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Supporting Information

Paired electrochemical conversion of nitroarenes to sulfonamides, diarylsulfones and bis(arylsulfonyl)aminophenols

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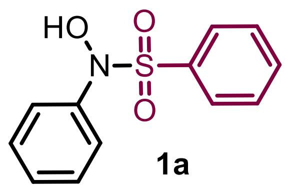
Contents

Characteristics of products

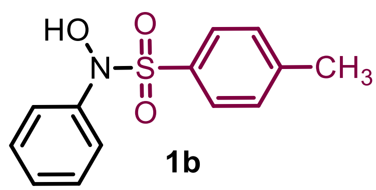
Compound 1a ($C_{12}H_{11}NO_3S$)



1a

Isolated yield: 70%. Mp=133-134 °C. IR (KBr, cm^{-1}): 3355, 1595, 1488, 1447, 1346, 1176, 765, 684, 564. ^{1}H NMR, δ ppm (500 MHz, acetone d_6): 7.17 (d, J = 7.5 Hz, 2H), 7.23-7.30 (m, 3H), 7.53 (m, 4H), 7.66 (d, J = 3.1 Hz, 1H), 10.15 (s, 1H, OH). ^{13}C NMR, δ ppm (125 MHz, acetone d_6): 123.1, 127.3, 128.5, 128.8, 129.9, 133.5, 134.2, 143.3. MS (EI) *m/z* (%): 51 (42), 77 (100), 141 (47), 233 (9), 248 [78, (M^+-1)].

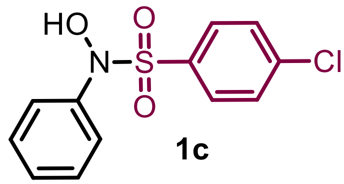
Compound 1b ($C_{13}H_{13}NO_3S$)



1b

Isolated yield: 75%. Mp=139-141°C. IR (KBr, cm^{-1}): 3372, 2815, 1565, 1487, 1353, 1161, 566, 543. ^{1}H NMR, δ ppm (500 MHz, acetone-d_6): 2.42 (s, 3H, CH_3), 7.18 (d, J = 7.6, 2H), 7.22-7.30 (m, 3H), 7.32 (d, J = 8.0, 2H), 7.40 (d, J = 8.1, 2H), 10.06 (s, 1H, OH). ^{13}C NMR, δ ppm (125 MHz, acetone-d_6): 21.1, 123.1, 127.2, 128.4, 129.1, 130.0, 130.7, 143.4, 145.1. MS (EI) *m/z* (%): 65 (3), 91 (100), 155 (77), 262 [75, (M^+-1)].

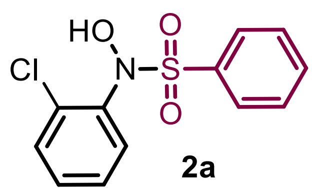
Compound 1c ($C_{12}H_{10}ClNO_3S$)



1c

Isolated yield: 78%. Mp=128-129°C. IR (KBr, cm^{-1}): 3359, 1577, 1487, 1350, 1177, 761, 567. ^{1}H NMR, δ ppm (500 MHz, acetone-d_6): 6.88 (d, J = 7.9 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 8.1 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H) 10.42 (s, H, OH). ^{13}C NMR, δ ppm (125 MHz, acetone-d_6): 123.1, 127.6, 128.7, 129.1, 131.6, 132.1, 140.2, 143.0. MS (EI) m/z (%): 52 (20), 75 (34), 111 (95), 175 (97), 282 [100, (M^+-1)].

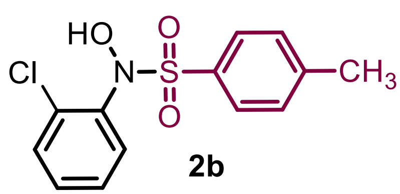
Compound 2a ($C_{12}H_{10}ClNO_3S$)



2a

Isolated yield: 73%. Mp=153-155°C. IR (KBr, cm^{-1}): 3359, 1577, 1487, 1350, 1177, 761, 567. ^{1}H NMR, δ ppm (500 MHz acetone-d_6): 6.81 (d, J = 7.9 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.65 (t, J = 7.6, 2H), 7.77-7.82 (m, 3H), 10.31 (s, 1H, OH). ^{13}C NMR, δ ppm (125 MHz, acetone-d_6): 126.9, 127.4, 129.1, 130.0, 130.4, 130.5, 133.0 134.2, 134.5 140.4. MS (EI) m/z (%): 51 (92), 77 (100), 142 (95), 266 (21), 283 [25, (M^+)].

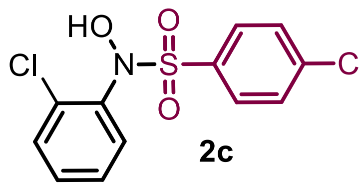
Compound 2b ($C_{13}H_{12}ClNO_3S$)



2b

Isolated yield: 75%. Mp=139-140ºC. IR (KBr, cm^{-1}): 3332, 2837, 1595, 1472, 1443, 1344, 1167, 765, 678, 576. ^{1}H NMR, δ ppm (500 MHz, acetone-d_6): 2.44 (s, 3H, CH_3), 6.76 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.1 Hz, 1H), 7.41 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 7.6 Hz, 2H), 10.26 (s, 1H, OH). ^{13}C NMR, δ ppm (125 MHz, acetone-d_6): 21.1 CH_3, 126.8, 127.4, 129.6, 130.0, 130.4, 130.5, 131.2, 133.0, 140.6, 145.5. MS (EI) m/z (%): 51 (36), 65 (71), 91 (100), 114 (54), 142 (78), 281 (11), 297 [22, (M^+)].

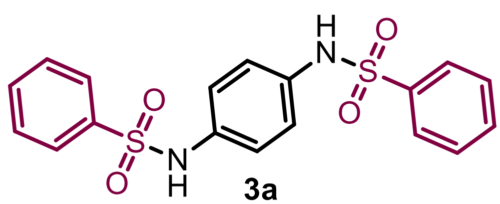
Compound 2c ($C_{12}H_9Cl_2NO_3S$)



2c

Isolated yield: 72%. Mp=143-145ºC. IR (KBr, cm^{-1}): 3377, 1578, 1474, 1396, 1350, 1169, 769, 661, 621, 574. ^{1}H NMR, δ ppm (500 MHz, acetone-d_6): 6.88 (d, J = 7.9 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.1 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.6 Hz , 2H), 10.41 (s, 1H, OH). ^{13}C NMR, δ ppm (125 MHz, acetone-d_6): 126.8, 127.6, 129.4, 130.2, 130.5, 132.1, 132.9, 133.1, 140.1, 140.MS (EI) m/z (%): 50 (11), 75 (41), 111 (100), 159 (20), 175 (95), 316 [39, (M^+-1)].

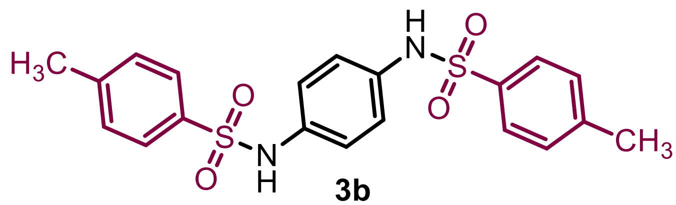
Compound 3a ($C_{18}H_{16}N_2O_4S_2$)



3a

Isolated yield: 60%. Mp = 170-172 ºC. IR (KBr, cm^{-1}): 3460, 3362, 3210, 1629, 1491, 1288, 1142, 688, 591. ^{1}H NMR, δppm (400 MHz, DMSO-d_6): 4.22 (s, 1H, NH), 5.70 (s, 1H, NH), 6.52-6.71 (m, 3H), 7.19 (s, 1H), 7.35 (s, 1H), 7.70 (s, 6H), 7.93-7.95 (d, J = 6.8 Hz, 3H). ^{13}C NMR, δppm (125 MHz, DMSO-d_6): 121.0, 122.0, 122.6, 124.1, 124.6, 126.1, 126.6, 126.7, 128.8, 129.1, 129.3, 129.5, 133.9, 140.2. MS (EI) m/z (%): 77 (100), 125 (26), 182 (71), 247 (62), 388 [64, (M^+)].

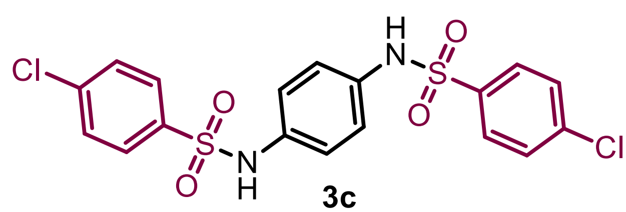
Compound 3b ($C_{20}H_{20}N_2O_4S_2$)



3b

Isolated yield: 72%. Mp =158-159°C. IR (KBr, cm^{-1}): 3376, 2962, 2925, 2853, 1599, 1508, 1446, 1305, 1142, 804, 724, 688, 588. ^{1}H NMR, δ ppm (400 MHz, DMSO-d_6 and acetone-d_6): 2.38 (s, 6H, CH_3), 4.20 (s, 1H, NH), 5.65 (s, 1H, NH), 6.62-6.64 (d, J = 8.4 Hz, 1H), 6.78, (t, J = 8.4 Hz, 3H), 7.10-7.13 (d, J = 9.6 Hz, 2H), 7.36-7.38 (d, J = 7.4 Hz, 3H), 7.83-7.85 (d, J = 8 Hz, 3H). ^{13}C NMR, δ ppm (100 MHz, acetone-d_6): 20.5 (CH_3), 113.2, 114.3, 118.1, 118.9, 119.4, 123.1, 126.8, 127.0, 127.7, 128.7, 129.2, 129.5, 129.6, 131.1. MS (EI) m/z (%): 72 (100), 149 (37), 222 (35), 279 (5), 346 (7), 401 (3), 414 [23, (M^+-2)].

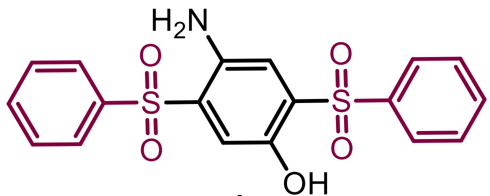
Compound 3c ($C_{18}H_{14}Cl_2N_2O_4S_2$)



3c

Isolated yield: 77%. Mp =156-158°C. IR (KBr, cm^{-1}): 3366, 3233, 1625, 1599, 1509, 1303, 1140, 722, 690. ^{1}H NMR, δ ppm (400 MHz, acetone-d_6): 7.29 (m, J = 7.6 Hz, 1H), 7.35-7.40 (m, 3H), 7.45-7.52 (m, 4H), 7.56-7.59 (d, J = 8.0 Hz, 2H), 7.64-7.66 (d, J = 8.0 Hz, 2H), 7.78 (t, J = 7.6, 2H). ^{13}C NMR, δ ppm (100 MHz, acetone-d_6): 118.7, 124.2, 126.1, 128.3, 128.8, 129.2, 130.6, 131.1, 131.8, 132.6, 133.9, 136.2, 142.1, 149.5. MS (EI) *m/z* (%): 50 (55), 72 (100), 105 (53), 182 (64), 250 (20), 312 (16), 383 (17), 455 [55, (M^{+}-1)].

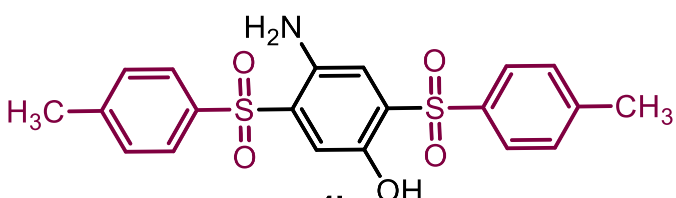
Compound 4a ($C_{18}H_{15}NO_5S_2$)



4a

Isolated yield: 70%. Mp=158-160°C. IR (KBr, cm^{-1}): 3344, 3274, 1611, 1512, 1447, 1280, 1141, 731, 602, 557. ^{1}H NMR, δ ppm (400 MHz, acetone-d_6): 6.72 (d, J = 8.4 Hz, 1H), 6.85-6.94 (m, 2H), 7.16-7.21 (m, 1H), 7.57-7.67 (m, 7H), 7.95-8.0 (m, 4H). ^{13}C NMR, δ ppm (100 MHz, acetone-d_6): 112.8, 115.9, 117.9, 118.4, 118.8, 119.4, 122.6, 127.3, 127.6, 127.7, 129.0, 129.1, 133.2, 133.3. MS (EI) *m/z* (%): 79 (100), 158 (98), 202 (76), 249 (36), 389 [36, (M^{+})].

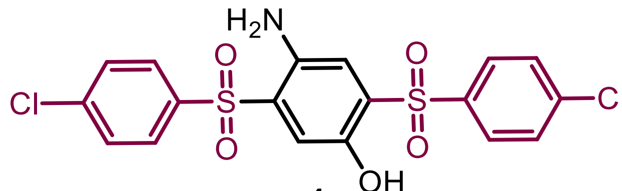
Compound 4b ($C_{20}H_{19}NO_5S_2$)



4b

Isolated yield: 70%. Mp=158-159°C. IR (KBr, cm^{-1}): 3352, 3292, 1617, 1596, 1451, 1298, 1146, 710, 657, 521. ^{1}H NMR, δ ppm (400 MHz, acetone-d_6): 2.39 (s, 6H, CH_3), 6.71 (d, J = 8.4 Hz, 1H), 6.84-6.87 (m, 1H), 6.91 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 2.8 Hz, 1H), 7.40 (t, J = 7.2, Hz, 4H), 7.49 (s, 1H), 7.82-7.89 (m, 4H). ^{13}C NMR, δ ppm (100 MHz, acetone-d_6): 21.4, 21.5, 113.6, 118.1, 119.3, 119.7, 120.1, 120.4, 123.4. 128.2, 128.4, 128.6, 128.7, 130.4, 130.5, 130.7. MS (EI) *m/z* (%): 52.2 (36), 107 (100), 199 (16), 263 (14), 417 [36, (M^{+})].

Compound 4c ($C_{18}H_{13}Cl_2NO_5S_2$)



4c

Isolated yield: 72%. Mp=157-159°C. IR (KBr, cm^{-1}): 3362, 3311, 3216, 1634, 1611, 1582, 1493, 1289, 1139, 731, 685, 605. ^{1}H NMR, δ ppm (400 MHz, DMSO-d_6): 6.74 (s, 1H, OH, disappeared after addition of D_2O), 6.87-6.93 (m, 3H, aryl H and NH, disappeared after addition of D_2O), 7.22 (d, *J* = 10.8 Hz, 2H), 7.62 (s, 4H, aryl H and NH, disappeared after addition of D_2O), 7.97-7.99 (m, 3H). ^{13}C NMR, δ ppm (125 MHz, DMSO-d_6): 113.7, 115.0, 119.1, 119.6, 120.3, 123.5, 128.6, 130.0, 130.4, 130.7, 142.0, 142.8, 145.1, 147.5. MS (EI) *m/z* (%): 79 (86), 183 (11), 283 (100), 457 [23, (M^+)].

Cyclic voltammograms of 1-chloro-2-nitrobenzene at different pHs

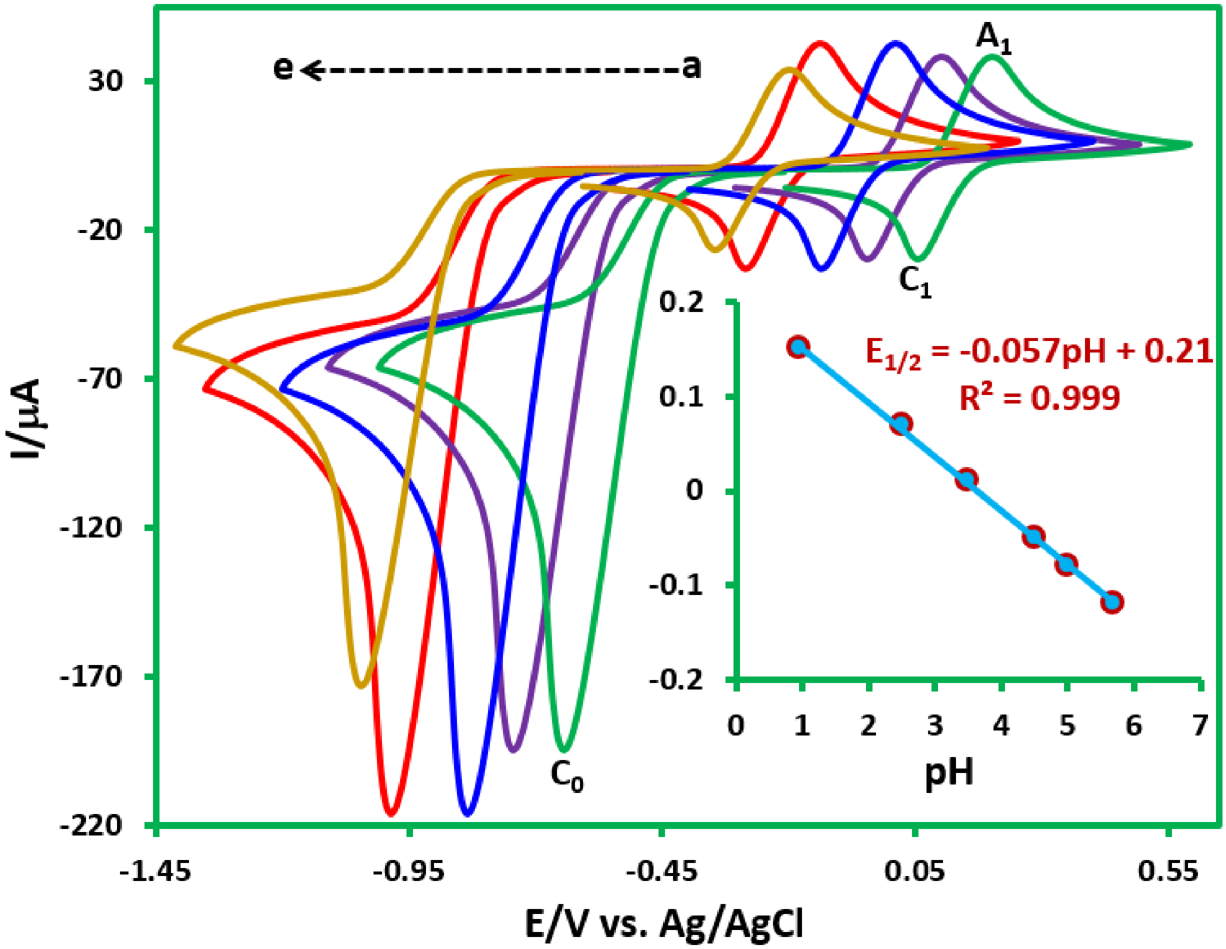


Fig. S1. Cyclic voltammograms of 1.0 mM1 -chloro-2-nitrobenzene at glassy carbon electrode, in water/ethanol (80/20) mixture with various pH values and same ionic strength. pHs from (a) to (e) are: 1.0, 2.5, 3.5, 4.5, 5.0 and 5.7. Working electrode: glassy carbon. Scan rate: 100 mV/s. Inset: The potential-pH diagram of phenylhydroxylamine/nitrosobenzene (redox couple A_1/C_1). t = 25 ± 1 °C.

Cyclic voltammograms of *p*-nitroaniline at different pHs

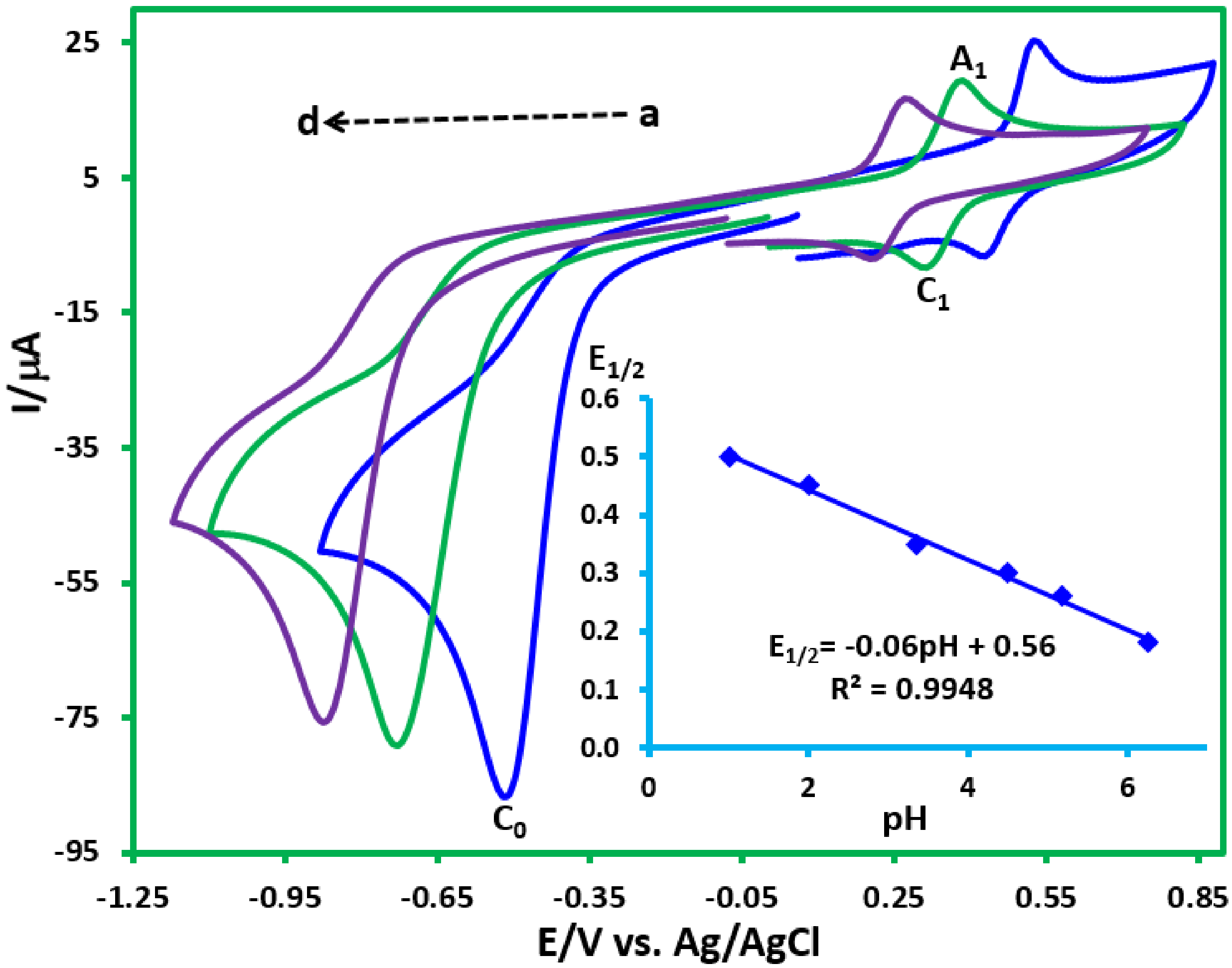


Fig. S2. Cyclic voltammograms of 1.0 mM *p*-nitroaniline at glassy carbon electrode, in water/ethanol (80/20) mixture with various pH values and same ionic strength. pHs from (a) to (d) are: 1.0, 3.35, 5.2 and 6.25. Working electrode: glassy carbon. Scan rate: 100 mV/s. Inset: The potential-pH diagram of phenylhydroxylamine/nitrosobenzene (redox couple A_1/C_1). t = 25 ± 1 ^{o}C.

Cyclic voltammograms of *p*-nitrophenol at different pHs

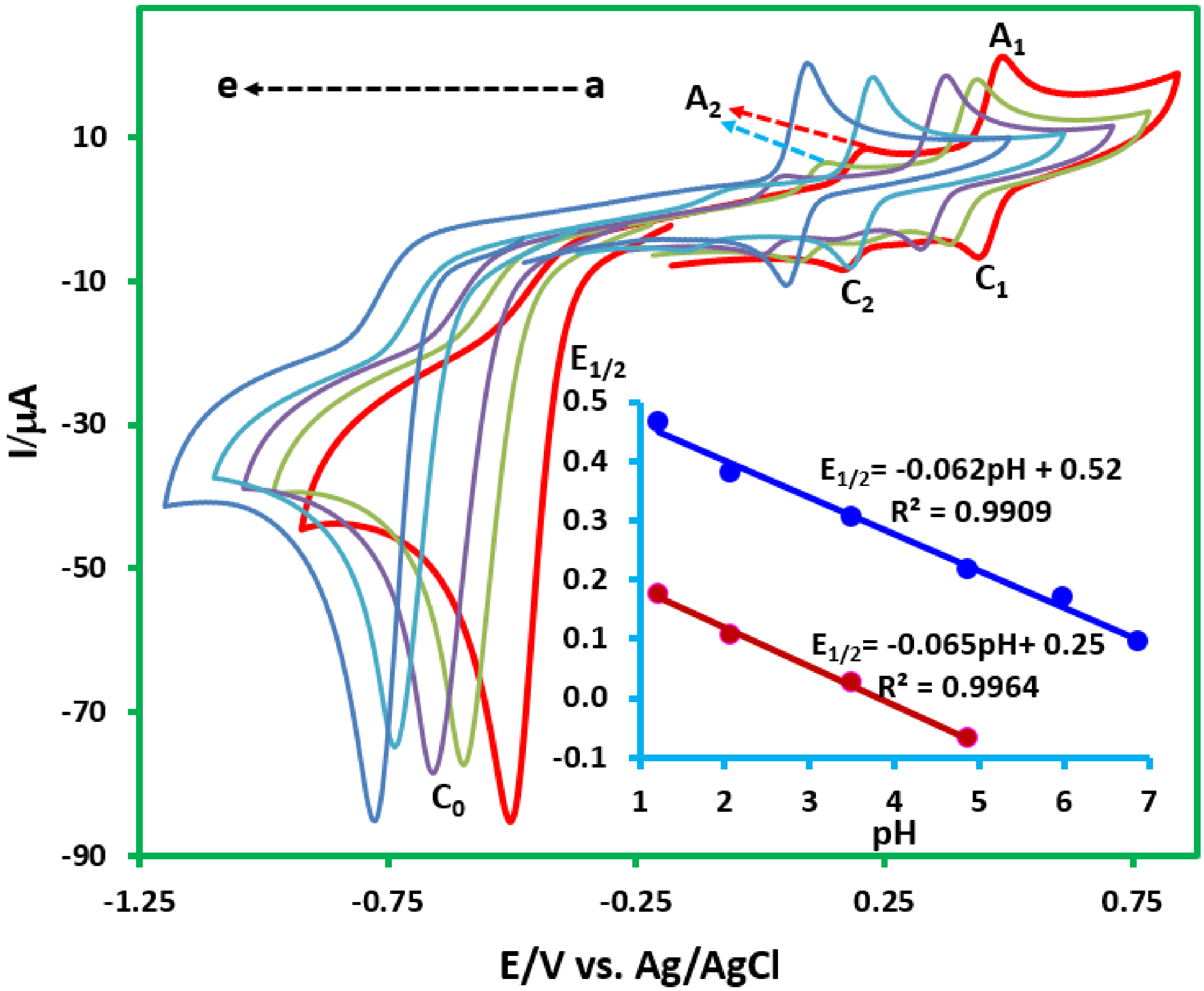


Fig. S3. Cyclic voltammograms of 1.0 mM *p*-nitrophenol at glassy carbon electrode, in water/ethanol (80/20) mixture with various pH values and same ionic strength. pHs from (a) to (e) are: 1.2, 2.1, 2.9, 5.0 and 6.8. Working electrode: glassy carbon. Scan rate: 100 mV/s. Inset: The potential-pH diagram of phenylhydroxylamine/nitrosobenzene (redox couple A_1/C_1) and *p*-aminophenol/*p*-aminoquinone (redox couple A_2/C_2). t = 25 ± 1 °C.

Cyclic voltammograms of nitrobenzene

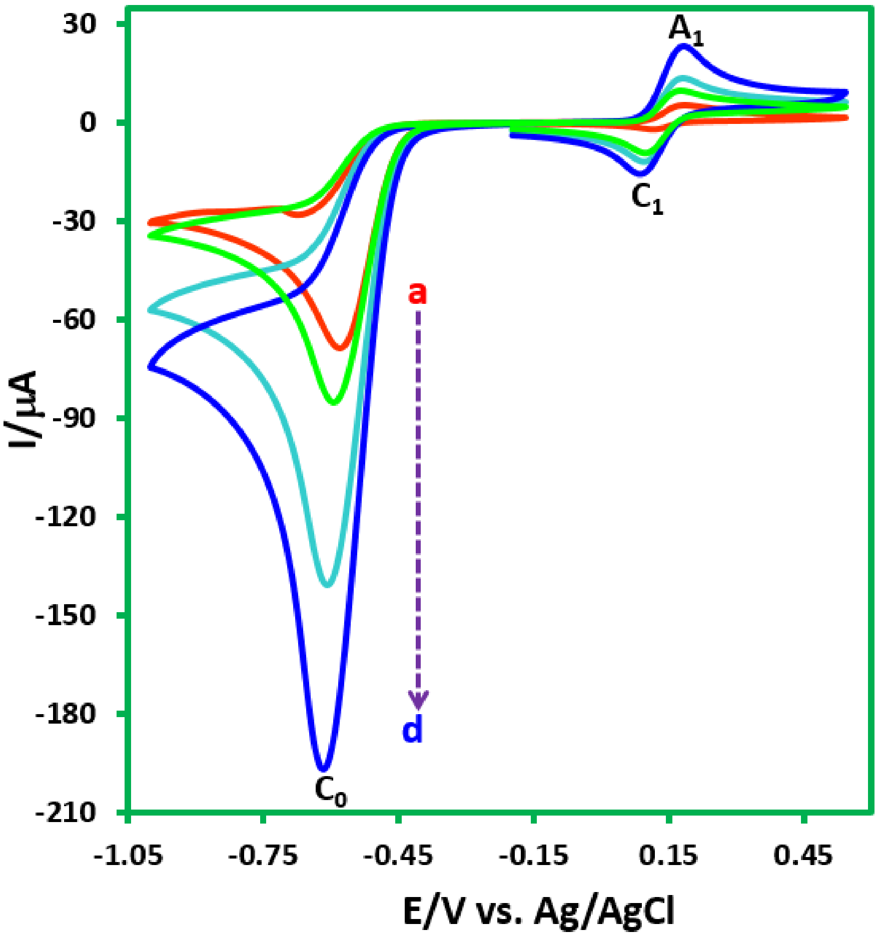


Fig. S4. Cyclic voltammograms of 1.0 mM nitrobenzene at glassy carbon electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.5) at different scan rates. Scan rate from (a) to (d) are: 10, 25, 50 and 100 mV/s respectively. t = 25 ± 1 °C.

Cyclic voltammograms of nitrobenzene in the absence and presence of benzenesulfinic acid

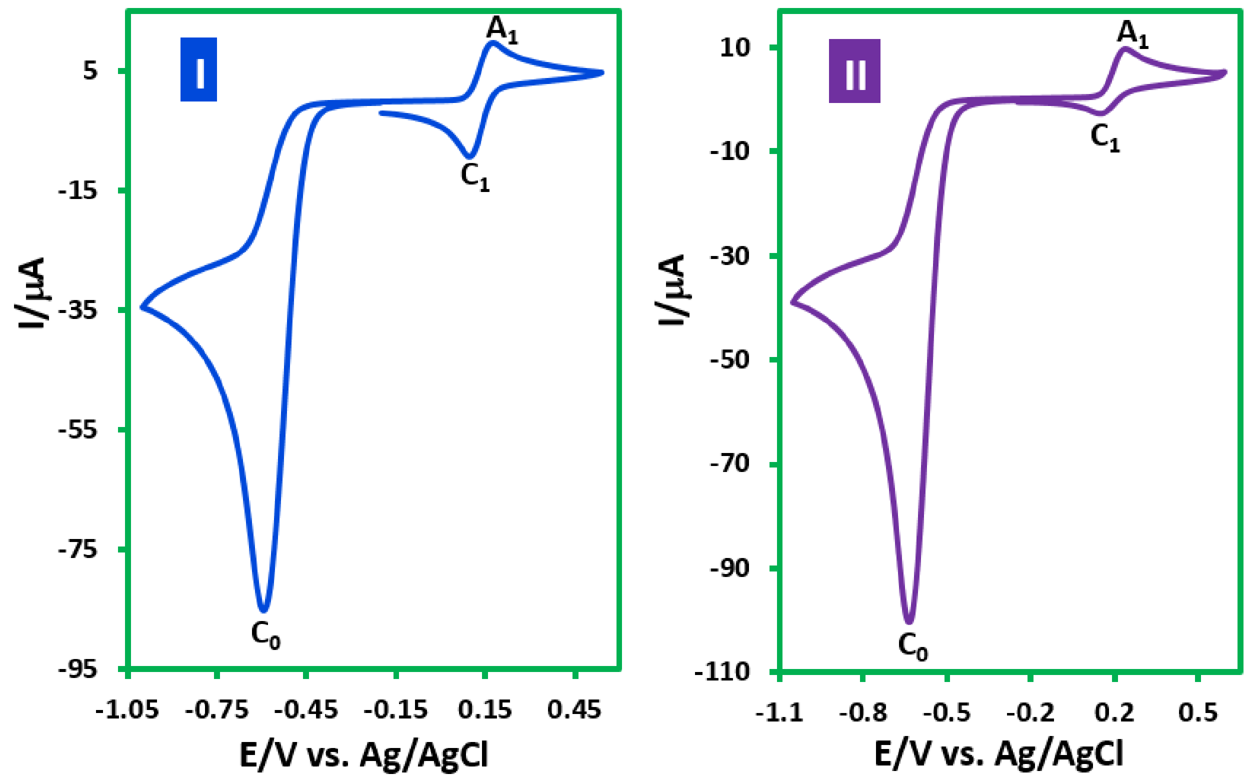


Fig. S5. Cyclic voltammograms of 1.0 mM nitrobenzene. Part I: in the absence and part II, in the presence of benzenesulfinic acid (1.0 mM) at glassy carbon electrode, in aqueous solution conta ining phosphate buffer (c = 0.2 M, pH = 3.5). Scan rate: 25. t = 25 ± 1 ^{o}C.

Cyclic voltammograms of nitrobenzene in the presence of benzenesulfinic acid

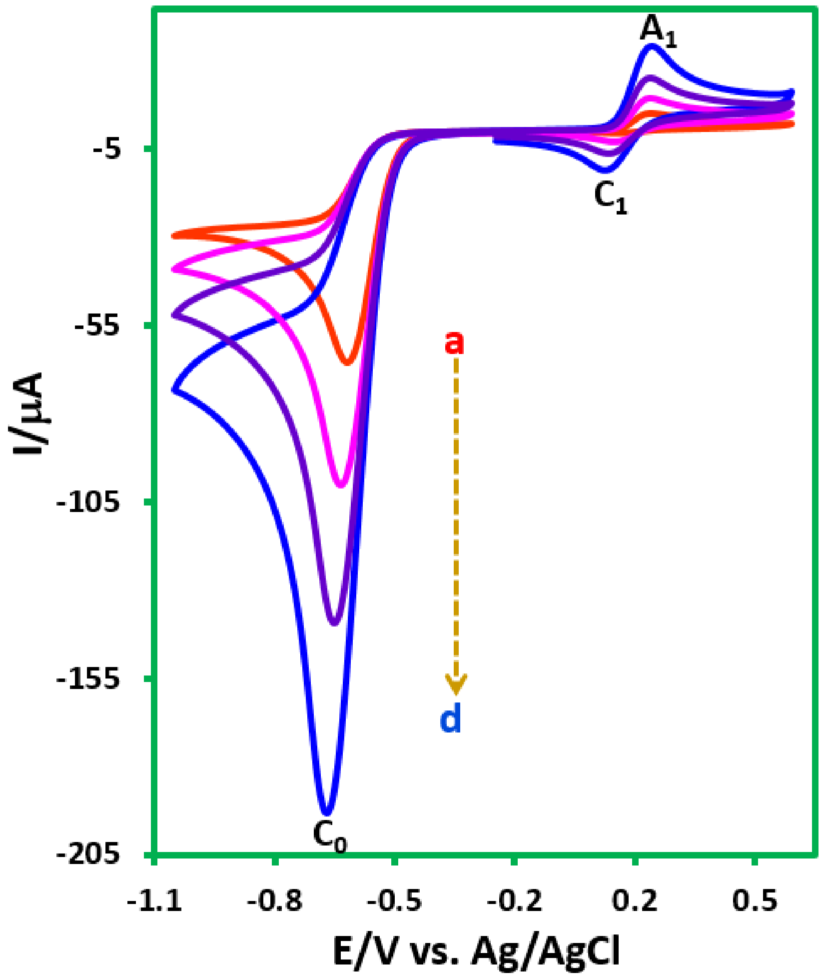


Fig. S6. Cyclic voltammograms of 1.0 mM nitrobenzene in the presence of benzenesulfinic acid (1.0 mM) at glassy carbon electrode, in aqueous solution containing phosphate buffer (*c* = 0.2 M, pH = 3.5) at different scan rates. Scan rate from (a) to (d) are: 10, 25, 50 and 100 mV/s respectively. *t* = 25 ± 1 ^{o}C.

