Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for

Copper catalysed synthesis of unsymmetrical diaryl sulfones from arenediazonium salt and sodium *p*-toluenesulfinate

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Experimental section

Materials

All reagents were of analytical grade, purchased from S. D. Fine Chemicals Pvt. Ltd., Sigma Aldrich and used without further purification. The solvents were HPLC and AR grade. The crude product was purified by column chromatography (silica gel; PE–EtOAc, 90:10). The products were characterized by MS analysis (GC-MS Shimadzu QP 2010), ^{13}C-NMR and ^{1}H-NMR analysis.

Preparation of Arenediazonium Salts:

Diazonium salt was prepared as per reported process.[1] To a 250 mL flask containing 12.5 mL of Conc. HCl and 12.5 mL of water was added 4.65 gm of aniline. Aniline hydrochloride crystals were formed at 0−5 °C, and then 3.65 gm of sodium nitrite in 7.5 mL water was added drop wise, followed by addition of 7.6 gm of sodium tetrafluoroborate in 15 mL of water. The reaction mixture was allowed to stir for another 10 min at temperature below 5 °C. The arenediazonium salt solids were filtered out and then washed with 5 mL of 5% sodium tetrafluoroborate three times, followed by 5 mL of methanol.

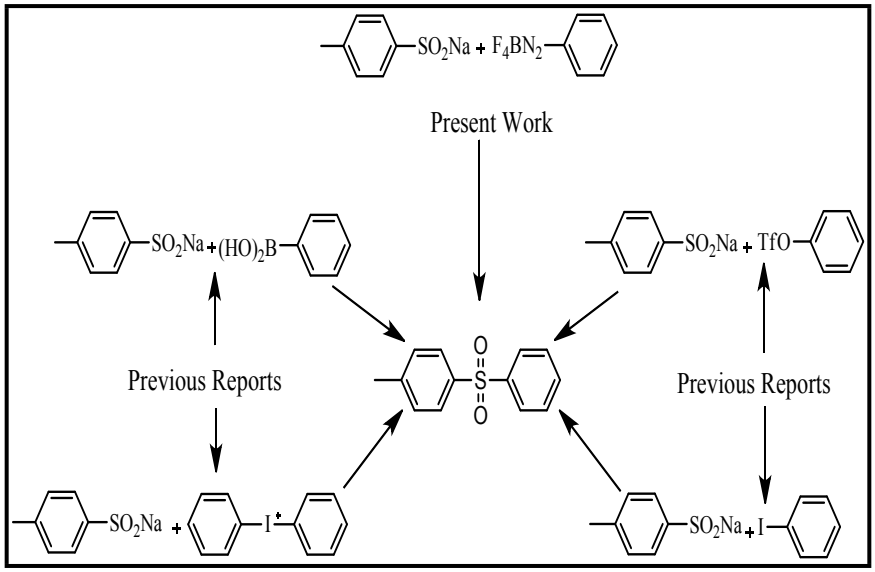


Fig. S1 The methods include various arylating agents for arylation of sulfones.

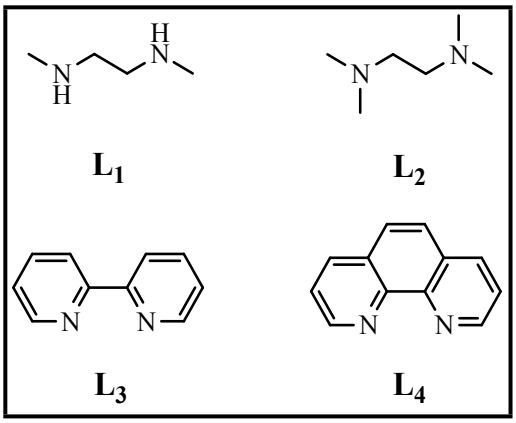


Fig. S2 Ligands screened for arylation of sulfones.

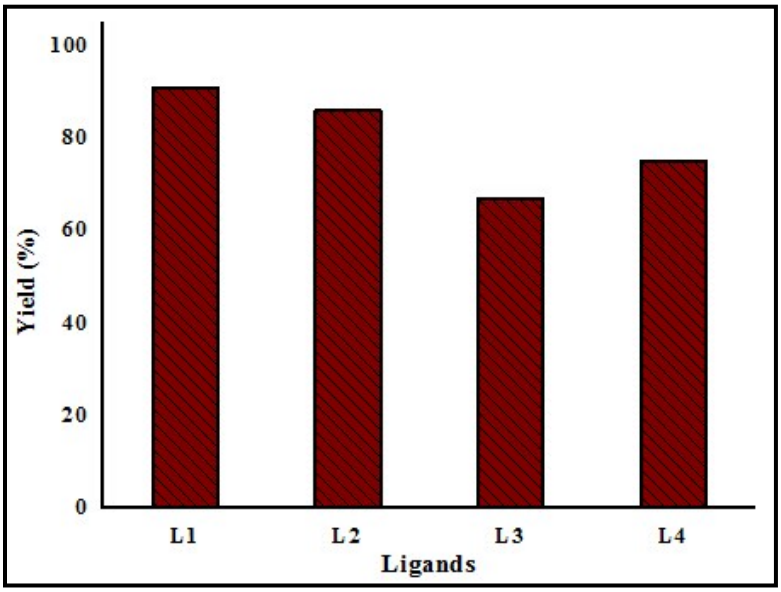


Fig. S3 The graph of Isolated yield (%) verses ligand $\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_3}$ and $\mathbf{L_4}$ screened for model reaction with CuI.

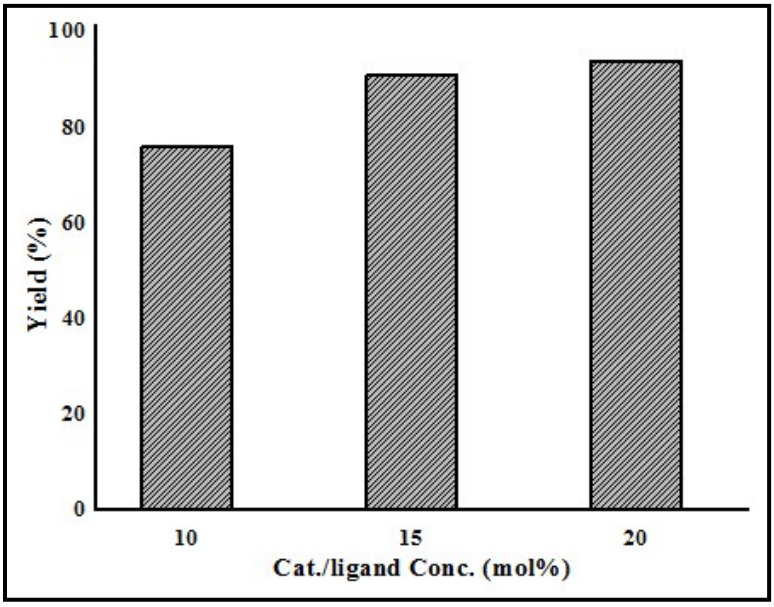


Fig. S4 The plot of isolated yield (%) verses catalyst/ligand concentrations screened for model reaction under the optimized parameters.

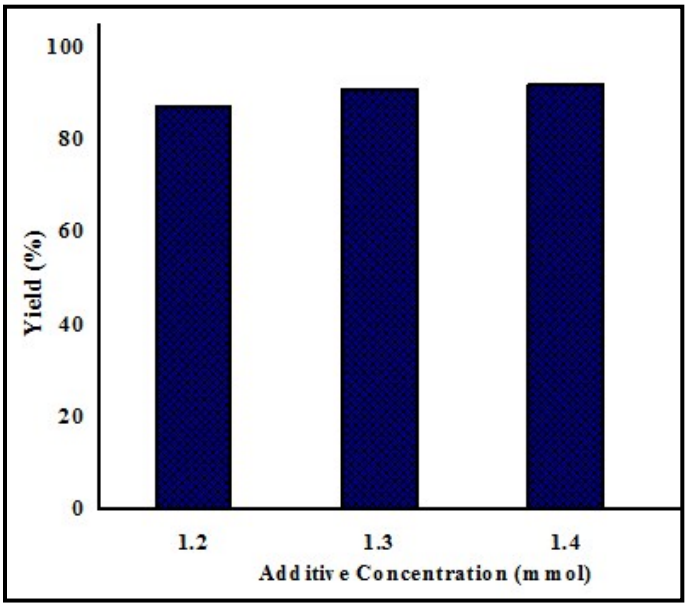


Fig. S5 The plot of isolated yield (%) verses additive concentrations screened for model reaction under the optimized parameters.

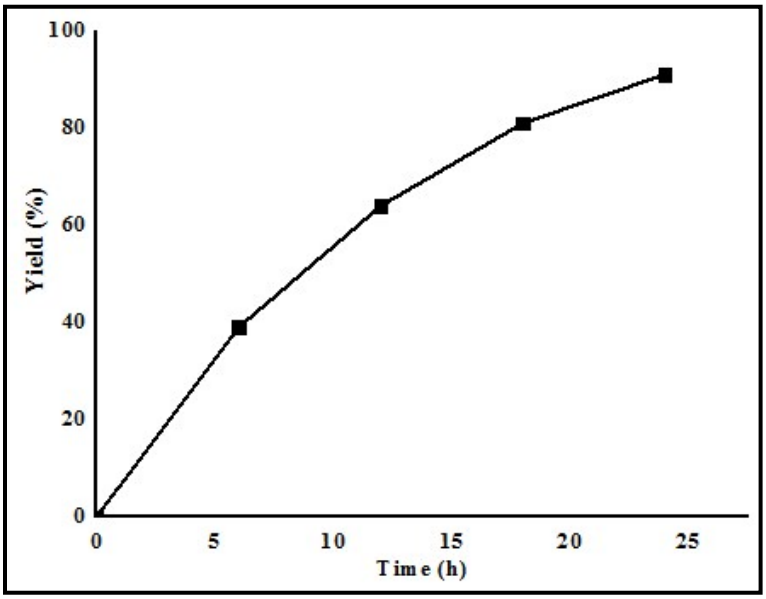
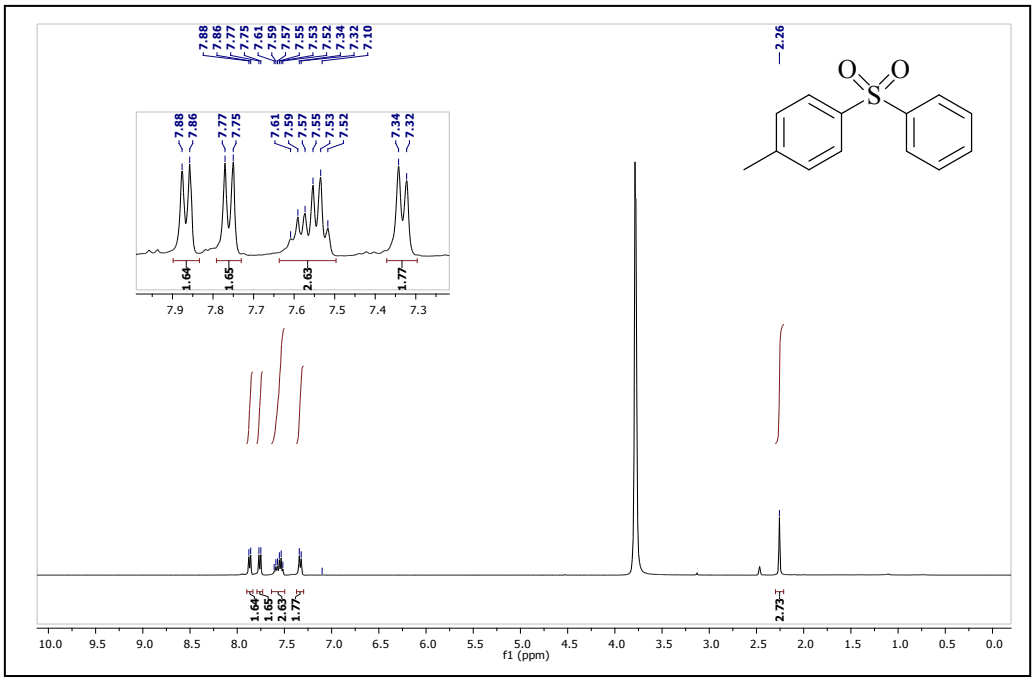


Fig. S6 The graph of isolated yield (%) verses time (h) for model reaction.

