Supporting Information

The *in situ* generation and conversion of a half-zirconocene catalyst for the synthesis of N-acylpyrazoles

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Contents

1. General information.

All reagents were purchased from commercial sources and were used as received. Solvents were of AR and the reactions were monitored by TLC (thin layer chromatography). All procedures were carried out under open atmosphere with no precautions taken to exclude ambient moisture. Purification of the reaction products was carried out by flash chromatography on silica gel (200–300 mesh). Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker EQUINX 55 (400 MHz for ^{1}H; 101 MHz for ^{13}C) spectrometer by using $CDCl_3$ as a solvent. For ^{1}H NMR, tetramethyl silane (TMS) served as internal standard ($\delta = 0$) and ^{1}H NMR chemical shifts are reported in ppm downfield of tetramethyl silane and referenced to residual solvent peak ($CDCl_3$ at 7.26 ppm) unless otherwise noted. The data are reported as following: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiple), and coupling constant in Hz. For ^{13}C NMR, $CDCl_3$ -d1 was used as internal standard ($\delta = 77.0$ ppm) and spectra were obtained with complete proton decoupling. ESI-MS measurement was performed in the positive-ion mode (m/z 50−2500 range) on a MAXIS instrument from Bruker. This instrument has a hybrid quadrupole/ion mobility/orthogonal acceleration time-of-flight (oa-TOF) geometry and was used in the TOF V+ mode. All samples were dissolved in methanol and were directly infused into the ESI source at a flow rate of 4.0 mL/min after 1 min at 180 °C. ESI source conditions were as follows: capillary voltage 4.0 kV, nebulizer 0.4 bar, scan begin 100 m/z, scan end 1300 m/z, collision cell RF 200.0 Vpp, end plate offset -500 V.

2. ESI(+)-MS spectra and ^{1}H NMR of organometallic zirconocene complexes.

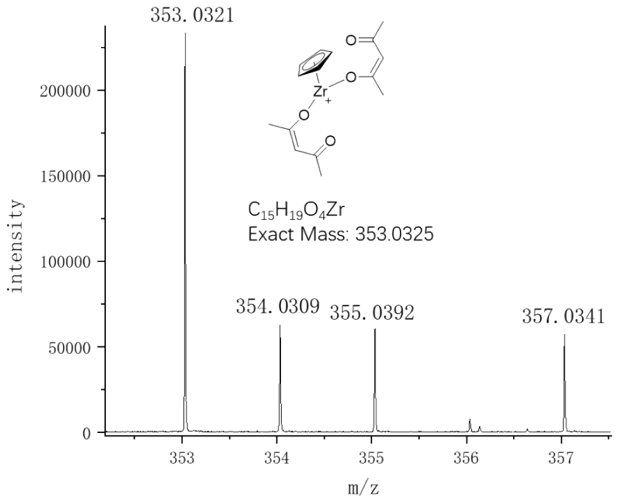


Figure S1. ESI(+)-MS spectra of organometallic zirconocene complexes

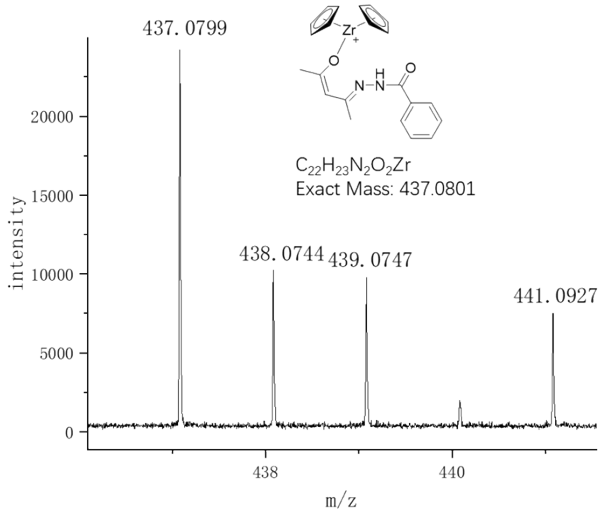


Figure S2. ESI(+)-MS spectra of organometallic zirconocene complexes

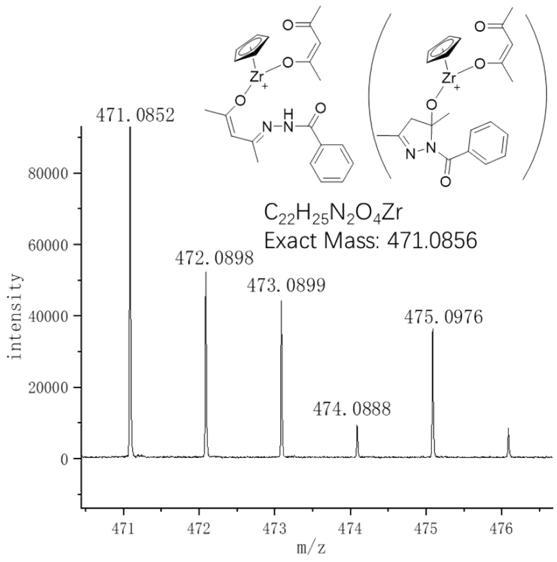


Figure S3. ESI(+)-MS spectra of organometallic zirconocene complexes

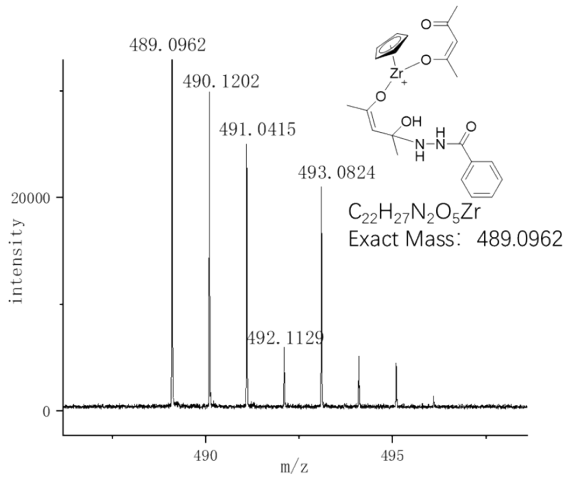


Figure S4. ESI(+)-MS spectra of organometallic zirconocene complexes

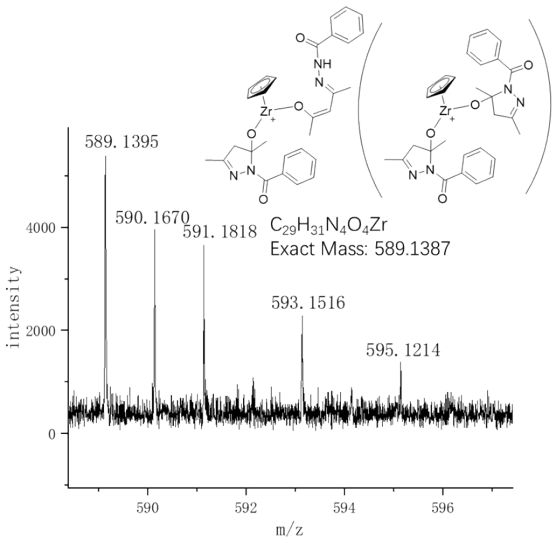


Figure S5. ESI(+)-MS spectra of organometallic zirconocene complexes

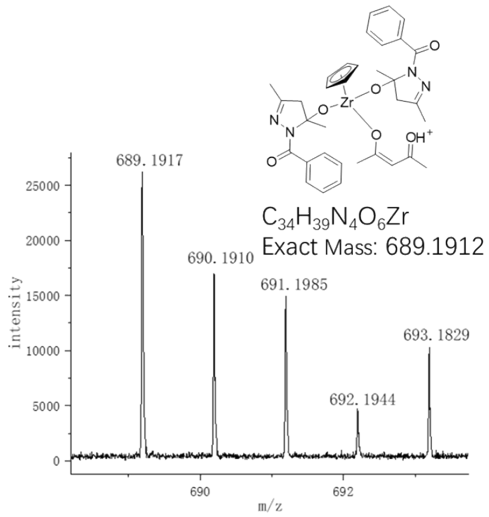


Figure S6. ESI(+)-MS spectra of organometallic zirconocene complexes

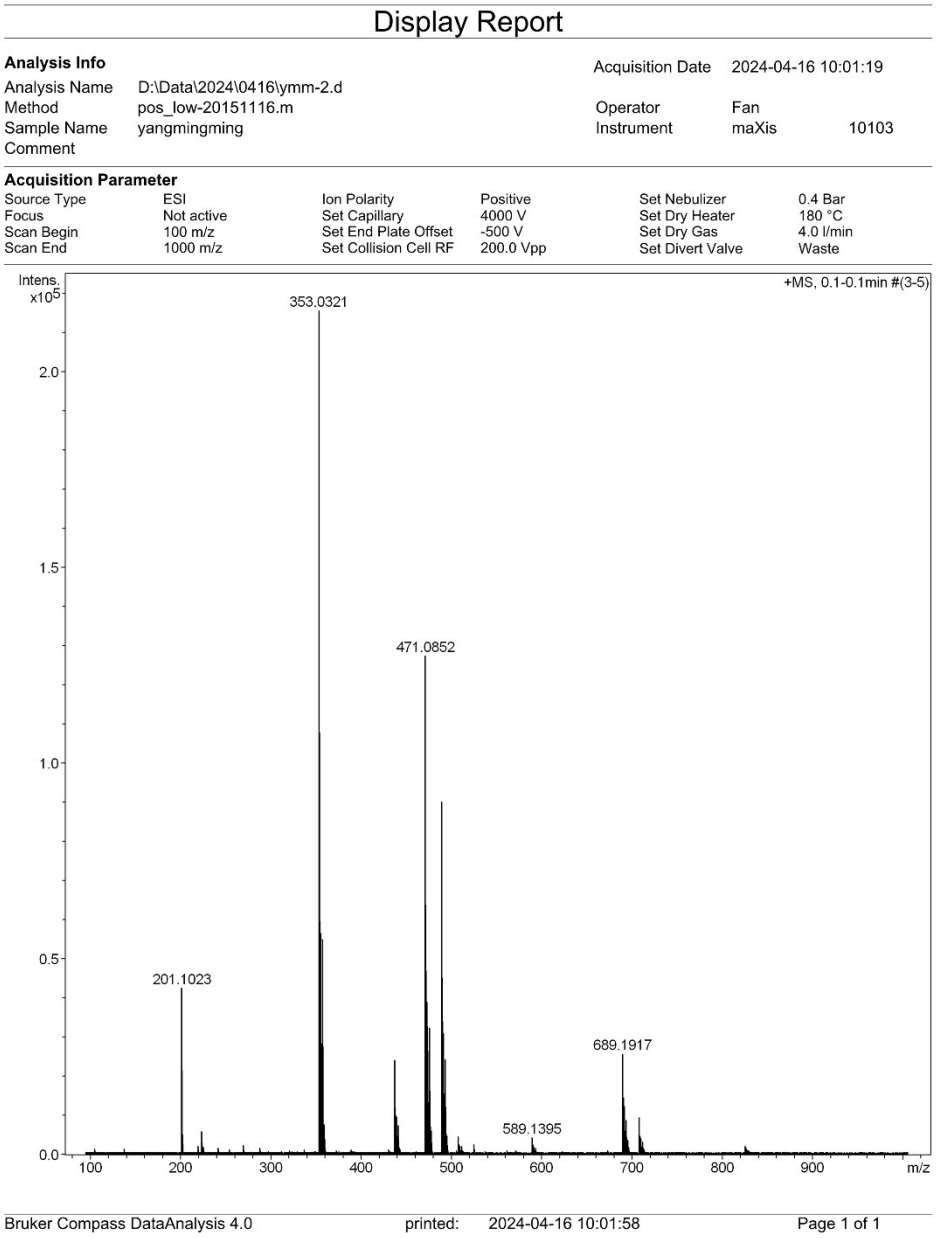


Figure S7. ESI(+)-MS spectra of *in situ* reaction.

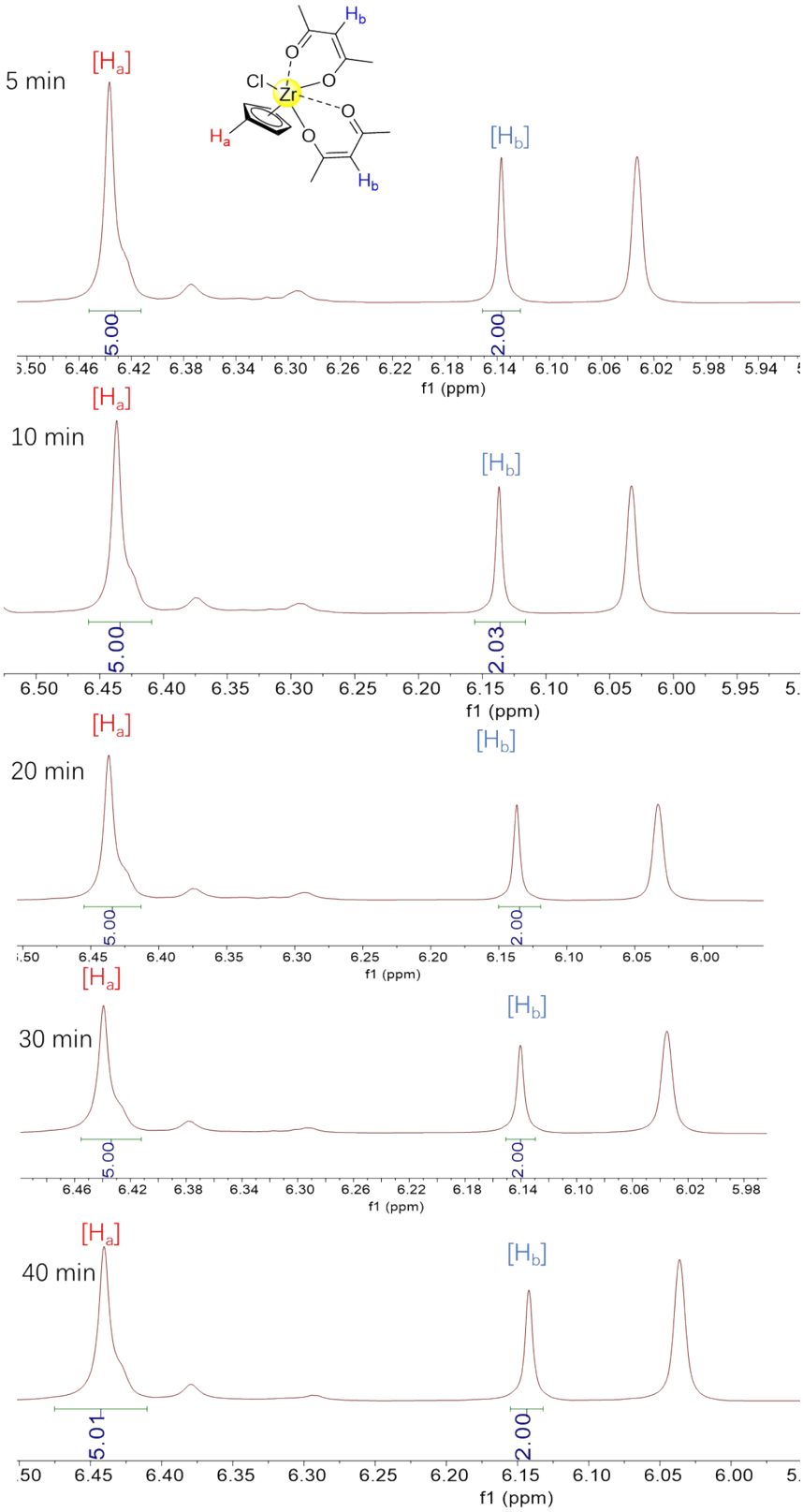


Figure S8. ^{1}H NMR of organometallic zirconocene complexes.

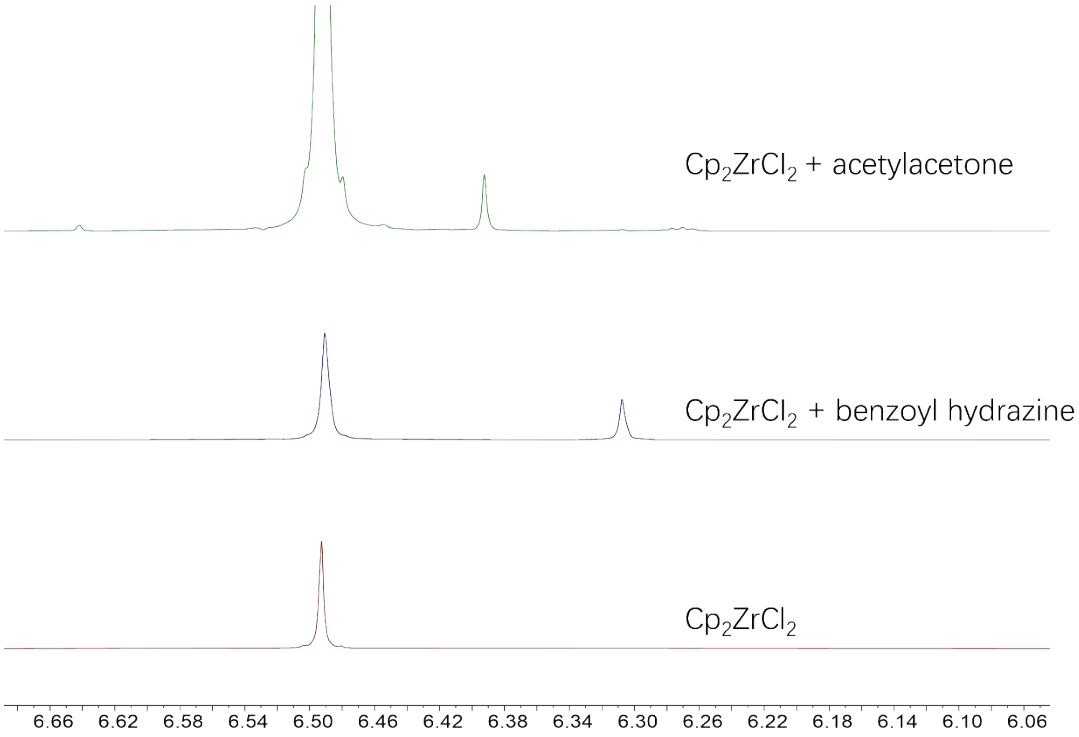
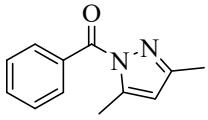
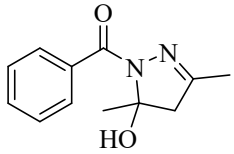


Figure S9. ^{1}H NMR of organometallic zirconocene complexes.

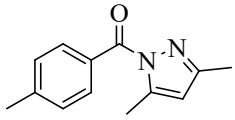
3. Experimental and characterization data of N-acylpyrazoles.



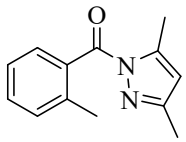
(3,5-dimethyl-1H-pyrazol-1-yl)(phenyl)methanone (3a). (Yellow liquid, 97mg, 97%);^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 (dd, *J* = 7.7, 2.5 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.43 (td, *J* = 7.8, 2.6 Hz, 2H), 6.03 (s, 1H), 2.61 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 168.5, 152.2, 145.1, 133.5, 132.5, 131.5, 127.9, 111.2, 14.4, 14.0; HRMS (ESI) calcd for $[C_{12}H_{12}N_2O+Na]^+$ 223.0842, found 223.0849.



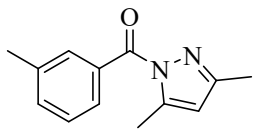
(5-hydroxy-3,5-dimethyl-4,5-dihydro-1H-pyrazol-1-yl)(phenyl)methanone (5a). (Yellow resin, 82.9 mg, 76%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.37 (dq, *J* = 14.1, 6.8 Hz, 3H), 5.36 (s, 1H), 2.97 (d, *J* = 18.4 Hz, 1H), 2.74 (d, *J* = 18.4 Hz, 1H), 1.92 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 155.6, 134.6, 131.2, 129.9, 127.8, 92.7, 51.1, 26.8, 16.3; HRMS (ESI) calcd for $[C_{12}H_{14}N_2O_2+Na]^+$ 241.0948, found 241.0951.



(3,5-dimethyl-1H-pyrazol-1-yl)(p-tolyl)methanone (3b). (Yellow oil, 103.8 mg, 97%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.03 (s, 1H), 2.61 (s, 3H), 2.40 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 152.0, 145.1, 143.4, 131.7, 130.5, 128.7, 111.0, 21.8, 14.40, 14.0; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O+Na]^+$ 237.0999, found 237.0997.

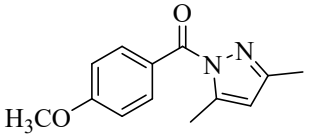


(3,5-dimethyl-1H-pyrazol-1-yl)(o-tolyl)methanone (3c). (Light yellow oil, 98.5 mg, 92%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.4 Hz, 1H), 7.38 (t, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 4.3 Hz, 2H), 6.04 (s, 1H), 2.66 (s, 3H), 2.34 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 170.2, 152.7, 144.6, 136.9, 134.8, 130.7, 129.1, 125.3, 111.6, 20.0, 14.5, 14.0; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O+Na]^+$ 237.0999, found 237.0995.

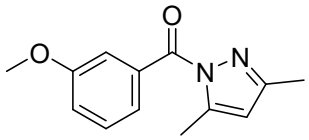


(3,5-dimethyl-1H-pyrazol-1-yl)(m-tolyl)methanone (3d). (Yellow oil, 96.3 mg, 90%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (t, *J* = 2.6 Hz, 2H), 7.37 – 7.30 (m, 2H), 6.04 (s, 1H),

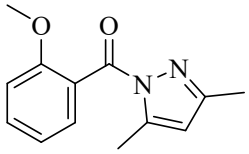
2.61 (s, 3H), 2.40 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 152.2, 145.1, 137.7, 133.4, 133.4, 131.7, 128.6, 127.8, 111.2, 21.5, 14.4, 14.0; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O+Na]^+$ 237.0999, found 237.0997.



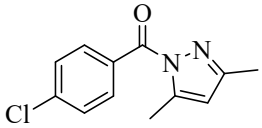
(3,5-dimethyl-1H-pyrazol-1-yl)(4-methoxyphenyl)methanone (3e). (Yellow oil, 112.8 mg, 98%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.00 (s, 1H), 3.82 (s, 3H), 2.57 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 163.3, 151.8, 145.0, 134.1, 125.4, 113.3, 110.8, 55.5, 14.3, 13.9; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O_2+Na]^+$ 253.0948, found 253.0947.



(3,5-dimethyl-1H-pyrazol-1-yl)(3-methoxyphenyl)methanone (3f). (Light yellow solid，m.p. 51-54 °C, 112.8 mg, 98%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.51 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 5.7 Hz, 1H), 6.06 (s, 1H), 3.84 (s, 3H), 2.62 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 159.1, 152.3, 145.2, 134.6, 129.0,124.0, 118.9, 116.1, 111.3, 55.5, 14.5, 14.0; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O_2+Na]^+$ 253.0948, found 253.0948.

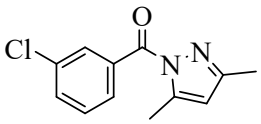


(3,5-dimethyl-1H-pyrazol-1-yl)(2-methoxyphenyl)methanone (3g). (Light yellow solid, m.p. 122-124 °C, 110.5 mg, 96%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.38 (m, 2H), 7.04 – 6.95 (m, 2H), 6.00 (s, 1H), 3.78 (s, 3H), 2.62 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 157.4, 152.3, 144.4, 132.1, 129.8, 124.9, 120.2, 111.8, 111.3, 56.0, 14.5, 14.0; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O_2+Na]^+$ 253.0948, found 253.0949.

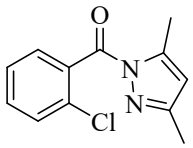


(4-chlorophenyl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone (3h). (Yellow oil, 101.8 mg, 87%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.05 (s, 1H), 2.61 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 152.6, 145.3, 138.9, 133.0, 131.8, 128.3, 111.4, 14.5, 14.0; HRMS (ESI) calcd for

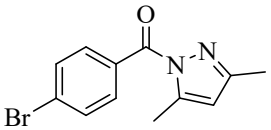
$[C_{12}H_{11}ClN_2O+Na]^+$ 257.0453, found 257.0459.



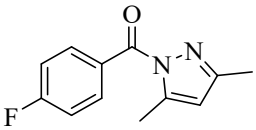
(3-chlorophenyl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone (3i). (Brown oil, 107.7 mg, 92%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 6.07 (s, 1H), 2.62 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 152.8, 145.4, 135.1, 134.0, 132.4, 131.4, 129.5, 129.3, 111.6, 14.5, 14.0; HRMS (ESI) calcd for $[C_{12}H_{11}ClN_2O+Na]^+$ 257.0453, found 257.0461.



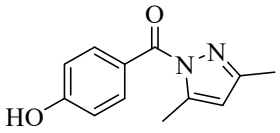
(2-chlorophenyl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone (3j). (Yellow oil, 108.8 mg, 93%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.40 (q, *J* = 9.2, 8.0 Hz, 2H), 7.36 – 7.30 (m, 1H), 6.04 (s, 1H), 2.65 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 153.4, 144.6, 135.2, 131.7, 131.3, 129.8, 129.4, 126.5, 111.9, 14.4, 14.0; HRMS (ESI) calcd for $[C_{12}H_{11}ClN_2O+Na]^+$ 257.0453, found 257.0451.



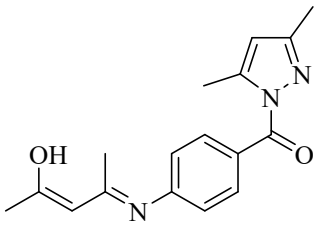
(4-bromophenyl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone (3k). (White solid, m.p. 36-40 °C, 127.9 mg, 92%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.05 (s, 1H), 2.61 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 152.6, 145.3, 133.0, 132.2, 131.3, 127.6, 111.5, 14.5, 14.0; HRMS (ESI) calcd for $[C_{12}H_{11}BrN_2O+Na]^+$ 300.9947, found 300.9934.



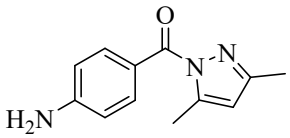
(3,5-dimethyl-1H-pyrazol-1-yl)(4-fluorophenyl)methanone (3l). (Brown solid, m.p. 38-42 °C, 97 mg, 89%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.06 (s, 1H), 2.62 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 166.7, 164.1, 152.4, 145.4, 134.3, 134.2, 129.5, 129.4, 115.3, 115.1, 111.3, 14.5, 14.0; HRMS (ESI) calcd for $[C_{12}H_{11}FN_2O+Na]^+$ 241.0748, found 241.0755.



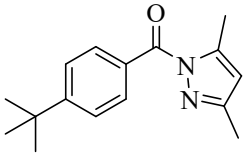
(3,5-dimethyl-1H-pyrazol-1-yl)(4-hydroxyphenyl)methanone (3m). (White resin, 71.3 mg, 66%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.5 Hz, 2H), 6.78 (s, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 6.07 (s, 1H), 2.58 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 152.6, 145.3, 133.0, 132.2, 131.3, 127.6, 111.5, 14.5, 14.0; HRMS (ESI) calcd for $[C_{12}H_{12}N_2O+H]^+$ 217.0972, found 217.0978.



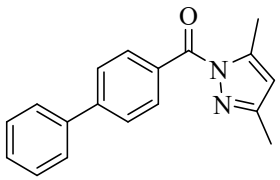
(Z)-4-((4-(3,5-dimethyl-1H-pyrazole-1-carbonyl)phenyl)amino)pent-3-en-2-one (3n). (Organe solid, m.p. 109-112 °C, 8.9 mg, 6%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.04 (s, 1H), 5.24 (s, 1H), 2.60 (s, 3H), 2.24 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.1, 167.4, 158.5, 152.2, 145.2, 143.1, 133.1, 128.9, 122.1, 111.1, 99.7, 29.6, 20.5, 14.4, 14.0; HRMS (ESI) calcd for $[C_{17}H_{19}N_3O_2+H]^+$ 298.1551, found 298.1551.



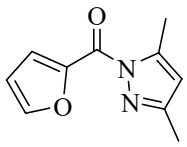
(4-aminophenyl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone (3o). (Yellow solid, m.p. 148-150 °C, 101.1 mg, 94%), ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 1H), 4.11 (s, 2H), 2.56 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 151.3, 151.3, 144.8, 134.4, 121.9, 113.5, 110.5, 14.2, 14.0; HRMS (ESI) calcd for $[C_{12}H_{13}N_3O+Na]^+$ 238.0951, found 238.0956.



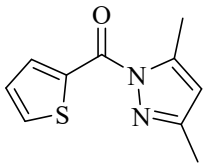
(4-(tert-butyl)phenyl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone (3p). (White soild, m.p. 67-69 °C, 119,1 mg, 93%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.04 (s, 1H), 2.61 (s, 3H), 2.25 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 156.2, 152.0, 145.1, 131.6, 130.4, 125.1, 111.0, 35.2, 31.2, 14.5, 14.0; HRMS (ESI) calcd for $[C_{16}H_{20}N_2O+Na]^+$ 279.1468, found 279.1473.



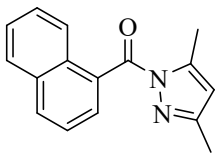
[1,1'-biphenyl]-4-yl(3,5-dimethyl-1H-pyrazol-1-yl)methanone (3q). (Yellow soild, m.p. 106-109 °C, 131.2 mg, 95%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 6.08 (s, 1H), 2.65 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 152.3, 145.4, 145.2, 140.3, 132.1, 132.0, 129.0, 128.2, 127.5, 126.8, 111.2, 14.5, 14.1; HRMS (ESI) calcd for $[C_{18}H_{16}N_2O+Na]^+$ 299.1155, found 299.1168.



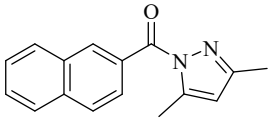
(3,5-dimethyl-1H-pyrazol-1-yl)(furan-2-yl)methanone (3r). (Yellow soild, m.p. 95-97 °C, 78.9 mg, 83%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 3.6 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 6.58 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.01 (s, 1H), 2.60 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.9, 152.8, 147.6, 145.9, 145.5, 124.1, 112.4, 111.1, 14.6, 14.0; HRMS (ESI) calcd for $[C_{10}H_{10}N_2O_2+Na]^+$ 213.0635, found 213.0635.



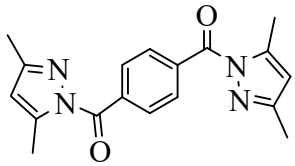
(3,5-dimethyl-1H-pyrazol-1-yl)(thiophen-2-yl)methanone (3s). (Light yellow oil, 97.9 mg, 95%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.73 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.18 – 7.12 (m, 1H), 6.03 (s, 1H), 2.62 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7, 152.3, 145.2, 137.9, 137.0, 134.1, 127.0, 111.4, 14.7, 14.0; HRMS (ESI) calcd for $[C_{10}H_{10}N_2OS+Na]^+$ 229.0407, found 229.0417.



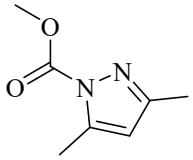
(3,5-dimethyl-1H-pyrazol-1-yl)(naphthalen-1-yl)methanone (3t). (White soild, m.p. 107-109 °C, 97.5 mg, 78%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.97 (m, 2H), 7.92 – 7.85 (m, 1H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.57 – 7.49 (m, 3H), 6.09 (s, 1H), 2.74 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 152.7, 145.0, 133.7, 132.0, 131.6, 131.0, 128.6, 127.3, 126.4, 125.4, 124.4, 111.8, 14.7, 14.0; HRMS (ESI) calcd for $[C_{16}H_{14}N_2O+Na]^+$ 273.0999, found 273.1012.



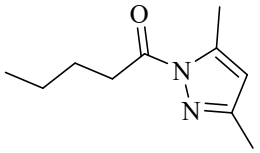
(3,5-dimethyl-1H-pyrazol-1-yl)(naphthalen-2-yl)methanone (3u). (White soild, m.p. 100-102 °C, 82.5 mg, 66%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.05 – 8.00 (m, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (t, *J* = 8.4 Hz, 2H), 7.62 – 7.51 (m, 2H), 6.10 (s, 1H), 2.68 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 152.4, 145.3, 135.3, 133.2, 132.3, 130.7, 129.6, 128.4, 127.8, 127.6, 127.1, 126.7, 111.2, 14.5, 14.1; HRMS (ESI) calcd for $[C_{16}H_{14}N_2O+Na]^+$ 273.0999, found 273.1012.



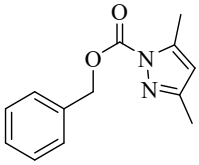
1,4-phenylenebis((3,5-dimethyl-1H-pyrazol-1-yl)methanone) (3v). (Yellow soild, m.p. 201-204 °C, 112.8 mg, 70%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 4H), 6.07 (s, 2H), 2.65 (s, 6H), 2.24 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 152.7, 145.3, 136.7, 130.6, 111.5, 14.5, 14.0; HRMS (ESI) calcd for $[C_{18}H_{18}N_4O_2+Na]^+$ 345.1322, found 345.1323.



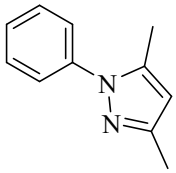
methyl 3,5-dimethyl-1H-pyrazole-1-carboxylate (3w). (White soild, m.p. 50-52 °C, 44.7 mg, 58%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.86 (s, 1H), 3.90 (s, 3H), 2.40 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.7, 150.8, 145.0, 110.6, 54.3, 14.0, 13.8; HRMS (ESI) calcd for $[C_7H_{10}N_2O_2+Na]^+$ 177.0635, found 177.0634.



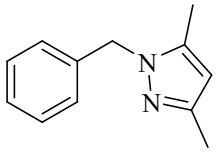
1-(3,5-dimethyl-1H-pyrazol-1-yl)pentan-1-one (3x). (Yellow liquid, 59.4 mg, 66%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.90 (s, 1H), 3.06 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 3H), 2.19 (s, 3H), 1.67 (p, *J* = 7.4 Hz, 2H), 1.38 (h, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 151.7, 144.0, 111.0, 34.9, 26.5, 22.3, 14.7, 14.0, 13.9; HRMS (ESI) calcd for $[C_{10}H_{16}N_2O+Na]^+$ 203.1155, found 203.1165.



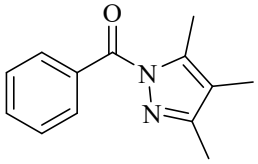
benzyl 3,5-dimethyl-1H-pyrazole-1-carboxylate (3y). (White soild, m.p. 54-56 °C, 94.3mg, 82%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 6.5 Hz, 2H), 7.36 (q, *J* = 7.8, 7.0 Hz, 3H), 5.95 (s, 1H), 5.43 (s, 2H), 2.48 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.8, 150.5, 145.1, 135.1, 128.9, 128.8, 128.7, 110.9, 69.3, 14.3, 14.0; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O_2+Na]^+$ 253.0948, found 253.0952.



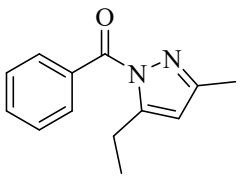
3,5-dimethyl-1-phenyl-1H-pyrazole (6a) (Brown oil, 76.6 mg, 89%), ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 – 7.41 (m, 4H), 7.36 – 7.29 (m, 1H), 6.02 (s, 1H), 2.23 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.3, 140.2, 139.6, 129.6, 127.4, 124.6, 107.6, 13.8, 12.7; J. Iran. Chem. Soc. 2013, 10, 213-219.



1-benzyl-3,5-dimethyl-1H-pyrazole (6b) (Yellow liquid, 72.6 mg, 78%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 2H), 5.84 (s, 1H), 5.20 (s, 2H), 2.24 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.6, 139.4, 137.4, 128.8, 127.5, 126.7, 105.7, 52.7, 13.6, 11.2; J. Org. Chem. 2021,86,14,9723-9732.

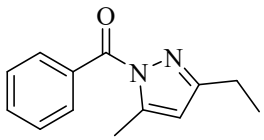


(E)-N'-(3-methyl-4-oxopent-2-en-2-yl)benzohydrazide (4a). (Yellow oil, 96.3 mg, 90%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 2.19 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 152.6, 140.6, 133.8, 132.3, 131.4, 127.9, 117.6, 12.7, 12.5, 7.8; HRMS (ESI) calcd for $[C_{13}H_{16}N_2O_2+Na]^+$ 237.0999, found 237.1006.

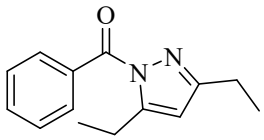


(5-ethyl-3-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4b). (Yellow oil, 27.8 mg, 26%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.10 (s, 1H), 2.63 (s, 3H), 2.62 – 2.57 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 157.9, 145.2, 133.4, 132.6, 131.6, 127.9,

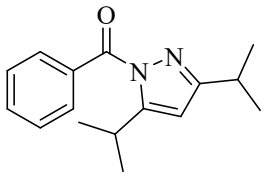
109.7, 21.7, 14.6, 13.3; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O+Na]^+$ 237.0999, found 237.1008.