Cyclic voltammograms of *p*-nitroaniline

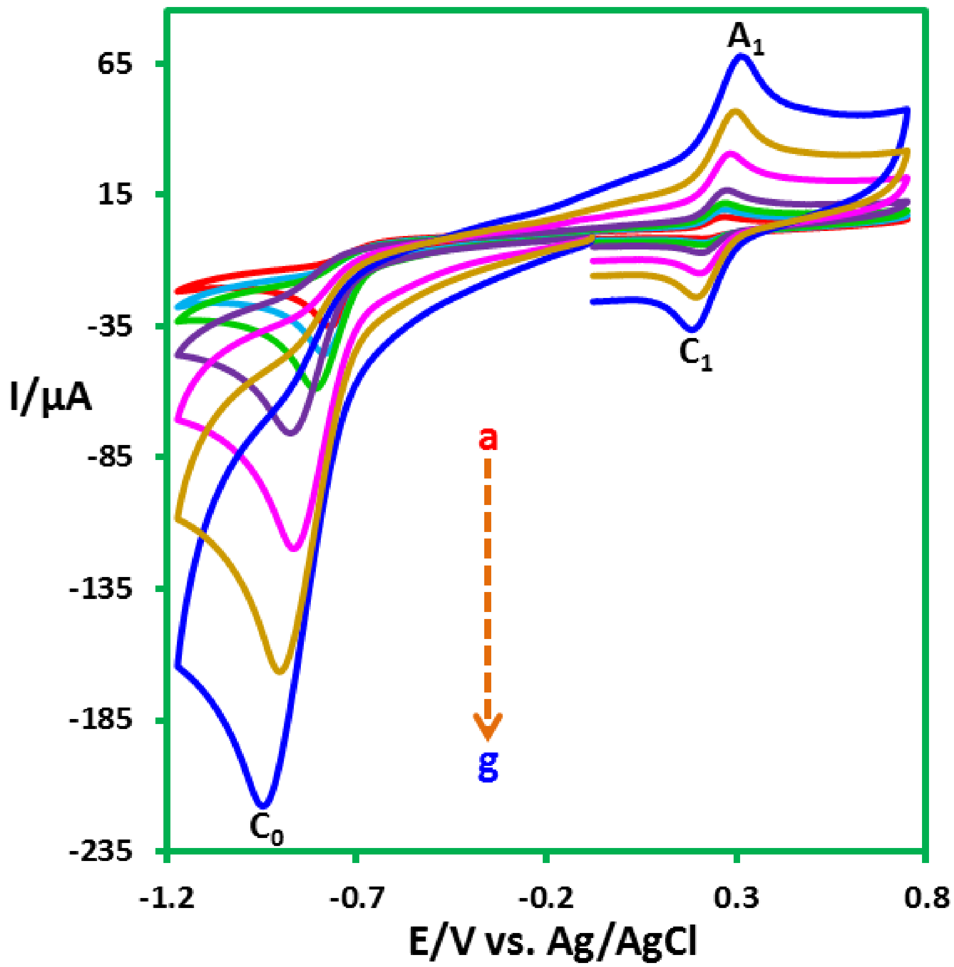


Fig. S7. Cyclic voltammograms of 1.0 mM *p*-nitroaniline in the presence of benzenesulfinic acid (1.0 mM) at glassy carbon electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.5) at different scan rates. Scan rate from (a) to (g) are: 10, 25, 50, 100, 250, 500 and 1000 mV/s respectively. t = 25 ± 1 ^{o}C.

Cyclic voltammograms of *p*-nitroaniline in the presence of benzenesulfinic acid

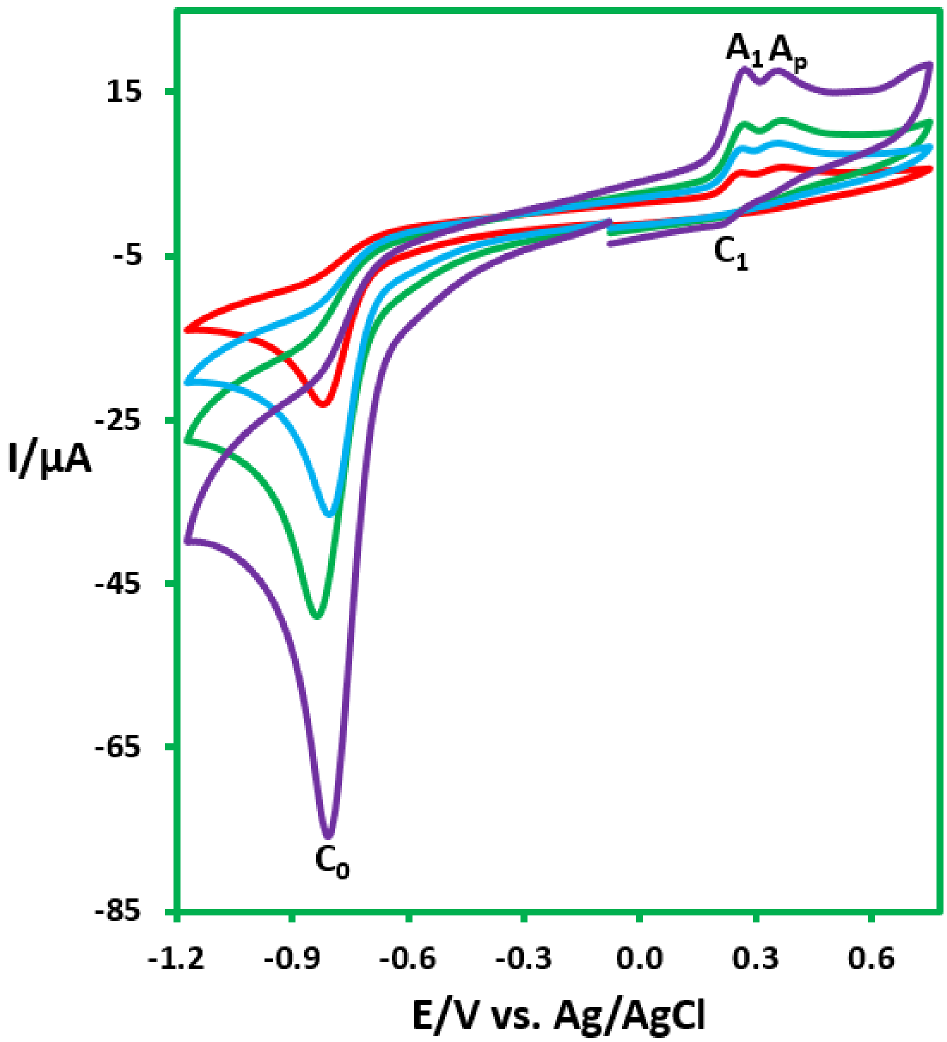


Fig. S8. Cyclic voltammograms of 1.0 mM *p*-nitroaniline in the presence of benzenesulfinic acid (1.0 mM) at glassy carbon electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.5) at different scan rates. Scan rate from (a) to (d) are: 10, 25, 50 and 100 mV/s respectively. t = 25 ± 1 °C.

Cyclic voltammograms of *p*-nitroaniline in the absence and presence of benzenesulfinic acid

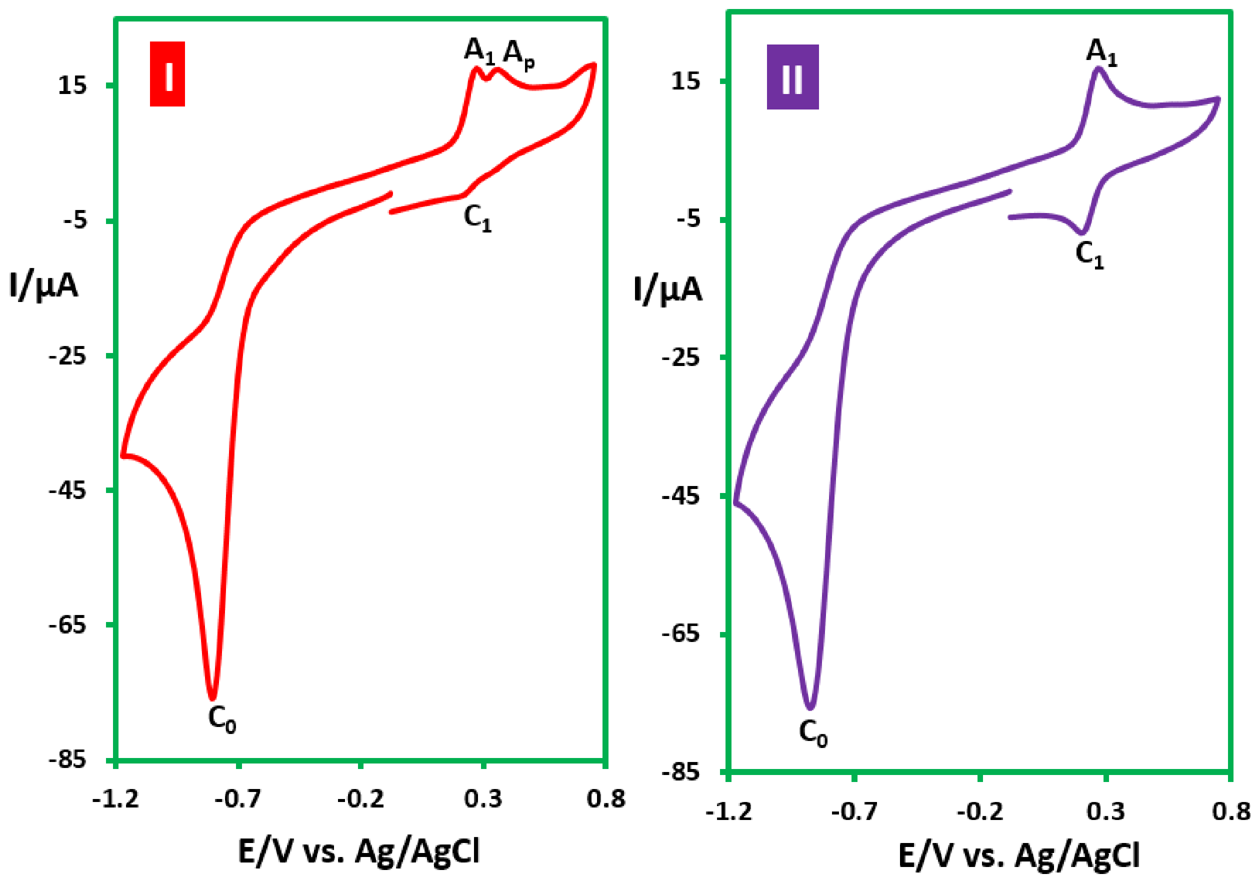


Fig. S9. Cyclic voltammograms of 1.0 mM *p*-nitroaniline. Part I: in the presence and part II, in the absence of benzenesulfinic acid (1.0 mM) at glassy carbon electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.5). Scan rate: 100 mV/s. t = 25 ± 1 °C.

Cyclic voltammograms of *p*-nitrophenol

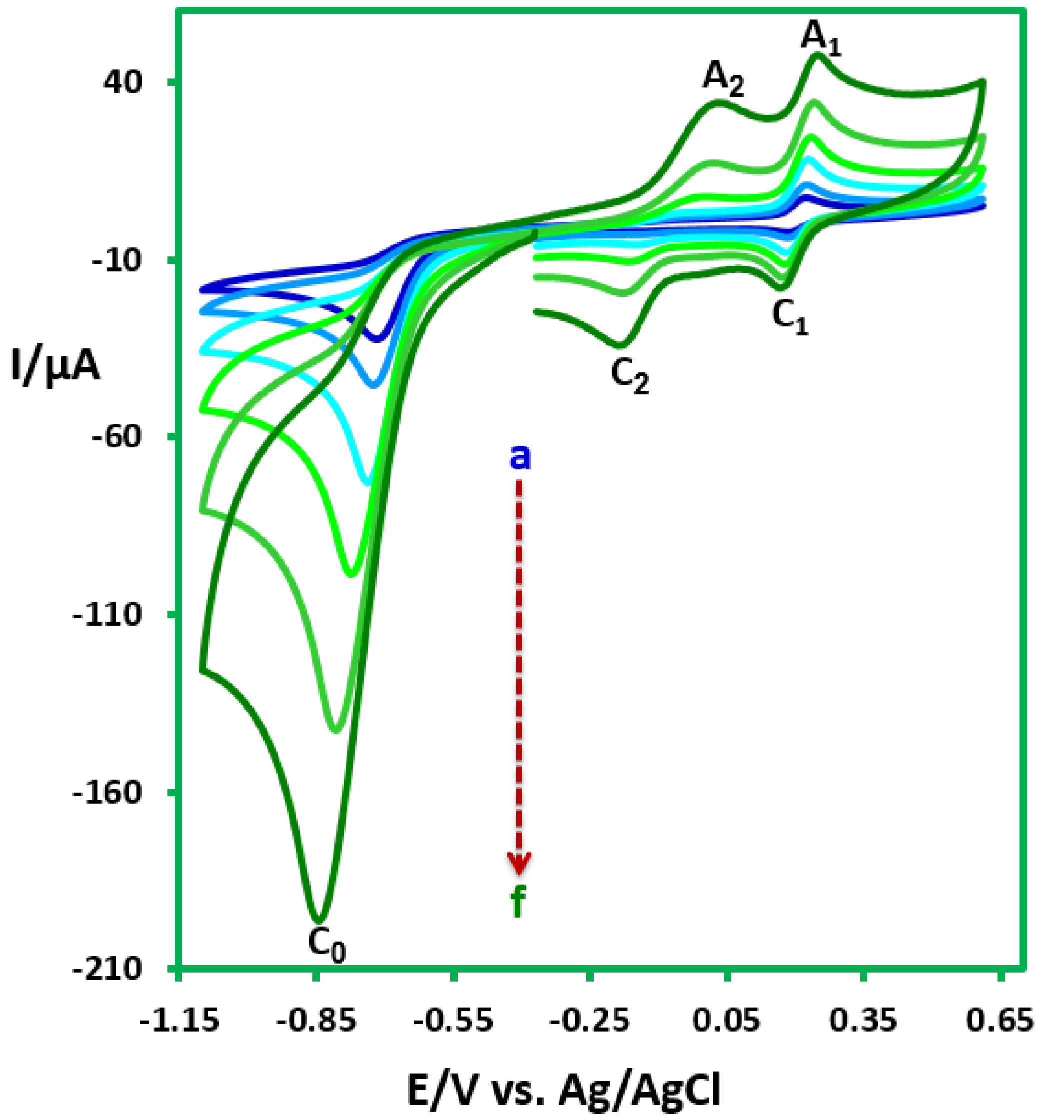


Fig. S10. Cyclic voltammograms of 1.0 mM *p*-nitrophenol at glassy carbon electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.5) at different scan rates. Scan rate fro m (a) to (f) are: 10, 50, 100, 250, 500 and 1000 mV/s respectively. t = 25 ± 1 ^{o}C.

Cyclic voltammograms of *p*-nitrophenol in the presence of benzenesulfinic acid

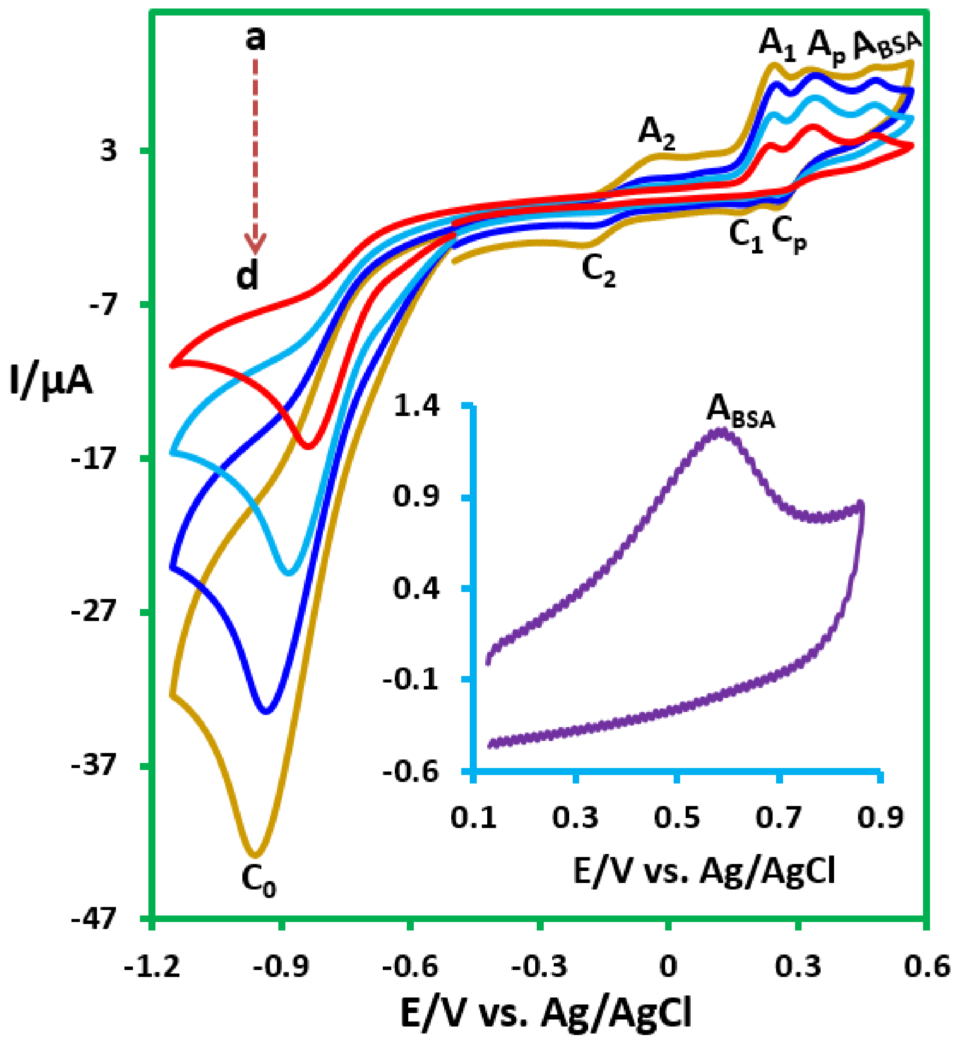


Fig. S11. Cyclic voltammograms of 1.0 mM *p*-nitrophenol in the presence of benzenesulfinic acid (**BSA**) (1.0 mM) at glassy carbon electrode, in aqueous solution containing phosphate buffer (*c* = 0.2 M, pH = 3.5) at different scan rates. Scan rate from (a) to (d) are: 10, 25, 50 and 100 mV/s respectively. *t* = 25 ± 1 ^{o}C. Inset: Cyclic voltammogram of 1.0 mM **BSA** in the same conditions at100 mV/s.

Cyclic voltammograms of *p*-nitrophenol in the absence and presence of BSA

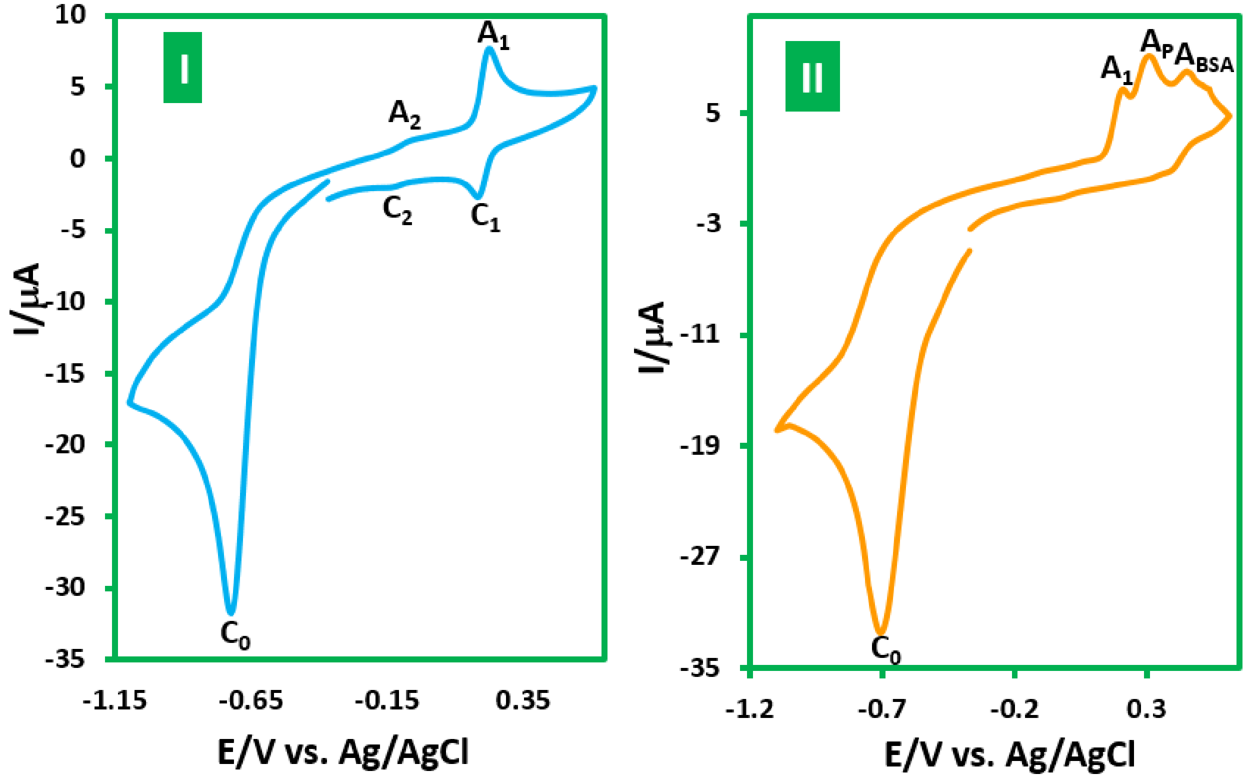
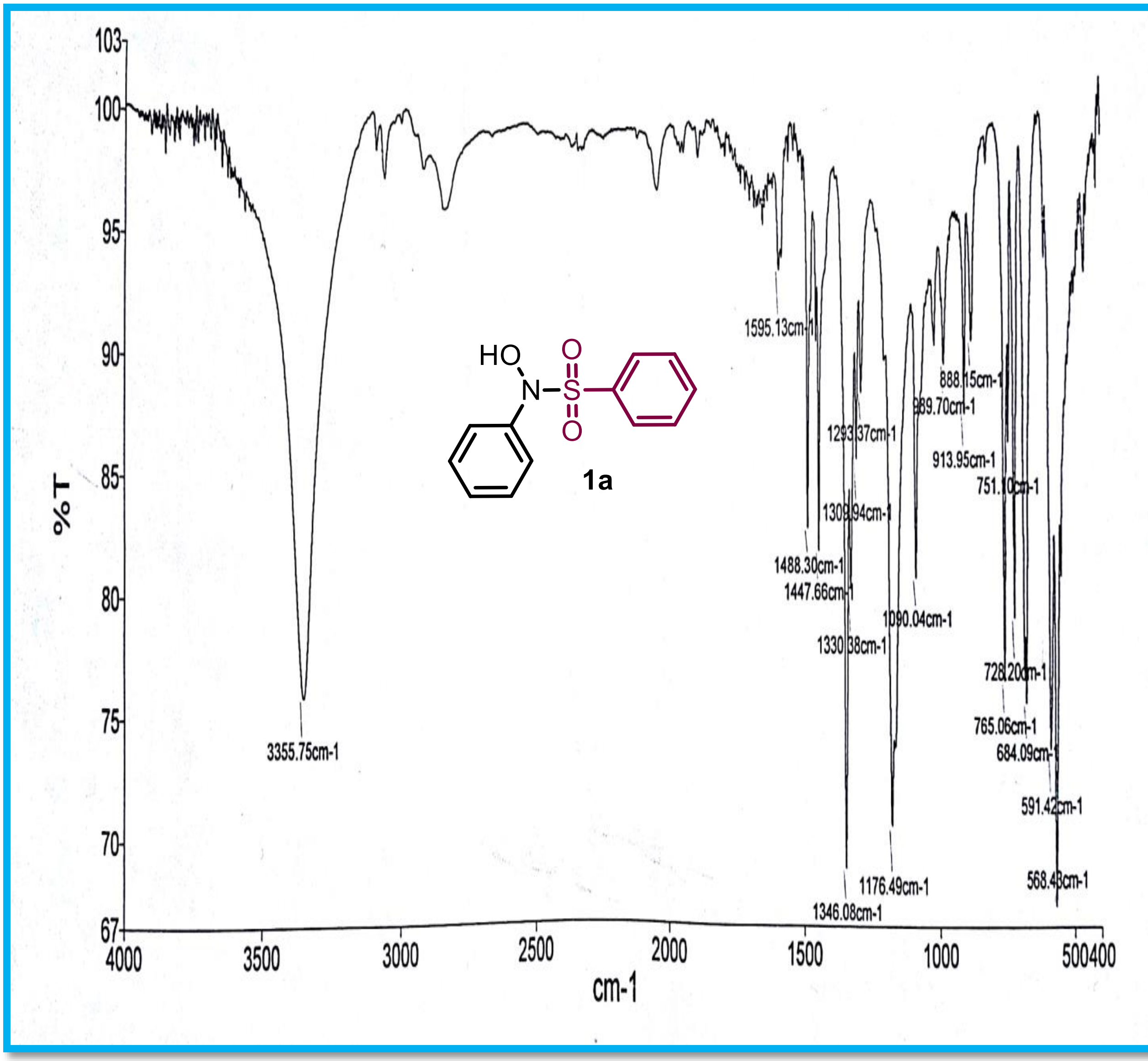
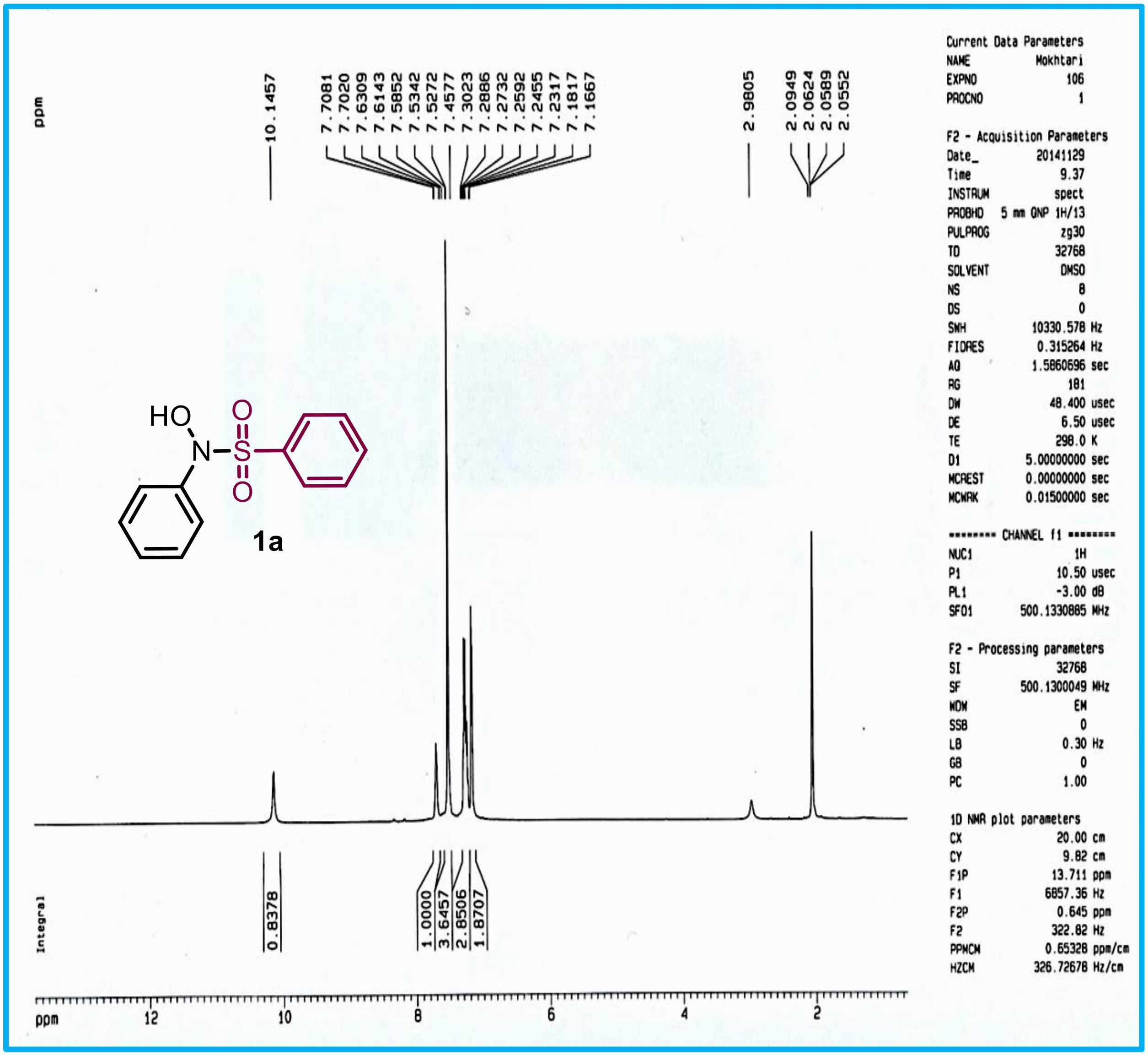


Fig. S12. Cyclic voltammograms of 1.0 mM *p*-nitrophenol. Part I: in the absence and part II, in th e presence of benzenesulfinic acid (1.0 mM) at glassy carbon electrode, in aqueous solution con taining phosphate buffer (c = 0.2 M, pH = 3.5). Scan rate: 50 mV/s. t = 25 ± 1 ^{o}C.

