Supporting Information

for

An easy direct arylation of 5-pyrazolones

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Experimental details and characterization data for all compounds

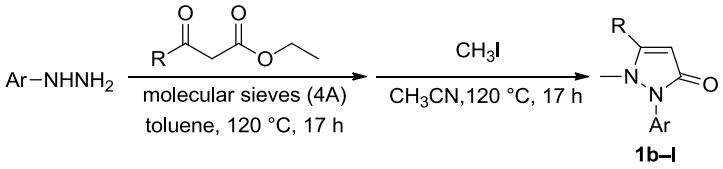
Contents

1. Experimental procedures

All commercially available reagents and solvents were obtained from the commercial providers and used without further purification. Melting points were recorded using a WRS-2A melting point apparatus and were uncorrected. IR spectra were obtained on a Nexus FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer. Chemical shifts were reported relative to tetramethylsilane (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C. High resolution mass spectra were determined using a Finnigan-NAT GC/MS/DS 8430 spectrometer. Flash column chromatography was performed on 300–400 mesh silica gel. 5-Pyrazolones **1** (except **1a**) were prepared according to literature procedures [1]. 5-Pyrazolone **1a** is a commercially available reagent.

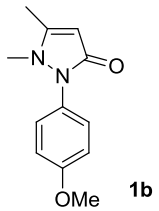
2. Experimental details and characterization data for 5-pyrazolones 1

1) Experimental details and characterization data for 1b–l



A reaction mixture containing aryl hydrazine (2 mmol), ethyl acetoacetate (2 mmol), molecular sieves (4 Å) and toluene (4 mL) was stirred in the dark in a sealed tube maintained at 120 °C in an oil bath. After 17 h, the reaction mixture was cooled to room temperature. To this mixture, acetonitrile (2 mL) and iodomethane (6 mmol) were added successively and stirred in the dark in the sealed tube maintained at 120 °C for additional 17 h, After the reaction was completed, the mixture was cooled to room temperature. The solvent was then evaporated in vacuo. The resulting residue was purified by flash column chromatography (ethyl acetate) to yield **1b–l**.

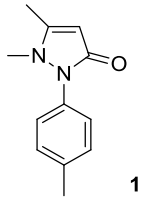
Spectral data of 1b–l



1b

2-(4-Methoxyphenyl)-1,5-dimethyl-1*H*-pyrazol-3(2*H*)-one(1b) [1**]:**

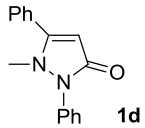
yellow solid, mp:124.7-125.8°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 5.40 (s, 1H), 3.85 (s, 3H), 3.07 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 158.8, 154.9, 127.9, 127.0 (2C), 114.6 (2C), 97.9, 55.6, 34.8, 12.9; IR (KBr): 3002, 2823, 1629, 1565, 1552, 1530, 1483, 1452, 1384, 1275 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{12}H_{14}N_2O_2$: 218.1126 $[M]^{+}$; found: 218.1135.



1c

1,2-Dihydro-2,3-dimethyl-1-*p*-tolylpyrazol-5-one (1c):

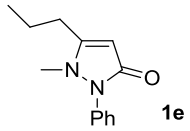
yellow solid, mp: 147.8-148.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25(s, 4H), 5.38 (s, 1H), 3.06 (s, 3H), 2.38 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 155.7, 136.9, 132.6, 129.8 (2C) , 124.7 (2C) , 98.4, 35.1, 21.1, 12.9; IR (KBr): 3060, 2911, 1630, 1565, 1547, 1513, 1483, 1384 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{12}H_{14}N_2O$: 202.1132 $[M]^+$; found: 202.1128.



1d

1,2-Dihydro-2-methyl-1,3-diphenylpyrazol-5-one (1d):

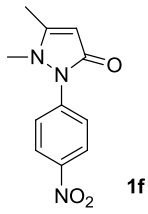
yellow solid, mp: 157.2-158.5°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.45 (m, 9H), 7.29 (t, *J* = 7.2 Hz, 1H), 5.82 (s, 1H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 161.6, 135.2, 130.6, 129.3, 129.2 (2C), 129.1 (2C), 128.4 (2C), 123.7 (2C), 126.5, 100.2, 39.1; IR (KBr): 3087, 2943, 2878, 1630, 1565, 1552, 1513, 1484 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{16}H_{14}N_2O$: 250.1107 $[M]^+$; found: 250.1103.



1e

1-Methyl-2-phenyl-5-propyl-1H-pyrazol-3(2H)-one (1e):

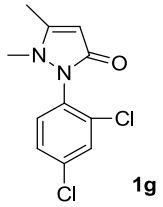
yellow solid, mp: 62.9-63.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 5.39 (s, 1H), 3.03 (s, 3H), 2.47 (t, *J* = 7.6 Hz, 2H), 1.76 -1.64 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 160.9, 135.2 , 129.2 (2C), 126.61, 124.3 (2C), 97.6, 35.6, 28.9, 20.8, 13.8. IR (KBr): 3085, 2958, 2931, 1658, 1594, 1569, 1454, 1396, 1312, 906, 833 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{13}H_{16}N_2O$: 216.1261$[M]^+$; found: 216.1275.



1f

1,2-Dihydro-2,3-dimethyl-1-(4-nitrophenyl)pyrazol-5-one (1f) [2]:

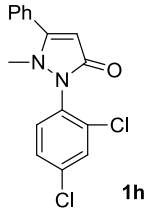
tan solid, mp:164.8-165.6 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 9.2 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 5.45 (s, 1H), 3.09 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 160.7, 144.7, 141.1, 124.7 (2C) , 122.2 (2C) , 100.0, 36.7,13.3; IR (KBr): 3010, 2944, 2893, 1630, 1563, 1530, 1513, 1481, 1352, 1324 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{11}H_{11}N_3O_3$: 233.0816 $[M]^+$; found: 233.0822.



1g

1-(2,4-Dichlorophenyl)-1,2-dihydro-2,3-dimethylpyrazol-5-one (1g):

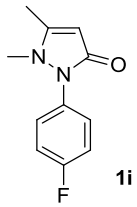
yellow solid, mp:139.2-140.1°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 1H), 7.33 (d, *J* = 8.0Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 5.28 (s, 1H), 3.02 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 155.1, 135.8, 134.9, 131.6, 131.5, 130.7, 128.1, 96.8, 34.2, 12.9; IR (KBr): 3042, 2930, 2839, 1672, 1599, 1552, 1530, 1481, 1468, 1332, 621 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{11}H_{10}{}^{35}Cl_2N_2O$: 256.0224 $[M]^+$; found: 256.0215.



1h

1-(2,4-Dichlorophenyl)-1,2-dihydro-2-methyl-3-phenylpyrazol-5-one (1h):

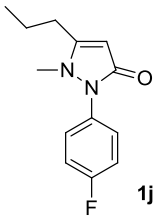
brown solid, mp: 119.6- 120.5°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.55 (s, 1H), 7.54-7.46 (m, 5H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 5.73 (s, 1H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 160.8, 135.7, 134.4, 131.5, 131.2, 130.7, 129.1 (2C), 130.6, 129.0, 128.4 (2C) , 128.1, 98.5, 37.6; IR (KBr): 3081, 2969, 1666, 1582, 1550, 1530, 1469, 1384, 841,735 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{16}H_{12}{}^{35}Cl_2N_2O$: 318.0321 $[M]^+$; found: 318.0316.



1i

2-(4-Fluorophenyl)-1,5-dimethyl-1*H*-pyrazol-3(2*H*)-one (1i) [1]:

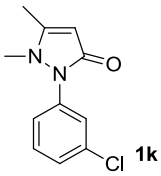
brown solid, mp: 94.3-95.1°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.27 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 5.29 (s, 1H), 3.08 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.2, 161.4 (d, *J* = 245.7 Hz, 1C), 156.1, 130.8 (d, *J* = 2.8 Hz, 1C), 126.8 (d, *J* = 8.4 Hz, 2C), 116.2 (d, *J* = 22.8 Hz, 2C), 97.7, 35.2, 13.1; IR (KBr): 3111, 3047, 2999, 1651, 1506, 1424, 1348, 836, 821, 770 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{11}H_{11}{}^{19}FN_2O$: 206.0864 $[M]^+$; found: 206.0854



1j

2-(4-Fluorophenyl)-1-methyl-5-propyl-1*H*-pyrazol-3(2*H*)-one (1j) :

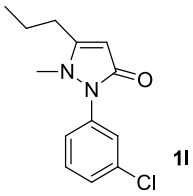
tan solid, mp: 95.8-96.7°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.30 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 5.37 (s, 1H), 3.02 (s, 3H), 2.46 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 161.13, 161.12 (d, *J* = 245.1 Hz, 1C), 131.2 (d, *J* = 2.8 Hz, 1C), 126.3 (d, *J* = 8.5 Hz, 2C), 116.1 (d, *J* = 22.7 Hz, 2C), 97.5, 35.5, 28.8, 20.8, 13.7; IR (KBr): 3050, 2962, 1661, 1602, 1505, 1422, 1333, 962, 836, 811, 780 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{13}H_{15}{}^{19}FN_2O$: 234.1157[M]$^+$; found: 234.1165.



1k

1-(3-Chlorophenyl)-1,2-dihydro-2,3-dimethylpyrazol-5-one (1k) [1]:

gray solid, mp:104.3-105.9°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 5.42 (s, 1H), 3.07 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 158.1, 136.6, 134.8, 130.1, 126.4, 123.6, 121.9, 99.2, 35.9, 13.1; IR (KBr): 3025, 2971, 1630, 1582, 1548, 1513, 1483, 1451, 1384, 769 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{11}H_{11}{}^{35}ClN_2O$: 222.0612 [M]$^+$; found: 222.0608.



1l

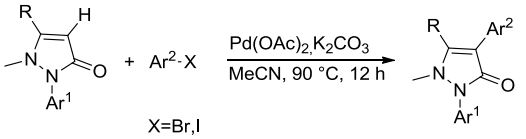
2-(3-Chlorophenyl)-1-methyl-5-propyl-1*H*-pyrazol-3(2*H*)-one (1l):

yellow solid, mp: 63.4-64.1°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.37 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 5.39 (s, 1H), 3.04 (s, 3H), 2.47 (t, *J* = 7.6 Hz, 2H), 1.76-1.65 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 162.5, 136.5, 134.7, 130.1, 126.4, 123.7, 121.9, 98.1, 36.0, 28.9, 20.8, 13.8; IR (KBr): 3072, 2987, 1655, 1573, 1531, 1465, 1432, 1314, 972, 894, 778 cm^{-1}; HR-MS (ESI): *m*/*z* calcd for $C_{13}H_{15}{}^{35}ClN_2O$: 250.0865 [M]$^+$; found: 250.0857.

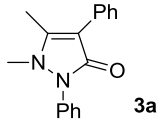
3. Experimental details and characterization data for products 3

A mixture of 5-pyrazolones **1** (0.3 mmol), aryl halids (0.6 mmol), $Pd(OAc)_2$ (0.03 mmol) and Ag_2CO_3 (0.6 mmol) in 2 mL MeCN was placed in a sealed tube. The tube was heated at 90 °C for 12 h using an oil bath. After the reaction was completed (as monitored by TLC), the mixture was cooled to room temperature, and then concentrated under reduced pressure to afford a crude product.

Purification by column chromatography on silica gel (EtOAc) to yield 4-aryl-5-pyrazolones **3**.



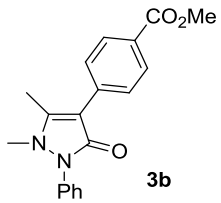
Spectral data of 3



3a

1,2-Dihydro-2,3-dimethyl-1,4-diphenylpyrazol-5-one (3a**):**

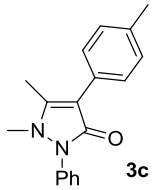
light yellow solid. mp:160.0-160.8 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 4.4 Hz, 4H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34-7.29 (m, 2H), 3.17 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 164.6, 152.2, 135.3, 131.3, 129.1(2C) , 128.9 (2C) , 128.3 (2C) , 126.8, 126.5, 124.1(2C), 111.2, 36.0, 12.1; IR (KBr): 3158, 3086, 3050, 1598, 1527, 1514, 1501, 1465, 1457, 1384, 1338, 1064, 994, 957, 855, 791, 757, 703, 685 cm^{-1}; HR-MS: m/z calcd for $C_{17}H_{16}N_2O$: 264.1284 $[M]^+$; found: 264.1276.



3b

Methyl 4-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)benzoate (3b) :

yellow solid. mp 148.2-149.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.52-7.45 (m, 4H), 7.34(t, *J* = 7.2 Hz, 1H), 3.94 (s, 3H),3.20 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 164.1, 152.2, 136.5, 135.0, 129.6 (2C), 129.2 (2C), 128.3 (2C), 127.9 , 126.9, 124.4 (2C), 109.54, 52.1, 35.8, 12.3; IR (KBr): 3064, 3028, 1716, 1651, 1608, 1588, 1453, 1376, 1344, 1056, 962, 890, 861, 760, 709, 699 cm^{-1}; HR-MS: m/z calcd for $C_{19}H_{18}N_2O_3$: 322.1324$[M]^+$; found: 322.1319.

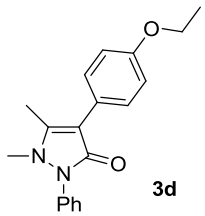


3c

1,5-Dimethyl-2-phenyl-4-(*p*-tolyl)-1*H*-pyrazol-3(2*H*)-one (**3c**):

white solid. mp 148.9-149.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.48 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.15 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 164.7, 152.2 , 136.4, 135.5, 129.1 (2C), 129.0 (2C), 128.8 (2C), 128.3, 126.3, 123.9 (2C), 111.4, 36.2, 21.3, 12.2. IR (KBr): 3100, 3056, 1650, 1590, 1510, 1494, 1456, 1372,

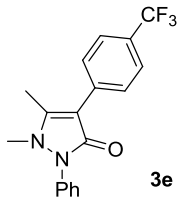
1345, 1056, 912, 889, 827, 782, 695 cm^{-1} ; HR-MS: m/z calcd for $C_{18}H_{18}N_2O$: 278.1422 $[M]^+$; found: 278.1428.



3d

4-(4-Ethoxyphenyl)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (**3d**):

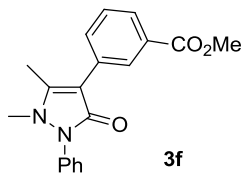
light yellow solid. mp: 158.2-158.9 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.48 (m, 6H), 7.32-7.29 (m, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 4.07 (q, *J* = 6.8 Hz, 2H), 3.14 (s, 3H), 2.38. (s, 3H), 1.4(t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 157.8, 152.0, 135.5, 130.5 (2C) 129.1 (2C), 126.3, 123.8 (2C), 123.4, 114.5 (2C), 111.3, 63.4, 36.2, 14.9, 12.2; IR (KBr): 3132, 3066, 1651, 1613, 1558, 1533, 1491, 1435, 1389, 1344, 971, 936, 850, 782, 713 cm^{-1}; HR-MS: m/z calcd for $C_{19}H_{20}N_2O_2$: 308.1532 $[M]^+$; found: 308.1527



3e

1,5-Dimethyl-2-phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-pyrazol-3(2*H*)-one (**3e**):

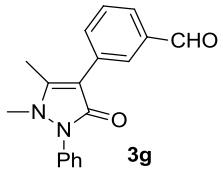
white solid. mp: 162.7-163.2 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.66 (m, 4H), 7.52-7.45 (m, 4H), 7.34 (t, *J* = 6.8 Hz, 1H), 3.21 (s, 3H), 2.43 (s, 3H); ^{13}C NMR(100 MHz,$CDCl_3$): δ = 164.1, 152.1, 135.2, 134.9, 129.2 (2C), 128.8 (2C), 128.4 (q, *J* = 64.1 Hz, 1C), 126.9 (2C), 125.2 (q, *J* = 5.7 Hz , 2C), 124.4, 124.3(q, *J* =270.1 Hz, 1C), 109.3, 36.7, 12.2; IR (KBr): 3071, 3024, 1646, 1616, 1591, 1496, 1458, 1404, 1376, 1324, 914, 855, 805, 751, 698 cm^{-1}; HR-MS: m/z calcd for $C_{18}H_{15}F_3N_2O$: 332.1145 $[M]^+$; found: 332.1138.



3f

Methyl 3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)benzoate (**3f**):

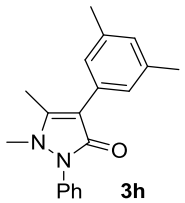
yellow solid. mp: 149.5-150.4 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.52-7.47 (m , 5H), 7.34-7.29 (m, 1H), 3.93 (s, 3H), 3.19(s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 164.4, 152.4, 135.2, 133.4, 131.8, 130.2, 129.7, 129.2 (2C), 128.5, 127.8, 126.6, 124.2 (2C), 110.0, 52.1, 35.9, 12.2; IR (KBr): 3060, 3027, 2945, 1723, 1649, 1581, 1488, 1414, 1325, 1306, 964, 879, 763, 694 cm^{-1}; HR-MS: m/z calcd for $C_{19}H_{18}F_3N_2O_3$: 322.1319 $[M]^+$; found: 322.1322.



3g

3-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)benzaldehyde (3g):

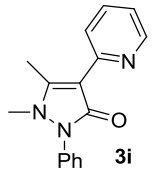
yellow soild, mp: 179.1-180.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 8.09 (s, 1H), 7.91(d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.59(t, *J* = 8.0 Hz, 1H), 7.53-7.46 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 1H), 3.22 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 164.3, 152.2, 136.5, 134.9, 134.7, 132.6, 130.3, 129.2 (2C), 129.1, 127.5, 126.9, 124.3 (2C), 103.3, 35.8, 12.2; IR (KBr): 3088, 3013, 1787, 1764, 1692, 1658, 1649, 1582, 1565, 1529, 1432, 945, 887, 763, 683 cm^{-1}; HR-MS: m/z calcd for $C_{18}H_{16}N_2O_2$: 292.1216 $[M]^+$; found: 292.1221



3h

4-(3,5-Dimethylphenyl)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (3h):

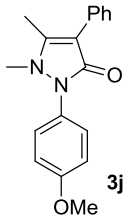
yellow solid. mp: 207.0-207.8^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.48 (m, 4H), 7.32-7.29 (m, 1H), 7.18 (s, 2H), 6.96 (s, 1H), 3.14 (s, 3H), 2.38 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 152.5, 137.7 (2C), 135.5, 131.0, 129.0 (2C), 128.5, 126.7 (2C), 126.3, 123.8 (2C), 111.5, 36.2, 21.4 (2C), 12.2; IR (KBr): 3084, 3053, 3013, 1655, 1620, 1592, 1468, 1455, 1373, 1323, 880, 855, 758, 700 cm^{-1}; HR-MS: m/z calcd for $C_{19}H_{20}N_2O$: 292.1566 $[M]^+$; found: 292.1558



3i

1,5-Dimethyl-2-phenyl-4-(pyridin-2-yl)-1*H*-pyrazol-3(2*H*)-one (**3i**):

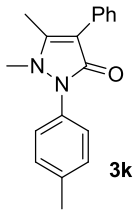
yellow solid. mp: 101.0-101.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 4.4 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.72-7.69 (m, 1H), 7.53-7.43 (m, 4H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.13-7.10(m, 1H) 3.25(s, 3H), 2.78(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 154.5, 152.4, 148.5, 136.2, 135.0, 129.2 (2C), 127.1, 124.9 (2C), 122.5, 120.7, 107.5, 35.1, 12.8; IR (KBr): 3150, 3027, 1754, 1737, 1581, 1529, 1493, 1468, 1366, 1330, 879, 752, 712 cm^{-1} ; HR-MS: m/z calcd for $C_{16}H_{15}N_3O$: 265.1219 $[M]^+$; found: 265.1216



3j

2-(4-Methoxyphenyl)-1,5-dimethyl-4-phenyl-1*H*-pyrazol-3(2*H*)-one (**3j**):

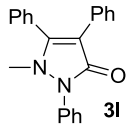
tan solid. mp: 134.4-135.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.2 Hz, 2H), 7.42-7.37 (m, 4H), 7.31 (s, 1H), 7.03-7.02 (m, 2H), 3.86 (s , 3H), 3.18 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 158.5, 150.9, 131.5, 128.8 (2C), 128.3 (2C), 128.1, 126.6, 126.5 (2C), 114.5 (2C), 110.6, 55.6, 35.5, 12.1; IR (KBr): 3060, 3035, 1660, 1622, 1592, 1510, 1454, 1335, 836, 807, 704, 670cm^{-1} ; HR-MS: m/z calcd for $C_{18}H_{18}N_2O_2$: 294.1365 $[M]^+$; found: 294.1372



3k

1,5-Dimethyl-4-phenyl-2-(*p*-tolyl)-1*H*-pyrazol-3(2*H*)-one (**3k**):

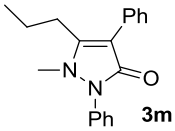
yellow solid. mp: 157.3-158.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30-7.28 (m, 3H), 3.15 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 151.6, 136.5, 132.7, 131.4, 129.7 (2C), 128.9 (2C), 128.3 (2C), 126.6, 124.3 (2C), 110.9, 35.8, 21.1, 12.1; IR (KBr): 3078, 3048, 1654, 1609, 1511, 1487, 1418, 1303, 935, 881, 803, 778, 741, 669 cm^{-1} ; HR-MS: m/z calcd for $C_{18}H_{18}N_2O$: 278.1432 $[M]^+$; found: 278.1439.



3l

1-Methyl-2,4,5-triphenyl-1*H*-pyrazol-3(2*H*)-one (**3l**) :

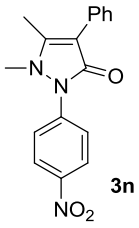
yellow solid. mp: 108.8-109.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.2 Hz, 2H) ,7.50 (t, *J* = 8.0 Hz, 3H) ,7.48-7.44 (m, 6H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2, 155.9, 135.4, 130.6, 130.2, 129.6 (2C), 129.5, 129.2(2C), 129.1 (2C), 128.9 (2C), 128.1 (2C), 126.7, 126.4, 123.6 (2C), 112.2, 38.7; IR (KBr): 3056, 2924, 1667, 1592, 1494, 1447, 1393, 1342, 911, 879, 803, 755, 695 cm^{-1} ; HR-MS: m/z calcd for $C_{22}H_{18}N_2O$: 326.1425 $[M]^+$; found: 326.1418.



3m

1-Methyl-2,4-diphenyl-5-propyl-1*H*-pyrazol-3(2*H*)-one (3m):

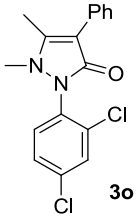
yellow solid. mp: 116.5-117.2 °C . ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 4.4 Hz, 4H), 7.42(t, *J* = 7.6 Hz, 2H), 7.32-7.29(m, 2H), 3.15 (s, 3H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.77(q, *J* = 7.6 Hz, 2H), 1.07(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 156.6, 135.4, 131.3, 129.1 (2C), 129.0 (2C), 128.4 (2C), 126.8, 126.4, 123.9 (2C), 111.6, 36.3, 27.4, 22.4, 14.0; IR (KBr): 3076, 3012, 1637, 1615, 1572, 1478, 1384, 1011, 972, 879, 724, 687 cm^{-1} ; HR-MS: m/z calcd for $C_{19}H_{20}N_2O$: 292.1627 $[M]^+$; found: 292.1622.



3n

1,5-Dimethyl-2-(4-nitrophenyl)-4-phenyl-1*H*-pyrazol-3(2*H*)-one (3n) :

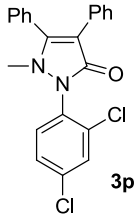
yellow solid. mp: 165.5-166.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 9.2 Hz, 2H), 7.72 (d, *J* = 9.2, 2H), 7.53-7.51 (m, 2H), 7.45 (t, *J* = 7.6, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 3.19 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 155.8, 144.7, 144.1, 130.2, 128.9 (2C), 128.5 (2C), 127.4, 124.8 (2C), 122.1 (2C), 122.7, 37.3, 12.4; IR (KBr): 3111, 3077, 1661, 1639, 1616, 1588, 1514, 1491, 1412, 1339, 1054, 859, 748, 706 cm^{-1}; HR-MS: m/z calcd for $C_{17}H_{15}N_3O_3$: 309.1089 $[M]^+$; found: 309.1096.



3o

2-(2,4-Dichlorophenyl)-1,5-dimethyl-4-phenyl-1*H*-pyrazol-3(2*H*)-one (3o):

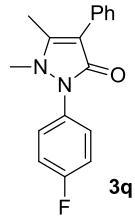
yellow solid.mp: 179.8-180.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.57(m, 3H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32-7.25 (m, 1H), 3.12 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 151.2, 135.6, 134.8, 131.9, 131.3, 131.2, 130.7, 128.8 (2C), 128.4 (2C), 128.1, 126.7, 109.6, 34.8, 12.1; IR (KBr): 3083, 3027, 1661, 1607, 1579, 1474, 1415, 1388, 1307, 837, 821, 759, 702, 667 cm^{-1}; HR-MS: m/z calcd for $C_{17}H_{14}{}^{35}Cl_2N_2O$: 332.0489 $[M]^+$; found: 332.0478.



3p

2-(2,4-Dichlorophenyl)-1-methyl-4,5-diphenyl-1*H*-pyrazol-3(2*H*)-one (3p):

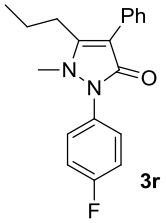
yellow solid. mp: 149.8-150.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 2.1 Hz, 1H), 7.53 -7.39 (m, 9H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 155.3, 135.6, 134.4, 131.8, 131.0, 130.8, 130.5, 130.3, 129.6 (2C), 129.3 , 129.2 (2C), 128.8 (2C), 128.1 (3C), 126.6, 110.6, 37.2; IR (KBr): 3062, 3031, 1667, 1639, 1581, 1480, 1441, 1415, 1396, 1315, 1022, 924, 880, 825, 783, 716 cm^{-1};HR-MS: m/z calcd for $C_{22}H_{16}{}^{35}Cl_2N_2O$: 394.0638 $[M]^+$; found: 394.0631.



3q

2-(4-Fluorophenyl)-1,5-dimethyl-4-phenyl-1*H*-pyrazol-3(2*H*)-one (3q):

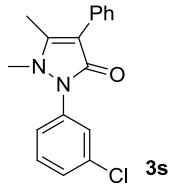
yellow solid. mp: 149.3-150.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* =7.3 Hz, 2H), 7.44 (m, 4H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 8.6 Hz, 2H), 3.15 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 161.1(d, *J* = 246.4 Hz, 1C), 152.5, 131.4, 131.1, 128.9 (2C), 128.4 (2C), 126.8, 125.9 (d, *J* = 8.5 Hz, 2C), 116.1 (d, *J* = 22.7 Hz, 2C), 111.3, 36.0, 12.2; IR (KBr): 3065, 3021, 1654, 1603, 1503, 1438, 1340, 1307, 1011, 881, 786, 763, 702 cm^{-1}; HR-MS: m/z calcd for $C_{17}H_{15}{}^{19}F_2N_2O$: 282.1174 $[M]^+$; found: 282.1171.



3r

2-(4-Fluorophenyl)-1-methyl-4-phenyl-5-propyl-1*H*-pyrazol-3(2*H*)-one (3r):

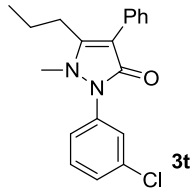
yellow solid. mp: 106.2-107.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.4 Hz, 2H), 7.48-7.39 (m, 4H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 8.6 Hz, 2H), 3.13 (s, 3H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.76 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.0, 161.0 (d, *J* = 246.3 Hz, 1C), 156.8, 131.5, 131.2, 129.0 (2C), 128.4 (2C), 126.9, 125.8 (d, *J* = 8.4 Hz, 2C), 116.0 (d, *J* = 22.8 Hz, 2C), 111.6, 36.2, 27.4, 22.4, 14.03; IR (KBr): 3051, 3014, 1649, 1603, 1582, 1457, 1414, 1322, 1017, 913, 837, 826, 743, 702 cm^{-1}; HR-MS: m/z calcd for $C_{19}H_{19}{}^{19}FN_2O$: 310.1472 $[M]^+$; found: 310.1481.



3s

2-(3-Chlorophenyl)-1,5-dimethyl-4-phenyl-1*H*-pyrazol-3(2*H*)-one (3s):

yellow solid. mp：203.6-204.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.4 Hz, 2H), 7.51 (s, 1H), 7.45-7.41(m, 4H), 7.33-7.26 (m, 2H), 3.19 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 153.7, 136.7, 134.8, 130.9, 130.1, 128.9 (2C), 128.4 (2C), 127.0, 126.3, 123.4, 121.6, 111.7, 36.5, 12.2; IR (KBr): 3071, 3028, 1764, 1662, 1629, 1586, 1549, 1462, 1310, 1022, 981, 917, 861, 786, 702 cm^{-1}; HR-MS: m/z calcd for $C_{17}H_{15}{}^{35}ClN_2O$: 298.0865 $[M]^+$; found: 298.0874.



3t

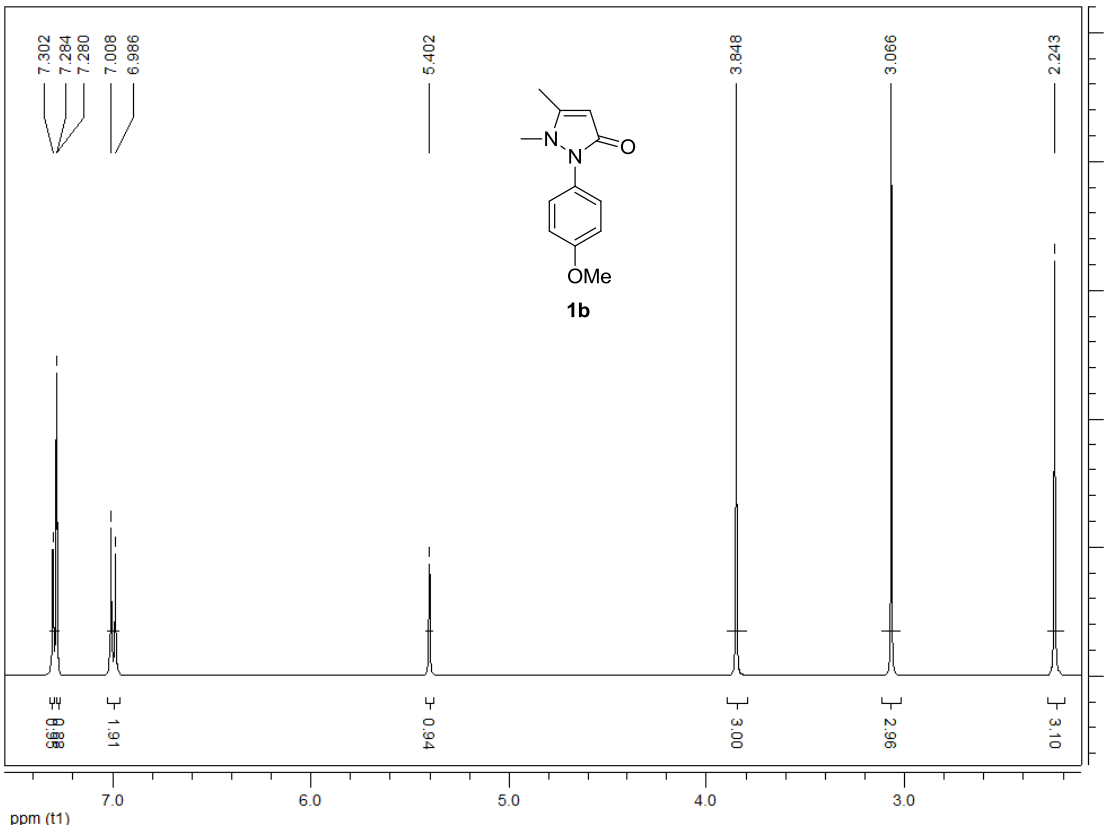
2-(3-chlorophenyl)-1-methyl-4-phenyl-5-propyl-1*H*-pyrazol-3(2*H*)-one (3t):

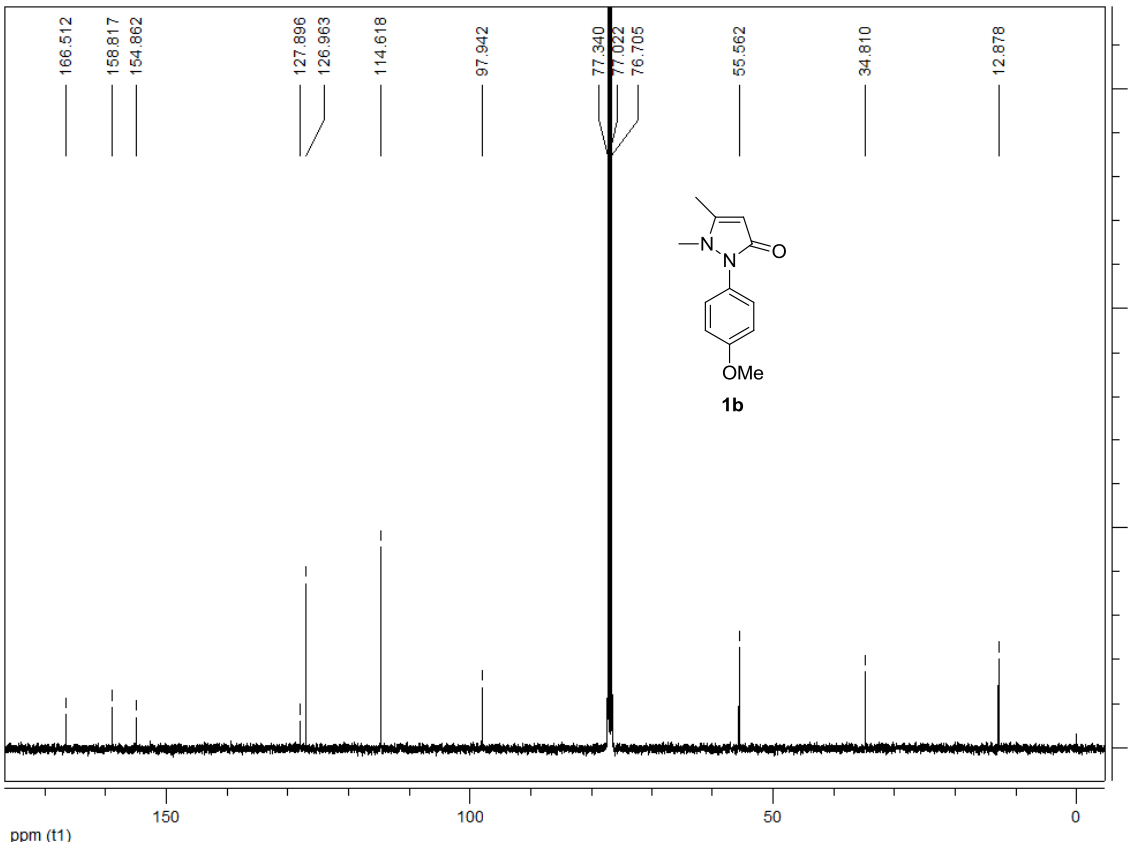
yellow solid. mp:115.5-116.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.49 (m, 3H), 7.44-7.41 (m, 4H), 7.32 (t, J = 7.3 Hz, 1H), 7.29-7.25 (m, 1H), 3.14 (s, 3H), 2.73-2.68 (t, *J* = 7.8 Hz, 2H), 1.80-1.74 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 157.9, 136.7, 134.7, 130.9, 130.1, 129.0 (2C), 128.4 (2C), 127.0, 126.2, 123.3, 121.6, 112.1, 36.7, 27.4, 22.4, 14.1. IR (KBr): 3129, 3080, 1657, 1612, 1590, 1481, 1429, 1399, 1342, 1018, 998, 860, 829, 774, 725, 697 cm^{-1}; HR-MS: m/z calcd for $C_{19}H_{19}{}^{35}ClN_2O$: 326.1174 $[M]^+$; found: 326.1182.

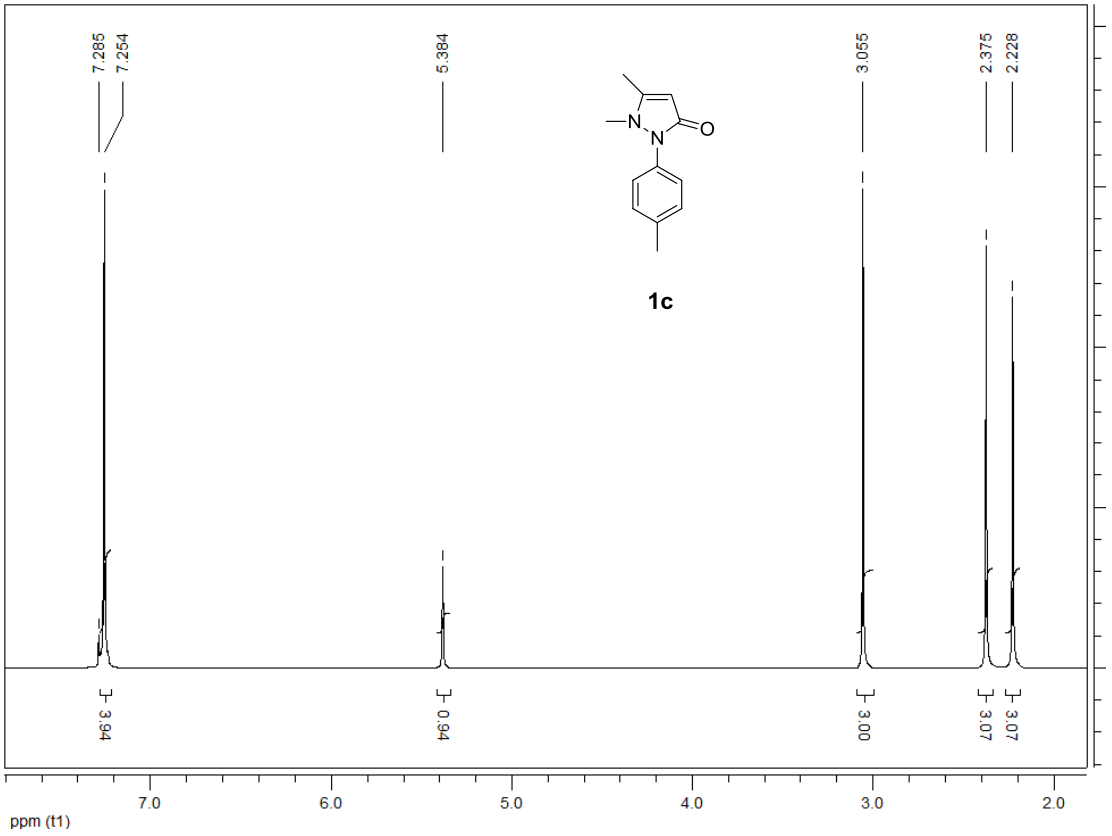
References

1. Balestra, M.; Bunting, H.; Chen, D.; Egle, I.; Forst, J.; Frey, J.; Isaac, M.; Ma, F.; Nugiel, D.; Slassi, A.; Steelman, G.; Sun, G.; Sundar, B.; Ukkiramapandian, R.; Urbanek, R.; Walsh, S. Pyrazolone Compounds as Metabotropic Glutamate Receptor Agonists for the Treatment of Neurological and Psychiatric Disorders. WO Patent 2006071730A1, July 6, 2006.
2. Ailawadi, S.; Jyoti, Yadav, M.; Pathak, D. *Der Pharma Chemica* **2011,** *3,* 215–222.

