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Supporting Information

Copper(I)-Catalysed Oxidative C-N Coupling of 2-aminopyridine with Terminal alkynes featuring an C≡C bond Cleavage promoted by Visible Light

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Experimental section

General: Unless otherwise stated, all reactions were conducted under an oxygen atmosphere and oven-dried glass wares were used. All the reactions were carried out using a blue-LED array as the light source (30 lamps, power density: 40 mW/cm^2 at 460 nm). All solvents were dried according to known methods and distilled prior to use. All other starting materials were directly used as purchased without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz and 600 MHz (125 MHz and 150 MHz for ^{13}C) instrument. ^{1}H and ^{13}C NMR spectra were reported relative to residual $CDCl_3$ (δ 7.24 ppm) and DMSO-d_6 (δ 2.49 ppm) and (δ 77.00 ppm) and DMSO-d_6 (δ 39.50 ppm) was used as internal reference. Chemical shifts (δ) were reported as parts per million (ppm) and the following abbreviations were used to identify the multiplicities: s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet, b= broad and all combinations thereof can be explained by their integral parts. EPR spectra were recorded by a Bruker ESP-300E instrument.

General procedure for preparation of pyridylbenzamides:

A dry test tube (20 mL) containing 5 mol% CuCl and then added dry CH_3CN (7 mL) via syringe, added 2-aminopyridine (0.5 mmol) and finally added terminal acetylene (0.6 mmol). The suspension was irradiated with blue LED light (40 mW/cm^2 at 460 nm) at room temperature in presence of 1 atm oxygen atmosphere for 10-18 h until completion of coupling reaction (it was determined by thin layer chromatography). The reaction mixture was diluted with 40 % ethyl acetate in hexane and stirred for 10 min. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired pyridyl-amides product.

General procedure for preparation of 2-oxo-2-phenyl-N-(pyridin-2-yl)acetamide (**3aa**):

A dry test tube (20 mL) containing 5 mol% CuCl and then added dry CH_3CN (7 mL) via syringe, added 2-aminopyridine (0.5 mmol) and finally added terminal acetylene (0.6 mmol). The suspension was irradiated with blue LED light (40 mW/cm^2 at 460 nm) at room temperature in presence of 1 atm oxygen atmosphere for **3 h** (it was determined by thin layer chromatography). The reaction mixture was diluted with 40 % ethyl acetate in hexane and stirred for 10 min. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate

was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired 2-oxo-2-phenyl-N-(pyridin-2-yl)acetamide product.

***Preparation of copper* phenylacetylide**,[s1] CuI (1.0 g, 5.0 mmol) was dissolved in ammonium hydroxide to form a blue solution. While stirring, this solution was added dropwise to the solution of phenylacetylene (0.5 g, 5.1 mmol) in 50 mL of ethanol. The system was allowed to stand for 15 min to form a yellow precipitate suspension. The precipitate was filtered out and washed with water, ethanol, and diethyl ether, three times each. The solid was vacuum-dried, and 0.65 g (yield 75%) of a bright yellow solid was obtained. The spectroscopic data for the yellow solid are shown below: IR (KBr, cm^{-1}) [s2:] 1931(C≡C), 1596, 1568; UV-Vis λ_{abs} = 476 nm.

Evaluation of Green metrics of the process;

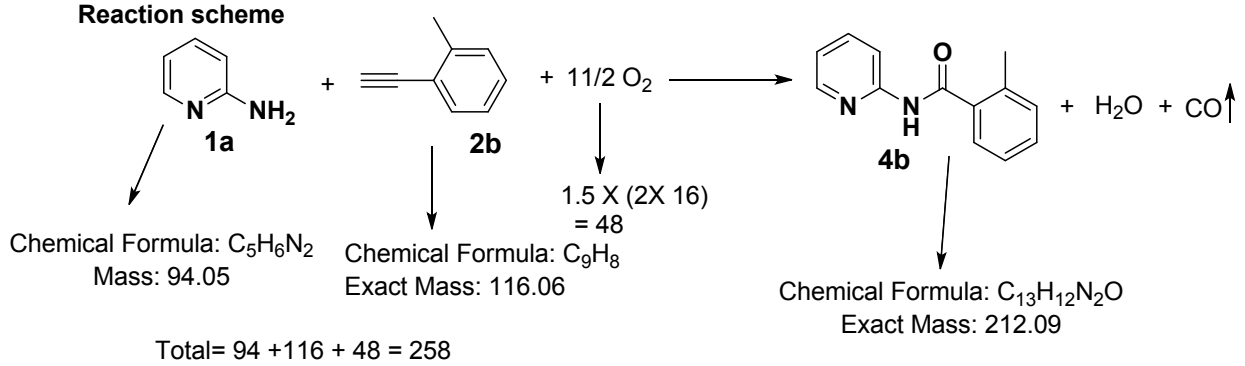
Atom economy defined as "how much of the reactants remain in the final desired product"

$$\text{Atom economy (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

Reaction mass efficiency (RME) defined as "the percentage of the mass of the reactants that remain in the product"

$$\text{Reaction mass efficiency (RME)} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

Reaction scheme



Total= 94 +116 + 48 = 258

Evaluation of Green metrics of the current photochemical process

Reactant A	2-amino-pyridine (**2a**)	0.14g	0.0015mol	FW 94.05
Reactant B	1-ethynyl-2-methylbenzene (**2b**)	0.225g	0.0019mol	FW 116.06
Solvent	ACN	12. 0g	---	---
Auxiliary	---	---	---	---
Product	Pyridyl benzamide (**4b**)	0.260g	0.0012 mol	FW 212.09

Product yield= 82%

E-factor $= \dfrac{0.14g + 0.225g + 12.0g - 0.260g}{0.260\ g}$ = 46 kg waste/ 1 kg product

Atom economy $= \dfrac{212}{258} \times 100$ = 82%

Atom efficiency = 82 % X 82% / 100 = 67%

Carbon efficiency $= \dfrac{13}{5 + 9} \times 100$ = 93%

Reaction mass efficiency $= \dfrac{0.260\ g}{0.14g + 0.225g} \times 100$ = 71%

EPR measurements. EPR spectra were recorded at room temperature on a Bruker ESP-300E(X band, 9.8 GHz) with parameters setting as shown below: receiver gain=30 n; receiver phase=0 deg; receiver harmonic=1; field modulation frequency=100000 Hz; microwave frequency [Hz]= 9.660469 e+09; field modulation amplitude [T]= 0.00016 ;receiver time constant[S] = 0.32768; microwave power= 0.015W; receiver offset [%FS]=0; DMPO (5-,5-dimethyl-1-pyrroline N-oxide) was employed as a radical trap for superoxide.

The reaction under a standard condition (**1a, 2a,** CuCl, 1 atm. O_2) in CH_3CN was irradiated with blue LEDs for 30 min in the presence of DMPO in an EPR chamber while recording the EPR spectra. The EPR signals shown in Figure S1 are corresponding to DMPO-OO(H). This result indicates that superoxide anion radical was formed in the reaction solution. No superoxide EPR signal was observed from the reaction solution under standard condition in the absence of CuCl (Fig. S2). These results indicate that copper(I) phenylacetylide undergoes single electron transfer to O_2, and generate superoxide free radical upon blue LEDs irradiation.

EPR spectra of the reaction mixture after blue LEDs irradiation

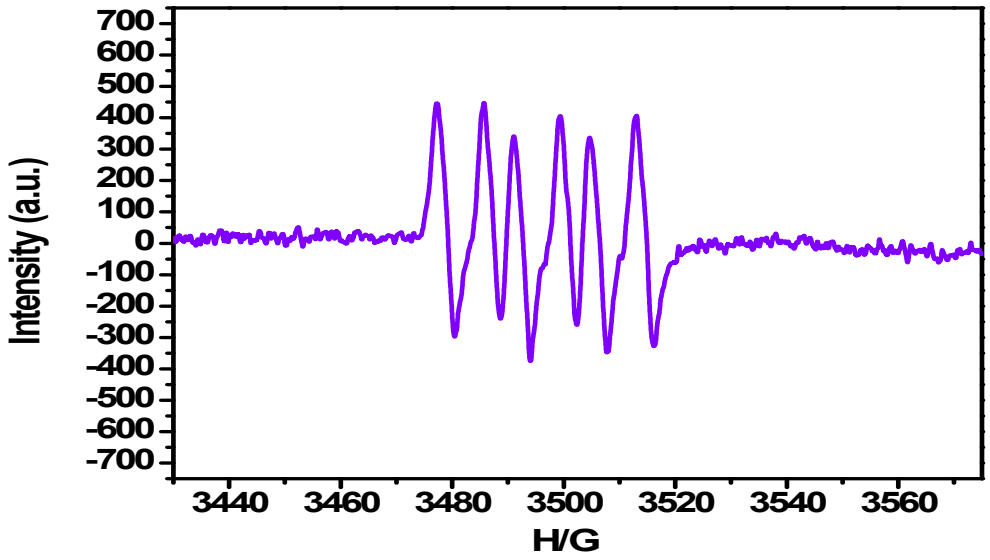


Figure S1: EPR spectra of the reaction mixture: 2-aminopyridine (**1a,** 0.5 mmol) phenylacetylene (**2a,** 0.6 mmol), and 5 mol% of CuCl in dry CH_3CN (7 mL), 0.5 ml of this reaction solution was taken out into a small vial, followed by the addition of 0.01 mL of DMPO

(5 x 10^{-2} M). The mixture was irradiated with blue LEDs at room temperature under an oxygen atmosphere (1 atm) for 30 minutes. The reaction mixture was then analysed by EPR spectra. There are classical 6 peaks, the signals corresponding to (DMPO-OO(H)).

EPR spectra of the reaction mixture in the absence of CuCl

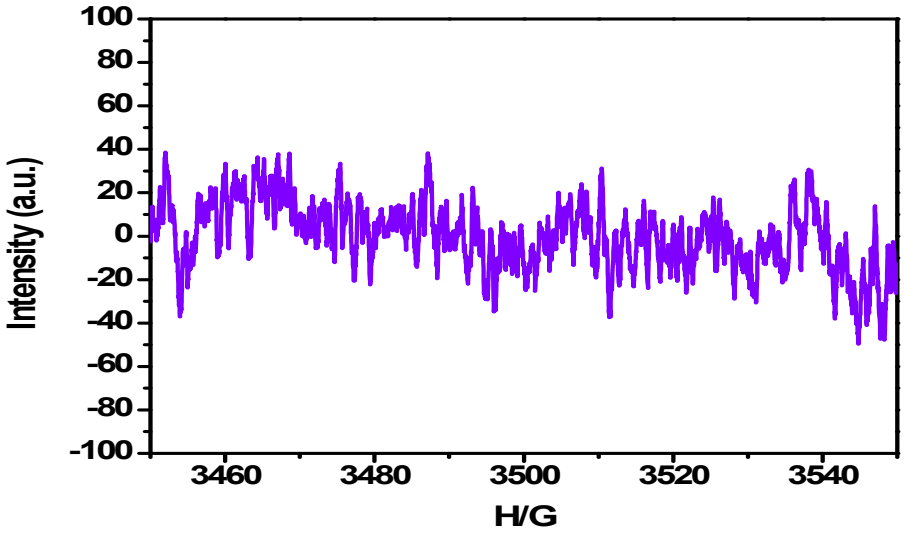


Figure S2: EPR spectra of the reaction mixture: 2-aminopyridine (**1a,** 0.5 mmol) phenylacetylene (**2a,** 0.6 mmol) in dry CH_3CN (7 mL), 0.5 mL of this reaction solution was taken out into a small vial, followed by the addition of 0.01 mL of DMPO (5 x 10^{-2} M). The mixture was irradiated with blue LEDs at room temperature under an oxygen atmosphere (1 atm) for 30 minutes (in the absence of CuCl). The reaction mixtures was analysed by EPR spectra. No signals were detected.

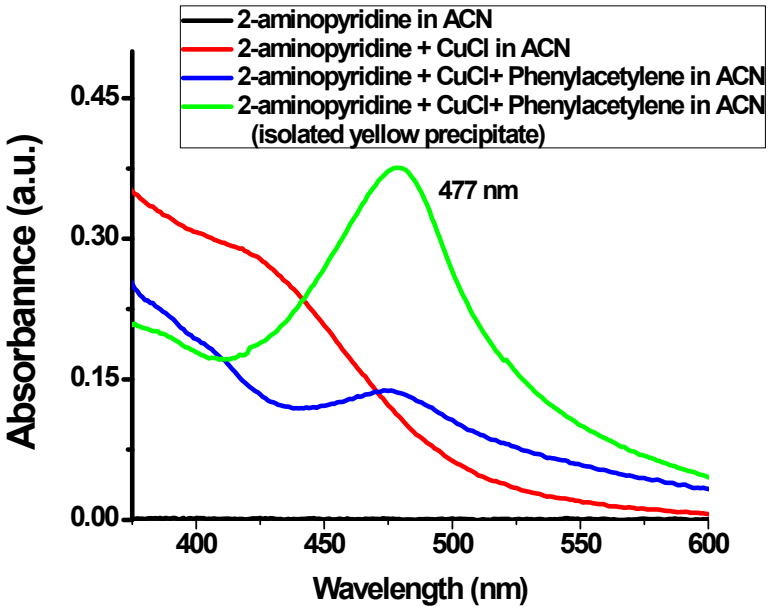
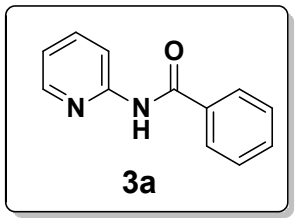


Figure S3: UV-visible spectra of the reaction mixture in CH_3CN. The black line indicates a 2-aminopyridine (**1a**), the red line indicates mixture of 2-aminopyridine (**1a**) and CuCl, the blue line indicates a mixture of 2-aminopyridine (**1a**), CuCl and phenylacetylene, the green line indicates isolation of a yellow suspension of copper(I) phenylacetylide

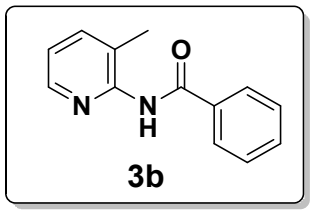
Spectroscopic Data

N-(pyridin-2-yl)benzamide (3a)[s3]



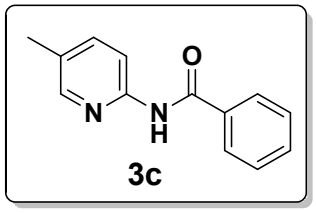
Yellow solid; m.p. 71-73 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): **δ** 9.03 (bs, 1 H), 8.37 (d, *J*= 6.0 Hz, 1 H), 8.14 (d, *J*= 6.0 Hz, 1 H), 7.90 (d, *J*= 6.0 Hz, 2 H), 7.72 (t, *J*= 6.0 Hz, 1 H), 7.53 (t, *J*= 6.0 Hz, 1 H), 7.45 (t, *J*= 6.0 Hz, 2 H), 7.00 (m, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.8, 151.6, 147.8, 138.4, 134.2, 132.1, 128.7, 127.2, 119.8, 114.2; **HRMS** calcd for $C_{12}H_{10}N_2O$: 198.0793, found: 198.0786.

N-(3-methylpyridin-2-yl)benzamide (3b)



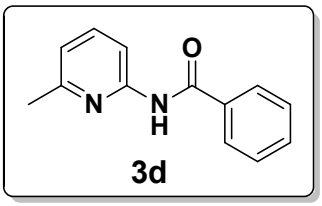
Pale white solid; m.p. 104-107 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.23 (s, 1 H), 7.74 (d, *J*= 12.0 Hz, 3 H), 7.56 (d, *J*= 6.0 Hz, 1 H), 7.42 (t, *J*= 6.0 Hz, 1 H), 7.31 (t, *J*= 6.0 Hz, 2 H), 7.12 (d, *J*= 6.0 Hz, 1 H), 2.33 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.9, 152.6, 147.1, 140.1, 134.7, 132.4, 130.4, 129.0, 128.5, 123.3, 17.7; **HRMS** calcd for $C_{13}H_{12}N_2O$: 212.0950, found: 212.0951

N-(5-methylpyridin-2-yl)benzamide (3c)[s3]



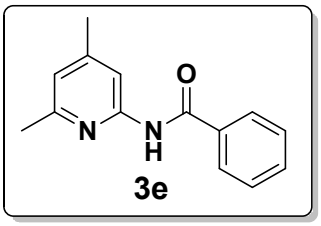
Yellow solid; m.p. 100-104 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.65 (s, 1 H), 8.27 (d, *J*= 12.0 Hz, 1 H), 8.07 (s, 1 H), 7.90 (d, *J*= 12.0 Hz, 2 H), 7.54 (t, *J*= 6.0 Hz, 2 H), 7.45 (d, *J*= 6.0 Hz, 2 H), 2.29 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.5, 149.3, 147.7, 139.0, 134.3, 132.1, 129.3, 128.7, 127.1, 113.6, 17.8; **HRMS** calcd for $C_{13}H_{12}N_2O$: 212.0950, found: 212.0951.

N-(6-methylpyridin-2-yl)benzamide (3d)



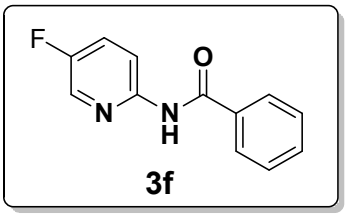
Yellow solid; m.p. 111-114 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.65 (s, 2 H), 8.18 (d, *J*= 6.0 Hz, 1 H), 7.91 (d, *J*= 6.0 Hz, 1 H), 7.64 (t, *J*= 6.0 Hz, 1 H), 7.54 (t, *J*= 6.0 Hz, 1 H), 7.46 (m, 2 H), 6.91(d, *J*= 6.0 Hz, 1 H), 2.45 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.6, 156.7, 150.7, 138.9, 134.2, 132.1, 128.7, 127.2, 119.4, 111.0, 23.8; **HRMS** calcd for $C_{13}H_{12}N_2O$: 212.0950, found: 212.0951.

N-(4, 6-dimethylpyridin-2-yl)benzamide (3e)



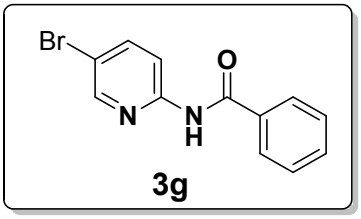
Yellow solid; m.p. 117-120 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.51 (s, 1 H), 8.03 (s, 1 H), 7.90 (t, *J*= 6.0 Hz, 2 H), 7.55-7.45 (m, 1 H), 7.47 (d, *J*= 6.0 Hz, 2 H), 6.75 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.5, 156.3, 150.7, 150.2, 134.3, 132.1, 128.7, 127.1, 120.6, 111.6, 23.7, 21.3; **HRMS** calcd for $C_{14}H_{14}N_2O$: 226.1106, found: 226.1104.

N-(5-fluoropyridin-2-yl)benzamide (3f) [s3]



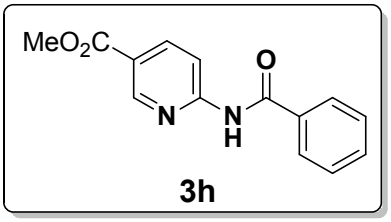
Pale white solid; m.p. 108-111˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.67 (s, 1 H), 8.43 (m, 1 H), 8.14 (s, 1 H), 7.90 (d, *J*= 6.0 Hz, 2 H), 7.56 (t, *J*= 6.0 Hz, 1 H), 7.49 (m, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.4, 156.5 (d, $J_{C\text{-}F}$ = 250 Hz), 147.7, 133.8, 132.4, 128.9, 127.1, 125.6, 125.5, 115.0, 114.9; **HRMS** calcd for $C_{12}H_9FN_2O$: 216.0699, found: 216.0696.

N-(5-bromopyridin-2-yl)benzamide (3g)



Brown solid; m.p. 168-171 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.69 (s, 1 H), 8.32 (d, *J*= 6.0 Hz, 1 H), 8.27 (s, 1 H), 7.88 (d, *J*= 6.0 Hz, 2 H), 7.83 (t, *J*= 6.0 Hz, 1 H), 7.56 (t, *J*= 6.0 Hz, 1 H), 7.48 (t, *J*= 6.0 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.8, 150.2, 148.7, 140.8, 133.8, 132.4, 128.9, 127.1, 115.3, 114.7; **HRMS** calcd for $C_{12}H_9BrN_2O$: 275.9898, found: 275.9892.

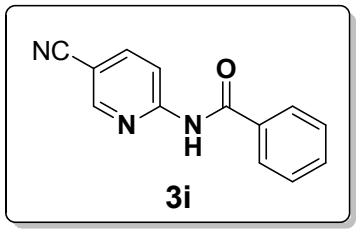
Methyl 6-benzamidonicotinate (3h)



Yellow solid; m.p. 163-166 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.03 (s, 1 H), 8.46 (s, 1 H), 8.33 (d, *J*= 6.0 Hz, 1 H), 7.91 (d, *J*= 6.0 Hz, 2 H), 7.58-7.55 (m, 1 H), 7.50 (d, *J*= 6.0 Hz, 3 H), 3.91

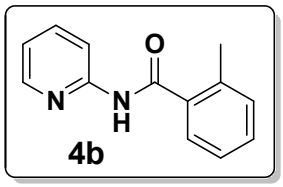
(s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.8, 165.3, 154.5, 149.8, 139.9, 132.6, 130.0, 128.9, 128.6, 127.3, 52.2; **HRMS** calcd for $C_{14}H_{12}N_2O_3$: 256.0848, found: 256.0842.

N-(5-cyanopyridin-2-yl)benzamide (3i)



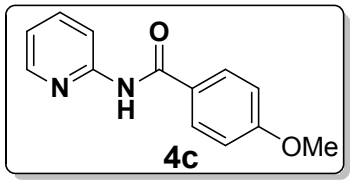
Yellow solid; m.p. 186-189 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.82 (s, 1 H), 8.53 (d, *J*= 6.0 Hz, 2 H), 7.97 (d, *J*= 6.0 Hz, 1 H), 7.90 (d, *J*= 6.0 Hz, 2 H), 7.59 (t, *J*= 6.0 Hz, 1 H), 7.51 (t, *J*= 6.0 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.7, 154.0, 151.6, 141.6, 133.3, 132.9, 129.0, 127.3, 116.6, 113.7, 105.2; **HRMS** calcd for $C_{13}H_9N_3O$: 223.0746, found: 223.0744.

2-methyl-N-(pyridin-2-yl)benzamide (4b)



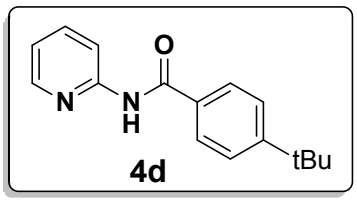
Yellow solid; m.p. 102-105 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.44 (s, 1 H), 8.31 (d, *J*= 6.0 Hz, 2 H), 7.93 (d, *J*= 6.0 Hz, 1 H), 7.76 (t, *J*= 6.0 Hz, 1 H), 7.46 (t, *J*= 6.0 Hz, 1 H), 7.29 (t, *J*= 6.0 Hz, 2 H), 7.13 (s, 1 H), 2.51 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 168.2, 151.5, 147.8, 138.4, 136.6, 135.8, 131.3, 130.6, 126.8, 125.9, 119.9, 114.0, 19.9; **HRMS** calcd for $C_{13}H_{12}N_2O$: 212.0950, found: 212.0951.

4-methoxy-N-(pyridin-2-yl)benzamide (4c) [s4]



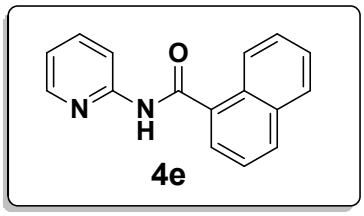
Yellow solid; m.p. 104-107 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.81 (s, 1 H), 8.38 (d, *J*= 6.0 Hz, 1 H), 8.24 (d, *J*= 6.0 Hz, 1 H), 7.90 (d, *J*= 6.0 Hz, 2 H), 7.76-7.73 (m, 1 H), 7.04 (t, *J*= 6.0 Hz, 3 H) 6.96 (d, *J*= 6.0 Hz, 2 H), 3.85 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.2, 162.8, 151.6, 147.2, 138.8, 129.2, 126.2, 119.6, 114.2, 114.0, 55.4; **HRMS** calcd for $C_{13}H_{12}N_2O_2$: 228.0899, found: 228.0898.

