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Green Chemistry

Solid acid-catalyzed domino cyclization reaction: regio- and diastereoselective synthesis of pyrido[2,3-*d*]pyrimidine derivatives bearing three contiguous stereocenters

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Electronic Supplementary Information (ESI)

Supplementary Information Available: complete product characterization data, analytical details.

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General information

All the reagents were commercially available and used without further purification, unless otherwise stated. IR spectra were determined on an FT-IR-Tensor 27 spectrometer. ^{1}HNMR spectra were recorded on a 400 MHz instrument (Bruker Avance 400 Spectrometer). Chemical shifts (δ) are given in ppm relative to TMS as the internal reference, with coupling constants (J) in Hz. ^{13}C NMR spectra were recorded at 100 MHz. Chemical shift were reported in ppm with the internal chloroform signal at 77.0 ppm or dimethyl sulphoxide signal at 39.9 ppm as a standard. HRMS (ESI) was measured with a Bruker Daltonics APEXII instrument. Single-crystal X-ray diffraction measurement was carried out on a Rigaku Saturn CCD diffractometer at 100(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program package. According to literature method,[1] the carbonaceous material catalyst was prepared using furaldehyde and hydroxyethylsulfonic acid as substrates.

X-ray Crystallography

Single-crystal X-ray diffraction measurement was carried out on a Rigaku Saturn CCD diffractometer at 100(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073

Å). An empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program package.

Synthesis and property of solid acid (C-SO_3H) catalyst

According to literature method,[1] furaldehyde (10 g), hydroxyethylsulfonic acid (5 g) were dropped into deionized water (80 mL) and placed in 100 mL Teflon-lined stainless steel autoclaves, which were heated in an oven at 200 °C for 4 h. The resulting products were filtered, washed with water and methanol, and dried in a vacuum oven at 110 °C for 5 h. The acidity of the solid acid was 2.4 mmol/g, which was determined through the neutralization titration. This solid acid owned much higher acidity than that of the sulfonated solid acid, which was obtained via the sulfonation of the inactive carbon. The acid strength of the catalyst was determined by thermodesorption of chemisorbed ammonia (NH_3-TPD). The result showed that the catalyst had great acid strength in which ammonia was desorbed at 400 to 600 °C. IR (KBr) = 3020 (Ar-H), 1704 (C=O), 1604 (C=C), 1204 (C-O), 1040 (S=O), 940 (S-O) cm^{-1}.

General procedure for the synthesis of 4

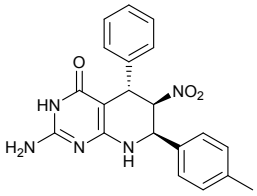
In a 10-mL reaction vial, 2,6-diaminopyrimidin-4(3*H*)-one (0.5 mmol), nitroolefin (0.5 mmol), aldehyde (0.5 mmol), carbonaceous material (C-SO_3H) (10 mg) as well as water (3.0 mL), were added respectively and then capped. The mixture was stirred until TLC revealed that conversion of the substrates was complete, then, the reaction mixture was cooled to room temperature. The resulted precipitate was filtered and dried along with the catalyst. The crude product was further purified by recrystallization from hot ethanol/*N*,*N*-dimethylformamide to give the pure desired product.

General procedure for the synthesis of 6

In a 10-mL reaction vial, 6-aminopyrimidine-2,4(1*H*,3*H*)-dione **5a** or 6-amino-2-thioxo-2,3-dihydropyrimidin-4(1*H*)-one **5b** (0.5 mmol), (*E*)-1-methyl-4-(2-nitrovinyl)benzene (0.5 mmol), 4-methylbenzaldehyde (0.5 mmol), carbonaceous material (C-SO_3H) (10 mg) as well as water (3.0 mL), were added respectively and then capped. The mixture

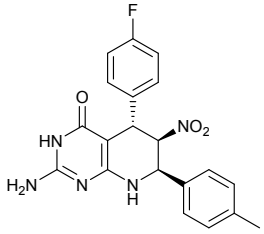
was stirred until TLC revealed that conversion of the substrates was complete, then, the reaction mixture was cooled to room temperature. The resulted precipitate was filtered and dried along with the catalyst. The crude product was further purified by recrystallization from hot ethanol/*N*,*N*-dimethylformamide to give the pure desired product.

Spectral data of the compounds



2-amino-6-nitro-5-phenyl-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4a)

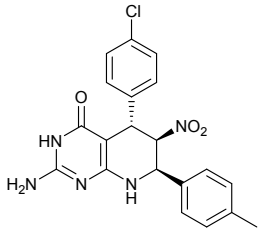
Yellow powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.09 (br, s, 1H, NH), 7.34-7.38 (m, 2H, ArH), 7.25-7.29 (m, 3H, ArH), 7.17 (s, 1H, NH), 7.11 (d, J = 8.4 Hz, 2H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 6.21 (br, s, 2H, NH_2), 4.92 (t, J = 2.6 Hz, 1H, CH), 4.50 (d, J = 3.2 Hz, 1H, CH), 4.39 (d, J = 2.0 Hz, 1H, CH), 2.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.8, 160.0, 154.4, 143.0, 138.0, 134.3, 130.2, 129.4, 129.0, 128.6, 127.8, 127.4, 127.1, 89.4, 83.0, 52.7, 21.1; IR (KBr, ν, cm^{-1}): 3499, 3393, 3064, 2901, 1642, 1594, 1545, 1474, 1385, 1322, 1285, 1075, 1030, 770, 621; HRMS (ESI) m/z calcd for $C_{20}H_{19}N_5O_3$ $[M + H]^+$: 378.1561, found: 378.1565.



2-amino-5-(4-fluorophenyl)-6-nitro-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4b)

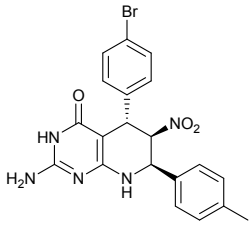
Purple powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.11 (br, s, 1H, NH), 7.29-7.33 (m, 2H, ArH), 7.17-7.20 (m, 3H, ArH+NH), 7.12 (d, J = 8.0 Hz, 2H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 6.23 (br, s, 2H, NH_2), 4.92 (t, J = 2.8 Hz, 1H, CH),

4.51 (d, J = 3.6 Hz, 1H, CH), 4.39 (d, J = 2.0 Hz, 1H, CH), 2.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.1 (J_{CF}^1 = 143.0 Hz), 159.9, 154.4, 139.1 (J_{CF}^4 = 2.8 Hz), 139.0, 137.9, 134.3, 130.5 (J_{CF}^3 = 8.0 Hz), 129.3, 127.1, 115.6 (J_{CF}^2 = 22.0 Hz), 89.3, 83.1, 52.7, 21.1; IR (KBr, ν, cm^{-1}): 3418, 2921, 1648, 1609, 1545, 1471, 1329, 1215, 1074, 1011, 866, 617; HRMS (ESI) calcd for $C_{20}H_{18}FN_5O_3$ $(M + H)^+$: 396.1466, found: 396.1476.



2-amino-5-(4-chlorophenyl)-6-nitro-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4c)

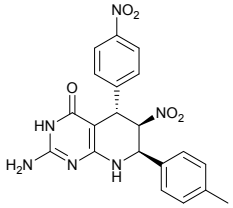
Green powder; Mp >300 ^oC; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 10.11 (br, s, 1H, NH), 7.39 (d, J = 8.4 Hz, 2H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH), 7.22 (s, 1H, NH), 7.12 (d, J = 8.0 Hz, 2H, ArH), 7.05 (d, J = 8.4 Hz, 2H, ArH), 6.23 (br, s, 2H, NH_2), 4.94 (t, J = 2.8 Hz, 1H, CH), 4.53 (d, J = 3.6 Hz, 1H, CH), 4.38 (d, J = 2.0 Hz, 1H, CH), 2.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.7, 160.0, 154.4, 142.0, 138.0, 134.3, 131.9, 130.6, 129.3, 128.8, 127.2, 89.1, 82.9, 52.8, 21.1; IR (KBr, ν, cm^{-1}): 3419, 2921, 1649, 1610, 1546, 1472, 1370, 1325, 1215, 1074, 846, 676; HRMS (ESI) calcd for $C_{20}H_{18}ClN_5O_3$ $(M + H)^+$: 412.1171, found: 412.1173.



2-amino-5-(4-bromophenyl)-6-nitro-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4d)

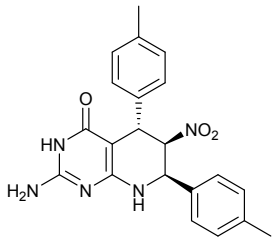
White powder; Mp >300 ^oC; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 11.01 (br, s, 1H, NH), 7.49 (d, J = 8.4 Hz, 2H, ArH), 7.09-7.15 (m, 4H, ArH),7.01 (d, J = 7.6 Hz, 2H, ArH), 5.43 (br, s, 1H, NH), 5.24 (br, s, 2H, NH_2), 4.80 (s, 1H, CH), 4.45 (s, 2H, CH), 2.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.0, 159.9, 154.2, 139.2, 138.3, 137.8,

132.5, 129.9, 129.8, 127.9, 126.3, 88.9, 83.7, 52.7, 40.8, 21.1; IR (KBr, ν, cm^{-1}): 3420, 2920, 1647, 1607, 1544, 1471, 1372, 1326, 1075, 1011, 845, 677; HRMS (ESI) calcd for $C_{20}H_{18}BrN_5O_3$ $(M + H)^+$: 456.0666, found: 456.0661.



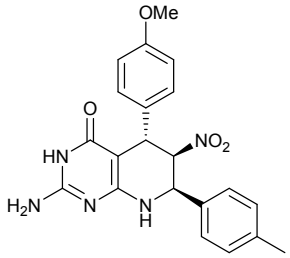
2-amino-6-nitro-5-(4-nitrophenyl)-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4e)

Brown powder; Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.21 (br, s, 1H, NH), 8.16 (d, J = 8.4 Hz, 2H, ArH), 7.54 (d, J = 8.4 Hz, 2H, ArH), 7.28 (s, 1H, NH), 7.10 (d, J = 8.0 Hz, 2H, ArH), 7.01 (d, J = 8.0 Hz, 2H, ArH), 6.31 (br, s, 2H, NH_2), 5.02 (t, J = 2.4 Hz, 1H, CH), 4.58 (d, J = 2.4 Hz, 1H, CH), 4.48 (d, J = 2.4 Hz, 1H, CH), 2.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.9, 160.1, 154.5, 150.5, 146.9, 138.2, 134.1, 130.1, 129.4, 127.1, 124.0, 88.5, 82.7, 53.2, 21.1; IR (KBr, ν, cm^{-1}): 3422, 2922, 1649, 1608, 1544, 1375, 1323, 1286, 1077, 845, 723; HRMS (ESI) calcd for $C_{20}H_{18}N_6O_5$ $(M + H)^+$: 413.1411, found: 413.1408.



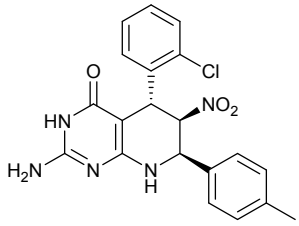
2-amino-6-nitro-5,7-di-*p*-tolyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4f)

Pale yellow powder; Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.91 (br, s, 1H, NH), 7.08-7.19 (m, 6H, ArH), 7.01 (d, J = 7.6 Hz, 2H, ArH), 5.35 (s, 1H, NH), 5.13 (br, s, 2H, NH_2), 4.83 (s, 1H, CH), 4.50 (d, J = 2.0 Hz, 1H, CH), 4.46 (s, 1H, CH), 2.36 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.0, 159.9, 154.2, 139.2, 138.3, 137.8, 132.5, 129.9, 129.8, 128.0, 126.3, 88.9, 83.7, 52.7, 40.8, 21.1; IR (KBr, ν, cm^{-1}): 3637, 3348, 1658, 1606, 1546, 1474, 1325, 1215, 1029, 850, 812, 668, 620; HRMS (ESI) calcd for $C_{21}H_{21}N_5O_3$ $(M + H)^+$: 392.1717, found: 392.1721.



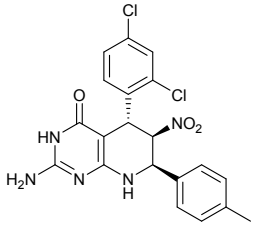
2-amino-5-(4-methoxyphenyl)-6-nitro-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4g)

Purple powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.09 (br, s, 1H, NH), 7.18-7.14 (m, 3H, ArH+NH), 7.10 (d, J = 8.0 Hz, 2H, ArH), 7.02(d, J = 8.0 Hz, 2H, ArH), 6.90 (d, J = 8.4 Hz, 2H, ArH), 6.19 (br, s, 2H, NH_2), 4.86 (s, 1H, CH), 4.47 (d, J = 3.2 Hz, 1H, CH), 4.32 (d, J = 2.0 Hz, 1H, CH), 3.73 (s, 3H, OMe), 2.25 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+ DMSO-d_6, TMS): δ 163.0, 160.0, 154.1, 141.4, 139.2, 134.1, 132.5, 129.8, 129.3, 128.1, 128.0, 126.3, 88.8, 83.6, 55.6, 52.7, 21.1; IR (KBr, ν, cm^{-1}): 3641, 3419, 3222, 2927, 1680, 1609, 1544, 1474, 1372, 1330, 1251, 1175, 1030, 843, 776; HRMS (ESI) calcd for $C_{21}H_{21}N_5O_4$ $(M + H)^+$: 408.1666, found: 408.1665.



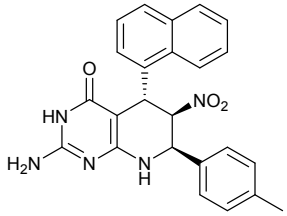
2-amino-5-(2-chlorophenyl)-6-nitro-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4h)

Light blue powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.69 (br, s, 1H, NH), 7.46-7.48 (m, 1H, ArH), 7.28-7.33 (m, 2H, ArH), 7.17-7.19 (m, 1H, ArH), 7.11 (d, J = 8.0 Hz, 2H, ArH), 7.02 (d, J = 8.0 Hz, 2H, ArH), 5.42 (s, 1H, NH), 5.38 (br, s, 2H, NH_2), 4.82-4.85 (m, 2H, CH), 4.46 (d, J = 3.2 Hz, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.0, 160.0, 154.2, 141.4, 139.2, 134.1, 132.5, 129.8, 129.3, 129.2, 128.1, 128.0, 126.3, 88.8, 83.6, 52.7, 41.2, 21.1; IR (KBr, ν, cm^{-1}): 3499, 3393, 2901, 1642, 1595, 1545, 1322, 1286, 1215, 1030, 848, 700, 620; HRMS (ESI) calcd for $C_{20}H_{18}ClN_5O_3$ $(M + H)^+$: 412.1171, found: 412.1170.



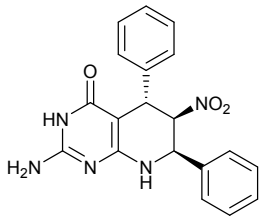
2-amino-5-(2,4-dichlorophenyl)-6-nitro-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4i)

Blue powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.80 (br, s, 1H, NH), 7.49 (d, J = 2.0 Hz, 1H, ArH), 7.28 (d, J = 1.6 Hz, 1H, ArH), 7.12-7.15 (m, 3H, ArH), 7.04 (d, J = 8.4 Hz, 2H, ArH), 5.45 (br, s, 2H, NH_2), 5.41 (s, 1H, NH), 4.80 (d, J = 2.8 Hz, 1H, CH), 4.77 (s, 1H, CH), 4.44 (d, J = 2.8 Hz, 1H, CH), 2.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 162.7, 160.4, 154.3, 139.5, 136.7, 134.7, 133.9, 131.9, 131.1, 129.9, 128.0, 126.3, 85.9, 82.7, 53.1, 38.2, 21.1; IR (KBr, ν, cm^{-1}): 3496, 3390, 2901, 1642, 1595, 1545, 1475, 1323, 1286, 1030, 770, 700; HRMS (ESI) calcd for $C_{20}H_{17}Cl_2N_5O_3$ $(M + H)^+$: 446.0781, found: 446.0781.



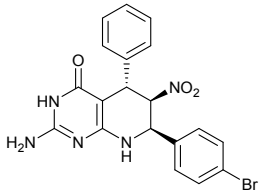
2-amino-5-(naphthalen-1-yl)-6-nitro-7-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4j)

Blue powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.62 (br, s, 1H, NH), 8.16 (d, J = 8.0 Hz, 1H, ArH), 7.96 (d, J = 7.6 Hz, 1H, ArH), 7.84 (d, J = 8.4 Hz, 1H, ArH), 7.55-7.61 (m, 2H, ArH), 7.43 (t, J = 7.2 Hz, 1H, ArH), 7.27 (s, 1H, ArH), 7.02 (d, J = 8.4 Hz, 2H, ArH), 6.93 (d, J = 8.0 Hz, 2H, ArH), 5.31 (s, 1H, NH), 5.23 (s, 1H, CH), 4.94 (s, 1H, CH), 4.50 (br, s, 3H, NH_2 + CH), 2.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 162.7, 160.1, 154.0, 139.2, 136.2, 134.1, 132.2, 130.1, 129.7, 129.0, 127.6, 126.9, 126.4, 125.7, 121.8, 86.7, 83.4, 53.1, 37.7, 21.1; IR (KBr, ν, cm^{-1}): 3388, 2925, 1639, 1550, 1475, 1328, 1105, 1047, 770, 620; HRMS (ESI) calcd for $C_{24}H_{21}N_5O_3$ $(M + H)^+$: 428.1717, found: 428.1731.



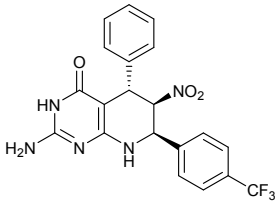
2-amino-6-nitro-5,7-diphenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4k)

Blue powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.13 (br, s, 1H, NH), 7.35-7.38 (m, 2H, ArH), 7.26-7.32 (m, 6H, ArH), 7.24 (s, 1H, NH), 7.15-7.17 (m, 2H, ArH), 6.24 (br, s, 2H, NH_2), 4.97 (t, J = 2.4 Hz, 1H, CH), 4.54 (d, J = 3.6 Hz, 1H, CH), 4.41 (s, d, J = 2.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 162.7, 161.8, 160.0, 154.4, 154.0, 142.9, 141.8, 137.4, 129.0, 128.8, 128.7, 128.6, 128.2, 127.4, 126.8, 89.3, 83.0, 53.0; IR (KBr, ν, cm^{-1}): 3385, 2920, 1639, 1550, 1474, 1364, 1328, 1104, 845, 770; HRMS (ESI) calcd for $C_{19}H_{17}N_5O_3$ $(M + H)^+$: 364.1404, found: 364.1410.



2-amino-7-(4-bromophenyl)-6-nitro-5-phenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4l)

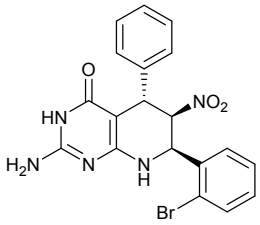
Light blue powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.13 (br, s, 1H, NH), 7.51 (d, J = 8.4 Hz, 2H, ArH), 7.34-7.38 (m, 2H, ArH), 7.27-7.29 (m, 4H, ArH + NH), 7.13 (d, J = 8.4 Hz, 2H, ArH), 6.23 (br, s, 2H, NH_2), 5.00 (s, 1H, CH), 4.54 (d, J = 3.2 Hz, 1H, CH), 4.42 (d, J = 2.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.2, 159.9, 154.4, 142.8, 136.9, 131.6, 129.6, 129.0, 128.6, 127.4, 121.7, 89.0, 83.1, 52.4; IR (KBr, ν, cm^{-1}): 3421, 2920, 1648, 1609, 1546, 1470, 1371, 1328, 1214, 1011, 845, 676; HRMS (ESI) calcd for $C_{19}H_{16}BrN_5O_3$ $(M + H)^+$: 442.0509, found: 442.0500.



2-amino-6-nitro-5-phenyl-7-(4-(trifluoromethyl)phenyl)-5,6,7,8-

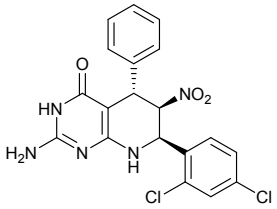
tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4m)

Light blue powder; Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 11.06 (br, s, 1H, NH), 7.58 (d, J = 8.0 Hz, 2H, ArH), 7.35-7.41 (m, 2H, ArH), 7.27-7.32 (m, 5H, ArH), 5.56 (s, 1H, NH), 5.24 (br, s, 2H, NH_2), 4.90 (s, 1H, CH), 4.64 (d, J = 2.4 Hz, 1H, CH), 4.57 (s, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.2, 159.9, 154.2, 141.0, 139.5, 129.4, 129.2, 128.1 (J_{CF}^1 = 11.0 Hz), 127.0, 126.1, 88.5, 83.9, 52.6; IR (KBr, ν, cm^{-1}): 3498, 3393, 2900, 1641, 1594, 1544, 1474, 1384, 1322, 1285, 1029, 847, 700, 620; HRMS (ESI) calcd for $C_{20}H_{16}F_3N_5O_3$ $(M + H)^+$: 432.1278, found: 432.1283.



2-amino-7-(2-bromophenyl)-6-nitro-5-phenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4n)

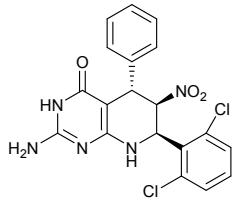
Light blue powder; Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.20 (br, s, 1H, NH), 7.56 (d, J = 7.6 Hz, 1H, ArH), 7.26-7.40 (m, 8H, ArH), 7.15 (s, 1H, NH), 6.25 (br, s, 2H, NH_2), 5.02 (s, 1H, CH), 4.83 (s, 1H, CH), 4.53 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.9, 160.3, 154.4, 142.6, 135.8, 133.1, 130.7, 129.5, 128.9, 128.6, 128.3, 127.5, 122.0, 86.1, 83.8, 52.0; IR (KBr, ν, cm^{-1}): 3421, 2920, 1649, 1608, 1544, 1372, 1329, 1285, 1074, 1012, 847, 677; HRMS (ESI) calcd for $C_{19}H_{16}BrN_5O_3$ $(M + H)^+$: 442.0509, found: 442.0511.



2-amino-7-(2,4-dichlorophenyl)-6-nitro-5-phenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4o)

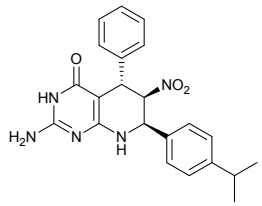
Light blue powder; Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.24 (br, s, 1H, NH), 7.57 (s, 1H, ArH), 7.23-7.43 (m, 8H, ArH + NH), 6.26 (br, s, 2H, NH_2), 5.02 (s, 1H, CH), 4.86 (s, 1H, CH), 4.57 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 162.0, 160.2, 154.4, 142.5, 134.0, 133.7, 132.5, 130.6, 129.1, 128.9, 128.6, 127.9, 127.5,

85.9, 83.9, 49.4; IR (KBr, ν, cm^{-1}): 3419, 2921, 1647, 1605, 1544, 1383, 1329, 1215, 1011, 847, 618; HRMS (ESI) calcd for $C_{19}H_{15}Cl_2N_5O_3$ $(M + H)^+$: 432.0625, found: 432.0629.



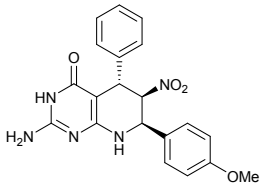
2-amino-7-(2,6-dichlorophenyl)-6-nitro-5-phenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4p)

Light blue powder; Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.14 (br, s, 1H, NH), 7.26-7.39 (m, 8H, ArH), 7.10 (s, 1H, NH), 6.24 (br, s, 2H, NH_2), 5.21 (s, 1H, CH), 4.79 (s, 1H, CH), 4.59 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 160.9, 158.9, 154.4, 142.9, 131.0, 130.8, 128.8, 128.7, 127.4, 84.5, 83.5, 51.7; IR (KBr, ν, cm^{-1}): 3644, 3421, 2921, 1649, 1609, 1547, 1472, 1329, 1216, 873, 677; HRMS (ESI) calcd for $C_{19}H_{15}Cl_2N_5O_3$ $(M + H)^+$: 432.0625, found: 432.0624.



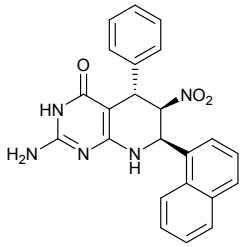
2-amino-7-(4-isopropylphenyl)-6-nitro-5-phenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4q)

White powder; Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.78 (br, s, 1H, NH), 7.35-7.42 (m, 3H, ArH), 7.34 (s, 2H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH), 7.06 (d, J = 8.0 Hz, 2H, ArH), 5.25 (s, 1H, NH), 5.02 (br, s, 2H, NH_2), 4.89 (s, 1H, CH), 4.51-4.53 (m, 2H, CH), 2.83-2.92 (m, 1H, CH), 1.21 (s, 3H, CH_3), 1.19 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.8, 159.9, 154.4, 148.8, 143.0, 134.7, 129.0, 128.6, 127.4, 127.2, 126.8, 89.3, 82.9, 52.8, 33.5, 24.2; IR (KBr, ν, cm^{-1}): 3401, 1644, 1598, 1475, 1388, 1331, 1284, 1215, 1037, 852, 775; HRMS (ESI) calcd for $C_{22}H_{23}N_5O_3$ $(M + H)^+$: 406.1874, found: 406.1878.