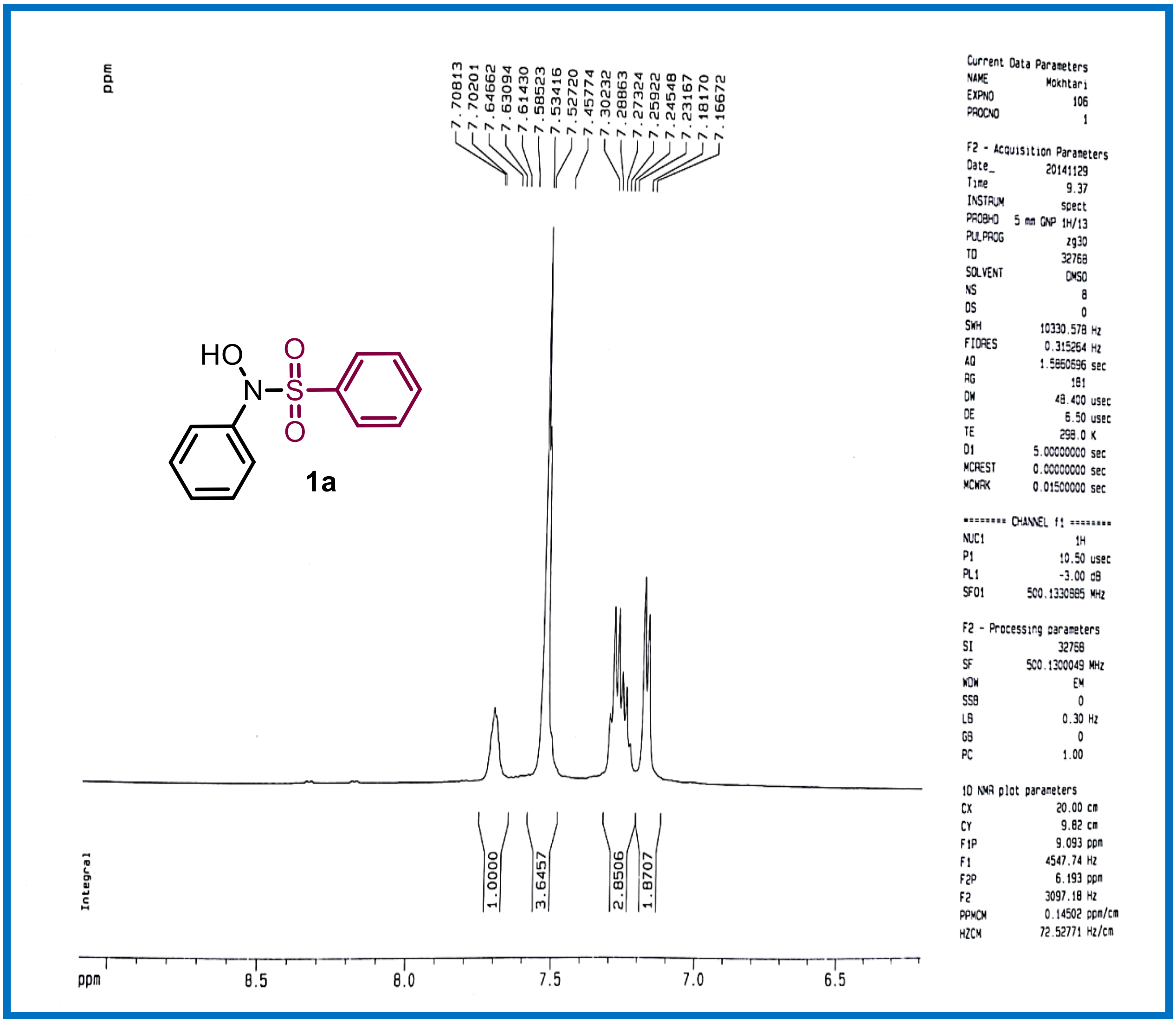
IR spectrum of 1a



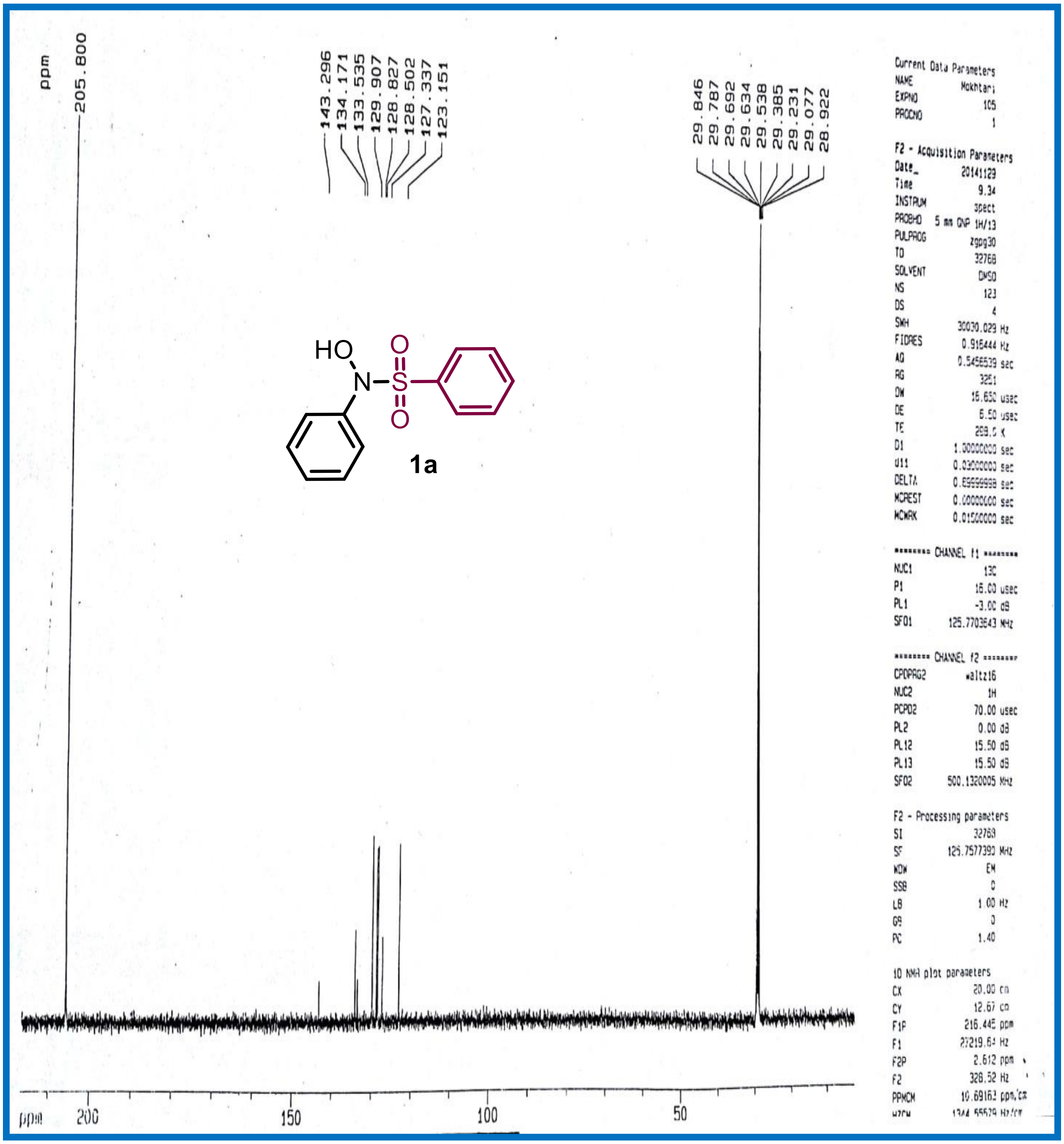
[1]H NMR spectrum of 1a



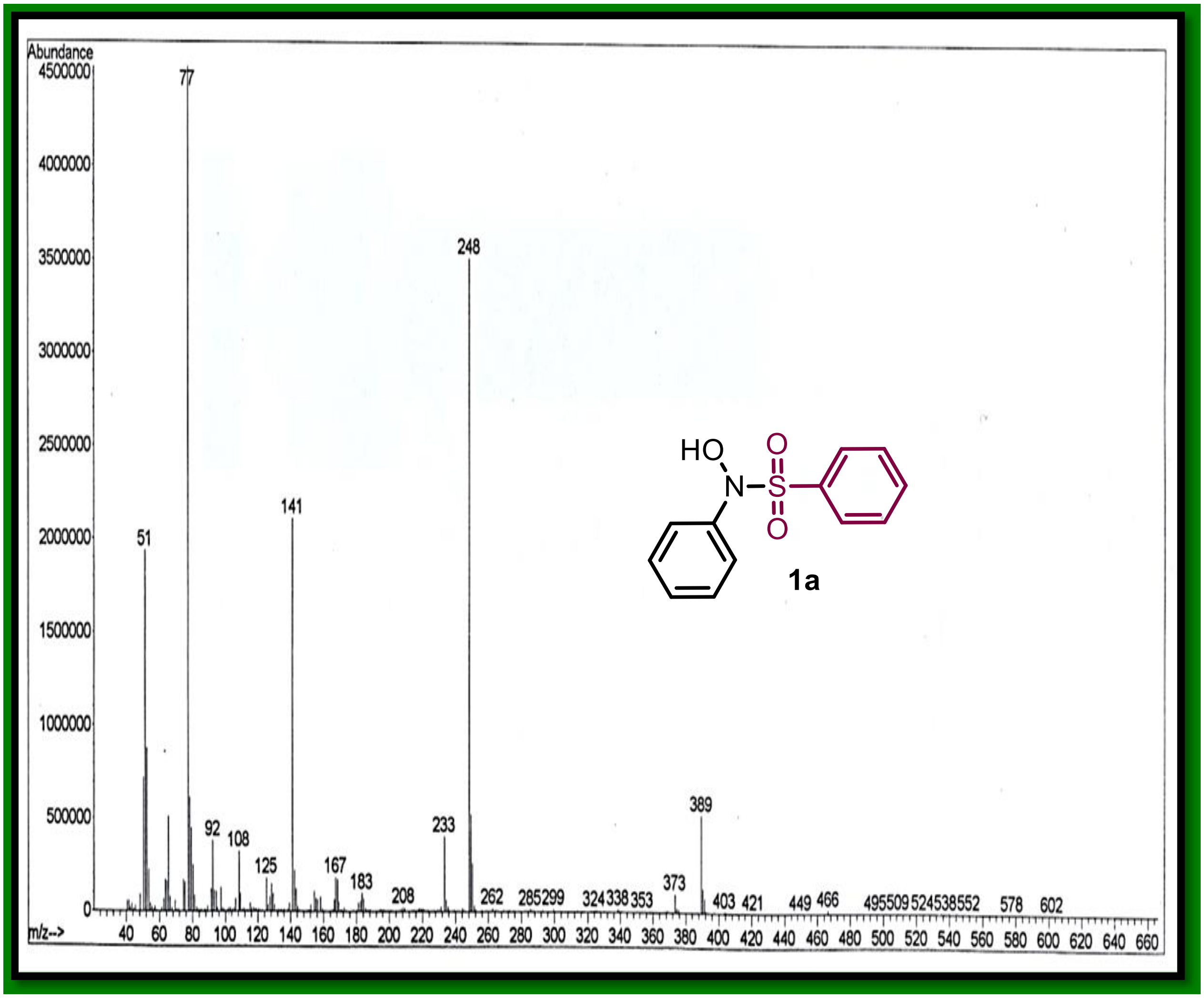
Expanded ^{1}H NMR spectrum of 1a



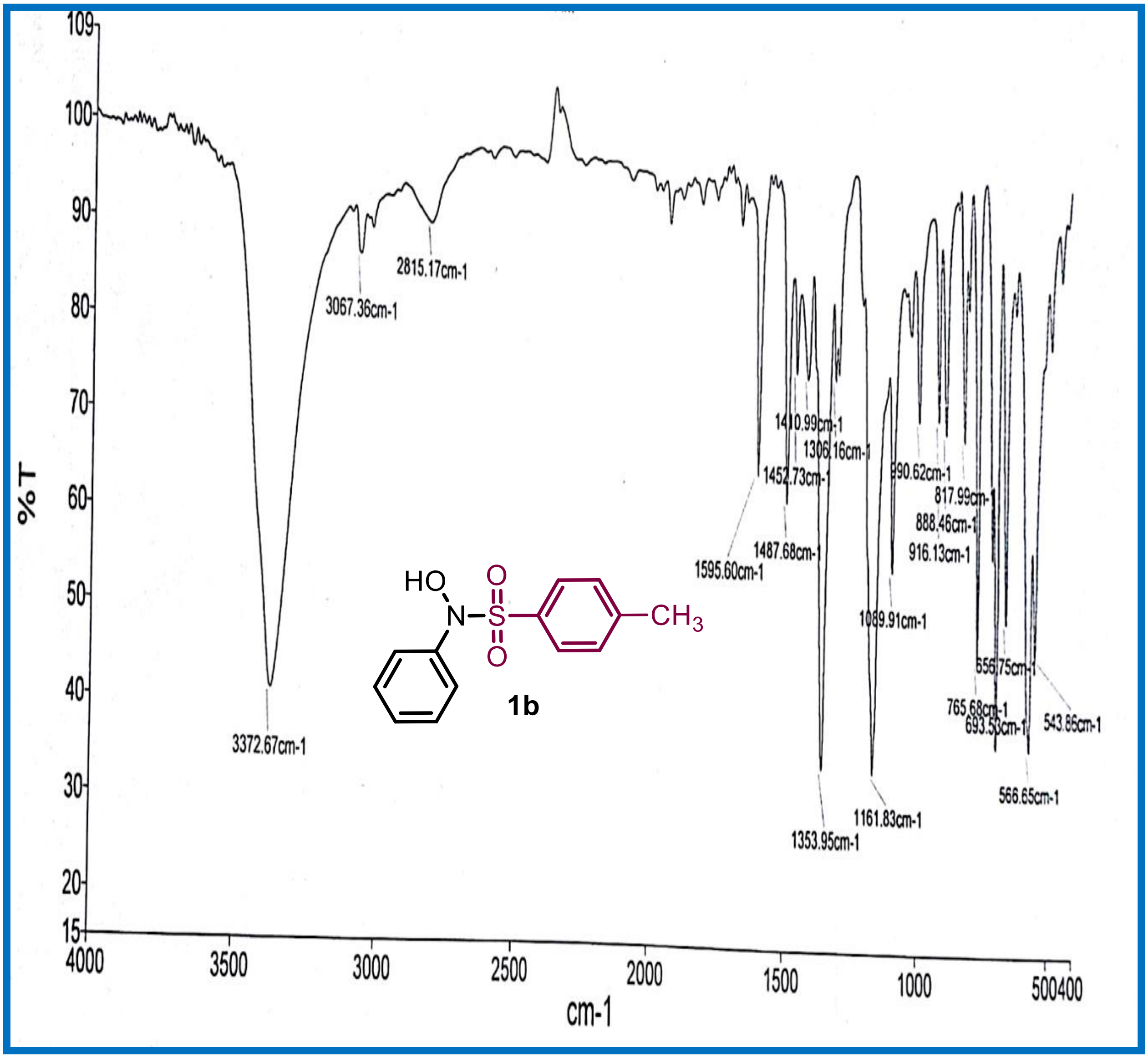
^{13}C NMR spectrum of 1a



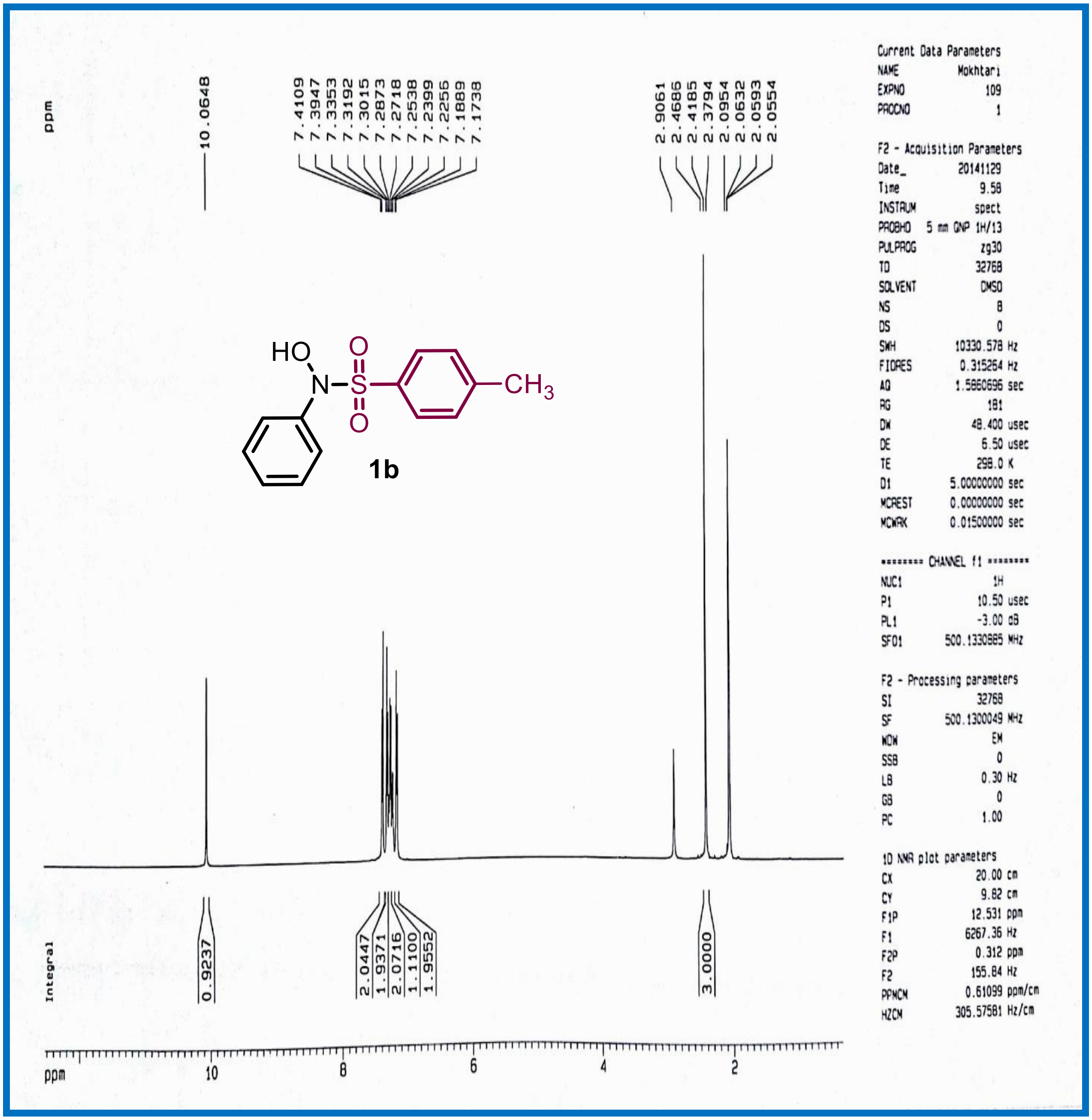
MS spectrum of 1a



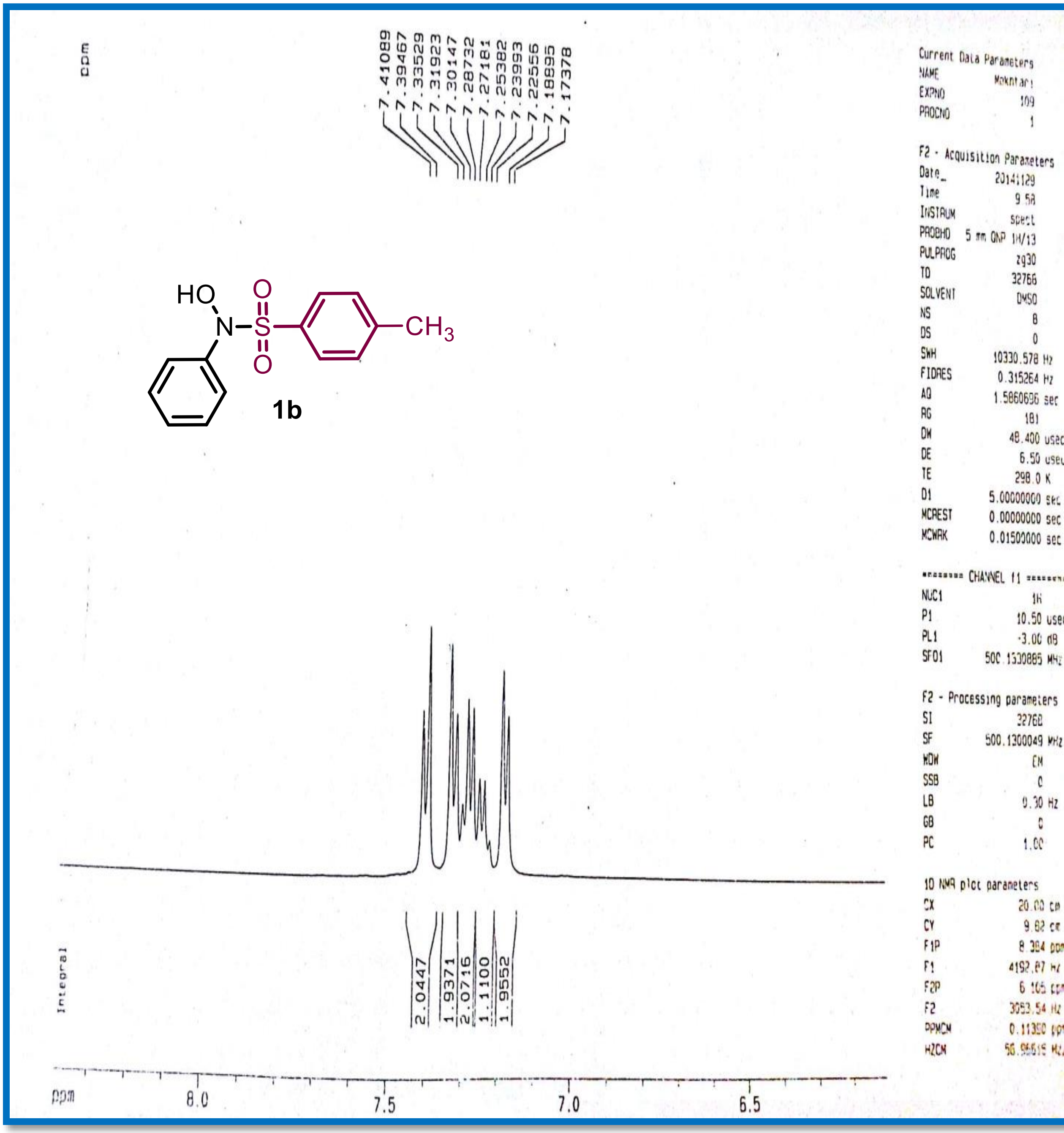
IR spectrum of 1b



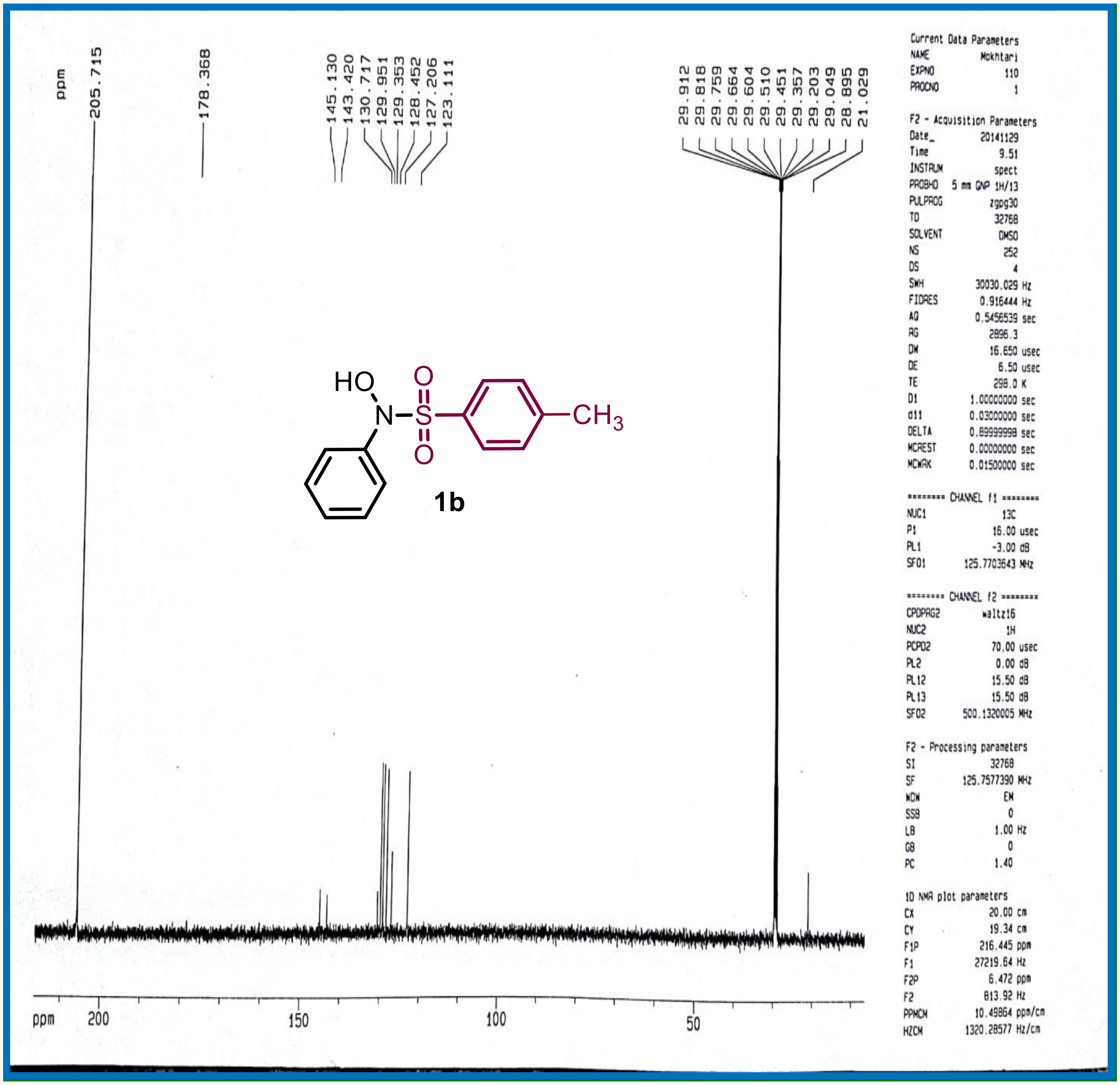
^{1}H NMR spectra of 1b



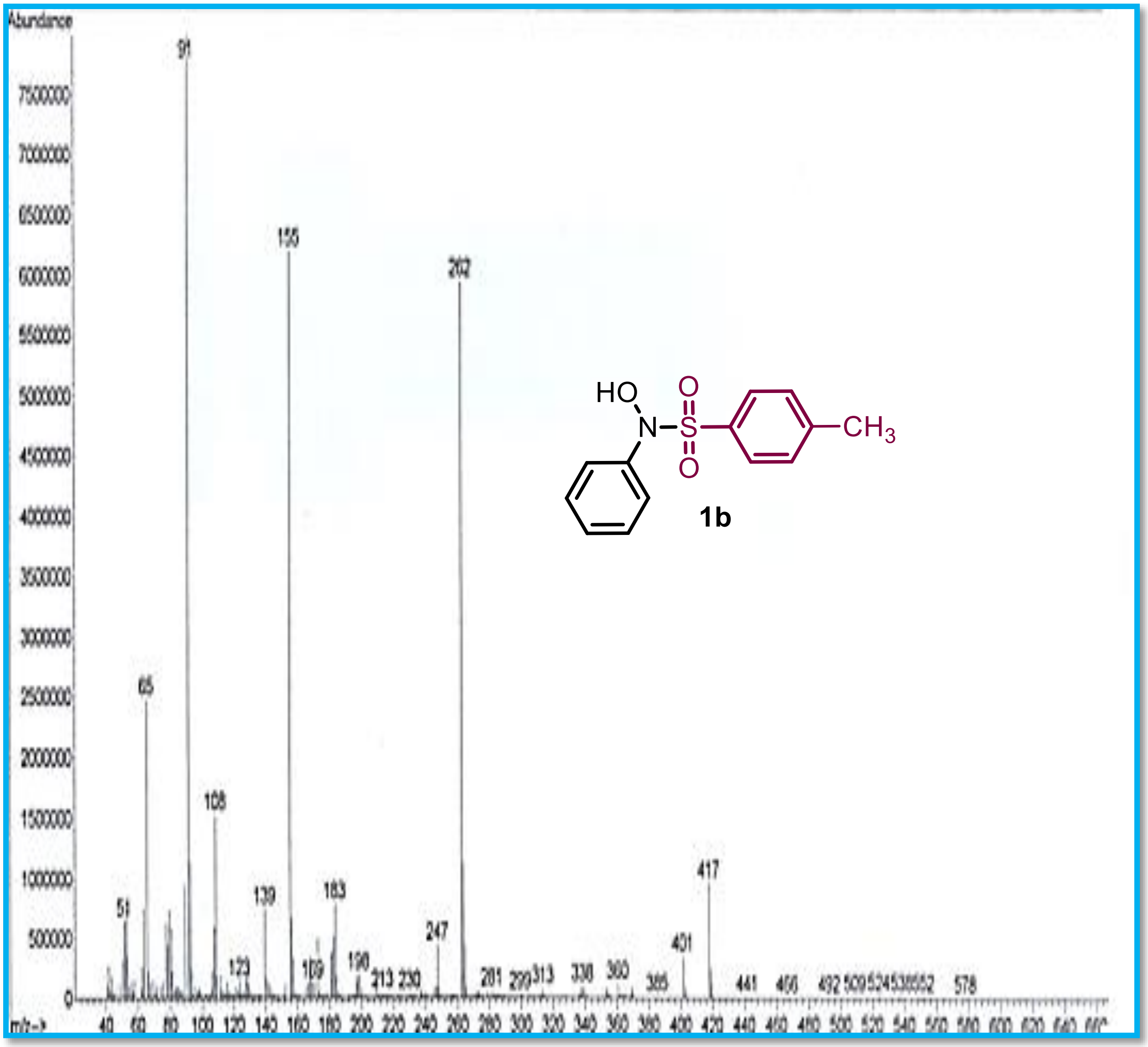
Expanded ^{1}H NMR spectrum of 1b



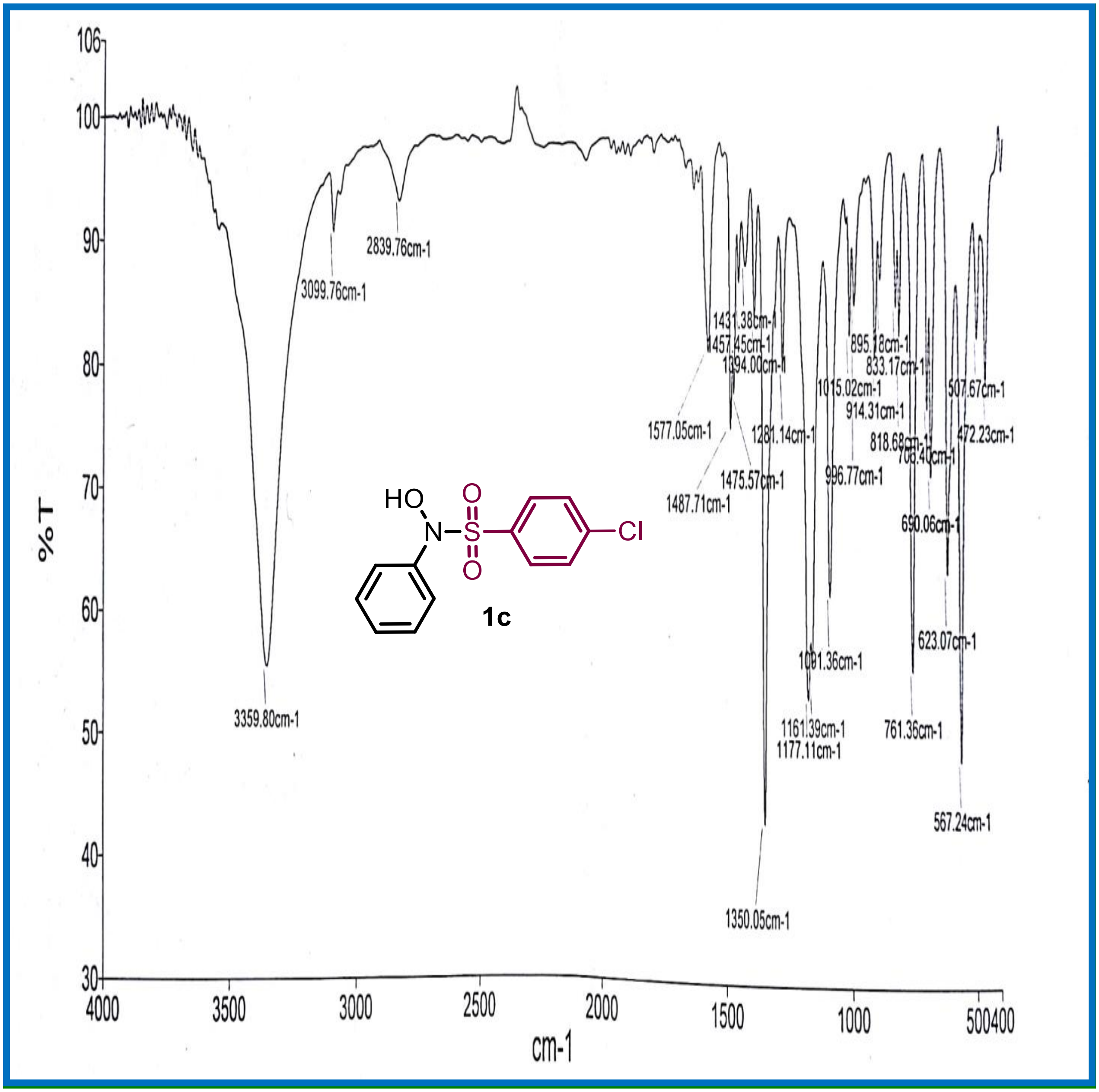
^{13}C NMR spectrum of 1b



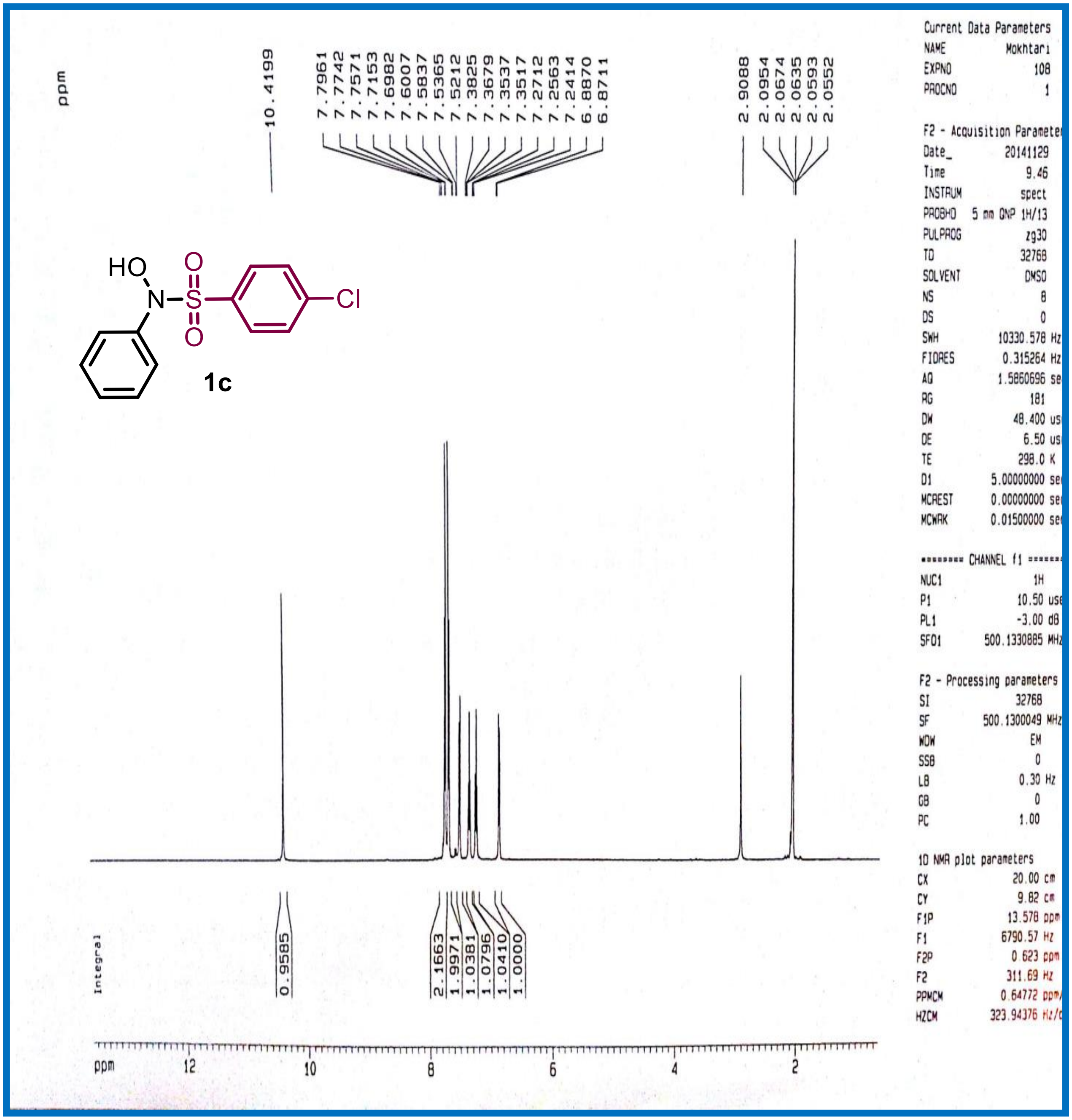
MS spectrum of 1b



