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Supporting Information

Imidazoles Synthesis by Transition Metal Free, Base-Mediated Deaminative Coupling of Benzylamines and Nitriles

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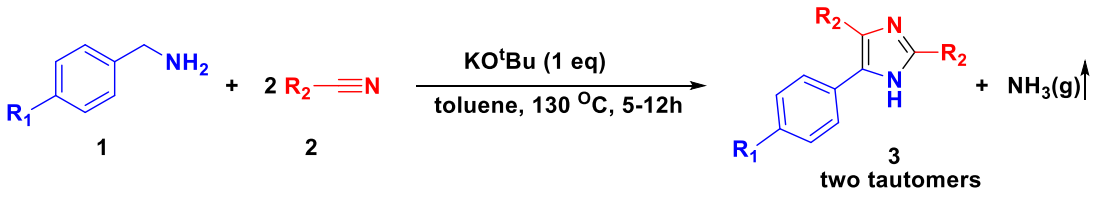
CONTENTS:

1. General Information:

All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenoneketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glove box over 4Å molecular sieves. Most of the chemicals used in the imidazole synthesis reactions were purified according to standard procedures (vacuum distillation). N-benzylbenzimidamide (**A**) was synthesized as per literature procedure.[1] All ^{1}H NMR (400 MHz, 300 MHz), ^{13}C NMR (100 MHz, 75 MHz) spectra were recorded on a Bruker AMX-400 NMR and Bruker AMX-300 NMR spectrometer for a DMSO-d_6 (3.3 and 2.5 ppm are solvent peaks) and $CDCl_3$ (7.28 ppm is solvent peak) solution and reported in ppm (δ). NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. GC–MS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. The HRMS/ESI-MS was carried out on Micromass ZQ Mass Spectrometer. IR spectra were recorded on Thermo Nicolet 6700 FT-IR.

2. Experimental procedures:

(a) General procedure for the synthesis of tri-substituted imidazoles (3a-3o):



Under a nitrogen atmosphere, 1 mmol of benzylamine (**1**), 2 mmol of nitrile (**2**) and 1 mmol of KO^{t}Bu (stored in a nitrogen atmosphere glove box) were dissolved in 3 mL toluene in a 10 mL vial. The reaction mixture was stirred for 3-5 min under N_2 atmosphere and transferred to a 50 mL pressure tube equipped with a stirring bar. The flask was tightly sealed with a Teflon screw cap and placed in a preheated oil bath at the indicated temperature (110 °C to 130 °C). The reaction mixture was stirred for the indicated time (5-12h). The reaction mixture was then cooled down to room temperature and the generated NH_3 was vented off. The potassium salt of the imidazole product precipitated from the reaction mixture (the corresponding potassium salt of 2,4,5-triphenyl-imidazole {**B**} was characterized by ^{1}H NMR in DMSO-d_6 {300 MHz, δ (ppm), 8.09 (d, J = 7.5 Hz, 2H) 7.53-7.43 (m, 7H), 7.36-7.30 (br m, 7H)}. The solvent was removed under reduced pressure, and the resulting residue was stirred with 10 ml distilled water. The aqueous layer was extracted with ethyl acetate (20 mL). The ethyl acetate solution was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel (60-120 mess) using 20% ethyl acetate in *n*-hexane solution as an eluent.

(b) Procedure for the large scale synthesis of 3a (Table 2, 3a$^{\#}$):

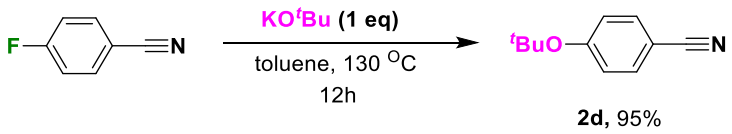
A mixture of benzylamine (1.07 g, 10 mmol), benzonitrile (2.06 g, 10 mmol) and KO^{t}Bu (1.122 g, 10 mmol) in toluene (20 mL) was added to a 100 mL pressure tube equipped with a stirring bar under an atmosphere of nitrogen in a Vacuum Atmospheres glove box. The flask was tightly sealed with a Teflon screw cap and placed in a preheated oil bath at the 130 °C. The reaction mixture was stirred for 5h. The reaction mixture was then cooled down to room temperature and the generated NH_3 was vented off. The

potassium salt of the imidazole product precipitated from the reaction mixture. The solvent was removed under reduced pressure, and the resulting residue was stirred with 100 mL distilled water. The aqueous layer was extracted with ethyl acetate (50 x 3 mL). The ethyl acetate solution was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography. **3a** was isolated as pure white crystalline solid (2.633 g, 89% yield).

(c) Reaction with radical scavenger (Scheme 2, reaction 2):

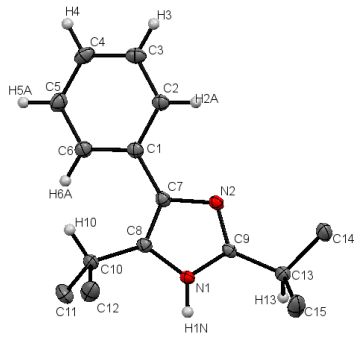
Under a nitrogen atmosphere, 1 mmol (107 mg) of benzylamine, 2 mmol (206 mg) of benzonitrile and 1 mmol (112 mg) of KO^{t}Bu (stored in a nitrogen atmosphere glove box) were dissolved in 5 mL toluene in a 10 mL vial. The reaction mixture was stirred for 5 min under N_2 and 1 mmol (156 mg) of TEMPO (or 1 mmol of Galvinoxyl radical) was added to the mixture. The mixture was transferred to a 50 mL pressure tube equipped with a stirring bar. The flask was tightly sealed with a Teflon screw cap and placed in a preheated oil bath at 130 °C. The reaction mixture was stirred for 6h. After workup and purification (same as **3a-3o**) **3a** was isolated as white solid (266 mg, 90% yield).

(d) Synthesis of 4-(*tert-butoxy*)benzonitrile (2d) from 4-fluorobenzonitrile:



Under a nitrogen atmosphere, 4-fluorobenzonitrile (0.250 g, 2 mmol) was dissolved in toluene (3 mL), and 2 mmol (0.225 g) of KO^{t}Bu (stored in a nitrogen atmosphere glove box) was then added. The reaction mixture was heated at 130 °C for 12 h, after which the organic solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography (1:20 mixture of EtOAc/ hexanes) to yield **2d** (0.331 g, 95%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 1.40 (s, 9H). ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$) 160.13, 133.63, 123.20, 119.38, 105.89, 80.43, 29.06. This is a known compound.[2]

3. X-ray Crystal structure determination of 3i: (full details can be found in the CIF file)



Crystal data: $C_{15}H_{20}N_2$, colorless prism, 0.303 x 0.087 x 0.075 mm^3, monoclinic *$P2_1/c$,* a=14.2280(2)Å, b=28.0486(5)Å, c=10.0680(15)Å, α=90°, β=98.7934(13)°, γ=90°, from 17643 reflections, T=100(2)K, V=3970.89(11)$Å^3$, Z=12, Fw=228.33 Dc=1.146 $Mg·m^{-3}$, μ=0.516 mm^{-1}.

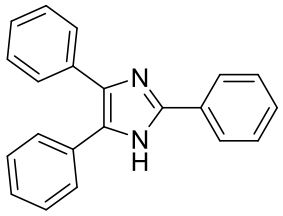
Data collection and processing: Rigaku XtaLab Pro diffractometer, MoKα (λ=1.54184Å), -17≤h≤17 -34≤k≤35, -12≤l≤12, frame scan width = 0.5°, scan speed 1.0° per 3.28 sec typical peak mosaicity 0.7°, 50218 reflections collected, 8808 independent reflections (R-int =0.0443). The data were processed with CrysAlisPro.

Solution and refinement: Structure solved with SHELXT-2016/4. Hydrogen atoms were placed in calculated positions with the exception of the hydrogens on N1 that was found in the electron density maps and refined freely. Full matrix least-squares refinement based on F^2 with SHELXL-2016/14 on 484 parameters with 0 restraints gave final R_1= 0.0544 (based on F^2) for data with I>2σ(I) and, wR_2= 0.0582 on 8808 reflections, goodness-of-fit on F^2 = 1.054 largest electron density peak 0.396 $e·Å^{-3}$. Largest hole – 0.234 $e·Å^{-3}$

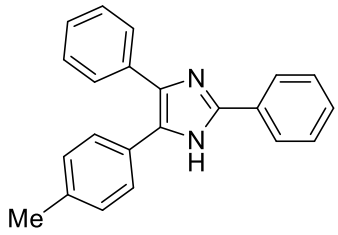
Table S1. Crystal data and structure refinement for **3i**.

Identification code	m2011
Empirical formula	C_{15} H_{20} N_2
Formula weight	228.33
Temperature	100(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 14.2280(2) A alpha = 90 deg.
	b = 28.0486(5) A beta = 98.7934(13) deg.
	c = 10.06860(15) A gamma = 90 deg.
Volume	3970.89(11) A^3
Z, Calculated density	12, 1.146 Mg/m^3
Absorption coefficient	0.516 mm^-1
F(000)	1488
Crystal size	0.303 x 0.087 x 0.075 mm
Theta range for data collection	4.453 to 74.504 deg.
Limiting indices	-17<=h<=17, -34<=k<=35, -12<=l<=12
Reflections collected / unique	50218 / 8088 [R(int) = 0.0443]
Completeness to theta	67.684 99.8
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.44165
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8088 / 0 / 484
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1583
R indices (all data)	R1 = 0.0582, wR2 = 0.1622
Extinction coefficient	n/a
Largest diff. peak and hole	0.396 and -0.234 e.A^-3

4. ^{1}H NMR and ^{13}C{^{1}H}NMR data of tri-substituted imidazoles (3a-3o):

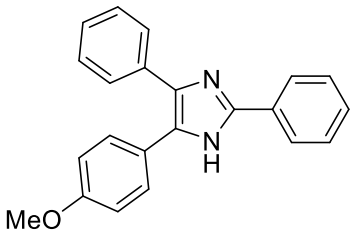


2,4,5-triphenyl-1*H*-imidazole (3a): Isolated as an colorless solid (0.284 g, 96%), mp 278-279°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.69 (br s, 1H,), 8.10 (d, J = 7.6 Hz, 2H), 7.54-7.24 (m, 13H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 145.49, 137.11, 135.18, 131.09, 130.35, 128.68, 128.46, 128.24, 127.78, 127.07, 126.52, 125.19. HRMS (ESI) for $C_{21}H_{17}N_2$ $[M+H]^+$: calcd 297.1392, found 297.1394. This is a known compound.[3]



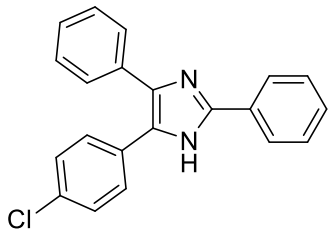
2,4(5)-diphenyl-5(4)-(*p*-tolyl)-1*H*-imidazole (3b): Isolated as a colorless solid (0.285 g, 92%, mixture of two tautomers), mp 233-234°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.64 (br s, 1H), 8.10 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.51-7.44 (m, 4H), 7.42-7.36 (m, 3H), 7.32-7.20 (m, 3H), 7.13 (d, J = 8 Hz, 1H), 2.36, 2.30 (2s, 3H for two isomers). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 145.86, 145.77, 137.70, 137.63, 137.27, 136.10, 135.77, 132.82, 131.65, 130.88, 129.69, 129.25, 129.14, 129.09, 128.94, 128.82, 128.63, 128.29, 128.11, 127.53, 127.48, 126.88, 125.63, 21.33, 21.25. HRMS (ESI) for $C_{22}H_{19}N_2$ $[M+H]^+$: calcd 311.1548, found 311.1551. This is a known compound.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.93 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.47-7.27 (m, 8H), 7.18 (d, J = 8.0, 2H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 145.76, 137.39, 129.77, 129.36, 128.88, 128.82, 128.61, 128.53, 127.78, 127.77, 127.48, 127.32, 125.31, 21.30.

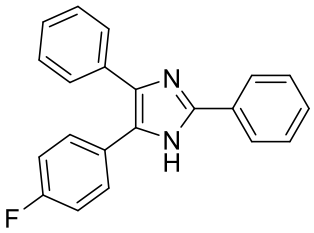


5(4)-(4-methoxyphenyl)-2,4(5)-diphenyl-1*H*-imidazole (3c): Isolated as a colorless solid (0.320 g, 98%, mixture of two tautomers), mp 226-227°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.61 (br s, 1H), 8.11 (d, J = 7.2 Hz, 2H), 7.56-7.32 (m, 10H), 7.01-6.91 (br m, 2H), 3.78 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 159.40, 158.65, 145.99, 145.62, 137.61, 136.93, 135.83, 131.78, 130.94, 130.37, 129.13, 128.71, 128.67, 127.99, 127.37, 126.77, 125.59, 123.85, 114.54, 114.18, 55.59. HRMS (ESI) for $C_{22}H_{19}N_2O$ $[M+H]^+$: calcd 327.1497, found 327.1499. This is a known compound.[4,5]

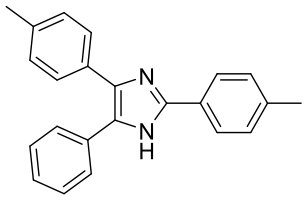
^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.92 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 7.2 Hz, 2H), 7.54-7.31 (m, 8H), 6.89 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 159.15, 145.98, 145.64, 133.01, 132.74, 130.14, 129.74, 129.65, 129.28, 128.86, 128.59, 128.54, 127.86, 127.70, 127.47, 127.29, 126.34, 125.36, 114.12, 114.06, 55.29. HRMS (ESI) for $C_{22}H_{19}N_2O$ $[M+H]^+$: calcd 327.1497, found 327.1499.



5(4)-(4-chlorophenyl)-2,4(5)-diphenyl-1*H*-imidazole (3d): Isolated as a colorless solid (0.254 g, 77%, mixture of two tautomers), mp 259-261°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.75 (br s, 1H), 8.10 (d, J = 7.6 Hz, 2H), 7.51-7.24 (m, 12H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 146.31, 146.17, 145.97, 138.18, 137.58, 136.26, 135.66, 135.44, 134.50, 132.71, 131.57, 131.43, 131.30, 130.83, 130.68, 130.47, 129.25, 129.17, 129.03, 128.84, 128.72, 128.50, 128.24, 127.74, 127.54, 127.23, 126.98, 125.71, 125.66. HRMS (ESI) for $C_{21}H_{16}ClN_2$ $[M+H]^+$: calcd 331.1002, found 331.1006. This is a known compound.[5]

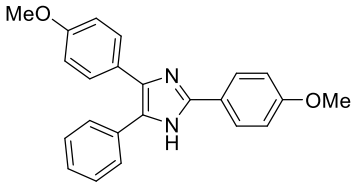


5(4)-(4-fluorophenyl)-2,4(5)-diphenyl-1*H*-imidazole (3e): Isolated as a colorless solid (0.257 g, 82%, mixture of two tautomers), mp 256-257°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.70 (br s, 1H), 8.09 (d, J = 7.2 Hz, 2H), 7.55-7.20 (m, 12H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 162.97, 160.53, 146.07, 131.67, 130.77, 129.93, 129.37, 129.16, 129.00, 128.89, 128.75, 128.66, 127.93, 125.67, 115.88, 115.67. HRMS (ESI) for $C_{21}H_{16}FN_2$ $[M+H]^+$: calcd 315.1298, found 315.1299. This is a known compound.[6]

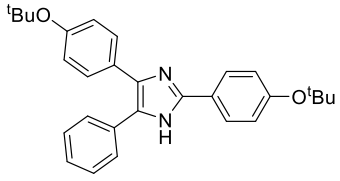


5(4)-phenyl-2,4(5)-di-*p-tolyl*-1*H*-imidazole (3f): Isolated as a yellowish white solid (0.301 g, 93%, mixture of two tautomers), mp 225-226°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.53 (br s, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.56-7.10 (m, 11H), 2.34, 2.29 (2s, 6H for two isomers). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 145.95, 138.06, 137.52, 137.08, 136.03, 135.85, 132.90, 131.72, 129.70, 129.24, 129.06, 128.77, 128.61, 128.22, 128.01, 127.48, 126.82, 125.61, 21.36, 21.31. IR (NaCl): 3442, 2917, 1604, 1495, 1446, 1125, 909, 820, 728 cm^{-1}. HRMS (ESI) for $C_{23}H_{21}N_2$ $[M+H]^+$: calcd 325.1705, found 325.1705.

^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 9.49 (br s, 1H), 7.80 (d, J = 8 Hz, 2H), 7.67-7.34 (br m, 6H), 7.26 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8 Hz, 2H), 7.18-7.14 (m, 1H), 2.40 (s, 6H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 146.06, 138.71, 129.55, 129.06, 129.02, 128.98, 128.84, 128.80, 128.26, 128.25, 127.75, 127.26, 126.78, 125.18, 124.36, 21.29. HRMS (ESI) for $C_{22}H_{19}N_2O$ $[M+H]^+$: calcd 327.1497, found 327.1499.

