Supporting Information

Cu-Catalyzed Iminative Hydroolefination of Unactivated Alkynes En route to 4-Imino-Tetrahydropyridines and 4-Aminopyridines

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I. General Information and methods.

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 400 MHz spectrometers for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 161.9 MHz for ^{31}P NMR Chemical shifts δ are given in ppm relative to the residual signals of tetramethylsilane in $CDCl_3$ or deuterated solvent $CDCl_3$/DMSO-d_6 and C_6D_6 for ^{1}H and ^{13}C NMR. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m), broad singlet (bs). HRMS were obtained using the electro spray ionization (ESI) technique and a time-of-flight (TOF) analyzer. Column chromatography was performed using silica gel (100-200 mesh) as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). The purity and characterization of these compounds were further established using HR/ESI Mass spectroscopy. Melting points were measured on a capillary melting point apparatus and are uncorrected.

II. General Procedure for the Preparation N-propargyl β-enaminone.

All the N-propargyl β-enaminone (**7a-x**) were prepared according to the literature procedure.[i]

III. General procedure for the synthesis of sulfonyl azide.

All the sulphonyl azide were synthesized according to our previously reported procedure.[i]

IV. General procedure for the synthesis of 4-Imino-Tetrahydropyridine (7).

In an oven dried round bottomed flask equipped with a stir bar, added appropriate *N*-propargyl β-enaminone (0.5 mmol), sulfonyl azide (0.6 mmol), TEA (1.2 equiv) and CuI (10 mol%) in 4.0 mL CH_2Cl_2 under N_2 environment and stirred at room temp until consumption of starting materials were observed (monitored by tlc). After completion of reaction the resulting mixture was diluted with water, and the reaction mixture was extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was

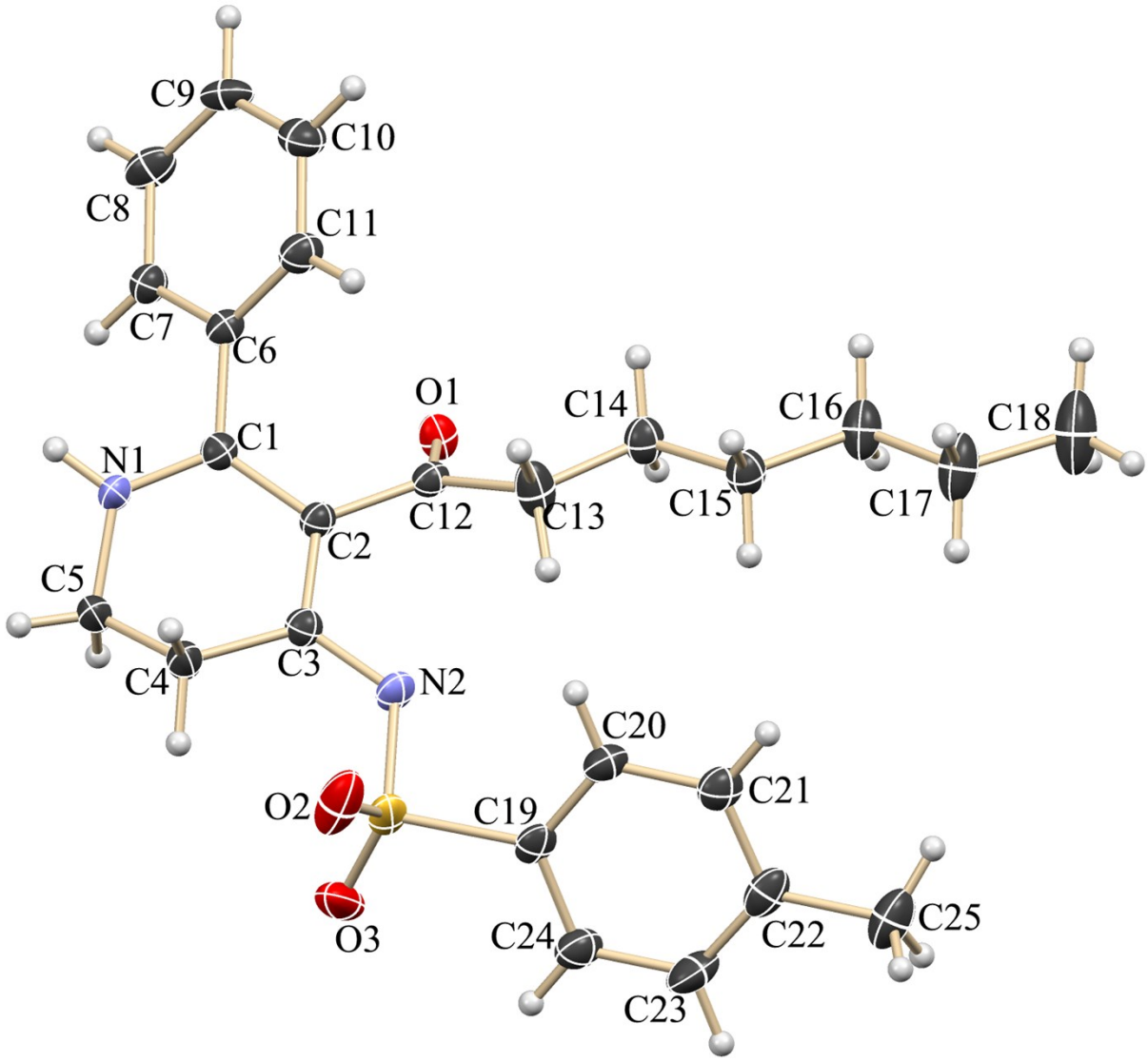
evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (DCM/EtOAc) to yield the products.

V. General procedure for the synthesis of 4-aminopyridines (9).

In an oven dried round bottomed flask equipped with a stir bar, added appropriate *N*-propargyl β-enaminone (0.5 mmol), sulfonyl azide (0.6 mmol), TEA (1.2 equiv) and CuI (10 mol%) in 4.0 mL CH_2Cl_2 under N_2 environment and stirred at room temp. until consumption of starting materials were observed (monitored by tlc). After completion of reaction following the work up the crude was again dissolved in CH_2Cl_2 and added 2.2 equiv of DDQ and stirred for 12 h. After completion of the reaction (monitored by tlc) the resulting mixture was passed through a short bed of celite and diluted with water, the reaction mixture was then extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (DCM/EtOAc) to yield the products.

VI. X-ray crystallographic data.

X-ray intensity data measurements of compound **7ta** was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073Å) radiation at 150(2) K. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 15 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was



monitored by APEX2 program (Bruker, 2006).[iii] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2.[iv] All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms except H atom bound to N atoms which was located in difference Fourier and refined isotropically. An *ORTEP* III[v] view of both compounds were drawn with 50% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii.

Crystal data of **7ta** $C_{25}H_{30}N_2O_3S$, M = 438.57, colorless block, 0.41 x 0.34 x 0.27 mm^3, monoclinic, space group $P2_1/n$, a = 15.6911(13) Å, b = 7.8759(7) Å, c = 19.8219(14) Å, β = 106.907(2)°, V = 2343.7(3) $Å^3$, Z = 4, T = 150(2) K, $2\theta_{max}$=50.00°, D_{calc} (g cm^{-3}) = 1.243, $F(000)$ = 936, μ (mm^{-1}) = 0.166, 30275 reflections collected, 4034 unique reflections (R_{int}=0.0488), 3356 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.9349, T_{max} = 0.9565, 286 refined parameters, S = 1.098, $R1$ = 0.0484, $wR2$ = 0.1176 (all data R = 0.0767, $wR2$ = 0.1417), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.615, $\Delta\rho_{min}$= -0.560 ($eÅ^{-3}$).

VII. Characteristic data of final compounds.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7aa)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 191 mg (89%); mp 191-193 °C; FT-IR (neat) 3398, 3018, 1646, 1402, 1216 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35 (bs, 1H), 7.71 (d, J = 7.32 Hz, 2H), 7.52 (t, J = 6.8 Hz, 1H), 7.41 (t, J = 6.6 Hz, 3H), 7.34 (s, 4H), 7.11-7.06 (m, 4H), 3.69 (s, 2H), 3.24 (t, J = 7.4, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.9, 172.3, 165.8, 142.0, 140.9, 139.9, 135.0, 132.4, 131.1, 129.3, 129.1, 128.8, 128.7, 128.4, 125.9, 109.5, 39.3, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{25}H_{23}N_2O_3S$ [M + H] 431.1429 found 431.1426.

***(E)-N-(5-benzoyl-6-(p-tolyl)-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7ba)*:** Beige solid; R_f = 0.36 (40% EtOAc/DCM); Yield = 189 mg (85%); mp 206-208 °C; FT-IR (neat) 3371, 2924, 1656, 1401, 1215 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.32 (bs, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.16-7.04 (m, 6H), 3.67 (s, 2H), 3.22 (t, J = 7.8 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.0, 172.2, 165.8, 141.9, 141.2, 140.9, 139.9, 132.4, 132.1,

129.4, 129.3, 129.2, 128.8, 128.4, 125.9, 109.4, 39.2, 28.4, 21.3, 21.3 ppm; HRMS (ESI) calcd for $C_{26}H_{25}N_2O_3S$ [M + H] 445.1586 found 445.1580.

***(E)-N-(5-benzoyl-6-(4-(tert-butyl)phenyl)-2,3-dihydro-pyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7ca)*:** Beige solid; R_f = 0.36 (40% EtOAc/DCM); Yield = 211 mg (87%); mp 127-129 °C; FT-IR (neat) 3390, 3019, 1645, 1403, 1215 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.30 (bs, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.44-7.37 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.68 (s, 3H), 3.23 (t, *J* = 7.3 Hz, 3H), 2.31 (s, 3H), 1.23 (s, 9H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.1, 172.2, 165.9, 154.1, 141.9, 140.9, 140.1, 132.3, 132.2, 129.2, 129.1, 128.8, 128.3, 125.9, 125.7, 109.4, 39.2, 35.0, 31.3, 28.3, 21.3 ppm; HRMS (ESI) calcd for $C_{29}H_{31}N_2O_3S$ [M + H] 487.2055 found 487.2054.

***(E)-N-(6-([1,1'-biphenyl]-4-yl)-5-benzoyl-2,3-dihydro-pyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7da)*:** Beige solid; R_f = 0.40 (40% EtOAc/DCM); Yield = 212 mg (84%); mp 158-160 °C; FT-IR (neat) 3399, 3019, 1650, 1403, 1215 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.40 (bs, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 4H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.47-7.36 (m, 7H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.71 (s, 2H), 3.26 (t, *J* = 7.7 Hz, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.0, 172.3, 165.5, 142.7, 142.0, 140.9, 140.1, 139.2, 133.9, 132.4, 129.5, 129.3, 129.2, 128.8, 128.6, 127.2, 126.9, 125.9, 109.5, 39.3, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{31}H_{27}N_2O_3S$ [M + H] 507.1742 found 507.1739.

***(E)-N-(5-benzoyl-6-(4-fluorophenyl)-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7ea)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 152 mg (68%); mp 200-202 °C; FT-IR (neat) 3386, 3017, 1646, 1402, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.38 (bs, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.42-7.39 (m, 4H), 7.21 (t, *J* =

8.8 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 3.69 (t, *J* = 6.6 Hz, 2H), 3.24 (t, *J* = 7.8 Hz, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.9, 172.3, 164.8, 162.5 142.0, 140.8, 140.0, 132.4, 131.4, 131.0 (d, *J* = 8.9 Hz,), 129.3, 129.1, 128.8, 125.9, 115.9 (d, *J* = 21.8 Hz), 109.6, 39.3, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3SF$ [M + H] 449.1335 found 449.1345.

***(E)-N-(5-benzoyl-6-(3,4-dichlorophenyl)-2,3-dihydro-pyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7fa)*:** Brown solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 170 mg (68%); mp 106-108 °C; FT-IR (neat) 3399, 3016, 1644, 1403, 1215 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.48 (bs, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.55-7.47 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 7.7 Hz, 2H), 3.70 (s, 2H), 3.24 (t, *J* = 7.8 Hz, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.7, 172.4, 163.3, 142.1, 140.6, 140.1, 135.5, 133.7, 132.4, 131.5, 131.0, 130.7, 129.3, 129.1, 128.8, 128.7, 125.9, 109.8, 39.4, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{25}H_{21}N_2O_3SCl_2$ [M + H] 499.0650 found 499.0646.

***(E)-N-(5-benzoyl-6-(4-methoxyphenyl)-2,3-dihydro-pyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7ga)*:** Beige solid; R_f = 0.28 (40% EtOAc/DCM); Yield = 186 mg (81%); mp 175-177 °C; FT-IR (neat) 3398, 3016, 1644, 1402, 1216 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28-7.27 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 7.6 Hz, 2H), 6.53 (bs, 1H), 3.74 (s, 3H), 3.68 (s, 2H), 3.38 (s, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 171.6, 164.7, 162.0, 141.9, 139.8, 131.9, 129.6, 129.1, 128.8, 128.3, 126.6, 126.1, 114.3, 110.3, 55.4, 39.6, 28.7, 21.4 ppm; HRMS (ESI) calcd for $C_{26}H_{25}N_2O_4S$ [M + H] 461.1535 found 461.1527.

***(E)-N-(5-benzoyl-6-butyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7ha)*:** Brown sticky mass; R_f = 0.36 (40% EtOAc/DCM); Yield = 133 mg (65%); FT-IR (neat) 3375, 3021, 1649, 1397, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.24 (bs, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 6.6 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 3.54 (s, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.35-2.32 (m, 2H), 2.29 (s, 3H), 1.42-1.40 (m, 2H), 1.24-1.22 (m, 2H), 0.77 (t, 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.3, 171.9, 169.5, 141.8, 140.9, 140.0, 132.4, 129.2, 128.9, 128.7, 125.8, 108.5, 38.9, 32.5, 30.3, 28.2, 22.2, 21.3, 13.9 ppm; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3S$ [M + H] 411.1742 found 411.1721.

***(E)-N-(5-benzoyl-6-hexyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7ia)*:** Brown sticky mass; R_f = 0.38 (40% EtOAc/DCM); Yield = 153 mg (70%); mp 146-148 °C; FT-IR (neat) 3385, 3019, 1647, 1401, 1215 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.26 (bs, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 3.53 (s, 2H), 3.07 (t, *J* = 7.7 Hz, 2H), 2.37-2.33 (m, 2H), 2.29 (s, 3H), 1.43-1.41 (m, 2H), 1.24-1.15 (m, 6H), 0.78 (t, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.3, 171.9, 169.5, 141.8, 140.9, 139.9, 132.4, 129.2, 128.9, 128.7, 125.8, 108.5, 38.9, 32.7, 31.1, 28.6, 28.2, 28.1, 22.2, 21.3, 14.2 ppm; HRMS (ESI) calcd for $C_{25}H_{31}N_2O_3S$ [M + H] 439.2055 found 439.2043.

***(E)-N-(5-benzoyl-6-cyclopropyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7ja)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 160 mg (81%); mp 189-191 °C; FT-IR (neat) 3380, 3015, 1640, 1401, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 8.36 (bs, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 6.9 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.45 (t, *J* = 6.1 Hz, 2H), 3.03 (t, *J* = 7.7 Hz, 2H), 2.30

(s, 3H), 1.75-1.71 (m, 1H), 0.97-0.96 (m, 2H), 0.90-0.88 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.6, 171.0, 169.4, 141.8, 141.2, 139.6, 132.7, 129.2, 129.1, 128.9, 125.8, 110.1, 38.9, 28.2, 21.3, 13.9, 9.5 ppm; HRMS (ESI) calcd for $C_{22}H_{23}N_2O_3S$ [M + H] 395.1429 found 395.1420.

***(E)-N-(5-benzoyl-6-cyclopentyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7ka)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 181 mg (86%); mp 106-108 °C; FT-IR (neat) 3390, 3019, 1647, 1403, 1216 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.78 (bs, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.53 (t, *J* = 6.2 Hz, 2H), 3.06 (t, *J* = 6.2 Hz, 2H), 2.79-2.71 (m, 1H), 2.30 (s, 3H), 1.76-1.60 (m, 7H), 1.46-1.45 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 171.4, 170.8, 141.9, 139.8, 139.4, 132.2, 129.0, 128.8, 128.3, 125.9, 110.4, 42.3, 39.8, 31.8, 28.6, 25.5, 21.4 ppm; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_3S$ [M + H] 423.1742 found 423.1728.

***(E)-N-(5-benzoyl-6-cyclohexyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7la)*:** Beige solid; R_f = 0.36 (40% EtOAc/DCM); Yield = 185 mg (85%); mp 212-214 °C; FT-IR (neat) 3391, 3019, 1646, 1402, 1216 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.83 (bs, 1H), 7.70 (d, *J* = 5.9 Hz, 2H), 7.57 (t, *J* = 5.6 Hz, 1H), 7.44 (t, *J* = 5.9 Hz, 2H), 7.08 (d, *J* = 6.4 Hz, 2H), 7.01 (d, *J* = 6.4 Hz, 2H), 3.51 (s, 2H), 3.05 (t, *J* = 6.2 Hz, 2H), 2.39-2.34 (m, 1H), 2.29 (s, 3H), 1.68 (bs, 4H), 1.59-1.57 (m, 1H), 1.48-1.42 (m, 2H), 1.13-1.03 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 172.2, 171.8, 141.9, 139.9, 139.7, 132.1, 128.9, 128.8, 128.3, 125.9, 109.3, 41.1, 39.5, 30.7, 28.5, 25.8, 25.5, 21.4 ppm; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_3S$ [M + H] 437.1899 found 437.1895.

***(E)-N-(5-benzoyl-6-((benzyloxy)methyl)-2,3-dihydro-pyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7ma)*:** Off white solid; R_f = 0.40 (40% EtOAc/DCM); Yield = 213 mg (90%); mp 149-151 °C; FT-IR (neat) 3384, 3019, 1637, 1402, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.27 (bs, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.30 (s, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 4.55 (s, 2H), 4.41 (s, 2H), 3.61 (t, *J* = 6.2 Hz, 2H), 3.13 (t, *J* = 7.8 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.2, 171.9, 166.1, 141.9, 140.8, 140.4, 137.6, 132.1, 129.2, 129.0, 128.7, 128.5, 128.3, 128.2, 125.8, 106.5, 72.9, 67.5, 39.1, 28.5, 21.3 ppm; HRMS (ESI) calcd for $C_{27}H_{27}N_2O_4S$ [M + H] 475.1692 found 475.1695.

***(E)-N-(5-(4-isopropylbenzoyl)-6-phenyl-2,3-dihydro-pyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7na)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 186 mg (79%); mp 107-109 °C; FT-IR (neat) 3390, 3019, 1645, 1402, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.31 (bs, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.40 (s, 1H), 7.35-7.34 (m, 4H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.07 (s, 4H), 3.69 (s, 2H), 3.24 (t, *J* = 7.6 Hz, 2H), 2.99-2.92 (m, 1H), 2.29 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (100 MHz, , DMSO-d_6): δ 195.5, 172.1, 165.7, 153.2, 141.9, 140.9, 137.8, 135.1, 131.2, 129.5, 129.2, 128.8, 128.4, 126.7, 125.9, 109.7, 39.3, 33.9, 28.3, 24.0, 21.3 ppm; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_5S$ [M + H] 473.1899 found 473.1894.

***(E)-N-(5-(benzo[d][1,3]dioxole-5-carbonyl)-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7oa)*:** Beige solid; R_f = 0.32 (40% EtOAc/DCM); Yield = 171 mg (72%); mp 180-182 °C; FT-IR (neat) 3391, 3019, 1644, 1402, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.26 (bs, 1H), 7.41-7.31 (m, 7H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.20-7.14 (m, 3H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.09 (s, 2H), 3.67 (s, 2H), 3.21 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, , DMSO-d_6): δ 194.1, 171.9, 165.4, 150.9, 147.8, 142.1, 140.9, 134.9, 134.7,

131.1, 129.3, 128.8, 128.4, 126.0, 125.4, 109.6, 108.7, 108.2, 102.2, 39.32, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N_2O_5S$ [M + H] 475.1382 found 472.1380.

***(E)-4-methyl-N-(5-(3-nitrobenzoyl)-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)benzene sulfonamide (7pa)*:** Beige solid; R_f = 0.34 (40% EtOAc/DCM); Yield = 183 mg (77%); mp 197-199 °C; FT-IR (neat) 3391, 3019, 1646, 1403, 1215 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.65 (bs, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 8.11 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.44-7.36 (m, 5H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 3.72 (s, 2H), 3.28 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 193.9, 171.9, 167.5, 148.5, 148.0, 142.2, 142.1, 140.1, 134.9, 134.8, 131.3, 130.3, 129.2, 128.9, 128.5, 125.9, 122.7, 108.3, 39.3, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{25}H_{22}N_3O_5S$ [M + H] 476.1280 found 476.1281.

***(E)-N-(5-(2-naphthoyl)-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzene sulfonamide (7qa)*:** Beige solid; R_f = 0.36 (40% EtOAc/DCM); Yield = 144 mg (69%); mp 196-198 °C; FT-IR (neat) 3392, 3020, 1650, 1403, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.41 (bs, 1H), 8.28 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.76-7.74 (m, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.41-7.38 (m, 3H), 7.5-7.31 (m, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 8.1 Hz, 2H), 3.74 (t, *J* = 6.5 Hz, 2H), 3.29 (t, *J* = 7.9 Hz, 2H), 2.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, , DMSO-d_6): δ 195.9, 172.2, 166.1, 141.7, 140.5, 137.7, 135.1, 132.9, 131.1, 130.0, 129.9, 128.9, 128.5, 128.3, 127.9, 126.8, 125.7, 125.5, 109.7, 39.4, 28.3, 21.3 ppm; HRMS (ESI) calcd for $C_{29}H_{25}N_2O_5S$ [M + H] 481.1586 found 481.1595.

***(E)-4-methyl-N-(6-phenyl-5-(thiophene-2-carbonyl)-2,3-dihydropyridin-4(1H)-ylidene)benzenesulfonamide (7ra)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 161 mg (74%); mp 200-202 °C; FT-IR (neat) 3400, 3019, 1644, 1402, 1216 cm^{-1}; ^1H NMR (400 MHz,

DMSO-d_6): δ 9.26 (bs, 1H), 7.82 (d, J = 3.8 Hz, 1H), 7.61 (d, J = 2.8 Hz, 1H), 7.43-7.34 (m, 7H), 7.21 (d, J = 6.4 Hz, 2H), 7.07 (t, J = 3.4 Hz, 1H), 3.69-3.66 (m, 2H), 3.21 (t, J = 6.4 Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 187.8, 172.3, 164.5, 146.8, 142.2, 141.0, 134.7, 134.2, 134.0, 131.3, 129.5, 128.9, 128.6, 128.5, 126.1, 109.9, 39.3, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{23}H_{21}N_2O_3S_2$ [M + H] 437.0994 found 437.0981.

***(E)-4-methyl-N-(5-nicotinoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)benzenesulfonamide (7sa)*:** Orange solid; R_f = 0.30 (50% EtOAc/DCM); Yield = 136 mg (63%); mp 204-206 °C; FT-IR (neat) 3399, 3020, 1648, 1403, 1218 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.56 (s, 1H), 8.78 (bs, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.43-7.35 (m, 7H), 7.15-7.09 (m, 4H), 3.71 (t, J = 6.2 Hz, 2H), 3.27 (t, J = 7.8 Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, , DMSO-d_6): δ 194.6, 172.4, 166.9, 152.2, 150.2, 142.2, 140.5, 136.1, 134.9, 131.2, 130.6, 129.4, 128.9, 128.5, 126.2, 125.9, 108.9, 39.3, 28.2, 21.3 ppm; HRMS (ESI) calcd for $C_{24}H_{22}N_3O_3S$ [M + H] 432.1382 found 432.1380.