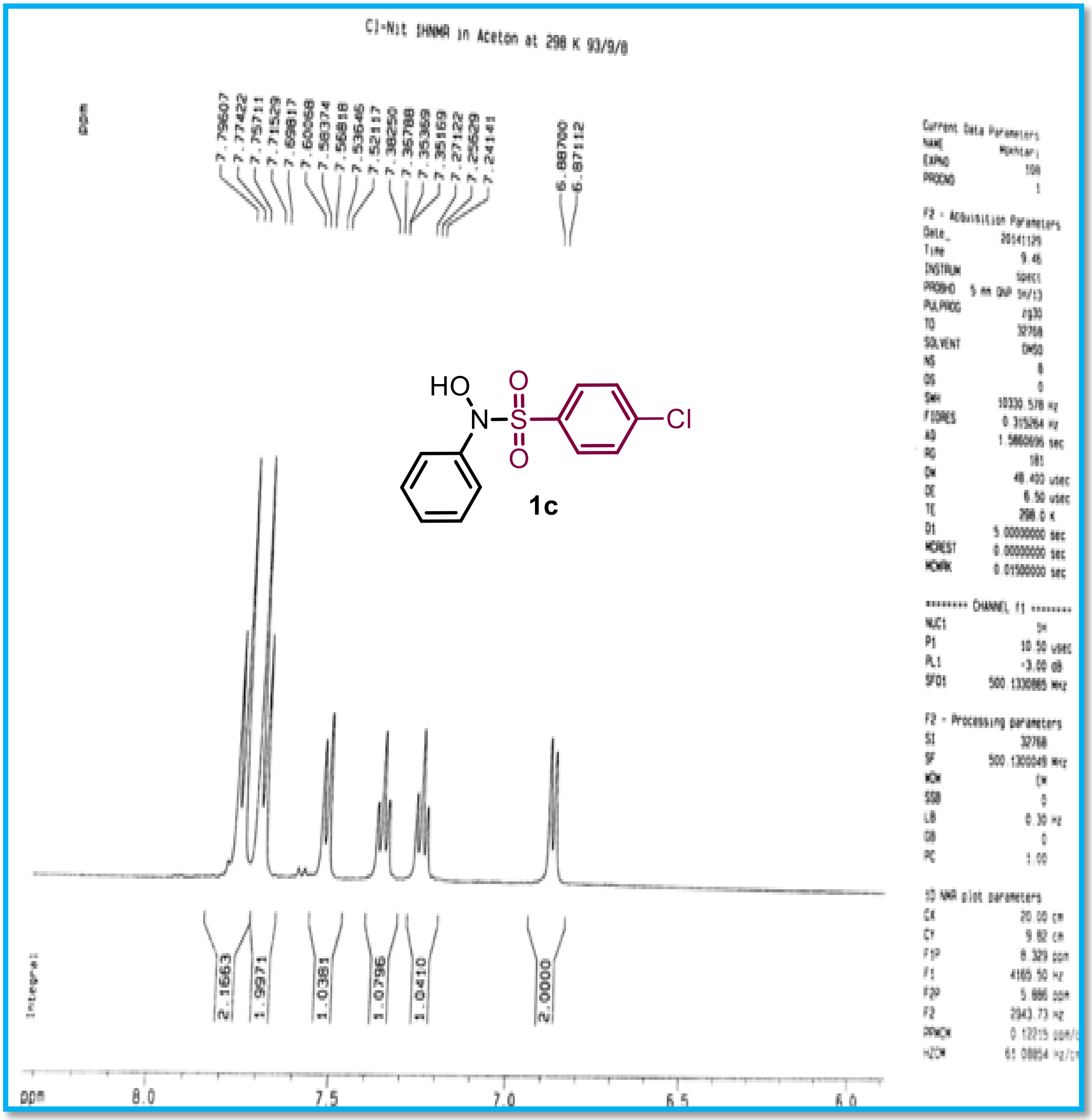
IR spectrum of 1c



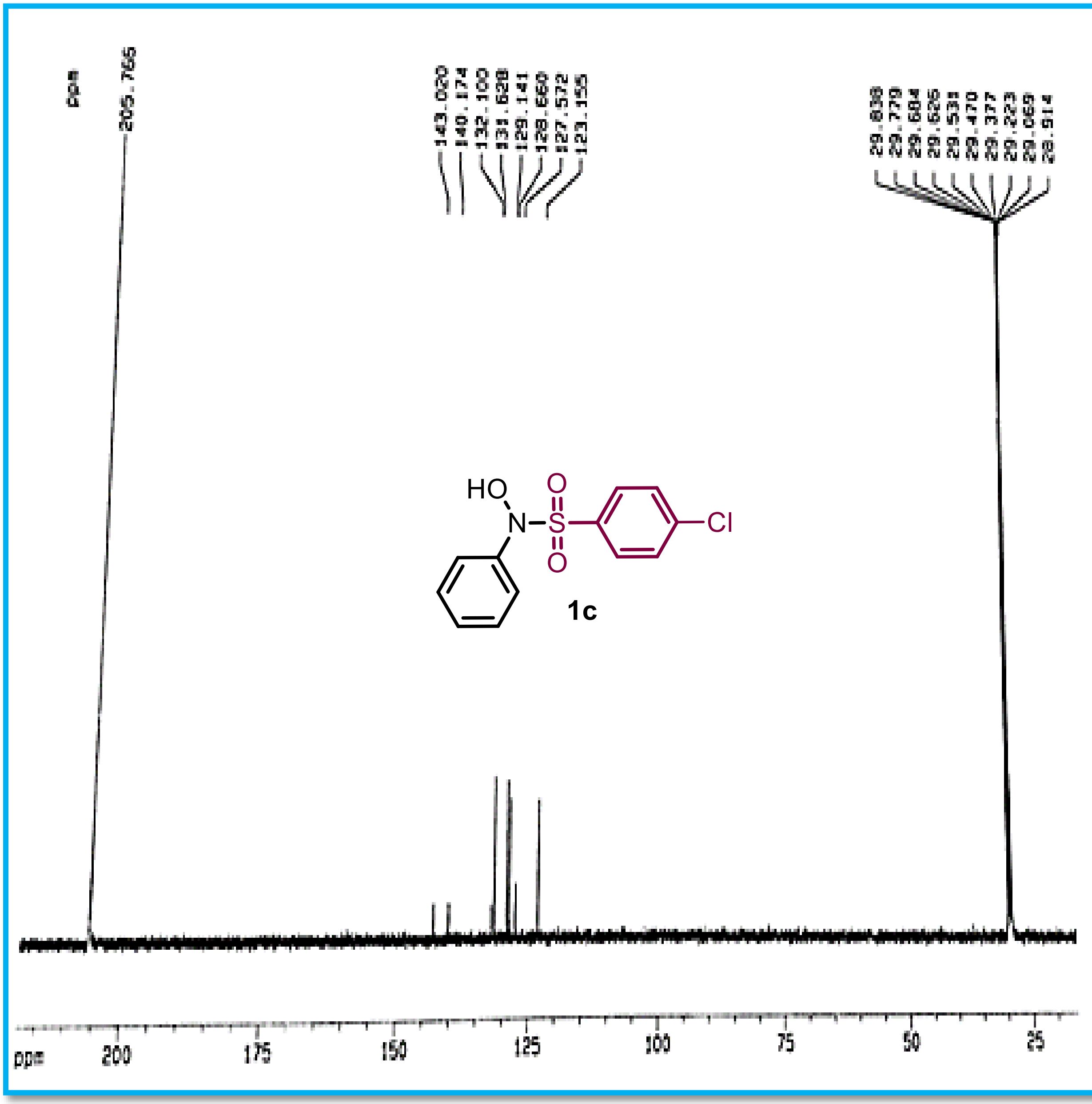
[1]H NMR spectrum of 1c



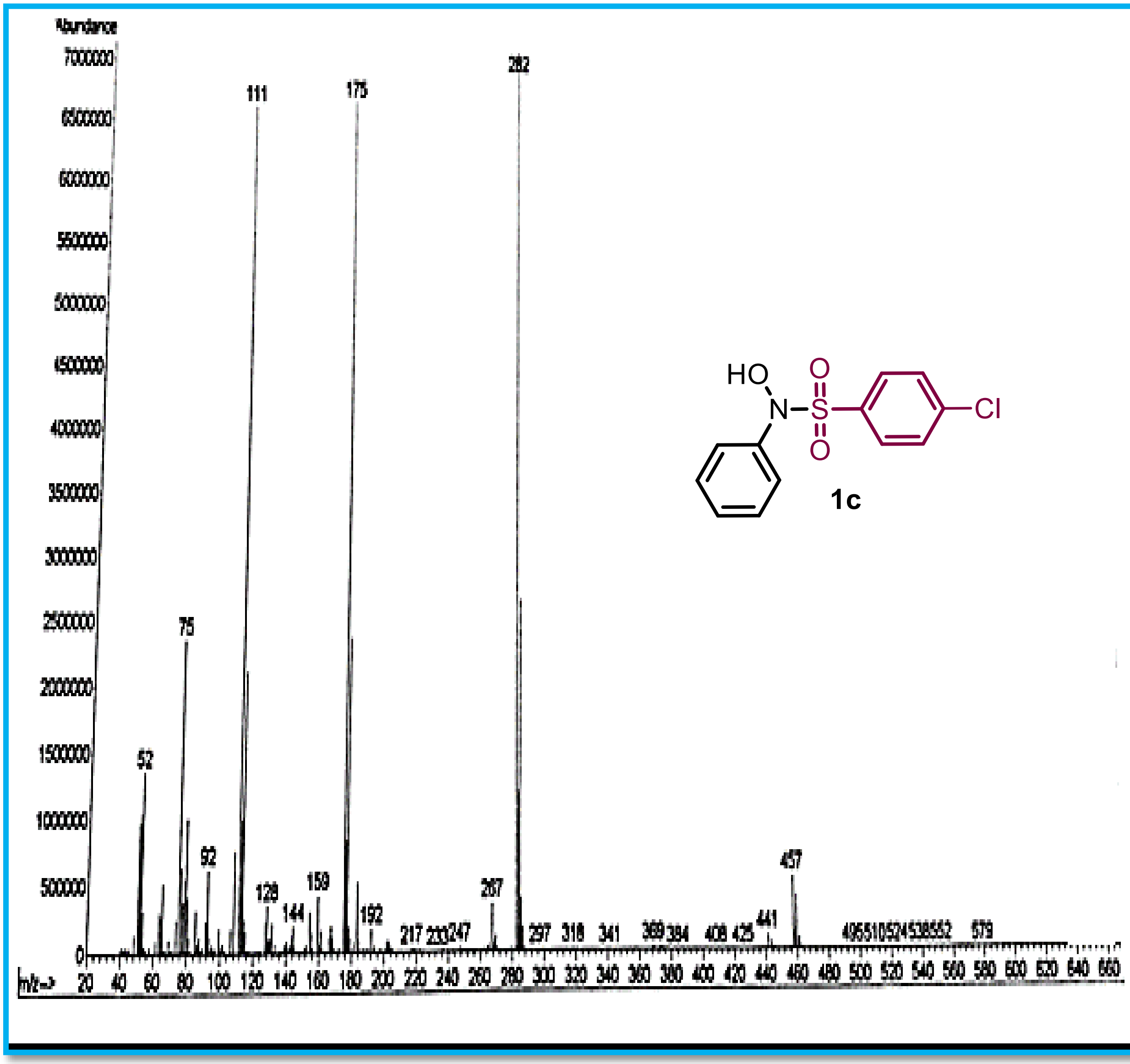
Expanded ^{1}H NMR spectrum of 1c



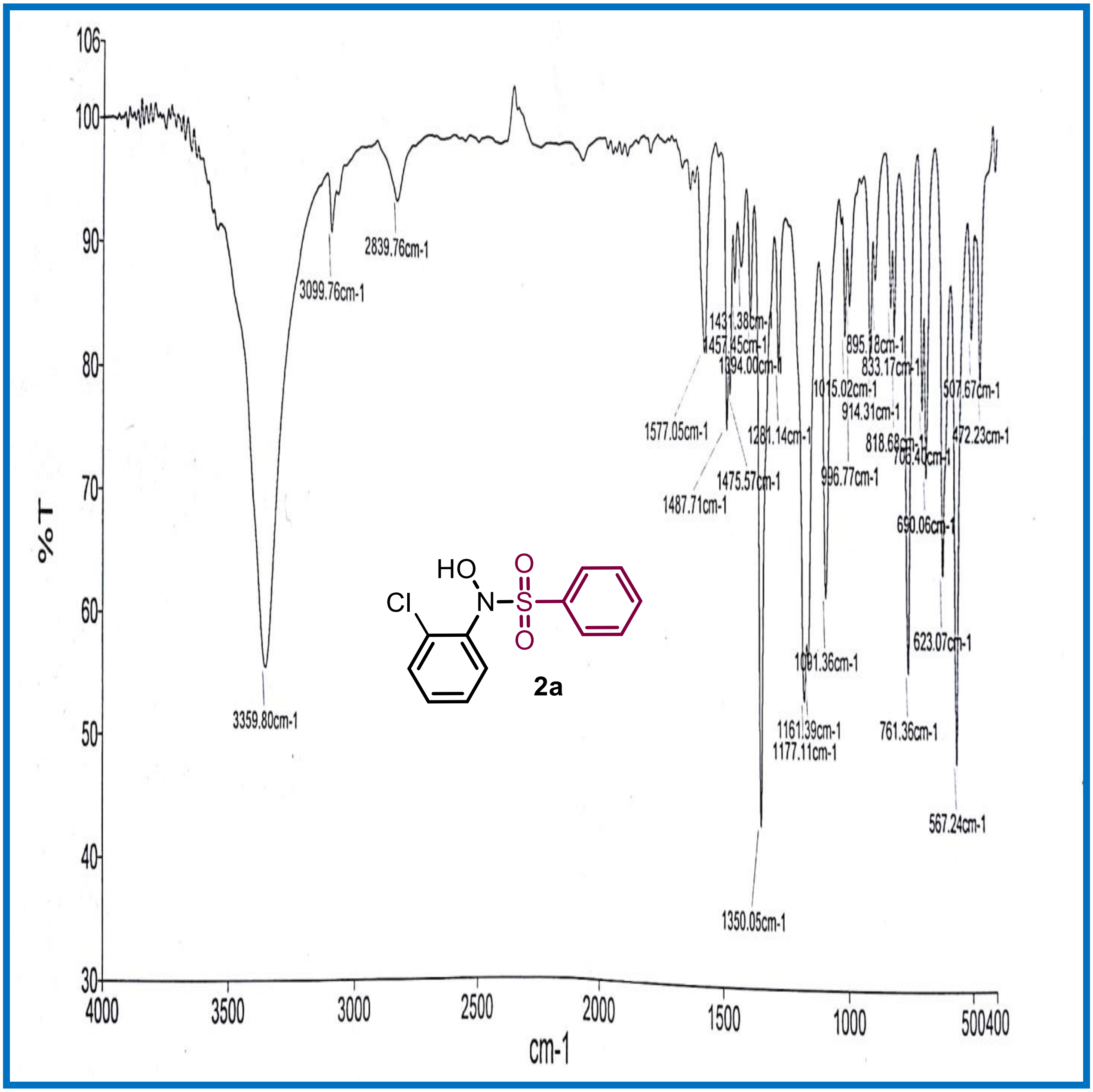
^{13}C NMR spectrum of 1c



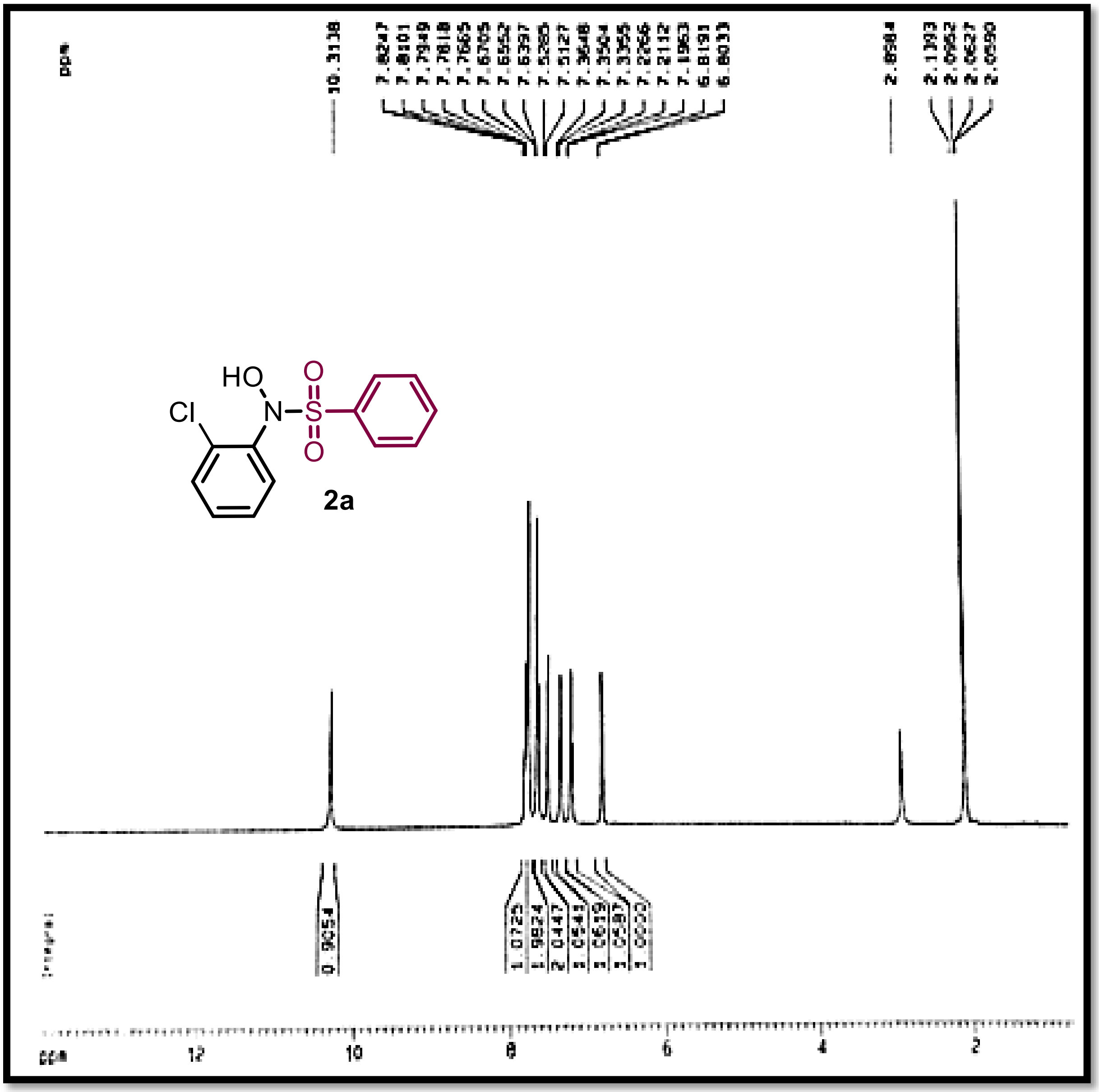
MS spectrum of 1c



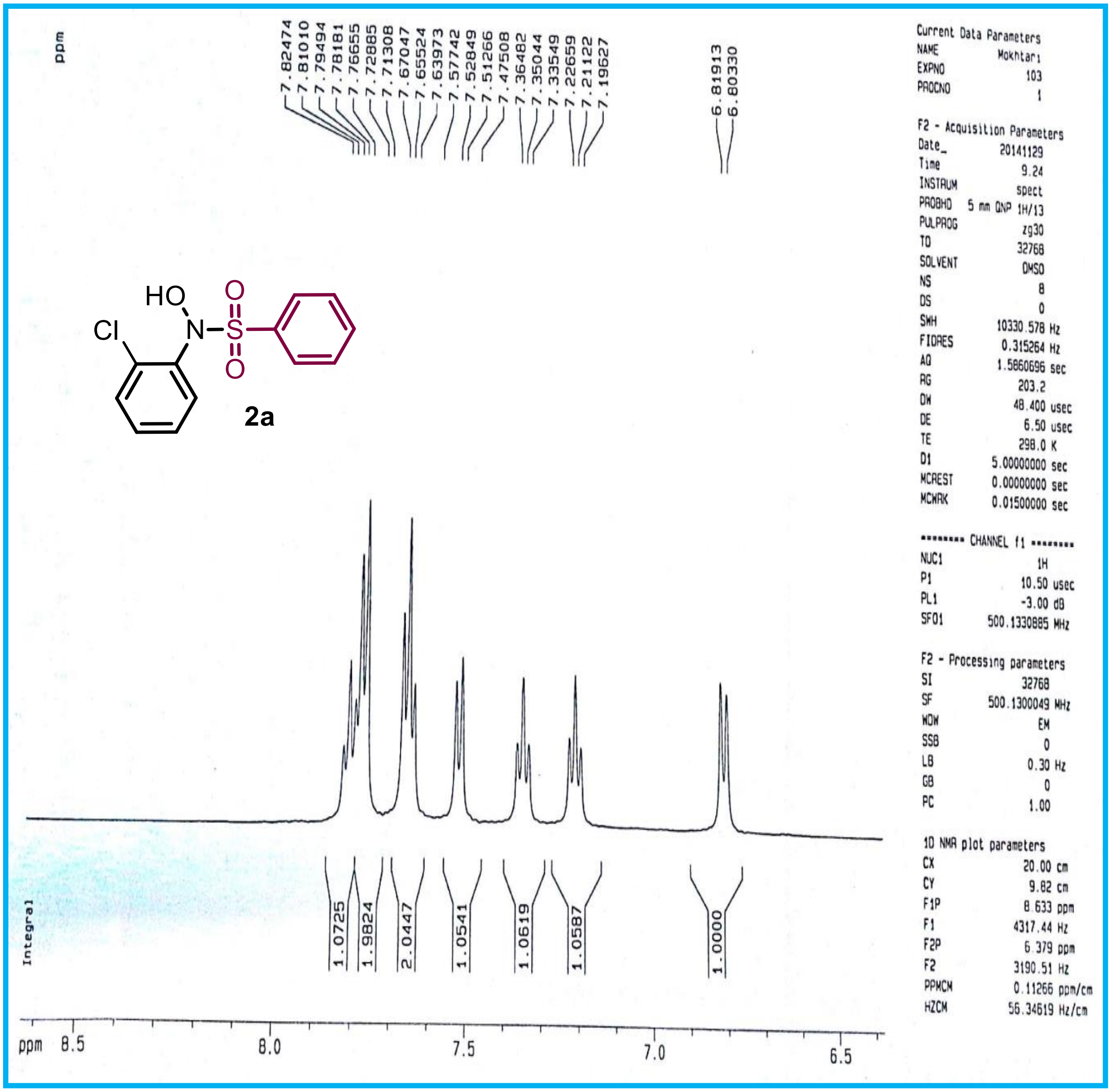
IR spectrum of 2a



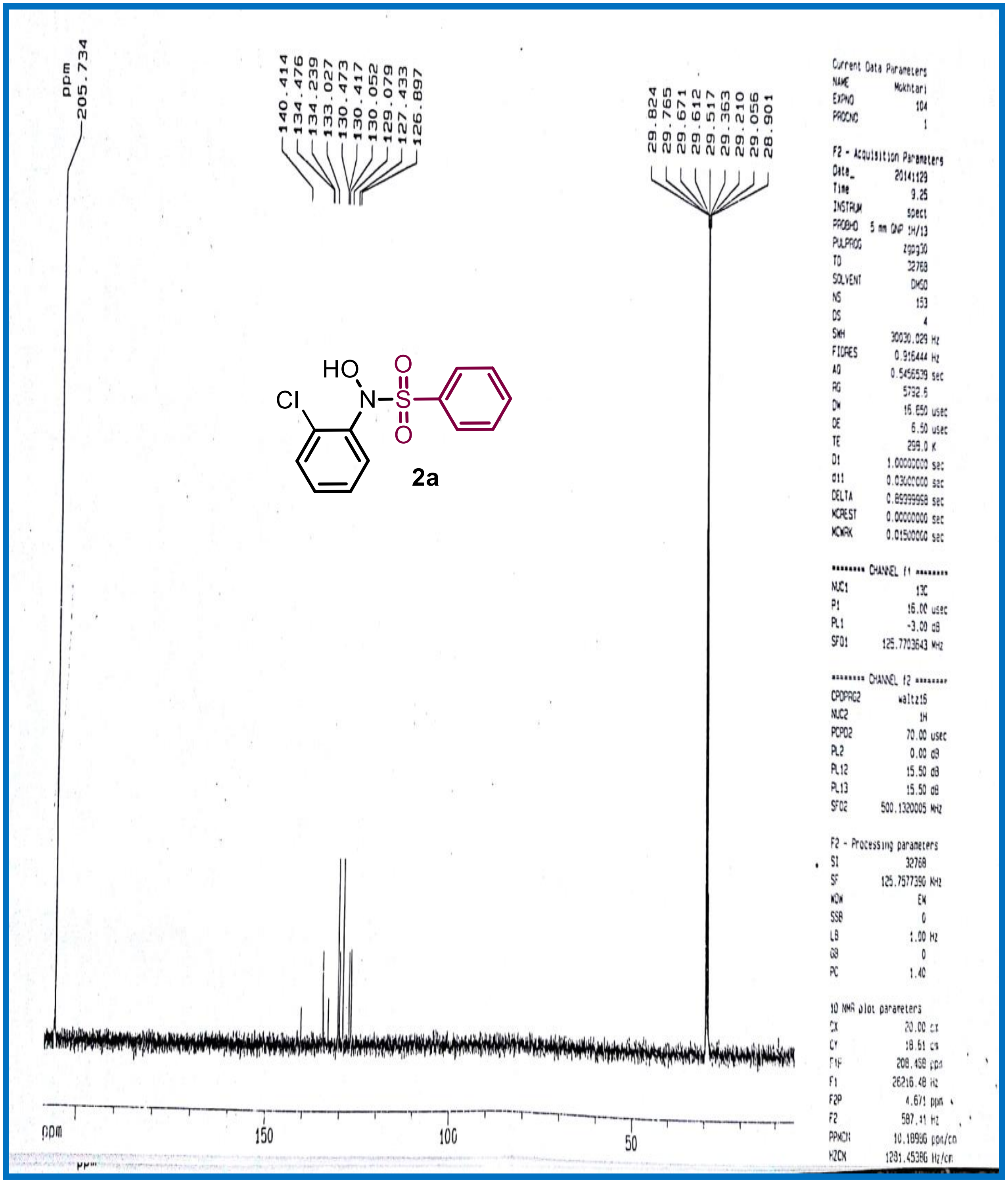
[1]H NMR spectrum of 2a



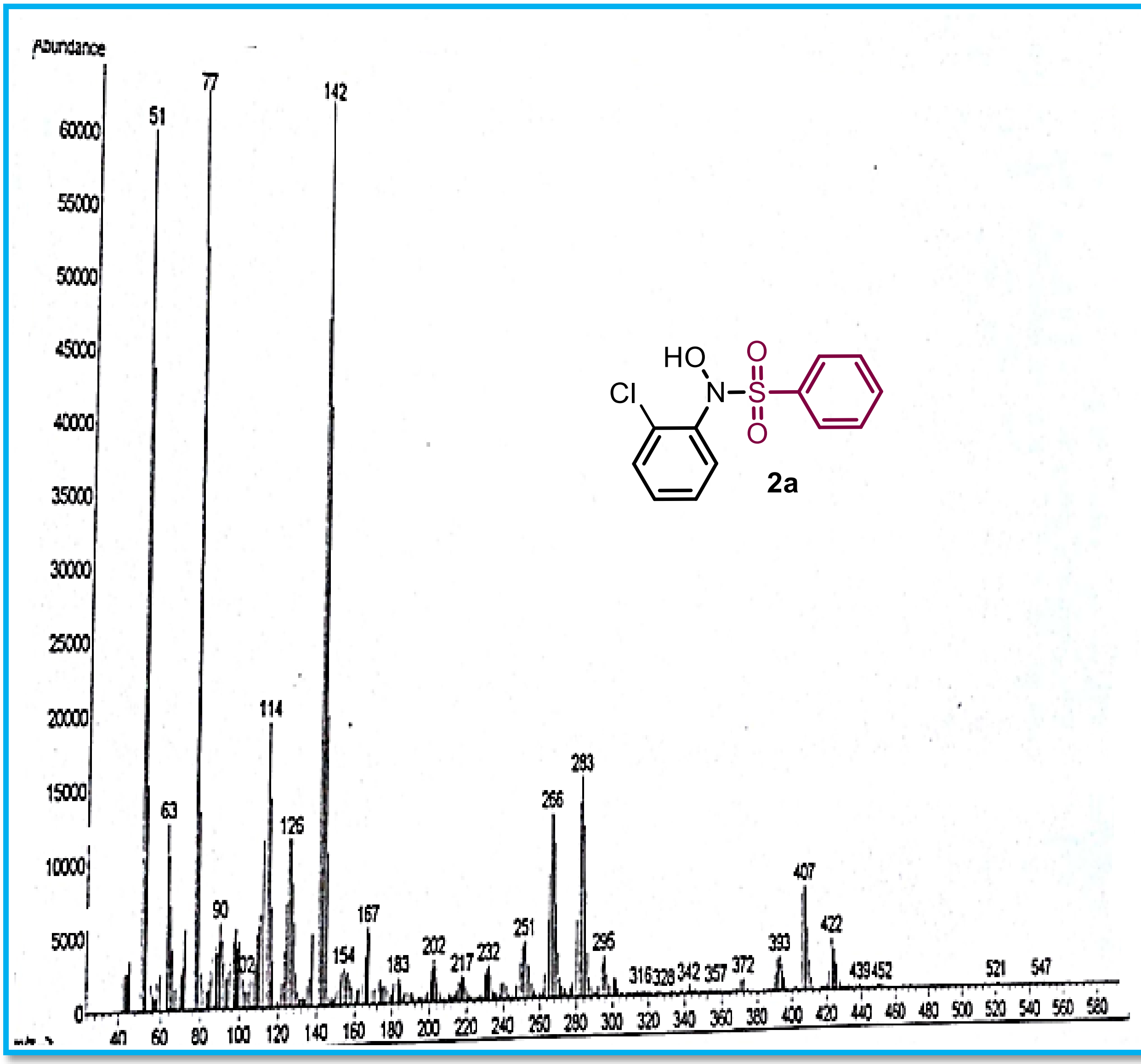
Expanded ^{1}H NMR spectrum of 2a



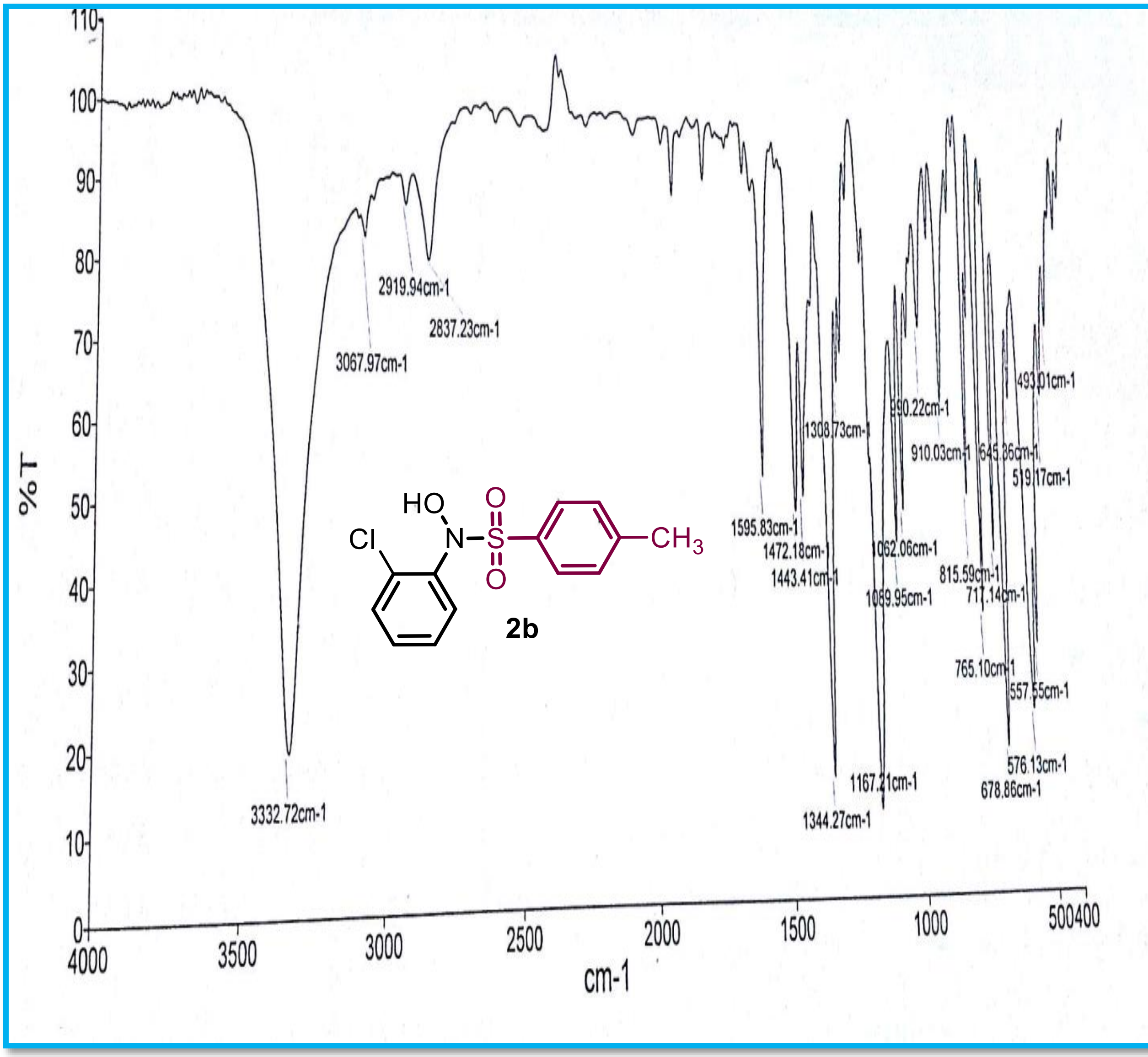
^{13}C NMR spectrum of 2a



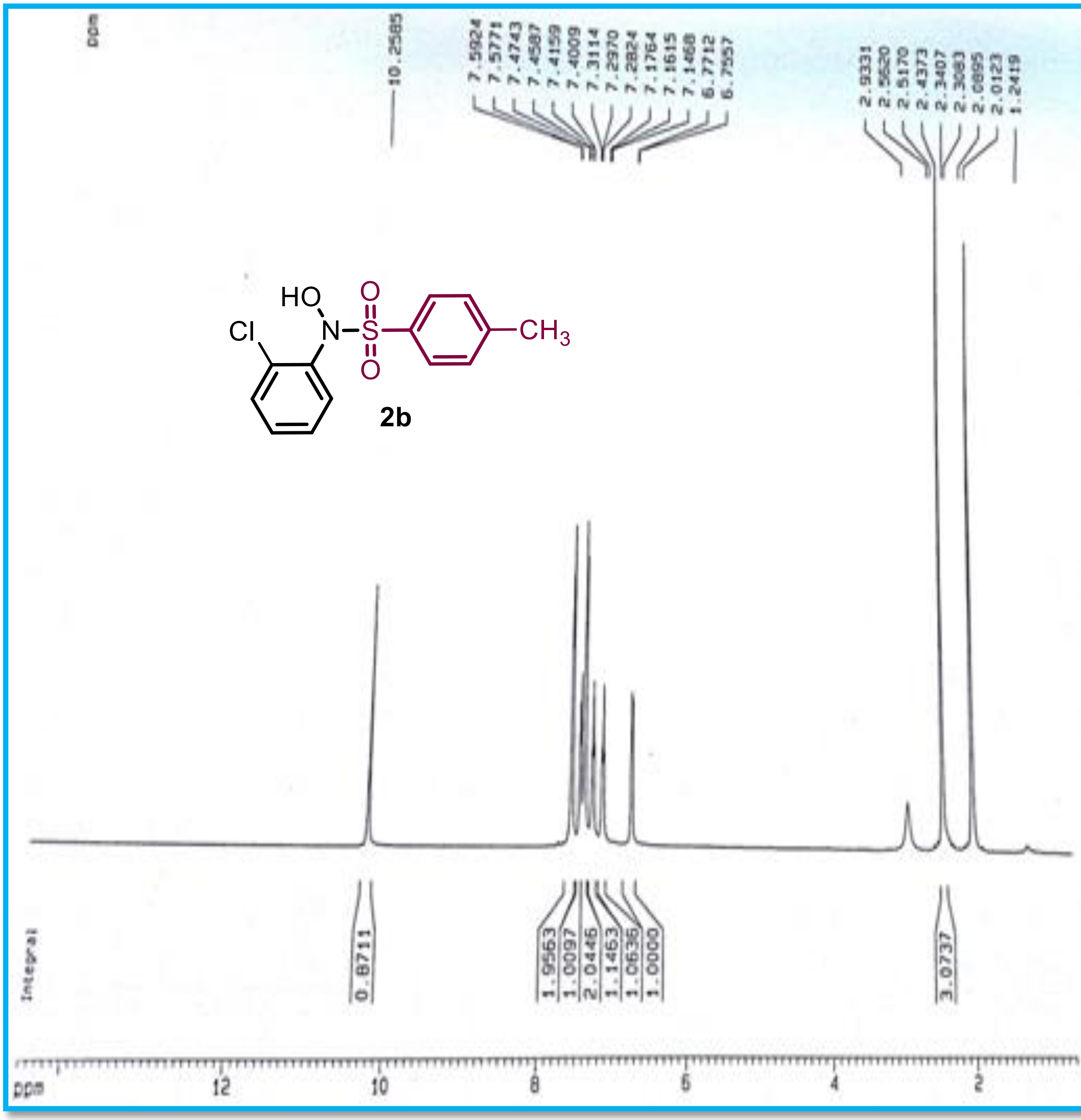
MS spectrum of 2a