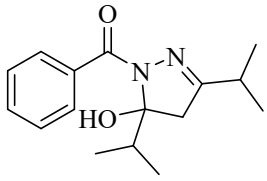
(3-ethyl-5-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4c). (Yellow oil, 69.6 mg, 65%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.10 (s, 1H), 3.08 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 152.3, 151.7, 133.6, 132.5, 131.4, 128.0, 109.3, 21.7, 14.1, 12.9; HRMS (ESI) calcd for $[C_{13}H_{14}N_2O+Na]^+$ 237.0999, found 237.1008.



(3-ethyl-5-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4d). (Yellow liquid, 98.1 mg, 86%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 6.14 (s, 1H), 3.10 (q, *J* = 7.3 Hz, 2H), 2.63 (q, *J* = 7.5 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 157.8, 151.6, 133.7, 132.5, 131.6, 127.9, 107.8, 21.8, 13.3, 12.9; HRMS (ESI) calcd for $[C_{14}H_{16}N_2O+H]^+$ 229.1336, found 229.1340.

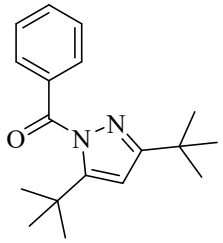


(3,5-diisopropyl-1H-pyrazol-1-yl)(phenyl)methanone (4e). (White oil, 116.6 mg, 91%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.16 (s, 1H), 3.77 (hept, *J* = 7.1 Hz, 1H), 2.93 (hept, *J* = 7.2 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.24 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 161.7, 156.5, 133.9, 132.4, 131.7, 127.8, 104.7, 28. 1, 27.0, 22.7, 22.3; HRMS (ESI) calcd for $[C_{16}H_{20}N_2O+Na]^+$ 279.1468, found 278.1469.

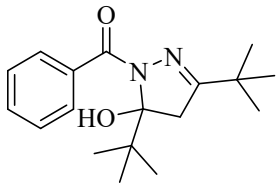


(5-hydroxy-3,5-diisopropyl-4,5-dihydro-1H-pyrazol-1-yl)(phenyl)methanone (5b). (Yellow solid, m.p. 86-89 ℃, 122 mg ,89%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 4.96 (s, 1H), 2.98 (p, *J* = 6.8

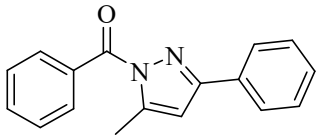
Hz, 1H), 2.90 (d, *J* = 18.6 Hz, 1H), 2.72 (d, *J* = 18.5 Hz, 1H), 2.64 (p, *J* = 6.8 Hz, 1H), 1.16 – 1.12 (m, 6H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168. 7, 163.3, 134.6, 131.2, 130.1, 127.7, 98.8, 39.8, 34.5, 30.0, 20.1, 20.0, 17.9, 16.8; HRMS (ESI) calcd for $[C_{16}H_{22}N_2O_2+Na]^+$ 297.1574, found 297.1577.



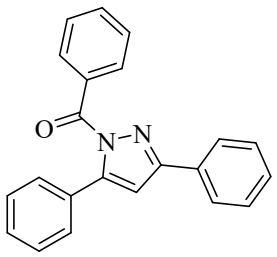
(3,5-di-tert-butyl-1H-pyrazol-1-yl)(phenyl)methanone (4f) (Light yellow resin, 88mg, 62%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 6.17 (s, 1H), 1.46 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 162.8, 157.7, 134.7, 132.3, 131.8, 127.7, 105.7, 33.2, 32.4, 30.0, 29.9; HRMS (ESI) calcd for $[C_{18}H_{24}N_2O+Na]^+$ 307.1781, found 307.1782.



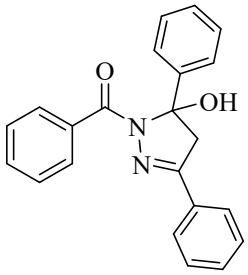
(3,5-di-tert-butyl-5-hydroxy-4,5-dihydro-1H-pyrazol-1-yl)(phenyl)methanone (5c). (Light yellow resin, 120.8 mg, 85%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 6.70 (s, 1H), 3.13 (d, *J* = 18.2 Hz, 1H), 2.88 (d, *J* = 18.2 Hz, 1H), 1.13 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 166.9, 135.0, 131.1, 130.2, 127.5, 102.3, 43.1, 41.6, 34.5, 27.9, 25.3; HRMS (ESI) calcd for $[C_{18}H_{26}N_2O_2+Na]^+$ 325.1877, found 325.1879.



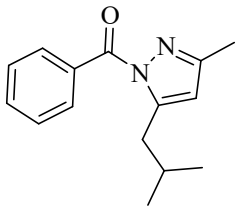
(5-methyl-3-phenyl-1H-pyrazol-1-yl)(phenyl)methanone (4g). (White solid, m.p. 82-84 ^{o}C, 30.14 mg, 23%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.09 (m, 2H), 7.85 – 7.79 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.36 (m, 3H), 6.59 (s, 1H), 2.74 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 153.6, 145.9, 133.2, 132.7, 132.1, 131.9, 129.1, 128.8, 127.9, 126.4, 108.1, 14.8; HRMS (ESI) calcd for $[C_{17}H_{14}N_2O+Na]^+$ 285.0999, found 285.1000.



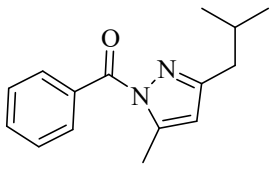
(3,5-diphenyl-1H-pyrazol-1-yl)(phenyl)methanone (4h). (Light yellow soild, m.p. 128-131 °C, 94 mg, 58%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 7.2 Hz, 2H), 7.90 (d, *J* = 6.8 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.50 (m, 4H), 7.47 – 7.38 (m, 6H), 6.89 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 153.7, 148.7, 133.3, 132.6, 132.1, 131.9, 130.9, 129.2, 128.9, 128.9, 128.6, 128.4, 128.2, 126.5, 109.1; HRMS (ESI) calcd for $[C_{22}H_{16}N_2O+Na]^+$ 347.1155, found 347.1172.



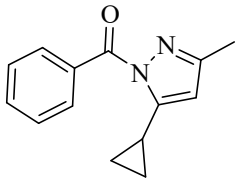
(5-hydroxy-3,5-diphenyl-4,5-dihydro-1H-pyrazol-1-yl)(phenyl)methanone (5d). (Yellow soild, m.p.130-132 °C, 71.8 mg, 42%), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.08 (m, 2H), 7.75 – 7.68 (m, 2H), 7.60 – 7.53 (m, 3H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.45 – 7.38 (m, 5H), 7.33 (t, *J* = 7.3 Hz, 1H), 5.55 (s, 1H), 3.77 (d, *J* = 18.2 Hz, 1H), 3.45 (d, *J* = 18.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) 163.1, 148.3, 138.6, 128.5, 126.7, 126.0, 125.5, 125.3, 123.7, 123.7, 123.1, 122.7, 121.7, 119.0, 90.0, 44.7; HRMS (ESI) calcd for $[C_{22}H_{18}N_2O_2+Na]^+$ 365.1261, found 365.1263.



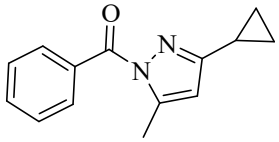
(5-isobutyl-3-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4i) (Colorless liquid, 38.7mg, 30%),^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.3 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.06 (s, 1H), 2.91 (d, *J* = 7.7 Hz, 2H), 2.25 (s, 3H), 2.02 (dp, *J* = 13.5, 6.6 Hz, 1H), 0.98 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 152.0, 148.9, 133.7, 132.5, 131.4, 128.0, 111.2, 36.7, 27.9, 22.6, 14.0.



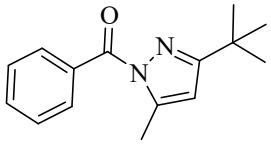
(3-isobutyl-5-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4j) (Colorless liquid, 71.4mg, 59%),[1]H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.07 (s, 1H), 2.64 (s, 3H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.96 (dp, *J* = 13.5, 6.7 Hz, 1H), 0.96 (s, 3H), 0.95 (s, 3H); [13]C NMR (101 MHz, Chloroform-*d*) δ 168.6, 155.8, 144.9, 133.5, 132.6, 131.6, 128.0, 110.7, 37.5, 28.5, 22.6, 14.6.



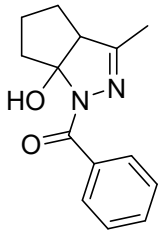
(5-cyclopropyl-3-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4k) (Yellow-green oil, 39.6mg, 35%), [1]H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 5.85 (s, 1H), 2.60 (tt, *J* = 8.5, 5.3 Hz, 1H), 2.22 (s, 3H), 1.05 (q, *J* = 6.4 Hz, 2H), 0.71 (q, *J* = 6.4, 5.6 Hz, 2H); [13]C NMR (101 MHz, Chloroform-*d*) δ 168.5, 152.4, 152.2, 133.6, 132.6, 131.5, 128.0, 106.9, 14.1, 8.9, 8.8; Chem. Eur. J. 2024, e202401105.



(3-cyclopropyl-5-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4l) (Yellow-green oil, 45mg, 40%), [1]H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.86 (s, 1H), 2.61 (s, 3H), 1.91 (tt, *J* = 8.6, 4.9 Hz, 1H), 0.93 (q, *J* = 6.7 Hz, 2H), 0.75 – 0.70 (m, 2H); [13]C NMR (101 MHz, Chloroform-*d*) δ 168.4, 158.6, 145.3, 133.4, 132.5, 131.5, 127.9, 107.2, 14.7, 9.5, 8.3; Chem. Eur. J. 2024, e202401105.



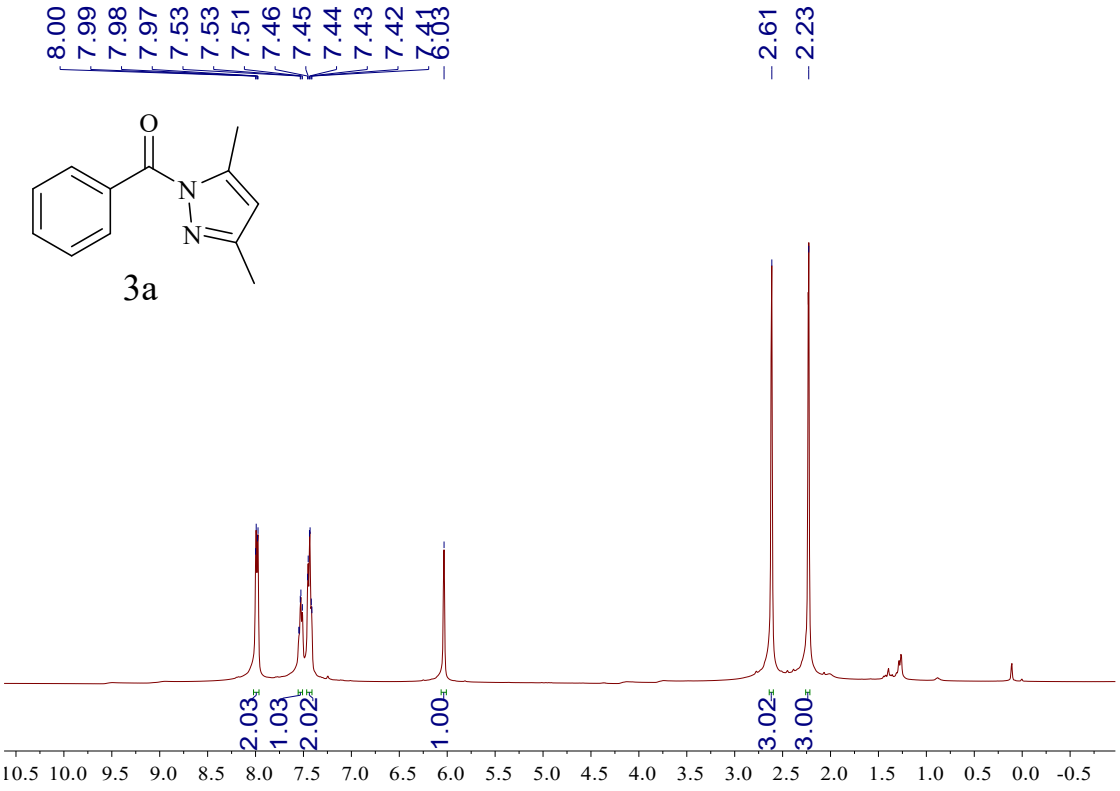
(3-(tert-butyl)-5-methyl-1H-pyrazol-1-yl)(phenyl)methanone (4m) (Colorless oil, 35mg, 29%), [1]H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.14 (s, 1H), 2.63 (s, 3H), 1.27 (s, 9H); [13]C NMR (101 MHz, Chloroform-*d*) δ 168.5, 164.5, 144.9, 133.4, 132.4, 132.0, 127.7, 108.0, 32.4, 29.8, 14.7.

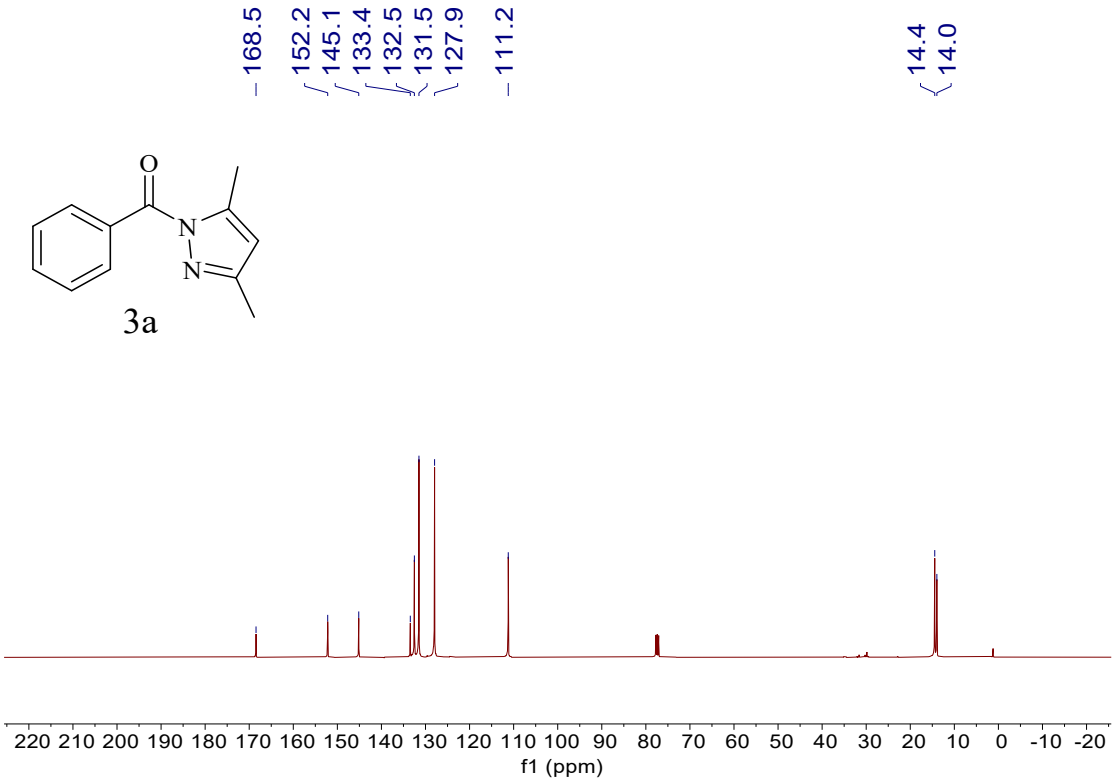


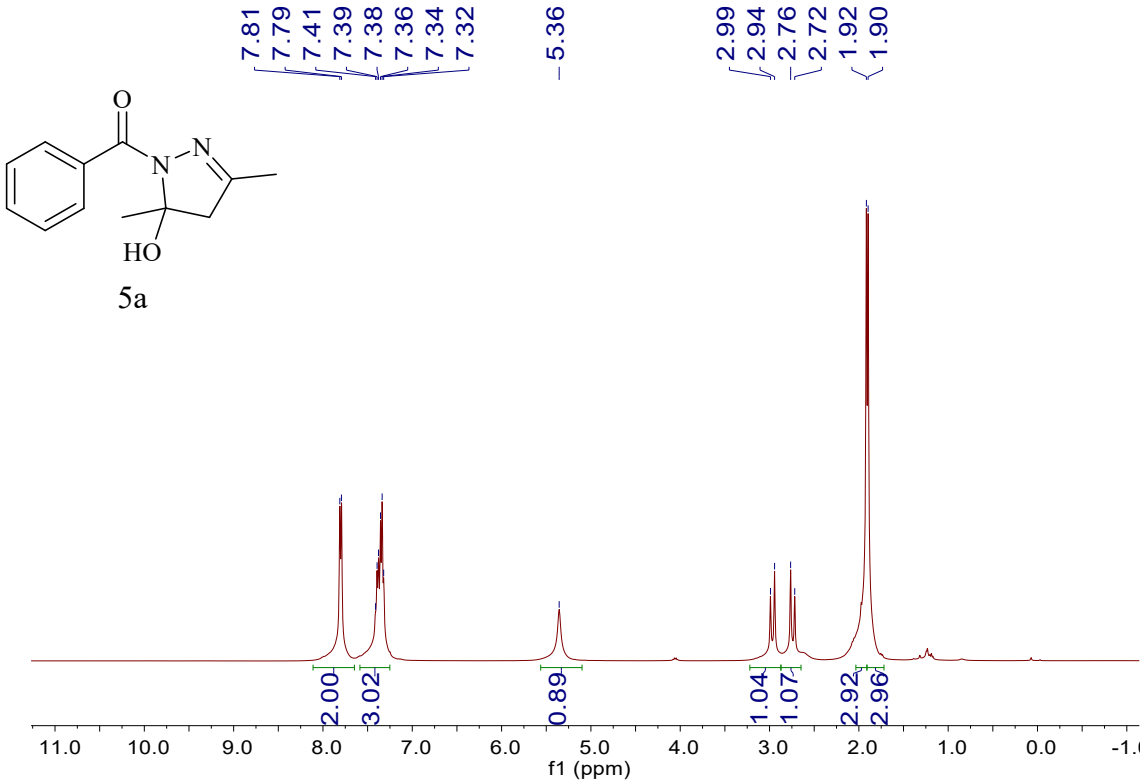
(6a-hydroxy-3-methyl-4,5,6,6a-tetrahydrocyclopenta[c]pyrazol-1(3aH)-yl)(phenyl)methanone (5e) (Colorless liquid, 100mg, 82%), [1]H NMR (400 MHz,

Chloroform-*d*) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 5.18 (s, 1H), 3.26 (d, *J* = 6.7 Hz, 1H), 2.66 (dq, *J* = 11.7, 5.0, 4.5 Hz, 1H), 2.23 – 2.15 (m, 1H), 2.15 – 2.07 (m, 1H), 1.99 (s, 3H), 1.88 (dtt, *J* = 13.3, 6.2, 3.8 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.65 – 1.52 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 159.2, 134.2, 131.3, 129.9, 127.8, 103.1, 59.7, 41.0, 29.7, 25.8, 14.9; US Patent 20080227840A1.

4. ^{1}H NMR and ^{13}C NMR Spectra for N-acylpyrazoles products.



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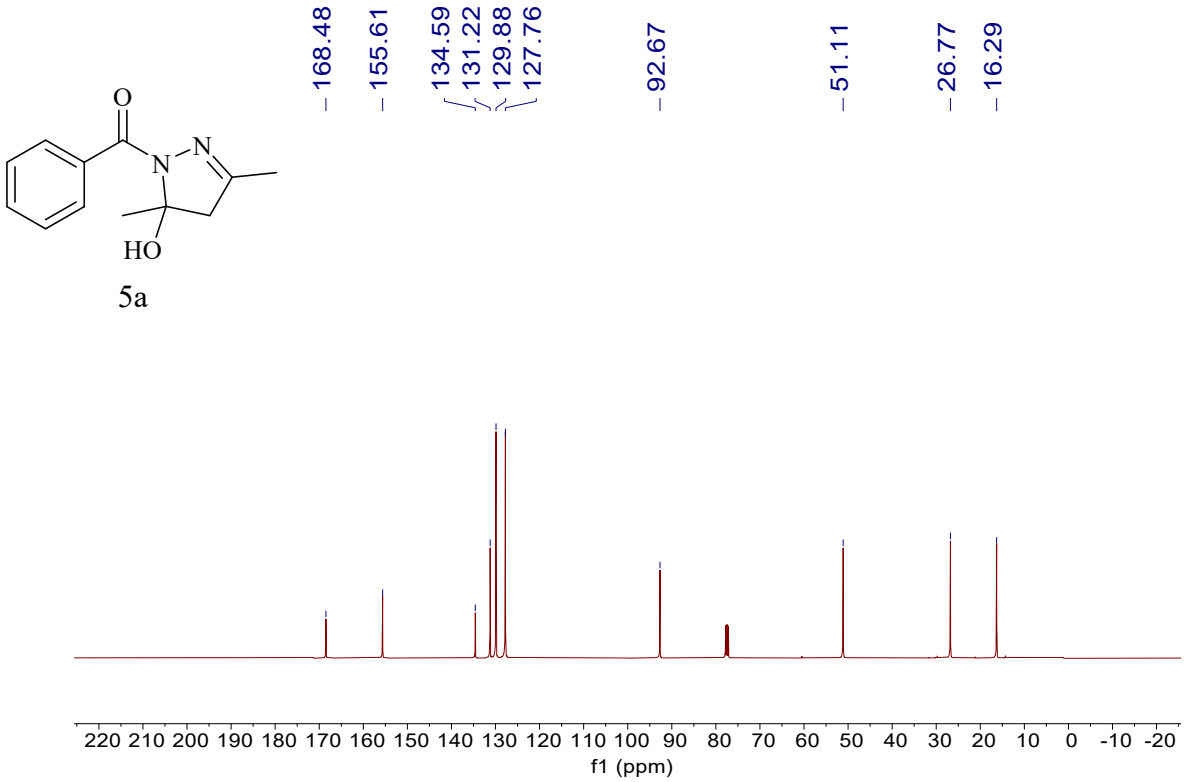
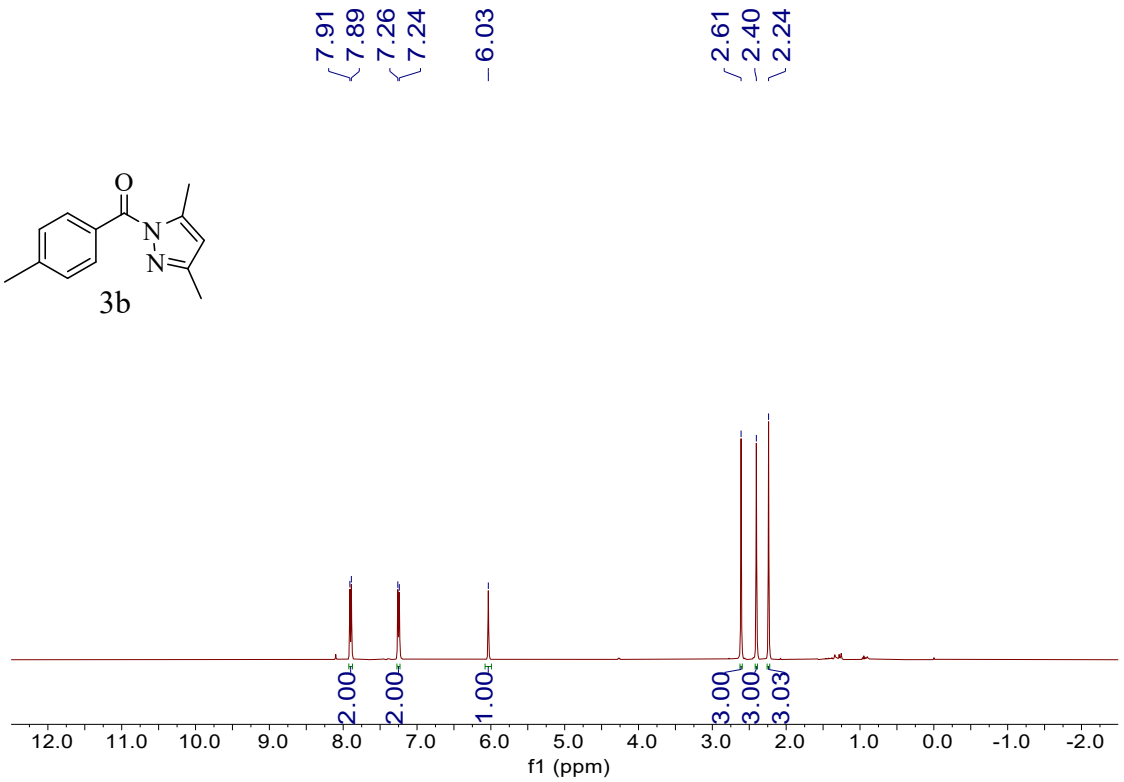
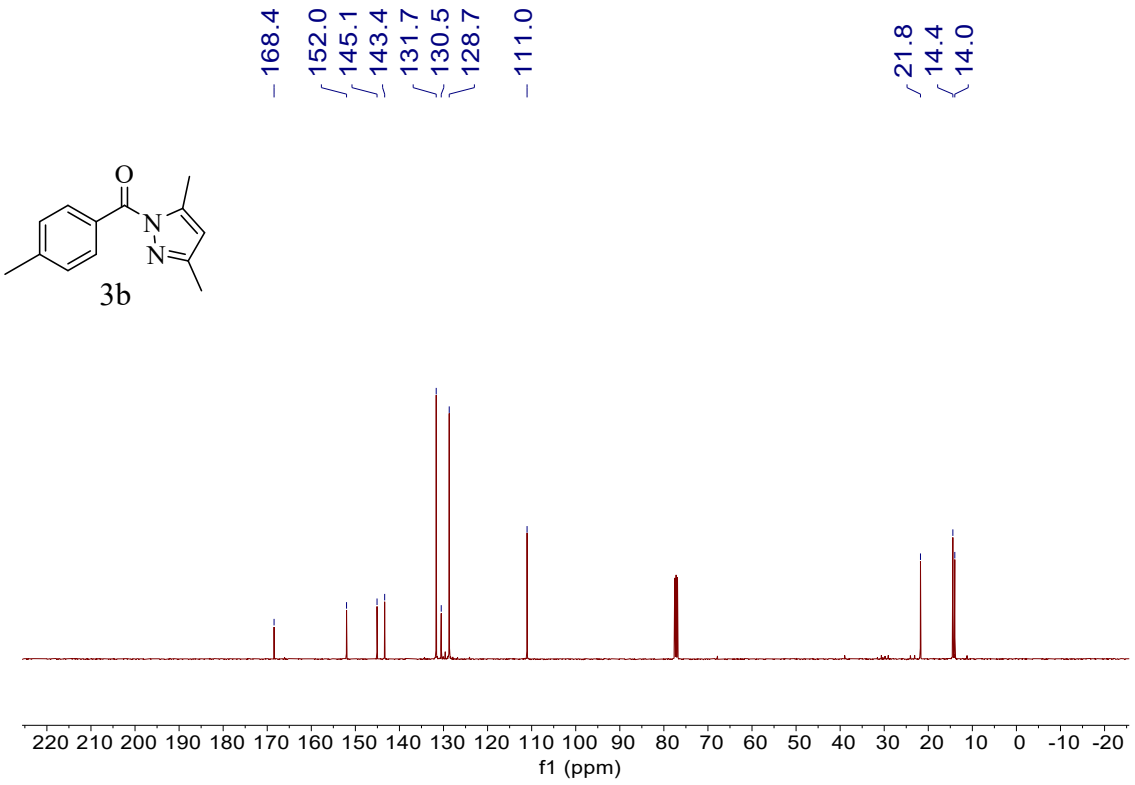
7.79
7.41
7.39
7.38
7.36
7.34
7.32
5.36
2.99
2.94
2.76
2.72
1.92
1.90
O
N
N
HO
2.00
3.02
0.89
1.04
1.07
2.92
2.96
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

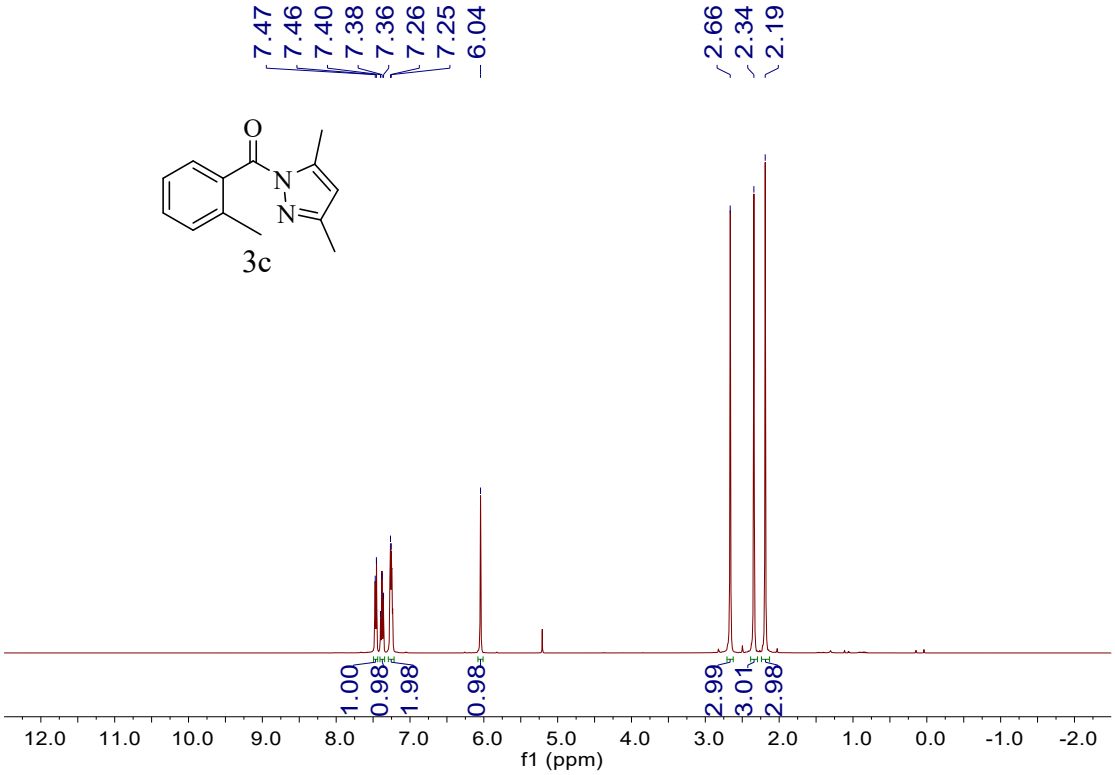
5a

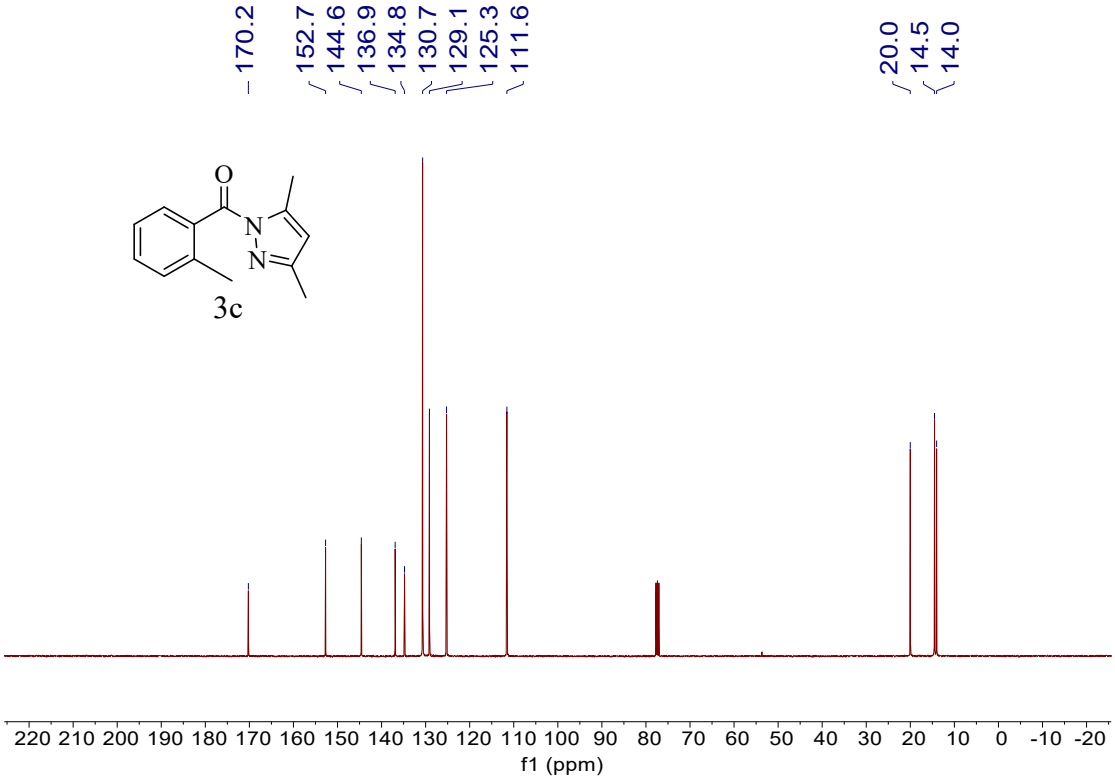

168.48
155.61
134.59
131.22
129.88
127.76
92.67
51.11
26.77
16.29
O
N
N
HO
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

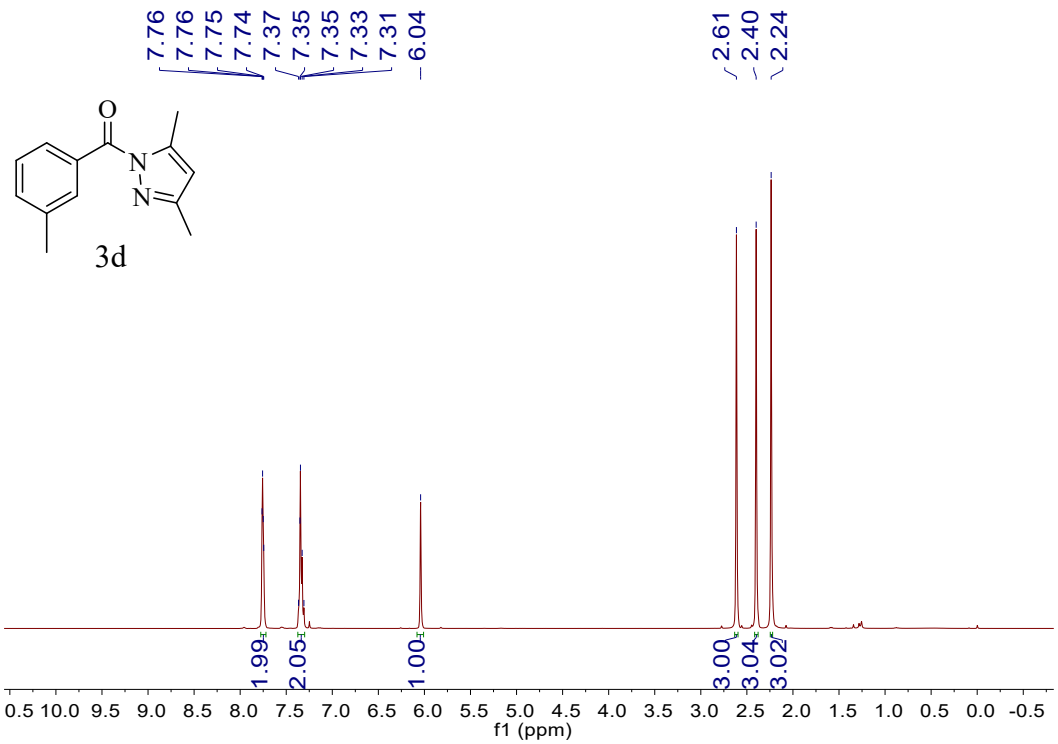
5a

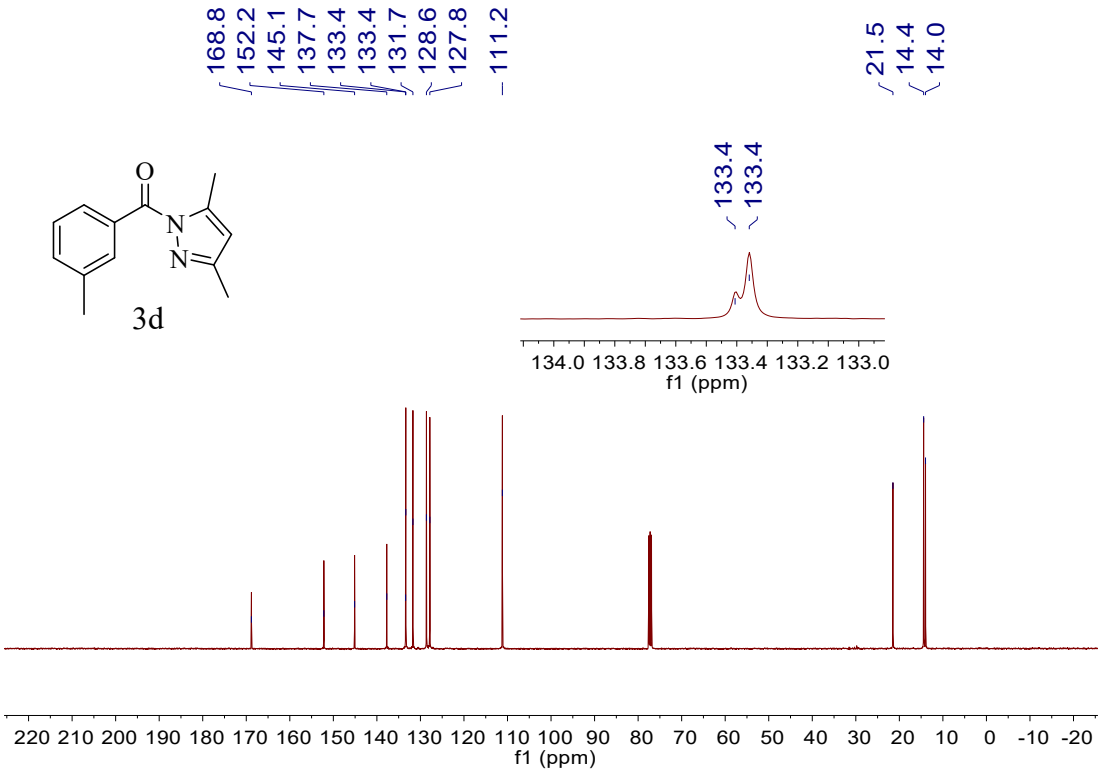

7.91
7.89
7.26
7.24
6.03
2.61
2.40
2.24
O
N
N
3b
2.00
2.00
1.00
3.00
3.00
3.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

