

Photochemical study of electrocyclization of 4-aryl-5-hetarylimidazolones for information optical recording

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1. General

Unless otherwise noted, all the reagents were purchased from commercial suppliers, and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 MHz and Bruker AV 400 MHz spectrometers in $\text{DMSO-}d_6$, chemical shift (δ) values for ^1H and ^{13}C NMR spectra are reported in parts per million (ppm) with the solvent resonance as the internal standard. High-resolution mass spectra (HRMS) were measured on the Bruker micrOTOF II instrument using electrospray ionization (ESI). IR spectra were registered on a Shimadzu IRAffinity-1 FTIR spectrophotometer in KBr pellets. The melting points were determined on a Kofler hot stage. UV irradiation was carried out by a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W).

2. General synthetic procedure

General procedure for the preparation of 1,3-dimethyl-1,3-dihydro-2H-imidazol-2-ones (7a,b and 9). A mixture of appropriate arylglyoxal (1 mmol), 4-hydroxycoumarin (1 mmol), and *N,N'*-dimethylurea (1 mmol) in MeOH (6 ml) was refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was recrystallized from 2-propanol to give the corresponding product.

General procedure for the preparation of photoproducts 8a, 8b and 10. In all cases, *N*-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich, ACS reagent) was used. A solution of compound **7a,b** or **9** (0.5 mmol) in NMP (5 ml) was irradiated with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) for 6–20 h at 20–25 °C. The reaction mixture was poured into water (100 ml), and the resulting precipitate was filtered off and recrystallized from MeOH to give the corresponding products **8a,b** and **10**.

3 General procedure for photochemical and photophysical studies of imidazolones 1-10.

Solutions were irradiated with the UV light from an L8253 xenon lamp of an LC-4 lighter (Hamamatsu) through the UFS-1 light filter. Spectral kinetic measurements were carried out on a Cary 60 bio spectrophotometer (Varian) in a quartz cell with a pathlength of 1 cm. The concentration of solutions was $C = 4 \times 10^{-5}$ M. The fluorescence characteristics were measured on a CARY ECLIPSE spectrofluorimeter (Varian) in a quartz cell with a pathlength of 1 cm. The concentration of solutions was $C = 4 \times 10^{-5}$ M. The spectral width of the gap of excitation and transmission monochromators was 5 nm. The quantum yields of the photochemical transformations were determined using a standard procedure with the ferrioxalate actinometer ($\phi = 0.9$). The quantum intensity of the incident actinic radiation was 1.24×10^{16} quantum s^{-1} . The concentration of the starting compounds was $C = 1 \times 10^{-3}$ M, the volume of the irradiated solution was 8 ml, and the thickness of the solution layer in the reaction flask was 2 cm, which provided 100% absorption of actinic light.

4. Characterization data of products.

4-(4-Chlorophenyl)-1,3-dimethyl-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dihydro-2H-imidazol-2-one **7a**: white powder; yield 30%; mp 284–285°C; ¹H NMR (300 MHz, DMSO-d₆) δ 7.84 (d, *J* = 6.7 Hz, 1H), 7.72–7.66 (m, 1H), 7.45–7.24 (m, 6H), 3.14 (s, 3H), 3.01 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 165.25, 161.66, 153.30, 152.98, 133.32, 132.64, 130.17, 128.71, 127.95, 124.22, 124.10, 122.33, 116.45, 115.52, 110.87, 93.08, 28.66, 27.56. IR spectrum, ν, cm⁻¹: 3630, 3422, 2986, 2952, 2929, 2857, 2684, 2529, 2477, 2365, 1989, 1918, 1813, 1701, 1699, 1674, 1653, 1608, 1556, 1493, 1460, 1423, 1400, 1392, 1331, 1285, 1260, 1228, 1205, 1176, 1155, 1100, 1091, 1031, 1011, 996, 915, 897, 869, 835, 765, 737, 596, 514. HRMS: Calculated for C₂₀H₁₅ClN₂O₄ [M+H]⁺: 383.0793. Found: 383.0788.

4-[5-(1,3-Dimethyl-4-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxo-2,3-dihydro-1H-imidazol-4-yl]benzotrile **7b**: white powder; yield 32%; mp > 300°C; ¹H NMR (300 MHz, DMSO-d₆) δ 7.85 (d, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.72–7.64 (m, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.41–7.32 (m, 2H), 3.20 (s, 3H), 3.02 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 165.47, 161.54, 153.40, 153.02, 133.84, 133.42, 132.52, 128.72, 124.25, 124.13, 122.10, 118.57, 116.48, 115.50, 112.55, 110.00, 92.86, 28.97, 27.62. IR spectrum, ν, cm⁻¹: 3443, 3089, 2929, 2855, 2363, 2231 (CN), 1705, 1672, 1609, 1559, 1503, 1496, 1448, 1424, 1394, 1373, 1206, 1150, 1101, 1033, 996, 868, 842, 789, 759, 582, 558. HRMS: Calculated for C₂₁H₁₅N₃O₄ [M+H]⁺: 374.1135. Found: 374.1131.

1,3-Dimethyl-4-(4-hydroxy-2-oxo-2H-chromen-3-yl)-5-(thiophen-3-yl)-1,3-dihydro-2H-imidazol-2-one **9**: white powder; yield 30%; mp > 300°C; ¹H NMR (300 MHz, DMSO-d₆) δ 7.88 (d, *J* = 6.3 Hz, 1H), 7.68 (s, 1H), 7.59–7.29 (m, 4H), 7.03 (s, 1H), 3.21 (s, 3H), 2.99 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 165.18, 161.53, 153.13, 152.98, 133.26, 129.00, 127.28, 126.53, 124.20, 124.11, 123.64, 119.11, 116.42, 115.57, 110.24, 93.46, 28.71, 27.53. IR spectrum, ν, cm⁻¹: 3443, 3125, 3100, 3084, 2825, 2360, 1701, 1669, 1653, 1606, 1560, 1493, 1451, 1424, 1395, 1363, 1270, 1213, 1171, 1098, 1032, 995, 841, 786, 755, 738, 590, 579. HRMS: Calculated for C₁₈H₁₄N₂O₄S [M+Na]⁺: 355.0747. Found: 355.0739.

11-Chloro-1,3-dimethyl-1,3-dihydrodibenzo[3,4:5,6]isochromeno[7,8-d]imidazole-2,4-dione **8a**: yellow powder; yield 61%; mp > 300°C; ¹H NMR (400 MHz, DMSO-d₆) δ 8.76 (s, 1H), 8.64 (d, *J* = 9.3 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 9.2, 1H), 7.61–7.47 (m, 3H),

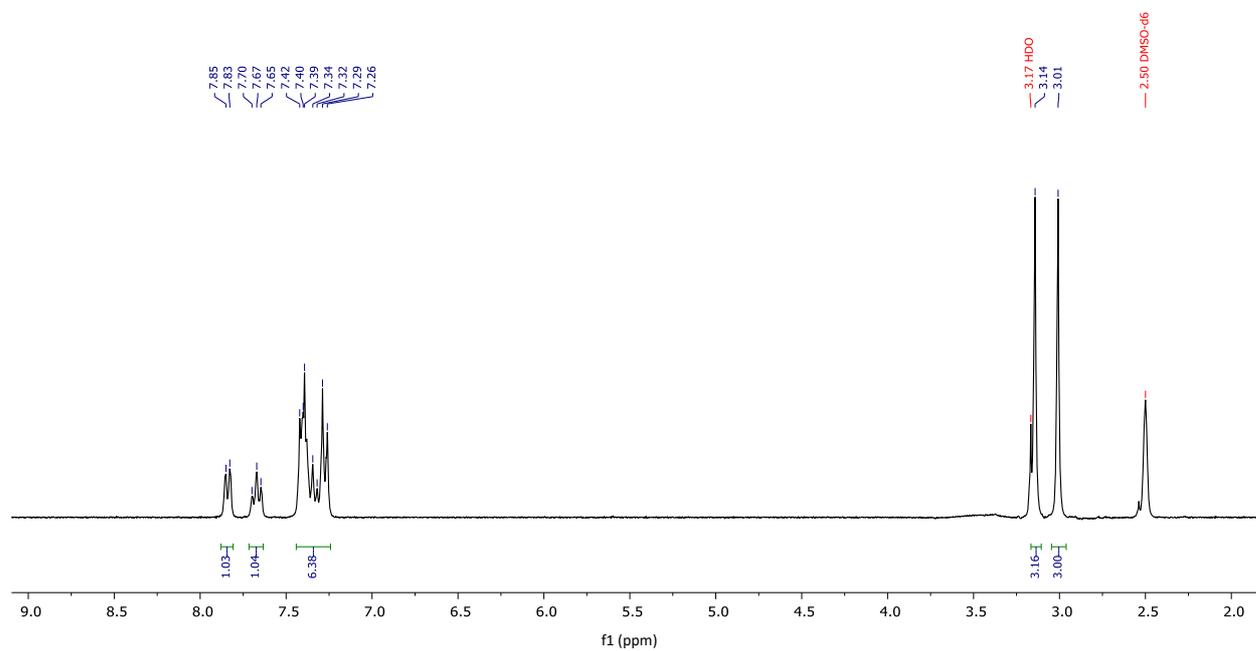
3.93 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 156.70, 155.34, 149.33, 129.92, 129.10, 128.94, 127.29, 127.23, 126.06, 125.23, 125.05, 124.38, 123.54, 121.20, 118.02, 116.75, 107.42, 32.98, 31.08. IR spectrum, ν , cm^{-1} : 3442, 3129, 3076, 2967, 2894, 2628, 2377, 2153, 1806, 1736, 1703, 1653, 1612, 1552, 1476, 1460, 1446, 1424, 1403, 1350, 1301, 1257, 1216, 1148, 1115, 1044, 1032, 1018, 960, 895, 889, 806, 792, 751, 689, 587, 569. HRMS: Calculated for $\text{C}_{20}\text{H}_{13}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 365.0687. Found: 365.0679.

