DBU-CATALYZED HIGHLY EFFICIENT SYNTHESIS OF 1,4-DIHYDROPYRIDINE DERIVATIVES FROM ARYLIDENEMALONONITRILES AND β-ENAMINO IMIDES

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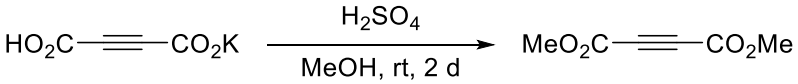
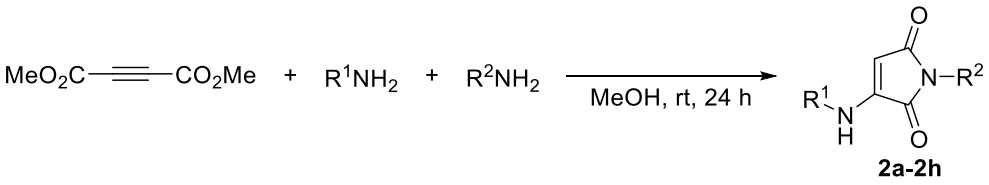
1. Synthesis of β-Enamino Imides[1]

1.1 Synthesis of Dimethyl Acetylenedicarboxylate



Monopotassium acetylenedicarboxylate (20.0 mmol, 3.04 g) was dissolved in MeOH and cooled to 0 ^{o}C in ice bath. Then conc. H_2SO_4 (8 mL) was added slowly to the flask. After stirred at room temperature for 2 days, the liquid in the flask was dissolved in EtOAc and then washed with cold water, sat. $NaHCO_3$, and brine respectively for one time. The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by Kugelrohr to give dimethyl acetylenedicarboxylate, DMAD (4.66 g, 16.4 mmol, 82%).

1.2 Synthesis of β-Enamino Imides 2



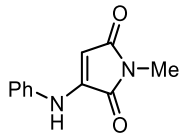
To a solution of DMAD (2.84 g, 20.0 mmol) in MeOH (20 ml), the corresponding amine R^1NH_2 (1.0 eq, 20.0 mmol) was added at 0 ^{o}C and stirred for 30 min. Then another amine R^2NH_2 (1.0 eq, 20.0 mmol) was added and reacted at rt for 24 h. The solvent was removed under redeuced pressure. The residue was recrystallized from EtOAc and hexane to afford pure β-enamino imides **2a-2h**.

2. References:

1. K. Kizaki, H. Imoto, T. Kato, and K. Naka, *Tetrahedron*, 2015, **71**, 643.

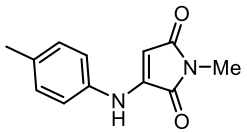
3. ^{1}H and ^{13}C NMR, IR Data

3.1 Analytical Data of β-Enamino Imides 2



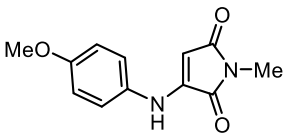
2a

1-methyl-3-(phenylamino)-1H-pyrrole-2,5-dione (2a): Yield: 83%. mp: 199-200 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 3.05 (3H, s), 5.51 (1H, s), 7.13-7.17 (3H, m), 7.23 (1H, brs), 7.46 (2H, t, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.7, 89.1, 118.7, 124.5, 129.8, 138.4, 142.5, 168.3, 172.7. IR (KBr, cm^{-1}): 3292, 3127, 2359, 1695, 1651, 1459, 1129, 1043, 753, 701.



2b

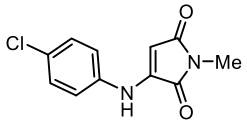
1-methyl-3-[(4-methylphenyl)amino]-1H-pyrrole-2,5-dione (2b): Yield: 53%. mp: 206-207 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.35 (3H, s), 3.04 (3H, s), 5.45 (1H, s), 7.04 (2H, d, *J* = 8.4 Hz), 7.17 (1H, brs), 7.20 (2H, d, *J* = 8.3 Hz).^{13}C NMR ($CDCl_3$, δ): 20.83, 23.69, 88.39, 118.92, 130.27, 134.44, 135.84, 142.84, 168.31, 172.79. IR (KBr, cm^{-1}): 3304, 3131, 2916, 1762, 1628, 1454, 1140, 1041, 815, 696.



2c

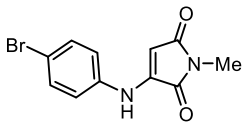
1-methyl-3-[(4-methoxyphenyl)amino]-1H-pyrrole-2,5-dione (2c): Yield: 40%. mp: 240-241 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 3.04 (3H, s), 3.82 (3H, s), 5.38 (1H, s), 6.93 (2H, d, *J*

= 9.0 Hz), 7.09 (2H, d, *J* = 9.0 Hz), 7.13 (1H, brs). ^{13}C NMR ($CDCl_3$, δ): 23.67, 55.58, 87.43, 115.02, 120.59, 131.43, 143.36, 156.80, 168.24, 172.82. IR (KBr, cm^{-1}): 3445, 3300, 3134, 1761, 1625, 1512, 1247, 1029, 842, 693.



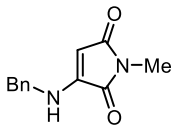
2d

1-methyl-3-[(4-chlorophenyl)amino]-1H-pyrrole-2,5-dione (2d): Yield: 55%. mp: 242-243 ºC. ^{1}H NMR ($CDCl_3$, δ): 3.05 (3H, s), 5.48 (1H, s), 7.08 (2H, d, *J* = 8.9 Hz), 7.20 (1H, brs), 7.37 (2H, d, *J* = 8.9 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.79, 89.62, 119.93, 129.79, 129.87, 137.00, 142.28, 168.11, 172.39. IR (KBr, cm^{-1}): 3304, 3128, 1764, 1634, 1495, 1408, 1138, 1091, 827, 691.



2e

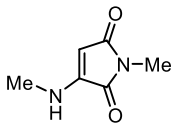
1-methyl-3-[(4-bromophenyl)amino]-1H-pyrrole-2,5-dione (2e): Yield: 27%. mp: 238-239 ºC. ^{1}H NMR ($CDCl_3$, δ): 3.05 (3H, s), 4.34 (2H, s), 4.86 (1H, s), 5.65 (1H, brs), 7.26-7.39 (5H, m). ^{13}C NMR ($CDCl_3$, δ): 23.78, 89.81, 117.27, 120.22, 132.82, 137.50, 168.09, 172.37. IR (KBr, cm^{-1}): 3304, 3127, 1704, 1630, 1542, 1457, 1117, 815, 645.



2f

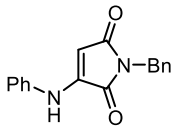
1-methyl-3-(benzylamino)-1H-pyrrole-2,5-dione (2f): Yield: 29%. mp: 130-132 ºC. ^{1}H NMR ($CDCl_3$, δ): 2.97 (3H, s), 5.51 (1H, s), 7.13-7.17 (3H, m), 7.23 (1H, brs), 7.46 (2H, t, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.47, 48.43, 85.55, 127.69, 128.44, 129.02,

135.68, 149.05, 167.61, 172.46. IR (KBr, cm^{-1}): 3325, 3101, 1751, 1625, 1454, 1125, 998, 782, 755.



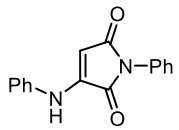
2g

1-methyl-3-(methylamino)-1H-pyrrole-2,5-dione (2g): Yield: 71%, mp: 146-147 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.93 (3H, d, *J* = 5.3 Hz), 2.97 (3H, s), 4.82 (1H, s), 5.33 (1H, brs). ^{13}C NMR ($CDCl_3$, δ): 23.40, 30.53, 84.20, 150.48, 167.47, 172.49. IR (KBr, cm^{-1}): 3341, 3109, 2929, 1638, 1449, 1245, 988, 794, 689.



2h

1-benzyl-3-(phenylamino)-1H-pyrrole-2,5-dione (2h): Yield: 36%. mp: 161-162 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 4.70 (2H, s), 5.52 (1H, s), 7.12-7.17 (3H, m), 7.22 (1H, brs), 7.27 (2H, m), 7.32 (2H, t, *J* = 3.6 Hz), 7.36-7.41 (4H, m). ^{13}C NMR ($CDCl_3$, δ): 41.45, 89.12, 118.79, 124.58, 127.75, 128.32, 128.66, 129.77, 136.47, 138.33, 142.50, 167.94, 172.23. IR (KBr, cm^{-1}): 3295, 3131, 3063, 2968, 2933, 1695, 1634, 1441, 1412, 1322, 1131, 748, 700.

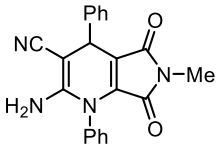


2i

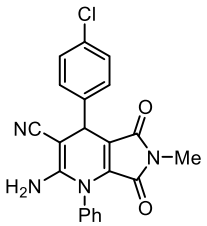
1-phenyl-3-(phenylamino)-1H-pyrrole-2,5-dione (2i): Yield: 3%, mp: 236-237 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 5.67 (1H, s), 7.18 (3H, m), 7.34-7.49 (8H, m). ^{13}C NMR ($CDCl_3$, δ): 89.18, 118.99, 119.84, 124.81, 125.59, 125.87, 127.61, 129.07, 129.31, 129.85, 131.64,

138.24, 142.41, 167.09, 171.28. IR (KBr, cm^{-1}): 3261, 3137, 3077, 1704, 1651, 1628, 1503, 1405, 1120, 750, 687.

3.2 Analytical Data of products 3

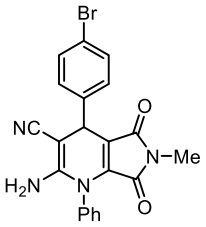


2-amino-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-1,4-diphenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3a**)[16] **:** Yield: 99%. Yellow powder. mp: 222-224 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.81 (3H, s), 4.32 (2H, brs), 4.77 (1H, s), 7.28-7.32 (1H, m), 7.35-7.42 (6H, m), 7.55-7.60 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 23.45, 36.71, 62.65, 112.46, 120.26, 127.73, 128.62, 129.30, 130.53, 131.02, 134.48, 136.78, 142.70, 151.23, 163.73, 168.37. IR (KBr, cm^{-1}): 3464, 2188, 1713, 1677, 1413, 1074, 987, 737.

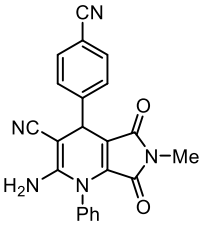


2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-chlorophenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3b**)**:** Yield: 97%. Yellow powder. mp: 233-234 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.81 (3H, s), 4.37 (2H, brs), 4.77 (1H, s), 7.34-7.38 (6H, m), 7.56-7.60 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 23.79, 36.30, 62.04, 111.84, 120.10, 127.46,

128.90, 129.14, 130.21, 130.57, 133.62, 134.28, 136.87, 141.18, 151.37, 163.54, 168.31. IR (KBr, cm^{-1}): 3472, 3370, 2181, 1712, 1677, 1564, 1381, 985, 791. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{21}H_{15}N_4NaClO_2$: 413.0776; found: 413.0794.

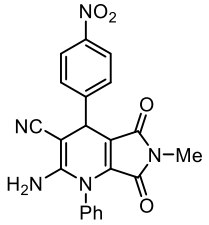


2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-bromophenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3c**)**:** Yield: 100%. Yellow powder. mp: 172-173 ^oC. ^1H NMR ($CDCl_3$, δ): 2.81 (3H, s), 4.35 (2H, brs), 4.76 (1H, s), 7.29 (2H, d, *J* = 7.9 Hz), 7.34-7.36 (6H, m), 7.53 (2H, d, *J* = 8.0 Hz), 7.56-7.60 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 23.48, 36.36, 62.18, 111.80, 119.97, 121.84, 129.01, 129.51, 130.48, 132.07, 132.39, 134.26, 136.86, 141.62, 151.27, 163.52, 168.26. IR (KBr, cm^{-1}): 3456, 2195, 1714, 1420, 1073, 791. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{21}H_{15}N_4NaBrO_2$: 457.0271; found: 457.0282.

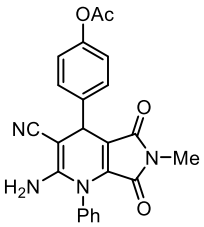


2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-cyanophenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3d**)**:** Yield: 97%. Orange powder. mp: 230-231 ^oC. ^1H NMR ($CDCl_3$, δ): 2.82 (3H, s), 4.44 (2H, brs), 4.86 (1H, s), 7.34-7.37 (2H, m), 7.54 (2H, d, *J* = 8.3 Hz), 7.57-7.63 (3H, m), 7.70 (2H, d, *J* = 8.2 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.56, 37.01, 61.17, 110.87, 111.69, 118.65, 119.81, 128.74, 128.99, 130.39, 130.81,

132.82, 133.98, 137.29, 147.46, 151.67, 163.27, 168.13. IR (KBr, cm^{-1}): 3461, 3322, 3215, 3215, 2229, 2186, 1713, 1680, 1560, 1414, 1076, 751. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{22}H_{15}N_5NaO_2$: 404.1118; found: 404.1130.

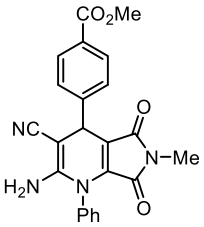


2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-nitrophenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3e**)**:** Yield: 54%. Orange powder. mp: 198-200 ^oC. ^1H NMR ($CDCl_3$, δ): 2.82 (3H, s), 4.46 (2H, brs), 4.93 (1H, s), 7.36-7.38 (2H, m), 7.58-7.62 (5H, m), 8.28 (2H, d, *J* = 8.8 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.55, 36.83, 61.17, 110.77, 119.73, 123.98, 125.95, 127.37, 128.92, 130.79, 133.95, 137.24, 147.48, 149.27, 151.69, 163.21, 168.08. IR (KBr, cm^{-1}): 3458, 2189, 1711, 1678, 1562, 1379, 1076. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{21}H_{15}N_5NaO_4$: 424.1016; found: 424.1019.

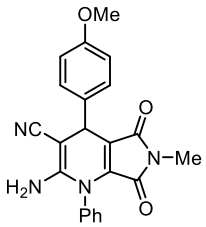


2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-acetyloxyphenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3f**)**:** Yield: 100%. Red powder. mp: 223-224 ^oC. ^1H NMR ($CDCl_3$, δ): 2.30 (3H, s), 2.81 (3H, s), 4.38 (2H, brs), 4.79 (1H, s), 7.12 (2H, d, *J* = 8.5 Hz), 7.33-7.35 (2H, m), 7.42 (2H, d, *J* = 8.5 Hz), 7.55-7.58 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 21.19, 23.47, 36.05, 62.24, 112.26, 120.15, 121.96, 128.74, 129.03, 130.27, 130.59, 134.35, 136.69, 140.04, 150.12, 151.34, 163.61, 168.31, 169.35. IR

(KBr, cm^{-1}): 3441, 3321.6, 3223, 2181, 1753, 1717, 1594, 1382, 1290, 1196, 1015. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{23}H_{18}N_4NaO_4$: 437.1220; found: 437.1232.

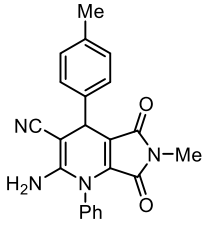


2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-methoxycarbonylphenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3g):** Yield: 100%. Yellow powder. mp: 221-222 °C. ^{1}H NMR ($CDCl_3$, δ): 2.81 (3H, s), 3.92 (3H, s), 4.37 (2H, brs), 4.85 (1H, s), 7.36-7.38 (2H, m), 7.49 (2H, d, *J* = 8.3 Hz), 7.56-7.61 (3H, m), 8.08 (2H, d, *J* = 8.4 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.50, 36.80, 52.13, 62.09, 111.64, 119.89, 127.86, 129.02, 129.65, 130.33, 130.68, 134.24, 137.09, 147.36, 151.34, 163.49, 166.75, 168.16. IR (KBr, cm^{-1}): 3482, 2951, 2184, 1712, 1562, 1436, 1283, 1106, 740. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{23}H_{18}N_4NaO_4$: 437.1220; found: 437.1233.

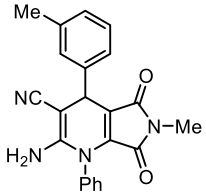


2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-methoxyphenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3h**)[14] **:** Yield: 93%. Orange powder. mp: 214-215 °C. ^{1}H NMR ($CDCl_3$, δ): 2.81 (3H, s), 3.81 (3H, s), 4.31 (2H, brs), 4.73 (1H, s), 6.93 (2H, d, *J* = 8.7 Hz), 7.32 (2H, d, *J* = 7.0 Hz), 7.35-7.37 (2H, m), 7.56-7.59 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 23.42, 29.35, 35.95, 55.29, 63.04, 112.69, 114.34, 120.30, 128.93, 130.30, 130.87, 134.55, 135.08, 136.44, 150.97, 159.15, 163.80, 168.48. IR (KBr, cm^{-1}):

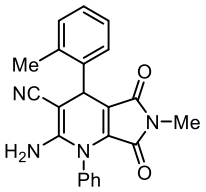
3452, 3332, 2173, 1713, 1679, 1562, 1441, 1284, 984.



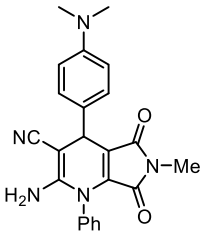
2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(4-methylphenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3i**)[16] **:** Yield: 98%. Orange powder. mp: 187-189 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.35 (3H, s), 2.80 (3H, s), 4.31 (2H, brs), 4.74 (1H, s), 7.20 (2H, d, *J* = 8.0 Hz), 7.29 (2H, d, *J* = 8.0 Hz), 7.35-7.37 (2H, m), 7.56-7.59 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 21.14, 23.72, 24.02, 36.31, 62.88, 112.65, 120.27, 127.76, 129.07, 129.65, 130.36, 134.55, 136.63, 137.44, 139.85, 151.05, 163.80, 168.43. IR (KBr, cm^{-1}): 3457, 2184, 1712, 1675, 1620, 1414, 1381, 984, 761.



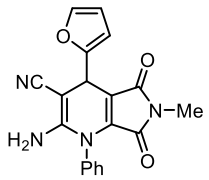
2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(3-methylphenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3j):** Yield: 91%. Orange powder. mp: 197-198 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.39 (3H, s), 2.81 (3H, s), 4.31 (2H, brs), 4.72 (1H, s), 7.10 (1H, d, *J* = 7.3 Hz), 7.19 (2H, d, *J* = 6.2 Hz), 7.28 (1H, d, *J* = 8.0 Hz), 7.35-7.37 (2H, m), 7.56-7.59 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 21.51, 23.74, 36.62, 112.60, 114.86, 120.25, 124.78, 125.66, 127.49, 128.67, 130.55, 131.80, 134.54, 136.74, 138.35, 142.65, 151.04, 160.79, 163.85, 168.37. IR (KBr, cm^{-1}): 3376, 2180, 1711, 1675, 1613, 1415, 1072. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{22}H_{18}N_4NaO_2$: 393.1327; found: 393.1339.



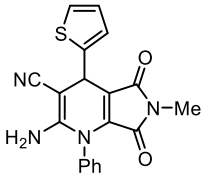
2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(2-methylphenyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3k**)**:** Yield: 93%. Orange powder. mp: 219-220 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.60 (3H, s), 2.79 (3H, s), 4.27 (2H, brs), 5.03 (1H, s), 7.16-7.18 (2H, m), 7.23-7.31 (2H, m), 7.38-7.40 (2H, m), 7.58-7.59 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 20.30, 23.39, 32.59, 63.35, 113.15, 120.22, 126.77, 127.53, 128.77, 129.11, 129.42, 130.37, 130.85, 134.58, 135.56, 136.96, 141.57, 150.89, 163.88, 168.28. IR (KBr, cm^{-1}): 3427, 2181, 1712, 1679, 1558, 1412, 1076. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{22}H_{18}N_4NaO_2$: 393.1322; found: 393.1344.



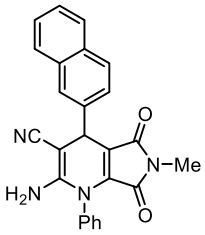
2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-[4-(dimethylamino)phenyl]-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3m**)**:** Yield: 30%. Red powder. mp: 243-244 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.80 (3H, s), 2.95 (6H, s), 4.26 (2H, brs), 4.67 (1H, s), 6.74 (2H, d, *J* = 8.7 Hz), 7.25 (2H, m), 7.34-7.36 (2H, m), 7.54-7.58 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 23.37, 35.67, 40.54, 63.46, 112.80, 113.17, 120.42, 128.38, 129.07, 130.16, 130.40, 130.83, 134.76, 136.07, 150.10, 150.76, 164.00, 168.58. IR (KBr, cm^{-1}): 3464, 3335, 2887, 2184, 1709, 1661, 1611, 1410, 1375, 985, 751, 526. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{23}H_{21}N_5NaO_2$: 422.1587; found: 422.1595.



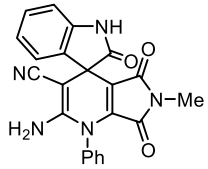
2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(2-furanyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3n**)**:** Yield: 88%. Yellow powder. mp: 204-205 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.85 (3H, s), 4.34 (2H, brs), 4.87 (1H, s), 6.32 (1H, d, *J* = 3.2 Hz), 6.36-6.37 (1H, m), 7.36-7.37 (2H, m), 7.38-7.40 (1H, m), 7.54-7.59 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 23.51, 23.56, 30.35, 106.83, 109.52, 110.80, 120.00, 129.12, 130.21, 130.56, 134.39, 137.77, 142.61, 151.48, 153.89, 163.63, 168.14. IR (KBr, cm^{-1}): 3435, 3322, 3225, 2189, 1715, 1680, 1634, 1381, 986, 748. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{19}H_{14}N_4NaO_3$: 369.0958; found: 369.0975.



