Palladium(II) *ortho*-cyano-aminothiophenolate (ocap) complexes

Electronic supplementary information

Experimental section

General methods, reagents and instrumentation

NMR spectra were recorded at room temperature on a Varian Unity 400 spectrometer using d^6-dmso as solvent, and referenced internally to residual solvent peaks or externally to $P(OMe)_3$ ($^{31}P\{^1H\}$). IR spectra were recorded on Shimadzu FT-IR 8400 spectrophotometer in the 400-4000 cm^{-1} range as KBr discs and in the 200-600 cm^{-1} as CsI discs Elemental analyses were carried out at Al Al-Bayt University, Jorden using a Euro vector EURO EA300 elemental analyser. Melting points measured on a Gallenkamp melting point apparatus and are uncorrected. Conductivity measurements were carried out on 10^{-3} molar solutions using a digital conductivity meter. Complexes **1a-b** were prepared as previously reported. [**1,2**].

Synthesis of 2a-b: These were prepared by two different procedures: (i) A solution of Na_2S (0.530 g, 6.80 mmol) in distilled water (5 ml) was added to a pale-yellow suspension of **1a** (2.368 g, 6.80 mmol) in EtOH (20 ml). The mixture was stirred at room temperature for 2 h. A black precipitate formed which was removed by filtration and to the yellow filtrate was added a suspension of $K_2[PdCl_4]$ (1.0 g, 3.40 mmol) in EtOH (5 ml). This mixture was heated at reflux for 2 h to afford a brown-red precipitate, which was collected by filtration, washed with distilled water and dried under vacuum (1.642 g, 95%). (ii) A solution of KOH (0.141 g, 2.52 mmol) in distilled water (5 ml) was added to a suspension of *trans*-$PdCl_2(abt)_2$ (**3a**) (0.30 g, 0.63 mmol) in EtOH (10 ml). The mixture was heated at reflux for 4 h to give a red-brown precipitate which was collected by filtration, washed with EtOH and dried under vacuum (0.113 g, 71%). Complex **2b** was prepared in a similar manner using route (i) and isolated as a brown solid (1.384, 78%). Characterising data for **2a:** Anal. Calc. for $C_7H_4PdN_2S$: C, 33.02; H, 1.58; N, 11.00. Found: C, 33.13; H, 1.96; N, 11.01%. IR (KBr): 3058m, 2158vs (CN), 1531s, 1467s, 1290m, 746m cm^{-1}. ^1H NMR (dmso-d^6): δ 7.01 (t, 1H, J 7.6), 7.23 (d, 1H, J 7.6), 7.40 (t, 1H, J 7.6), 7.67 (d, 1H, J 7.6). $^{13}C\{^1H\}$ NMR (dmso-d^6): 110.9 (CN), 120.8, 122.0, 123.7, 126.4, 131.9, 149.1 ppm. Melting point: 228 °C decomposes. Characterising data for **2b:** Anal.

Calc. for $C_8H_6PdN_2S$: C, 35.77; H, 2.25; N, 10.43C, 35.77; H, 2.25; N, 10.43. Found: C, 35.45; H, 2.11; N, 10.21 %. IR (KBr): 3022w, 2916w, 2158s (CN), 1517s, 1489s, 1280m, 804s cm^{-1}. ^1H NMR (dmso-d^6): δ 2.15 (s, 3H, CH_3), 6.87 (d, 1H, J 7.9), 7.06 (d, 1H, J 7.9), 7.29 (s, 1H). $^{13}C\{^1H\}$ NMR (dmso-d^6): 21.2, 113.9 (CN), 121.4, 126.8, 127.5, 130.2, 144.5, 161.7 ppm. Melting point: 300 ^oC decomposes.

Synthesis of 3a-b: Addition of abt (0.301g, 2.00 mmol) in EtOH (10 ml) to a solution of $K_2[PdCl_4]$ (0.326g, 1.00 mmol) in EtOH (10ml) immediately afforded a yellow precipitate. The mixture was heated at reflux for 2 h and then cooled to room temperature. The yellow precipitate was collected by filtration, washed with EtOH and dried under vacuum. Characterising data for **3a:** Yellow, 0.411g, 86%. Anal. Calc. for $C_{14}H_{12}Cl_2PdN_4S_2$: C, 35.20; H, 2.53; N, 11.73. Found: C, 35.33; H, 2.61; N, 11.97 %. IR (KBr): 3382s, 3284s (NH_2) 3058m, 1608s (CN), 1528s, 1343s, 782m, 372 (Pd-Cl) cm^{-1}. ^1H NMR (dmso-d^6): δ 7.08 (t, 2H, J 7.9), 7.24 (t, 2H, J 7.9), 7.38 (d, 2H, J 7.9), 7.53 (s, 4H, NH_2), 7.76 (d, 2H, J 8.0). Melting point: 272^oC decomposes. Characterising data for **3b:** Brown-yellow, 0.428g, 85%. Anal. Calc. for $C_{16}H_{16}Cl_2PdN_4S_2$: C, 37.99; H, 3.19; N, 11.08. Found: C, 38.17; H, 3.44; N, 11.34 %. IR (KBr): 3375s, 3288s (NH_2) 3028m, 2912w, 1610s (CN), 1533s, 1355s, 802m, 366 (Pd-Cl) cm^{-1}. ^1H NMR (dmso-d^6): δ 2.29 (s, 6H, CH_3), 6.99 (d, 2H, J 7.7), 7.19 (d, 2H, J 7.7), 7.28 (s, 4H, NH_2), 7.42 (s, 2H). $^{13}C\{^1H\}$ NMR (dmso-d^6): 21.2, 117.8, 122.3, 126.5, 128.2, 131.9, 143.9, 158.6 ppm. Melting point: 260 ^oC decomposes.

Synthesis of 4a-b: A solution of PPh_3 (0.164 g, 0.628 mmol) in $CHCl_3$ (10 ml) was added to a red suspension of **2a** (0.080 g, 0.314 mmol) in $CHCl_3$ (10 ml). The mixture was heated at reflux for 2 h. A red solution formed which was left to stand at room temperature, allowing solvent to evaporate to give dark red needle crystals which were collected by filtration and dried under vacuum. Characterising data for **4a:** Red-brown, 0.144 g, 84%. Anal. Calc. for $C_{50}H_{38}Pd_2P_2N_4S_2$: C, 58.09; H, 3.71, N, 5.42. Found: C, 57.85; H, 4.10; N, 5.50 %. IR (KBr) 3055w, 2169vs (CN), 1469s, 1434s, 1319m, 536s cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.03 (dd,1H, J 6.8, 1.6), 6.61 (dd, 2H, J 6.7, 1.6), 7.02 (dd, 1H, J 7.0, 1.5), 7.33-7.74 (m, 15H). $^{31}P\{^1H\}$ NMR: δ 31.6 (s) ppm. Melting point: 219-222 ^oC (decomposes). Characterising data for **4b:** Dark brown, 0.165 g, 73%. Anal. Calc. for $C_{52}H_{42}Pd_2P_2N_4S_2$: C, 58.82; H, 3.99; N, 5.28. Found: C, 58.69; H, 4.07; N, 5.43 %. IR (KBr) 3055w, 2958w, 2162s (CN), 1471s, 1436s, 494s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.38 (s, 3H, CH_3), 7.11-7.67 (m, 18H, Ph). $^{31}P\{^1H\}$ NMR: δ 29.2 (s) ppm. Melting point: 127-130 ^oC.

Synthesis of 5a-b: These complexes were prepared by two procedures as follows: (i) A solution of dppm (0.120 g, 0.314 mmol) in $CHCl_3$ (10 ml) was added to a red suspension of **2a** (0.080 g, 0.314 mmol) in $CHCl_3$ (10 ml). The mixture was stirred at room temperature for 2 h. The red solution formed was filtered and left for solvent to evaporate at room temperature to give orange lozenge crystals which were collected and dried under vacuum (0.142 g, 71%). (ii) A solution of Na_2S (0.111 g, 1.434 mmol) in distilled water (5 ml) was added to a pale-yellow suspension of **1a** (0.500 g, 1.434 mmol) in EtOH (10 ml). The mixture was stirred at room temperature for 2 h. The black precipitate of HgS formed was filtered off. The yellow filtrate was added to an orange suspension of $[Pd(dppm)_2]Cl_2$ (0.135 g, 1.434 mmol) in a mixture of EtOH (10 ml) and distilled water (5 ml). The resulting orange solution was refluxed for 2 h. The resulting dark orange precipitate was filtered off, dried under vacuum, and recrystallised from $CHCl_3$ to give orange lozenge crystals (0.595 g, 65%). Characterising data for **5a**: Orange, 0.142 g, 71%. Anal. Calc. for $C_{32}H_{26}PdP_2N_2S$: C, 60.15; H, 4.10; N, 4.38. Found: C, 60.36; H, 4.22; N, 4.61 %. IR (KBr) 3053w, 2904w, 2156vs (CN), 1465s, 1433s, 1278m, 1101m, 734s, 688s, 505m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.25 (s, 2H, CH_2), 6.78 (t, 1H, J 7.3), 6.99 (t, 1H, J 7.3), 7.13 (m, 2H), 7.26-7.93 (m, 20H). $^{31}P\{^1H\}$ NMR: δ -45.5 (d, J 99), -28.6 (d, J 99) ppm. Melting point: 130-133°C. Characterising data for **5b:** Dark brown, 0.162g, 81%. Anal. Calc. for $C_{33}H_{28}PdP_2N_2S$: C, 60.70; H, 4.32; N, 4.29. Found: C, 61.02; H, 4.50; N, 4.31 %. IR (KBr) 3055w, 2918w, 2154s (CN), 1469s, 1434s, 1184s, 690s, 501s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.40 (s, 3H, CH_3), 4.24 (s, 2H, CH_2), 7.11-7.86 (m, 23H, Ph). $^{31}P\{^1H\}$ NMR: δ -45.4 (d, J 52.0), 28.9 (d, J 52.0) ppm. Melting point: 142-145°C.

Synthesis of 6a-b: These complexes were prepared by two different procedures in a similar manner to those described for **5.** (i) A solution of dppe (0.125 g, 0.314 mmol) in $CHCl_3$ (10 ml) was added to a red suspension of **2a** (0.080 g, 0.314 mmol) in $CHCl_3$ (10 ml). The mixture was stirred at room temperature for 2 h. The red solution formed was filtered and left to evaporate at room temperature to give red lozenge crystals, which were collected and dried under vacuum to give **6a** (0.187g, 91%). (ii) A pale yellow suspension of **1a** (0.071 g, 0.205 mmol) in EtOH (10 ml) was added to a red suspension of $[Pd(\kappa^2\text{-dppe})_2]Cl_2$ (0.200 g, 0.205 mmol) in EtOH (10 ml). The mixture was stirred at room temperature for 3 h. The red solution formed was filtered and the solvent left to evaporate at room temperature to give red lozenge crystals of **6a** (0.124 g, 93%). Characterising data for **6a:** Red, 0.124 g, 93%. Anal. Calc. for $C_{33}H_{28}PdN_2P_2S$: C, 60.70, H, 4.32, N, 4.29. Found: C, 61.00; H, 4.45; N, 4.32 %. IR (KBr)

3051w, 2918w, 2158s (CN), 1527s, 1434s, 1101m, 750m, 692s, 532s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.82 (s, 4H, CH_2), 7.14 (t,1H, J 7.6), 7.33 (d, 1H, J 7.6), 7.45-7.92 (m, 22H, Ph) $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 55.9 (d, J 29.6), 64.1 (d, J 29.6) ppm. Melting point: 146-149 ^{o}C decomposes. Characterising data for **6b:** Brown, 0.120 g, 90%. Anal. Calc. for $C_{34}H_{30}PdN_2P_2S$: C, 61.22; H, 4.53; N, 4.20. Found: C, 61.38; H, 4.58; N, 4.23 %. IR (KBr) 3053w, 2918w, 2156vs (CN), 1471s, 1436s, 1172s, 1103s, 729s, 690s, 501s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 4H, CH_2), 2.52 (s, 3H, CH_3), 7.00-7.90 (m, 23H, Ph). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 53.4 (d, J 29), 60.0 (d, J 29) ppm. Melting point: 117-120 ^{o}C.

Synthesis of 7a-b: Prepared and isolated in a similar procedure as that described for **6a** synthesis (i). Characterising data for **7a:** Red, 0.445 g, 71%. Anal. Calc. for $C_{34}H_{30}PdN_2P_2S$: C, 61.22; H, 4.53, N, 4.20. Found: C, 61.38; H, 4.61; N, 4.45 %. IR (KBr) 3051w, 2921w, 2156vs (CN), 1465m, 1433s,1285s, 1101s, 744s, 690s, 509s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.27-1.33 (m, 4H, $2CH_2$), 1.37-1.43 (m, 2H, CH_2), 6.72 (t, 1H, J 7.4), 6.81 (t, 1H J 7.4), 6.91 (d, 1H, J 7.4), 7.01 (d, 1H, J 7.4), 7.28-7.48 (m, 20H, Ph). $^{31}P\{^{1}H\}$ NMR: 1.1 (d, J 52.6), 12.9 (d, J 52.6) ppm. Melting point: 156-159 ^{o}C decomposes. Characterising data for **7b:** Brown, 0.489 g,78%. Anal. Calc.for $C_{35}H_{32}PdN_2P_2S$: C, 61.72, H, 4.74, N, 4.11. Found: C, 61.84; H, 4.82; N, 4.37 %. IR (KBr) 3053w, 2912w, 2154vs (CN), 1481s, 1434s, 1182m, 1099s, 742m, 692s, 509s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.83 (bs, 2H, CH_2), 2.18 (bs, 4H, CH_2), 2.39 (s, 3H, CH_3), 7.04-7.90 (m, 23H, Ph). $^{31}P\{^{1}H\}$ NMR: 1.3 (d, J 52.6), 13.1 (d, J 52.6) ppm. Melting point: 158-161 ^{o}C.

Synthesis of 8a-b: Prepared and isolated in a similar procedure as that described for **6a** synthesis (i). Characterising data for **9a:** Red, 0.142 g, 85%. Anal. Calc. for $C_{35}H_{32}PdN_2P_2S$: C, 61.72; H, 4.74, N, 4.11. Found: C, 61.75; H, 5.15; N, 4.22 %. IR (KBr) 3053w, 2927w, 2156vs (CN), 1536m, 1434s, 1182s, 1099s, 746s, 692s, 509m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.74 (bs, 4H, $2CH_2$), 2.22 (bs, 4H, $2CH_2$), 6.66 (t, 1H, J 7.3), 6.86 (t, 1H, J 7.4), 7.10 (d, 1H, J 7.4), 7.15 (d, 1H, J 7.4), 7.32-7.89 (m, 20H, Ph). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 9.1 (d, J 44.5), 37.4 (d, J 44.5) ppm. Melting point: 159-162 ^{o}C decomposes. Characterising data for **9b:** Brown, 0.182 g, 83%. Anal. Calc.for $C_{36}H_{34}PdN_2P_2S$: C, 62.20; H, 4.93; N, 4.03 Found: C, 62.44; H, 5.19; N, 4.18 %. IR (KBr) 3053w, 2912w, 2154m (CN), 1481s, 1434s, 1182m, 1099s, 742s, 692s, 509s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.73 (bs, 4H, $2CH_2$), 2.27 (bs, 4H, $2CH_2$), 2.39 (s, 3H, CH_3), 6.89-7.86 (m, 23H, Ph). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 9.3 (d, J 43.7), 36.9 (d, J 43.7) ppm Melting point: 169-172 ^{o}C.

Synthesis of 9a-b: A solution of 2,2'-bipy (0.061 g, 0.393 mmol) in $CHCl_3$ (10 ml) was added to a suspension of **2a** (0.100 g, 0.393 mmol) in $CHCl_3$ (10 ml) and the resulting dark brown solution was refluxed for 4 h and then filtered and left for solvent to evaporate at room temperature to give a red-brown solid which was filtered off and dried under vacuum (0.130 g, 81%). Characterising data for **9a**: Yellow solid, 0.130 g, 81%. Anal. Calc. for $C_{17}H_{12}PdN_4S$: C, 49.71; H, 2.94; N, 13.64. Found: C, 49.57; H, 2.74; N, 13.67%. IR (KBr): 3066w, 2160s (CN), 1572m, 1562m, 1450s, 753s cm^{-1}. ^1H NMR (dmso-d^6): δ 6.38 (dt, 1H, J 7.7, 1.6), 6.45 (d, 1H, J 7.6), 6.90-6.94 (m, 2H), 7.14 (dt, 2H, J 8.0, 1.9), 8.52 (d, 2H, J 7.1), 8.81 (d, 2H, J 8.0). Melting point: 158-161 ^oC. Characterising data for **9b**: Dark brown solid, 0.236 g, 61%. Anal. Calc. for $C_{18}H_{14}PdN_4S$: C, 50.89; H, 3.32; N, 13.19. Found: C, 51.07; H, 3.62; N, 13.51 %. IR (KBr): 3051w, 2915, 2154s (CN), 1608s, 1572s, 1460s, 1280s, 1181m, 804m, 740s cm^{-1}. ^1H NMR (dmso-d^6): δ 2.40 (s, 3H, CH_3), 6.99 (d, 1H, J 7.8), 7.13-7.33 (m, 3H), 7.38 (s, 1H), 7.80-7.84 (m, 2H), 8.91 (m, 2H, J 7.8), 8.89 (d, 2H, J 7.8): Melting point: 214-217 ^oC.

Synthesis of 10a-b: A solution of 1,10-phen (0.071 g, 0.393 mmol) in $CHCl_3$ (10 ml) was added to a red suspension of **2a** (0.100 g, 0.393 mmol) in $CHCl_3$ (10 ml). The dark brown solution was refluxed for 4 h, then filtered and left to evaporate at room temperature to give a red-brown solid which was filtered off and dried under vacuum. Characterising data for **10a**: Red-brown, 0.194 g, 76%. Anal. Calc. for $C_{19}H_{12}PdN_4S$: C, 52.48; H, 2.78, N, 12.89. Found: C, 52.36; H, 2.98; N, 12.65 %. IR (KBr) 3062w, 2158vs (CN), 1583m, 1502vs, 1450s, 1288m, 1161m, 846s, 736s, 680s, 521m cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.28 (t, 1H, J 8.0), 7.34 (d, 1H, J 7.6), 6.62 (dd, 1H, J 7.8, 1.4), 7.14 (dt, 2H, J 7.6, 1.4), 7.91(s, 2H), 8.41 (dd, 2H, J 7.8, 1.4), 9.03 (dd, 2H, J 7.6,1.4). Melting point: 210-214 ^oC. **10b**: Dark brown, 0.167 g, 76%. Anal. Calc. for $C_{20}H_{14}PdN_4S$: C, 53.52; H, 3.14; N, 12.48. Found: C, 53.23; H, 3.36; N, 12.59 %. IR (KBr): 3058w, 2923w, 2160s (CN), 1597m, 1452s, 752m cm^{-1}. ^1H NMR (dmso-d^6): δ 2.39 (s, 3H, CH_3), 7.08 (d, 1H, J 7.4), 7.13 (d, 1H, J 7.4), 7.32 (dd, 2H, J 7.5, 1.3), 7.43 (s, 1H), 7.67 (dd, 2H, J 8.0, 2.1), 8.12 (d, 2H, J 8.0), 8.43 (d, 2H, J 8.0). Melting point: 220-224 ^oC.