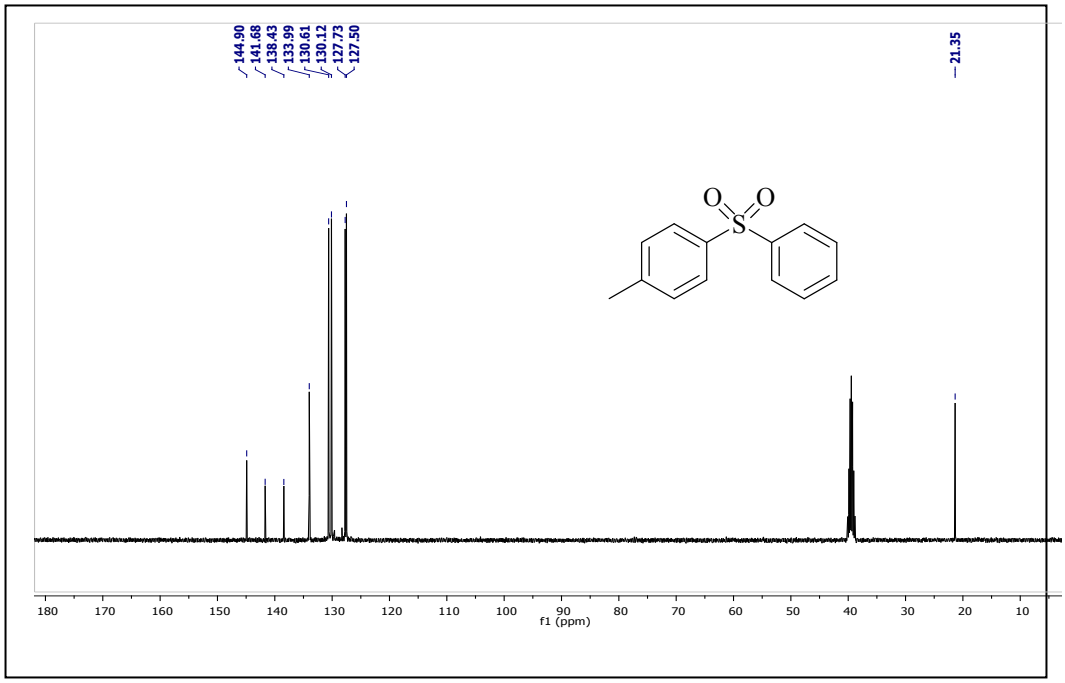
1. Table 2, entry 1

^{1}H NMR (400 MHz, DMSO) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.63 – 7.50 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.26 (s, 3H).



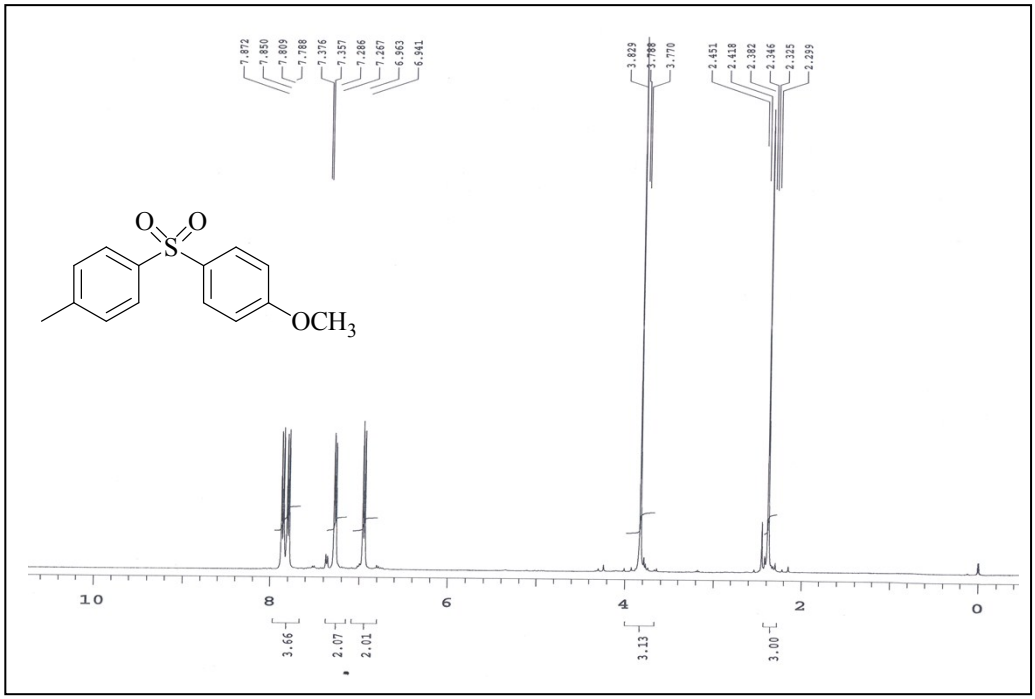
2. Table 2, entry 1

^{13}C NMR (100 MHz, DMSO): δ 144.90, 141.68, 138.43, 133.99, 130.61, 130.12, 127.73, 127.50, 21.35.



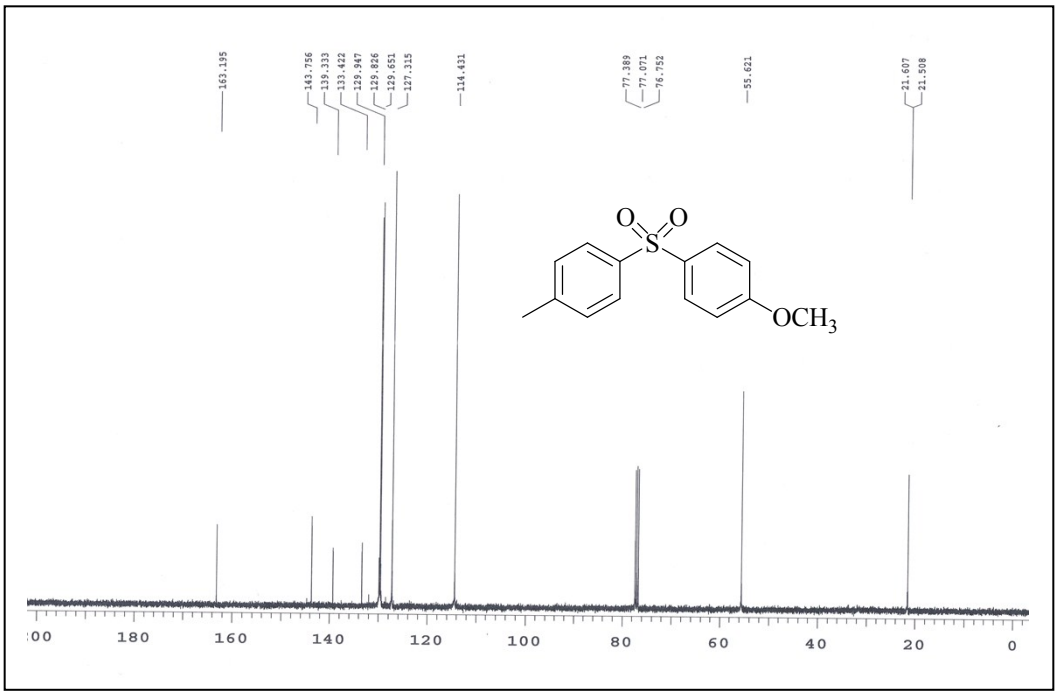
3. Table 2, entry 2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 3.78 (s, 3H), 2.34 (s, 3H).



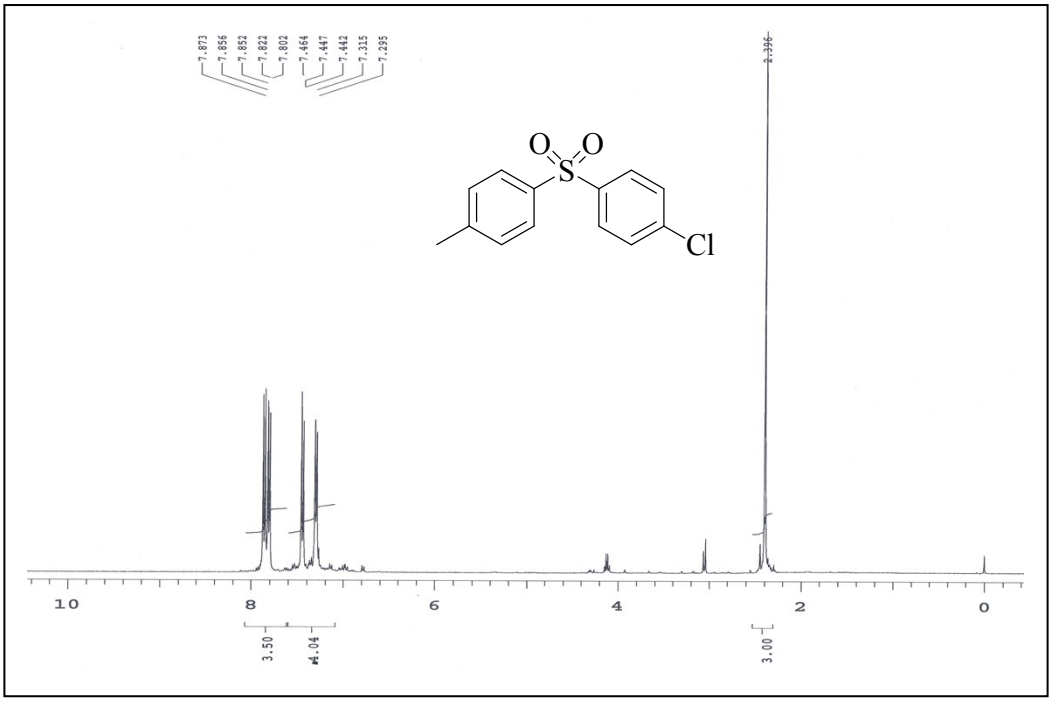
4. Table 2, entry 2

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.19, 143.75, 139.33, 133.42, 129.94, 129.82, 129.65, 127.31, 114.43, 55.62, 21.50.