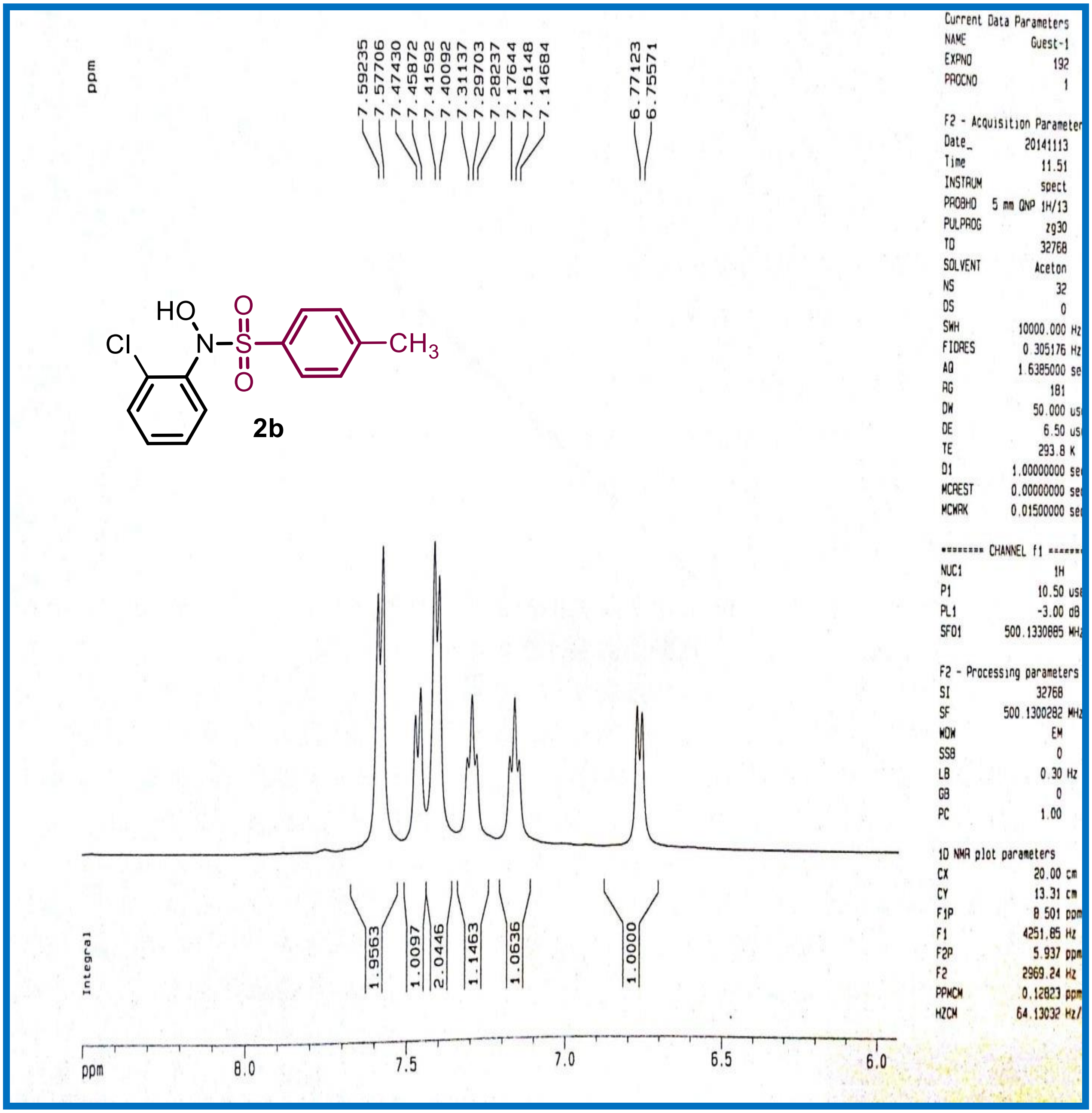
IR spectrum of 2b



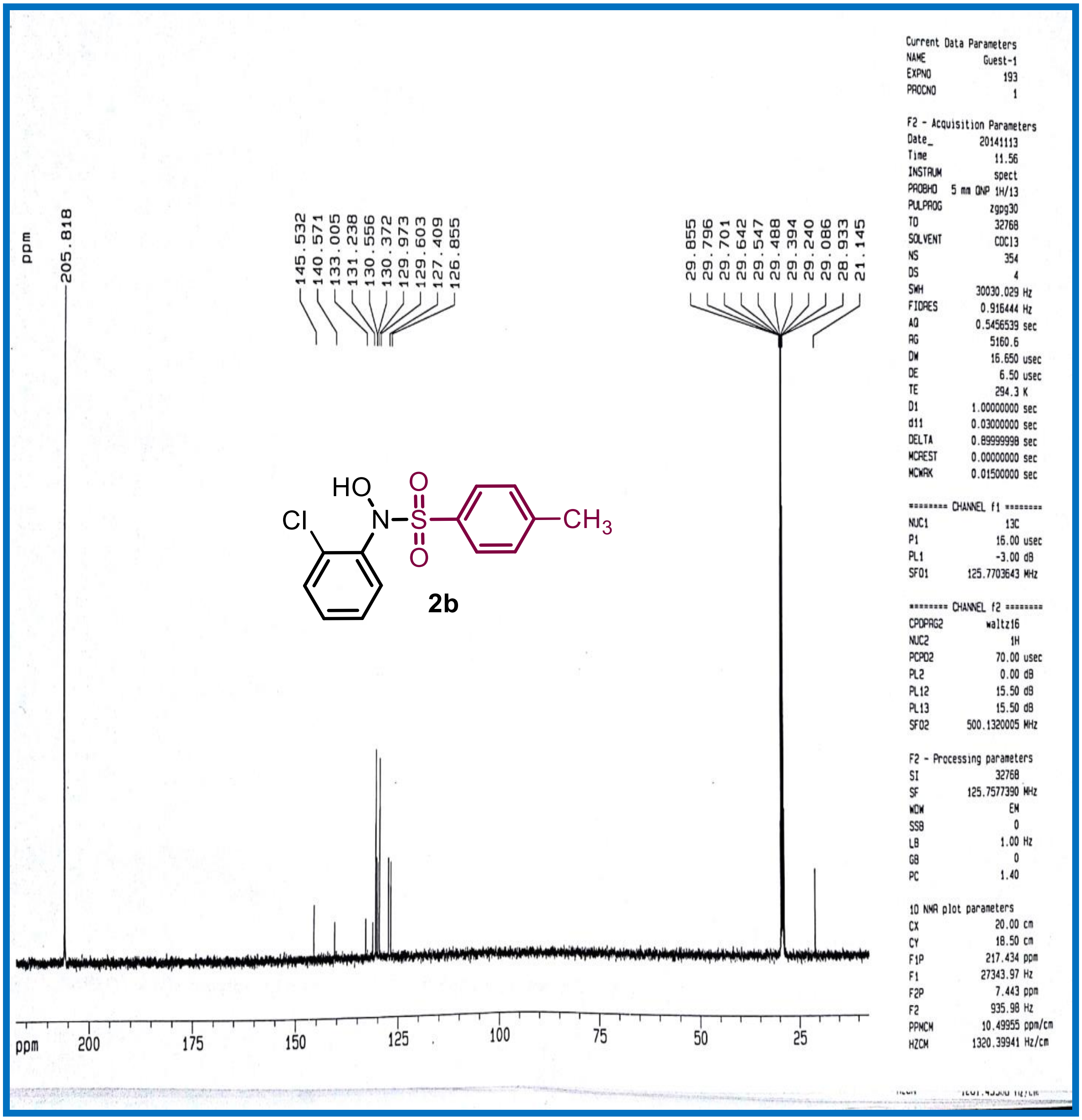
¹H NMR spectrum of 2b



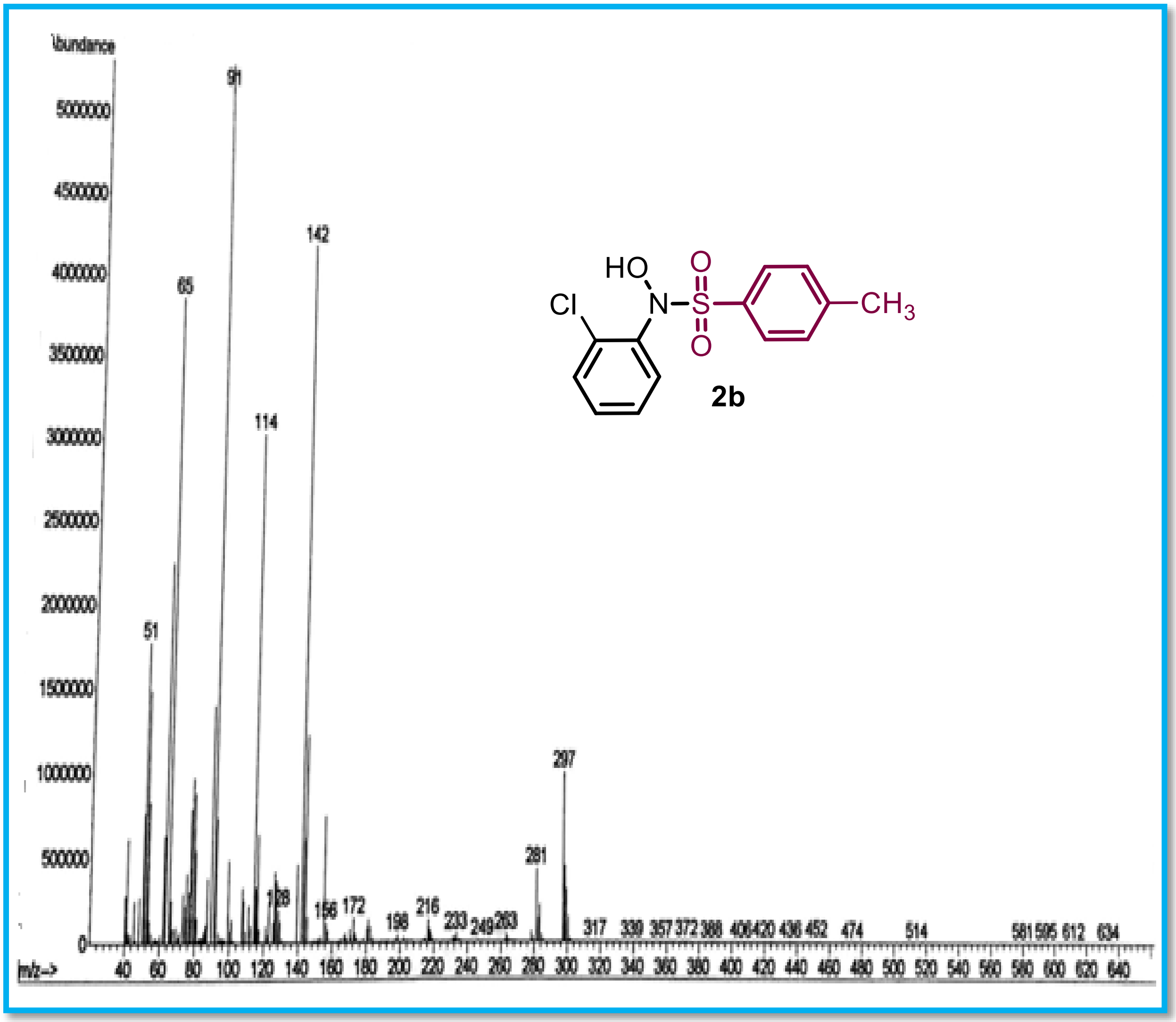
Expanded ^1H NMR spectrum of 2b



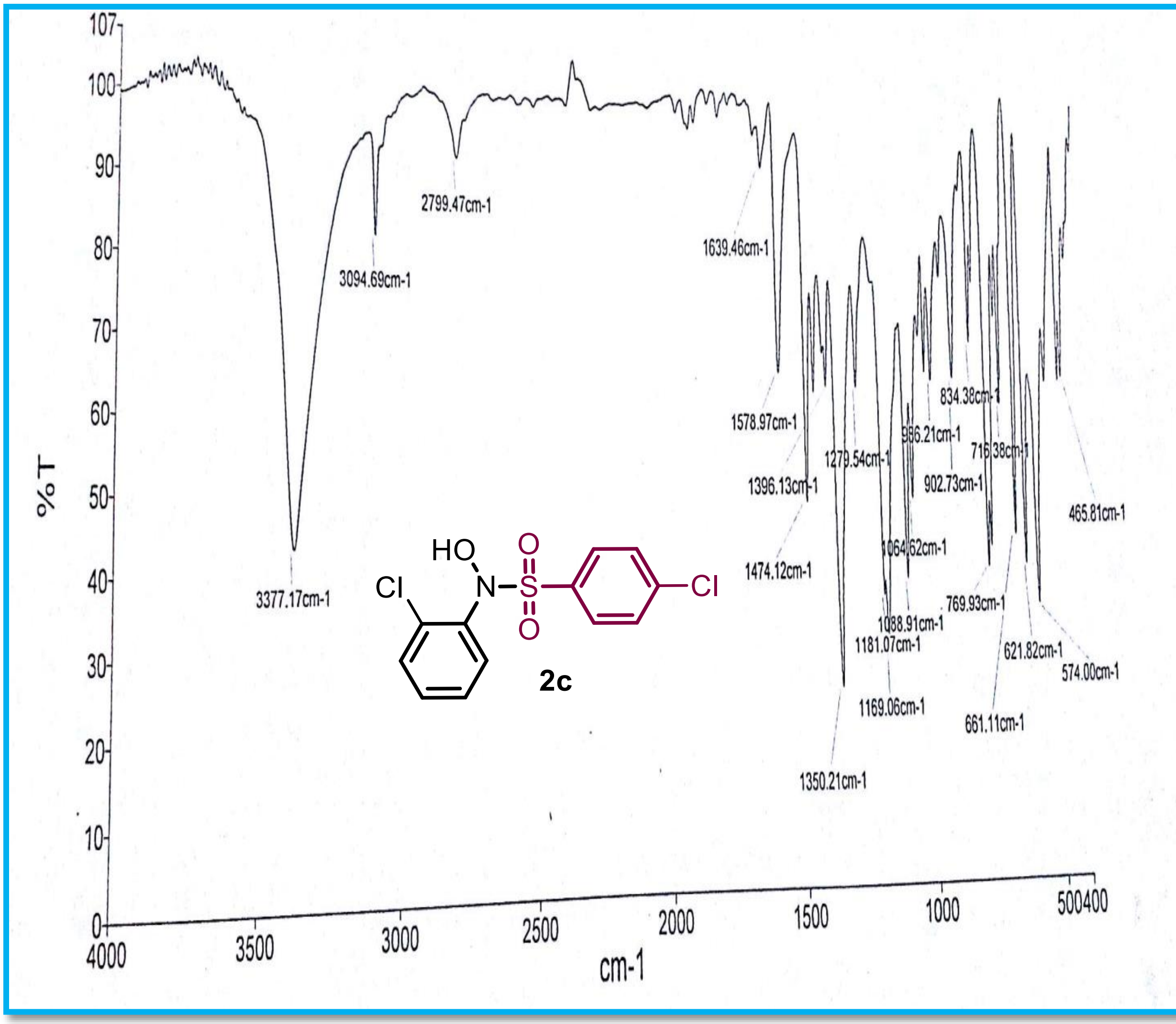
[13]C NMR spectrum of 2b



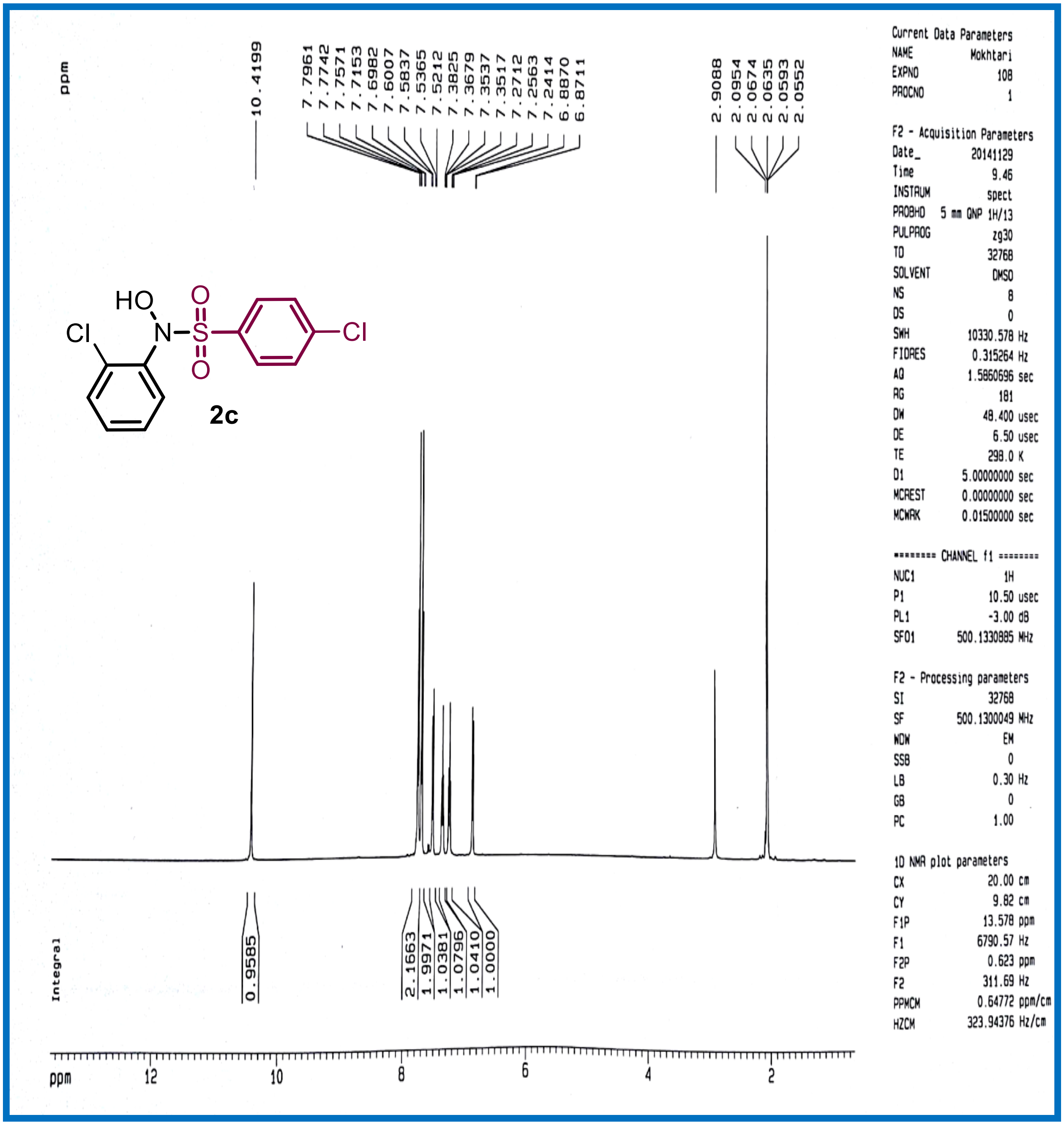
MS spectrum of 2b



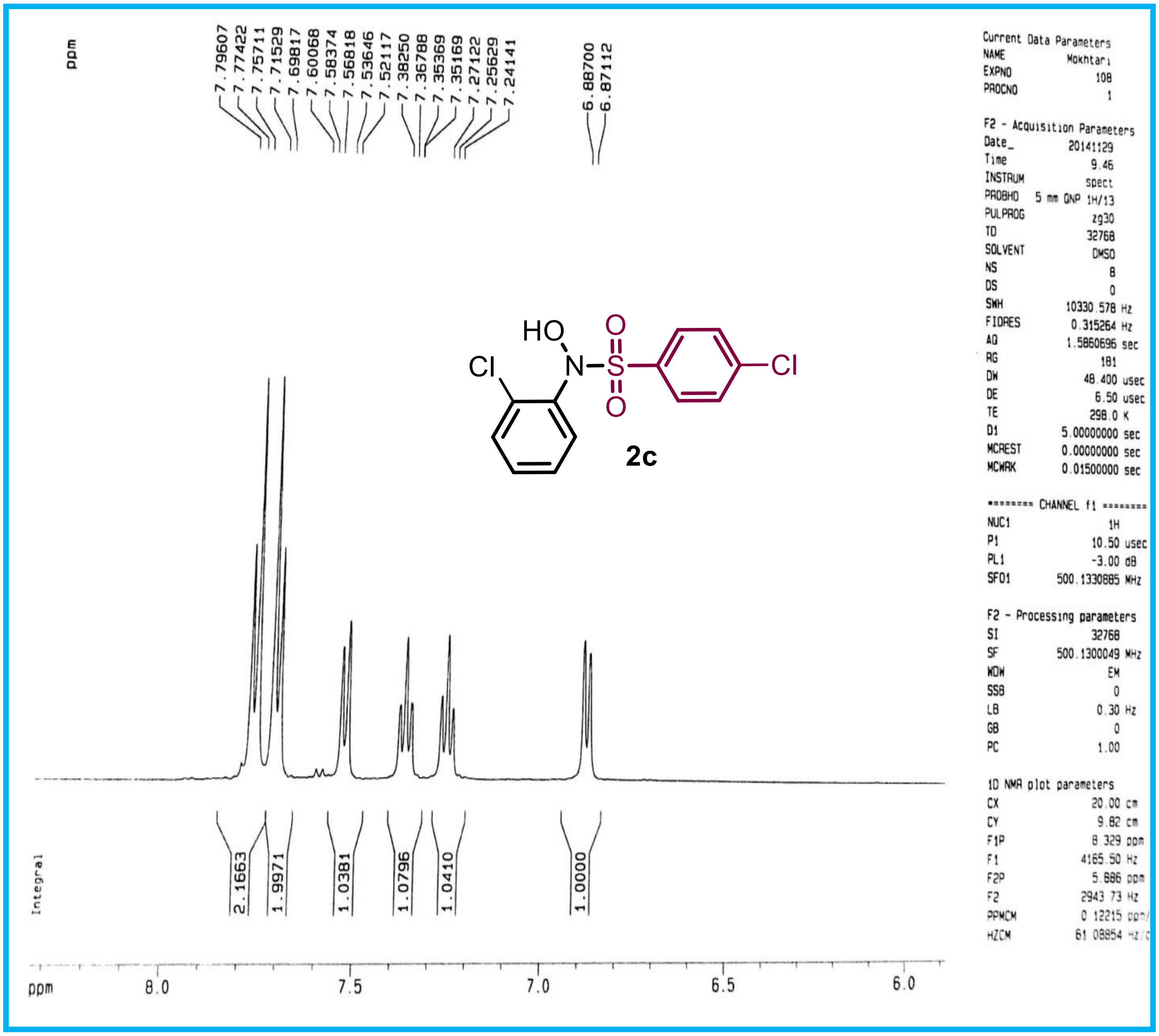
IR spectrum of 2c



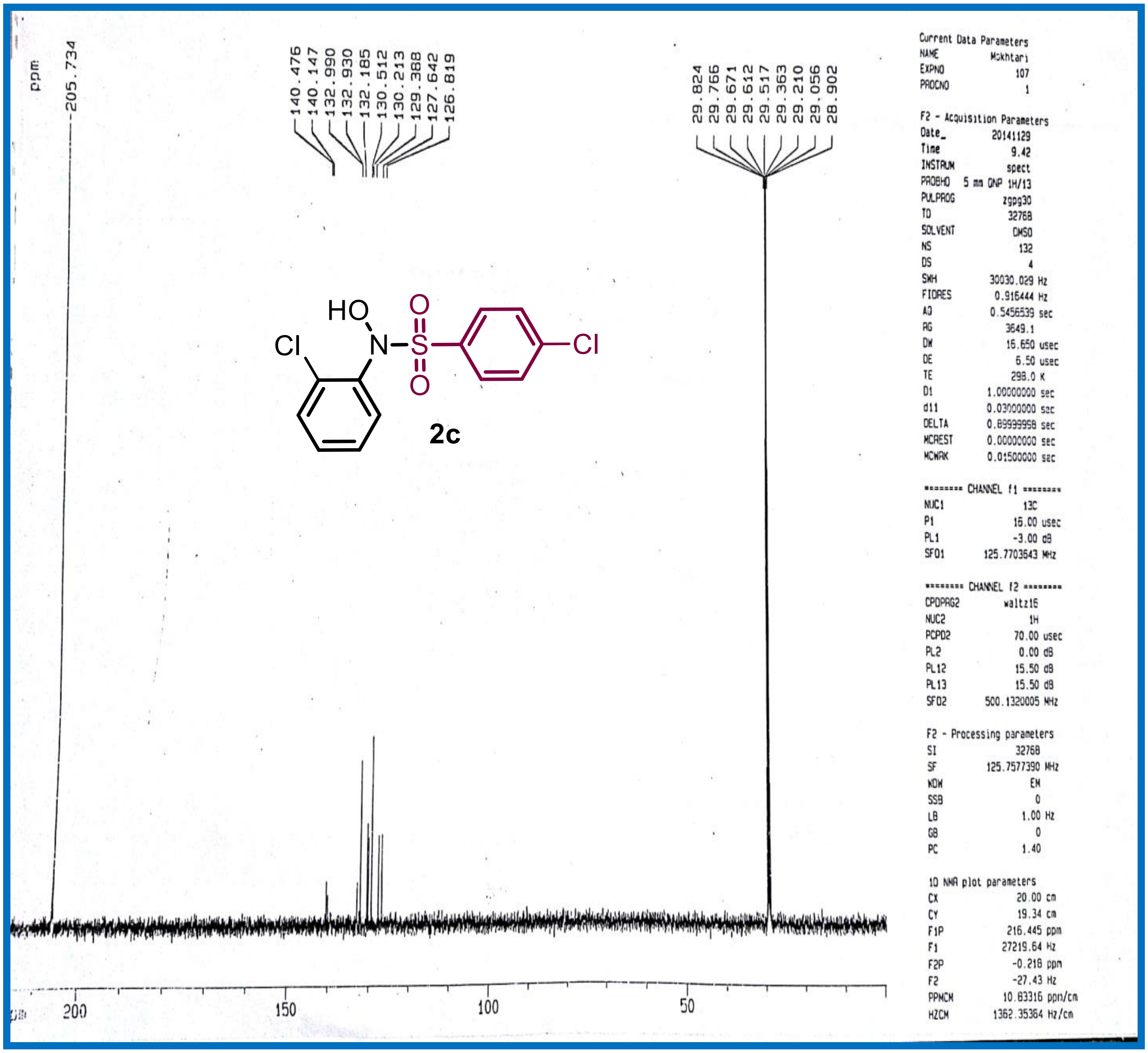
[1]H NMR spectrum of 2c



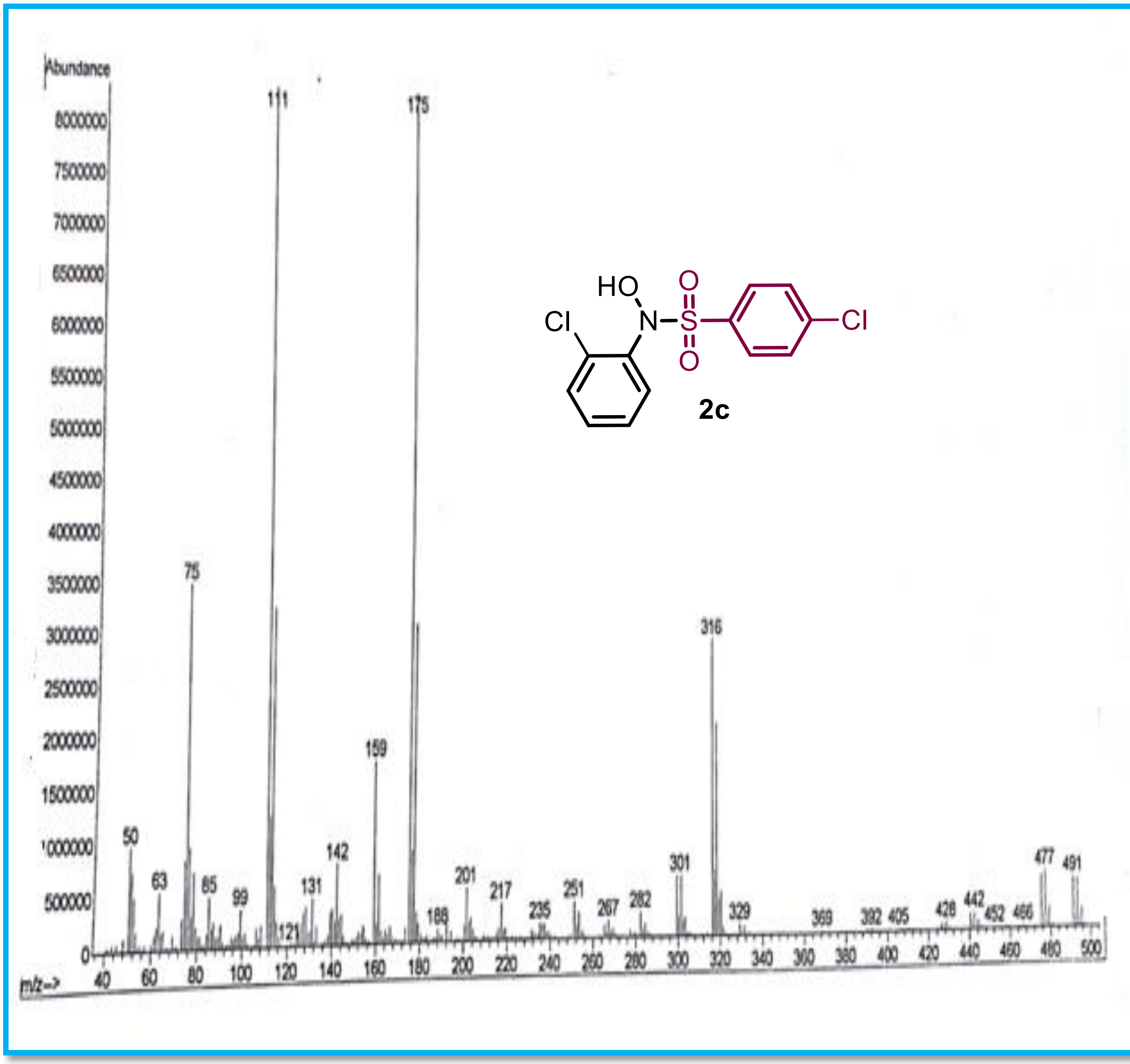
Expanded ^{1}H NMR spectrum of 2c



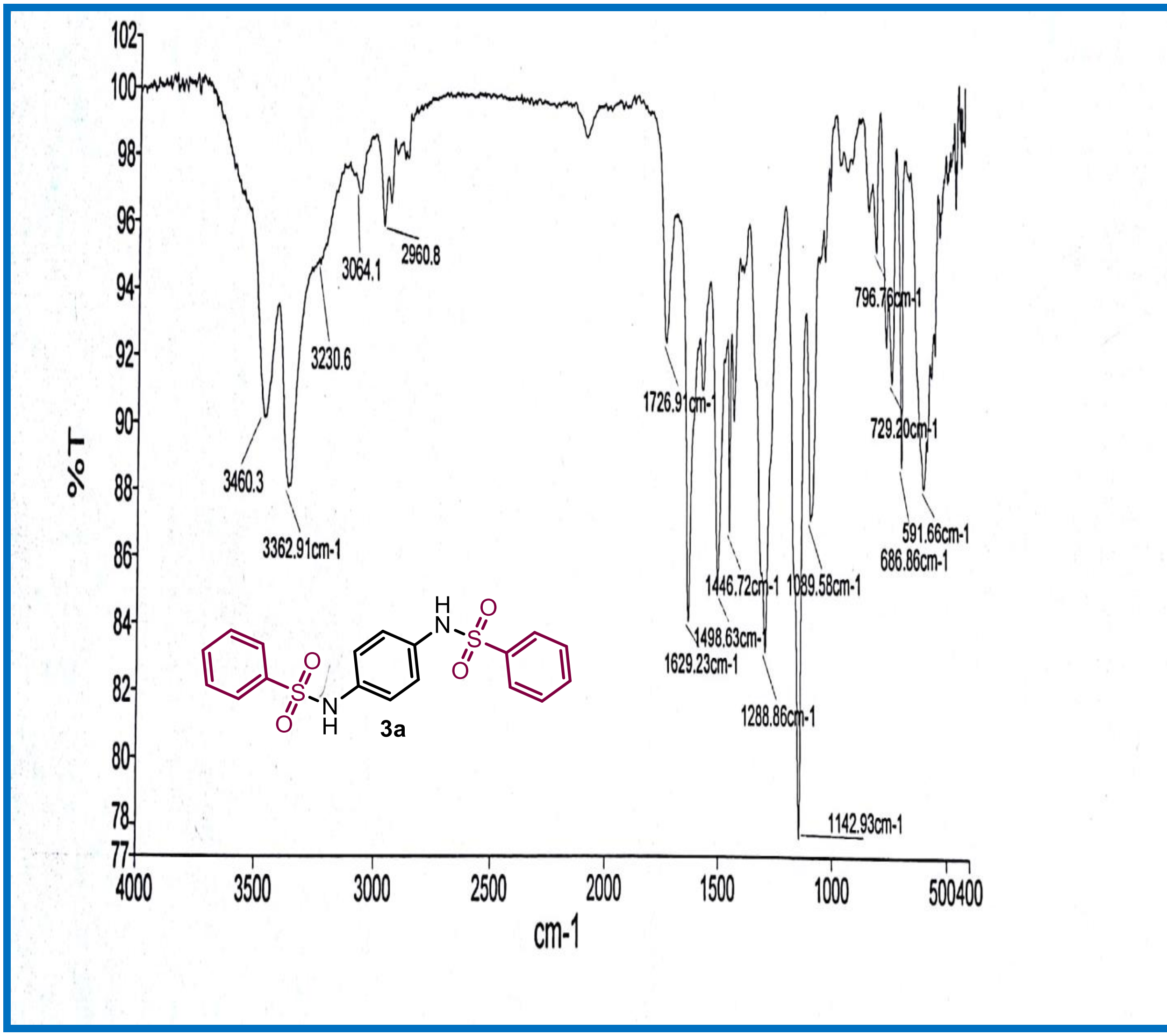
[13]C NMR spectrum of 2c



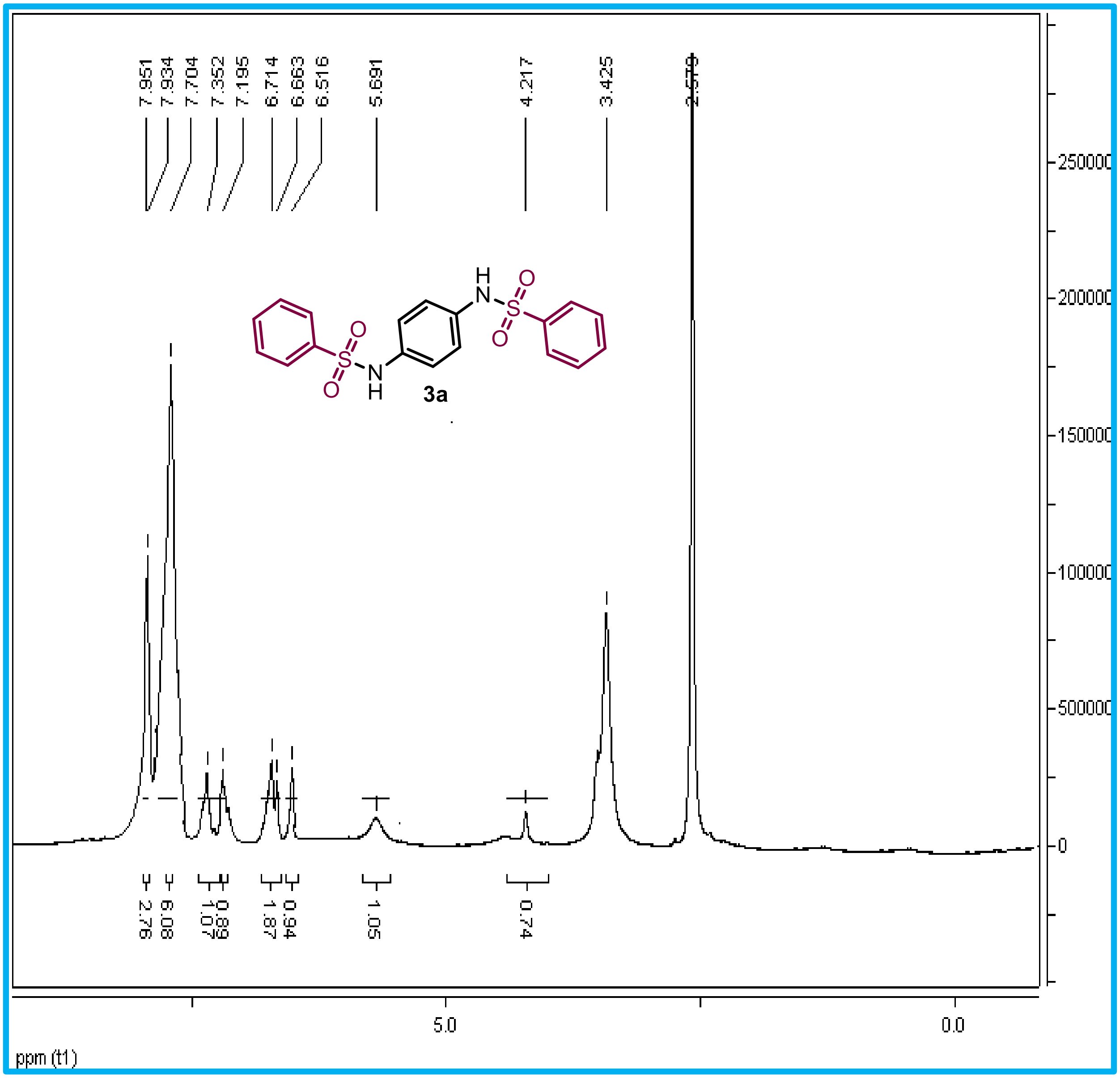
MS spectrum of 2c



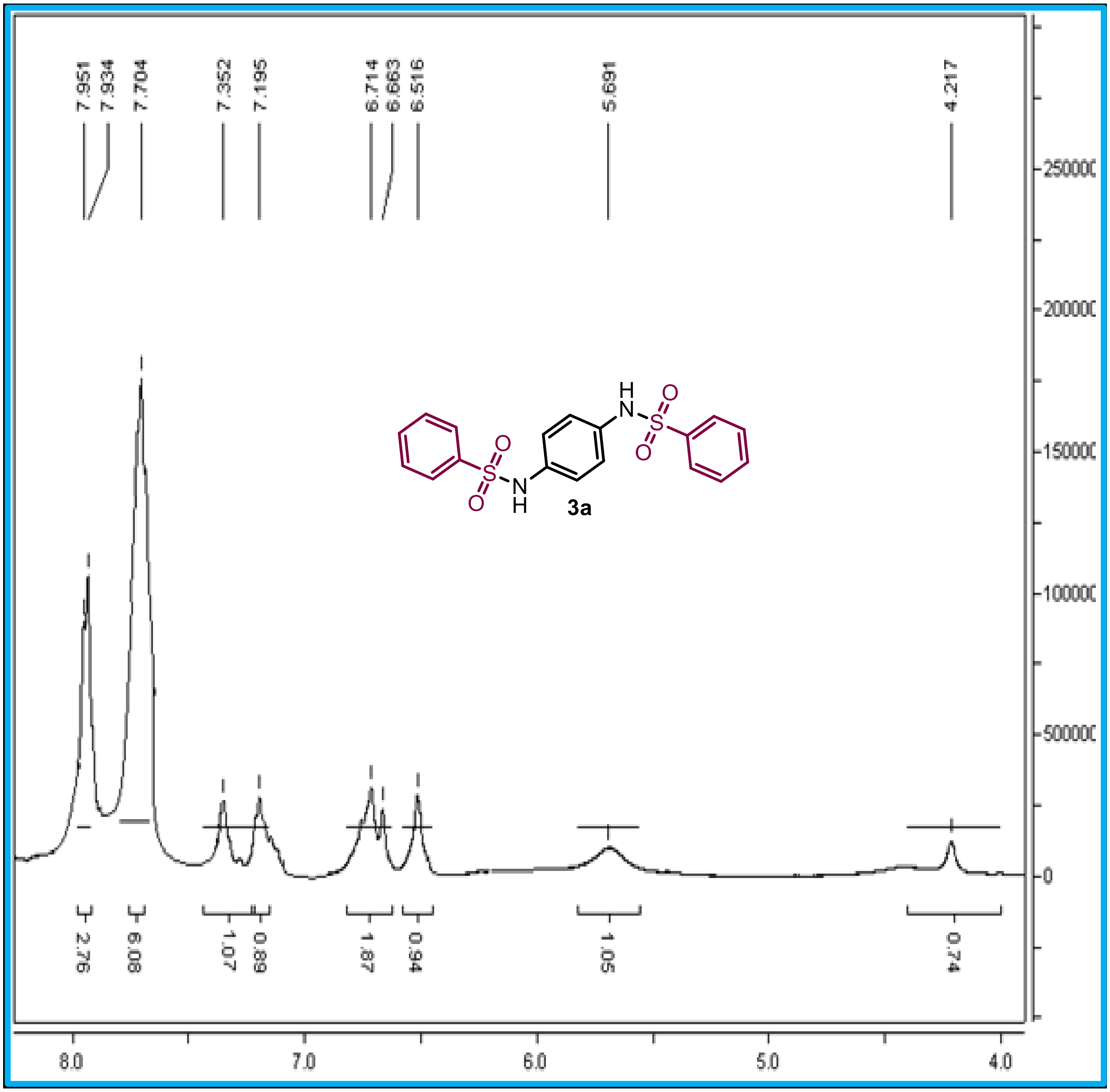
