spectrum of compound **IIe**



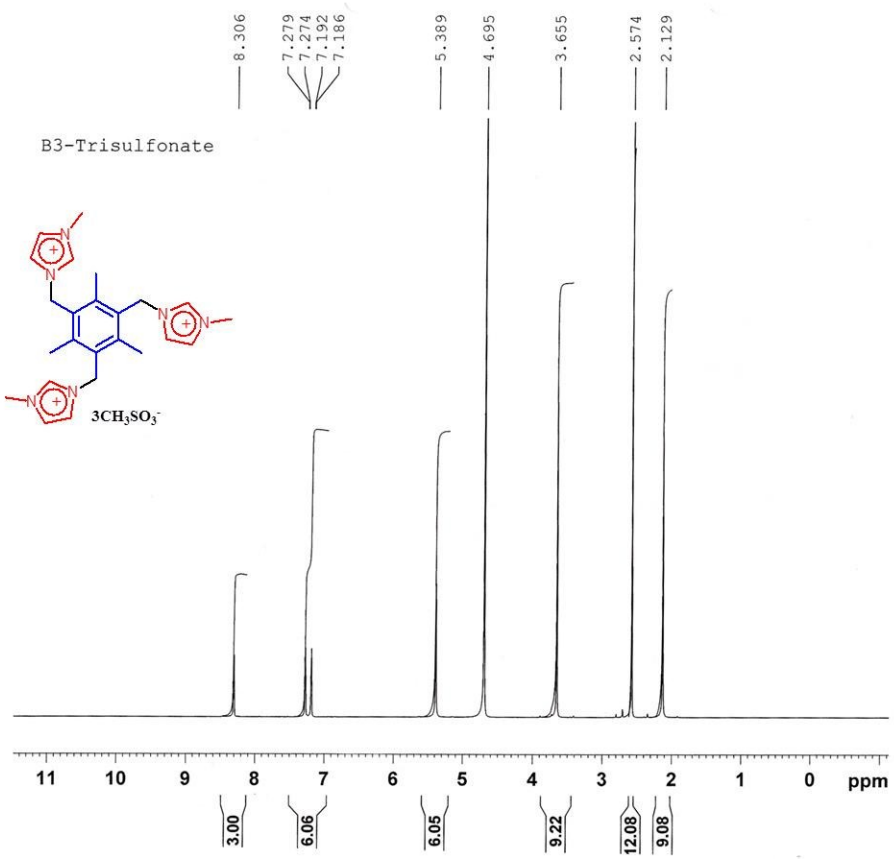
Spectra 32. ^{1}H NMR spectrum of compound **IIe**



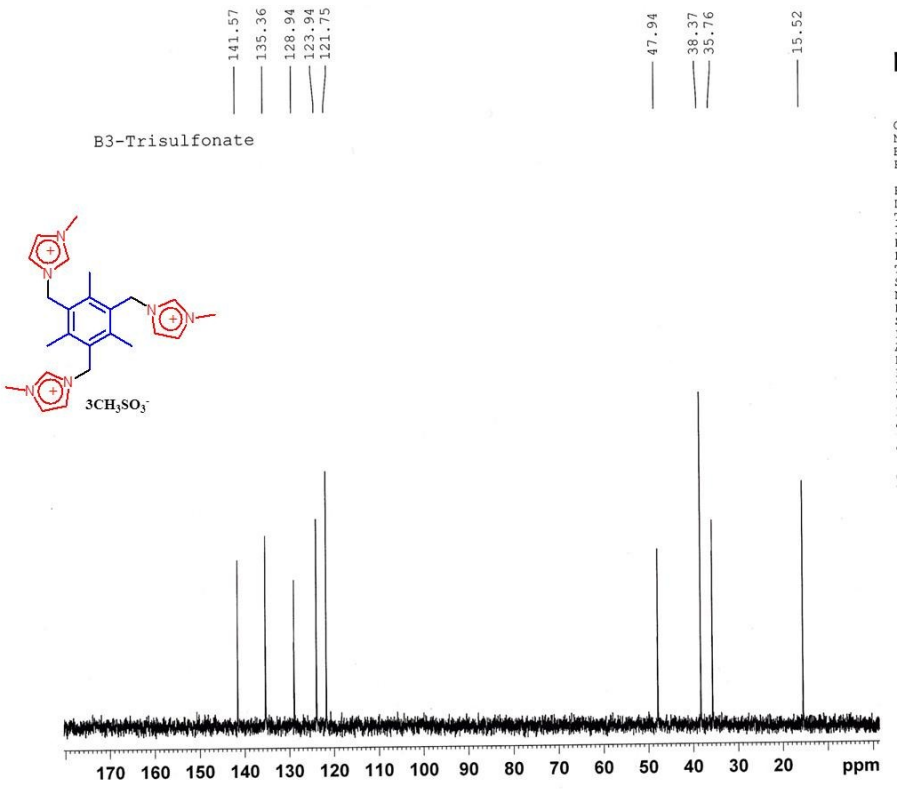
Spectra 33. ^{13c} NMR spectrum of compound **IIe**