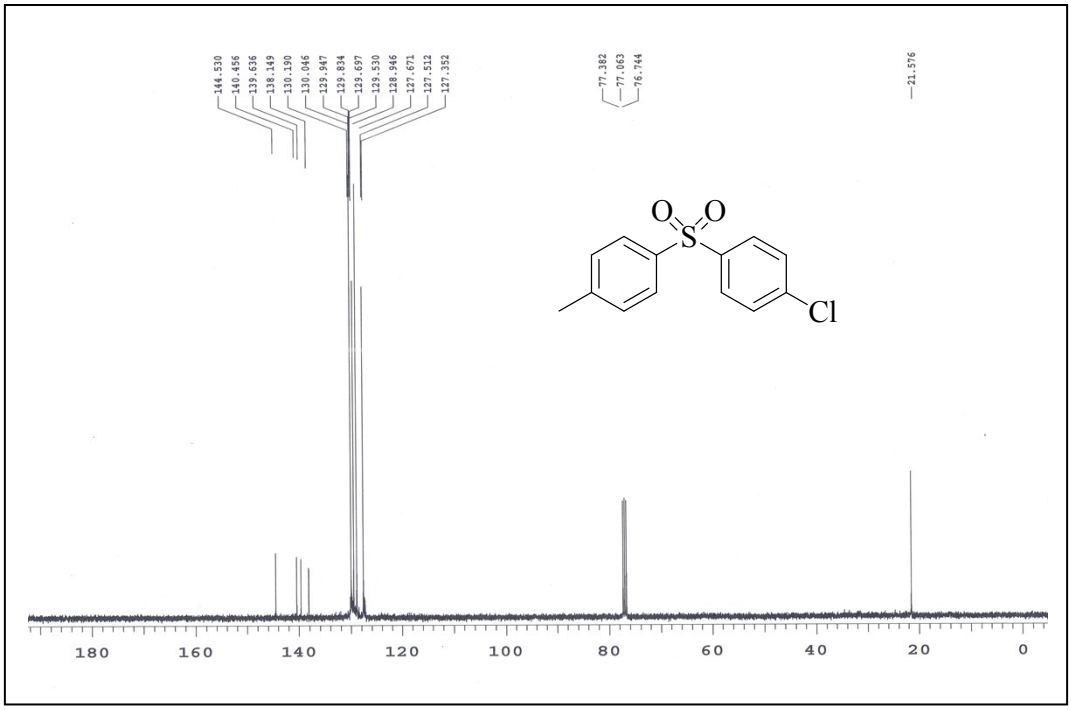
5. Table 2, entry 3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 7.9 Hz, 2H), 7.44 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H).



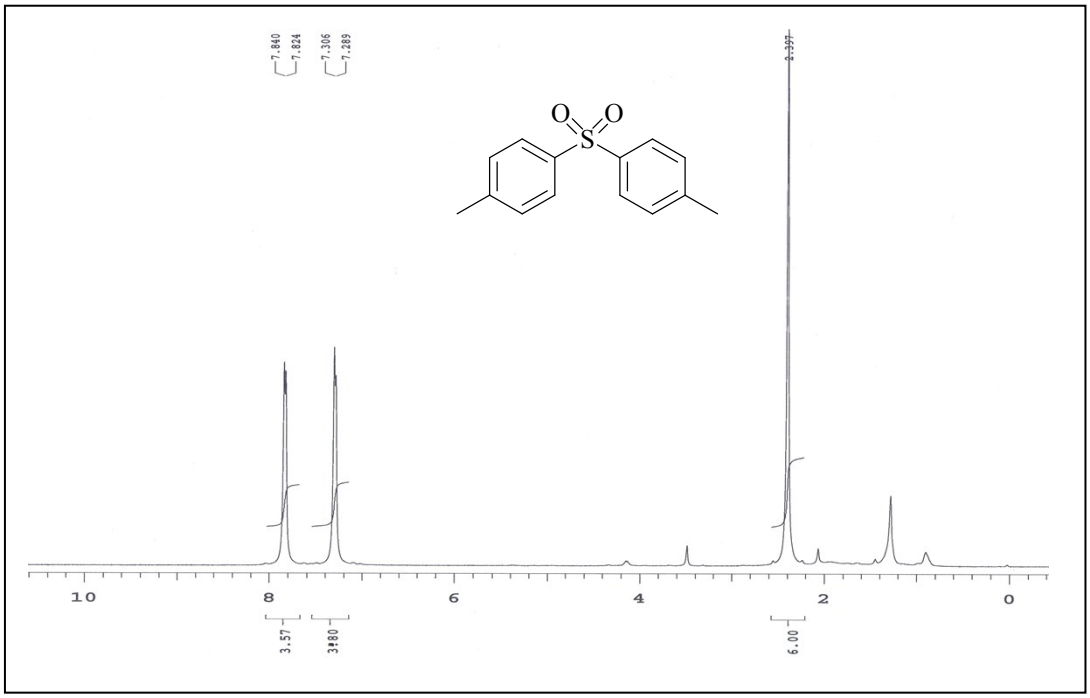
6. Table 2, entry 3

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.53, 140.45, 139.63, 138.14, 130.19, 130.04, 129.83, 129.53, 128.94, 127.67, 127.51, 127.35, 21.57.



7. Table 2, entry 5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 4H), 7.28 (d, J = 8.5 Hz, 4H), 2.39 (s, 6H).

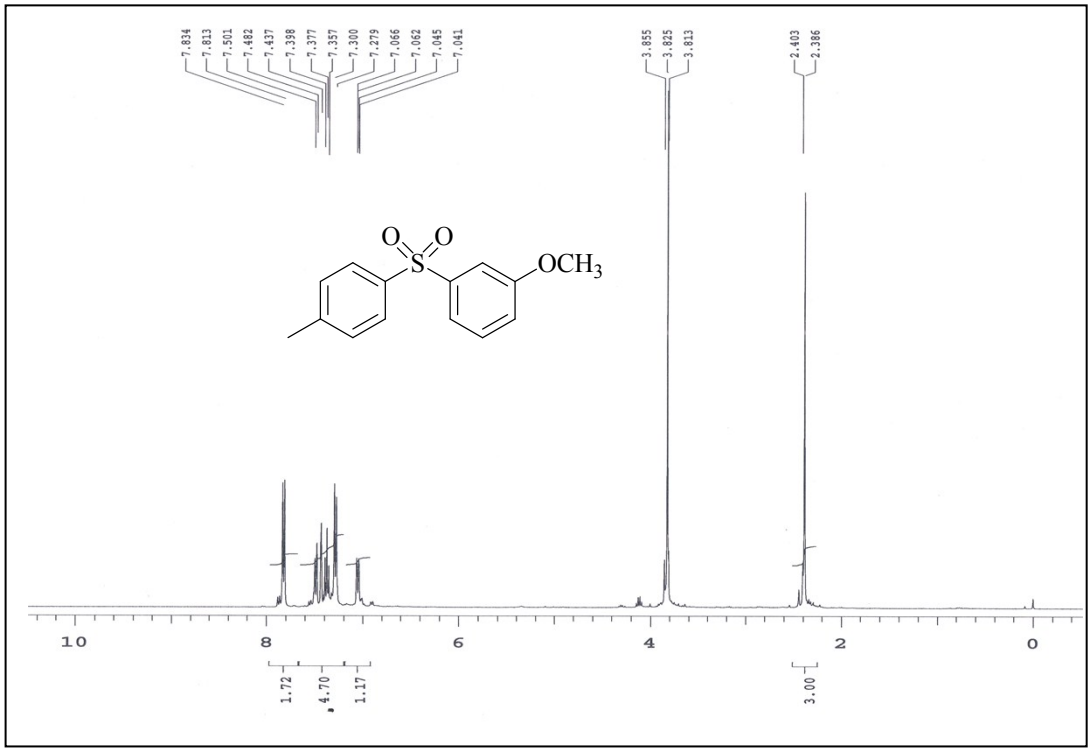


8. Table 2, entry 5

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.94, 138.94, 129.84, 127.49, 21.51.

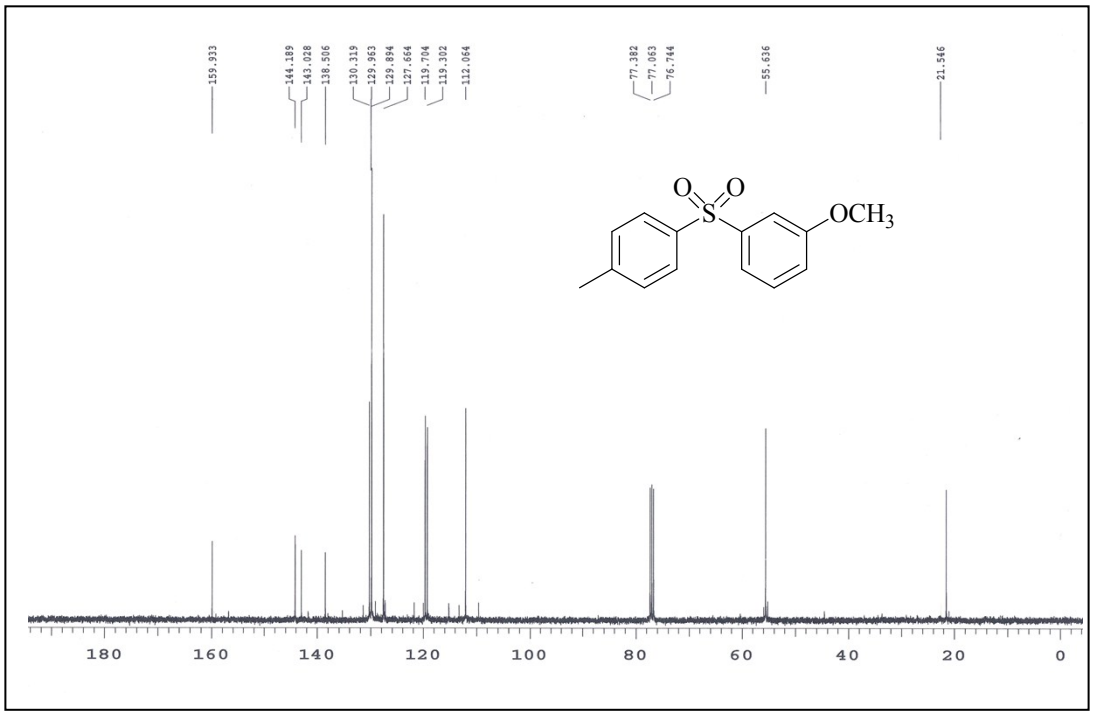
9. Table 2, entry 6

^{1}H NM R (400 MHz, $CDCl_3$) δ 7.81(d, *J* = 8.3 Hz, 2H), 7.50-7.27 (m, 5H), 7.04 (m, 1H), 3.81 (s, 3H), 2.38 (s, 3H).



