An expedient synthesis of new imino-thiazolidinone grafted dispiro-pyrrolidine-oxindole/indeno hybrids *via* multicomponent [3+2] cycloaddition reaction in deep eutectic solvent

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Supporting Data

1. General procedure for synthesis of dispiro-pyrrolidine-oxindole/indeno hybrid **4a-l** and **7a-d**.
2. The spectroscopic data revealed the formation of the final products.
3. Spectra (^{1}HNMR, ^{13}CNMR, Mass (S1-S34). (In ^{1}HNMR spectra the peaks at around δ 3.31 and δ 2.46 ppm and around multiple signal at around δ 40 ppm in ^{13}CNMR is comes due to solvent DMSO-d_6.
4. Crystal data and structure refinement for **4d.**

Experimental Section

Analytical grade solvents and commercially available reagents were used without further purification. The melting points of all compounds were determined on a Digital melting point apparatus. The purity of compounds was checked on thin layers of silica Gel-G coated glass plates and benzene: ethyl acetate (8:2) as eluent. ^{1}H and ^{13}C NMR spectra were recorded in dimethyl sulfoxide (DMSO-d_6) and chloroform ($CDCl_3$) as a solvent on a Jeol Resonance at 400 MHz and 100MH_Z, respectively. Chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The Mass spectra of representative compounds were obtained using Xevo G2-SQTof (water, USA). Elemental analysis was carried out on a Euro-E 3000 CHN Elemental analyzer**.** Single crystal X-ray structural studies were performed on Make/Model: Bruker Kappa Apex II diffractometer at SAIF Cochin/Eranakulam, Kerala.

General procedure for the synthesis of dispiro-pyrrolidines 4 / 7.

An equimolar mixture of appropriate 4-oxo-3-aryl-2-(arylimino)thiazolidin-5-ylidenes **1** (1 mmol), isatin **2/** ninhydrine **6** and sarcosine **3** (1 mmol) in DES (10 ml) were taken in a round bottom flask and stirred the reaction mixture at 80 ^oC for 2-2.5 hrs. At the end of

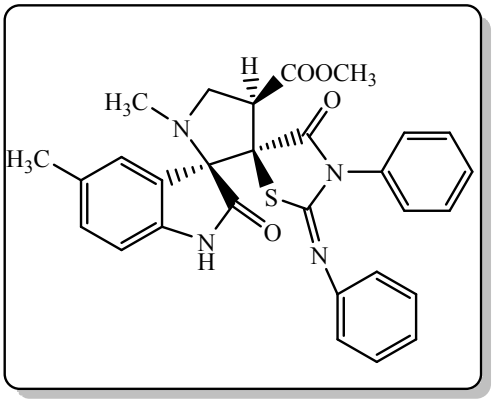
reaction confirmed by TLC, the reaction mixture was cooled at room temperature. Then, it was extracted using ethyl acetate. The ethyl acetate phase containing product was separated from undissolved DES and extra ethyl acetate was evaporated under reduced pressure to obtained crude solid residue that was then crystallized from ethanol to obtain pure cyclo adducts. All compounds **4a-l** and **7a-d** was prepared by this manner (Table 2 and 3). Synthesized compounds were well characterized by ^{1}H NMR, ^{13}C NMR, Mass and single crystal X-ray analysis of representative compound. For crystallography the crystals of compound was grown by slow evaporation technique using ethanol as solvent.

To recover the used deep eutectic solvent, it was washed with ethyl acetate to remove all material traces, deep eutectic solvent showed comparable yield in three subsequent reactions.

Characterization data

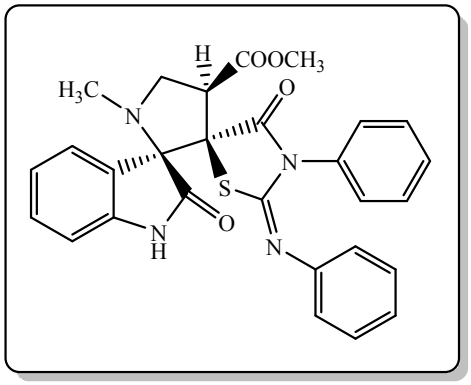
Methyl-1',5-dimethyl-2,4''-dioxo-3''-phenyl-2''-(phenylimino)dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4a):

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.18 (s, 3H, N-CH_3), 2.25 (s, 3H, CH_3), 3.54 (t, 1H, CH, *J* = 8.8 Hz), 3.76 (s, 3H, OCH_3), 4.03 (t, 1H, CH, *J* = 9.2 Hz), 4.25 (t, 1H, CH, *J* = 8.8 Hz), 6.65-7.41 (m, 13H, Ar-H), 7.91 (s, 1H, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.1, 35.7, 49.9, 52.4, 54.0, 65.8 (spiro carbon), 79.8 (spiro carbon) 110.0, 120.8, 122.0, 124.7, 128.0, 128.4, 128.9, 129.1, 131.5, 134.1, 136.1, 140.0, 147.65, 152.1 (aromatic carbons), 169.8, 173.2, 175.6 (three C=O) ppm; MS (m/z): 527.17 $[M+H]^+$; Anal. calcd. for $C_{29}H_{26}N_4O_4S$: C 66.14; H 4.98; N 10.64 %. Found: C 66.29, H 4.95, N 10.60 %.



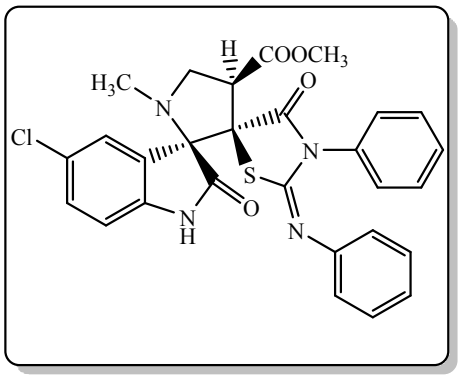
Methyl-1'-methyl-2,4''-dioxo-3''-phenyl-2''-(phenylimino)dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4b):

^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.01 (s, 3H, N-CH_3), 3.33-3.54 (m, 1H, CH), 3.69 (s, 3H, OCH_3), 4.33 (t, 1H, CH, *J* = 6.8 Hz), 4.91 (t, 1H, CH, *J* = 6.8, 7.6 Hz), 6.74 - 7.42 (m, 14H, Ar-H), 10.55 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 35.6, 51.1, 52.9, 56.5, 70.2 (spiro carbon), 78.5 (spiro carbon), 110.3, 120.7, 122.6, 123.5, 126.1, 128.2, 129.5, 129.8, 130.0, 131.4, 134.1, 143.9, 148.3, 152.8 (aromatic



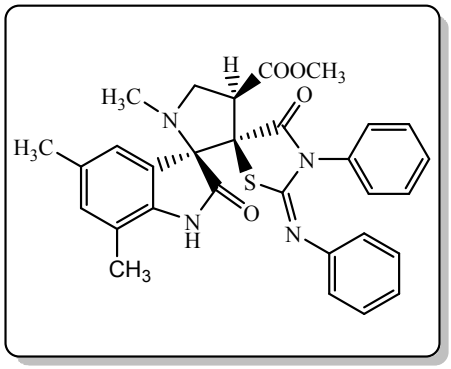
carbons), 170.0, 170.1, 175.3 (three C=O) ppm; MS (m/z): 513.19 $[M+H]^+$; Anal. calcd. for $C_{28}H_{24}N_4O_4S$: C 65.61; H 4.72; N 10.93 %. Found: C 65.76, H 4.75, N 10.90 %.

Methyl-5-chloro-1'-methyl-2,4''-dioxo-3''-phenyl-2''-(phenylimino)dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4c):



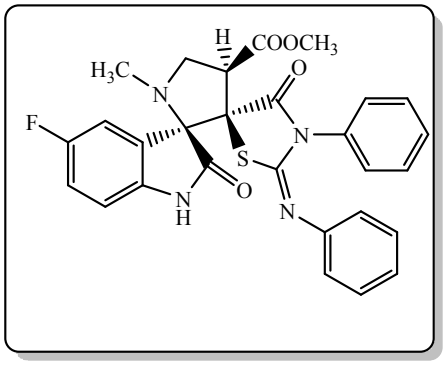
^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.18 (s, 3H, N-CH_3), 3.52 (t, 1H, CH, *J* = 8.8 Hz), 3.77 (s, 3H, OCH_3), 4.01 (t, 1H, CH, *J* = 9.2, 8.8 Hz), 4.22 (t, 1H, CH, *J* = 8.4 Hz), 6.66 - 7.45 (m, 13H, Ar-H), 8.15 (s, 1H, NH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.7, 50.3, 52.5, 53.9, 65.8 (spiro carbon), 79.7 (spiro carbon), 111.3, 120.7, 124.8, 128.0, 128.1, 129.2, 129.4, 129.8, 132.5, 134.7, 141.3, 147.5, 151.7 (aromatic carbons), 169.6, 173.1, 175.4 (three C=O) ppm; MS (m/z): 547.11 $[M+H]^+$; Anal. calcd. for $C_{28}H_{23}ClN_4O_4S$: C 61.48; H 4.24; N 10.24 %. Found: C 61.28, H 4.27, N 10.21 %.

Methyl-1',5,7-trimethyl-2,4''-dioxo-3''-phenyl-2''-(phenylimino)dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4d):



^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.97 (s, 3H, N-CH_3), 2.14 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.33 (t, 1H, CH, *J* = 6.4 Hz), 3.64 (s, 3H, OCH_3), 3.75 (t, 1H, CH, *J* = 8.8, 9.2 Hz), 4.10 (t, 1H, CH, *J* = 8.8, 8.4 Hz), 6.58-7.46 (m, 12H, Ar-H), 10.67 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 21.1, 24.9, 35.1, 47.0, 52.8, 53.0, 65.3 (spiro carbon), 74.3 (spiro carbon), 111.0, 111.1, 117.5, 117.8, 122.5, 126.5, 126.6, 129.6, 130.0, 133.4, 134.2, 139.2, 146.8, 152.7, 156.6, 159.0 (aromatic carbons), 168.8, 169.5, 176.5 (three C=O) ppm; MS (m/z): 541.10 $[M+H]^+$; Anal. calcd. for $C_{30}H_{28}N_4O_4S$: C 66.65; H 5.22; N 10.36 %. Found: C 66.50, H 5.25, N 10.33 %.

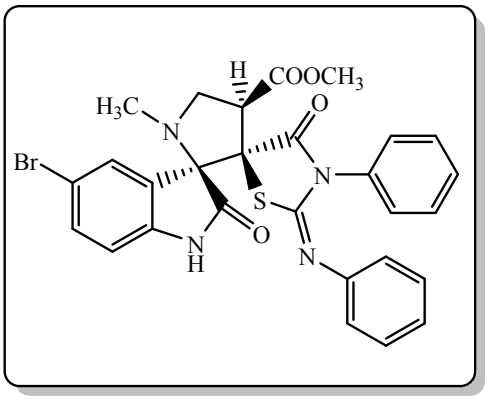
Methyl-5-fluoro-1'-methyl-2,4''-dioxo-3''-phenyl-2''-(phenylimino)dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4e):



^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.25 (s, 3H, N-CH_3), 3.62 (t, 1H, CH, *J* = 8.8, 9.2 Hz), 3.97 (s, 3H, OCH_3), 4.29 (t, 1H, CH, *J* = 8.8 Hz), 4.42 (t, 1H, CH, *J* = 8.4 Hz), 6.86-7.85 (m, 13H, Ar-H) , 8.24 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 31.2, 47.0, 52.4, 52.8, 65.3 (spiro carbon), 74.3 (spiro carbon), 119.1, 120.8, 126.1,

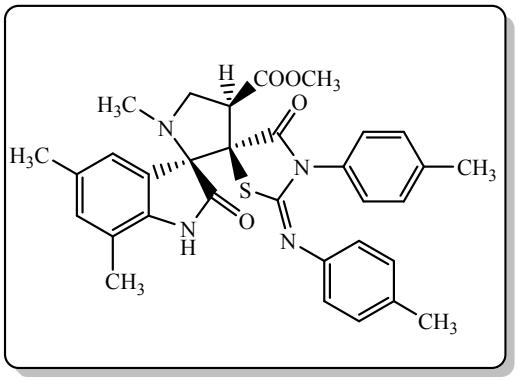
128.2, 129.4, 129.8, 129.9, 130.2, 132.6, 135.0, 138.9, 148.3, 152.4 (aromatic carbons), 169.3, 169.7, 177.2 (three C=O) ppm; MS (m/z): 531.57 $[M+H]^+$; Anal. calcd. for $C_{28}H_{23}FN_4O_4S$: C 63.39; H 4.37; N 10.56 %. Found: C 63.54, H 4.42, N 10.53 %.

Methyl-5-bromo-1'-methyl-2,4''-dioxo-3''-phenyl-2''-(phenylimino)dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4f):



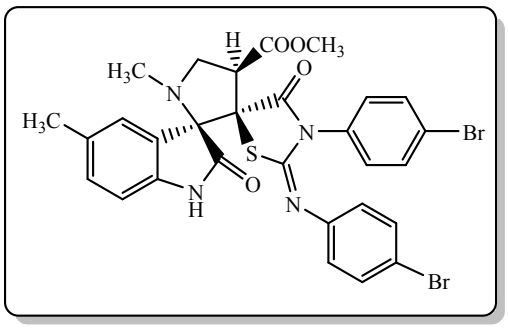
^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.00 (s, 3H, N-CH_3), 3.34 (t, 1H, CH, *J* = 8.8, 8 Hz), 3.66 (s, 3H, OCH_3), 3.72 (t, 1H, CH, *J* = 9.2 Hz), 4.14 (t, 1H, CH, *J* = 8.4, 9.2 Hz), 6.64-7.55 (m, 13H, Ar-H) ,10.92 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 35.4, 50.6, 52.6, 53.4, 66.4 (spiro carbon), 79.4 (spiro carbon), 112.6, 114.4, 120.8, 125.1, 128.5, 129.8, 129.9, 130.0, 134.1, 134.9, 143.8, 147.9, 152.6 (aromatic carbons), 169.7, 173.3, 175.8 (three C=O) ppm; MS (m/z): 591.48 $[M+H]^+$; Anal. calcd. for $C_{28}H_{23}BrN_4O_4S$: C 56.86; H 3.92; N 9.47 %. Found: C 56.71, H 3.95, N 9.43 %.

Methyl-1',5,7-trimethyl-2,4''-dioxo-3''-(p-tolyl)-2''-(p-tolylimino)dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4g):



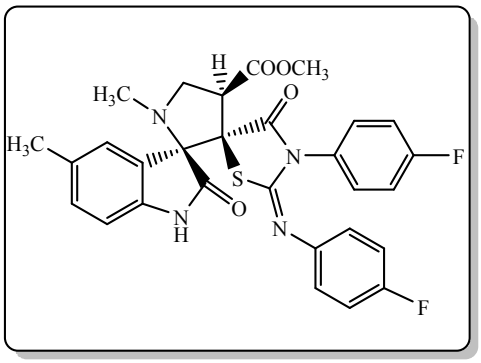
^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.97 (s, 3H,N-CH_3), 2.14 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.18 (s, 3H,CH_3), 2.20 (s, 3H, CH_3), 3.63 (s, 3H, OCH_3), 3.75 (t, 1H, CH, *J* = 8.8, 9.2 Hz), 4.08 (t, 1H, CH, *J* = 8.8, 8.4 Hz), 4.89 (t, 1H, CH, *J* = 7.2 Hz) , 6.46-7.23 (m, 10H, Ar-H), 10.64 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ16.6, 16.7, 20.9, 21.2, 35.5, 49.8, 52.4, 53.5, 66.2 (spiro carbon), 79.8 (spiro carbon), 119.5, 120.7, 123.1, 128.2, 130.0, 132.4, 132.9, 134.2, 138.9, 140.6, 145.7, 152.8, 152.9 (aromatic carbons), 170.1, 173.4, 176.8 (three C=O) ppm; MS (m/z): 569.21 $[M+H]^+$; Anal. calcd. for $C_{32}H_{32}N_4O_4S$: C 67.59; H 5.67; N 9.85 %. Found: C 67.39, H 5.62, N 9.89 %.

Methyl-3''-(4-bromophenyl)-2''-(4-bromophenyl)imino)-1',5-dimethyl-2,4''-dioxodispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4h):



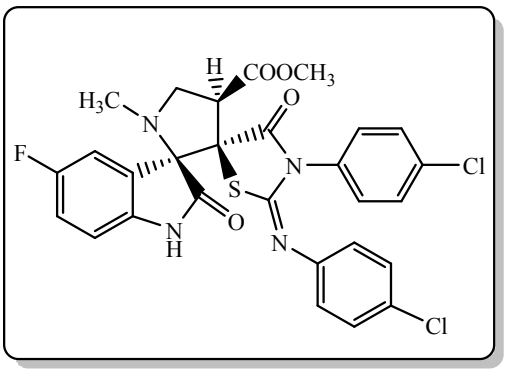
^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.16 (s, 3H, N-CH_3), 2.26 (s, 3H,CH_3), 3.44 (t, 1H, CH, J = 7.2, 9.2 Hz), 3.68 (s, 3H, OCH_3), 4.36 (t, 1H, CH, J = 6.4, 6 Hz), 4.92 (t, 1H, CH, J = 7.2, 7.6 Hz), 6.55-7.76 (m, 11H, Ar-H) ,10.47 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 21.3, 36.0, 48.5, 51.1, 52.9, 64.9 (spiro carbon), 79.6 (spiro carbon), 110.0, 110.7, 117.5, 123.2, 126.5, 130.3, 130.5, 131.7, 132.7, 132.9, 141.9, 147.0, 147.4, 153.1, 153.4 (aromatic carbons), 169.9, 171.3, 176.7 (three C=O) ppm; MS (m/z): 682.99 $[M+H]^+$; Anal. calcd. for $C_{29}H_{24}Br_2N_4O_4S$: C 50.89; H 3.53; N 8.19 %. Found: C 50.69, H 3.58, N 8.16 %

Methyl-3''-(4-fluorophenyl)-2''-(4-fluorophenyl)imino)-1',5-dimethyl-2,4''-dioxodispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4i):



^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.98 (s, 3H, N-CH_3), 2.18 (s, 3H,CH_3), 3.32 (t, 1H, CH, J = 7.6, 9.2 Hz), 3.65 (s, 3H, OCH_3), 3.75 (t, 1H, CH, J = 9.2 Hz), 4.13 (t, 1H, CH, J=8.8 Hz), 6.61-7.45 (m, 11H, Ar-H), 10.63 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 21.2, 35.8, 50.2, 52.5, 53.50, 66.4 (spiro carbon), 79.6 (spiro carbon), 110.2, 120.9, 124.0, 127.9, 128.5, 129.6, 129.8, 131.5, 142.0, 148.0, 152.9 (aromatic carbons), 169.9, 173.4, 176.2 (three C=O) ppm; MS (m/z): 563.15 $[M+H]^+$; Anal. calcd. for $C_{29}H_{24}F_2N_4O_4S$: C 61.91; H 4.30; N 9.96 %. Found: C 61.76, H 4.35, N 9.93%.