1,3-Dimethyl-2,4-dioxo-1,2,3,4-tetrahydrodibenzo[3,4:5,6]isochromeno[7,8-d]imidazole-11-carbonitrile 8b: yellow powder; yield 47%; mp 274-275°C; ^1H NMR (400 MHz, DMSO- d_6) δ 9.10 (s, 1H), 8.69 (d, $J = 8.9$ Hz, 1H), 8.22 (d, $J = 7.6$ Hz, 1H), 7.99 (d, $J = 8.8$ Hz, 1H), 7.66–7.57 (m, 1H), 7.57–7.44 (m, 2H), 3.92 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 156.69, 155.37, 149.64, 134.08, 129.80, 129.09, 128.25, 126.97, 124.89, 124.81, 123.68, 122.93, 122.44, 118.70, 117.80, 116.99, 107.75, 107.53, 33.36, 31.36. IR spectrum, ν , cm^{-1} : 3556., 3503, 3403, 3092, 3036, 2957, 2852, 2632, 2375, 2236, 1984, 1819, 1724, 1702, 1650, 1613, 1560, 1508, 1480, 1448, 1430, 1347, 1302, 1253, 1218, 1156, 1074, 1049, 1026, 924, 899, 827, 791, 747, 690, 584. HRMS: Calculated for $\text{C}_{21}\text{H}_{13}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 356.1030. Found: 356.1020.

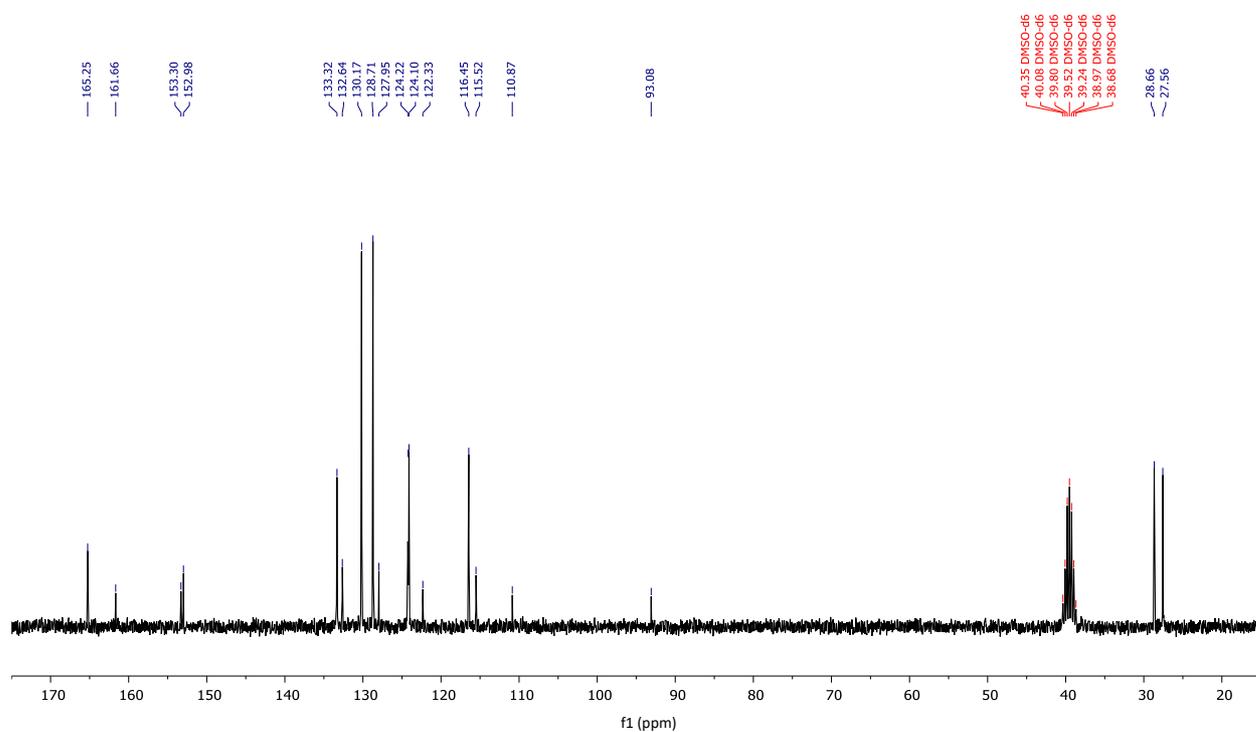
1,3-Dimethyl-1,3-dihydrobenzo[3,4]thieno[2',3':5,6]isochromeno[7,8-d]imidazole-2,4-dione 10: yellow powder; yield 46%; mp > 300°C; ^1H NMR (400 MHz, DMSO- d_6) δ 8.56 (d, $J = 7.8$ Hz, 1H), 8.28 (d, $J = 5.7$ Hz, 1H), 8.07 (d, $J = 5.7$ Hz, 1H), 7.61–7.47 (m, 3H), 3.80 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 157.23, 155.05, 149.42, 132.46, 129.09, 128.22, 128.00, 126.53, 125.95, 124.55, 124.29, 123.22, 119.40, 117.68, 116.64, 104.03, 33.46, 29.43. IR spectrum, ν , cm^{-1} : 3434, 3088, 3005, 2956, 2921, 2853, 1848, 1727, 1701, 1607, 1560, 1473, 1446, 1560, 1343, 1320, 1274, 1253, 1221, 1195, 1142, 1079, 1051, 1016, 926, 847, 757, 743, 706, 584. HRMS: Calculated for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3\text{S}$ $[\text{M}]^+$: 336.0563. Found: 336.0551.

5. Copies of NMR ^1H and ^{13}C spectra for all new compounds.

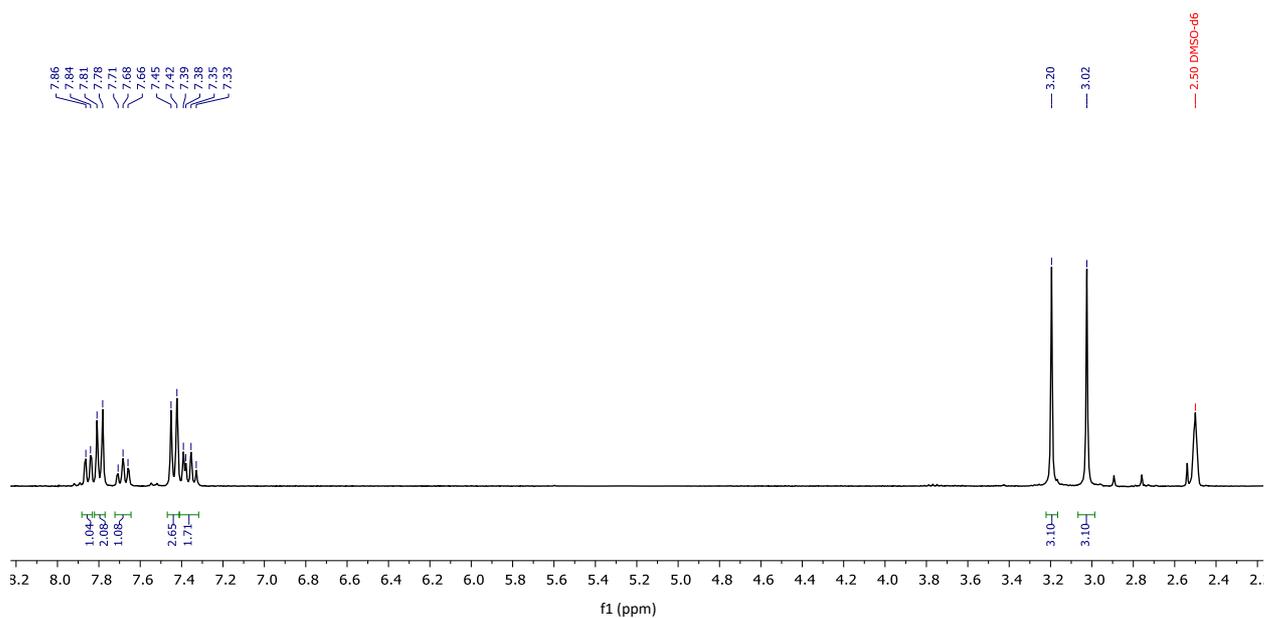
300 MHz ^1H NMR spectrum of **7a** in $\text{DMSO-}d_6$