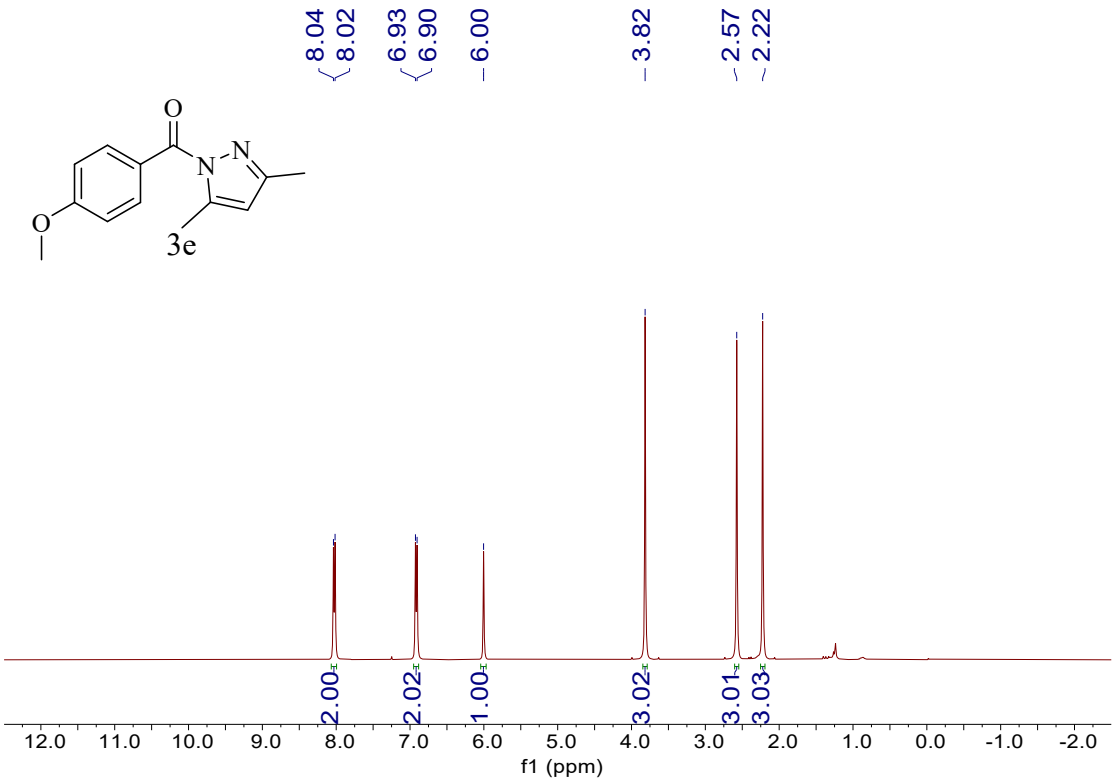

168.4
152.0
145.1
143.4
131.7
130.5
128.7
111.0
21.8
14.4
14.0
O
N
N
3b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.47
7.46
7.40
7.38
7.36
7.26
7.25
6.04
2.66
2.34
2.19
O
N
N
3c
1.00
0.98
1.98
0.98
2.99
3.01
2.98
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)


170.2
152.7
144.6
136.9
134.8
130.7
129.1
125.3
111.6
20.0
14.5
14.0
O
N
N
3c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.76
7.76
7.75
7.74
7.37
7.35
7.35
7.33
7.31
6.04
2.61
2.40
2.24
O
N
N
3d
1.99
2.05
1.00
3.00
3.04
3.02
0.5 10.0 9.5 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 0.0 -0.5
f1 (ppm)


168.8
152.2
145.1
137.7
133.4
133.4
131.7
128.6
127.8
111.2
21.5
14.4
14.0
O
N
N
3d
133.4
133.4
134.0 133.8 133.6 133.4 133.2 133.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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8.02
6.93
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6.00
3.82
2.57
2.22
O
N
N
O
3e
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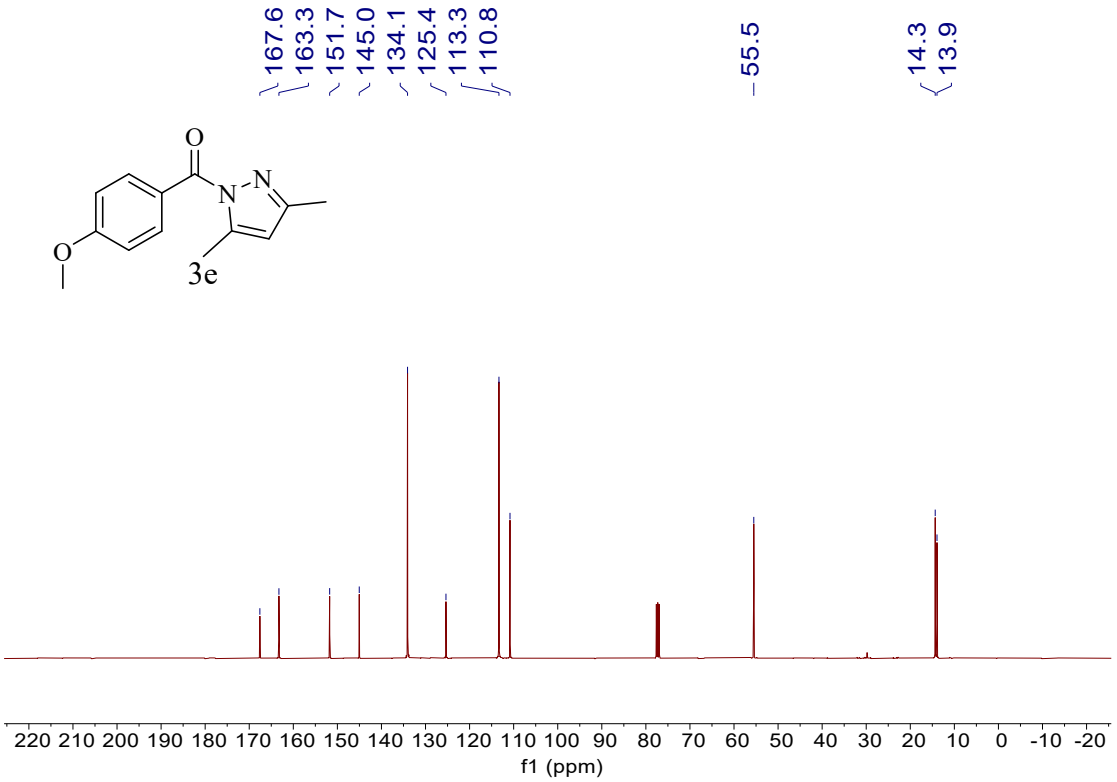
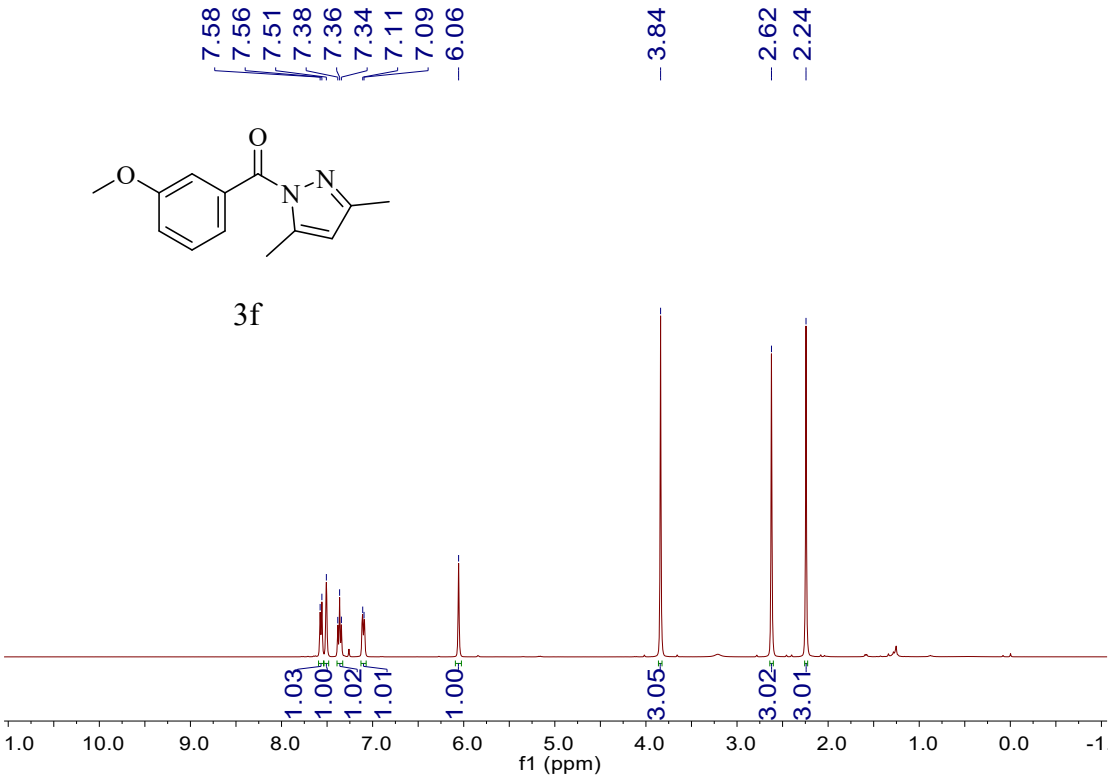
2.02
1.00
3.02
3.01
3.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)


167.6
163.3
151.7
145.0
134.1
125.4
113.3
110.8
55.5
14.3
13.9
O
N
N
O
3e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.51
7.38
7.36
7.34
7.11
7.09
6.06
3.84
2.62
2.24
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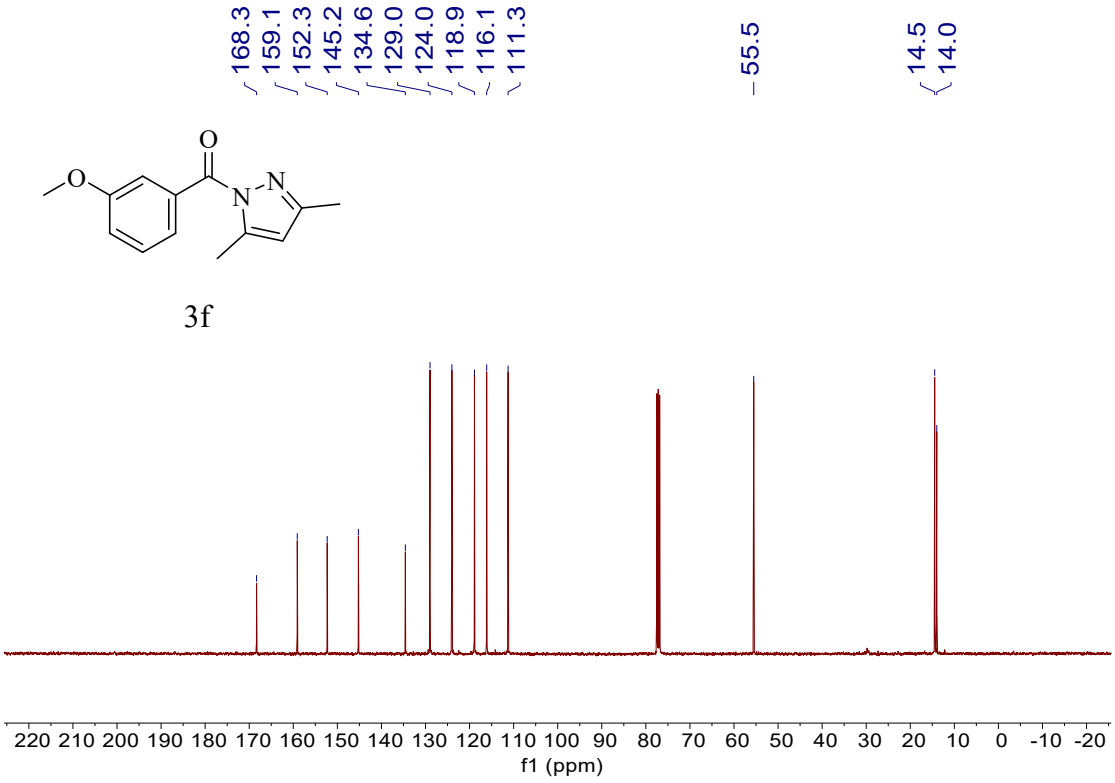
O
N
N
1.03
1.00
1.02
1.01
1.00
3.05
3.02
3.01
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)

3f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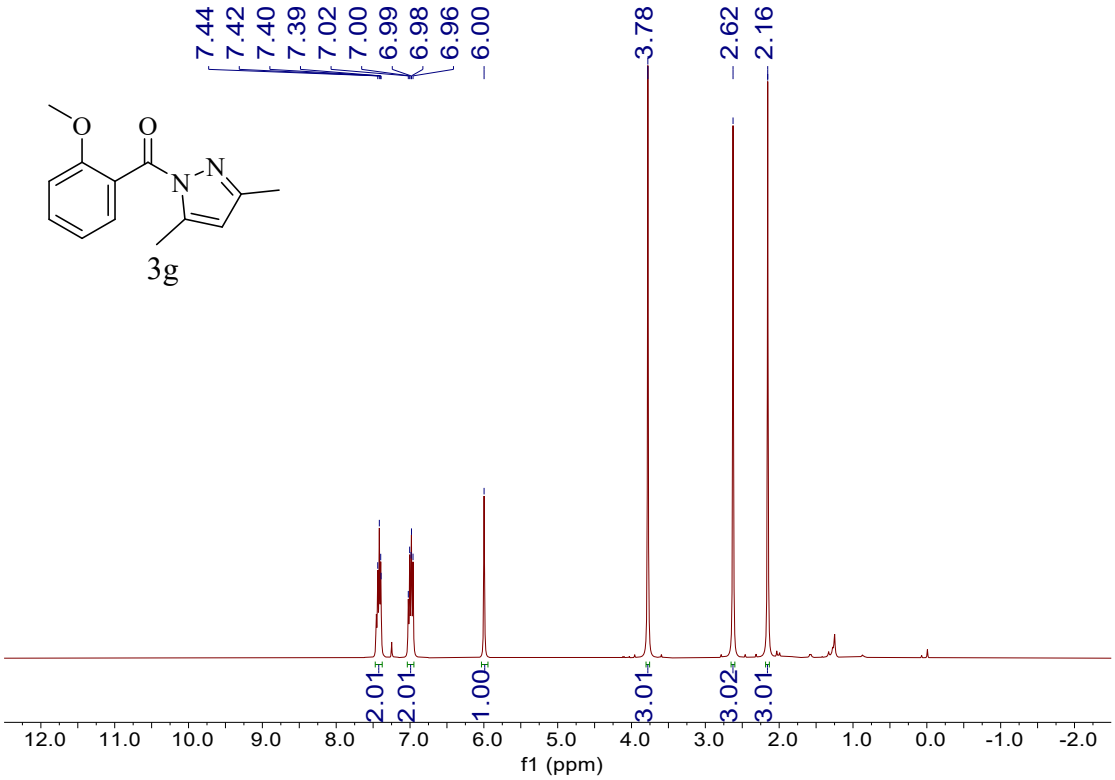
152.3
145.2
134.6
129.0
124.0
118.9
116.1
111.3
55.5
14.5
14.0
O
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

3f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7.42
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7.39
7.02
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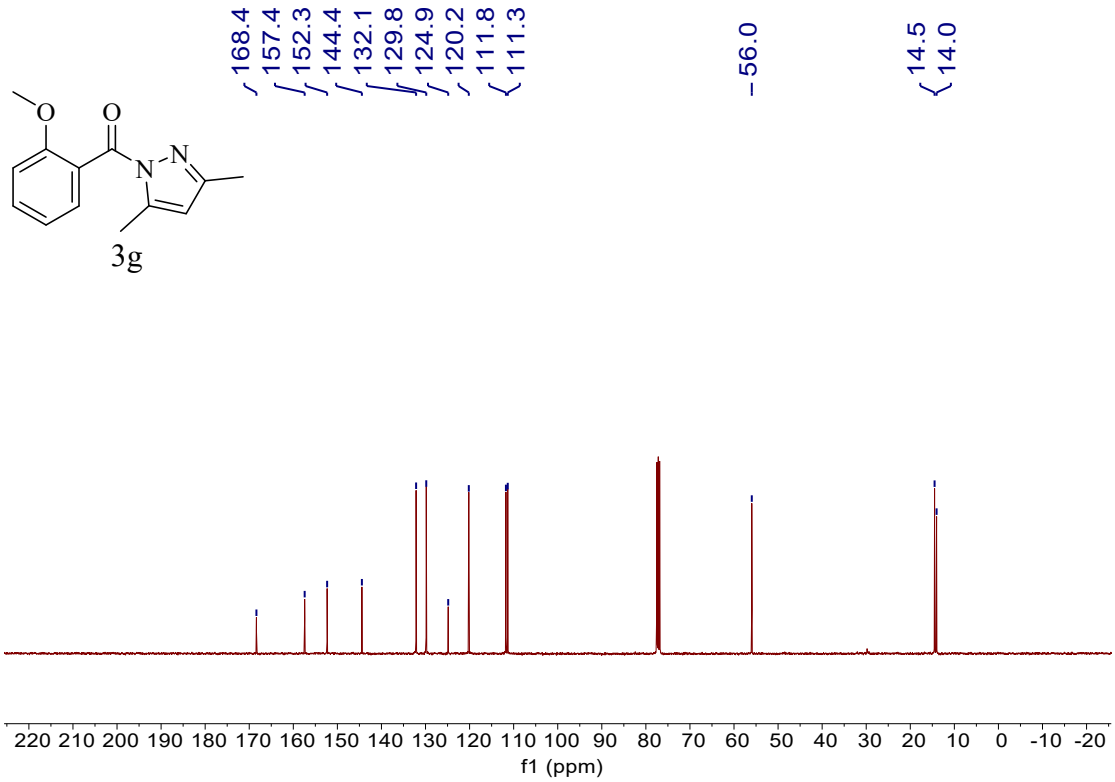
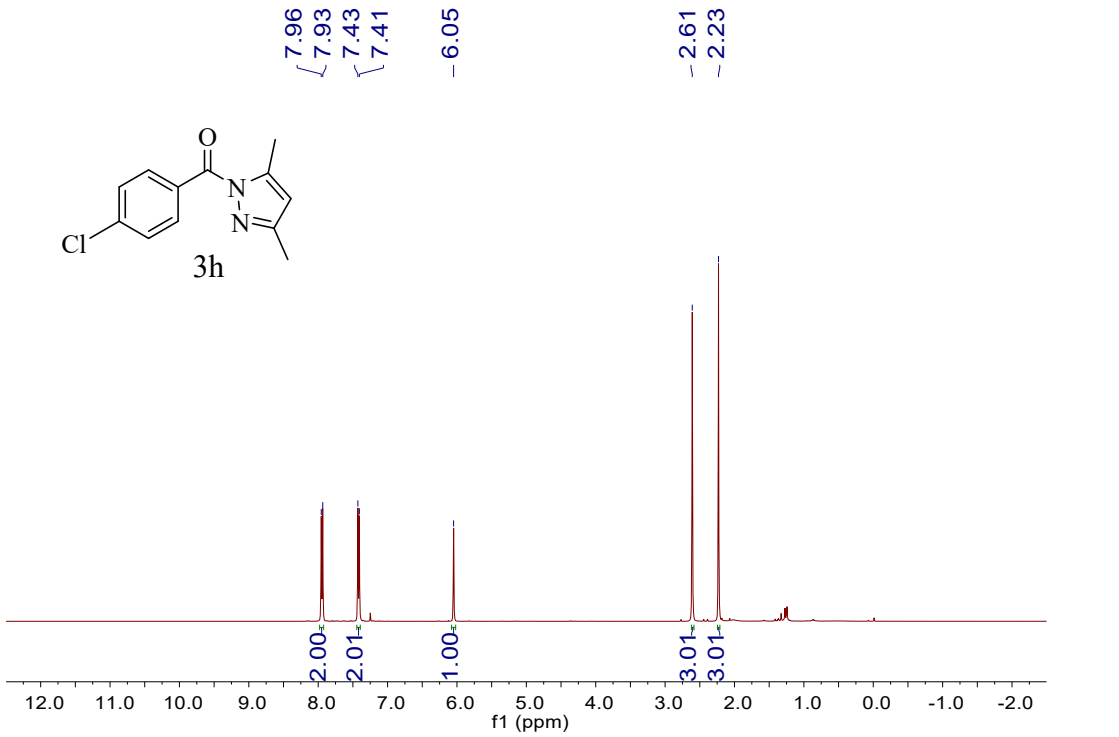
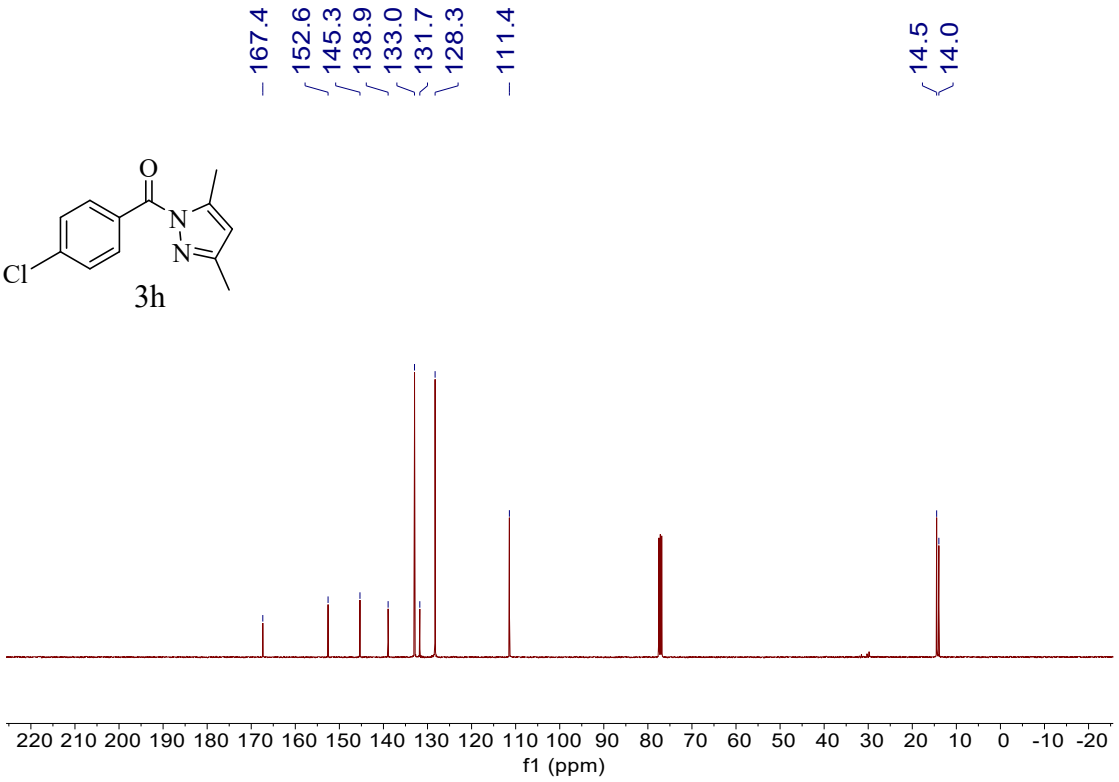
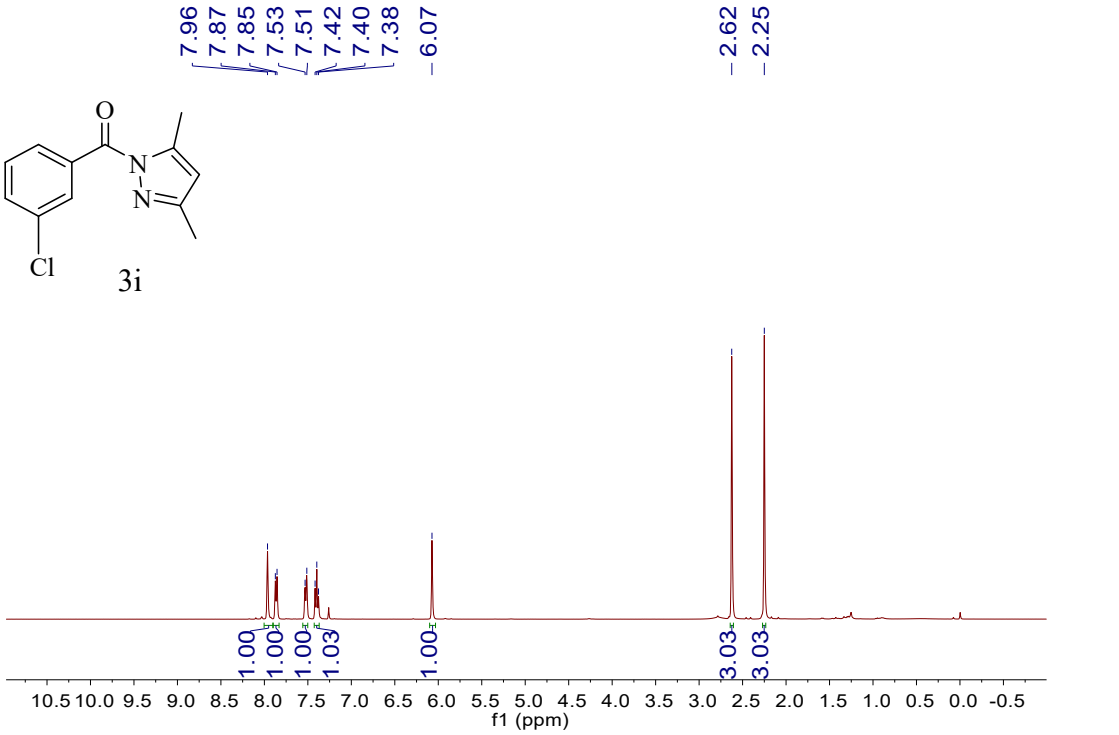
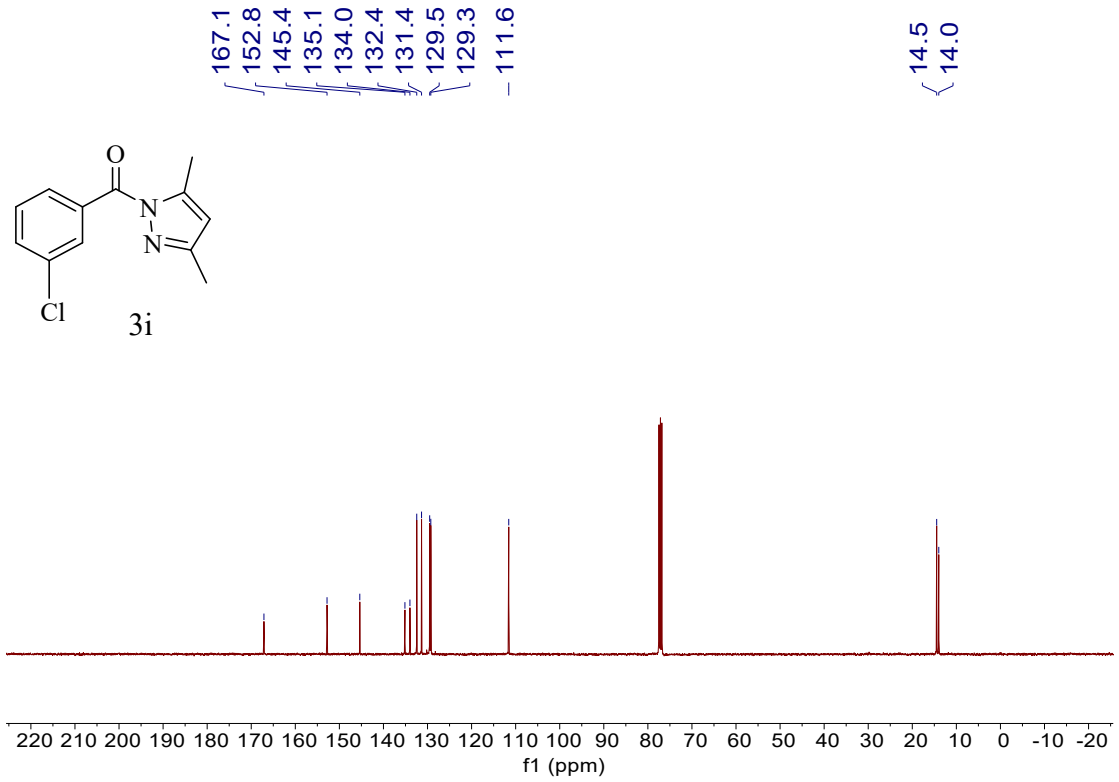
6.99
6.98
6.96
6.00
3.78
2.62
2.16
O
O
N
N
3g
2.01
2.01
1.00
3.01
3.02
3.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

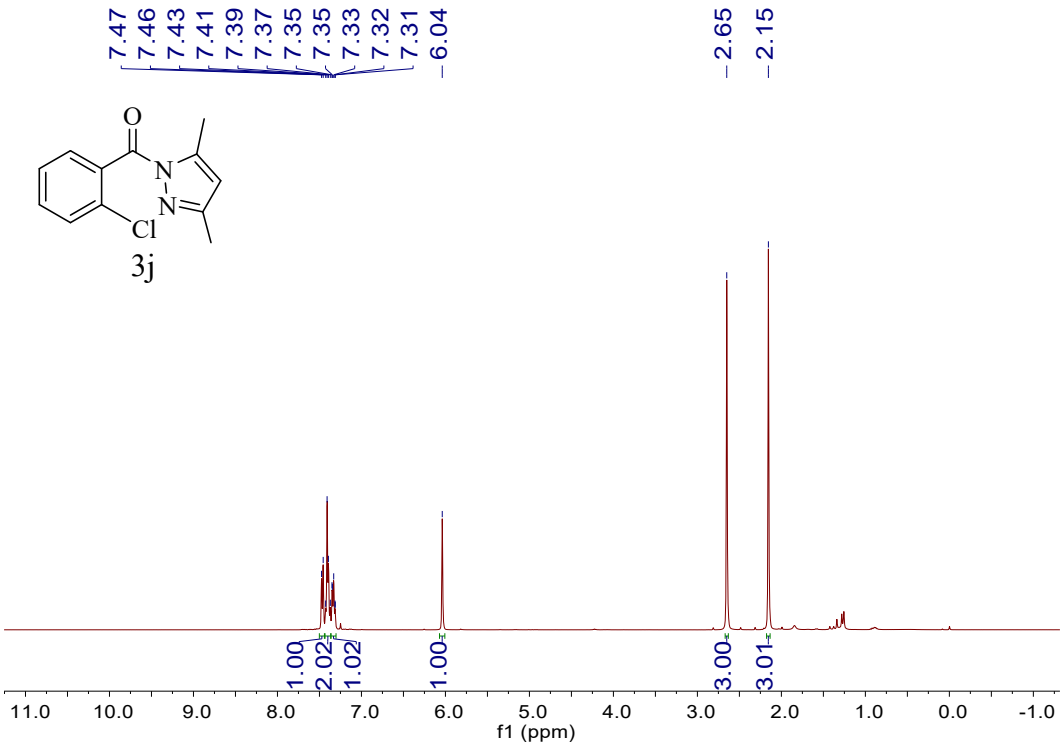

168.4
157.4
152.3
144.4
132.1
129.8
124.9
120.2
111.8
111.3
56.0
14.5
14.0
O
O
N
N
3g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

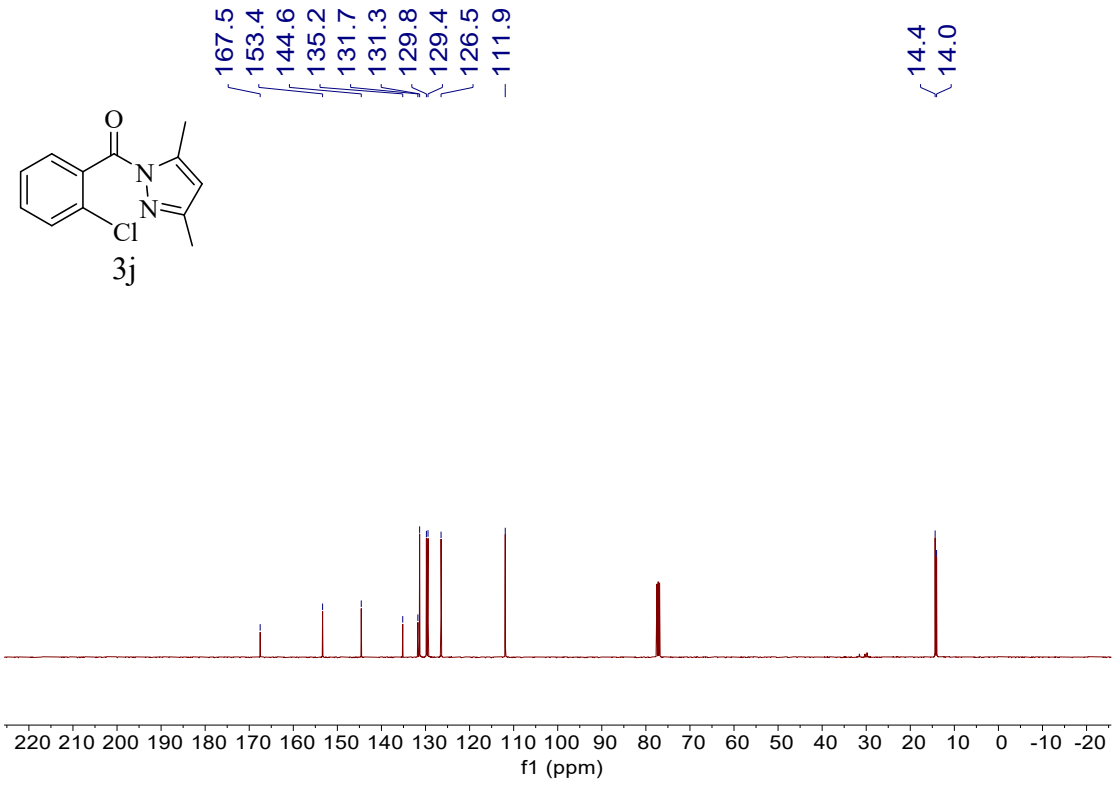

7.96
7.93
7.43
7.41
6.05
2.61
2.23
O
N
N
Cl
3h
2.00
2.01
1.00
3.01
3.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