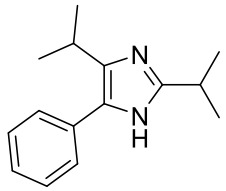


2,4(5)-*bis*(4-methoxyphenyl)-5(4)-phenyl-1*H*-imidazole (3g): Isolated as a colorless solid (0.320 g, 90%, mixture of two tautomers) mp 224-225°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ, ppm: 12.44 (br s, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.57-7.19 (m, 7H), 7.05-7.03 (m, 3H), 6.89 (d, J = 8.1 Hz, 1H), 3.81, 3.80, 3.75 (3s, 6H for two isomers). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 159.80, 159.30, 158.48, 145.86, 145.64, 137.26, 136.50, 135.95, 130.28, 129.06, 128.82, 128.60, 128.31, 128.06, 127.82, 127.30, 127.12, 127.06, 126.63, 124.01, 123.71, 114.55, 114.10, 55.66, 55.48. HRMS (ESI) for $C_{23}H_{21}N_2O_2$ $[M+H]^+$: calcd 357.1603, found 357.1605. This is a known compound.[7]

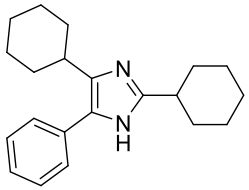


2,4(5)-*bis*(4-(*tert*-butoxy)phenyl)-5(4)-phenyl-1*H*-imidazole (3h): Isolated as a yellowish white solid (0.347 g, 89%, mixture of two tautomers), mp 115-116°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.51 (br s, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.56-7.20 (m, 8H), 7.08-7.03 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 1.34 (s, 14H), 1.30 (s, 4H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 155.95, 155.79, 155.28, 154.22, 145.97,

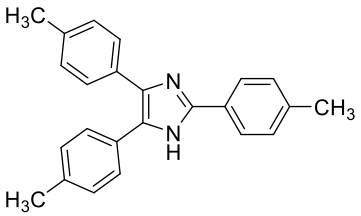
145.79, 145.64, 137.22, 136.93, 135.83, 134.16, 131.75, 130.64, 129.76, 129.13, 129.08, 128.83, 128.74, 128.59, 128.14, 128.01, 127.73, 127.51, 127.33, 126.76, 126.62, 126.51, 126.29, 125.87, 125.56, 123.92, 123.75, 123.01, 78.82, 78.74, 78.33, 29.08, 29.06. IR (NaCl): 3441, 2976, 1611, 1511, 1492, 1365, 1240, 1160, 895, 697 cm^{-1}. HRMS (ESI) for $C_{29}H_{33}N_2O_2$ $[M+H]^+$: calcd 341.2542, found 341.2542.



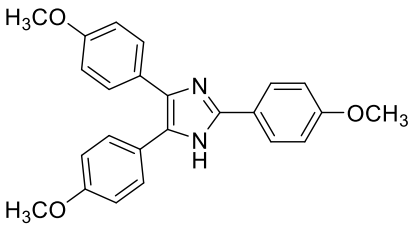
2,4(5)-diisopropyl-5(4)-phenyl-1*H*-imidazole (3i): Isolated as a colorless solid (0.215g, 94%, mixture of two tautomers) mp 179-180°C. ^{1}H NMR for major isomer (400 MHz, DMSO-d_6) δ, ppm: 11.38 (br s, 1H), 7.51 (d, J = 7.2 Hz, 2H), 7.43-7.38 (m, 1H), 7.36 (t, J = 7.6 Hz, 2H), 3.27-3.20 (m, 1H), 2.98-2.91 (m, 1H), 1.27 (d, J = 2.4 Hz, 6H), 1.25 (d, J = 2.4 Hz, 6H). ^{1}H NMR for minor isomer (400 MHz, DMSO-*d6*) δ, ppm: 11.49 (br s, 1H), 7.43-7.38 (m, 2H), 7.26-7.23 (m, 1H), 7.19 (t, J = 7.2 Hz, 2H), 3.06-2.99 (m, 1H), 2.98-2.91 (m, 1H), 1.20 (br s, 6H), 1.18 (br s, 6H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 152.58, 151.93, 142.34, 136.81, 133.19, 132.34, 129.01, 128.58, 127.21, 126.47, 125.77, 28.36, 28.16, 26.24, 25.12, 23.67, 23.14, 22.26. IR (NaCl): 3430, 2965, 2358, 1606, 1531, 1450, 1365, 1011, 772, 700 cm^{-1}. HRMS (ESI) for $C_{15}H_{21}N_2$ $[M+H]^+$: calcd 229.1705, found 229.1709.



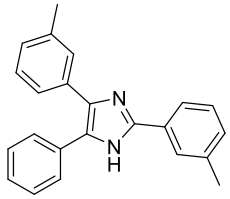
2,4(5)-dicyclohexyl-5(4)-phenyl-1*H*-imidazole (3j): Isolated as a colorless solid (0.262 g, 85%, mixture of two tautomers), mp 190-291°C. ^{1}H NMR for major isomer (400 MHz, DMSO-d_6) δ, ppm: 11.33 (br 2s, 1H), 7.50 (d, J = 7.2, 2H), 7.42-7.39 (m, 1H), 7.36 (t, J = 7.6 Hz, 2H), 2.86-2.81 (m, 1H), 2.64-2.59 (m, 1H), 1.79-1.74 (m, 8H), 1.61-1.48 (m, 4H), 1.37-1.15 (m, 8H). ^{1}H NMR for minor isomer (400 MHz, DMSO-d_6) δ, ppm: 11.47 (br 2s, 1H), 7.41 (d, J = 7.6, 2H), 7.24-7.21 (m, 3H), 7.18 (t, J = 7.2 Hz, 1H), 2.86-2.81 (m, 1H), 2.64-2.59 (m, 1H),1.92-1.89 (m, 4H), 1.68-1.66 (m, 8H), 1.37-1.15 (m, 8H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 151.89, 151.16, 142.04, 136.89, 133.40, 132.29, 131.64, 129.02, 128.59, 127.13, 126.37, 125.71, 123.85, 123.37, 37.92, 37.74, 36.41, 35.13, 33.39, 33.01, 32.09, 29.22, 27.33, 26.74, 26.22, 26.10, 26.02, 25.19, 24.02. IR (NaCl): 3440, 2926, 2851, 1642, 1607, 1531, 1449, 988, 771, 698 cm^{-1}. HRMS (ESI) for $C_{21}H_{29}N_2$ $[M+H]^+$: calcd 309.2331, found 309.2335.



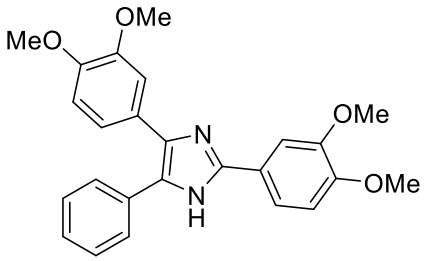
2,4,5-*tris*(*p-tolyl*)-1*H*-imidazole (3k): Isolated as a colorless solid (0.287 g, 85%), mp 238-239°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.48 (br s, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 6.8 Hz, 2H), 7.39 (d, J = 6.8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.11 (d, J = 7.2 Hz, 2H), 2.34 (s, 6H), 2.29 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 145.82, 137.97, 137.35, 137.20, 135.90, 133.02, 129.67, 129.62, 129.20, 128.80, 128.66, 128.29, 128.03, 127.47, 125.59, 21.35, 21.28. HRMS (ESI) for $C_{24}H_{23}N_2$ $[M+H]^+$: calcd 339.1861, found 339.1863. This is a known compound.[3]



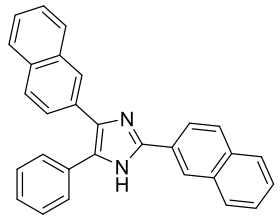
2,4,5-*tris*(4-methoxyphenyl)-1*H*-imidazole (3l): Isolated as a colorless solid (0.347 g, 90%), mp 226-227°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.34 (br s, 1H), 8.01 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.75 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 159.71, 159.13, 158.31, 145.40, 136.51, 130.11, 128.60, 128.50, 127.01, 124.19, 123.84, 114.53, 114.06, 55.64, 55.45. HRMS (ESI) for $C_{24}H_{23}N_2O_3$ $[M+H]^+$: calcd 387.1709, found 387.1711. This is a known compound.[3]



5(4)-phenyl-2,4(5)-di-*m-tolyl*-1*H*-imidazole (3m): Isolated as a colorless solid (0.291 g, 90%, mixture of two tautomers), mp 259-260°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 12.61 (s br, 1H), 7.93 (s, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.41-7.45 (m, 1H), 7.04-7.37 (m, 8H), 2.38 (s, 3H), 2.27, 2.33 (2s, 3H for two isomers). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 21.49, 21.57, 122.82, 122.84, 124.70, 126.08, 126.20, 126.91, 127.50, 127.63, 128.14, 128.30, 128.44, 128.53, 128.59, 128.70, 128.84, 128.97, 129.04, 129.35, 129.38, 130.76, 131.50, 131.59, 135.60, 135.71, 137.39, 137.64, 138.26, 145.96, 146.01. IR (NaCl): 3431, 2920, 2358, 1645, 1498, 1451, 1120, 788, 695 cm^{-}1. HRMS (ESI) for $C_{23}H_{21}N_2$ $[M+H]^+$: calcd 325.1705, found 325.1705.

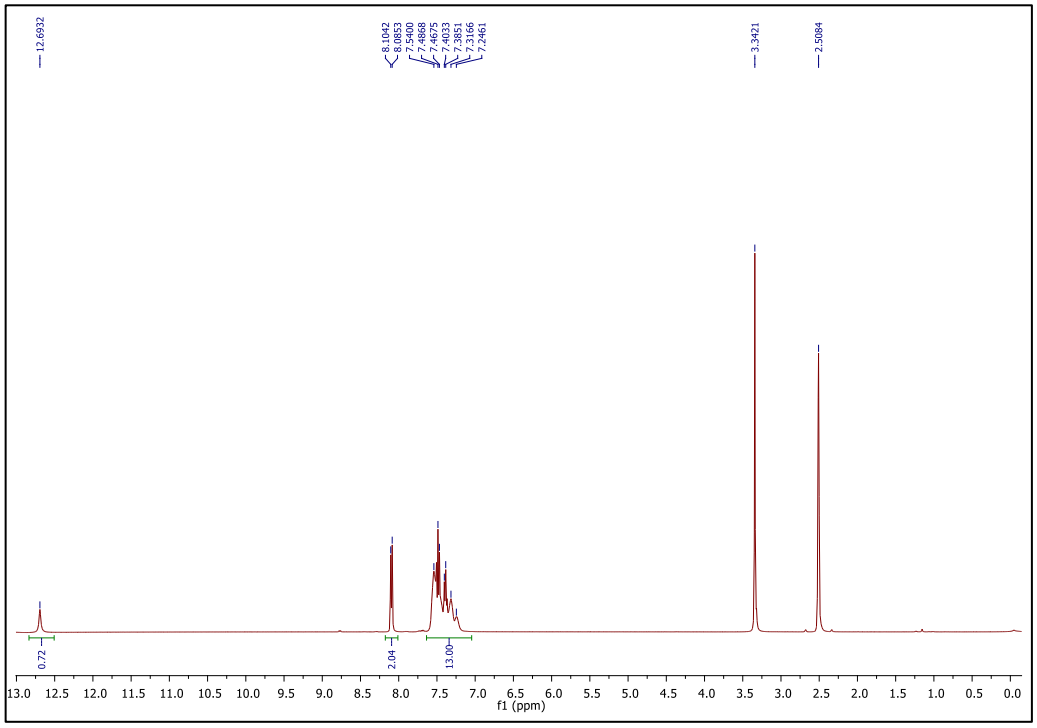


2,4-bis(3,4-dimethoxyphenyl)-5-phenyl-1H-imidazole (3n): Isolated as a colorless solid (0.262 g, 63%, mixture of two tautomers), mp 85-86°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.60 (s, 1H), 7.55 (d, *J* = 6.4 Hz, 2H), 7.29-7.38 (m, 4H), 7.07-7.12 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.92(s, 3H), 3.89 (s, 3H), 3.70 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): 149.78, 149.42, 148.85, 148.49, 145.81, 128.55, 127.86, 127.38, 122.97, 120.27, 117.48, 111.28, 111.23, 111.11, 109.02, 56.06, 55.97, 55.88, 55.74. IR (NaCl): 3441, 2936, 2836, 2360, 2254, 1606, 1515, 1504, 1259, 1025, 855, 812, 732 cm^{-}1. HRMS (ESI) for $C_{25}H_{25}N_2O_4$ [M+H]$^{+}$: calcd 417.1814, found 417.1815.

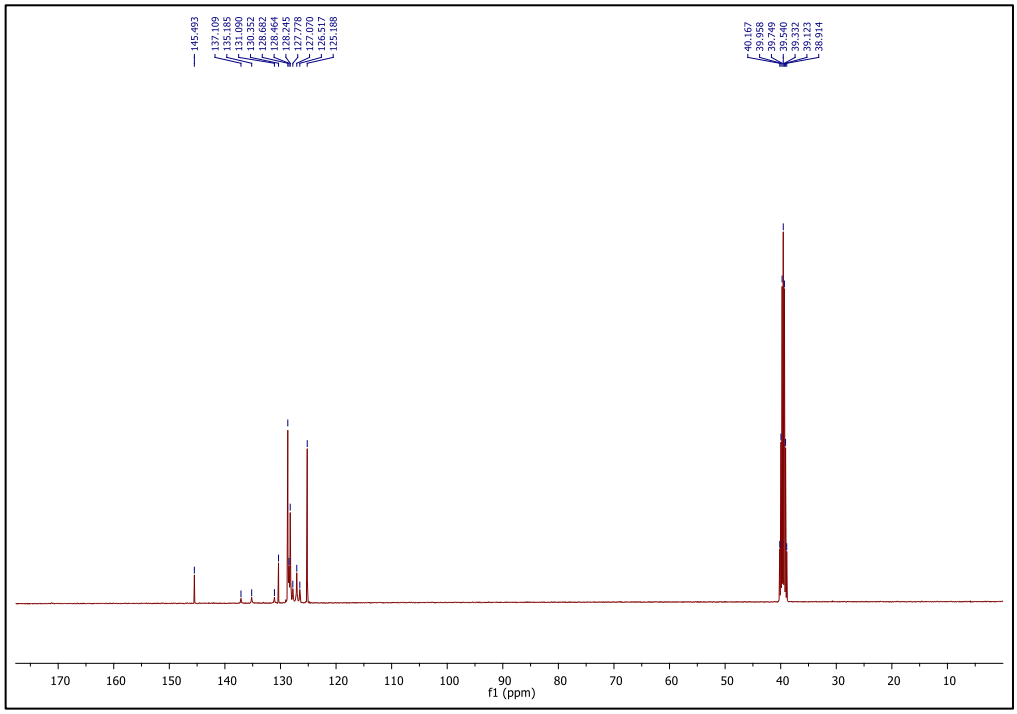


2,4(5)-di(naphthalen-2-yl)-5(4)-phenyl-1*H*-imidazole (3o): Isolated as a yellowish solid (0.340 g, 86%, mixture of two tautomers), mp above 300°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ, ppm: 7.33-7.35 (m, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.48-7.65 (m, 7H), 7.87-7.91 (m, 3H), 7.94-8.04 (m, 3H), 8.18 (s, 1H), 8.32 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.69 (s, 1H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 124.04, 124.24, 126.46, 126.66, 126.82, 126.88, 127.18, 127.79, 128.07, 128.21, 128.32, 128.34, 128.60, 128.73, 128.95, 132.56, 133.23, 133.51, 133.58, 146.34. IR (NaCl): 3426, 1631, 1404, 1109, 889, 855, 811, 766, 752, 698 cm^{-}1. HRMS (ESI) for $C_{29}H_{21}N_2$ [M+H]$^{+}$: calcd 397.1705, found 397.1704.

