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Supporting Information

Functional group manoeuvring for tuning stability and reactivity: Synthesis of Cicerfuran, Moracin (D, E, M) and Chromene fused benzofuran natural products

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Table of contents

1. **General information:** All cross-coupling reactions were performed in an oven-dried Schlenk tubes under N_2 atmosphere conditions. All other reactions were performed under anhydrous conditions using dry solvents.

2. Experimental procedures:

Compound 11:[1]

A solution of compound **10** (3 g, 21.72 mmol) and DMAP (0.265 g, 2.17 mmol) in 100 mL of CH_2Cl_2 was taken in a 250 mL RB flask at 0 ^oC. To this, NEt_3 (2.42 g, 23.89 mmol) was added initially followed by the slow addition of acetyl chloride (1.87 g, 23.89 mmol). The reaction mixture was stirred at rt for 2 h and then poured into cold water. The organic layer was separated and washed with water followed by brine. It was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 10:90) to give compound **11** (2.1 g, 54%) as colourless solid, m.p. 56-58 ^oC.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.22 (s, 1H), 9.85 (s, 1H), 7.57 (d, J = 8.55 Hz, 1H), 6.78 (dd, J = 8.25, 2.15 Hz, 1H), 6.75 (d, J = 1.8 Hz, 1H), 2.32 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ =195.47, 168.35, 163.05, 157.21, 134.93, 118.60, 113.87, 110.66, 21.15 ppm. IR (KBr): $\tilde{\nu}$ = 3214, 2941, 2857, 1752, 1663, 1625, 1586, 1502, 1444, 1378, 1303, 1198, 1145, 1117 cm^{-1}. HRMS (EI): calcd for $C_9H_8O_4$ $[M]^+$ 180.0423; found 180.0424.

General procedure A for *ortho-gem*-dibromovinylphenols (Compounds 12b, 12c and 22)

A solution of CBr_4 (3 equiv) in CH_2Cl_2 (1.0 mL per mmol CBr_4) was put into a 250 mL round-bottomed flask and cooled to 0 °C. To this, a solution of PPh_3 (6 equiv) in CH_2Cl_2 (1.0 mL per mmol PPh_3) was added dropwise for about 15 minutes time period. The resulting mixture was stirred for 30 min and thereafter triethylamine (6 equiv) was added and stirred for 5 minutes. To this, a solution of salicylaldehyde derivative (1 equiv) in CH_2Cl_2 (1.0 mL per mmol salicylaldehyde) was added dropwise in 30 minutes time period. The resulting mixture was brought to rt and

stirred for additional 14 h. To this, hexane (one fourth volume of total CH_2Cl_2 was used) was added and stirred for 15 minutes. The resulting suspension was filtered through 100–200 silica and the filtrate was concentrated. The crude product was subjected to silica gel column chromatography to obtain *ortho-gem*-dibromovinylphenols.

Compound 12b:[2]

Following the general procedure A, reaction of compound **11b** (2 g, 8.76 mmol), CBr_4 (8.71 g, 26.28 mmol), PPh_3 (13.78 g, 52.57 mmol), NEt_3 (5.32 g, 52.57 mmol) gave **compound 12b** as a pale yellow solid (1.5 g, 50%), m.p. 88-90 ^oC.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.73 Hz, 1H), 7.49 (s, 1H), 7.43-734 (m, 5H), 6.59 (dd, J = 8.73, 2.43 Hz, 1H), 644 (d, J = 2.43 Hz, 1H), 5.04 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.19, 153.72, 136.47, 131.78, 129.91, 128.64, 128.12, 127.46, 115.83, 107.25, 102.40, 90.42, 70.11 ppm. IR (KBr): $\tilde{\nu}$ = 3393, 3031, 2943, 1610, 1513, 1435, 1299, 1222, 1109, 1176, 1015, 852, 735 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{13}Br_2O_2$ $[M+H]^+$ 382.9282; found 382.9282.

Compound 12c:

Following the general procedure A, reaction of compound **11** (1.2 g, 6.66 mmol), CBr_4 (6.62 g, 19.98 mmol), PPh_3 (10.48 g, 39.96 mmol), NEt_3 (4.04 g, 39.96 mmol) gave **compound 12c** as a colourless solid (1.63 g, 73%), m.p. 120-122 ^oC.

^1H NMR (400 MHz, DMSO-d_6): δ = 10.31 (s, 1H), 7.59-7.57 (m, 2H), 6.63-6.60 (m, 2H), 2.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.87, 155.61, 151.36, 132.52, 128.97, 119.78, 112.21, 108.97, 88.98, 20.89 ppm. IR (KBr): $\tilde{\nu}$ = 3316, 3022, 1718, 1605, 1513, 1430, 1366, 1257, 1149, 1100, 1018, 844 cm^{-1}. HRMS (ESI): calcd for $C_{10}H_7Br_2O_3$ $[M-H]^-$ 332.8762; found 332.8766.

Compound 22:

Following the general procedure A, reaction of compound **20** (1.2 g, 5.82 mmol), CBr_4 (5.79 g, 17.47 mmol), PPh_3 (9.16 g, 34.93 mmol), NEt_3 (3.53 g, 34.93 mmol) gave **compound 22** as an off-white solid (1.2 g, 57%), m.p. 78-81 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 1H), 7.36 (s, 1H), 6.23 (s, 1H), 4.86 (s, 1H), 2.71 (t, *J* = 6.84 Hz, 2H), 1.79 (t, *J* = 6.84 Hz, 2H), 1.33 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.27, 152.05, 131.87, 129.51, 114.98, 113.42, 103.73, 88.87, 74.97, 32.82, 26.86, 21.74 ppm. IR (KBr): $\tilde{\nu}$ = 3335, 2975, 2931, 1620, 1590, 1501, 1387, 1318, 1192, 1104, 902 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{15}Br_2O_2$ $[M+H]^+$ 360.9439; found 360.9435.

General procedure B for acetyl protected *ortho-gem*-dibromovinylphenols (Compounds 12ba, 12ca, 22a and 22b)

A solution of CBr_4 (2 equiv) and acetyl protected salicylaldehyde derivative (1 equiv) in CH_2Cl_2 (1.0 mL per each mmol) was put into a 250 mL round-bottomed flask, and cooled to 0 °C. To this, a solution of PPh_3 (4 equiv) in CH_2Cl_2 (1.0 mL per mmol PPh_3) was added dropwise for about 30 minutes time period. After complete addition, the mixture was brought to rt and stirred for 14 h. Then hexane (one fourth volume of total CH_2Cl_2 was used) was added with stirring for 15 minutes. The resulting suspension was filtered through 100–200 silica and the filtrate was concentrated. The crude product was purified by silica gel column chromatography to obtain the corresponding *gem*-dibromide.

Compound 12ba

Following the general procedure B, reaction of compound **11c** (1.5 g, 5.5 mmol), CBr_4 (3.7 g, 11.1 mmol), PPh_3 (5.8 g, 22.2 mmol) gave **compound 12ba** as a pale yellow solid (1.95 g, 83%), m.p. 46-48 ^{o}C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.59 Hz, 1H), 7.41-7.35 (m, 5H), 7.29 (s, 1H), 6.88 (dd, *J* = 8.59, 2.29 Hz, 1H), 6.75 (d, *J* = 2.29 Hz, 1H), 5.05 (s, 2H) 2.33 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ =168.73, 159.67, 148.89, 136.19, 131.44, 129.95, 128.64, 128.19, 127.53, 121.15, 112.46, 108.99, 91.19, 70.31, 20.89 ppm. IR (KBr): $\tilde{\nu}$ = 3032, 1766, 1613, 1497, 1369, 1199, 1160, 1100 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{18}Br_2NO_3$ $[M+NH_4]^+$ 441.9653; found 441.9656.

Compound 12ca

Following the general procedure B, reaction of compound **11a** (1 g, 4.5 mmol), CBr_4 (3 g, 9 mmol), PPh_3 (4.7 g, 18 mmol) gave **compound 12ca** as a pale yellow solid (1.7 g, 82%), m.p. 34-36 ^oC.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.61 Hz, 1H), 7.32 (s, 1H), 7.03 (dd, *J* = 8.61, 2.27 Hz, 1H), 6.97 (d, *J* = 2.27 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.68, 168.40, 150.90, 148.18, 131.21, 129.78, 126.00, 118.99, 116.12, 92.88, 21.09, 20.88 ppm. IR (KBr): $\tilde{\nu}$ = 3023, 2923, 1769, 1650, 1491, 1369, 1192, 1145, 1096, 1014 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{14}Br_2NO_4$ $[M+NH_4]^+$ 393.9290; found 393.9290.

Compound 22a

Following the general procedure B, reaction of compound **21** (1.5 g, 6.04 mmol), CBr_4 (4 g, 12.08 mmol), PPh_3 (6.34 g, 24.17 mmol) gave **compound 22a** as a colourless solid (2 g, 82%), m.p. 60-62 ^oC.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 1H), 7.25 (s, 1H), 6.50 (s, 1H), 2.76 (t, *J* = 6.64 Hz, 2H), 2.29 (s, 3H), 1.80 (t, *J* = 6.64 Hz, 2H), 1.33 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.05, 155.14, 147.20, 131.69, 129.69, 119.84, 118.74, 110.97, 90.28, 75.13, 32.56, 27.03, 22.19, 20.99 ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2975, 1766, 1617, 1576, 1485, 1369, 1198, 1152, 1098, 1013, 928, 911 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{20}Br_2NO_3$ $[M+NH_4]^+$ 419.9810; found 419.9815.

Compound 22b

Following the general procedure B, reaction of compound **21a** (1.2 g, 4.87 mmol), CBr_4 (4.85 g, 14.62 mmol), PPh_3 (7.67 g, 29.24 mmol) gave **compound 22b** as a pale yellow liquid (1.5 g, 76%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 1H), 7.24 (s, 1H), 6.52 (s, 1H), 6.29 (d, *J* = 9.62 Hz, 1H), 5.60 (d, *J* = 9.62 Hz, 1H), 2.30 (s, 3H), 1.44 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.73, 153.99, 148.37, 131.39, 130.60, 126.38, 121.22, 120.63, 118.85, 110.39, 90.73, 77.11,

28.38, 29.91 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 2932, 1768, 1640, 1613, 1566, 1485, 1366, 1289, 1198, 1164, 913, 787 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{18}Br_2NO_3$ $[M+NH_4]^+$ 417.9653; found 417.9653.

Compound 13a:

Compound **12b** (0.5 g, 1.30 mmol), CuI (0.012 g, 0.065 mmol), K_3PO_4 (0.552 g, 2.6 mmol) and THF (3 mL) were put into an oven dried Schlenk tube under a nitrogen atmosphere. The mixture was heated in an oil bath at 65 °C for 7 h. The reaction mixture was then cooled to rt and extracted with ethyl acetate. The combined organic extract was washed with water, brine, dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane 03:97) to obtain compound **13a** (0.320 g, 81%) as a pale yellow solid, m.p. 40-42 ^oC.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.46-7.45 (m, 2H), 7.42-7.33 (m, 4H), 7.06 (d, *J* = 2.29 Hz, 1H), 6.95 (dd, *J* = 8.59, 2.29 Hz, 1H), 6.64 (d, *J* = 0.86 Hz, 1H), 5.10 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.88, 156.46, 136.70, 128.62, 128.06, 127.48, 126.20, 122.26, 120.16, 113.02, 108.01, 97.07, 70.62 ppm. IR (KBr): $\tilde{\nu}$ = 3090, 2902, 1533, 1292, 1035, 911, 825 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{12}BrO_2$ $[M+H]^+$ 303.0021; found 303.0028.

Triarylbismuth reagent (TAB-3):

To a solution of 5-bromo-6-methoxybenzo[d][1,3]dioxole (5 g, 5 equiv) in dry THF (20 mL), *n*-BuLi (14.87 mL, 1.6 M, 5.5 equiv) was added dropwise at -78 ^oC and stirred for 2 h. The reaction mixture was brought to rt and $ZnCl_2$ (47.6 mL, 0.5 M in THF) was added and stirred for 30 minutes. To this, a solution of $BiCl_3$ (1.36 g, 1 equiv) in dry THF (20 mL) was added dropwise in about 30 minutes at 0 ^oC and stirred at rt for further 18 h. After that, the solvent was evaporated and the crude residue obtained was dissolved in $CHCl_3$ (100 mL), washed with saturated $NaHCO_3$ solution followed by brine. It was quickly passed through silica bed and concentrated. The crude product was triturated with hexane (10 mLx2), hexane:ethanol (1:1) (10 mLx2) and the solid obtained was washed with hexane (5 mL). This procedure furnished the triarylbmuth **TAB-3** (1.8 g, 63%) as colourless solid, m.p. 222-224 ^oC.

$C_{24}H_{21}BiO_9$ (662.10): calcd C 43.52, H 3.20; found C 43.47, H 3.08%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (s, 1H), 6.64 (s, 1H), 5.88 (s, 2H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.11, 148.52, 145.38, 133.64, 117.62, 100.91, 94.75, 56.62 ppm. IR (KBr): $\tilde{\nu}$ = 2896, 1615, 1592, 1495, 1455, 1443, 1379, 1264, 1189, 1163, 1107, 1038, 943, 927, 869, 817 cm^{-1}.

Compound 13b:

Compound **13a** (0.825 mmol, 0.25 g, 3.3 equiv), **TAB-2** (0.25 mmol, 0.155 g, 1.0 equiv), Cs_2CO_3 (0.75 mmol, 0.244 g, 3.0 equiv), $Pd(OAc)_2$ (0.025 mmol, 5.6 mg, 0.1 equiv), PPh_3 (0.1 mmol, 26 mg, 0.4 equiv), and NMP (3 mL) were put into an oven-dried Schlenk tube under a nitrogen atmosphere. The mixture was heated in an oil bath at 90 °C for 1 h. The contents were cooled to rt, and extracted with ethyl acetate. The combined organic extract was washed with water, brine, dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane 05:95) to give compound **13 b** (0.219 g, 81%) as a colourless solid, m.p. 76-78 ^{o}C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49-7.33 (m, 6H), 7.13 (d, J = 2 Hz, 1H), 6.98-6.94 (m, 4H), 6.45 (t, J = 2.29 Hz, 1H), 5.13 (s, 2H), 3.87 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.04, 157.21, 155.67, 155.02, 136.89, 132.38, 128.61, 128.00, 127.49, 122.68, 121.07, 112.77, 102.53, 101.68, 100.59, 97.08, 70.57, 55.46 ppm. IR (KBr): $\tilde{\nu}$ = 2932, 1599, 1572, 1489, 1455, 1204, 1154, 821 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}O_4$ $[M+H]^+$ 361.1440; found 361.1446.

Procedure for domino couplings (compounds 13, 23 and 27):

1,1-Dibromide (0.825 mmol), $BiAr_3$ (0.250 mmol), Cs_2CO_3 (2.25 mmol), $Pd(PPh_3)_4$ (0.022 mmol), and DMF (6 mL) were put into an oven-dried Schlenk tube under a nitrogen atmosphere. The mixture was heated in an oil bath at 90 °C for 7 h. The contents were cooled to rt and extracted with ethyl acetate. The organic portion was washed with water, brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by silica gel column chromatography to obtain the benzofuran product.

Compound 13:[3]

Colourless solid (0.130 g, 64%), m.p. 110-112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.32 Hz, 1H), 7.01 (d, *J* = 1.96 Hz, 1H), 6.97 (d, *J* = 2.44 Hz, 2H), 6.93 (d, *J* = 0.76 Hz, 1H), 6.78 (dd, *J* = 8.28, 2.2 Hz, 1H), 6.45 (t, *J* = 2.32 Hz, 1H), 4.99 (bs, 1H), 3.87 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.01, 155.65, 155.02, 153.66, 132.32, 122.75, 121.20, 112.08, 102.57, 101.68, 100.60, 98.24, 55.48 ppm. IR (KBr): $\tilde{\nu}$ = 3399, 2937, 2838, 1574, 1600, 1488, 1461, 1423, 1153, 1204, 1064, 825 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{15}O_4$ $[M+H]^+$ 271.0970; found 271.0972.

Compound 23

Yellow colour solid (0.165 g, 65%), m.p. 104-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 1H), 6.96 (d, *J* = 2.28 Hz, 2H), 6.93 (s, 1H), 6.86 (s, 1H), 6.43 (t, *J* = 2.30 Hz, 1H), 3.86 (s, 6H), 2.89 (t, *J* = 6.88 Hz, 2H), 1.85 (t, *J* = 6.64 Hz, 2H), 1.37 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.05, 154.65, 152.40, 132.61, 122.19, 120.24, 117.40, 102.58, 101.31, 100.52, 99.28, 74.42, 55.48, 33.02, 26.91, 22.78 ppm. IR (KBr): $\tilde{\nu}$ = 2934, 2973, 1598, 1573, 1460, 1422, 1353, 1326, 1204, 1155, 1113, 1066, 928, 836 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{23}O_4$ $[M+H]^+$ 339.1596; found 339.1592.

Compound 27:[4]

Pale yellow solid (0.162 g, 70%), m.p 170-172 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, 8.72 Hz, 2H), 7.19 (s, 1H), 6.95 (d, 8.72Hz, 2H), 6.92 (s, 1H), 6.74 (s, 1H), 3.85 (s, 3H), 2.89 (t, *J* = 6.86 Hz, 2H), 1.84 (t, *J* = 6.86 Hz, 2H), 1.37 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.52, 155.03, 154.49, 151.84, 125.94, 123.79, 122.56, 120.47, 117.07, 114.15, 99.21, 99.07, 74.30, 55.34, 33.05, 26.89, 22.77 ppm. IR (KBr): $\tilde{\nu}$ = 2972, 1504, 1460, 1249, 1180, 1116, 1033, 879, 831, 797 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{21}O_3$ $[M+H]^+$ 309.1490; found 309.1498.

Compound 27a

Pale yellow solid (0.181 g, 69%), m.p. 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 9.16 Hz, 2H), 7.25 (s, 1H), 6.85 (d, *J* = 9.20 Hz, 2H), 6.53 (s, 1H), 3.82 (s, 3H), 2.74 (t, *J* = 7.10 Hz, 2H), 2.33 (s, 3H), 1.80 (t, *J* = 6.88 Hz, 2H), 1.33 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =168.99, 159.43, 154.84, 150.56, 133.25, 132.76, 118.87, 115.58, 113.93, 111.04, 108.56, 92.04, 83.18, 75.09, 55.27, 32.42, 26.87,

21.84, 20.86 ppm. IR (KBr): ṽ = 3416, 1766, 1616, 1571, 1513, 1249, 1202, 1149, 1119 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{23}O_4$ $[M+H]^+$ 351.1596; found 351.1591.

Compound 13c:[5]

A solution of compound **13** (0.150 g, 0.555 mmol) and DMAP (0.007 g, 0.055 mmol) in 100 mL of CH_2Cl_2 was put in a 250 mL RB flask at 0 ^oC. To this, NEt_3 (0.084 g, 0.832 mmol) was added followed by the slow addition of acetyl chloride (0.065 g, 0.832 mmol). This reaction mixture was stirred for 2 h at rt and poured in to cold water. The CH_2Cl_2 layer was separated, washed with water and brine solution. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude obtained was purified by silica gel column chromatography (EtOAc/hexane, 10:90) to obtain compound **13c** (0.161 g, 93%) as colourless solid. m.p. 110–112 ^oC

^1H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.25 Hz, 1H), 7.30 (d, *J* = 1.5 Hz, 1H), 6.99-6.97 (m, 4H), 6.48 (t, *J* = 2.12 Hz, 1H), 3.87 (s, 6H), 2.34 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.78, 161.06, 156.69, 154.56, 147.90, 131.92, 126.98, 120.89, 117.13, 105.11, 102.91, 101.57, 101.04, 55.49, 21.17 ppm. IR (KBr): ṽ = 2937, 2839, 1762, 1598, 1573, 1482, 1459, 1431, 1205, 1155, 1132, 1109, 966 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{17}O_5$ $[M+H]^+$ 313.1076; found 313.1074.

Moracin M (1): [3]

To a solution of compound **13c** (0.100 g, 0.320 mmol) in CH_2Cl_2 (20 mL), BBr_3 (0.240 g, 0.960 mmol) solution in CH_2Cl_2 (5 mL) was added dropwise at –78 °C. The reaction mixture brought to rt and stirred for 24 h. It was then cooled to 0 °C, quenched with water (5 mL), and extracted with ethyl acetate. The organic extract was dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by column chromatography (EtOAc/hexane, 80:20) to give compound **1** (0.063 g, 81%) as a pale yellow solid, m.p. 260-262 ^oC.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.60 (s, 1H), 9.46 (s, 2H), 7.38 (d, *J* = 8.24 Hz, 1H), 7.08 (s, 1H), 6.93 (d, *J* = 1.84 Hz, 1H), 6.74 (dd, *J* = 8.70, 2.30 Hz, 1H), 6.68 (d, *J* = 2.28 Hz, 2H), 6.21 (t, *J* = 2.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.86, 155.79, 155.33,

154.01, 131.75, 121.22, 120.86, 112.53, 102.68, 102.36, 101.66, 97.54 ppm. IR (KBr): $\tilde{\nu}$ = 3414, 2255, 2128, 1653, 1049, 1025, 1002, 826, 764 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_9O_4$ $[M-H]^-$ 241.0501; found 241.0503.

Compound 2:[6]

1,1-Dibromide (0.412 mmol), $BiAr_3$ (0.125 mmol), Cs_2CO_3 (0.75 mmol), $Pd(PPh_3)_4$ (0.11 mmol), CuI (0.025mmol) and DMF (4 mL) were put into an oven-dried Schlenk tube under a nitrogen atmosphere. The mixture was heated in an oil bath at 90 °C for 7 h. The contents were cooled to rt and Cs_2CO_3 (0.375 mmol) was added again, stirred at 90 °C for additional 3 h. Thereafter, it was cooled to rt and extracted with ethyl acetate. The organic extract was washed with water, brine, dried over $MgSO_4$, and concentrated. The crude product was purified by silica gel column chromatography to obtain benzofuran **2** (0.045 g, 42%) as a colourless solid, m.p. 150-152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (S, 1H), 7.38 (d, J = 8.72 Hz, 1H), 7.14 (s, 1H), 6.97 (d, J = 1.8 Hz, 1H), 6.75 (dd, J = 8.24, 2.28 Hz, 1H), 6.63 (s, 1H), 5.98 (s. 2H), 4.81 (s, 1H), 3.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.40, 153.15, 152.22, 151.64, 147.93, 141.47, 123.65, 120.95, 112.30, 111.59, 106.08, 104.43, 101.47, 97.91, 94.70, 56.27 ppm. IR (KBr): $\tilde{\nu}$ = 2896, 1615, 1593, 1495, 1444, 1455, 1264, 1189, 1164, 1038, 928 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{12}NaO_5$ $[M+Na]^+$ 307.0582; found 307.0588.

Compound 14:

A solution of compound **13** (0.3 g, 1.11 mmol) and methanesulfonyl chloride (0.190 g, 1.66 mmol) in 100 mL of CH_2Cl_2 were put in a 250 mL RB flask at 0 °C. To this, NEt_3 (0.168 g, 1.66 mmol) was added with stirring for 2 h at rt. Thereafter, CH_2Cl_2 layer was separated and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 30:70) to obtain compound **14** (0.310 g, 81%) as a pale brown solid, m.p. 106-108 °C .

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.55 Hz, 1H), 7.51 (d, J= 1.55 Hz, 1H), 7.18 (dd, J = 8.55, 2.15 Hz, 1H), 7.01 (s, 1H), 6.99 (d, J = 2.40 Hz, 2H), 6.49 (t, J = 2.3 Hz, 1H), 3.87 (s, 6H), 3.17 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.12, 157.65, 154.30, 146.19,

131.52, 128.41, 121.34, 117.42, 105.85, 103.05, 101.37, 55.50, 37.17 ppm. IR (KBr): $\tilde{\nu}$ = 3012, 2938, 2839, 1572, 1598, 1431, 1420, 1331, 1364, 1204, 1156, 1180, 1102, 960, 836.98 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{12}O_6S$ $[M]^+$ 348.0668; found 348.0664.

Compound 15:

To a solution of compound **14** (0.3 g, 0.861 mmol) in CH_2Cl_2 (20 mL), BBr_3 (0.863 g, 3.44 mmol) solution in CH_2Cl_2 (5 mL) was added dropwise at –78 °C. The reaction mixture brought to rt and stirred for 24 h. The contents were cooled to 0 °C, quenched with water (5 mL), and extracted with ethyl acetate. The organic extract was dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by column chromatography (methanol/DCM, 05:95) to obtain compound **15** (0.260 g, 94%) as a brown solid, m.p. 170-172 ^oC.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.54 (s, 2H), 7.70-7.68 (m, 2H), 7.30 (s, 1H), 7.25 (dd, J = 8.56, 2.20 Hz, 1H), 6.76 (d, J = 1.96 Hz, 2H), 6.28 (t, J = 2.20 Hz, 1H), 3.40 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 158.96, 157.32, 153.61, 146.19, 130.83, 128.01, 121.59, 118.06, 105.98, 103.63, 102.95, 101.50, 37.22 ppm. IR (KBr): $\tilde{\nu}$ = 3419, 2923, 1614, 1578, 1475, 1428, 1408, 1323, 1179, 1143, 1106, 962, 873, 851, 819 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{13}O_6S$ $[M+H]^+$ 321.0433; found 321.0439.

Compound 16:

A mixture of compound **15** (0.433 g, 1.352 mmol), **15a** (0.257 g, 1.622 mmol), 3-picoline (0.031 g, 0.337 mmol) and xylene (9 mL) were taken in an oven-dried Schlenk tube under nitrogen atmosphere. It was heated in an oil bath at 130 °C for 24 h and then cooled to rt. The xylene was evaporated and extracted with ethylacetate. The organic extract was washed with water, brine, dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 40:60) to obtain compound mixture **16** (0.407 g, 78%) as a pale brown solid.

Compound 17: To a solution of compound mixture **16** (0.283 g, 0.732 mmol) in 1, 4-dioxane (10 mL), teraethyammoniumhydroxide (4 mL) was added and stirred for 8 h at rt. Thereafter, it was extracted with ethyacetate. The organic extract was washed with water, brine, dried over

anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 60:40) to obtain compound mixture **17** as colourless solid (0.206 g, 91%).

Compounds 18a and **18b:**

A solution of compound **17** (0.210 g, 0.681 mmol) and DMAP (0.008 g, 0.068 mmol) in 25 mL of CH_2Cl_2 put in a 100 mL RB flask at 0 ^oC. To this, NEt_3 (0.206 g, 2.04 mmol) was added followed by the slow addition of acetyl chloride (0.160 g, 2.04 mmol). The reaction mixture was stirred for 3 h. The contents were poured into cold water and extracted with CH_2Cl_2. The organic extract was washed with water, brine and dried over anhydrous $MgSO_4$, concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 10:90) to obtain compound **18a** (0.163 g, 61%) as a colourless solid, m.p. 102-104 ^oC and compound **18b** (0.074 g, 28%) as a colourless solid, m.p. 64-66 ^oC.

Compound 18a (Moarcin D diacetate):[7]

^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.24 Hz, 1H), 7.24 (s, 1H), 7.15 (d, J = 0.92 Hz, 1H), 7.11 (d, J = 1.40 Hz, 1H), 6.96 (dd, J = 8.46, 2.06 Hz, 1H), 6.93 (d, J = 0.88 Hz, 1H), 6.33 (d. J = 9.64 Hz, 1H), 5.69 (d, J = 10.08 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.46 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.69, 168.99, 155.85, 154.62, 154.04, 148.02, 146.65, 131.83, 130.62, 126.90, 120.92, 117.19, 115.92, 114.65, 110.94, 110.34, 105.04, 101.80, 76.56, 27.89, 21.13, 20.81 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 2931, 1766, 1618, 1553, 1484, 1369, 1205, 1132, 1114, 1059, 1009, 972.18, 907.83 cm^{-1}. HRMS (EI): calcd for $C_{23}H_{20}O_6$ $[M]^+$ 392.1260; found 392.1268.

Compound 18b (Moracin E diacetate):[8]

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.24 Hz, 1H), 7.30 (bs, 1H), 7.02-6.98 (m, 2H), 6.84 (s, 1H), 6.82 (d, J = 10.04 Hz, 1H), 6.63 (d, J = 2.28 Hz, 1H), 5.71 (d, J = 10.08 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 1.48 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.74, 169.14, 154.89, 154.60, 150.68, 148.06, 130.96, 127.83, 126.68, 121.00, 119.95, 117.23, 116.90, 113.62, 110.70, 106.03, 105.16, 75.76, 27.68, 21.12 ppm. IR (KBr): $\tilde{\nu}$ = 3070, 2975, 2929, 1766, 1618, 1553, 1484, 1435, 1419, 1369, 1205, 1132, 1114 cm^{-1} HRMS (EI): calcd for $C_{23}H_{20}O_6$ $[M]^+$ 392.1260; found 392.1261.

Compound 3 (Moracin D):[7]

A solution of compound **18a** (0.05 g, 0.127 mmol) and 1:1 mixture of aqueous ammonia in methanol (8 mL) stirred for 2 h at rt. It was extracted with ethyl acetate and washed with water and brine solution. The organic extract was dried over anhydrous $MgSO_4$, concentrated and dried under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc / hexane, 50:50) to obtain moracin D (0.036 mg, 92%) as a off white solid, m.p. 122-124 ^oC.

^1H NMR (500 MHz, Acetone-d_6): δ = 8.97 (bs, 1H), 8.77 (bs, 1H), 7.39 (d, J = 8.45 Hz, 1H), 7.05 (d, J = 0.72 Hz, 1H), 6.97 (d, J = 2.15 Hz, 1H), 6.93 (d, J = 1.43 Hz, 1H), 6.80 (dd, J = 8.45, 2.15 Hz, 1H), 6.77 (dd, J = 1.43, 0.72 Hz, 1H), 6.69 (dd, J = 9.88, 0.72 Hz, 1H), 5.67 (d, J = 9.88 Hz, 1H), 1.41 (s, 6H). ^{13}C NMR (125 MHz, Acetone-d_6): δ = 156.99, 156.89, 155.30, 154.40, 132.10, 129.72, 122.59, 122.07, 117.69, 113.42, 110.58, 104.83, 104.50, 102.56, 98.47, 76.65, 28.12 ppm. IR (KBr): $\tilde{\nu}$ = 3351, 2975, 2925, 2854, 1616, 1561, 1488, 1425, 1146, 1115, 1062, 898, 818 cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{15}O_4$, $[M-H]^-$ 307.0971; found 307.0960.

Compound 4 (Moracin E):[8]

A solution of compound **18b** (0.05 mg, 0.127 mmol) and 1:1 mixture of aqueous ammonia in methanol (8 mL) stirred for 2 h at rt. It was extracted with ethyl acetate and washed with water and brine solution. The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 50:50) to obtain moracin E (0.0365 g, 93%) as a pale brown solid, m.p. 166-168 ^oC.

^1H NMR (500 MHz, Acetone-d_6): δ = 8.65 (bs, 2H), 7.46 (d, J = 8.31 Hz, 1H), 7.00 (d, J = 2.15 Hz, 1H), 6.87 (d, J = 0.72 Hz, 1H), 6.84 (dd, J = 8.31, 2.15 Hz, 1H), 6.83 (dd, J = 10.10, 0.57 Hz, 1H), 6.79 (d, J = 2.43 Hz, 1H), 6.35 (dd, J = 2.43, 0.57 Hz, 1H), 5.67 (d, J = 10.02 Hz, 1H), 1.42 (s, 6H) ppm. ^{13}C NMR (125 MHz, Acetone-d_6): δ = 159.08, 156.95, 156.89, 156.26, 154.29, 129.54, 128.97, 122.43, 122.25, 121.29,

113.41, 112.29, 108.15, 106.71, 104.83, 98.48, 76.04, 27.83 ppm. IR (KBr): $\tilde{\nu}$ = 3341, 2975, 2926, 2854, 1609, 1575, 1489, 1440, 1146, 1119, 1018, 969, 826 cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{17}O_4$ $[M+H]^+$ 309.1127; found 309.1120.

Compound 19:[9]

To a solution of resorcinol **9** (8.3 g, 75.47 mmol) in dichloroethane (150 mL) was added *p*-toluenesulfonic acid (1 g, 5.80 mmol). To this 2-methyl-3-buten-2-ol (5 g, 58.05 mmol) in dichloroethane (20 mL) was added dropwise in 30 minutes and stirred for 2 h at rt. Thereafter, it was refluxed at 80 ^oC for 10 h and cooled to rt. Then solvent was evaporated and the crude was extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane 05:95) to obtain compound **19** (6.2 g, 60%) as a colourless solid, m.p. 62-64 ^oC.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.90 (d, *J* = 8.24 Hz, 1H), 6.34 (dd, *J* = 8.24, 2.29 Hz, 1H), 6.28 (d, *J* = 2.29 Hz, 1H), 4.65 (bs, 1H) 2.69 (t, *J* = 6.87 Hz, 2H), 1.78 (t, *J* = 6.87 Hz, 2H), 1.32 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.77, 154.72, 130.10, 113.30, 107.29, 103.71, 74.40, 32.89, 26.80, 21.72 ppm. IR (KBr): $\tilde{\nu}$ = 3352, 2974, 2930, 1596, 1623, 1507, 1458, 1304, 1149, 1118, 994, 847 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{15}O_2$ $[M+H]^+$ 179.1072; found 179.1071.

Compound 20:[10]

A mixture of compound **19** (5 g, 28.05 mmol), $MgCl_2$ (4 g, 42.08 mmol) and NEt_3 (10.64 g, 105.18 mmol) in dry THF (150 mL) stirred for 20 minutes at rt. Then paraformaldehyde (5.68 g, 189.34 mmol) was added portion wise, stirred for 1 h followed by reflux for 7 h. It was the cooled to rt, evaporated THF and extracted with ethyl acetate. The organic extract was washed with dil. HCl, water followed by brine. The crude product was purified by column chromatography (EtOAc/hexane, 10:90) to obtain compound **20** (3.18 g, 55%) as a yellow solid, m.p. 82-84 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.06 (s, 1H), 9.66 (s, 1H), 7.21 (s, 1H), 6.31 (s, 1H), 2.75 (t, *J* = 6.64 Hz, 2H), 1.83 (t, *J* = 6.64 Hz, 2H), 1.36 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =194.16, 162.11, 162.01, 135.28, 115.19, 113.76, 104.34, 76.25, 32.54, 26.95, 21.42 ppm. IR (KBr): $\tilde{\nu}$ = 3023, 2933, 2978, 2844, 2742, 1629, 1652, 1582, 1493, 1458, 1327, 1344, 1296, 1173, 851, 760 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{15}O_3$ $[M+H]^+$ 207.1021; found 207.1029.

Compound 20a:[11]

A solution of compound **20** (2 g, 9.7 mmol) and DDQ (2.42 g, 10.7 mmol) in 1,4-dioxane (30 mL) was refluxed at 100 ^{o}C for 10 h then cooled to rt. It was extracted with ethyl acetate and washed with water followed by brine. The organic extract was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 15:85) to obtain compound **20a** (1.4 g, 70%) as a pale yellow solid, m.p. 88-90 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.43 (s, 1H), 9.66 (s, 1H), 7.11 (s, 1H), 6.33 (s, 1H), 6.29 (d, *J* = 9.62 Hz, 1H), 5.59 (d, *J* = 9.62 Hz, 1H), 1.45 (s, 6H) ppm. ^{13}C NMR (100, $CDCl_3$): δ = 194.06, 164.26, 161.22, 131.34, 128.95, 120.59, 115.19, 114.42, 104.15, 78.28, 28.61 ppm. IR (KBr): $\tilde{\nu}$ = 3059, 2971, 2934, 1643, 1589, 1487, 1370, 1340, 1286, 1261, 1214, 1169, 1140, 1105, 882, 777, 763 cm^{-1}. HRMS (ESI): calcd for. $C_{12}H_{13}O_3$ $[M+H]^+$ 205.0865; found 205.0860.

Compound 21:

A solution of compound **20** (4 g, 19.33 mmol) and DMAP (0.236 g, 1.93 mmol) in 100 mL of CH_2Cl_2 were put in a 250 mL RB flask at 0 ^{o}C. To this, NEt_3 (3.92 g, 38.77 mmol) was added followed the by slow addition of acetyl chloride (3.04 g, 38.77 mmol). The reaction mixture was stirred for 3 h at rt and poured into cold water. The organic layer was separated and washed with water followed by brine. The organic extract was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 20:80) to obtain compound **21** (4.4 g, 92%) as a yellow solid, m.p. 78-80 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.58 (s, 1H), 6.53 (s, 1H), 2.80 (t, *J* = 6.42 Hz, 2H), 2.36 (s, 3H), 1.84 (t, *J* = 6.64 Hz, 2H), 1.36 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =187.60, 169.34, 160.29, 151.09, 133.34, 120.75, 119.22, 111.85, 76.32, 32.24, 26.94, 21.76, 20.85 ppm. IR (KBr): $\tilde{\nu}$ = 2977, 2935, 2853, 1767, 1688, 1610, 1572, 1491, 1370, 1290, 1200, 1149, 1111, 912 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{17}O_4$ $[M+H]^+$ 249.1127; found 249.1123.

Compound 21a:

A solution of compound **20a** (1.1 g, 5.4 mmol) and DMAP (0.066 g, 0.54 mmol) in 60 mL of CH_2Cl_2 wete put in a 100 mL RB flask at 0 ^{o}C. To this, NEt_3 (1.09 g, 10.77 mmol) was added followed by the slow addition of acetyl chloride (0.845 g, 10.77 mmol). The reaction mixture was stirred for 2 h and poured into cold water. Thereafter, organic layer was separated, washed with water and brine. The organic extract was dried under anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 20:80) to obtain compound **21a** (0.900 g, 68%) as a pale yellow solid, m.p. 72-74 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.47 (s, 1H), 6.54 (s, 1H), 6.34 (d, *J* = 10.02 Hz, 1H), 5.66 (d, *J* = 10.02 Hz, 1H), 2.36 (s, 3H), 1.46 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.27, 169.07, 159.20, 152.84, 130.88, 129.00, 121.44, 120.58, 119.02, 111.11, 78.38, 28.67, 20.87 ppm. IR (KBr): $\tilde{\nu}$ = 2977, 2934, 2855, 1769, 1687, 1642, 1605, 1568, 1486, 1365, 1286, 912, 770 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{14}NaO_4$ $[M+Na]^+$ 269.0790; found 269.0799.

Compound 24:

To a solution of compound **23** (0.610 g, 1.80 mmol) in CH_2Cl_2 (50 mL), BBr_3 (1.129 g, 4.50 mmol) solution in CH_2Cl_2 (10 mL) was added dropwise at –78 °C. The reaction mixture was brought to rt and stirred for 24 h. The mixture was then cooled to 0 °C, quenched with water (10 mL) and extracted with ethyl acetate. The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography (EtOAc/hexane, 60:40) to obtain compound **24** (0.475 g, 85%) as pale brown solid, m.p. 120-124 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.43 (s, 2H), 7.28 (s, 1H), 7.06 (s, 1H), 6.91 (s, 1H), 6.68 (d, J = 2.28 Hz, 2H), 6.21 (t, J = 2.06 Hz, 1H), 2.84 (t, J = 6.64 Hz, 2H), 1.78 (t, J = 6.64 Hz, 2 H), 1.30 (s, 6H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 158.77, 154.35, 153.71, 151.86, 131.54, 121.73, 120.51, 117.37, 102.72, 102.38, 101.08, 98.51, 74.29, 32.25, 26.59, 22.06 ppm. IR (KBr): $\tilde{\nu}$ = 3364, 2975, 2931, 1702, 1621, 1578, 1460, 1354, 1325, 1264, 1148, 1108, 948.82, 926.90 cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{17}O_4$ $[M-H]^-$ 309.1127; found 309.1126.

Compound 25:

A solution of compound **24** (0.250 g, 0.805 mmol) and DMAP (0.010 g, 0.080 mmol) in 50 mL of CH_2Cl_2 put in a 100 mL RB flask at 0 ^{o}C. To this, NEt_3 (0.326 g, 3.22 mmol) was added followed by the slow addition of acetyl chloride (0.253 g, 3.22 mmol). The reaction mixture was stirred for 2 h and then poured into cold water. Thereafter, organic layer was washed with water followed by brine. It was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 5:95) to obtain compound **25** (0.302 g, 95%) as a colourless solid, m.p. 178-180 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 1.8 Hz, 2H), 7.22 (s, 1H), 6.90 (s, 1H), 6.88 (s, 1H), 6.86 (t, J = 2.06 Hz, 1H), 2.89 (t, J = 6.86 Hz, 2H), 2.32 (s, 6H), 1.84 (t, J = 6.86 Hz, 2H), 1.37 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.97, 154.77, 152.92, 152.74, 151.35, 132.86, 121.90, 120.56, 117.65, 114.95, 114.66, 102.37, 99.26, 74.55, 32.91, 26.90, 22.75, 21.14 ppm. IR (KBr): $\tilde{\nu}$ = 2975, 2932, 1770, 1615, 1594, 1573, 1459, 1369, 1352, 1195, 1147, 1123, 1022, 1065, 1023 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{23}O_6$ $[M+H]^+$ 395.1495; found 395.1492.

Compound 26:

A solution of compound **25** (0.100 g, 0.253 mmol) and DDQ (0.057 g, 0.253 mmol) in 1,4-dioxane (5 mL) was refluxed at 100 ^{o}C for 20 h. The contents were brought to rt, extracted with ethyl acetate, washed with water followed by brine. The organic extract was dried over anhydrous $MgSO_4$, concentrated. The crude was purified by silica gel column chromatography (EtOAc/hexane, 5:95) to obtain compound **26** (0.089 g, 89%) as colourless solid, m.p. 138-140 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 1.84 Hz, 2H), 7.14 (s, 1H), 6.92 (s, 1H), 6.90 (s, 1H), 6.87 (t, *J* = 2.06 Hz, 1H), 6.41 (d, *J* = = 9.6 Hz, 1H), 5.64 (d, *J* = 10.08 Hz, 1H), 2.32 (s, 6H), 1.46 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.91, 155.65, 153.22, 151.95, 151.40, 132.62, 130.20, 122.61, 122.47, 118.53, 117.87, 114.94, 114.77, 102.74, 99.50, 76.43, 27.86, 21.12 ppm. IR (KBr): $\tilde{\nu}$ = 3042, 2926, 2971, 1769, 1616, 1574, 1462, 1433, 1370, 1346, 1197, 1126, 1023 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}O_6$ $[M+H]^+$ 393.1338; found 393.1336.

Compound 6:[12]

A solution of compound **23** (0.500 g, 1.478 mmol) and DDQ (0.336 g, 1.478 mmol) in 1,4-dioxane (15 mL) was refluxed at 100 ^{o}C for 20 h. Thereafter, contents were cooled to rt and extracted with ethyl acetate, washed with water followed by brine. The organic extract was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 5:95) to obtain compound **5** (0.447 g, 90%) as a yellow solid, m.p. 114-116 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 1H), 6.96-6.95 (m, 3H), 6.88 (s, 1H), 6.44 (t, 2.3 Hz, 1H) 6.42 (d, 9.6 Hz, 1H), 5.64 (d, *J* = 9.6 Hz, 1H), 3.86 (s, 6H), 1.46 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.03, 155.46, 154.94, 151.55, 132.34, 130.05, 122.74, 118.34, 117.62, 102.51, 101.69, 100.57, 99.51, 76.31, 55.47, 27.79 ppm. IR (KBr): $\tilde{\nu}$ = 2973, 2936, 2837, 1574, 1599, 1461, 1350, 1423, 1204, 1156, 1126, 1066, 1035, 911, 837, 732 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1440 found 337.1440.