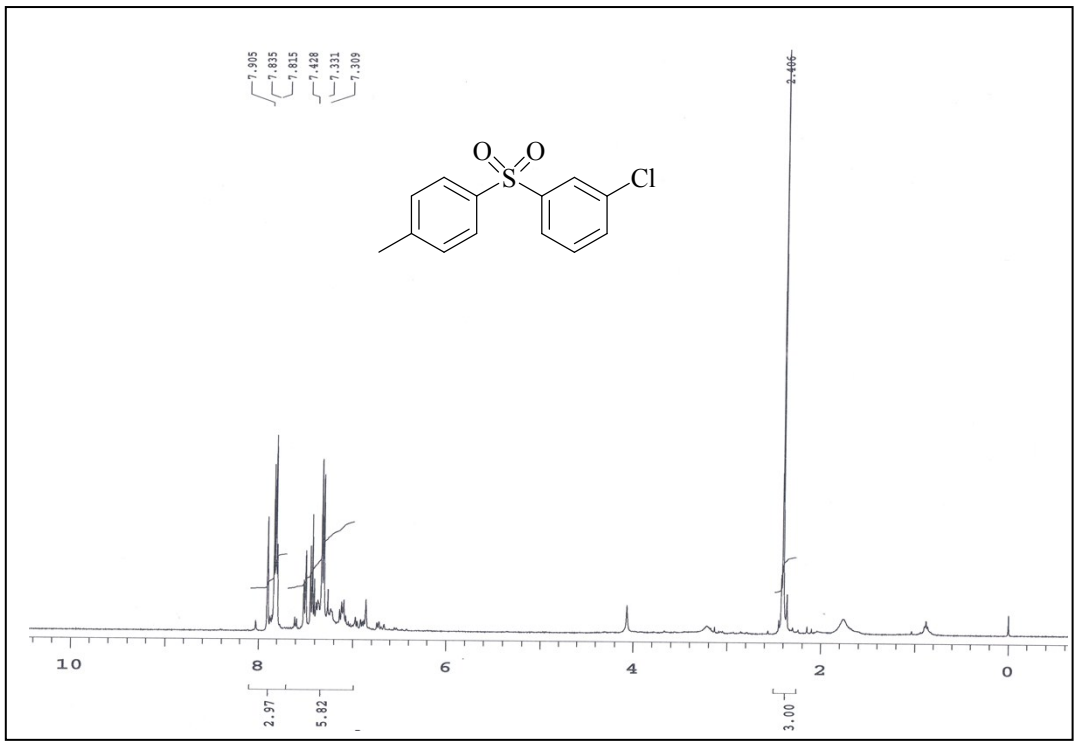
10. Table 2, entry 6

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.93, 144.18, 143.02, 138.50, 130.31, 129.96, 129.89, 127.66, 119.70, 119.30, 112.06, 55.63, 21.54.



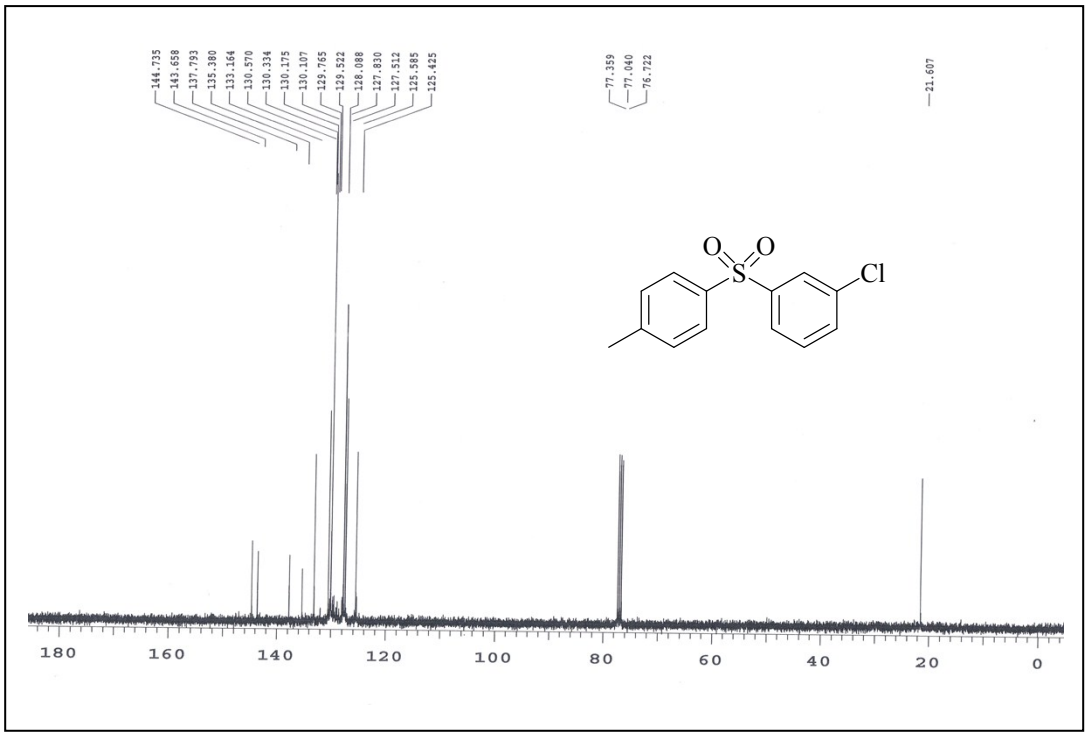
11. Table 2, entry 7

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.81 (m, 2H), 7.42-7.30 (m, 6H), 2.40 (s, 3H).



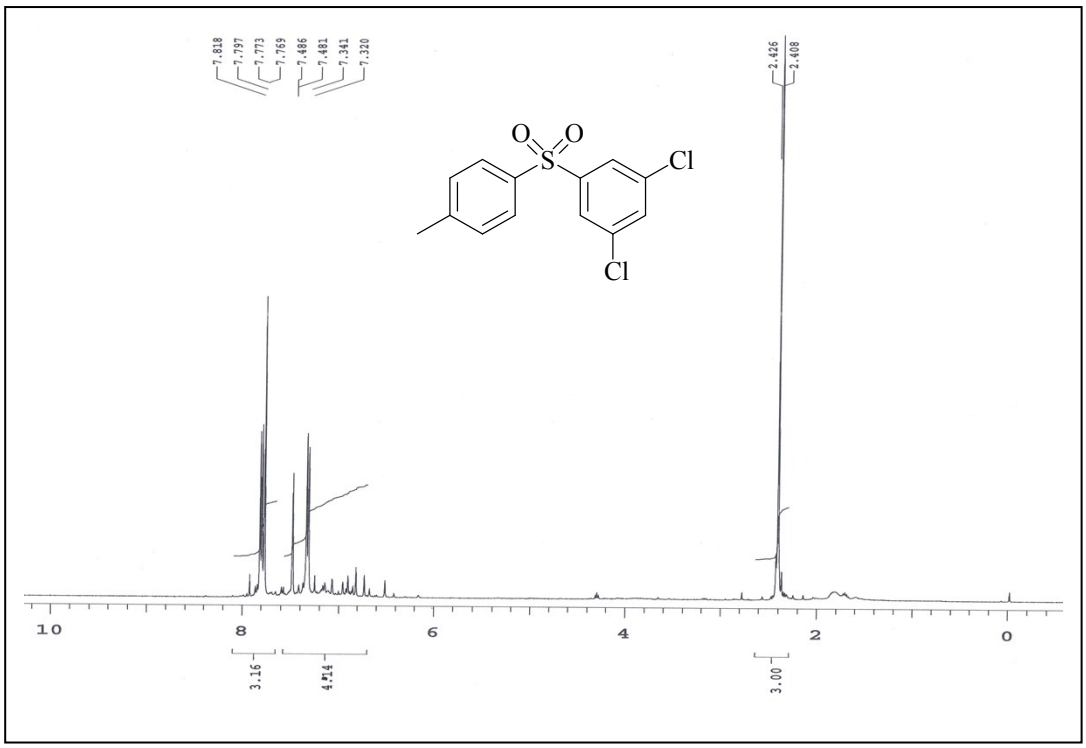
12. Table 2, entry 7

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.73, 143.65, 137.79, 135.38, 133.16, 130.57, 130.17, 129.52, 127.83, 127.51, 125.58, 21.60.



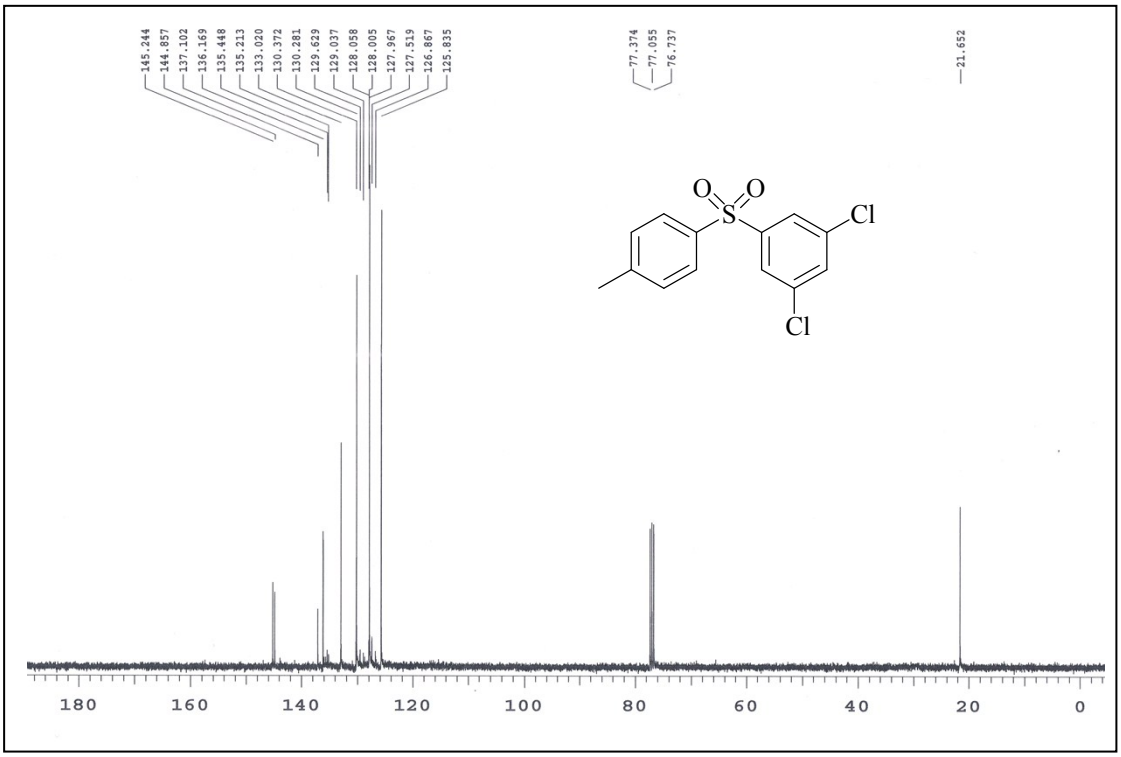
13. Table 2, entry 12

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 3H), 7.48-7.32 (m, 4H), 2.40 (s, 3H).