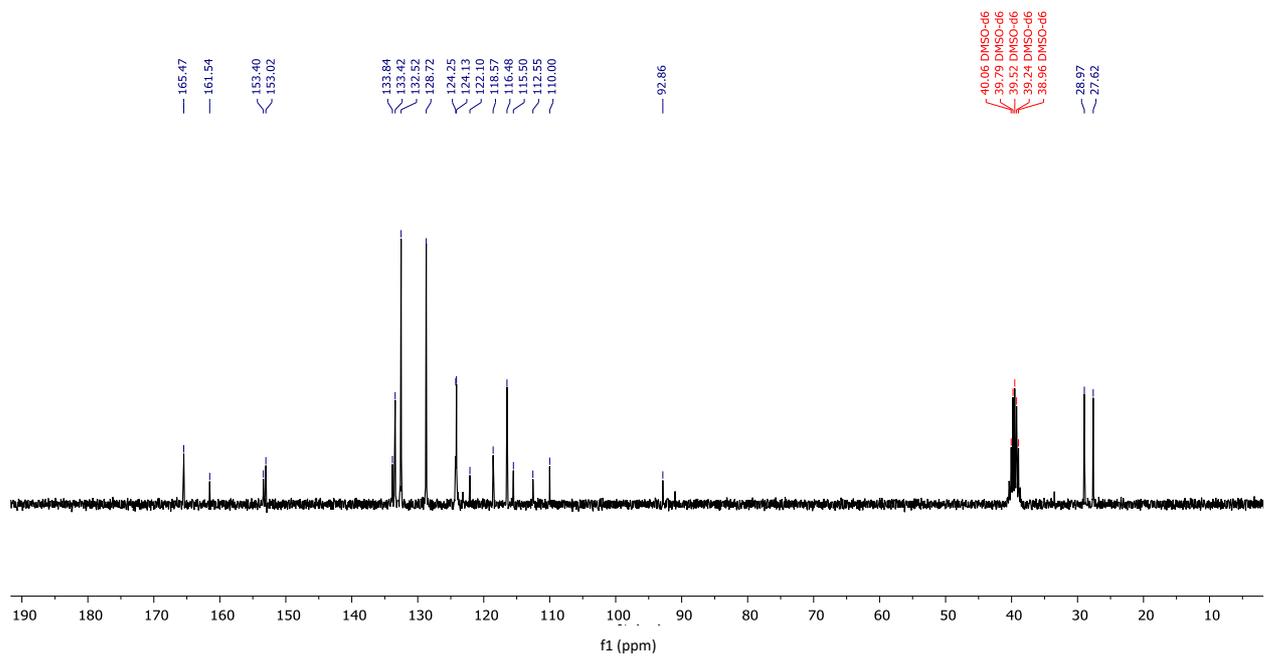
75 MHz ^{13}C NMR spectrum of **7a** in $\text{DMSO-}d_6$



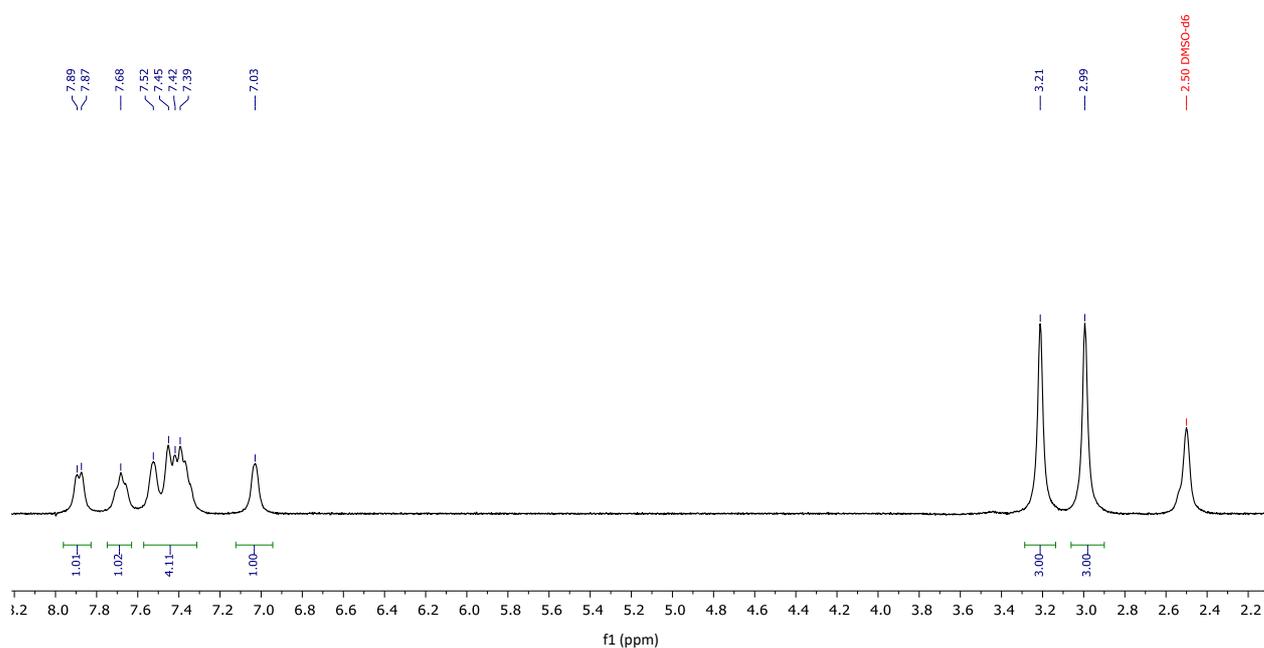
300 MHz ^1H NMR spectrum of **7b** in $\text{DMSO-}d_6$



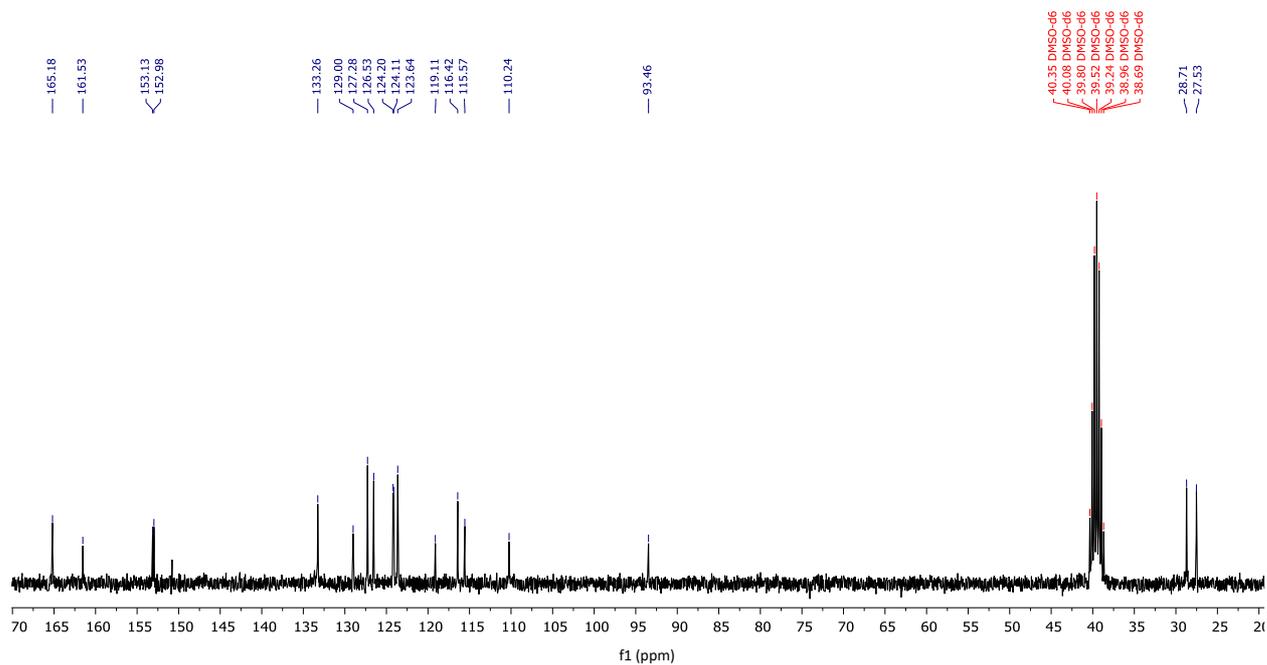
75 MHz ^{13}C NMR spectrum of **7b** in $\text{DMSO-}d_6$



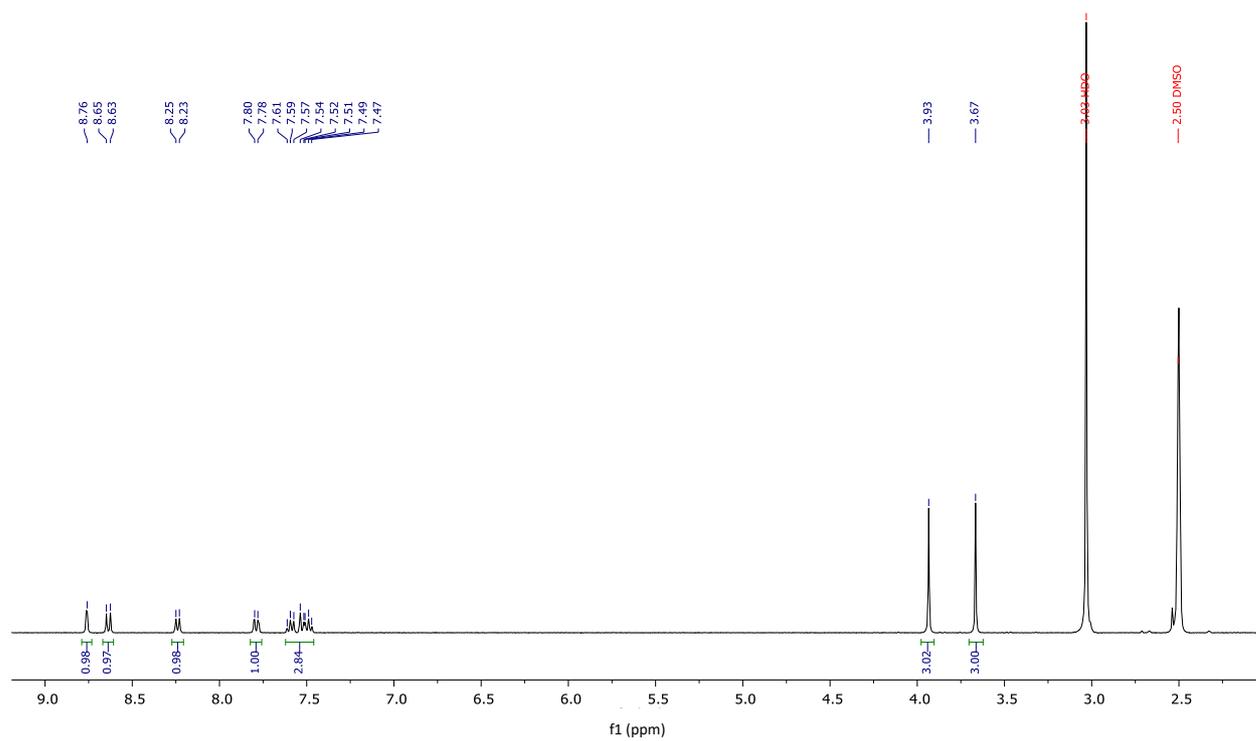
300 MHz ^1H NMR spectrum of **9** in $\text{DMSO-}d_6$