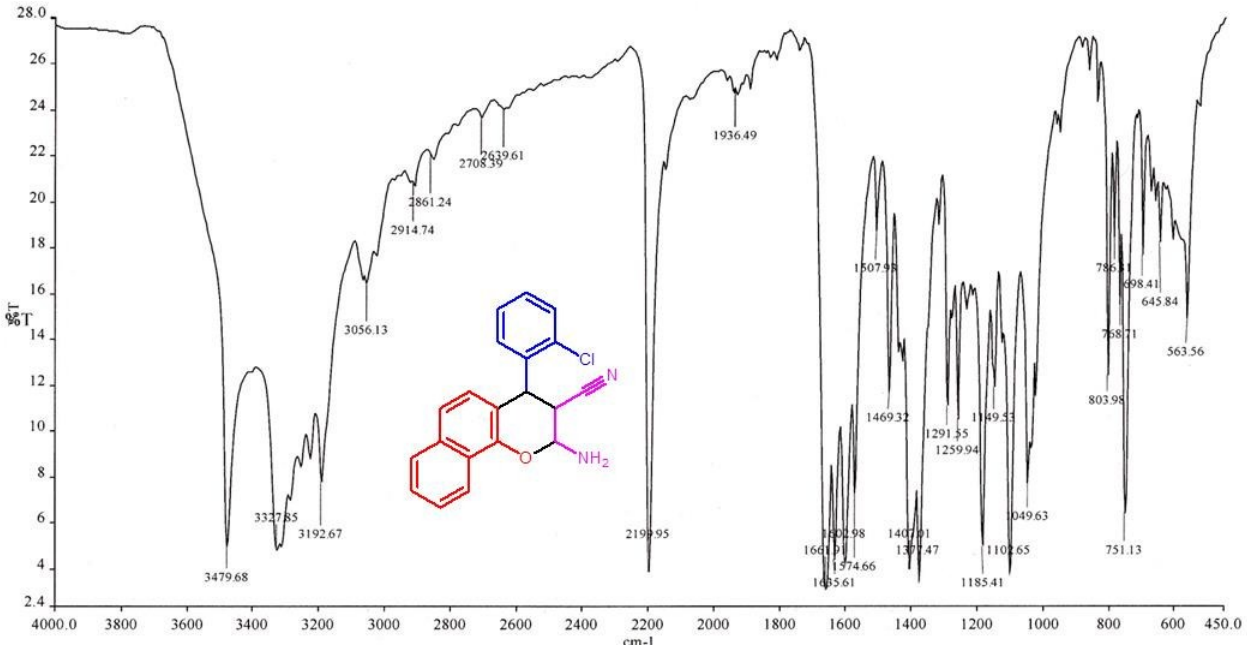
Spectra 34. IR spectrum of compound **IIIe**



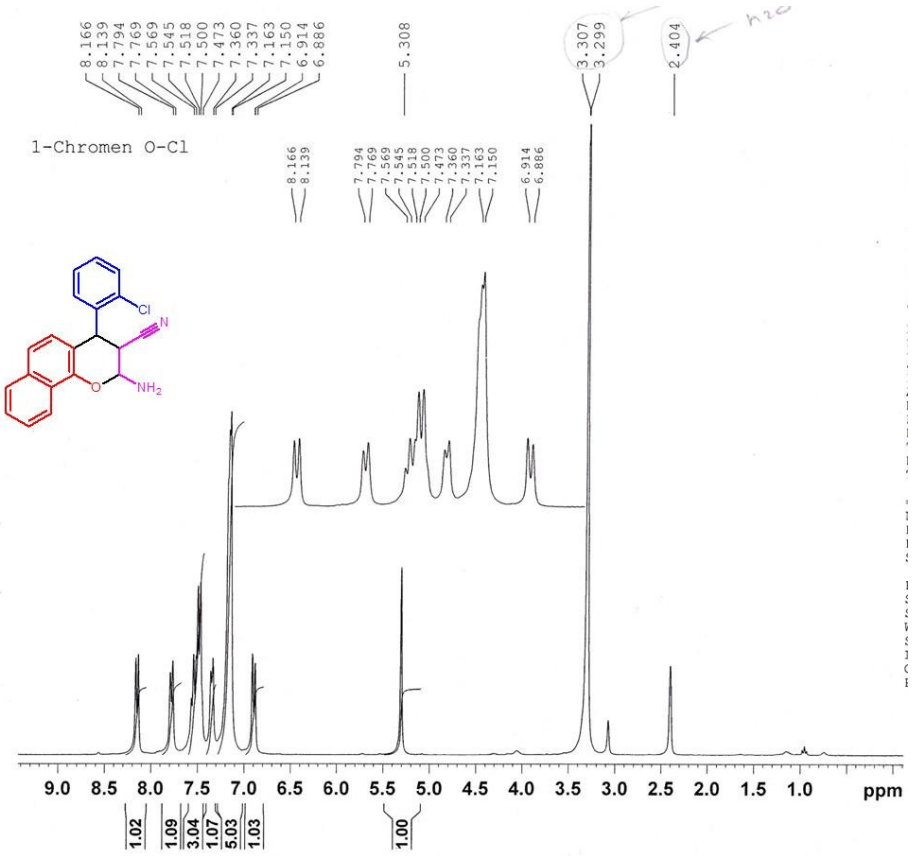
Spectra 35. [1]H NMR spectrum of compound **IIIe**



