Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Salicyldimine based schiff's complex of copper (II) as an efficient catalyst for the synthesis of nitrogen and oxygen heterocycles

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Supplementary Information

The XRD pattern of SiO_2-$Cu(OAc)_2$ has been shown in the following **fig.**

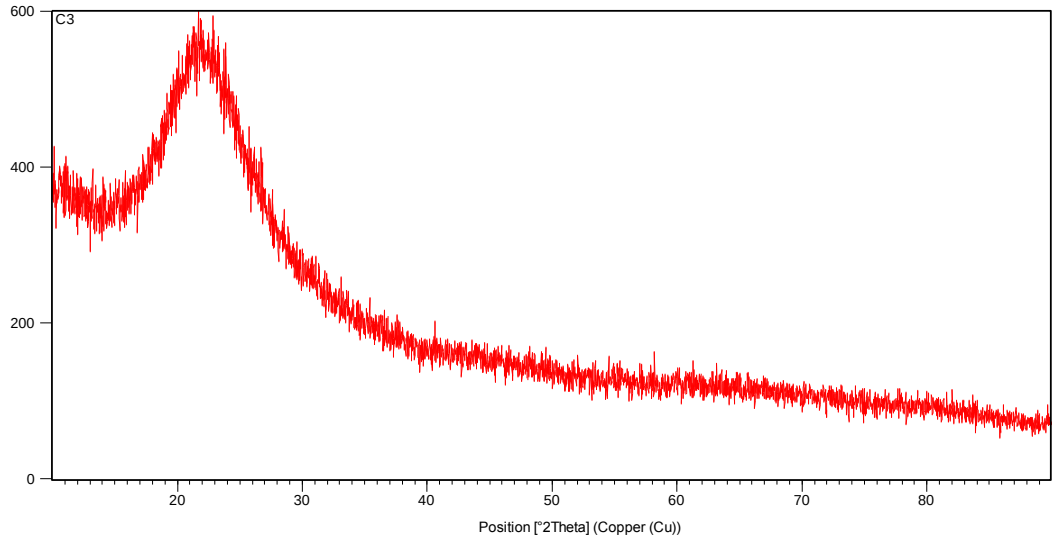
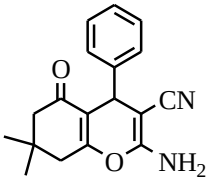


Fig. XRD graph of SiO_2-$Cu(OAc)_2$

Spectral details of some compounds

2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4*H*-chromene-3-carbonitrile (entry 1, table 2)



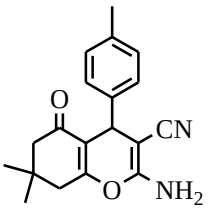
IR (υ_{max} in cm^{-1}, KBr): 1110 (C-N str.), 1565 (aromatic C=C str.), 3022 (aromatic C-H str.), 3432 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.93 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 2.04-2.29 (m, 4H, 2 X CH_2), 4.25 (s, 1H, CH), 6.40 (s, 1H, NH_2), 7.11-7.42 (m, 5H, ArH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 28.01, 29.25, 31.02, 34. 02, 51.55, 54.32, 118.01, 124.78, 127.61, 128.49, 128.69, 140.09, 156.76, 176.18, 190.39.

MS: *m/z* 294 (M^+).

2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-*p*-tolyl-4*H*-chromene-3-carbonitrile (entry 2, table 2)



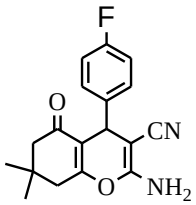
IR (υ_{max} in cm^{-1}, KBr): 1289 (C-N str.), 1513 (aromatic C=C str.), 3033 (aromatic C-H str.), 3325 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.95 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.00-2.11 (m, 4H, 2 X CH_2), 2.25 (s, 3H, CH_3), 4.13 (s, 1H, CH), 6.99 (s, 1H, NH_2), 7.01-7.10 (m, 4H, ArH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 20.24, 27.14, 28.72, 32.11, 35.64, 50.63, 58.74, 113.05, 120.28, 127.25, 129.54, 136.09, 142.29, 158.78, 162.62, 182.27, 196.11

MS: *m/z* 308 (M^+).

2-amino--4-(4-fluorophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile (entry 5, table 2)



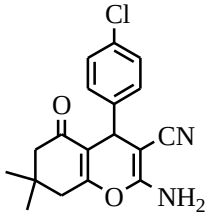
IR (υ_{max} in cm^{-1}, KBr): 1145 (C-N str.), 1595 (aromatic C=C str.), 3078 (aromatic C-H str.), 3435 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.91 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.89-2.34 (m, 4H, 2 X CH_2), 4.27 (s, 1H, CH), 6.87 (s, 1H, NH_2), 7.11-7.85 (m, 4H, ArH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 28.82, 33.75, 39.60, 40.82, 51.49, 54.39, 114.01, 118.31, 124.78, 129.77, 136.09, 156.71, 162.21, 176.18, 190.39.

MS: *m/z* 620 (M^+).

2-amino-4-(4-chlorophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile (entry 8, table 2)



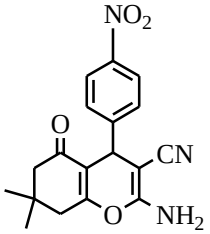
IR (υ_{max} in cm^{-1}, KBr): 1266 (C-N str.), 1491 (aromatic C=C str.), 3070 (aromatic C-H str.), 3379 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.95 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.09-2.28 (m, 4H, 2 X CH_2), 4.20 (s, 1H, CH), 7.09 (s, 1H, NH_2), 7.17-7.19 (d, 2H, ArH), 7.35-7.37 (d, 2H, ArH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 27.04, 28.26, 31.75, 35.63, 50.20, 58.01, 112.79, 119.87, 128.84, 129.18, 131.57, 144.45, 158.57, 162.91, 196.10.

MS: *m/z* 328 (M^+), 330 (M+2)

2-amino--6,6,8,8-tetrahydro-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-4*H*-chromene-3-carbonitrile (entry 8, table 2)



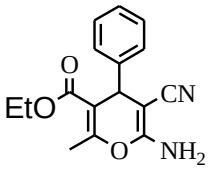
IR (υ_{max} in cm^{-1}, KBr): 1090 (C-N str.), 1498 (aromatic C=C str.), 3076 (aromatic C-H str.), 3389 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.93 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 2.19-2.30 (m, 4H, 2 X CH_2), 4.26 (s, 1H, CH), 6.54 (s, 1H, NH_2), 7.19-7.39 (m, 4H, ArH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 28.82, 33.77, 39.60, 40.89, 51.45, 53.87, 118.45, 123.19, 124.79, 129.00, 145.89, 149.32, 156.90, 178.09, 190.46.

MS: *m/z* 339 (M^+).

Ethyl-6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate (entry 15, table 2)



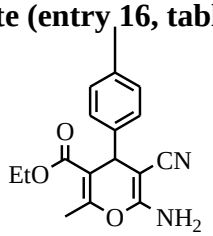
IR (υ_{max} in cm^{-1}, KBr): 1165 (C-N str.), 1532 (aromatic C=C str.), 3099 (aromatic C-H str.), 3474 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.36 (t, 3H, CH_3), 2.13 (s, 3H, CH_3), 4.14 (q, 2H, CH_2), 4.36 (s, 1H, CH), 6.44 (s, 1H, NH_2), 7.24-7.37 (m, 5H, ArH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 14.70, 15.82, 40.54, 55.64, 61.58, 106.54, 118.43, 127.54, 128.49, 128.69, 140.52, 152.95, 157.62, 165.53.

MS: *m/z* 284 (M^+).

Ethyl-6-amino-5-cyano-2-methyl-4-*p*-tolyl-4*H*-pyran-3-carboxylate (entry 16, table 2)



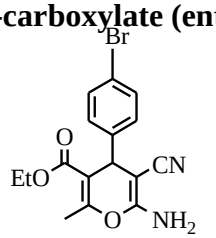
IR (υ_{max} in cm^{-1}, KBr): 1262 (C-N str.), 1514 (aromatic C=C str.), 3042 (aromatic C-H str.), 3329 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.06 (t, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.94 (q, 2H, CH_2), 4.25 (s, 1H, CH), 6.89 (s, 1H, NH_2), 7.01-7.13 (m, 4H, ArH).

^{13}C NMR (400 MHz, DMSO-d$_6$): δ 14.01, 17.96, 21.21, 57.37, 60.53, 107.86, 120.24, 127.35, 129.34, 136.10, 142.51, 156.75, 158.75, 165.96.

MS: *m/z* 298 (M^+).

Ethyl-6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate (entry 19, table 2)



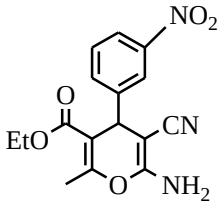
IR (υ_{max} in cm^{-1}, KBr): 1150 (C-N str.), 1632(aromatic C=C str.), 3011 (aromatic C-H str.), 3487 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.16 (t, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.54 (q, 2H, CH_2), 4.67 (s, 1H, CH), 6.67 (s, 1H, NH_2), 7.21-7.45 (m, 4H, ArH).

^{13}C NMR (400 MHz, DMSO-d$_6$): δ 12.01, 17.56, 22.01, 58.76, 61.53, 107.87, 121.24, 127.39, 129.56, 137.09, 141.51, 157.89, 157.75, 165.90.

MS: *m/z* 362 (M^+), 364 (M+2).

Ethyl-6-amino-5-cyano-2-methyl-4-(3-nitrophenyl)-4*H*-pyran-3-carboxylate (entry 23, table 2)



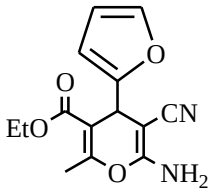
IR (υ_{max} in cm^{-1}, KBr): 1269 (C-N str.), 1593 (aromatic C=C str.), 3076 (aromatic C-H str.), 3399 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.03 (t, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.97 (q, 2H, CH_2), 4.50 (s, 1H, CH), 6.99 (s, 1H, NH_2), 7.60-8.07 (m, 4H, ArH).

^{13}C NMR (400 MHz, DMSO-d$_6$): δ 13.79, 18.57, 39.25, 56.85, 60.68, 106.71, 119.74, 121.71, 130.30, 134.46, 147.72, 148.22, 158.22, 159.09, 165.41.

MS: *m/z* 329 (M^+).

Ethyl-6-amino-5-cyano -4-(furan-2-yl)-2-methyl-4*H*-pyran-3-carboxylate (entry 25, table 2)



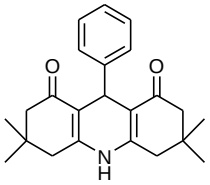
IR (υ_{max} in cm^{-1}, KBr): 1167 (C-N str.), 1589 (aromatic C=C str.), 3049 (aromatic C-H str.), 3432 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.38 (t, 3H, CH_3), 2.01 (s, 3H, CH_3), 4.22 (q, 2H, CH_2), 4.44 (s, 1H, CH), 6.06 (d, 1H, CH), 6.19 (t, 1H, CH), 6.99 (s, 1H, NH_2), 7.17 (d, 1H, CH).

^{13}C NMR (400 MHz, DMSO-d_6): δ14.70, 15.82, 39.11, 61.50, 64.58, 104.39, 110.96, 113.41, 116.68, 140.56, 148.96, 150.96, 160.52, 164.93.

MS: *m/z* 274 (M^+).

3,3,6,6-Tetramethyl -9-phenyl -1,8-dioxodecahydroacridine [entry 1, table 3]



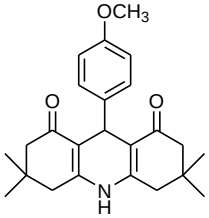
IR (υ_{max} in cm^{-1}, KBr): 1132 (C-N str.), 1590 (aromatic C=C str.), 1712 (C=O str.), 3034 (aromatic C-H str.), 3463 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.11 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 2.22-2.40 (m, 8H, 4 X CH_2), 4.99 (s, 1H, CH), 7.21-7.30 (m, 5H, Ar-H), 11.55 (bs, 1H, NH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 27.67, 28.99, 30.99, 31.77, 46.11, 46.72, 114.90, 127.89, 131.21, 135.45, 189.99, 190.03.

MS: *m/z* 349 (M^+).

3,3,6,6-Tetramethyl -9-(4-methoxyphenyl) -1,8-dioxodecahydroacridine [entry 3, table 3]



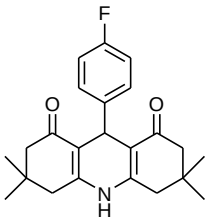
IR (υ_{max} in cm^{-1}, KBr): 1139 (C-N str.), 1550 (aromatic C=C str.), 1756 (C=O str.), 3087 (aromatic C-H str.), 3466 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.18 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 2.42-2.55 (m, 8H, 4 X CH_2), 3.79 (s, 3H, CH_3), 4.67 (s, 1H, CH), 7.18-7.31 (m, 4H, Ar-H), 11.68 (bs, 1H, NH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 28.63, 28.89, 30.39, 31.57, 47.01, 46.77, 113.90, 129.89, 132.21, 137.45, 189.98, 190.13.

MS: *m/z* 379 (M^+).

3,3,6,6-Tetramethyl -9-(4-fluorophenyl) -1,8-dioxodecahydroacridine [entry 6, table 3]



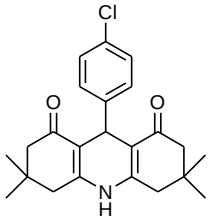
IR (υ_{max} in cm^{-1}, KBr): 1132 (C-N str.), 1558 (aromatic C=C str.), 1764 (C=O str.), 3089 (aromatic C-H str.), 3465 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.20 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 2.35-2.49 (m, 8H, 4 X CH_2), 4.45 (s, 1H, CH), 7.28-7.39 (m, 4H, Ar-H), 11.22 (bs, 1H, NH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 28.63, 28.89, 30.39, 31.57, 47.01, 46.77, 113.90, 129.89, 132.21, 137.45, 189.98, 190.13.

MS: *m/z* 367 (M^+).

3,3,6,6-Tetramethyl -9-(4-chlorophenyl) -1,8-dioxodecahydroacridine [entry 8, table 3]



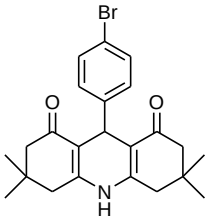
IR (υ_{max} in cm^{-1}, KBr): 1132 (C-N str.), 1593 (aromatic C=C str.), 1681 (C=O str.), 3377 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.12 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 2.36-2.46 (m, 8H, 4 X CH_2), 5.50 (s, 1H, CH), 7.02-7.29 (m, 4H, Ar-H), 11.90 (bs, 1H, NH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 27.26, 29.67, 31.17, 31.98, 46.14, 46.93, 115.21, 128.20, 131.33, 136.40, 189.36, 190.60.

MS: *m/z* 383 (M^+), 385 (M+2).

3,3,6,6-Tetramethyl -9-(4-bromophenyl) -1,8-dioxodecahydroacridine [entry 11, table 3]



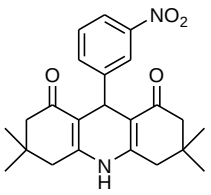
IR (υ_{max} in cm^{-1}, KBr): 1190 (C-N str.), 1498 (aromatic C=C str.), 1712 (C=O str.), 3097 (aromatic C-H str.), 3432 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.02 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 2.26-2.40 (m, 8H, 4 X CH_2), 5.56 (s, 1H, CH), 7.12-7.26 (m, 4H, Ar-H), 11.89 (bs, 1H, NH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 27.34, 30.06, 31.45, 32.08, 45.14, 47.93, 115.43, 129.20, 131.79, 136.54, 190.36, 190.78.

MS: *m/z* 428 (M^+), 430 (M+2).

3,3,6,6-Tetramethyl -9-(3-nitrophenyl)-1,8-dioxodecahydroacridine [entry 13, table 3]



IR (υ_{max} in cm^{-1}, KBr): 1252 (C-N str.), 1499 (aromatic C=C str.), 1697 (C=O str.), 3060 (aromatic C-H str.), 3410 (N-H str.).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.15 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.38-2.50 (m, 8H, 4 X CH_2), 5.57 (s, 1H, CH), 7.29-8.08 (m, 4H, Ar-H), 11.89 (bs, 1H, NH).

^{13}C NMR (400 MHz, DMSO-d_6): δ 27.08, 29.36, 31.30, 32.88, 41.03, 42.94, 46.43, 47.15, 114.85, 121.06, 122.24, 129.10, 133.01, 140.36, 148.52, 189.46, 191.01.

MS: *m/z* 394 (M^+).

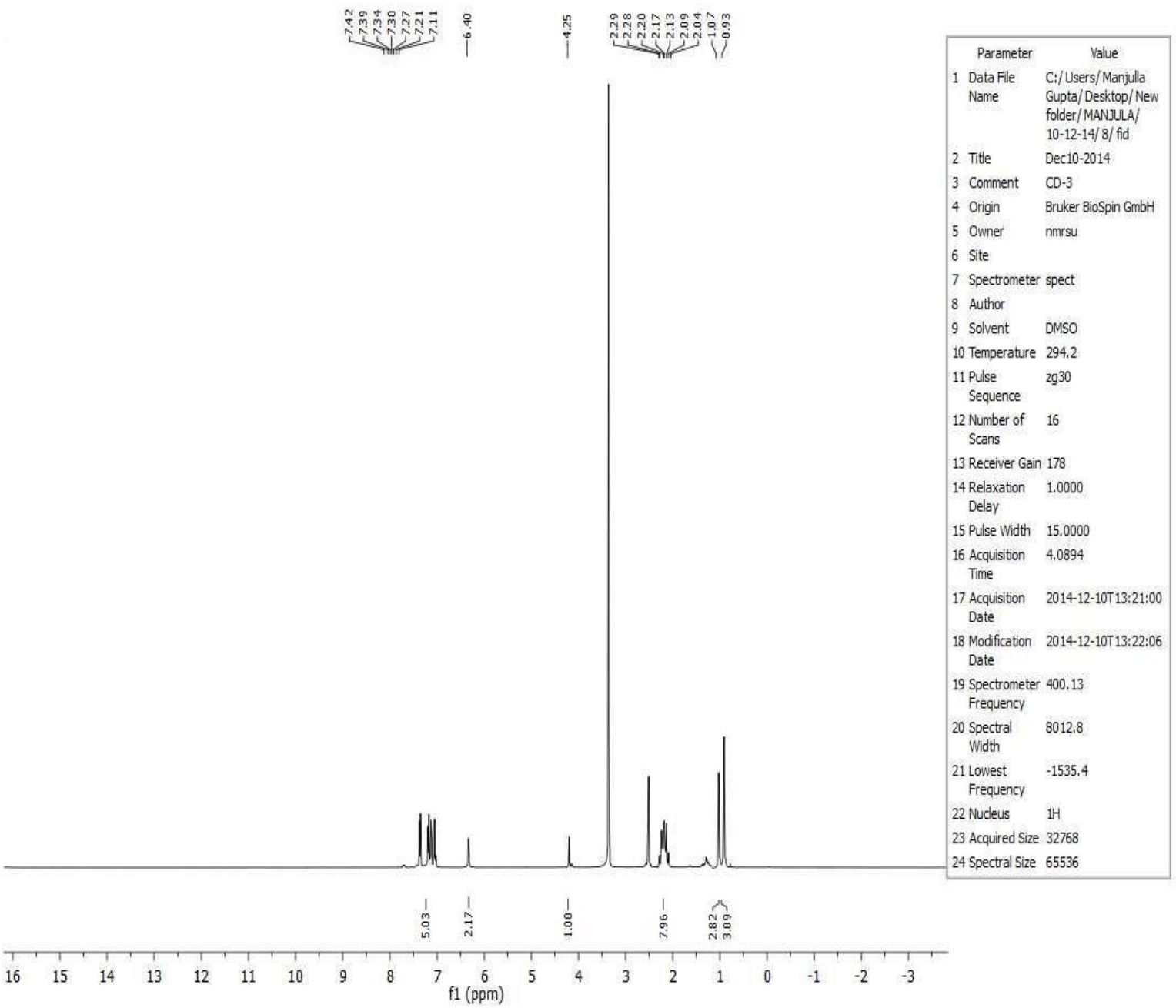


Fig. 1 ^{1}H NMR spectra of 2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4*H*-chromene-3-carbonitrile