Synthesis of 11: A solution of 1,10-phenanthrolien (phen) (0.038 g, 0.196 mmol) in $CHCl_3$ (10 ml) was added to a red suspension of **2a** (0.050 g, 0.196 mmol) in $CHCl_3$ (10 ml). The mixture was stirred for 1 h and after this time solid $HgCl_2(\kappa^2$-phen) (0.092 g, 0.196 mmol) was added. The resulted mixture was stirred for 2 h and refluxed for a further 2 h. The red-brown solid

produced was collected by filtration and dried under vacuum. Slow evaporation of the filtrate gave a small number of red-brown cubic crystals. Characterising data for **11:** Red-brown, 0.123 g, 71%. Anal. Calc. for $C_{34}H_{23}Cl_{11}PdHgN_6S$: C, 32.81; H, 1.86, N, 6.75. Found: C, 32.72; H, 2.09; N, 6.97 %. IR (KBr) 3055w, 2156vs (CN), 1618m, 1562m, 1469s, 1421m, 1280m, 852s, 738m, 622m, 540m cm^{-1}. Melting point: >300^{o}C (decomposes). The poor solubility of **11** in all common solvents has meant that we have been unable to record NMR data.

Crystal structure determinations: Crystals of **4a**, **5a** and **11**.3$CHCl_3$ were mounted on glass fibers and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer with graphite-monochromater Mo-Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data collection, indexing and initial cell refinements were done using SMART software. Data reduction was carried out with SAINT PLUS and absorption corrections applied using the programme, SADABS [**3**] All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package [**4**]. Crystals of **6a** were mounted on a glass fiber and all geometric and intensity data were taken from this sample using a SuperNova Dual diffractometer with Mo-Kα radiation (λ = 0.7103 Å) at 150 ± 2 K. Data collection, indexing and initial cell refinements were done using OLEX2 software [**5**] and the structure was solved with the SHELXS [**6**] structure solution program using Direct Methods and refined with the SHELXL [**6**] refinement package using Least Squares minimisation. Crystals of **7b** were mounted on a glass fiber and all geometric and intensity data were taken from this sample using a STOE-IPDS diffractometer with Mo-Kα radiation (λ = 0.7103 Å, graphite monochromator) at 200 ± 2 K. Absorption corrections were made using the IPDS software package [**7**]. All structures were solved by direct methods and refined using full-matrix least-square routines against F^2 with SHELXL-97 [**8**]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models by calculating the positions (riding model) and refined with calculated isotropic displacement parameters. Illustrations were generated using DIAMOND 3.0 [**9**]. A summary of crystallographic and refinement parameters is given below in Table S1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 2114233 (**4a**), 2114230 (**5a**), 2201775 (**6a**), 2181464 (**7b**) 2114234 (**11**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road,

Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

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IR and NMR spectra

Fig. SI 1.IR spectrum of 2a

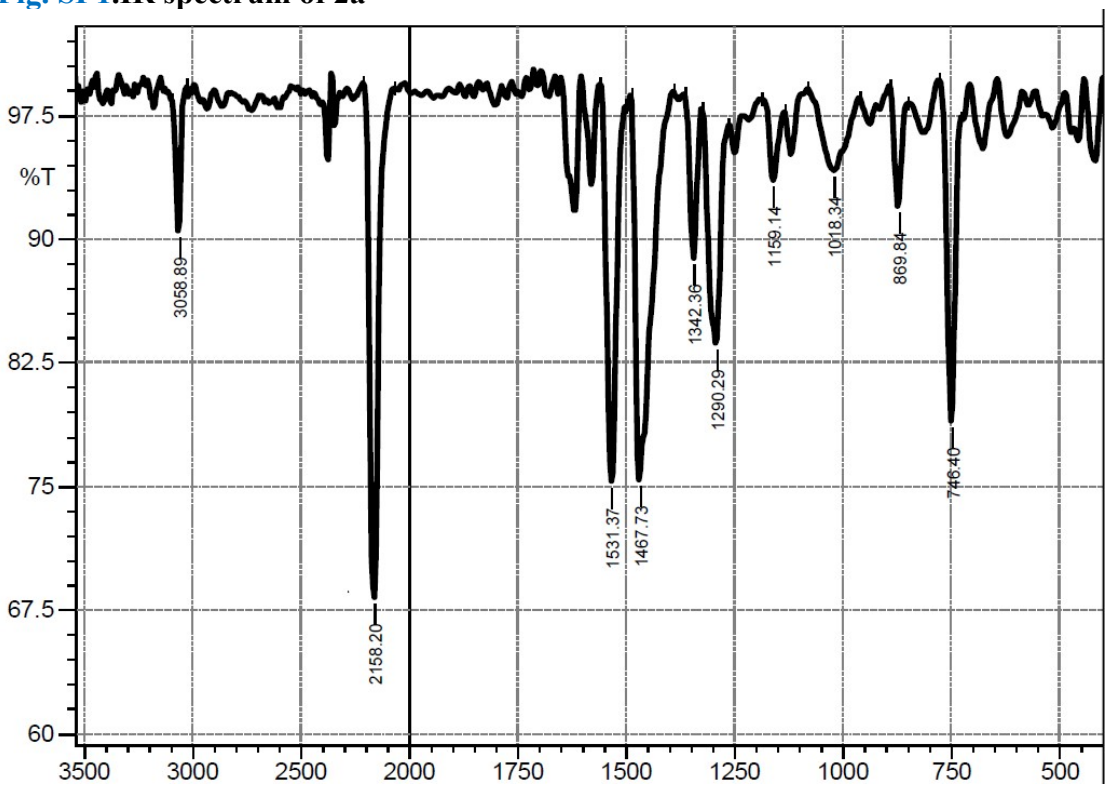


Fig. SI 2. ^{1}H NMR spectrum of 2a

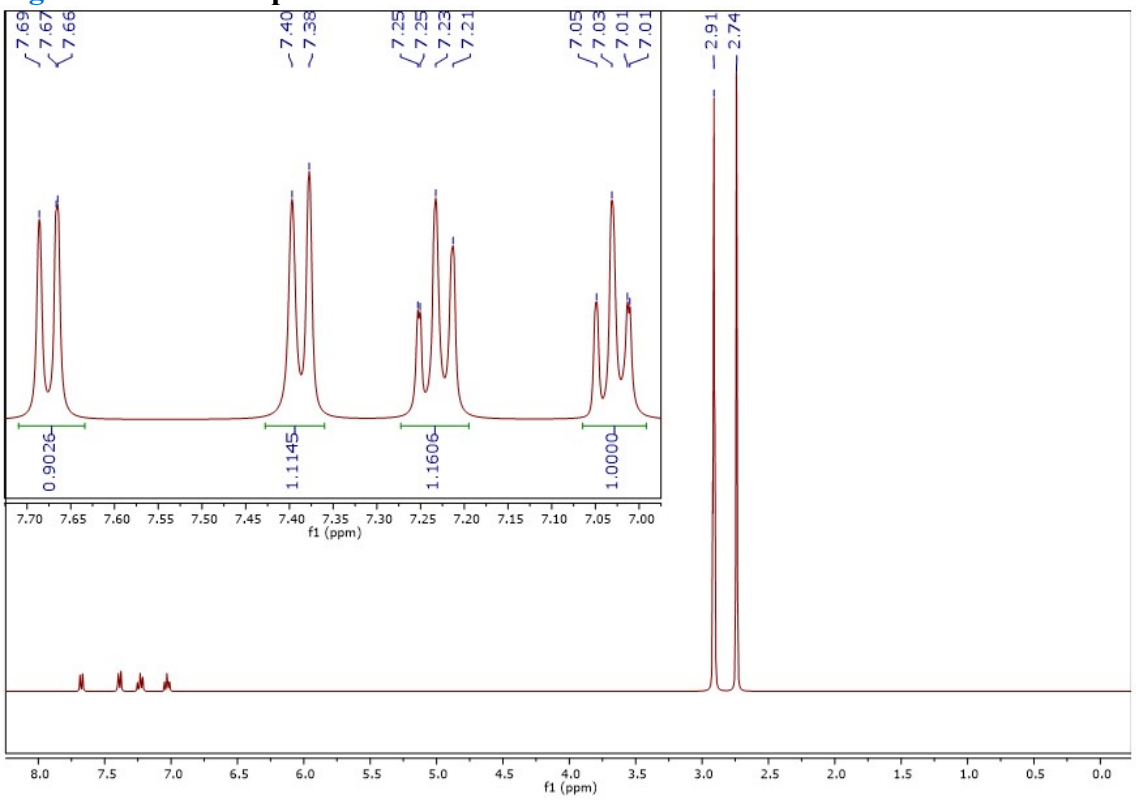


Fig. SI 3. ^{13}C{^{1}H} NMR spectrum of 2a

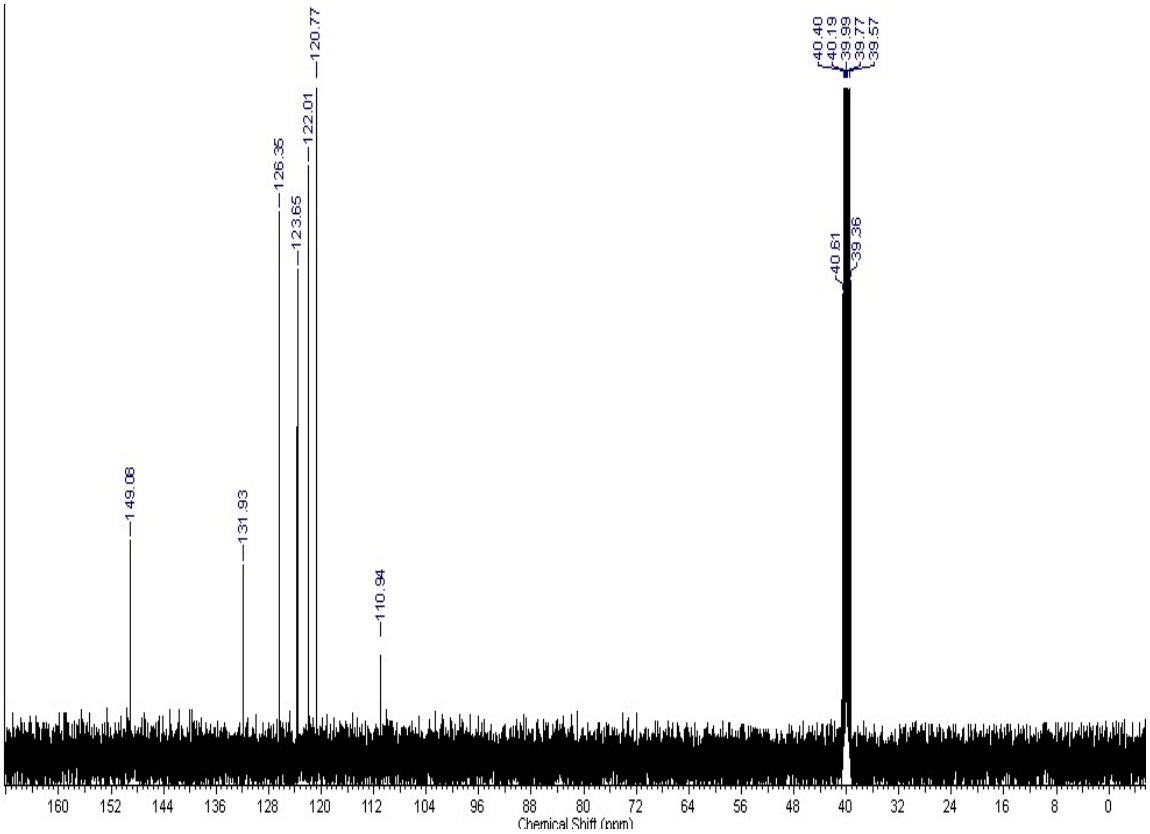


Fig. SI 4.IR spectrum of 2b

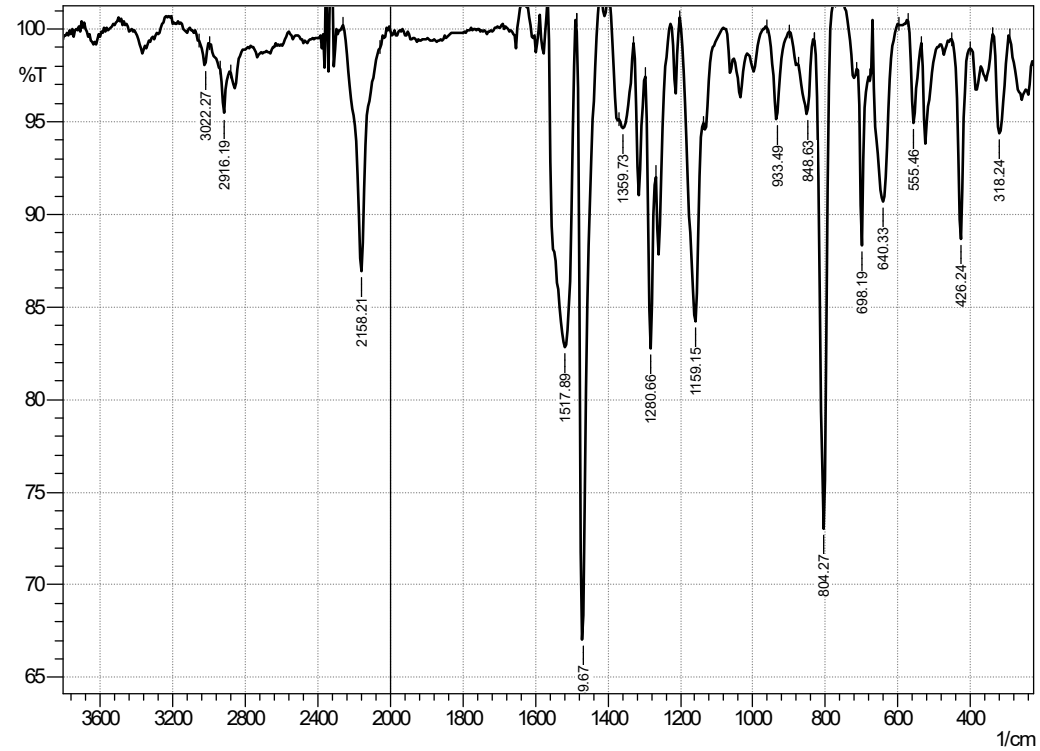
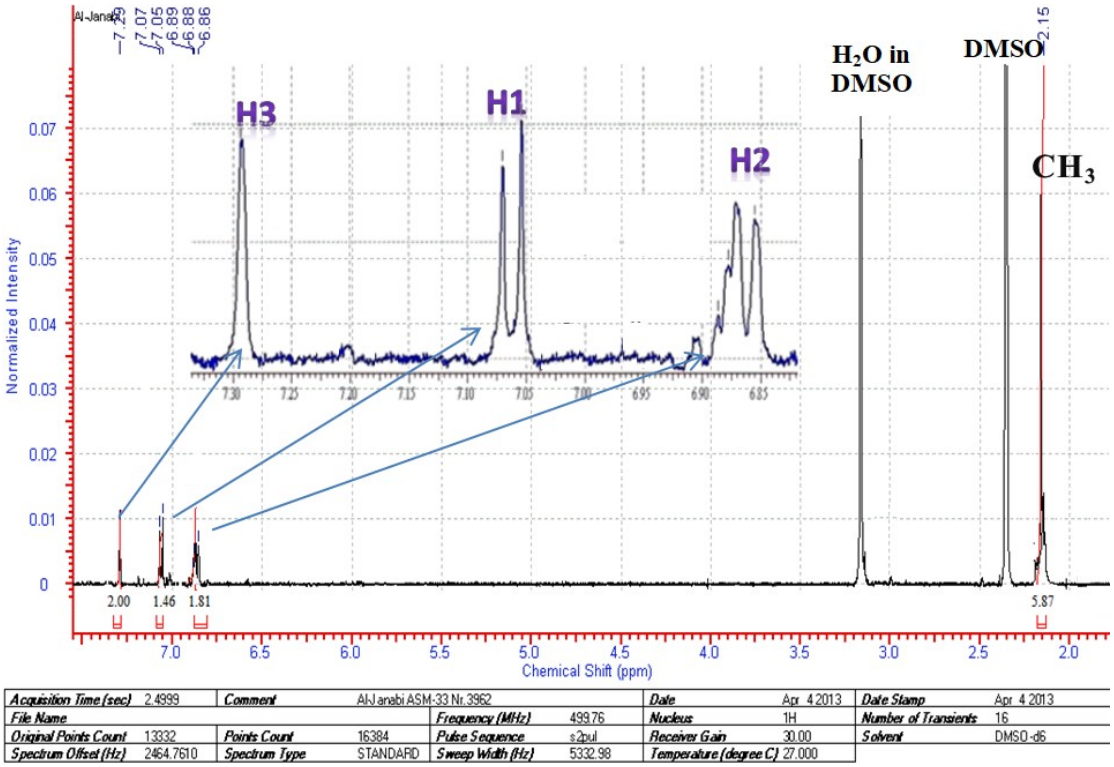


Fig. SI 5. ^{1}H NMR spectrum of 2b



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File Name				*Frequency (MHz)*	499.76	*Nucleus*	1H	*Number of Transients*	16
Original Points Count	13332	*Points Count*	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	DMSO-d6
Spectrum Offset (Hz)	2464.7610	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	5332.98	*Temperature (degree C)*	27.000		