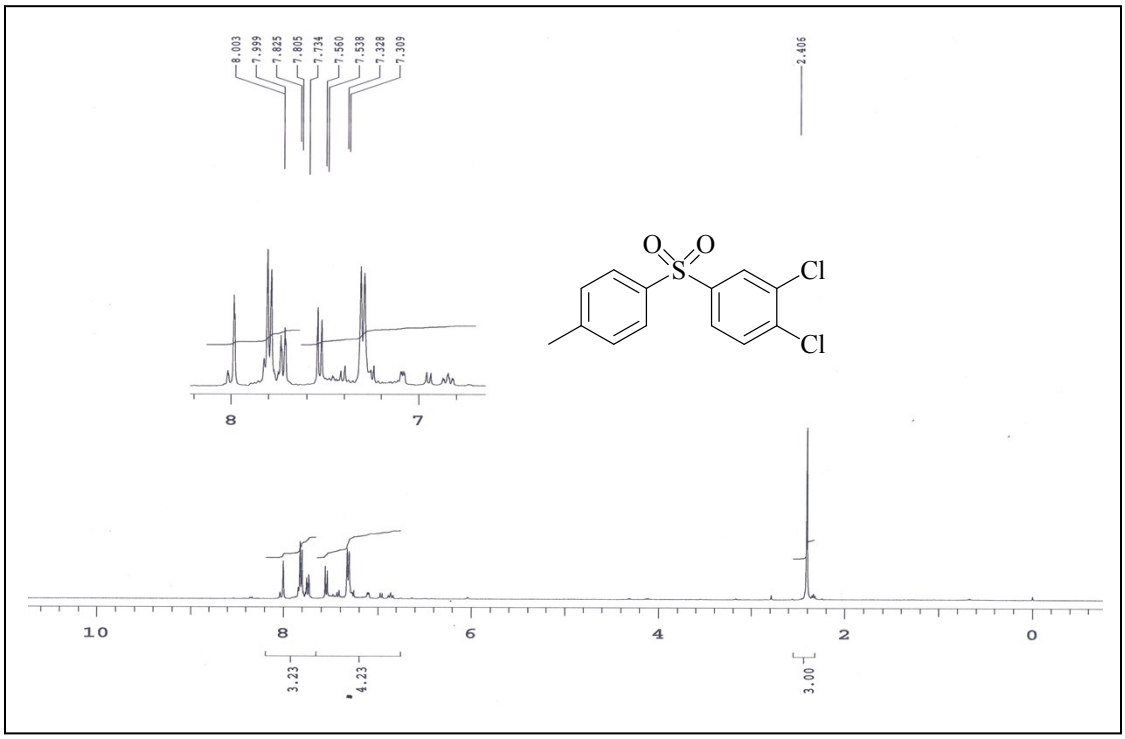
14. Table 2, entry 12

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.24, 144.85, 137.10, 136.16, 133.02, 130.37, 130.28, 129.62, 128.00, 127.96, 126.86, 125.83, 21.65.



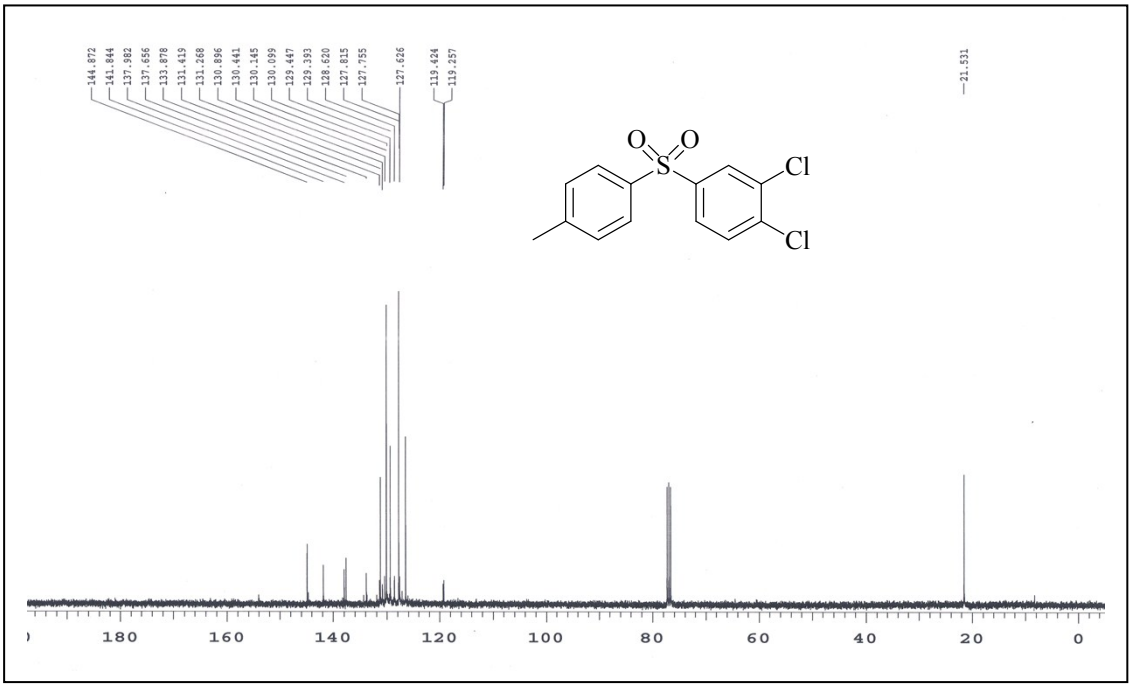
15. Table 2, entry 13

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 - 7.73(m, 3H), 7.56 - 7.53(d, 2H), 7.32 –7.30 (d, 2H), 2.40 (s, 3H).

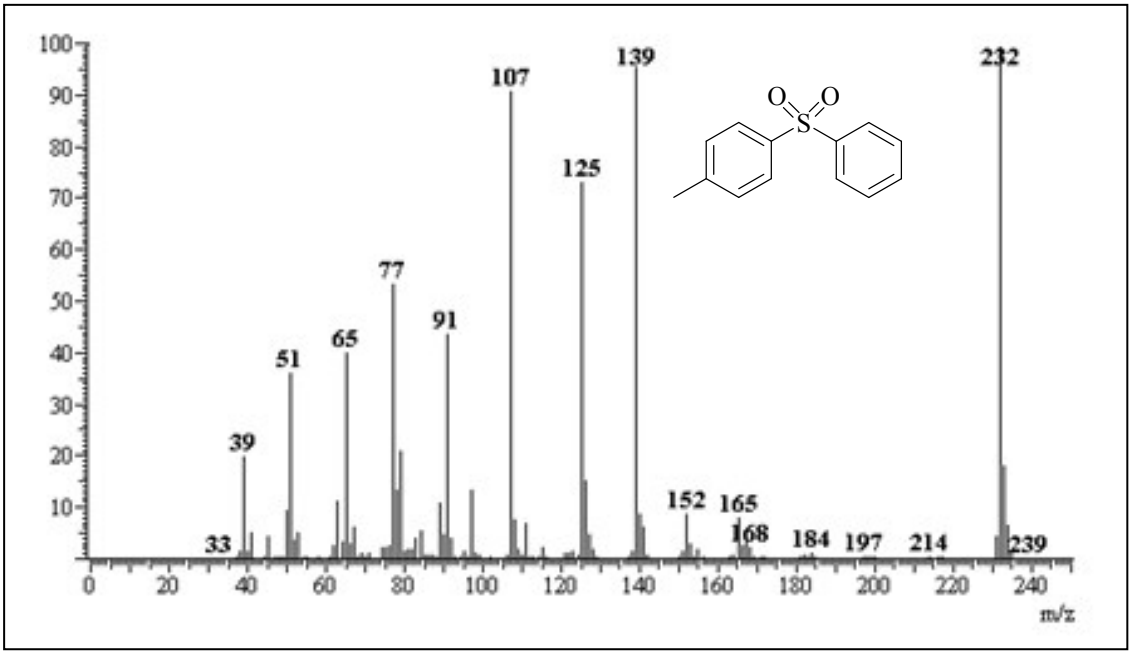


16. Table 2, entry 13

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.87, 141.84, 137.98, 137.65, 131.41, 130.89, 130.44, 130.09, 129.44, 128.62, 127.81, 127.62, 21.53.

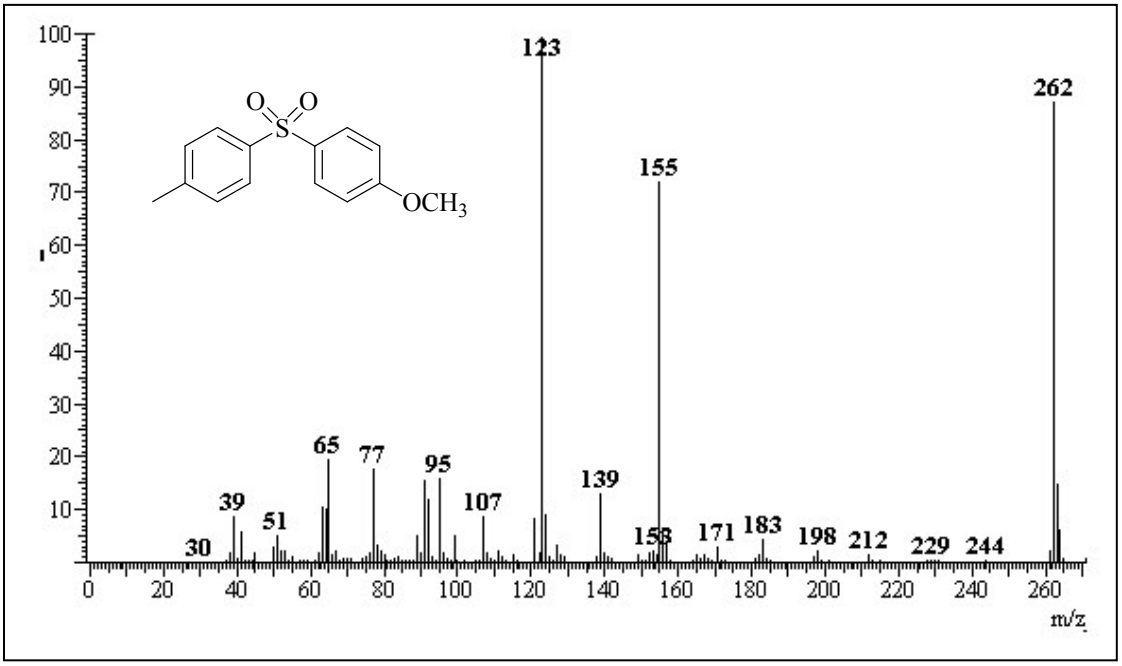


17. Table 2, entry 1



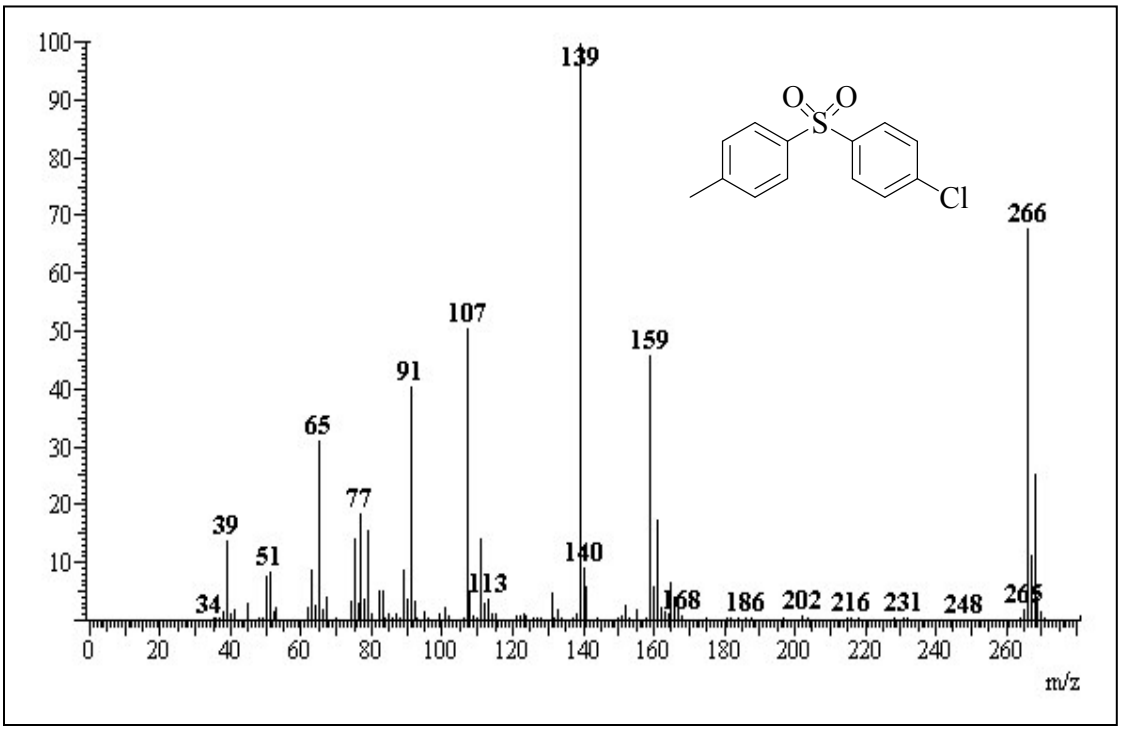
MS (m/z/rel.int.): 232(M^+): 51(35.0), 77(55.2), 107(93.1), 139(100), 232(79.9).