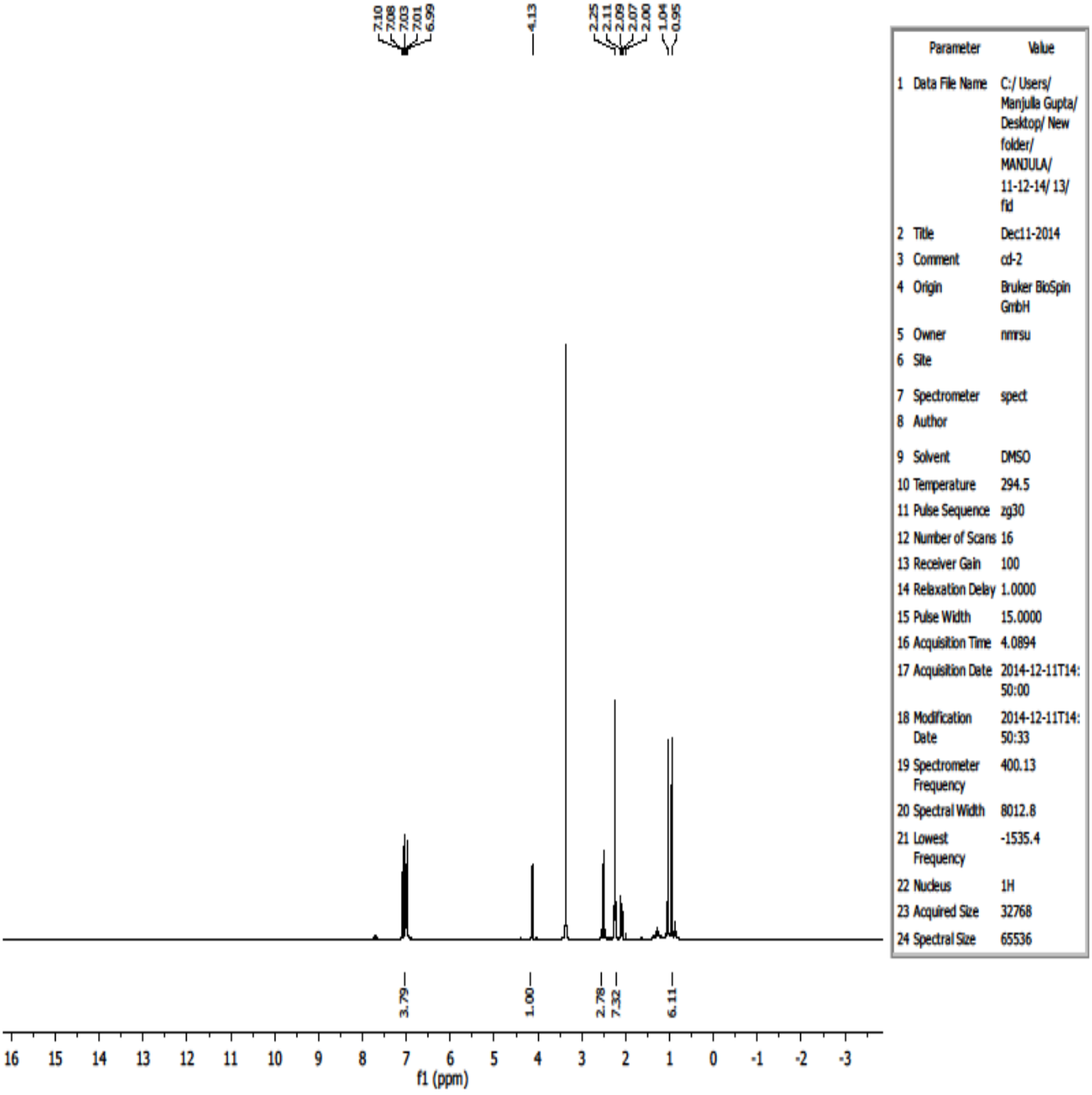


Fig. 2 ^{1}H NMR spectra of 2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-*p*-tolyl-4*H*-chromene-3-carbonitrile

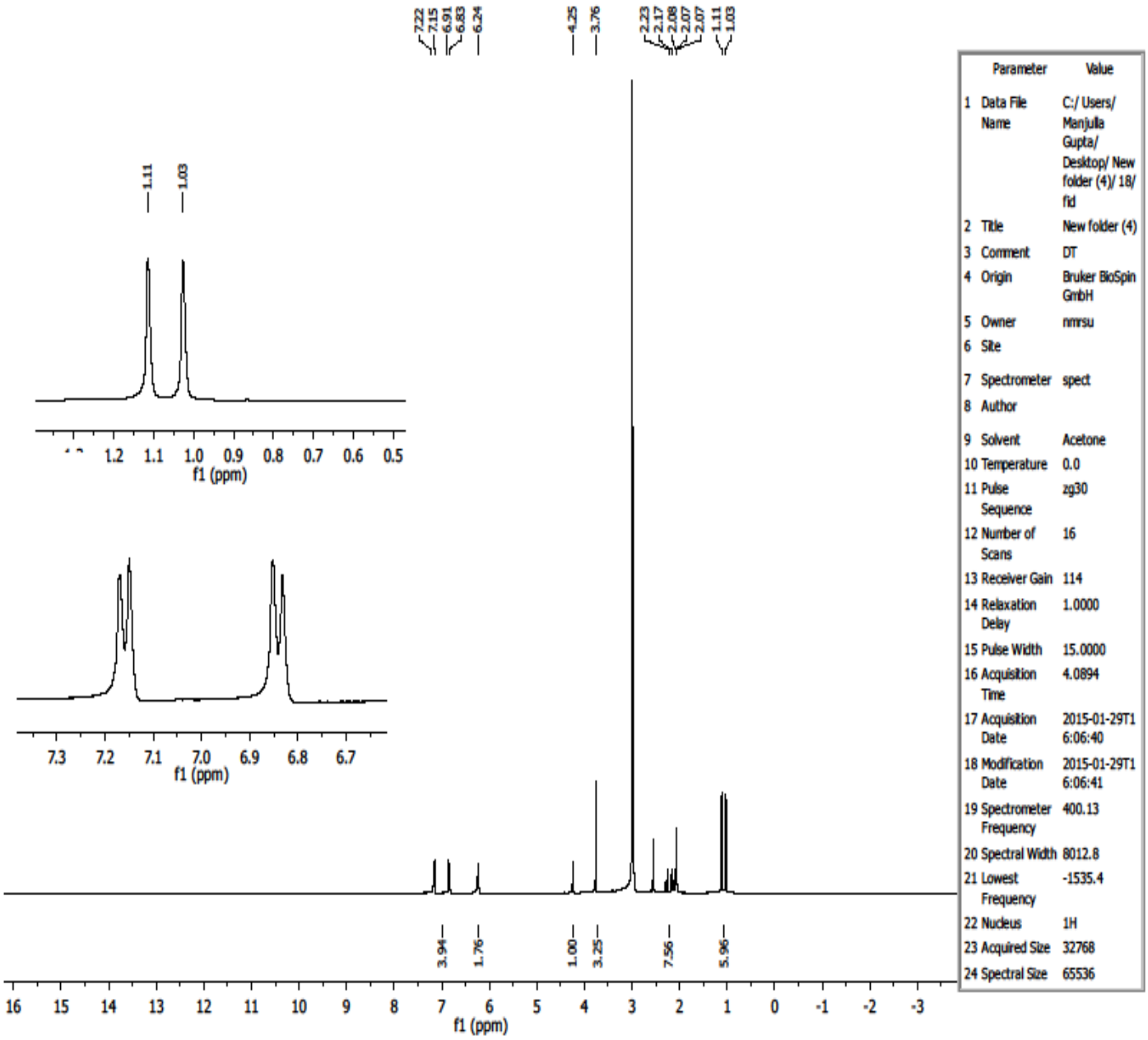


Fig. 3 ^{1}H NMR spectra of 2-amino-4-(4-methoxyphenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

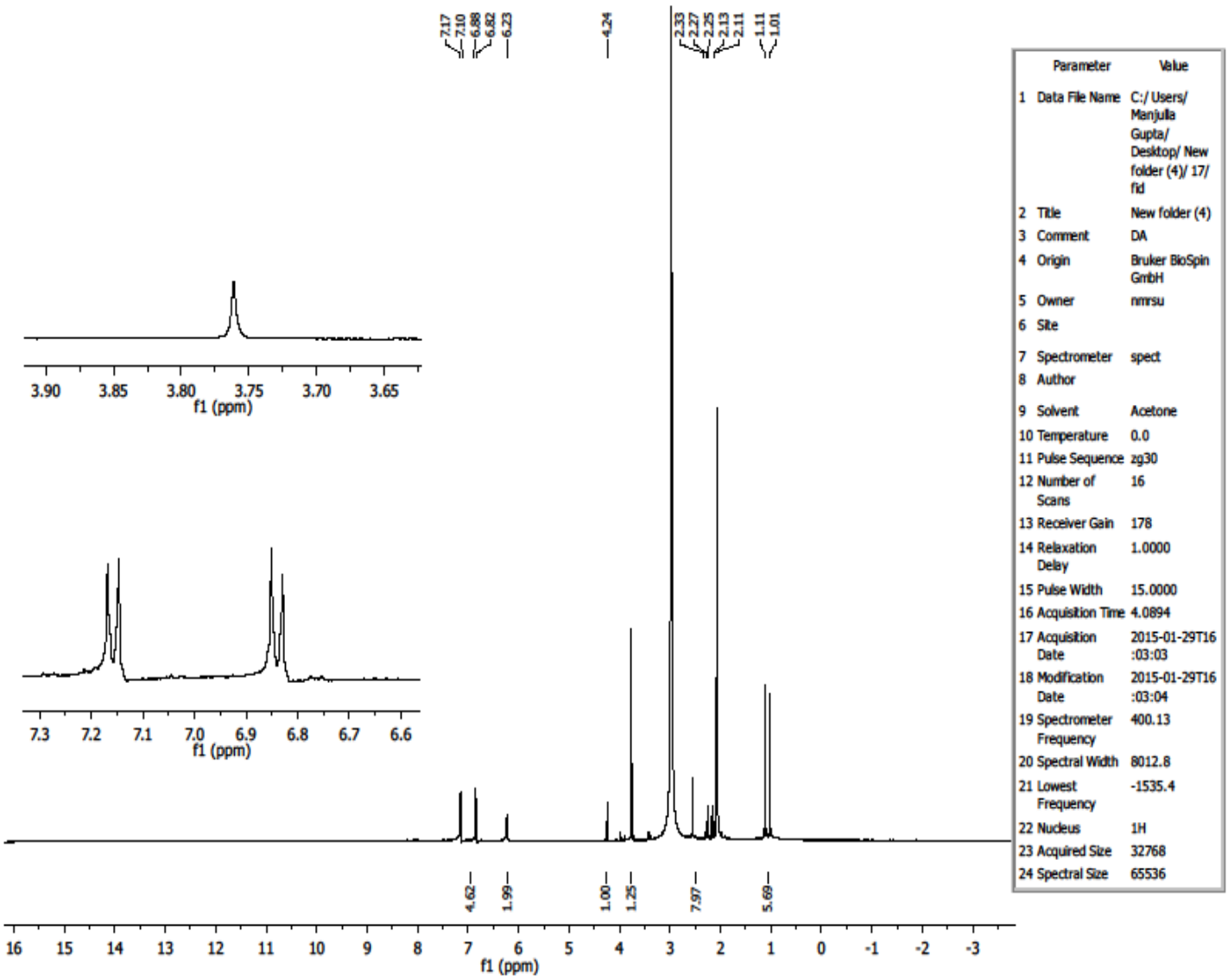


Fig. 4 ^{1}H NMR spectra of 2-amino-4-(4-hydroxyphenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

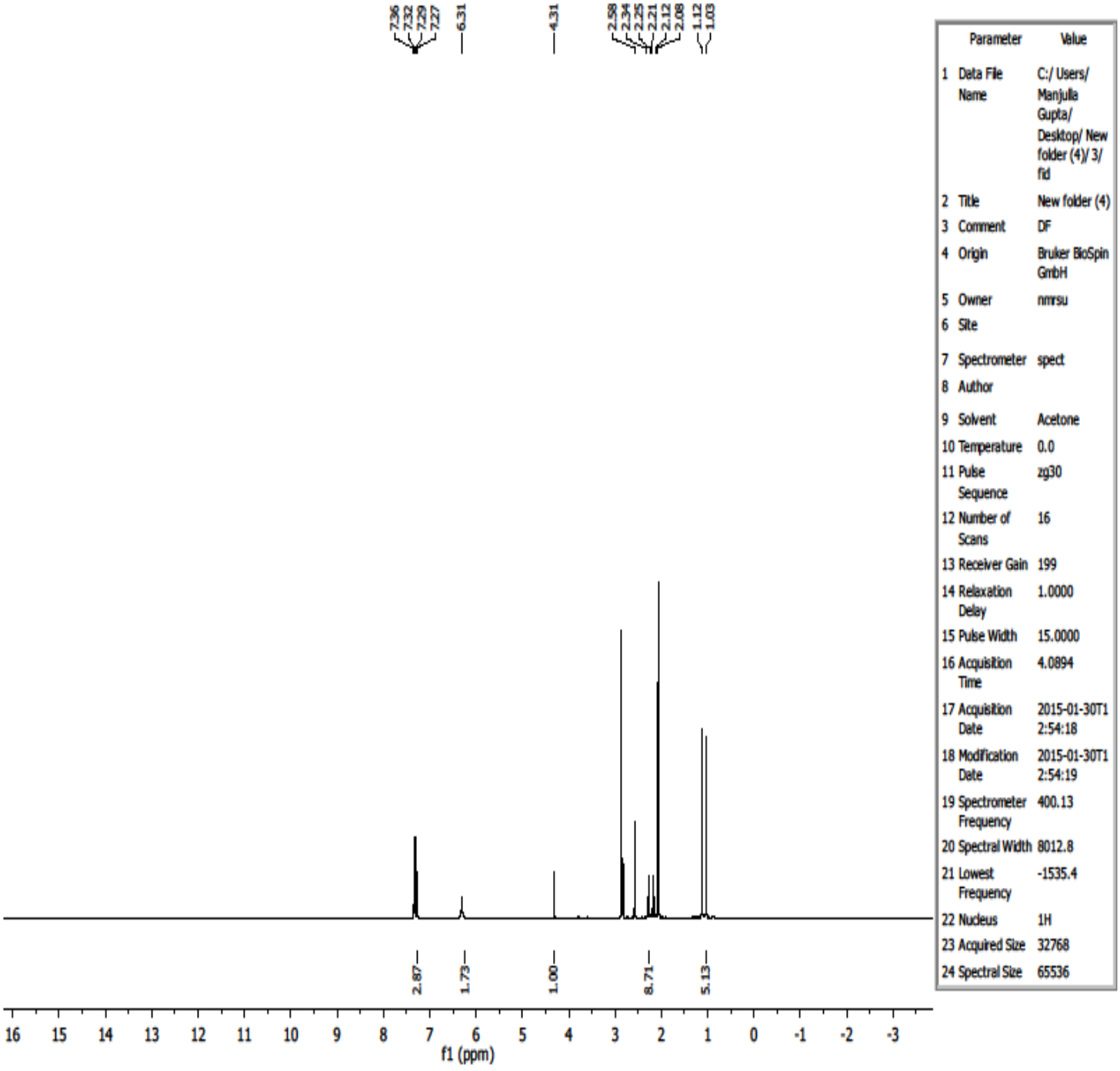


Fig. 5 ^{1}H NMR spectra of 2-amino-4-(4-fluorophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

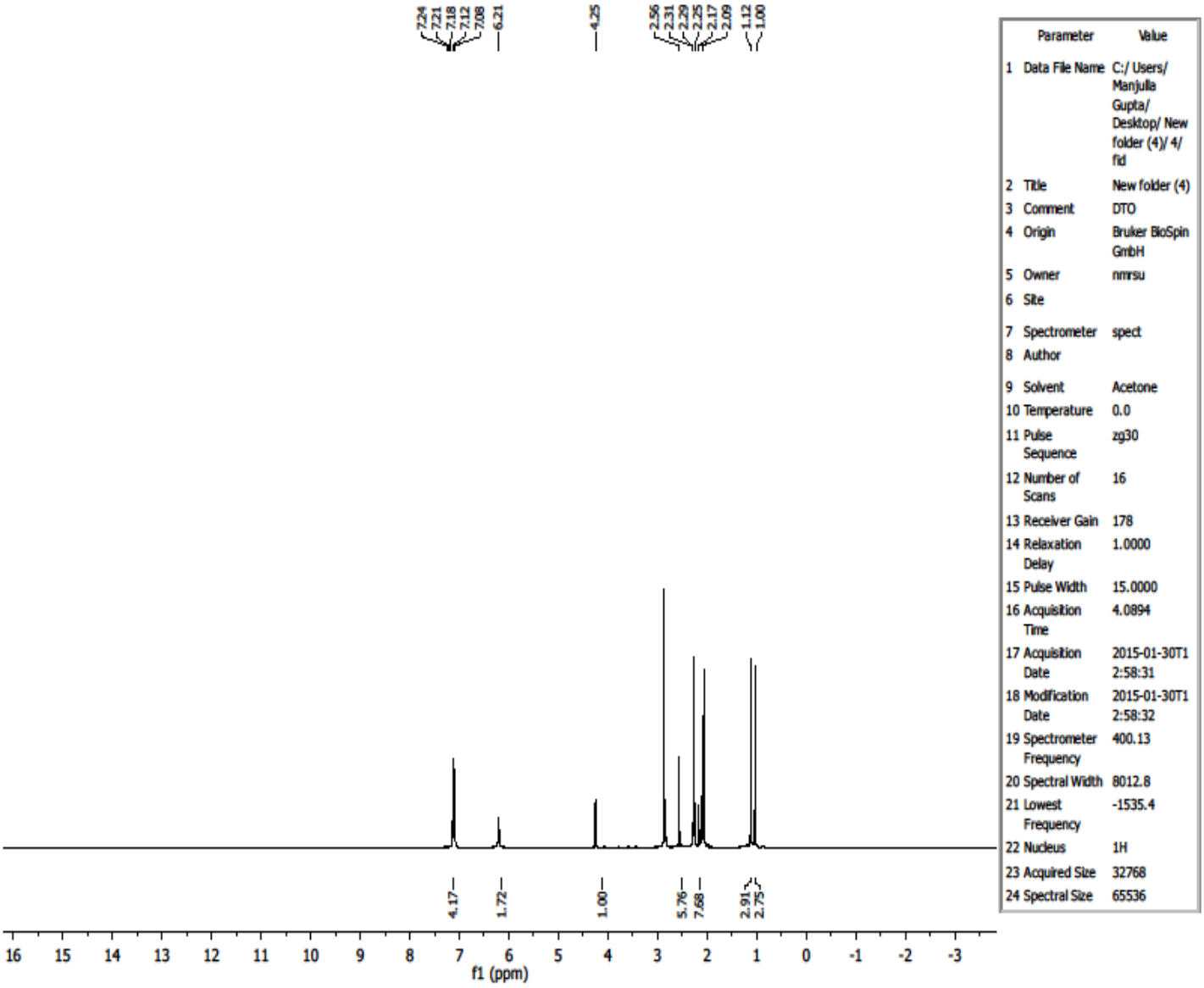


Fig. 6 ^{1}H NMR spectra of 2-amino-4-(4-(dimethylamino)phenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