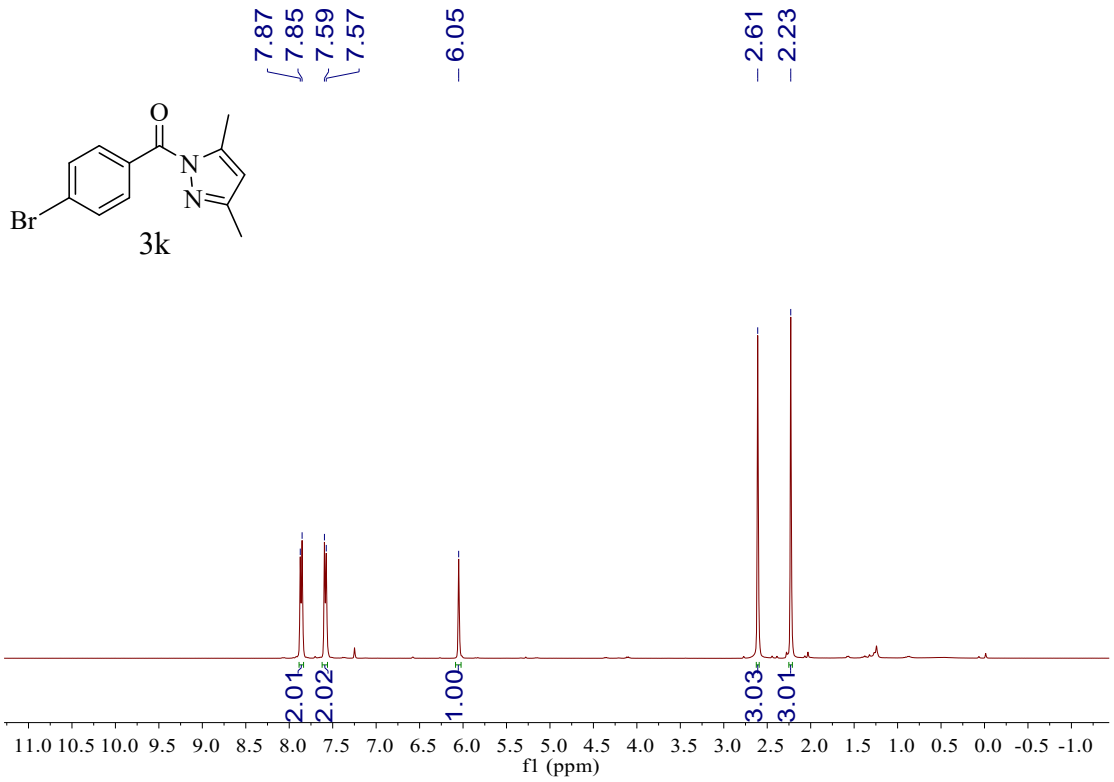

167.4
152.6
145.3
138.9
133.0
131.7
128.3
111.4
14.5
14.0
O
N
N
Cl
3h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

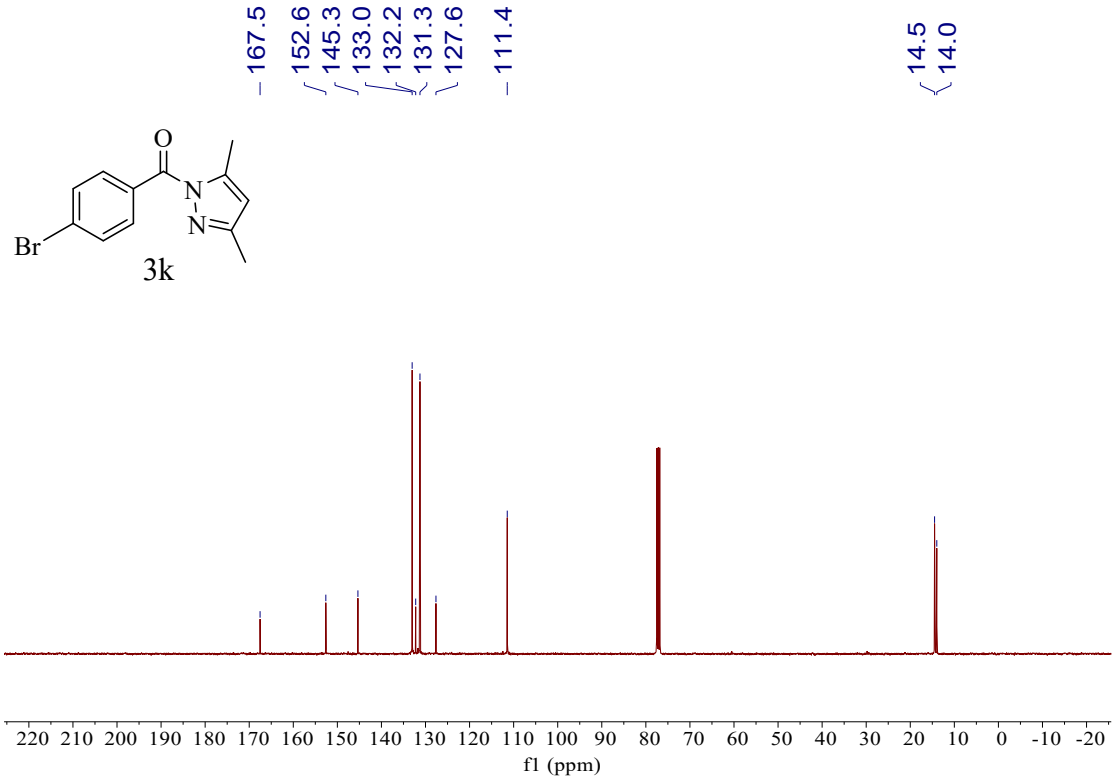

7.96
7.87
7.85
7.53
7.51
7.42
7.40
7.38
6.07
2.62
2.25
O
N
N
Cl
3i
1.00
1.00
1.00
1.03
1.00
3.03
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

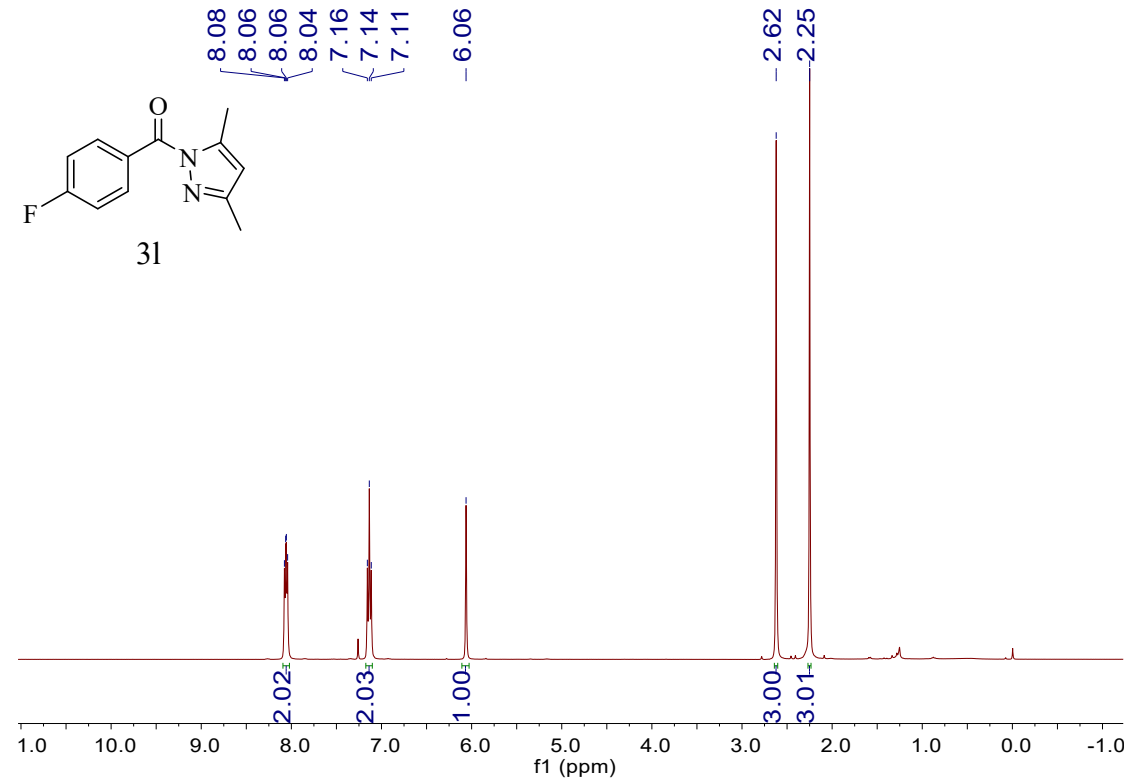

167.1
152.8
145.4
135.1
134.0
132.4
131.4
129.5
129.3
111.6
14.5
14.0
O
N
N
Cl
3i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.47
7.46
7.43
7.41
7.39
7.37
7.35
7.35
7.33
7.32
7.31
6.04
2.65
2.15
O
N
N
Cl
3j
1.00
2.02
1.02
1.00
3.00
3.01
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

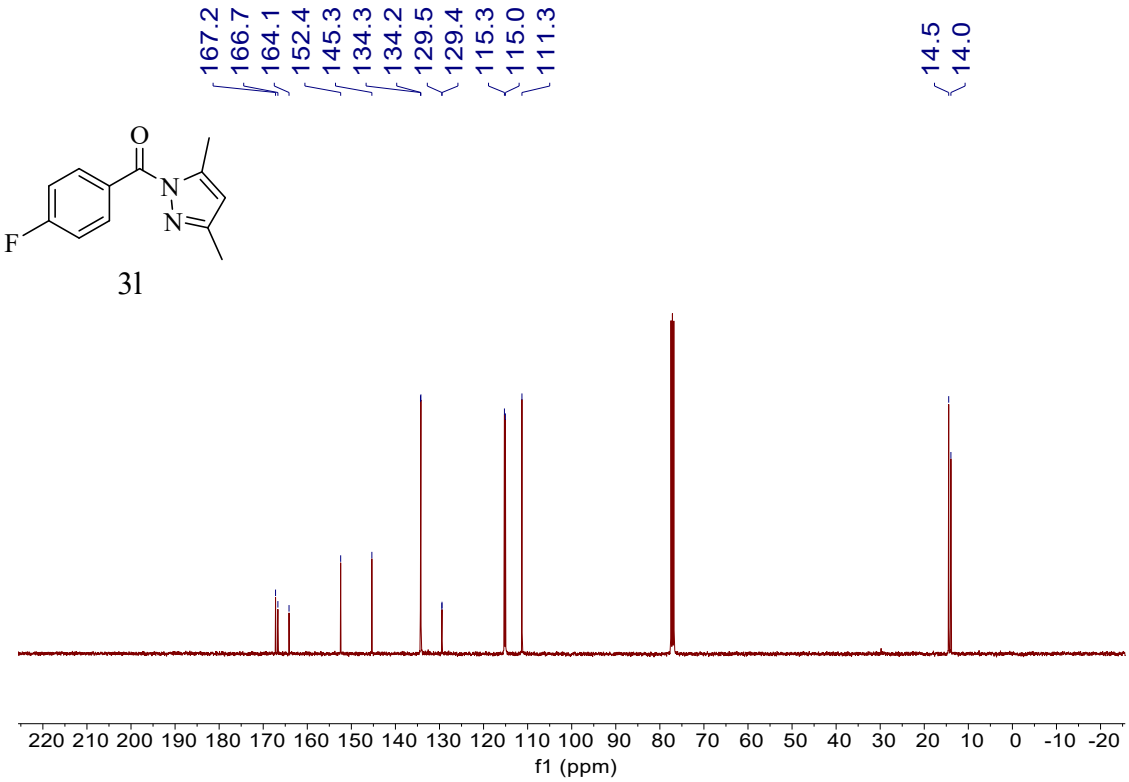

167.5
153.4
144.6
135.2
131.7
131.3
129.8
129.4
126.5
111.9
14.4
14.0
O
N
N
Cl
3j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.87
7.85
7.59
7.57
6.05
2.61
2.23
Br
3k
2.01
2.02
1.00
3.03
3.01
11.0 10.5 10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)

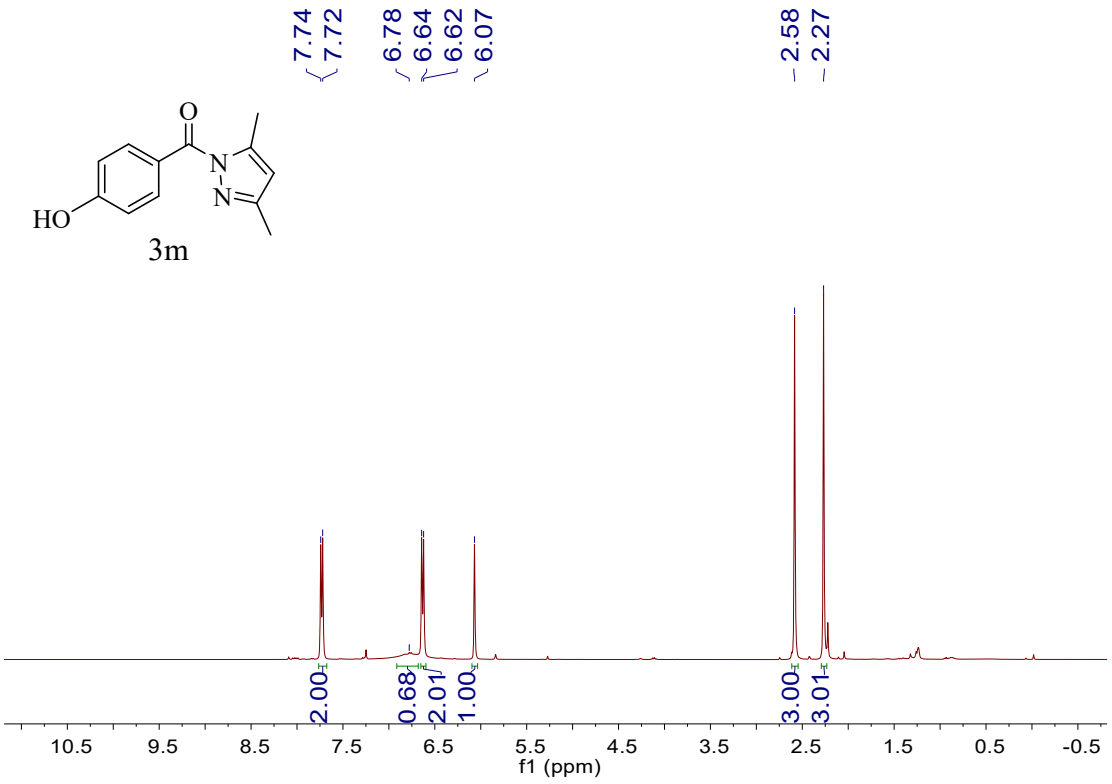

167.5
152.6
145.3
133.0
132.2
131.3
127.6
111.4
14.5
14.0
Br
3k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

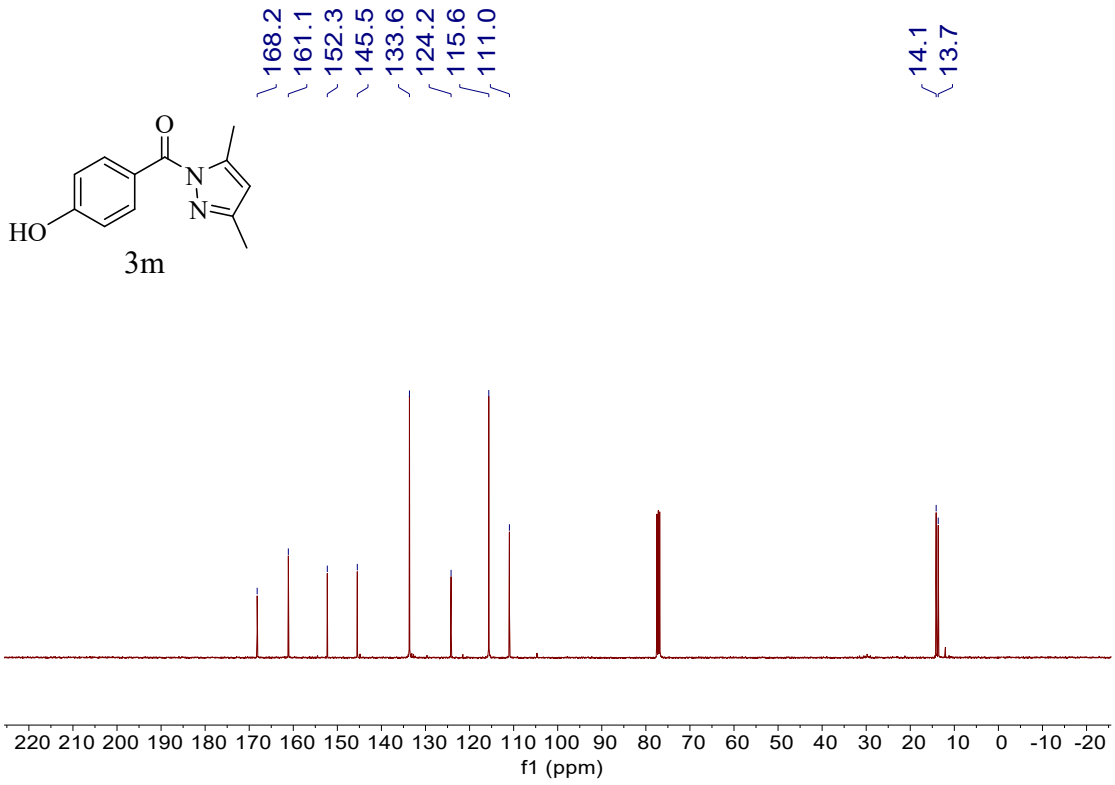

8.08
8.06
8.06
8.04
7.16
7.14
7.11
6.06
2.62
2.25
O
N
N
F
2.02
2.03
1.00
3.00
3.01
1.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

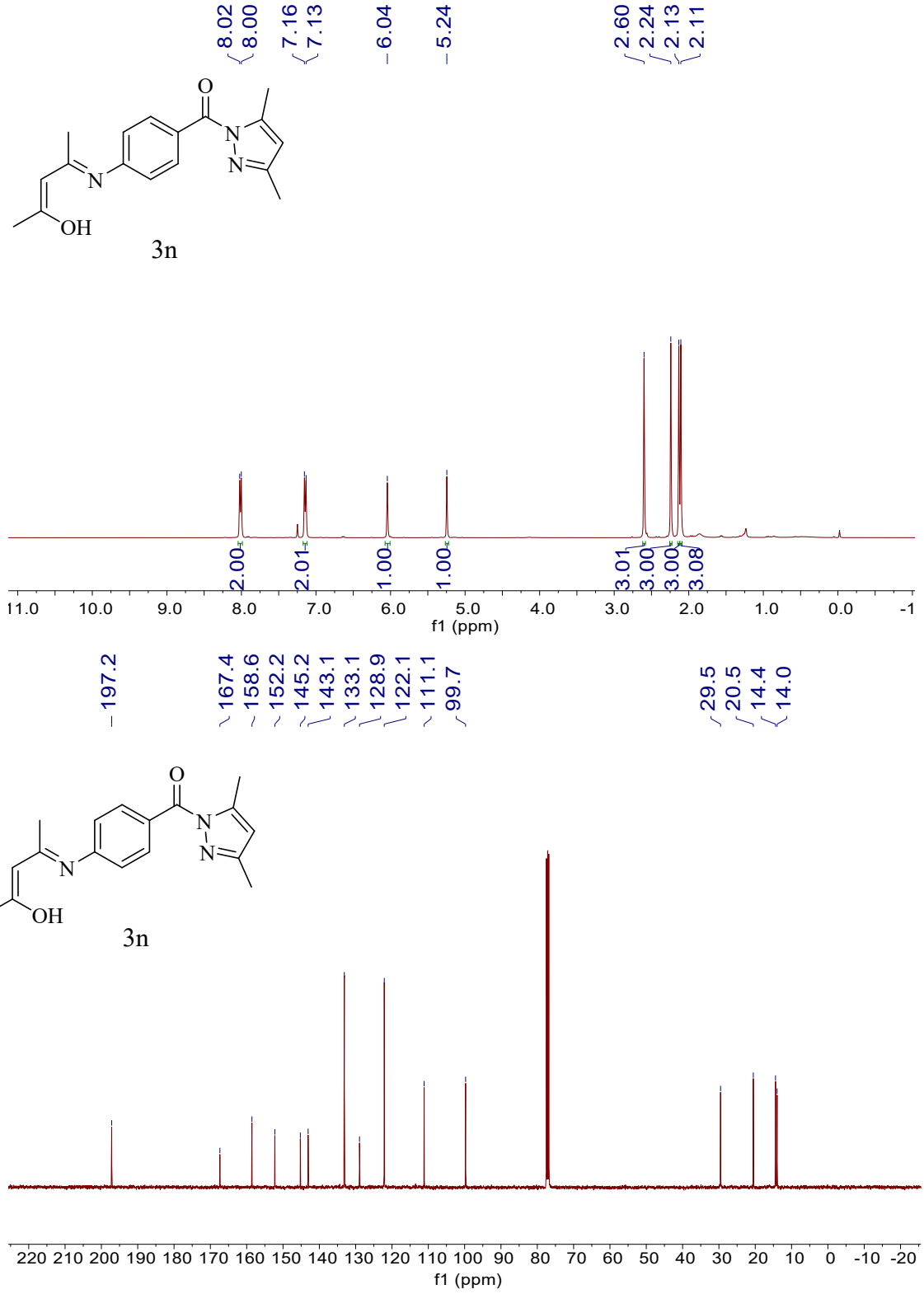
31

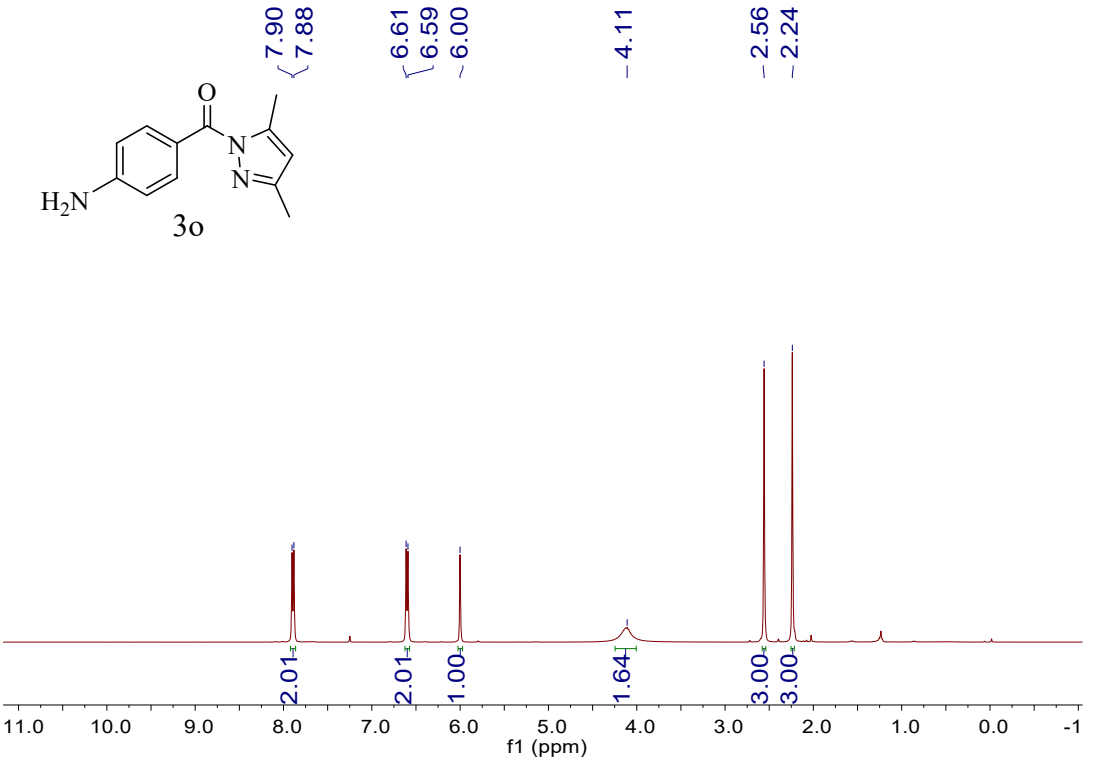

167.2
166.7
164.1
152.4
145.3
134.3
134.2
129.5
129.4
115.3
115.0
111.3
14.5
14.0
O
N
N
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

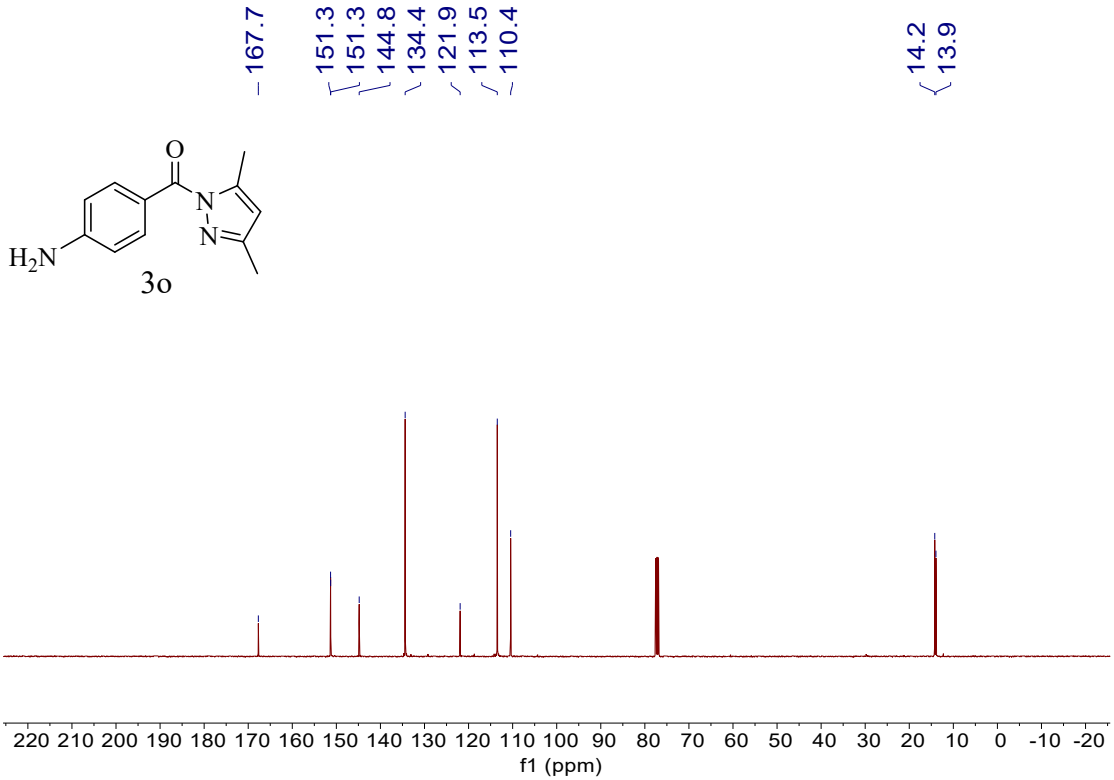
31

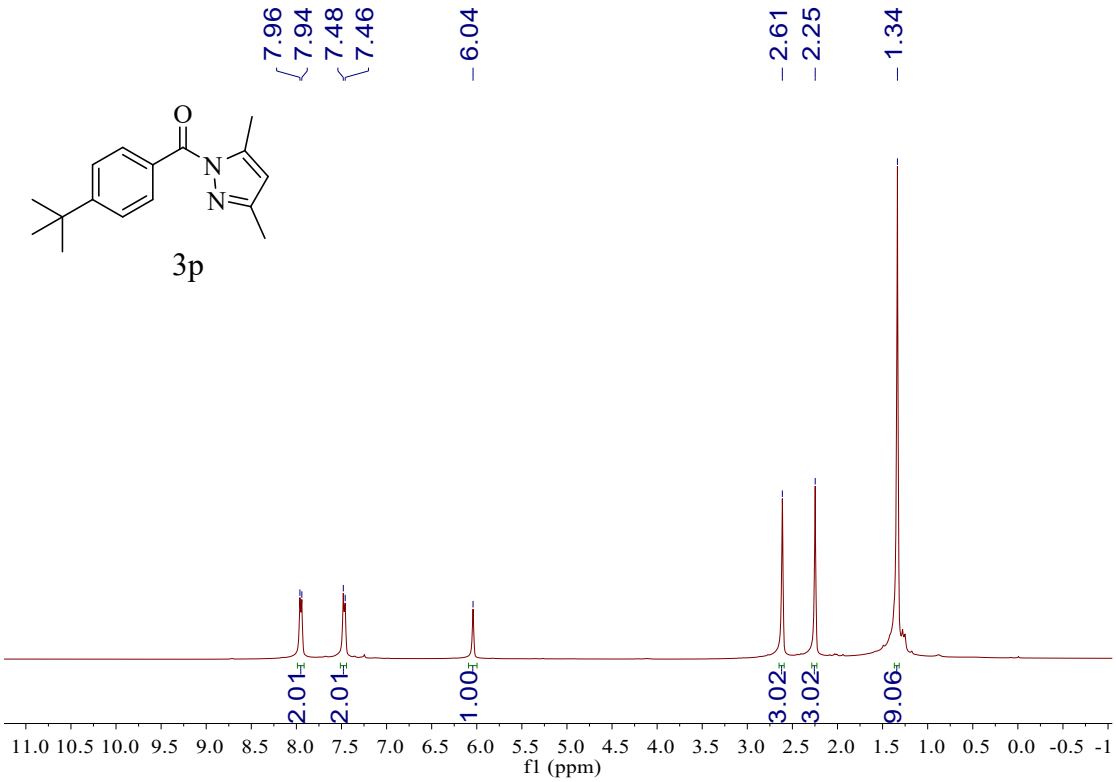

7.74
7.72
6.78
6.64
6.62
6.07
2.58
2.27
O
N
N
HO
3m
2.00
0.68
2.01
1.00
3.00
3.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

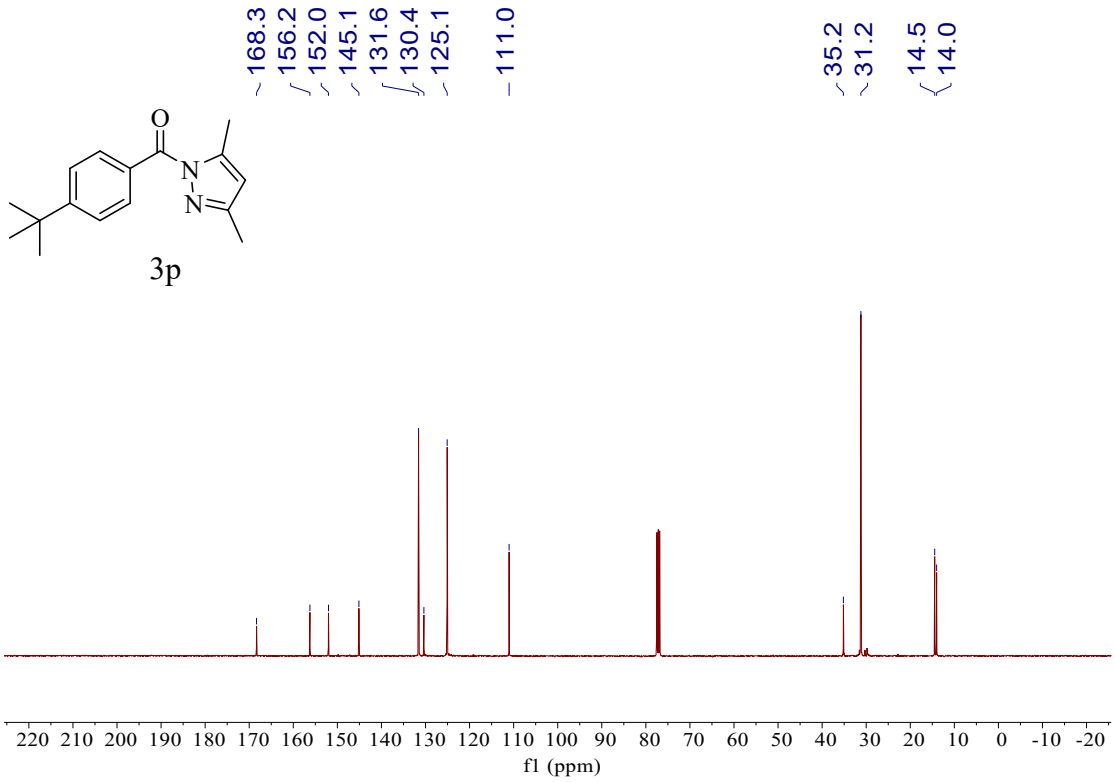

168.2
161.1
152.3
145.5
133.6
124.2
115.6
111.0
14.1
13.7
O
N
N
HO
3m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

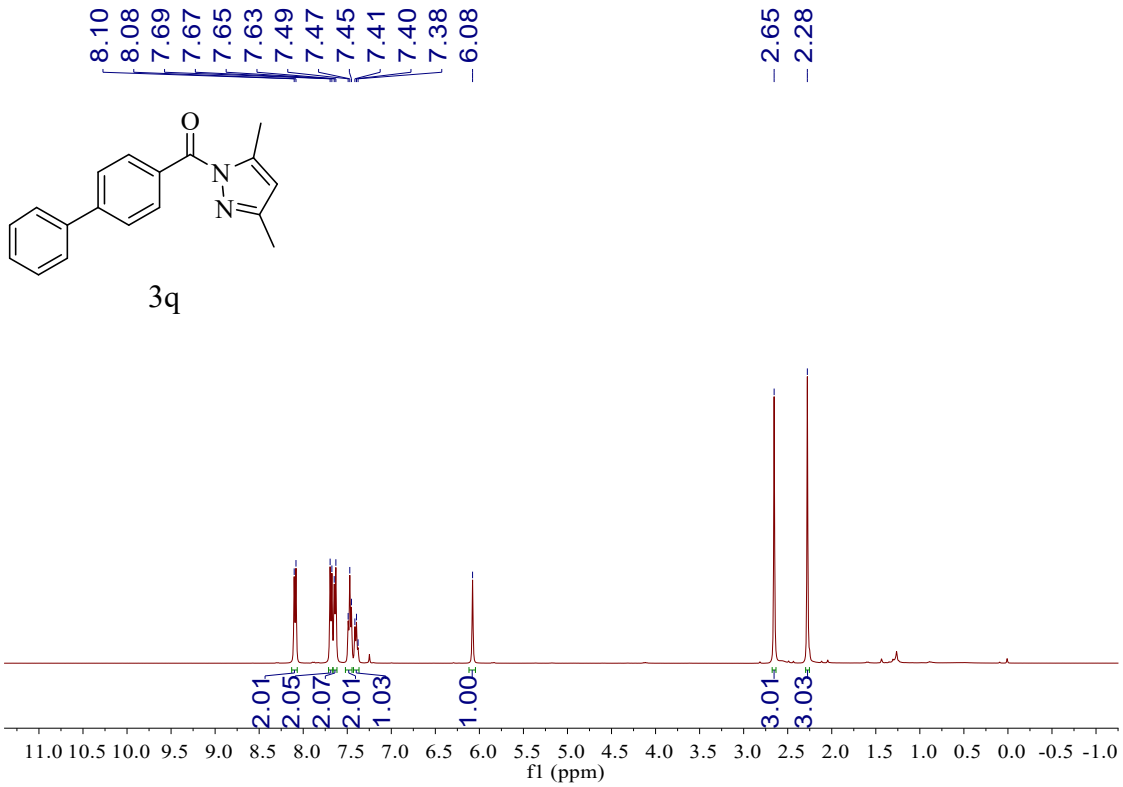

8.02
8.00
7.16
7.13
6.04
5.24
2.60
2.24
2.13
2.11
O
N
N
N
OH
3n
2.00
2.01
1.00
1.00
3.01
3.00
3.00
3.08
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1
f1 (ppm)
197.2
167.4
158.6
152.2
145.2
143.1
133.1
128.9
122.1
111.1
99.7
29.5
20.5
14.4
14.0
O
N
N
N
OH
3n
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.90
7.88
6.61
6.59
6.00
4.11
2.56
2.24
O
N
N
H_2N
3o
2.01
2.01
1.00
1.64
3.00
3.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1
f1 (ppm)

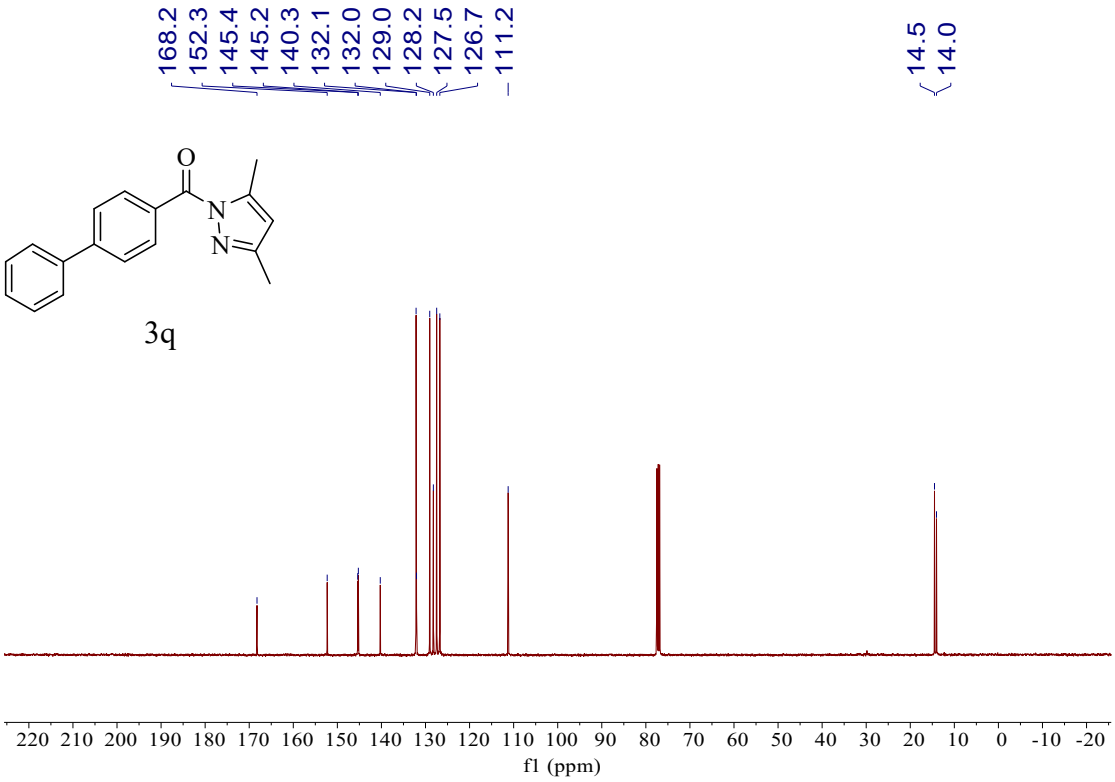

167.7
151.3
151.3
144.8
134.4
121.9
113.5
110.4
14.2
13.9
O
N
N
H_2N
3o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.96
7.94
7.48
7.46
6.04
2.61
2.25
1.34
O
N
N
3p
2.01
2.01
1.00
3.02
3.02
9.06
11.0 10.5 10.0 9.5 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 0.0 -0.5 -1
f1 (ppm)