***(E)-N-(5-heptanoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7ta)*:** White solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 175 mg (80%); mp 191-193 °C; FT-IR (neat) 3378, 3016, 1642, 1403, 1215 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.44 (bs, 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 7.3 Hz, 2H), 3.56 (t, J = 6.4 Hz, 2H), 3.16 (t, J = 7.8 Hz, 2H), 2.38 (s, 3H), 1.23-1.09 (m, 5H), 1.02-0.90 (m, 5H), 0.79 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 203.1, 171.3, 166.9, 142.4, 141.1, 135.8, 130.9, 129.7, 128.7, 128.4, 126.4, 112.4, 44.3, 39.0, 31.6, 28.8, 28.8, 24.6, 22.5, 21.4, 14.3 ppm; HRMS (ESI) calcd for $C_{25}H_{31}N_2O_3S$ [M + H] 439.2055 found 439.2036.

***(E)-N-(5-butyryl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7ua)*:** White solid; R_f = 0.34 (40% EtOAc/DCM); Yield = 162 mg (82%); mp 206-208 °C; FT-IR (neat) 3389, 3019, 1646, 1402, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.42 (bs, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43-7.36 (m, 4H), 7.32 (d, *J* = 7.1 Hz, 2H), 3.56-3.53 (m, 2H), 3.15 (t, *J* = 7.9 Hz, 2H), 2.53-2.49 (m, 2H), 2.38 (s, 3H), 1.28-1.22 (m, 2H), 0.58 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 203.0, 171.4, 167.0, 142.5, 141.0, 135.7, 130.9, 129.7, 128.7, 128.4, 126.3, 112.3, 46.3, 39.0, 28.7, 21.4, 17.9, 13.9 ppm; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_3S$ [M + H] 397.1586 found 397.1581.

***(E)-N-(5-isobutyryl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-methylbenzenesulfonamide (7va)*:** White solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 151 mg (76%); mp 128-130 °C; FT-IR (neat) 3388, 3019, 1648, 1403, 1214 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.37 (bs, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.49-7.46 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38-7.33 (m, 4H), 3.56 (t, *J* = 7.6 Hz, 2H), 3.16 (t, *J* = 7.9 Hz, 2H), 2.99-2.89 (m, 1H), 2.38 (s, 3H), 0.73 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 206.8, 171.6, 166.5, 142.5, 140.9, 135.6, 130.9, 129.7, 128.6, 128.5, 126.3, 111.7, 39.1, 28.5, 21.4, 19.0 ppm; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_5S$ [M + H] 397.1586 found 397.1587.

***(E)-4-methyl-N-(5-(3-methylbutanoyl)-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)benzene sulfonamide (7wa)*:** White solid; R_f = 0.40 (40% EtOAc/DCM); Yield = 154 mg (75%); mp 137-139 °C; FT-IR (neat) 3390, 3019, 1645, 1402, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.44 (bs, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.49-7.46 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 3.54 (t, *J* = 6.5 Hz, 2H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.47 (d, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 1.82-1.74 (m, 1H), 0.8 (d, *J* = 6.6 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 201.9, 171.3, 167.1, 142.4, 141.1, 135.8, 130.9, 129.7, 128.7, 128.5, 126.4,

112.4, 53.1, 38.9, 28.9, 24.1, 22.7, 21.4 ppm; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3S$ [M + H] 411.1742 found 411.1743.

***(E)-4-methyl-N-(6-phenyl-5-(2-phenylacetyl)-2,3-dihydropyridin-4(1H)-ylidene)benzene sulfonamide (7xa)*:** Off white solid; R_f = 0.36 (40% EtOAc/DCM); Yield = 158 mg (71%); mp 148-150 °C; FT-IR (neat) 3400, 3019, 1644, 1403, 1215 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.49 (bs, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), `7.39 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.20-7.14 (m, 5H), 6.88-6.86 (m, 2H), 3.97 (s, 2H), 3.59-3.54 (m, 2H), 3.20 (t, *J* = 7.9 Hz, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.3, 171.7, 167.2, 142.6, 140.9, 136.1, 135.5, 130.9, 130.2, 129.9, 128.6, 128.3, 128.2, 126.6, 126.5, 111.5, 50.3, 39.0, 28.6, 21.4 ppm; HRMS (ESI) calcd for $C_{26}H_{25}N_2O_3S$ [M + H] 445.1586 found 445.1571.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)benzenesulfonamide (7ab)*:** Beige solid; R_f = 0.42 (40% EtOAc/DCM); Yield = 181 mg (87%); mp 116-118 °C; FT-IR (neat) 3399, 3019, 1644, 1403, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.40 (bs, 1H), 7.72-7.67 (m, 2H), 7.61 (t, *J* = 6.6 Hz, 1H), 7.52-7.45 (m, 3H), 7.42-7.39 (m, 3H), 7.35-7.28 (m, 4H), 7.19 (d, *J* = 7.7 Hz, 2H), 3.71 (s, 2H), 3.26 (t, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.9, 172.3, 166.0, 143.6, 140.0, 134.0, 132.4, 131.2, 129.3, 129.2, 128.9, 128.8, 128.7, 128.4, 125.8, 109.5, 39.3, 28.3 ppm; HRMS (ESI) calcd for $C_{24}H_{21}N_2O_3S$ [M + H] 417.1273 found 417.1268.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-chlorobenzenesulfonamide (7ac)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 191 mg (85%); mp 207-209 °C; FT-IR (neat) 3391, 3019, 1645, 1402, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.50 (bs, 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.44-7.39 (m, 3H), 7.37-7.34 (m, 6H), 7.17 (d, *J* = 8.5 Hz, 2H), 3.74-3.69 (m, 2H), 3.25 (t, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-

d_6): δ 195.8, 172.3, 166.5, 142.5, 140.0, 136.7, 134.9, 132.4, 131.2, 129.3, 128.9, 128.8, 128.7, 128.4, 127.8, 109.6, 39.3, 28.4 ppm; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3SCl$ [M + H] 451.0883 found 451.0901.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-fluorobenzenesulfonamide (7ad)*:** Beige solid; R_f = 0.36 (40% EtOAc/DCM); Yield = 176 mg (81%); mp 160-162 °C; FT-IR (neat) 3299, 3017, 1649, 1494, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d_6*): δ 9.46 (bs, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41-7.38 (m, 4H), 7.35 (d, *J* = 4.2 Hz, 3H), 7.25-7.21 (m, 2H), 7.12 (t, *J* = 8.8 Hz, 2H), 3.17 (t, *J* = 6.4 Hz, 2H), 3.25 (t, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-*d_6*): δ 195.9, 172.2, 166.3, 163.9 (d, *J* = 249.0 Hz), 140.1, 134.9, 132.3, 131.2, 129.2, 129.1, 128.8, 128.7, 128.6, 128.4, 115.9 (d, *J* = 22.2 Hz), 109 .5, 39.4, 28.3 ppm; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3SF$ [M + H] 435.1179 found 435.1172.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-(trifluoromethyl)benzene sulfonamide (7ae)*:** Beige solid; R_f = 0.34 (40% EtOAc/DCM); Yield = 155 mg (64%); mp 207-209 °C; FT-IR (neat) 3392, 3019, 1650, 1403, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d_6*): δ 9.58 (bs, 1H), 7.67 (t, *J* = 7.7 Hz, 4H), 7.47-7.39 (m, 4H), 7.36-7.33 (m, 6H), 3.75-3.71 (m, 2H), 3.27 (t, *J* = 6.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-*d_6*): δ 195.9, 172.3, 166.9, 147.1, 139.9, 134.7, 132.3, 131.9, 131.3, 129.0, 128.9, 128.7, 128.4, 126.8, 126.1, 125.3, 109.6, 39.3, 28.5 ppm; HRMS (ESI) calcd for $C_{25}H_{20}N_2O_3SF_3$ [M + H] 485.1147 found 485.1142.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)-4-nitrobenzenesulfonamide (7af)*:** Beige solid; R_f = 0.30 (40% EtOAc/DCM); Yield = 182 mg (79%); mp 163-165 °C; FT-IR (neat) 3390, 3019, 1645, 1402, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d_6*): δ 9.66 (bs, 1H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.50-7.46 (m, 1H), 7.43-7.39 (m, 4H), 7.38-7.35 (m, 5H), 3.75 (s, 2H), 3.28 (t, *J* = 7.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-*d_6*): δ

195.7, 172.3, 167.1, 149.2, 148.9, 139.9, 134.7, 132.4, 131.3, 129.1, 128.9, 128.8, 128.4, 127.4, 124.3, 109.7, 39.3, 28.6 ppm; HRMS (ESI) calcd for $C_{24}H_{20}N_3O_5S$ [M + H] 462.1124 found 462.1120.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)thiophene-2-sulfonamide (7ag)*:** Beige solid; R_f = 0.36 (40% EtOAc/DCM); Yield = 152 mg (72%); mp 168-170 °C; FT-IR (neat) 3391, 3019, 1644, 1402, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.47 (bs, 1H), 7.73-7.71 (m, 3H), 7.48 (t, *J* = 6.9 Hz, 2H), 7.43-7.32 (m, 6H), 7.09 (d, *J* = 2.9 Hz, 1H), 6.96 (t, *J* = 4.2 Hz, 1H), 3.70 (s, 2H), 3.24 (t, *J* = 7.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.6, 172.0, 166.2, 145.0, 139.6, 134.8, 132.6, 131.8, 131.2, 130.1, 129.3, 128.8, 128.7, 128.4, 127.2, 109.6, 39.4, 28.0 ppm; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_3S_2$ [M + H] 423.0837 found 423.0827.

***(E)-N-(5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)methanesulfonamide (7ah)*:** Greenish solid; R_f = 0.46 (40% EtOAc/DCM); Yield = 145 mg (82%); mp 110-112 °C; FT-IR (neat) 3392, 3018, 1644, 1403, 1218 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.20 (bs, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.51-7.47 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 3H), 7.37 (d, *J* = 4.0 Hz, 4H), 3.66 (s, 2H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.9, 172.0, 165.4, 140.3, 135.1, 132.2, 131.1, 128.9, 128.8, 128.6, 128.5, 108.8, 42.9, 39.2, 28.3 ppm; HRMS (ESI) calcd for $C_{19}H_{19}N_2O_3S$ [M + H] 355.1116 found 355.1113.

***N-(3-benzoyl-2-phenylpyridin-4-yl)-4-methylbenzene-sulfonamide (9a)*:** Yellow solid; R_f = 0.44 (40% EtOAc/DCM); Yield = 173 mg (81%); mp 205-207 °C; FT-IR (neat) 3392, 3019, 1650, 1402, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 13.21 (bs, 1H), 8.08 (d, *J* = 7.1 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.47-7.41 (m, 4H), 7.40-7.34 (m, 6H), 7.19 (d, *J* = 7.9 Hz, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.4, 161.6,

147.4, 141.5, 141.4, 139.6, 137.1, 134.0, 132.3, 130.8, 129.4, 129.3, 129.2, 129.0, 127.3, 126.2, 111.9 ppm; HRMS (ESI) calcd for $C_{25}H_{21}N_2O_3S$ [M + H] 429.1273 found 429.1285.

***N-(3-(4-isopropylbenzoyl)-2-phenylpyridin-4-yl)-4-methylbenzenesulfonamide (9b)*:** White solid; R_f = 0.40 (40% EtOAc/DCM); Yield = 176 mg (75%); mp 198-200 °C; FT-IR (neat) 3392, 3018, 1637, 1403, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 13.18 (bs, 1H), 8.07 (d, *J* = 7.1 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.38-7.37 (m, 6H), 7.35-7.31 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.99-2.93 (m, 1H), 2.32 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 193.9, 161.8, 154.9, 147.1, 141.4, 139.4, 135.2, 132.3, 131.9, 130.8, 129.6, 129.3, 129.3, 129.0, 127.5, 127.2, 126.2, 111.9, 33.9, 23.9, 21.3 ppm; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3S$ [M + H] 471.1742 found 471.1734.

***N-(3-benzoyl-2-(p-tolyl)pyridin-4-yl)-4-methylbenzene-sulfonamide (9c)*:** White solid; R_f = 0.41 (40% EtOAc/DCM); Yield = 172 mg (78%); mp >250 °C; FT-IR (neat) 3394, 3019, 1650, 1405, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 13.13 (bs, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19-7.17 (m, 4H), 2.32 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.5, 161.8, 147.3, 141.5, 140.7, 139.4, 137.1, 134.0, 129.6, 129.3, 129.2, 129.2, 127.2, 126.2, 111.8, 21.3, 21.2 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N_2O_3S$ [M + H] 443.1429 found 443.1430.

***N-(3-butyryl-2-phenylpyridin-4-yl)-4-methylbenzene-sulfonamide (9d)*:** White solid; R_f = 0.42 (40% EtOAc/DCM); Yield = 142 mg (72%); mp 194-196 °C; FT-IR (neat) 3392, 3019, 1623, 1403, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 13.10 (bs, 1H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.54-7.48 (m, 3H), 7.46-7.43 (m, 2H), 7.35-7.30 (m, 3H), 2.49 (s, 2H), 2.35 (s, 3H), 1. 39-1.29 (m, 2H), 0.64 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6):

δ 204.0, 160.7, 146.2, 141.7, 141.5, 139.0, 132.2, 130.9, 130.0, 129.6, 129.5, 129.1, 126.4, 112.0, 45.7, 21.3, 16.7, 13.7 ppm; HRMS (ESI) calcd for $C_{22}H_{23}N_2O_3S$ [M + H] 395.1429 found 395.1425.

***N-(3-benzoyl-2-phenylpyridin-4-yl)-4-(trifluoromethyl)benzenesulfonamide (9e)*:** Beige solid; R_f = 0.38 (40% EtOAc/DCM); Yield = 183 mg (76%); mp 207-209 °C; FT-IR (neat) 3398, 3019, 1642, 1403, 1216 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 13.43 (bs, 1H), 8.15 (d, *J* = 6.9 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.67-7.57 (m, 5H), 7.48-7.39 (m, 8H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.3, 161.6, 147.9 (d, *J* = 34.0 Hz), 139.9, 137.7, 134.0, 132.1, 131.6, 131.3, 130.9, 129.3, (d, *J* = 8.0 Hz), 129.0, 127.6, 126.9, 125.5, 122.7, 112.2 ppm; HRMS (ESI) calcd for $C_{25}H_{20}N_2O_3SF_3$ [M + H] 483.0990 found 483.0992.

***N-(3-benzoyl-2-phenylpyridin-4-yl)methanesulfonamide (9f)*:** White solid; R_f = 0.44 (40% EtOAc/DCM); Yield = 128 mg (73%); mp 187-189 °C; FT-IR (neat) 3391, 3019, 1649, 1403, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 13.06 (bs, 1H), 8.08 (d, *J* = 4.9 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.46-7.39 (m, 8H), 2.59 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.5, 161.6, 147.2, 139.1, 137.2, 133.9, 133.3, 130.7, 129.7, 129.2, 129.2, 129.0, 126.5, 111.9, 41.5 ppm; HRMS (ESI) calcd for $C_{19}H_{17}N_2O_3S$ [M + H] 353.0960 found 353.0953.

***(E)-diphenyl (5-benzoyl-6-phenyl-2,3-dihydropyridin-4(1H)-ylidene)phosphoramidate (10aa)*:** Greenish solid; R_f = 0.28 (40% EtOAc/DCM); Yield = 71 mg (28%); mp 158-160 °C; FT-IR (neat) 3340, 3019, 1645, 1403, 1217 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.16 (bs, 1H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 6.4 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 3H), 7.38 (s, 4H), 7.24 (t, *J* = 6.5 Hz, 4H), 7.11 (t, *J* = 6.9 Hz, 2H), 6.87 (d, *J* = 7.4 Hz, 4H), 3.65 (s, 2H), 3.06 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.3, 177.5, 165.2, 151.5, 151.4, 139.6, 135.1, 132.6, 131.0,

129.9, 129.3, 128.8, 128.7, 128.4, 124.6, 120.6, 38.6, 28.8 ppm; ^{31}P NMR (161.9 MHz, DMSO-d_6): δ -4.52 ppm; HRMS (ESI) calcd for $C_{30}H_{26}N_2O_4P$ [M + H] 509.1630 found 509.1626.

References:

(i) Cai, S.; Yang, K.; Wang, D. Z. *Org. Lett.* **2014**, *16*, 2606. (b) Wang, G.-W.; Miao, C.-B. *Green Chem.* **2006**, *8*, 1080. (c) Cox, R. J.; Ritson, D. J.; Dane, T. A.; Berge, J.; Charmant, J. P. H.; Kantacha, A. *Chem. Commun.* **2005**, 1037.

(ii) Kumar, Y. K.; Kumar, G. R.; Reddy, T. J.; Sridhar, B.; Reddy, M. S. *Org. Lett.*, **2015**, *17*, 2226.

(iii) Bruker (2006). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

(iv) Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112. (v) Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.