IR spectrum of 3a



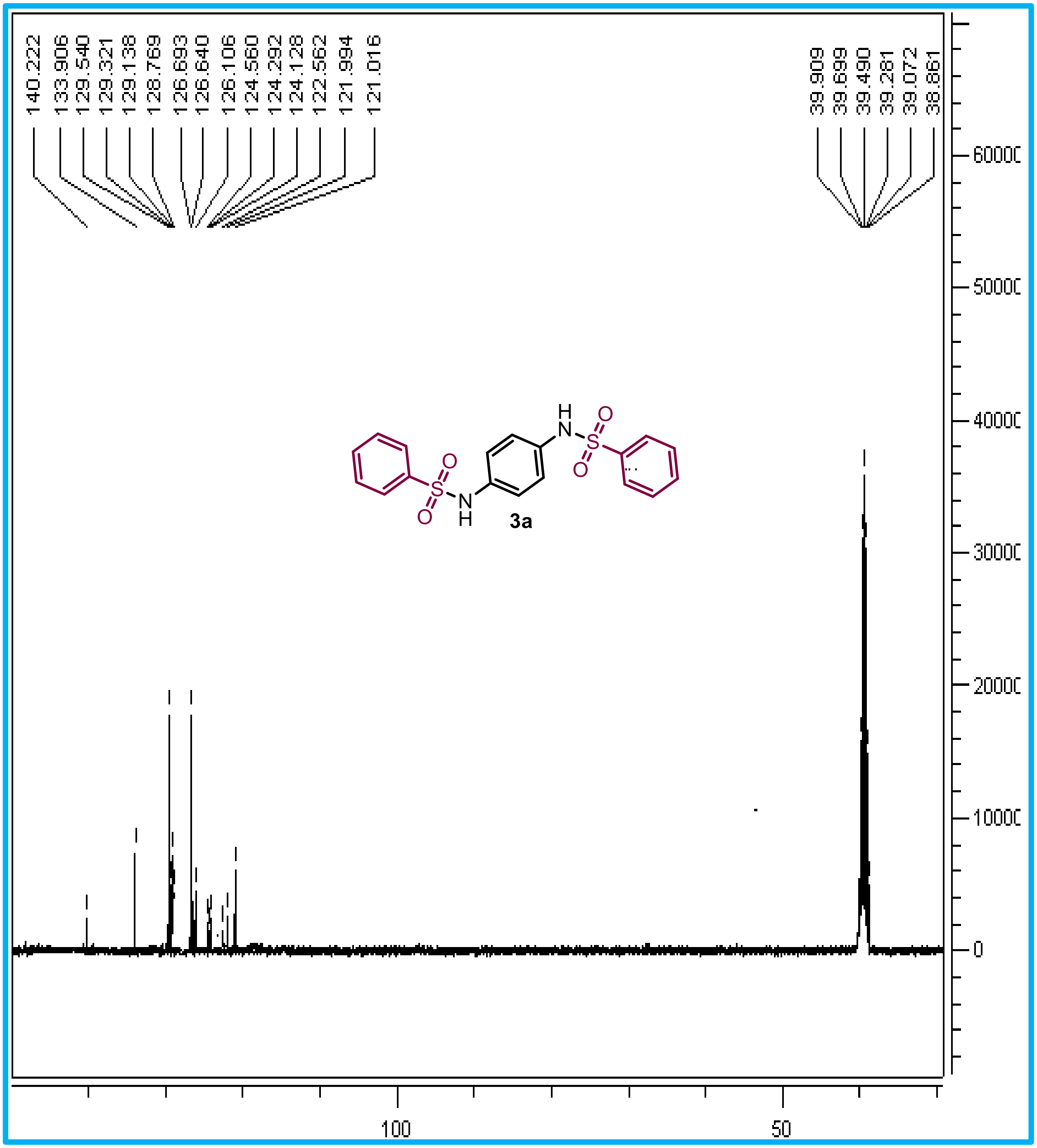
[1]H NMR spectrum of 3a



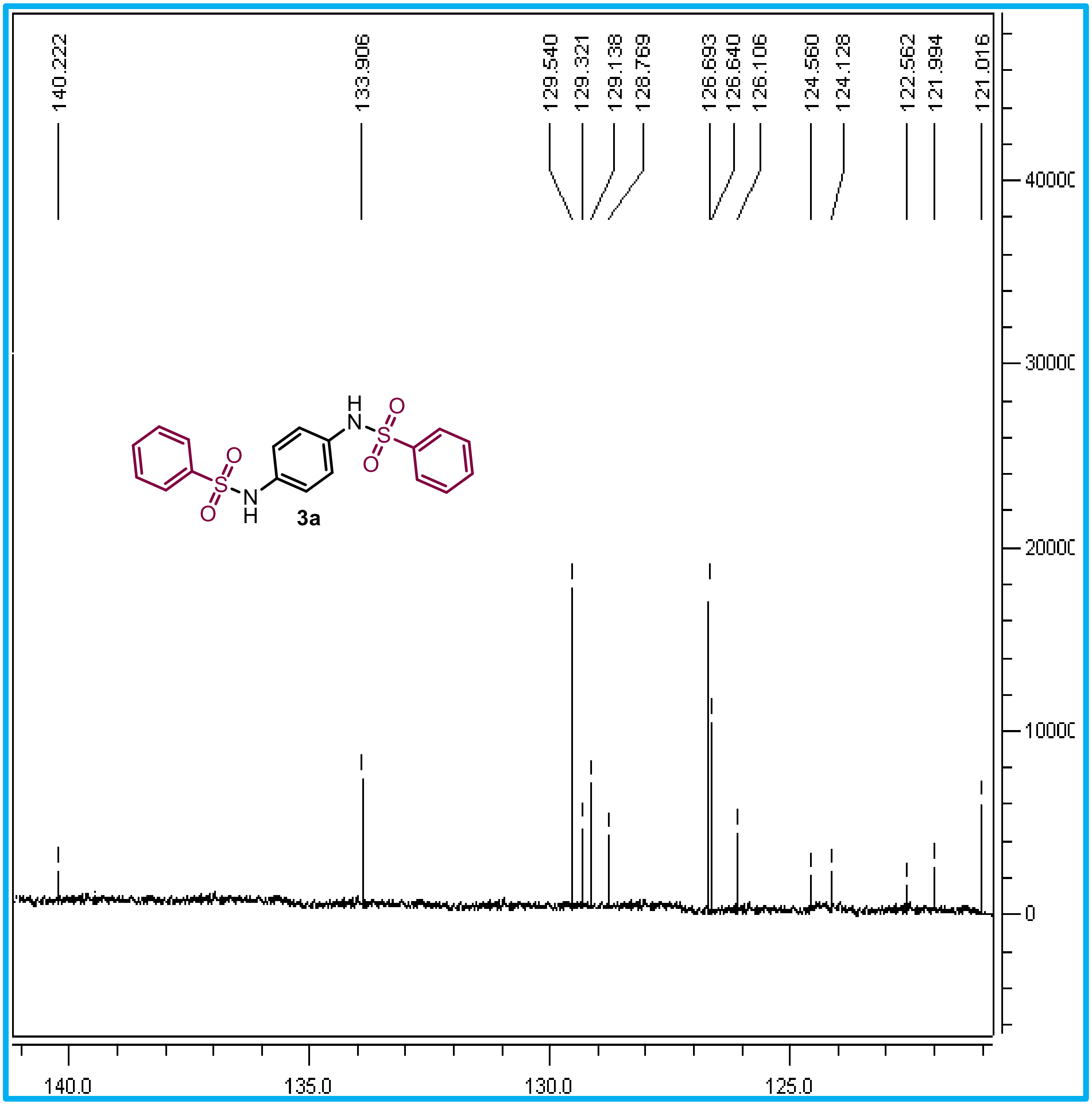
Expanded ^{1}H NMR spectrum of 3a



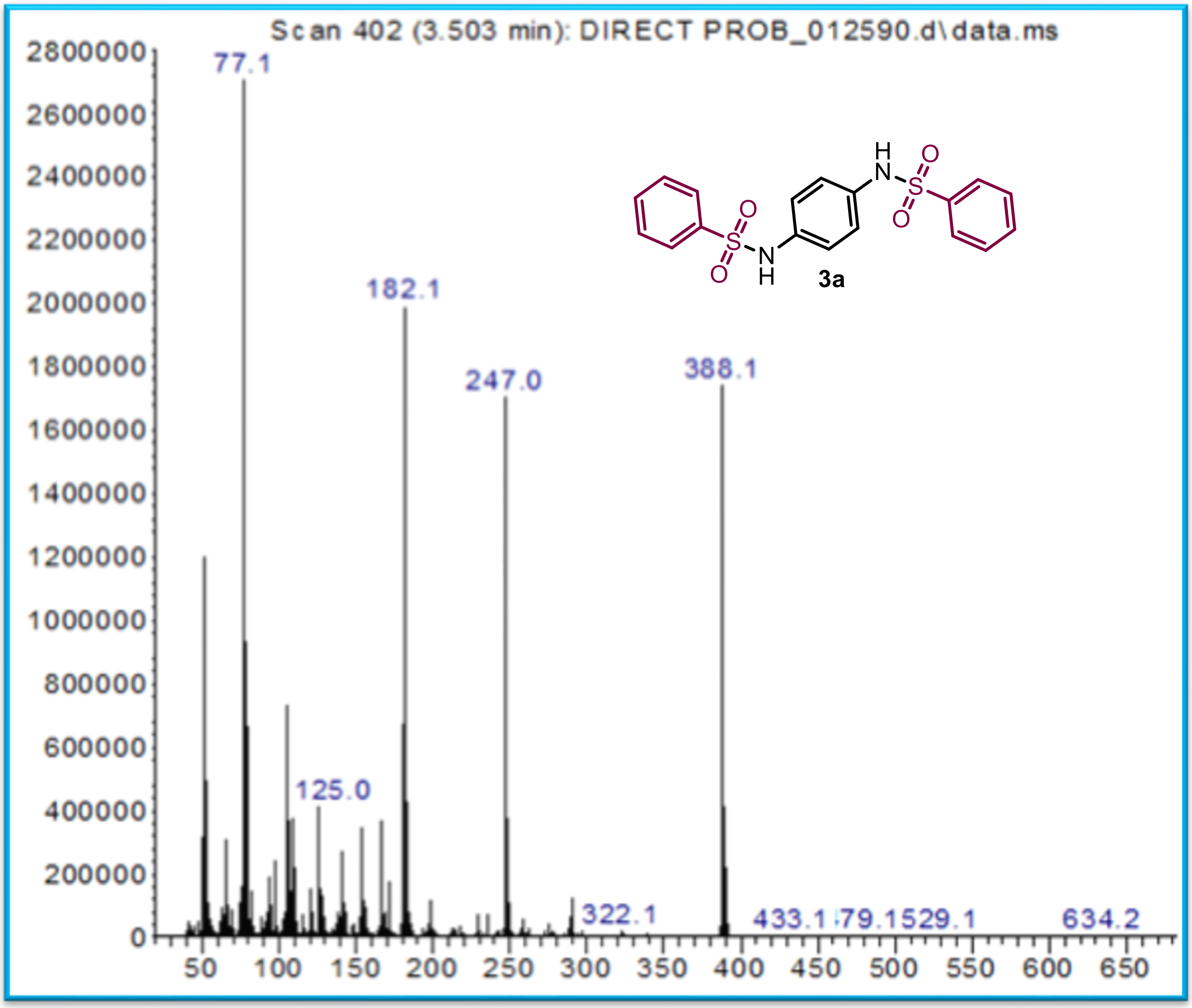
^{13}C NMR spectrum of 3a



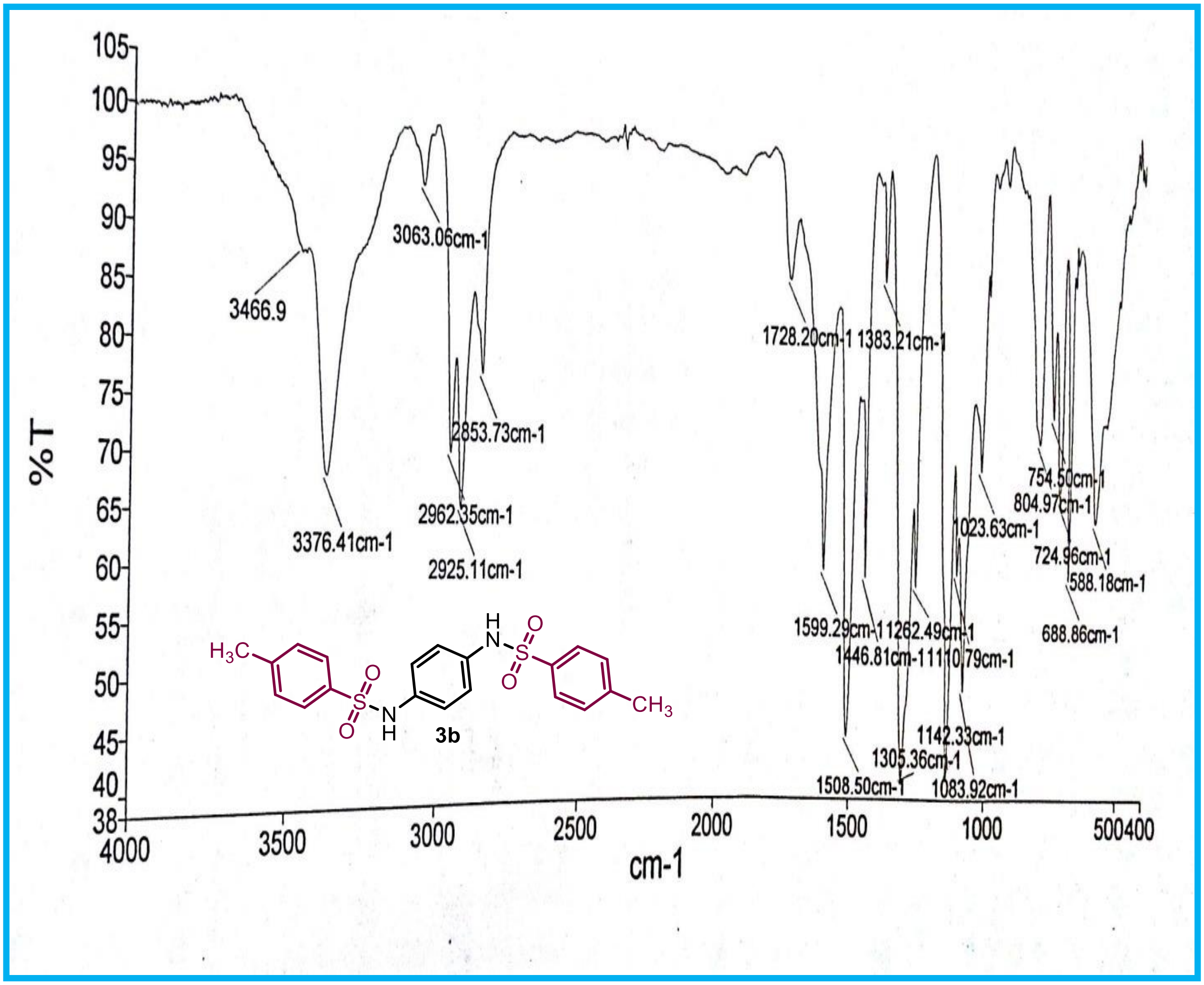
Expanded ^{13}C NMR spectrum of 3a



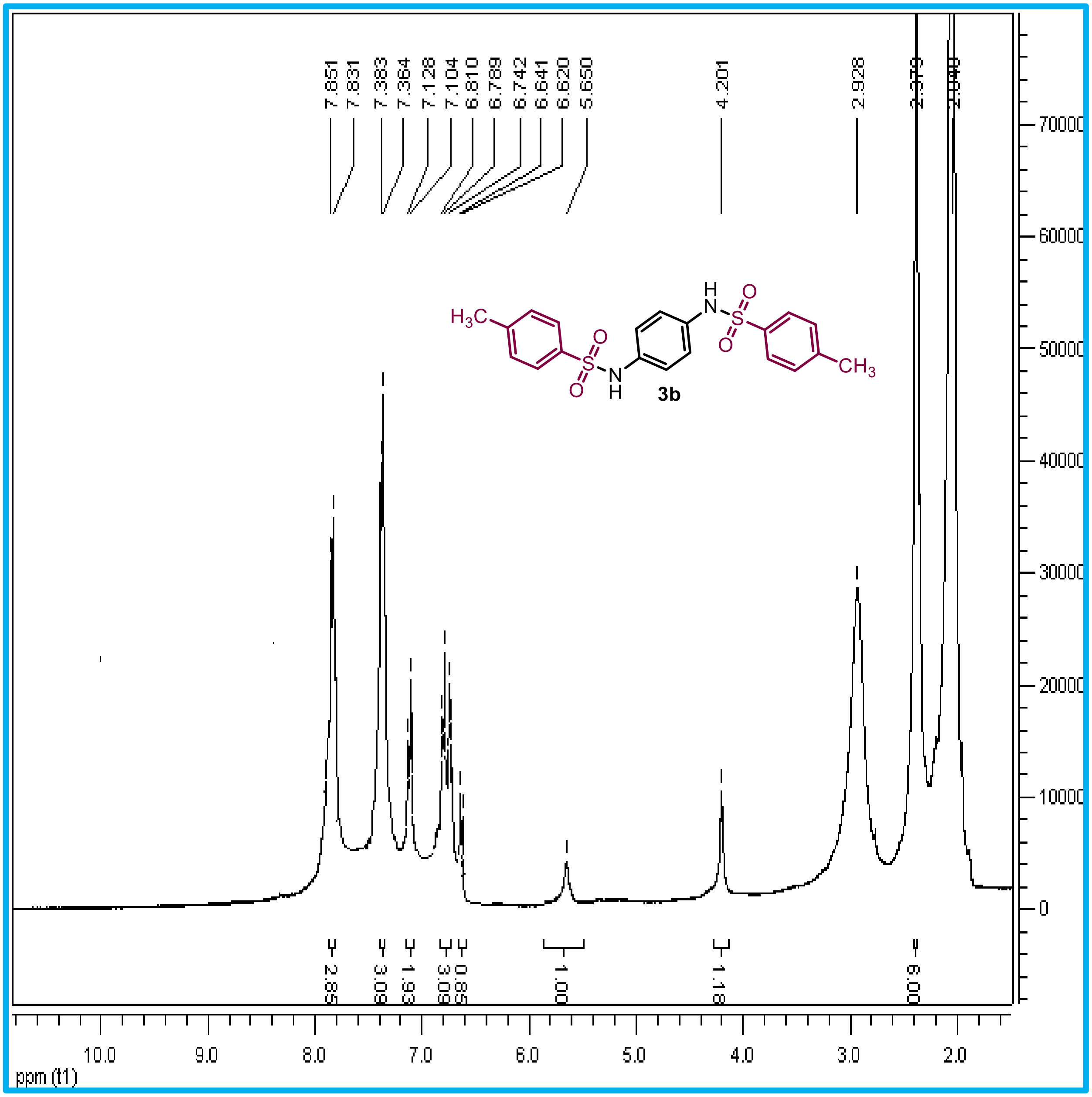
MS spectrum of 3a



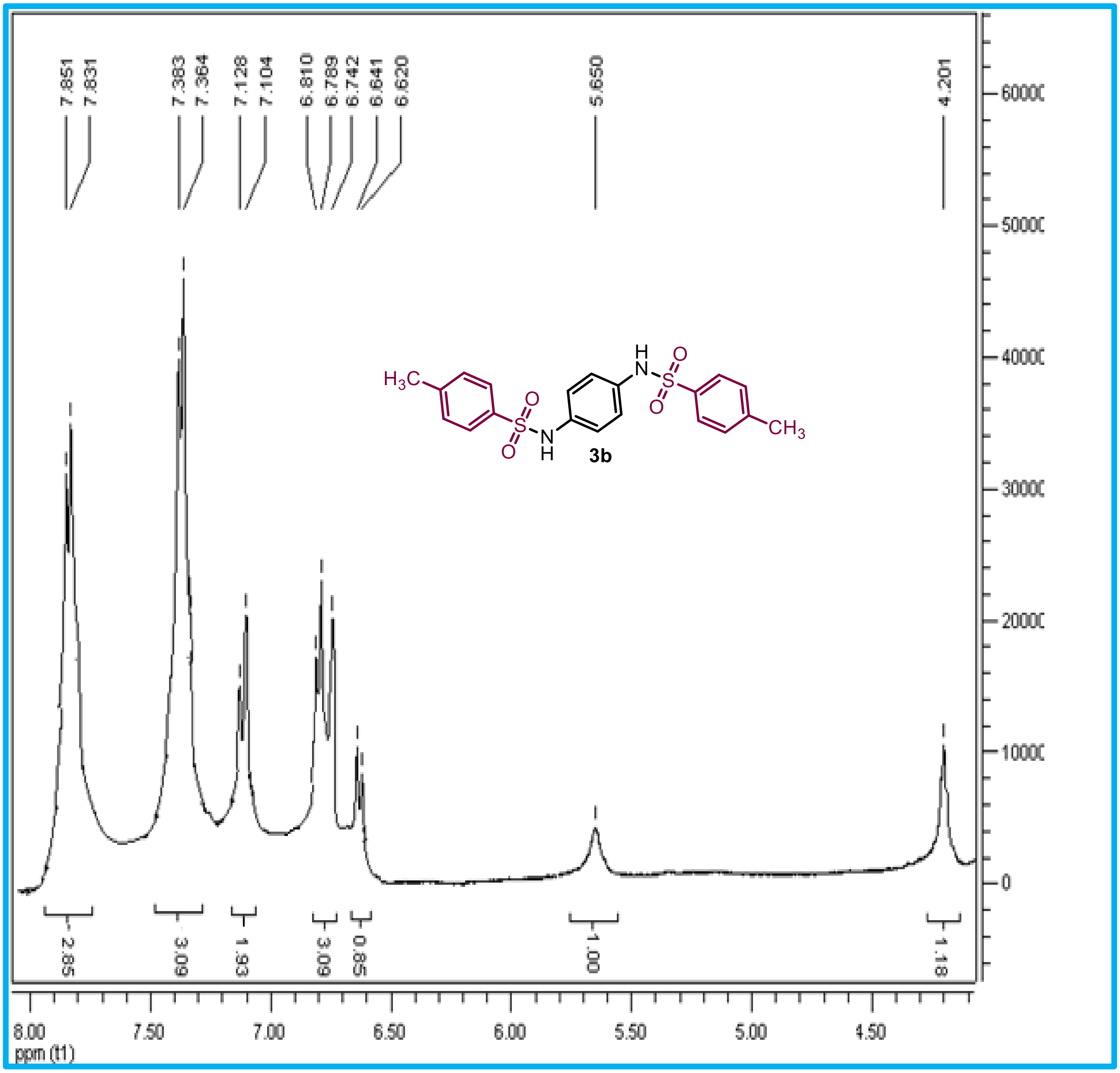
IR spectrum of 3b



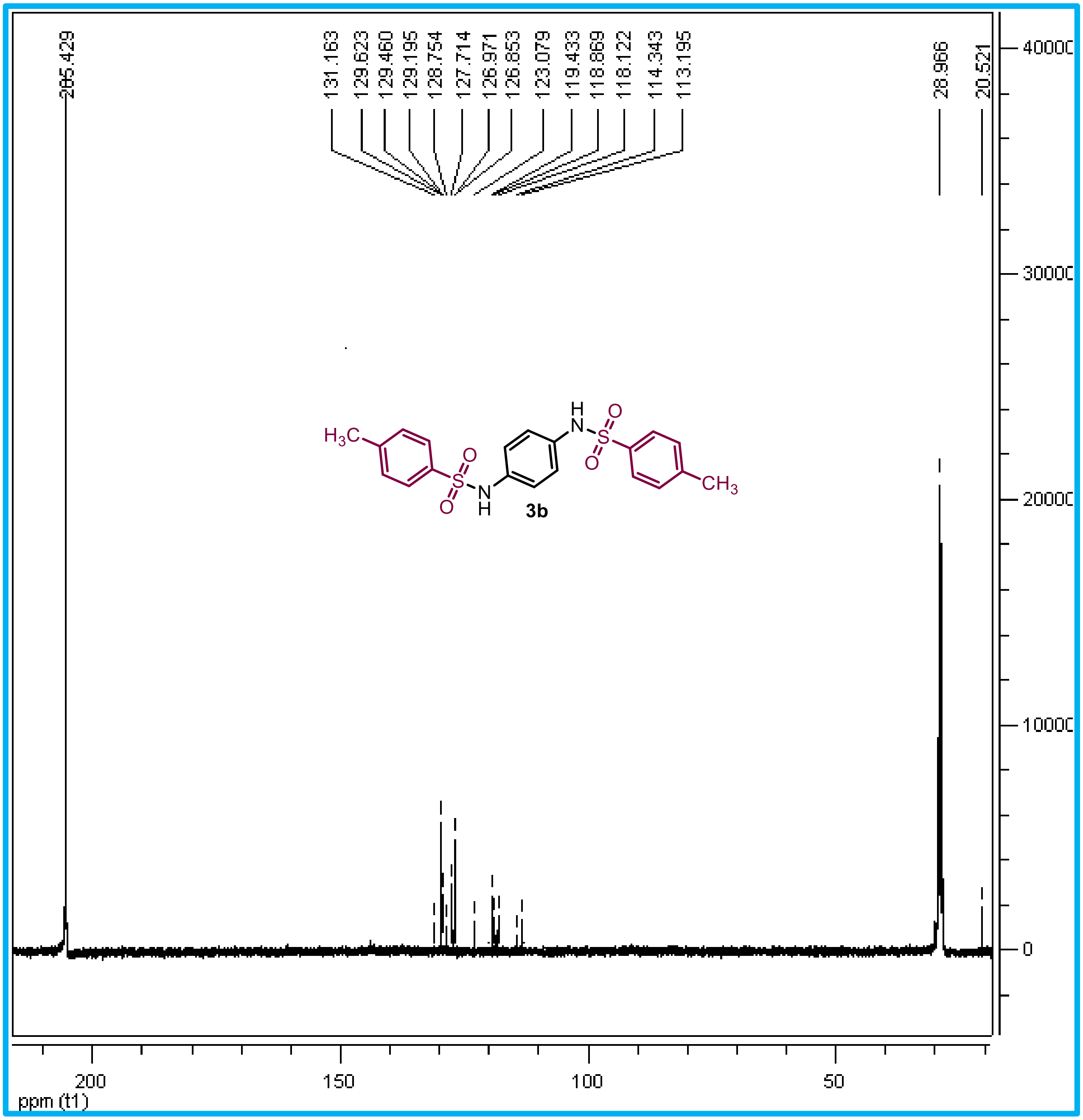
[1]H NMR spectrum of 3b



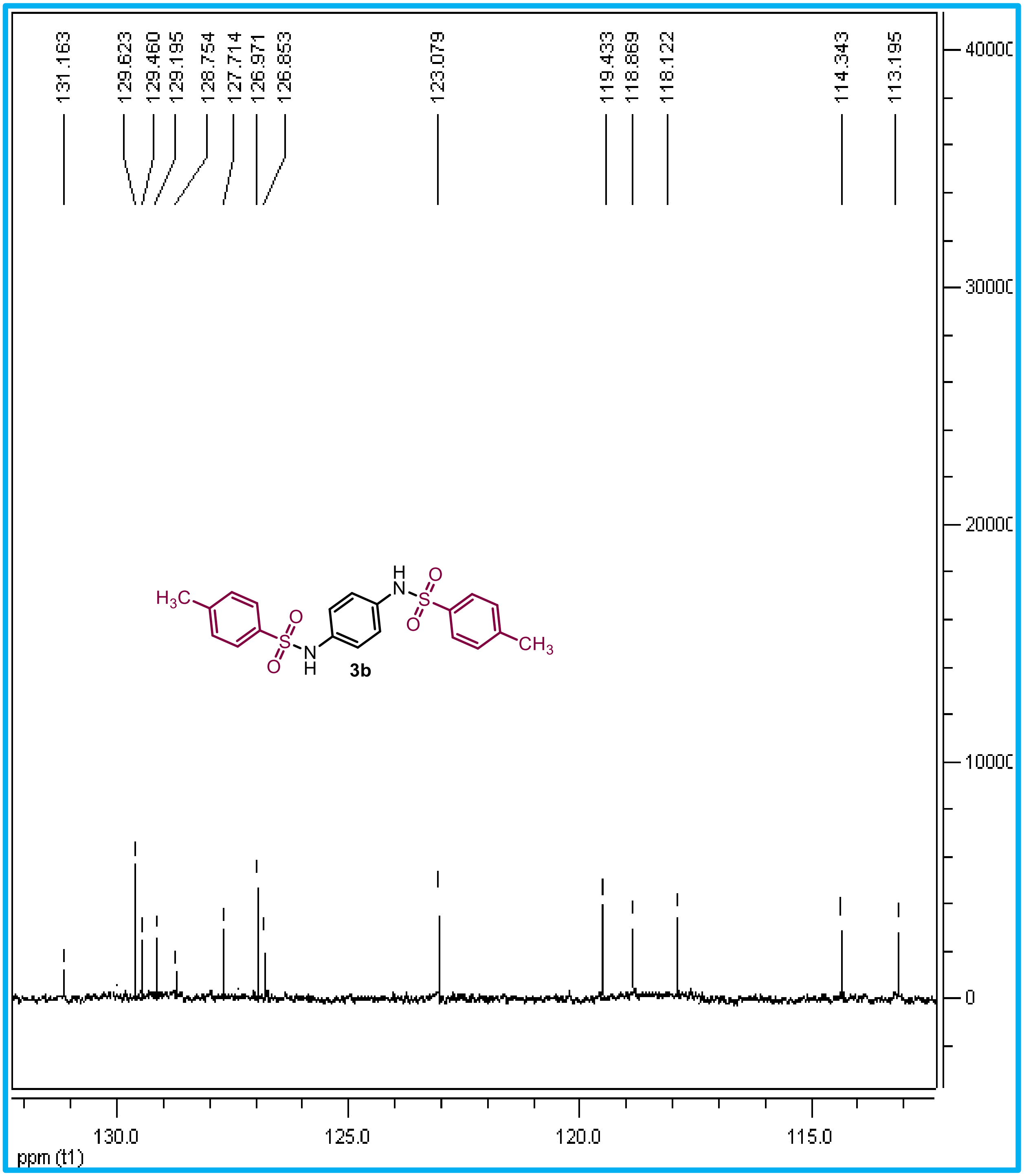
Expanded ^{1}H NMR spectrum of 3b



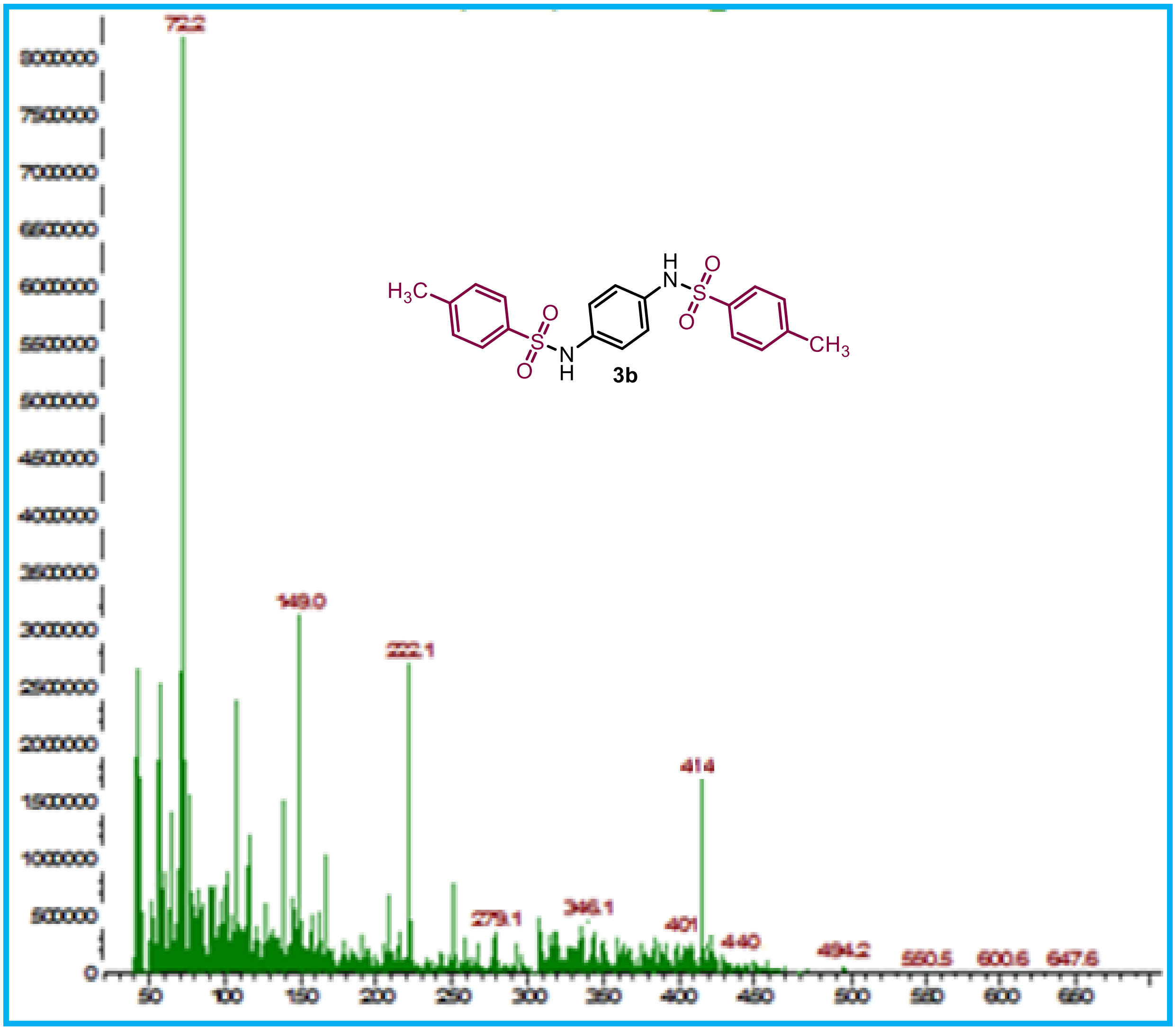
^{13}C NMR spectrum of 3b