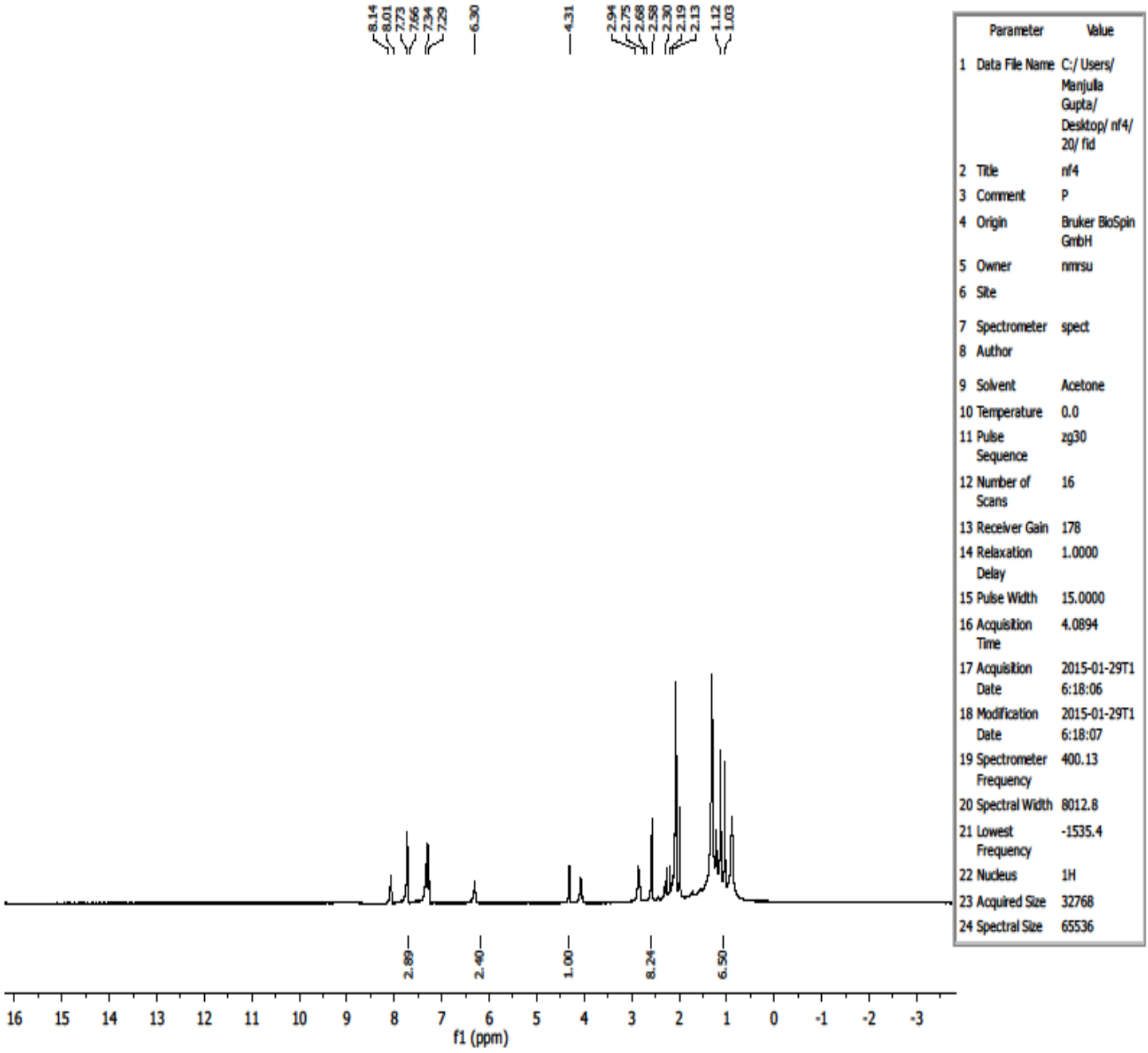


Fig. 7 ^{1}H NMR spectra of 2-amino-4-(furan-2-yl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

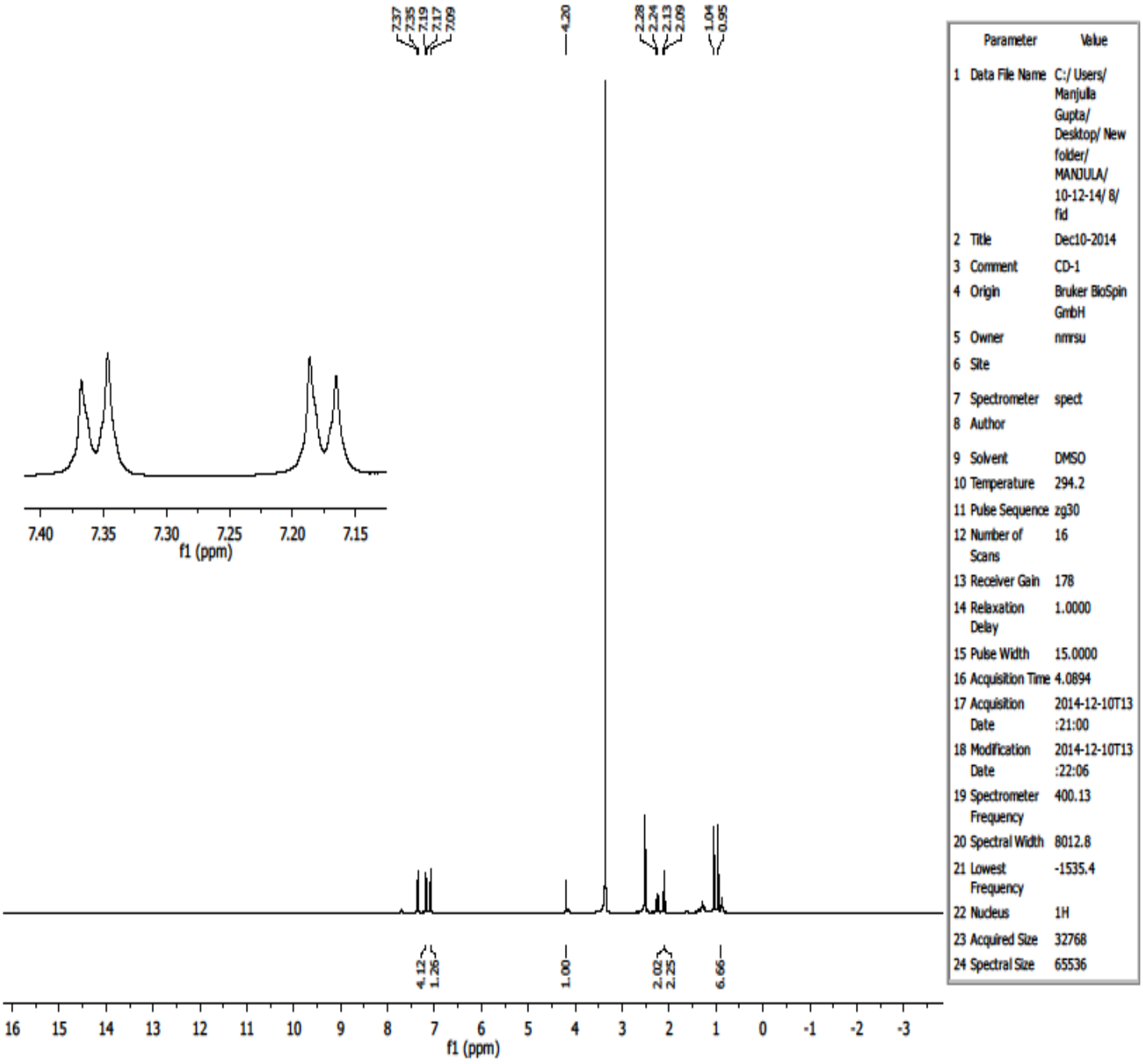


Fig. 8 ^{1}H NMR spectra of 2-amino-4-(4-chlorophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

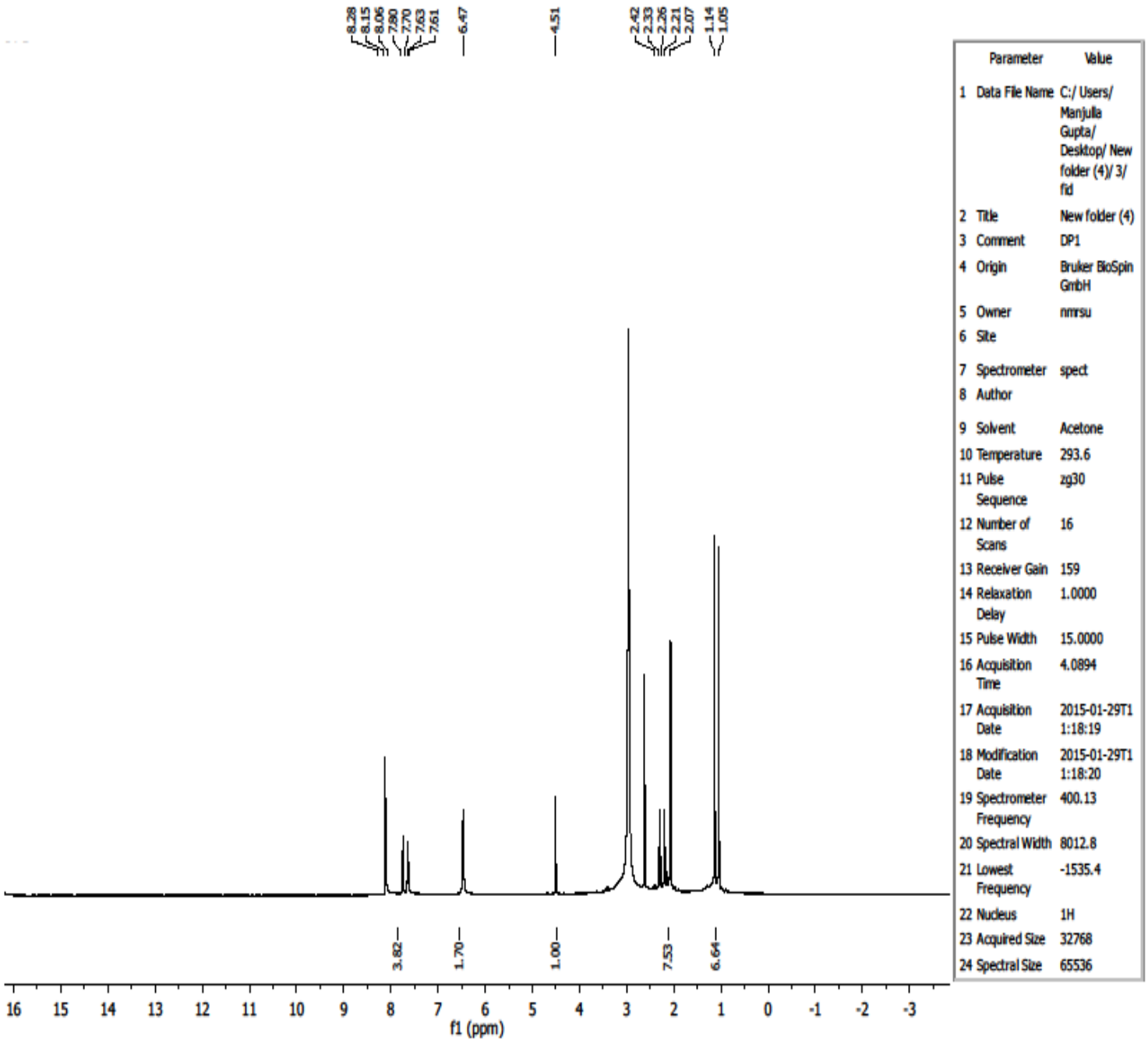


Fig. 9 ^{1}H NMR spectra of 2-amino-4-(2-chlorophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

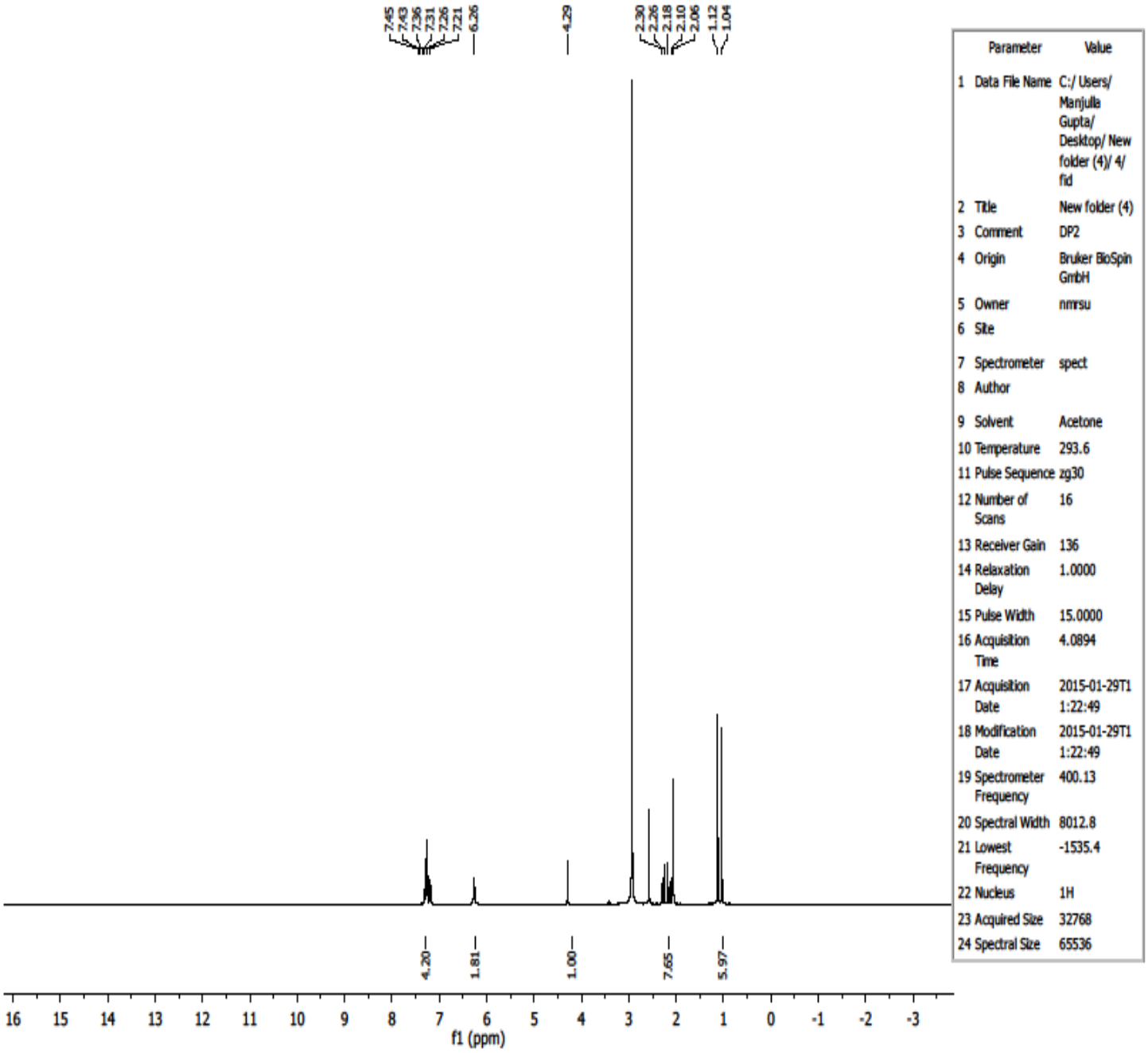


Fig. 10 ^{1}H NMR spectra of 2-amino-4-(4-bromophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

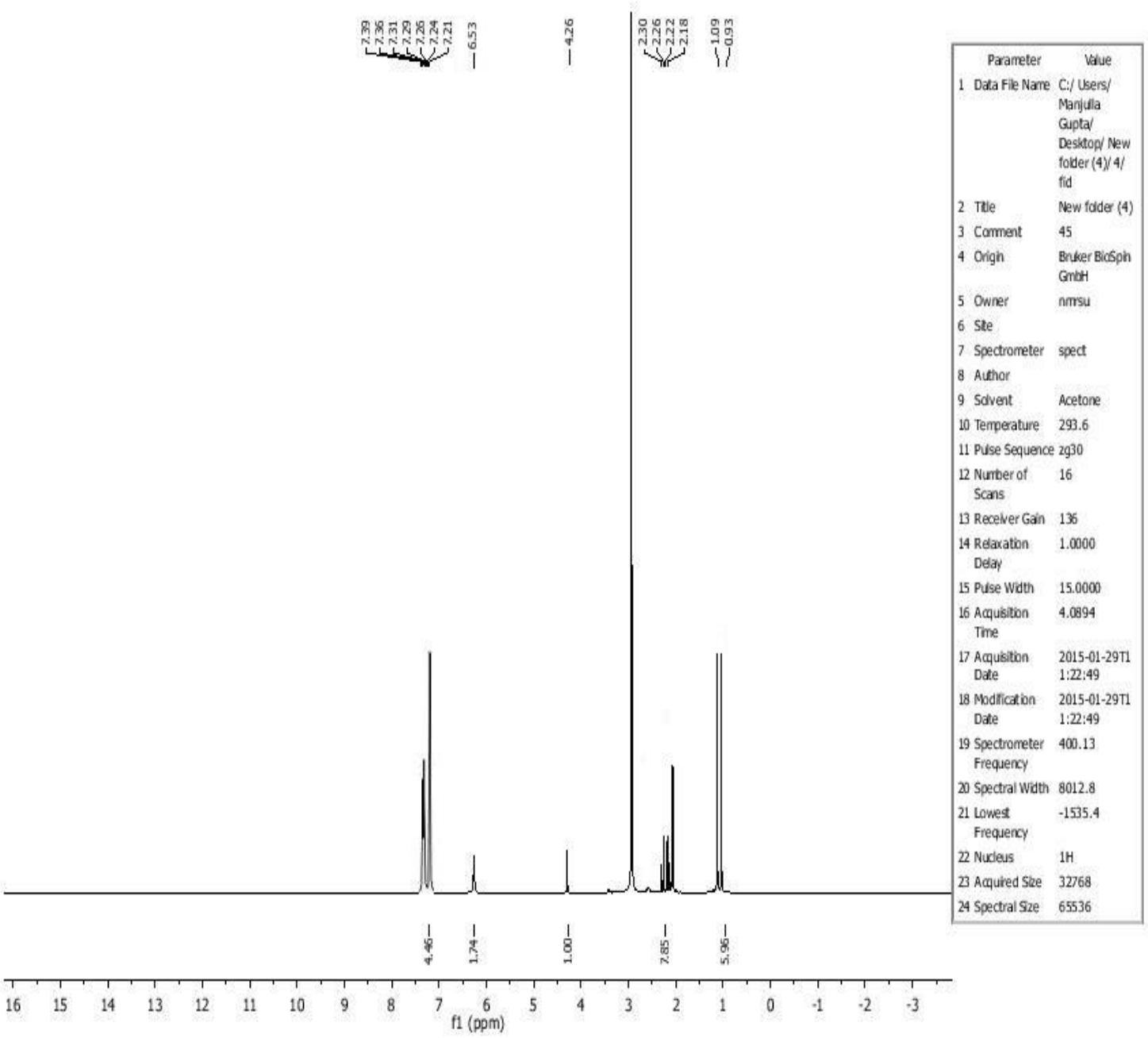


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Fig. 11 ^{1}H NMR spectra of 2-amino-4-(4-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

