Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

N-Triflination of pyrazolones: A new method for N-S bond formation

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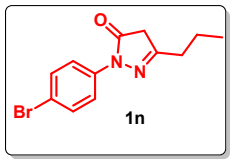
General experimental

All reactions were carried out using commercially available solvents. Reactions were monitored by using precoated silica TLC plates. All ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a BRUKER-AV400 spectrometer in $CDCl_3$ (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR), where tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal standard. The corresponding residual non-deuterated solvent signal ($CDCl_3$; δ = 77.00 ppm) was used as an internal standard for ^{13}C NMR. IR spectra were measured using a Perkin-Elmer FT-IR Spectrometer. Mass spectra were measured with Micromass Q-Tof (ESI-HRMS). Column chromatography was carried out on silica gel 230-400 mesh or 100-200 mesh (Merck), and thin-layer chromatography was carried out using SILICA GEL GF-254. Chemicals obtained from commercial suppliers were used without further purification.

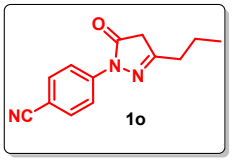
Starting material 3-Methyl-1-phenyl-2-pyrazolin-5-one was purchased from Alfa Aesar, and 1-(4-chlorophenyl)-3-methyl-5-pyrazolone was purchased from TCI, whereas the rest of the pyrazolone derivatives were prepared according to the reported literature procedure.[1-6] Substrate **1n-1v** were isolated in quantitative yield following the literature report.[1] Sodium triflinate was purchased from TCI. PIFA was purchased from a local supplier.

Characterization data for the starting materials:

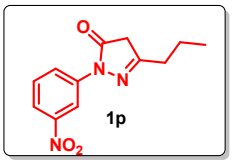
1. **2-(4-Bromophenyl)-5-propyl-2,4-dihydro-3H-pyrazol-3-one (1n).** Light brown solid; ***mp***: 116-120 °C; R_f (20% EtOAc/petroleum ether) 0.5; **IR** (neat, cm^{-1}): 2963, 1717, 1488, 1325; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 3.40 (s, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.63 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 160.3, 137.3, 131.8, 120.2, 117.8, 41.8, 33.2, 20.0, 13.8; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{14}BrN_2O$ $(M + H)^+$: 281.0290, found $(M + H)^+$: 281.0293.



2. **4-(5-Oxo-3-propyl-4,5-dihydro-1H-pyrazol-1-yl)benzonitrile (1o).** Pale yellow solid; ***mp***: 130-134 °C; R_f (20% EtOAc/petroleum ether) 0.4; **IR** (neat, cm^{-1}): 2963, 2226, 1724, 1600, 1508, 1312; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.2 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 3.47 (s, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 161.1, 141.6, 133.0, 118.9, 118.1, 107.4, 41.8, 33.1, 19.7, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{14}N_3O$ $(M + H)^+$: 228.1137, found $(M + H)^+$: 228.1139.

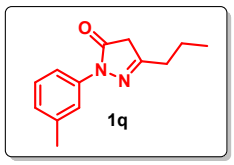


3. **2-(3-Nitrophenyl)-5-propyl-2,4-dihydro-3H-pyrazol-3-one (1p).** yellow semi solid, R_f (20% EtOAc/ petroleum ether) 0.4; **IR** (neat, cm^{-1}): 2965, 1723, 1530, 1483, 1350; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 1H) 8.00 (dd, *J* = 8, 1.2 Hz, 1H), 7.54 (t, *J* = 8 Hz, 1H), 3.48 (s, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.67 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 161.0, 148.6, 139.1, 129.7, 123.8, 119.2, 113.3,

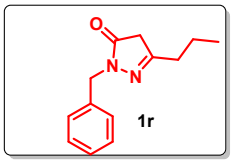


41.9, 33.2, 20.0, 13.8; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{14}N_3O_3$ $(M + H)^+$: 248.1035, found $(M + H)^+$: 248.1037.

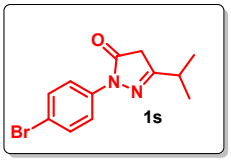
4. **5-Propyl-2-(m-tolyl)-2,4-dihydro-3H-pyrazol-3-one (1q).** Colourless oily; R_f (20% EtOAc/petroleum ether) 0.4; **IR** (neat, cm^{-1}): 2967, 1715, 1633, 1491,1336; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 7.26 (td, *J* = 8, 1.2 Hz, 1H); 6.99 (d, *J* = 7.2 Hz, 1H), 3.39 (s, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.72 – 1.63 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 159.9, 138.8, 138.1, 128.7, 125.9, 119.6, 116.2, 41.8, 33.2, 21.6, 20.1, 13.8; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{17}N_2O$ $(M + H)^+$: 217.1341, found $(M + H)^+$: 217.1344.



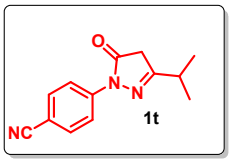
5. **2-Benzyl-5-propyl-2,4-dihydro-3H-pyrazol-3-one (1r)** Colourless solid; ***mp***: 116-118 °C; R_f (20% EtOAc/petroleum ether) 0.1; **IR** (neat, cm^{-1}): 2962, 1707, 1599, 1555, 1296; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 5H), 4.80 (s, 2H), 3.19 (s, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.62 – 1.53 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 159.5, 136.7, 128.6, 128.2, 127.7, 47.8, 40.1, 33.1, 20.2, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{17}N_2O$ $(M + H)^+$: 217.1341, found $(M + H)^+$: 217.1340.



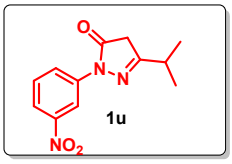
6. **2-(4-Bromophenyl)-5-isopropyl-2,4-dihydro-3H-pyrazol-3-one (1s).** Brown solid; ***mp***: 135-138 °C; R_f (20% EtOAc/petroleum ether) 0.4; **IR** (neat, cm^{-1}): 2968, 1715, 1488, 1333; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 3.41 (s, 2H), 2.82 – 2.72 (m, 1H), 1.24 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 164.7, 137.3, 131.8, 120.1, 117.6, 39.9, 30.8, 20.1; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{14}BrN_2O$ $(M + H)^+$: 281.0290, found $(M + H)^+$: 281.0290.



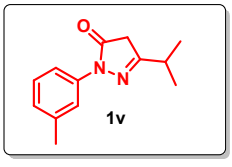
7. **4-(3-Isopropyl-5-oxo-4,5-dihydro-1H-pyrazol-1-yl)benzonitrile (1t).** Brown solid; ***mp***: 124-128 °C; R_f(20% EtOAc/petroleum ether) 0.3; **IR** (neat, cm^{-1}): 2967, 2224, 1718, 1603, 1508, 1337; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H); 7.66 (d, *J* = 8.8 Hz, 2H), 3.47 (s, 2H), 2.86 – 2.75 (m, 1H), 1.27 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 165.4, 141.7, 133.1, 119.0, 118.3, 107.6, 40.1, 30.9, 20.0; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{14}N_3O$ $(M + H)^+$: 228.1137, found $(M + H)^+$: 228.1139.



8. **5-Isopropyl-2-(3-nitrophenyl)-2,4-dihydro-3H-pyrazol-3-one (1u).** yellow oily; R_f (20% EtOAc/petroleum ether) 0.3; **IR** (neat, cm^{-1}): 2971, 1725, 1531, 1483, 1358; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.32 (dd, *J* = 8, 0.8 Hz, 1H); 8.00 – 7.97 (m, 1H), 7.53 (t, *J* = 8.4 Hz, 1H), 3.50 (s, 2H), 2.88 – 2.78 (m, 1H), 1.28 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 165.4, 148.5, 139.1, 129.7, 123.7, 119.1, 113.2, 40.0, 30.8, 20.0; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{14}N_3O_3$ $(M + H)^+$: 248.1035, found $(M + H)^+$: 248.1037.



9. **5-Isopropyl-2-(m-tolyl)-2,4-dihydro-3H-pyrazol-3-one (1v).** Brown oily; R_f (20% EtOAc/petroleum ether) 0.4; **IR** (neat, cm^{-1}): 2962, 1715, 1613, 1490, 1328; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.66 (m, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* =



7.2 Hz, 1H), 3.38 (s, 2H), 2.82 – 2.71 (m, 1H), 2.37 (s, 3H), 1.23 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 164.2, 138.7, 138.1, 128.6, 125.8, 119.5, 116.2, 39.8, 30.7, 21.6, 20.1; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{17}N_2O$ $(M + H)^+$: 217.1341, found $(M + H)^+$: 217.1344.

Typical experimental procedure for trifluoromethyl sulfonylation of pyrazolones

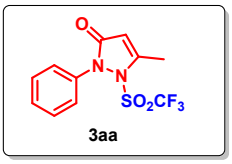
Pyrazolone derivative (0.30 mmol, 1 equiv), Langlois reagent (0.45 mmol, 1.5 equiv), PIFA (0.60 mmol, 2 equiv) were dissolved in 1 mL of TFE/H_2O mixture (3:1) in a 8-mL screw-cap reaction vial and the reaction mixture was stirred at rt for 5 minutes. After the completion of the reaction (monitored by TLC), the reaction mixture was transferred to a 10mL RB and subjected to a rotary evaporator to remove TFE, followed by extraction of the organic component using DCM water workup. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel column using EtOAc/petroleum ether to get the pure products.

Scale-up experimental procedure

Pyrazolone 1a (500mg, 2.87 mmol, 1 equiv), Langlois reagent 2 (672mg, 4.31 mmol, 1.5equiv), PIFA (2.471gm, 5.74 mmol, 2equiv) were dissolved in 10 mL of TFE/H_2O mixture (3:1) in a 24-neck 50ml RB, and the reaction mixture was stirred at the room temperature for 40 minutes. After completing the reaction (monitored by TLC), the TFE was removed under vacuum, followed by extraction of the organic layer using CH_2Cl_2 (3 ×20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel column using EtOAc/petroleum ether to get pure product **3aa** in 72% (636mg).

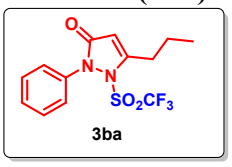
Characterization data for the products:

1. **5-Methyl-2-phenyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3aa).** Colourless solid; Yield– (77mg, 83%); ***mp***: 130-134 °C; R_f (30% EtOAc/petroleum ether) 0.5; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1709, 1624, 1419, 1215, 1129; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.39 – 7.30 (m, 3H), 5.91 (s, 1H), 2.55 (d, J = 1.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 157.2, 137.9, 129.1, 128.2, 124.7, 120.0 (q, $J_{C\text{-}F}$ = 329 Hz), 110.1, 15.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.8; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_{10}F_3N_2O_3S$ $(M+H)^+$: 307.0364, found $(M+H)^+$: 307.0363.



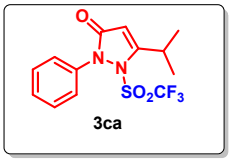
3aa

2. **2-Phenyl-5-propyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ba).** Yellow solid; Yield– (55mg, 55%); ***mp***: 90-94 °C; R_f (20% EtOAc/petroleum ether) 0.7; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1723, 1623, 1423, 1226, 1130; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.37 – 7.31 (m, 3H), 5.92 (s, 1H), 2.85 (t, J = 7.2 Hz, 2H), 1.77-1.86 (m, 2H), 1.08 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 161.9, 138.0, 129.1, 128.1, 124.5, 120.0 (q, $J_{C\text{-}F}$ = 329 Hz), 109.3, 31.1, 21.3, 13.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.8; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{14}F_3N_2O_3S$ $(M+H)^+$: 335.0677, found $(M+H)^+$: 335.0678.



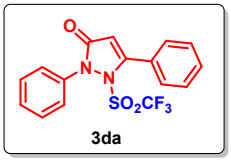
3ba

3. **5-Isopropyl-2-phenyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ca).** Yellow solid; Yield– (66mg, 66%); ***mp***: 127-130 °C; R_f (20% EtOAc/petroleum ether) 0.7; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1733, 1617, 1420, 1220, 1128; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.36 – 7.31 (m, 3H), 5.92 (s, 1H), 3.40 – 3.30 (m, 1H), 1.39 (d, J = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 167.7, 138.2, 129.1, 128.0, 124.2, 120.0 (q, $J_{C\text{-}F}$ = 329 Hz), 107.7, 28.7, 21.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.8; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{14}F_3N_2O_3S$ $(M+H)^+$: 335.0677, found $(M+H)^+$: 335.0674.



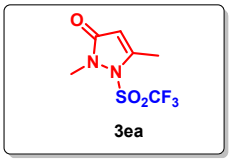
3ca

4. **2,5-Diphenyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3da).** Colourless solid; Yield– (18mg, 16%); ***mp***: 113-118 °C; R_f (20% EtOAc/petroleum ether) 0.6; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1740, 1622, 1424, 1238, 1128; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.2 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.49 – 7.44 (m, 6H), 7.36 – 7.32 (m, 1H), 6.16 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 159.6, 137.9, 132.3, 129.2, 129.1, 128.7, 127.9, 127.7, 124.1, 120.0 (q, $J_{C\text{-}F}$ = 330 Hz), 110.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.3; **HRESI-MS** *(m/z)*: Calculated for $C_{16}H_{11}F_3N_2O_3SNa$ $(M+Na)^+$: 391.0340, found $(M+Na)^+$: 391.0339.



3da

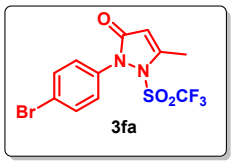
5. **2,5-Dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ea).** yellow oily; Yield– (37.5mg, 51%); R_f (30% EtOAc/ petroleum ether) 0.5; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1726, 1629, 1416, 1230, 1131; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.85 (s, 1H), 3.42 (s, 3H), 2.44 (d, J



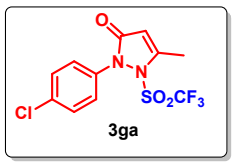
3ea

= 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 156.1, 120.0(q, J_{C-F} = 328 Hz), 110.4, 35.9, 15.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.1; **HRESI-MS** *(m/z)*: Calculated for $C_6H_8F_3N_2O_3S$ $(M + H)^+$: 245.0208, found $(M + H)^+$: 245.0207.

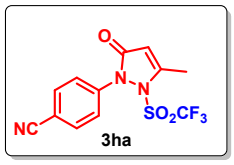
6. **2-(4-Bromophenyl)-5-methyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3fa).** yellow solid; Yield– (67mg, 58%); ***mp***: 125-129 °C; R_f (30% EtOAc/petroleum ether) 0.7; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1729, 1630, 1486, 1422, 1226, 1128; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 5.91 (s, 1H), 2.55 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 157.6, 136.9, 132.3, 126.1, 121.9, 120.0 (q, J_{C-F} = 329 Hz), 110.1, 15.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.0; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{12}F_3N_2O_3S$ $(M + H)^+$: 384.9469, found $(M + H)^+$: 384.9465.



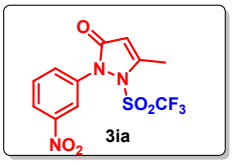
7. **2-(4-Chlorophenyl)-5-methyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ga).** Pale yellow solid; Yield– (72mg, 71%); ***mp***: 130-134 °C; R_f (30% EtOAc/petroleum ether) 0.6; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1725, 1628, 1490, 1418, 1315, 1228, 1131; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 5.91 (s, 1H), 2.56 (d, J = 0.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 157.6, 136.4, 134.0, 129.4, 125.9, 120.0 (q, J_{C-F} = 329 Hz), 110.1, 15.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.0; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_8ClF_3N_2O_3SNa$ $(M + Na)^+$: 362.9794, found $(M + Na)^+$: 362.9791.



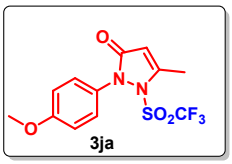
8. **4-(3-Methyl-5-oxo-2-((trifluoromethyl)sulfonyl)-2,5-dihydro-1H-pyrazol-1-yl)benzonitrile (3ha).** Pale yellow solid; Yield – (52mg, 52%); ***mp***: 146-149 °C; R_f (30% EtOAc/petroleum ether) 0.4; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 2230, 1735, 1631, 1419, 1226, 1126; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 5.95 (s, 1H), 2.59 (d, J = 1.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 158.3, 141.5, 133.0, 124.1, 120.0 (q, J_{C-F} = 329 Hz), 118.1, 111.3, 110.1, 15.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.6; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_9F_3N_3O_3S$ $(M + H)^+$: 332.0317, found $(M + H)^+$: 332.0319.



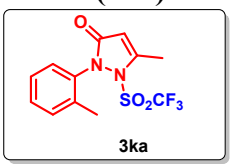
9. **5-Methyl-2-(3-nitrophenyl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ia).** Yellow solid; Yield– (46mg, 44%); ***mp***: 149-154 °C; R_f (30% EtOAc/petroleum ether) 0.5; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1730, 1631, 1533, 1421, 1352, 1226, 1129; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 – 8.21 (m, 2H), 7.74 – 7.71 (m, 1H), 7.67 – 7.62 (m, 1H), 5.96 (s, 1H), 2.61 (d, J = 0.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 158.5, 148.6, 138.9, 130.1, 130.0, 122.6, 120.0 (q, J_{C-F} = 329 Hz), 119.0, 109.9, 15.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.7; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_9F_3N_3O_5S$ $(M + H)^+$: 352.0215, found $(M + H)^+$: 352.0211.



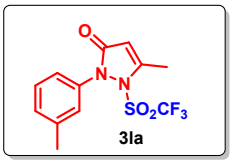
10. **2-(4-Methoxyphenyl)-5-methyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ja).** Pale yellow solid; Yield– (51mg, 51%); ***mp***: 105-109 °C; R_f (30% EtOAc/petroleum ether) 0.4; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1730, 1620, 1509, 1421, 1225, 1129; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 5.91 (s, 1H), 3.82 (s, 3H), 2.54 (d, J = 0.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 159.6, 156.9, 130.4, 126.9, 120.0(q, J_{C-F} = 329 Hz), 114.4, 110.0, 55.5, 15.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.3; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{11}F_3N_2O_4SNa$ $(M + Na)^+$: 359.0289, found $(M + Na)^+$: 359.0285.



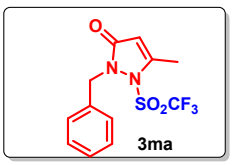
11. **5-Methyl-2-(o-tolyl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ka).** Pale yellow solid; Yield– (70mg, 73%); ***mp***: 86-90 °C; R_f(30% EtOAc/petroleum ether)) 0.6; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1734, 1631, 1421, 1230, 1130; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, J = 4.0 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 5.92 (s, 1H), 2.54 (d, J = 1.1 Hz, 3H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 156.8, 137.3, 136.2, 131.5,129.3, 126.7, 126.5, 120.1 (q, J_{C-F} = 328 Hz), 110.1, 17.7, 15.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.2; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{12}F_3N_2O_3S$ $(M + H)^+$: 321.0521, found $(M + H)^+$: 321.0517.



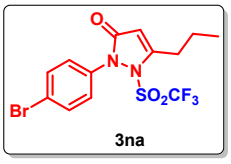
12. **5-Methyl-2-(m-tolyl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3la).** Pale yellow solid; Yield– (49mg, 51%); ***mp***: 108-113 °C; R_f (30% EtOAc/petroleum ether) 0.6; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1724, 1633, 1421, 1229, 1128; **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 7.32 (t, J = 7.7 Hz, 1H), 7.17- 7.10 (m, 3H), 5.90 (s, 1H), 2.54 (d, J = 0.8 Hz, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 157.1, 139.2, 137.8, 129.2, 128.9, 125.5, 121.9, 120.1(q, J_{C-F} = 329 Hz), 110.2, 21.5, 15.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.162; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{11}F_3N_2O_3SNa$ $(M + Na)^+$: 343.0340, found $(M + Na)^+$: 343.0337.



13. **2-Benzyl-5-methyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ma).** Yellow oily; Yield– (61mg, 63%); R_f (20% EtOAc/petroleum ether) 0.6; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1735, 1629, 1416, 1236, 1134; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 3H), 7.25 – 7.22 (m, 2H), 5.84 (s, 1H), 5.12 (s, 2H), 3.31 (d, J = 0.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 157.5, 134.3, 128.9, 128.7, 128.5, 120.0 (q, J_{C-F} = 328 Hz), 111.1, 51. 9, 15.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.4; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{11}F_3N_2O_3SNa$ $(M + Na)^+$: 343.0340, found $(M + Na)^+$: 343.0341.

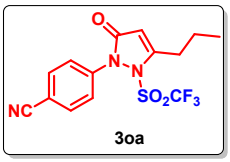


14. **2-(4-Bromophenyl)-5-propyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3na).** Yellow oily; Yield– (87mg, 70%); R_f (20% EtOAc/petroleum ether) 0.8; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1731, 1623, 1424, 1225, 1129; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 5.91 (s, 1H), 2.84 (td, J = 7.7, 0.8 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.07 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz,

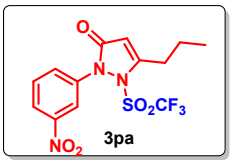


$CDCl_3$) δ 167.3, 162.3, 137.0, 132.3, 125.9, 121.8, 120.0 (q, $J_{C\text{-}F}$ = 263 Hz), 109.2, 31.1, 21.3, 13.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.7; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{13}BrF_3N_2O_3S$ $(M + H)^+$: 412.9782, found $(M + H)^+$: 412.9779.

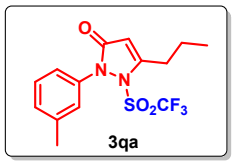
15. **4-(5-Oxo-3-propyl-2-((trifluoromethyl)sulfonyl)-2,5-dihydro-1H-pyrazol-1-yl)benzonitrile (3oa).** Yellow solid; Yield– (56mg, 52%); ***mp***: 97-101 °C; R_f (20% EtOAc/petroleum ether) 0.5; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1734, 1627, 1422, 1224, 1127; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 163.0, 141.6, 133.0, 123.9, 120.0(q, $J_{C\text{-}F}$ = 329 Hz), 118.2, 111.2, 109.2, 31.1, 21.3, 13.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{13}F_3N_3O_3S$ $(M + H)^+$: 360.0630, found $(M + H)^+$: 360.0627.



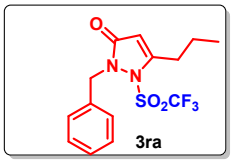
16. **2-(3-Nitrophenyl)-5-propyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3pa).** Yellow oily; Yield– (48mg, 42%); R_f (20% EtOAc/ petroleum ether) 0.4; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1711, 1622, 1529,1435,1352, 1232, 1133; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 8.22 (m, 2H), 7.75 – 7.73 (m, 1H), 7.69 – 7.65 (m, 1H), 5.98 (s, 1H), 2.91 (td, *J* = 7.3, 0.7 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.14 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 163.1, 148.5, 138.9, 129.9, 129.8, 122.5, 120.0 (q, $J_{C\text{-}F}$ = 329 Hz), 118.8, 108.9, 31.1, 21.2, 13.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{13}F_3N_3O_5S$ $(M + H)^+$: 380.0528, found $(M + H)^+$: 380.0530.



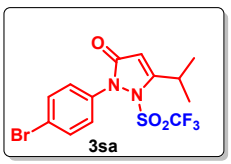
17. **5-Propyl-2-(m-tolyl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3qa).** Colourless solid; Yield– (67mg, 64%); ***mp***: 80-85°C; R_f (20% EtOAc/petroleum ether) 0.6; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1732, 1619, 1422, 1225, 1130; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.7 Hz, 1H), 7.16 – 7.09 (m, 3H), 5.91 (s, 1H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.86 – 1.77 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 161.8, 139.2, 137.9, 129.1, 128.9, 125.3, 121.7, 120.0(q, $J_{C\text{-}F}$ = 330 Hz), 109.3, 31.1, 21.5, 21.3, 13.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.8; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{15}F_3N_2O_3SNa$ $(M + Na)^+$: 371.0653, found $(M + Na)^+$: 371.0648.



18. **2-Benzyl-5-propyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ra)** Yellow oily; Yield– (72mg, 69%); R_f(20% EtOAc/petroleum ether) 0.8; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1727, 1622, 1427, 1230, 1132; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2H), 5.83 (s, 1H), 5.10 (s, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.52 – 1.43 (m, 2H), 0.73 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 162.6, 134.1, 128.9, 128.7, 128.5, 120.0 (q, $J_{C\text{-}F}$ = 328 Hz), 110.6, 52.4, 30.8, 21.2, 12.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.2; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{15}F_3N_2O_3SNa$ $(M + Na)^+$: 371.0653, found $(M + Na)^+$: 371.0651.

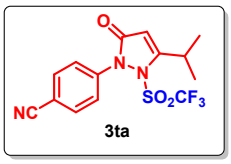


19. **2-(4-Bromophenyl)-5-isopropyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3sa).** Pale yellow solid; Yield– (57.5mg,

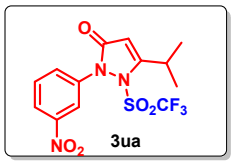


46%); ***mp***: 118-122 °C; R_f (20% EtOAc/petroleum ether) 0.7; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1722, 1618, 1429, 1225, 1123; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 5.91 (s, 1H), 3.36 – 3.33 (m, 1H), 1.39 (d, *J* = 6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 167.3, 137.2, 132.3, 125.6, 121.6, 120.0 (q, J_{C-F} = 330 Hz), 107.6, 28.7, 21.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.6; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{13}BrF_3N_2O_3S$ $(M + H)^+$: 412.9782, found $(M + H)^+$: 412.9779.

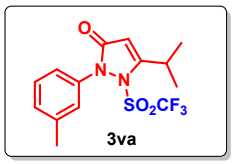
20. 4-(3-Isopropyl-5-oxo-2-((trifluoromethyl)sulfonyl)-2,5-dihydro-1H-pyrazol-1-yl)benzonitrile (3ta). Colourless solid; Yield– (55mg, 51%); ***mp***: 117-122 °C R_f (20% EtOAc/petroleum ether) 0.7; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1735, 1624, 1424, 1224, 1126; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H); 7.50 (d, *J* = 8.4 Hz, 2H), 5.94 (s, 1H), 3.38 – 3.34 (m, 1H), 1.41 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 166.5, 141.7, 133.0, 123.6, 120.0 (q, J_{C-F} = 329 Hz), 118.2, 111.0, 107.6, 28.8, 21.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{13}F_3N_3O_3S$ $(M + H)^+$: 360.0630, found $(M + H)^+$: 360.0627.



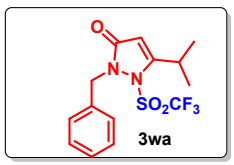
21. 5-Isopropyl-2-(3-nitrophenyl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3ua). Pale yellow solid; Yield– (53mg, 46%); ***mp***: 126-130 °C; R_f (20% EtOAc/petroleum ether) 0.4; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1737, 1618, 1534, 1425, 1351, 1225, 1127; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.19 (m, 2H), 7.72 – 7.70 (m, 1H), 7.66 – 7.62 (m, 1H), 5.95 (s, 1H), 3.43 – 3.33 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 166.9, 148.5, 139.1, 130.0, 129.5, 122.4, 120.0 (q, J_{C-F} = 329 Hz), 118.6, 107.5, 28.8, 21.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{13}F_3N_3O_5S$ $(M + H)^+$: 380.0528, found $(M + H)^+$: 380.0524.



22. 5-Isopropyl-2-(m-tolyl)-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3va). Colourless solid; Yield– (38mg, 36%); ***mp***: 113-117 °C; R_f (20% EtOAc/petroleum ether) 0.6; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1716, 1613, 1426, 1224, 1126; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.08 (m, 3H), 5.91 (s, 1H), 3.38 – 3.32 (m, 1H), 2.40 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 167.8, 139.2, 138.1, 129.0, 128.9, 125.0, 121.4, 120.0 (q, J_{C-F} = 329 Hz), 107.7, 28.7, 21.9, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.8; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{16}F_3N_2O_3S$ $(M + H)^+$: 349.0834, found $(M + H)^+$: 349.0829.



23. 2-Benzyl-5-isopropyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydro-3H-pyrazol-3-one (3wa). Yellow oily; Yield– (64mg, 61%); R_f (20% EtOAc/petroleum ether) 0.8; Prepared as shown in general experimental procedure. **IR** (neat, cm^{-1}): 1732, 1617, 1419, 1231, 1132; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.27 (m, 3H), 7.21 – 7.19 (m, 2H), 5.82 (s, 1H), 5.09 (s, 2H), 3.17 – 3.06 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 169.6, 134.0, 128.8, 128.6, 128.5, 120.0 (q, J_{C-F} = 329 Hz), 108.6, 53.0, 28.4, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.2; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{15}F_3N_2O_3SNa$ $(M + Na)^+$: 371.0653, found $(M + Na)^+$: 371.0649.



Crystal data for compound 3ca

Translucent yellow tabular crystals of approximate dimension 0.092 x 0.189 x 0.324mm were selected under a polarizing microscope for single-crystal x-ray diffraction studies. With the help of paratone oil, the sample was taken on a fiber loop and mounted over a diffractometer head. Data collection was done at low temperature (100K or-173.15°C) using the Oxford cyrostream device (N_2 flow). The X-ray intensity data were collected using Bruker APEX-II Ultra (3-circle machine) operated at 40KV voltage and 80mA current. Collected raw images were corrected for Lorentz and polarization effects. Multi-scan absorption corrections were applied using the program SADABS[7]. The structure was solved and refined using SHELXT[8] and SHELXL[9] programs, respectively. Spherical atomic-scattering factors were assumed (Independent Atom Model, IAM). All non-hydrogen atoms were modeled anisotropically, and hydrogen atoms were refined as a riding model using HFIX cards.Aromatic phenyl hydrogens and double bond α-hydrogen-bonded to C4 atom were added to the model through HFIX 43 card and methyl hydrogen atoms (bonded to C32 and C33) were given HFIX 137(X-C torsion refined) and methine hydrogen (bonded to C31) were added through HFIX 13 cards. For all hydrogen atoms, Uiso values are constrained to 1.2 times that of the parent atom's Uiso (1.5 times for methyl hydrogens). Software used for creating molecular graphics is ORTEP3 for windows[10] and packages used for computing publication materials are SHELXLE[11] and WinGX[10].Crystallographic and refinement data are reported in Table 1, and selected bond lengths and angles are reported in Table 2.

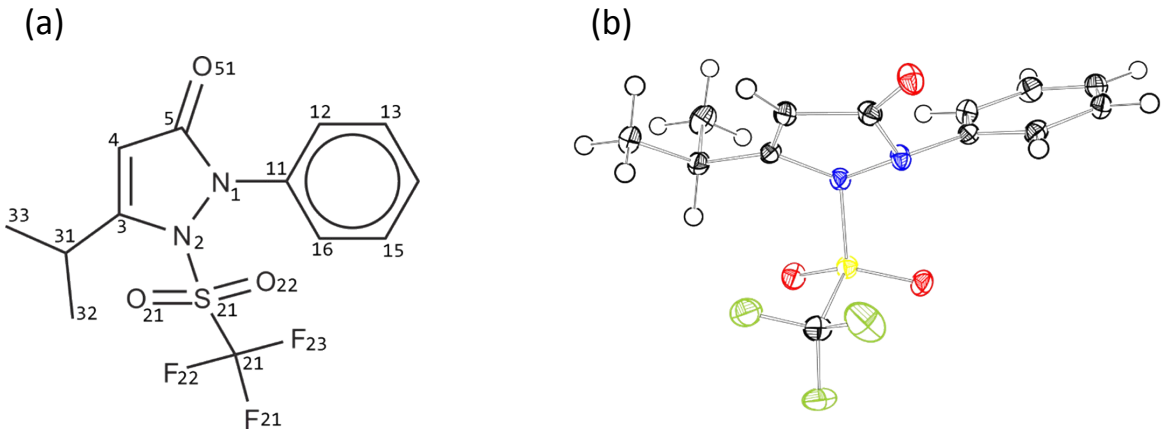


Figure 1:(a) Schematic representation of the compound 3ca with atom numbering scheme; (b) ORTEP plot with 50% probability ellipsoid; Color code:C=Black, H=Hollow Sphere with arbitrary radius, N=Blue, O=Red,F=Green,S=Yellow.

Largest positive difference peak of 0.524eÅ^{-3} located at (0.1598, 0.5281, 0.1205) was attributed to the bonding electrons. It is located equidistant between S21 and C21 atoms.Deepest hole of -0.357eÅ^{-3}at (0.2008, 0.5042, 0.1535) was found near S21(distance of 0.37Å). IAM model was

inadequate to model such features. Electron density synthesis with coefficient [F_o-F_c] was calculated using the program PLATON[12].

Table 1: Crystal data and structure refinement for **3ca**

Identification code	3ca
Empirical formula	C_{13} H_{13} F_3 N_2 O_3 S
Formula weight	334.31
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*P* b c a
Unit cell dimensions	a = 8.6070(5) Å b = 14.6316(8) Å c = 22.5134(14) Å
Volume	2835.2(3) $Å^3$
Z	8
Density (calculated)	1.566 mg/m^3
Absorption coefficient	0.277 mm^{-1}
F(000)	1376
Crystal size(mm)	0.324 x 0.189 x 0.092
Theta range for data collection	1.809 to 28.349°
Index ranges	-11<=h<=11, -19<=k<=19, -30<=l<=30
Reflections collected	60045
Independent reflections	3541 [R(int) = 0369]
Completeness to theta = 25.242°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5914
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3541 / 0 / 201
Goodness-of-fit on F^2	1.153
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0923
R indices (all data)	R1 = 0.0401, wR2 = 0.0938
Extinction coefficient	constrained to zero
Largest diff. peak and hole	0.524 and -0.357e.$Å^{-3}$

Table 2: Selected Bond length and angles of 5-membered pyrazol-3-one ring (Å and °)

N1-C5	1.417(2)
N1-N2	1.422(2)
N1-C11	1.437(2)
N2-C3	1.442(2)
N2-S21	1.678(1)
C3-C4	1.338(2)
C3-C31	1.496(2)
C4-C5	1.455(2)
C5-O51	1.213(2)
C5-N1-N2	108.2(1)
C5-N1-C11	120.0(1)
N2-N1-C11	117.2(1)
N1-N2-C3	107.1(1)
N1-N2-S21	112.4(9)
C3-N2-S21	119.4(1)
C4-C3-N2	108.7(1)
C4-C3-C31	129.8(1)
N2-C3-C31	121.4(1)
C3-C4-C5	110.1(1)
O51-C5-N1	123.4(1)
O51-C5-C4	130.7(1)
N1-C5-C4	105.9(1)

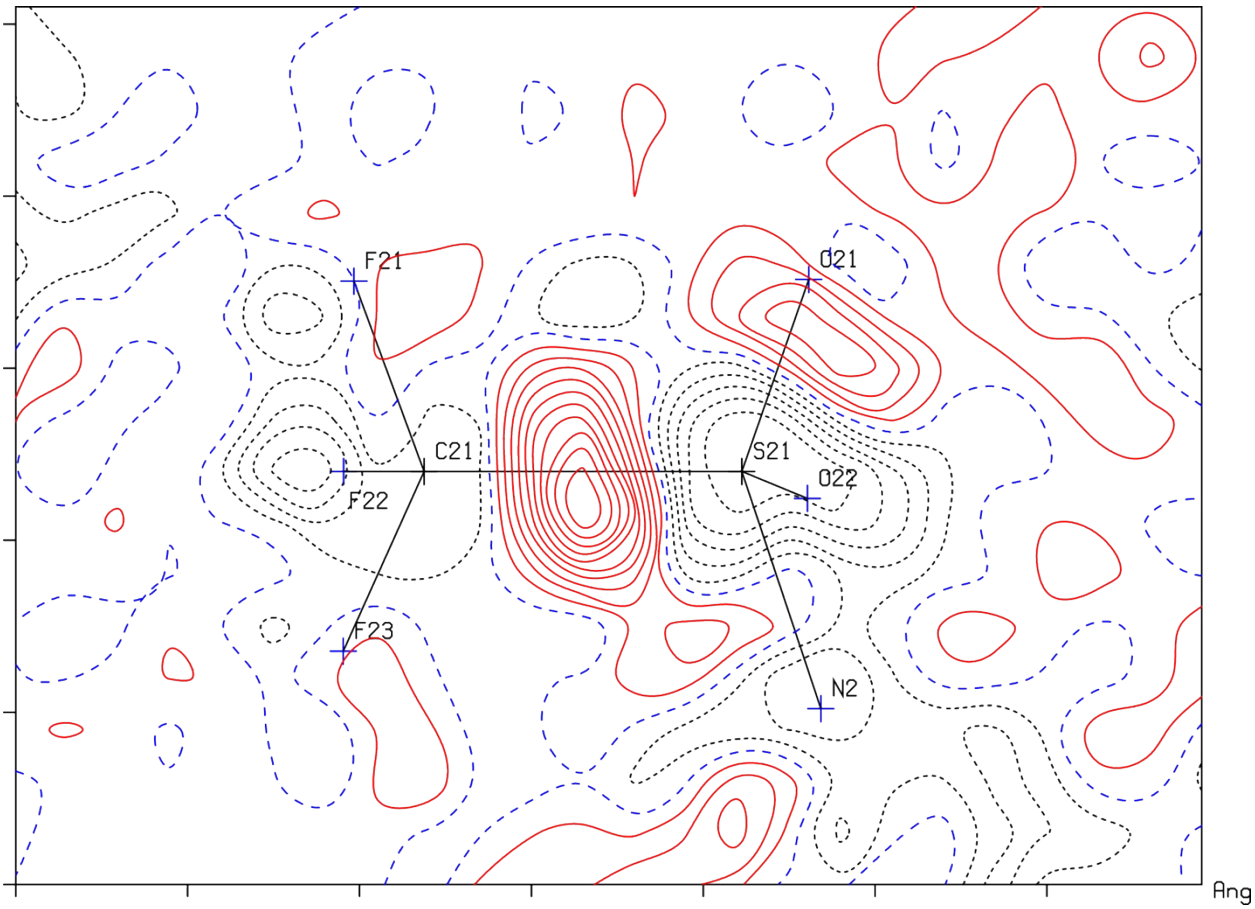


Figure 2: Final difference Fourier synthesis with Coefficients [F_o-F_c]; Dashed blue lines represent -ve contours, dotted black represent zero contour,solid red lines represent +ve contours. High +ve contour was found equidistant between S21 and C21.
Plane definition: 8.5399x-0.9813y+2.3649z=5.9550; Contour level(eÅ^{-3}): -0.30 0.50 0.05

Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2071406 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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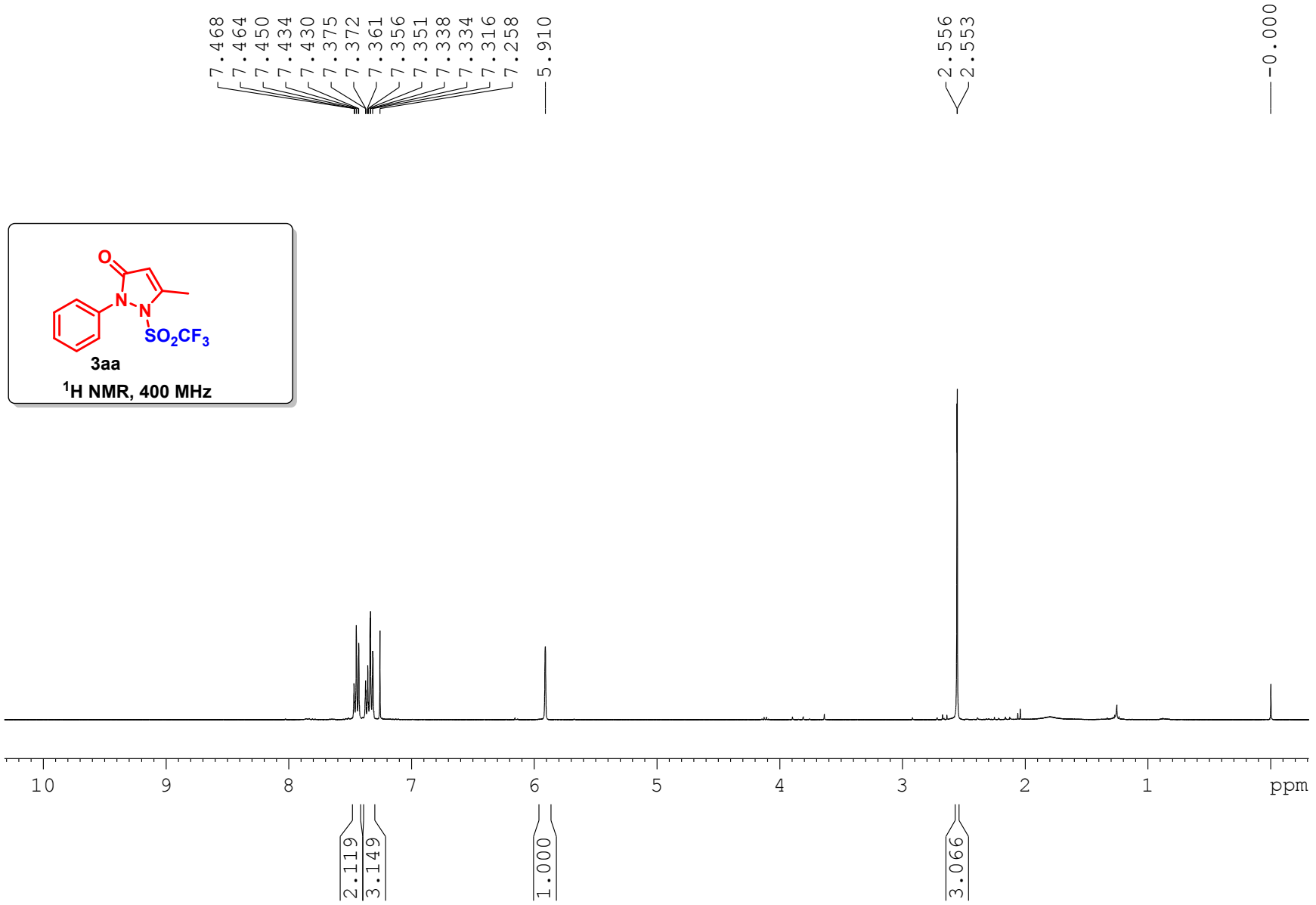
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7.375
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7.316
7.258
5.910
2.556
2.553
0.000
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N
N
SO2CF3
3aa
1H NMR, 400 MHz
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9
8
7
6
5
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1
ppm
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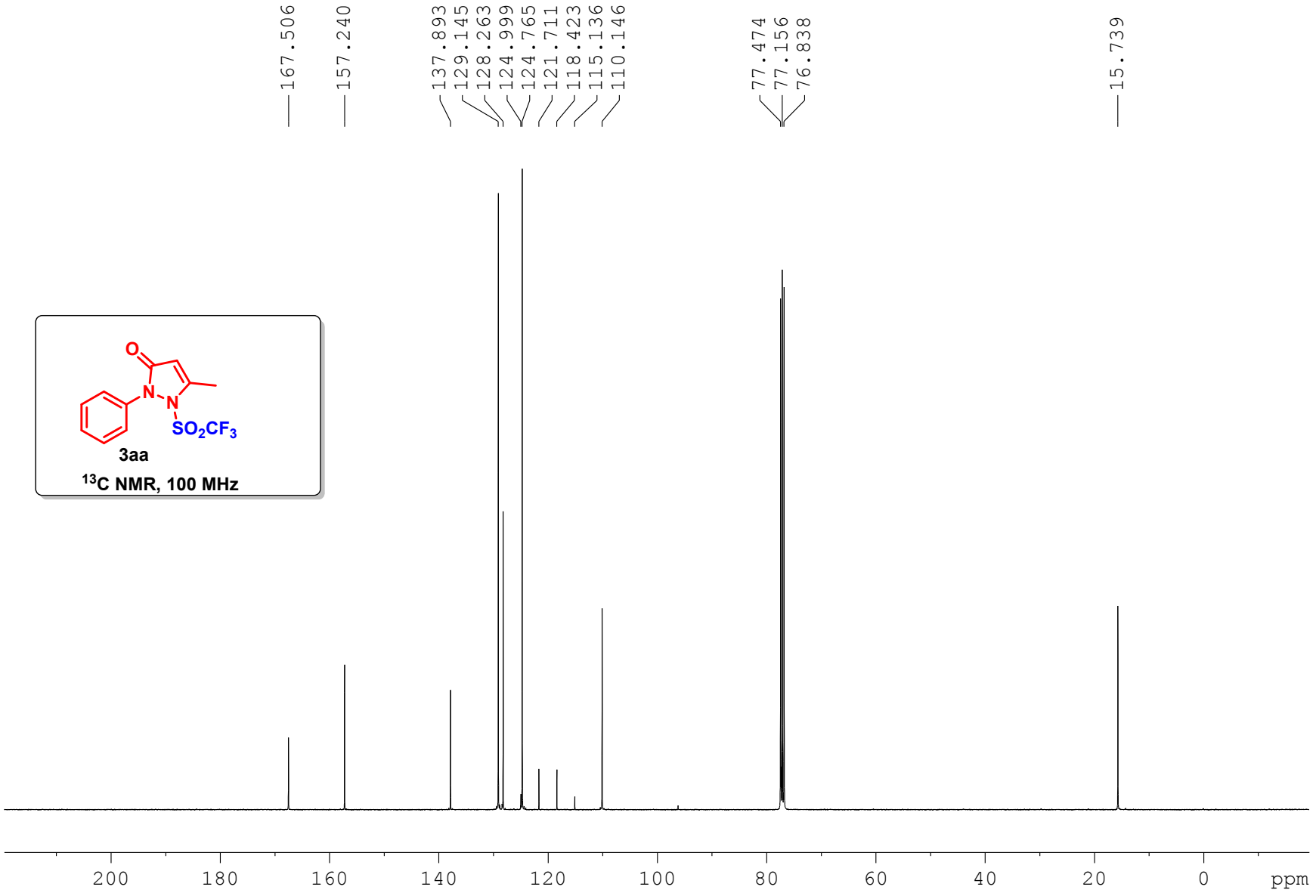
1.000
3.066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76.838
15.739
O
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13C NMR, 100 MHz
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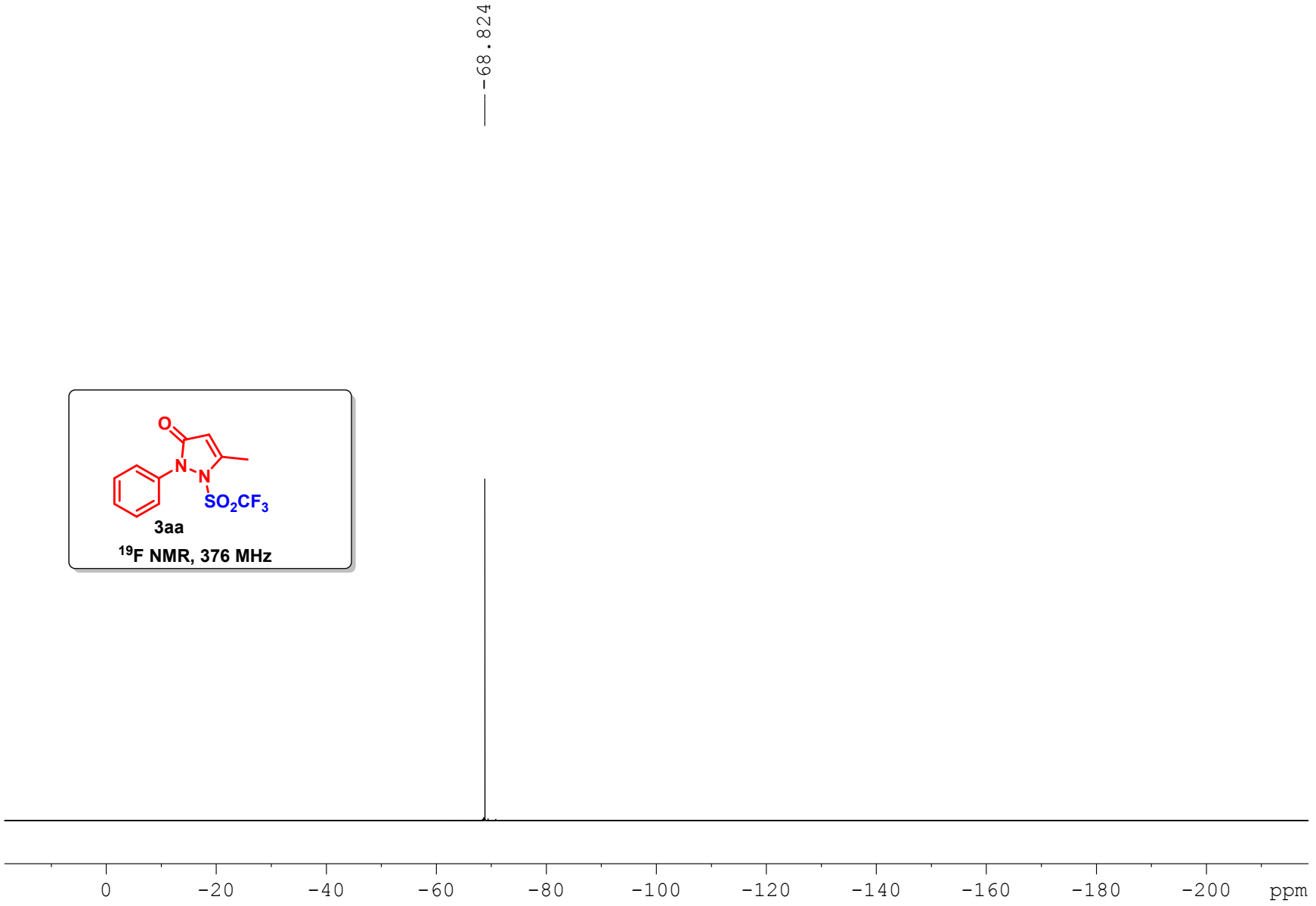
160
140
120
100
80
60
40
20
0
ppm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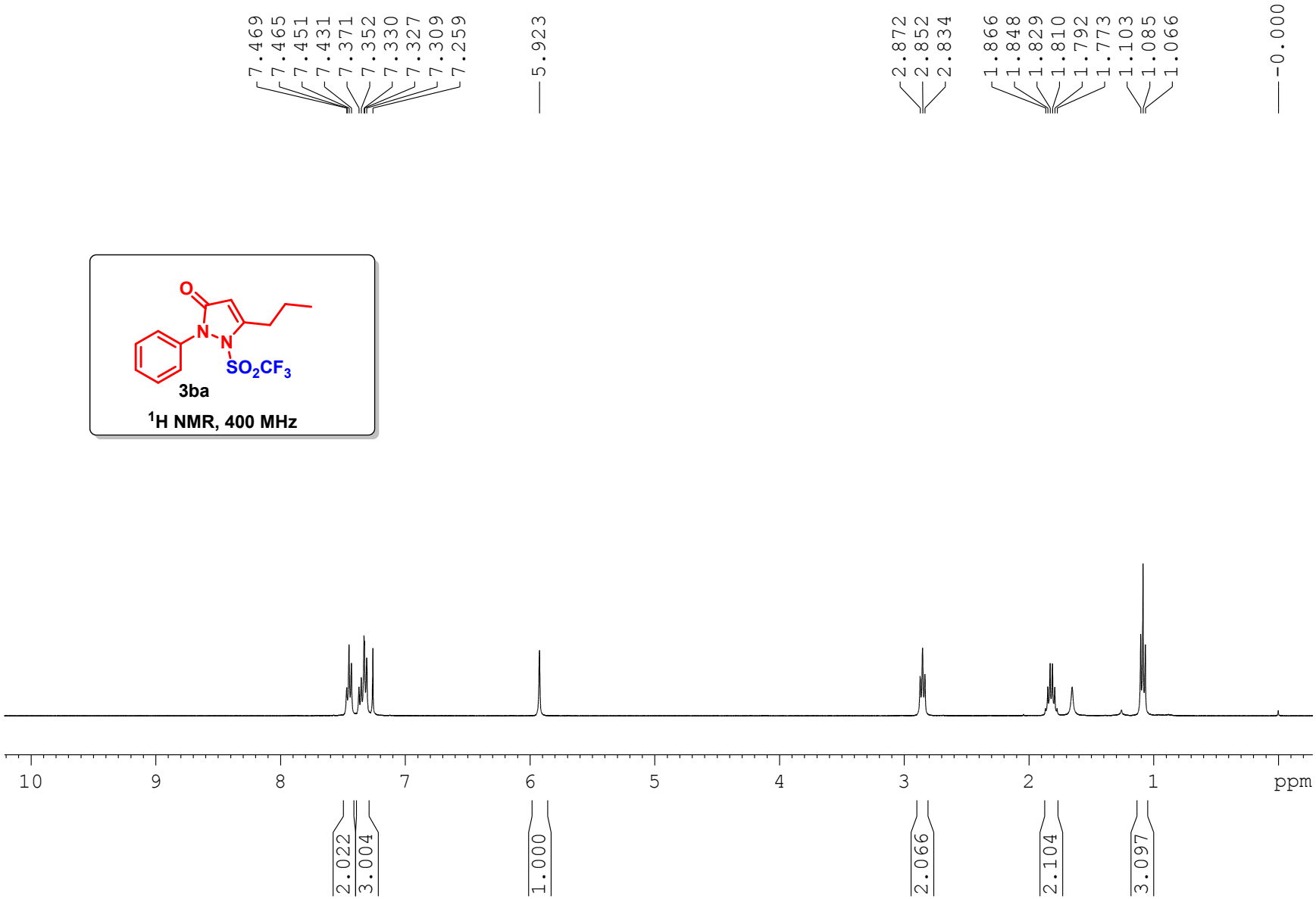
ppm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7.259
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2.834
1.866
1.848
1.829
1.810
1.792
1.773
1.103
1.085
1.066
0.000
O
N
N
SO2CF3
3ba
1H NMR, 400 MHz
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9
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7
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5
4
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2
1
ppm
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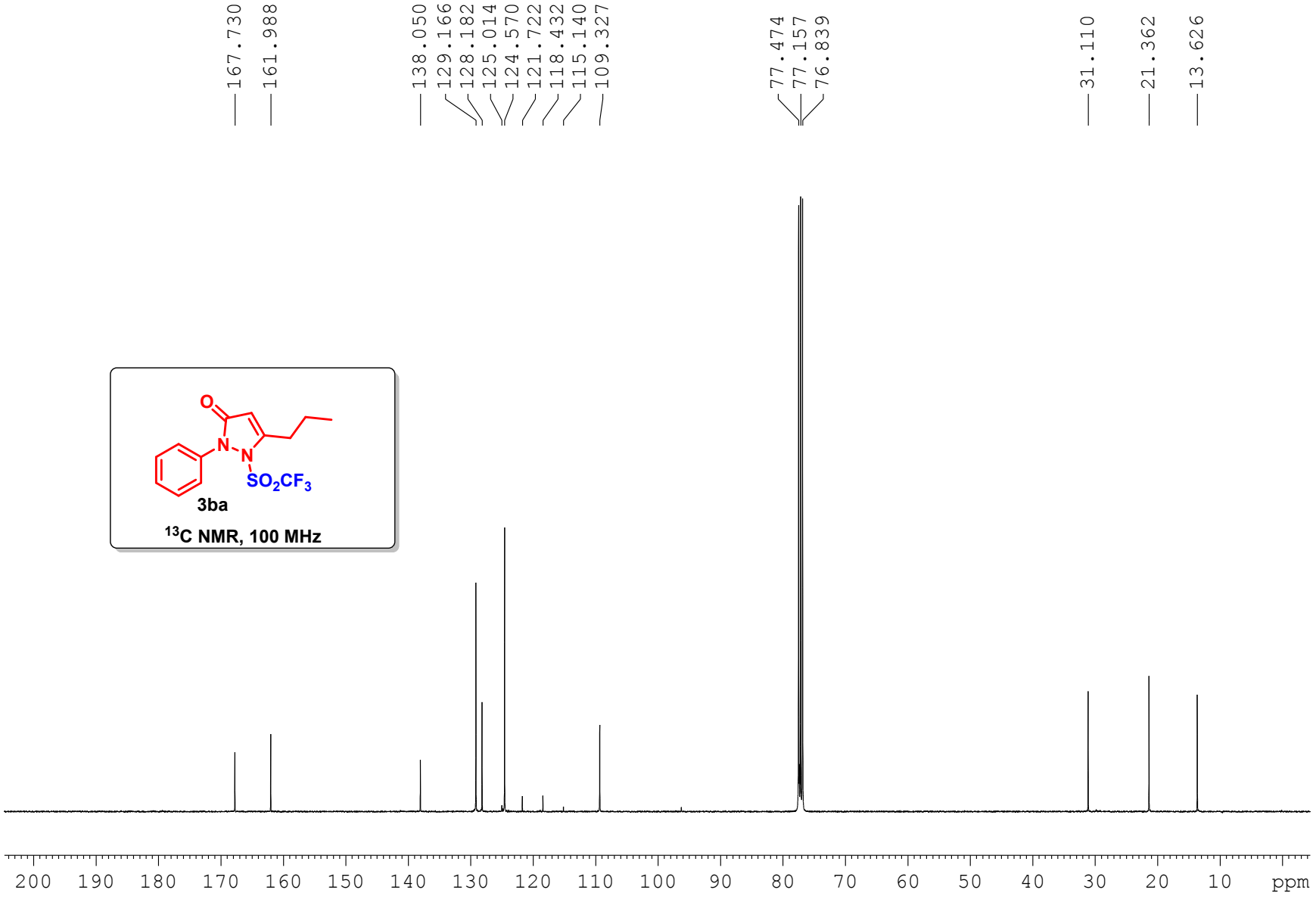
2.104
3.097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77.157
76.839
31.110
21.362
13.626
O
N
N
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3ba
13C NMR, 100 MHz
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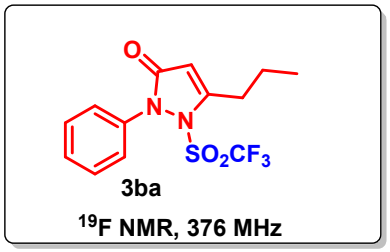
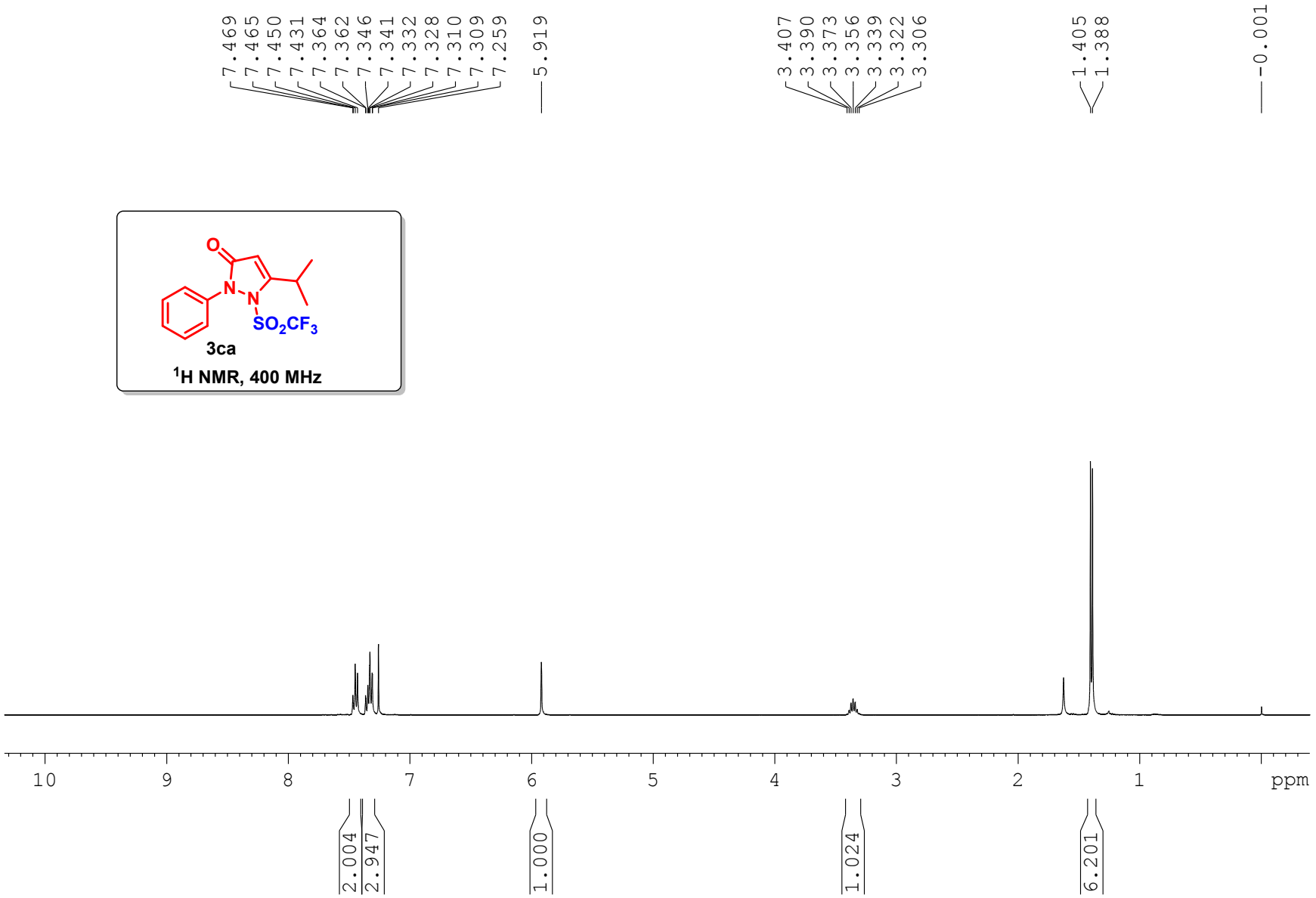


3ba

^{19}F NMR, 376 MHz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7.431
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7.328
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5.919
3.407
3.390
3.373
3.356
3.339
3.322
3.306
1.405
1.388
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O
N
N
SO2CF3
3ca
1H NMR, 400 MHz
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9
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6
5
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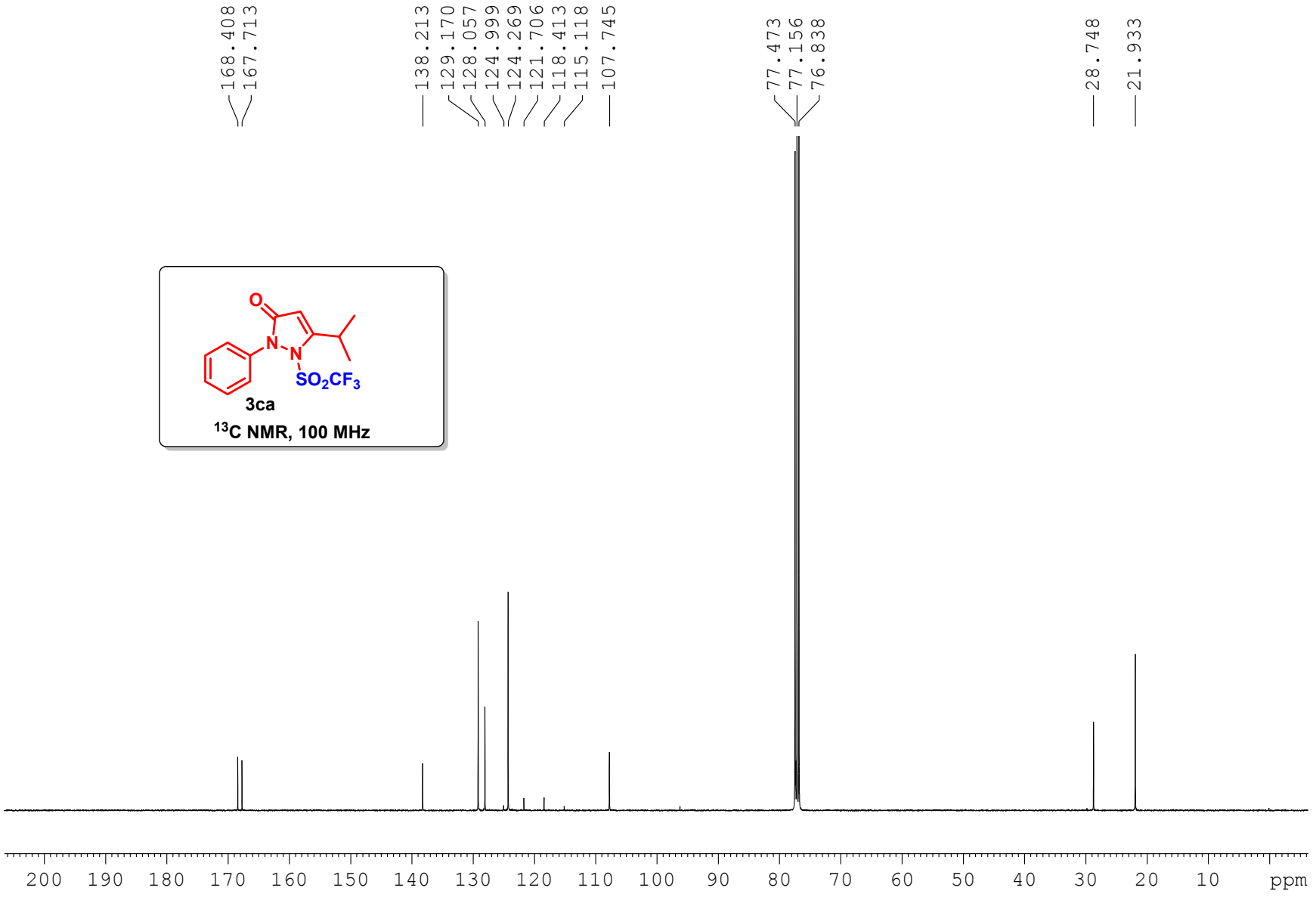
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76.838
28.748
21.933
O
N
N
SO2CF3
3ca
13C NMR, 100 MHz
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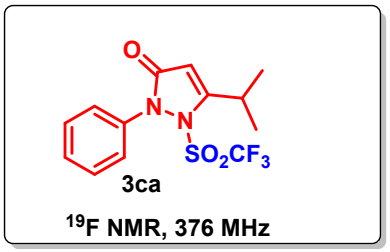
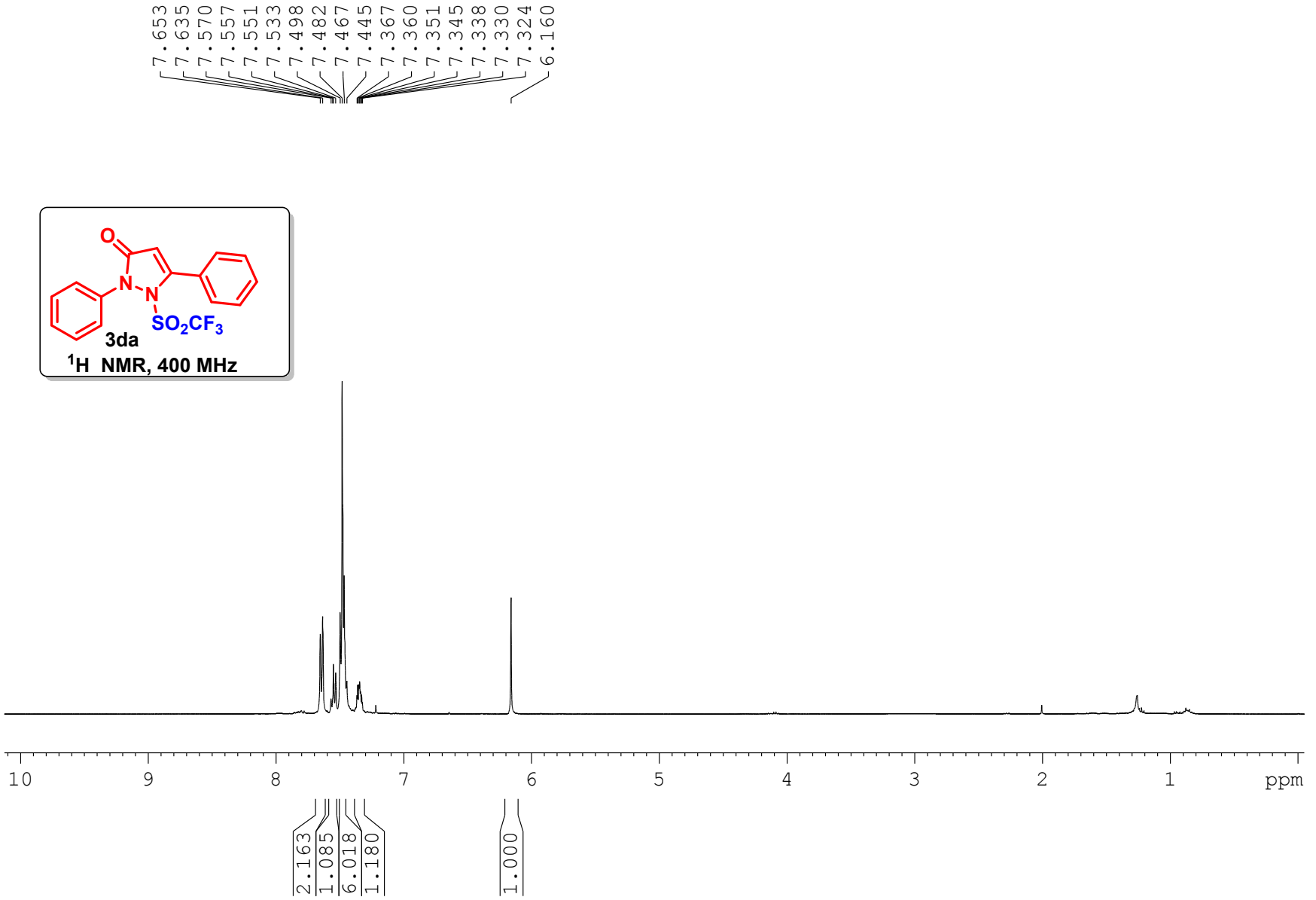
ppm



3ca

^{19}F NMR, 376 MHz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7.351
7.345
7.338
7.330
7.324
6.160
O
N
N
SO2CF3
3da
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.163
1.085
6.018
1.180
1.000

166.730
159.676
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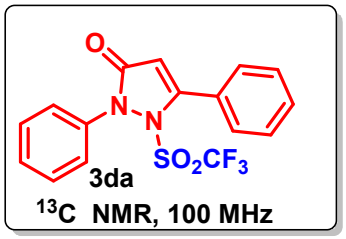
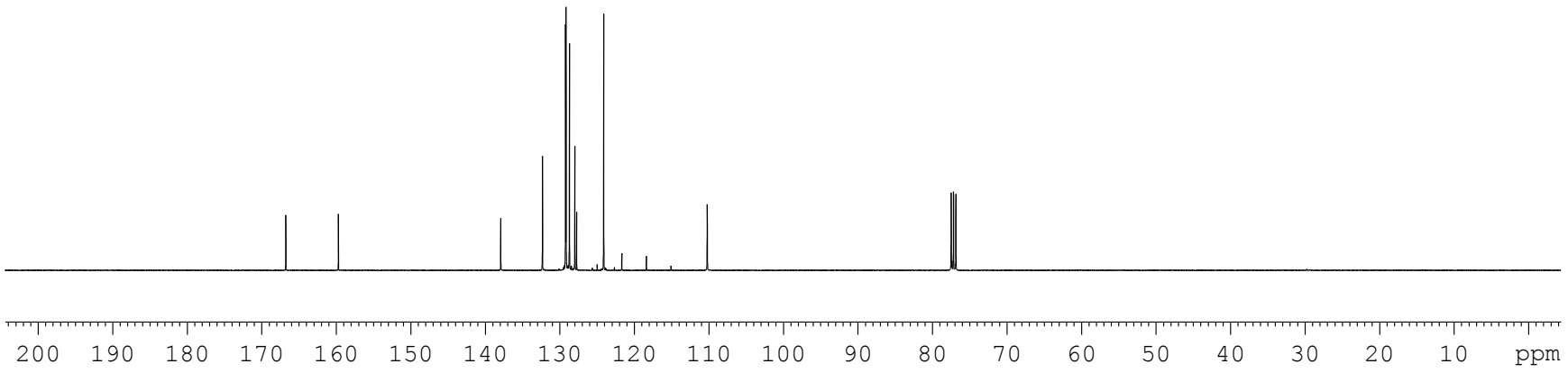
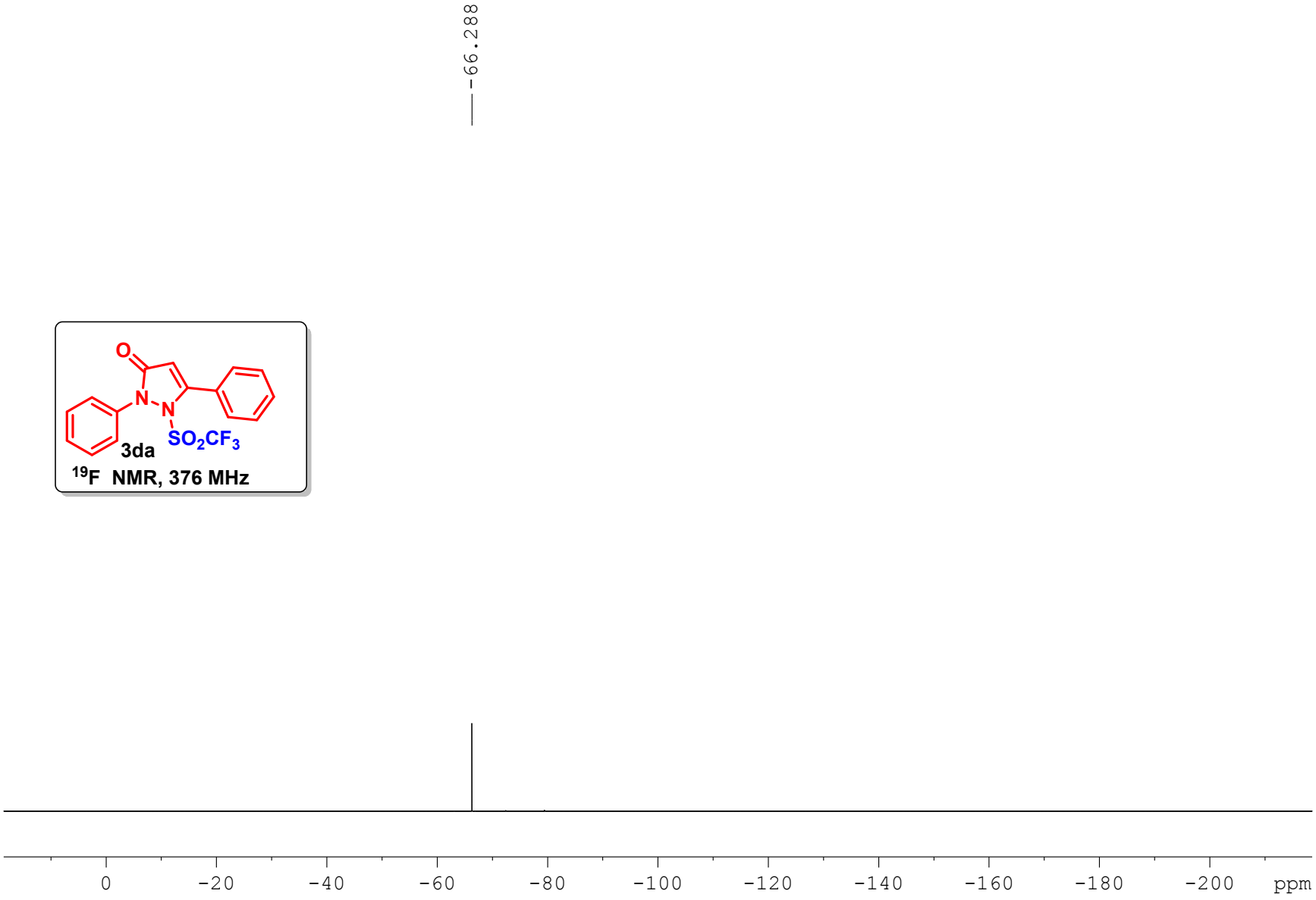


