Electronic Supplementary Information

Unexpected manganese(III) acetate-mediated reactions of β-enamino carbonyl compounds with 1-(pyridin-2-yl)-enones under mechanical milling conditions

Zi Liu,[a] Guang-Peng Fan,[a] Guan-Wu Wang*[a,b]

[a] CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.
Fax: (+86)551-360-7864; E-mail: gwang@ustc.edu.cn
[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

Table of contents

General Procedure for 3

A mixture of 3-amino-5,5-dimethylcyclohex-2-enone **1a** (or **1b-1h**, 0.2 mmol), enone **2a** (or **2b-2q**, 0.1 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (107.2 mg, 0.4 mmol) and DMAP (12.2 mg, 0.1 mmol) was added to a stainless-steel jar containing two stainless-steel balls. The vessel was vibrated in Spex SamplePrep 5100 Mixer Mill at room temperature (~25 ^oC) for 2 h. The same reaction was repeated again. Then, the two reaction mixtures were washed with acetone and collected into a round-bottomed flask together with silica and the solvent was removed *in vacuo*. The residue was purified on a silica gel column with petroleum ether and ethyl acetate (3:1 v/v) as the eluent.

6,6-Dimethyl-2-picolinoyl-3-*p*-tolyl-6,7-dihydrobenzofuran-4(5*H*)-one (3aa): ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dt, J = 4.8, 1.2 Hz, 1H), 7.69 (dt, J = 7.6, 1.2 Hz, 1H), 7.65 (td, J = 7.5, 1.6 Hz, 1H), 7.19 (ddd, J = 7.1, 4.8, 1.7 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 2.92 (s, 2H), 2.43 (s, 2H), 2.25 (s, 3H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 183.9, 169.4, 154.3, 148.6, 147.4, 138.1, 136.5, 134.3, 130.3 (2C), 128.2 (2C), 127.1, 125.8, 123.9, 119.8, 53.3, 38.1, 34.8, 28.6 (2C), 21.3; FT-IR (KBr) ν/cm^{-1} 2957, 2871, 1687, 1648, 1579, 1541, 1499, 1442, 1344, 1274, 1238, 1169, 1049, 987, 928, 811, 750, 698, 616; HR-MS (+APCI) calcd for $C_{23}H_{22}NO_3$ $[M+1]^+$ 360.1594, found 360.1594.

6,6-Dimethyl-2-picolinoyl-3-*o*-tolyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ab): ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dt, J = 4.8, 1.3 Hz, 1H), 7.61-7.56 (m, 2H), 7.14 (ddd, J = 6.6, 4.8, 2.9 Hz, 1H), 7.07-7.02 (m, 2H), 6.87-6.81 (m, 2H), 2.95 (s, 2H), 2.43 (d, J = 16.4 Hz, 1H), 2.39 (d, J = 16.4 Hz, 1H), 2.19 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 183.5, 169.3, 154.3, 148.4, 147.9, 137.1, 136.3, 133.3, 130.8, 129.8, 129.4, 128.2, 125.9, 124.9, 123.3, 120.8, 53.0, 38.1, 34.9, 28.9, 28.4, 20.1; FT-IR (KBr) ν/cm^{-1} 2960, 2929, 1681, 1651, 1569, 1534, 1452, 1425, 1338, 1287, 1231, 1173, 1050, 994, 931, 753, 695, 616; HR-MS (+EI) calcd for $C_{23}H_{21}NO_3$ (M^+) 359.1521, found 359.1523.

3-(3,4-Dimethylphenyl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ac): ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dt, J = 4.7, 1.2 Hz, 1H), 7.66-7.64 (m, 1H), 7.63 (td, J = 7.3, 1.6 Hz, 1H), 7.16 (ddd, J = 6.8, 4.7, 2.0 Hz, 1H), 7.05 (dd, J = 7.8, 1.5 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.88 (s, 1H), 2.91 (s, 2H), 2.43 (s, 2H), 2.14 (s, 3H), 2.03 (s, 3H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 183.9, 169.5, 154.5, 148.5, 147.4, 136.7, 136.3, 135.4, 134.5, 131.6, 128.8, 127.8, 127.3, 125.6, 123.7, 119.7, 53.3, 38.1, 34.8, 28.6 (2C), 19.6, 19.4; FT-IR (KBr) ν/cm^{-1} 2956, 2871, 1684, 1640, 1577, 1536, 1494, 1444, 1345, 1279, 1238, 1050, 981, 943, 817, 752, 696, 615; HR-MS (+EI) calcd for $C_{24}H_{23}NO_3$ (M^+) 373.1678, found 373.1675.

3-(4-Methoxyphenyl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ad): ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (dt, J = 4.8, 1.5 Hz, 1H), 7.70-7.67 (m, 1H), 7.66 (td, J = 7.4, 1.5 Hz, 1H), 7.22-7.19 (m, 1H), 7.19 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H), 2.91 (s, 2H), 2.43 (s, 2H), 1.19 (s, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 193.1, 183.7, 169.4, 159.5, 154.2, 148.5, 147.1, 136.4, 133.9, 131.7 (2C), 125.9, 123.8, 122.1, 119.6, 112.9 (2C), 55.2, 53.2, 37.9, 34.7, 28.5 (2C); FT-IR (KBr) ν/cm^{-1} 2955, 2873, 1687, 1641, 1579, 1540, 1498, 1443, 1344, 1296, 1256, 1166, 1106, 1043, 983, 926, 814, 749, 699, 614; HR-MS (+EI) calcd for $C_{23}H_{21}NO_4$ (M^+) 375.1471, found 375.1478.

3-(3-Methoxyphenyl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ae): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 4.7 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.65 (td, J = 7.8, 1.5 Hz, 1H), 7.19 (ddd, J = 7.3, 4.7, 1.4 Hz, 1H), 7.00 (t, J = 8.0 Hz, 1H), 6.80-6.78 (m, 2H), 6.70-6.67 (m, 1H), 3.68 (s, 3H), 2.93 (s, 2H), 2.44 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 183.9, 169.4, 158.7, 154.2, 148.6, 147.5, 136.4, 133.7, 131.4, 128.4, 126.0, 123.7, 123.0, 119.7, 115.4, 114.7, 55.2, 53.3, 38.0, 34.8, 28.6 (2C); FT-IR (KBr) ν/cm^{-1} 2956, 1688, 1641, 1573, 1488, 1442, 1422, 1342, 1286, 1276, 1220, 1052, 1004, 941, 772, 745, 696, 681, 617; HR-MS (+EI) calcd for $C_{23}H_{21}NO_4$ (M^+) 375.1471, found 375.1476.

3-(2-Methoxyphenyl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3af): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (ddd, J = 4.7, 1.5, 1.0 Hz, 1H), 7.66 (dt, J = 7.7, 1.0 Hz, 1H), 7.60 (td, J = 7.6, 1.5 Hz, 1H), 7.13 (ddd, J = 7.4, 4.7, 1.4 Hz, 1H), 7.12-7.06 (m, 2H), 6.72 (td, J = 7.5, 0.9 Hz, 1H), 6.59 (d, J = 8.2 Hz, 1H), 3.58 (s, 3H), 2.92 (s, 2H), 2.41 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 183.7, 169.1, 156.5, 154.1, 148.3, 147.8, 136.1, 131.4, 129.8, 129.2, 125.9, 123.3, 120.3, 120.2, 119.9, 110.0, 55.2, 53.2, 38.0, 34.8, 28.6 (2C); FT-IR (KBr) ν/cm^{-1} 2959, 2936, 2872, 1683, 1644, 1582, 1537, 1489, 1436, 1336, 1297, 1269, 1238, 1167, 1109, 1050, 1026, 985, 927, 748, 689; HR-MS (+EI) calcd for $C_{23}H_{21}NO_4$ (M^+) 375.1471, found 375.1477.

6,6-Dimethyl-3-phenyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ag): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 4.6 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.63 (td, J = 7.6, 1.6 Hz, 1H), 7.22 (dd, J = 7.9, 1.5 Hz, 1H), 7.16 (ddd, J = 7.4, 4.6, 1.2 Hz, 1H), 7.14-7.07 (m, 3H), 2.92 (s, 2H), 2.43 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 183.8, 169.4, 154.0, 148.5, 147.4, 136.4, 134.0, 130.3 (2C), 130.2, 128.1, 127.3 (2C), 126.0, 123.8, 119.7, 53.2, 38.0, 34.8, 28.5 (2C); FT-IR (KBr) ν/cm^{-1} 3052, 2958, 2927, 2869, 1691, 1642, 1577, 1535, 1487, 1414, 1342, 1274, 1241, 1166, 1047, 986, 926, 769, 740, 701, 615; HR-MS (+EI) calcd for $C_{22}H_{19}NO_3$ (M^+) 345.1365, found 345.1366.

3-(4-Chlorophenyl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ah): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddd, J = 4.9, 1.5, 1.1 Hz, 1H), 7.74 (dt, J = 7.2, 1.1 Hz, 1H), 7.71 (td, J = 7.5, 1.5 Hz, 1H), 7.26 (ddd, J = 6.9, 4.9, 1.9 Hz, 1H), 7.18 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 2.92 (s, 2H), 2.44 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 183.6, 169.5, 154.0, 148.6, 147.5, 136.7, 134.3, 132.7, 131.7 (2C), 128.8, 127.6 (2C), 126.2, 123.9, 119.6, 53.2, 38.0, 34.9, 28.6 (2C); FT-IR (KBr) ν/cm^{-1} 3073, 2959, 2878, 1682, 1585, 1544, 1481, 1435, 1334,

1234, 1171, 1089, 1048, 1004, 916, 814, 746, 699; HR-MS (+EI) calcd for $C_{22}H_{18}{}^{35}ClNO_3$ (M^+) 379.0975, found 379.0973.

3-(2-Chlorophenyl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ai): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dt, J = 4.5, 0.9 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.64 (td, J = 7.7, 1.7 Hz, 1H), 7.24 (dd, J = 7.9, 1.0 Hz, 1H), 7.18 (ddd, J = 7.5, 4.5, 1.2 Hz, 1H), 7.11 (td, J = 7.7, 1.8 Hz, 1H), 7.08 (dd, J = 8.0, 1.8 Hz, 1H), 7.02 (td, J = 7.4, 1.0 Hz, 1H), 2.97 (d, J = 17.9 Hz, 2H), 2.92 (d, J = 17.9 Hz, 2H), 2.46 (d, J = 16.1 Hz, 1H), 2.38 (d, J = 16.1 Hz, 1H), 1.21 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 183.1, 169.1, 154.0, 148.4, 148.0, 136.5, 133.8, 131.5, 130.7, 130.2, 129.4, 129.0, 126.1, 126.0, 123.7, 120.6, 52.8, 38.0, 35.0, 28.7, 28.6; FT-IR (KBr) ν/cm^{-1} 2958, 1688, 1653, 1580, 1542, 1470, 1445, 1272, 1228, 1049, 990, 931, 750, 695; HR-MS (+EI) calcd for $C_{22}H_{18}{}^{35}ClNO_3$ (M^+) 379.0975, found 379.0975.

3-(Benzo[*d*][1,3]dioxol-5-yl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3aj): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dt, J = 4.8, 1.2 Hz, 1H), 7.71-7.69 (m, 2H), 7.25 (ddd, J = 5.6, 4.8, 3.2 Hz, 1H), 6.80 (d, J = 1.7 Hz, 1H), 6.67 (dd, J = 8.0, 1.7 Hz, 1H), 6.52 (d, J = 8.0 Hz, 1H), 5.88 (s, 2H), 2.91 (s, 2H), 2.44 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 183.8, 169.4, 154.4, 148.6, 147.7, 147.4, 146.9, 136.6, 133.7, 126.0, 124.8, 123.8, 123.7, 119.7, 110.8, 107.5, 101.1, 53.3, 38.0, 34.8, 28.6 (2C); FT-IR (KBr) ν/cm^{-1} 2957, 2874, 1687, 1641, 1577, 1540, 1487, 1444, 1329, 1278, 1240, 1095, 1044, 993, 938, 865, 809, 746, 695, 614; HR-MS (+EI) calcd for $C_{23}H_{19}NO_5$ (M^+) 389.1263, found 389.1266.

4-(6,6-Dimethyl-4-oxo-2-picolinoyl-4,5,6,7-tetrahydrobenzofuran-3-yl)benzonitrile (3ak): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 4.8 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.76 (td, J = 7.5, 1.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.30 (ddd, J = 7.3, 4.8, 1.3 Hz, 1H), 2.94 (s, 2H), 2.45 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 183.0, 169.4, 153.5, 148.4, 147.5, 136.8, 135.5, 131.4, 130.9 (4C), 126.5, 123.9, 119.3, 118.6, 111.5, 52.9, 37.8, 34.8, 28.5 (2C); FT-IR (KBr) ν/cm^{-1} 2958, 2887, 2874, 2223, 1686, 1656, 1580, 1540, 1495, 1443, 1408, 1340, 1297, 1275, 1235, 1052, 1008, 926, 903, 853, 808, 752, 707, 691, 561; HR-MS (+EI) calcd for $C_{23}H_{18}N_2O_3$ (M^+) 370.1317, found 370.1312.

6,6-Dimethyl-3-(4-nitrophenyl)-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3al): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 8.03 (d, J = 8.9 Hz, 2H), 7.83 (dt, J = 7.8, 1.1 Hz, 1H), 7.76 (td, J = 7.7, 1.6 Hz, 1H), 7.44 (d, J = 8.9 Hz, 2H), 7.27 (ddd, J = 7.5, 4.8, 1.3 Hz, 1H), 2.95 (s, 2H), 2.46 (s, 2H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 183.0, 169.4, 153.6, 148.4, 147.6, 147.2, 137.6, 136.9, 131.2 (2C), 131.0, 126.6, 124.0, 122.4 (2C), 119.4, 52.9, 37.8, 34.8, 28.5 (2C); FT-IR (KBr) ν/cm^{-1} 2961, 1688, 1644, 1576, 1511, 1444, 1341, 1291, 1238, 1050, 1009, 926, 853, 814, 750, 699; HR-MS (+EI) calcd for $C_{22}H_{18}N_2O_5$ (M^+) 390.1216, found 390.1212.

6,6-Dimethyl-3-(3-nitrophenyl)-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3am): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 8.06 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.03 (t, J = 1.7 Hz, 1H), 7.83 (dt, J = 7.8, 1.1 Hz, 1H), 7.74 (td, J = 7.7, 1.6 Hz, 1H), 7.71 (ddd, J = 7.7, 1.5, 1.2 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.24 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 2.96 (s, 2H), 2.46 (s, 2H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 183.1, 169.6, 153.7, 148.4, 147.8, 147.3, 137.0, 136.4, 132.2, 131.1, 128.4, 126.5, 125.4, 124.2, 122.9, 119.4, 53.0, 37.9, 35.0, 28.6 (2C); FT-IR (KBr) ν/cm^{-1} 3057, 2952, 2920, 2869, 1681, 1655, 1522, 1479, 1442, 1344, 1285, 1179, 1052, 940, 811, 739, 685, 619; HR-MS (+EI) calcd for $C_{22}H_{18}N_2O_5$ (M^+) 390.1216, found 390.1210.

6,6-Dimethyl-2-picolinoyl-3-(thiophen-2-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (3an): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 7.79 (dt, J = 7.8, 1.1 Hz, 1H), 7.73 (td, J = 7.7, 1.6 Hz, 1H), 7.27 (ddd, J = 7.5, 4.8, 1.3 Hz, 1H), 7.24 (dd, J = 5.1, 1.2 Hz, 1H), 7.12 (dd, J = 3.6, 1.2 Hz, 1H), 6.78 (dd, J = 5.1, 3.6 Hz, 1H), 2.89 (s, 2H), 2.45 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 183.6, 169.2, 154.2, 148.7, 147.6, 136.6, 131.3, 130.2, 128.1, 126.4, 126.2, 126.1, 123.8, 119.5, 53.2, 37.9, 34.7, 28.5 (2C); FT-IR (KBr) ν/cm^{-1} 3086, 2959, 2928, 2869, 1691, 1637, 1578, 1502, 1445, 1410, 1321, 1245, 1162, 1050, 963, 898, 838, 735, 695; HR-MS (+EI) calcd for $C_{20}H_{17}NO_3S$ (M^+) 351.0929, found 351.0924.

3-(Benzo[*b*]thiophen-2-yl)-6,6-dimethyl-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ao): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 7.82 (dt, J = 7.8, 0.9 Hz, 1H), 7.70-7.67 (m, 1H), 7.65 (td, J = 7.7, 1.6 Hz, 1H), 7.58-7.56 (m, 1H), 7.30 (d, J = 0.3 Hz, 1H), 7.25-7.23 (m, 2H), 7.09 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 2.91 (s, 2H), 2.47 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 183.7, 169.3, 154.2, 148.7, 148.3, 141.3, 139.1, 136.6, 131.1, 127.9, 126.3, 125.9, 124.7, 124.1, 123.82, 123.77, 121.9, 119.8, 53.2, 38.0, 34.8, 28.6 (2C); FT-IR (KBr) ν/cm^{-1} 2954, 2925, 2868, 1688, 1641, 1582, 1501, 1444, 1417, 1341, 1322, 1290, 1232, 1155, 1107, 1050, 961, 751, 697, 567; HR-MS (+EI) calcd for $C_{24}H_{19}NO_3S$ (M^+) 401.1086, found 401.1082.

6,6-Dimethyl-3-phenyl-2-(pyrazine-2-carbonyl)-6,7-dihydrobenzofuran-4(5*H*)-one (3ap): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 1.4 Hz, 1H), 8.44 (d, J = 2.3 Hz, 1H), 8.10 (dd, J = 2.3, 1.4 Hz, 1H), 7.22-7.11 (m, 5H), 2.94 (s, 2H), 2.45 (s, 2H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 181.9, 170.0, 149.4, 147.1, 146.5, 144.9, 143.1, 135.0, 130.4 (2C), 129.7, 128.6, 127.6 (2C), 119.8, 53.2, 38.1, 34.9, 28.6 (2C); FT-IR (KBr) ν/cm^{-1} 2961, 2928, 2871, 1691, 1650, 1570, 1542, 1489, 1452, 1421, 1345, 1267, 1164, 1050, 1016, 985, 926, 767, 731, 700, 580; HR-MS (+EI) calcd for $C_{21}H_{18}N_2O_3$ (M^+) 346.1317, found 346.1293.

3-(4-Methoxyphenyl)-6,6-dimethyl-2-(pyrazine-2-carbonyl)-6,7-dihydrobenzofuran-4(5*H*)-one (3aq): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 1.4 Hz, 1H), 8.48 (d, J = 2.4 Hz, 1H), 8.20 (dd, J = 2.4, 1.5 Hz, 1H), 7.19 (d, J = 8.7 Hz, 2H), 6.68 (d, J =

8.7 Hz, 2H), 3.74 (s, 3H), 2.92 (s, 2H), 2.45 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 181.8, 170.0, 159.9, 149.6, 146.8, 146.3, 144.8, 143.1, 135.0, 131.9 (2C), 121.5, 119.7, 113.1 (2C), 55.2, 53.1, 38.0, 34.7, 28.5 (2C); FT-IR (KBr) ν/cm^{-1} 2959, 1689, 1642, 1610, 1578, 1539, 1500, 1443, 1412, 1341, 1296, 1250, 1172, 1053, 1019, 987, 928, 821, 774, 730, 595, 543; HR-MS (+EI) calcd for $C_{22}H_{20}N_2O_4$ (M^+) 376.1423, found 376.1425.

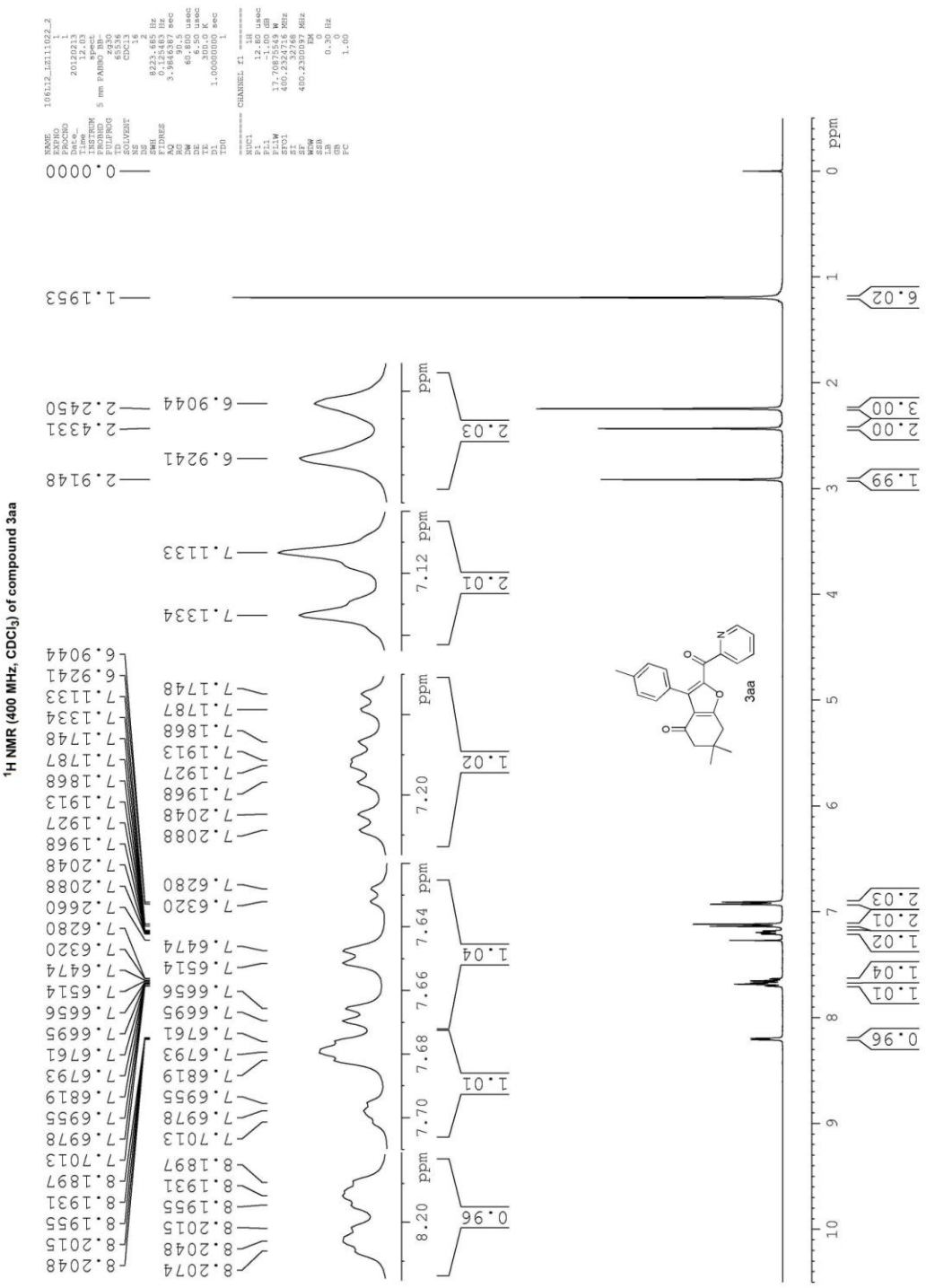
2-Picolinoyl-3-*p*-tolyl-6,7-dihydrobenzofuran-4(5*H*)-one (3ha): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 4.4 Hz, 1H), 7.70-7.64 (m, 2H), 7.22-7.19 (m, 1H), 7.13 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 7.9 Hz, 2H), 3.06 (t, J = 6.4 Hz, 2H), 2.57-2.54 (m, 2H), 2.25 (s, 3H), 2.24 (quintet, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 183.9, 170.1, 154.3, 148.6, 146.9, 138.0, 136.4, 134.3, 130.2 (2C), 128.1 (2C), 127.1, 125.8, 123.8, 120.8, 38.9, 24.3, 22.1, 21.3; FT-IR (KBr) ν/cm^{-1} 2943, 1679, 1656, 1579, 1543, 1504, 1440, 1426, 1401, 1348, 1263, 1229, 1173, 1066, 1011, 952, 877, 818, 754, 680, 514; HR-MS (+EI) calcd for $C_{21}H_{17}NO_3$ (M^+) 331.1208, found 331.1211.