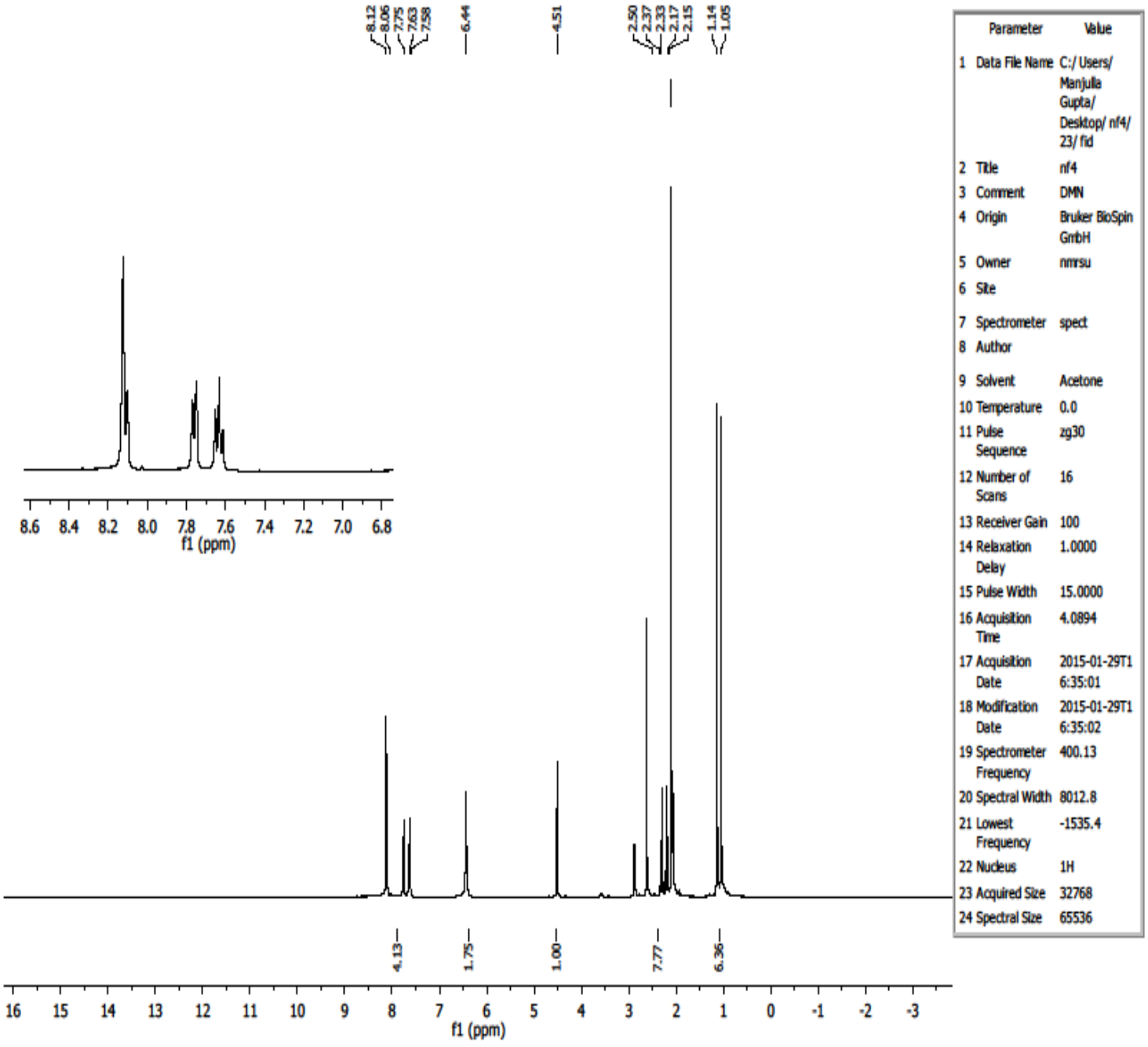

Fig. 12 ^{1}H NMR spectra of 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

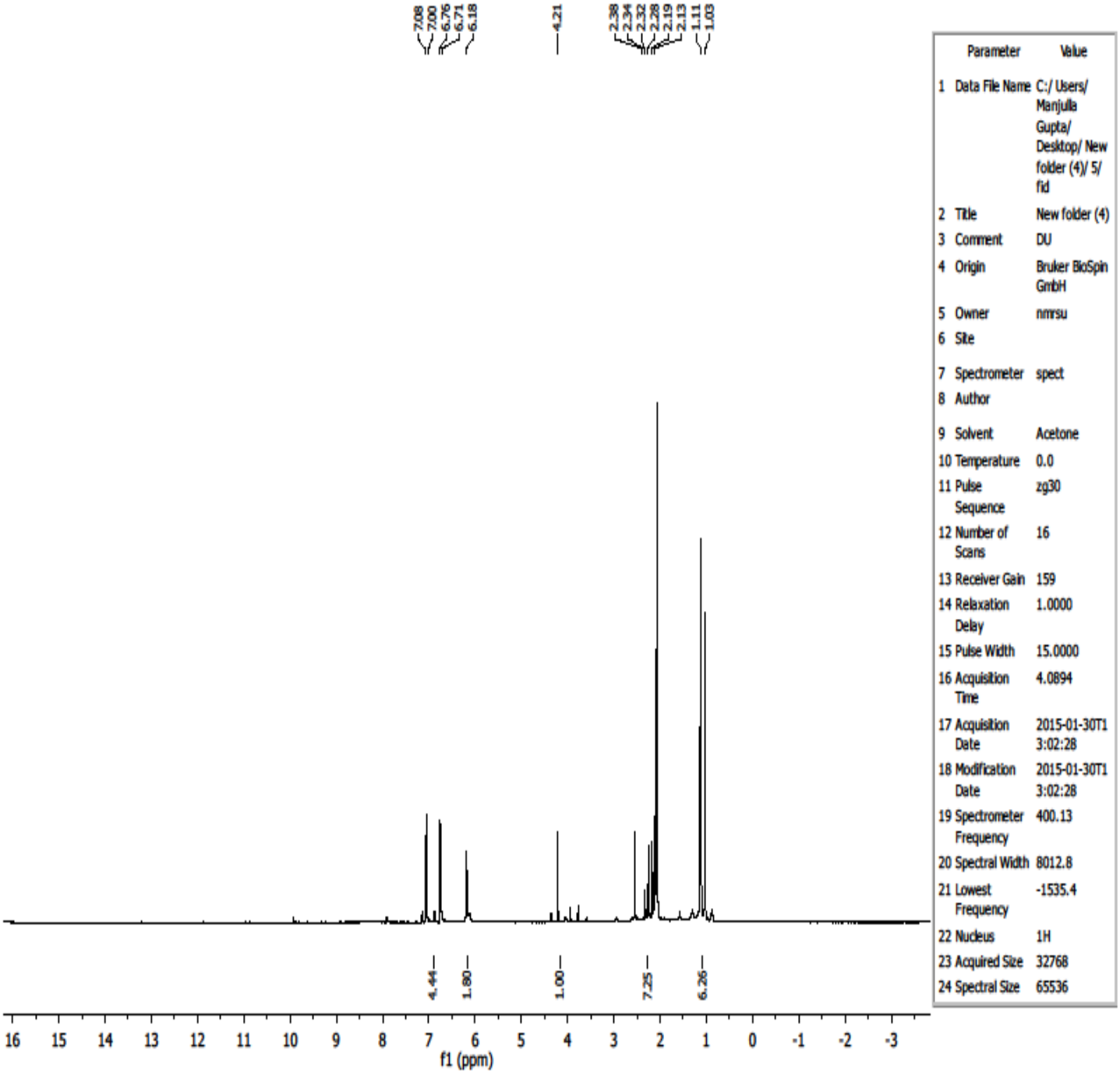

Fig. 13 ^{1}H NMR spectra of 2-amino-4-(2-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

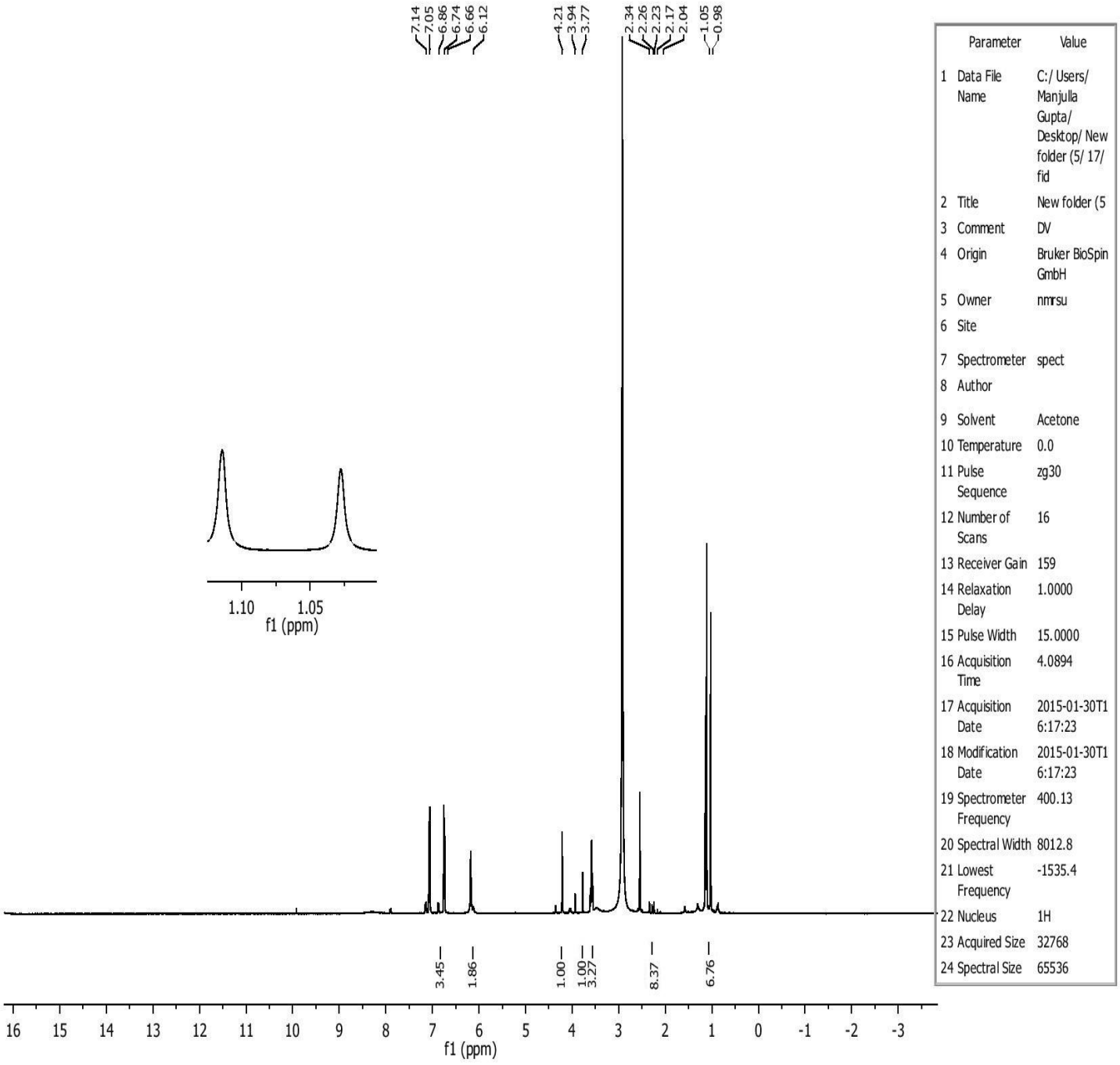

Fig. 14 ^{1}H NMR spectra of 2-amino-4-(4-hydroxy-3-methoxyphenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

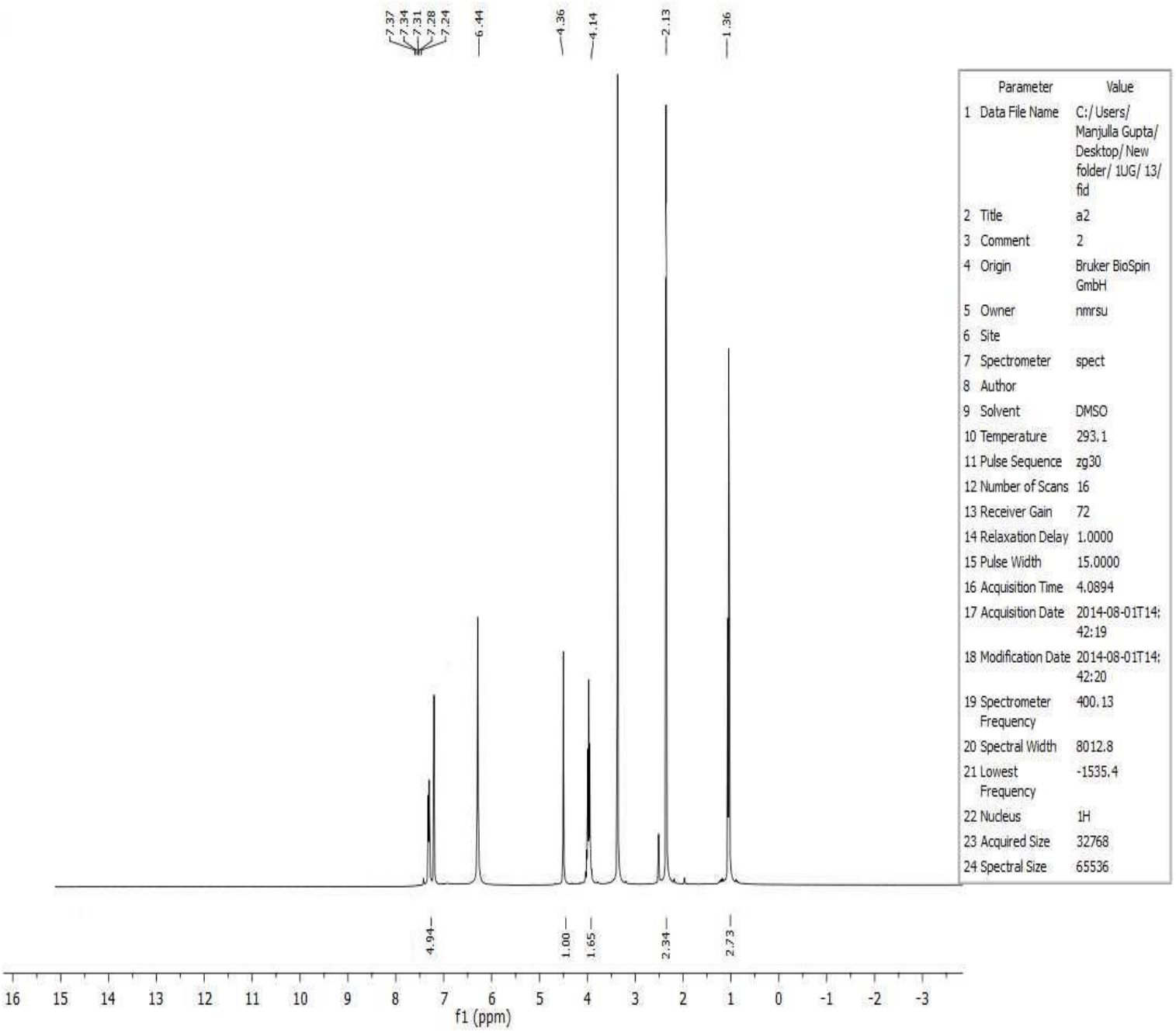

Fig. 15 ^{1}H NMR spectra of Ethyl-6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate

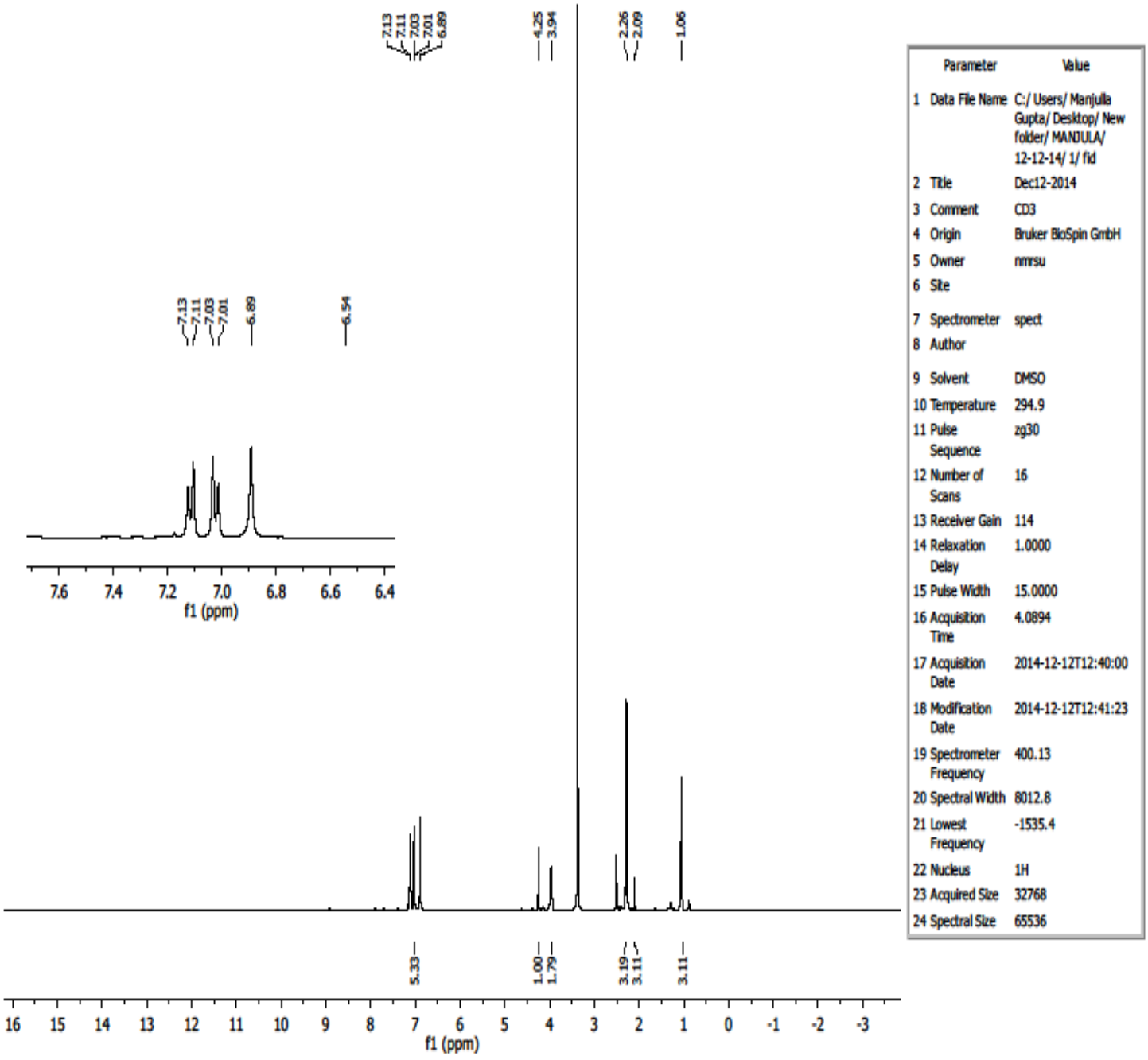

Fig. 16 ^{1}H NMR spectra of Ethyl-6-amino-5-cyano-2-methyl-4-*p*-tolyl-4*H*-pyran-3-carboxylate