Compound 5:[12]

A solution of compound **26** (0.050 g, 0.127 mmol) in 1:1 mixture of aqueous ammonia and methanol (8 mL) was stirred at rt for 5 h. It was extracted with ethyl acetate and washed with water followed by brine. The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 70:30) to obtain compound **6** (0.035 g, 90%) as a brown solid, m.p. 138-140 ^{o}C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.43 (s, 2H), 7.28 (s, 1H), 7.10 (s, 1H), 6.99 (s, 1H), 6.69 (d, J = 2.3 Hz, 2H), 6.50 (d, J = 9.7 Hz, 1H), 6.22 (t, J = 2.42 Hz, 1H), 5.75 (d, J = 9.7 Hz, 1H), 1.39 (s, 6H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 158.80, 154.76, 154.53, 150.96, 131.33, 130.23, 122.41, 122.26, 118.04, 117.87, 102.85, 102.41, 101.52, 98.90, 76.15, 27.49 ppm. IR (KBr): $\tilde{\nu}$ = 3615, 3290, 2972, 2923, 2852, 1613, 1581, 1466, 1440, 1353, 1149, 1128, 1001, 838 cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{17}O_4$ $[M+H]^+$ 309.1127; found 309.1125.

Compound 7:[4,12,13]

A solution of compound **27** (0.100 g, 0.324 mmol) and DDQ (0.074 g, 0.324 mmol) in 1,4-dioxane (5 mL) was refluxed at 100 ^{o}C for 20 h. Thereafter, it was cooled to rt and extracted with ethyl acetate and washed with water followed by brine. The organic layer was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc / hexane, 5:95) to obtain compound **7** (0.092 g, 93%) as a semi white solid, m.p.172-174 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.68 Hz, 2H), 7.11 (s, 1H), 6.96 (s, 1H), 6.95 (d, J = 8.72 Hz, 2H), 6.75 (d, J = 0.92 Hz, 1H), 6.42 (d, J = 9.6 Hz, 1H), 5.63 (d, J = 9.6 Hz, 1H), 3.85 (s, 3H), 1.46 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.53, 155.27, 150.99, 129.85, 125.89, 123.47, 123.08, 122.81, 118.09, 117.26, 114.14, 99.44, 76.18, 55.30, 27.73 ppm. IR (KBr): $\tilde{\nu}$ = 2965, 1612, 1504, 1461, 1250, 1179, 1087, 1033, 832, 797, 732 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1334; found 307.1331.

Compound 28:

To a solution of compound **27** (0.100 g, 0.324 mmol) in CH_2Cl_2 (15 mL), BBr_3 (0.097 g, 0.389 mmol) solution in CH_2Cl_2 (5 mL) was added dropwise at –78 °C. The reaction mixture was brought to rt and stirred for 12 h. Thereafter, the mixture was cooled to 0 °C, quenched with water (5 mL) and extracted with ethyl acetate. The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography (EtOAc/hexane 20:80) to obtain compound **28** (0.076 g, 80%) as a semi white solid, m.p. 178-180 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.72 Hz, 2H), 7.19 (s, 1H), 6.92 (s, 1H), 6.88 (d, *J* = 8.72 Hz, 2H), 6.73 (s, 1H), 2.89 (t, *J* = 6.64 Hz, 2H), 1.84 (t, *J* = 6.64 Hz, 2H), 1.37 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.47, 154.94, 154.47, 151.85, 126.18, 124.05, 122.54, 119.88, 117.12, 115.63, 99.21, 99.10, 74.36, 33.04, 26.89, 22.78 ppm. IR (KBr): $\tilde{\nu}$ = 3411, 2973, 1596, 1507, 1459, 1353, 1252, 1147, 1116, 836.98, 798, 518.70 cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1334; found 295.1330.

Compound 29:

A solution of compound **28** (0.200 g, 0.679 mmol) and DMAP (0.008 g, 0.068 mmol) in 50 mL of CH_2Cl_2 were put in a 100 mL RB flask at 0 ^{o}C. To this, NEt_3 (0.137 g, 1.359 mmol) was added followed by the slow addition of acetyl chloride (0.107 g, 1.359 mmol). The reaction mixture was stirred for 2 h and poured into cold water. The organic portion was separated and washed with water followed by brine. It was was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 5:95) to obtain compound **29** (0.194 g, 85%) as a colourless solid, m.p. 156-158 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.72 Hz, 2H), 7.22 (s, 1H), 7.14 (d, *J* = 8.72 Hz, 2H), 6.93 (s, 1H), 6.84 (s, 1H), 2.89 (t, *J* = 6.64 Hz, 2H), 2.32 (s, 3H), 1.85 (t, *J* = 6.88 Hz, 2H), 1.37 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.44, 154.70, 154.12, 152.29, 150.22, 128.63, 125.55, 122.23, 121.89, 120.24, 117.38, 100.83, 99.27, 74.43, 32.96, 26.89, 22.76, 21.16 ppm. IR (KBr): $\tilde{\nu}$ = 2969, 2927, 1755, 1629, 1590, 1499, 1459, 1368, 1199, 1149, 1119, 913, 849 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1440; found 337.1441.

Compound 30:

A solution of compound **29** (0.100 g, 0.297 mmol) and DDQ (0.067 g, 0.297 mmol) in 1,4-dioxane (5 mL) was refluxed at 100 ^{O}C for 20 h. The contents were brought to rt and extracted with ethyl acetate, washed with water followed by brine. The organic extract was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography (EtOAc/hexane, 5:95) to obtain compound **30** (0.090 g, 90%) as a semi white solid, m.p. 154-156 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, 8.72 Hz, 2H), 7.15 (d, 8.68 Hz, 2H), 7.13 (s, 1H), 6.95 (s, 1H), 6.86 (s, 1H), 6.42 (d, 10.08Hz, 1H), 5.64 (d, 10.08 Hz, 1H), 2.32 (s, 3H), 1.46 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.38, 155.56, 154.40, 151.51, 150.34, 130.06, 128.42, 125.54, 122.72, 121.94, 118.34, 117.59, 101.22, 99.53, 76.31, 27.80, 21.15 ppm. IR (KBr): $\tilde{\nu}$ = 2973, 1754, 1593, 1503, 1461, 1368, 1345, 1227, 1210, 1195, 1166, 1013, 838, 849 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{19}O_4$ $[M+H]^+$ 335.1283; found 335.1286.

Compound 8:[12,13]

A solution of compound **29** (0.050 g, 0.149 mmol) in 1:1 mixture of aqueous ammonia and methanol (5 mL) was stirred at rt for 5 h. Thereafter, it was extracted with ethyl acetate, washed with water followed by brine. The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 70:30) to obtain compound **8** (0.039 g, 89%) as a brown solid, m.p. 140-142 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.78 (s, 1H), 7.64 (d, J = 8.68 Hz, 2H), 7.24 (s, 1H), 7.02 (s, 1H), 6.95 (s, 1H), 6.84 (d, J = 8.72 Hz, 2H), 6.49 (d, J = 10.08 Hz, 1H), 5.73 (d, J = 10.08 Hz, 1H), 1.38 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.87, 155.16, 154.42, 150.46, 130.14, 125.90, 122.83, 122.38, 121.08, 117.92, 117.50, 115.81, 99.24, 98.91, 76.10, 27.51 ppm. IR (KBr): $\tilde{\nu}$ = 2971, 2925, 1612, 1507, 1461, 1347, 1253, 1127, 837 cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{15}O_3$ $[M-H]^-$ 291.1021; found 291.1023.

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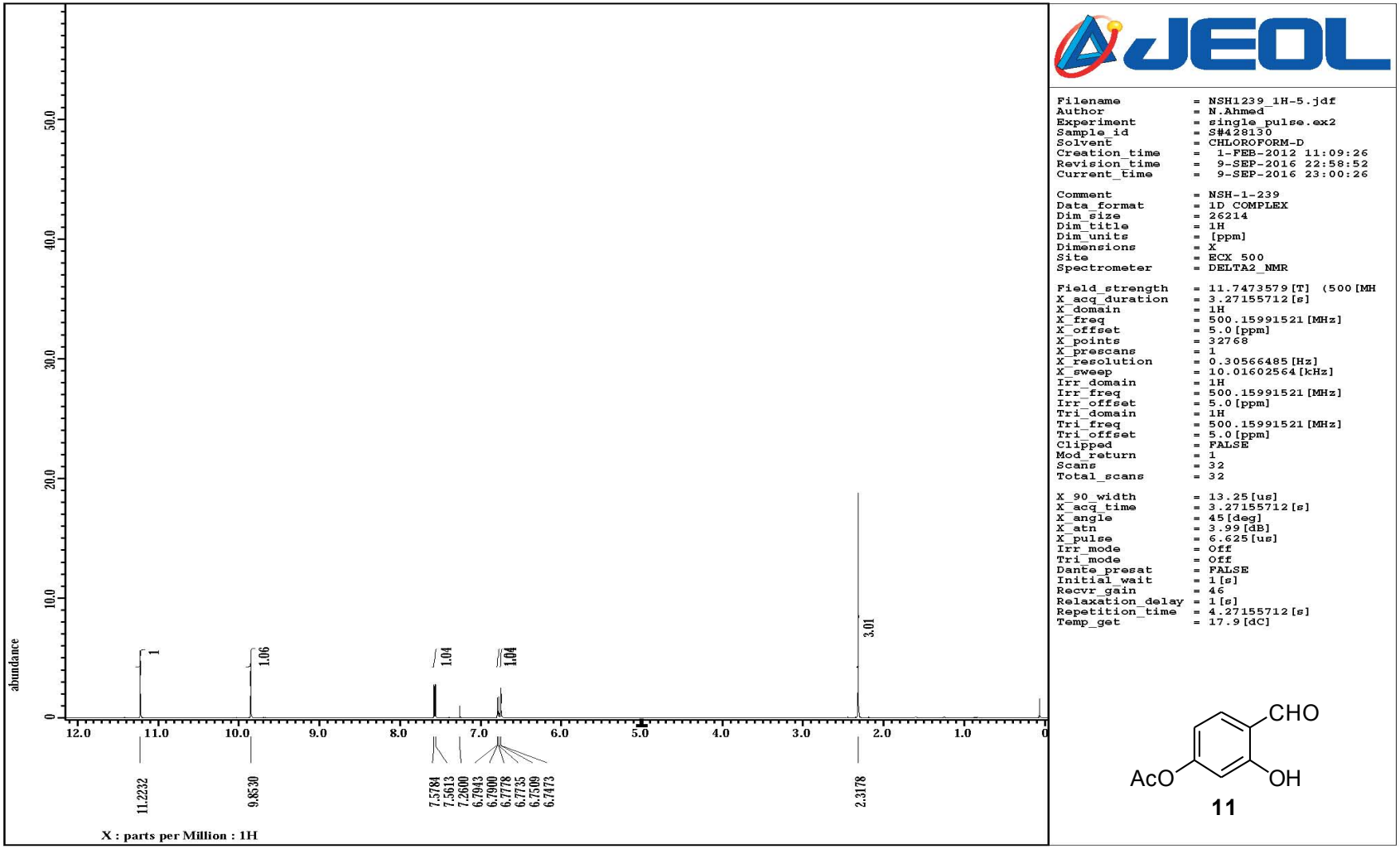
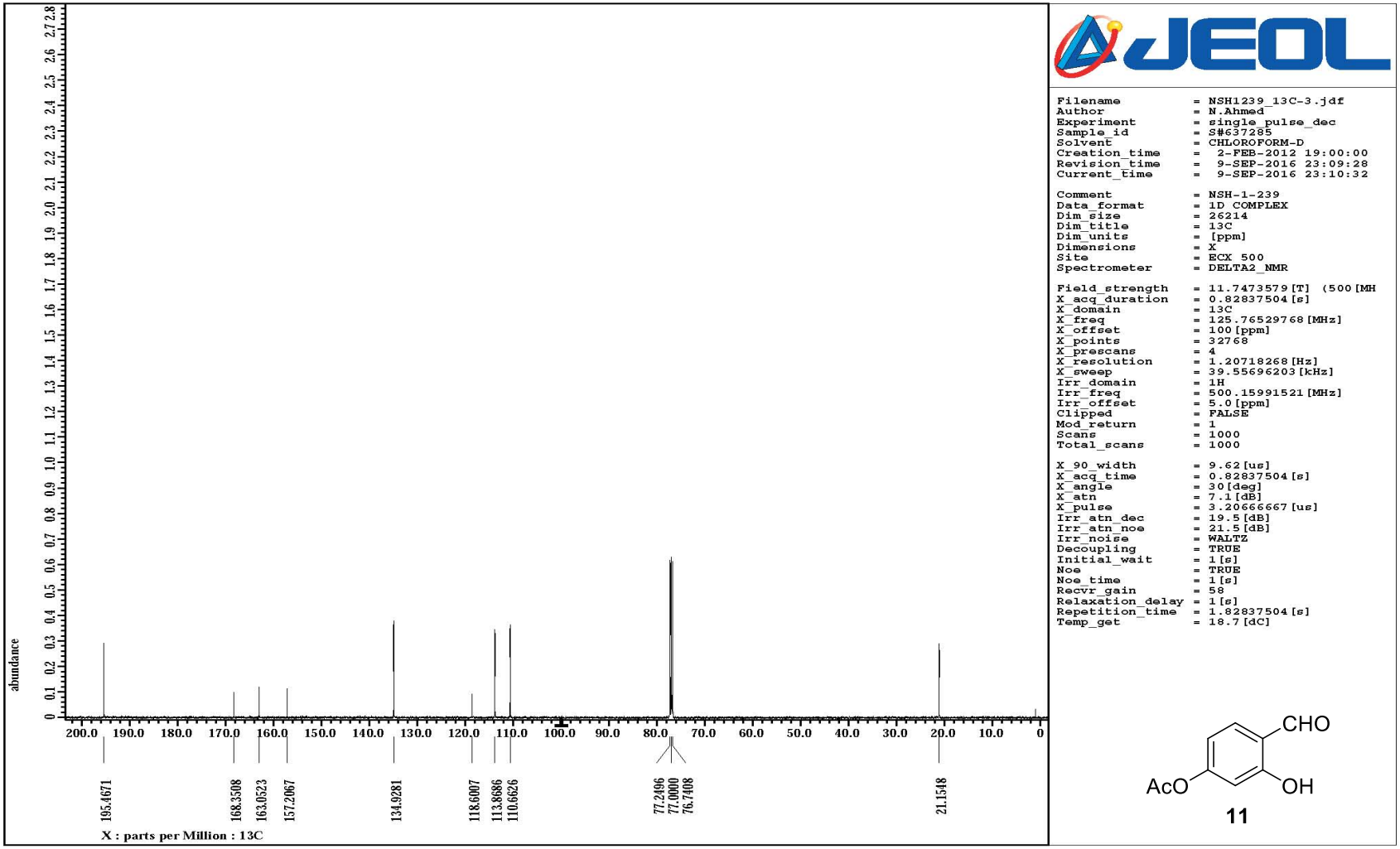
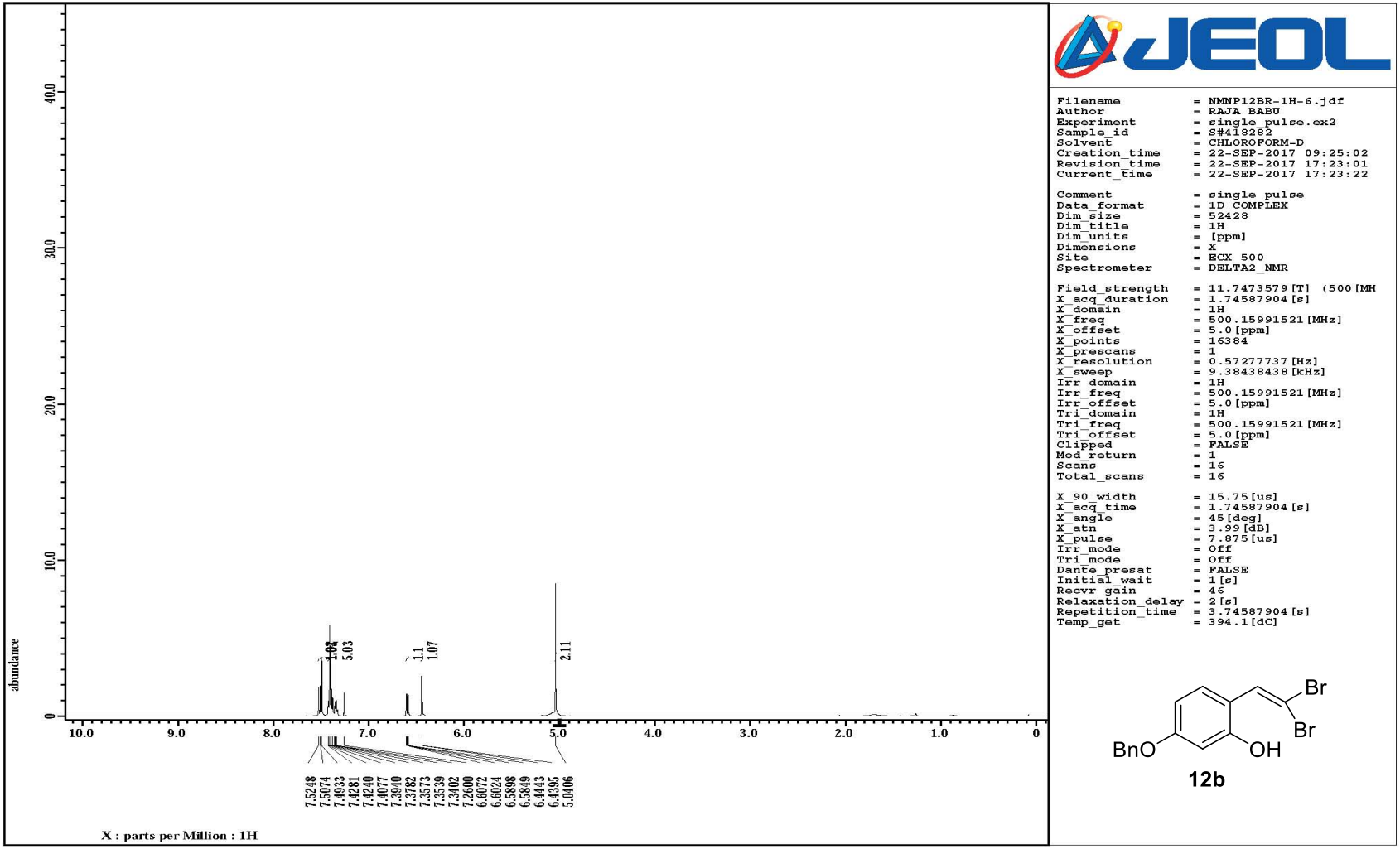


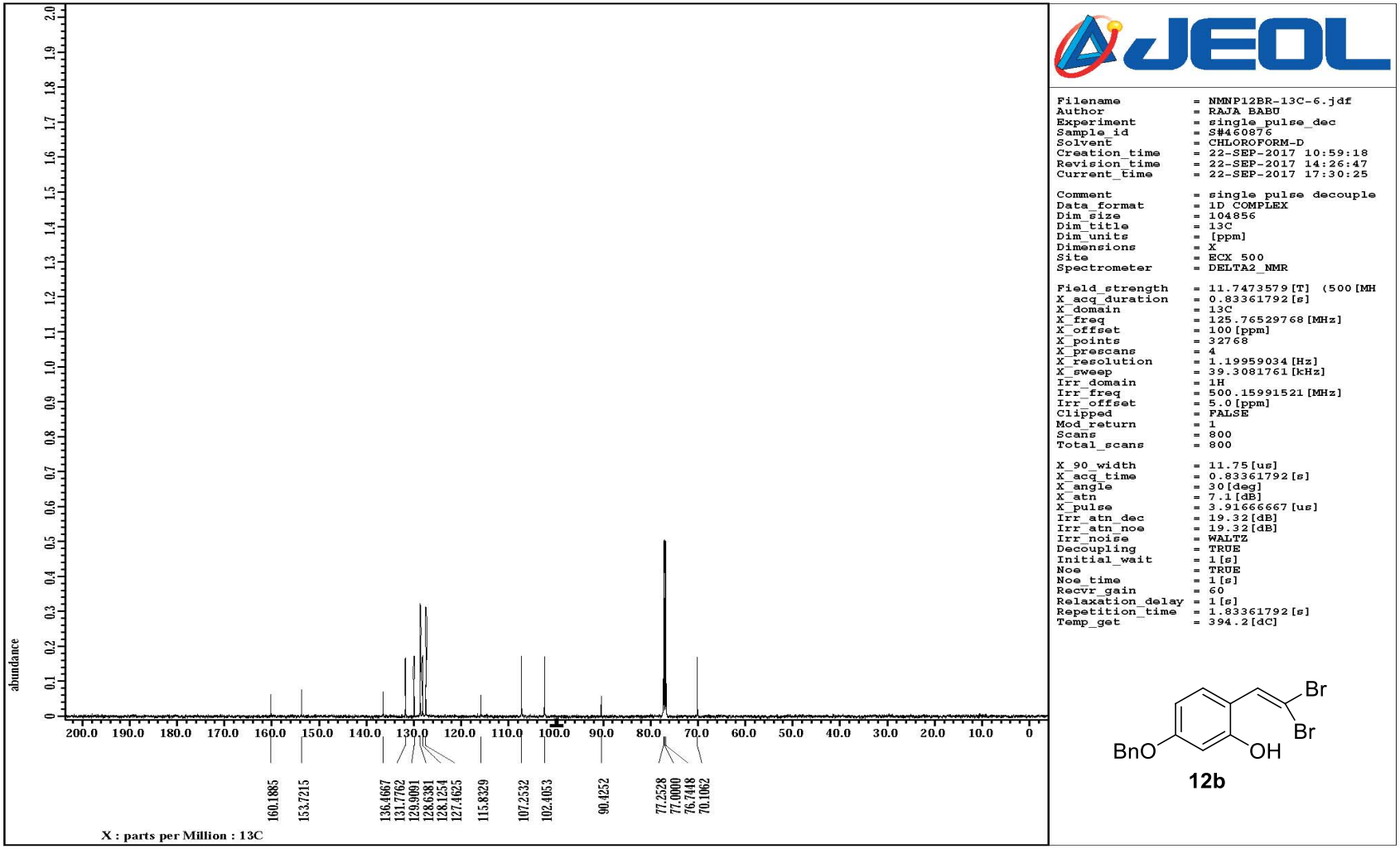
^{1}H NMR spectrum of Compound **11**



^{13}C NMR spectrum of Compound **11**



^{1}H NMR spectrum of Compound **12b**



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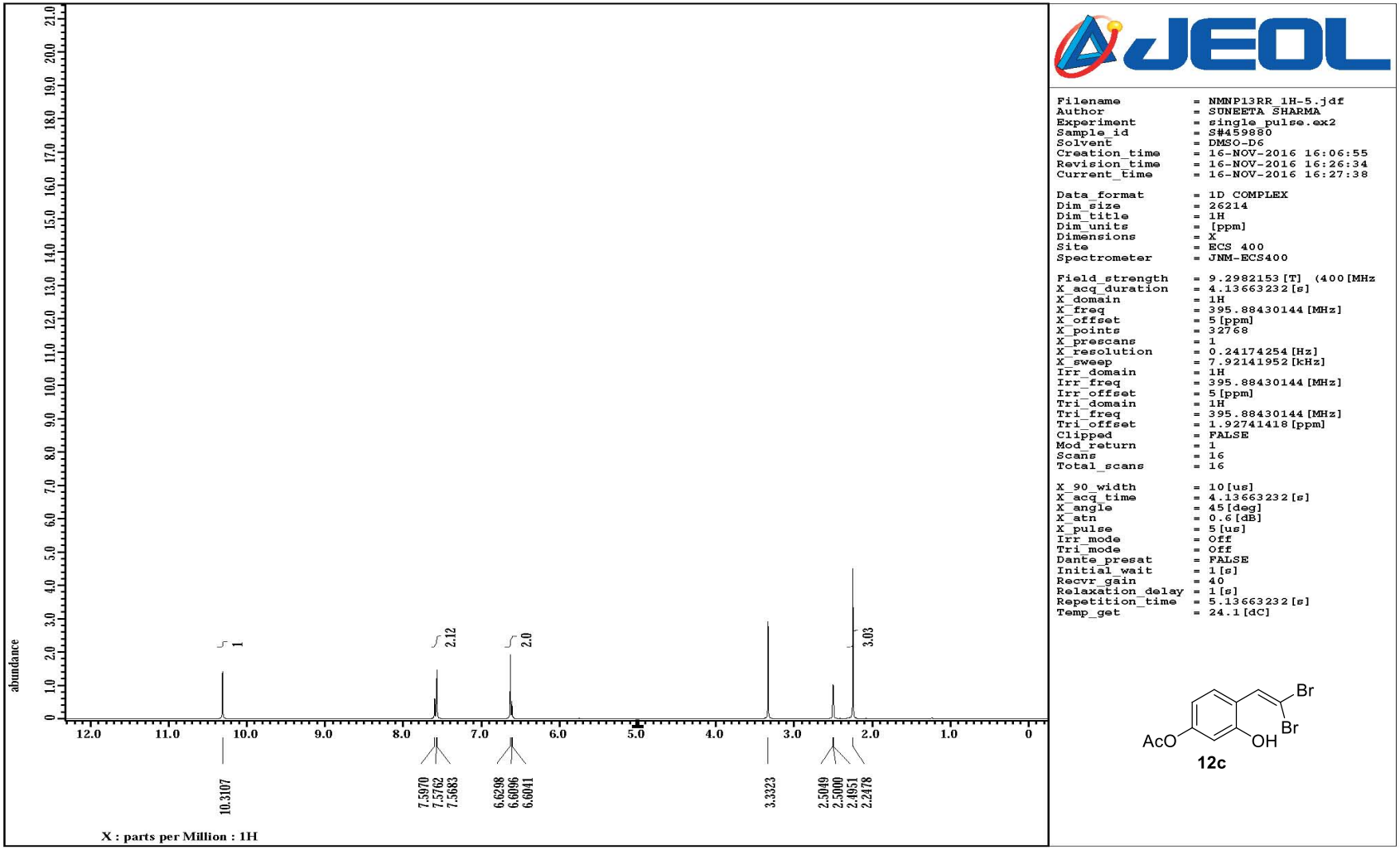
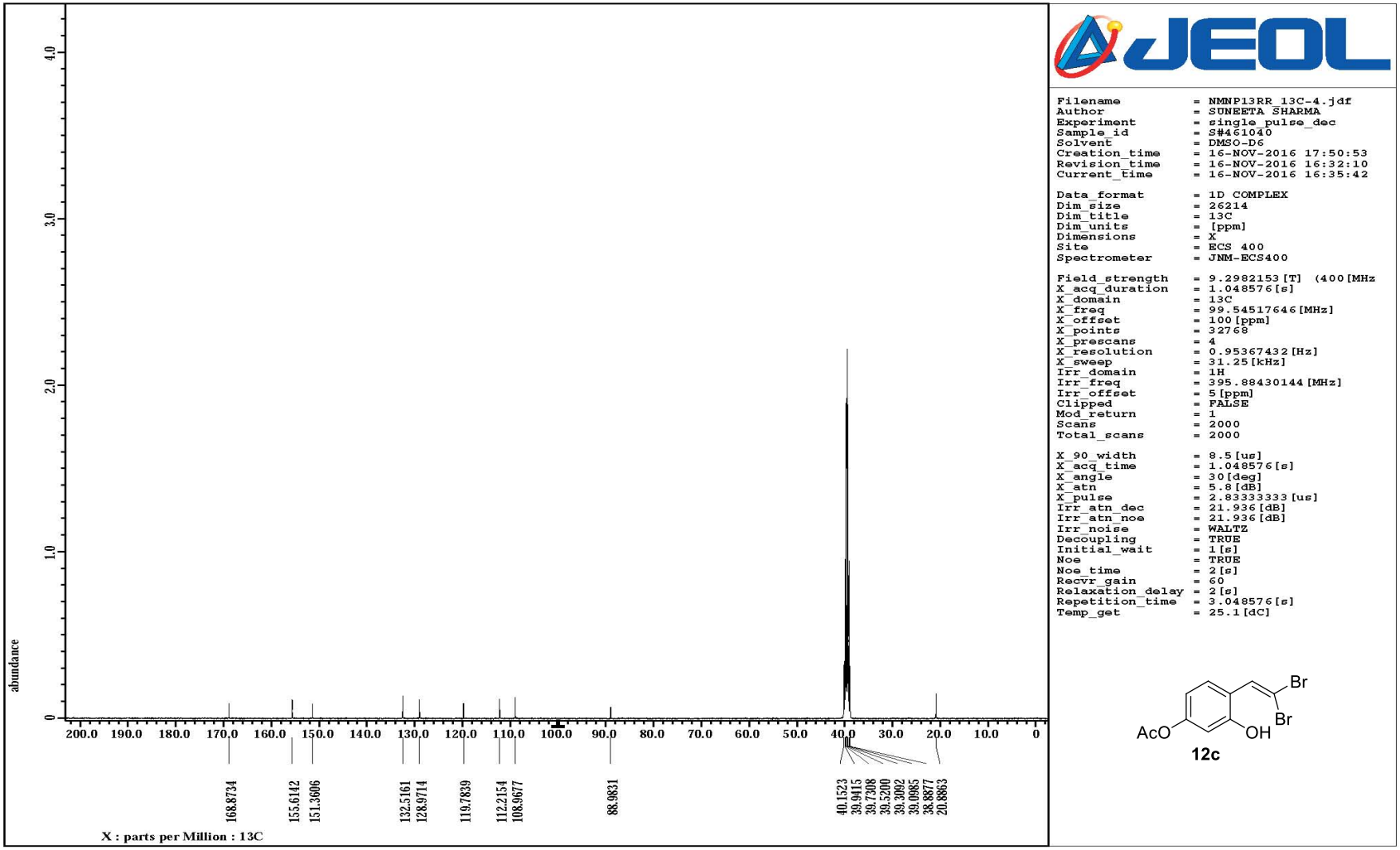
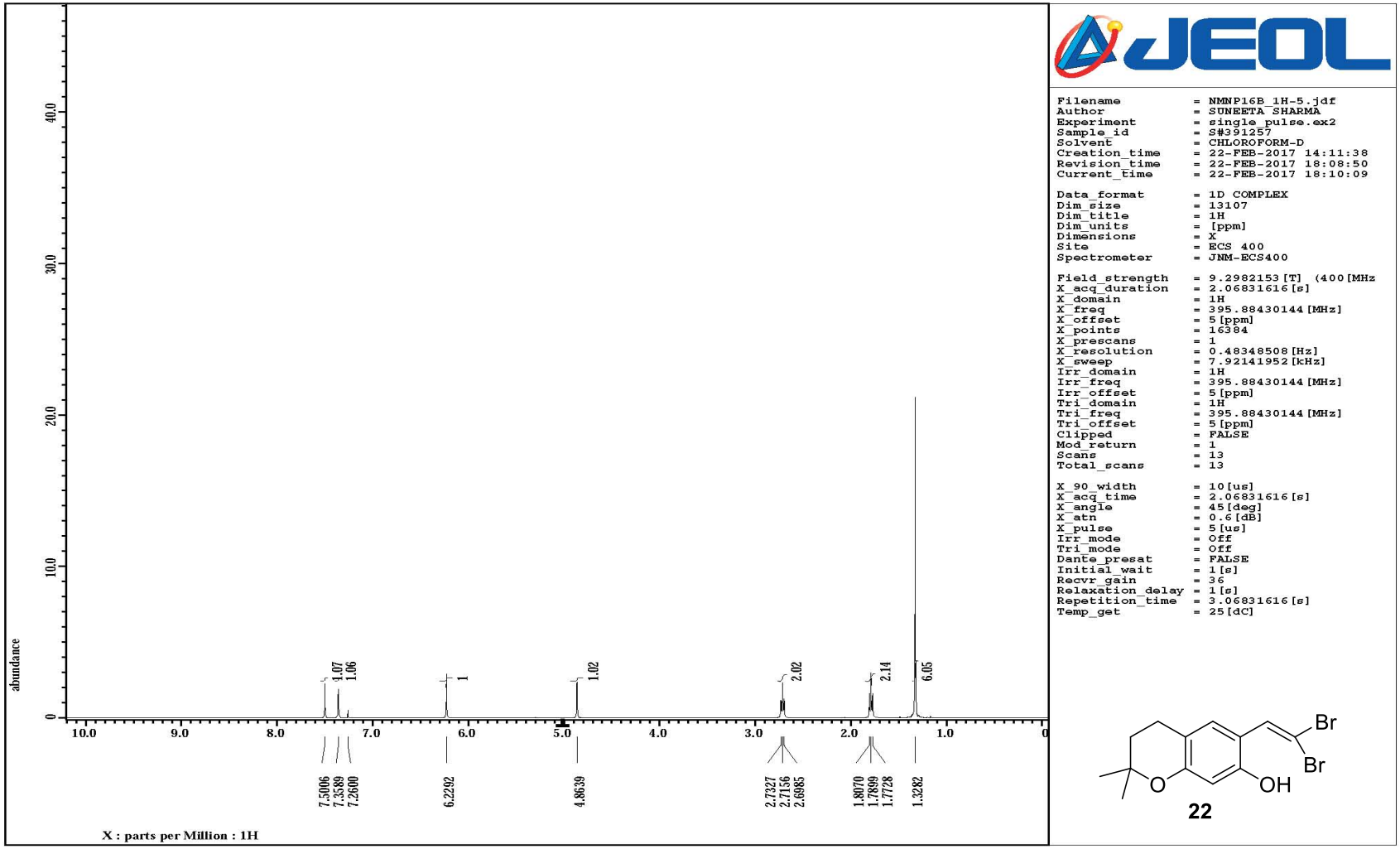