4-(tert-butyl)-N-(pyridin-2-yl)benzamide (4d)



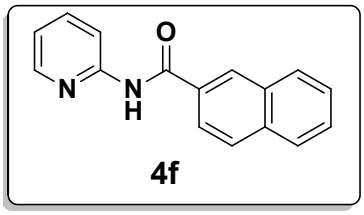
Yellow solid; m.p. 122-125 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.86 (b, 1 H), 8.40 (d, *J*= 6.0 Hz, 1 H), 8.27 (s, 1 H), 7.87 (d, *J*= 6.0 Hz, 2 H), 7.77-7.74 (m, 1 H), 7.49 (d, *J*= 6.0 Hz, 2 H), 7.06 (t, *J*= 6.0 Hz, 1 H), 1.33 (s, 9 H); **^{13}CNMR** (150 MHz, $CDCl_3$): δ 165.6, 155.9, 151.6, 147.3, 138.7, 131.6, 127.1, 125.7, 119.7, 114.3, 35.0, 31.1; **HRMS** calcd for $C_{16}H_{18}N_2O$: 254.1419, found: 254.1417.

N-(pyridin-2-yl)-1-naphthamide (4e) [s3]



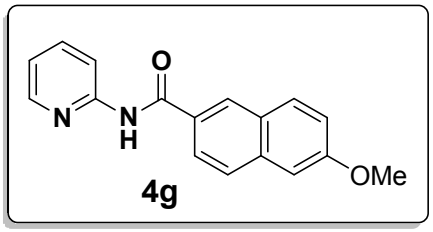
Yellow solid; m.p. 158-161 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.50 (s, 1 H), 8.40 (d, *J*= 6.0 Hz, 1 H), 8.01 (d, *J*= 6.0 Hz, 1 H), 7.96 (d, *J*= 6.0 Hz, 1 H), 7.88 (d, *J*= 6.0 Hz, 1 H), 7.81-7.78 (m, 2 H), 7.58-7.47 (m, 3 H), 7.02 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 167.8, 151.4, 146.8, 139.2, 133.7, 133.3, 131.6, 130.1, 128.4, 127.4, 126.6, 125.7, 125.1, 124.6, 119.8, 114.5; **HRMS** calcd for $C_{16}H_{12}N_2O$: 248.0950, found: 248.0948.

N-(pyridin-2-yl)-2-naphthamide (4f) [s4]



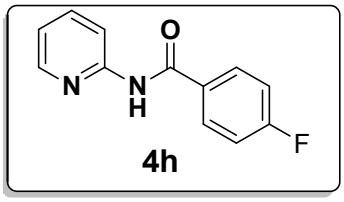
Yellow solid; m.p. 164-167 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.85 (s, 1 H), 8.43 (d, *J*= 6.0 Hz, 2 H), 8.30 (d, *J*= 6.0 Hz, 1 H), 7.98-7.93 (m, 3 H), 7.88 (d, *J*= 6.0 Hz, 1 H), 7.78 (q, *J*= 6.0 Hz, 1 H), 7.75-7.54 (m, 2 H), 7.07 (d, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.7, 151.5, 147.8, 138.6, 135.0, 132.5, 131.3, 129.1, 128.8, 128.1, 127.9, 127.8, 127.0, 123.5, 119.9, 114.2; **HRMS** calcd for $C_{16}H_{12}N_2O$: 248.0950, found: 248.0948.

6-methoxy-N-(pyridin-2-yl)-2-naphthamide (4g)



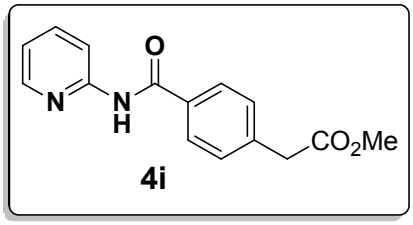
Yellow solid; m.p. 175-178 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.00 (s, 1 H), 8.43 (d, *J*= 6.0 Hz, 1 H), 8.35 (s, 1 H), 8.24 (s, 1 H), 7.93 (d, *J*= 6.0 Hz, 1 H), 7.79-7.73 (m, 1 H), 7.14 (s, 1 H), 7.03 (t, *J*= 6.0 Hz, 1 H), 3.91 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.8, 159.3, 151.7, 147.7, 138.5, 136.6, 130.6, 129.0, 127.9, 127.8, 127.3, 124.1, 119.9, 119.7, 114.2, 105.6, 55.3; **HRMS** calcd for $C_{17}H_{14}N_2O_2$: 278.1055, found: 278.1052.

4-fluoro-N-(pyridin-2-yl)benzamide (4h)[s3]



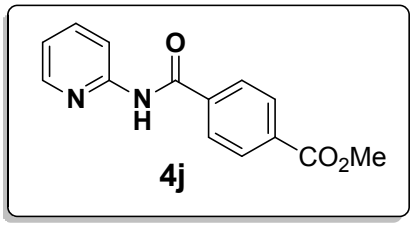
Pale white solid; m.p. 127-130 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.85 (s, 1 H), 8.34 (d, *J*= 6.0 Hz, 1 H), 8.19 (d, *J*= 6.0 Hz, 1 H), 7.94-7.91 (m, 2 H), 7.75-7.72 (m, 1 H), 7.14 (t, *J*= 6.0 Hz, 2 H), 7.04 (d, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.1 (d, $J_{C\text{-}F}$ = 255.2 Hz), 164.7, 151.4, 147.8, 138.5, 130.4, 129.7, 129.6, 120.0, 115.7, 115.8, 114.2; **HRMS** calcd for $C_{12}H_9FN_2O$: 216.0699,found: 216.0696.

Methyl 2-(4-(pyridin-2-ylcarbamoyl) phenyl) acetate (4i)



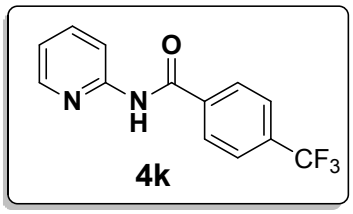
Yellow solid; m.p. 137-140 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.81 (s, 1 H), 8.37 (d, *J*= 6.0 Hz, 1 H), 8.25 (s, 1 H), 7.88 (d, *J*= 6.0 Hz, 2 H), 7.75 (t, *J*= 6.0 Hz, 1 H), 7.39 (d, *J*= 6.0 Hz, 2 H), 7.05 (t, *J*= 6.0 Hz, 1 H), 3.69 (s, 3 H), 3.68 (s, 2 H); **^{13}CNMR** (150 MHz, $CDCl_3$): δ 171.2, 165.3, 151.5, 147.6, 138.6, 138.4, 129.7, 127.5, 119.9, 114.3, 52.2, 40.9; **HRMS** calcd for $C_{15}H_{14}N_2O_3$: 270.1004, found: 270.1008.

Methyl 4-(pyridin-2-ylcarbamoyl) benzoate (4j)



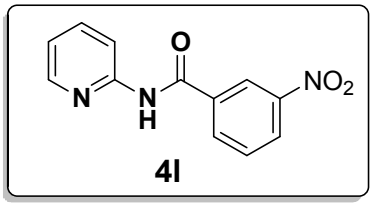
Yellow solid; m.p. 130-135 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.89 (s, 1 H), 8.38 (d, *J*= 6.0 Hz, 1 H), 8.27 (d, *J*= 6.0 Hz, 1 H), 8.14 (d, *J*= 6.0 Hz, 2 H), 7.98 (d, *J*= 6.0 Hz, 2 H), 7.79-7.76 (m, 1 H), 7.09 (d, *J*= 6.0 Hz, 1 H), 3.94 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 166.1, 164.8, 151.2, 147.5, 138.8, 137.9, 133.3, 130.0, 127.3, 120.2, 114.4, 52.4; **HRMS** calcd for $C_{14}H_{12}N_2O_3$: 256.0848, found: 256.0842.

N-(pyridin-2-yl)-4-(trifluoromethyl)benzamide (4k)



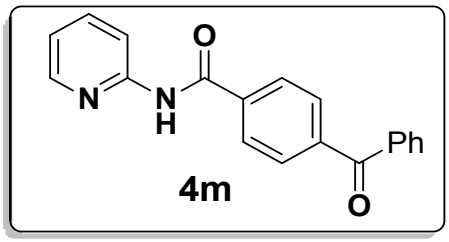
Yellow solid; m.p. 108-113 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.76 (s, 1 H), 8.36 (d, *J*= 6.0 Hz, 1 H), 8.25 (s, 1 H), 8.02 (d, *J*= 6.0 Hz, 2 H) 7.78-7.74 (m, 3 H), 7.08 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 164.3, 151.3, 147.9, 138.6, 137.5, 134.0, 133.7, 127.7, 125.9, 125.8, 124.6, 122.4, 120.3, 114.3; **HRMS** calcd for $C_{13}H_9F_3N_2O$: 266.0667, found: 266.0666.

3-nitro-N-(pyridin-2-yl)benzamide (4l)



Dark yellow solid; m.p. 223-226 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.94 (s, 1 H), 8.79 (s, 1 H), 8.42-8.37 (m, 2 H), 8.30 (t, *J*= 6.0 Hz, 1 H), 7.82-7.78(m, 1 H), 7.71 (t, *J*= 6.0 Hz, 1 H), 7.12 (d, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.2, 150.9, 147.6, 139.0, 135.8, 133.1, 130.15, 130.13, 126.7, 122.3, 120.5, 114.4; **HRMS** calcd for $C_{12}H_9N_3O_3$: 243.0644, found: 243.0646.

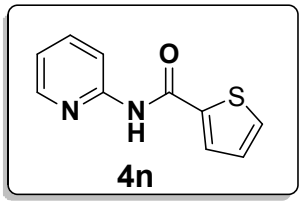
4-benzoyl-N-(pyridin-2-yl)benzamide (4m)



Yellow solid; m.p. 181-184 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.84 (s, 1 H), 8.39 (d, *J*= 6.0 Hz, 1 H), 8.28 (d, *J*= 6.0 Hz, 1 H), 8.01 (d, *J*= 6.0 Hz, 1 H), 7.90-7.79 (m, 5 H), 7.62-7.50 (m, 1 H), 7.49 (d, *J*= 6.0 Hz, 2 H), 7.10-7.08 (m, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 195.7, 164.8,

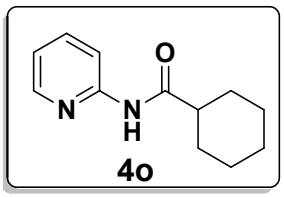
151.3, 147.8, 140.7, 138.6, 137.3, 136.9, 132.9, 130.3, 130.0, 128.4, 127.2, 120.2, 114.3. **HRMS** calcd for $C_{19}H_{14}N_2O_2$: 302.1055, found: 302.1051.

N-(pyridin-2-yl) thiophene-2-carboxamide (4n) [s3]



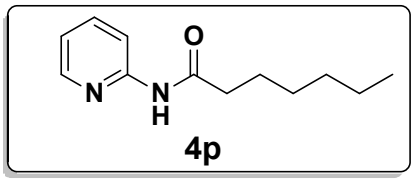
Yellow solid; m.p. 142-145 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.81 (s, 1 H), 8.83 (d, *J*= 6.0 Hz, 1 H), 8.26 (s, 1 H), 7.71-7.61 (m, 2 H), 7.56 (d, *J*= 6.0 Hz, 1 H), 7.12 (t, *J*= 6.0 Hz, 1 H), 7.06 (d, *J*= 6.0 Hz, 1 H); **^{13}CNMR** (150 MHz, $CDCl_3$): δ 160.0, 151.1, 147.2, 138.9, 138.8, 131.7, 129.0, 128.0, 119.9, 114.4; **HRMS** calcd for $C_{10}H_8N_2OS$: 204.0357,found: 204.0353.

N-(pyridin-2-yl)cyclohexanecarboxamide (4o) [s3]



Yellow solid; m.p. 73-75 ˚C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.57 (s, 1 H), 8.22 (d, *J*= 6.0 Hz, 2 H), 7.68-7.65 (m, 1 H), 6.99 (t, *J*= 6.0 Hz, 1 H), 2.26-2.21 (m, 1 H), 1.92 (m, 2 H), 1.80-1.64 (m, 5 H), 1.48-1.32 (m, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 175.0, 151.7, 147.3, 138.5, 119.5, 114.2, 46.3, 29.4, 25.6, 25.5; **HRMS** calcd for $C_{12}H_{16}N_2O$: 204.1263,found: 204.1261.

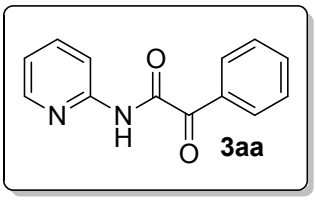
N-(pyridin-2-yl)heptanamide (4p)



Yellow solid; m.p. 88-91 ˚C; ^{1}H **NMR** (600 MHz, $CDCl_3$): δ 8.57(s, 1 H), 8.21 (d, *J*= 6.0 Hz, 2 H), 7.69-7.65 (m, 1 H), 7.00 (t, *J*= 6.0 Hz, 1 H), 2.35 (t, *J*= 6.0 Hz, 2 H), 1.71-1.65 (m, 2 H),

1.34-1.27 (m, 6 H), 0.85 (t, *J*= 6.0 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.0, 151.5, 147.4, 138.4, 119.5, 114.1, 33.7, 31.4, 28.8, 25.3, 22.4, 13.9; **HRMS** calcd for $C_{12}H_{18}N_2O$: 206.1419,found: 206.1418.

2-oxo-2-phenyl-N-(pyridin-2-yl)acetamide (3aa)[s5]



Yellow solid; m.p. 105-108 ˚C; **^{1}H NMR** (500 MHz, $CDCl_3$): **δ** 9.47 (s, 1 H), 8.36 (d, *J*= 10.0 Hz, 3 H), 8.30 (d, *J*= 10.0 Hz, 1 H), 7.76 (d, *J*= 10.0 Hz, 1 H), 7.64 (t, *J*= 10.0 Hz, 1 H), 7.50 (t, *J*= 10.0 Hz, 2 H), 7.11 (t, *J*= 5.0 Hz, 1 H); **^{13}CNMR** (125 MHz, $CDCl_3$): δ 186.6, 159.3, 150.2, 148.4, 138.4, 134.6, 132.8, 131.3, 128.6, 120.7, 114.1; **HRMS** calcd for $C_{13}H_{10}N_2O_2$: 226.0742, found: 226.0740.

References:

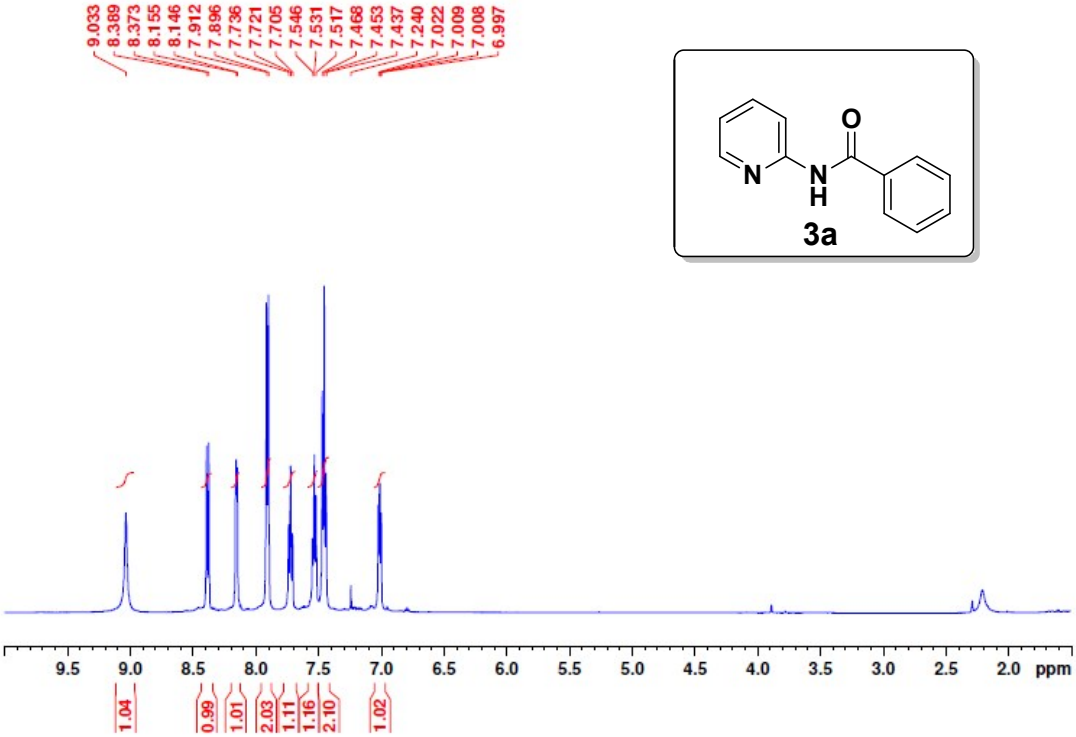
S1. W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang and A. Lei, *J. Am. Chem. Soc.* 2008, **130**, 14713.

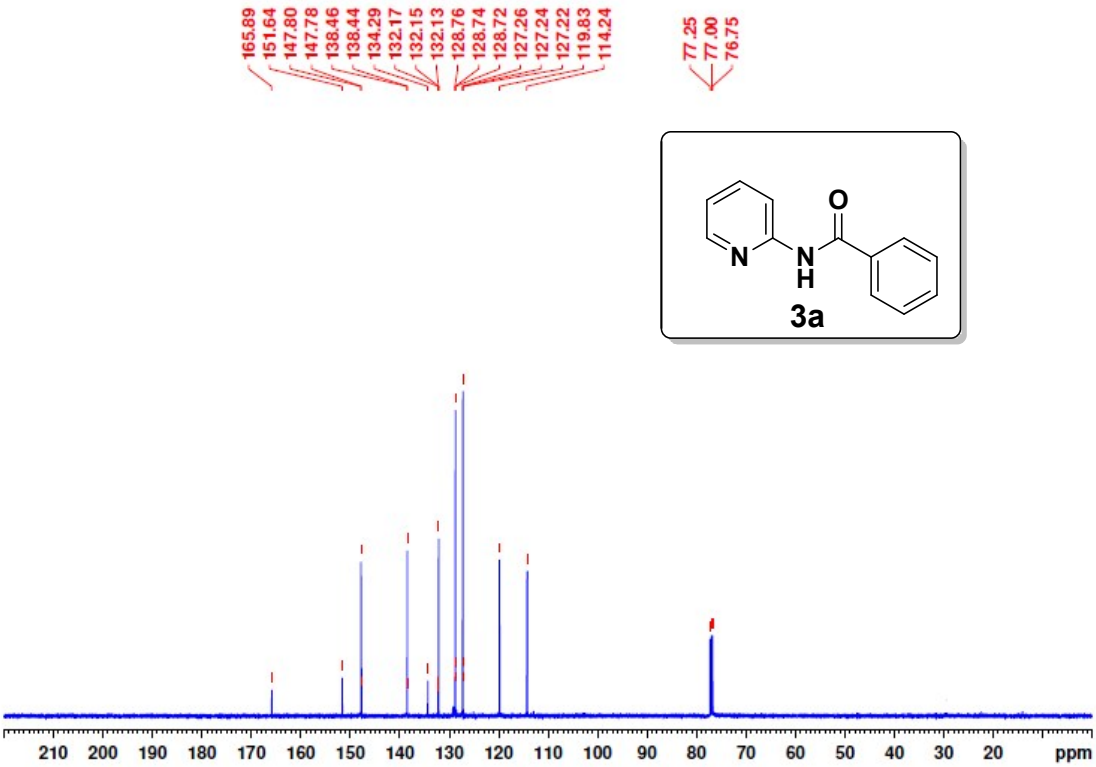
S2. Y. Okamoto and S. K. Kundu, *J. Phys. Chem.* 1973, **77**, 2677.

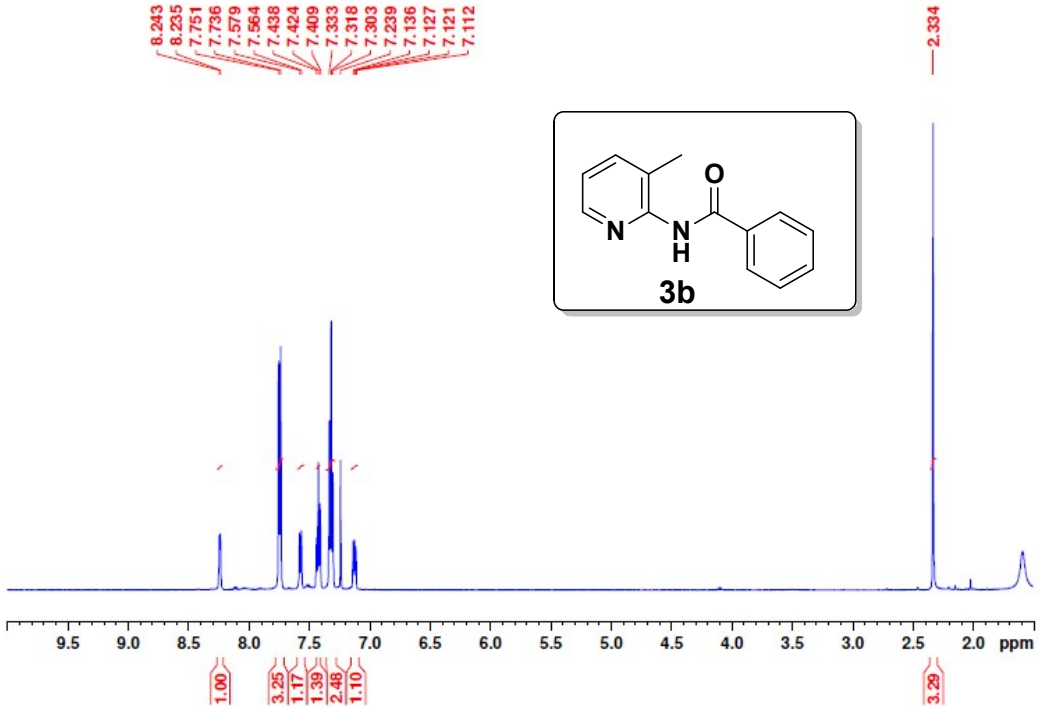
S3. Om P. S. Patel, D. Anand, R. K. Maurya and P. P. Yadav, *Green Chem.* 2015, **17**, 3728.

S4. P. Subramanian, S. Indu, and K. P. Kaliappan, *Org. Lett.* 2014., **16**, 6212.

S5. J. Sun, Q. Tan, W. Yang, B. Liu, and B. Xu, *Adv. Synth. Catal.* 2014, **356**, 388.