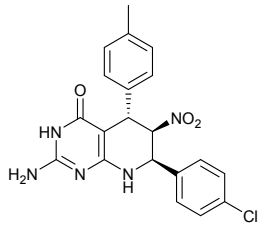
2-amino-7-(4-methoxyphenyl)-6-nitro-5-phenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4r)

Grey powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.09 (br, s, 1H, NH), 7.32-7.35 (m, 2H, ArH), 7.24-7.26 (m, 3H, ArH), 7.14 (s, 1H, NH) 7.05 (d, J = 8.4 Hz, 2H, ArH), 6.84 (d, J = 8.8 Hz, 2H, ArH), 6.19 (br, s, 2H, NH_2), 4.88 (t, J = 2.6 Hz, 1H, CH), 4.48 (d, J = 3.6 Hz, 1H, CH), 4.36 (d, J = 2.0 Hz, 1H, CH), 3.70 (s, 3H, OMe); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.8, 160.0, 159.6, 154.4, 143.1, 129.1, 129.0, 128.6, 128.4, 127.4, 114.2, 89.5, 83.0, 55.5, 52.5; IR (KBr, ν, cm^{-1}): 3640, 3419, 3223, 2926, 1608, 1543, 1373, 1250, 1174, 1030, 842, 774, 621; HRMS (ESI) calcd for $C_{20}H_{19}N_5O_4$ $(M + H)^+$: 394.1510, found: 394.1522.



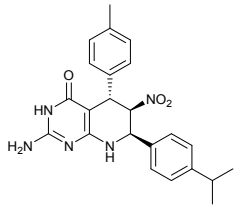
2-amino-7-(naphthalen-1-yl)-6-nitro-5-phenyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4s)

Grey powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.22 (br, s, 1H, NH), 7.87-7.95 (m, 2H, ArH), 7.38-7.49 (m, 7H, ArH), 7.20 (t, J = 7.6 Hz, 1H, ArH), 7.11 (s, 1H, NH), 6.73 (d, J = 8.4 Hz, 1H, ArH), 6.24 (br, s, 2H, NH_2), 5.35 (s, 1H, CH), 5.02 (s, 1H, CH), 4.56 (s, 1H, CH) ; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 162.1, 160.9, 154.3, 143.2, 133.6, 132.1, 129.8, 129.7, 129.1, 128.8, 128.4, 127.7, 127.1, 126.2, 125.8, 125.1, 120.3, 87.7, 84.1, 48.6; IR (KBr, ν, cm^{-1}): 3400, 1645, 1599, 1542, 1399, 1332, 1284, 852, 775; HRMS (ESI) calcd for $C_{23}H_{19}N_5O_3$ $(M + H)^+$: 414.1561, found: 414.1557.



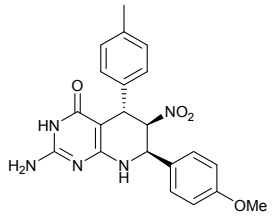
2-amino-7-(4-chlorophenyl)-6-nitro-5-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4t)

White powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.85 (br, s, 1H, NH), 7.24-7.39 (m, 4H, ArH), 7.09 (d, J = 8.0 Hz, 2H, ArH), 7.00 (d, J = 8.0 Hz, 2H, ArH), 5.34 (s, 1H, NH), 5.11 (br, s, 2H, NH_2), 4.85 (s, 1H, CH), 4.50 (s, 2H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.0, 160.0, 154.1, 141.4, 139.2, 134.1, 132.5, 129.8, 129.3, 129.2, 128.1, 128.0, 126.3, 88.8, 83.6, 52.7, 41.2, 21.1; IR (KBr, ν, cm^{-1}): 3645, 3418, 2920, 1648, 1608, 1546, 1470, 1371, 1328, 1286, 1011, 846; HRMS (ESI) calcd for $C_{20}H_{18}ClN_5O_3$ $(M + H)^+$: 412.1171, found: 412.1179.



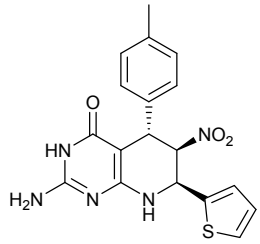
2-amino-7-(4-isopropylphenyl)-6-nitro-5-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4u)

White powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS):δ 10.08 (br, s, 1H, NH), 7.16-7.19 (m, 6H, ArH), 7.11 (s, 1H, NH), 7.06 (d, J = 8.0 Hz, 2H, ArH), 6.21 (br, s, 2H, NH_2), 4.91 (s, 1H, CH), 4.49 (d, J = 2.8 Hz, 1H, CH), 4.36 (s, 1H, CH), 2.82-2.89 (m, 1H, CH), 2.30 (s, 3H, CH_3), 1.16 (d, J = 6.8 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.8, 159.9, 154.4, 148.8, 140.0, 136.5, 134.7, 129.6, 128.4, 127.2, 126.8, 89.3, 83.0, 52.7, 33.5, 24.2, 21.1; IR (KBr, ν, cm^{-1}): 3400, 2961, 1643, 1598, 1541, 1476, 1388, 1329, 1215, 1035, 851, 776; HRMS (ESI) calcd for $C_{23}H_{25}N_5O_3$ $(M + H)^+$: 420.2030, found: 420.2026.



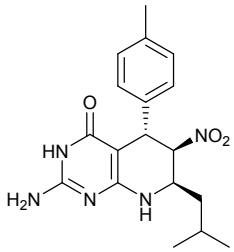
2-amino-7-(4-methoxyphenyl)-6-nitro-5-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4v)

White powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.08 (br, s, 1H, NH), 7.07-7.15 (m, 7H, ArH + NH), 6.86 (s, 2H, ArH), 6.20 (br, s, 2H, NH_2), 4.87 (s, 1H, CH), 4.49 (s, 1H, CH), 4.34 (s, 1H, CH), 3.71 (s, 3H, OMe), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.8, 159.9, 159.6, 154.3, 140.0, 136.5, 129.6, 129.1, 128.4, 114.2, 89.5, 83.1, 55.5, 52.4, 21.1; IR (KBr, ν, cm^{-1}): 3640, 3420, 2926, 1703, 1608, 1544, 1473, 1373, 1288, 1251, 1031, 843, 774, 621; HRMS (ESI) calcd for $C_{21}H_{21}N_5O_4$ $(M + H)^+$: 408.1666, found: 408.1671.



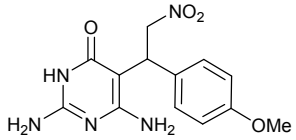
2-amino-6-nitro-5-phenyl-7-(thiophen-2-yl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4w)

Brown powder; Mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6, TMS): δ 10.49 (br, s, 1H, NH), 7.42 (s, 1H, ArH), 7.13 (s, 4H, ArH), 6.33 (d, J = 2.0 Hz, 1H, ArH), 6.14 (s, 1H, ArH), 5.97 (s, 1H, NH), 5.87 (br, s, 2H, NH_2), 5.08 (s, 1H, CH), 4.61 (d, J = 10.4 Hz, 2H, CH), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6, TMS): δ 164.0, 159.1, 158.3, 147.1, 143.4, 137.8, 134.5, 134.3, 131.3, 115.4, 113.5, 89.8, 86.8, 58.3, 39.9, 25.9; IR (KBr, ν, cm^{-1}): 3636, 3349, 2917, 1658, 1606, 1546, 1474, 1326, 1287, 1215, 1028, 851, 812, 668; HRMS (ESI) calcd for $C_{18}H_{17}N_5O_3S$ $(M + H)^+$: 384.1125, found: 384.1131.



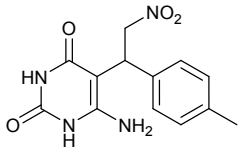
2-amino-7-isobutyl-6-nitro-5-(*p*-tolyl)-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidin-4(3*H*)-one (4x)

Sheet solid; Mp 214-216 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.86 (br, s, 1H, NH), 7.07-7.13 (m, 4H, ArH), 5.10 (br, s, 2H, NH_2), 4.91 (s, 1H, NH), 4.66 (s, 1H, CH), 4.45 (s, 1H, CH), 3.45 (t, J = 6.0 Hz, 1H, CH), 2.31 (s, 3H, CH_3), 1.65-1.72 (m, 1H, CH), 1.38 (t, J = 6.8 Hz, 1H, CH_2), 0.82 (d, J = 6.4 Hz, 3H, CH_3), 0.75 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.0, 159.8, 154.2, 138.4, 137.5, 129.8, 127.9, 86.5, 84.1, 46.4, 40.9, 39.8, 29.3, 24.4, 22.5, 22.0, 21.0; IR (KBr, ν, cm^{-1}): 3395, 2958, 1645, 1544, 1474, 1331, 1216, 1173, 813, 618; HRMS (ESI) calcd for $C_{18}H_{23}N_5O_3$ $(M + H)^+$: 358.1874, found: 358.1889.



2,6-diamino-5-(1-(4-methoxyphenyl)-2-nitroethyl)pyrimidin-4(3*H*)-one (intermediate C)

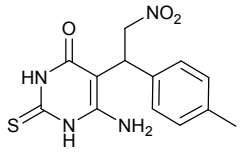
White solid; mp: >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 9.86 (br, s, 1H, NH), 7.42 (d, J = 8.0 Hz, 2H, ArH), 6.79 (d, J = 8.0 Hz, 2H, ArH), 6.10 (br, s, 4H, NH_2), 5.38-5.43 (m, 1H, CH_2), 5.21-5.26 (m, 1H, CH_2), 4.47 (t, J = 7.6 Hz, 1H, CH), 3.69 (s, 3H, OMe); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 162.6, 158.3, 154.0, 133.8, 129.3, 113.3, 86.8, 78.5, 55.4.



6-amino-5-(2-nitro-1-(*p*-tolyl)ethyl)pyrimidine-2,4(1*H*,3*H*)-dione (6a)

White solid; mp: >300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.28 (s, 1H), 10.00 (br, s, 1H, NH), 7.29 (d, J = 8.0 Hz, 2H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 6.36 (br, s,

2H, NH_2), 5.33-5.39 (m, 1H, CH_2), 5.21-5.26 (m, 1H, CH_2), 4.51 (t, J = 8.0 Hz, 1H, CH), 2.22 (s, 3H, CH_3).

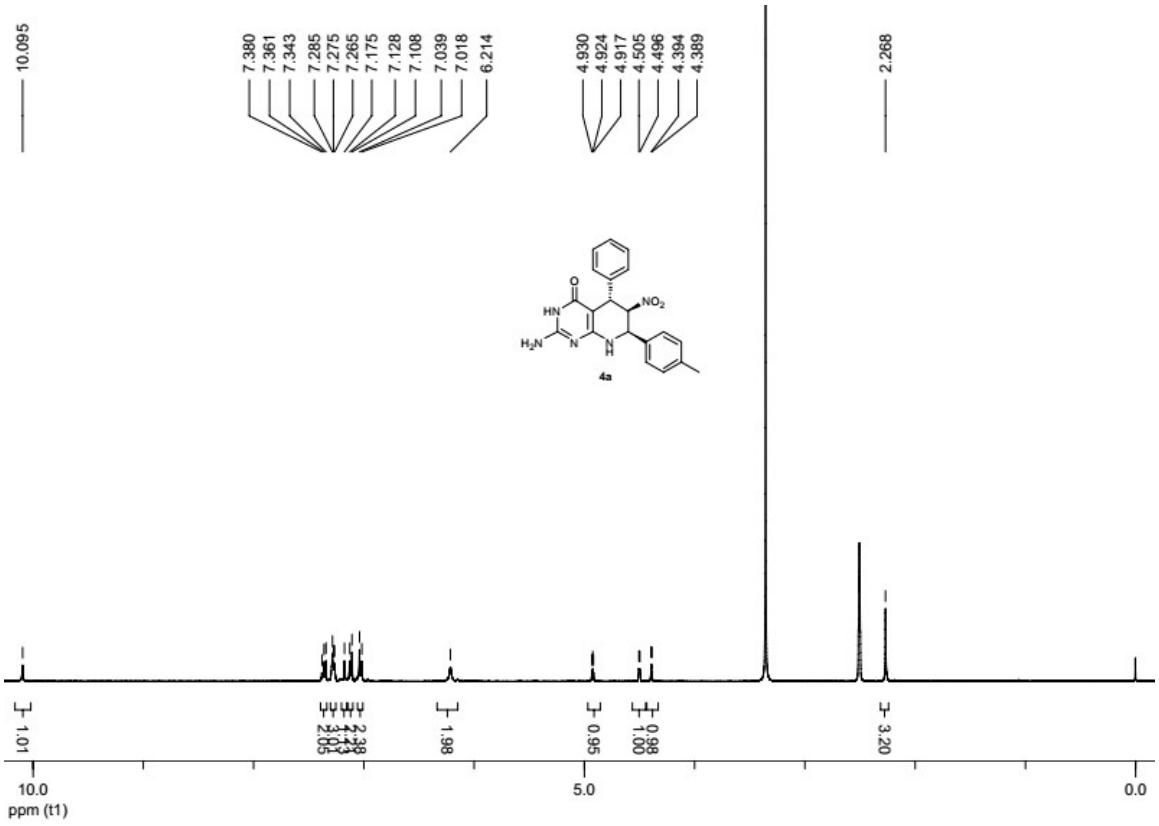


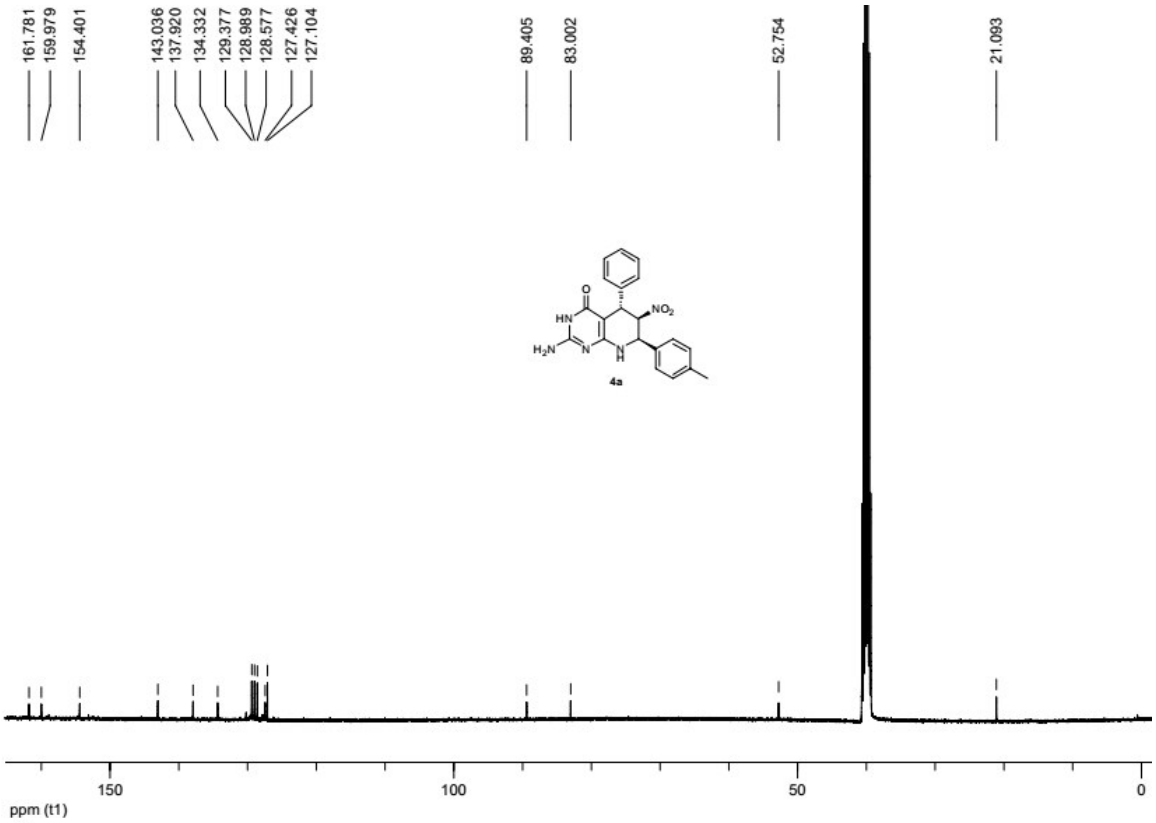
6-amino-5-(2-nitro-1-(*p*-tolyl)ethyl)-2-thioxo-2,3-dihydropyrimidin-4(1*H*)-one (6b)
Yellow solid; mp: >300 ^oC; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 11.70 (br, s, 2H, NH), 7.28 (d, J = 8.0 Hz, 2H, ArH), 7.05 (d, J = 8.0 Hz, 2H, ArH), 6.59 (br, s, 2H, NH_2), 5.35-5.41 (m, 1H, CH_2), 5.23-5.28 (m, 1H, CH_2), 4.55 (t, J = 7.6 Hz, 1H, CH), 2.22 (s, 3H, CH_3).

References:

1. X. Z. Liang, M. F. Zeng, C. Z. Qi, *Carbon*, 2010, **48**, 1844-1848.

^1H and ^{13}C NMR Spectra

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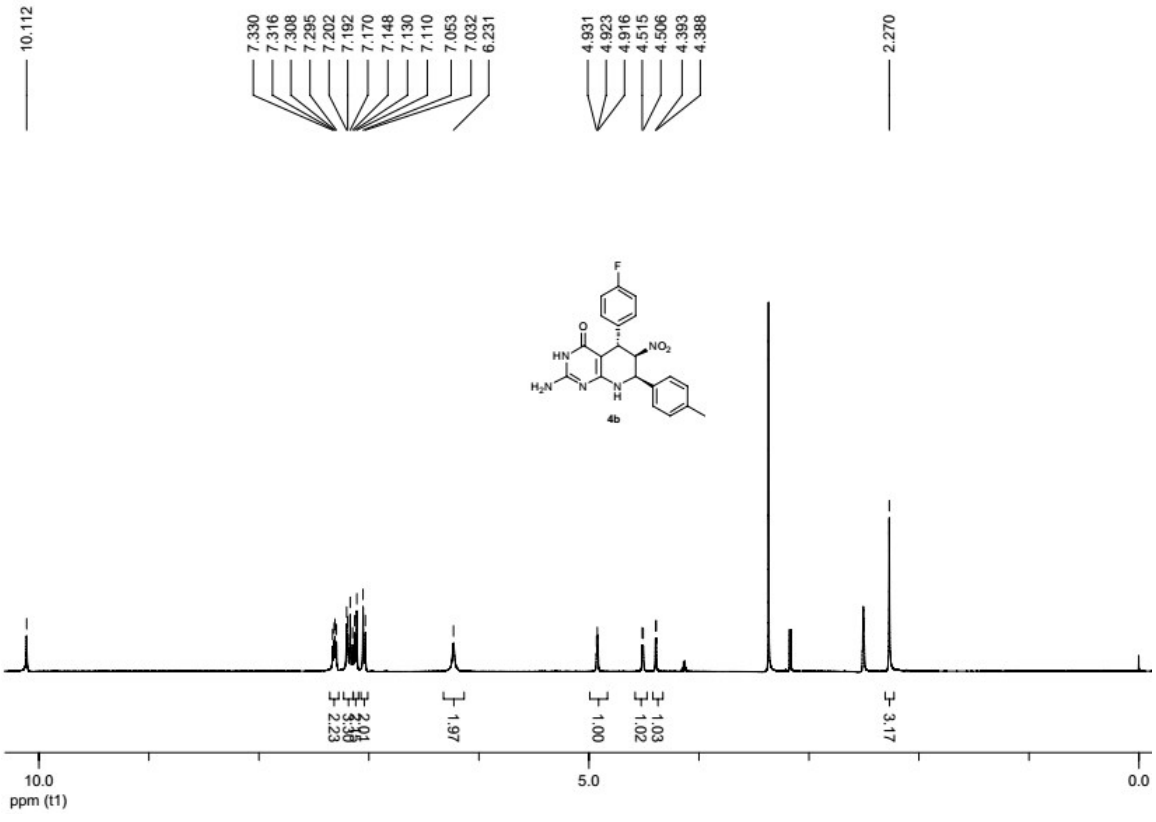
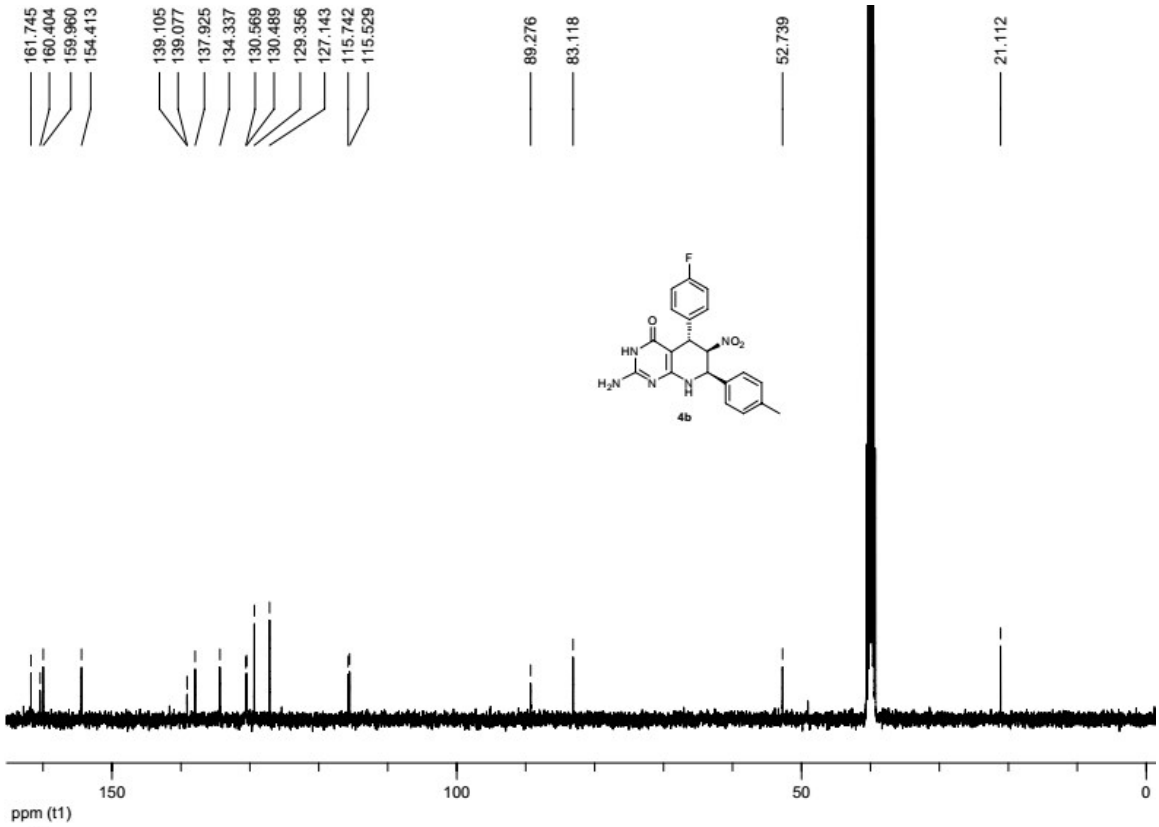
159.979
154.401
143.036
137.920
134.332
129.377
128.989
128.577
127.426
127.104
89.405
83.002
52.754
21.093
4a
150
100
50
0
ppm (t1)