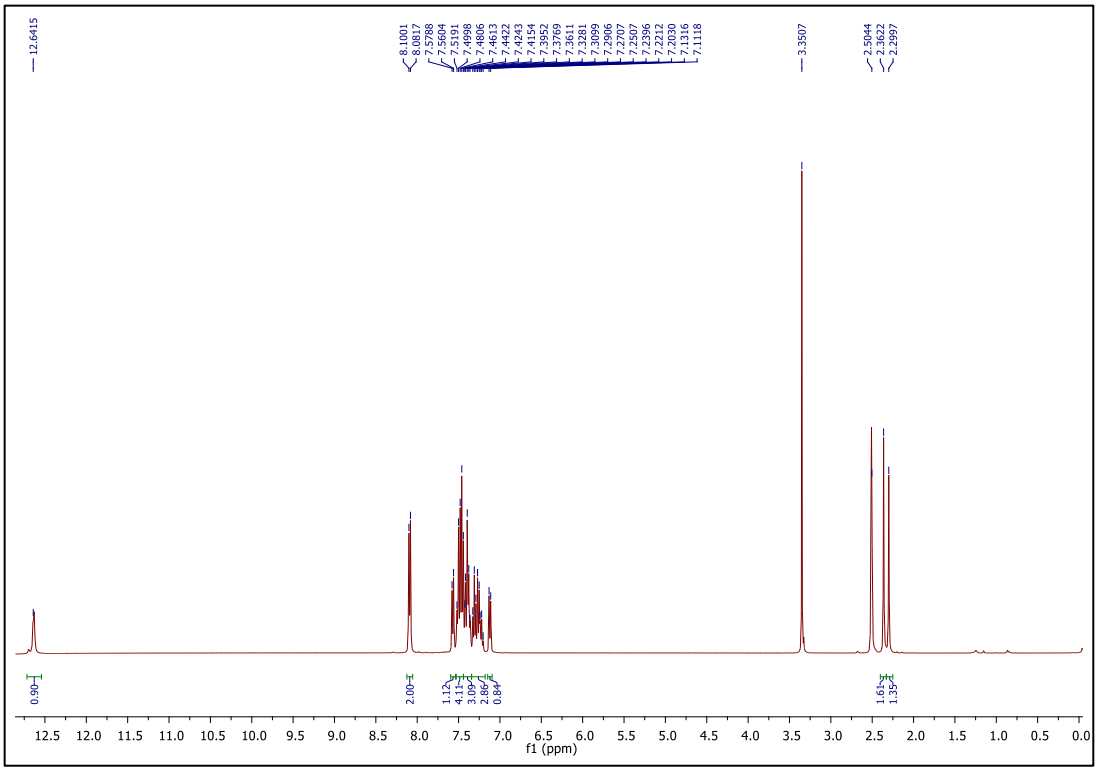
5. ^{1}H NMR and ^{13}C NMR spectrum of tri-substituted imidazoles (3a-3o):



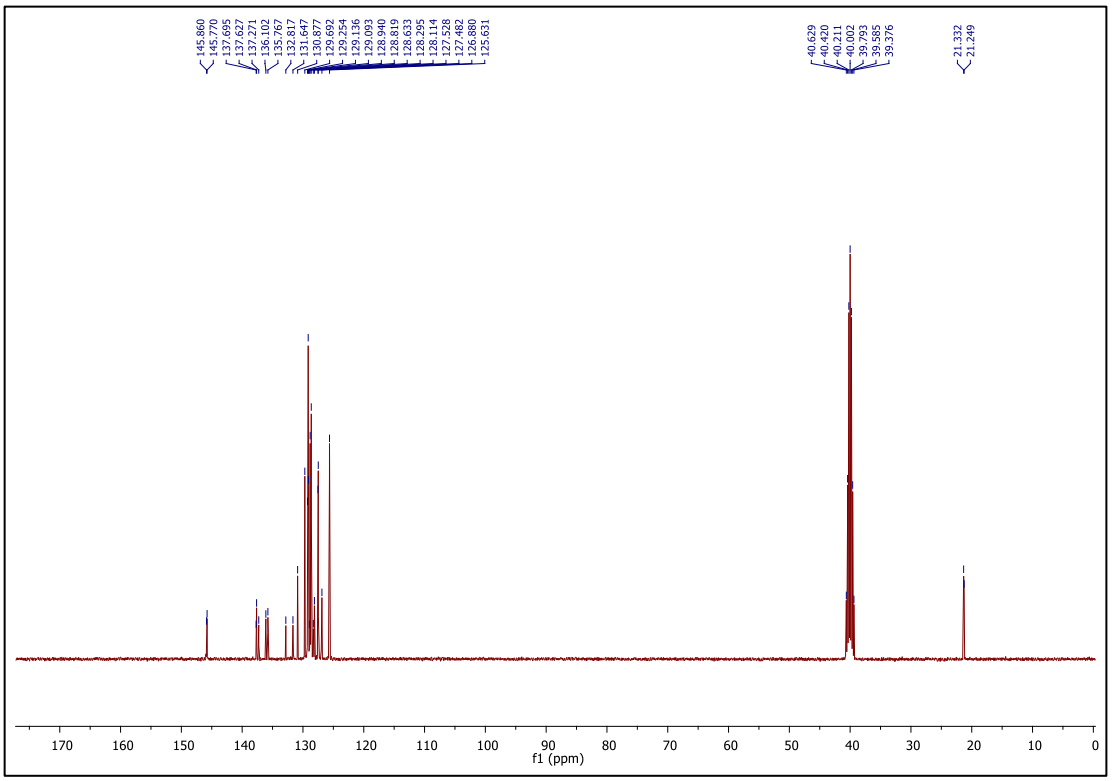
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3a** (peaks at 3.3 and 2.5 ppm are solvent and water peaks)



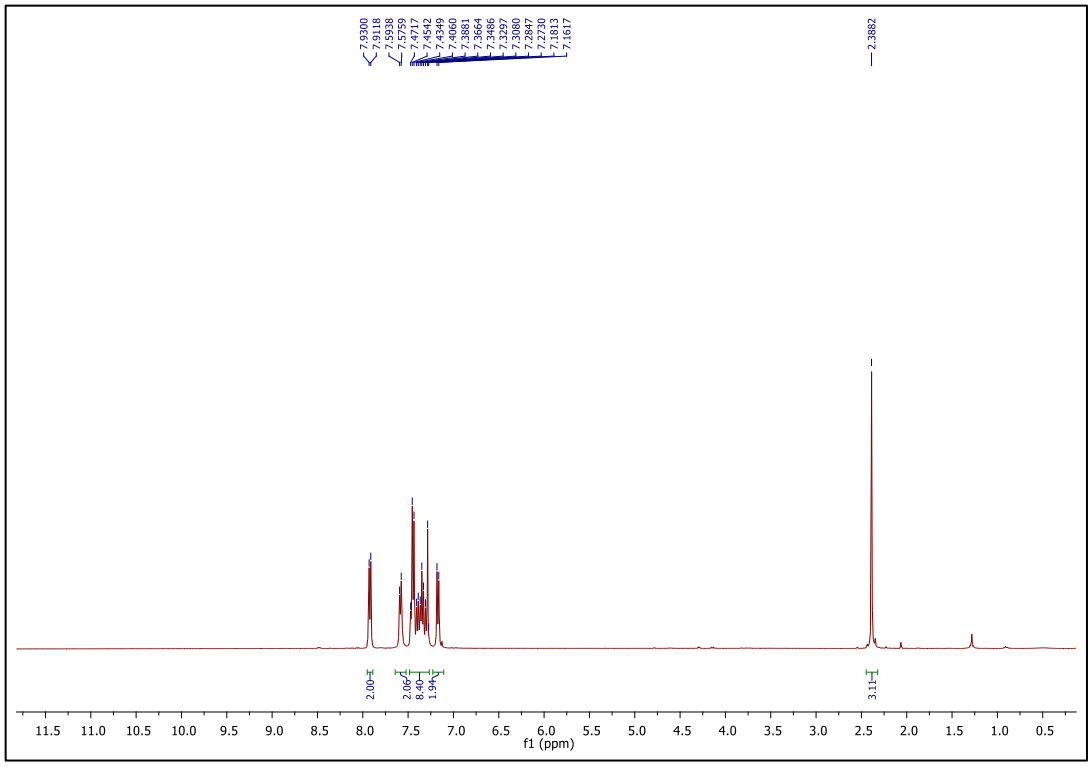
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3a**



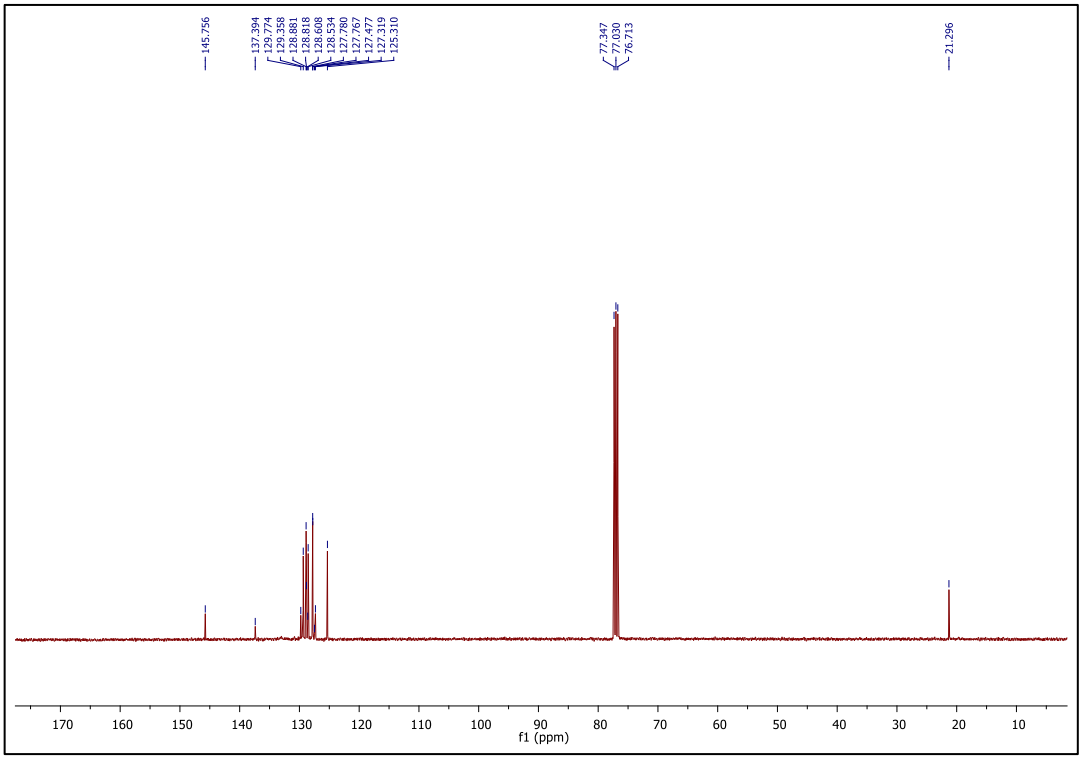
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3b** (mixture of two tautomers), peaks at 3.3 and 2.5 ppm are solvent and water peaks



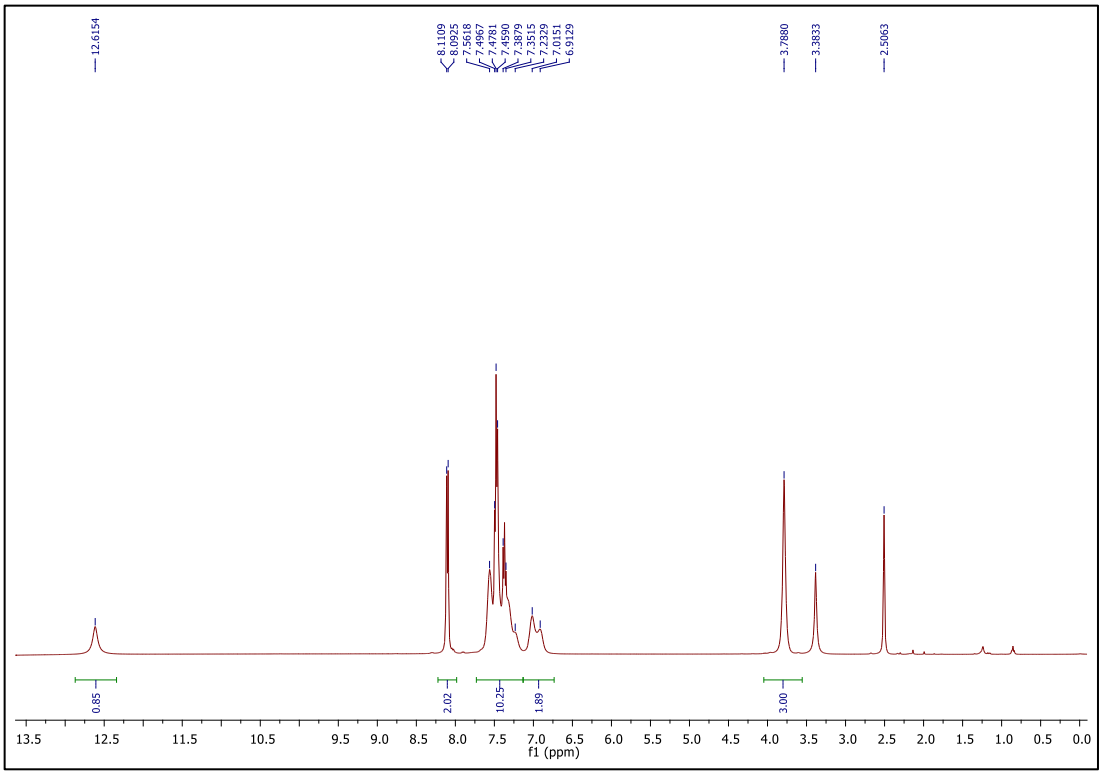
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3b** (mixture of two tautomers)



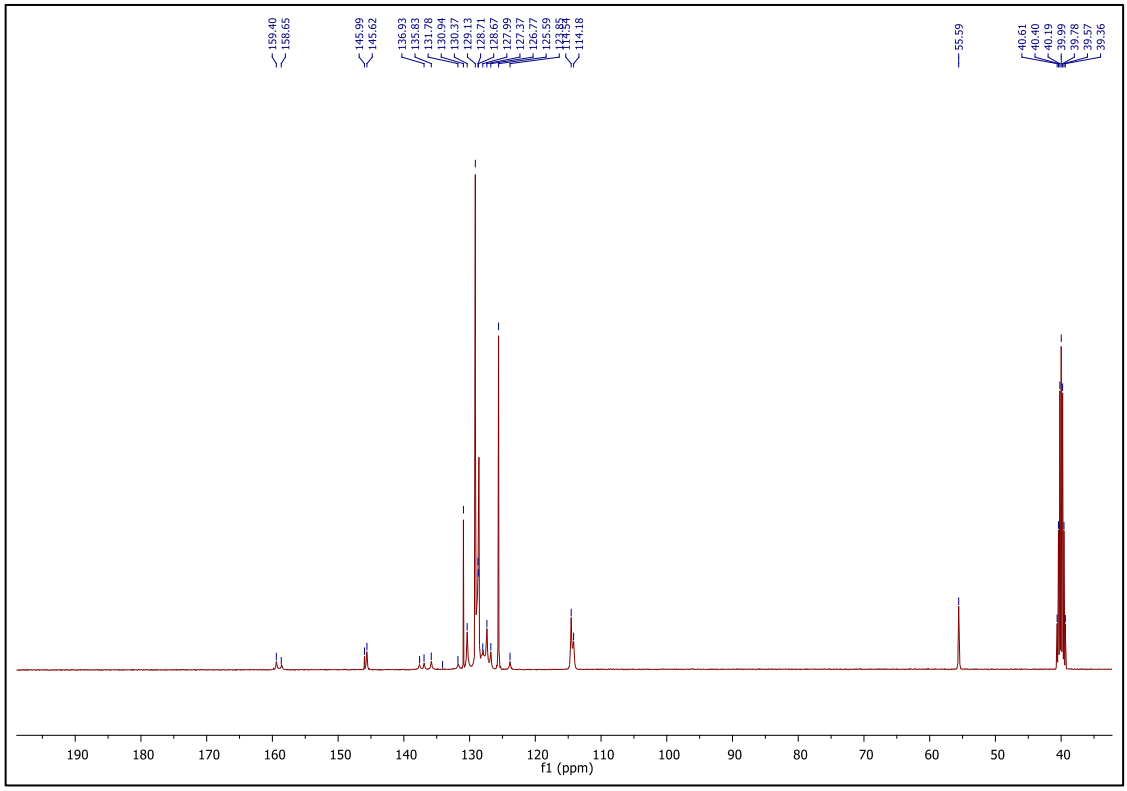
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b** (mixture of two tautomers)



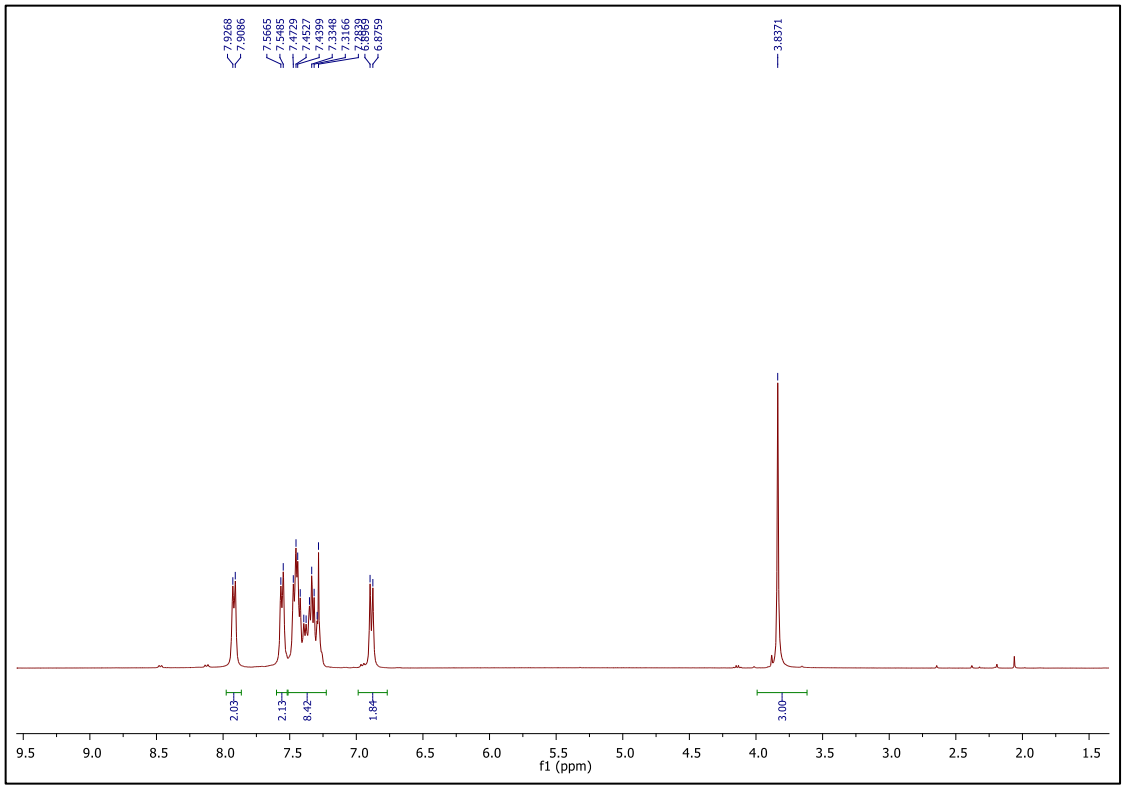
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3b** (mixture of two tautomers)