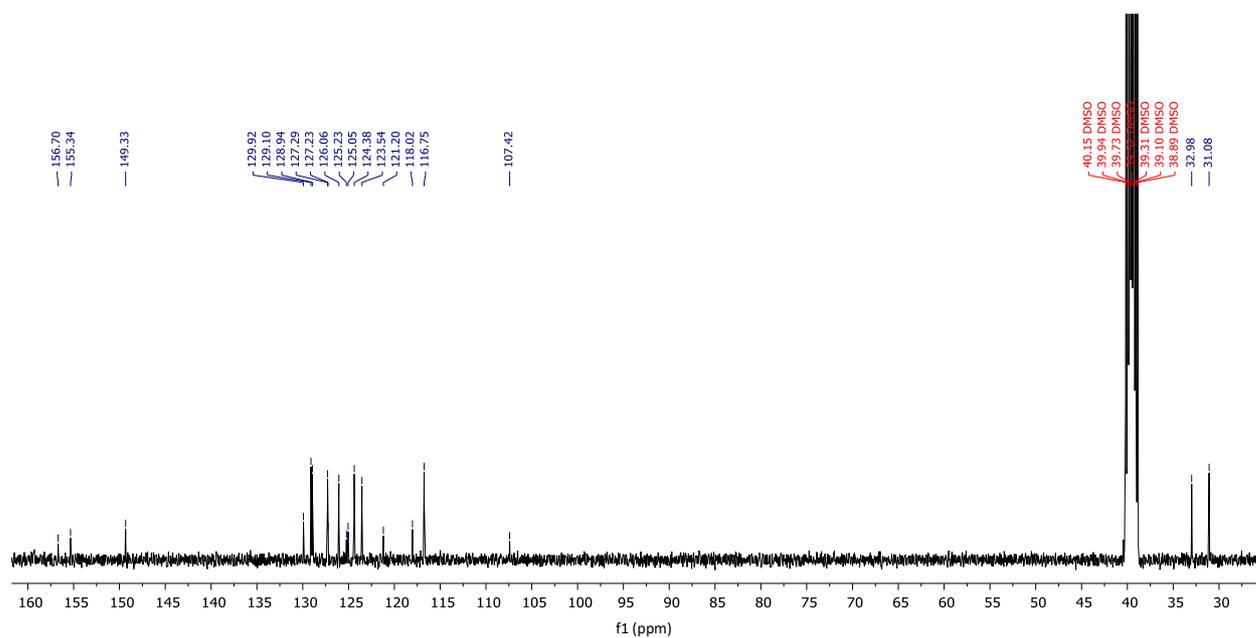
75 MHz ^{13}C NMR spectrum of **9** in $\text{DMSO-}d_6$



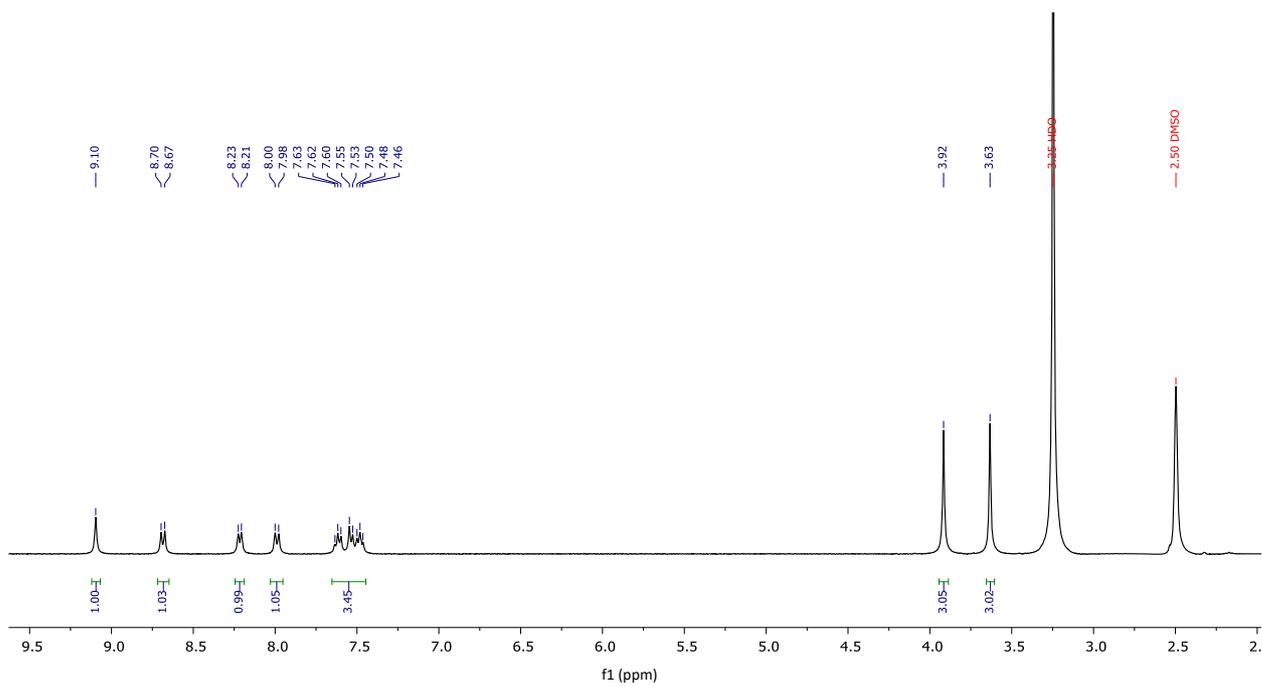
400 MHz ^1H NMR spectrum of **8a** in $\text{DMSO-}d_6$



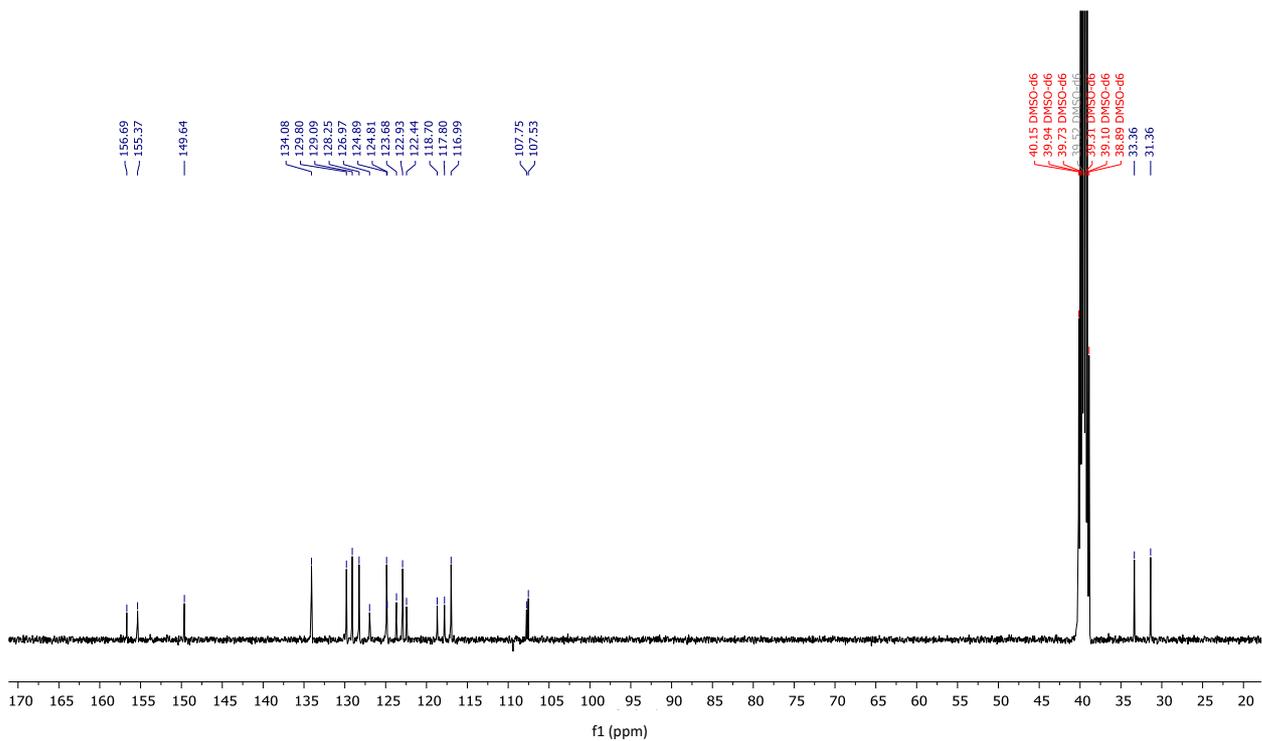
101 MHz ^{13}C NMR spectrum of **8a** in $\text{DMSO-}d_6$