VII. Copies of ^{1}H, ^{13}C and ^{31}P NMR spectra.

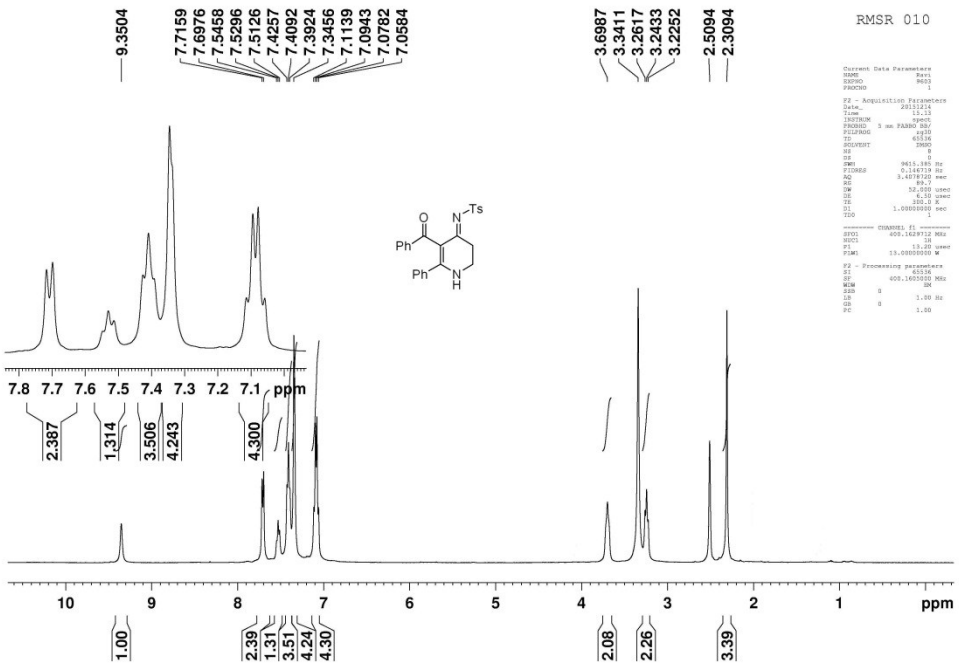


Fig. 1: ^{1}H NMR of 7aa

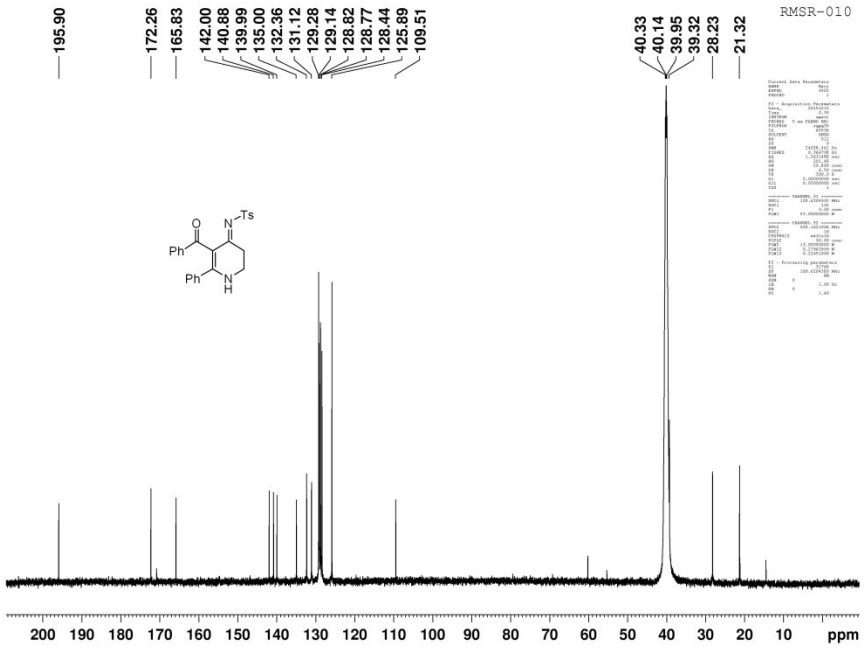


Fig. 2: ^{13}C NMR of 7aa

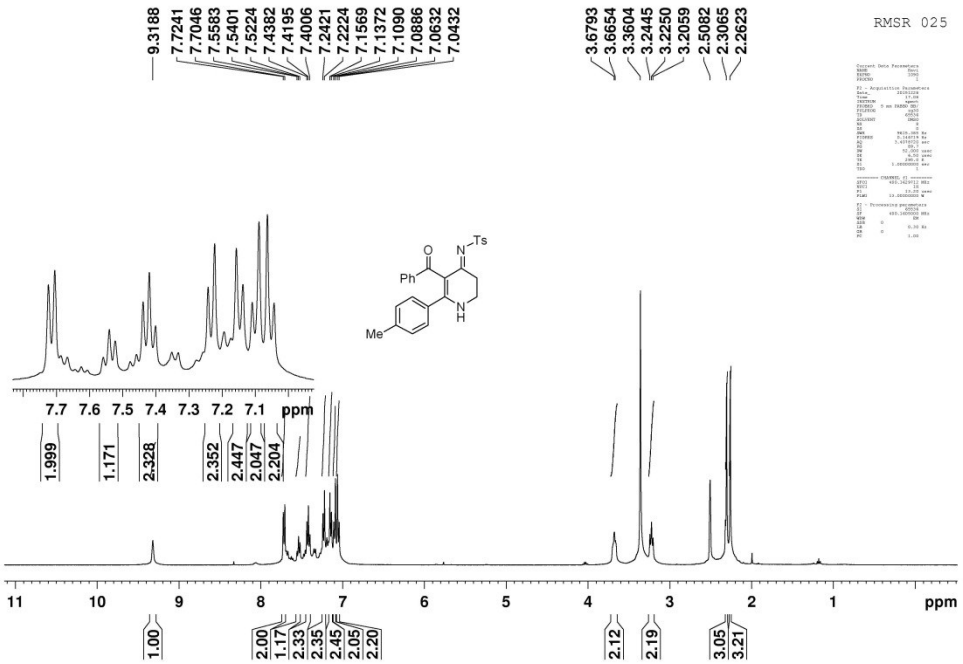


Fig. 3: ^{1}H NMR of 7ba

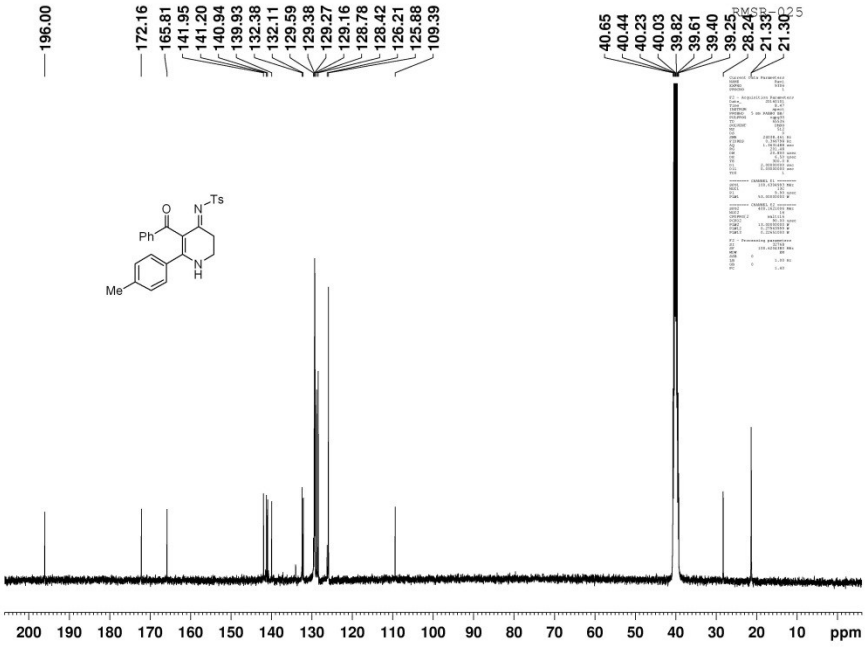


Fig. 4: ^{13}C NMR of 7ba

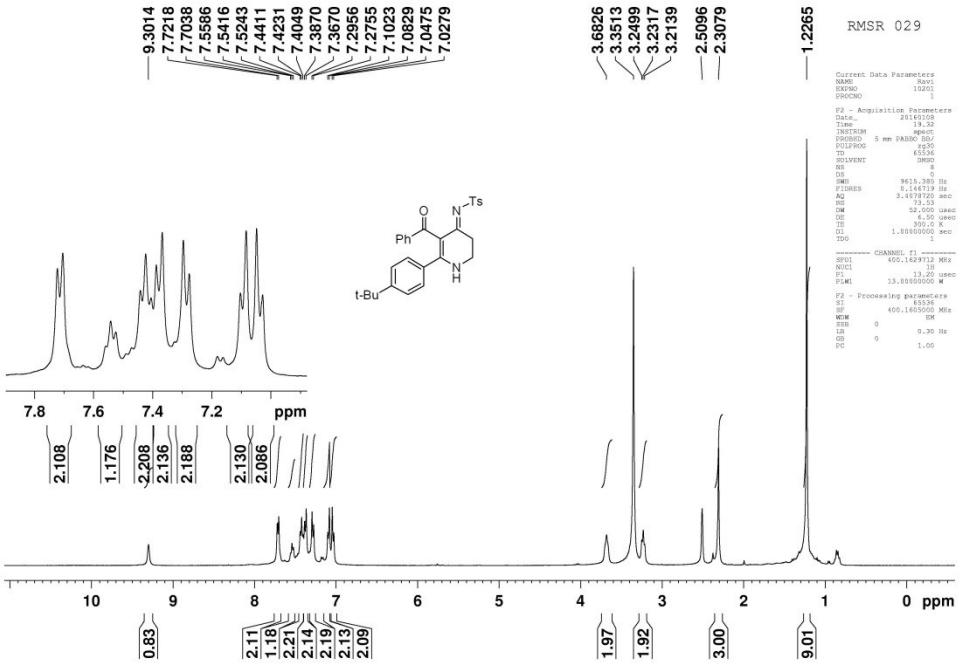


Fig. 5: ^{1}H NMR of 7ca

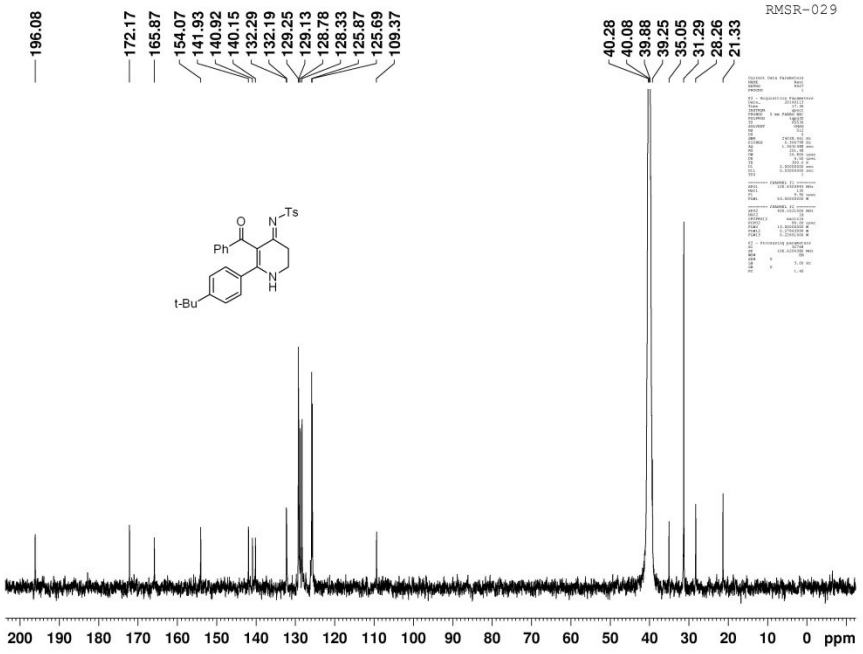


Fig. 6: ^{13}C NMR of 7ca

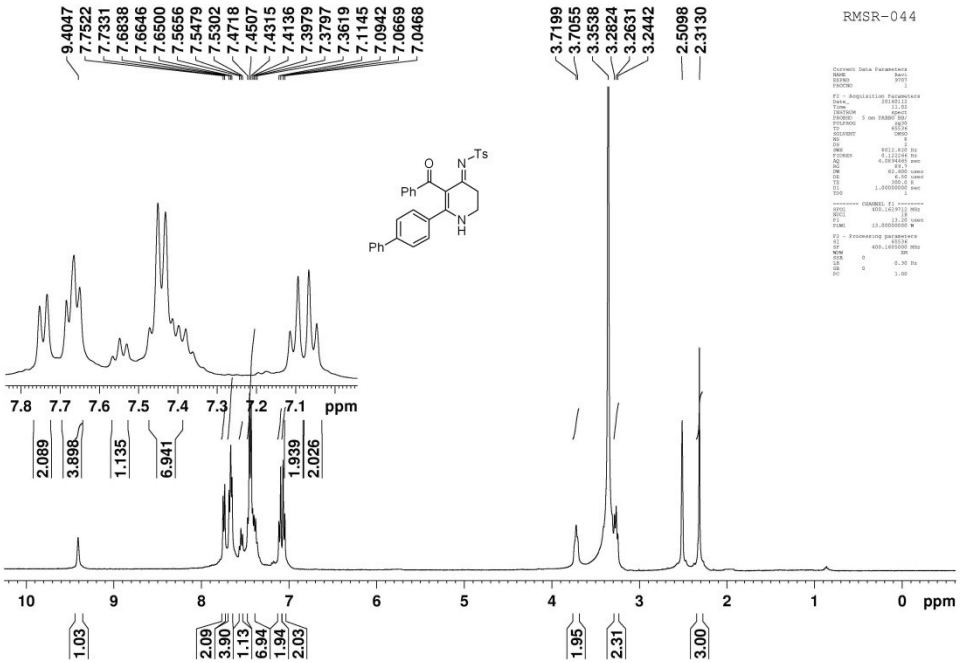


Fig. 7: ^{1}H NMR of 7da

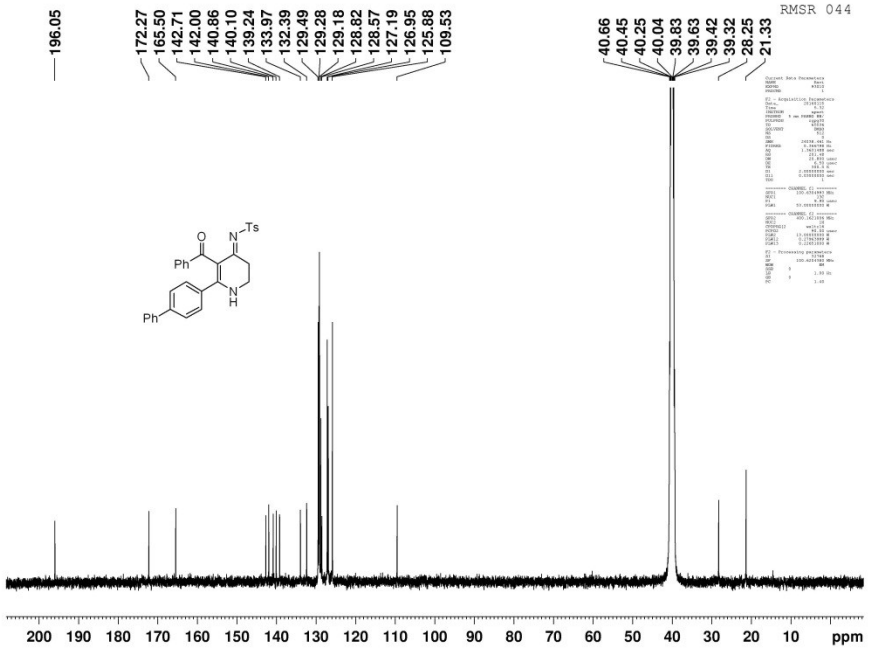


Fig. 8: ^{13}C NMR of 7da

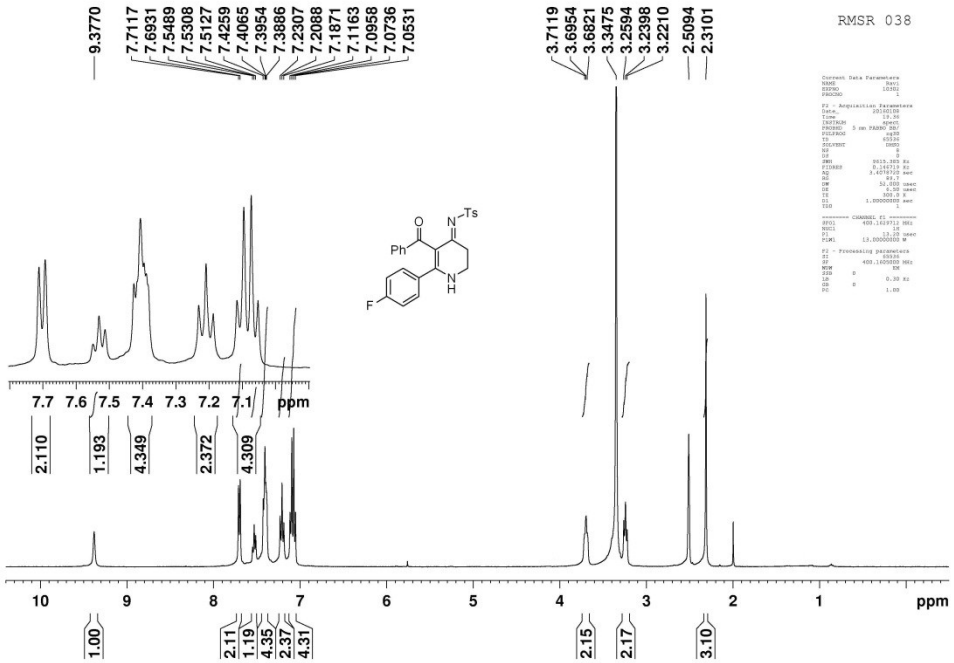


Fig. 9: ^{1}H NMR of 7ea

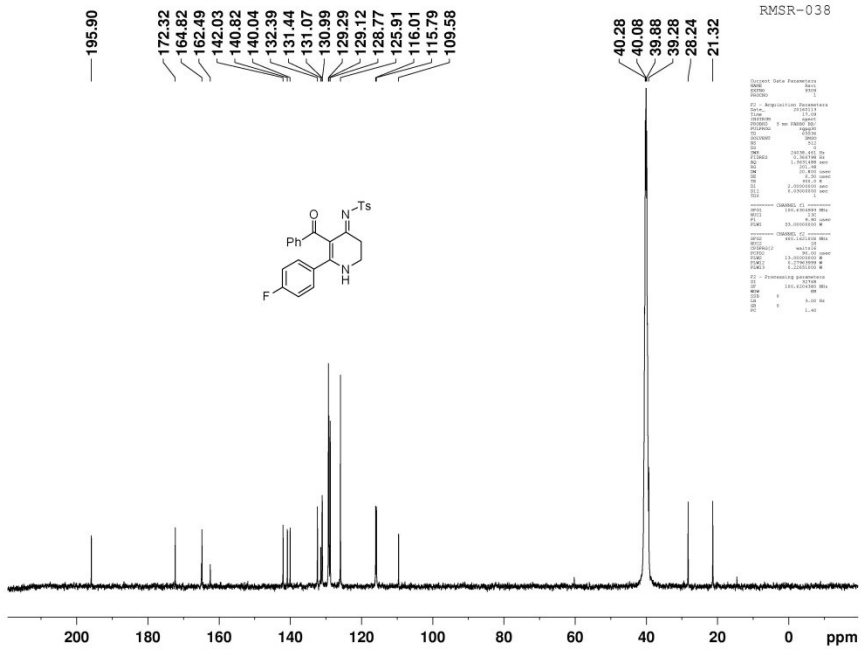


Fig. 10: ^{13}C NMR of 7ea

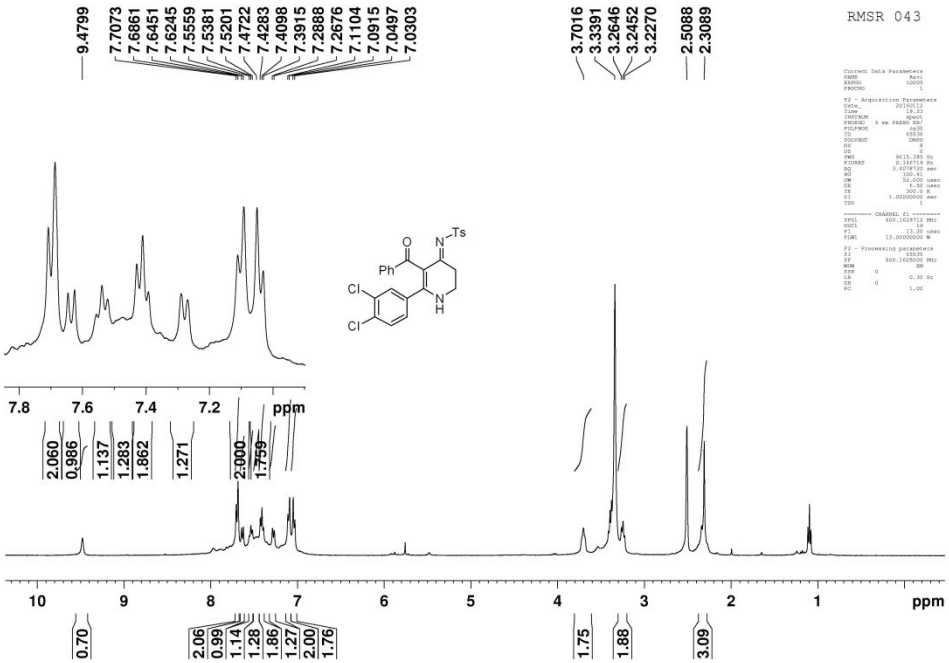


Fig. 11: ^{1}H NMR of 7fa

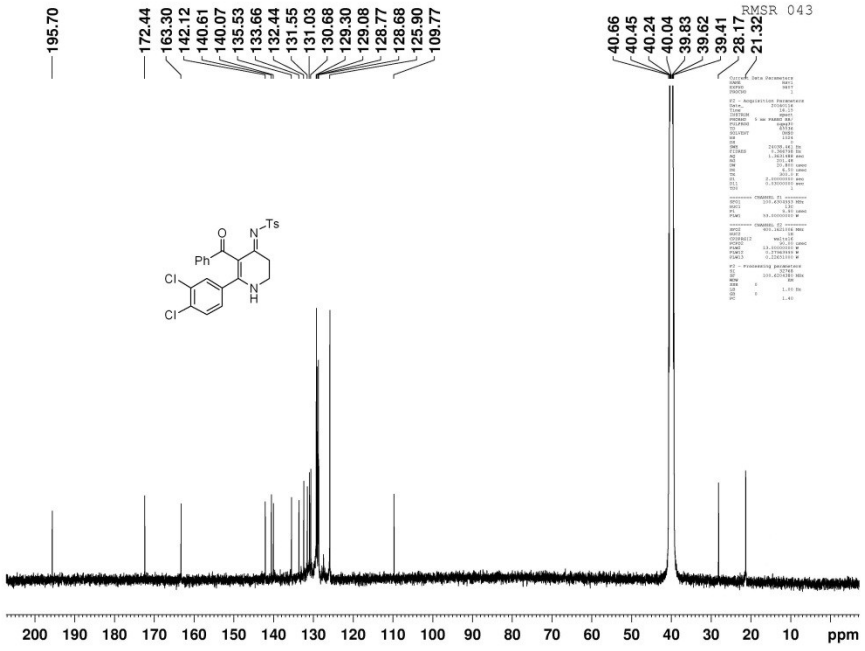


Fig. 12: ^{13}C NMR of 7fa

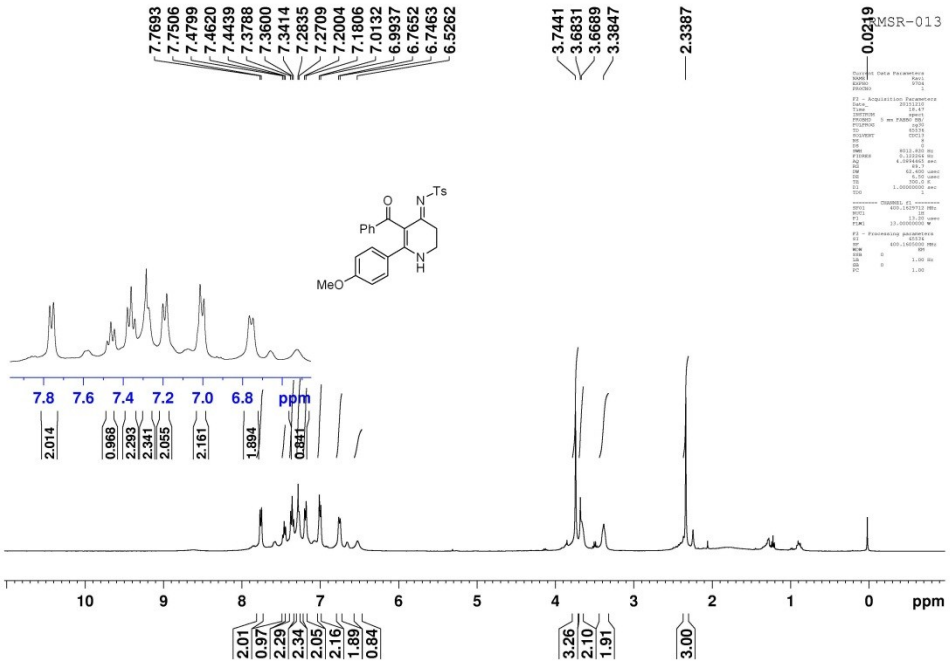


Fig. 13: ^{1}H NMR of 7ga

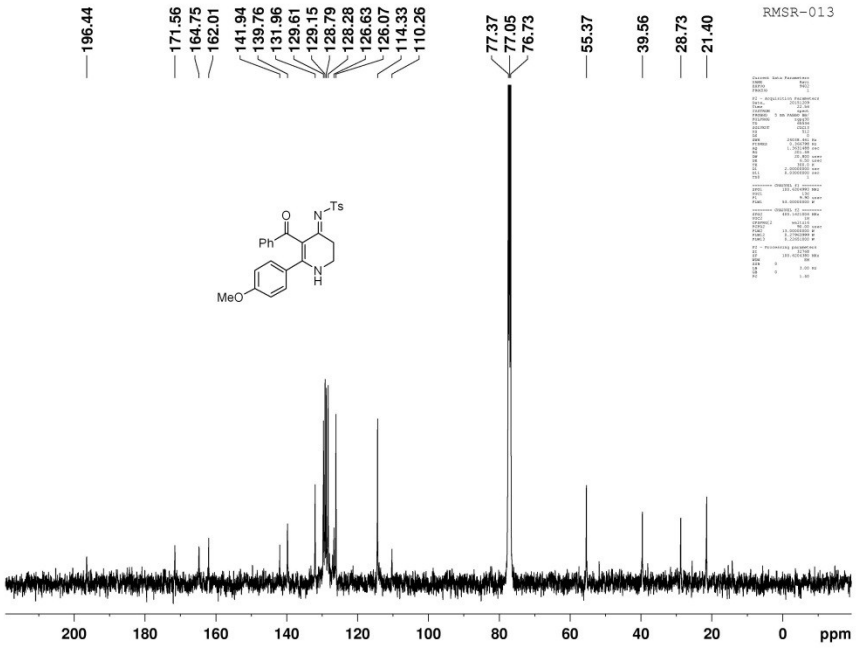
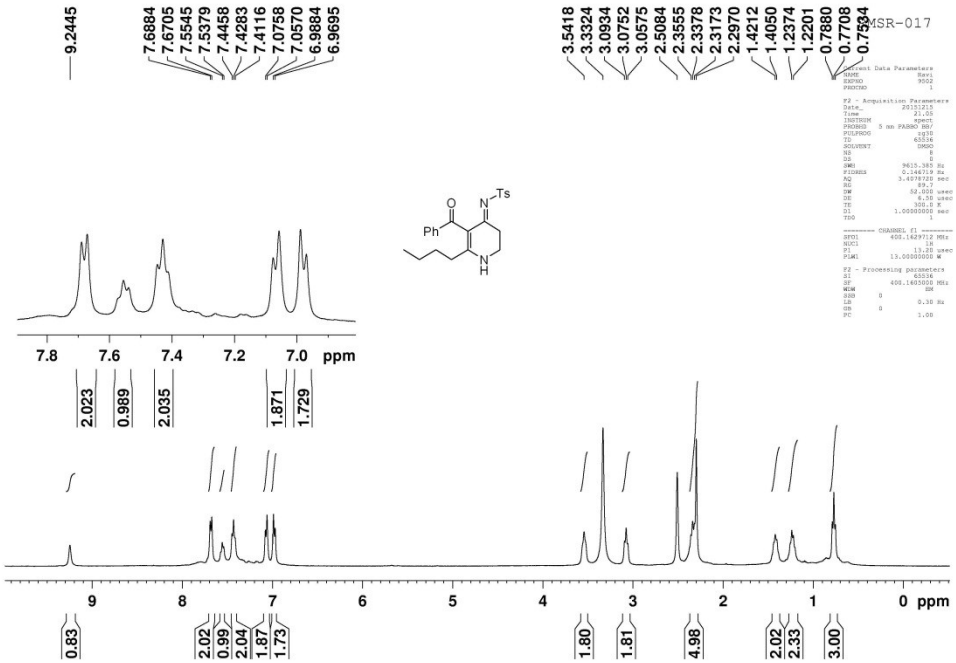