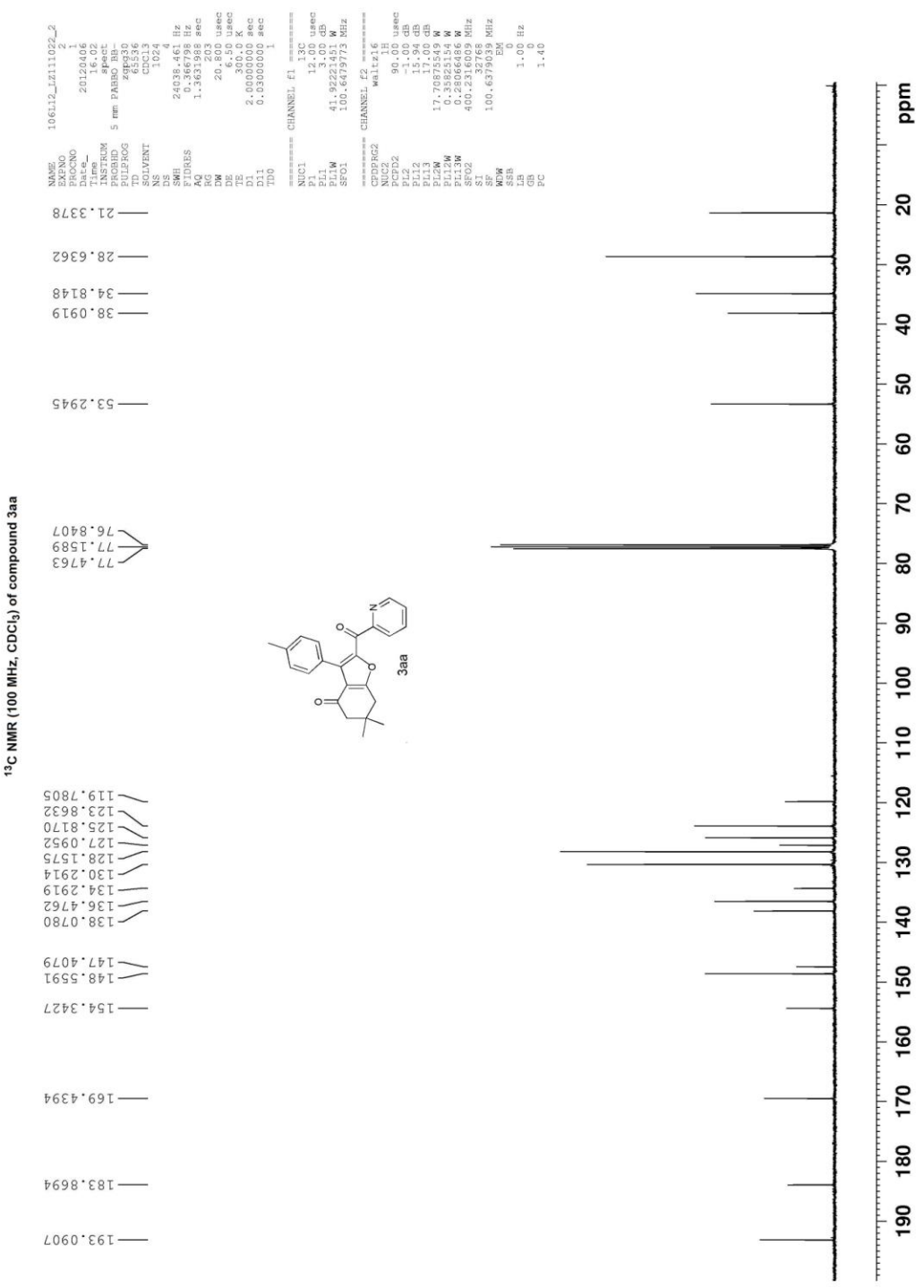
3-(4-Methoxyphenyl)-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3hd): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dt, J = 4.7, 1.4 Hz, 1H), 7.69-7.67 (m, 1H), 7.65 (td, J = 7.3, 1.4 Hz, 1H), 7.23-7.20 (m, 1H), 7.19 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 3.03 (t, J = 6.4 Hz, 2H), 2.56-2.53 (m, 2H), 2.22 (quintet, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 183.8, 170.2, 159.6, 154.3, 148.6, 146.8, 136.5, 134.0, 131.7 (2C), 125.9, 123.8, 122.2, 120.7, 112.9 (2C), 55.2, 38.9, 24.2, 22.0; FT-IR (KBr) ν/cm^{-1} 2942, 1680, 1650, 1614, 1541, 1504, 1440, 1403, 1349, 1296, 1264, 1250, 1171, 1067, 1035, 1011, 950, 875, 838, 759, 683, 585; HR-MS (+EI) calcd for $C_{21}H_{17}NO_4$ (M^+) 347.1158, found 347.1159.

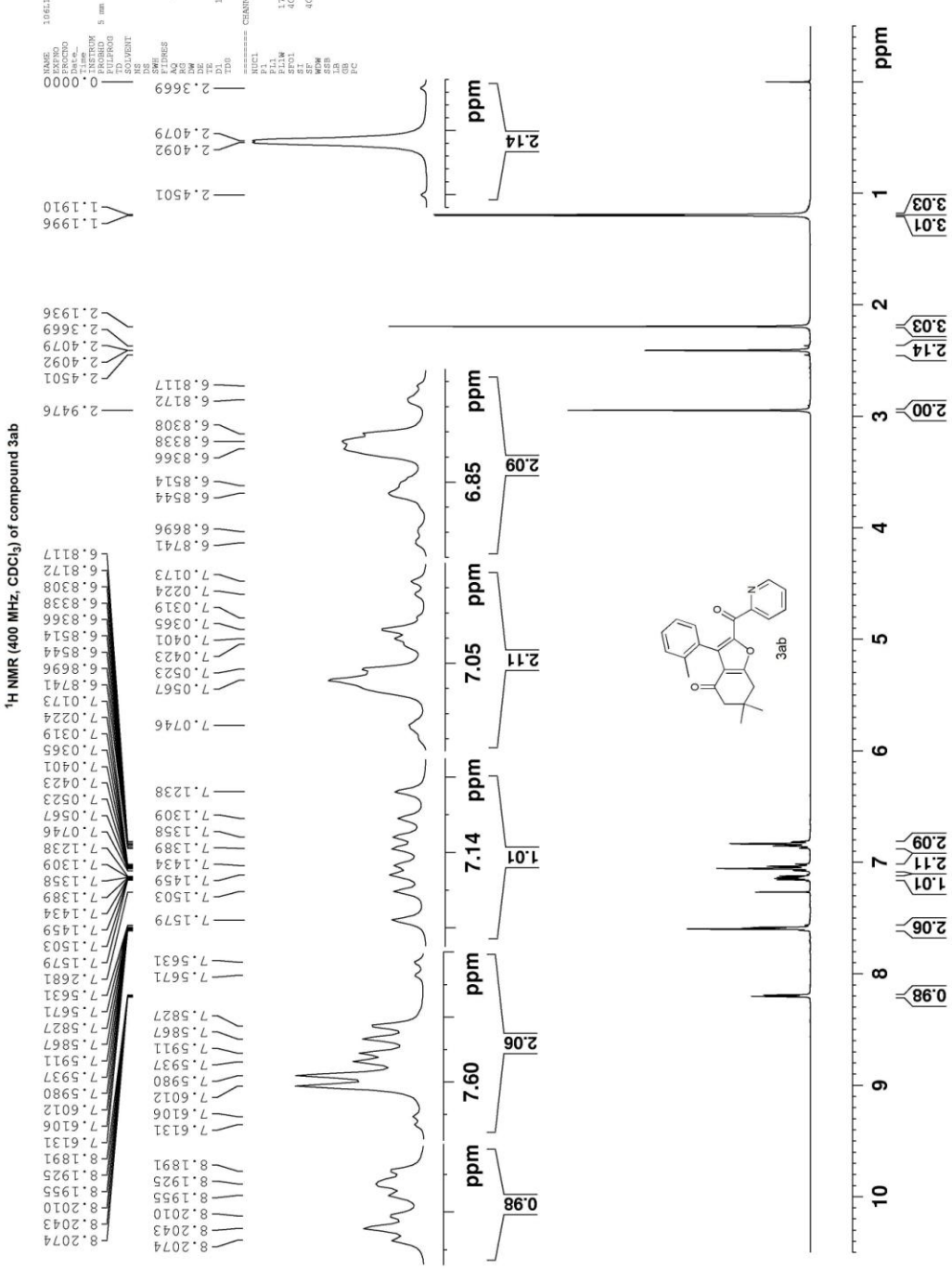
3-(4-Nitrophenyl)-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3hl): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 4.8 Hz, 1H), 8.05 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 7.4 Hz, 1H), 7.81 (td, J = 7.6, 1.5 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.34 (ddd, J = 7.2, 4.8, 1.5 Hz, 1H), 3.10 (t, J = 6.4 Hz, 2H), 2.60-2.56 (m, 2H), 2.28 (quintet, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 182.7, 170.4, 153.3, 148.2, 147.4, 147.2, 137.6, 137.5, 131.4, 131.3 (2C), 126.9, 124.2, 122.6 (2C), 120.6, 38.7, 24.2, 22.0; FT-IR (KBr) ν/cm^{-1} 3110, 3052, 2926, 1682, 1661, 1578, 1515, 1441, 1346, 1294, 1230, 1063, 1013, 948, 855, 747, 698; HR-MS (+EI) calcd for $C_{20}H_{14}N_2O_5$ (M^+) 362.0903, found 362.0902.

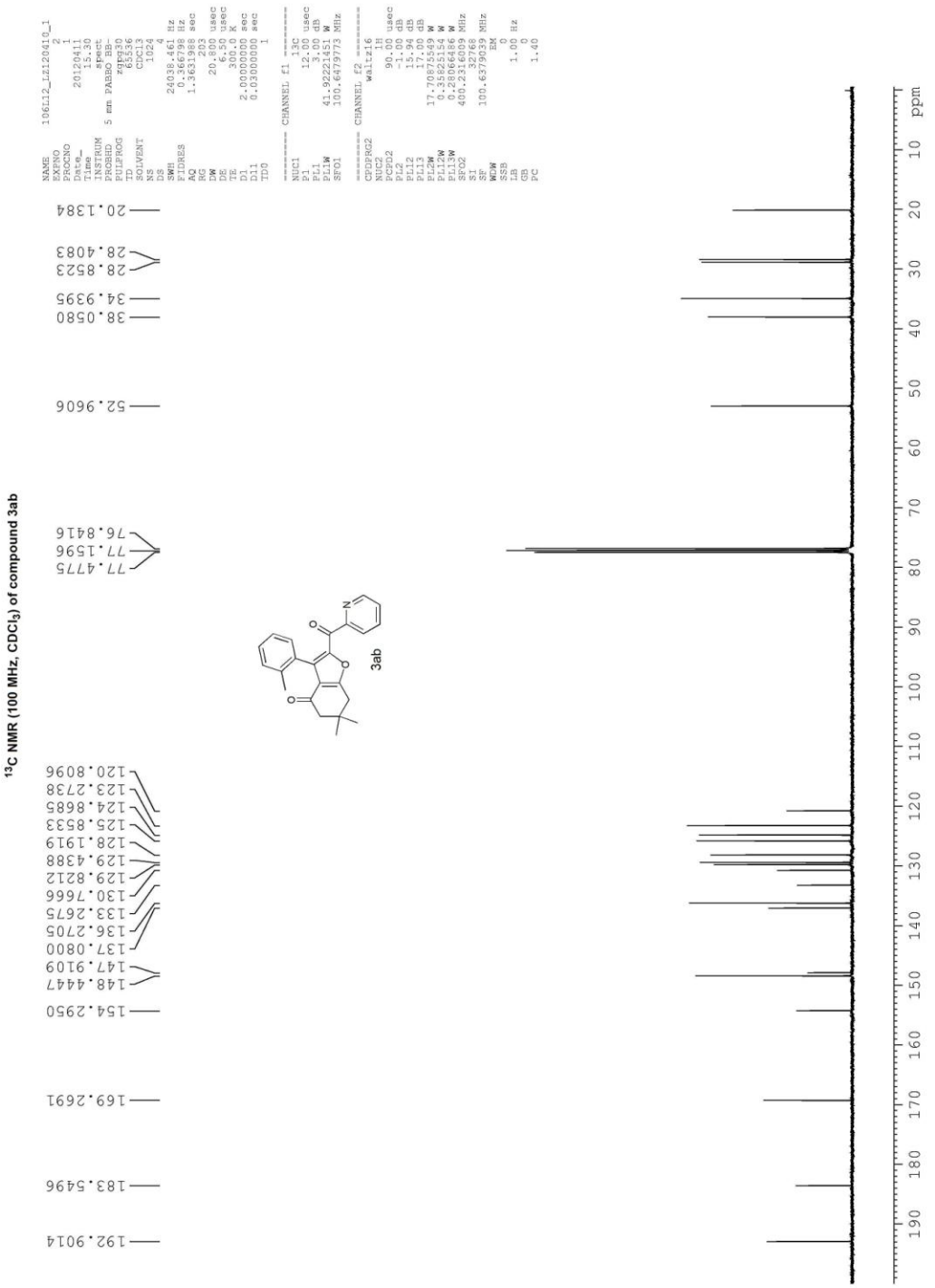
3-(3-Nitrophenyl)-2-picolinoyl-6,7-dihydrobenzofuran-4(5*H*)-one (3hm): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 8.08-8.05 (m, 2H), 7.82 (dt, J = 7.8, 0.9 Hz, 1H), 7.74 (td, J = 7.7, 1.6 Hz, 1H), 7.70 (dt, J = 7.8, 1.3 Hz, 1H), 7.40 (td, J = 7.8, 0.9 Hz, 1H), 7.25 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 3.09 (t, J = 6.4 Hz, 2H), 2.60-2.56 (m, 2H), 2.28 (quintet, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 183.2, 170.3, 153.8, 148.5, 147.42, 147.38, 137.0, 136.4, 132.3, 131.1, 128.4, 126.6, 125.4, 124.2, 123.0, 120.5, 38.7, 24.2, 22.1; FT-IR (KBr) ν/cm^{-1}

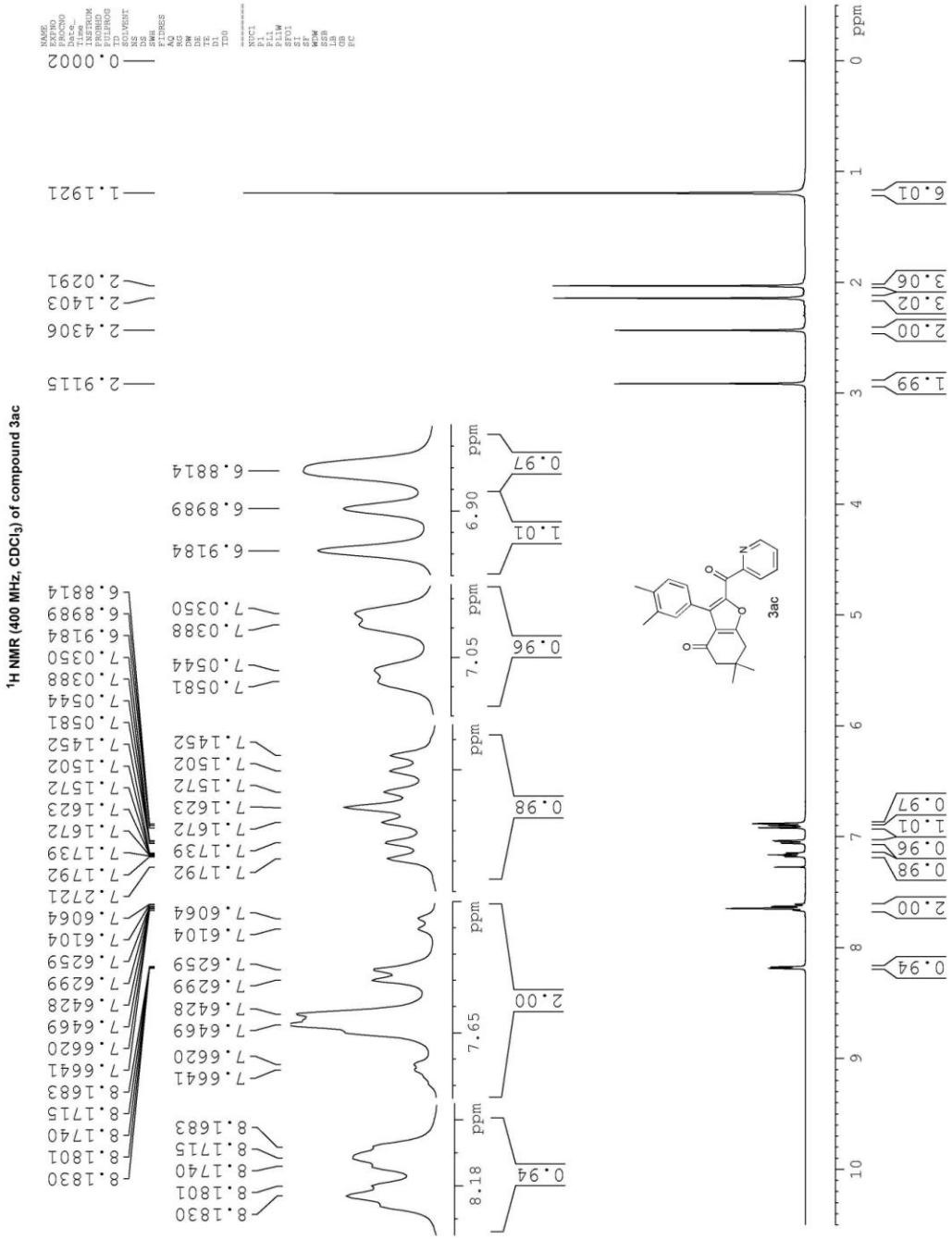
3081, 2955, 2877, 1686, 1655, 1582, 1524, 1478, 1445, 1410, 1347, 1229, 1065, 1014, 953, 863, 810, 741, 685; HR-MS (+EI) calcd for $C_{20}H_{14}N_2O_5$ (M^+) 362.0903, found 362.0905.

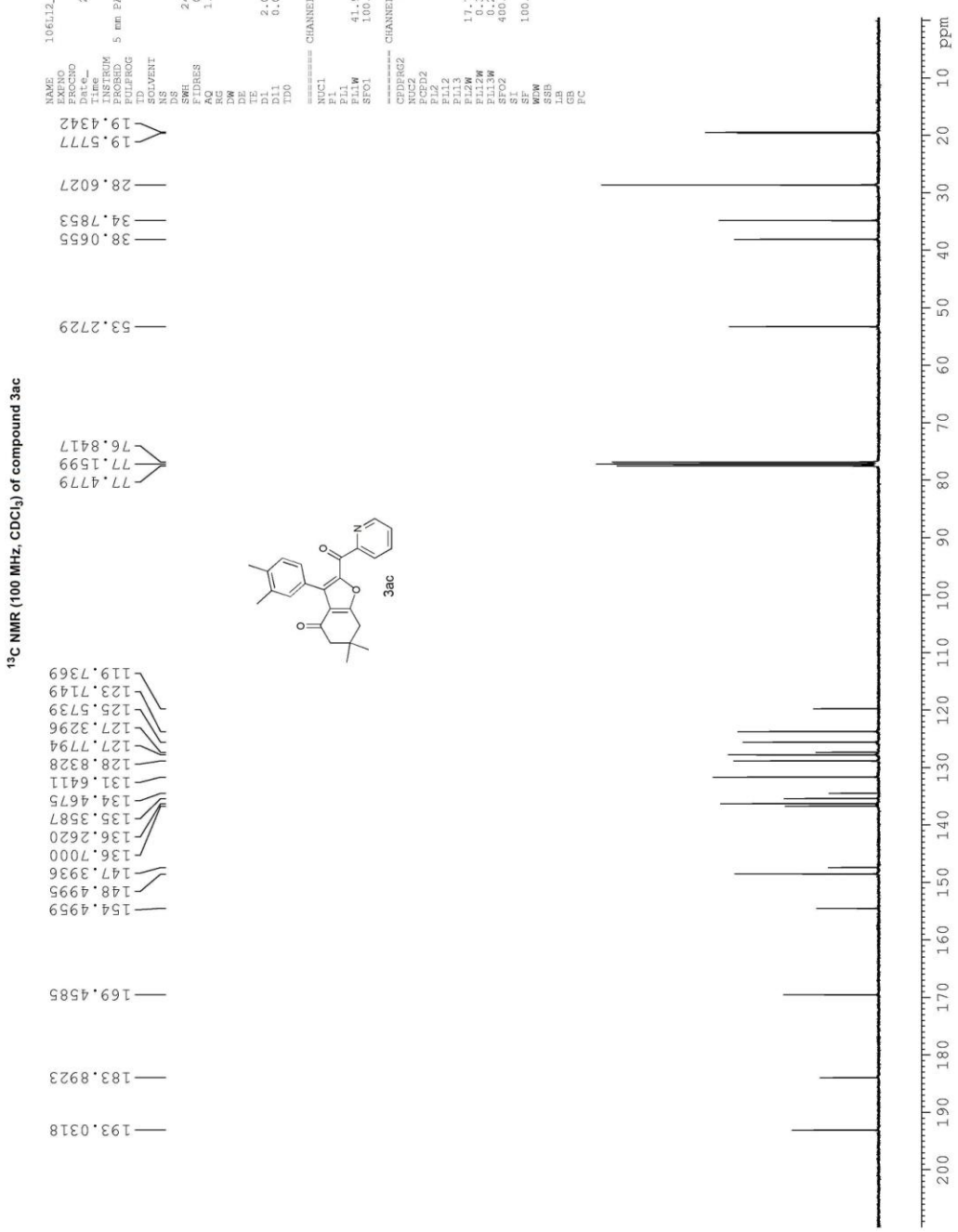

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3aa
3aa

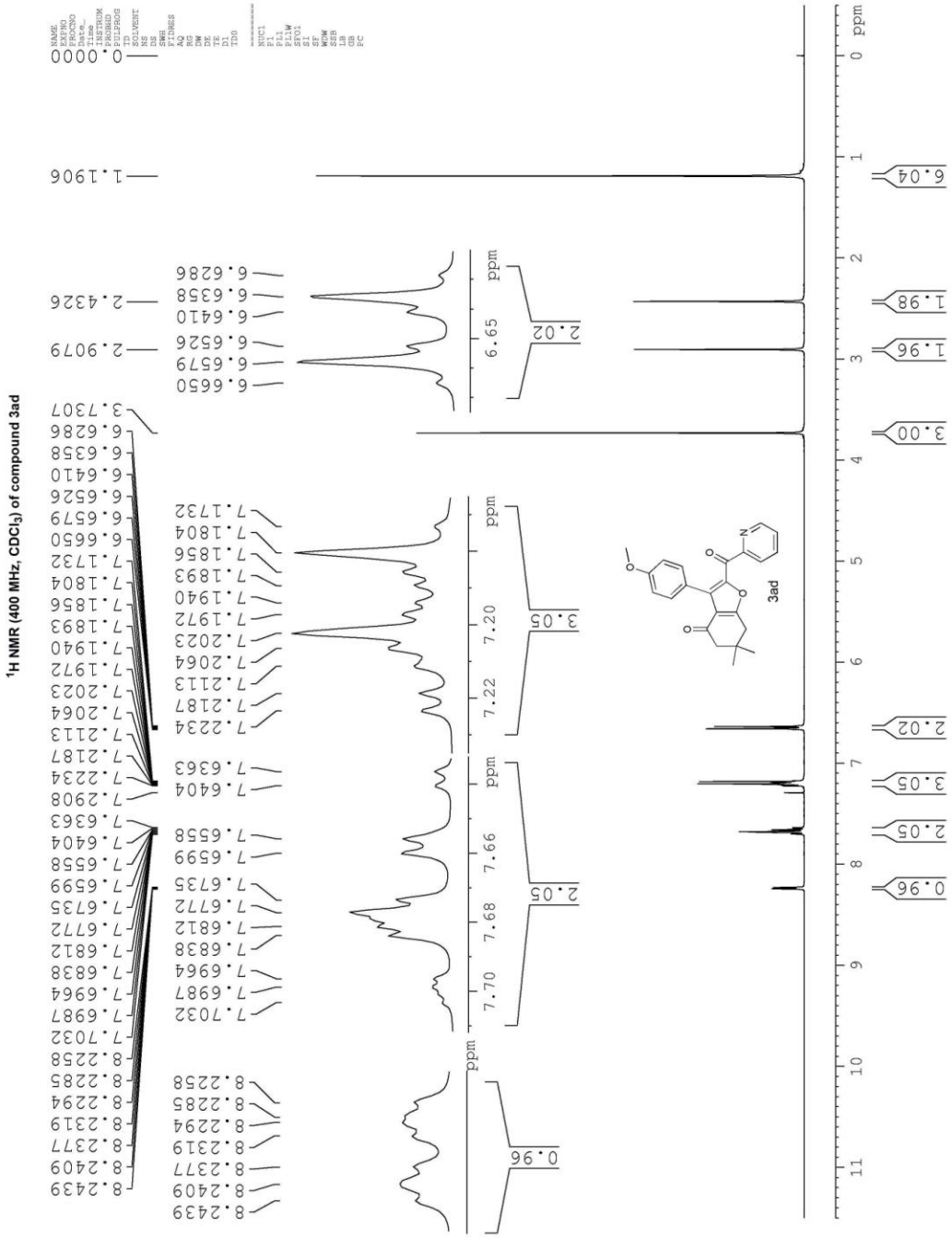

13C NMR (100 MHz, CDCl3) of compound 3aa
21.3378
28.6362
34.8148
38.0919
53.2945
76.8407
77.1589
77.4763
119.7805
123.8632
125.8170
127.0952
128.1575
130.2914
134.2919
136.4762
138.0780
147.4079
148.5591
154.3427
169.4394
183.8694
193.0907
3aa
ppm