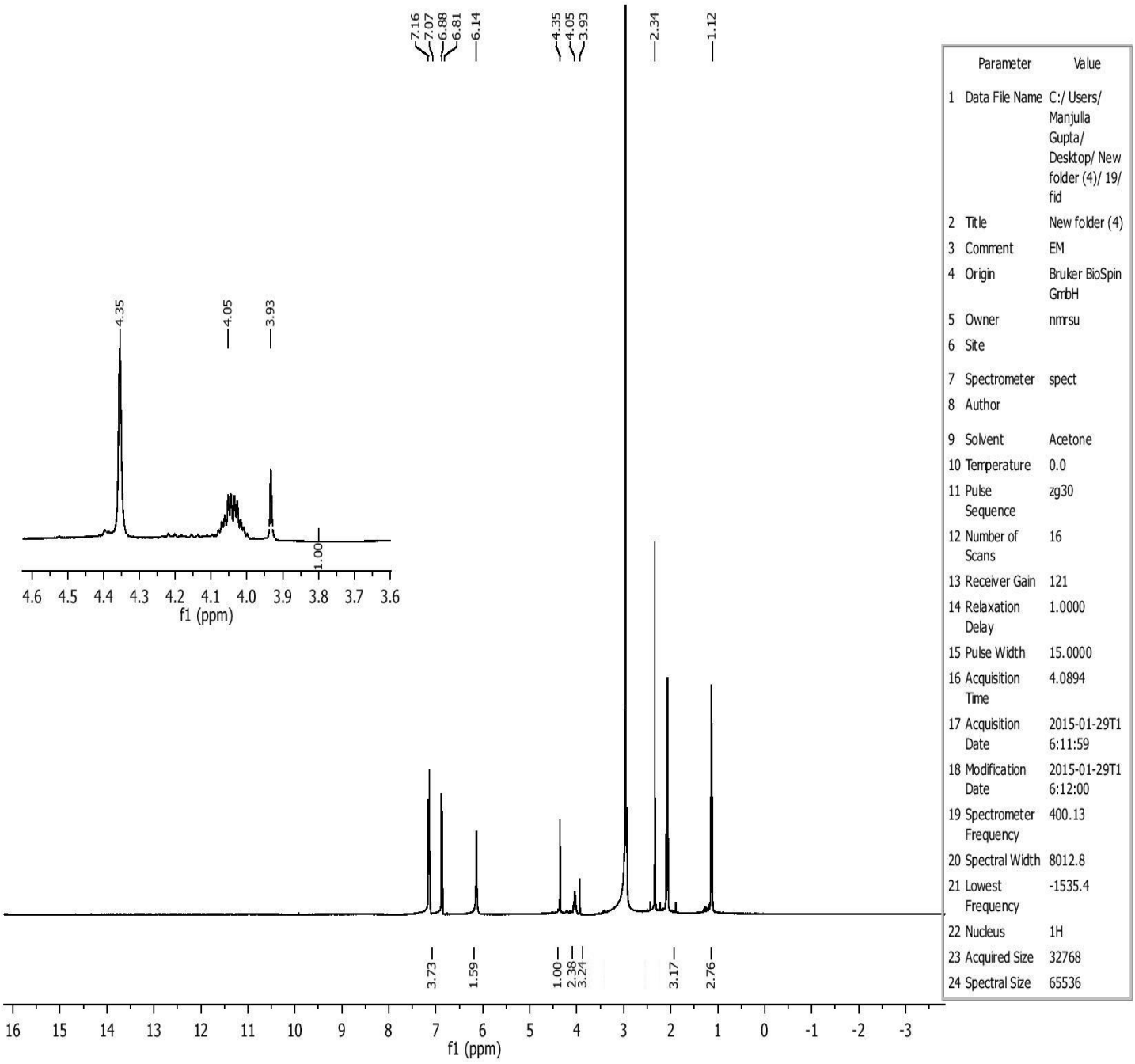

Fig. 17 ^{1}H NMR spectra of Ethyl-6-amino-4-(4-methoxyphenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

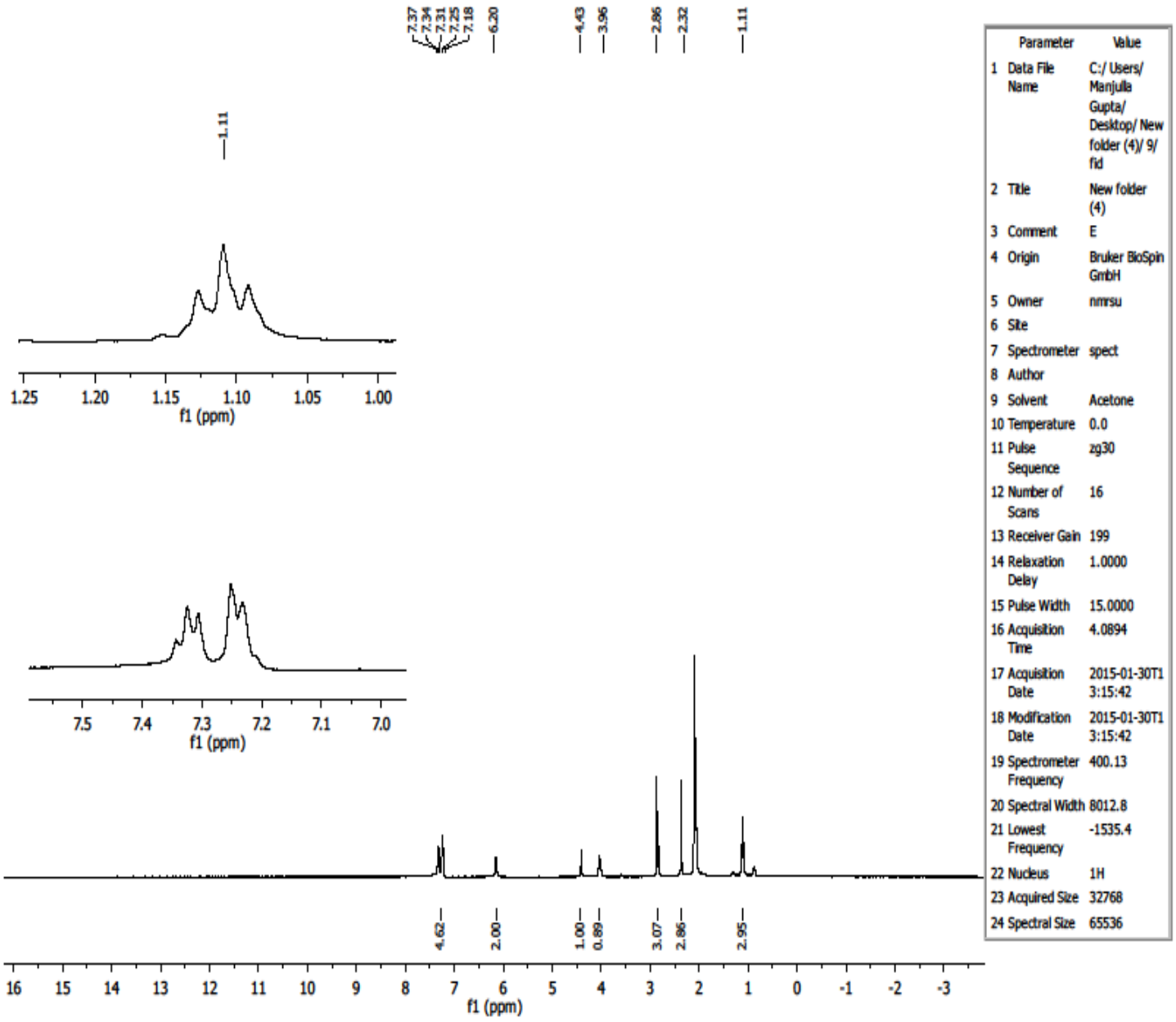

Fig. 18 ^{1}H NMR spectra of Ethyl-6-amino-4-(4-hydroxyphenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

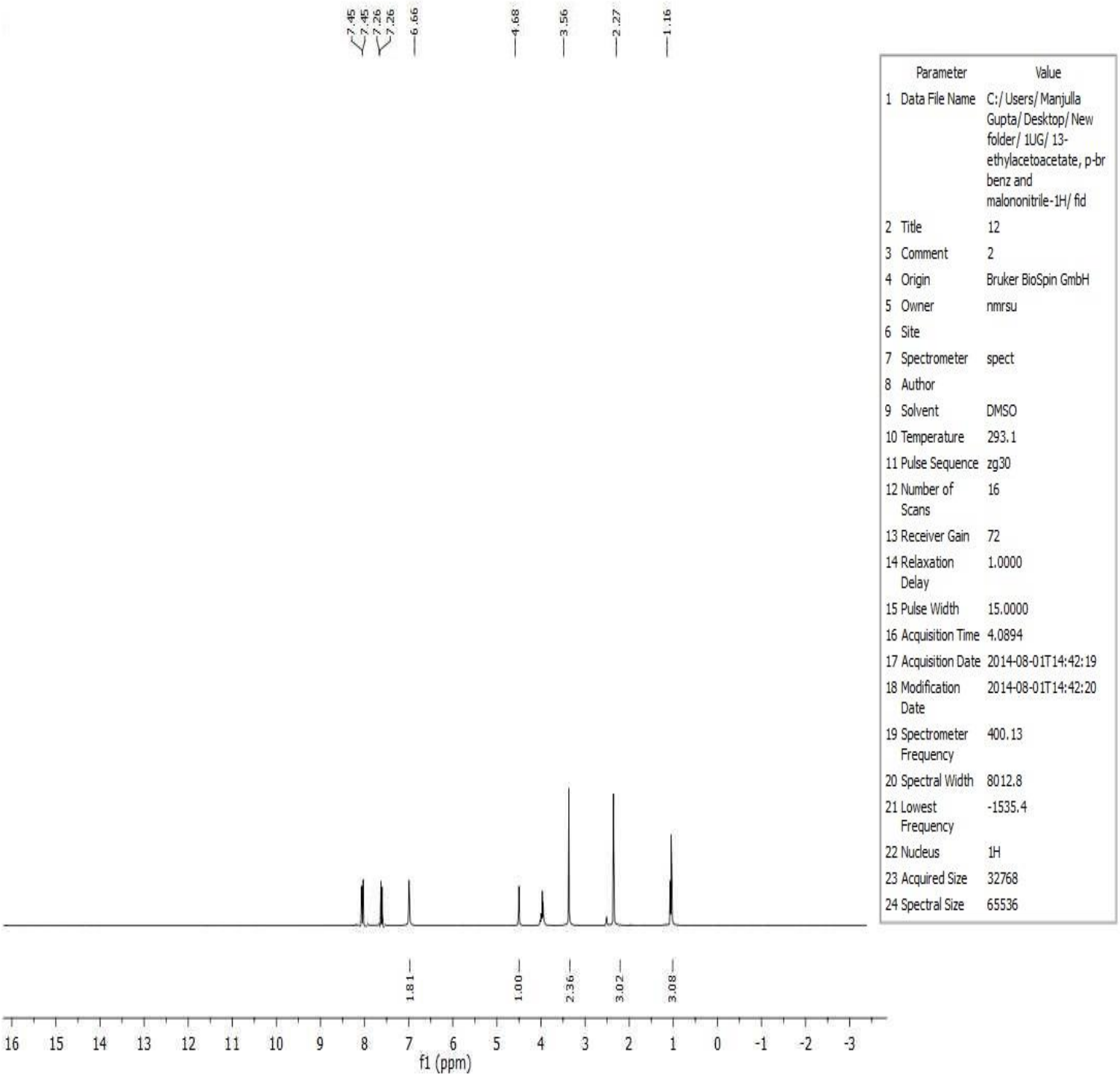

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Fig. 19 ^{1}H NMR spectra of Ethyl-6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

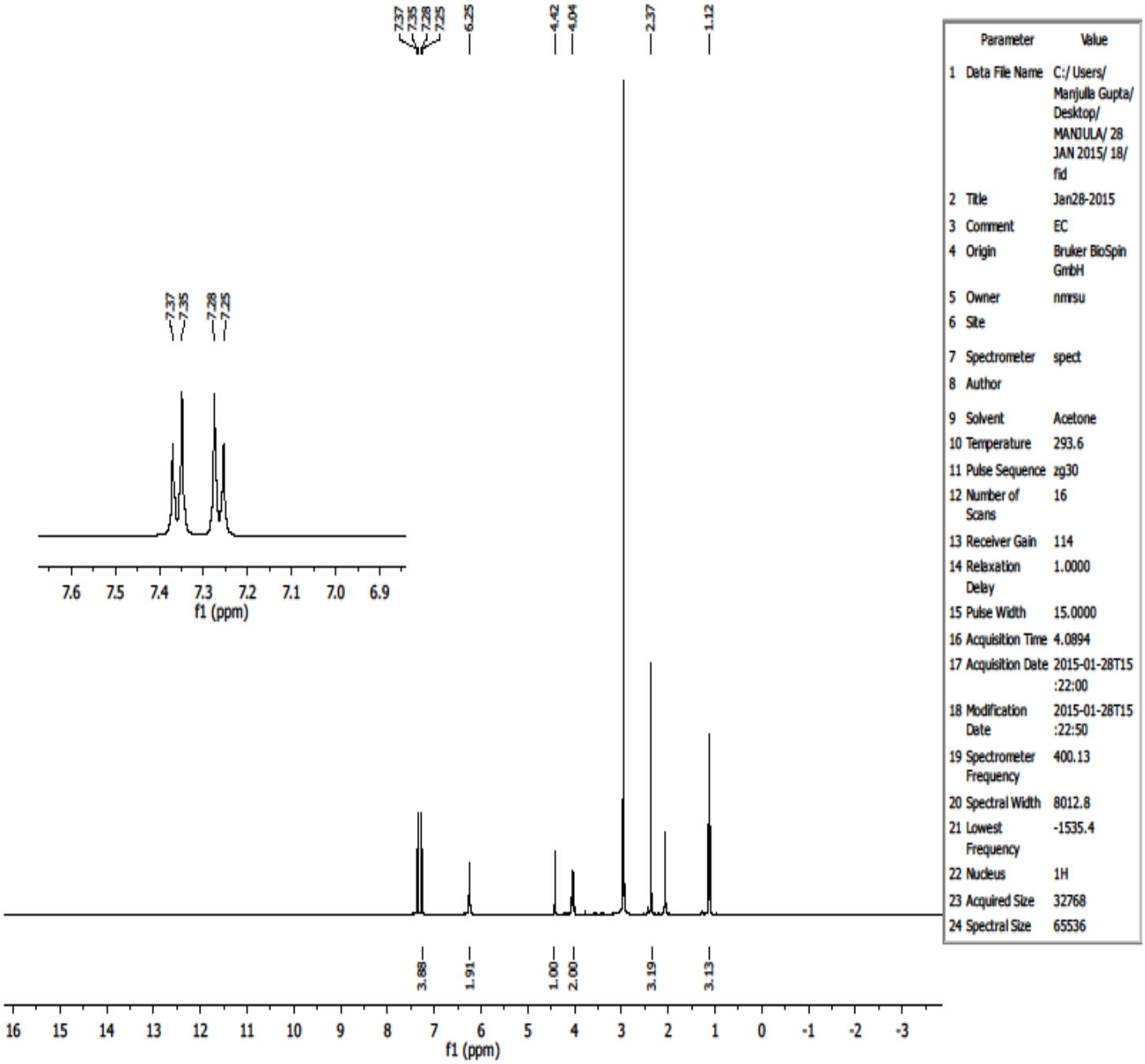

Fig. 20 ^{1}H NMR spectra of Ethyl-6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

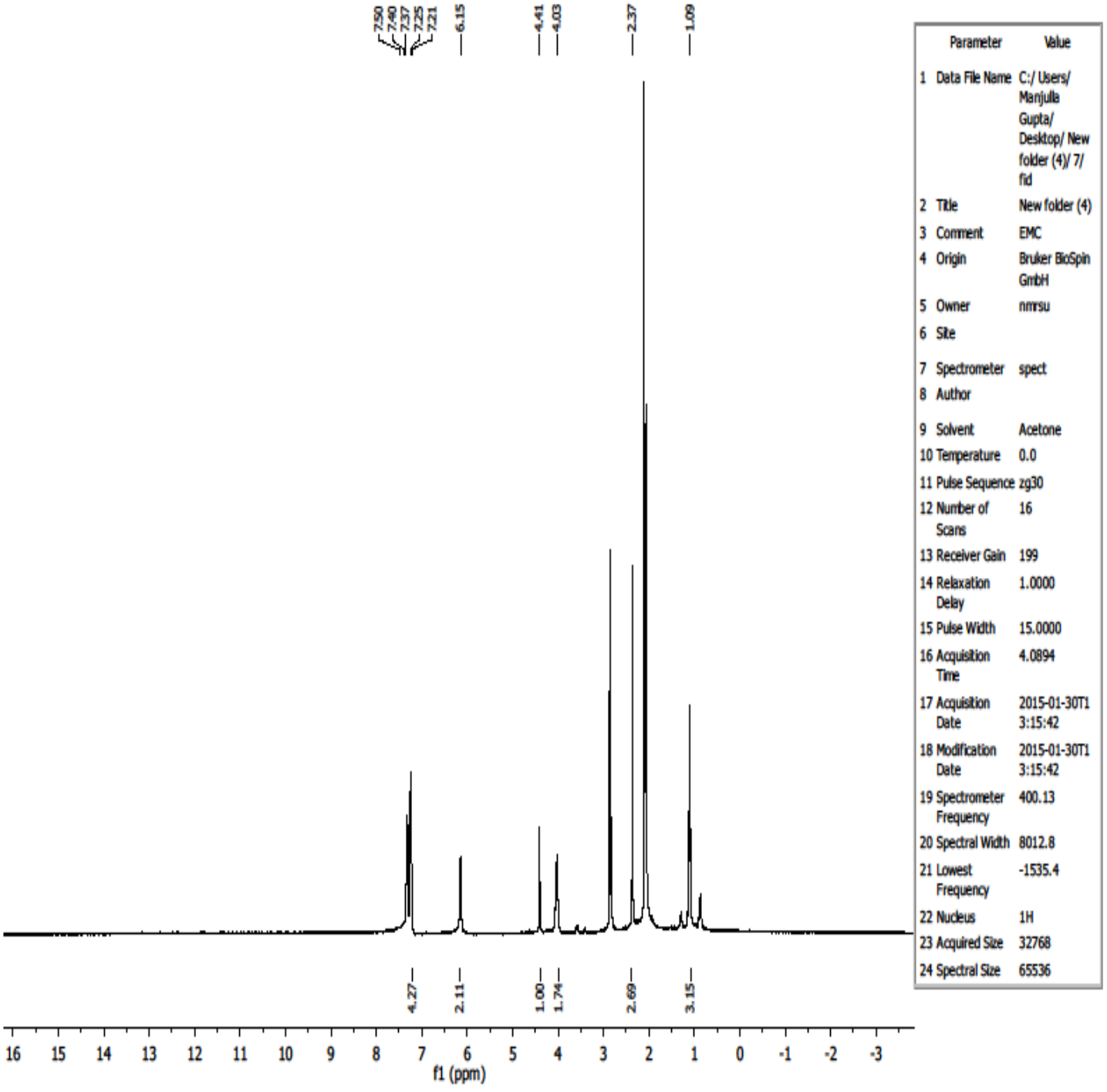

Fig. 21 ^{1}H NMR spectra of Ethyl-6-amino-4-(2-chlorophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

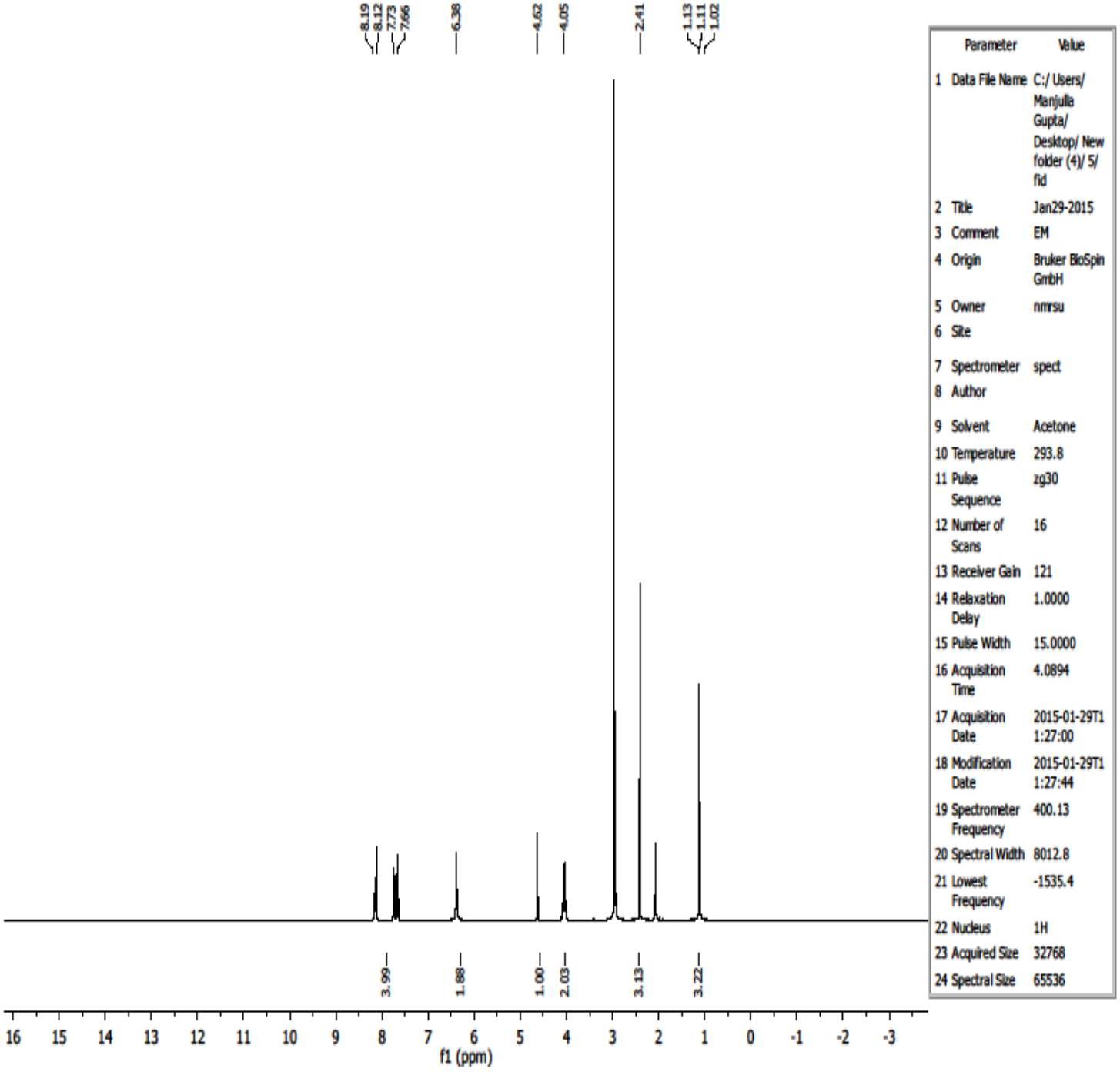

Fig. 22 ^{1}H NMR spectra of Ethyl-6-amino-4-(4-nitrophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