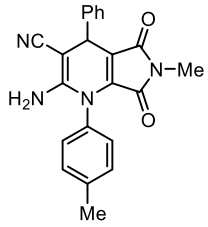
2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(2-thienyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3o**)**:** Yield: 95%. Yellow powder. mp: 196-197 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.84 (3H, s), 4.36 (1H, brs), 5.07 (1H, s), 7.00 (1H, m), 7.10 (1H, d, *J* = 3.5 Hz), 7.26-7.27 (1H, m), 7.35-7.37 (2H, m), 7.55-7.59 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 23.51, 31.63, 63.20, 111.97, 120.00, 124.90, 125.39, 127.51, 129.08, 130.26, 130.62, 134.32, 136.42, 147.91, 151.05, 163.59, 168.15. IR (KBr, cm^{-1}): 3460, 3428, 3226, 2186, 1714, 1678, 1416, 1382, 743. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{19}H_{14}N_4NaO_2S$: 385.0730; found: 385.0734.



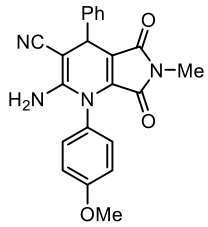
2-amino-1-phenyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-(2-naphthyl)-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3p):** Yield: 98%. Yellow powder. mp: 213-214 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.80 (3H, s), 4.38 (2H, brs), 4.95 (1H, s), 7.40-7.42 (2H, m), 7.46-7.51 (2H, m), 7.54-7.61 (4H, m), 7.82-7.90 (4H, m). ^{13}C NMR ($CDCl_3$, δ): 23.45, 36.96, 62.65, 112.32, 120.65, 125.65, 126.03, 126.31, 126.63, 127.72, 128.18, 128.92, 129.08, 130.25, 130.56, 133.00, 133.51, 134.48, 136.86, 140.00, 151.26, 163.74, 168.40. IR (KBr, cm^{-1}): 3730, 3444, 2923, 2183, 1712, 1676, 1563, 1440, 1381, 1072. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{25}H_{18}N_4NaO_2$: 429.1322; found: 429.1343.



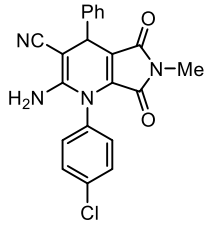
2'-amino-1,1',2,5',6',7'-hexahydro-6'-methyl-2,5',7'-trioxo-1'-phenyl-spiro[3H-indole-3,4'-[4H]pyrrolo[3,4-b]pyridine]-3'-carbonitrile. (**3q):** Yield: 99%. Orange powder. mp: 260-262 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.78 (3H, s), 4.47 (2H, brs), 6.93 (1H, d, *J* = 7.9 Hz), 7.13 (1H, t, *J* = 7.0 Hz), 7.29-7.33 (2H, t, *J* = 7.5 Hz), 7.37 (1H, brs), 7.41-7.43 (2H, m), 7.58-7.62 (3H, m). ^{13}C NMR (DMSO-d_6, δ): 23.60, 48.22, 60.60, 108.63, 110.04, 119.14, 122.69, 125.67, 129.63, 130.28, 134.62, 135.02, 139.56, 141.35, 141.50, 153.23, 163.29, 167.63, 170.80, 177.88. IR (KBr, cm^{-1}): 3348, 2189, 1714, 1619, 1378, 985, 752. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{22}H_{15}N_5NaO_3$: 420.1067; found: 420.1087.



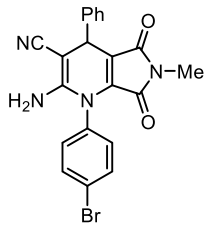
2-amino-1-(4-methylphenyl)-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-phenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3s**)[16] **:** Yield: 100%. Yellow powder. mp: 184-185 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.46 (s, 3H), 2.81 (s, 3H), 4.33 (brs, 2H), 4.76 (s, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.27-7.31 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.39-7.40 (m, 3H). ^{13}C NMR ($CDCl_3$, δ): 21.35, 23.42, 36.68, 62.70, 112.33, 120.23, 127.72, 128.69, 128.92, 130.87, 131.74, 136.88, 140.89, 142.74, 151.29, 163.79, 168.38. IR (KBr, cm^{-1}): 3451, 2925, 2186, 1713, 1563, 1416, 983, 740.



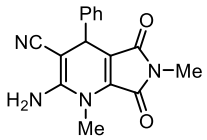
2-amino-1-(4-methoxyphenyl)-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-phenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3t**)[16] **:** Yield: 100%. Yellow powder. mp: 183-184 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.81 (3H, s), 3.88 (3H, s), 4.34 (2H, brs), 4.76 (1H, s), 7.04 (2H, d, *J* = 9.0 Hz), 7.26 (2H, d, *J* = 9.0 Hz), 7.28-7.31 (1H, m), 7.39-7.40 (4H, m). ^{13}C NMR ($CDCl_3$, δ): 23.42, 36.66, 55.60, 62.66, 112.27, 115.31, 120.24, 126.58, 127.71, 128.91, 130.14, 136.96, 142.74, 151.50, 160.90, 163.84, 168.38. IR (KBr, cm^{-1}): 3432, 2185, 1712, 1511, 1381, 1251, 985, 741.



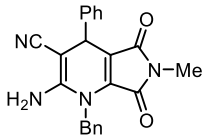
2-amino-1-(4-chlorophenyl)-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-phenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3u**)[16] **:** Yield: 98%. Yellow powder. mp: 217-218 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.82 (3H, s), 4.29 (2H, brs), 4.76 (1H, s), 7.31 (3H, m), 7.39-7.40 (4H, m), 7.54 (2H, d, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.77, 36.68, 63.37, 89.58, 112.91, 119.93, 127.71, 127.84, 128.98, 129.76, 130.45, 132.93, 136.79, 142.38, 150.81, 163.70, 168.14. IR (KBr, cm^{-1}): 3455, 2918, 2185, 1715, 1679, 1561, 1380, 1086.



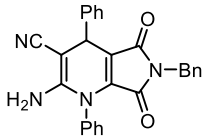
2-amino-1-(4-bromophenyl)-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-phenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3v**)[16] **:** Yield: 98%. Yellow powder. mp: 212-213 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.82 (3H, s), 4.29 (2H, brs), 4.76 (1H, s), 7.24 (2H, d, *J* = 8.5 Hz), 7.28-7.32 (2H, m), 7.38-7.42 (3H, m), 7.70 (2H, d, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$, δ): 23.48, 36.68, 63.48, 112.95, 119.83, 124.88, 127.71, 127.85, 128.98, 130.70, 133.48, 133.50, 136.42, 142.35, 150.68, 163.69, 168.11. IR (KBr, cm^{-1}): 3455, 2186, 1715, 1560, 1379, 1070, 761.



2-amino-4,5,6,7-tetrahydro-1,6-dimethyl-5,7-dioxo-4-phenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3w**)**:** Yield: 87%. Red powder. mp: 200-202 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.93 (3H, s), 3.65 (3H, s), 4.42 (2H, brs), 4.68 (1H, s), 7.24-7.36 (5H, m). ^{13}C NMR ($CDCl_3$, δ): 23.62, 31.20, 36.37, 64.25, 112.15, 120.39, 127.52, 127.65, 128.87, 137.14, 142.71, 152.28, 165.25, 168.24. IR (KBr, cm^{-1}): 3442, 3251, 2180, 1706, 1669, 1556, 1419, 1383, 975. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{16}H_{14}N_4NaO_2$: 317.1009; found: 317.1043.

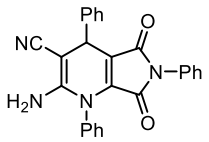


2-amino-1-benzyl-4,5,6,7-tetrahydro-6-methyl-5,7-dioxo-4-phenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3x**)**:** Yield: 96%. Red powder. mp: 197-198 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 2.35 (s, 3H), 2.80 (s, 3H), 4.31 (brs, 2H), 4.74 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.35-7.37 (m, 2H), 7.56-7.59 (m, 3H). ^{13}C NMR ($CDCl_3$, δ): 23.69, 36.57, 48.14, 65.98, 113.06, 120.03, 126.21, 127.59, 128.51, 128.68, 128.89, 129.58, 135.77, 137.20, 142.42, 152.33, 165.18, 168.14. IR (KBr, cm^{-1}): 3440, 2182, 1708, 1672, 1428, 1064. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{22}H_{18}N_4NaO_2$: 393.1322; found: 393.1339.



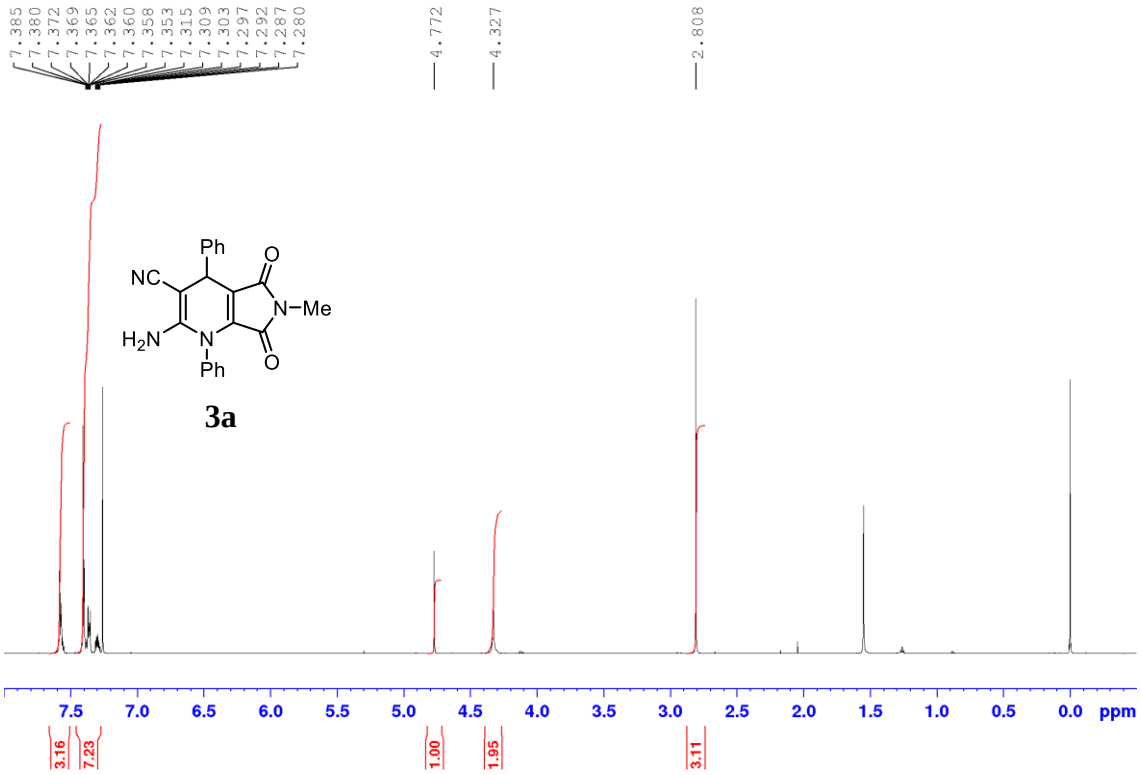
2-amino-4,5,6,7-tetrahydro-6-benzyl-5,7-dioxo-1,4-diphenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3y**)**:** Yield: 99%. Yellow powder. mp: 204-206 ^{o}C. ^{1}H NMR ($CDCl_3$, δ): 4.33 (2H, brs), 4.44 (2H, s), 4.76 (1H, s), 7.20-7.25 (5H, m), 7.28-7.31 (1H,

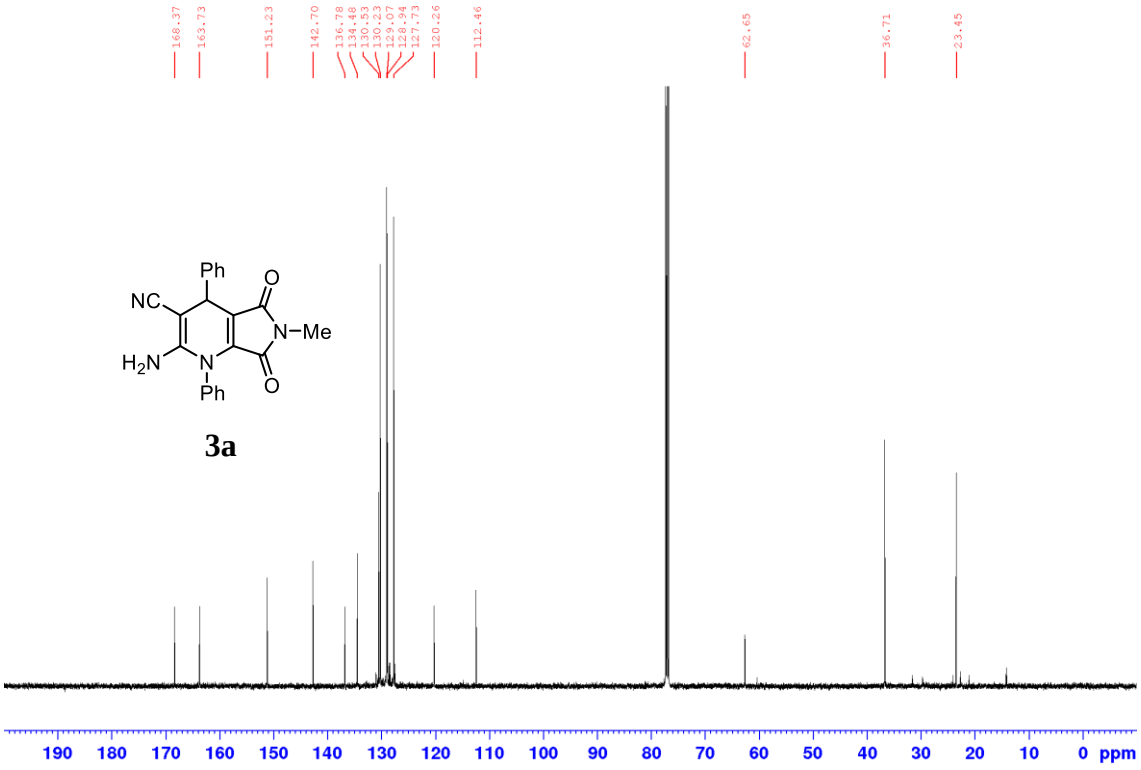
m), 7.33-7.35 (2H, m), 7.39-7.40 (4H, m), 7.53-7.58 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 30.90, 36.71, 41.32, 62.54, 112.32, 120.23, 127.71, 127.74, 128.55, 128.57, 128.93, 129.06, 130.19, 130.49, 134.32, 136.18, 136.70, 142,62, 151.20, 163.22, 168.06. IR (KBr, cm^{-1}): 3459, 3328, 3226, 2191, 1714, 1679, 1566, 1389, 1047, 697. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{27}H_{20}N_4NaO_2$: 455.1478; found: 455.1497.

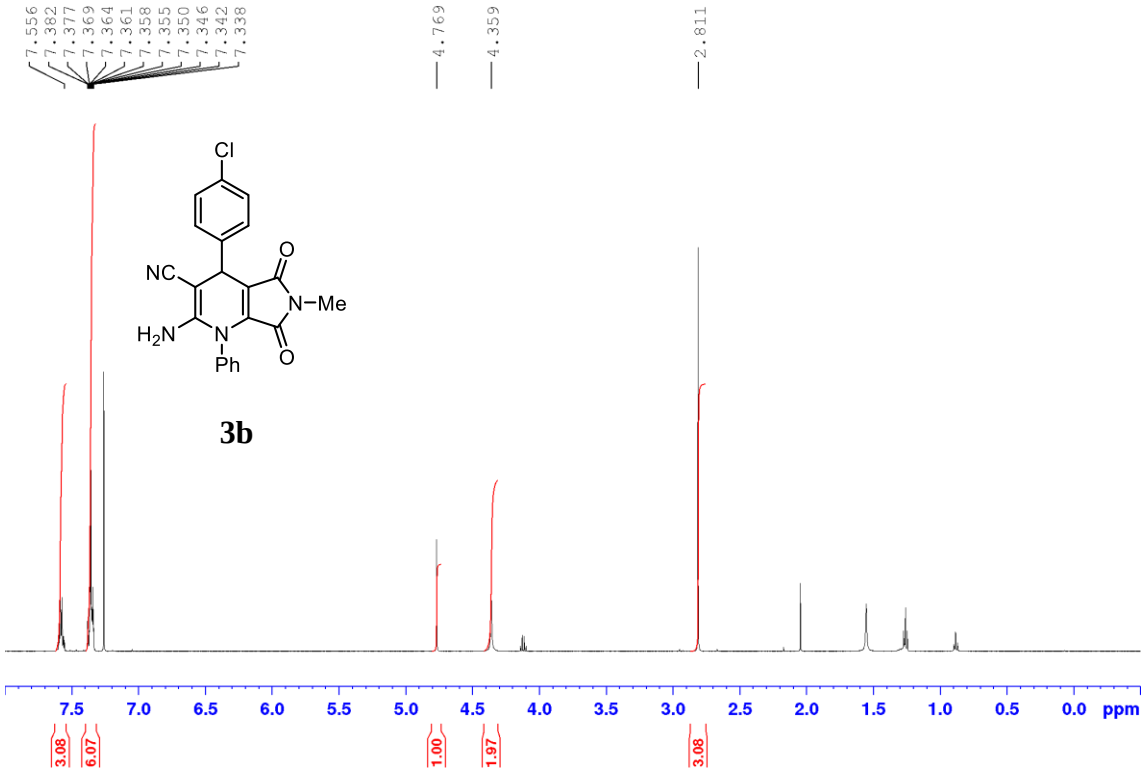


2-amino-4,5,6,7-tetrahydro-5,7-dioxo-1,4,6-triphenyl-1H-pyrrolo[3,4-b]pyridine-3-carbonitrile. (**3z**)**:** Yield: 87%. Yellow powder. mp: 198-199 ºC. ^{1}H NMR ($CDCl_3$, δ): 4.39 (2H, brs), 4.86 (1H, s), 7.17-7.19 (2H, m), 7.22-7.25 (1H, m), 7.30-7.33 (3H, m), 7.39-7.43 (4H, m), 7.46-7.47 (2H, m), 7.56-7.57 (3H, m). ^{13}C NMR ($CDCl_3$, δ): 36.73, 62.87, 112.59, 120.06, 125.88, 127.52, 127.82, 128.79, 129.01, 130.28, 130.60, 131.04, 134.36, 136.44, 142.46, 151.25, 162.43, 167.64. IR (KBr, cm^{-1}): 3445, 3374, 3063, 2183, 1722, 1680, 1566, 1557, 1380, 1219, 754, 732, 694. HRMS (ESI): *m*/*z* $[M+Na]^+$, calcd for $C_{26}H_{18}N_4NaO_2$: 441.1322; found: 441.1339.

3.3 ^{1}H and ^{13}C NMR Data of products 3



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7.338
4.769
4.359
2.811
Cl
NC
O
N–Me
H2N
N
Ph
O
3b
7.5
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6.0
5.5
5.0
4.5
4.0
3.5
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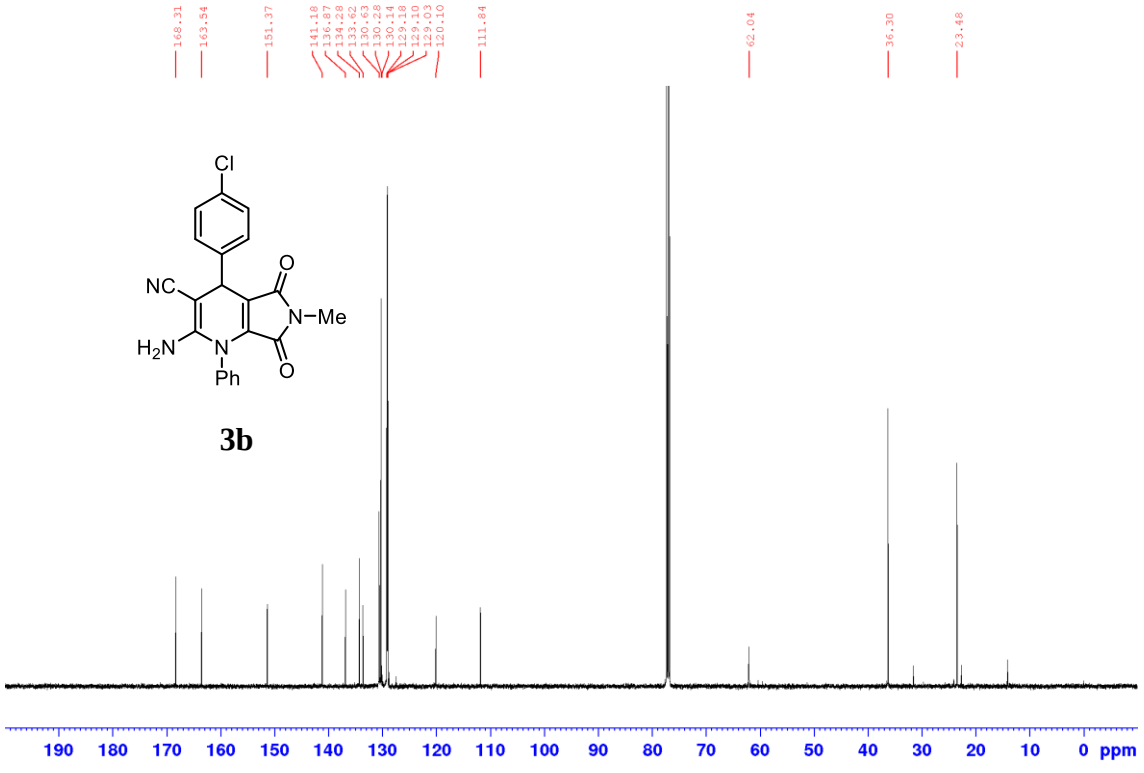
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111.84
62.04
36.30
23.48
Cl
NC
O
N–Me
H2N
N
Ph
O
3b
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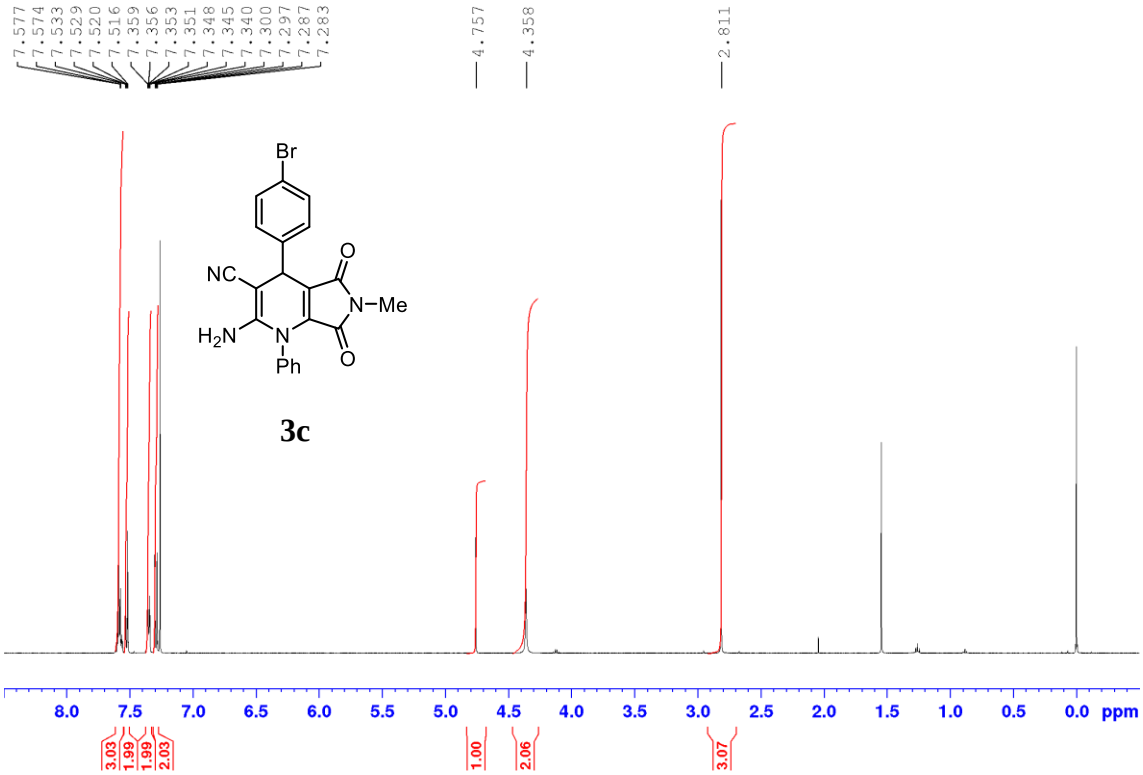
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7.340
7.300
7.297
7.287
7.283
4.757
4.358
2.811
Br
NC
O
N–Me
H2N
N
Ph
O
3c
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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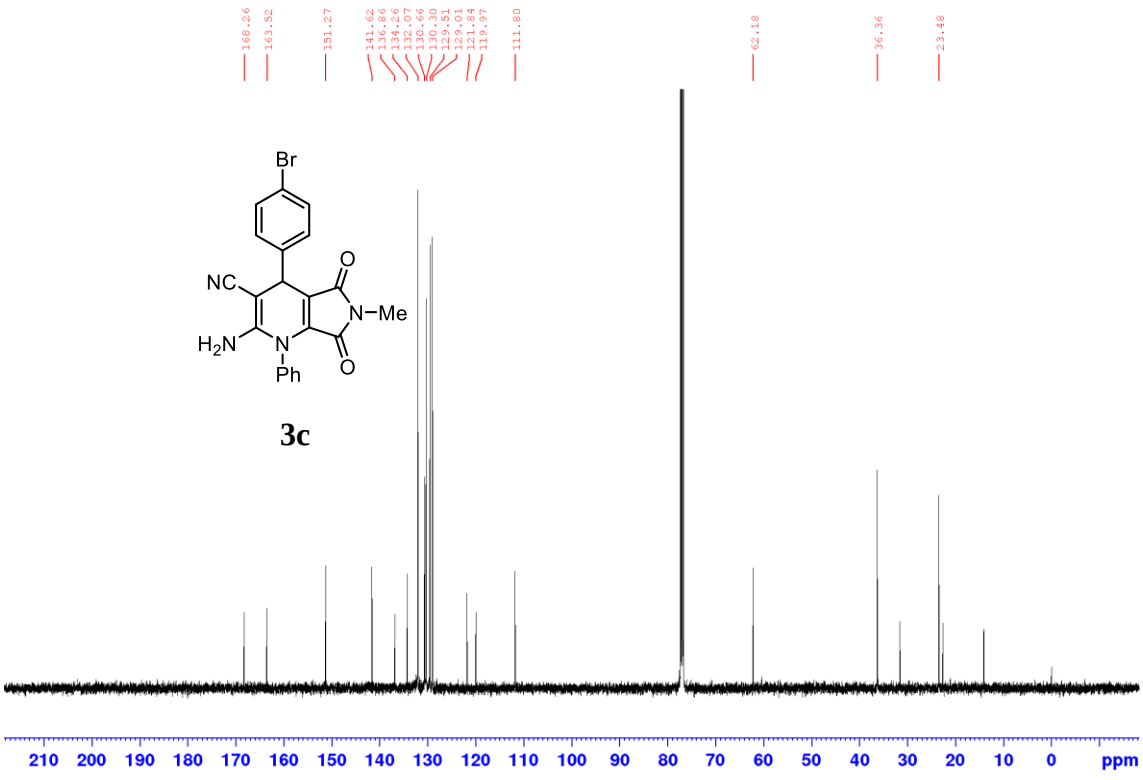
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111.80
62.18
36.36
23.48
Br
NC
O
N–Me
H2N
N
Ph
O
3c
210
200
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140
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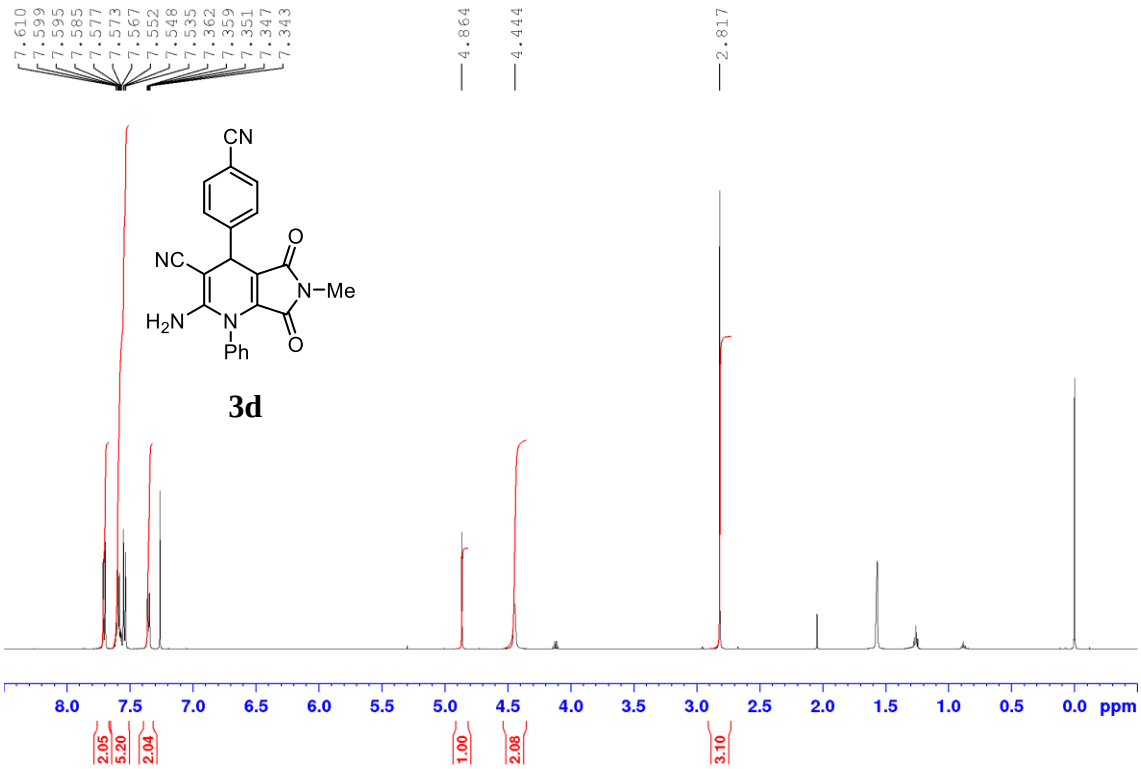
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7.351
7.347
7.343
4.864
4.444
2.817
CN
NC
O
N–Me
H2N
N
Ph
O
3d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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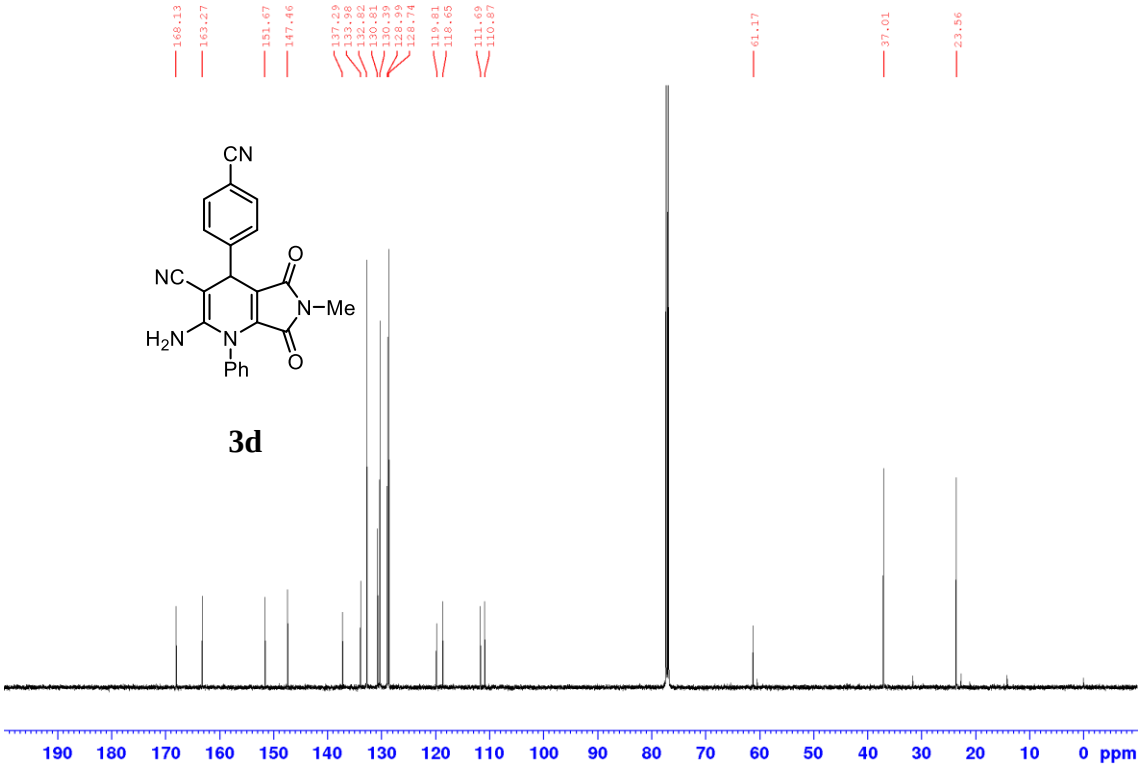
3.10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118.65
111.69
110.87
61.17
37.01
23.56
CN
NC
O
N–Me
H2N
N
Ph
O
3d
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140
130
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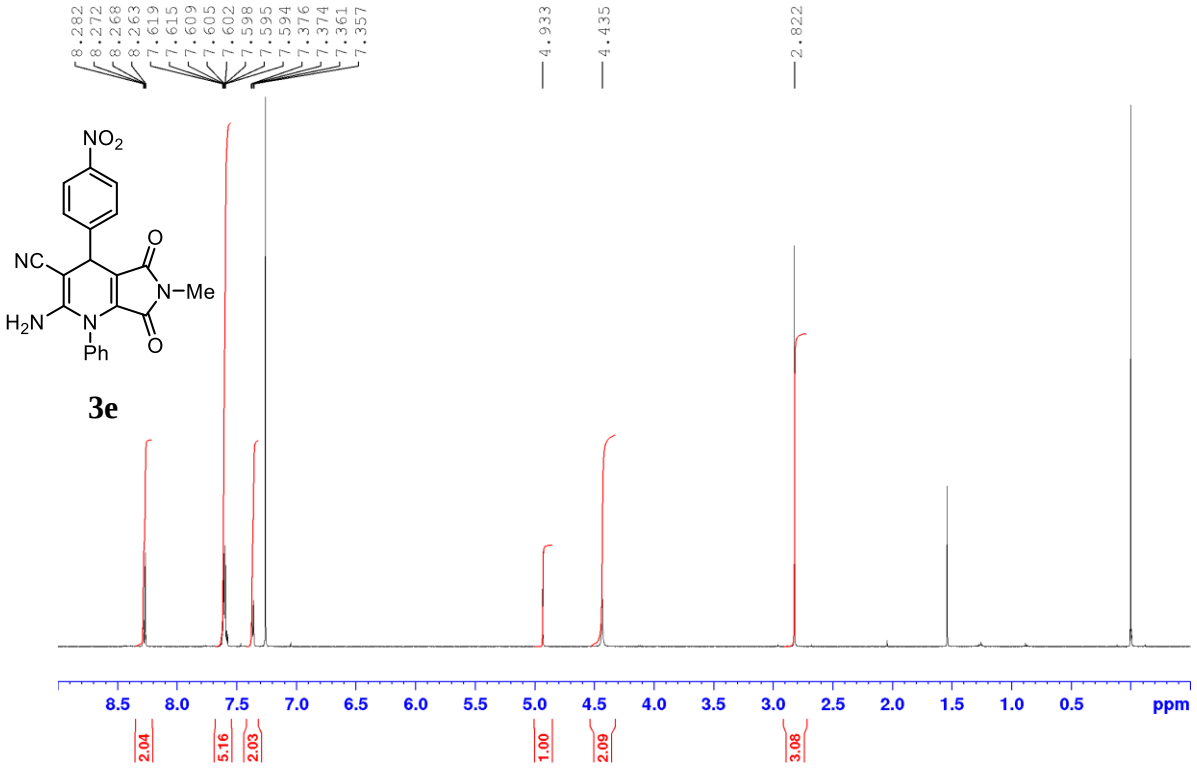
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7.605
7.602
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7.595
7.594
7.376
7.374
7.361
7.357
4.933
4.435
2.822
NO2
NC
O
N–Me
H2N
N
Ph
O
3e
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
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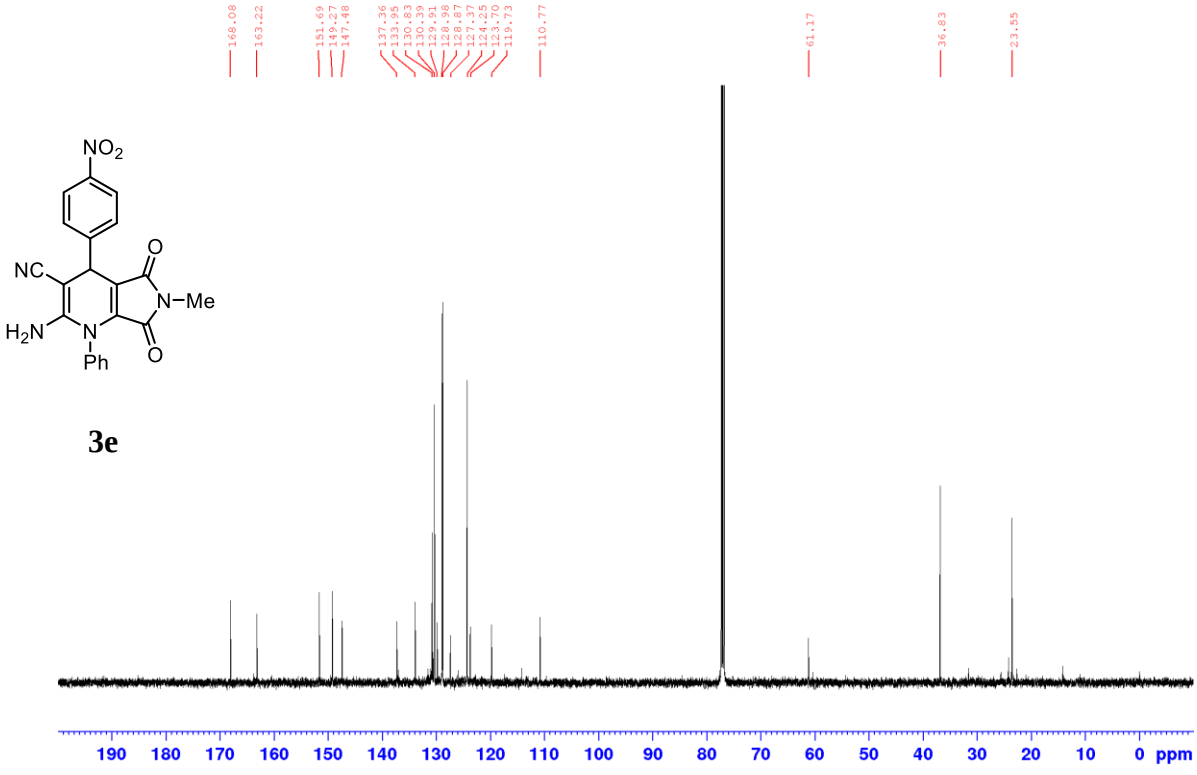
3.08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130.83
130.39
129.91
128.98
128.87
127.37
124.25
123.70
119.73
110.77
61.17
36.83
23.55
NO2
NC
O
N–Me
H2N
N
Ph
O
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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40
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20
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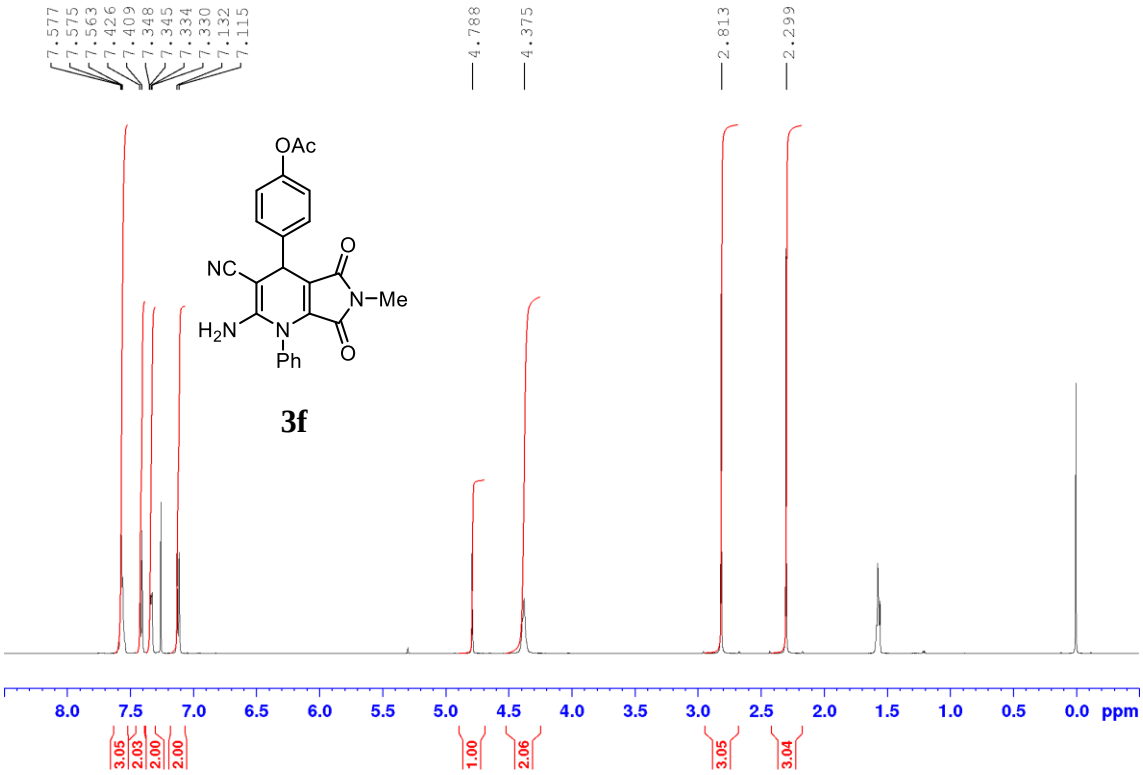
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7.330
7.132
7.115
4.788
4.375
2.813
2.299
OAc
NC
O
N–Me
H2N
N
Ph
O
3f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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0.0
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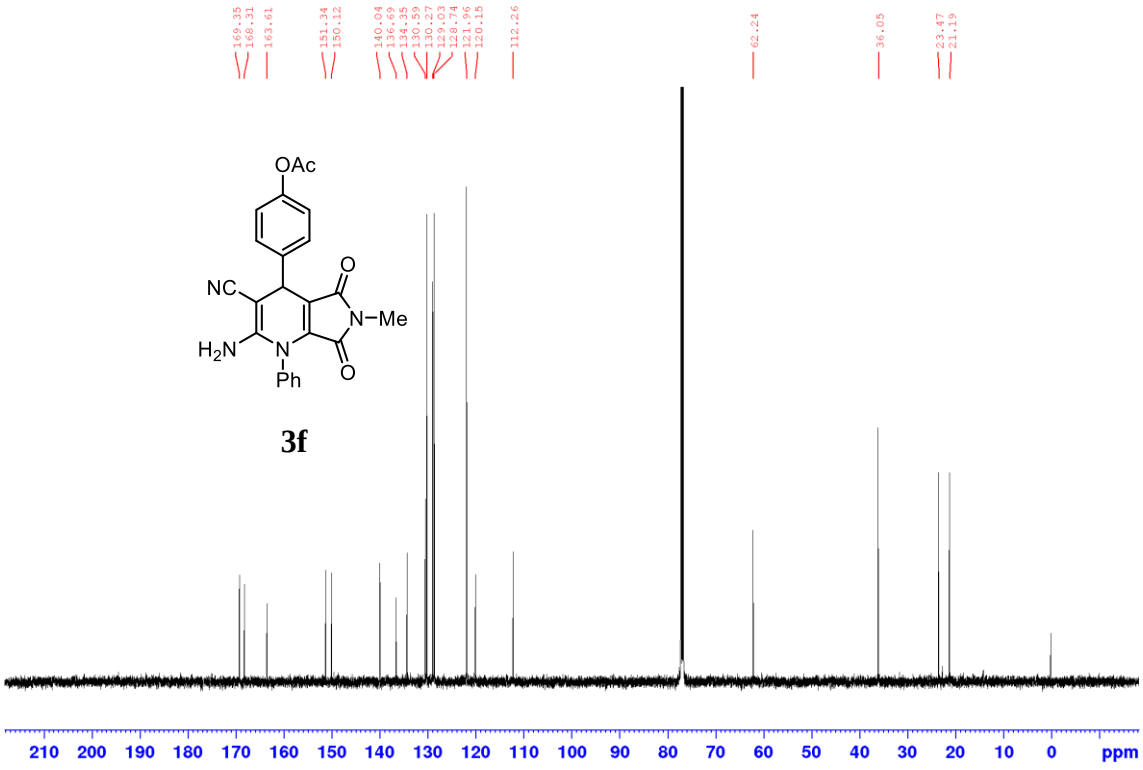
2.00
1.00
2.06
3.05
3.04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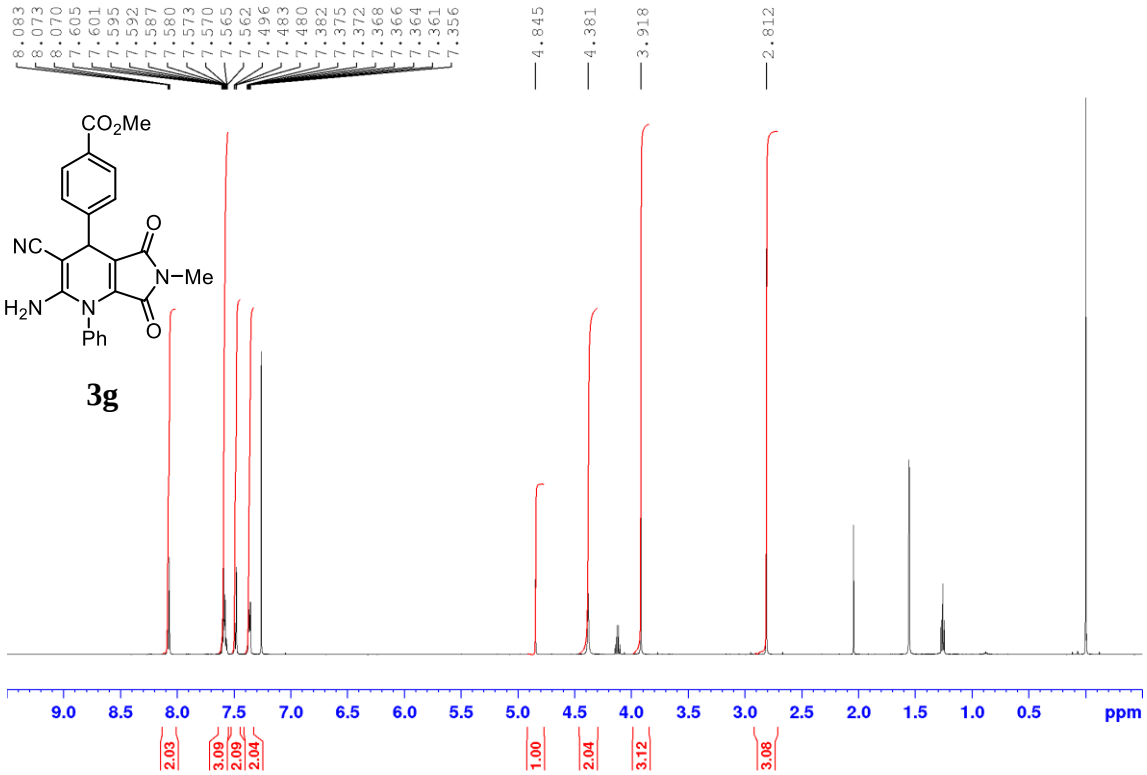
134.35
130.59
130.27
129.03
128.74
121.96
120.15
112.26
62.24
36.05
23.47
21.19
OAc
NC
O
N–Me
H2N
N
Ph
O
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.565
7.562
7.496
7.483
7.480
7.382
7.375
7.372
7.368
7.366
7.364
7.361
7.356
4.845
4.381
3.918
2.812
CO2Me
NC
O
N–Me
H2N
N
Ph
O
3g