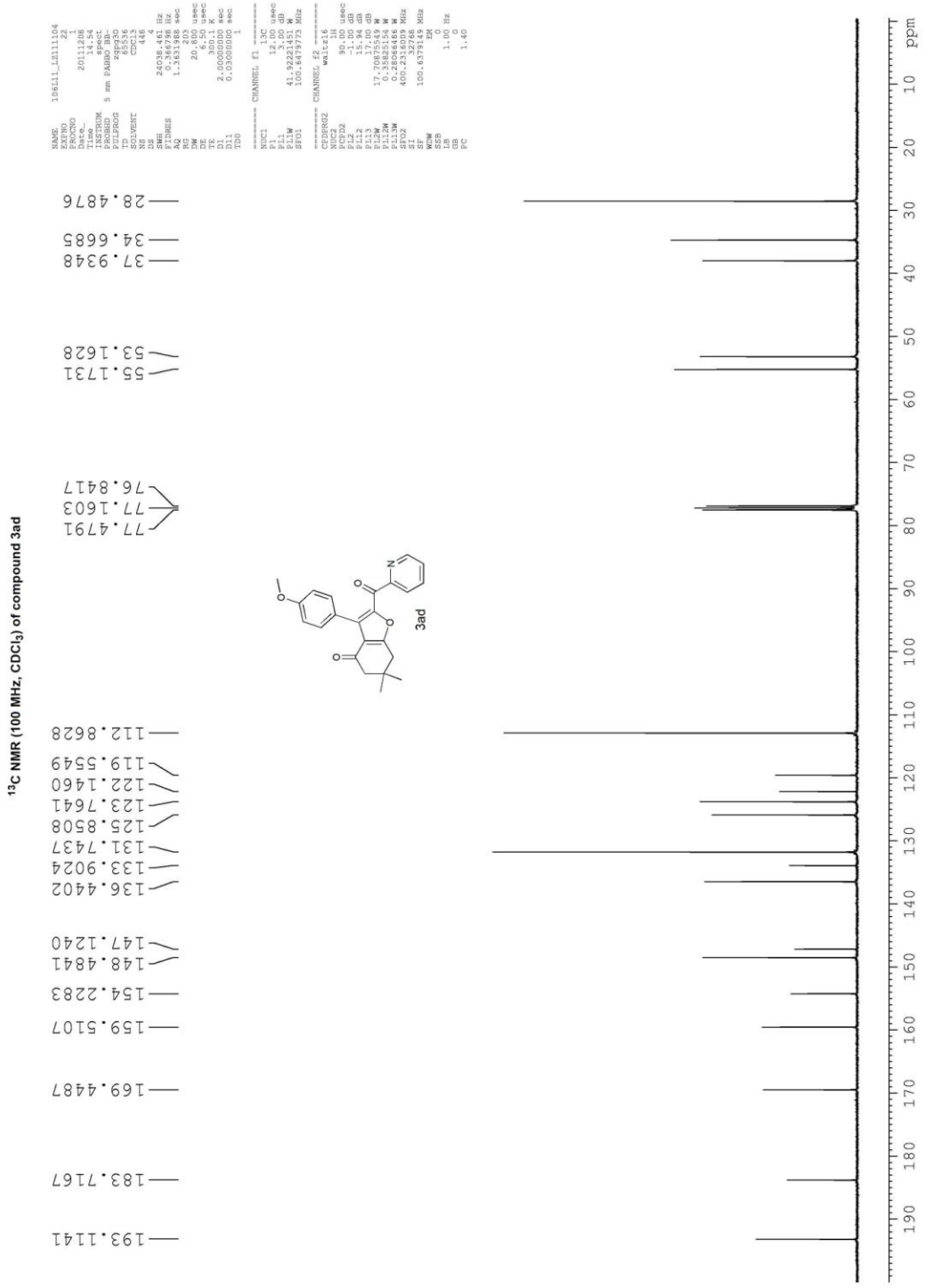

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ab
3ab
ppm

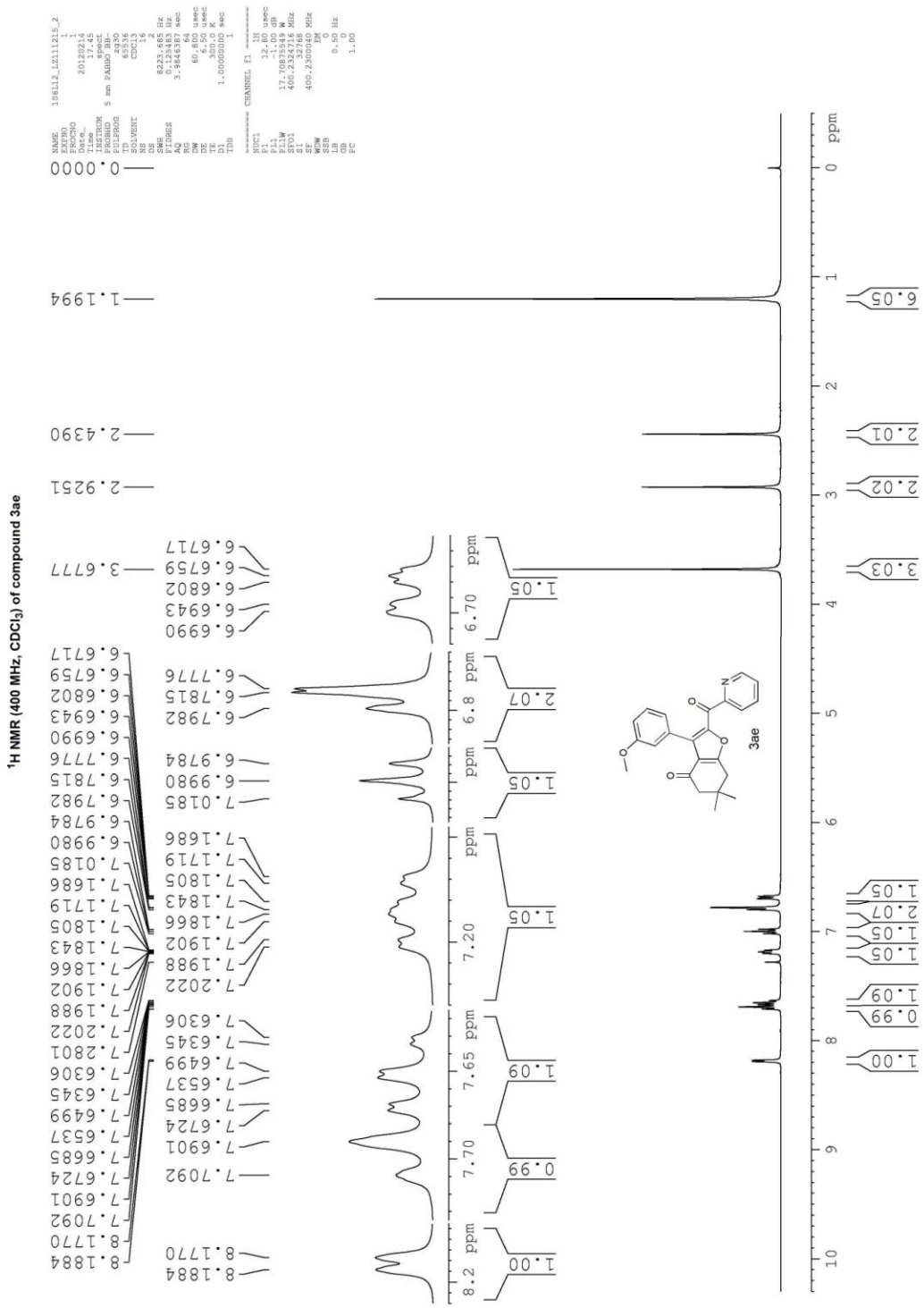

13C NMR (100 MHz, CDCl3) of compound 3ab
3ab
20.1384
28.4083
28.8523
34.9395
38.0580
52.9606
76.8416
77.1596
77.4775
120.8096
123.2738
124.8685
125.8533
128.1919
129.4388
129.8212
130.7666
133.2675
136.2705
137.0800
147.9109
148.4447
154.2950
169.2691
183.5496
192.9014
ppm

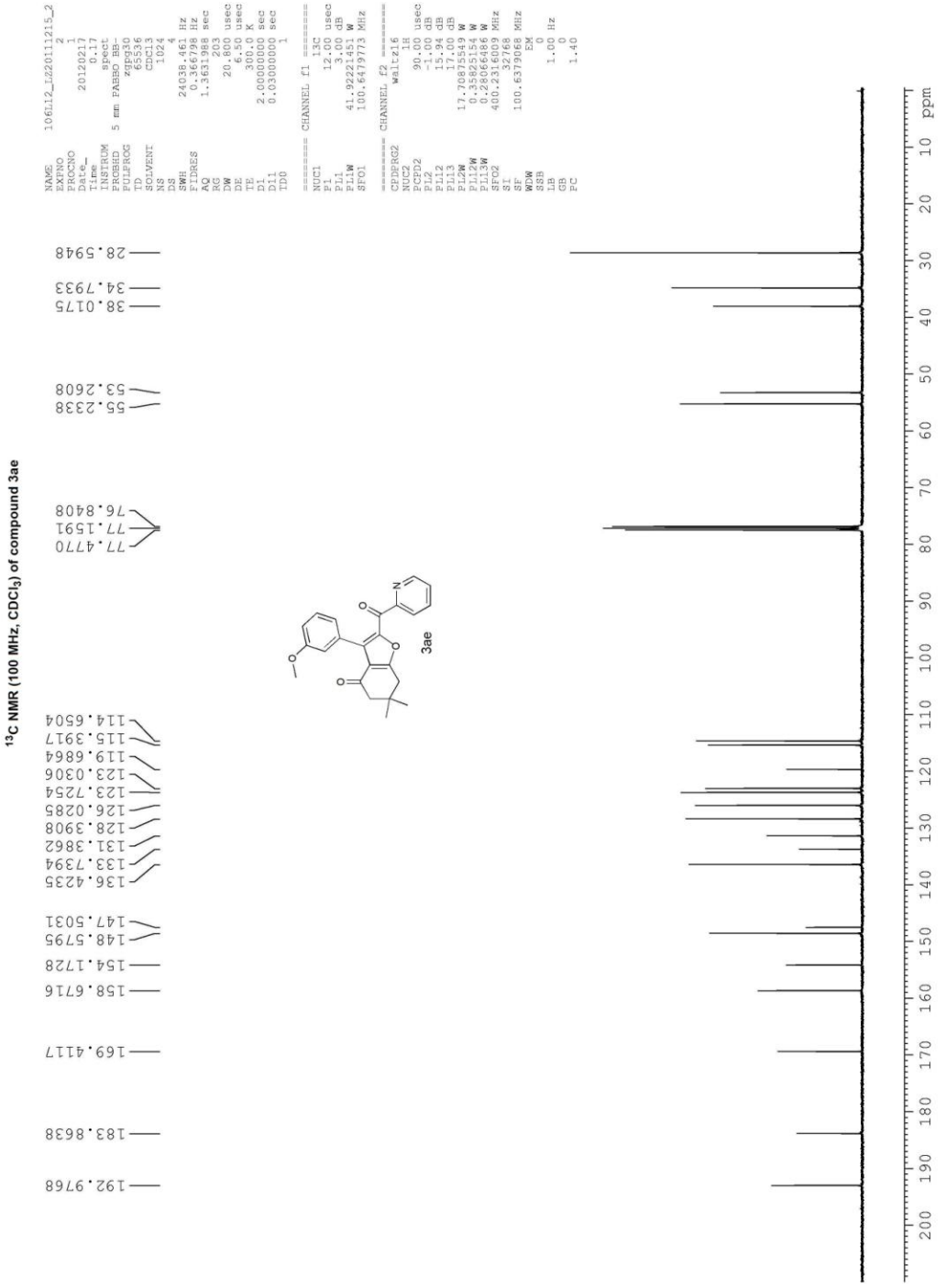

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ac
3ac

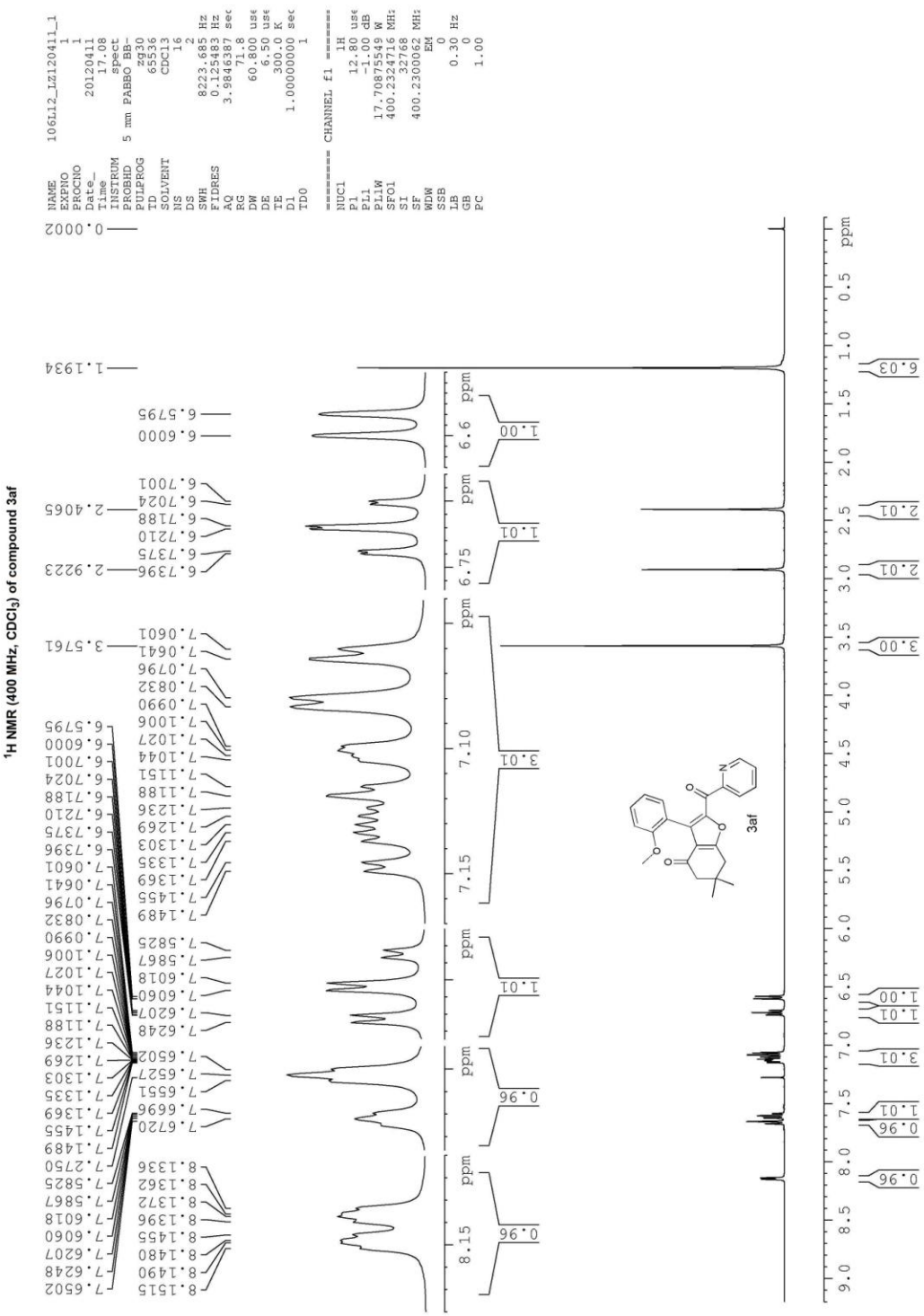

^{13}C NMR (100 MHz, CDCl$_3$) of compound 3ac
19.4342
19.5777
28.6027
34.7853
38.0655
53.2729
76.8417
77.1599
77.4779
119.7369
123.7149
125.5739
127.3296
127.7794
128.8328
131.6411
134.4675
135.3587
136.2620
136.7000
147.3936
148.4995
154.4959
169.4585
183.8923
193.0318
3ac
ppm

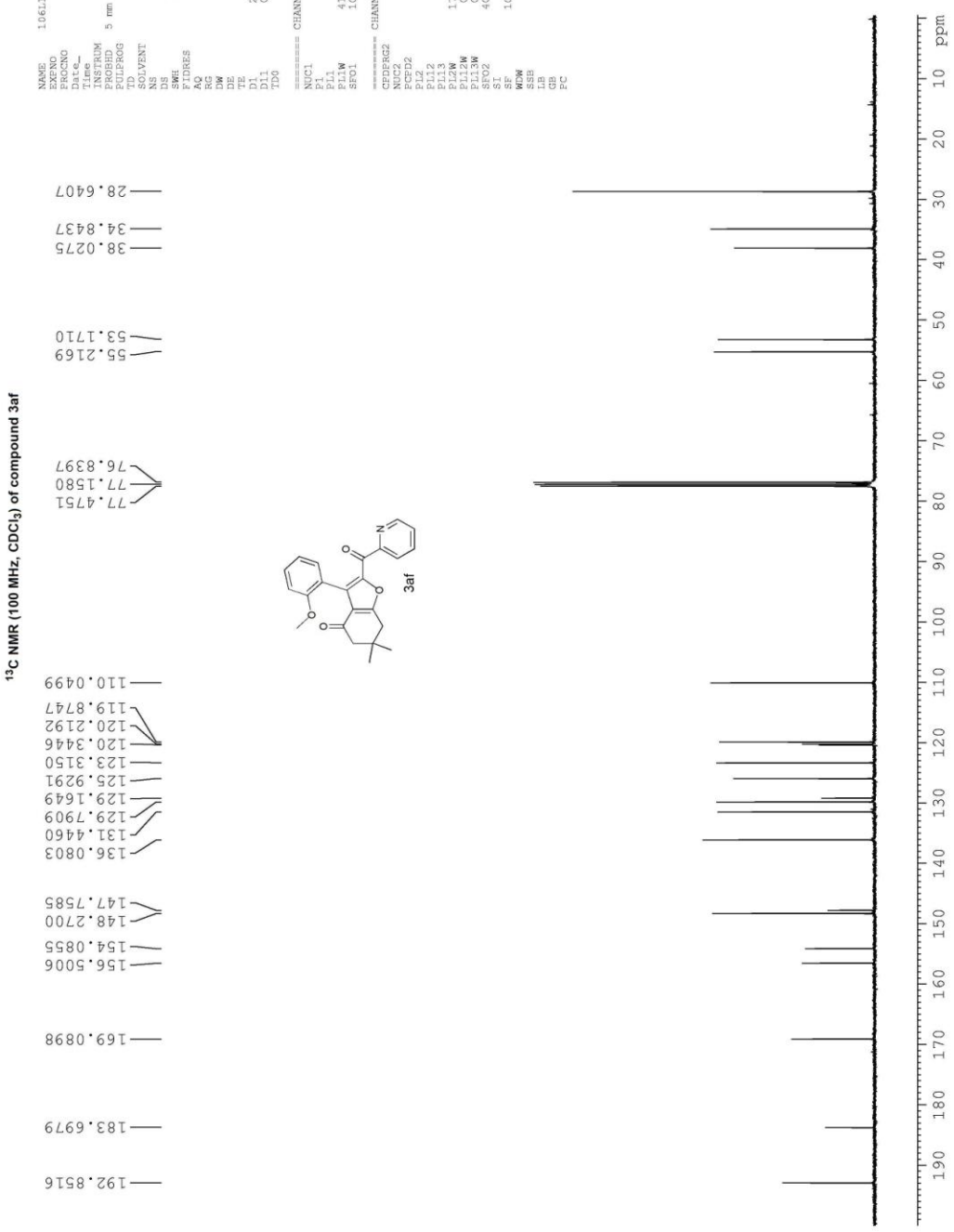

^{1}H NMR (400 MHz, CDCl$_3$) of compound 3ad
3ad

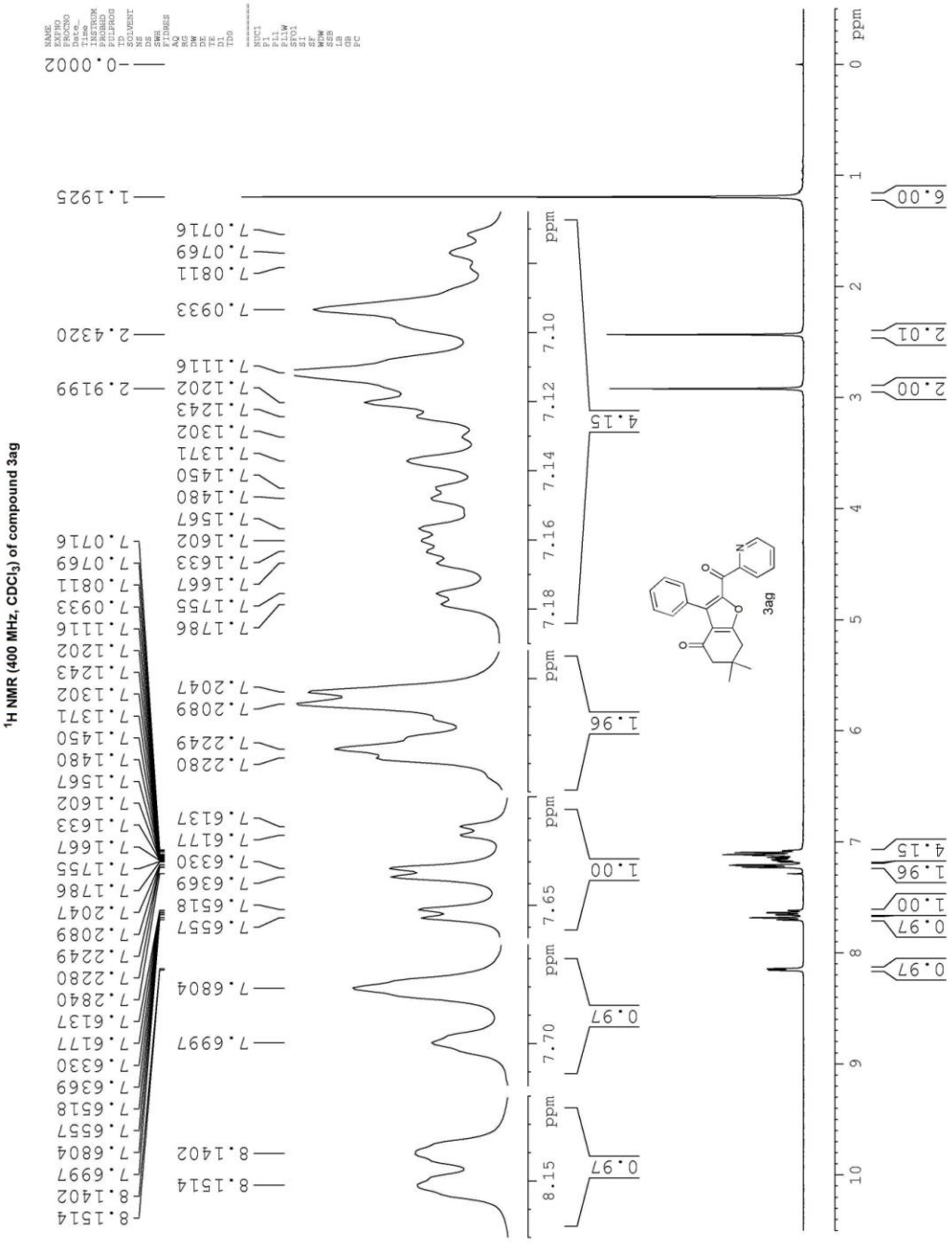

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ad
28.4876
34.6685
37.9348
53.1628
55.1731
76.8417
77.1603
77.4791
112.8628
119.5549
122.1460
123.7641
125.8508
131.7437
133.9024
136.4402
147.1240
148.4841
154.2283
159.5107
169.4487
183.7167
193.1141
3ad
ppm