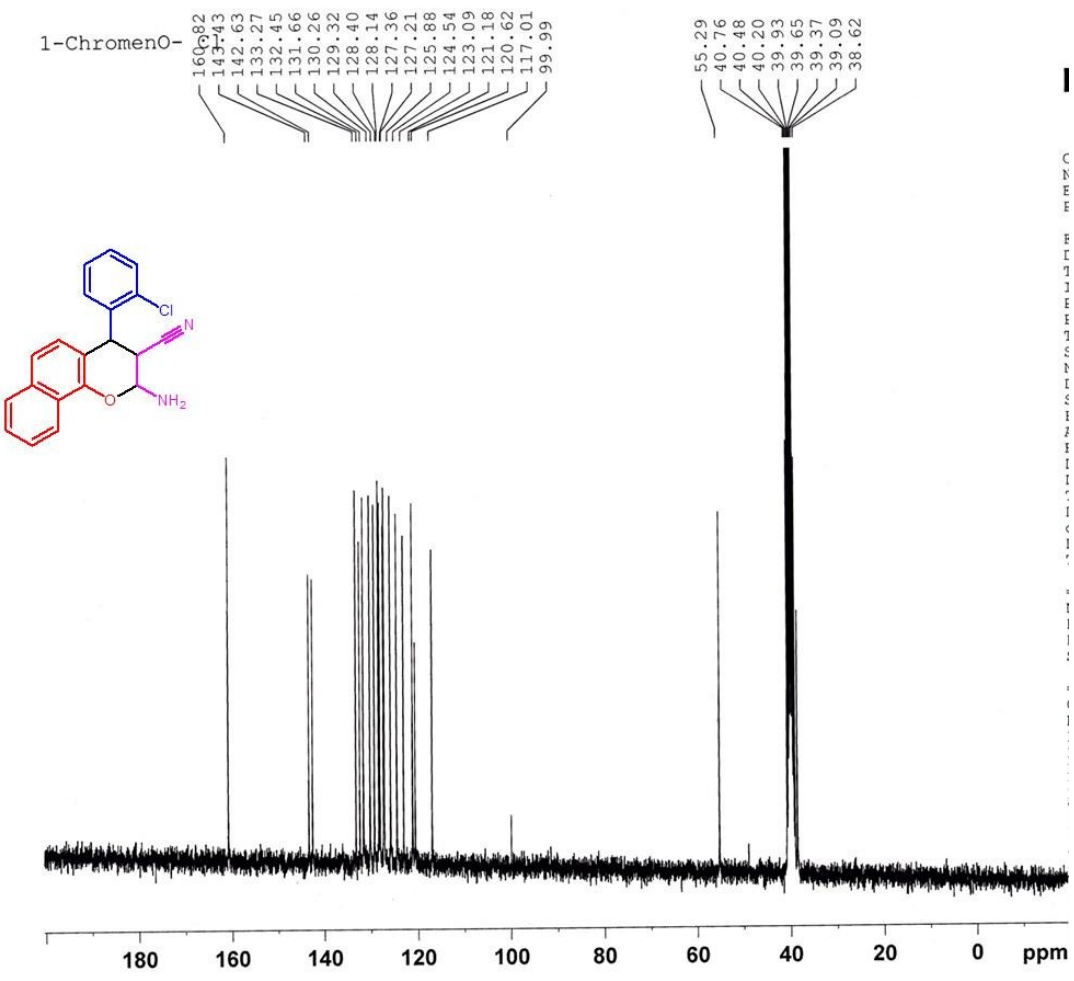
Spectra 36. [13]C NMR spectrum of compound **IIIe**



Spectra 37. IR spectrum of compound chromene



Spectra 38. [1]H NMR spectrum of compound **chromene**



Spectra 39. ^{13c} NMR spectrum of compound **chromene**