NMR spectra data for all compounds



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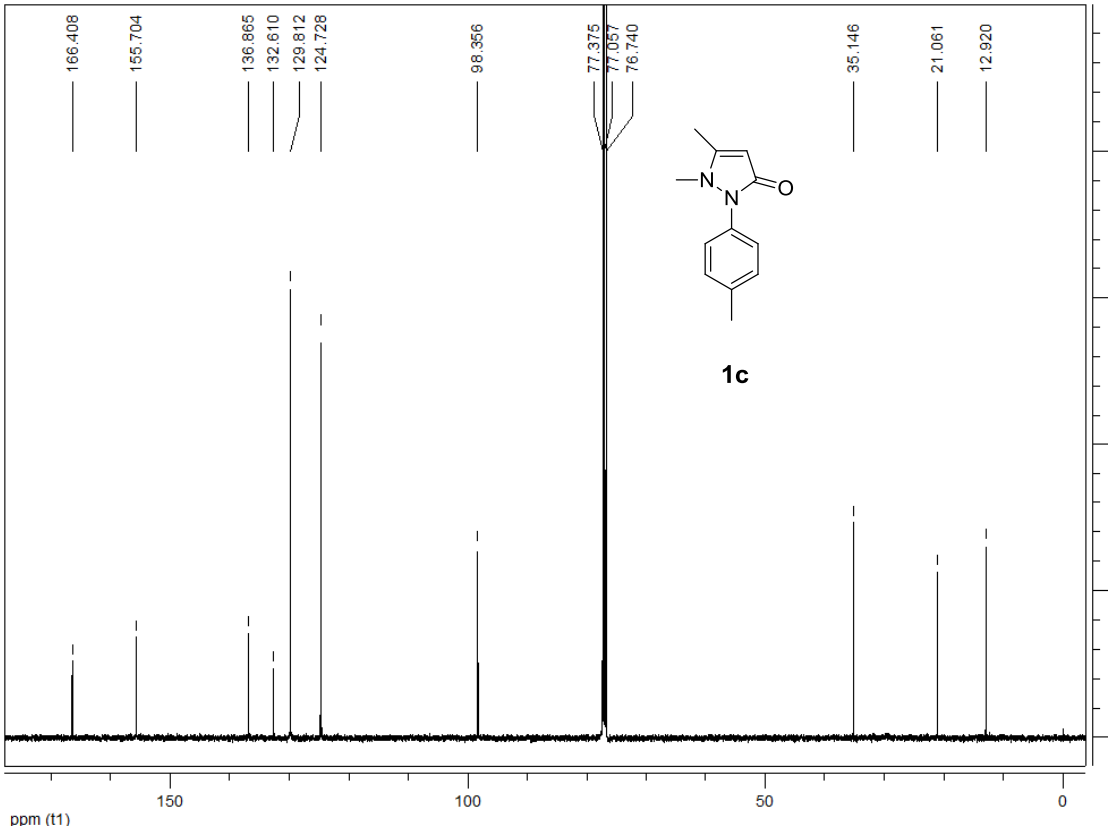
5.384
3.055
2.375
2.228
3.94
0.94
3.00
3.07
3.07
1c
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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155.704
136.865
132.610
129.812
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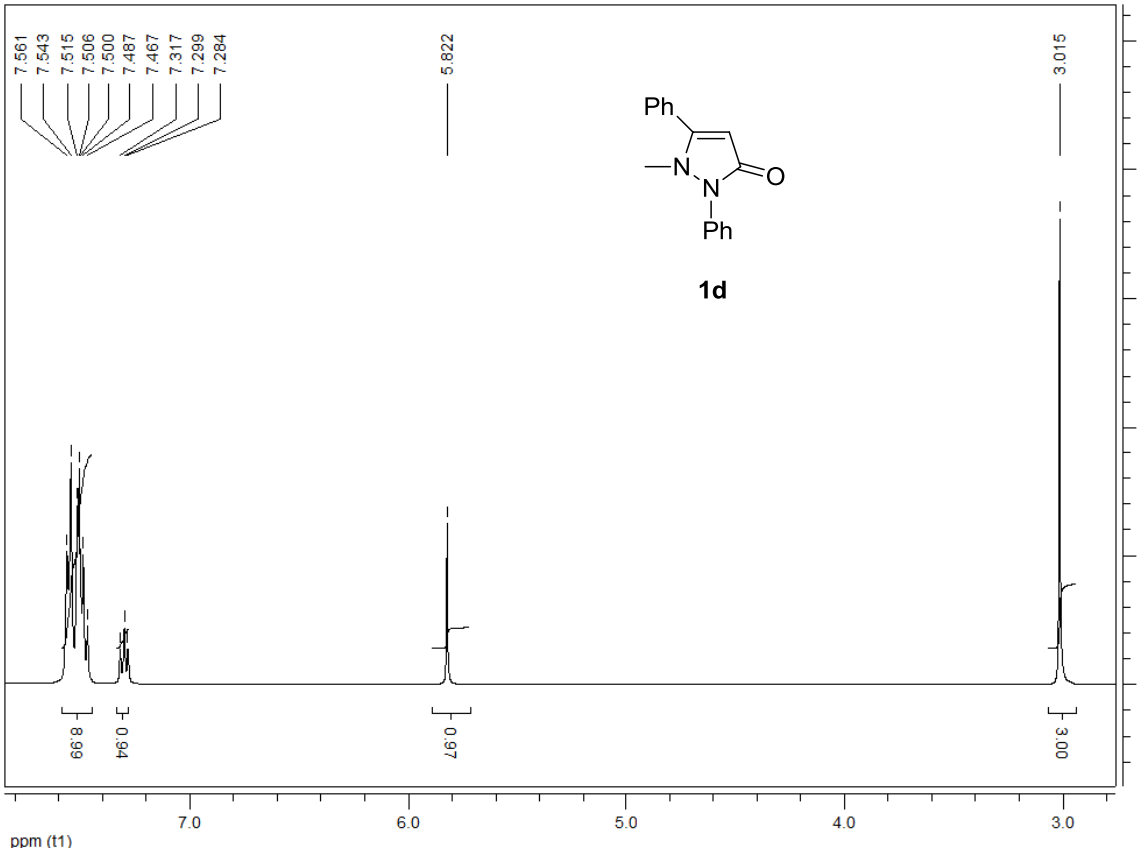
77.057
76.740
35.146
21.061
12.920
1c
150
100
50
0
ppm (t1)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7.543
7.515
7.506
7.500
7.487
7.467
7.317
7.299
7.284
5.822
3.015
Ph
N
N
O
Ph
1d
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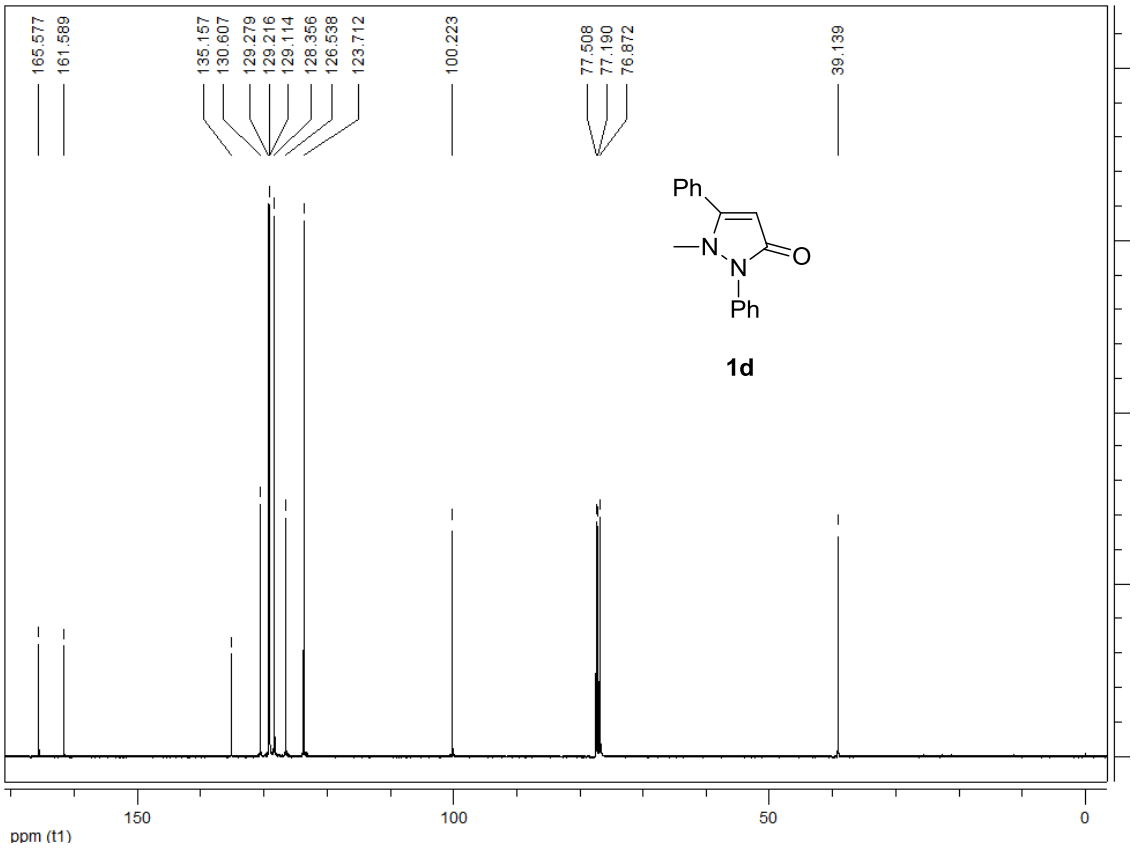
0.94
0.97
3.00
7.0
6.0
5.0
4.0
3.0
ppm (t1)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161.589
135.157
130.607
129.279
129.216
129.114
128.356
126.538
123.712
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77.190
76.872
39.139
Ph
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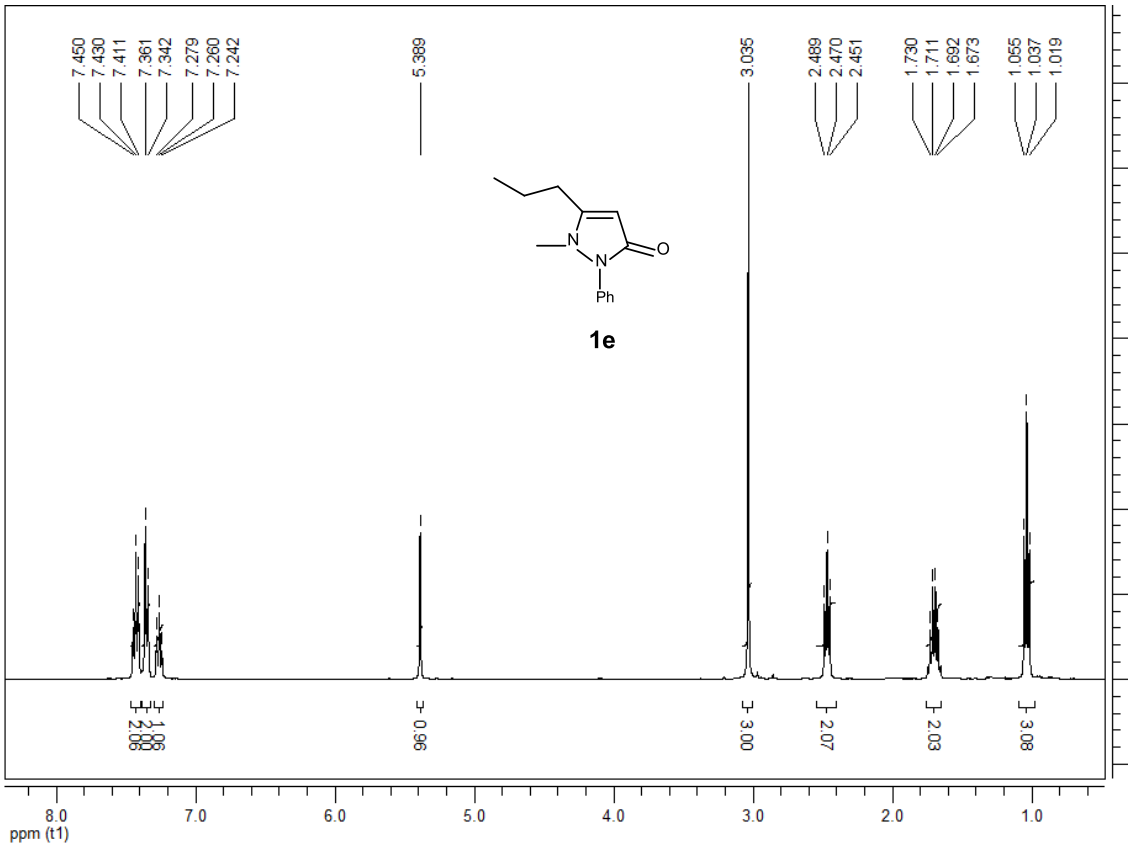
N
O
Ph
1d
150
100
50
0
ppm (t1)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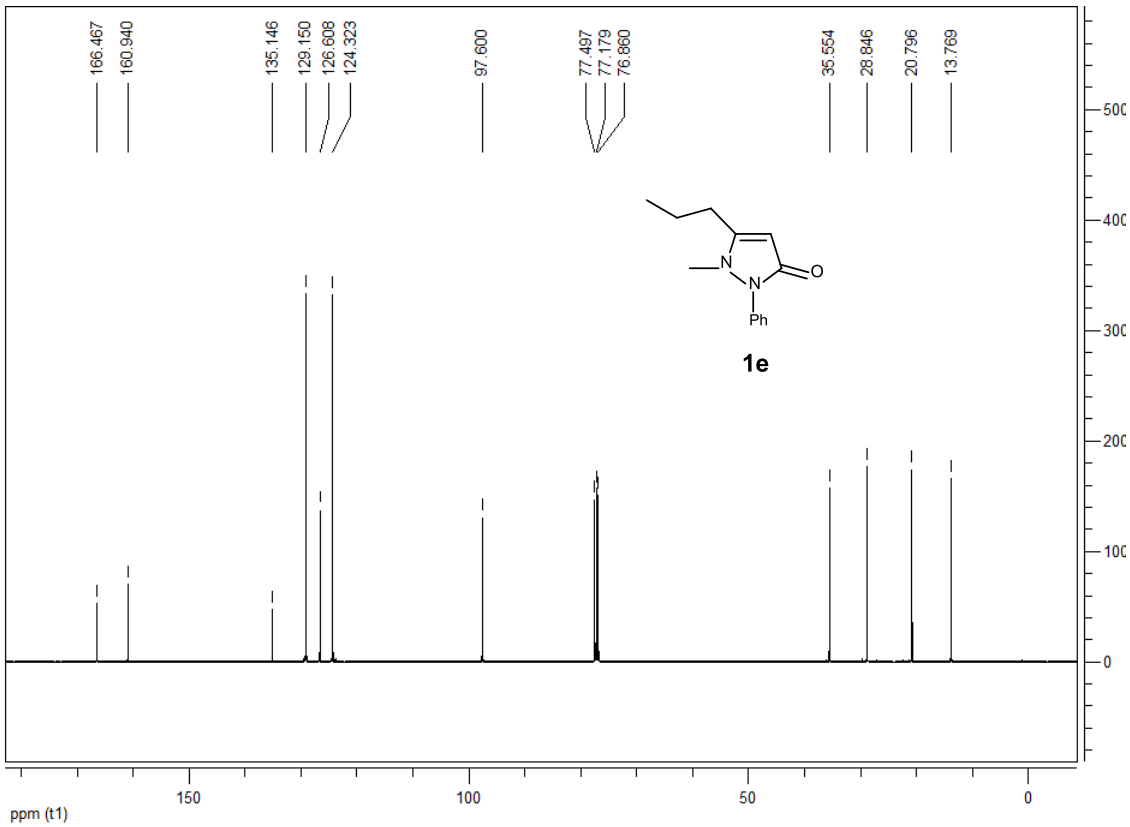
7.430
7.411
7.361
7.342
7.279
7.260
7.242
5.389
3.035
2.489
2.470
2.451
1.730
1.711
1.692
1.673
1.055
1.037
1.019
1e
2.08
3.13
2.00
0.96
3.00
2.07
2.03
3.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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135.146
129.150
126.608
124.323
97.600
77.497
77.179
76.860
35.554
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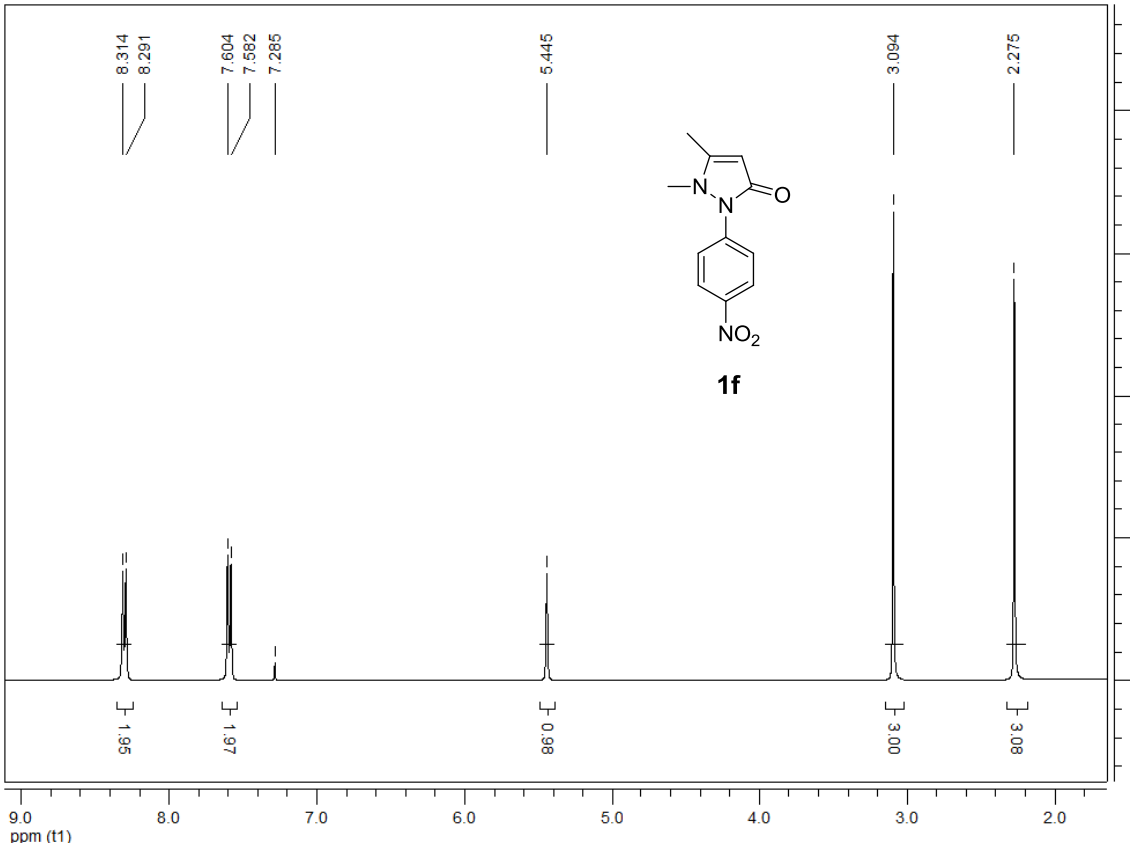
20.796
13.769
1e
500
400
300
200
100
0
150
100
50
0
ppm (t1)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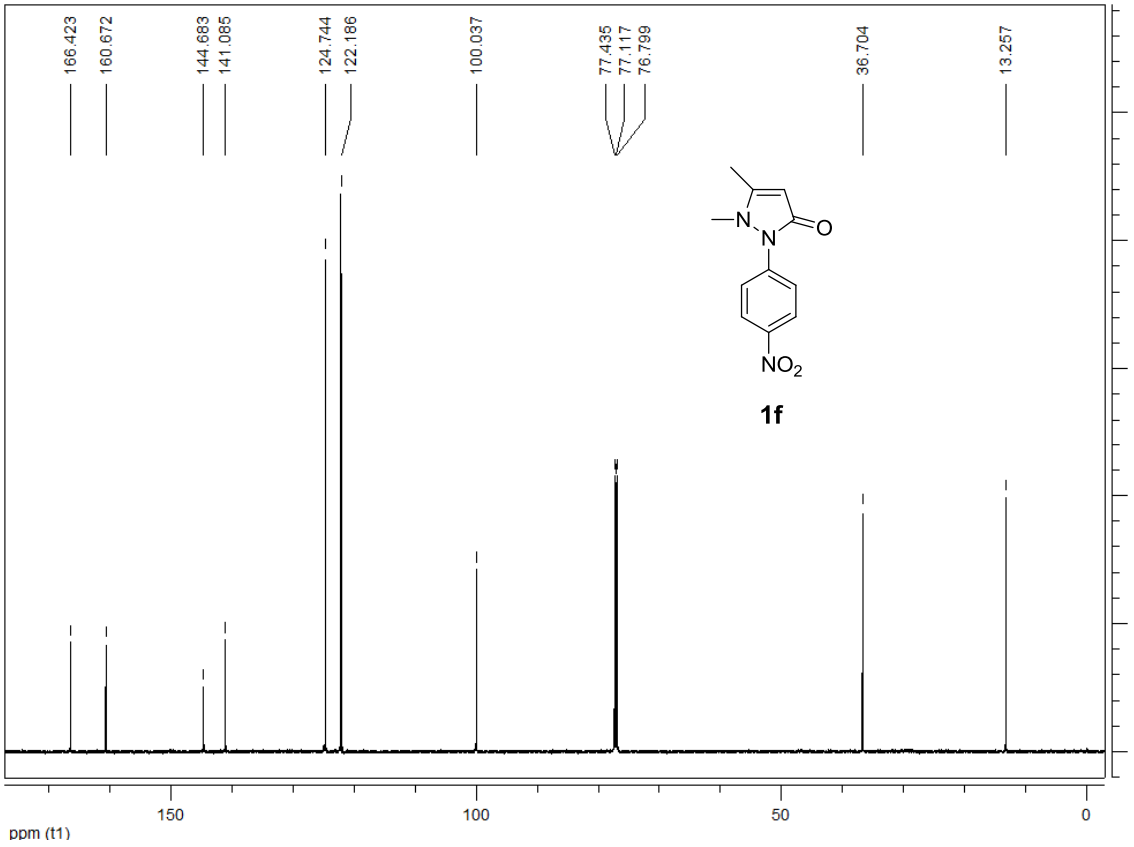
8.291
7.604
7.582
7.285
5.445
3.094
2.275
1.95
1.97
0.98
3.00
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
O
N
N
NO2
1f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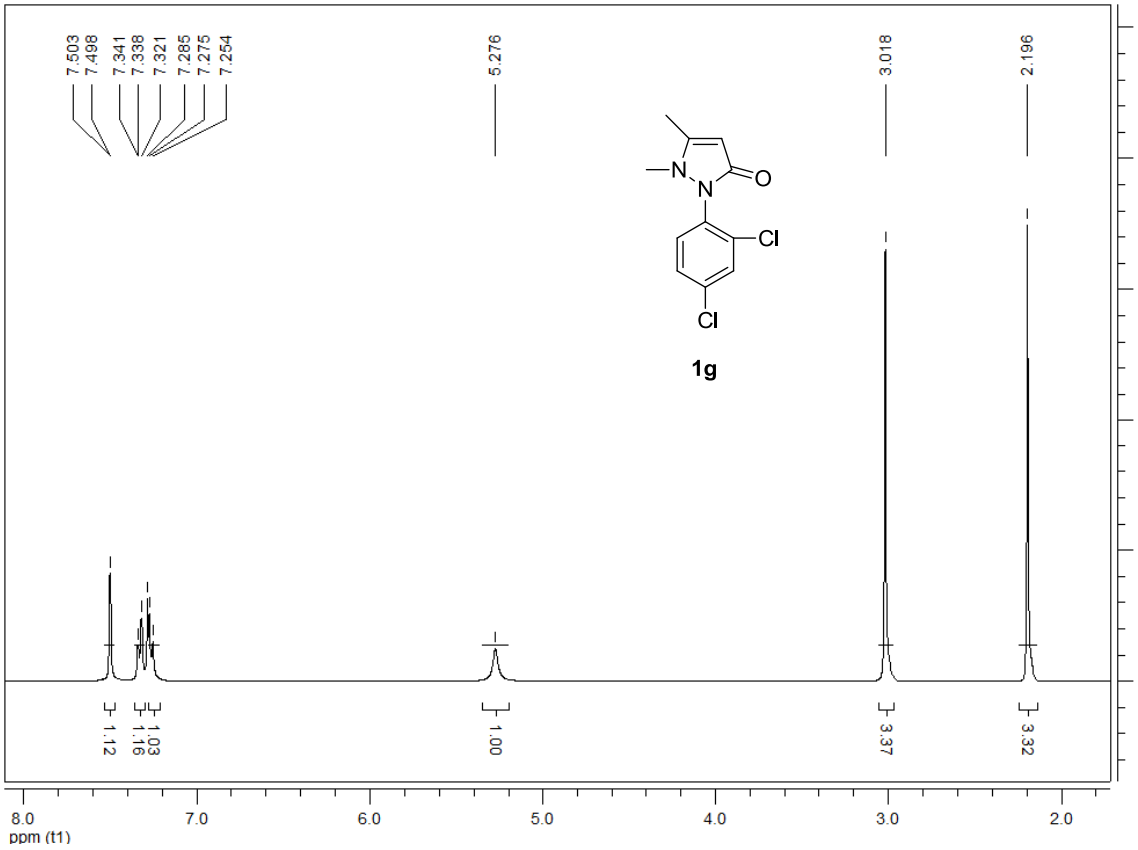
144.683
141.085
124.744
122.186
100.037
77.435
77.117
76.799
36.704
13.257
150
100
50
0
ppm (t1)
O
N
N
NO2
1f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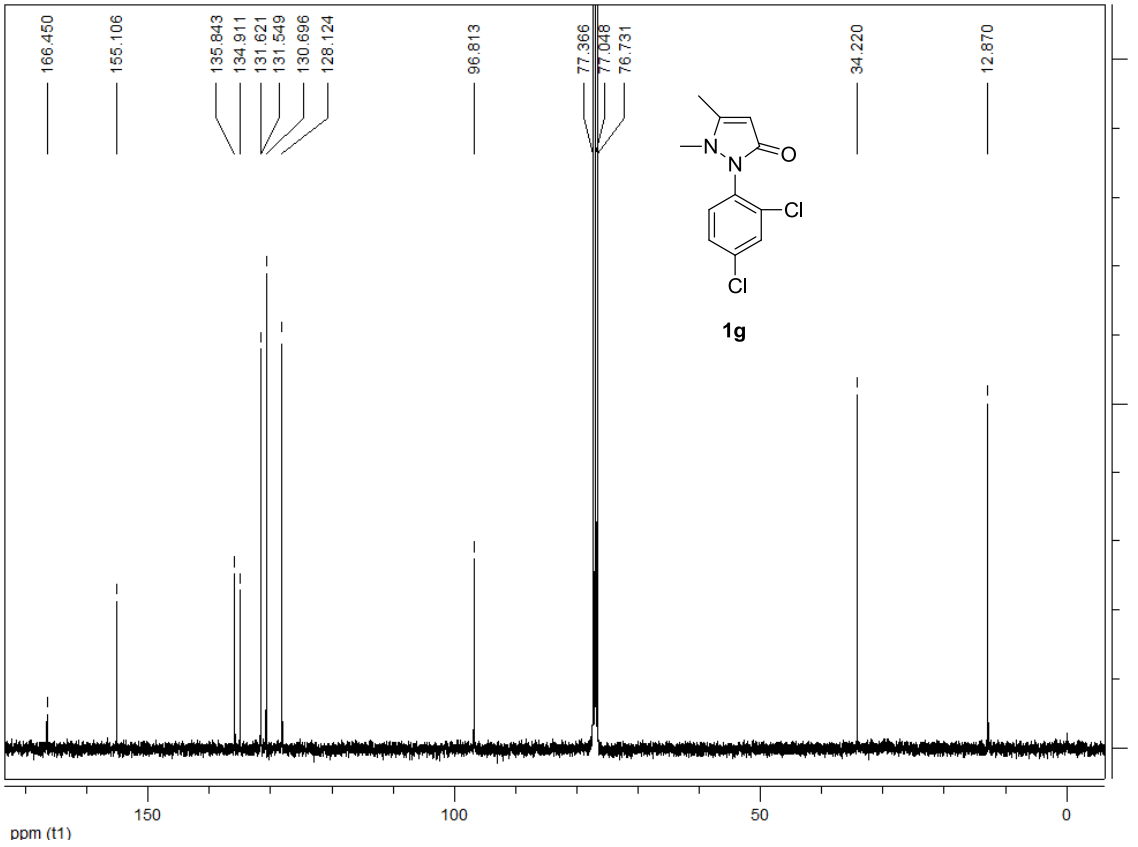
7.498
7.341
7.338
7.321
7.285
7.275
7.254
5.276
3.018
2.196
1g
1.12
1.16
1.03
1.00
3.37
3.32
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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155.106
135.843
134.911
131.621
131.549
130.696
128.124
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77.366
77.048
76.731
34.220
12.870
1g
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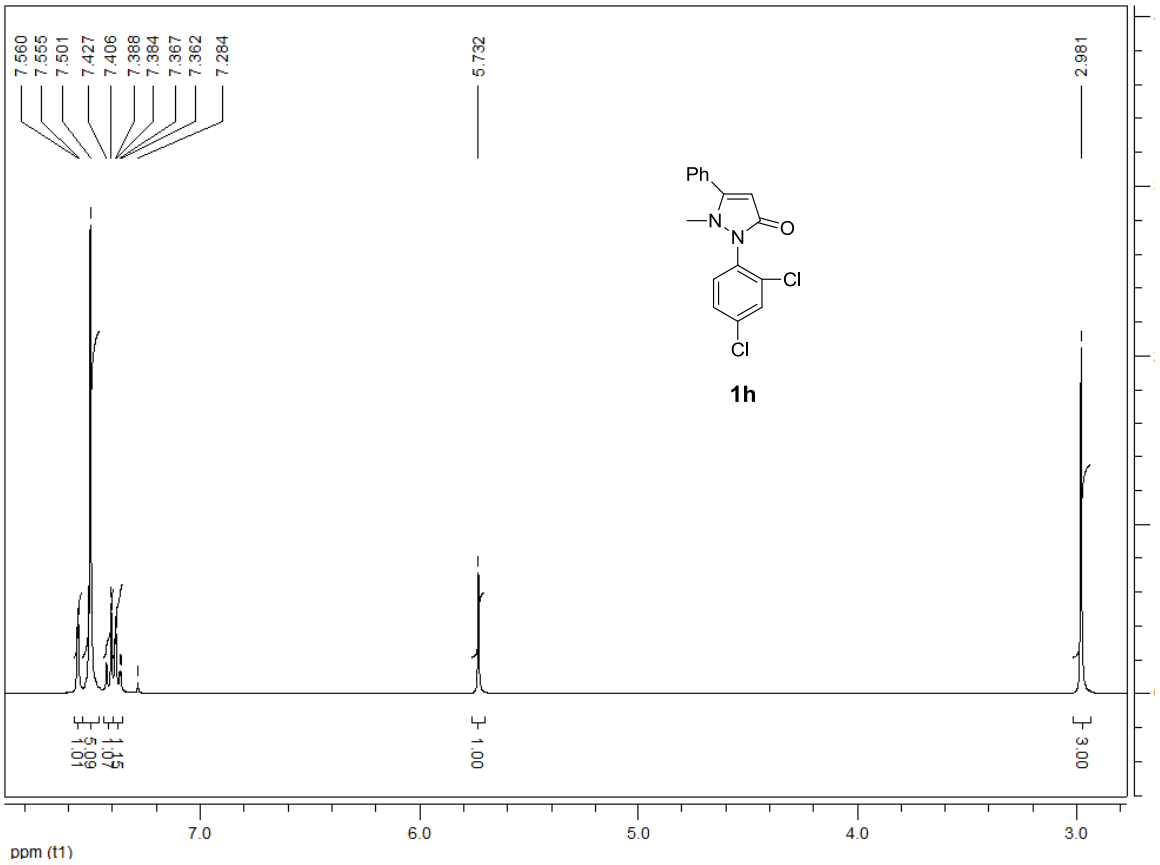
50
0
ppm (t1)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7.555
7.501
7.427
7.406
7.388
7.384
7.367
7.362
7.284
5.732
2.981
1.01
1.59
1.37
1.15
1.00
3.00
Ph
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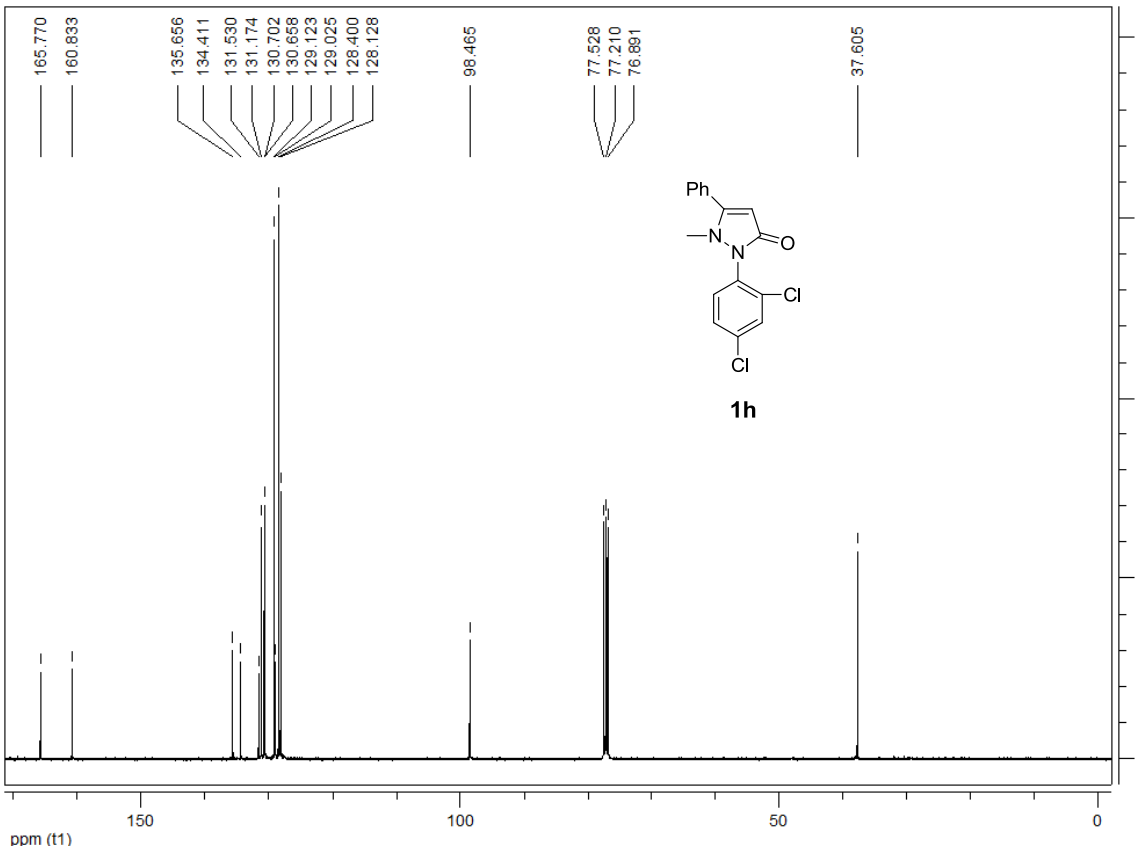
N
O
Cl
Cl
1h
7.0
6.0
5.0
4.0
3.0
ppm (t1)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135.656
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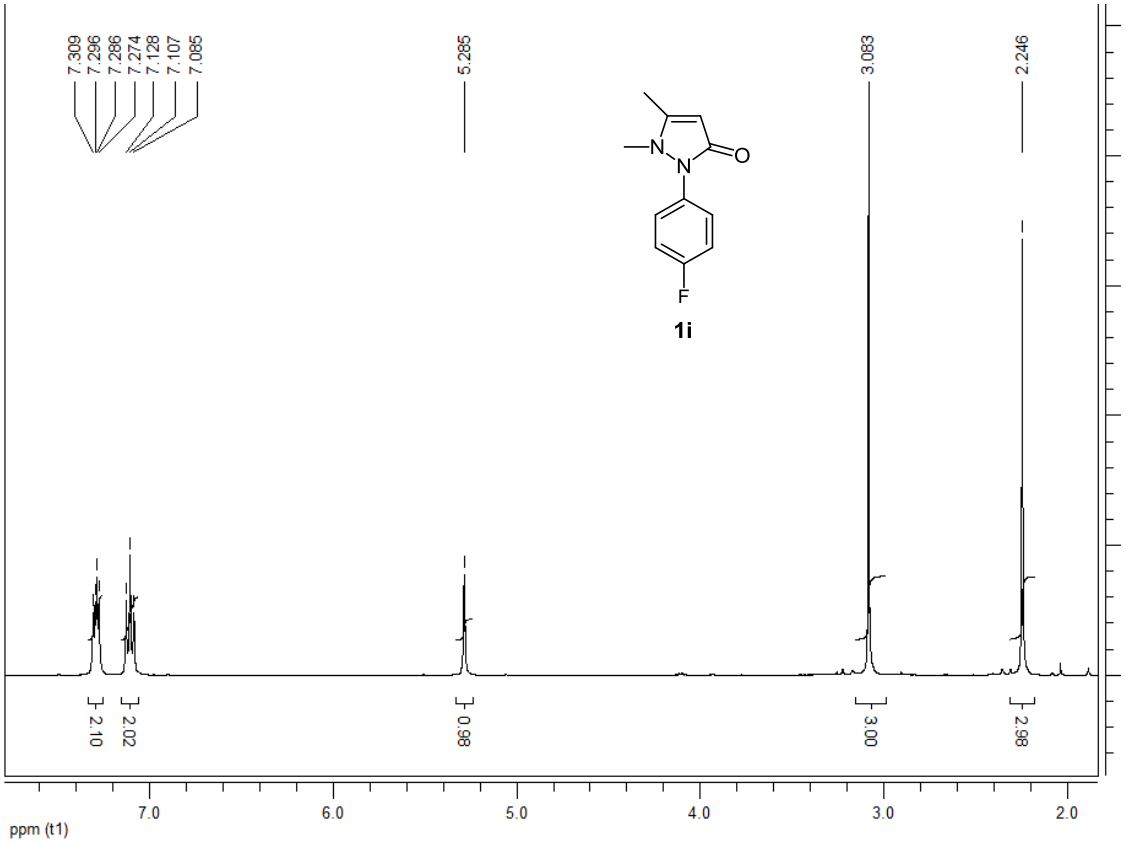
131.530
131.174
130.702
130.658
129.123
129.025
128.400
128.128
98.465
77.528
77.210
76.891
37.605
Ph
N
N
O
Cl
Cl
1h
150
100
50
0
ppm (t1)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7.296
7.286
7.274
7.128
7.107
7.085
5.285
3.083
2.246
2.10
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2.98
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6.0
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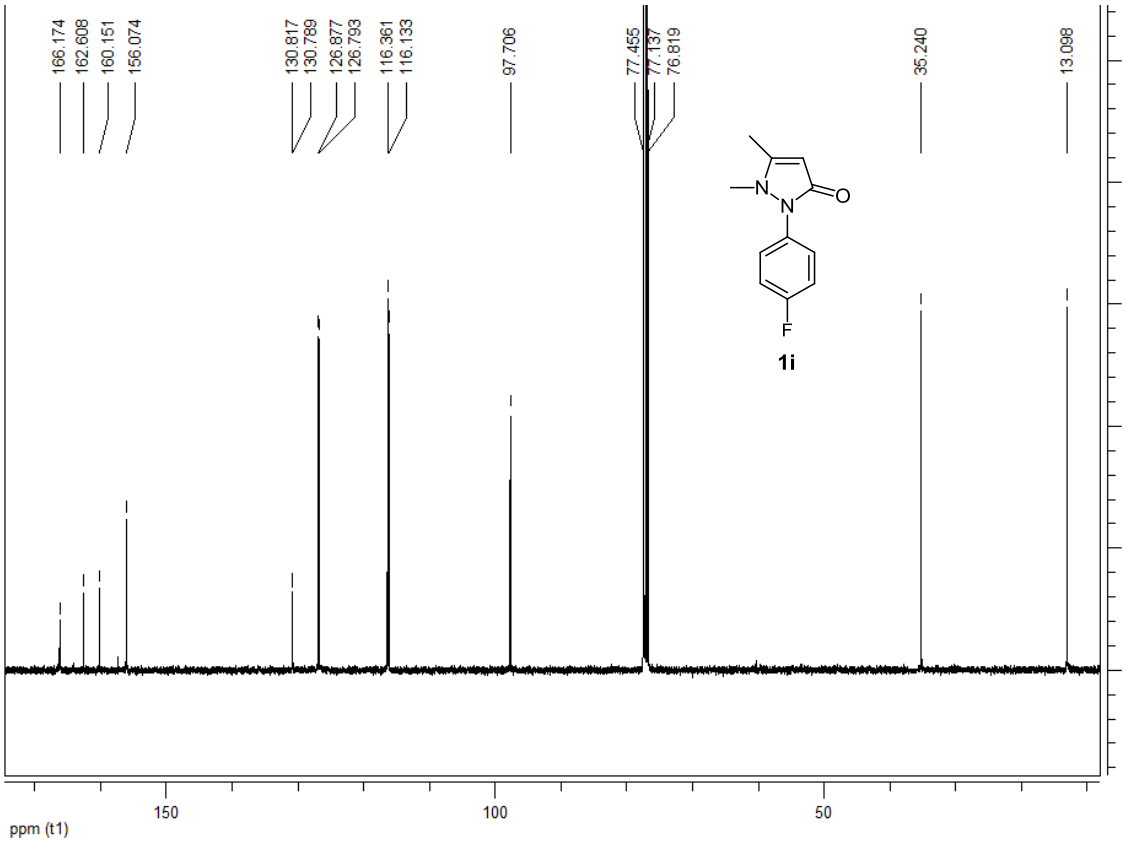
4.0
3.0
2.0
ppm (t1)
1i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160.151
156.074
130.817
130.789
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126.793
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116.133
97.706
77.455
77.137
76.819
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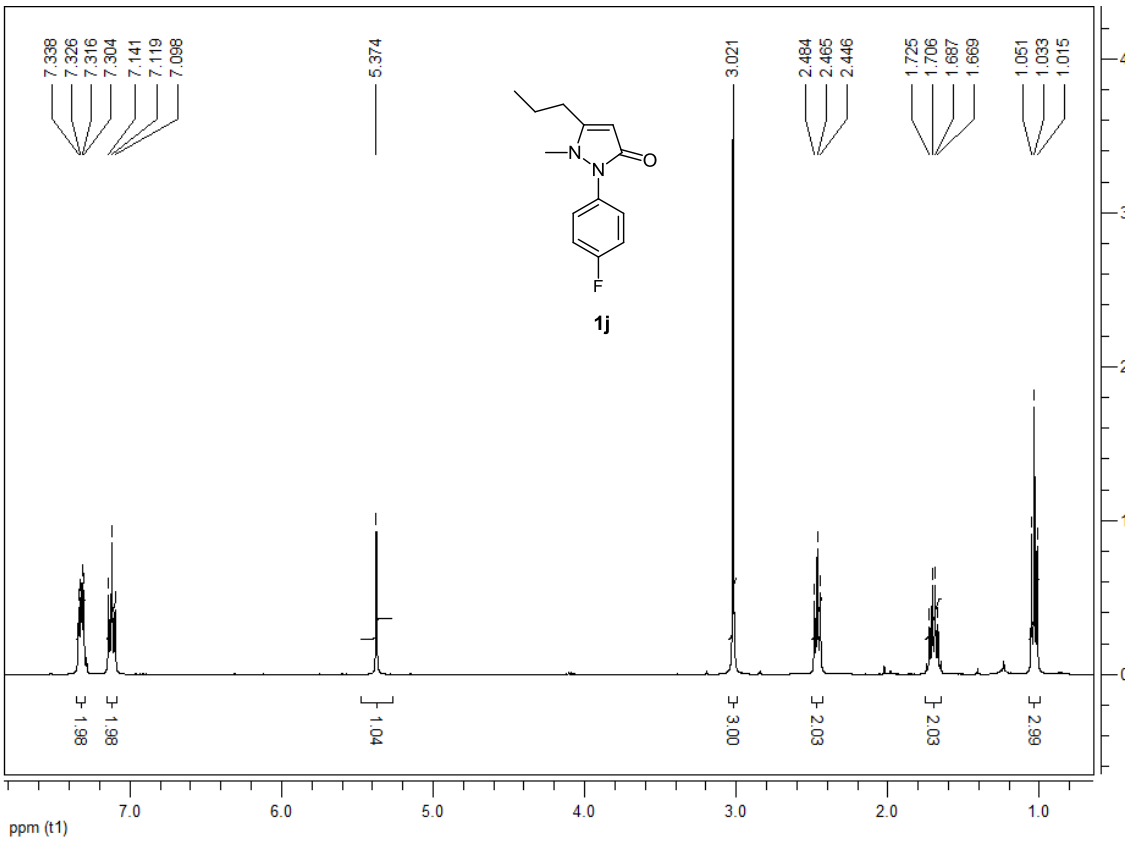
13.098
150
100
50
ppm (t1)
1i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7.141
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5.374
3.021
2.484
2.465
2.446
1.725
1.706
1.687
1.669
1.051
1.033
1.015
1j
1.98
1.98
1.04
3.00
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2.03
2.99
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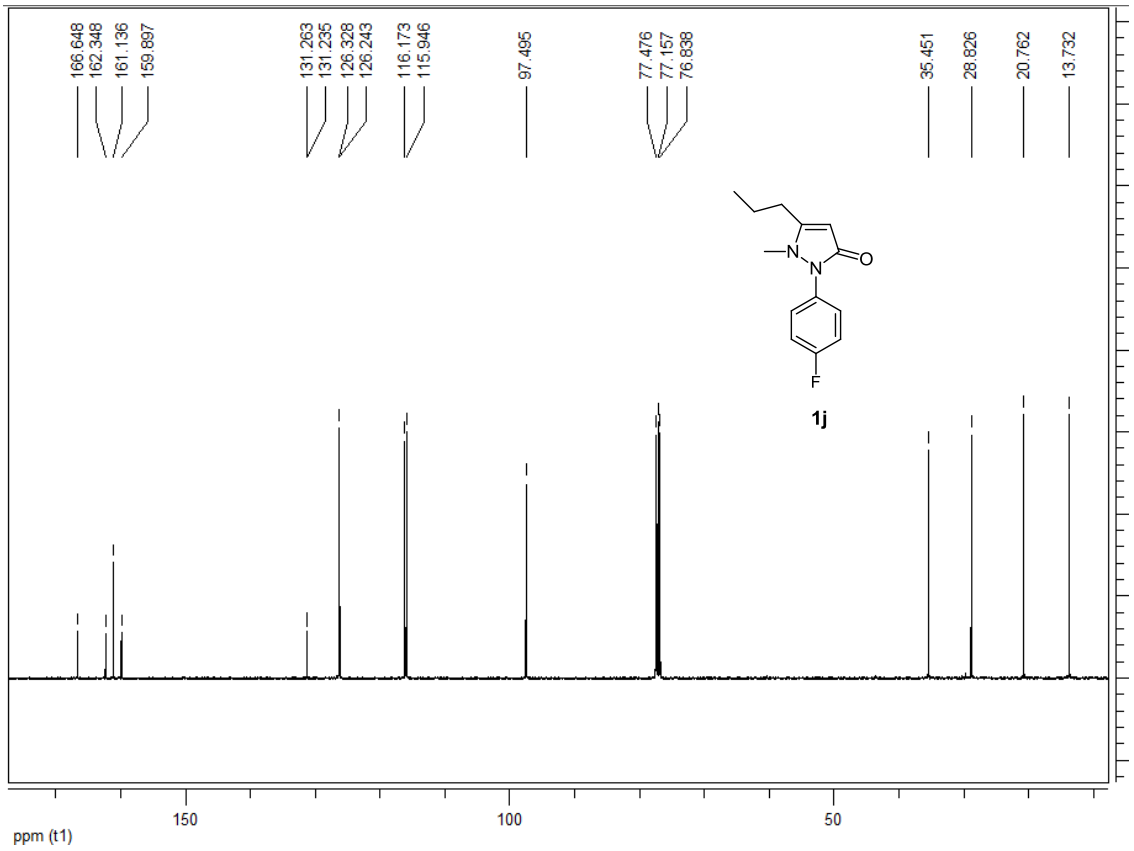
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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161.136
159.897
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131.235
126.328
126.243
116.173
115.946
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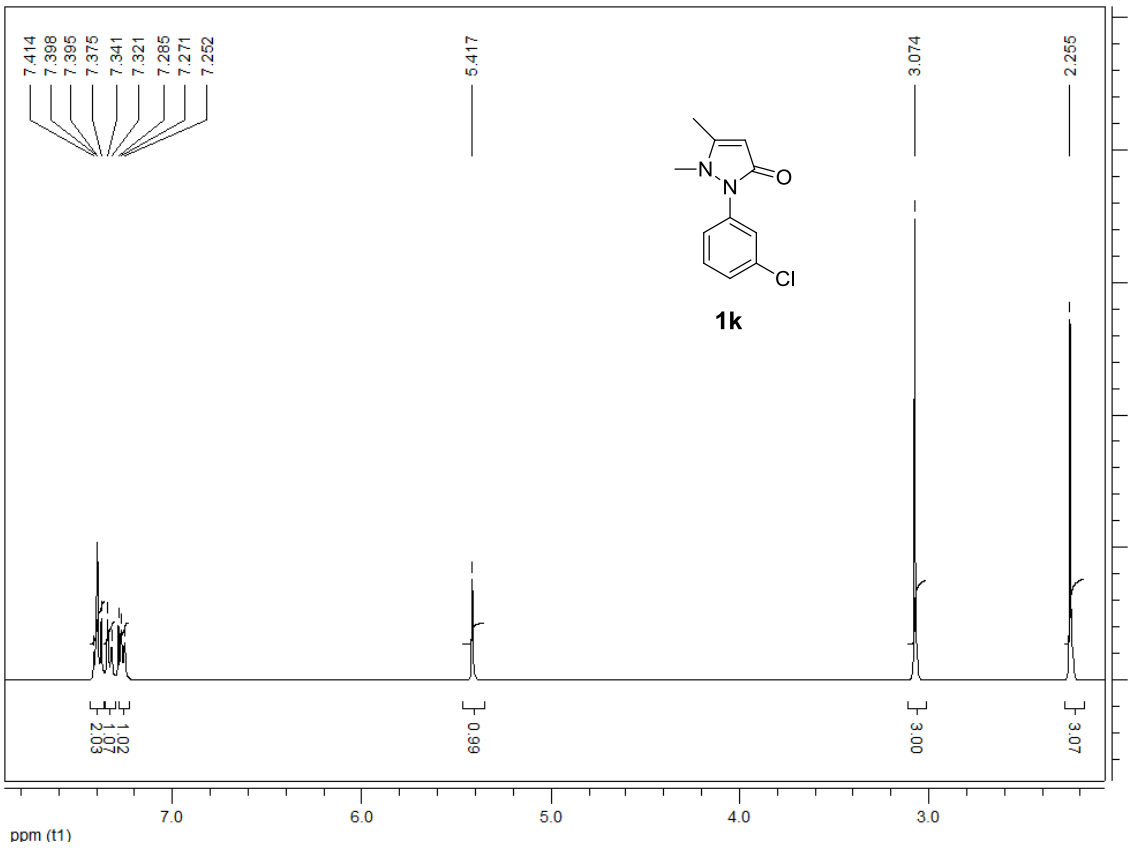
77.157
76.838
35.451
28.826
20.762
13.732
1j
150
100
50
ppm (t1)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7.321
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7.271