9.033
8.389
8.373
8.155
8.146
7.912
7.896
7.736
7.721
7.705
7.546
7.531
7.517
7.468
7.453
7.437
7.240
7.022
7.009
7.008
6.997
O
N
N
H
3a
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 ppm
1.04
0.99
1.01
2.03
1.11
1.16
2.10
1.02


165.89
151.64
147.80
147.78
138.46
138.44
134.29
132.17
132.15
132.13
128.76
128.74
128.72
127.26
127.24
127.22
119.83
114.24
77.25
77.00
76.75
O
N
N
H
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.235
7.751
7.736
7.579
7.564
7.438
7.424
7.409
7.333
7.318
7.303
7.239
7.136
7.127
7.121
7.112
2.334
3b
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 ppm
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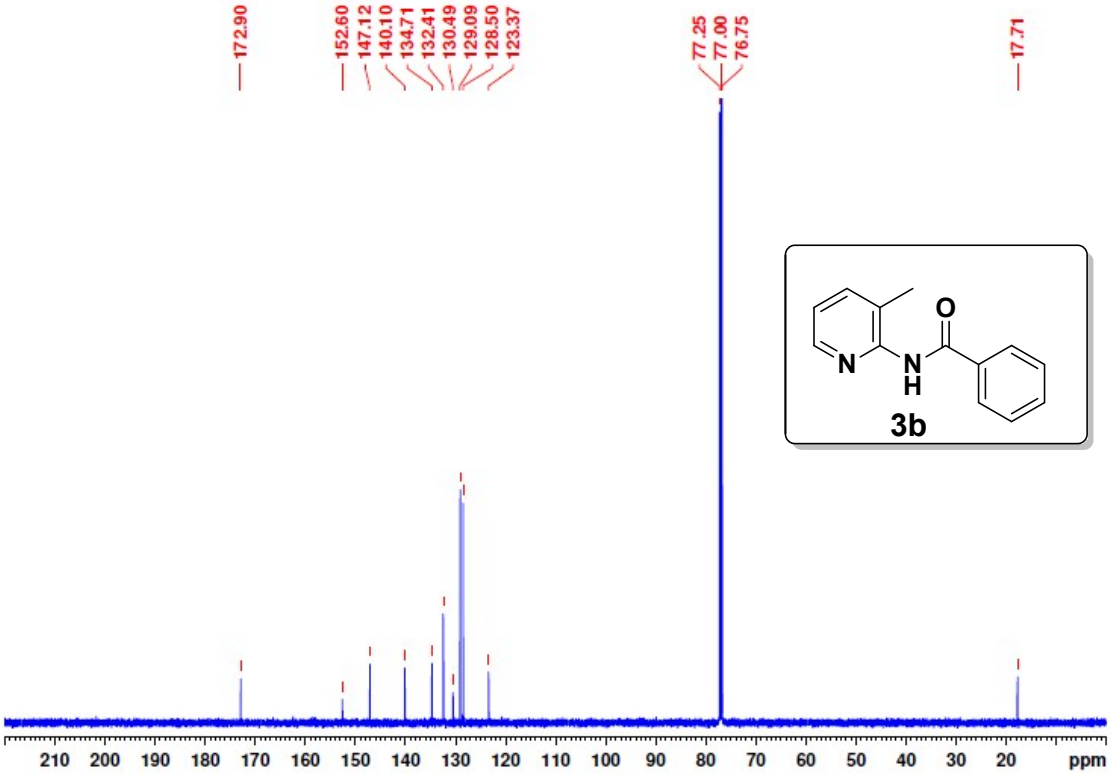
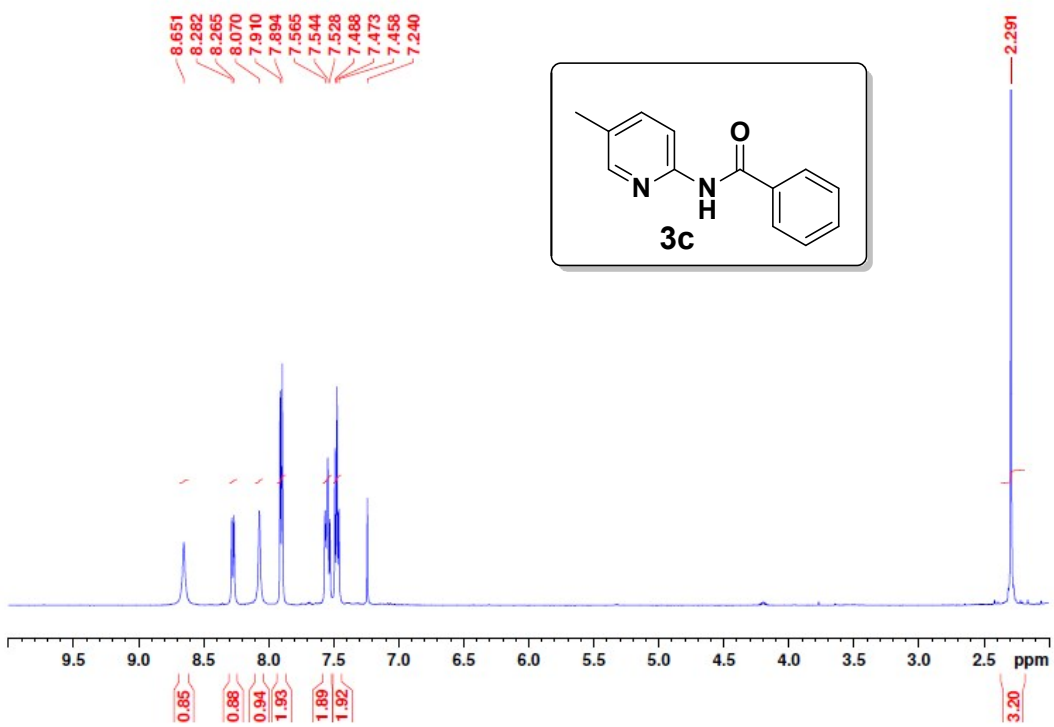
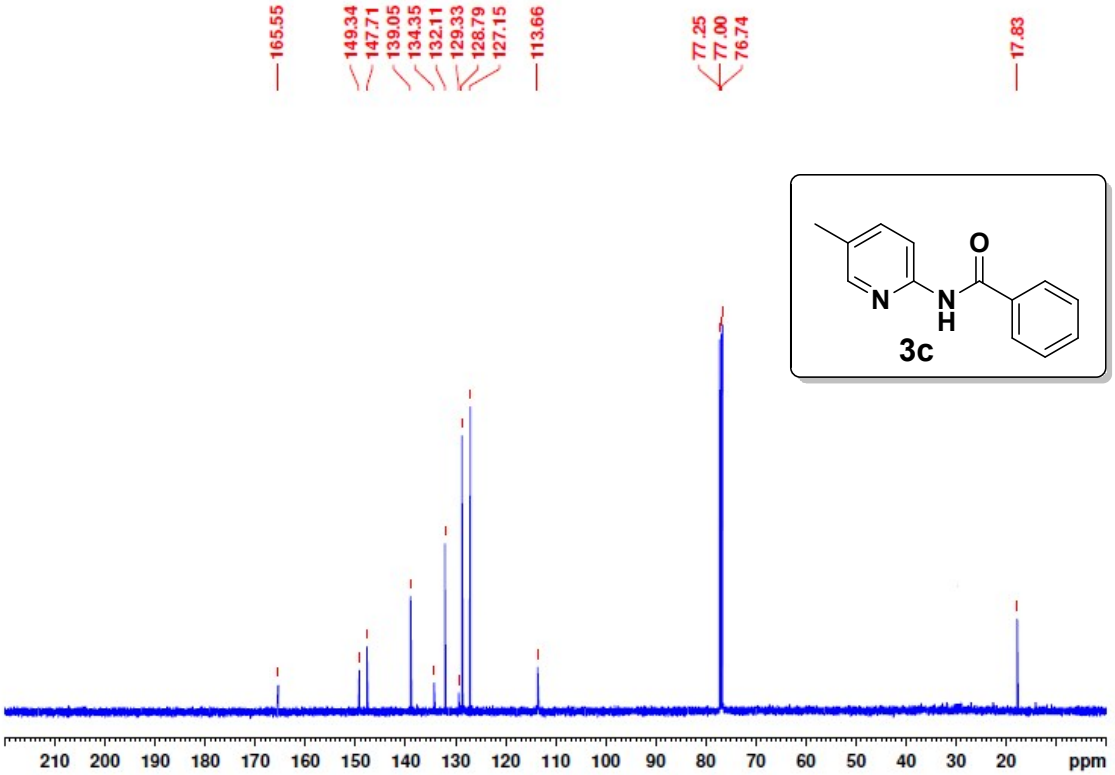
3.25
1.17
1.39
2.46
1.10
3.29


172.90
152.60
147.12
140.10
134.71
132.41
130.49
129.09
128.50
123.37
77.25
77.00
76.75
17.71
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.651
8.282
8.265
8.070
7.910
7.894
7.565
7.544
7.528
7.488
7.473
7.458
7.240
2.291
O
N
N
H
3c
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 ppm
0.85
0.88
0.94
1.93
1.89
1.92
3.20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149.34
147.71
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134.35
132.11
129.33
128.79
127.15
113.66
77.25
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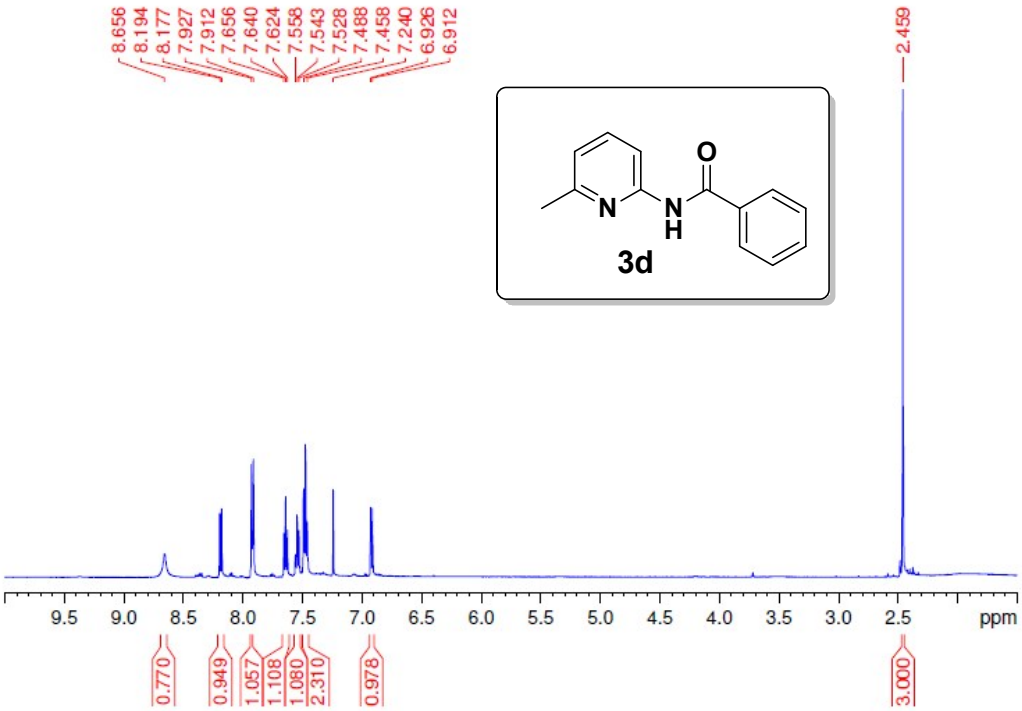
76.74
17.83
O
N
N
H
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.177
7.927
7.912
7.656
7.640
7.624
7.558
7.543
7.528
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7.458
7.240
6.926
6.912
2.459
3d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
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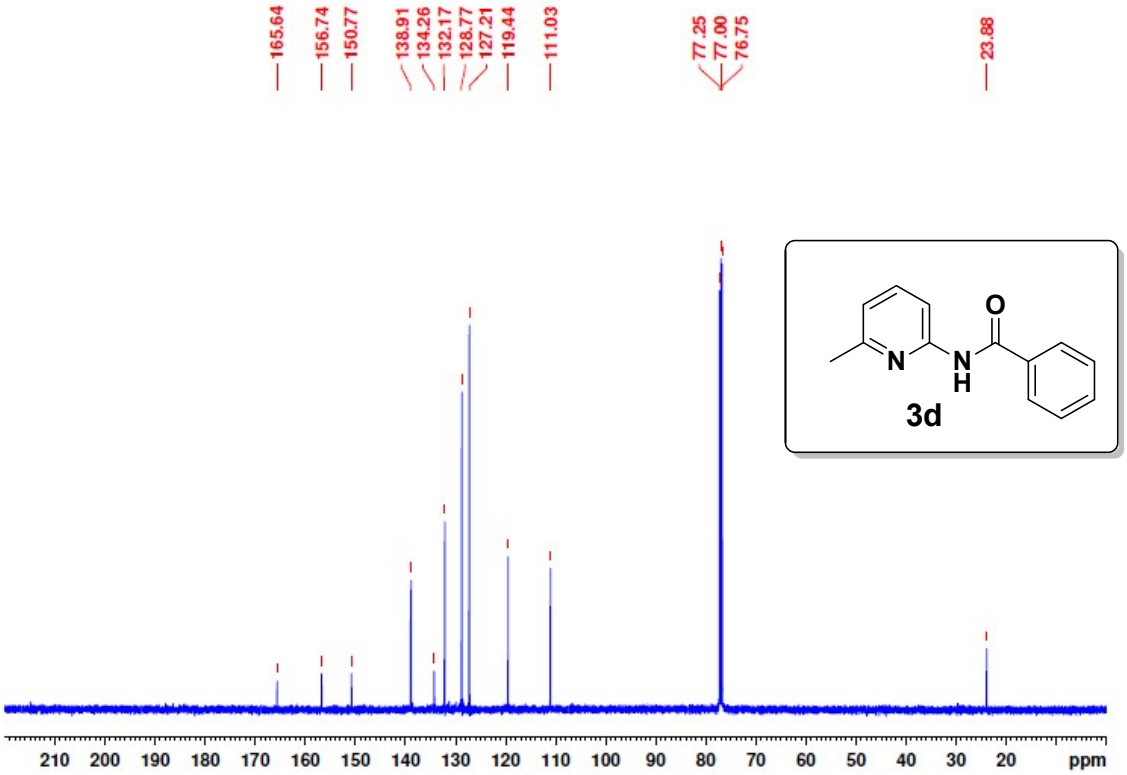
1.108
1.080
2.310
0.978
3.000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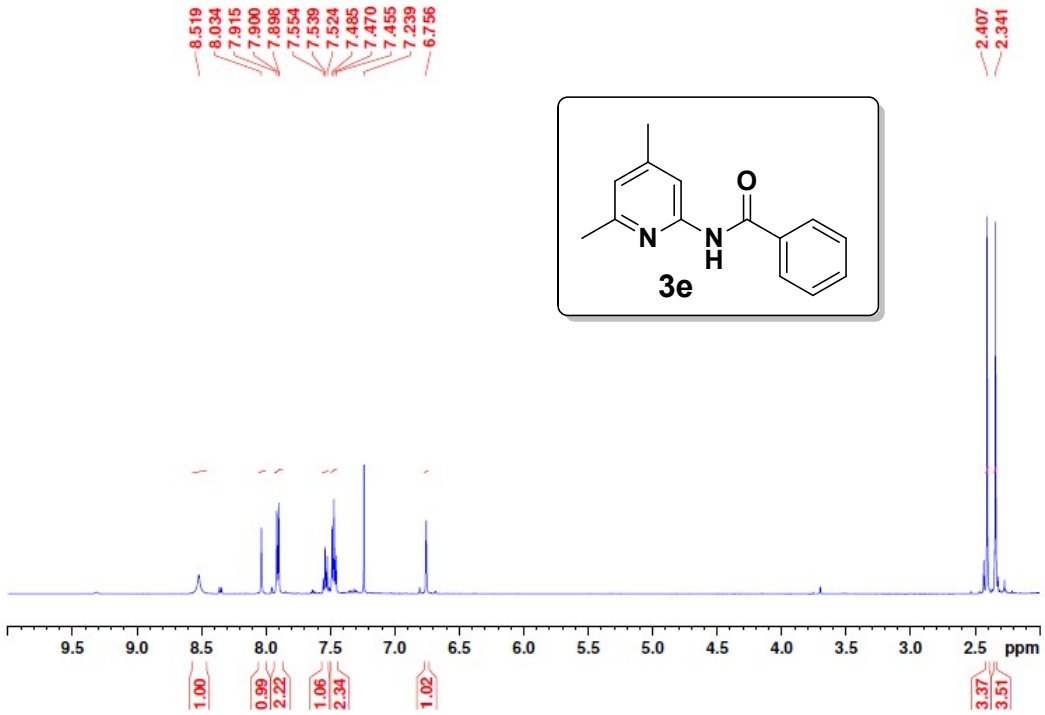
134.26
132.17
128.77
127.21
119.44
111.03
77.25
77.00
76.75
23.88
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.034
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7.898
7.554
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7.524
7.485
7.470
7.455
7.239
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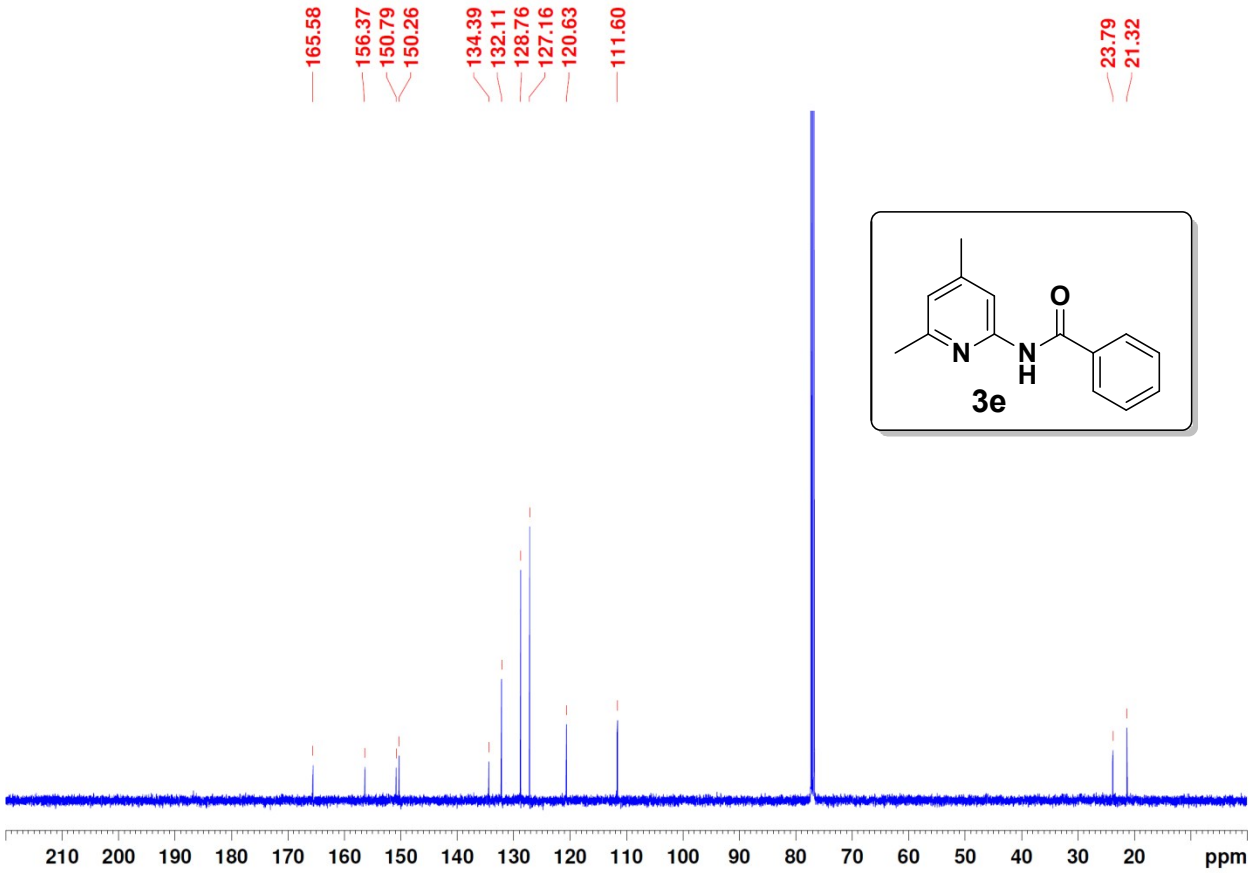
2.407
2.341
O
N
N
H
3e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.00
0.99
2.22
1.06
2.34
1.02
3.37
3.51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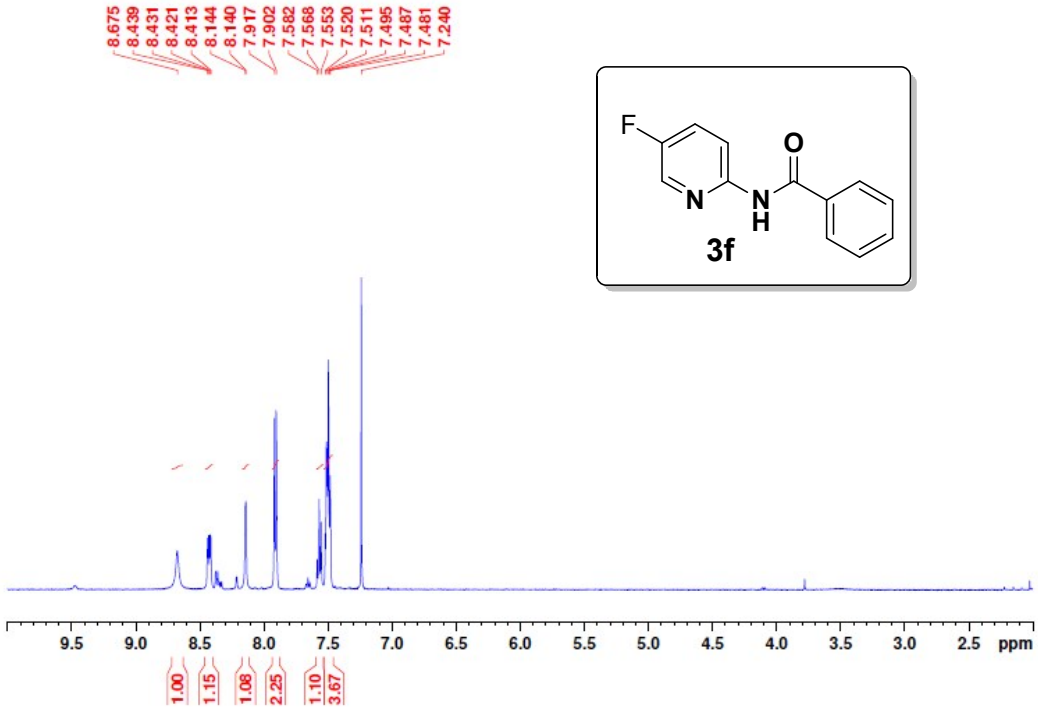
156.37
150.79
150.26
134.39
132.11
128.76
127.16
120.63
111.60
23.79
21.32
O
N
N
H
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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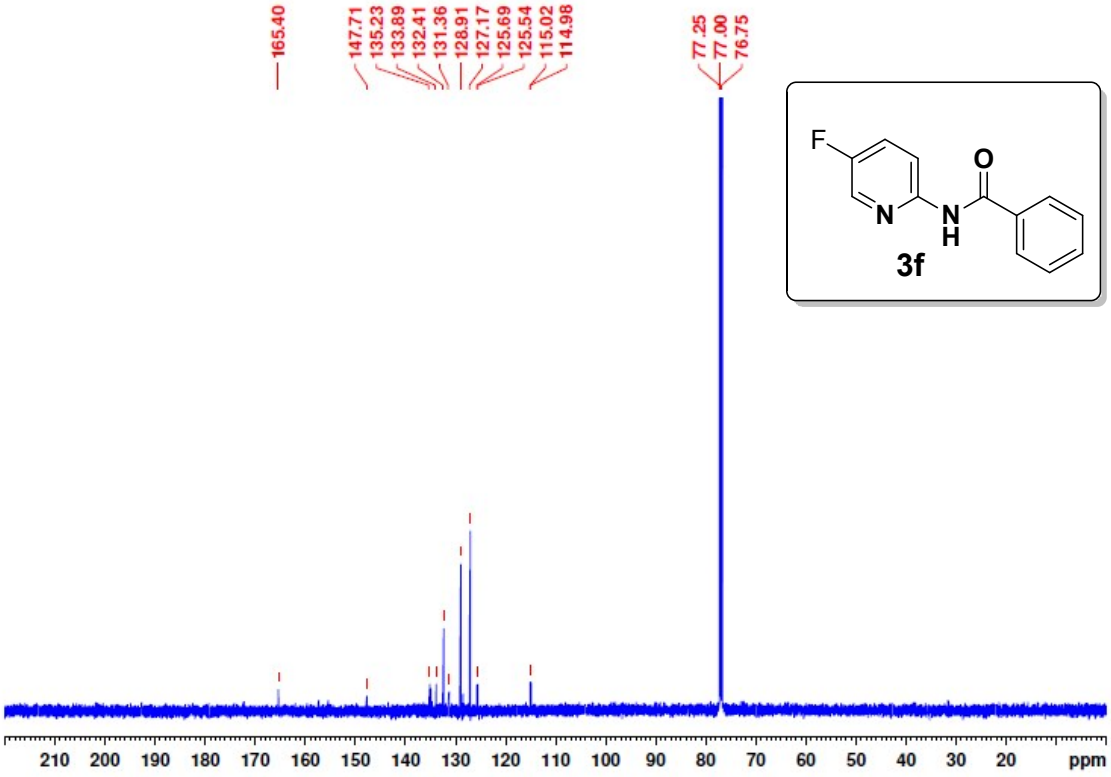
8.439
8.431
8.421
8.413
8.144
8.140
7.917
7.902
7.582
7.568
7.553
7.520
7.511
7.495
7.487
7.481
7.240
F
O
N
N
H
3f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.00
1.15
1.08
2.25
1.10
3.67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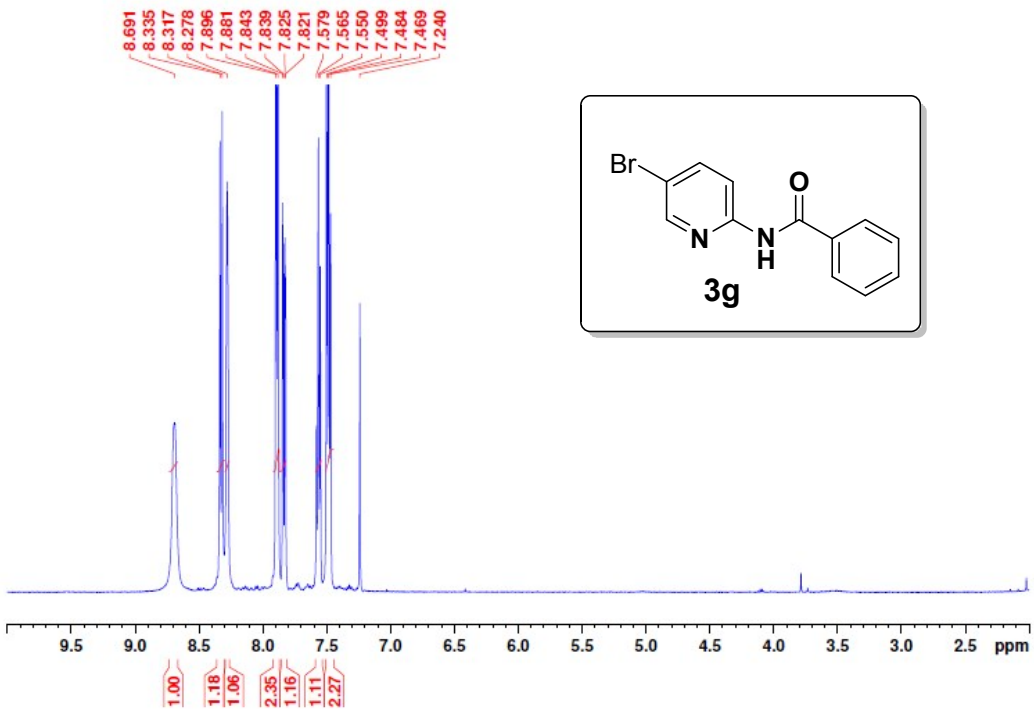
147.71
135.23
133.89
132.41
131.36
128.91
127.17
125.69
125.54
115.02
114.98
77.25
77.00
76.75
F
O
N
N
H
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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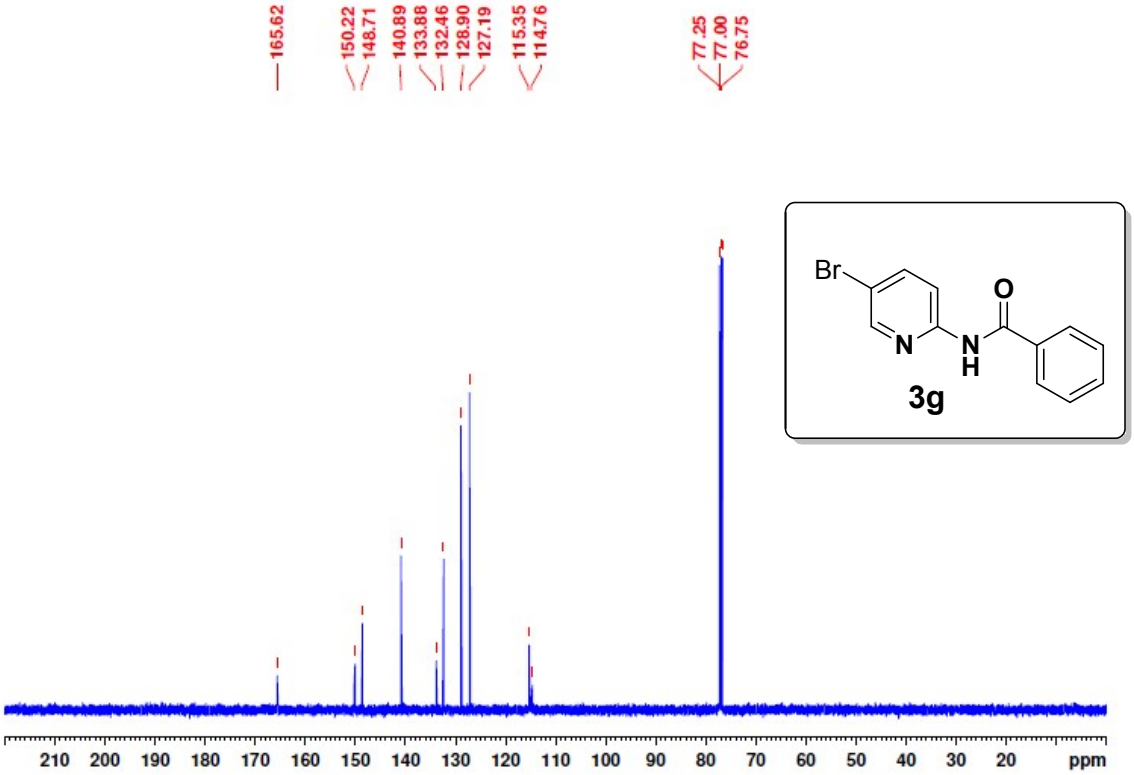
8.335
8.317
8.278
7.896
7.881
7.843
7.839
7.825
7.821
7.579
7.565
7.550
7.499
7.484
7.469
7.240
Br
O
N
N
H
3g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.00
1.18
1.06
2.35
1.16
1.11
2.27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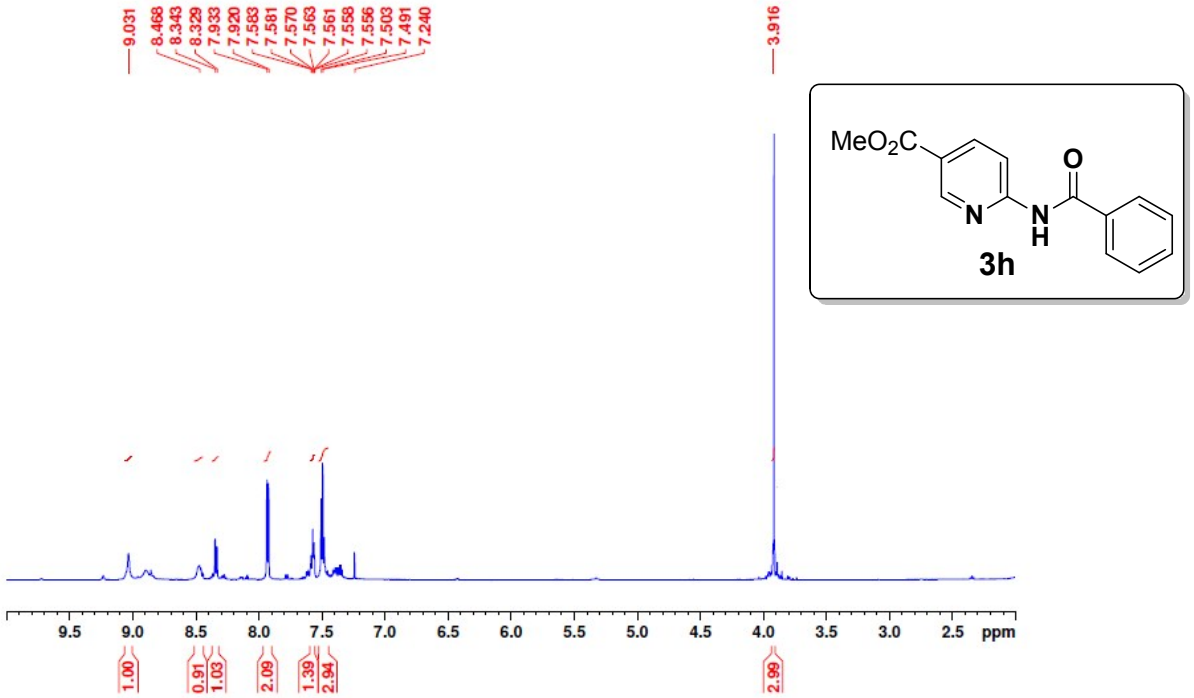
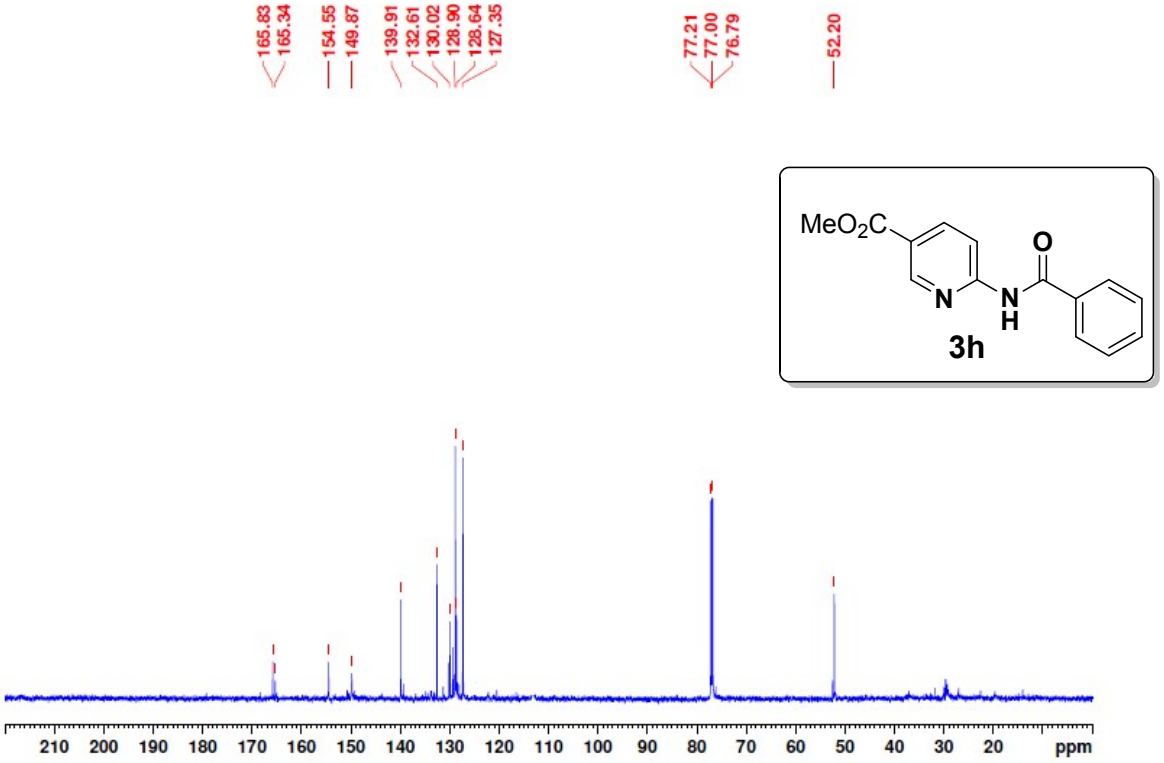
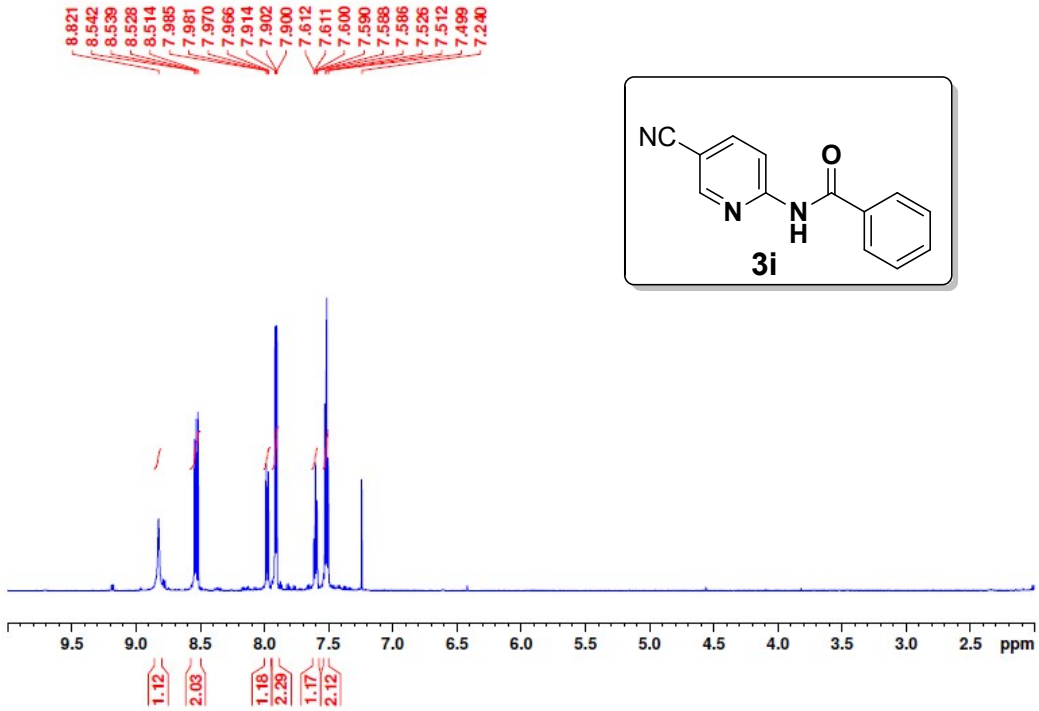
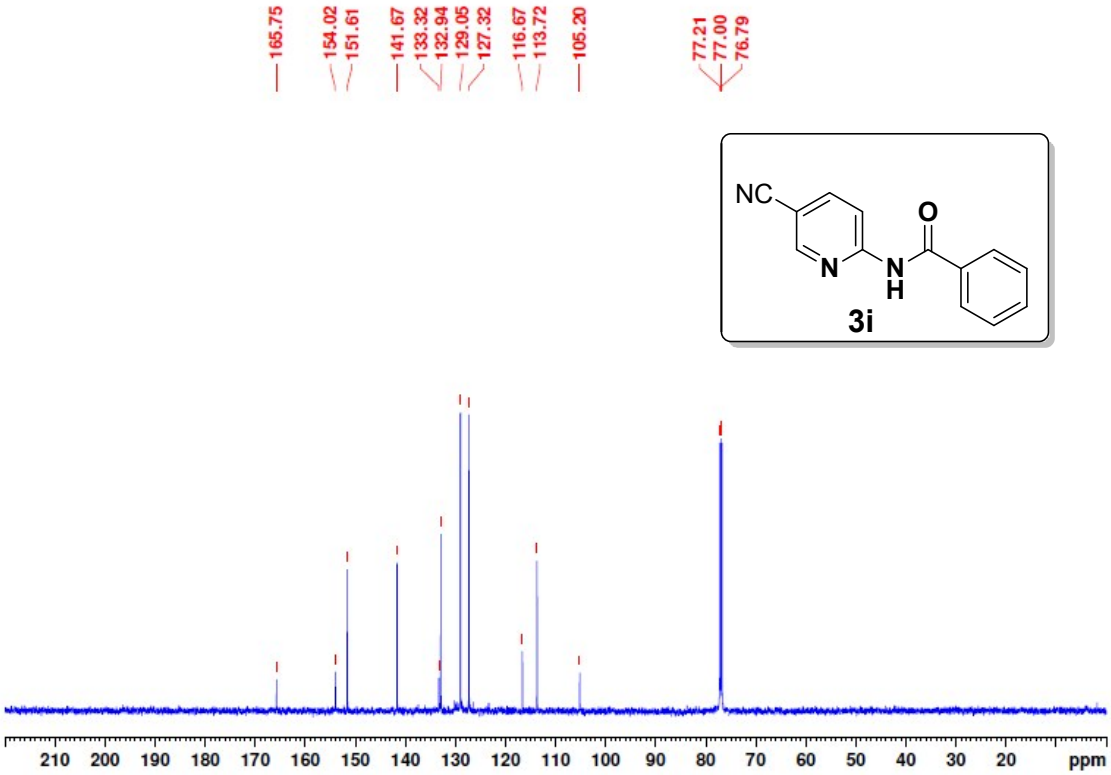
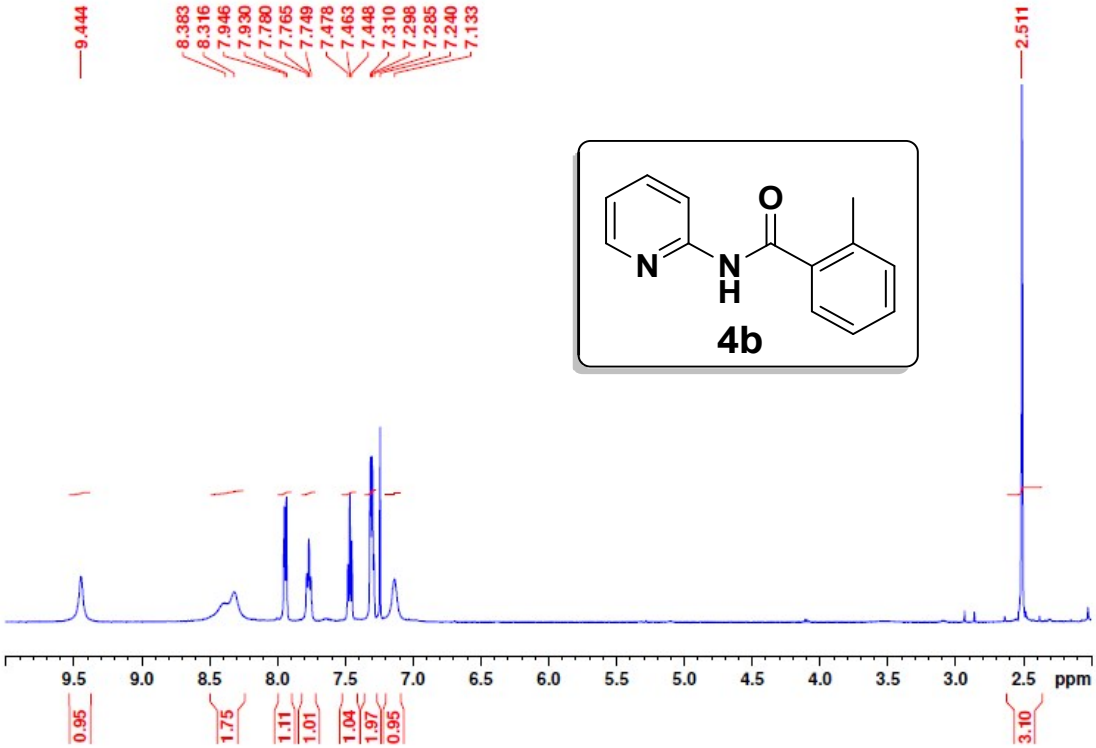
150.22
148.71
140.89
133.88
132.46
128.90
127.19
115.35
114.76
77.25
77.00
76.75
Br
O
N
N
H
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