Fig. 14: ^{13}C NMR of 7ga



-Fig. 15: ^{1}H NMR of 7ha

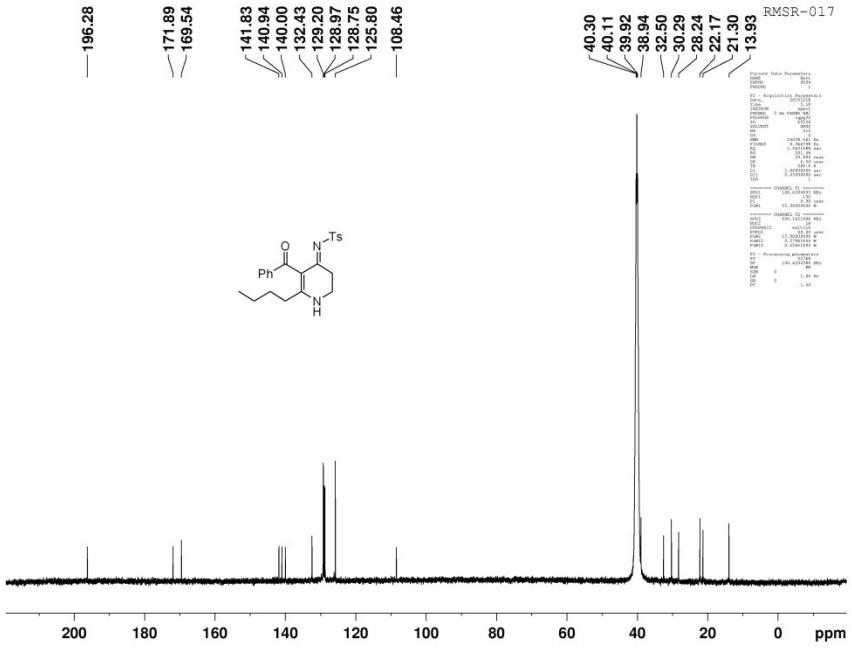


Fig. 16: ^{13}C NMR of 7ha

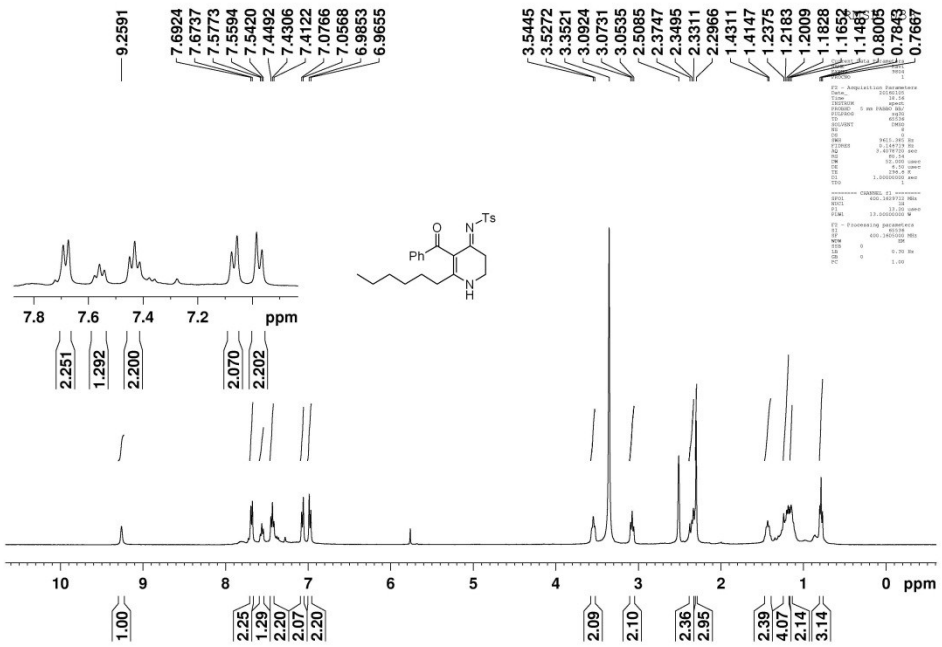


Fig. 17: ^{1}H NMR of 7ia

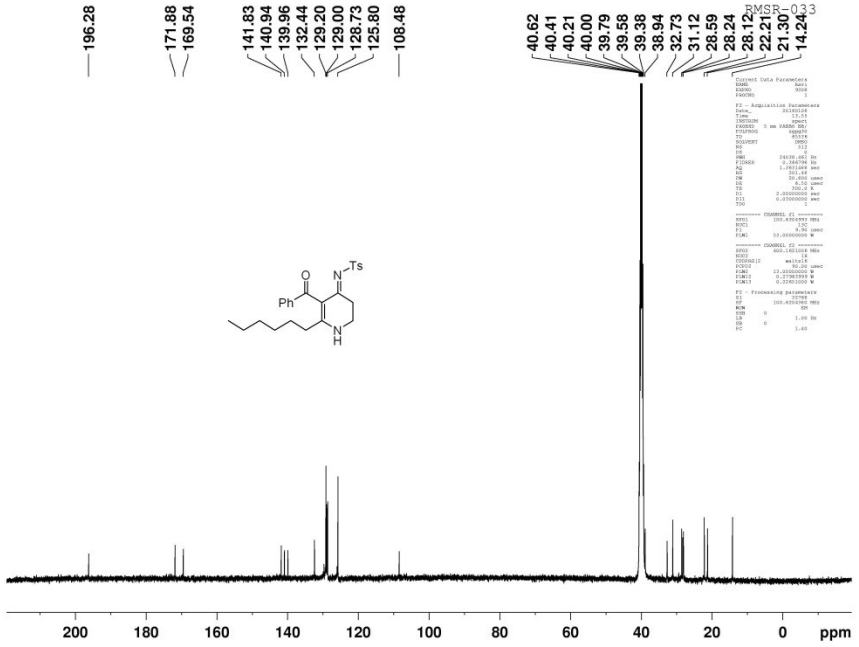


Fig. 18: ^{13}C NMR of 7ia

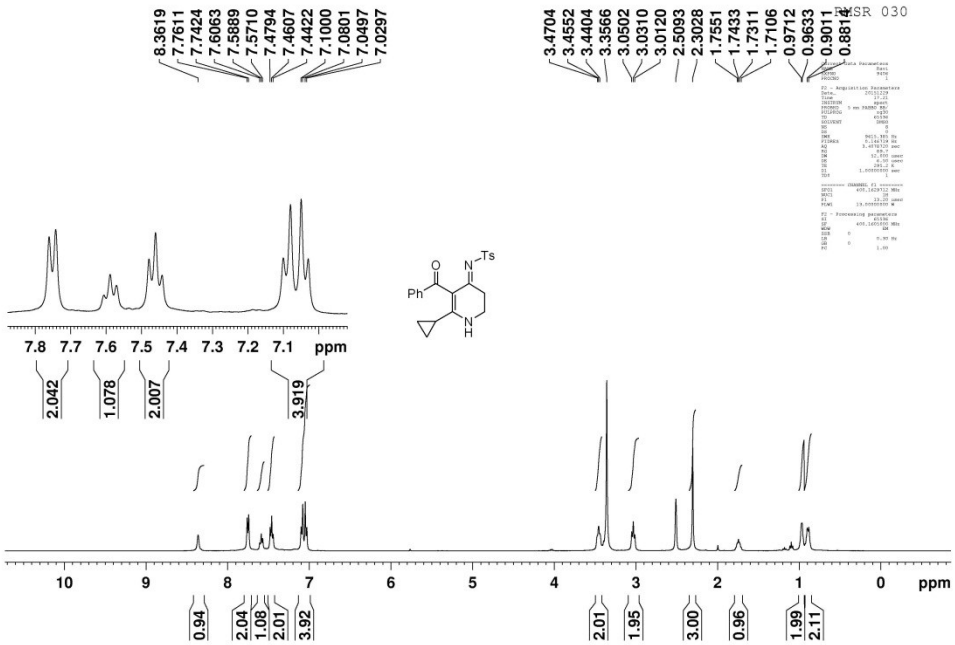


Fig. 19: ^{1}H NMR of 7ja

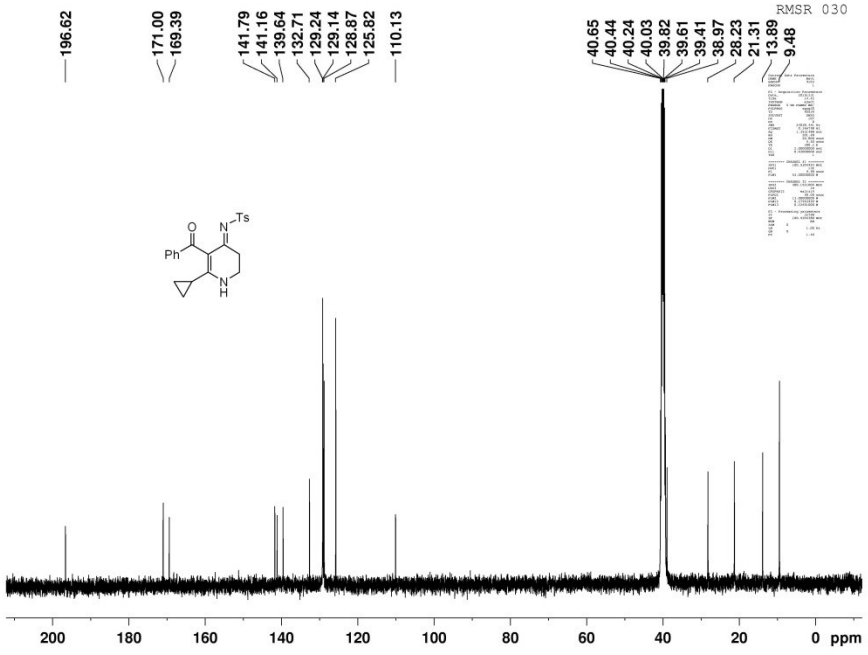


Fig. 20: ^{13}C NMR of 7ja

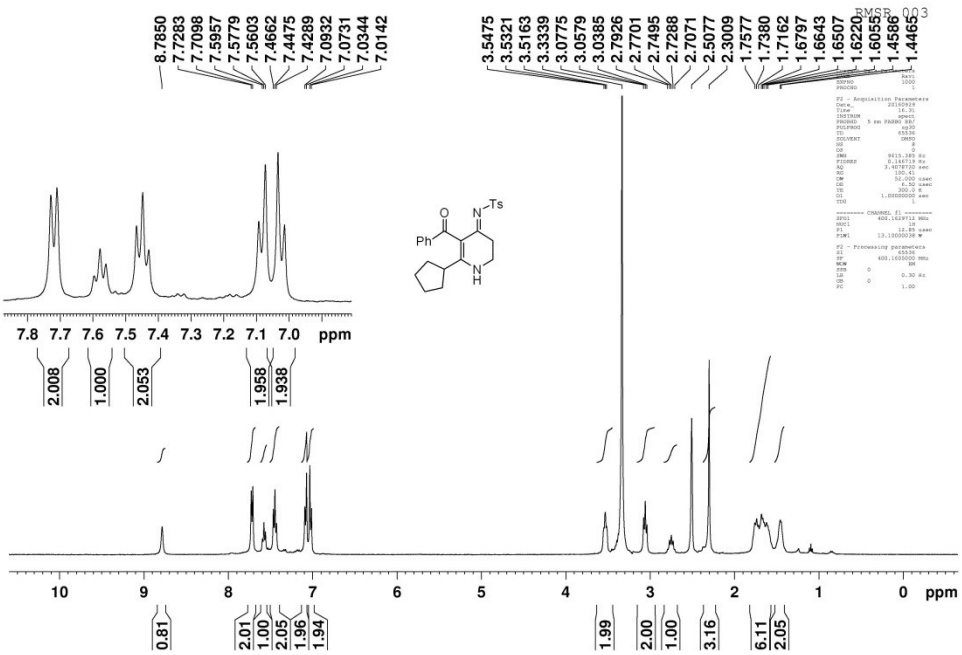


Fig. 21: ^{1}H NMR of 7ka

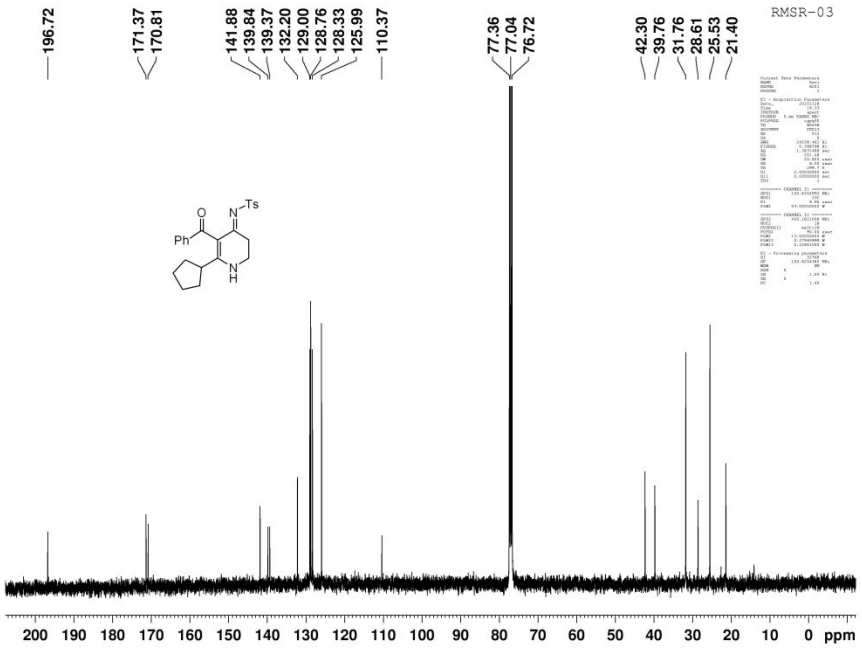


Fig. 22: ^{13}C NMR of 7ka

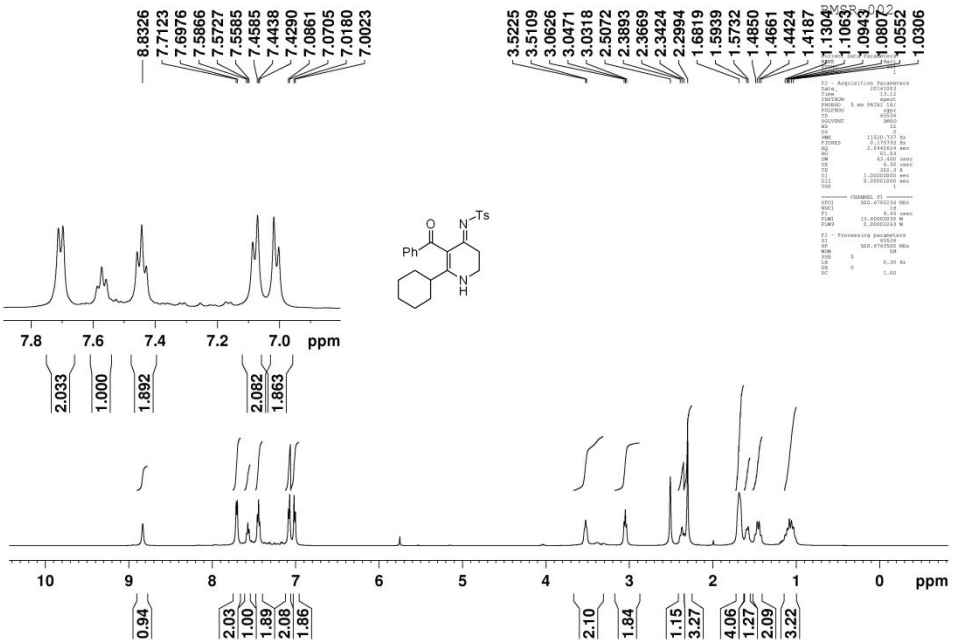


Fig. 23: ^{1}H NMR of 7la

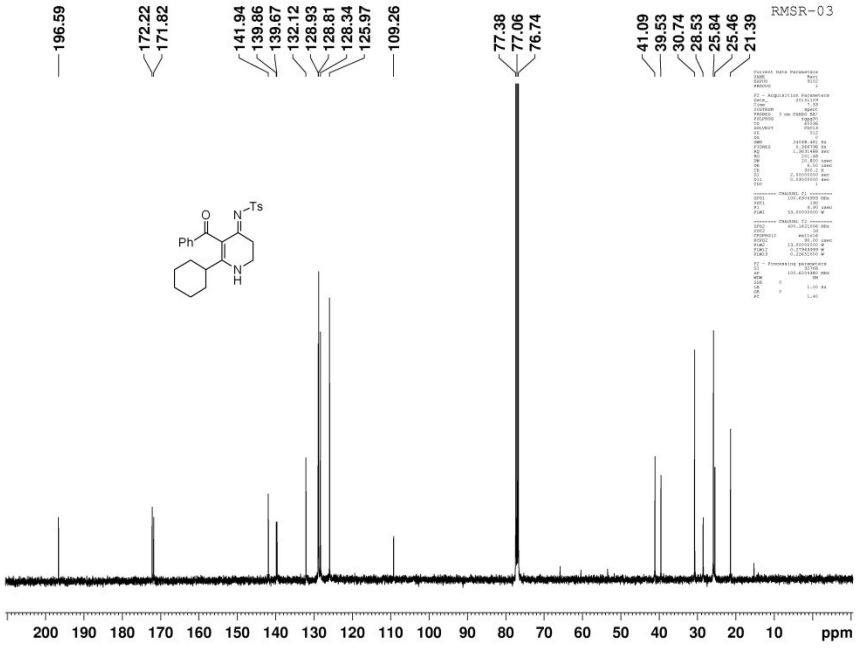


Fig. 24: ^{13}C NMR of 7la

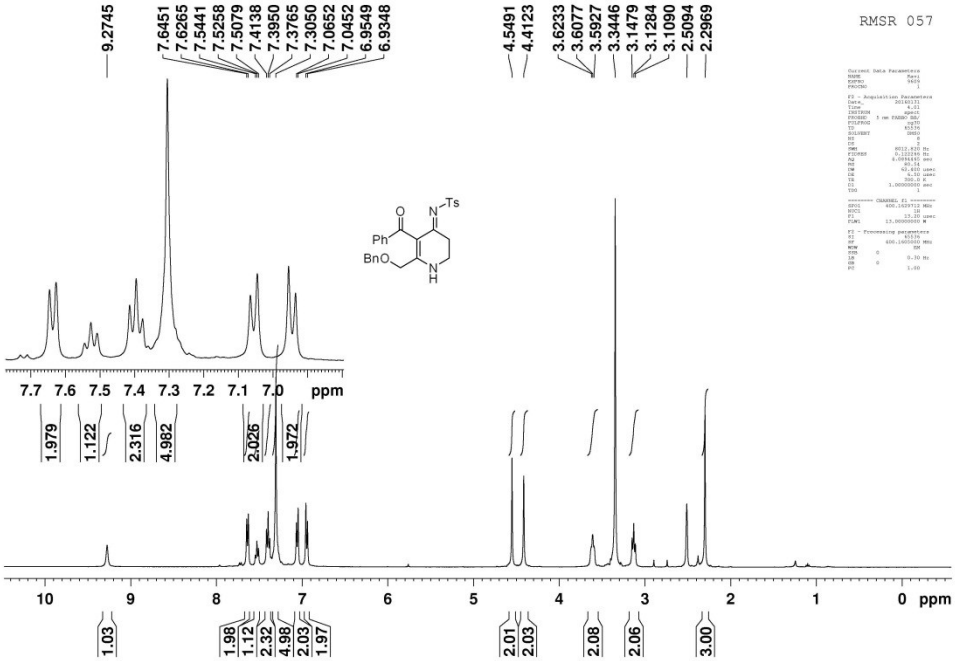


Fig. 25: ^{1}H NMR of 7ma

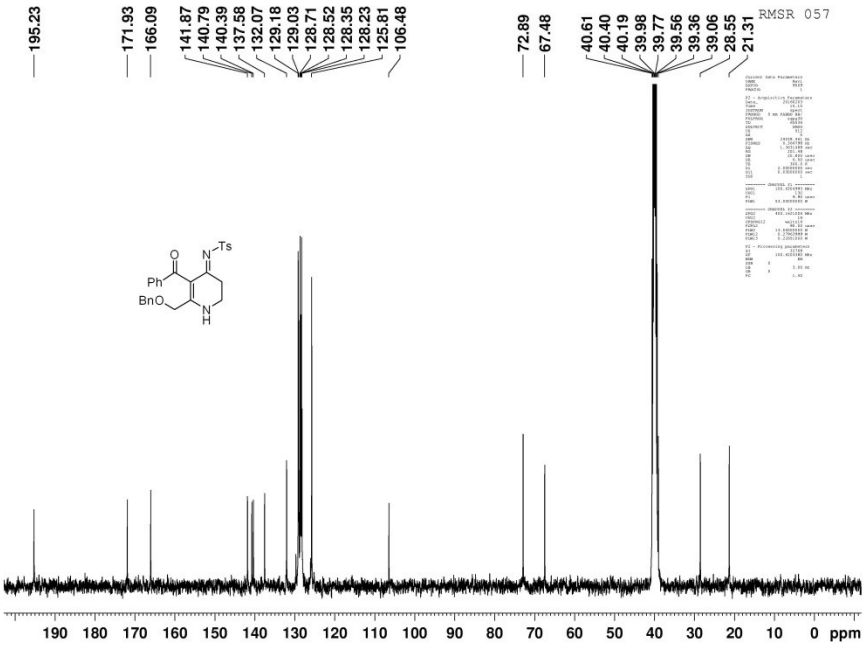


Fig. 26: ^{13}C NMR of 7ma

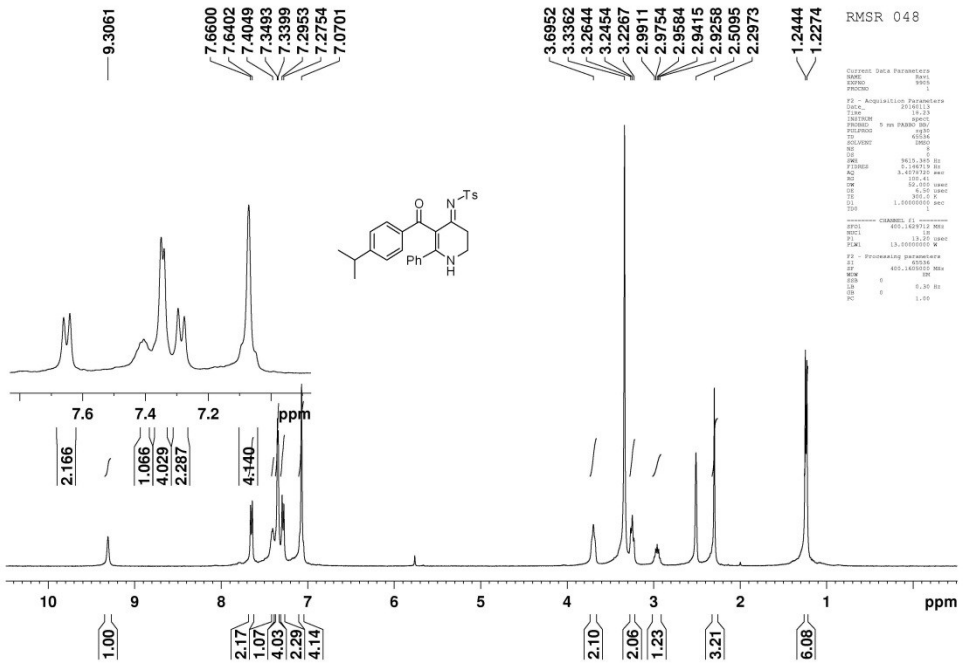