18. Table 2, entry 2



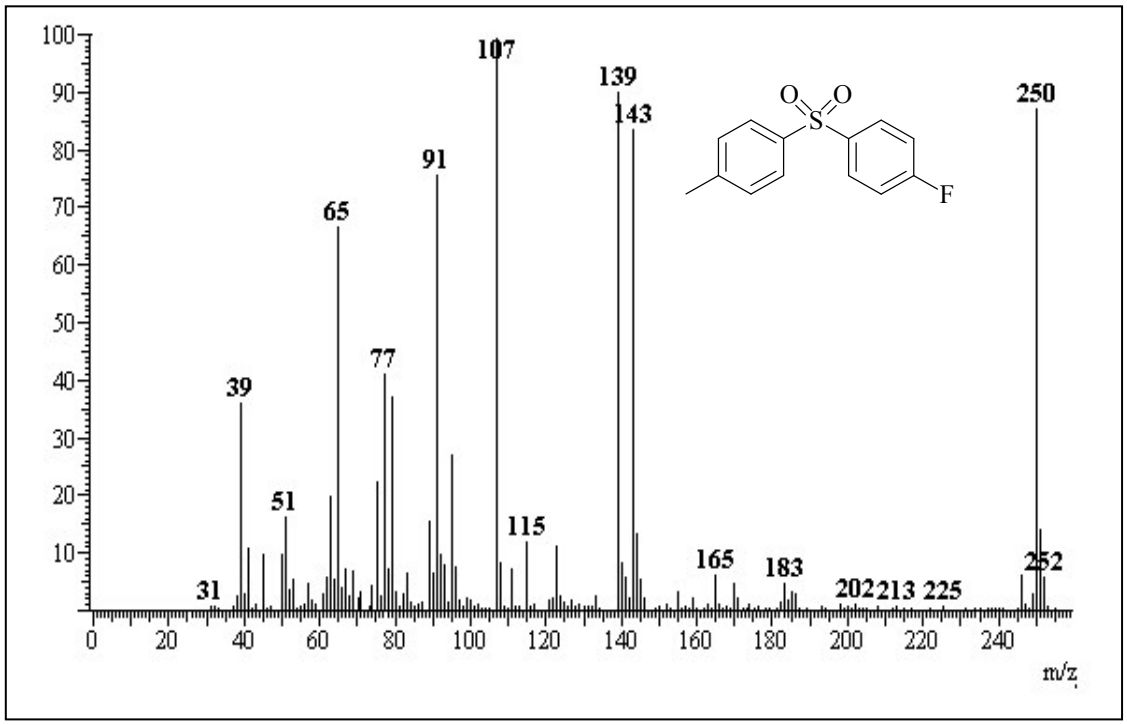
MS (m/z/rel.int.): 262(M^+): 65(21.3), 77(19.3), 123(100), 155(68.5), 262(77.7).

19. Table 2, entry 3



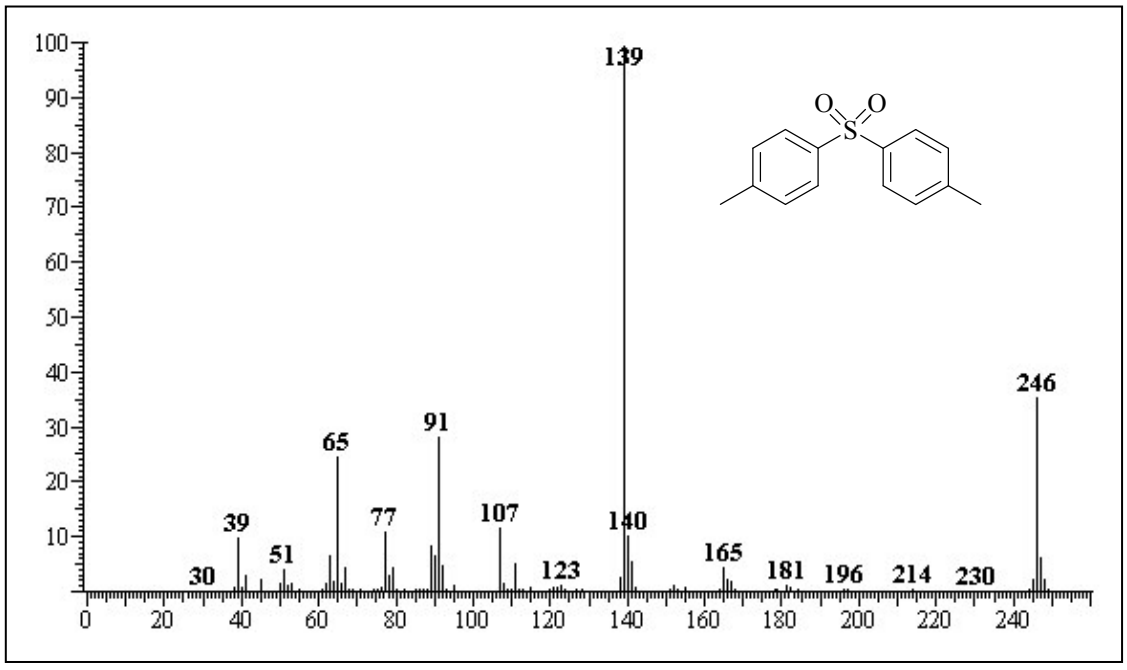
MS (m/z/rel.int.): 266(M^+): 91(43.8), 107(52.3), 139(100), 158(41.3), 266(47.7).

20. Table 2, entry 4



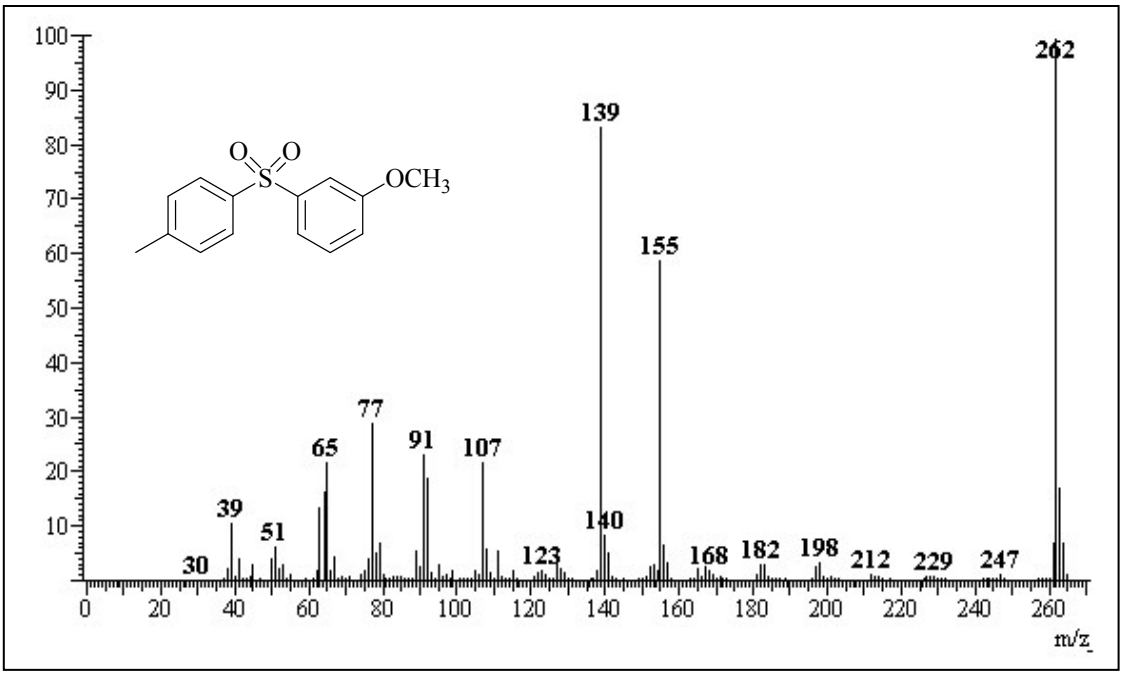
MS (m/z/rel.int.): 250(M^+): 65(68.2), 79(38.2), 91(74.2), 107(100), 143(88.1), 250(77.2).

21. Table 2, entry 5



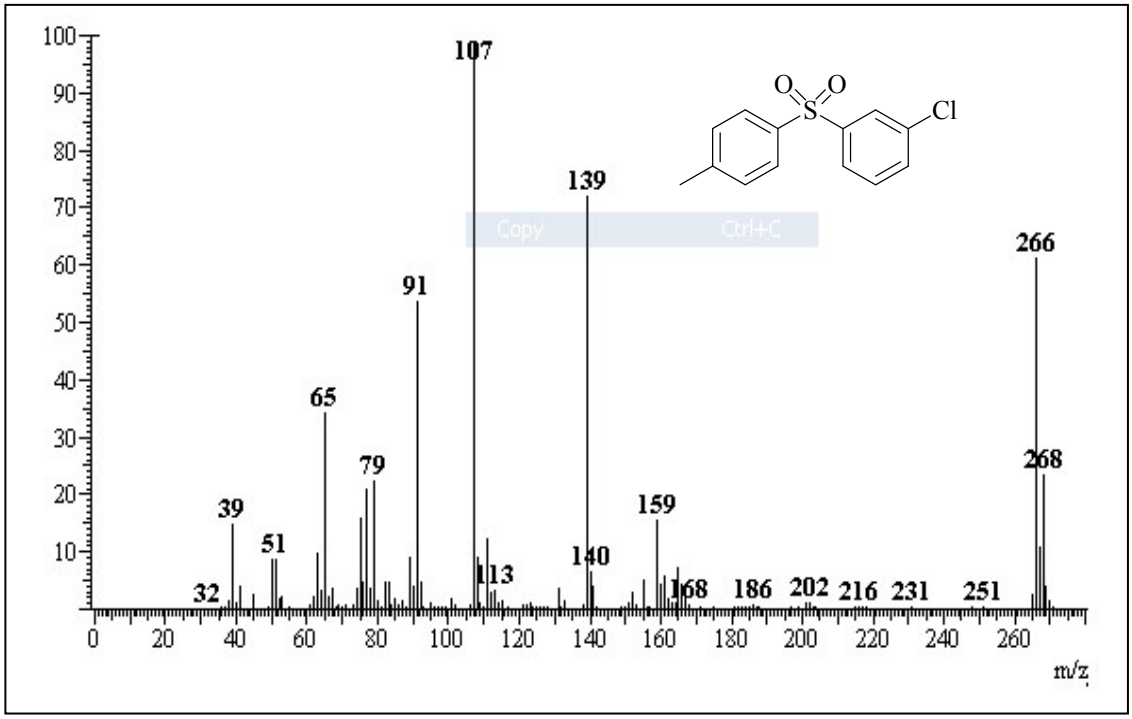
MS (m/z/rel.int.): 246(M^+): 65(24.2), 91(28.1), 107(10.9), 139(100), 246(34.6).