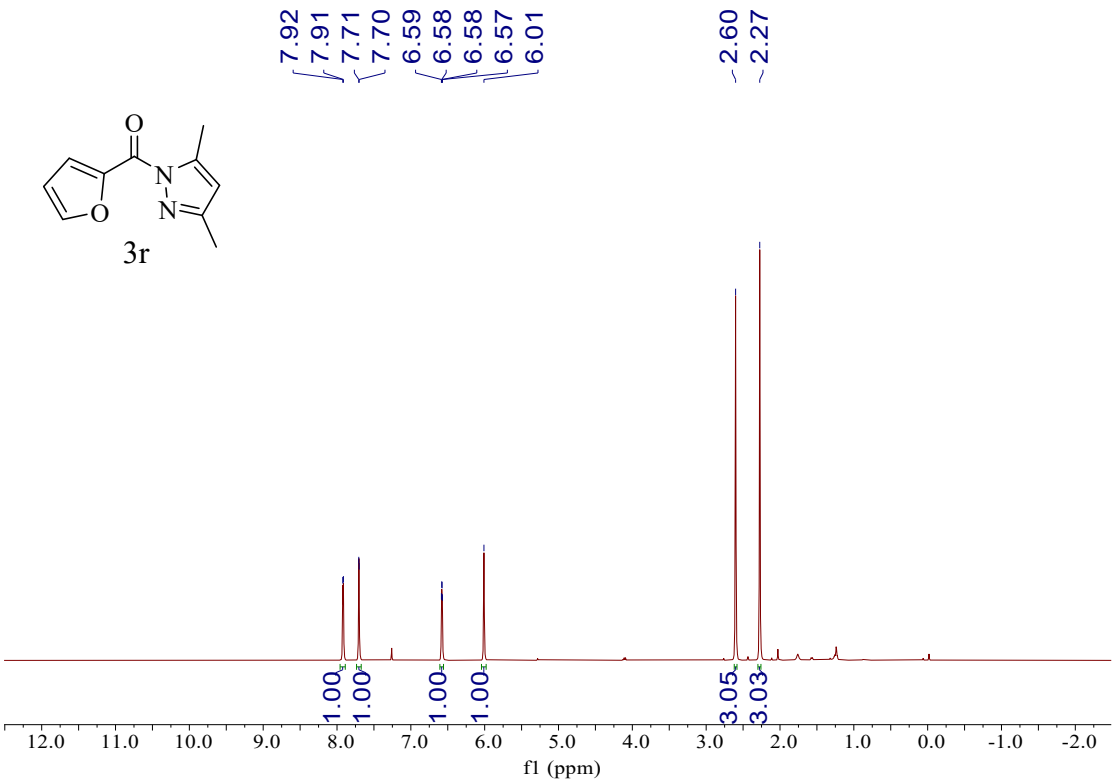

168.3
156.2
152.0
145.1
131.6
130.4
125.1
111.0
35.2
31.2
14.5
14.0
O
N
N
3p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

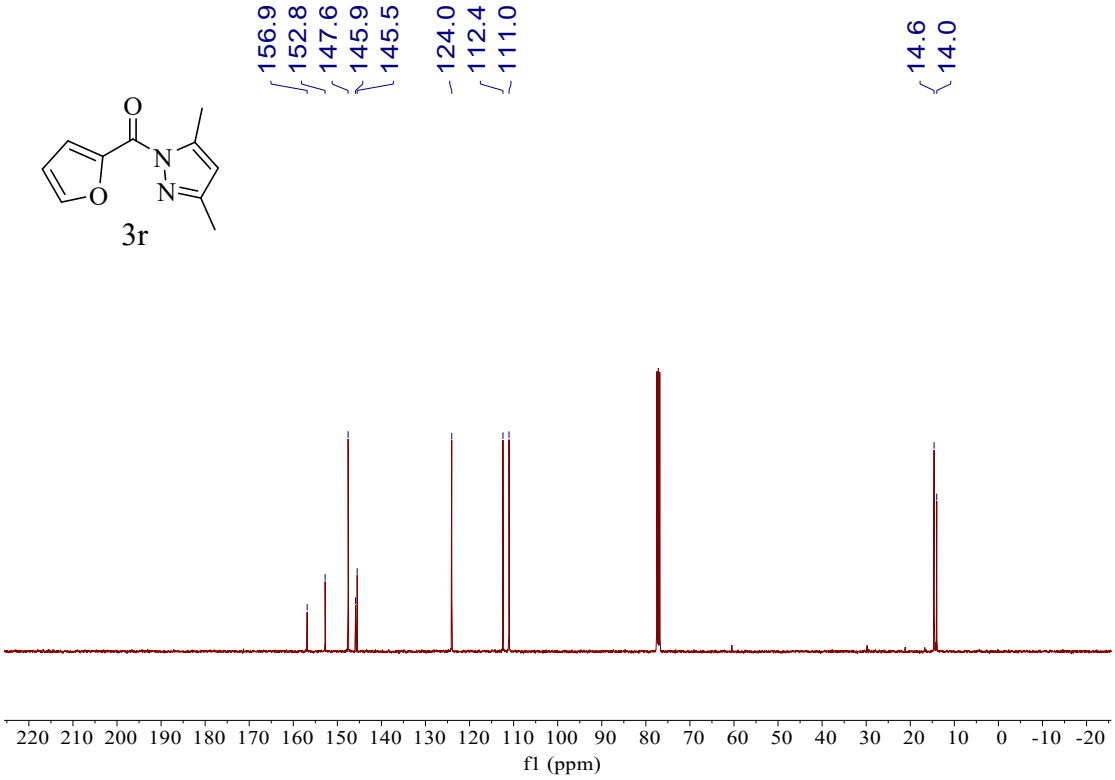

8.10
8.08
7.69
7.67
7.65
7.63
7.49
7.47
7.45
7.41
7.40
7.38
6.08
2.65
2.28
O
N
N
2.01
2.05
2.07
2.01
1.03
1.00
3.01
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

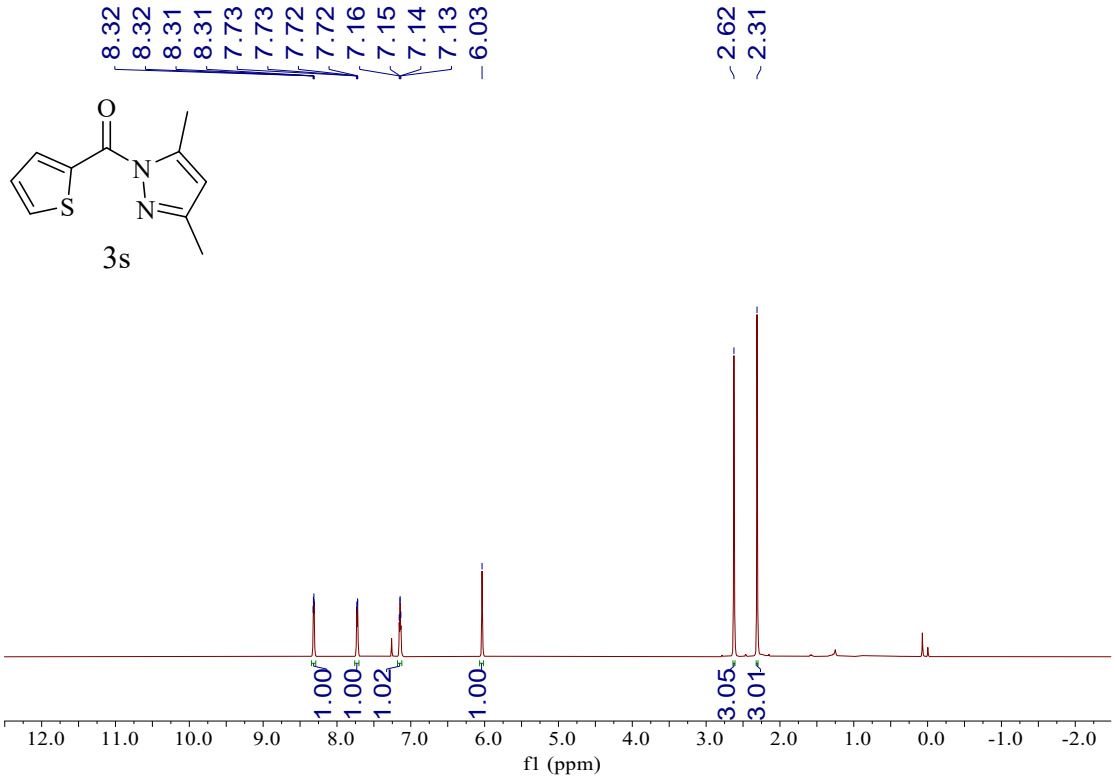
3q

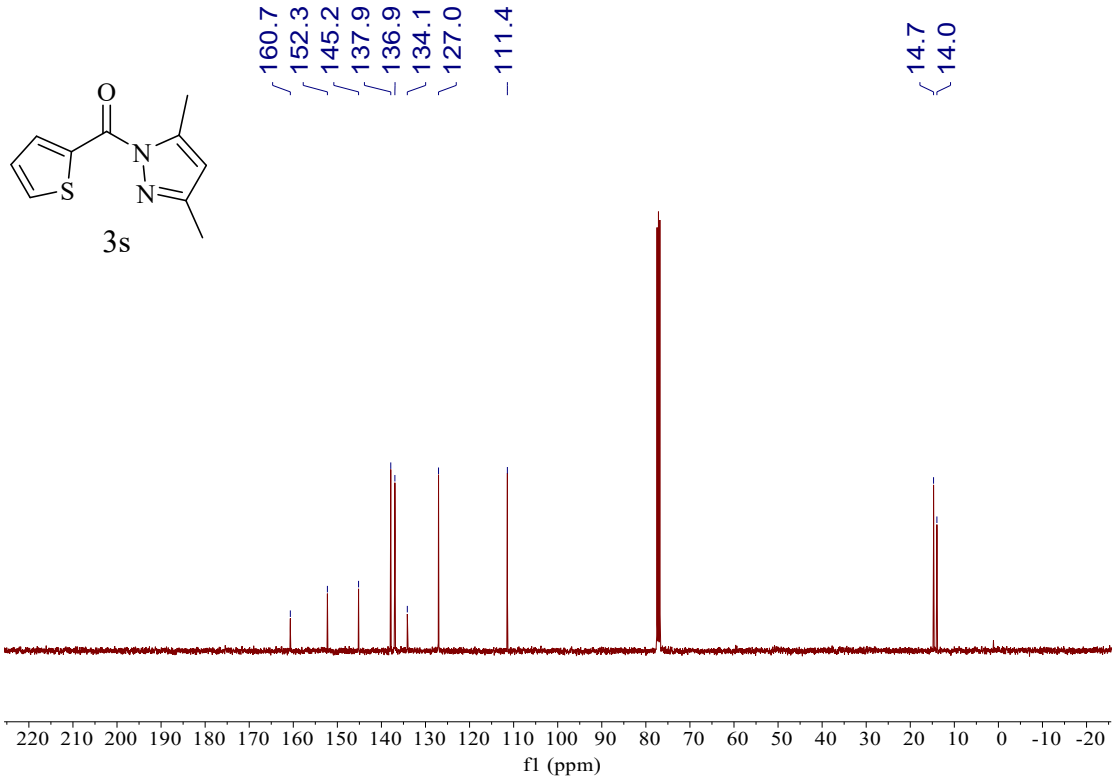

168.2
152.3
145.4
145.2
140.3
132.1
132.0
129.0
128.2
127.5
126.7
111.2
14.5
14.0
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

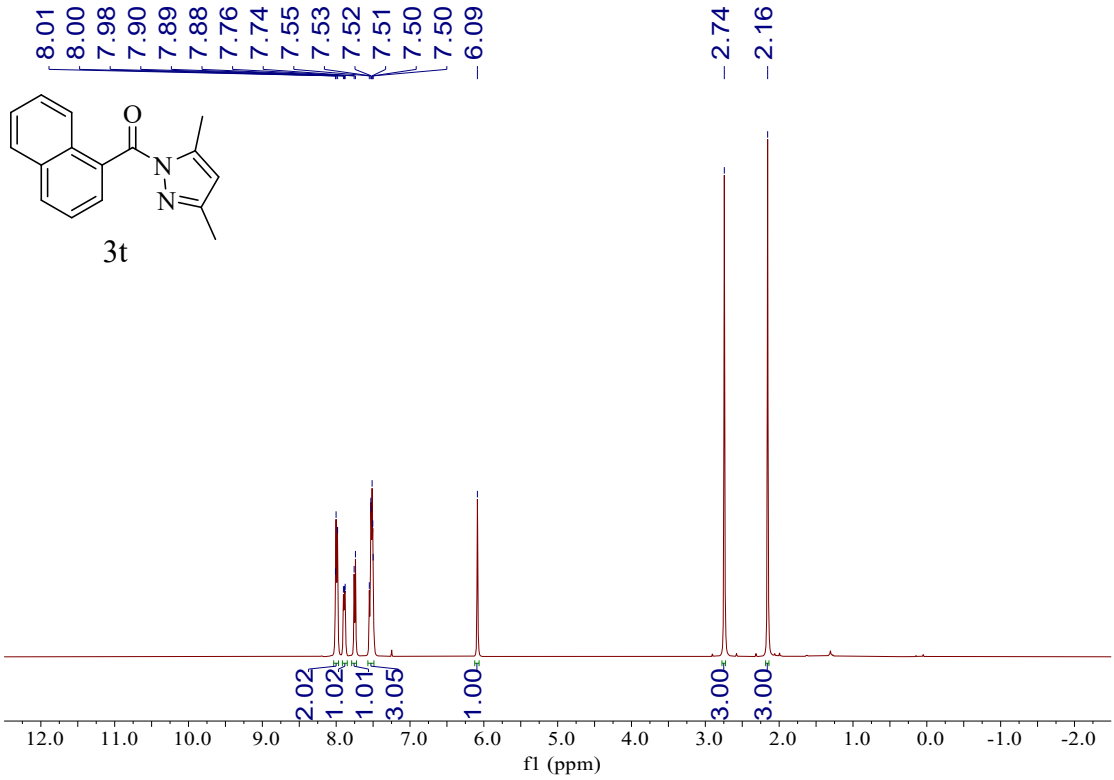
3q

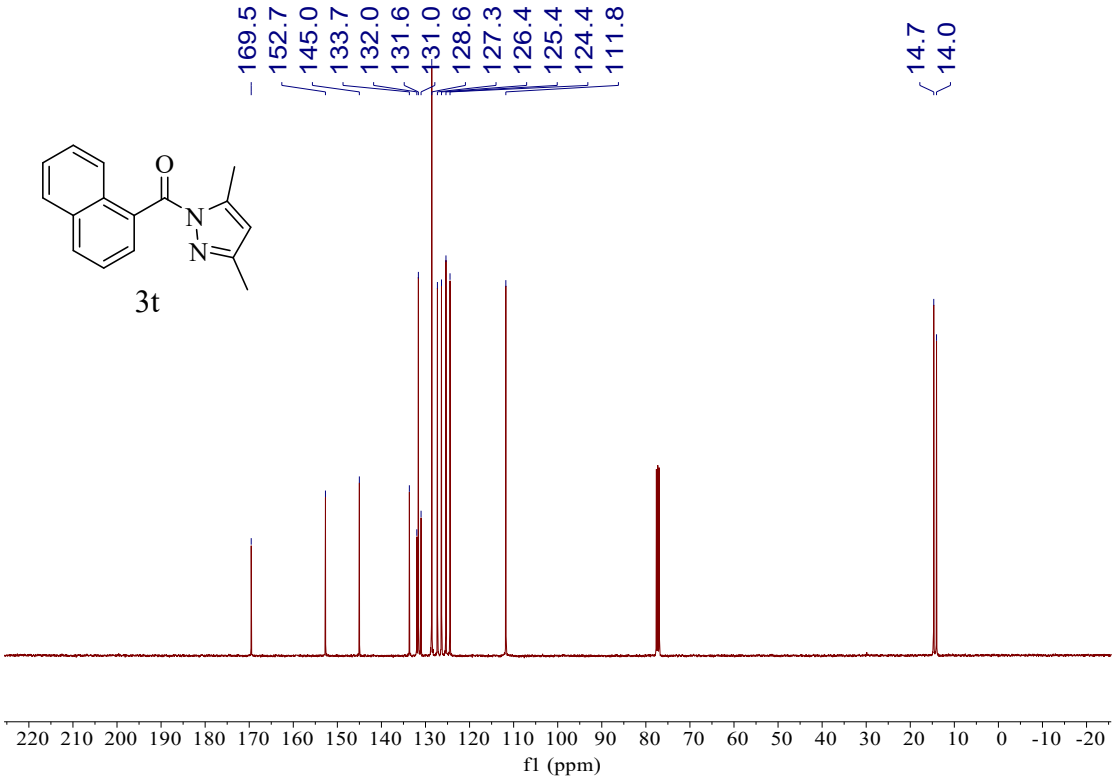

7.92
7.91
7.71
7.70
6.59
6.58
6.58
6.57
6.01
2.60
2.27
O
N
N
O
3r
1.00
1.00
1.00
1.00
3.05
3.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

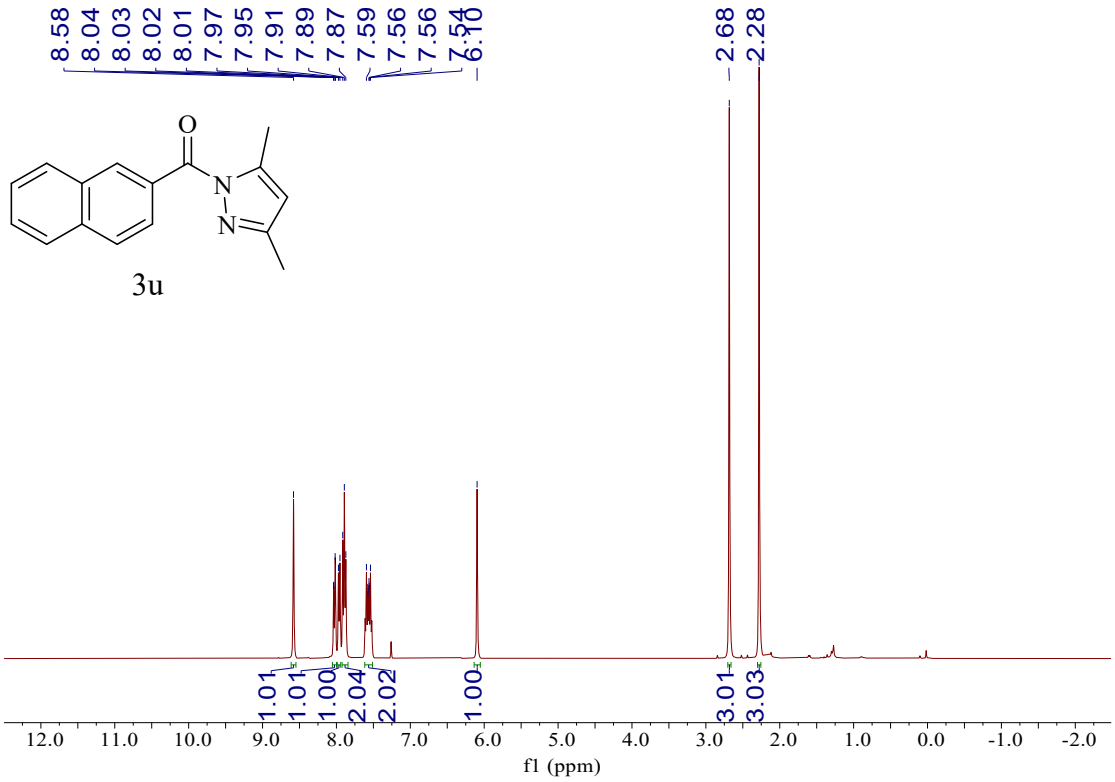

156.9
152.8
147.6
145.9
145.5
124.0
112.4
111.0
14.6
14.0
O
N
N
O
3r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.32
8.32
8.31
8.31
7.73
7.73
7.72
7.72
7.16
7.15
7.14
7.13
6.03
2.62
2.31
O
N
N
S
3s
1.00
1.00
1.02
1.00
3.05
3.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

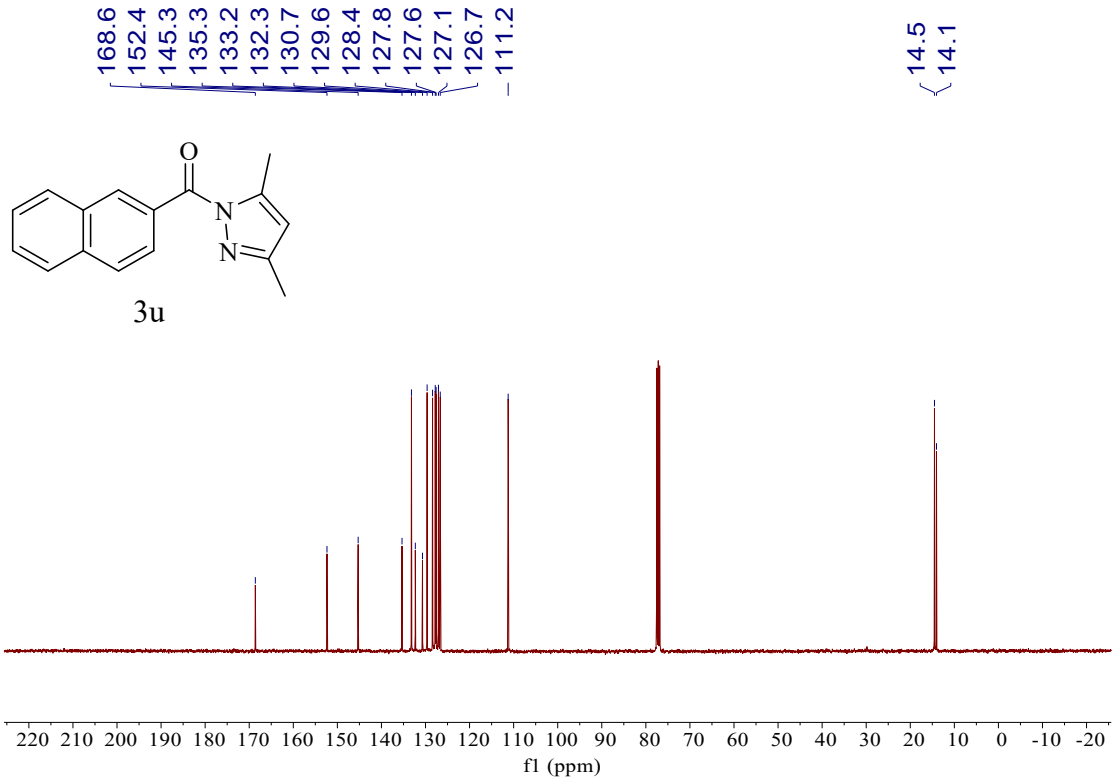

160.7
152.3
145.2
137.9
136.9
134.1
127.0
111.4
14.7
14.0
O
N
N
S
3s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.01
8.00
7.98
7.90
7.89
7.88
7.76
7.74
7.55
7.53
7.52
7.51
7.50
7.50
6.09
2.74
2.16
O
N
N
3t
2.02
1.02
1.01
3.05
1.00
3.00
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

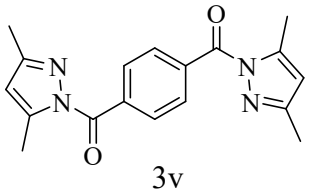

169.5
152.7
145.0
133.7
132.0
131.6
131.0
128.6
127.3
126.4
125.4
124.4
111.8
14.7
14.0
O
N
N
3t
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.58
8.04
8.03
8.02
8.01
7.97
7.95
7.91
7.89
7.87
7.59
7.56
7.56
7.54
6.10
2.68
2.28
O
N
N
1.01
1.01
1.00
2.04
2.02
1.00
3.01
3.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

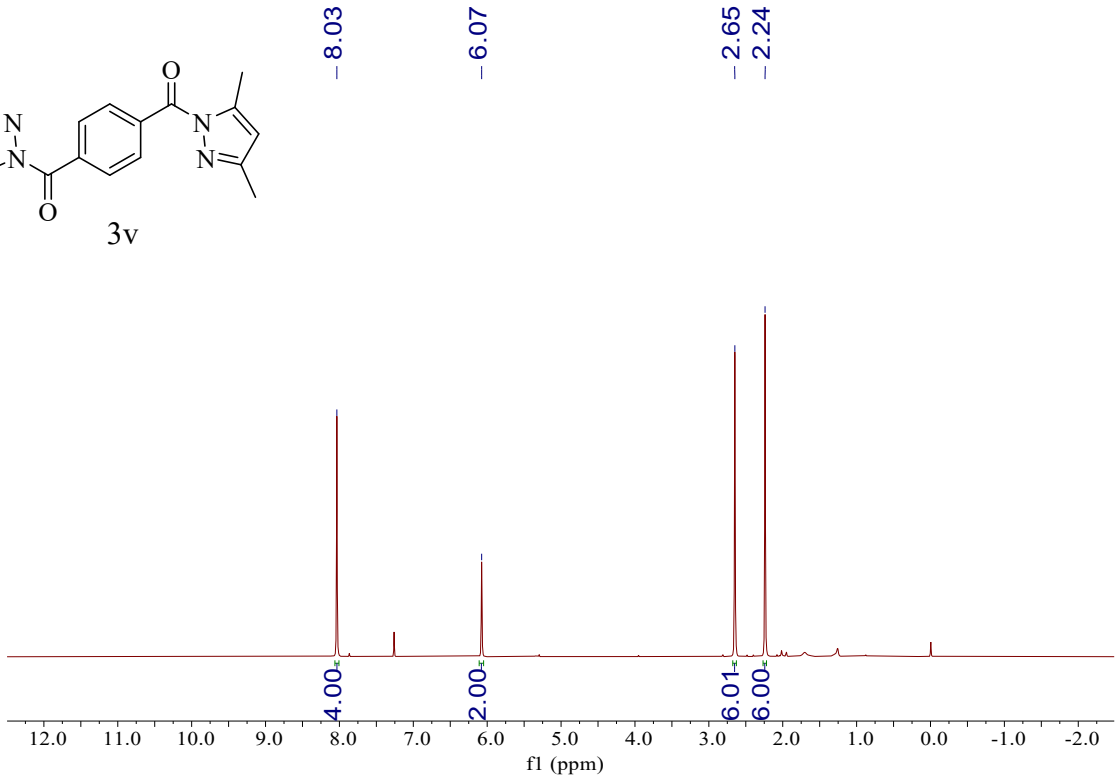
3u


168.6
152.4
145.3
135.3
133.2
132.3
130.7
129.6
128.4
127.8
127.6
127.1
126.7
111.2
14.5
14.1
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

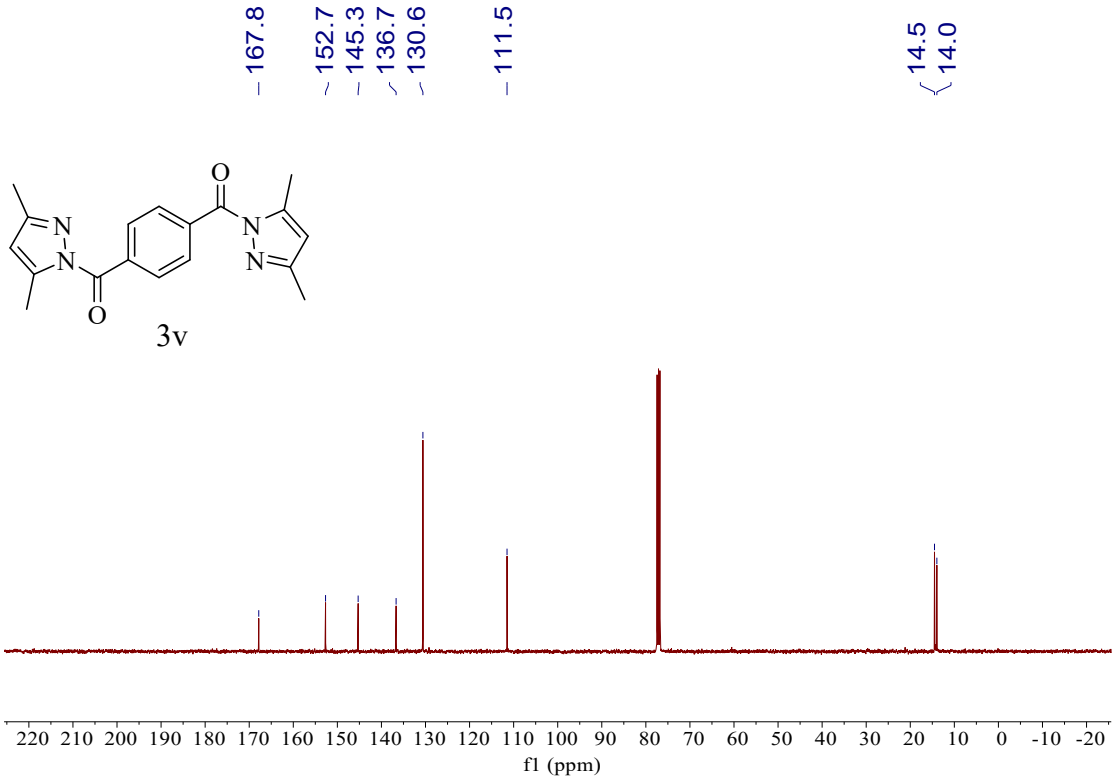
3u



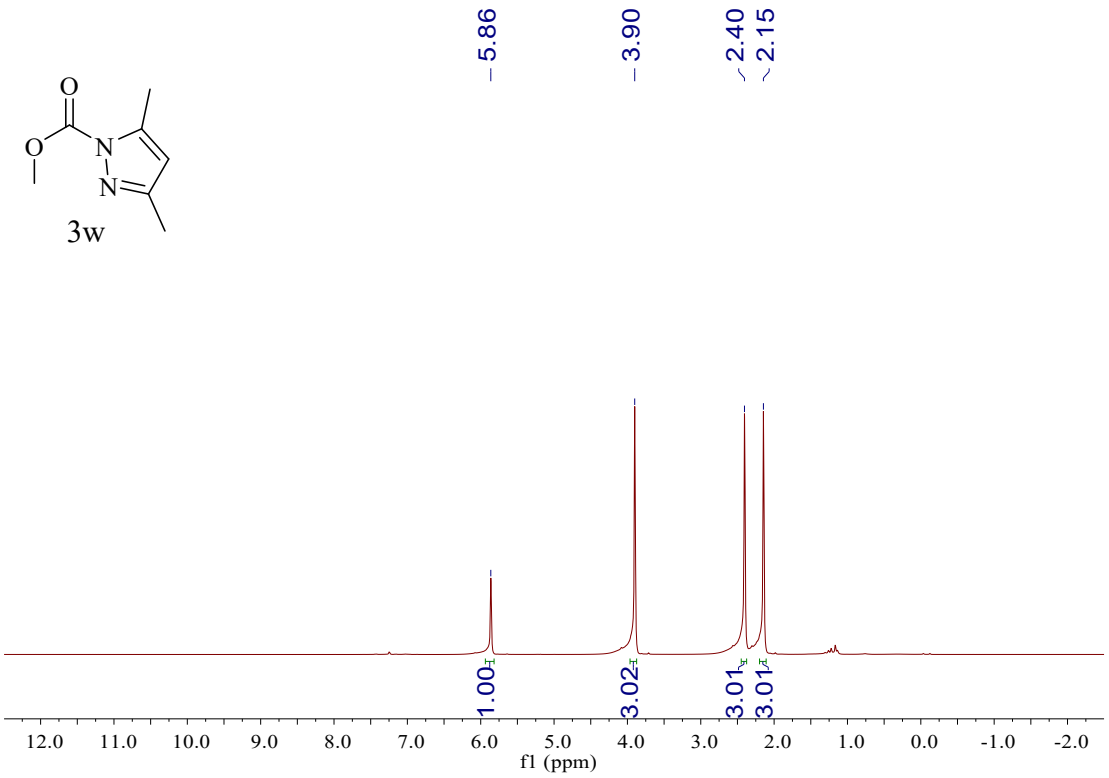
3v


8.03
6.07
2.65
2.24
4.00
2.00
6.01
6.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

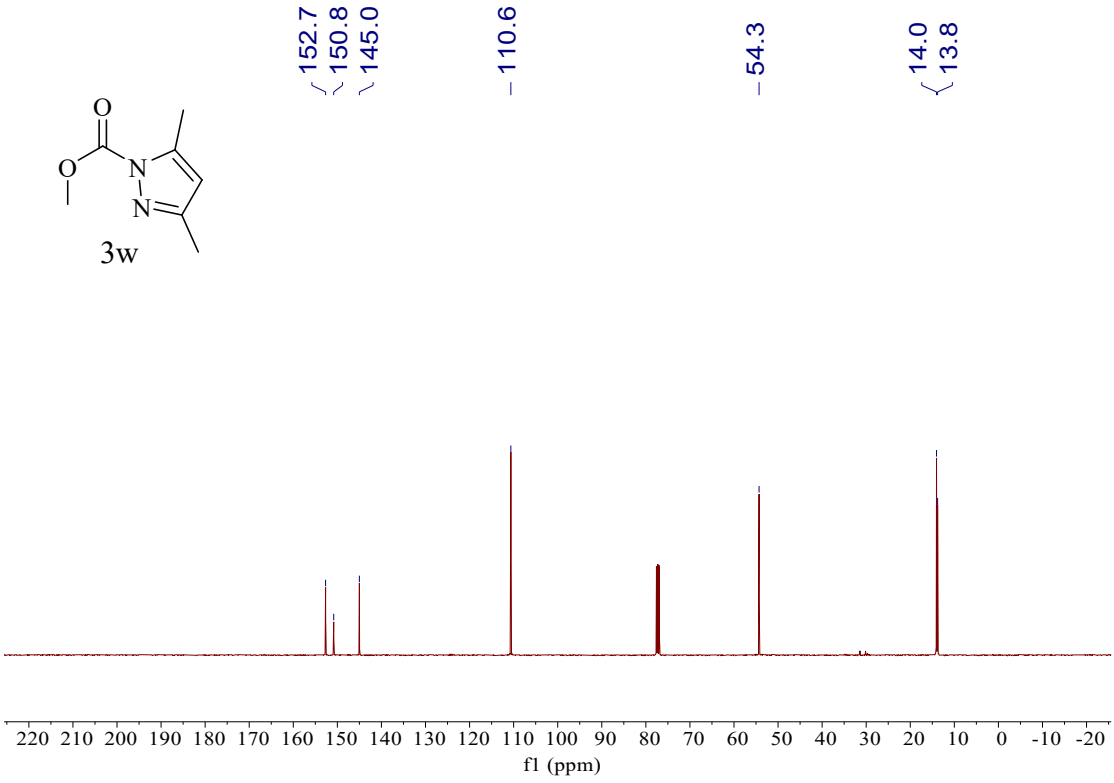
3v

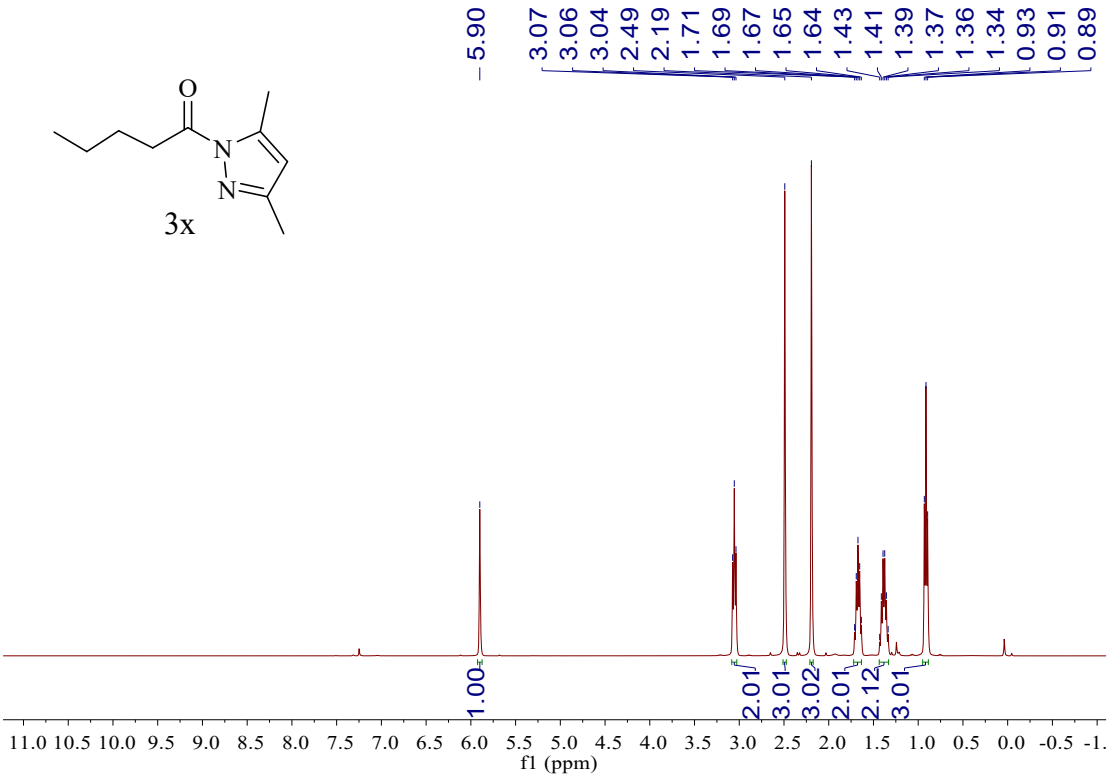

167.8
152.7
145.3
136.7
130.6
111.5
14.5
14.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

3w


5.86
3.90
2.40
2.15
1.00
3.02
3.01
3.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

3w


152.7
150.8
145.0
110.6
54.3
14.0
13.8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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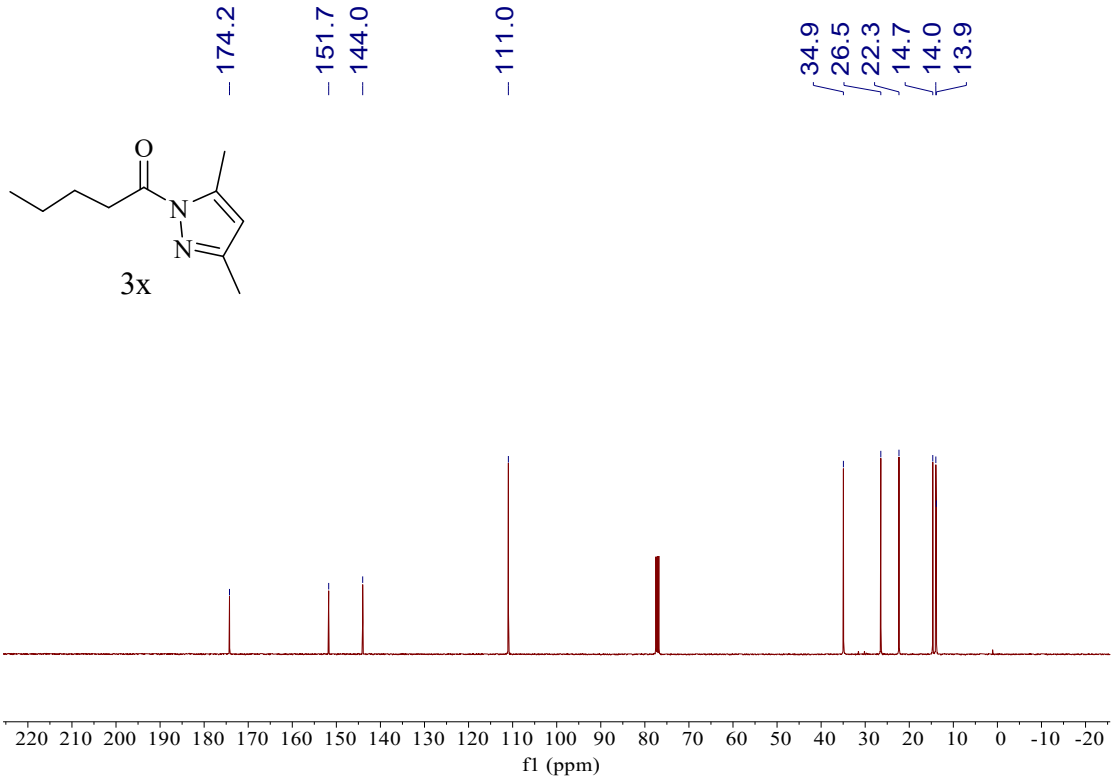
3.07
3.06
3.04
2.49
2.19
1.71
1.69
1.67
1.65
1.64
1.43
1.41
1.39
1.37
1.36
1.34
0.93
0.91
0.89
1.00
2.01
3.01
3.02
2.01
2.12
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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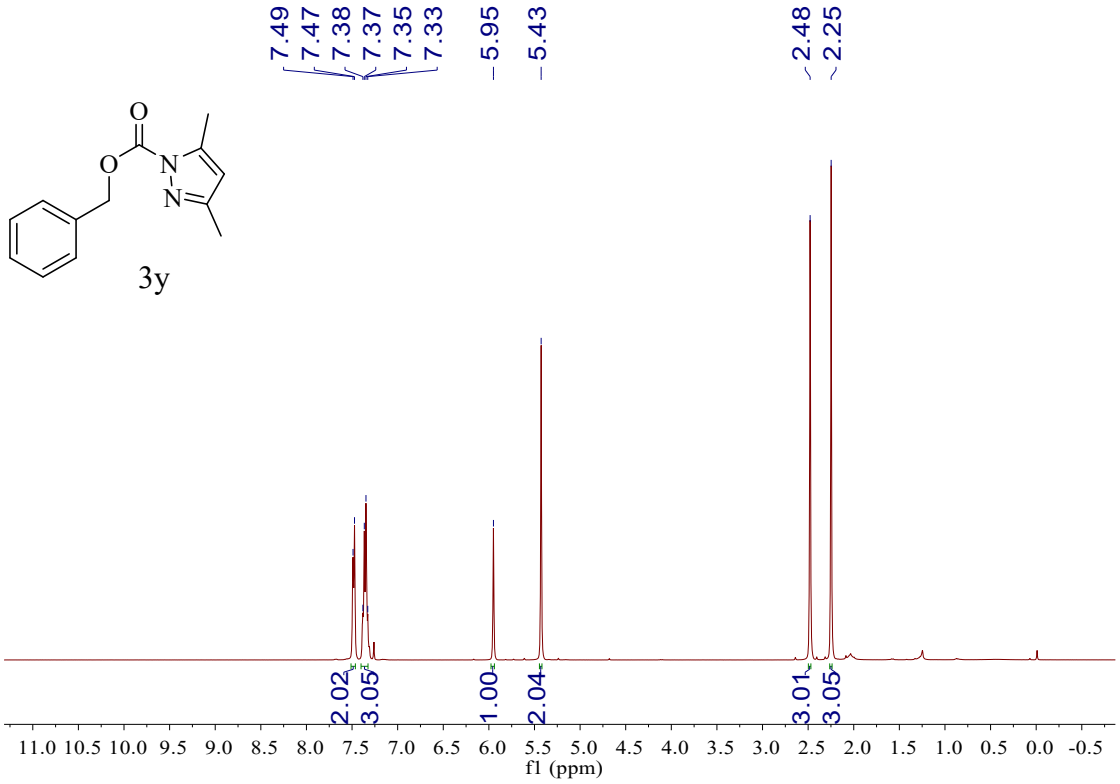
151.7
144.0
111.0
34.9
26.5
22.3
14.7
14.0
13.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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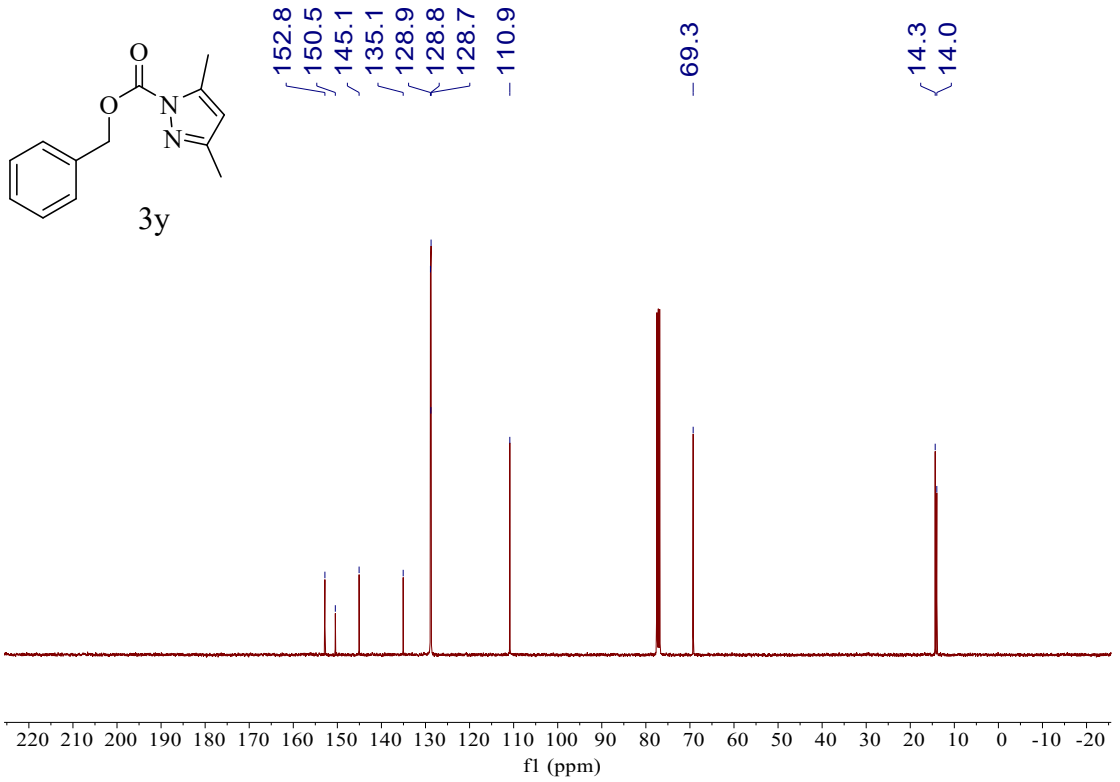
7.47
7.38
7.37
7.35
7.33
5.95
5.43
2.48
2.25
O
O
N
N
3y
2.02
3.05
1.00
2.04
3.01
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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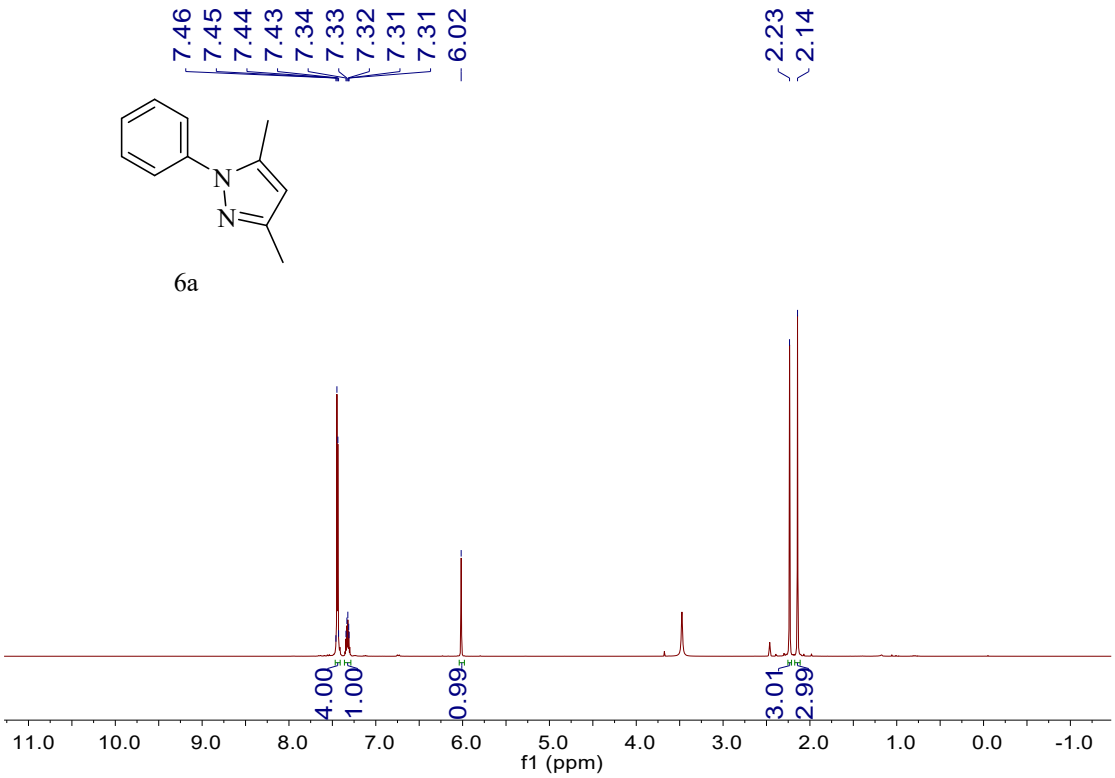
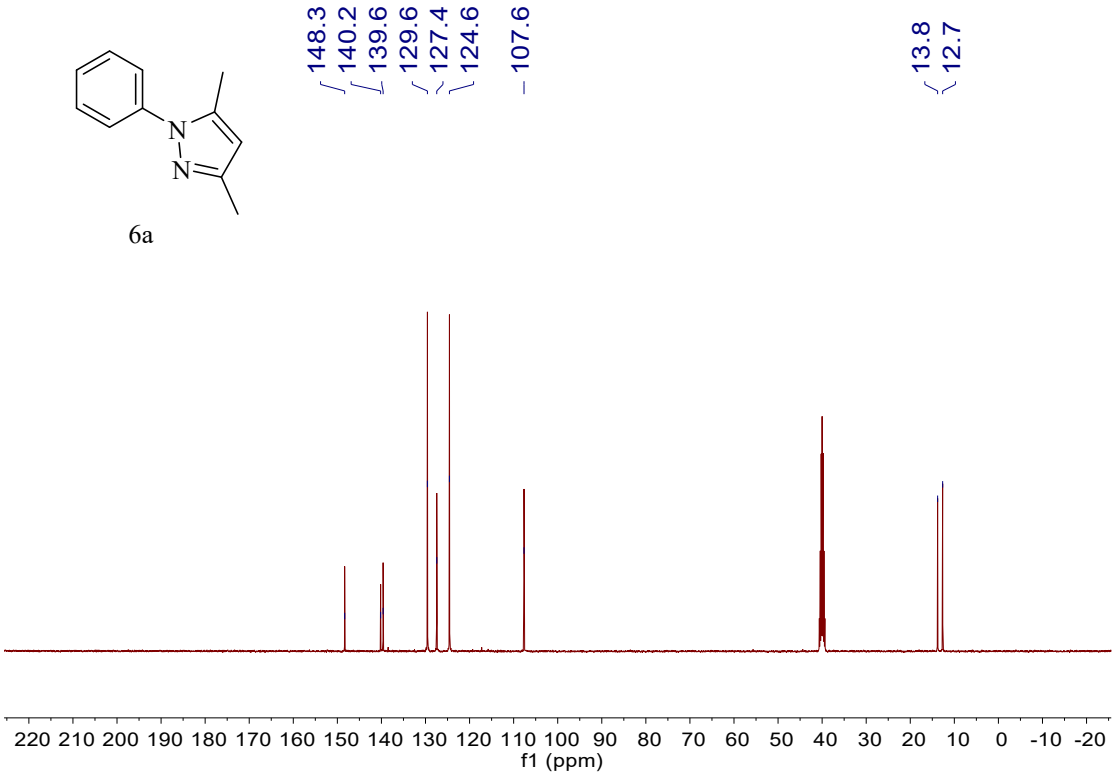
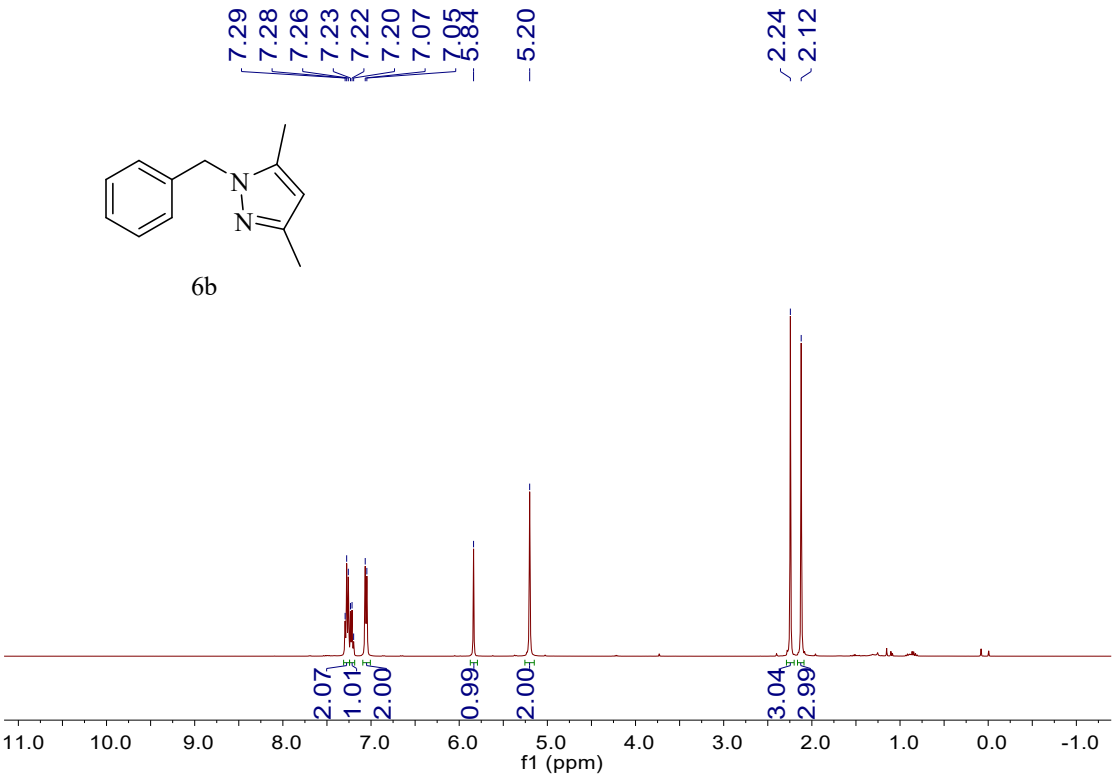
150.5
145.1
135.1
128.9
128.8
128.7
110.9
69.3
14.3
14.0
O
O
N
N
3y
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

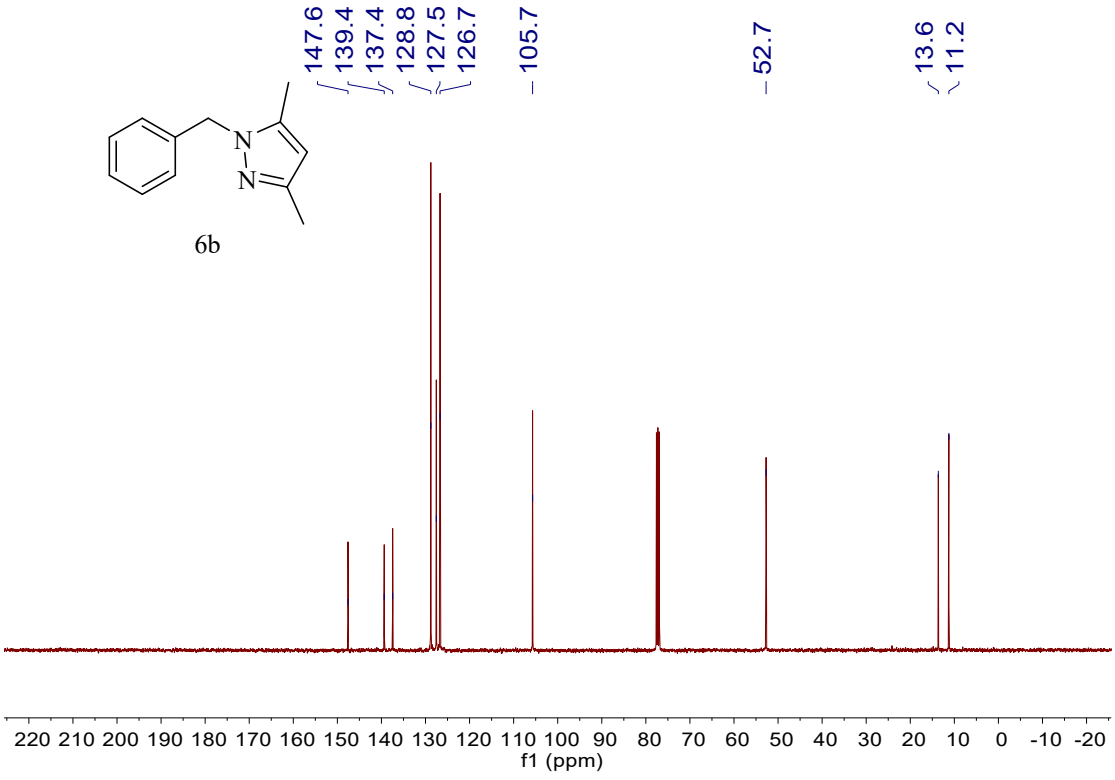

7.46
7.45
7.44
7.43
7.34
7.33
7.32
7.31
7.31
6.02
2.23
2.14
N
N
4.00
1.00
0.99
3.01
2.99
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

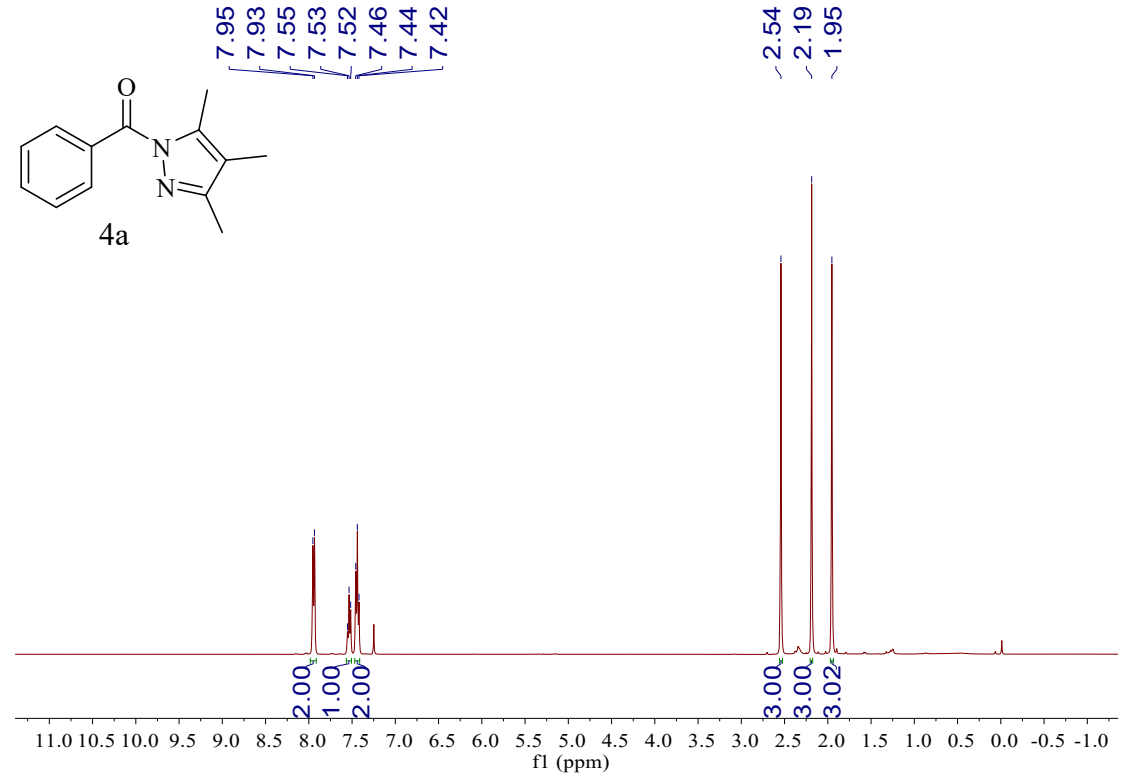
6a

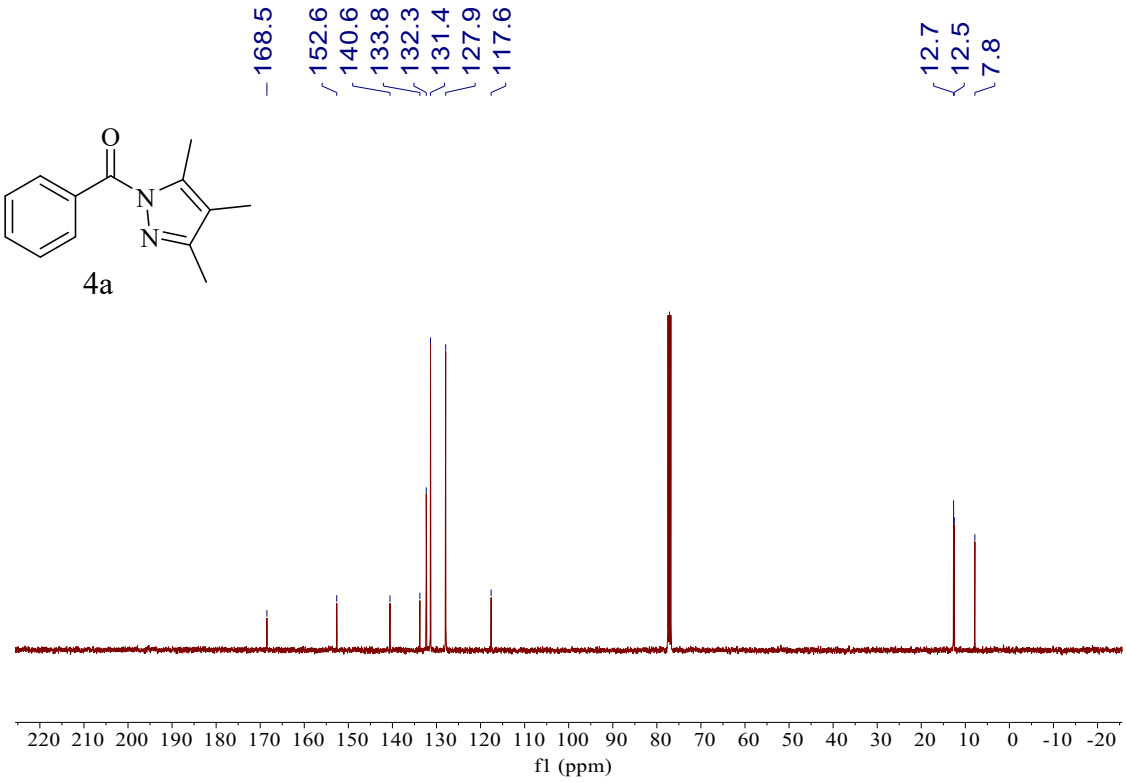

148.3
140.2
139.6
129.6
127.4
124.6
107.6
13.8
12.7
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

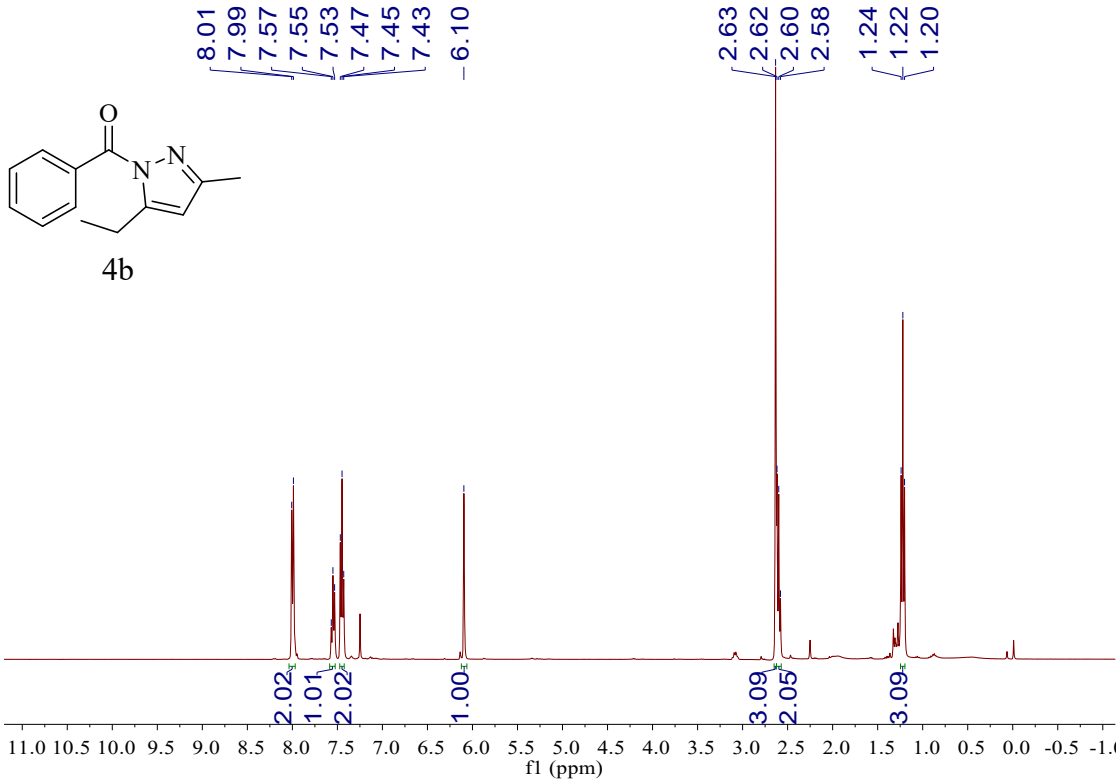
6a


7.29
7.28
7.26
7.23
7.22
7.20
7.07
7.05
5.84
5.20
2.24
2.12
N
N
6b
2.07
1.01
2.00
0.99
2.00
3.04
2.99
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

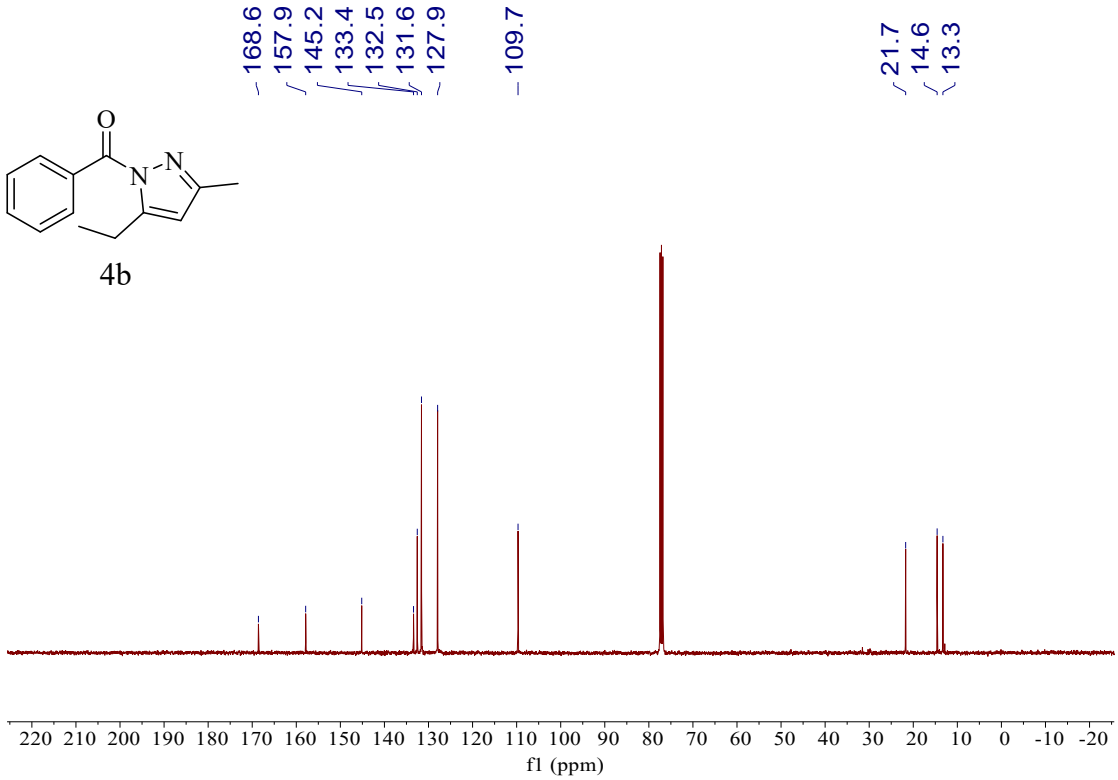

147.6
139.4
137.4
128.8
127.5
126.7
105.7
52.7
13.6
11.2
N
N
6b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.95
7.93
7.55
7.53
7.52
7.46
7.44
7.42
2.54
2.19
1.95
O
N
N
4a
2.00
1.00
2.00
3.00
3.00
3.02
11.0 10.5 10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)

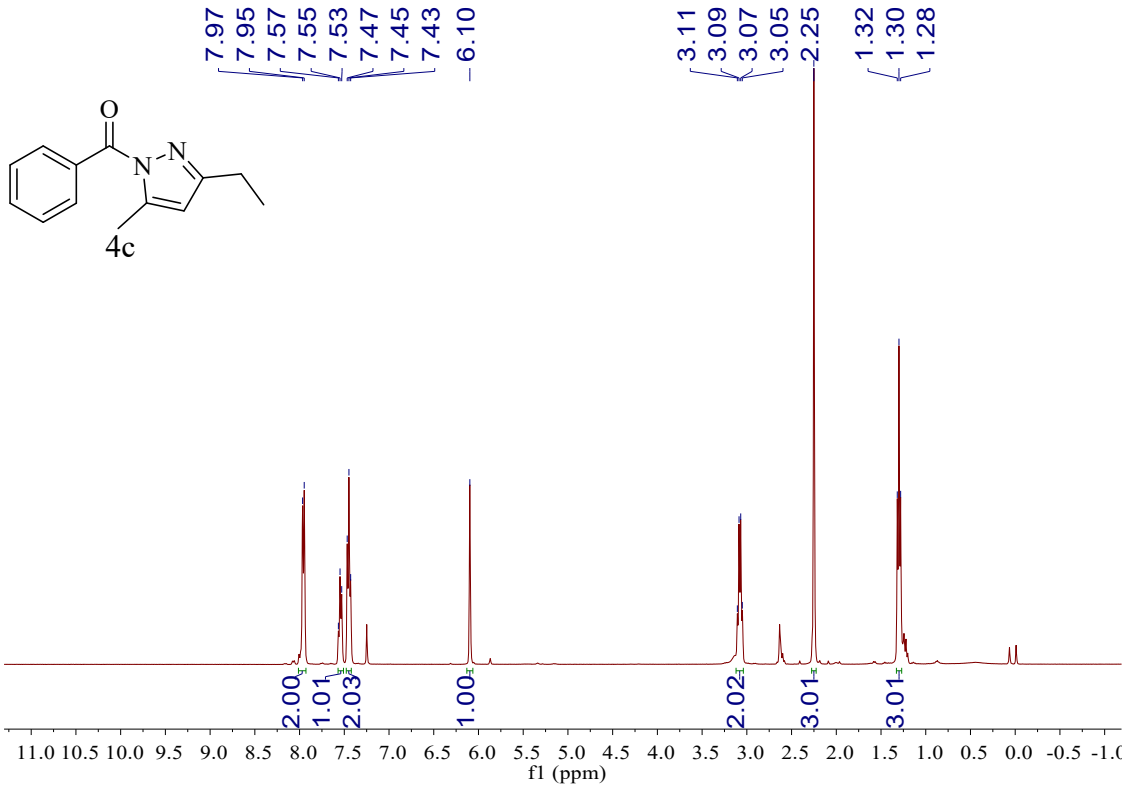

168.5
152.6
140.6
133.8
132.3
131.4
127.9
117.6
12.7
12.5
7.8
O
N
N
4a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