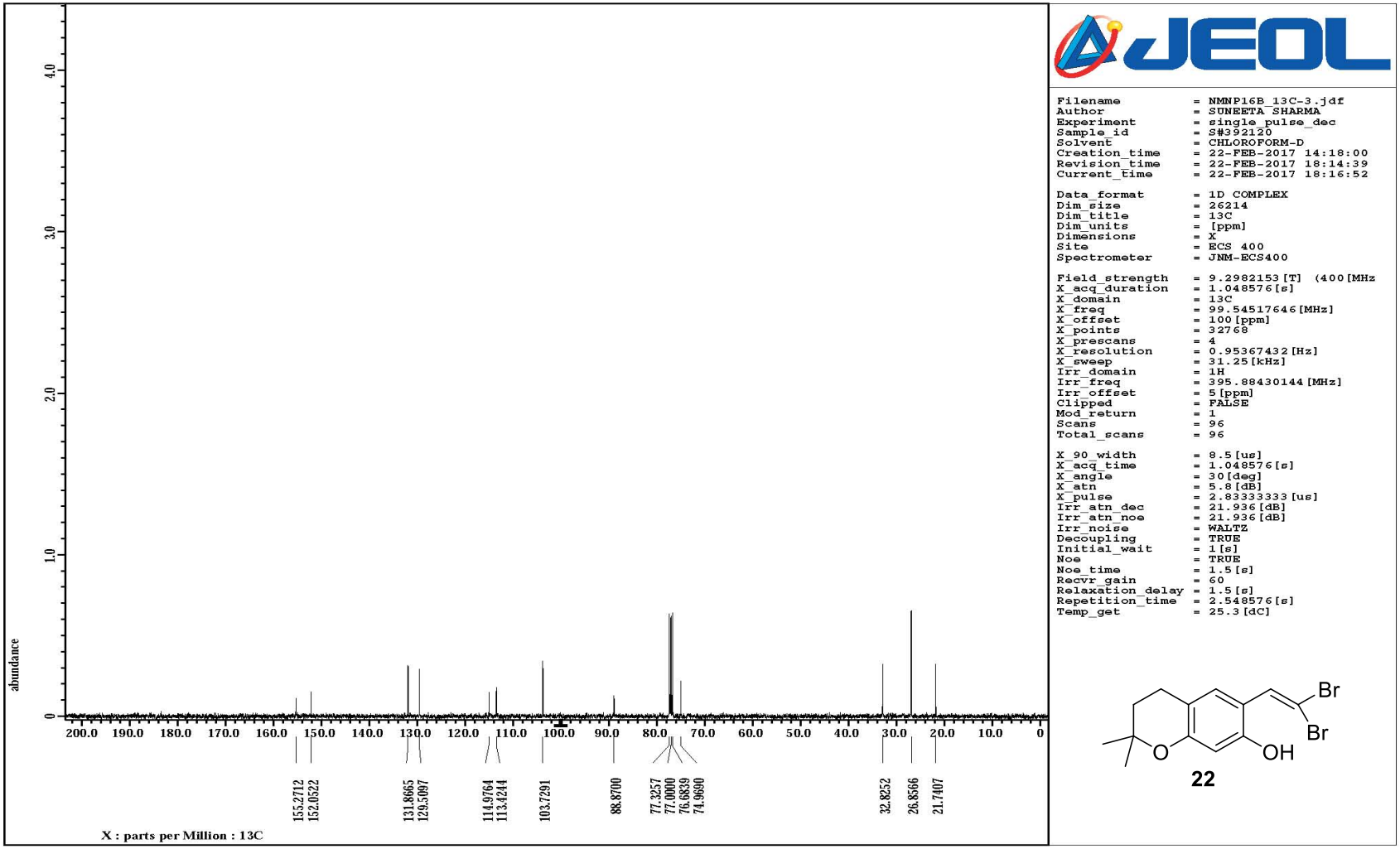
^{1}H NMR spectra of Compound **12c**



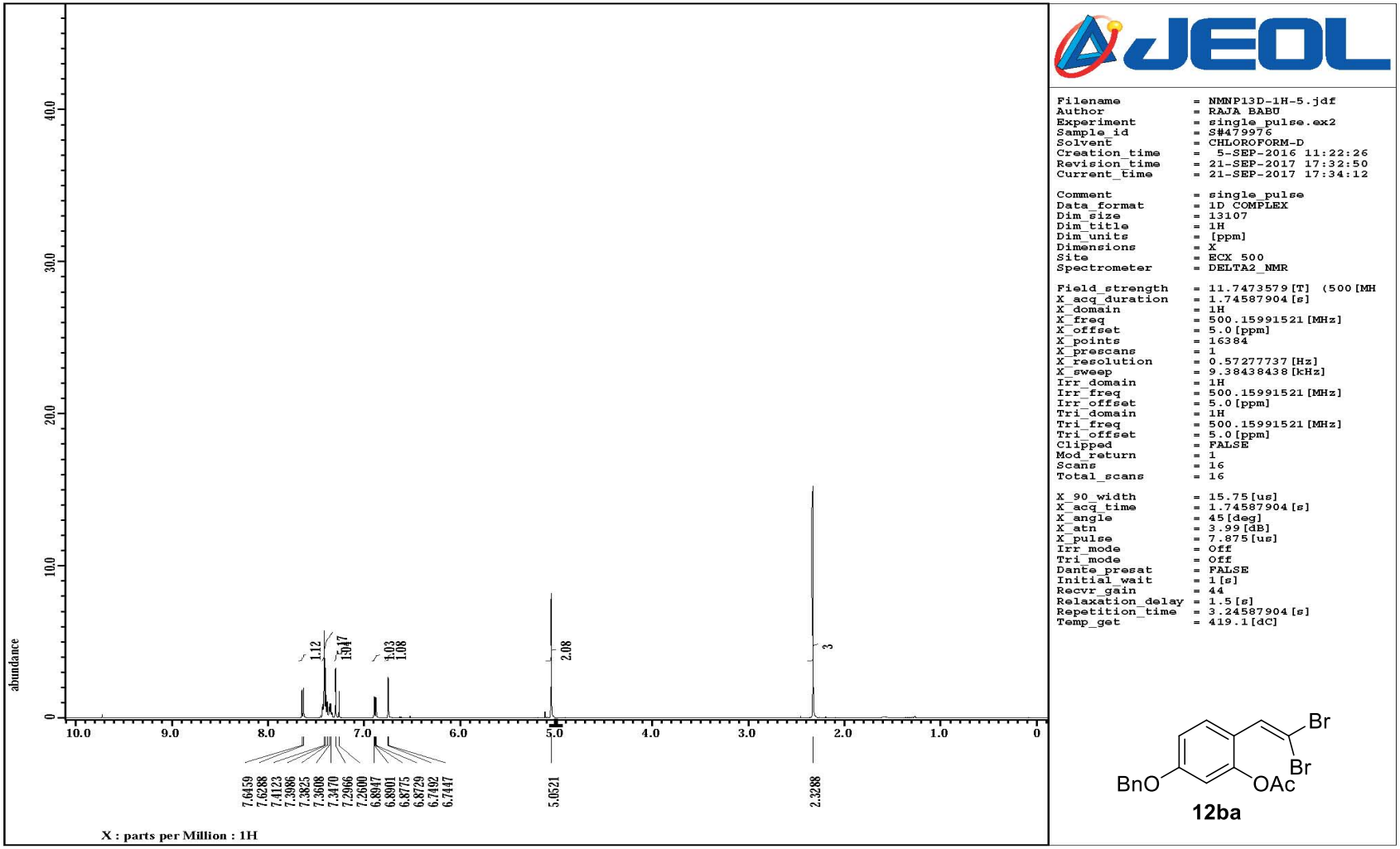
^{13}C NMR spectra of Compound **12c**



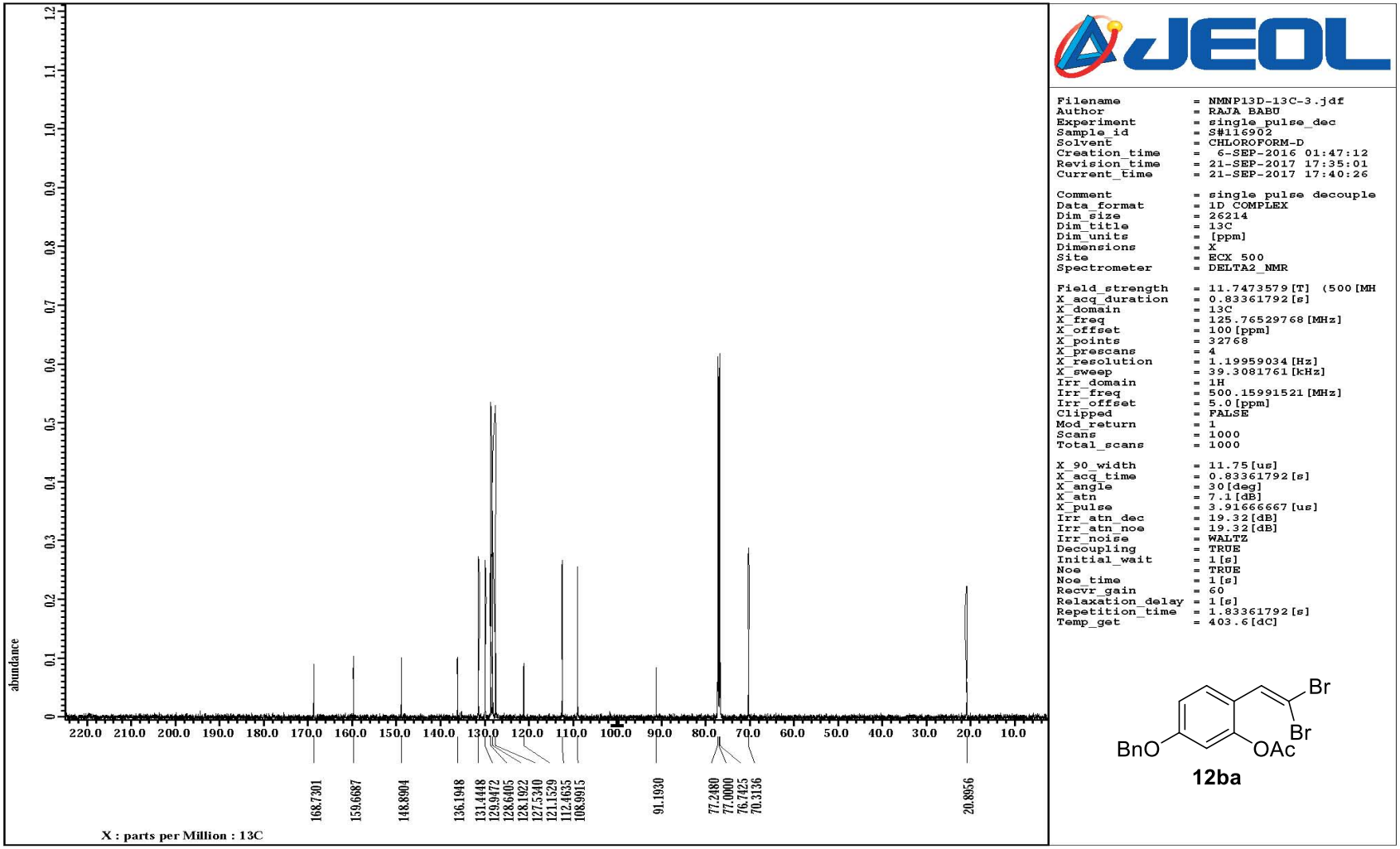
^{1}H NMR spectra of Compound **22**



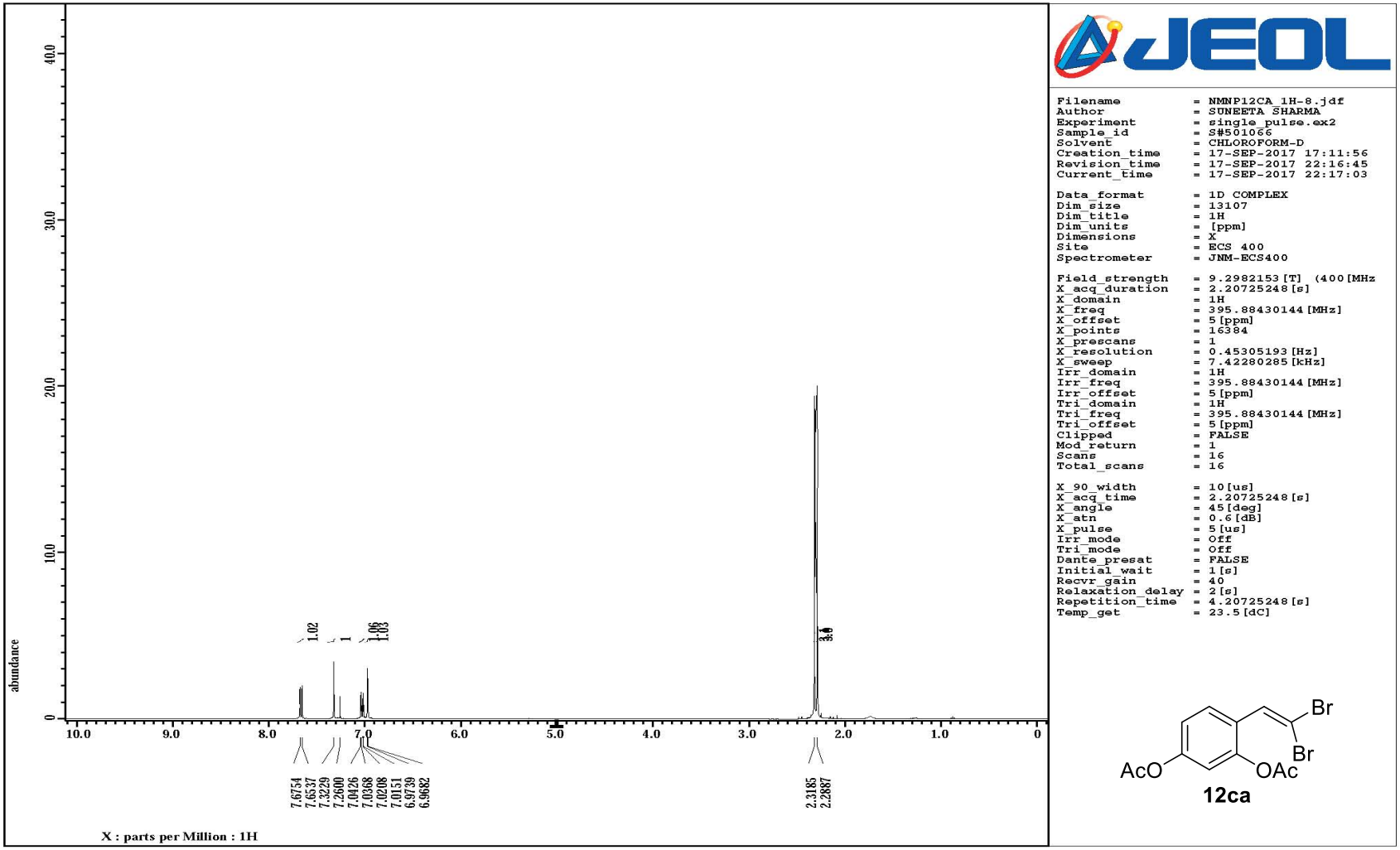
^{13}C NMR spectra of Compound **22**



^{1}H NMR spectrum of Compound **12ba**



^{13}C NMR spectrum of Compound **12ba**



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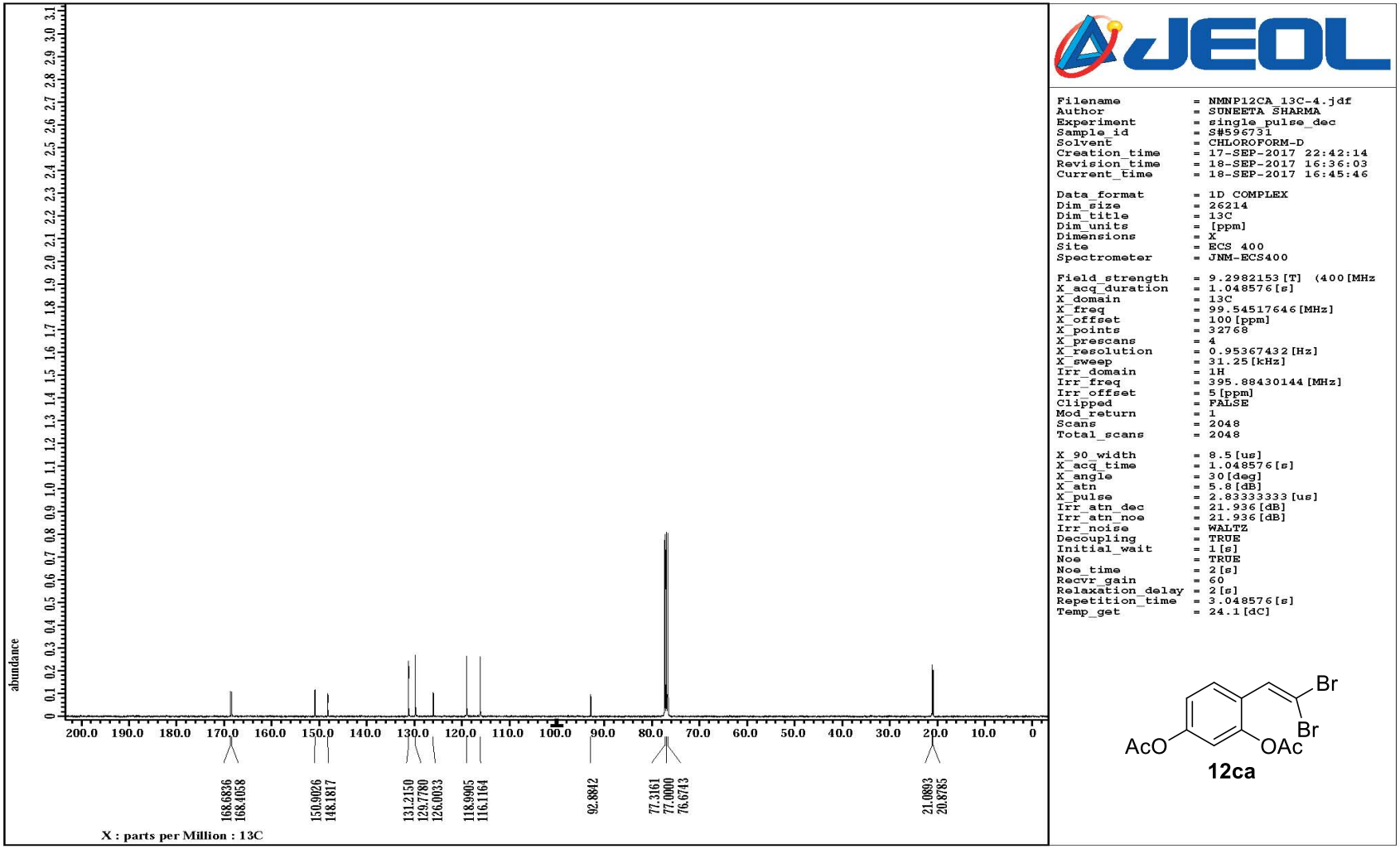
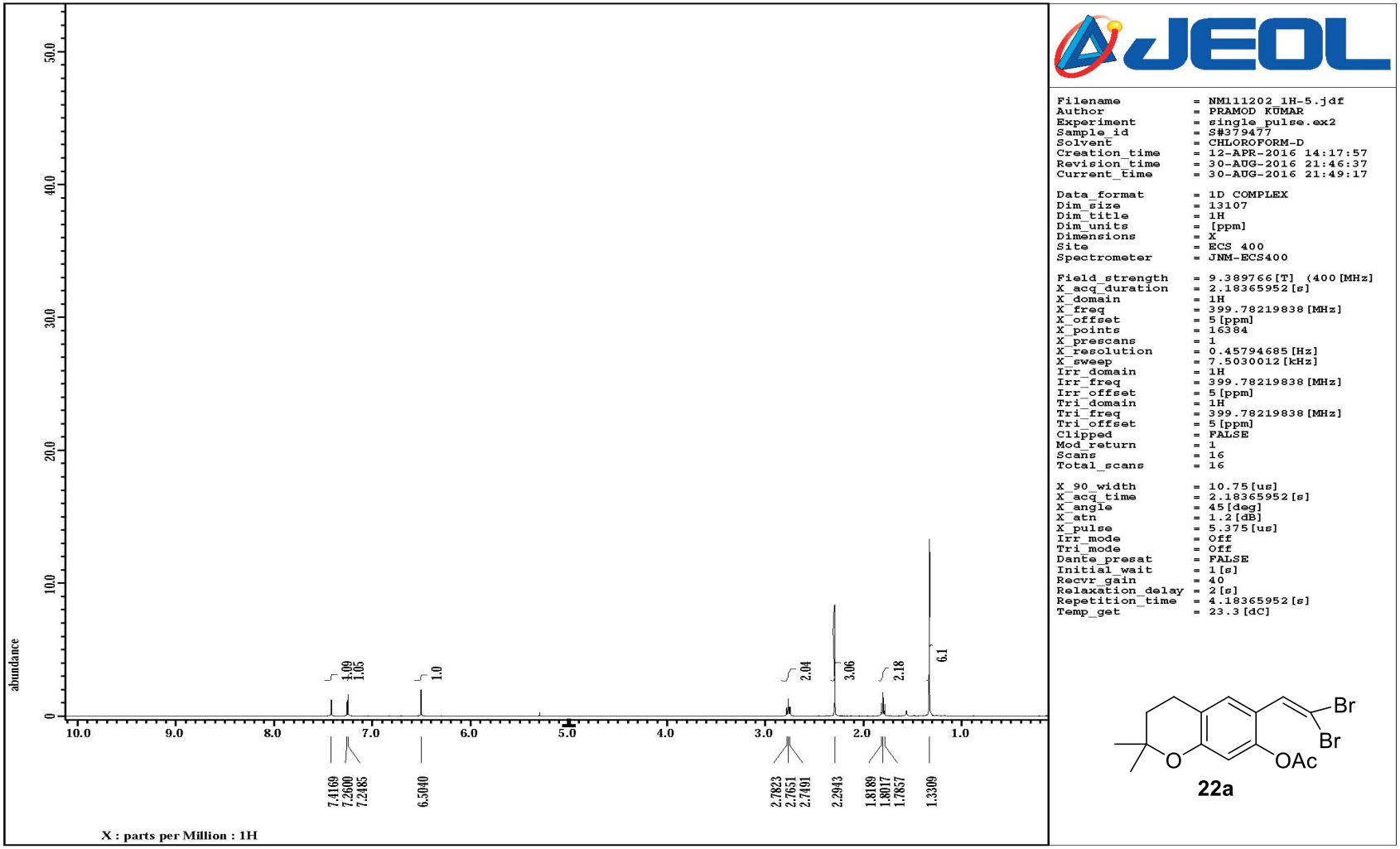
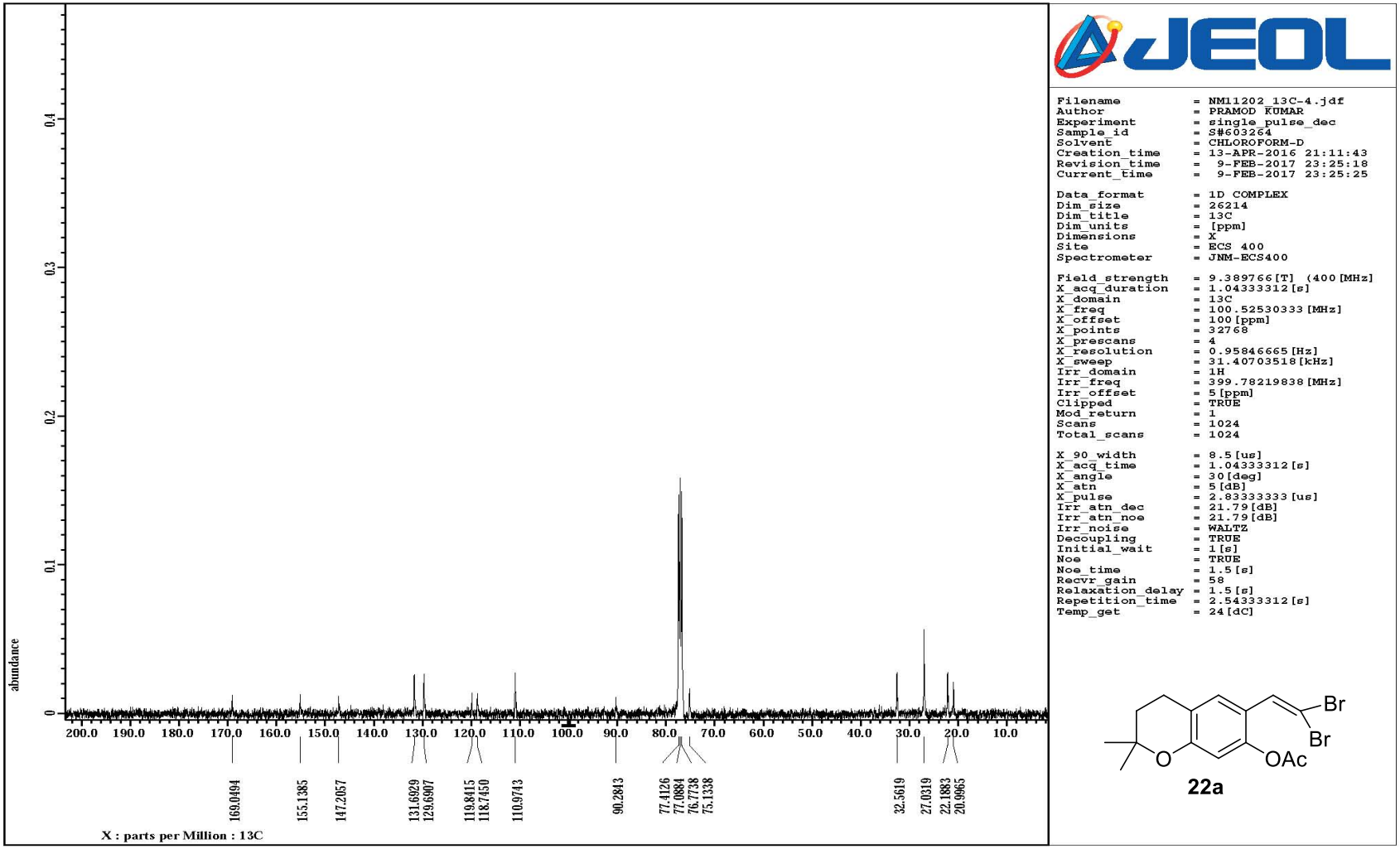


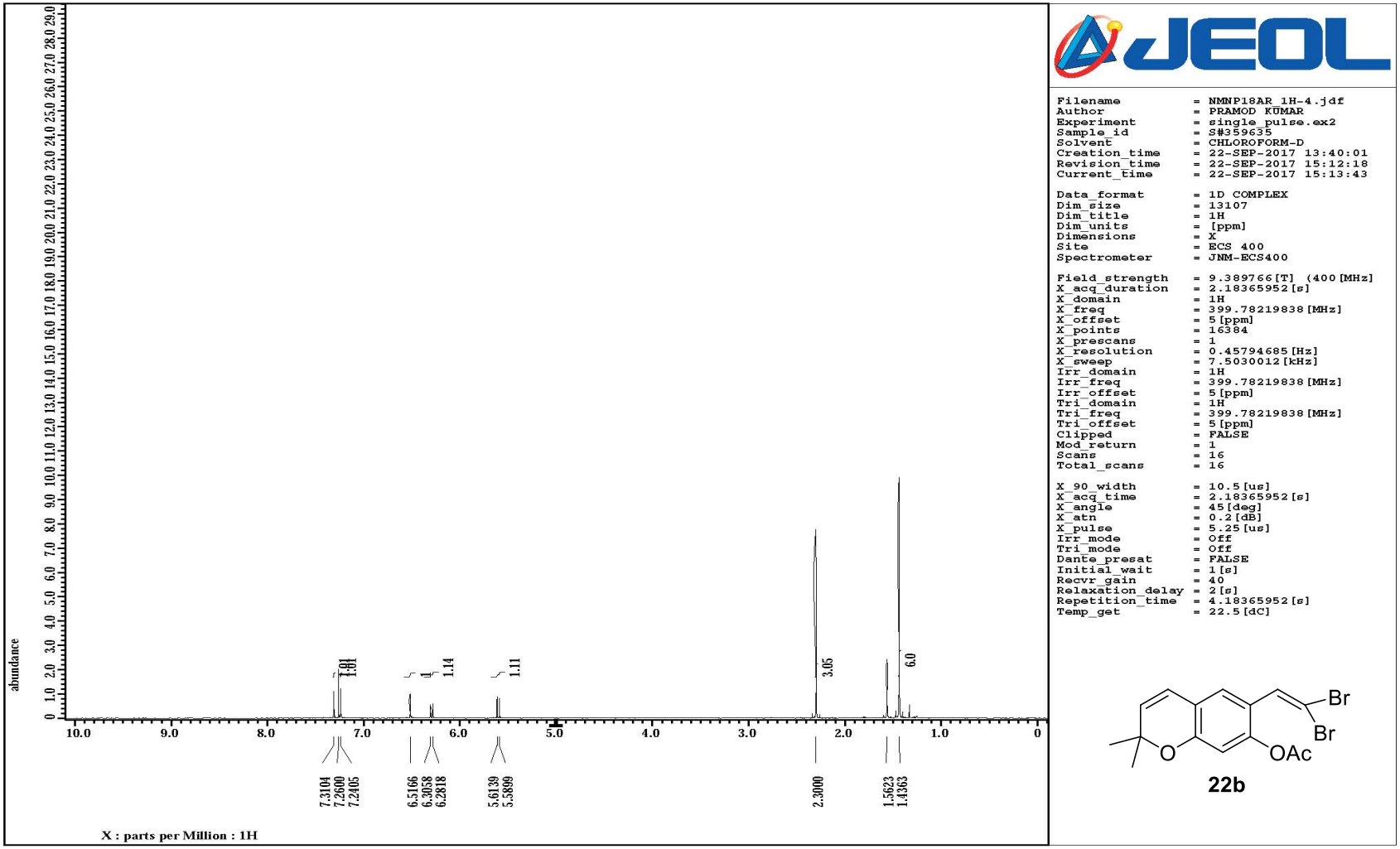
^{13}C NMR spectrum of Compound **12ca**



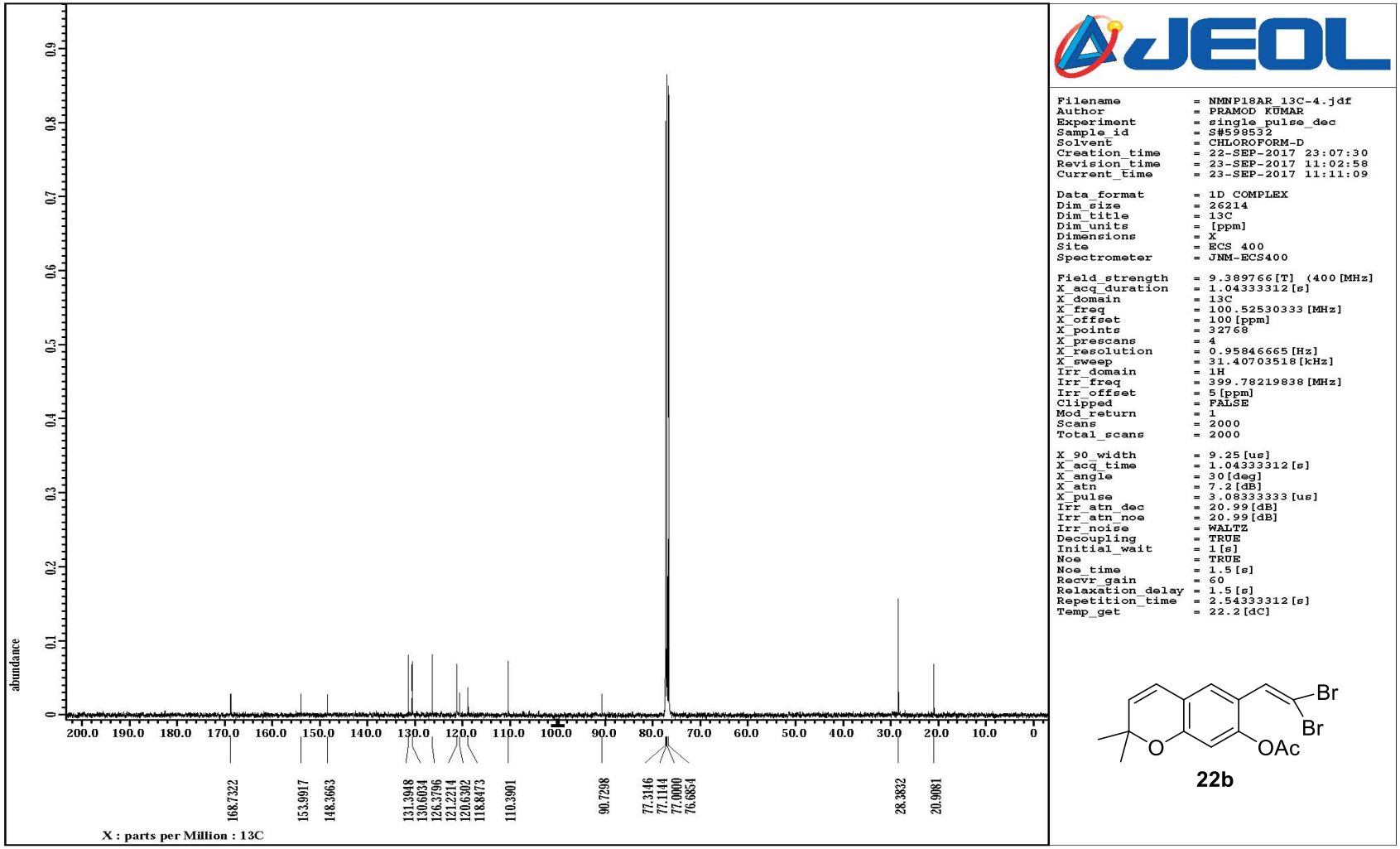
^{1}H NMR spectra of Compound **22a**



^{13}C NMR spectra of Compound **22a**



^{1}H NMR spectrum of Compound **22b**



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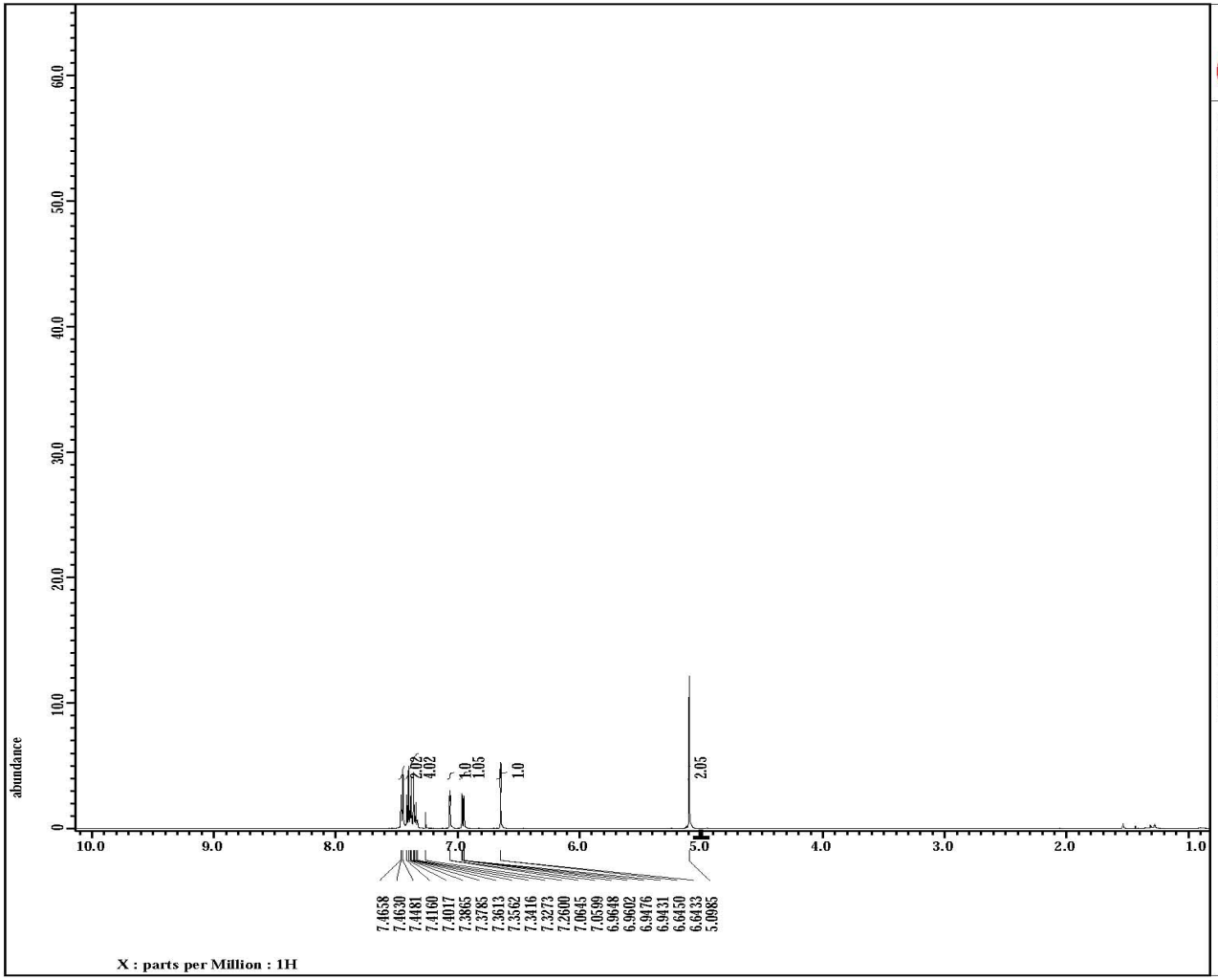


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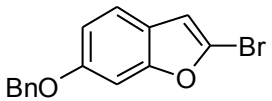
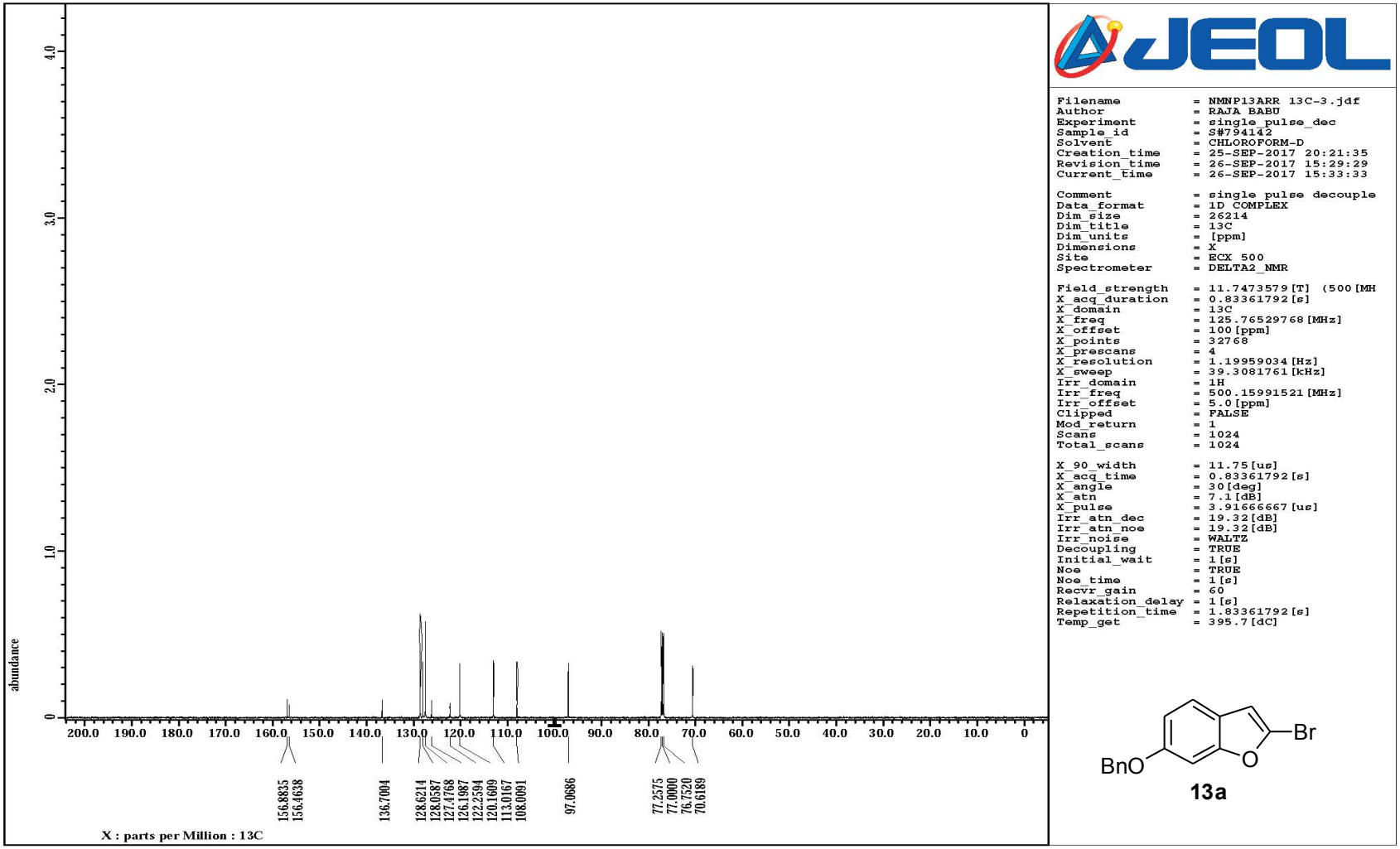
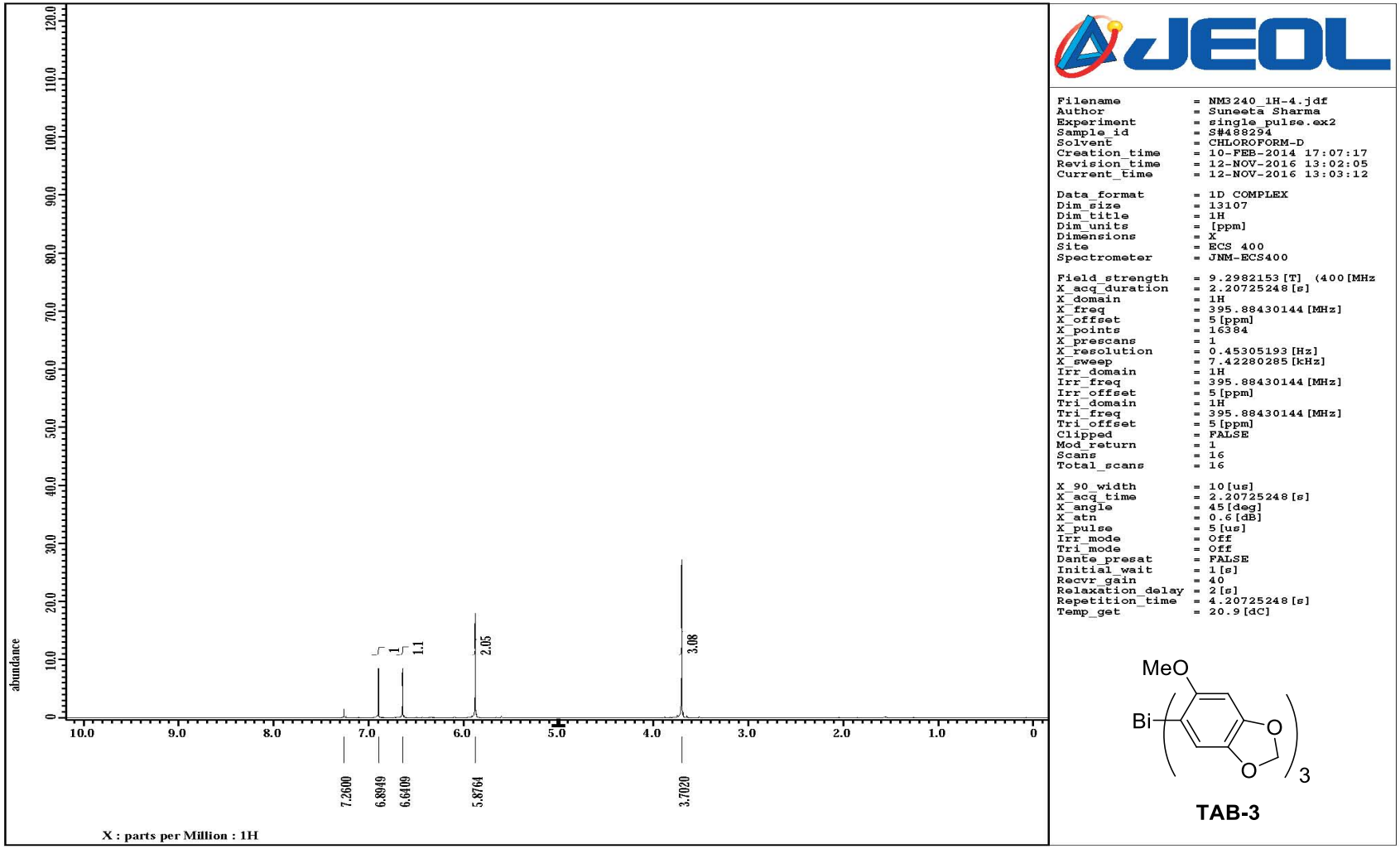