Fig. 27: ^{1}H NMR of 7na

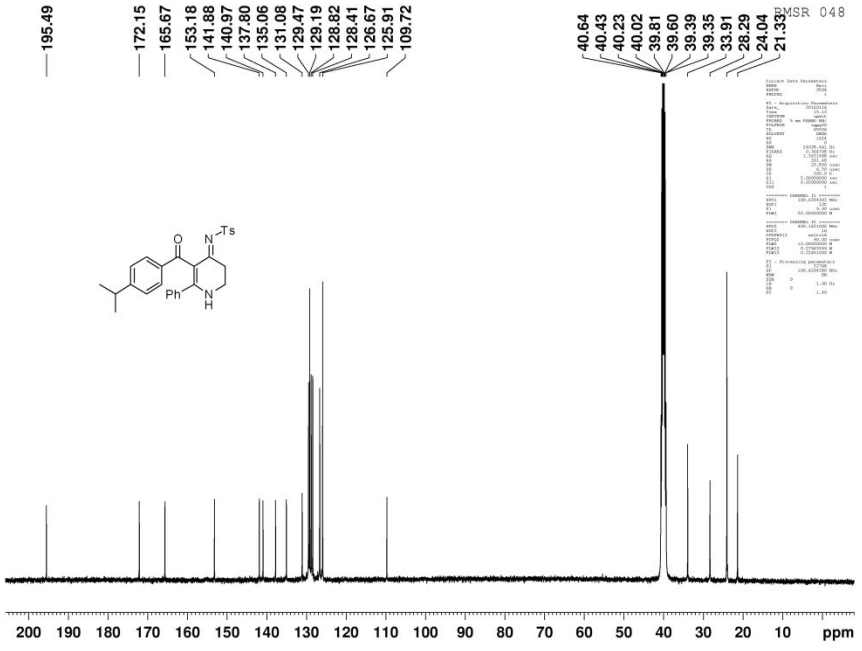


Fig. 28: ^{13}C NMR of 7na

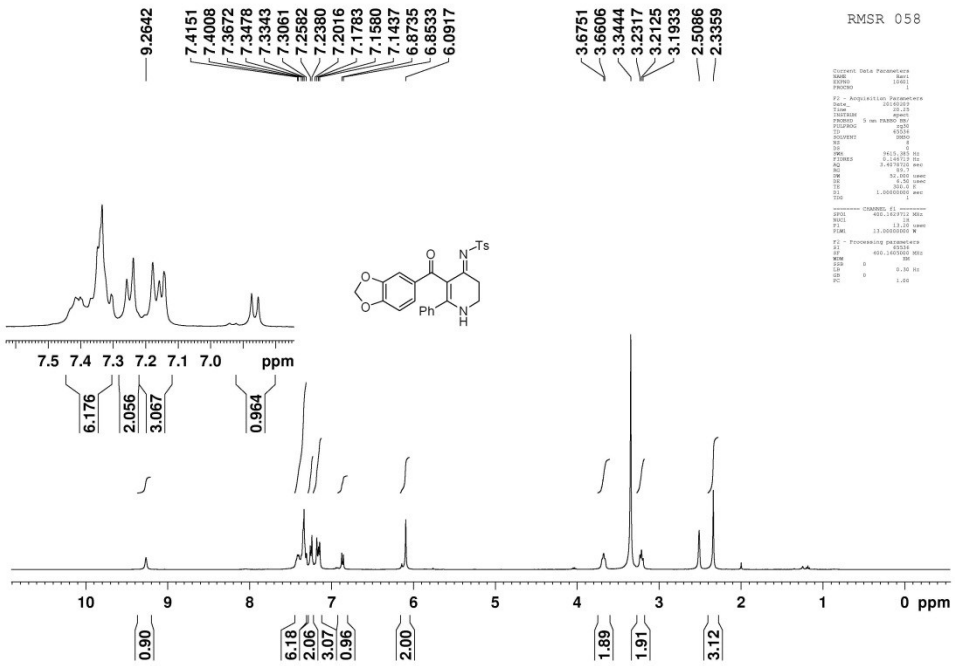


Fig. 29: ^{1}H NMR of 7oa

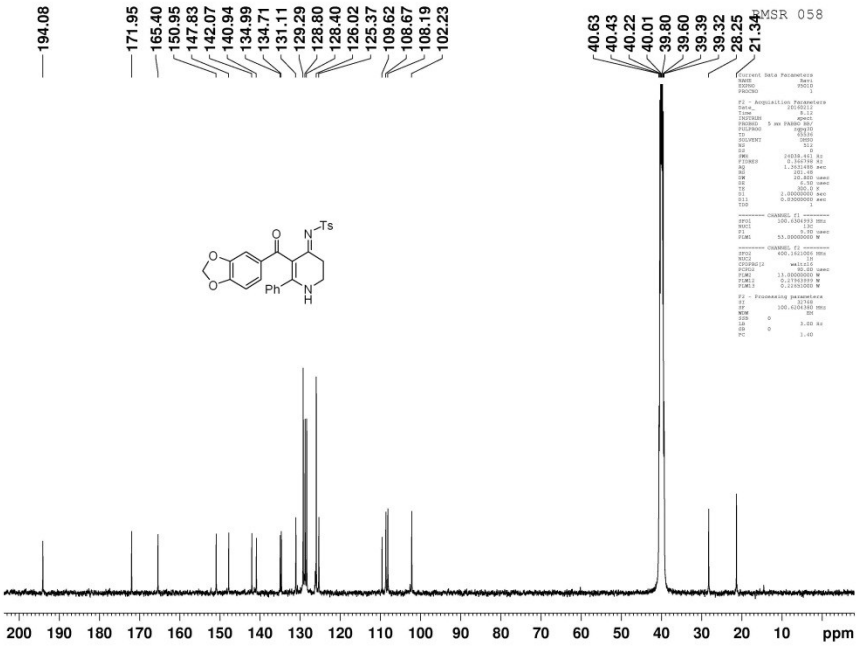


Fig. 30: ^{13}C NMR of 7oa

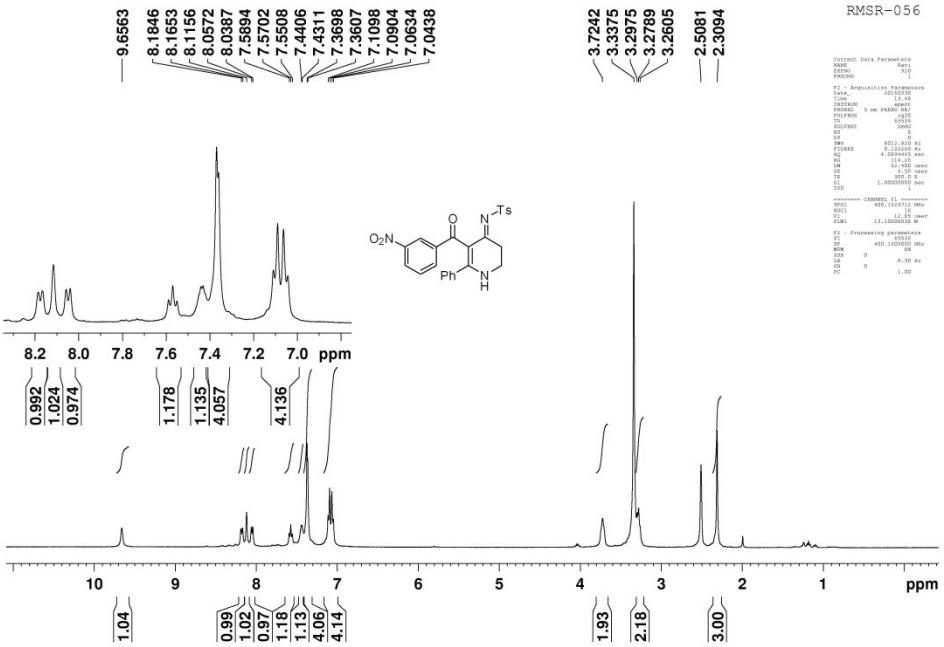


Fig. 31: ^{1}H NMR of 7pa

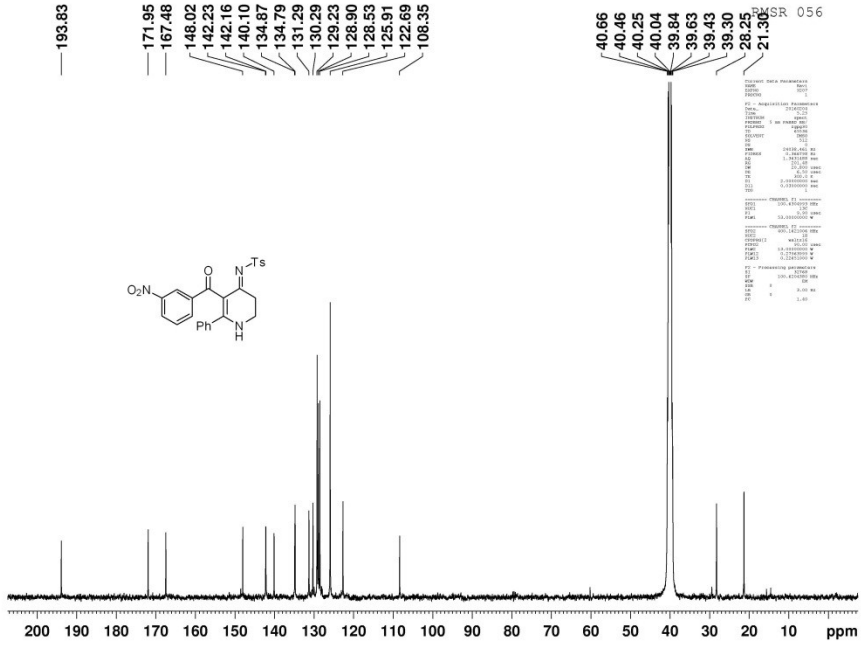


Fig. 32: ^{13}C NMR of 7pa

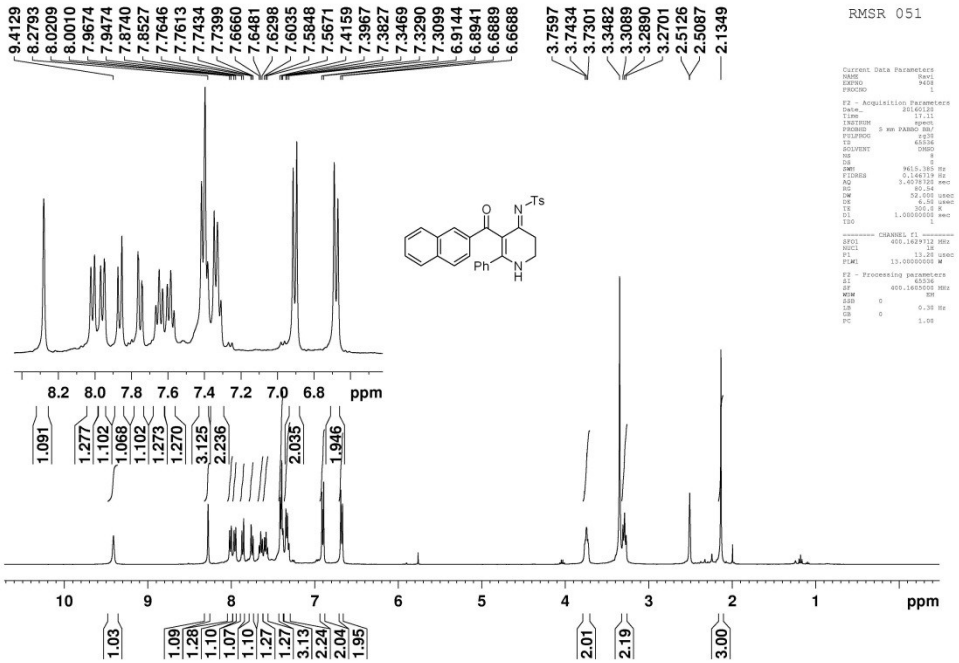


Fig. 33: ^{1}H NMR of 7qa

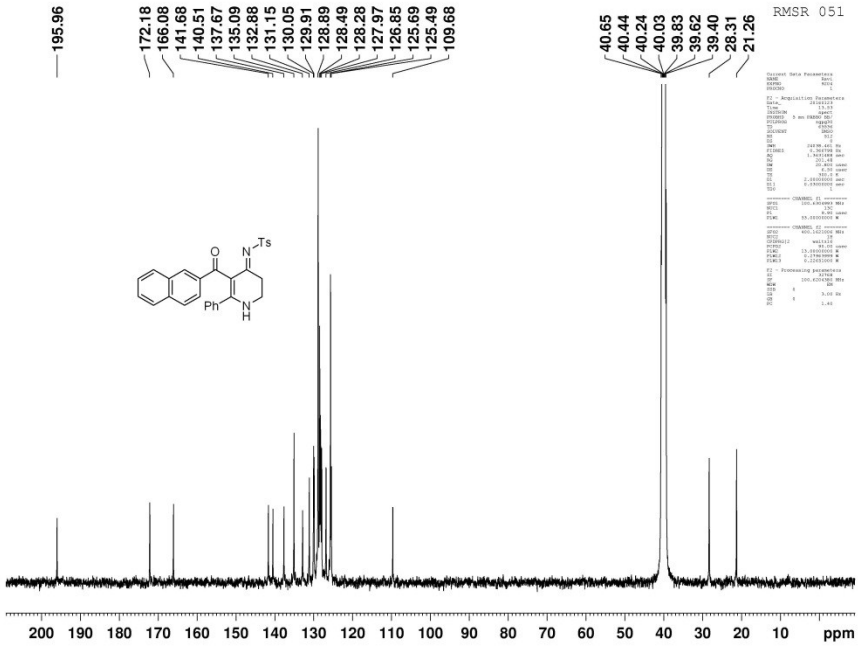


Fig. 34: ^{13}C NMR of 7qa

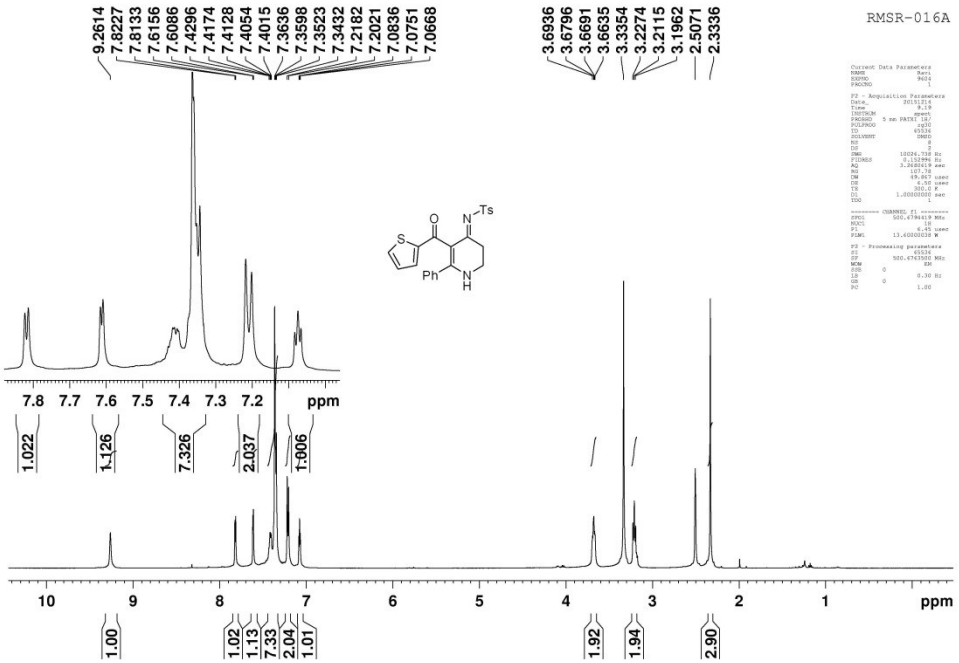


Fig. 35: ^{1}H NMR of 7ra

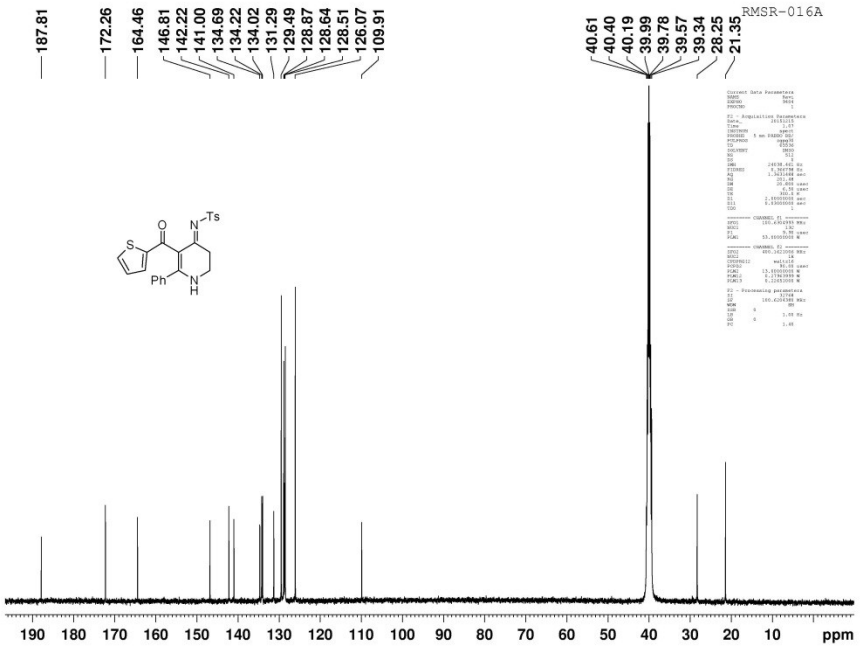


Fig. 36: ^{13}C NMR of 7ra

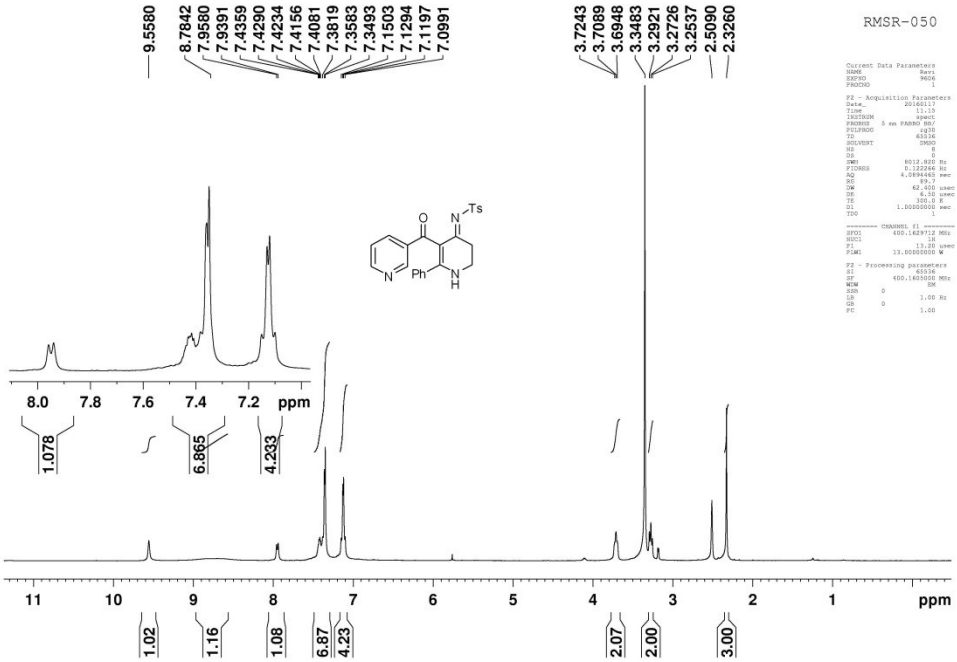


Fig. 37: ^{1}H NMR of 7sa

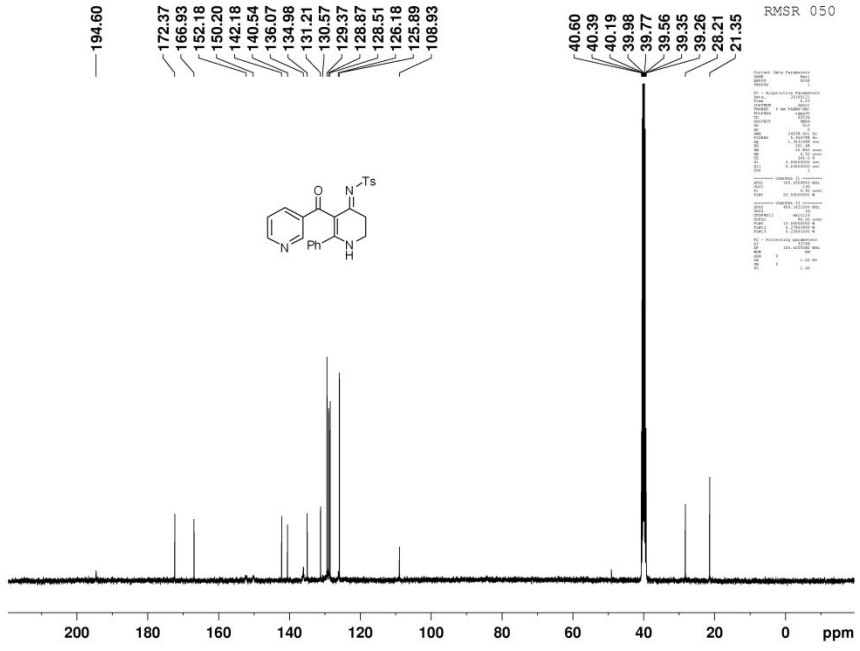


Fig. 38: ^{13}C NMR of 7sa

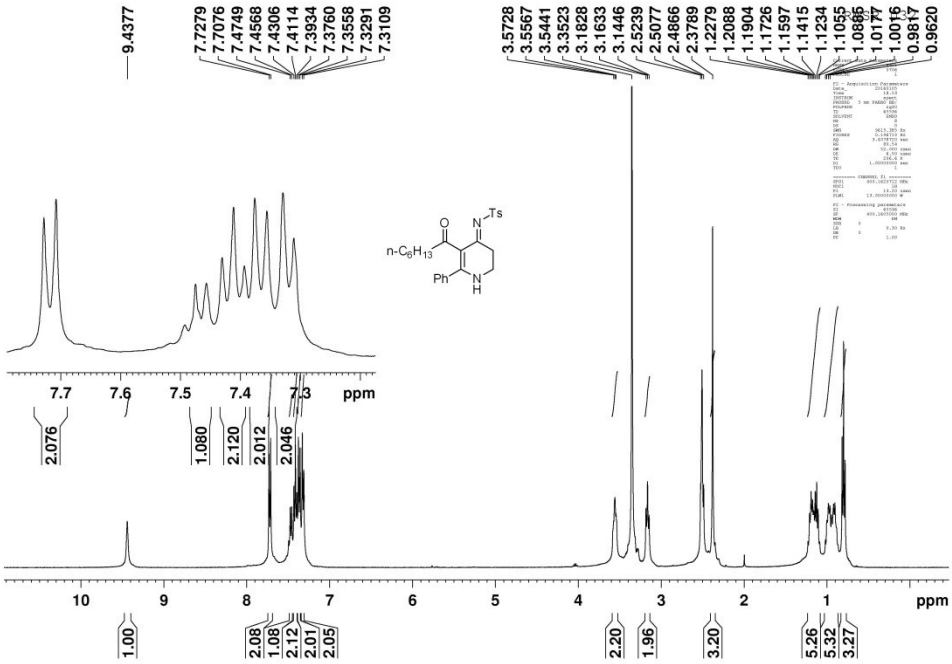


Fig. 39: ^{1}H NMR of 7ta