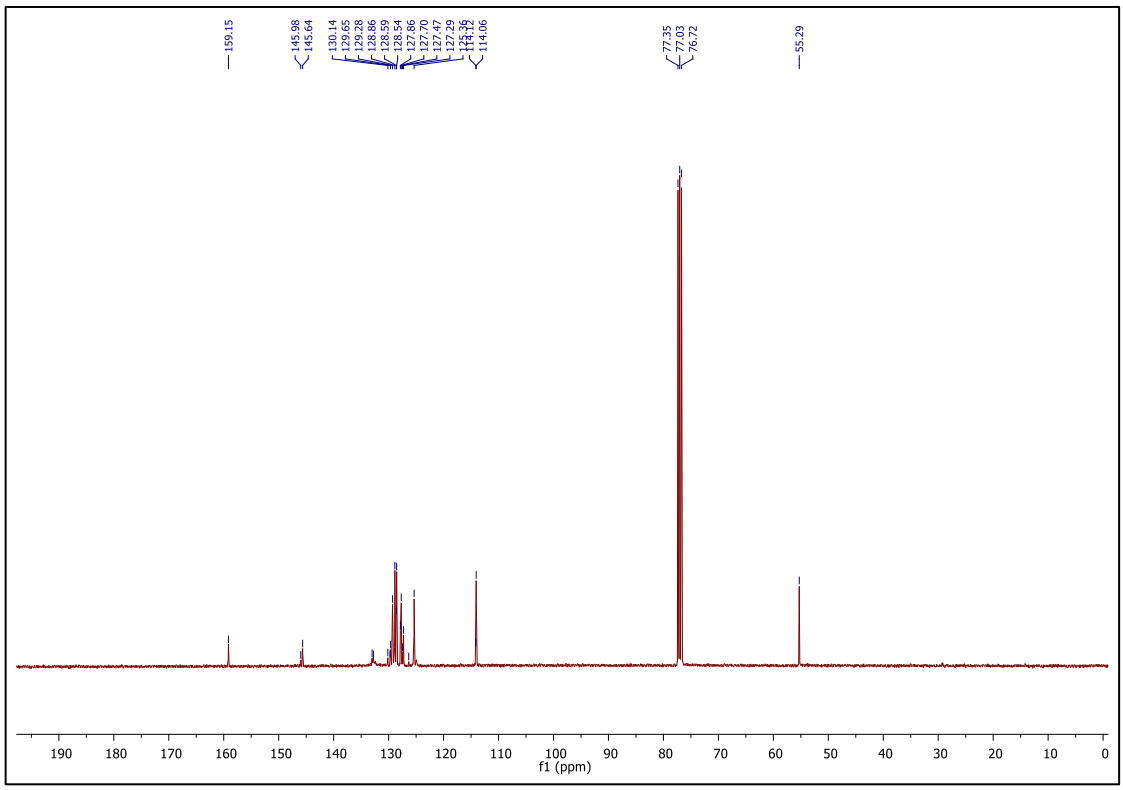
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3c** (mixture of two tautomers), peaks at 3.3 and 2.5 ppm are solvent and water peaks



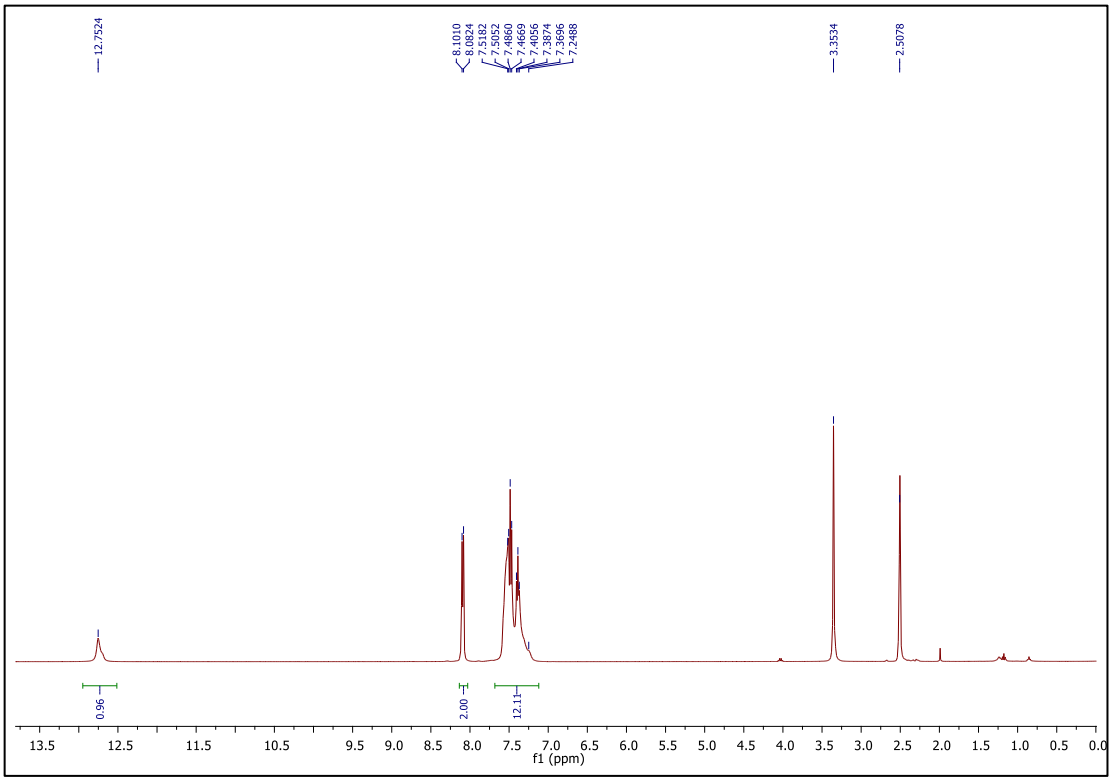
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3c** (mixture of two tautomers)



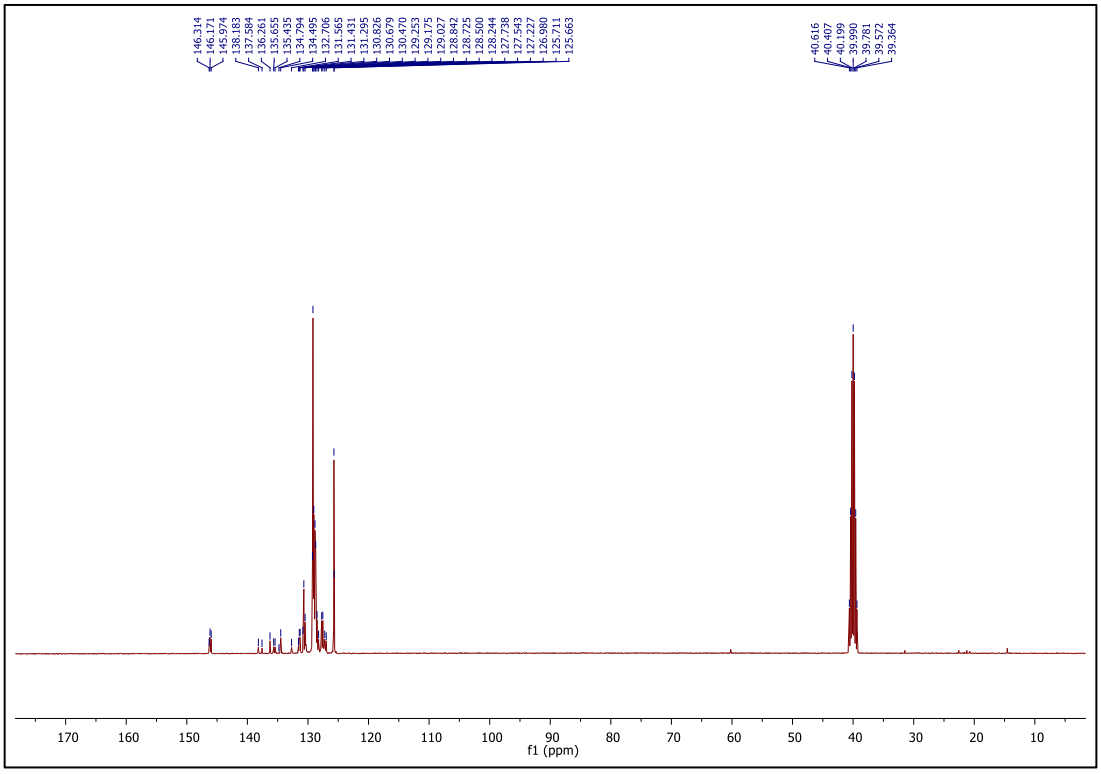
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c** (mixture of two tautomers)



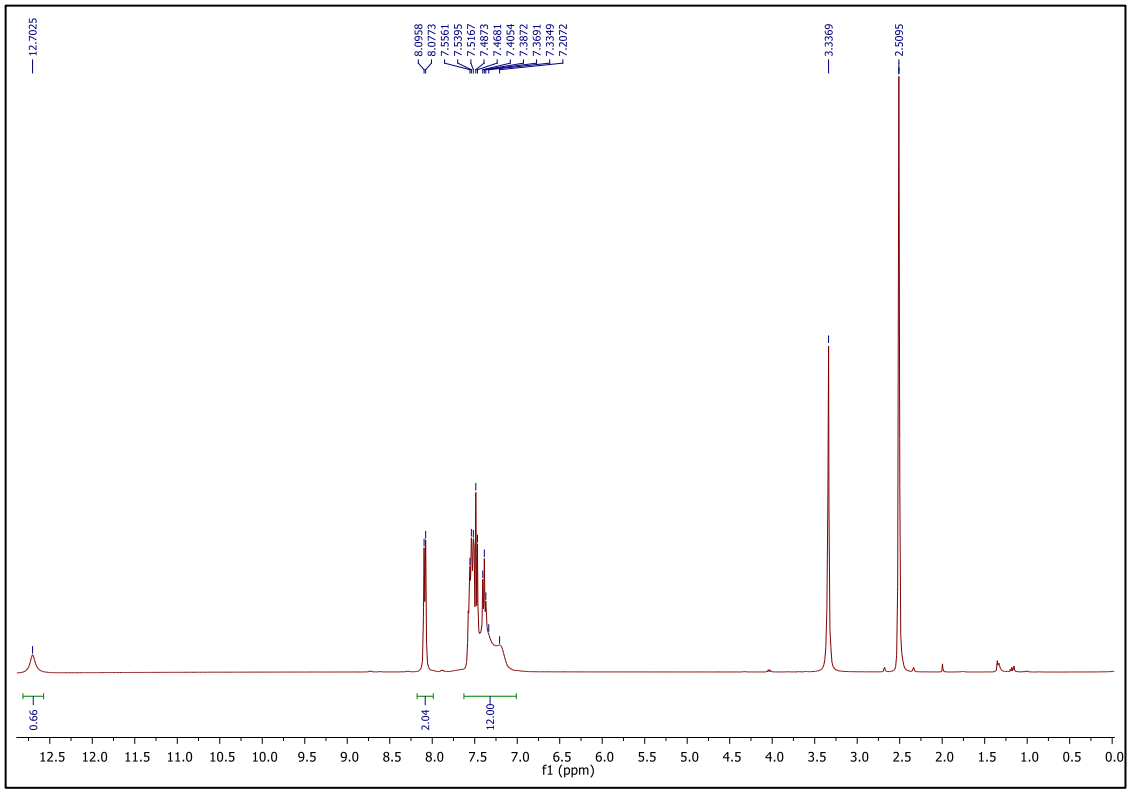
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3c** (mixture of two tautomers)



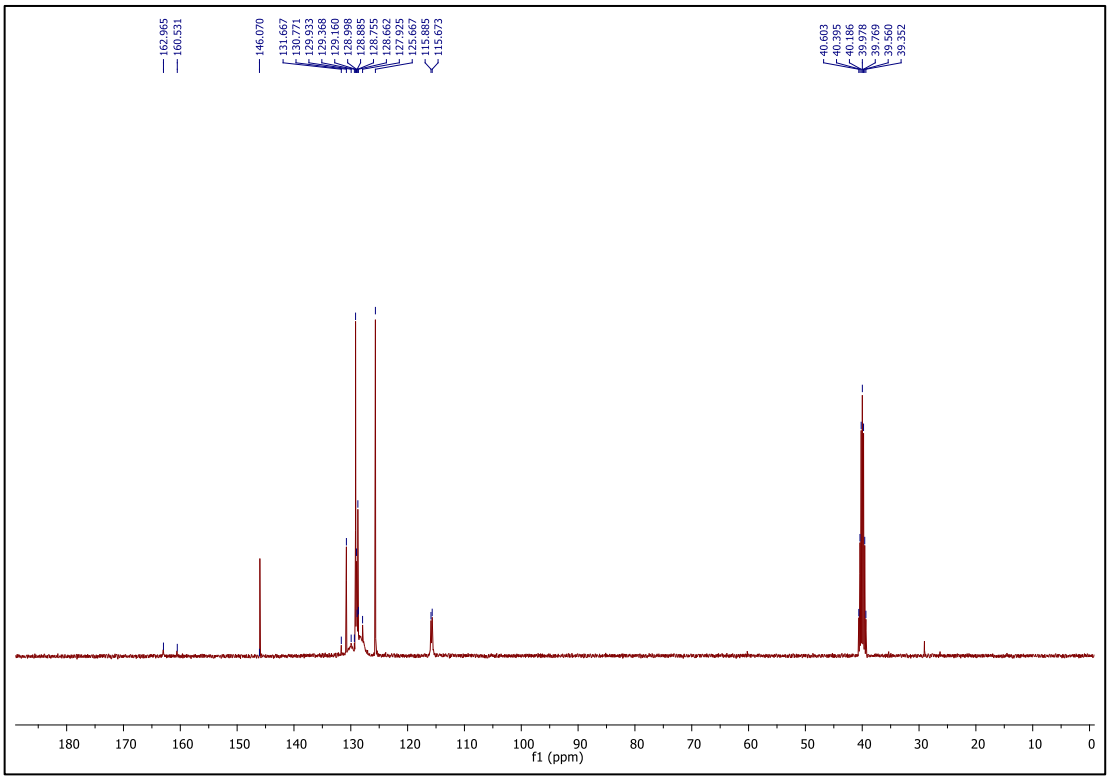
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3d** (mixture of two tautomers), 3.3 and 2.5 ppm are solvent and water peaks



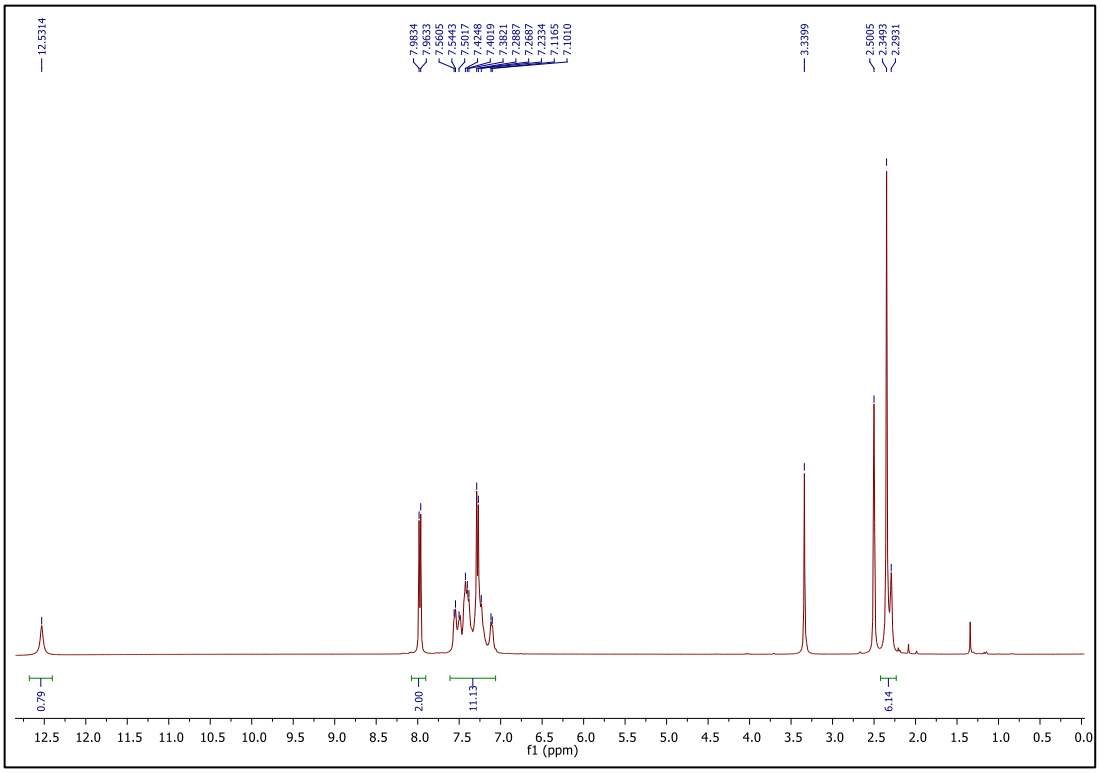
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3d** (mixture of two tautomers)