13a

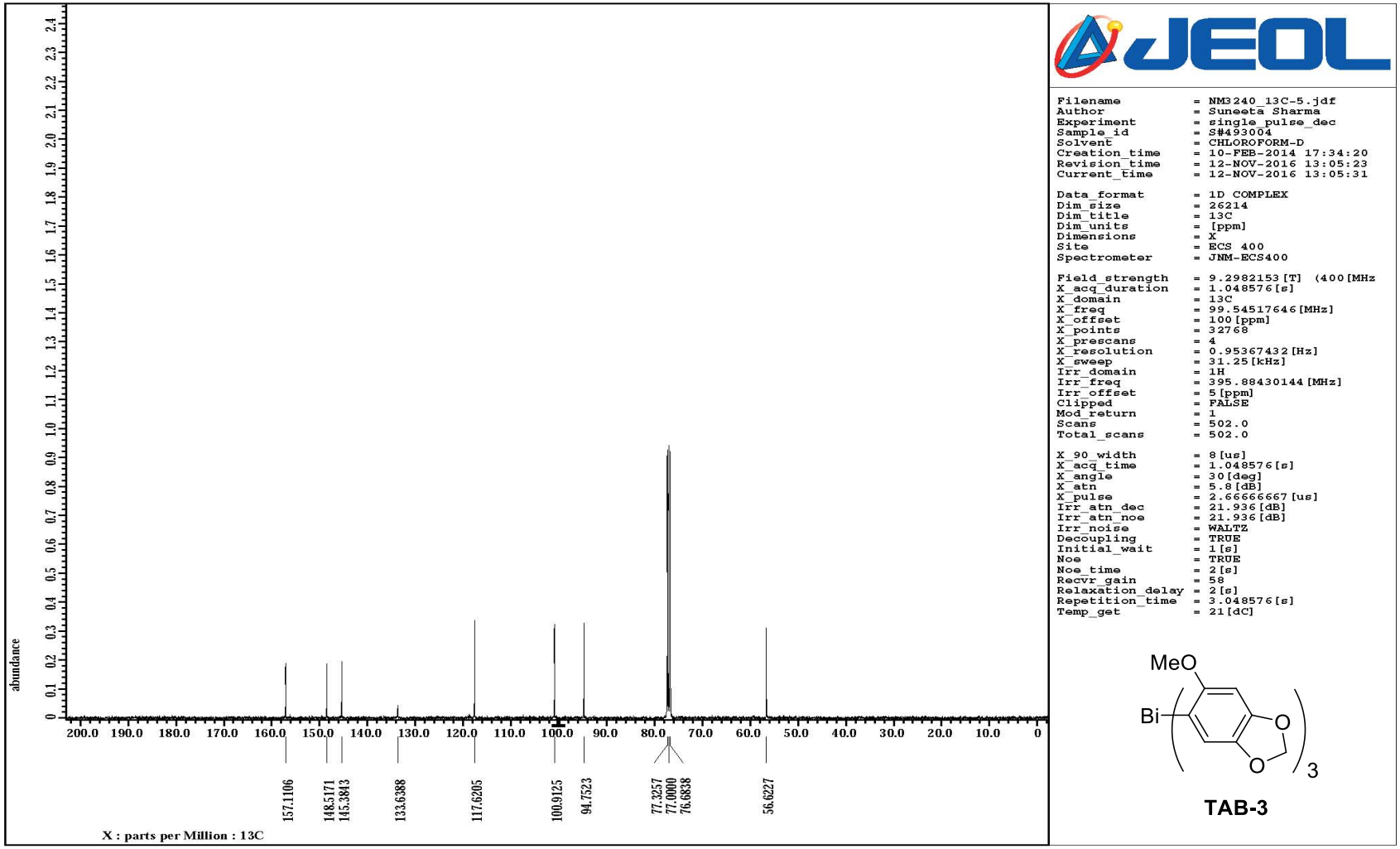
^{1}H NMR spectrum of Compound **13a**



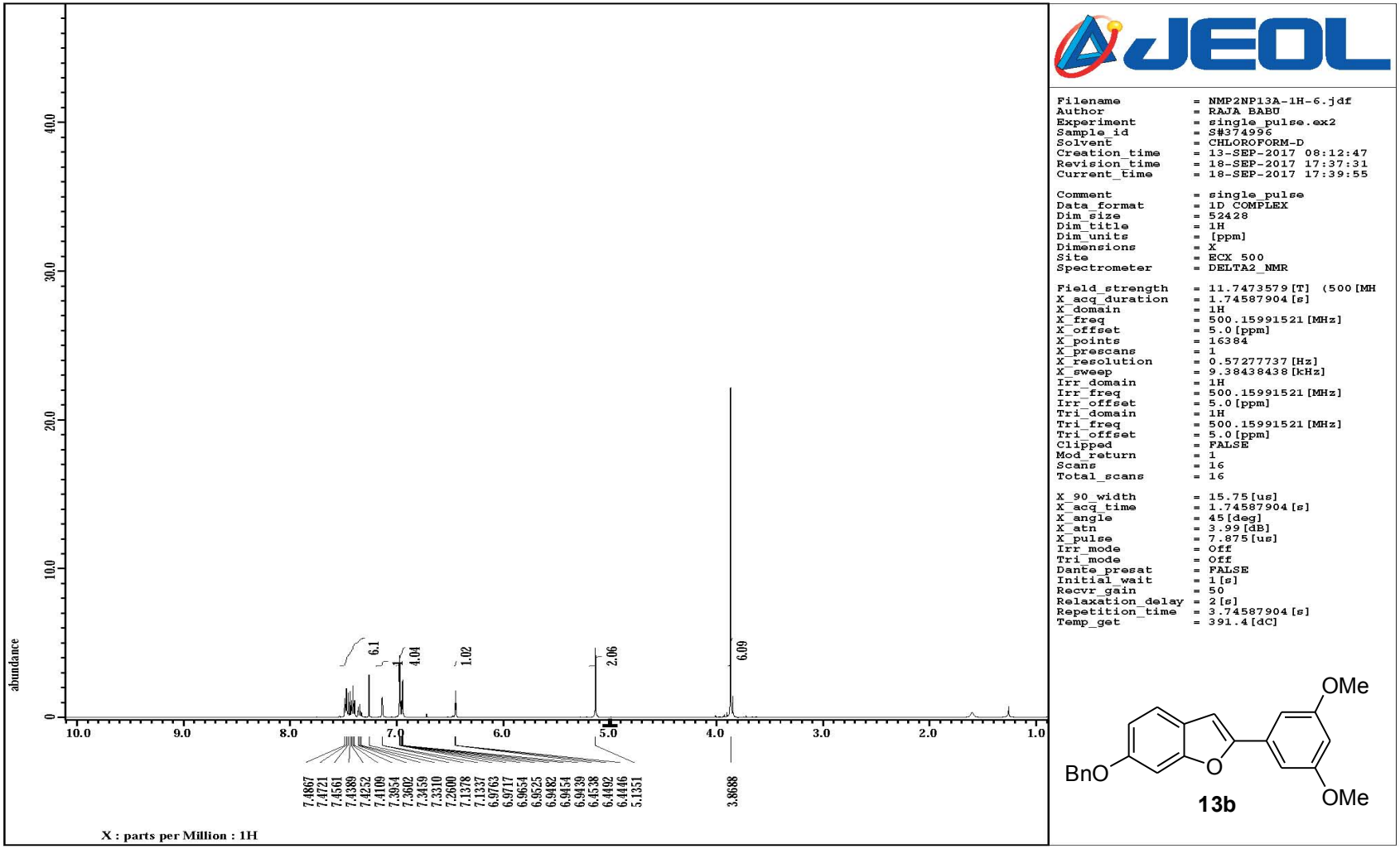
^{13}C NMR spectrum of Compound **13a**



^{1}H NMR spectra of **TAB-3**



^{13}C NMR spectra of **TAB-3**



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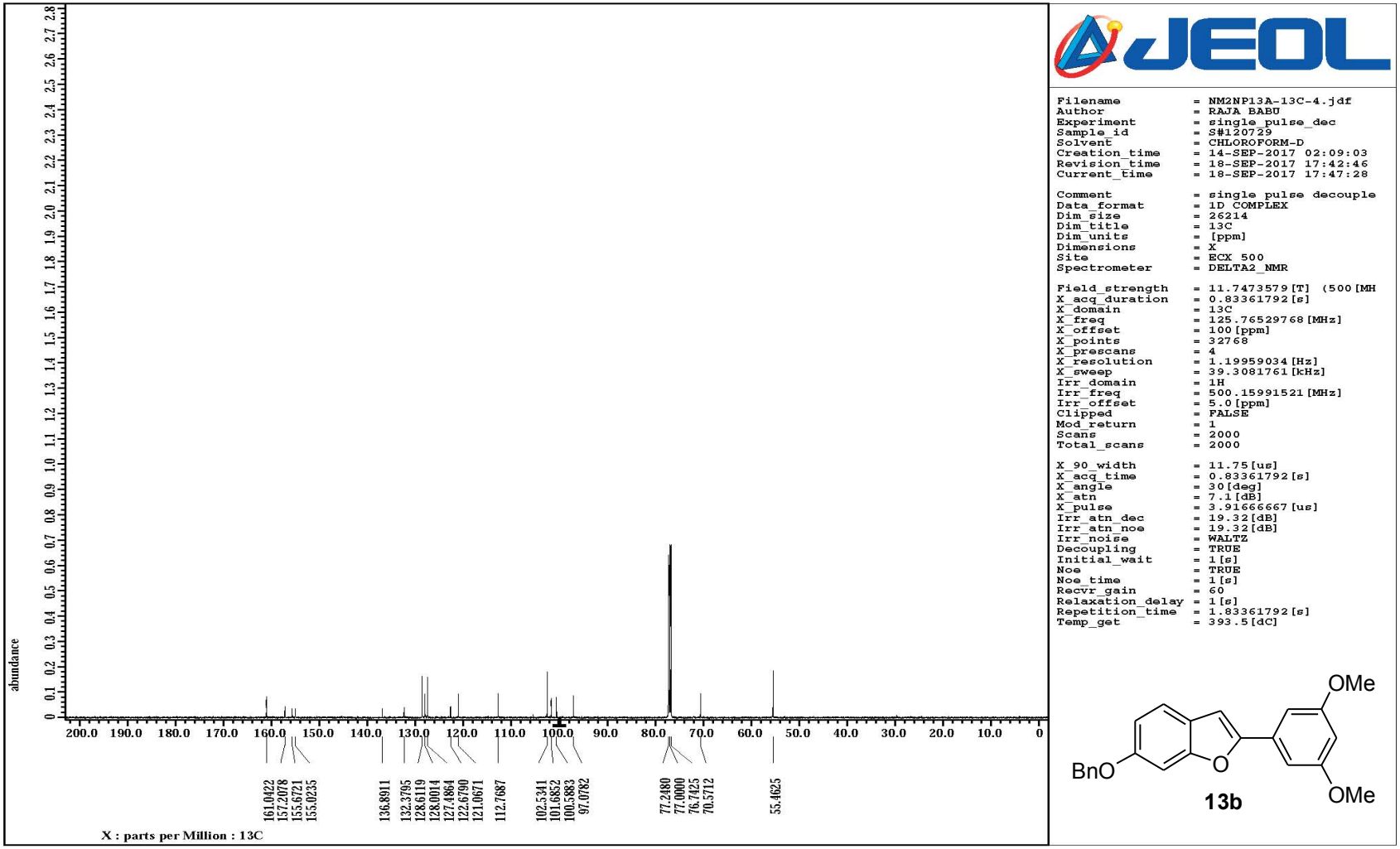
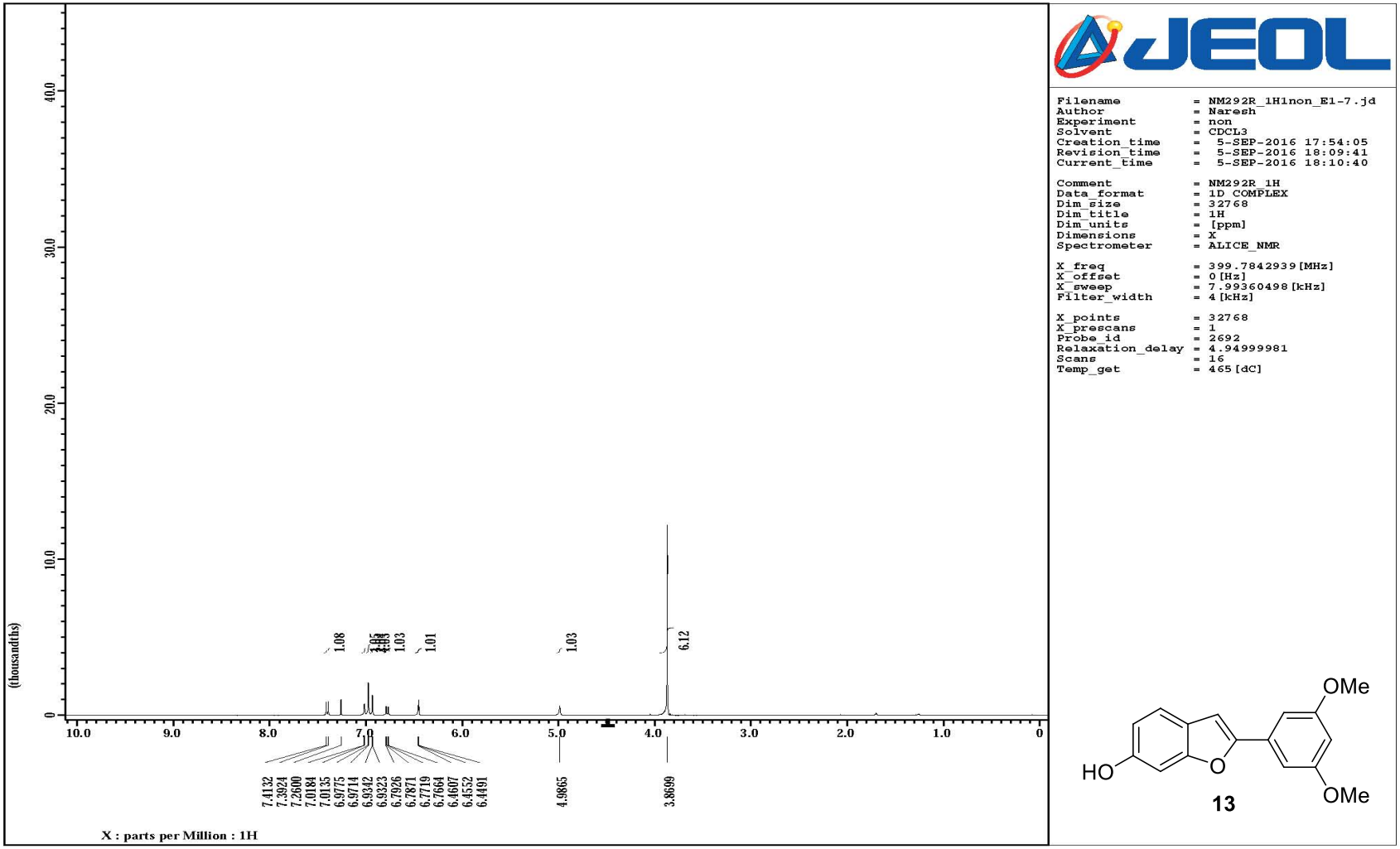
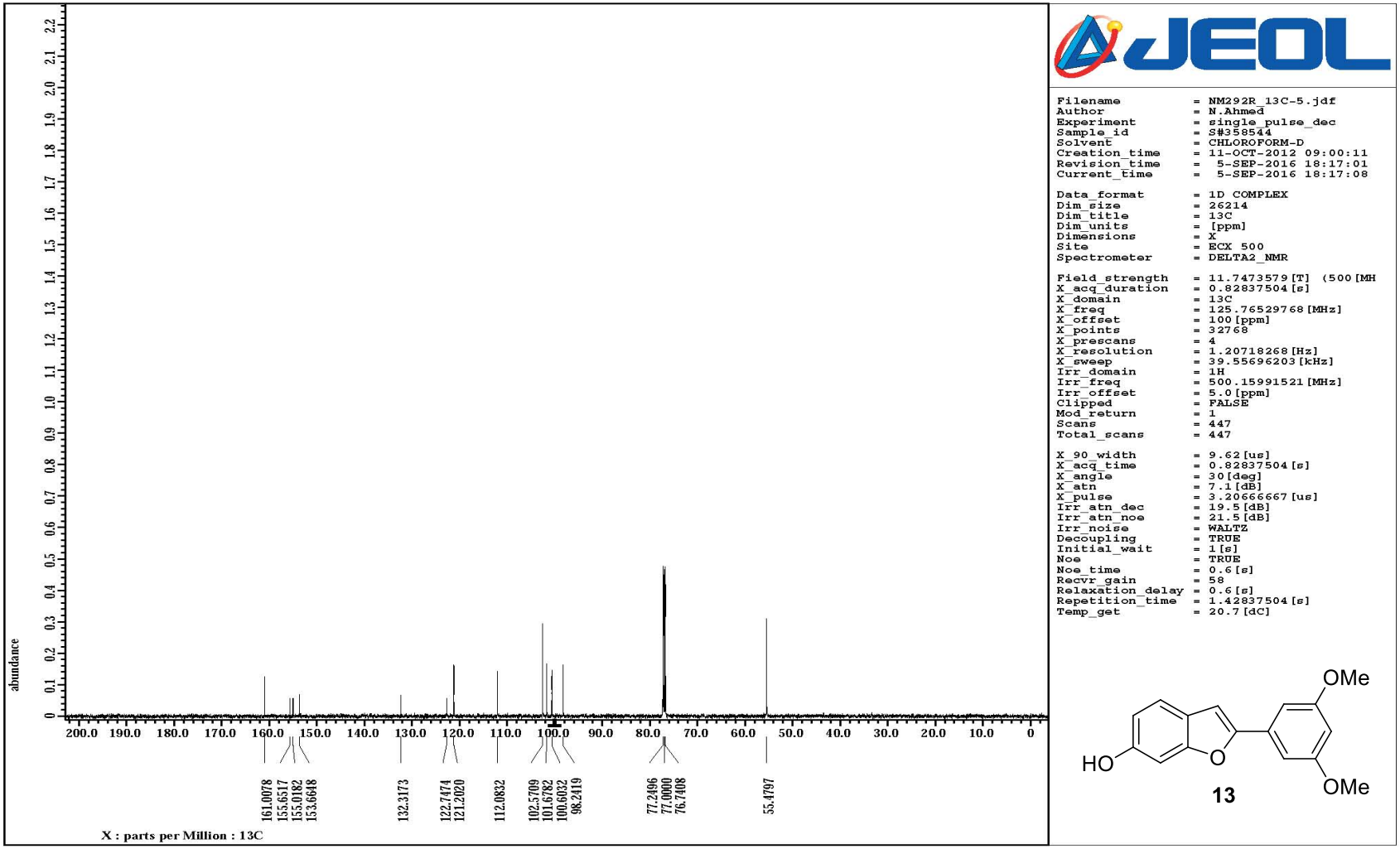


^{13}C NMR spectrum of Compound **13b**



^{1}H NMR spectra of Compound **13**



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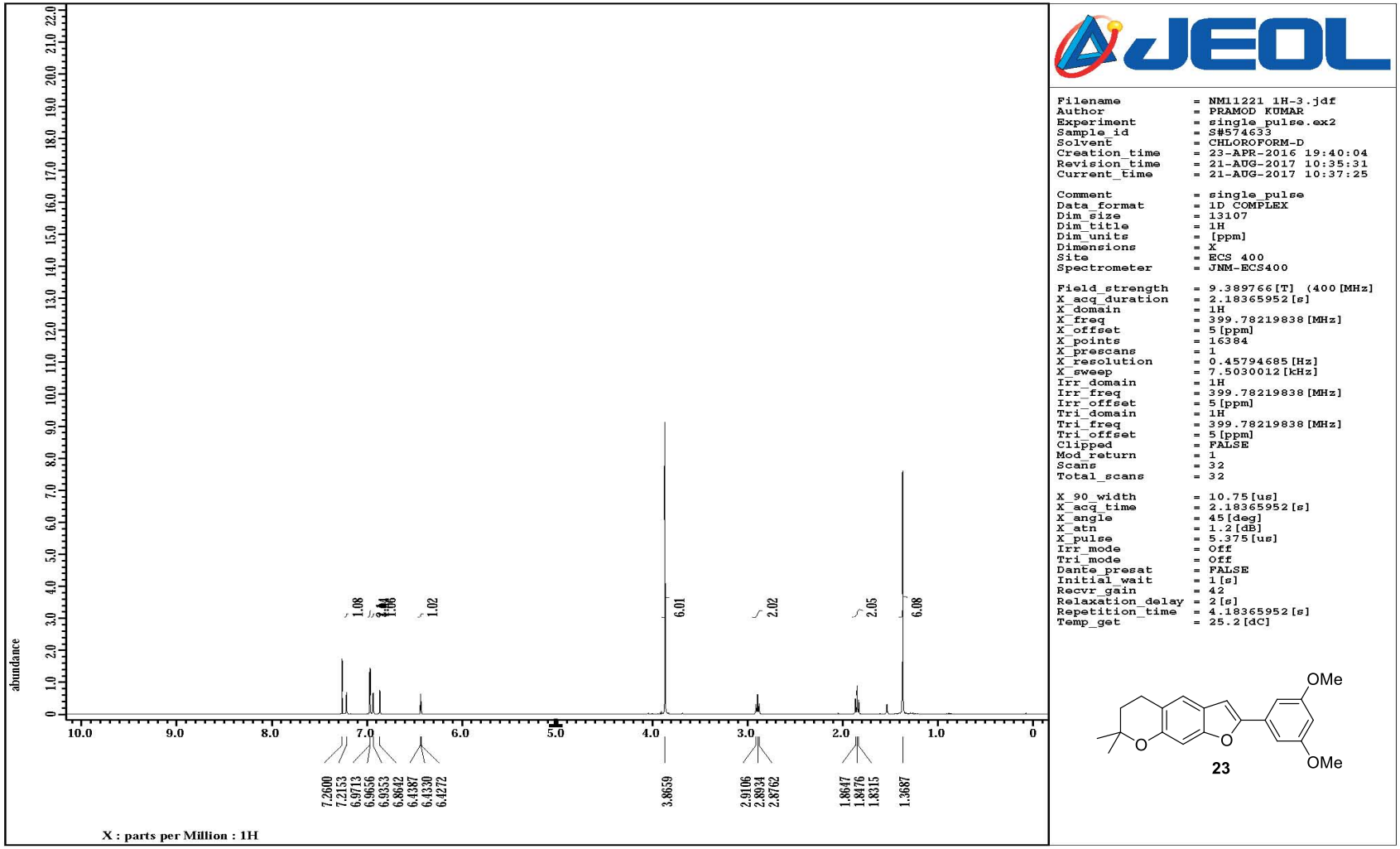
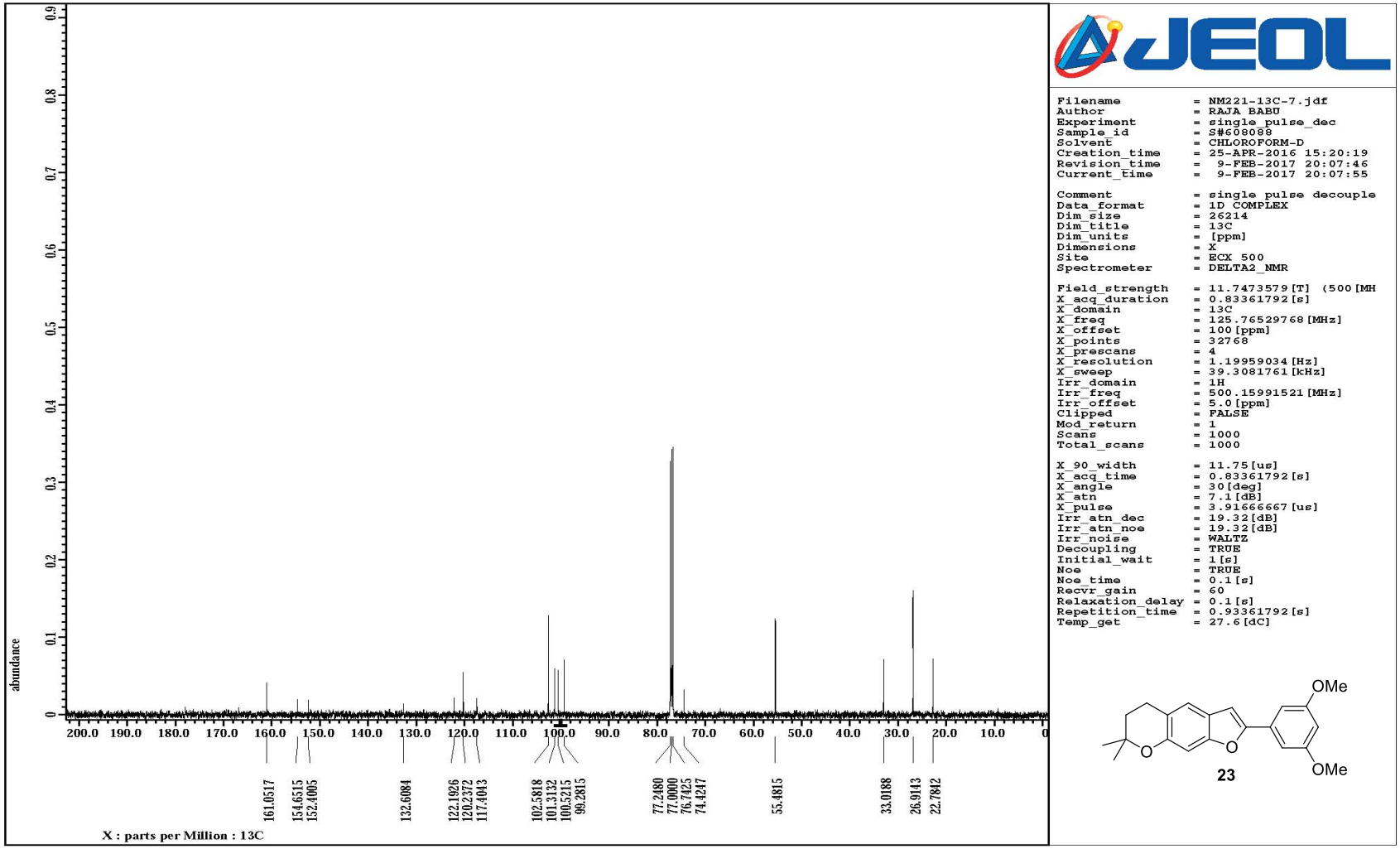
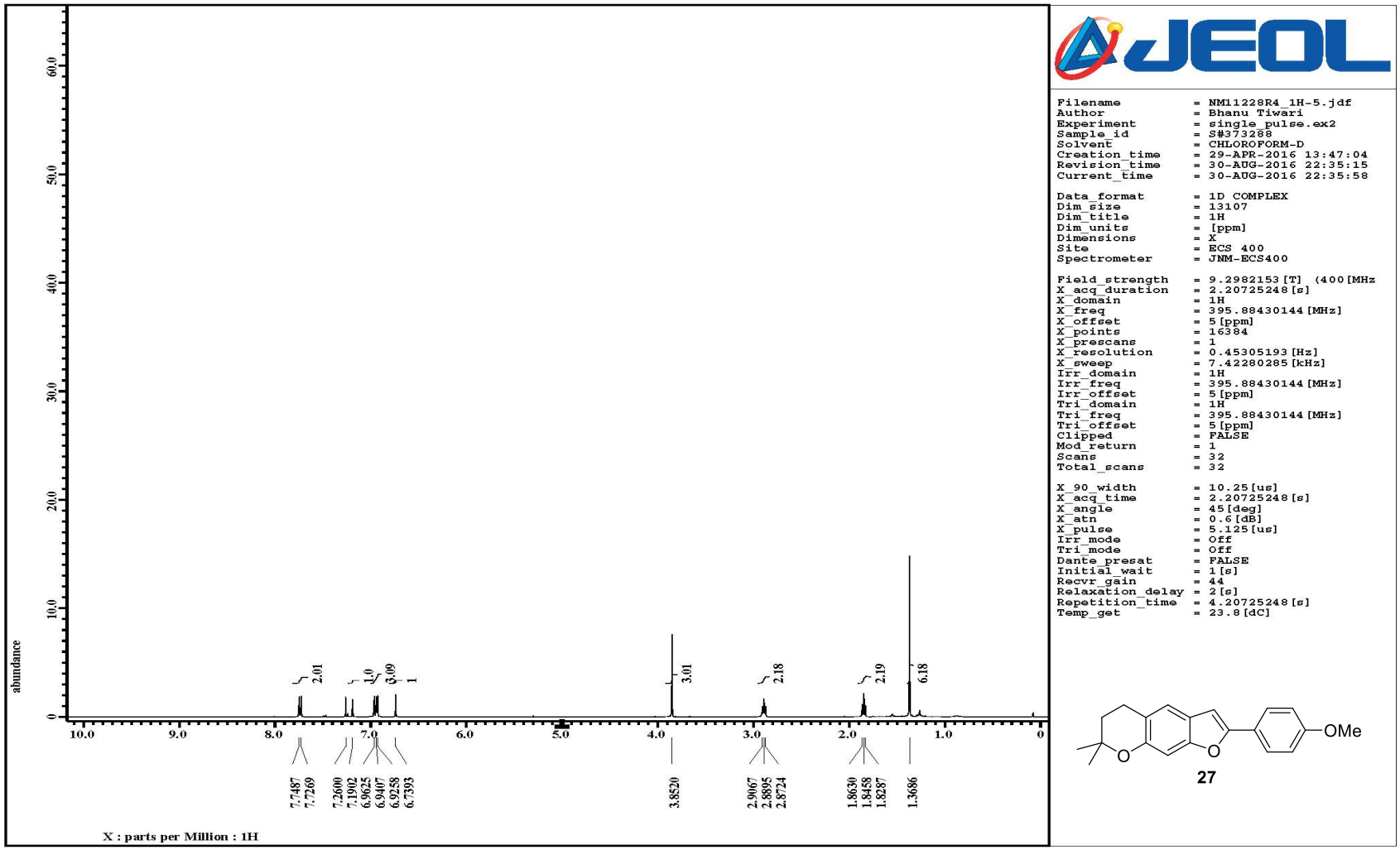