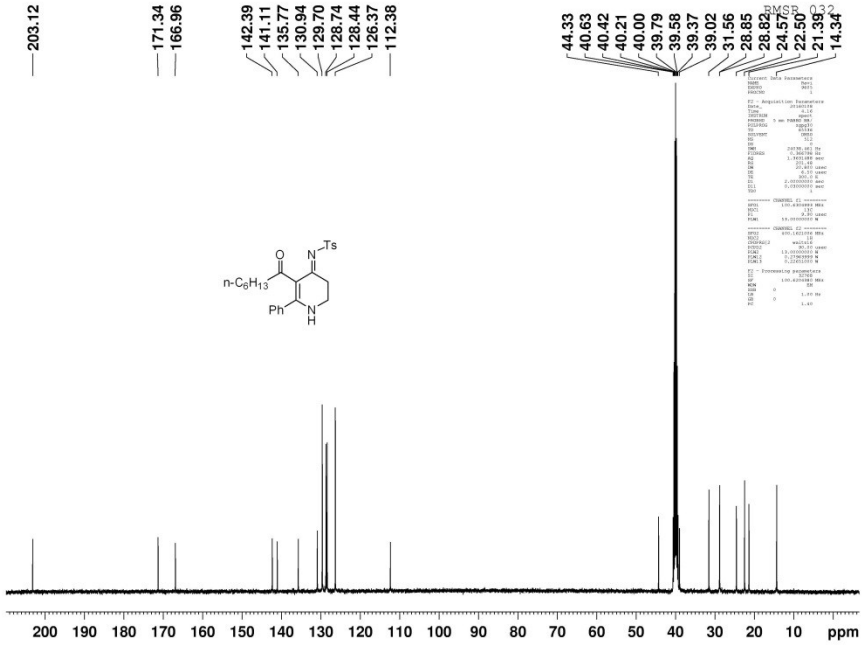


Fig. 40: ^{13}C NMR of 7ta

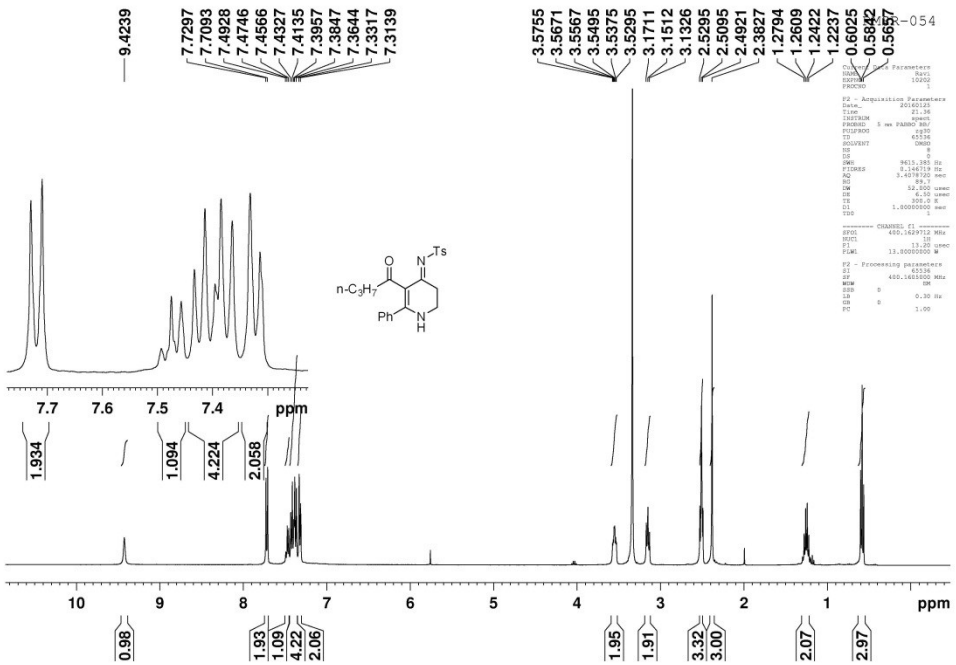


Fig. 41: ^{1}H NMR of 7ua

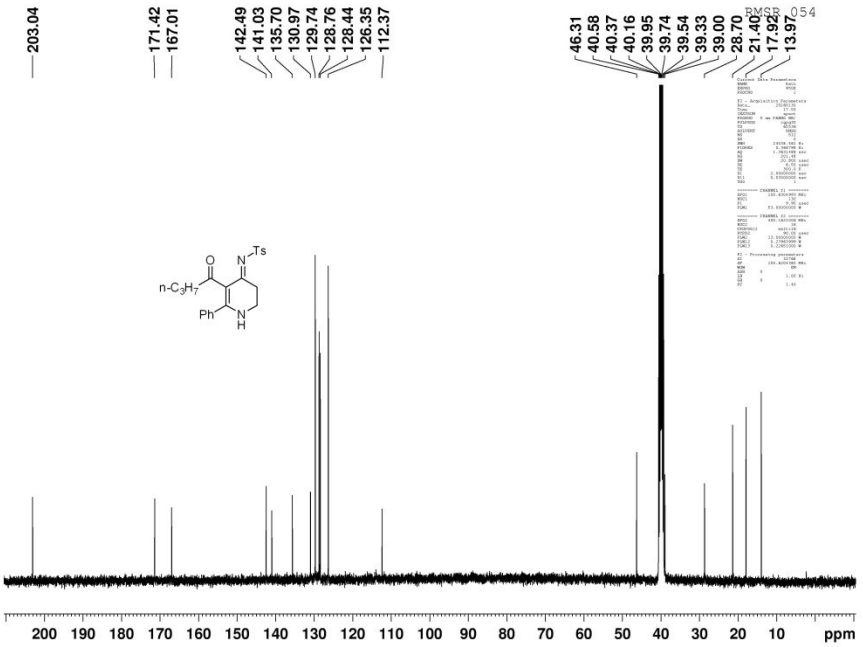


Fig. 42: ^{13}C NMR of 7ua

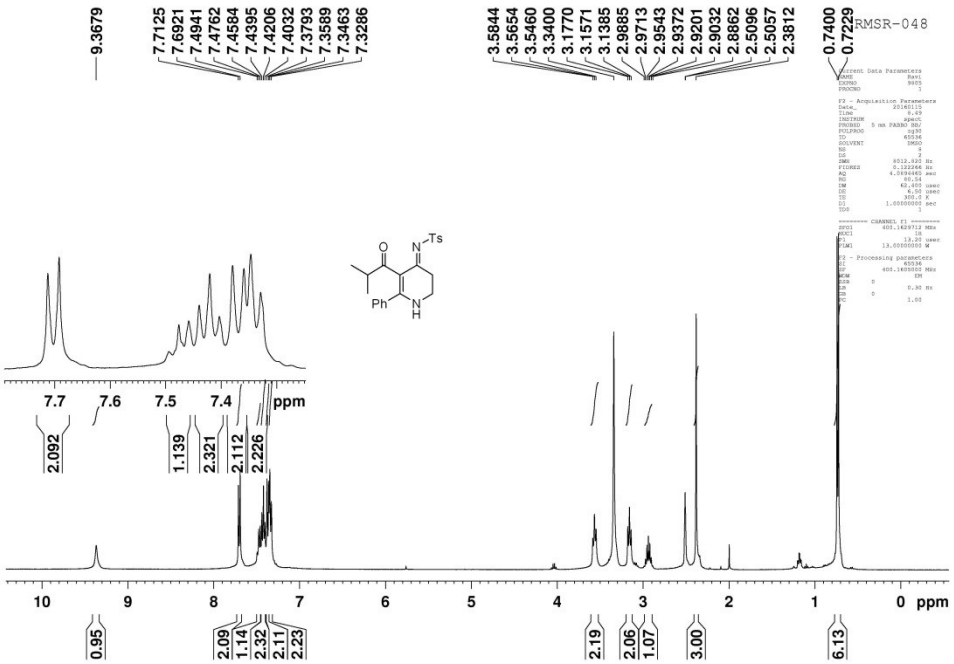


Fig. 43: ^{1}H NMR of 7va

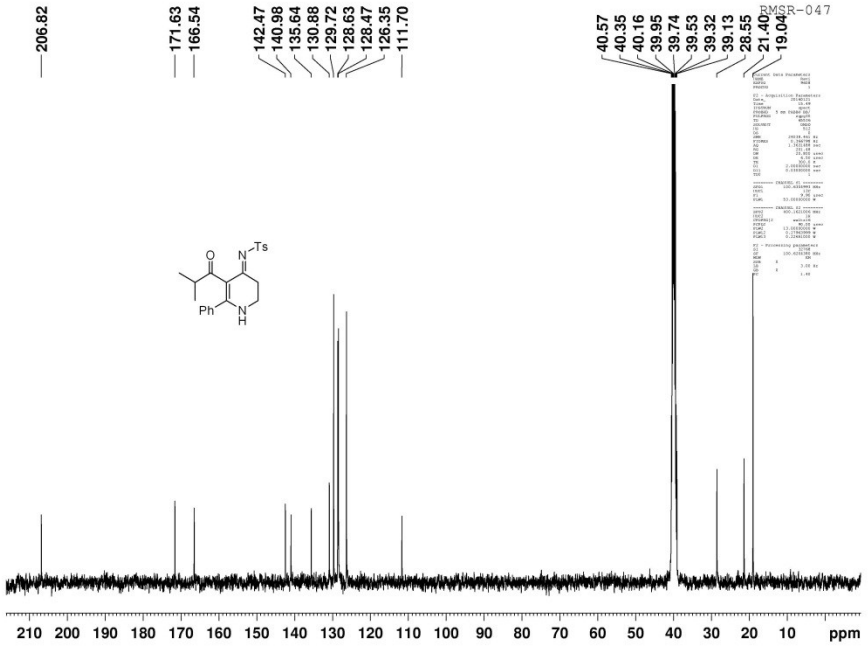


Fig. 44: ^{13}C NMR of 7va

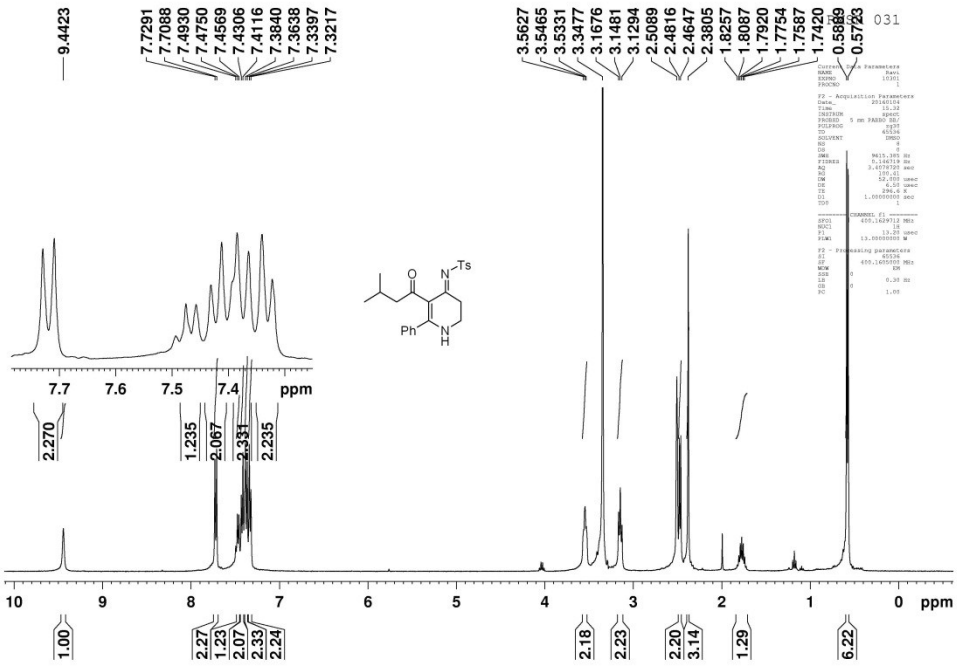


Fig. 45: ^{1}H NMR of 7wa

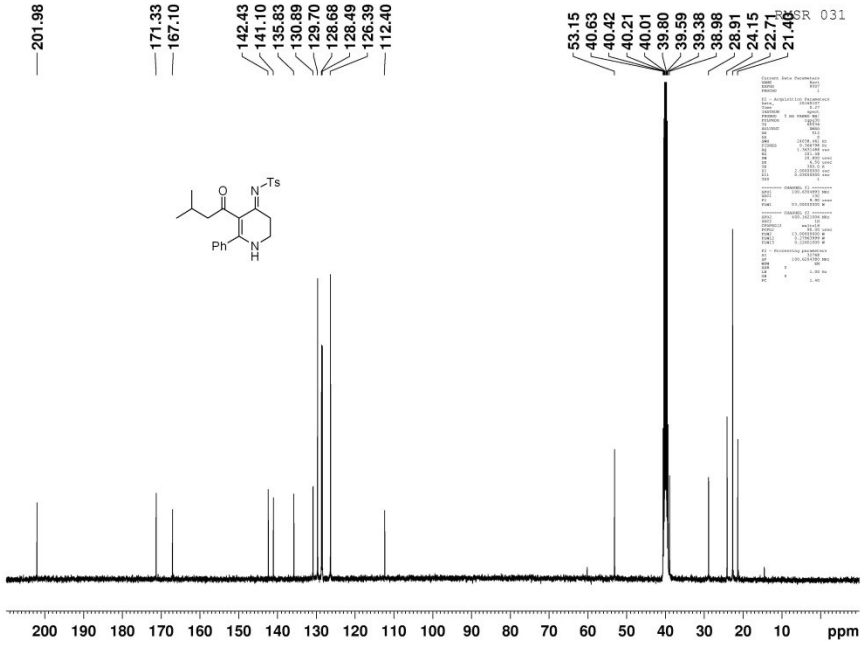


Fig. 46: ^{13}C NMR of 7wa

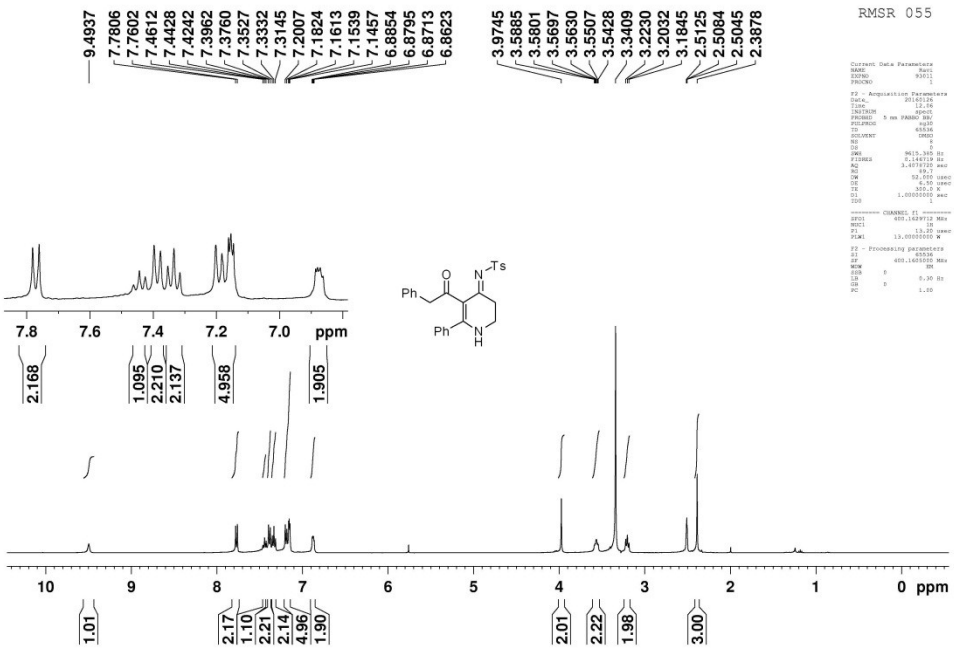


Fig. 47: ^{1}H NMR of 7xa

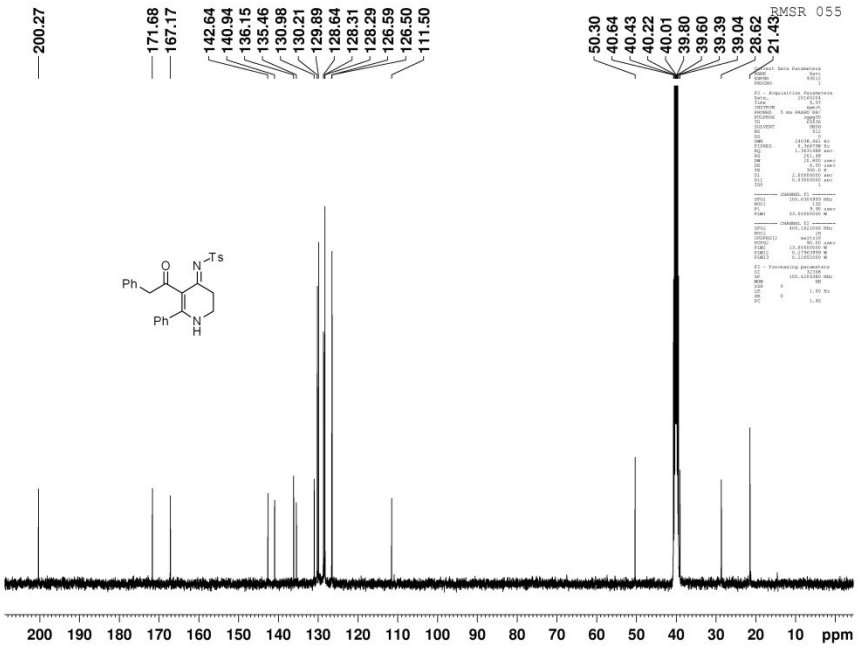


Fig. 48: ^{13}C NMR of 7xa

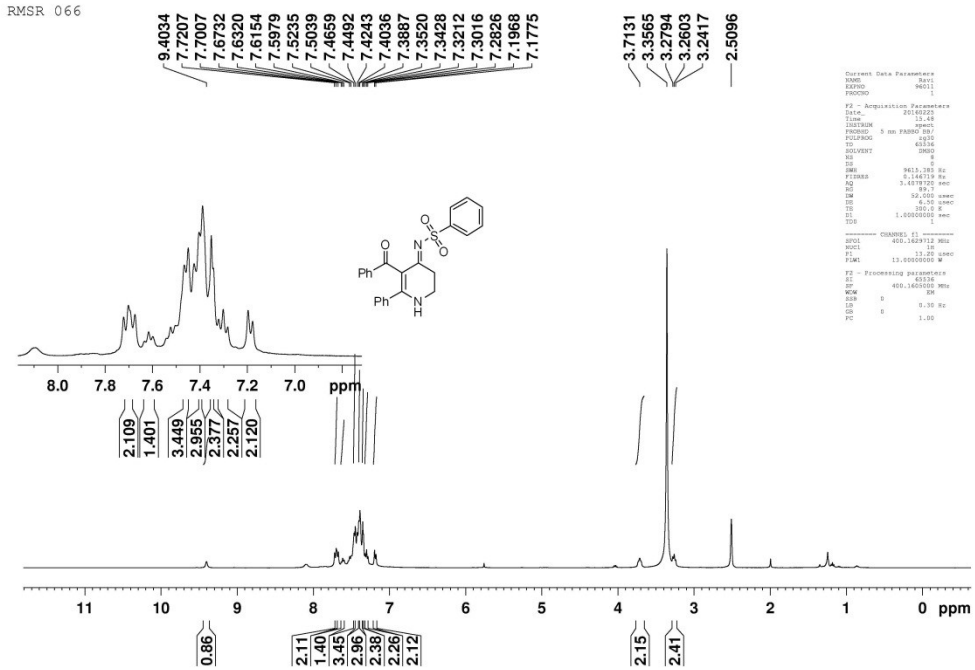


Fig. 49: ^{1}H NMR of 7ab

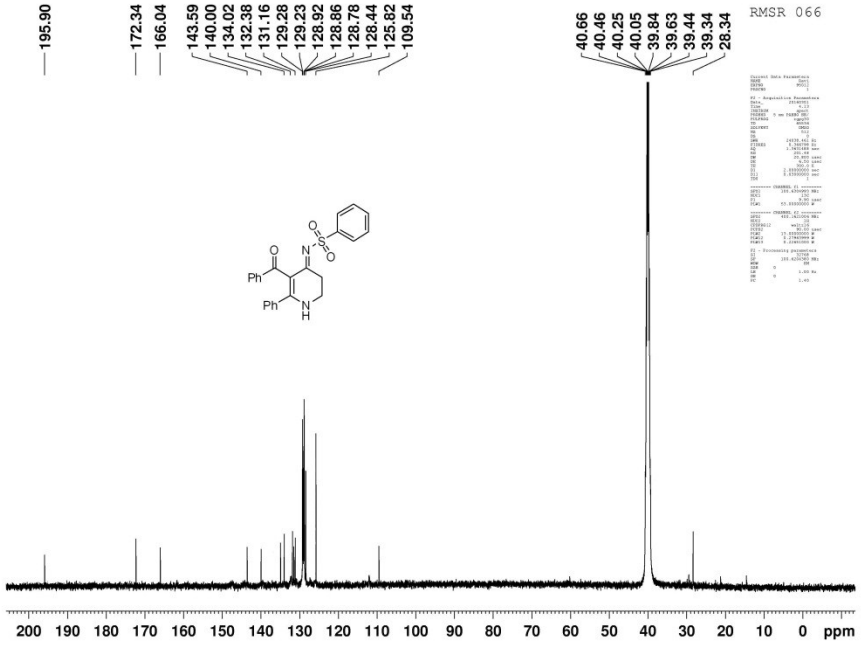


Fig. 50: ^{13}C NMR of 7ab

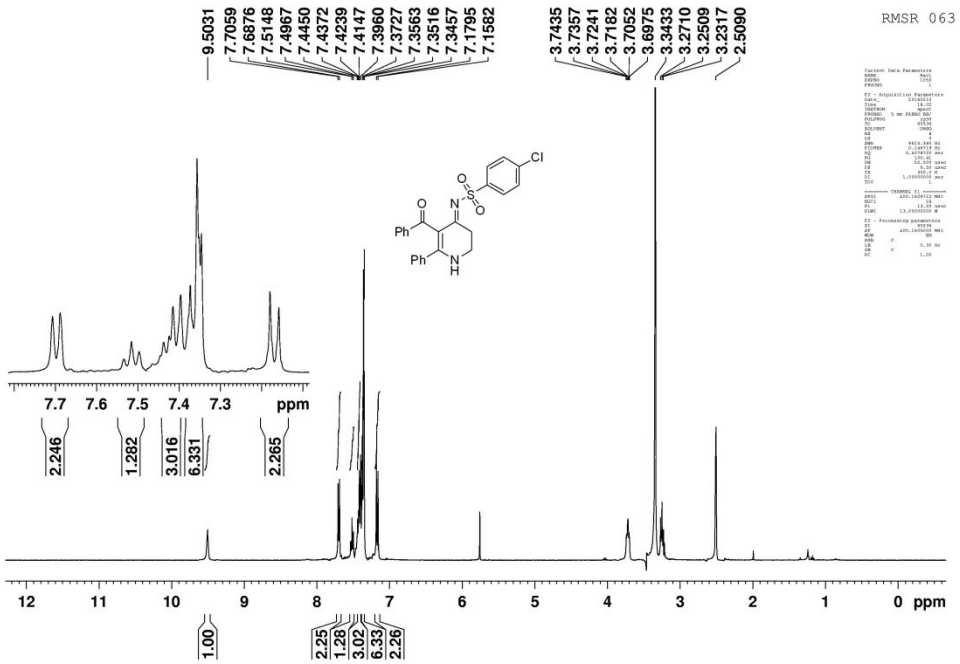


Fig. 51: ^{1}H NMR of 7ac

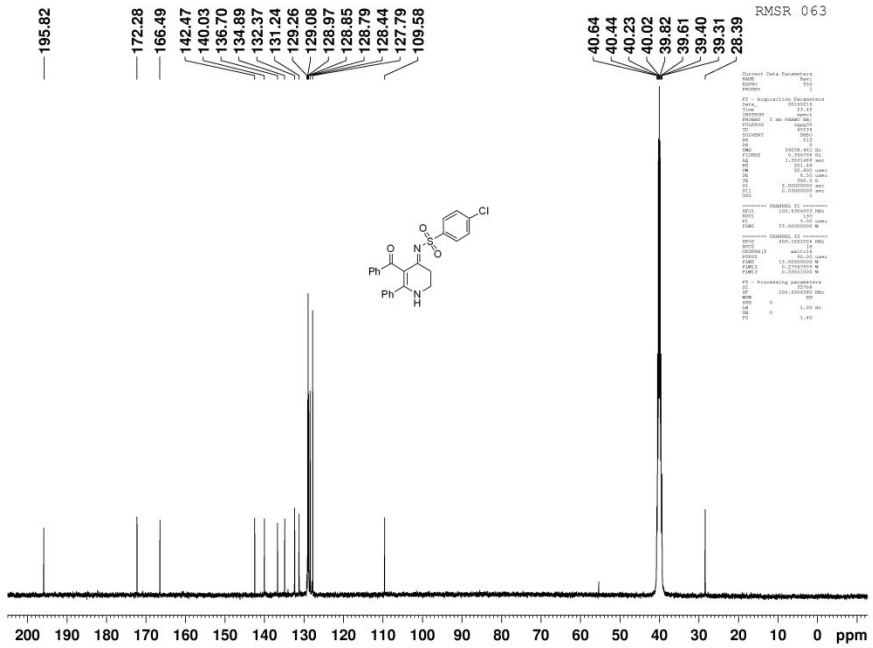