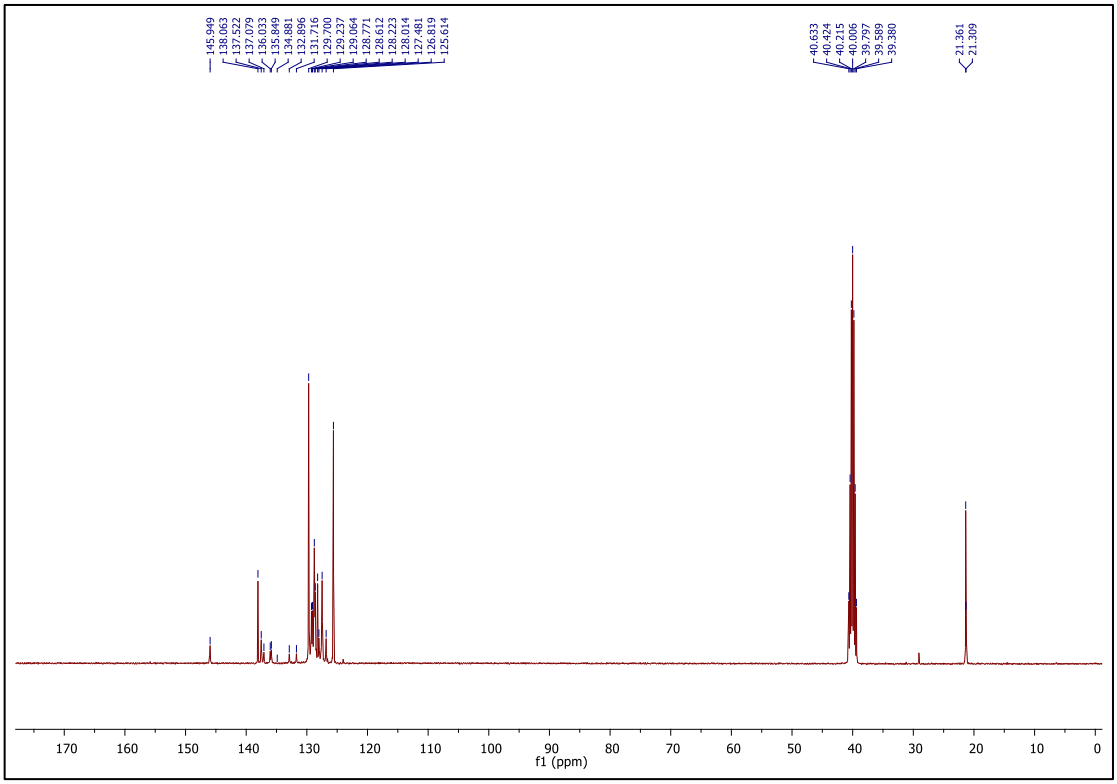
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3e** (mixture of two tautomers), peaks at 3.3 and 2.5 ppm are solvent and water peaks



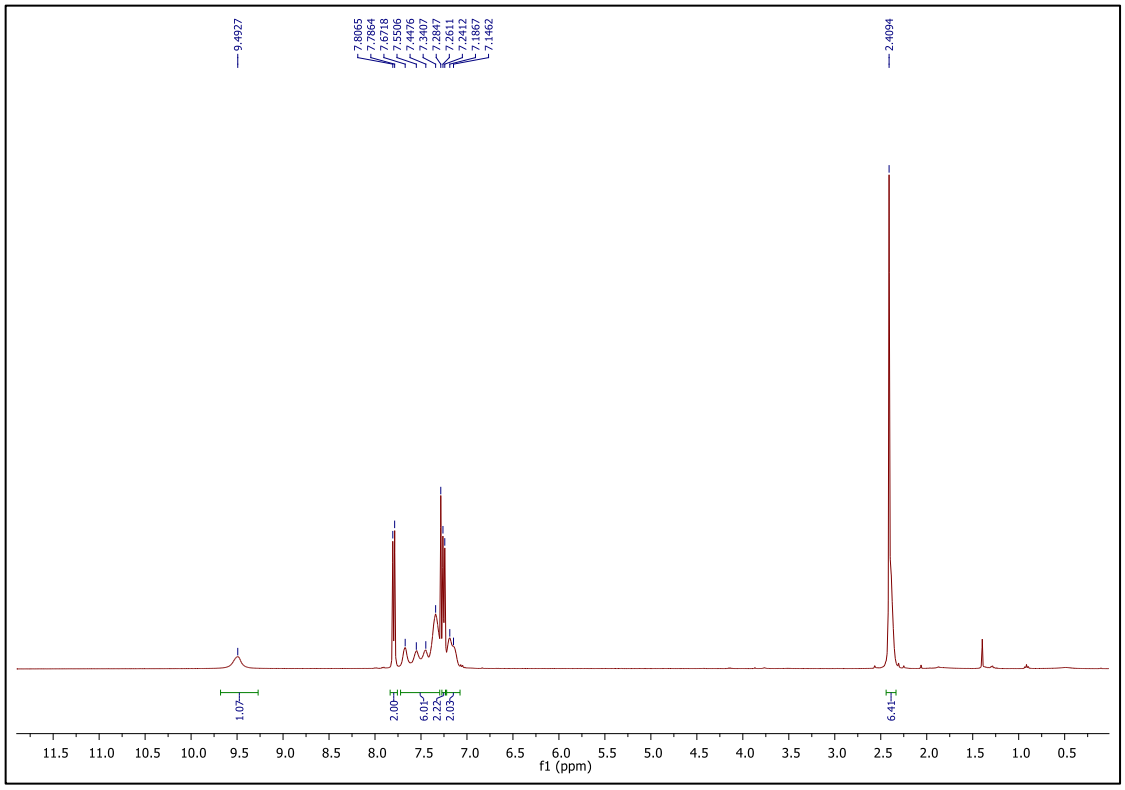
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3e** (mixture of two tautomers)



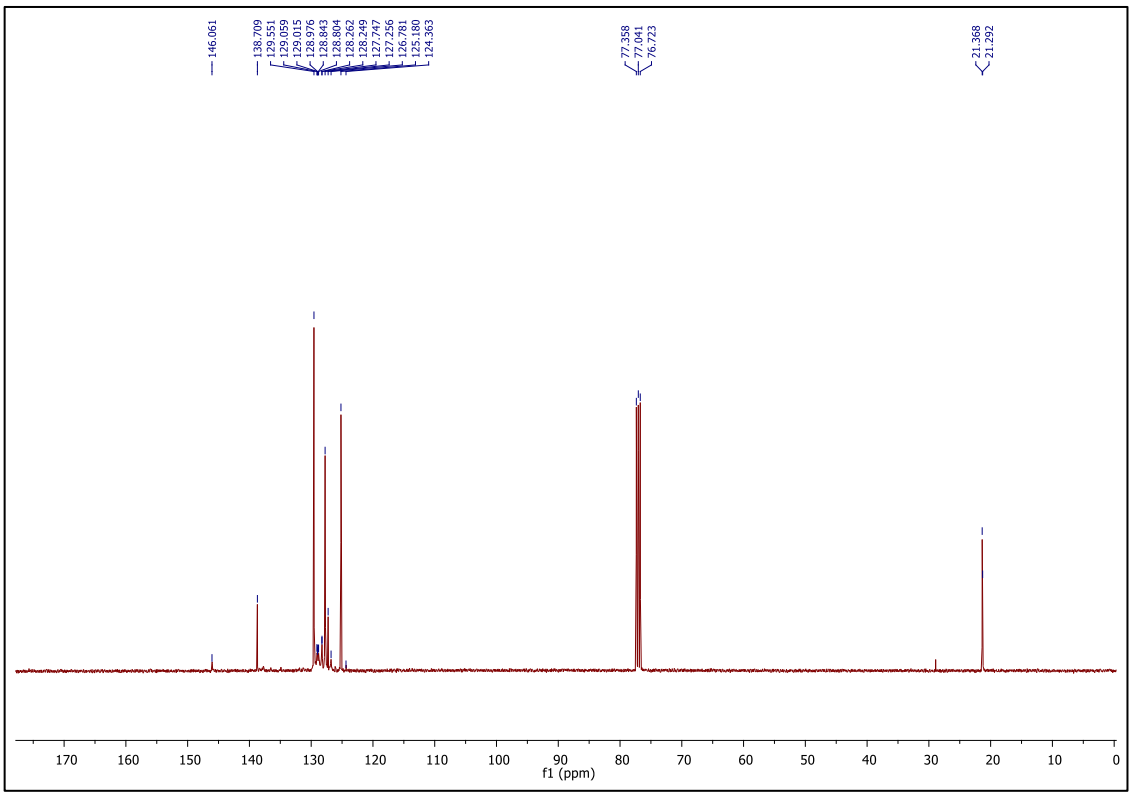
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3f** (mixture of two tautomers), peaks at 3.3 and 2.5 ppm are solvent and water peaks



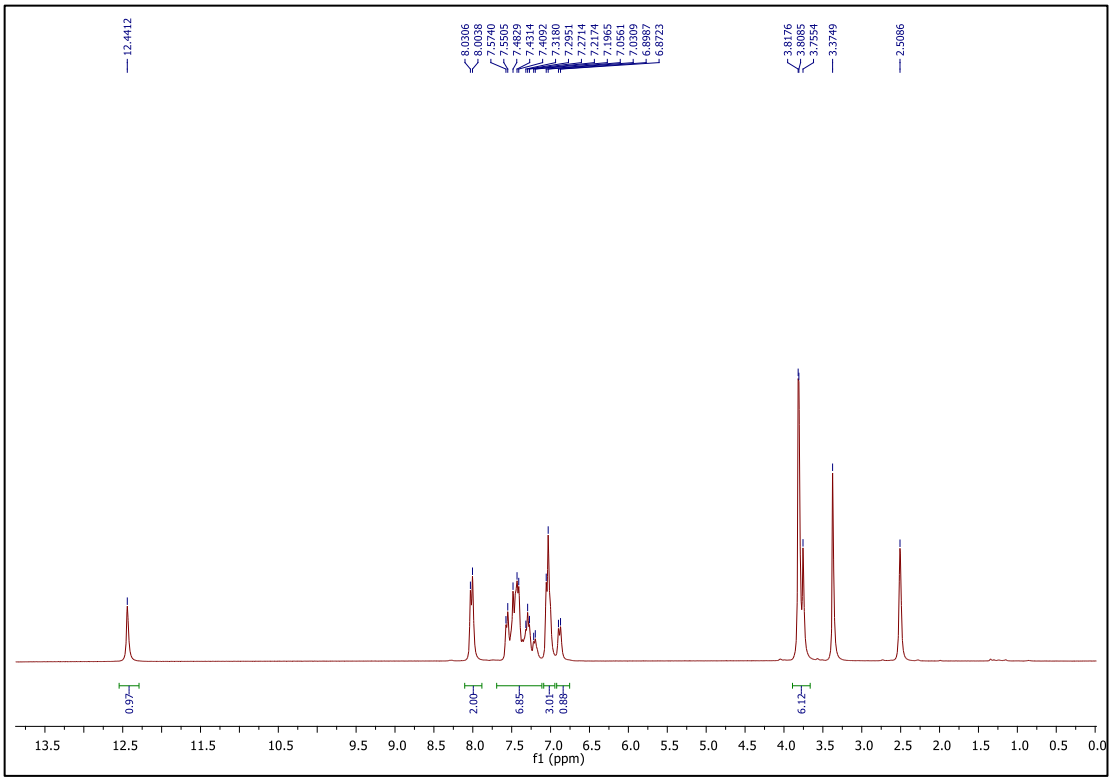
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3f** (mixture of two tautomers)



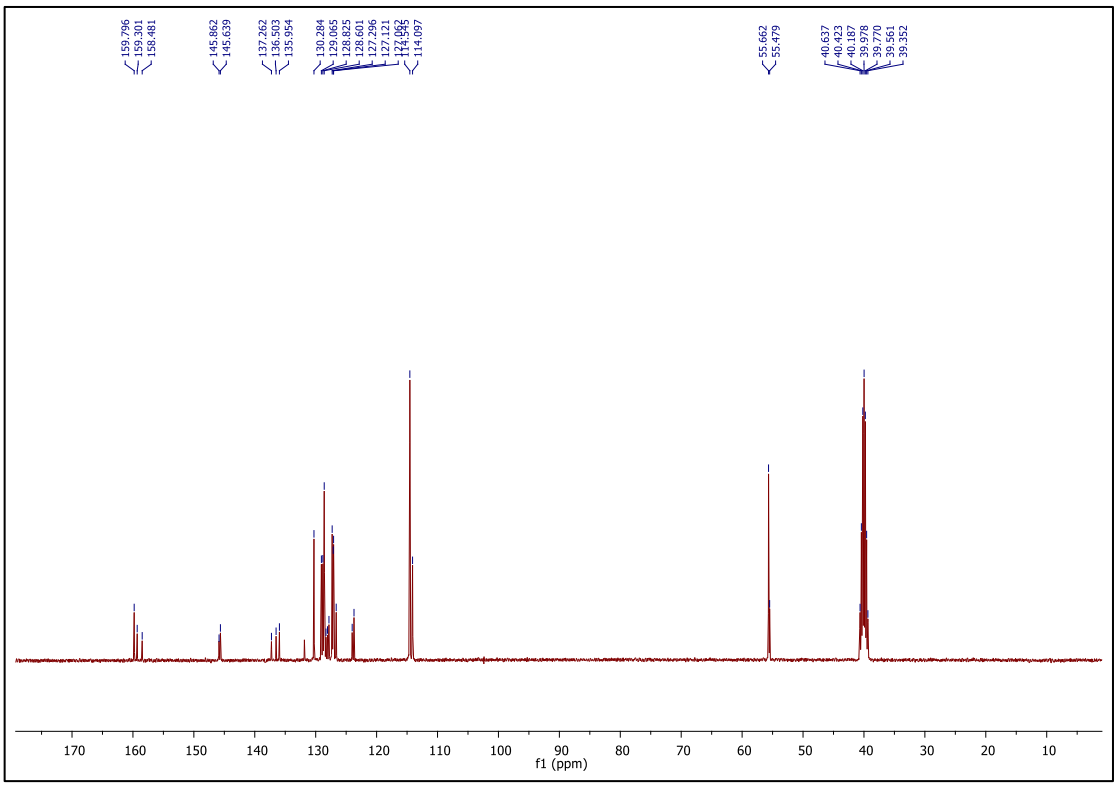
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f** (mixture of two tautomers)



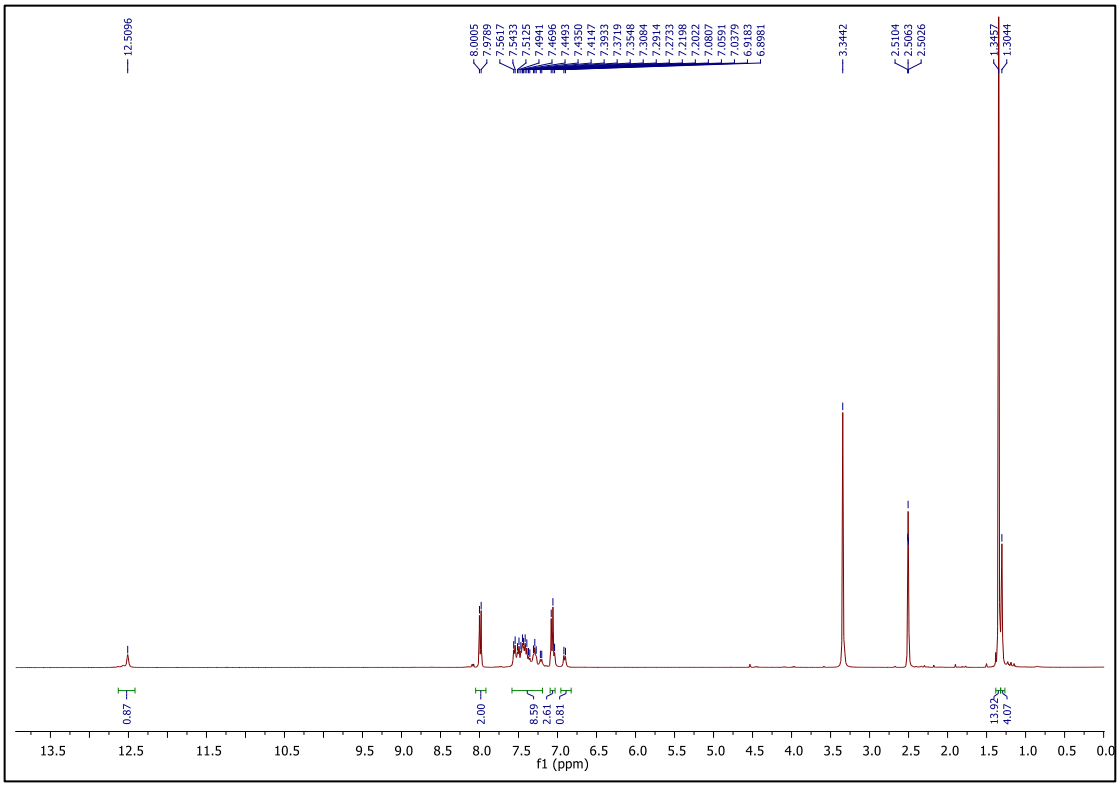
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3f** (mixture of two tautomers)