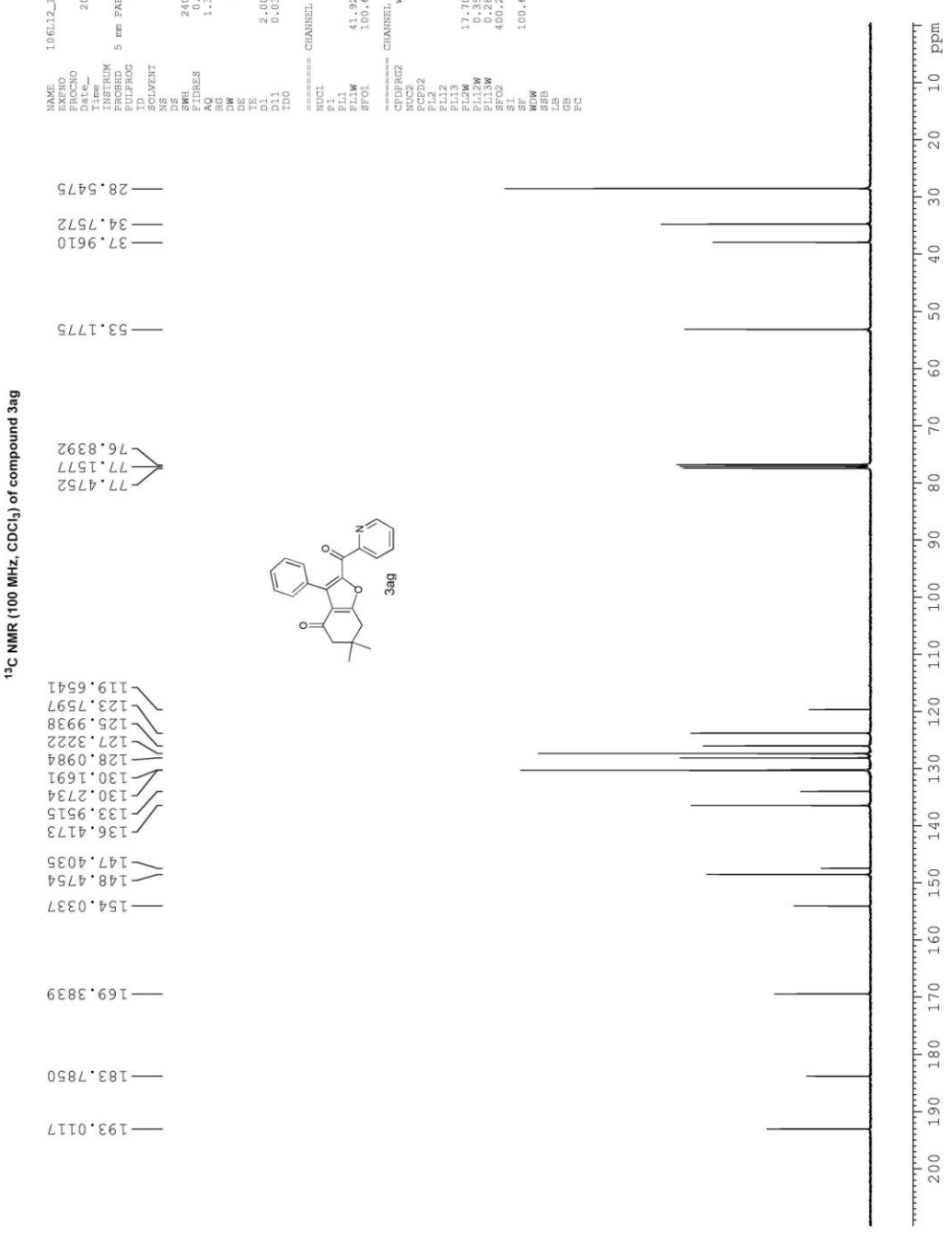

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ae
3ae
ppm

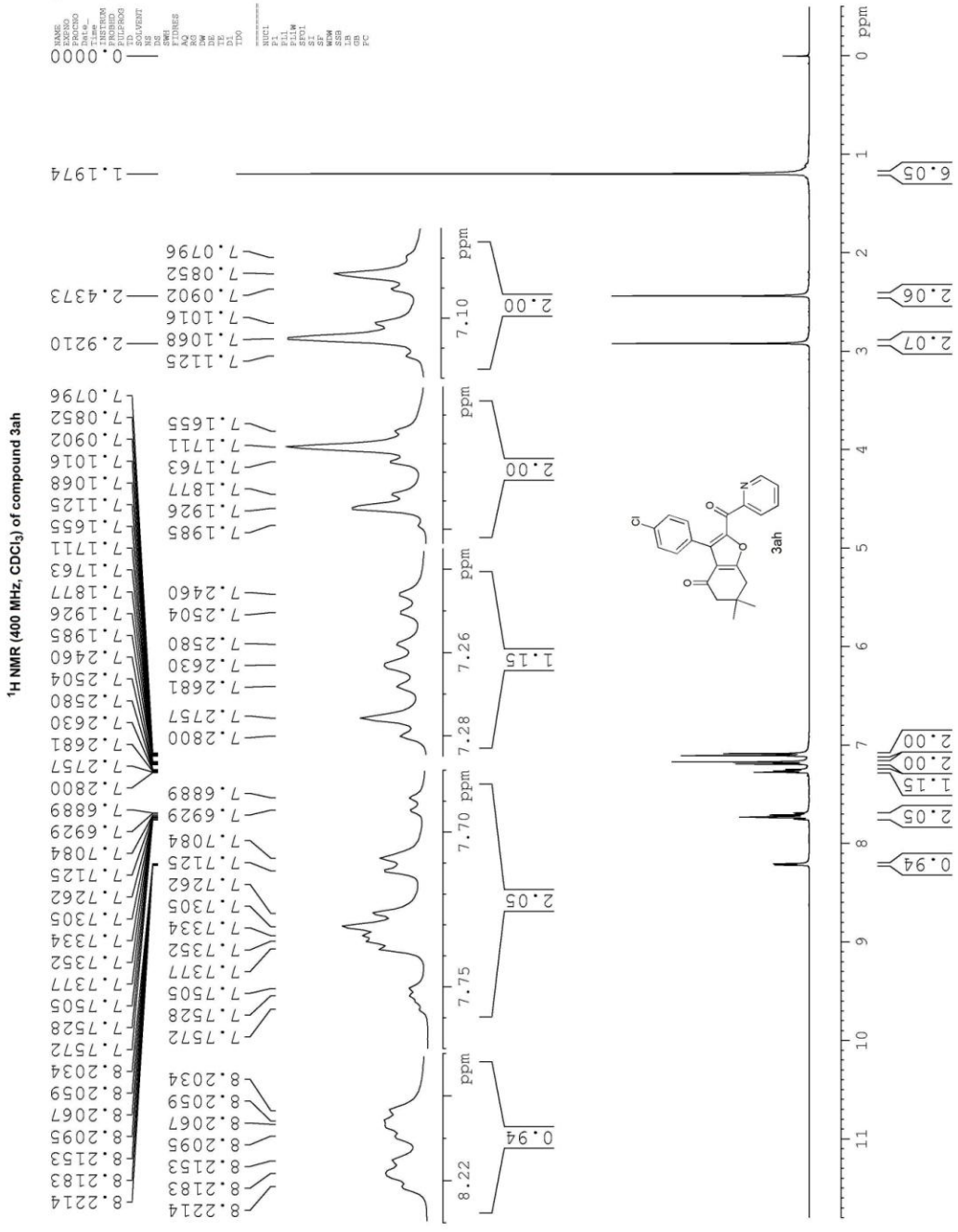

13C NMR (100 MHz, CDCl3) of compound 3ae
3ae
28.5948
34.7933
38.0175
53.2608
55.2338
76.8408
77.1591
77.4770
114.6504
115.3917
119.6864
123.0306
123.7254
126.0285
128.3908
131.3862
133.7394
136.4235
147.5031
148.5795
154.1728
158.6716
169.4117
183.8638
192.9768
ppm

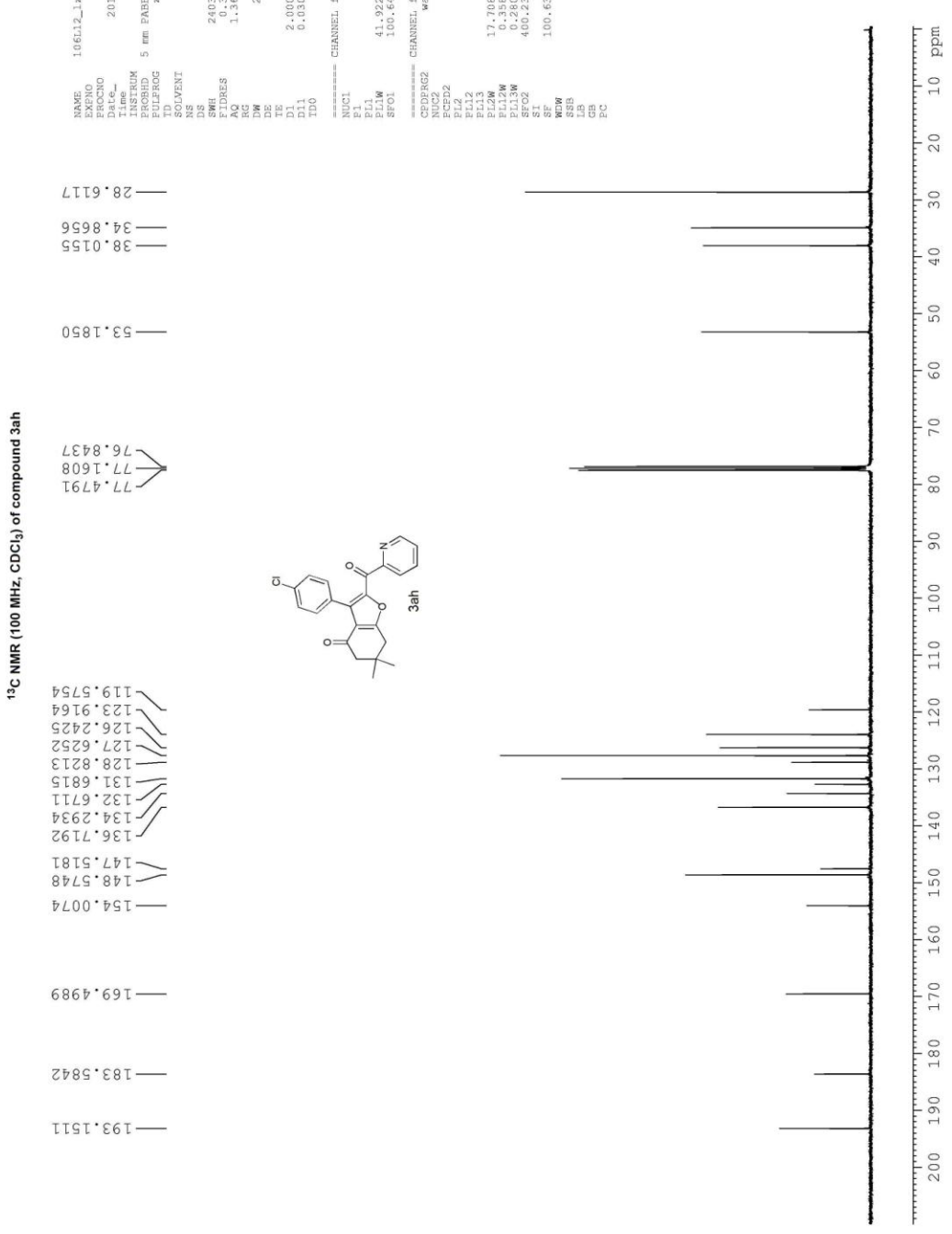

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3af
3af

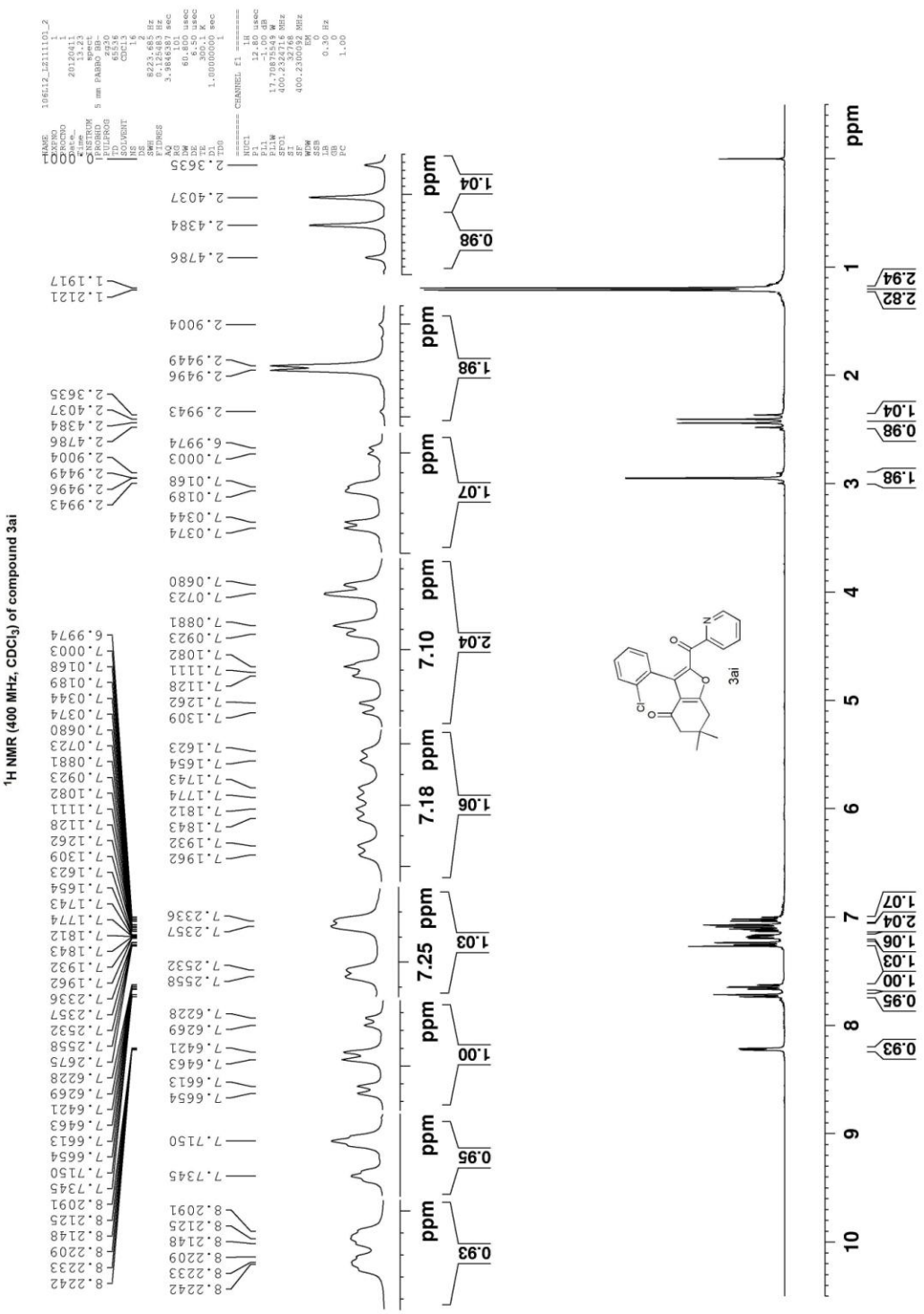

13C NMR (100 MHz, CDCl3) of compound 3af
3af
28.6407
34.8437
38.0275
53.1710
55.2169
76.8397
77.1580
77.4751
110.0499
119.8747
120.2192
120.3446
123.3150
125.9291
129.1649
129.7909
131.4460
136.0803
147.7585
148.2700
154.0855
156.5006
169.0898
183.6979
192.8516
ppm

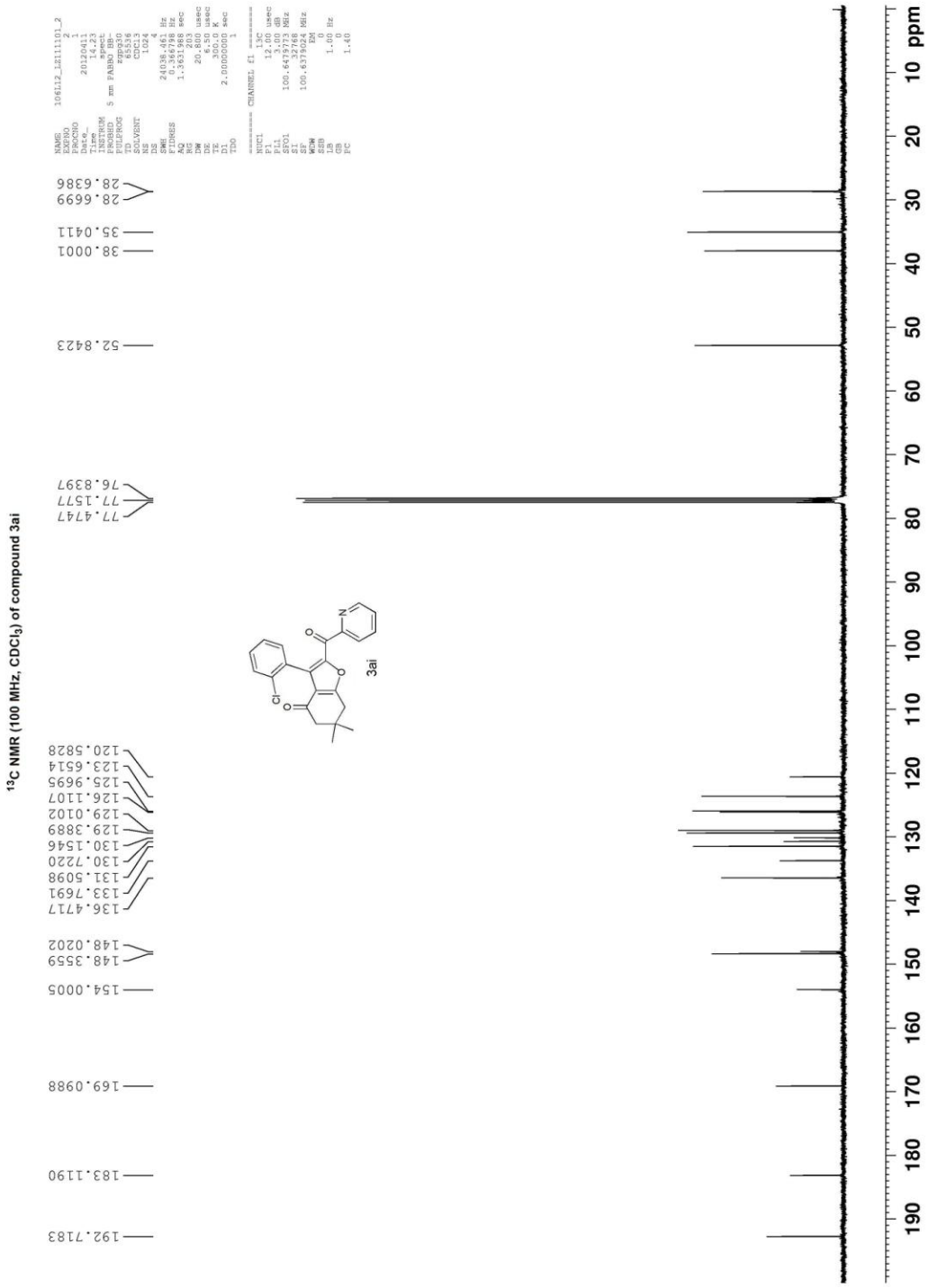

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ag
3ag

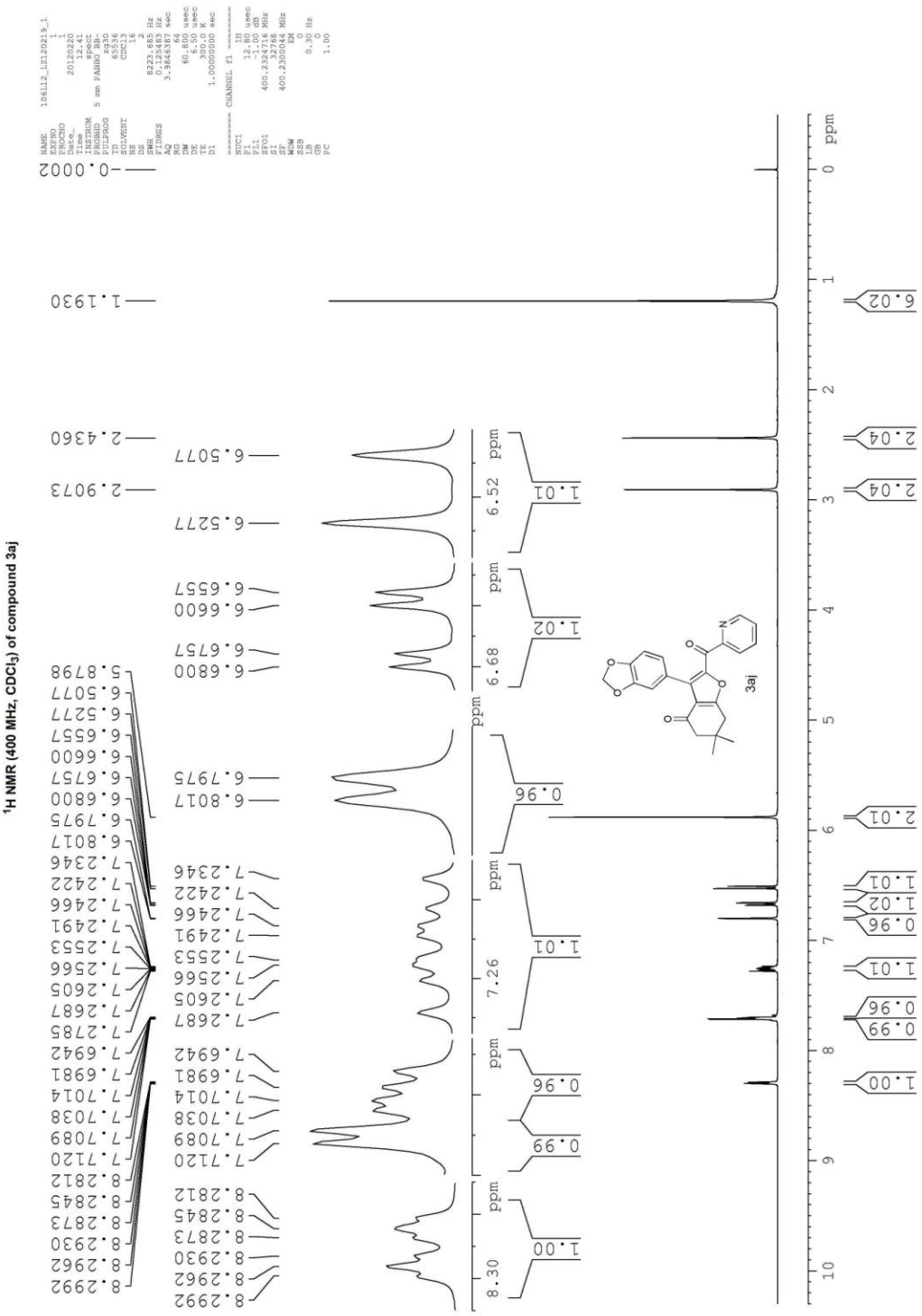

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ag
28.5475
34.7572
37.9610
53.1775
76.8392
77.1577
77.4752
119.6541
123.7597
125.9938
127.3222
128.0984
130.1691
130.2734
133.9515
136.4173
147.4035
148.4754
154.0337
169.3839
183.7850
193.0117
3ag
ppm