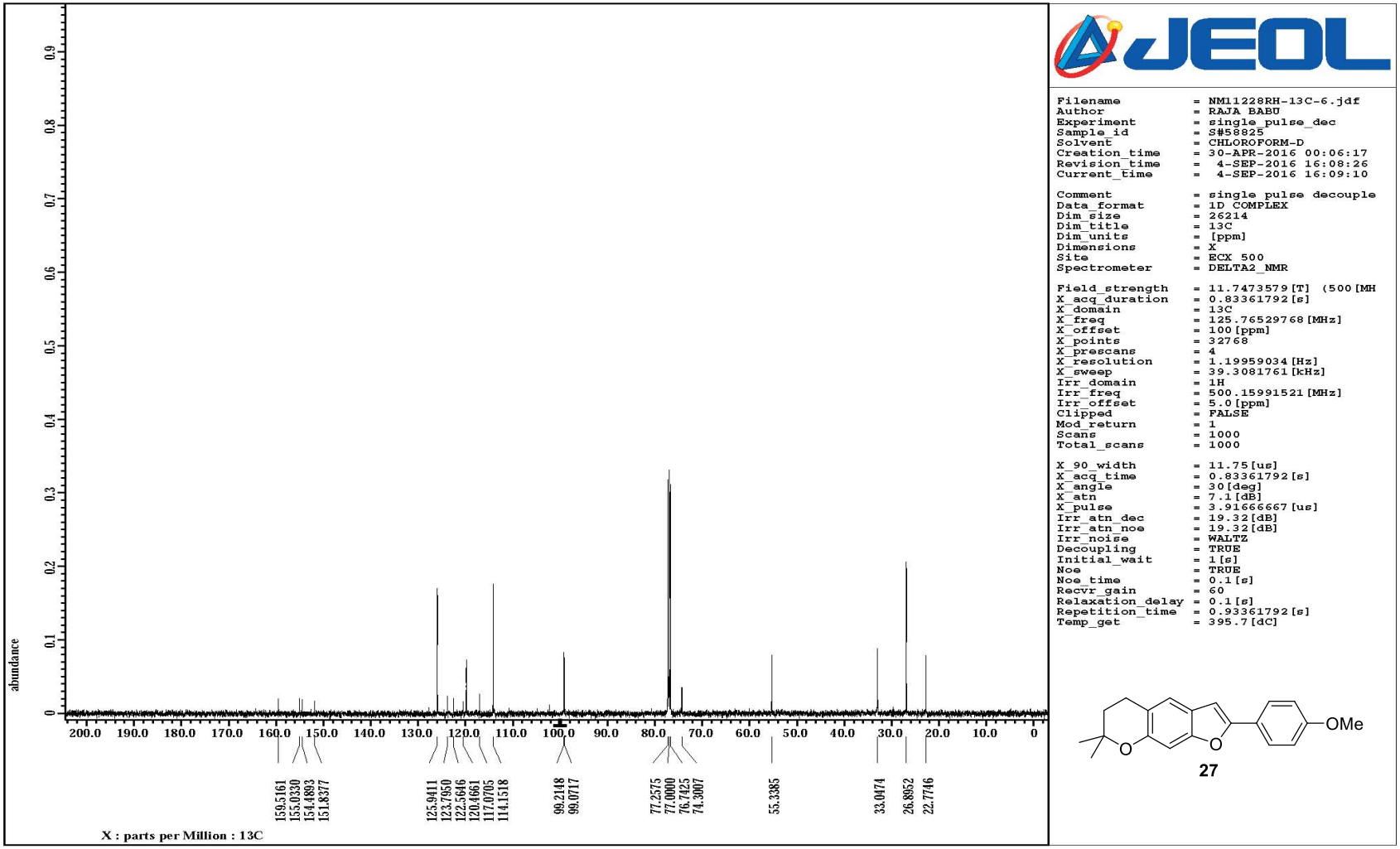
^{1}H NMR spectra of Compound **23**



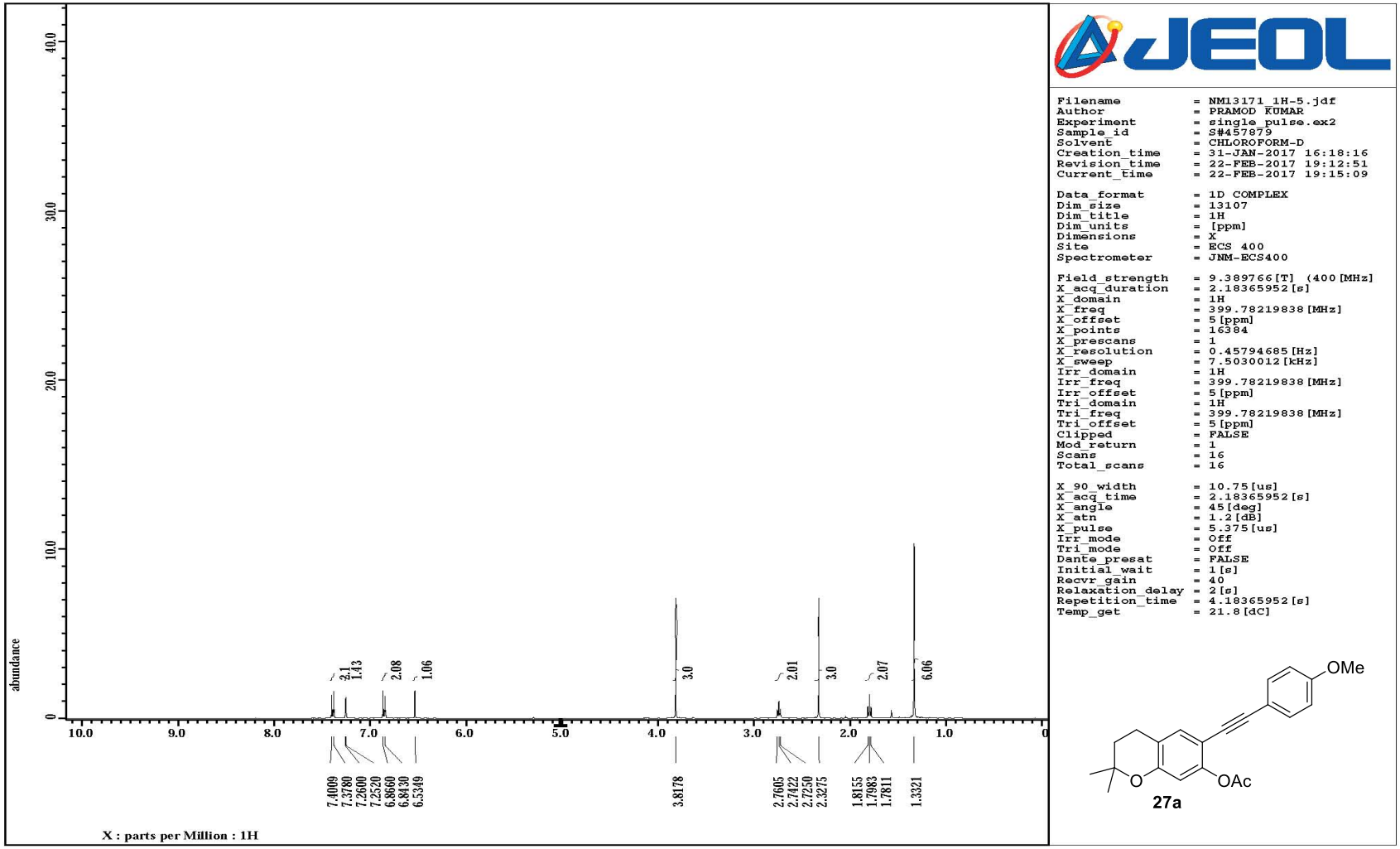
^{13}C NMR spectra of Compound **23**



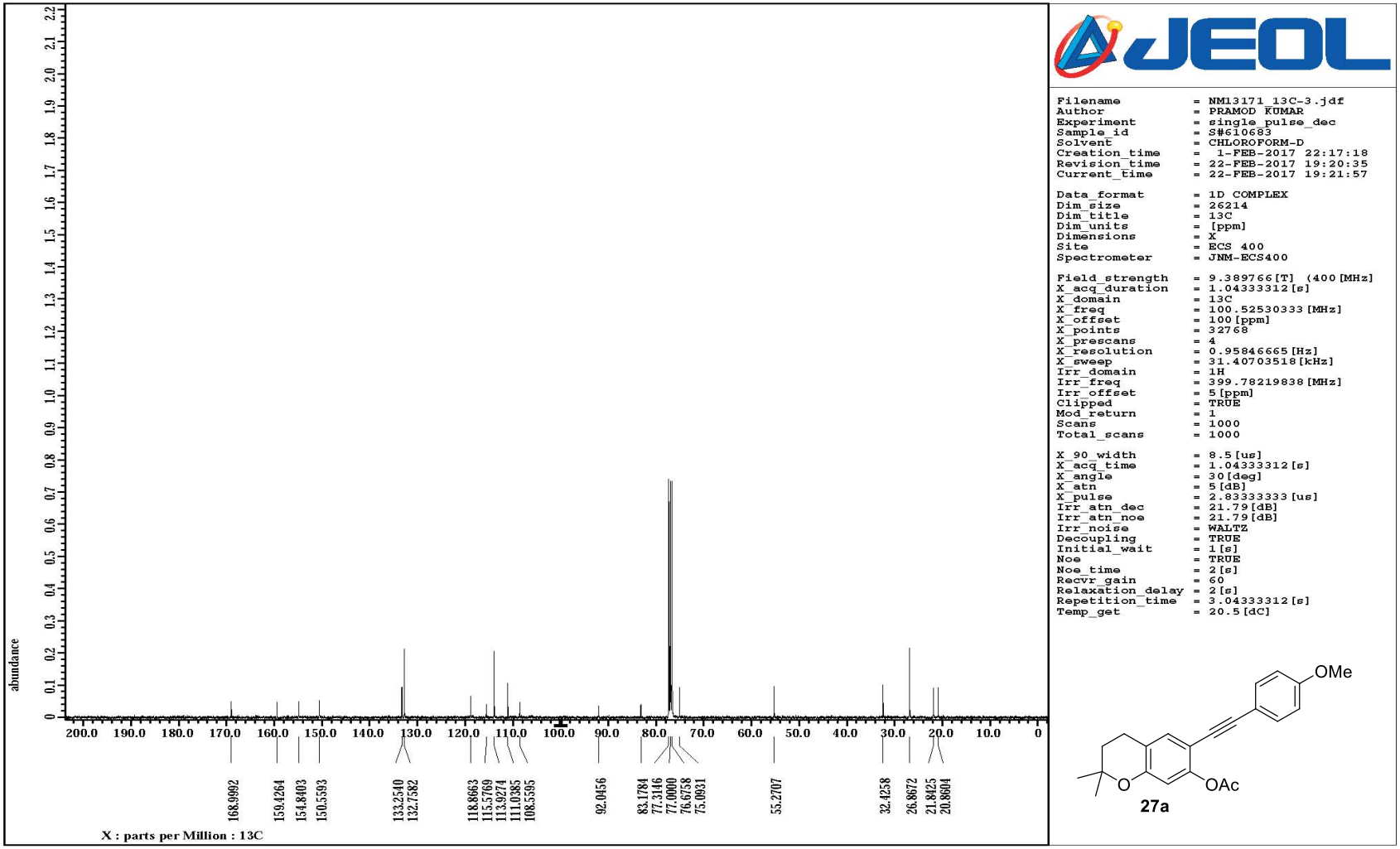
^{1}H NMR spectra of Compound **27**



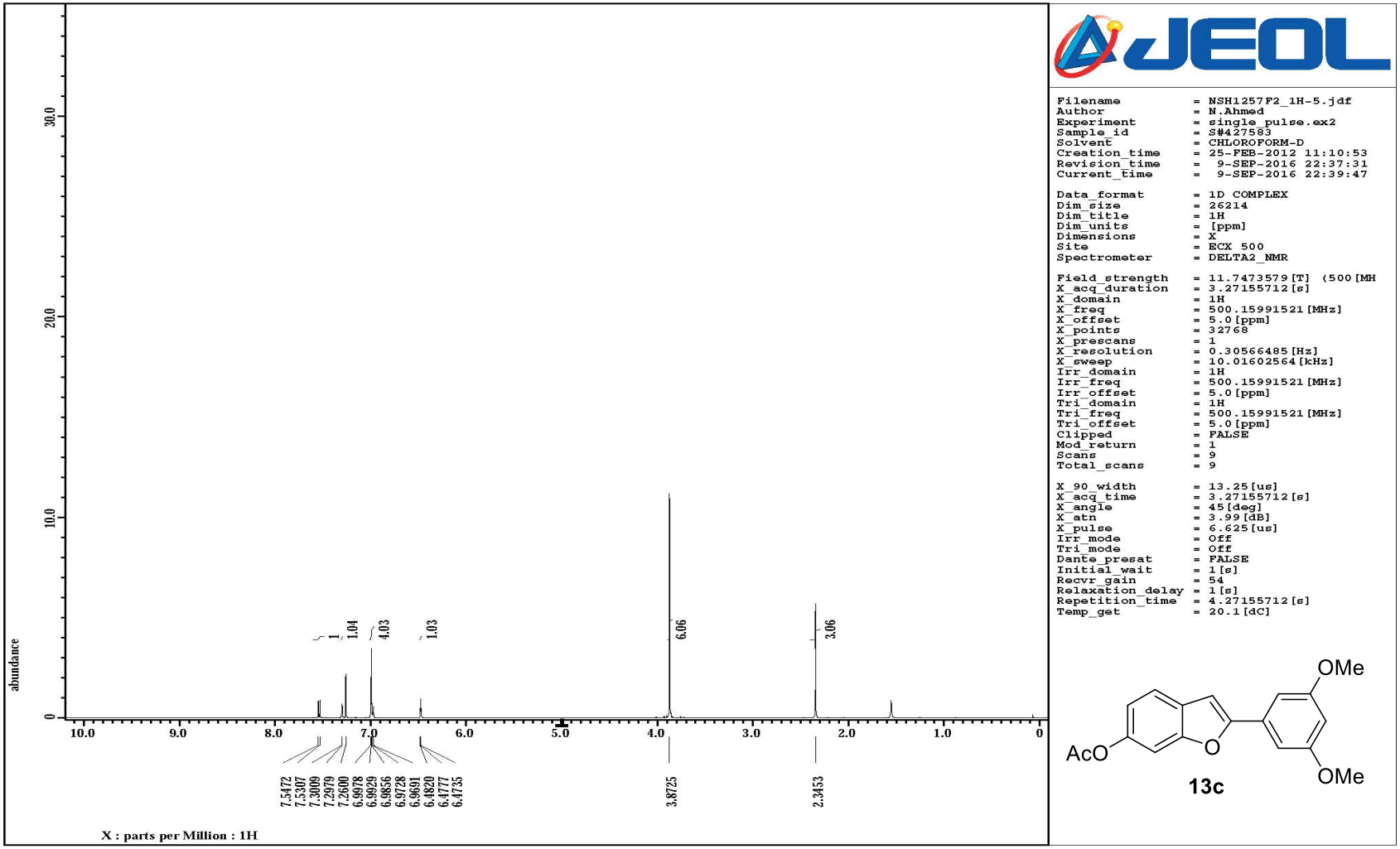
^{13}C NMR spectra of Compound **27**



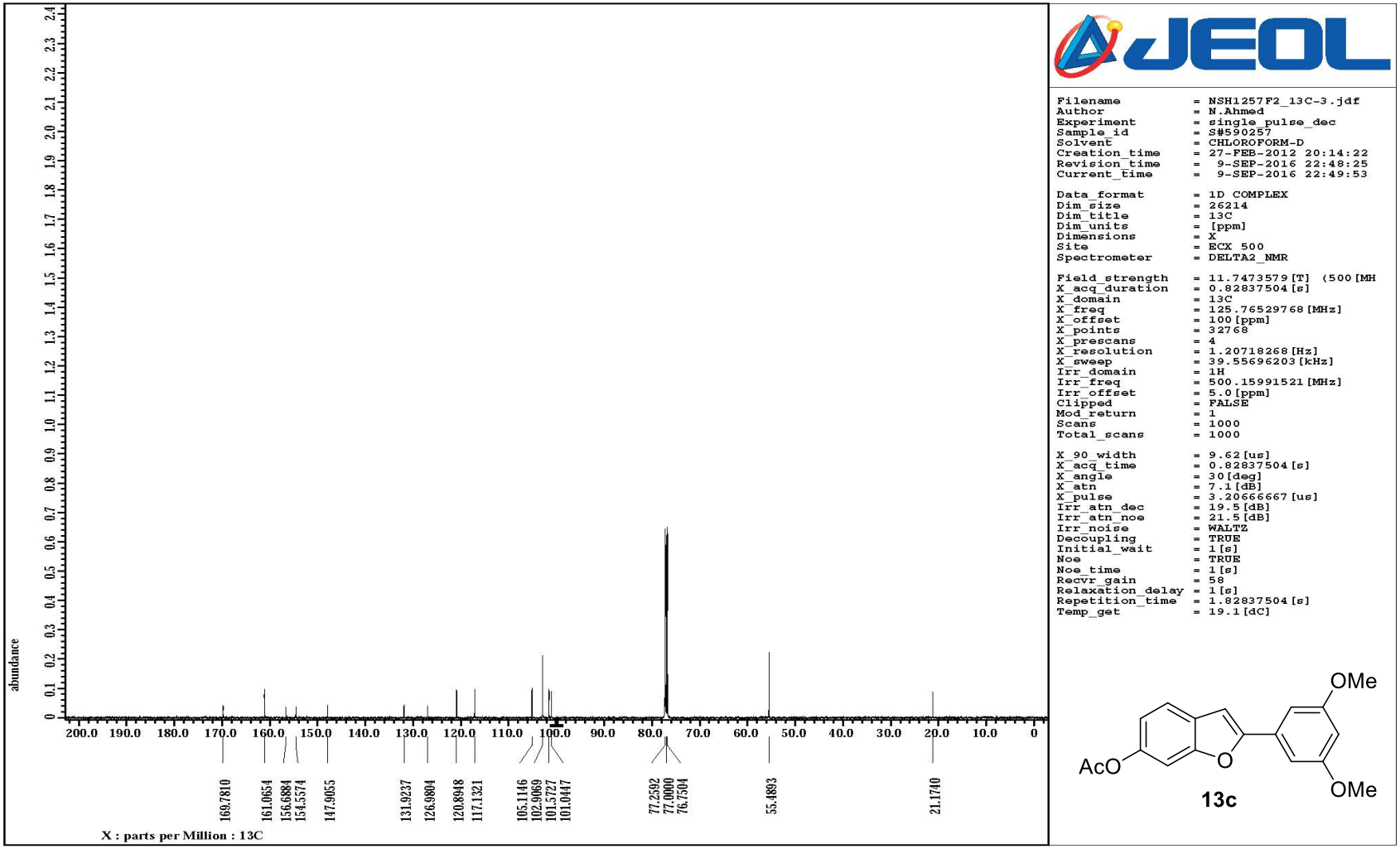
^{1}H NMR spectra of Compound **27a**



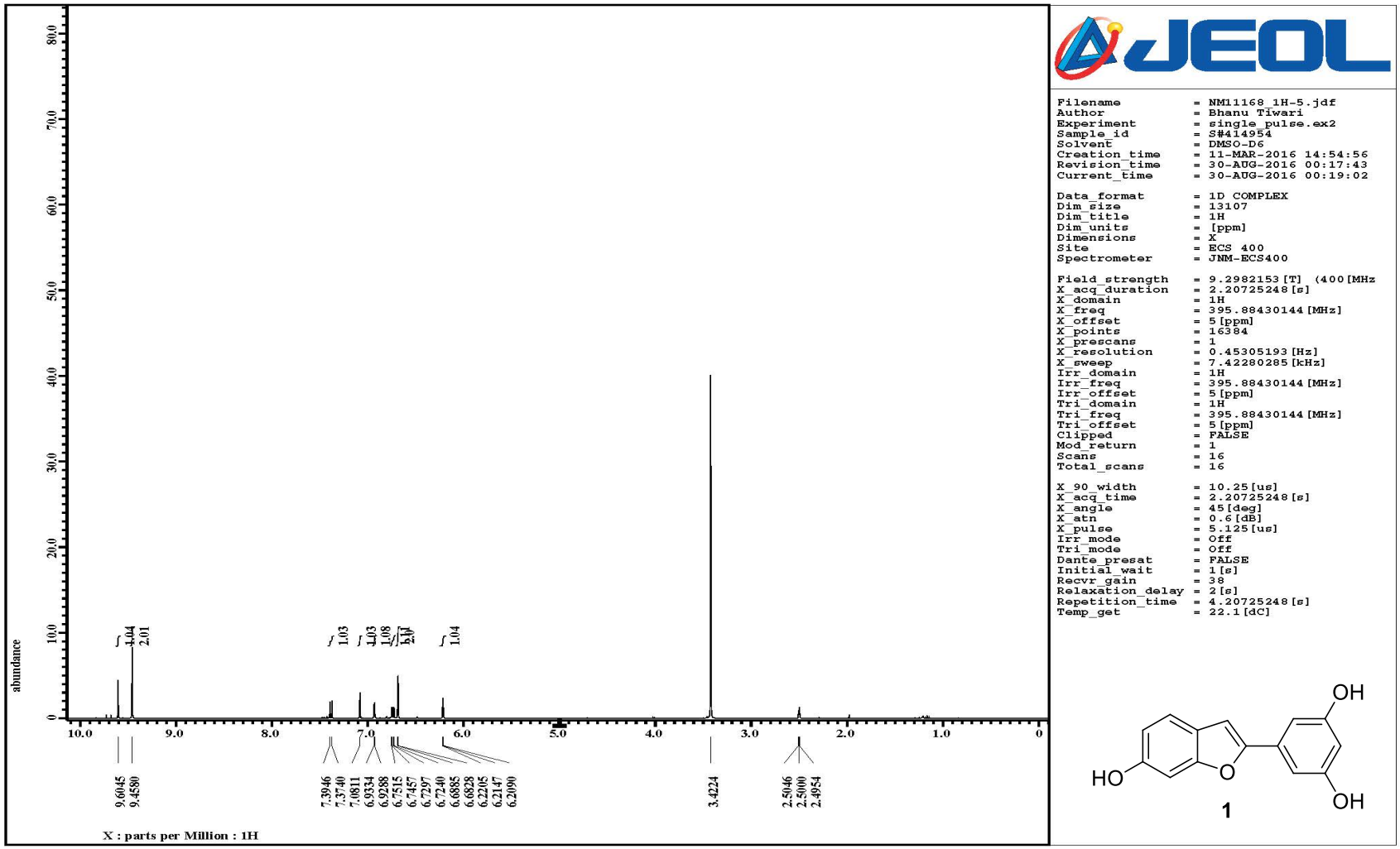
^{13}C NMR spectra of Compound **27a**



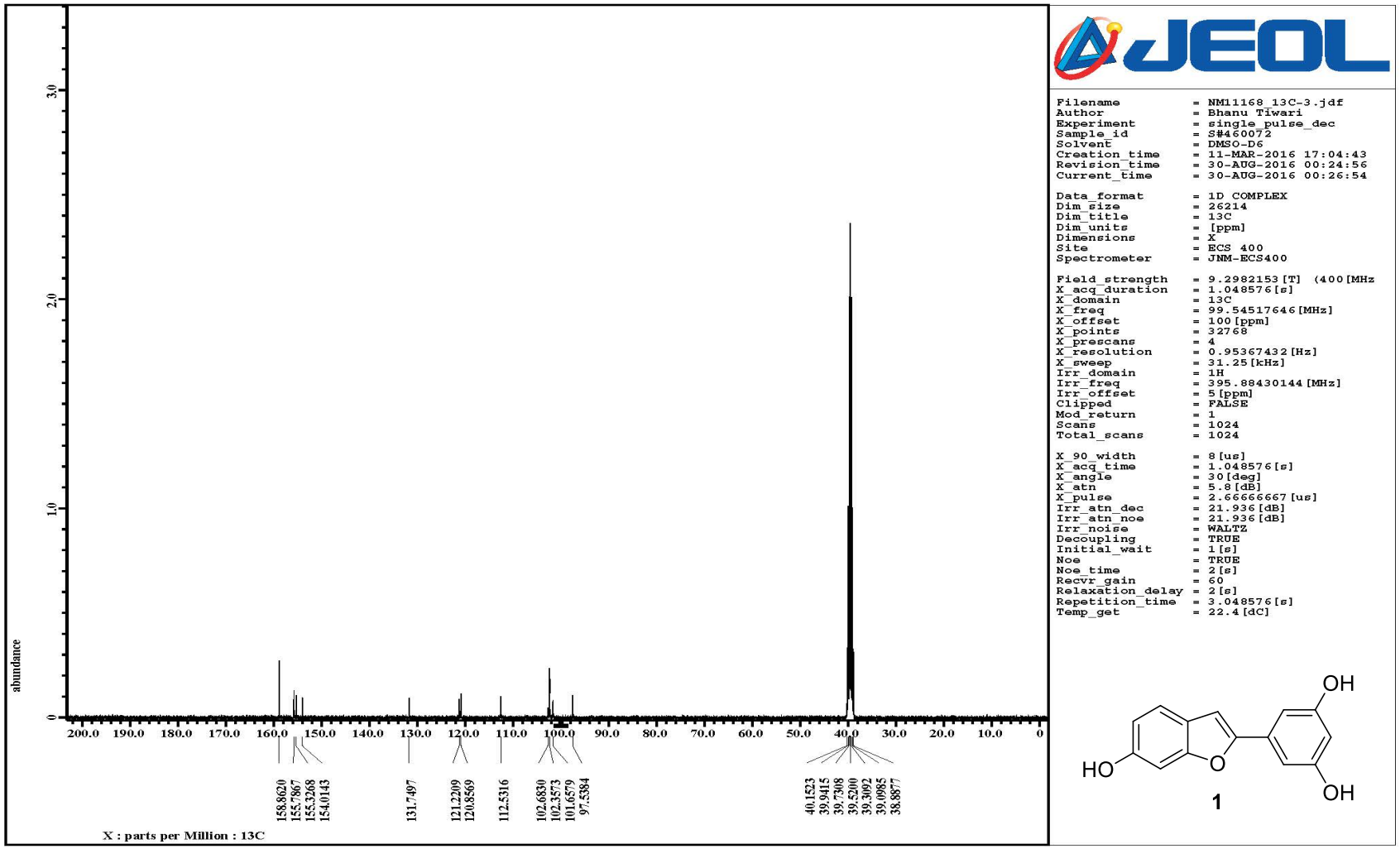
^{1}H NMR spectra of Compound **13c**



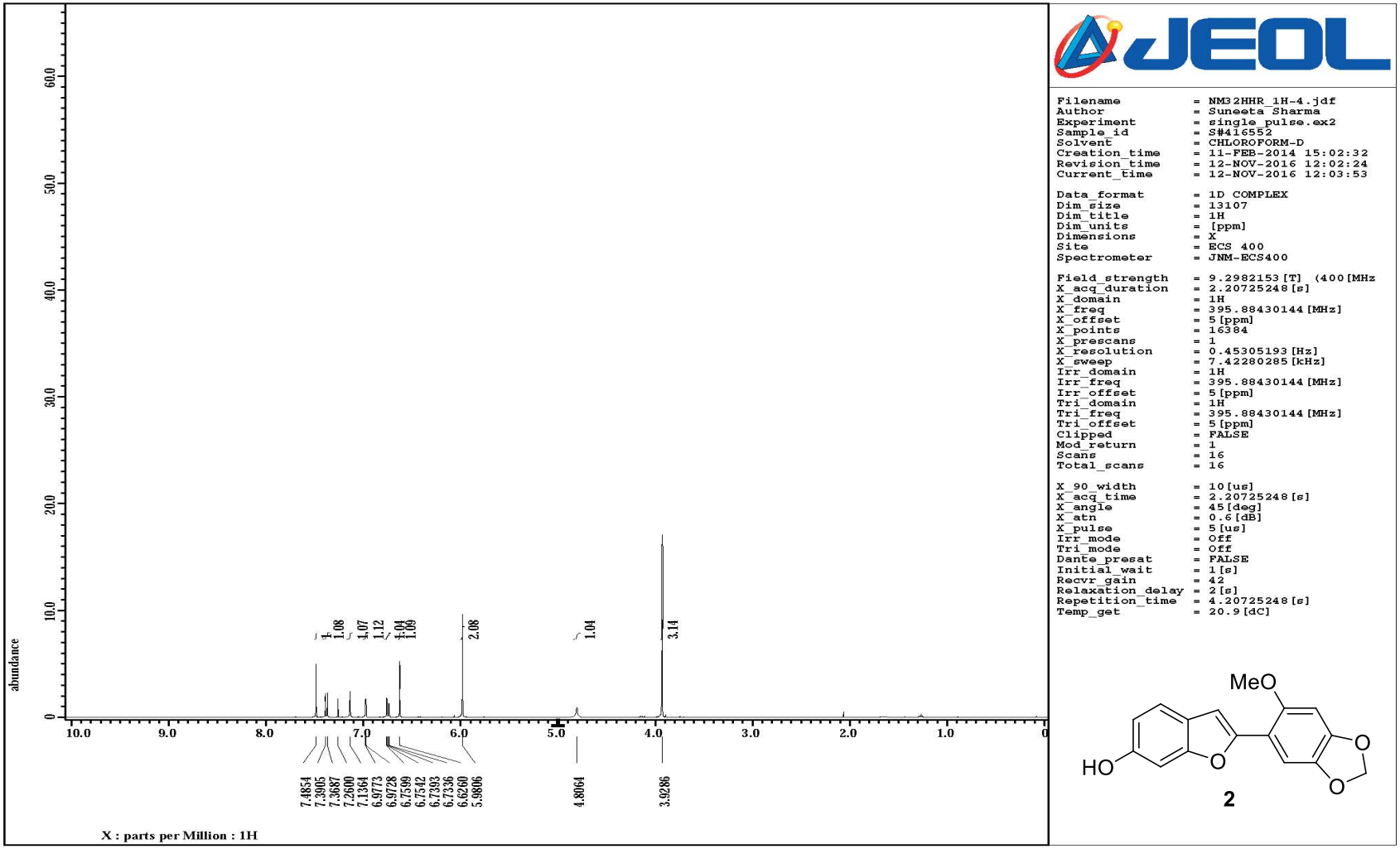
^{13}C NMR spectra of Compound **13c**



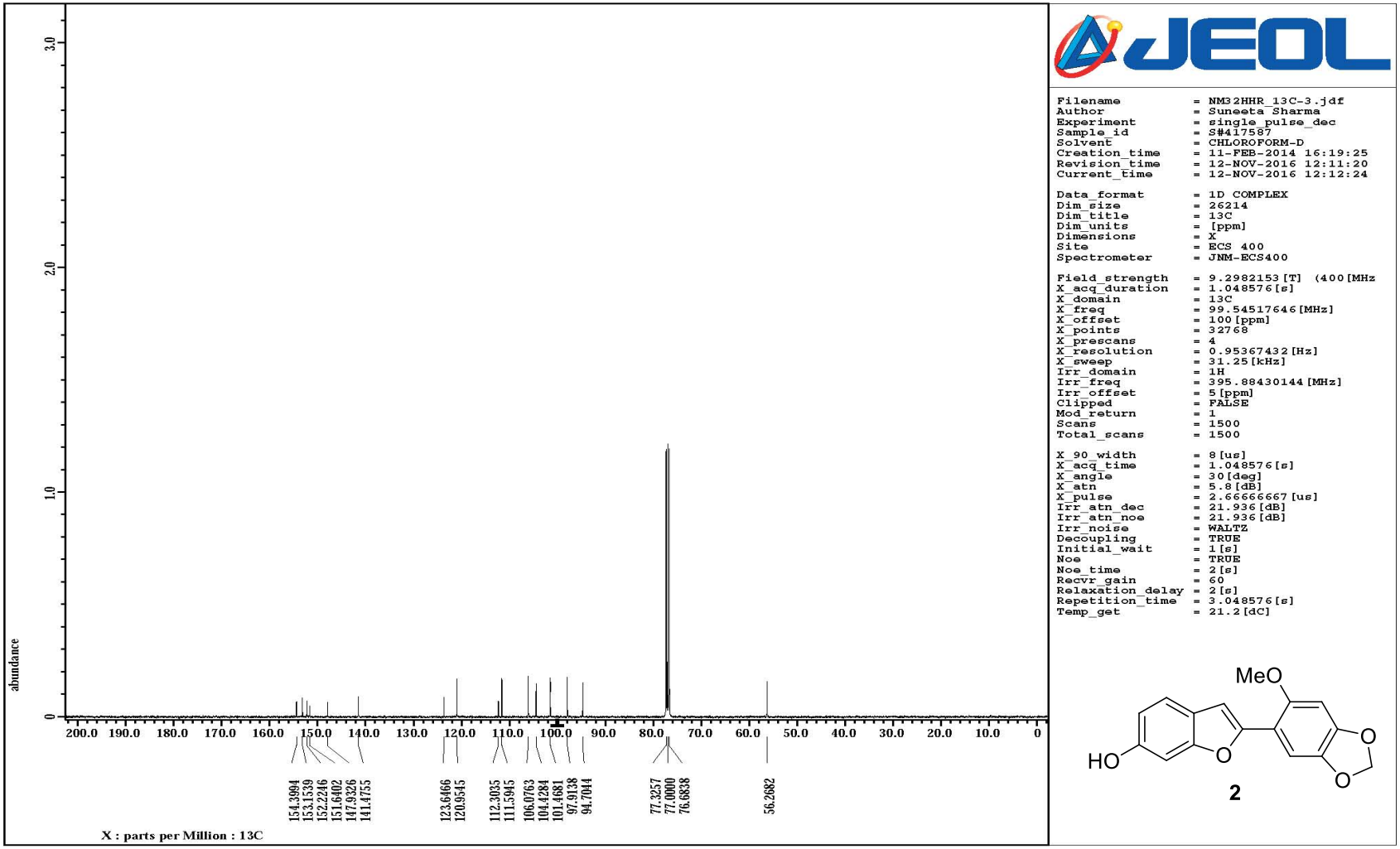
^{1}H NMR spectra of moracin M (**1**)



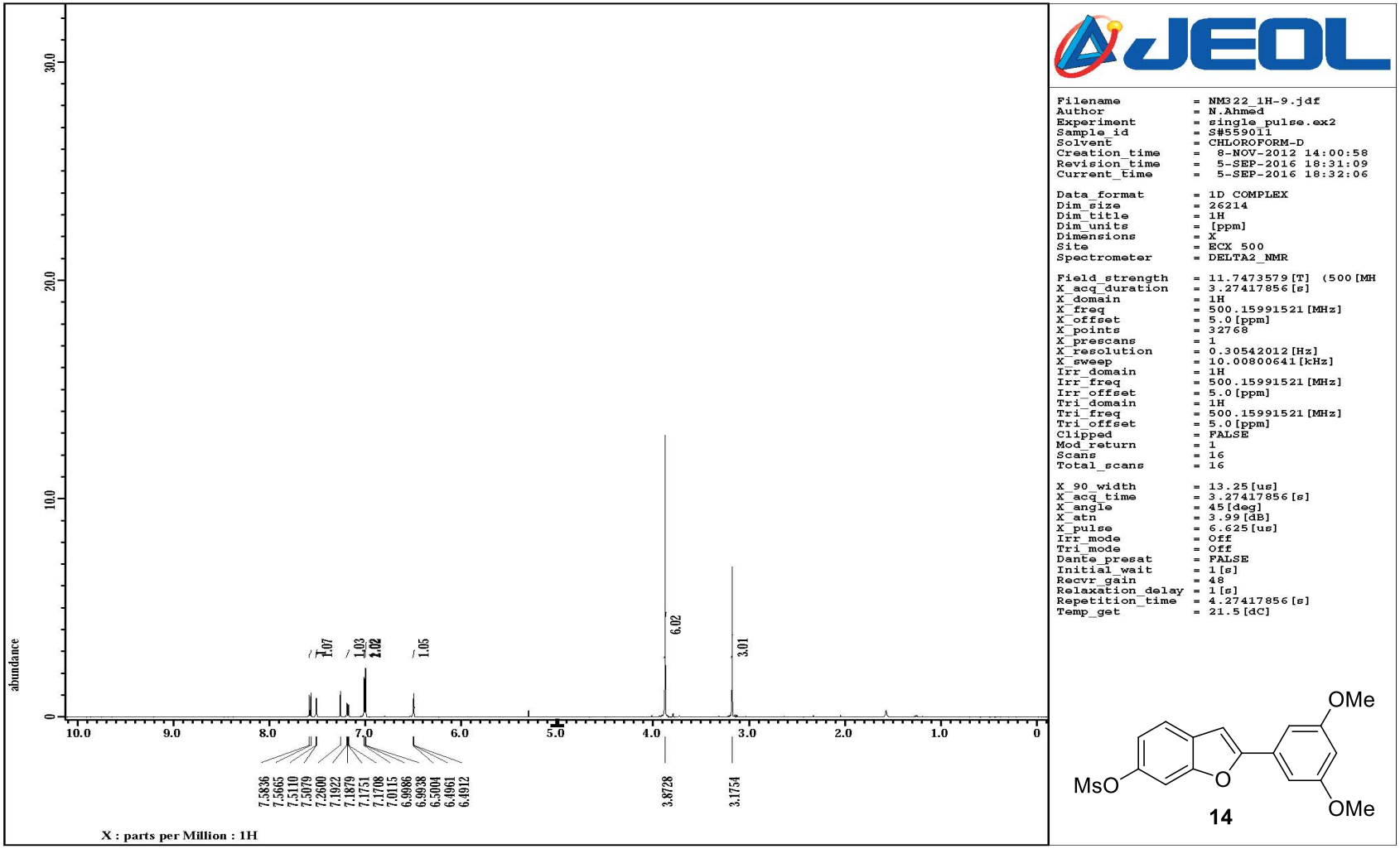
^{13}C NMR spectra of moracin M (**1**)



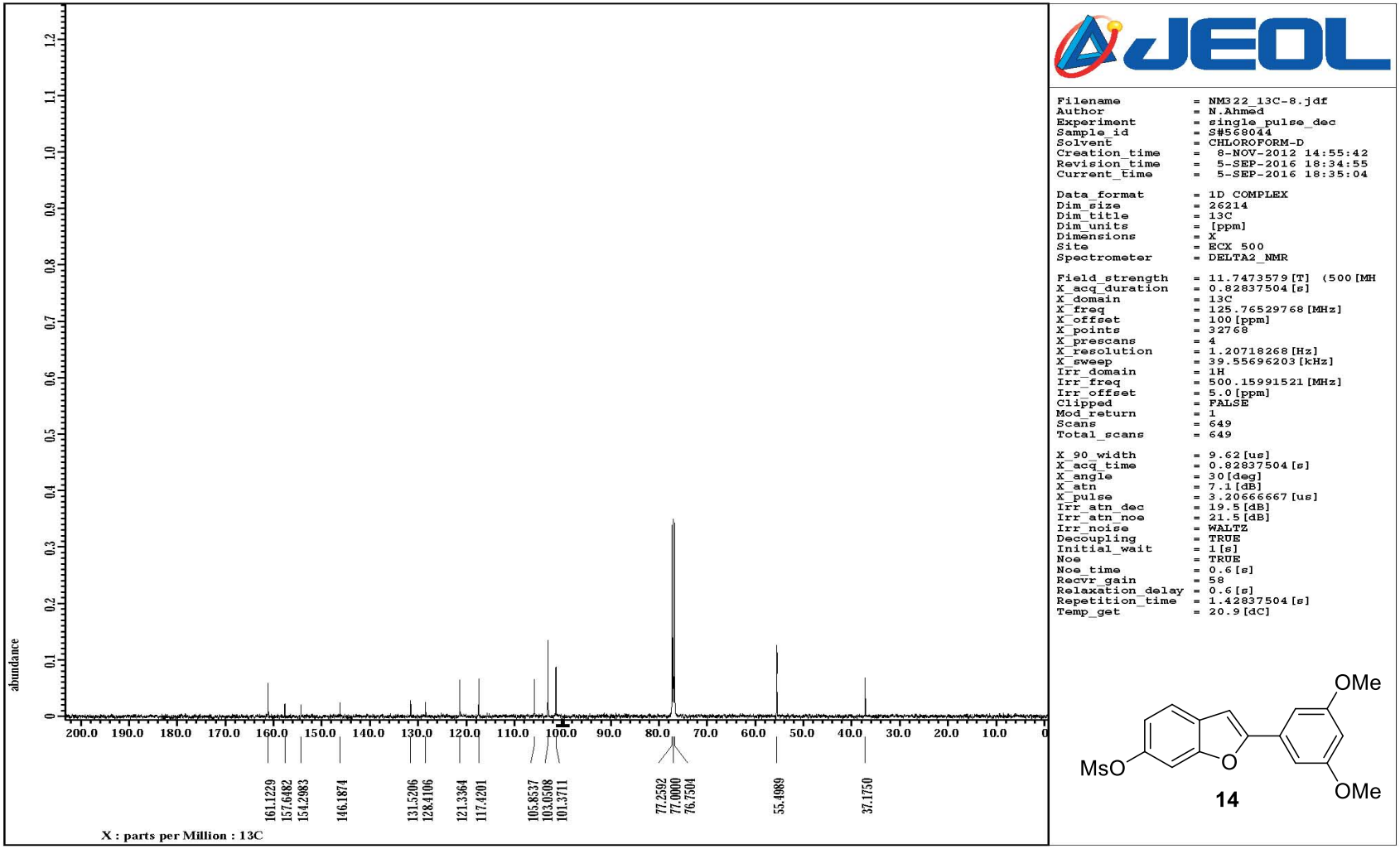
^{1}H NMR spectra of cicerfuran (**2**)



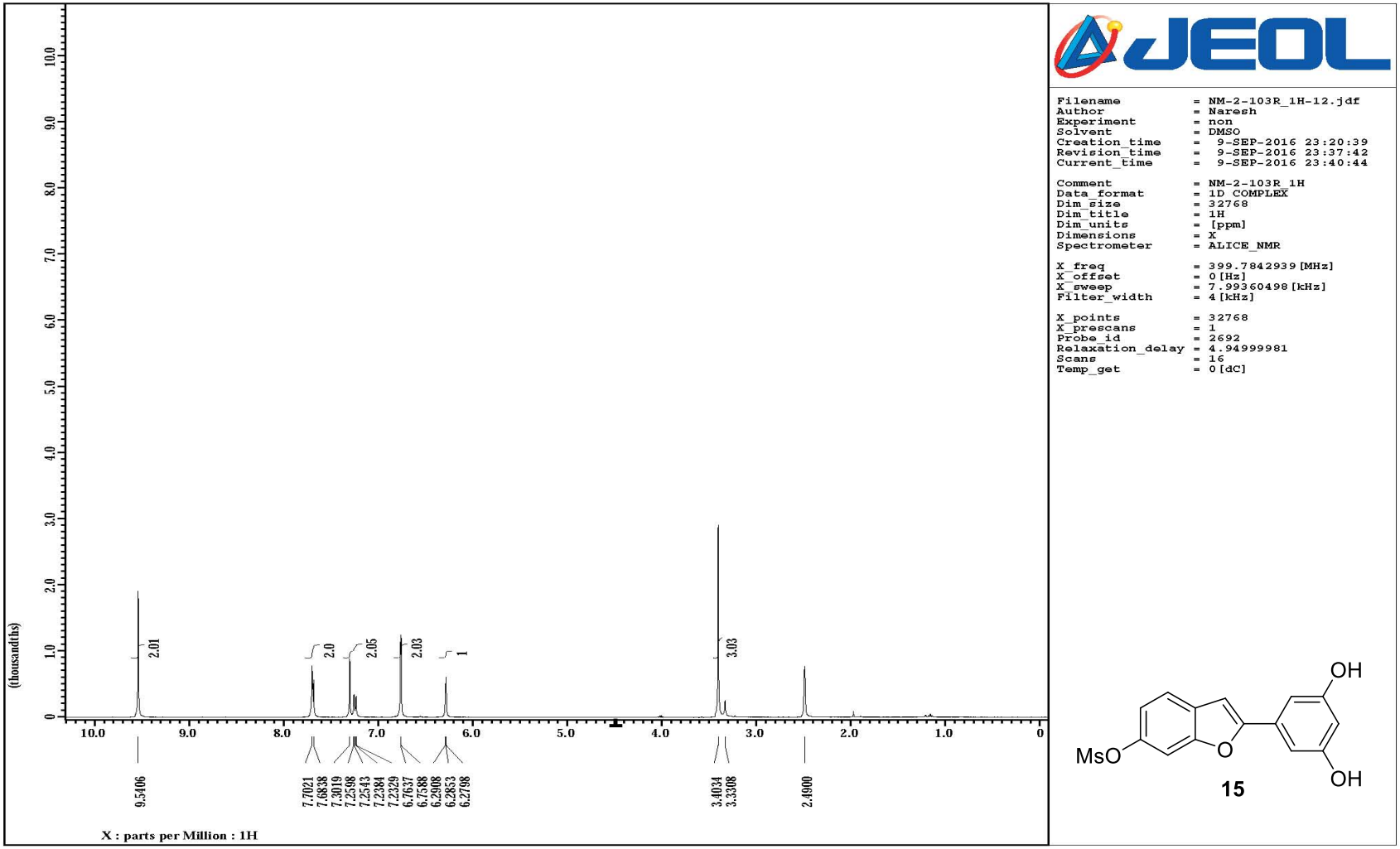
^{13}C NMR spectra of cicerfuran (**2**)