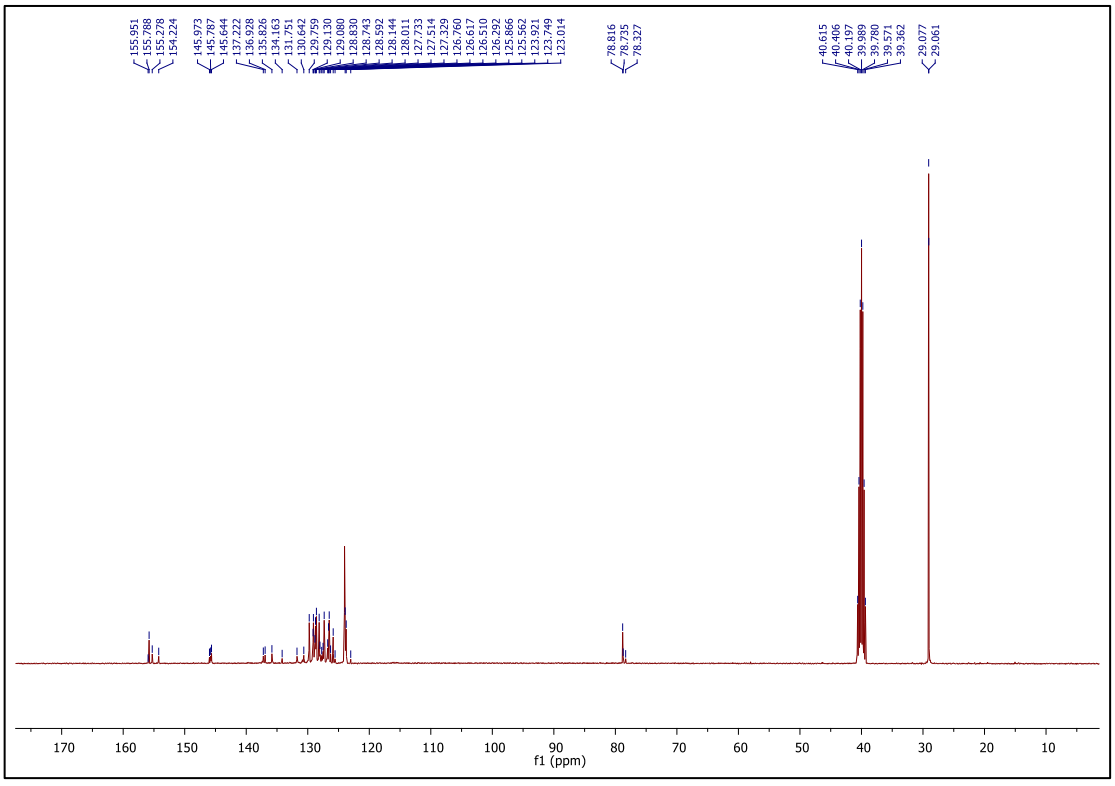
^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **3g** (mixture of two tautomers), 3.3 and 2.5 ppm are solvent and water peaks



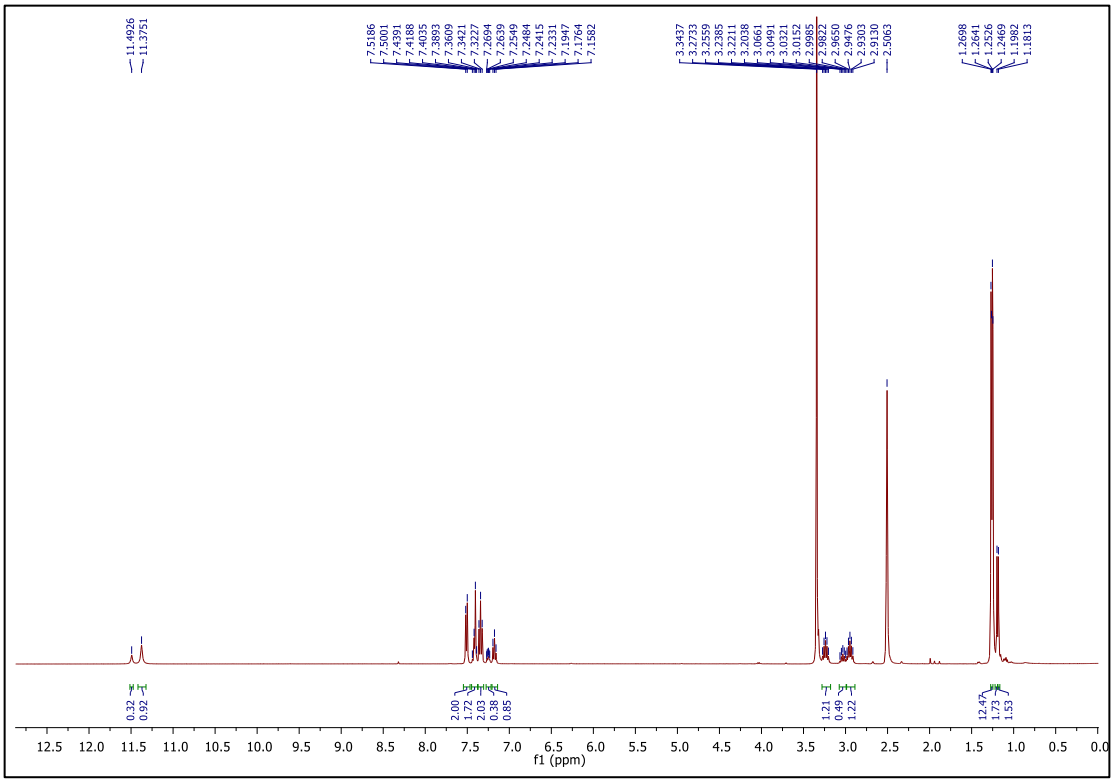
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3g** (mixture of two tautomers)



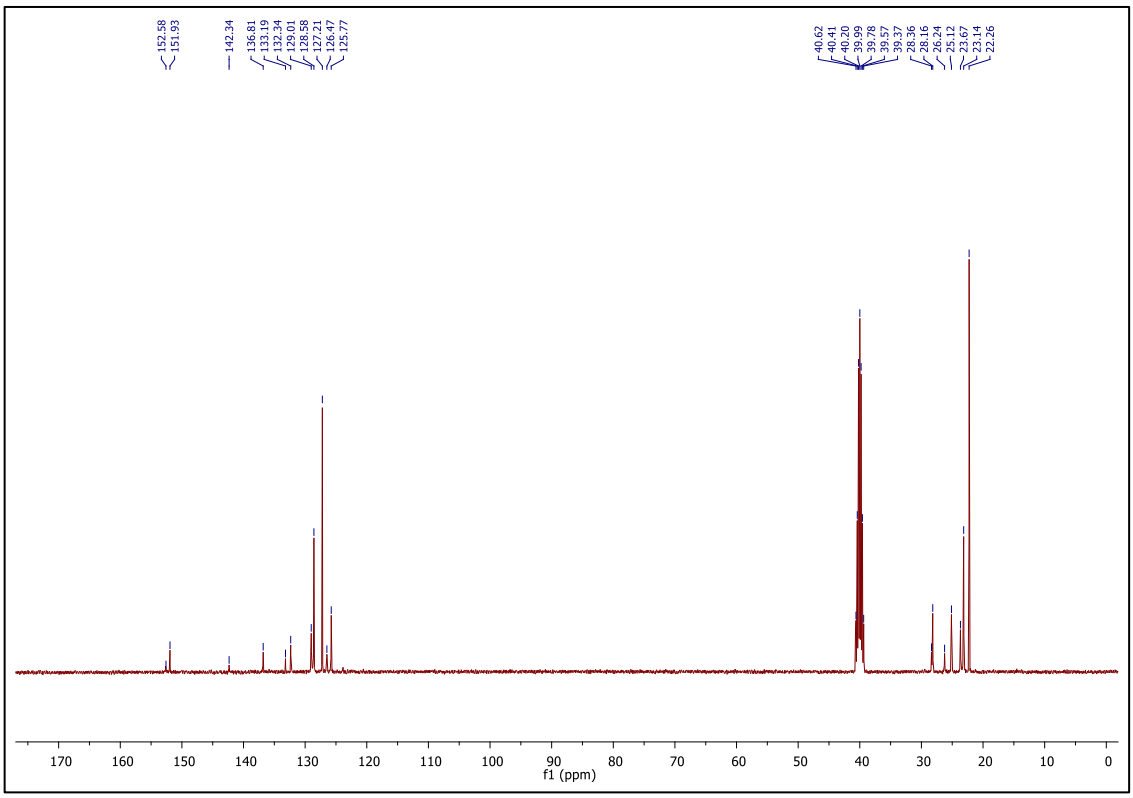
^{11}H NMR (400 MHz, DMSO-d_6) spectrum of **3h** (mixture of two tautomers), 3.3 and 2.5 ppm are solvent and water peaks



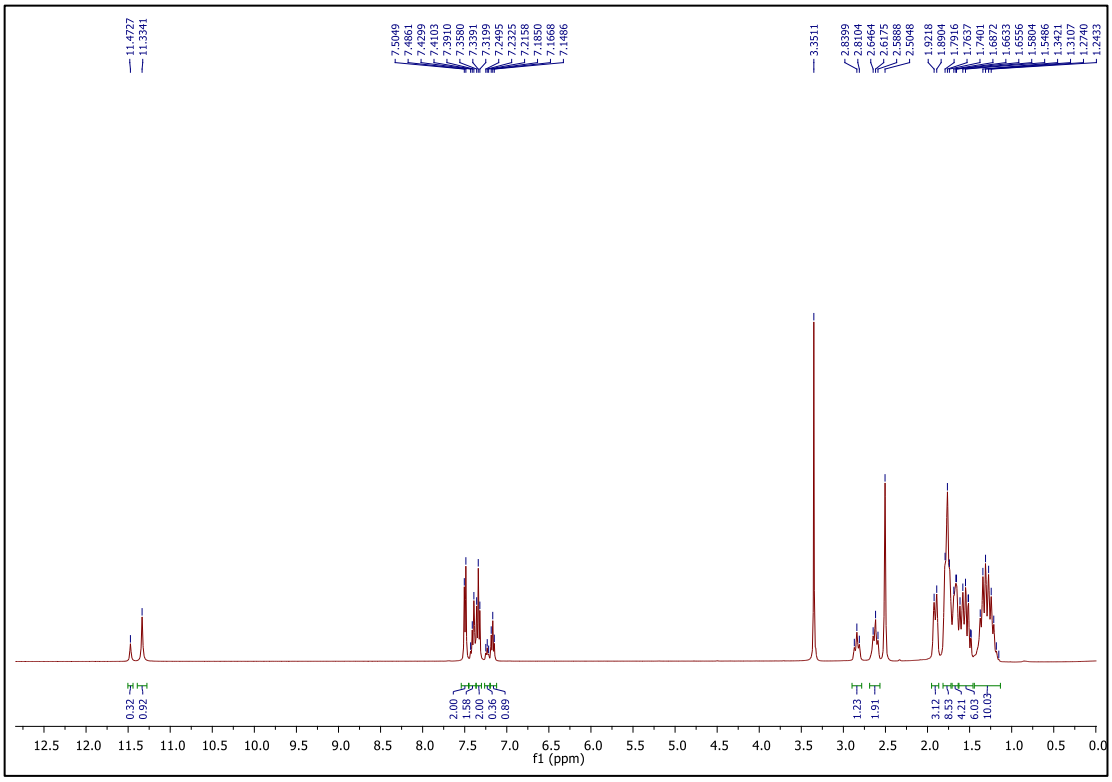
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3h** (mixture of two tautomers)



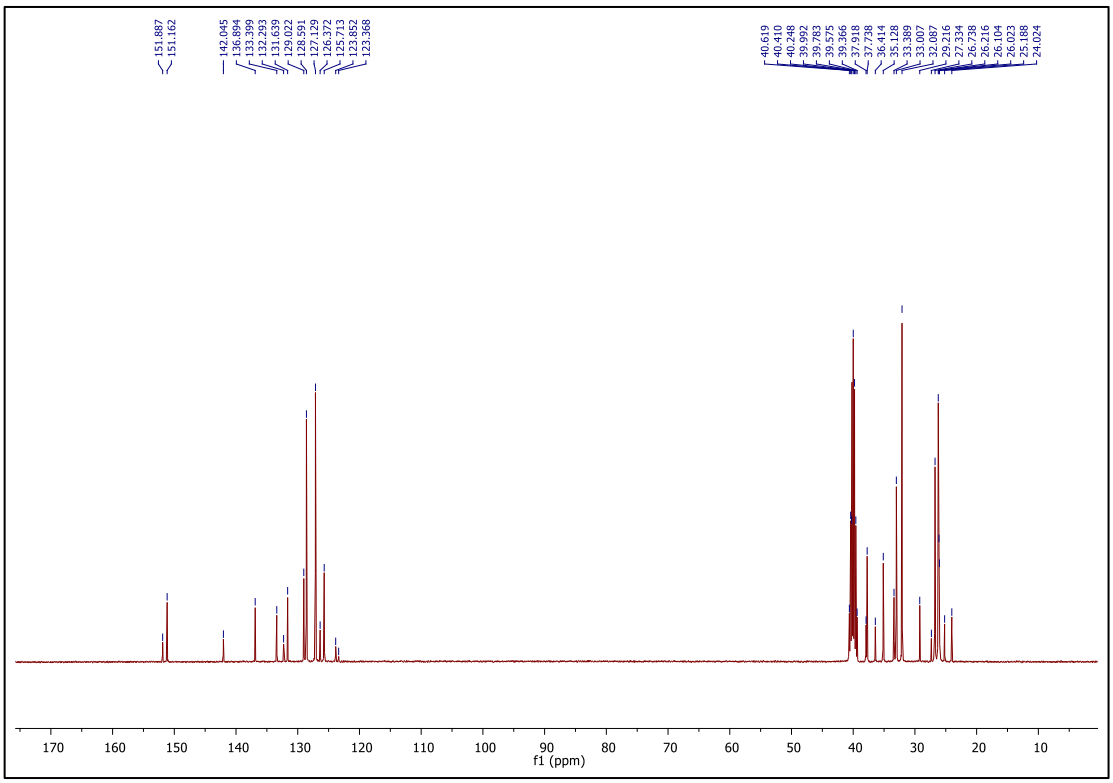
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3i** (mixture of two tautomers), peaks at 3.3 and 2.5 ppm are solvent and water peaks



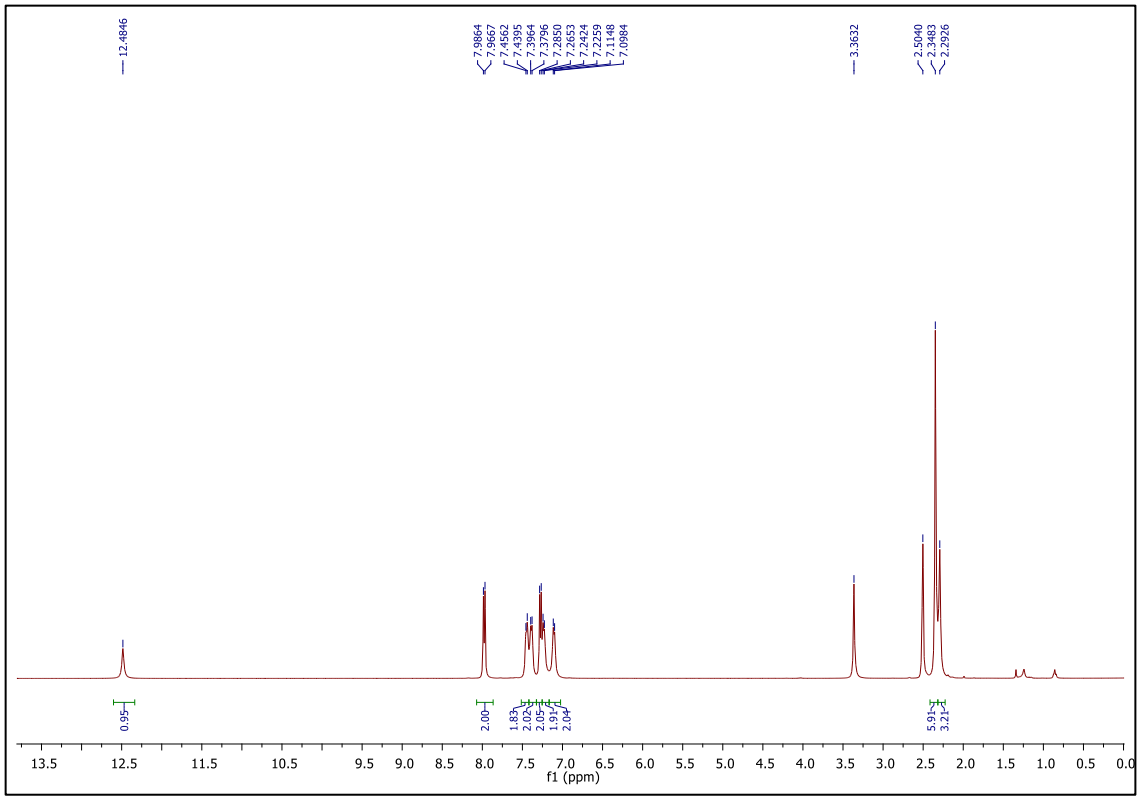
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3i** (mixture of two tautomers)