10.112
7.330
7.316
7.308
7.295
7.202
7.192
7.170
7.148
7.130
7.110
7.053
7.032
6.231
4.931
4.923
4.916
4.515
4.506
4.393
4.388
2.270
4b
2.23
2.39
2.01
1.97
1.00
1.02
1.03
3.17
10.0
5.0
0.0
ppm (t1)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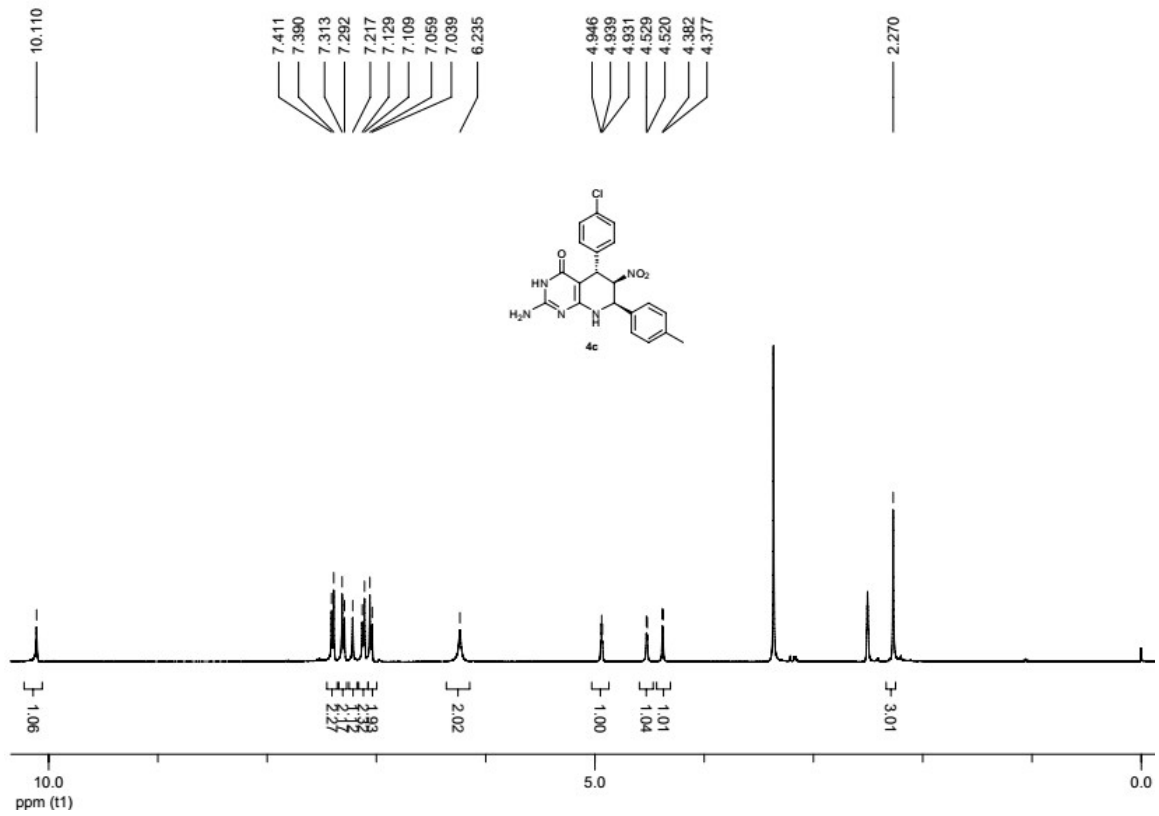
160.404
159.960
154.413
139.105
139.077
137.925
134.337
130.569
130.489
129.356
127.143
115.742
115.529
89.276
83.118
52.739
21.112
F
O
HN
NO_2
H_2N
N
H
4b
150
100
50
0
ppm (t1)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7.411
7.390
7.313
7.292
7.217
7.129
7.109
7.059
7.039
6.235
4.946
4.939
4.931
4.529
4.520
4.382
4.377
2.270
Cl
O
HN
NO_2
H_2N
N
H
4c
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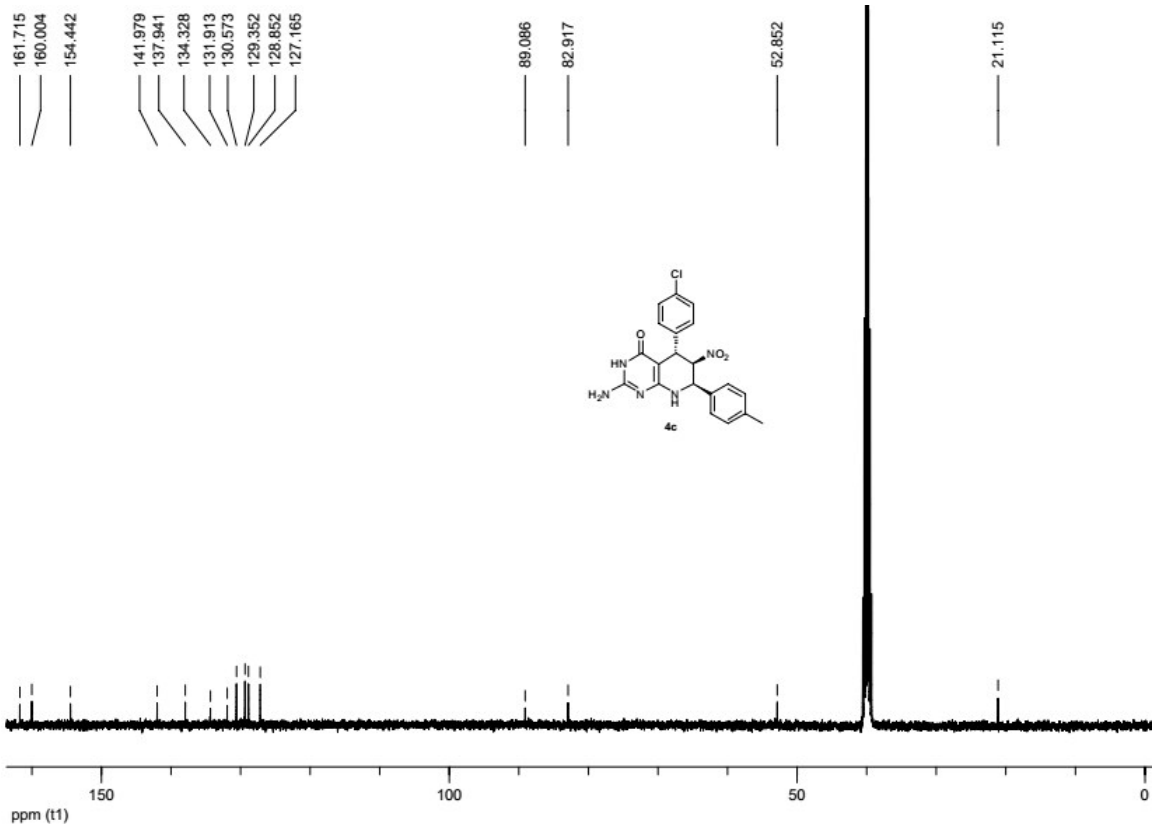
2.02
1.00
1.04
1.01
3.01
10.0
5.0
0.0
ppm (t1)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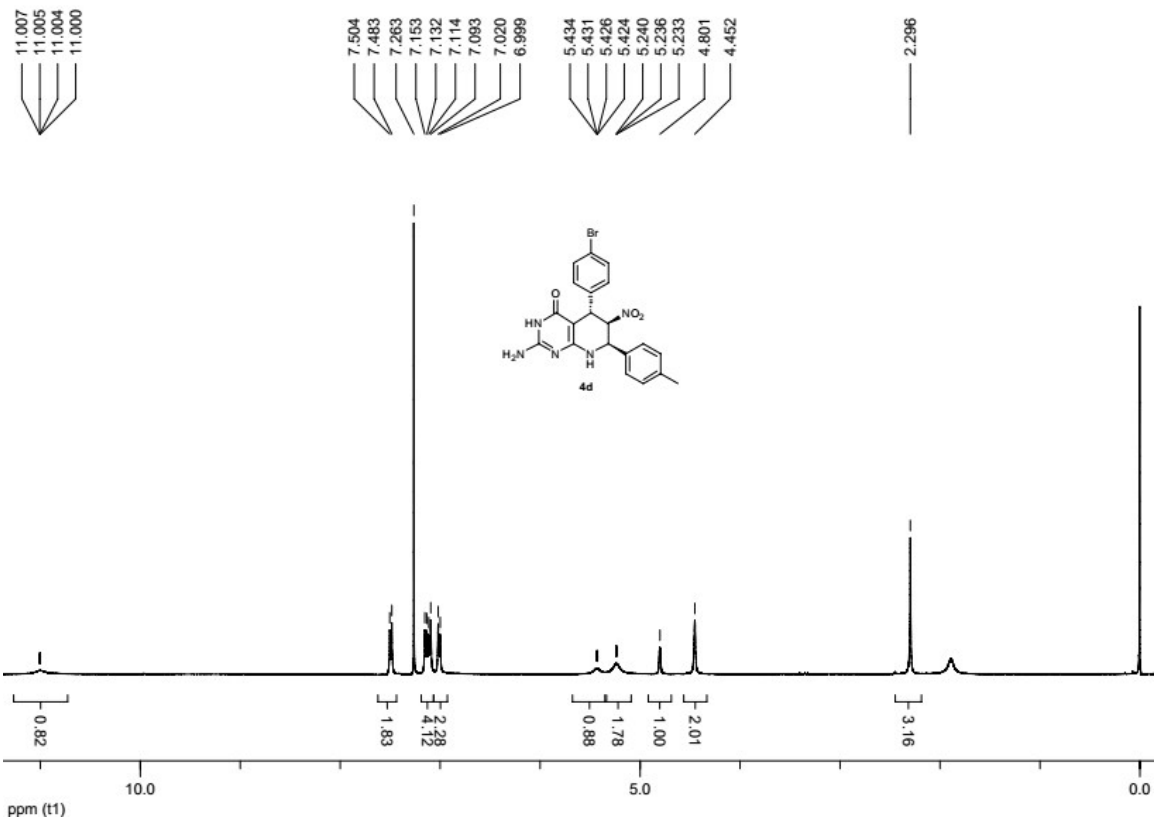
160.004
154.442
141.979
137.941
134.328
131.913
130.573
129.352
128.852
127.165
89.086
82.917
52.852
21.115
Cl
O
HN
NO_2
H_2N
N
H
4c
150
100
50
0
ppm (t1)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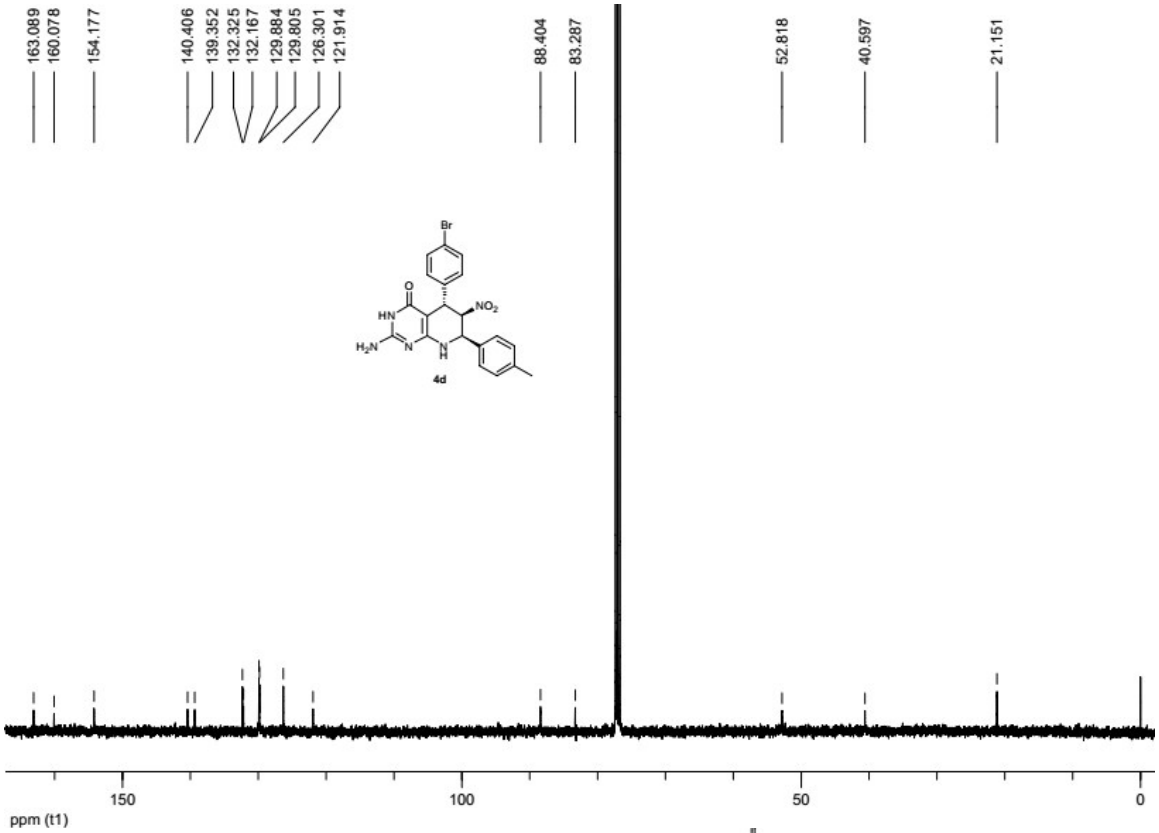
11.005
11.004
11.000
7.504
7.483
7.263
7.153
7.132
7.114
7.093
7.020
6.999
5.434
5.431
5.426
5.424
5.240
5.236
5.233
4.801
4.452
2.296
Br
O
HN
NO_2
H_2N
N
H
4d
0.82
1.83
2.28
4.12
0.88
1.78
1.00
2.01
3.16
10.0
5.0
0.0
ppm (t1)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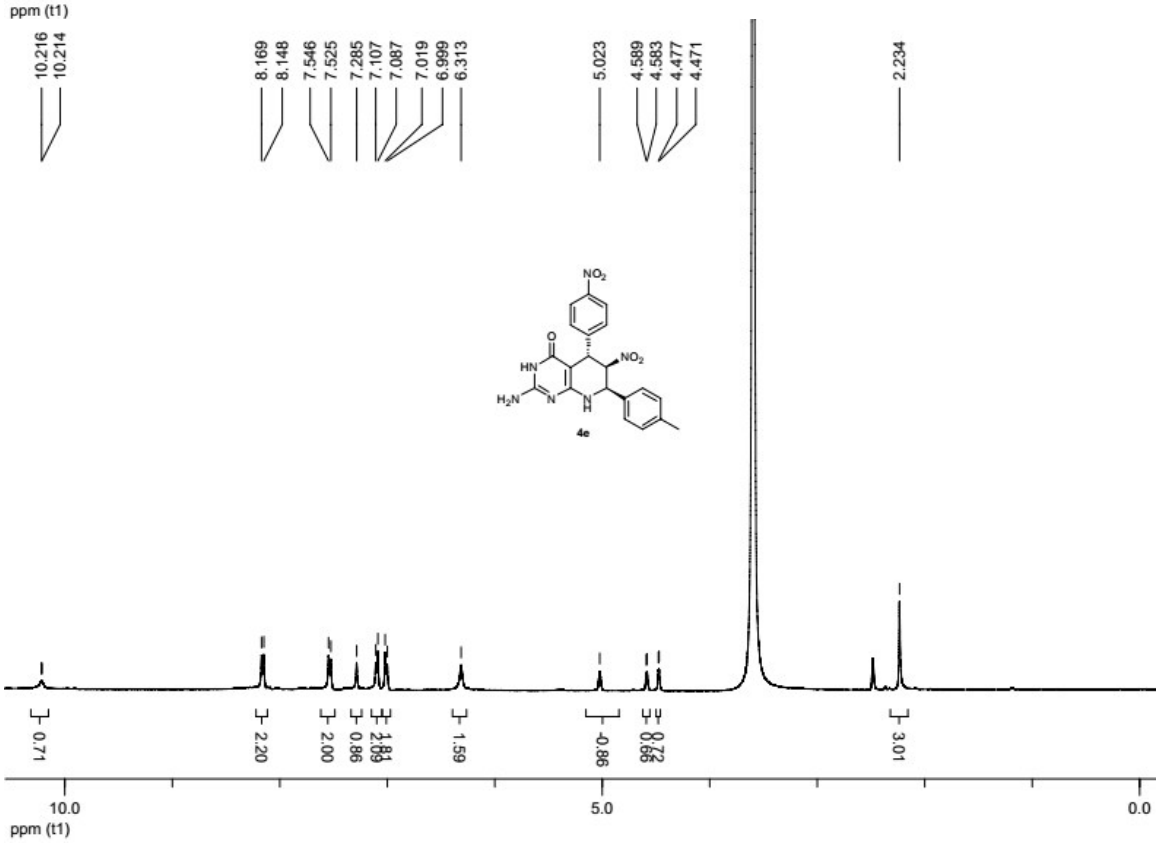
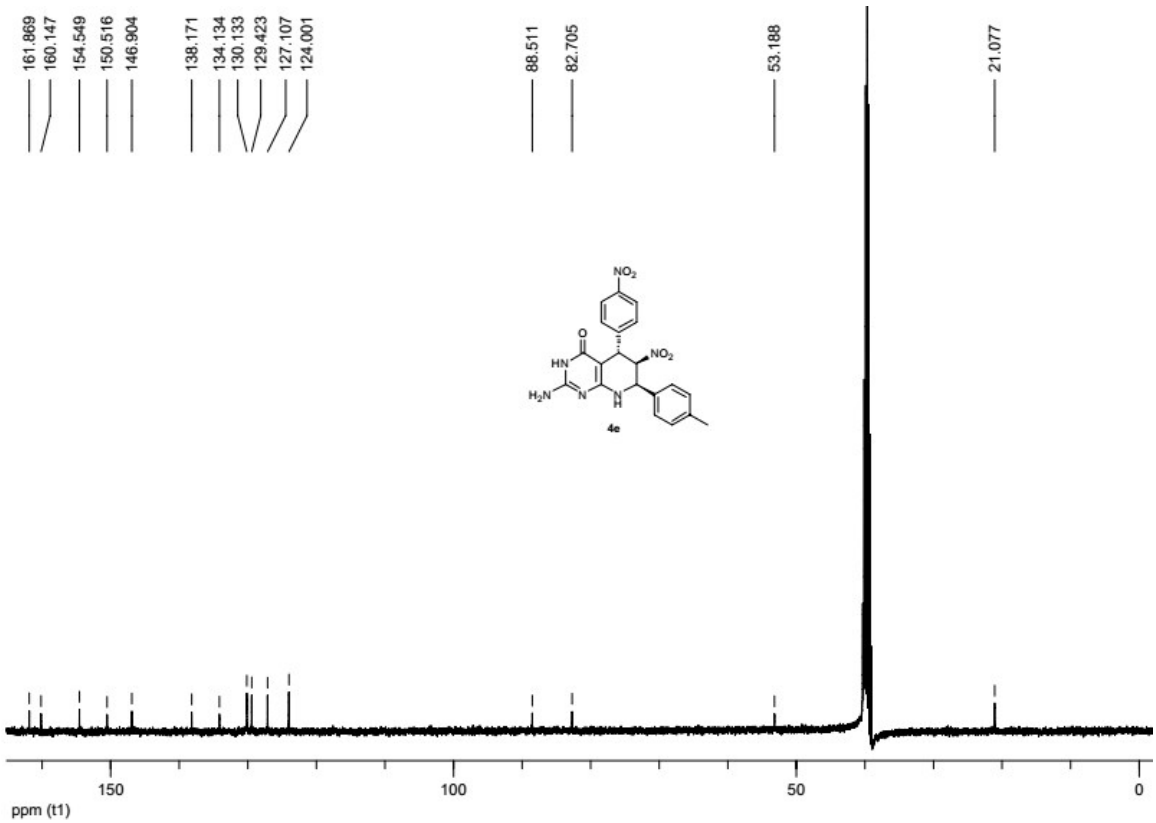
160.078
154.177
140.406
139.352
132.325
132.167
129.884
129.805
126.301
121.914
88.404
83.287
52.818
40.597
21.151
Br
NO2
HN
O
H2N
N
H
4d
150
100
50
0
ppm (t1)


10.216
10.214
8.169
8.148
7.546
7.525
7.285
7.107
7.087
7.019
6.999
6.313
5.023
4.589
4.583
4.477
4.471
2.234
NO2
NO2
HN
O
H2N
N
H
4e
0.71
2.20
2.00
0.86
1.59
0.96
3.01
10.0
5.0
0.0
ppm (t1)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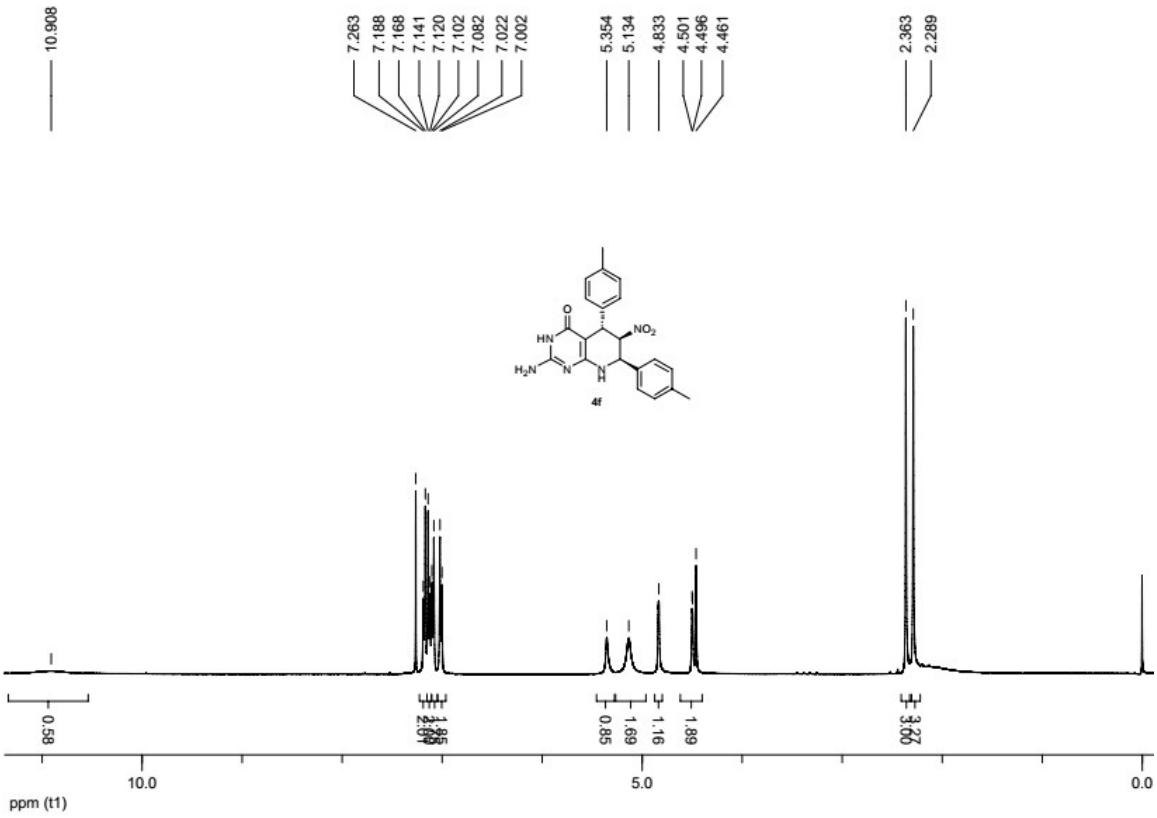
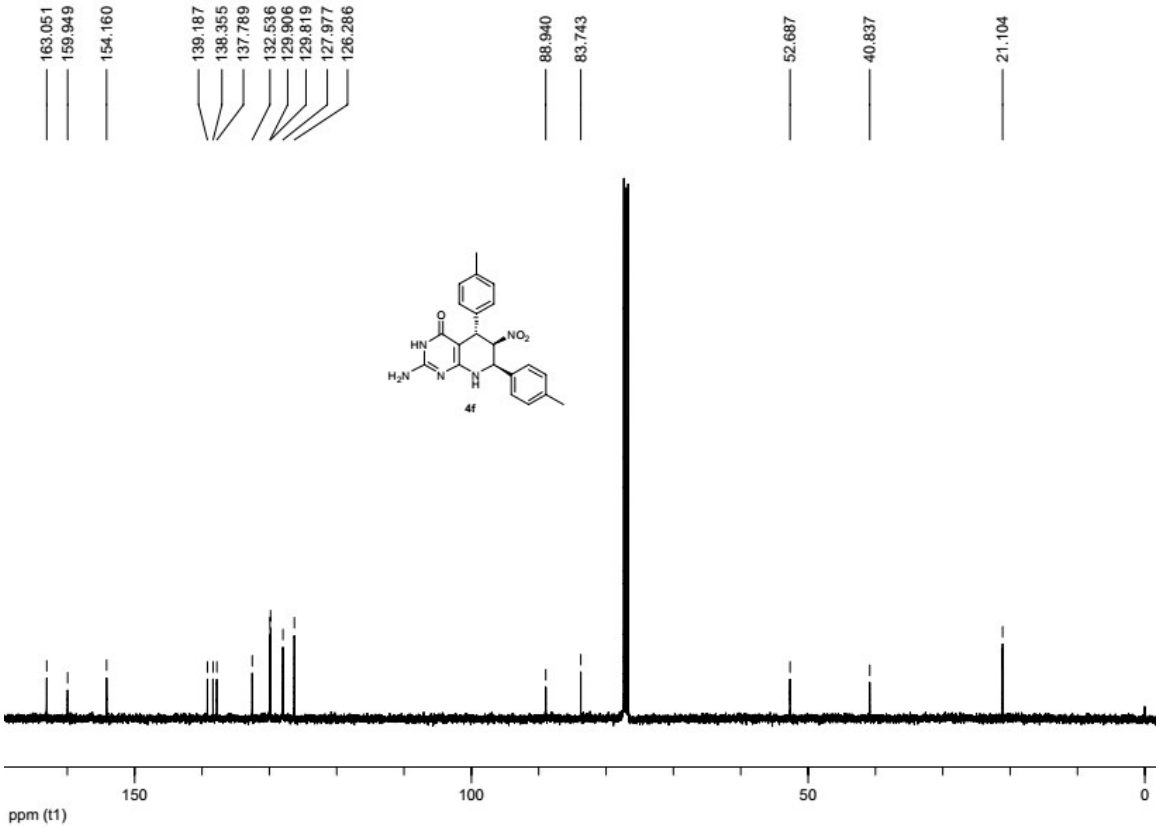
160.147
154.549
150.516
146.904
138.171
134.134
130.133
129.423
127.107
124.001
88.511
82.705
53.188
21.077
4e
150
100
50
0
ppm (t1)