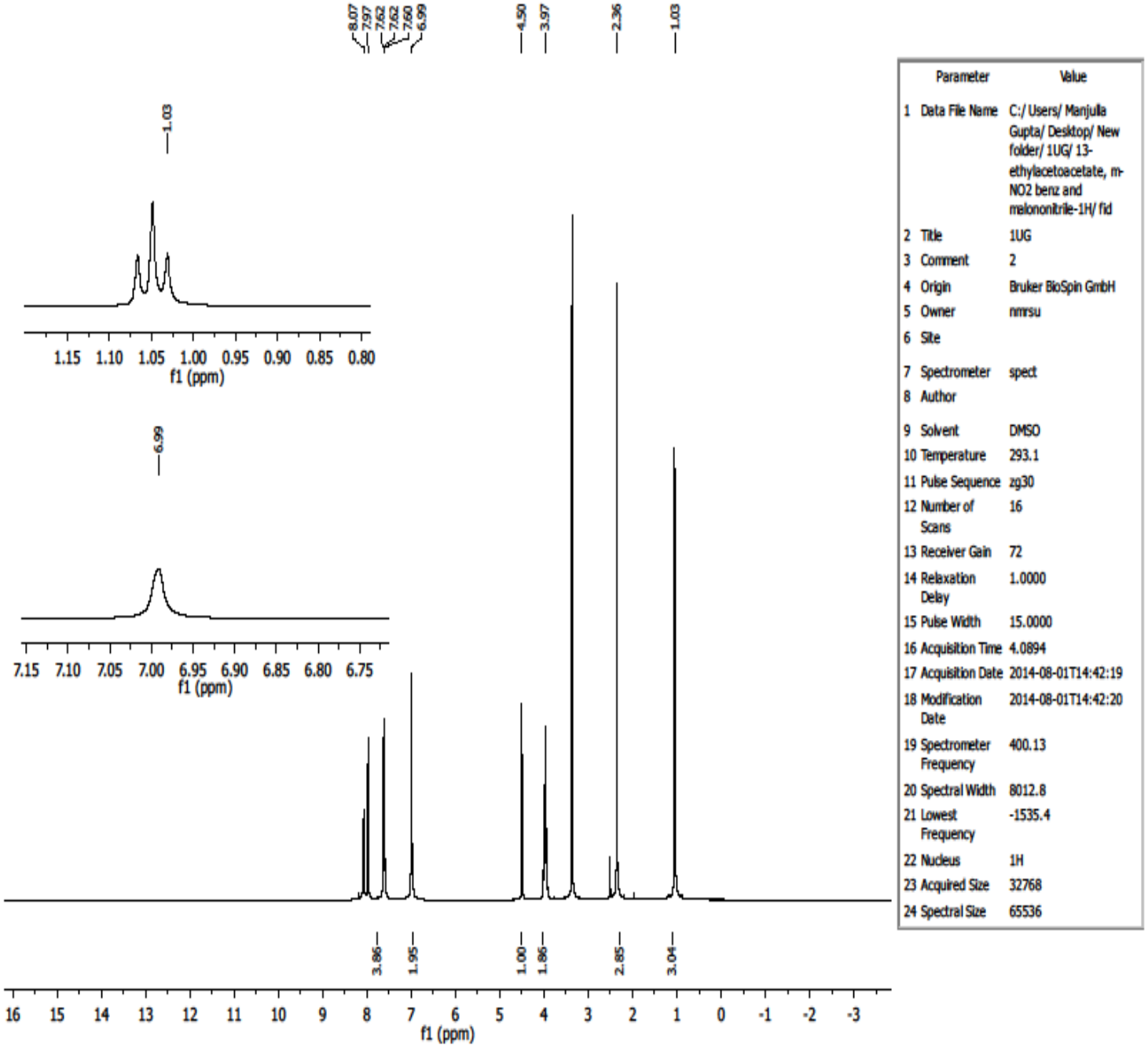

Fig. 23 ^{1}H NMR spectra of Ethyl-6-amino-4-(3-nitrophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

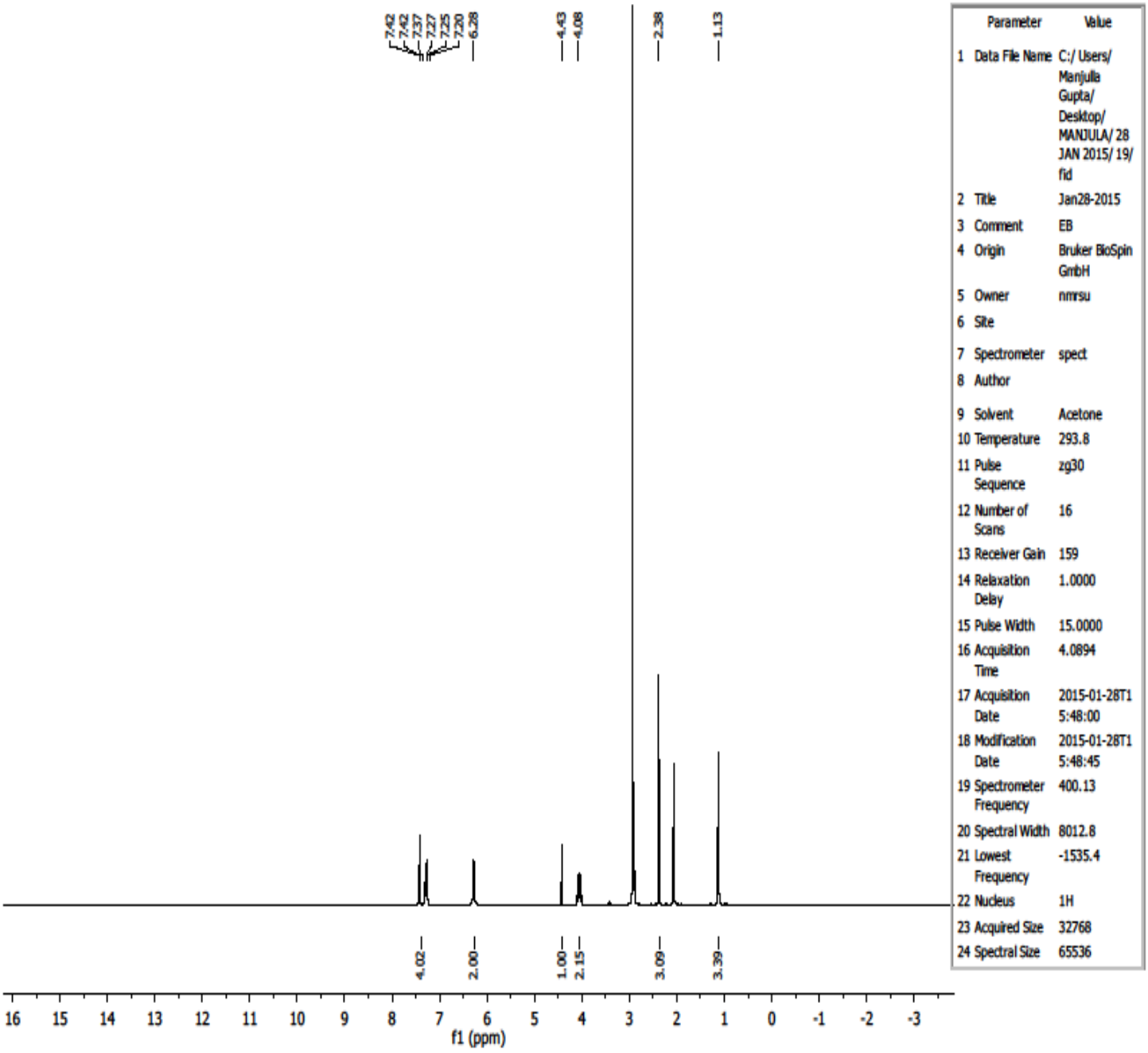

Fig. 24 ^{1}H NMR spectra of Ethyl-6-amino-4-(2-nitrophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

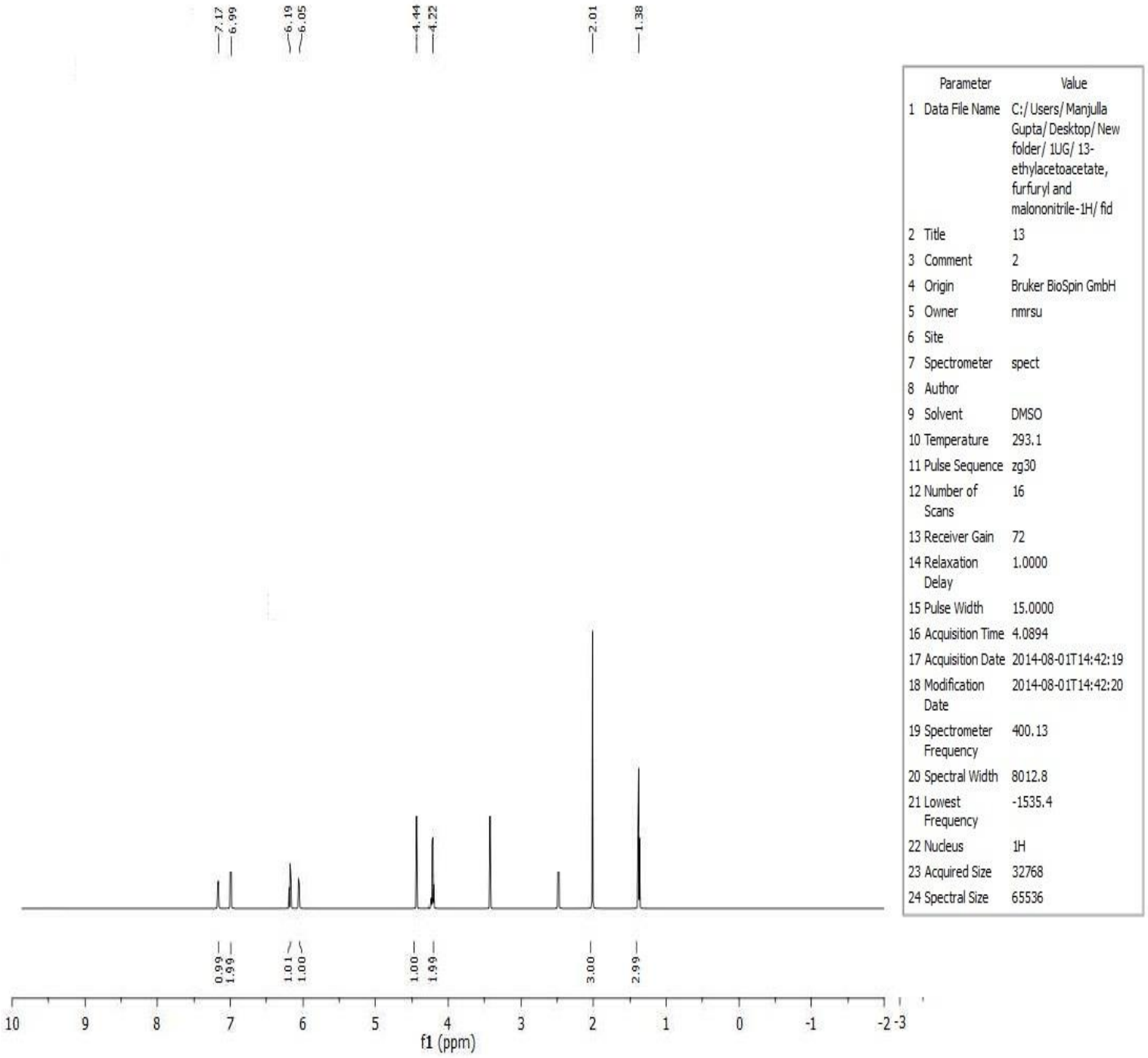

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Fig. 25 ^{1}H NMR spectra of Ethyl-6-amino-5-cyano -4-(furan-2-yl)-2-methyl-4*H*-pyran-3-carboxylate

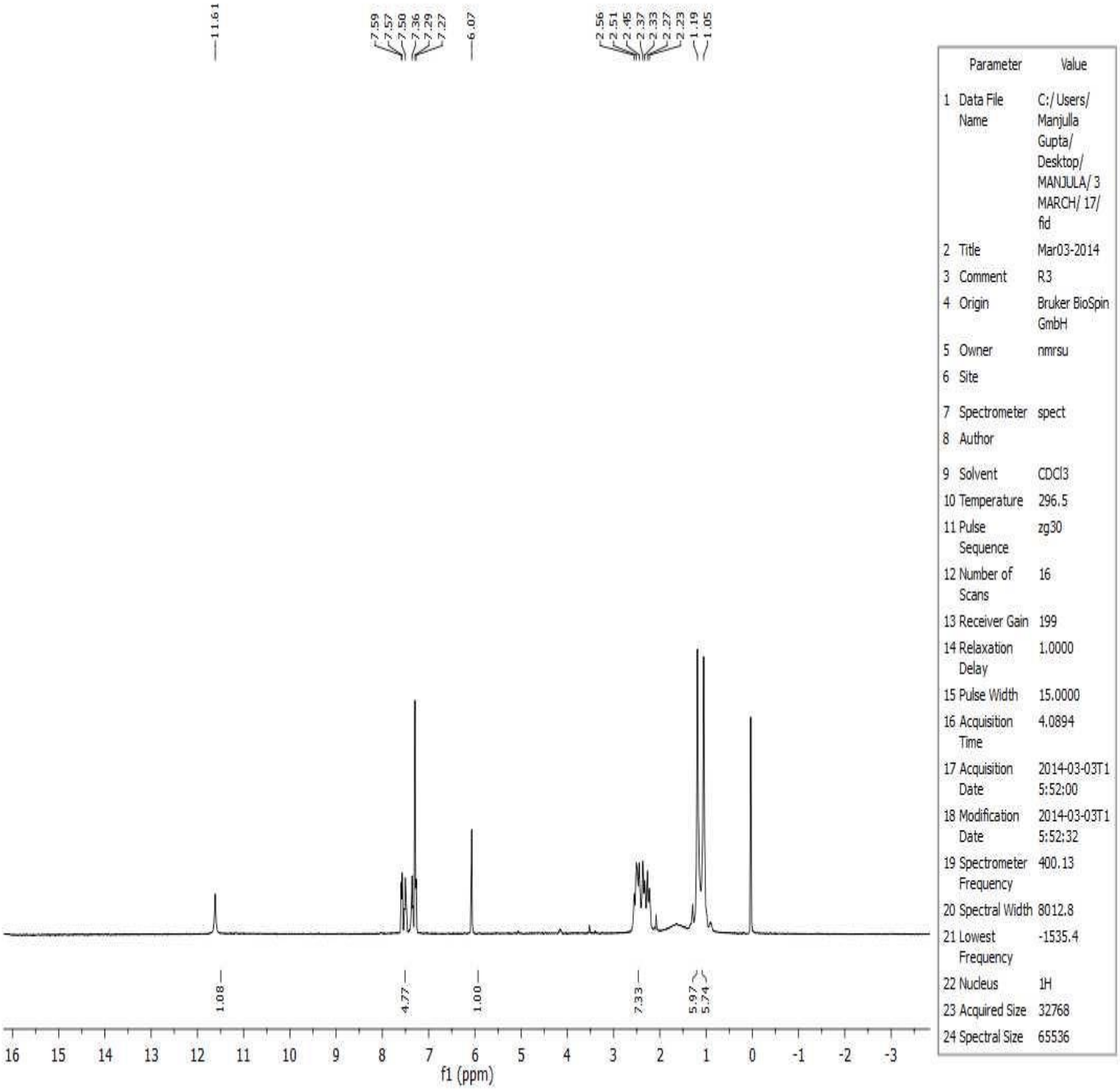

Fig. 26 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-phenyl -1,8-dioxodecahydroacridine

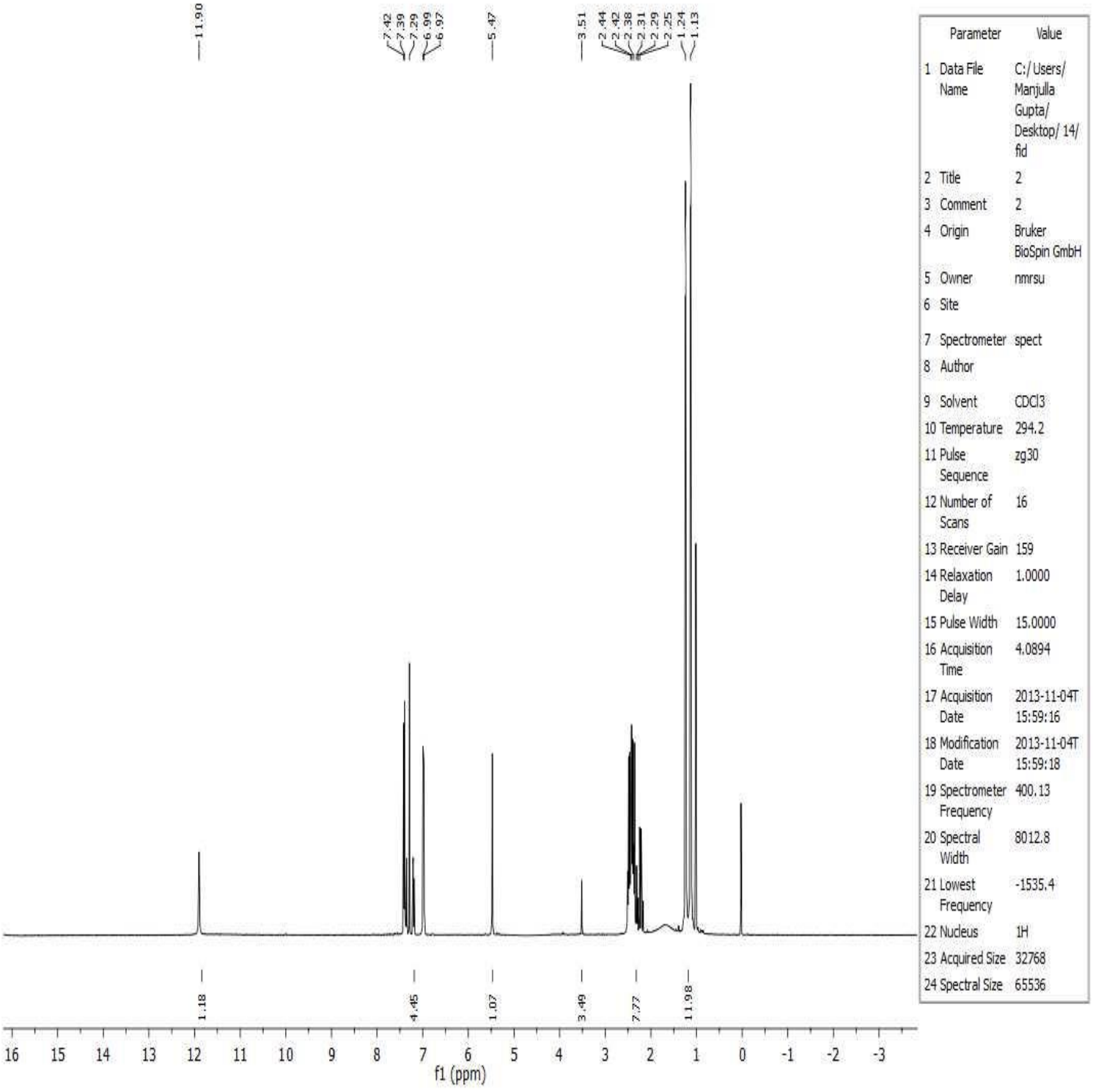

Fig. 27 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-methylphenyl)-1,8-dioxodecahydroacridine