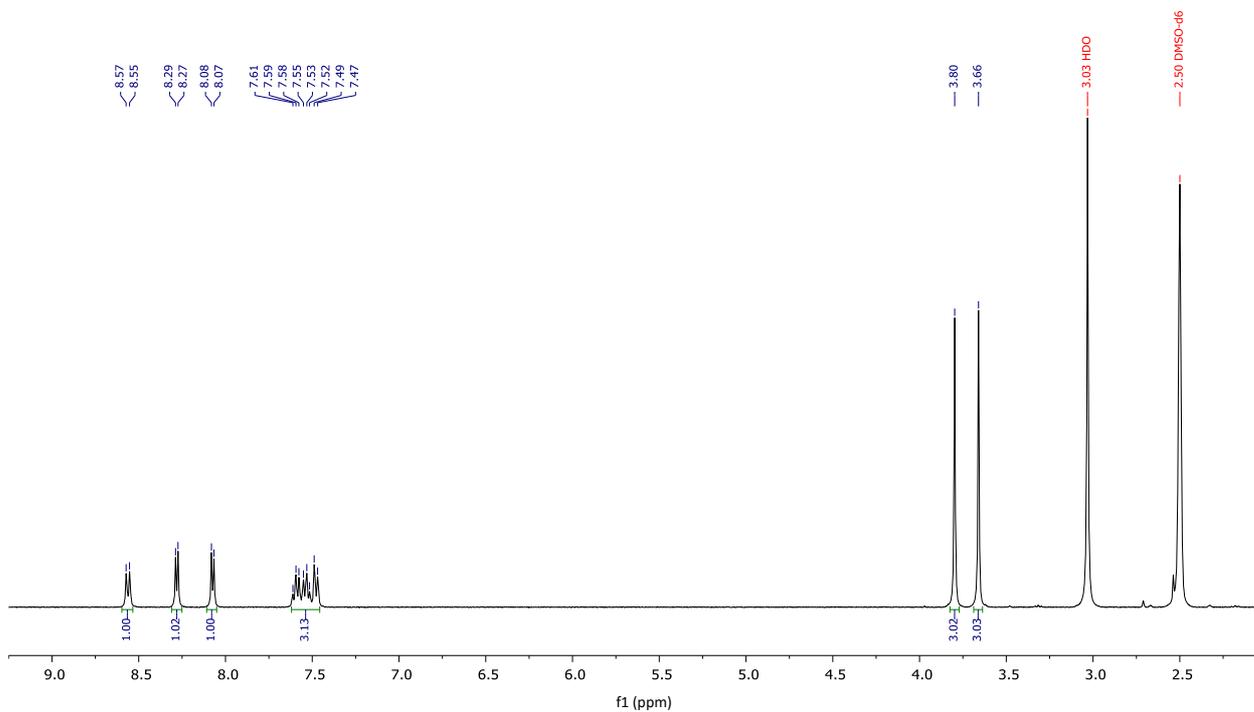
400 MHz ^1H NMR spectrum of **8b** in $\text{DMSO-}d_6$



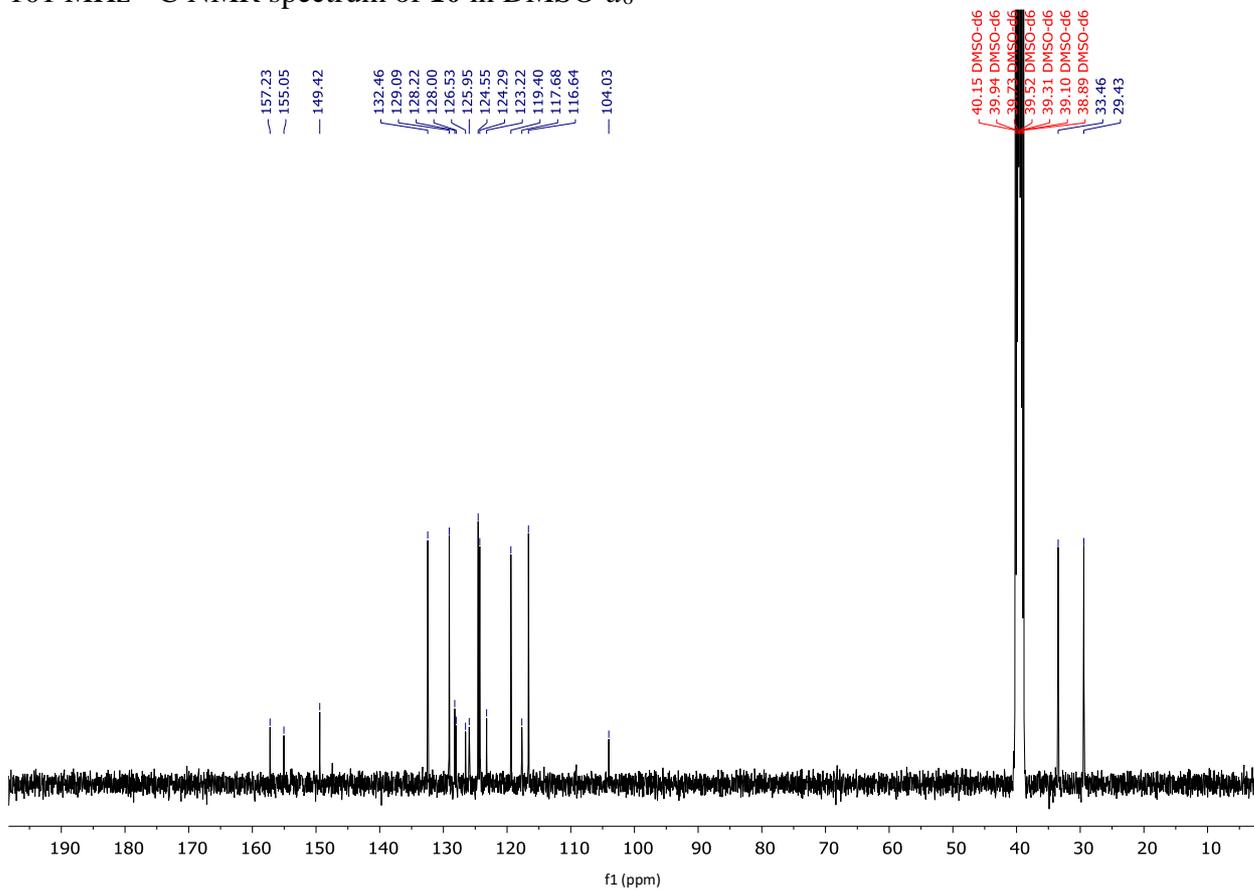
101 MHz ^{13}C NMR spectrum of **8b** in $\text{DMSO-}d_6$