7.252
5.417
3.074
2.255
2.03
1.07
1.02
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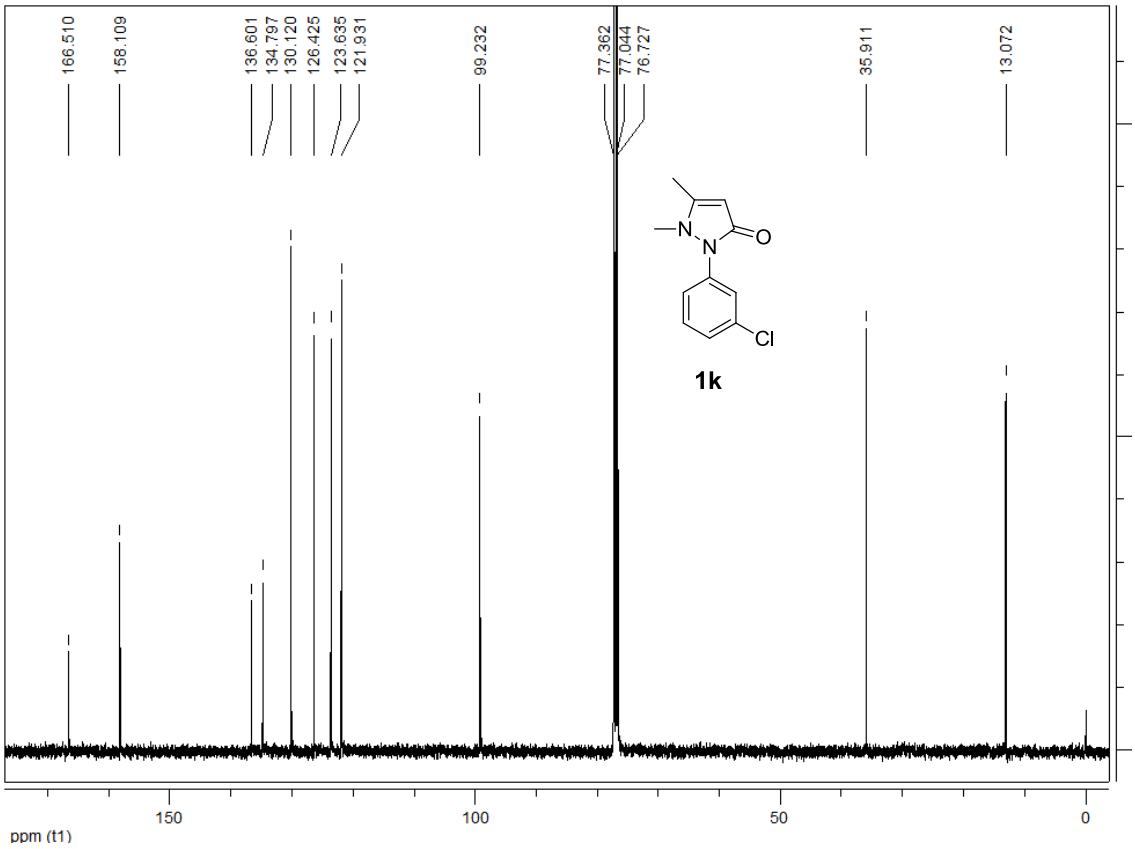
3.00
3.07
7.0
6.0
5.0
4.0
3.0
ppm (t1)
O
N
N
Cl
1k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134.797
130.120
126.425
123.635
121.931
99.232
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76.727
35.911
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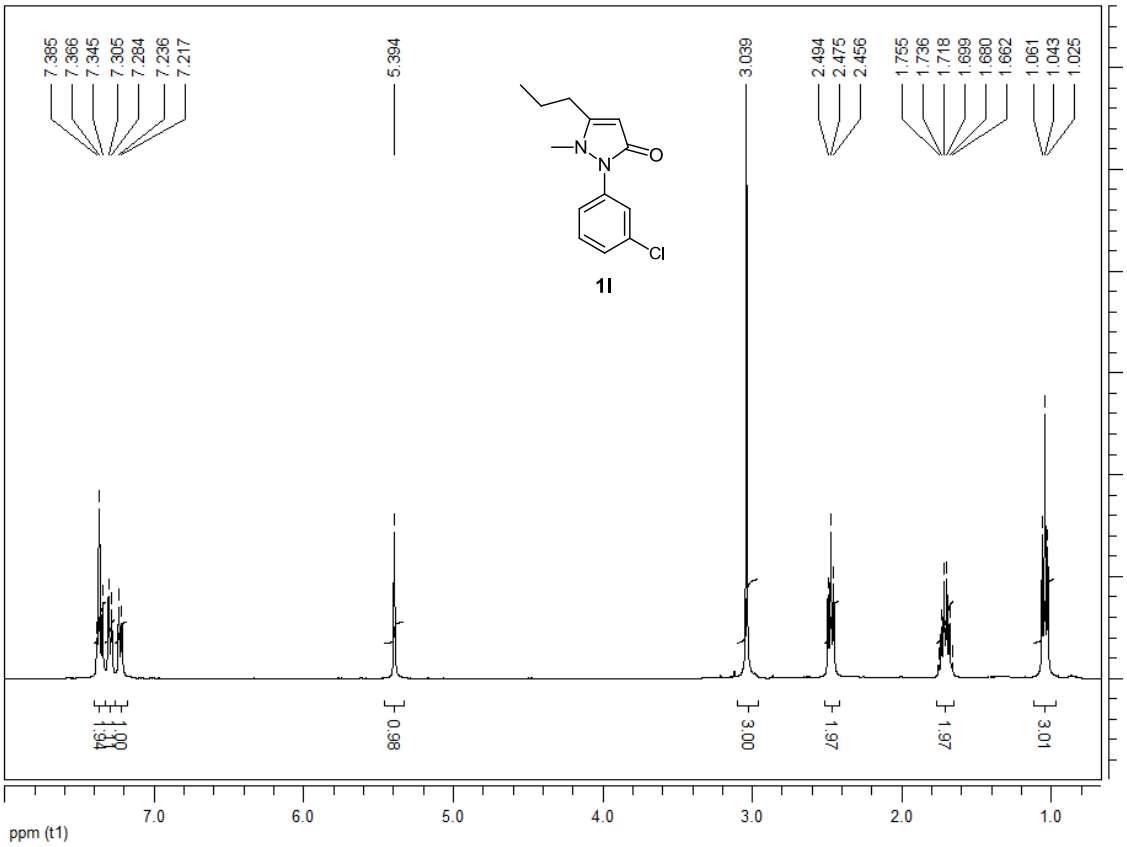
50
0
ppm (t1)
O
N
N
Cl
1k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2.456
1.755
1.736
1.718
1.699
1.680
1.662
1.061
1.043
1.025
1.94
1.00
0.98
3.00
1.97
1.97
3.01
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5.0
4.0
3.0
2.0
1.0
ppm (t1)
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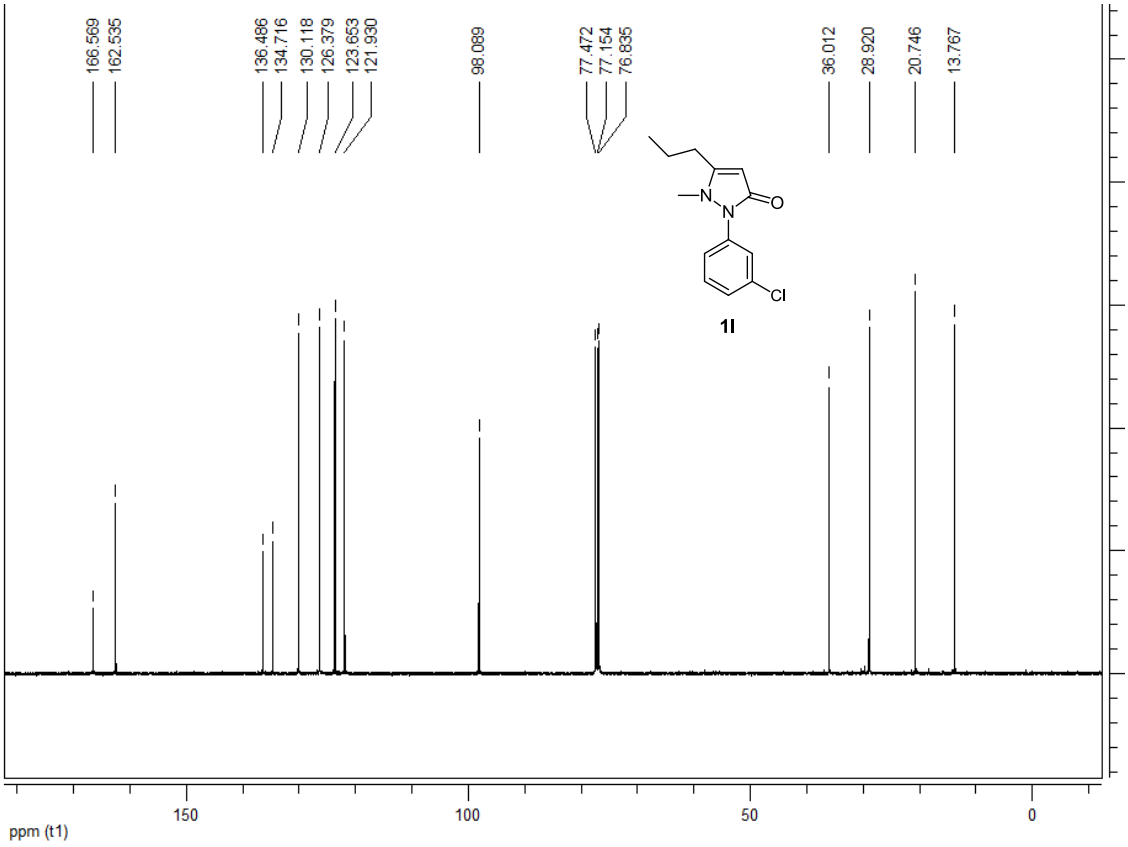
N
O
Cl
1l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121.930
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77.472
77.154
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20.746
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ppm (t1)
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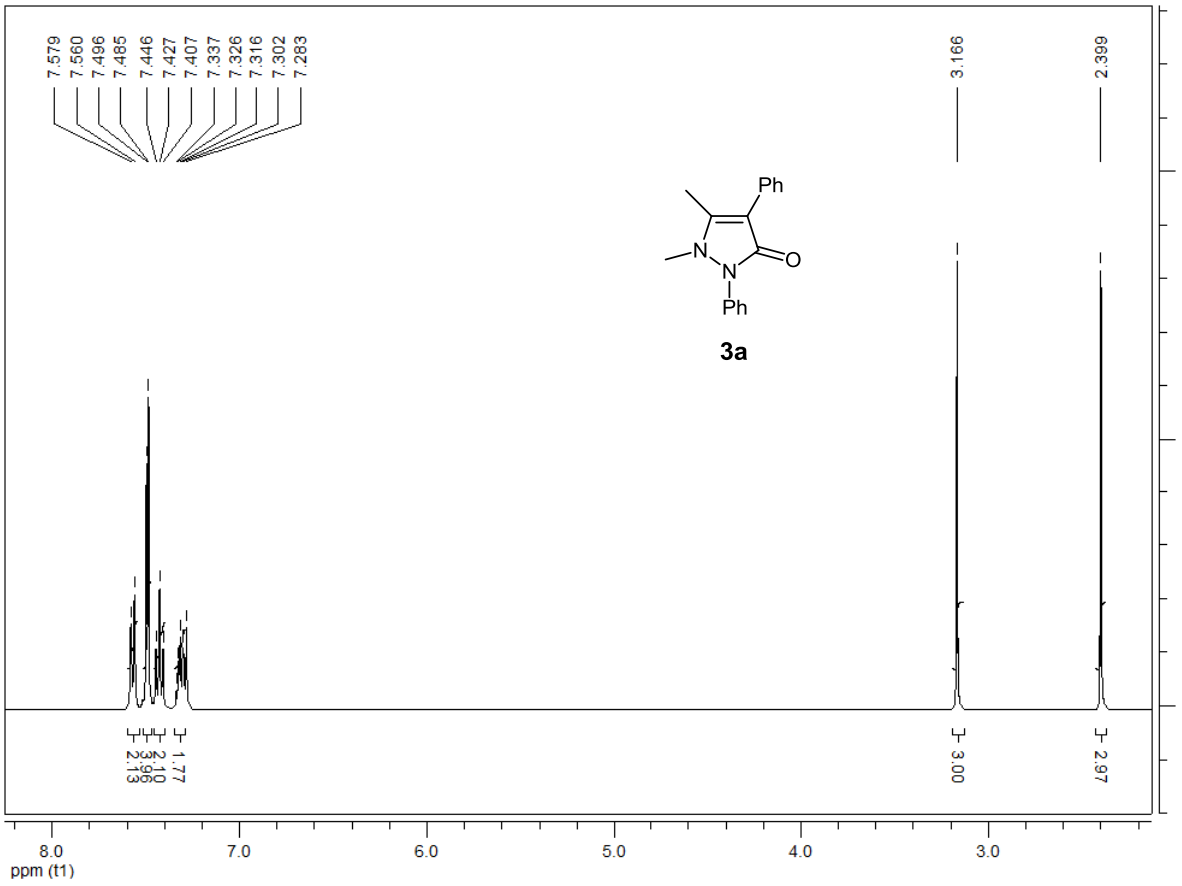
N
O
Cl
1l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7.337
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7.316
7.302
7.283
3.166
2.399
Ph
N
N
O
Ph
3a
2.13
2.03
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3.00
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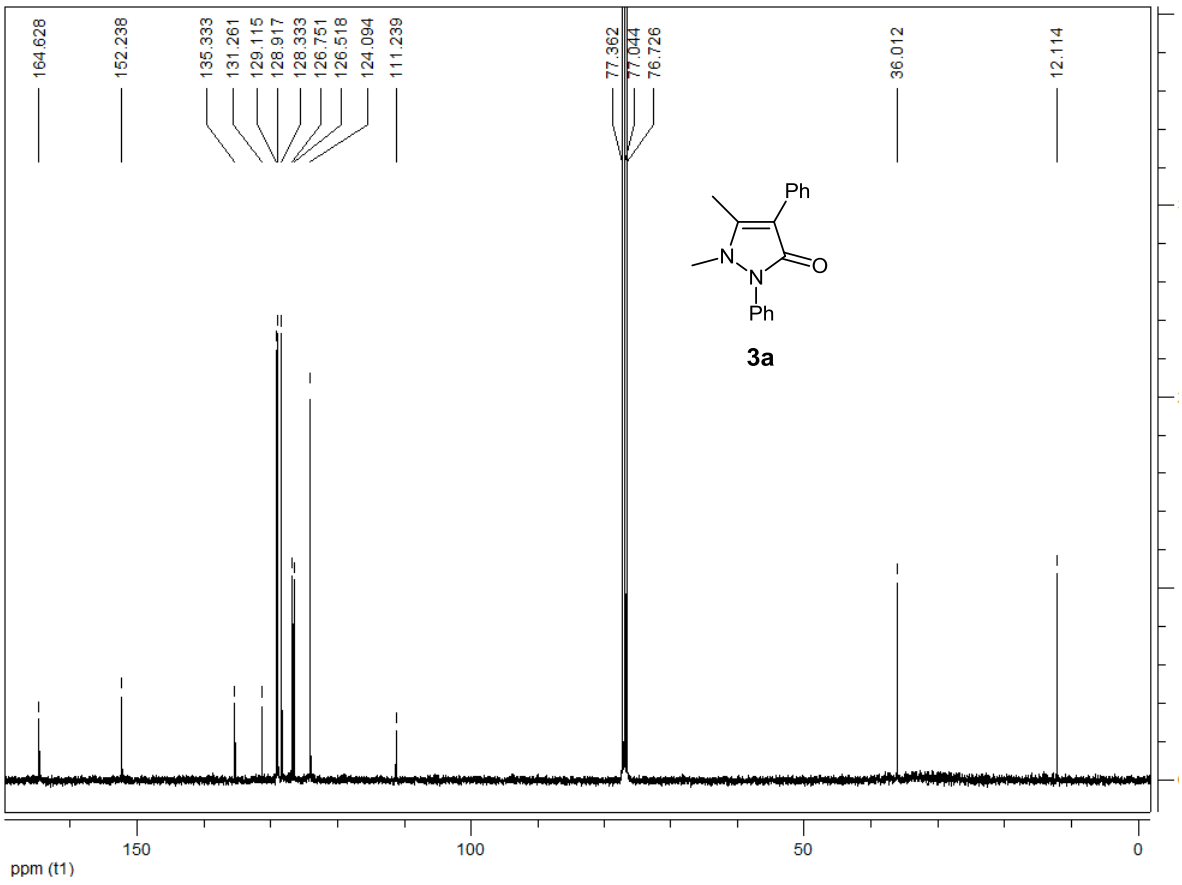
7.0
6.0
5.0
4.0
3.0
ppm (t1)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131.261
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128.333
126.751
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124.094
111.239
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12.114
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Ph
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50
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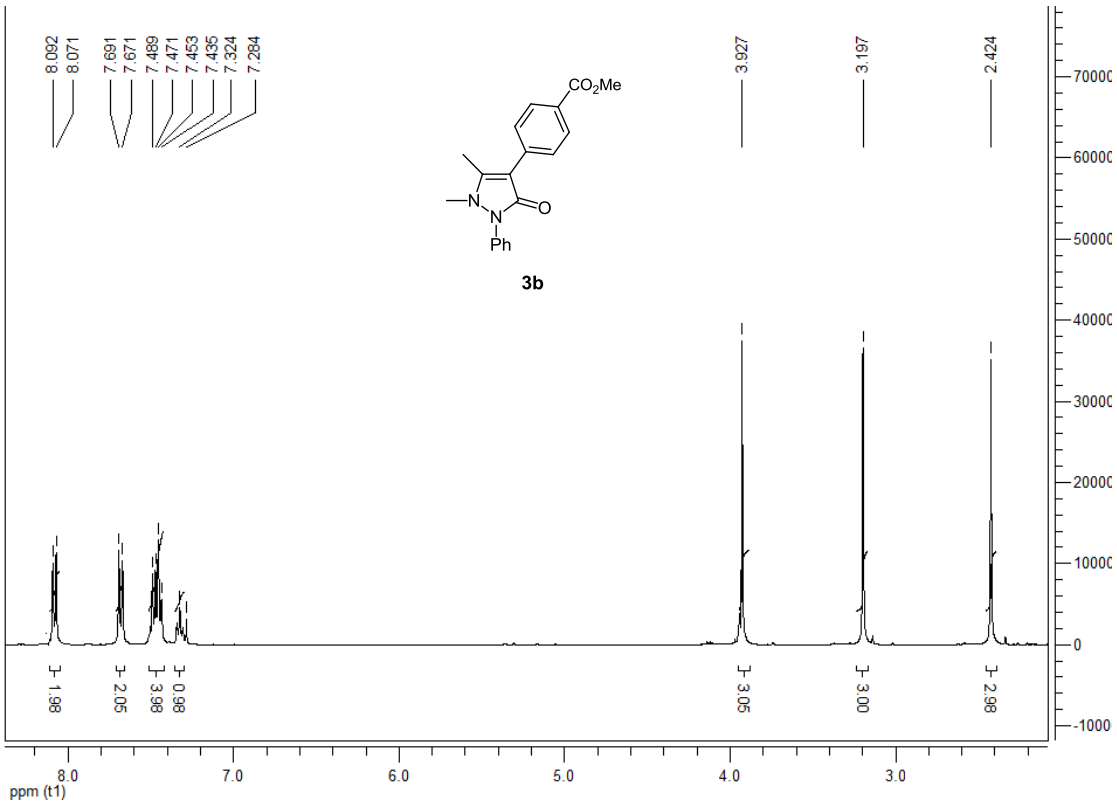
ppm (t1)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7.489
7.471
7.453
7.435
7.324
7.284
3.927
3.197
2.424
CO2Me
N
N
O
Ph
3b
1.98
2.05
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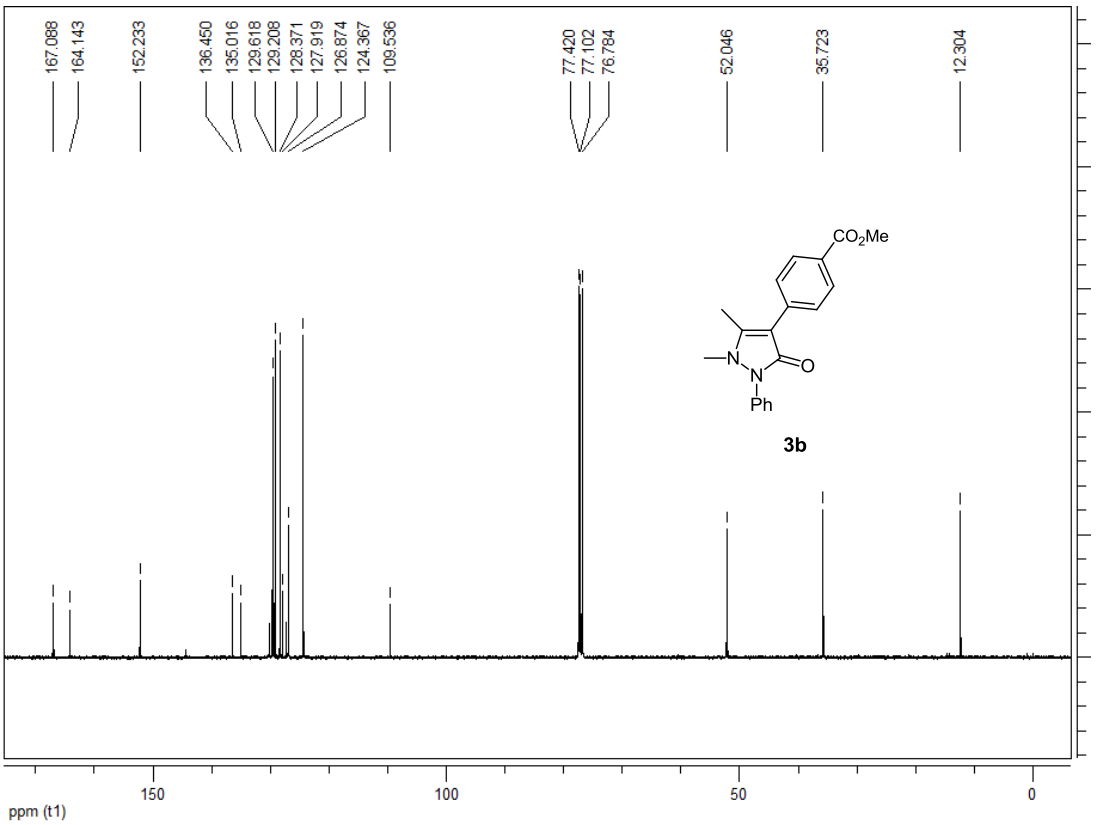
3.05
3.00
2.98
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)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129.208
128.371
127.919
126.874
124.367
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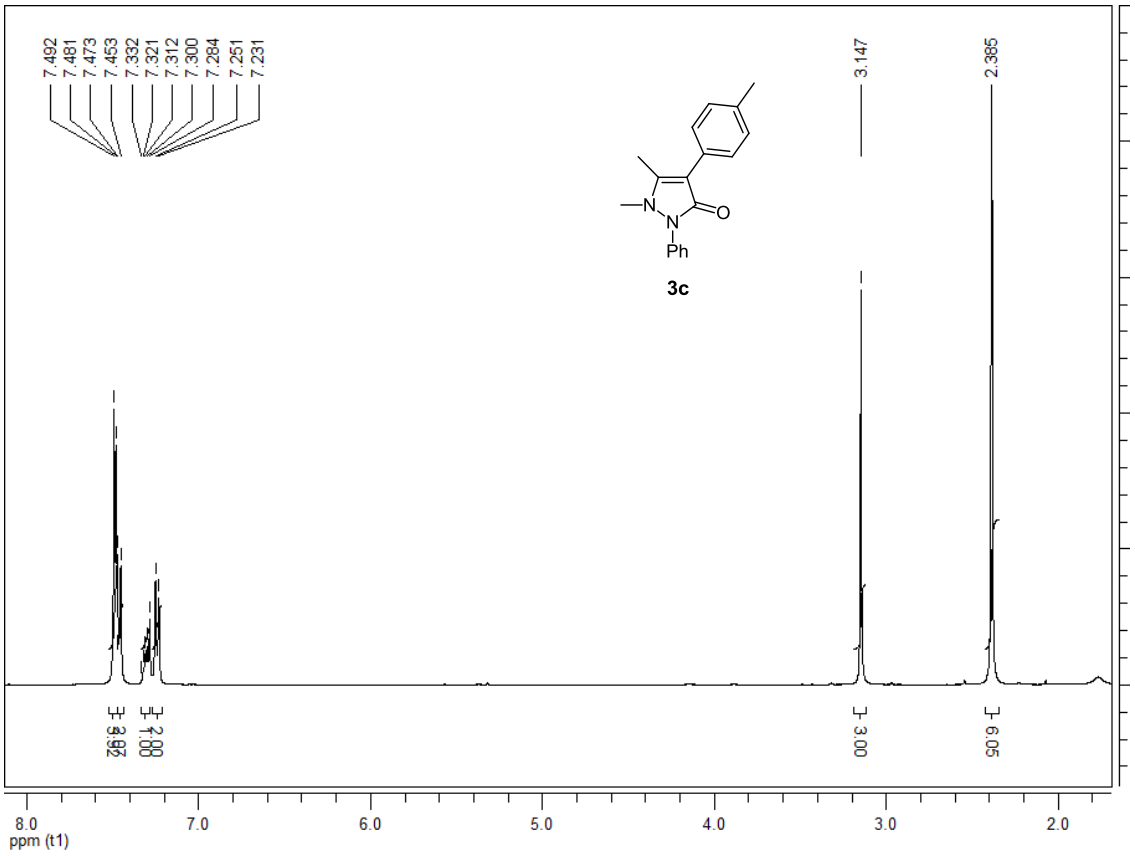
77.420
77.102
76.784
52.046
35.723
12.304
CO2Me
N
N
O
Ph
3b
150
100
50
0
ppm (t1)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7.321
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7.300
7.284
7.251
7.231
3.147
2.385
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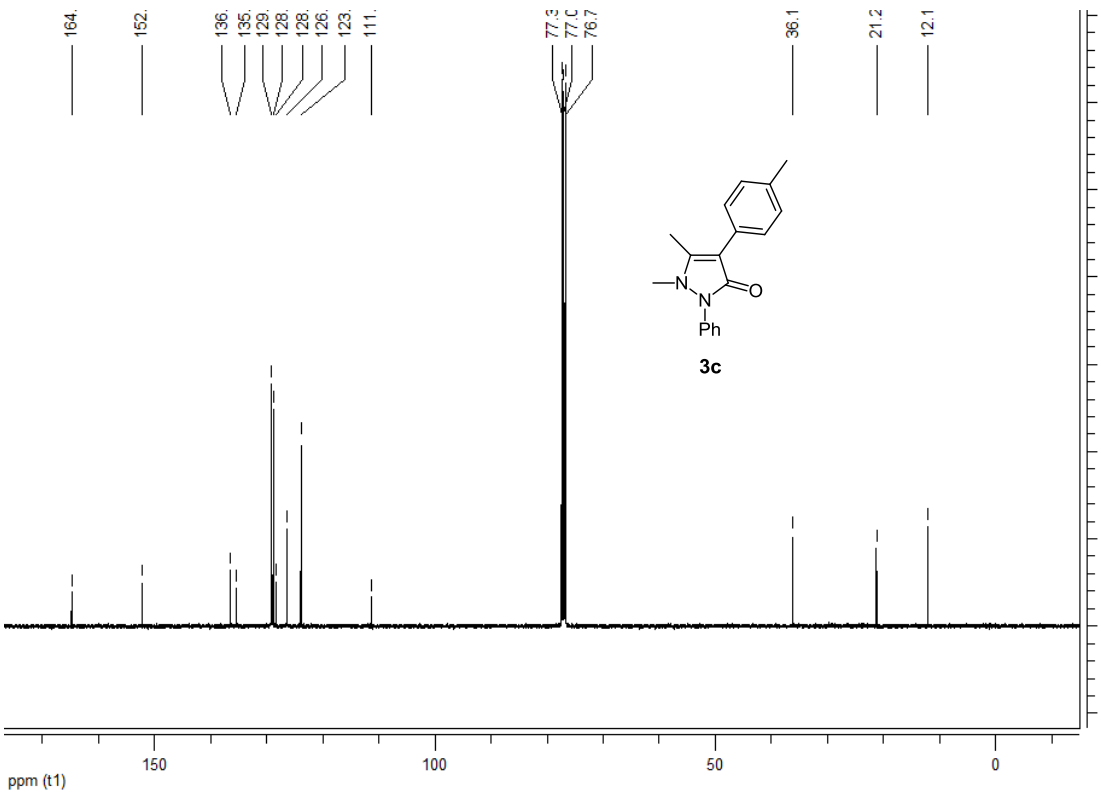
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
Ph
3c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136.
135.
129.
128.
128.
126.
123.
111.
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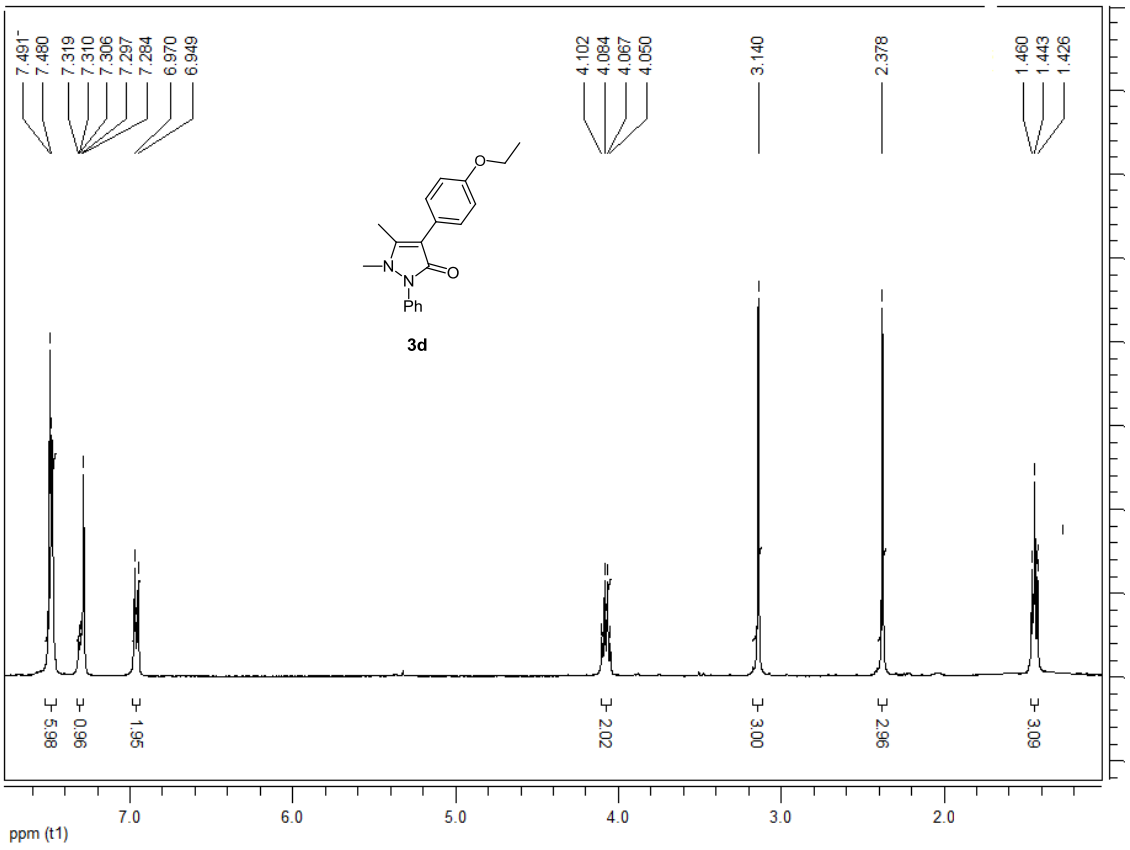
100
50
0
ppm (t1)
Ph
3c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4.067
4.050
3.140
2.378
1.460
1.443
1.426
3d
5.98
0.96
1.95
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2.96
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6.0
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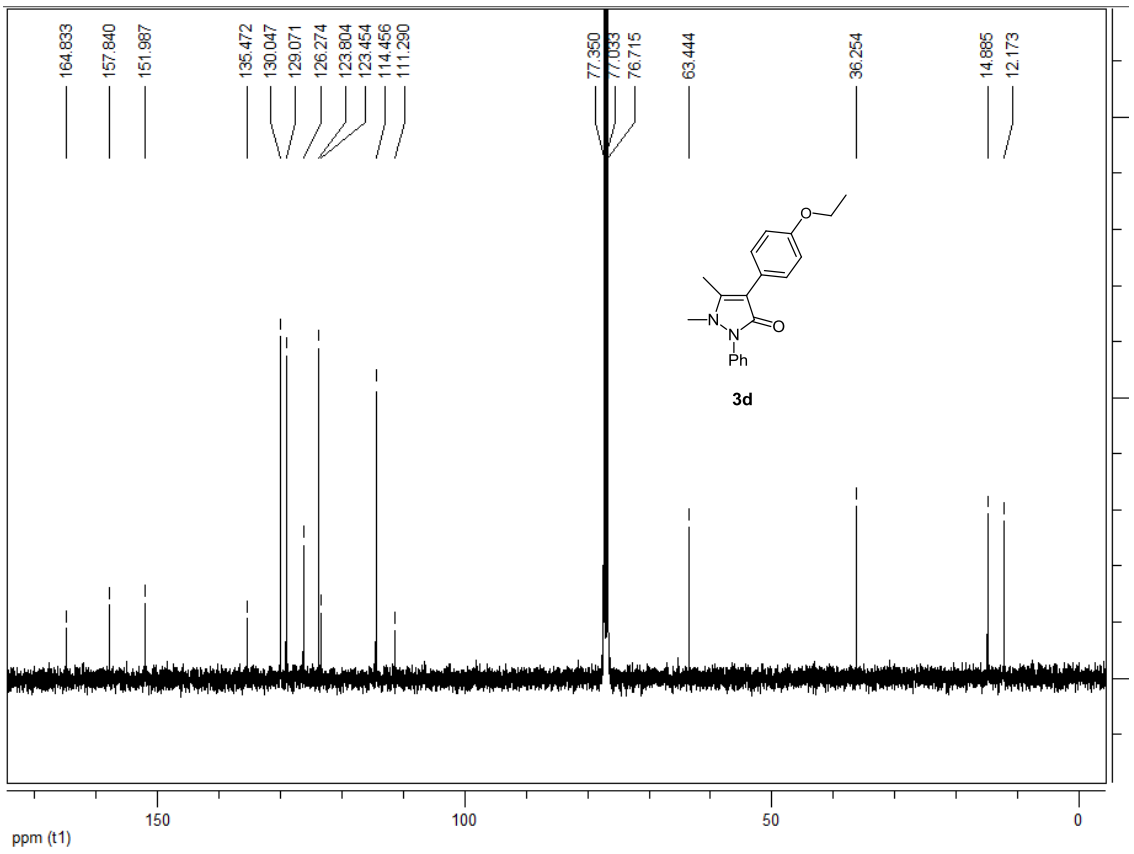
4.0
3.0
2.0
ppm (t1)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129.071
126.274
123.804
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114.456
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76.715
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14.885
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100
50
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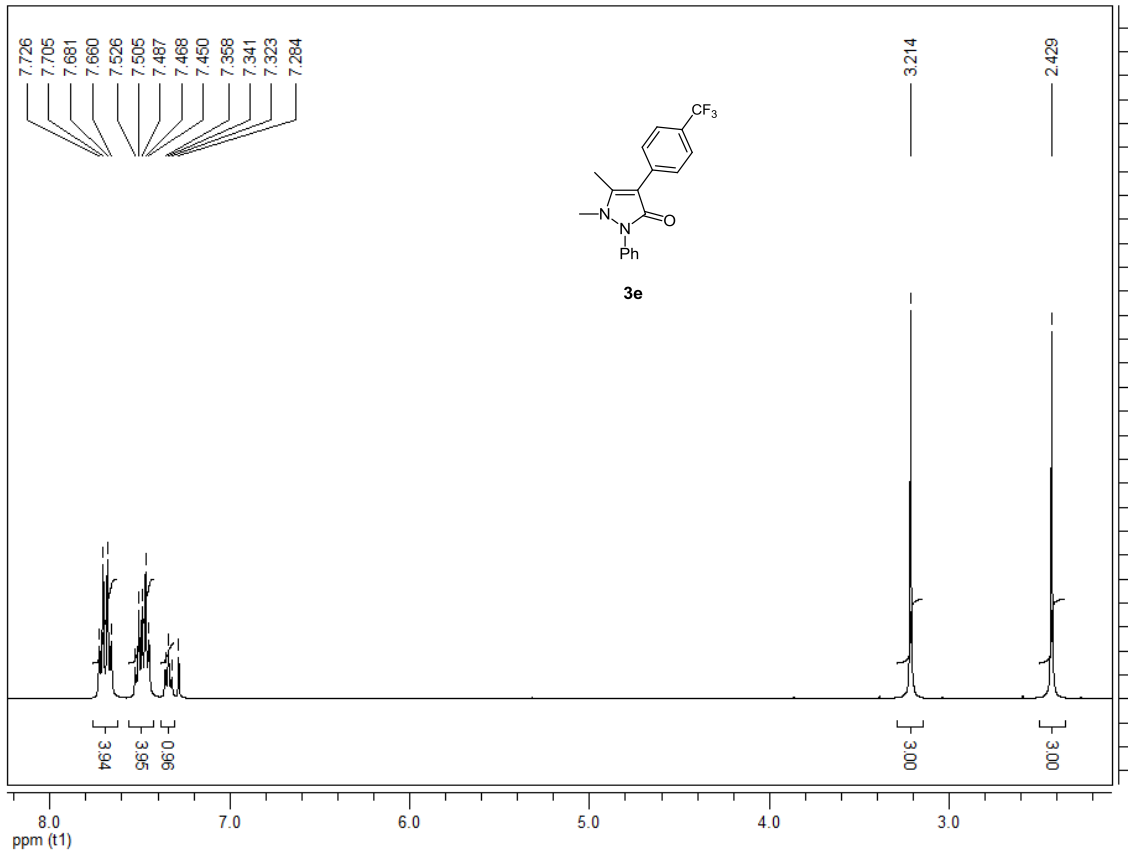
ppm (t1)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7.487
7.468
7.450
7.358
7.341
7.323
7.284
3.214
2.429
CF3
N
N
O
Ph
3e
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3.96
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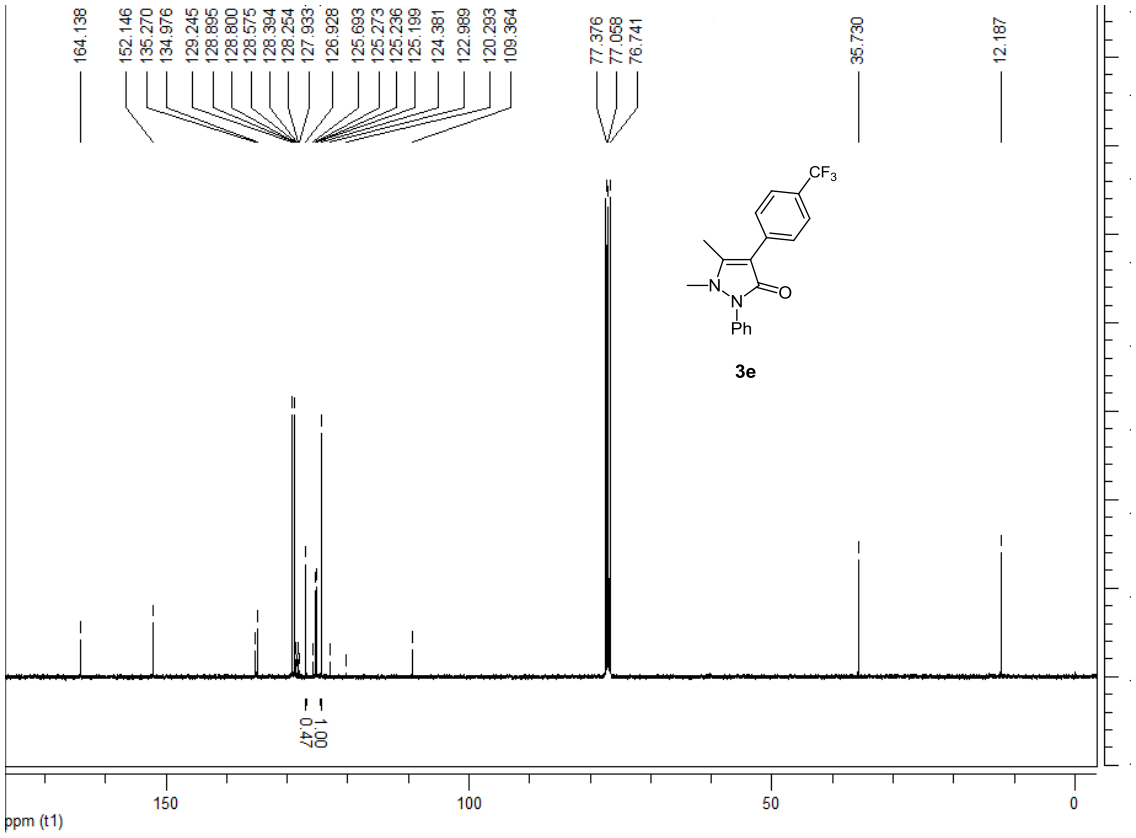
3.0
ppm (t1)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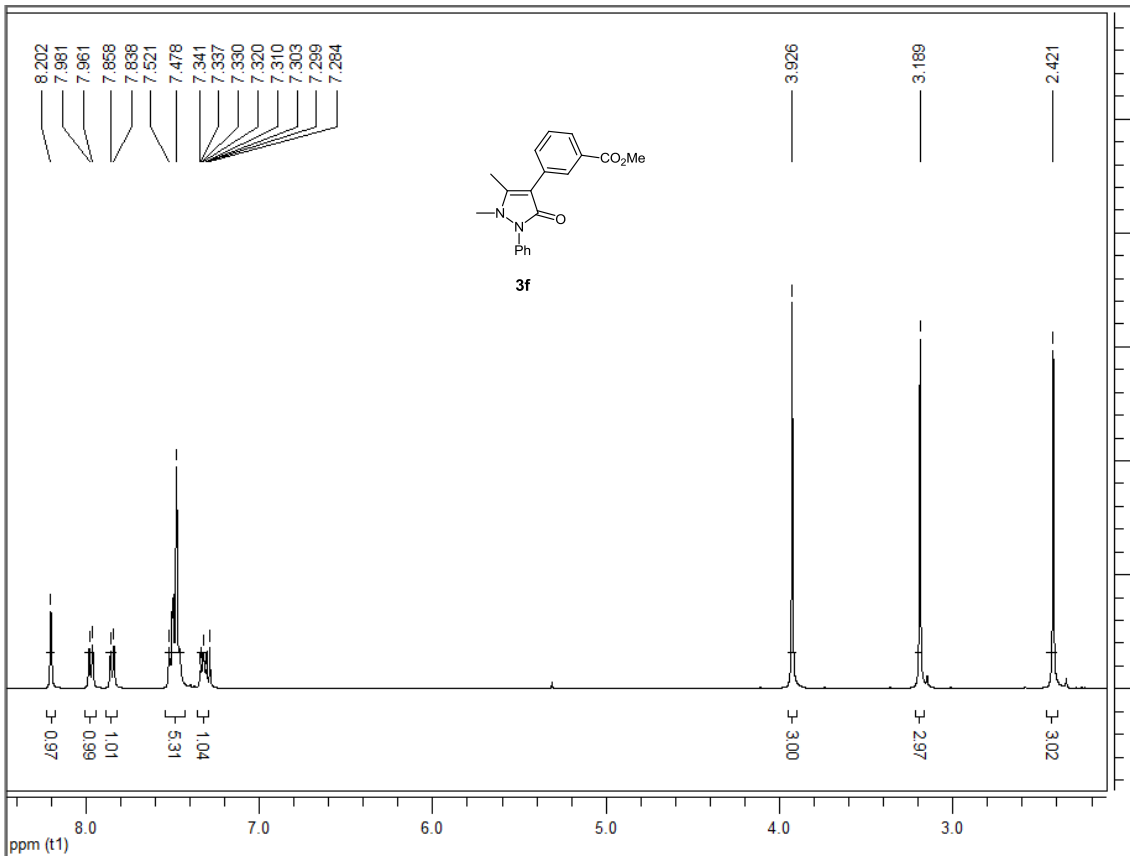
128.254
127.933
126.928
125.693
125.273
125.236
125.199
124.381
122.989
120.293
109.364
77.376
77.058
76.741
35.730
12.187
CF3
N
N
O
Ph
3e
1.00
0.47
150
100
50
0
ppm (t1)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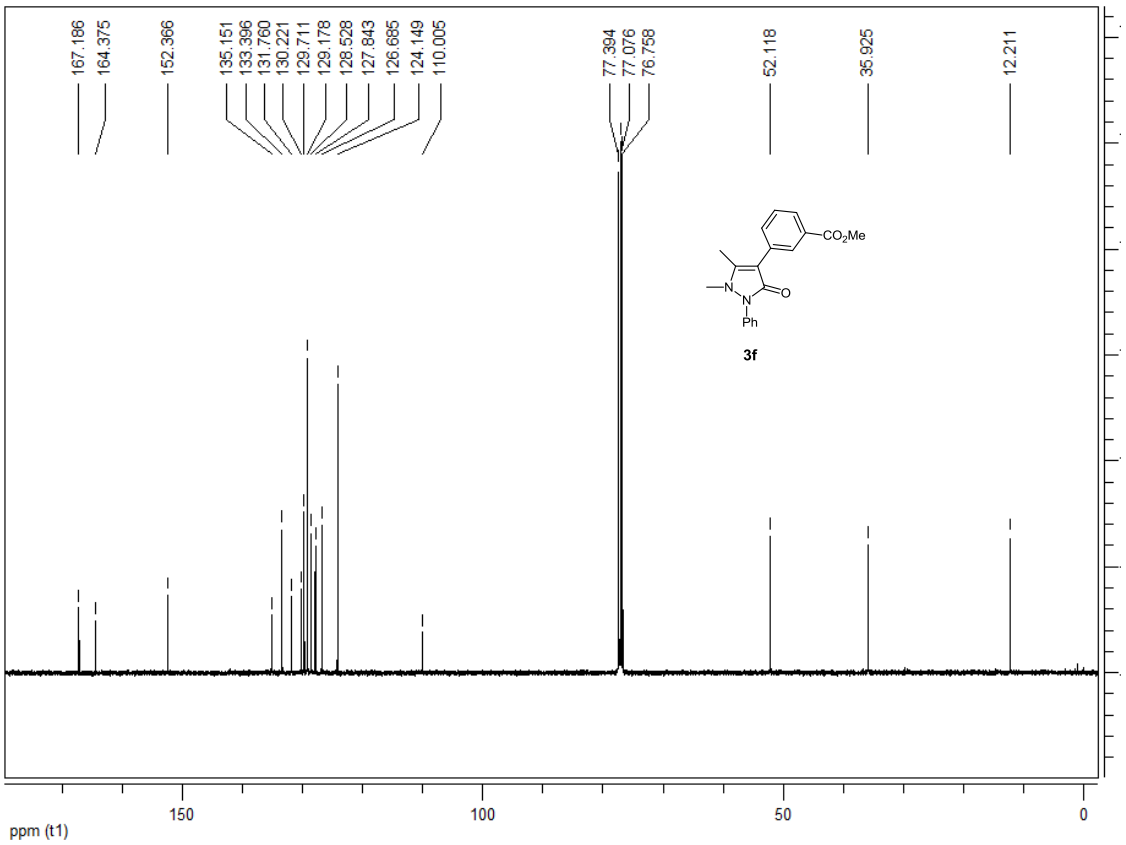
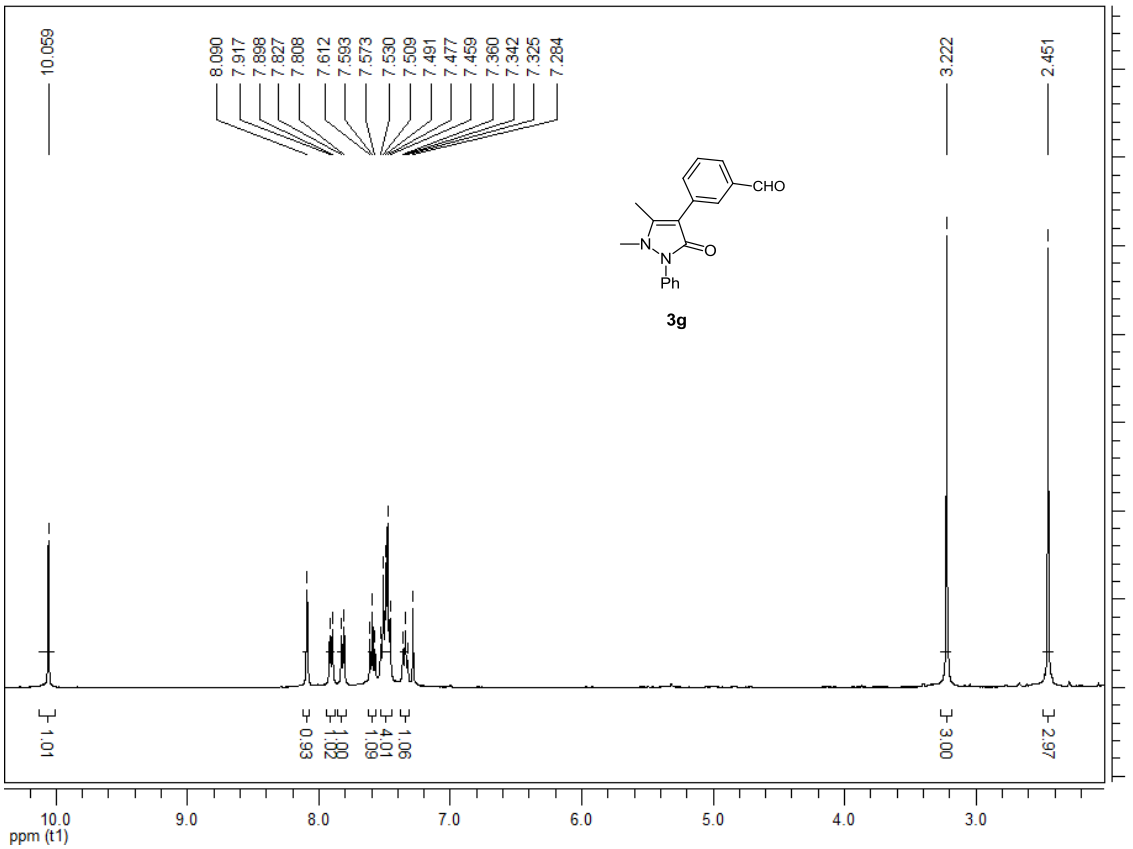
7.981
7.961
7.858
7.838
7.521
7.478
7.341
7.337
7.330
7.320
7.310
7.303
7.299
7.284
3.926
3.189
2.421
CO2Me
N
N
O
Ph
3f
0.97
0.99
1.01
5.31
1.04
3.00
2.97
3.02
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