10.908
7.263
7.188
7.168
7.141
7.120
7.102
7.082
7.022
7.002
5.354
5.134
4.833
4.501
4.496
4.461
2.363
2.289
4f
0.58
2.00
1.85
1.69
1.16
1.89
3.00
2.27
10.0
5.0
0.0
ppm (t1)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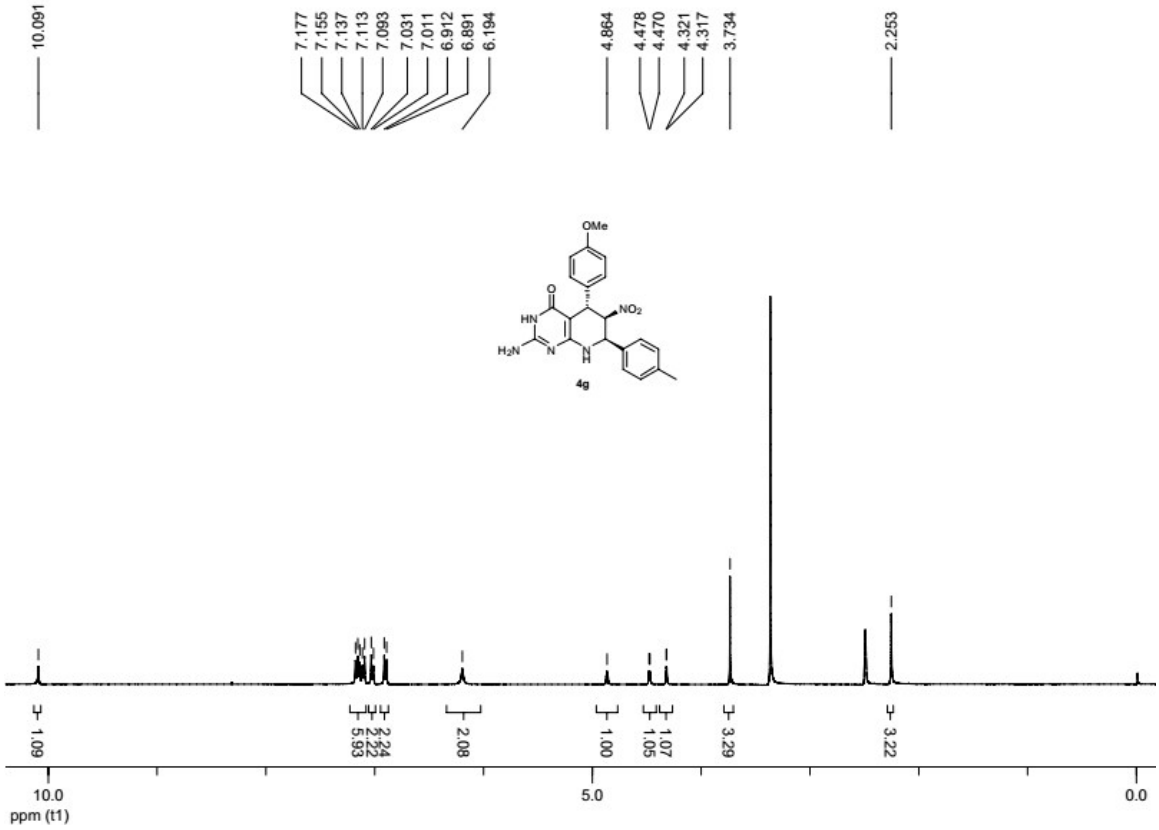
159.949
154.160
139.187
138.355
137.789
132.536
129.906
129.819
127.977
126.286
88.940
83.743
52.687
40.837
21.104
4f
150
100
50
0
ppm (t1)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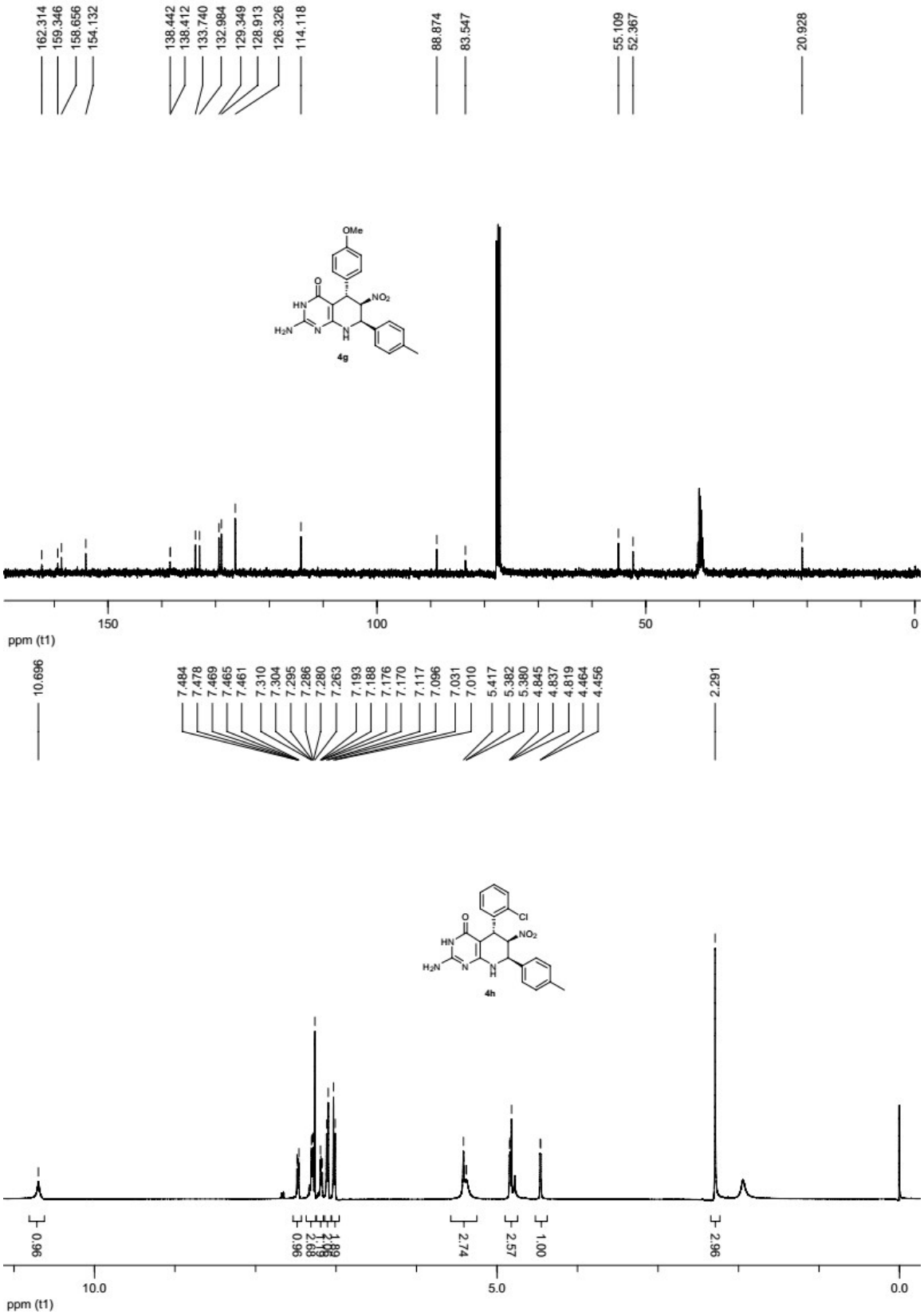
7.177
7.155
7.137
7.113
7.093
7.031
7.011
6.912
6.891
6.194
4.864
4.478
4.470
4.321
4.317
3.734
2.253
OMe
4g
1.09
5.93
2.24
2.22
2.08
1.00
1.05
1.07
3.29
3.22
10.0
5.0
0.0
ppm (t1)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158.656
154.132
138.442
138.412
133.740
132.984
129.349
128.913
126.326
114.118
88.874
83.547
55.109
52.367
20.928
OMe
NO2
HN
O
H2N
N
H
4g
150
100
50
0
ppm (t1)
10.696
7.484
7.478
7.469
7.465
7.461
7.310
7.304
7.295
7.286
7.280
7.263
7.193
7.188
7.176
7.170
7.117
7.096
7.031
7.010
5.417
5.382
5.380
4.845
4.837
4.819
4.464
4.456
2.291
Cl
NO2
HN
O
H2N
N
H
4h
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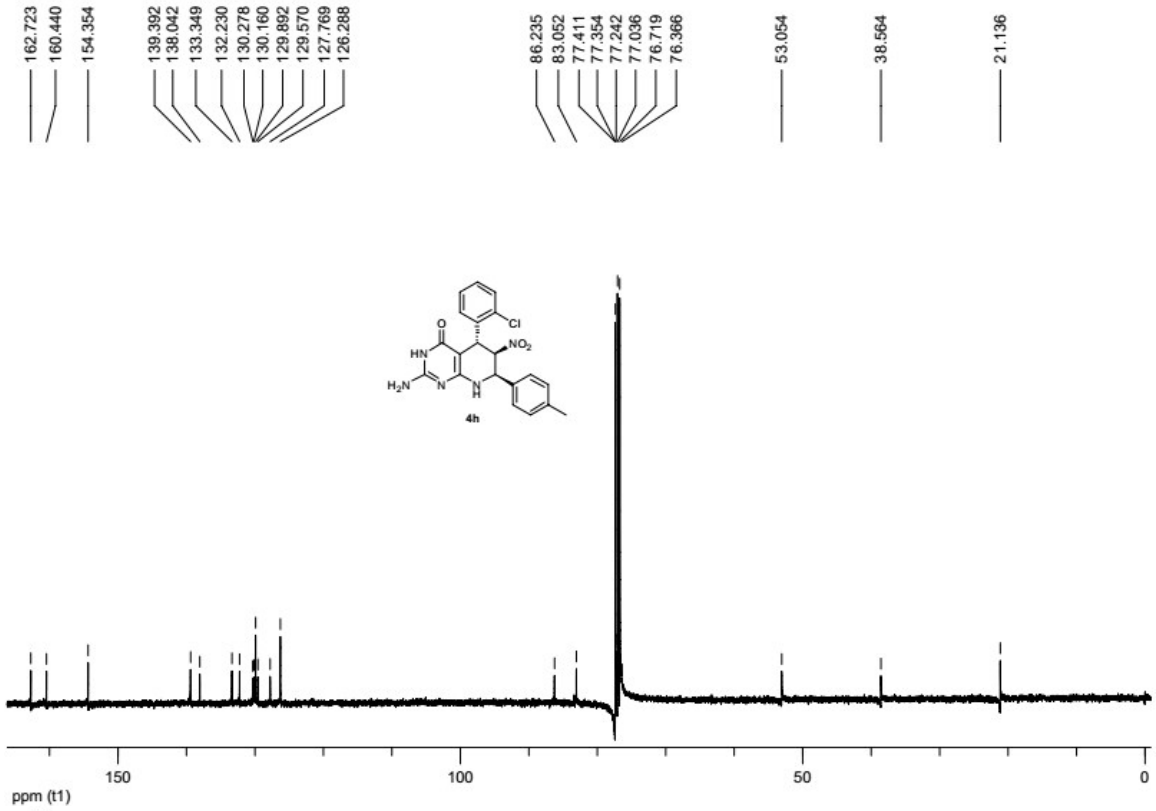
0.96
2.74
2.57
1.00
2.96
10.0
5.0
0.0
ppm (t1)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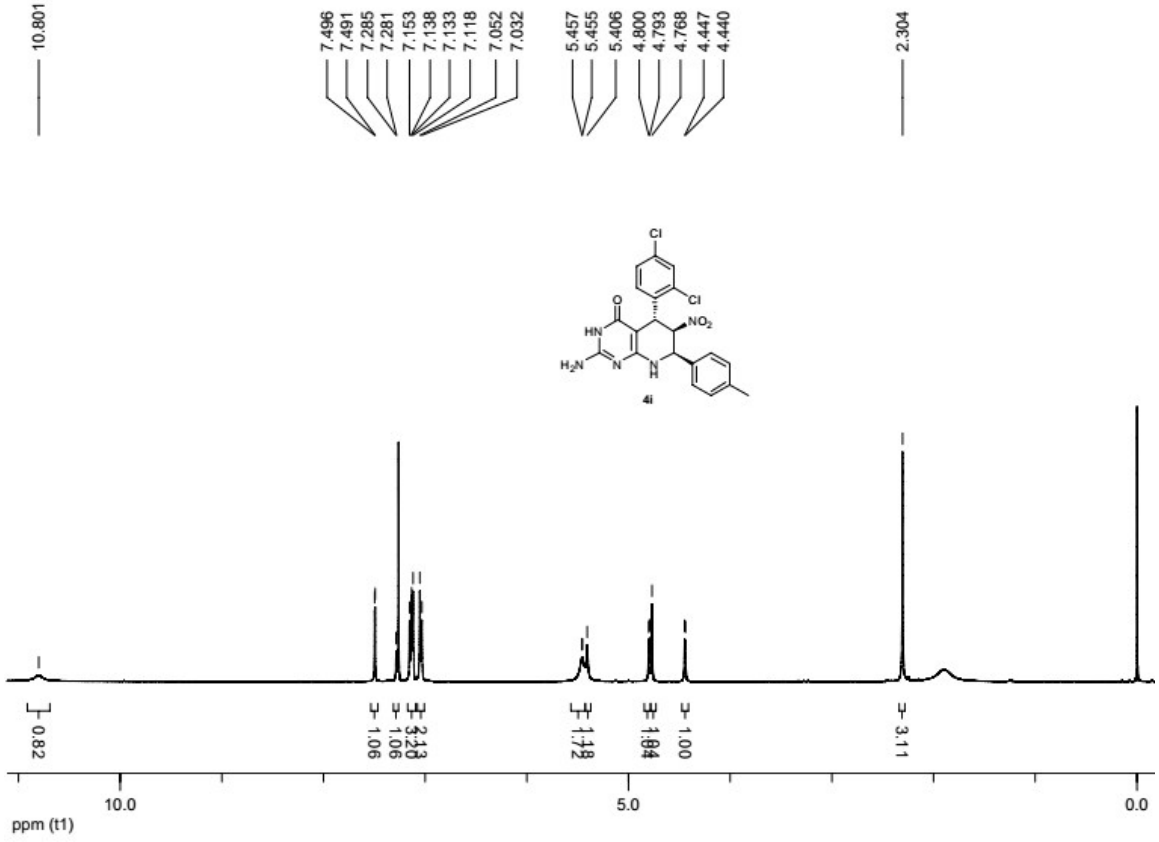
154.354
139.392
138.042
133.349
132.230
130.278
130.160
129.892
129.570
127.769
126.288
86.235
83.052
77.411
77.354
77.242
77.036
76.719
76.366
53.054
38.564
21.136
4h
150
100
50
0
ppm (t1)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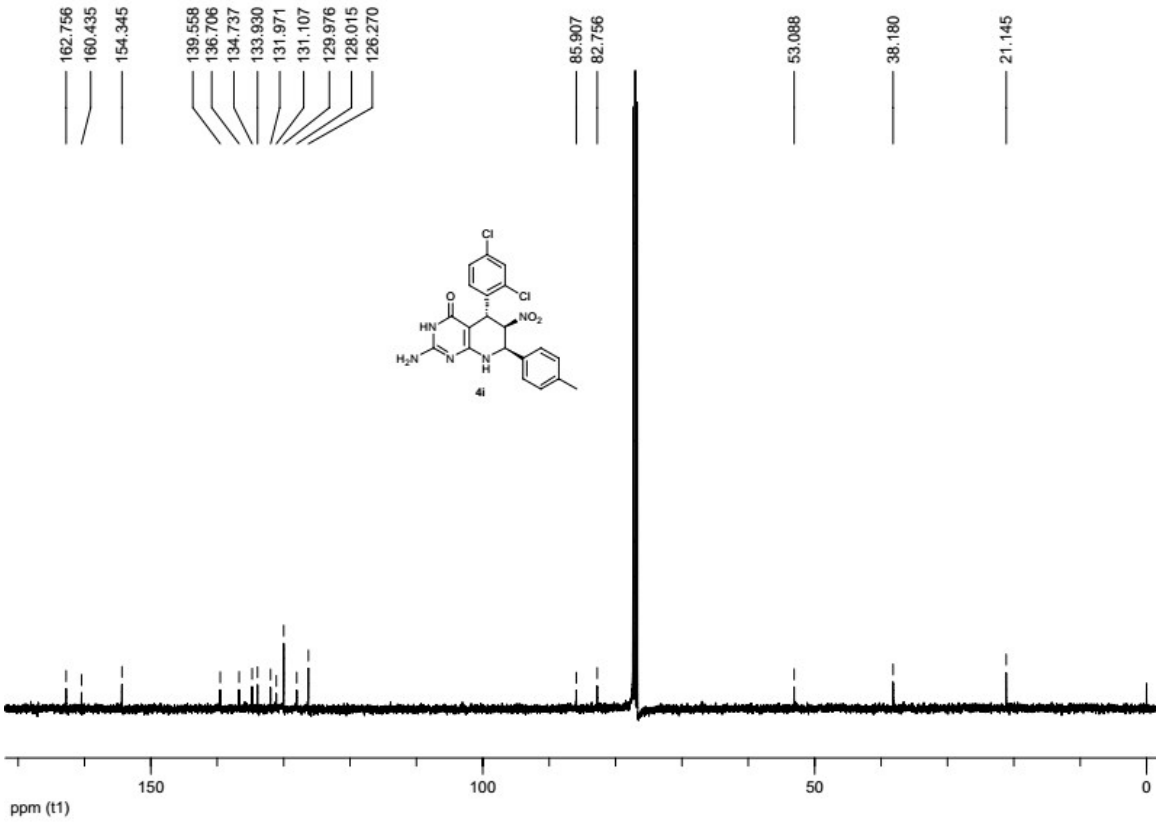
7.491
7.285
7.281
7.153
7.138
7.133
7.118
7.052
7.032
5.457
5.455
5.406
4.800
4.793
4.768
4.447
4.440
2.304
4i
0.82
1.09
1.06
1.00
3.11
10.0
5.0
0.0
ppm (t1)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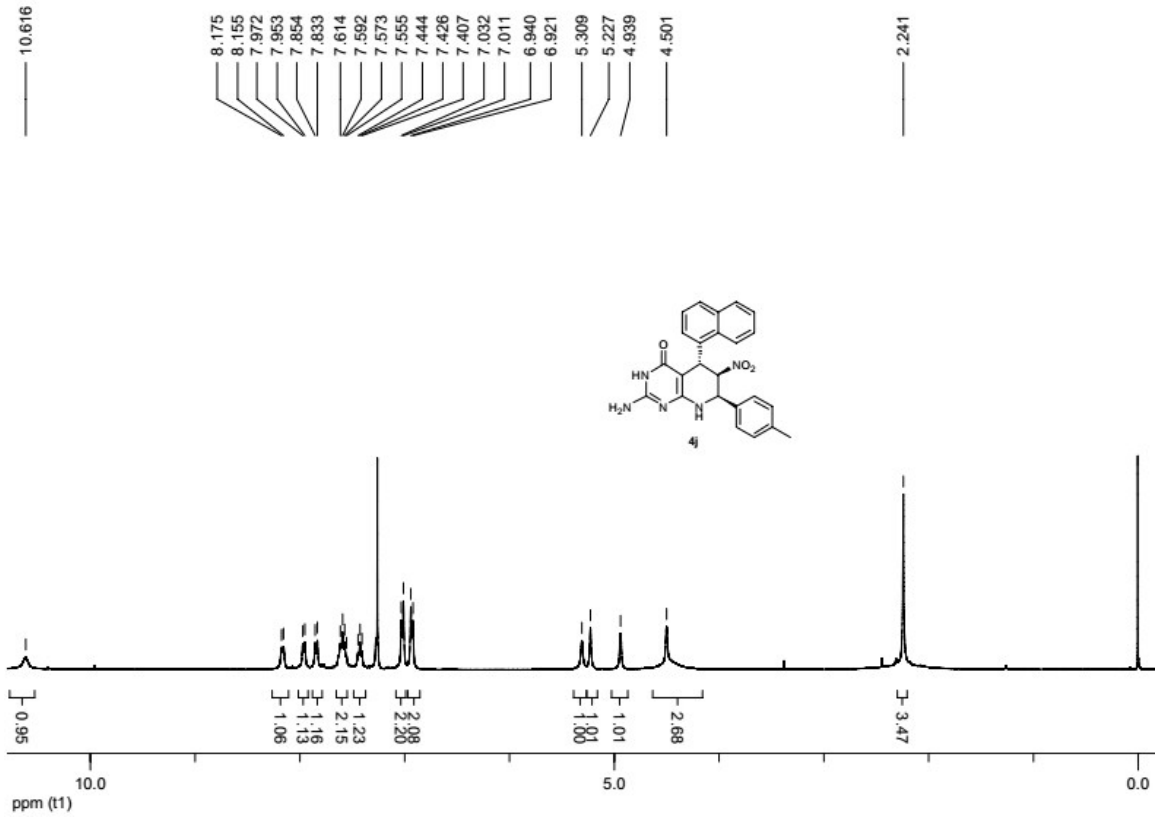
139.558
136.706
134.737
133.930
131.971
131.107
129.976
128.015
126.270
85.907
82.756
53.088
38.180
21.145
Cl
Cl
O
HN
NO2
H2N
N
N
H
4i
150
100
50
0
ppm (t1)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8.155
7.972
7.953
7.854
7.833
7.614
7.592
7.573
7.555
7.444
7.426
7.407
7.032
7.011
6.940
6.921
5.309
5.227
4.939
4.501
2.241
O
HN
NO2
H2N
N
N
H
4j
0.95
1.06
1.13
1.16
2.15
1.23
2.20
2.08
1.00
1.01
1.01
2.68
3.47
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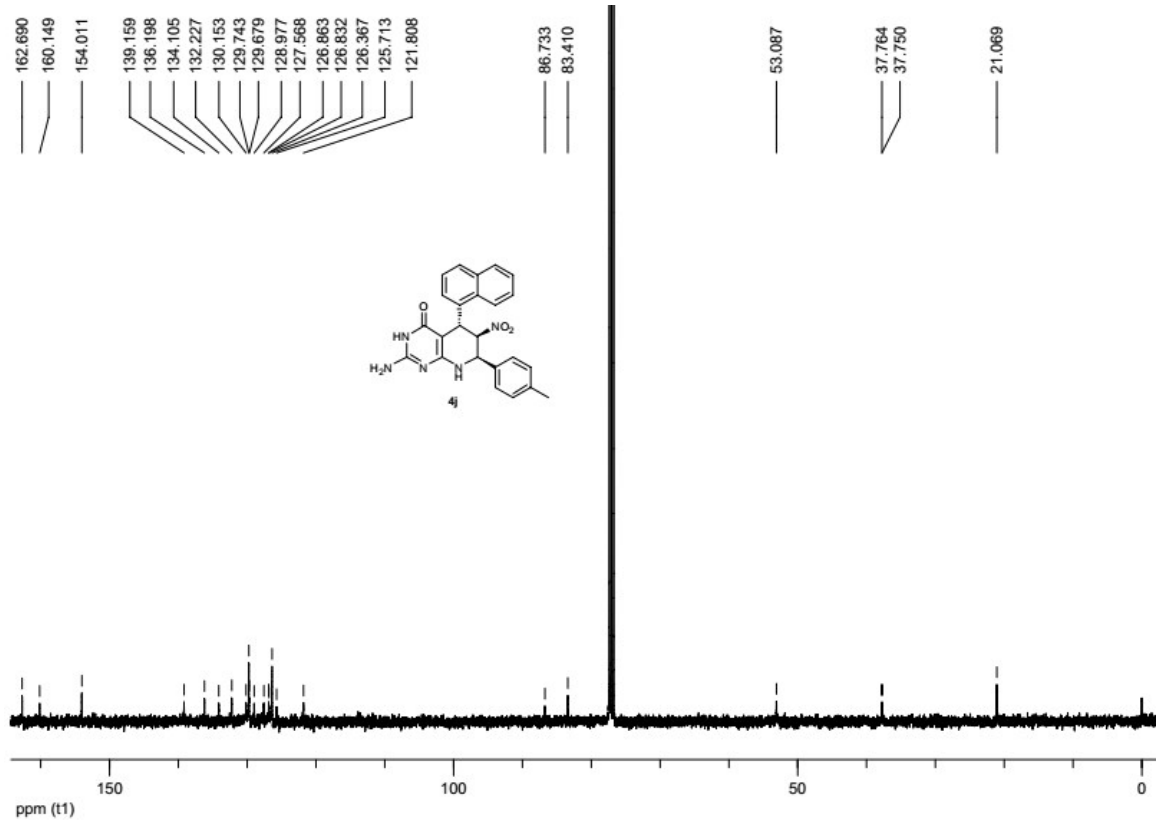
ppm (t1)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132.227
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129.743
129.679
128.977
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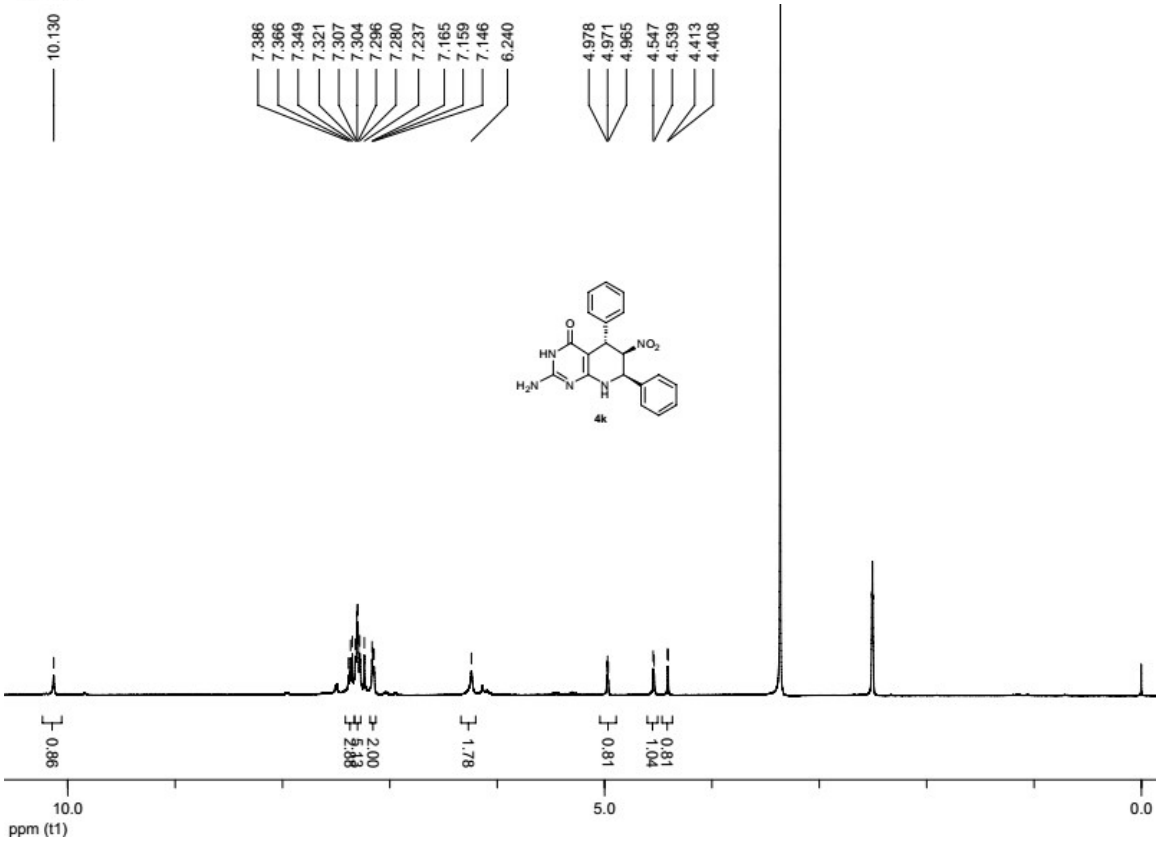
126.832
126.367
125.713
121.808
86.733
83.410
53.087
37.764
37.750
21.069
4j
150
100
50
0
ppm (t1)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7.366
7.349
7.321
7.307
7.304
7.296
7.280
7.237
7.165
7.159
7.146
6.240
4.978
4.971
4.965
4.547
4.539
4.413
4.408
4k
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2.00
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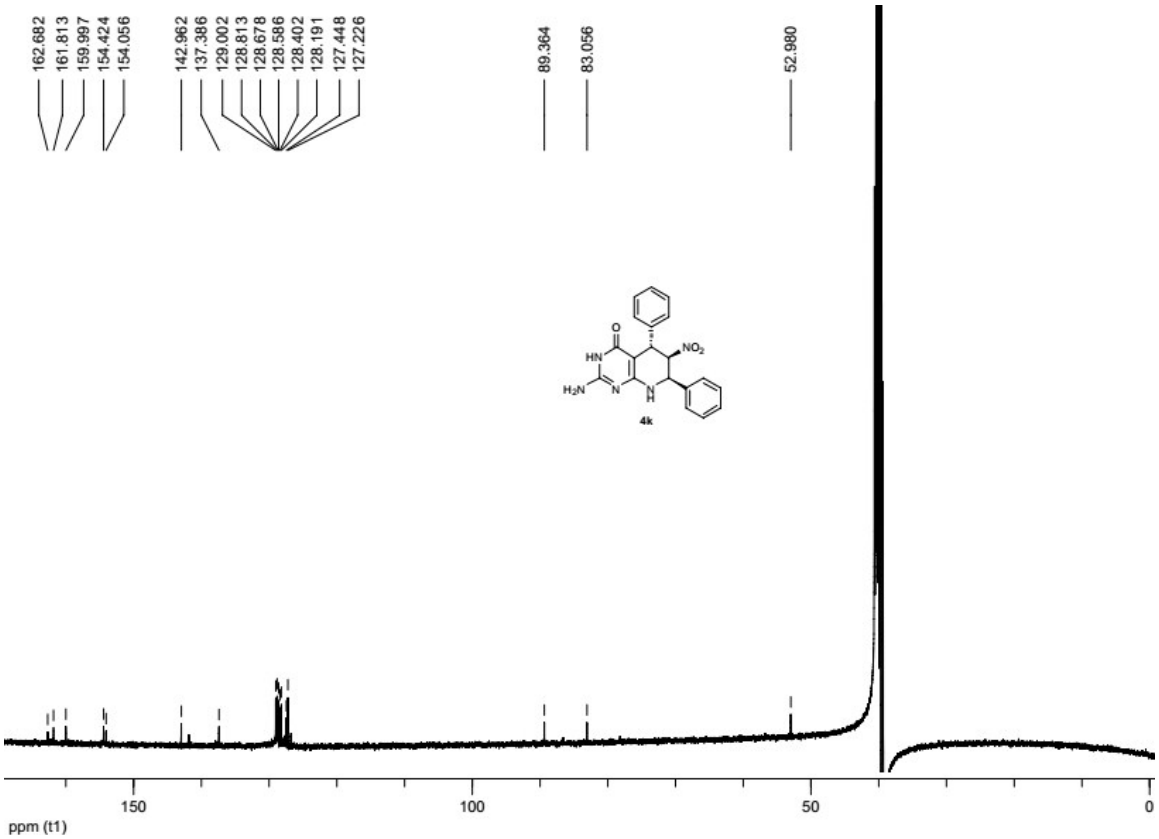
0.81
0.81
1.04
10.0
5.0
0.0
ppm (t1)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159.997
154.424
154.056
142.962
137.386
129.002
128.813
128.678
128.586
128.402
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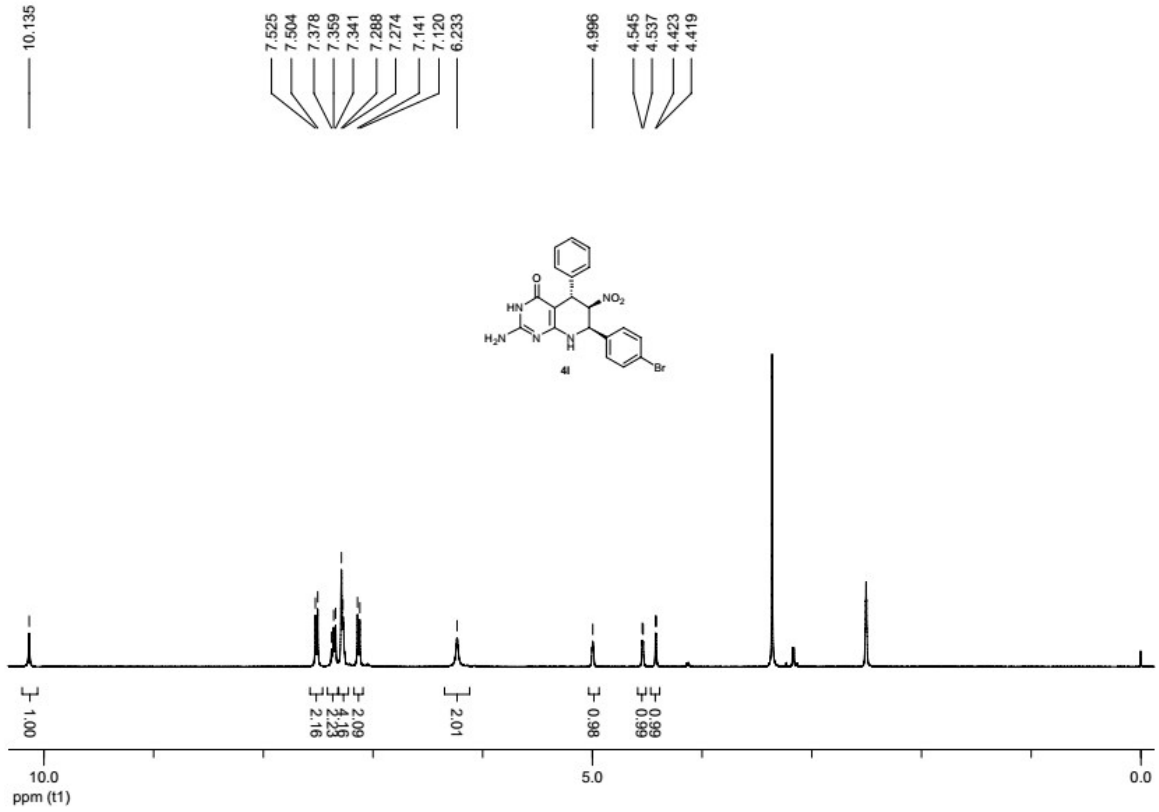
127.448
127.226
89.364
83.056
52.980
4k
150
100
50
0
ppm (t1)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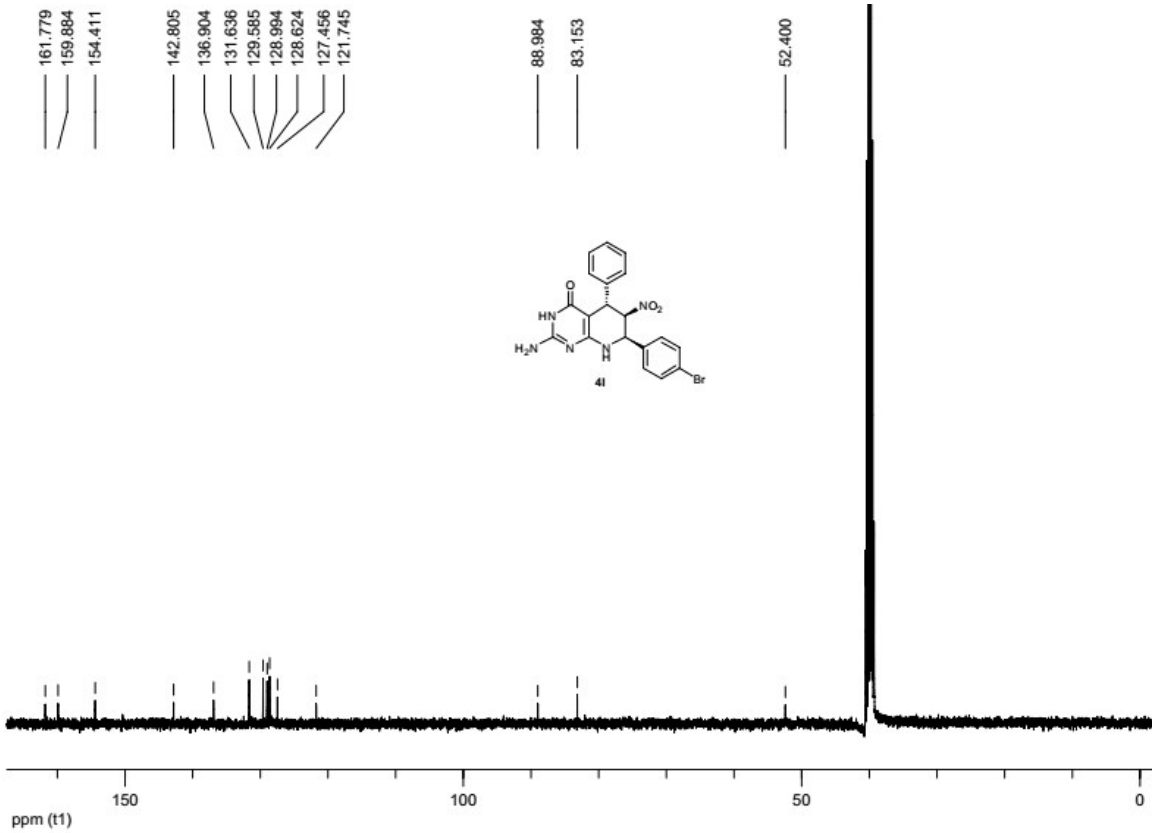
7.504
7.378
7.359
7.341
7.288
7.274
7.141
7.120
6.233
4.996
4.545
4.537
4.423
4.419
4l
1.00
2.19
2.23
4.16
2.09
2.01
0.98
0.99
0.99
10.0
5.0
0.0
ppm (t1)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131.636
129.585
128.994
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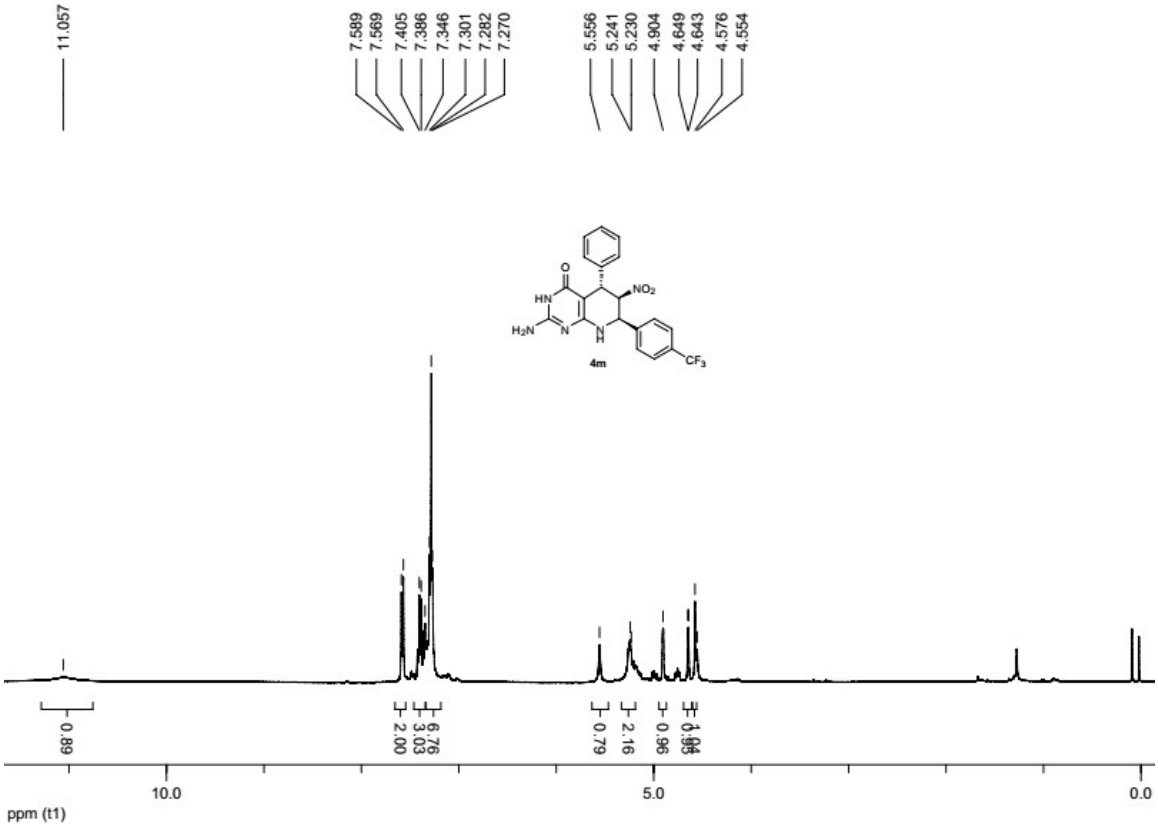
127.456
121.745
88.984
83.153
52.400
4l
150
100
50
0
ppm (t1)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7.405
7.386
7.346
7.301
7.282
7.270
5.556
5.241
5.230
4.904
4.649
4.643
4.576
4.554
4m
0.89
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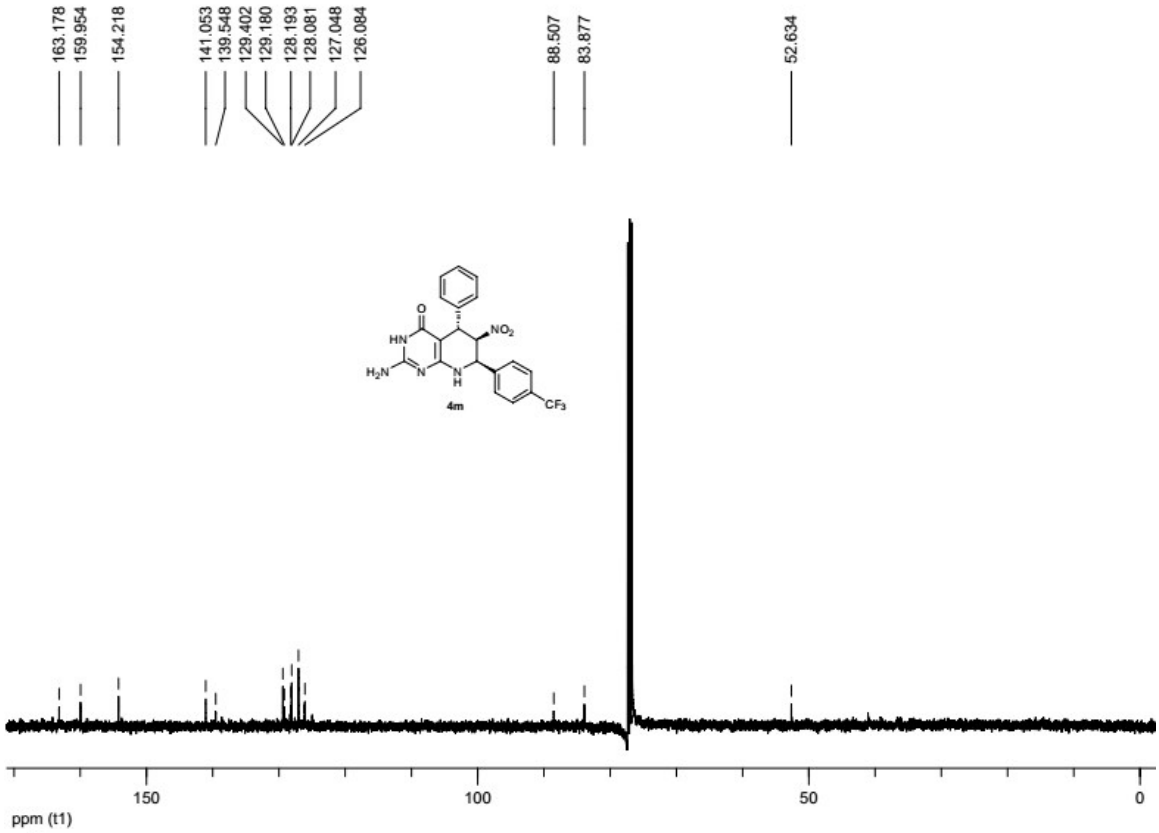
6.03
6.76
0.79
2.16
0.96
1.00
10.0
5.0
0.0
ppm (t1)