22. Table 2, entry 6



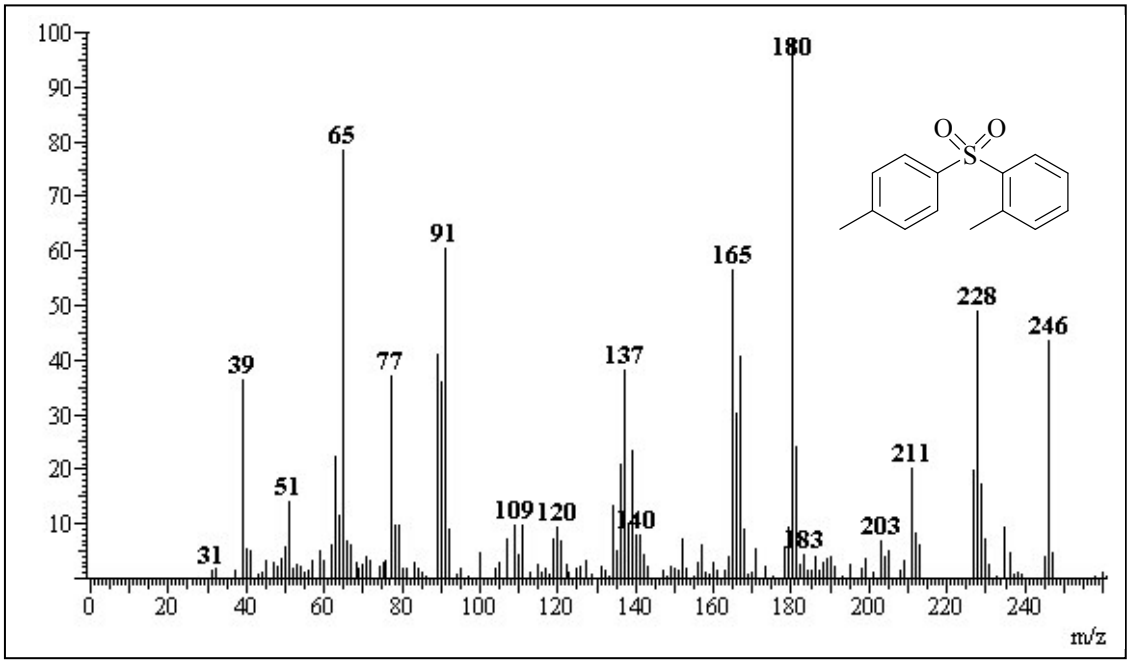
MS (m/z/rel.int.): 262(M^+): 77(31.4), 91(25.5), 139(88.0), 155(60.6), 262(100)

23. Table 2, entry 7



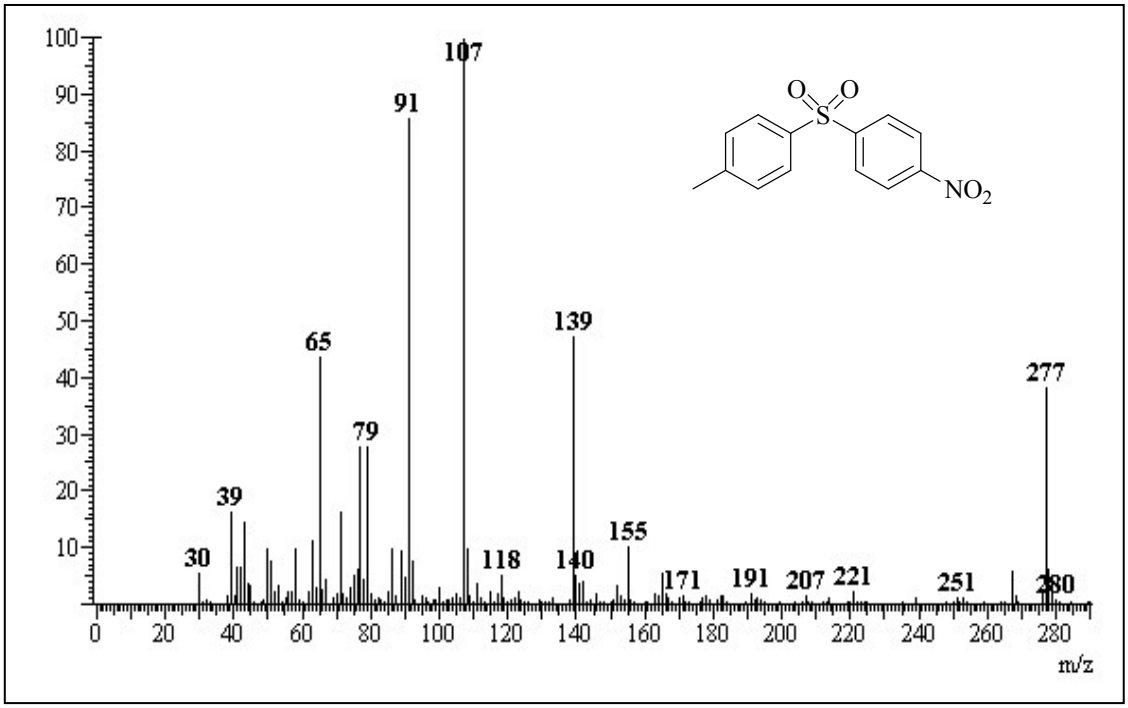
MS (m/z/rel.int.): 268(M^+): 65(34.1), 91(53.4), 107(100), 139(70.2), 265(60.1), 267(22.5).

24. Table 2, entry 8



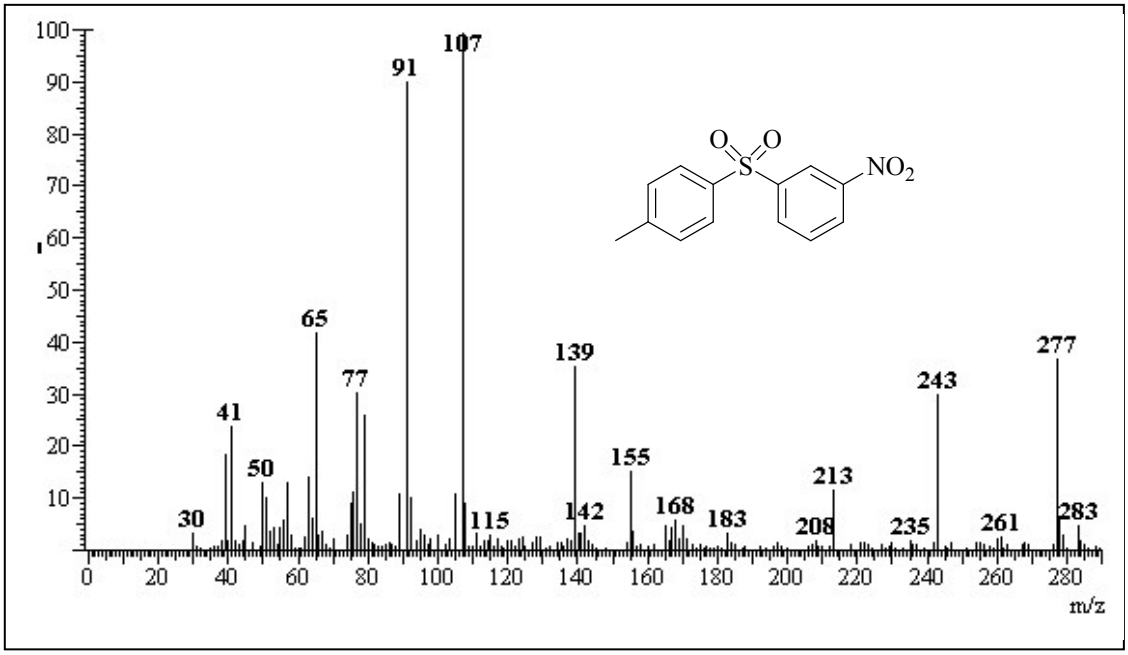
MS (m/z/rel.int.): 246(M^+): 65(100), 77(48.0), 91(74.3), 180(74.0), 228(60.0), 246(31.0).

25. Table 2, entry 9



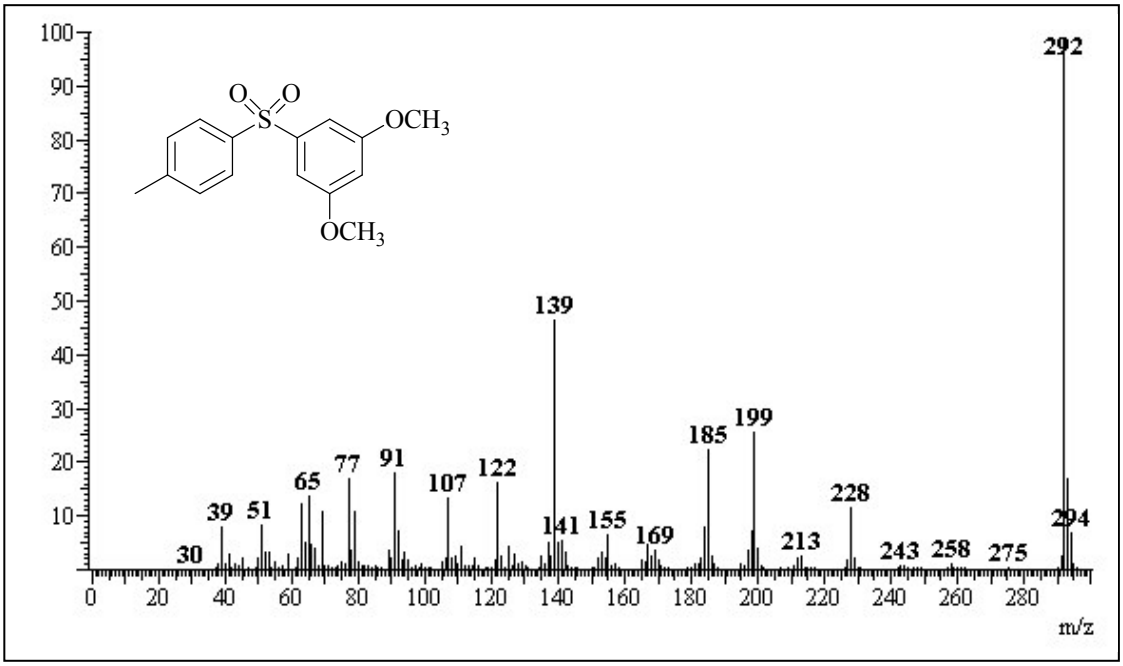
MS (m/z/rel.int.): 277(M^+): 65(44.5), 91(86.3), 107(100), 139(50.1), 277(38.8).