Fig. SI 6. $^{13}C\{^{1}H)$ NMR spectrum of 2a

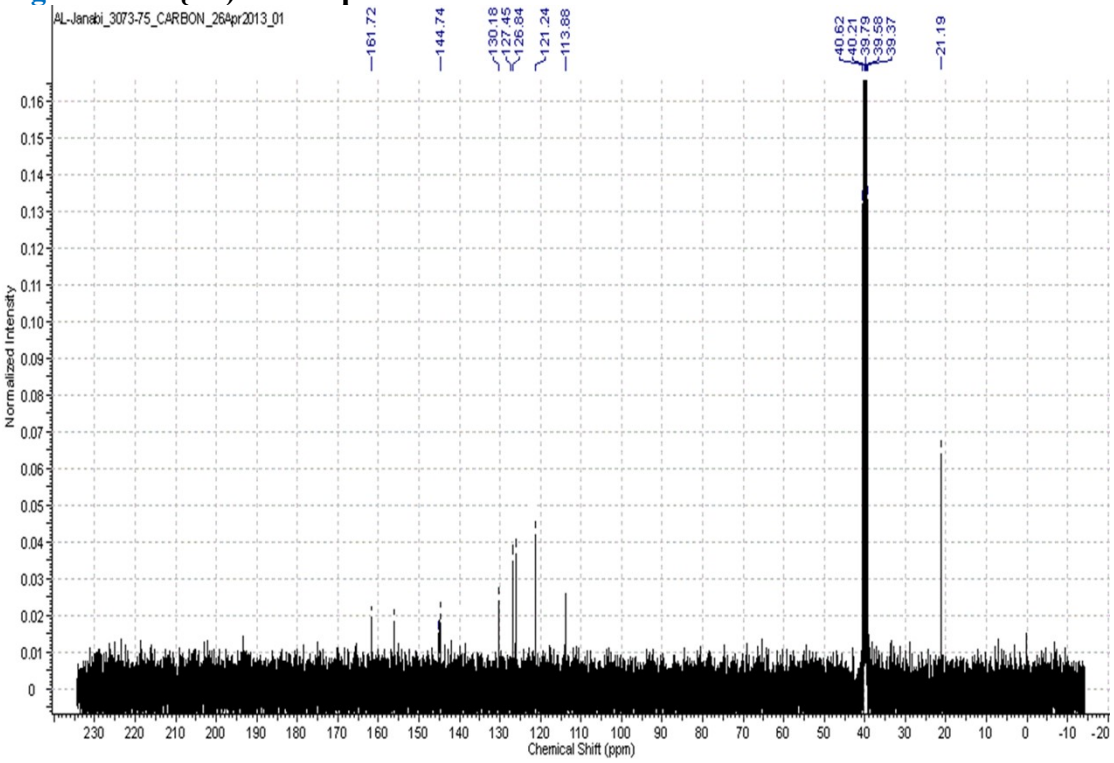


Fig. SI 7.IR spectrum of 3b

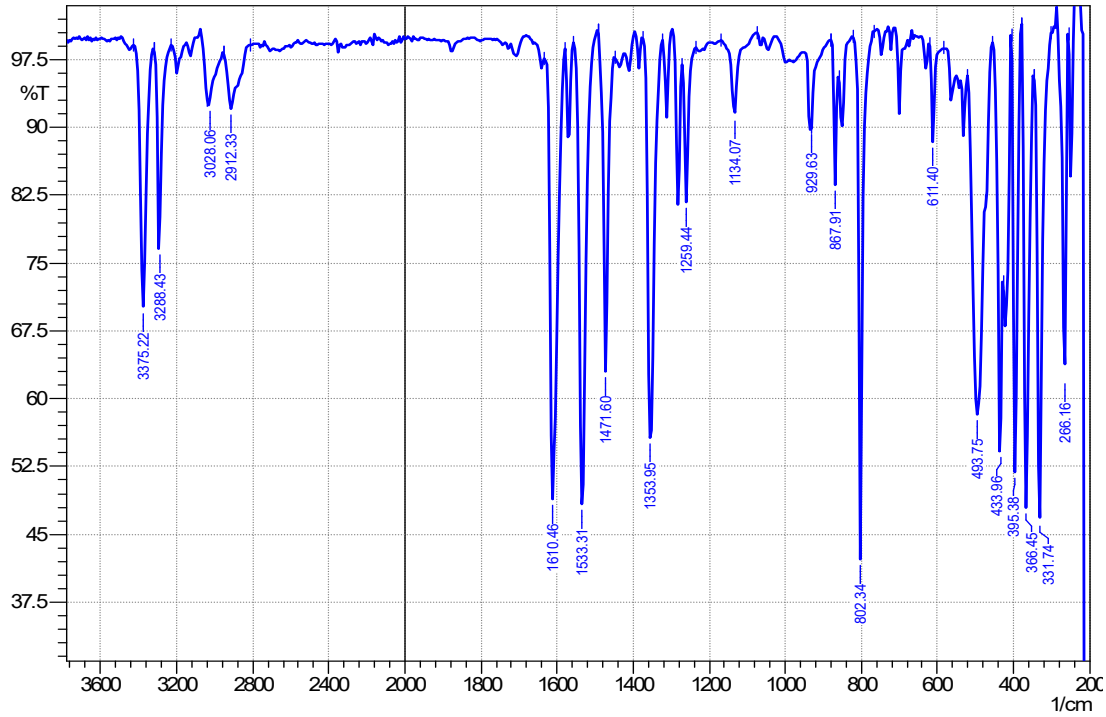
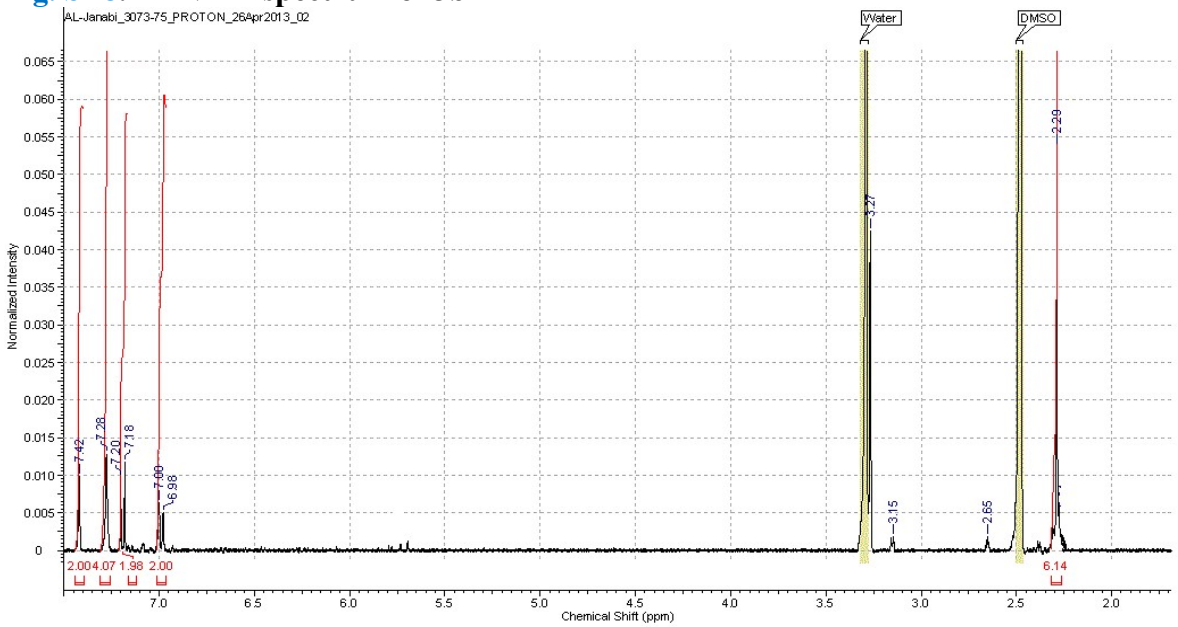


Fig. SI 8. ^{1}H NMR spectrum of 3b



Acquisition Time (sec)	5.1119	*Comment*	AL-Janabi 3073-75 ASM148			*Date*	Apr 26 2013
Date Stamp	Apr 26 2013	*File Name*	E:\اطياف الرنين المغناطيسي\data\04_2013\AL-Janabi_3073-75\AL-Janabi_3073-75_PROTON_26Apr2013_02.fid\fid				
Frequency (MHz)	399.96	*Nucleus*	1H	*Number of Transients*	16	*Original Points Count*	16136
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	46.00	*Solvent*	DMSO-d6
Spectrum Offset (Hz)	1940.6350	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	3156.57	*Temperature (degree C)*	27.000