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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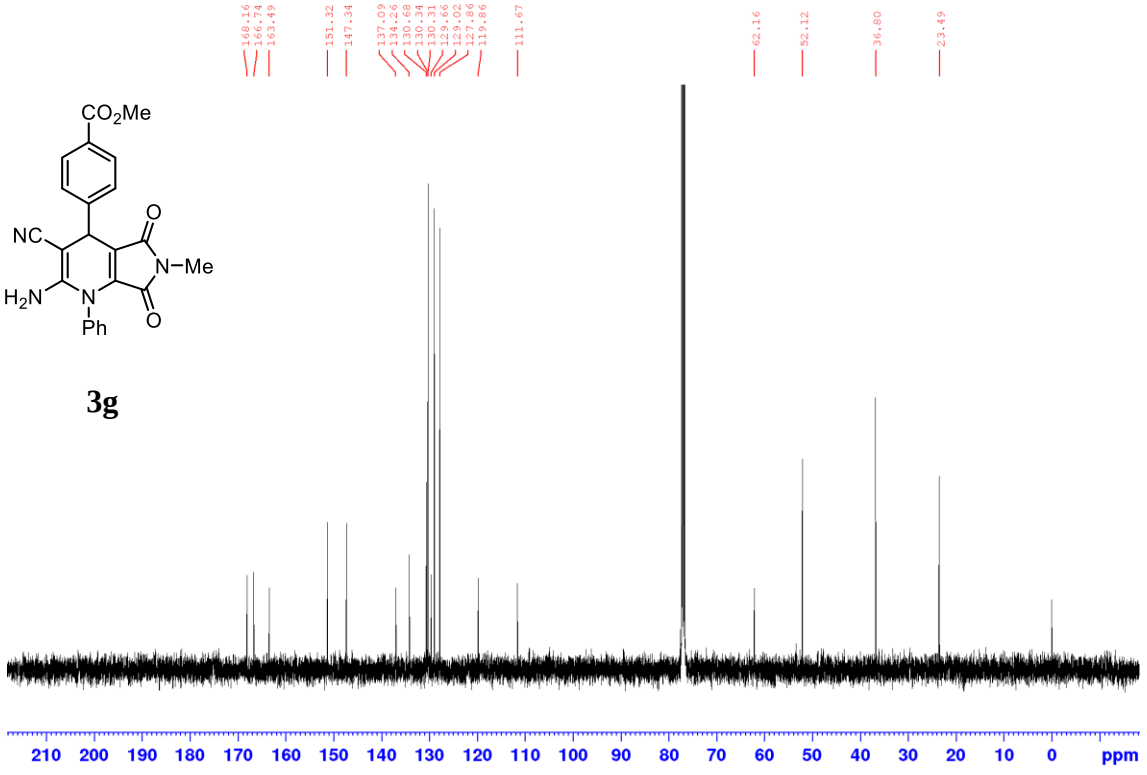
3.09
2.09
2.04
1.00
2.04
3.12
3.08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130.31
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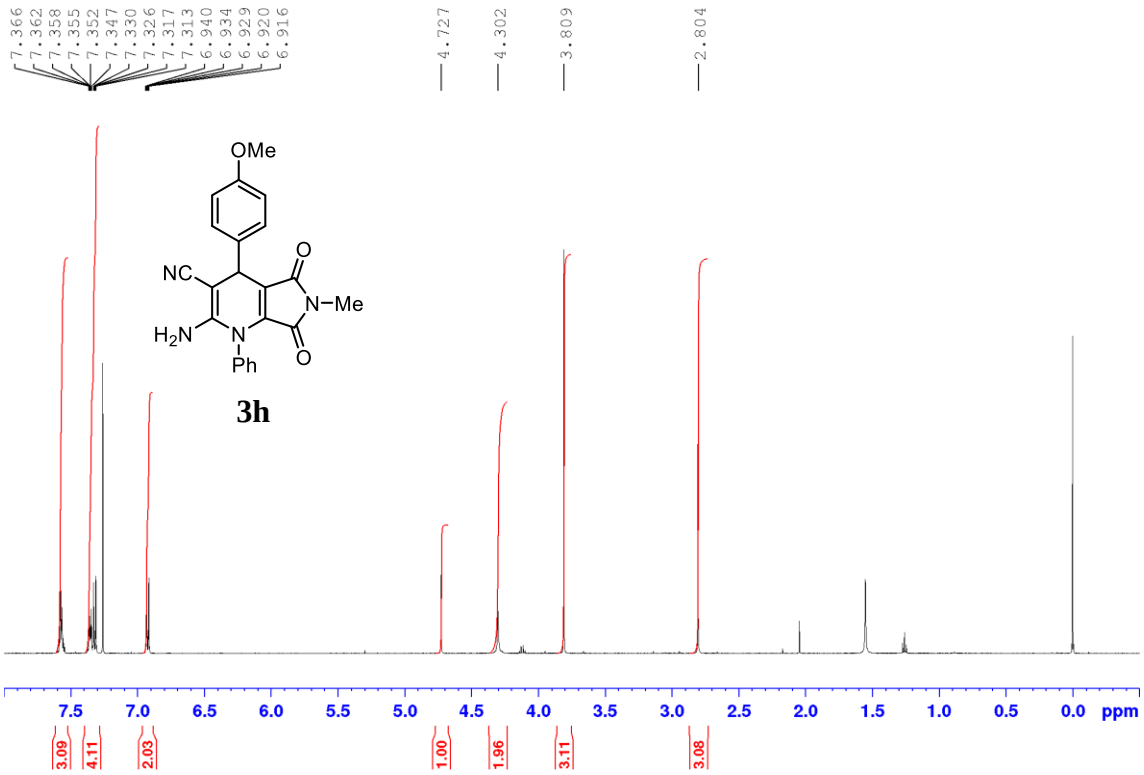
129.02
127.86
119.86
111.67
62.16
52.12
36.80
23.49
CO2Me
NC
O
N–Me
H2N
N
Ph
O
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.313
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6.934
6.929
6.920
6.916
4.727
4.302
3.809
2.804
OMe
NC
O
N–Me
H2N
N
Ph
O
3h
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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0.0
ppm
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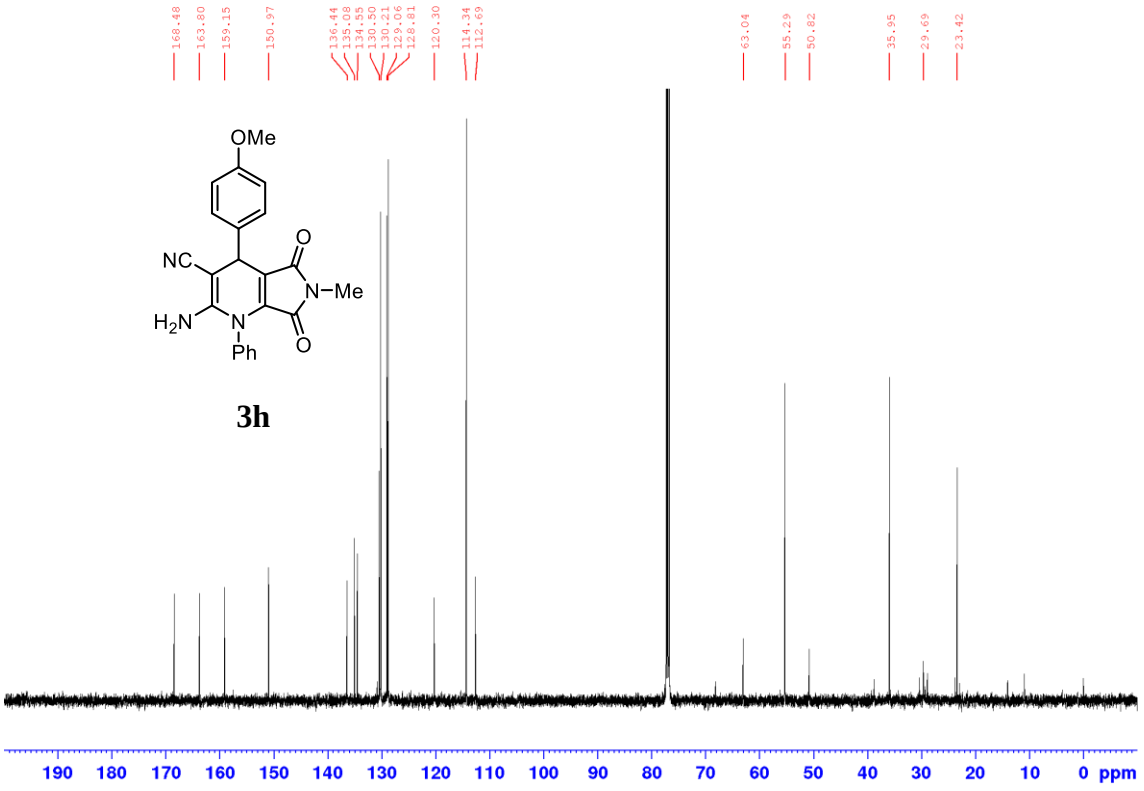
2.03
1.00
1.96
3.11
3.08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130.50
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129.06
128.81
120.30
114.34
112.69
63.04
55.29
50.82
35.95
29.69
23.42
OMe
NC
O
N–Me
H2N
N
Ph
O
3h
190
180
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150
140
130
120
110
100
90
80
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60
50
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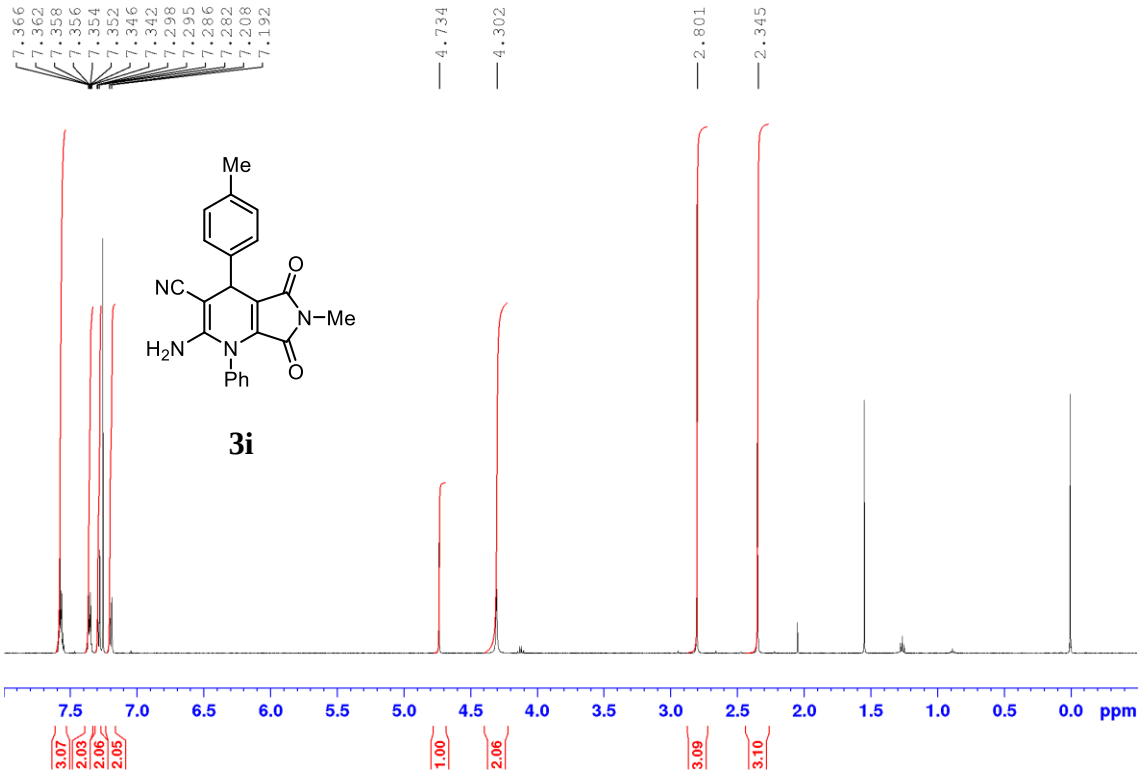
30
20
10
0
ppm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7.192
4.734
4.302
2.801
2.345
Me
NC
O
N–Me
H2N
N
Ph
O
3i
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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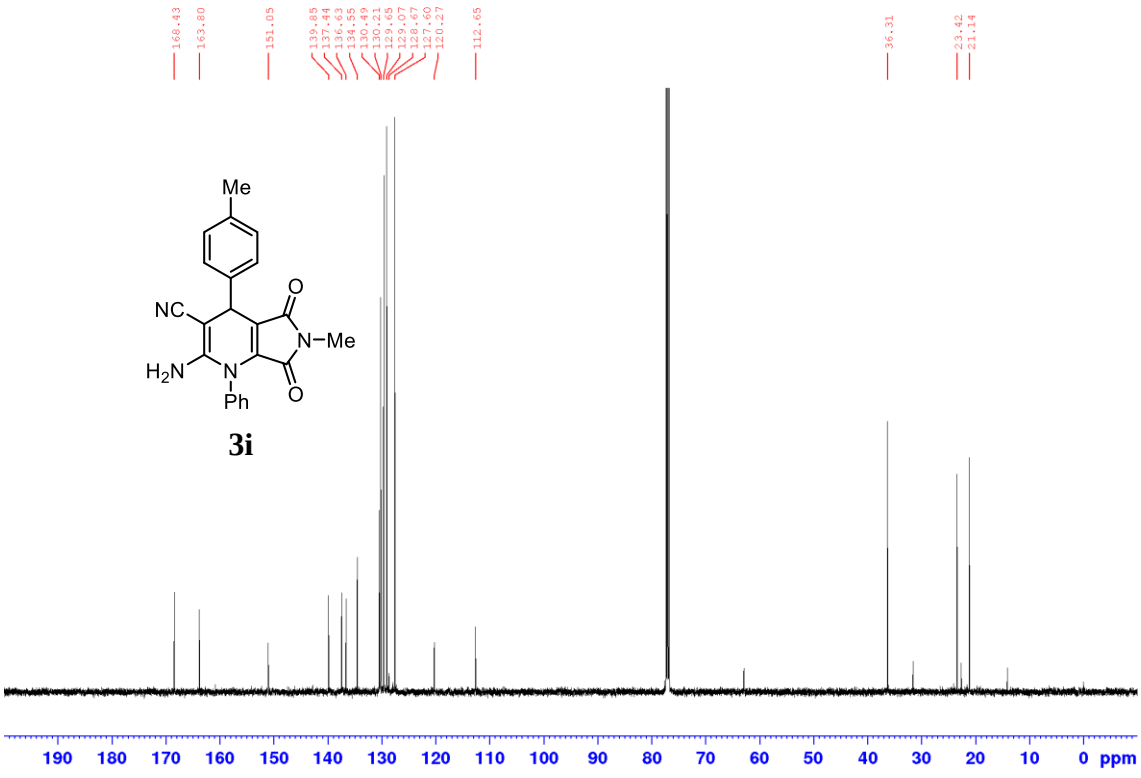
2.05
1.00
2.06
3.09
3.10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127.60
120.27
112.65
36.31
23.42
21.14
Me
NC
O
N–Me
H2N
N
Ph
O
3i
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140
130
120
110
100
90
80
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60
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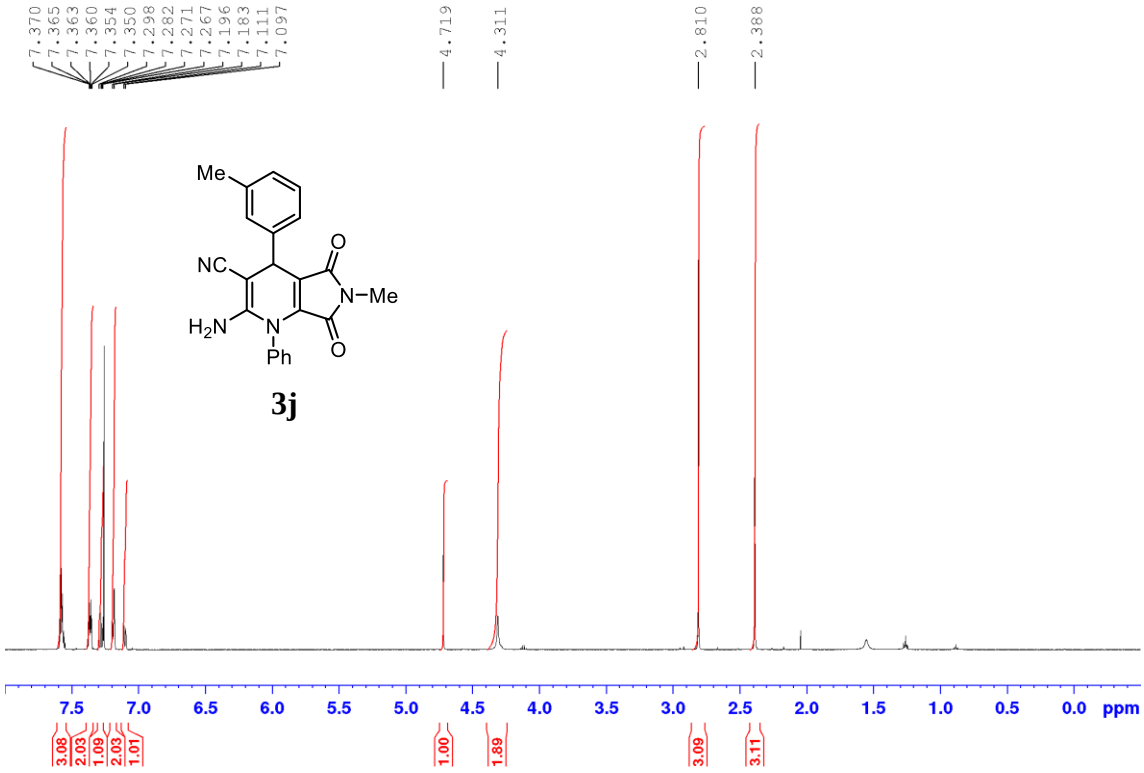
30
20
10
0
ppm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7.111
7.097
4.719
4.311
2.810
2.388
Me
NC
O
N–Me
H2N
N
Ph
O
3j
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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1.01
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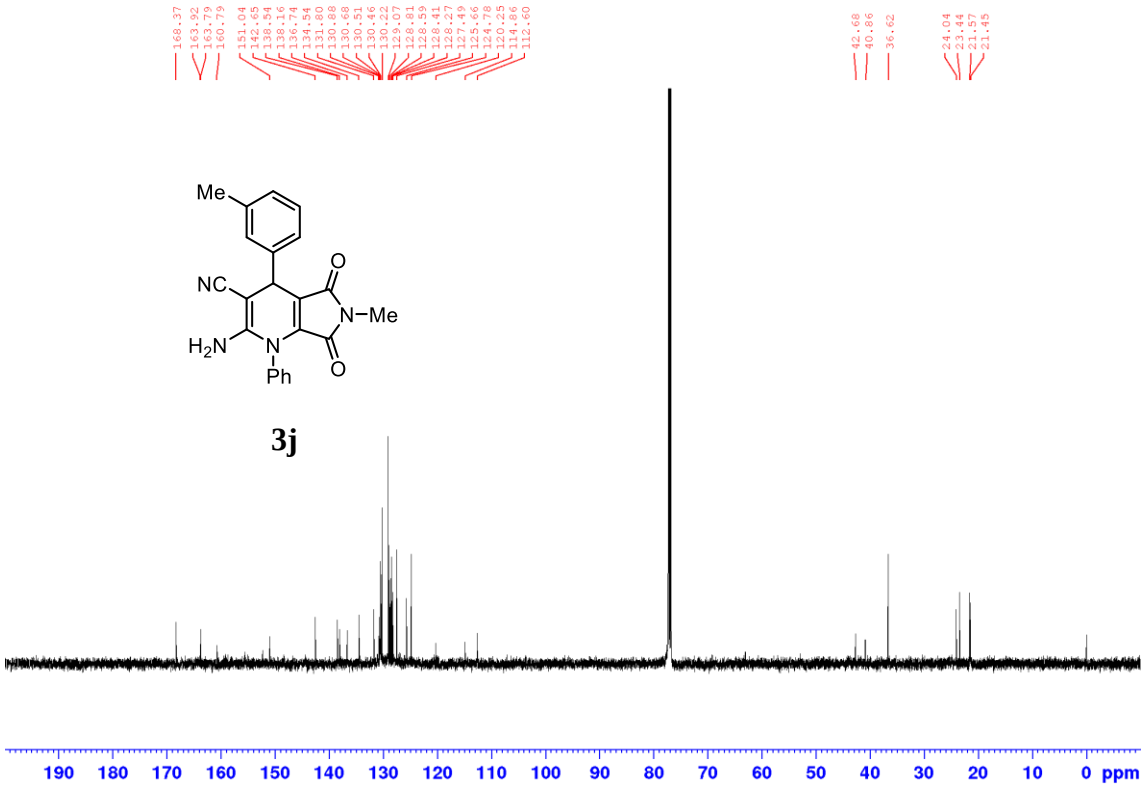
3.11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130.51
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128.27
127.49
125.66
124.78
120.25
114.86
112.60
42.68
40.86
36.62
24.04
23.44
21.57
21.45
Me
NC
O
N–Me
H2N
N
Ph
O
3j
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140
130
120
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100
90
80
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60
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10
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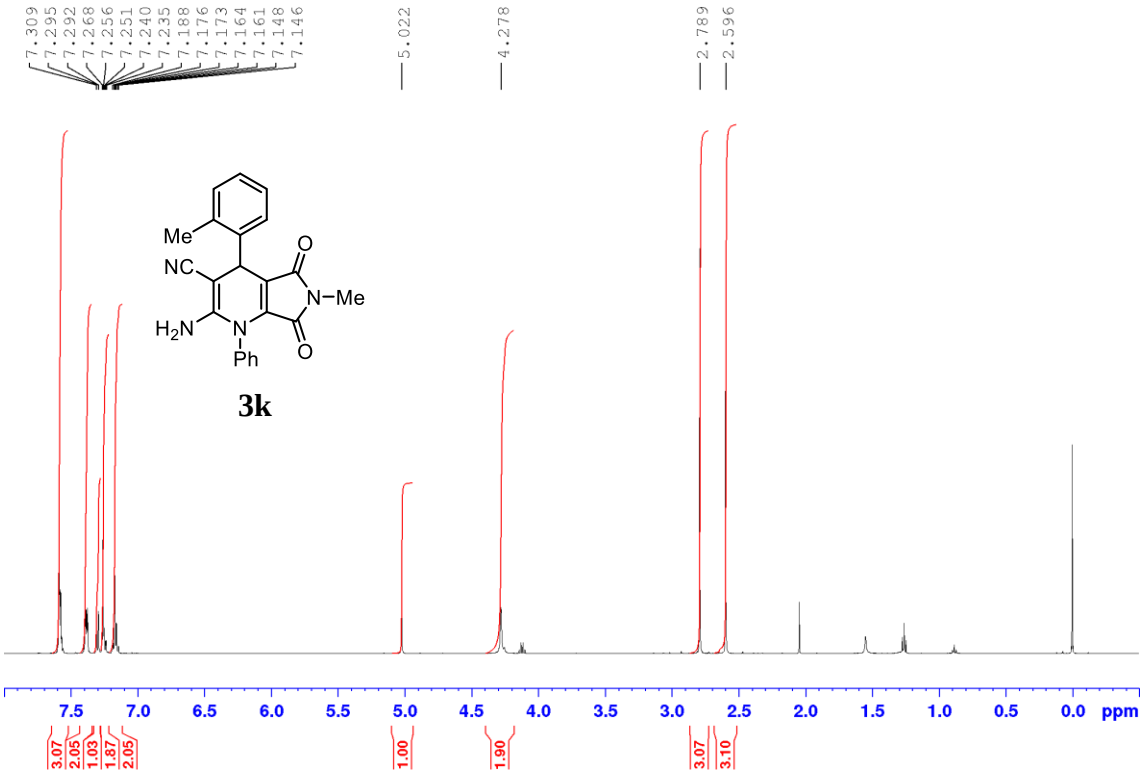
ppm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7.161
7.148
7.146
5.022
4.278
2.789
2.596
Me
NC
O
N–Me
H2N
N
Ph
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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1.00
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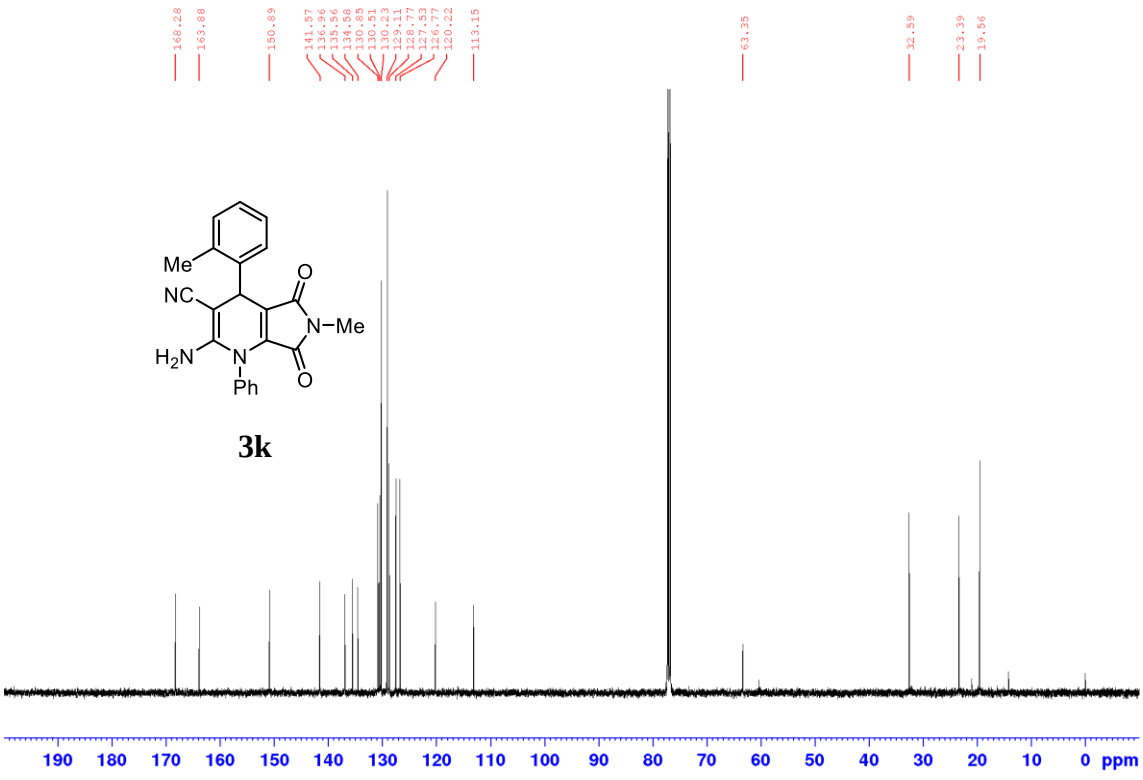
3.07
3.10

3k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126.77
120.22
113.15
63.35
32.59
23.39
19.56
Me
NC
O
N–Me
H2N
N
Ph
O
190
180
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130
120
110
100
90
80
70
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50
40
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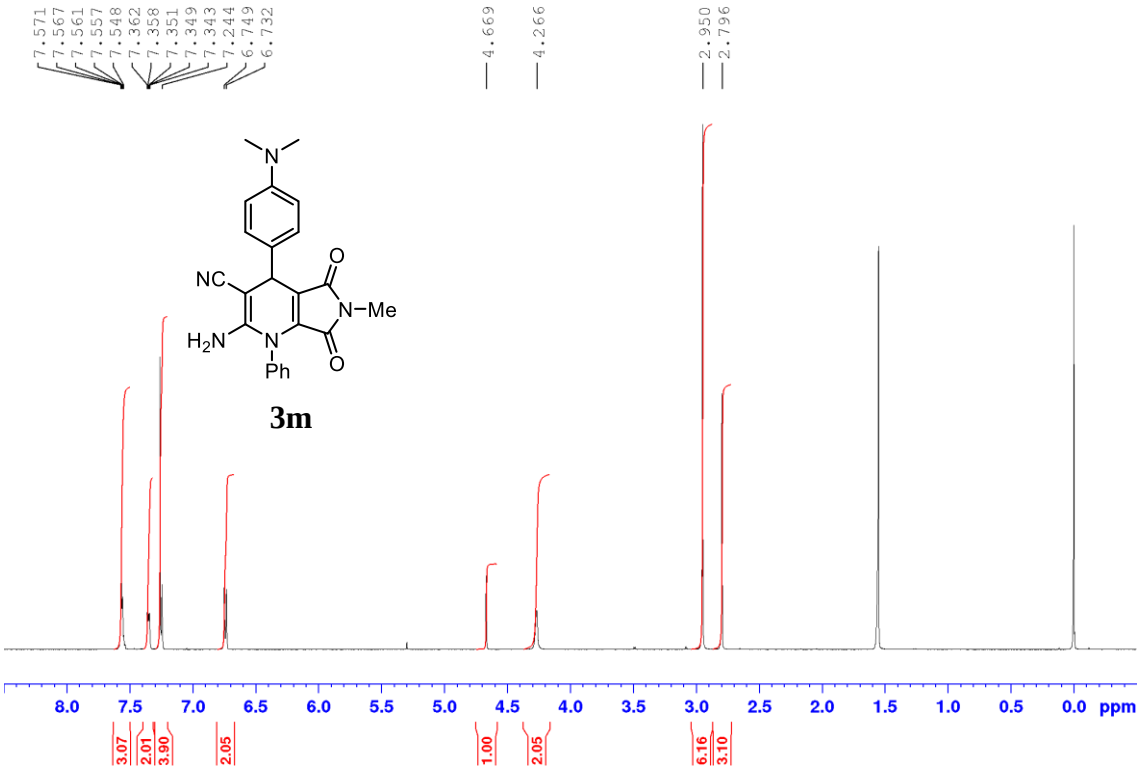
10
0
ppm

3k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4.669
4.266
2.950
2.796
NC
N–Me
H2N
N
Ph
O
3m
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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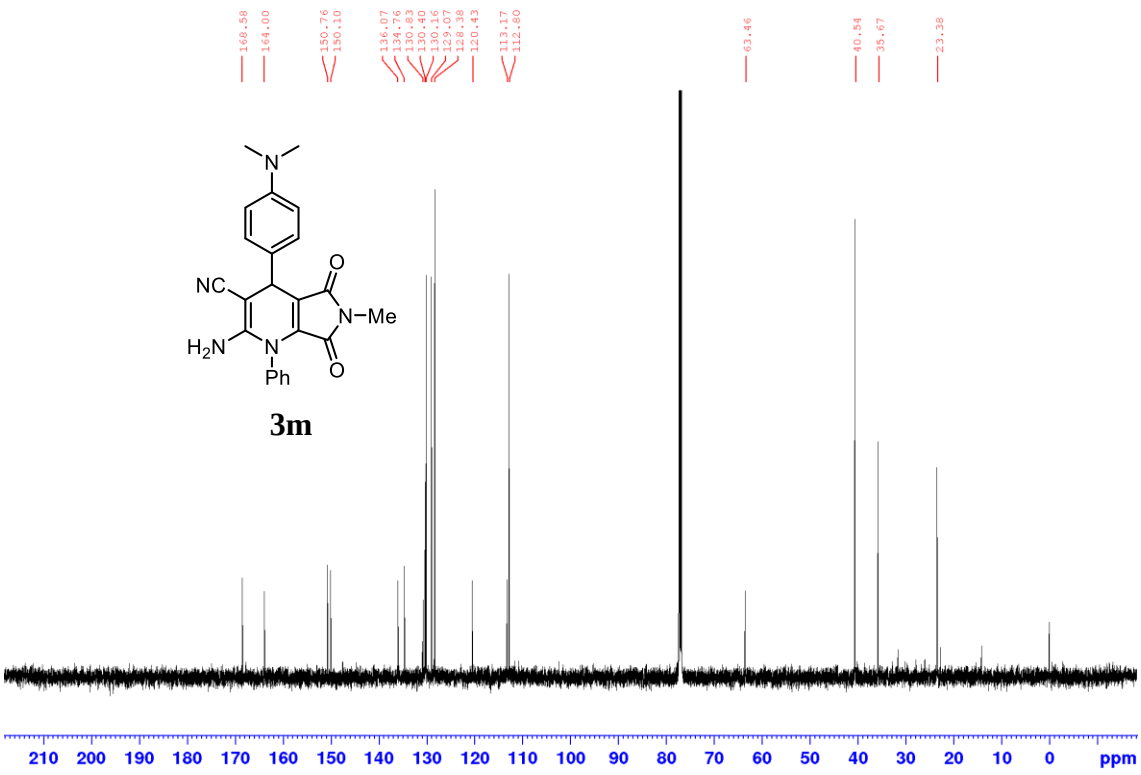
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129.07
128.38
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113.17
112.80
63.46
40.54
35.67
23.38
NC
N–Me
H2N
N
Ph
O
3m
210
200
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140
130
120
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100
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60
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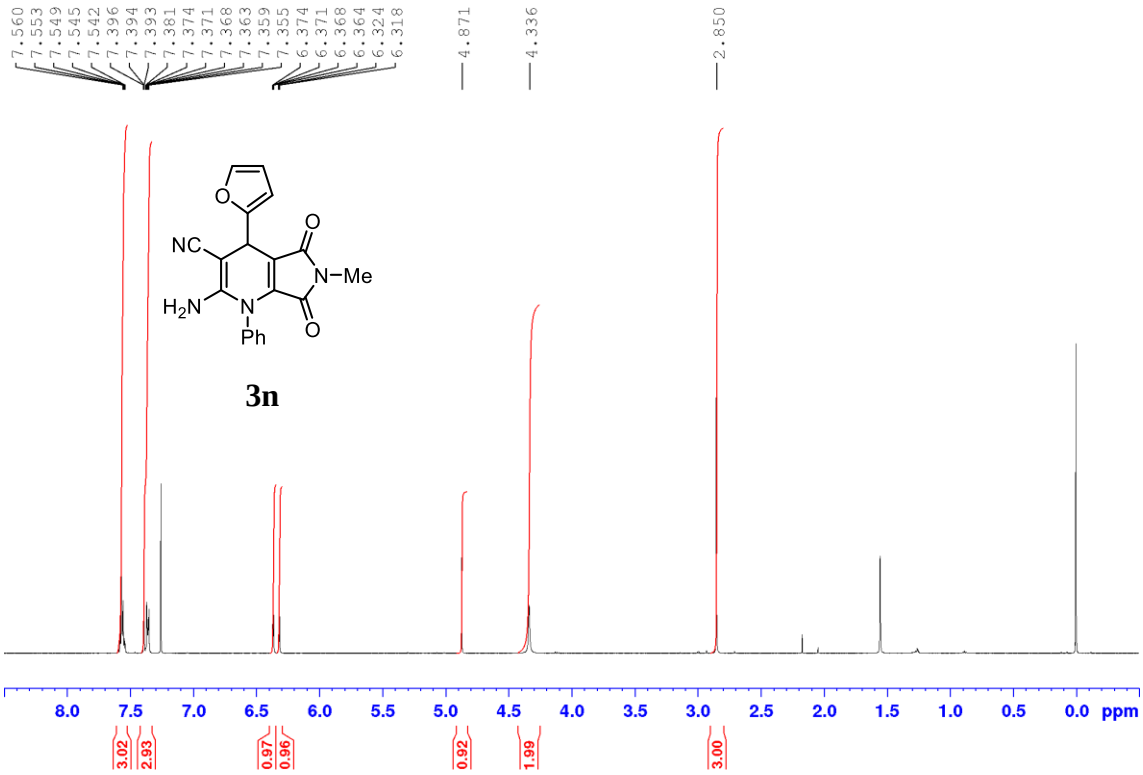
0
ppm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7.363
7.359
7.355
6.374
6.371
6.368
6.364
6.324
6.318
4.871
4.336
2.850
O
NC
O
N–Me
H2N
N
Ph
O
3n
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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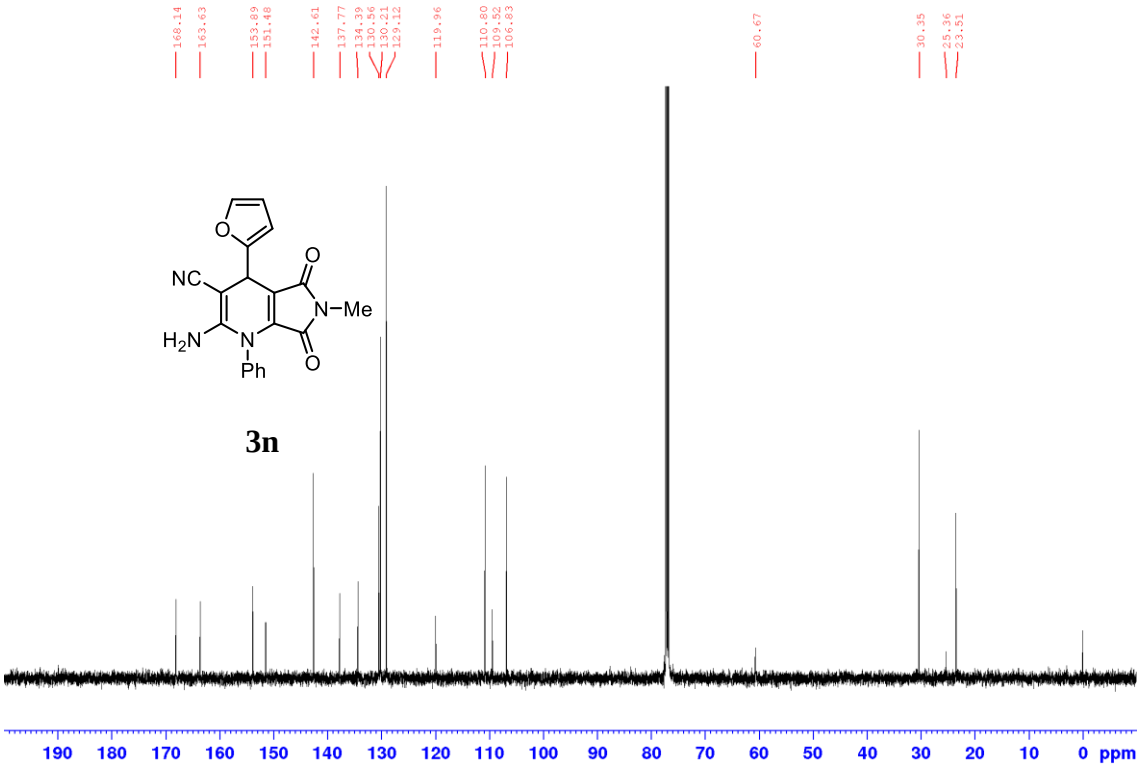
3.00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60.67
30.35
25.36
23.51
O
NC
O
N–Me
H2N
N
Ph
O
3n
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140
130
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110
100
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80
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50
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20
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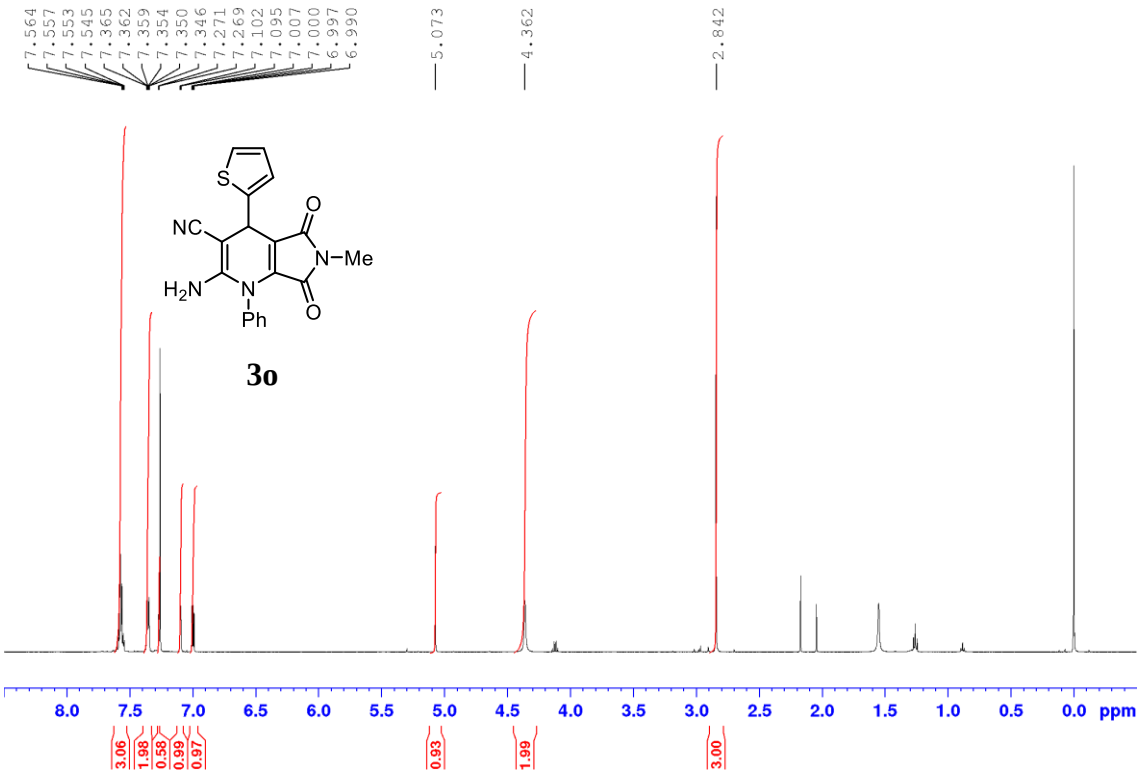
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7.354
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7.269
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7.095
7.007
7.000
6.997
6.990
5.073
4.362
2.842
S
NC
O
N–Me
H2N
N
Ph
O
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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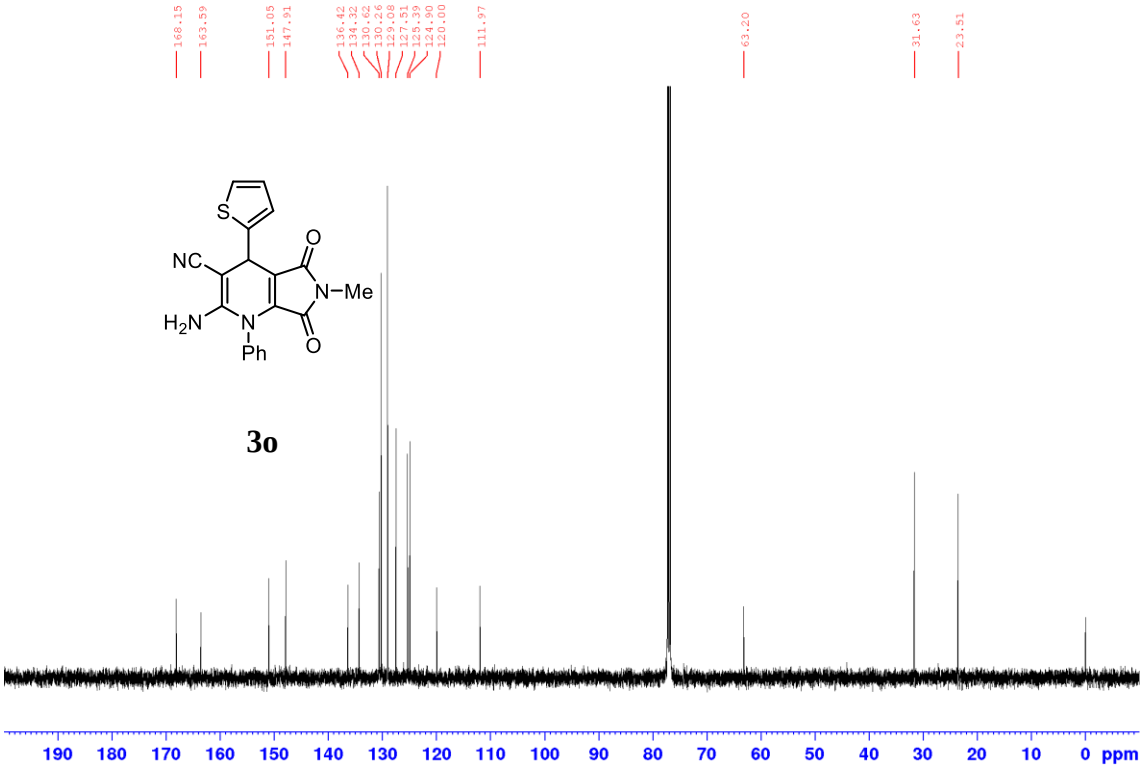
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130.26
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127.51
125.39
124.90
120.00
111.97
63.20
31.63
23.51
S
NC
O
N–Me
H2N
N
Ph
O
190
180
170
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150
140
130
120
110
100
90
80
70
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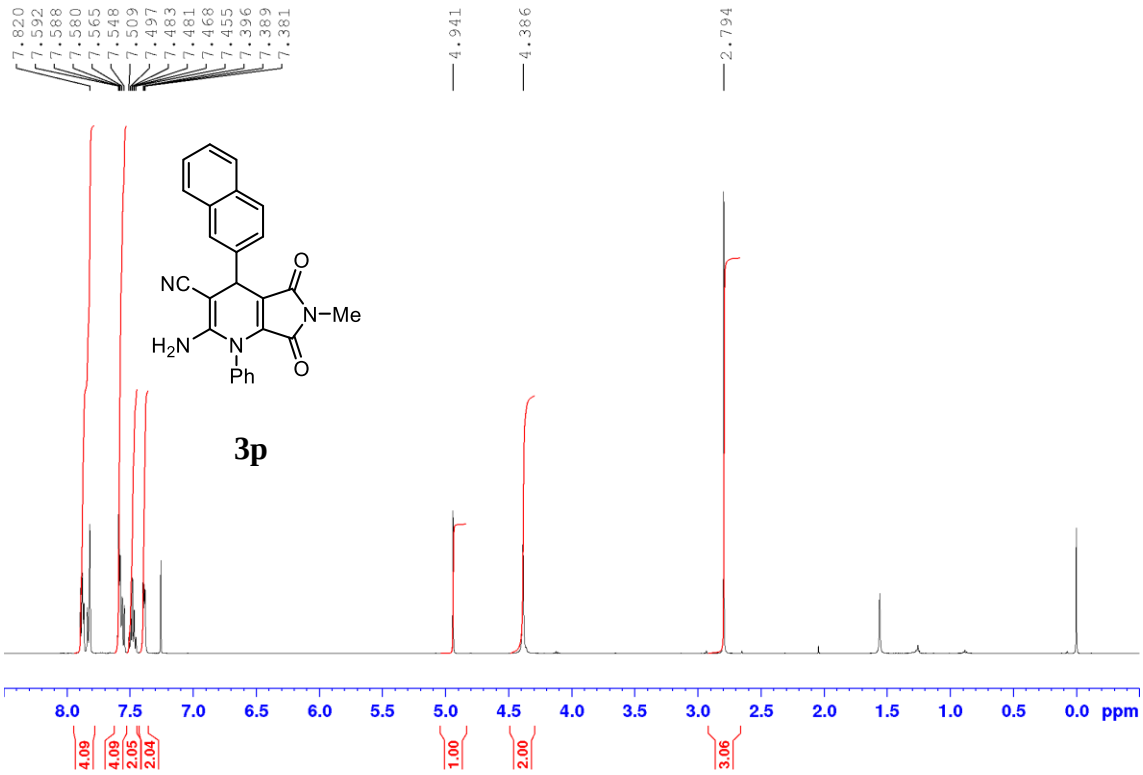
50
40
30
20
10
0
ppm

3o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7.497
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7.396
7.389
7.381
4.941
4.386
2.794
NC
O
N–Me
H2N
N
Ph
O
3p
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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0.5
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ppm
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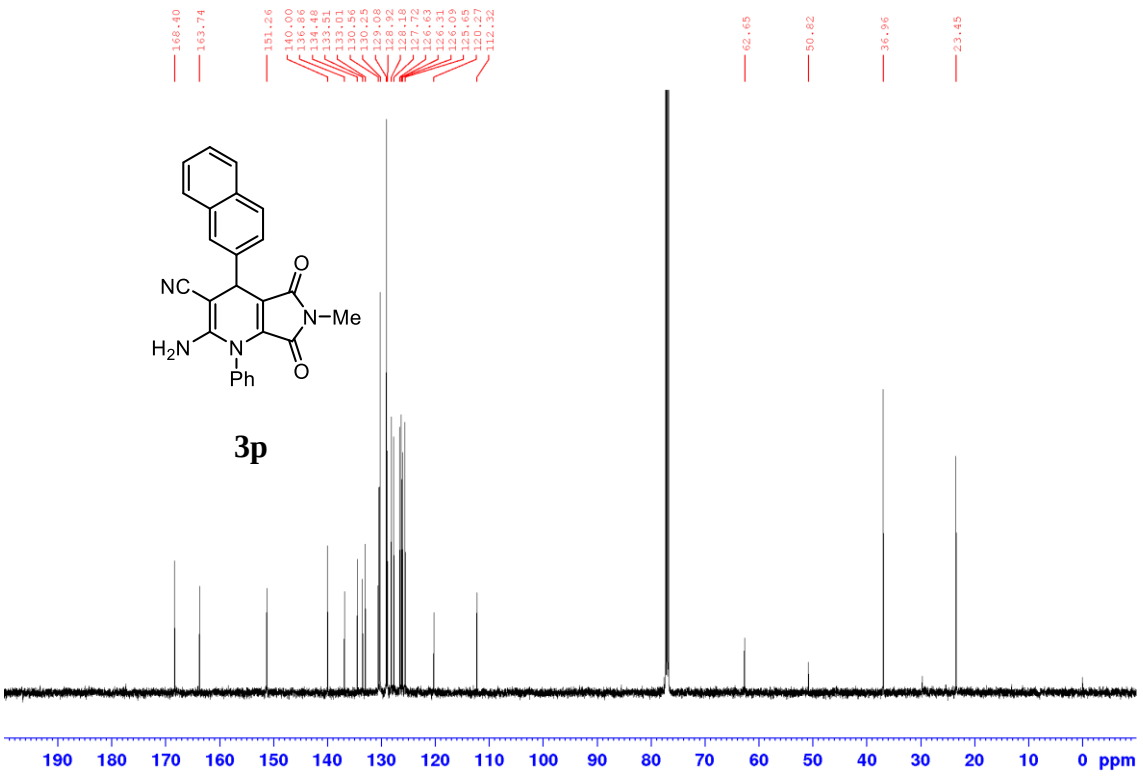
2.04
1.00
2.00
3.06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133.01
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128.92
128.18
127.72
126.63
126.31
126.09
125.65
120.27
112.32
62.65
50.82
36.96
23.45
NC
O
N–Me
H2N
N
Ph
O
3p
190
180
170
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140
130
120
110
100
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80
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50
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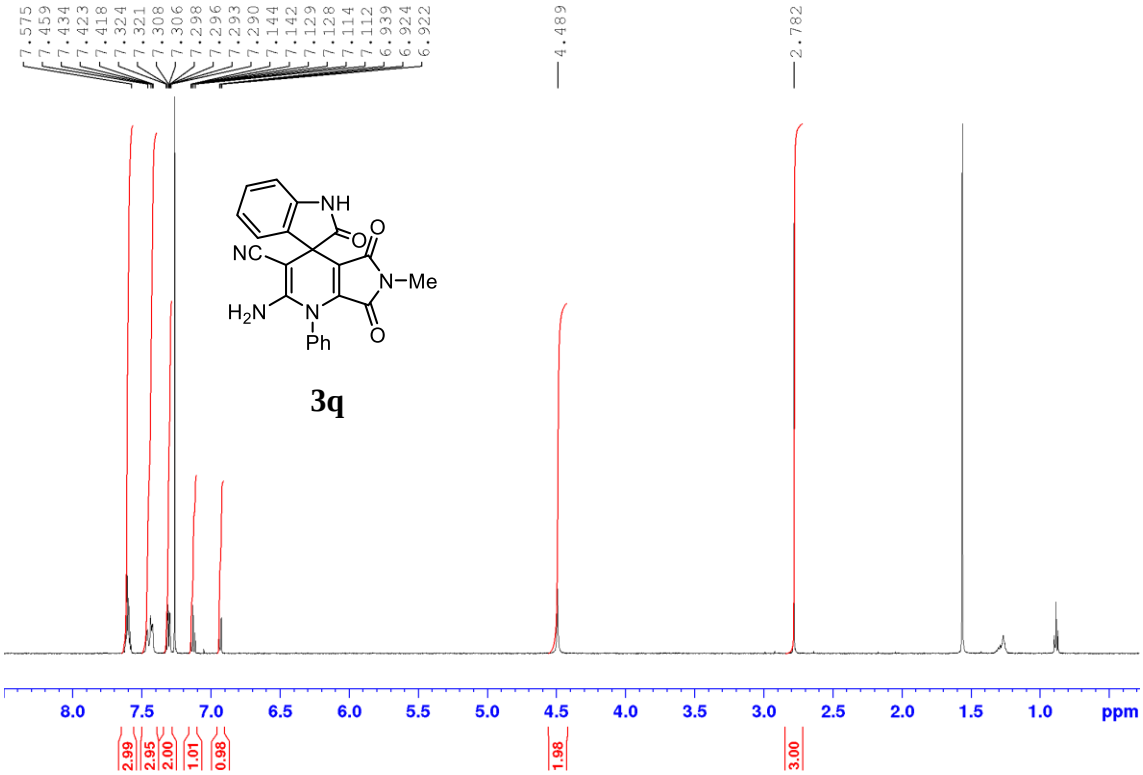
30
20
10
0
ppm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7.308
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7.296
7.293
7.290
7.144
7.142
7.129
7.128
7.114
7.112
6.939
6.924
6.922
4.489
2.782
NH
O
O
NC
N–Me
H2N
N
Ph
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
ppm
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2.00
1.01
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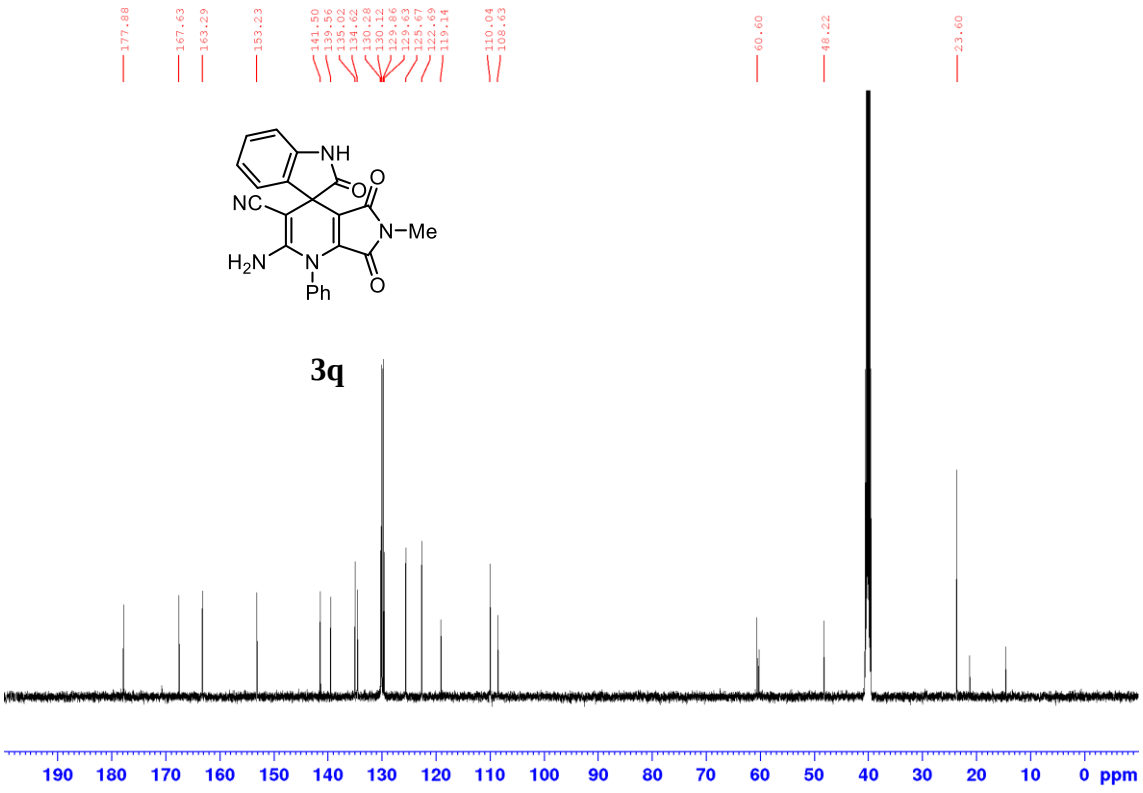
1.98
3.00