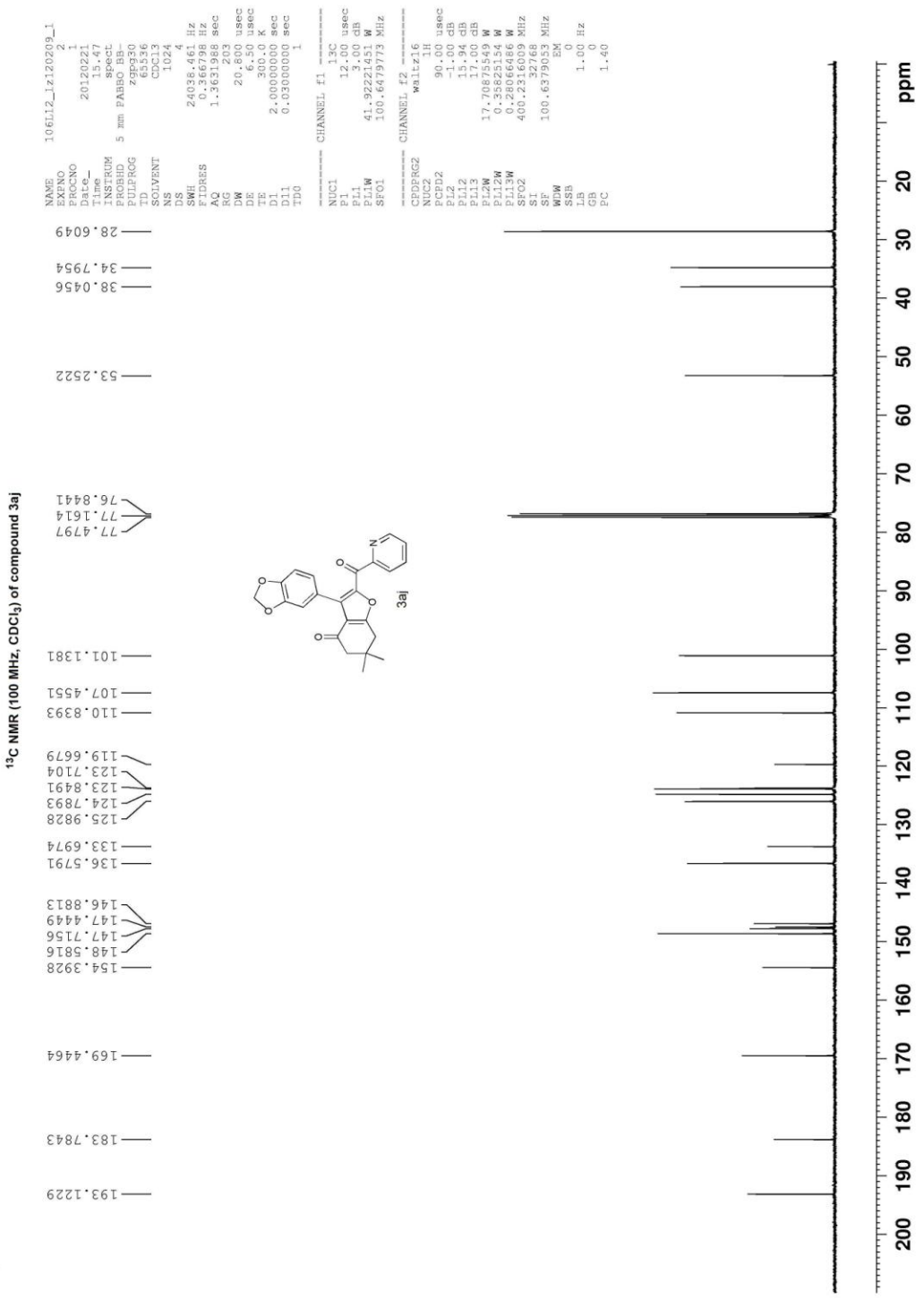

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ah
3ah

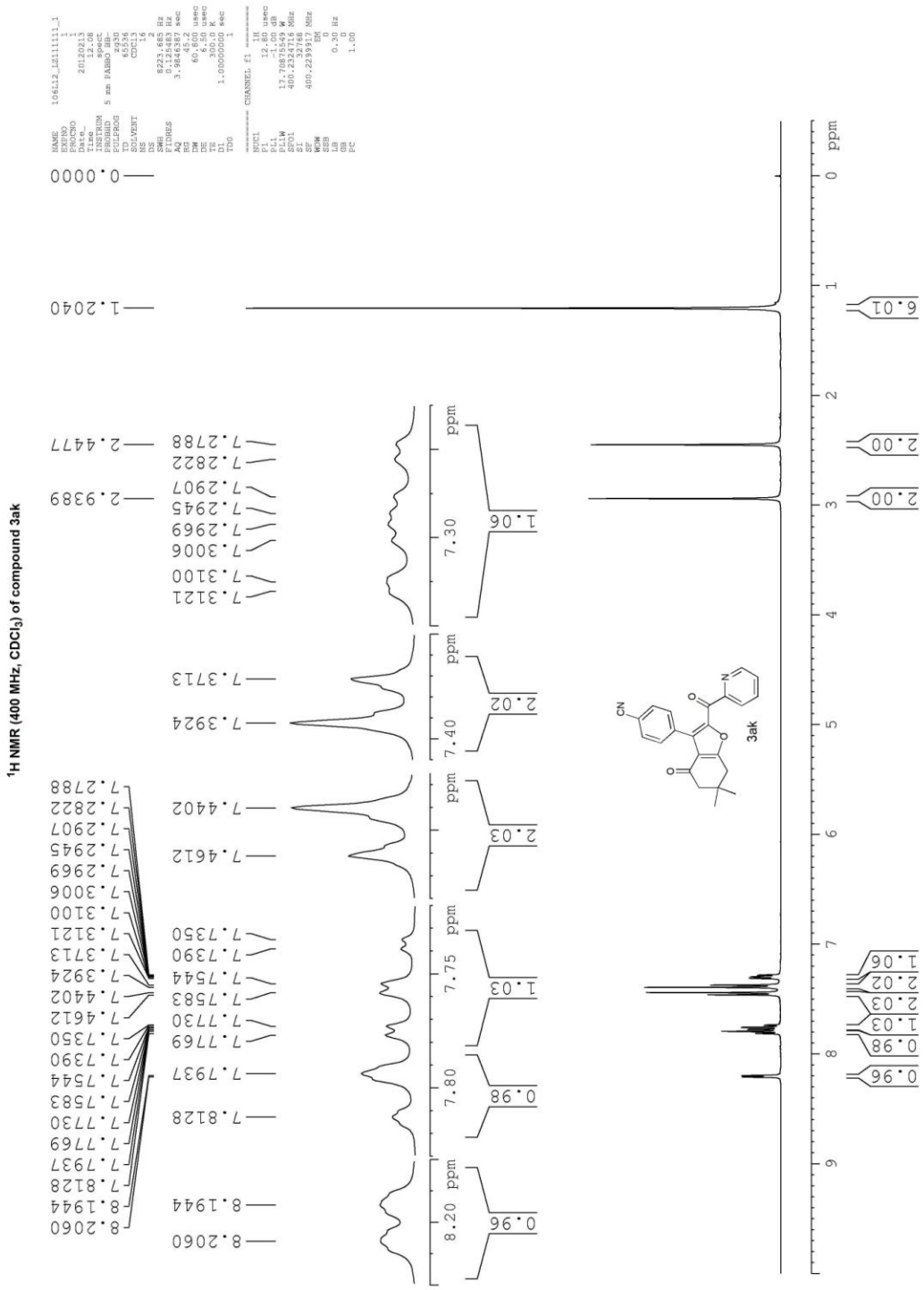

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ah
3ah
28.6117
34.8656
38.0155
53.1850
76.8437
77.1608
77.4791
119.5754
123.9164
126.2425
127.6252
128.8213
131.6815
132.6711
134.2934
136.7192
147.5181
148.5748
154.0074
169.4989
183.5842
193.1511
ppm

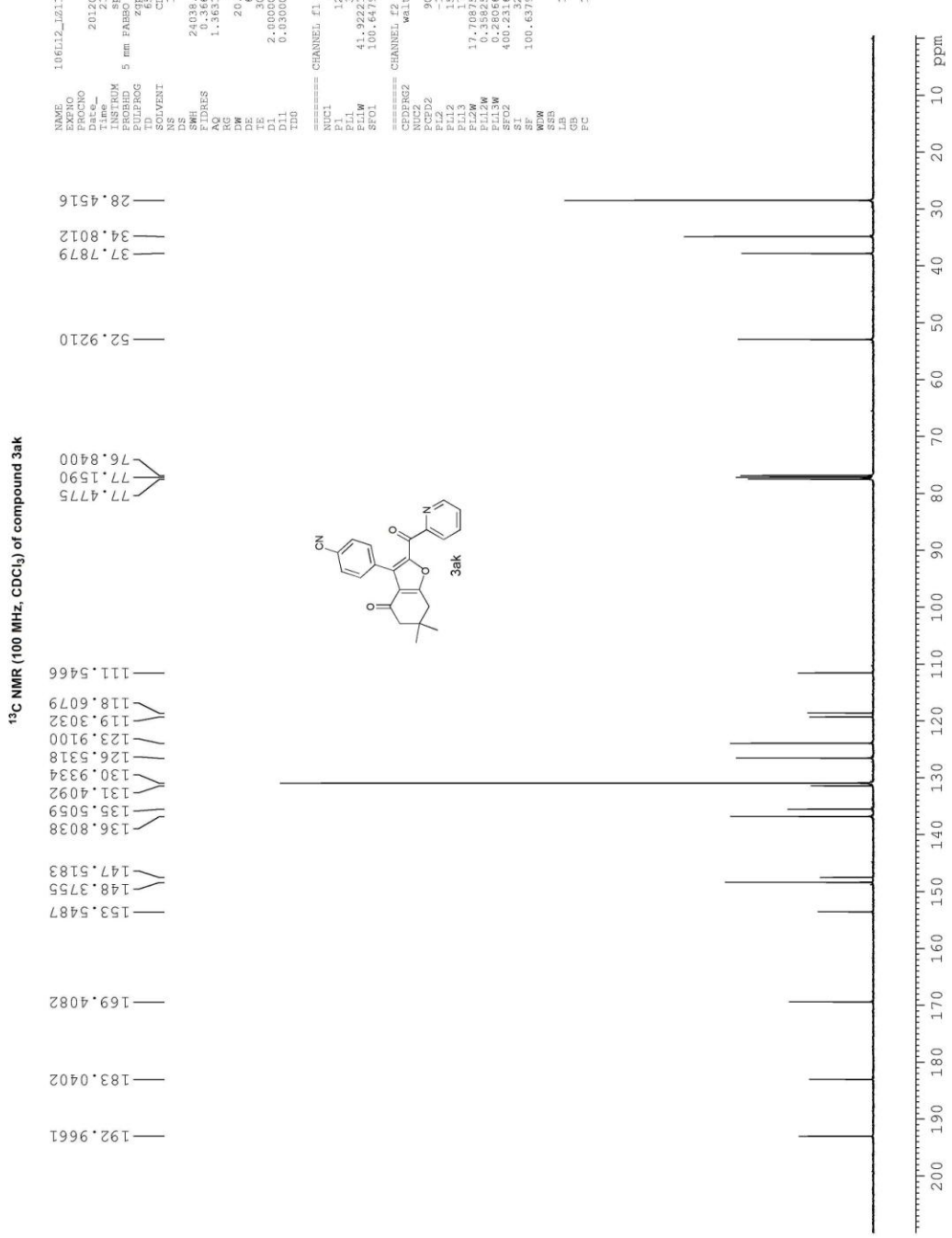

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ai
3ai
ppm

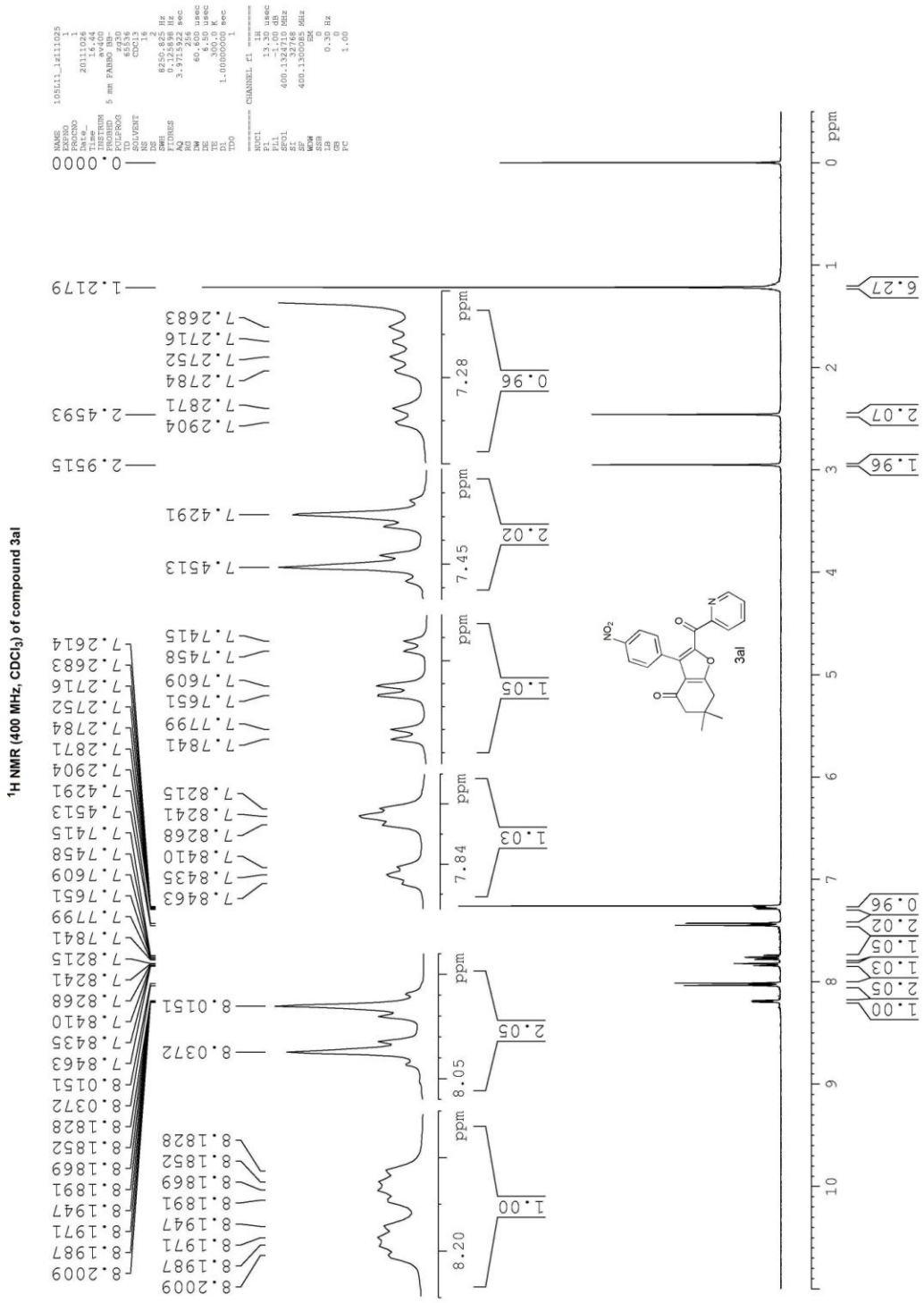

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ai
3ai
192.7183
183.1190
169.0988
154.0005
148.3559
148.0202
136.4717
133.7691
131.5098
130.7220
130.1546
129.3889
129.0102
126.1107
125.9695
123.6514
120.5828
77.4747
77.1577
76.8397
52.8423
38.0001
35.0411
28.6699
28.6386
ppm