Fig. SI 9.IR spectrum of 4a

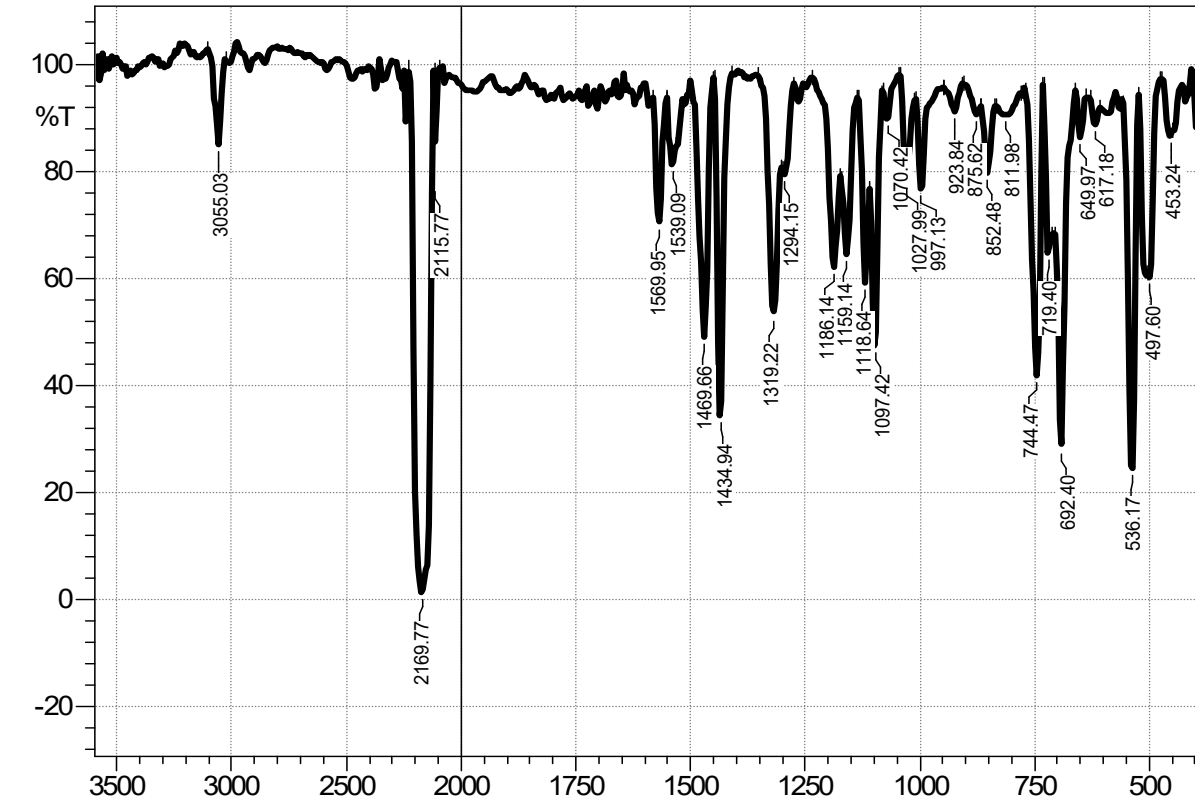


Fig. SI 10. $^{31}P\{^{1}H\}$ NMR spectrum of 4a

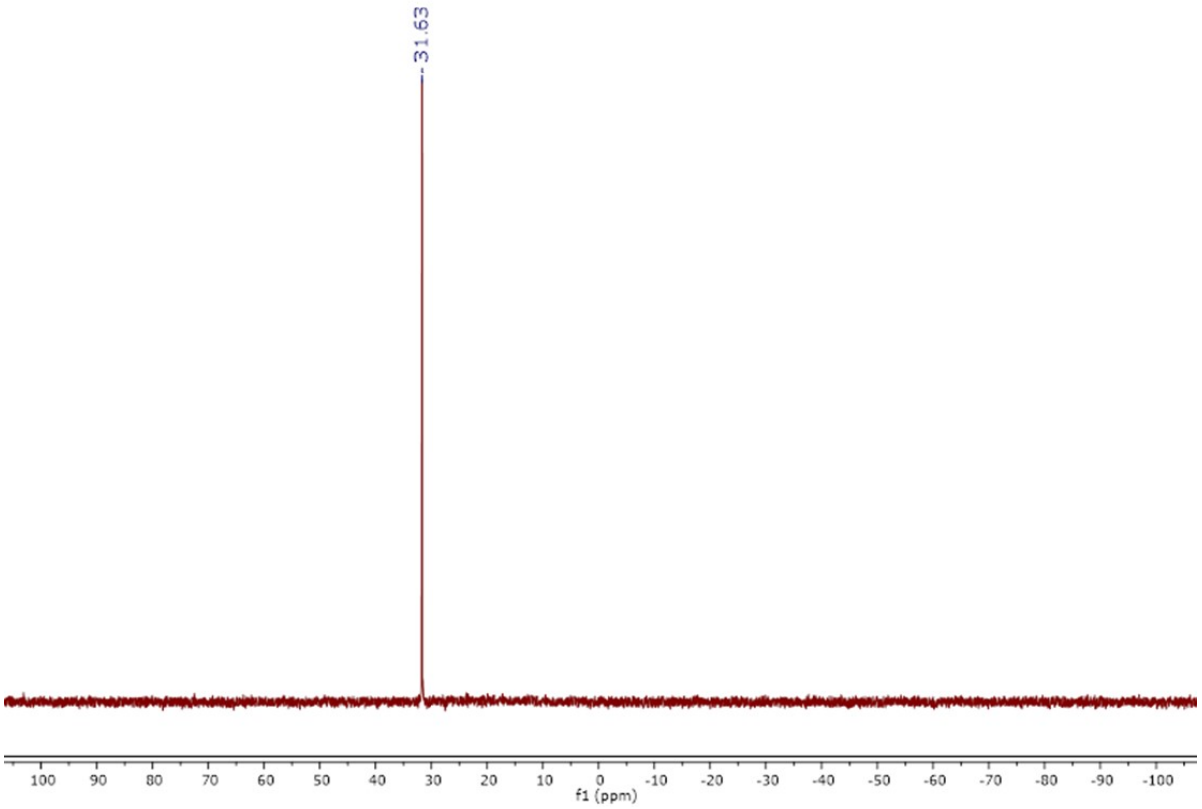


Fig. SI 11. ^{1}H NMR spectrum of 4a

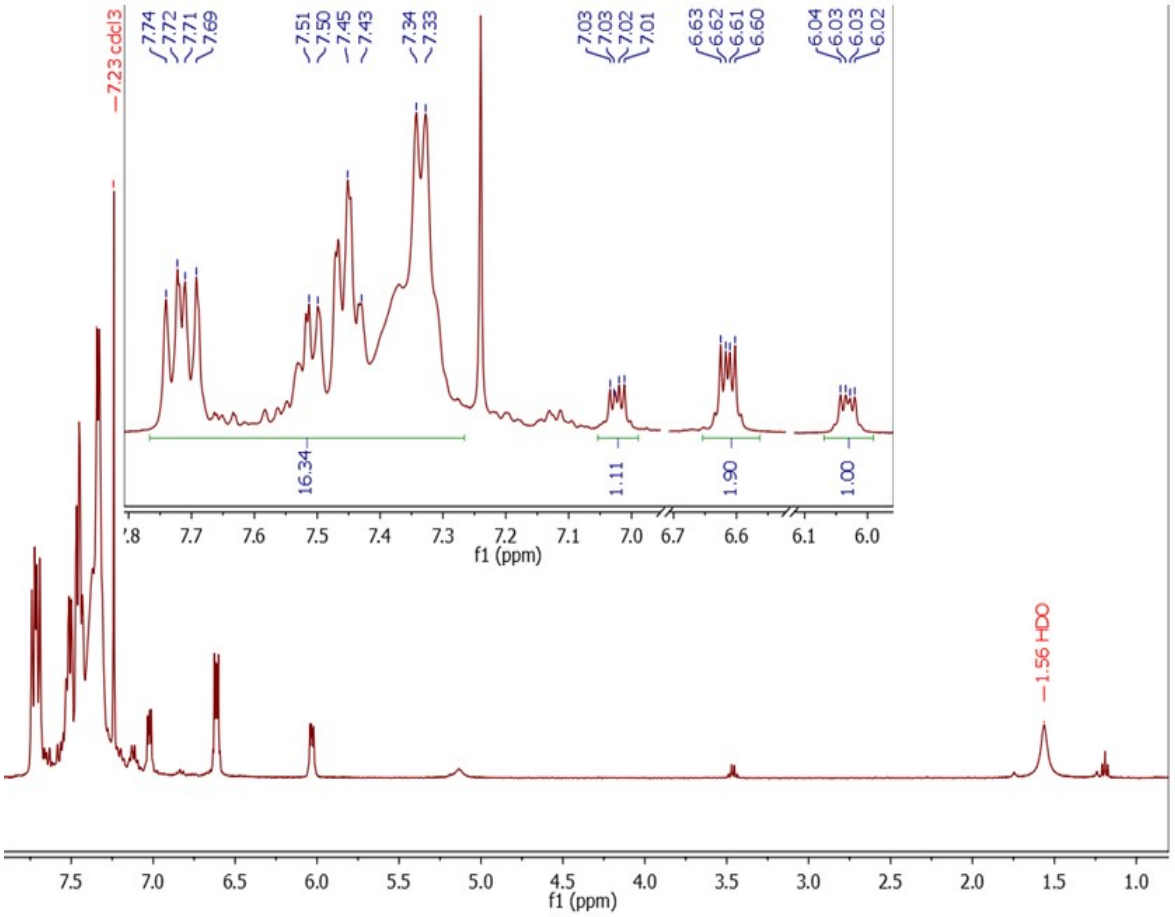


Fig. SI 12.IR spectrum of 4b

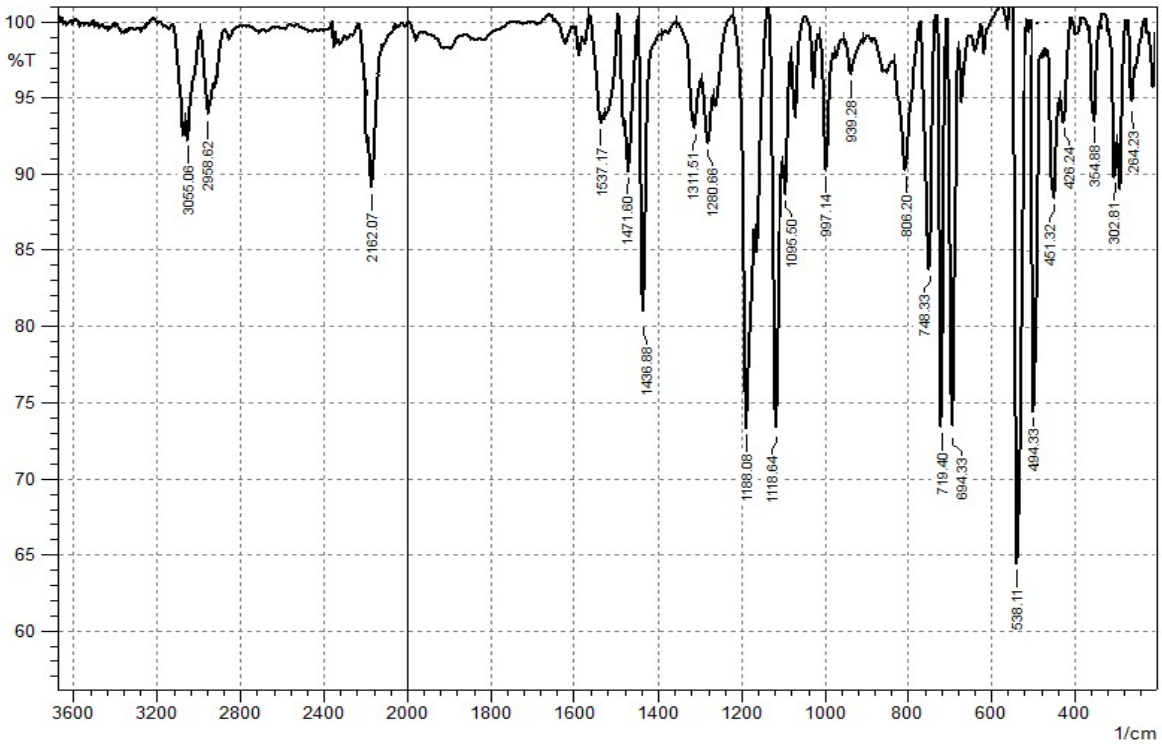


Fig. SI 13. $^{31}P\{^{1}H\}$ NMR spectrum of 4b

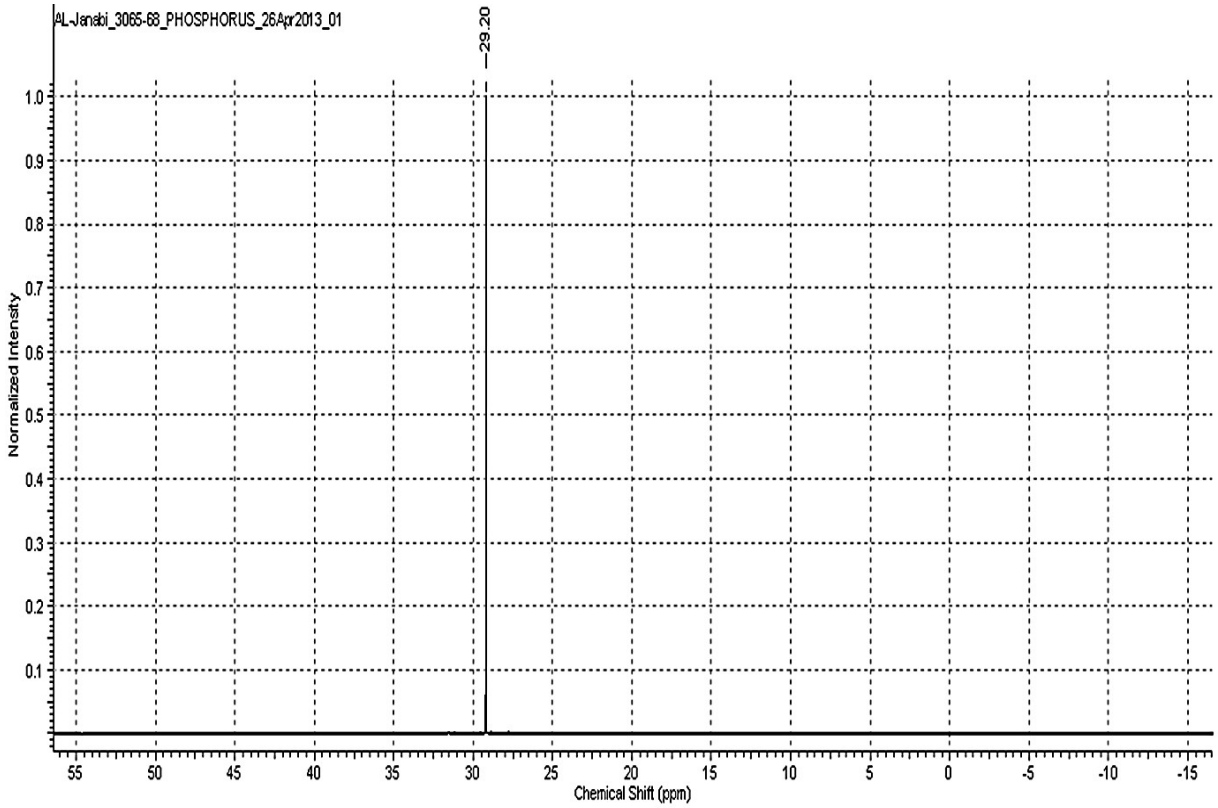


Fig. SI 14. ^{1}H NMR spectrum of 4b

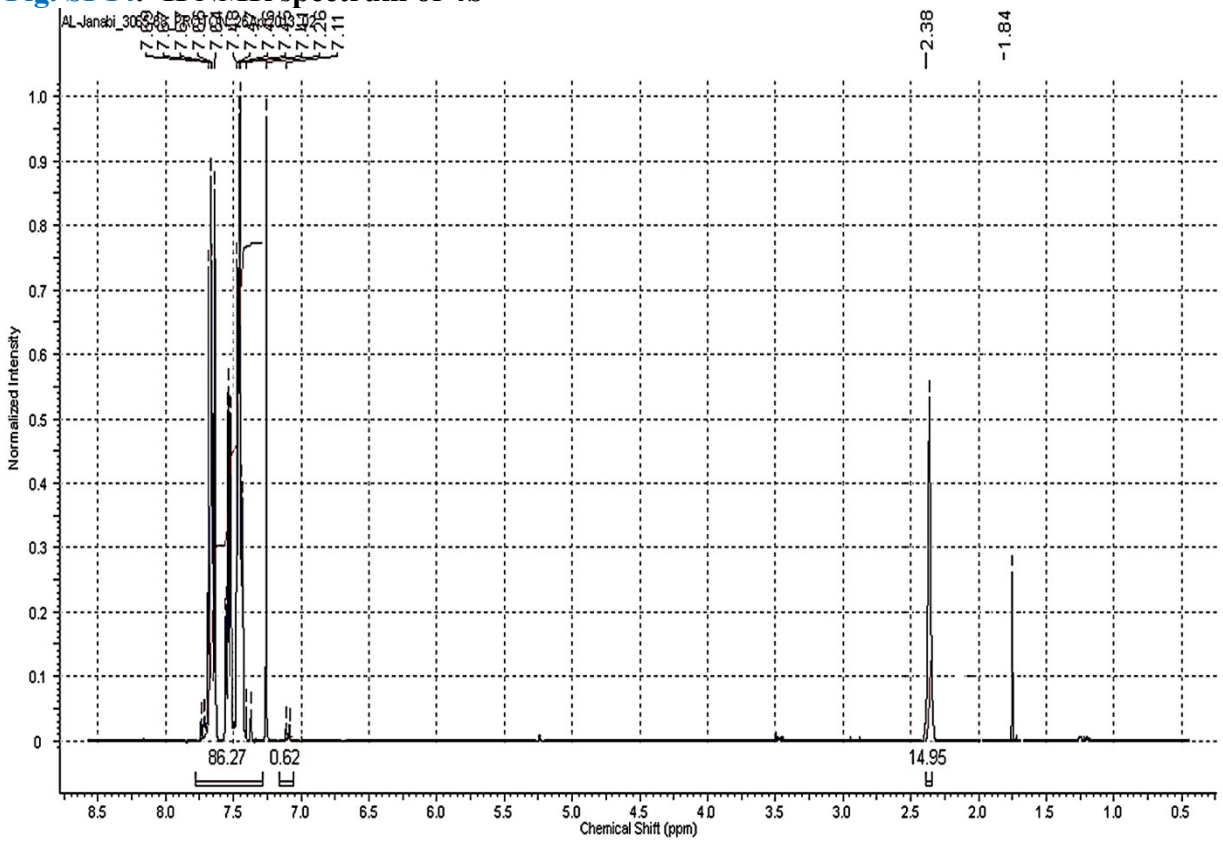


Fig. SI 15.IR spectrum of 5a

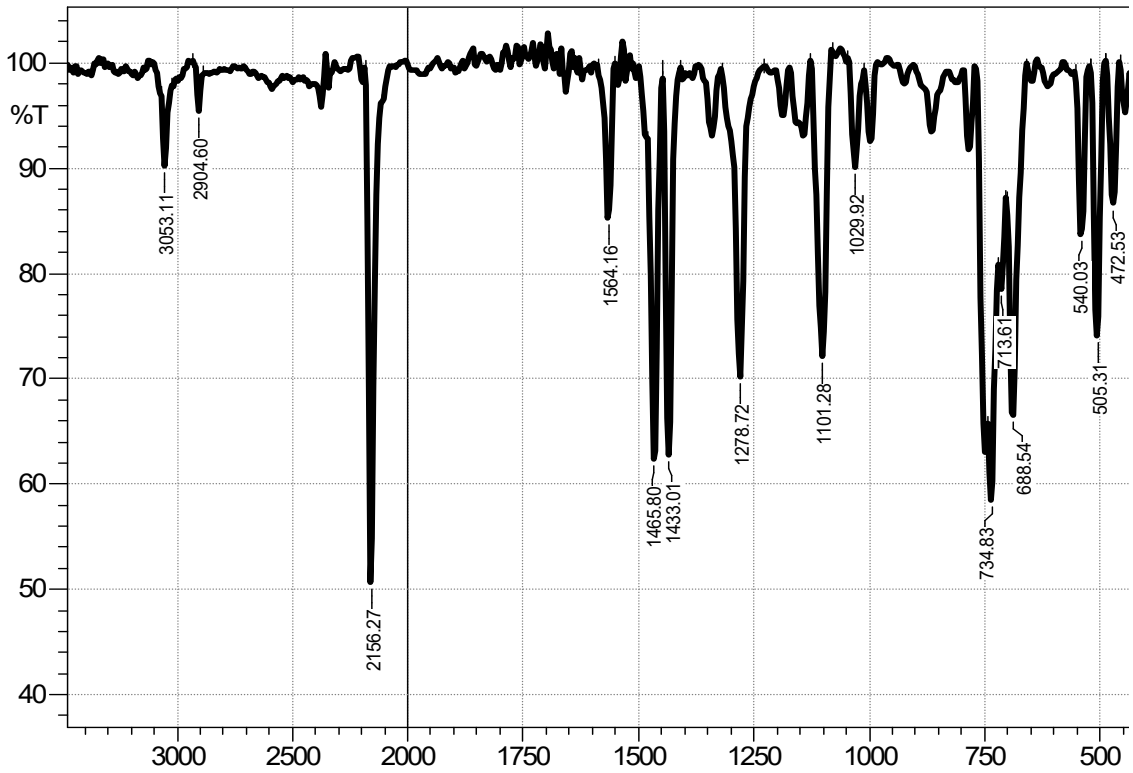


Fig. SI 16. $^{31}P\{^{1}H\}$ NMR spectrum of 5a

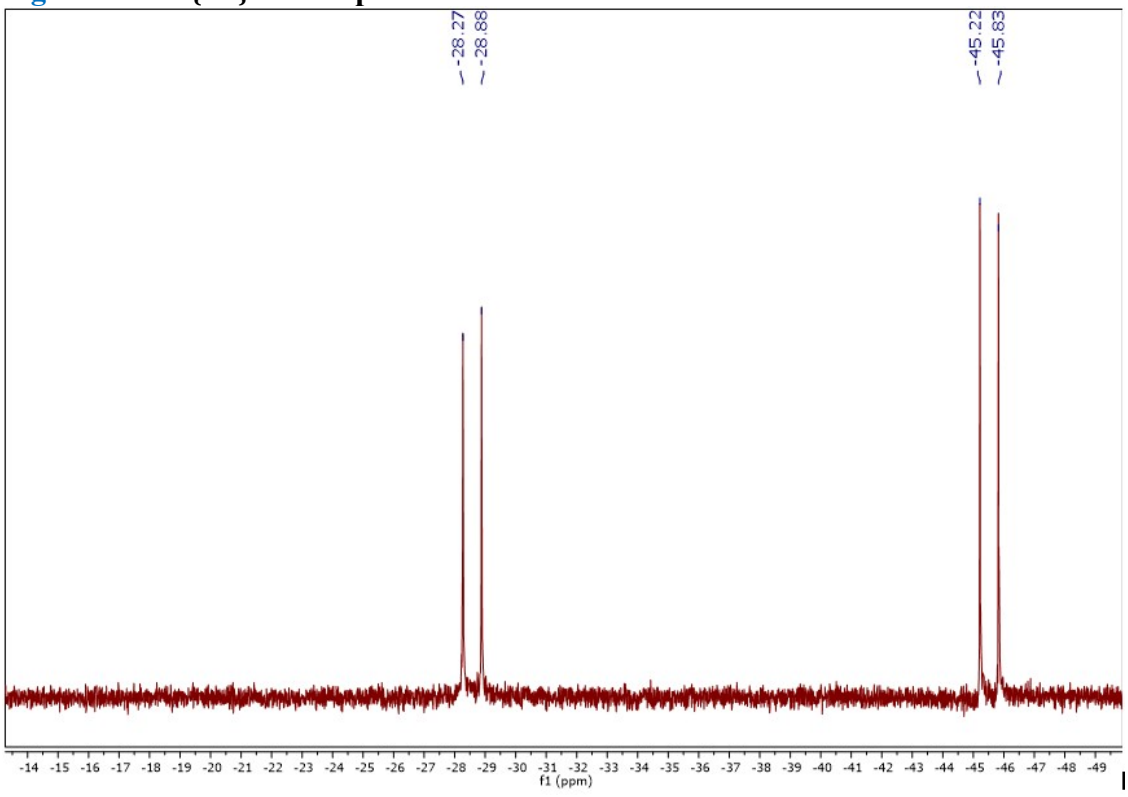


Fig. SI 17. ^{1}H NMR spectrum of 5a

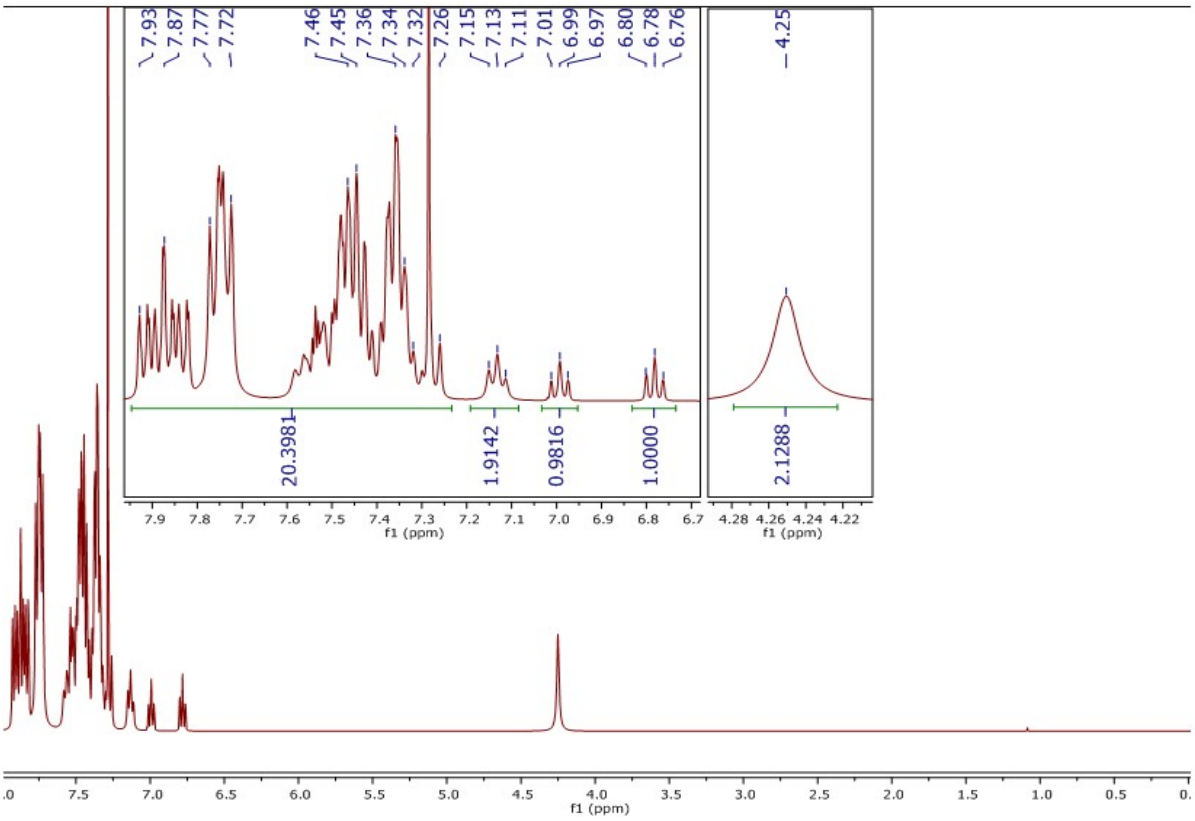