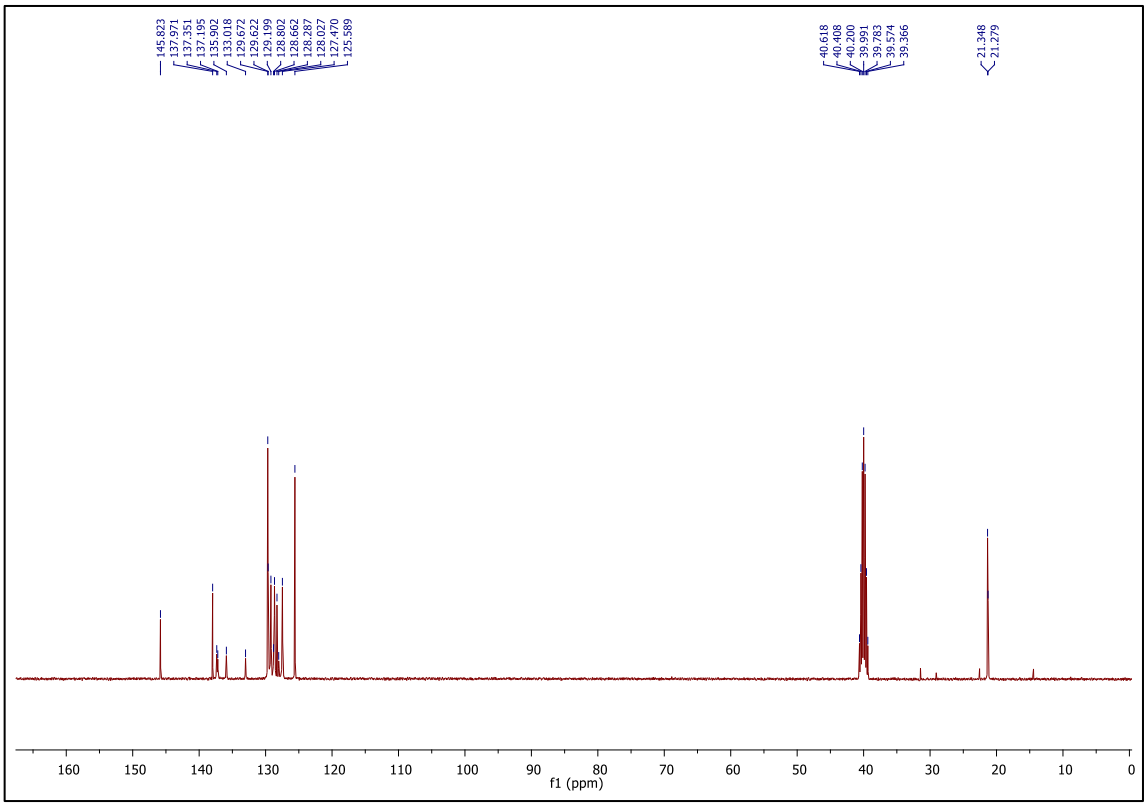
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3j** (mixture of two tautomers), peaks at 3.3 and 2.5 ppm are solvent and water peaks



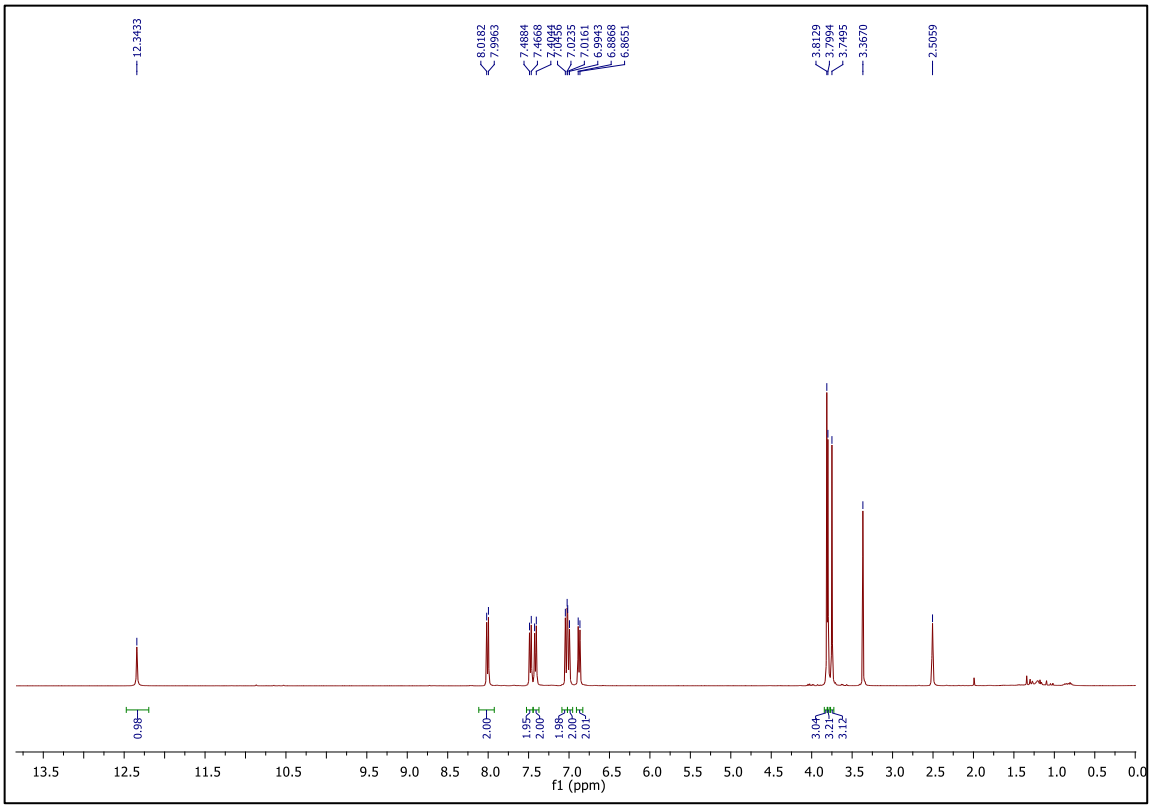
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3j** (mixture of two tautomers)



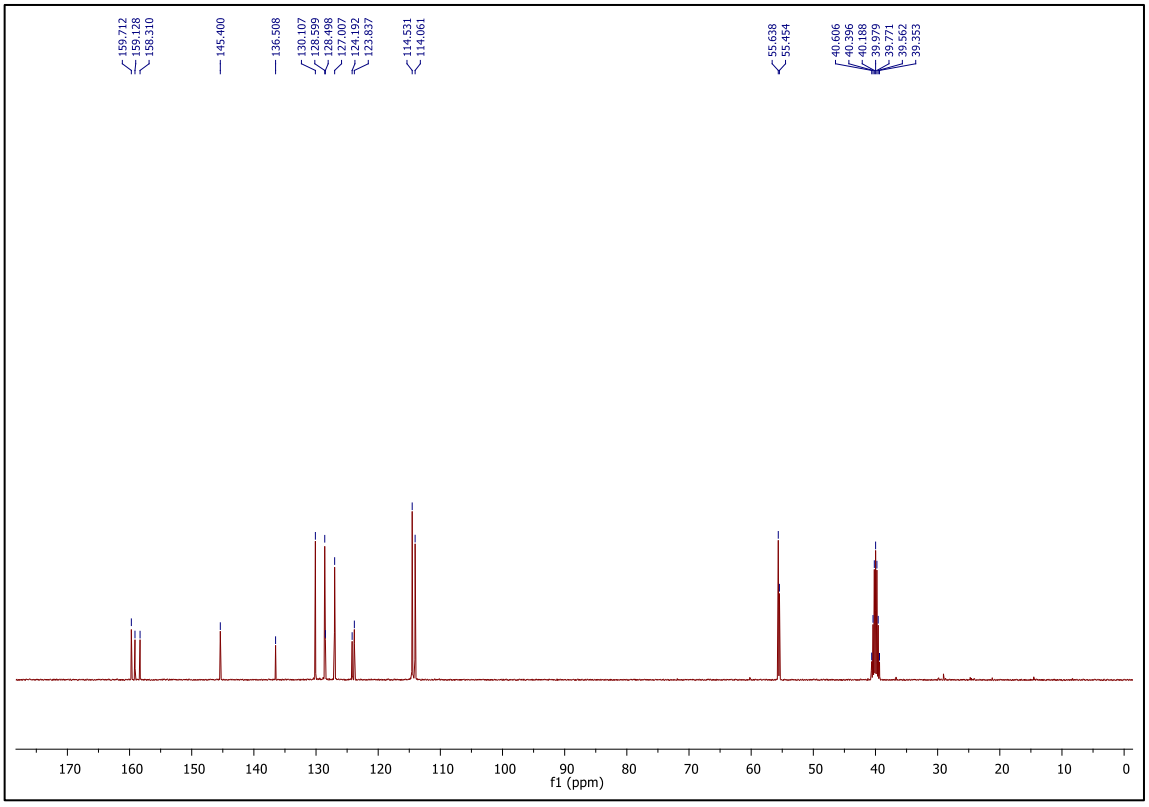
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3k** (peaks at 3.3 and 2.5 ppm are solvent and water peaks)



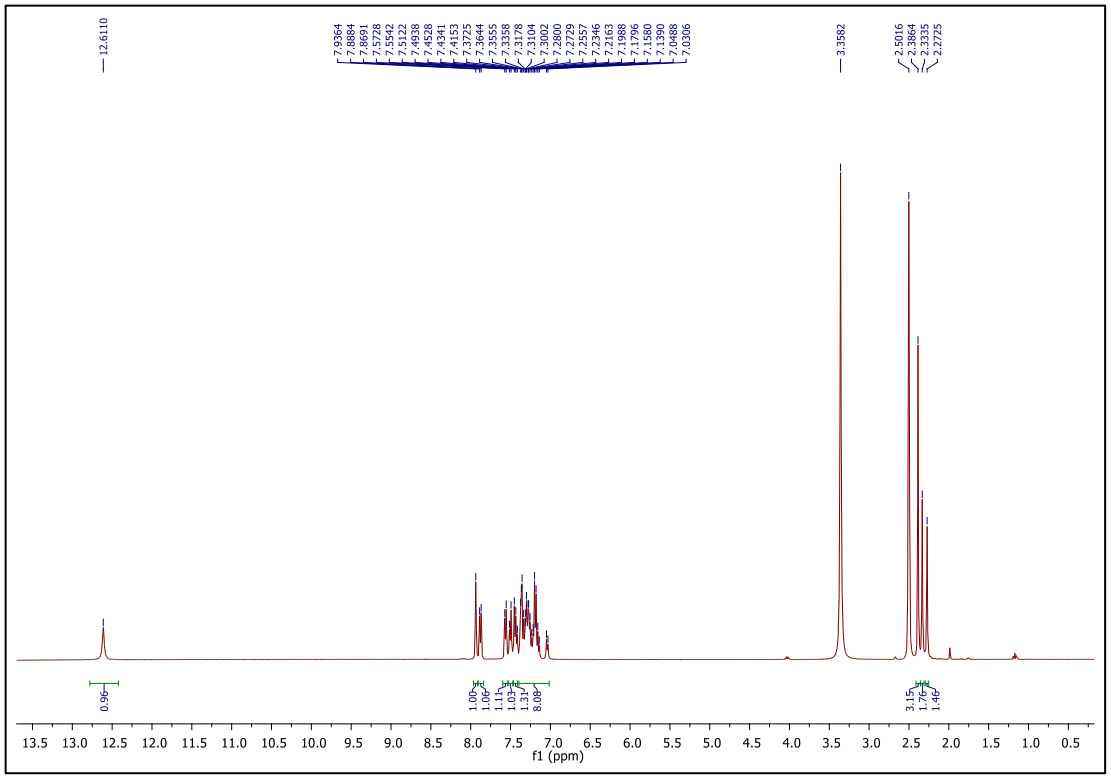
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3k**



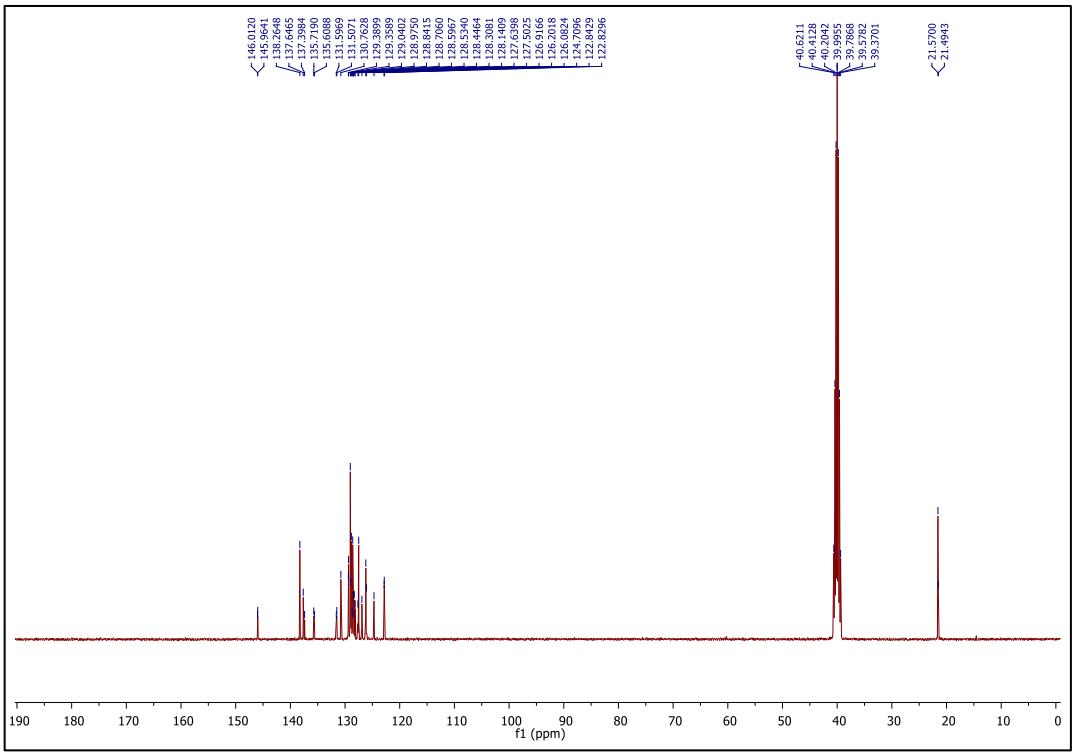
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3l** (peaks at 3.3 and 2.5 ppm are solvent and water peaks)



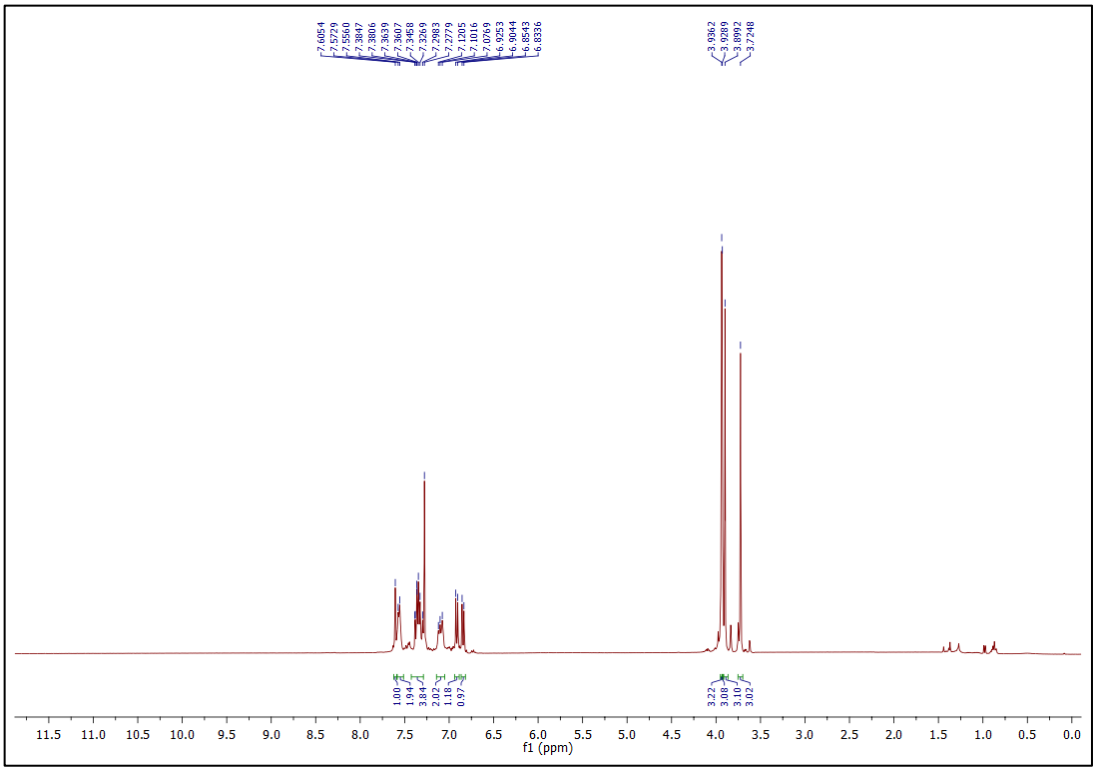
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3l**