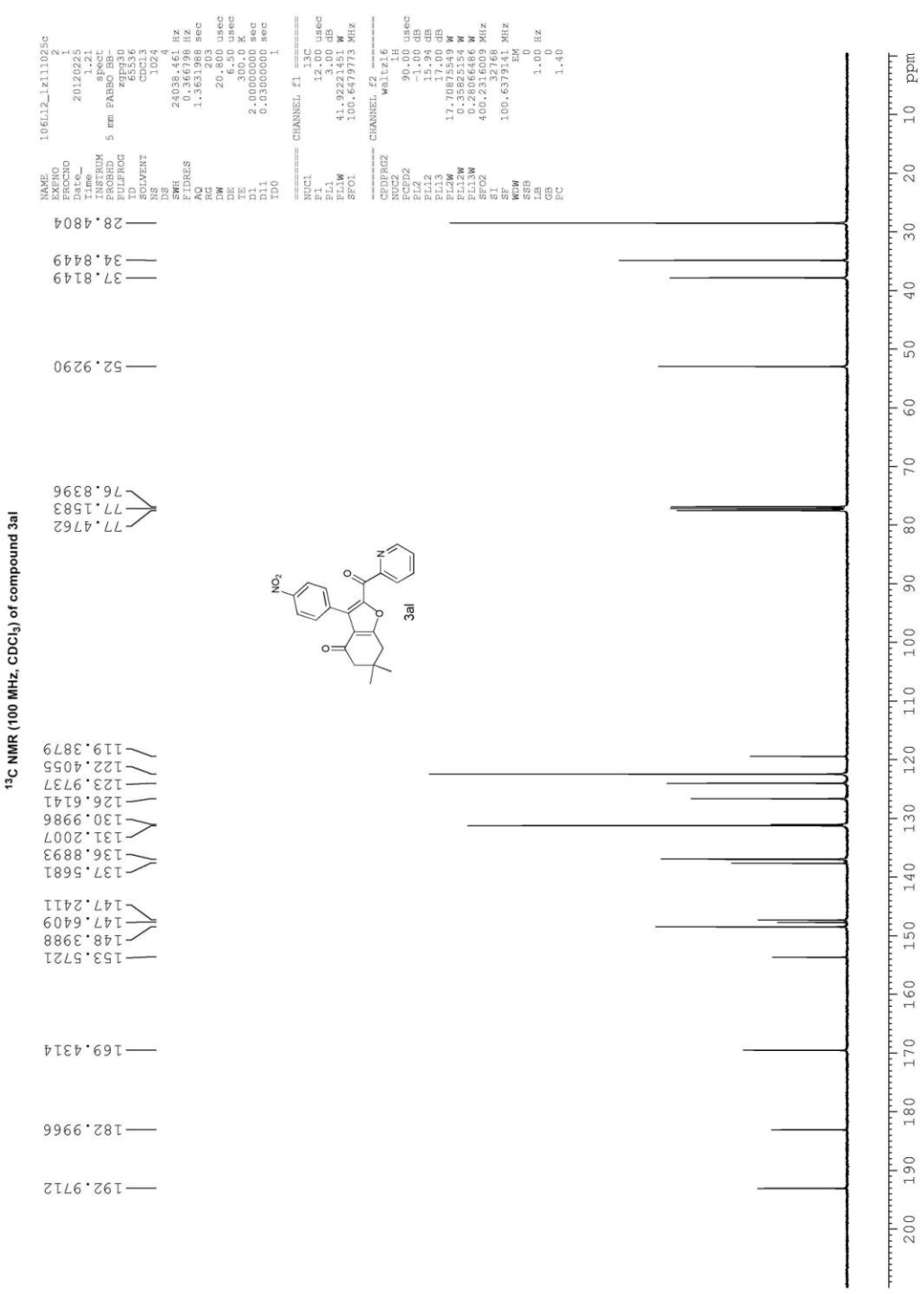

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3aj
3aj

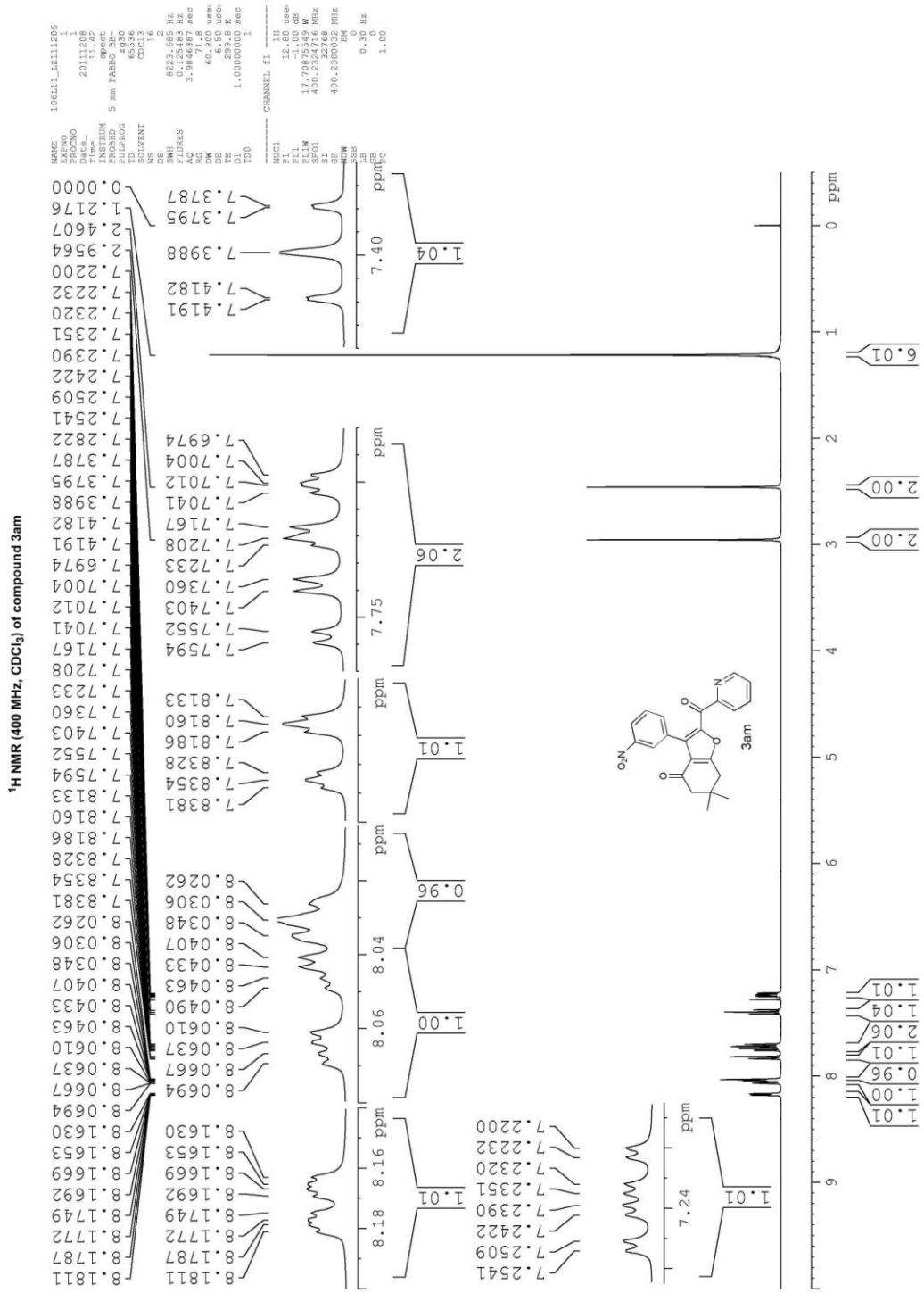

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3aj
3aj
ppm

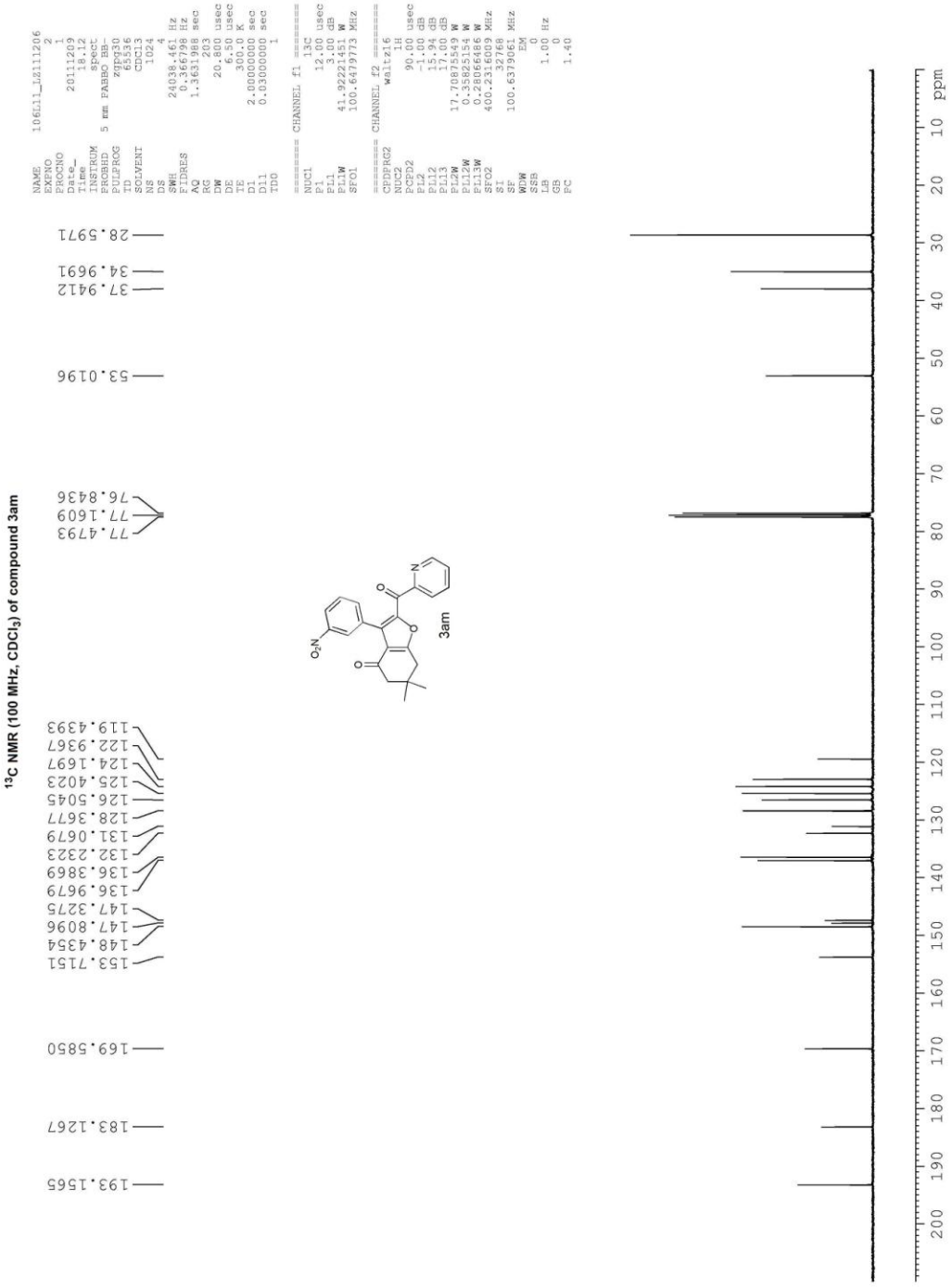

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ak
3ak
CN
O
N
O
O
ppm
8.20
7.80
7.75
7.40
7.30
0
1
2
3
4
5
6
7
8
9
6.01
2.00
2.00
1.06
0.98
2.02
2.03
1.03
0.96
1.2040
2.4477
2.9389
7.2788
7.2822
7.2907
7.2945
7.2969
7.3006
7.3100
7.3121
7.3713
7.3924
7.4402
7.4612
7.7350
7.7390
7.7544
7.7583
7.7730
7.7769
7.7937
7.8128
8.1944
8.2060

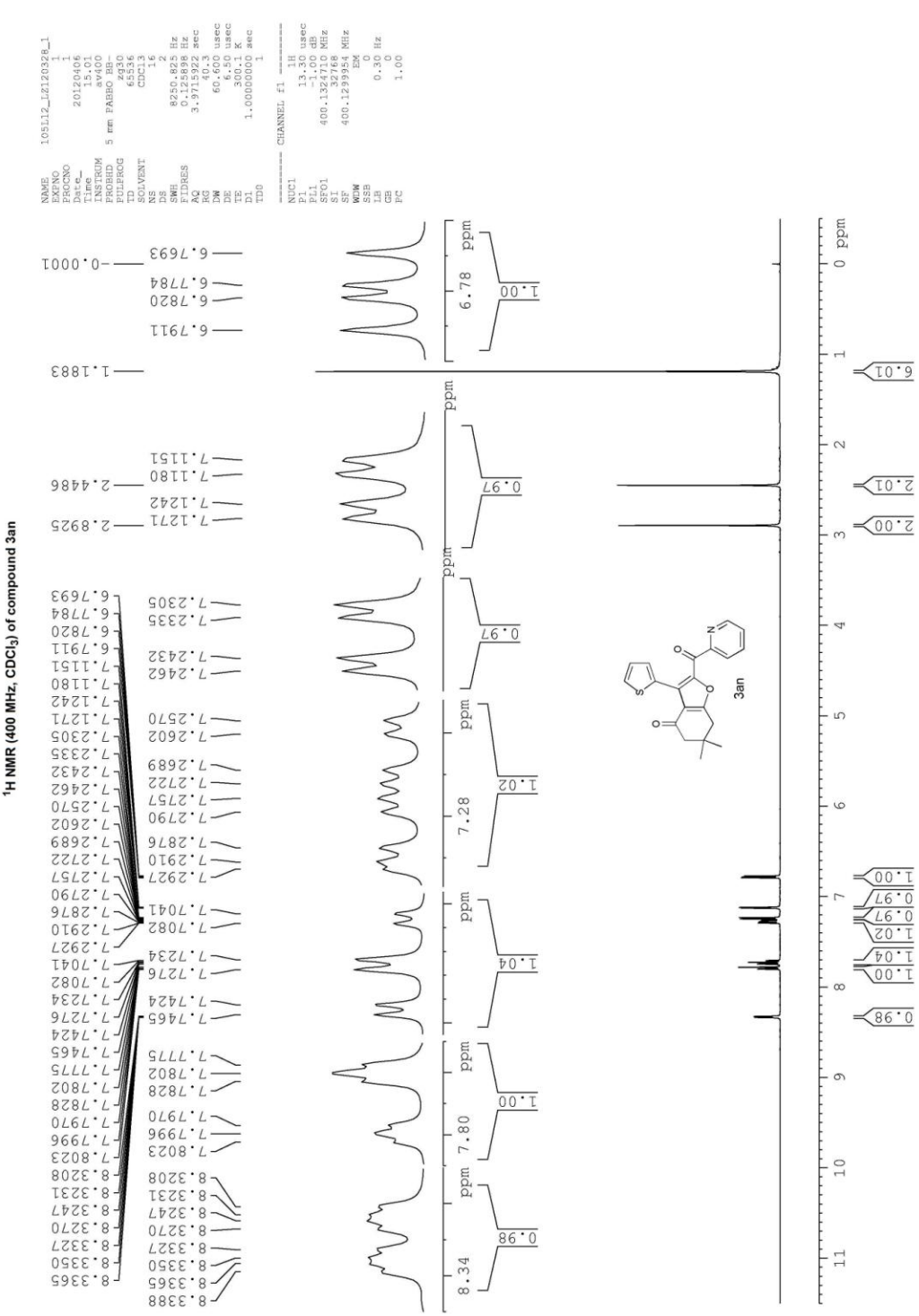

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ak
28.4516
34.8012
37.7879
52.9210
76.8400
77.1590
77.4775
111.5466
118.6079
119.3032
123.9100
126.5318
130.9334
131.4092
135.5059
136.8038
147.5183
148.3755
153.5487
169.4082
183.0402
192.9661
3ak
ppm

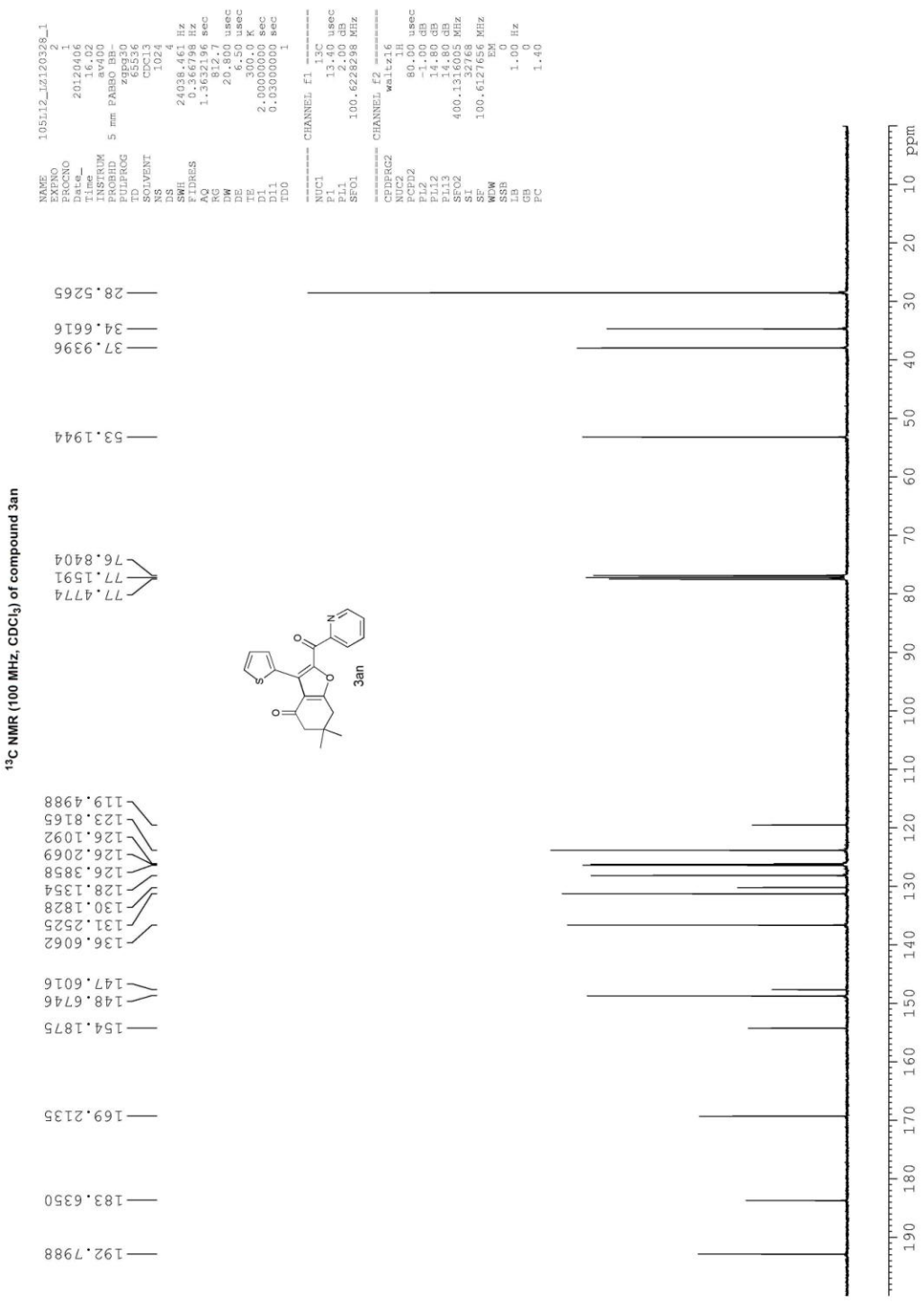

^{1}H NMR (400 MHz, CDCl$_3$) of compound 3al
3al

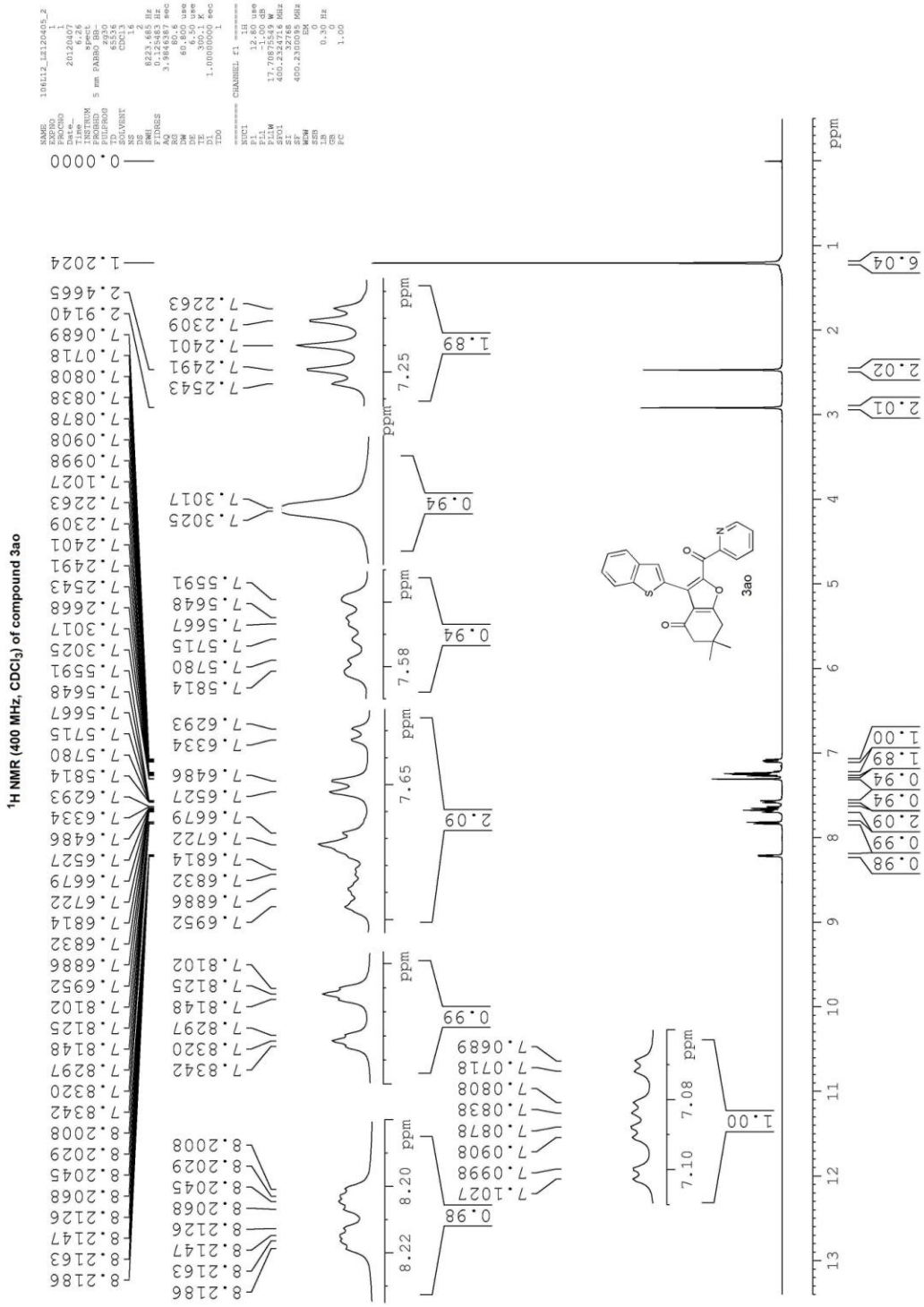

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3al
28.4804
34.8449
37.8149
52.9290
76.8396
77.1583
77.4762
119.3879
122.4055
123.9737
126.6141
130.9986
131.2007
136.8893
137.5681
147.2411
147.6409
148.3988
153.5721
169.4314
182.9966
192.9712
3al
ppm

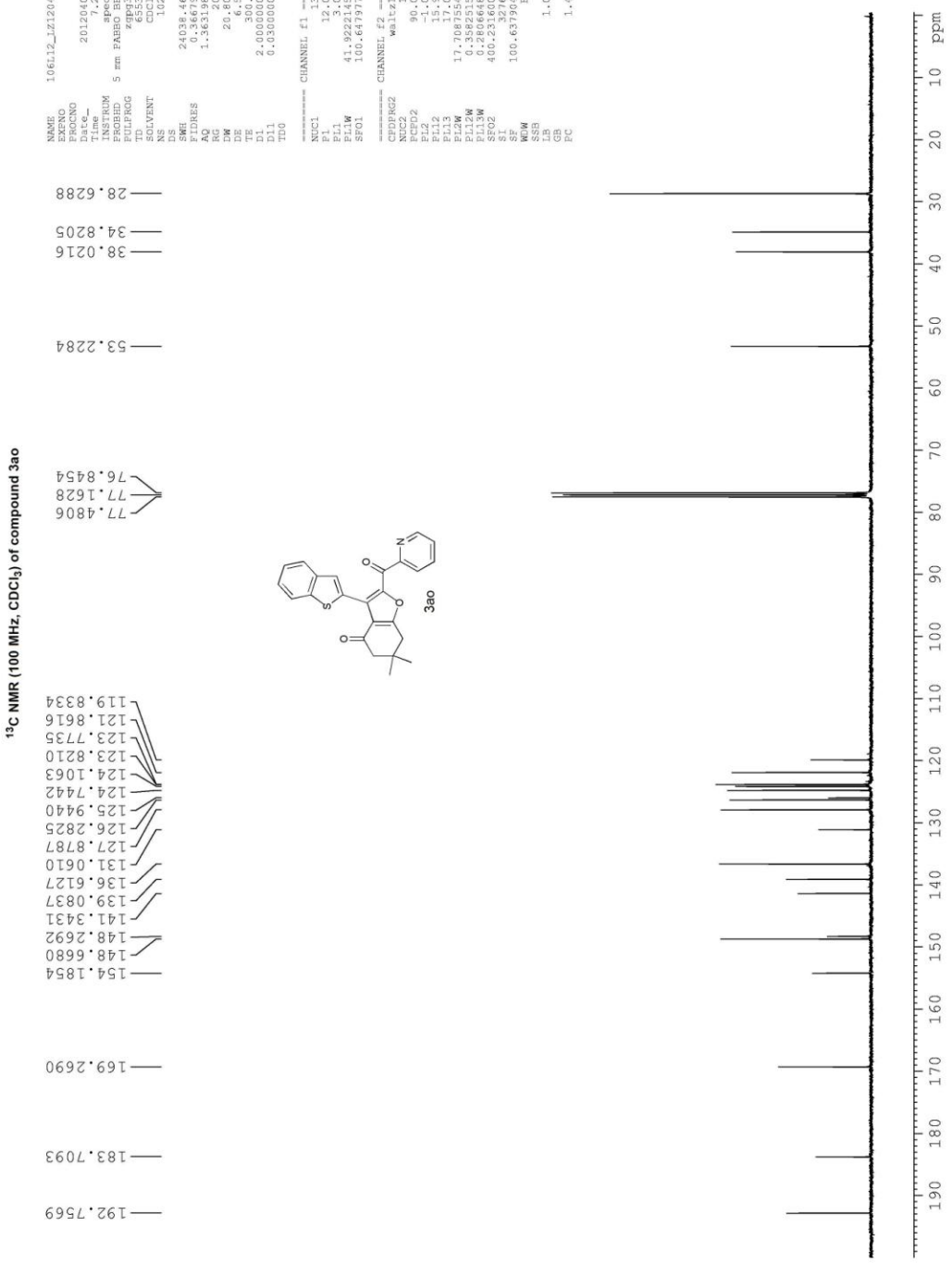

^{1}H NMR (400 MHz, CDCl$_3$) of compound 3am
3am

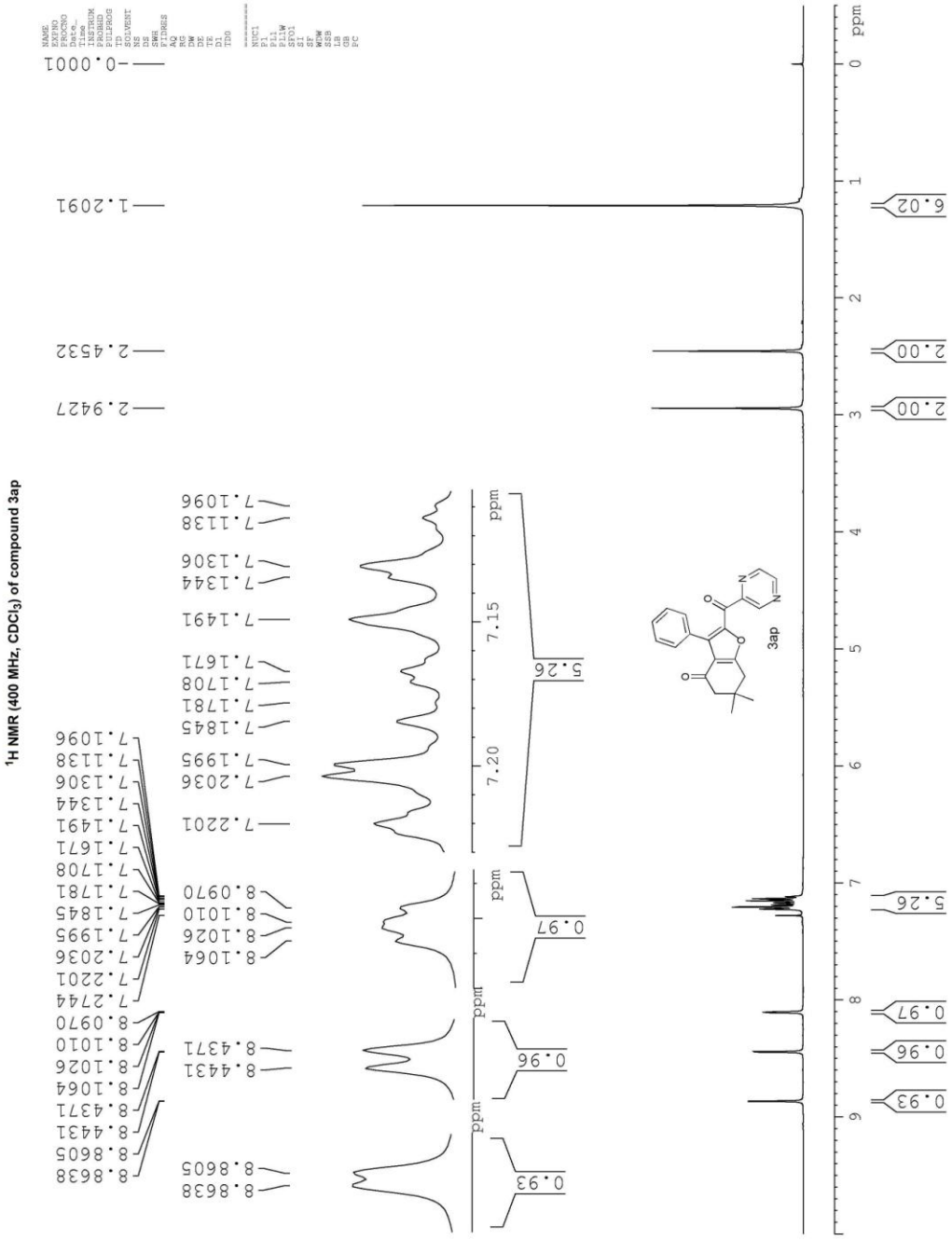

13C NMR (100 MHz, CDCl3) of compound 3am
3am
28.5971
34.9691
37.9412
53.0196
76.8436
77.1609
77.4793
119.4393
122.9367
124.1697
125.4023
126.5045
128.3677
131.0679
132.2323
136.3869
136.9679
147.3275
147.8096
148.4354
153.7151
169.5850
183.1267
193.1565
ppm

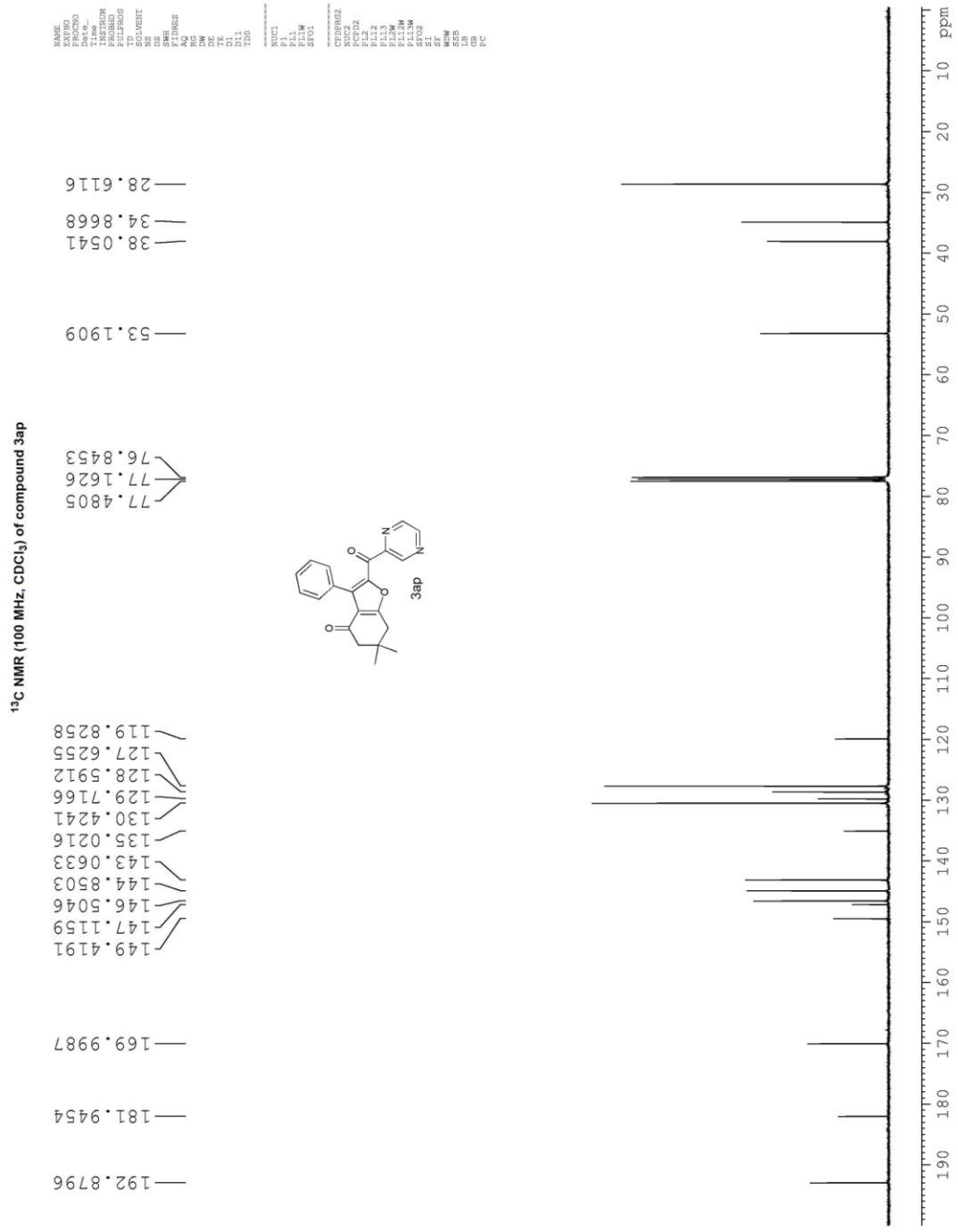

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3an
3an

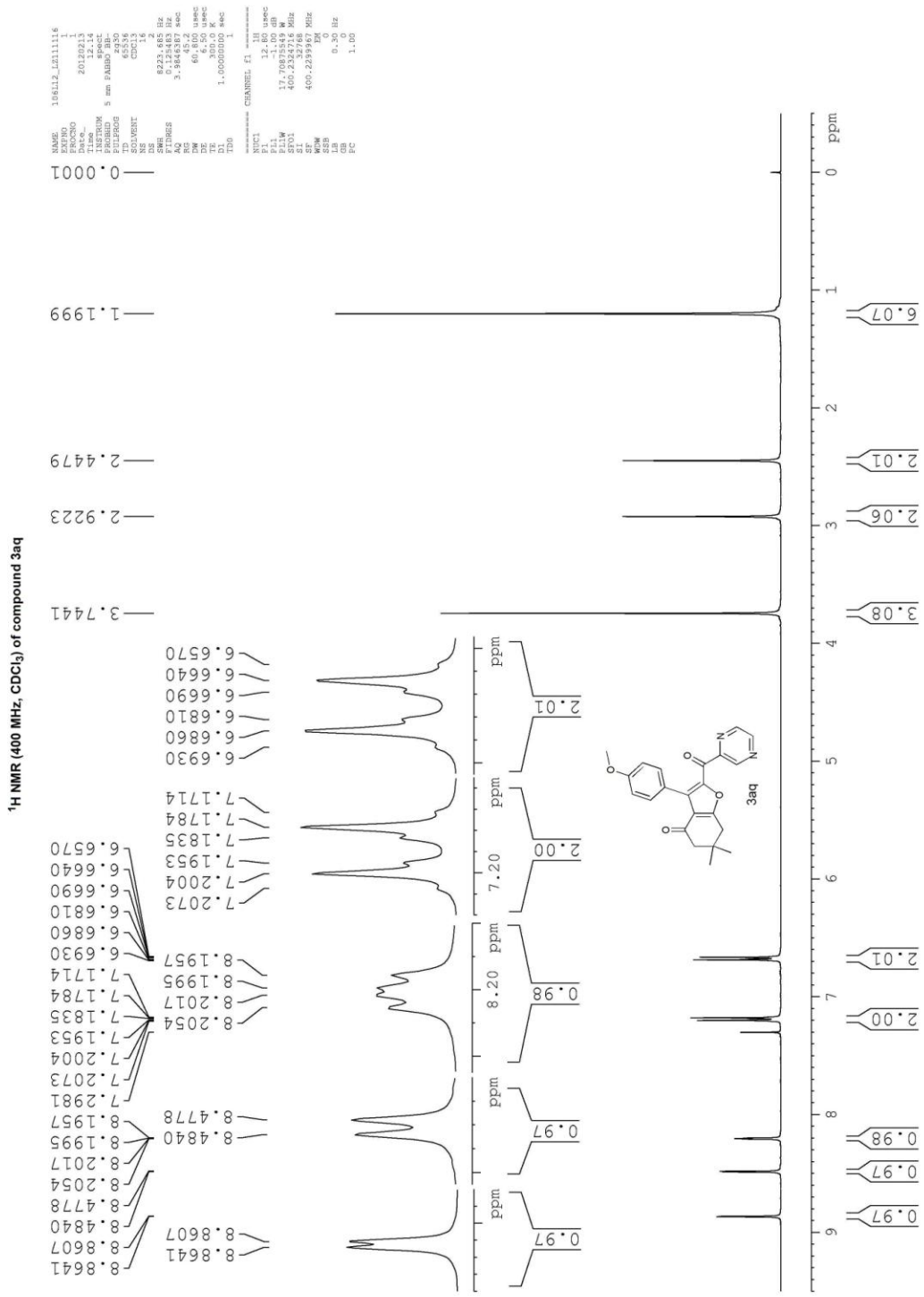

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3an
3an
28.5265
34.6616
37.9396
53.1944
76.8404
77.1591
77.4774
119.4988
123.8165
126.1092
126.2069
126.3858
128.1354
130.1828
131.2525
136.6062
147.6016
148.6746
154.1875
169.2135
183.6350
192.7988
ppm

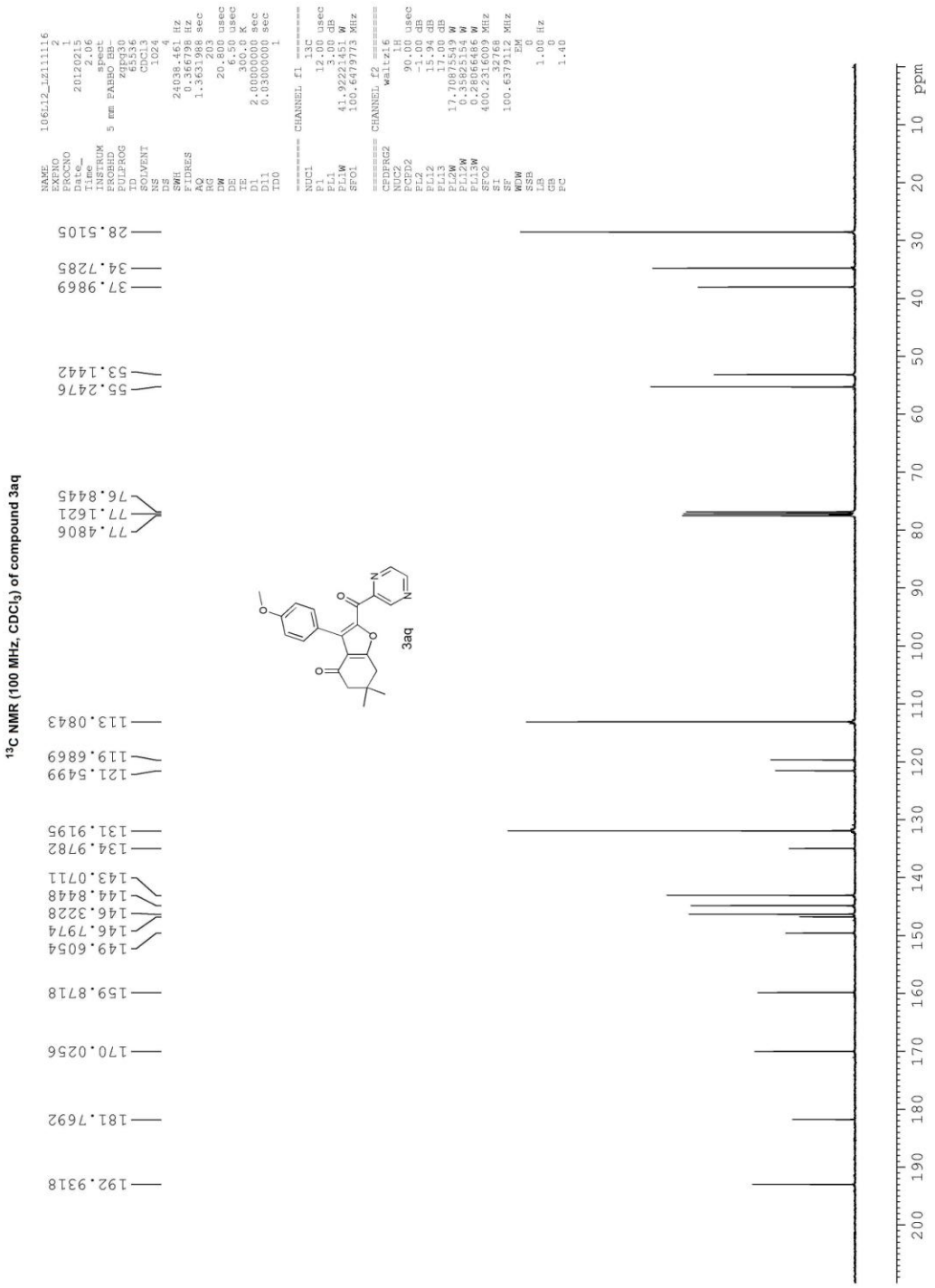

^{1}H NMR (400 MHz, CDCl$_3$) of compound 3ao
3ao

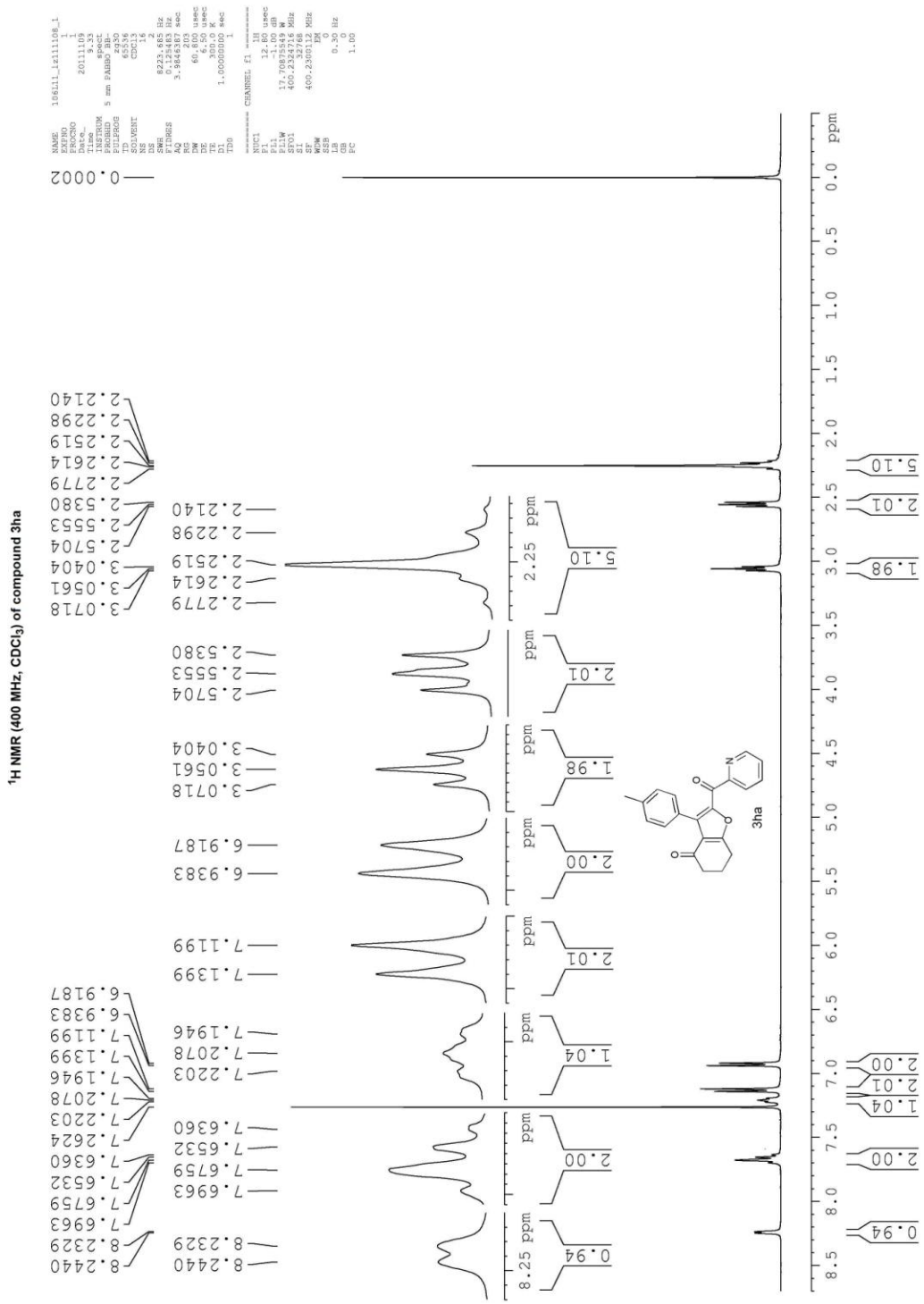

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ao
28.6288
34.8205
38.0216
53.2284
76.8454
77.1628
77.4806
119.8334
121.8616
123.7735
123.8210
124.1063
124.7442
125.9440
126.2825
127.8787
131.0610
136.6127
139.0837
141.3431
148.2692
148.6680
154.1854
169.2690
183.7093
192.7569
3ao
ppm

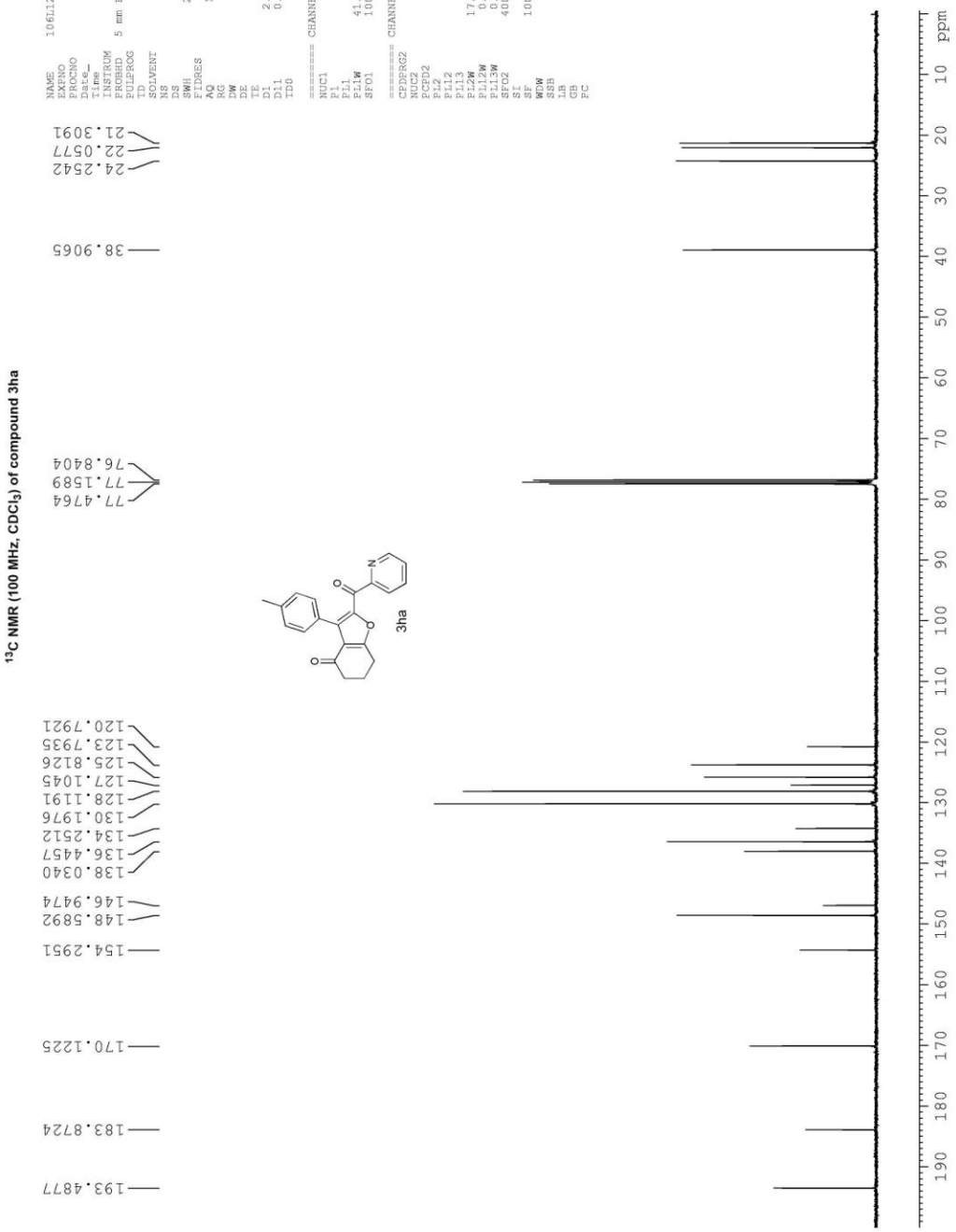

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ap
3ap
ppm

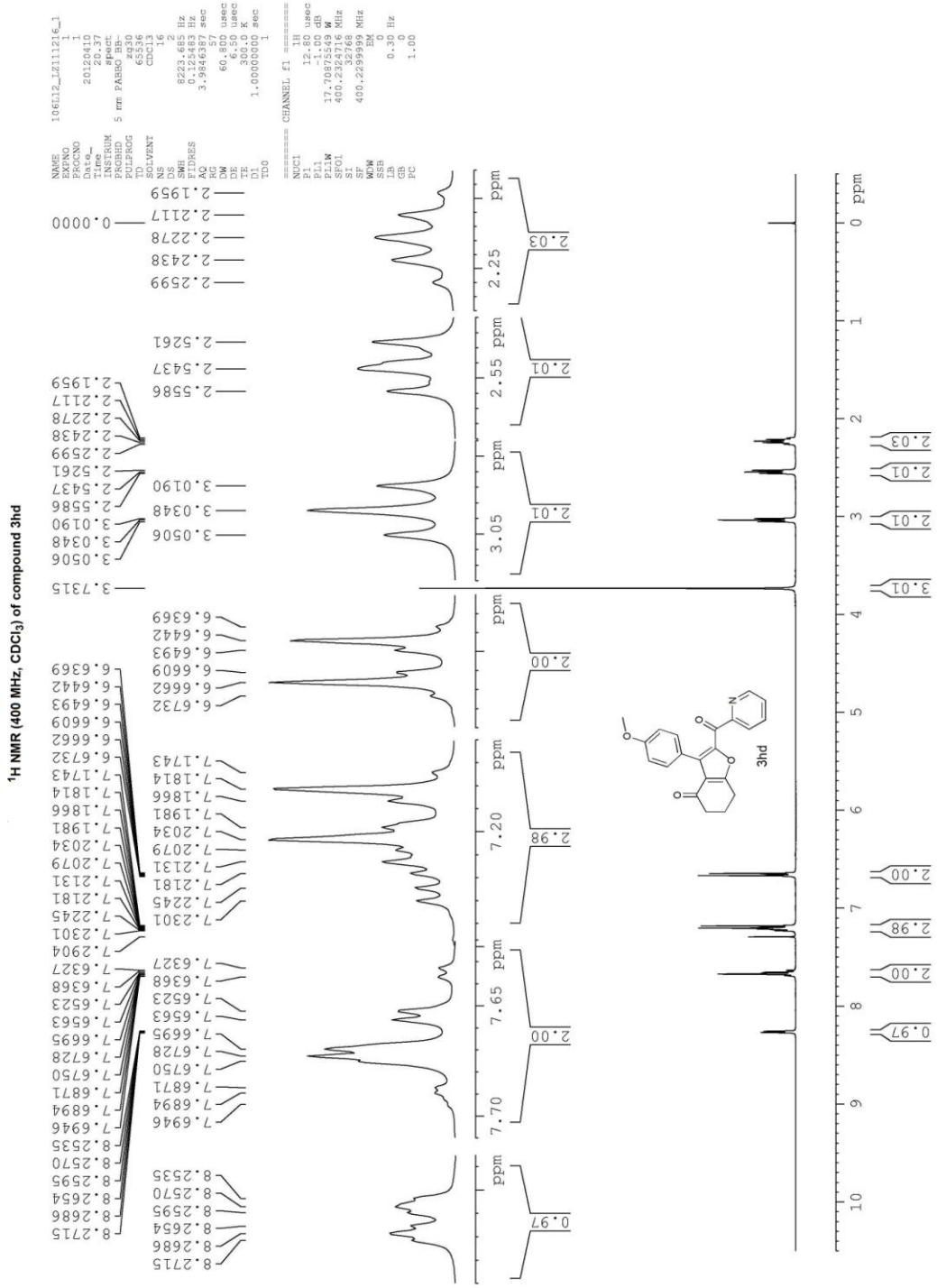

^{13}C NMR (100 MHz, CDCl$_3$) of compound 3ap
28.6116
34.8668
38.0541
53.1909
76.8453
77.1626
77.4805
119.8258
127.6255
128.5912
129.7166
130.4241
135.0216
143.0633
144.8503
146.5046
147.1159
149.4191
169.9987
181.9454
192.8796
3ap
ppm