400 MHz ^1H NMR spectrum of **10** in $\text{DMSO-}d_6$

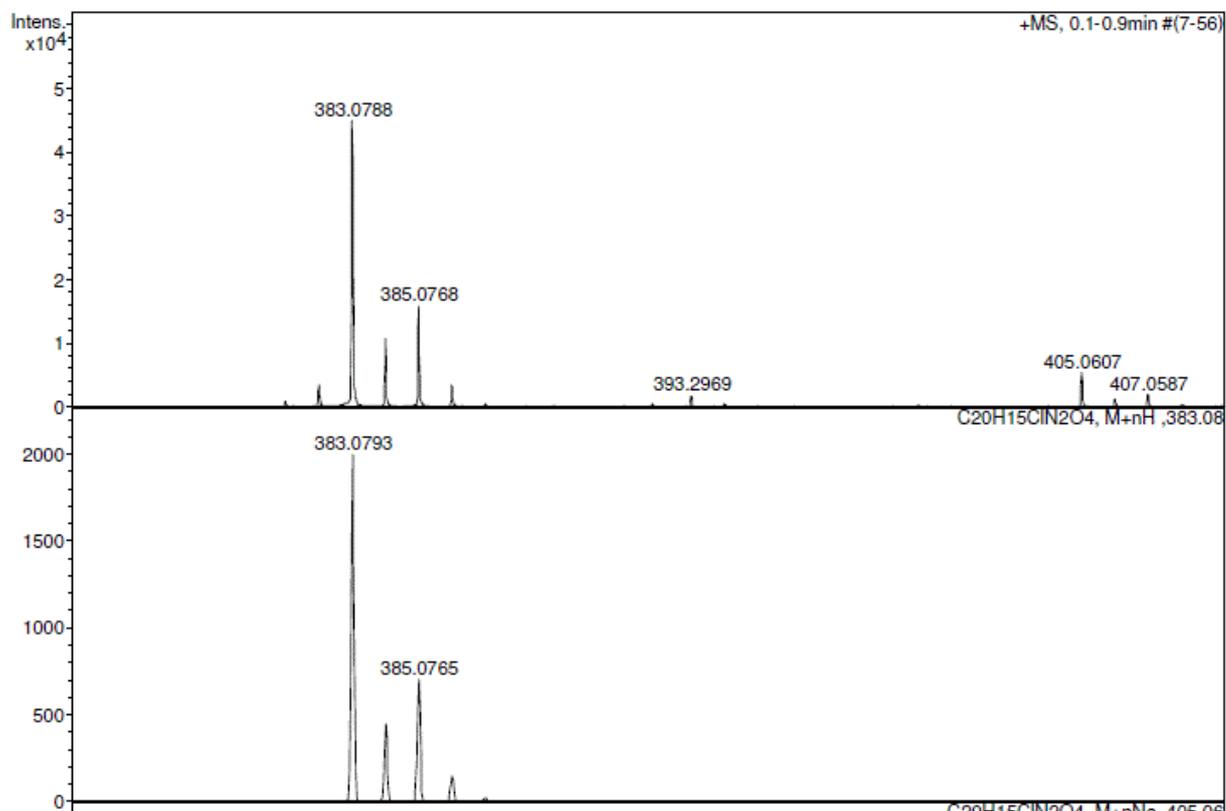


101 MHz ^{13}C NMR spectrum of **10** in $\text{DMSO-}d_6$

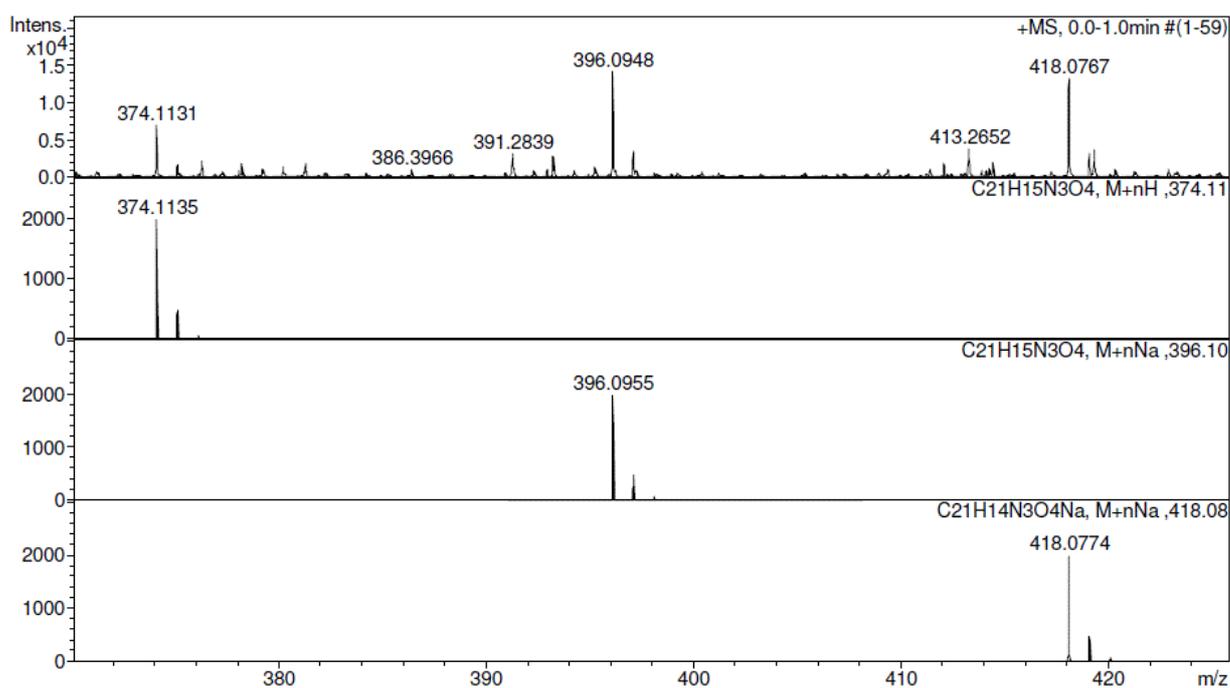


6. Copies of HRMS for new compounds

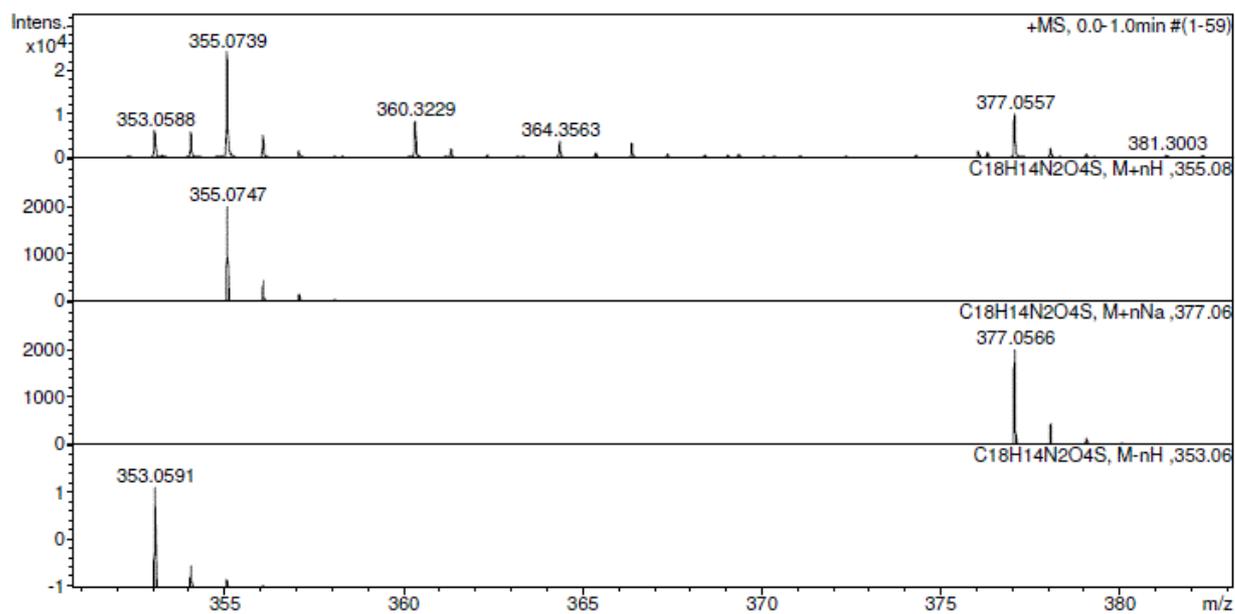