26. Table 2, entry 10



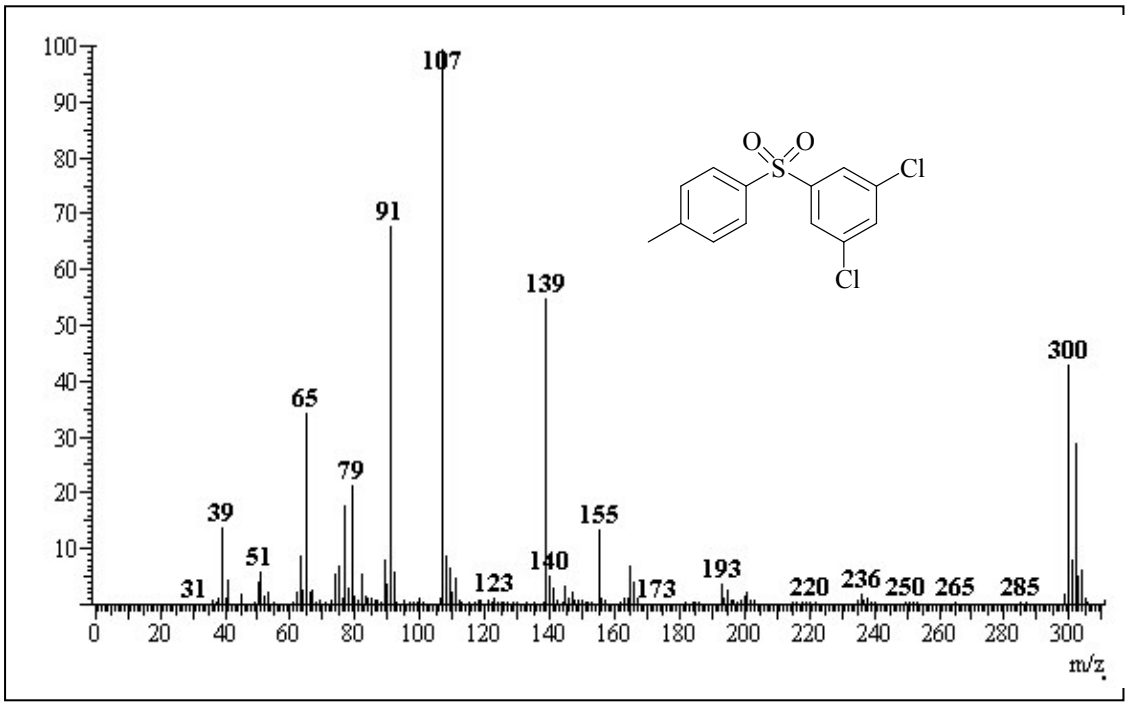
MS (m/z/rel.int.): 277(M^+): 41(33.8), 79(46.4), 91(90.8), 107(100), 277(36.2).

27. Table 2, entry 11



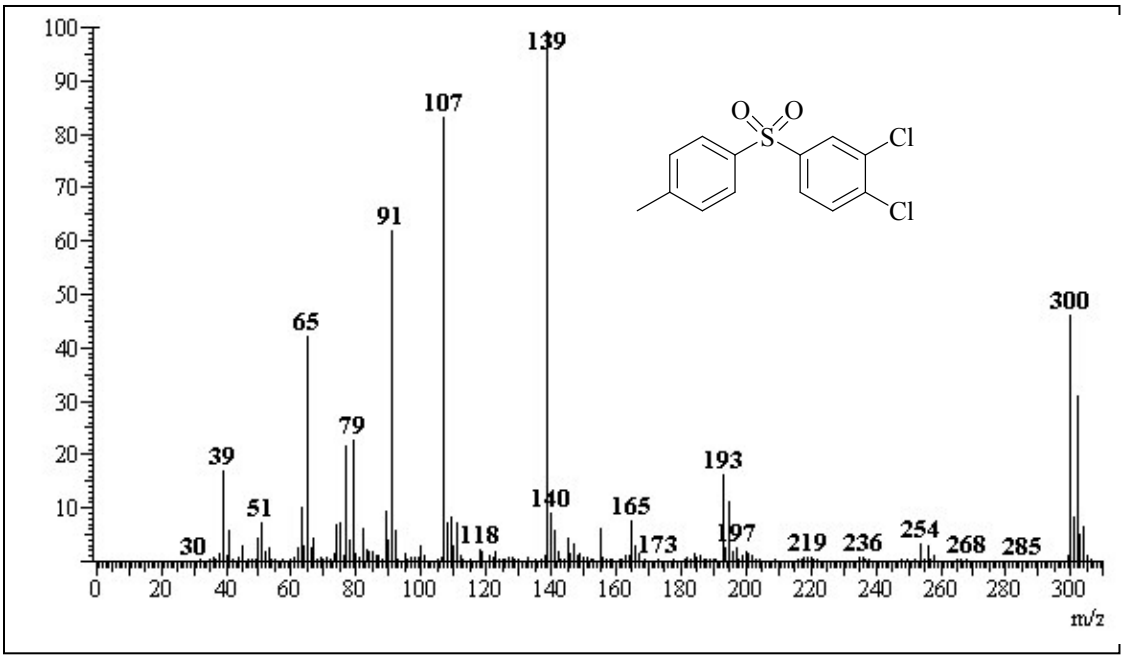
MS (m/z/rel.int.): 292(M^+): 65(16.2), 91(20.6), 139(48.8), 199(25.7), 292(100).

28. Table 2, entry 12



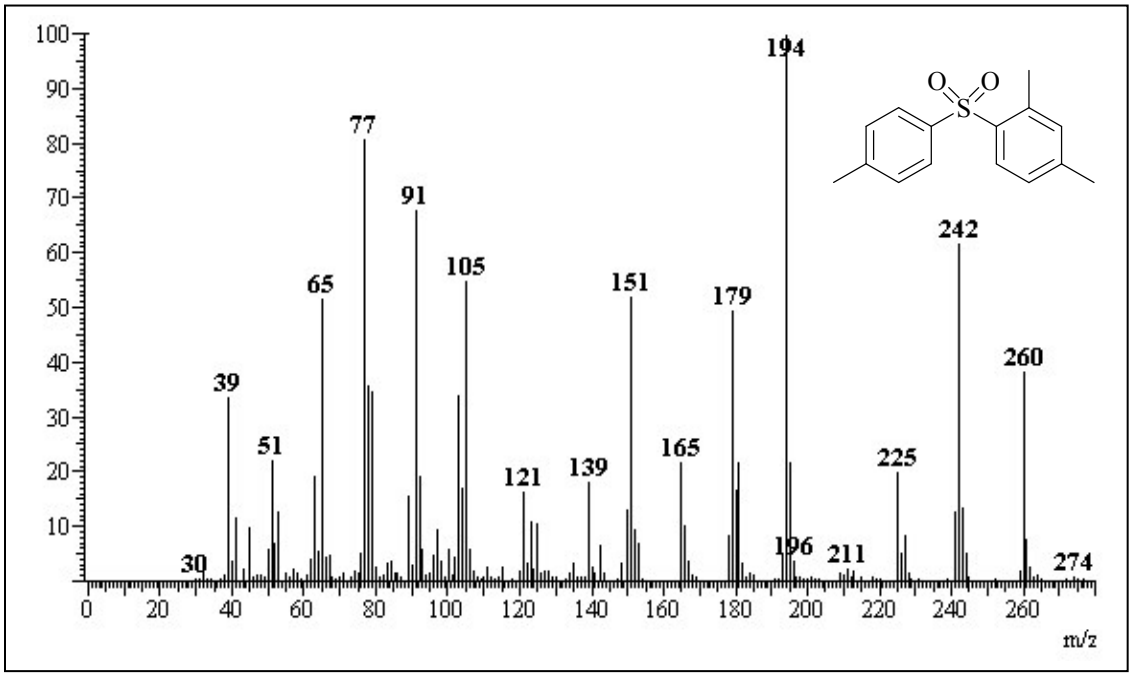
MS (m/z/rel.int.): 302(M^+): 65(37.7), 79(22.2), 91(70.4), 107(100), 302(20.6).

29. Table 2, entry 13



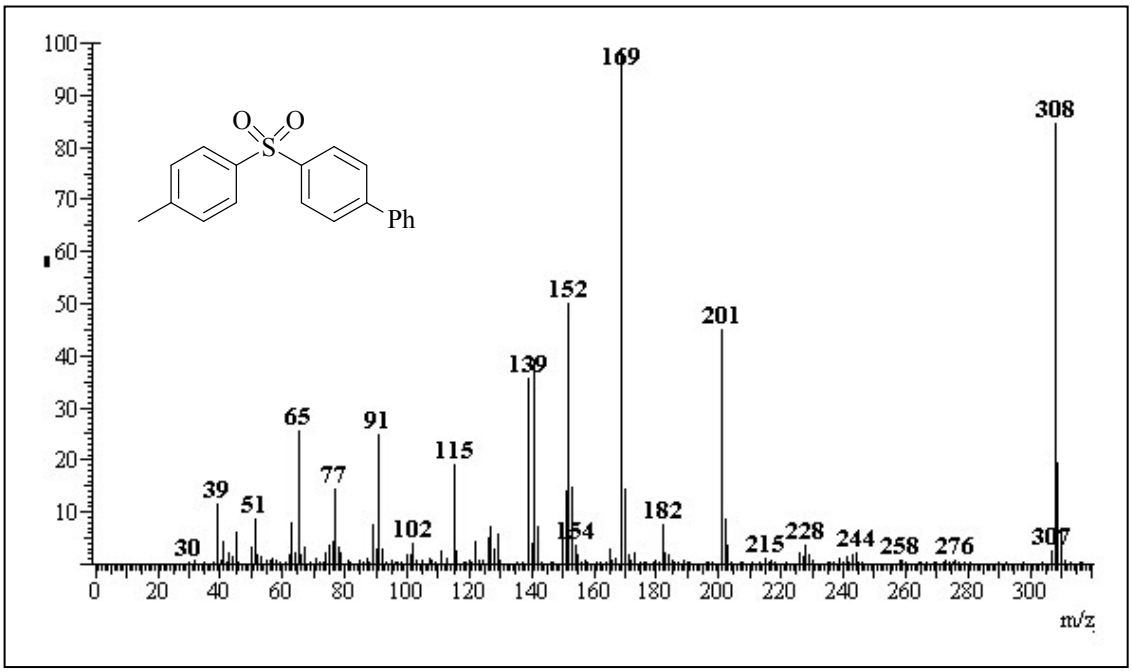
MS (m/z/rel.int.): 302(M^+): 65(43.6), 91(63.9), 107(79.7), 139(100), 300(35.1), 302(24.6).

30. Table 2, entry 14



MS (m/z/rel.int.): 260(M^+): 39(46.0), 77(89.9), 91(80.2), 151(52.7), 194(100), 260(37.0).

31. Table 2, entry 15



MS (m/z/rel.int.): 308(M^+): 65(26.3), 141(41.0), 169(100), 200(43.9), 308(87.1).

Reference:

1. K. Cheng, C. Wang, Y. Ding, Q. Song, C. Qi and Xian-Man Zhang, *J. Org. Chem*., 2011, **76**, 9261.