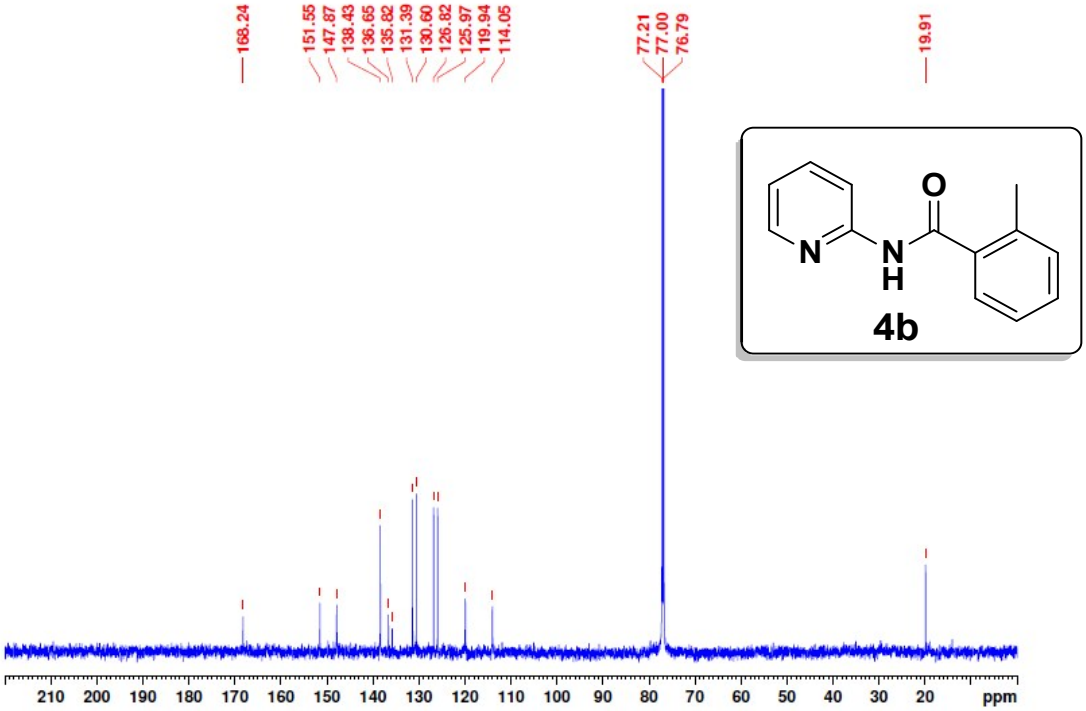

9.031
8.468
8.343
8.329
7.933
7.920
7.583
7.581
7.570
7.563
7.561
7.558
7.556
7.503
7.491
7.240
3.916
MeO2C
O
N
N
H
3h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.00
0.91
1.03
2.09
1.39
2.94
2.99

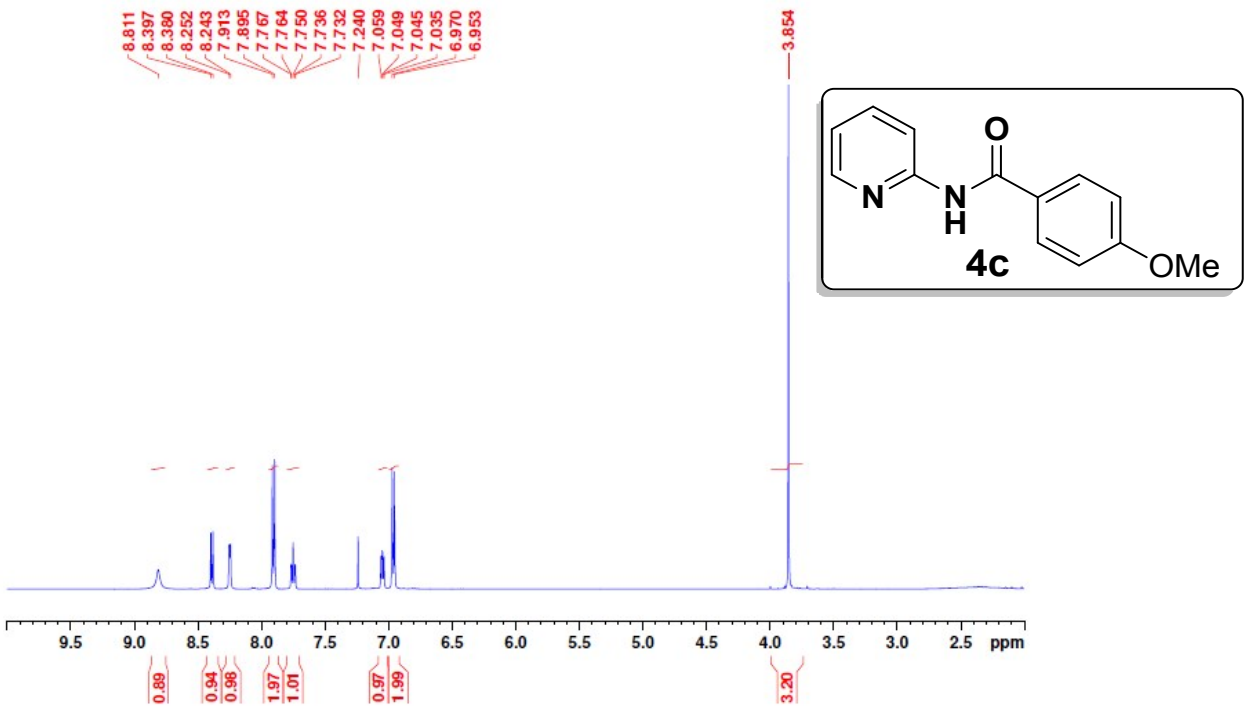

165.83
165.34
154.55
149.87
139.91
132.61
130.02
128.90
128.64
127.35
77.21
77.00
76.79
52.20
MeO2C
O
N
N
H
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

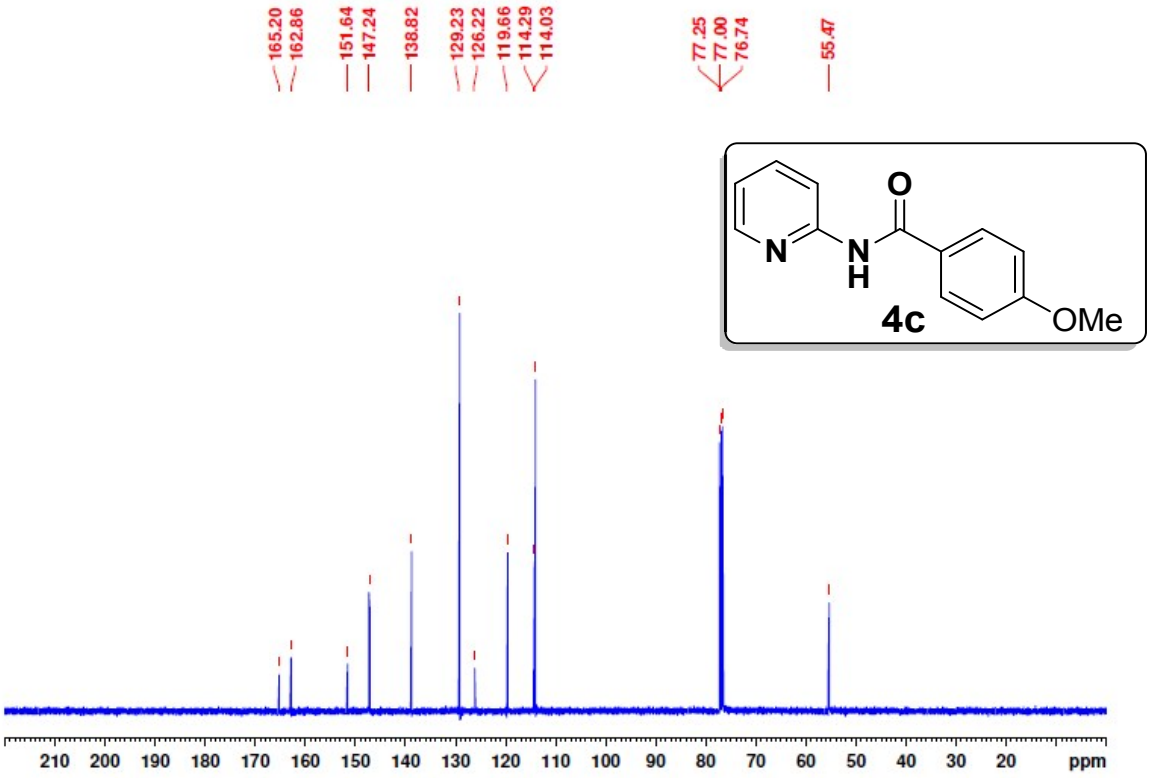

8.821
8.542
8.539
8.528
8.514
7.985
7.981
7.970
7.966
7.914
7.902
7.900
7.612
7.611
7.600
7.590
7.588
7.586
7.526
7.512
7.499
7.240
NC
O
N
N
H
3i
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.12
2.03
1.18
2.29
1.17
2.12

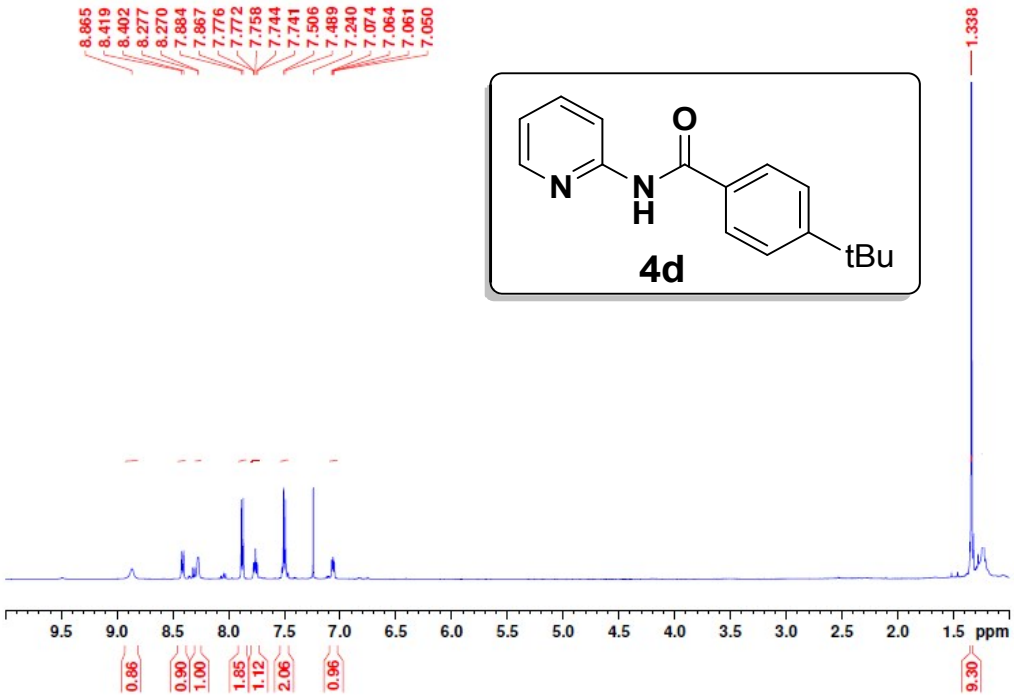

165.75
154.02
151.61
141.67
133.32
132.94
129.05
127.32
116.67
113.72
105.20
77.21
77.00
76.79
NC
O
N
N
H
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

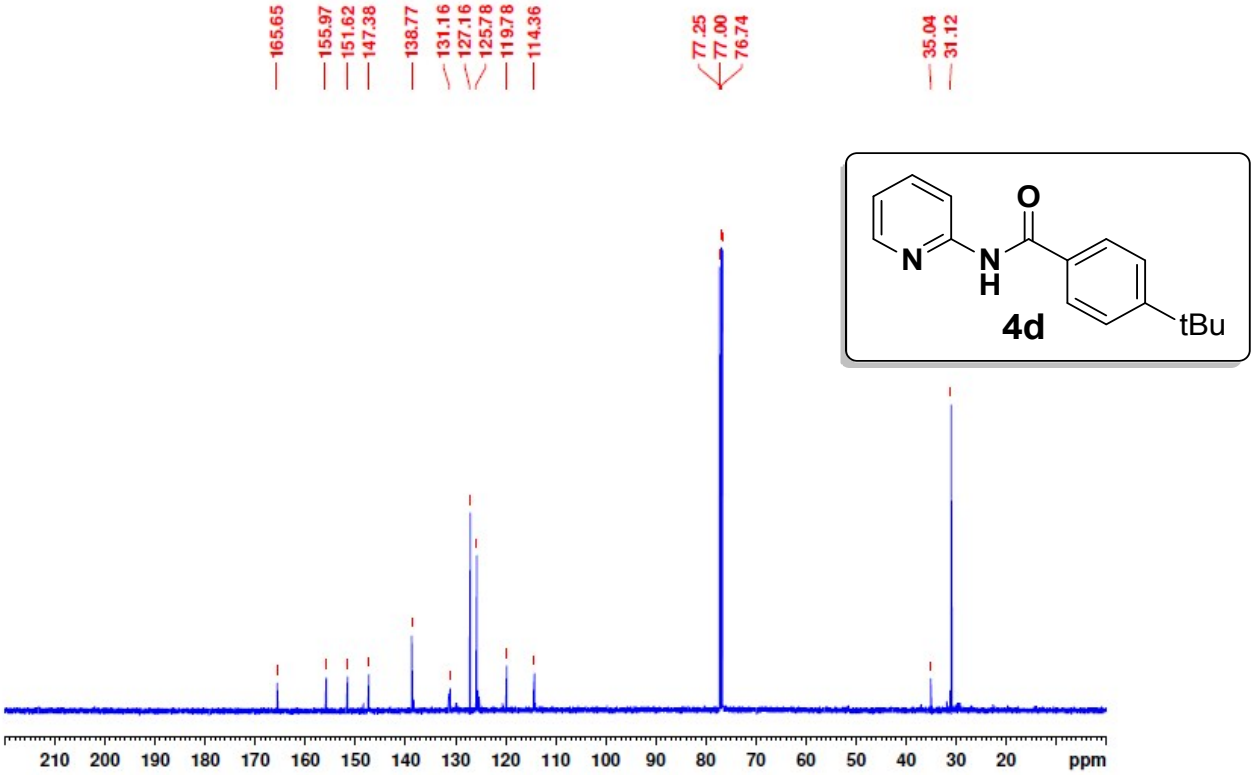

9.444
8.383
8.316
7.946
7.930
7.780
7.765
7.749
7.478
7.463
7.448
7.310
7.298
7.285
7.240
7.133
2.511
O
N
N
H
4b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
0.95
1.75
1.11
1.01
1.04
1.97
0.95
3.10

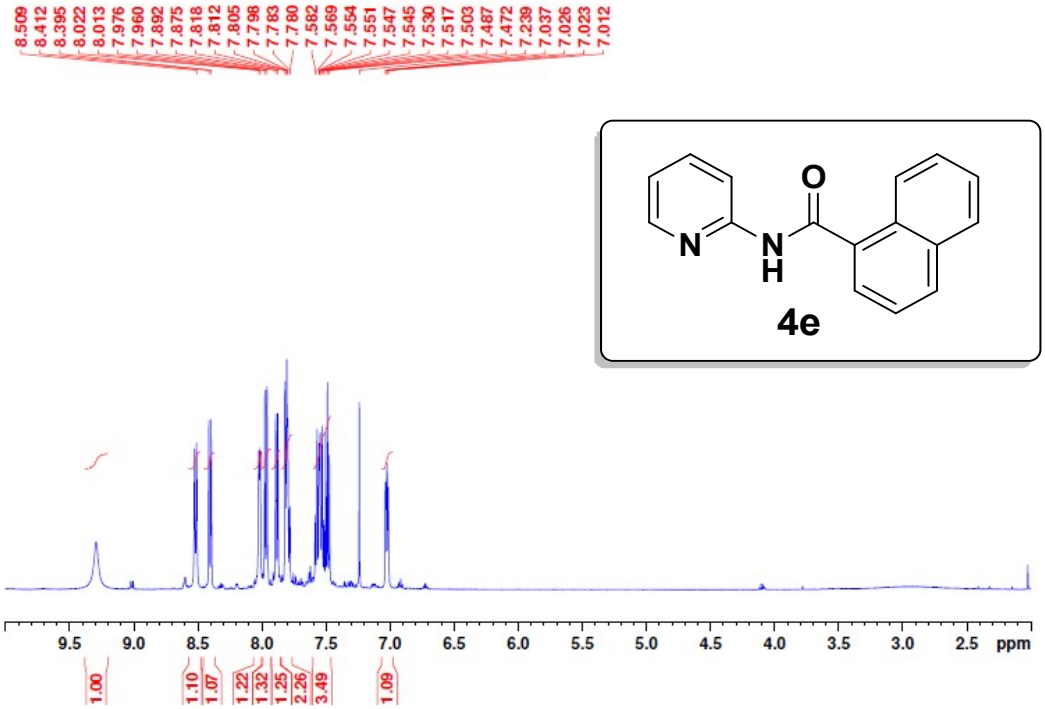

168.24
151.55
147.87
138.43
136.65
135.82
131.39
130.60
126.82
125.97
119.94
114.05
77.21
77.00
76.79
19.91
O
N
N
H
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

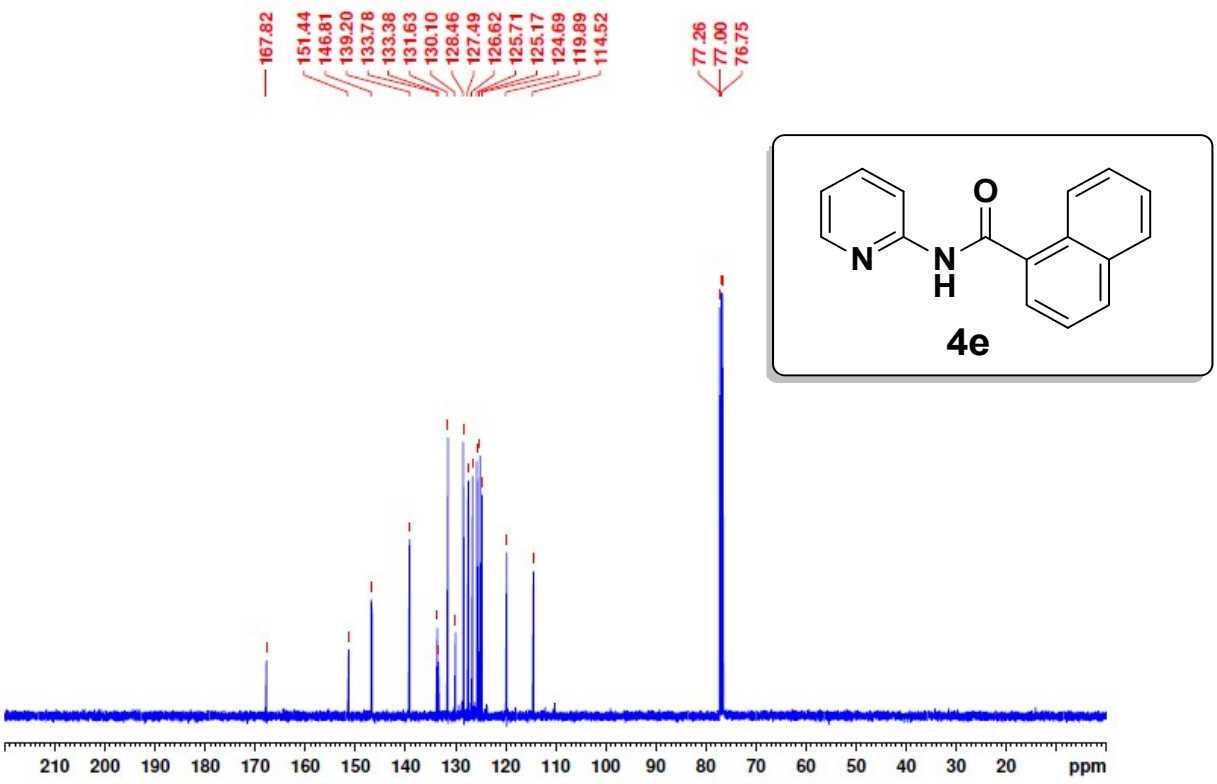

8.811
8.397
8.380
8.252
8.243
7.913
7.895
7.767
7.764
7.750
7.736
7.732
7.240
7.059
7.049
7.045
7.035
6.970
6.953
3.854
O
N
N
H
4c
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
0.89
0.94
0.98
1.97
1.01
0.97
1.99
3.20

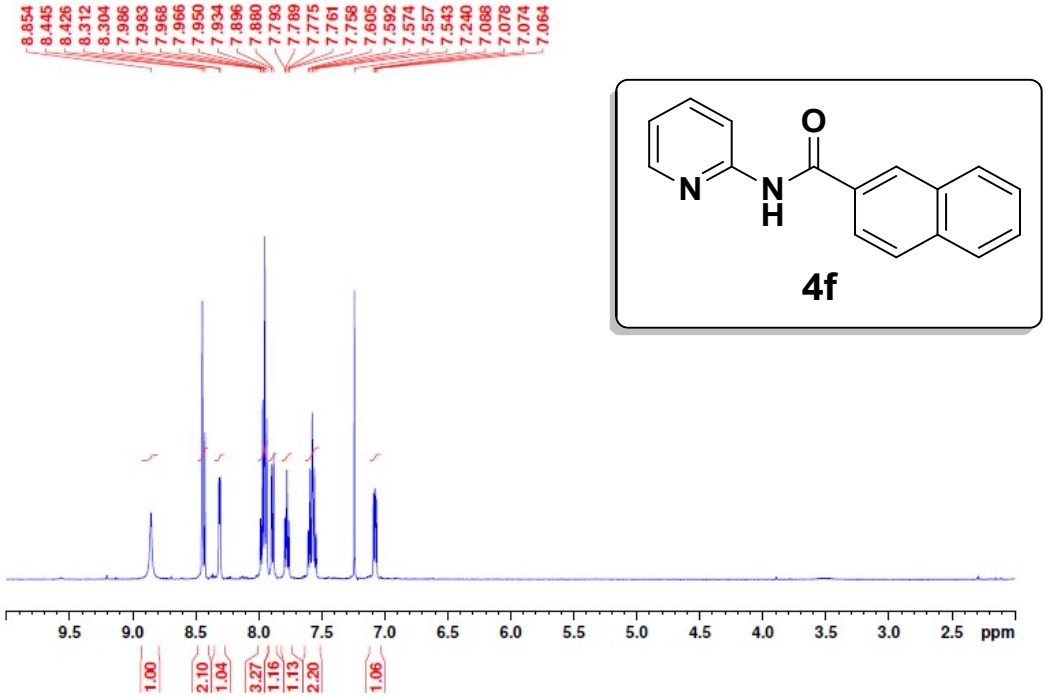

165.20
162.86
151.64
147.24
138.82
129.23
126.22
119.66
114.29
114.03
77.25
77.00
76.74
55.47
O
N
N
H
4c
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.865
8.419
8.402
8.277
8.270
7.884
7.867
7.776
7.772
7.758
7.744
7.741
7.506
7.489
7.240
7.074
7.064
7.061
7.050
1.338
O
N
N
H
4d
tBu
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 ppm
0.86
0.90
1.00
1.85
1.12
2.06
0.96
9.30


165.65
155.97
151.62
147.38
138.77
131.16
127.16
125.78
119.78
114.36
77.25
77.00
76.74
35.04
31.12
O
N
N
H
4d
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.509
8.412
8.395
8.022
8.013
7.976
7.960
7.892
7.875
7.818
7.812
7.805
7.798
7.783
7.780
7.582
7.569
7.554
7.551
7.547
7.545
7.530
7.517
7.503
7.487
7.472
7.239
7.037
7.026
7.023
7.012
O
N
N
H
4e
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
ppm
1.00
1.10
1.07
1.22
1.32
1.25
2.26
3.49
1.09


167.82
151.44
146.81
139.20
133.78
133.38
131.63
130.10
128.46
127.49
126.62
125.71
125.17
124.69
119.89
114.52
77.26
77.00
76.75
O
N
N
H
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.445
8.426
8.312
8.304
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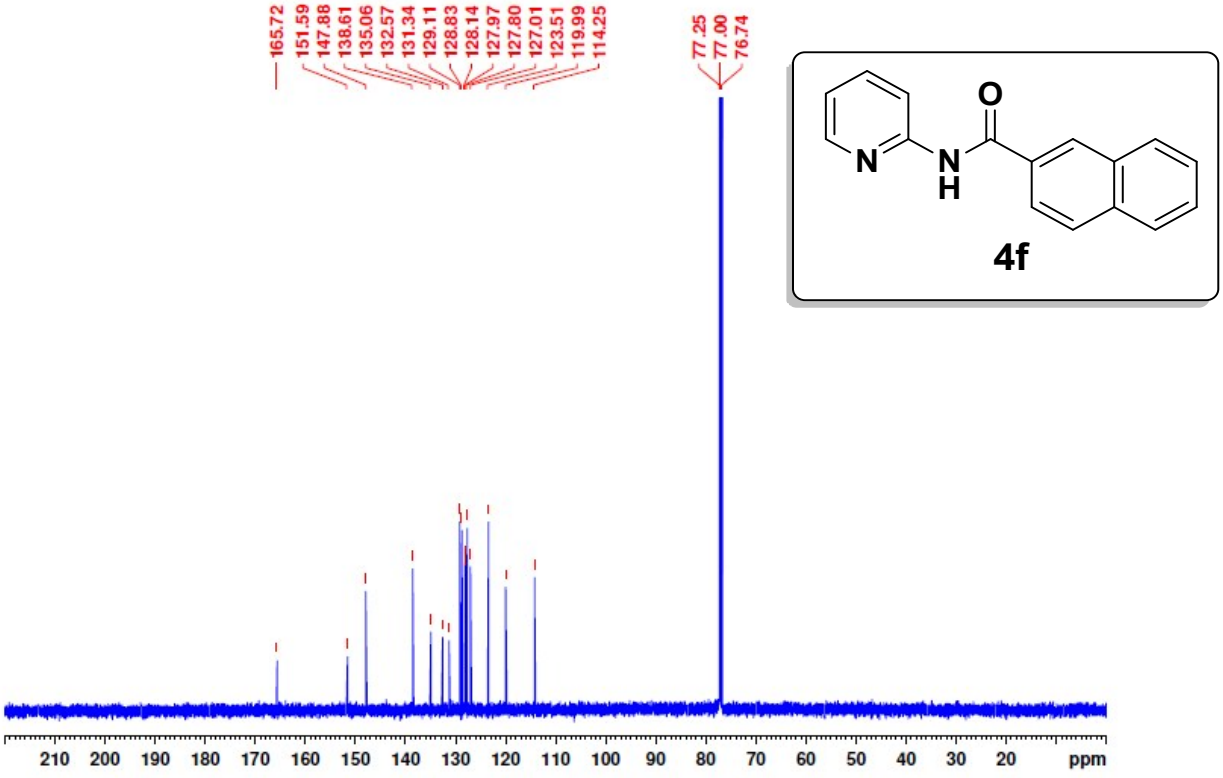
7.983
7.968
7.966
7.950
7.934
7.896
7.880
7.793
7.789
7.775
7.761
7.758
7.605
7.592
7.574
7.557
7.543
7.240
7.088
7.078
7.074
7.064
O
N
N
H
4f
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.00
2.10
1.04
3.27
1.16
1.13
2.20
1.06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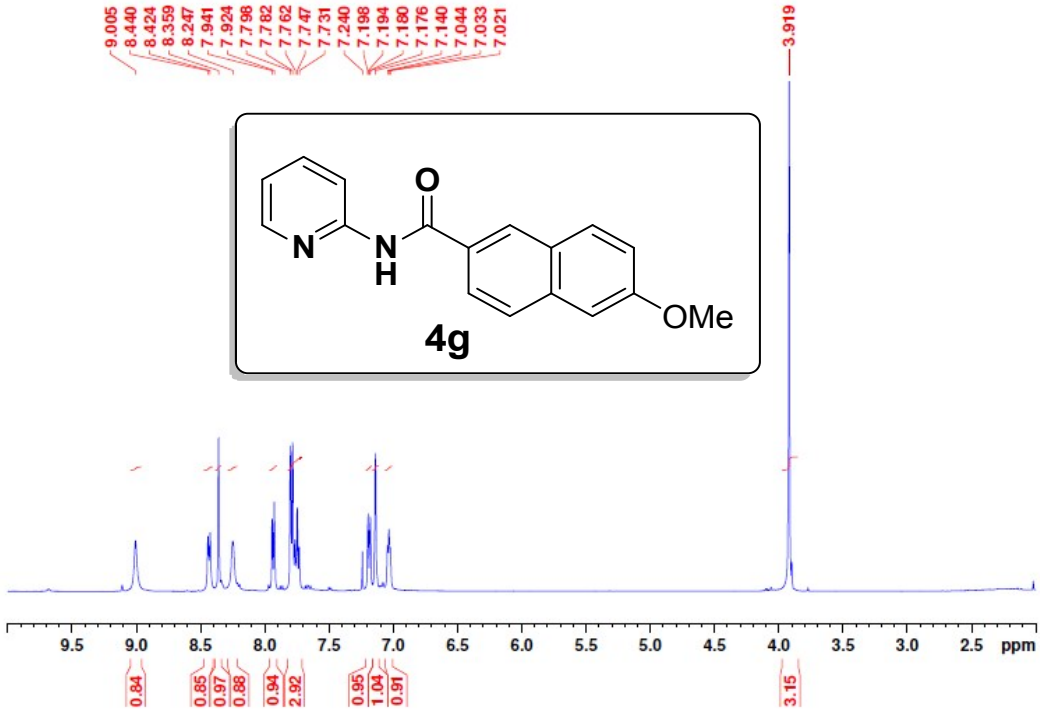
147.88
138.61
135.06
132.57
131.34
129.11
128.83
128.14
127.97
127.80
127.01
123.51
119.99
114.25
77.25
77.00
76.74
O
N
N
H
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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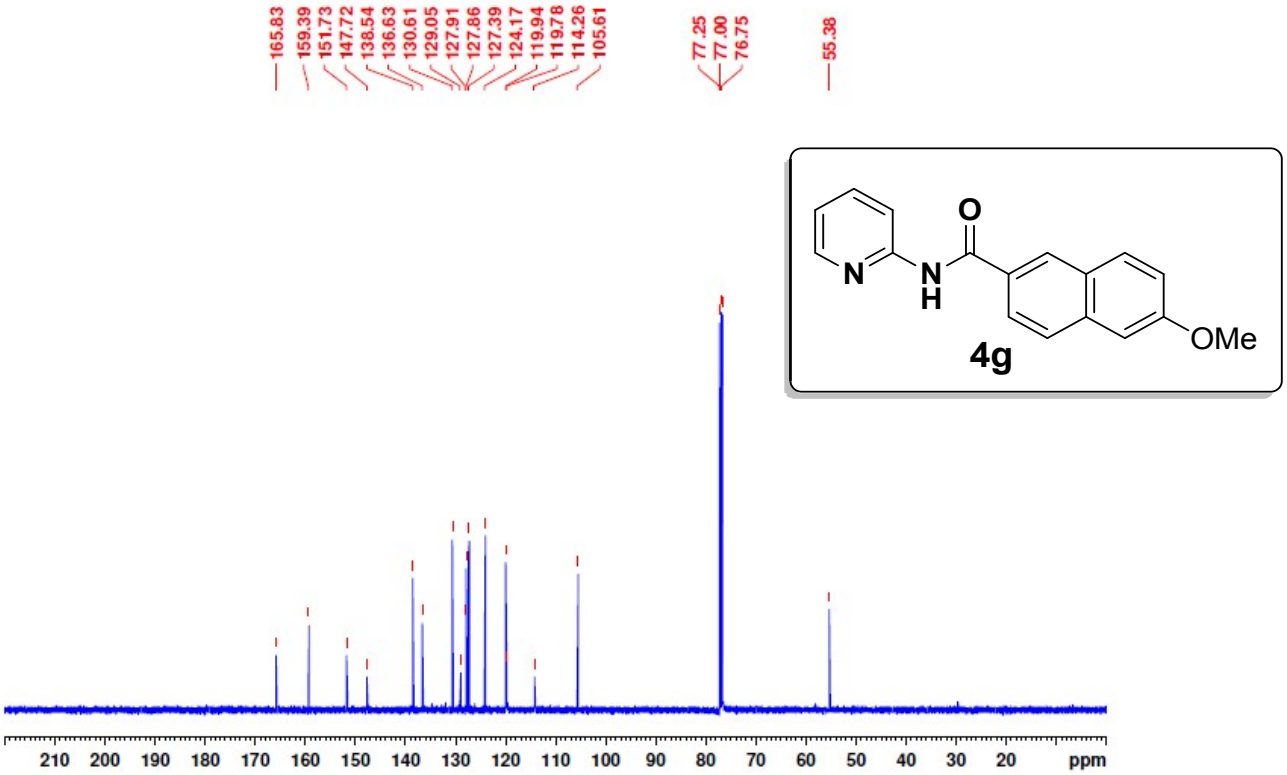
8.440
8.424
8.359
8.247
7.941
7.924
7.798
7.782
7.762
7.747
7.731
7.240
7.198
7.194
7.180
7.176
7.140
7.044
7.033
7.021
3.919
O
N
N
H
OMe
4g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
0.84
0.85
0.97
0.88
0.94
2.92
0.95
1.04
0.91
3.15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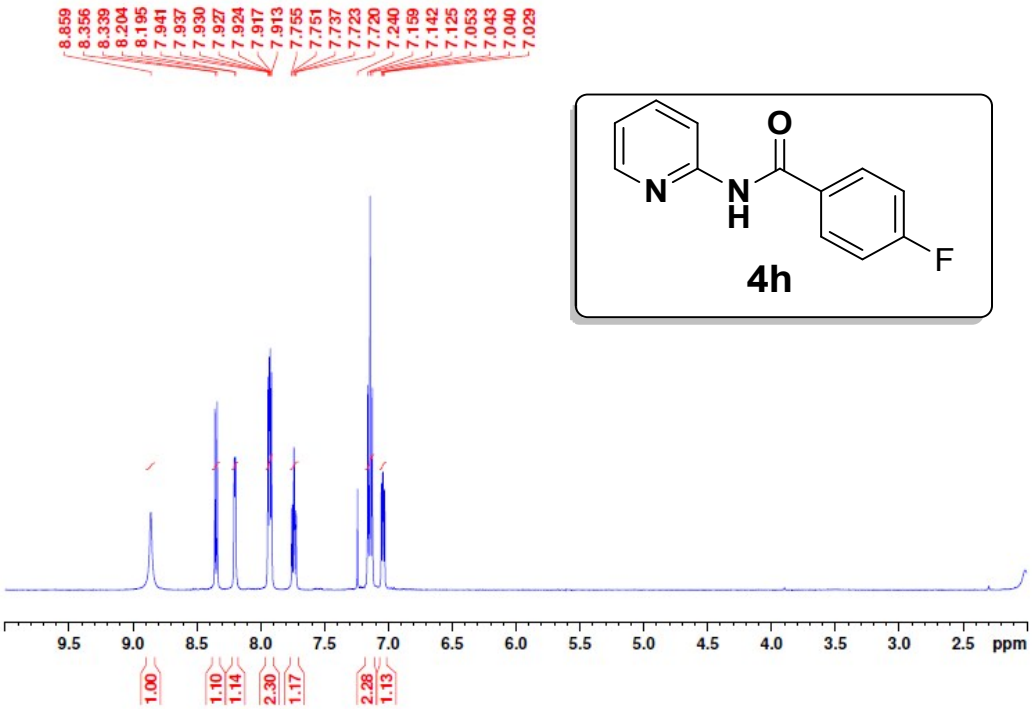
159.39
151.73
147.72
138.54
136.63
130.61
129.05
127.91
127.86
127.39
124.17
119.94
119.78
114.26
105.61
77.25
77.00
76.75
55.38
O
N
N
H
OMe
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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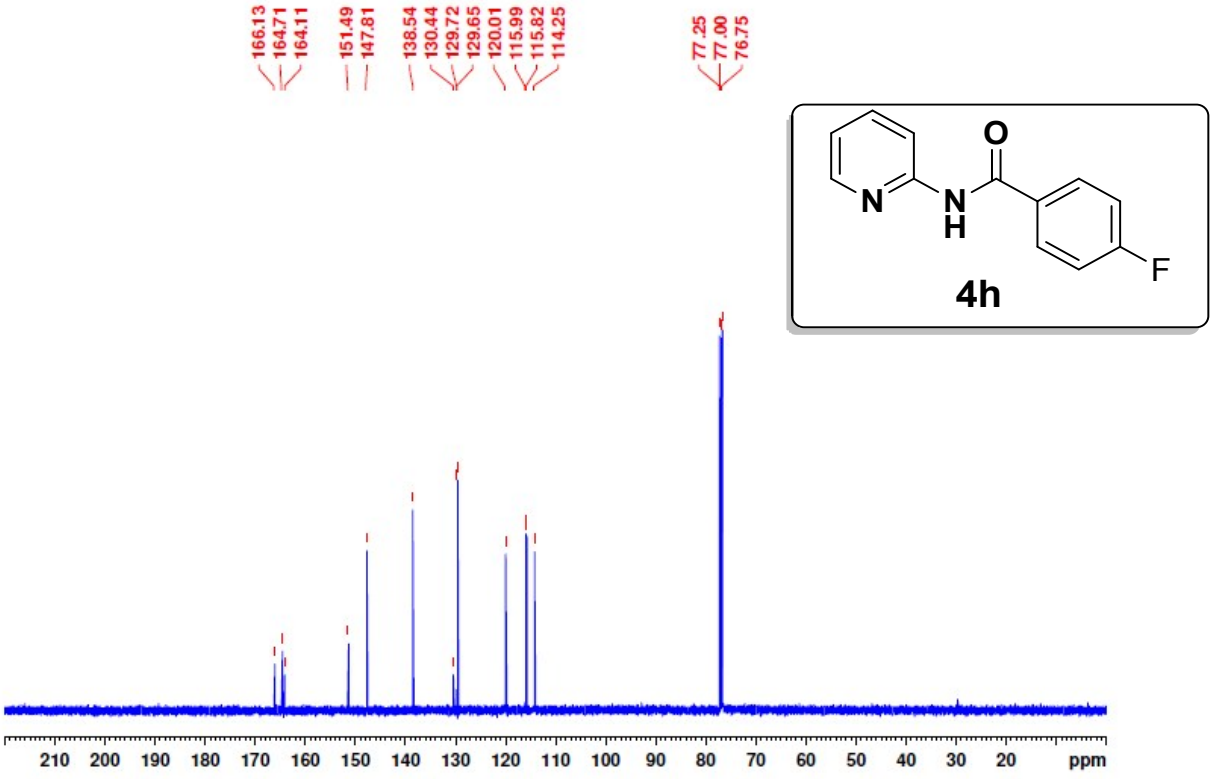
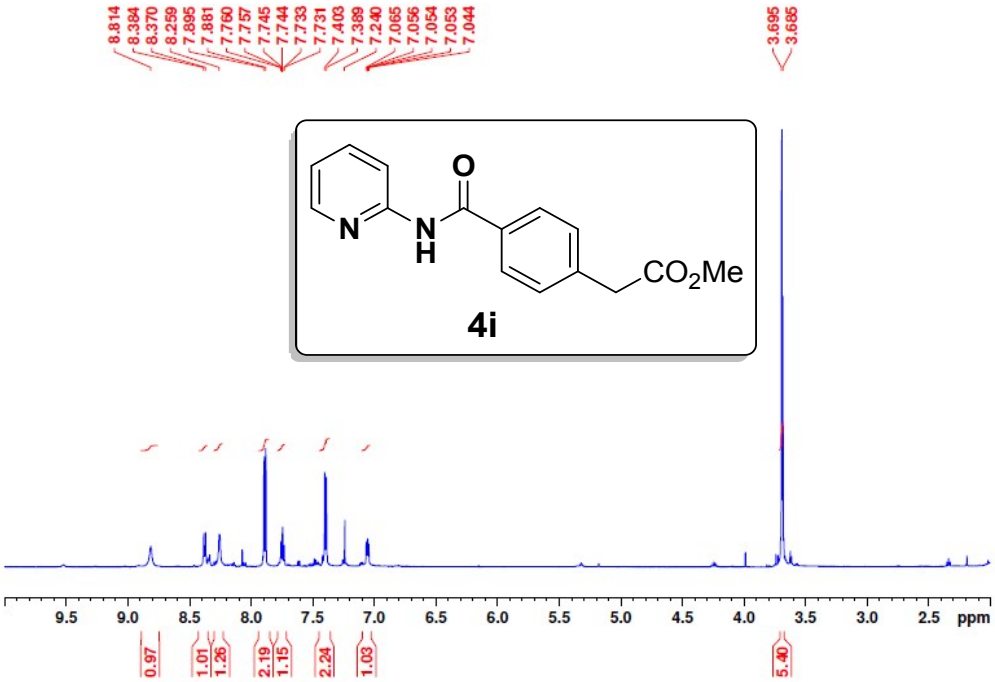
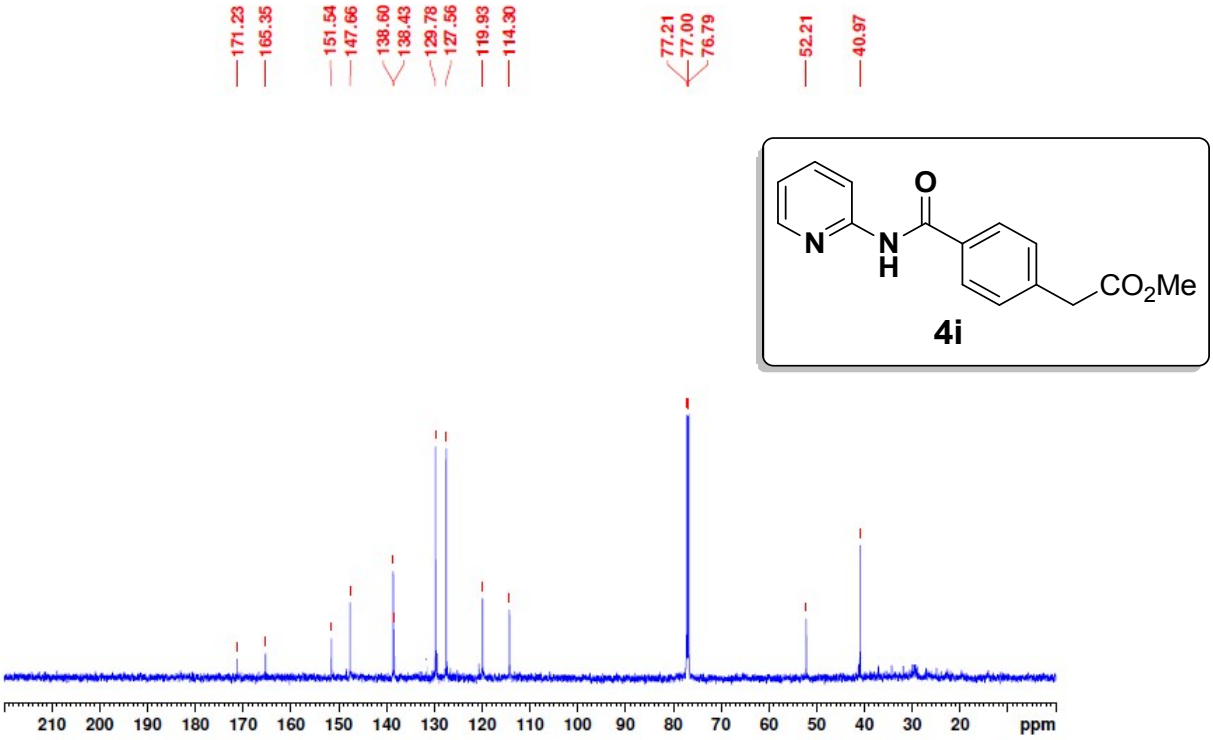
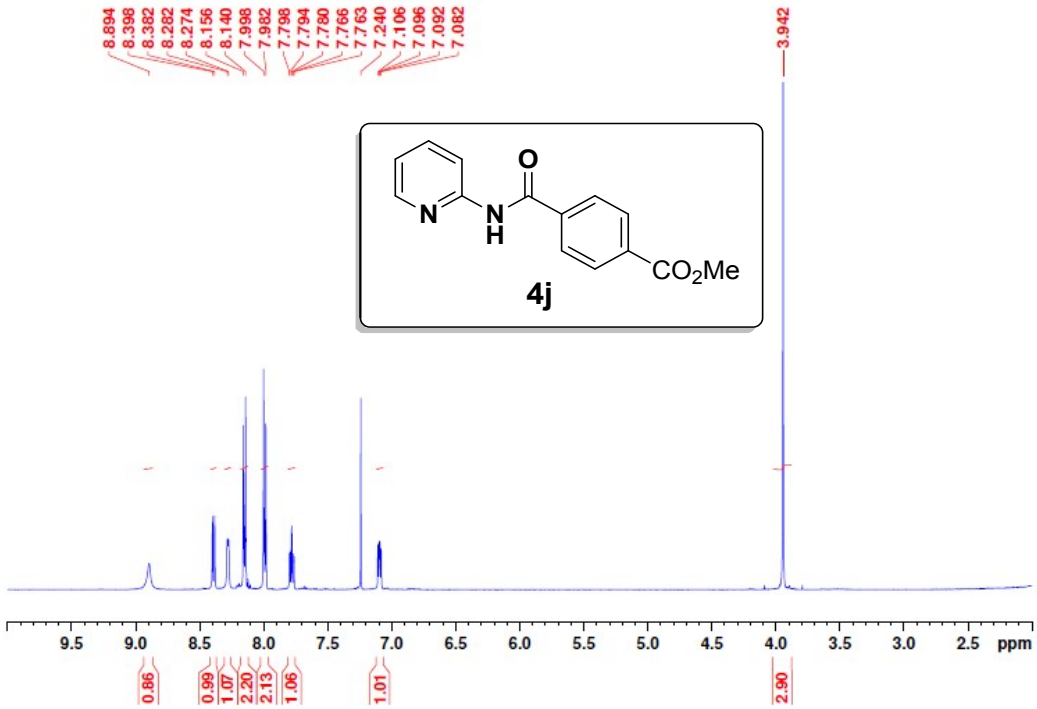
8.339
8.204
8.195
7.941
7.937
7.930
7.927
7.924
7.917
7.913
7.755
7.751
7.737
7.723
7.720
7.240
7.159
7.142
7.125
7.053
7.043
7.040
7.029
O
N
N
H
F
4h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.00
1.10
1.14
2.30
1.17
2.28
1.13


166.13
164.71
164.11
151.49
147.81
138.54
130.44
129.72
129.65
120.01
115.99
115.82
114.25
77.25
77.00
76.75
O
N
N
H
F
4h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.814
8.384
8.370
8.259
7.895
7.881
7.760
7.757
7.745
7.744
7.733
7.731
7.403
7.389
7.240
7.065
7.056
7.054
7.053
7.044
3.695
3.685
O
N
N
H
CO2Me
4i
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 ppm
0.97
1.01
1.26
2.19
1.15
2.24
1.03
5.40


171.23
165.35
151.54
147.66
138.60
138.43
129.78
127.56
119.93
114.30
77.21
77.00
76.79
52.21
40.97
O
N
N
H
CO2Me
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.894
8.398
8.382
8.282
8.274
8.156
8.140
7.998
7.982
7.798
7.794
7.780
7.766
7.763
7.240
7.106
7.096
7.092
7.082
3.942
O
N
N
H
CO2Me
4j
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 ppm
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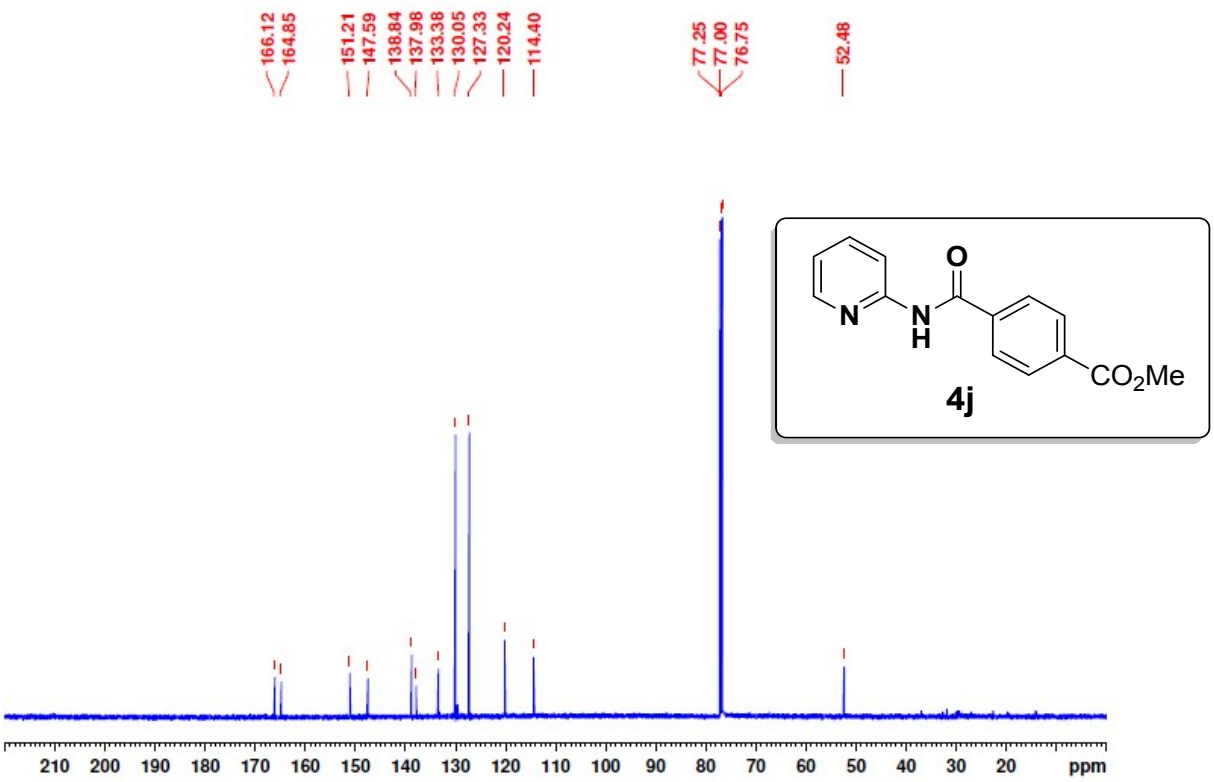
0.99
1.07
2.20
2.13
1.06
1.01
2.90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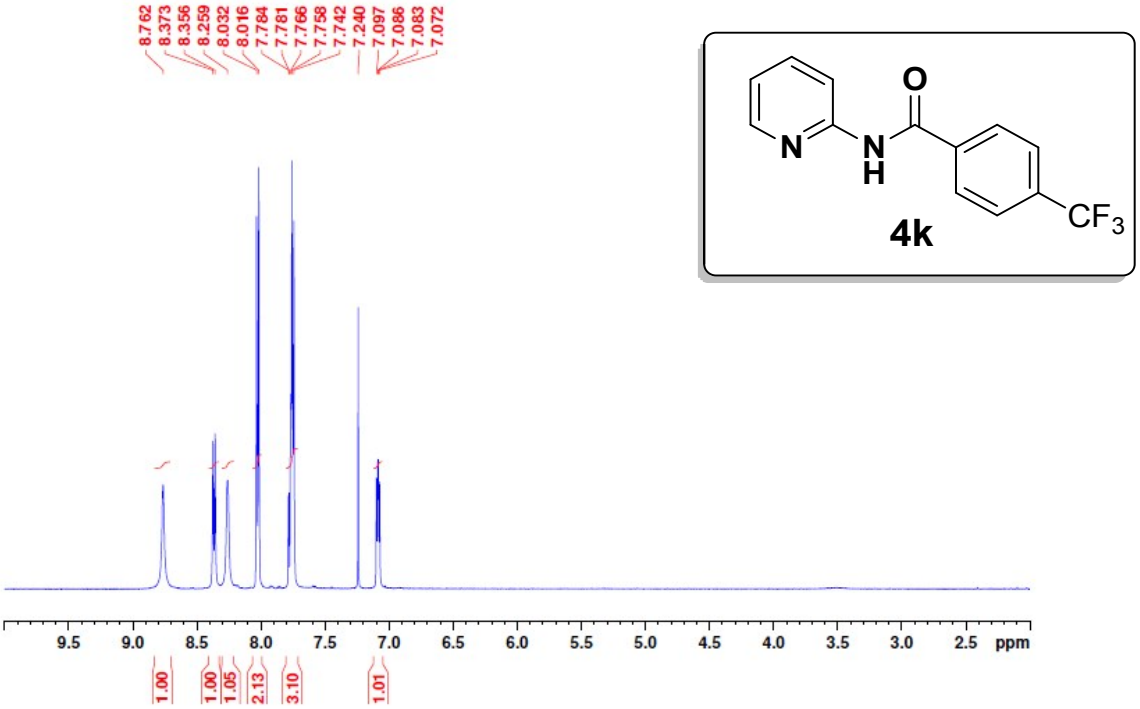
137.98
133.38
130.05
127.33
120.24
114.40
77.25
77.00
76.75
52.48
O
N
N
H
CO2Me
4j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.016
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7.758
7.742
7.240
7.097
7.086
7.083
7.072
O
N
N
H
CF3
4k
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 ppm
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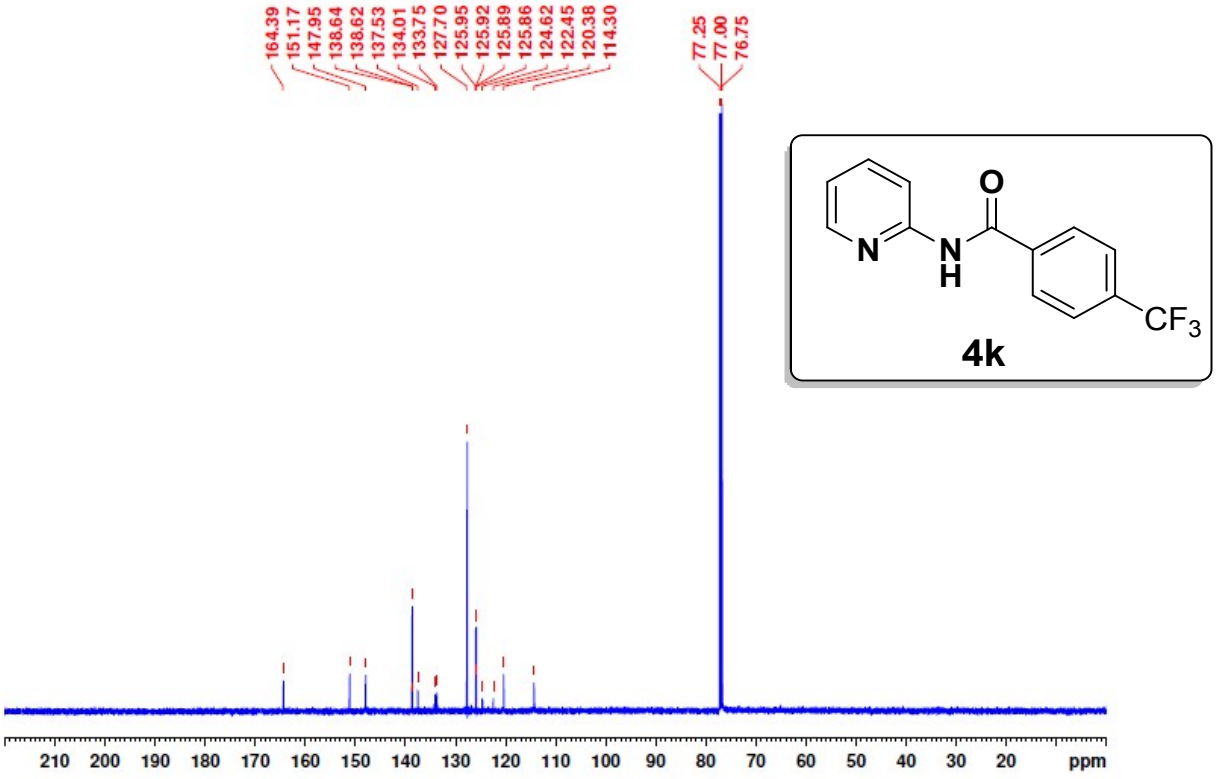
1.00
1.05
2.13
3.10
1.01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133.75
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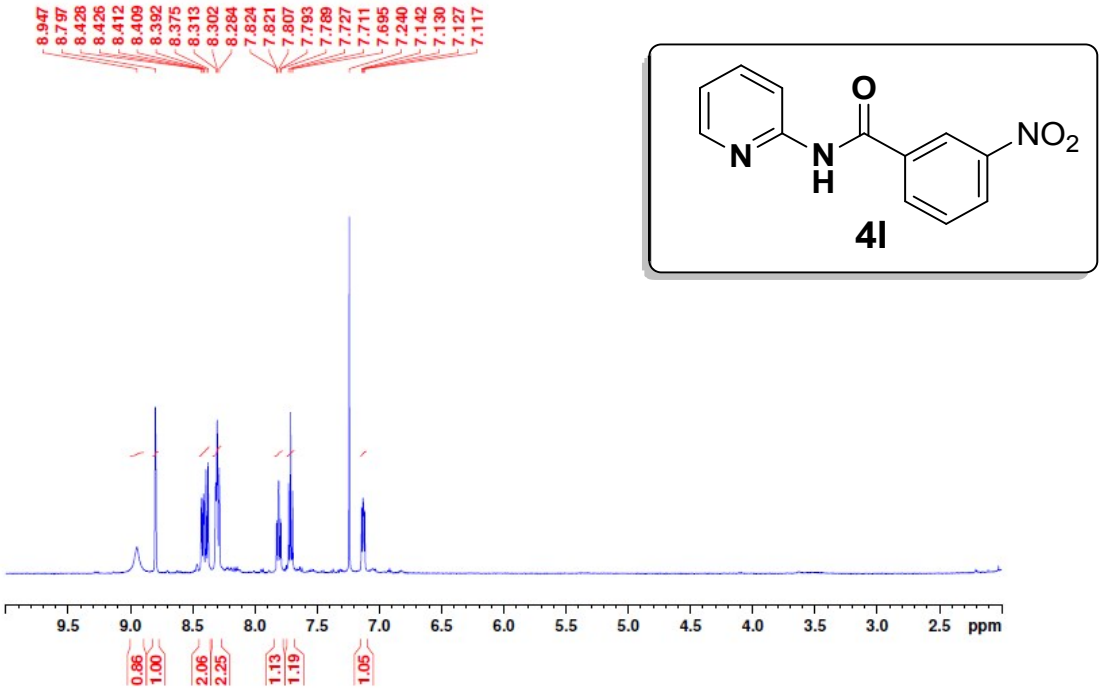
125.95
125.92
125.89
125.86
124.62
122.45
120.38
114.30
77.25
77.00
76.75
O
N
N
H
CF3
4k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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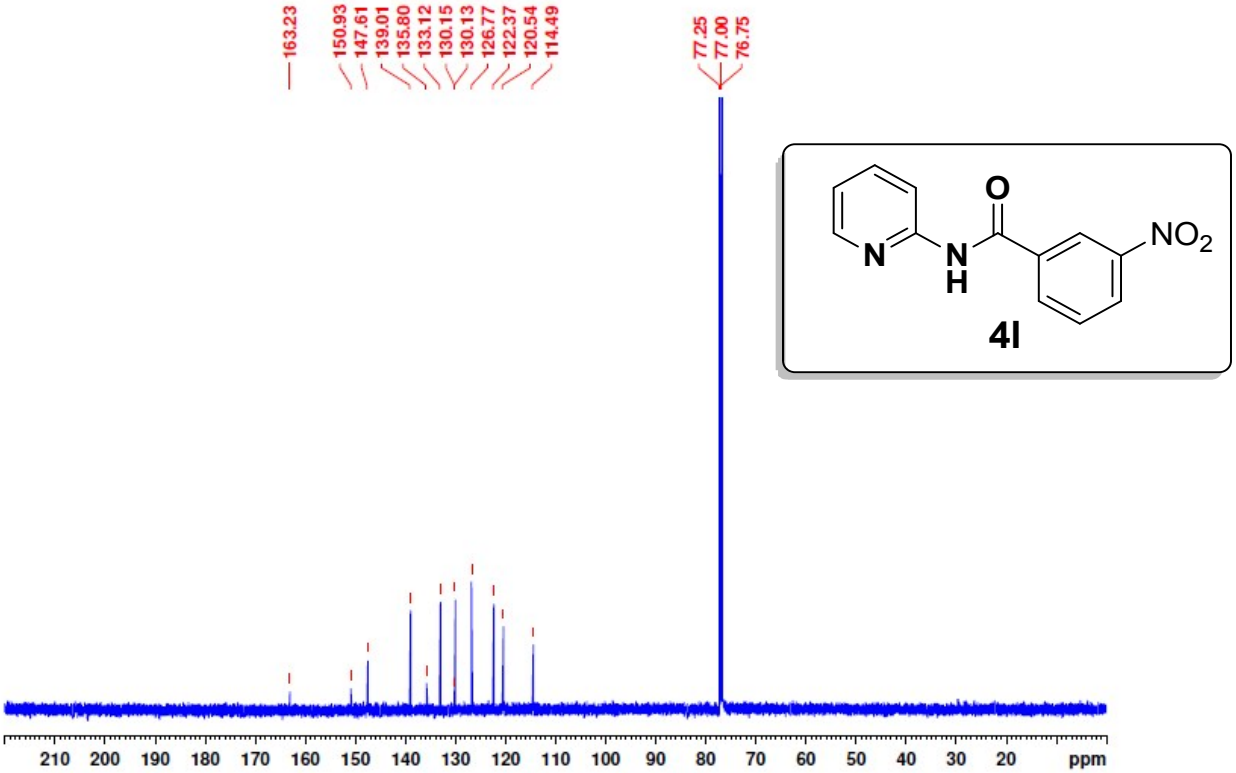
7.821
7.807
7.793
7.789
7.727
7.711
7.695
7.240
7.142
7.130
7.127
7.117
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
0.86
1.00
2.06
2.25
1.13
1.19
1.05
O
N
N
H
NO2
4l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133.12
130.15
130.13
126.77
122.37
120.54
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76.75
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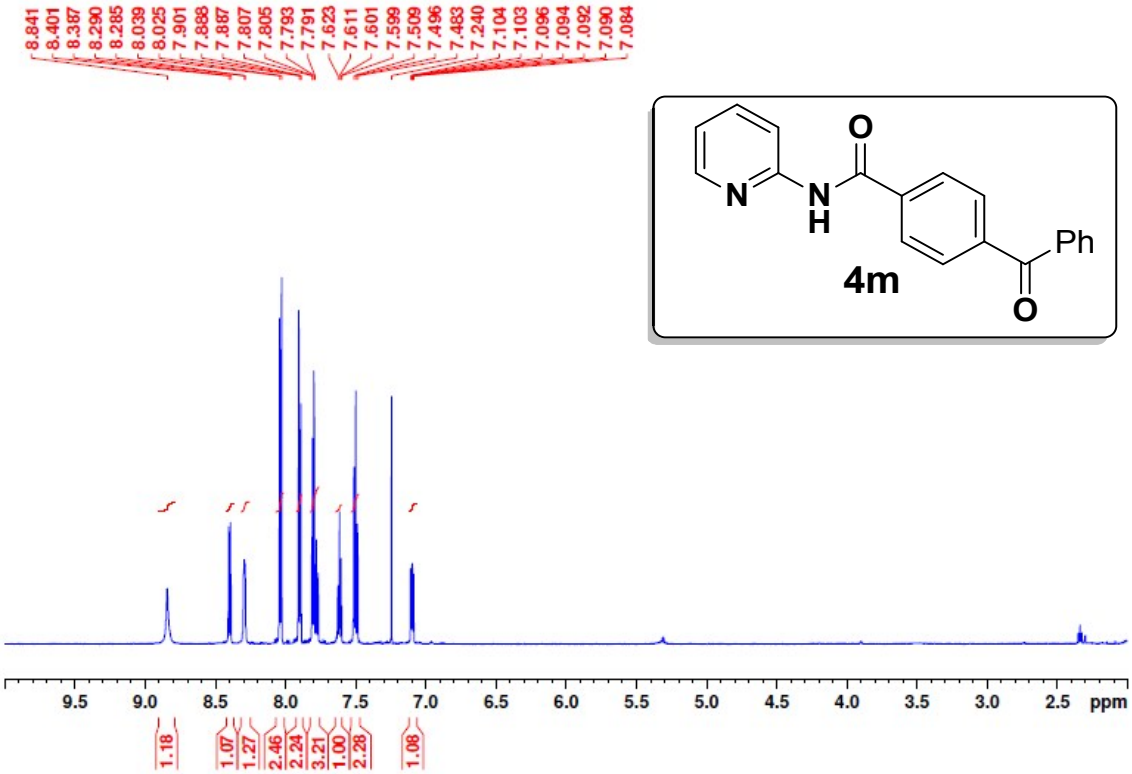
O
N
N
H
NO2
4l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7.793
7.791
7.623
7.611
7.601
7.599
7.509
7.496
7.483
7.240
7.104
7.103
7.096
7.094
7.092
7.090
7.084
O
N
N
H
Ph
4m
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
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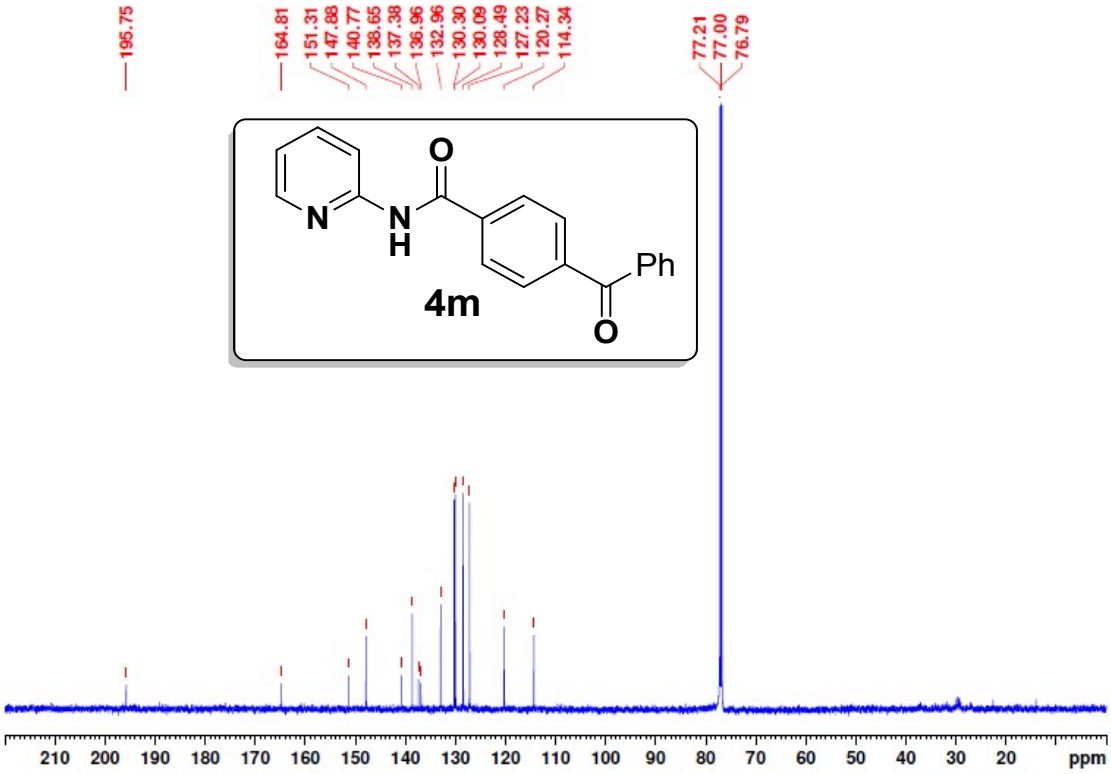
3.21
1.00
2.28
1.08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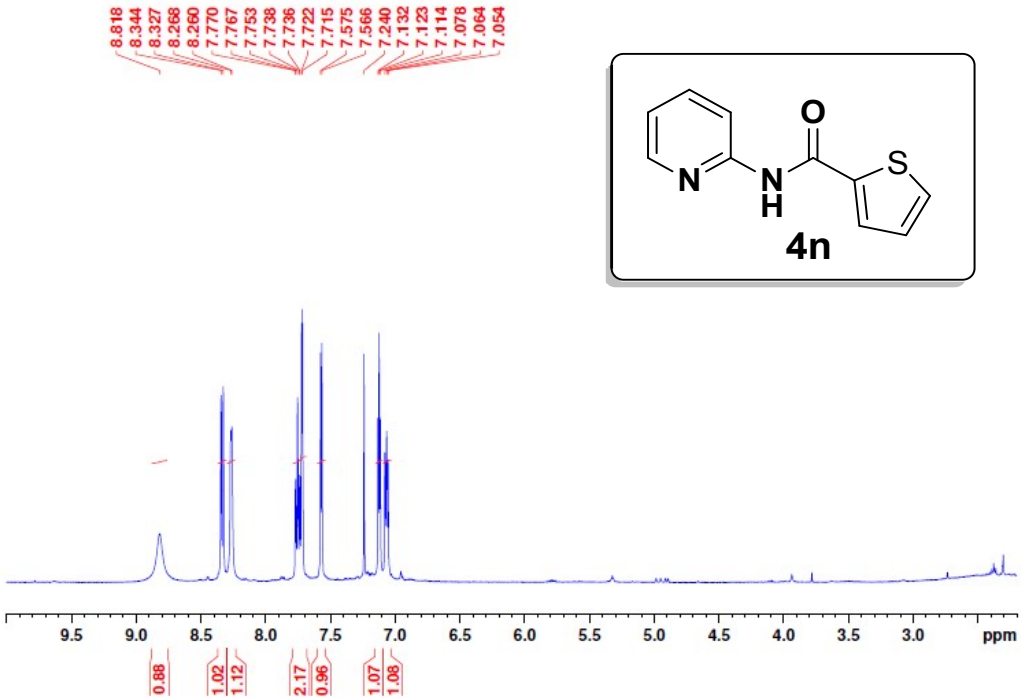
127.23
120.27
114.34
77.21
77.00
76.79
O
N
N
H
Ph
4m
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.260
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7.767
7.753
7.738
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7.715
7.575
7.566
7.240
7.132
7.123
7.114
7.078
7.064
7.054
O
N
N
H
S
4n
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
ppm
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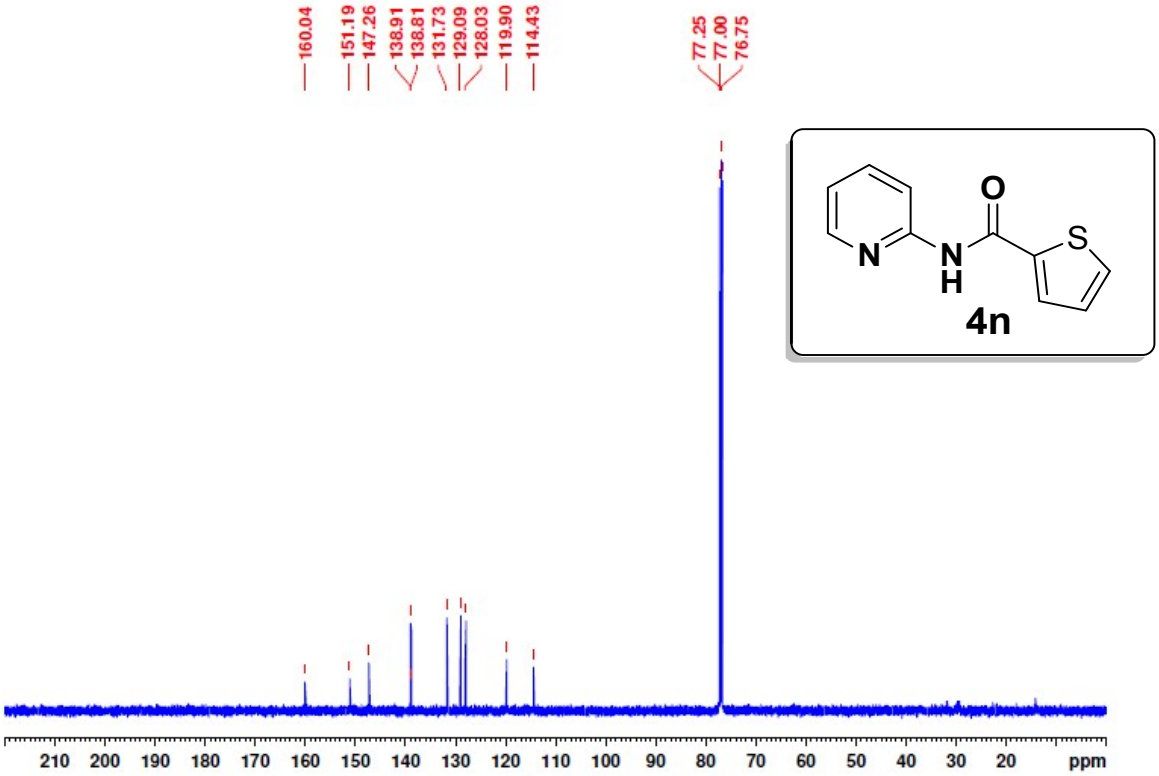
1.12
2.17
0.96
1.07
1.08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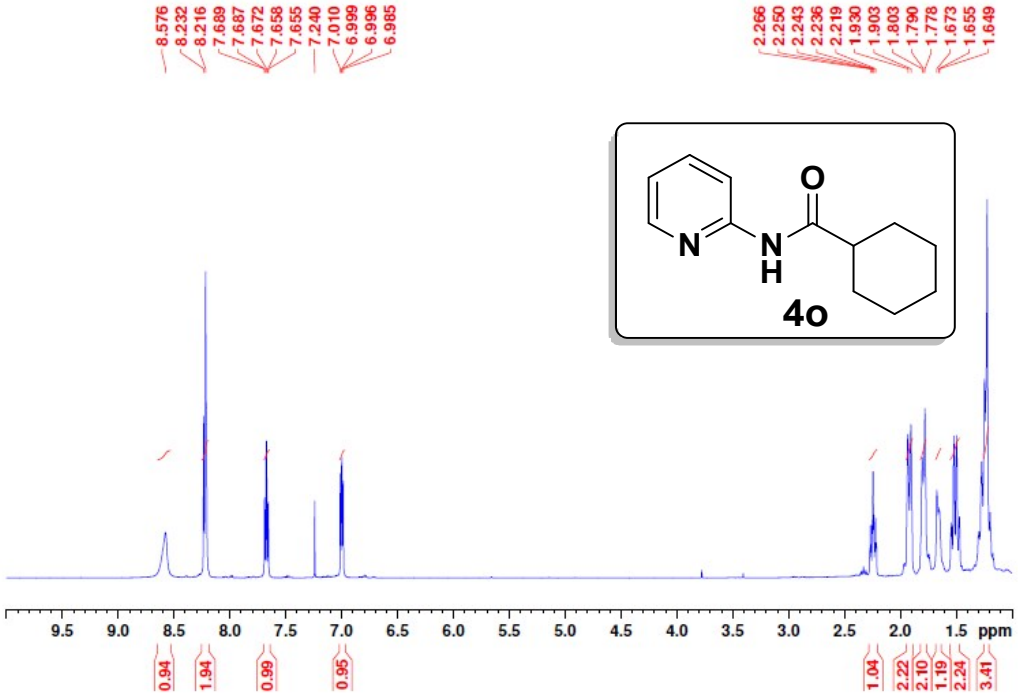
138.81
131.73
129.09
128.03
119.90
114.43
77.25
77.00
76.75
O
N
N
H
S
4n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.216
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7.687
7.672
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7.655
7.240
7.010
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6.996
6.985
2.266
2.250
2.243
2.236
2.219
1.930
1.903
1.803
1.790
1.778
1.673
1.655
1.649
O
N
N
H
4o
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 ppm
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1.94
0.99
0.95
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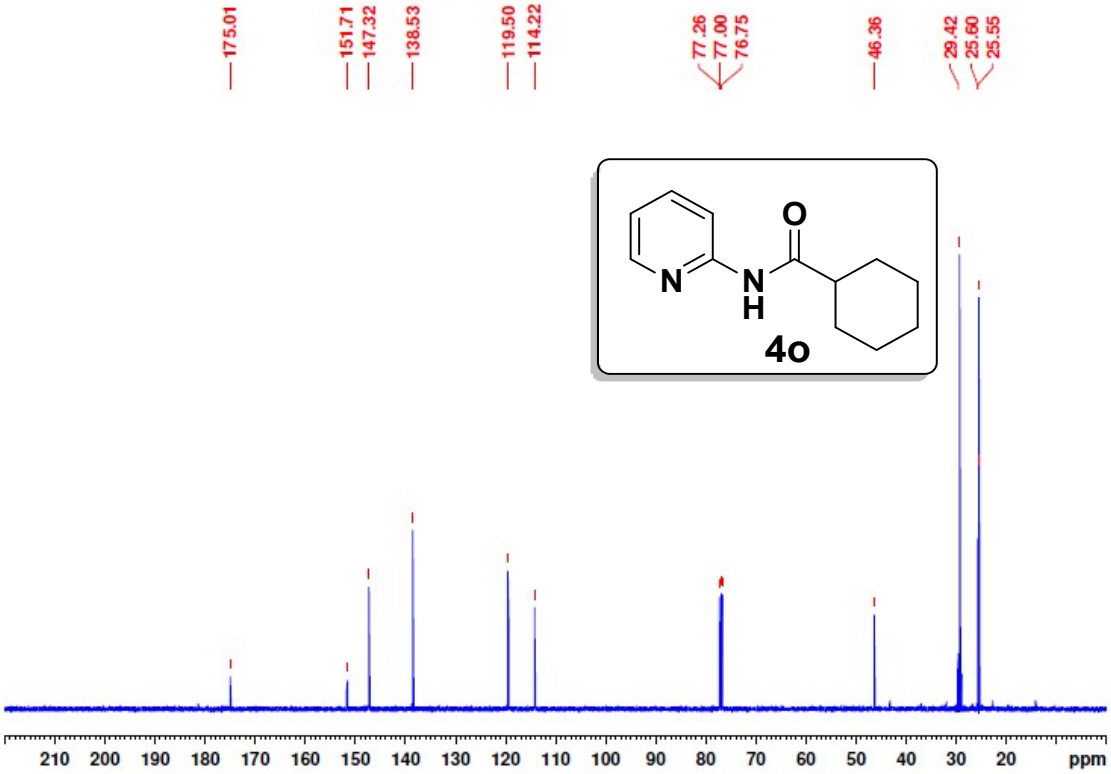
2.10
1.19
2.24
3.41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77.00
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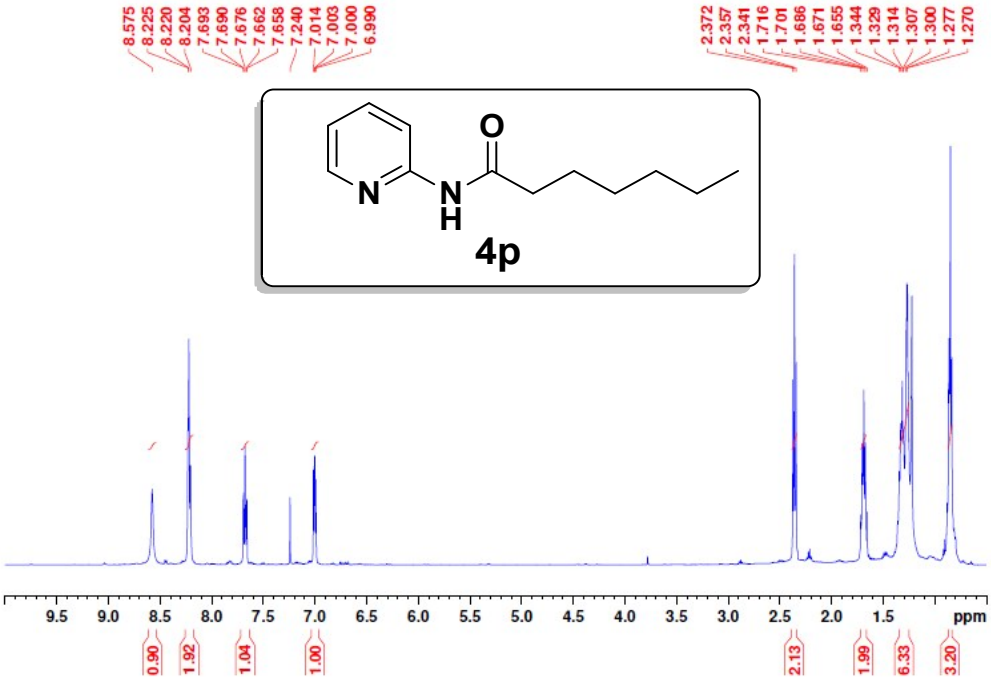
25.55
O
N
N
H
4o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.676
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7.000
6.990
2.372
2.357
2.341
1.716
1.701
1.686
1.671
1.655
1.344
1.329
1.314
1.307
1.300
1.277
1.270
O
N
N
H
4p
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 ppm
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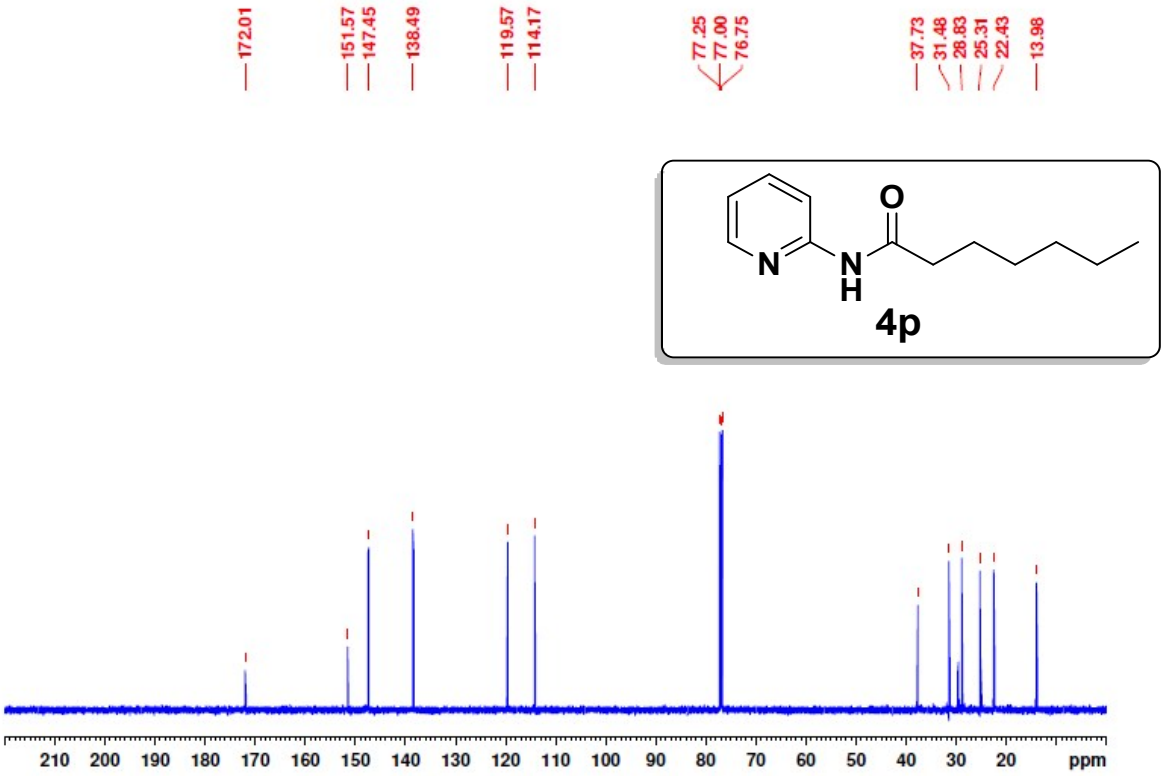
1.92
1.04
1.00
2.13
1.99
6.33
3.20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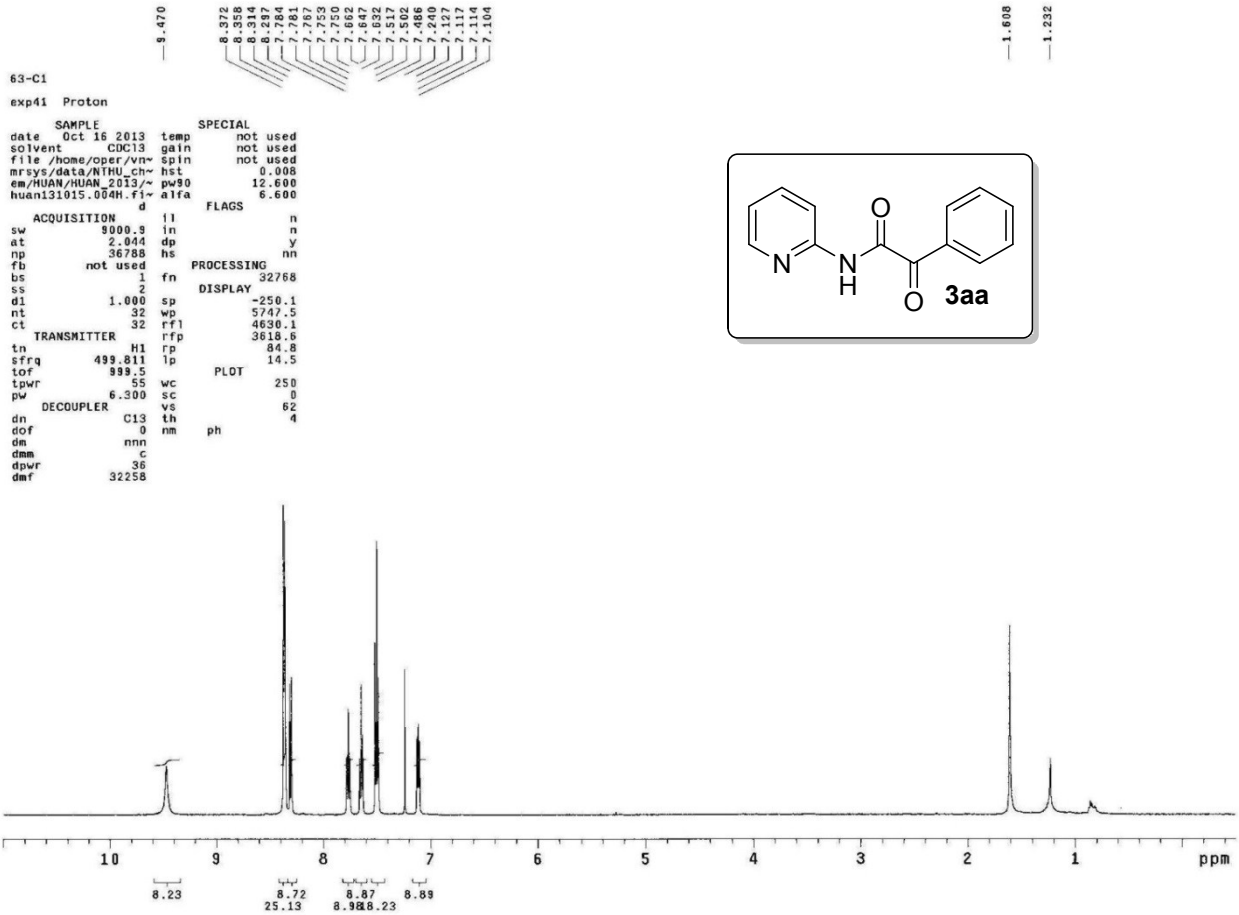
138.49
119.57
114.17
77.25
77.00
76.75
37.73
31.48
28.83
25.31
22.43
13.98
O
N
N
H
4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.750
7.662
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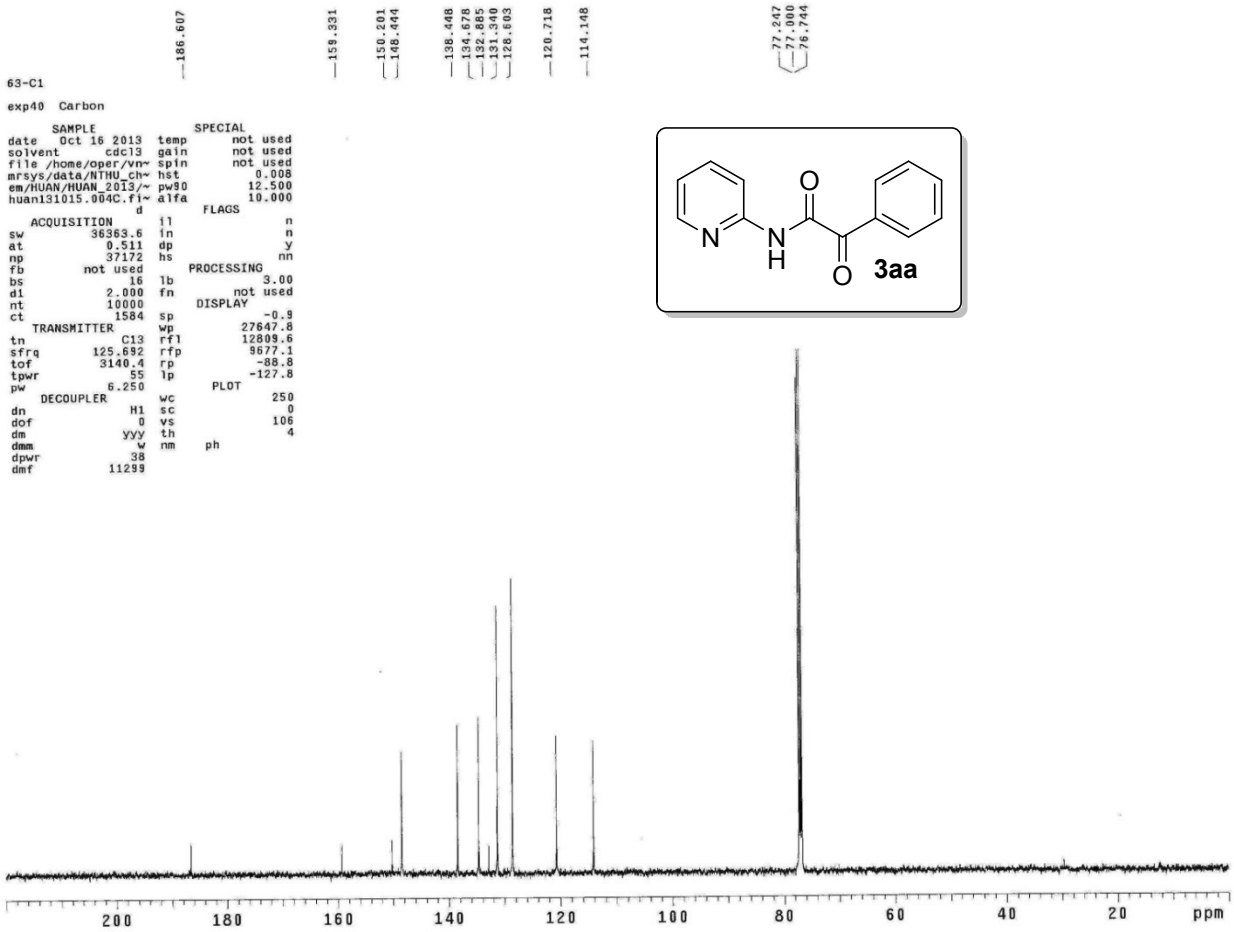
7.632
7.517
7.502
7.486
7.240
7.127
7.117
7.114
7.104
1.608
1.232
63-C1
exp41 Proton
SAMPLE
date Oct 16 2013
solvent CDCl3
file /home/oper/vn~
mrsys/data/NTHU_ch~
em/HUAN/HUAN_2013/~
huan131015.004H.fi~
d
ACQUISITION
sw 9000.9
at 2.044
np 36788
fb not used
bs 1
ss 2
d1 1.000
nt 32
ct 32
TRANSMITTER
tn H1
sfrq 499.811
tof 999.5
tpwr 55
pw 6.300
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 36
dmf 32258
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pw90 12.600
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 32768
DISPLAY
sp -250.1
wp 5747.5
rfl 4630.1
rfp 3618.6
rp 84.8
lp 14.5
PLOT
wc 250
sc 0
vs 62
th 4
nm ph
O
N
N
H
O
3aa
10
9
8
7
6
5
4
3
2
1
ppm
8.23
8.72
25.13
8.87
8.98
8.23
8.89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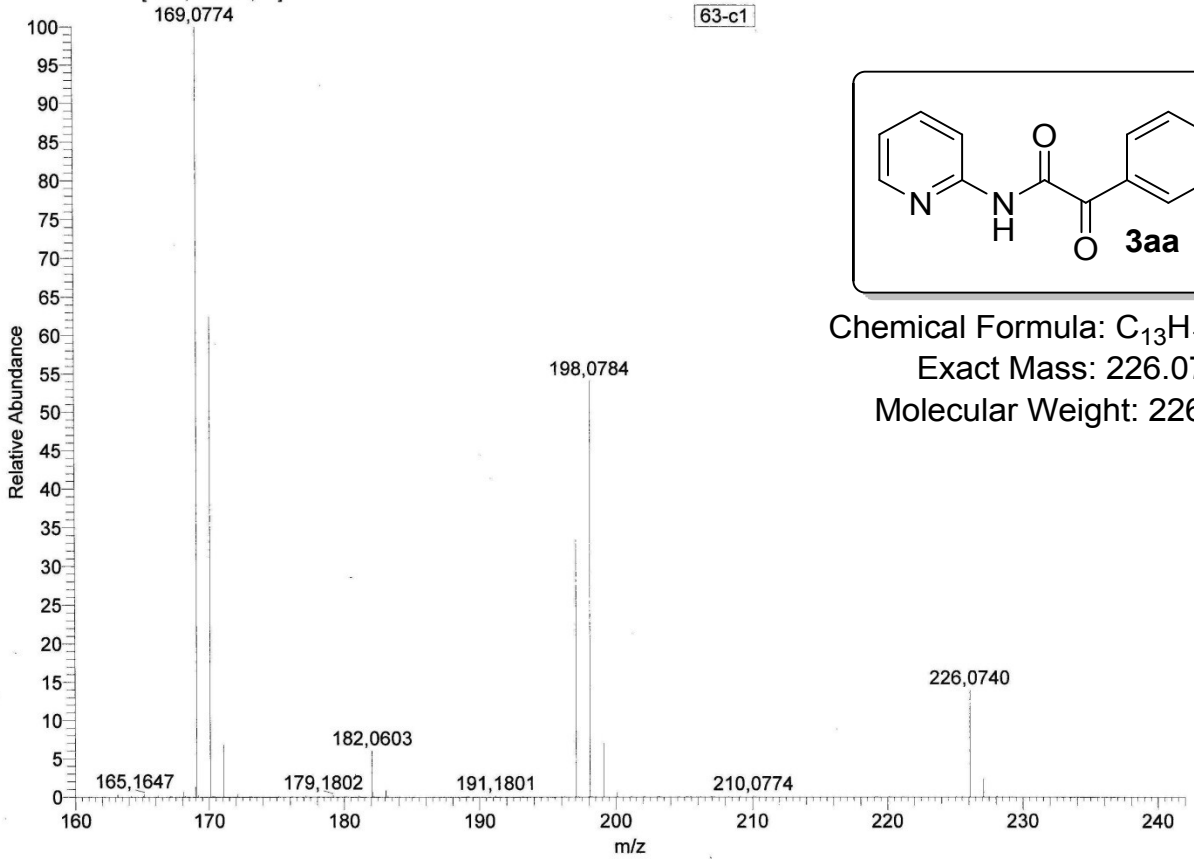
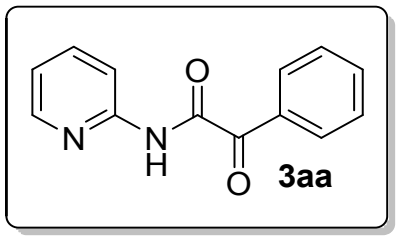
150.201
148.444
138.448
134.678
132.865
131.340
128.603
120.718
114.148
77.247
77.000
76.744
63-C1
exp40 Carbon
SAMPLE
date Oct 16 2013
solvent cdcl3
file /home/oper/vn~
mrsys/data/NTHU_ch~
em/HUAN/HUAN_2013/~
huan131015.004C.fi~
d
ACQUISITION
sw 36363.6
at 0.511
np 37172
fb not used
bs 16
d1 2.000
nt 10000
ct 1584
TRANSMITTER
tn C13
sfrq 125.692
tof 3140.4
tpwr 55
pw 6.250
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11299
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 3.00
fn not used
DISPLAY
sp -0.9
wp 27647.8
rf1 12809.6
rfp 9677.1
rp -88.8
lp -127.8
PLOT
wc 250
sc 0
vs 106
th 4
nm ph
N
N
H
O
O
3aa
200
180
160
140
120
100
80
60
40
20
ppm

D:\Xcalibur\...\LIN-14-01\22\1eihr-86-c1 22.01.2014 15:47:54

1eihr-86-c1 #3 RT: 1,40 AV: 1 NL: 1,09E7
T: + c EI Full ms [159,50-245,50]

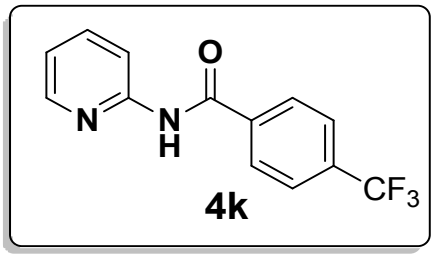




Chemical Formula: $C_{13}H_{10}N_2O_2$
Exact Mass: 226.07
Molecular Weight: 226.23

\

Figure **S4**. ORTEP diagram of Compound **4k**



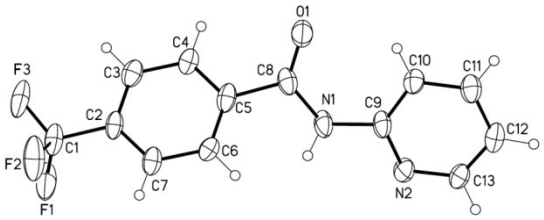


Table S1. Crystal data and structure refinement for 131023LT_0M.

Identification code	131023lt_0m	
Empirical formula	C13 H9 F3 N2 O	
Formula weight	266.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.6170(11) Å	a= 75.267(13)°.
	b = 7.3899(16) Å	b= 80.383(12)°.
	c = 14.156(3) Å	g = 88.880(13)°.
Volume	560.1(2) $Å^3$	
Z	2	
Density (calculated)	1.578 Mg/m^3	
Absorption coefficient	0.136 mm^{-1}	
F(000)	272	
Crystal size	0.15 x 0.09 x 0.04 mm^3	
Theta range for data collection	1.509 to 26.984°.	
Index ranges	-6<=h<=7, -9<=k<=9, -17<=l<=17	
Reflections collected	6889	
Independent reflections	2216 [R(int) = 0.0783]	
Completeness to theta = 25.242°	96.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9484 and 0.6356
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2216 / 0 / 173
Goodness-of-fit on F^2	1.378
Final R indices [I>2sigma(I)]	R1 = 0.1230, wR2 = 0.3629
R indices (all data)	R1 = 0.1601, wR2 = 0.4026
Extinction coefficient	0.02(2)
Largest diff. peak and hole	0.832 and -0.681 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) For 131023LT_0M. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6676(12)	7684(9)	4331(4)	33(2)
C(2)	6409(11)	7747(7)	3292(4)	26(1)
C(3)	4304(11)	6967(8)	3113(4)	29(1)
C(4)	4175(11)	6971(8)	2149(4)	31(2)
C(5)	5978(12)	7637(8)	1381(4)	29(2)
C(6)	8061(10)	8412(8)	1558(4)	26(1)
C(7)	8244(11)	8483(8)	2518(4)	28(1)
C(8)	5670(11)	7560(8)	349(4)	29(2)
C(9)	8113(11)	7134(8)	-1224(4)	29(1)
C(10)	6499(11)	7872(8)	-1866(4)	28(1)
C(11)	7195(12)	7900(8)	-2848(4)	32(2)
C(12)	9410(11)	7191(8)	-3166(4)	31(2)
C(13)	10792(11)	6436(9)	-2456(4)	31(2)
F(1)	8351(8)	6445(6)	4635(3)	52(1)
F(2)	7325(10)	9330(5)	4421(3)	58(2)
F(3)	4678(8)	7149(6)	5001(3)	50(1)
N(1)	7705(10)	7137(8)	-212(4)	36(2)
N(2)	10184(9)	6359(7)	-1496(4)	33(1)
O(1)	3731(8)	7885(6)	73(3)	36(1)

Table S3. Bond lengths [Å] and angles [°] for 131023LT_0M.

C(1)-F(2)	1.319(7)
C(1)-F(3)	1.337(7)
C(1)-F(1)	1.345(7)
C(1)-C(2)	1.493(8)
C(2)-C(7)	1.378(8)
C(2)-C(3)	1.412(9)
C(3)-C(4)	1.378(8)
C(3)-H(3)	0.9500
C(4)-C(5)	1.353(9)
C(4)-H(4)	0.9500
C(5)-C(6)	1.399(9)
C(5)-C(8)	1.514(8)
C(6)-C(7)	1.395(8)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-O(1)	1.217(7)
C(8)-N(1)	1.358(7)
C(9)-N(2)	1.329(8)
C(9)-C(10)	1.396(8)
C(9)-N(1)	1.413(7)
C(10)-C(11)	1.375(8)
C(10)-H(10)	0.9500
C(11)-C(12)	1.390(9)
C(11)-H(11)	0.9500
C(12)-C(13)	1.372(9)
C(12)-H(12)	0.9500
C(13)-N(2)	1.332(7)
C(13)-H(13)	0.9500
N(1)-H(1)	0.8800
F(2)-C(1)-F(3)	105.9(4)
F(2)-C(1)-F(1)	108.1(5)
F(3)-C(1)-F(1)	105.1(5)
F(2)-C(1)-C(2)	111.9(5)
F(3)-C(1)-C(2)	114.7(5)

F(1)-C(1)-C(2)	110.6(4)
C(7)-C(2)-C(3)	120.3(5)
C(7)-C(2)-C(1)	120.3(5)
C(3)-C(2)-C(1)	119.3(5)
C(4)-C(3)-C(2)	117.6(6)
C(4)-C(3)-H(3)	121.2
C(2)-C(3)-H(3)	121.2
C(5)-C(4)-C(3)	123.2(6)
C(5)-C(4)-H(4)	118.4
C(3)-C(4)-H(4)	118.4
C(4)-C(5)-C(6)	119.1(5)
C(4)-C(5)-C(8)	119.2(6)
C(6)-C(5)-C(8)	121.7(5)
C(7)-C(6)-C(5)	119.7(5)
C(7)-C(6)-H(6)	120.2
C(5)-C(6)-H(6)	120.2
C(2)-C(7)-C(6)	120.1(6)
C(2)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
O(1)-C(8)-N(1)	124.8(5)
O(1)-C(8)-C(5)	120.7(5)
N(1)-C(8)-C(5)	114.5(5)
N(2)-C(9)-C(10)	123.9(5)
N(2)-C(9)-N(1)	113.0(5)
C(10)-C(9)-N(1)	123.1(5)
C(11)-C(10)-C(9)	117.2(6)
C(11)-C(10)-H(10)	121.4
C(9)-C(10)-H(10)	121.4
C(10)-C(11)-C(12)	120.2(6)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	117.0(5)
C(13)-C(12)-H(12)	121.5
C(11)-C(12)-H(12)	121.5
N(2)-C(13)-C(12)	124.9(6)
N(2)-C(13)-H(13)	117.5

C(12)-C(13)-H(13)	117.5
C(8)-N(1)-C(9)	129.1(5)
C(8)-N(1)-H(1)	115.4
C(9)-N(1)-H(1)	115.4
C(9)-N(2)-C(13)	116.6(5)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x 10^3$) for 131023LT_0M. The anisotropic Displacement factor exponent takes the form: $-2p^2 [h2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	50(4)	29(3)	21(3)	-9(3)	-3(3)	10(3)
C(2)	35(3)	22(3)	22(3)	-10(2)	1(2)	3(2)
C(3)	36(3)	27(3)	22(3)	-4(2)	-1(2)	5(3)
C(4)	38(4)	29(3)	27(3)	-10(3)	-6(3)	6(3)
C(5)	44(4)	22(3)	21(3)	-6(2)	-5(3)	10(3)
C(6)	24(3)	27(3)	23(3)	-7(2)	3(2)	2(2)
C(7)	35(3)	24(3)	24(3)	-7(2)	1(2)	2(2)
C(8)	43(4)	23(3)	24(3)	-9(2)	-8(3)	5(3)
C(9)	40(4)	31(3)	22(3)	-13(2)	-9(3)	7(3)
C(10)	33(3)	28(3)	24(3)	-9(2)	-4(2)	8(3)
C(11)	47(4)	27(3)	23(3)	-7(2)	-7(3)	6(3)
C(12)	42(4)	29(3)	22(3)	-8(2)	1(3)	-6(3)
C(13)	32(3)	32(3)	31(3)	-18(3)	2(3)	1(3)
F(1)	70(3)	63(3)	23(2)	-11(2)	-10(2)	28(2)
F(2)	111(4)	35(2)	28(2)	-14(2)	-3(2)	-7(2)
F(3)	69(3)	56(3)	24(2)	-17(2)	4(2)	7(2)
N(1)	42(3)	47(3)	25(3)	-19(2)	-14(2)	24(3)
N(2)	33(3)	39(3)	31(3)	-18(2)	-8(2)	11(2)
O(1)	35(3)	48(3)	25(2)	-10(2)	-8(2)	6(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) For 131023LT_0M.

	x	y	z	U(eq)
H(3)	3023	6459	3639	35
H(4)	2749	6481	2018	37
H(6)	9344	8887	1027	31
H(7)	9635	9040	2639	34
H(10)	4983	8336	-1634	34
H(11)	6158	8406	-3311	38
H(12)	9943	7228	-3844	38
H(13)	12297	5929	-2665	37
H(1)	8943	6820	98	43