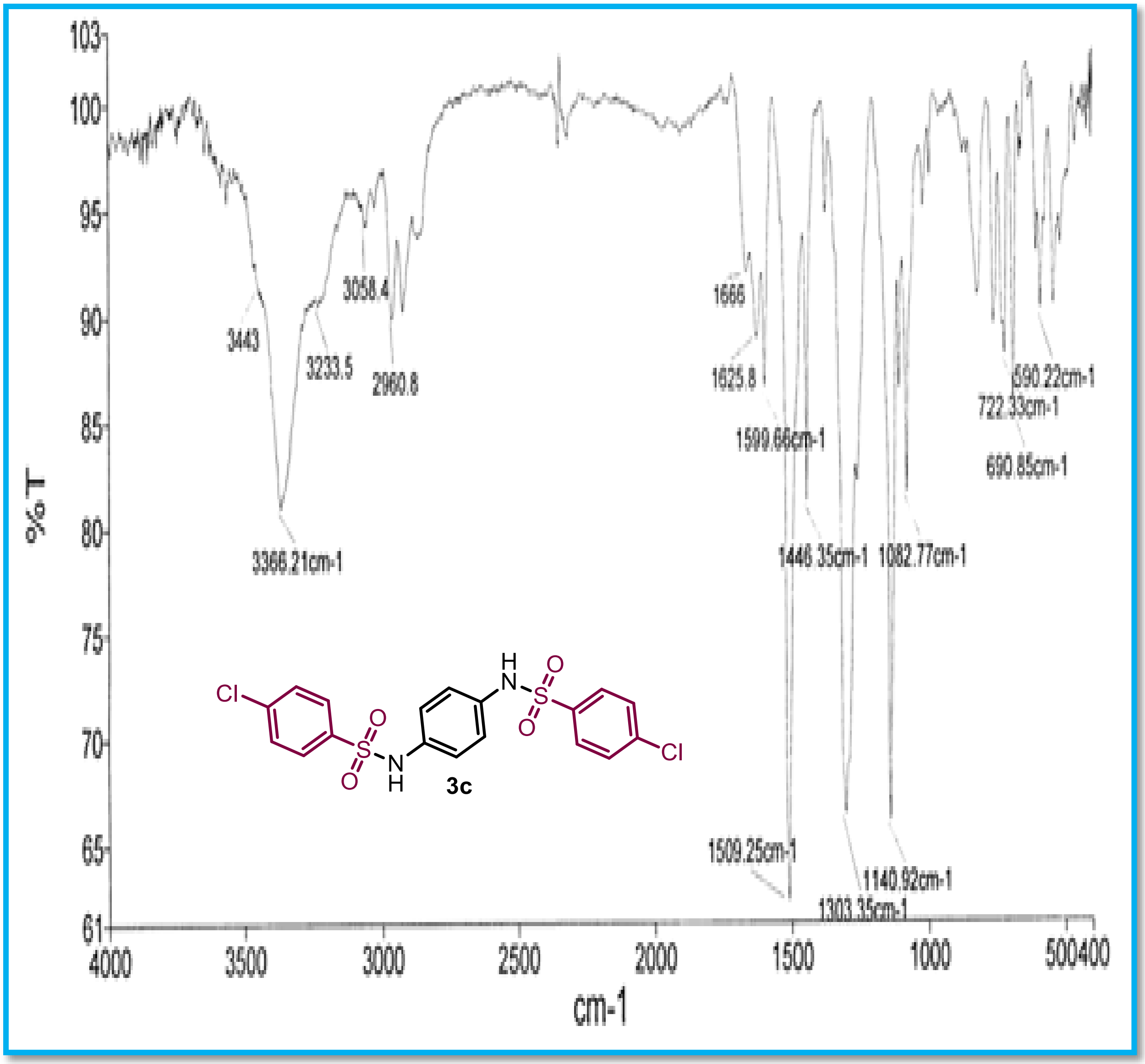
Expanded ^{13}C NMR spectrum of 3b



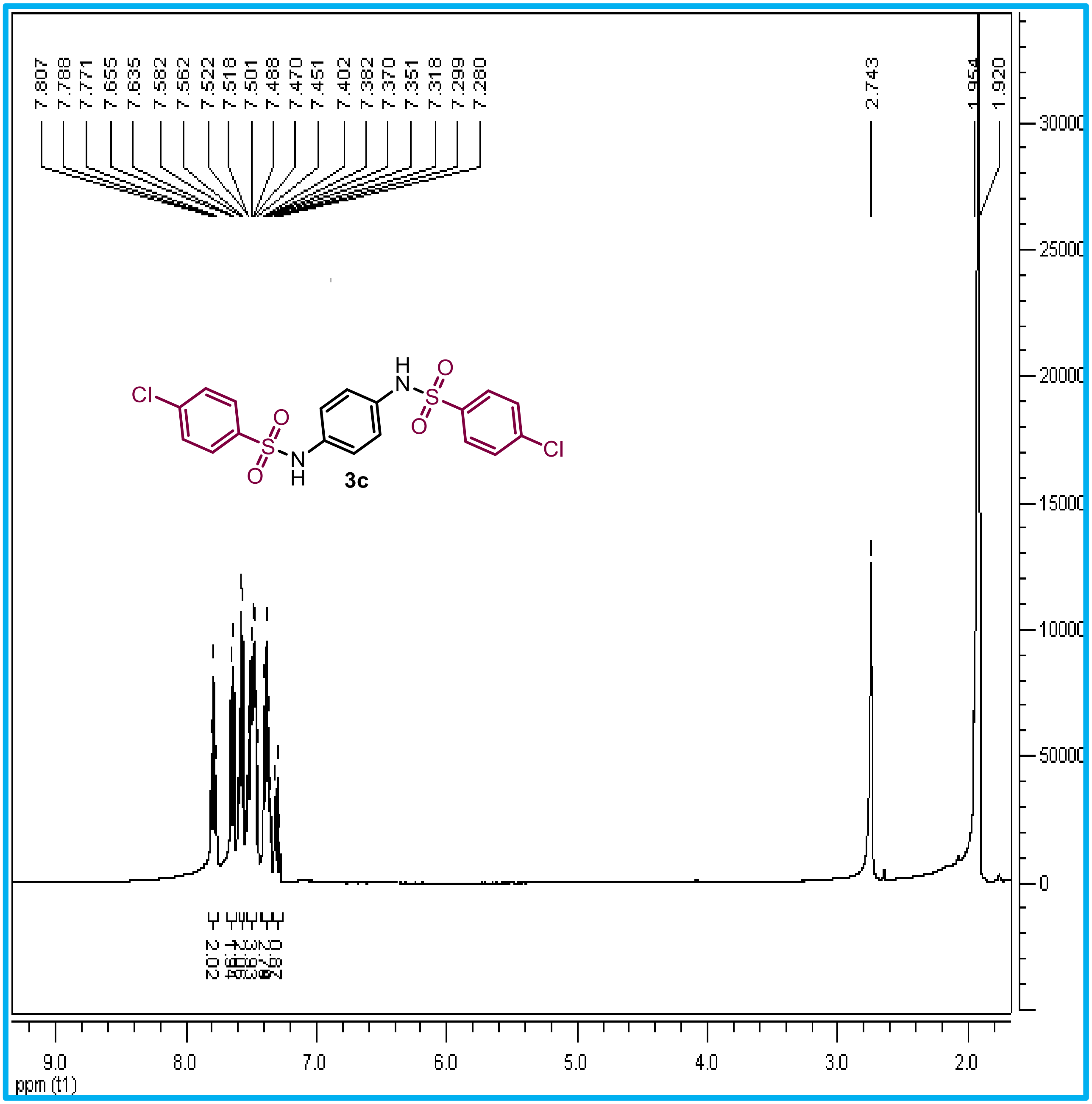
MS spectrum of 3b



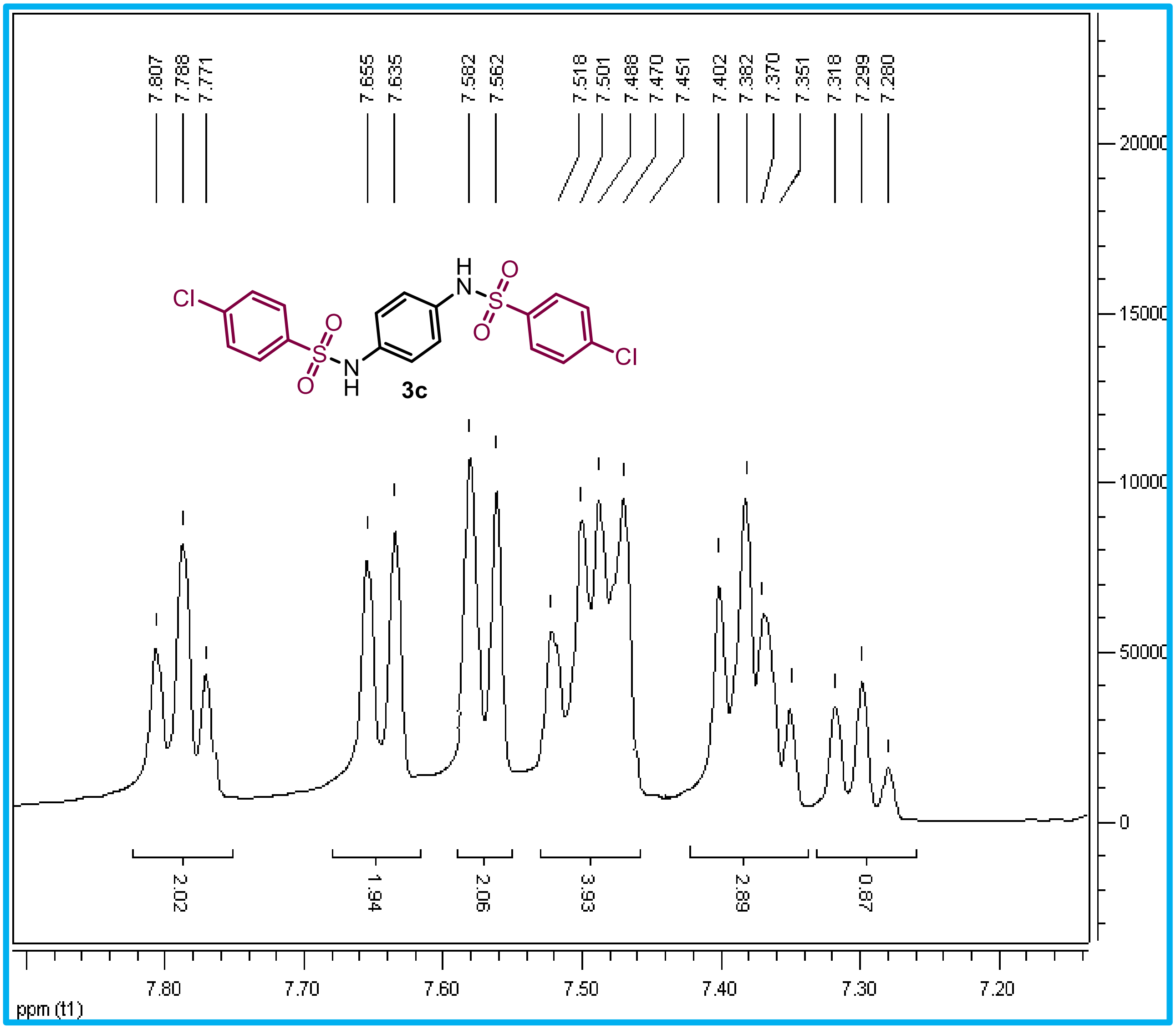
IR spectrum of 3c



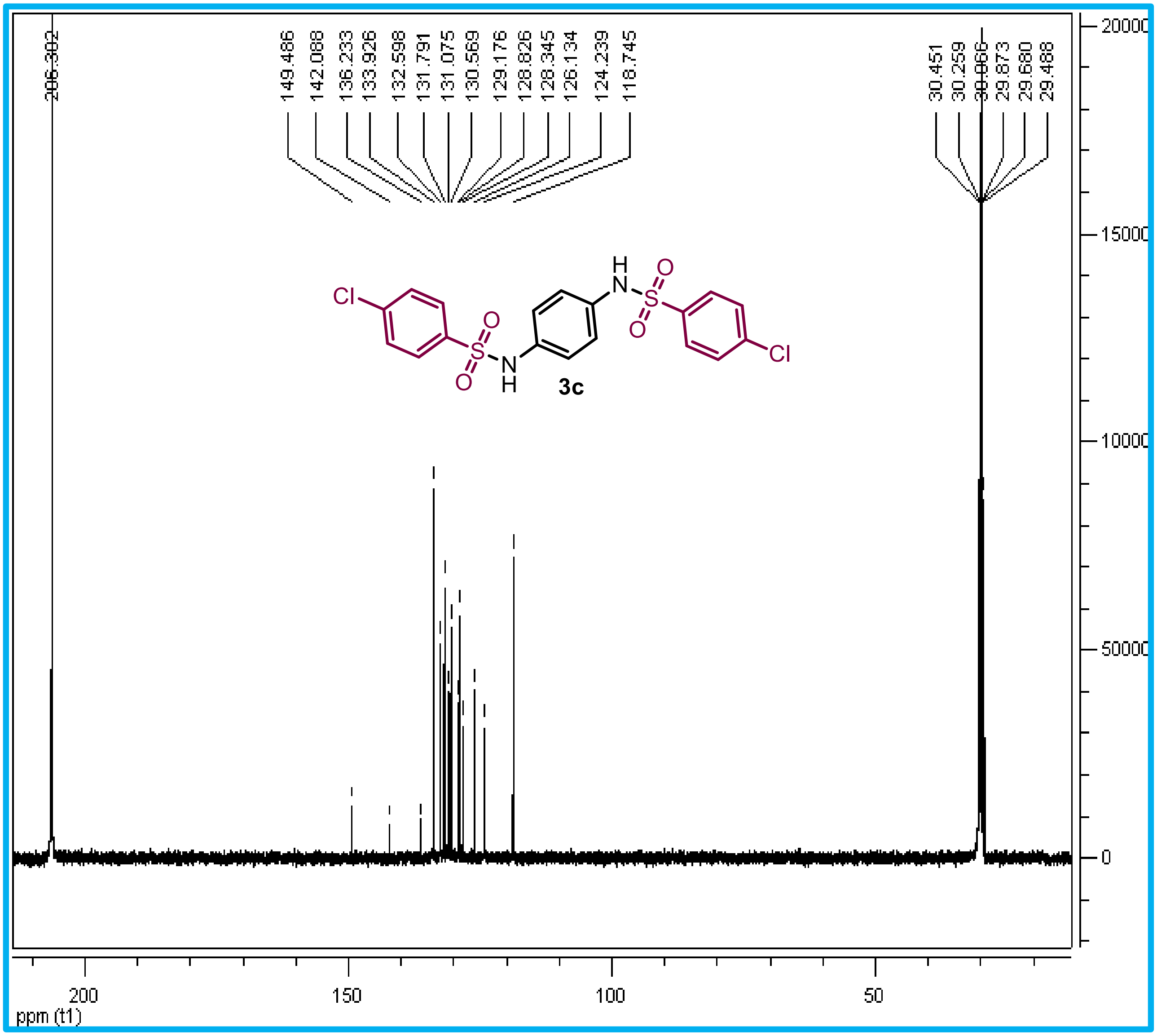
[1]H NMR spectrum of 3c



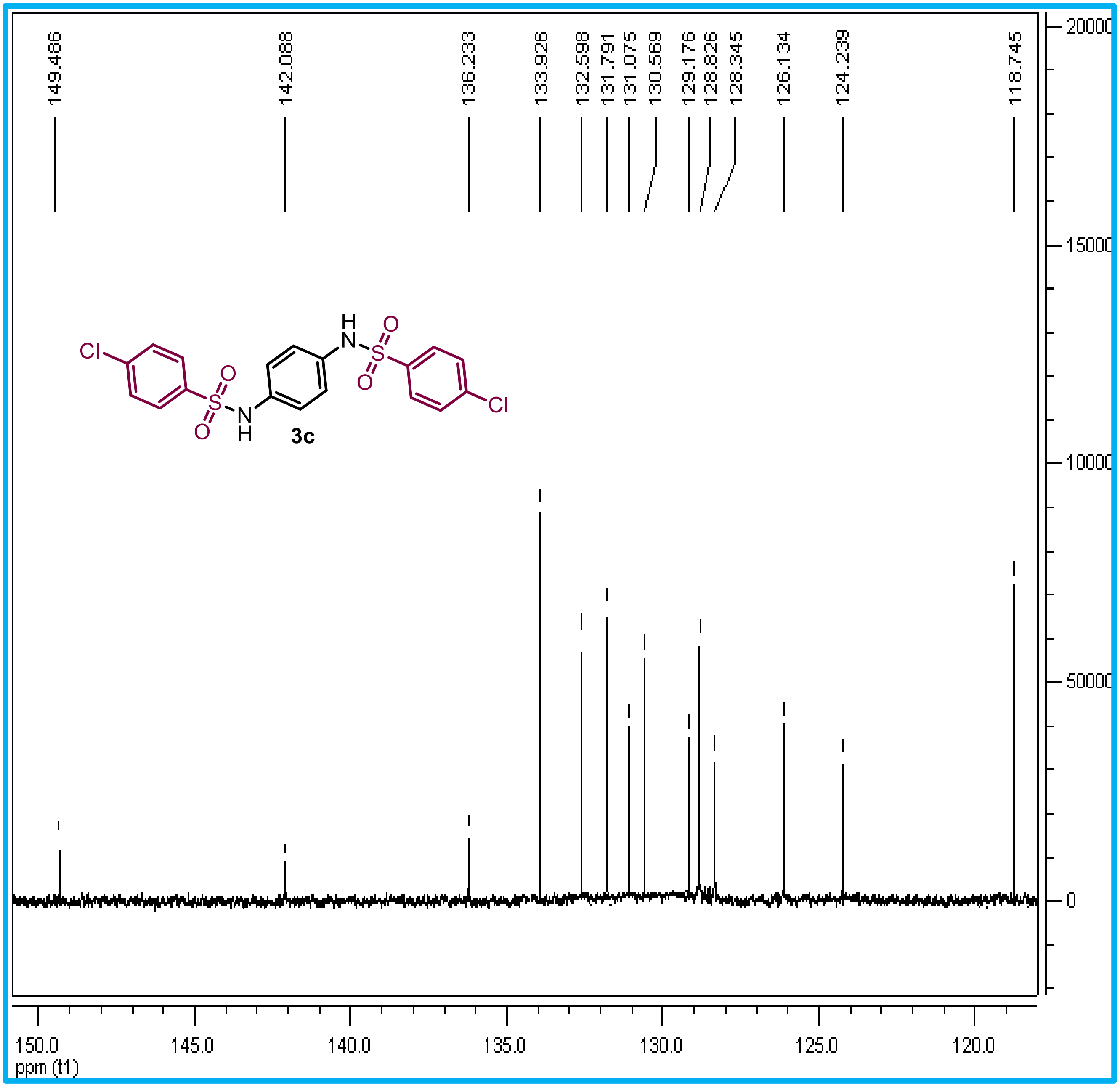
Expanded ^{1}H NMR spectrum of 3c



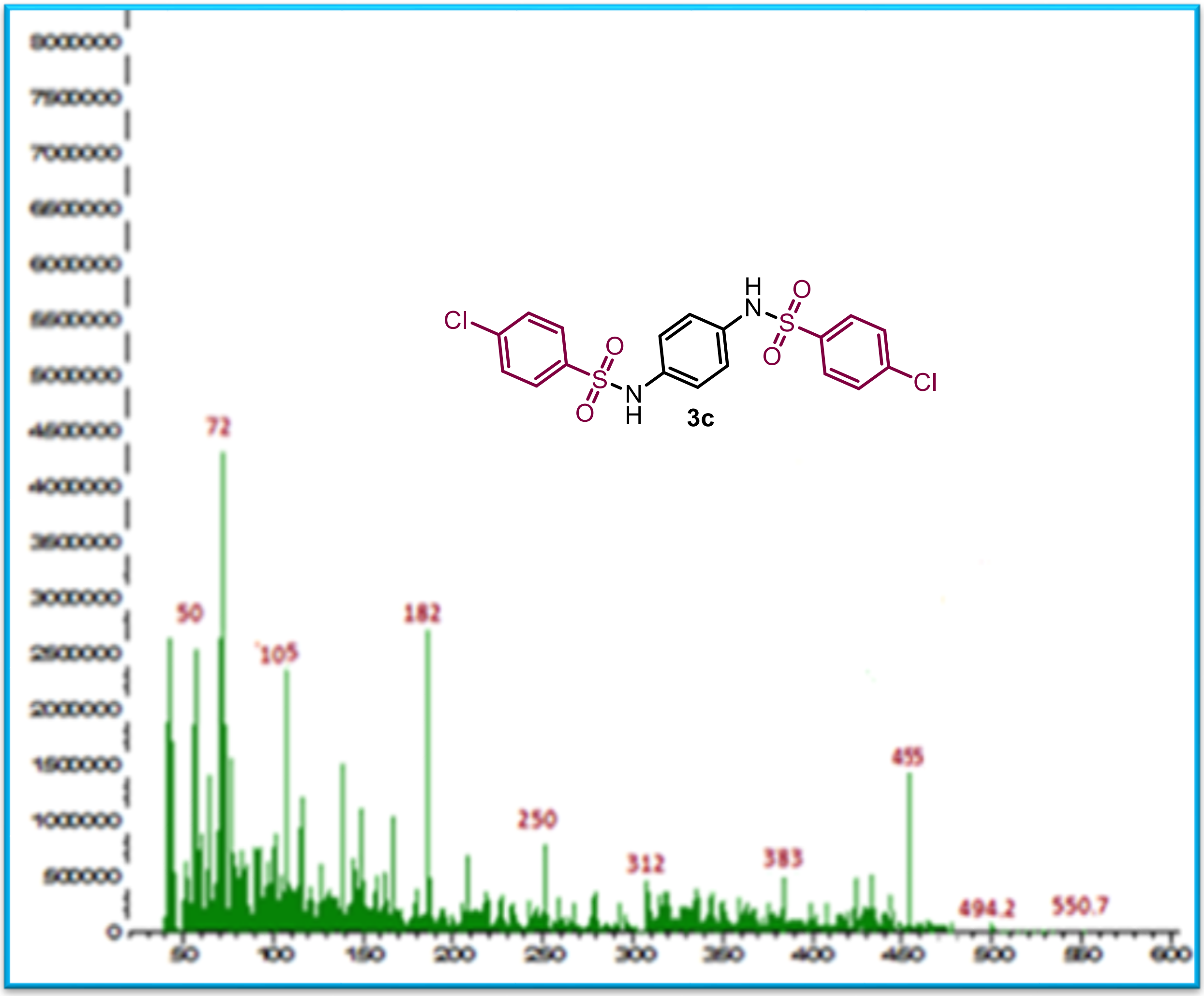
[13]C NMR spectrum of 3c



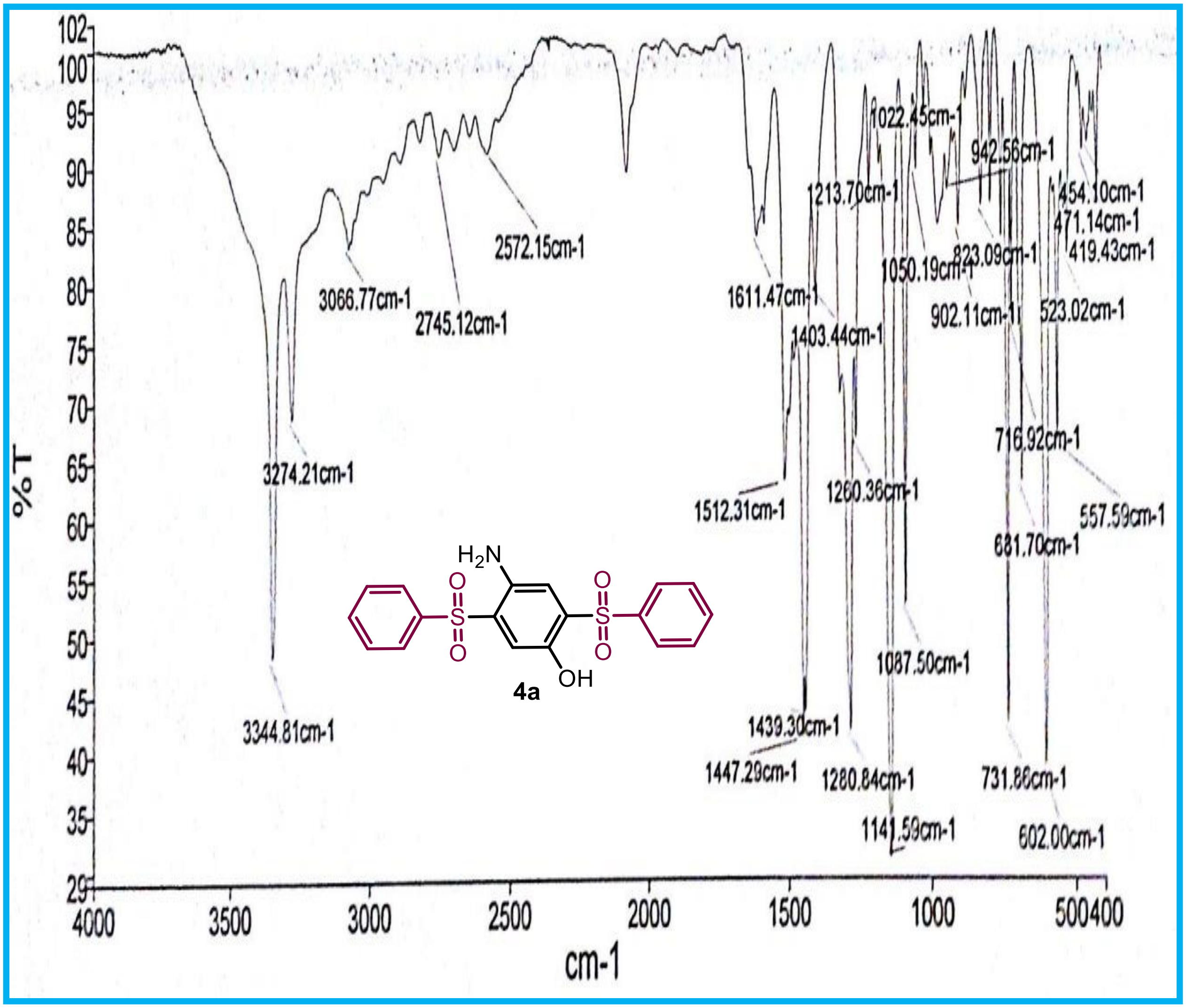
Expanded ^{13}C NMR spectrum of 3c



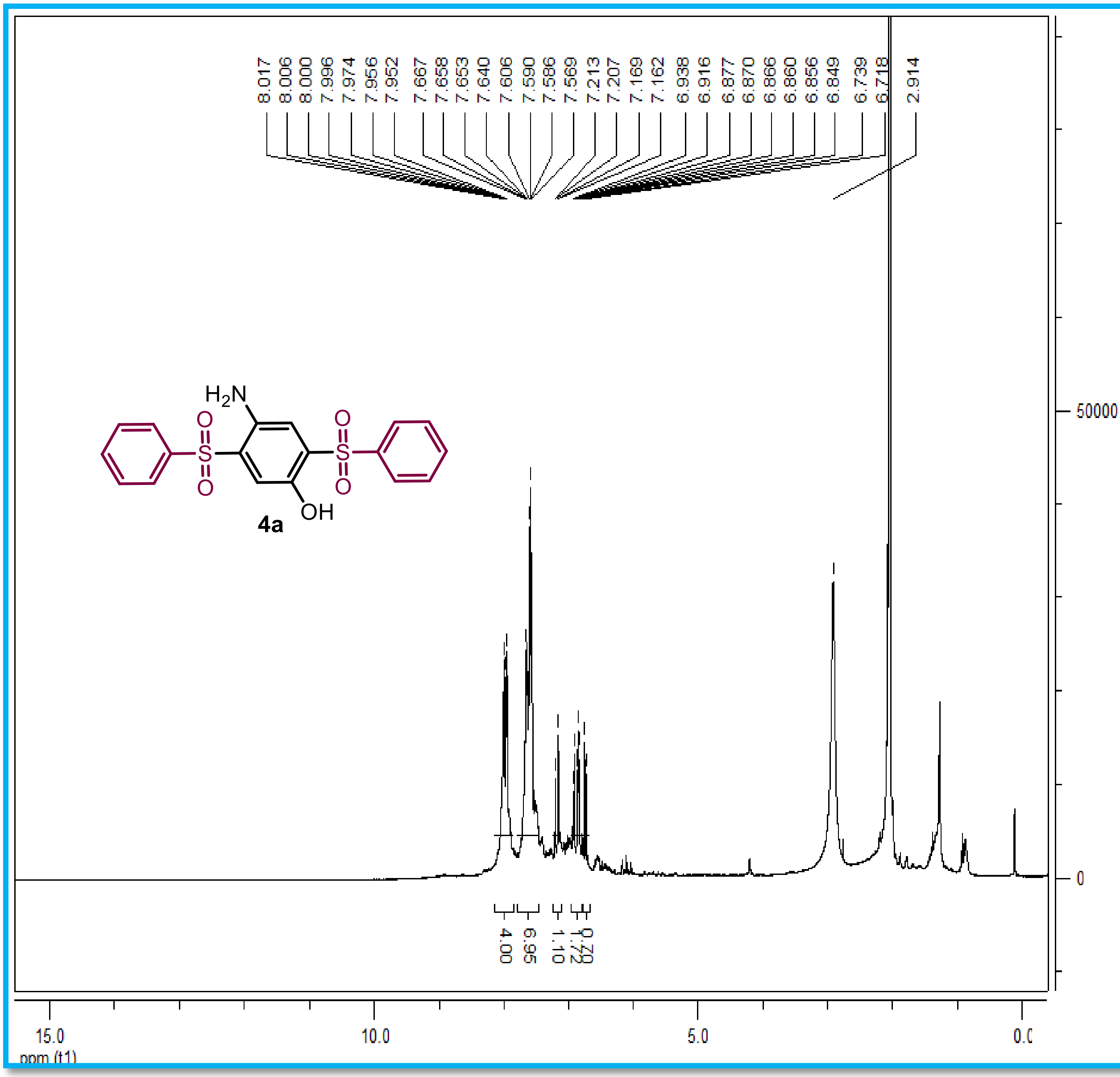
MS spectrum of 3c



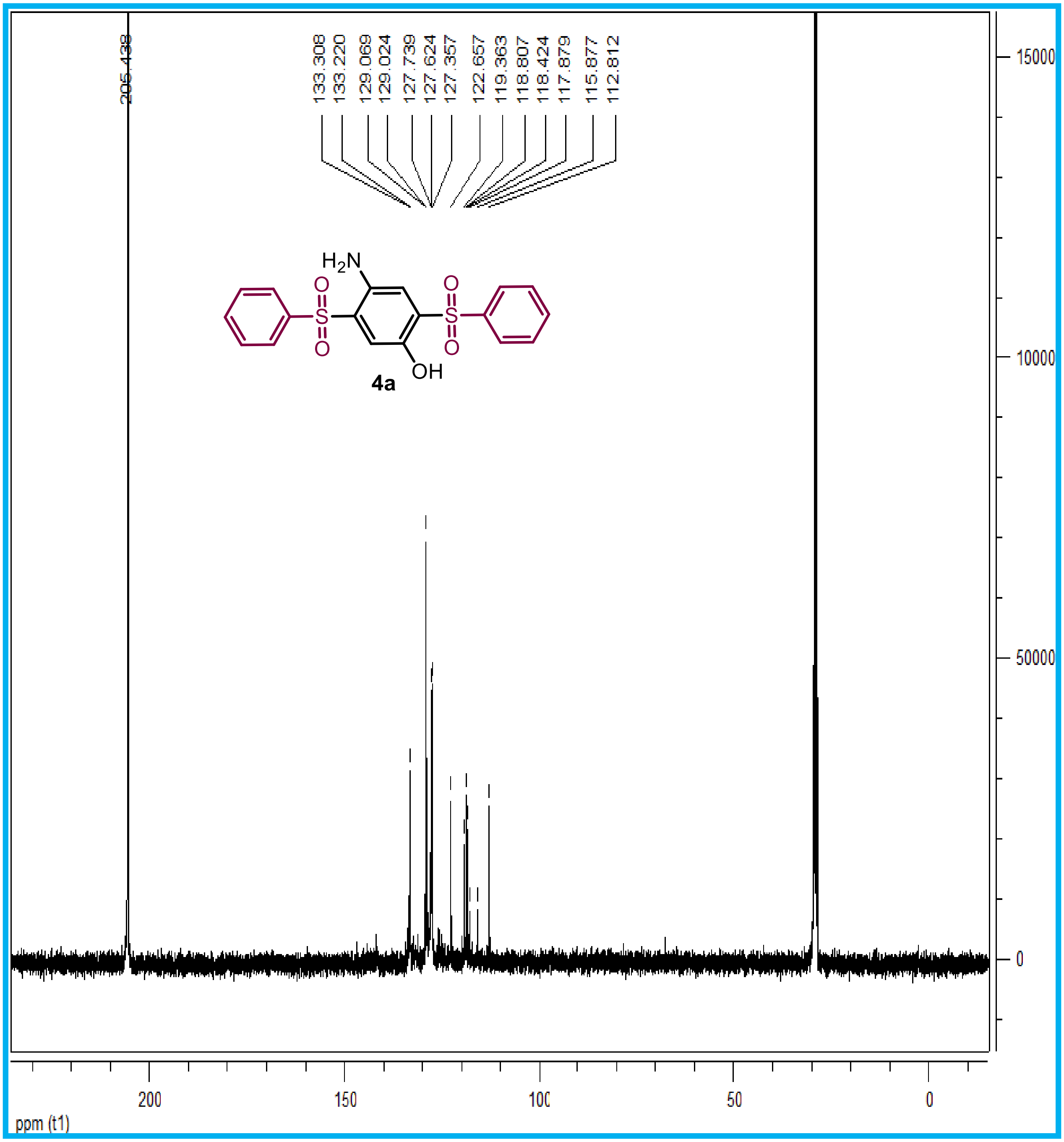
IR spectrum of 4a



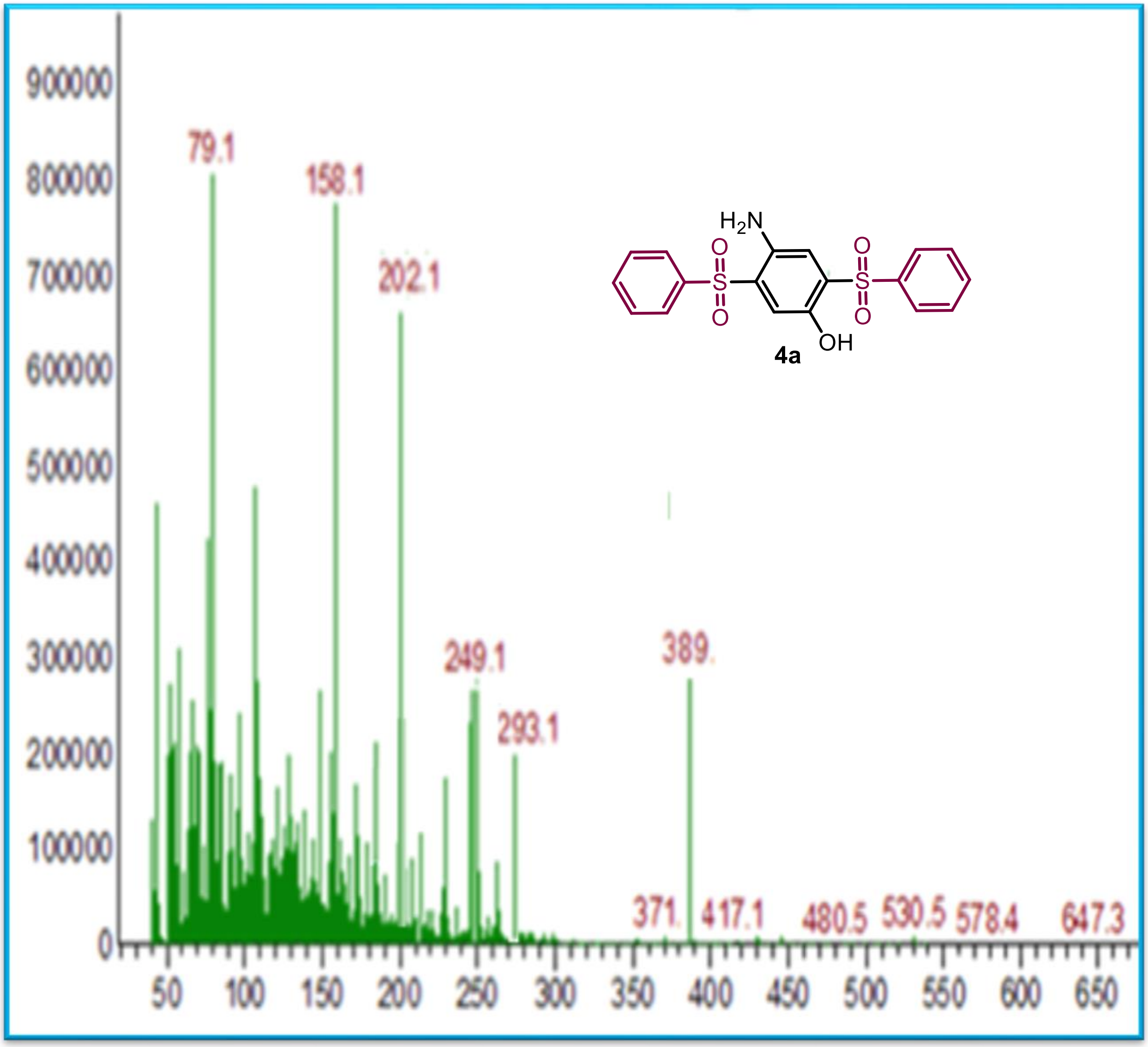
[1]H NMR spectrum of 4a