3da

^{13}C NMR, 100 MHz

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SO2CF3
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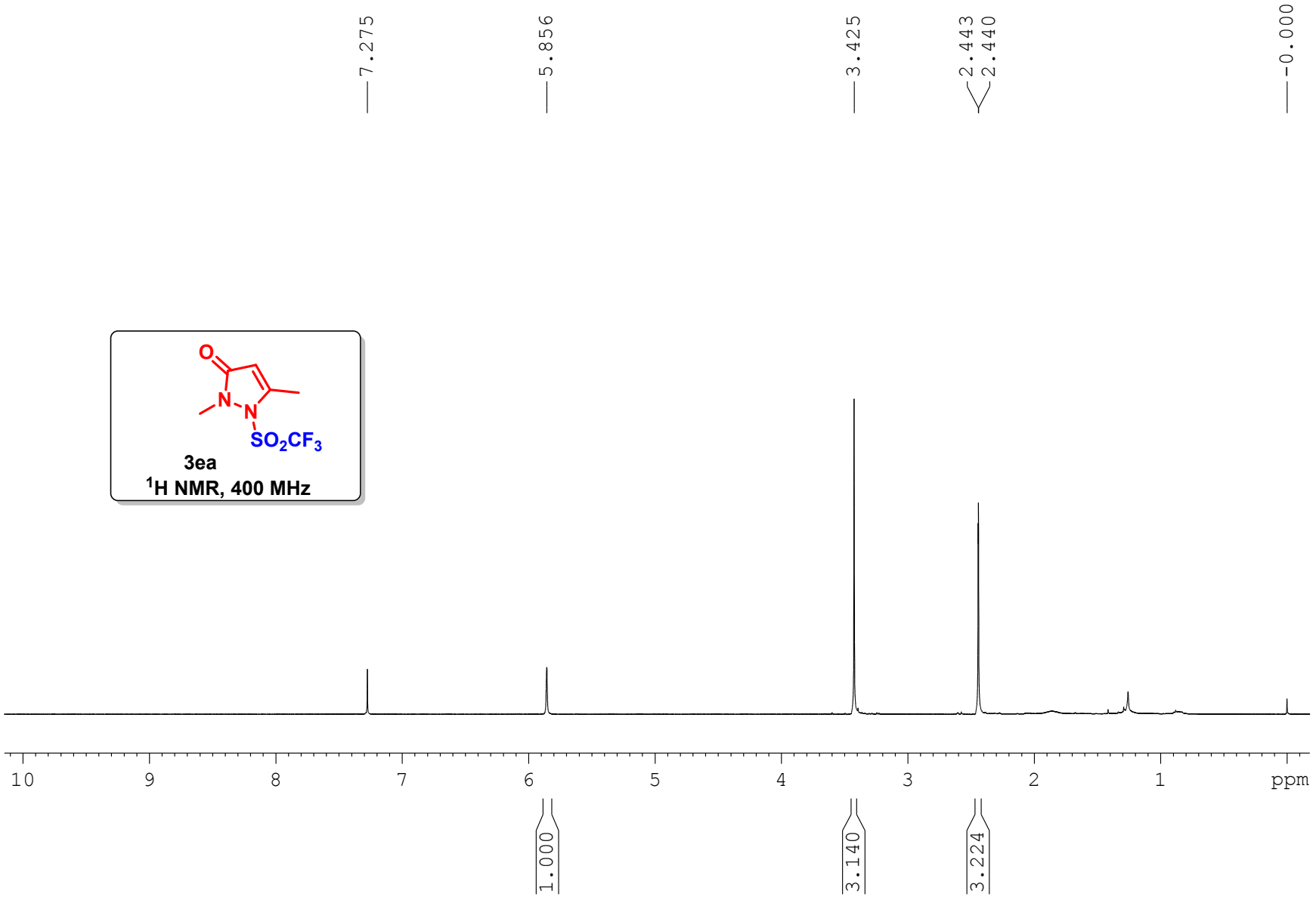
-200
ppm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SO2CF3
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7
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3
2
1
ppm
1.000
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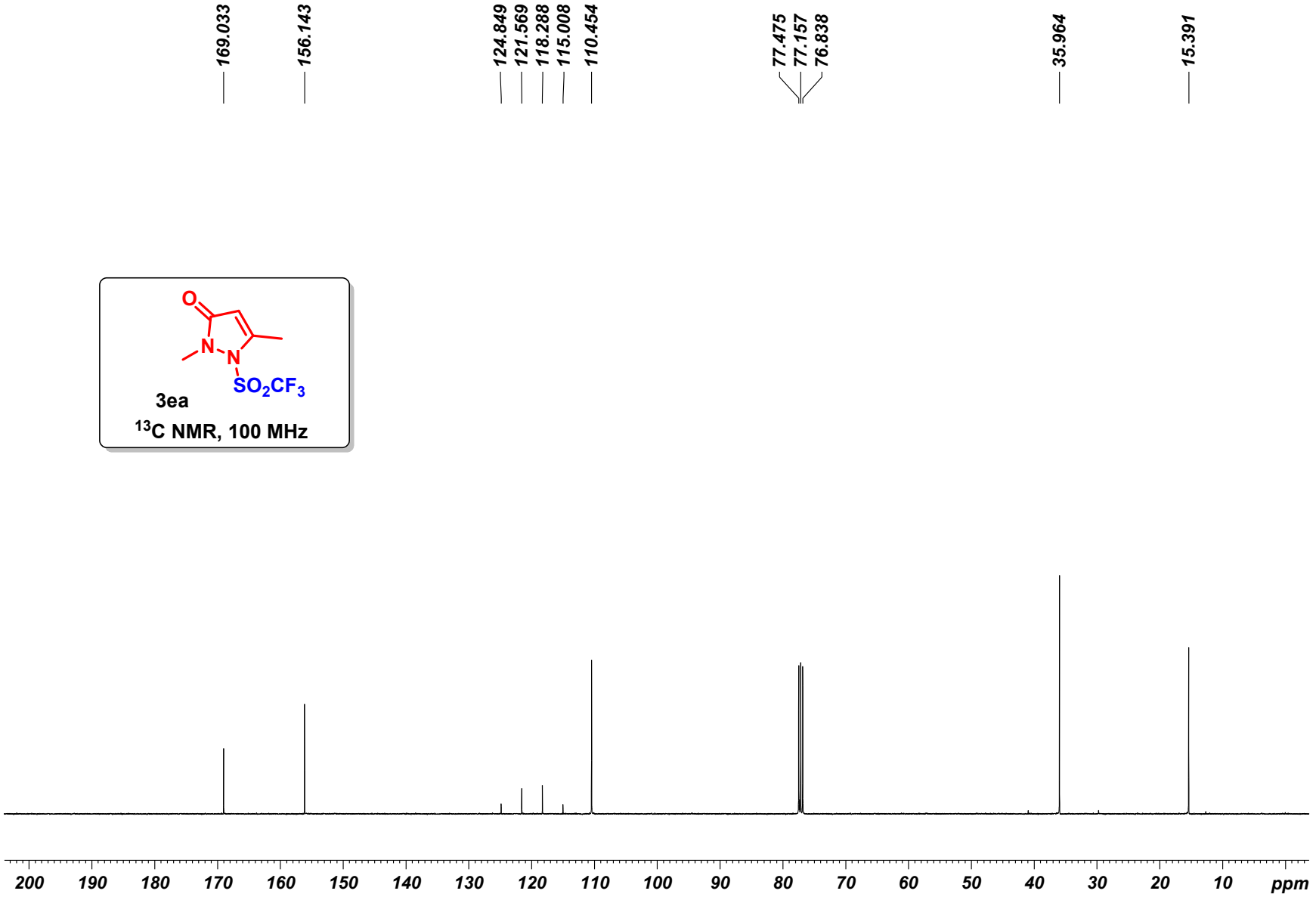
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O
N
N
SO2CF3
3ea
13C NMR, 100 MHz
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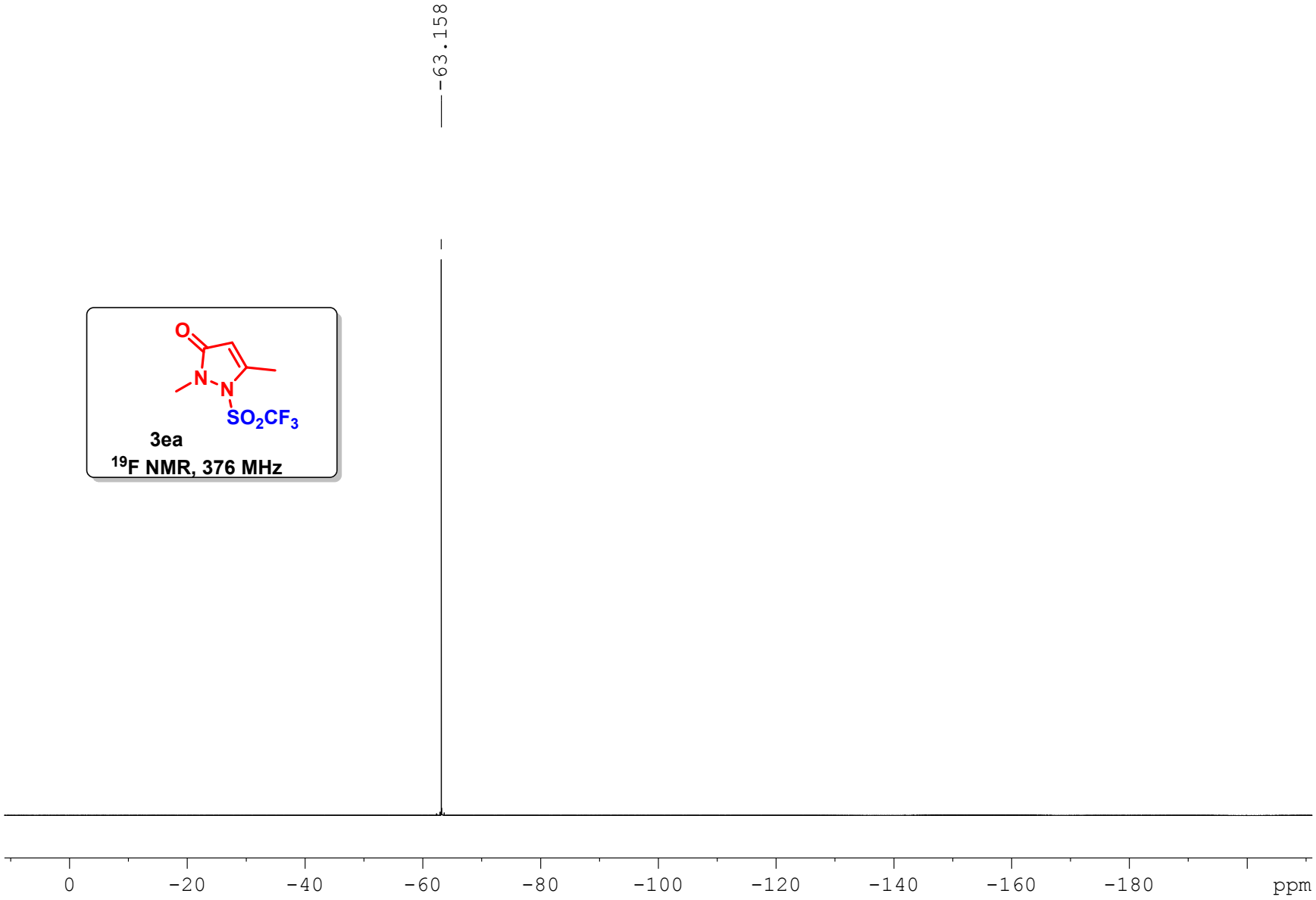
10
ppm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-40
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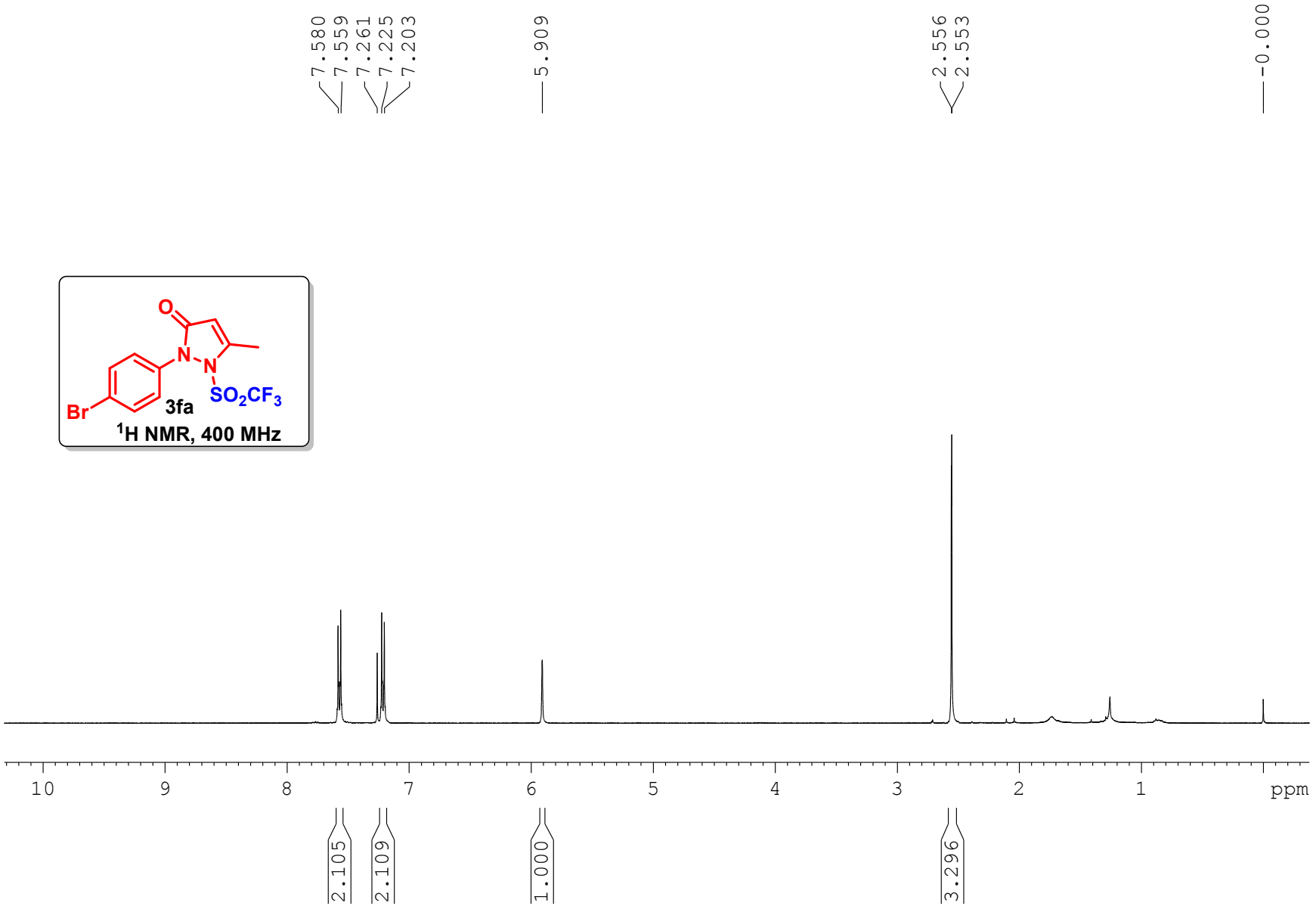
-180
ppm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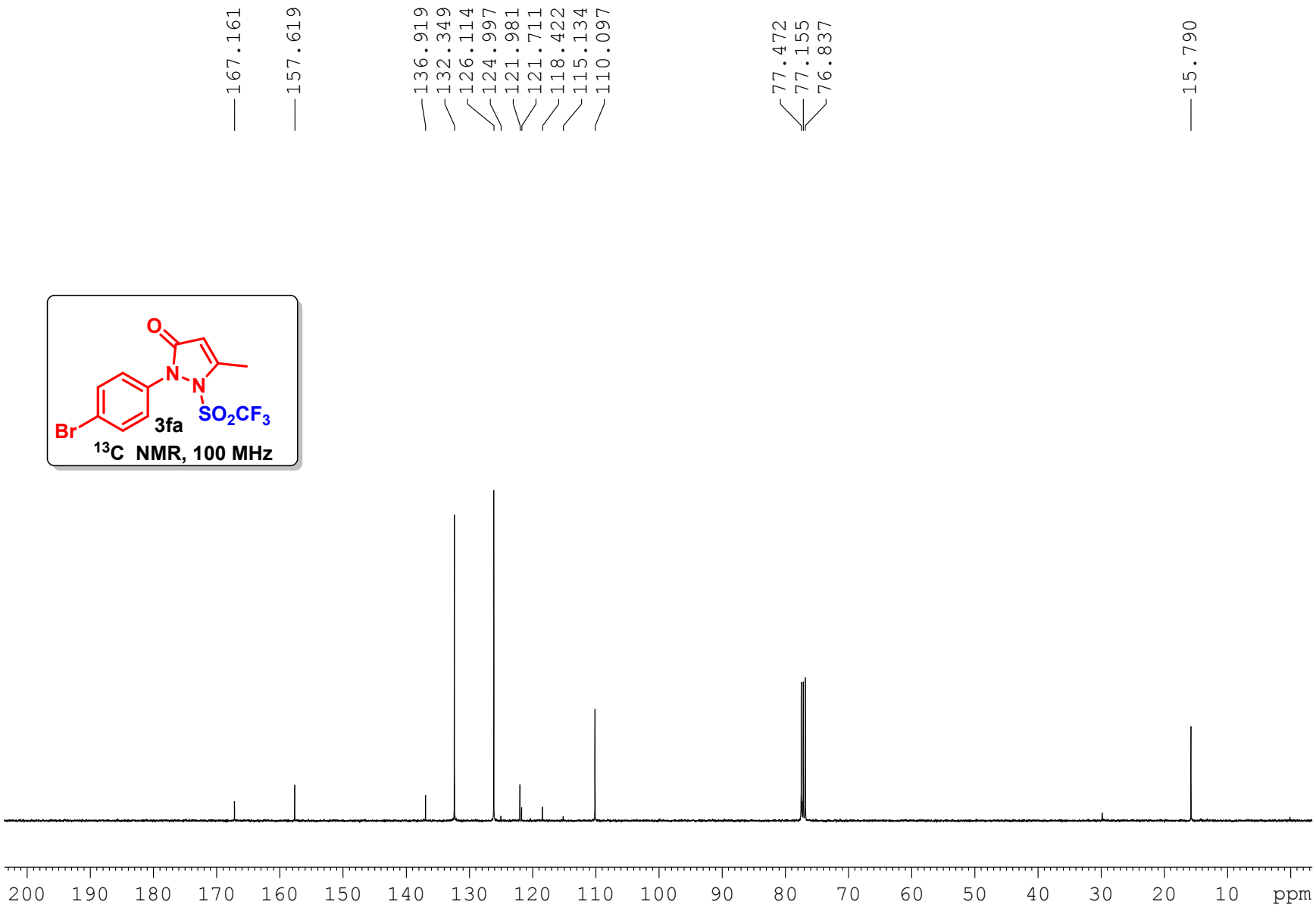
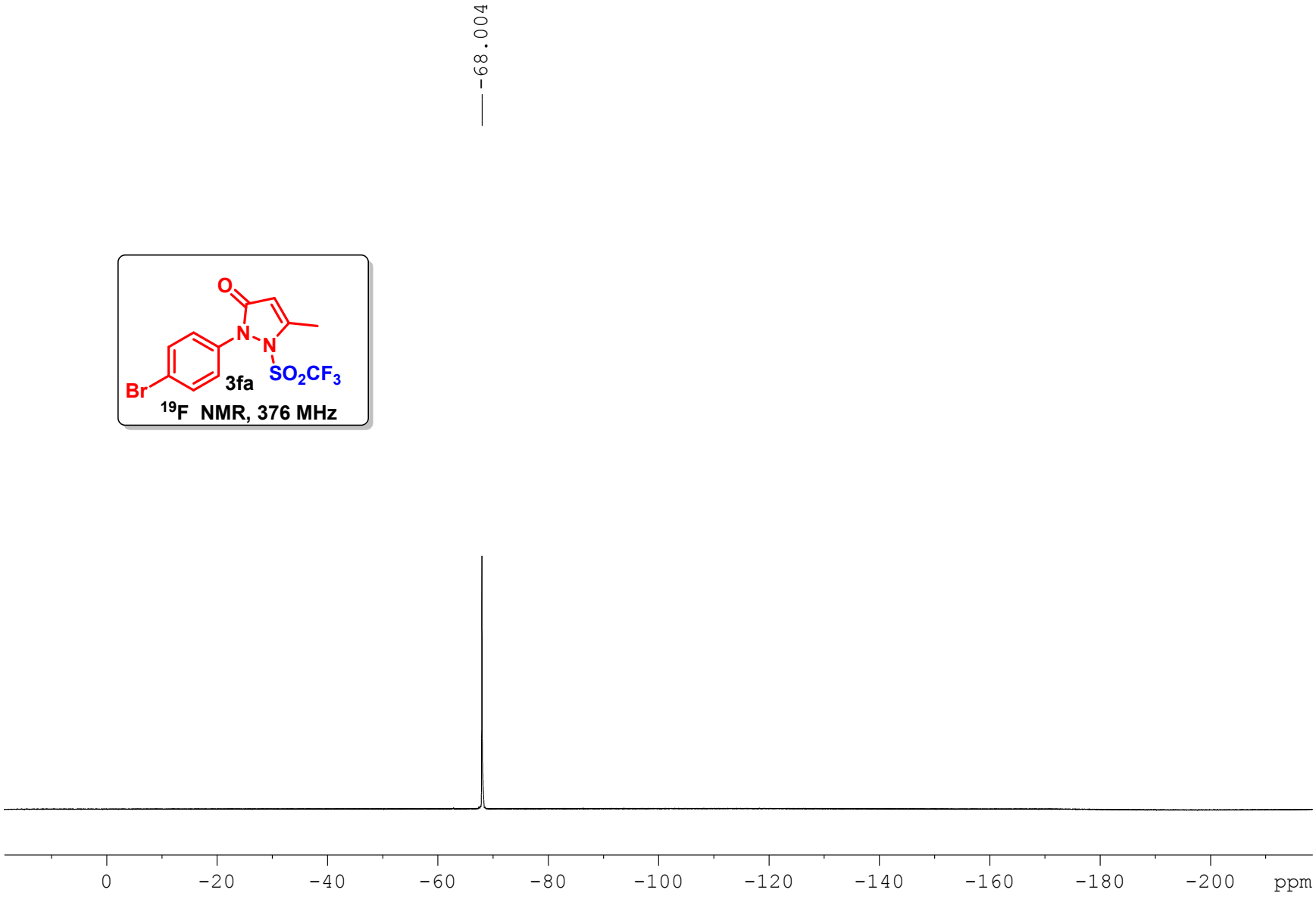
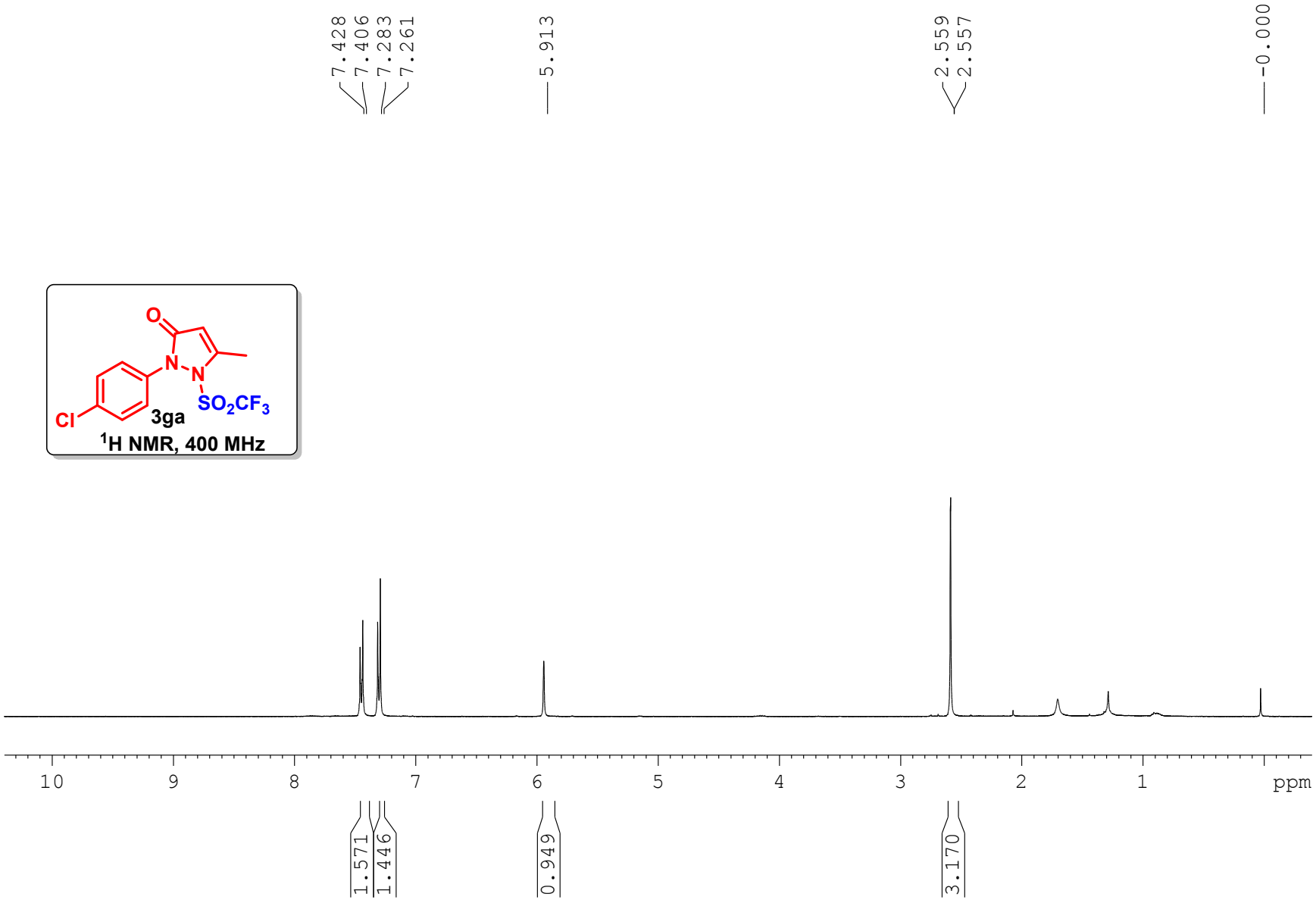
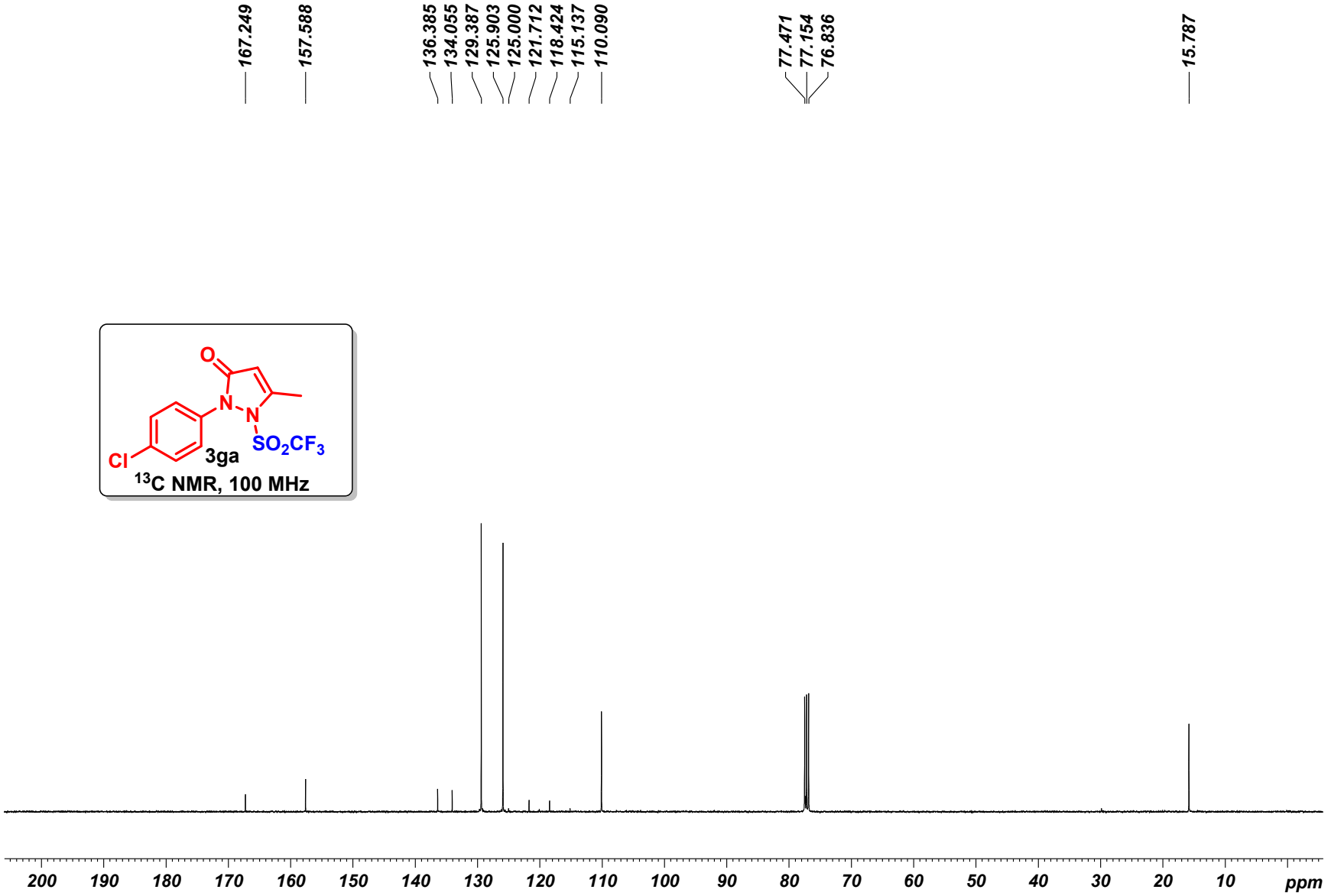
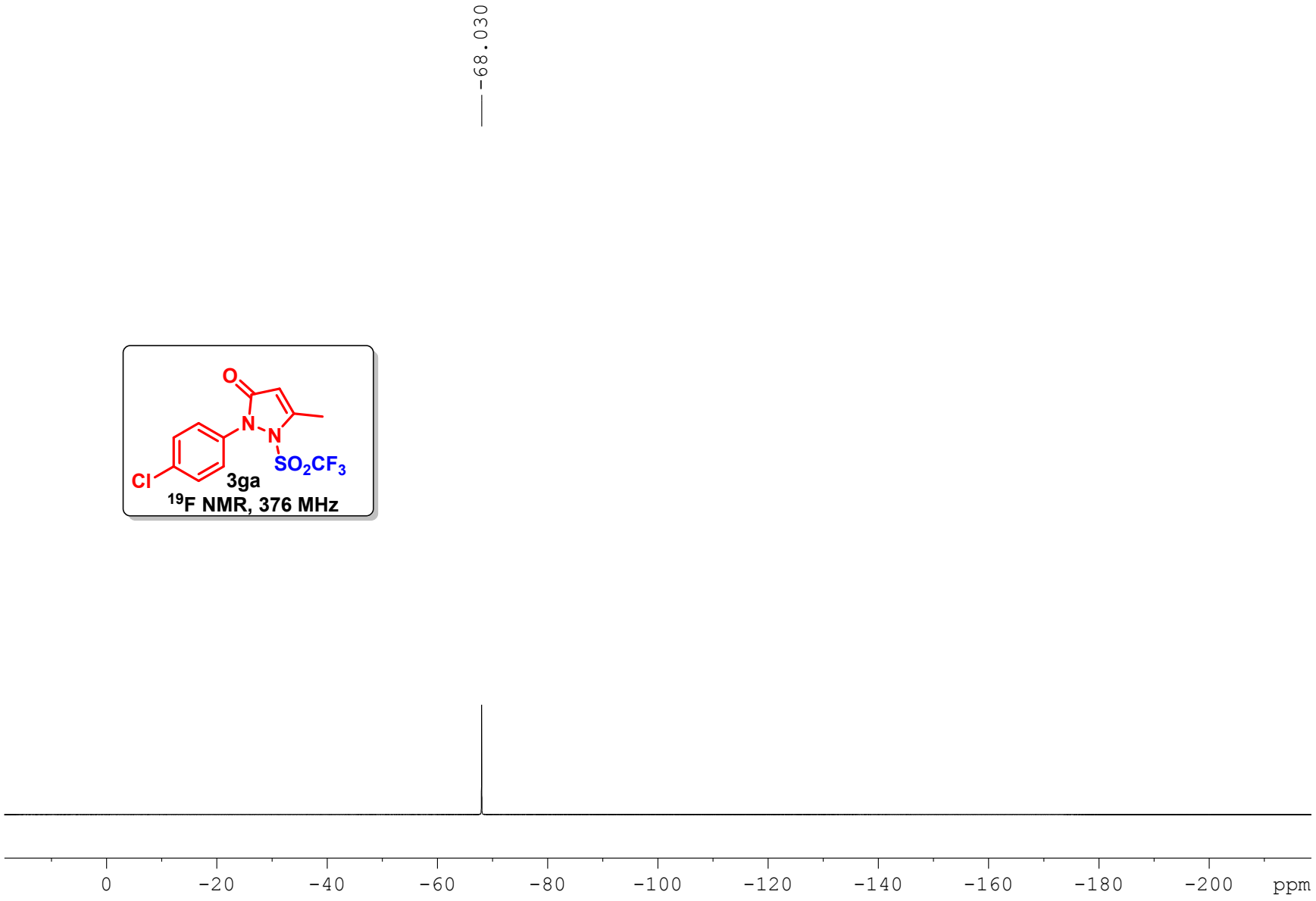
7.559
7.261
7.225
7.203
5.909
2.556
2.553
0.000
O
N
N
Br
SO2CF3
3fa
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.105
2.109
1.000
3.296

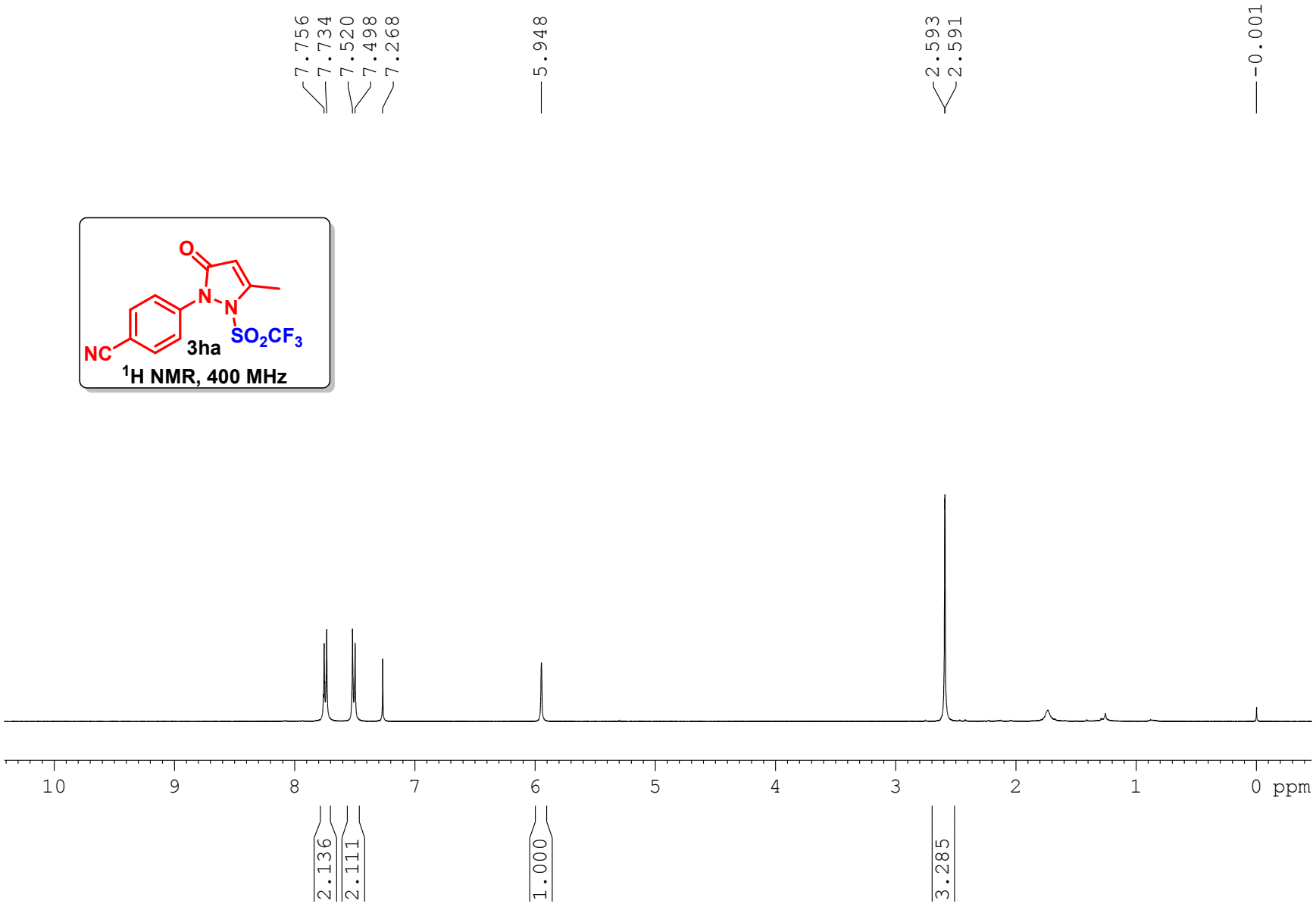

167.161
157.619
136.919
132.349
126.114
124.997
121.981
121.711
118.422
115.134
110.097
77.472
77.155
76.837
15.790
O
N
N
SO2CF3
Br
3fa
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

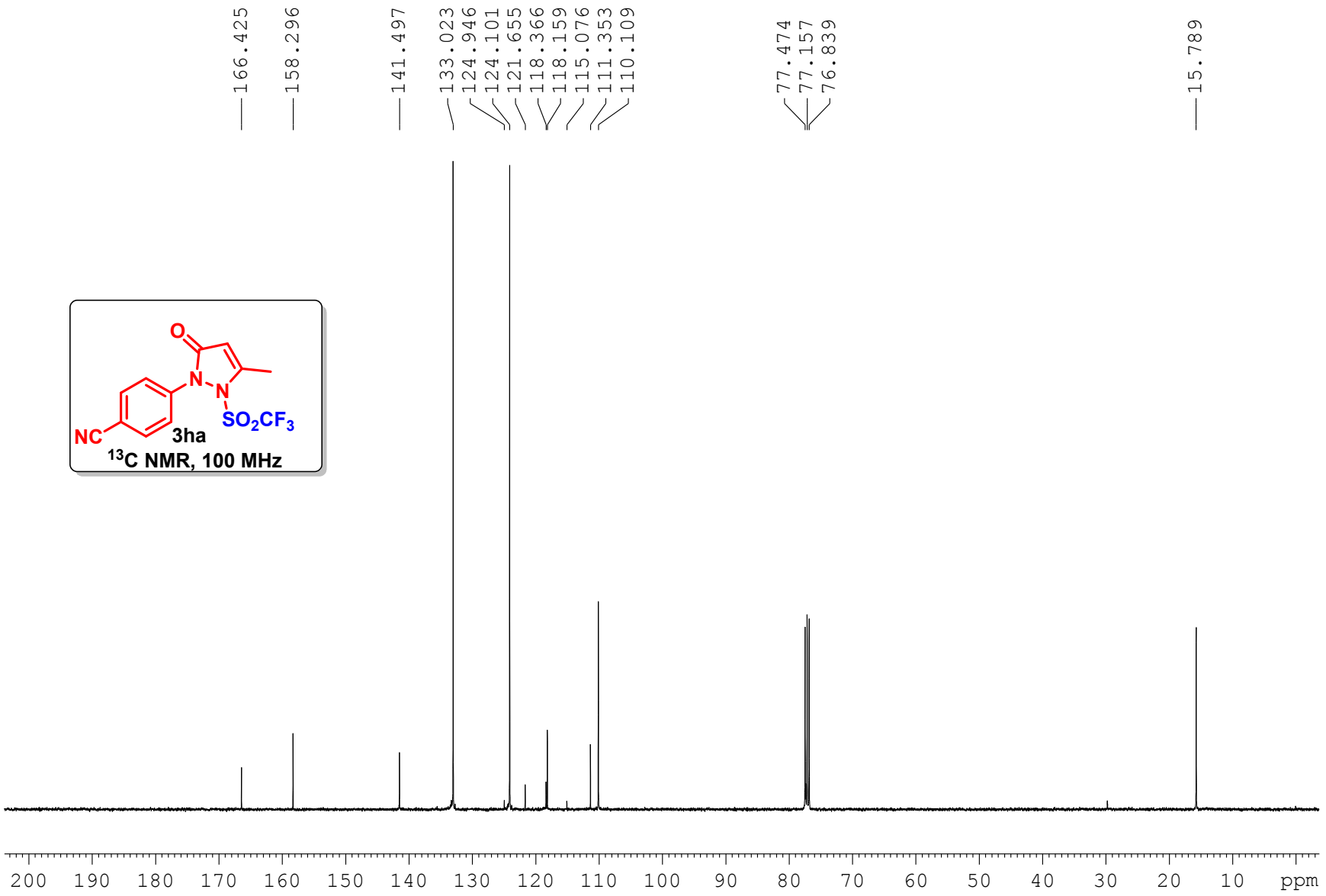

-68.004
O
N
N
SO2CF3
Br
3fa
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

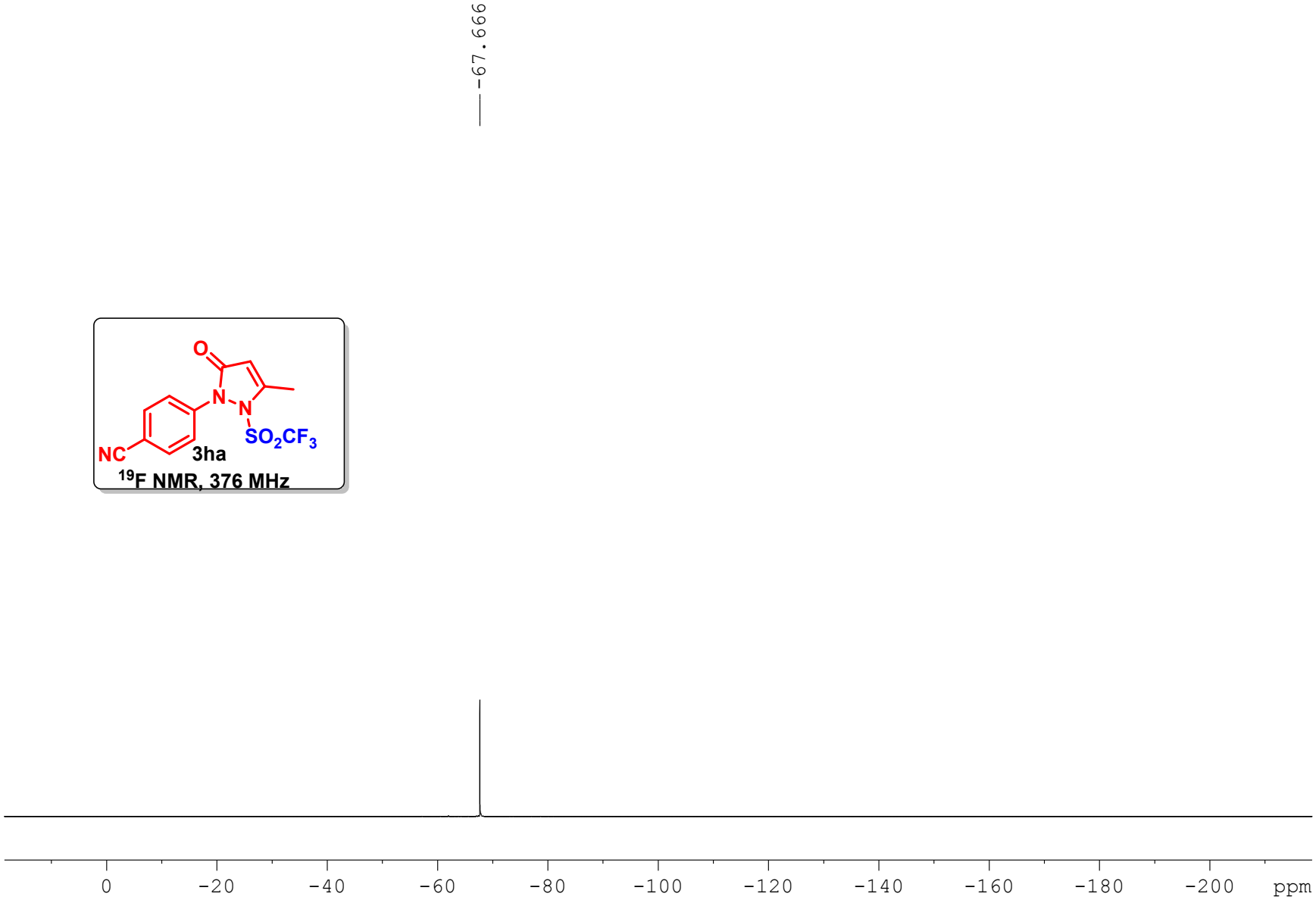

7.428
7.406
7.283
7.261
5.913
2.559
2.557
-0.000
O
N
N
SO2CF3
Cl
3ga
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.571
1.446
0.949
3.170

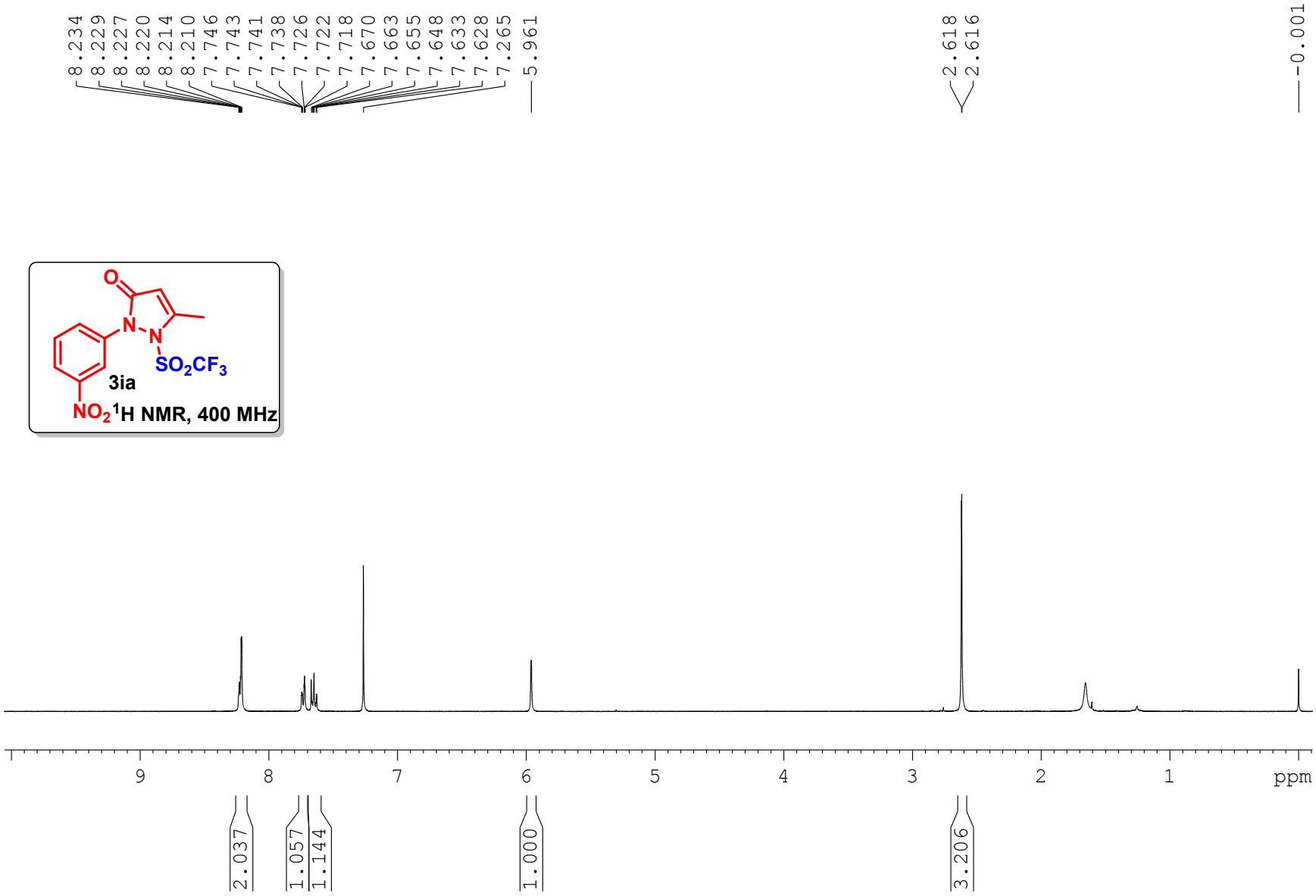

167.249
157.588
136.385
134.055
129.387
125.903
125.000
121.712
118.424
115.137
110.090
77.471
77.154
76.836
15.787
O
N
N
SO2CF3
Cl
3ga
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

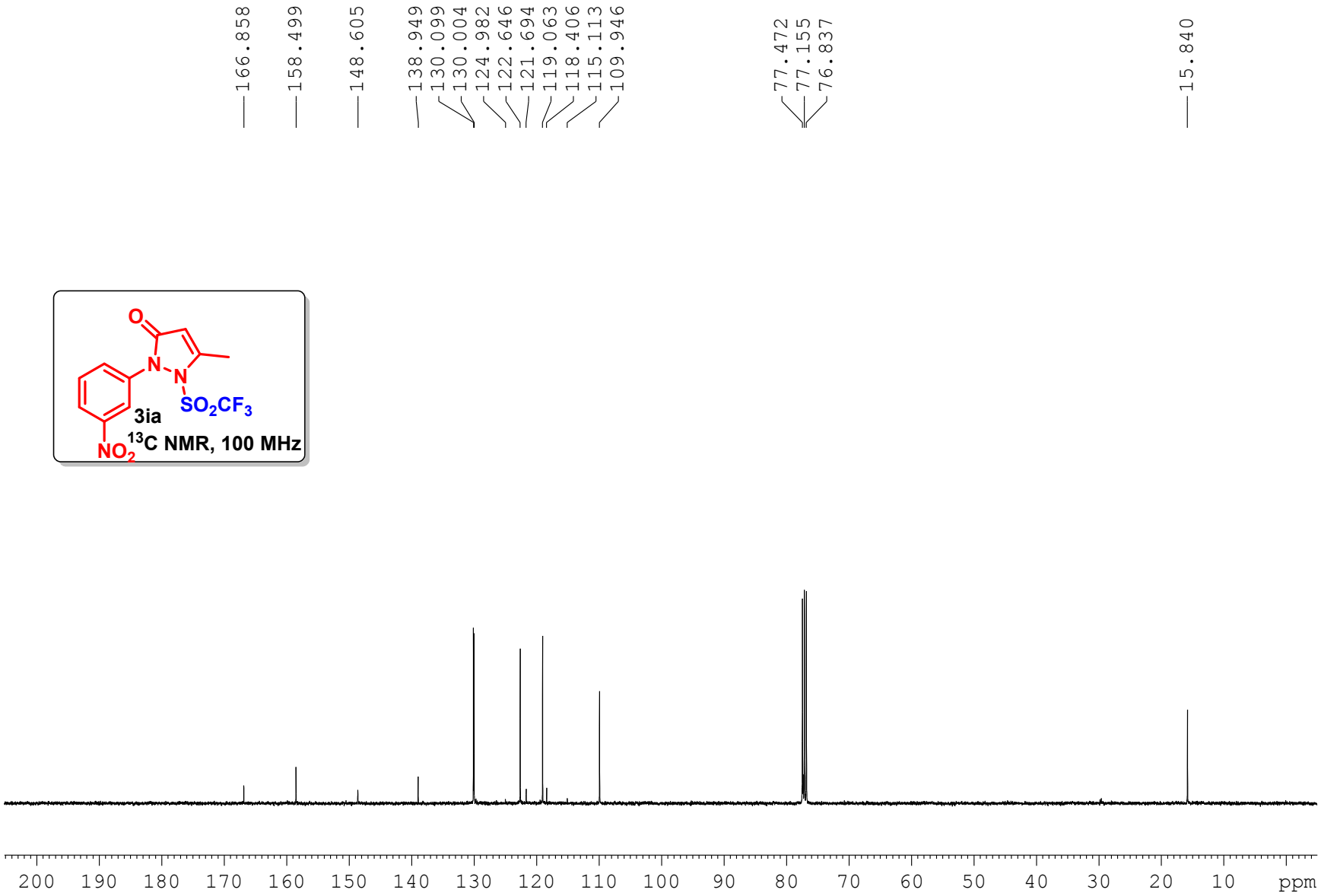

-68.030
O
N
N
SO2CF3
Cl
3ga
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

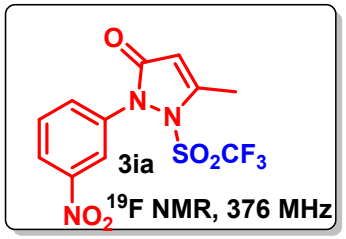

7.756
7.734
7.520
7.498
7.268
5.948
2.593
2.591
-0.001
O
N
N
SO2CF3
NC
3ha
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
2.136
2.111
1.000
3.285


166.425
158.296
141.497
133.023
124.946
124.101
121.655
118.366
118.159
115.076
111.353
110.109
77.474
77.157
76.839
15.789
O
N
N
SO2CF3
NC
3ha
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-67.666
O
N
N
SO2CF3
NC
3ha
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