163.178
159.954
154.218
141.053
139.548
129.402
129.180
128.193
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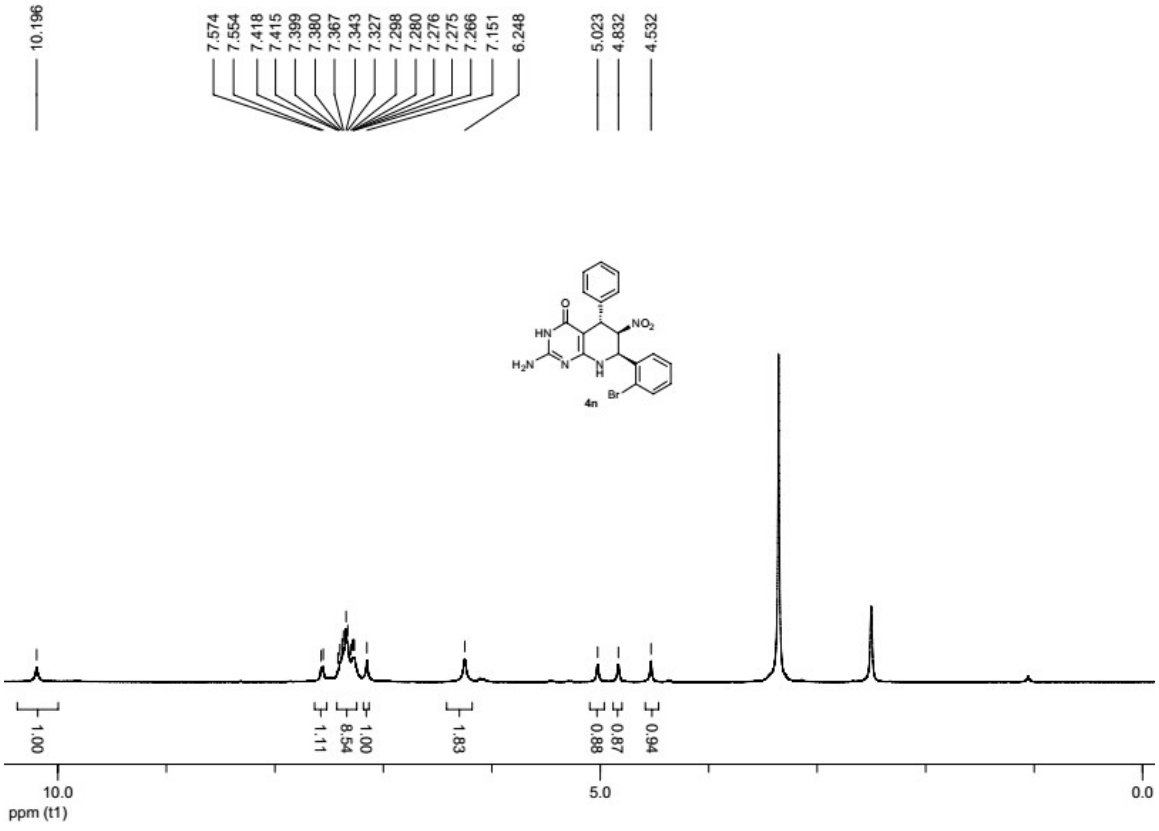
127.048
126.084
88.507
83.877
52.634
4m
150
100
50
0
ppm (t1)


10.196
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7.418
7.415
7.399
7.380
7.367
7.343
7.327
7.298
7.280
7.276
7.275
7.266
7.151
6.248
5.023
4.832
4.532
4n
1.00
1.11
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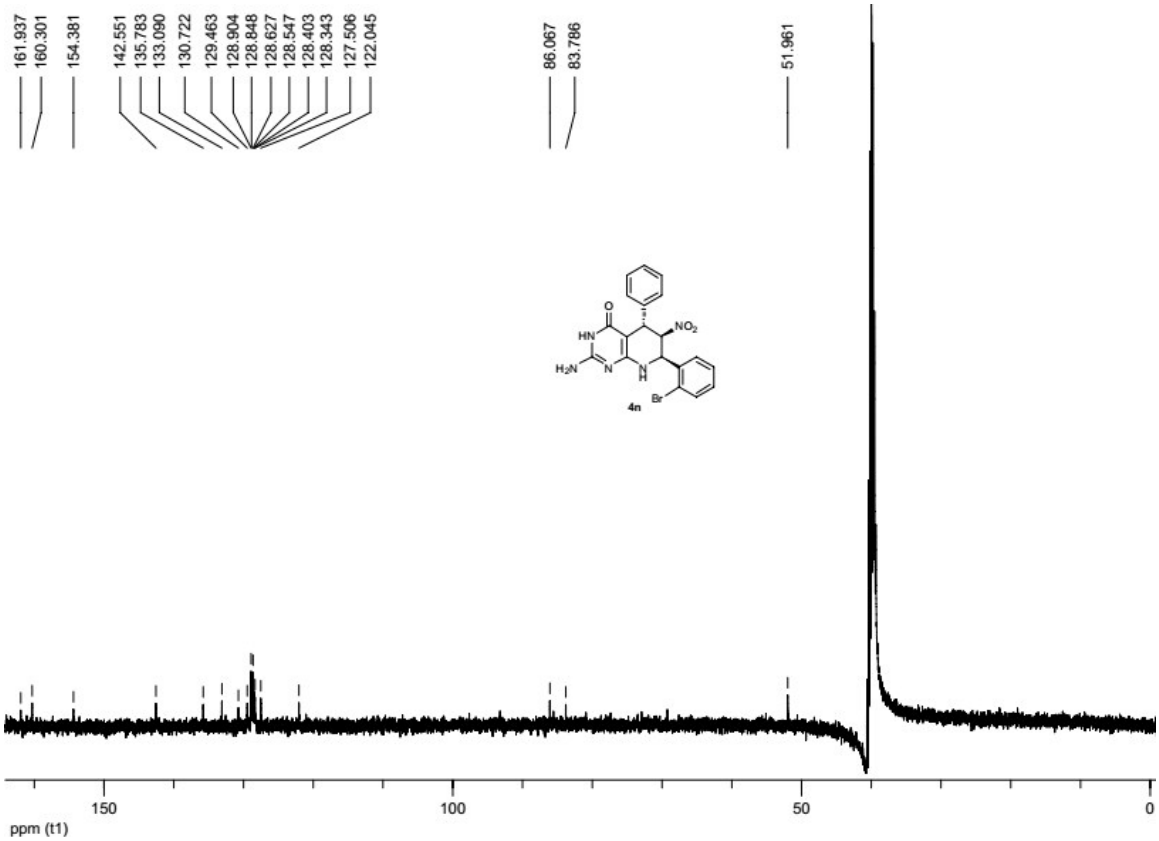
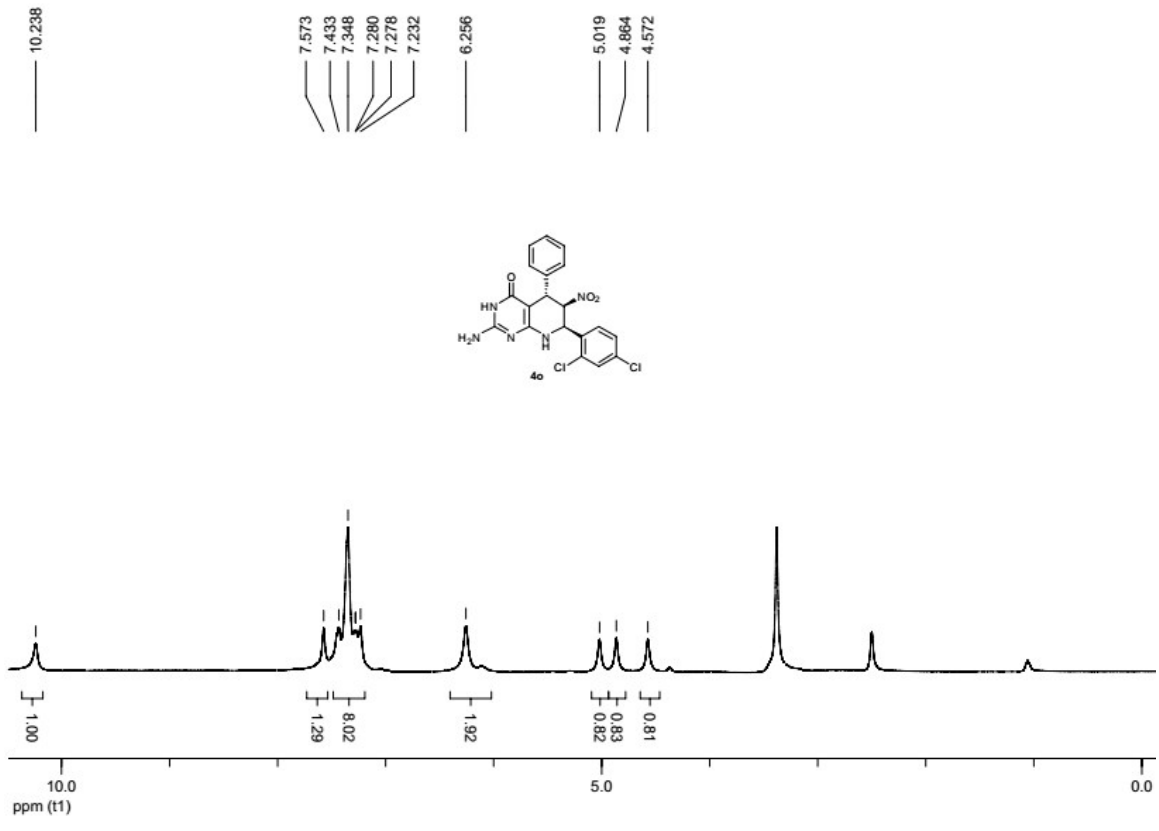
1.00
1.83
0.88
0.87
0.94
10.0
5.0
0.0
ppm (t1)


161.937
160.301
154.381
142.551
135.783
133.090
130.722
129.463
128.904
128.848
128.627
128.547
128.403
128.343
127.506
122.045
86.067
83.786
51.961
4n
150
100
50
0
ppm (t1)


10.238
7.573
7.433
7.348
7.280
7.278
7.232
6.256
5.019
4.864
4.572
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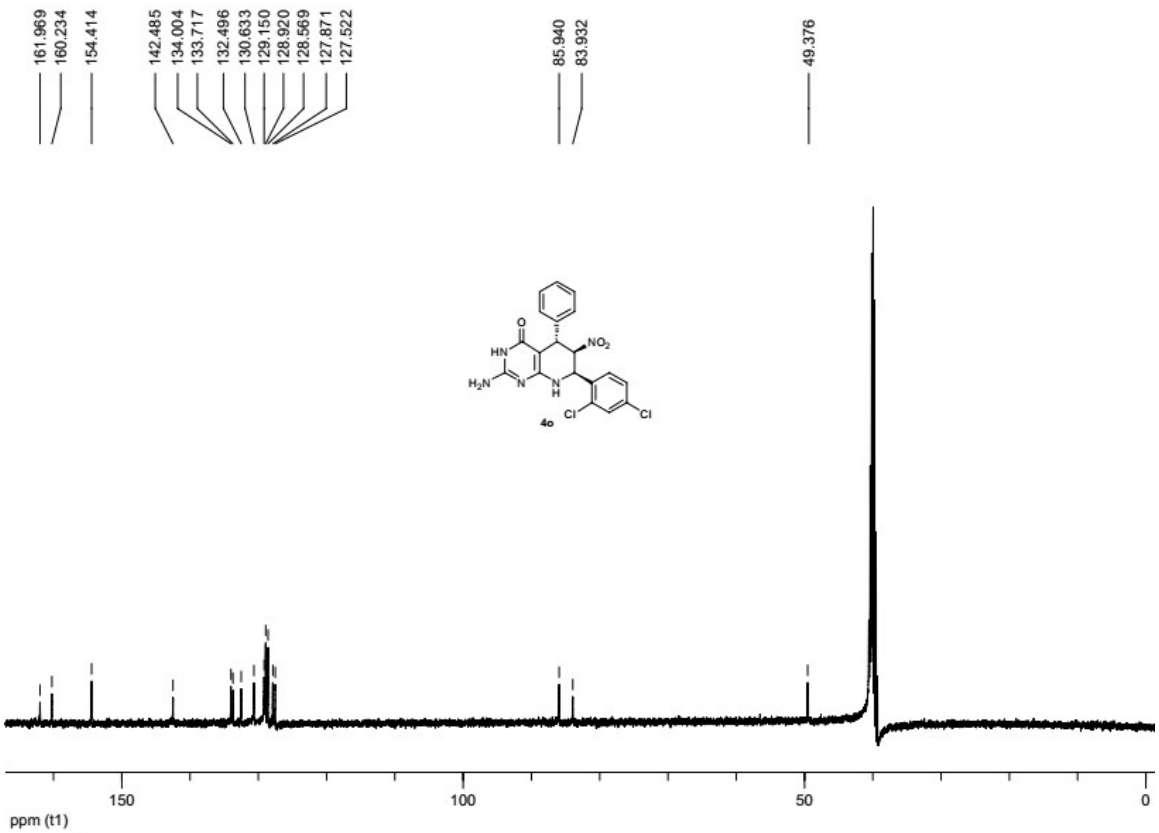
1.29
8.02
1.92
0.82
0.83
0.81
10.0
5.0
0.0
ppm (t1)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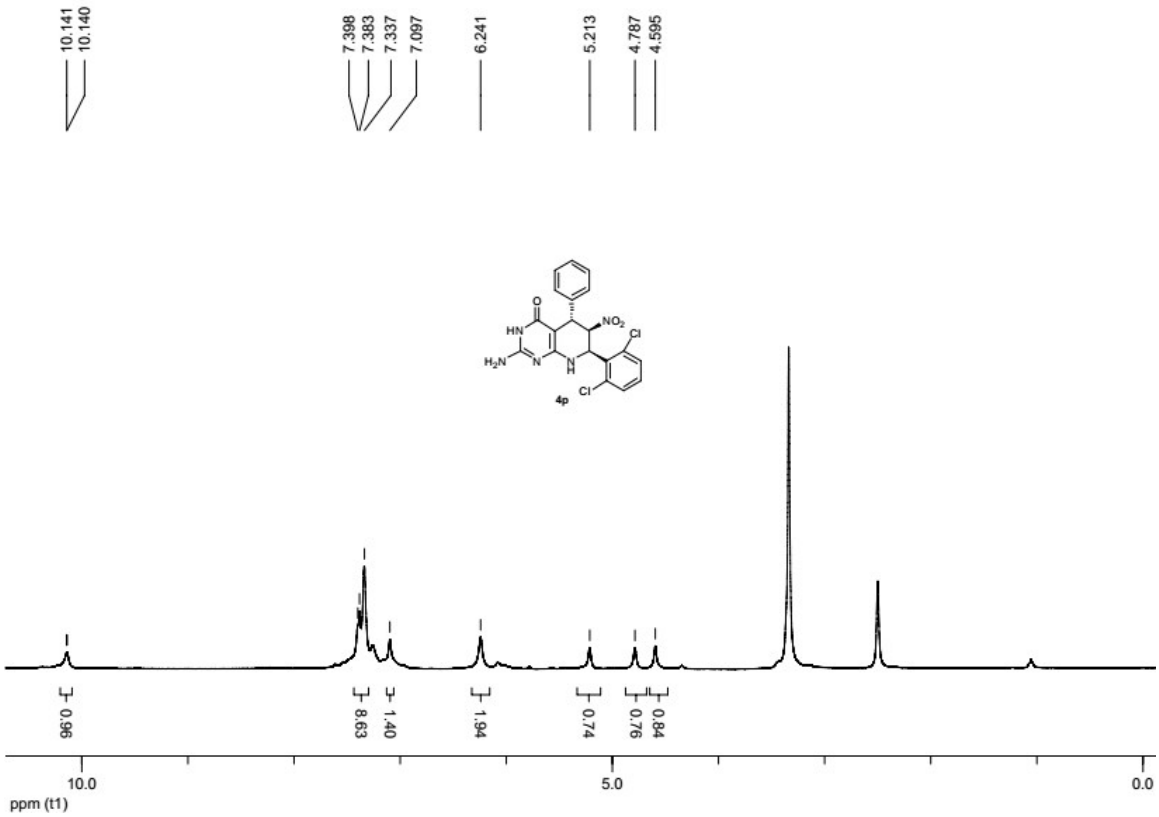
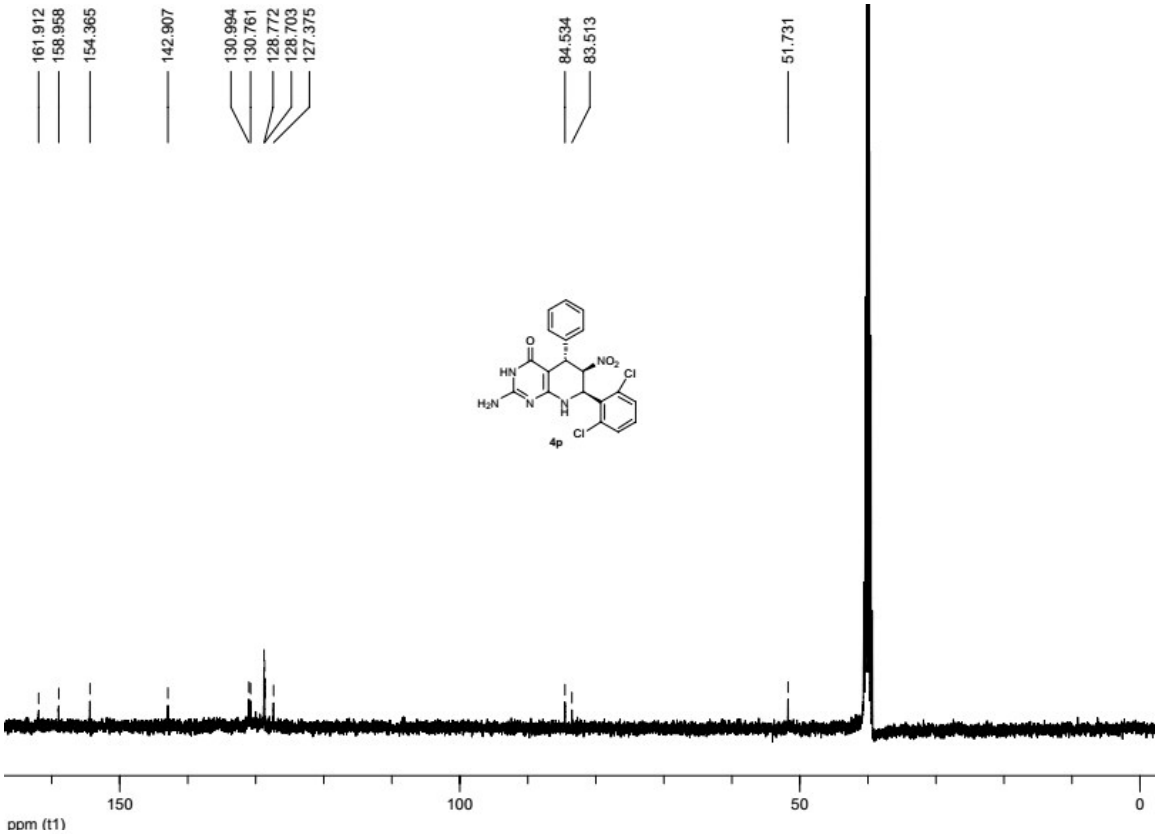
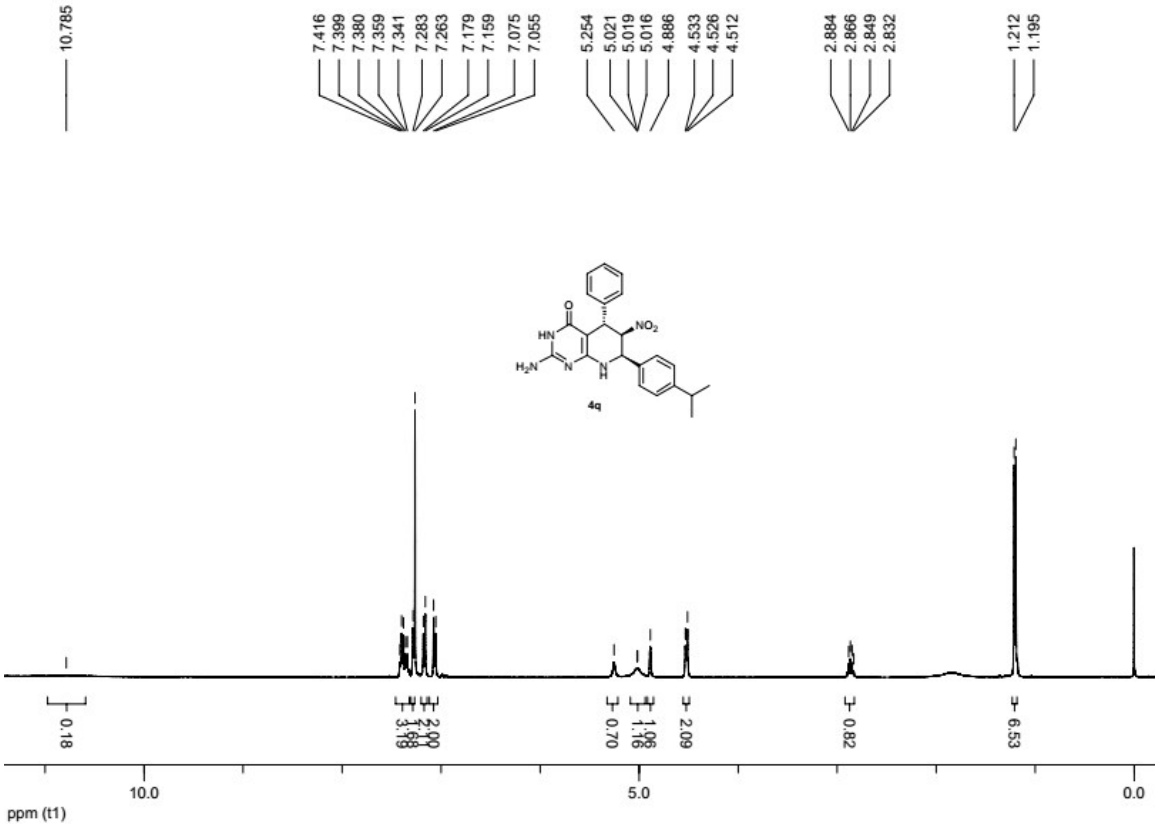
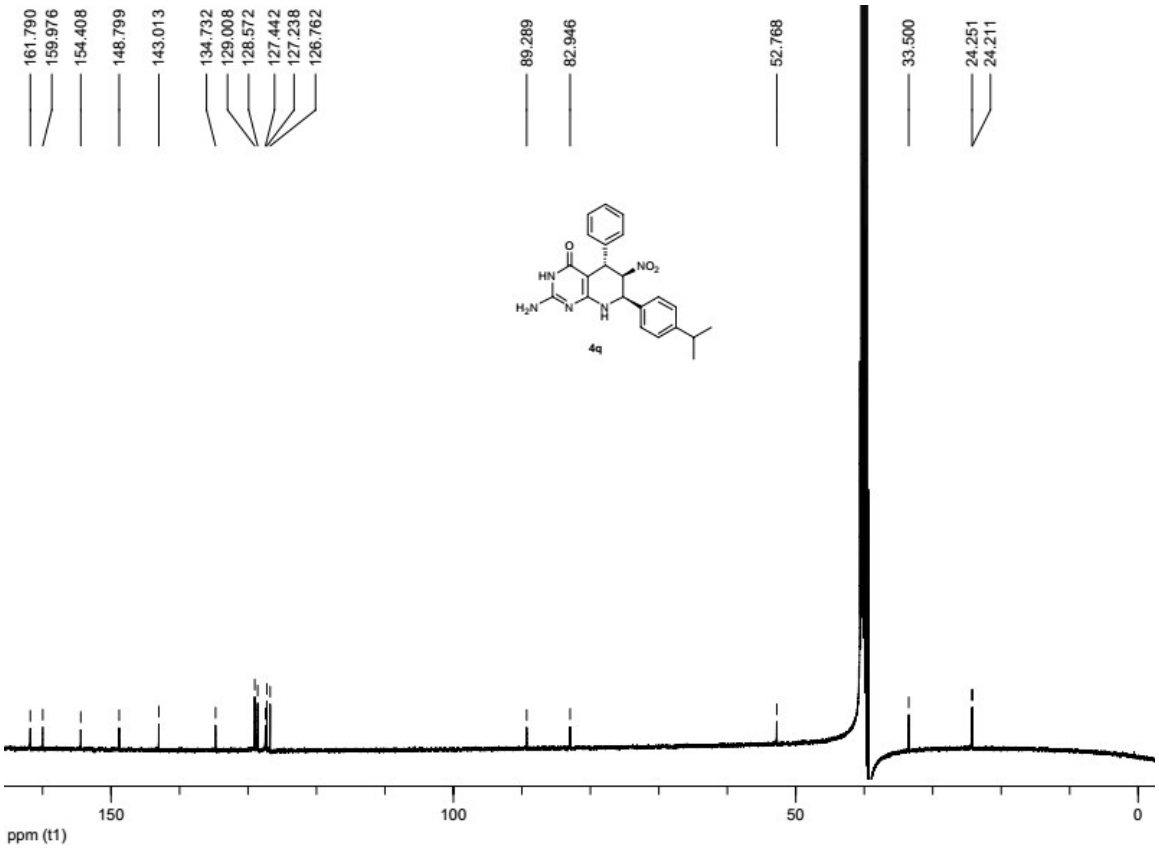
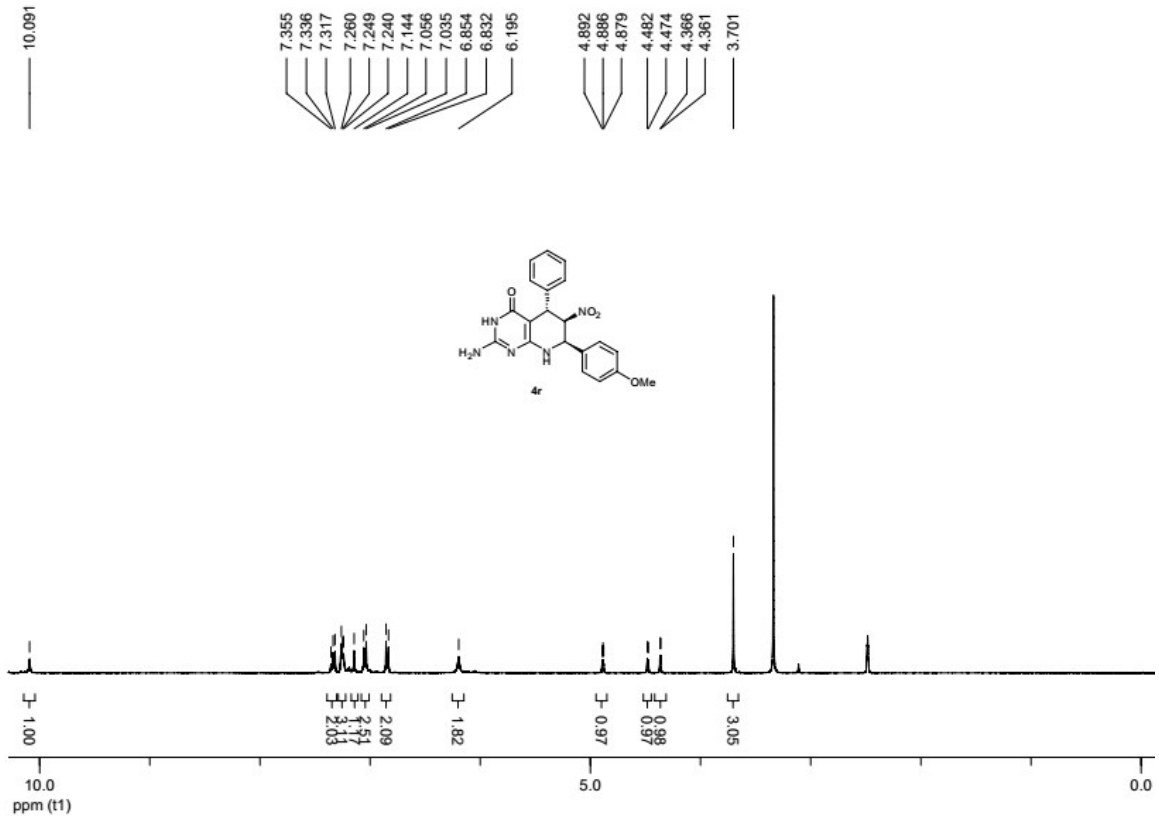
160.234
154.414
142.485
134.004
133.717
132.496
130.633
129.150
128.920
128.569
127.871
127.522
85.940
83.932
49.376
4o
150
100
50
0
ppm (t1)