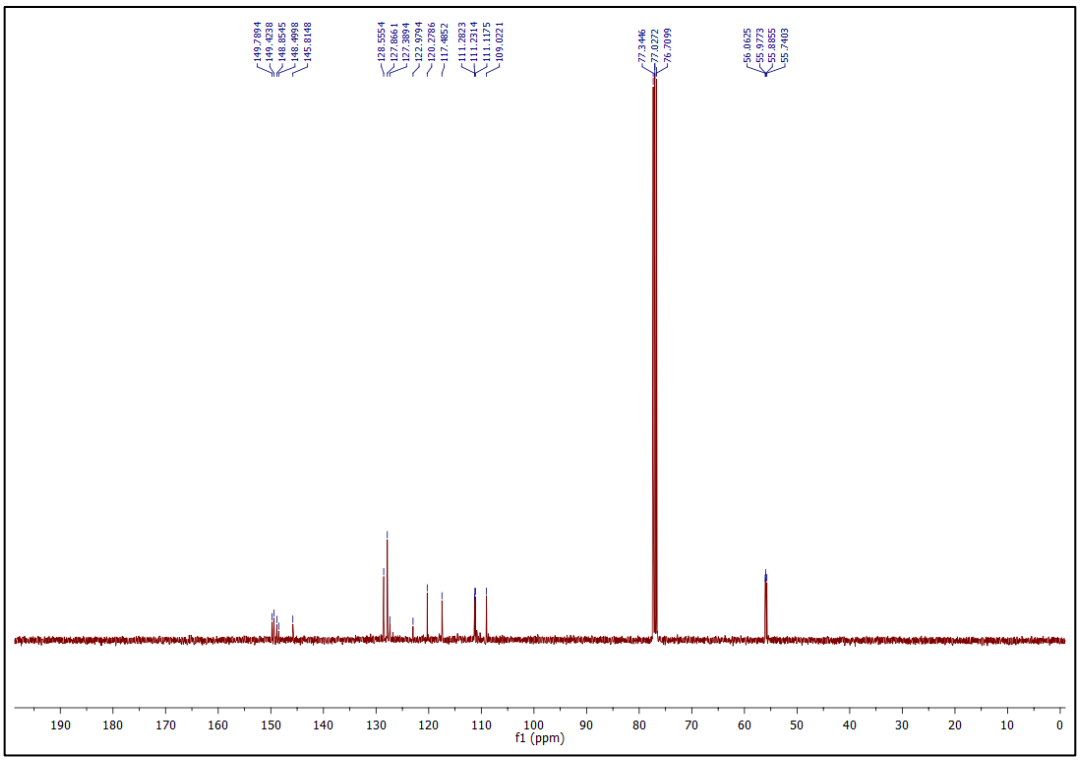
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3m** (mixture of two tautomers), peaks at 3.3 and 2.5 ppm are solvent and water peaks



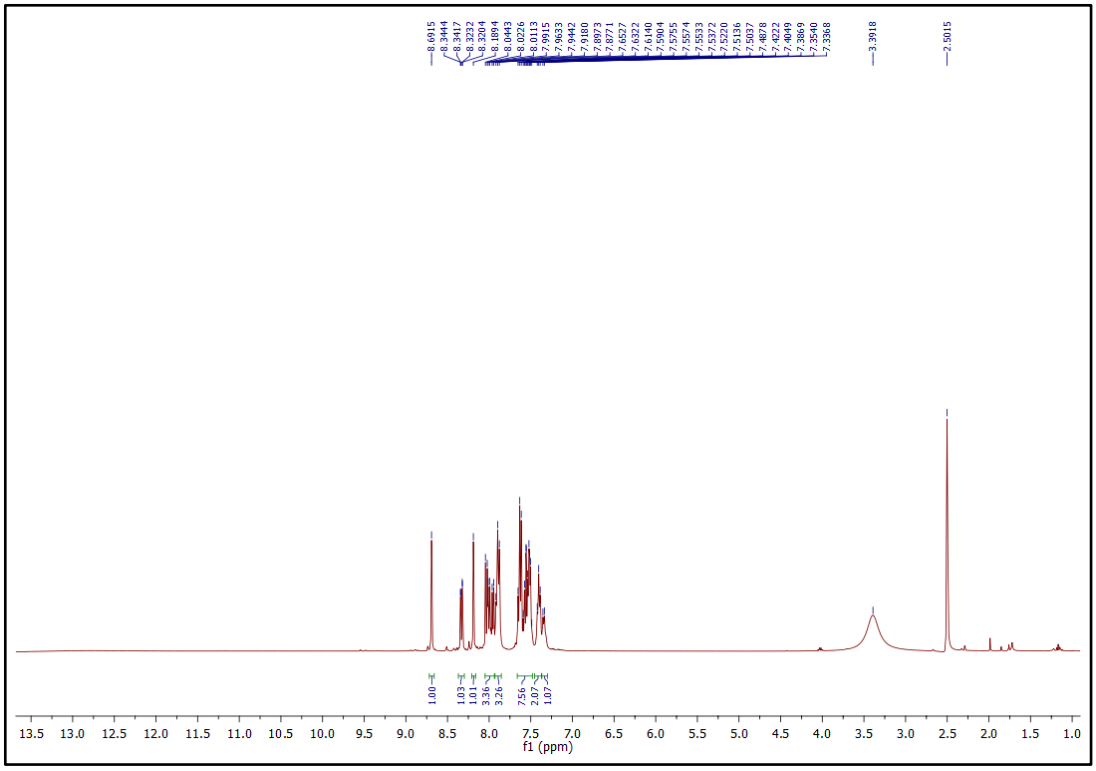
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3m** (mixture of two tautomers)



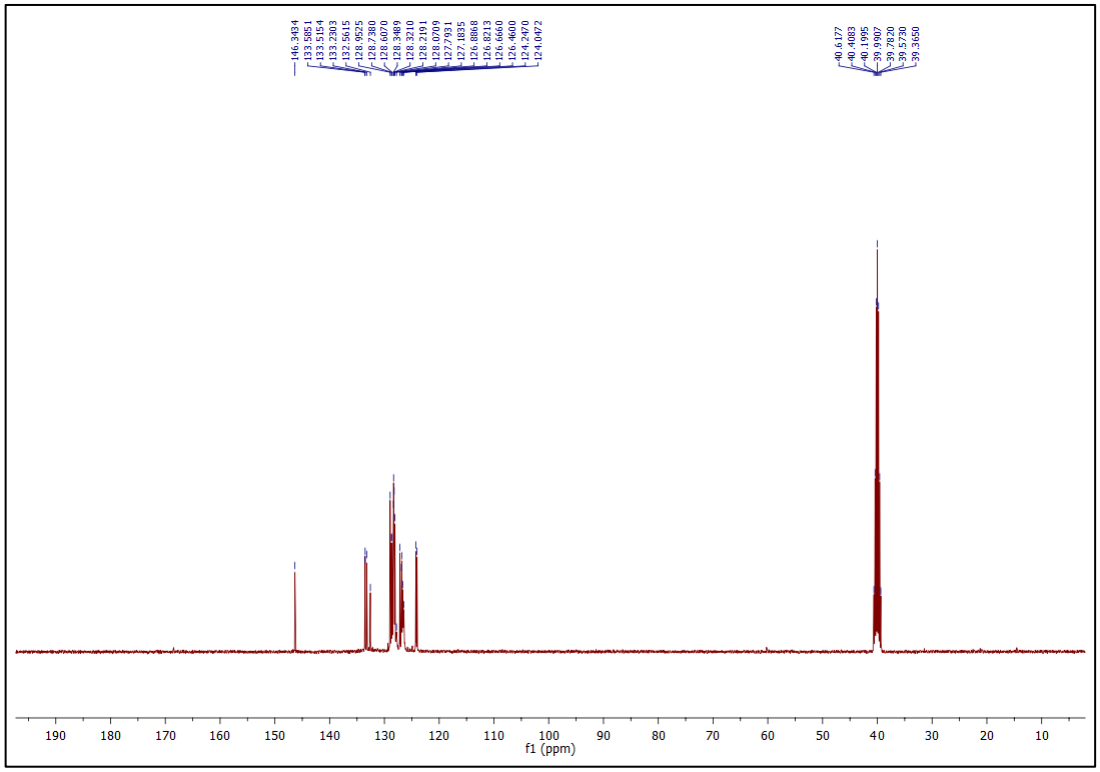
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n** (mixture of two tautomers)



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3n** (mixture of two tautomers)

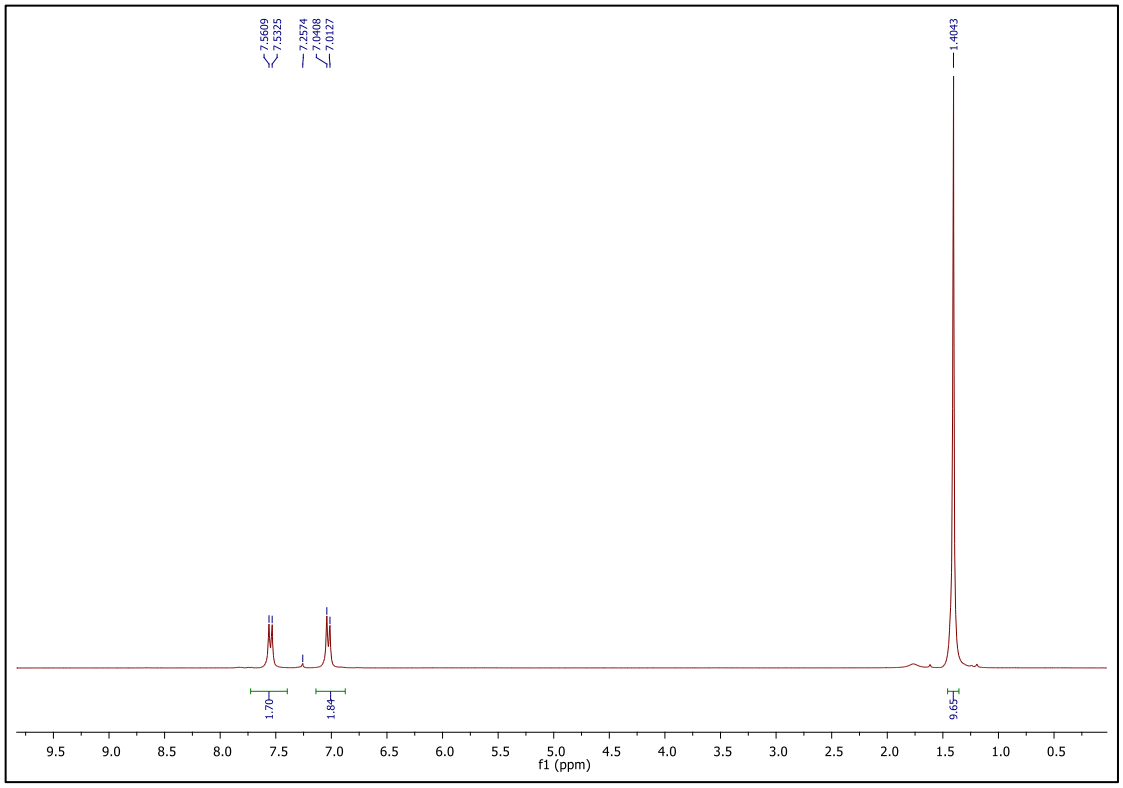


^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3o** (mixture of two tautomers), 3.3 and 2.5 ppm are solvent and water peaks

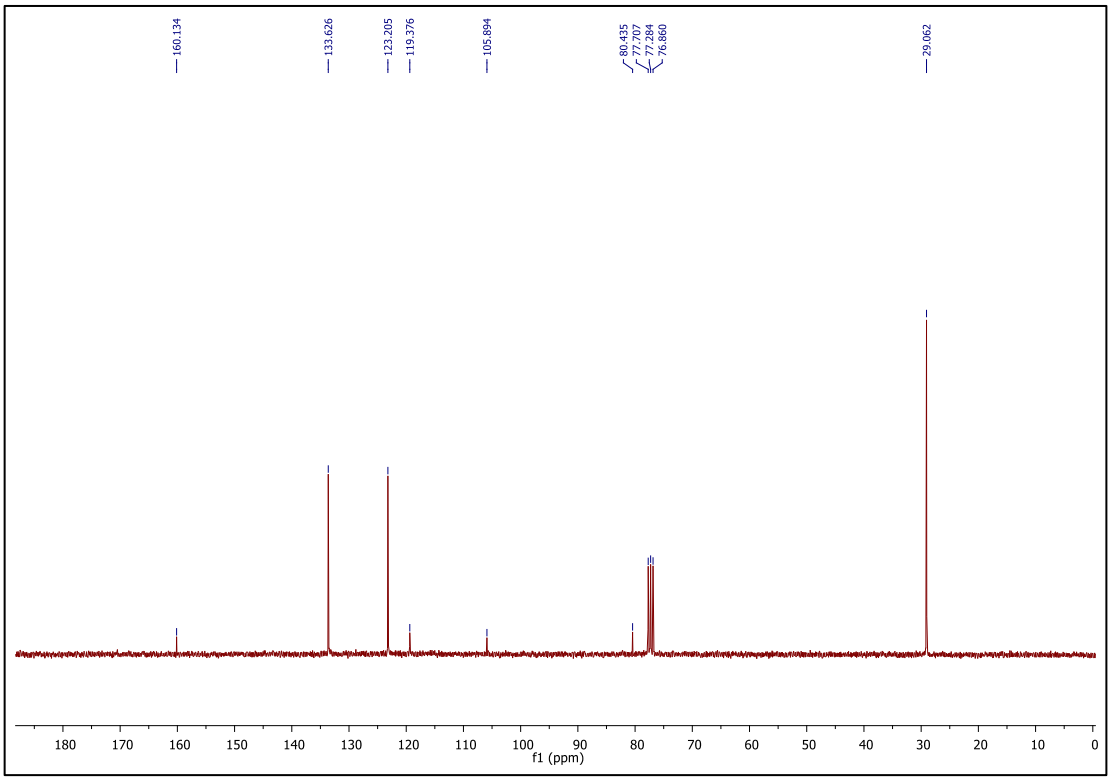


^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3o** (mixture of two tautomers)

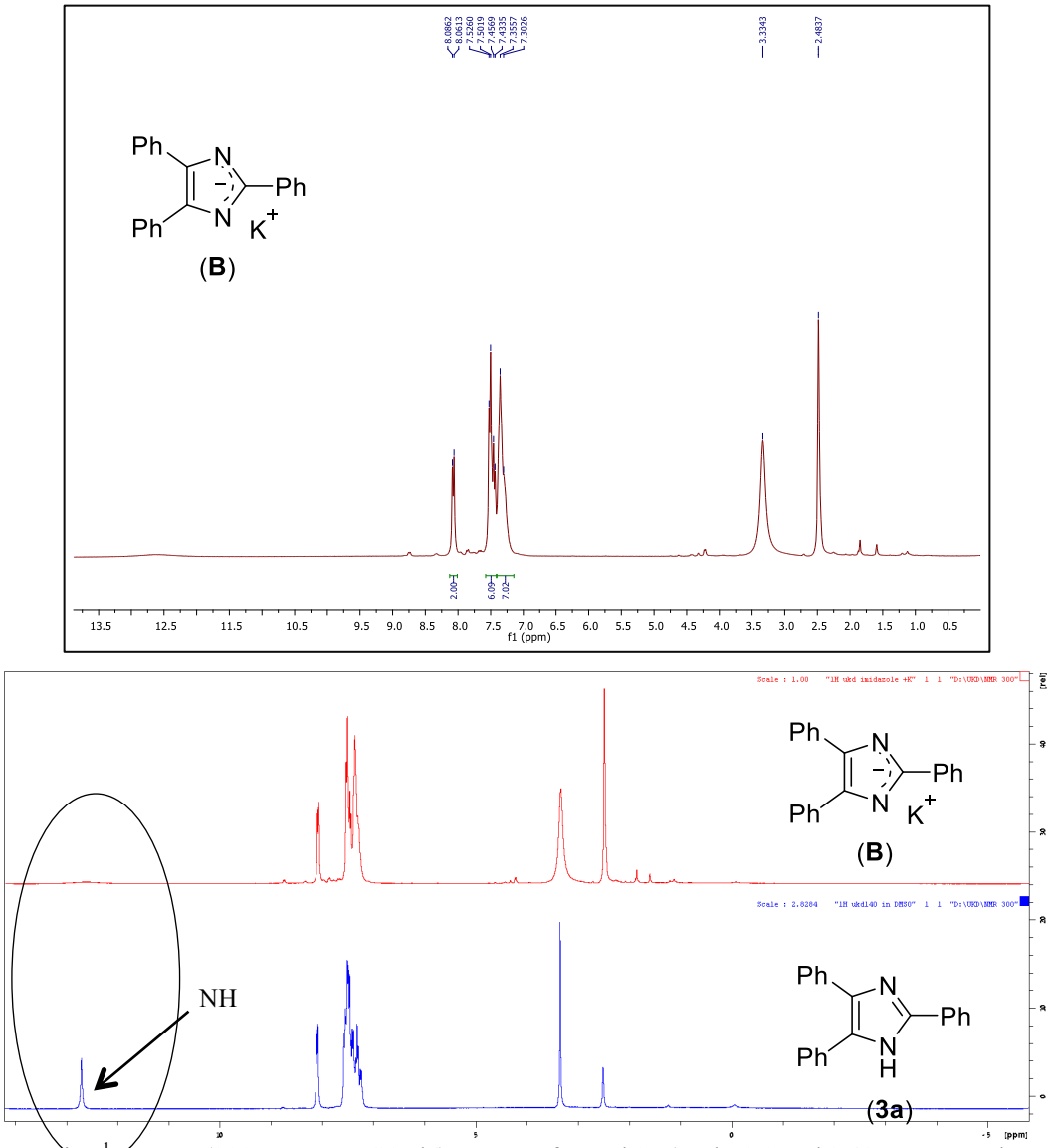
6. ^{1}H NMR and ^{13}C NMR spectra of compounds 2d:



^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2d**



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **2d**



Comparative ^{1}H NMR (300 MHz, DMSO-d6) spectra of **B** and **3a** (peaks 3.3 and 2.48 ppm are solvent and water peaks)

7. References:

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