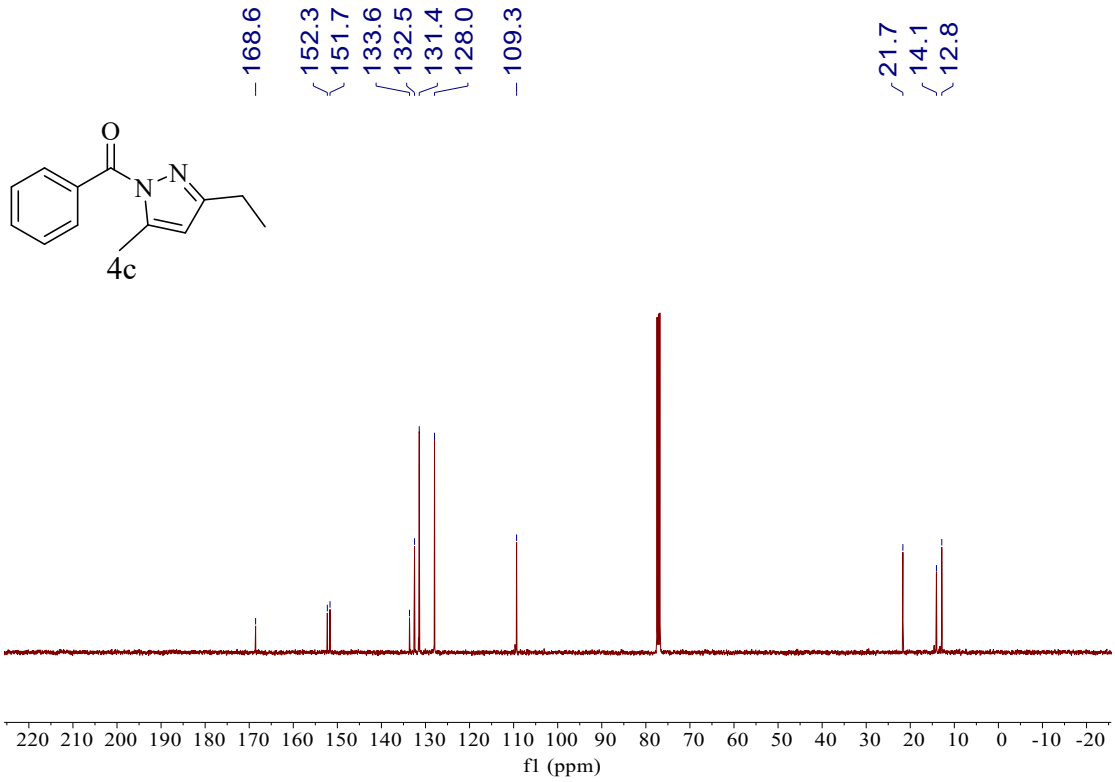

8.01
7.99
7.57
7.55
7.53
7.47
7.45
7.43
6.10
2.63
2.62
2.60
2.58
1.24
1.22
1.20
O
N
N
2.02
1.01
2.02
1.00
3.09
2.05
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

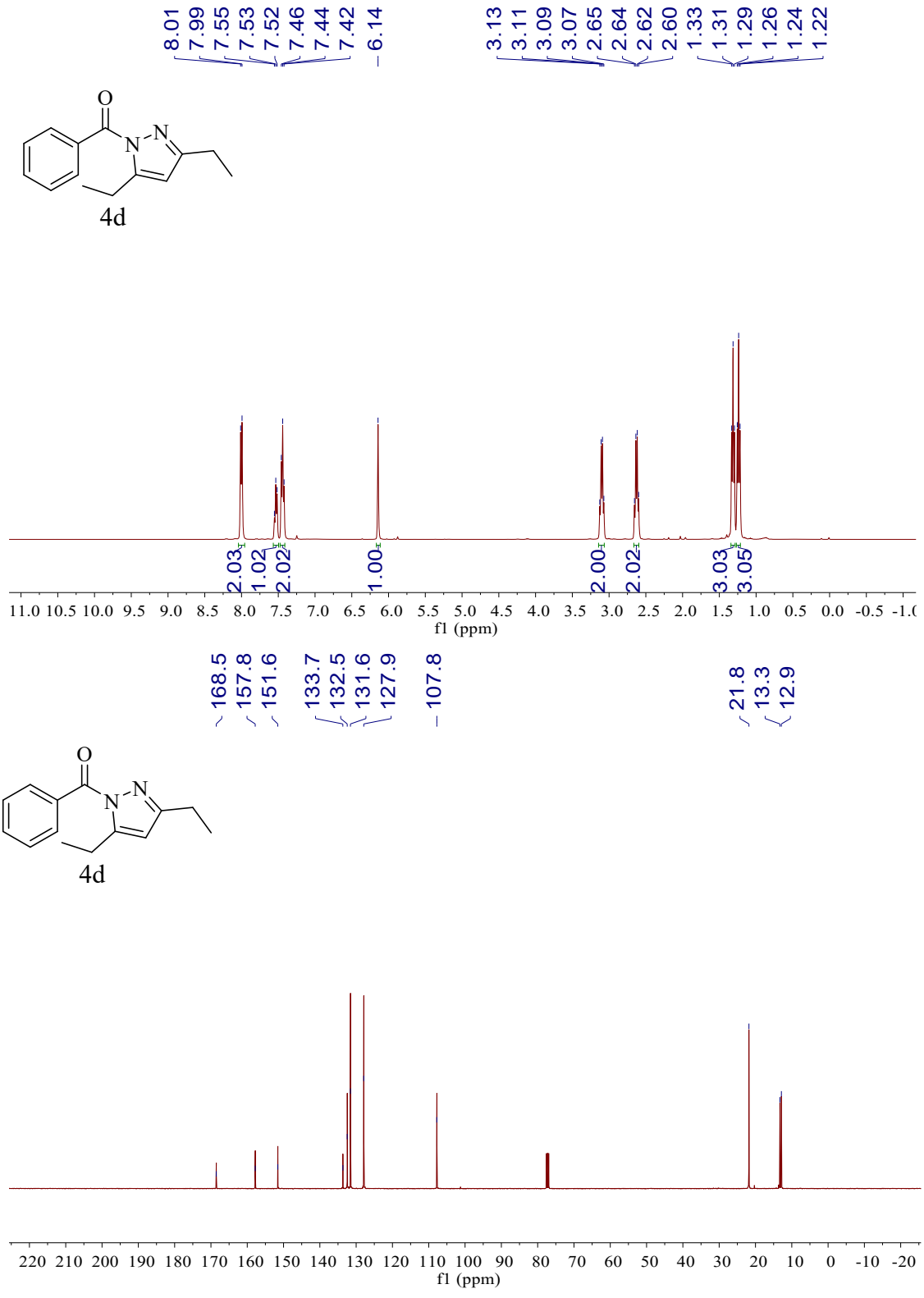
4b

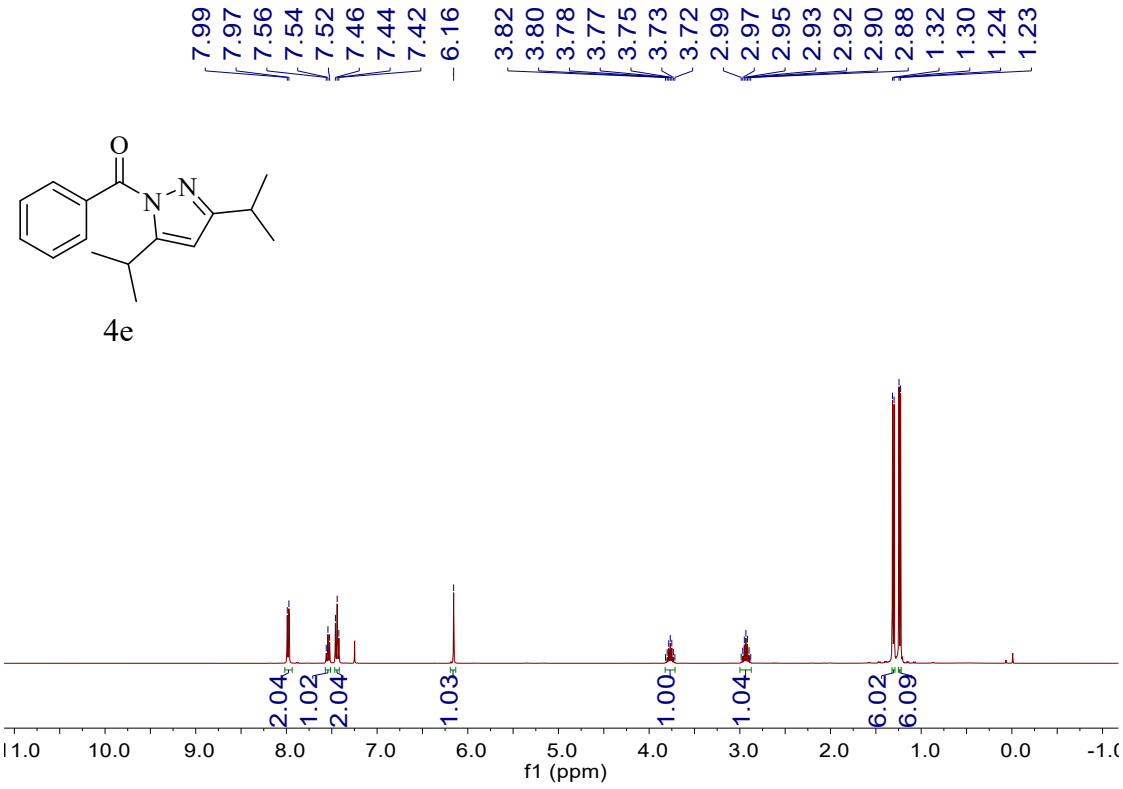

168.6
157.9
145.2
133.4
132.5
131.6
127.9
109.7
21.7
14.6
13.3
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

4b


7.97
7.95
7.57
7.55
7.53
7.47
7.45
7.43
6.10
3.11
3.09
3.07
3.05
2.25
1.32
1.30
1.28
O
N
N
4c
2.00
1.01
2.03
1.00
2.02
3.01
3.01
11.0 10.5 10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)


168.6
152.3
151.7
133.6
132.5
131.4
128.0
109.3
21.7
14.1
12.8
O
N
N
4c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.01
7.99
7.55
7.53
7.52
7.46
7.44
7.42
6.14
3.13
3.11
3.09
3.07
2.65
2.64
2.62
2.60
1.33
1.31
1.29
1.26
1.24
1.22
O
N
N
4d
2.03
1.02
2.02
1.00
2.00
2.02
3.03
3.05
11.0 10.5 10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)
168.5
157.8
151.6
133.7
132.5
131.6
127.9
107.8
21.8
13.3
12.9
O
N
N
4d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.97
7.56
7.54
7.52
7.46
7.44
7.42
6.16
3.82
3.80
3.78
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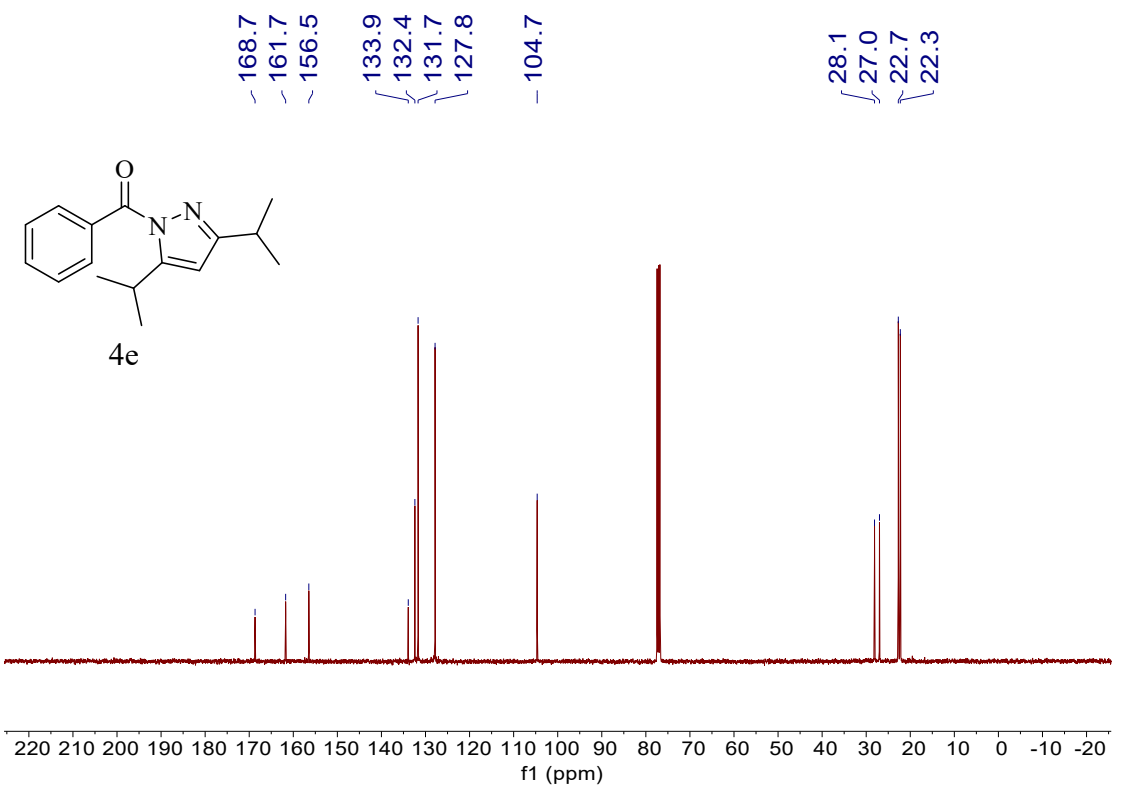
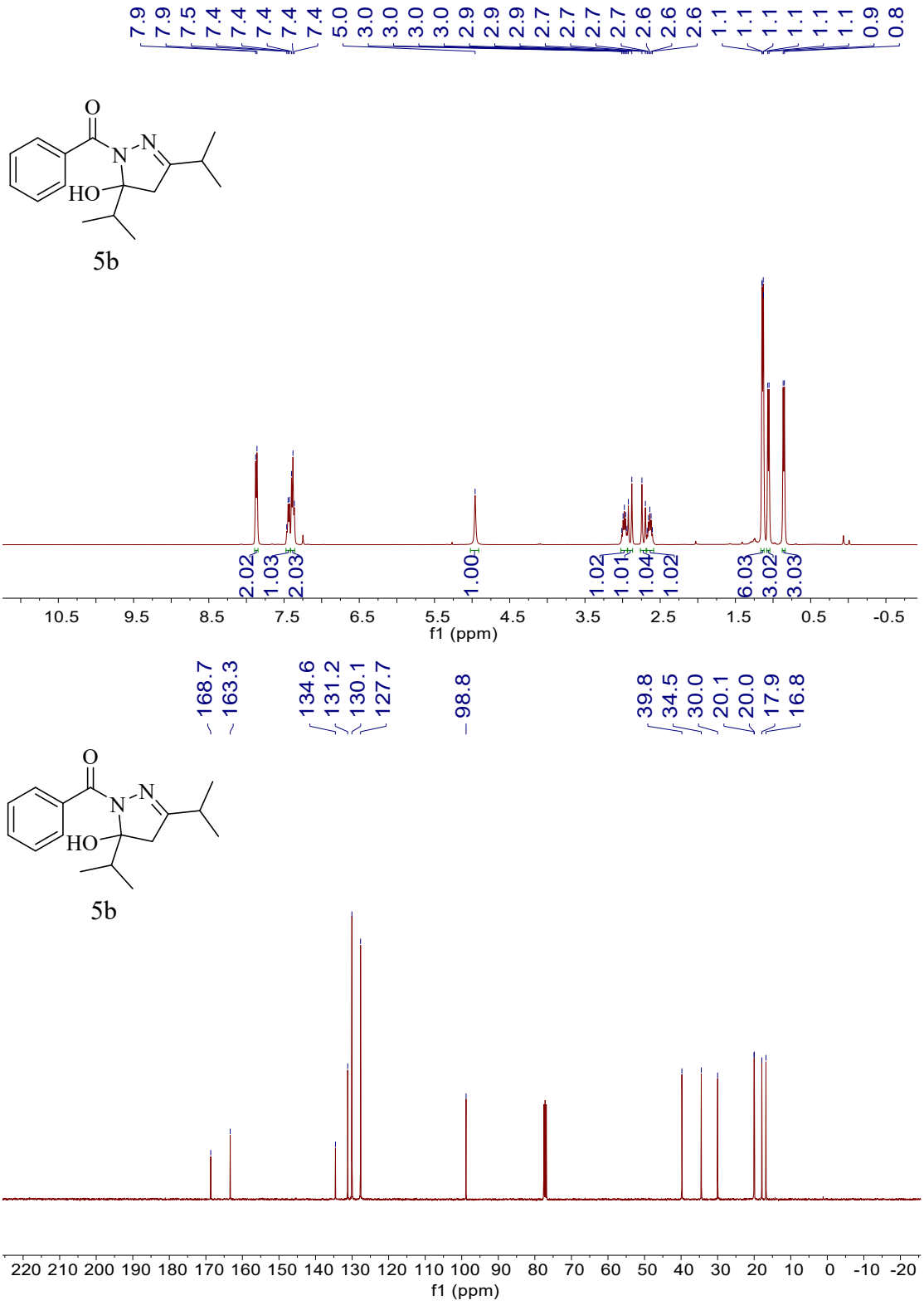
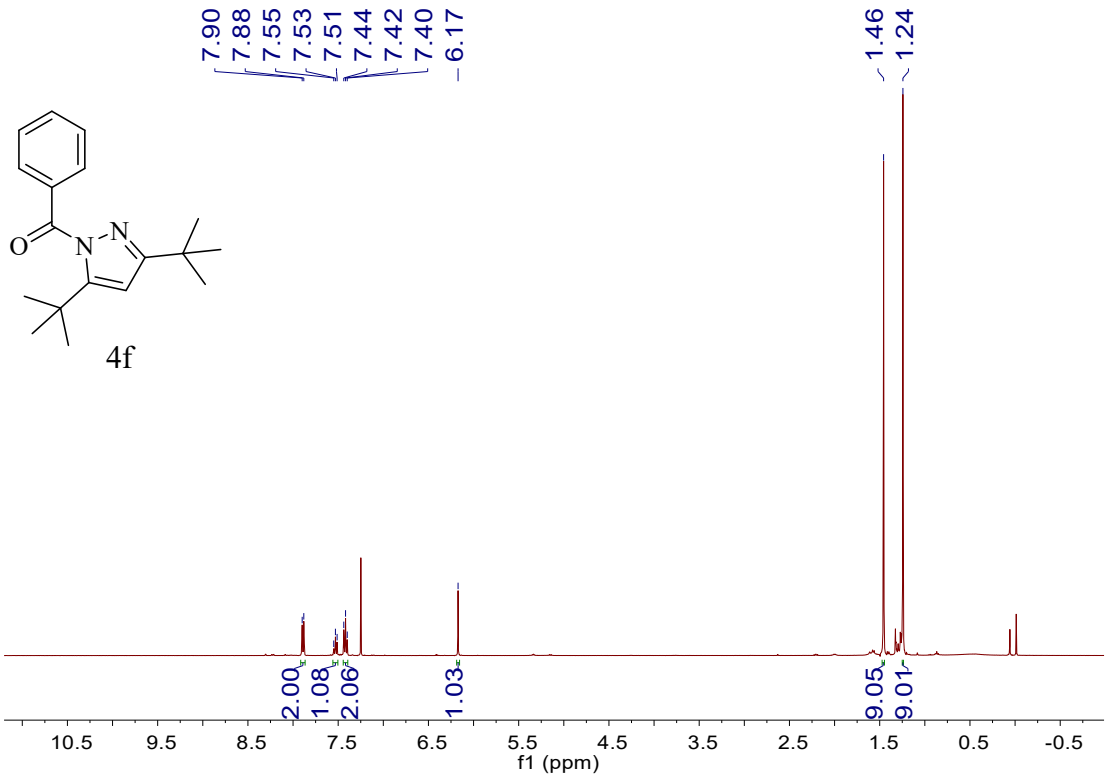
3.75
3.73
3.72
2.99
2.97
2.95
2.93
2.92
2.90
2.88
1.32
1.30
1.24
1.23
O
N
N
4e
2.04
1.02
2.04
1.03
1.00
1.04
6.02
6.09
f1 (ppm)


168.7
161.7
156.5
133.9
132.4
131.7
127.8
104.7
28.1
27.0
22.7
22.3
O
N
N
4e
f1 (ppm)


7.9 7.9 7.5 7.4 7.4 7.4 7.4 7.4 5.0 3.0 3.0 3.0 3.0 2.9 2.9 2.9 2.7 2.7 2.7 2.7 2.6 2.6 2.6 1.1 1.1 1.1 1.1 1.1 1.1 0.9 0.8
O
N
N
HO
5b
2.02 1.03 2.03 1.00 1.02 1.01 1.04 1.02 6.03 3.02 3.03
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)
168.7 163.3 134.6 131.2 130.1 127.7 98.8 39.8 34.5 30.0 20.1 20.0 17.9 16.8
O
N
N
HO
5b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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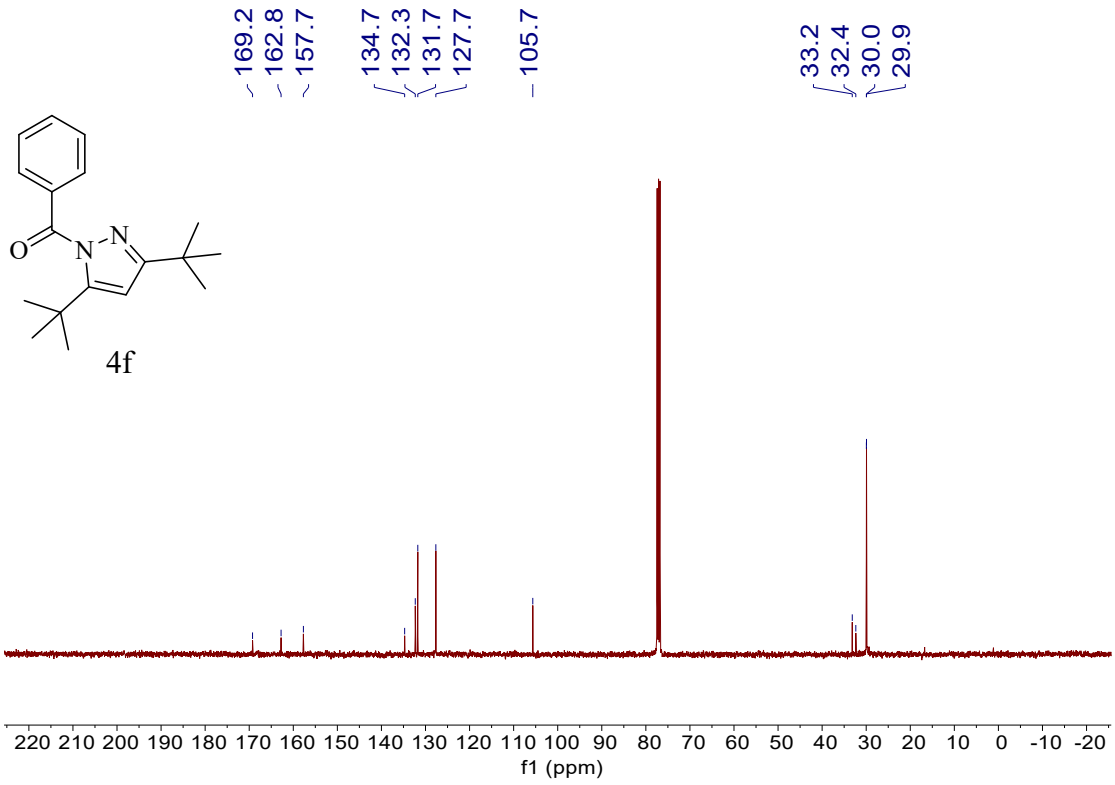
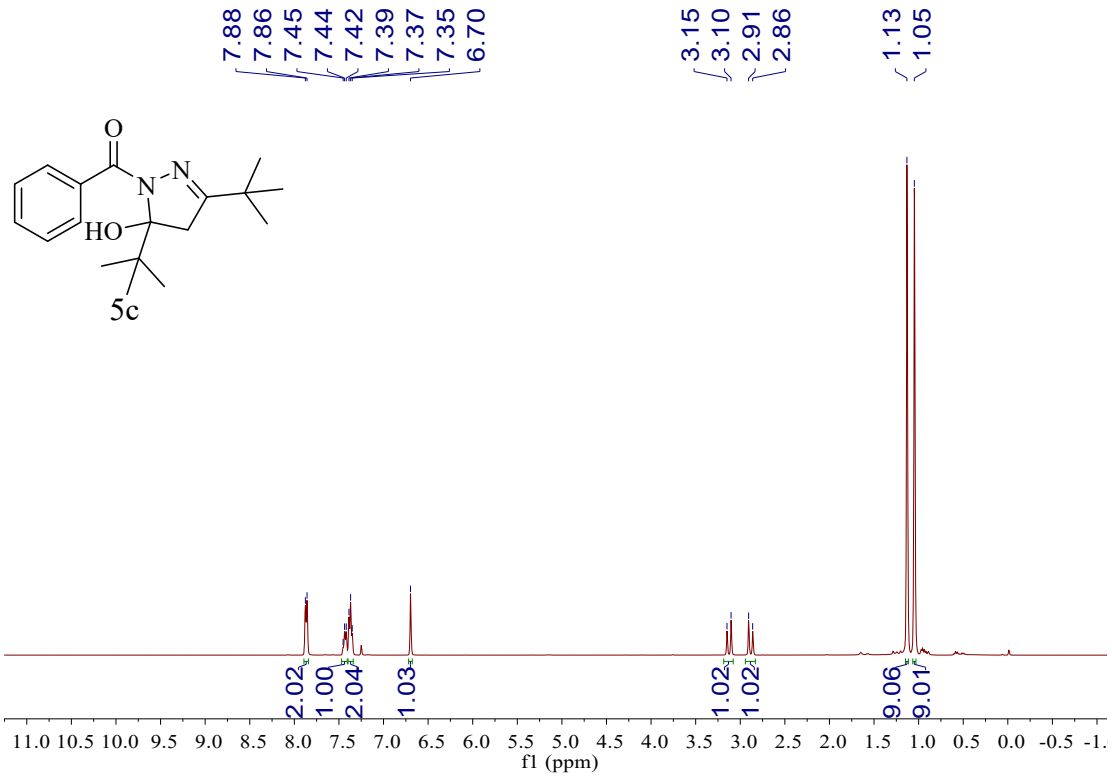
7.88
7.55
7.53
7.51
7.44
7.42
7.40
6.17
1.46
1.24
O
N
N
2.00
1.08
2.06
1.03
9.05
9.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

4f


169.2
162.8
157.7
134.7
132.3
131.7
127.7
105.7
33.2
32.4
30.0
29.9
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

4f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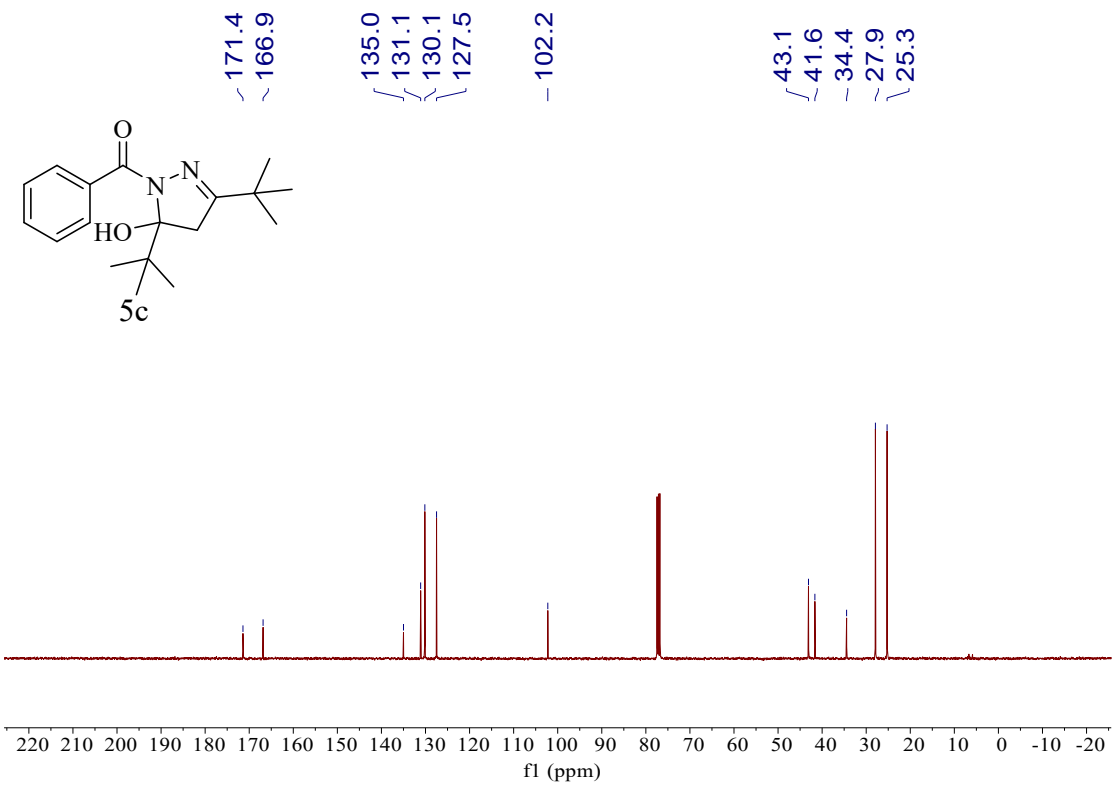
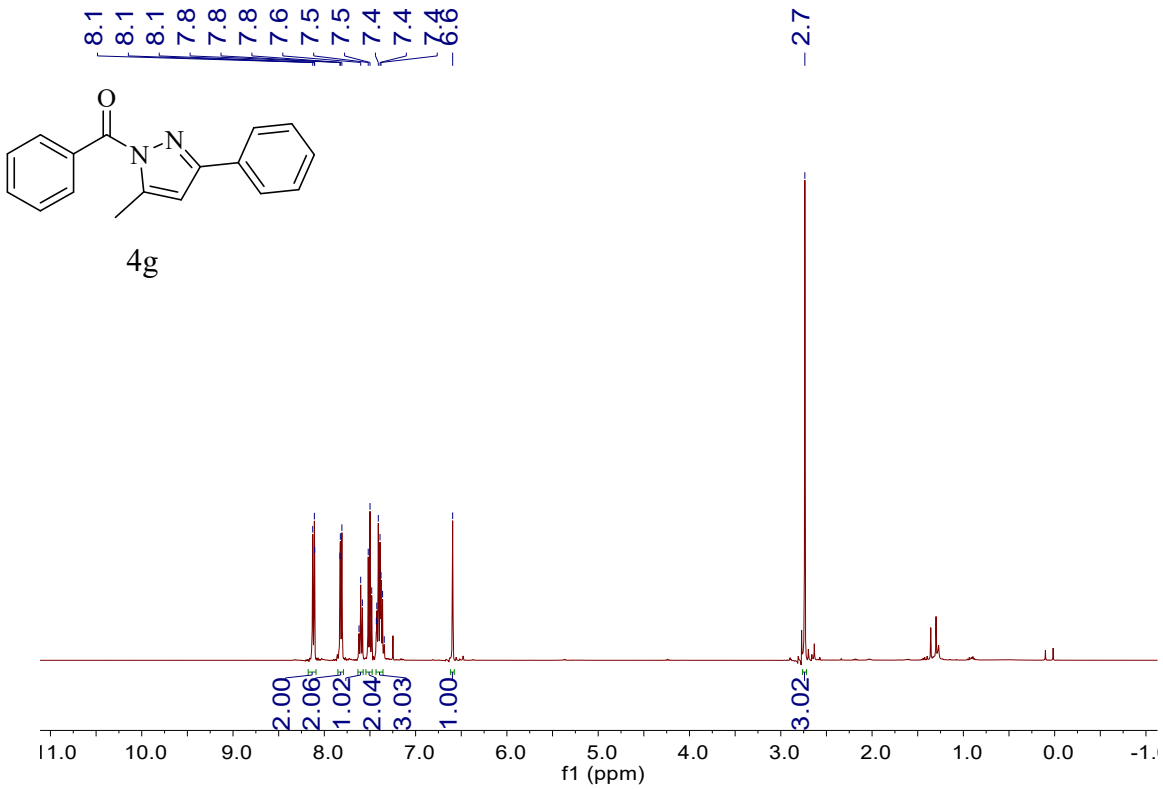
7.86
7.45
7.44
7.42
7.39
7.37
7.35
6.70
3.15
3.10
2.91
2.86
1.13
1.05
O
N
N
HO
5c
2.02
1.00
2.04
1.03
1.02
1.02
9.06
9.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


171.4
166.9
135.0
131.1
130.1
127.5
102.2
43.1
41.6
34.4
27.9
25.3
O
N
N
HO
5c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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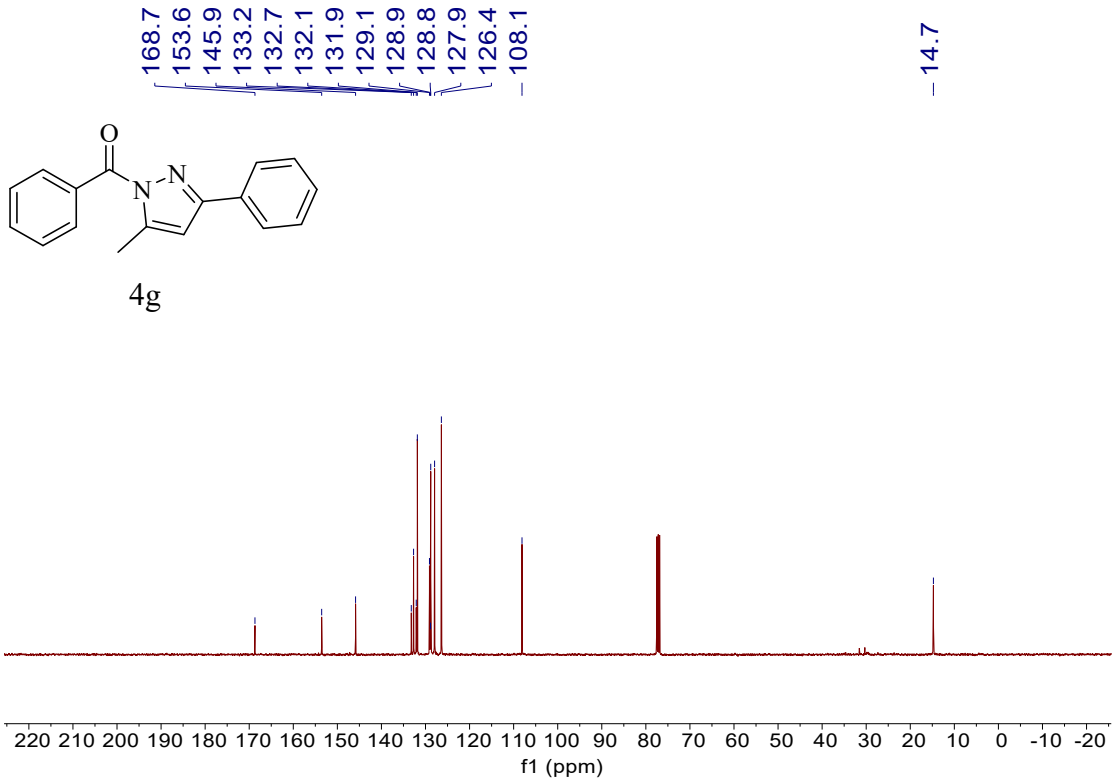
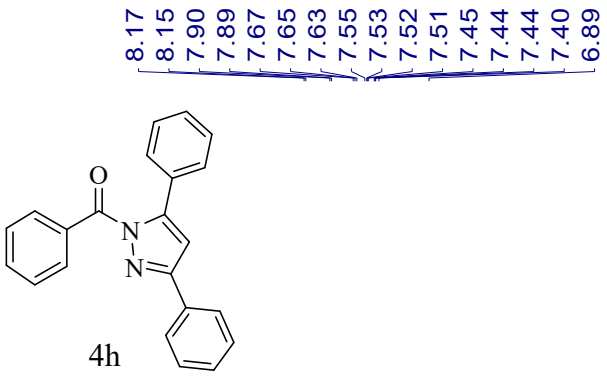
8.1
8.1
7.8
7.8
7.8
7.6
7.5
7.5
7.4
7.4
7.4
6.6
2.7
O
N
N
4g
2.00
2.06
1.02
2.04
3.03
1.00
3.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