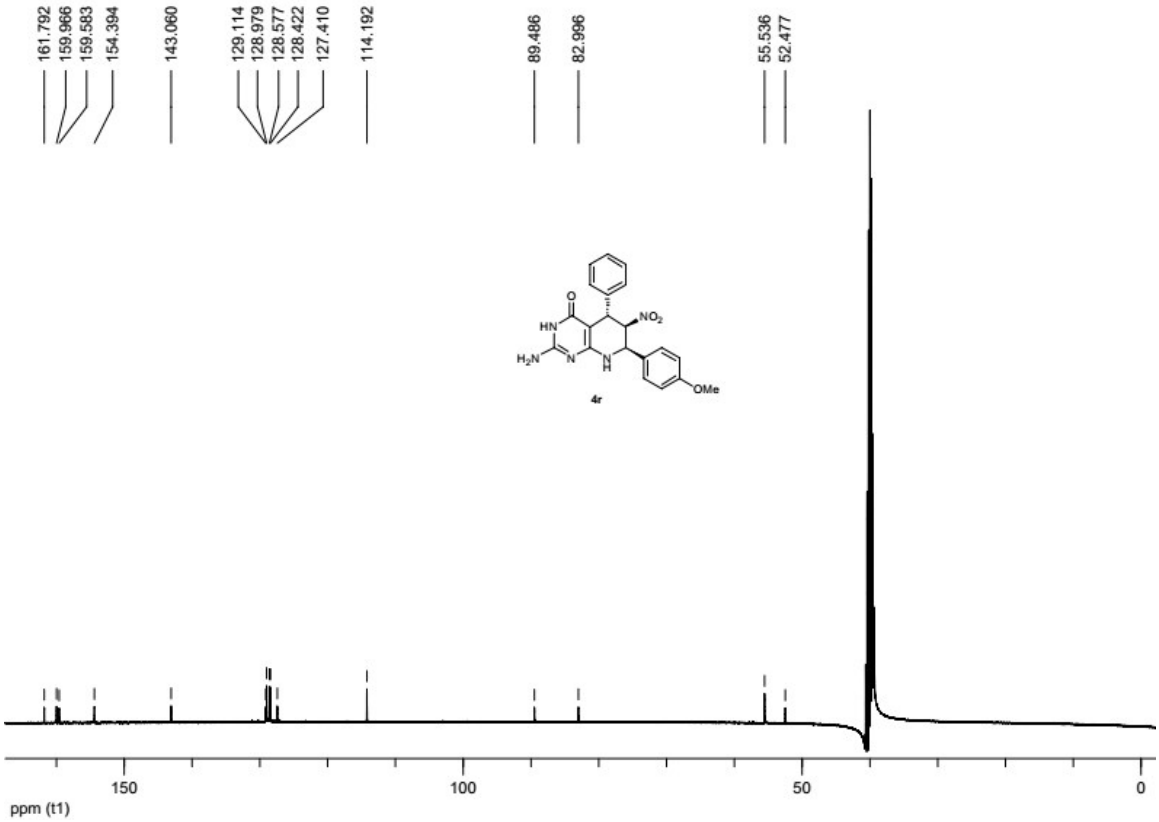

10.141
10.140
7.398
7.383
7.337
7.097
6.241
5.213
4.787
4.595
4p
0.96
8.63
1.40
1.94
0.74
0.76
0.84
10.0
5.0
0.0
ppm (t1)

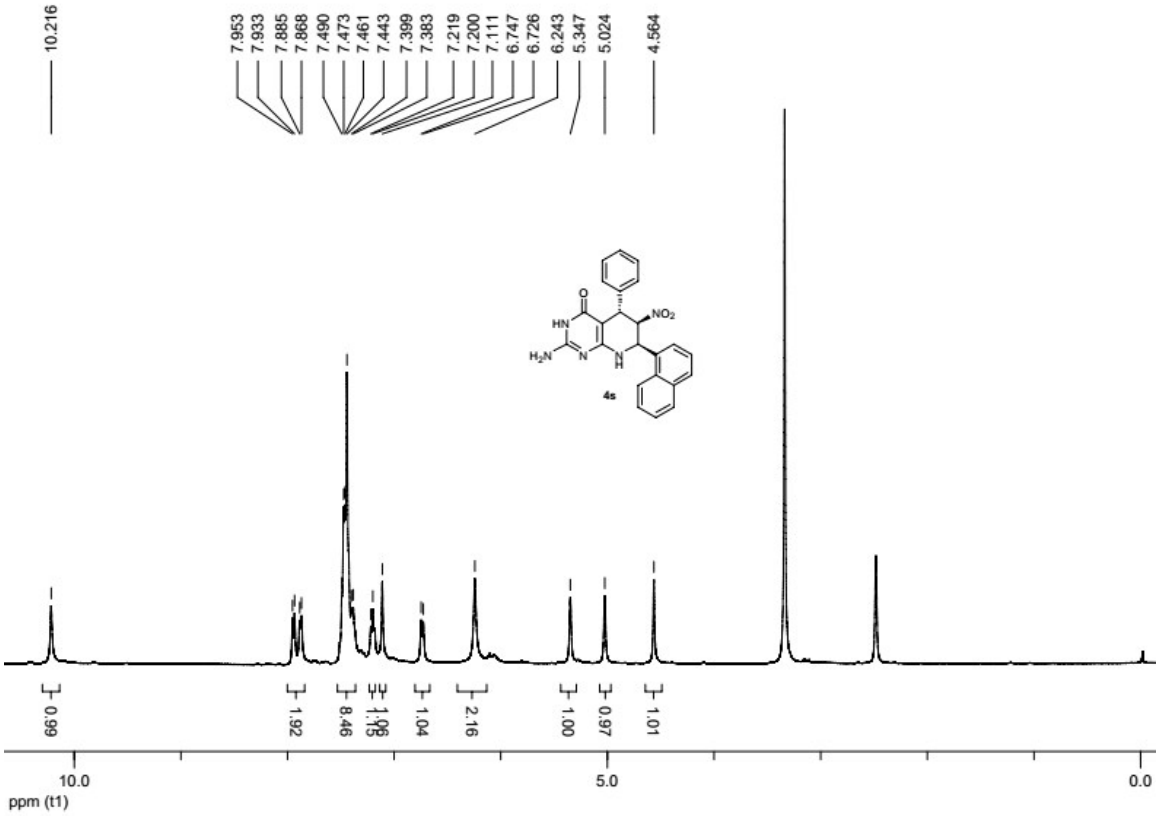

161.912
158.958
154.365
142.907
130.994
130.761
128.772
128.703
127.375
84.534
83.513
51.731
4p
150
100
50
0
ppm (t1)

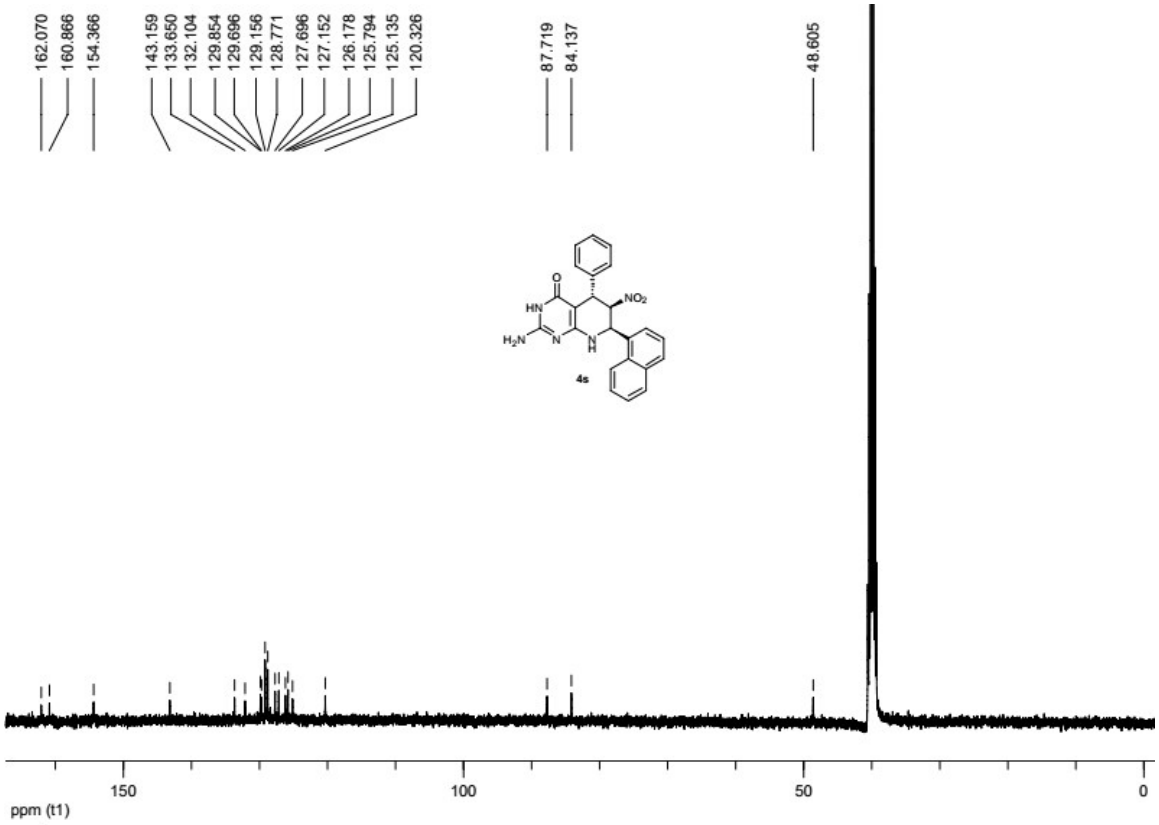

10.785
7.416
7.399
7.380
7.359
7.341
7.283
7.263
7.179
7.159
7.075
7.055
5.254
5.021
5.019
5.016
4.886
4.533
4.526
4.512
2.884
2.866
2.849
2.832
1.212
1.195
4q
1.18
3.19
1.68
2.00
0.70
1.06
1.16
2.09
0.82
9.53
10.0
5.0
0.0
ppm (t1)

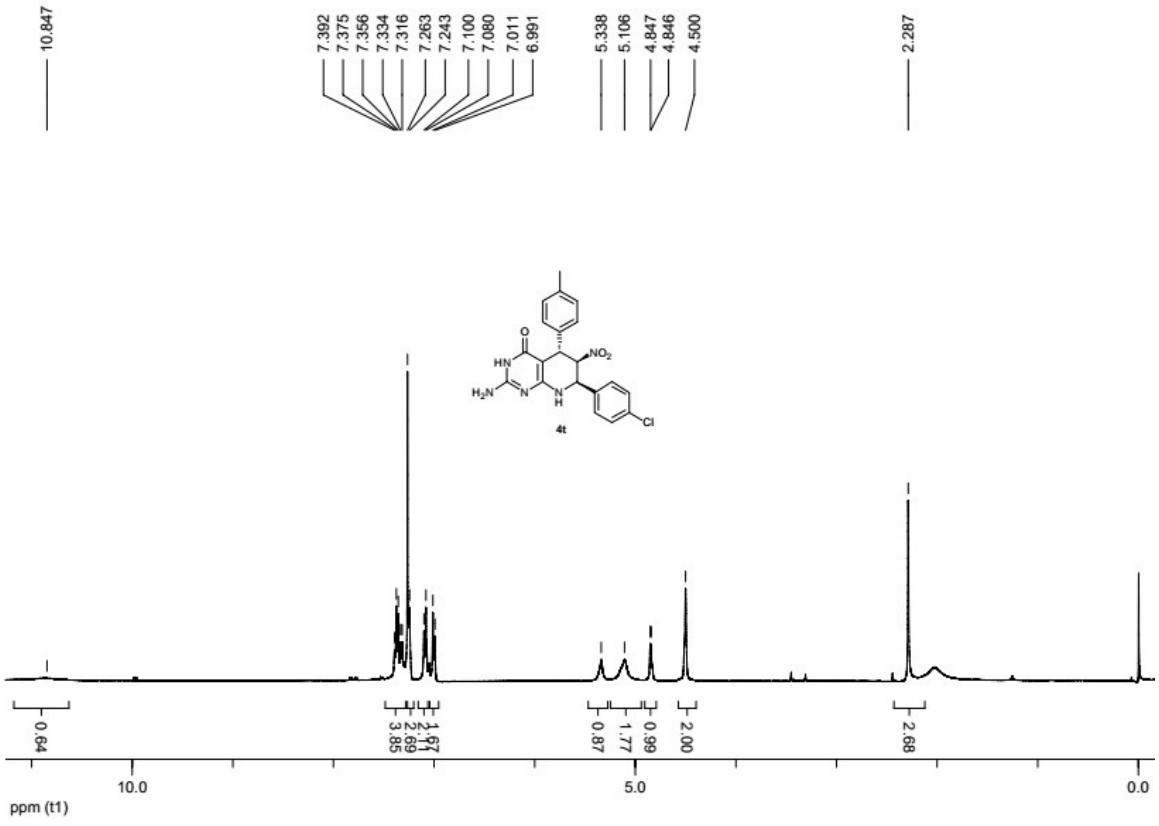

161.790
159.976
154.408
148.799
143.013
134.732
129.008
128.572
127.442
127.238
126.762
89.289
82.946
52.768
33.500
24.251
24.211
4q
150
100
50
0
ppm (t1)

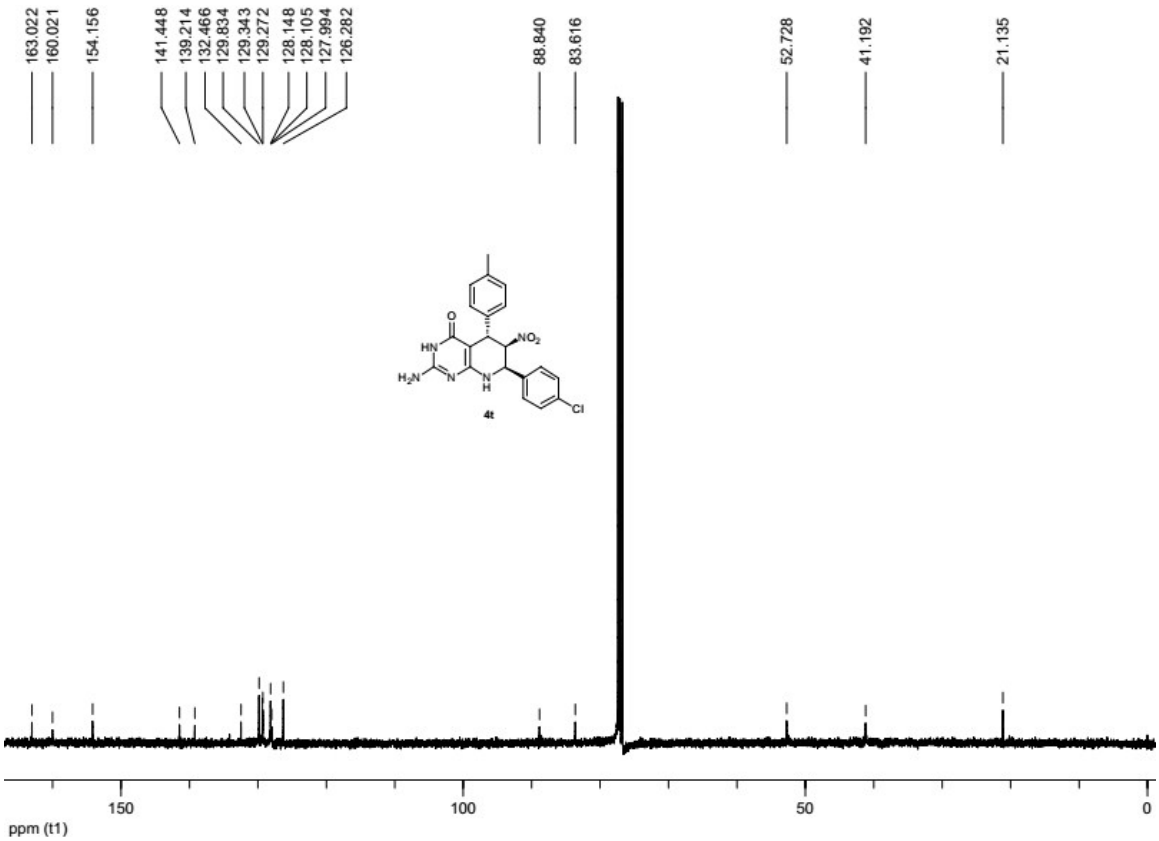

10.091
7.355
7.336
7.317
7.260
7.249
7.240
7.144
7.056
7.035
6.854
6.832
6.195
4.892
4.886
4.879
4.482
4.474
4.366
4.361
3.701
4r
1.00
2.03
3.11
2.51
2.09
1.82
0.97
0.98
0.97
3.05
10.0
5.0
0.0
ppm (t1)

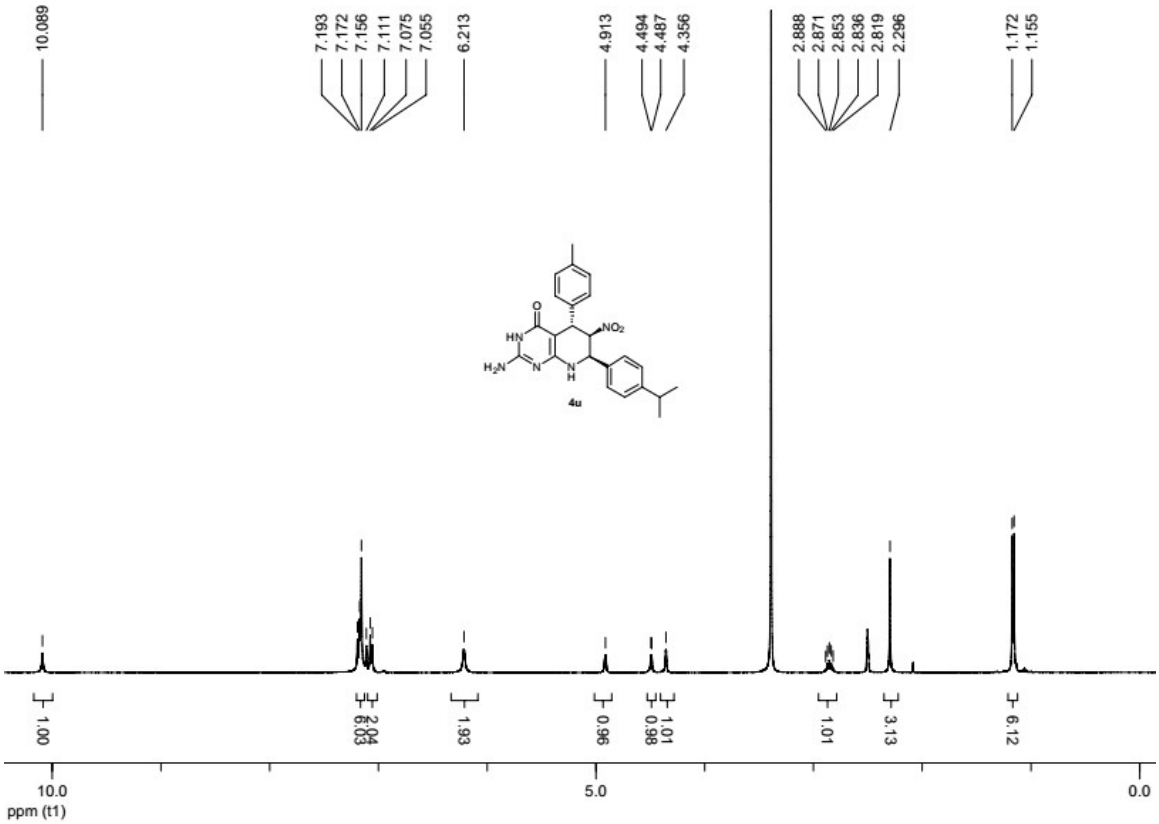

161.792
159.966
159.583
154.394
143.060
129.114
128.979
128.577
128.422
127.410
114.192
89.486
82.996
55.536
52.477
4r
150
100
50
0
ppm (t1)

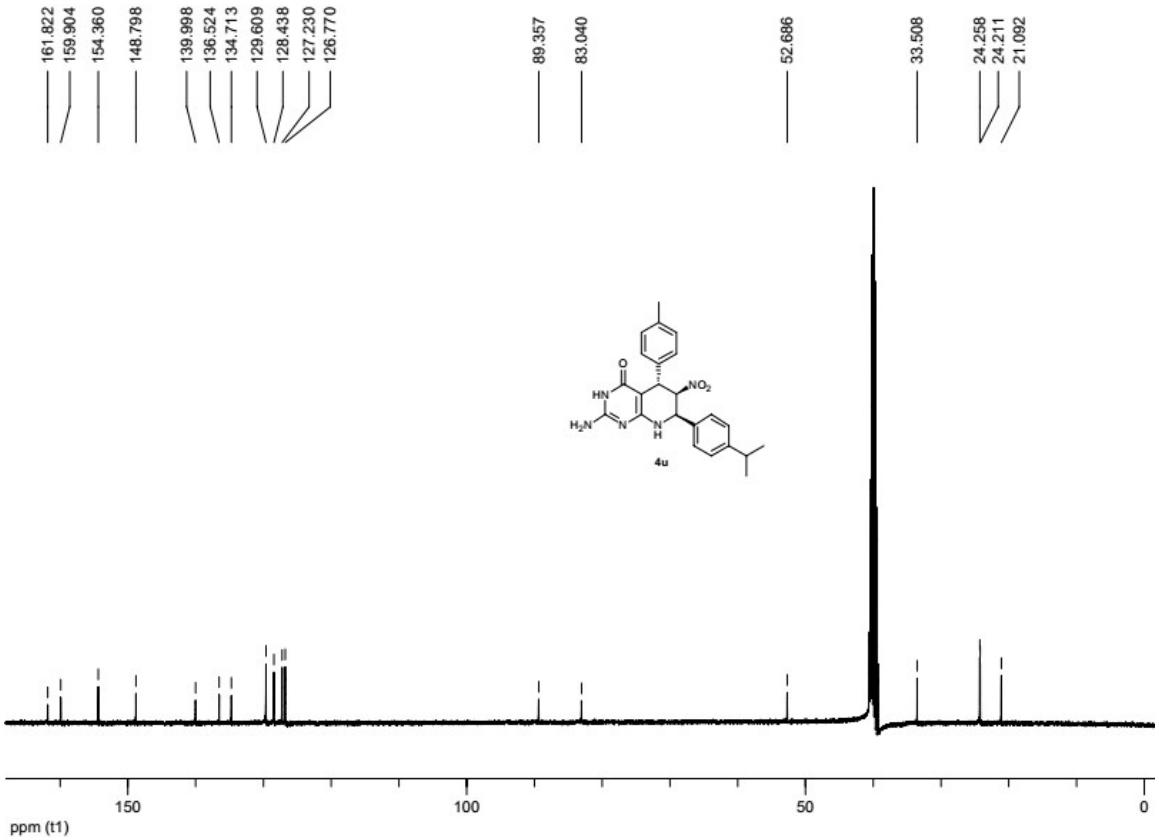

10.216
7.953
7.933
7.885
7.868
7.490
7.473
7.461
7.443
7.399
7.383
7.219
7.200
7.111
6.747
6.726
6.243
5.347
5.024
4.564
4s
0.99
1.92
8.46
1.05
1.04
2.16
1.00
0.97
1.01
10.0
5.0
0.0
ppm (t1)

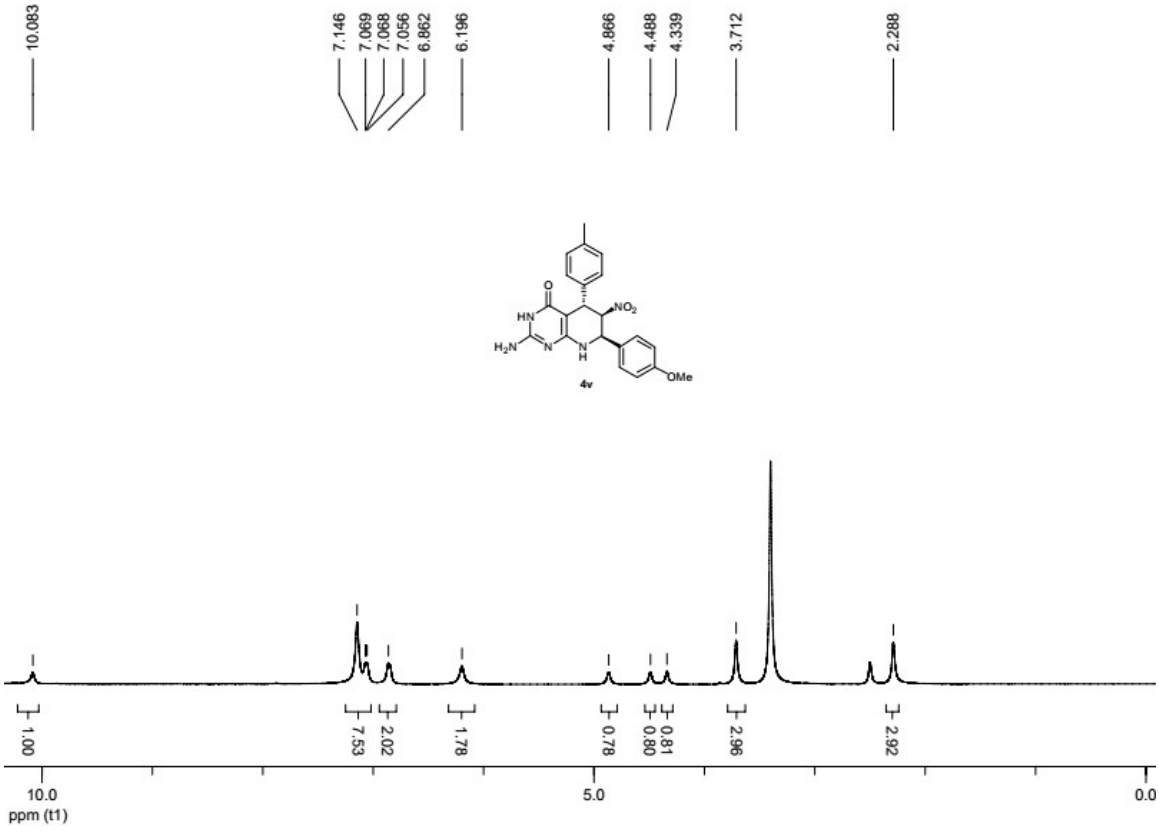

162.070
160.866
154.366
143.159
133.650
132.104
129.854
129.696
129.156
128.771
127.696
127.152
126.178
125.794
125.135
120.326
87.719
84.137
48.605
4s
150
100
50
0
ppm (t1)