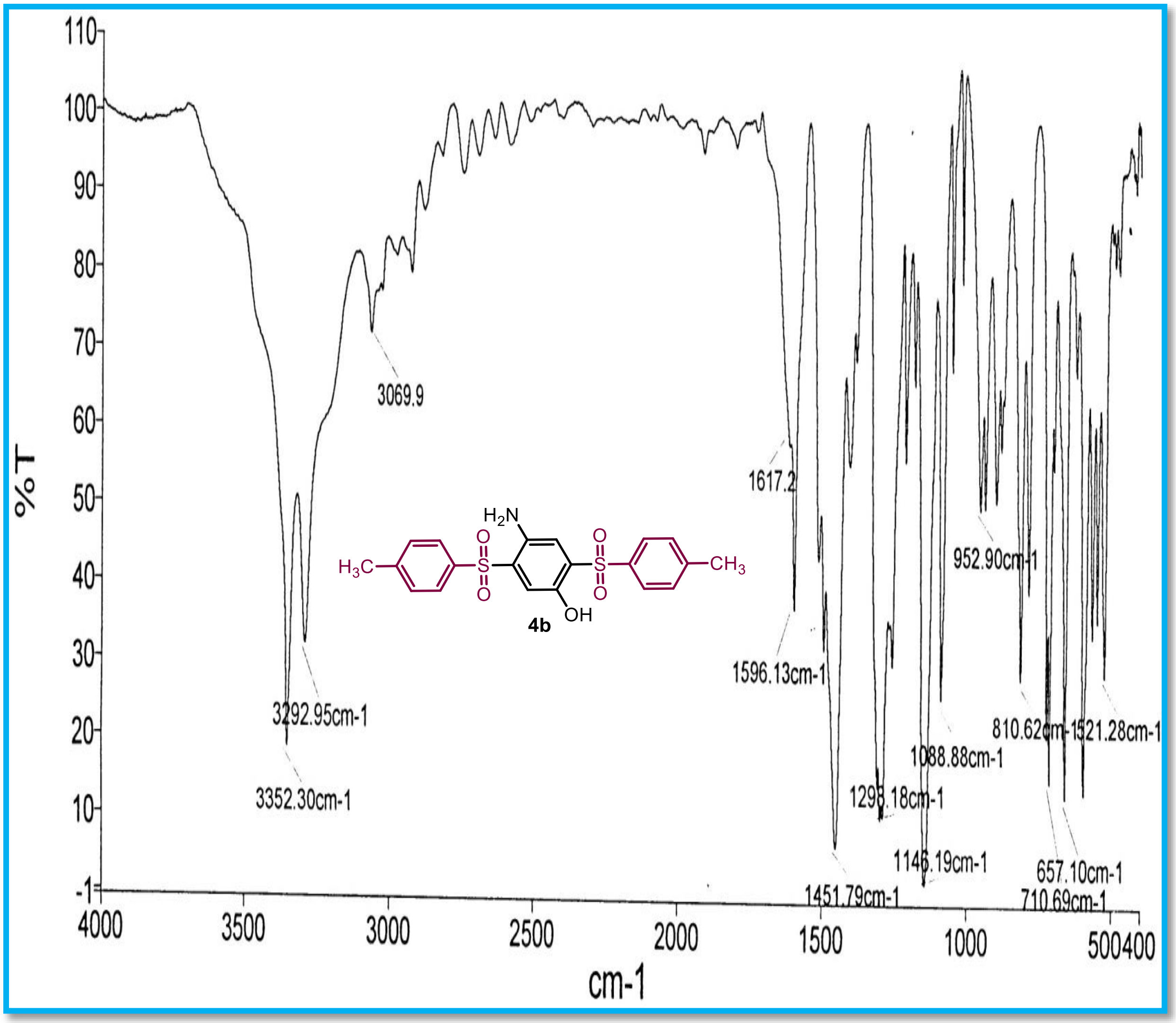
^{13}C NMR spectrum of 4a



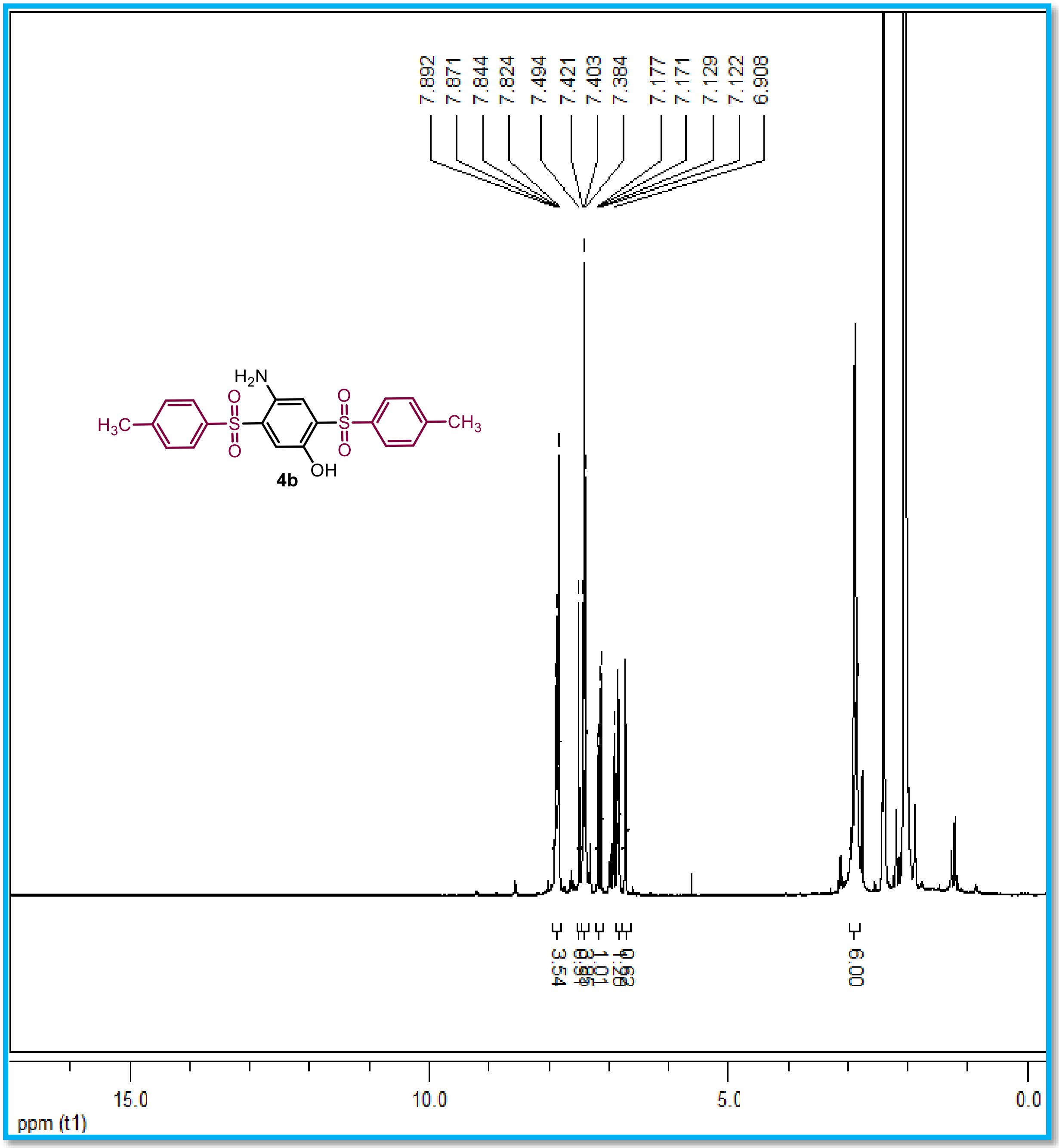
MS spectrum of 4a



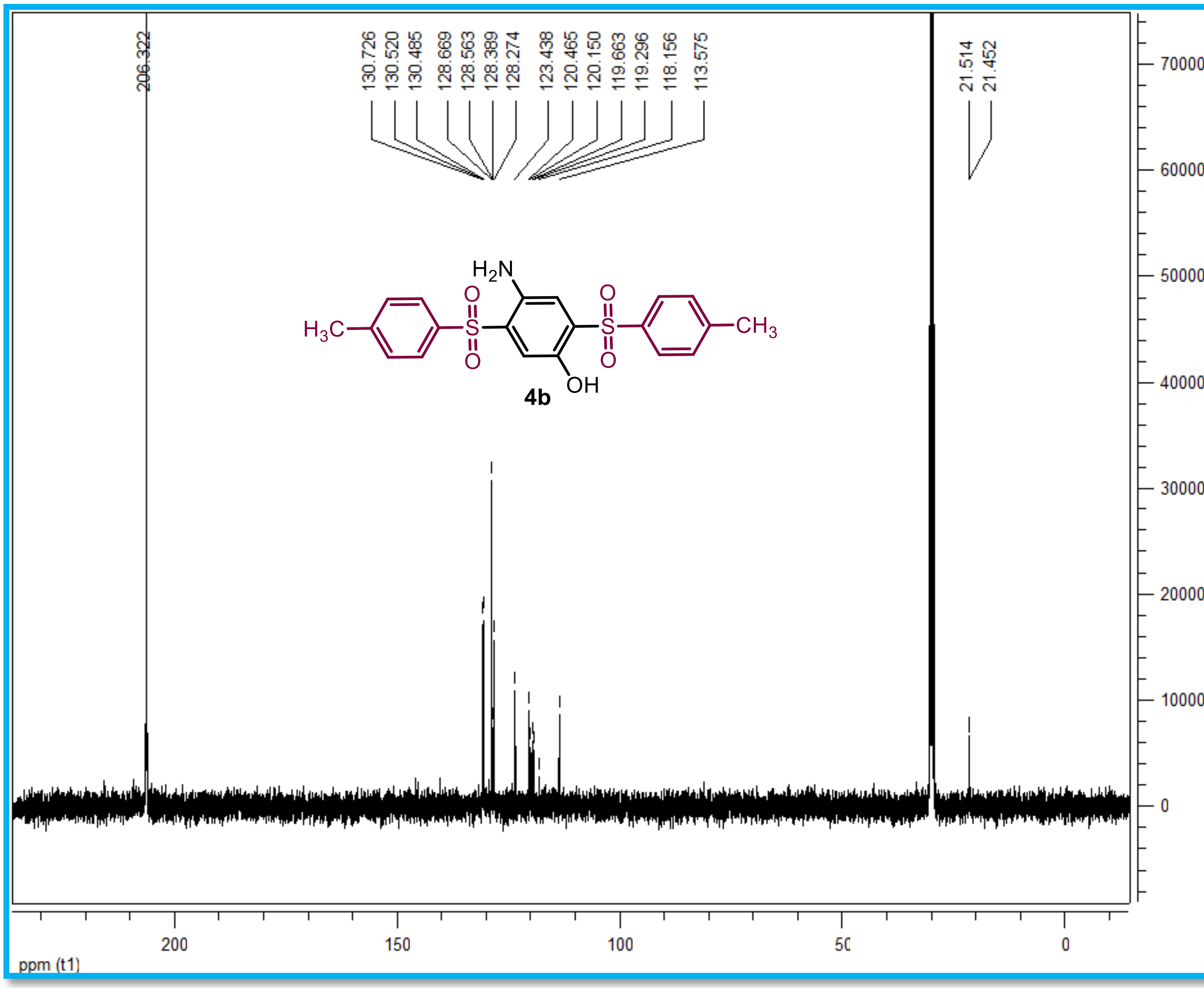
IR spectrum of 4b



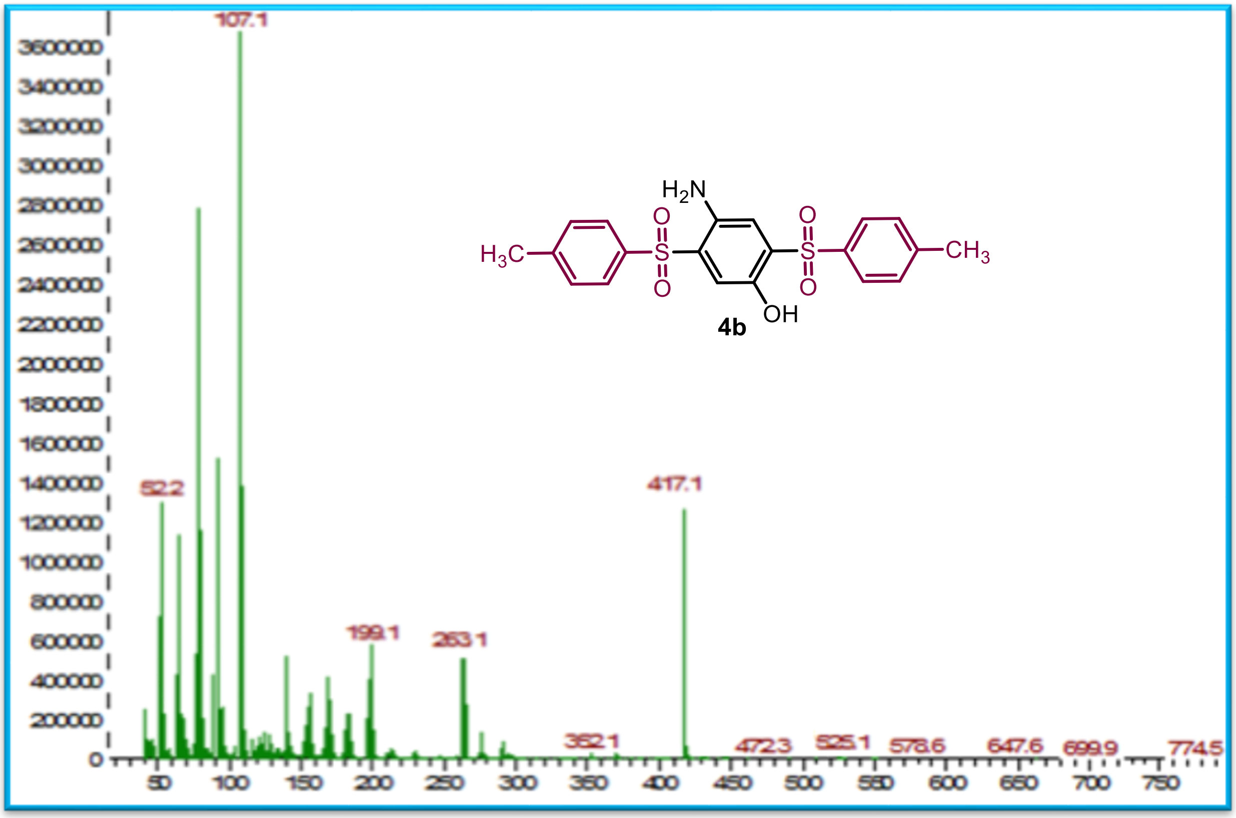
[1]H NMR spectrum of 4b



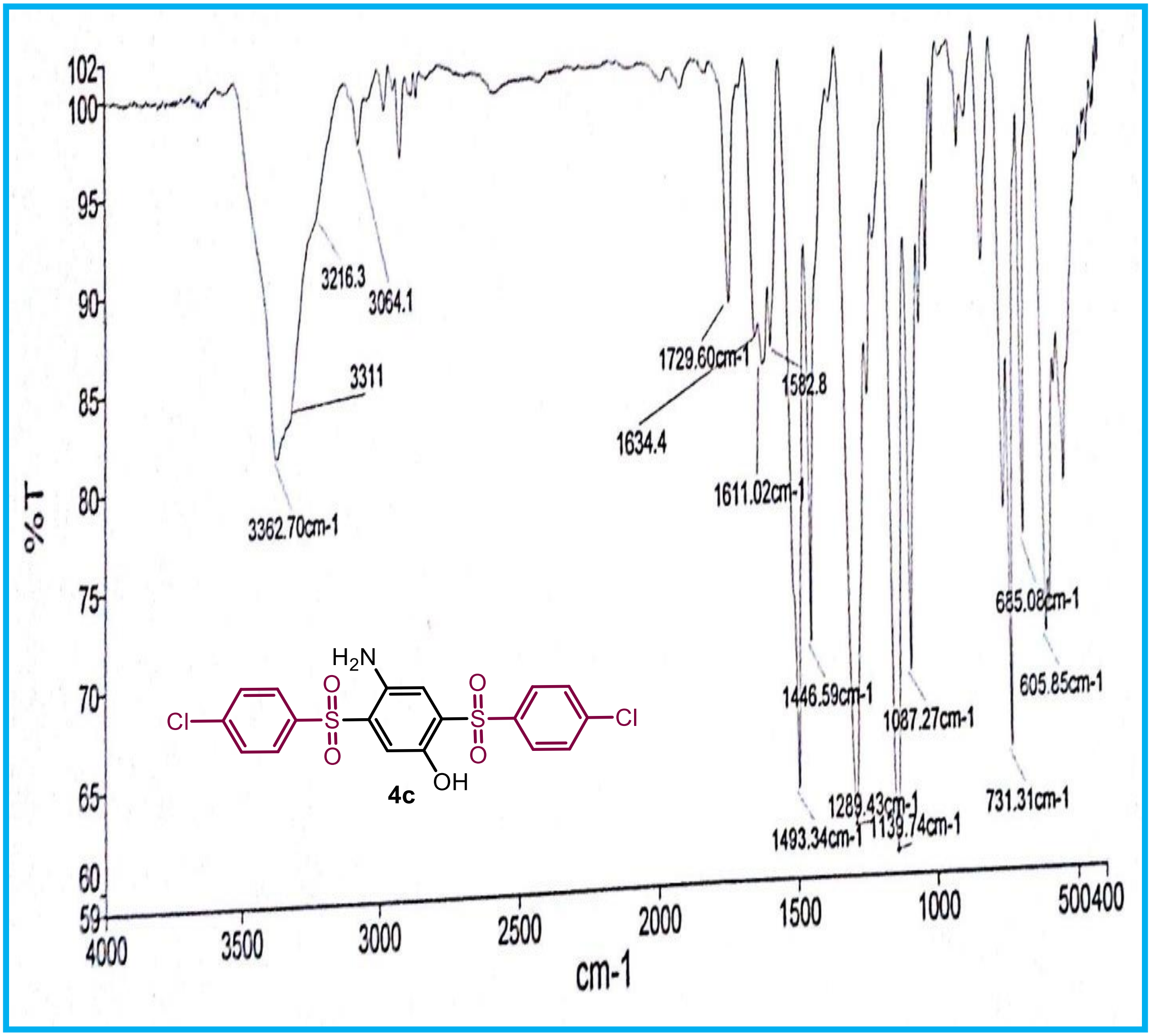
[13]C NMR spectrum of 4b



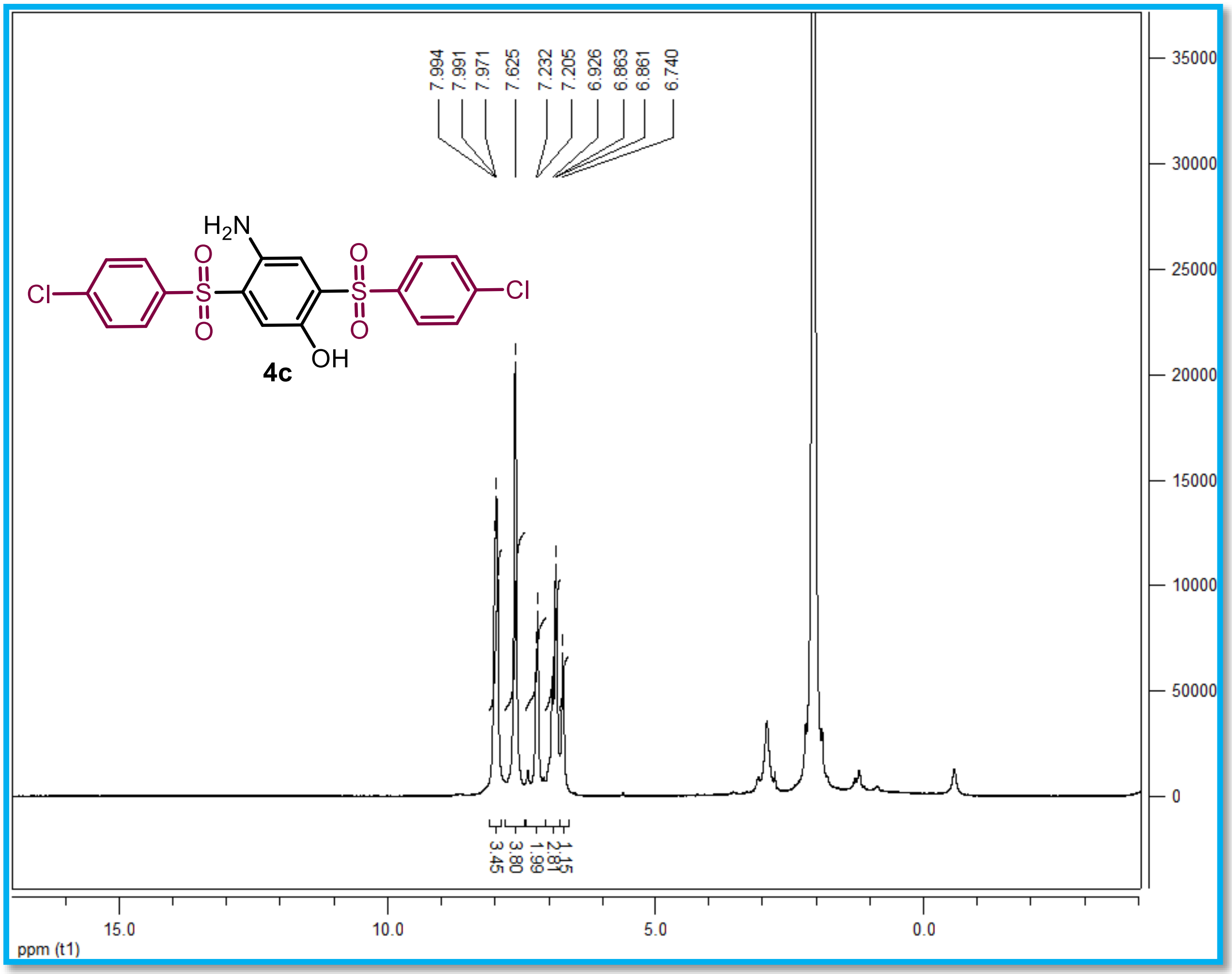
MS spectrum of 4b



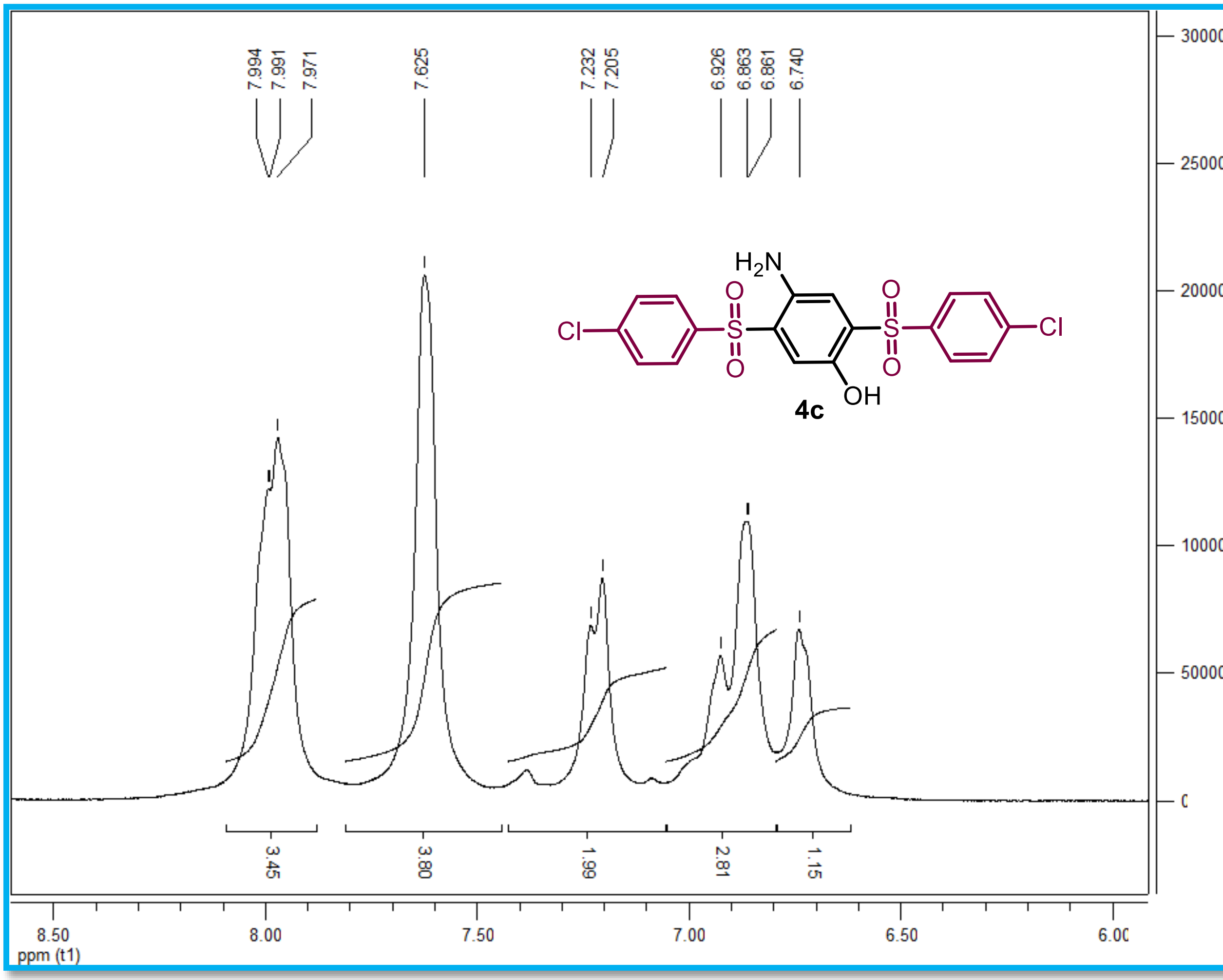
IR spectrum of 4c



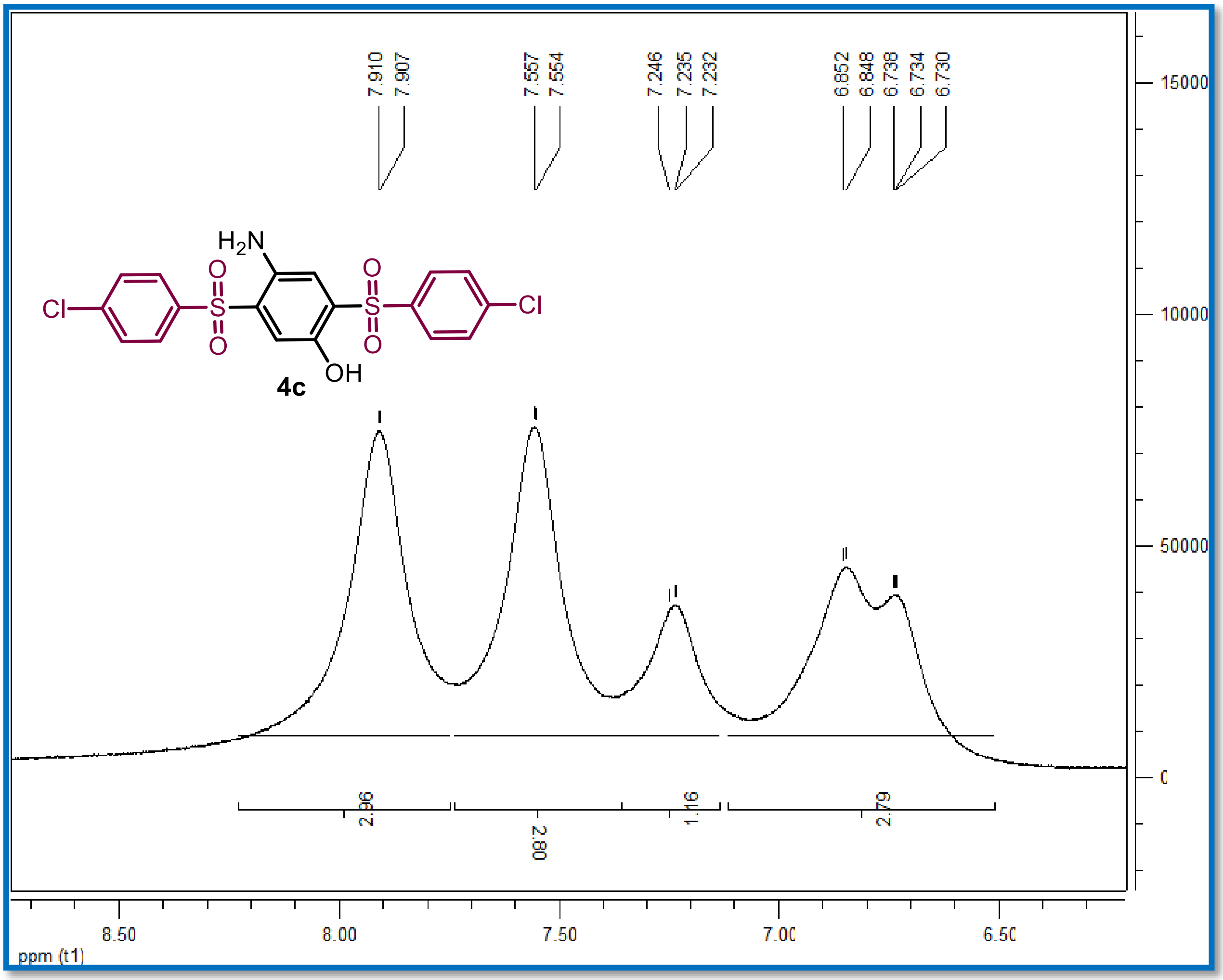
[1]H NMR spectrum of 4c



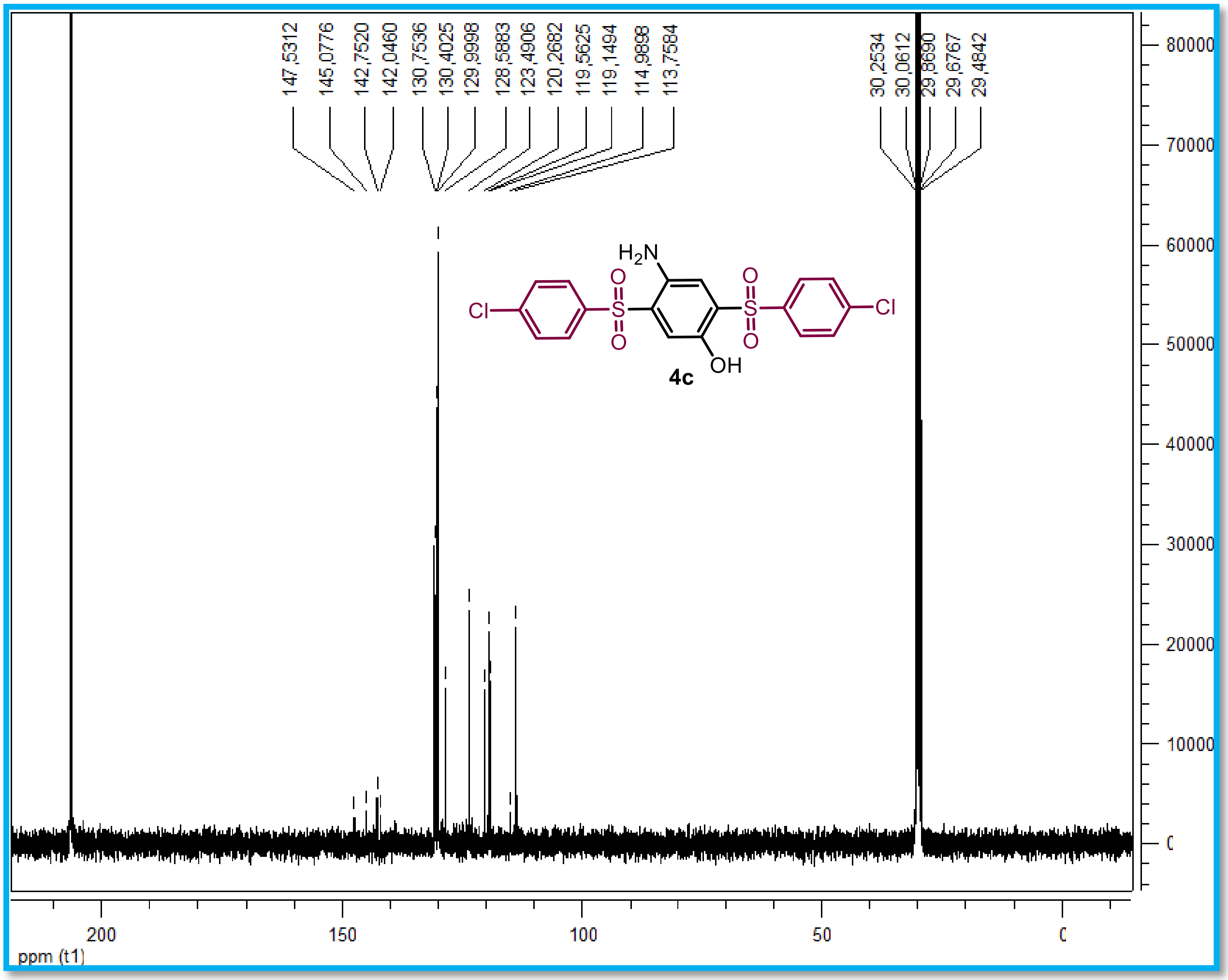
Expanded ^{1}H NMR spectrum of 4c



Expanded ^{1}H NMR spectrum of 4c (with D_2O)



[13]C NMR spectrum of 4c



MS spectrum of 4c