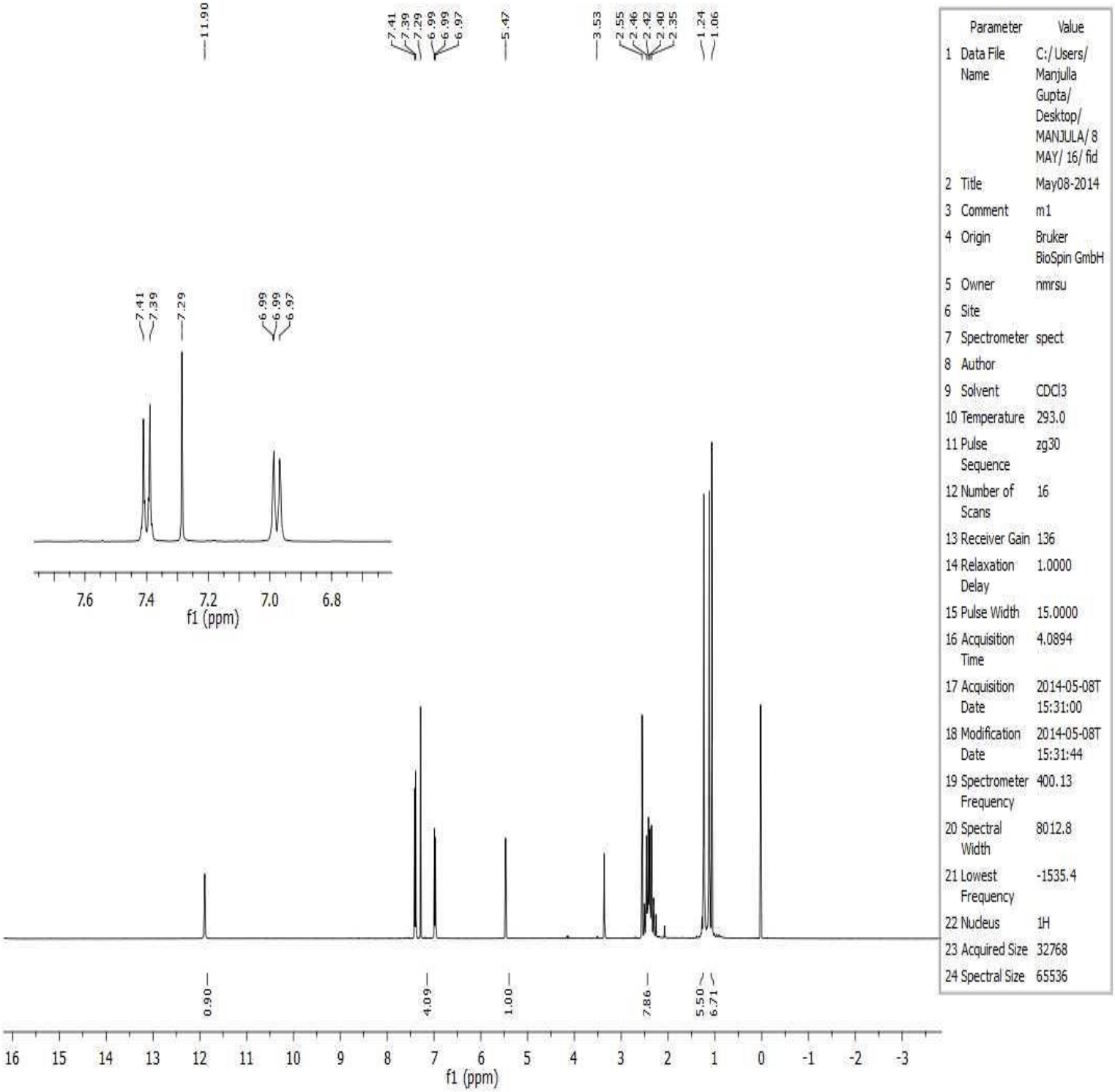

Fig. 28 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-methoxyphenyl)-1,8-dioxodecahydroacridine

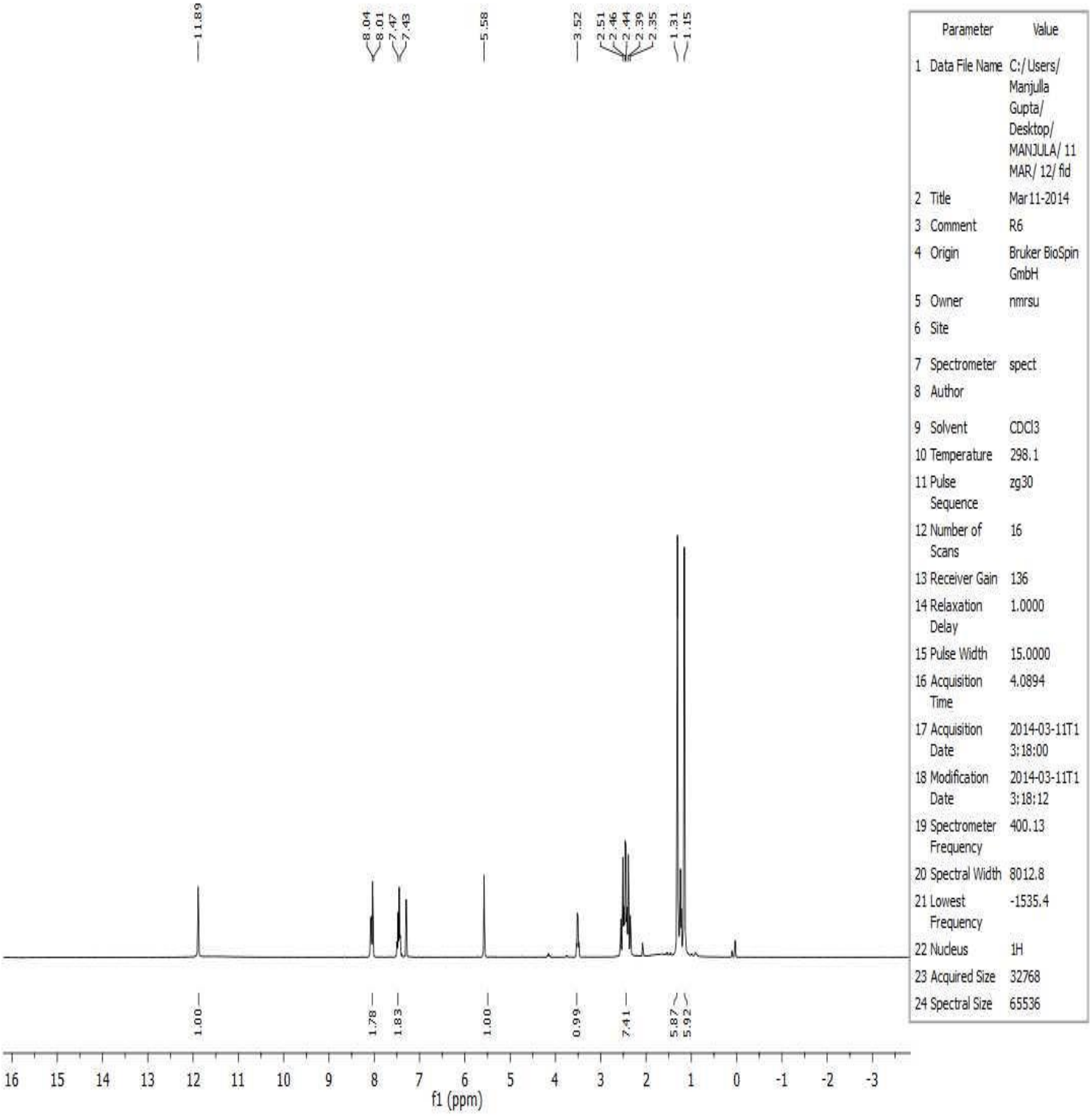

Fig. 29 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-hydroxyphenyl)-1,8-dioxodecahydroacridine

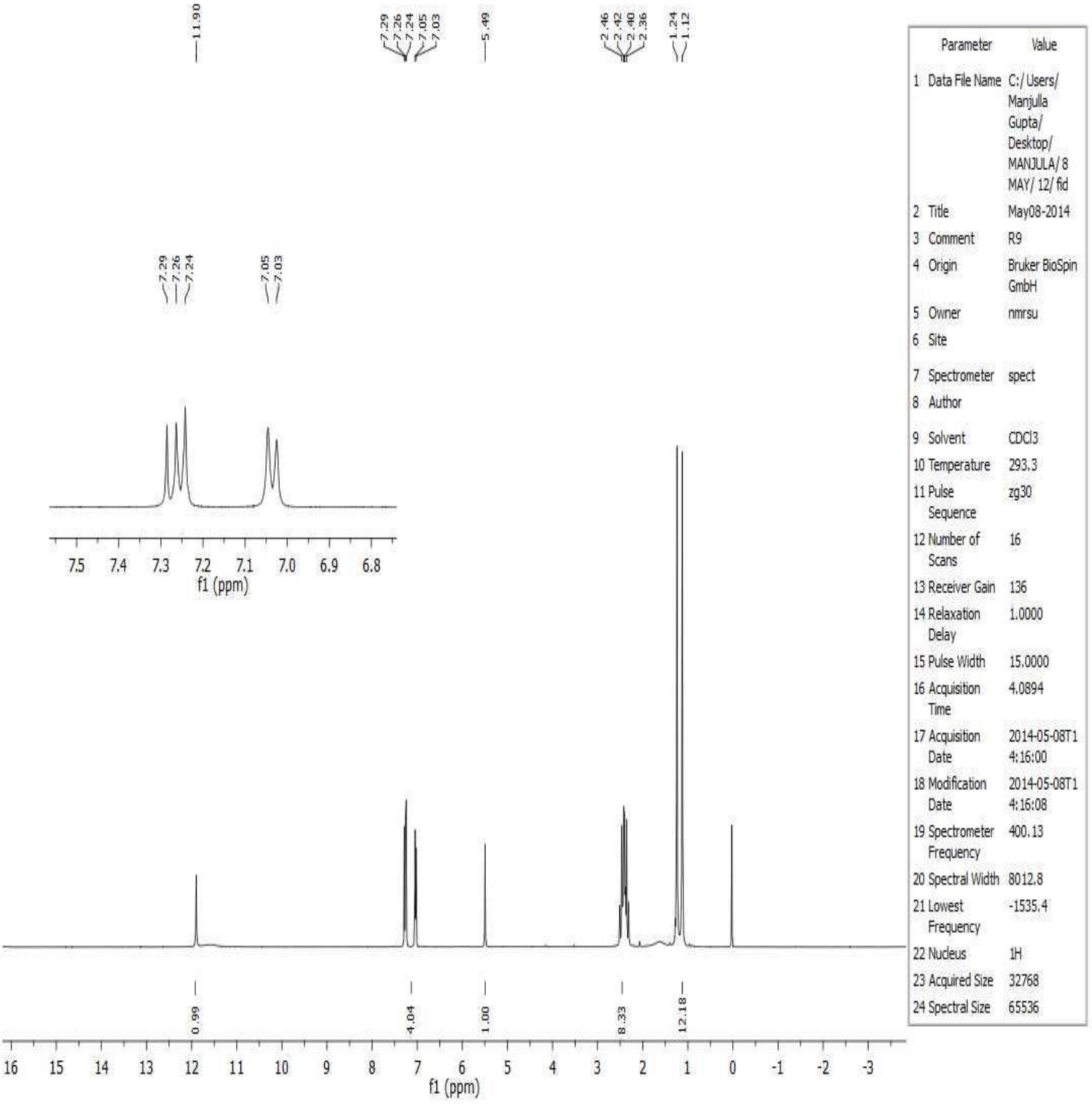

Fig. 30 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-fluorophenyl)-1,8-dioxodecahydroacridine

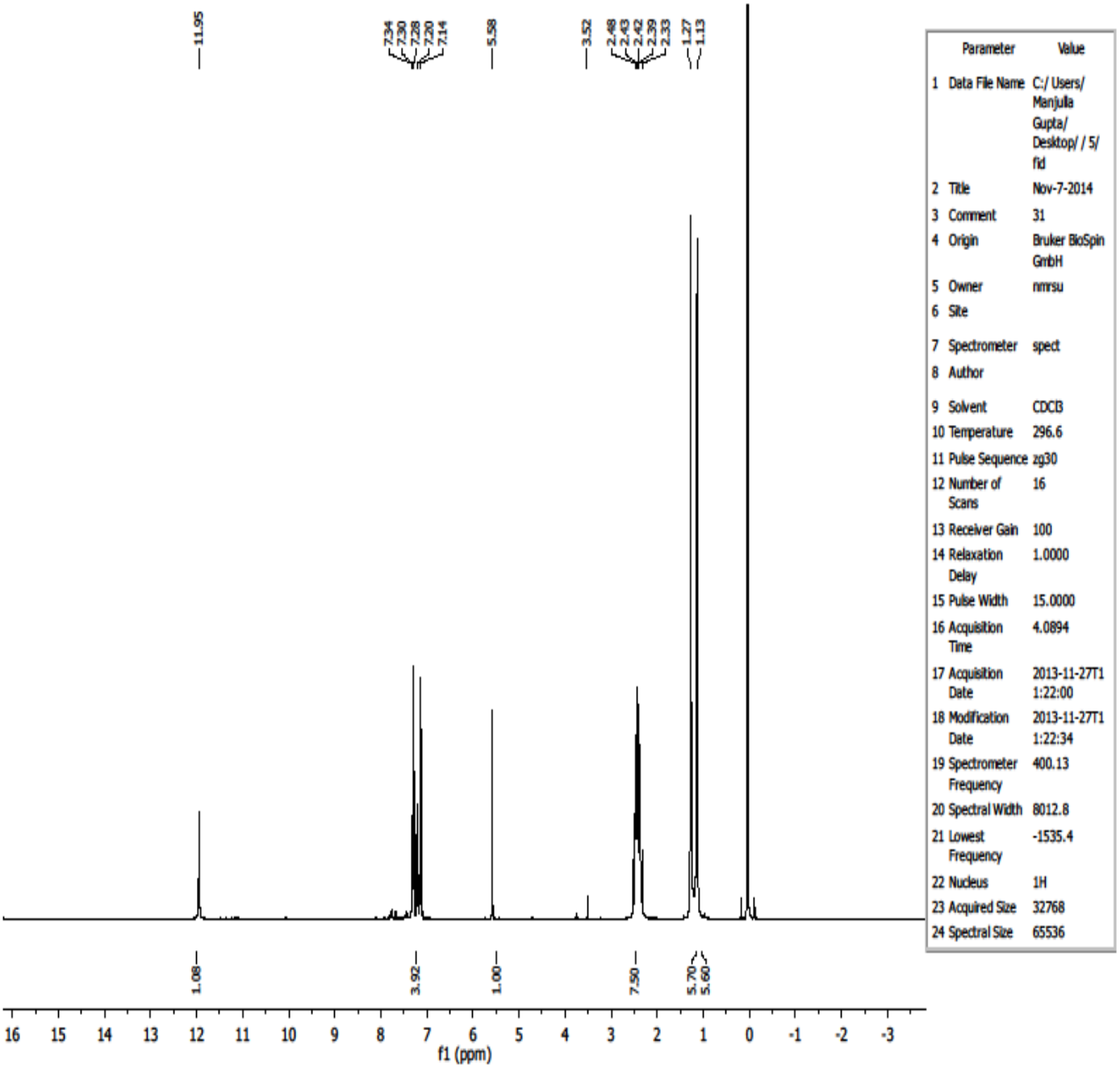

Fig. 31 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-(dimethylamino)phenyl)-1,8-dioxodecahydroacridine

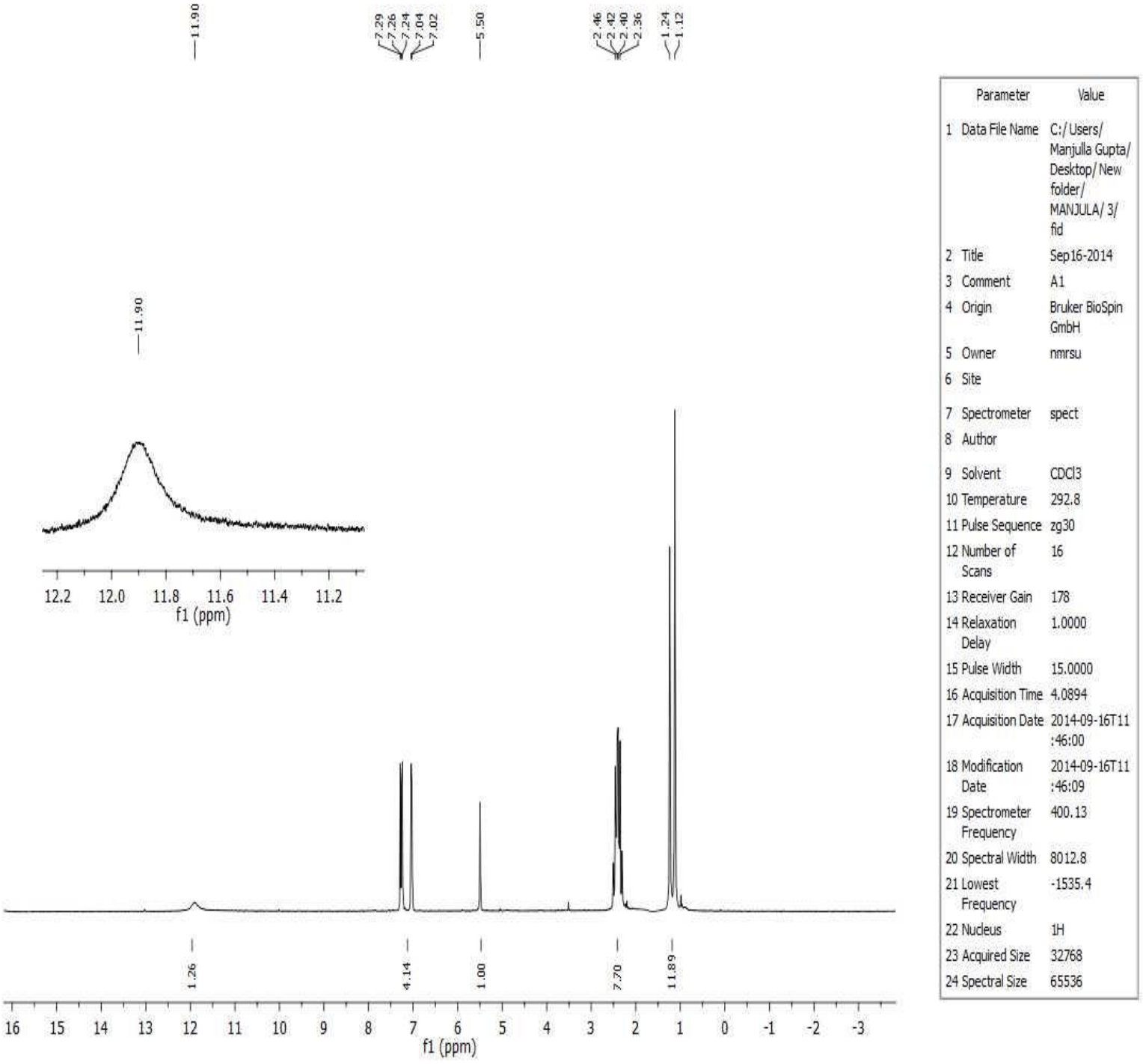

Fig. 32 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-chlorophenyl)-1,8-dioxodecahydroacridine