Fig. 52: ^{13}C NMR of 7ac

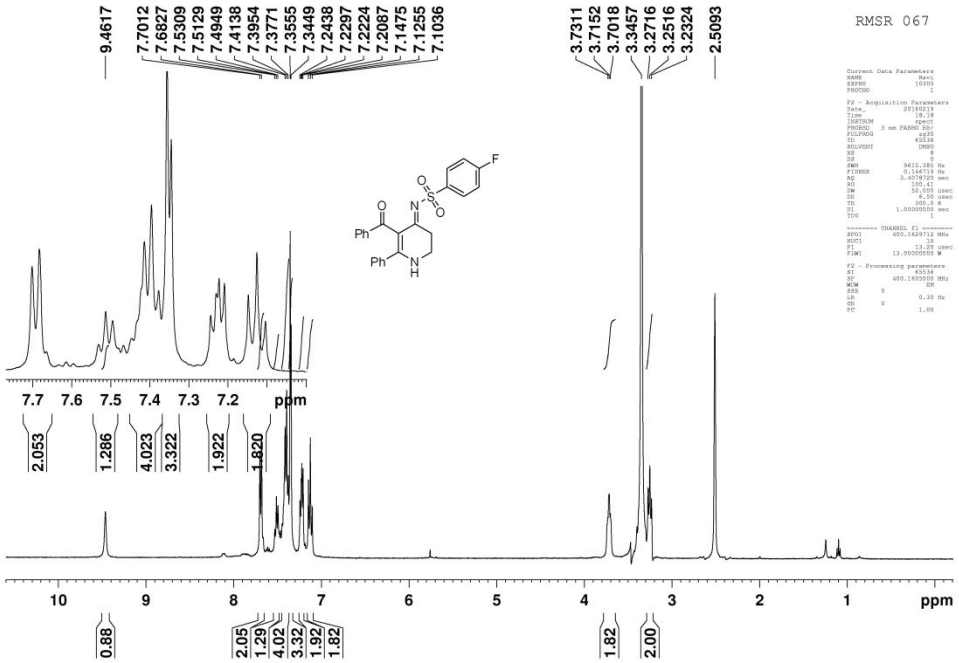


Fig. 53: ^{1}H NMR of 7ad

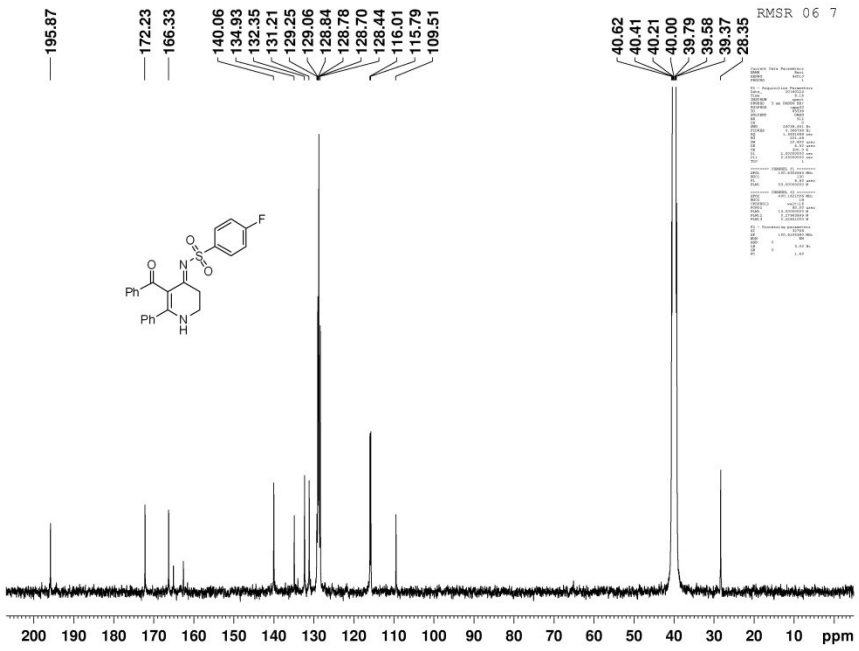


Fig. 54: ^{13}C NMR of 7ad

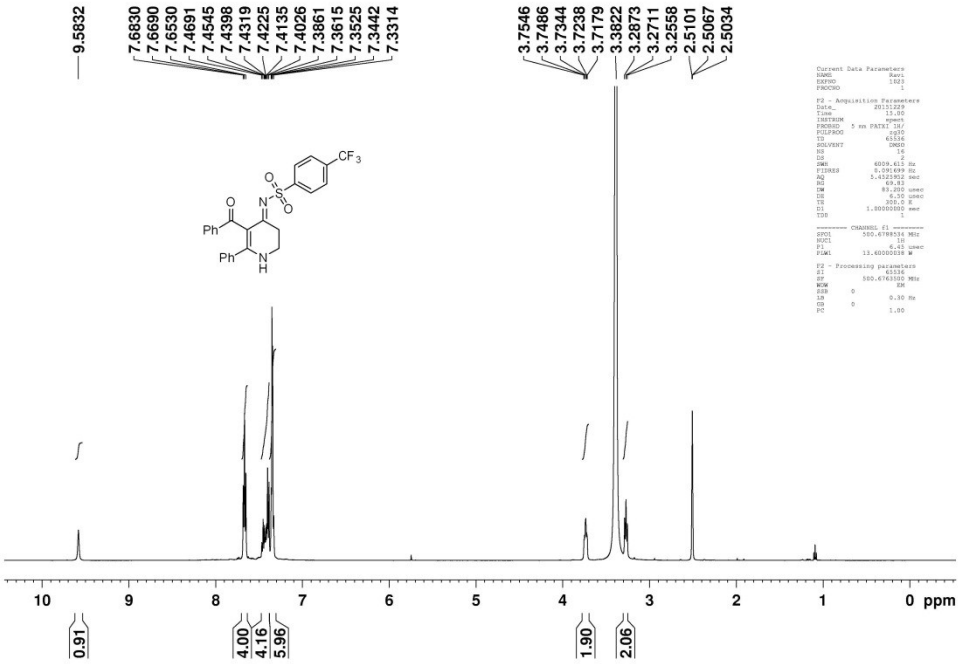


Fig. 55: ^{1}H NMR of 7ae

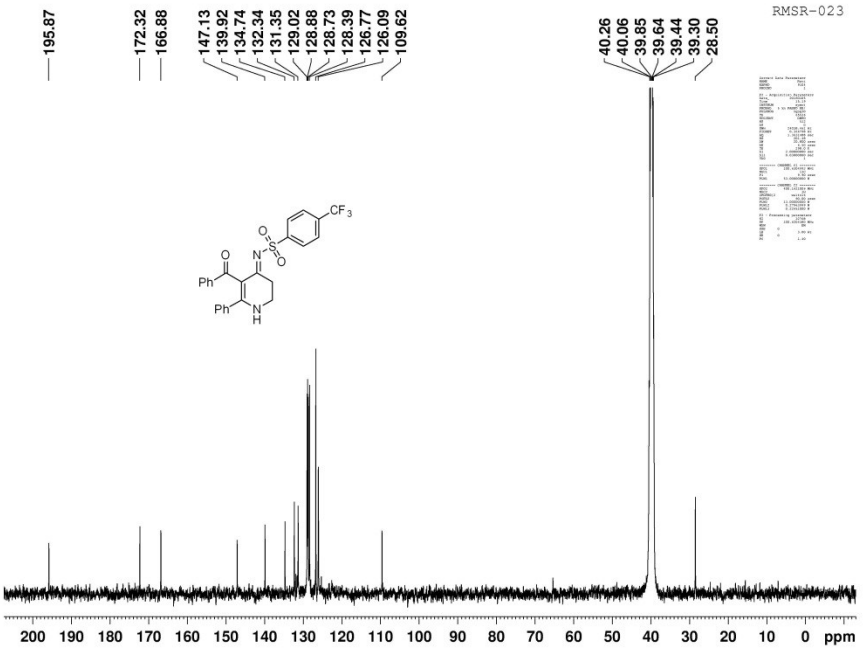


Fig. 56: ^{13}C NMR of 7ae

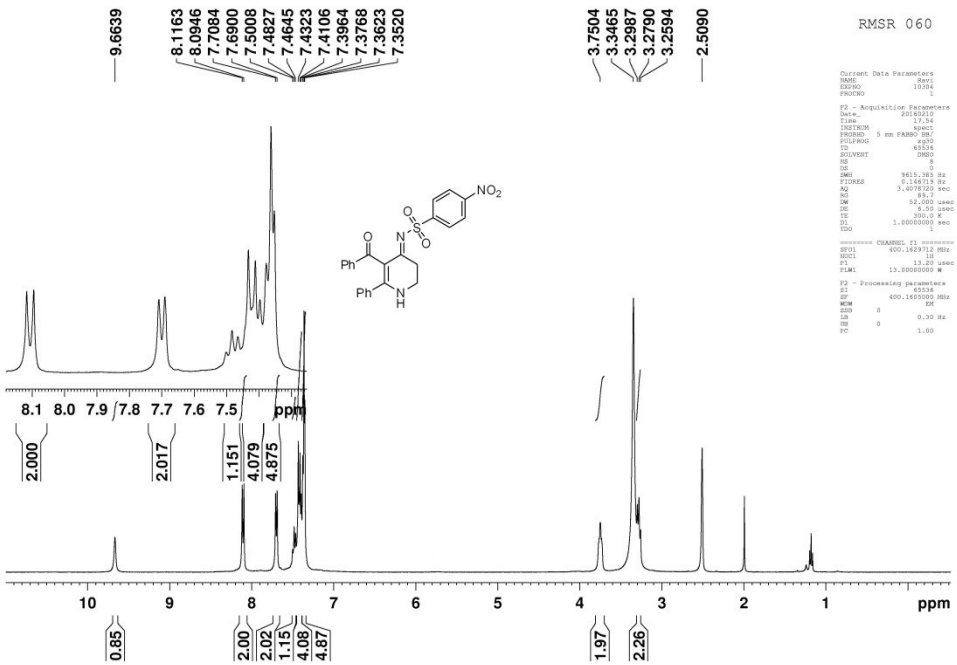


Fig. 57: ^{1}H NMR of 7af

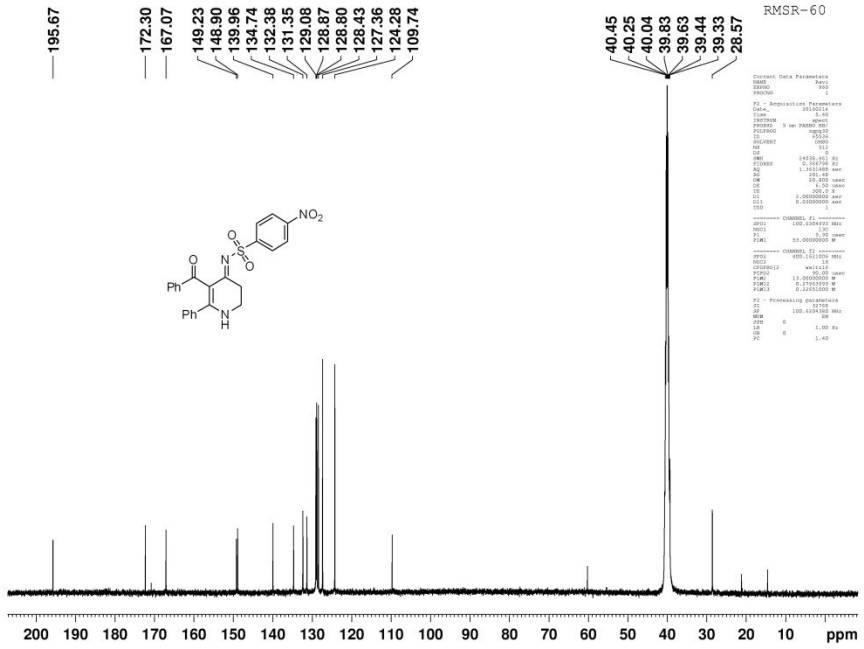


Fig. 58: ^{13}C NMR of 7af

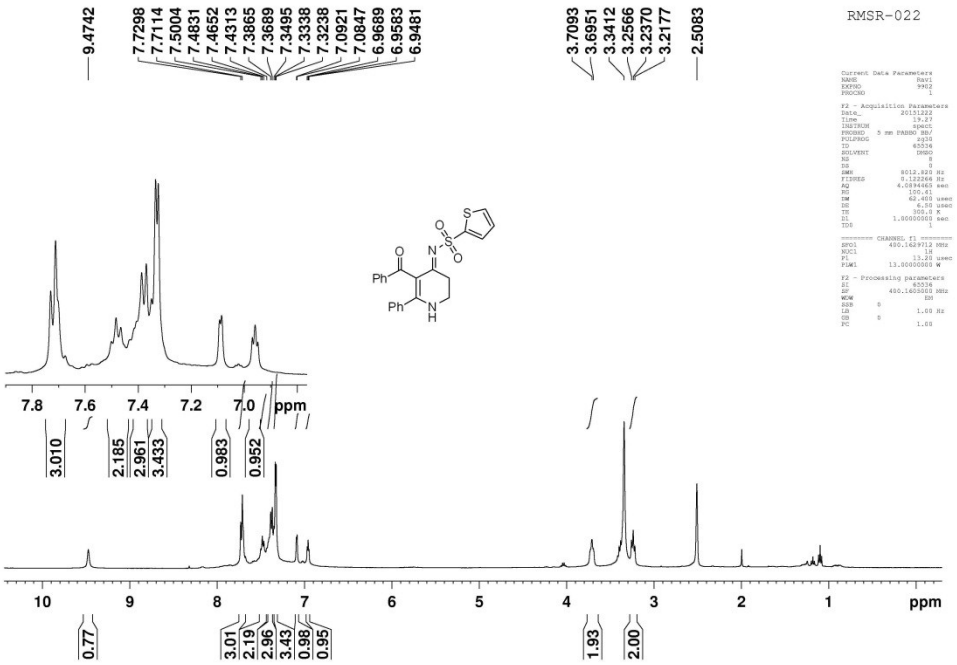


Fig. 59: ^{1}H NMR of 7ag

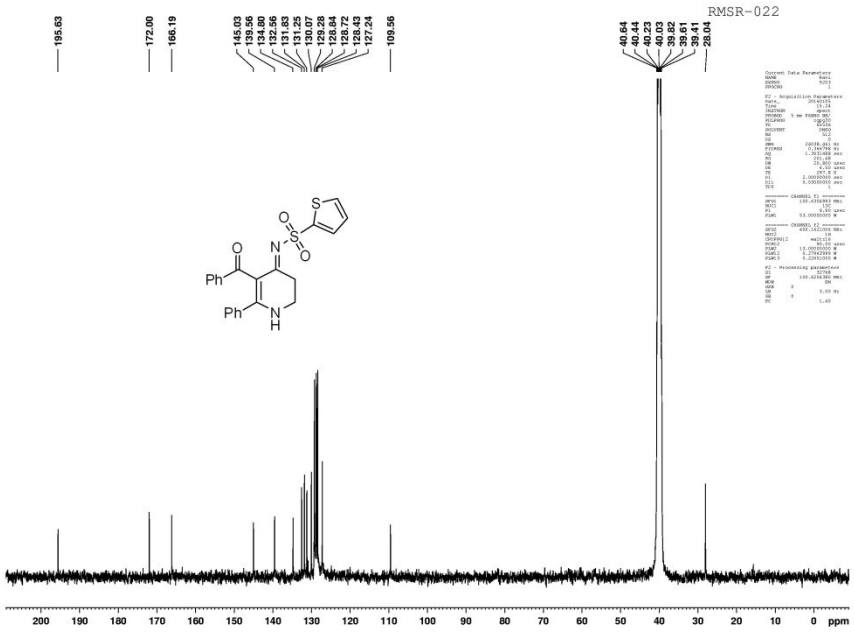


Fig. 60: ^{13}C NMR of 7ag

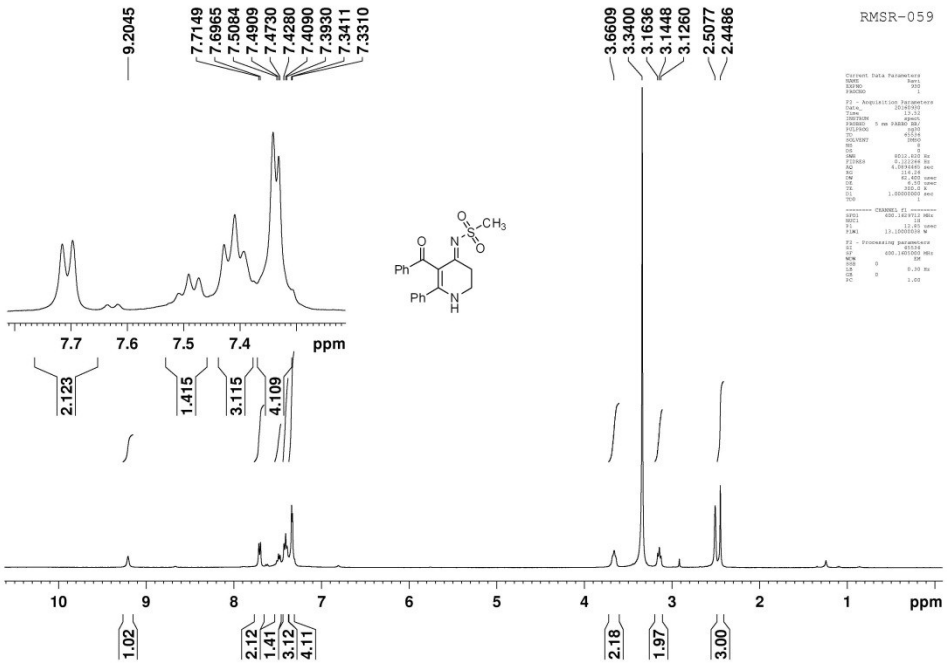


Fig. 61: ^{1}H NMR of 7ah

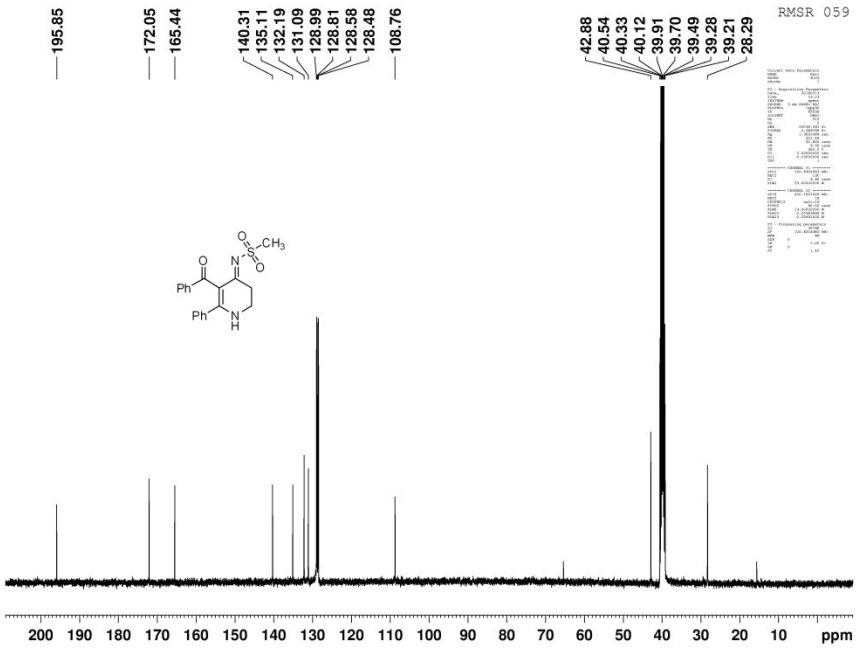


Fig. 62: ^{13}C NMR of 7ah

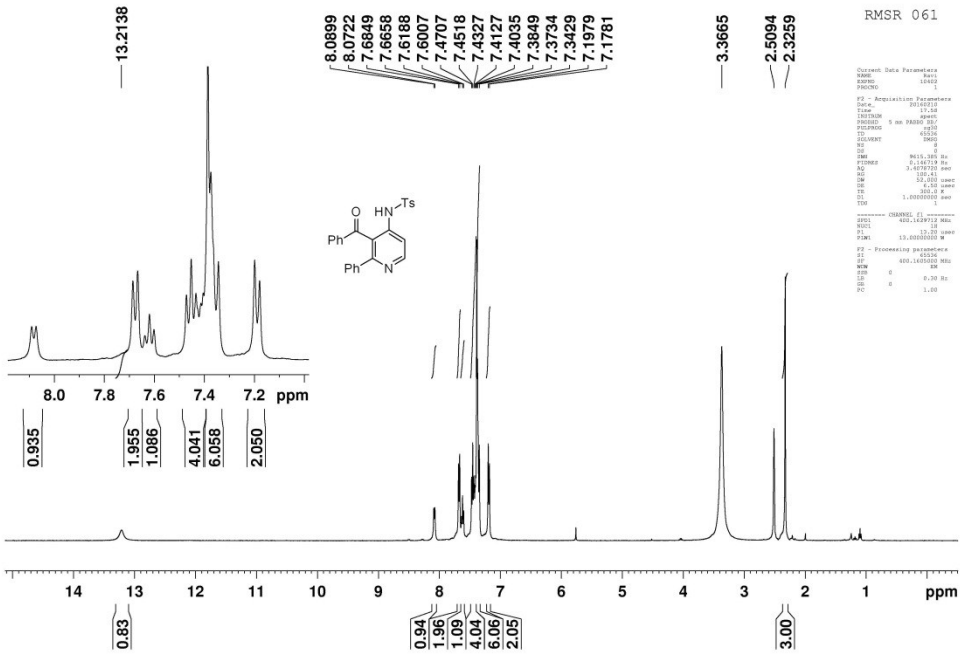


Fig. 63: ^{1}H NMR of 9a

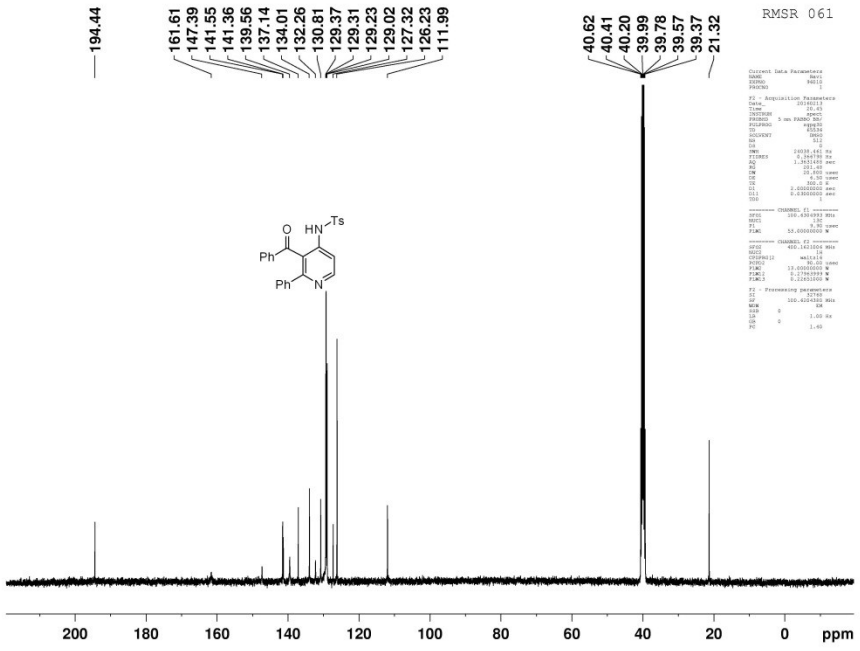


Fig. 64: ^{13}C NMR of 9a

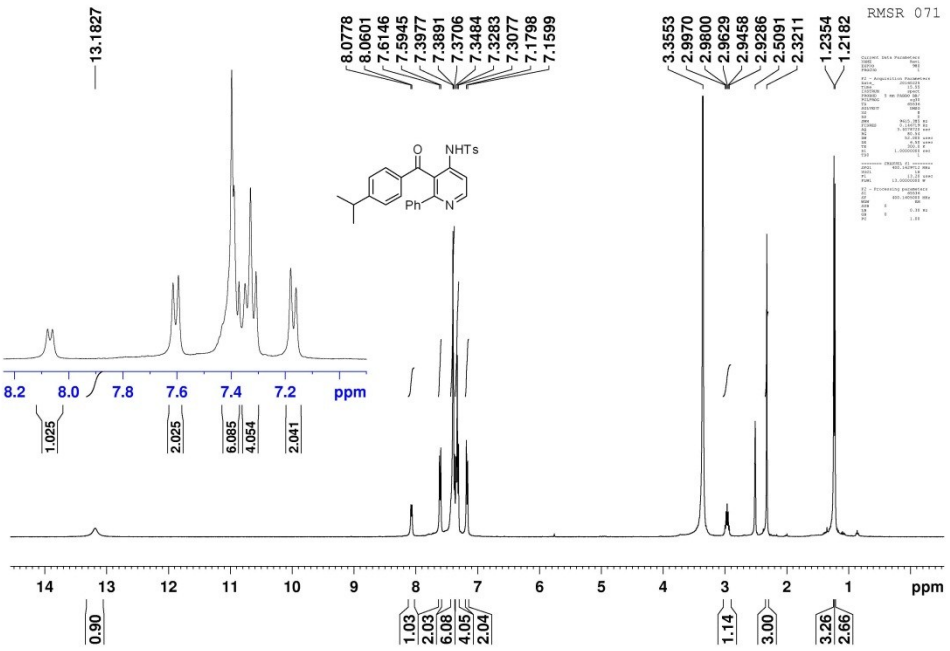


Fig. 65: ^{1}H NMR of 9b

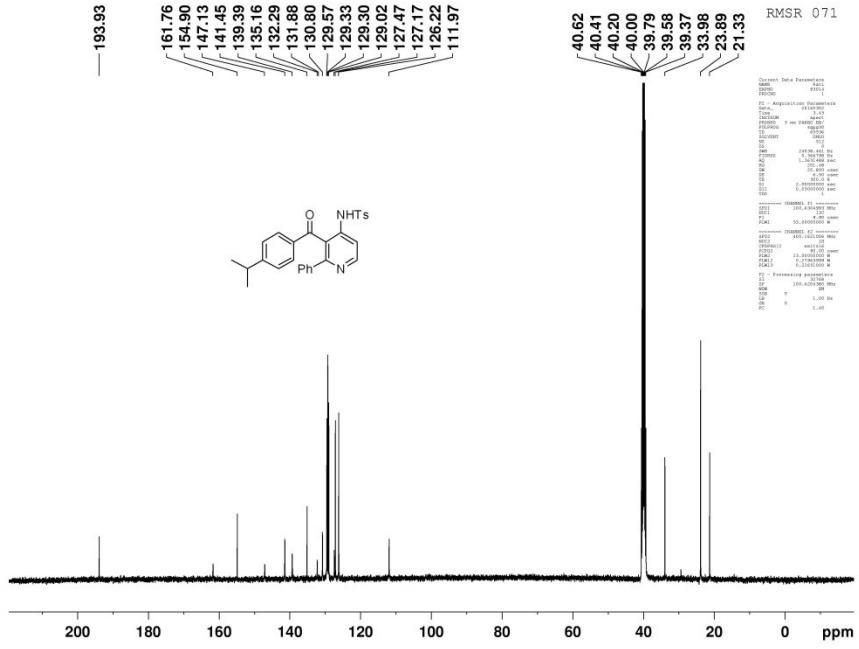


Fig. 66: ^{13}C NMR of 9b

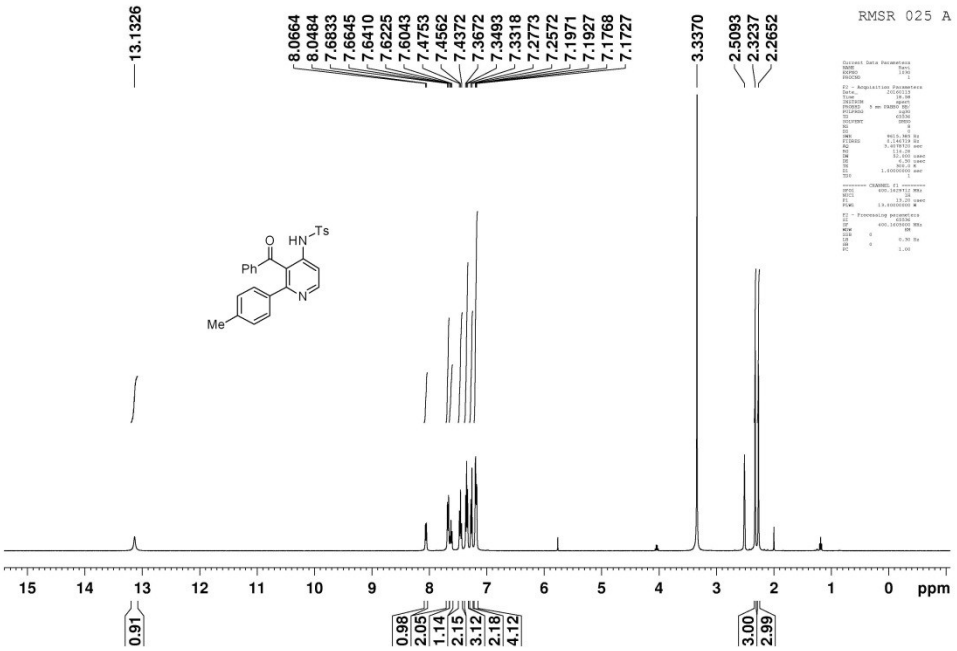


Fig. 67: ^{1}H NMR of 9c

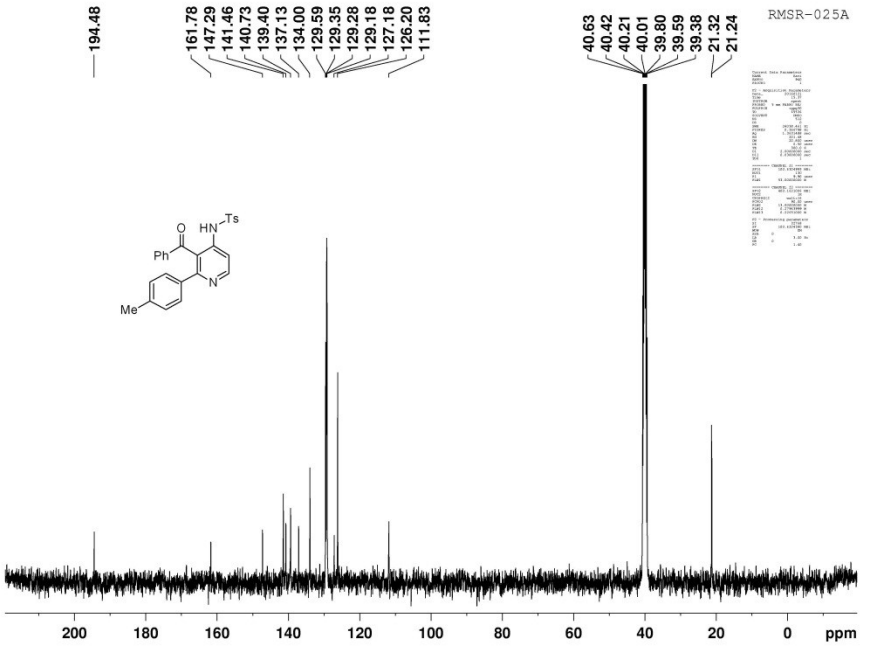


Fig. 68: ^{13}C NMR of 9c

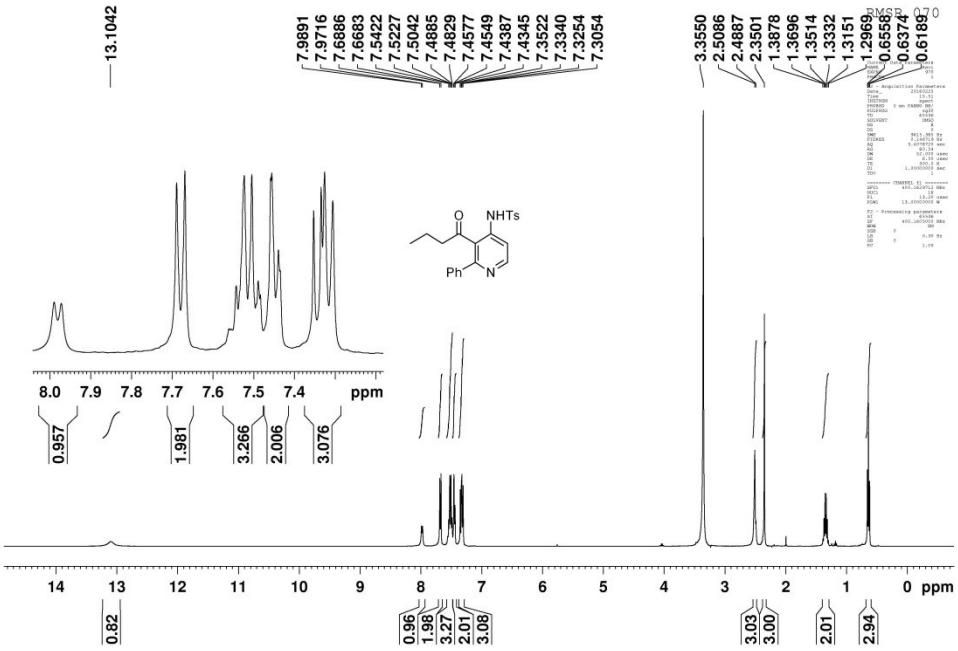


Fig. 69: ^{1}H NMR of 9d

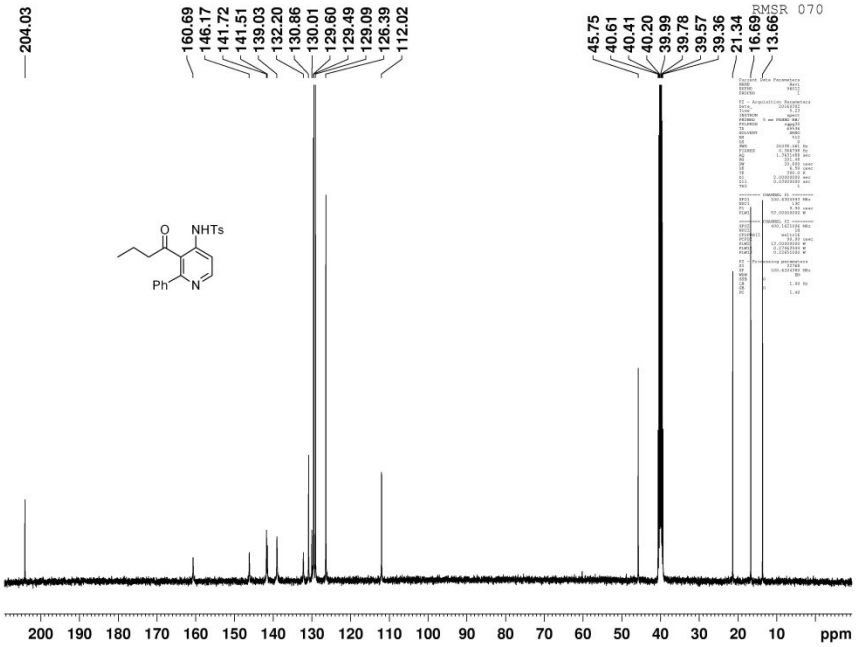


Fig. 70: ^{13}C NMR of 9d

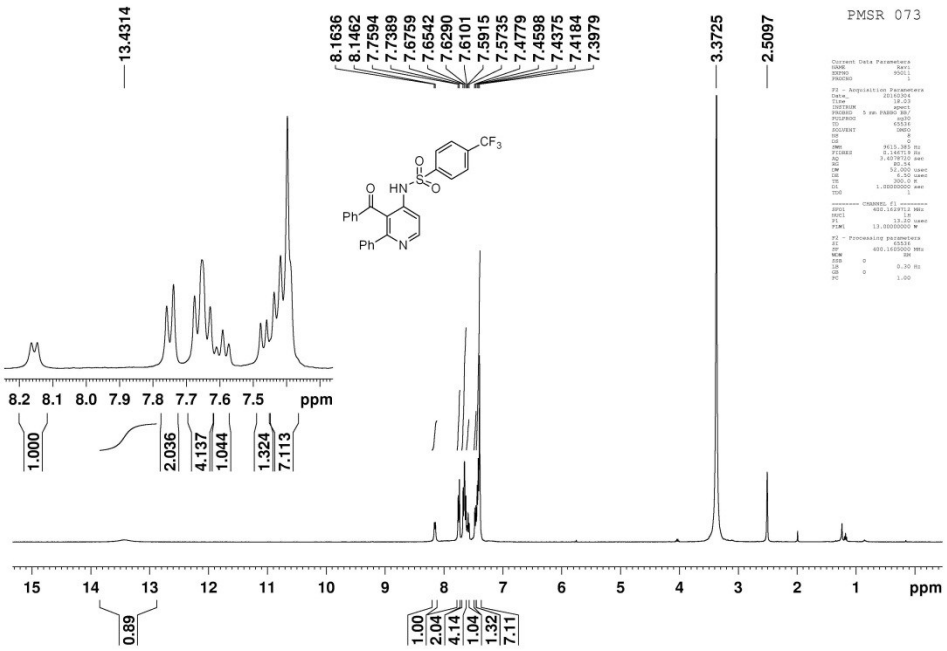


Fig. 71: ^{1}H NMR of 9e

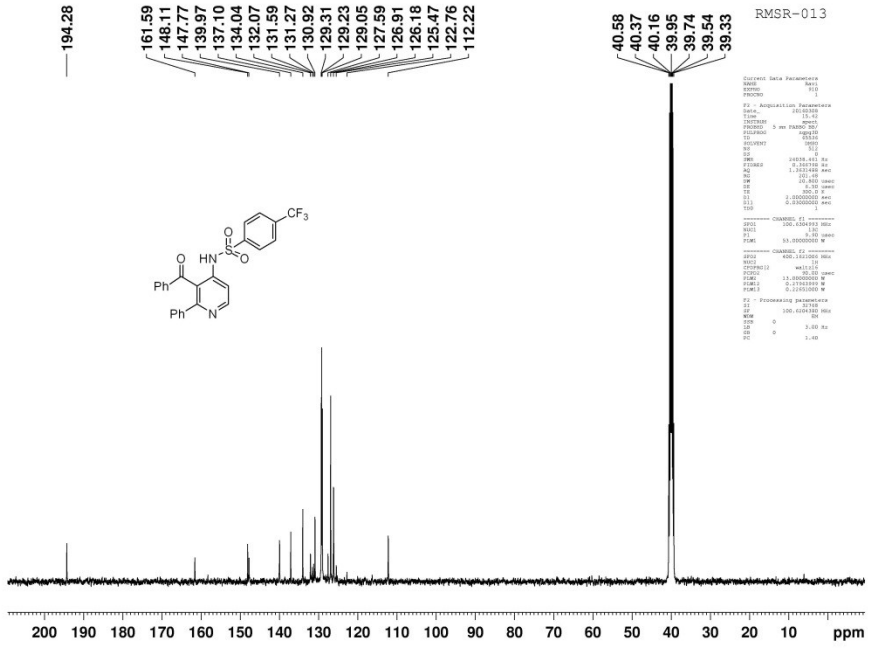


Fig. 72: ^{13}C NMR of 9e

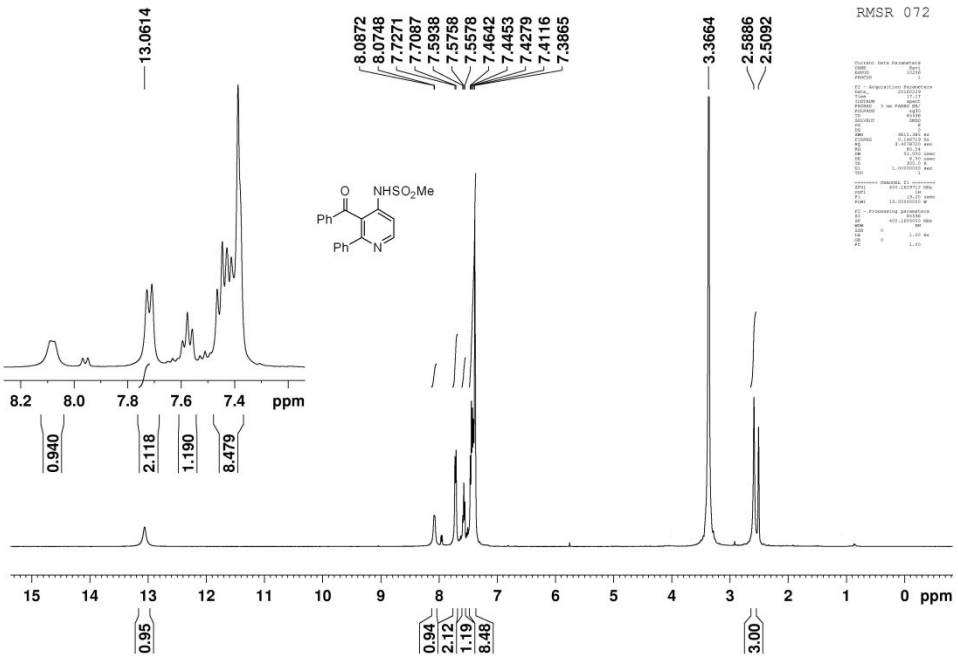


Fig. 73: ^{1}H NMR of 9f

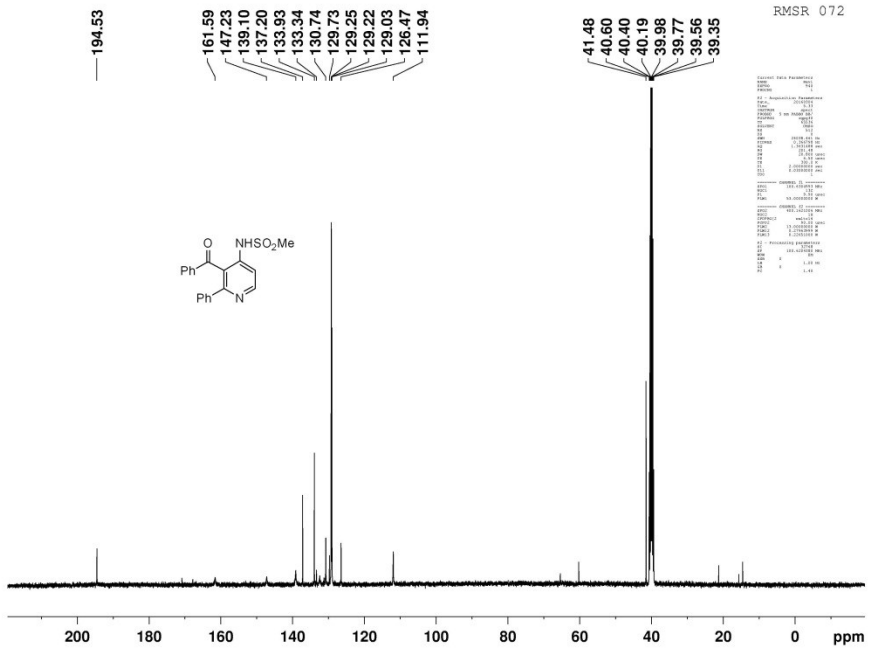


Fig. 74: ^{13}C NMR of 9f

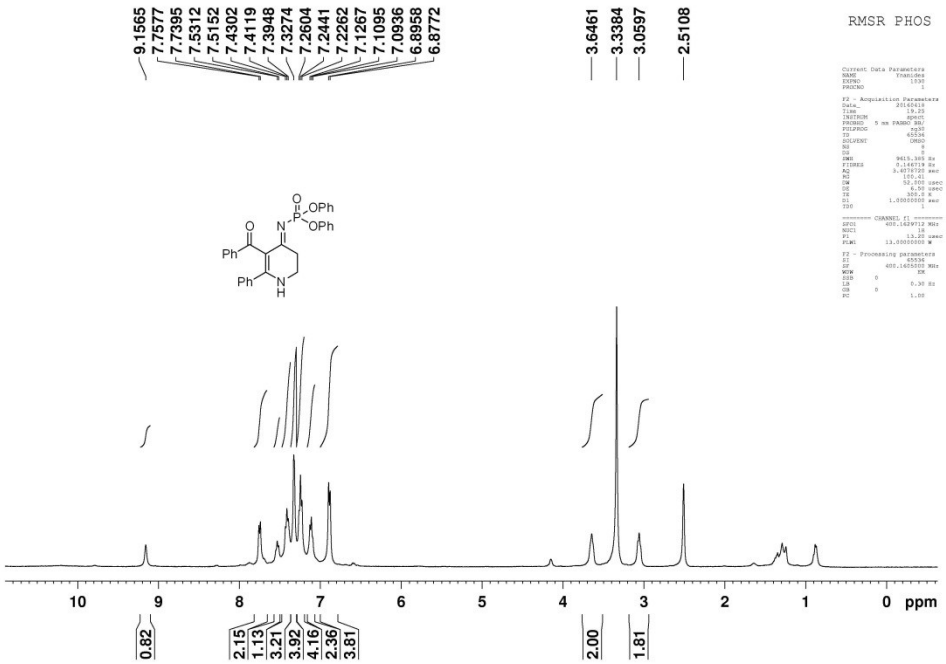


Fig. 75: ^{1}H NMR of 10

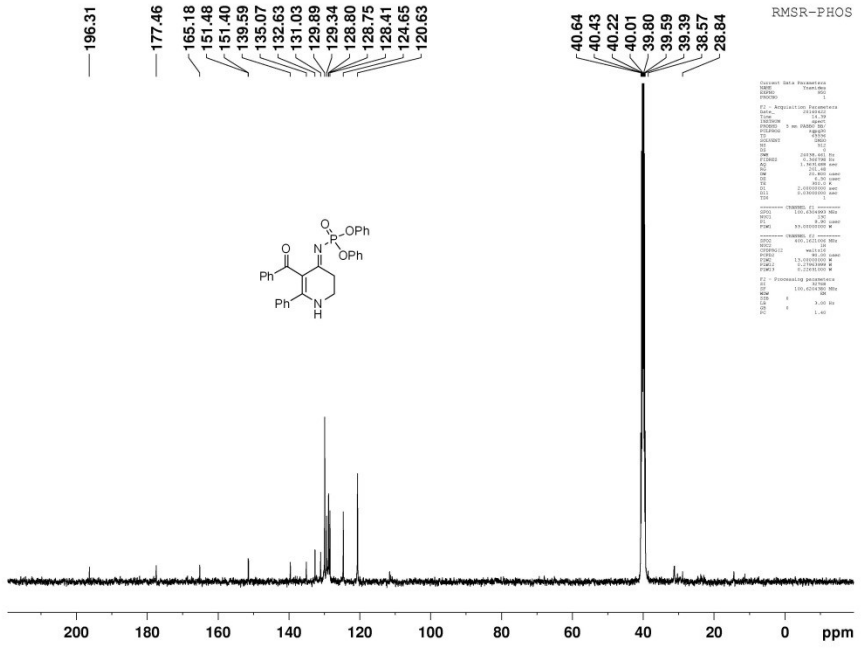


Fig. 76: ^{13}C NMR of 10

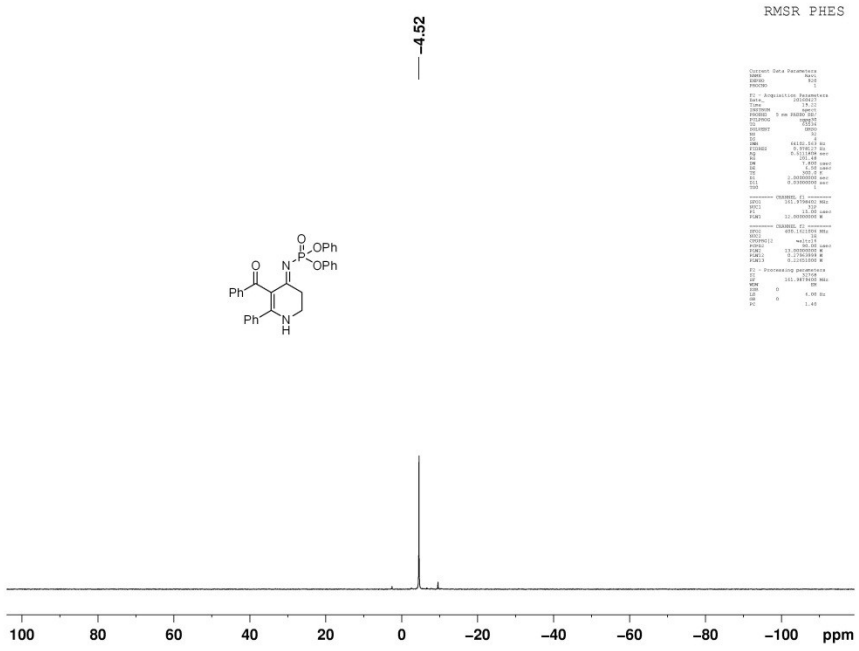


Fig. 77: ^{31}P NMR of 10