HRMS of 7a



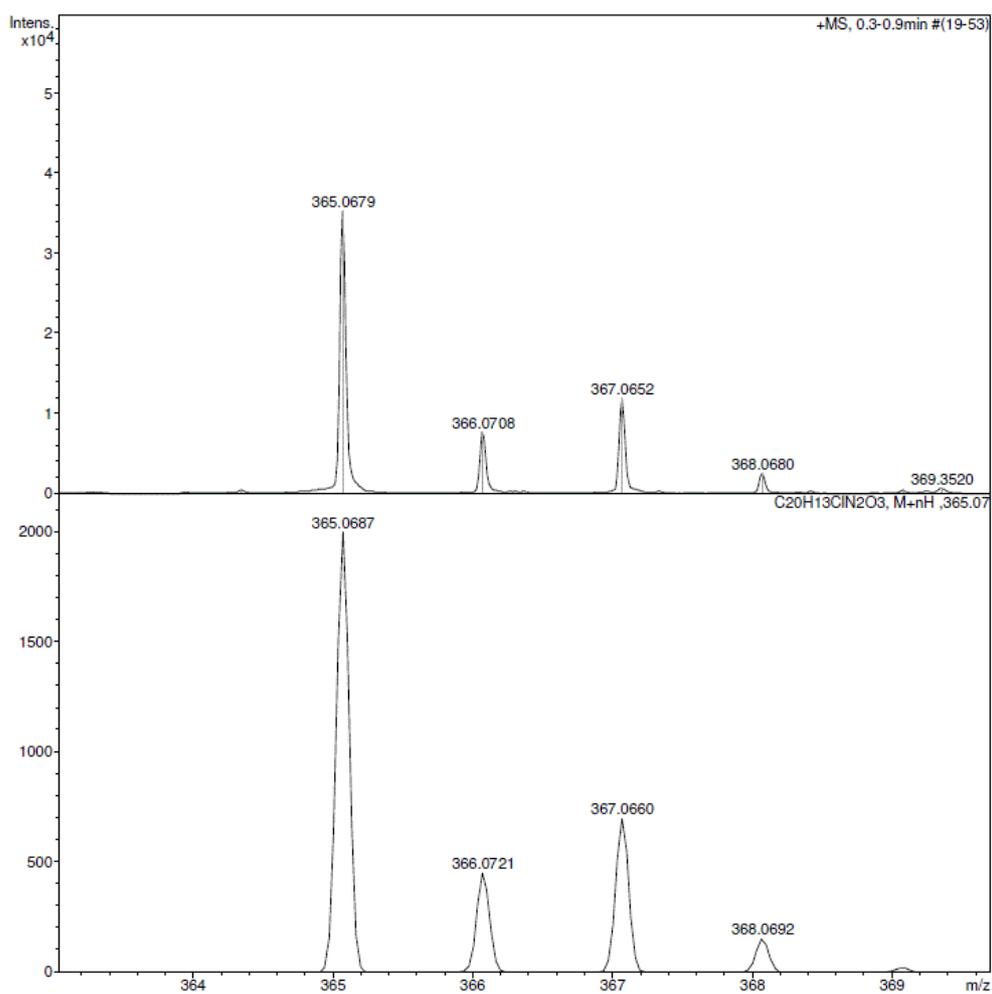
HRMS of 7b



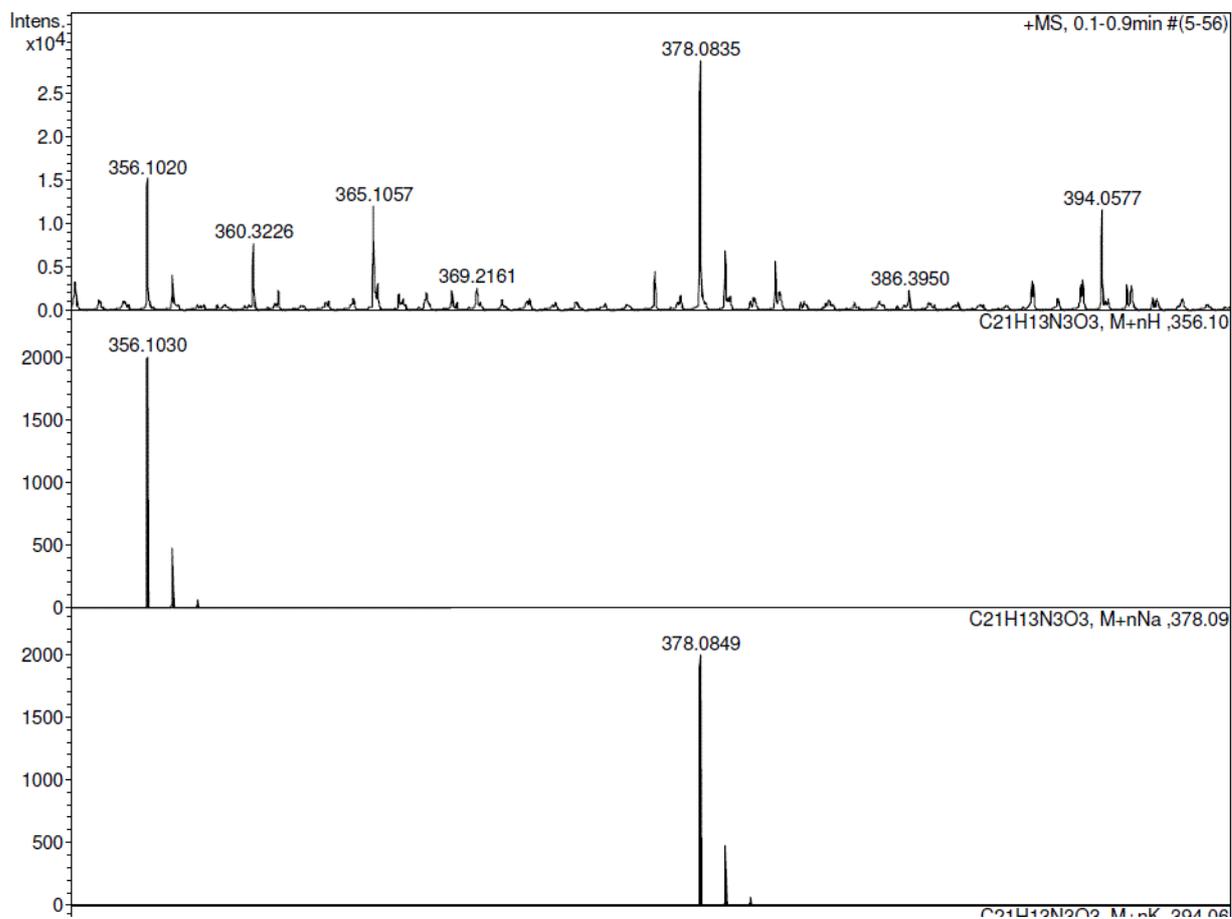
HRMS of 9



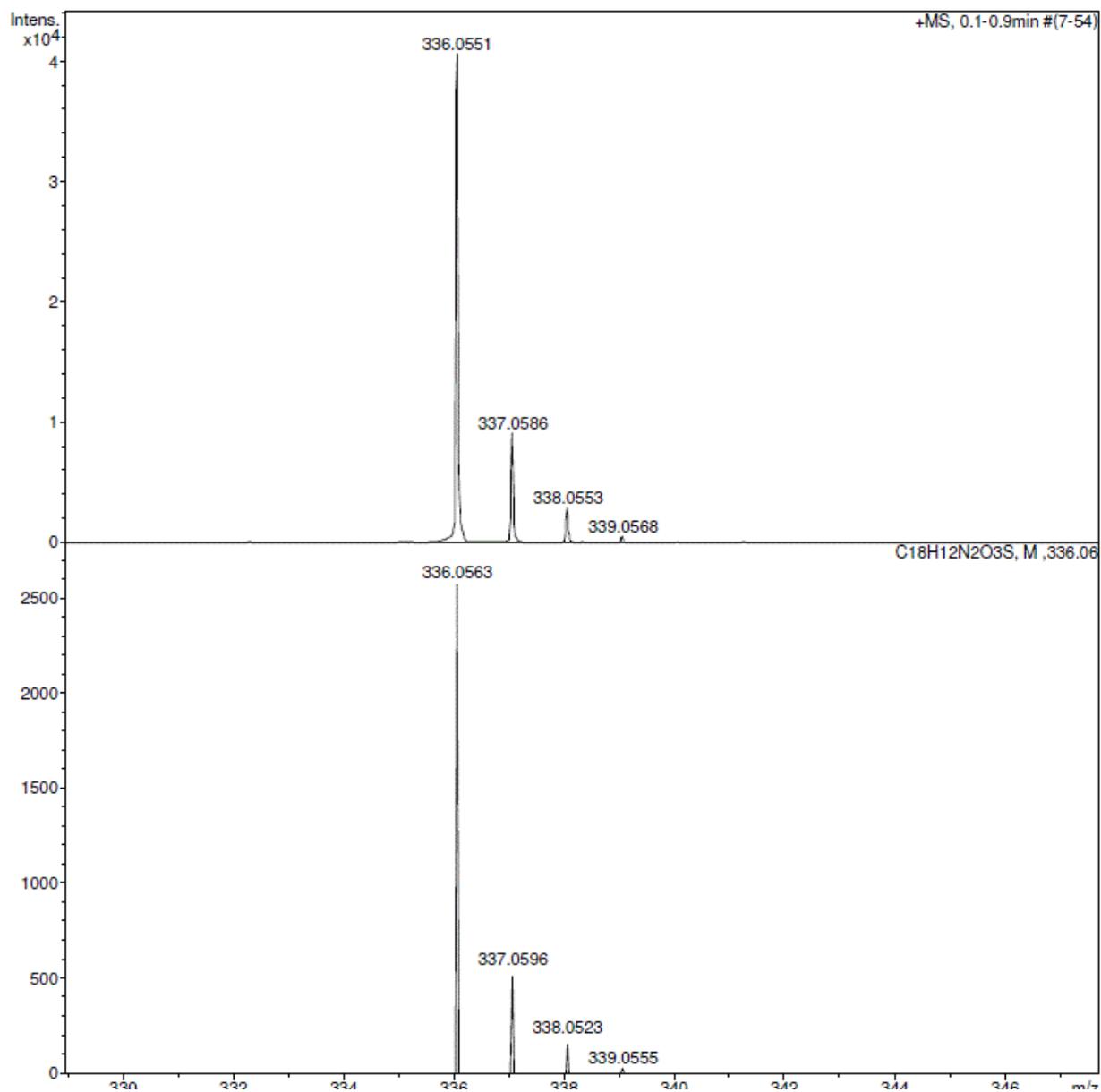
HRMS of 8a



HRMS of 8b

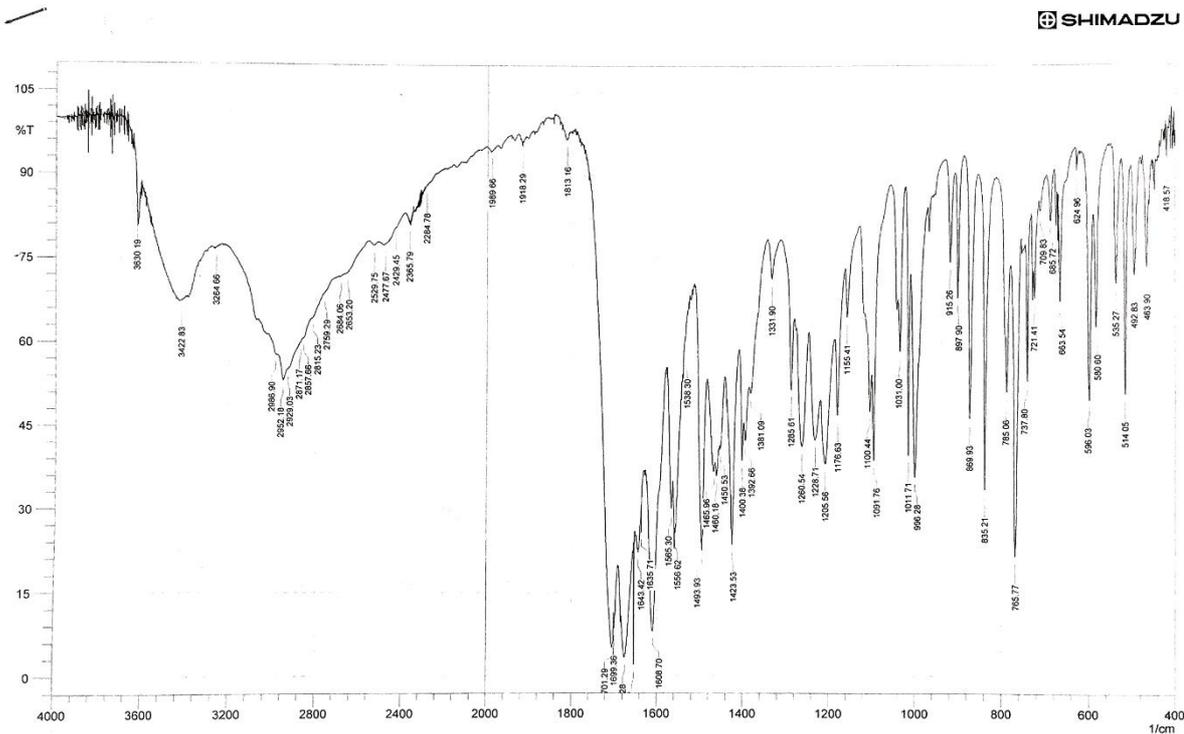


HRMS of 10