Fig. SI 18.IR spectrum of 5b

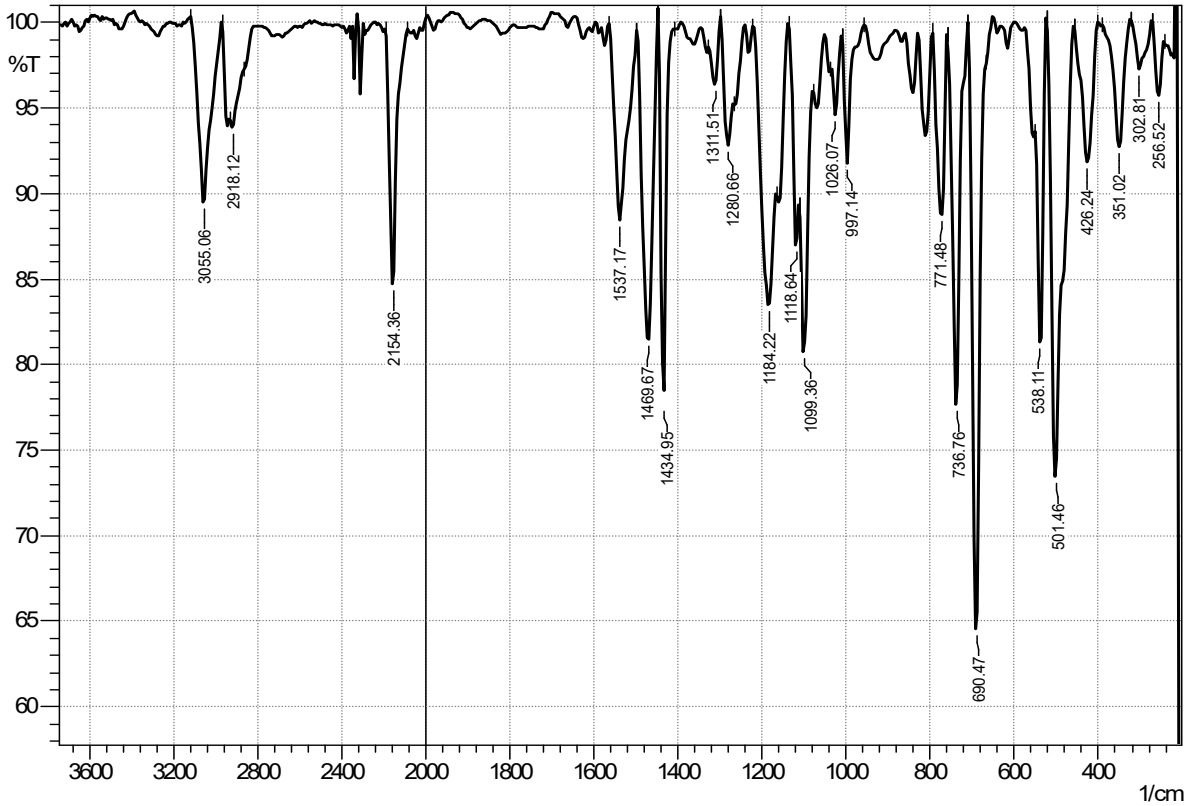


Fig. SI 19. $^{31}P\{^{1}H\}$ NMR spectrum of 5b

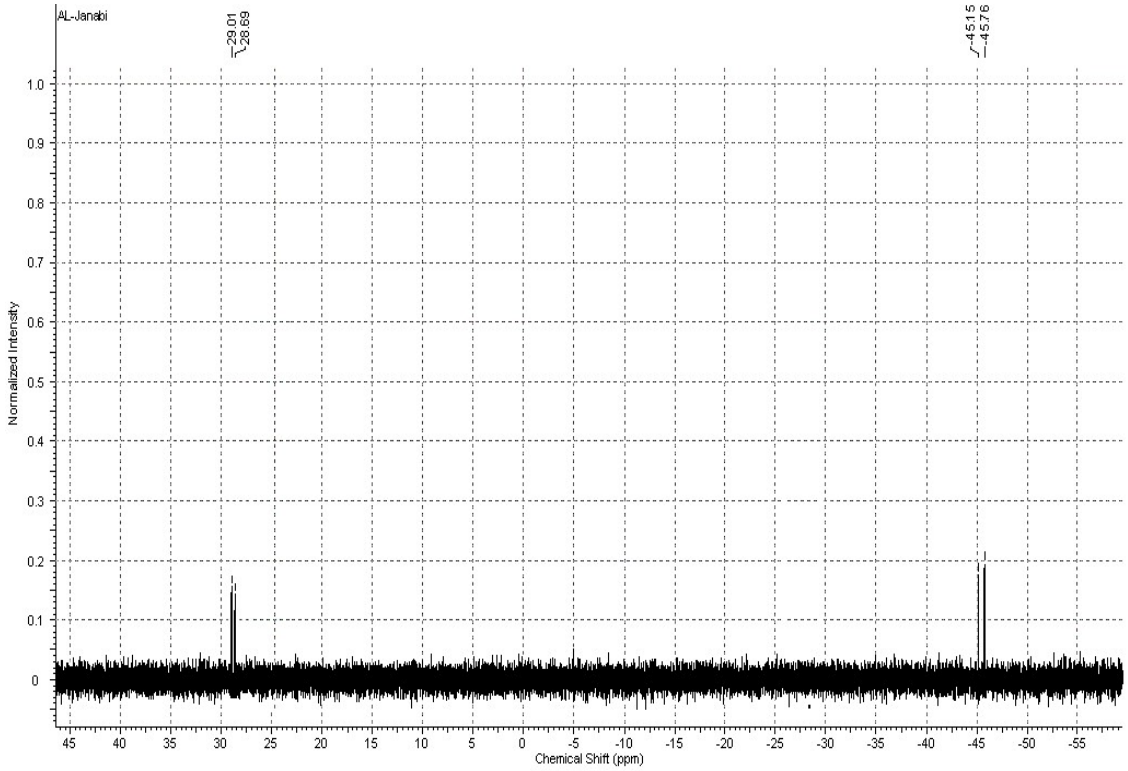


Fig. SI 20. ^{1}H NMR spectrum of 5b

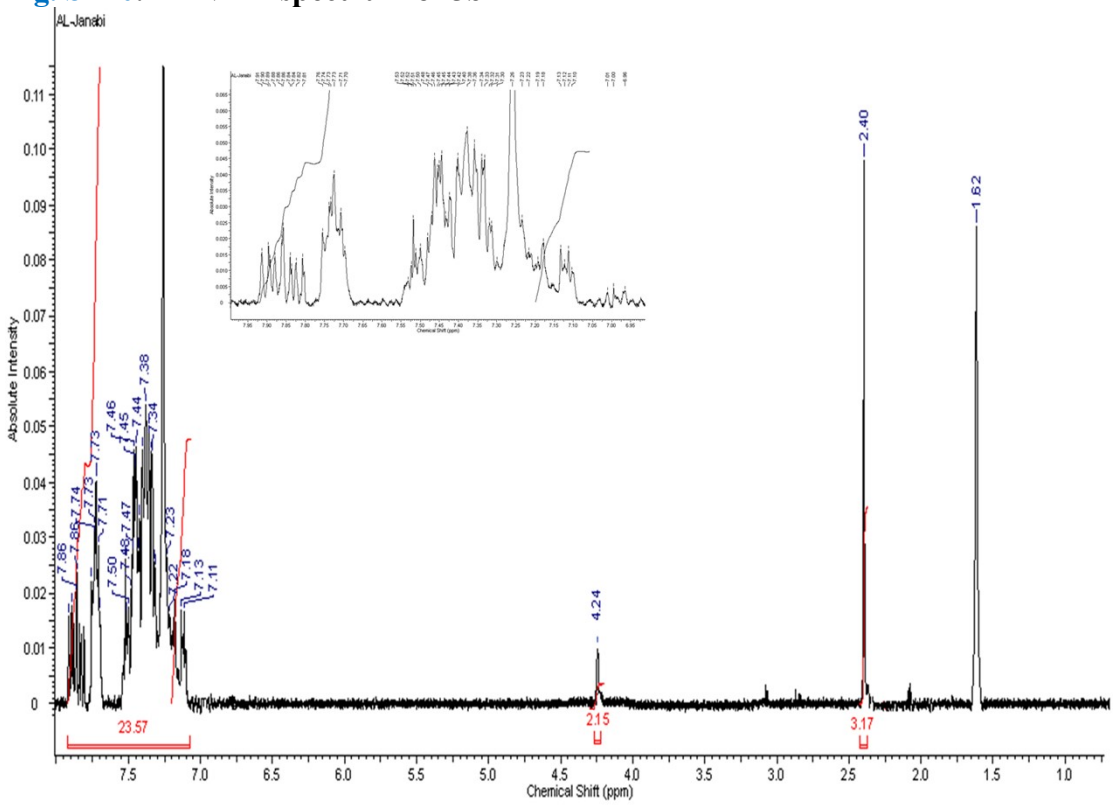


Fig. SI 21.IR spectrum of 6a

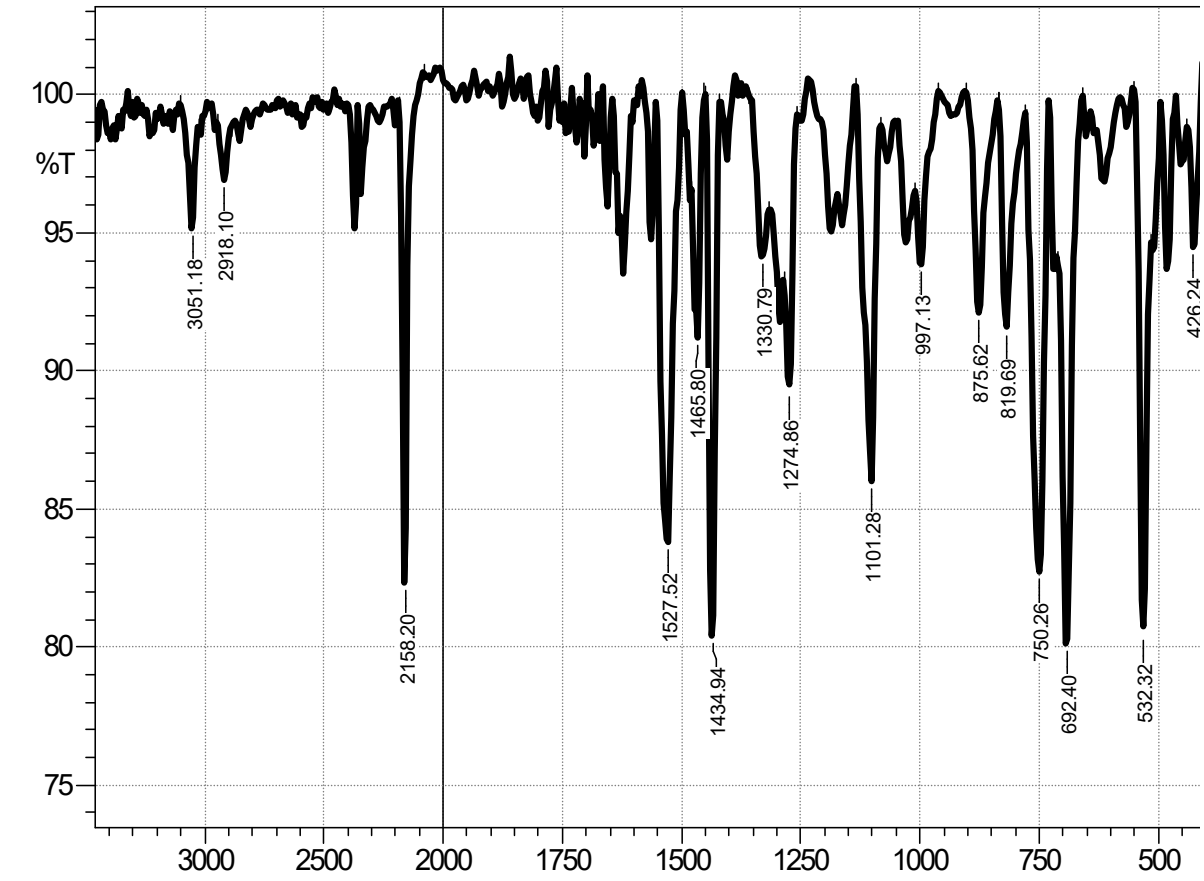


Fig. SI 22. $^{31}P\{^{1}H\}$ NMR spectrum of 6a

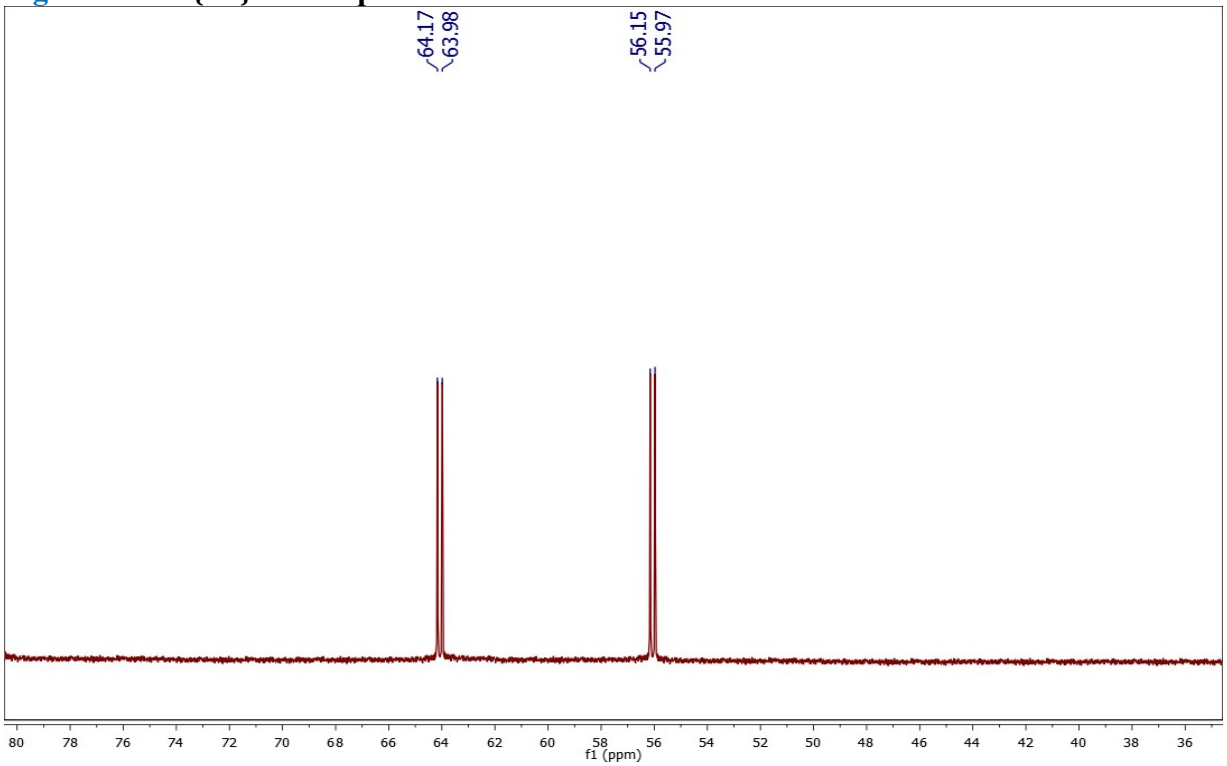


Fig. SI 23. ^{1}H NMR spectrum of 6a

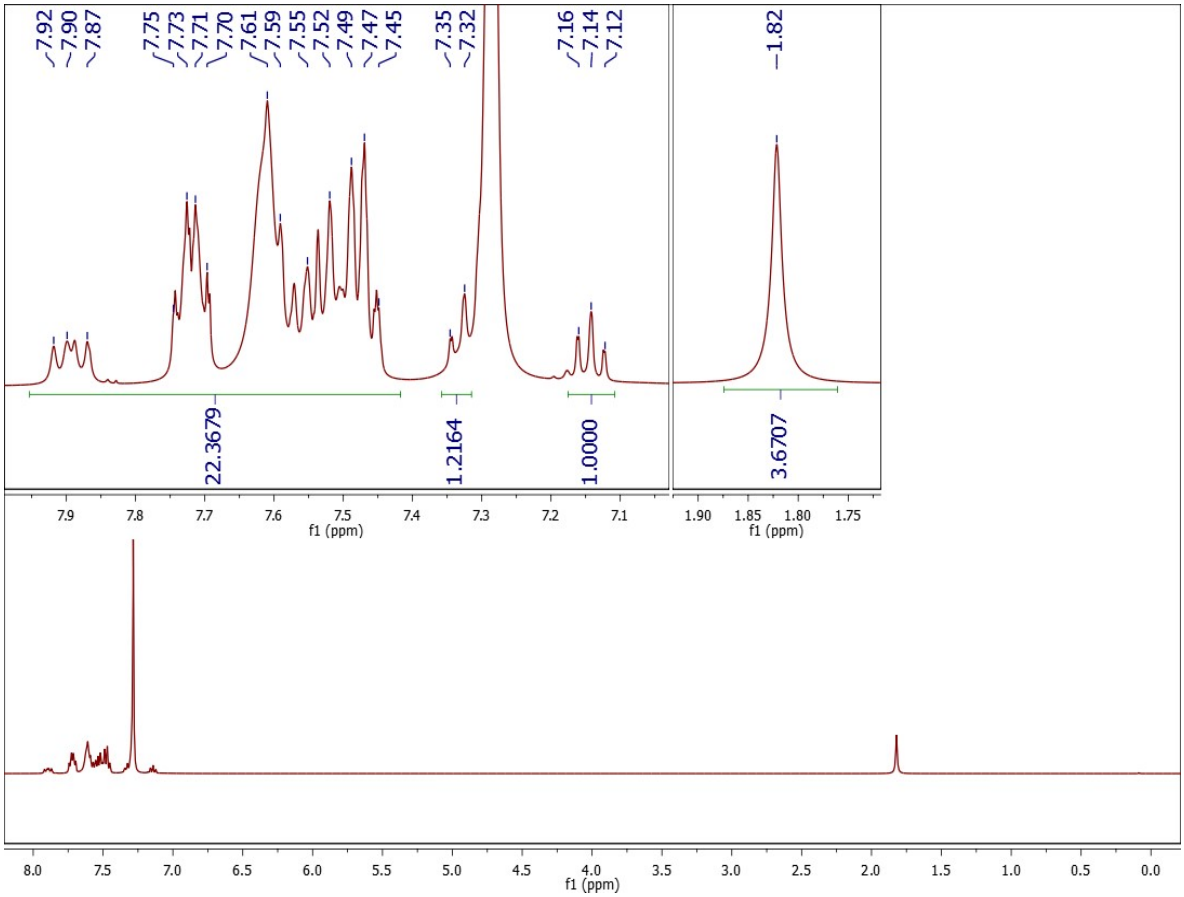


Fig. SI 24.IR spectrum of 6b

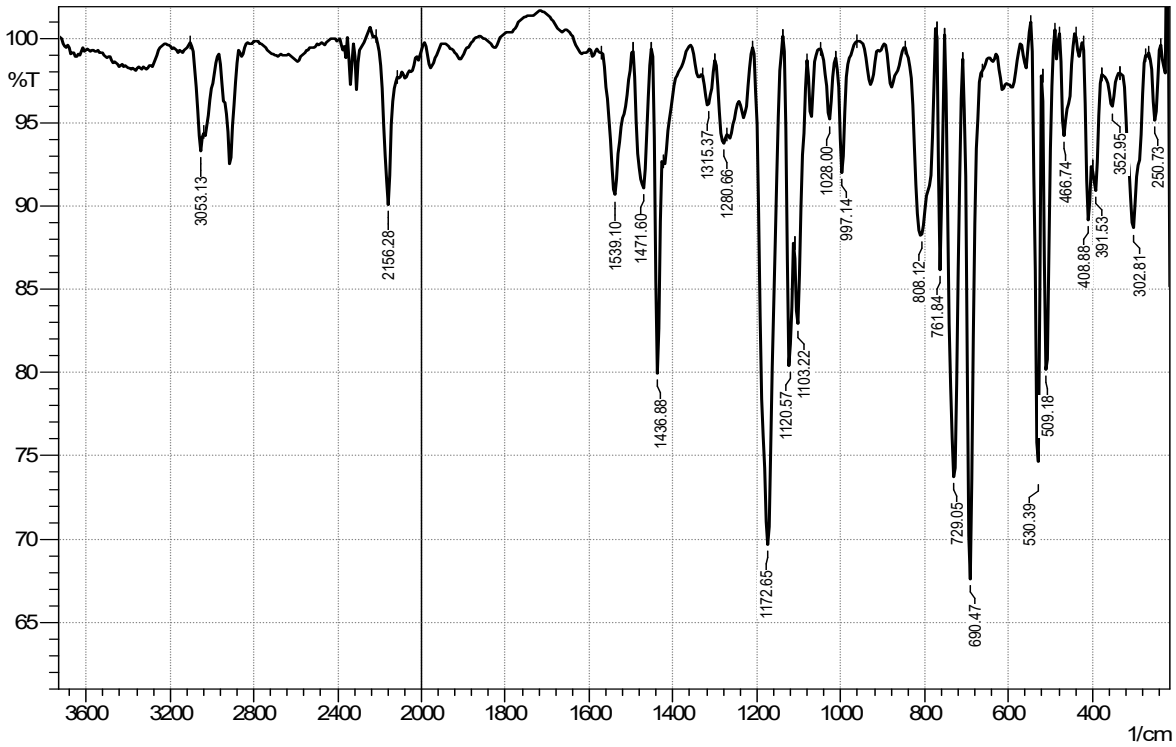


Fig. SI 25. $^{31}P\{^{1}H\}$ NMR spectrum of 6b

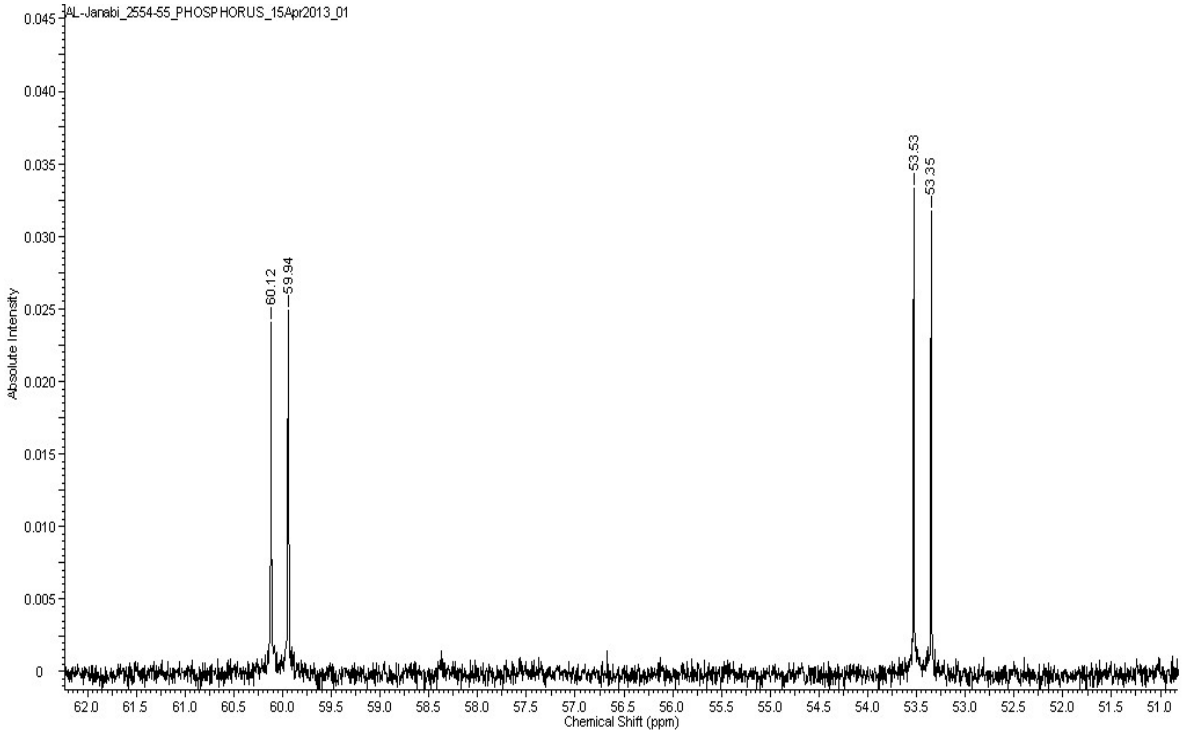
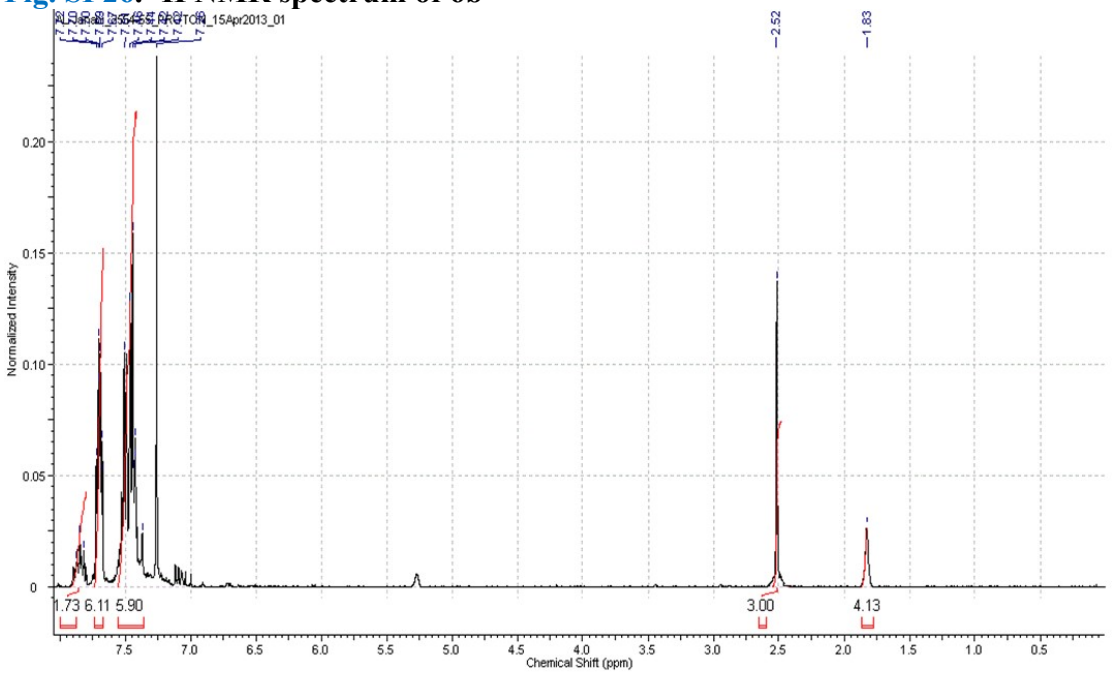