167.186
164.375
152.366
135.151
133.396
131.760
130.221
129.711
129.178
128.528
127.843
126.685
124.149
110.005
77.394
77.076
76.758
52.118
35.925
12.211
CO2Me
N
N
O
Ph
3f
150
100
50
0
ppm (t1)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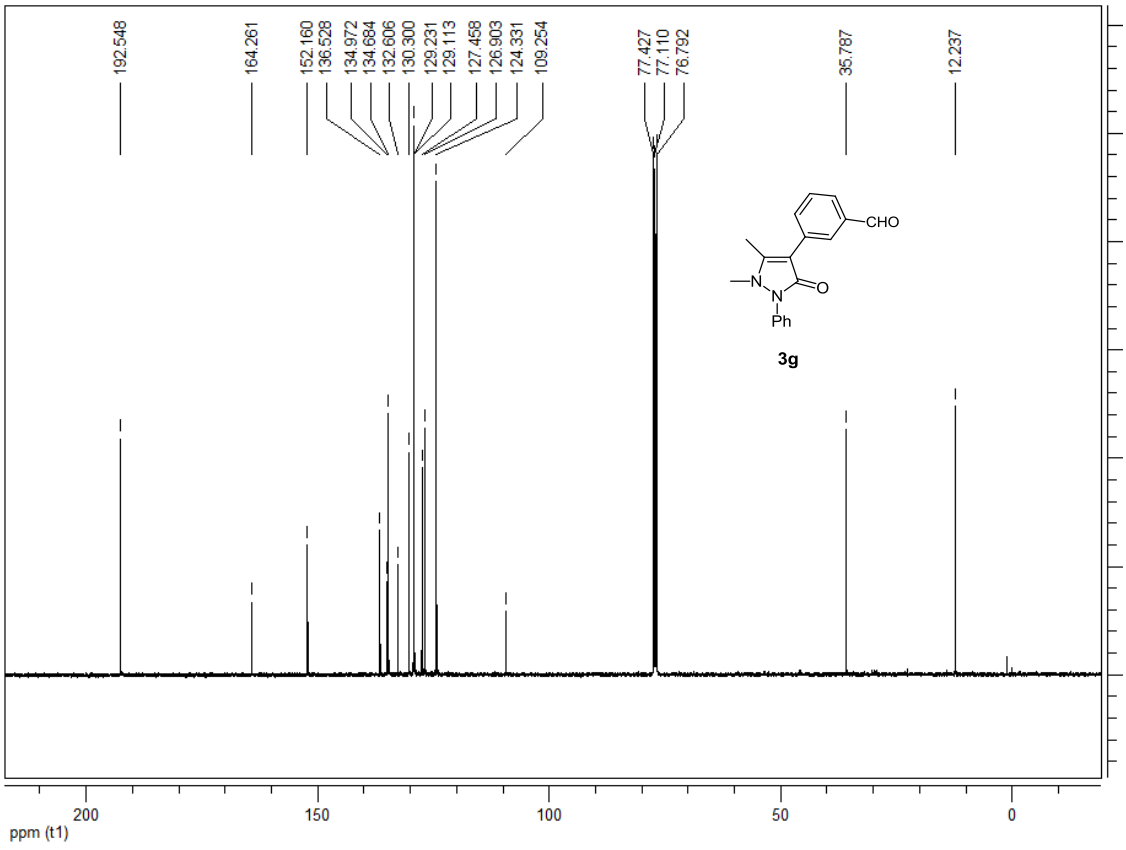
8.090
7.917
7.898
7.827
7.808
7.612
7.593
7.573
7.530
7.509
7.491
7.477
7.459
7.360
7.342
7.325
7.284
3.222
2.451
CHO
N
N
O
Ph
3g
1.01
0.93
1.02
1.09
4.01
1.06
3.00
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


192.548
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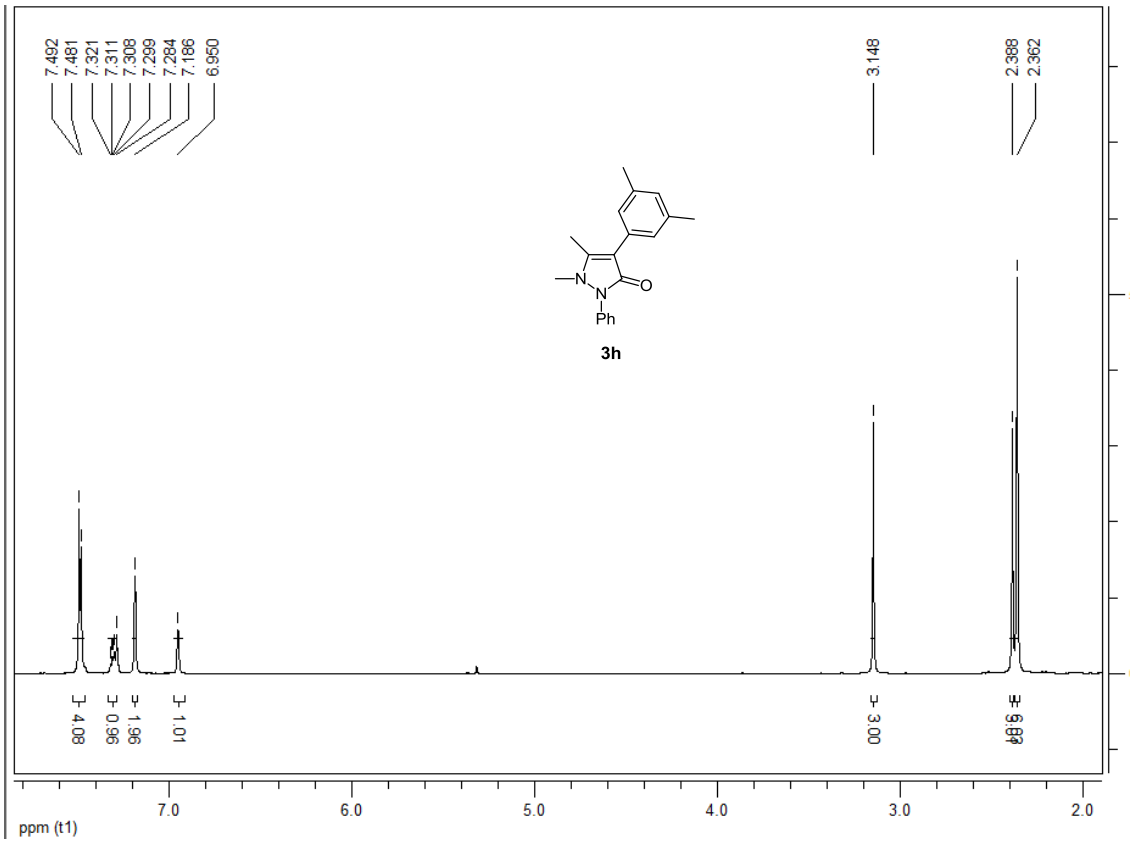
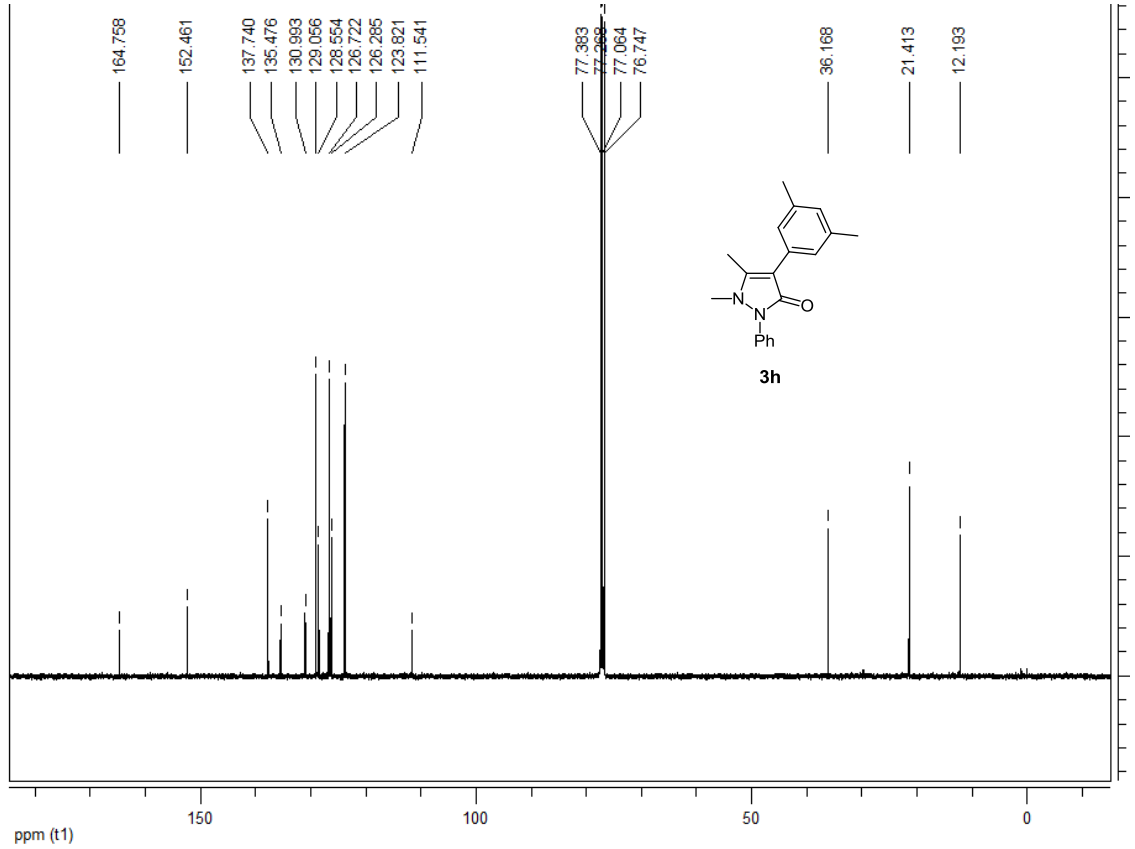
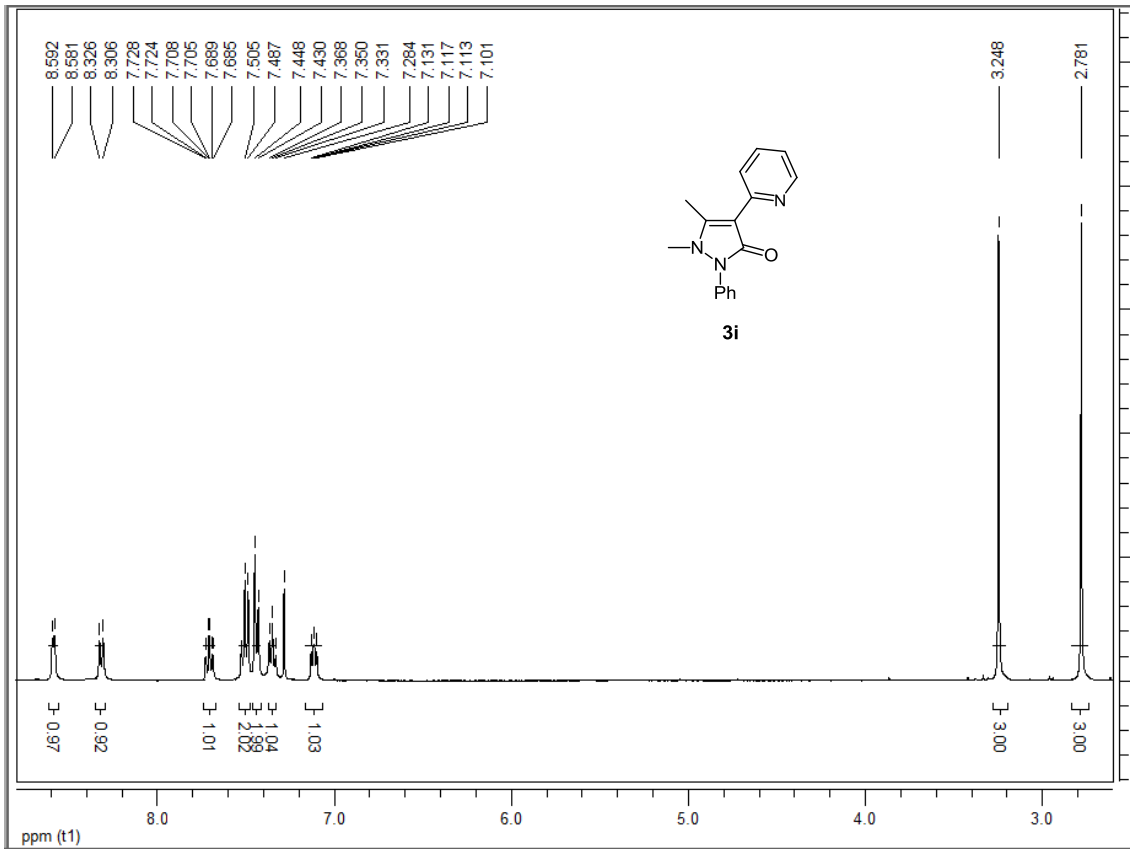
152.160
136.528
134.972
134.684
132.606
130.300
129.231
129.113
127.458
126.903
124.331
109.254
77.427
77.110
76.792
35.787
12.237
CHO
N
N
O
Ph
3g
200
150
100
50
0
ppm (t1)


7.492
7.481
7.321
7.311
7.308
7.299
7.284
7.186
6.950
3.148
2.388
2.362
3h
4.08
0.96
1.96
1.01
3.00
9.18
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


164.758
152.461
137.740
135.476
130.993
129.056
128.554
126.722
126.285
123.821
111.541
77.383
77.064
76.747
36.168
21.413
12.193
3h
150
100
50
0
ppm (t1)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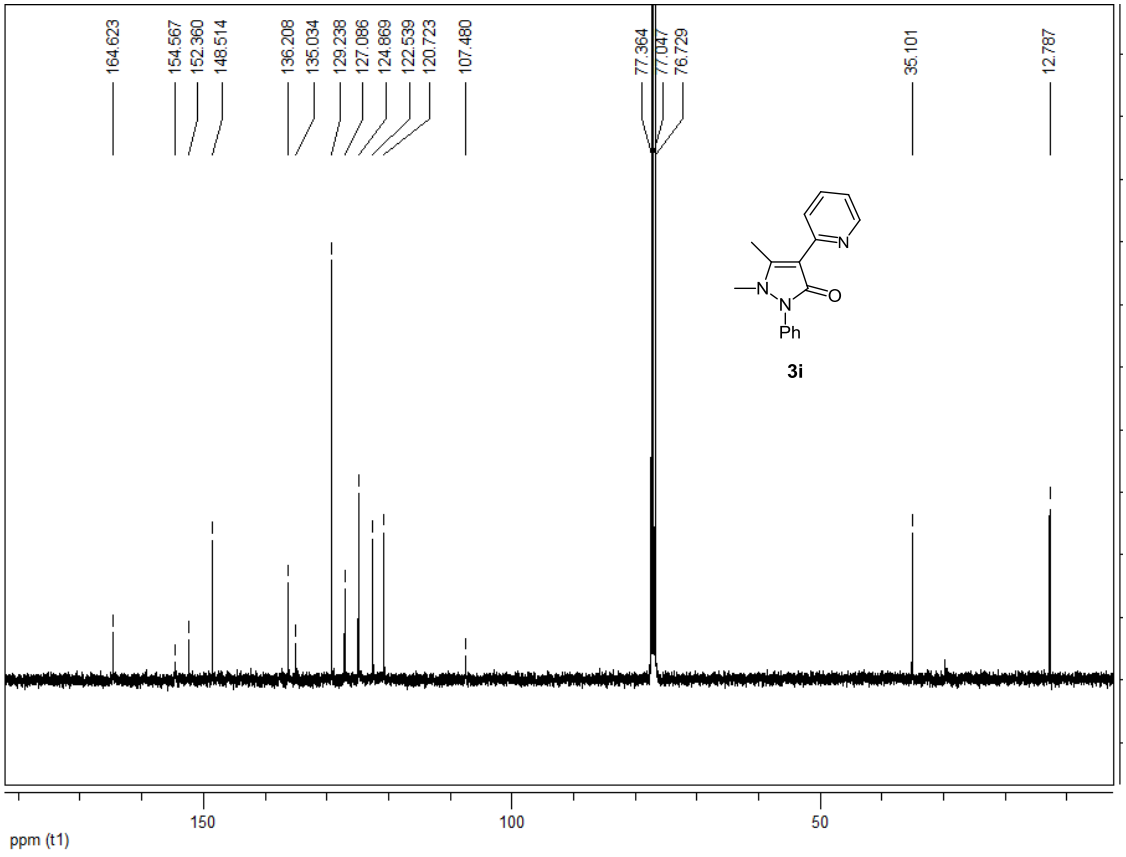
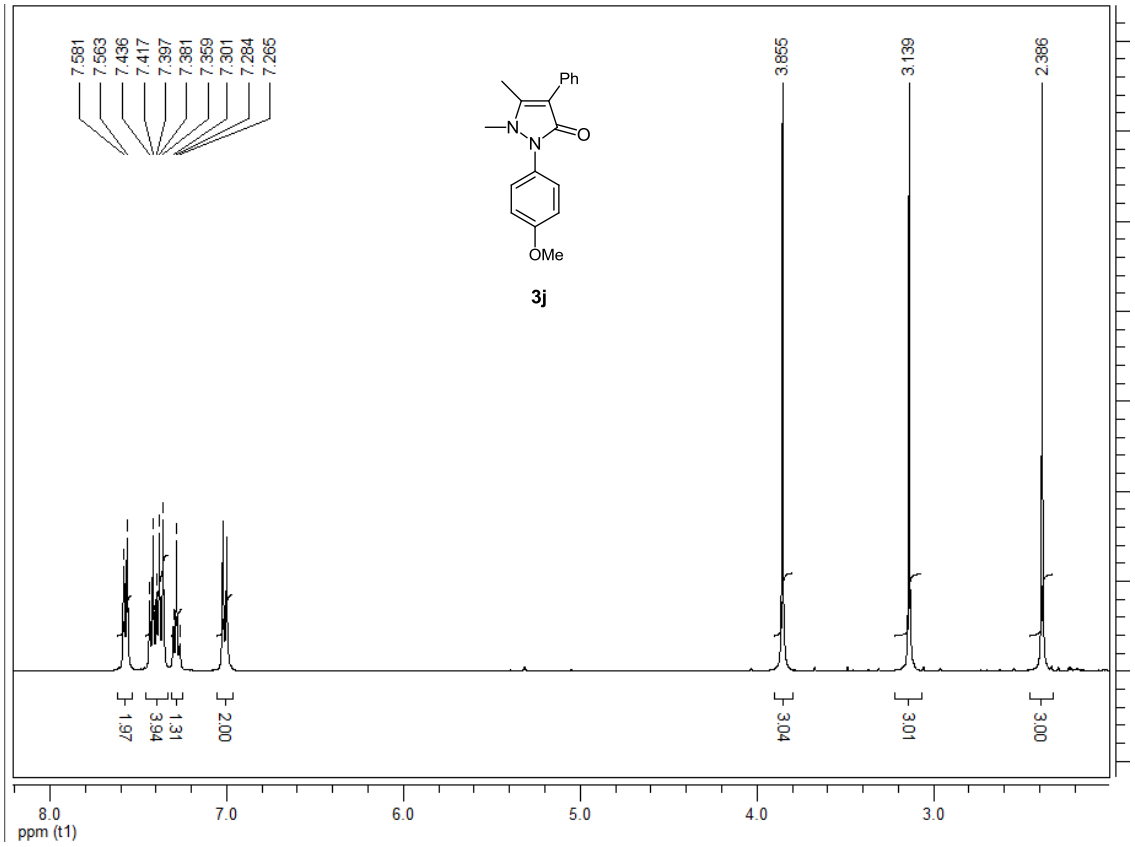
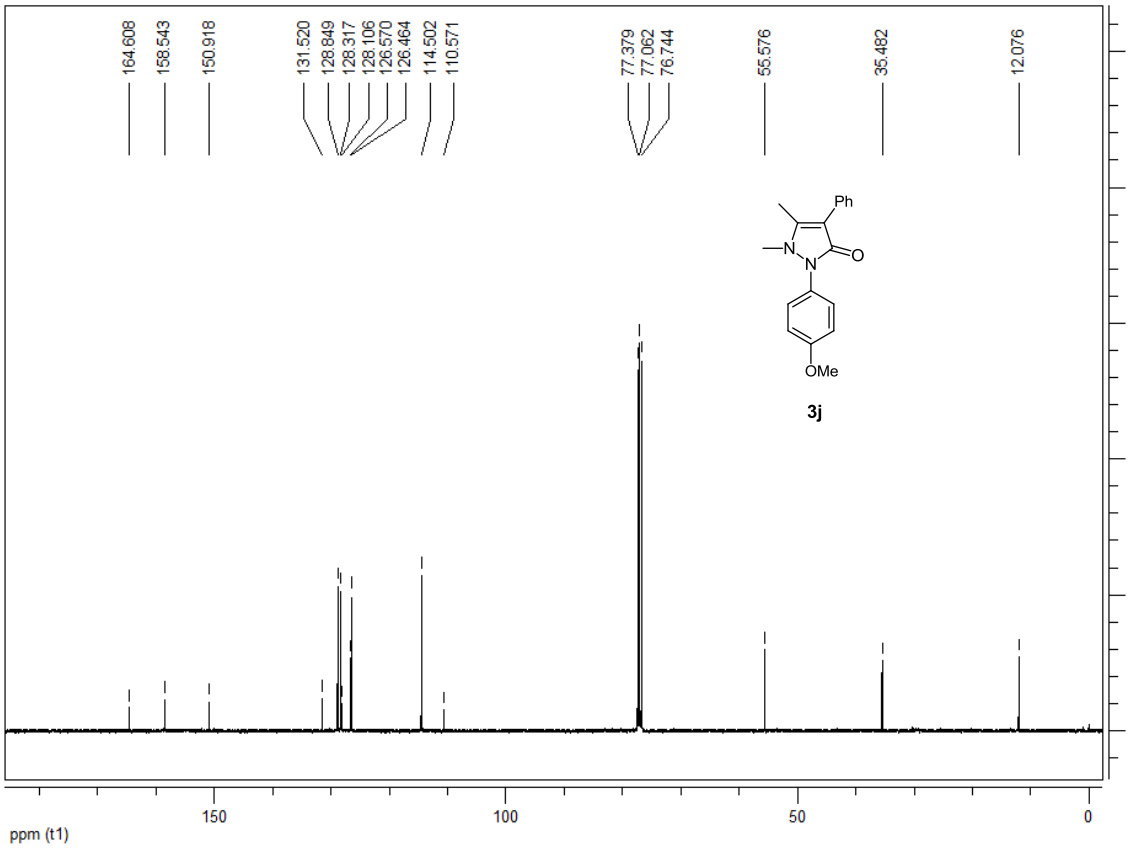
8.581
8.326
8.306
7.728
7.724
7.708
7.705
7.689
7.685
7.505
7.487
7.448
7.430
7.368
7.350
7.331
7.284
7.131
7.117
7.113
7.101
3.248
2.781
0.97
0.92
1.01
2.02
1.04
1.03
3.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)
N
N
N
O
Ph

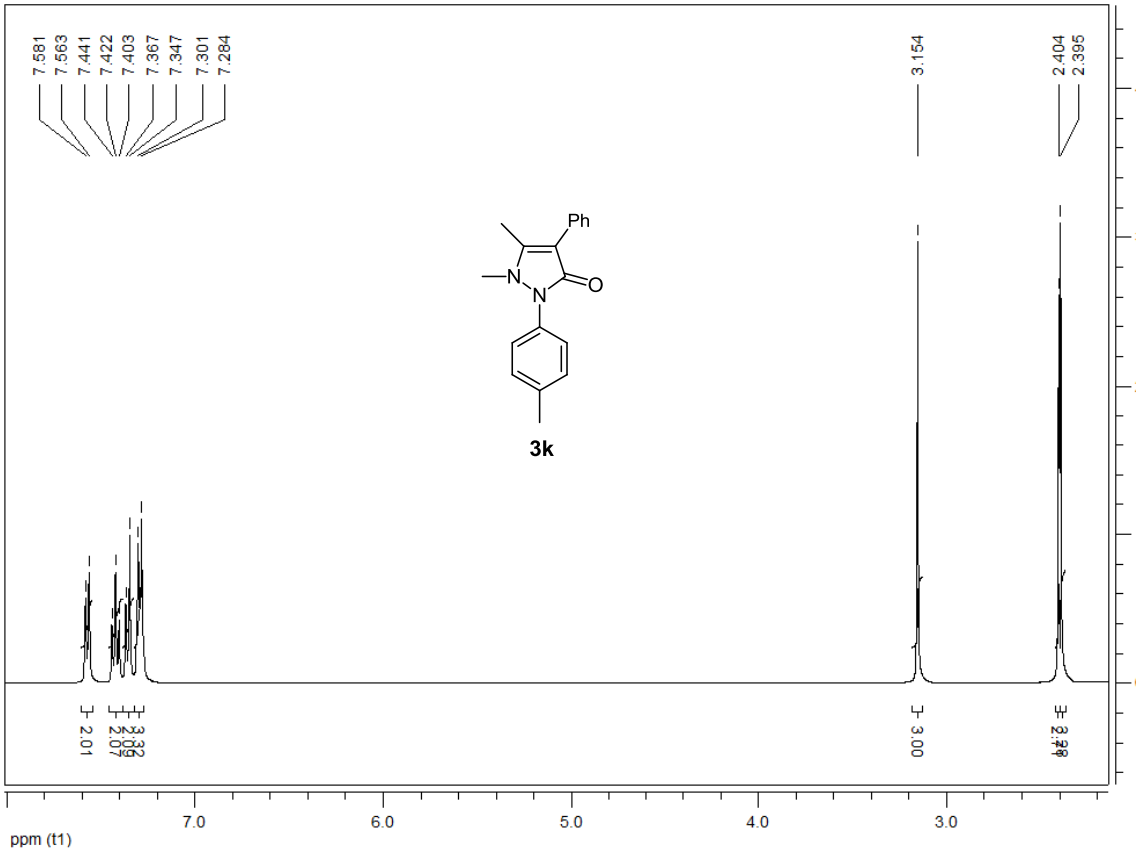
3i

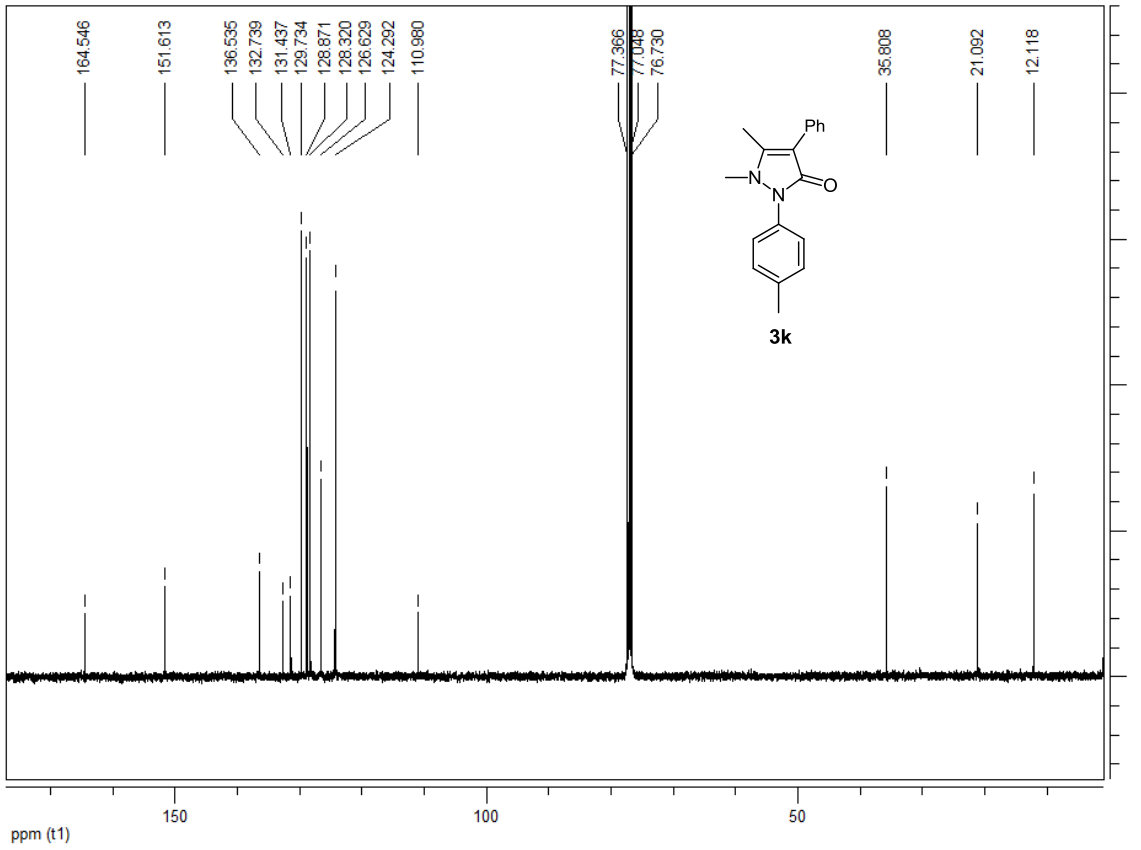

164.623
154.567
152.360
148.514
136.208
135.034
129.238
127.086
124.869
122.539
120.723
107.480
77.364
77.047
76.729
35.101
12.787
150
100
50
ppm (t1)
N
N
N
O
Ph

3i


7.581
7.563
7.436
7.417
7.397
7.381
7.359
7.301
7.284
7.265
3.855
3.139
2.386
Ph
N
N
O
OMe
3j
1.97
3.94
1.31
2.00
3.04
3.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


164.608
158.543
150.918
131.520
128.849
128.317
128.106
126.570
126.464
114.502
110.571
77.379
77.062
76.744
55.576
35.482
12.076
Ph
N
N
O
OMe
3j
150
100
50
0
ppm (t1)


7.581
7.563
7.441
7.422
7.403
7.367
7.347
7.301
7.284
3.154
2.404
2.395
Ph
N
N
O
3k
2.01
2.07
2.32
3.00
2.39
7.0
6.0
5.0
4.0
3.0
ppm (t1)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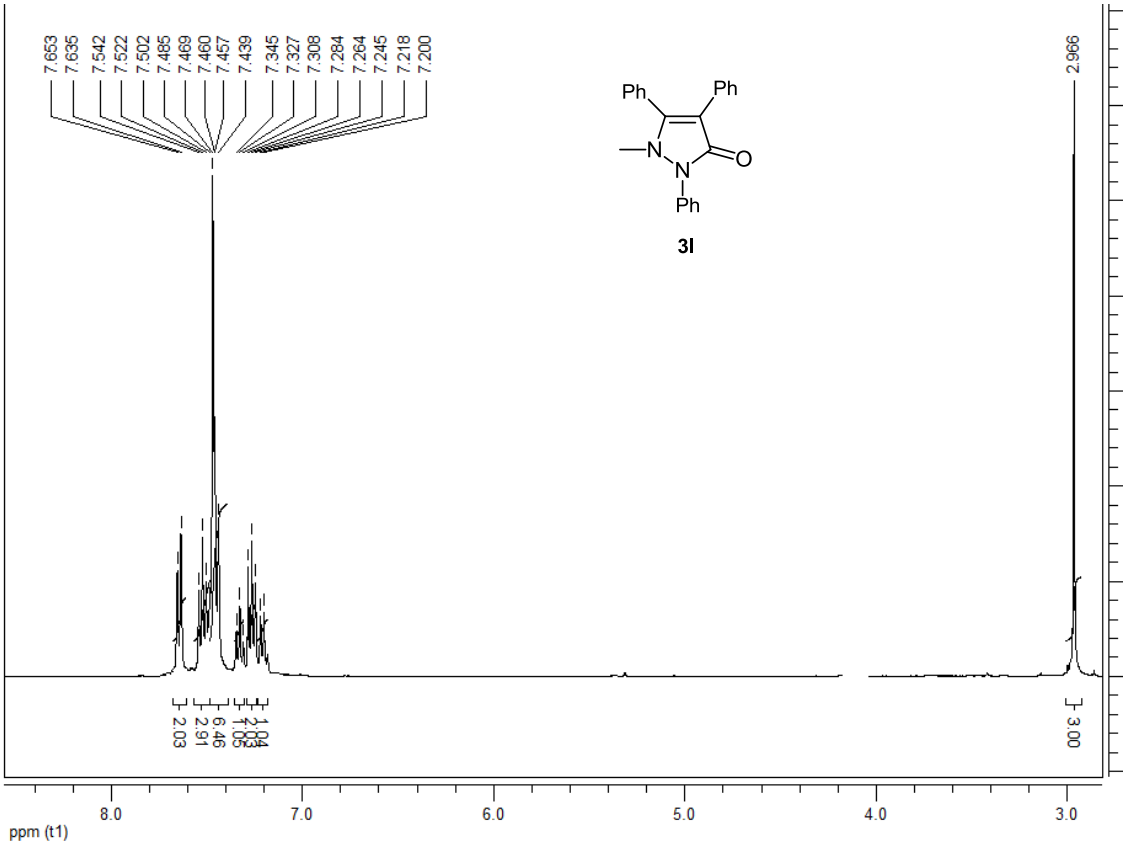
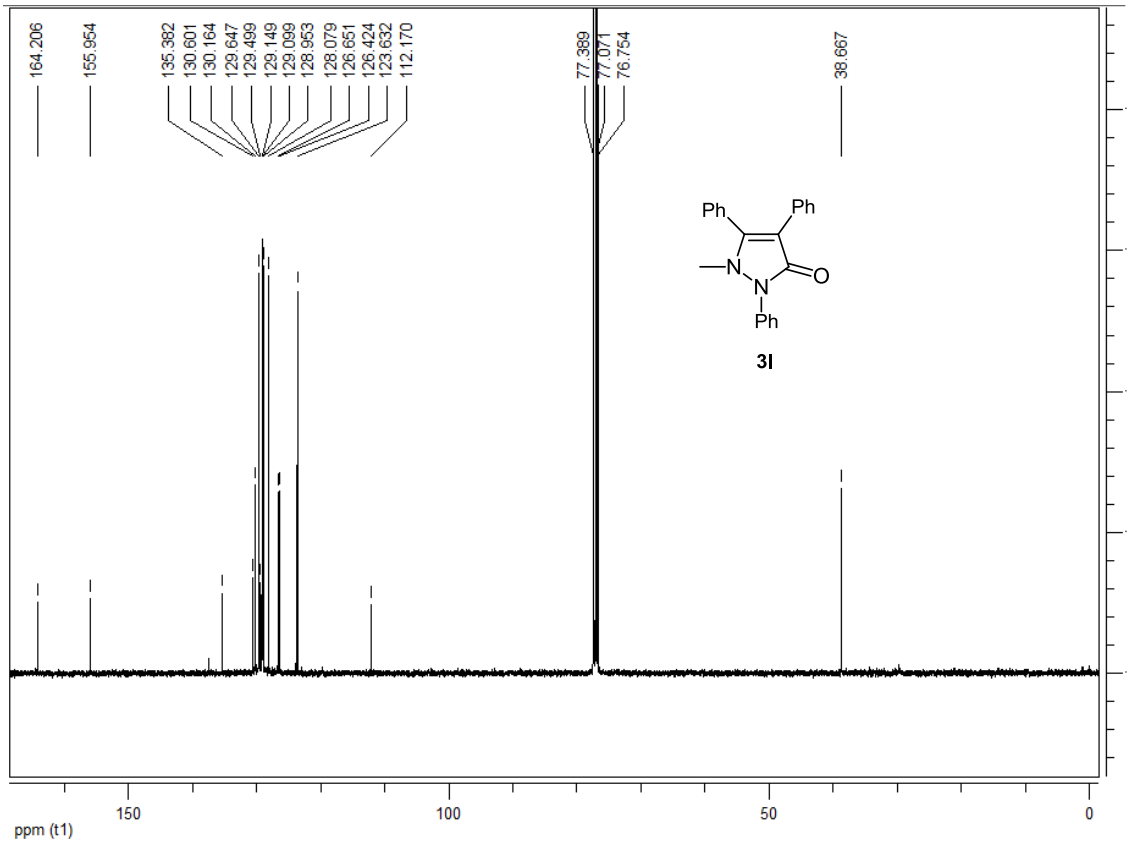
136.535
132.739
131.437
129.734
128.871
128.320
126.629
124.292
110.980
77.366
77.048
76.730
35.808
21.092
12.118
Ph
N
N
O
3k
150
100
50
ppm (t1)


7.653
7.635
7.542
7.522
7.502
7.485
7.469
7.460
7.457
7.439
7.345
7.327
7.308
7.284
7.264
7.245
7.218
7.200
2.966
Ph
Ph
N
N
O
Ph
3l
2.03
2.91
6.46
3.00
ppm (t1)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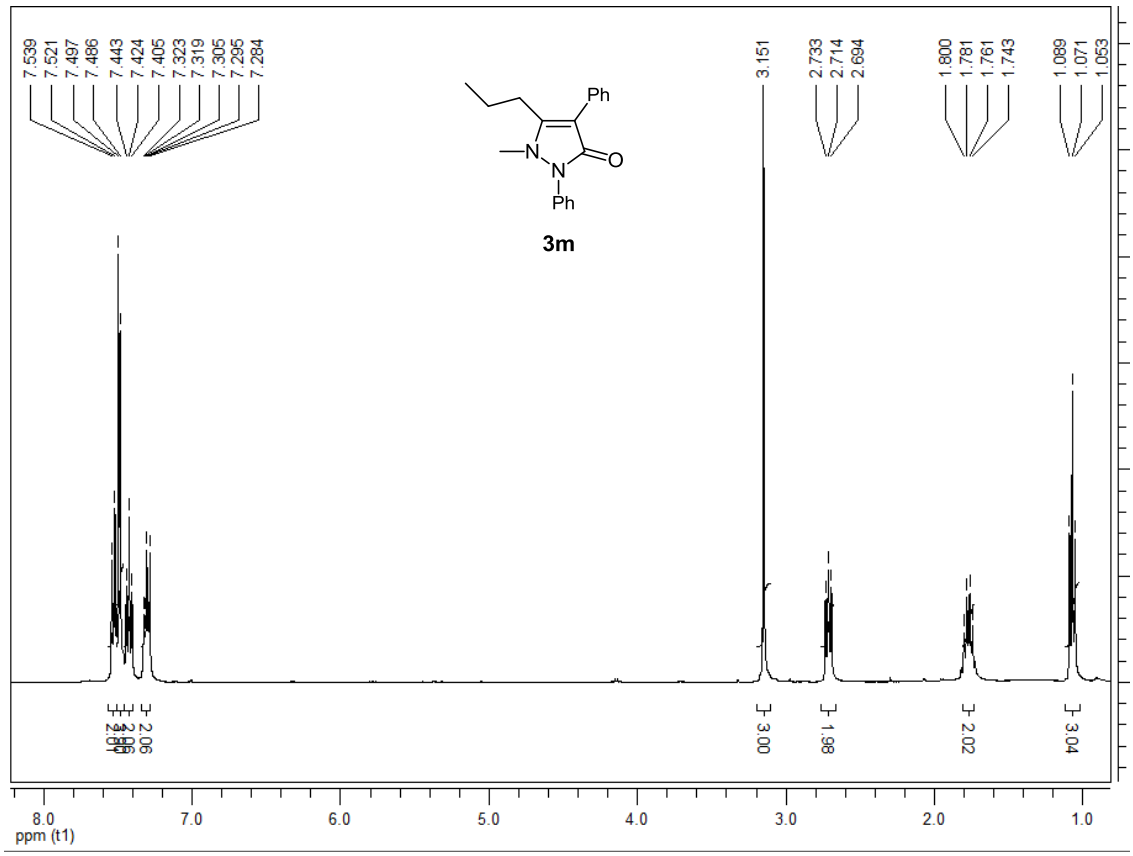
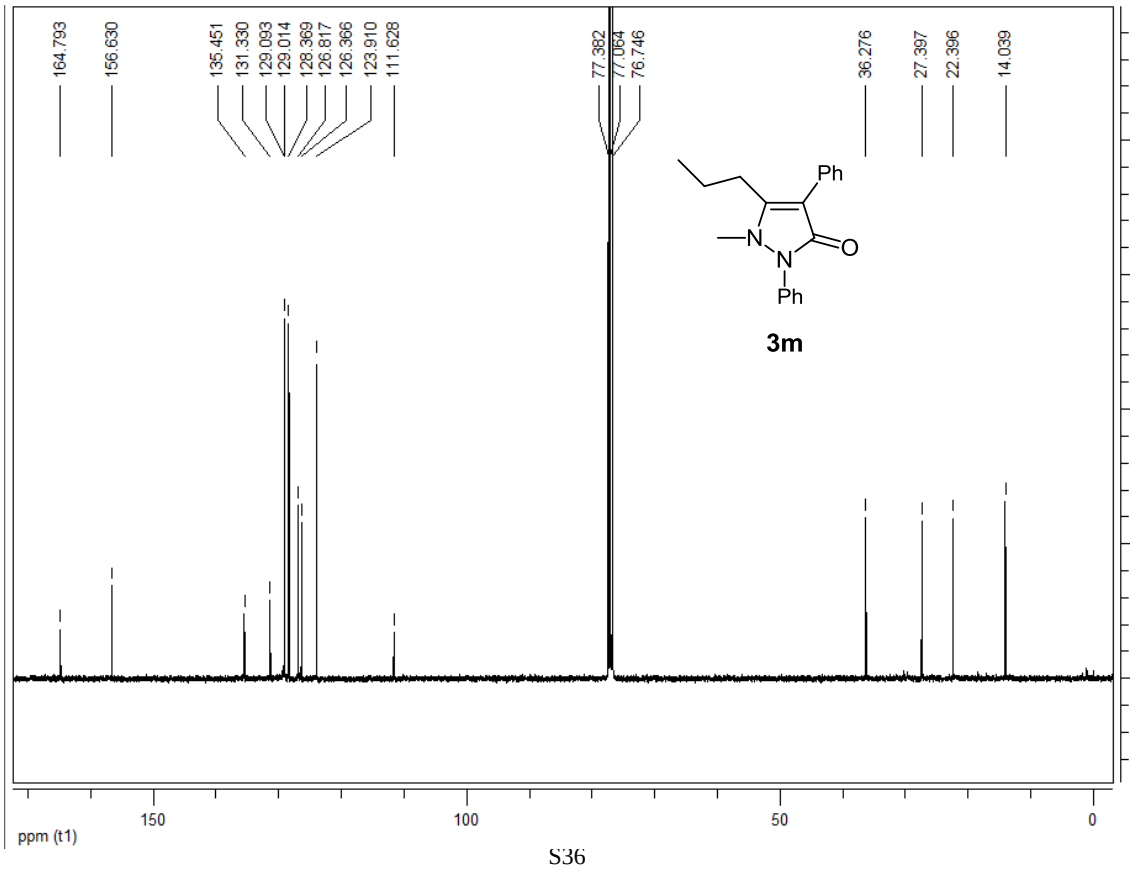
135.382
130.601
130.164
129.647
129.499
129.149
129.099
128.953
128.079
126.651
126.424
123.632
112.170
77.369
77.071
76.754
38.667
Ph
Ph
N
N
O
Ph
3l
ppm (t1)


7.539
7.521
7.497
7.486
7.443
7.424
7.405
7.323
7.319
7.305
7.295
7.284
3.151
2.733
2.714
2.694
1.800
1.781
1.761
1.743
1.089
1.071
1.053
Ph
N
N
O
Ph
3m
2.06
3.00
1.98
2.02
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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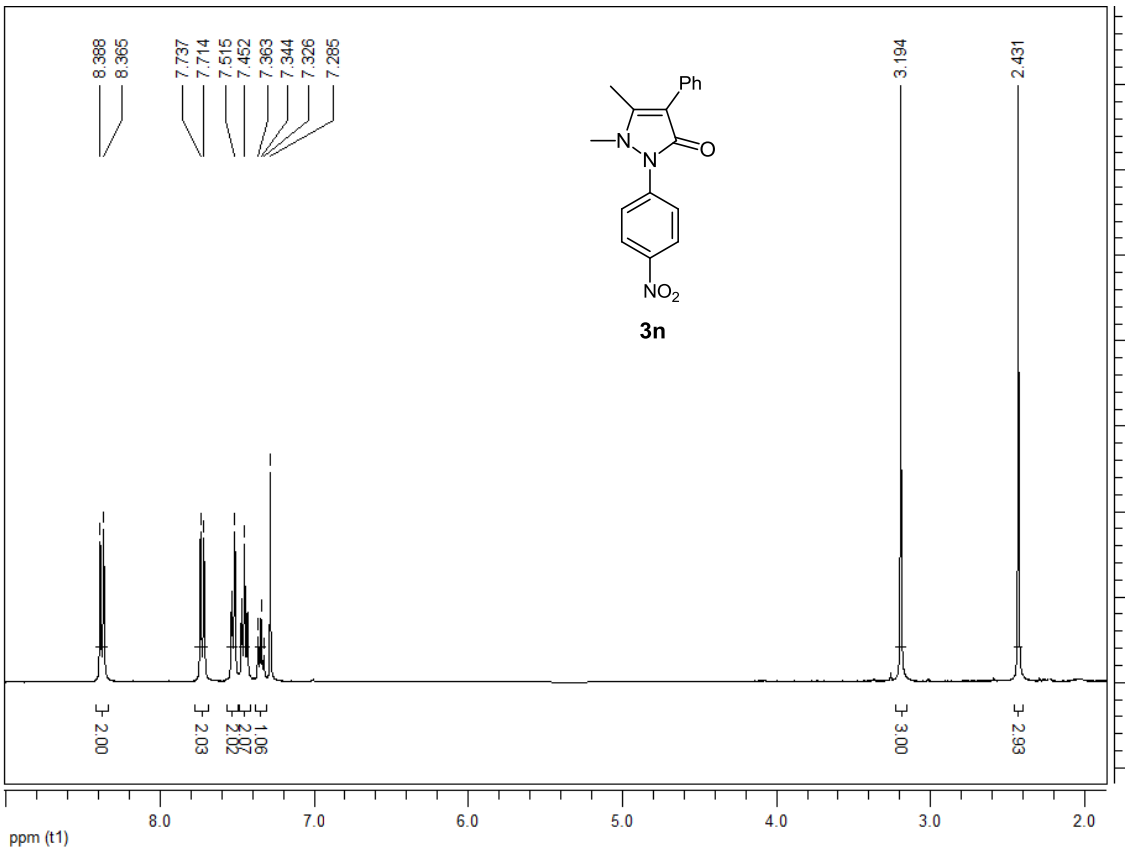
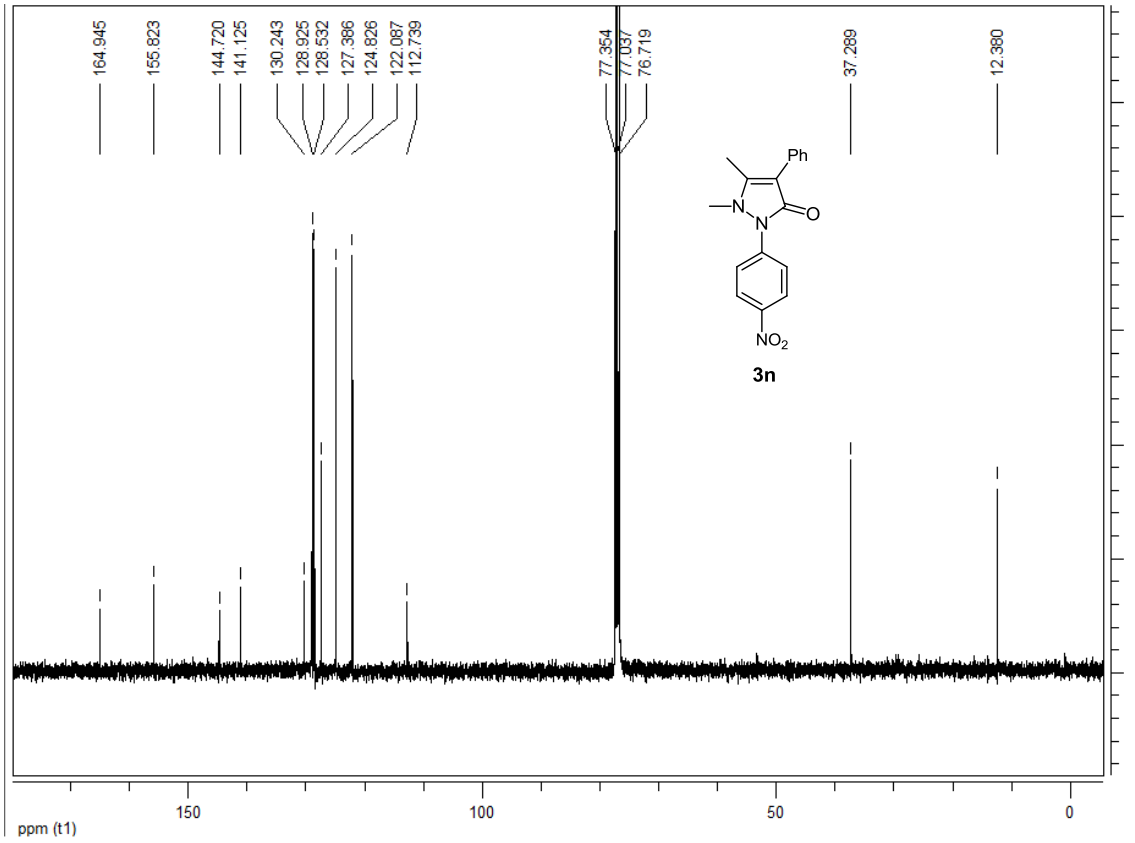
129.093
129.014
128.369
126.817
126.366
123.910
111.628
77.382
77.064
76.746
36.276
27.397
22.396
14.039
Ph
N
N
O
Ph
3m
150
100
50
0
ppm (t1)


8.388
8.365
7.737
7.714
7.515
7.452
7.363
7.344
7.326
7.285
3.194
2.431
Ph
N
N
O
NO2
3n
2.00
2.03
2.02
2.02
1.06
3.00
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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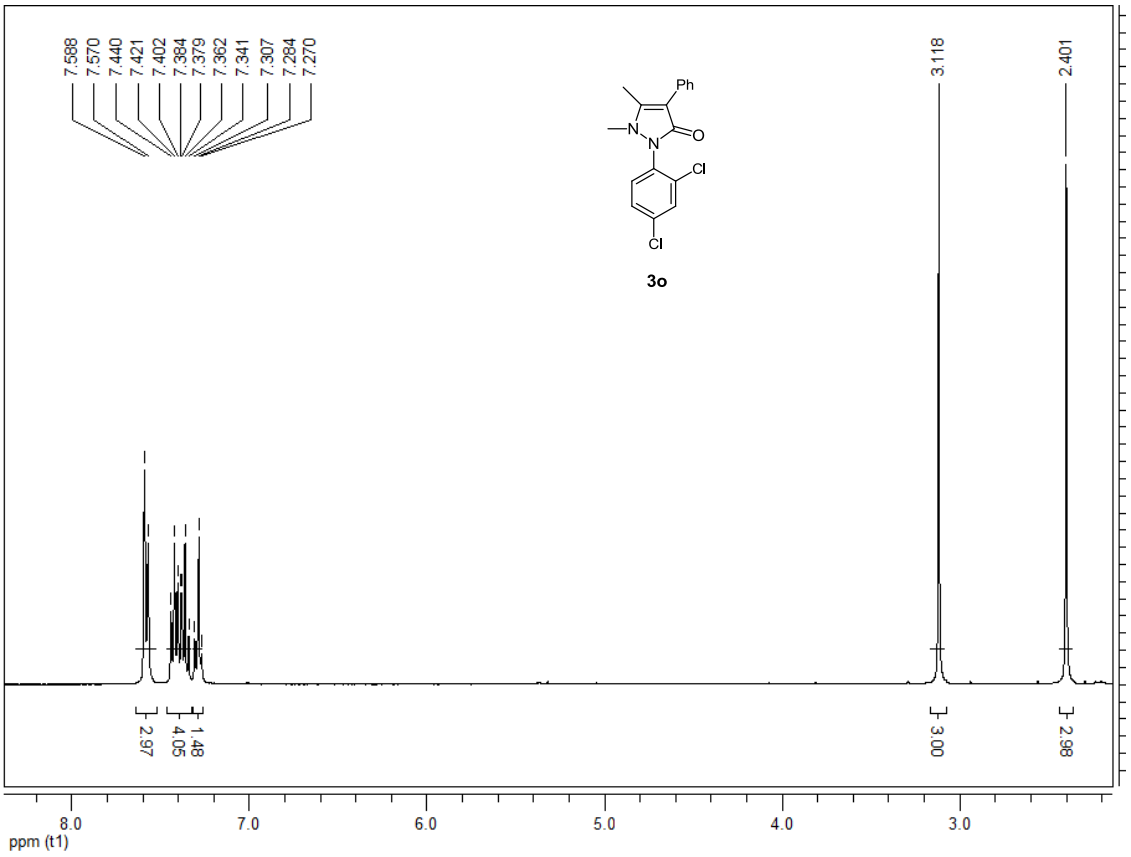
141.125
130.243
128.925
128.532
127.386
124.826
122.087
112.739
77.354
77.037
76.719
37.269
12.380
Ph
N
N
O
NO2
3n
150
100
50
0
ppm (t1)


7.588
7.570
7.440
7.421
7.402
7.384
7.379
7.362
7.341
7.307
7.284
7.270
3.118
2.401
Ph
N
N
O
Cl
Cl
3o
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4.06
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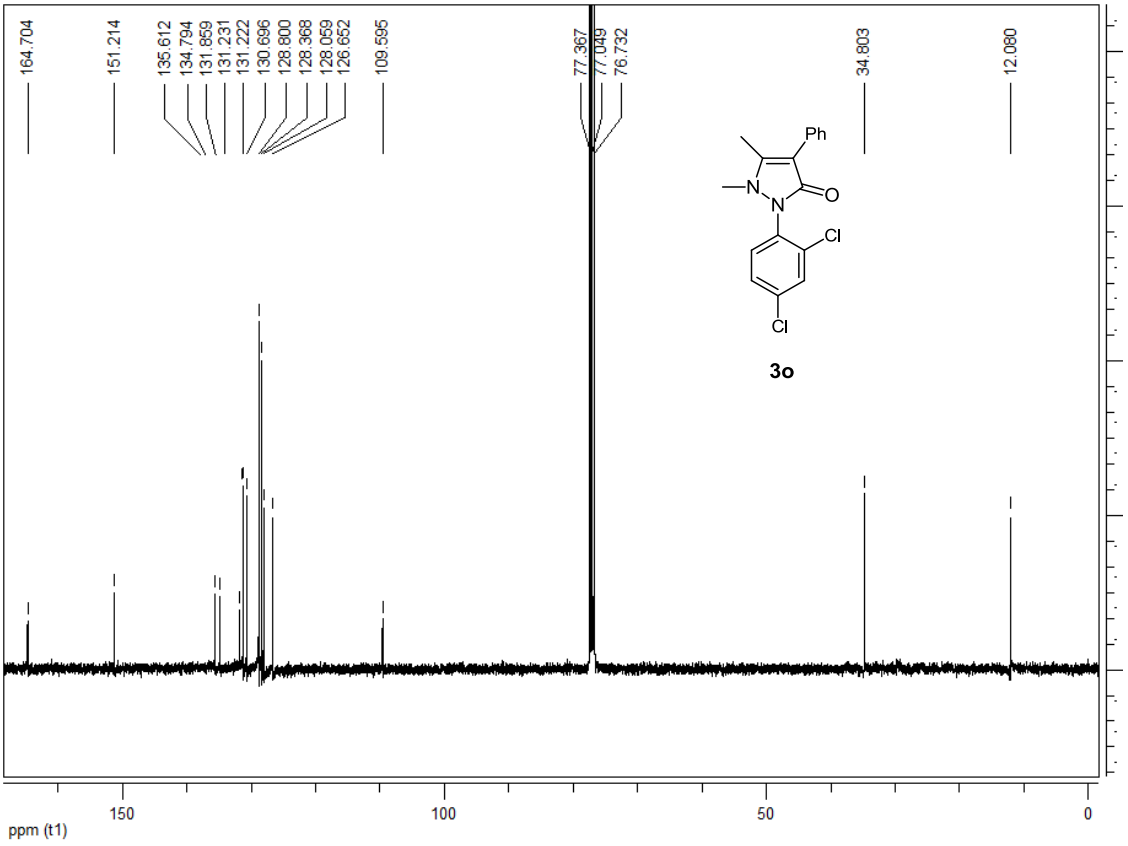
3.00
2.98
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)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131.231
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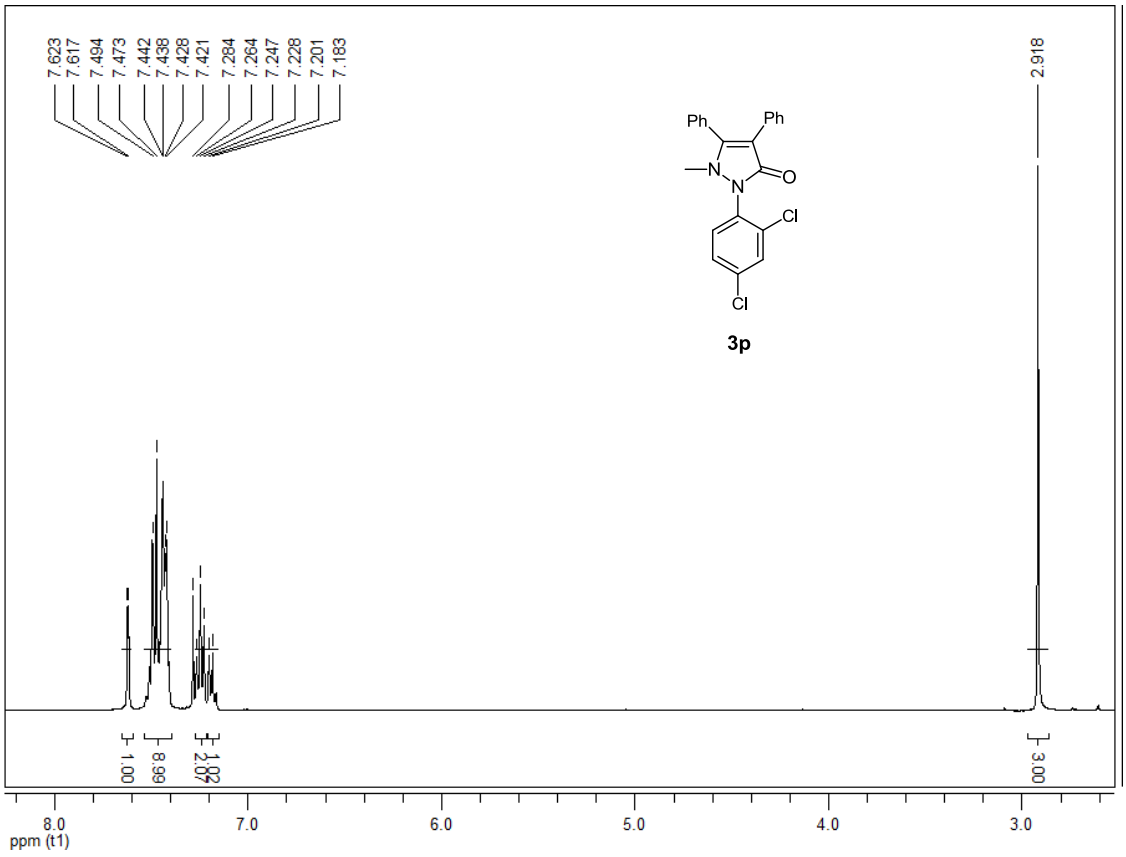
130.696
128.800
128.368
128.059
126.652
109.595
77.367
77.049
76.732
34.803
12.080
Ph
N
N
O
Cl
Cl
3o
150
100
50
0
ppm (t1)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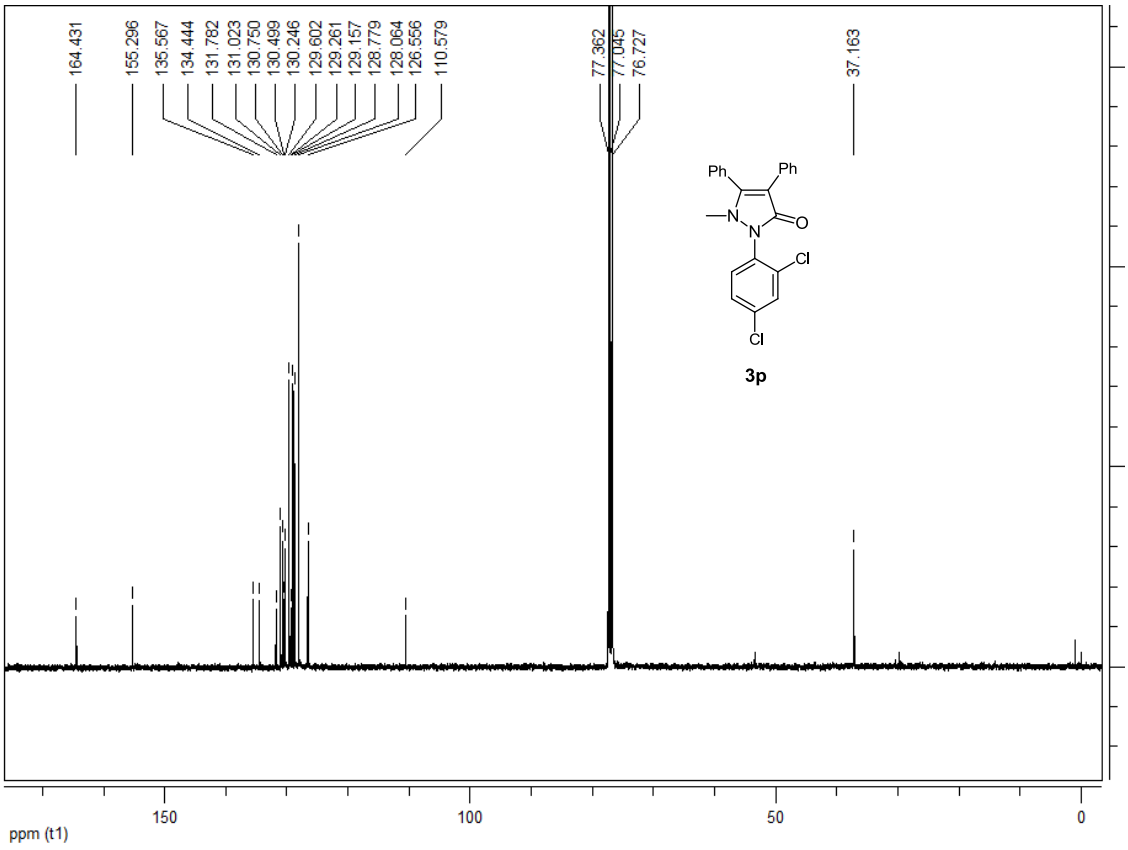
7.438
7.428
7.421
7.284
7.264
7.247
7.228
7.201
7.183
2.918
Ph
Ph
N
N
O
Cl
Cl
3p
1.00
8.99
2.07
3.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


164.431
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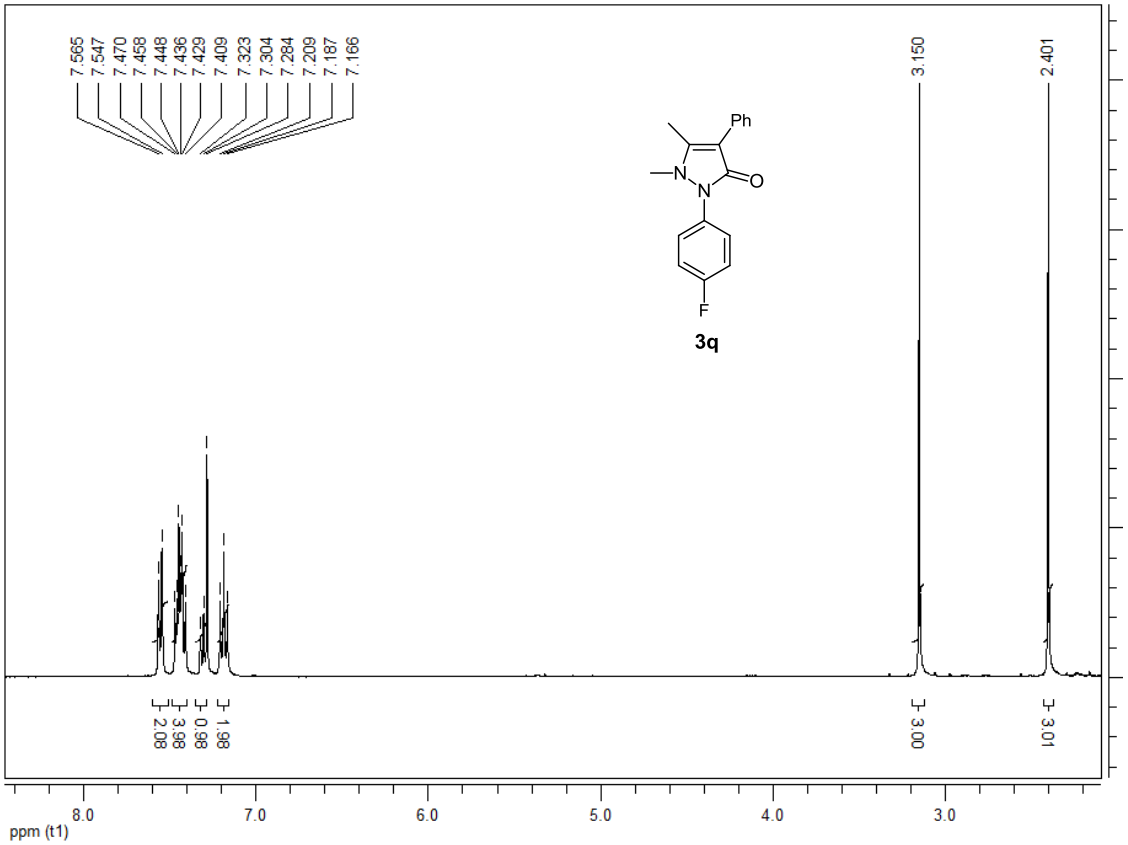
134.444
131.782
131.023
130.750
130.499
130.246
129.602
129.261
129.157
128.779
128.064
126.556
110.579
77.362
77.045
76.727
37.163
Ph
Ph
N
N
O
Cl
Cl
3p
150
100
50
0
ppm (t1)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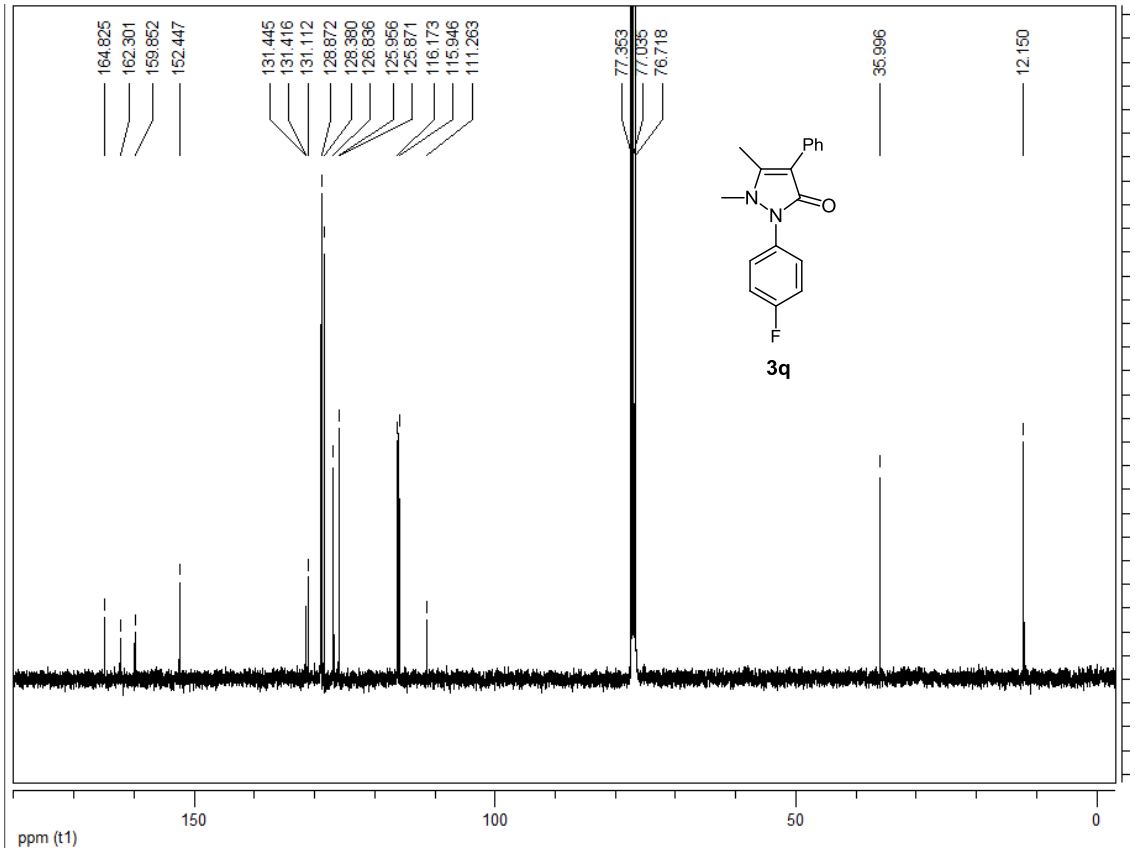
7.470
7.458
7.448
7.436
7.429
7.409
7.323
7.304
7.284
7.209
7.187
7.166
3.150
2.401
Ph
N
N
O
F
3q
2.08
3.98
0.98
1.98
3.00
3.01
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)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152.447
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131.416
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128.872
128.380
126.836
125.956
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116.173
115.946
111.263
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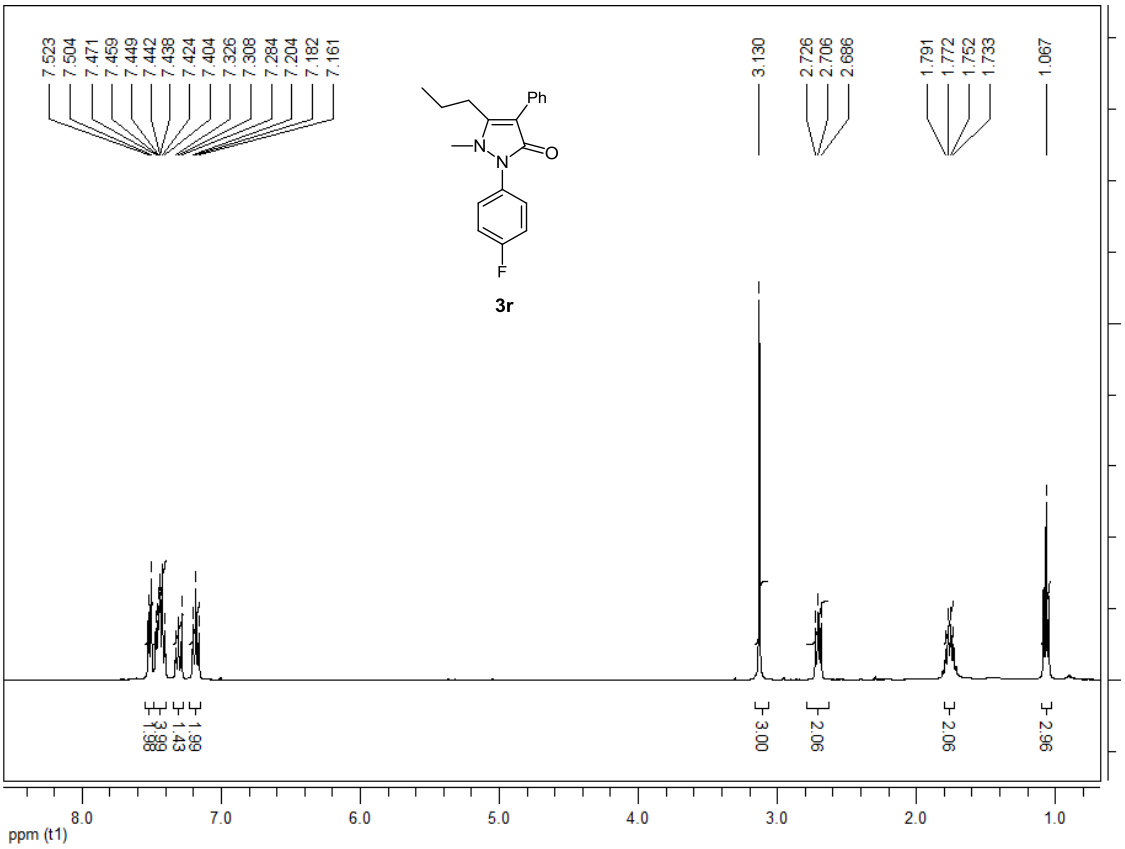
77.035
76.718
35.996
12.150
Ph
N
N
O
F
3q
150
100
50
0
ppm (t1)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7.442
7.438
7.424
7.404
7.326
7.308
7.284
7.204
7.182
7.161
3.130
2.726
2.706
2.686
1.791
1.772
1.752
1.733
1.067
Ph
N
N
O
F
3r
1.98
3.98
1.43
1.99
3.00
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2.06
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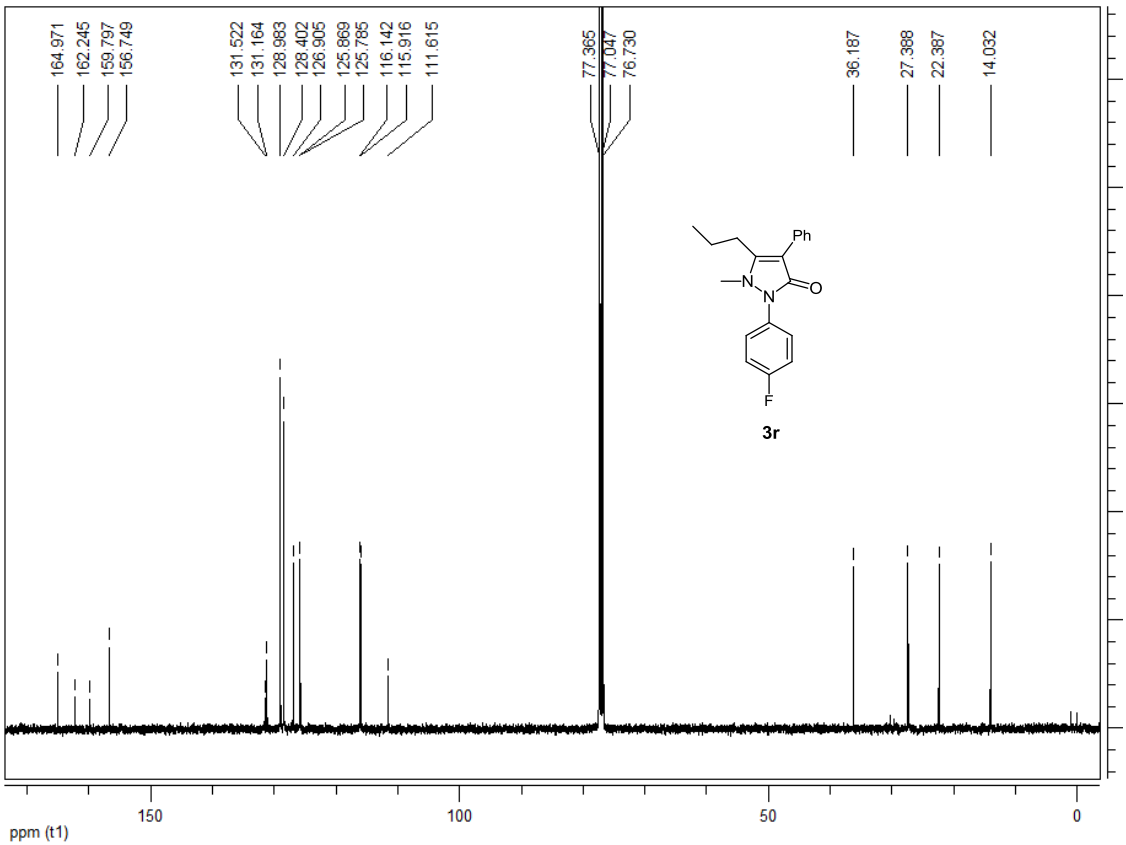
3.0
2.0
1.0
ppm (t1)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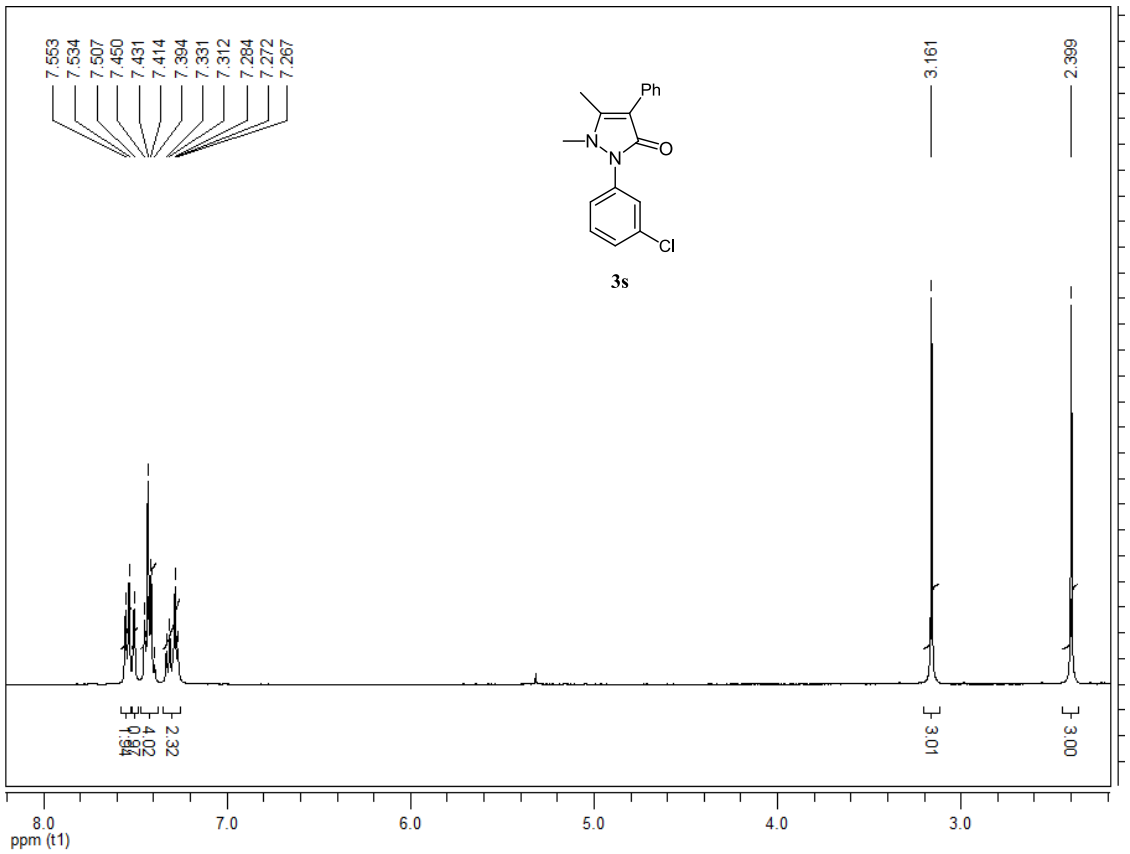
131.164
128.983
128.402
126.905
125.869
125.785
116.142
115.916
111.615
77.365
77.047
76.730
36.187
27.388
22.387
14.032
Ph
N
N
O
F
3r
150
100
50
0
ppm (t1)


7.553
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7.431
7.414
7.394
7.331
7.312
7.284
7.272
7.267
3.161
2.399
Ph
N
N
O
Cl
3s
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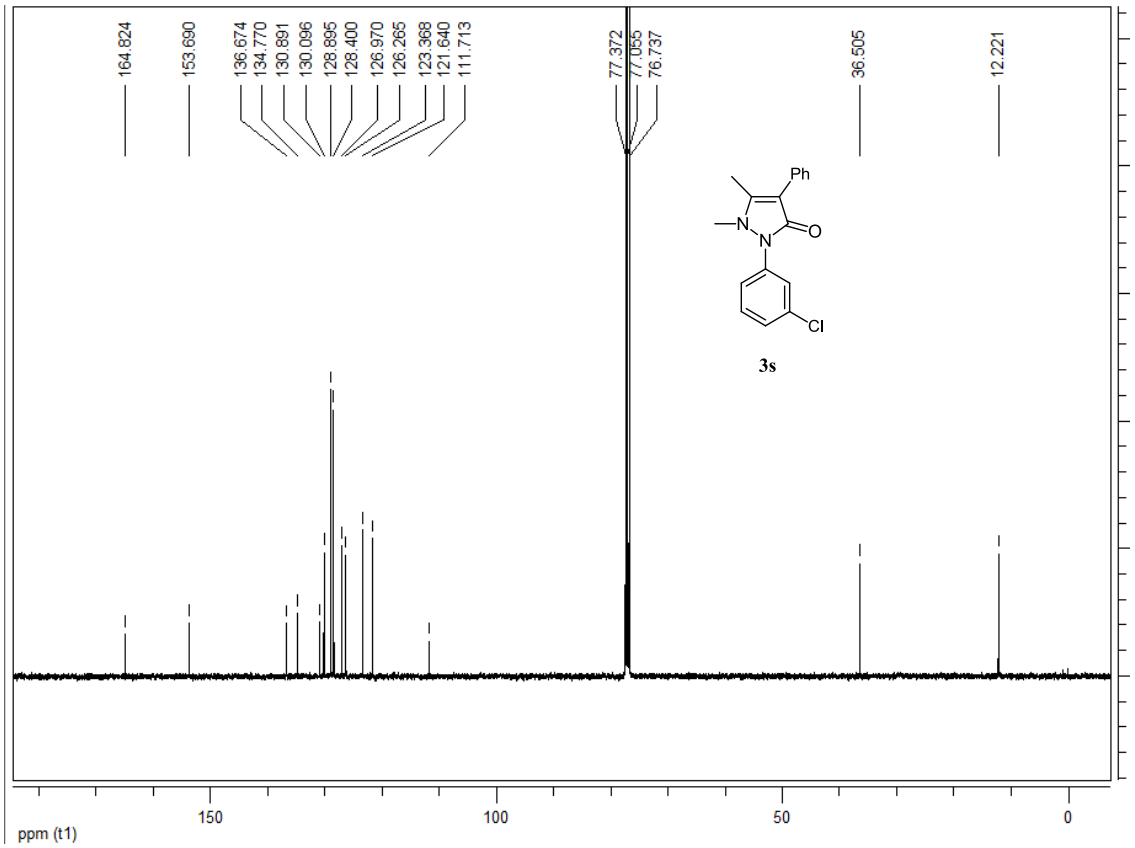
3.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)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128.400
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126.265
123.368
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111.713
77.372
77.055
76.737
36.505
12.221
Ph
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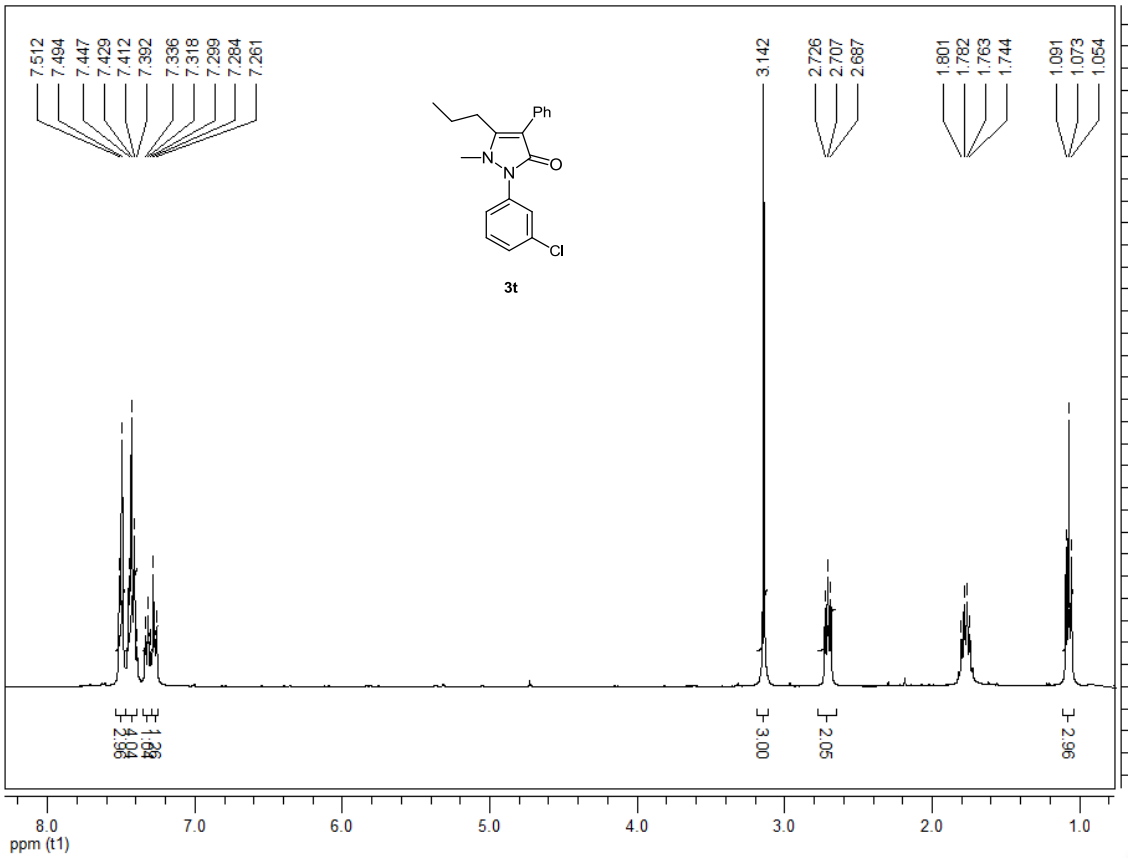
N
O
Cl
3s
150
100
50
0
ppm (t1)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7.494
7.447
7.429
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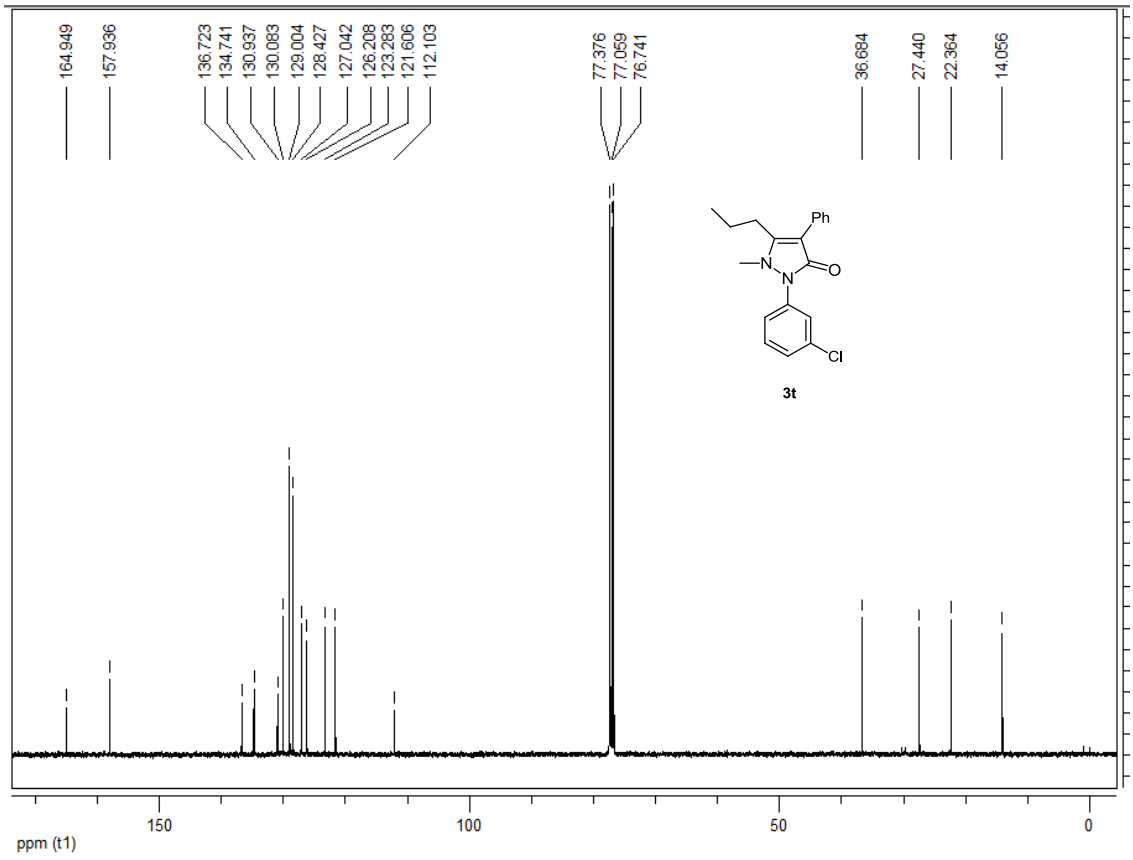
7.392
7.336
7.318
7.299
7.284
7.261
3.142
2.726
2.707
2.687
1.801
1.782
1.763
1.744
1.091
1.073
1.054
Ph
N
N
O
Cl
3t
3.00
2.05
2.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


164.949
157.936
136.723
134.741
130.937
130.083
129.004
128.427
127.042
126.208
123.283
121.606
112.103
77.376
77.059
76.741
36.684
27.440
22.364
14.056
Ph
N
N
O
Cl
3t
150
100
50
0
ppm (t1)