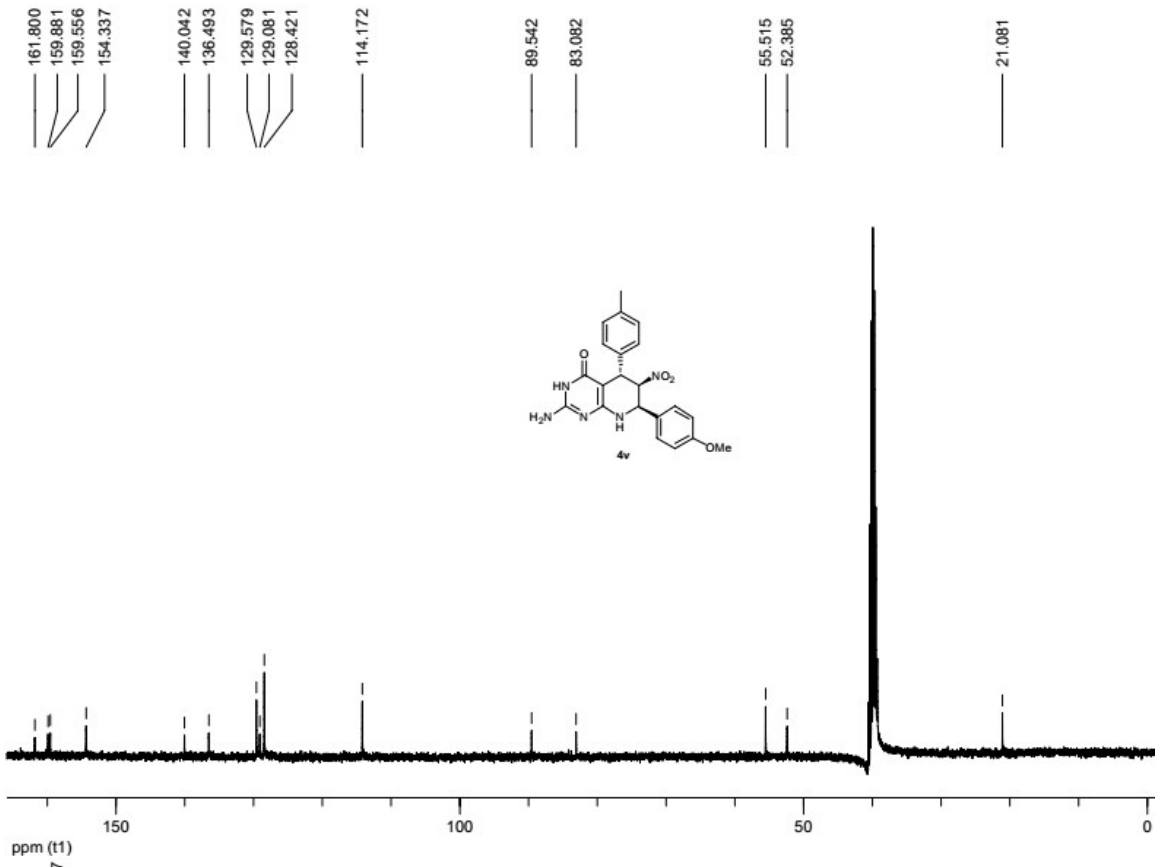

10.847
7.392
7.375
7.356
7.334
7.316
7.263
7.243
7.100
7.080
7.011
6.991
5.338
5.106
4.847
4.846
4.500
2.287
4t
0.64
3.85
2.69
2.17
1.67
0.87
1.77
0.99
2.00
2.68
10.0
5.0
0.0
ppm (t1)

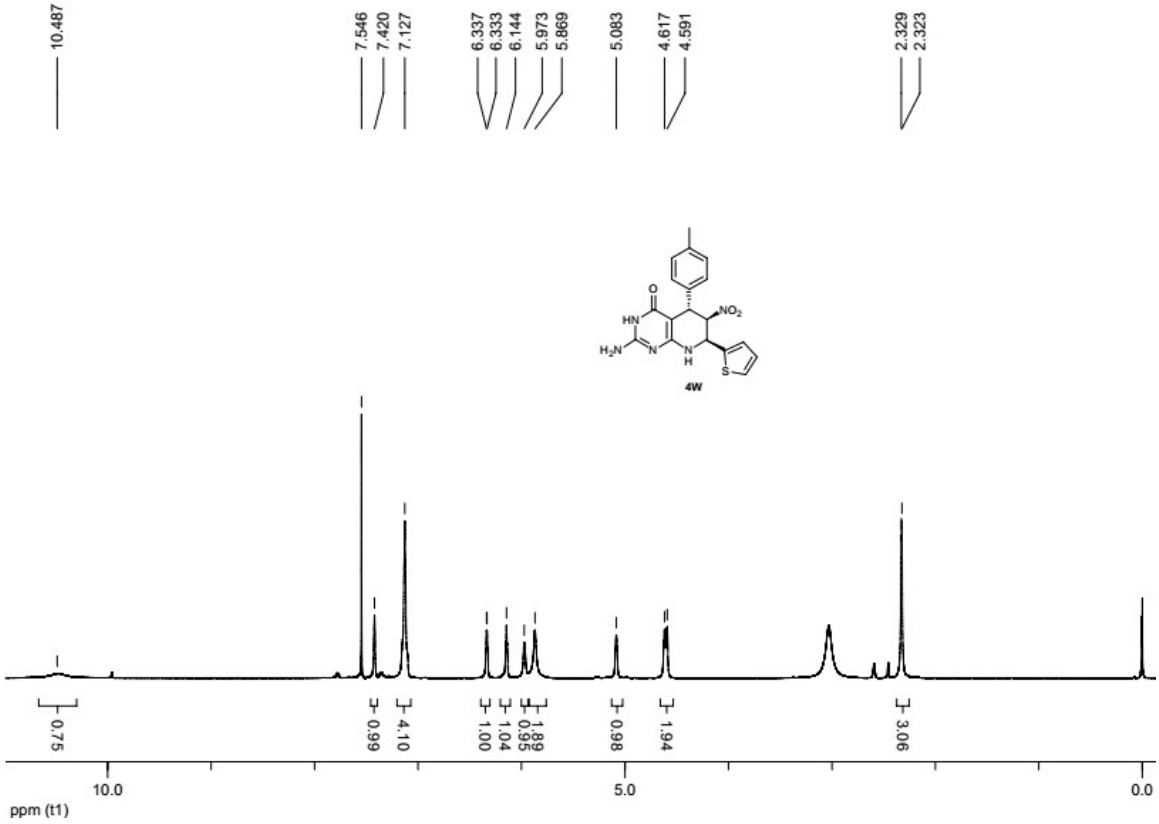

163.022
160.021
154.156
141.448
139.214
132.466
129.834
129.343
129.272
128.148
128.105
127.994
126.282
88.840
83.616
52.728
41.192
21.135
4t
150
100
50
0
ppm (t1)

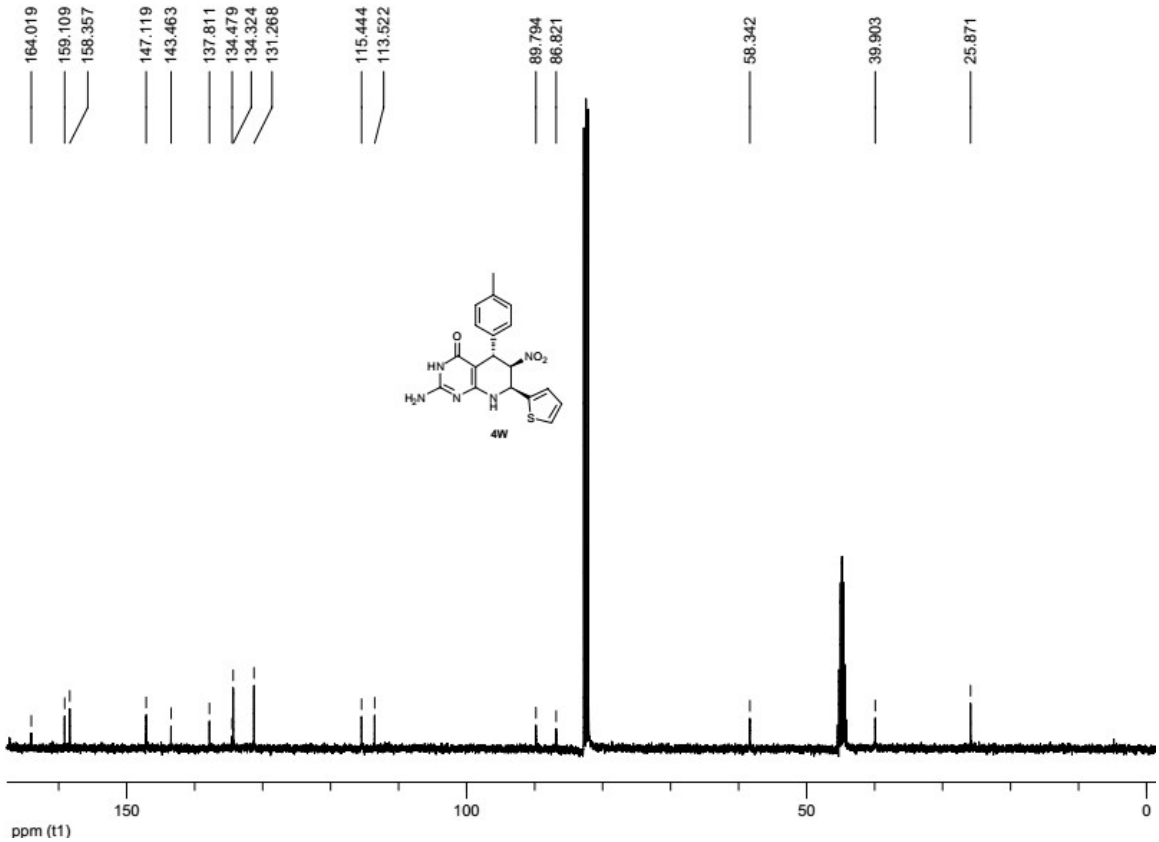

10.089
7.193
7.172
7.156
7.111
7.075
7.055
6.213
4.913
4.494
4.487
4.356
2.888
2.871
2.853
2.836
2.819
2.296
1.172
1.155
4u
1.00
6.03
2.04
1.93
0.96
0.98
1.01
1.01
3.13
6.12
10.0
5.0
0.0
ppm (t1)

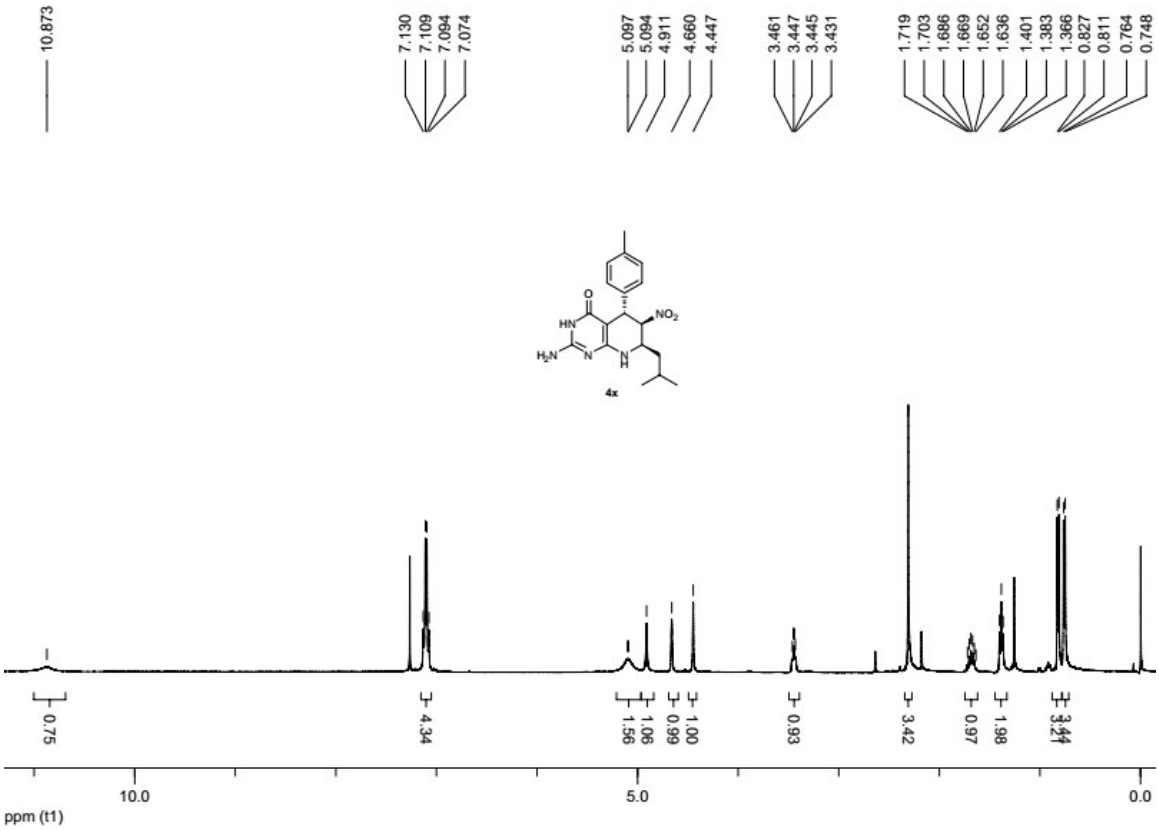

161.822
159.904
154.360
148.798
139.998
136.524
134.713
129.609
128.438
127.230
126.770
89.357
83.040
52.686
33.508
24.258
24.211
21.092
4u
150
100
50
0
ppm (t1)

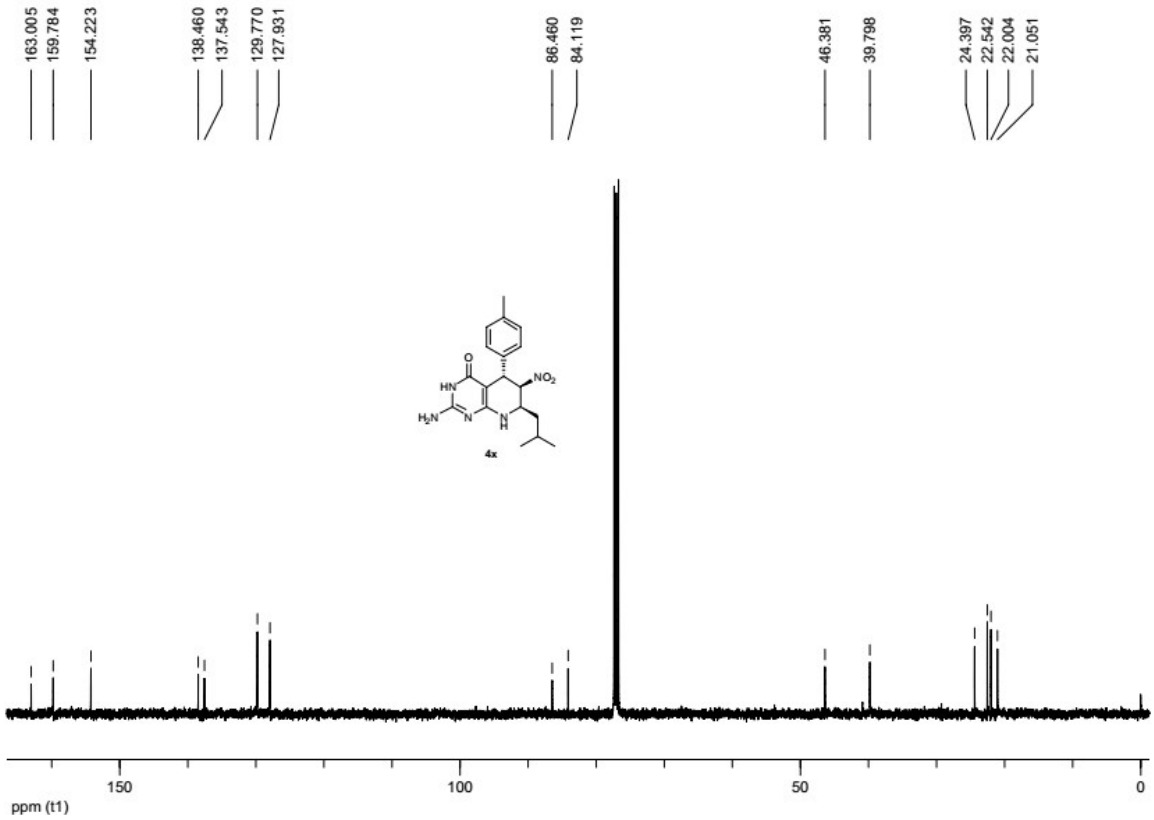

10.083
7.146
7.069
7.068
7.056
6.862
6.196
4.866
4.488
4.339
3.712
2.288
4v
OMe
1.00
7.53
2.02
1.78
0.78
0.80
0.81
2.96
2.92
10.0
5.0
0.0
ppm (t1)

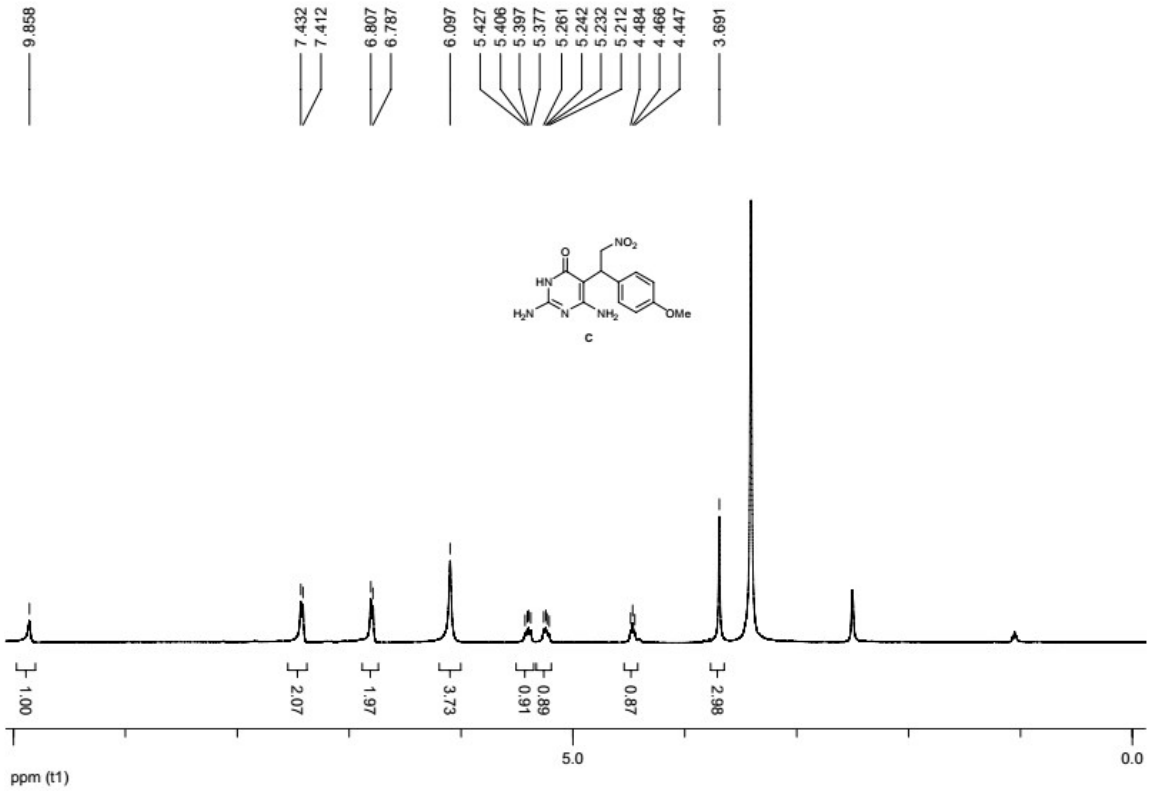

161.800
159.881
159.556
154.337
140.042
136.493
129.579
129.081
128.421
114.172
89.542
83.082
55.515
52.385
21.081
4v
150
100
50
0
ppm (t1)

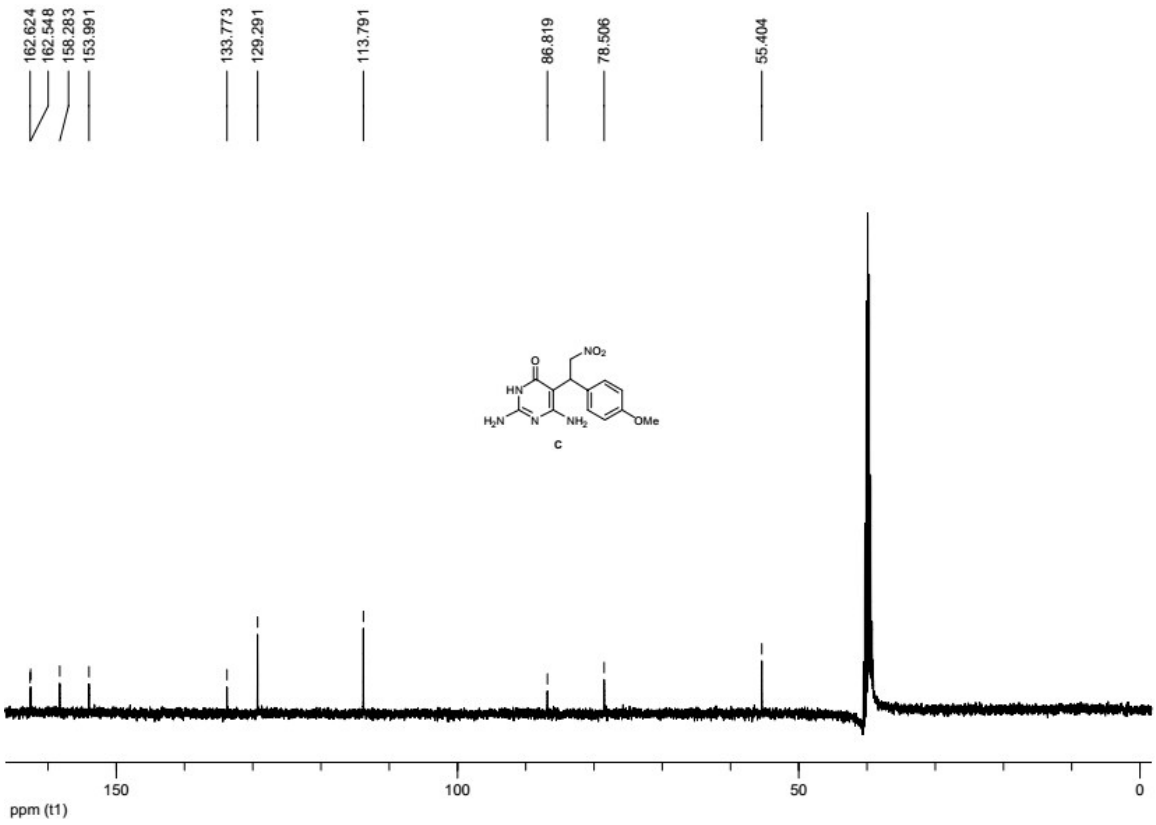

10.487
7.546
7.420
7.127
6.337
6.333
6.144
5.973
5.869
5.083
4.617
4.591
2.329
2.323
4w
0.75
0.99
4.10
1.00
1.04
0.95
1.86
0.98
1.94
3.06
10.0
5.0
0.0
ppm (t1)


164.019
159.109
158.357
147.119
143.463
137.811
134.479
134.324
131.268
115.444
113.522
89.794
86.821
58.342
39.903
25.871
4W
150
100
50
0
ppm (t1)


10.873
7.130
7.109
7.094
7.074
5.097
5.094
4.911
4.660
4.447
3.461
3.447
3.445
3.431
1.719
1.703
1.686
1.669
1.652
1.636
1.401
1.383
1.366
0.827
0.811
0.764
0.748
4x
0.75
4.34
1.96
1.06
0.99
1.00
0.93
3.42
0.97
1.98
10.0
5.0
0.0
ppm (t1)


163.005
159.784
154.223
138.460
137.543
129.770
127.931
86.460
84.119
46.381
39.798
24.397
22.542
22.004
21.051
4x
150
100
50
0
ppm (t1)


9.858
7.432
7.412
6.807
6.787
6.097
5.427
5.406
5.397
5.377
5.261
5.242
5.232
5.212
4.484
4.466
4.447
3.691
c
1.00
2.07
1.97
3.73
0.91
0.89
0.87
2.98
5.0
0.0
ppm (t1)


162.624
162.548
158.283
153.991
133.773
129.291
113.791
86.819
78.506
55.404
NO2
O
HN
H2N
N
NH2
OMe
c
150
100
50
0
ppm (t1)