Fig. SI 26. ^{1}H NMR spectrum of 6b



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Frequency (MHz)	399.96	*Nucleus*	1H	*Number of Transients*	16	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.7400	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	27.000

Fig. SI 27.IR spectrum of 7a

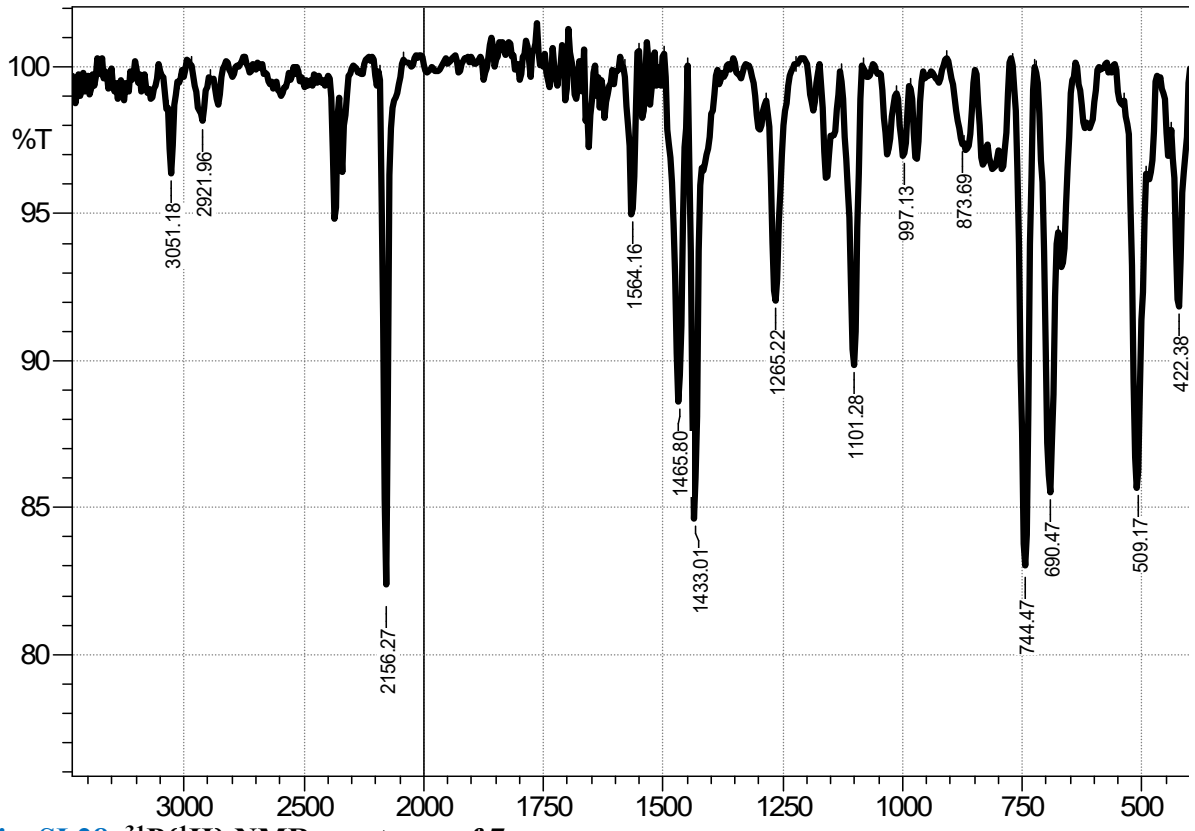


Fig. SI 28. $^{31}P\{^{1}H\}$ NMR spectrum of 7a

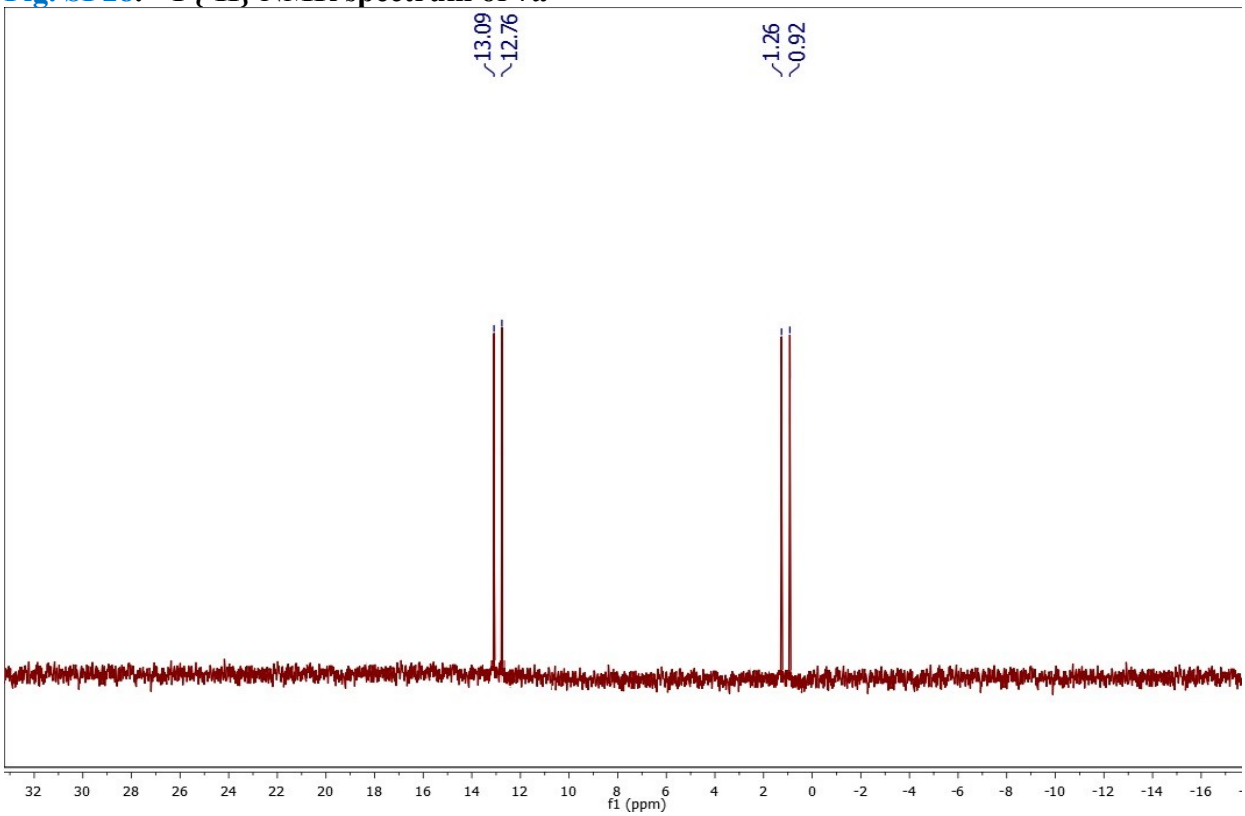


Fig. SI 29. ^{1}H NMR spectrum of 7a

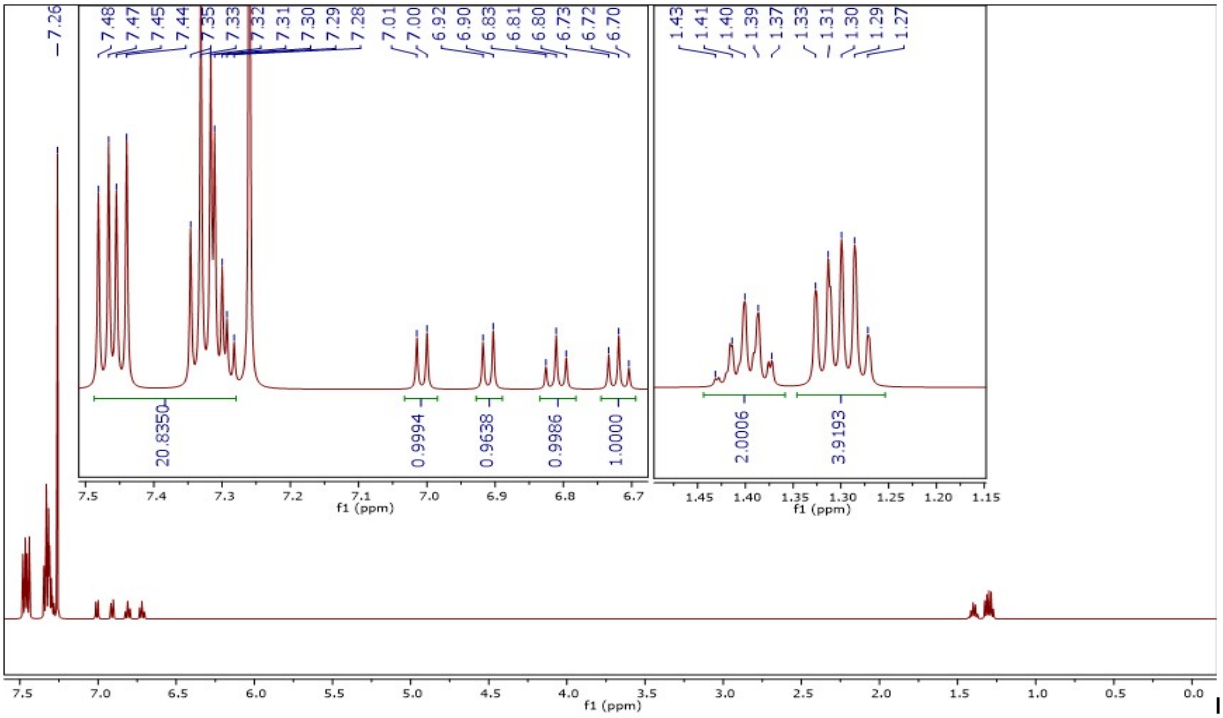


Fig. SI 30.IR spectrum of 7b

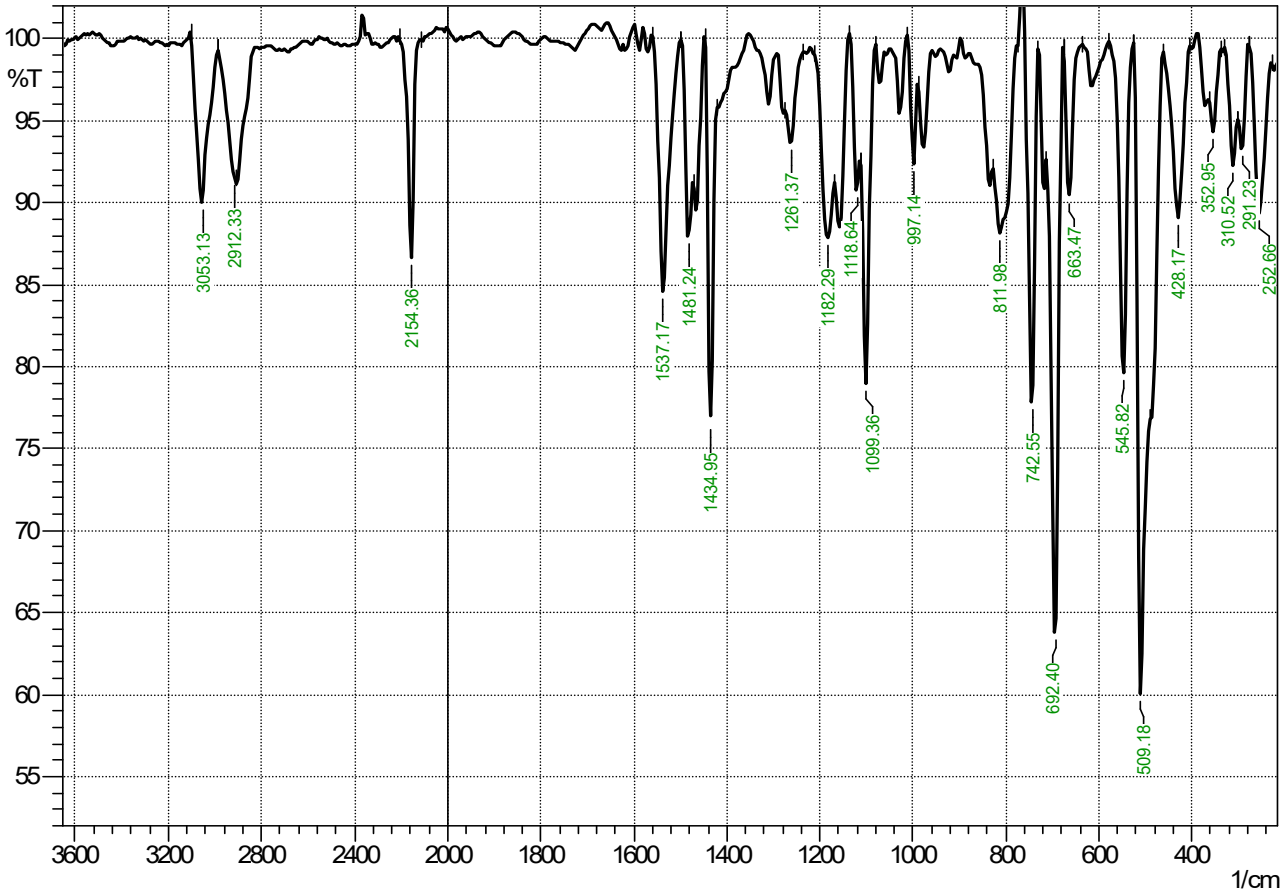


Fig. SI 31. $^{31}P\{^{1}H\}$ NMR spectrum of 7b

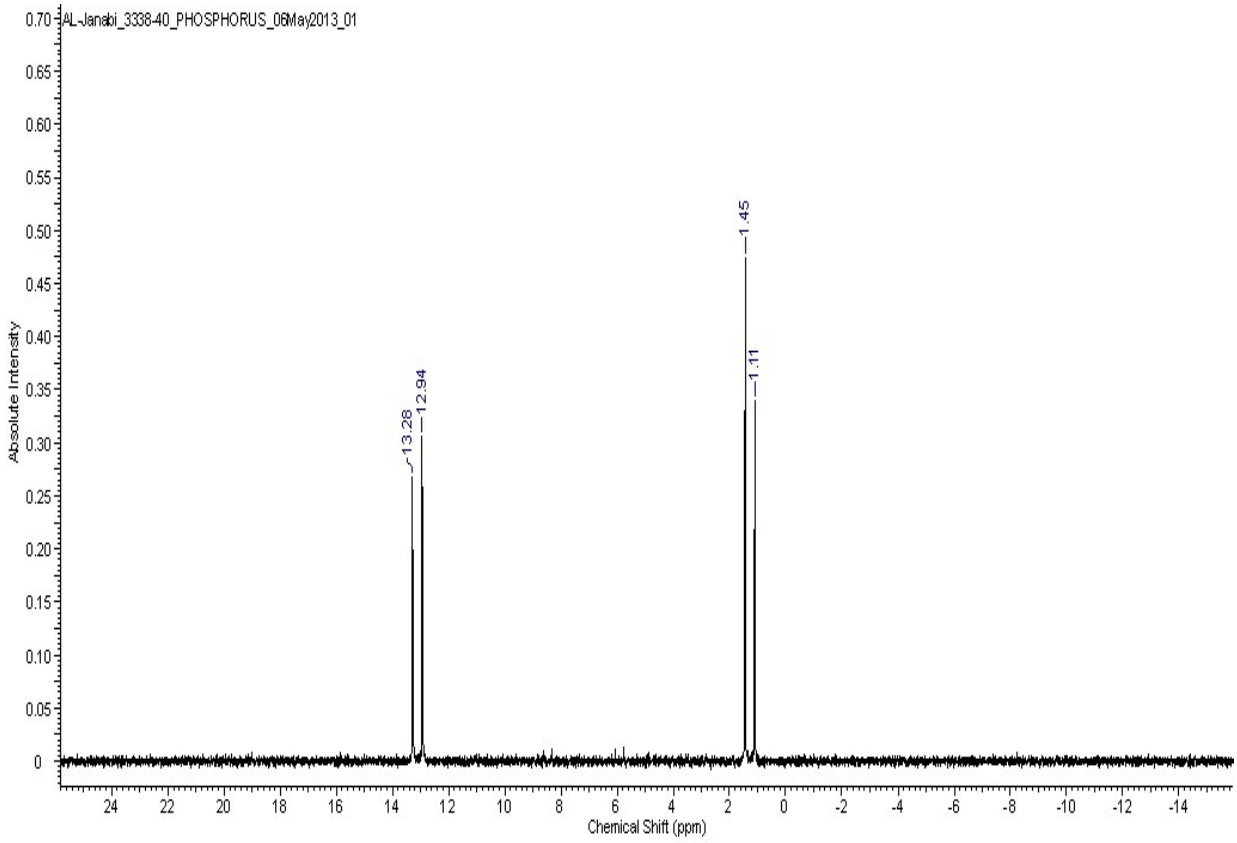


Fig. SI 32.IR spectrum of 8a

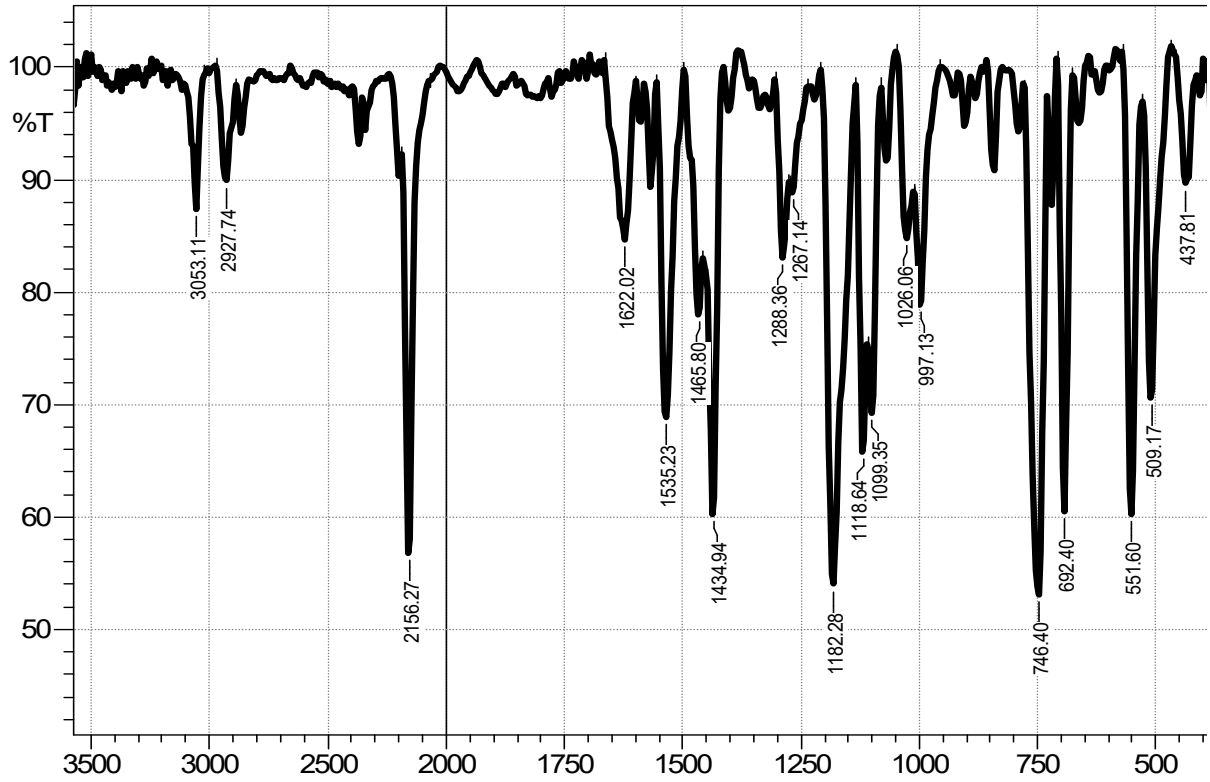


Fig. SI 33. $^{31}P\{^{1}H\}$ NMR spectrum of 8a