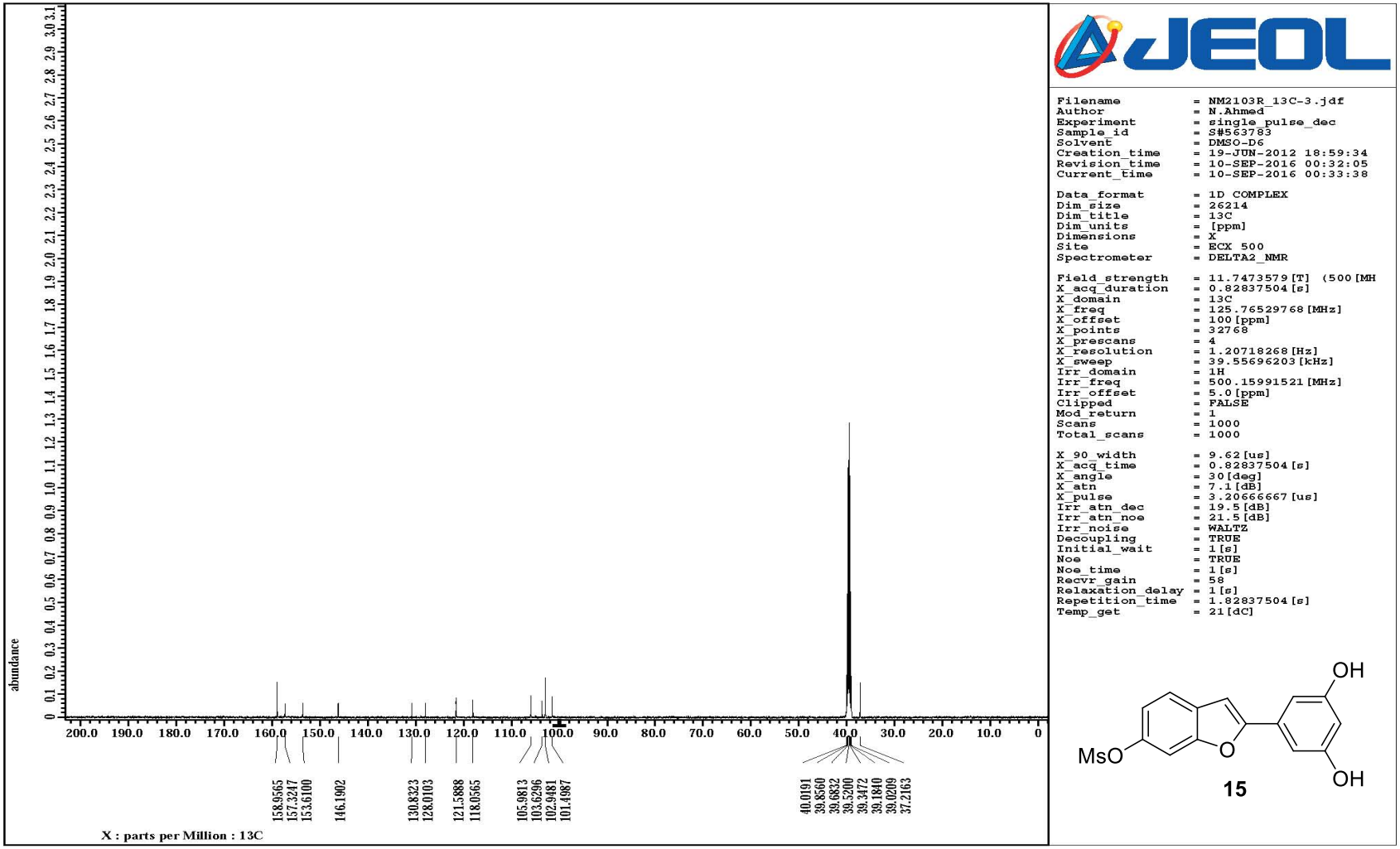
^{1}H NMR spectra of compound **14**



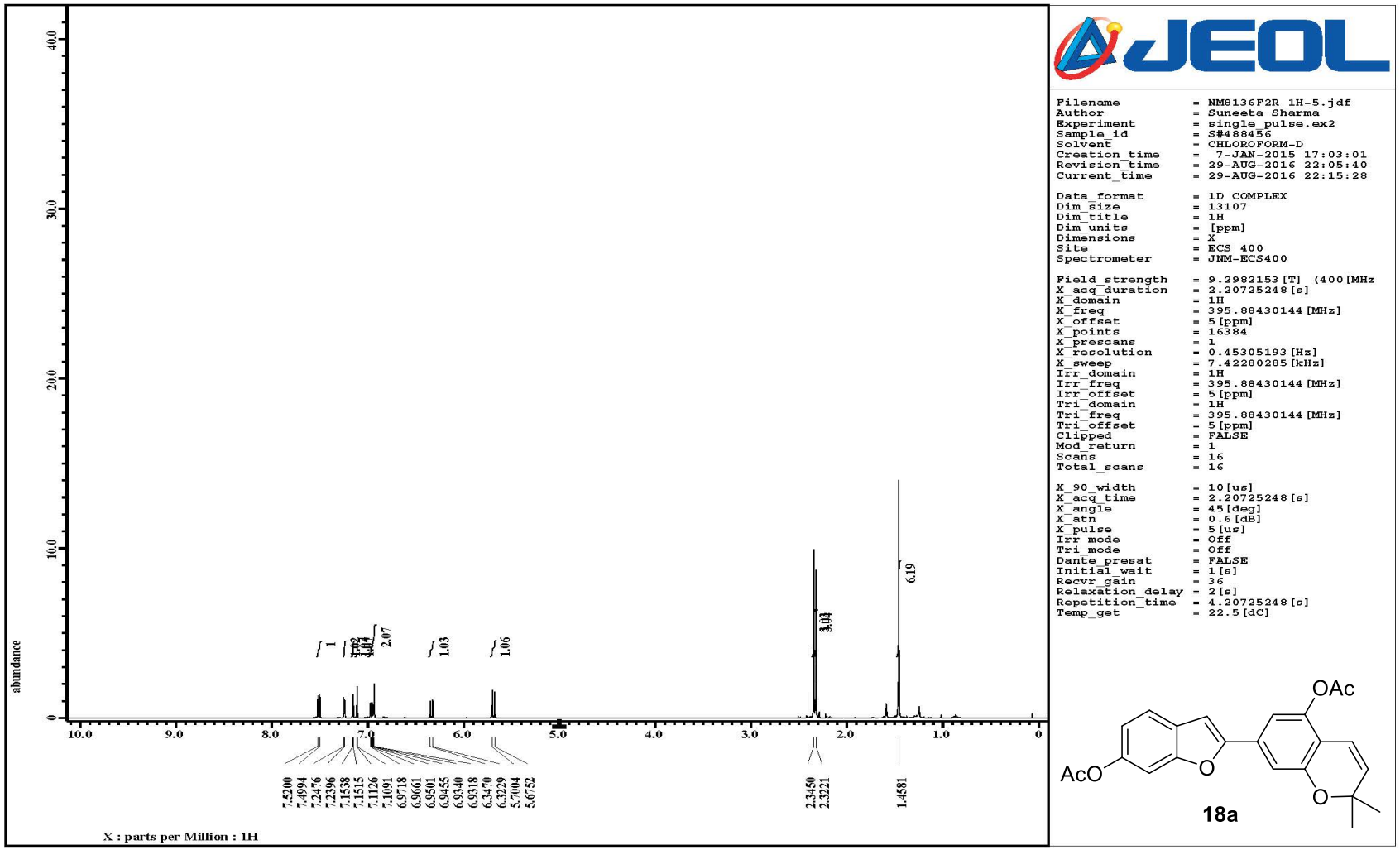
^{13}C NMR spectra of Compound **14**



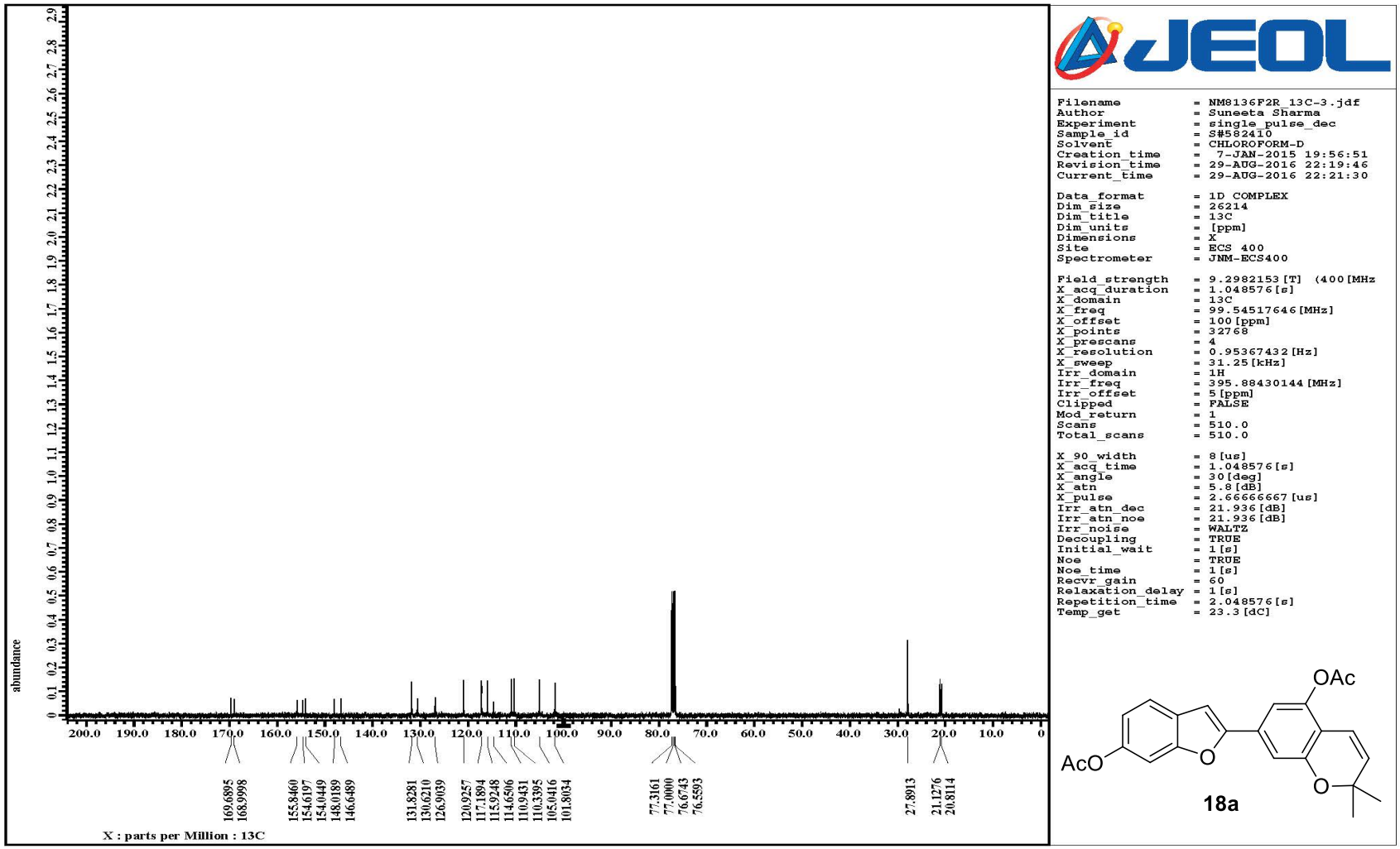
^{1}H NMR spectra of Compound **15**



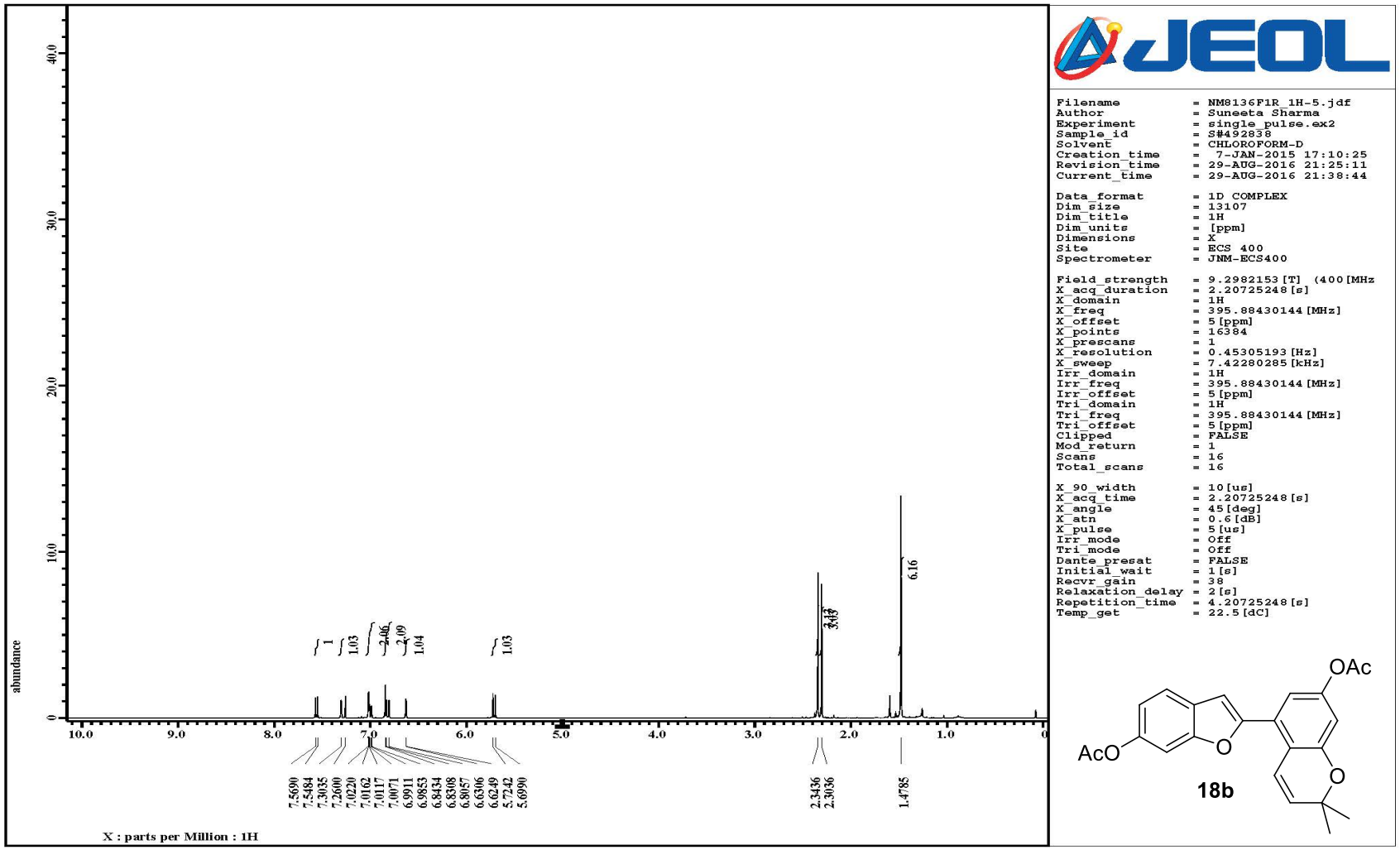
^{13}C NMR spectra of Compound **15**



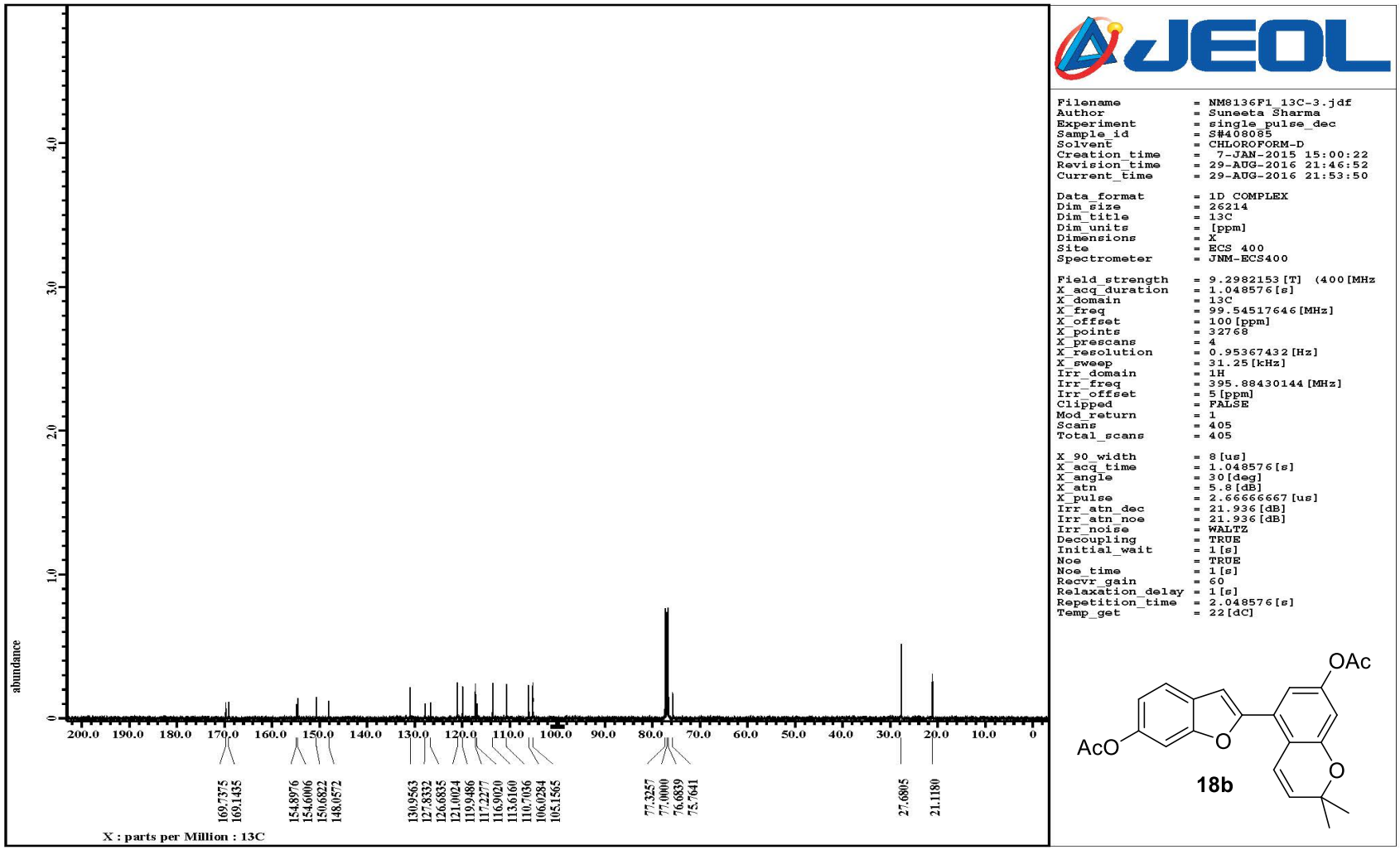
^{1}H NMR spectra of Compound **18a**



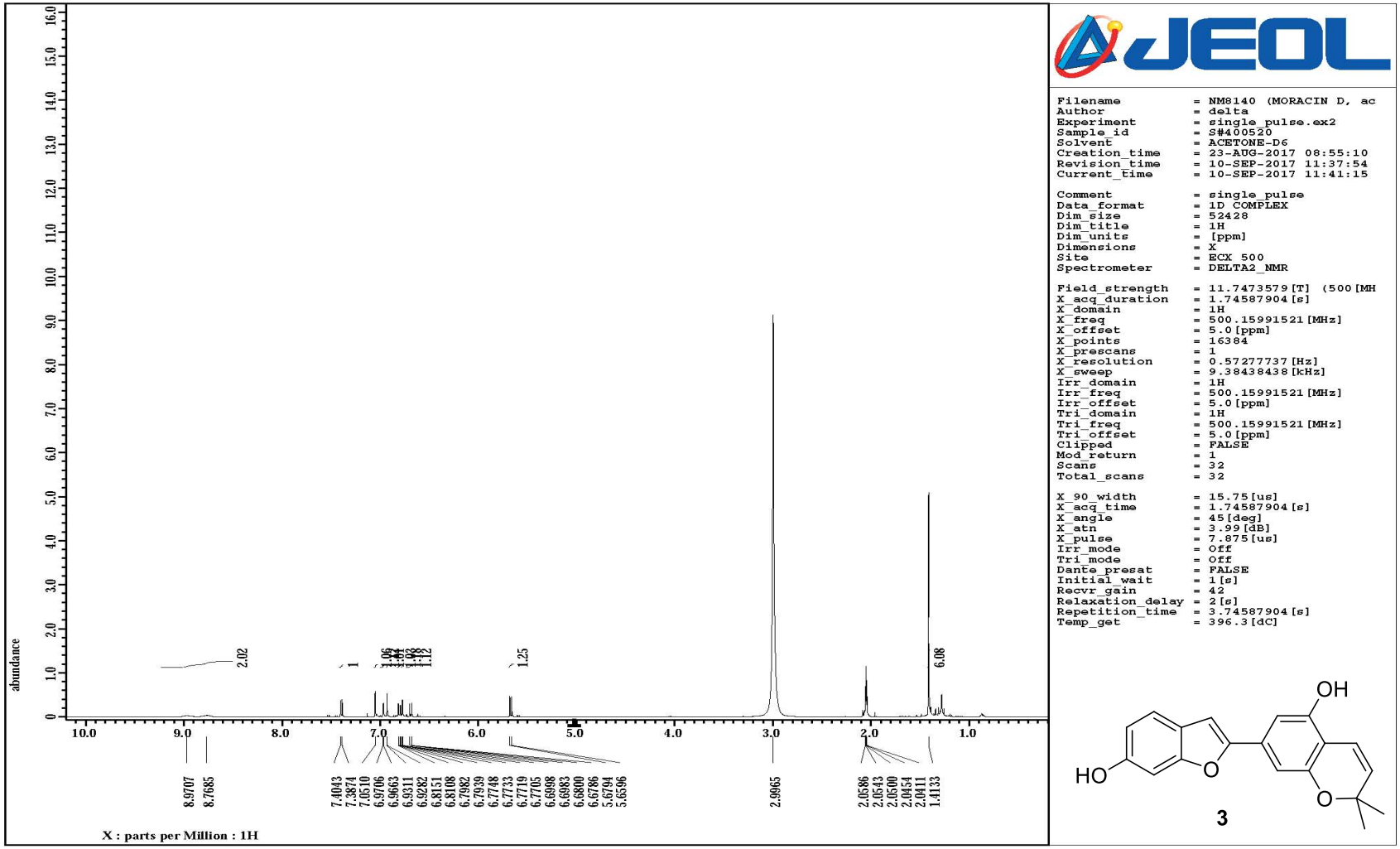
^{13}C NMR spectra of Compound **18a**



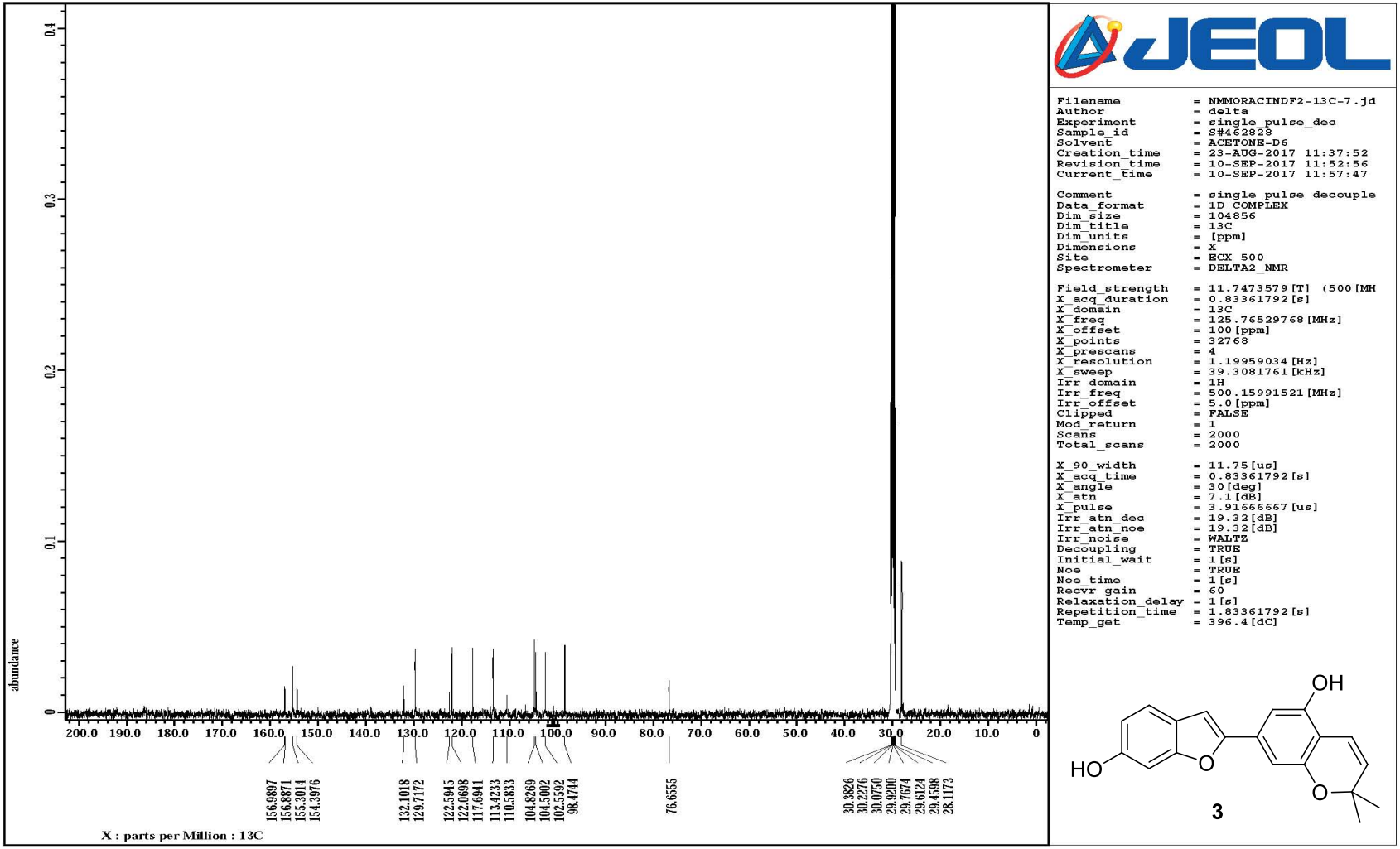
^{1}H NMR spectra of Compound **18b**



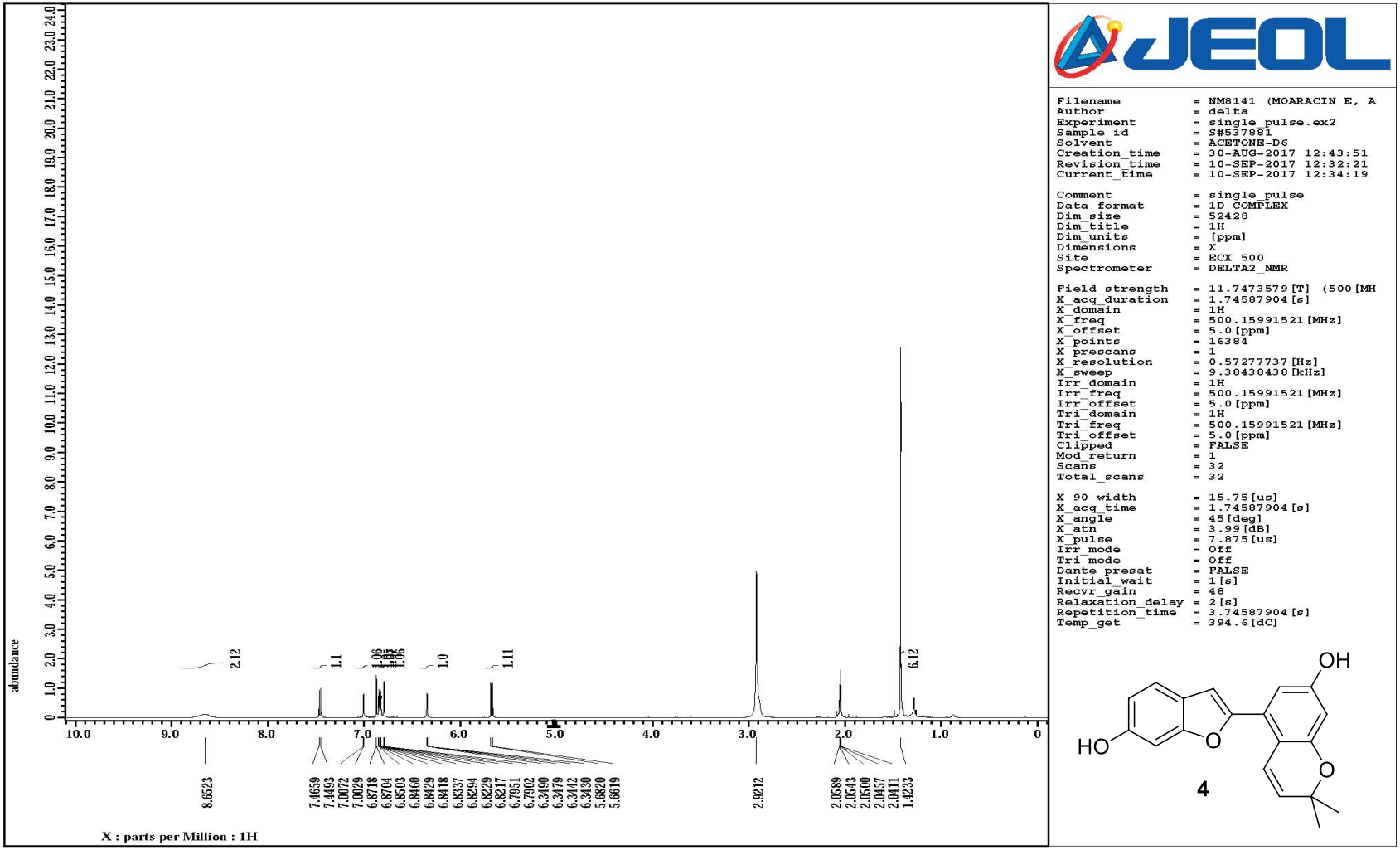
^{13}C NMR spectra of Compound **18b**



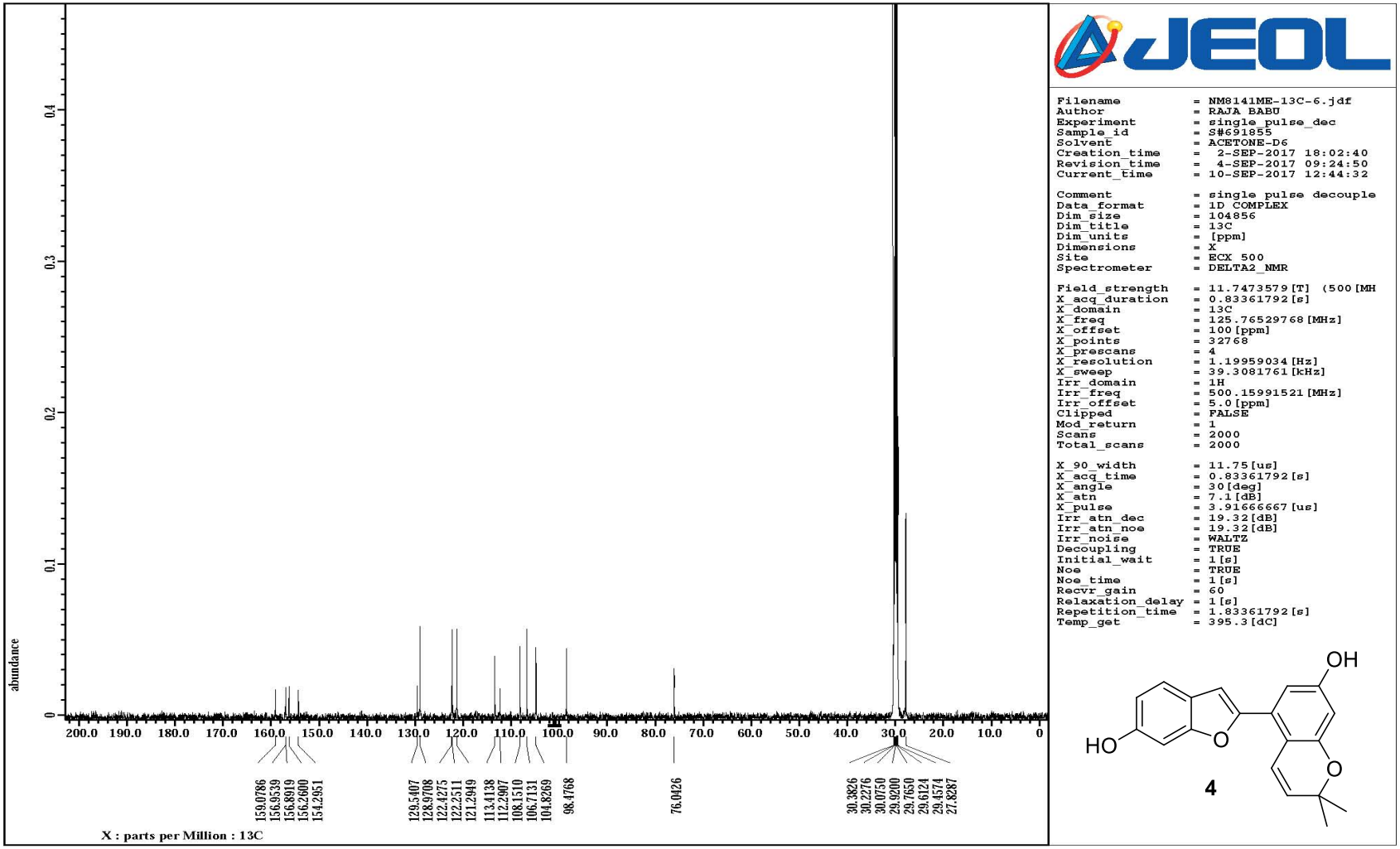
^{1}H NMR spectra of moracin D (**3**)



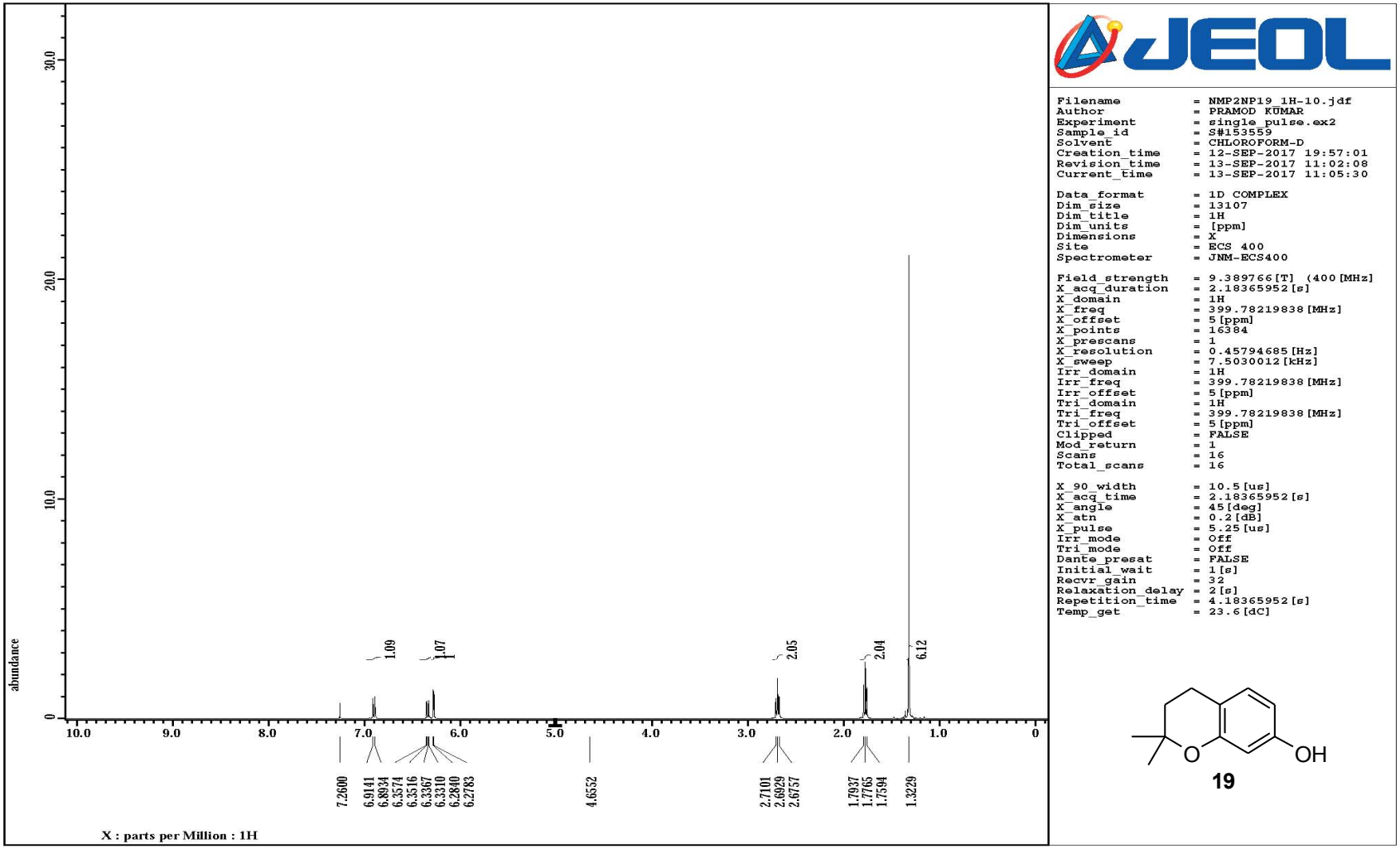
^{13}C NMR spectra of moracin D (**3**)



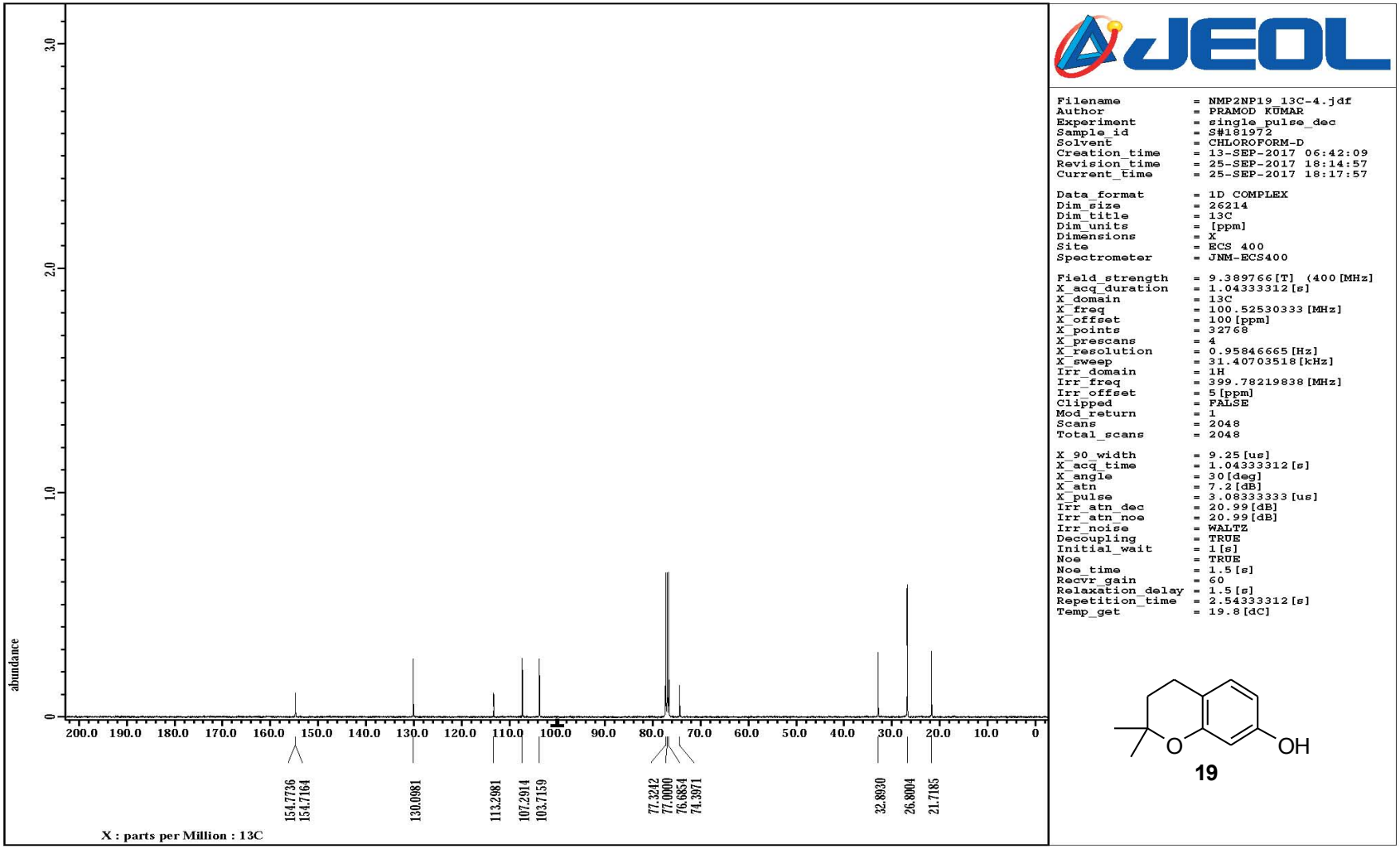
^{1}H NMR spectra of moracin E (**4**)



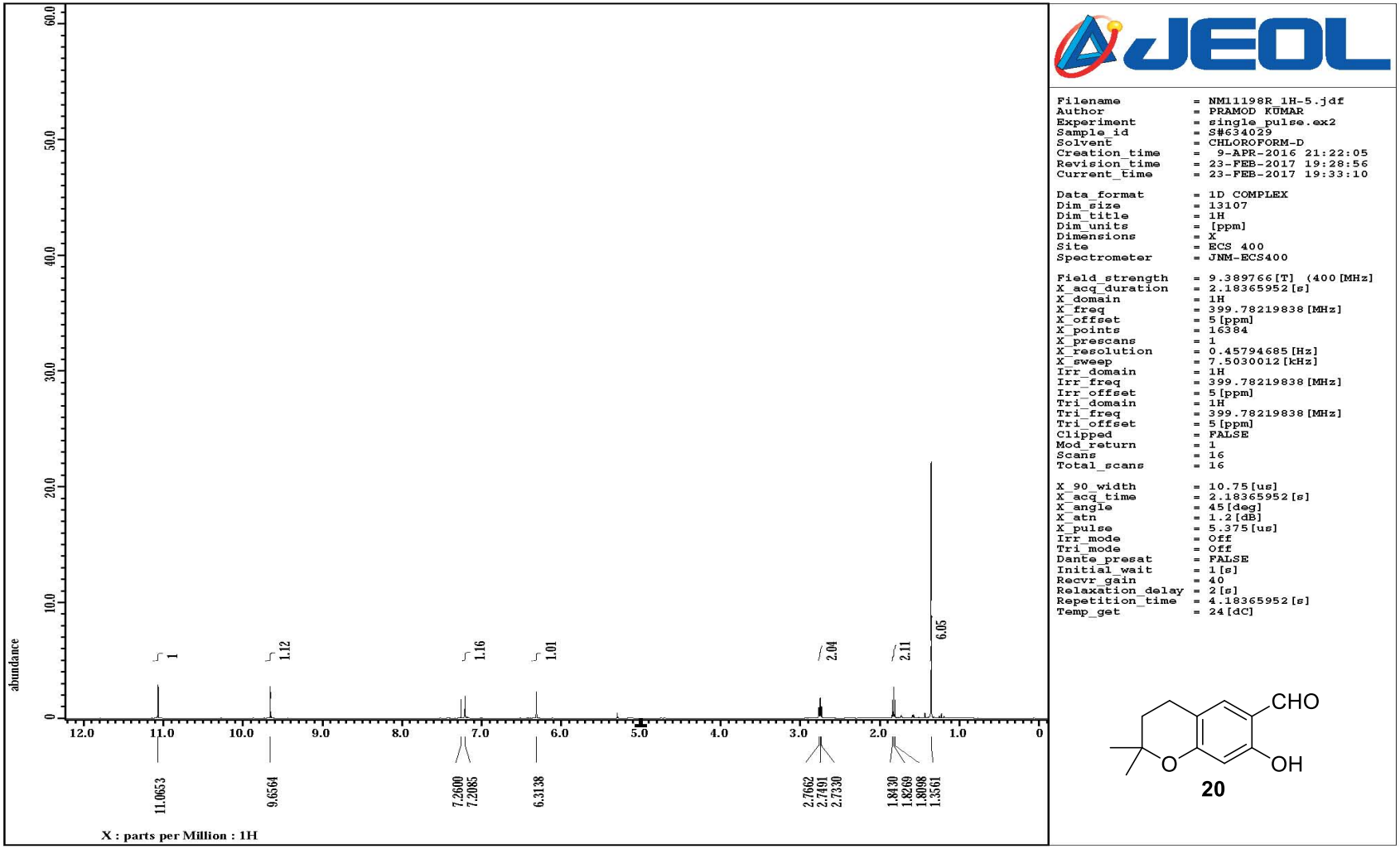
^{13}C NMR spectra of moracin E (**4**)



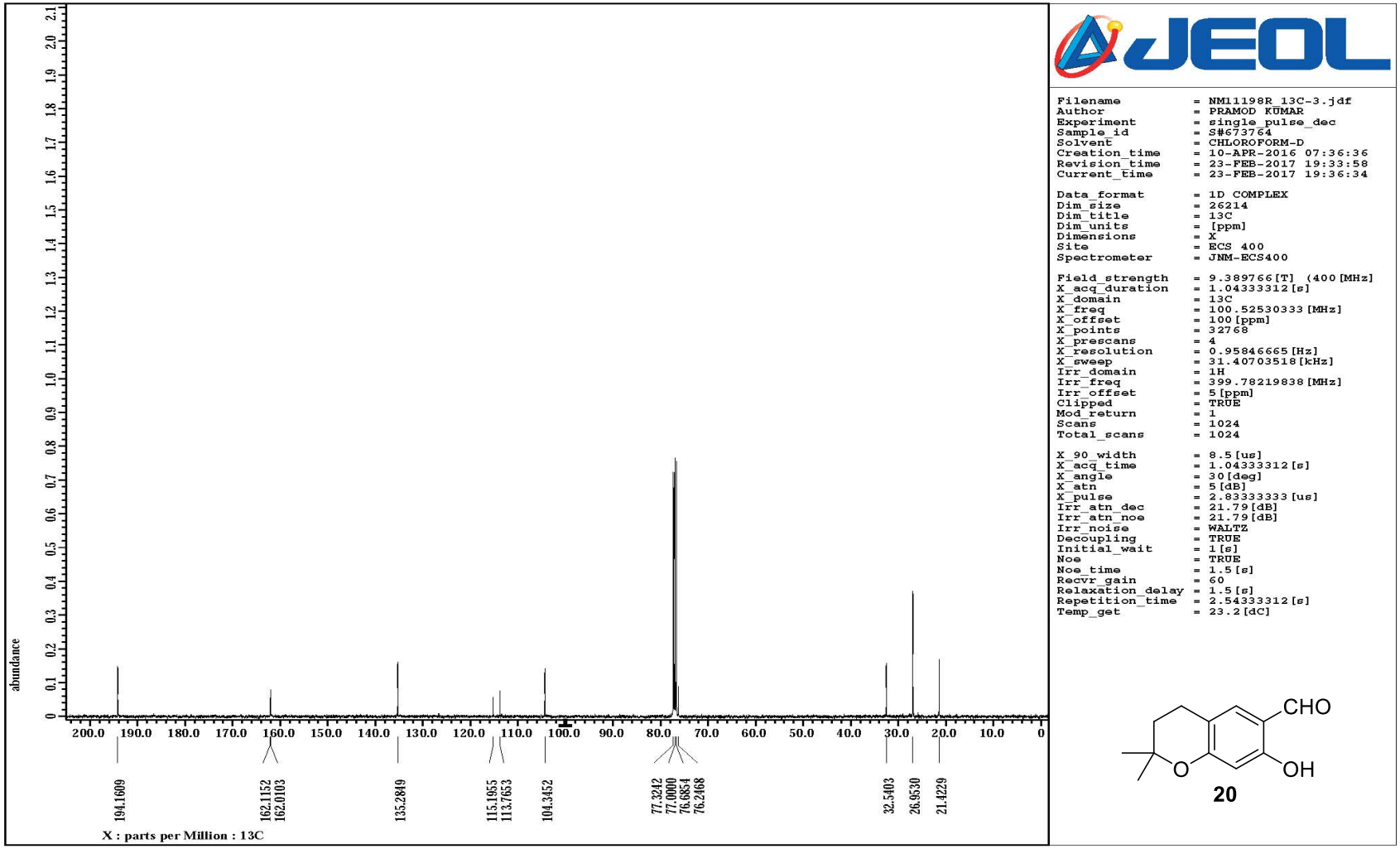
^{1}H NMR spectrum of Compound **19**



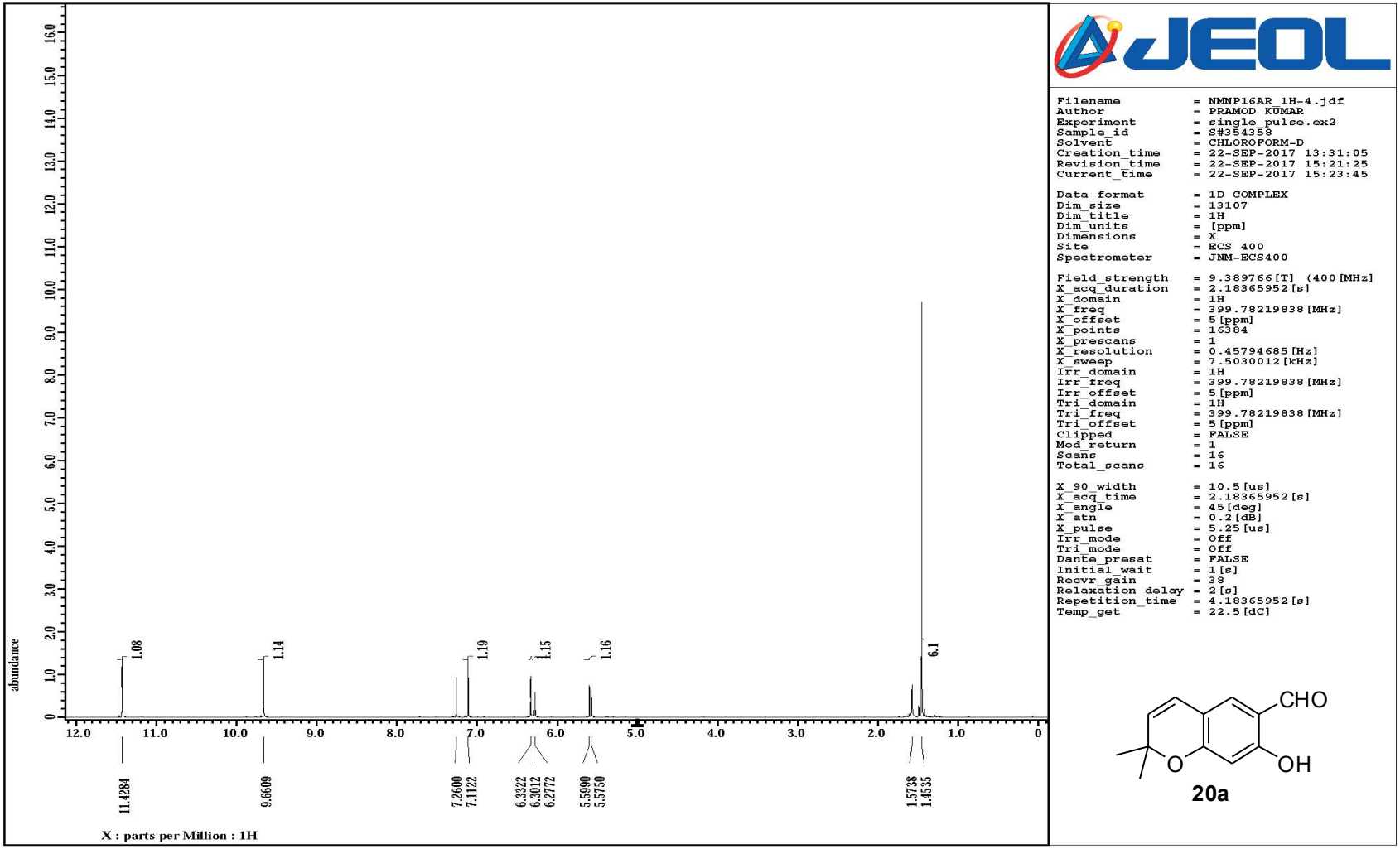
^{13}C NMR spectrum of Compound **19**



^{1}H NMR spectra of Compound **20**



^{13}C NMR spectra of Compound **20**



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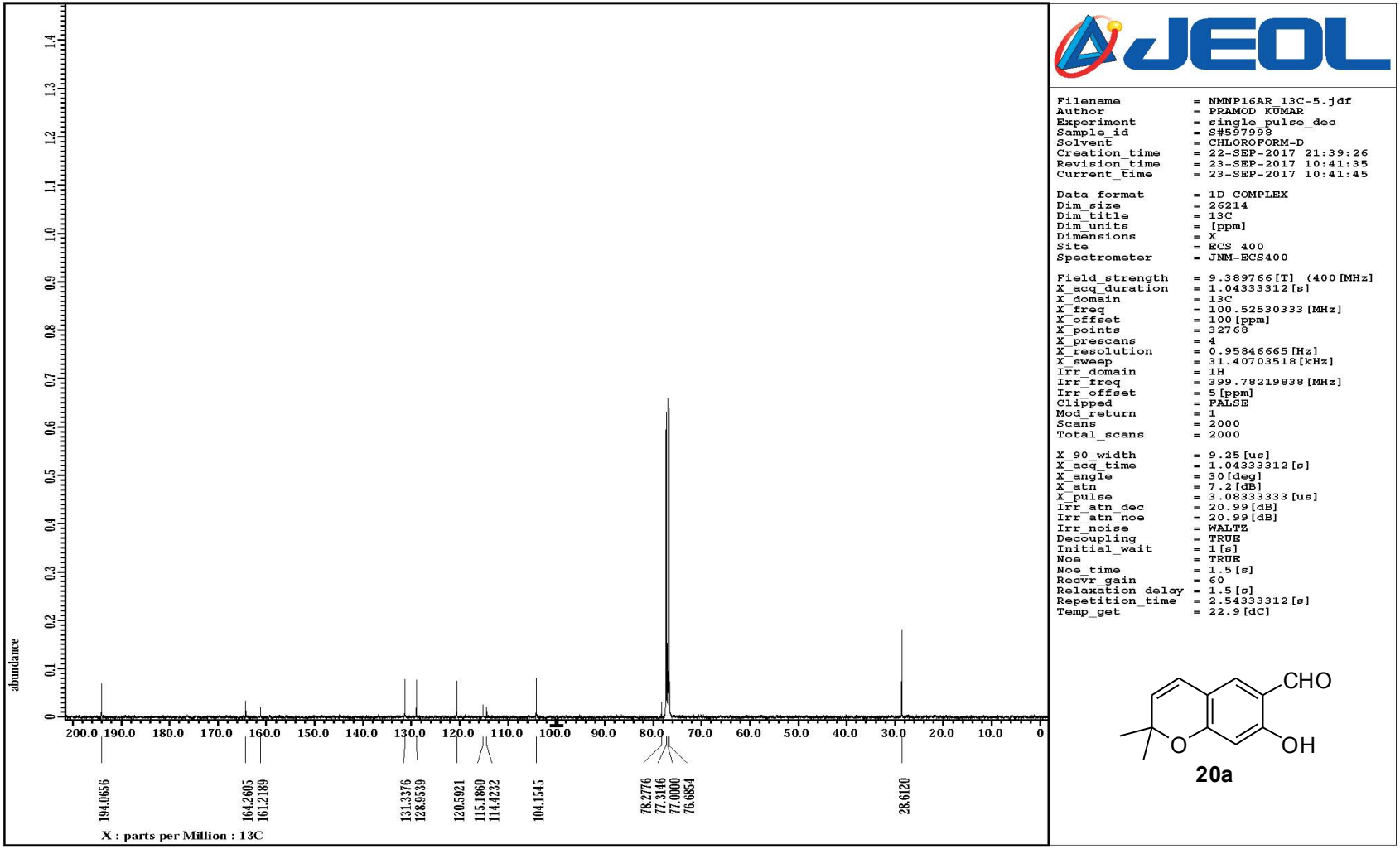

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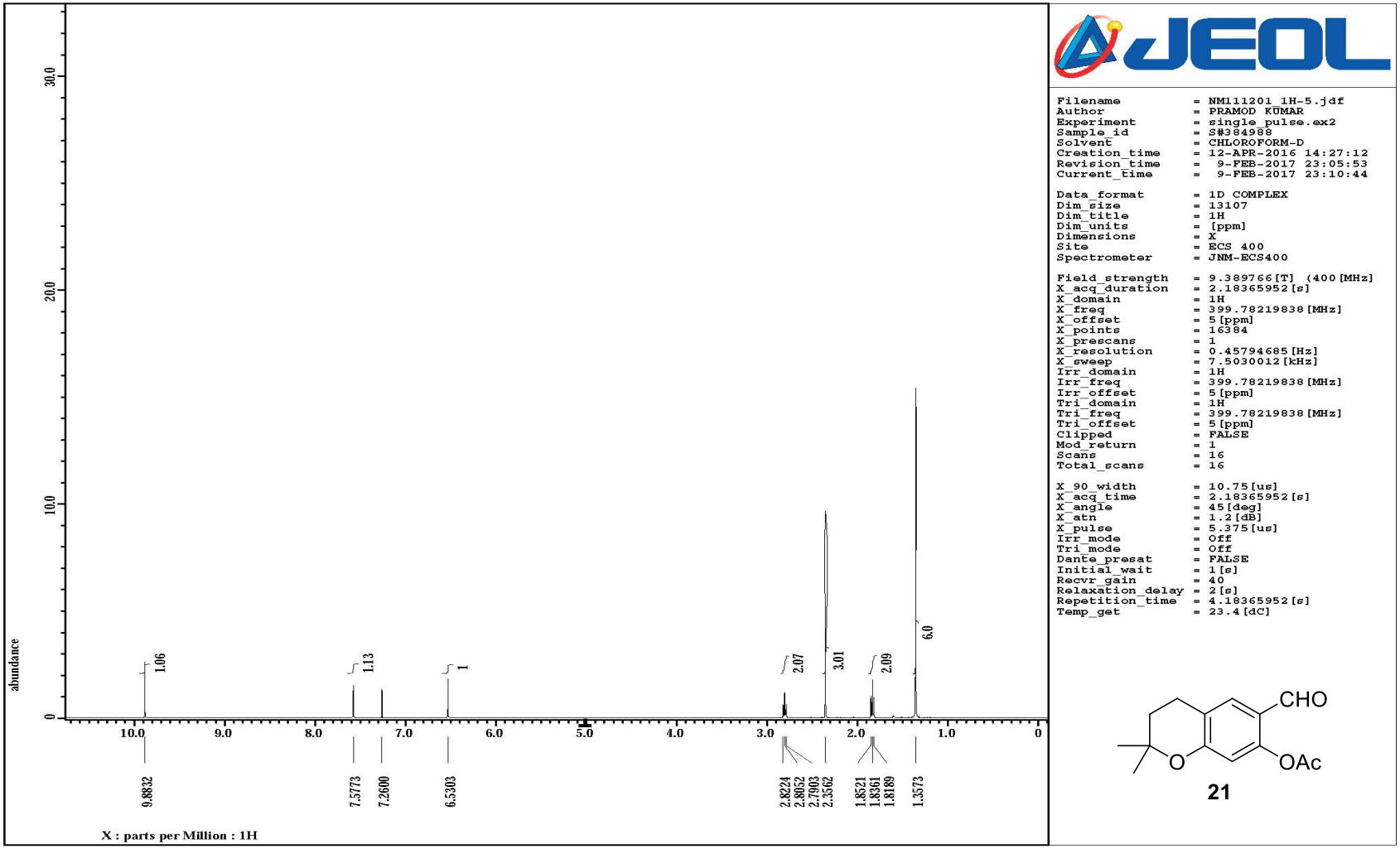
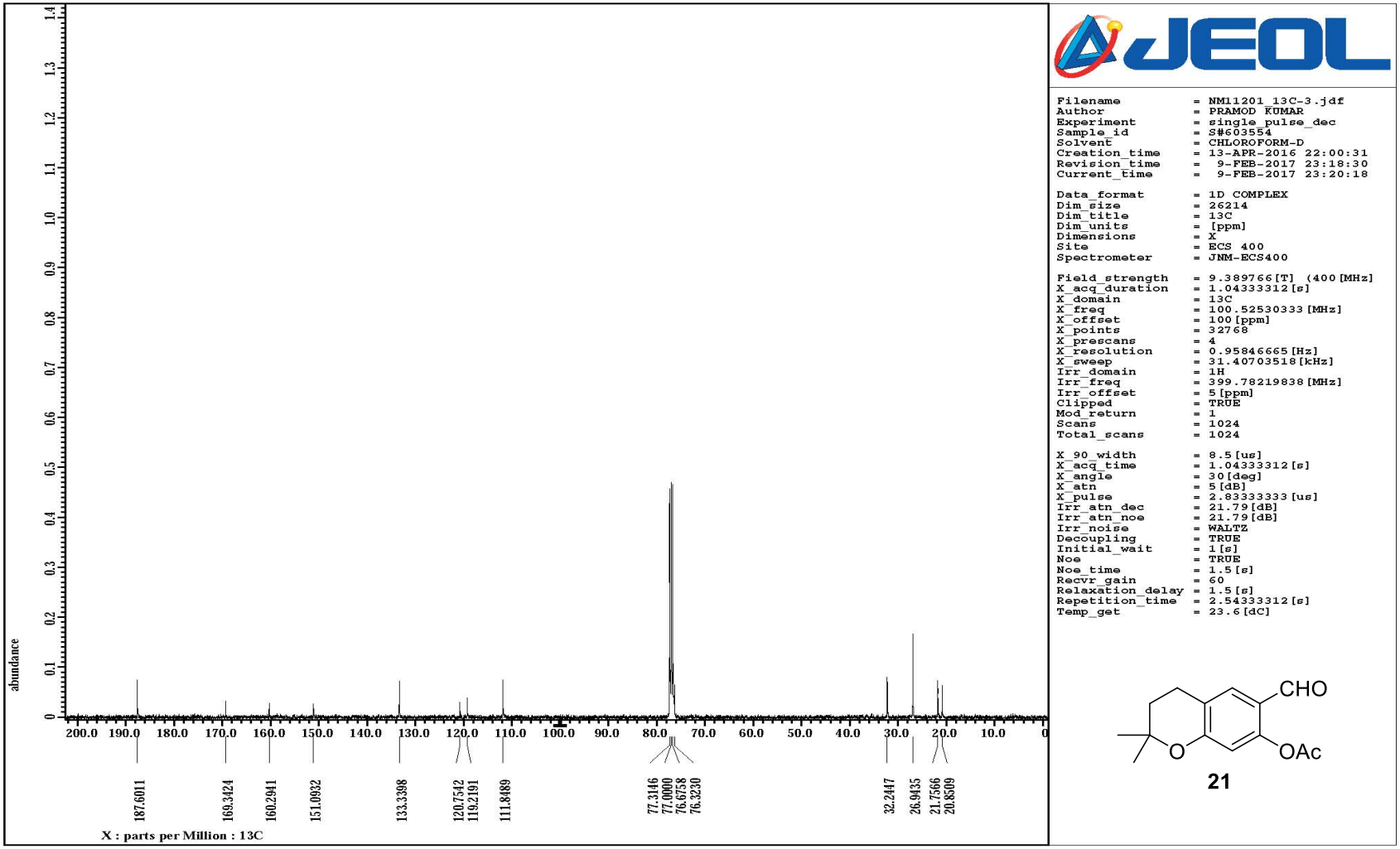
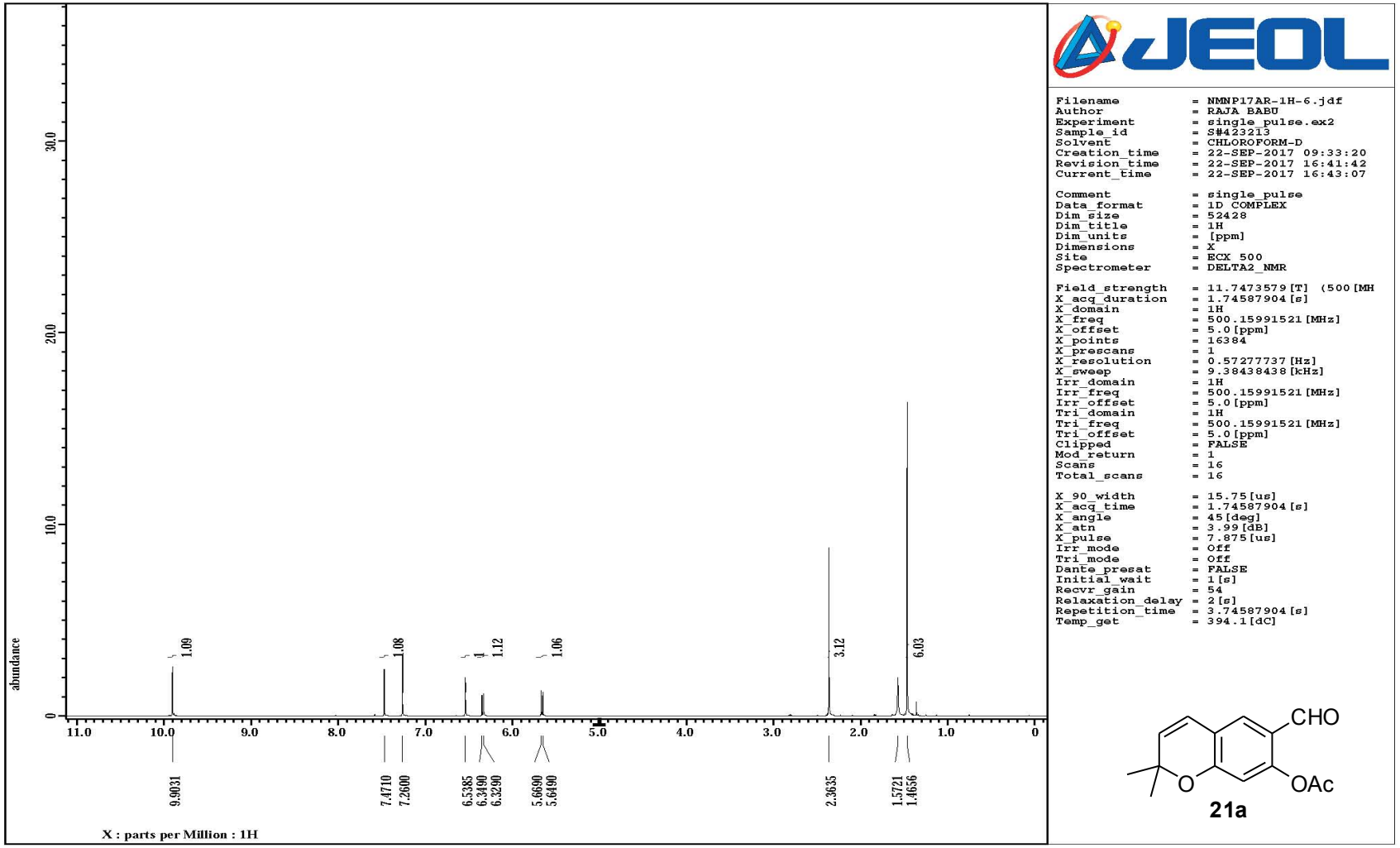