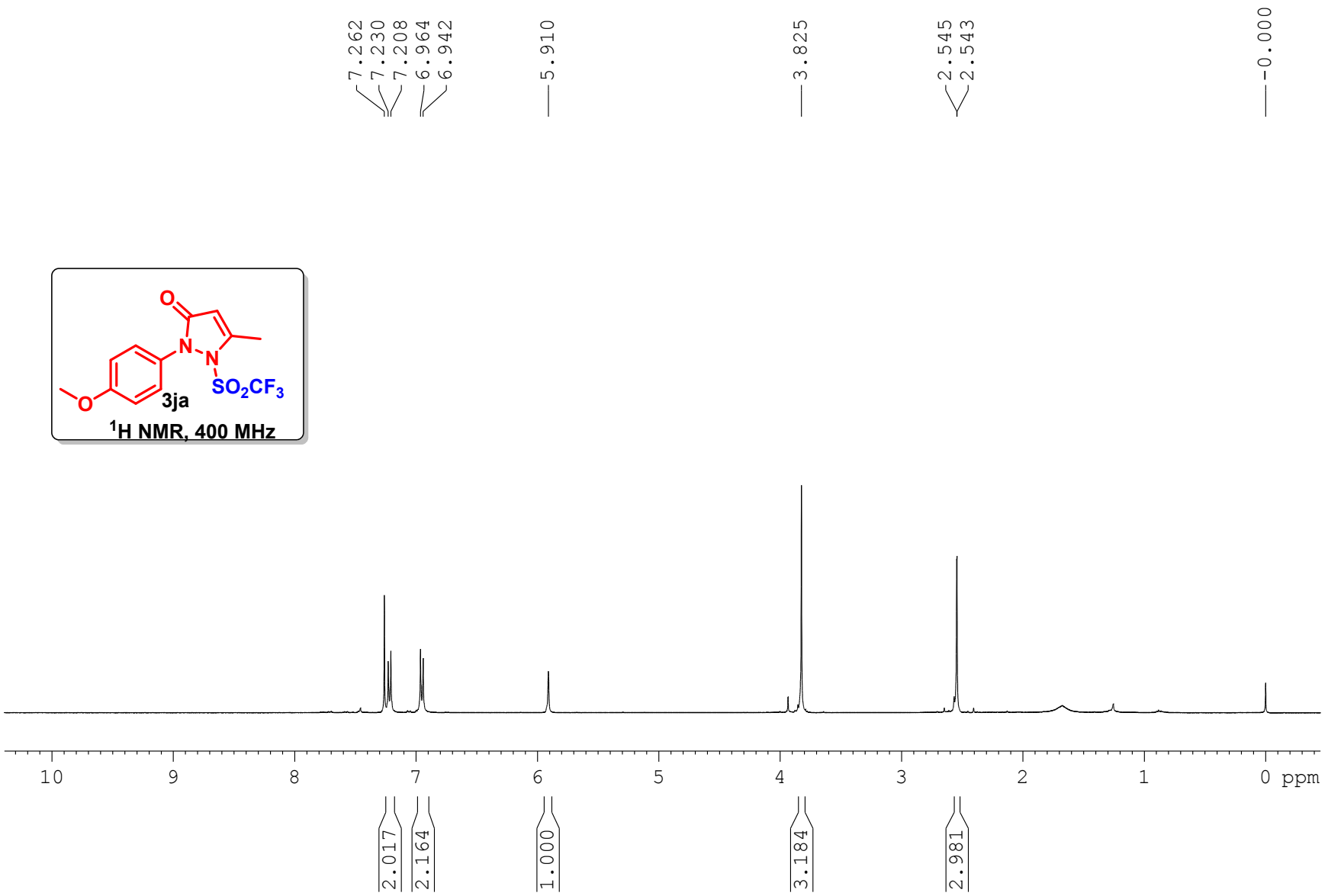

8.234
8.229
8.227
8.220
8.214
8.210
7.746
7.743
7.741
7.738
7.726
7.722
7.718
7.670
7.663
7.655
7.648
7.633
7.628
7.265
5.961
2.618
2.616
-0.001
O
N
N
SO2CF3
3ia
NO2
1H NMR, 400 MHz
9
8
7
6
5
4
3
2
1
ppm
2.037
1.057
1.144
1.000
3.206

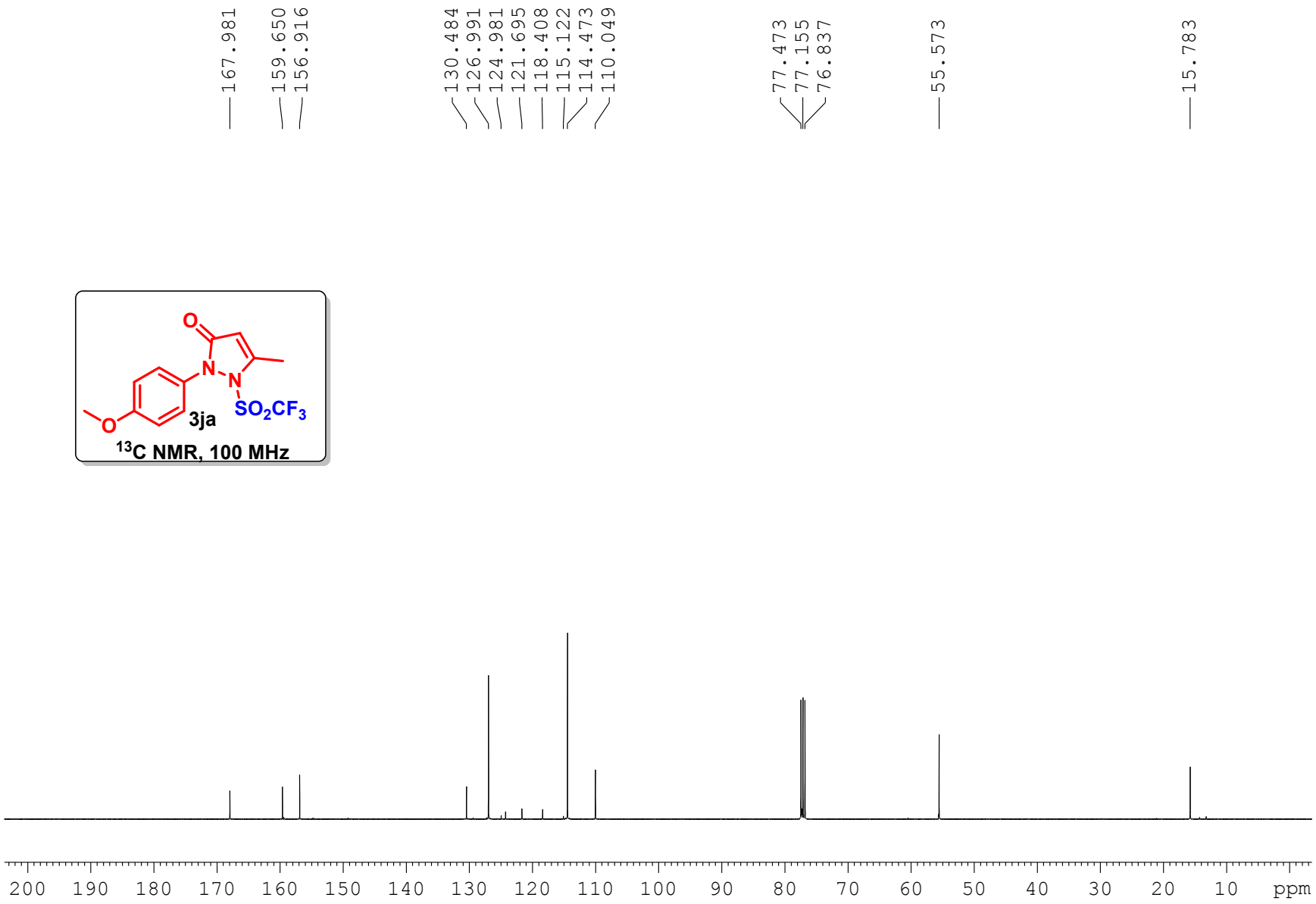

166.858
158.499
148.605
138.949
130.099
130.004
124.982
122.646
121.694
119.063
118.406
115.113
109.946
77.472
77.155
76.837
15.840
O
N
N
SO2CF3
NO2
3ia
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

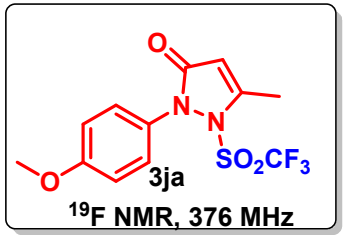


3ia

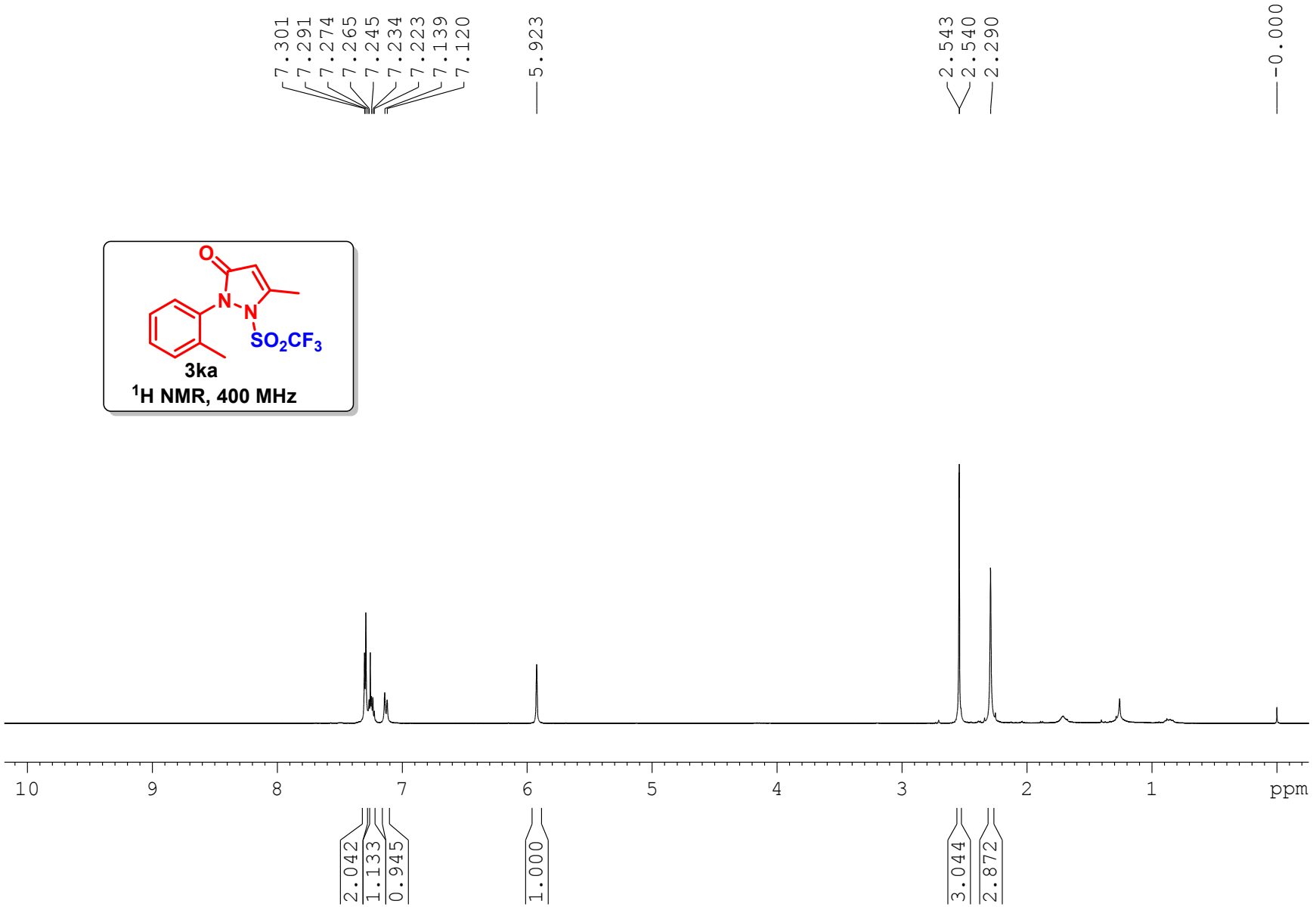
^{19}F NMR, 376 MHz

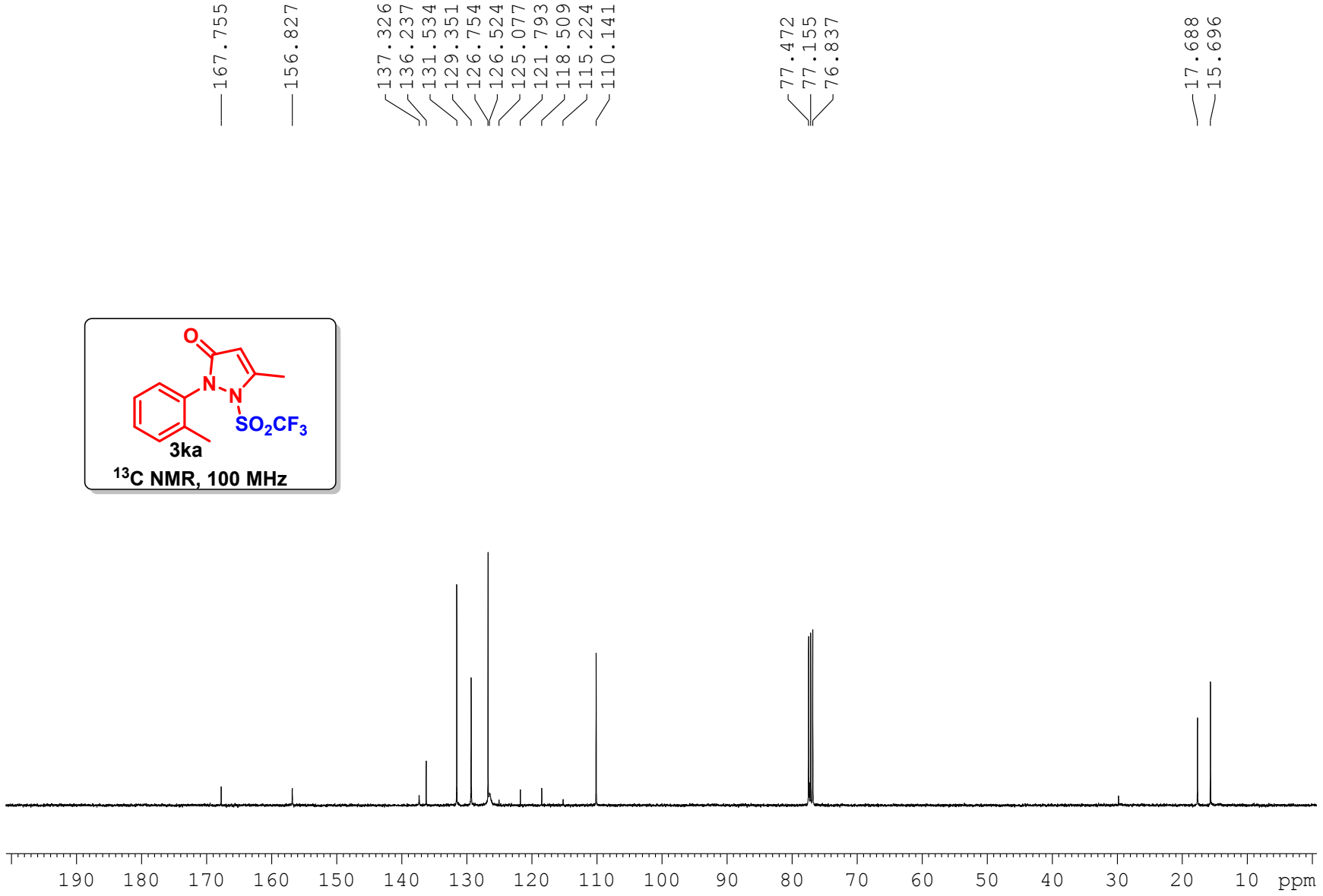

7.262
7.230
7.208
6.964
6.942
5.910
3.825
2.545
2.543
-0.000
O
N
N
SO2CF3
O
3ja
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
2.017
2.164
1.000
3.184
2.981

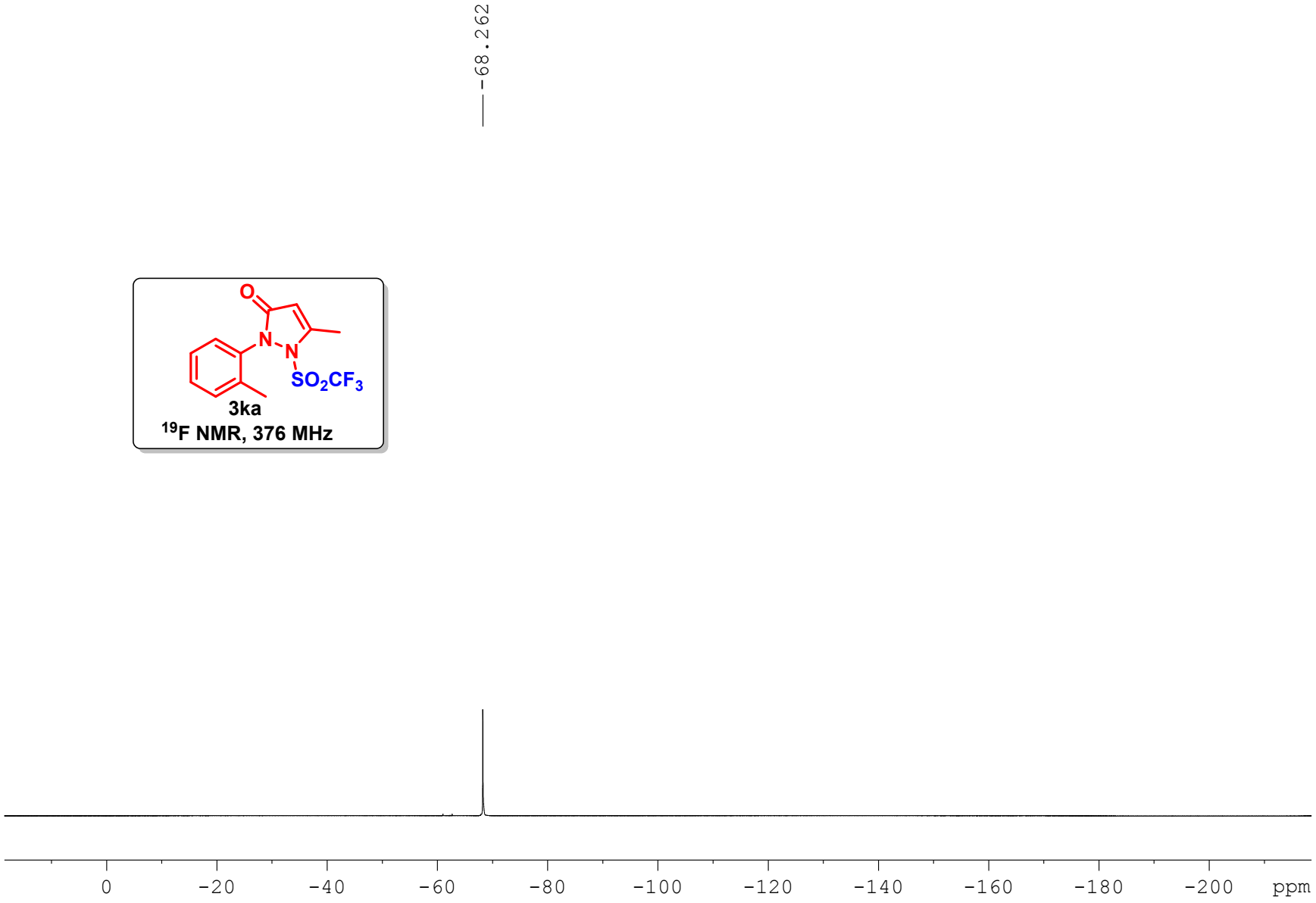

167.981
159.650
156.916
130.484
126.991
124.981
121.695
118.408
115.122
114.473
110.049
77.473
77.155
76.837
55.573
15.783
O
N
N
SO2CF3
O
3ja
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

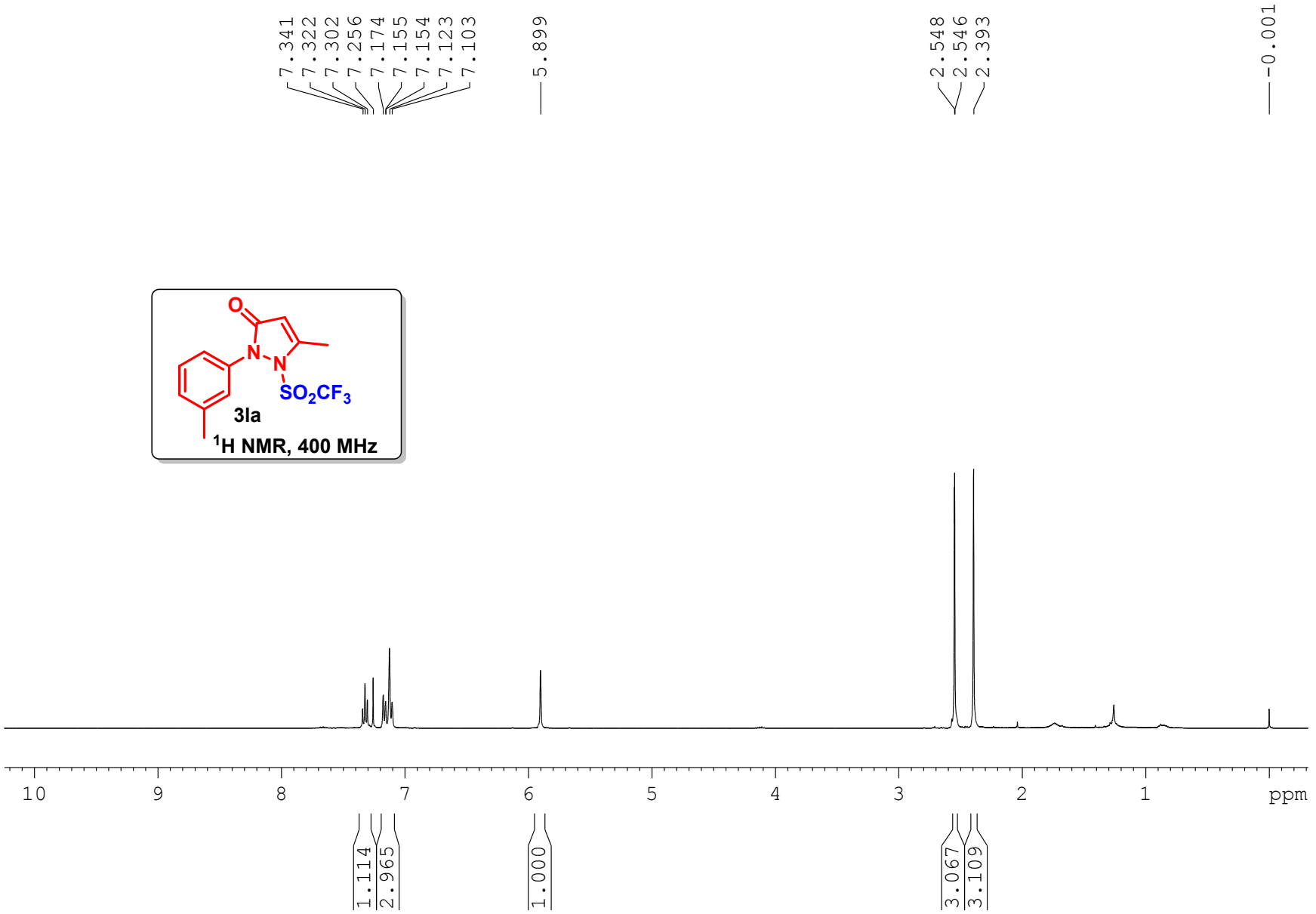


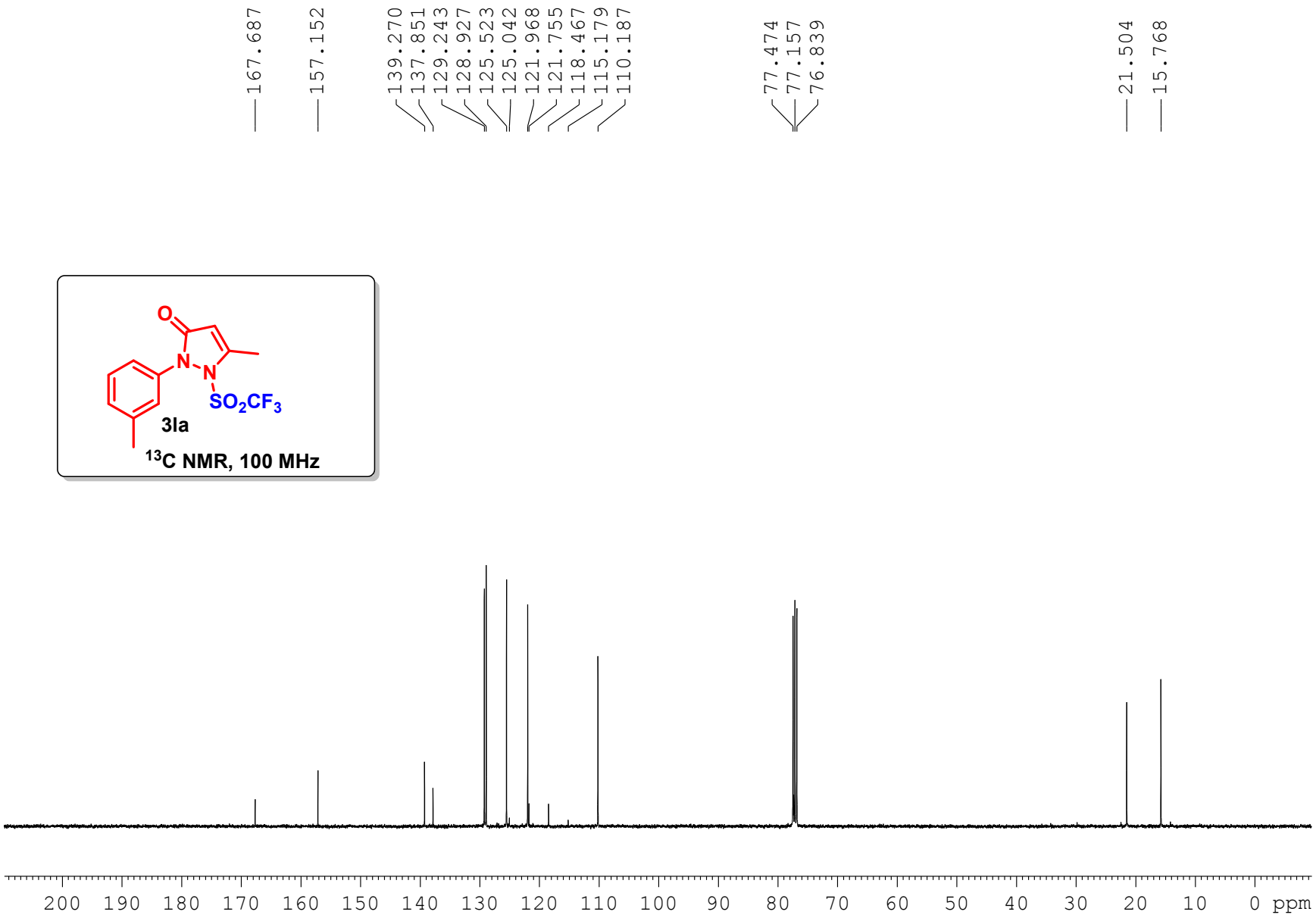
^{19}F NMR, 376 MHz

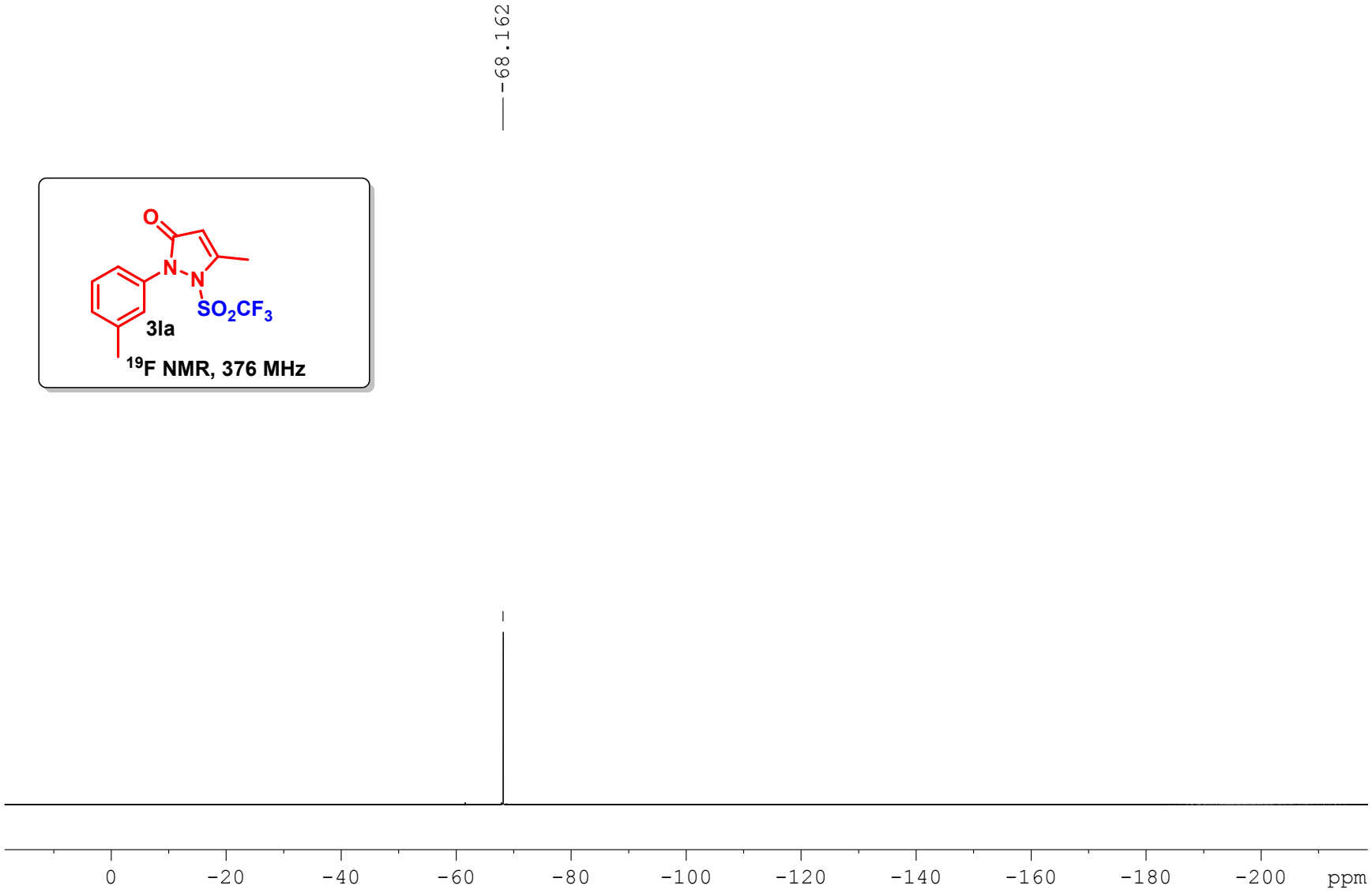

7.301
7.291
7.274
7.265
7.245
7.234
7.223
7.139
7.120
5.923
2.543
2.540
2.290
0.000
O
N
N
SO2CF3
3ka
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.042
1.133
0.945
1.000
3.044
2.872

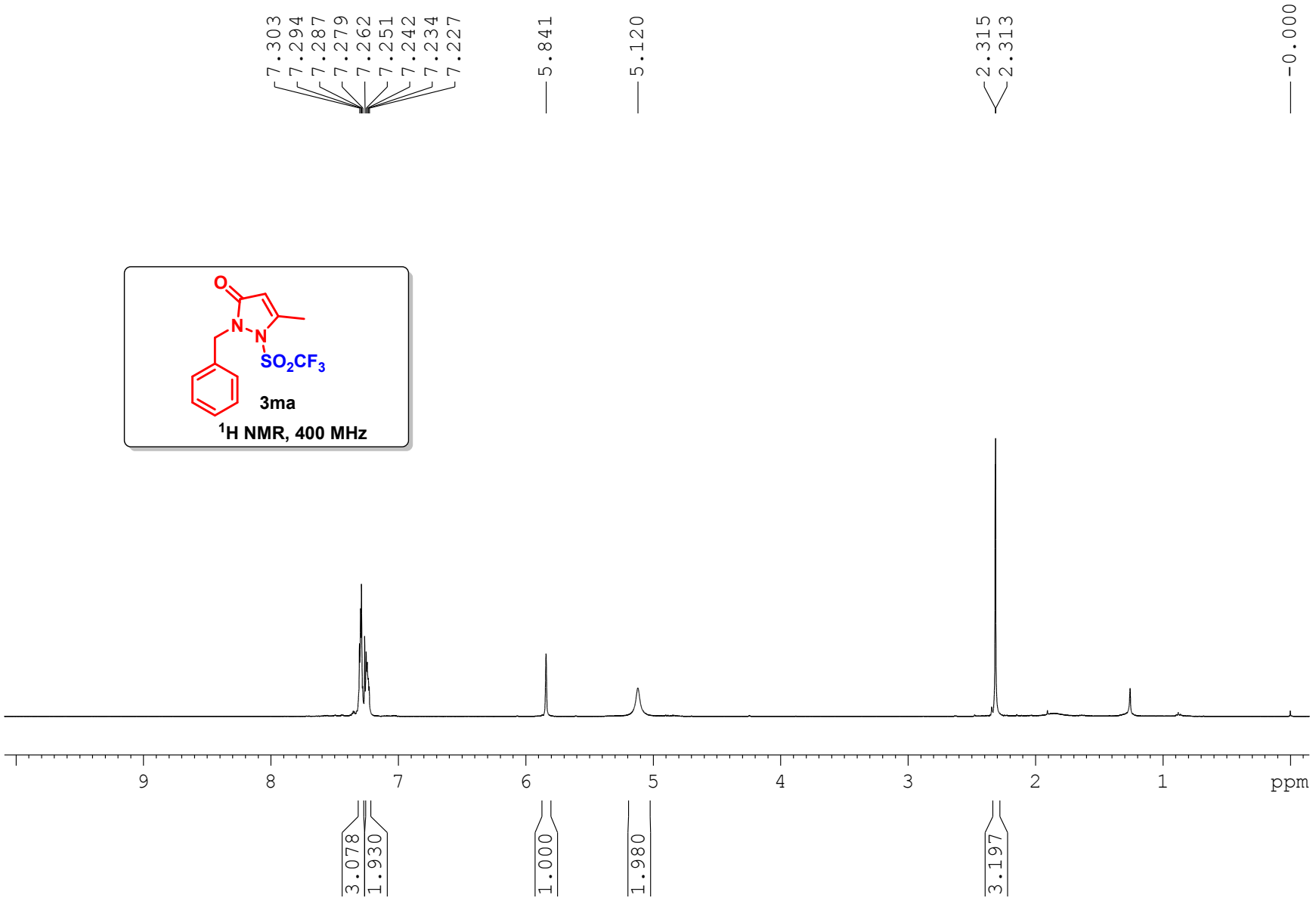

167.755
156.827
137.326
136.237
131.534
129.351
126.754
126.524
125.077
121.793
118.509
115.224
110.141
77.472
77.155
76.837
17.688
15.696
O
N
N
SO2CF3
3ka
13C NMR, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

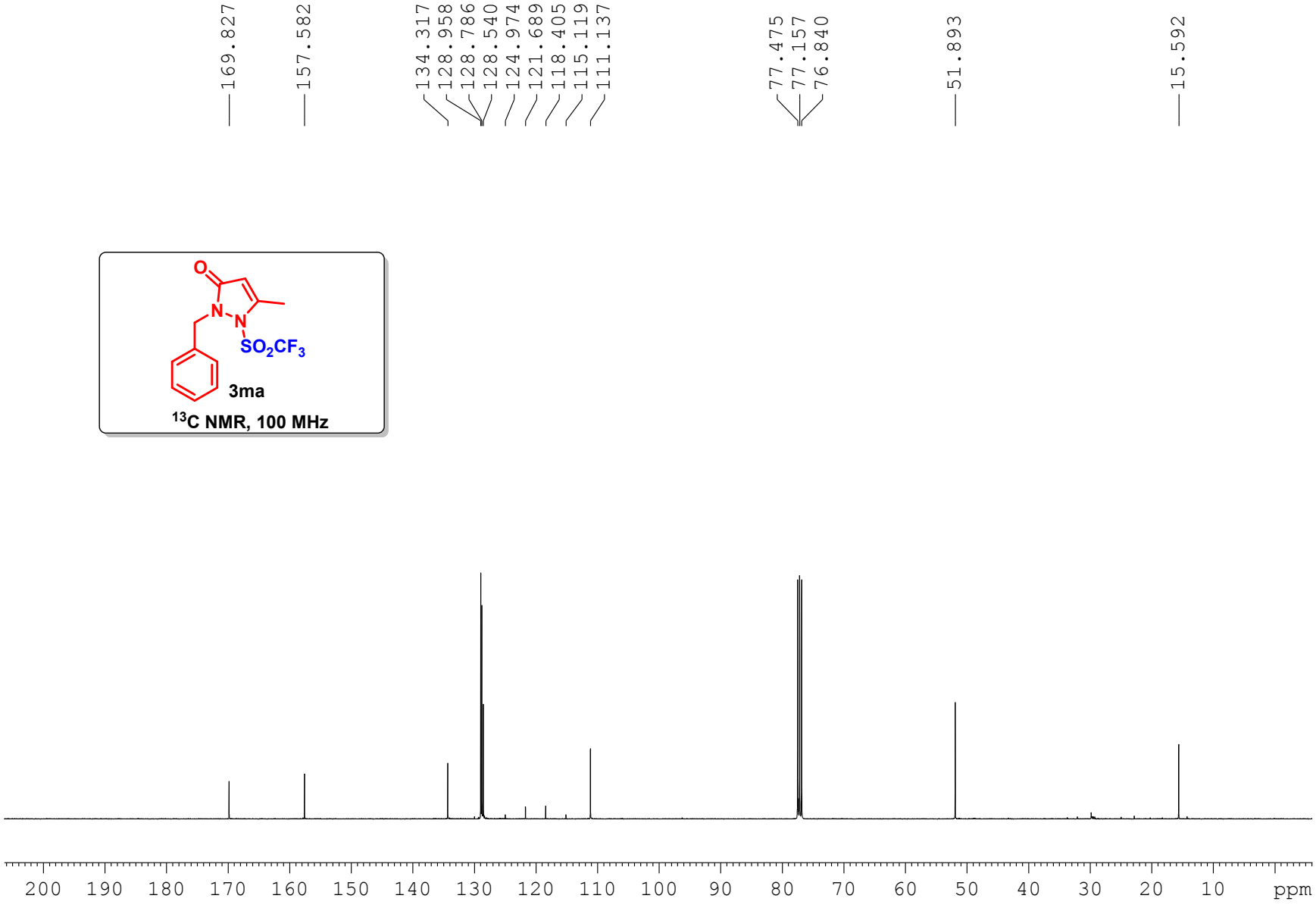

-68.262
O
N
N
SO2CF3
3ka
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

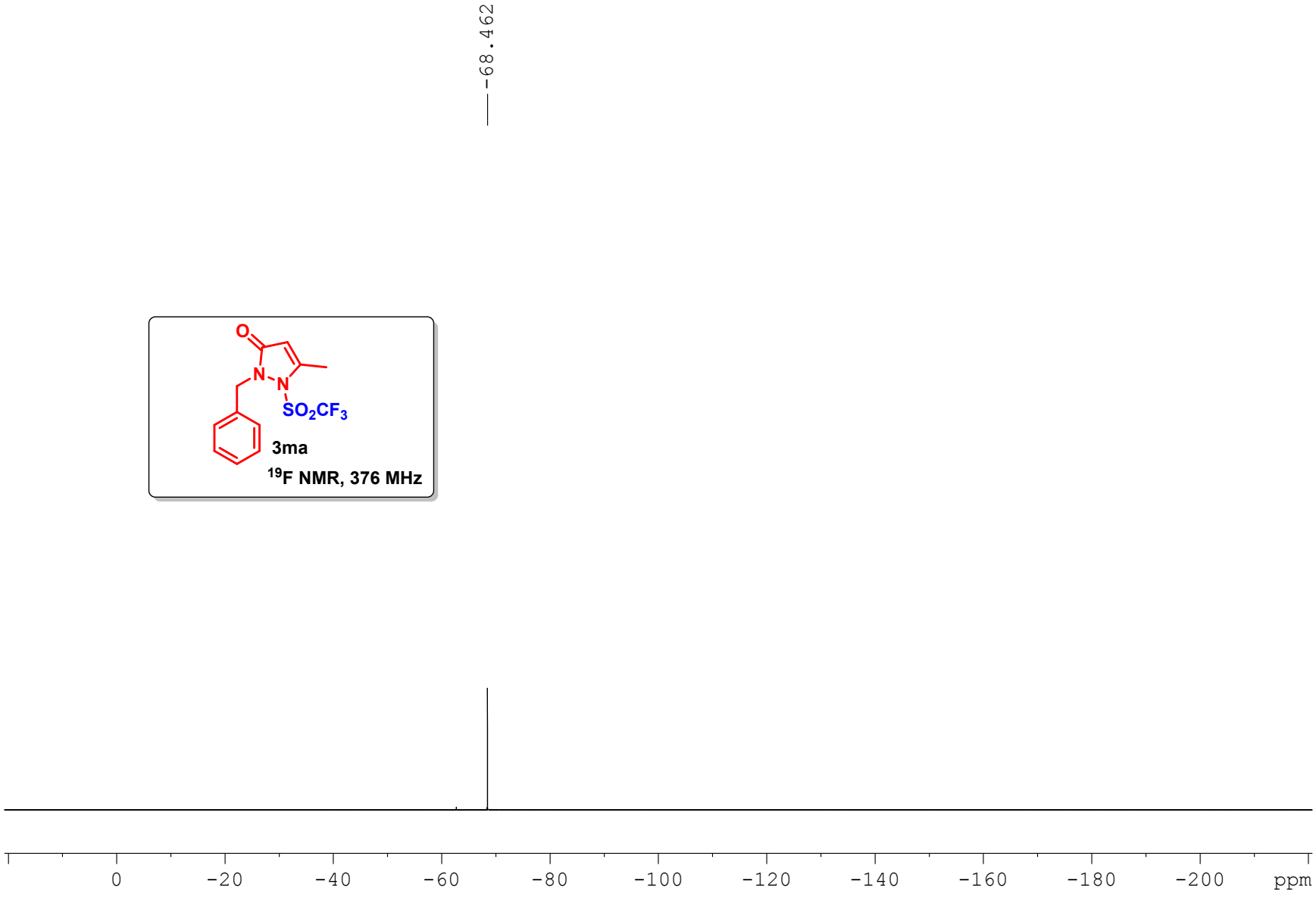

7.341
7.322
7.302
7.256
7.174
7.155
7.154
7.123
7.103
5.899
2.548
2.546
2.393
-0.001
O
N
N
SO2CF3
3Ia
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.114
2.965
1.000
3.067
3.109

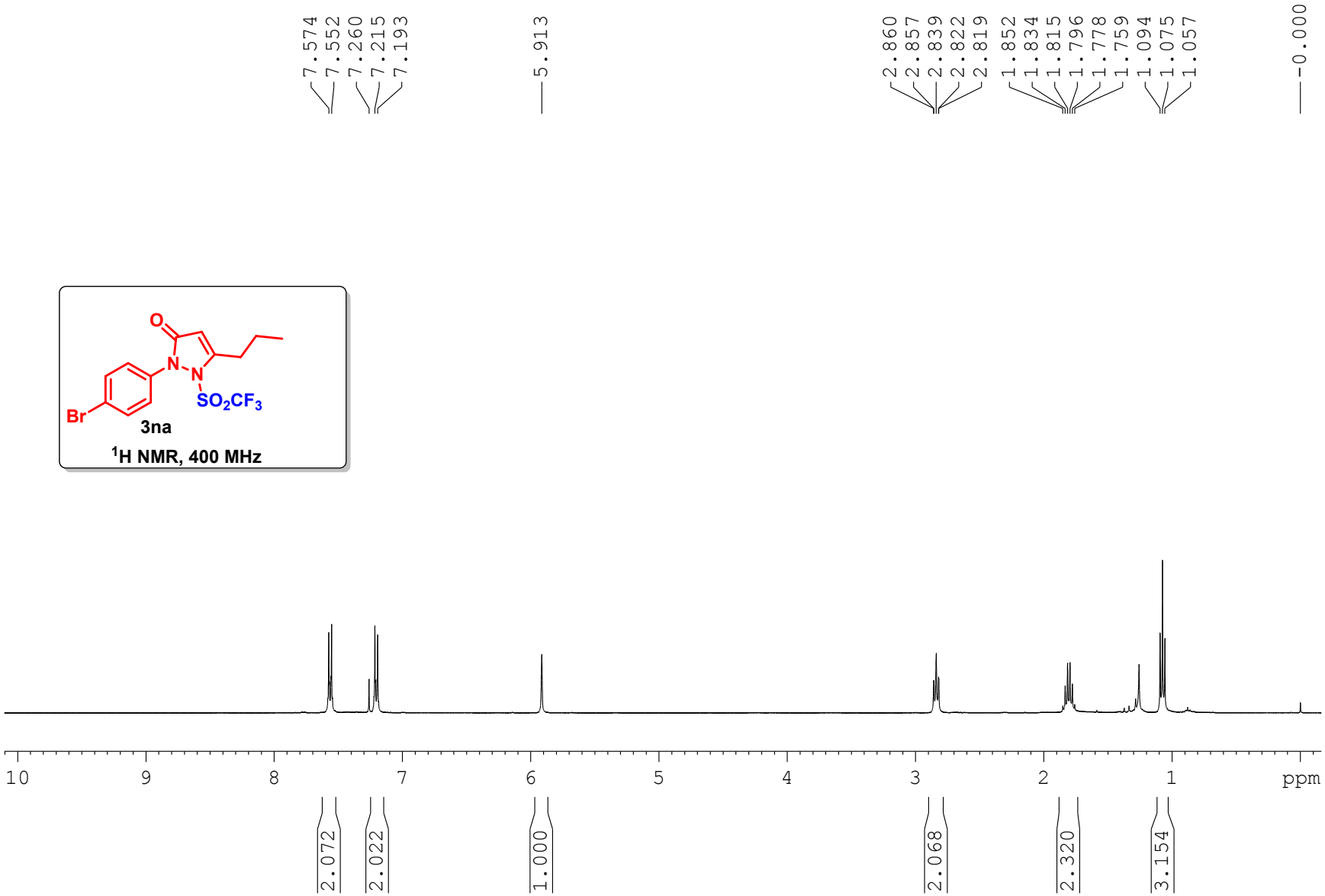

167.687
157.152
139.270
137.851
129.243
128.927
125.523
125.042
121.968
121.755
118.467
115.179
110.187
77.474
77.157
76.839
21.504
15.768
O
N
N
SO2CF3
3la
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-68.162
O
N
N
SO2CF3
3la
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