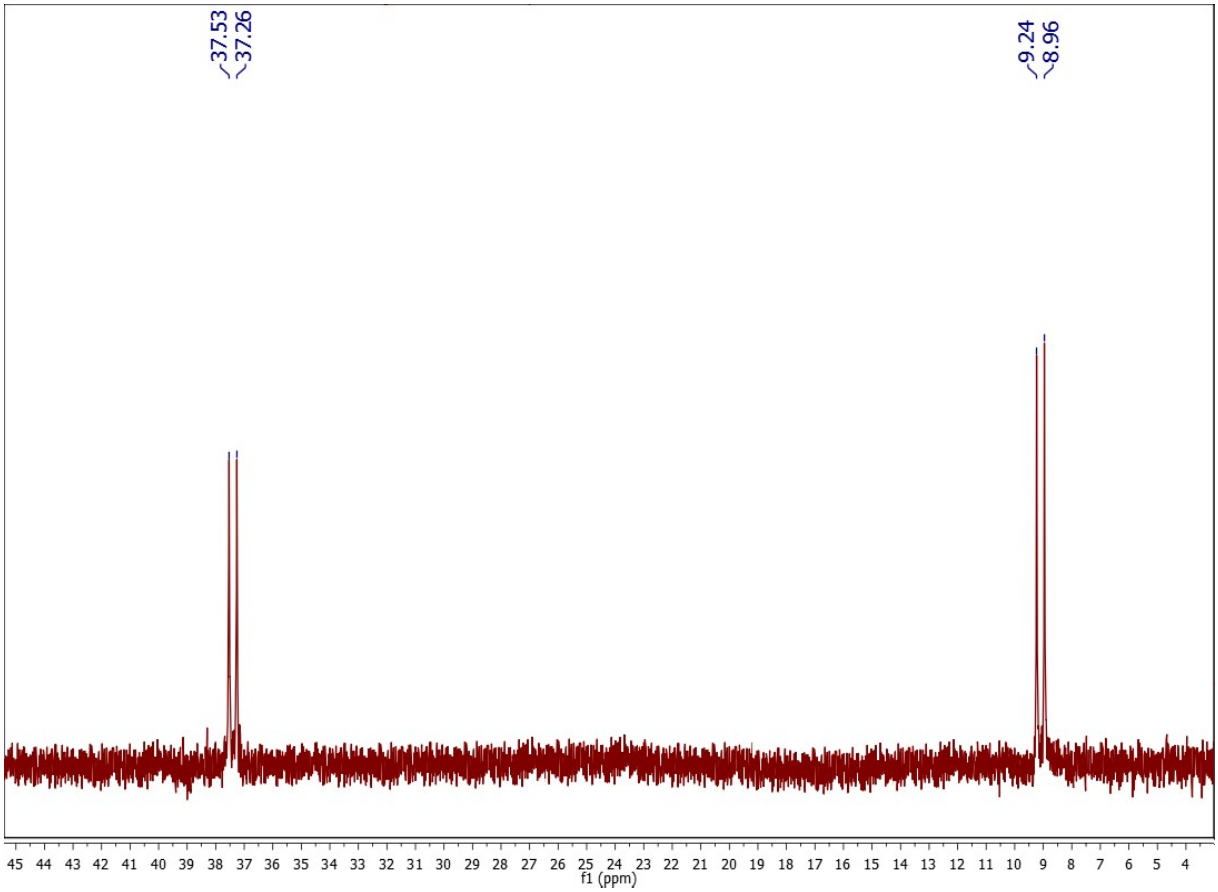


Fig. SI 34. ^{1}**H NMR spectrum of 8a**

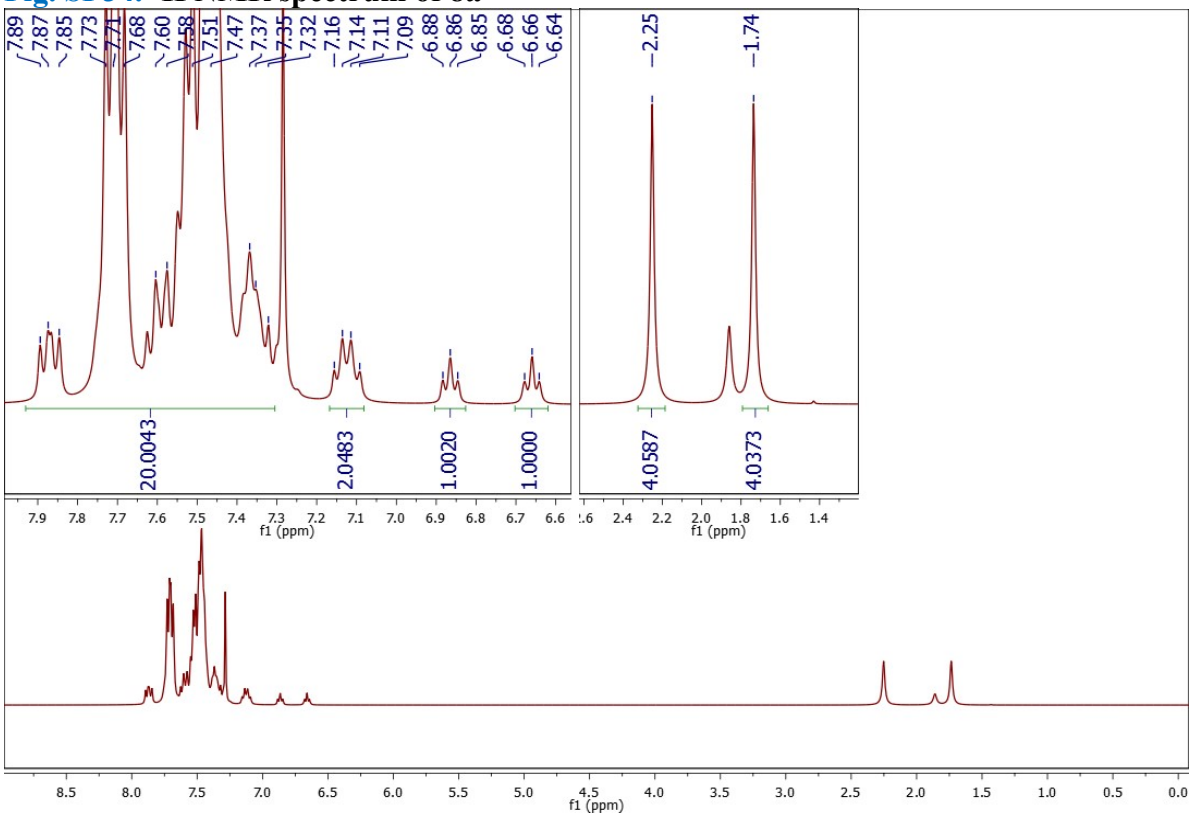


Fig. SI 35.IR spectrum of 8b

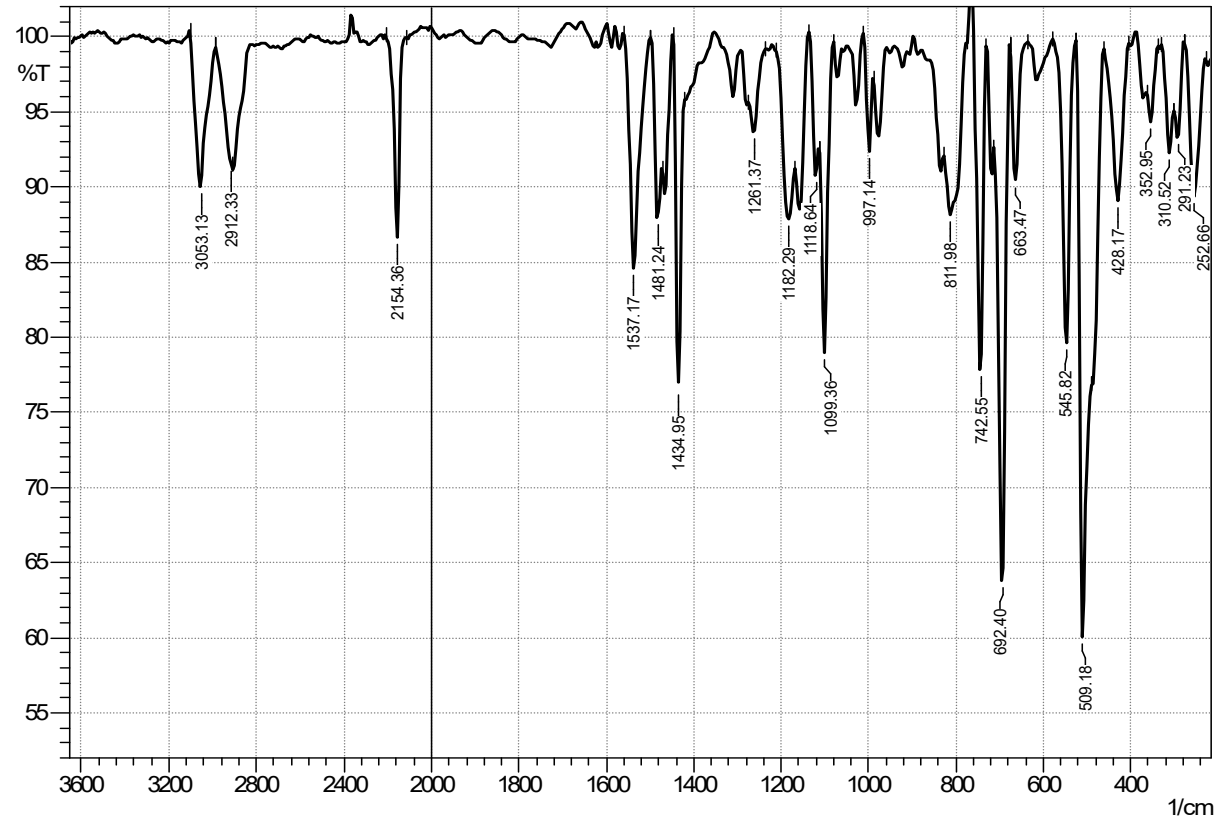


Fig. SI 36. $^{31}P\{^{1}H\}$ NMR spectrum of 8b

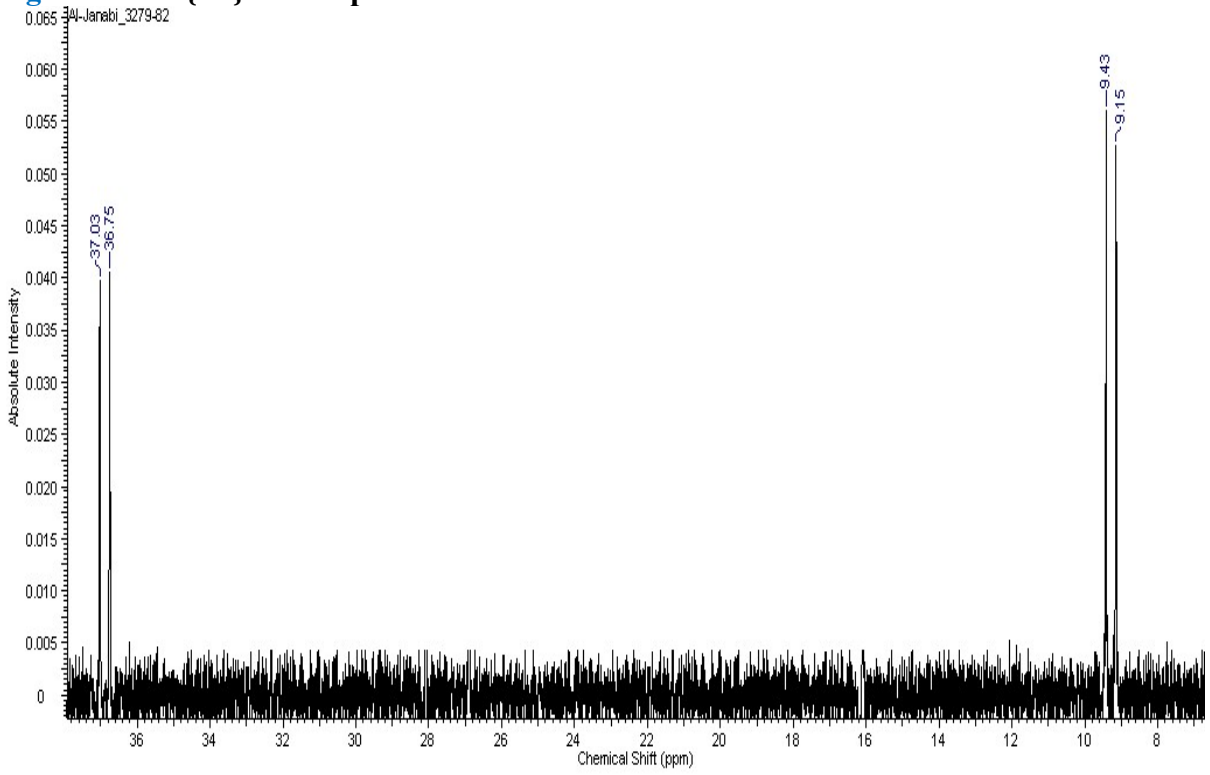
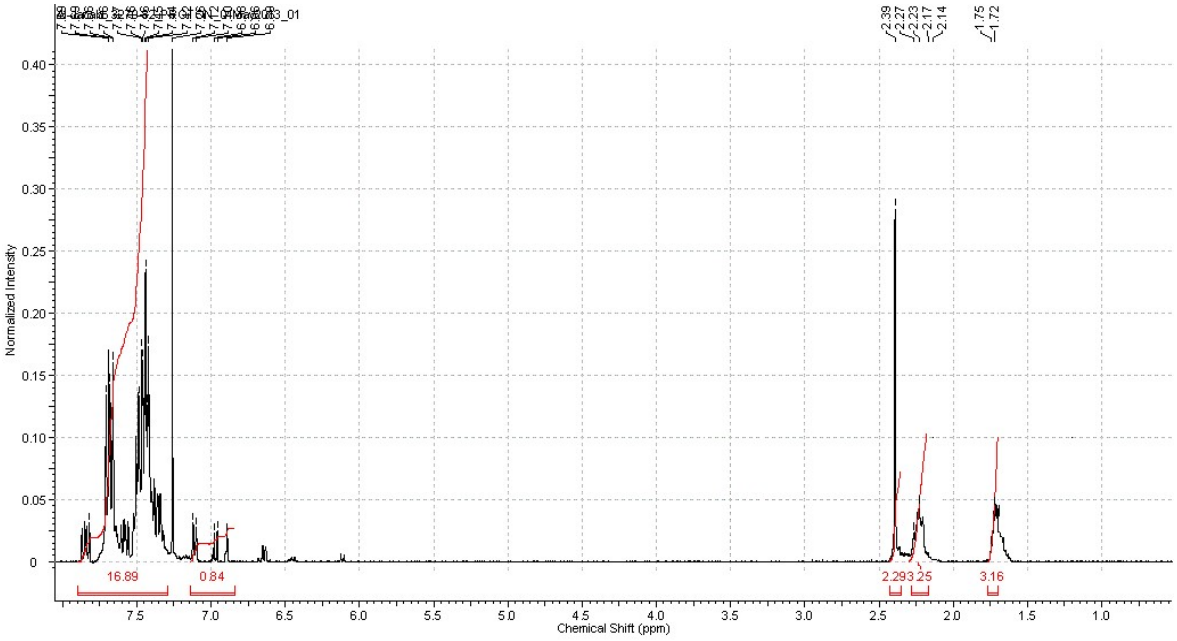


Fig. SI 37. ^{1}H NMR spectrum of 8b



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Date Stamp	May 4 2013	*File Name*	E:\٢٠١٣-٥-٦\اطياف الرنين المقناسة\data\05_2013\Al-Janabi_3279-82\Al-Janabi_3279-82_PROTON_04May2013_01.fid\fid				
Frequency (MHz)	399.96	*Nucleus*	1H	*Number of Transients*	64	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	44.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.7400	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	27.000