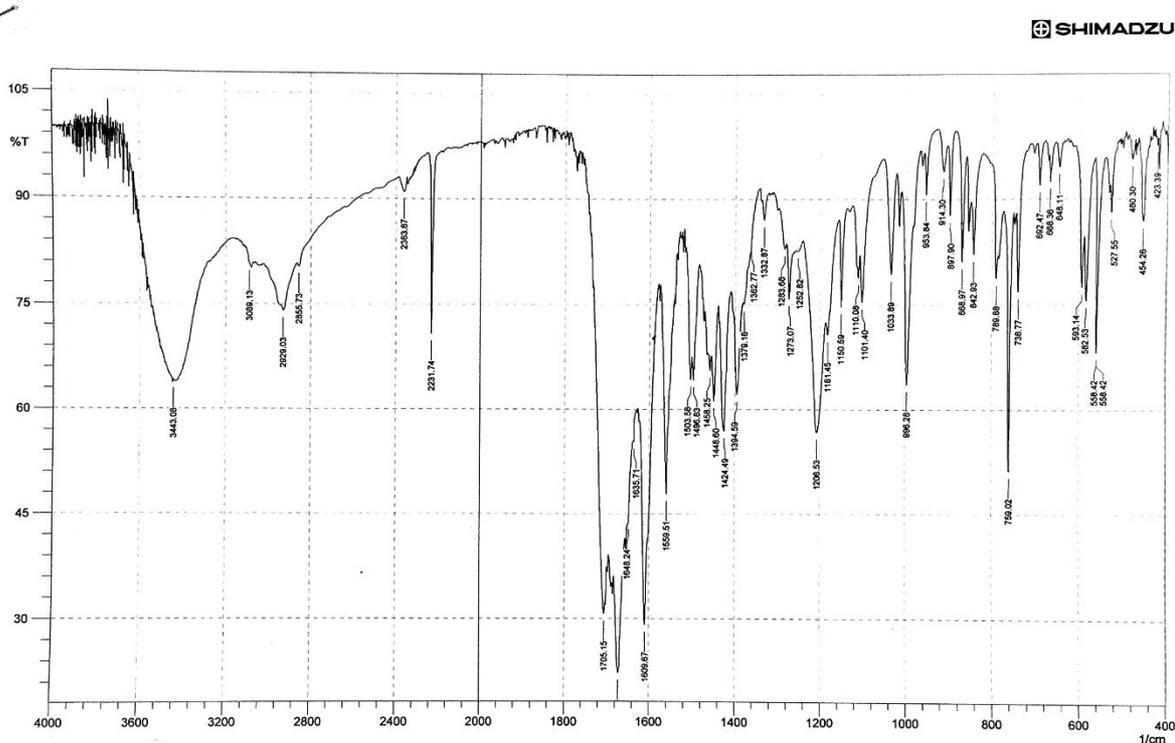


Copies of IR spectra for new compounds

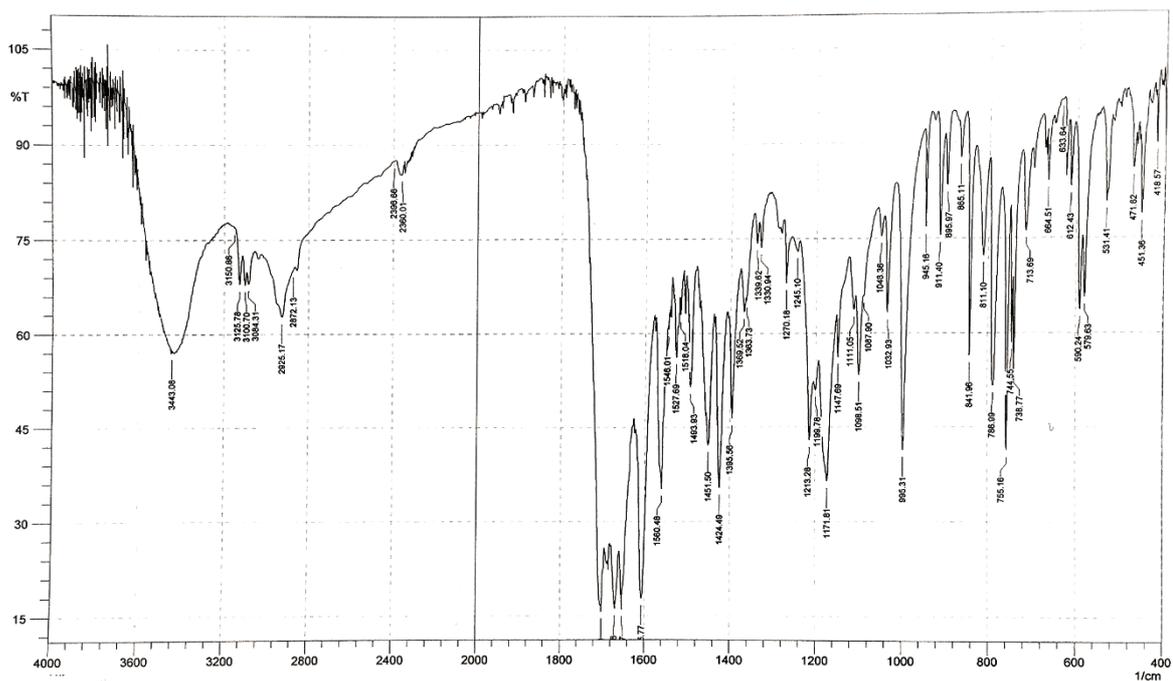
IR of 7a



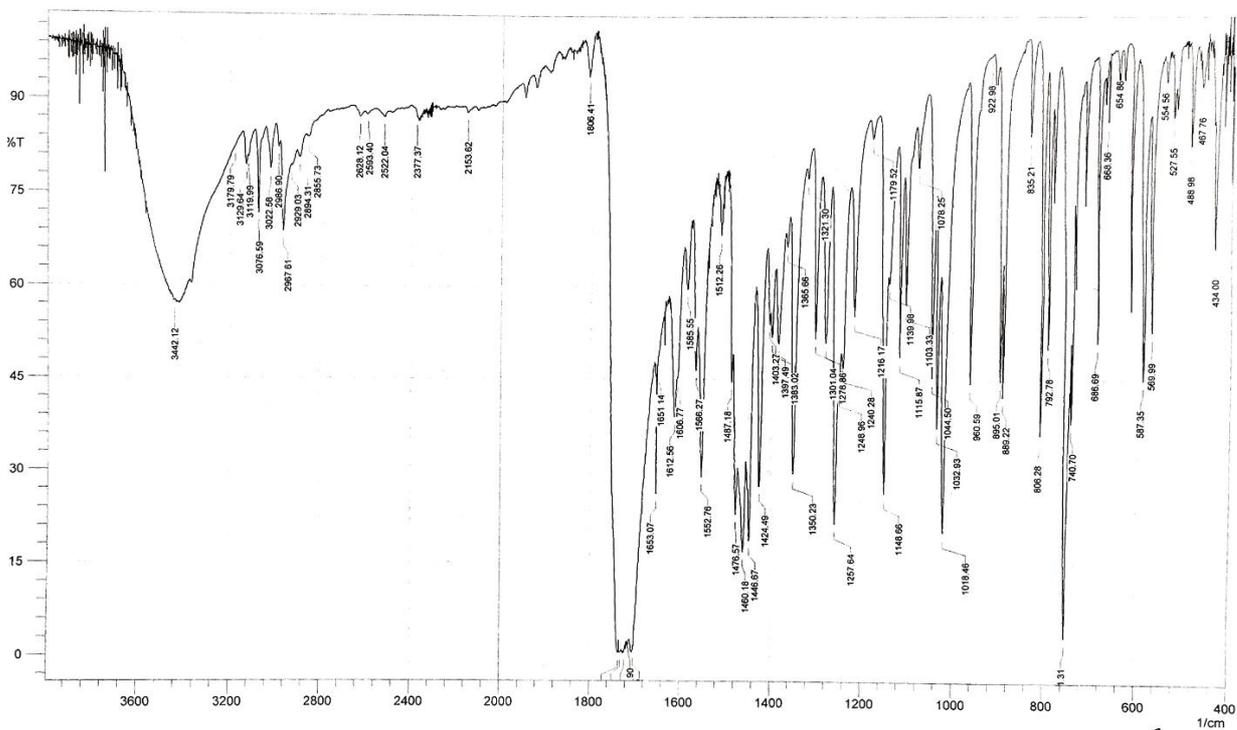
IR of 7b



IR of 9

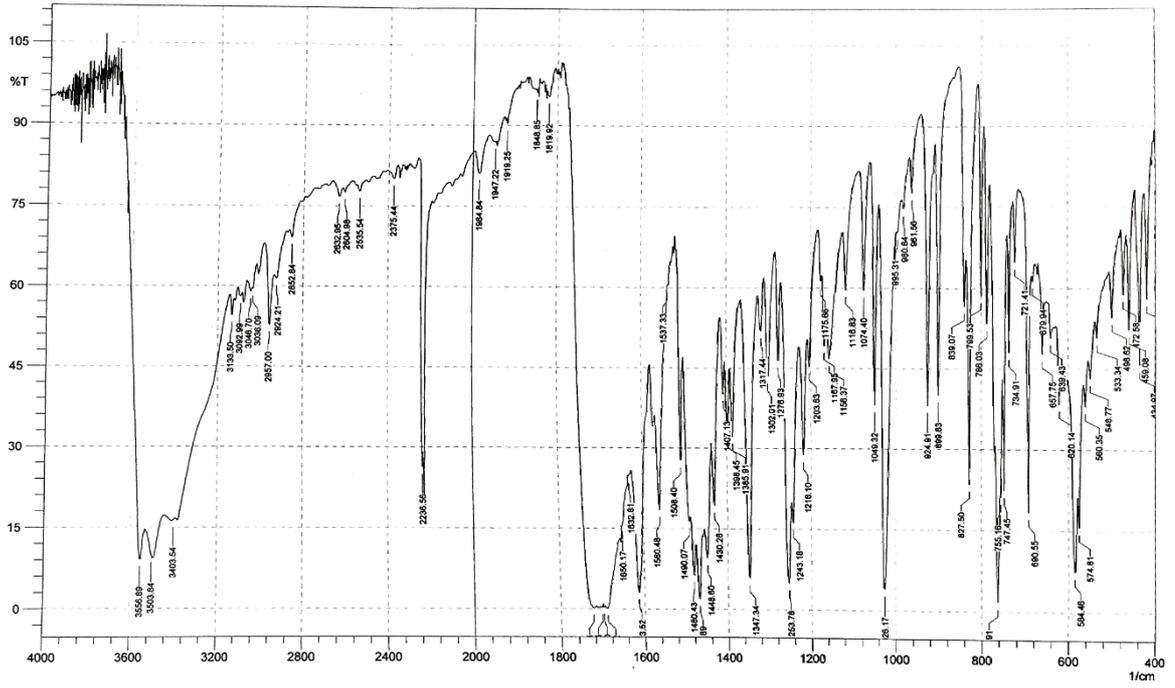


IR of 8a



IR of 8b

SHIMADZU



IR of 10

SHIMADZU