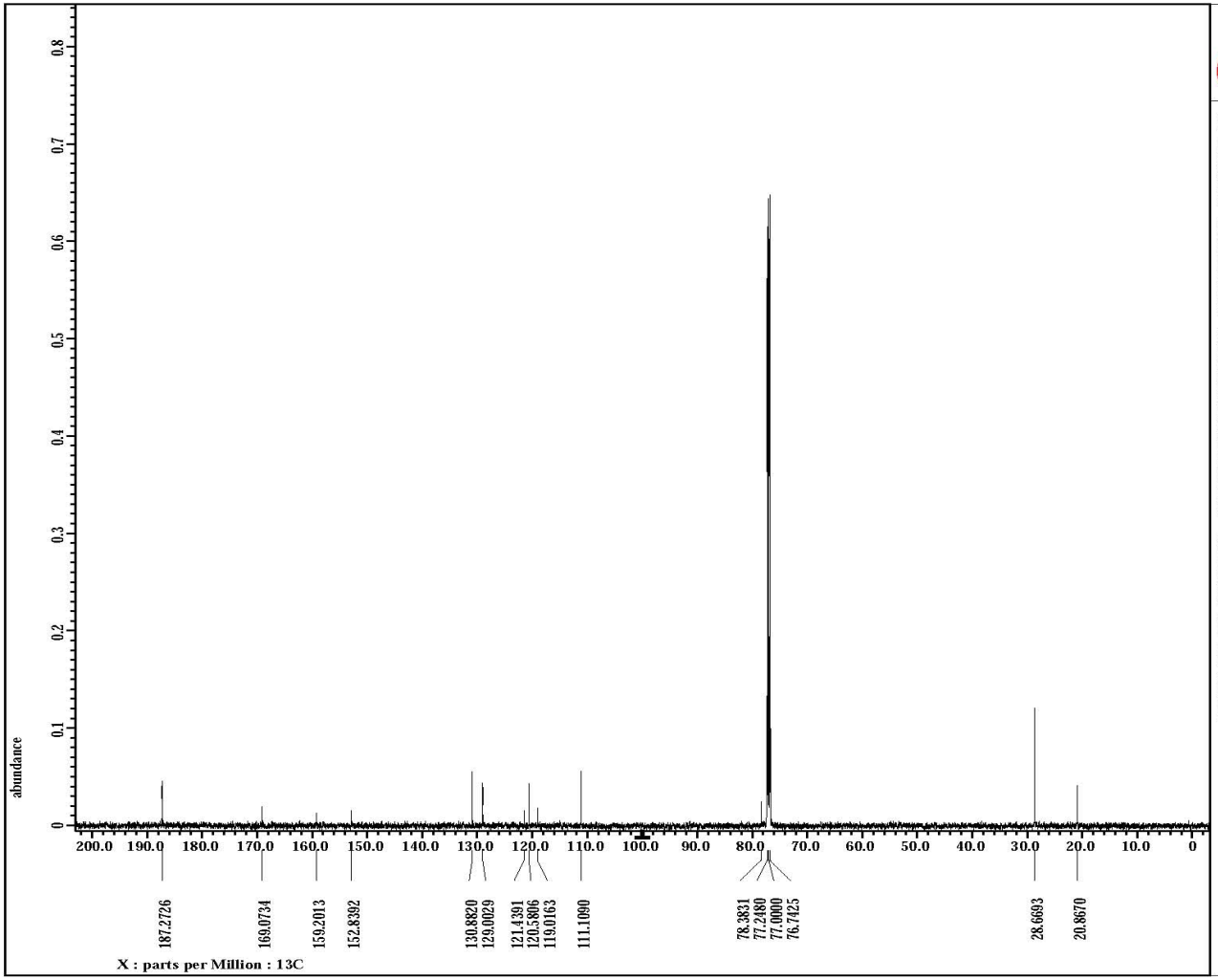
^{1}H NMR spectra of Compound **21**

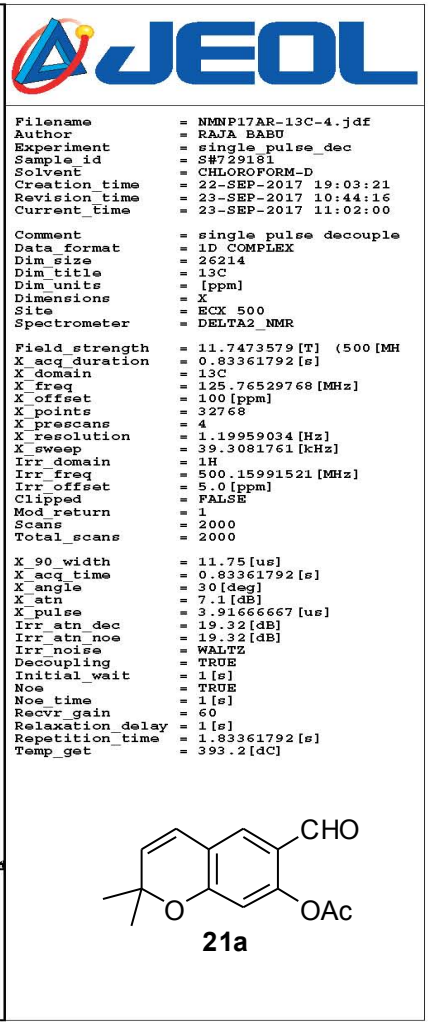


^{13}C NMR spectra of Compound **21**



^{1}H NMR spectrum of Compound **21a**





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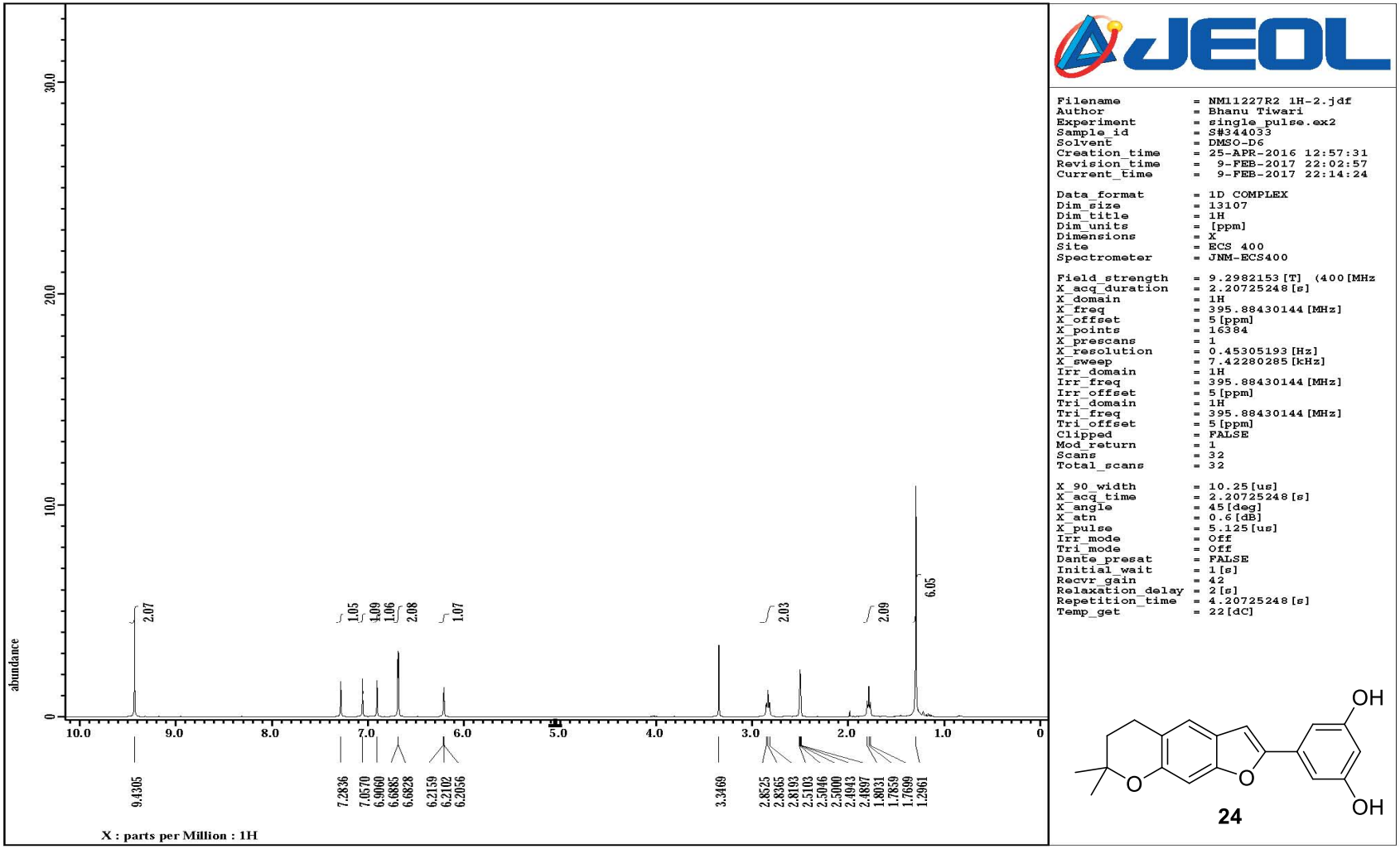

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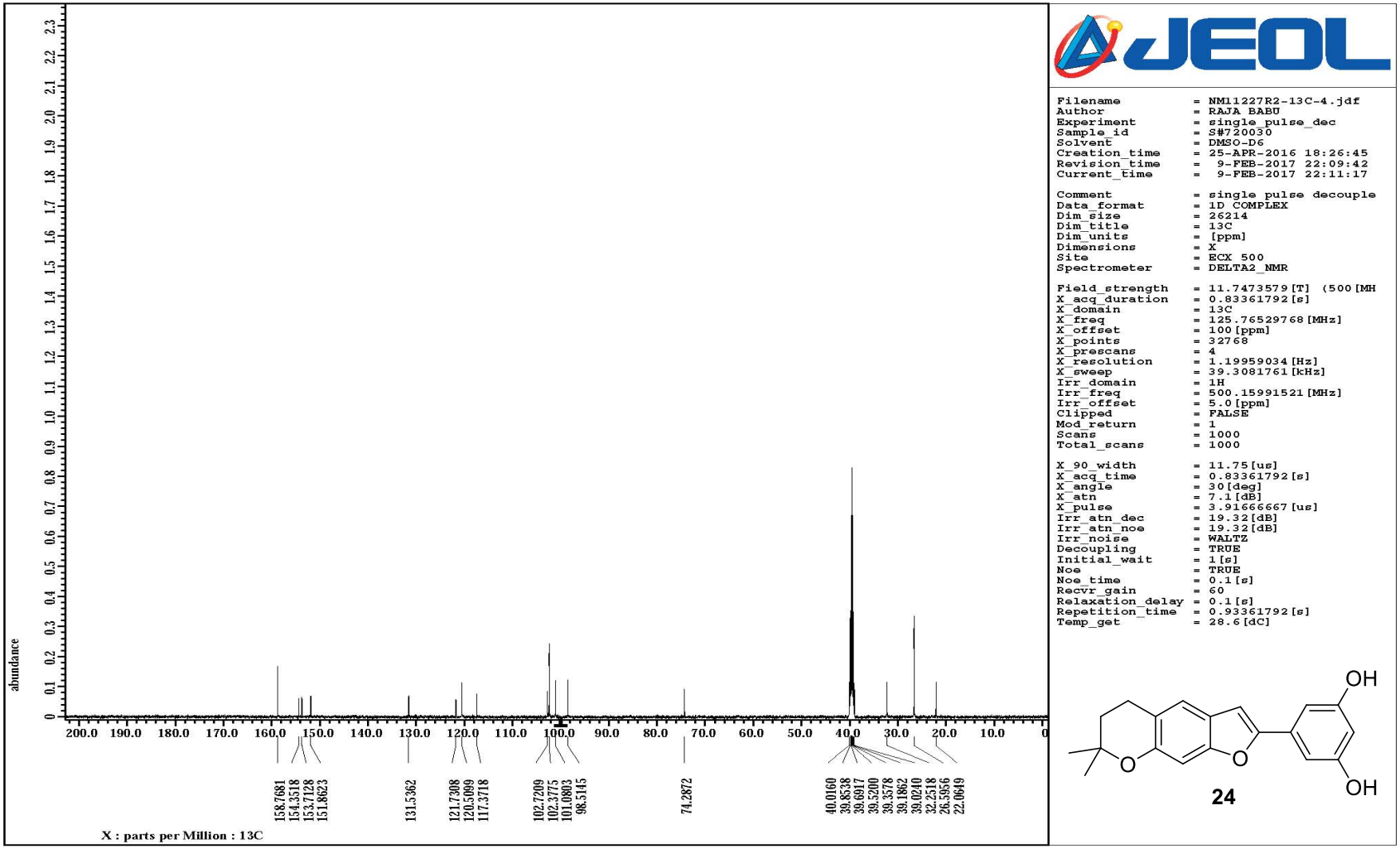
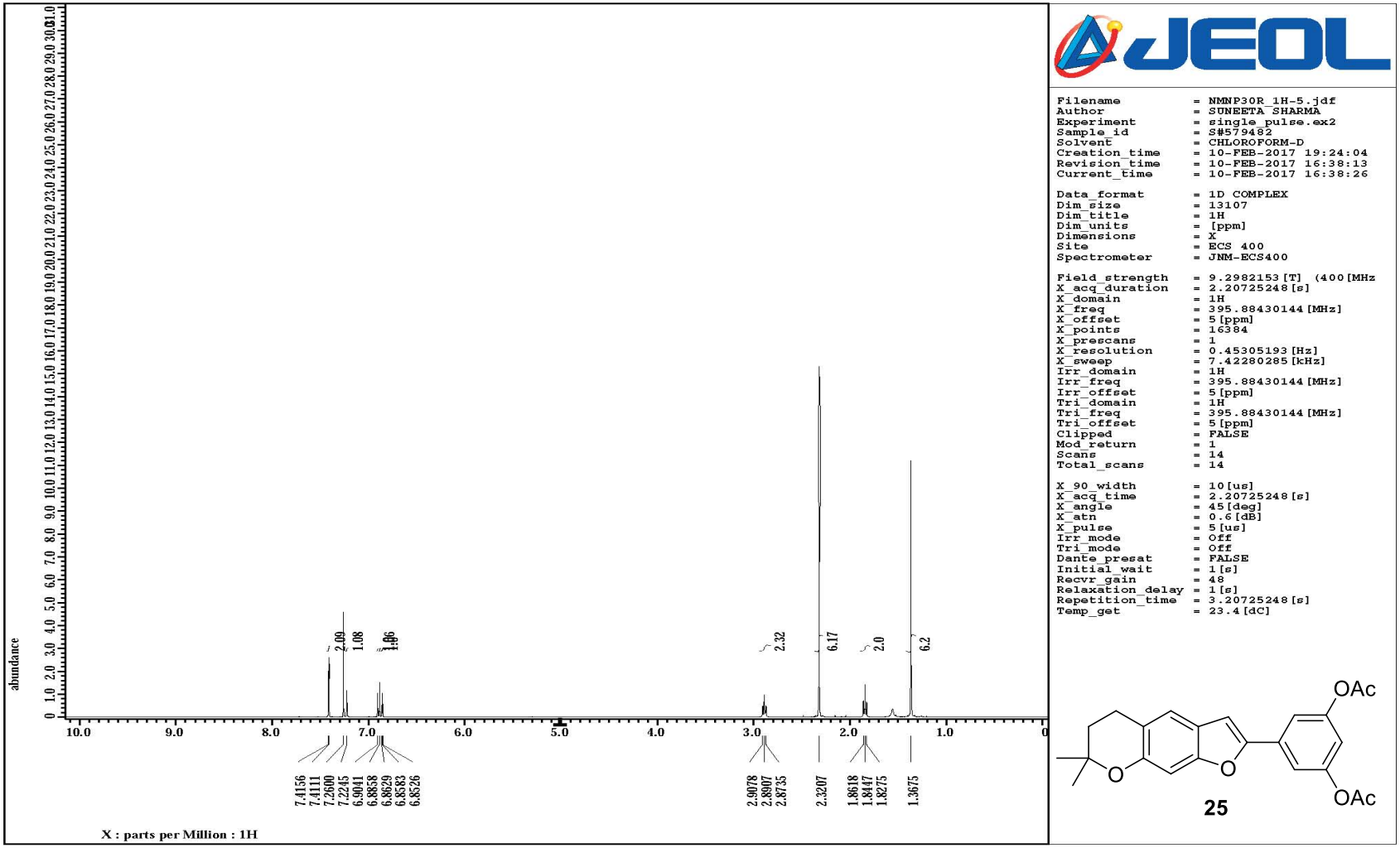


^{13}C NMR spectra of Compound **24**



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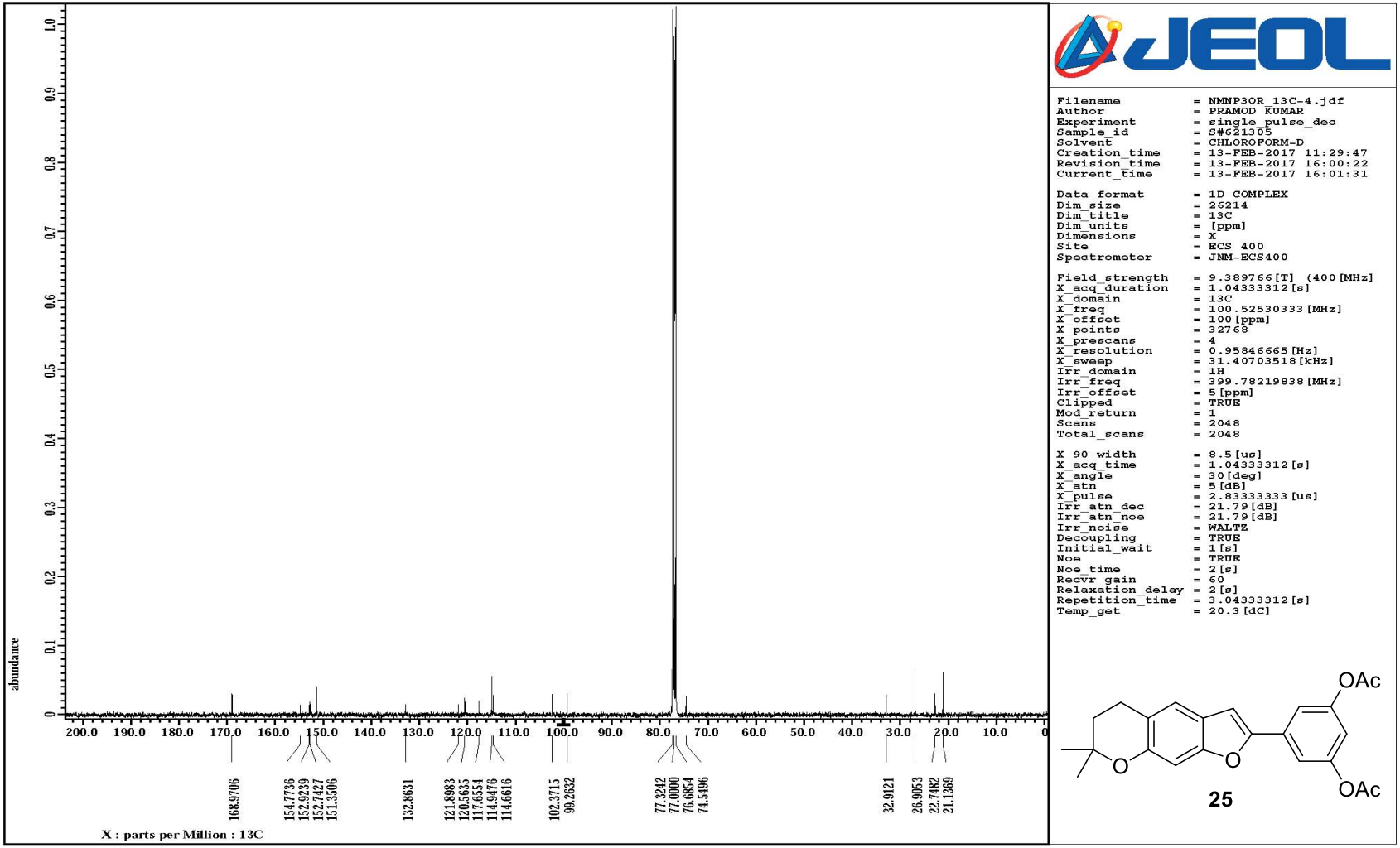

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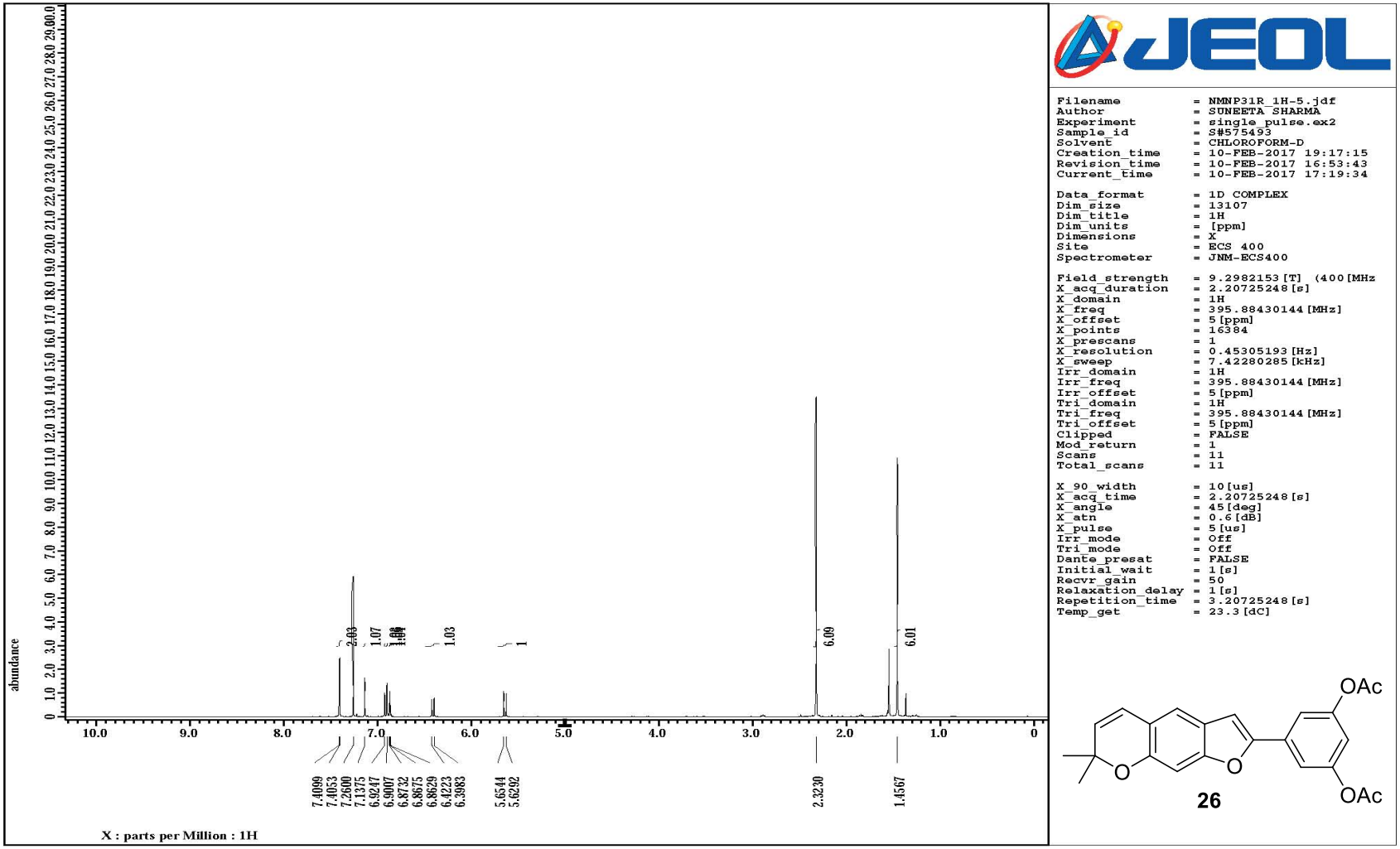

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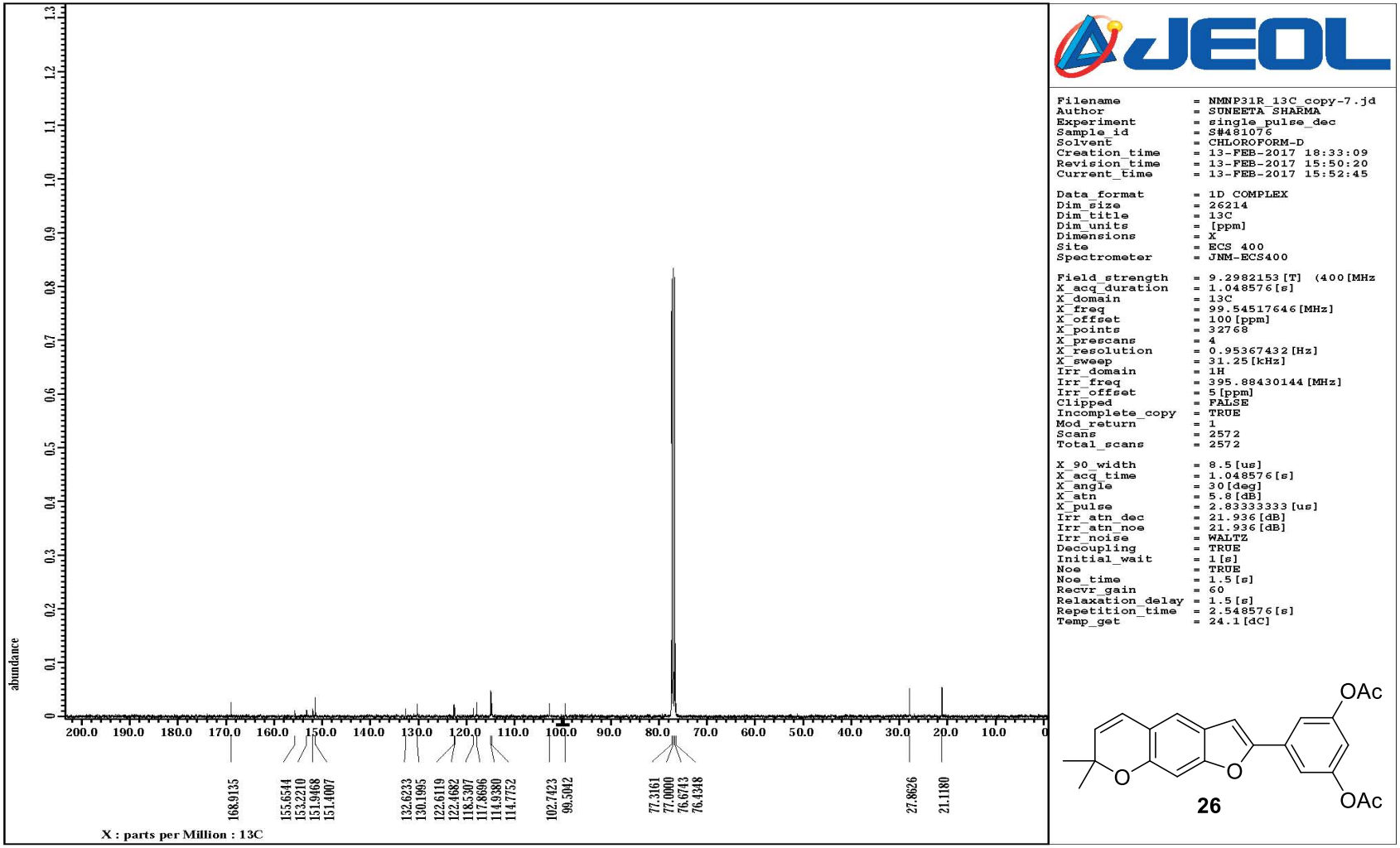
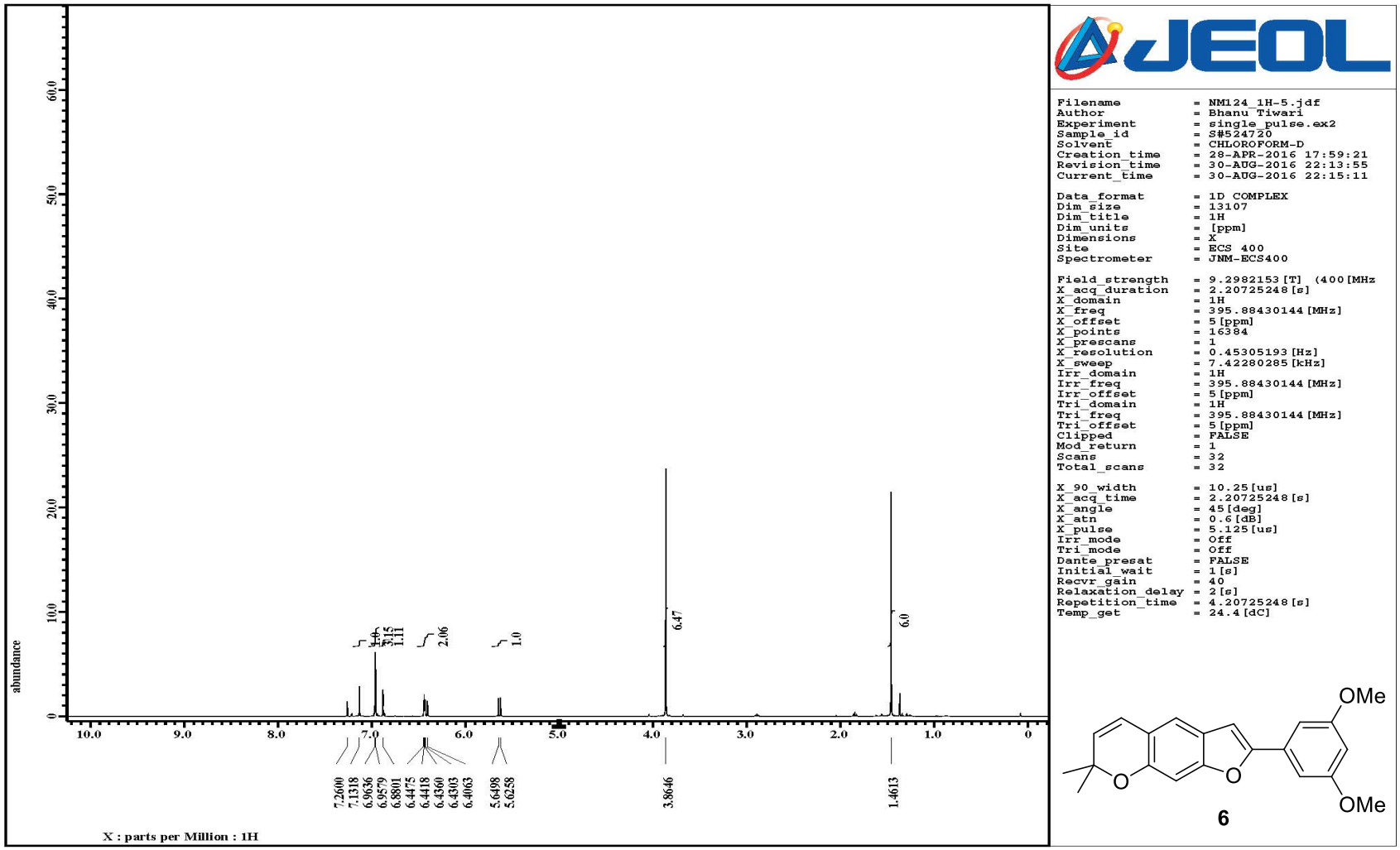


^{13}C NMR spectra of Compound **26**



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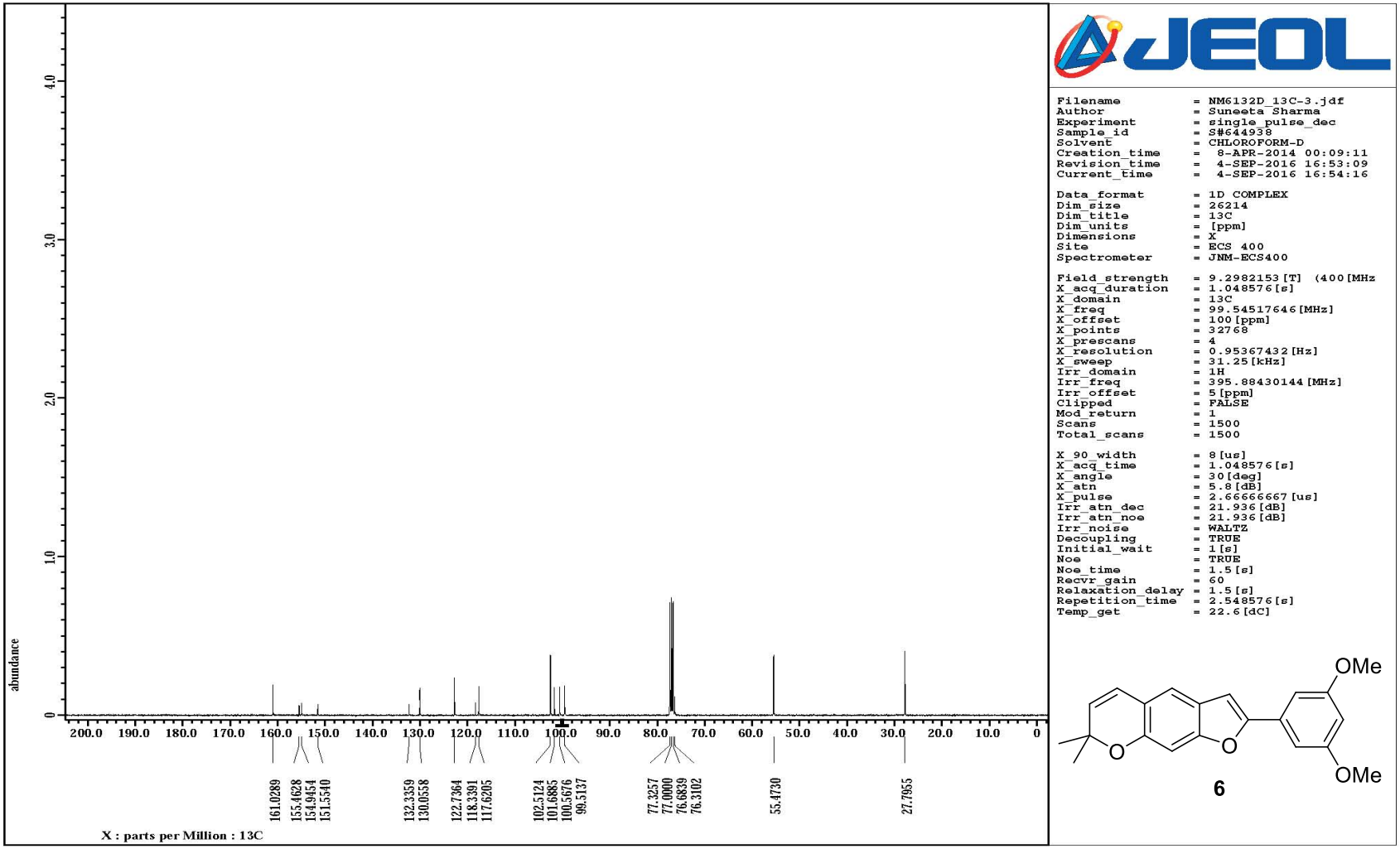
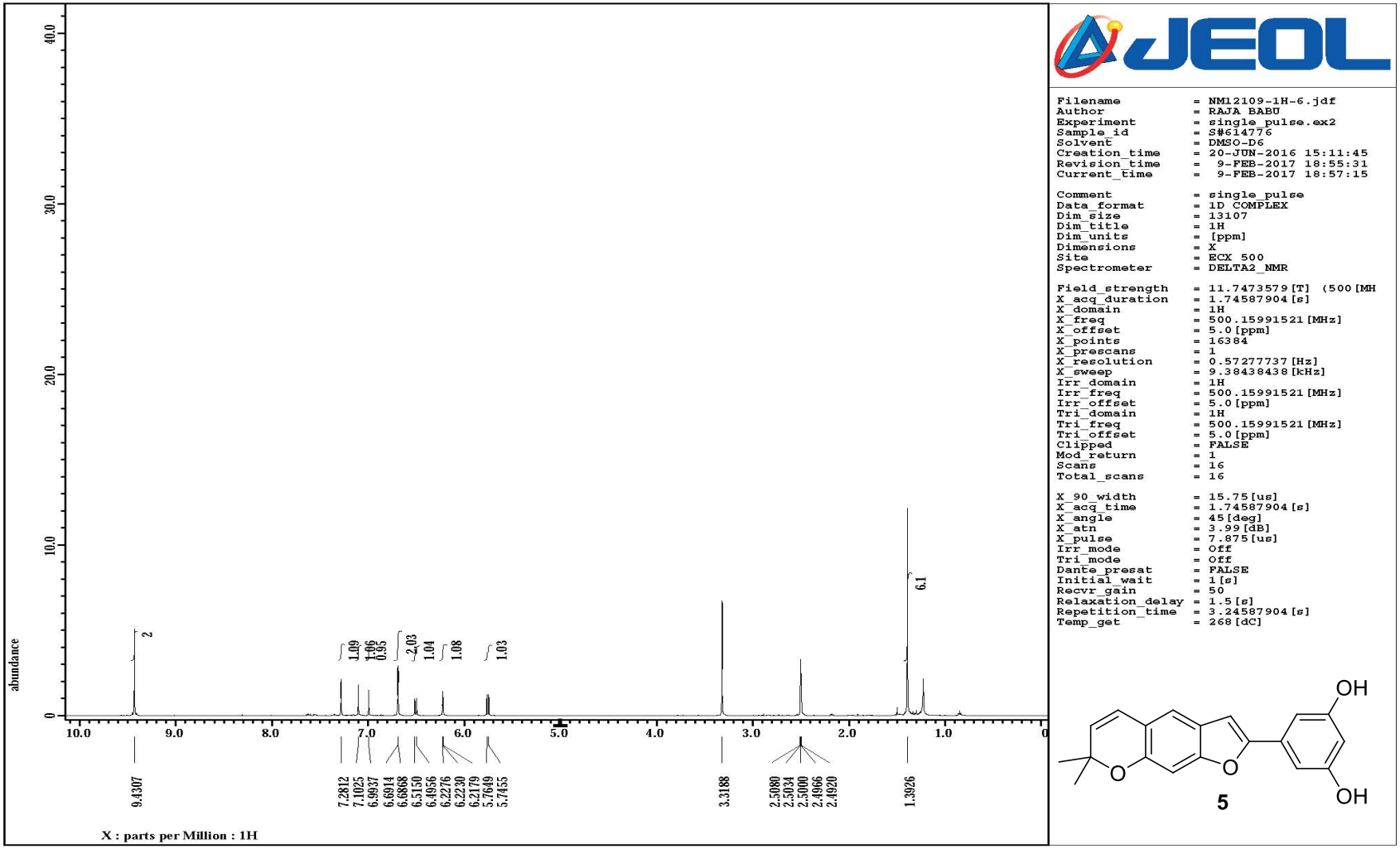


^{13}C NMR spectra of Compound **6**



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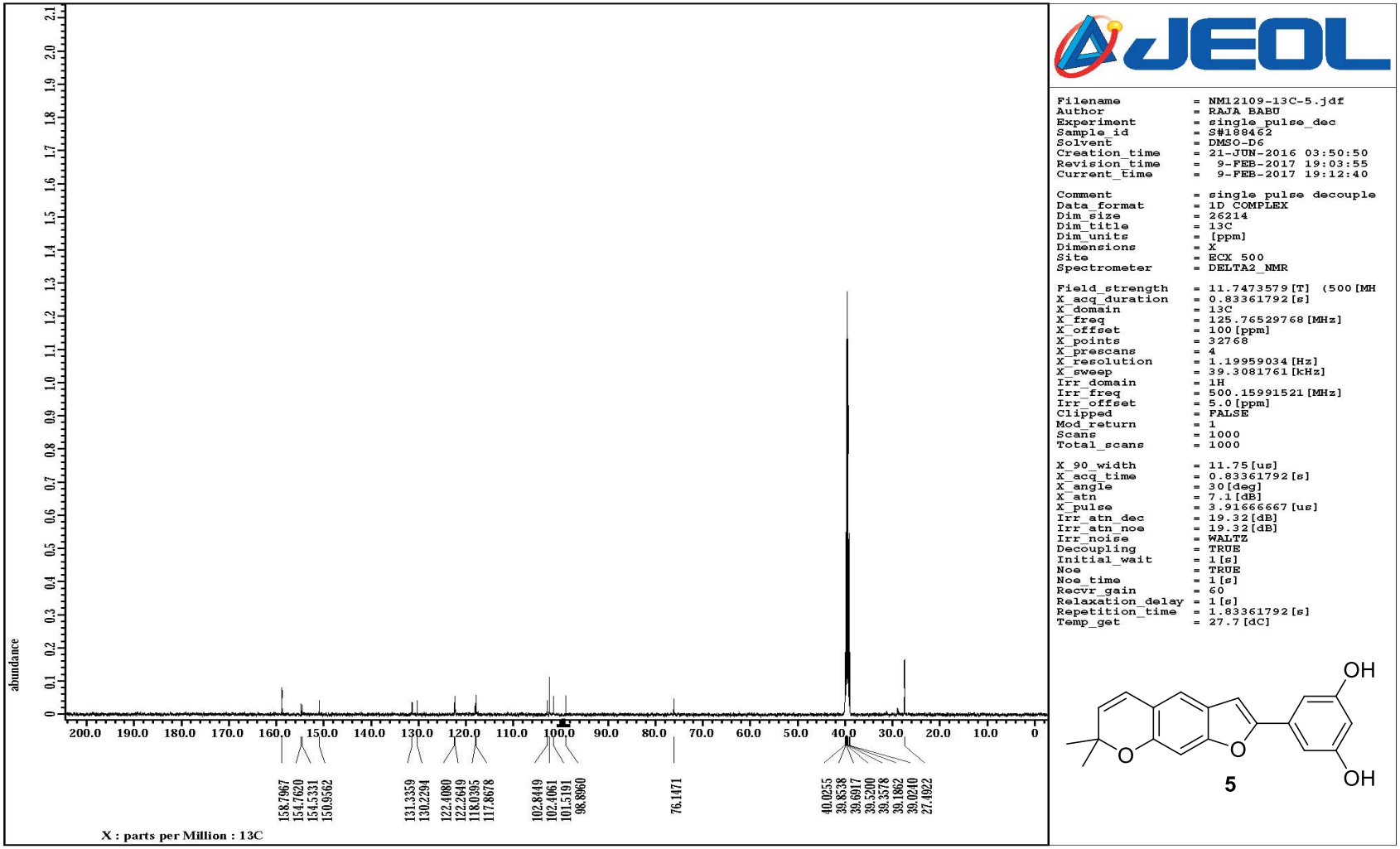
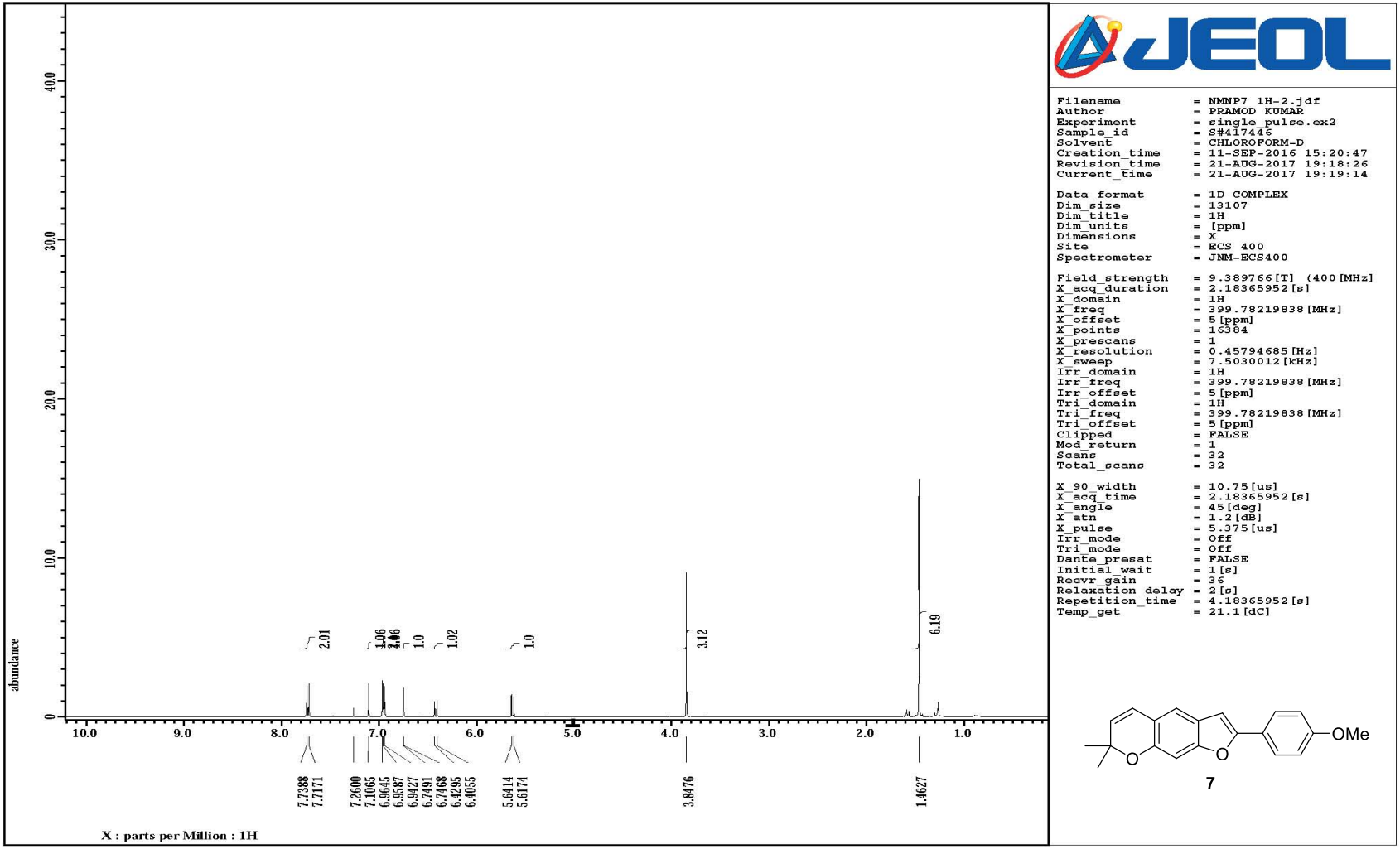
5

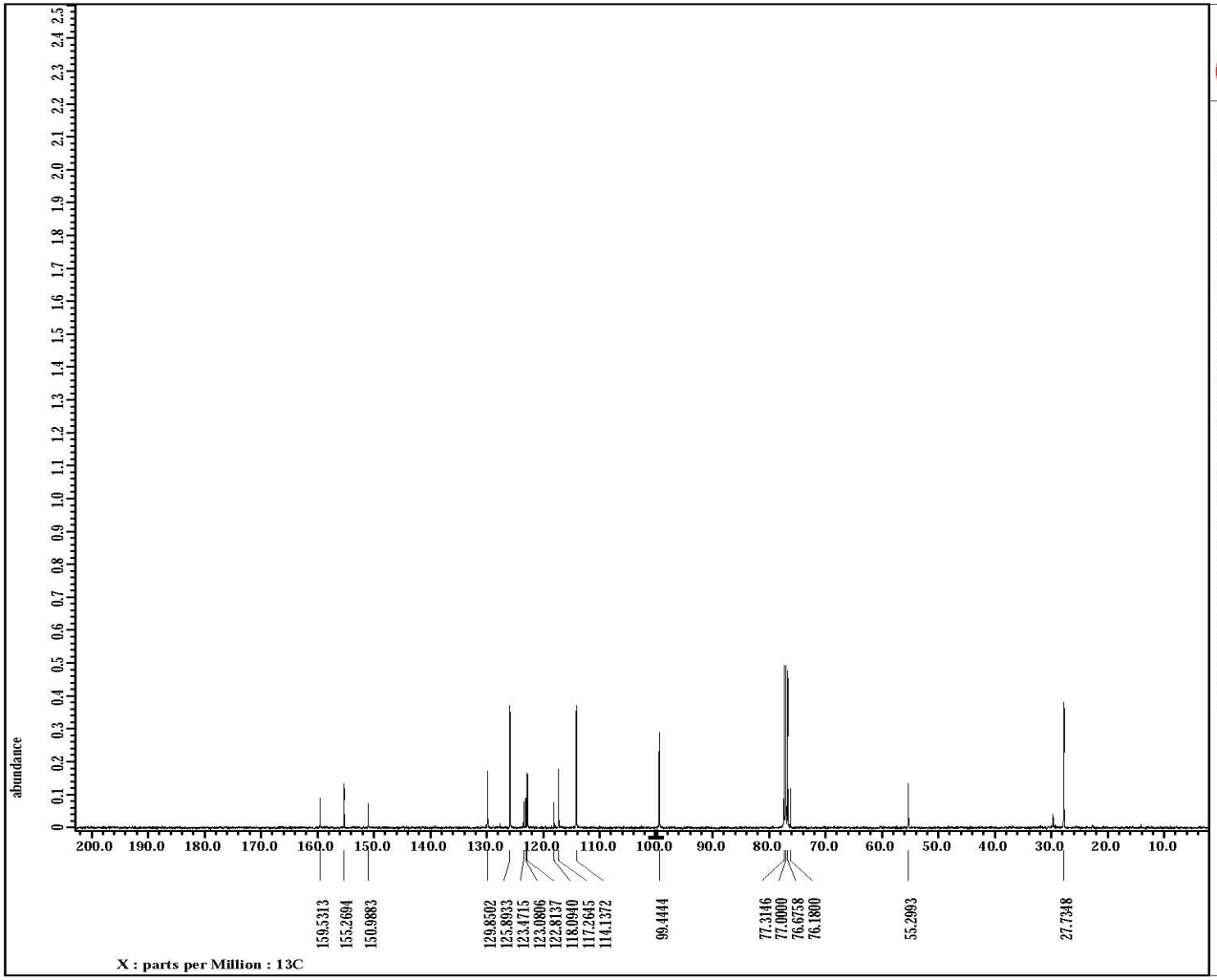
^{1}H NMR spectra of Compound **5**



^{13}C NMR spectra of Compound **5**



^{1}H NMR spectra of Compound 7



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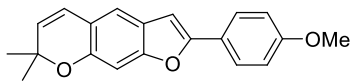
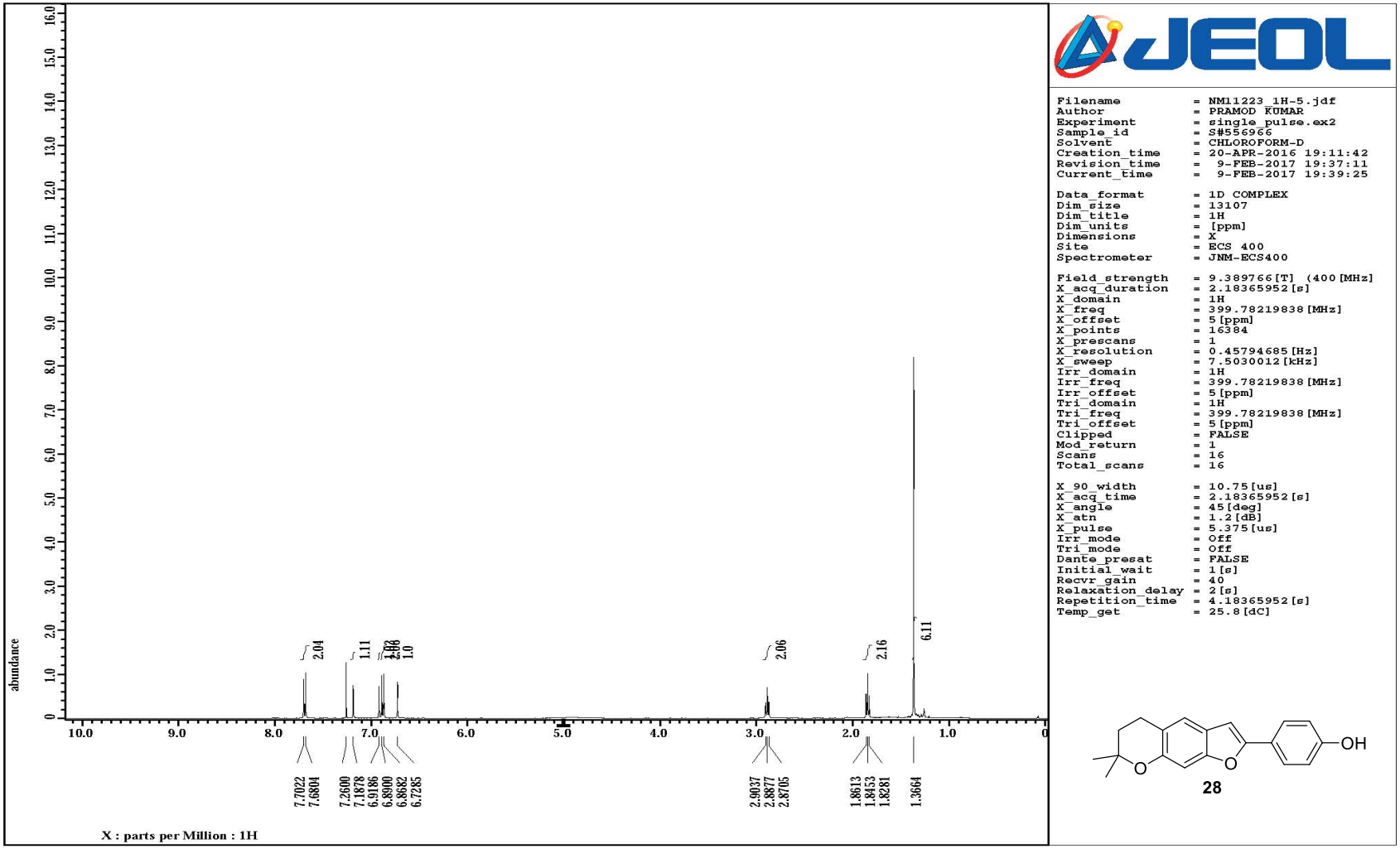
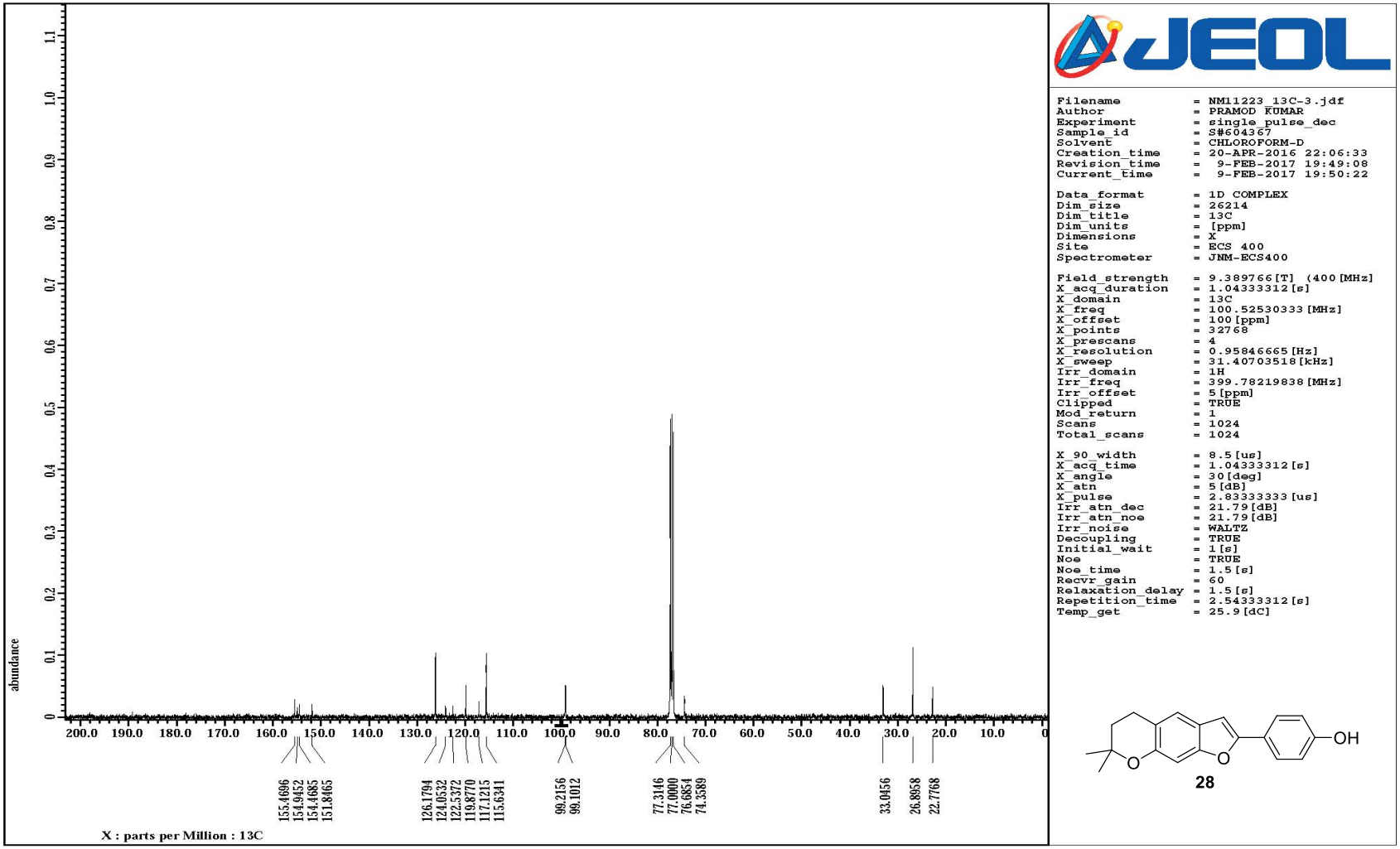


7

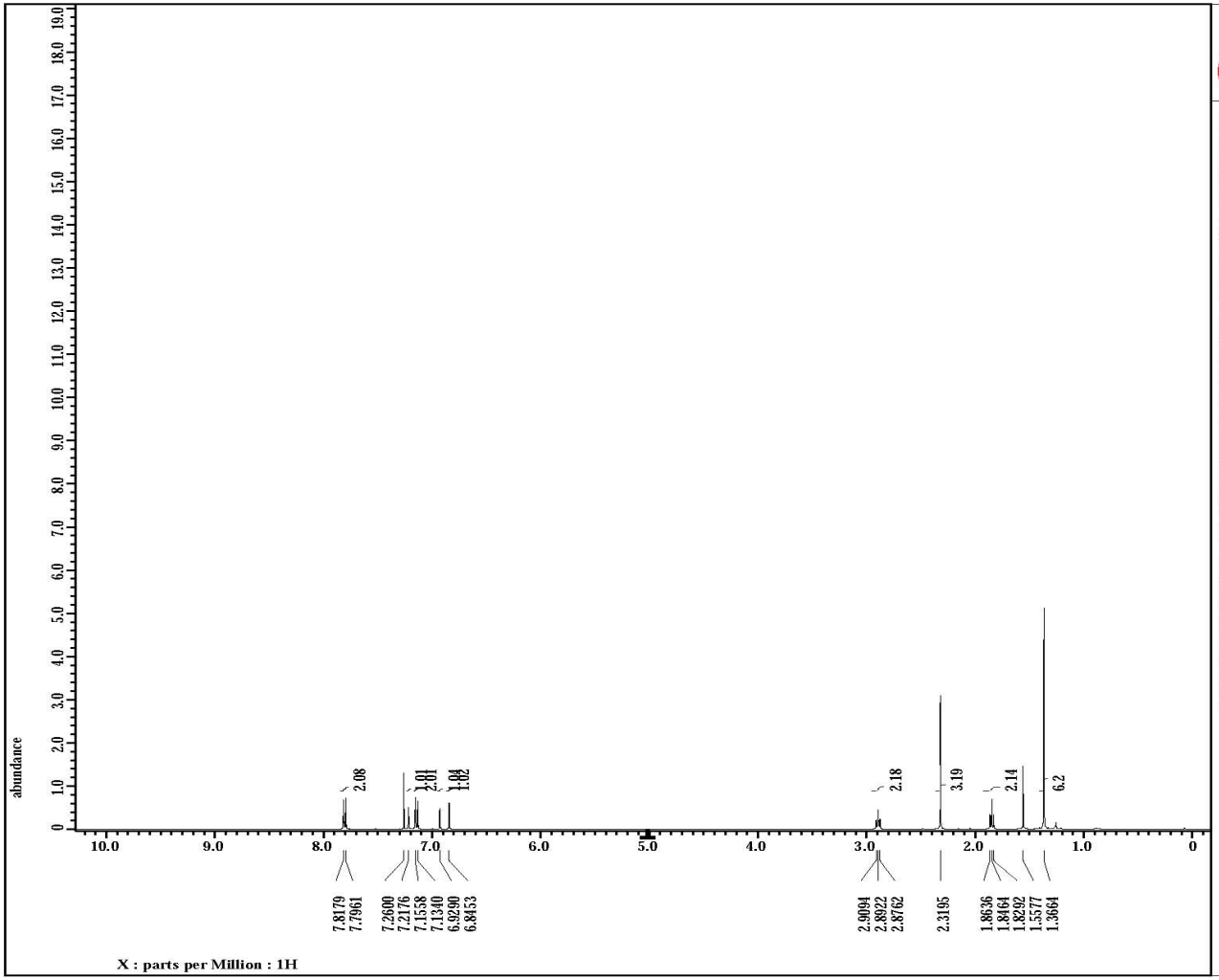
^{13}C NMR spectra of Compound 7

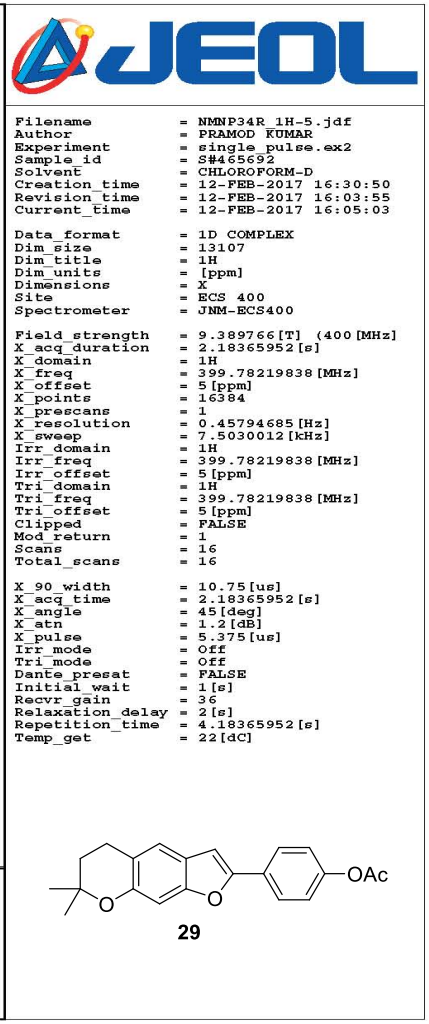


^{1}H NMR spectra of Compound **28**



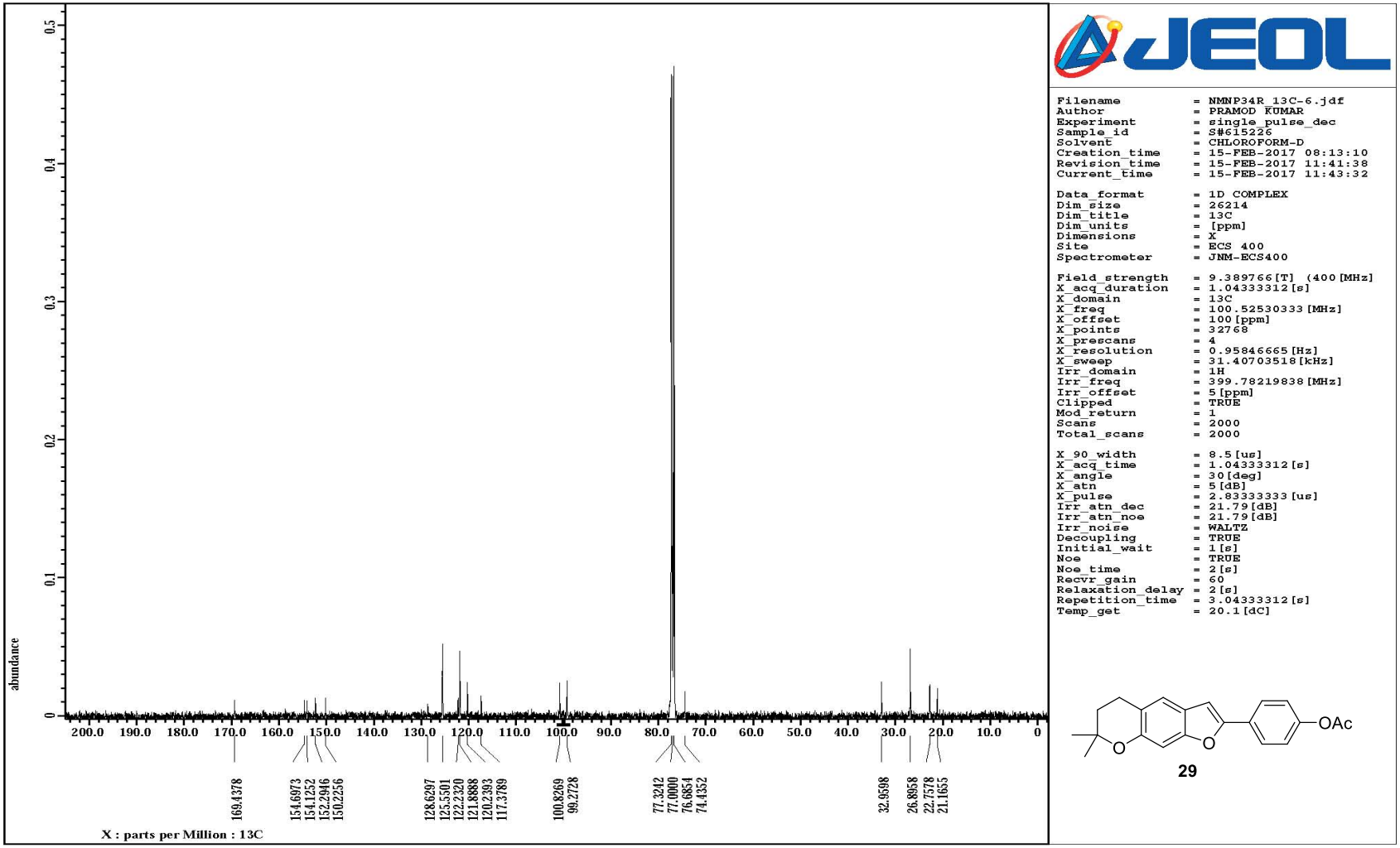
^{13}C NMR spectra of Compound **28**



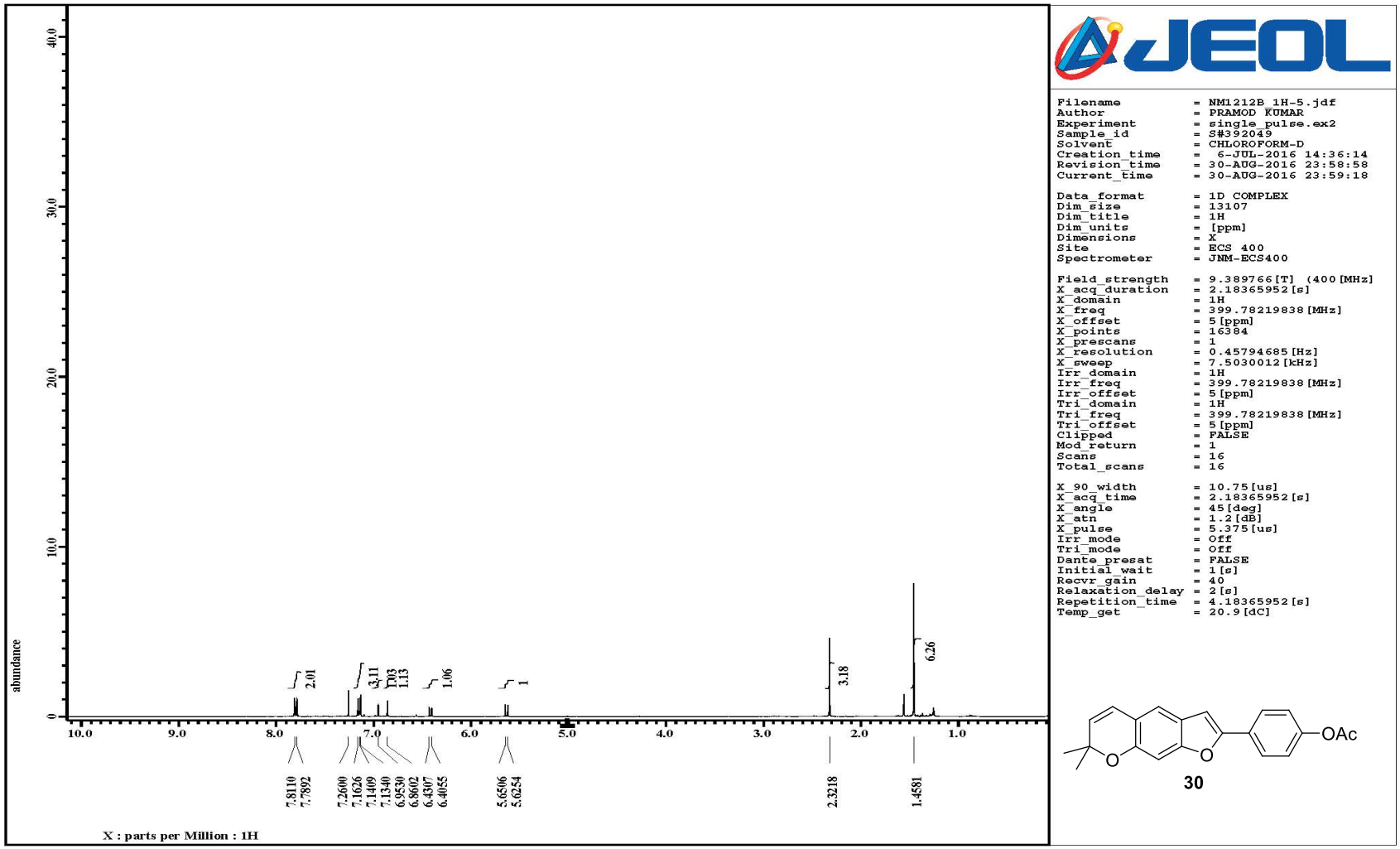


29

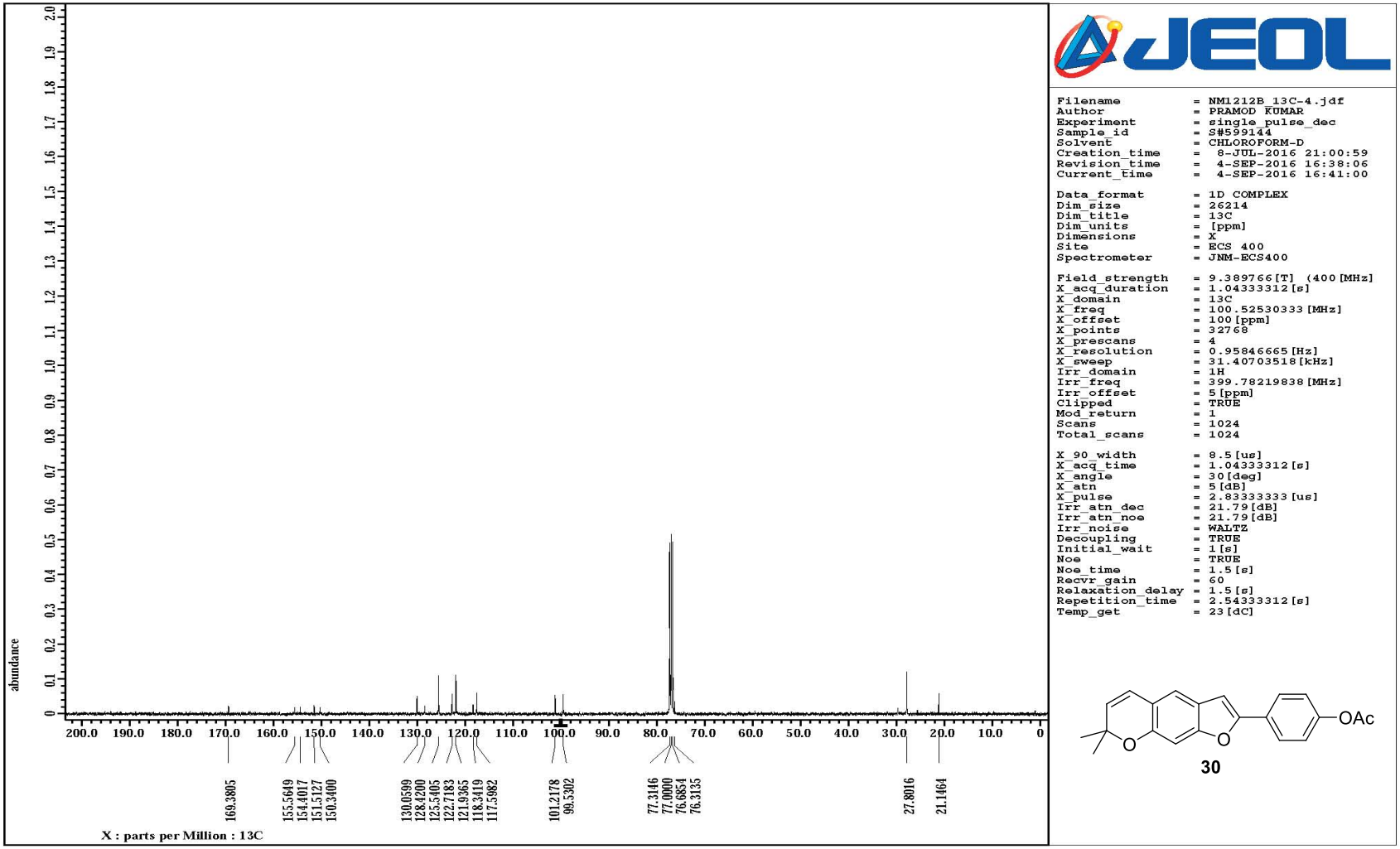
^{1}H NMR spectra of Compound **29**



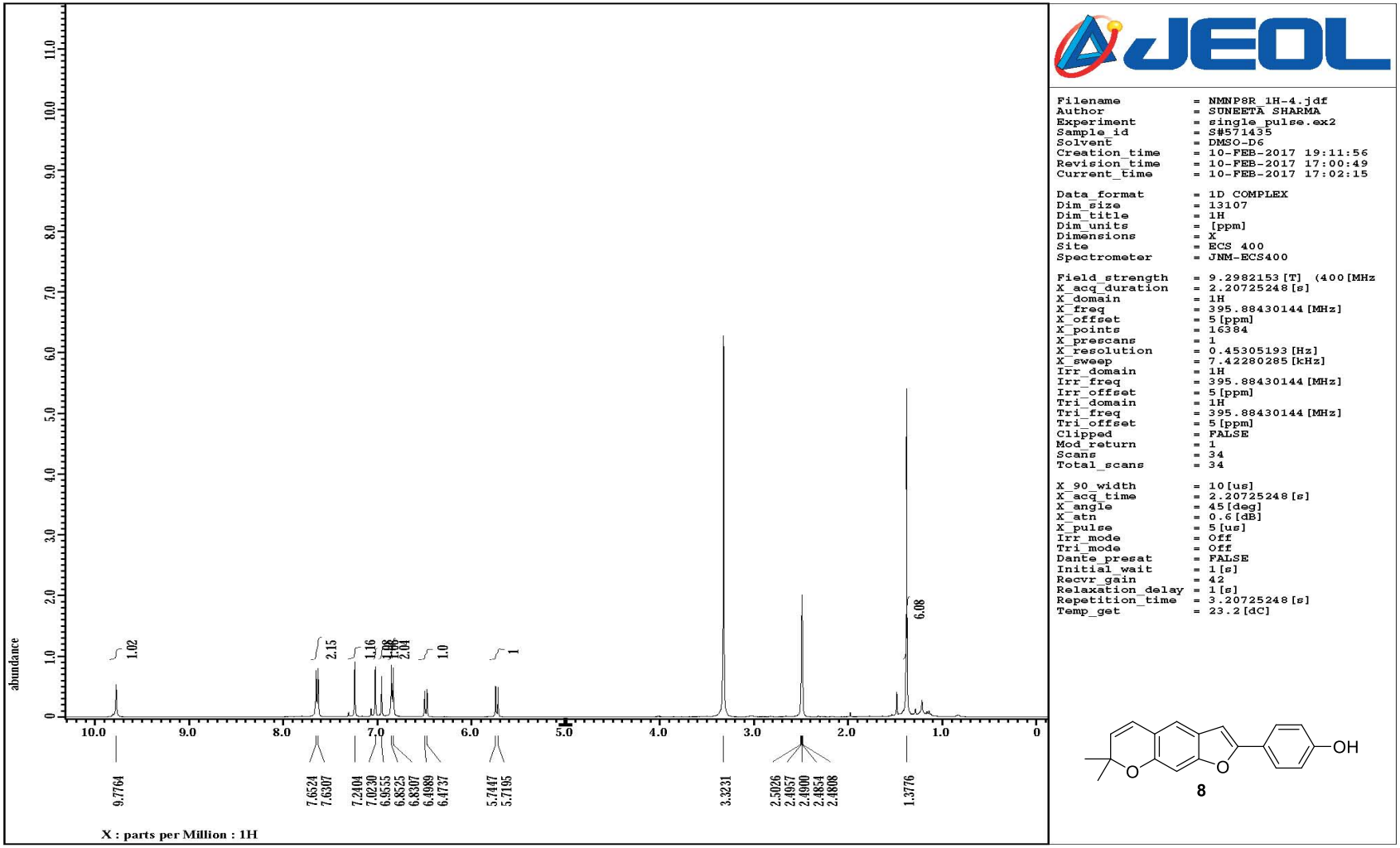
^{13}C NMR spectra of Compound **29**



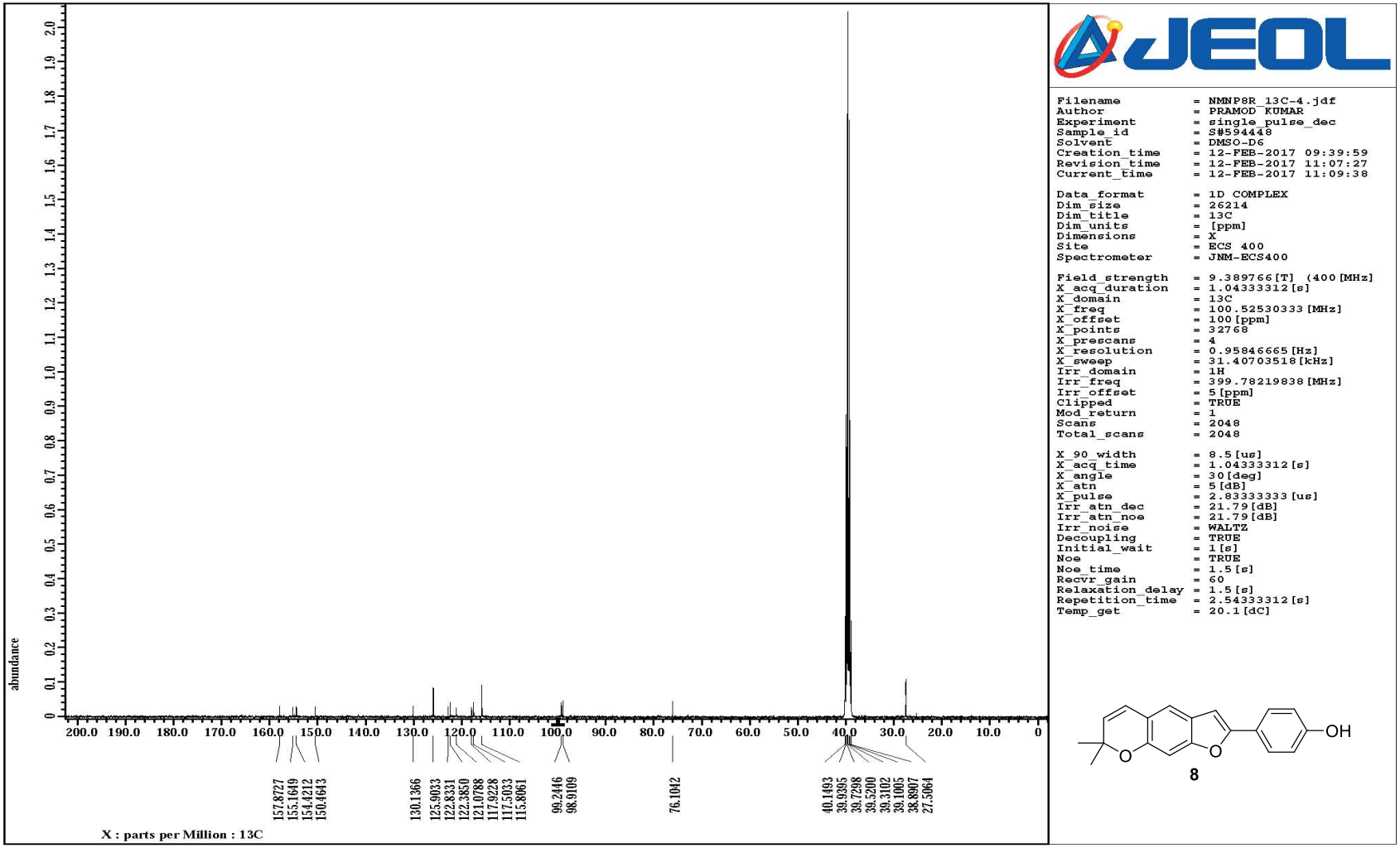
^{1}H NMR spectra of Compound **30**



^{13}C NMR spectra of Compound **30**



^{1}H NMR spectra of Compound **8**



^{13}C NMR spectra of Compound **8**