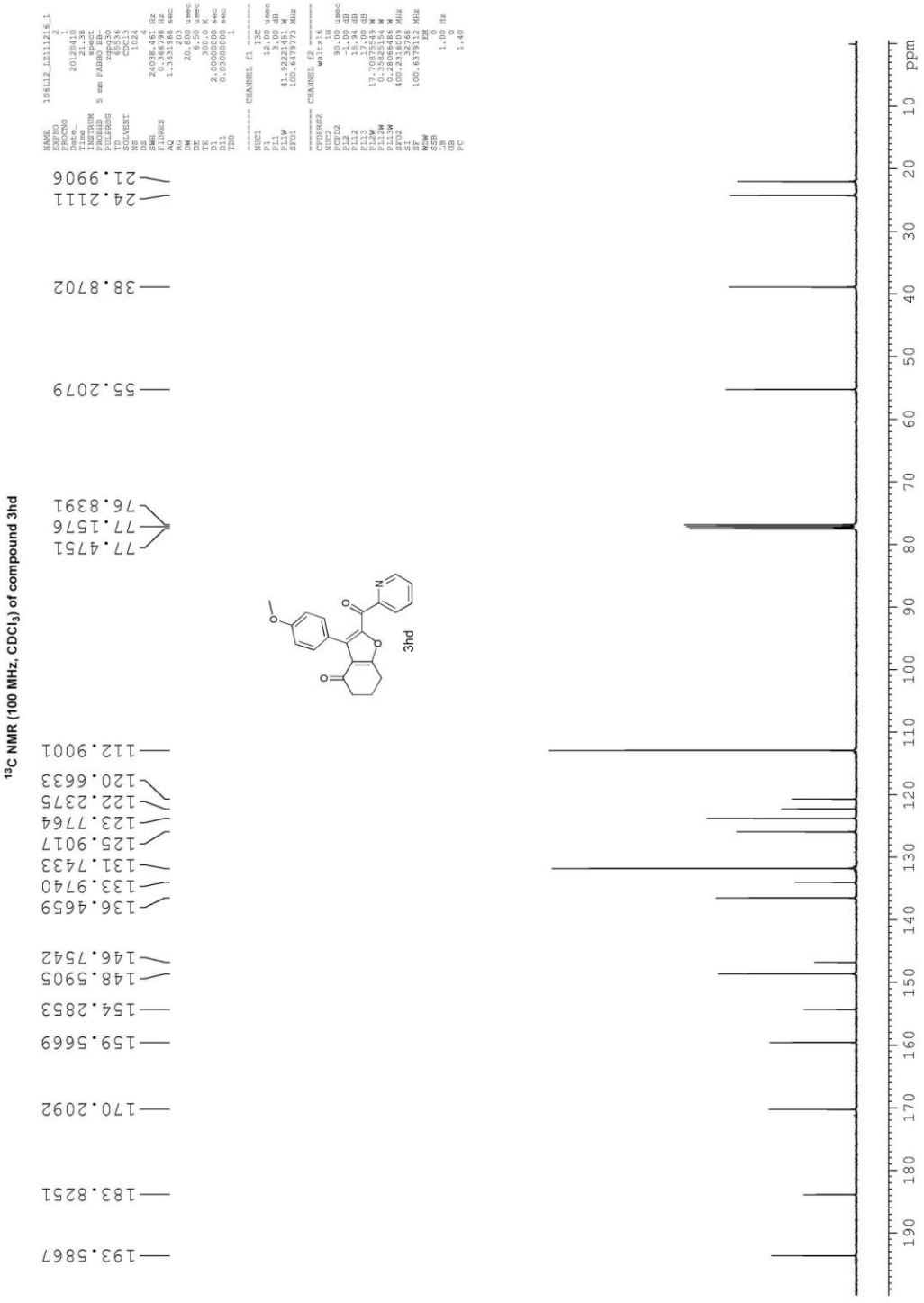

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3aq
3aq

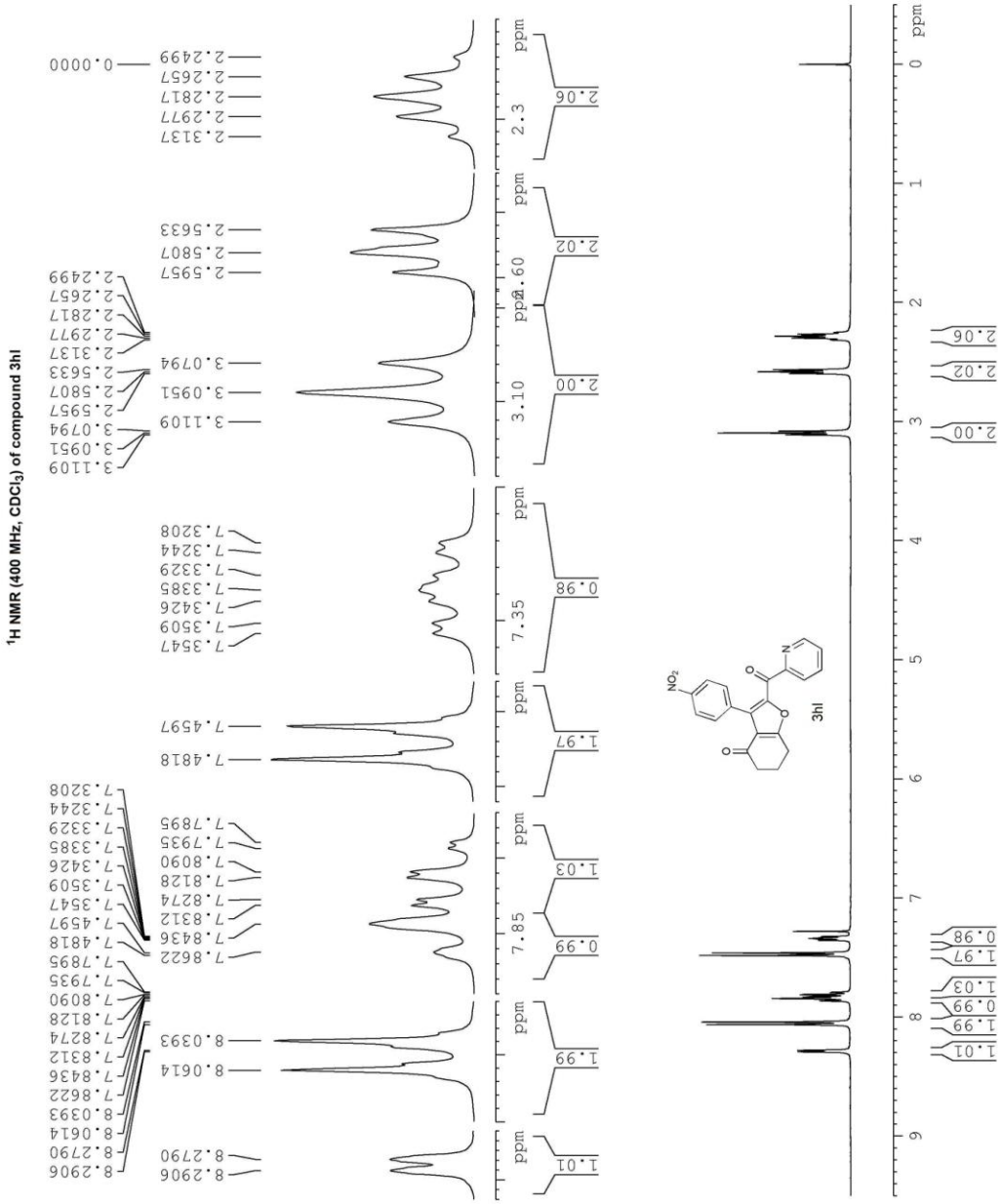

13C NMR (100 MHz, CDCl3) of compound 3aq
3aq
28.5105
34.7285
37.9869
53.1442
55.2476
76.8445
77.1621
77.4806
113.0843
119.6869
121.5499
131.9195
134.9782
143.0711
144.8448
146.3228
146.7974
149.6054
159.8718
170.0256
181.7692
192.9318
ppm

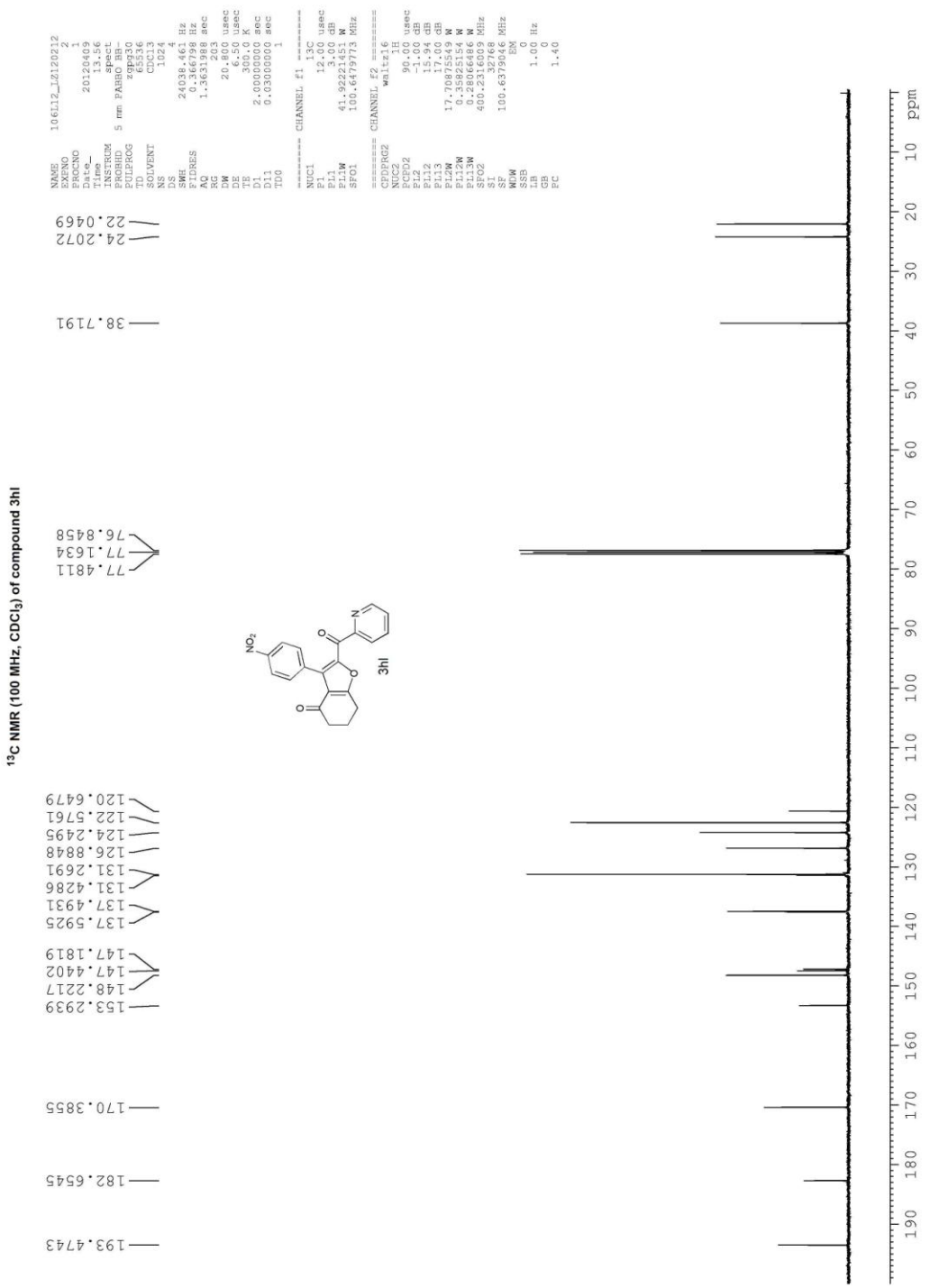

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ha
3ha

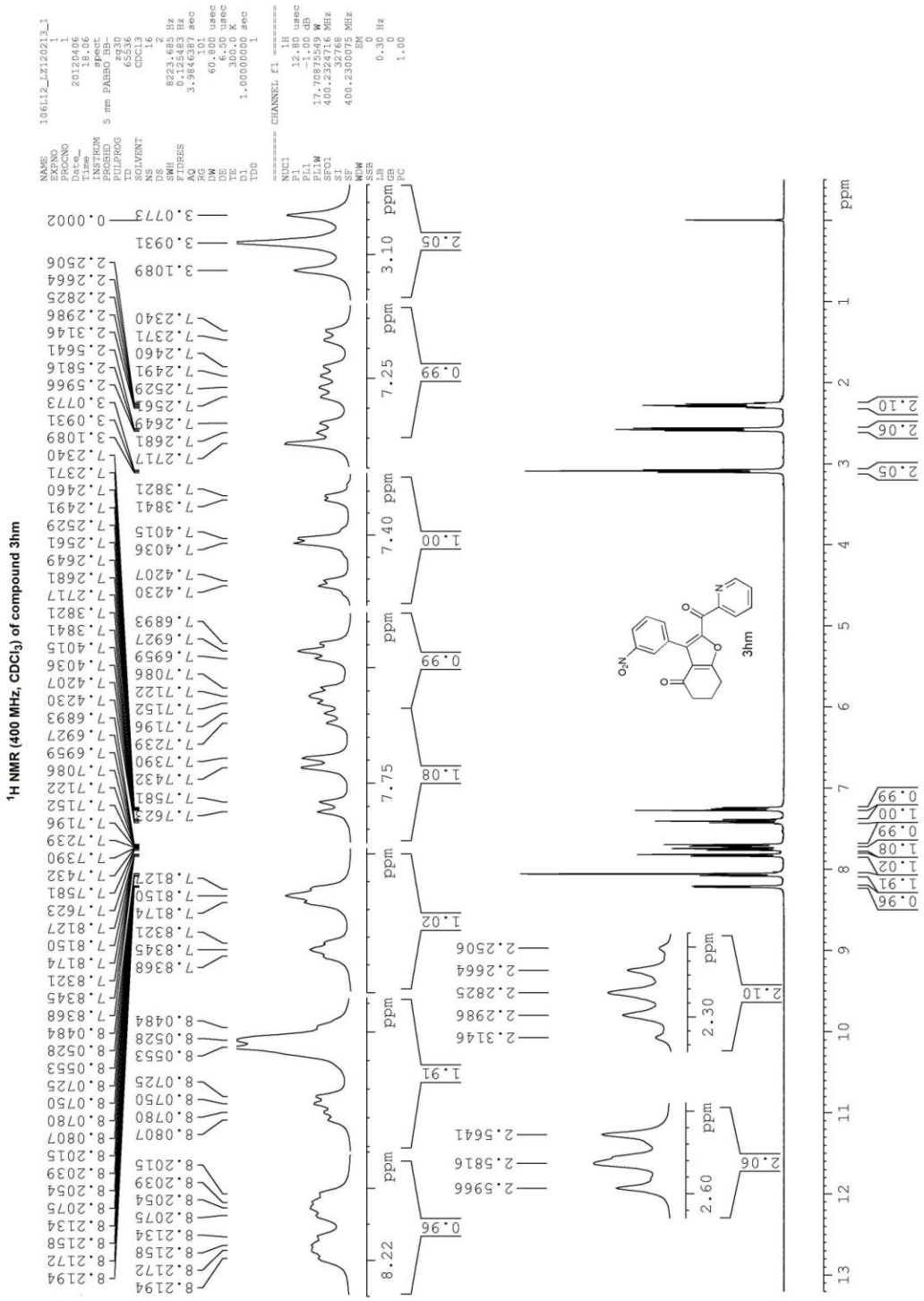

^{13}C NMR (100 MHz, CDCl$_3$) of compound 3ha
3ha
21.3091
22.0577
24.2542
38.9065
76.8404
77.1589
77.4764
120.7921
123.7935
125.8126
127.1045
128.1191
130.1976
134.2512
136.4457
138.0340
146.9474
148.5892
154.2951
170.1225
183.8724
193.4877
ppm

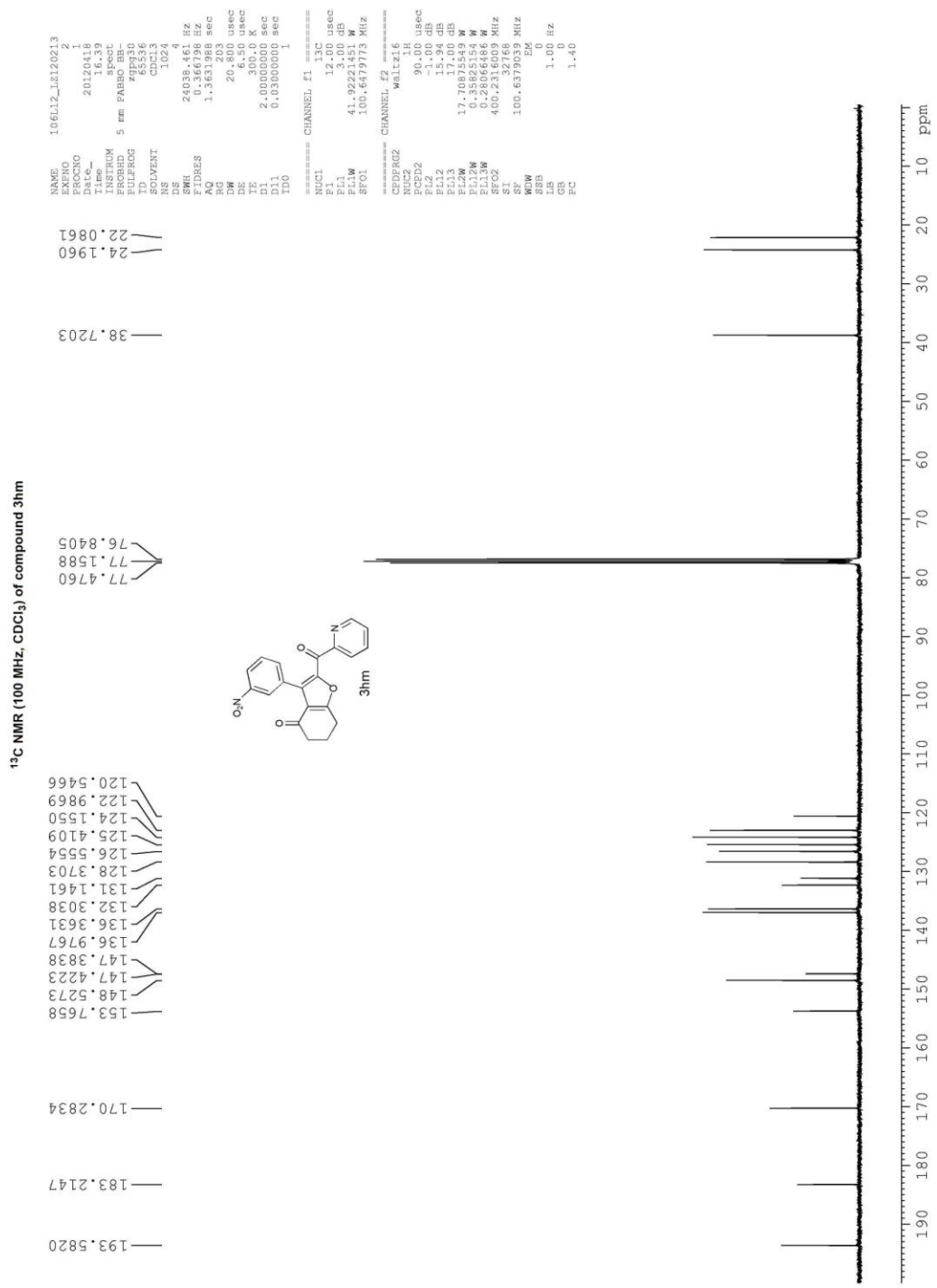

^{1}H NMR (400 MHz, $CDCl_3$) of compound 3hd
3hd

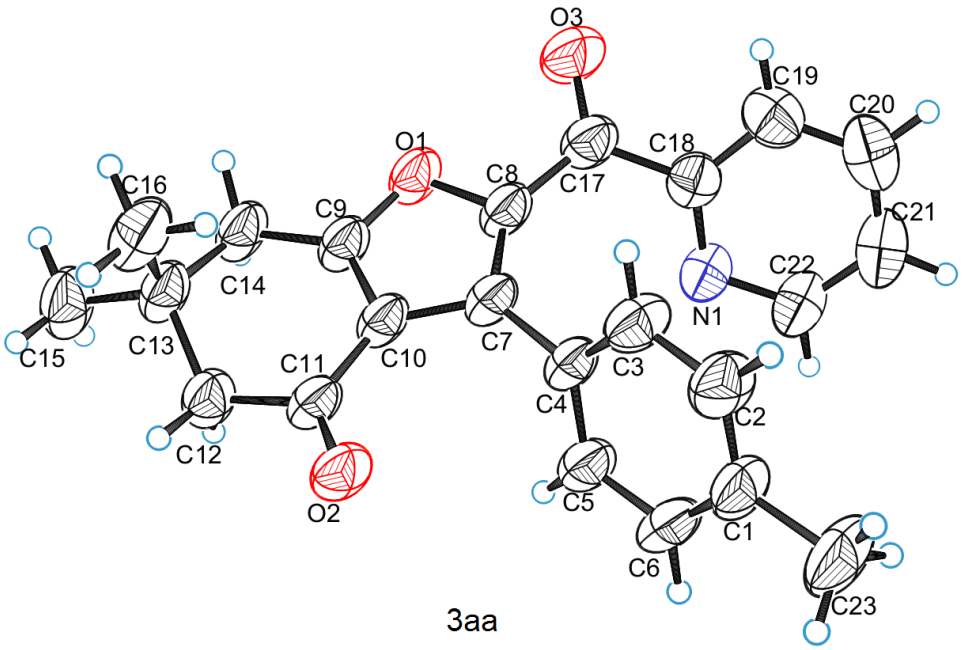

^{13}C NMR (100 MHz, $CDCl_3$) of compound 3hd
3hd
ppm


^{1}H NMR (400 MHz, $CDCl_3$) of compound 3hl
3hl


^{13}C NMR (100 MHz, $CDCl_3$) of compound 3hl
22.0469
24.2072
38.7191
76.8458
77.1634
77.4811
120.6479
122.5761
124.2495
126.8848
131.2691
131.4286
137.4931
137.5925
147.1819
147.4402
148.2217
153.2939
170.3855
182.6545
193.4743
3hl
ppm


^{1}H NMR (400 MHz, CDCl$_3$) of compound 3hm
3hm


^{13}C NMR (100 MHz, $CDCl_3$) of compound 3hm
3hm
22.0861
24.1960
38.7203
76.8405
77.1588
77.4760
120.5466
122.9869
124.1550
125.4109
126.5554
128.3703
131.1461
132.3038
136.3631
136.9767
147.3838
147.4223
148.5273
153.7658
170.2834
183.2147
193.5820
ppm



X-ray crystal structure of 3aa

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 111123

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 111123

```
Bond precision:  C-C = 0.0031 A          Wavelength=1.54184

Cell:            a=18.5722(6)    b=6.3147(3)        c=16.7573(7)
                 alpha=90        beta=93.197(3)     gamma=90
Temperature:     290 K
```

	Calculated	Reported
Volume	1962.20(14)	1962.20(14)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	?
Moiety formula	C23 H21 N O3	?
Sum formula	C23 H21 N O3	C23 H21 N O3
Mr	359.41	359.41
Dx,g cm-3	1.217	1.217
Z	4	4
Mu (mm-1)	0.645	0.645
F000	760.0	760.0
F000’	762.27	
h,k,lmax	22,7,20	22,7,20
Nref	3702	3615
Tmin,Tmax	0.793,0.857	0.787,0.864
Tmin’	0.773	

```
Correction method= MULTI-SCAN

Data completeness= 0.976          Theta(max)= 69.520

R(reflections)= 0.0503( 2540)     wR2(reflections)= 0.1614( 3615)

S = 1.031                 Npar= 248
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low 0.976
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C1

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 04/07/2012; check.def file version of 28/06/2012

Datablock 111123 - ellipsoid plot