Fig. SI 38.IR spectrum of 9a

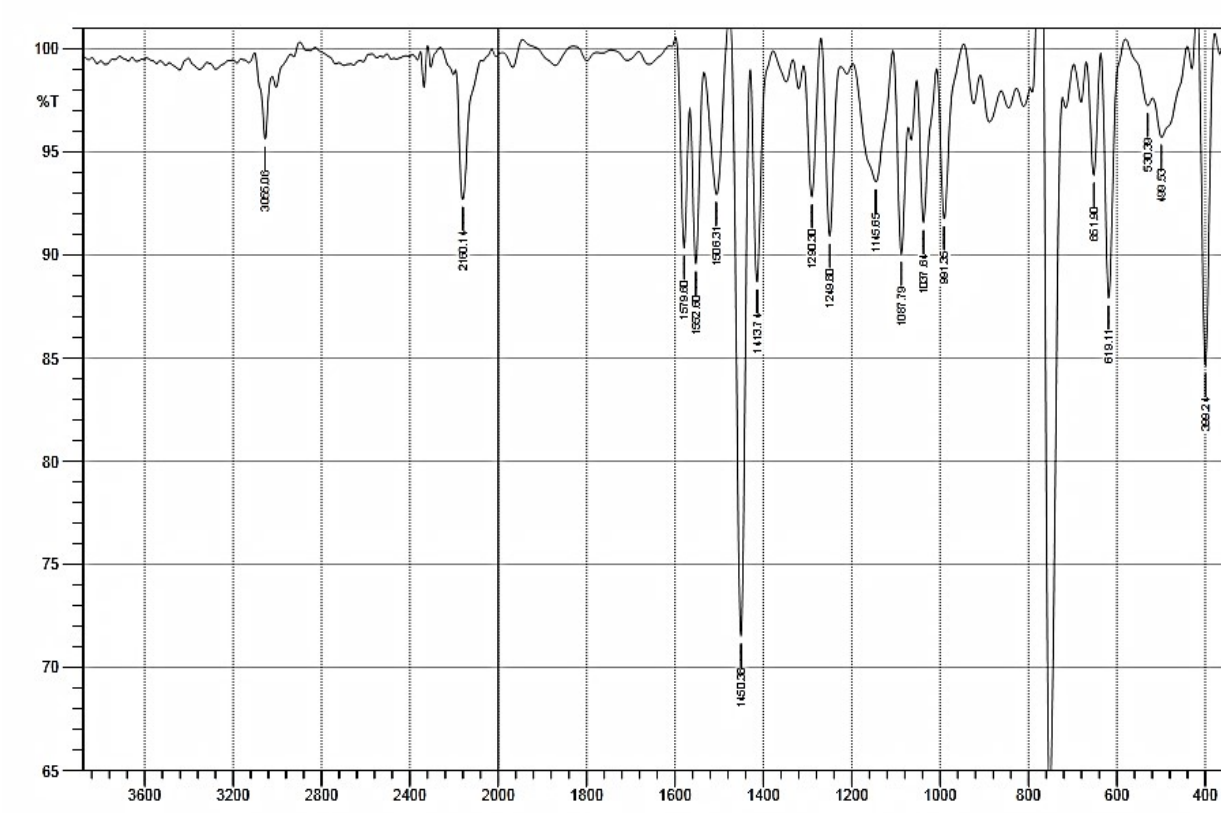

Fig. SI 39. ^{1}H NMR spectrum of 9a

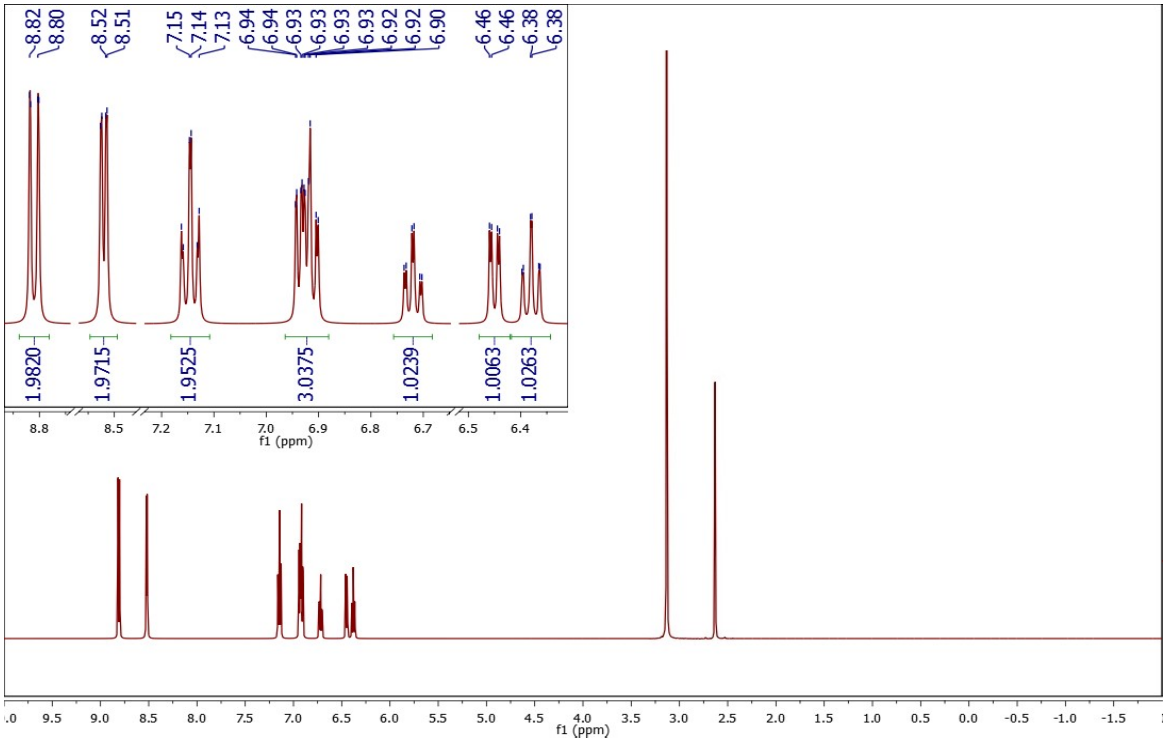

Fig. SI 40.IR spectrum of 9b

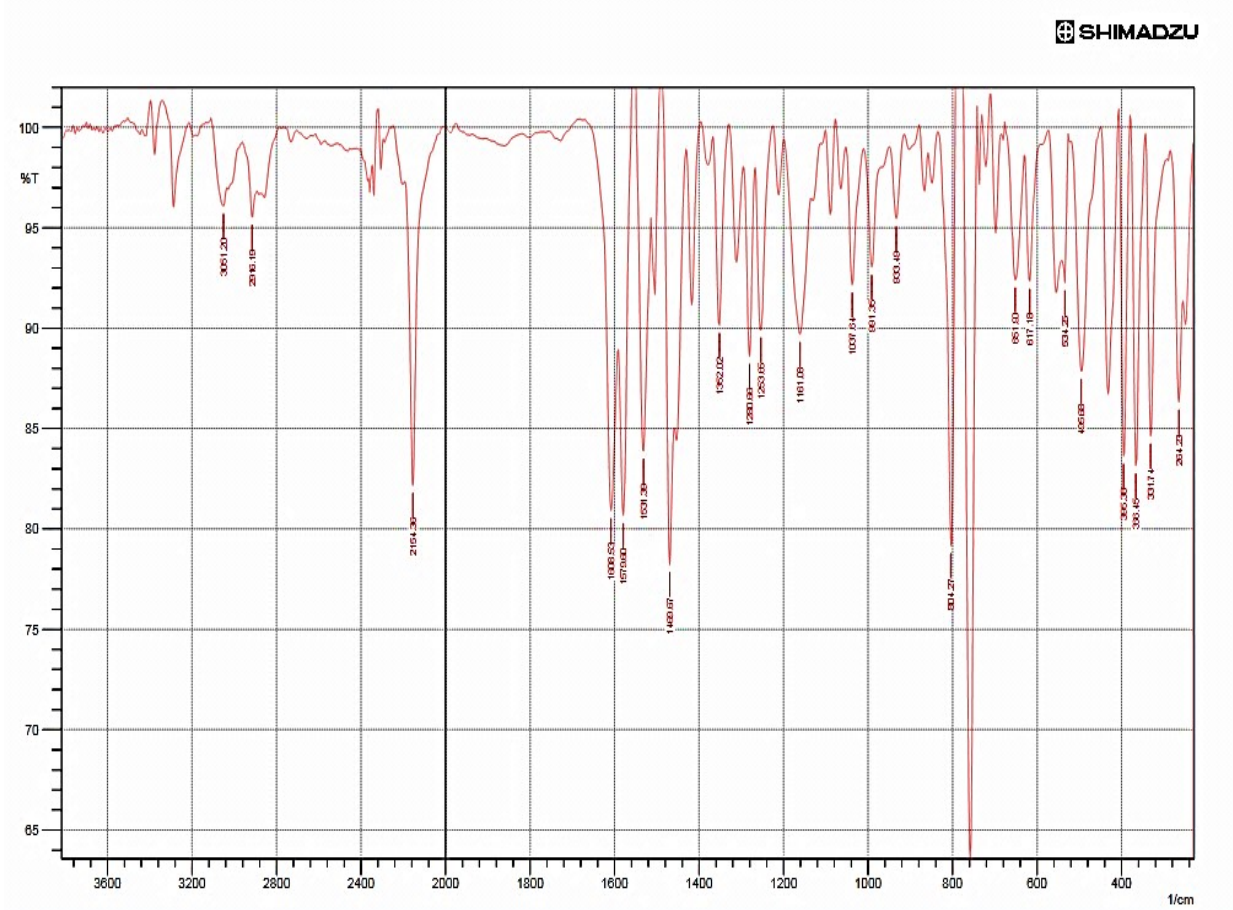

Fig. SI 41. ^{1}H NMR spectrum of 9b

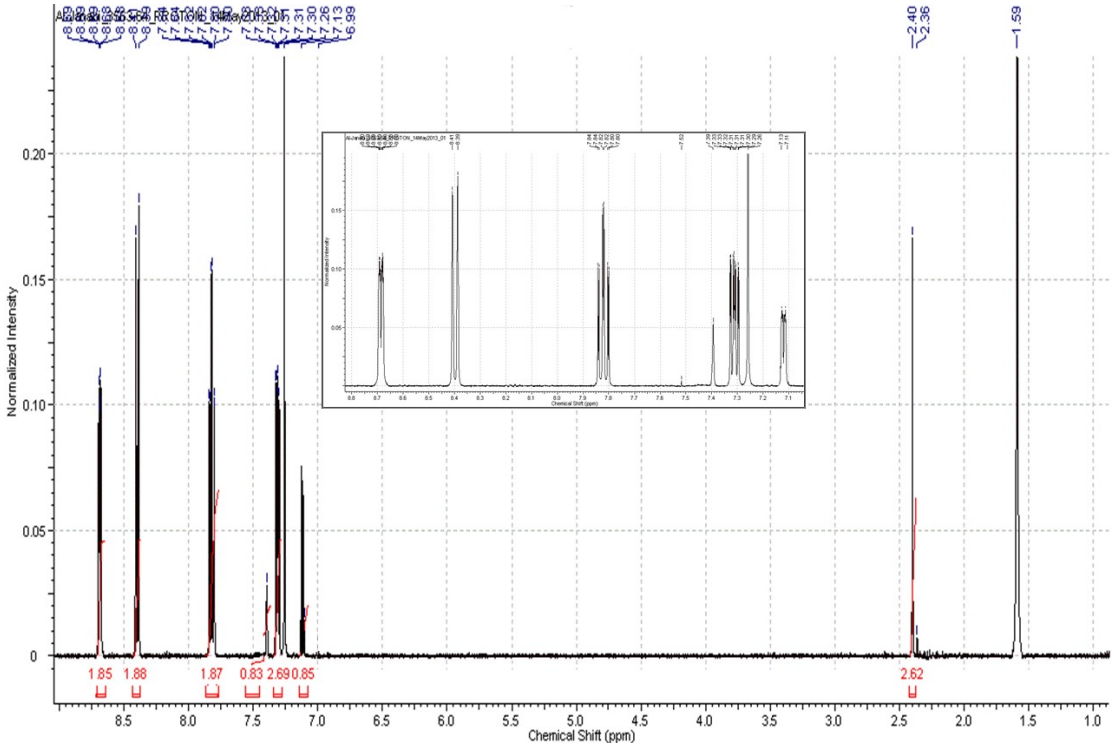

Fig. SI 42.IR spectrum of 10a

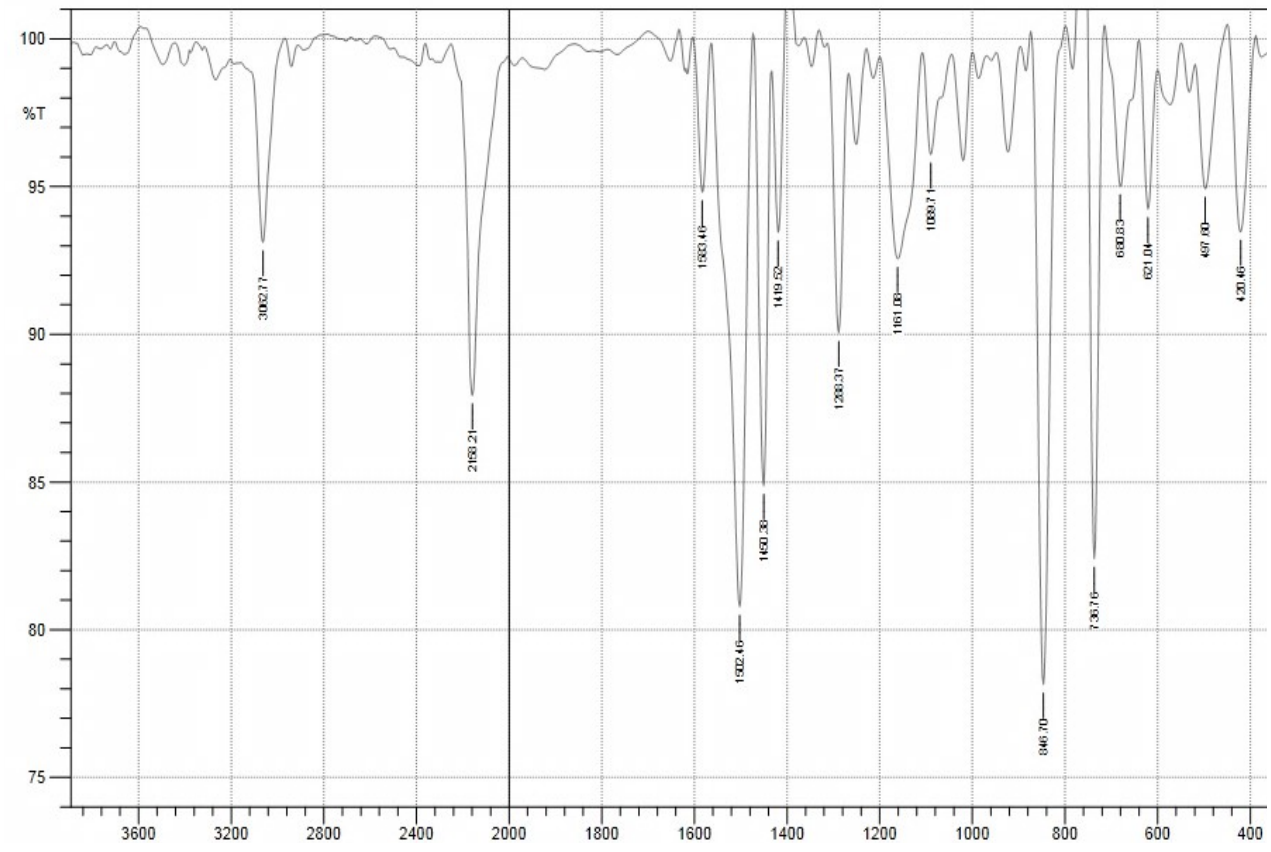

Fig. SI 43. ^{1}H NMR spectrum of 10a

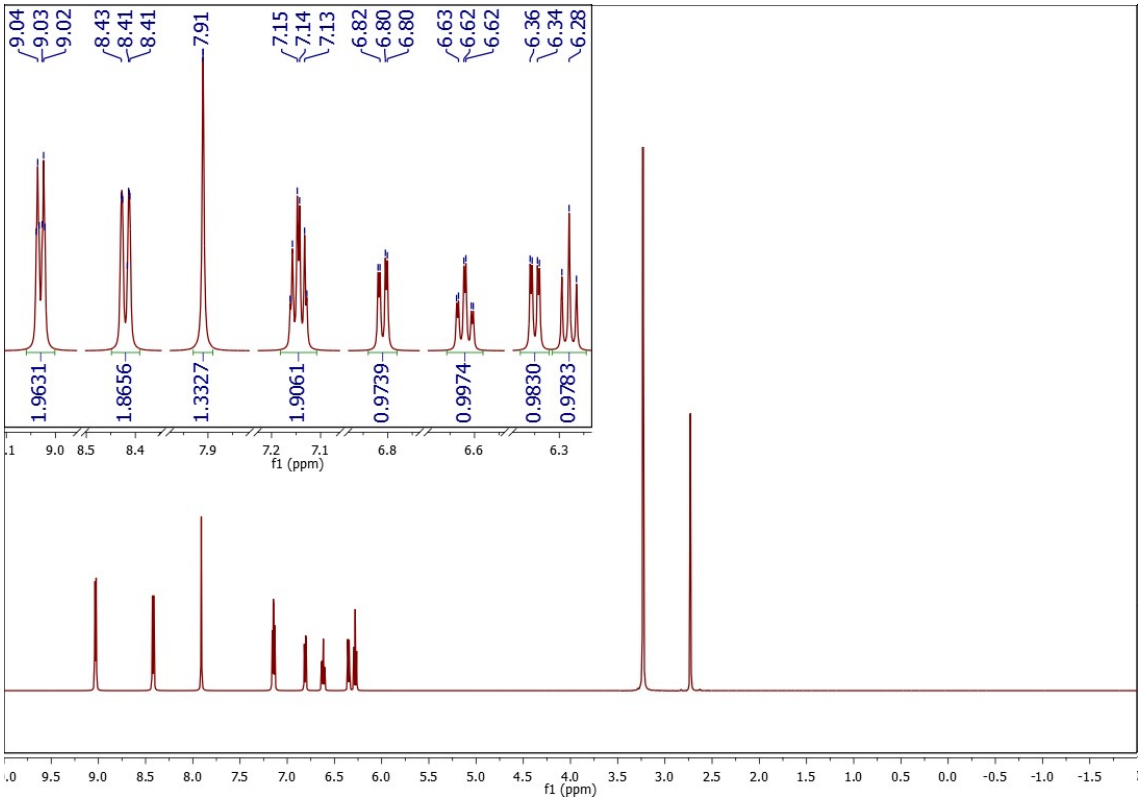
9.04
9.03
9.02
8.43
8.41
8.41
7.91
7.15
7.14
7.13
6.82
6.80
6.80
6.63
6.62
6.62
6.36
6.34
6.28
1.9631
1.8656
1.3327
1.9061
0.9739
0.9974
0.9830
0.9783
f1 (ppm)
f1 (ppm)

Table S1: Crystallographic data and structure refinement

	4a	**5a**	**6a**	**7b**	**11 .3CHCl$_3$**
CCDC number	2114233	2114230	2201775	2181464	2114234
Empirical formula	$C_{50}H_{38}N_4P_2Pd_2S_2$	$C_{32}H_{26}N_2P_2PdS$	$C_{33}H_{28}N_2P_2PdS$	$C_{35}H_{32}N_2P_2PdS$	$C_{34}H_{23}Cl_{11}N_6PdHgS$
Formula weight	1033.70	638.95	653.03	681.03	1244.58
Temperature (K)	150(2)	150(2)	150(2)	200(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P* -1	*P2$_1$/n*	*P2$_1$/c*	*P2$_1$/a*	*P2$_1$/n*
a (Å)	9.387(3)	12.904(3)	11.5387(3)	14.2842(16)	13.321(3)
b (Å)	15.923(6)	13.160(3)	19.3845(5)	14.4067(8)	12.444(3)
c (Å)	16.389(6)	16.640(4)	13.6921(4)	15.4064(12)	24.332(6)
α (°)	60.702(5)	90	90	90	90
β (°)	78.798(6)	105.465(4)	105.998(3)	102.516(8)	97.025(4)
γ (°)	82.205(6)	90	90	90	90
Volume (Å^3)	2086.3(13)	2713.3(11)	2943.92(15)	3095.1(5)	4003.3(16)
Z	2	4	4	4	4
Density (calc.) (g/cm^3)	1.645	1.558	1.473	1.461	2.065
Absorption coefficient	1.081	0.901	0.836	0.798	5.103
F(000)	1040	1296	1326	1392	2392
Crystal size (mm)	0.36 × 0.32 × 0.08	0.48 × 0.46 × 0.36	0.20 × 0.17 × 0.07	0.37 × 0.08 × 0.07	0.24 × 0.22 × 0.15
θ Range for data collection (°)	2.53 to 28.48	2.32 to 28.31	5.22 to 59.18	1.96 to 26.50	3.01 to 28.50
Index ranges	-11 ≤ h ≤ 11	-15 ≤ h ≤ 15	-15 ≤ h ≤ 15	-17 ≤ h ≤ 17	-15 ≤ h ≤ 15
	-18 ≤ k ≤ 18	-15 ≤ k ≤ 15	-18 ≤ k ≤ 24	-18 ≤ k ≤ 16	-14 ≤ k ≤ 14
	-19 ≤ l ≤ 19	-19 ≤ l ≤ 19	-16 ≤ l ≤ 17	-19 ≤ l ≤ 19	-28 ≤ l ≤ 28
Reflections collected	14547	14381	21359	16457	32724
Independent reflections	7206	4205	7054	6342	9331
Data / restraints / parameters	7206/0/541	4205/0/284	7054/0/351	6342/0/370	9331/0/488
Goodness-of-fit on F^2	0.839	0.940	1.045	0.914	0.851
Final *R* indices [I>2σ(I)]	R_1 = 0.0411	R_1 = 0.0385	R_1 = 0.0359	R_1 = 0.0576,	R_1 = 0.0349
	wR_2 = 0.0755	wR_2 = 0.0929	wR_2 = 0.0775	wR_2 = 0.1022	wR_2 = 0.0600
R indices (all data)	R_1 = 0.0700	R_1 = 0.0527	R_1 = 0.0440	R_1 = 0.1332	R_1 = 0.0561
	wR_2 = 0.0795	wR_2 = 0.0968	wR_2 = 0.0820	wR_2 = 0.1482	wR_2 = 0.0628
Larg. diff. peak and hole (e/Å^3)	0.85/-0.60	0.41/-0.50	1.00/-0.78	0.61/-0.84	1.31/-1.34