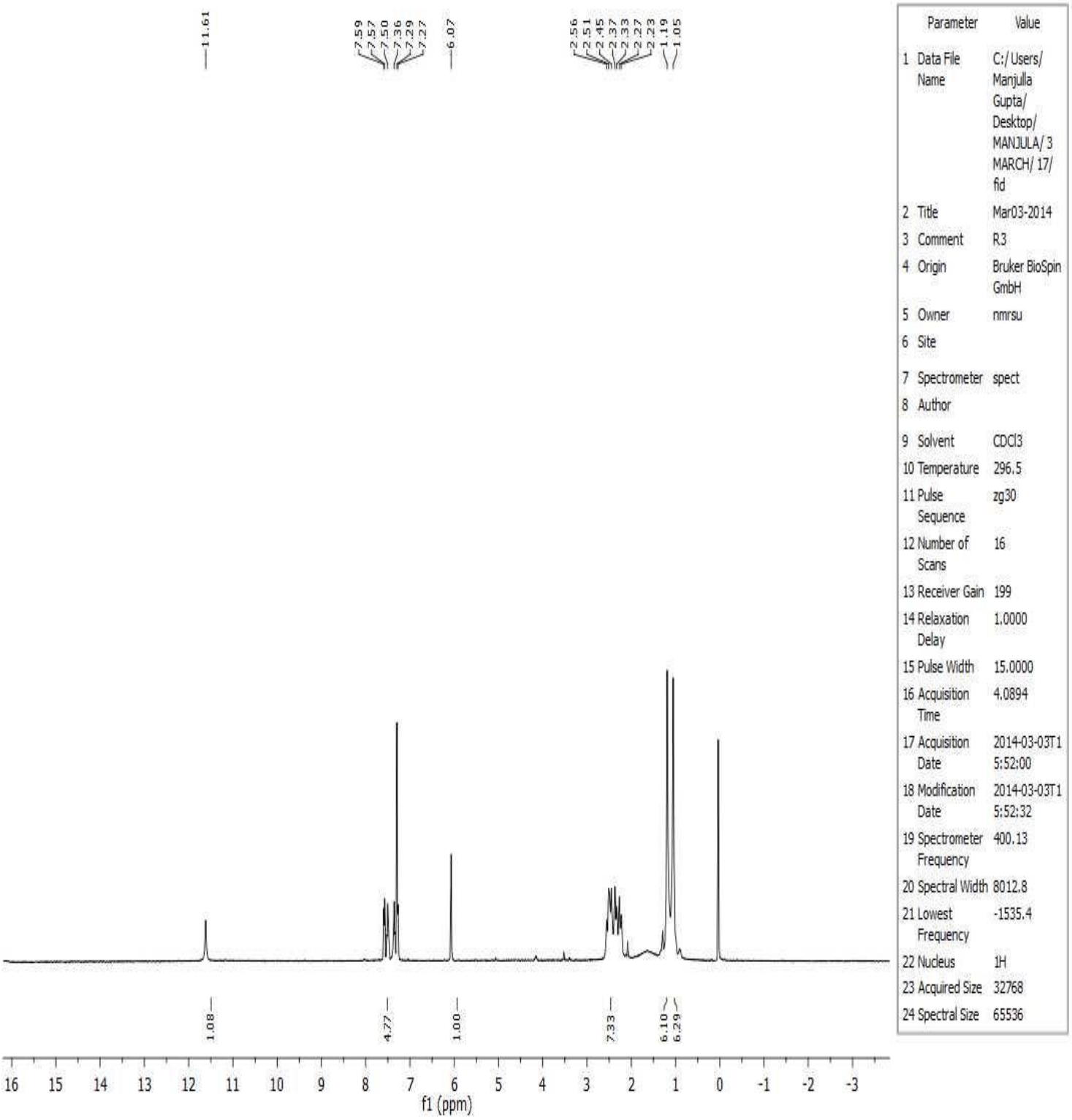

Fig. 33 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(2-chlorophenyl)-1,8-dioxodecahydroacridine

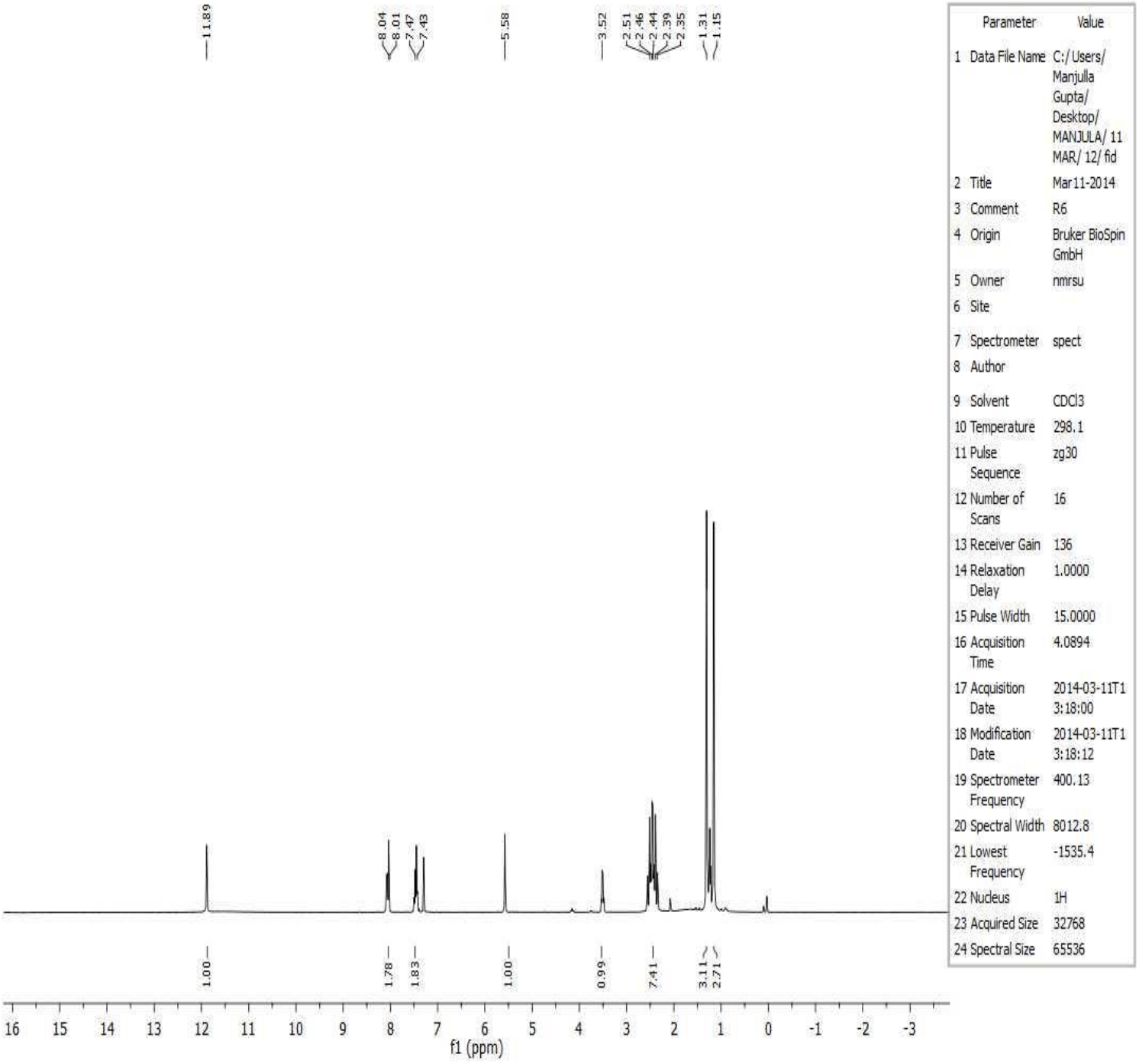

Fig. 34 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(3-chlorophenyl)-1,8-dioxodecahydroacridine

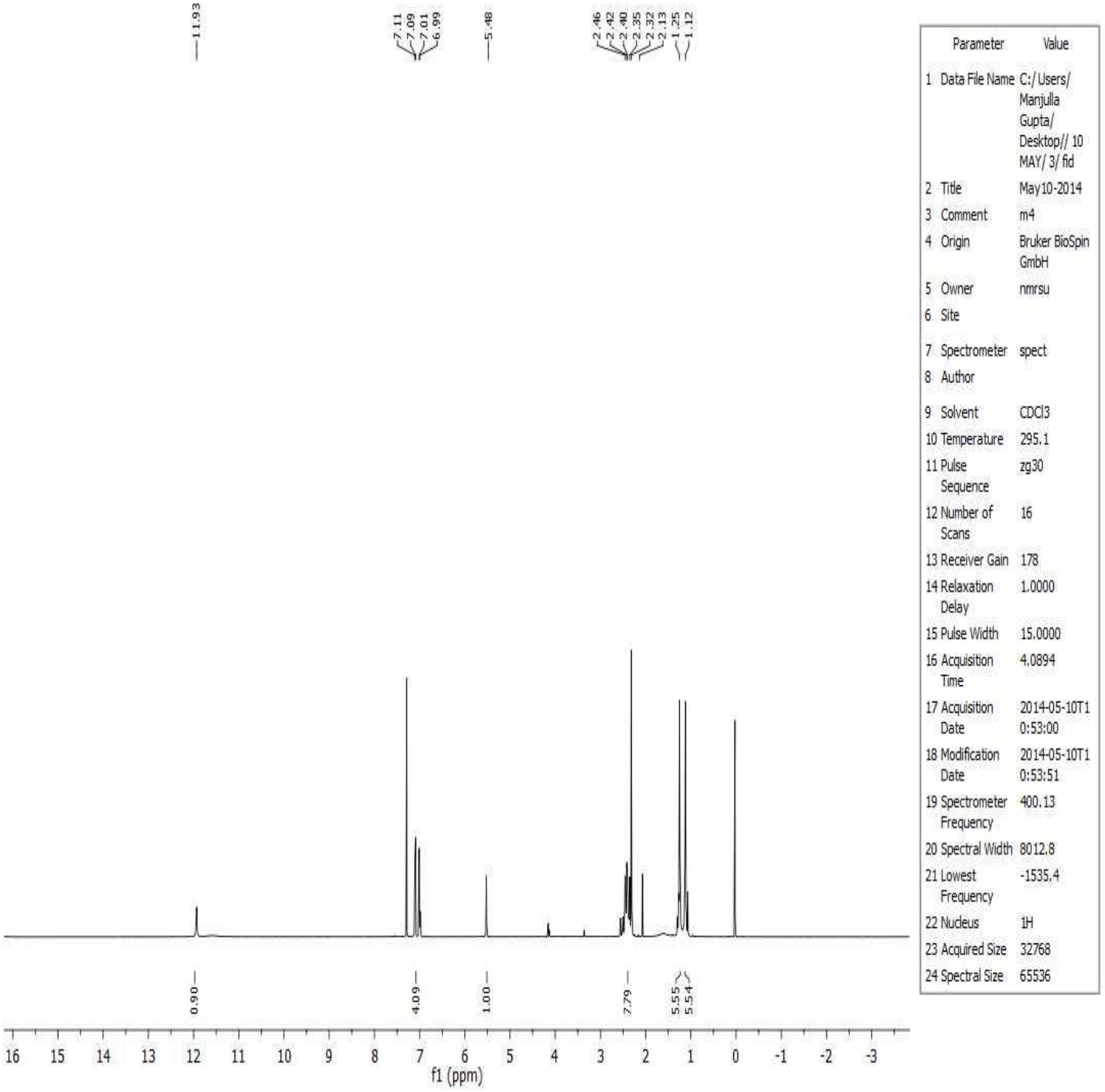

Fig. 35 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-bromophenyl)-1,8-dioxodecahydroacridine

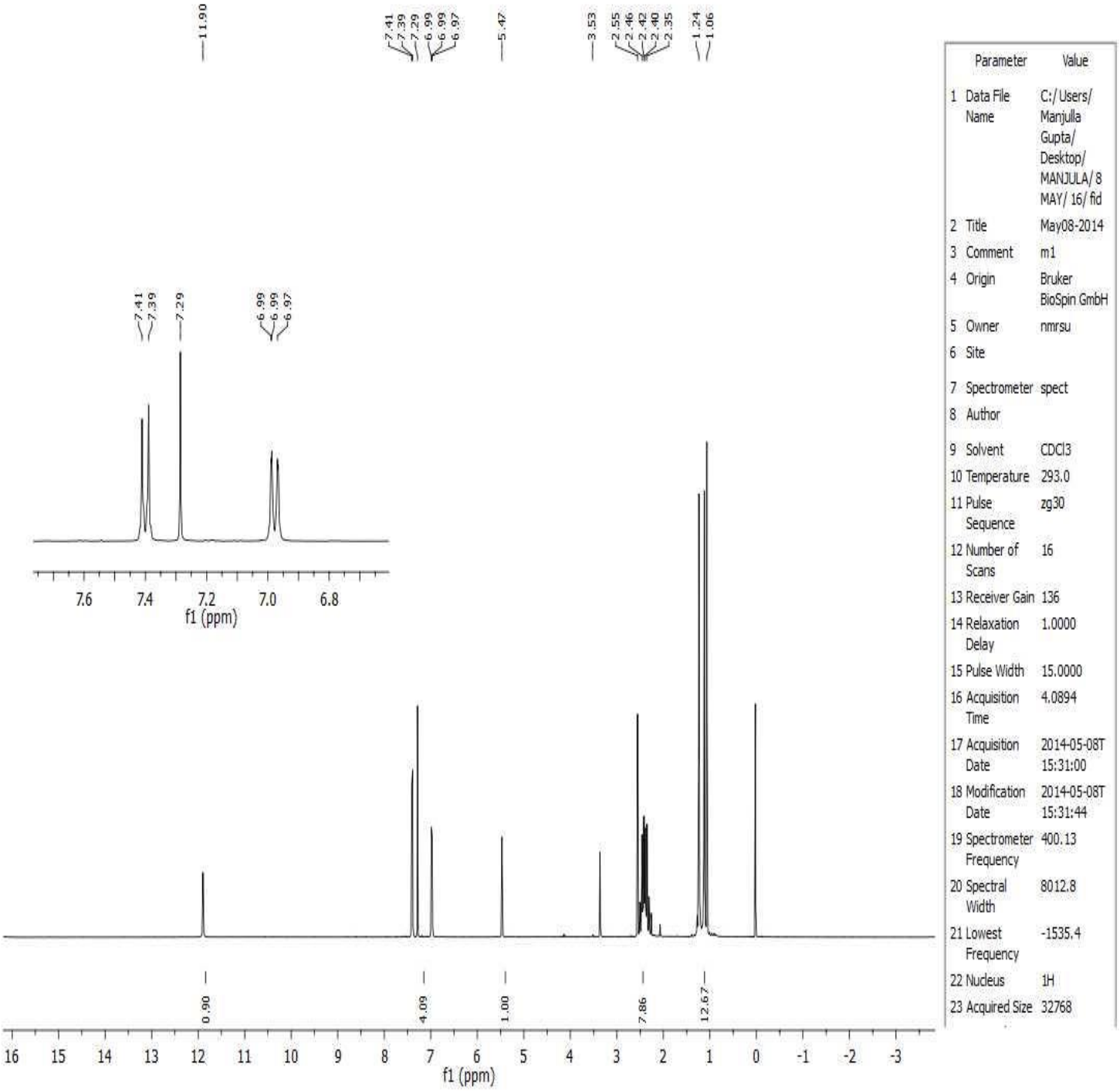

Fig. 36 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(4-nitrophenyl)-1,8-dioxodecahydroacridine

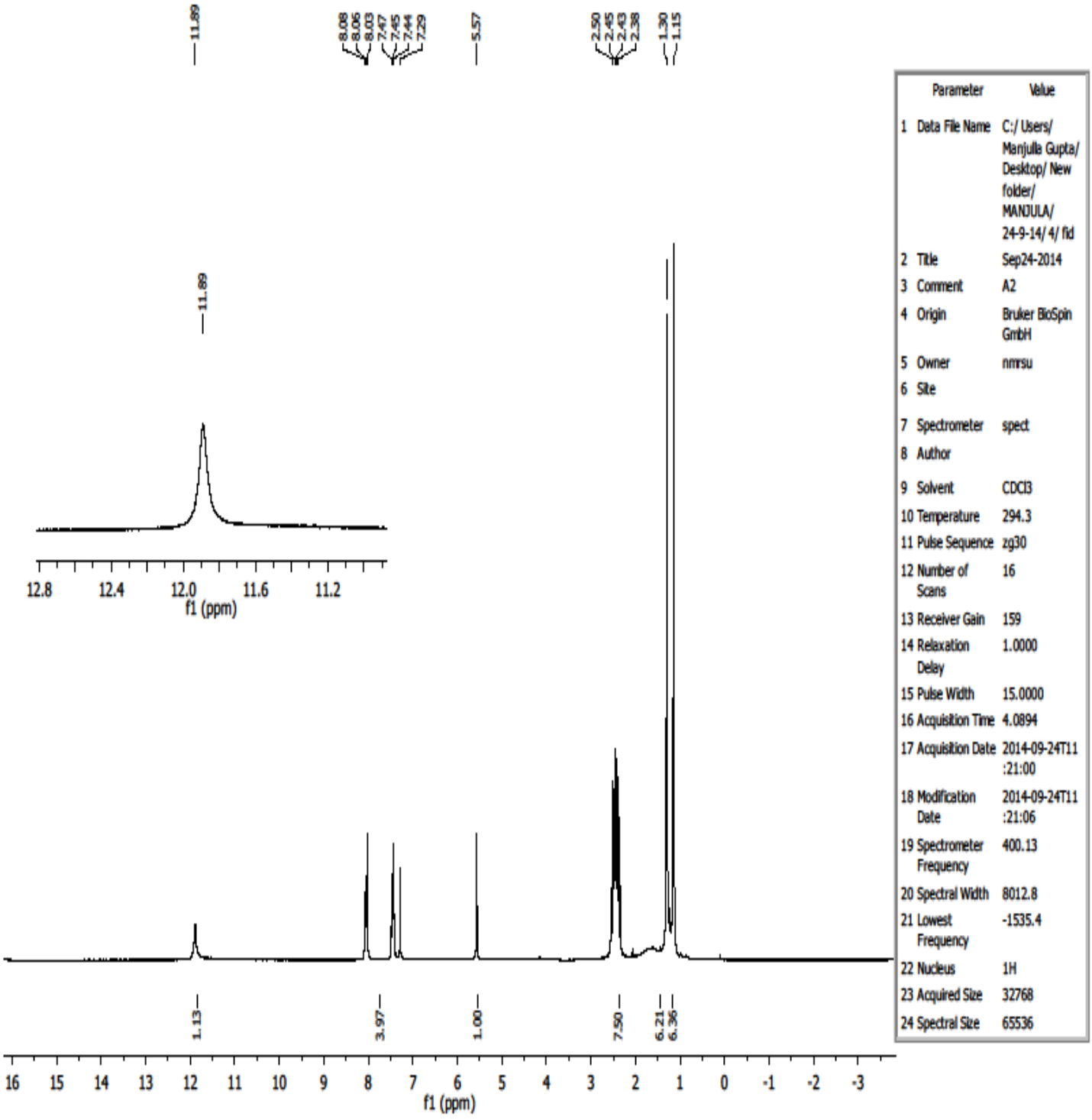

Fig. 37 ^{1}H NMR spectra of 3,3,6,6-Tetramethyl -9-(3-nitrophenyl)-1,8-dioxodecahydroacridine