3q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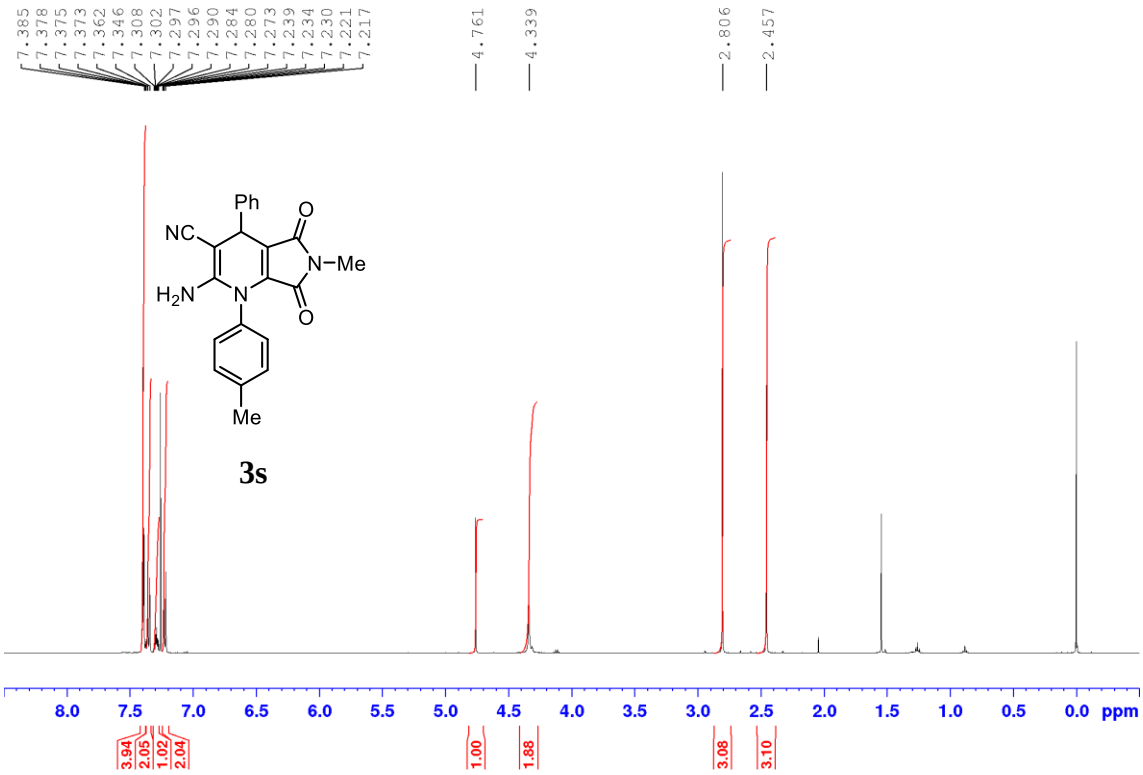
167.63
163.29
153.23
141.50
139.56
135.02
134.62
130.28
130.12
129.86
129.63
125.67
122.69
119.14
110.04
108.63
60.60
48.22
23.60
NH
O
O
NC
N–Me
H2N
N
Ph
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3q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7.302
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7.296
7.290
7.284
7.280
7.273
7.239
7.234
7.230
7.221
7.217
4.761
4.339
2.806
2.457
Ph
NC
O
N–Me
H2N
N
O
Me
3s
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
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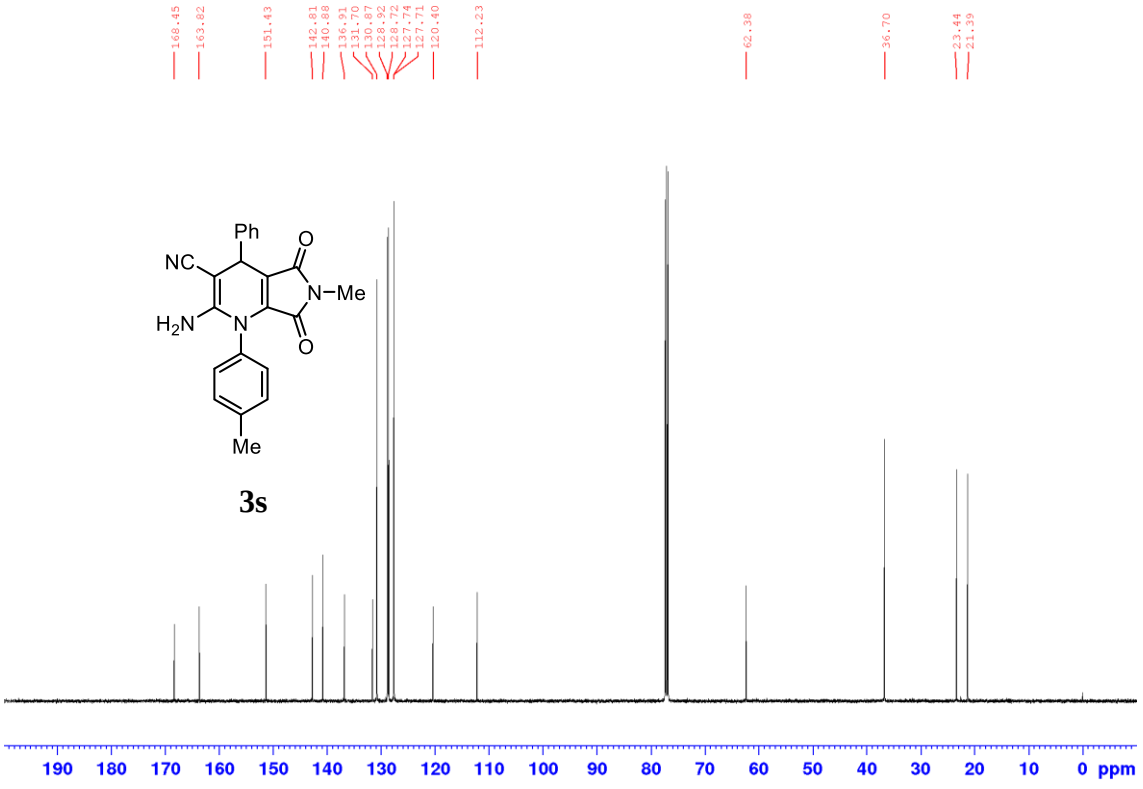
2.05
1.02
2.04
1.00
1.88
3.08
3.10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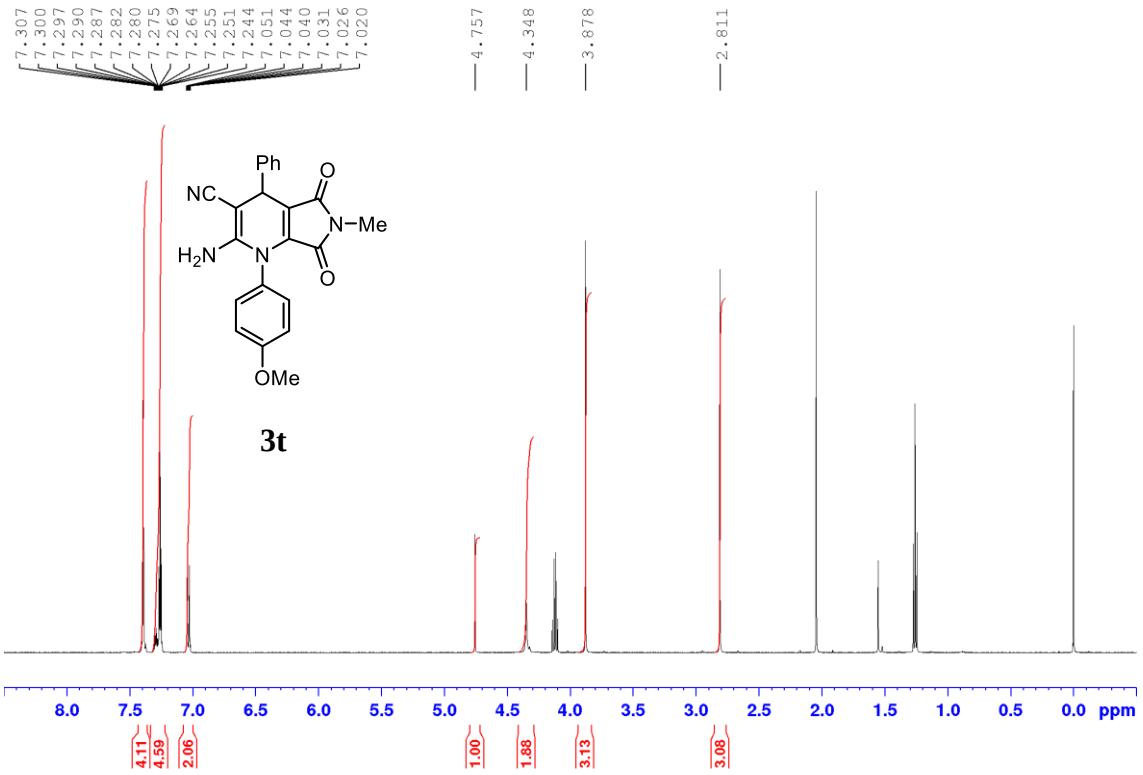
136.91
131.70
130.87
128.92
128.72
127.74
127.71
120.40
112.23
62.38
36.70
23.44
21.39
Ph
NC
O
N–Me
H2N
N
O
Me
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.280
7.275
7.269
7.264
7.255
7.251
7.244
7.051
7.044
7.040
7.031
7.026
7.020
4.757
4.348
3.878
2.811
Ph
NC
O
N–Me
H2N
N
O
OMe
3t
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
0.0
ppm
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2.06
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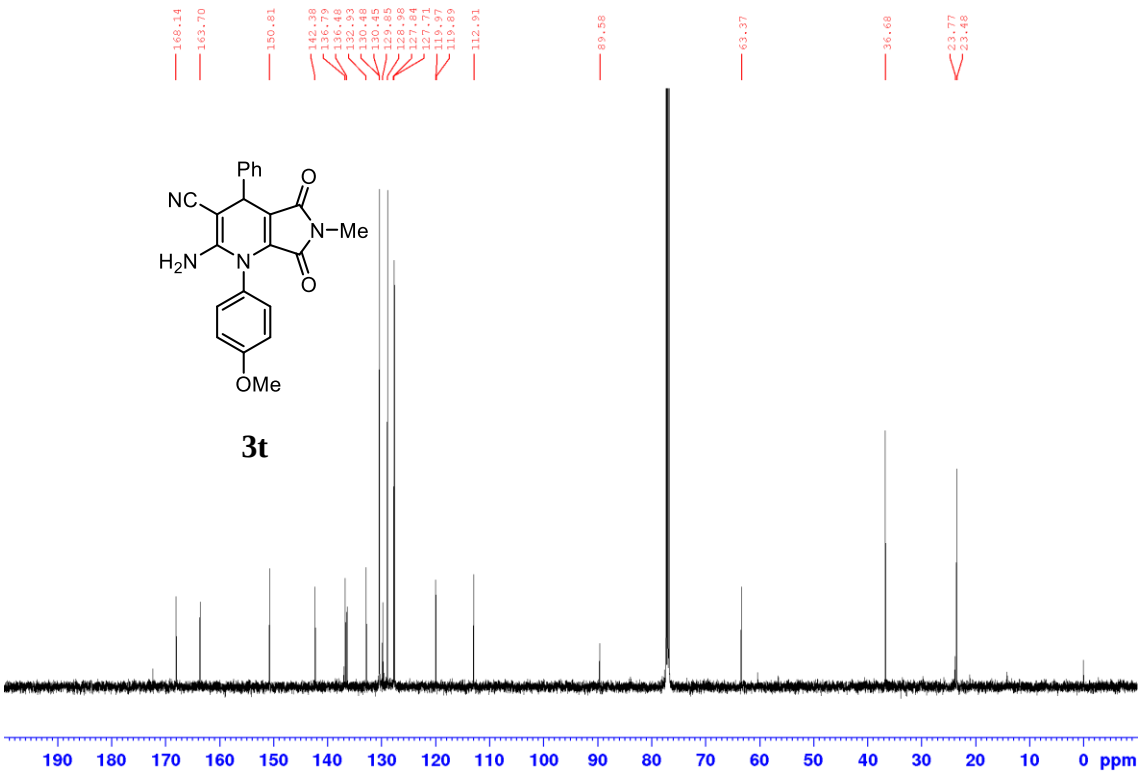
1.88
3.13
3.08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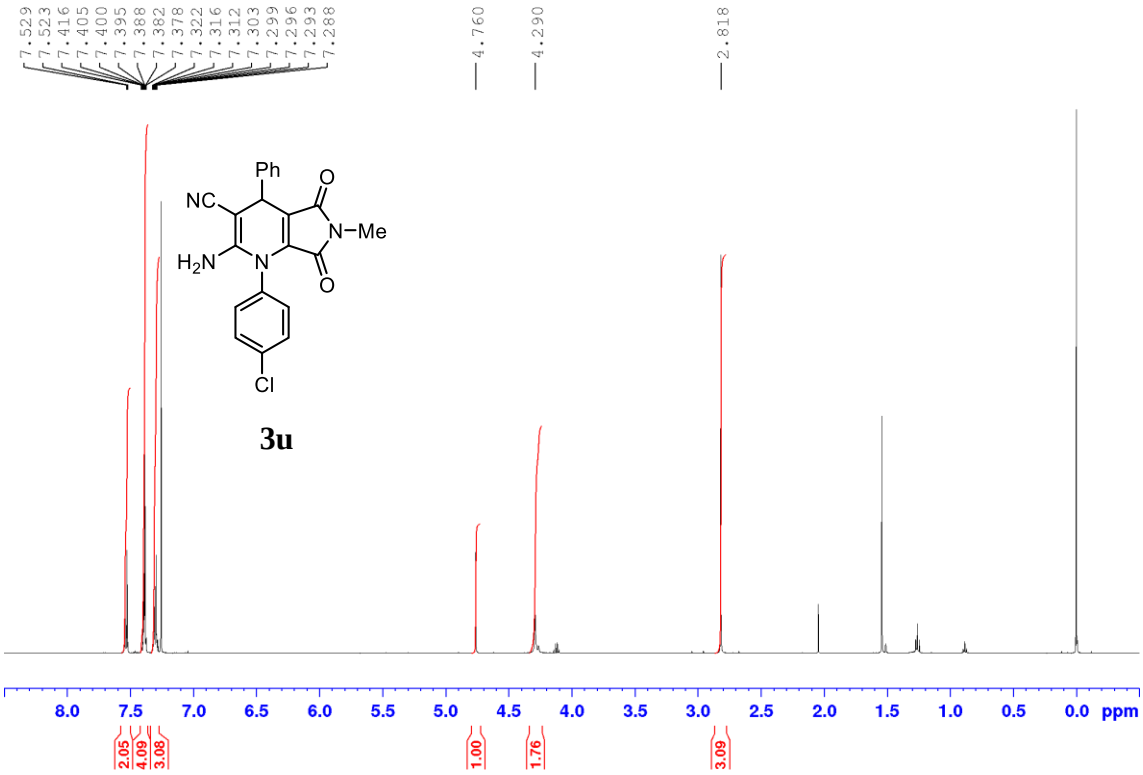
136.48
132.93
130.48
130.45
129.85
128.98
127.84
127.71
119.97
119.89
112.91
89.58
63.37
36.68
23.77
23.48
Ph
NC
O
N–Me
H2N
N
O
OMe
3t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.388
7.382
7.378
7.322
7.316
7.312
7.303
7.299
7.296
7.293
7.288
4.760
4.290
2.818
Ph
NC
O
N–Me
H2N
N
O
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
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ppm
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3.08
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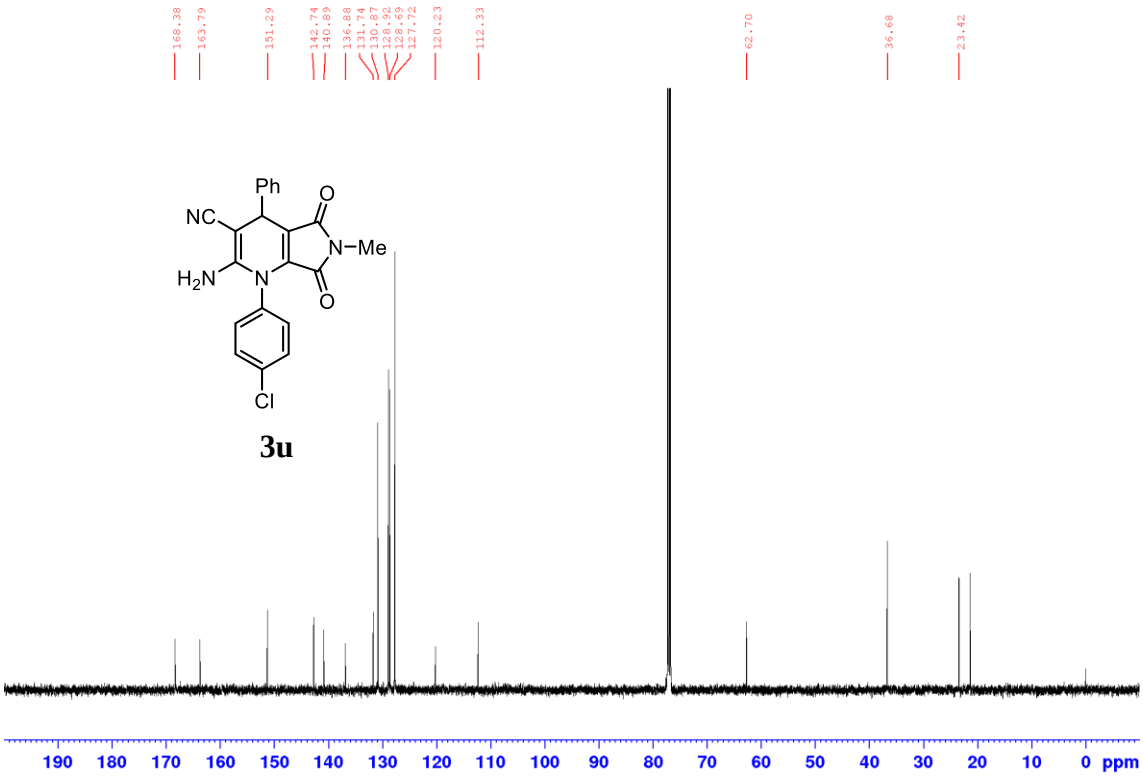
1.76
3.09