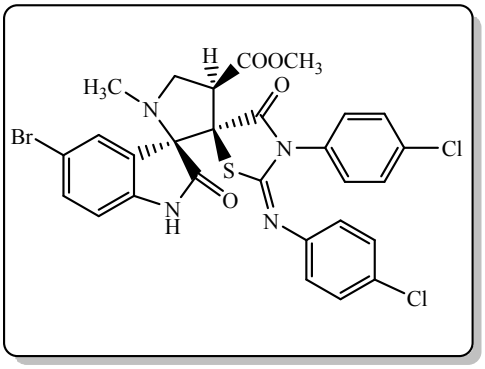
Methyl-3''-(4-chlorophenyl)-2''-(4-chlorophenyl)imino)-5-fluoro-1'-methyl-2,4''-dioxodispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4j):



^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.02 (s, 3H, N-CH_3), 3.45 (t, 1H, CH, J = 7.2, 9.2 Hz), 3.69 (s, 3H, OCH_3), 4.38 (t, 1H, CH, J = 6.4 Hz), 4.93 (t, 1H, CH, J = 7.2, 7.6 Hz), 6.62 - 7.62 (m, 11H, Ar-H), 10.64 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 36.0, 48.9, 52.7, 53.0, 64.9 (spiro carbon), 78.9 (spiro carbon), 112.1, 113.3, 118.1, 118.4, 122.7, 129.8, 130.0, 133.6, 134.3, 140.5, 146.5, 152.9, 153.1 (aromatic carbons), 169.8, 171.3, 176.8 (three C=O) ppm; MS (m/z): 599.06

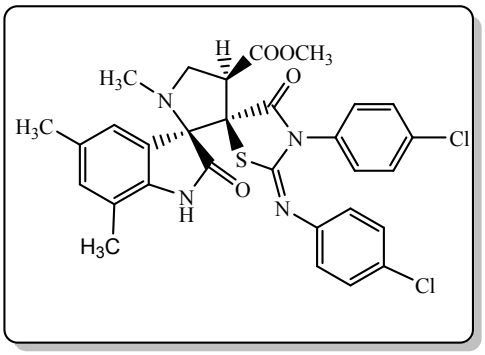
[M+H]$^+$; Anal. calcd. for $C_{28}H_{21}Cl_2FN_4O_4S$: C 56.10; H 3.53; N 9.35 %. Found: C 56.25, H 3.58, N 9.38 %.

Methyl-3''-(4-chlorophenyl)-2''-(4-chlorophenyl)imino)-5-bromo-1'-methyl-2,4''-dioxodispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4k):



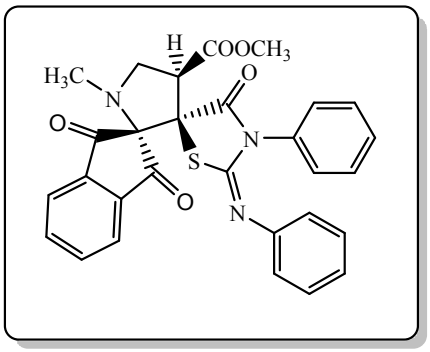
^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.97 (s, 3H, N-CH_3), 3.56 (t, 1H, CH, *J* = 8.8 Hz), 3.78 (s, 3H, OCH_3), 4.22 (t, 1H, CH, *J* = 8.4 Hz), 4.72 (t, 1H, CH, *J* = 7.2, 8.4 Hz), 7.08-7.76 (m, 11H, Ar-H), 10.47 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 36.8, 50.5, 52.7, 53.2, 66.2 (spiro carbon), 74.2 (spiro carbon), 110.8, 120.5, 125.1, 127.8, 129.5, 134.5, 137.2, 143.8, 157.2, 159.6, (aromatic carbon), 169.0, 173.4, 177.8 (three C=O) ppm; MS (m/z): 659.98 [M+H]$^+$; Anal. calcd. for $C_{28}H_{21}BrCl_2N_4O_4S$: C 50.93; H 3.21; N 8.48 %. Found: C 50.77, H 3.26, N 8.45 %.

Methyl-3''-(4-chlorophenyl)-2''-(4-chlorophenyl)imino)-1',5,7-trimethyl-2,4''-dioxodispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (4l):



^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.98 (s, 3H, N-CH_3), 2.12 (s, 3H,CH_3), 2.17 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 3.74 (t, 1H, CH, *J*= 8.8 Hz), 4.11 (t, 1H, CH, *J*= 8.4 Hz), 4.93 (t, 1H, CH, *J* = 7.2 Hz),6.61-7.30 (m, 10H, Ar-H), 10.69 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 16.7, 21.1, 35.5, 49.5, 52.5, 53.7, 66.3 (spiro carbon), 79.8 (spiro carbon), 116.4, 116.6, 119.6, 122.5, 122.6, 124.9, 126.0, 130.7, 133.0, 140.6, 144.4, 153.8, 158.4, 160.9 (aromatic carbons), 170.0, 173.2, 176.8 (three C=O) ppm; MS (m/z): 609.11 [M+H]$^+$; Anal. calcd. for $C_{30}H_{26}Cl_2N_4O_4S$: C 59.12; H 4.30; N 9.19 %. Found: C 59.27, H 4.35, N 9.16 %.

Methyl-1'-methyl-1,3,4''-trioxo-3''-phenyl-2''-(phenylimino)-1,3-dihydrodispiro[indene-2,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (7a):

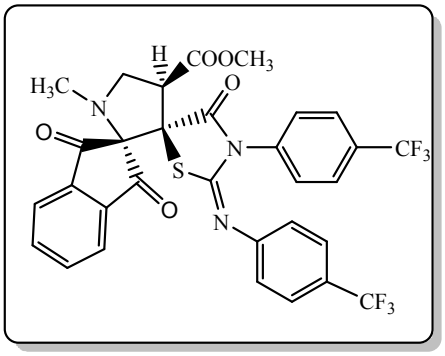


^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.31 (s, 3H, N-CH_3), 3.53 (t, 1H, CH, *J* = 9.2 Hz), 3.74 (t, 1H, CH, *J* = 7.2, 8.4 Hz), 3.76 (s, 3H, OCH_3), 4.69 (t, 1H, CH, *J* = 7.6, 8 Hz), 6.84 – 8.02 (m, 14H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.5, 51.8, 52.6, 52.8, 69.0 (spiro carbon), 79.92 (spiro

carbon), 120.9, 123.4, 123.6, 124.9, 127.4, 129.08, 129.3, 129.3, 136.0, 137.3, 147.5 (aromatic carbons), 168.8, 170.1, 194.4, 198.1 (four C=O) ppm; MS (m/z): 526.14 $[M+H]^+$; Anal. calcd. for $C_{29}H_{23}N_3O_5S$: C 66.27; H, 4.41; N, 8.00%. Found: C 66.42, H 4.46, N 8.03 %.

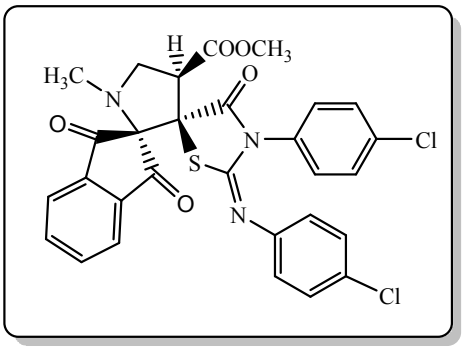
Methyl-1'-methyl-1,3,4''-trioxo-3''-(4-(trifluoromethyl)phenyl)-2''-(4-(trifluoromethyl)phenyl)imino)-1,3-dihydrodispiro[indene-2,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (7b):

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.26 (s, 3H, N-CH_3), 3.11 (t, 1H, CH, *J* = 7.2, 9.2 Hz), 3.30 (t, 1H, CH, *J* = 6.4 Hz), 3.43 (s, 3H, OCH_3), 4.27 (t, 1H, CH, *J* = 7.6 Hz), 6.82 – 8.18 (m, 12H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.6, 51.1, 52.3, 52.5, 69.2 (spiro carbon), 79.9 (spiro carbon), 120.9, 121.9, 124.7, 127.7, 128.8, 129.0, 129.2, 129.9, 129.9, 130.5, 130.8, 144.4, 152.4, 153.9, 161.0 (aromatic carbons), 172.1, 174.2, 192.6, 196.5 (four C=O) ppm; MS (m/z): 662.11 $[M+H]^+$; Anal. calcd. for $C_{31}H_{21}F_6N_3O_5S$: C 56.28; H, 3.20; N, 6.35%. Found: C 56.43, H 3.25, N 6.32 %.

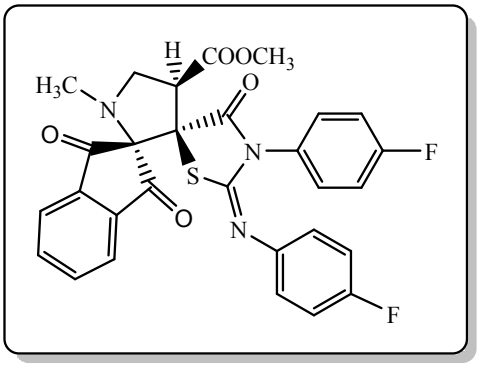


Methyl-3''-(4-chlorophenyl)-2''-(4-chlorophenyl)imino)-1'-methyl-1,3,4''-trioxo-1,3-dihydrodispiro[indene-2,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (7c):

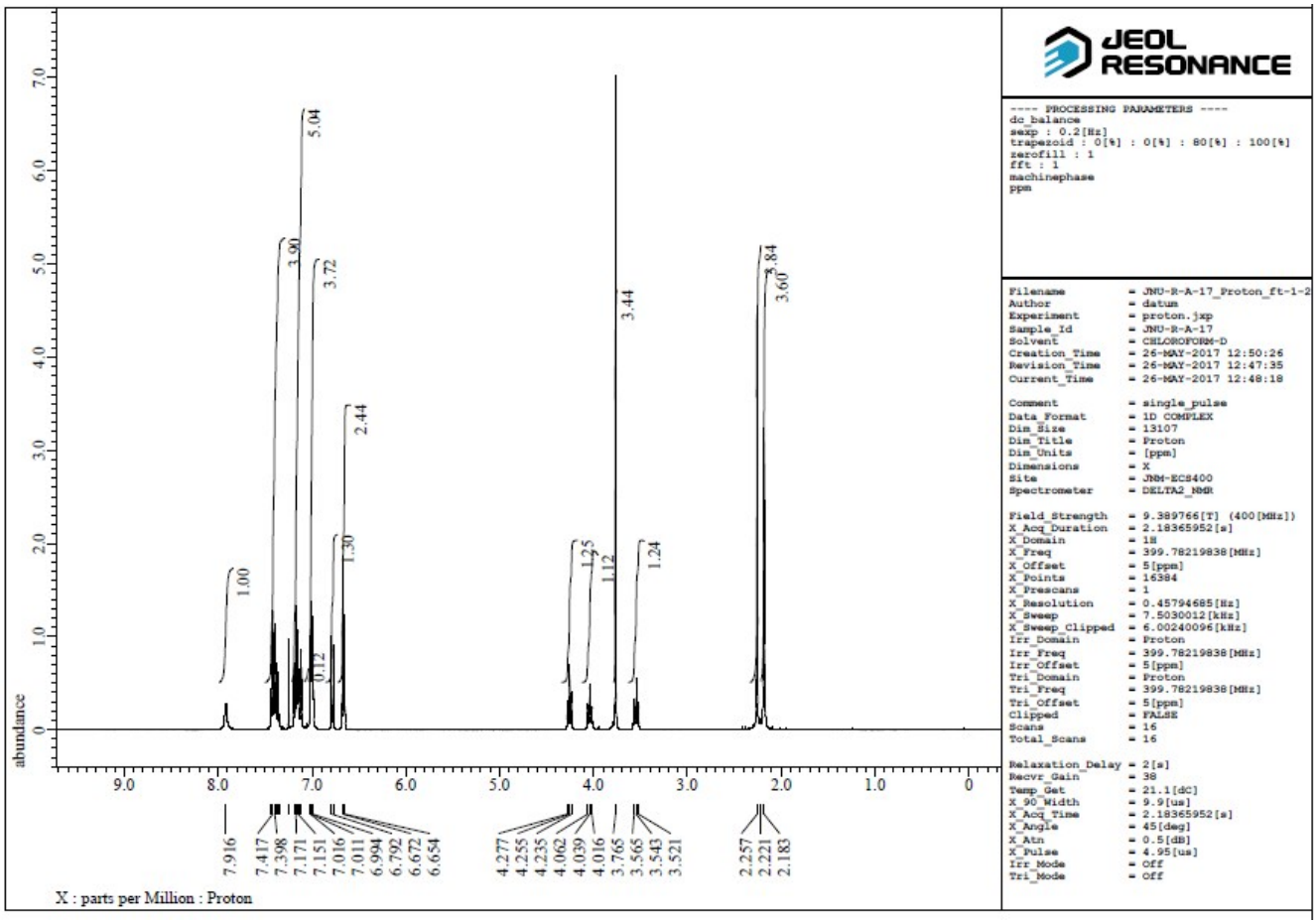
^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.17 (s, 3H, N-CH_3), 3.64 (s, 3H, OCH_3), 3.75 (t, 1H, CH, *J*= 8 Hz), 4.10 (t, 1H, CH, *J* = 7.4 Hz), 4.72 (t, 1H, CH, *J*= 8.6, 9.2 Hz), 6.54 – 8.32 (m, 12H, Ar-H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 35.8, 50.8, 54.5, 55.2, 67.2 (spiro carbon), 75.2 (spiro carbon), 121.9, 124.1, 127.1, 128.2, 129.5, 129.6, 130.5, 133.3, 136.7, 140.3, 156.8 (aromatic carbons), 172.1, 174.2, 192.6, 196.8 (four C=O) ppm; MS (m/z): 595.46 $[M+H]^+$; Anal. calcd. for $C_{29}H_{21}Cl_2N_3O_5S$: C 58.59; H, 3.56; N, 7.07%. Found: C 58.34, H 3.51, N 7.05 %.



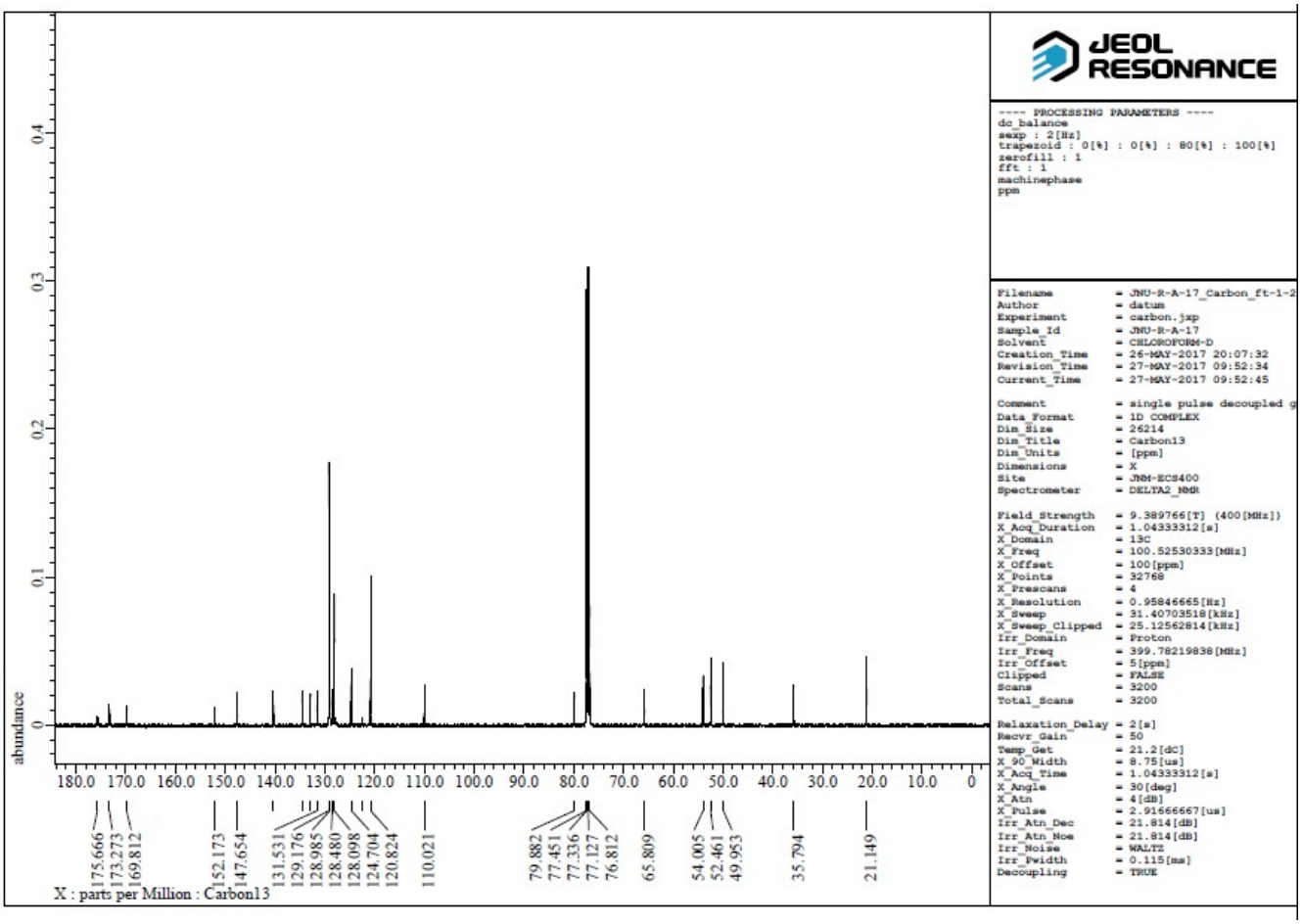
Methyl-3''-(4-fluorophenyl)-2''-(4-fluorophenyl)imino)-1'-methyl-1,3,4''-trioxo-1,3-dihydrodispiro[indene-2,2'-pyrrolidine-3',5''-thiazolidine]-4'-carboxylate (7d):



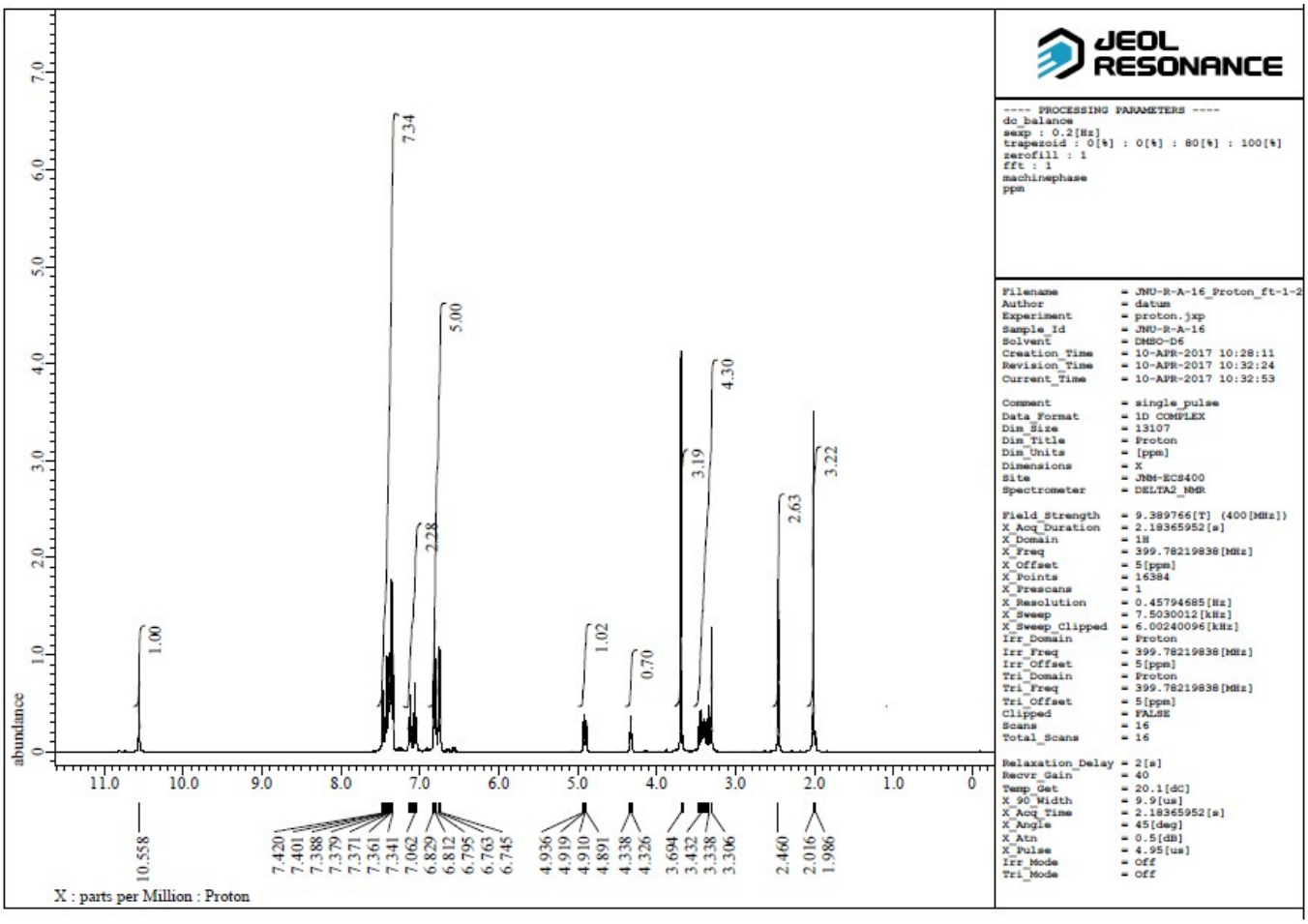
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.61 (s, 3H, N-CH_3), 3.79 (s, 3H, OCH_3), 4.03 (t, 1H, CH, *J* = 7.4 Hz), 4.23 (t, 1H, CH, *J* = 7.4 Hz), 5.11 (t, 1H, CH, *J* = 7.6 Hz), 6.76 – 7.67 (m, 12H, Ar-H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 34.5, 51.1, 52.2, 58.5, 66.8 (spiro carbon), 71.8 (spiro carbon), 110.0, 111.1, 117.5, 117.8, 122.5, 126.5, 126.6, 129.6, 130.0, 133.4, 134.2, 139.2, 146.8, 152.7 (aromatic carbons), 170.9, 172.0, 192.4, 197.6 (four C=O) ppm; MS (m/z): 562.12 $[M+H]^+$; Anal. calcd. for $C_{29}H_{21}F_2N_3O_5S$: C 62.03; H, 3.77; N, 7.48%. Found: C 62.27, H 3.72, N 7.45 %.



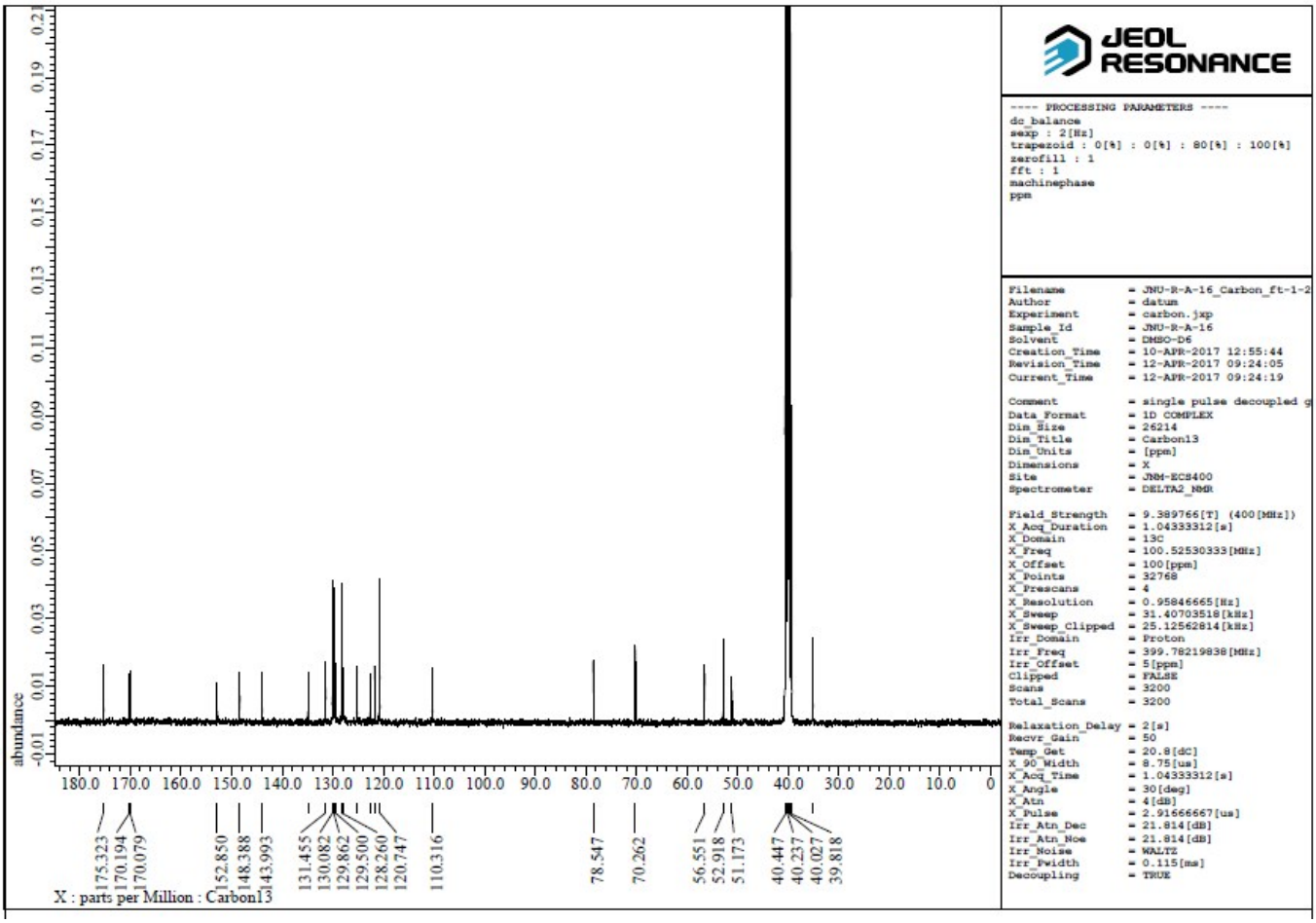
S-1: ^{1}H-NMR of 4a



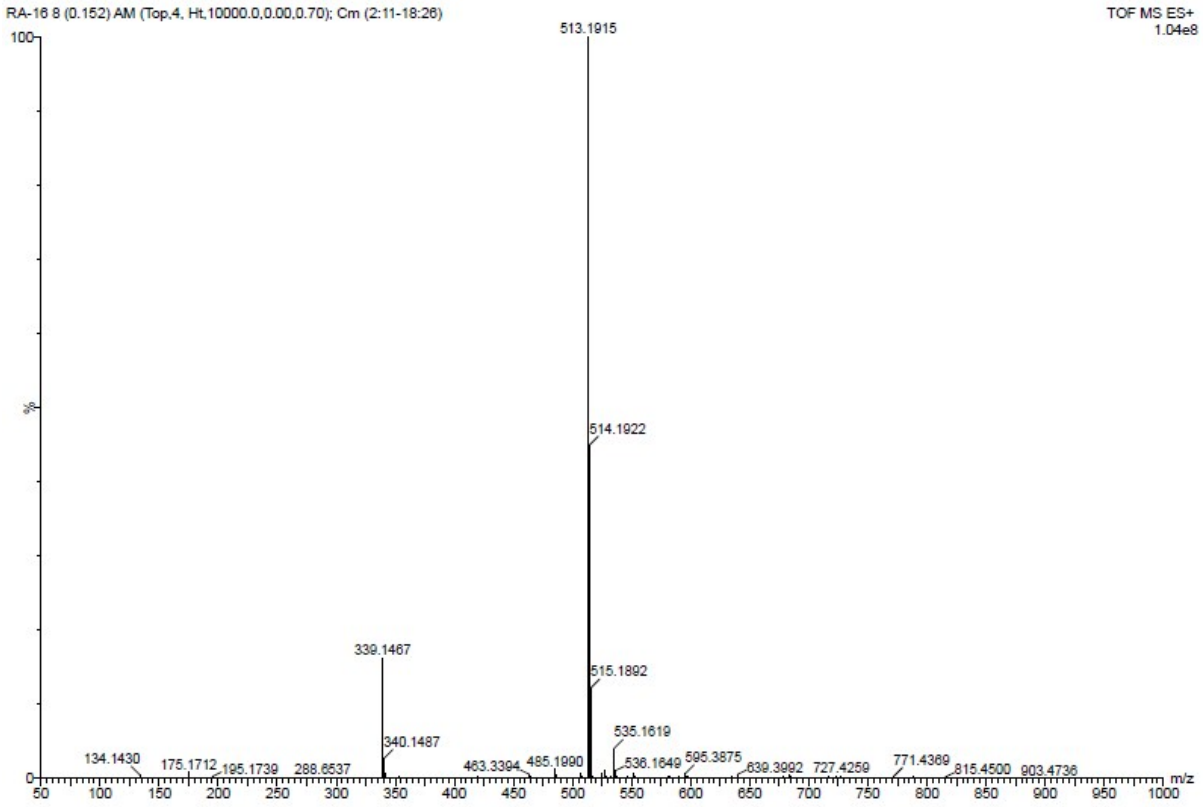
S-2: ^{13}C-NMR of 4a



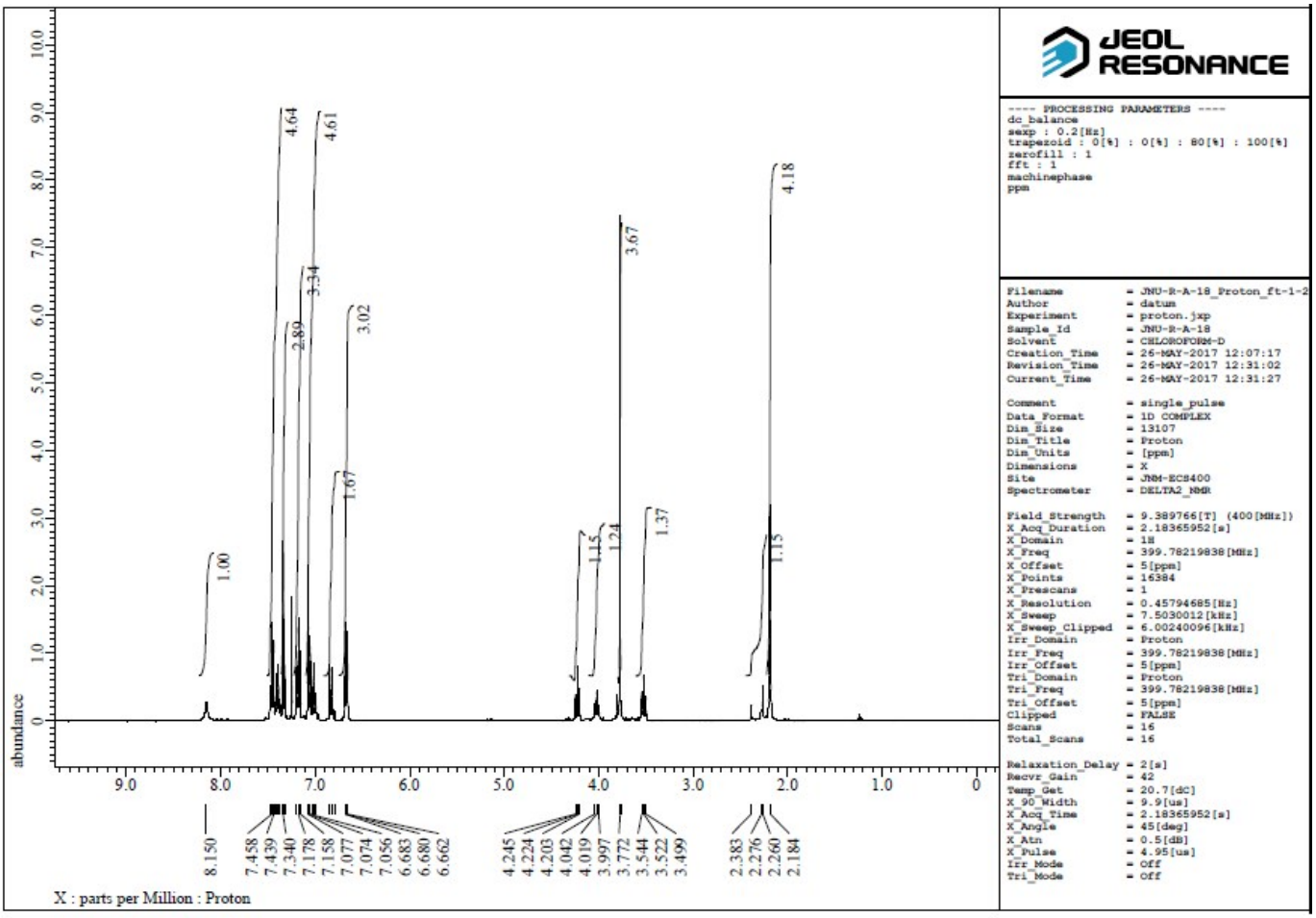
S-3: ^{1}H-NMR of 4b



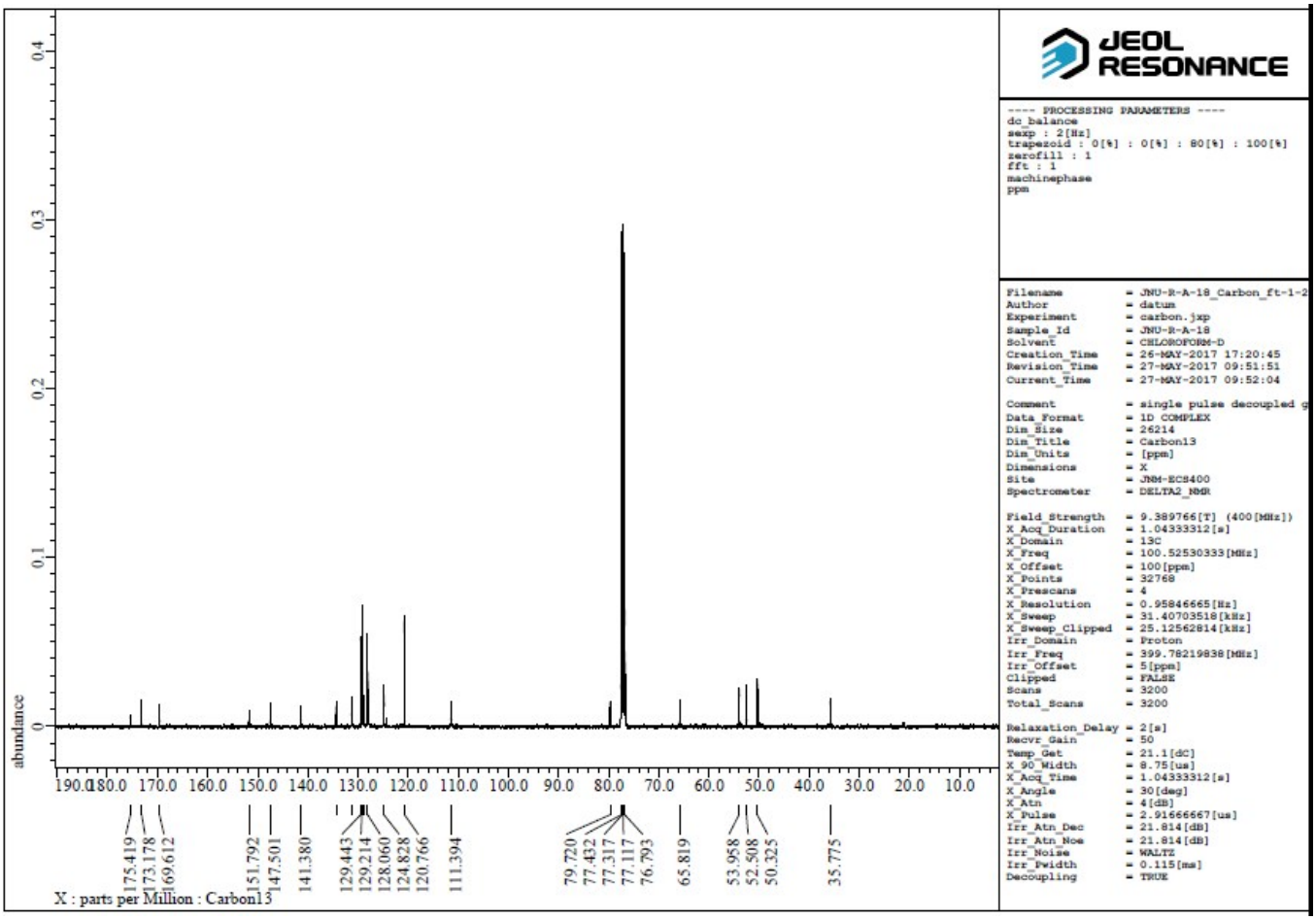
S-4: ^{13}C-NMR of 4b



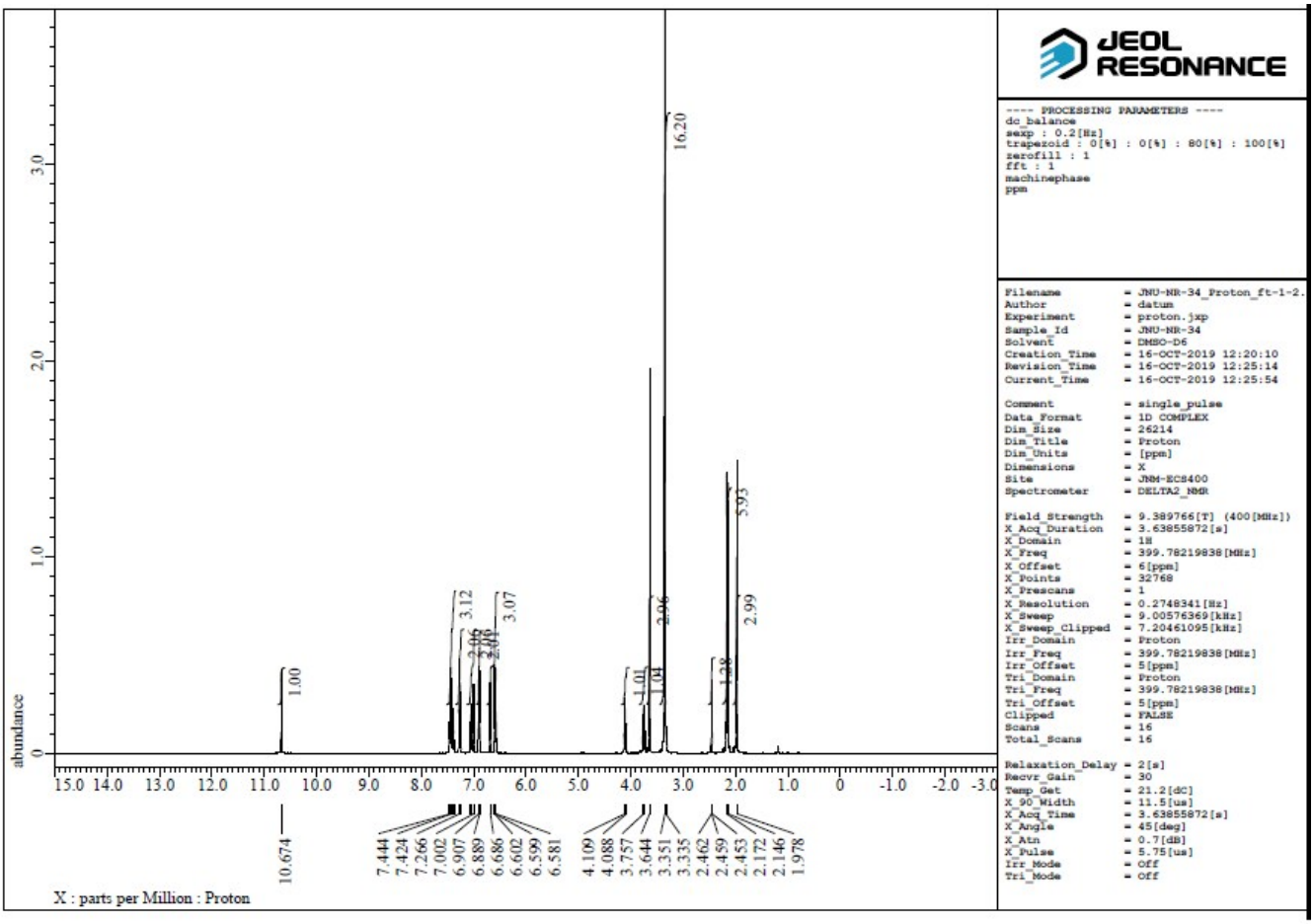
S-5: Mass spectrum of 4b



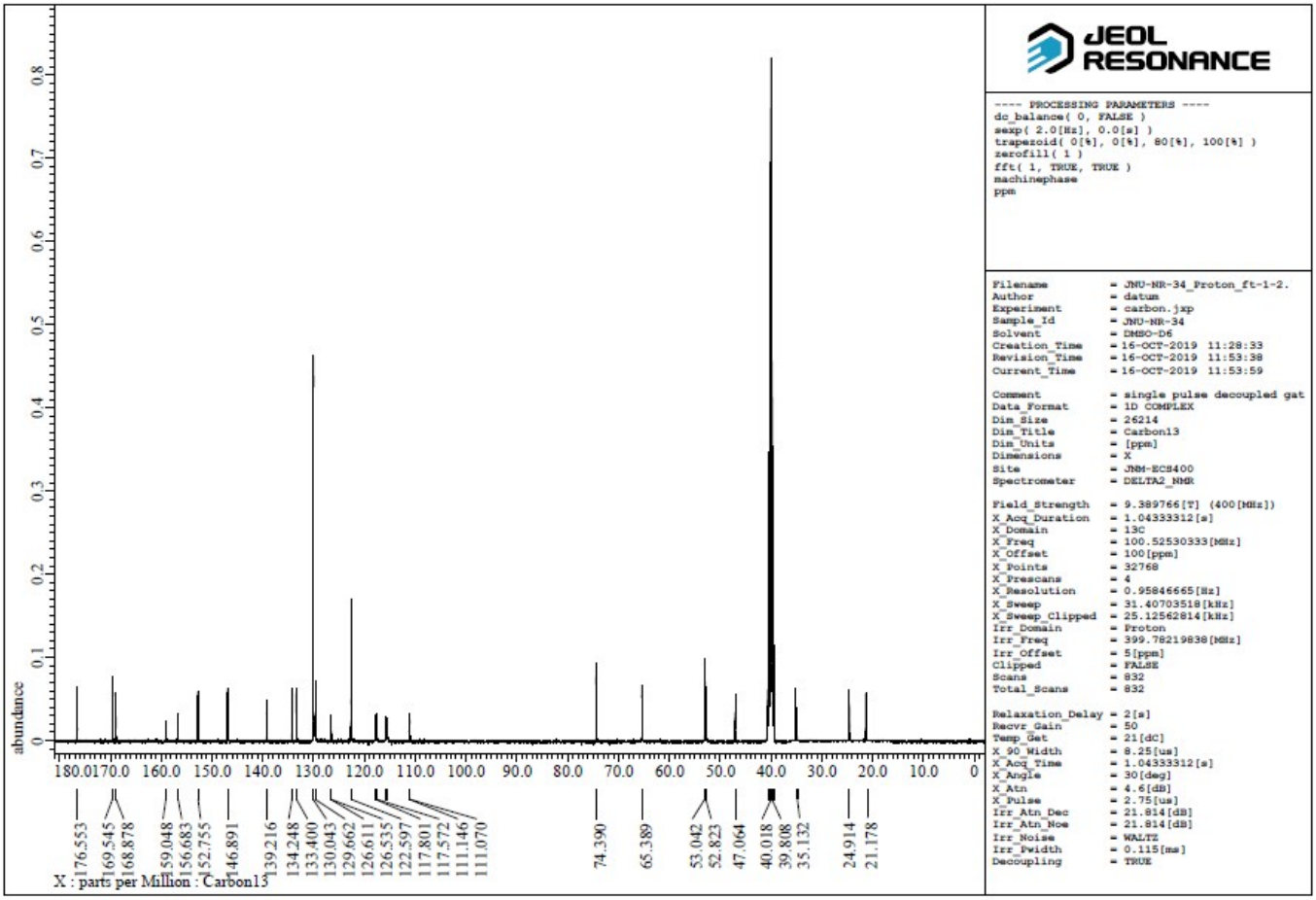
S-6: ^{1}H-NMR of 4c



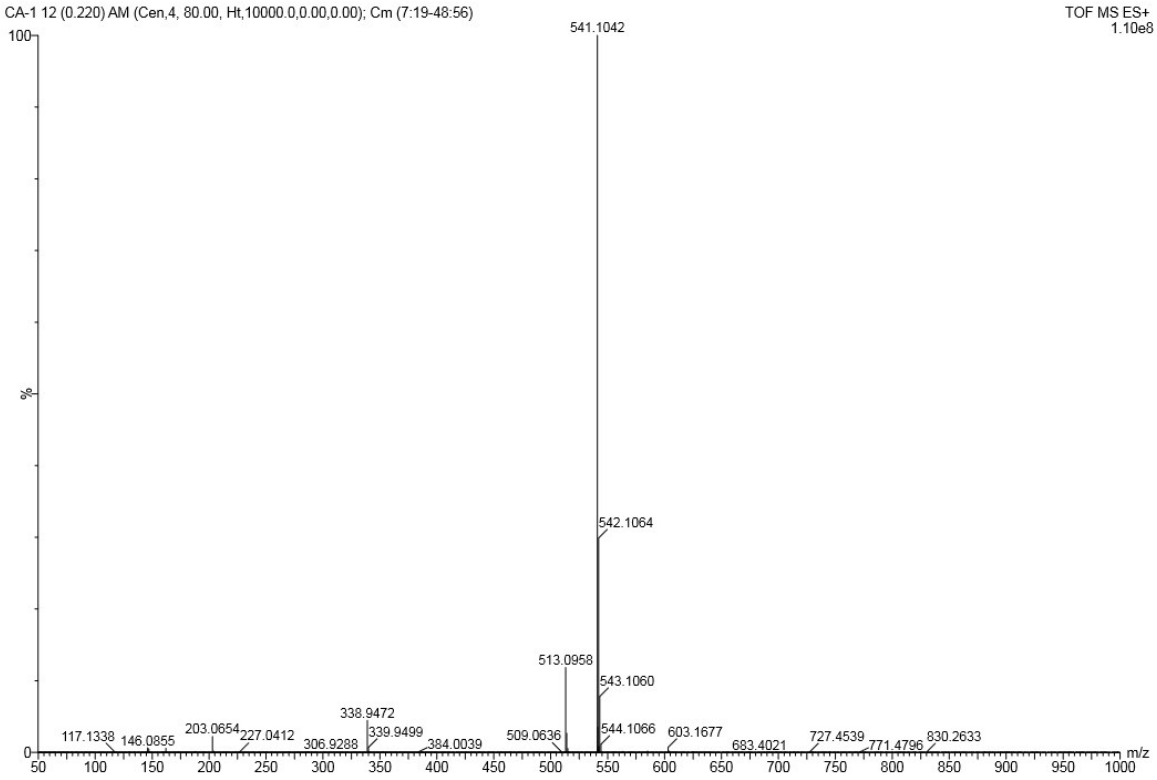
S-7: ^{13}C-NMR of 4c



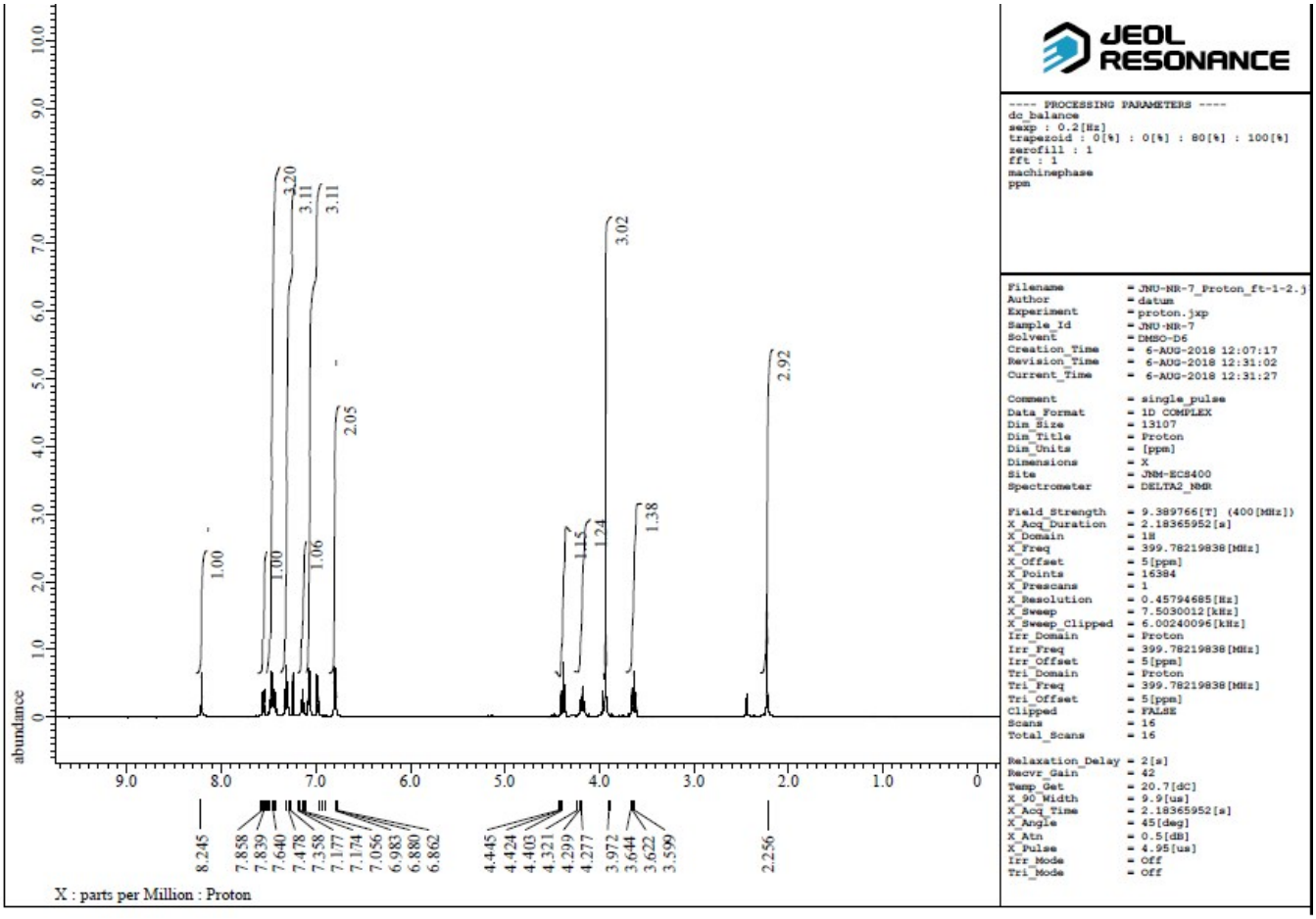
S-8: ^{1}H-NMR of 4d



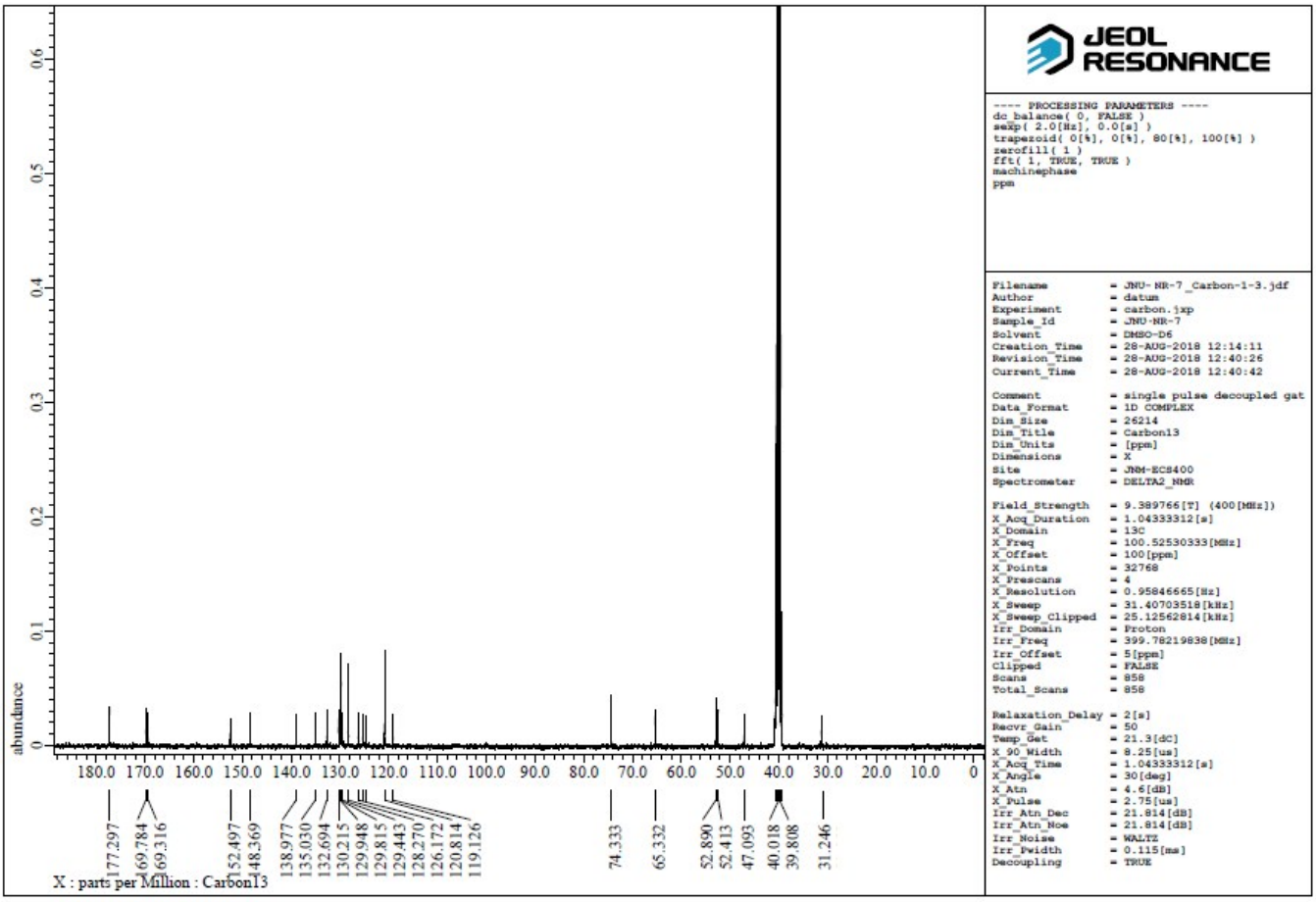
S-9: ^{13}C-NMR of 4d



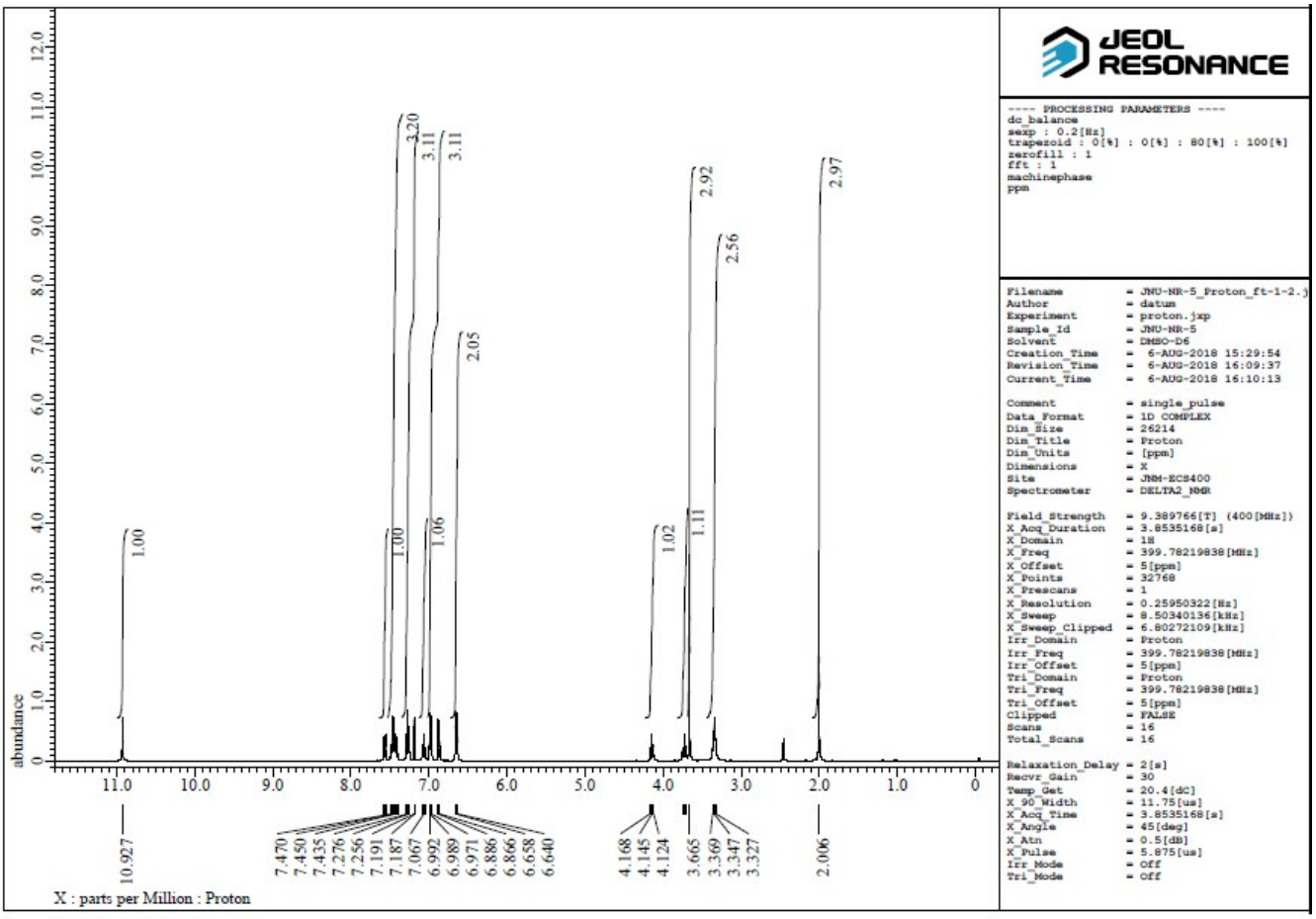
S-10: Mass spectrum of 4d



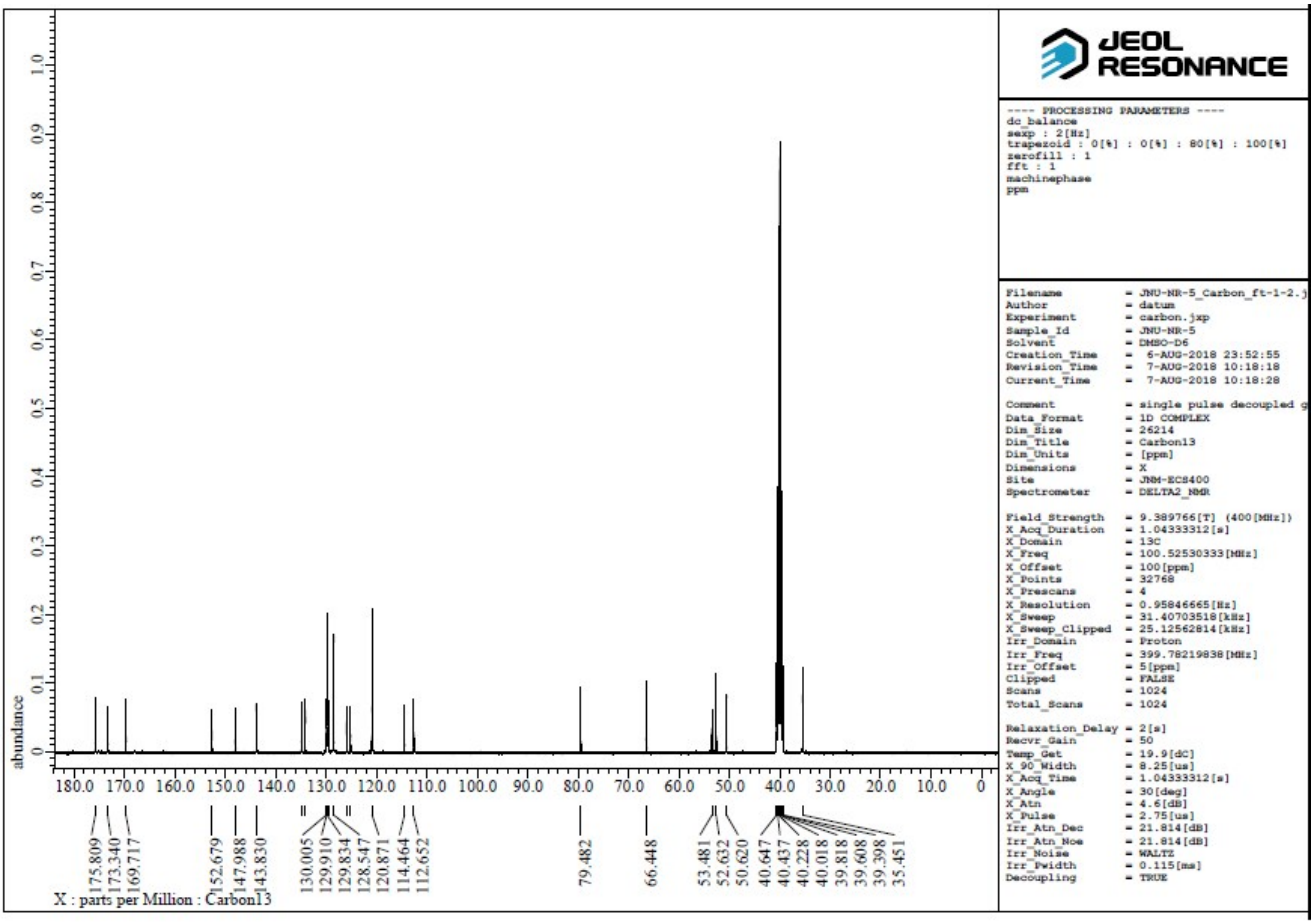
S-11: ^{1}H-NMR of 4e



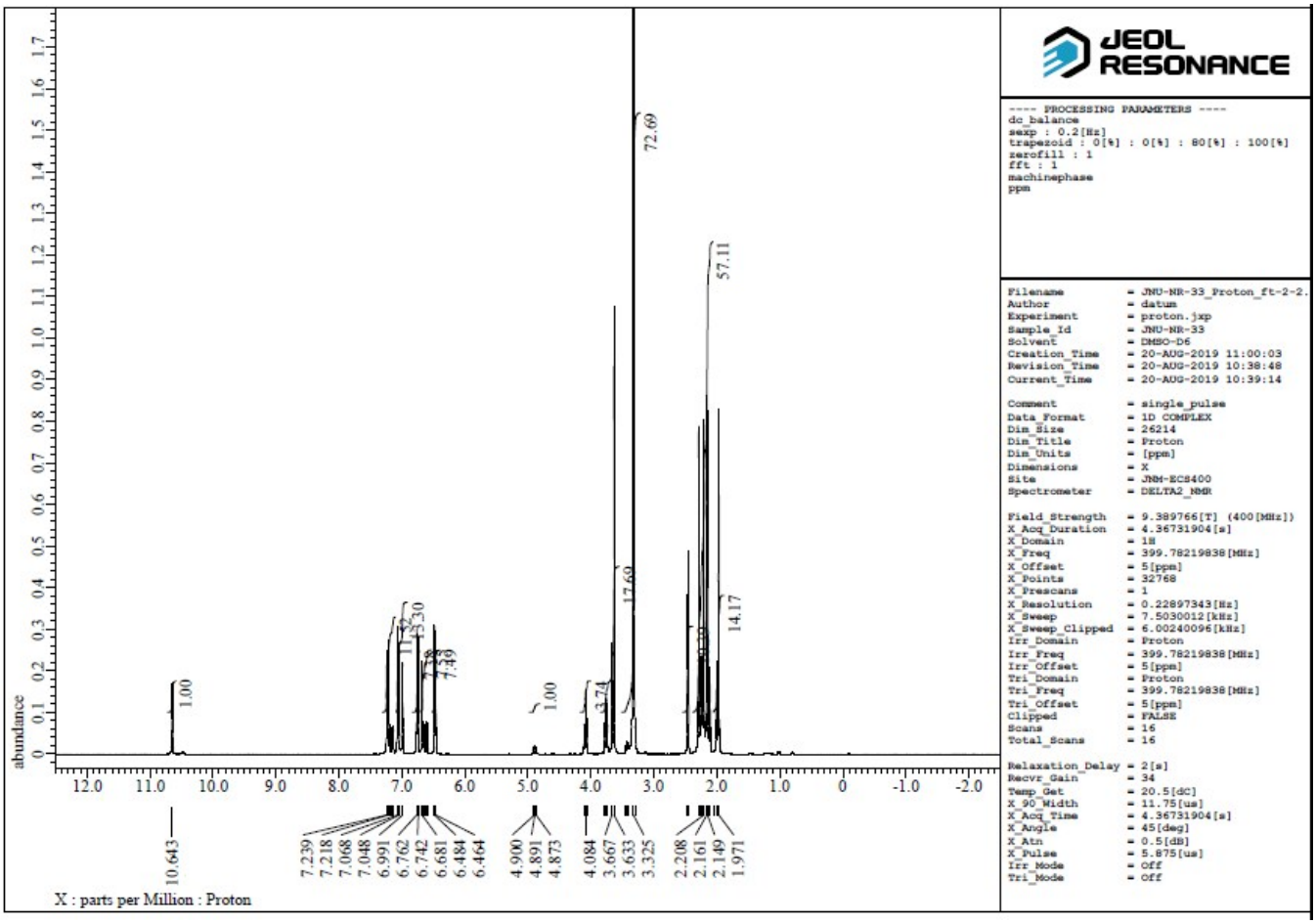
S-12: ^{13}C-NMR of 4e



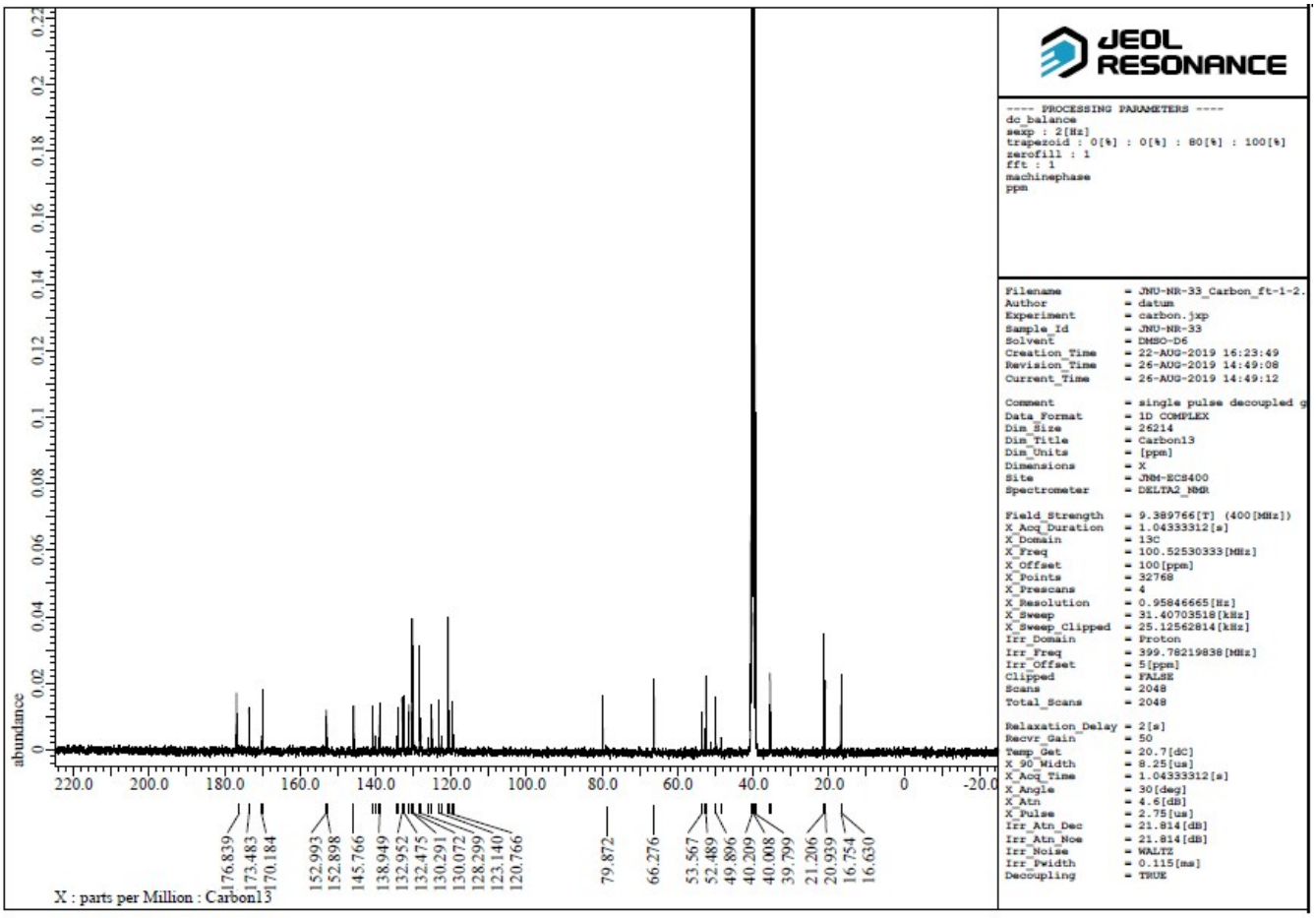
S-13: ^{1}H-NMR of 4f



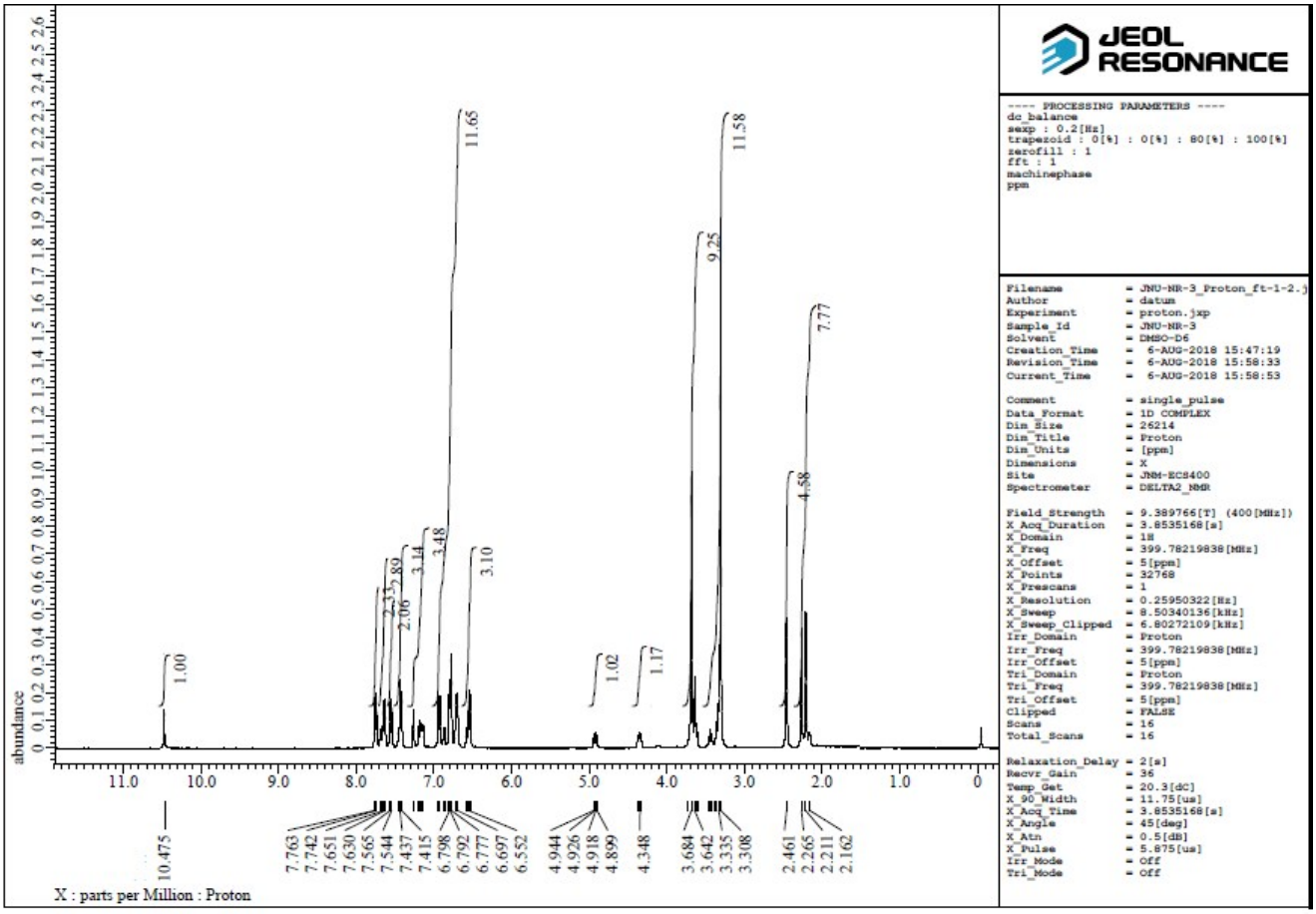
S-14: ^{13}C-NMR of 4f



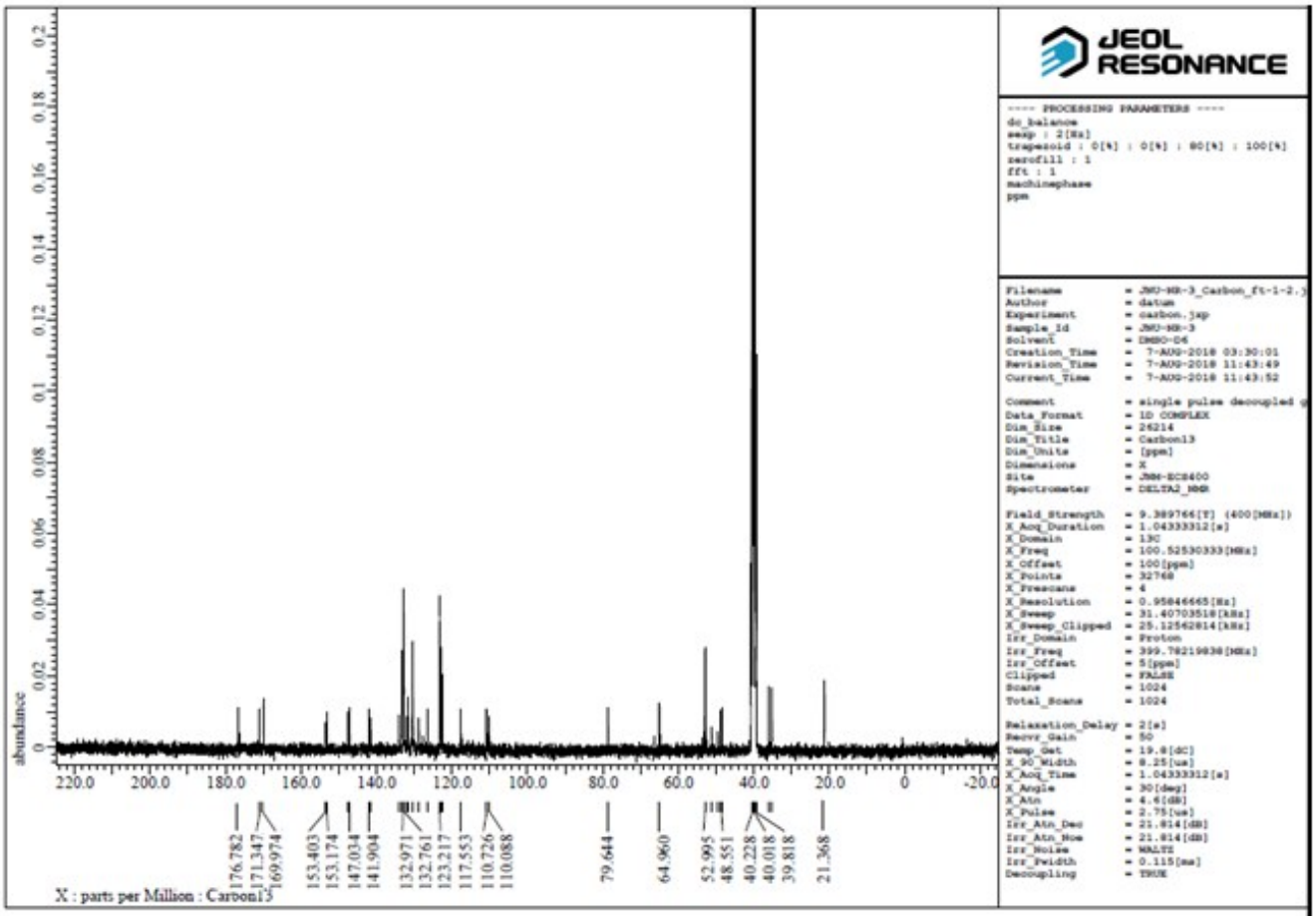
S-15: ^{1}H-NMR of 4g



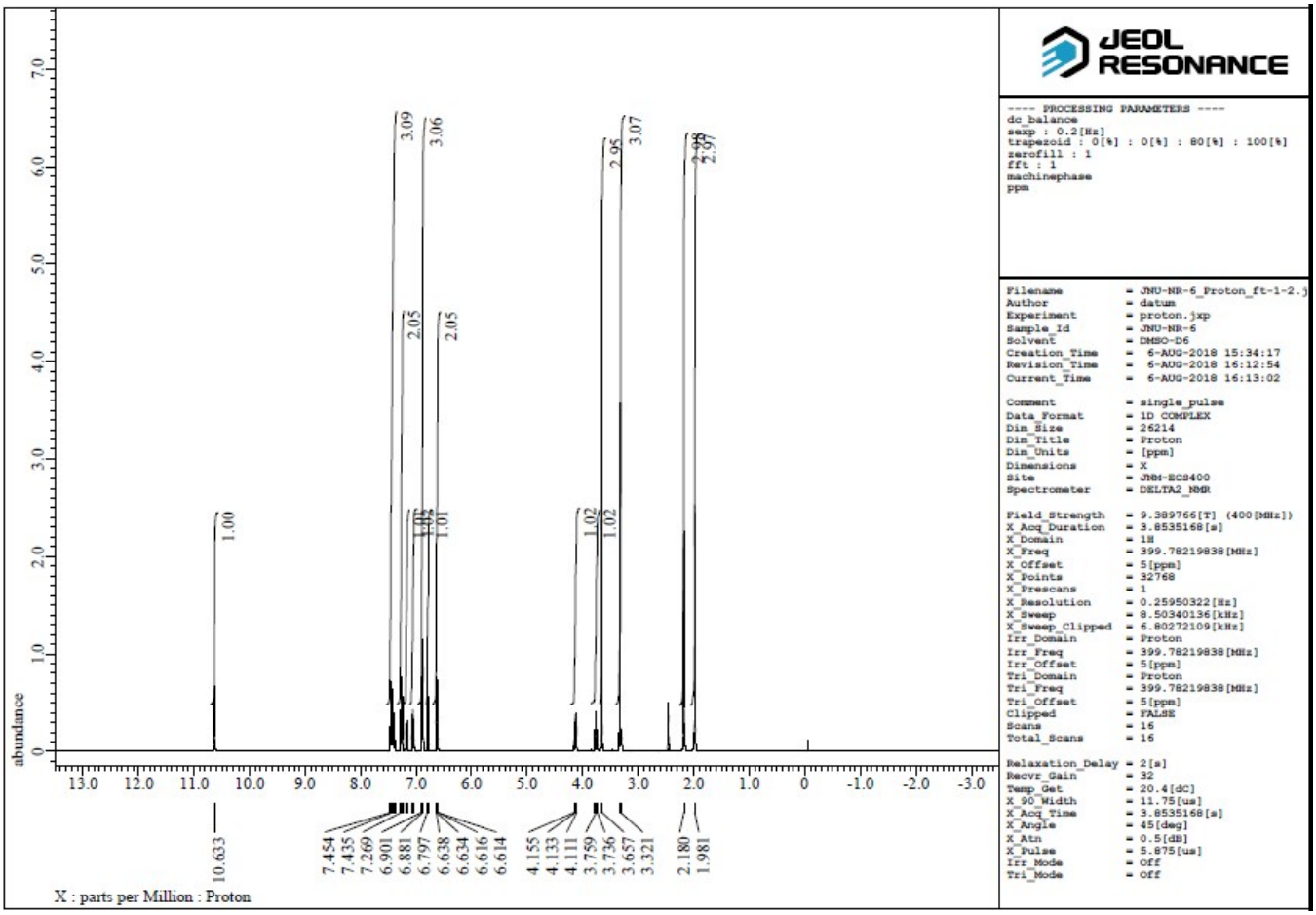
S-16: ^{13}C-NMR of 4g



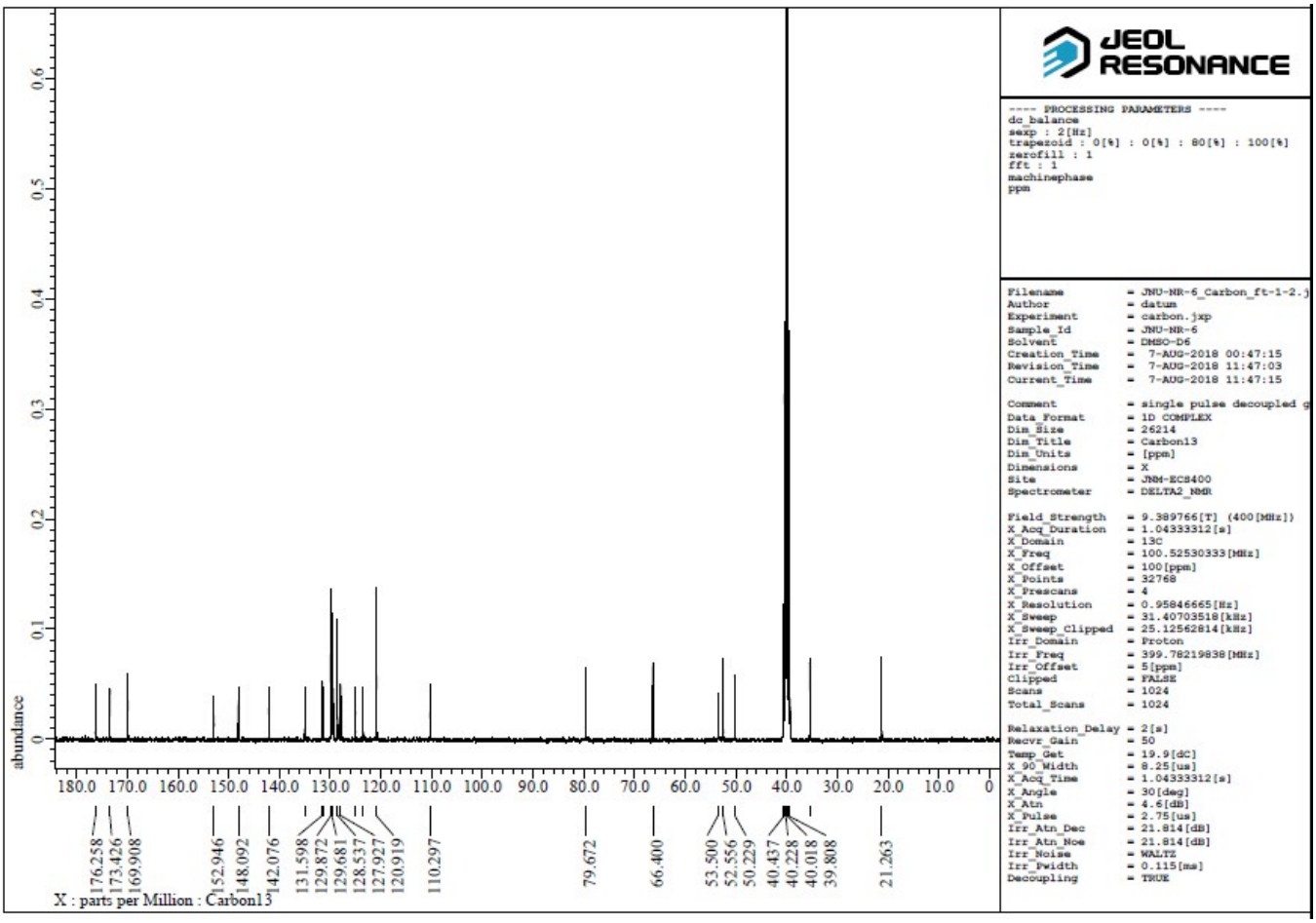
S-17: ^{1}H-NMR of 4h



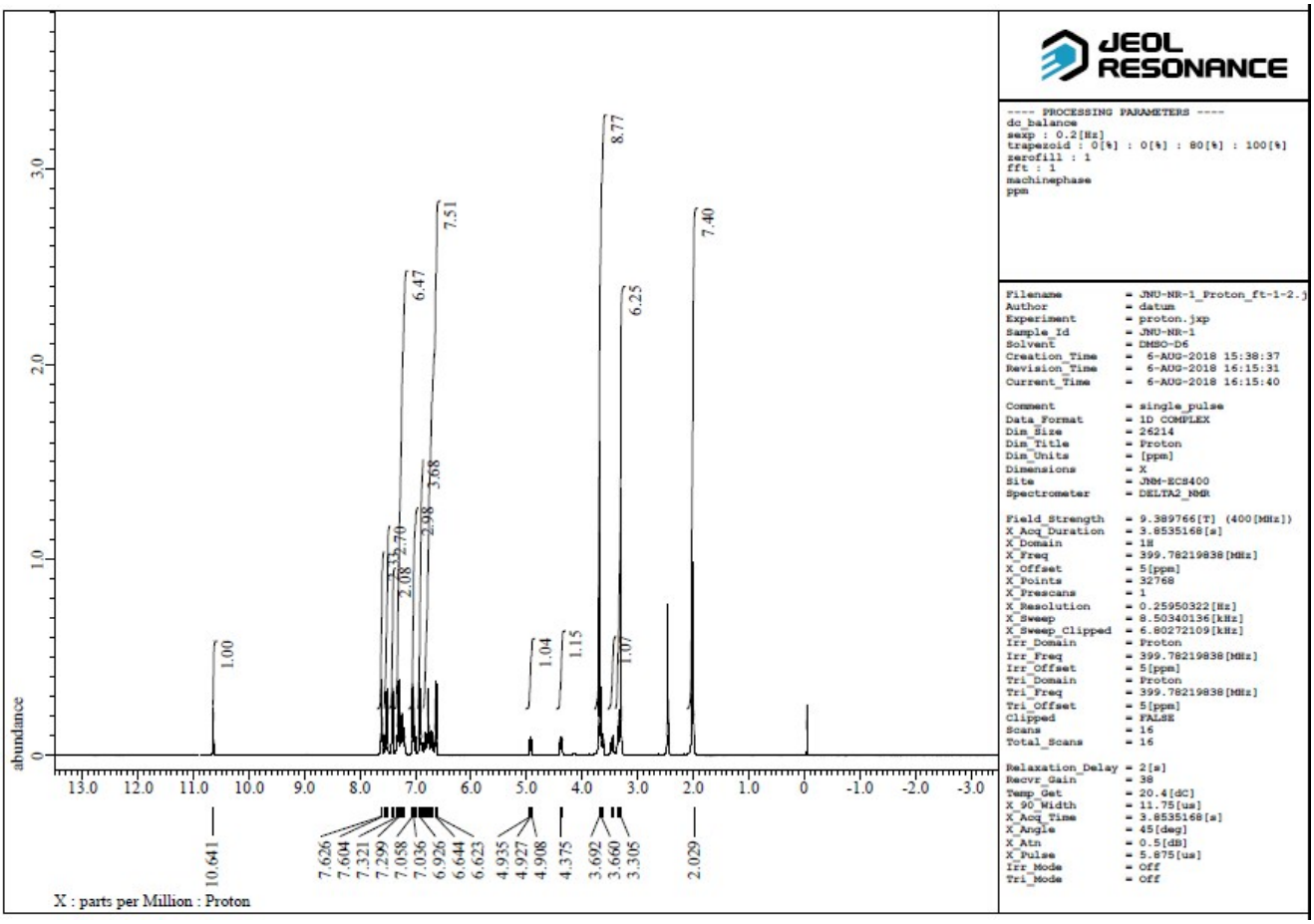
S-18: ^{13}C-NMR of 4h



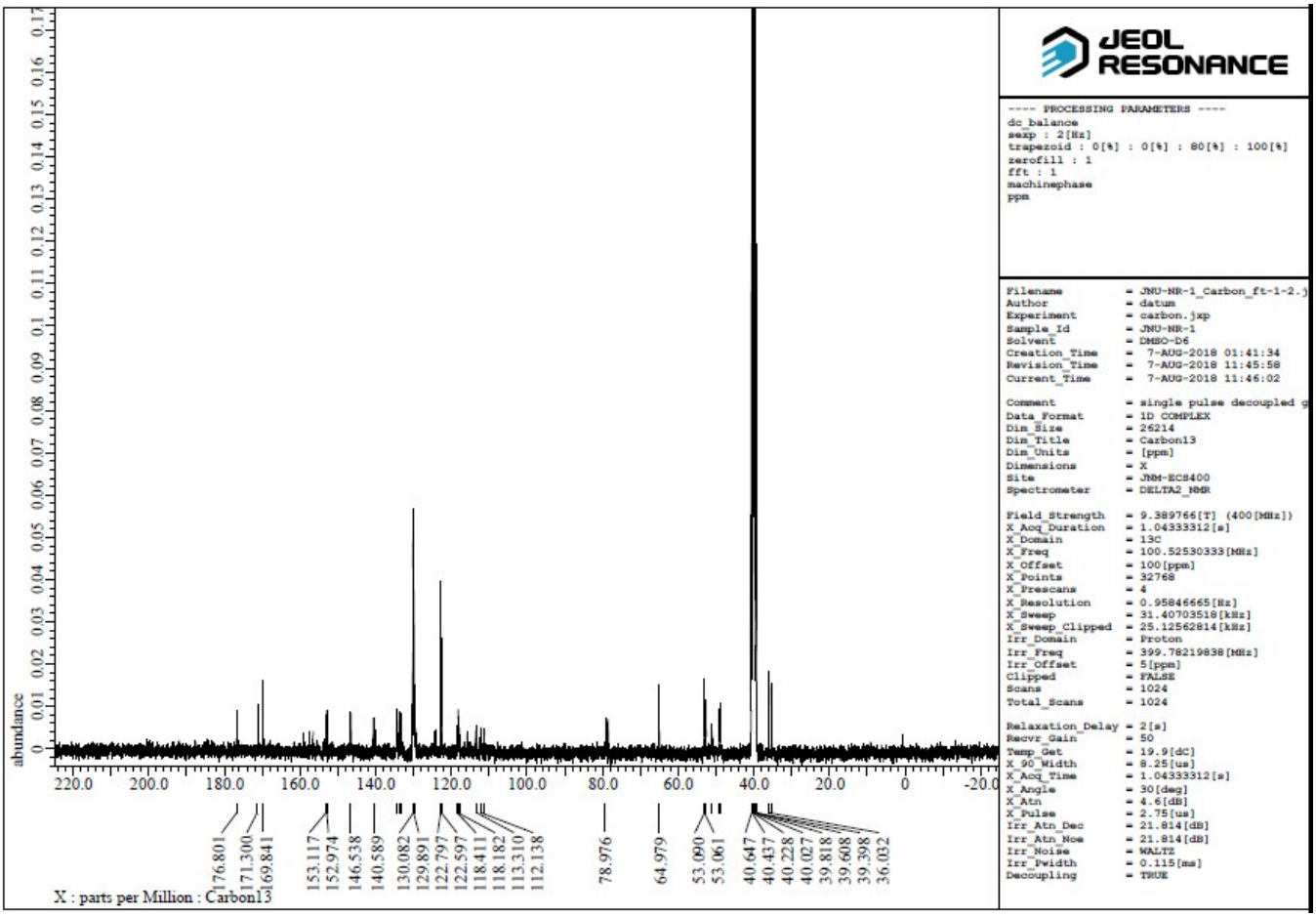
S-19: ^{1}H-NMR of 4i



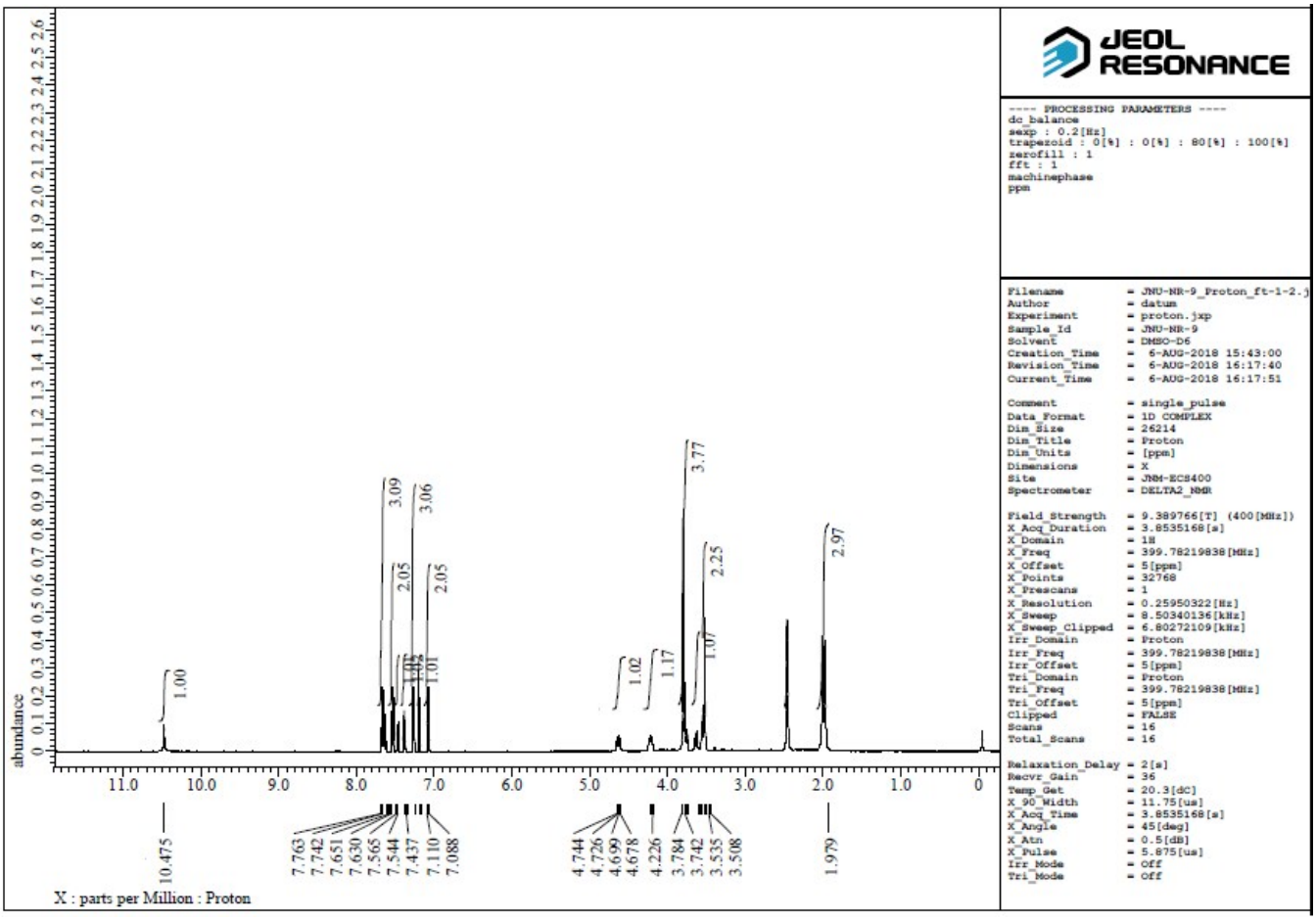
S-20: ^{13}C-NMR of 4i



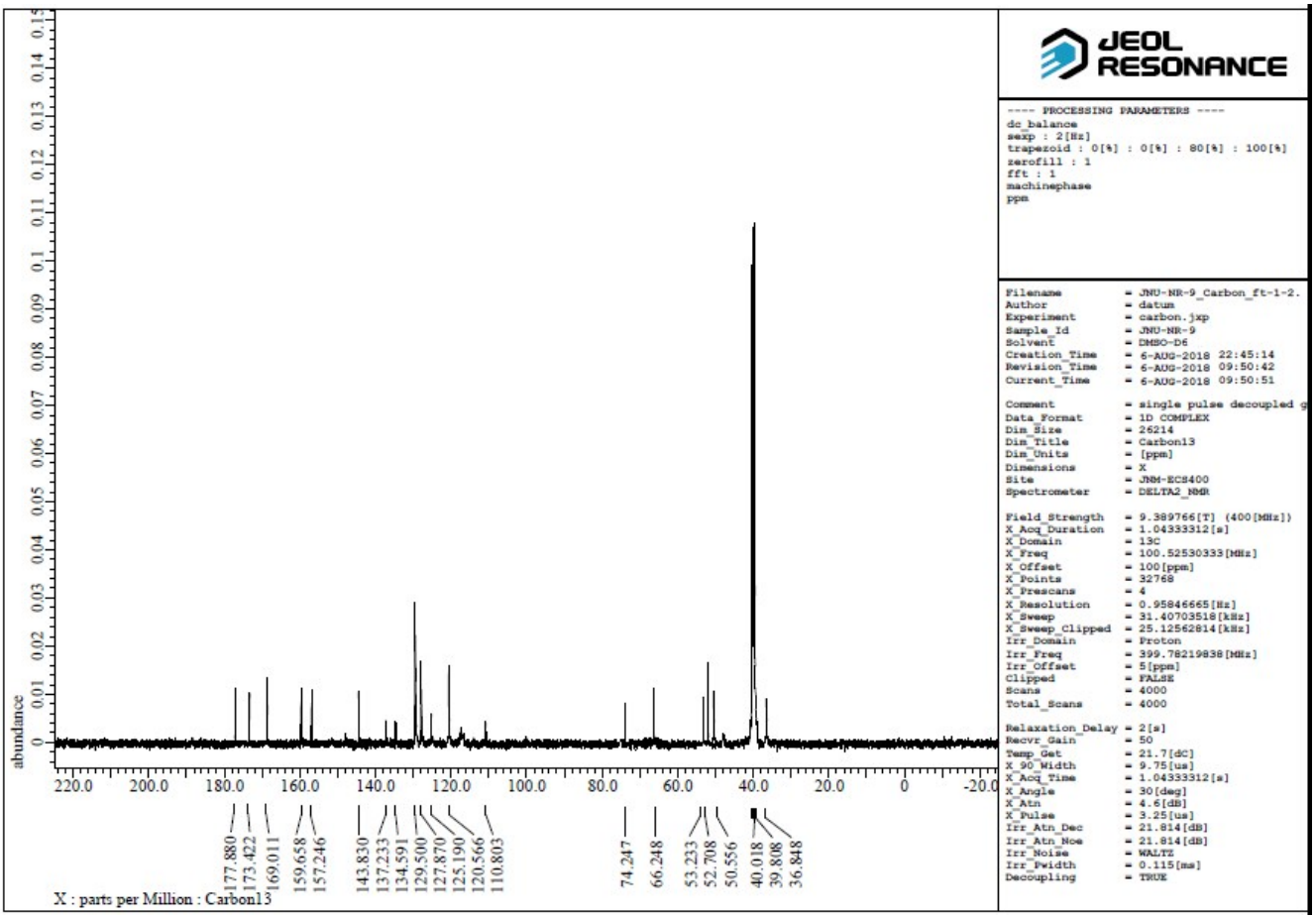
S-21: ^{1}H-NMR of 4j



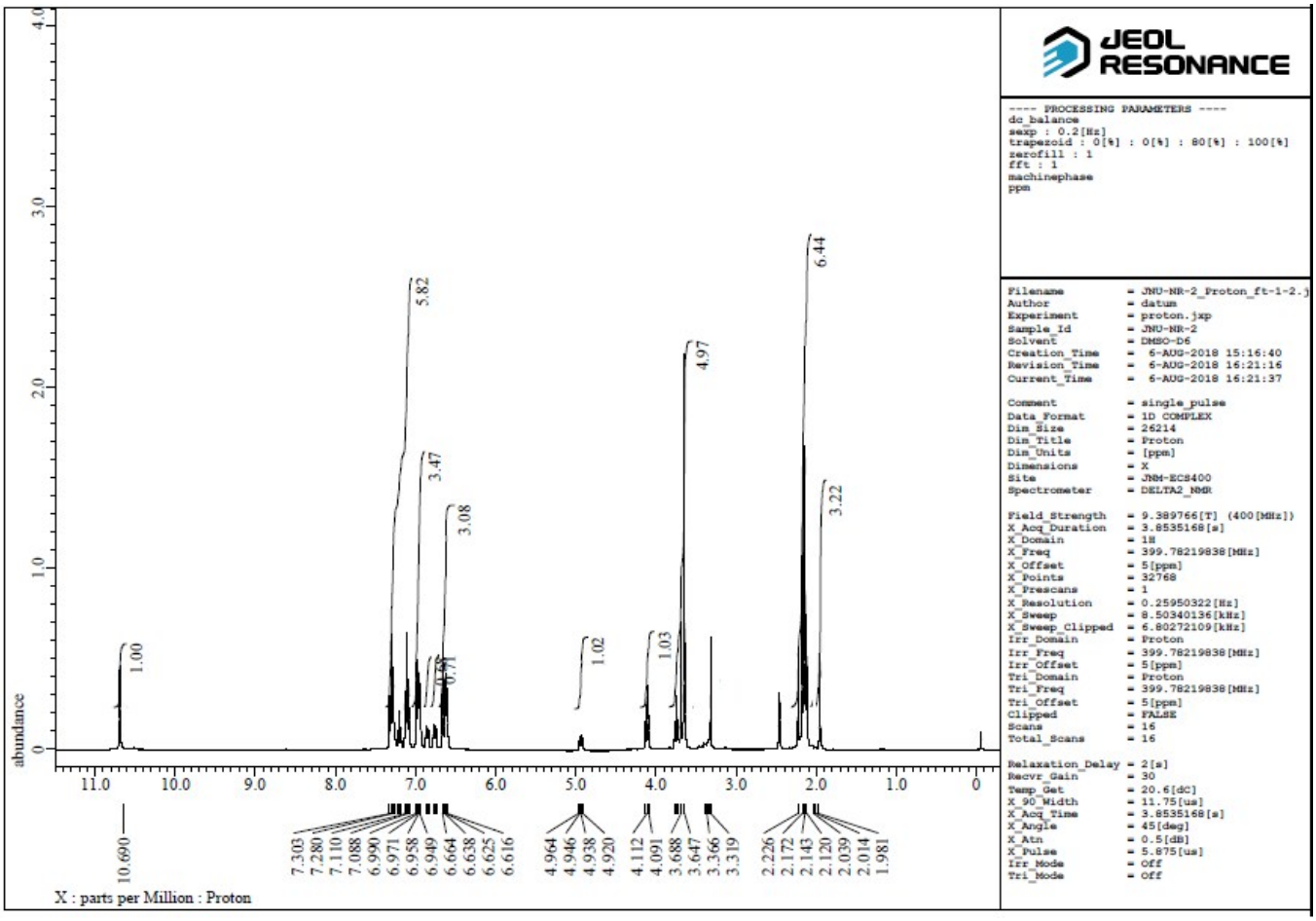
S-22: ^{13}C-NMR of 4j



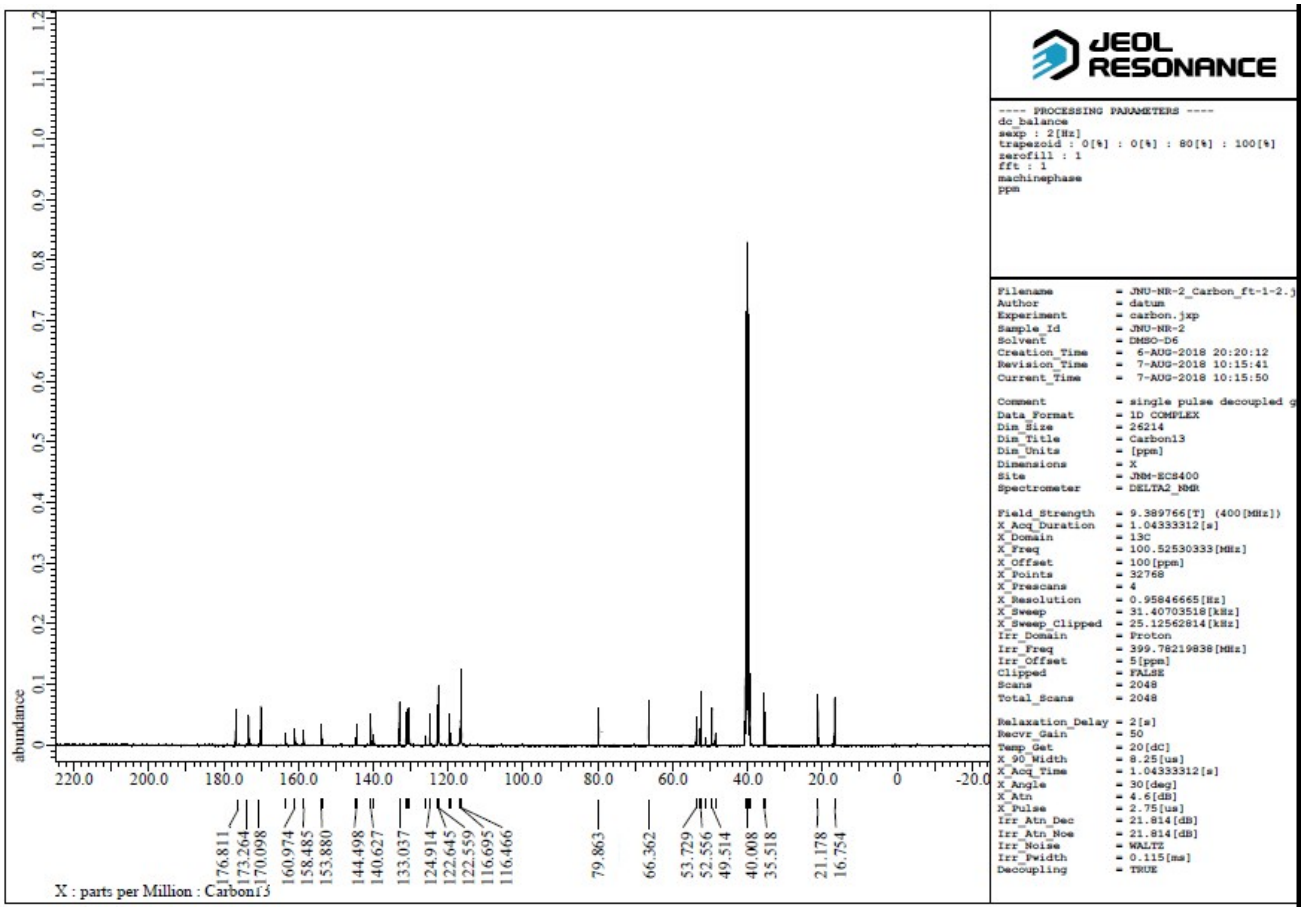
S-23: ^{1}H-NMR of 4k



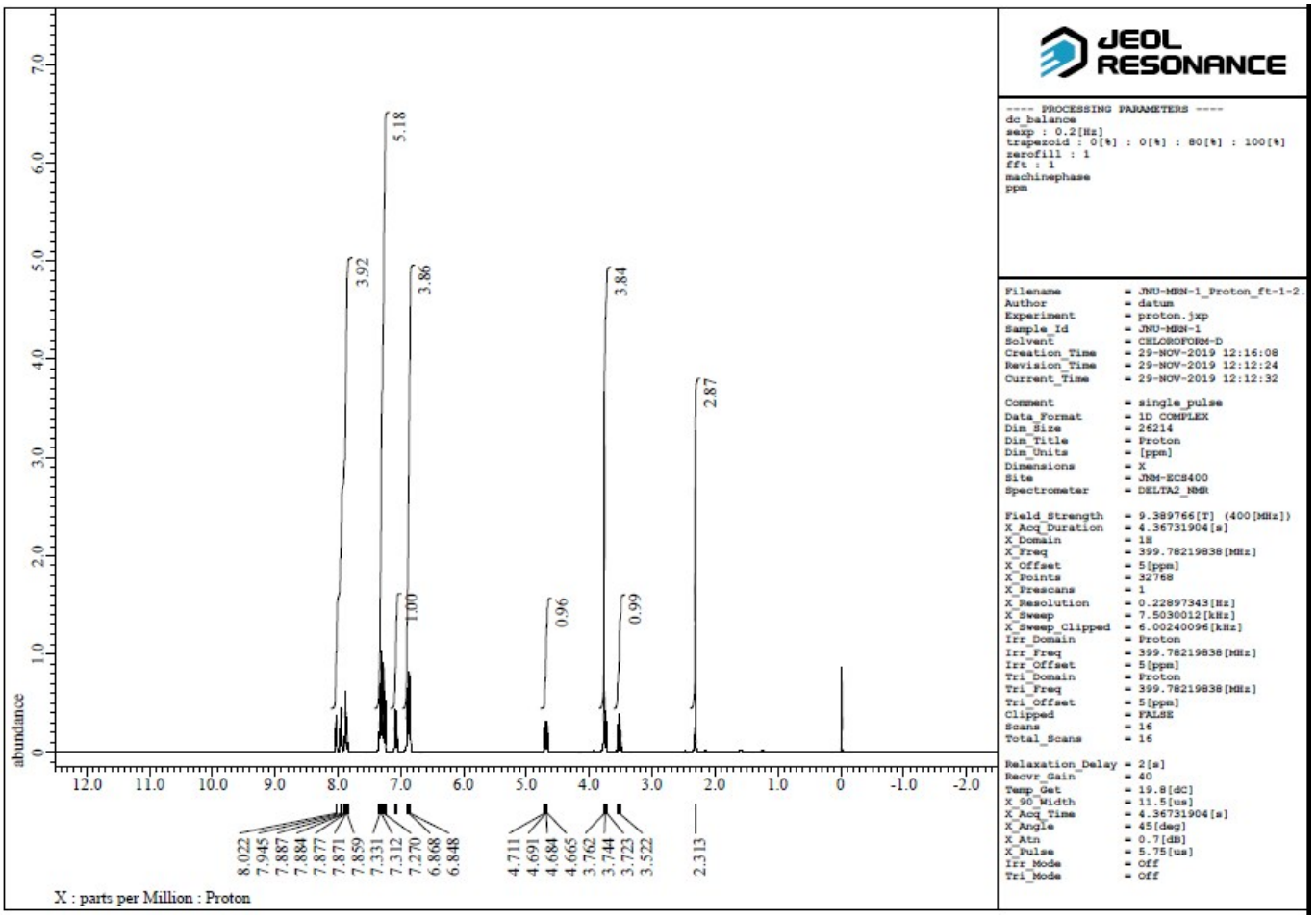
S-24: ^{13}C-NMR of 4k



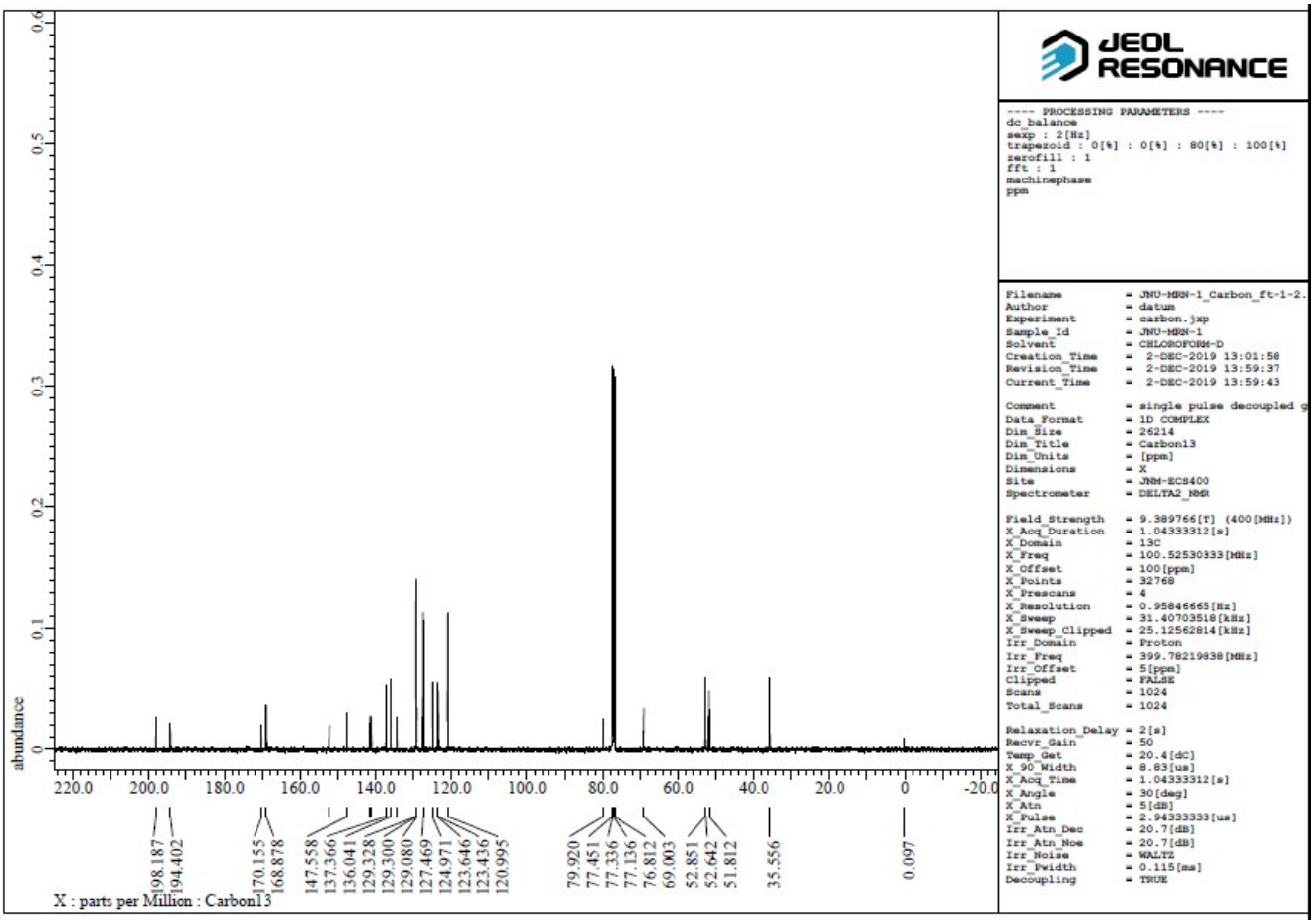
S-25: ^{1}H-NMR of 4l



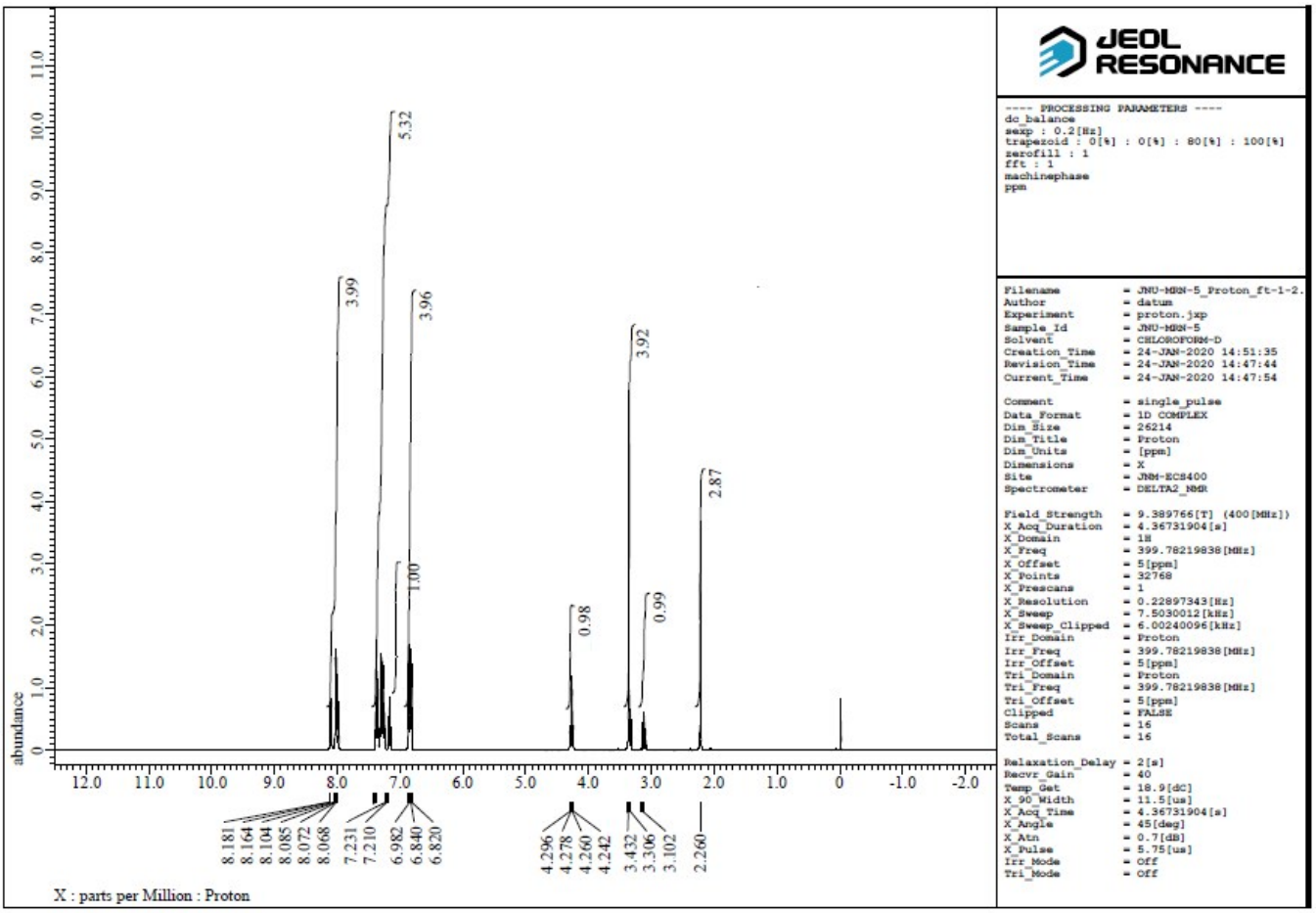
S-26: ^{13}C-NMR of 4l



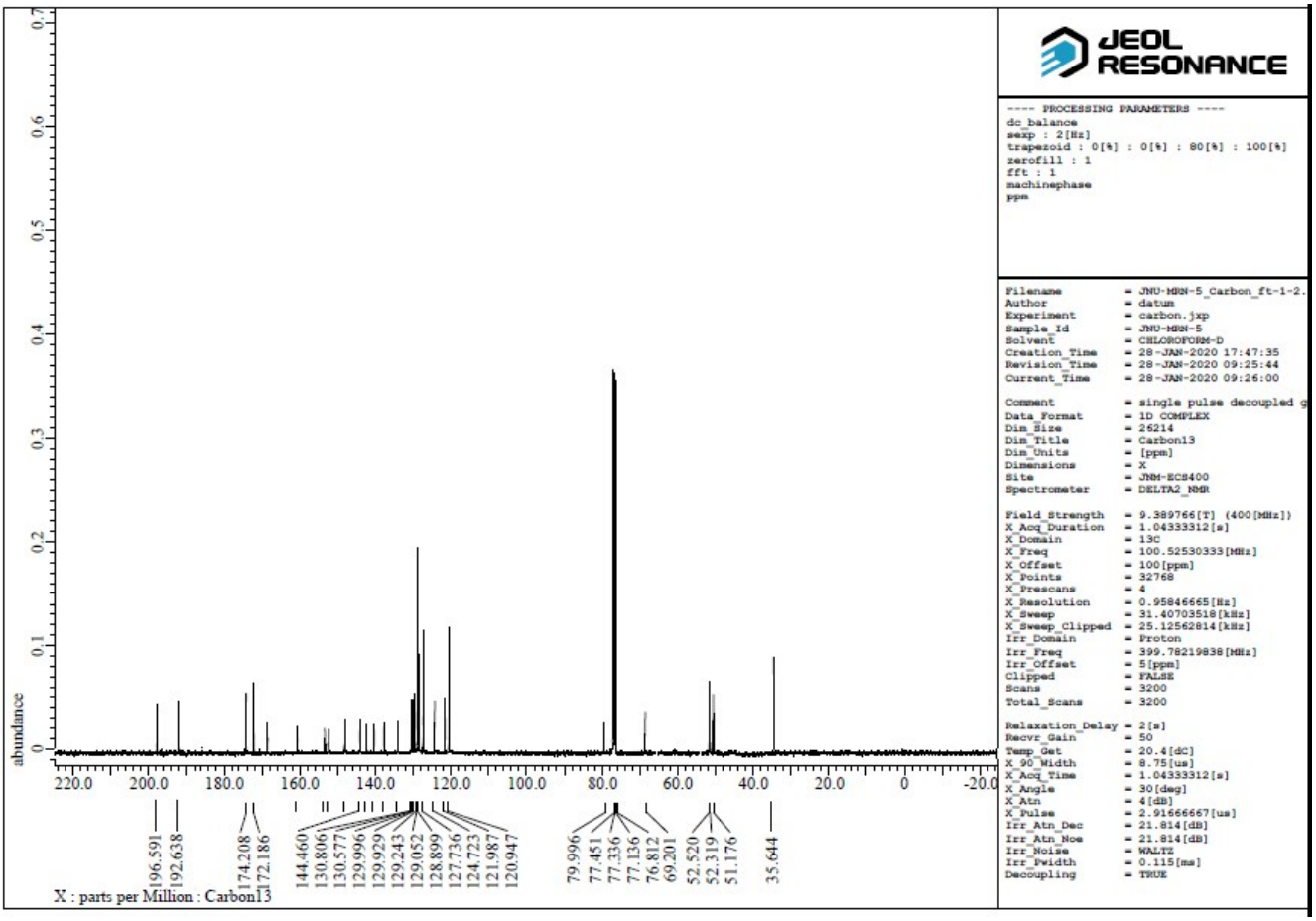
S-27: ^{1}H-NMR of 7a



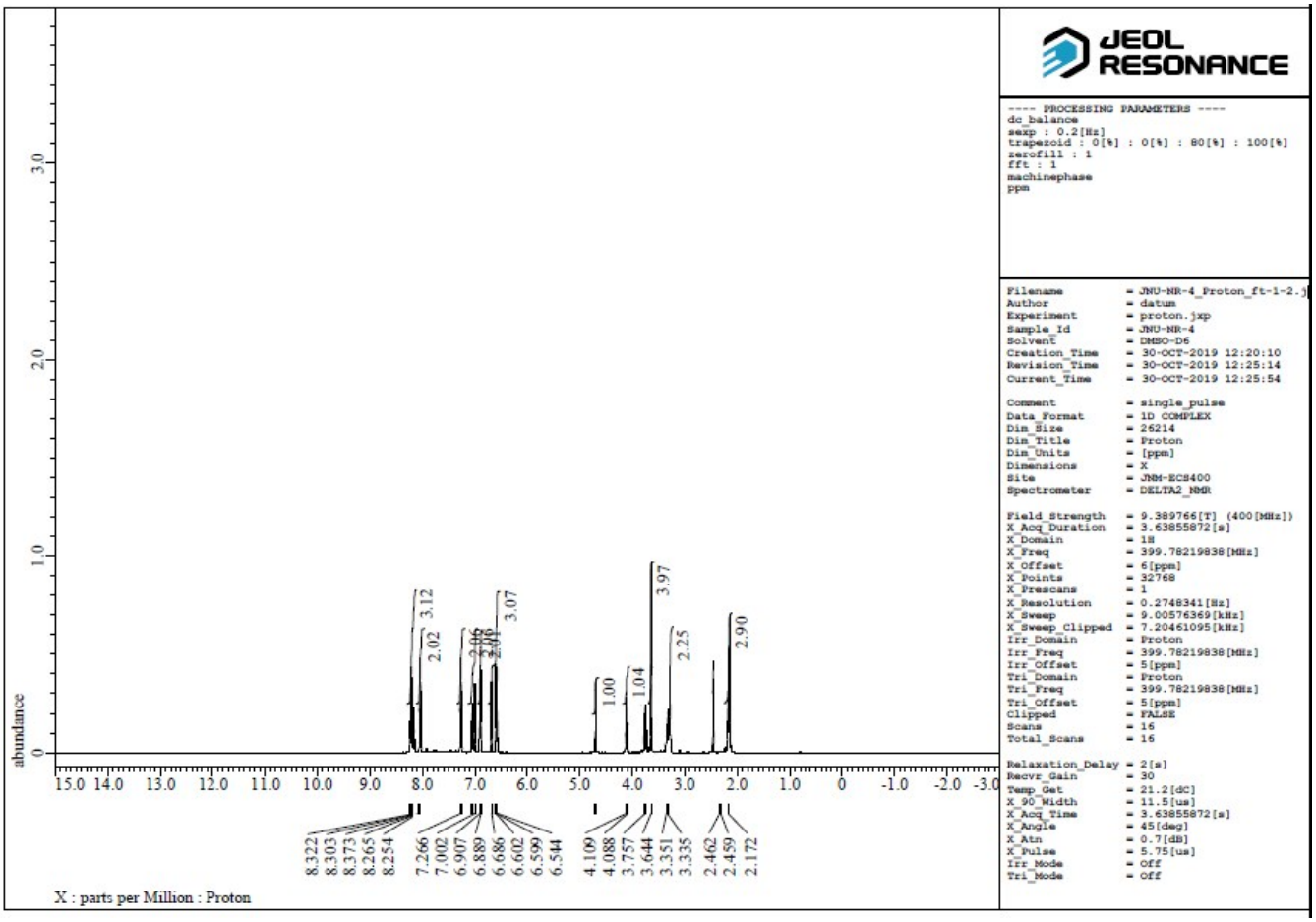
S-28: ^{13}C-NMR of 7a



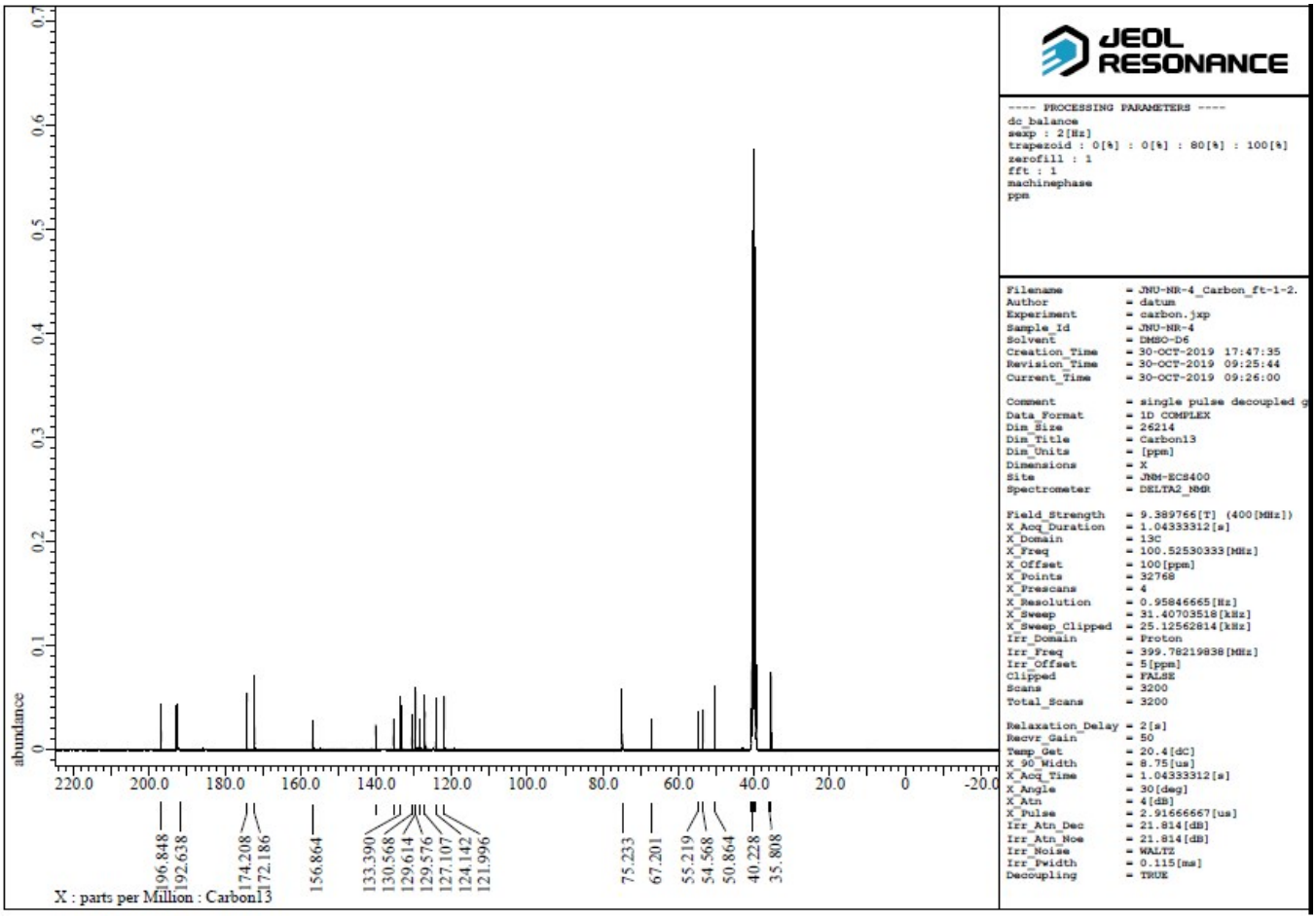
S-29: ^{1}H-NMR of 7b



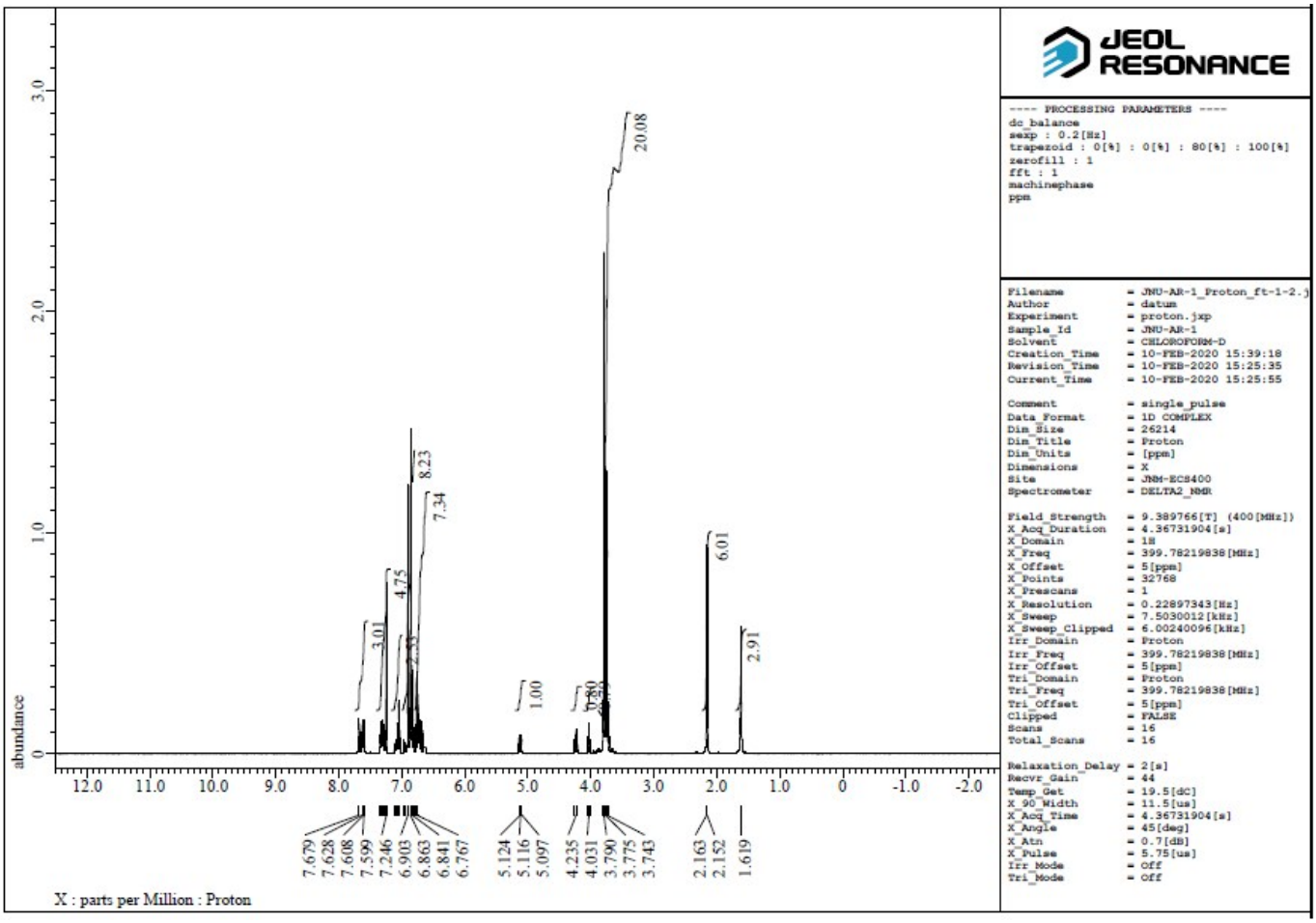
S-30: ^{13}C-NMR of 7b



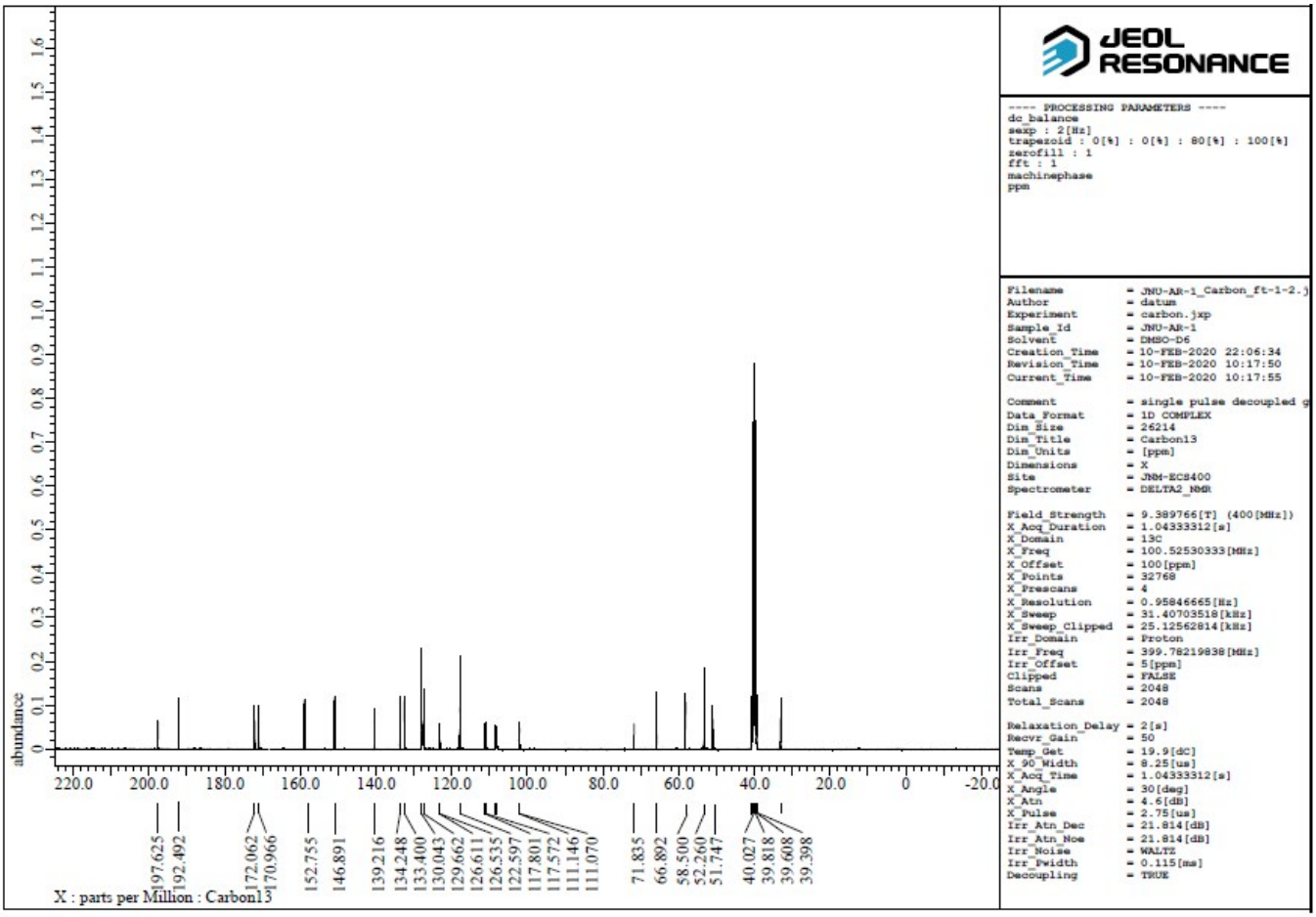
S-31: ^{1}H-NMR of 7c



S-32: ^{13}C-NMR of 7c



S-33: ^{1}H-NMR of 7d



S-34: ^{13}C-NMR of 7d

Crystal data and structure refinement for **4d**.

Identification code	Shelxl
Empirical formula	C_{30} H_{28} N_4O_4S
Formula weight	540
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 13.2006(11) A alpha = 113.018(3) deg.
	b = 14.2388(11) A beta = 103.338(4) deg.
	c = 17.0243(12) A gamma = 97.930(4) deg.
Volume	2771.1(4) A^3
Z, Calculated density	2, 1.297 Mg/m^3
Absorption coefficient	0.159 mm^-1
F(000)	1138
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	1.59 to 28.32 deg.
Limiting indices	-16<=h<=17, -17<=k<=18, -22<=l<=16
Reflections collected / unique	23290 / 12528 [R(int) = 0.0255]
Completeness to theta =	28.32 90.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9688 and 0.9538
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12528 / 0 / 711
Goodness-of-fit on F^2	0.845
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1612
R indices (all data)	R1 = 0.0873, wR2 = 0.2025
Largest diff. peak and hole	0.823 and -0.559 e.A^-3