168.7
153.6
145.9
133.2
132.7
132.1
131.9
129.1
128.9
128.8
127.9
126.4
108.1
14.7
O
N
N
4g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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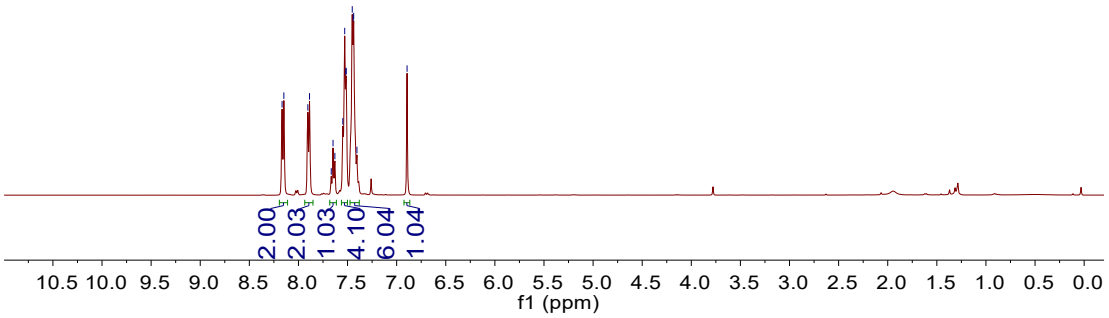
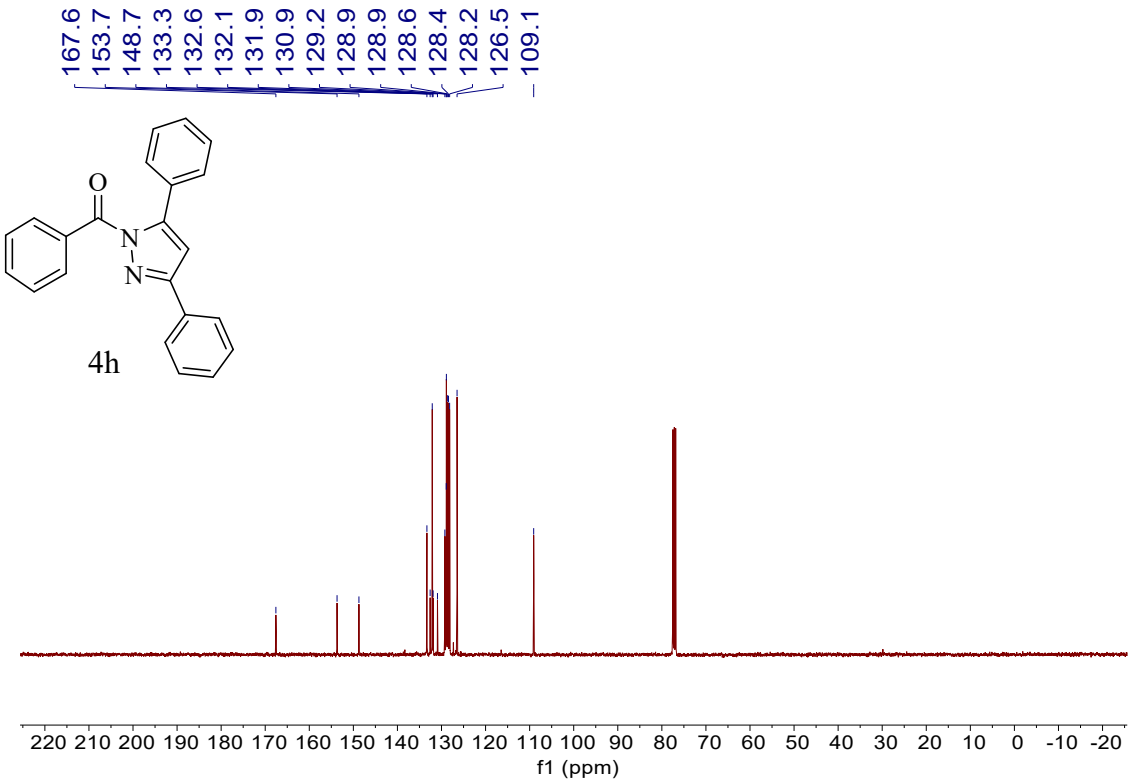
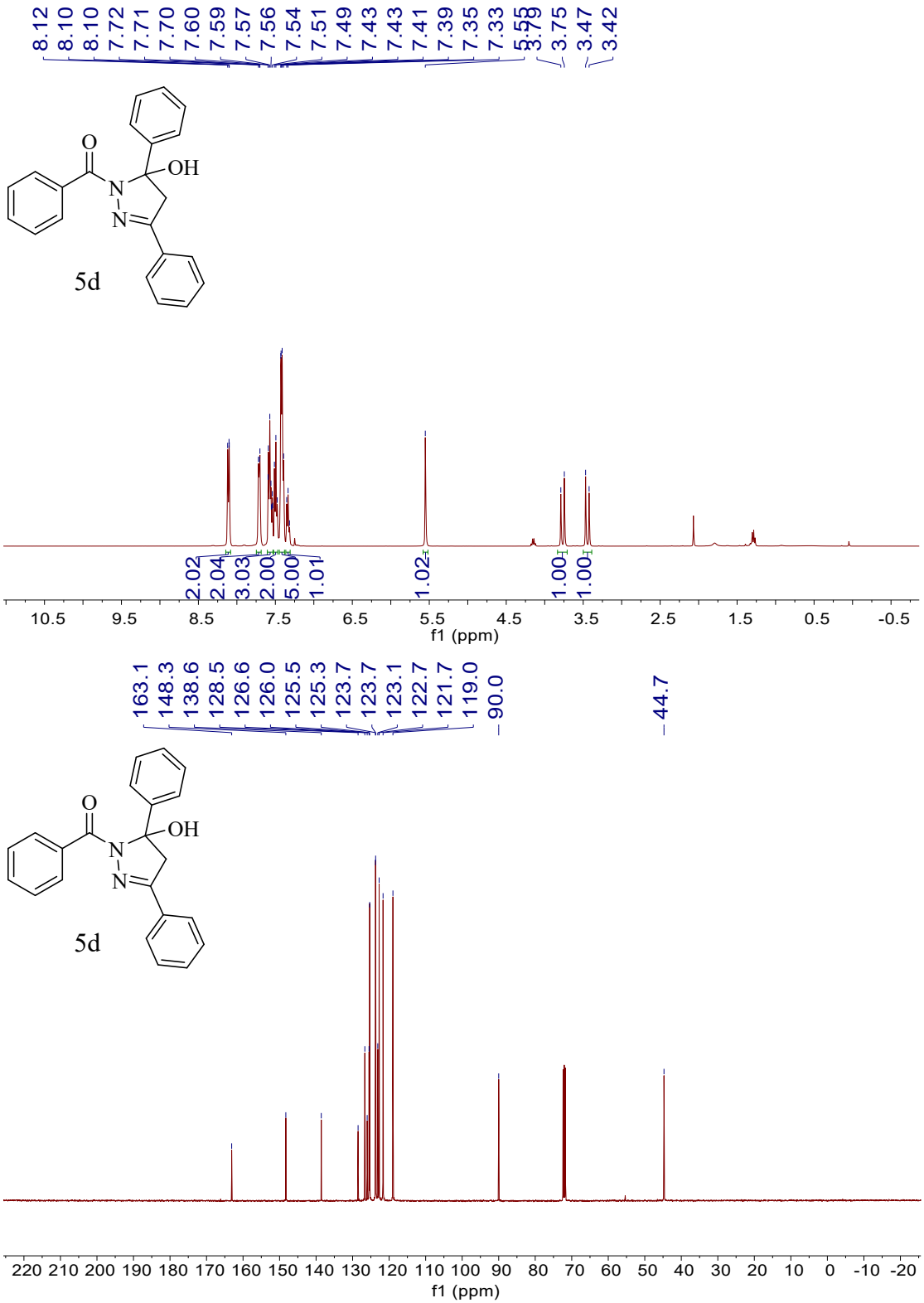
7.53
7.52
7.51
7.45
7.44
7.44
7.40
6.89
O
N
N

4h


2.00
2.03
1.03
4.10
6.04
1.04
10.5 10.0 9.5 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 0.0
f1 (ppm)


167.6
153.7
148.7
133.3
132.6
132.1
131.9
130.9
129.2
128.9
128.9
128.6
128.4
128.2
126.5
109.1
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

4h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8.10
7.72
7.71
7.70
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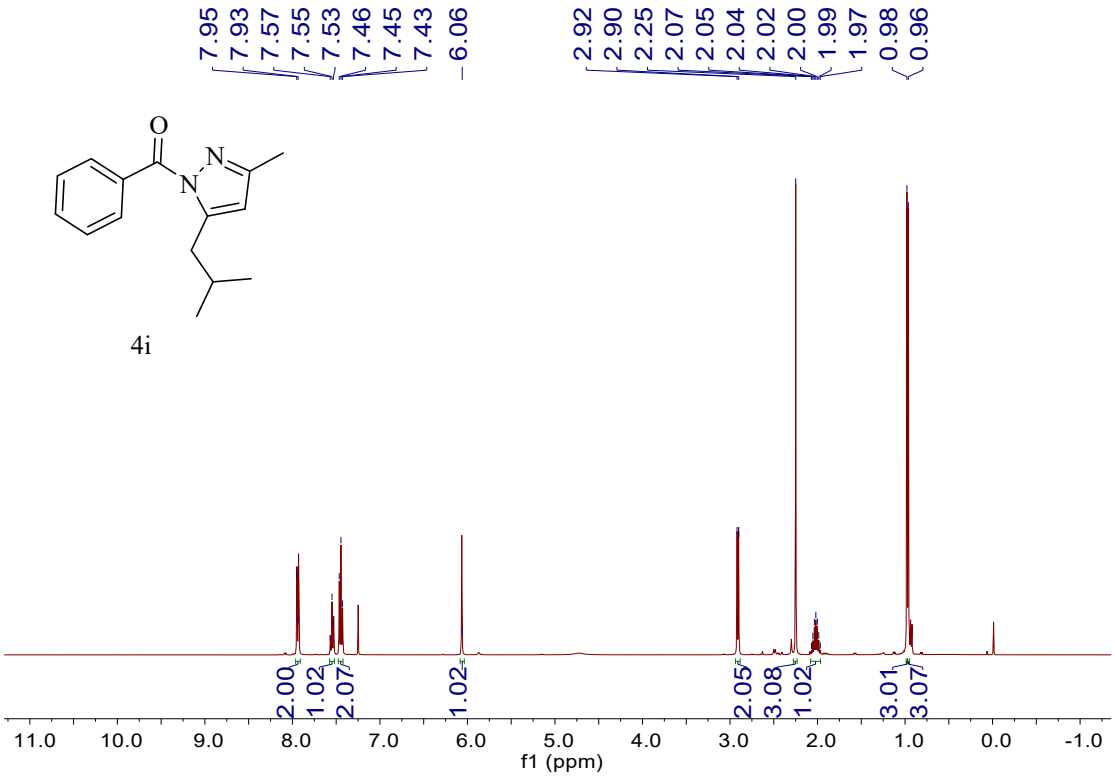
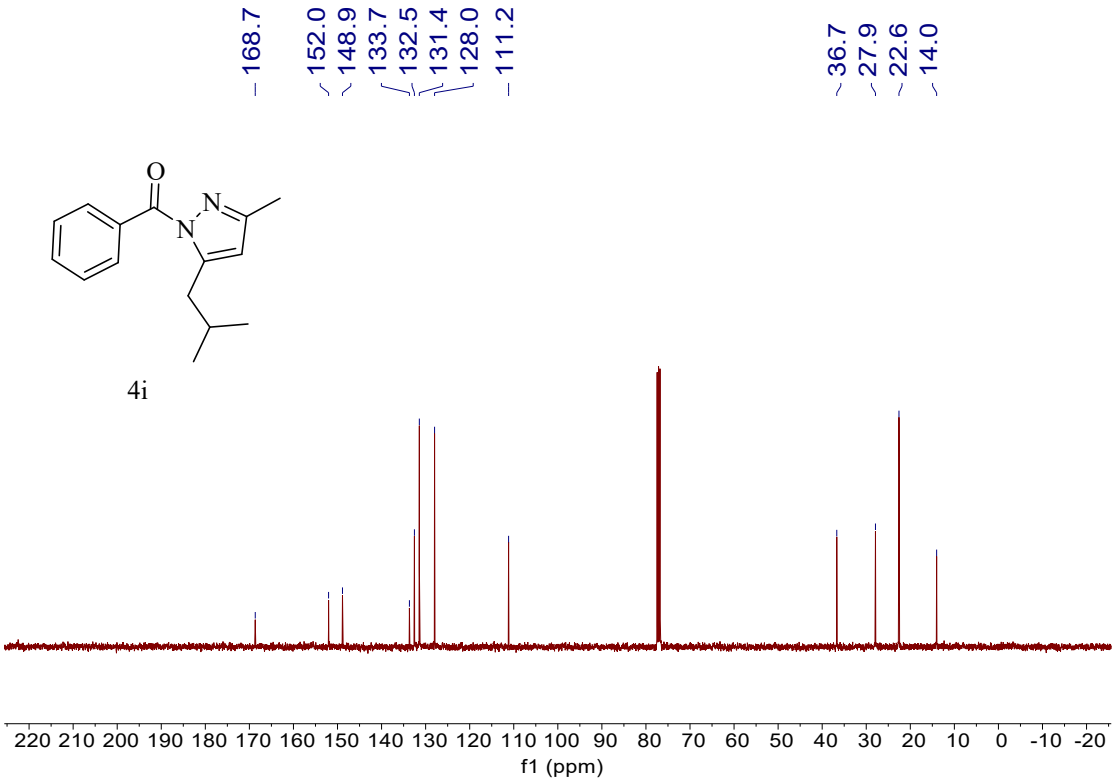
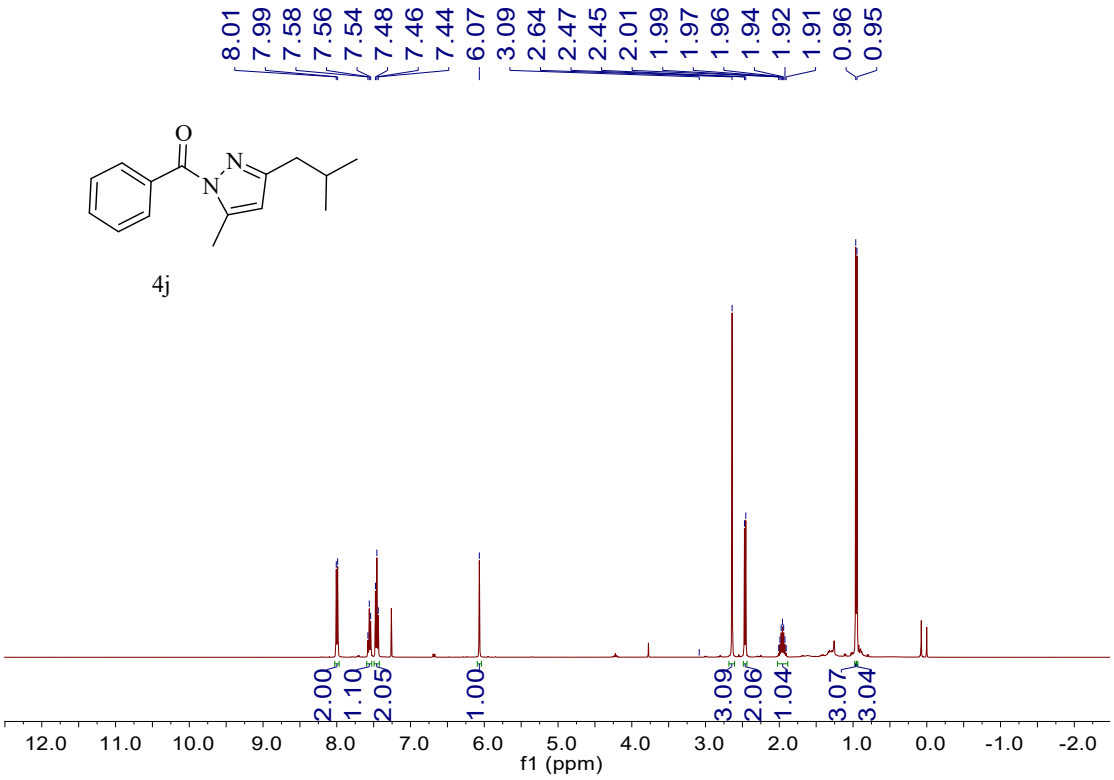
7.59
7.57
7.56
7.54
7.51
7.49
7.43
7.43
7.41
7.39
7.35
7.33
5.55
3.79
3.75
3.47
3.42
O
OH
N
N
5d
2.02
2.04
3.03
2.00
5.00
1.01
1.02
1.00
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)
163.1
148.3
138.6
128.5
126.6
126.0
125.5
125.3
123.7
123.7
123.1
122.7
121.7
119.0
90.0
44.7
O
OH
N
N
5d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

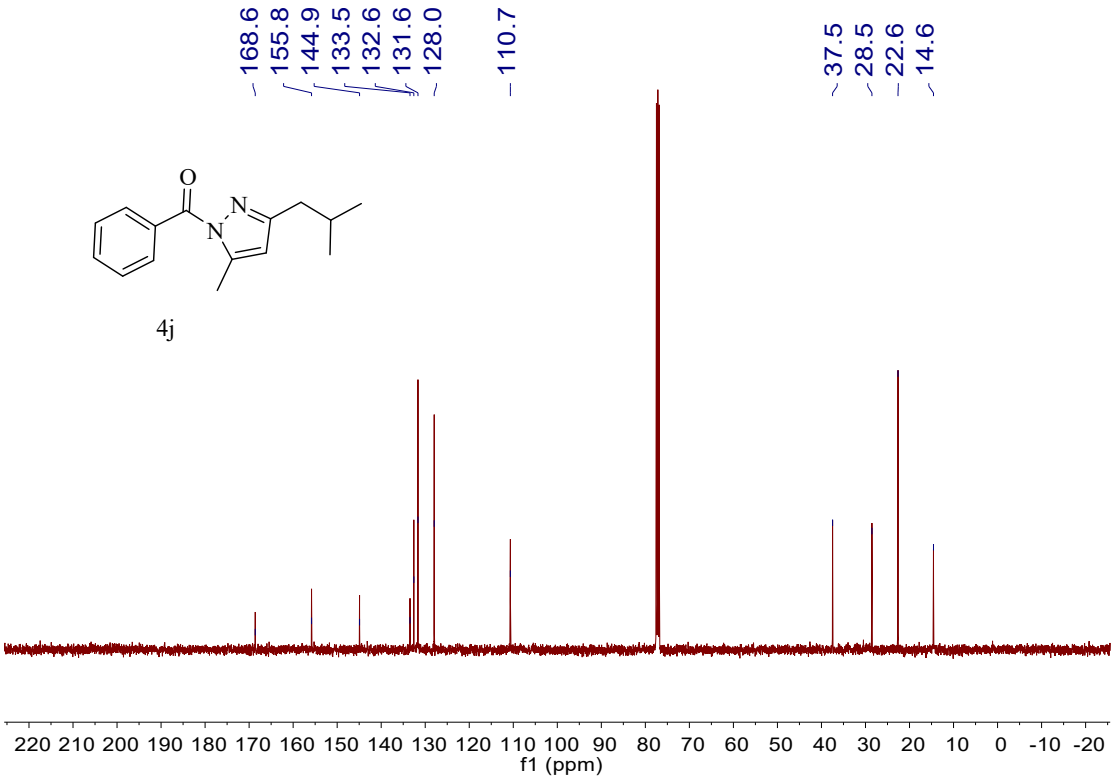

7.95
7.93
7.57
7.55
7.53
7.46
7.45
7.43
6.06
2.92
2.90
2.25
2.07
2.05
2.04
2.02
2.00
1.99
1.97
0.98
0.96
O
N
N
2.00
1.02
2.07
1.02
2.05
3.08
1.02
3.01
3.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

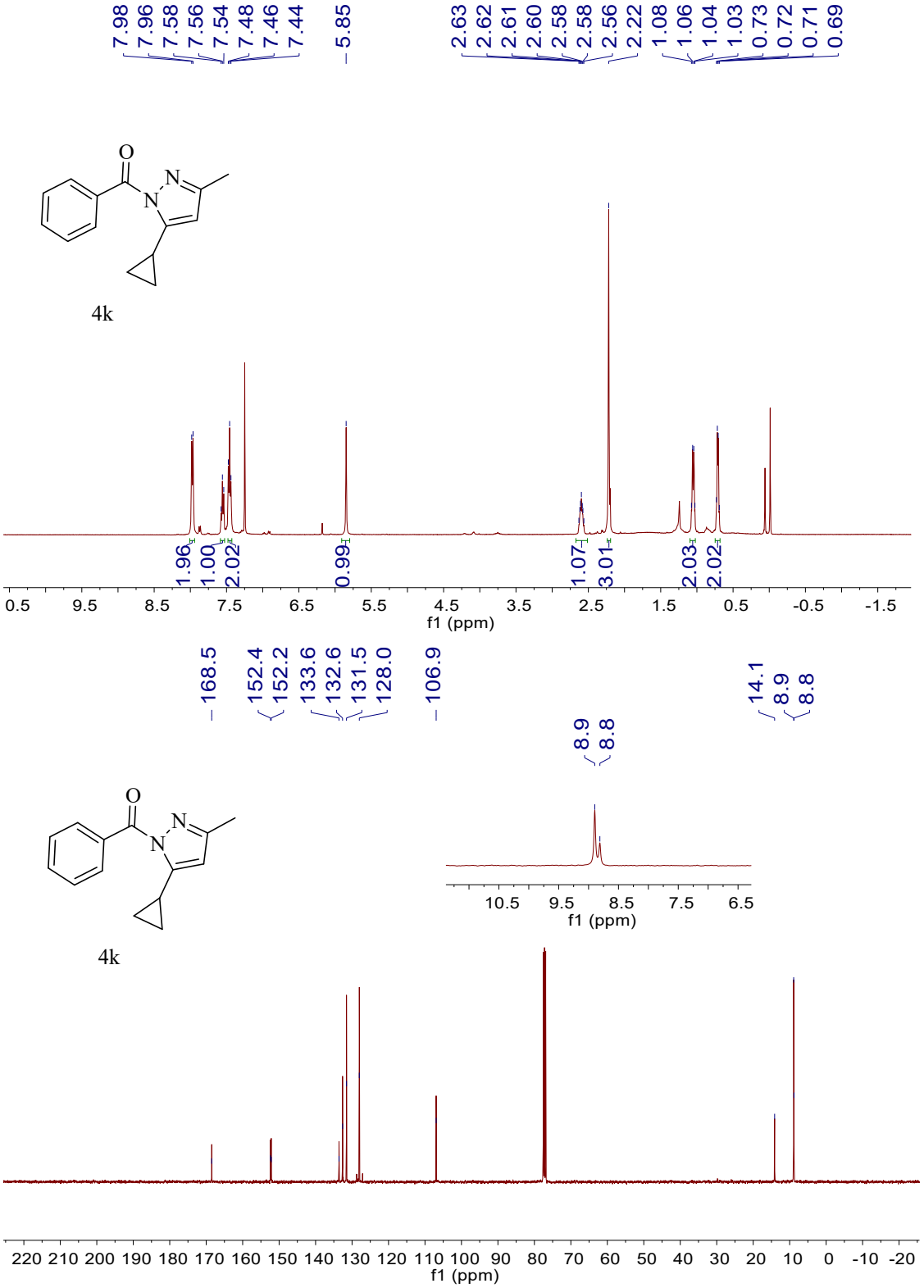
4i

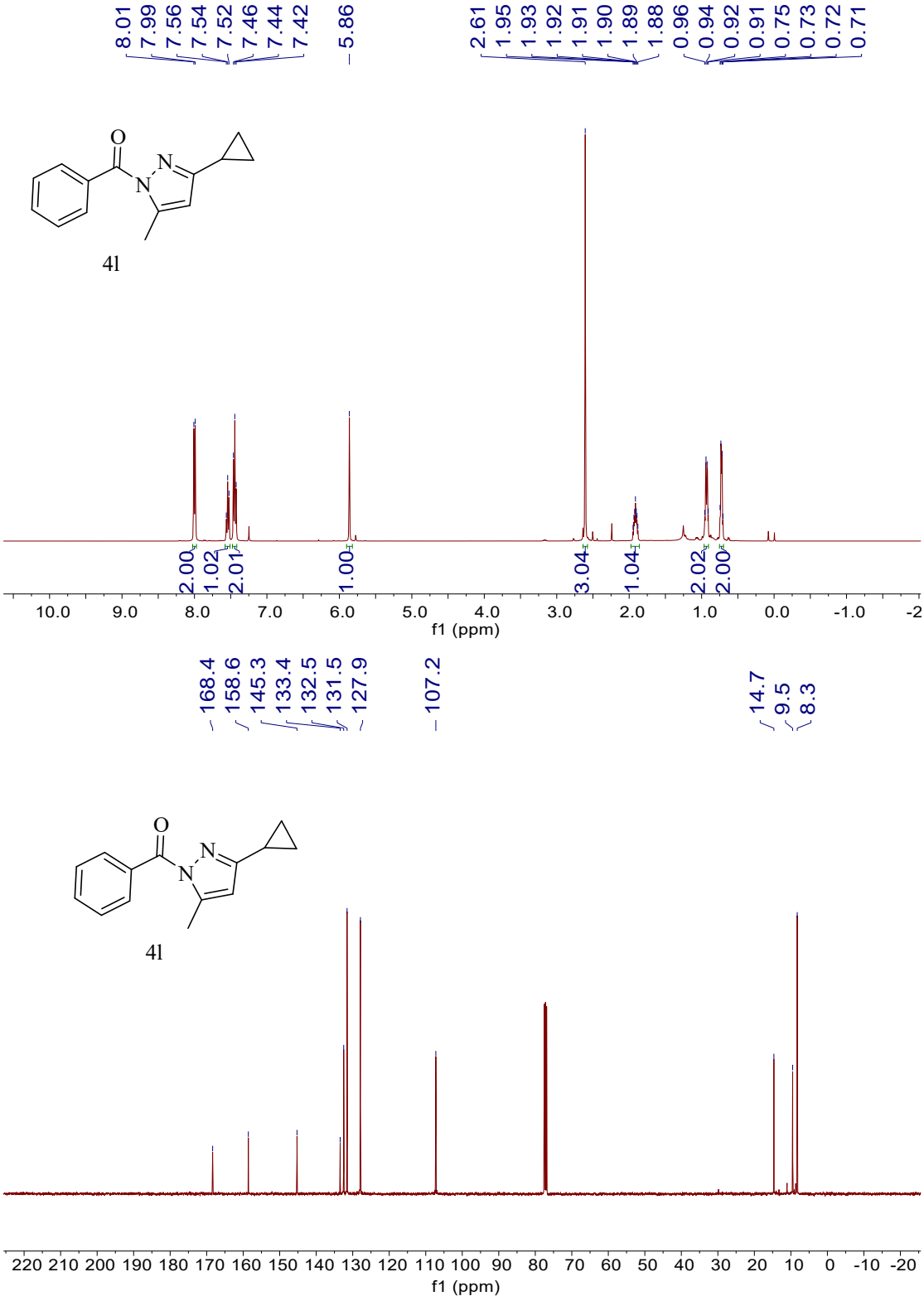

168.7
152.0
148.9
133.7
132.5
131.4
128.0
111.2
36.7
27.9
22.6
14.0
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

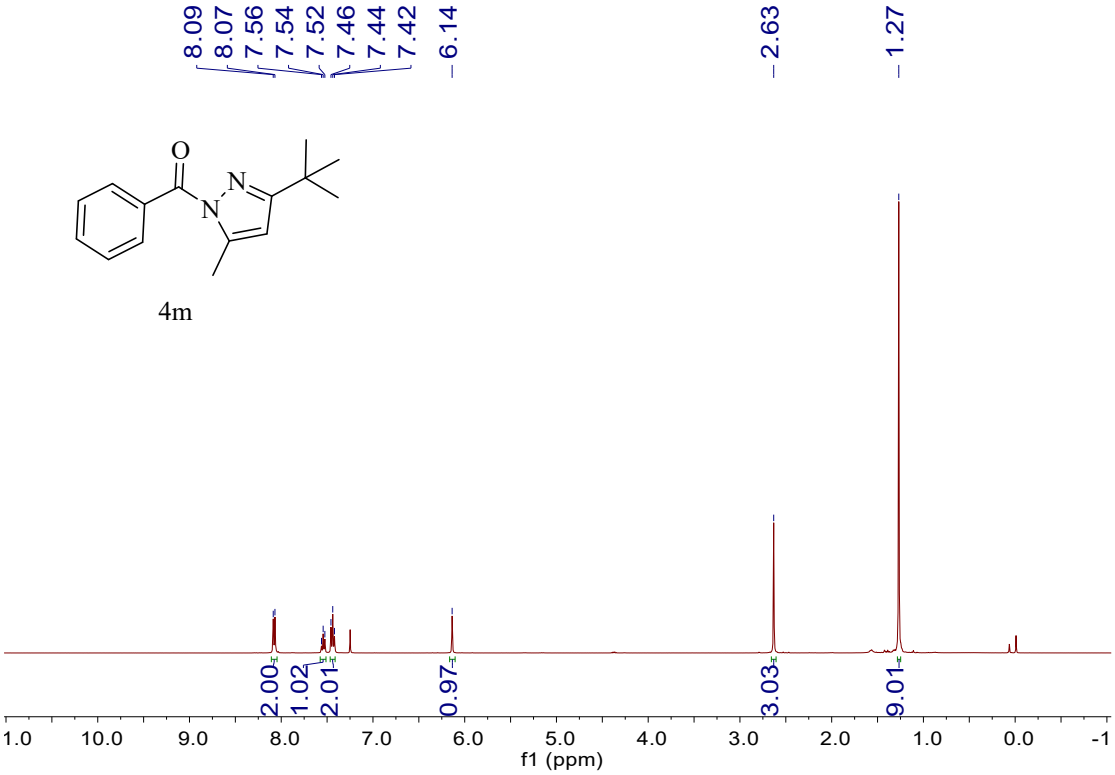
4i

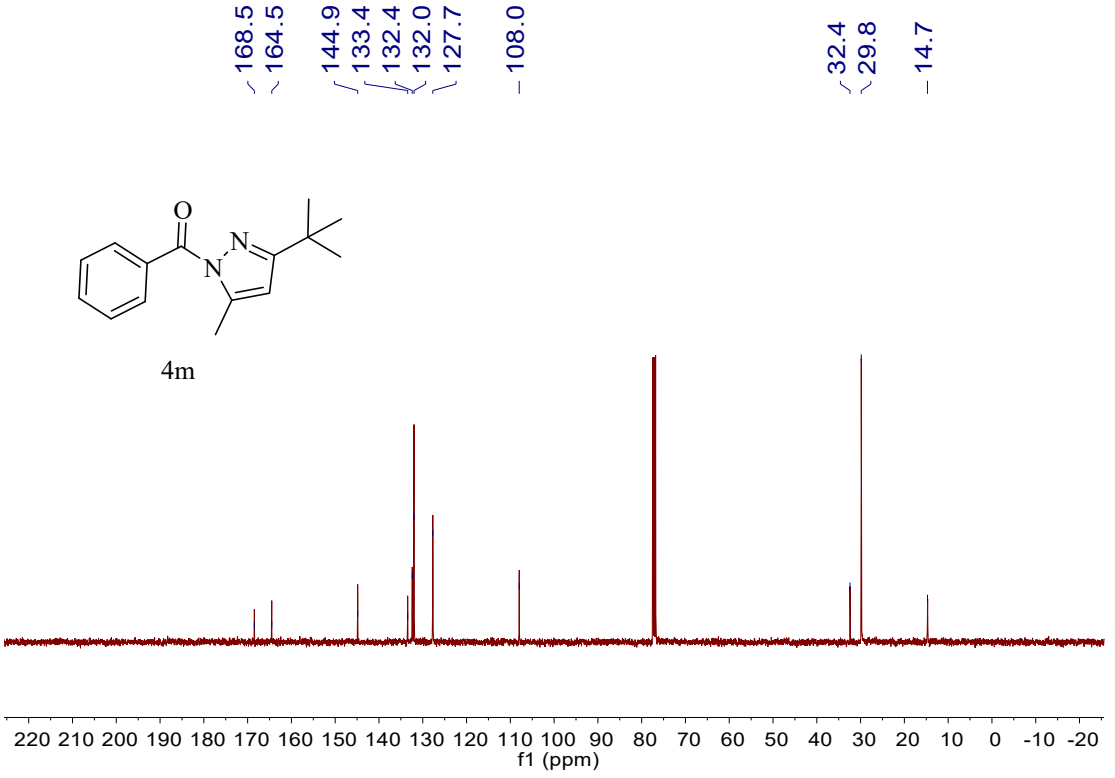

8.01
7.99
7.58
7.56
7.54
7.48
7.46
7.44
6.07
3.09
2.64
2.47
2.45
2.01
1.99
1.97
1.96
1.94
1.92
1.91
0.96
0.95
O
N
N
4j
2.00
1.10
2.05
1.00
3.09
2.06
1.04
3.07
3.04
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

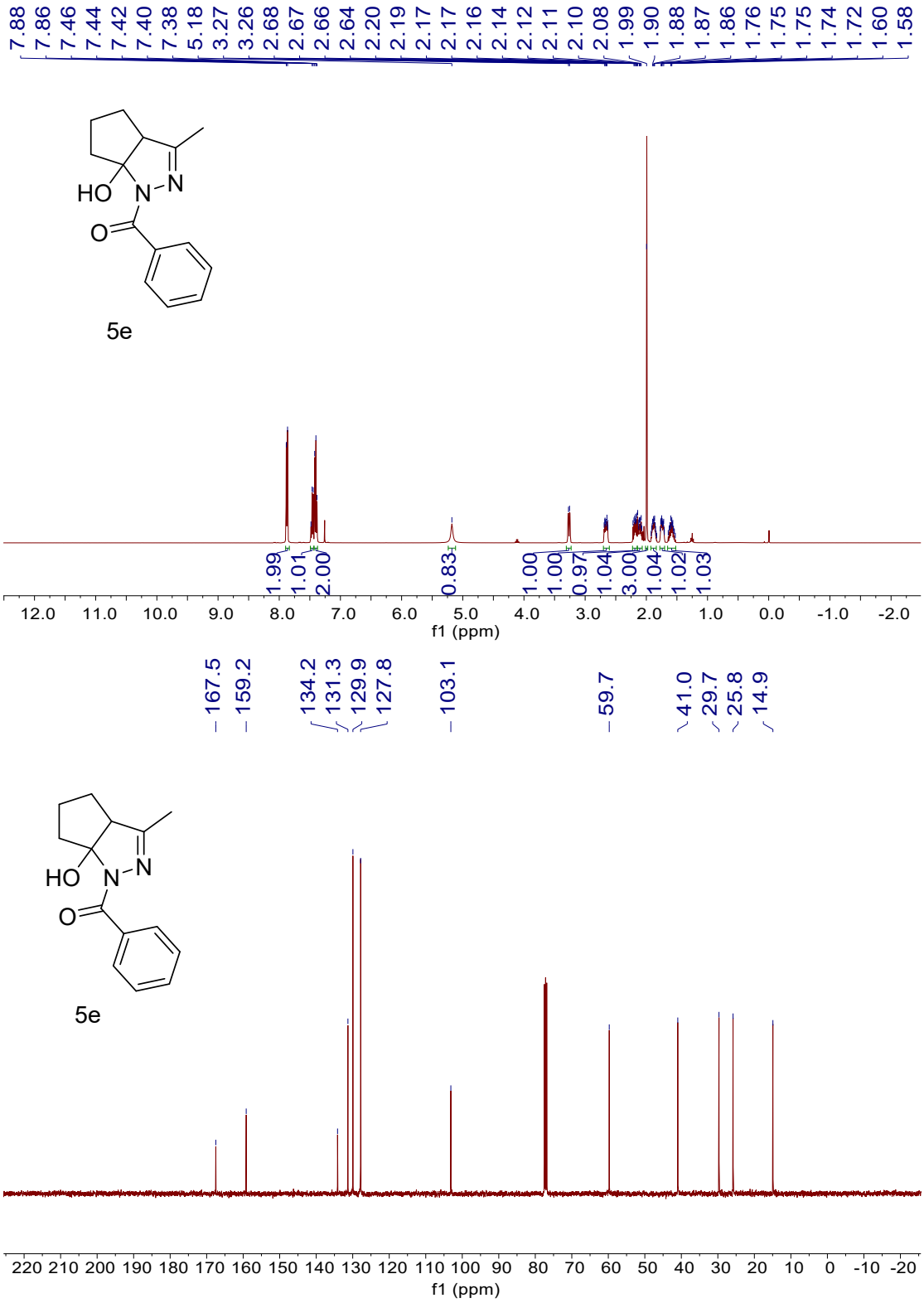

168.6
155.8
144.9
133.5
132.6
131.6
128.0
110.7
37.5
28.5
22.6
14.6
O
N
N
4j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.98
7.96
7.58
7.56
7.54
7.48
7.46
7.44
5.85
2.63
2.62
2.61
2.60
2.58
2.58
2.56
2.22
1.08
1.06
1.04
1.03
0.73
0.72
0.71
0.69
O
N
N
4k
1.96
1.00
2.02
0.99
1.07
3.01
2.03
2.02
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)
168.5
152.4
152.2
133.6
132.6
131.5
128.0
106.9
14.1
8.9
8.8
8.9
8.8
10.5
9.5
8.5
7.5
6.5
f1 (ppm)
O
N
N
4k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.01
7.99
7.56
7.54
7.52
7.46
7.44
7.42
5.86
2.61
1.95
1.93
1.92
1.91
1.90
1.89
1.88
0.96
0.94
0.92
0.91
0.75
0.73
0.72
0.71
O
N
N
4l
2.00
1.02
2.01
1.00
3.04
1.04
2.02
2.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2
f1 (ppm)
168.4
158.6
145.3
133.4
132.5
131.5
127.9
107.2
14.7
9.5
8.3
O
N
N
4l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.09
8.07
7.56
7.54
7.52
7.46
7.44
7.42
6.14
2.63
1.27
O
N
N
4m
2.00
1.02
2.01
0.97
3.03
9.01
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)


168.5
164.5
144.9
133.4
132.4
132.0
127.7
108.0
32.4
29.8
14.7
O
N
N
4m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.88 7.86 7.46 7.44 7.42 7.40 7.38 5.18 3.27 3.26 2.68 2.67 2.66 2.64 2.20 2.19 2.17 2.17 2.16 2.14 2.12 2.11 2.10 2.08 1.99 1.90 1.88 1.87 1.86 1.76 1.75 1.75 1.74 1.72 1.60 1.58
HO
N
N
O
5e
1.99 1.01 2.00 0.83 1.00 1.00 0.97 1.04 3.00 1.04 1.02 1.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)
167.5 159.2 134.2 131.3 129.9 127.8 103.1 59.7 41.0 29.7 25.8 14.9
HO
N
N
O
5e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)