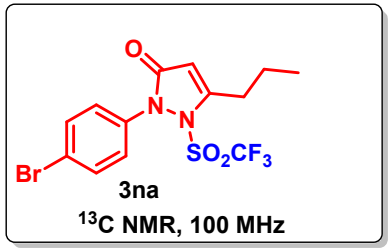

7.303
7.294
7.287
7.279
7.262
7.251
7.242
7.234
7.227
5.841
5.120
2.315
2.313
0.000
3ma
1H NMR, 400 MHz
9
8
7
6
5
4
3
2
1
ppm
3.078
1.930
1.000
1.980
3.197


169.827
157.582
134.317
128.958
128.786
128.540
124.974
121.689
118.405
115.119
111.137
77.475
77.157
76.840
51.893
15.592
O
N
N
SO2CF3
3ma
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-68.462
O
N
N
SO2CF3
3ma
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

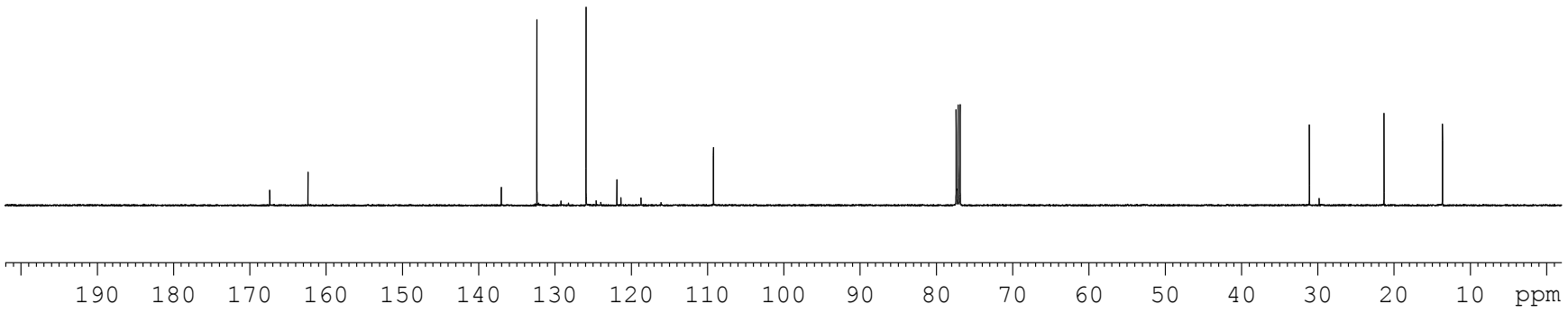

7.574
7.552
7.260
7.215
7.193
5.913
2.860
2.857
2.839
2.822
2.819
1.852
1.834
1.815
1.796
1.778
1.759
1.094
1.075
1.057
0.000
O
N
N
SO2CF3
Br
3na
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.072
2.022
1.000
2.068
2.320
3.154

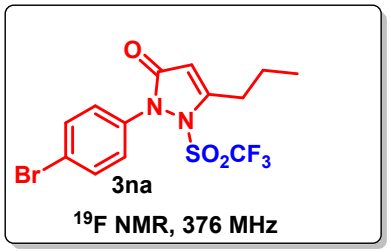
167.364
162.352
137.012
132.345
125.902
123.973
121.853
121.338
118.704
116.070
109.200
77.410
77.157
76.902
31.107
21.324
13.651



3na

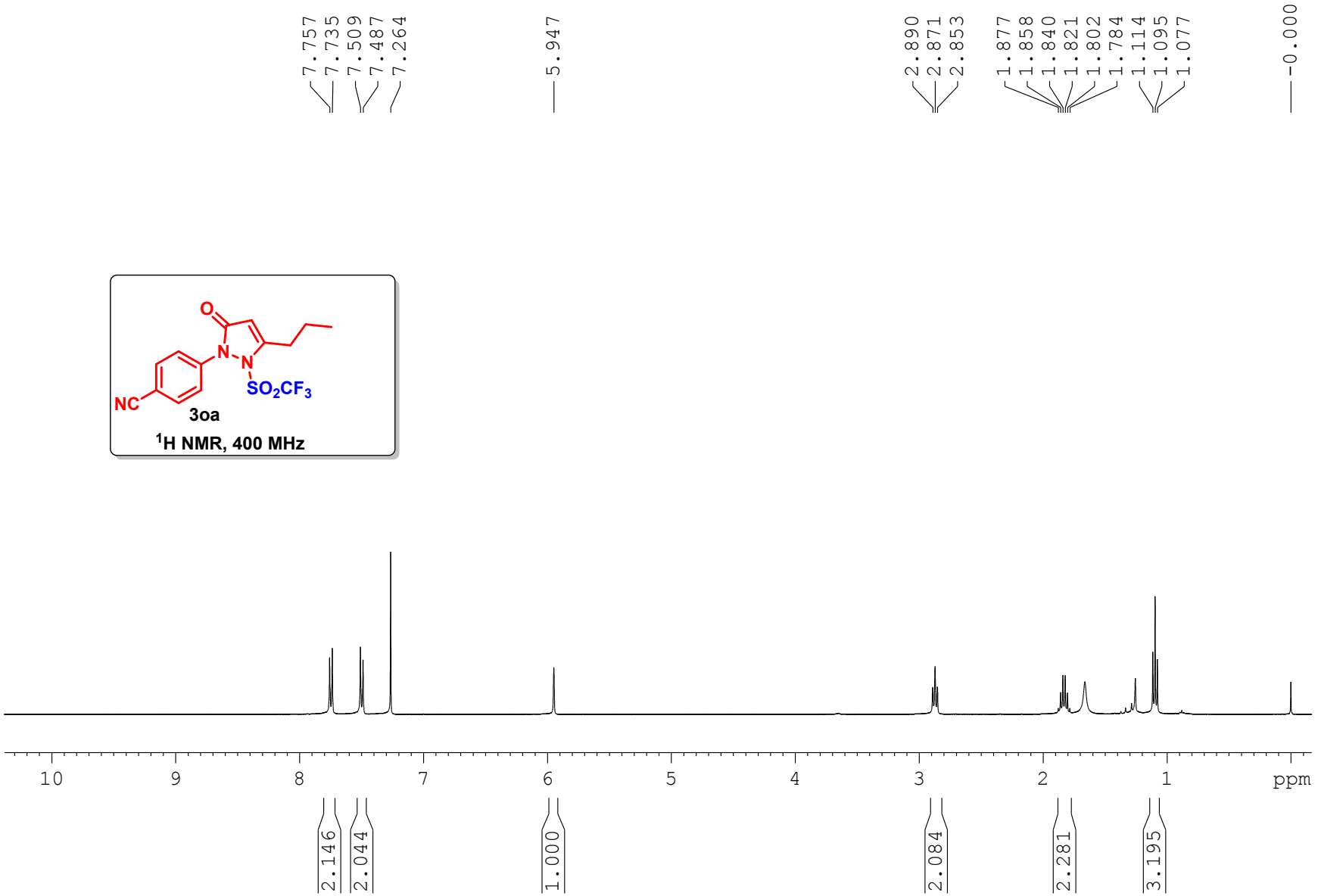
^{13}C NMR, 100 MHz

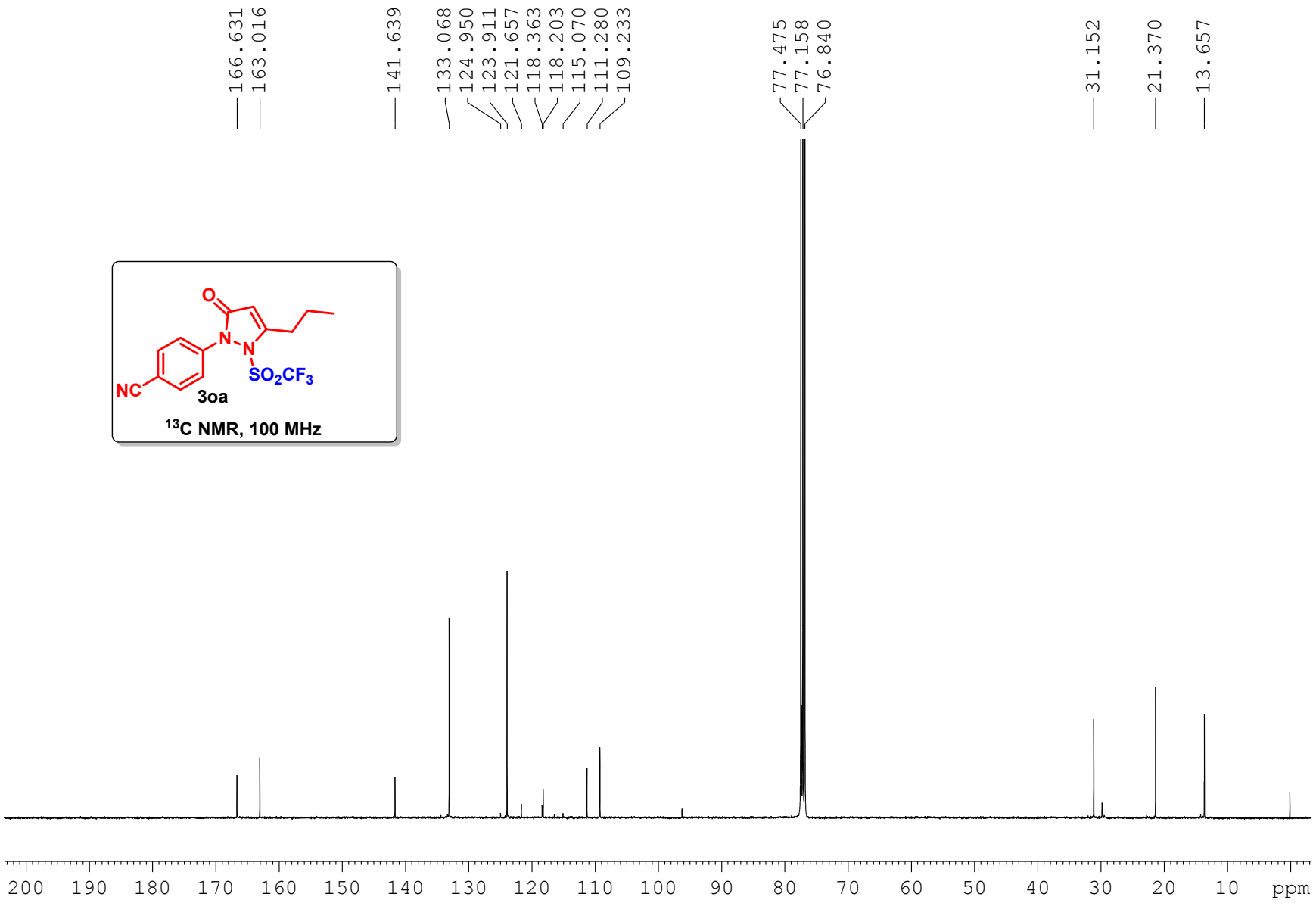


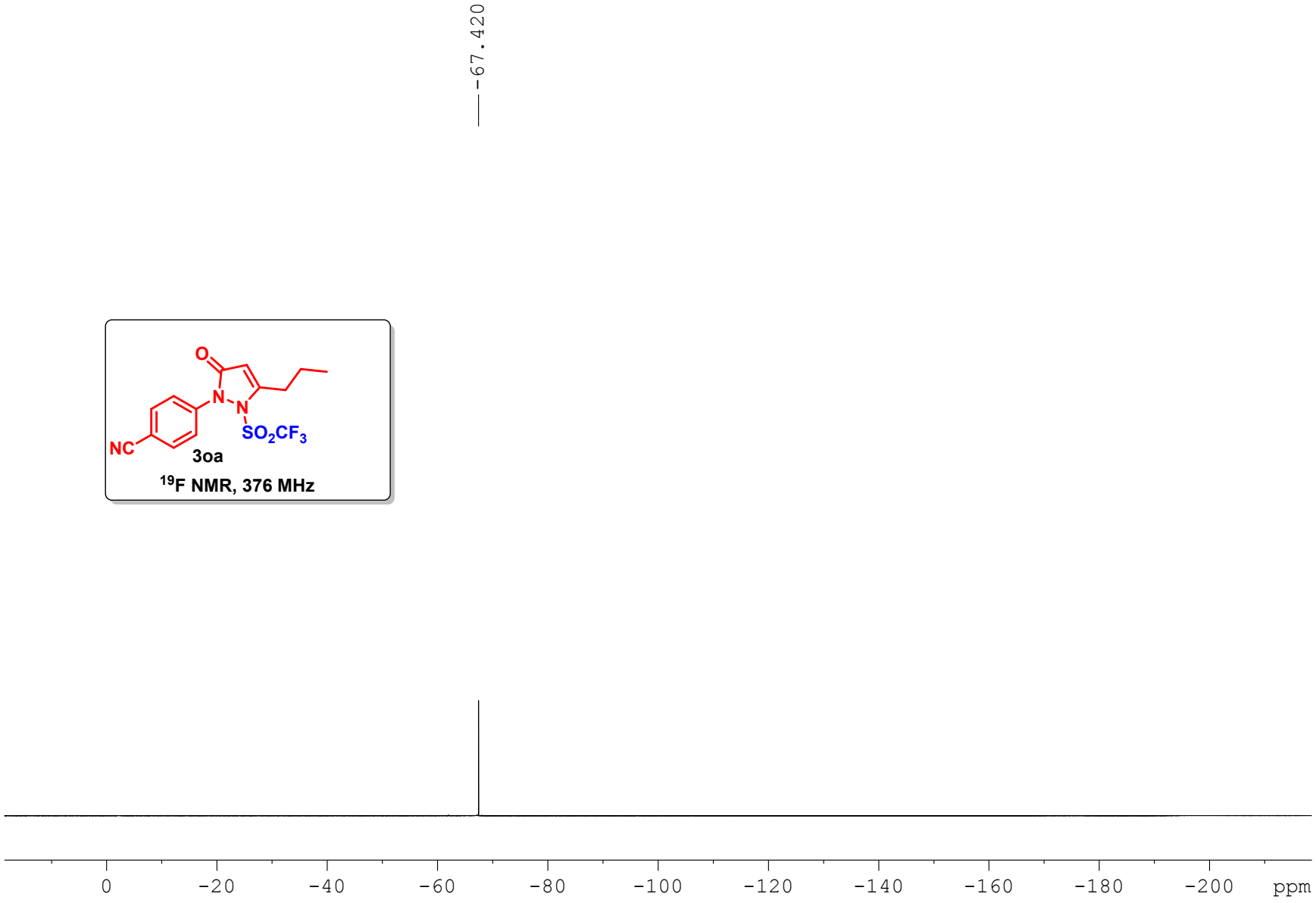


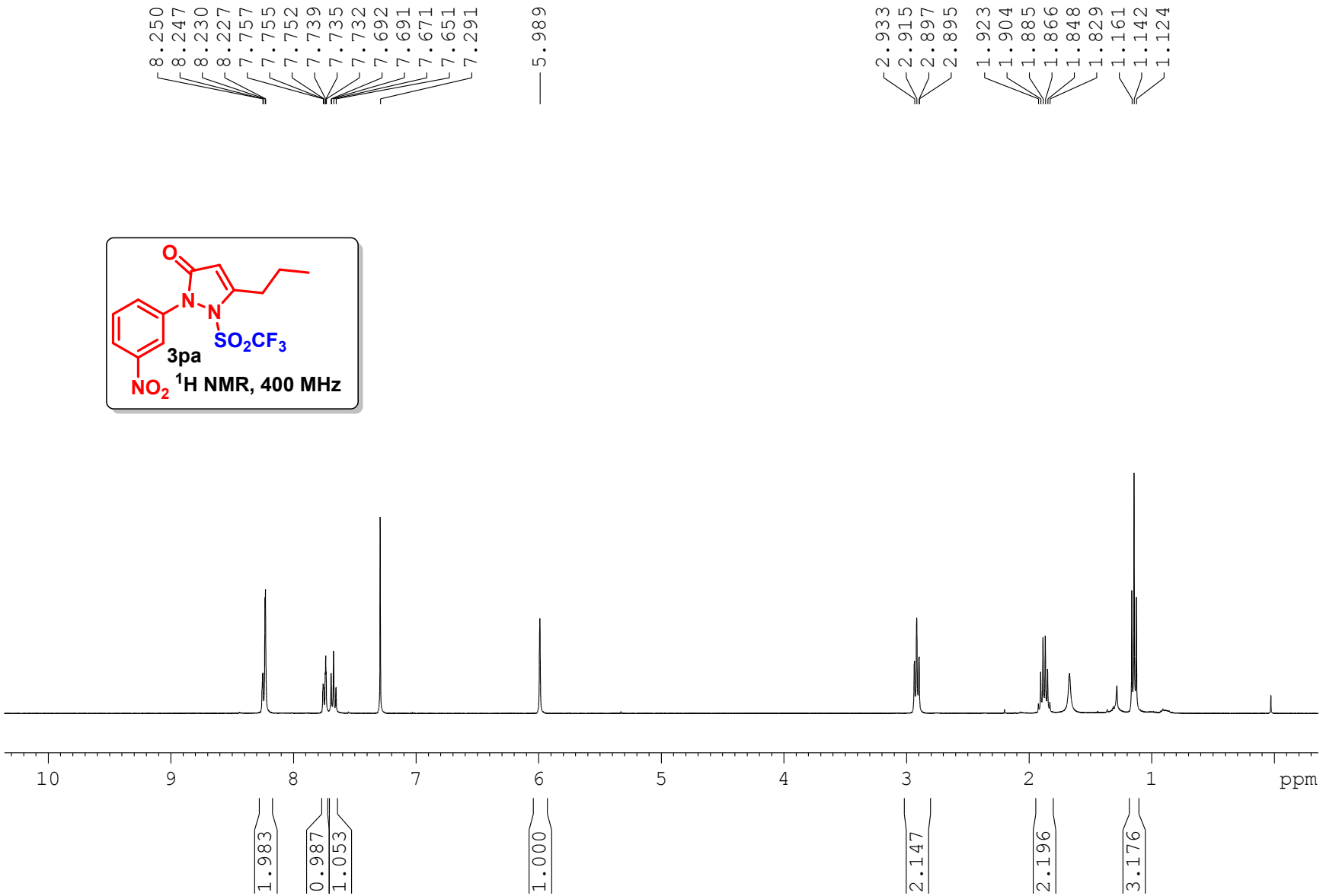
3na

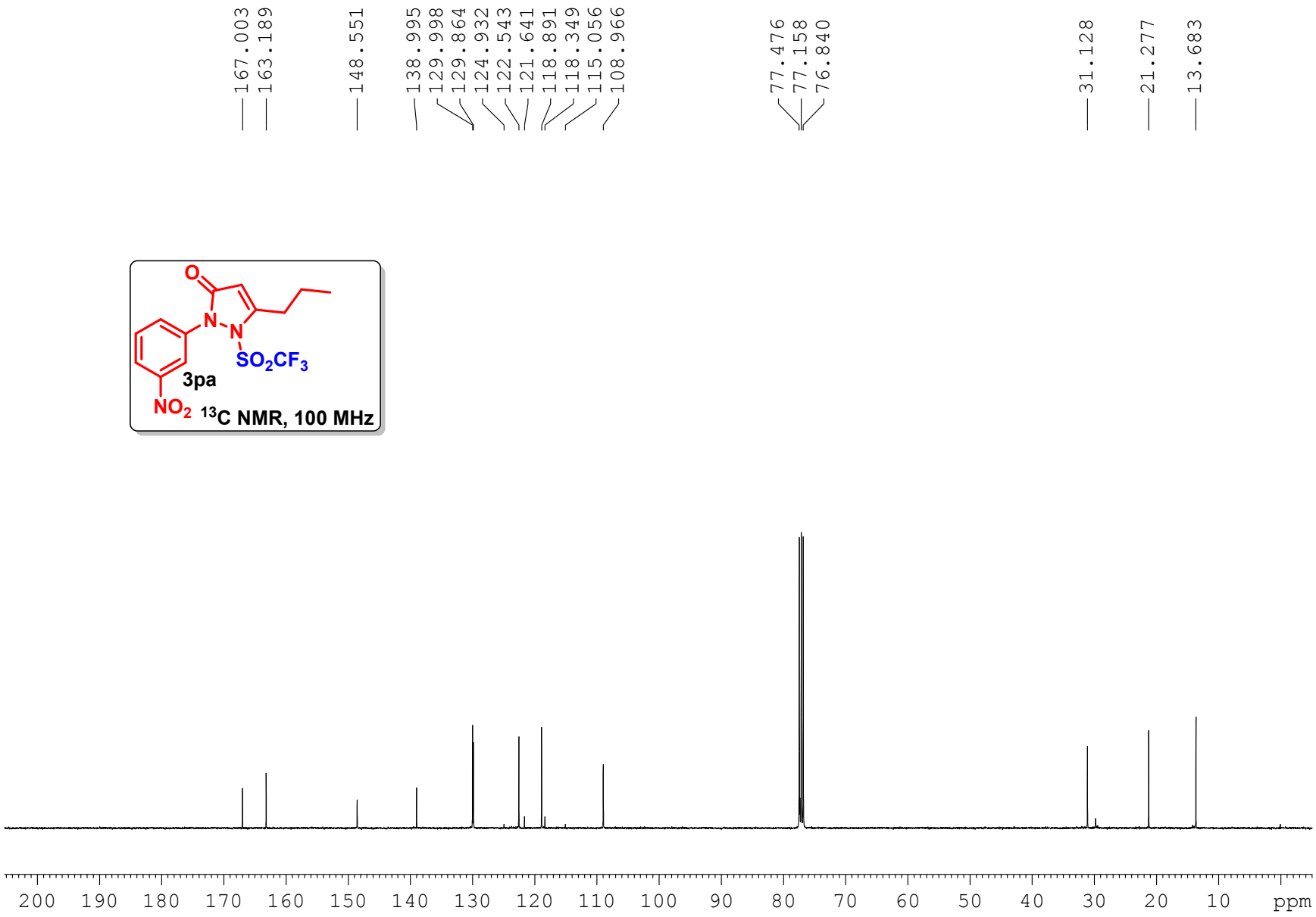
^{19}F NMR, 376 MHz

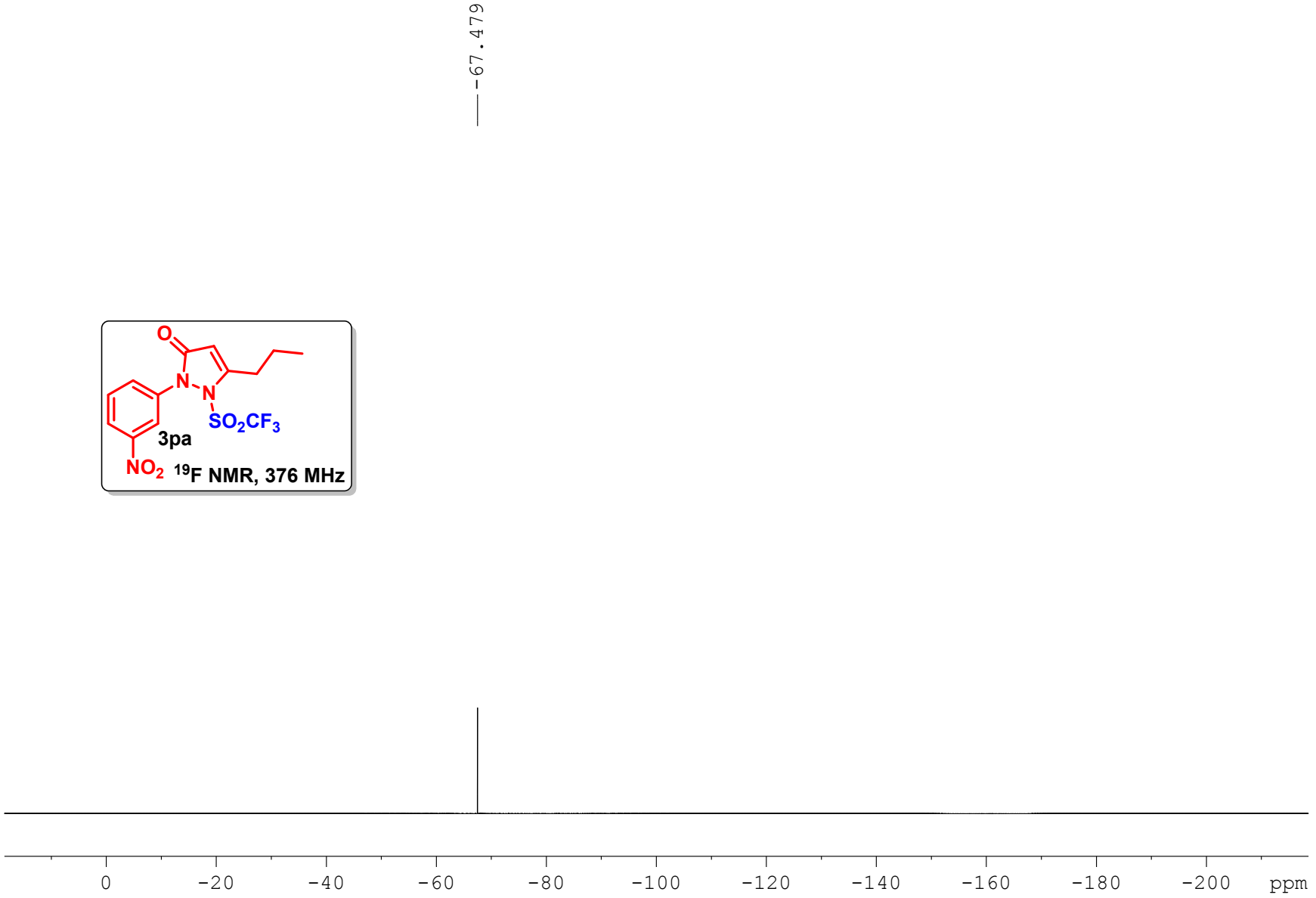

7.757
7.735
7.509
7.487
7.264
5.947
2.890
2.871
2.853
1.877
1.858
1.840
1.821
1.802
1.784
1.114
1.095
1.077
0.000
O
N
N
SO2CF3
NC
3oa
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.146
2.044
1.000
2.084
2.281
3.195

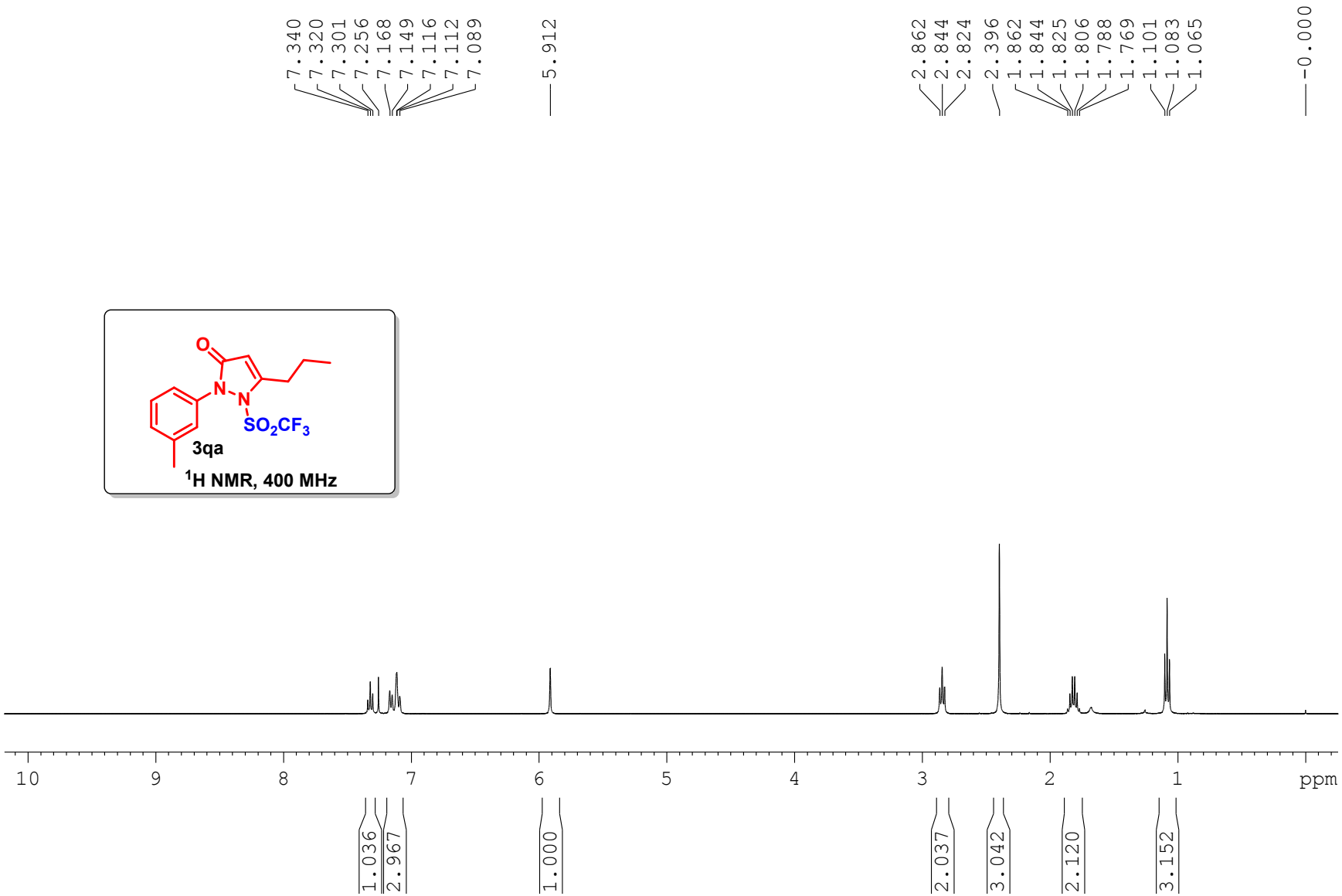

166.631
163.016
141.639
133.068
124.950
123.911
121.657
118.363
118.203
115.070
111.280
109.233
77.475
77.158
76.840
31.152
21.370
13.657
O
N
N
SO2CF3
NC
3oa
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

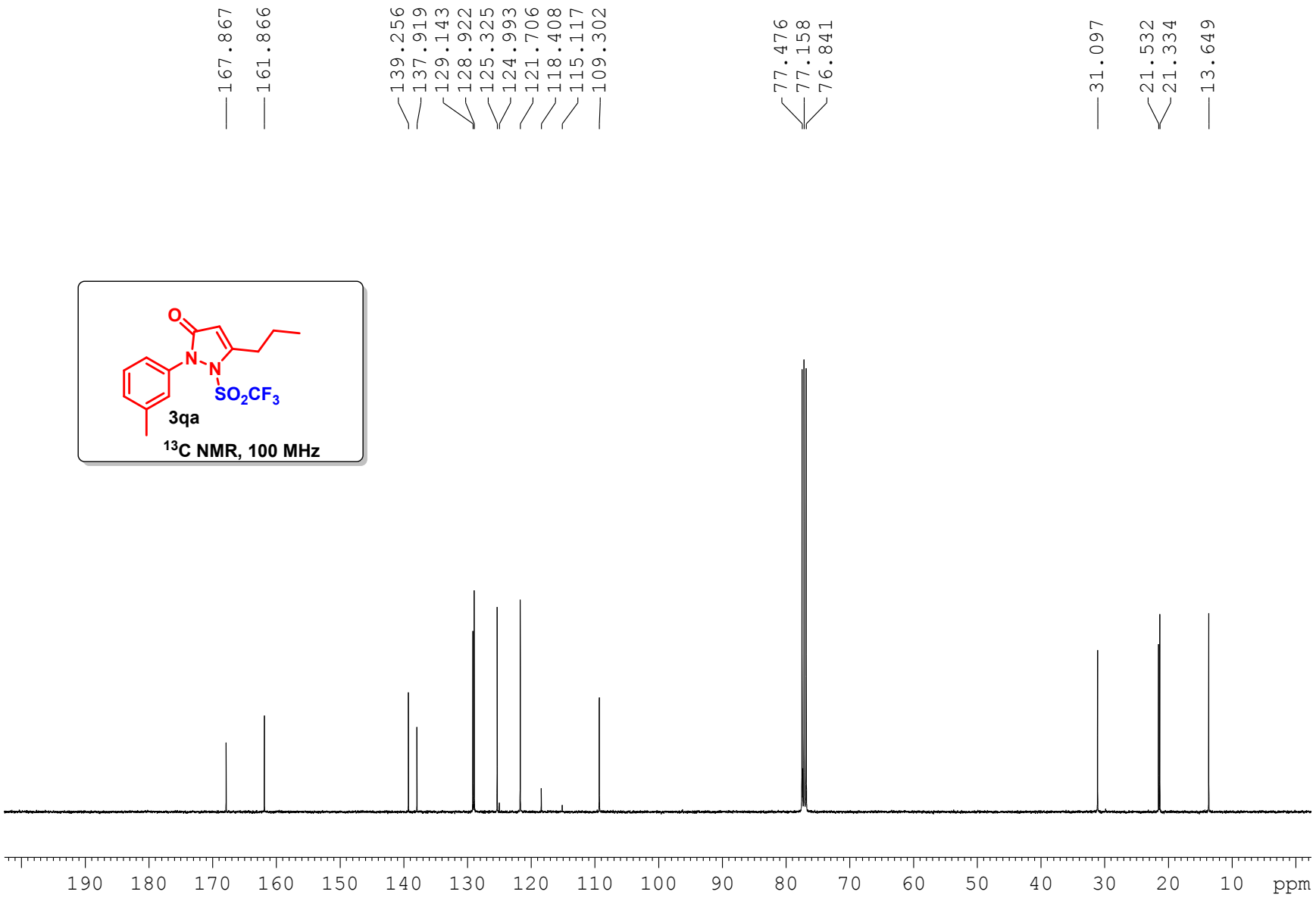

-67.420
O
N
N
SO2CF3
NC
3oa
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

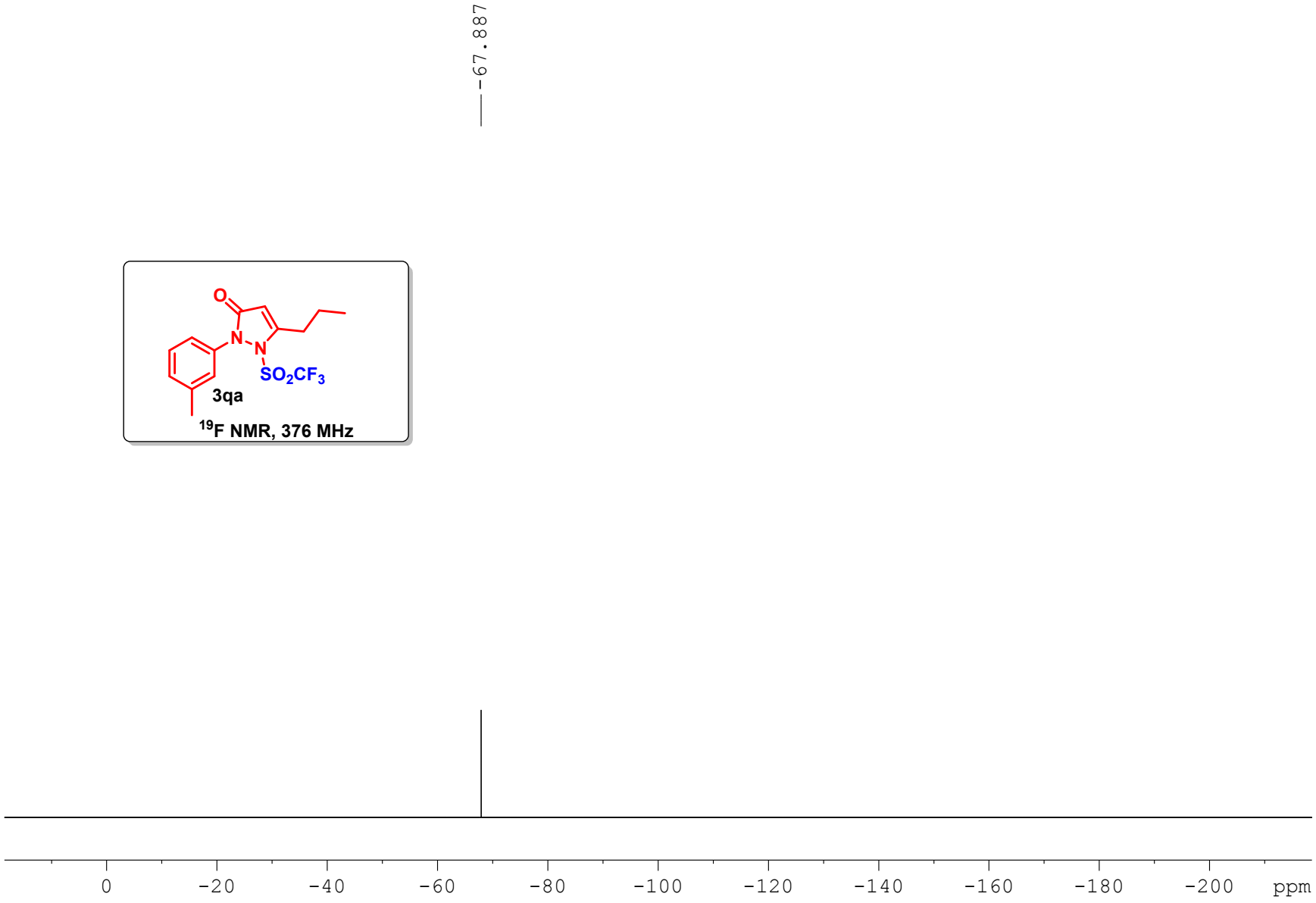

8.250
8.247
8.230
8.227
7.757
7.755
7.752
7.739
7.735
7.732
7.692
7.691
7.671
7.651
7.291
5.989
2.933
2.915
2.897
2.895
1.923
1.904
1.885
1.866
1.848
1.829
1.161
1.142
1.124
O
N
N
SO2CF3
3pa
NO2
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.983
0.987
1.053
1.000
2.147
2.196
3.176


167.003
163.189
148.551
138.995
129.998
129.864
124.932
122.543
121.641
118.891
118.349
115.056
108.966
77.476
77.158
76.840
31.128
21.277
13.683
O
N
N
SO2CF3
3pa
NO2
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-67.479
3pa
SO_2CF_3
NO_2
^{19}F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


7.340
7.320
7.301
7.256
7.168
7.149
7.116
7.112
7.089
5.912
2.862
2.844
2.824
2.396
1.862
1.844
1.825
1.806
1.788
1.769
1.101
1.083
1.065
0.000
O
N
N
SO2CF3
3qa
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.036
2.967
1.000
2.037
3.042
2.120
3.152


167.867
161.866
139.256
137.919
129.143
128.922
125.325
124.993
121.706
118.408
115.117
109.302
77.476
77.158
76.841
31.097
21.532
21.334
13.649
O
N
N
SO2CF3
3qa
13C NMR, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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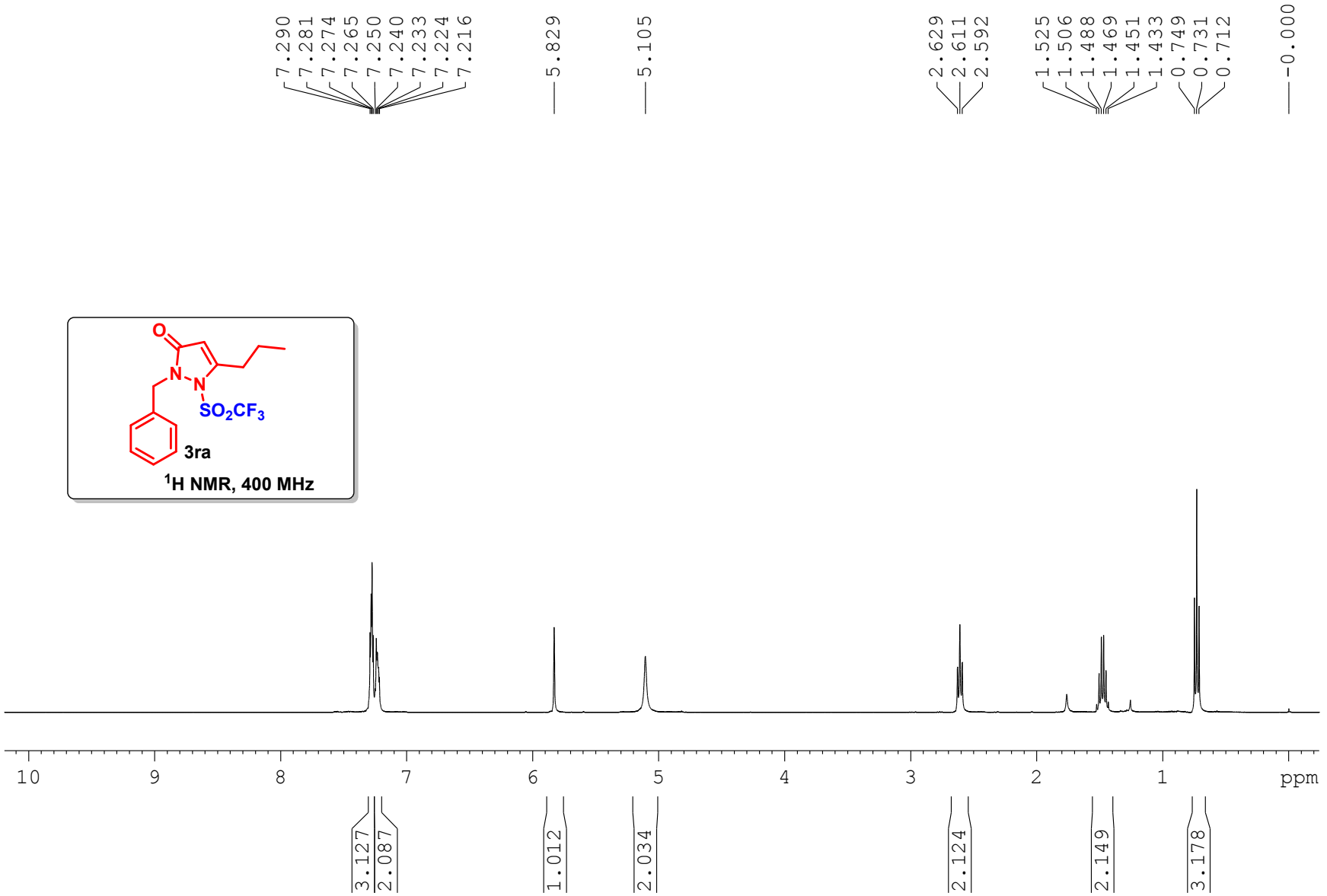
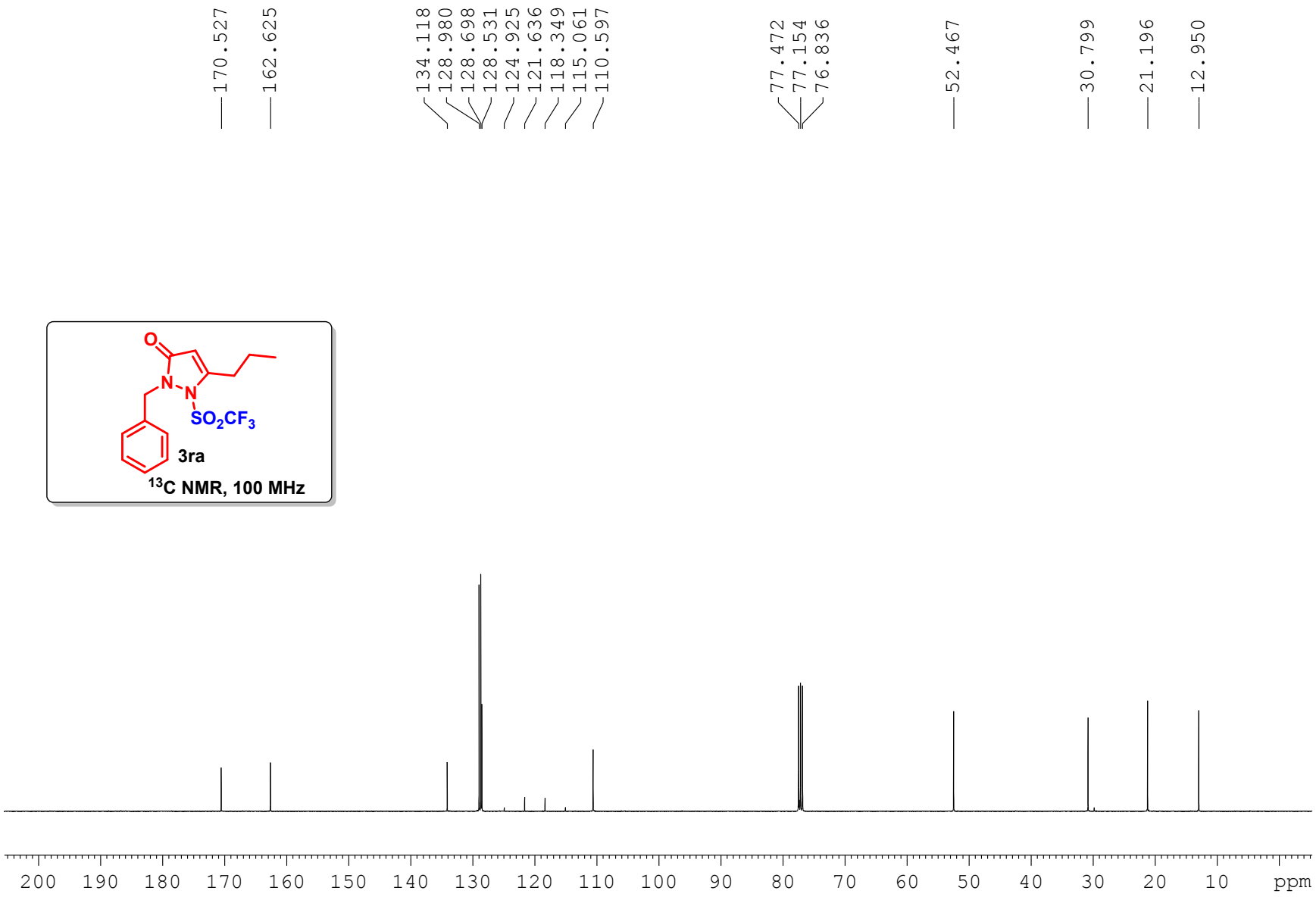
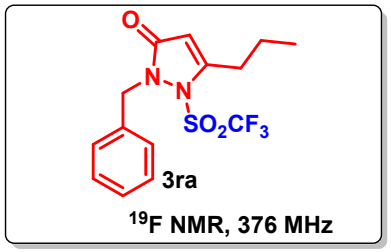
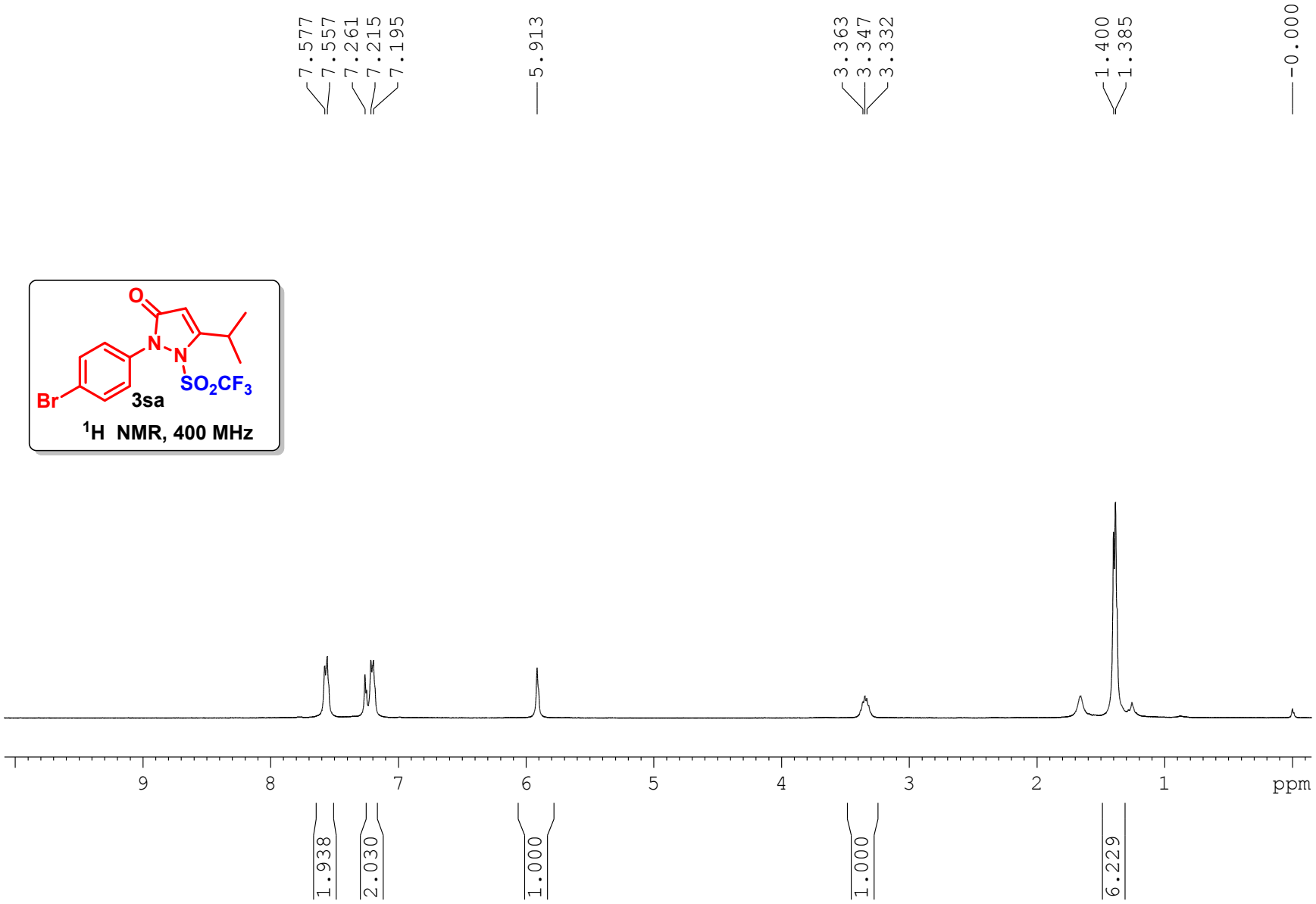
O
N
N
SO2CF3
3qa
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

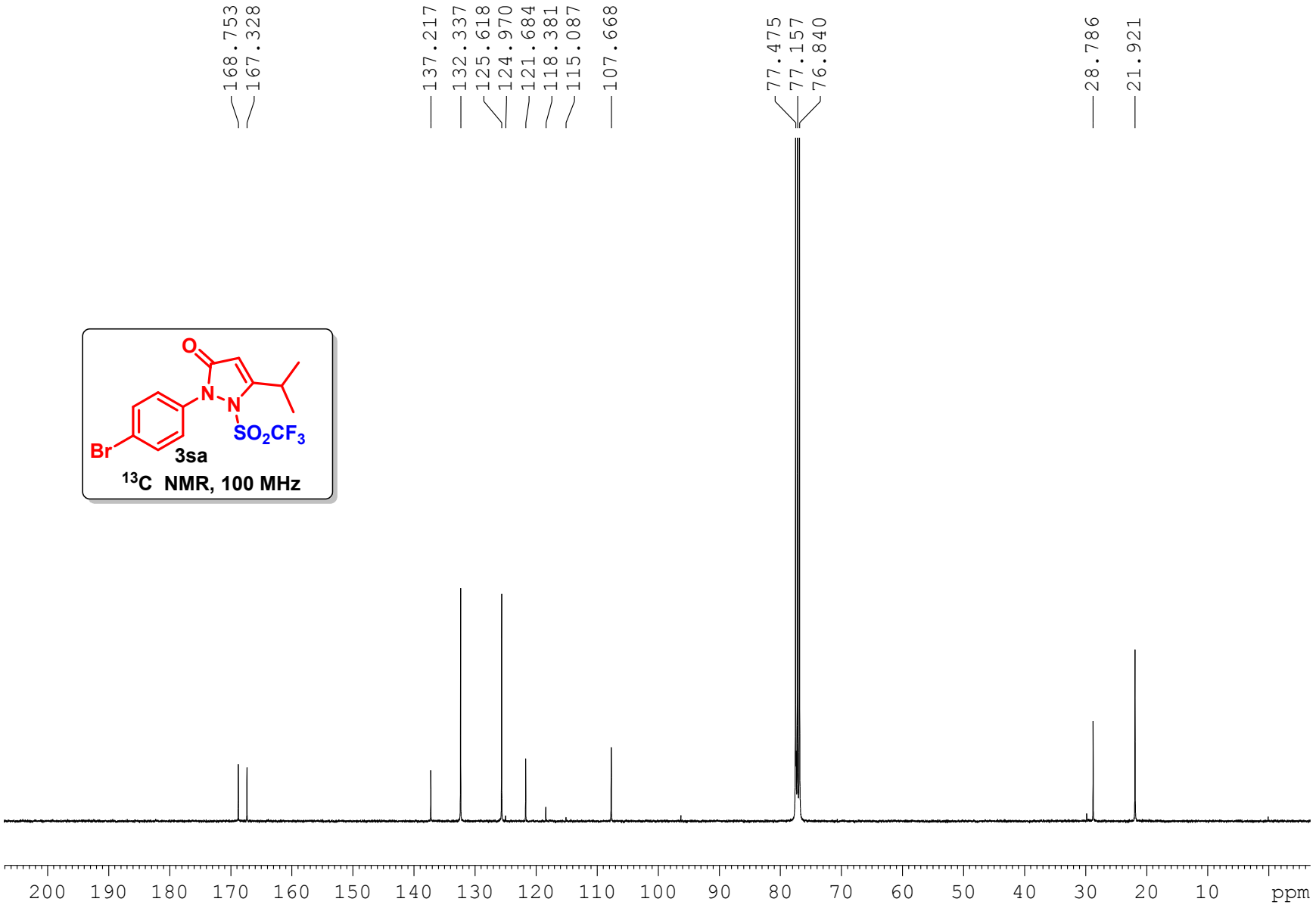

7.290
7.281
7.274
7.265
7.250
7.240
7.233
7.224
7.216
5.829
5.105
2.629
2.611
2.592
1.525
1.506
1.488
1.469
1.451
1.433
0.749
0.731
0.712
0.000
O
N
N
SO2CF3
3ra
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
3.127
2.087
1.012
2.034
2.124
2.149
3.178

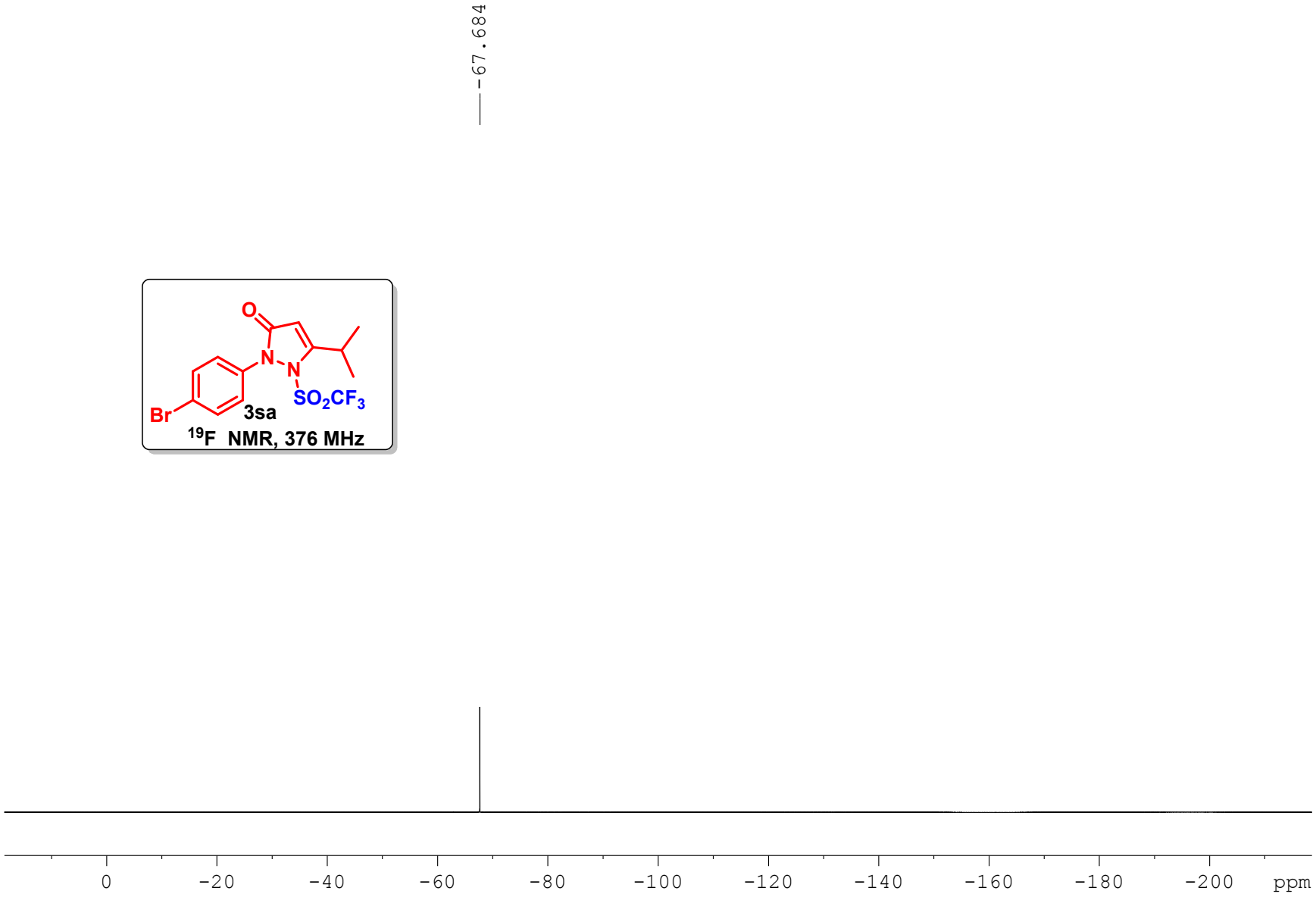

170.527
162.625
134.118
128.980
128.698
128.531
124.925
121.636
118.349
115.061
110.597
77.472
77.154
76.836
52.467
30.799
21.196
12.950
O
N
N
SO2CF3
3ra
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

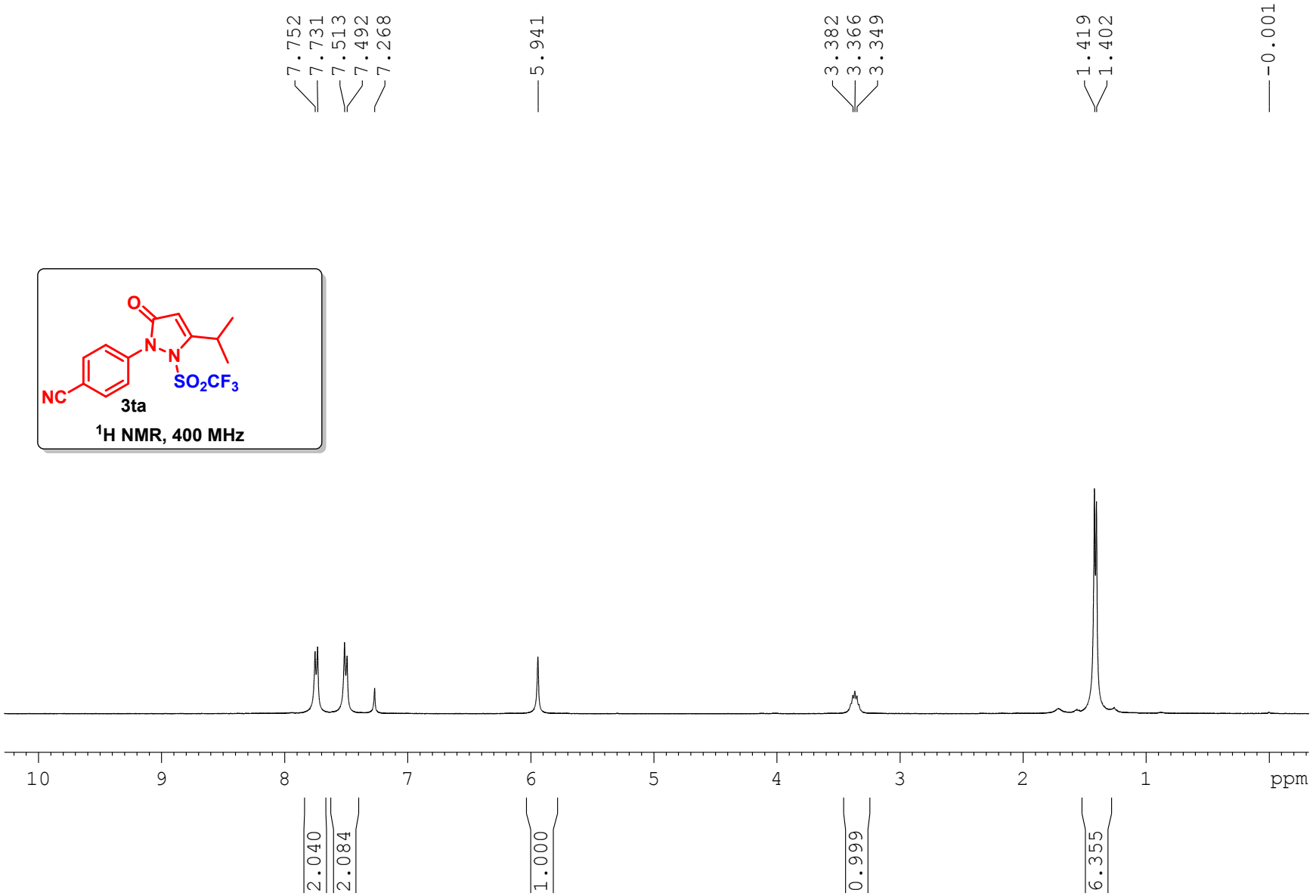

O
N
N
SO2CF3
3ra
19F NMR, 376 MHz

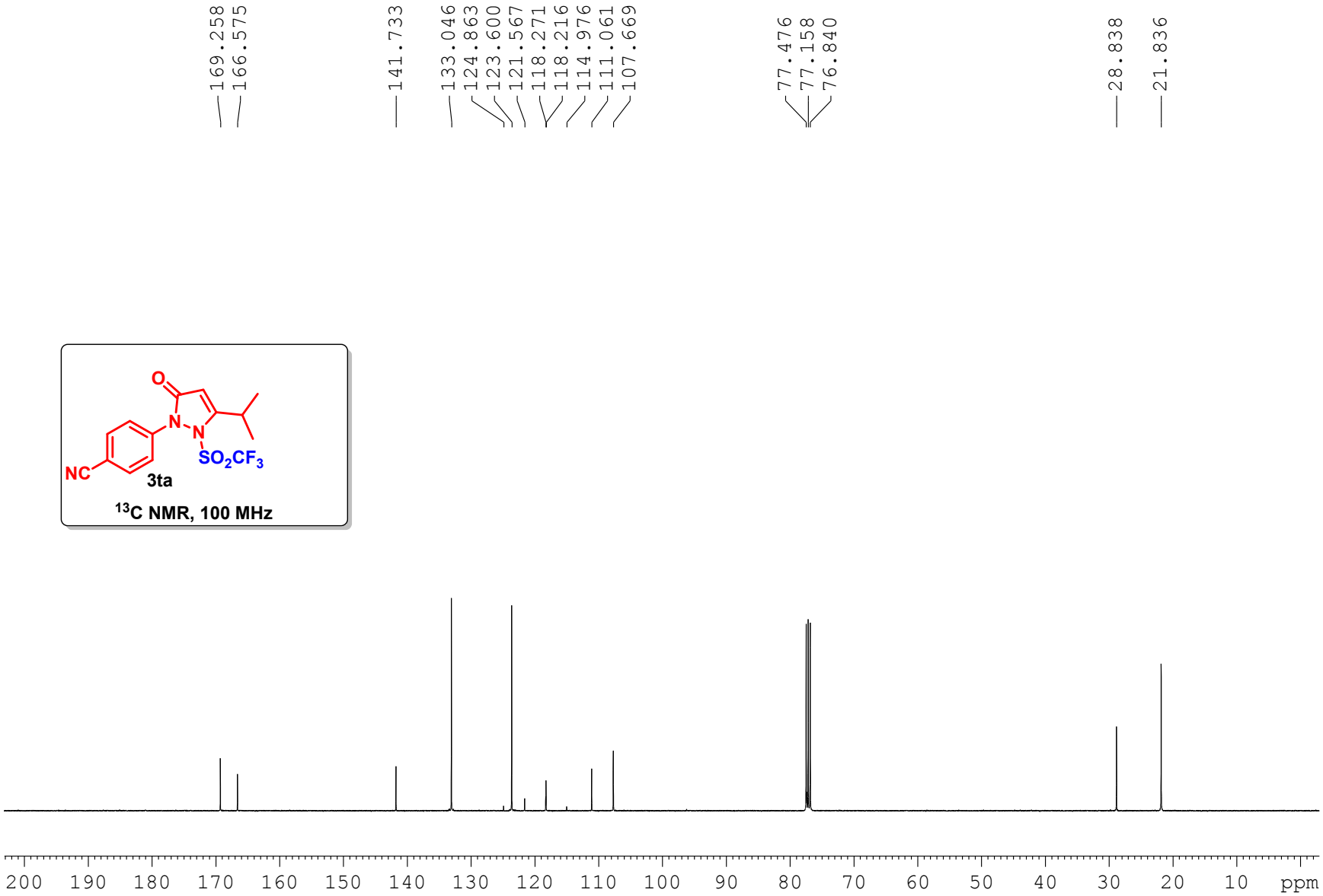
-68.244
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

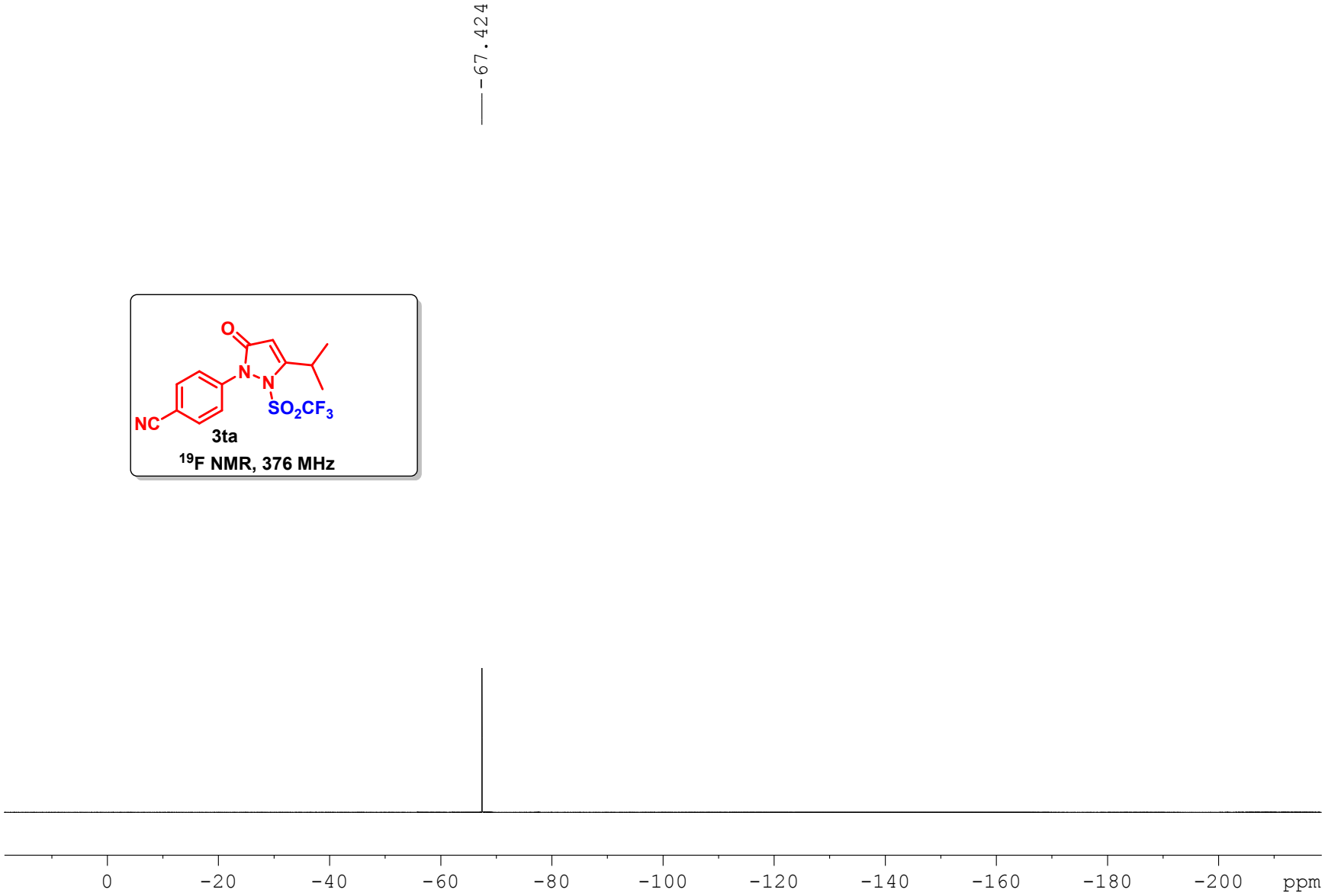

7.577
7.557
7.261
7.215
7.195
5.913
3.363
3.347
3.332
1.400
1.385
0.000
O
N
N
SO2CF3
Br
3sa
1H NMR, 400 MHz
9
8
7
6
5
4
3
2
1
ppm
1.938
2.030
1.000
1.000
6.229

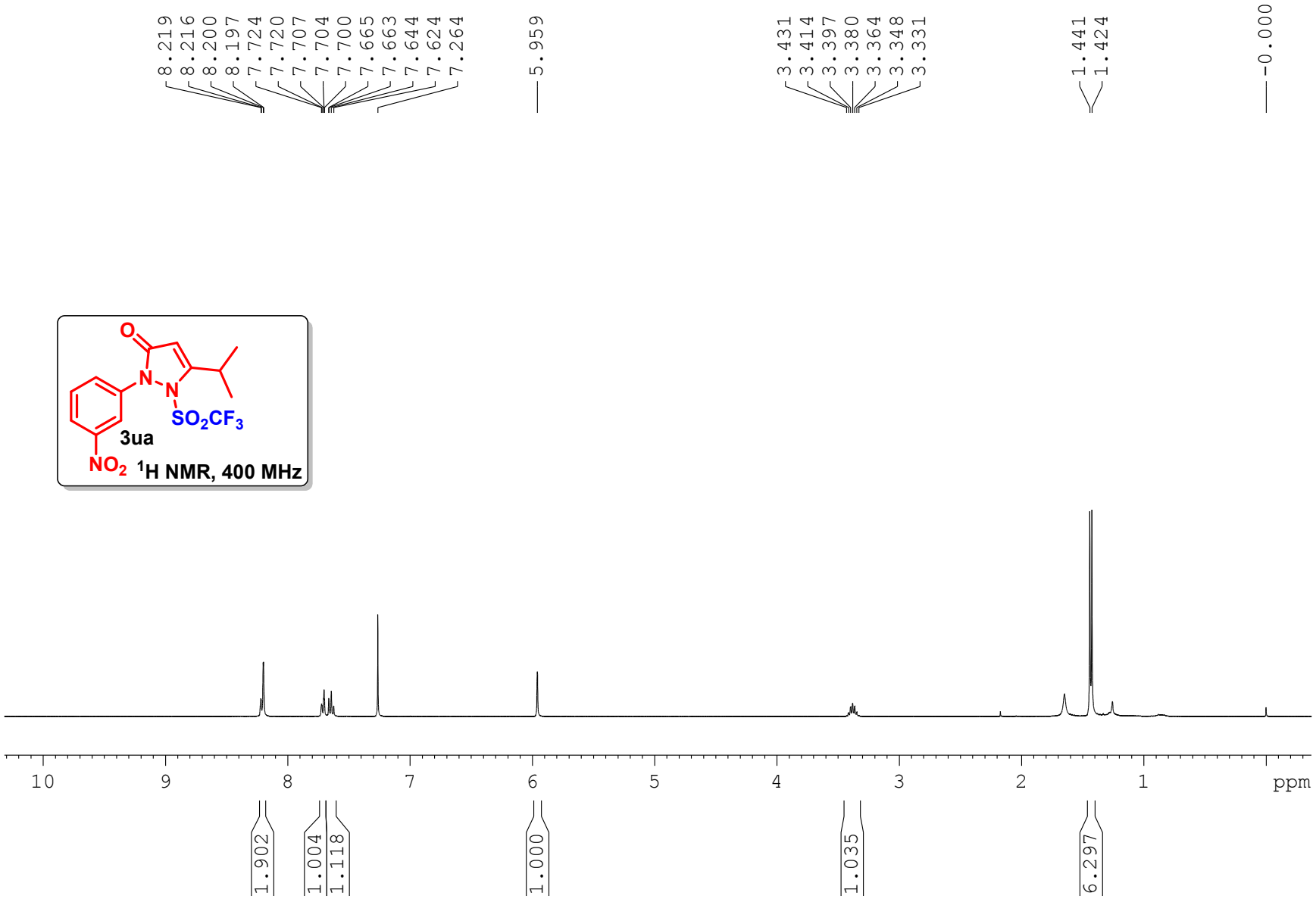

168.753
167.328
137.217
132.337
125.618
124.970
121.684
118.381
115.087
107.668
77.475
77.157
76.840
28.786
21.921
O
N
N
SO2CF3
Br
3sa
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

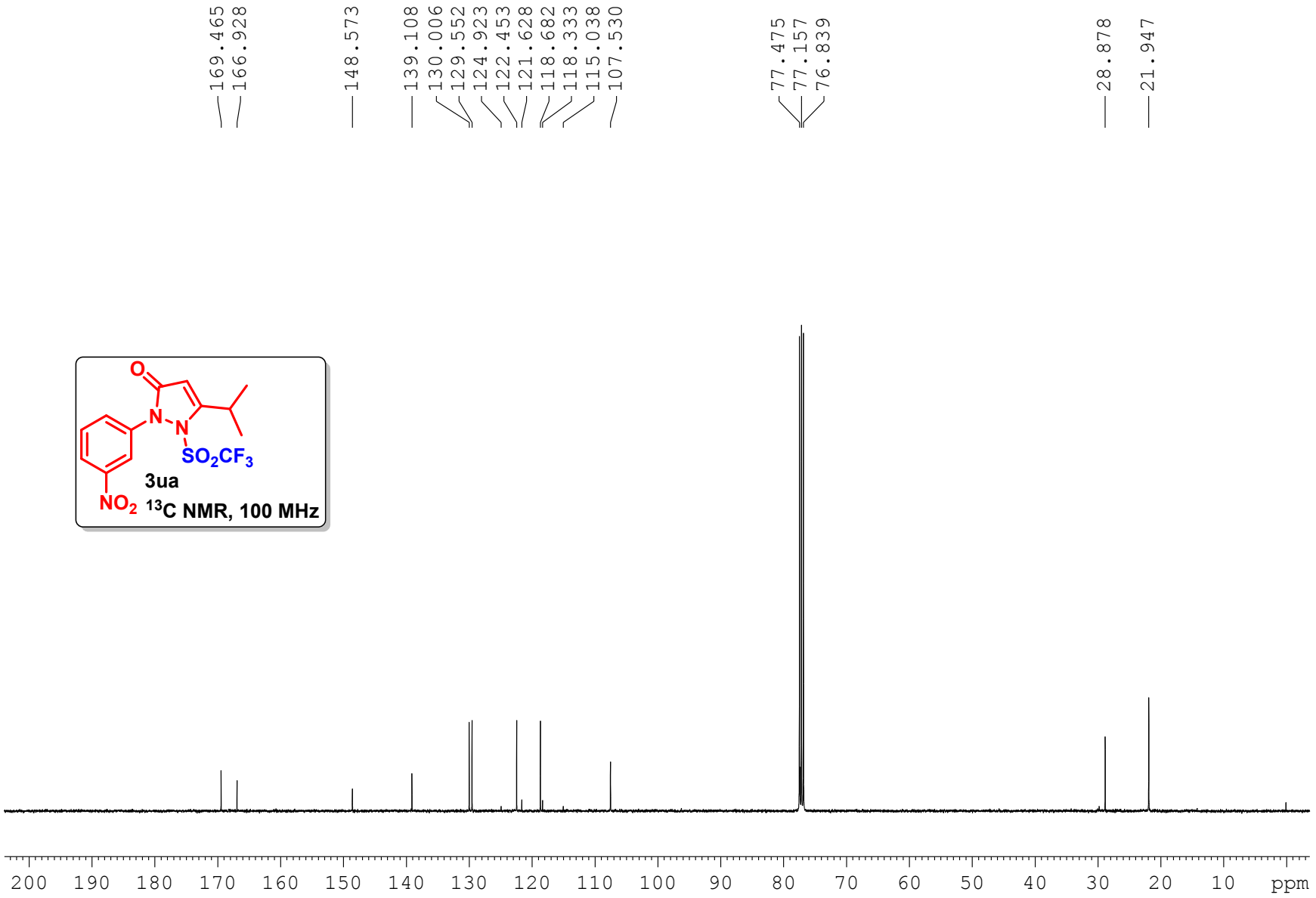

-67.684
O
N
N
SO2CF3
Br
3sa
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

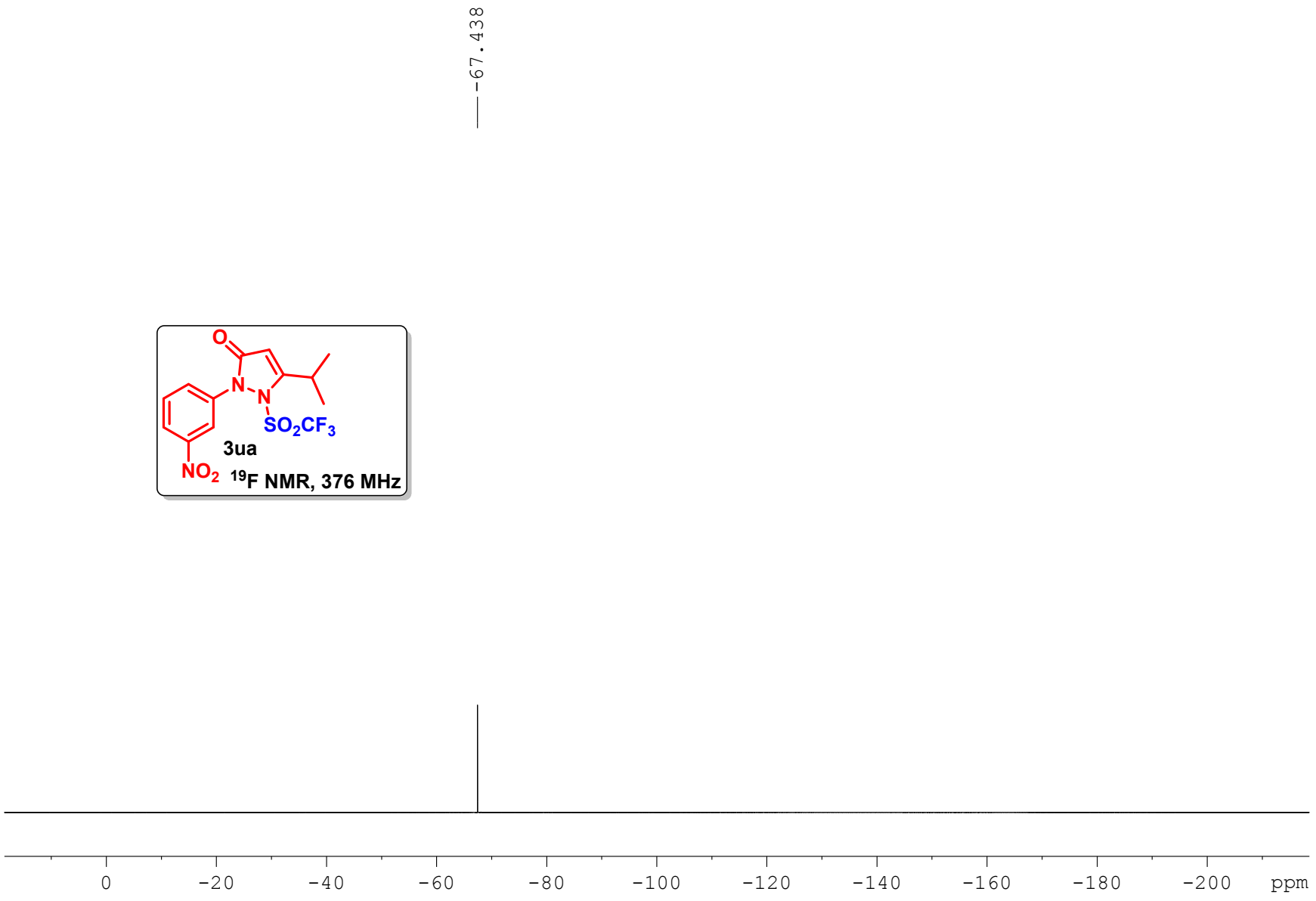

7.752
7.731
7.513
7.492
7.268
5.941
3.382
3.366
3.349
1.419
1.402
-0.001
NC
SO2CF3
3ta
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.040
2.084
1.000
0.999
6.355


169.258
166.575
141.733
133.046
124.863
123.600
121.567
118.271
118.216
114.976
111.061
107.669
77.476
77.158
76.840
28.838
21.836
O
N
N
SO2CF3
NC
3ta
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-67.424
O
N
N
SO2CF3
NC
3ta
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


8.219
8.216
8.200
8.197
7.724
7.720
7.707
7.704
7.700
7.665
7.663
7.644
7.624
7.264
5.959
3.431
3.414
3.397
3.380
3.364
3.348
3.331
1.441
1.424
0.000
O
N
N
SO2CF3
3ua
NO2
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.902
1.004
1.118
1.000
1.035
6.297