3u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131.74
130.87
128.92
128.69
127.72
120.23
112.33
62.70
36.68
23.42
Ph
NC
O
N–Me
H2N
N
O
Cl
190
180
170
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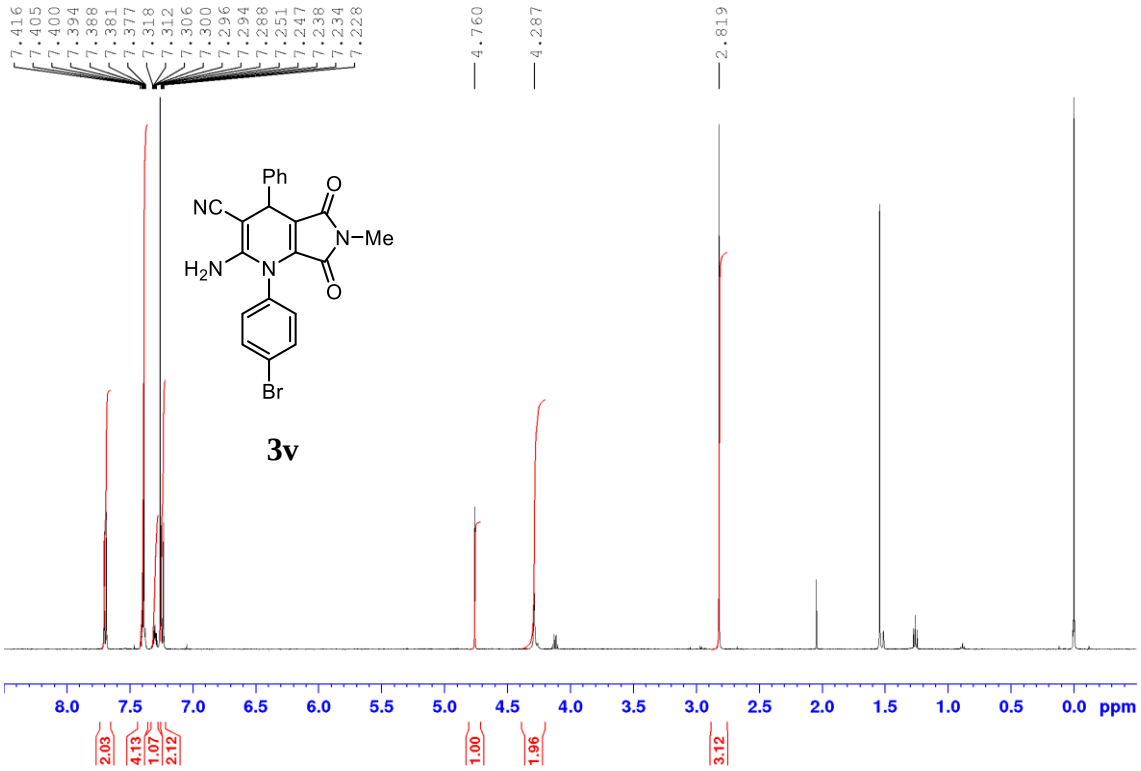
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3u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7.381
7.377
7.318
7.312
7.306
7.300
7.296
7.294
7.288
7.251
7.247
7.238
7.234
7.228
4.760
4.287
2.819
Ph
NC
O
N–Me
H2N
N
O
Br
3v
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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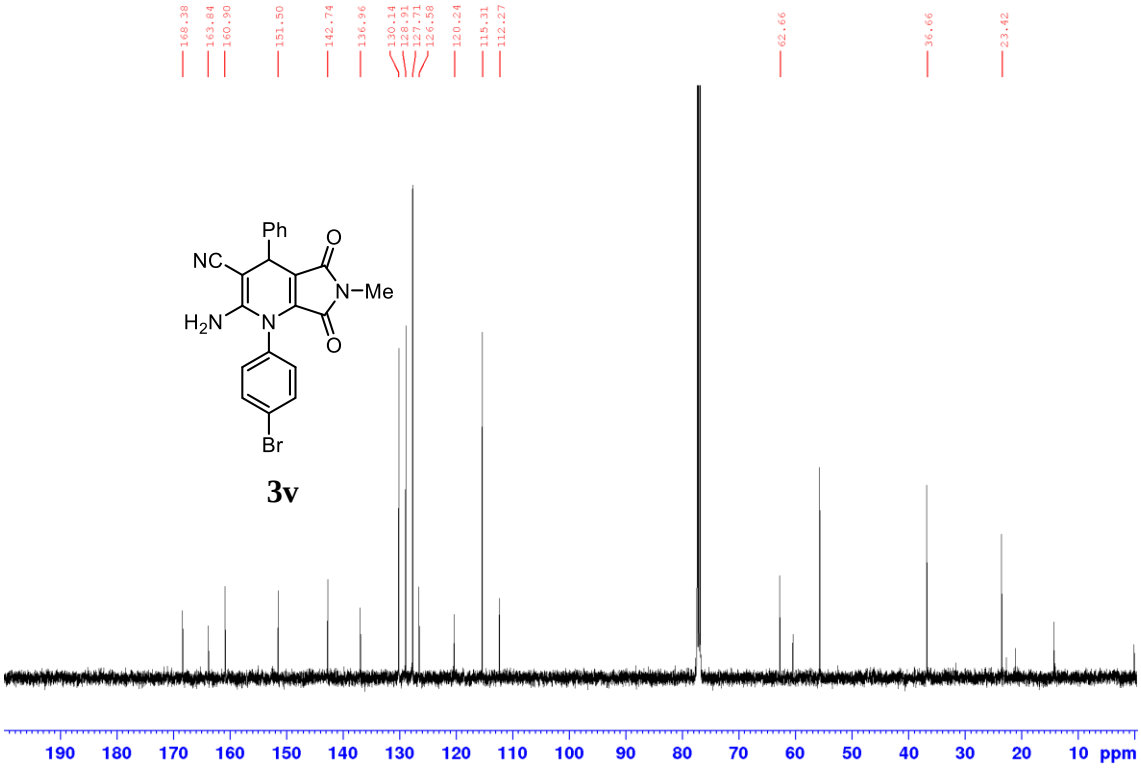
4.13
1.07
2.12
1.00
1.96
3.12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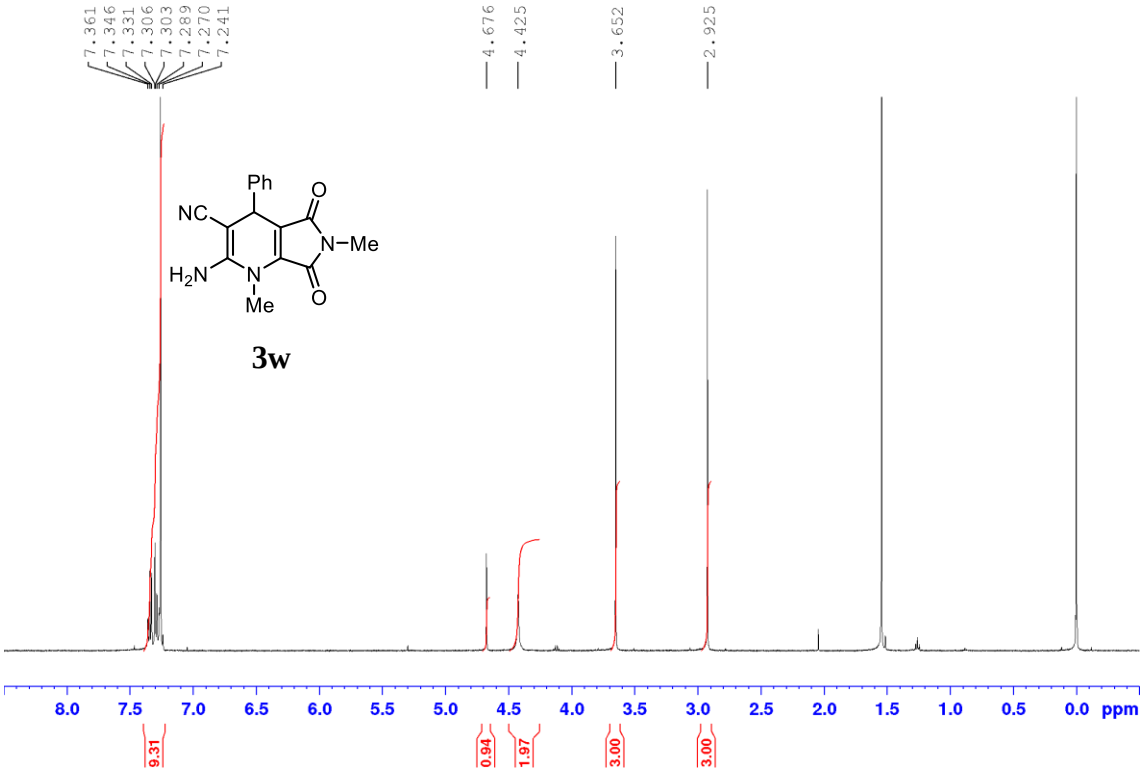
130.14
128.91
127.71
126.58
120.24
115.31
112.27
62.66
36.66
23.42
Ph
NC
O
N–Me
H2N
N
O
Br
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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2.925
Ph
NC
O
N–Me
H2N
N
Me
O
3w
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
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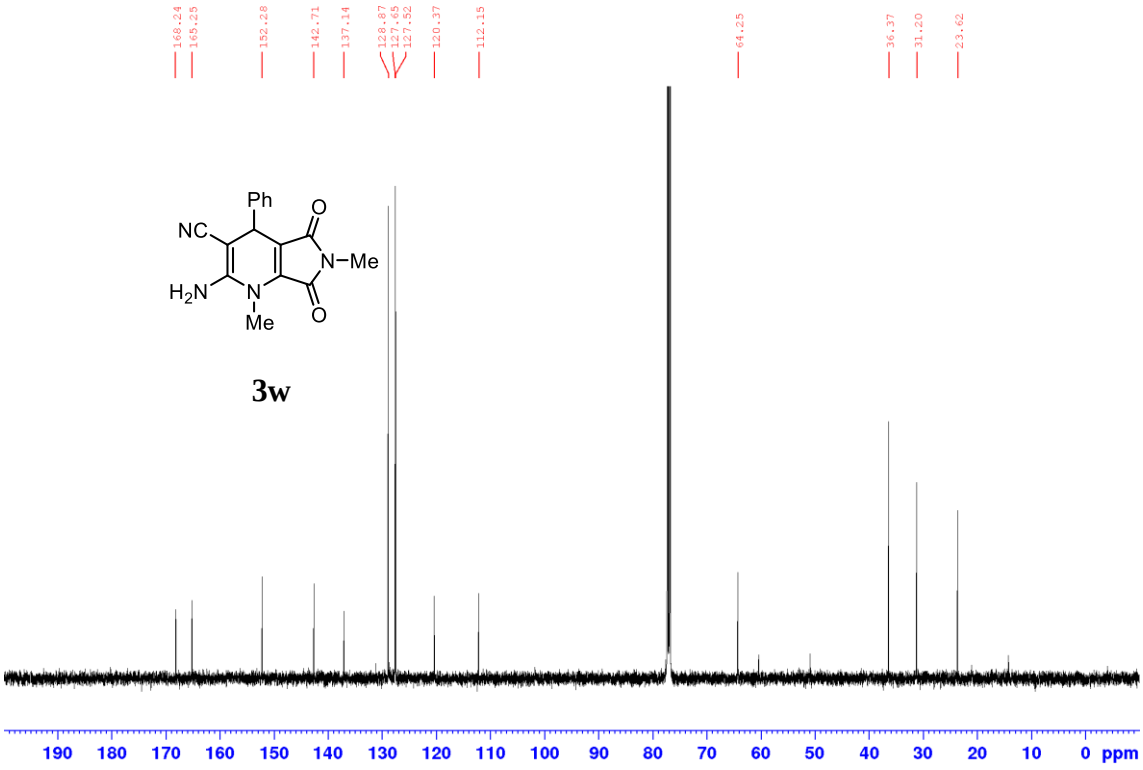
0.94
1.97
3.00
3.00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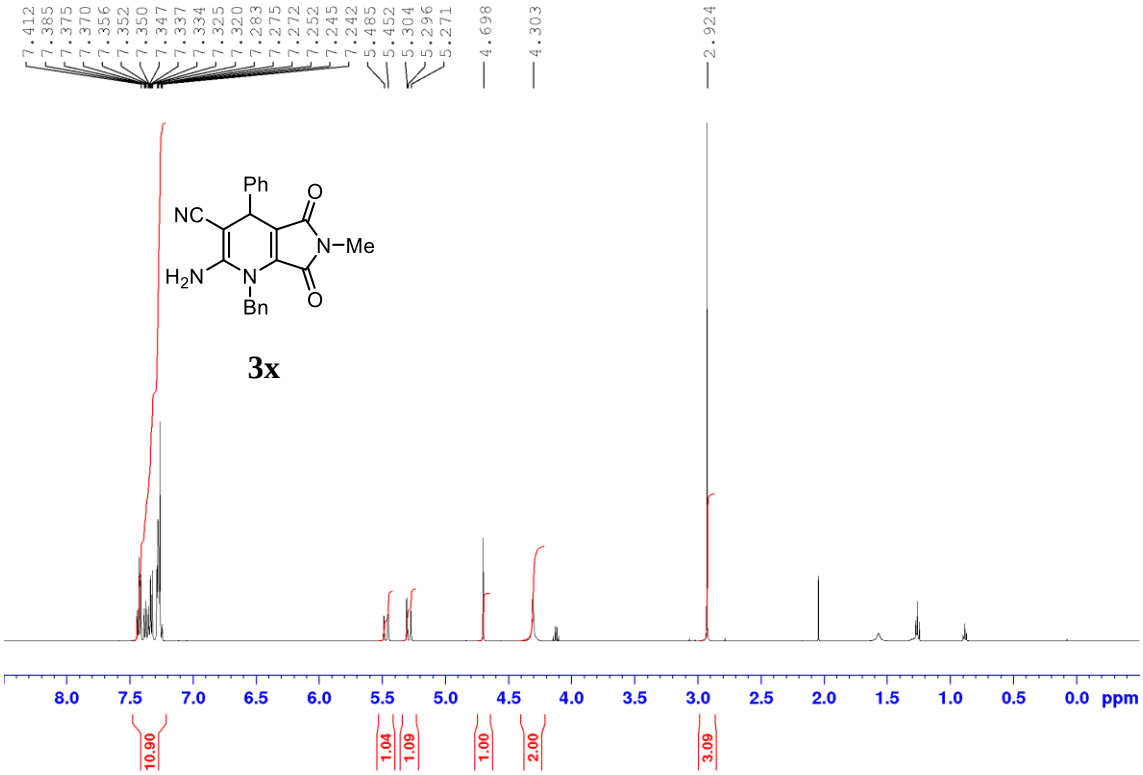
127.52
120.37
112.15
64.25
36.37
31.20
23.62
Ph
NC
O
N–Me
H2N
N
Me
O
3w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.325
7.320
7.283
7.275
7.272
7.252
7.245
7.242
5.485
5.452
5.304
5.296
5.271
4.698
4.303
2.924
Ph
NC
O
N–Me
H2N
N
Bn
O
3x
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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ppm
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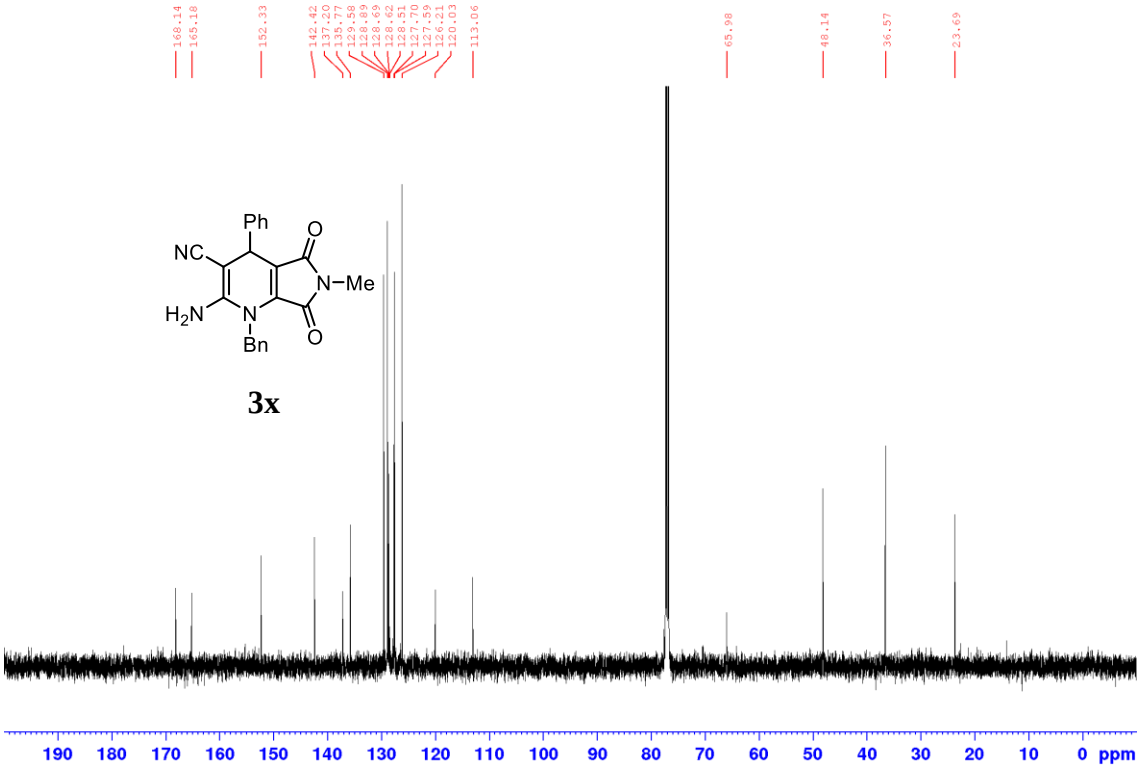
1.00
2.00
3.09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128.69
128.62
128.51
127.70
127.59
126.21
120.03
113.06
65.98
48.14
36.57
23.69
Ph
NC
O
N–Me
H2N
N
Bn
O
3x
190
180
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140
130
120
110
100
90
80
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60
50
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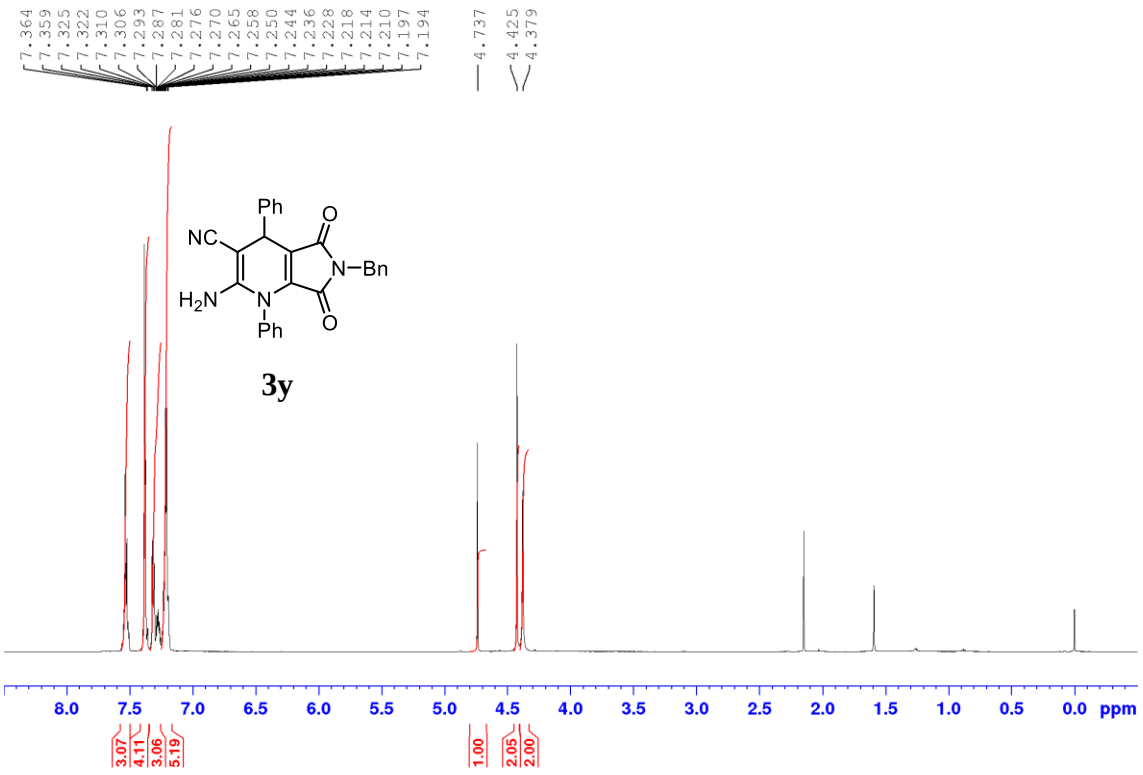
30
20
10
0
ppm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7.258
7.250
7.244
7.236
7.228
7.218
7.214
7.210
7.197
7.194
4.737
4.425
4.379
Ph
NC
O
N–Bn
H2N
N
Ph
O
3y
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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3.06
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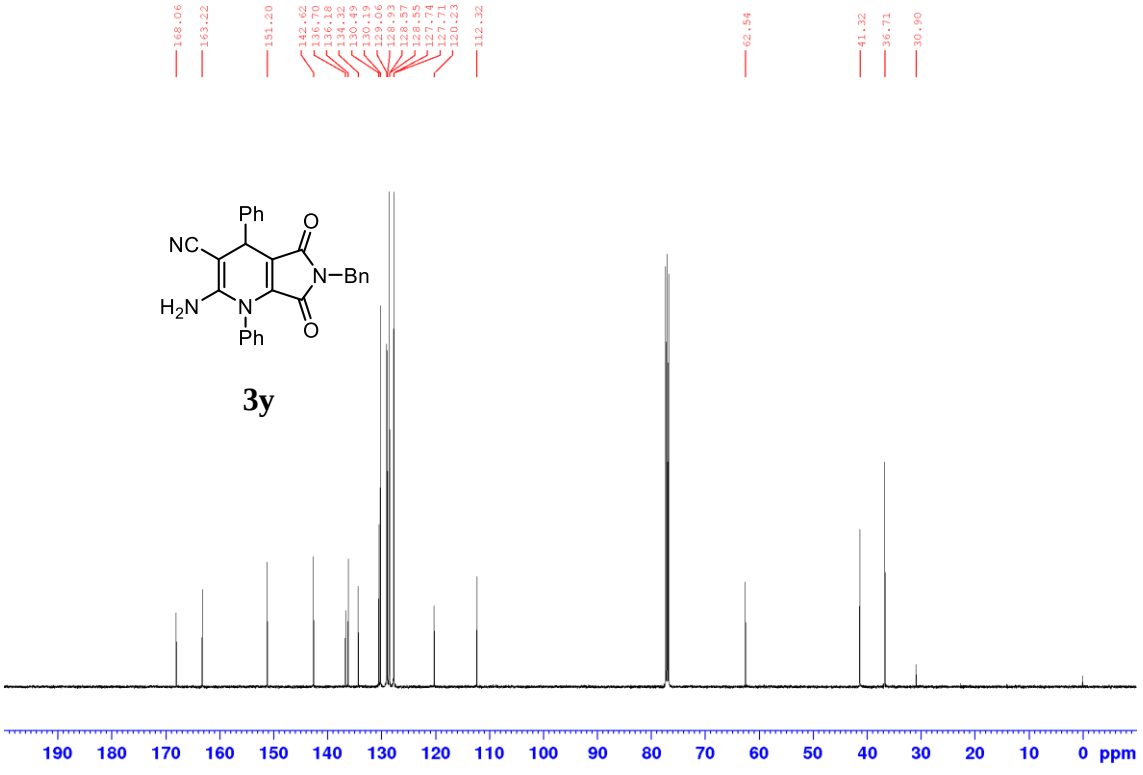
2.05
2.00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130.19
129.06
128.93
128.57
128.55
127.74
127.71
120.23
112.32
62.54
41.32
36.71
30.90
Ph
NC
O
N–Bn
H2N
N
Ph
O
3y
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160
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140
130
120
110
100
90
80
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60
50
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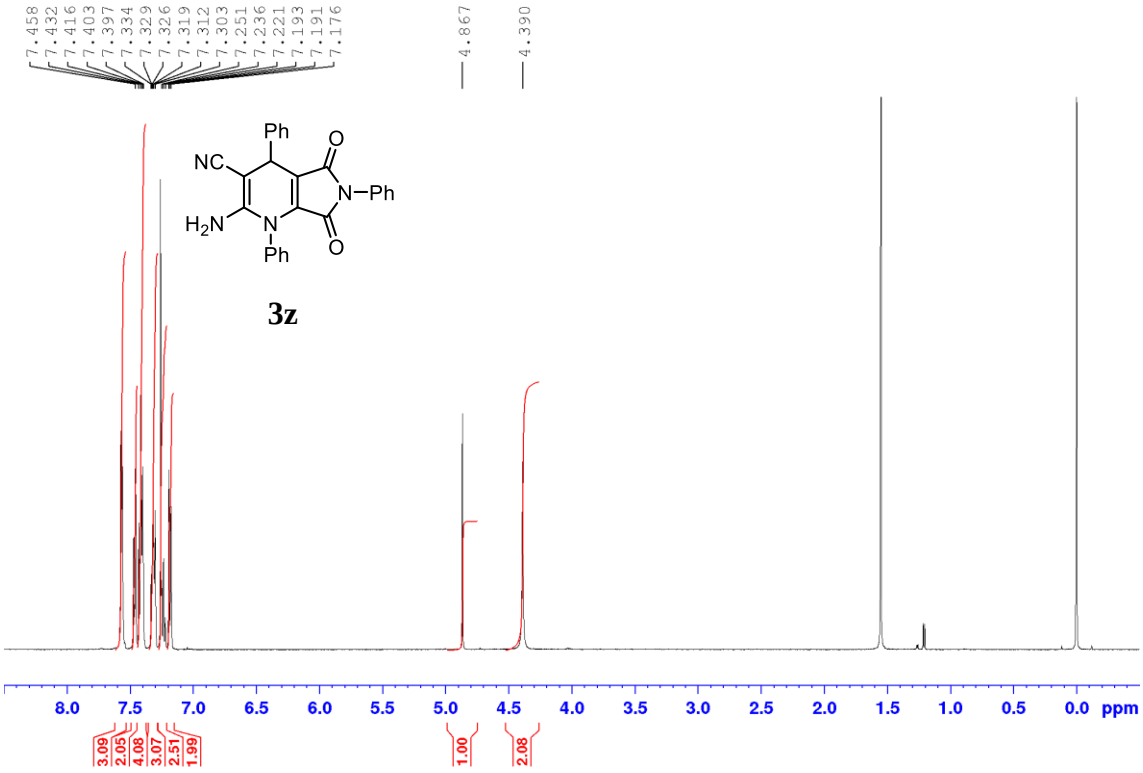
30
20
10
0
ppm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7.312
7.303
7.251
7.236
7.221
7.193
7.191
7.176
4.867
4.390
Ph
NC
O
N–Ph
H2N
N
Ph
O
3z
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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0.0
ppm
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4.08
3.07
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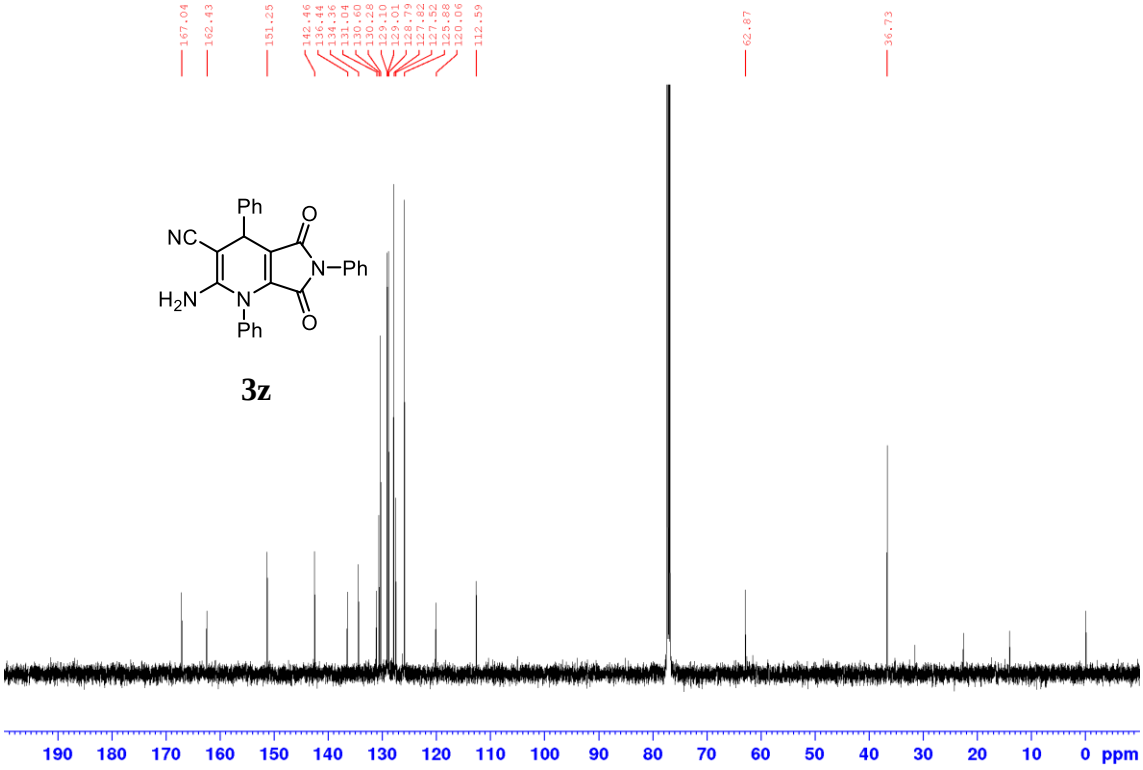
1.00
2.08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131.04
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130.28
129.10
129.01
128.79
128.62
127.52
125.88
120.06
112.59
62.67
36.73
Ph
NC
O
N–Ph
H2N
N
Ph
O
3z
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm