Supplementary Information

Keggin Heteropolyacid in Auto-Tandem Catalysis: Confinement Effects over Ordered Mesoporous Silica in the Synthesis of 2-Pyridones.

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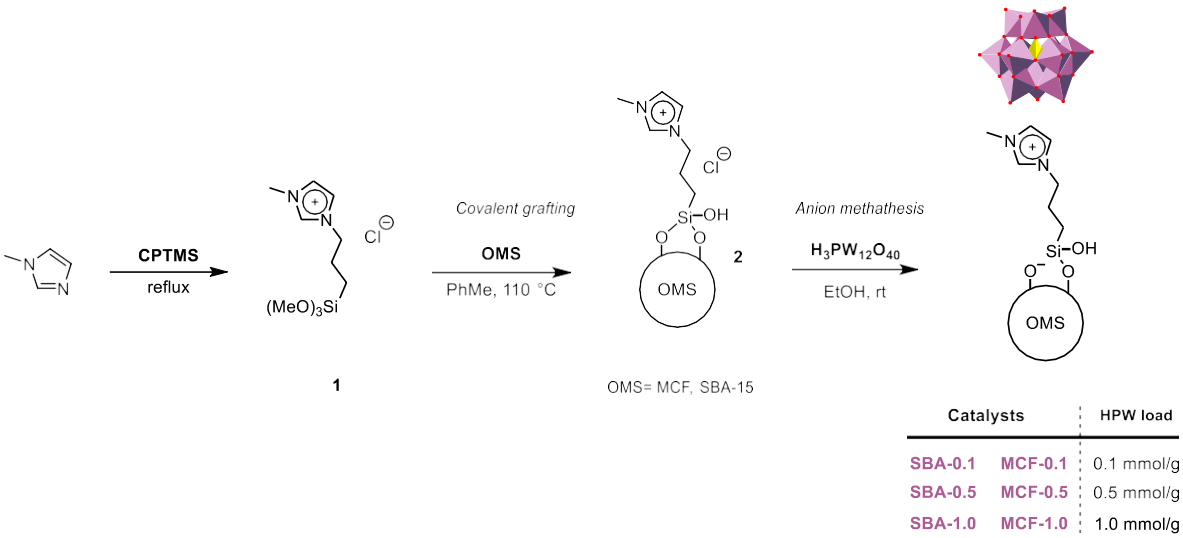
1. CATALYST PREPARATION

For the catalyst synthesis, ordered mesoporous silicas (SBA-15 and MCF) were synthetized according to the reported procedures in the literature.[1] Then functionalization of the porous supports was achieved by covalent grafting with the ionic liquid 3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium chloride. Finally, the Keggin acid $H_3PW_{12}O_{40}$ (0.1-1.0 mmol/g) was immobilized by anion metathesis.



Scheme S1. General strategy to generate the catalysts.

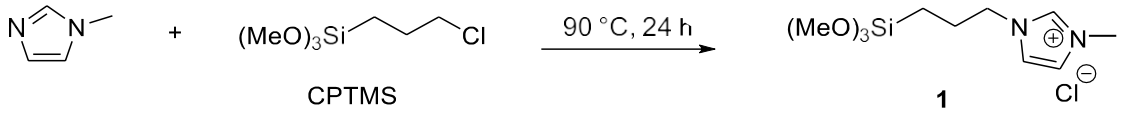
1.1. SBA-15 silica synthesis

Mesoporous silica SBA-15 was synthetized according to literature.[1] For the typical procedure, Pluronic P123 (16.2 g) were dissolved in 375 mL of HCl 1.6 M solution in distilled water with stirring at 35-40 °C for at least 4 h. Then, 37.0 mL of tetraethylorthosilicate (TEOS) were added to the previous mixture dropwise. The resulting mixture was stirred at the same temperature for 20 h. After hydrolysis, reaction temperature was increased at 80 °C and kept for 24 h under static conditions. The resulting solid was filtered, fully washed with 650 mL of distilled water, and dried at 60 °C overnight. Finally, the surfactant was eliminated by calcination at 550 °C for 6 h.

1.2. MCF silica synthesis

Mesocellular silica foam was synthetized according to literature.[2] For the typical procedure, Pluronic P123 (16.2 g) and 6.7 mL for 1,3,5-trimethylbencene (TMB) were dissolved in 375 mL of HCl 1.6 M solution in distilled water with stirring at 35-40 °C for at least 2 h. Then, 37.0 mL of tetraethylorthosilicate (TEOS) were added to the previous mixture dropwise. The resulting mixture was stirred at the same temperature for 24 h. After hydrolysis, reaction temperature was increased at 110 °C and kept for 24 h under static conditions. The resulting solid was filtered, fully washed with 650 mL of EtOH: H_2O (1:1) mixture and dried at 60 °C overnight. Finally, the surfactant was eliminated by calcination at 550 °C for 6 h.

1.3. 3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium chloride (1) [3]



CPTMS **1**

In a dry and degassed 25 mL round flask containing *N*-methylimidazol (0.03 mol, 5.6 mL) was added CPTMS (0.03 mol, 2.5 mL). The reaction mixture was stirred under N_2 atmosphere at 100 °C for 24 h. Then, the orange liquid was washed with anhydrous Et_2O (3x20 mL). Finally, dried under vacuo and stored under N_2 atmosphere.

3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium chloride (1)

Amber liquid, 95% yield. NMR ^{1}H (500 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.59 (t, J = 1.6 Hz, 1H), 7.36 (t, J = 1.7 Hz, 1H), 4.26 (t, J = 7.3 Hz, 2H), 4.06 (s, 3H), 3.50 (s, 9H), 1.99 – 1.89 (m, 3H), 0.60-0.52. (m, 2H). NMR ^{13}C (125 MHz, $CDCl_3$) δ 137.1, 124.4, 120.8, 51.1, 50.5, 36.4, 22.8, 7.5. Spectral data are consistent with the literature.

1.4. MIM-OMS (OMS= SBA-15, MCF)[3]

In a dry and degassed 50 mL round flask containing ionic liquid (**1**, 1.78 mmol, 0.5 g) was added the mesoporous silica (16.7 mmol, 1.0 g) and anhydrous PhMe (25 mL). The reaction mixture was stirred under reflux for 24 h. Then, cooled down to room temperature and filtered under vacuo. The resulting solid was washed successively with 20 mL of anhydrous PhMe and 20 mL of anhydrous DCM. The exceeding ionic liquid was removed by Soxhlet extraction with DCM for 24 h. Finally, the ionic liquid functionalized mesoporous silicas were dried under vacuo.

1.5. $H_3PW_{12}O_{40}$ immobilization

In a 50 mL round flask was dissolved the phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) in 25 mL of absolute EtOH. Then, 1.0 g of MIM-OMS (OMS= SBA-15, MCF) was suspended on the previous solution and stirred at room temperature for 12 h. The resulting solid was filtered under vacuo and washed three times with 25 mL of absolute EtOH. Finally, the catalyst was fully dried under vacuo (50 mbar, 40 °C, 1 h). Several catalysts were prepared using 1.0, 0.5 and 0.1 mmol/g of HPW.

2. Small-angle X-ray scattering and high-resolution transmission electron microscopy.

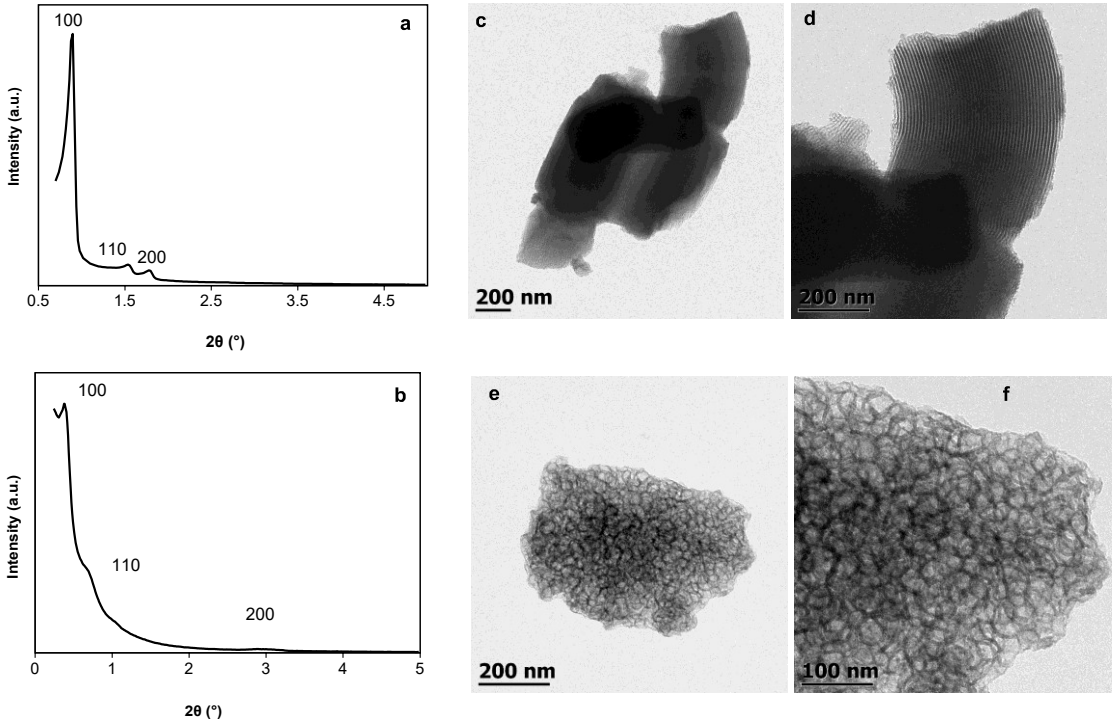


Figure S1. SAXS profile and HR-TEM images of pristine supports, SBA-15 (a, c, d) and MCF (b, e, f).

SAXS profile of synthetized SBA-15 is shown in Figure S1a, characteristic peaks at 0.89, 1.53 y 1.71 ° which corresponds to the diffracting planes (100) =9.9 nm, (110) = 5.8 nm and (200) = 5.1 nm respectively; d-spacing was determined according to Bragg's law. XRD pattern is consistent with a 2D hexagonal pore network (space group pmm6). D_{100} and D_p (measured by N_2 adsorption-desorption) data were used to calculate wall thickness, δ= 5.5 nm. Figures S1c-d shows HR-TEM images for SBA-15, where the tubular nature of the silica pores can be appreciated. Figure S1b presents the SAXS profile for synthetized MCF silica with peaks at 0.46° on 2θ scale, which corresponds to d-spacing at 19.1 nm, close to the D_p determined by N_2 physisorption (18.6 nm). Figures S1e-f includes HR-TEM images for MCF, where sponge like structure and interconected sphericall pores can be observed.

3. X-ray diffraction (XRD)

The XRD patterns for pure silica (SBA-15 and MCF), ionic liquid-functionalized silica (MIM-SBA-15 and MIM-MCF), and catalysts (SBA-1.0 and MCF-1.0) are compared to those of HPW hexahydrate (Figure 5). One broad peak was found at 2θ = 15-30°, corresponding to the amorphous nature of the silica walls of SBA-15 (Figure 5a) and MCF (Figure 5b). The same behavior was observed for the covalent grafting and HPW immobilization steps, which indicates good dispersion of ionic liquid groups and the HPW heteropolyanion throughout the mesoporous matrix.

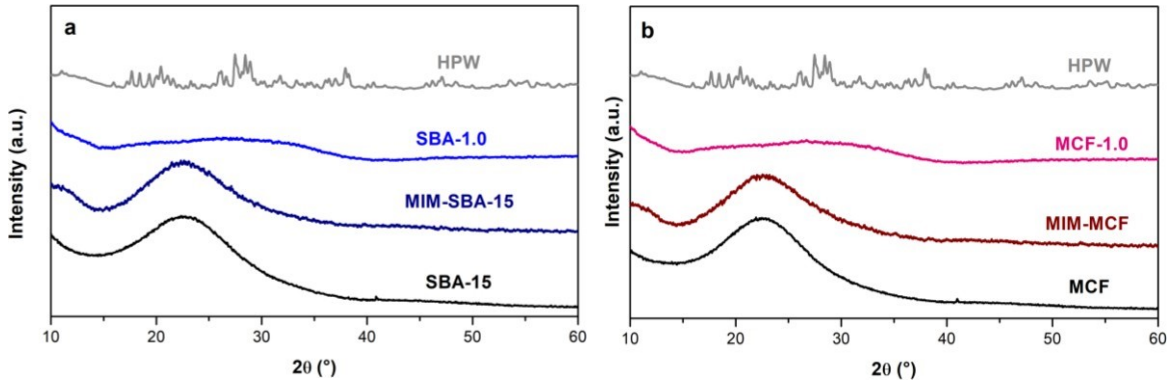


Figure S2. X-ray diffraction (XRD) patterns for SBA-1.0 and MCF-1.0 catalysts (in their pure form and afterbeing functionalized on silica) compared to HPW.

4. Thermogravimetric analysis (TGA)

The thermal stability of the catalysts grafted to the support material (SBA-1.0 or MCF-1.0) was determined by TGA (Figure 12). Weight loss with exposure to 150 °C corresponds to physiosorbed water. Further transformation from 250-350 °C can be explained by ionic liquid decomposition.

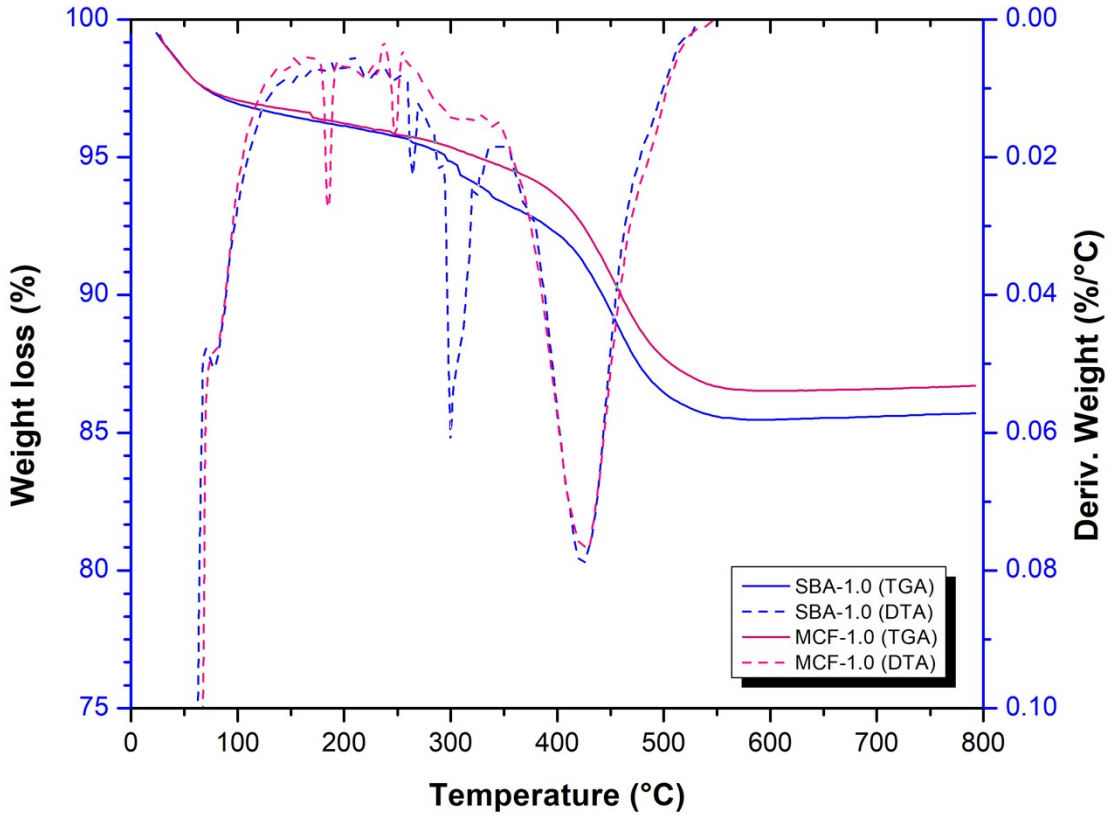


Figure S3. Thermogravimetric analysis (TGA) and Differentialfor the synthesized catalysts on support material.

5. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectra are shown for the complexes consisting of the catalysts plus SBA-15 (Figure 6a) or MCF (Figure 6b). For both cases, the stretching vibration for Si-O-Si appears at ~960 and 1080 cm^{-1}. The incorporation of ionic liquid moieties on mesoporous silica is reflected as absorption at 1460 cm^{-1} for C-H bending, and 1570 and 1630 cm^{-1} for C=C and C=N stretching vibrations.[4] The HPW hybrids exhibit absorption at 810 cm^{-1} for W-O_e-W (edge-sharing oxygen), 900 cm^{-1} for W-O_c-W (corner-sharing oxygen), 980 cm^{-1} for W=O_t (terminal oxygen), and 1080 cm^{-1} for P-O (central oxygen). The latter overlaps with the Si-O-Si stretching vibration.[5]

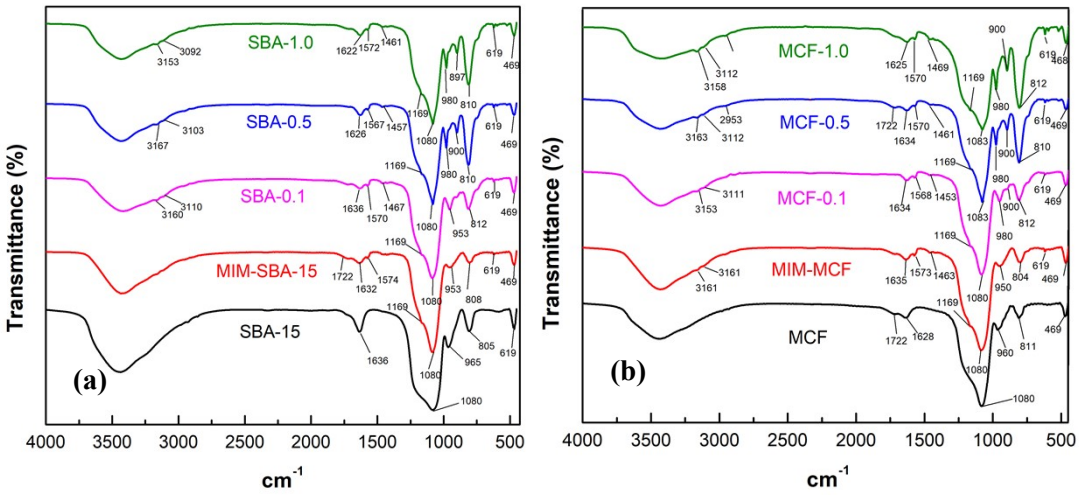


Figure S4. FT-IR spectra for SBA-15 (a) and MCF (b) material.

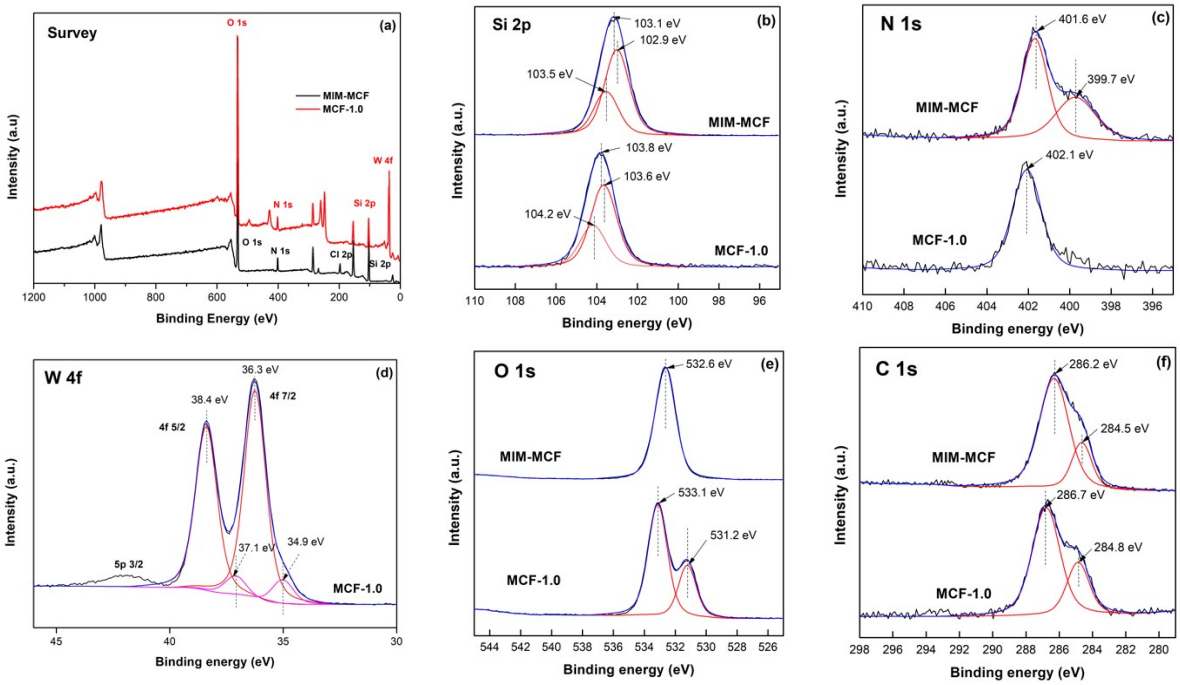


Figure S5. X-ray photoelectron (XPS) spectra for MIM-MCF and MCF-1.0.

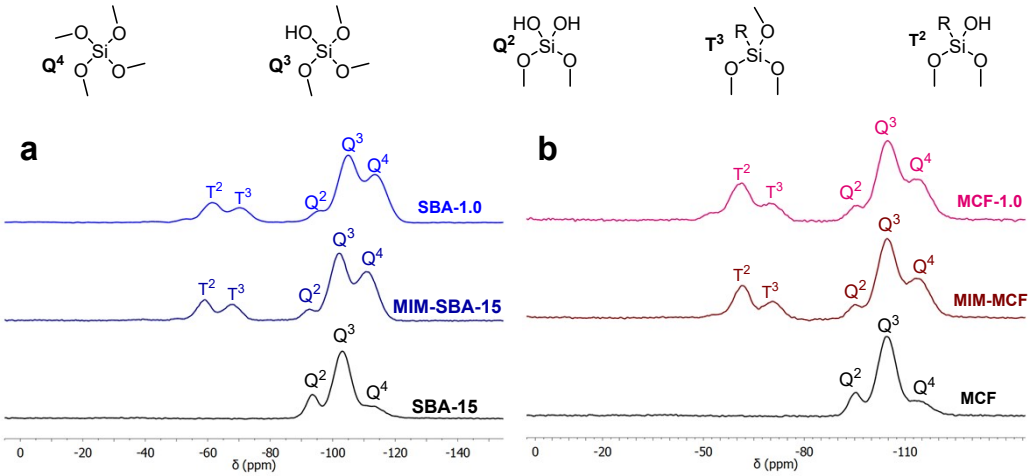


Figure S6. Solid-state[29] Si CP-MAS NMR spectra for the catalysts on the SBA-15 (a) and MCF (b) support material.

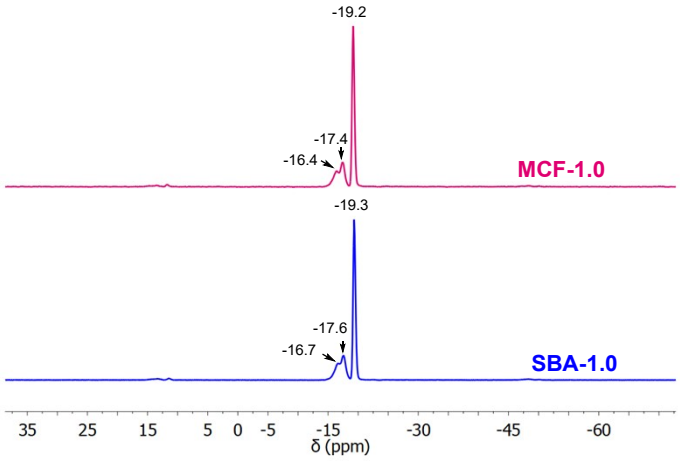


Figure S7. Solid-state ^{31}P NMR CP-MAS spectra for the hybrid catalysts SBA-1.0 and MCF-1.0.

After running model reaction along eight cycles the catalyst MCF-1.0 was recovered, dried, and analyzed by N_2 adsorption-desorption technique (Figure S8); the specific area S_{BET} corresponds to 45 m^2/g, pore size (D_p) 4.5-9.3 nm and pore volume (V_p) 0.18 cm^3/g.

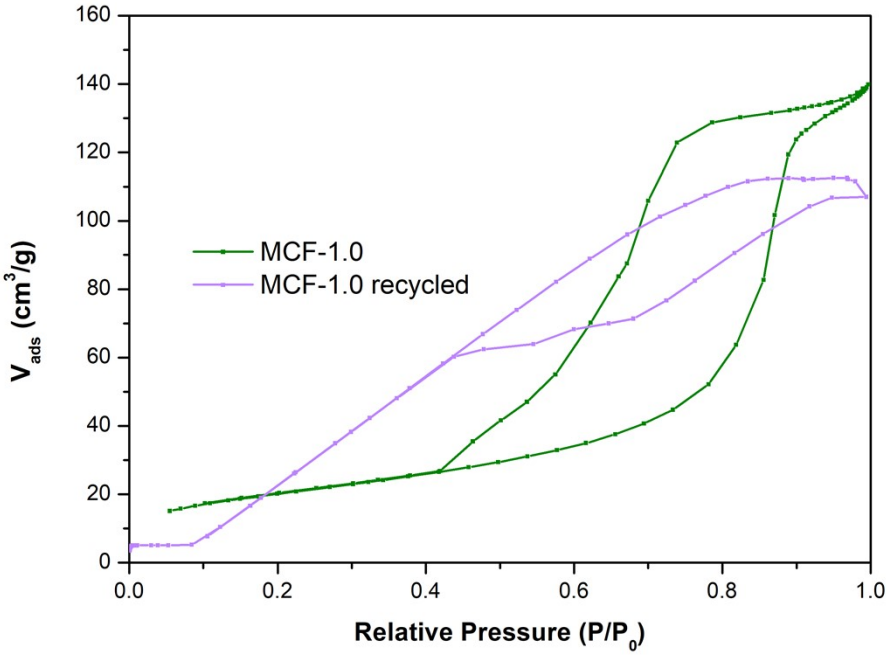
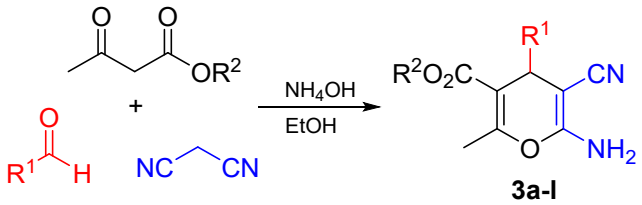


Figure S8. Adsorption-desorption analysis for the reused catalyst MCF-1.0.

6. CATALYTIC EVALUATION

6.1. General procedure for the synthesis of 2-amino-3-cyano-4*H*-pyrans (3a-l)[6]



3a-l

In a 50 mL round flask was placed the corresponding aldehyde (3.0 mmol), 1,3-dicarbonyl compound (3.0 mmol, 1.0 equiv.), malononitrile (3.0 mmol, 1.0 equiv.) and 6.0 mL of absolute EtOH. The mixture was stirred at room temperature until complete dissolution of starting materials. Then, 10% wt of NH_4OH (aqueous solution, 28% w/w) was added dropwise with vigorous stirring. The reaction mixture was stirred at room temperature until aldehyde was consumed; reaction progress was monitored by TLC with EtOAc: Hexane (3:7) as eluent. Product was recovered by filtration and purified by recrystallization with EtOH/H_2O.

2-amino-3-cyano-5-ethoxycarbonyl-6-methyl-4-(1-propyl)-4*H*-pyran (**3a**)

White solid, 88% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 6.79 (2H, s), 4.22-4.07 (2H, m), 3.32 (1H, s), 3.21 (1H, t, J = 4.9 Hz), 2.20 (3H, s), 1.41-1.31 (2H, m), 1.26-1.17 (5H, m), 0.85 (3H, t, J = 7.3 Hz). NMR ^{13}C (125 MHz, DMSO-d_6) δ 165.9, 160.1, 157.2, 120.3, 107.9, 60.2, 54.6, 38.7, 32.3, 18.1, 17.7, 13.9, 13.8.

2-amino-3-cyano-5-ethoxycarbonyl-6-methyl-4-phenyl-4*H*-pyran (**3b**)

White solid, 90% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 7.31 (2H, t, J = 7.6 Hz), 7.21 (1H, t, J = 7.3 Hz), 7.15 (2H, d, J = 7.1 Hz), 6.90 (2H, s), 4.29 (1H, s), 4.04-3.88 (2H, m), 2.31 (3H, s), 1.02 (3H, t, J = 7.1 Hz). NMR ^{13}C (125 MHz, DMSO-d_6) δ 165.4, 158.5, 156.6, 144.9, 128.4, 127.2, 126.8, 119.7, 107.2, 60.1, 57.25, 38.8, 18.1, 13.7.

2-amino-3-cyano-5-ethoxycarbonyl-6-methyl-4-(4-bromophenyl)-4*H*-pyran (**3c**)

White solid, 95% yield. NMR ^{1}H (500 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 8.4 Hz), 7.08 (2H, d, J = 8.4 Hz), 4.57 (2H, s), 4.41 (1H, s), 4.13-3.96 (2H, m), 3.01 (3H, s), 1.11 (3H, t, J = 7.1 Hz). NMR ^{13}C (125 MHz, $CDCl_3$) δ 165.8, 157.7, 157.2, 143.0, 131.8, 129.4, 121.2, 118.8, 107.6, 61.8, 60.9, 38.5, 18.6, 14.0.

2-amino-3-cyano-5-ethoxycarbonyl-6-methyl-4-(4-methoxyphenyl)-4*H*-pyran (**3d**)

White solid, 89% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 7.05 (2H, d, J = 8.6 Hz), 6.86 (4H, m), 4.24 (1H, s), 4.02-3.91 (2H, m), 3.72 (3H, s), 2.29 (3H, s), 1.06 (3H, t, J = 7.1 Hz). NMR ^{13}C (125 MHz, DMSO-d_6) δ 165.5, 158.4, 158.1, 156.0, 136.9, 128.3, 119.8, 113.8, 107.6, 60.1, 57.5, 55.0, 38.0, 18.1, 13.8.

2-amino-3-cyano-5-ethoxycarbonyl-6-methyl-4-(3-nitrophenyl)-4*H*-pyran (**3e**)

White solid, 94% yield. NMR ^{1}H (500 MHz, $CDCl_3$) δ 8.10 (1H, ddd, *J* = 8.1, 2.2, 1.0 Hz), 8.05 (1H, t, *J* = 1.9 Hz), 7.58 (1H, d, *J* = 7.7 Hz), 7.49 (1H, t, *J* = 7.9 Hz), 4.64 (2H, s), 4.58 (1H, s), 4.10-3.99 (2H, m), 2.41 (3H, s), 1.12 (3H, t, *J* = 7.1 Hz). NMR ^{13}C (125 MHz, $CDCl_3$) δ 165.4, 158.1, 157.9, 148.6, 146.2, 134.2, 129.7, 122.7, 122.6, 118.5, 107.1, 61.2, 61.1, 38.9, 18.8, 14.1.

2-amino-3-cyano-5-ethoxycarbonyl-6-methyl-4-(2-thienyl)-4*H*-pyran (**3f**)

White solid, 72% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 7.35 (1H, dd, *J* = 5.1, 1.1 Hz), 7.04 (2H, s), 6.93 (1H, dd, *J* = 5.1, 3.5 Hz), 6.85 (1H, d, *J* = 3.0 Hz), 4.65 (1H, s), 4.15-4.01 (2H, m), 3.34 (2H, s), 2.28 (3H, s), 1.15 (3H, t, *J* = 7.1 Hz). NMR ^{13}C (125 MHz, DMSO-d_6) δ 165.3, 159.1, 156.7, 149.4, 126.9, 124.8, 124.0, 119.6, 107.7, 60.4, 56.9, 33.8, 18.2, 13.8.

2-amino-3-cyano- *tert*-butoxycarbonyl-6-methyl-4-(1-propyl)-4*H*-pyran (**3g**)

White solid, 90% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 6.65 (1H, s), 3.14 (1H, t, *J* = 5.0 Hz), 2.16 (3H, s), 1.44 (9H, s), 1.39-1.29 (2H, m), 1.28-1.18 (2H, m), 0.86 (3H, t, *J* = 7.2 Hz). NMR ^{13}C (125 MHz, DMSO-d_6) δ 165.1, 160.1, 156.1, 120.4, 109.2, 80.4, 54.8, 38.7, 32.4, 27.7, 18.0, 17.8, 13.9.

2-amino-3-cyano-5-*tert*-butoxycarbonyl-6-methyl-4-phenyl-4*H*-pyran (**3h**)

White solid, 87% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 7.32 (2H, t, *J* = 7.6 Hz), 7.22 (1H, t, *J* = 7.3 Hz), 7.14 (2H, d, *J* = 7.0 Hz), 6.85 (2H, s), 4.23 (1H, s), 2.28 (3H, s), 1.20 (9H, s). NMR ^{13}C (125 MHz, DMSO-d_6) δ 164.7, 158.0, 155.7, 144.9, 128.3, 127.3, 126.7, 119.8, 108.2, 80.5, 57.2, 39.1, 27.4, 17.9.

2-amino-3-cyano-5- *tert*-butoxycarbonyl-6-methyl-4-(4-bromophenyl)-4*H*-pyran (**3i**)

White solid, 93% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 7.52 (2H, d, *J* = 8.4 Hz), 7.10 (2H, d, *J* = 8.4 Hz), 6.91 (2H, s), 4.23 (1H, s), 2.27 (3H, s), 1.22 (9H, s). NMR ^{13}C (125 MHz, DMSO-d_6) δ 164.5, 158.3, 156.2, 144.4, 131.2, 129.5, 119.7, 119.6, 107.7, 80.7, 56.9, 38.6, 27.5, 17.9.

2-amino-3-cyano-5- *tert*-butoxycarbonyl-6-methyl-4-(4-methoxyphenyl)-4*H*-pyran (**3j**)

White solid, 86% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 7.05 (2H, d, *J* = 8.6 Hz), 6.88 (2H, d, *J* = 8.6 Hz), 6.80 (2H, s), 4.18 (1H, s), 3.72 (3H, s), 2.27 (3H, s), 1.22 (9H, s). NMR ^{13}C (125 MHz, DMSO-d_6) δ 164.8, 158.3, 158.1, 155.15, 136.9, 128.4, 119.9, 113.7, 108.6, 80.5, 57.4, 55.0, 39.5, 38.3, 27.5, 17.8.

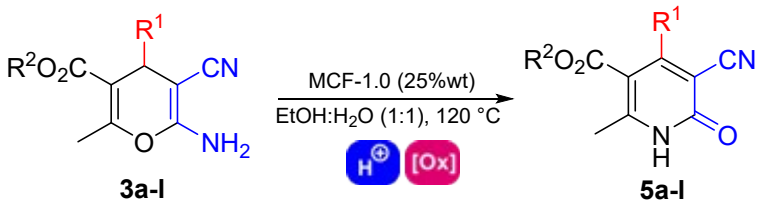
2-amino-3-cyano-5- *tert*-butoxycarbonyl-6-methyl-4-(3-nitrophenyl)-4*H*-pyran (**3k**)

White solid, 96% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 8.16-8.10 (1H, m), 7.98 (1H, s), 7.66 (2H, d, *J* = 5.1 Hz), 4.47 (1H, s), 2.31 (3H, s), 1.21 (9H, s). NMR ^{13}C (125 MHz, DMSO-d_6) δ 164.3, 158.6, 156.9, 147.7, 147.4, 134.2, 130.2, 121.9, 121.8, 119.5, 107.2, 80.9, 56.2, 38.8, 27.4, 18.1.

2-amino-3-cyano-5- *tert*-butoxycarbonyl-6-methyl-4-(2-thienyl)-4*H*-pyran (**3l**)

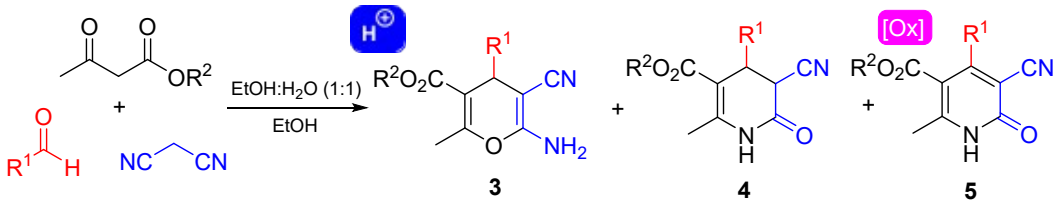
White solid, 80% yield. NMR ^{1}H (500 MHz, DMSO-d_6) δ 7.36 (1H, dd, *J* = 5.0, 0.8 Hz), 6.98 (2H, s), 6.94 (1H, dd, *J* = 5.0, 3.5 Hz), 6.84 (1H, dd, *J* = 3.1 Hz), 4.58 (1H, s), 2.25 (3H, s), 1.33 (9H, s). NMR ^{13}C (125 MHz, DMSO-d_6) δ 164.5, 158.3, 155.9, 149.4, 126.8, 124.7, 124.0, 119.7, 108.6, 80.9, 56.9, 34.1, 27.6, 18.0

6.2. General procedure for the synthesis of 3-cyano-3,4-dihydro-2-pyridones (5a-l)



In a 5 mL ace-glass pressure tube were placed 100 mg of the corresponding 2-amino-3-cyano-4*H*-pyran (**3a-r**), 25 mg of PW-MIM-MCF catalyst and the mixture EtOH: H_2O (1:1) as solvent (0.2 M). The reaction mixture was stirred at 120 °C until starting material was consumed. The reaction progress was monitored by TLC using EtOAc: hexane (5:5) as eluent. Product was recovered precipitation and recrystallization with EtOH. Column chromatography was performed when needed using EtOAc: hexaneas eluent and pure product was collected under vacuum.

6.3. General procedure for the one-pot synthesis of 3-cyano-3,4-dihydro-2-pyridones



In a 5 mL ace-glass pressure tube were placed aldehyde (0.27 mmol), 1,3-dicarbonyl compound (0.27 mmol, 1.0 equiv.), malononitrile (0.27 mmol, 1.0 equiv.), 25 mg of PW-MIM-MCF catalyst and the mixture EtOH: H_2O (1:1) as solvent. The reaction mixture was stirred at 120 °C until starting material was consumed. The reaction progress was monitored by TLC using EtOAc: hexane (3:7) and (5:5) as eluent. Product was recovered precipitation and recrystallization with EtOH. Column chromatography was performed when needed using EtOAc: hexane as eluent and pure product was collected under vacuum.

Ethyl 5-cyano-2-methyl-4-(1-propyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5a**)

White solid, 80% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.19 (q, J = 7.0 Hz, 2H), 2.32 (t, J = 8.1 Hz, 2H),), 2.32 (s, 3H), 1.59-1.53 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.50, 165.64, 152.81, 141.94, 113.91, 106.24, 99.14, 61.03, 33.76, 23.03, 19.42, 14.11.

Ethyl 5-cyano-2-methyl-4-phenyl-6-oxo-1,6-dihydropyridine-3-carboxylate (**5b**)

Light brown solid, 83 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dt, J = 5.9, 3.0 Hz, 3H), 7.39 – 7.33 (m, 2H), 3.90 (q, J = 7.1 Hz, 2H), 2.62 (s, 3H), 0.80 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 162.8, 161.1, 152.4, 135.6, 130.1, 128.8, 127.4, 114.9, 114.6, 101.6, 61.8, 19.0, 13.4.

Ethyl 5-cyano-2-methyl-4-(4-bromophenyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5c**)

White solid, 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.68 (s, 1H), 7.47 (dd, J = 5.0, 1.8 Hz, 2H), 7.42 – 7.30 (m, 2H), 3.91 (q, J = 7.1 Hz, 2H), 2.62 (s, 3H), 0.80 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 163.3, 154.0, 145.4, 134.3, 128.8, 126.2, 119.9, 114.3, 102.4, 99.8, 61.0, 19.4, 14.1.

Ethyl 5-cyano-2-methyl-4-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5d**)

White solid, 86% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.07 (s, 1H), 7.55 – 7.51 (m, 1H), 7.03 – 6.99 (m, 1H), 4.19 (q, J = 7.0 Hz, 1H), 3.81 (s, 1H), 2.36 (s, 1H), 1.26 (t, J = 7.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.2, 160.3, 159.9, 159.1, 152.6, 128.9, 127.7, 115.7, 113.8, 111.4, 101.2, 61.0, 55.3, 18.1, 13.3.

Ethyl 5-cyano-2-methyl-4-(3-nitrophenyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5e**)

Beige solid, 90% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.14 (s, 1H), 8.37 (d, J = 7.3 Hz, 1H), 8.20 (s, 1H), 7.84 (s, 2H), 3.84 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 0.72 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.3, 159.5, 157.3, 154.7, 147.6, 137.8, 134.1, 130.4, 124.2, 122.1, 115.1, 111.2, 101.5, 61.0, 18.7, 13.2

Ethyl 5-cyano-2-methyl-4-(2-thienyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5f**)

White solid, 56% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.00 (s, 1H), 7.85 (dd, J = 5.0, 1.2 Hz, 1H), 7.31 (dd, J = 3.6, 1.2 Hz, 1H), 7.21 (dd, J = 5.0, 3.6 Hz, 1H), 3.95 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 0.90 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.4, 160.2, 153.2, 152.2, 135.4, 130.3, 130.0, 128.2, 115.9, 112.9, 101.12, 61.8, 18.6, 13.8.

Tert-butyl 5-cyano-2-methyl-4-(1-propyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5g**)

Beige solid, 77% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.36 (3H, s), 2.29 (t, J = 5.0 Hz, 3H), 1.49-1.39 (m, 2H), 1.38-1.28 (m, 2H), 1.34 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) 168.7, 166.5, 152.8, 141.5, 113.9, 109.2, 99.4, 81.9, 30.8, 28.7, 28.1, 22.6, 19.4, 13.7.

Tert-butyl 5-cyano-2-methyl-4-phenyl-6-oxo-1,6-dihydropyridine-3-carboxylate (**5h**)

Brown solid, 87% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.43 – 7.33 (m, 3H), 7.27 – 7.18 (m, 2H), 2.36 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.4, 164.0, 151.8, 143.3, 132.6, 129.4, 129.3, 128.96, 114.7, 105.6, 99.0, 81.9, 28.2, 19.4.

Tert-butyl 5-cyano-2-methyl-4-(4-bromophenyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5i**)

Brown yellowish solid, 89% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 2.36 (s, 3H), 1.32 (s, 9H). δ 166.8, 166.3, 154.1, 145.4, 134.3, 128.8, 126.2, 119.8, 114.3, 105.5, 99.8, 81.6, 28.2, 19.4.

Tert-butyl 5-cyano-2-methyl-4-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5j**)

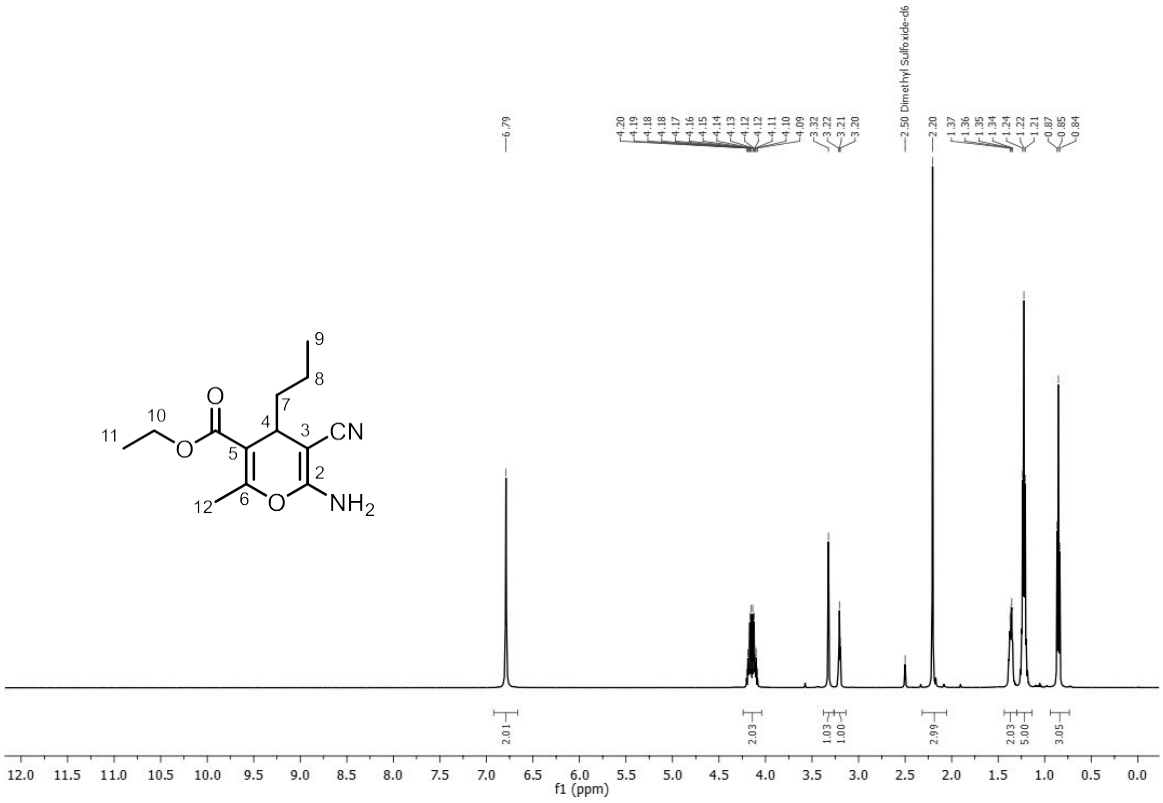
Beige solid, 85% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.54 (d, J = 8.8 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H), 3.81 (s, 1H), 2.36 (s, 1H), 1.32 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.8, 166.5, 157.9, 154.0, 145.4, 131.3, 130.1, 114.2, 113.0, 105.5, 99.8, 81.9, 55.4, 28.0, 19.4.

Tert-butyl l 5-cyano-2-methyl-4-(3-nitrophenyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5k**)

Red brown solid, 90% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.13 (dt, J = 8.0, 1.6 Hz, 1H), 7.91 (t, J = 1.9 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.57 (t, J = 8.0 Hz, 1H), 2.36 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.8, 166.4, 154.1, 147.0, 146.1, 134.5, 131.1, 129.4, 125.0, 124.3, 114.7, 105.50, 100.3, 81.9, 28.0, 19.2.

Tert-butyl 5-cyano-2-methyl-4-(2-thienyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (**5l**)

Dark brown solid, 45% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.63 (dd, J = 6.7, 1.7 Hz, 1H), 9.30 (dd, J = 5.1, 1.6 Hz, 1H), 7.94 (dd, J = 6.8, 5.1 Hz, 1H), 2.36 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.6, 154.7, 154.3, 144.5, 143.8, 138.5, 133.8, 128.5, 127.6, 115.4, 105. 6, 81.9, 28.1, 19.4.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4.11
4.10
4.09
3.32
3.22
3.21
3.20
2.50 Dimethyl Sulfoxide-d6
2.20
1.37
1.36
1.35
1.34
1.24
1.22
1.21
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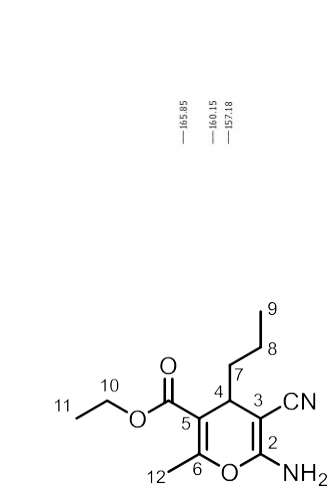
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10
11
O
5
2
12
6
O
NH2

165.85
160.15
157.18
120.35
107.86
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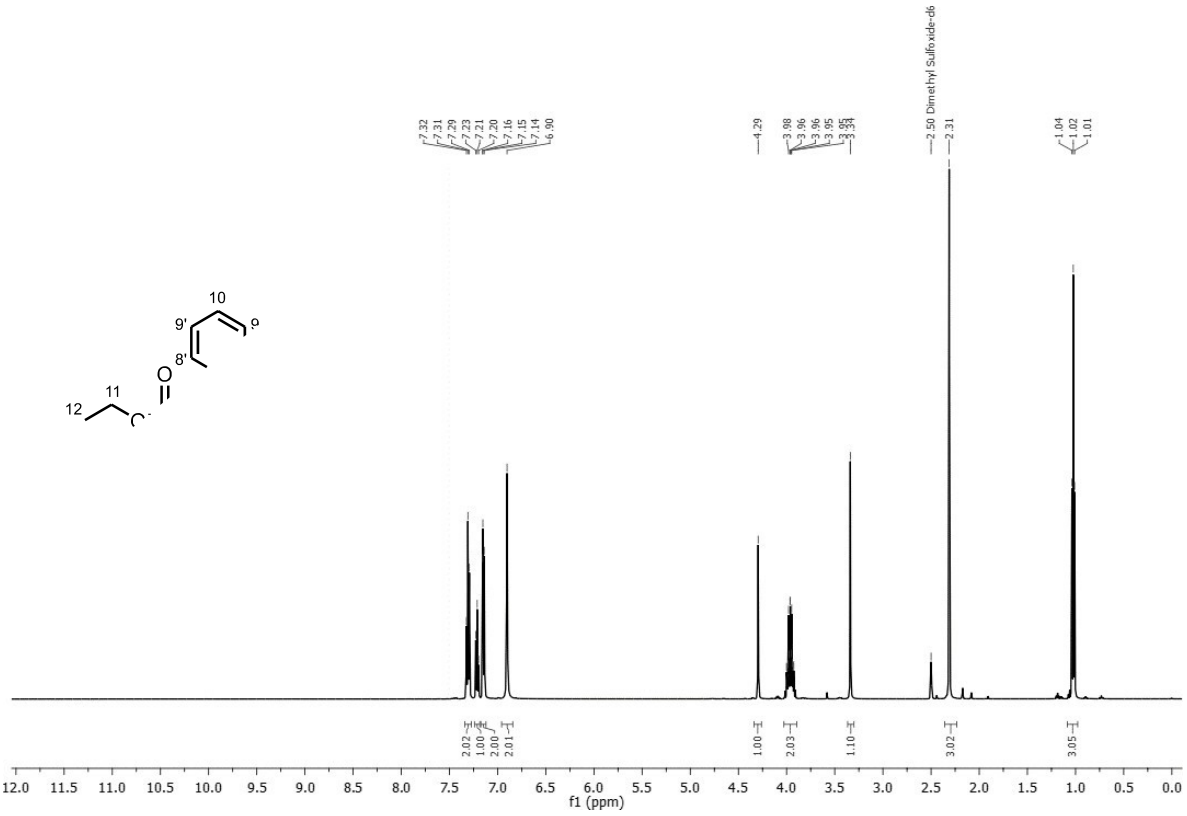
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3.96
3.96
3.95
3.95
3.94
2.50 Dimethyl Sulfoxide-d6
2.31
1.04
1.02
1.01
10
9'
8'
O
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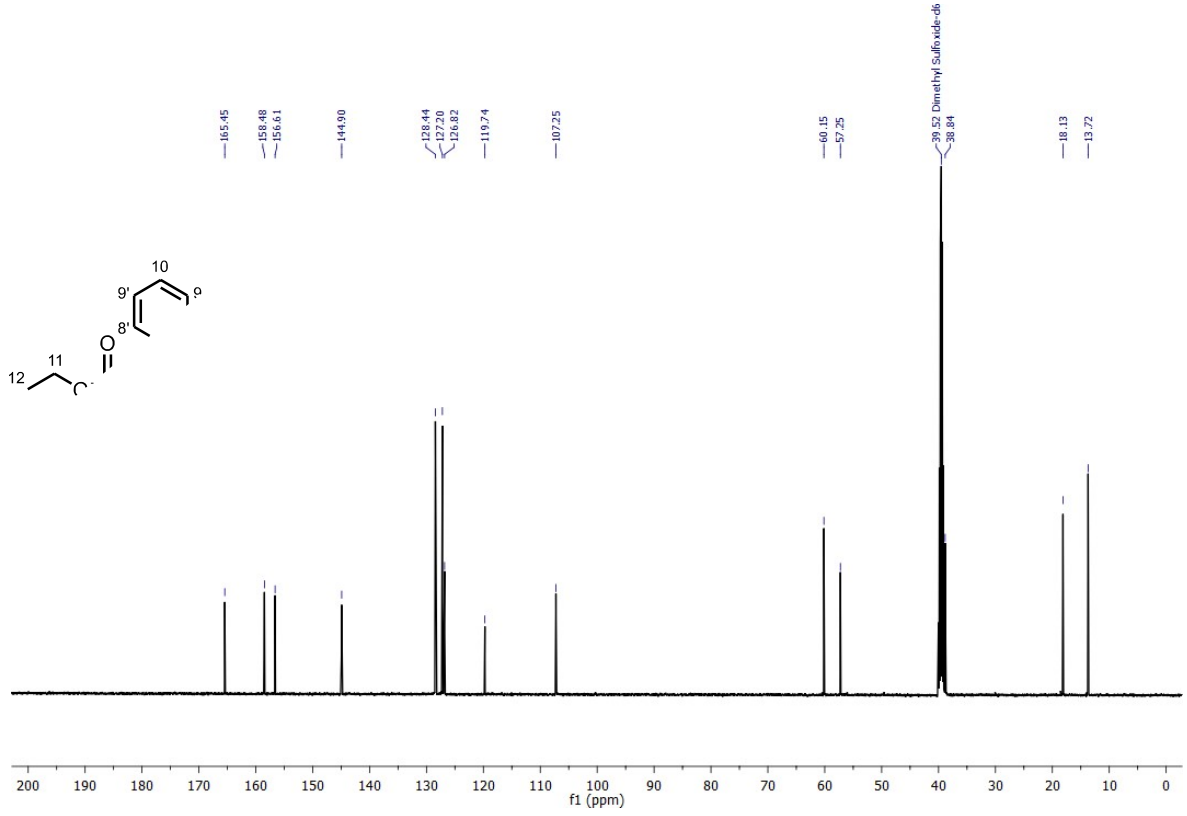
2.00
2.01
1.00
2.03
1.10
3.02
3.05
f1 (ppm)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18.13
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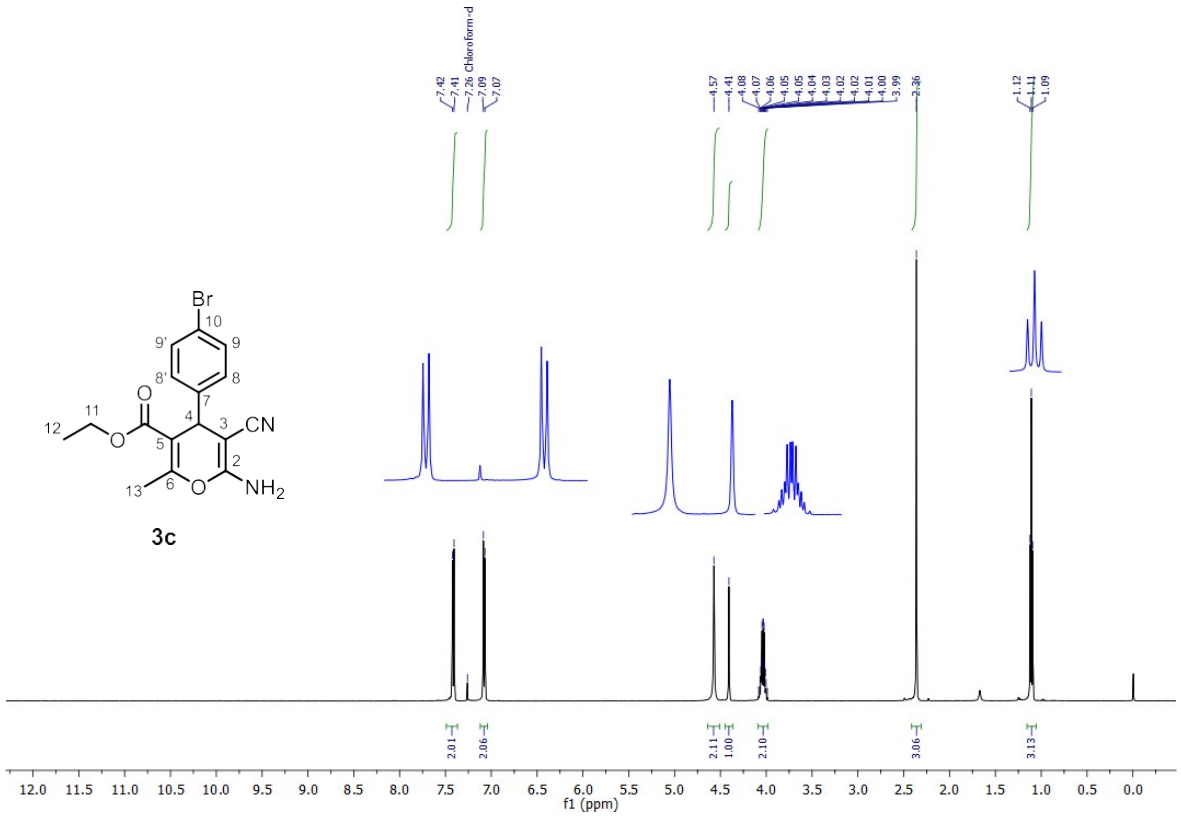
9'
8'
O
11
12
f1 (ppm)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4.04
4.03
4.02
4.02
4.02
4.01
4.00
3.99
2.36
1.12
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1.09
Br
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9
9'
8
8'
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2
NH2
6
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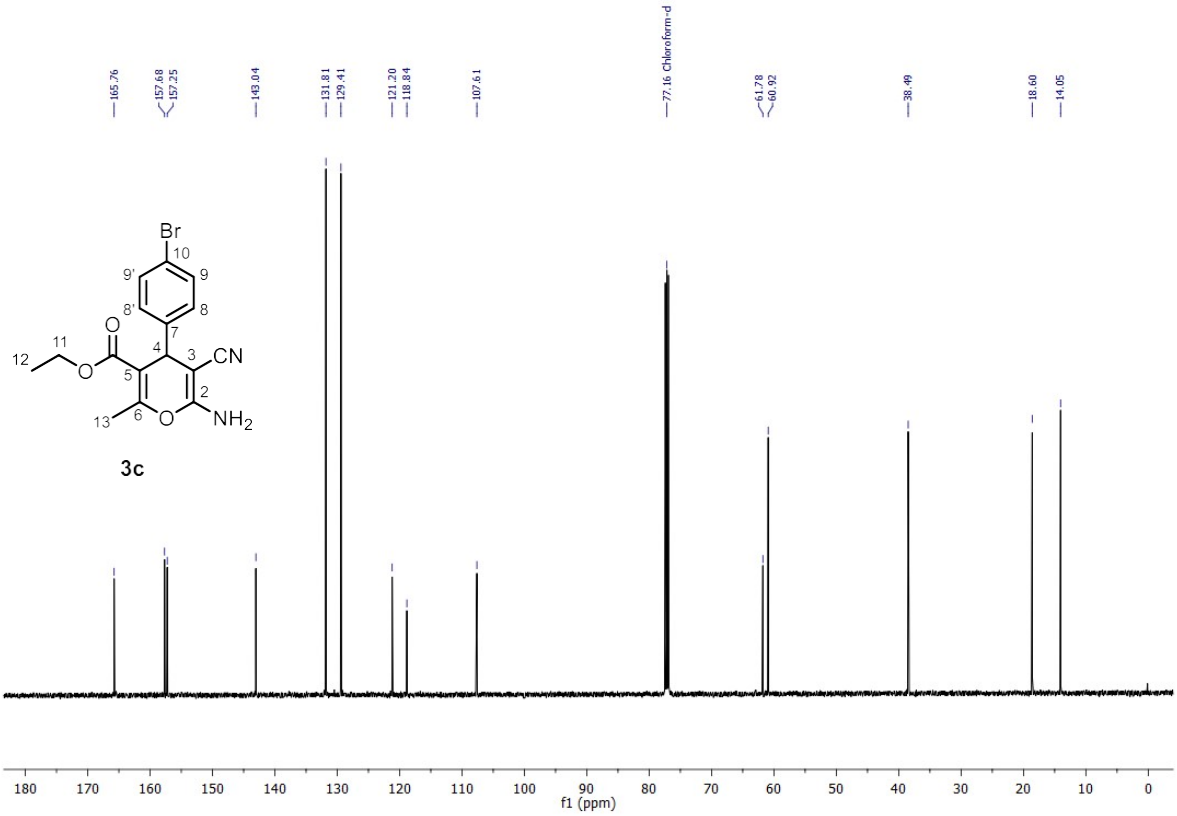
3.13
f1 (ppm)

3c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118.84
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60.92
38.49
18.60
14.05
Br
10
9
9'
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4
3
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NH2
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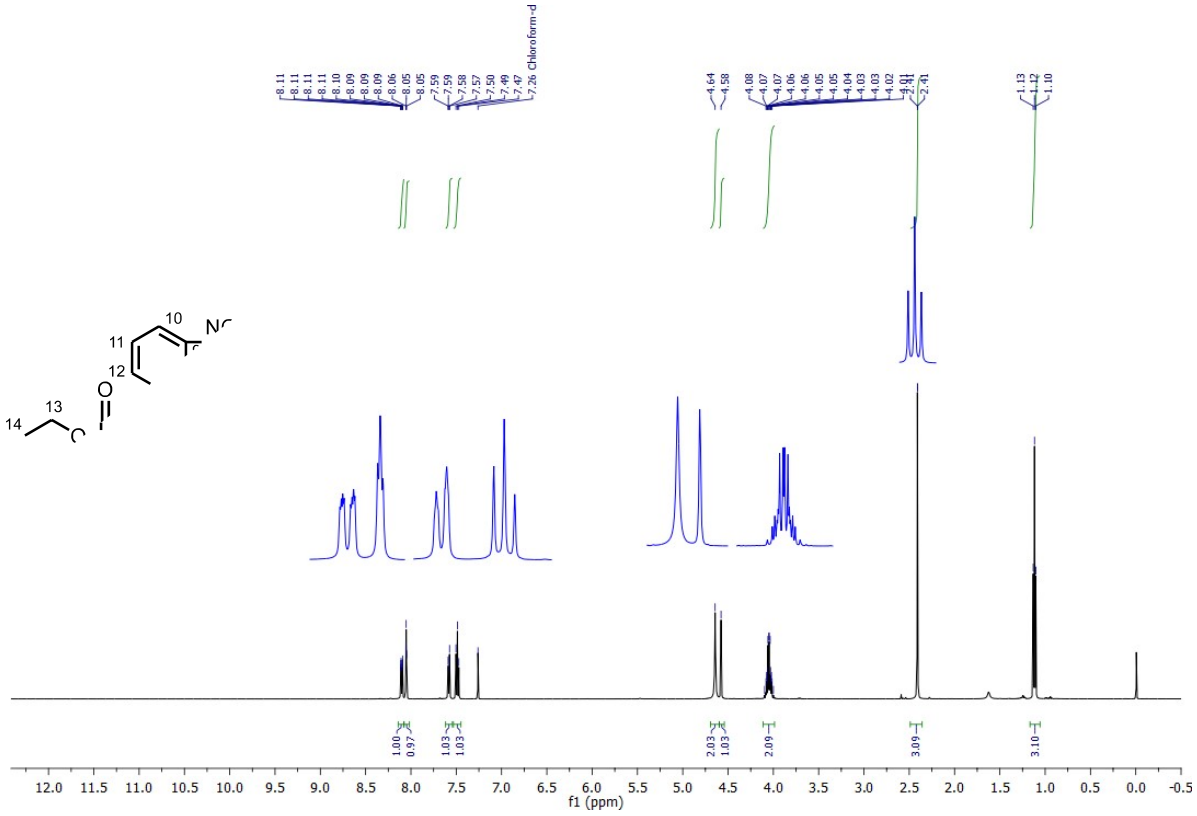
O
11
12
13
f1 (ppm)

3c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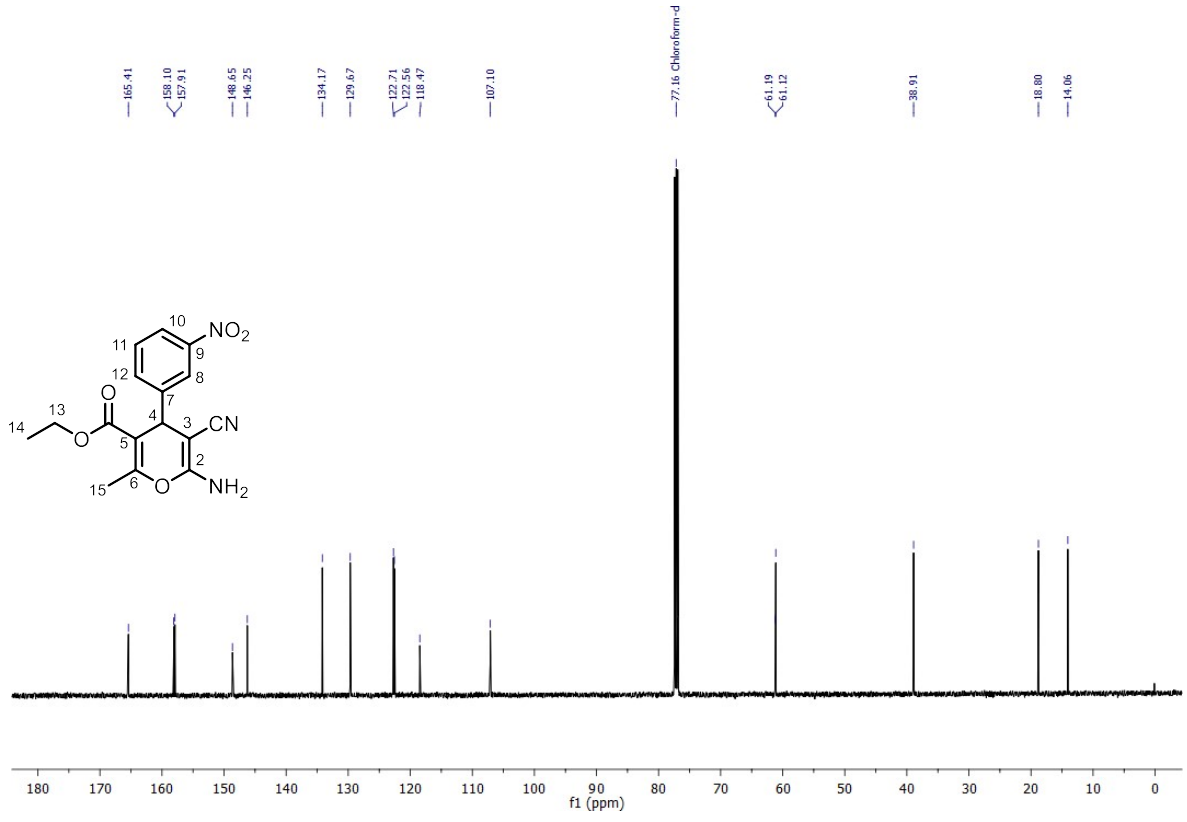
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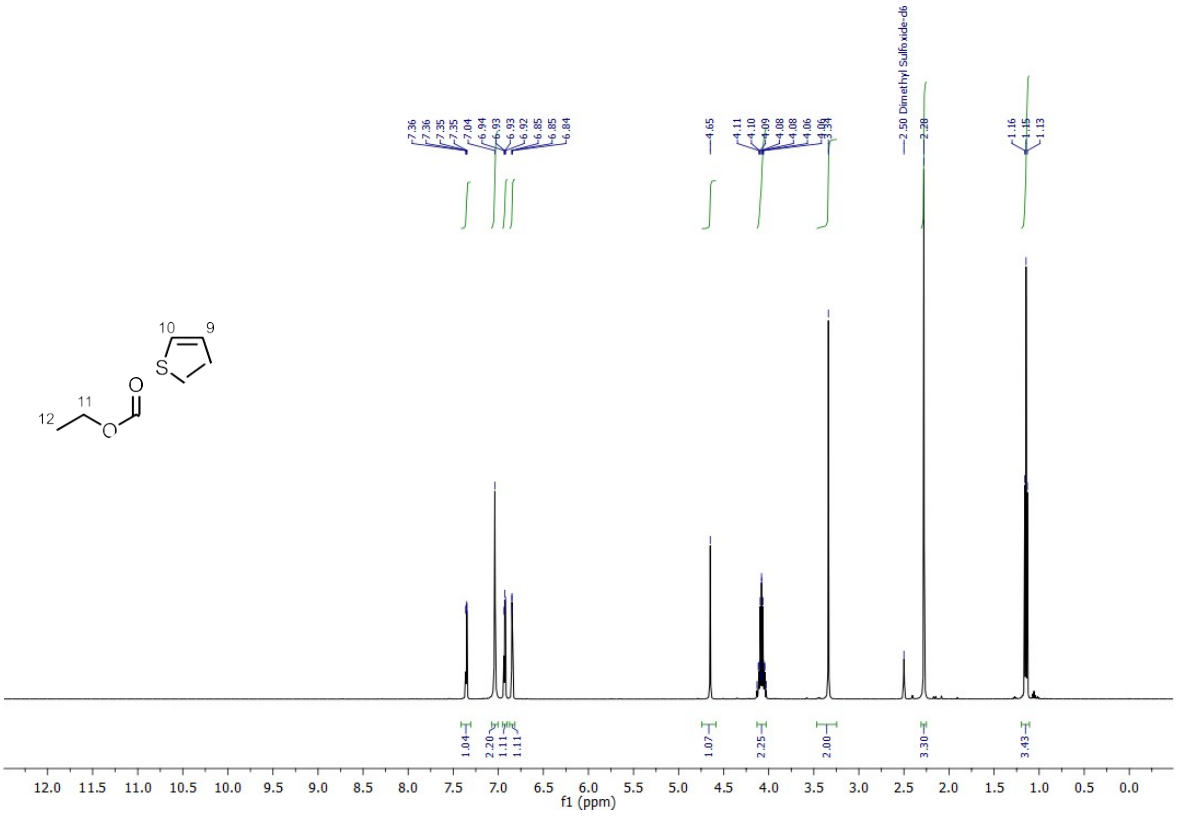
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6.93
6.92
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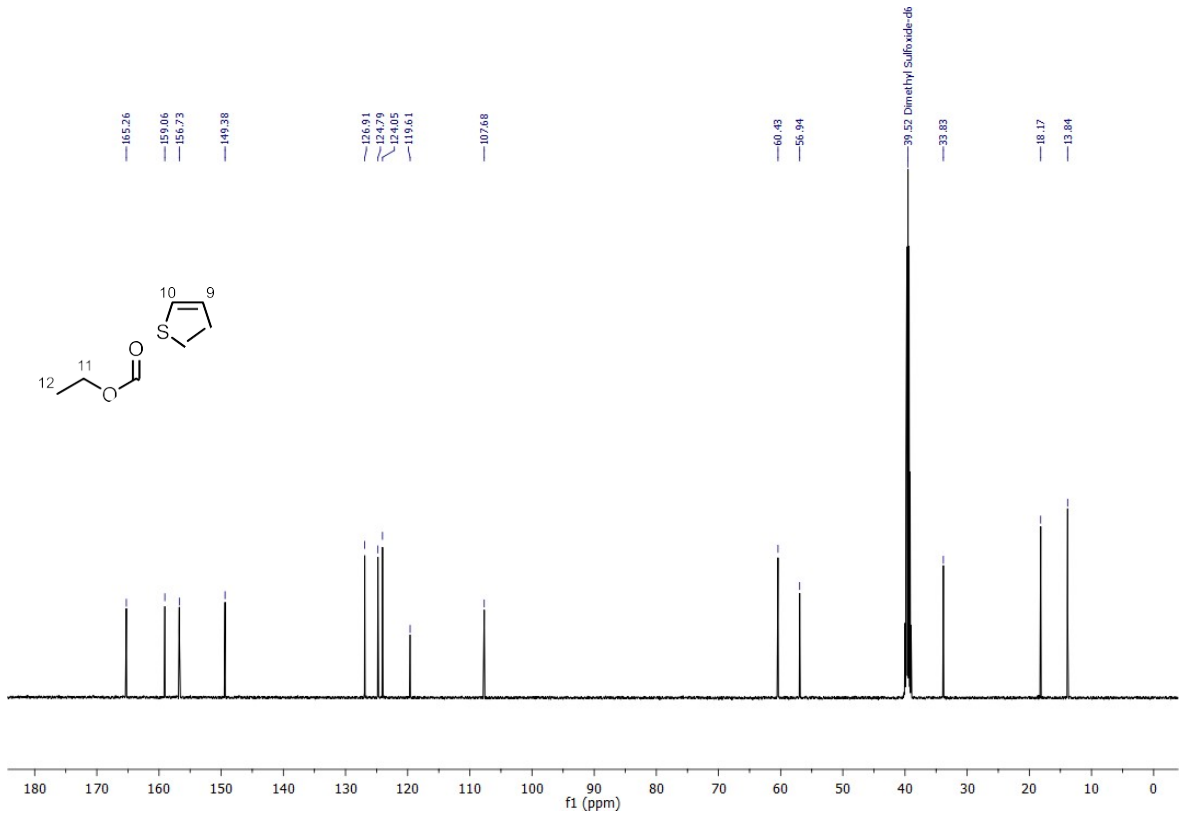
6.85
6.84
4.65
4.11
4.10
4.09
4.08
4.08
4.06
3.34
2.50 Dimethyl Sulfoxide-d6
2.20
1.16
1.15
1.13
10
9
S
O
11
12
O
1.04
2.20
1.11
1.11
1.07
2.25
2.00
3.30
3.43
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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33.83
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O
11
12
O
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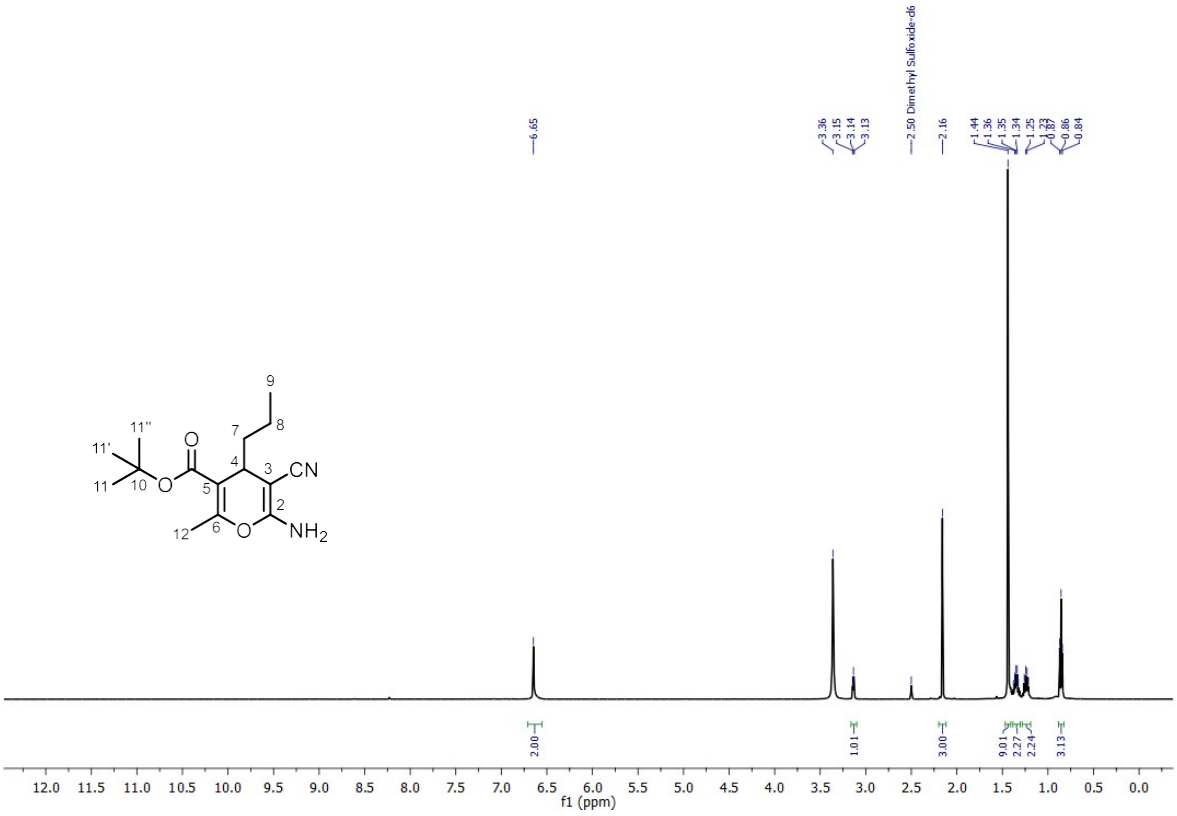
f1 (ppm)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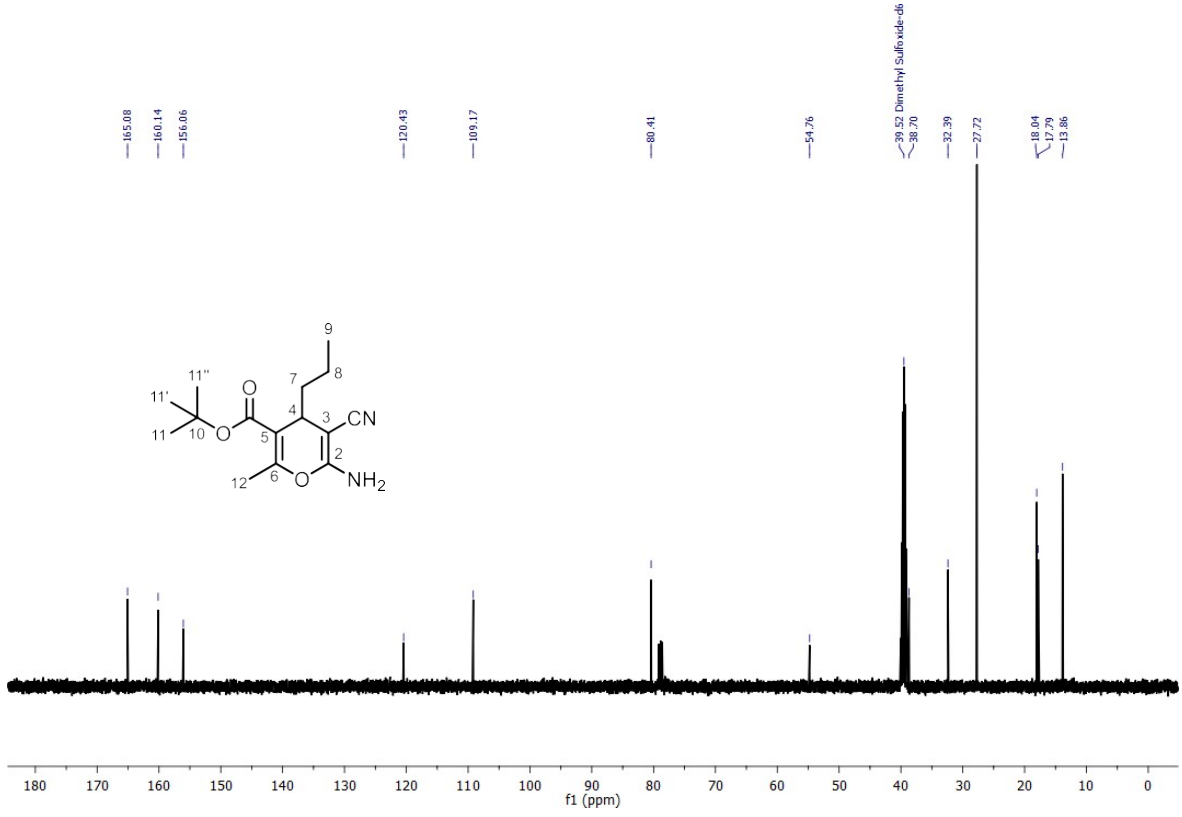
3.13
f1 (ppm)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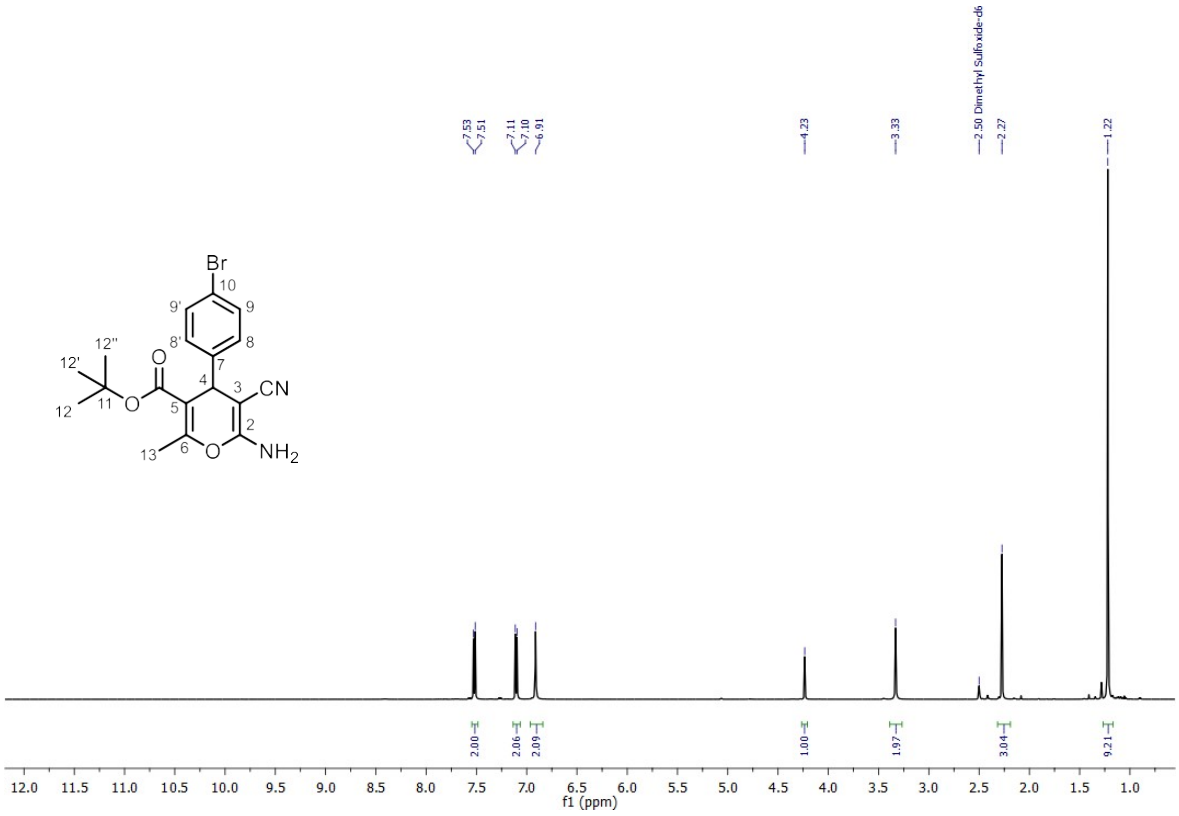
13.86
f1 (ppm)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8'
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NH2
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5
O
11
12
12'
12''
13
7.53
7.51
7.11
7.10
6.91
4.23
3.33
2.50 Dimethyl Sulfoxide-d6
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1.97
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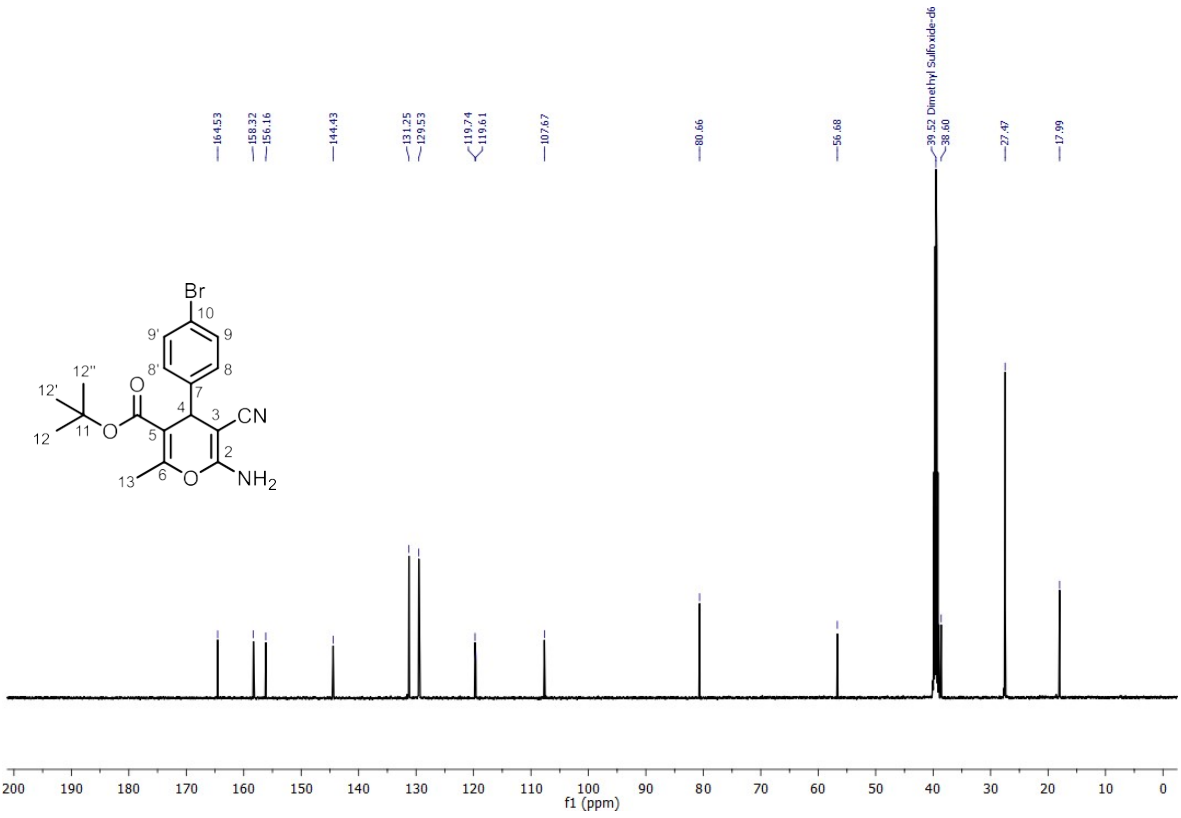
f1 (ppm)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9'
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8'
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NH2
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O
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12
12'
12''
13
164.53
158.32
156.16
144.43
131.25
129.53
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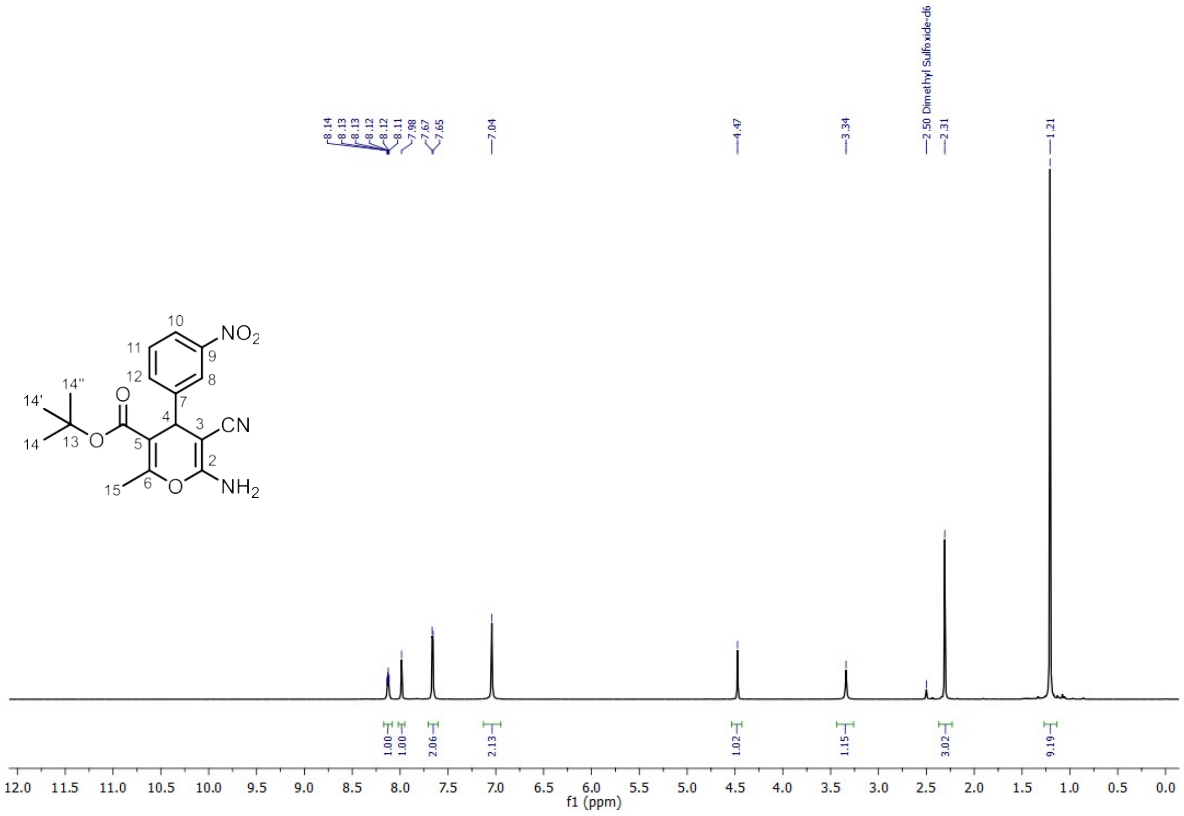
17.99
f1 (ppm)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7.65
7.04
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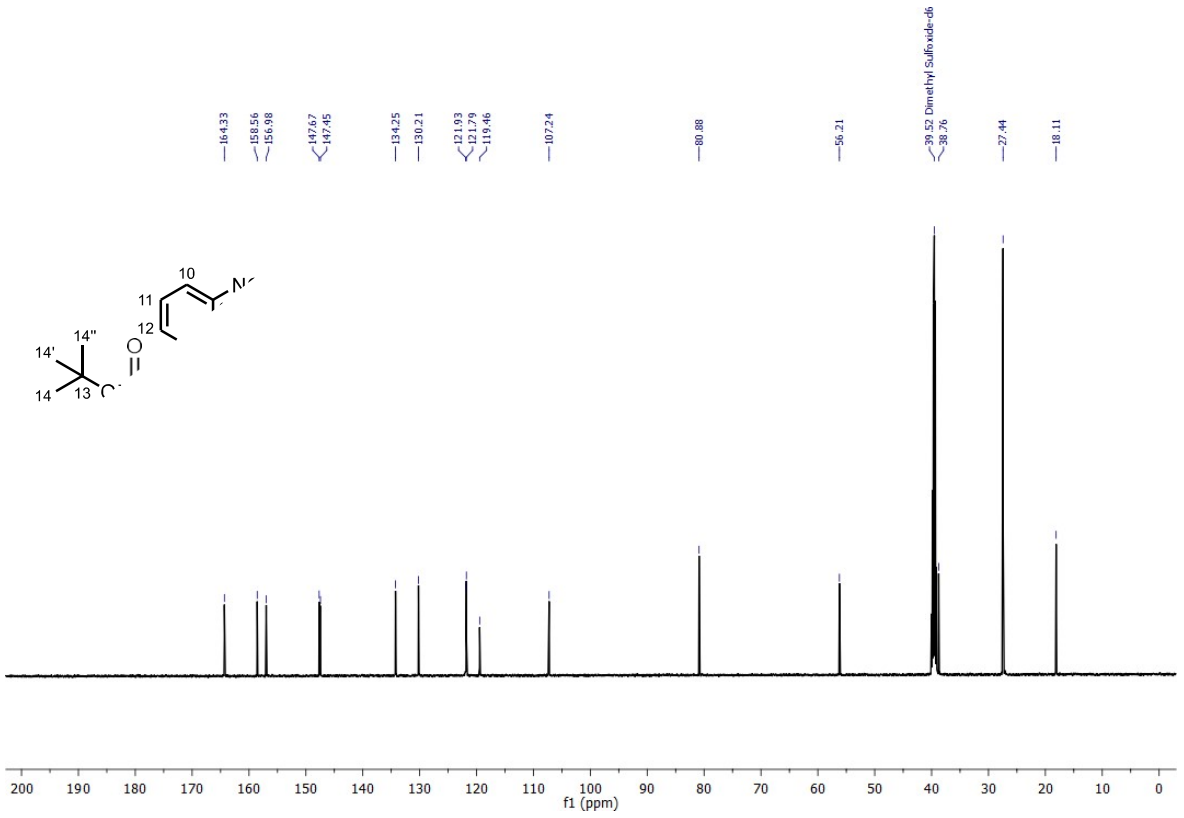
9.19
f1 (ppm)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39.52 Dimethyl Sulfoxide-d6
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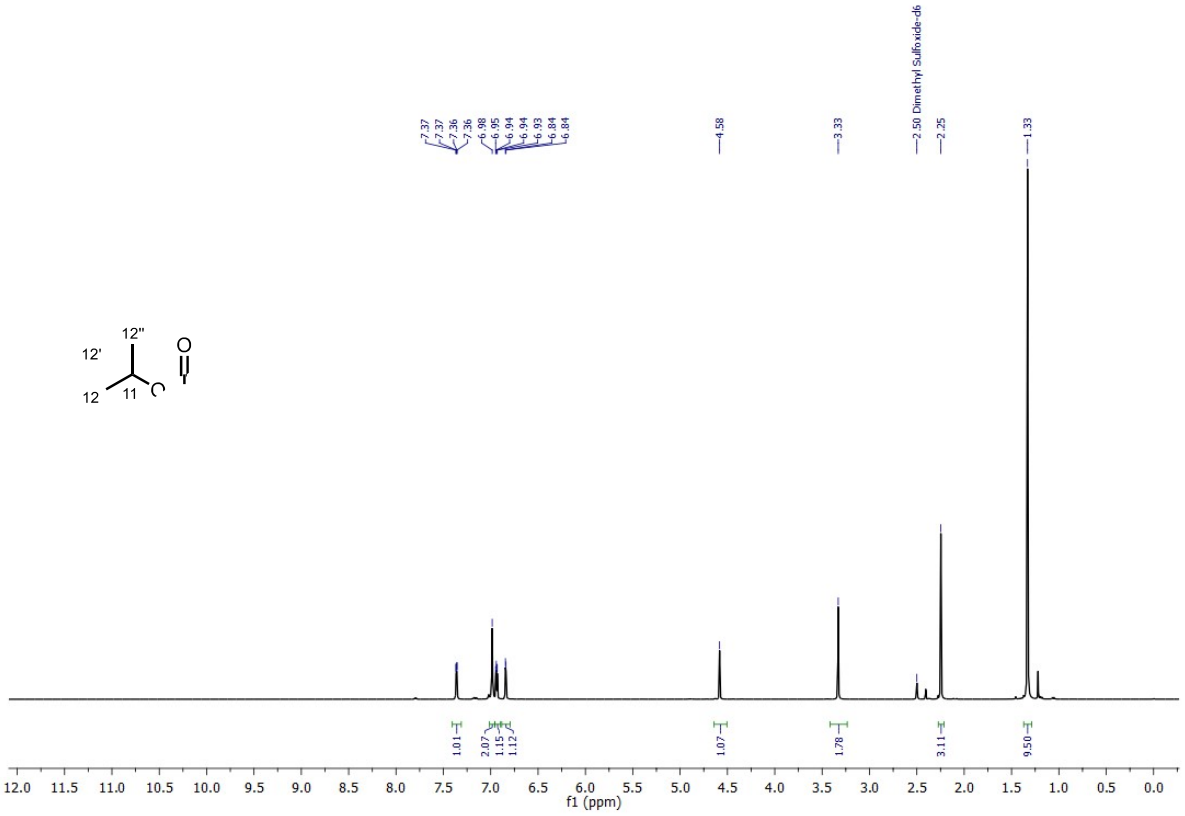
18.11
f1 (ppm)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6.94
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6.93
6.84
6.84
4.58
3.33
2.50 Dimethyl Sulfoxide-d6
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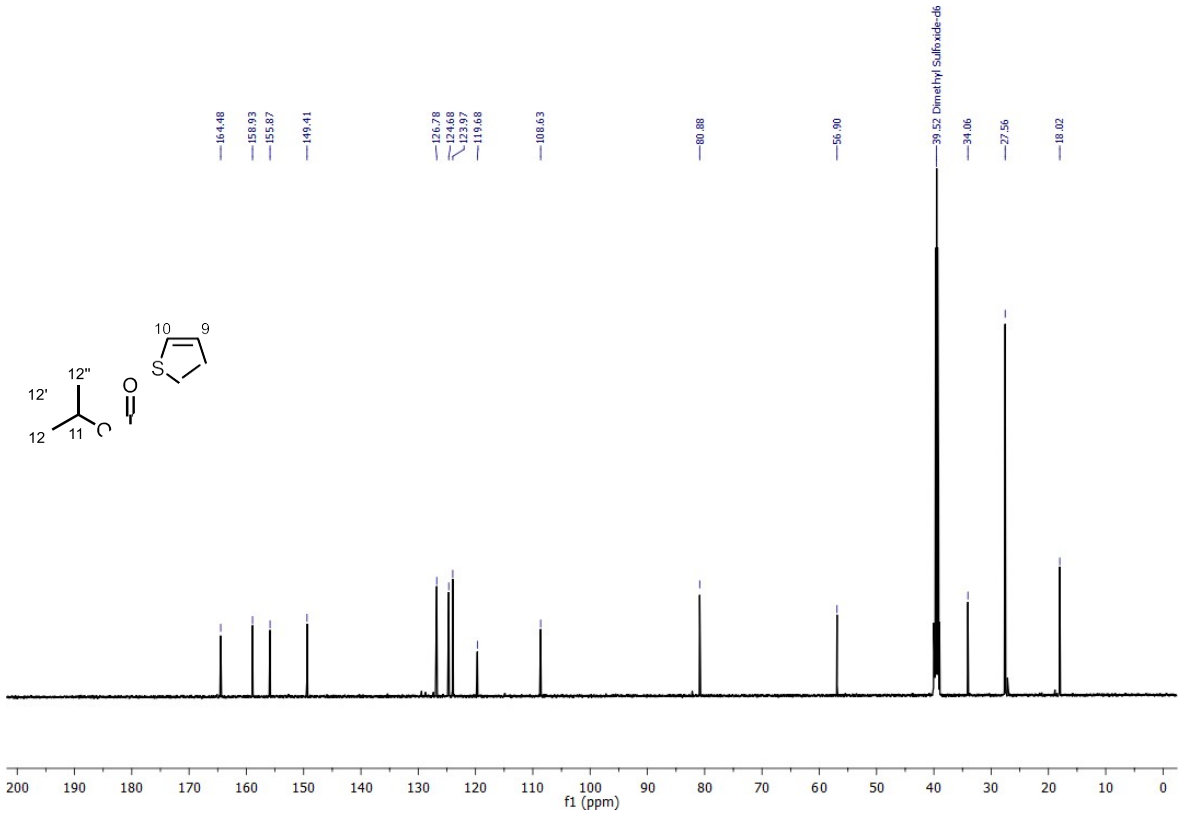
1.78
3.11
9.50
f1 (ppm)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12'
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O
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155.87
149.41
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124.68
123.97
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108.63
80.88
56.90
39.52 Dimethyl Sulfoxide-d6
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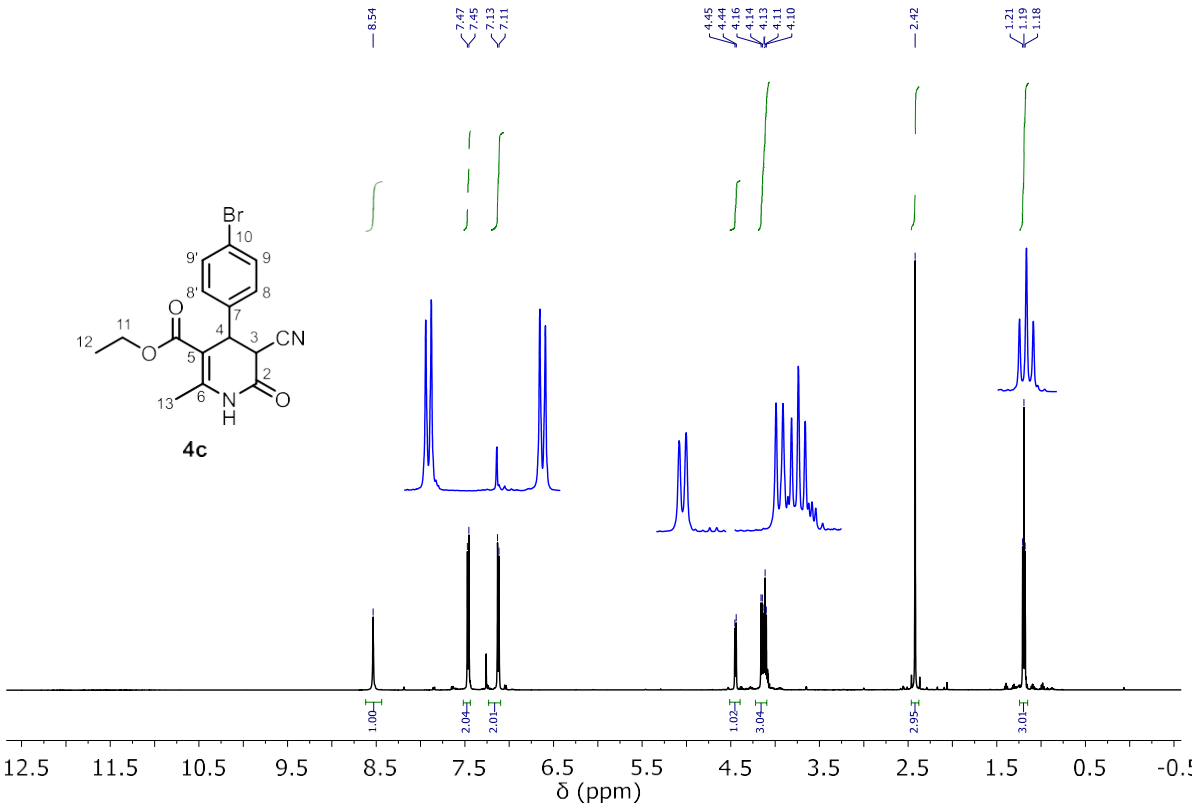
27.56
18.02
f1 (ppm)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1.21
1.19
1.18
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CN
O
N
H
4c
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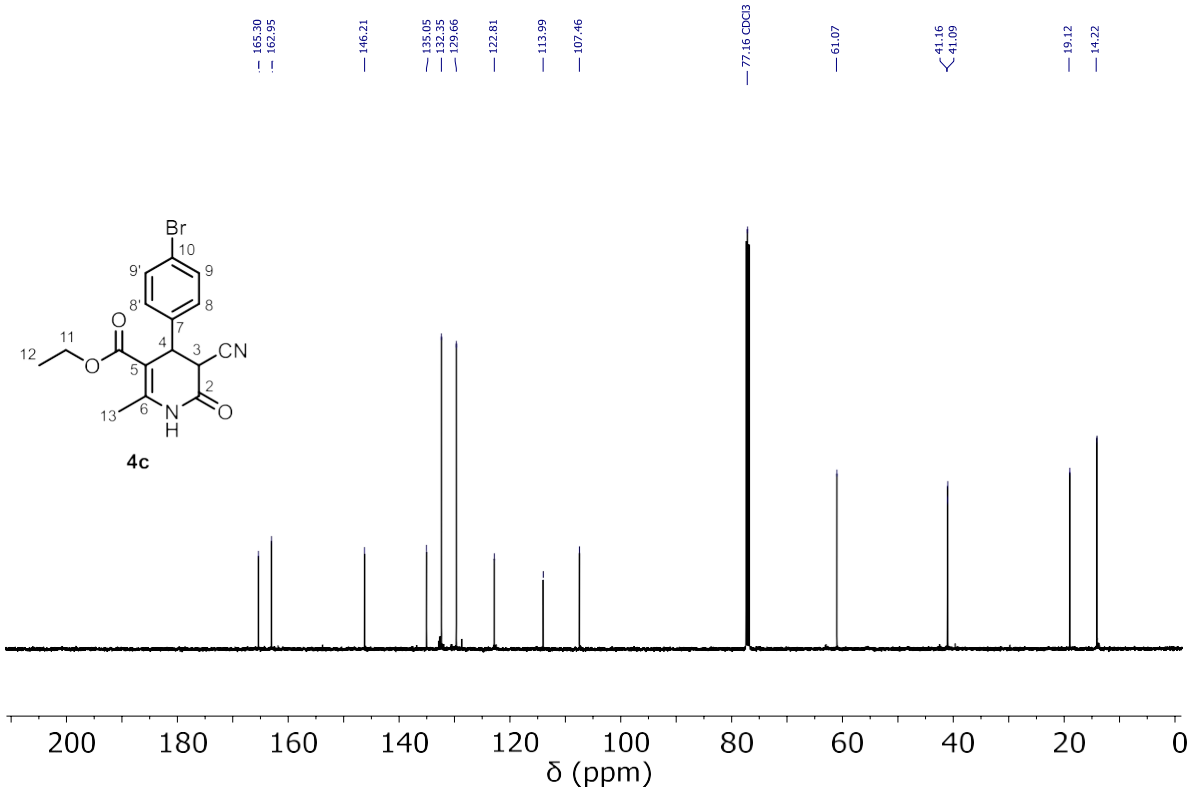
2.01
1.02
3.04
2.95
3.01
δ (ppm)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41.09
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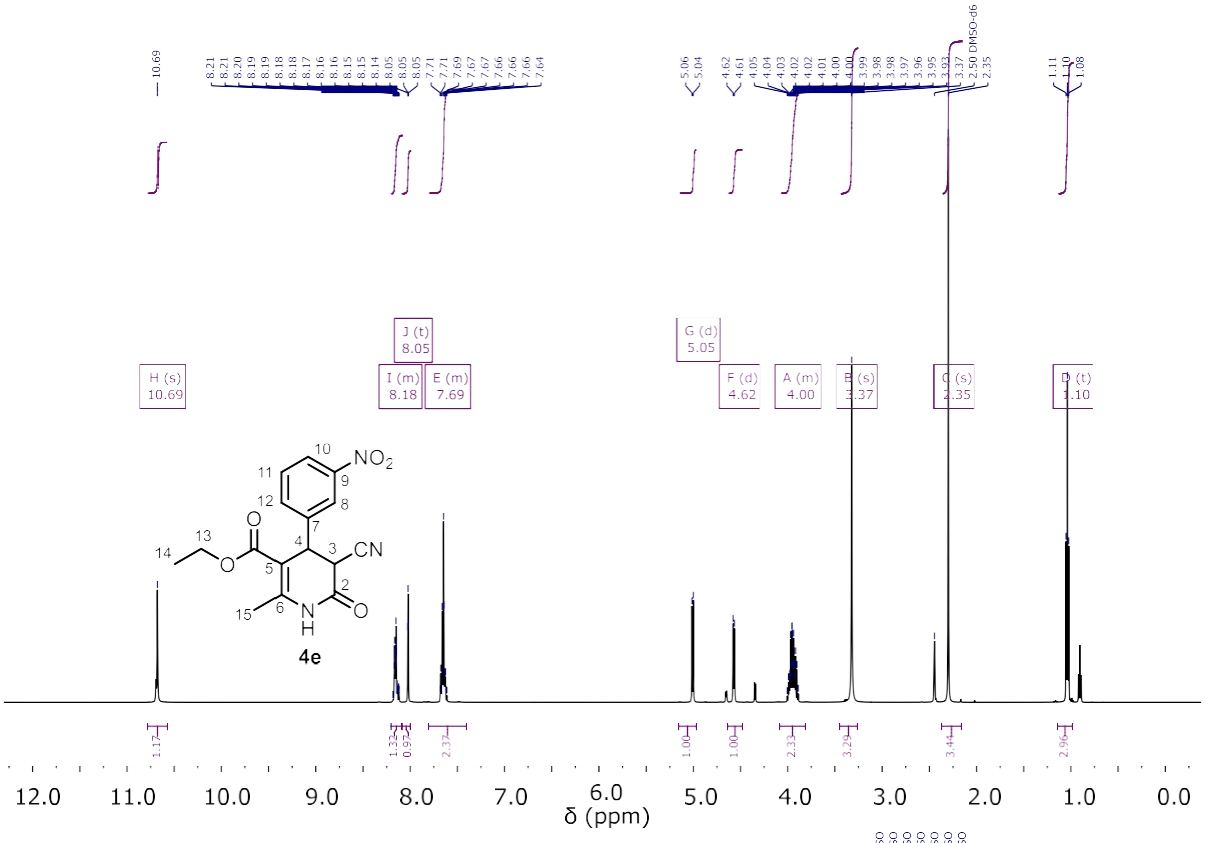
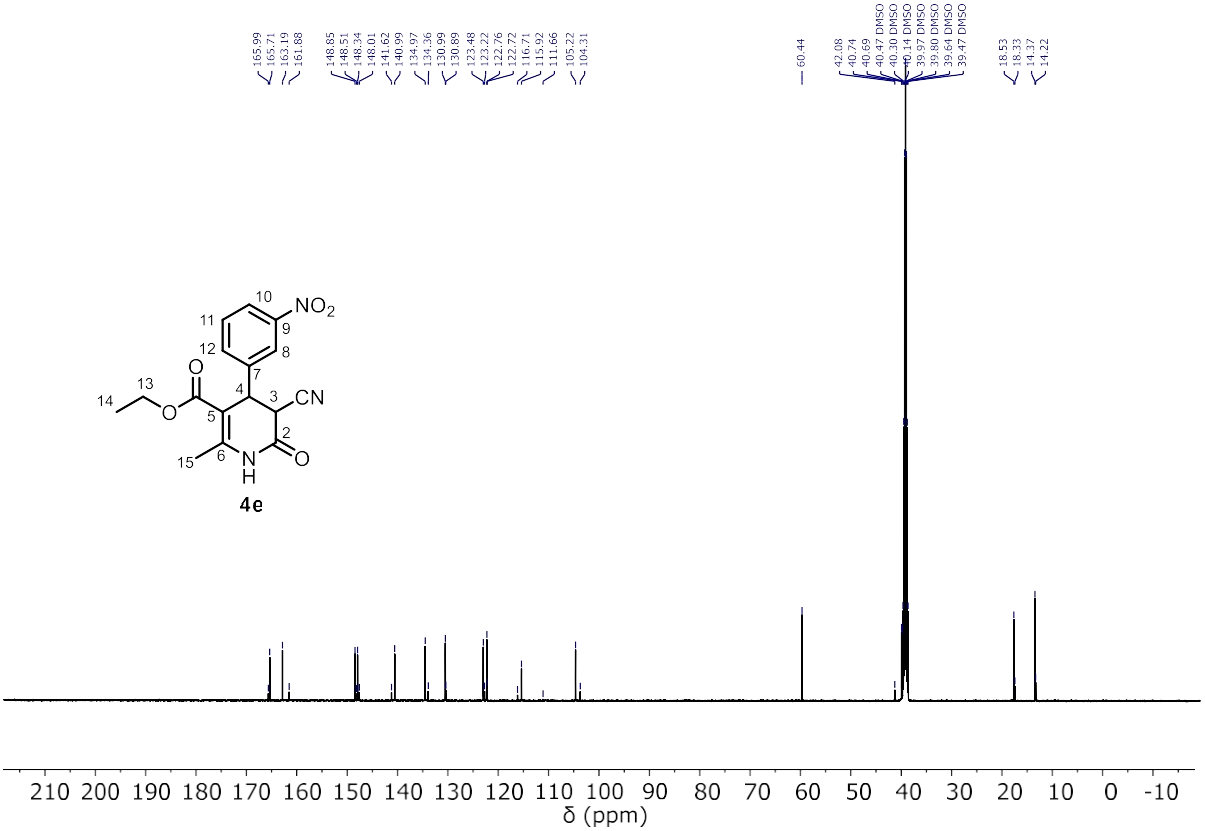
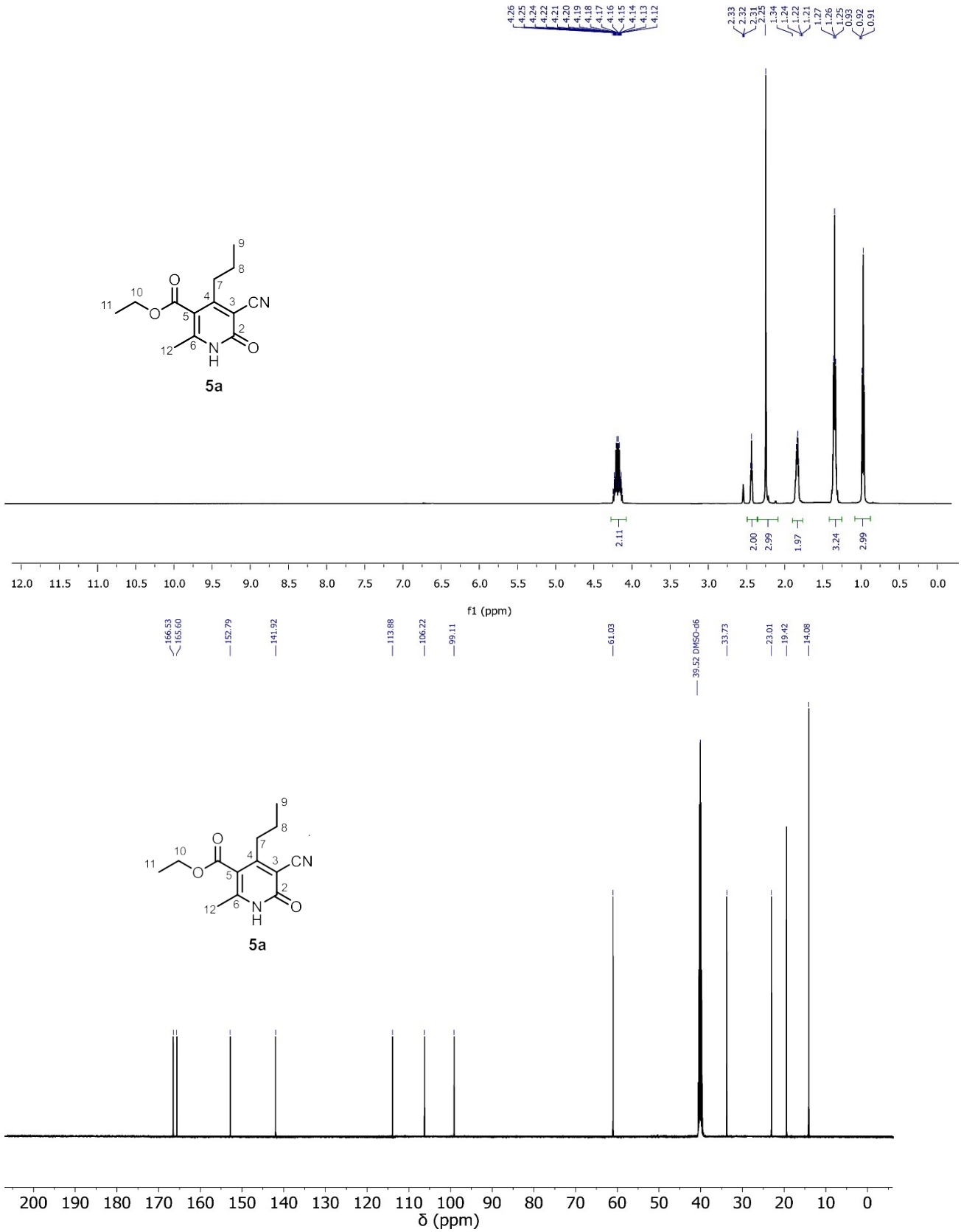
14.22
Br
CN
O
N
H
4c
δ (ppm)

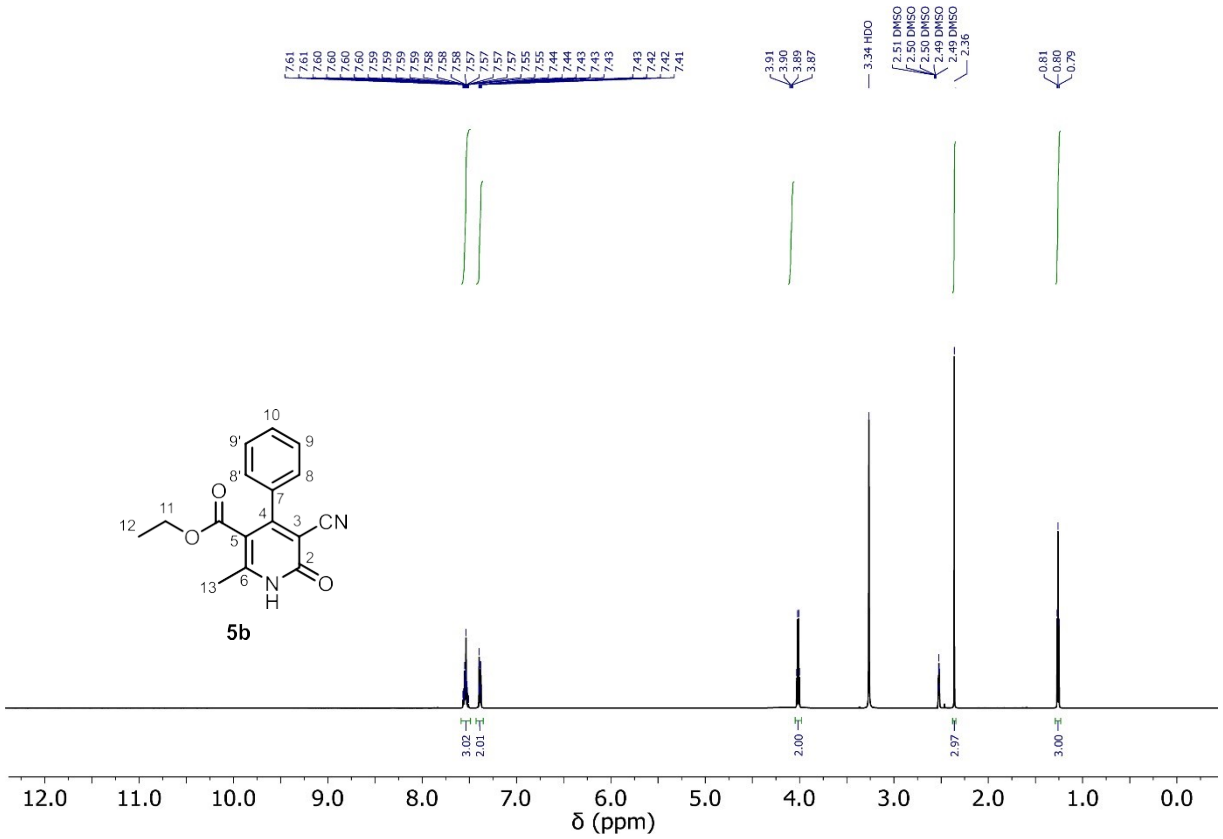

H (s) 10.69
J (t) 8.05
I (m) 8.18
E (m) 7.69
G (d) 5.05
F (d) 4.62
A (m) 4.00
B (s) 3.37
C (s) 2.35
D (t) 1.10
δ (ppm)

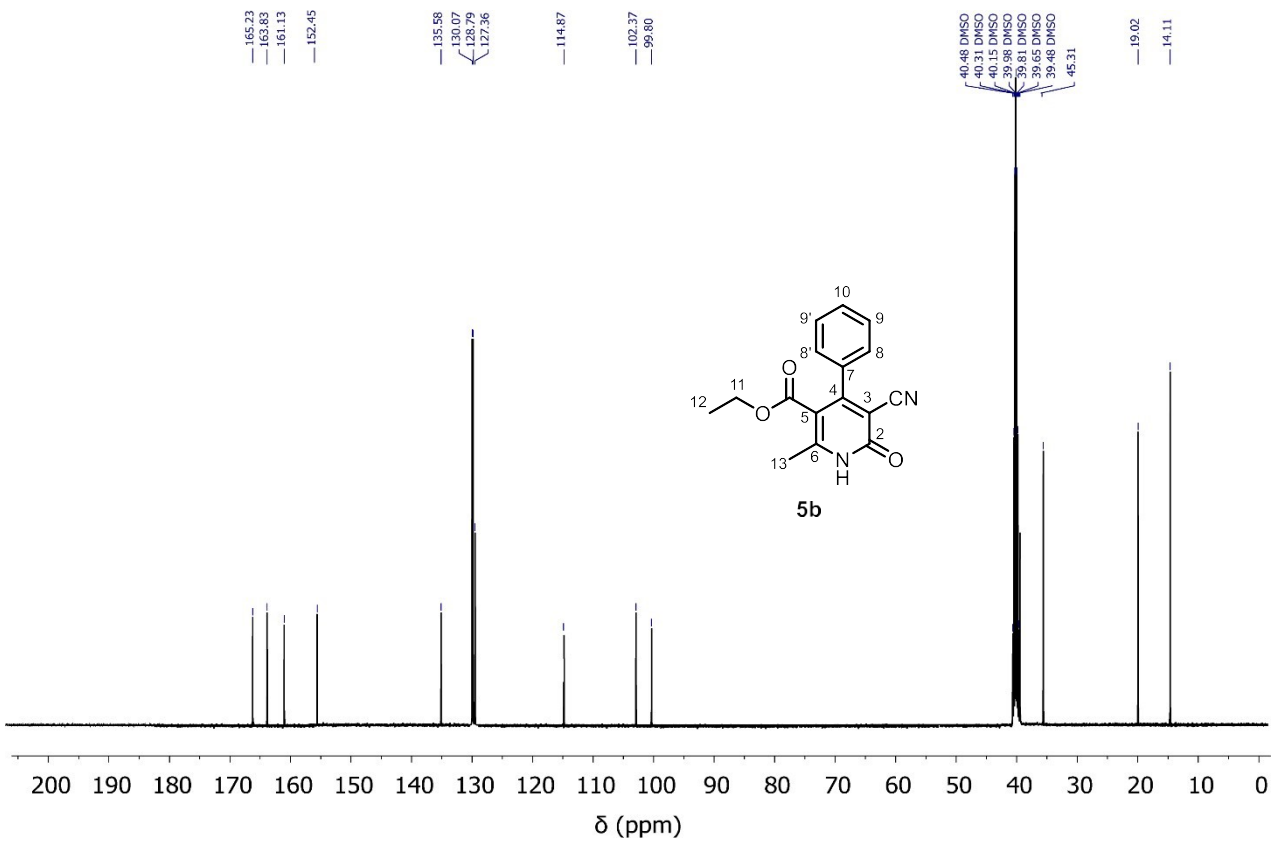
4e

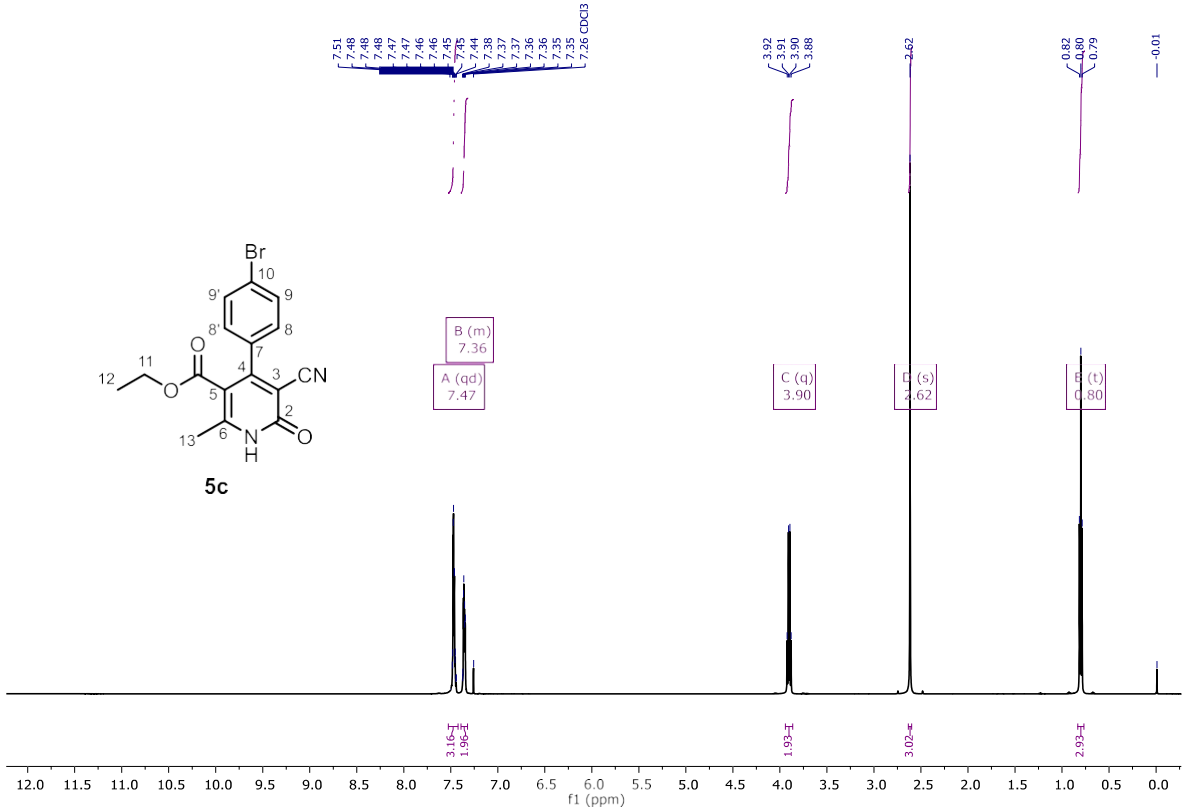

δ (ppm)

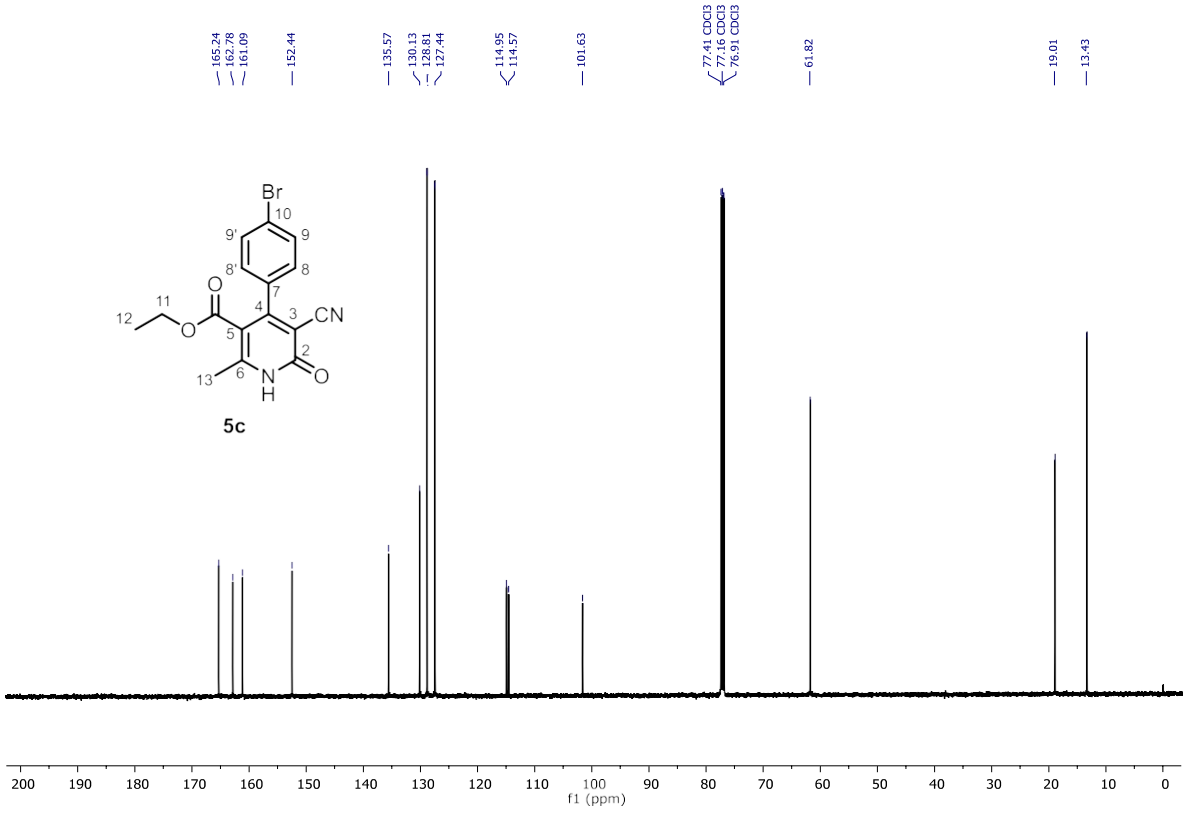
4e

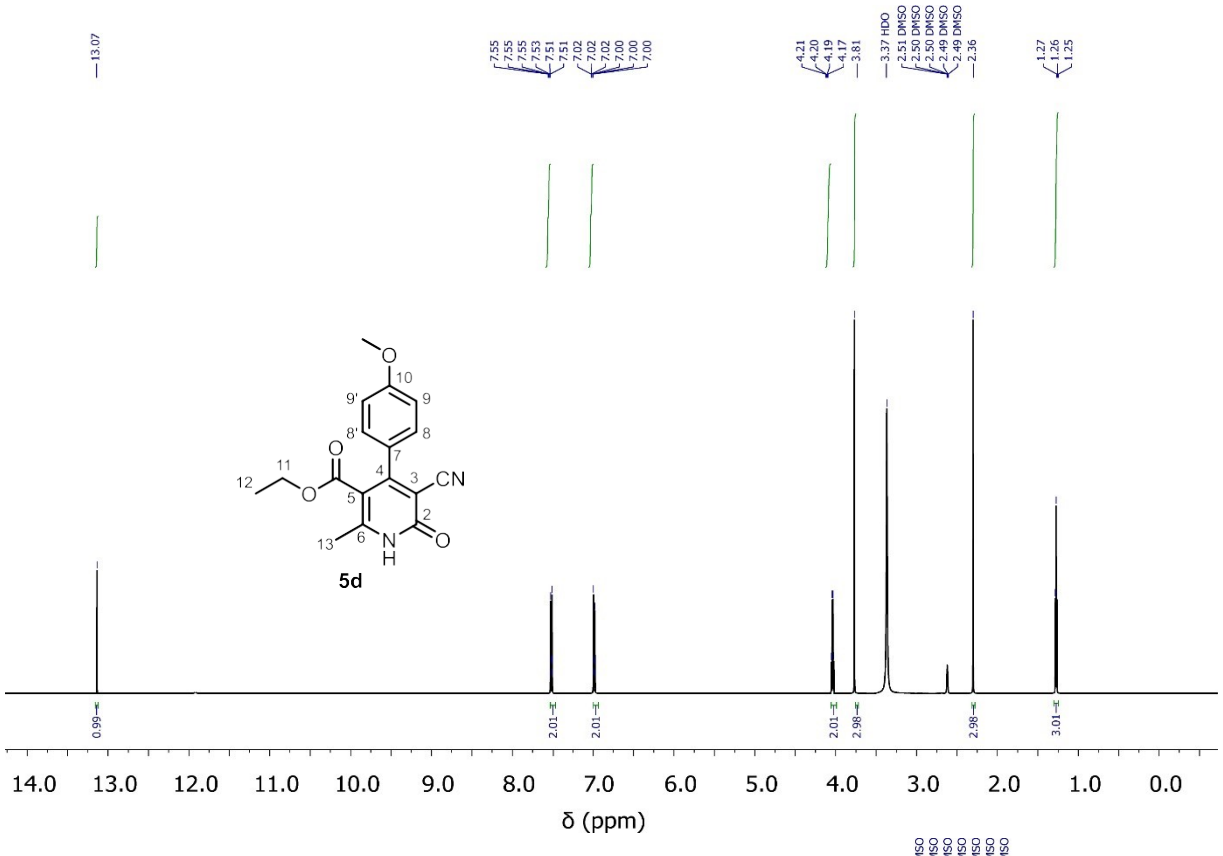

4.26
4.25
4.24
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
2.33
2.32
2.31
2.25
1.34
1.24
1.22
1.21
1.27
1.26
1.25
0.93
0.92
0.91
9
8
7
4
3
CN
10
11
O
5
2
O
12
6
N
H
O
5a
2.11
2.00
2.99
1.97
3.24
2.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
166.53
165.60
152.79
141.92
113.88
106.22
99.11
61.03
39.52 DMSO-d6
33.73
23.01
19.42
14.08
9
8
7
4
3
CN
10
11
O
5
2
O
12
6
N
H
O
5a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.61
7.61
7.60
7.60
7.60
7.60
7.59
7.59
7.59
7.59
7.58
7.58
7.58
7.58
7.57
7.57
7.57
7.57
7.57
7.55
7.44
7.44
7.43
7.43
7.43
7.43
7.42
7.42
7.41
3.91
3.90
3.89
3.87
3.34 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
2.36
0.81
0.80
0.79
10
9'
9
8'
8
7
4
3
CN
2
O
11
12
O
5
6
13
N
H
O
5b
3.02
2.01
2.00
2.97
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
δ (ppm)

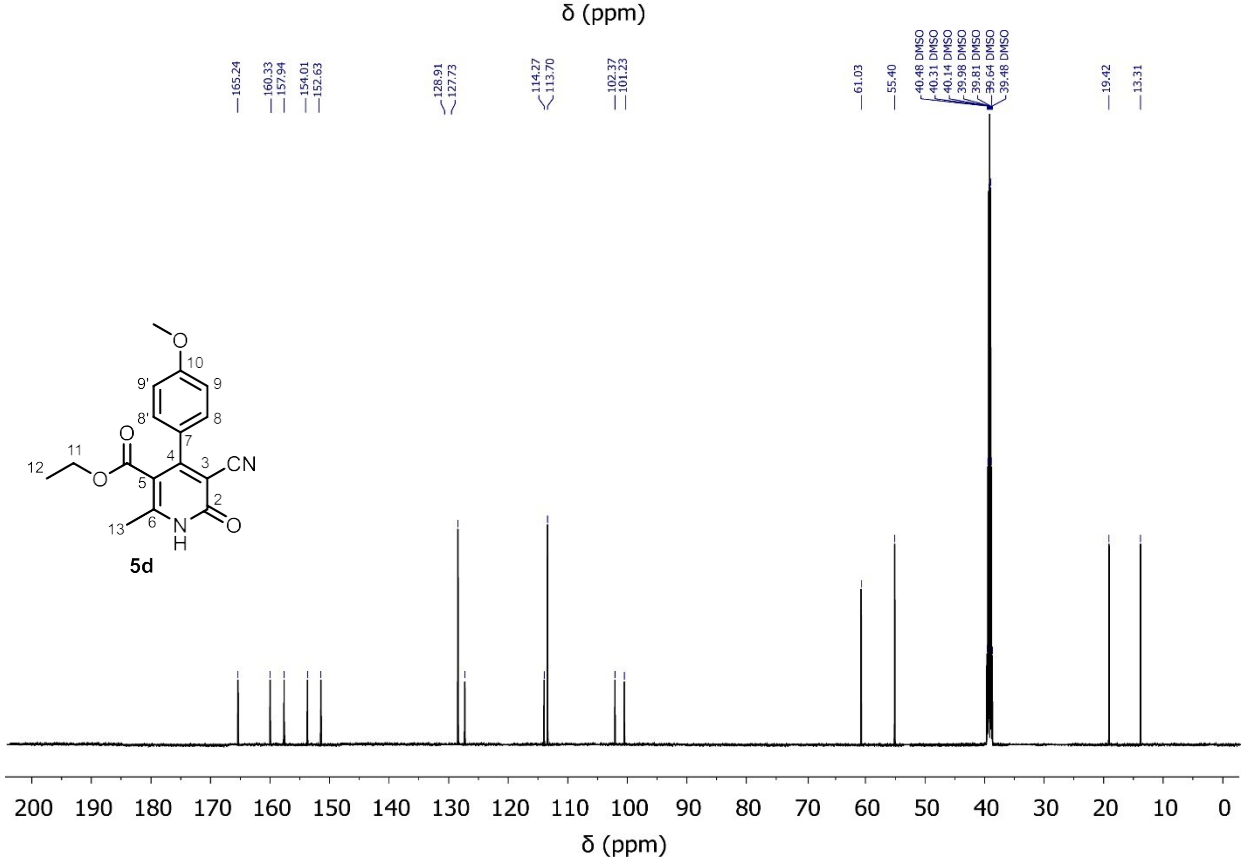

165.23
163.83
161.13
152.45
135.58
130.07
128.79
127.36
114.87
102.37
99.80
40.48 DMSO
40.31 DMSO
40.15 DMSO
39.98 DMSO
39.81 DMSO
39.65 DMSO
39.48 DMSO
45.31
19.02
14.11
10
9'
9
8'
8
7
4
3
CN
2
O
11
12
O
5
6
13
N
H
O
5b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.51
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.26 CDCl3
3.92
3.91
3.90
3.88
2.62
0.82
0.80
0.79
-0.01
Br
10
9'
9
8'
8
7
4
3
CN
2
O
11
12
O
5
6
13
N
H
O
B (m)
7.36
A (qd)
7.47
C (q)
3.90
D (s)
2.62
E (t)
0.80
5c
3.16
1.96
1.93
3.02
2.93
12.0
11.5
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
f1 (ppm)

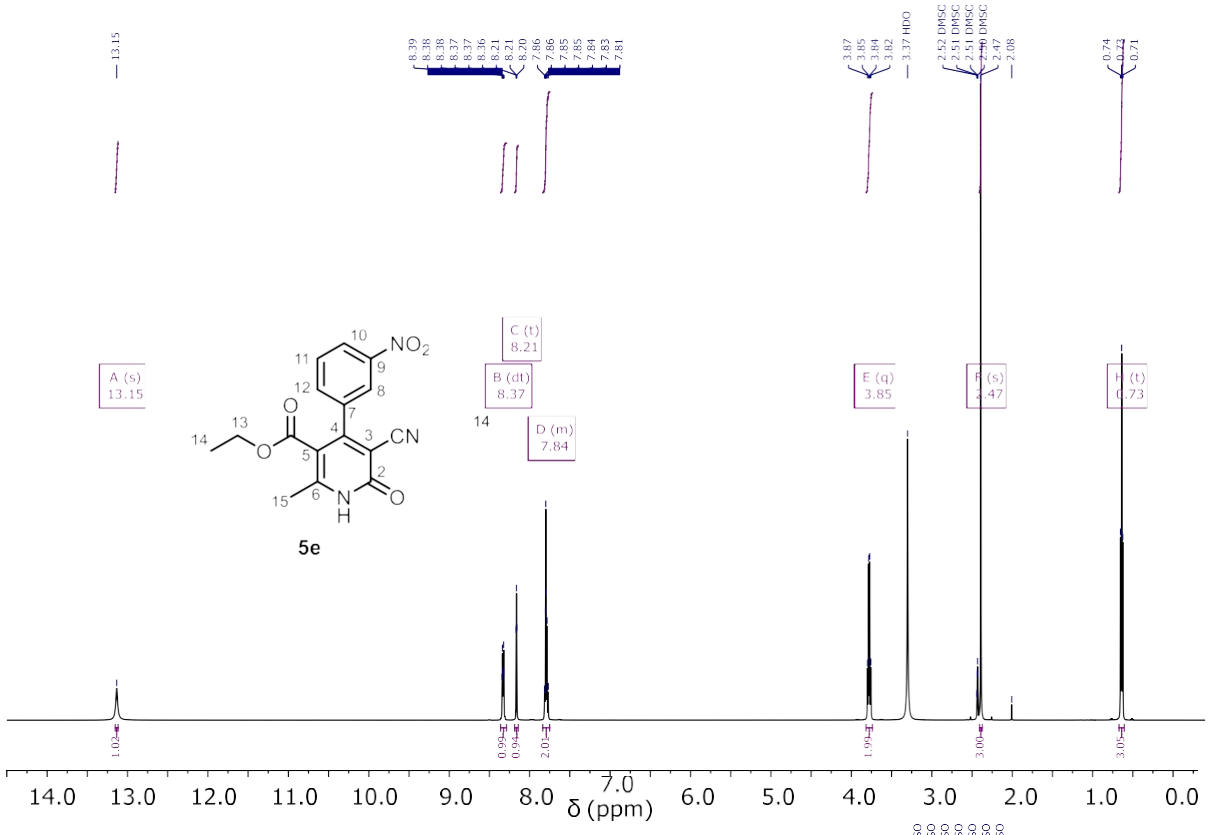

165.24
162.78
161.09
152.44
135.57
130.13
128.81
127.44
114.95
114.57
101.63
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
61.82
19.01
13.43
Br
10
9'
9
8'
8
7
4
3
CN
2
O
11
12
O
5
6
13
N
H
O
5c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

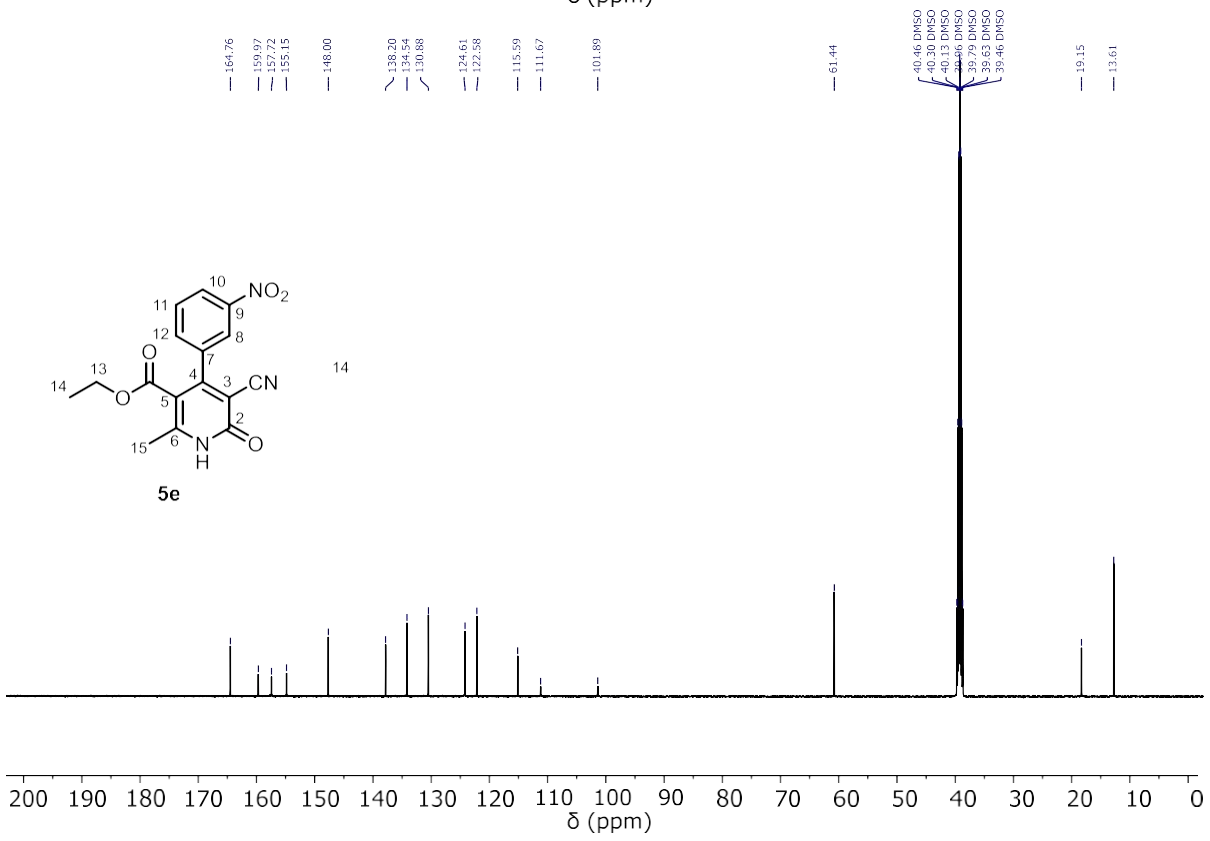

13.07
7.55
7.55
7.55
7.53
7.51
7.51
7.02
7.02
7.02
7.00
7.00
7.00
7.00
4.21
4.20
4.19
4.17
3.81
3.37 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
2.36
1.27
1.26
1.25
0.99
2.01
2.01
2.01
2.98
2.98
3.01
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

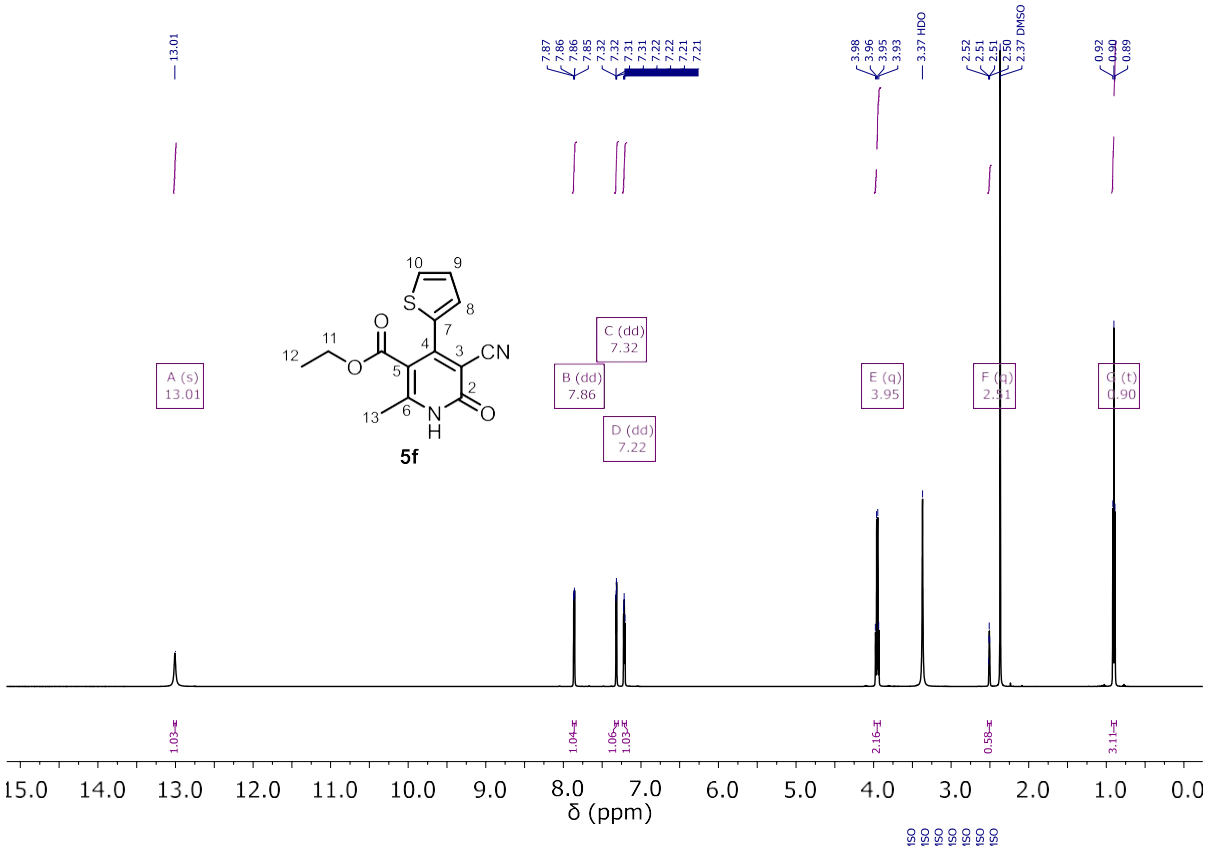
5d

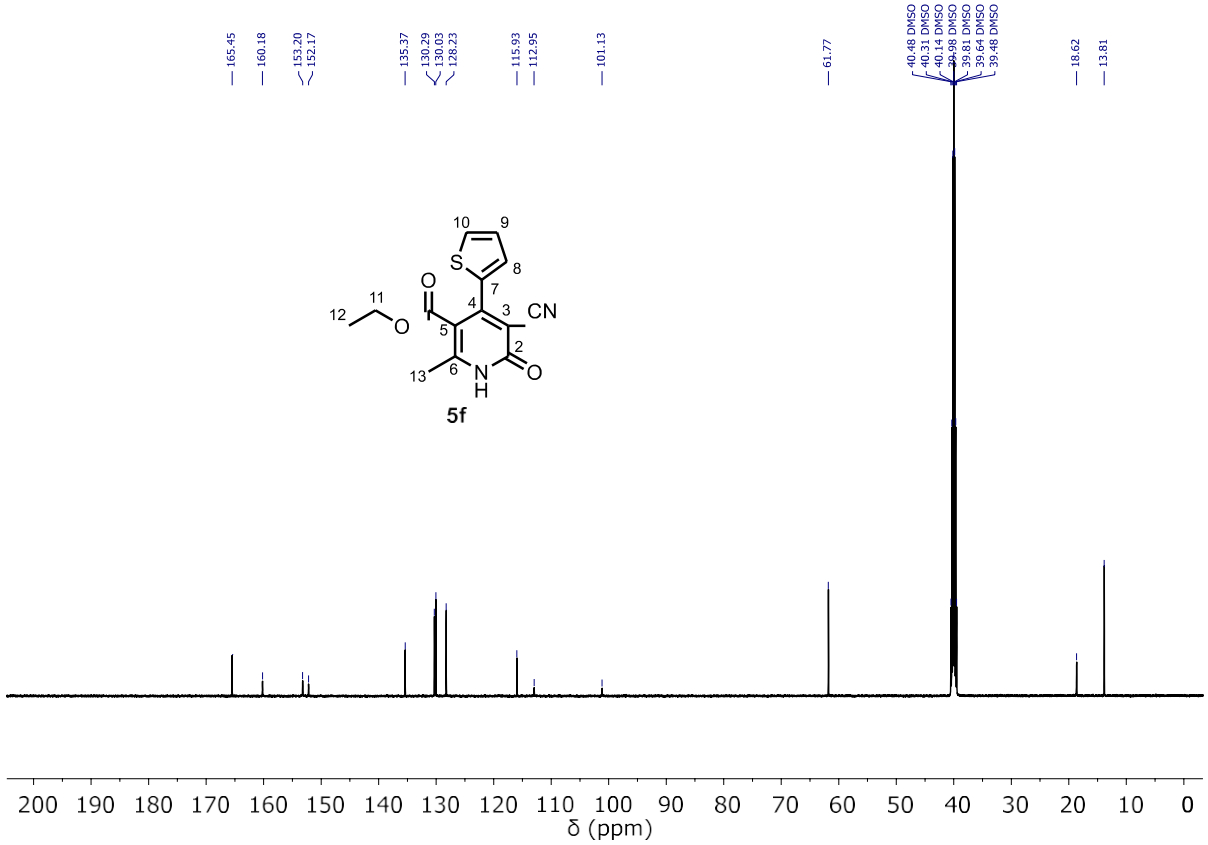

165.24
160.33
157.94
154.01
152.63
128.91
127.73
114.27
113.70
102.37
101.23
61.03
55.40
40.48 DMSO
40.31 DMSO
40.14 DMSO
39.98 DMSO
39.81 DMSO
39.64 DMSO
39.48 DMSO
19.42
13.31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

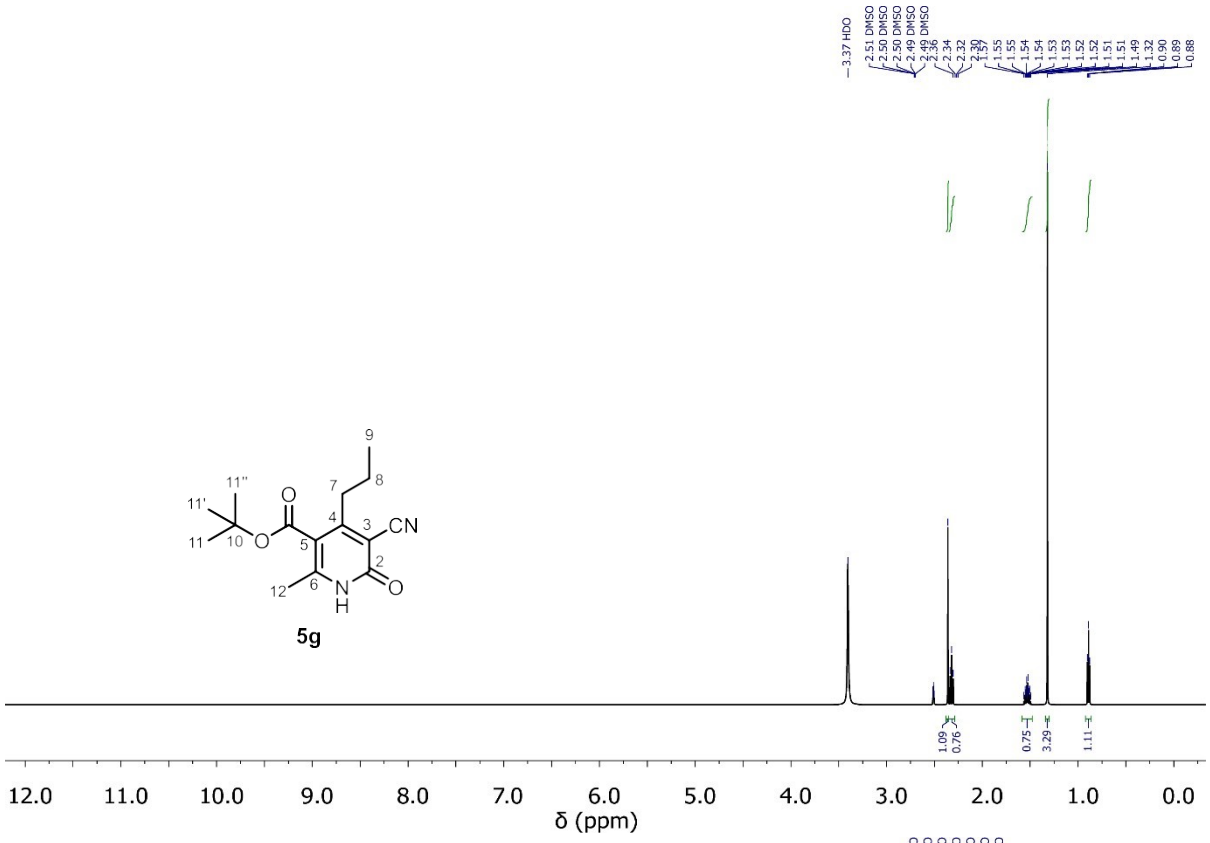
5d

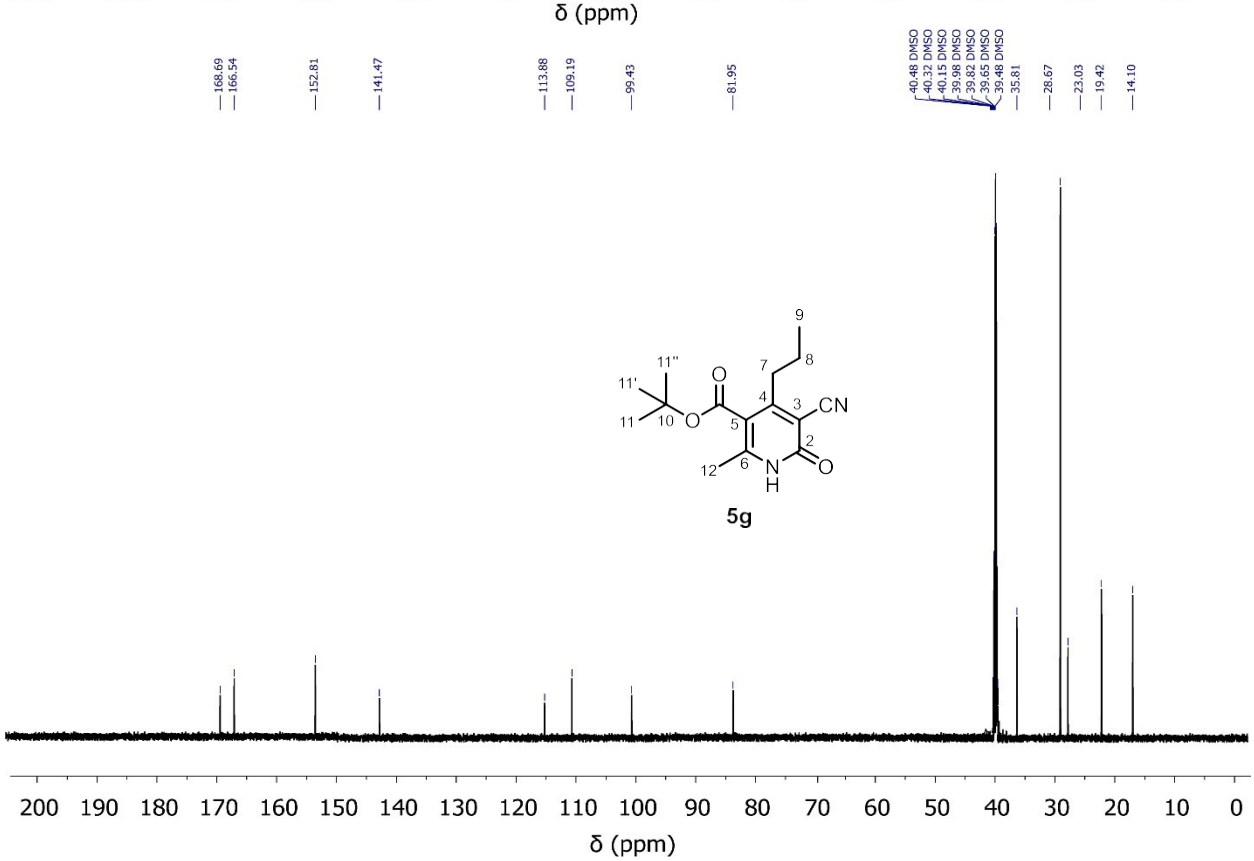

13.15
8.39
8.38
8.38
8.37
8.37
8.36
8.21
8.21
8.20
7.86
7.86
7.85
7.85
7.84
7.83
7.81
3.87
3.85
3.84
3.82
3.37 HDO
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.47
2.08
0.74
0.72
0.71
A (s) 13.15
B (dt) 8.37
C (t) 8.21
D (m) 7.84
E (q) 3.85
F (s) 2.47
G (t) 0.73
NO2
CN
O
N
H
5e
14
1.02
0.99
0.94
2.05
1.99
3.00
3.05
14.0 13.0 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
δ (ppm)

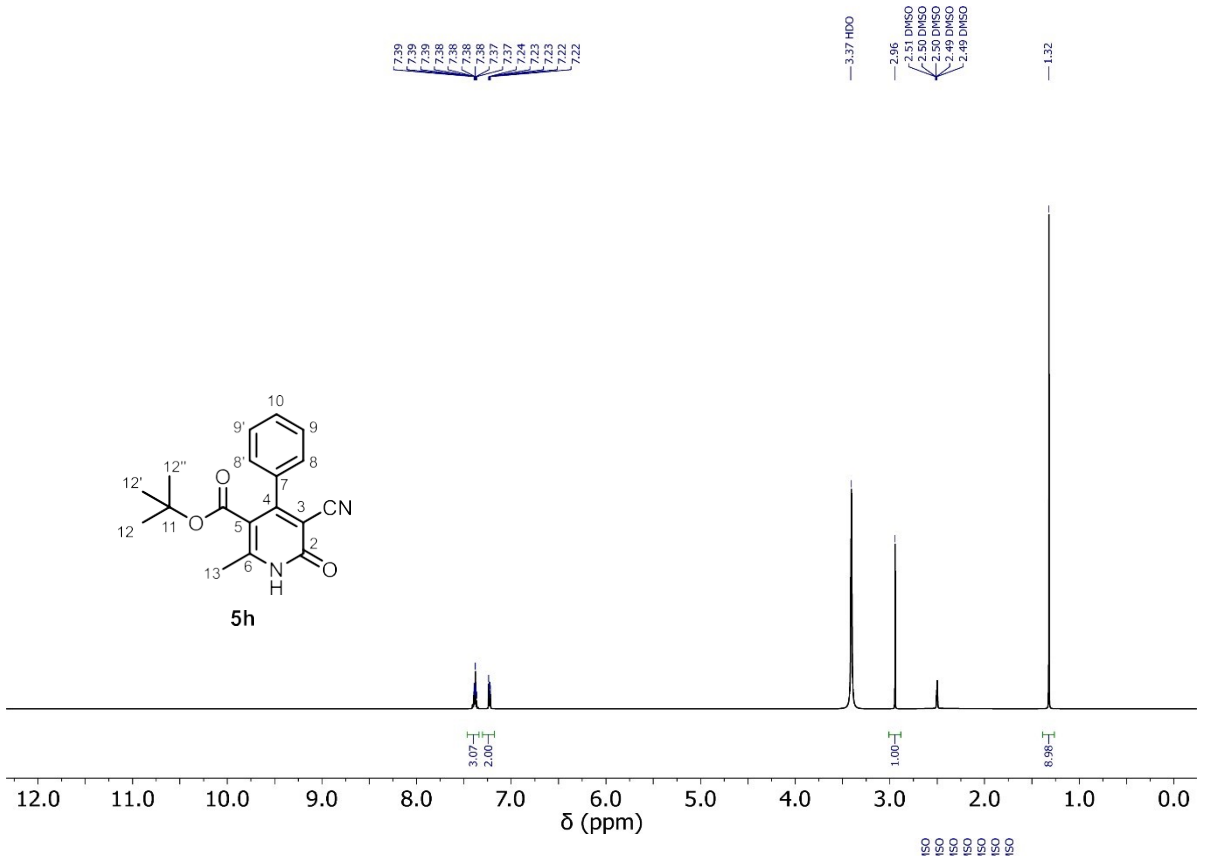

164.76
159.97
157.72
155.15
148.00
138.20
134.54
130.88
124.61
122.58
115.59
111.67
101.89
61.44
40.46 DMSO
40.30 DMSO
40.13 DMSO
39.96 DMSO
39.79 DMSO
39.63 DMSO
39.46 DMSO
19.15
13.61
NO2
CN
O
N
H
5e
14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

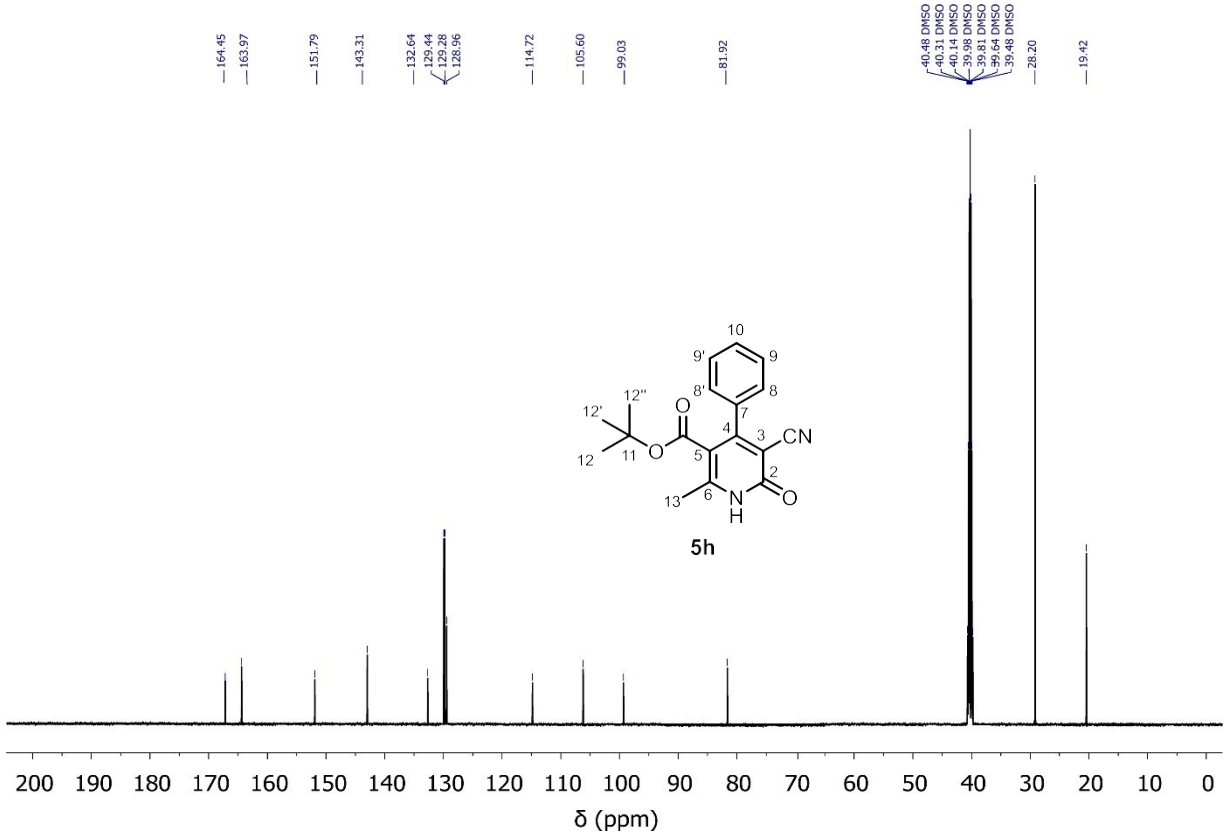

13.01
7.87
7.86
7.86
7.85
7.32
7.32
7.31
7.31
7.22
7.22
7.21
7.21
3.98
3.96
3.95
3.93
3.37 HDO
2.52
2.51
2.51
2.50
2.37 DMSO
0.92
0.90
0.89
A (s)
13.01
B (dd)
7.86
C (dd)
7.32
D (dd)
7.22
E (q)
3.95
F (q)
2.51
G (t)
0.90
5f
1.03
1.04
1.06
1.03
2.16
0.58
3.11
δ (ppm)

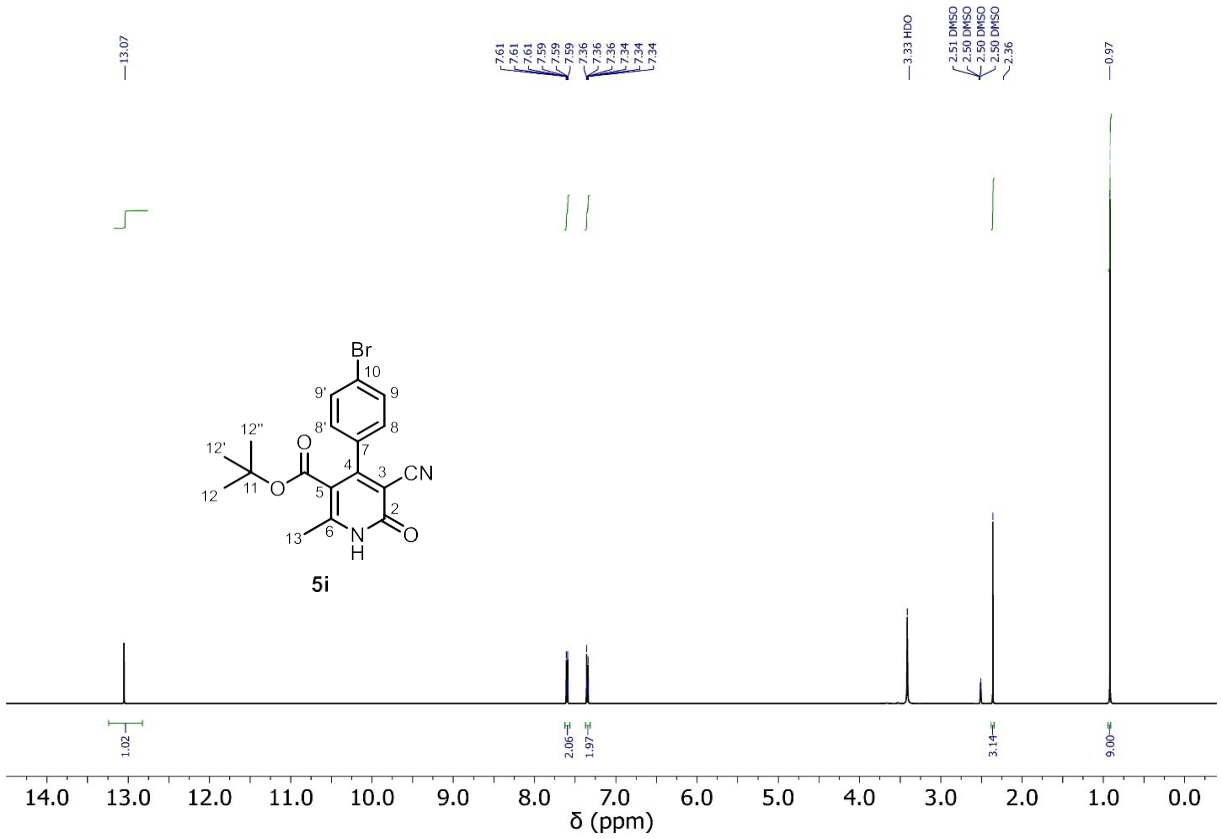

165.45
160.18
153.20
152.17
135.37
130.29
130.03
128.23
115.93
112.95
101.13
61.77
40.48 DMSO
40.31 DMSO
40.14 DMSO
39.98 DMSO
39.81 DMSO
39.64 DMSO
39.48 DMSO
18.62
13.81
5f
δ (ppm)

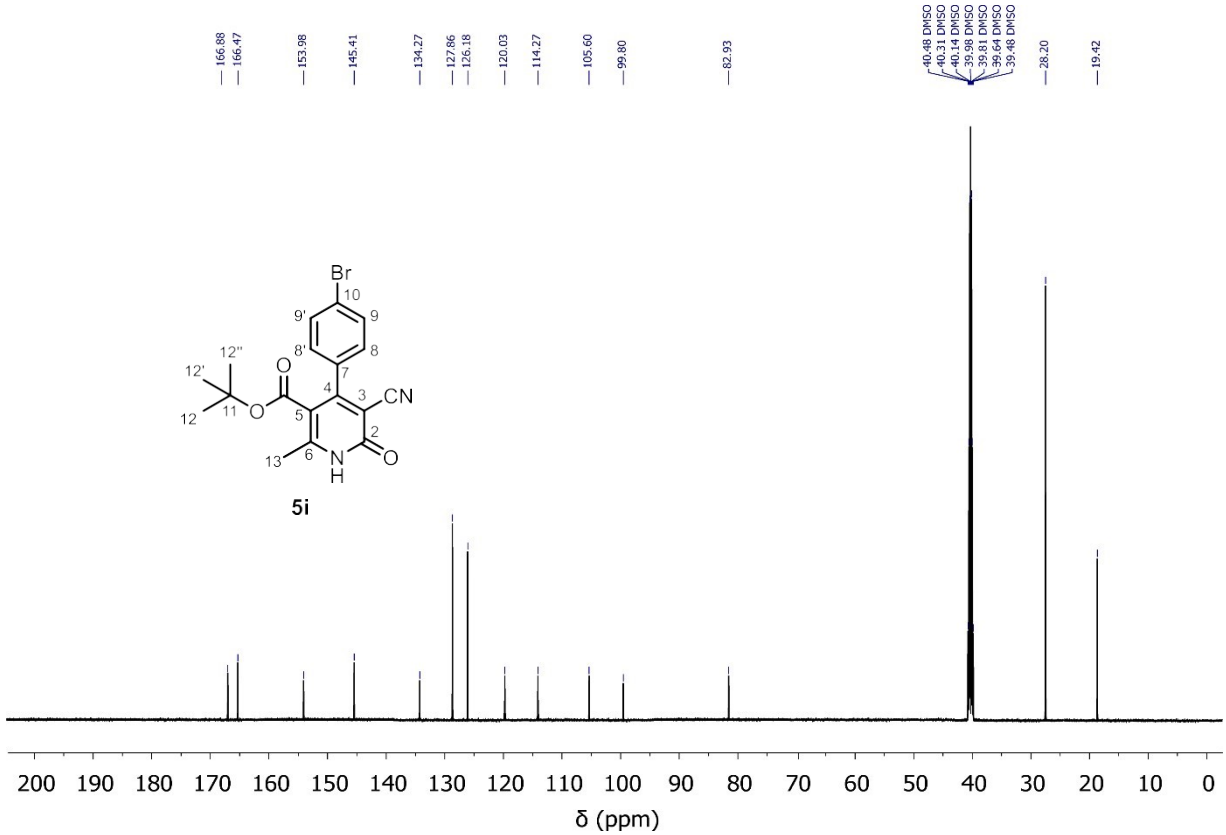

3.37 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
2.36
2.34
2.32
2.30
1.57
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.49
1.32
0.90
0.89
0.88
1.09
0.76
0.75
3.29
1.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)
5g

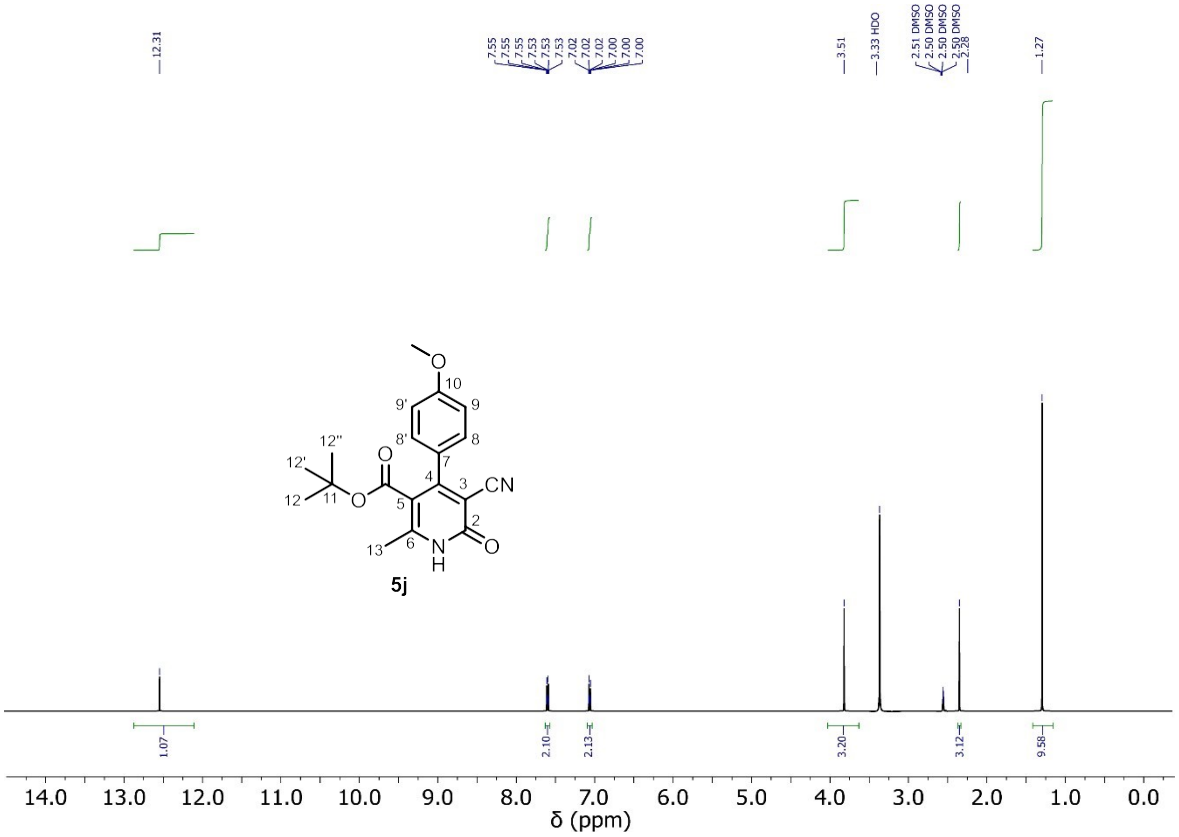

168.69
166.54
152.81
141.47
113.88
109.19
99.43
81.95
40.48 DMSO
40.32 DMSO
40.15 DMSO
39.98 DMSO
39.82 DMSO
39.65 DMSO
39.48 DMSO
35.81
28.67
23.03
19.42
14.10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)
5g

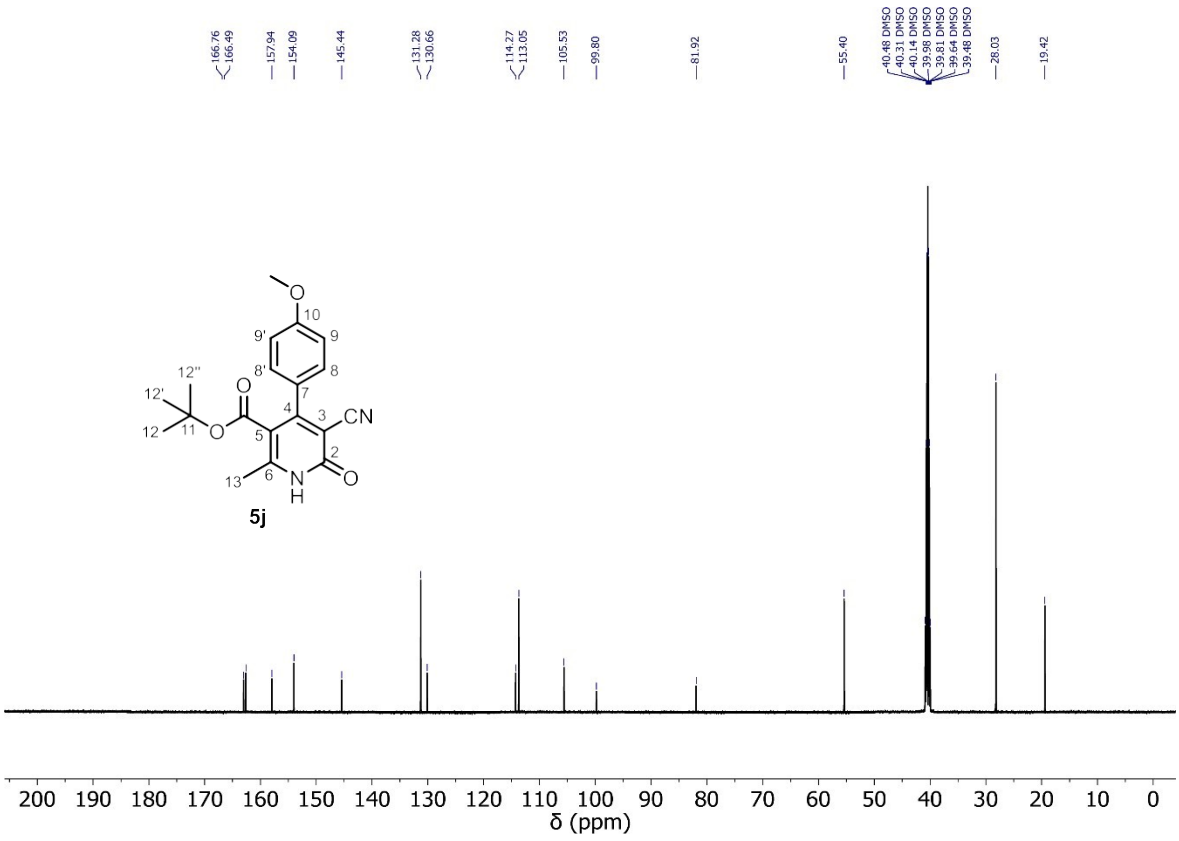

7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
7.24
7.23
7.23
7.22
7.22
3.37 HDO
2.96
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
1.32
10
9'
9
8'
8
7
4
3
CN
12"
12'
12
11
O
5
2
O
13
6
N
H
5h
3.07
2.00
1.00
8.98
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

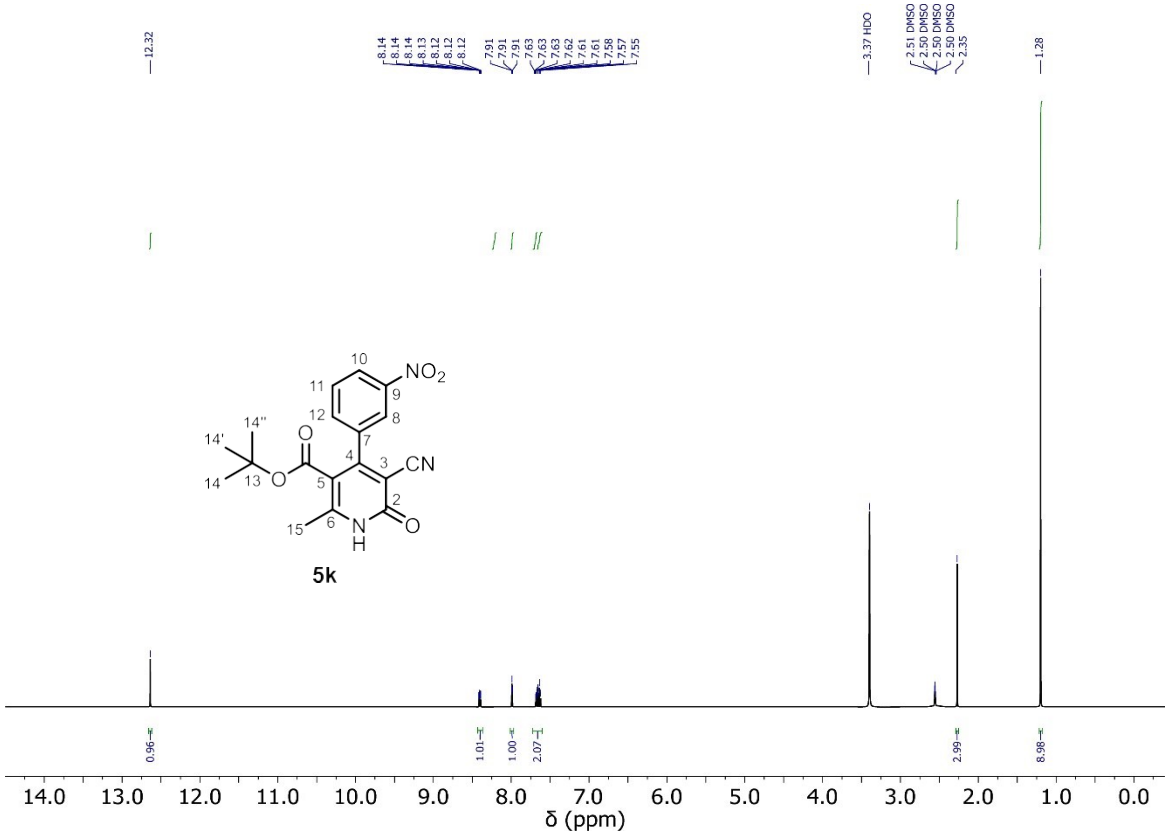

164.45
163.97
151.79
143.31
132.64
129.44
129.28
128.96
114.72
105.60
99.03
81.92
40.48 DMSO
40.31 DMSO
40.14 DMSO
39.98 DMSO
39.81 DMSO
39.64 DMSO
39.48 DMSO
28.20
19.42
10
9'
9
8'
8
7
4
3
CN
12"
12'
12
11
O
5
2
O
13
6
N
H
5h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


13.07
7.61
7.61
7.61
7.59
7.59
7.59
7.36
7.36
7.36
7.34
7.34
7.34
3.33 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.36
0.97
Br
10
9'
9
8'
8
12''
12'
7
4
O
3
CN
12
11
O
5
2
13
6
N
H
O
5i
1.02
2.06
1.97
3.14
9.00
14.0
13.0
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
δ (ppm)

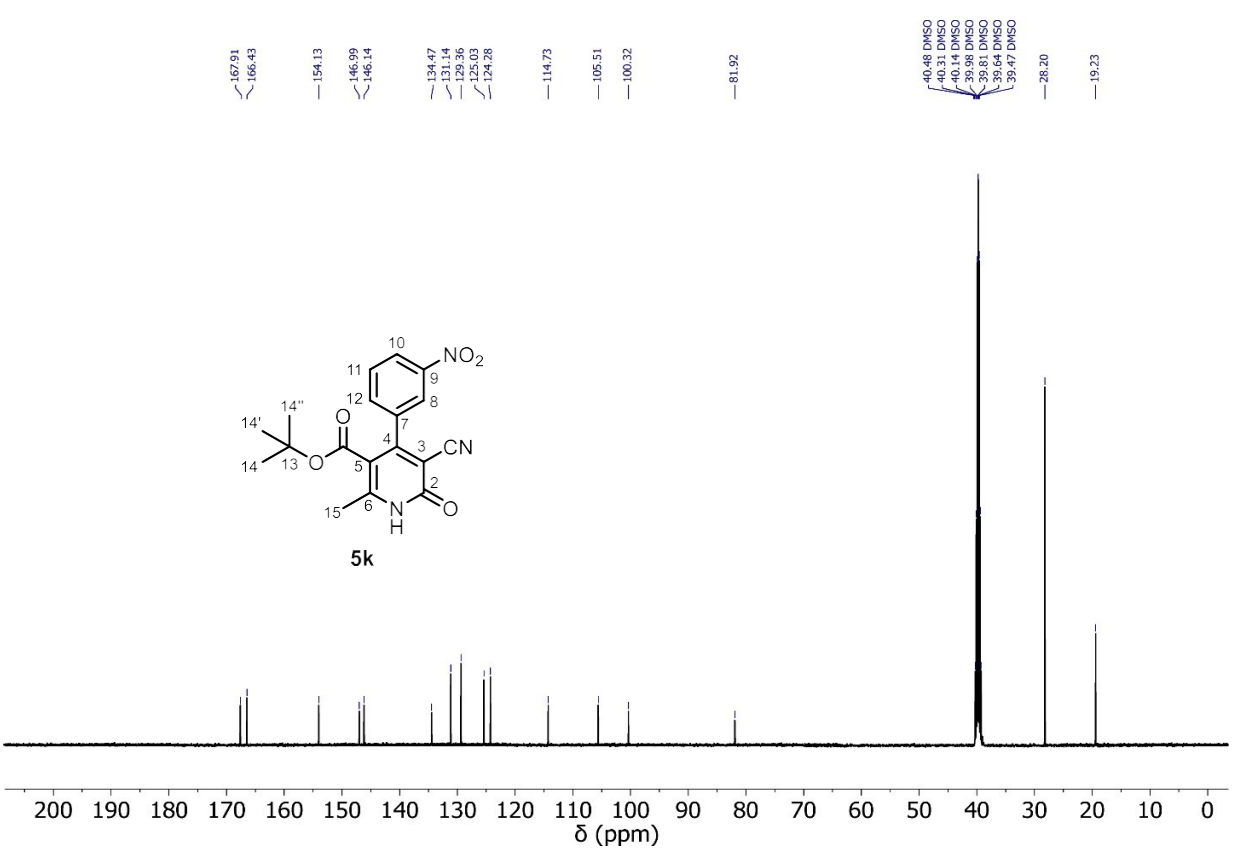

166.88
166.47
153.98
145.41
134.27
127.86
126.18
120.03
114.27
105.60
99.80
82.93
40.48 DMSO
40.31 DMSO
40.14 DMSO
39.98 DMSO
39.81 DMSO
39.64 DMSO
39.48 DMSO
28.20
19.42
Br
10
9'
9
8'
8
12''
12'
7
4
O
3
CN
12
11
O
5
2
13
6
N
H
O
5i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


12.31
7.55
7.55
7.55
7.53
7.53
7.53
7.02
7.02
7.02
7.00
7.00
7.00
3.51
3.33 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.28
1.27
5j
1.07
2.10
2.13
3.20
3.12
9.58
14.0
13.0
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
δ (ppm)

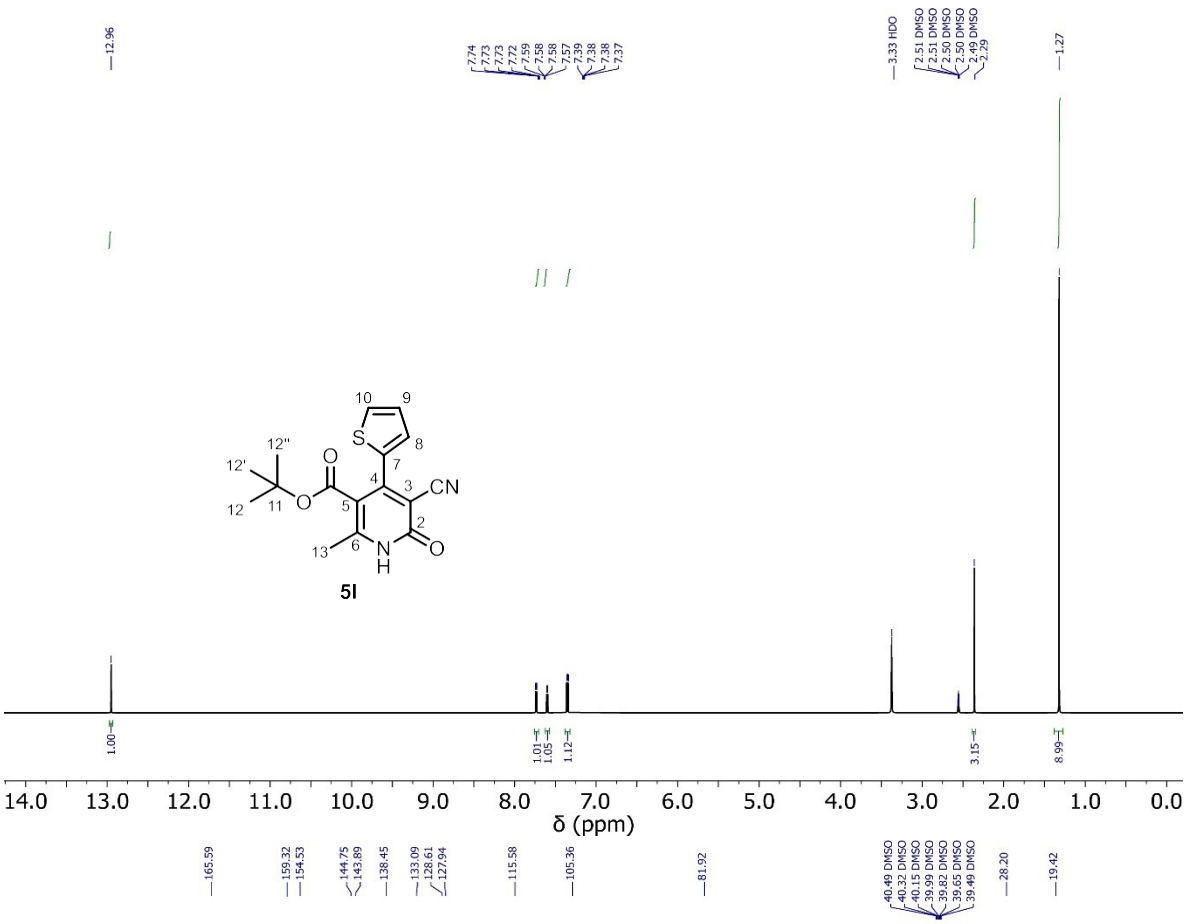

166.76
166.49
157.94
154.09
145.44
131.28
130.66
114.27
113.05
105.53
99.80
81.92
55.40
40.48 DMSO
40.31 DMSO
40.14 DMSO
39.98 DMSO
39.81 DMSO
39.64 DMSO
39.48 DMSO
28.03
19.42
5j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


12.32
8.14
8.14
8.14
8.13
8.12
8.12
8.12
7.91
7.91
7.91
7.63
7.63
7.63
7.62
7.61
7.61
7.58
7.57
7.55
3.37 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.35
1.28
0.96
1.01
1.00
2.07
2.99
8.98
δ (ppm)

5k

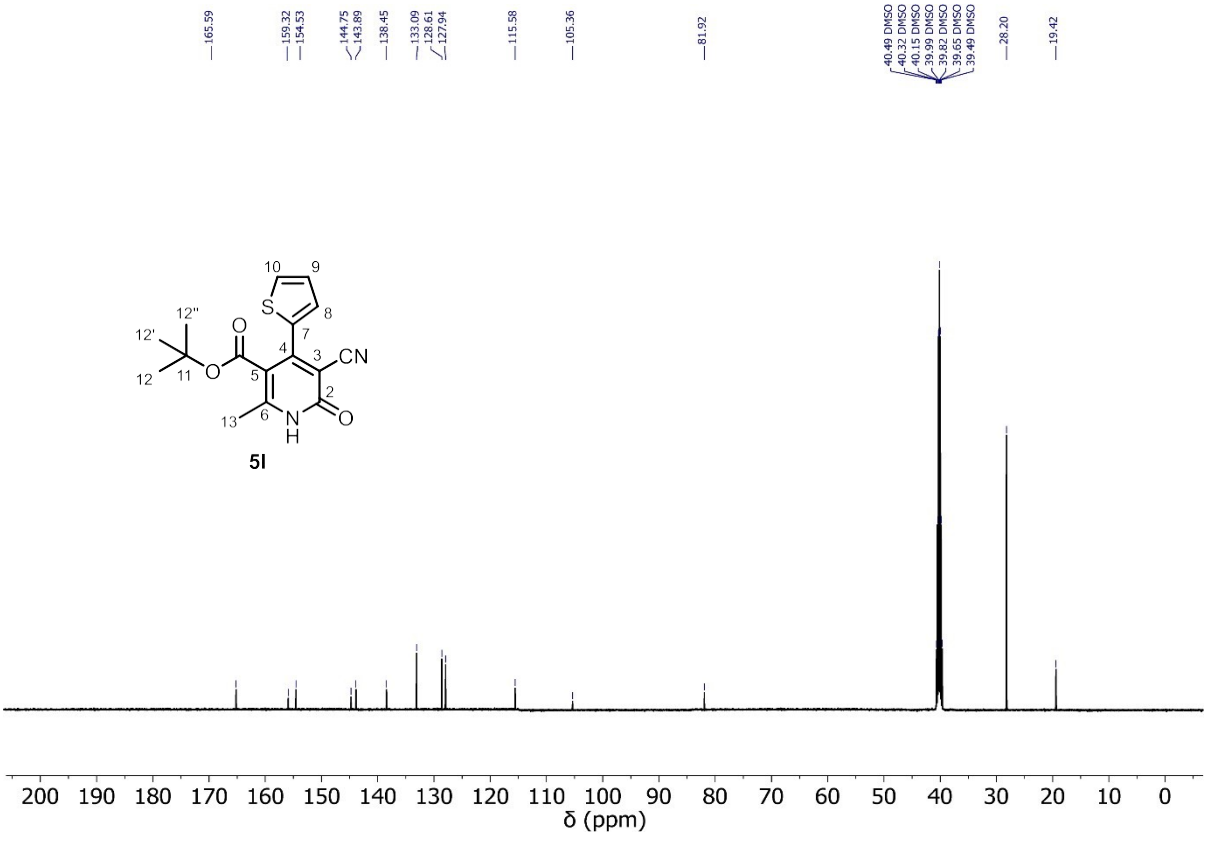

167.91
166.43
154.13
146.99
146.14
134.47
131.14
129.36
125.03
124.28
114.73
105.51
100.32
81.92
40.48 DMSO
40.31 DMSO
40.14 DMSO
39.98 DMSO
39.81 DMSO
39.64 DMSO
39.47 DMSO
28.20
19.23
δ (ppm)

5k


12.96
7.74
7.73
7.73
7.72
7.59
7.58
7.58
7.57
7.39
7.38
7.38
7.37
3.33 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.29
1.27
1.00
1.01
1.05
1.12
3.15
8.99
14.0
13.0
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
δ (ppm)

10
9
S
8
7
4
3
CN
2
O
12''
12'
O
12
11
O
5
6
N
H
13
O

5l


165.59
159.32
154.53
144.75
143.89
138.45
133.09
128.61
127.94
115.58
105.36
81.92
40.49 DMSO
40.32 DMSO
40.15 DMSO
39.99 DMSO
39.82 DMSO
39.65 DMSO
39.49 DMSO
28.20
19.42
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

10
9
S
8
7
4
3
CN
2
O
12''
12'
O
12
11
O
5
6
N
H
13
O

5l

References

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