169.465
166.928
148.573
139.108
130.006
129.552
124.923
122.453
121.628
118.682
118.333
115.038
107.530
77.475
77.157
76.839
28.878
21.947
O
N
N
SO2CF3
3ua
NO2 13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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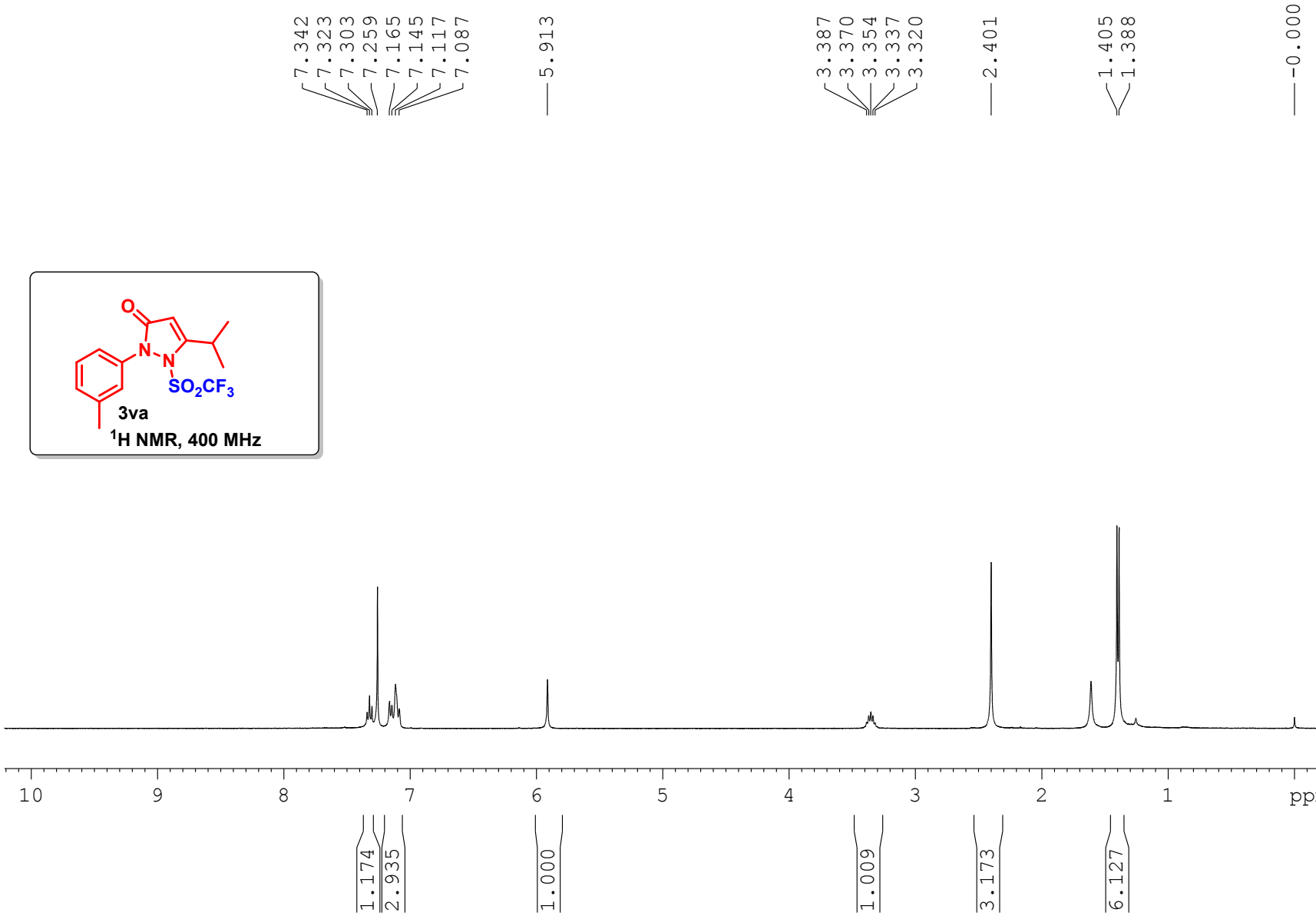
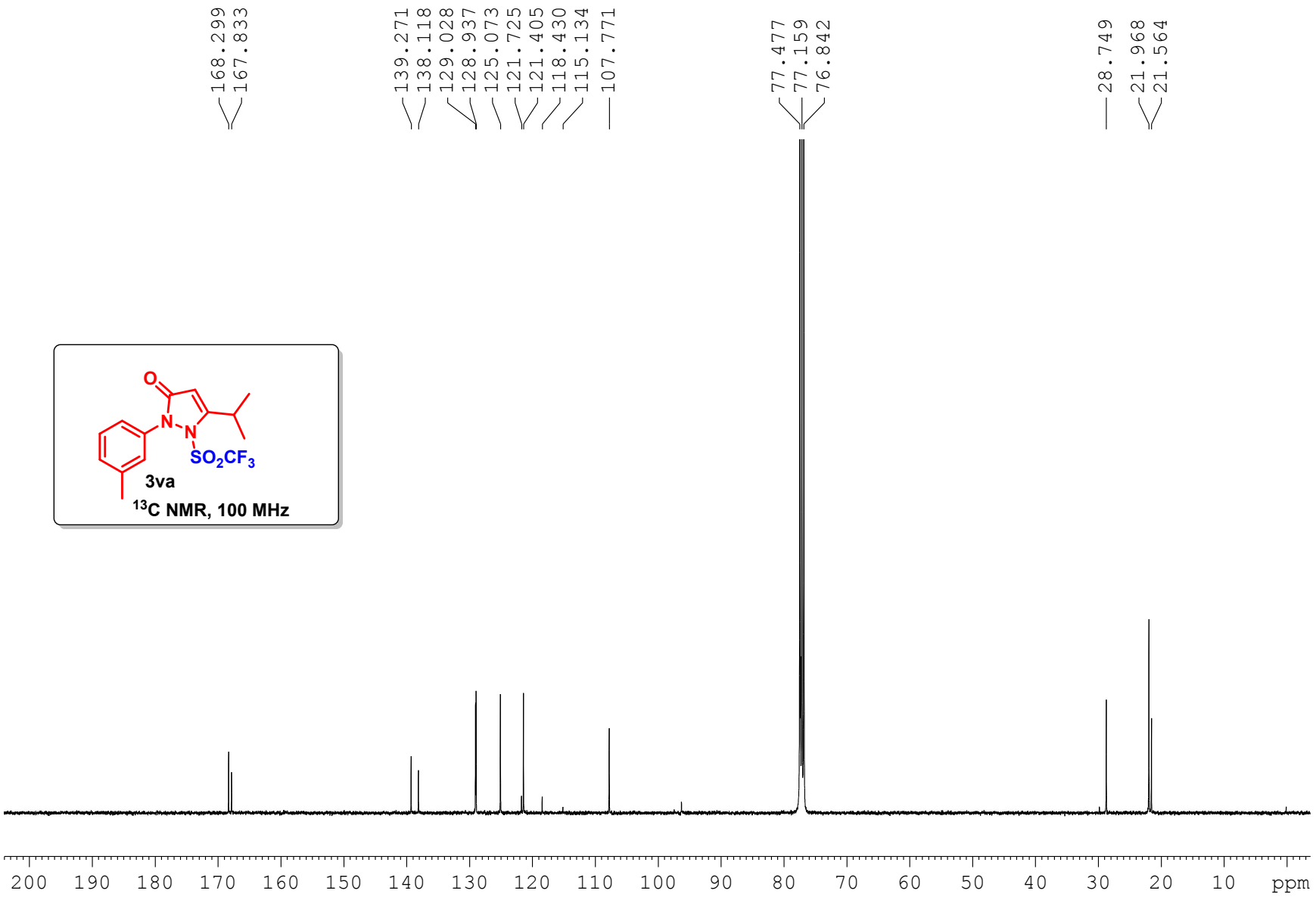
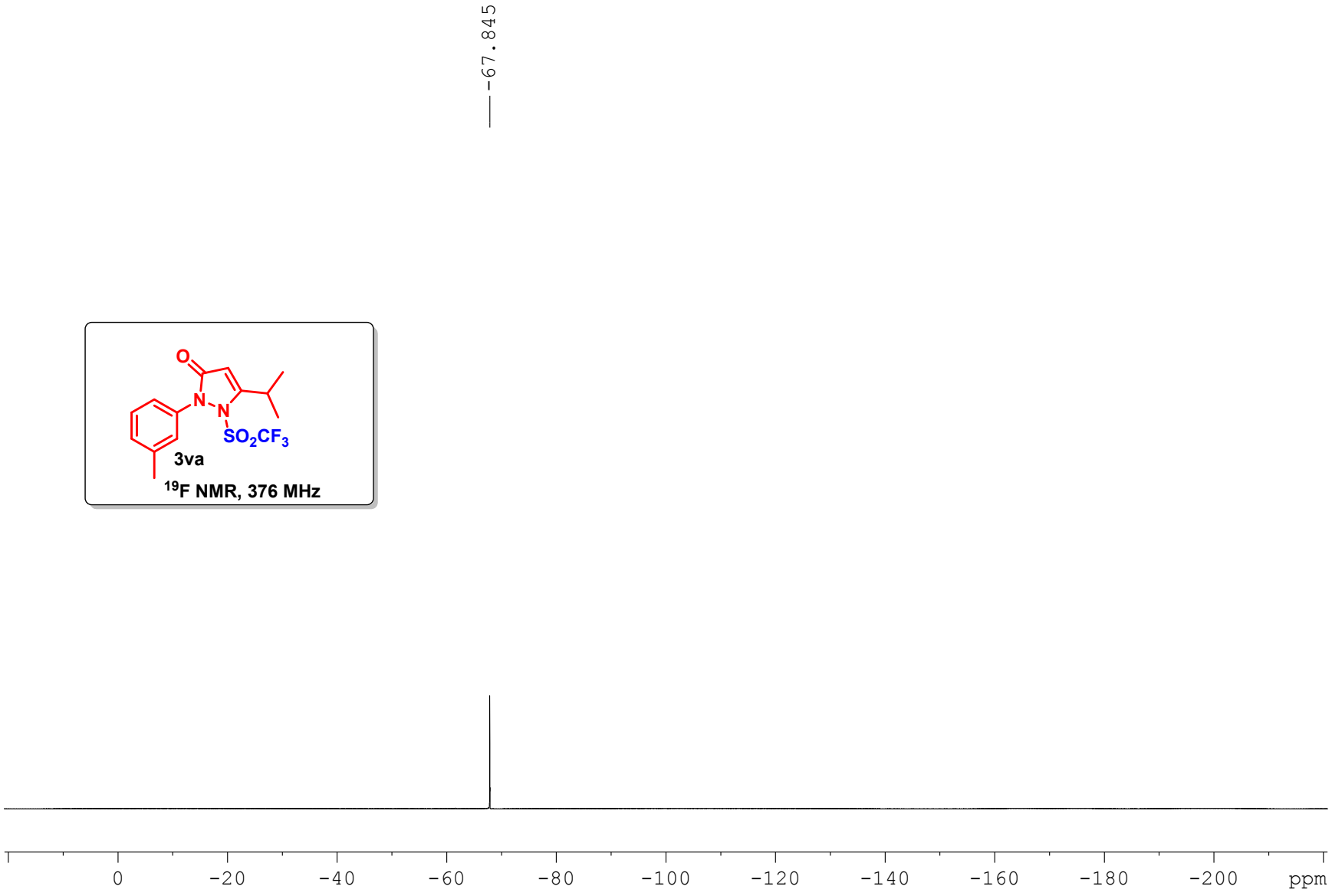
O
N
N
SO2CF3
3ua
NO2
19F NMR, 376 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


7.342
7.323
7.303
7.259
7.165
7.145
7.117
7.087
5.913
3.387
3.370
3.354
3.337
3.320
2.401
1.405
1.388
0.000
O
N
N
SO2CF3
3va
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.174
2.935
1.000
1.009
3.173
6.127


168.299
167.833
139.271
138.118
129.028
128.937
125.073
121.725
121.405
118.430
115.134
107.771
77.477
77.159
76.842
28.749
21.968
21.564
O
N
N
SO2CF3
3va
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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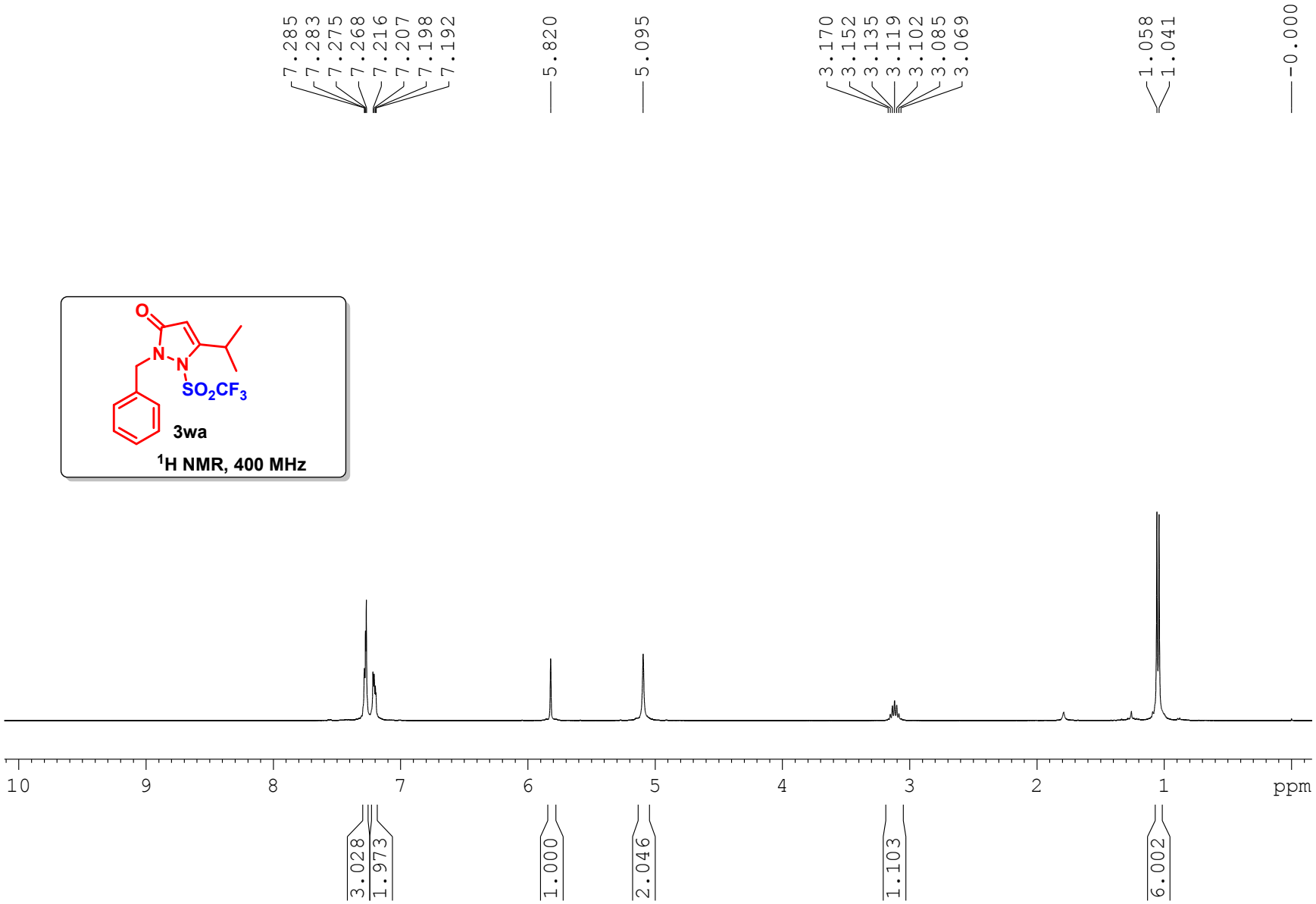
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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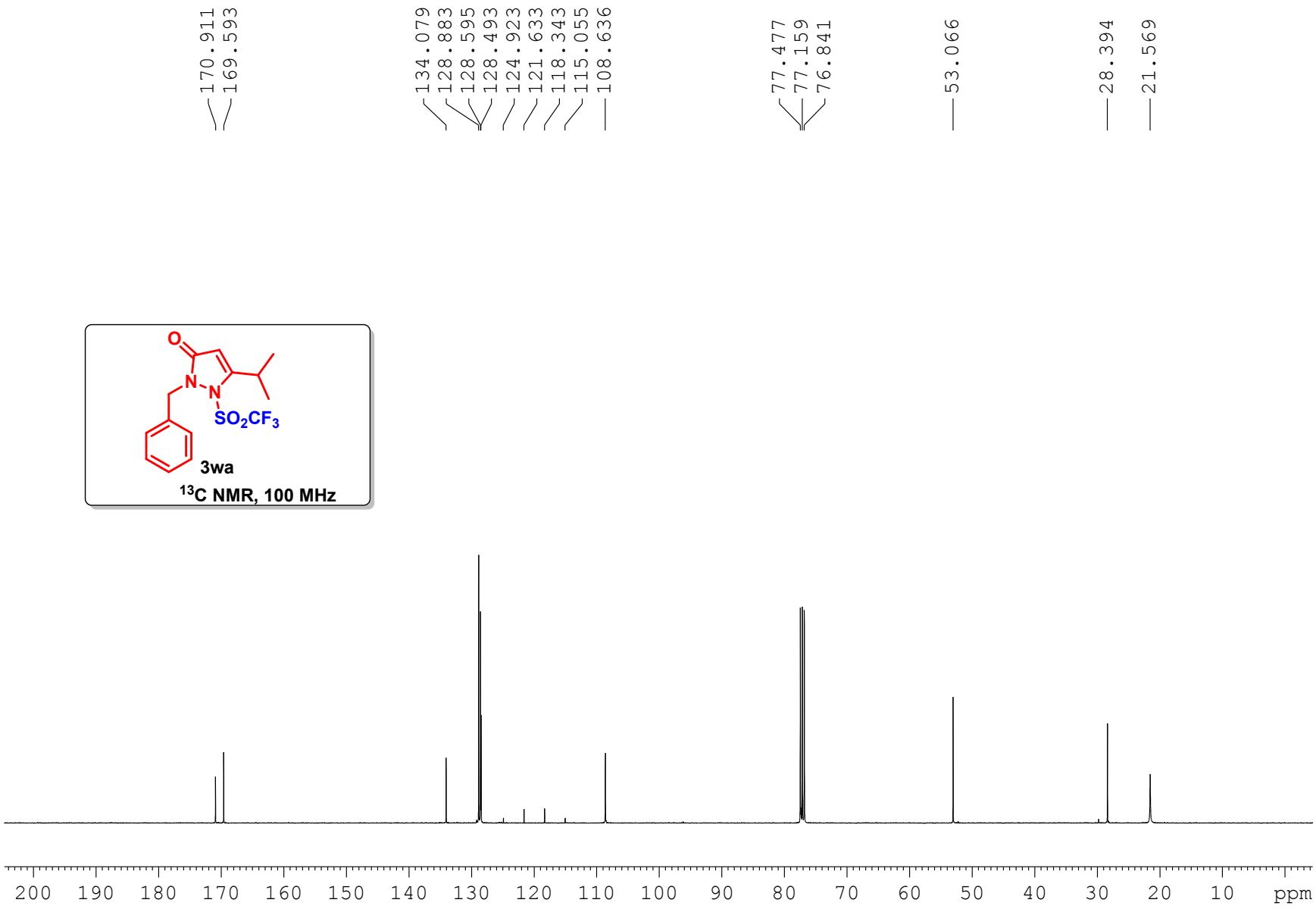
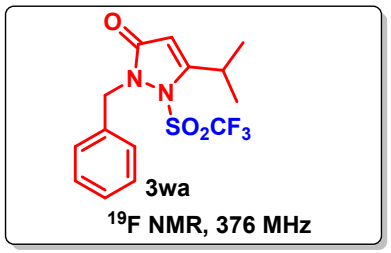
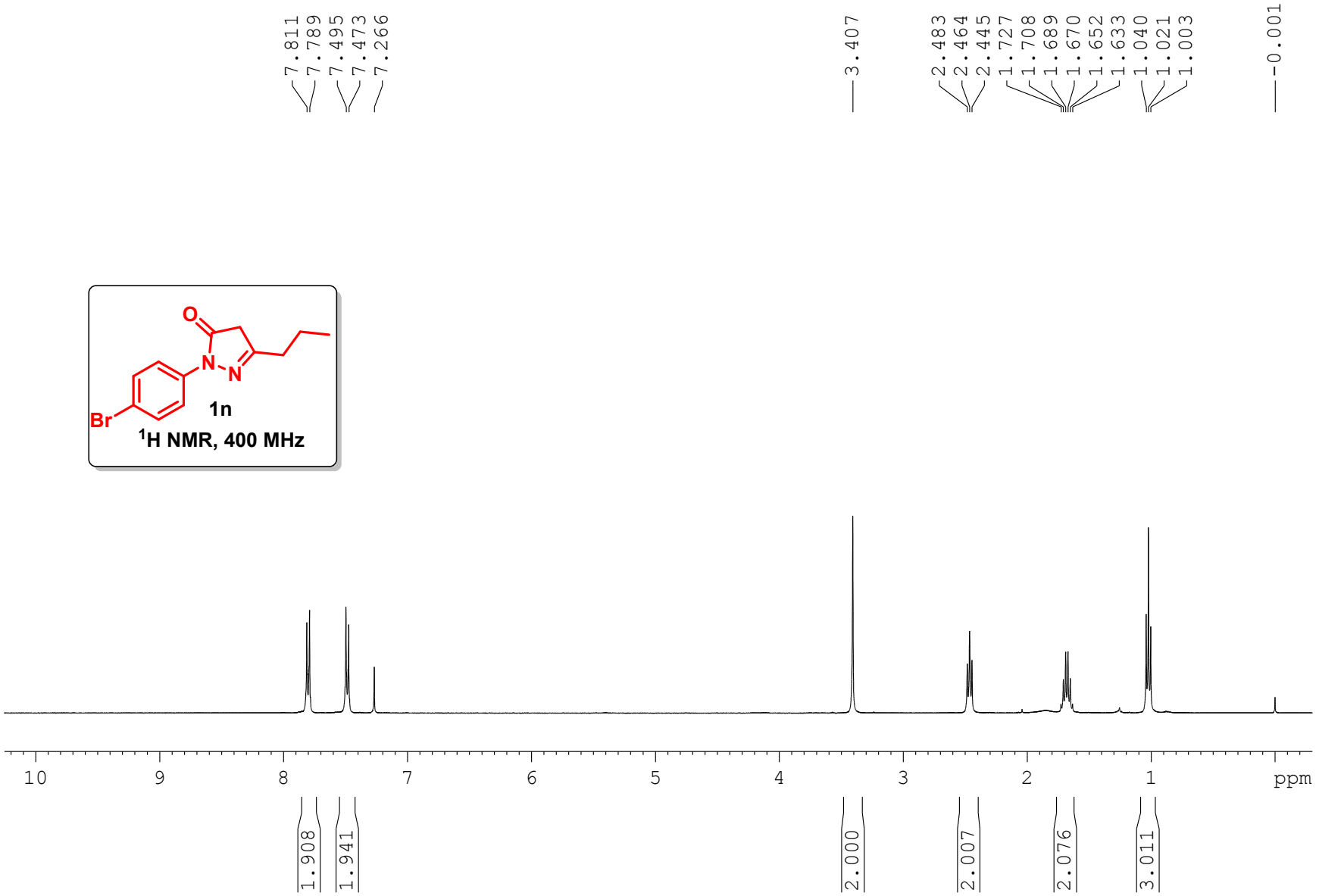
7.283
7.275
7.268
7.216
7.207
7.198
7.192
5.820
5.095
3.170
3.152
3.135
3.119
3.102
3.085
3.069
1.058
1.041
0.000
O
N
N
SO2CF3
3wa
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
3.028
1.973
1.000
2.046
1.103
6.002

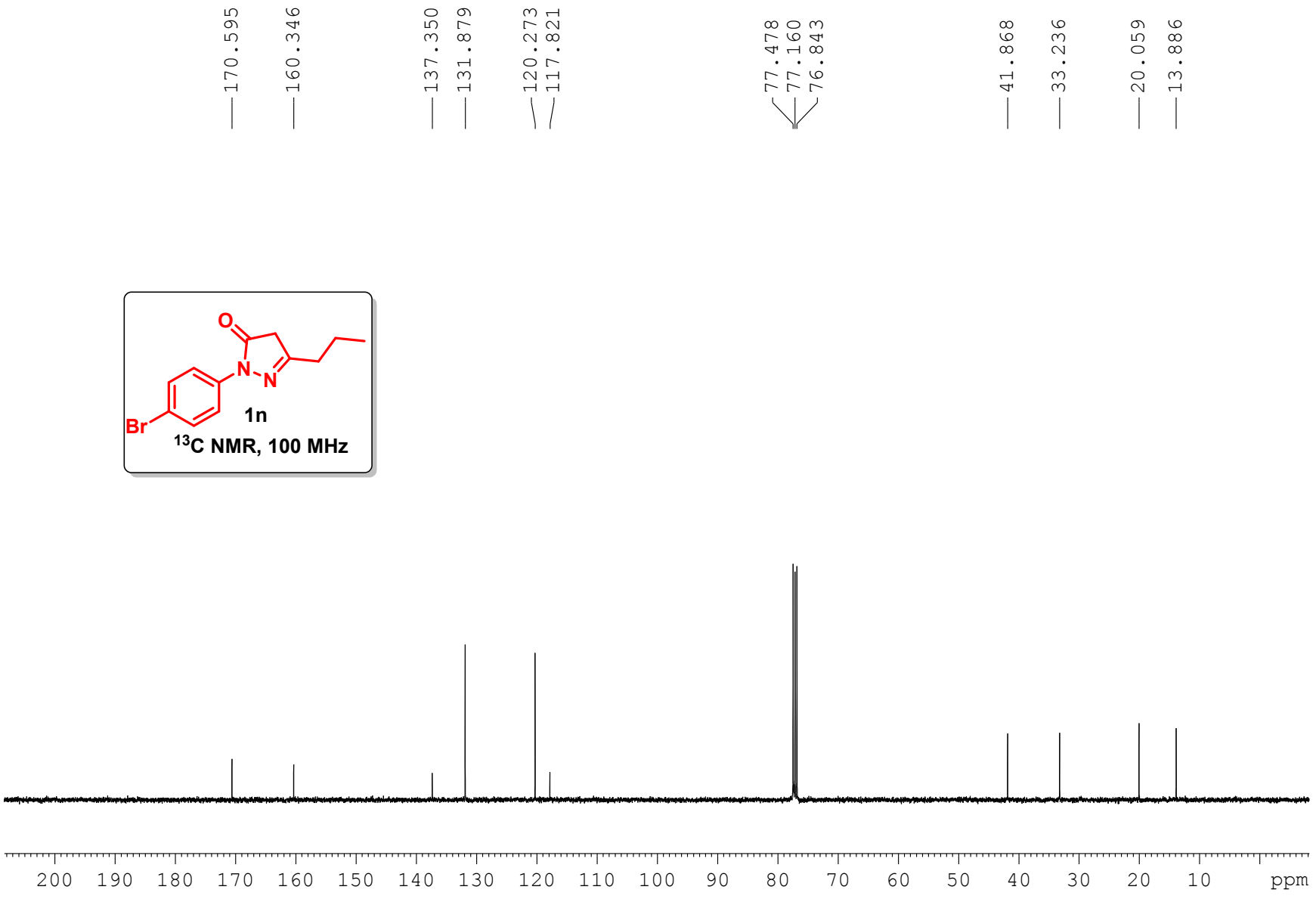

170.911
169.593
134.079
128.883
128.595
128.493
124.923
121.633
118.343
115.055
108.636
77.477
77.159
76.841
53.066
28.394
21.569
O
N
N
SO2CF3
3wa
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

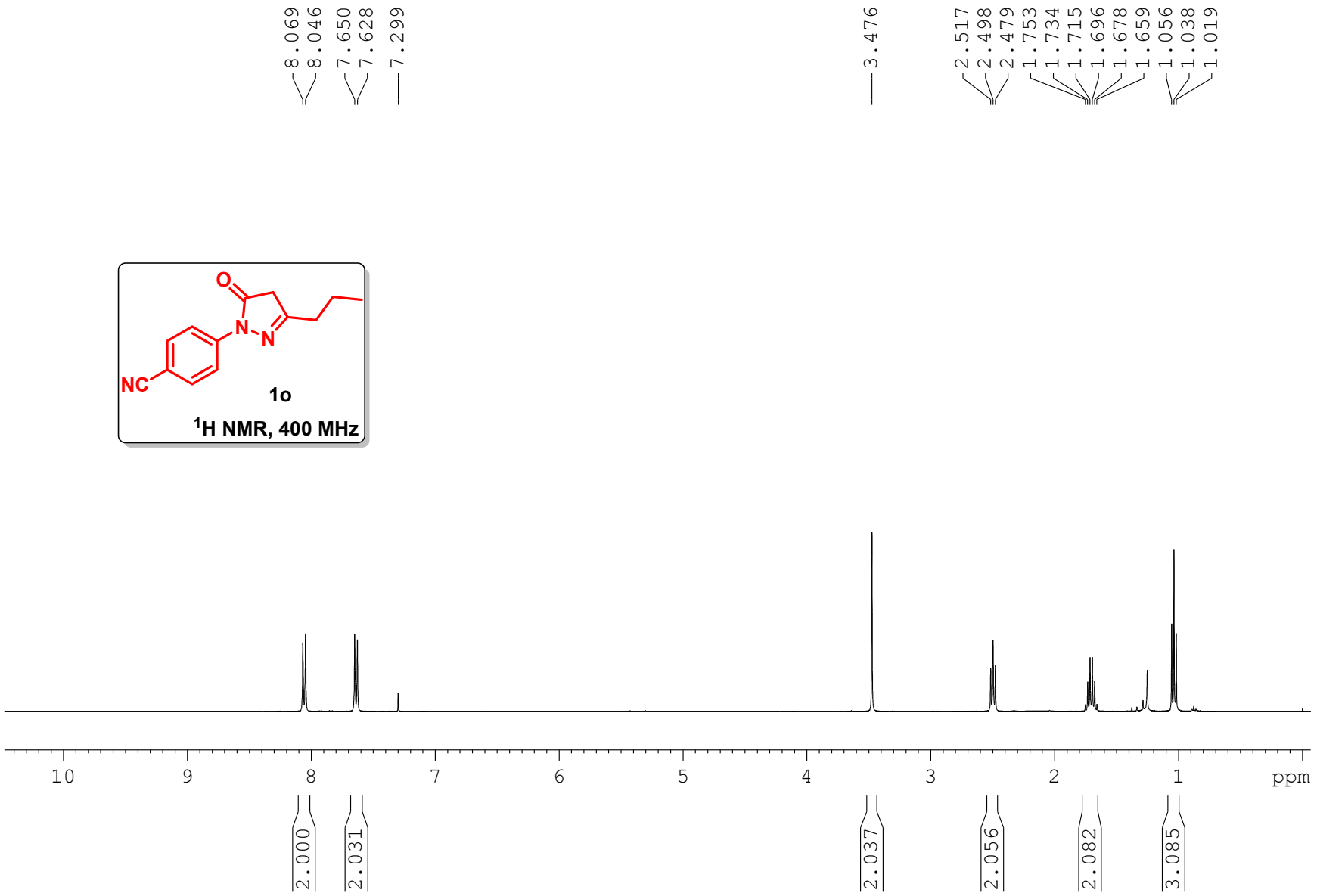


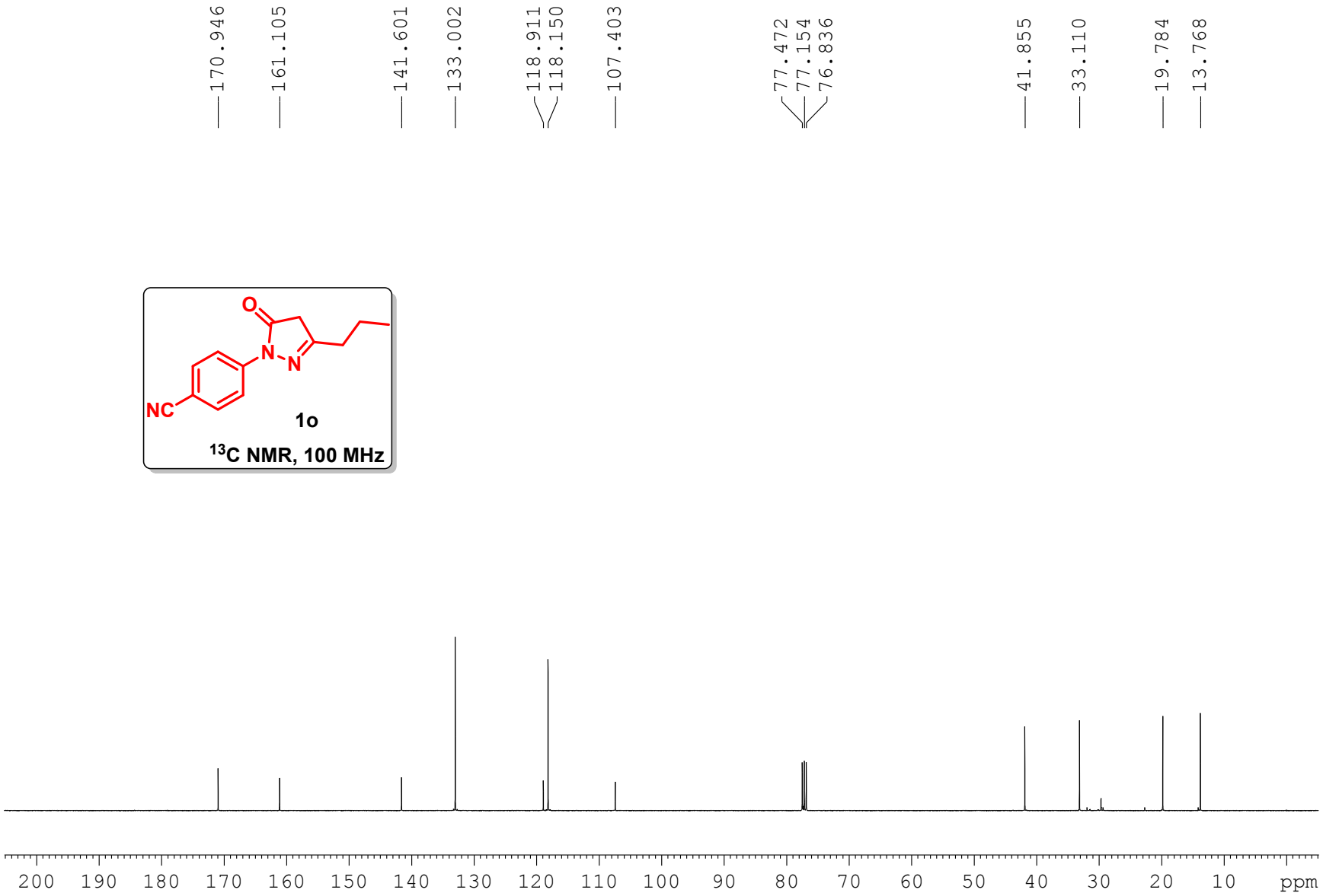
3wa

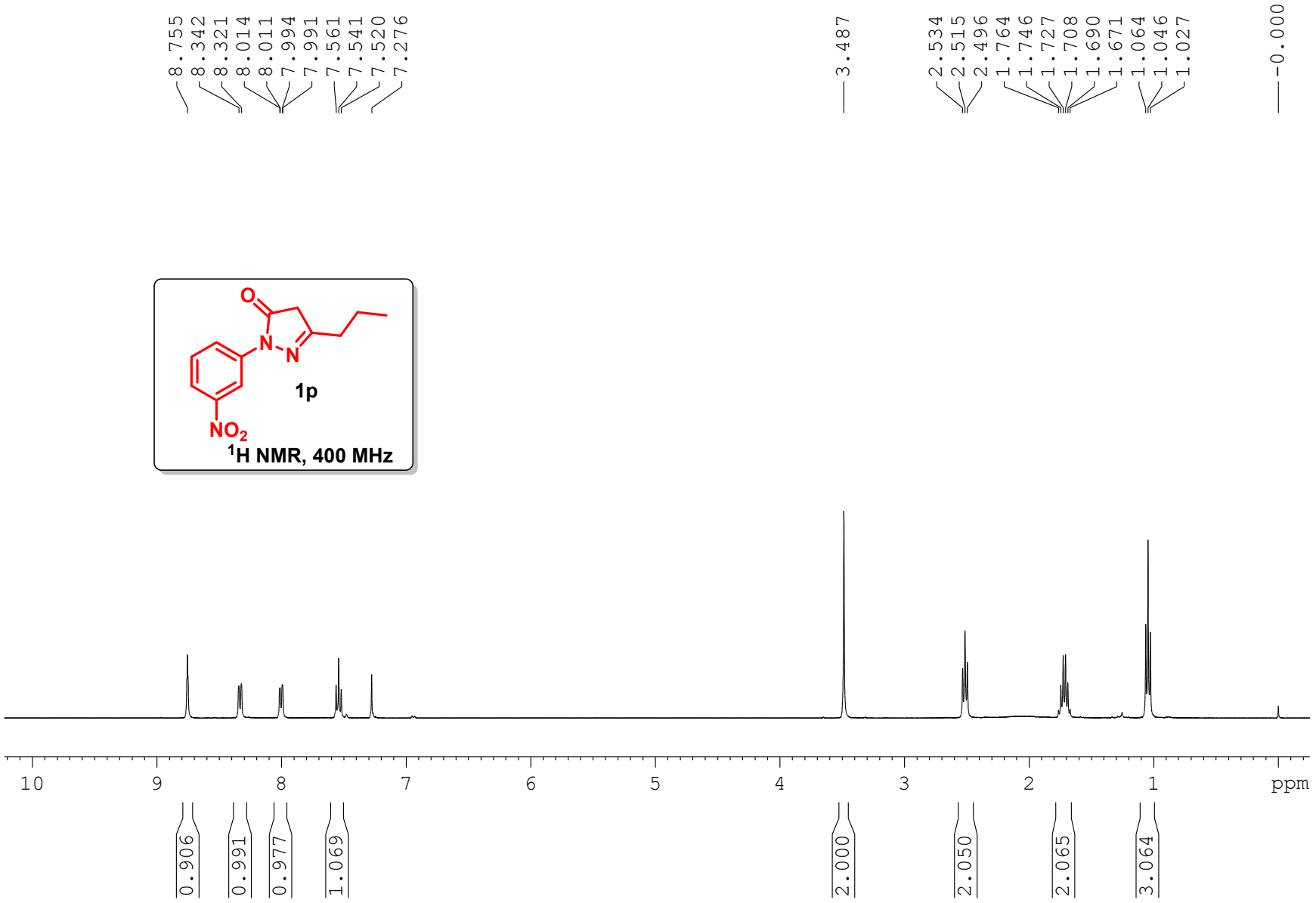
^{19}F NMR, 376 MHz

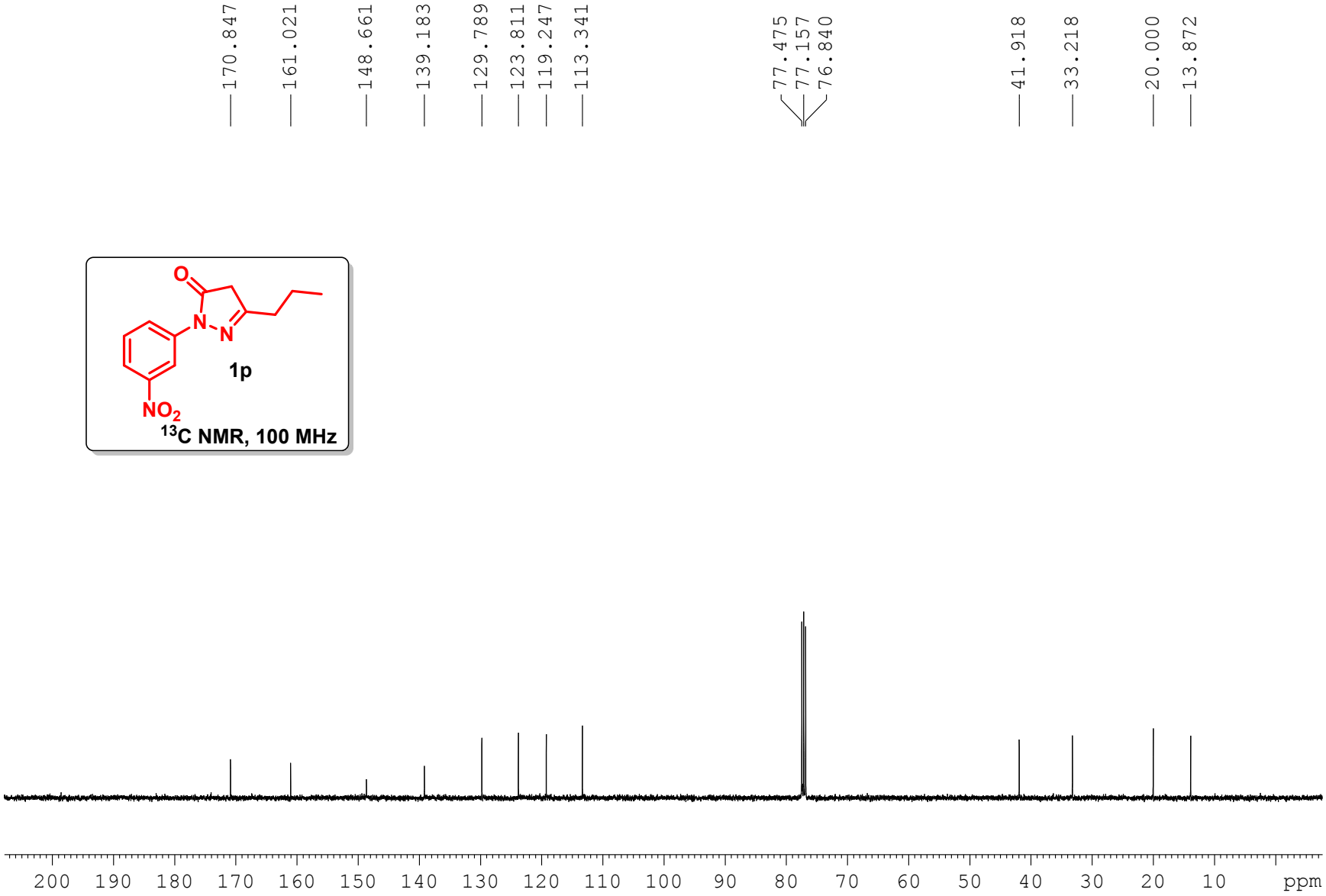

7.811
7.789
7.495
7.473
7.266
3.407
2.483
2.464
2.445
1.727
1.708
1.689
1.670
1.652
1.633
1.040
1.021
1.003
0.001
O
N
N
Br
1n
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.908
1.941
2.000
2.007
2.076
3.011

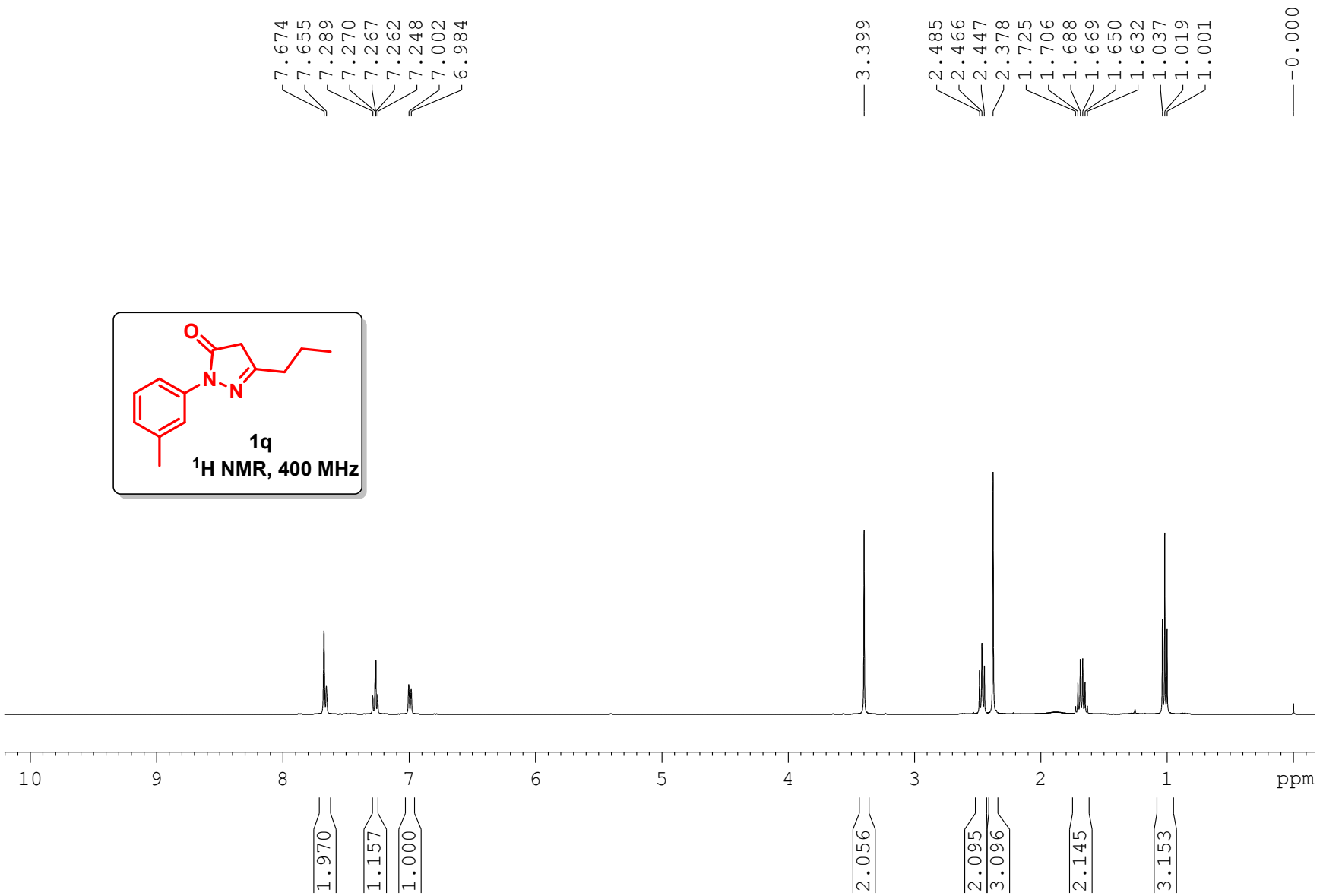

170.595
160.346
137.350
131.879
120.273
117.821
77.478
77.160
76.843
41.868
33.236
20.059
13.886
O
N
N
Br
1n
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

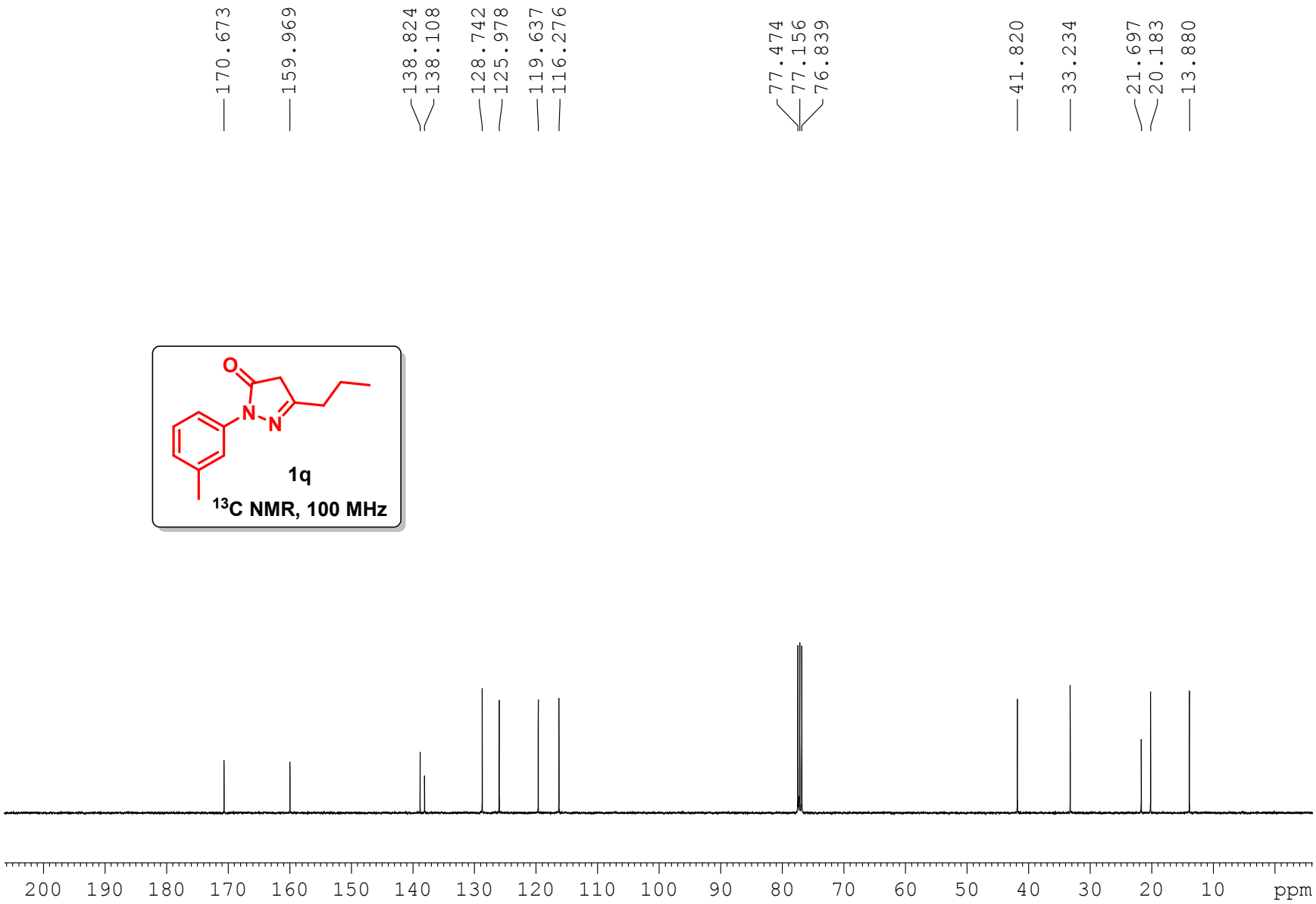

8.069
8.046
7.650
7.628
7.299
3.476
2.517
2.498
2.479
1.753
1.734
1.715
1.696
1.678
1.659
1.056
1.038
1.019
O
N
N
NC
1o
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.000
2.031
2.037
2.056
2.082
3.085

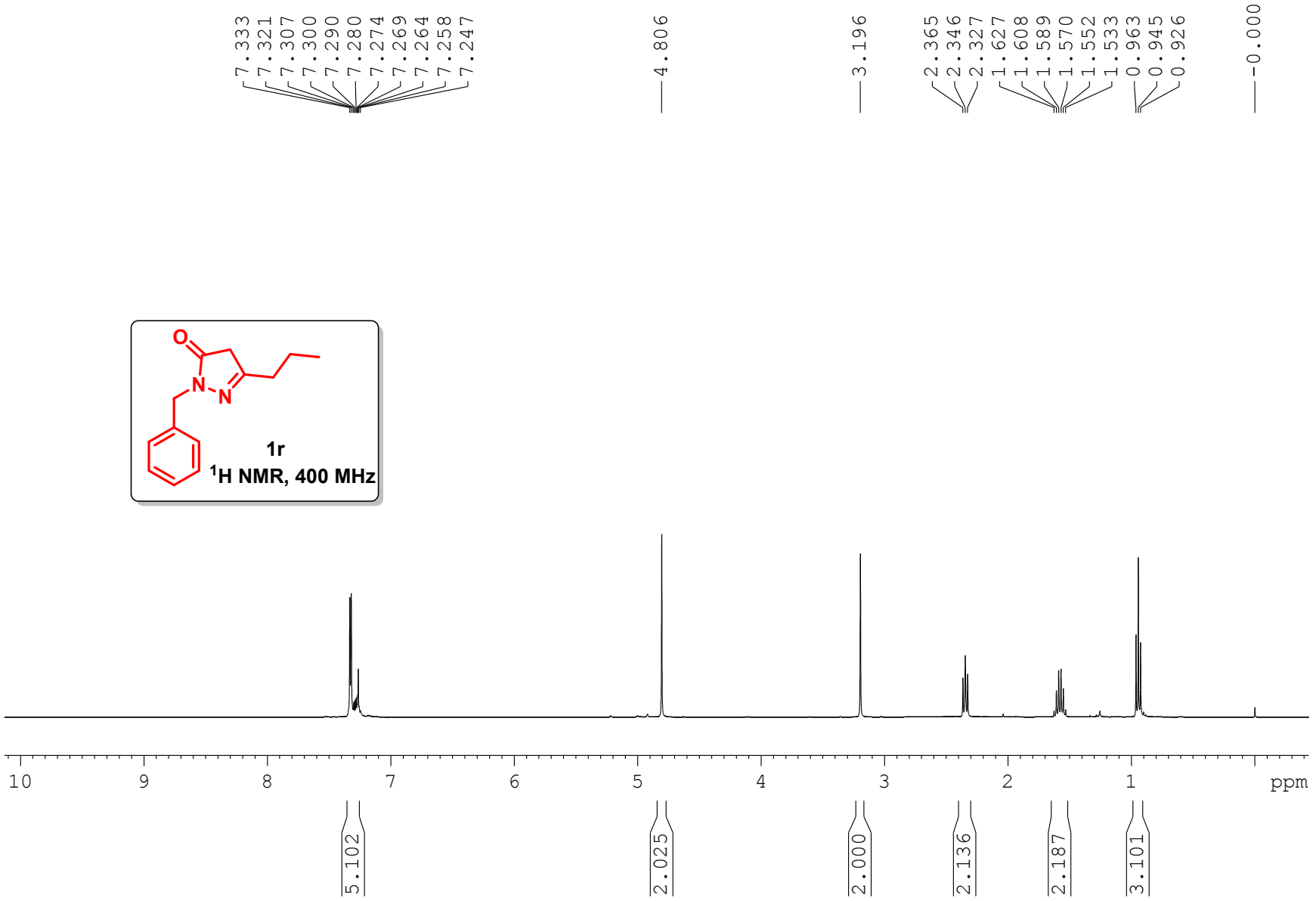

170.946
161.105
141.601
133.002
118.911
118.150
107.403
77.472
77.154
76.836
41.855
33.110
19.784
13.768
O
N
N
NC
1o
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

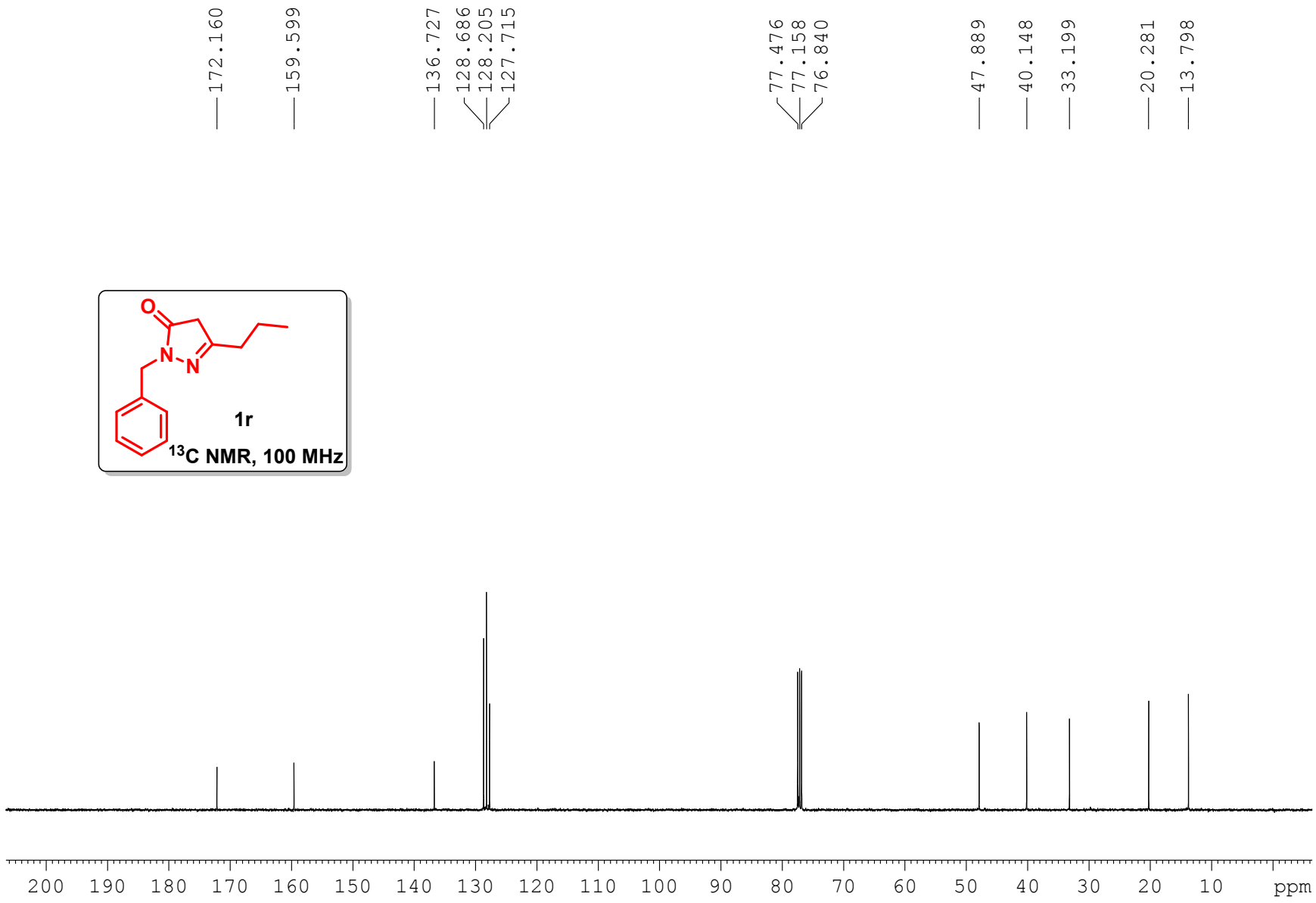

8.755
8.342
8.321
8.014
8.011
7.994
7.991
7.561
7.541
7.520
7.276
3.487
2.534
2.515
2.496
1.764
1.746
1.727
1.708
1.690
1.671
1.064
1.046
1.027
0.000
O
N
N
NO2
1p
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
0.906
0.991
0.977
1.069
2.000
2.050
2.065
3.064

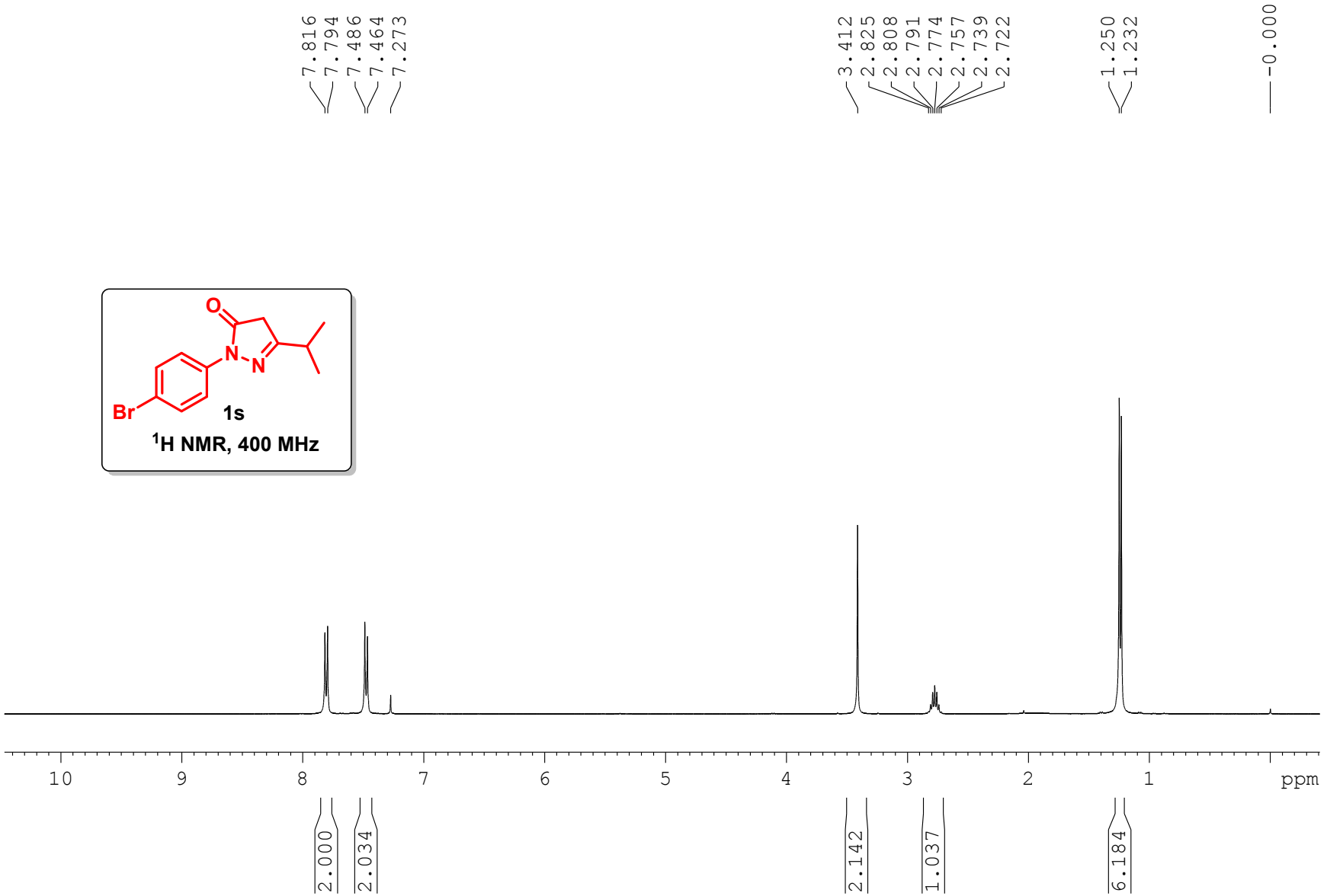

170.847
161.021
148.661
139.183
129.789
123.811
119.247
113.341
77.475
77.157
76.840
41.918
33.218
20.000
13.872
1p
^{13}C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

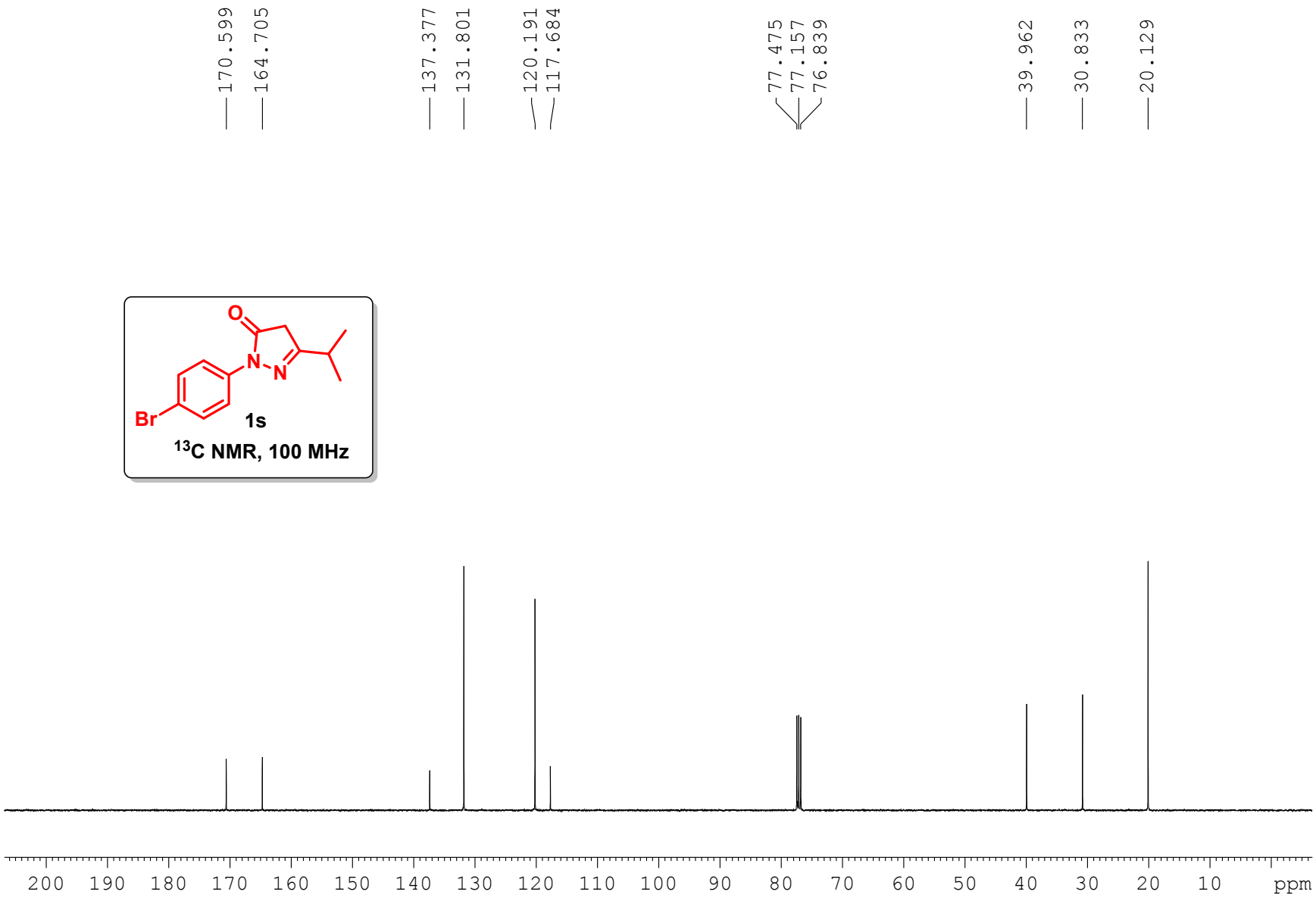

7.674
7.655
7.289
7.270
7.267
7.262
7.248
7.002
6.984
3.399
2.485
2.466
2.447
2.378
1.725
1.706
1.688
1.669
1.650
1.632
1.037
1.019
1.001
0.000
1q
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.970
1.157
1.000
2.056
2.095
3.096
2.145
3.153

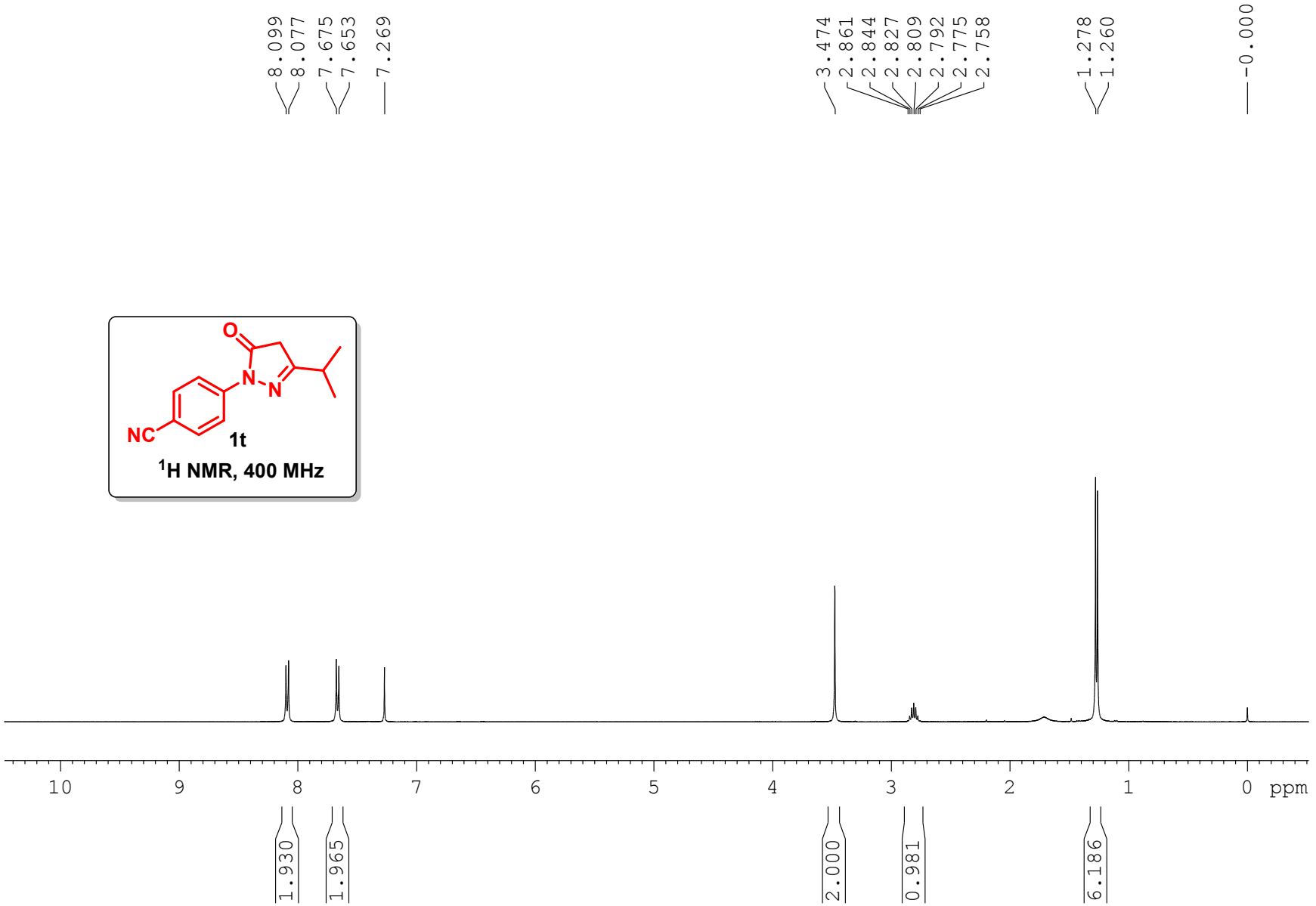

170.673
159.969
138.824
138.108
128.742
125.978
119.637
116.276
77.474
77.156
76.839
41.820
33.234
21.697
20.183
13.880
1q
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

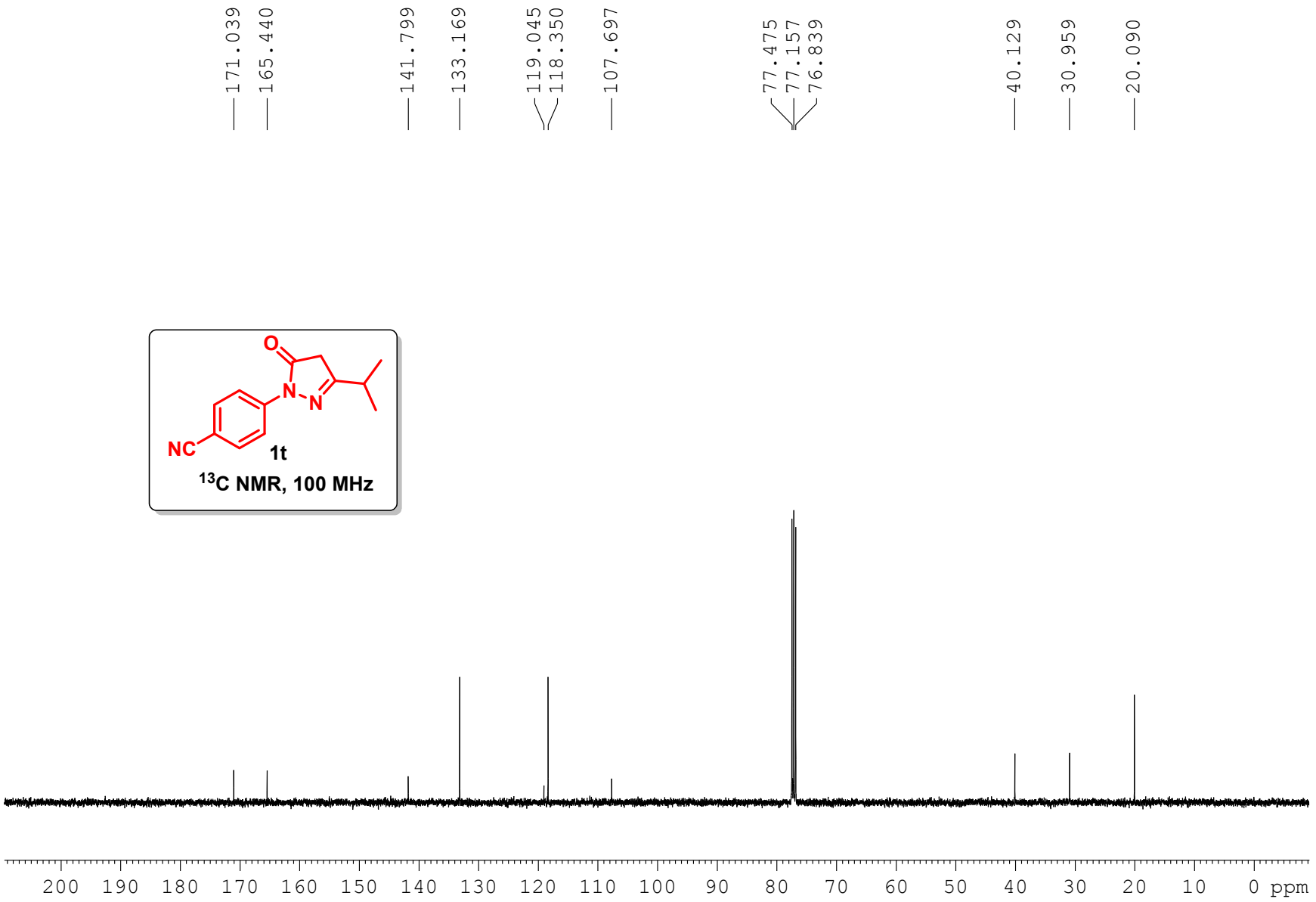

7.333
7.321
7.307
7.300
7.290
7.280
7.274
7.269
7.264
7.258
7.247
4.806
3.196
2.365
2.346
2.327
1.627
1.608
1.589
1.570
1.552
1.533
0.963
0.945
0.926
-0.000
O
N
N
1r
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
5.102
2.025
2.000
2.136
2.187
3.101

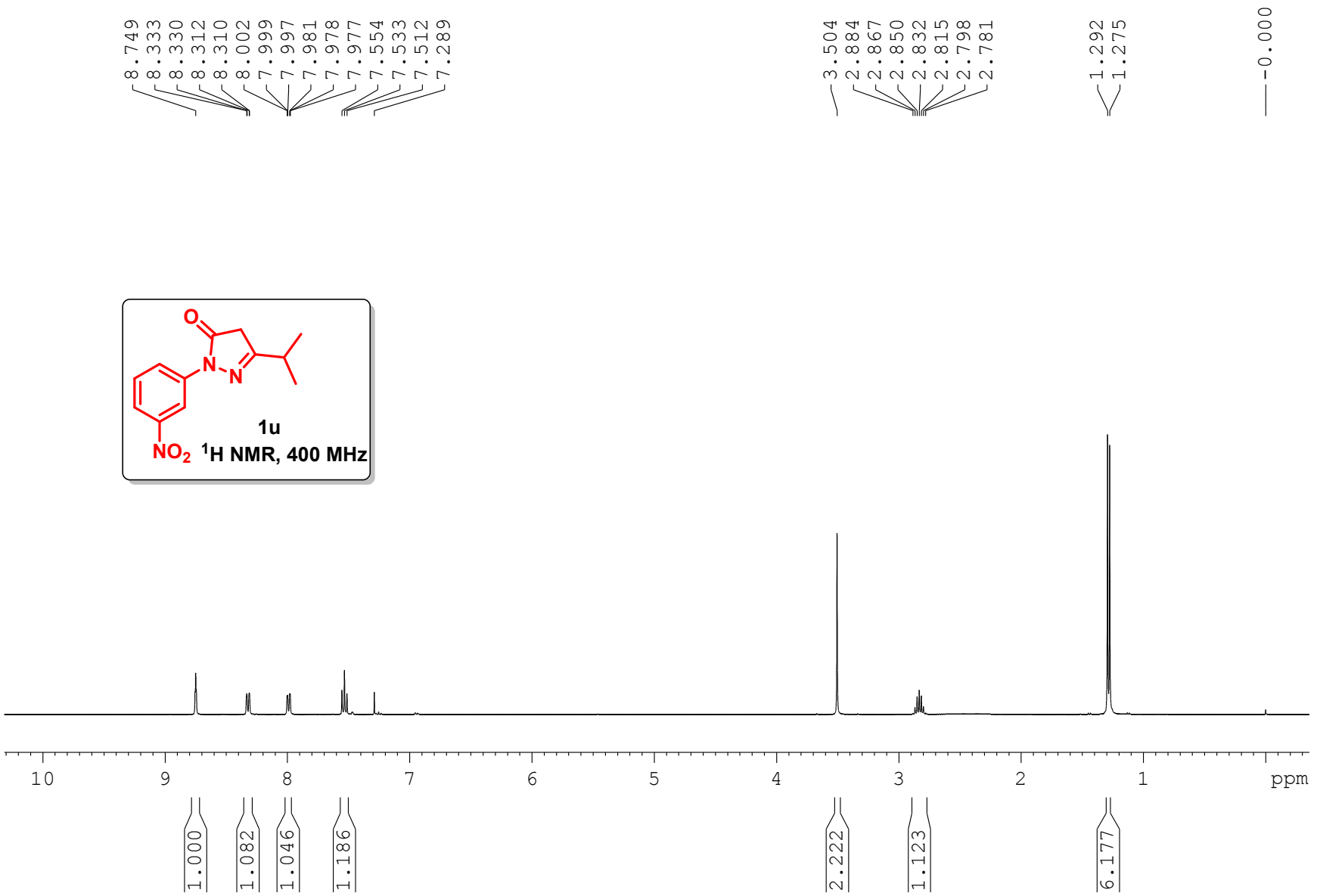

172.160
159.599
136.727
128.686
128.205
127.715
77.476
77.158
76.840
47.889
40.148
33.199
20.281
13.798
1r
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

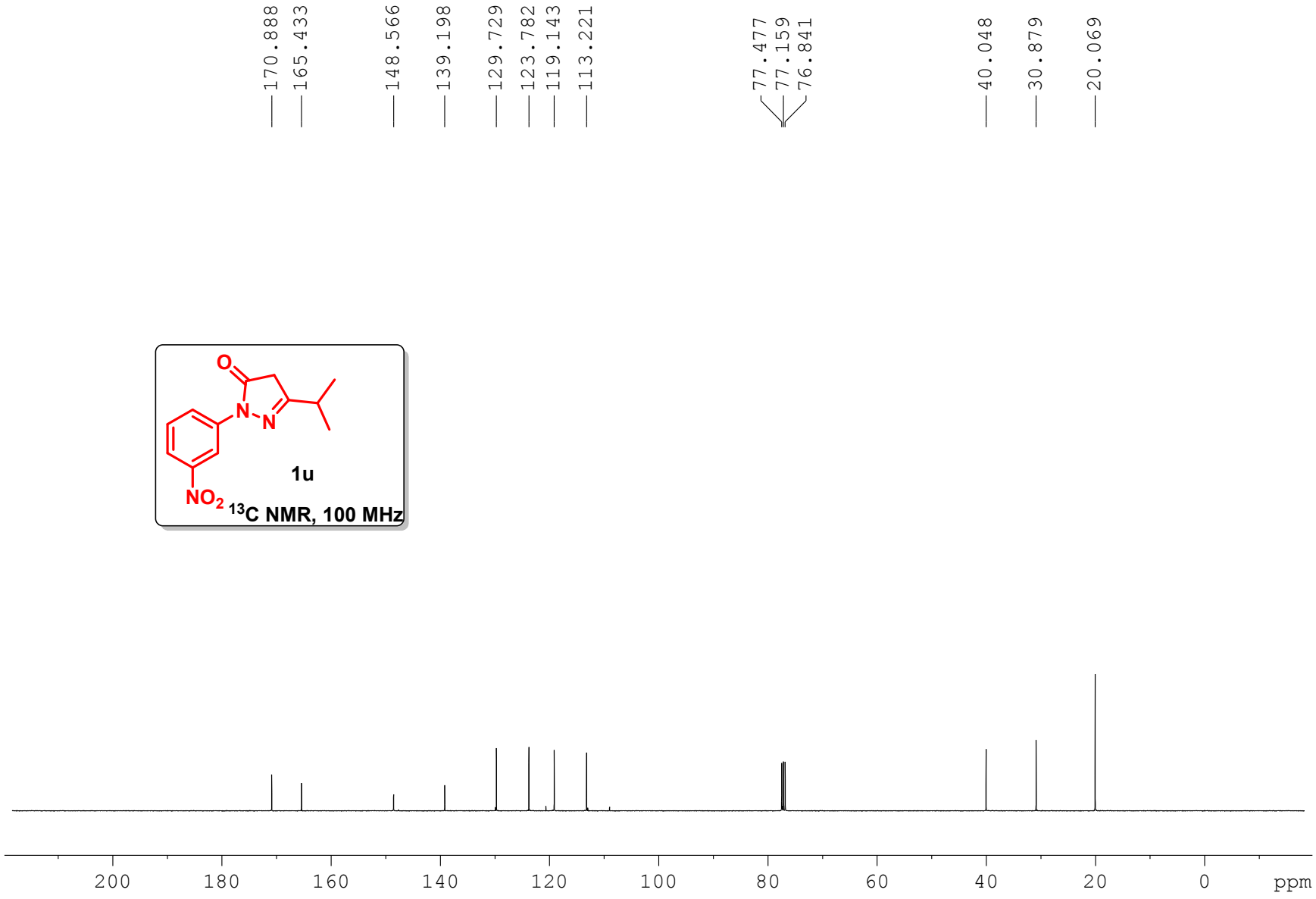

7.816
7.794
7.486
7.464
7.273
3.412
2.825
2.808
2.791
2.774
2.757
2.739
2.722
1.250
1.232
0.000
O
N
N
Br
1s
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
2.000
2.034
2.142
1.037
6.184

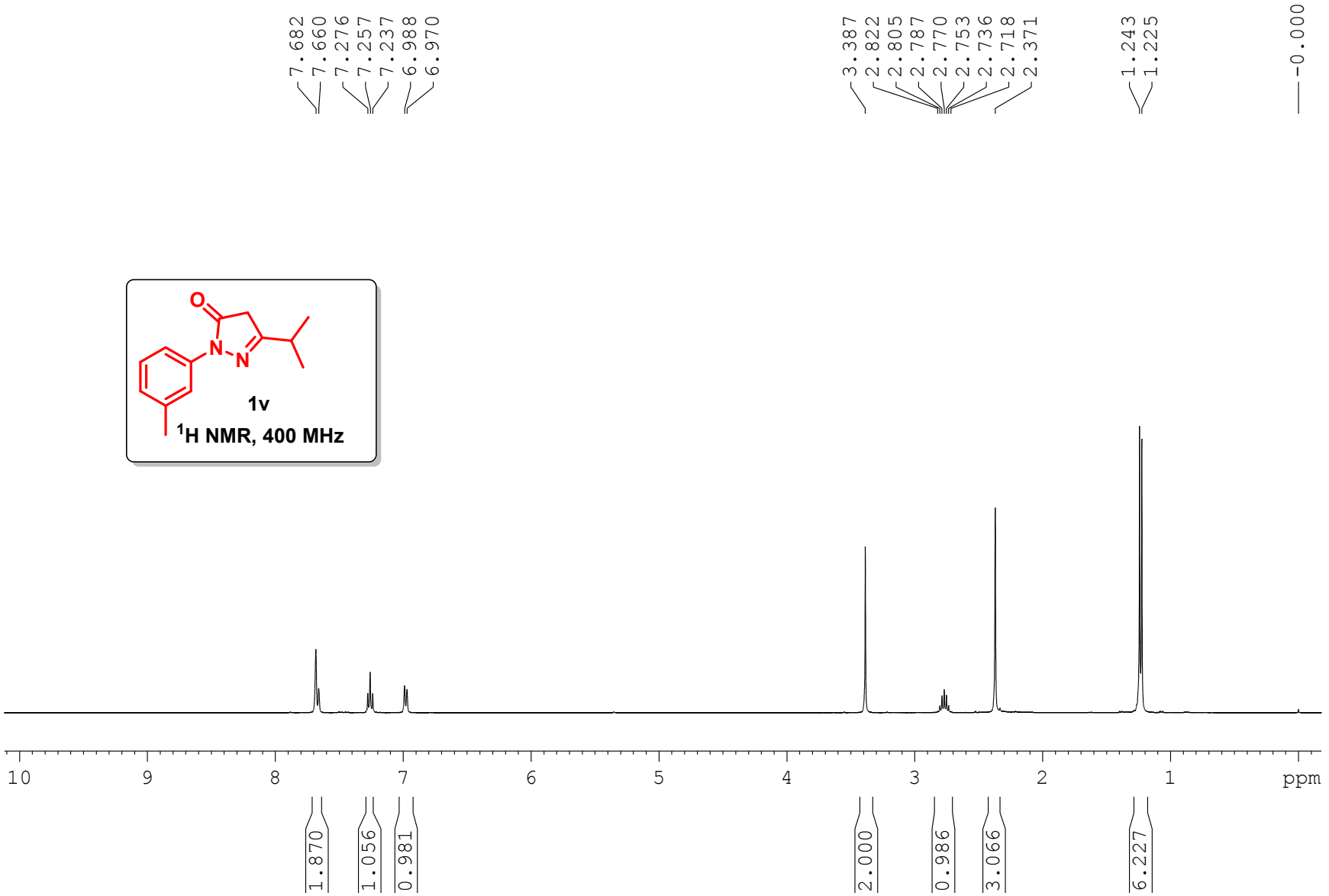

170.599
164.705
137.377
131.801
120.191
117.684
77.475
77.157
76.839
39.962
30.833
20.129
O
N
N
Br
1s
13C NMR, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

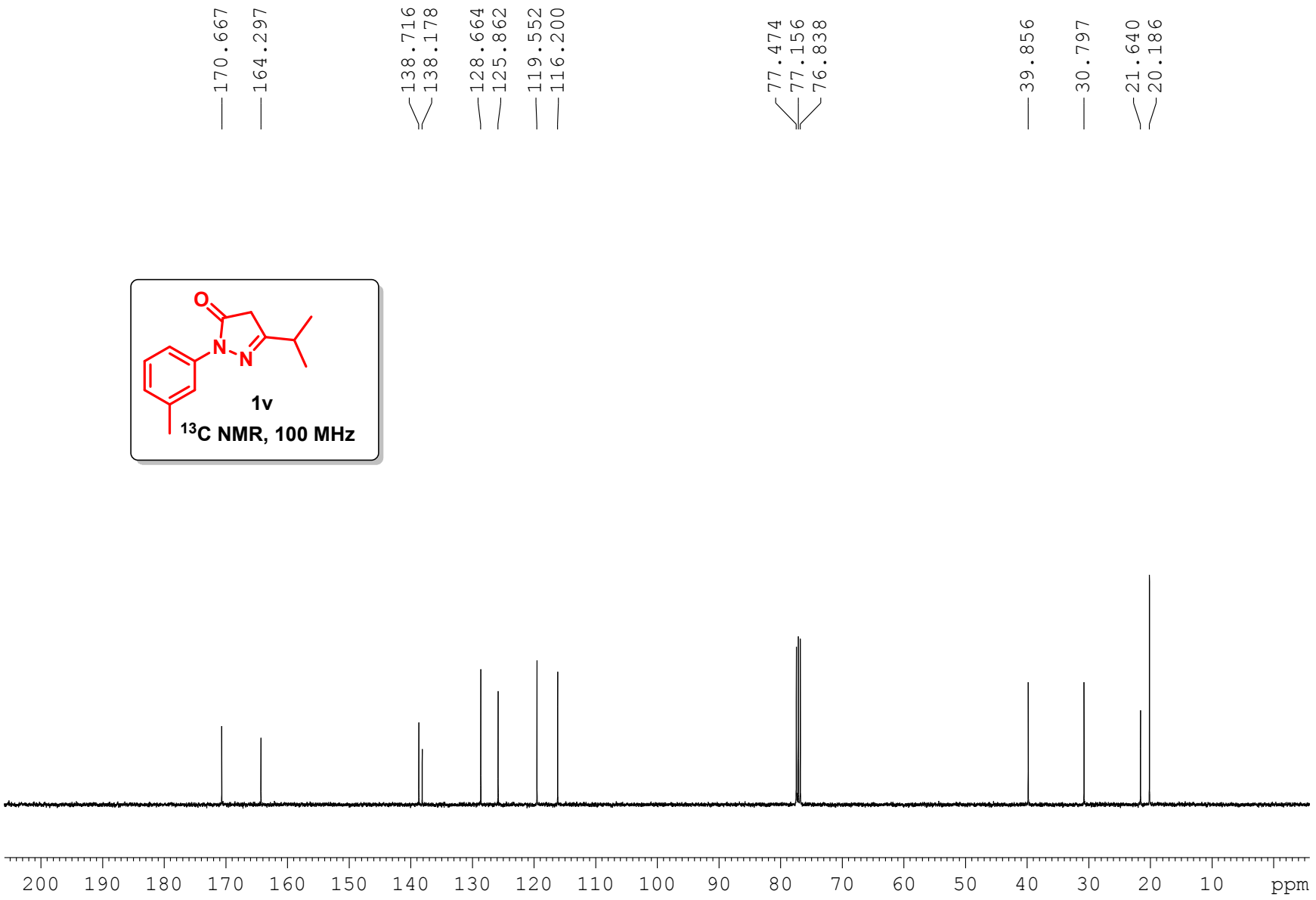

8.099
8.077
7.675
7.653
7.269
3.474
2.861
2.844
2.827
2.809
2.792
2.775
2.758
1.278
1.260
0.000
O
N
N
NC
1t
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.930
1.965
2.000
0.981
6.186


171.039
165.440
141.799
133.169
119.045
118.350
107.697
77.475
77.157
76.839
40.129
30.959
20.090
O
N
N
NC
1t
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.749
8.333
8.330
8.312
8.310
8.002
7.999
7.997
7.981
7.978
7.977
7.554
7.533
7.512
7.289
3.504
2.884
2.867
2.850
2.832
2.815
2.798
2.781
1.292
1.275
0.000
O
N
N
NO2
1u
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.000
1.082
1.046
1.186
2.222
1.123
6.177


170.888
165.433
148.566
139.198
129.729
123.782
119.143
113.221
77.477
77.159
76.841
40.048
30.879
20.069
O
N
N
NO2
1u
13C NMR, 100 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm


7.682
7.660
7.276
7.257
7.237
6.988
6.970
3.387
2.822
2.805
2.787
2.770
2.753
2.736
2.718
2.371
1.243
1.225
-0.000
O
N
N
1v
1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
ppm
1.870
1.056
0.981
2.000
0.986
3.066
6.227


170.667
164.297
138.716
138.178
128.664
125.862
119.552
116.200
77.474
77.156
76.838
39.856
30.797
21.640
20.186
1v
13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm