Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Visible-Light Induced Copper(I)-Catalysed Denitrogenative Oxidative Coupling of hydrazinylpyridines with Terminal Alkynes

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Experimental section

General: All reactions were conducted in oven-dried glasswares. All reactions were conducted using a blue light-emitting diode (LED) array (30 lamps, power density: 40 mW/cm^2 at 460 nm) was used as the visible-light source under oxygen (O_2) atmosphere in all reactions. All solvents were dried according to known methods and distilled prior to use. Starting materials were commercially available (Sigma-Aldrich or Alfa-Aesar or TCI-chemicals) and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 600 MHz using deuterated $CDCl_3$ or $CDCl_3$-DMSO-d_6 mixture. 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. Unless otherwise specified, the proton/carbon signal of 2 residual solvents (at δ 7.24 or 2.50 and δ 77.00 or 39.51 ppm, respectively) was used as the internal reference.

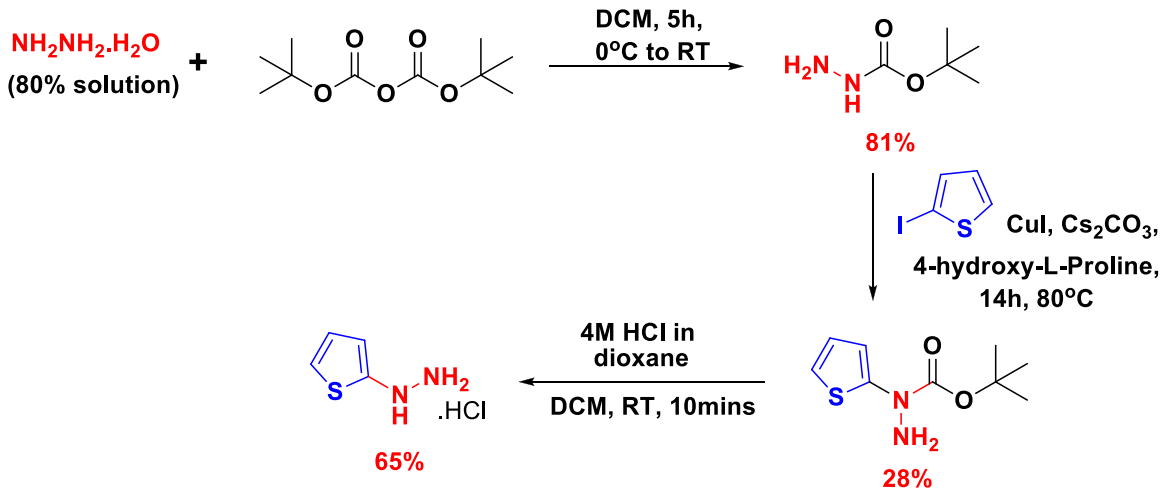
General procedure: To a dry test tube (20 mL) containing 5 mol% CuCl, K_2CO_3 (1.2 equiv.), 2-Hydrazino pyridine (0.5 mmol) and terminal acetylene (0.55 mmol), was added 7 mL of dry MeOH, via syringe. The reaction mixture was then irradiated with blue LEDs (40 mW/cm^2 at 460 nm) under an oxygen atmosphere at room temperature (25-28 ^{o}C) until completion of the reaction (monitored by TLC). The reaction mixture was then 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 column chromatography on silica gel.

Experimental procedure for the synthesis of potent mGluR5 noncompetitive antagonists MPEP (3e) and M-MPEP (3f):

Preparation of 2-methyl-6-(phenylethynyl)pyridine (3e) **(MPEP):** To a dry test tube (20 mL) containing 5 mol% CuCl, K_2CO_3 (1.2 equiv.), 2-hydrazinyl-6-methylpyridine (0.5 mmol) and phenyl acetylene (0.55 mmol), was added 7 mL of dry MeOH, via syringe. The reaction mixture was then irradiated with blue LEDs (40 mW/cm^2 at 460 nm) under an oxygen atmosphere/balloon at room temperature (25-28 ^{o}C) for 10 h. The reaction mixture was diluted with 40 % ethyl acetate in hexane and stirred for 10 min. The mixture was filtered through celite/silica gel pads and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to collect the product (yield 88%).

Preparation of 2-((3-methoxyphenyl)ethynyl)-6-methylpyridine (3f) **(M-MPEP):** To a dry test tube (20 mL) containing 5 mol% CuCl, K_2CO_3 (1.2 equiv.), 2-hydrazinyl-6-methylpyridine (0.5 mmol) and 1-ethynyl-3-methoxybenzene (0.55 mmol), was added 7 mL of dry MeOH, via syringe. The reaction mixture was then irradiated with blue LEDs (40 mW/cm^2 at 460 nm) under an oxygen atmosphere/balloon at room temperature (25-28 ^oC) for 10 h. The reaction mixture was diluted with 40 % ethyl acetate in hexane and stirred for 10 min. The mixture was filtered through celite/silica gel pads and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to collect the product (yield 83%).

Experimental procedure for the preparation of thiophen-2-ylhydrazine (1ad)[s1]:



Step1: Tert-butyl hydrazinecarboxylate was synthesized by condensation of hydrazine hydrate (80% slution) with di-tert-butyl dicarbonate in DCM solvent at 0 ^oC to RT for 5 h.

Setp2: To a solution of 2-bromo thiophene (5g, 0.0238 mol) in DMSO (120mL) was added tert-butyl hydrazinecarboxylate (8.2 g, 0.0621 mol), Cs_2CO_3 (16 g, 0.0491 mol), followed by CuI (0.6 g, 0.0031 mol) and 4-hydroxy-L-Proline (0.8 g, 0.0062 mol) at RT under nitrogen. The reaction mixture was then stirred at 80 ^oC for 14 h. After 14 h, the reaction mixture was cooled to RT and quenched with water (100 mL) and then extracted with ethylacetate (3x 100 mL). The combined organic layer was washed with water (100 mL x 2), dried over sodium sulphate, and evaporated under vacuum. The crude product was purified by column chromatography to get the

desired compound **tert-butyl 1-(thiophen-2-yl)hydrazinecarboxylate** (28% yield) as brown liquid.

Step3: To a solution of tert-butyl 1-(thiophen-2-yl)hydrazinecarboxylate in DCM (5 mL) was added 5 mL of a 4 M HCl solution in dioxane. The reaction mixture was stirred for 10 mins at RT. The reaction mixture was the evaporated and residue was used without further purification.

Preparation of copper (I) phenylacetylide:[s2] CuI (1.0 g, 5.0 mmol) was dissolved in ammonium hydroxide to form a blue solution. While stirring, phenylacetylene (0.5 g, 5.1 mmol in 50 mL ethanol) was added drop wise to the solution. The mixture 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. The bright yellow solid was obtained with 73% yield. The spectroscopic data for the yellow solid are shown below: IR (KBr, cm^{-1}) [s3:] 1929 (C≡C), 1596, 1568; UV-Vis λ_{abs} = 476 nm.

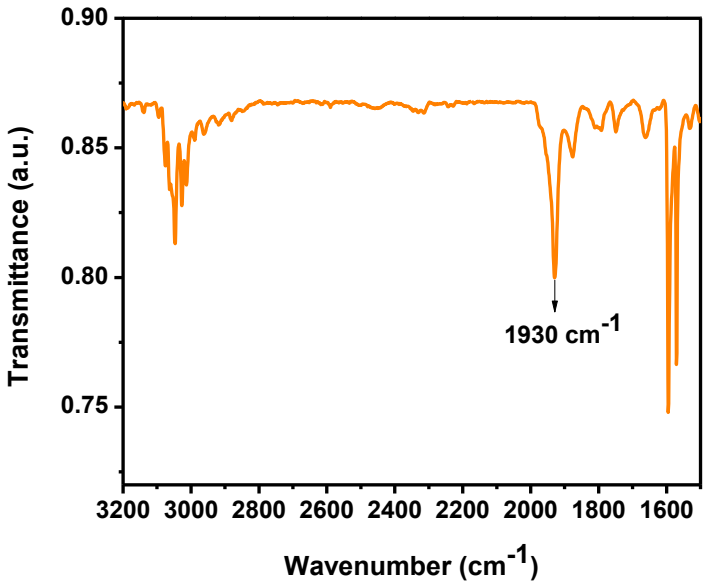
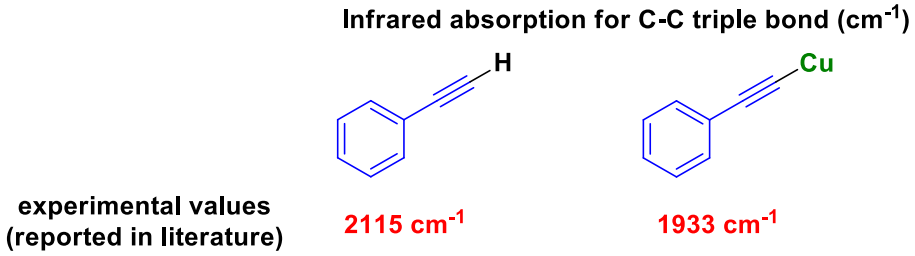


Figure S1: FT-IR spectrum of reaction in-situ generated copper(I)-phenylacetylide. IR (KBr, cm^{-1}): 1930(C≡C-Cu^{I}), 1595, 1569 in KBr.

Theoretical calculation for FT-IR vibrational frequency of C≡C triple bond in copper(I) phenylacetylide.

A) Experimental wave number (1/λ) for phenylacetylene and copper(I)-phenylacetylide

(reported in literature)



(ref S3**:** Y. Okamoto and S. K. Kundu, *J. Phys. Chem.* 1973, **77**, 2677**)**

B) Experrmental wave number (1/λ) for copper(I) phenylacetylide (present work)

- From IR-spectra of in-situ generated copper(I) phenylacetylide, the C≡C triple bond stretching frequency found to be **1930 cm^{-1}** (C≡C-Cu^{I}).
- Our experimental value is consistent with the reported experimental value[S2].

C) Theoretically calculated C≡C triple bond stretching frequency (in terms of wavenumber, 1/λ) for copper(I)-phenylacetylide

According to **Hook's Law**,
Force (F)= force constant (K) x displacement (or Total possible deformation of the spring) (x)

i.e., F= K x

In terms of **Harmonic oscillator**, Hook's Law can be represented as:

$$\nu(\text{frequency}) = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \quad \text{-------- eqn 1}$$

where, K= force constant and μ = reduced mass

$$\mu = \frac{m1x\ m2}{m1 + m2}$$

wave number (1/λ) = v/ c --------eqn 2

where, v= frequency, and c= speed of light

Therefore, from eqn 1 and eqn 2,

$$\text{wave number } \mathbf{(1/\lambda)} = \frac{\mathbf{1}}{\mathbf{2\pi c}}\sqrt{\frac{\boldsymbol{K}}{\boldsymbol{\mu}}} \quad \ldots\ldots \text{ eqn 3}$$

Further to convert the reduced mass (μ) unit in amu (atomic mass unit), the μ is divided by Avogodro's number.

$$\text{Thus, wave number } (1/\lambda) = \frac{1}{2\pi c}\sqrt{\frac{K}{(\mu/6.02\times10^{23})}}$$

$$\text{wave number } (1/\lambda) = \frac{1}{2\times3.14\times3\times(10^{10})}\sqrt{\frac{K}{(\mu/6.02\times10^{23})}}$$

The equation further simplified to form:

$$\text{wave number } (1/\lambda) = 4.12\sqrt{\frac{K}{\mu}}$$

The force constant K for typical single bond (bond order= 1), double bond and triple bond are 5 x 10^5, 10 x 10^5, and 15 x 10^5 dynes/cm, respectively.

Reduced mass (μ) = (m1xm2)/(m1+m2) = (CxC)/ (C+C)

= (12x12)/(12+12) = 144/24

=6

$$\text{wave number } (1/\lambda) = 4.12\sqrt{\frac{15\times(10^5)}{6}}$$

= 4.12 x 5 x 100

= 2060 cm^{-1}

The ideal FT-IR stretching wave number for typical C≡C triple bond (with a bond order of 3.0) is 2060 cm^{-1}, which is clearly different from the experimentally observed value of 1930 cm^{-1} for copper phenylacetylide. The difference is due to the electron-withdrawing character of Cu(I) ion in copper phenylacetylide. If we substitute the observed 1930 cm^{-1} wavenumber back to the equation (3),

$$1930 = = 4.12\sqrt{\frac{K\prime}{6}}$$

One obtains, K'= 13.166 x 10^5 dyne/cm.

The bond order in C≡C triple bond of copper phenylacetylide= (13.166 x 10^5) / (5 x 10^5)= 2.63, which is reasonable due to the electron-withdrawing character of Cu(I) in copper phenylacetylide and thus weakening of the adjacent C≡C triple bond.

Evaluation of Green metrics for the current photochemical process

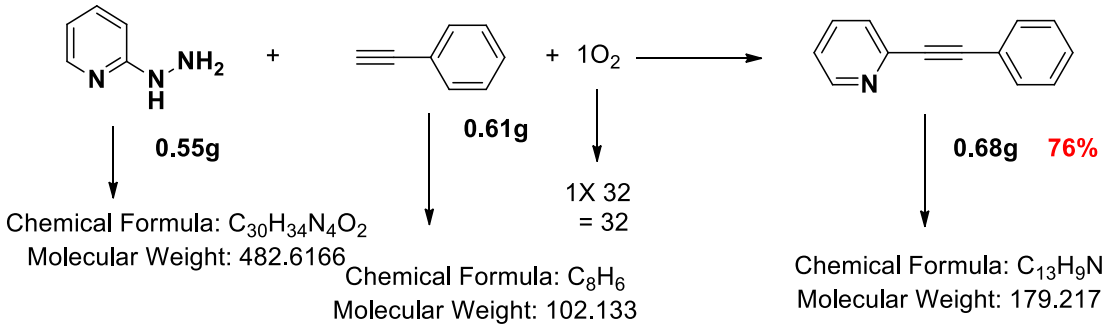
Atom economy defined as “how much of the reactants remain in the final desired product"

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

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= 109+102+32 = 243

Reactant 1	2-hydrazinylpyridine	0.55g	5.0 mmol	FW 109.12
Reactant 2	Phenylacetylene	0.61g	6.0 mmol	FW 102.13
Base	K_2CO_3 (1.2equiv.)	0.83g	6.0 mmol	FW 138.2
Solvent	MeOH	9.5g	---	---
Auxiliary	---	---	---	---
Product	2-(phenylethynyl)pyridine	0.68g	3.8 mmol	FW 179.22

Product yield= 76%

$$\text{E-factor} = \frac{0.55g + 0.61g + 0.83g + 9.5g - 0.68g}{0.68\ g} = \textbf{15.9 kg waste/ 1 kg product}$$

$$\text{Atom economy} = \frac{179}{243} \times 100 = 73.7\%$$

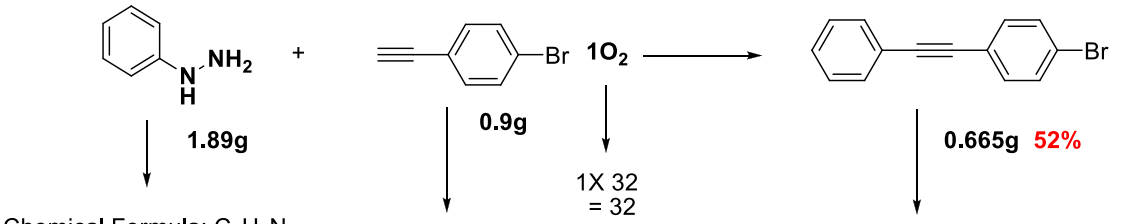
$$\text{Atom efficiency} = 76\ \% \times 73.7\% / 100 = 56\%$$

$$\text{Carbon efficiency} = \frac{13}{5 + 8} \times 100 = 100\%$$

$$\text{Reaction mass efficiency} = \frac{0.68\ g}{0.55g + 0.61g} \times 100 = 58.6\%$$

Evaluation of Green metrics for the reported thermal process [s4]

Reaction scheme (Pd-catalysed thermal reaction of arylhydrazine with terminal alkyne)



Chemical Formula: $C_6H_8N_2$
Molecular Weight: 108.141

Chemical Formula: C_8H_5Br
Molecular Weight: 181.029

Chemical Formula: $C_{14}H_9Br$
Molecular Weight: 257.125

Total= 108+181+32 = 321

Reactant 1	Phenylhydrazine (3.5equiv)	1.89g	17.5 mmol	FW 108.14
Reactant 2	1-bromo-4-ethynylbenzene	0.9g	5.0 mmol	FW 181.02
Additive	Acetic acid (3.0equiv.)	3.15g	52.4 mmol	FW 60.05
Solvent	DMF	18.9g	---	---
Auxiliary	---	---	---	---
Product	1-bromo-4-(phenylethynyl)benzene	0.665g	2.586mmol	FW 257.12

Product yield= 52%

$$\text{E-factor} = \frac{1.89\text{g} + 0.9\text{g} + 3.15\text{g} + 18.9\text{g} - 0.665\text{g}}{0.665\text{ g}} = \textbf{36.4 kg waste/ 1 kg product}$$

$$\text{Atom economy} = \frac{257}{321} \times 100 = 80\%$$

$$\text{Atom efficiency} = 52\,\% \times 80\% / 100 = 41.6\%$$

$$\text{Carbon efficiency} = \frac{14}{6 + 8} \times 100 = 100\%$$

$$\text{Reaction mass efficiency} = \frac{0.665\text{ g}}{1.89\text{g} + 0.9\text{g}} \times 100 = 23.8\%$$

Price Evaluation for the current photochemical process

Price of chemicals required for the reaction:

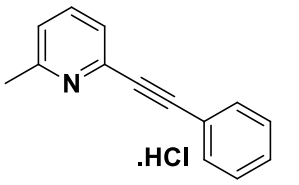
Sr.no	Chemical name	Chemical company	Amount/Price (USD)
1.	2-hydrazinylpyridine	Sigma Aldrich	1g /29 USD
2.	Phenylacetylene	Alfa Aesar	25g /33 USD
3.	Copper chloride (CuCl) Reagent grade, 97%	Sigma Aldrich	25g / 53 USD
4.	Potassium carbonate (K_2CO_3)	Showa	500g/ 15.4 USD
5.	Methanol, anhydrous 99.8%	Sigma Aldrich	1L/ 71 USD

Price estimation for the gram scale reaction for the formation of 2-(phenylethynyl)pyridine (3a)

Sr.no	Chemicals	Amount (g)	Estimated price (USD)
1.	2-hydrazinylpyridine	0.55	15.9
2.	Phenylacetylene	0.61	0.8
3.	Copper chloride (CuCl)	0.025	0.05
4.	Potassium carbonate (K_2CO_3)	0.83	0.03
5.	Methanol	9.5 (12mL)	0.9
6.	**2-(phenylethynyl)pyridine (Product, 3a)**	**0.68g (3.8 mmol)**	**Total= 17.68 USD**

Inference:

1. 0.68 g of product 2-(phenylethynyl)pyridine (**3a**) is synthesized in $17.68 USD, which is equivalent to $26 USD/g**.**
2. The product (3a) is not commercially available. The only product 3e in salt form is commercially available and provided by Sigma Aldrich Company at the price of 5 mg /109USD and 25mg /391USD**,** which is quite expensive.



(3e)

2-methyl-6-(phenylethynyl)pyridine hydrochloride

3. Thus, this current protocol is eco-friendly and economically feasible. In addition, this method could be applicable to the industrial scale synthesis of 2-(alkyl/arylethynyl) pyridines.

Note: In the above price estimation, the amount of electricity (power) consumed by the blue LEDs, stirrer and the cooling fans is not included.

Price Evaluation for the thermal process[s5]

Price of chemicals required for the reaction

Sr.no	Chemical name	Chemical company	Amount/Price (USD)
1.	2-bromopyridine	Sigma Aldrich	25g /$35.1 USD
2.	Phenylacetylene	Alfa Aesar	25g /$33 USD
3.	Palladium (II) acetate Reagent grade	Sigma Aldrich	1g /$94.4 USD
4.	Dimethylformamide, DMF anhydrous, 99.8% (Solvent)	Sigma Aldrich	0.1L/$64.5 USD
5.	Cesium carbonate, Reagentplus, 99%	Sigma Aldrich	5g/$21 USD
6.	Cu(Xantphos)I	Sigma Aldrich	0.5g/$63.6 USD

Price estimation for the 1.0mmol scale reaction for the formation of 2-(phenylethynyl)pyridine

Sr.no	Chemicals	Amount (g)	Estimated price (USD)
1.	2-bromopyridine (1.0mmol)	0.158	$0.22
2.	Phenylacetylene (1.2mmol)	0.123	$0.16
3.	Palladium (II) acetate (0.01mmol)	0.00225	$0.21
4.	Dimethylformamide, DMF	5mL	$3.23
5.	Cesium carbonate (2.0mmol)	0.65	$2.74
6.	Cu(Xantphos)I (0.01mmol)	0.0077	$0.98
7.	**2-(phenylethynyl)pyridine (Product) %Yield=94%**	**0.168 g** (0.94 mmol)	**Total= $7.54 USD**

Note: In the above price estimation, the amount of electricity (power) consumed by stirrer for maintaining the temperature of 60 ^{o}C for 16h is not included.

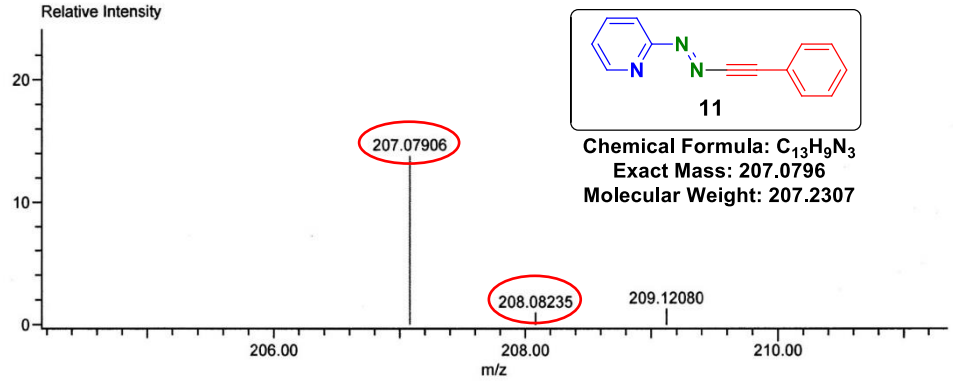
Inference: The reported thermal reaction can synthesize 0.168 g of 2-(phenylethynyl)pyridine (product) in $7.54 USD, which is equivalent to $44.9 USD/g.

Mass spectra of reaction mixture (intermediate 11)

Data:60-a
Comment:
Description:
Ionization Mode:ESI+
History:Average(MS[1] 0.56..0.97)

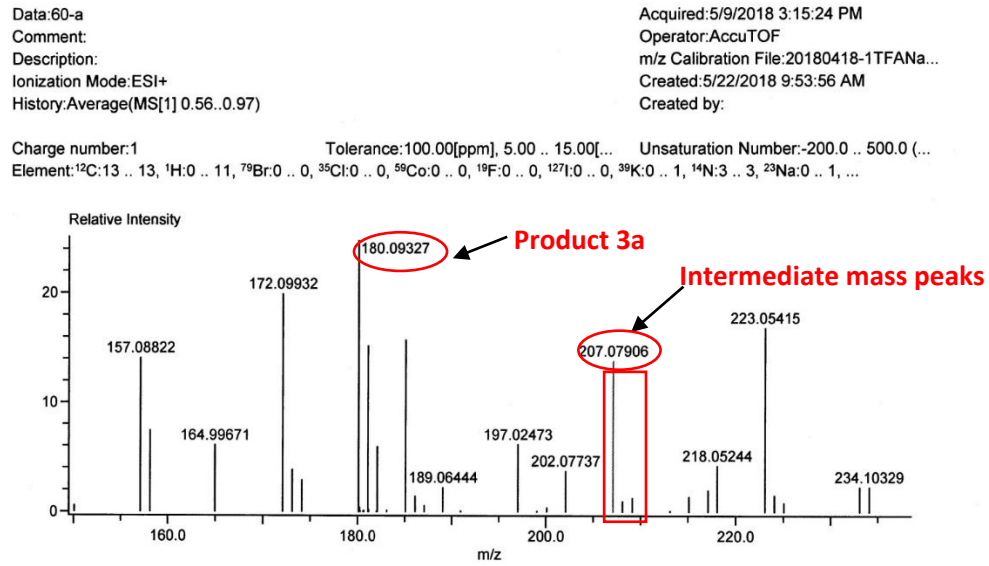
Acquired:5/9/2018 3:15:24 PM
Operator:AccuTOF
m/z Calibration File:20180418-1TFANa...
Created:5/22/2018 9:53:56 AM
Created by:

Charge number:1 Tolerance:100.00[ppm], 5.00 .. 15.00[... Unsaturation Number:-200.0 .. 500.0 (...
Element:^{12}C:13 .. 13, ^{1}H:0 .. 11, ^{79}Br:0 .. 0, ^{35}Cl:0 .. 0, ^{59}Co:0 .. 0, ^{19}F:0 .. 0, ^{127}I:0 .. 0, ^{39}K:0 .. 1, ^{14}N:3 .. 3, ^{23}Na:0 .. 1, ...



Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula
207.07906	2961.42	207.07965	-0.59	-2.83	$^{12}C_{13}{}^{1}H_{9}{}^{14}N_{3}$

Full ESI mass Spectrum



Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula
207.07906	2961.42	207.07965	-0.59	-2.83	$^{12}C_{13}{}^{1}H_{9}{}^{14}N_{3}$

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=30n; receiver phase=0deg; receiver harmonic=1; field modulation frequency=100000 Hz; microwave frequency[Hz]= 9.660469e^{+09}; field modulation amplitude [T]= 0.00016; receiver time constant[S] = 0.32768; microwave power= 0.015 W; receiver offset [%FS]=0; DMPO (5-,5-dimethyl-1-pyrroline N-oxide) was employed as a radical trap for superoxide.

The reaction under standard condition (**1a**, phenylacetylene, base, CuCl, O_2) in CH_3OH was irradiated with blue LED light for 30 min in the presence of DMPO in an EPR chamber while recording the EPR spectra. The EPR signals shown in Figure S1 is corresponding to DMPO-OO(H). This result indicates that superoxide free radical was formed in the reaction solution. No superoxide EPR signals were observed from the reaction solution under standard condition in absence of CuCl (Figure 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

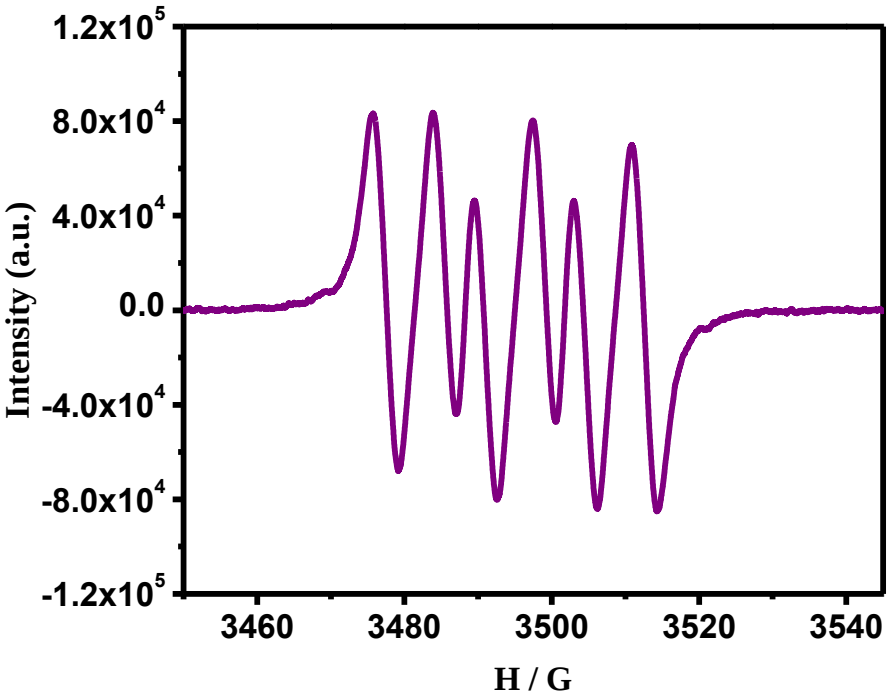


Figure S2: EPR spectra of the reaction mixture: 2-hydrazinopyridine (**1a**) (0.5 mmol), phenylacetylene (0.6 mmol), K_2CO_3 (1.2 equiv.) and 5 mol% of CuCl in MeOH (7 mL), 0.5 ml of this reaction solution was taken out into a small vial, followed by the addition of 0.01 mL of DMPO (5×10^{-2} M). The 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

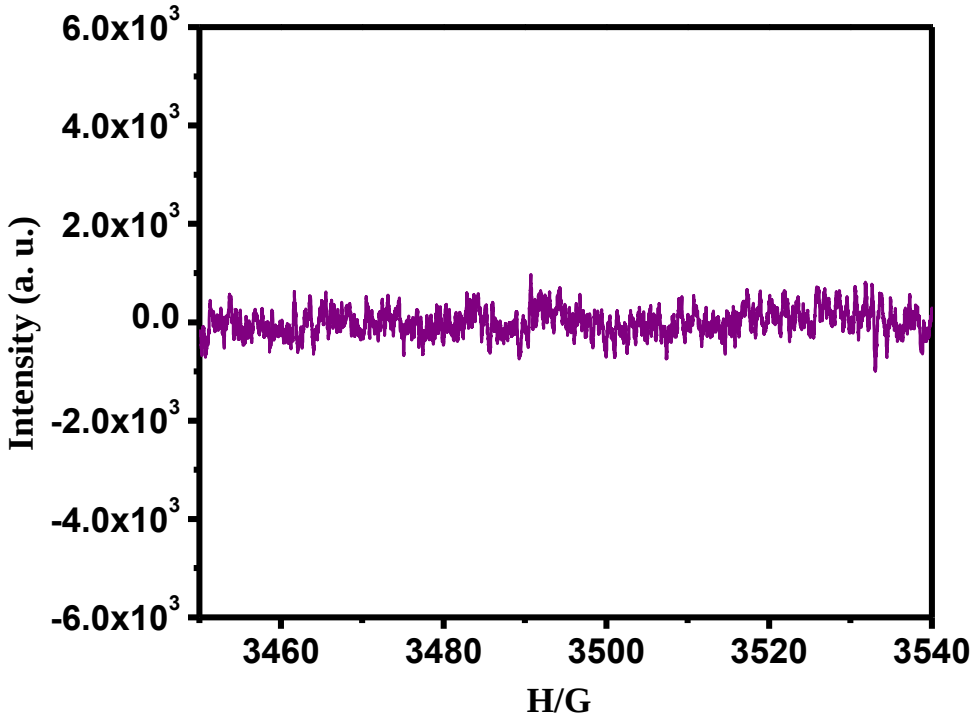


Figure S3: EPR spectra of the reaction mixture: 2-hydrazinopyridine (**1a**) (0.5 mmol) phenylacetylene (0.6 mmol), K_2CO_3 (1.2 equiv.) in MeOH (7 mL), 0.5 mL of this reaction solution was taken out into a small vial, followed by the addition of 0.01 mL of DMPO (5×10^{-2} M). The mixture was then irradiated 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.

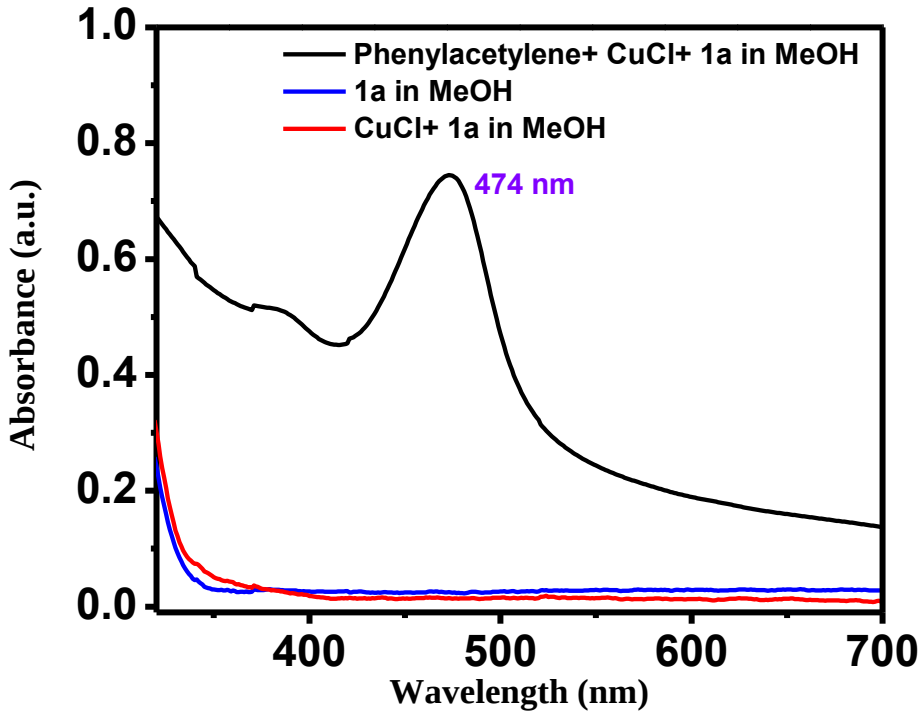
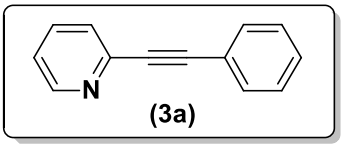


Figure S4: UV-visible spectra of the reaction mixture in MeOH. The black line indicates a mixture of 2- hydrazinopyridine **(1a)**, CuCl, phenlacetylene in MeOH, the blue line indicates **1a** in MeOH and the red line indicates a mixture of **1a** and CuCl in MeOH.

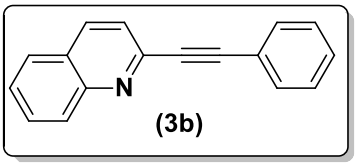
Spectroscopic Data

2-(phenylethynyl)pyridine (3a)



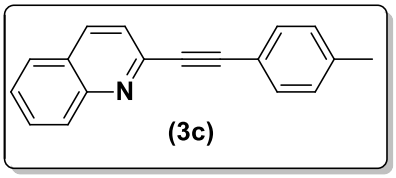
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.57 (d, *J*= 6.0Hz, 1 H), 7.62-7.55 (m, 3 H), 7.47 (d, *J*= 6.0Hz, 1 H), 7.31 (t, *J*= 6.0Hz, 3 H), 7.17 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.9, 143.3, 136.0,131.9, 128.8, 128.2, 127.0, 122.6, 122.1, 89.0 and 88.5; ESI-MS (M+H) calcd for $C_{13}H_9N$ (M+H): 179.0735, found: 180.0803.

2-(phenylethynyl)quinoline (3b)



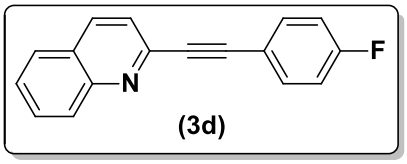
White semi-solid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.12 (q, *J*= 6.0Hz, 2 H), 7.79 (d, *J*= 12.0Hz, 1 H), 7.73-7.70 (m, 1 H), 7.64 (t, *J*= 12.0Hz, 2 H), 7.59 (d, *J*= 12.0 Hz, 1 H), 7.55-7.51 (m, 1 H), 7.37-7.36 (m, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 148.0, 143.4, 135.9, 132.0, 129.9, 129.1, 129.0, 128.2, 127.3, 126.9, 124.2, 122.0, 89.8 and 89.2; **ESI-MS** calcd for $C_{17}H_{11}N$ (M+H):229.0891, found: 230.09645.

2-(p-tolylethynyl)quinoline (3c)



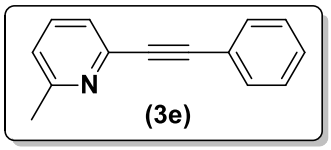
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.10 (d, *J*= 6.0Hz, 2 H), 7.77 (t, *J*= 6.0Hz, 1 H), 7.71 (t, *J*= 6.0Hz, 1 H), 7.58-7.50 (m, 4 H), 7.17 (d, *J*= 6.0 Hz, 2 H), 2.36 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 148.8, 139.4, 136.0, 132.1, 129.2, 129.1, 127.4, 127.0, 126.9, 124.3, 119.0, 90.3, 88.8 and 21.5; **ESI-MS** calcd for $C_{18}H_{13}N$ (M+H): 243.1048, found: 244.11314.

2-((4-fluorophenyl)ethynyl)quinoline (3d)



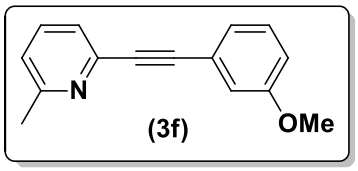
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.11 (t, *J*= 6.0Hz, 2 H), 7.78 (d, *J*= 6.0Hz, 1 H), 7.72-7.69 (m, 1 H), 7.63-7.57 (m, 4 H), 7.0.7 (t, *J*= 12.0 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.8, 162.1, 148.2, 143.4, 136.1, 134.2, 134.1, 130.0, 129.2, 127.4, 127.1, 124.2, 118.2, 115.8, 115.7, 89.0 and 88.7; **ESI-MS** calcd for $C_{17}H_{10}FN$ (M+H): 247.0797, found: 248.08762.

2-methyl-6-(phenylethynyl)pyridine (3e)



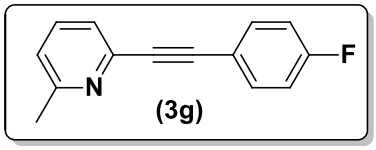
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58-7.53 (m, 3 H), 7.32 (t, *J*= 6.0Hz, 4 H), 7.08 (d, *J*= 6.0Hz, 1 H), 2.56 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 158.9, 142.7, 136.3,132.0, 128.8, 128.3, 124.3, 122.5, 122.3, 88.8, 88.7 and 24.5.

2-((3-methoxyphenyl)ethynyl)-6-methylpyridine (3f)



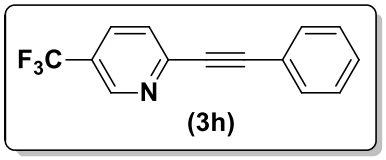
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54 (t, *J*= 6.0Hz, 1 H), 7.33 (d, *J*= 12.0Hz, 1 H), 7.23-7.16 (m, 1 H), 7.12 (d, *J*= 6.0Hz, 1 H), 7.09-6.90 (m, 2 H), 6.89(d, *J*= 6.0Hz, 1 H), 3.79 (s, 3 H), 2.56 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.2, 158.9, 142.6, 136.3, 129.4, 124.5, 124.3,123.3, 122.5, 116.6, 115.6, 88.6, 88.5, 55.2 and 24.2; **ESI-MS** calcd for $C_{15}H_{13}NO$ (M+H):223.0997, found: 224.10826

4-benzoyl-2,6-dimethylcyclohexa-2,5-dienone (3g)



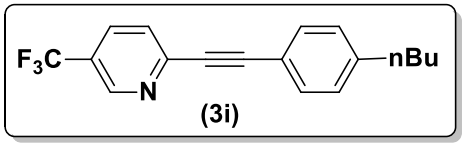
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56-7.54 (m, 3 H), 7.31 (d, *J*= 6.0Hz, 1 H), 7.09 (d, *J*= 6.0Hz, 1 H), 7.02 (t, *J*= 6.0Hz, 2 H), 2.55 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.6, 162.0, 159.0, 142.5, 136.3, 134.0, 133.9, 124.2, 122.6, 118.5, 115.7, 115.6, 88.5, 87.6 and 24.5.

2-(phenylethynyl)-5-(trifluoromethyl)pyridine (3h)



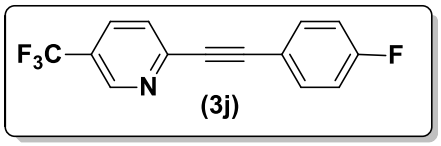
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.85 (s, 1 H), 7.90 (d, *J*= 6.0 Hz, 1 H), 7.60 (t, *J*= 12.0 Hz, 3 H), 7.39-7.35 (m, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 146.8, 133.3, 132.2, 129.5, 128.4, 126.6, 125.3, 125.0, 124.8, 124.2, 122.4, 121.4, 91.9 and 87.6.

2-((4-butylphenyl)ethynyl)-5-(trifluoromethyl)pyridine (3i)



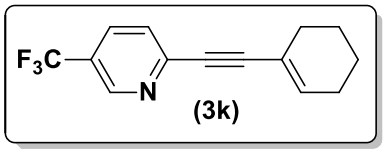
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.84 (s, 1 H), 7.88 (d, *J*= 6.0 Hz, 1 H), 7.59 (d, *J*= 12.0 Hz, 1 H), 7.51 (d, *J*= 6.0 Hz, 2 H), 7.18 (d, *J*= 6.0 Hz, 2 H), 2.61 (t, *J*= 6.0 Hz, 2 H), 1.61-1.55 (m, 2 H), 1.37-1.30 (m, 2 H), 0.91 (t, *J*= 6.0 Hz, 3 H) ; **^{13}C NMR** (150 MHz, $CDCl_3$): δ 147.0, 146.9, 146.8, 145.0, 133.3, 133.2, 132.3, 132.1, 129.4, 128.6, 126.5, 125.1, 124.8, 118.6, 92.4, 87.2, 35.6, 33.2, 22.2 and 13.8.

2-((4-fluorophenyl)ethynyl)-5-(trifluoromethyl)pyridine (3j)



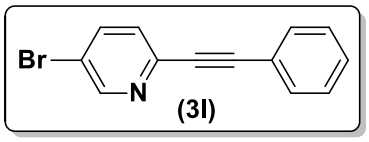
White solid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.85 (s, 1 H), 7.90 (t, *J*= 6.0 Hz, 1 H), 7.60-7.57 (m, 3 H), 7.06 (t, *J*= 12.0 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 164.1, 162.4, 146.9, 146.6, 134.3, 134.2, 133.4, 126.5, 125.4, 125.1, 117.6, 116.0, 115.8, 90.8 and 87.4; **ESI-MS** calcd for $C_{14}H_7F_4N_2$ (M+H): 265.0515, found: 266.06069.

2-(cyclohex-1-en-1-ylethynyl)-5-(trifluoromethyl)pyridine (3k)



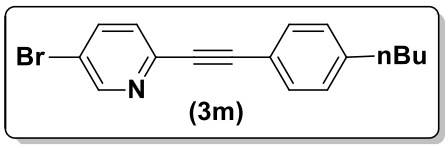
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.78 (s, 1 H), 7.82 (t, *J*= 6.0 Hz, 1 H), 7.47 (d, *J*= 6.0 Hz, 1 H), 6.37 (t, *J*= 6.0 Hz, 1 H), 2.22 (q, *J*= 6.0 Hz, 2 H), 2.14 (t, *J*= 6.0 Hz, 2 H), 1.67-1.65 (m, 4 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 147.2, 146.8, 146.7, 138.8, 133.2, 133.1, 126.3, 124.7, 124.5, 119.7, 94.1, 85.4, 28.6, 25.9, 22.1, 21.3 and 21.2.

5-bromo-2-(phenylethynyl)pyridine (3l)



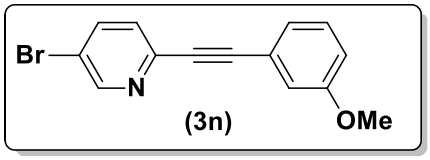
Pale yellow liquid **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.65 (s, 1 H), 7.78 (t, *J*= 6.0 Hz, 1 H), 7.56 (d, *J*= 6.0 Hz, 2 H), 7.39-7.33 (m, 4 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 151.1, 141.7, 138.8, 132.0, 129.2, 128.4, 128.0, 121.9, 119.5, 90.5 and 87.7; **ESI-MS** calcd for $C_{13}H_8BrN$ (M+H): 256.9840, found: 257.9910.

5-bromo-2-((4-butylphenyl)ethynyl)pyridine (3m)



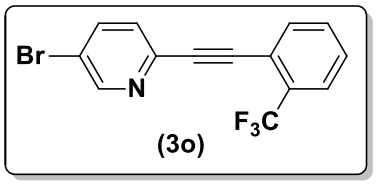
Pale yellow liquid **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.64 (s, 1 H), 7.76 (t, *J*= 6.0 Hz, 1 H), 7.48 (d, *J*= 6.0 Hz, 2 H), 7.36 (d, *J*= 12.0 Hz, 1 H), 7.15 (d, *J*= 6.0 Hz, 2 H), 2.60 (t, *J*= 6.0 Hz, 2 H), 1.60-1.55 (m, 2 H), 1.36-1.30 (m, 2 H), 0.90 (t, *J*= 6.0 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 151.1, 144.5, 141.9, 138.7, 131.9, 128.5, 127.9, 119.6, 118.9, 90.9, 87.1, 35.6, 33.2, 22.2 and 13.8; **ESI-MS** calcd for $C_{17}H_{16}BrN$ (M+H): 313.0466, found: 314.05274.

5-bromo-2-((3-methoxyphenyl)ethynyl)pyridine (3n)



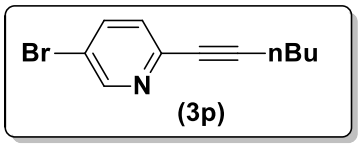
Pale yellow liquid **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.65 (s, 1 H), 7.78 (t, *J*= 6.0 Hz, 1 H), 7.39 (d, *J*= 6.0 Hz, 1 H), 7.25 (t, *J*= 6.0 Hz, 1 H), 7.16 (d, *J*= 6.0 Hz, 1 H), 7.10 (d, *J*= 6.0 Hz, 1 H), 6.91(t, *J*= 6.0 Hz, 1 H), 3.79 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.3, 151.2, 141.7, 138.8, 129.5, 128.0, 124.5, 122.8, 120.0, 116.6, 116.0, 90.4, 87.4 and 55.3; **ESI-MS** calcd for $C_{14}H_{10}BrNO$ (M+H): 286.9946, found: 288.0024.

5-bromo-2-((2-(trifluoromethyl)phenyl)ethynyl)pyridine (3o)



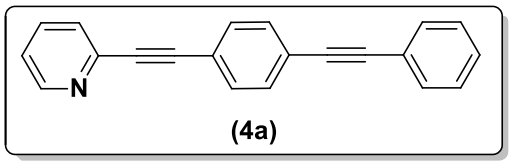
Pale yellow liquid **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.61 (s, 1 H), 7.74 (d, *J*= 6.0 Hz, 1 H), 7.69-7.66 (m, 2H), 7.54-7.50 (m, 1 H), 7.43 (t, *J*= 12.0 Hz, 1 H), 7.25 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.1, 142.9, 136.2, 134.2, 132.0, 131.7, 131.4, 128.6, 127.6, 126.0, 125.9, 125.8, 125.6, 123.1, 122.3, 120.5, 93.6 and 84.9.

5-bromo-2-(hex-1-yn-1-yl)pyridine (3p)



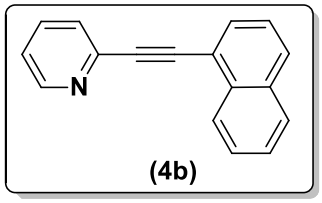
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.56 (s, 1 H), 7.70 (d, *J*= 6.0 Hz, 1 H), 7.22 (d, *J*= 12.0 Hz, 1 H), 2.40 (t, *J*= 6.0 Hz, 2 H), 1.62-1.55 (m, 2 H), 1.48-1.41 (m, 2 H), 0.91 (t, *J*= 6.0 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.8, 142.3, 138.6, 127.7, 119.3, 92.5, 79.4, 30.2, 22.0, 19.0 and 13.5.

2-((4-(phenylethynyl)phenyl)ethynyl)pyridine (4a)



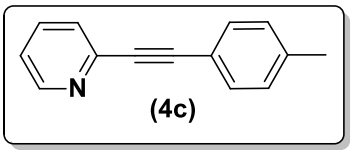
Semisolid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 6.61 (s, 1 H), 7.66 (t, *J*= 6.0 Hz, 1 H), 7.56-7.49 (m, 7 H), 7.33 (t, *J*= 6.0 Hz, 3 H), 7.22 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.1, 143.2, 136.1, 131.9, 131.6, 131.5, 131.0, 128.5, 128.3, 127.1, 123.8, 122.8, 121.9, 91.5, 90.2, 88.9 and 88.7; **ESI-MS** calcd for $C_{21}H_{13}N$ (M+H): 279.1048, found: 280.11327.

2-(naphthalen-1-ylethynyl)pyridine (4b)



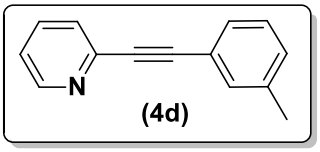
Viscous liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.64 (s, 1 H), 8.47 (d, *J*= 12.0 Hz, 1 H), 7.84 (t, *J*= 6.0 Hz, 3 H), 7.68-7.57 (m, 3 H), 7.52-7.42 (m, 2 H), 7.22 (d, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.1, 143.5, 136.1, 133.2, 133.0, 131.1, 129.4, 128.2, 127.2, 126.9, 126.4, 126.1, 125.1, 122.7, 119.8, 93.4 and 87.3; **ESI-MS** calcd for $C_{17}H_{11}N$ (M+H): 229.0891, found: 230.09759.

2-(p-tolylethynyl)pyridine (4c)



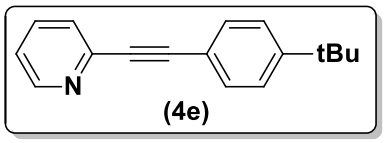
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.58 (d, *J*= 6.0 Hz, 1 H), 7.65-7.62 (m, 1 H), 7.47 (t, *J*= 6.0 Hz, 3 H), 7.20-7.18 (m, 1 H), 7.14 (q, *J*= 6.0 Hz, 2 H), 2.34 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.9, 143.5, 139.2, 136.0, 131.9, 129.1, 127.0, 122.5, 119.1, 89.5, 88.0. and 21.5; **ESI-MS** calcd for $C_{14}H_{11}N$ (M+H): 193.0891, found: 194.09766.

2-(m-tolylethynyl)pyridine (4d)



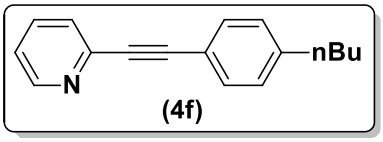
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.57 (s, 1 H), 7.63 (t, *J*= 6.0 Hz, 1 H), 7.48 (d, *J*= 6.0 Hz, 1 H), 7.38 (t, *J*= 12.0 Hz, 1 H), 7.21 (t, *J*= 6.0 Hz, 1 H), 7.19-7.14 (m, 3 H), 2.32 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.9, 143.4, 138.0, 136.0, 132.5, 129.8, 129.0, 128.2, 127.0, 122.5, 121.9, 89.4, 88.2 and 21.1; **ESI-MS** calcd for $C_{14}H_{11}N$ (M+H): 193.0891, found: 194.09784.

2-((4-(tert-butyl)phenyl)ethynyl)pyridine (4e)



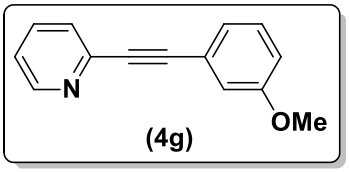
Pale yellow liquid;**^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.57 (d, *J*= 6.0 Hz, 1 H), 7.62-7.60 (m, 1 H), 7.51-7.46(m, 3 H), 7.35 (d, *J*= 6.0 Hz, 2 H), 7.17(t, *J*= 6.0 Hz, 1 H), 1.28 (s, 9 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 152.2, 149.9, 143.5, 136.0, 131.7, 127.0, 125.3, 122.4, 119.1, 89.4, 88.0, 34.7 and 31.0; **ESI-MS** calcd for $C_{17}H_{17}N$ (M+H): 235.1361, found: 236.14442.

2-((4-butylphenyl)ethynyl)pyridine (4f)



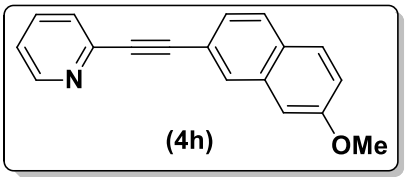
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.58 (d, *J*= 6.0 Hz, 1 H), 7.63 (t, *J*= 6.0 Hz, 1 H), 7.48 (d, *J*= 12.0 Hz, 3 H), 7.20-7.14 (m, 3 H), 2.59 (t, *J*= 6.0 Hz, 2 H), 1.59-1.54 (m, 2 H), 1.35-1.29 (m, 2 H), 0.90 (t, *J*= 6.0 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.9, 144.1, 143.6, 136.0, 131.9, 128.4, 127.0, 122.5, 119.2, 89.5, 88.0, 35.5, 33.2, 22.2 and 13.8; **ESI-MS** calcd for $C_{17}H_{17}N$ (M+H): 235.1361, found: 236.1430.

2-((3-methoxyphenyl)ethynyl)pyridine (4g)



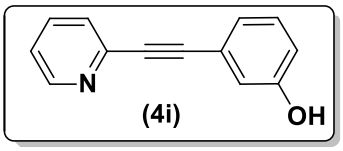
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.56 (s, 1 H), 7.60 (t, *J*= 6.0 Hz, 1 H), 7.46 (d, *J*= 12.0 Hz, 1 H), 7.22-7.08 (m, 4 H), 6.87 (t, *J*= 6.0 Hz, 1 H), 3.74 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.1, 149.9, 143.2, 136.0, 129.3, 127.0, 124.4, 123.0, 122.6, 116.5, 115.6, 89.0, 88.2 and 55.1; **ESI-MS** calcd for $C_{14}H_{11}NO$ (M+H): 209.0841, found: 210.09220.

2-((7-methoxynaphthalen-2-yl)ethynyl)pyridine (4h)



Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.61 (s, 1 H), 8.03 (s, 1 H), 7.71-7.57 (m, 3 H), 7.53 (d, *J*= 6.0 Hz, 2 H), 7.21 (t, *J*= 6.0 Hz, 1 H), 7.16 (t, *J*= 6.0 Hz, 1 H), 7.10 (d, *J*= 6.0 Hz, 1 H), 3.90 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 158.6, 150.0, 143.6, 136.1, 134.5, 132.1, 129.4, 129.0, 128.3,127.0, 126.8, 122.5, 119.4, 117.0, 105.8, 89.6, 88.3 and 55.3.

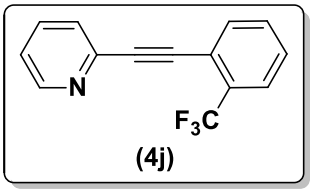
3-(pyridin-2-ylethynyl)phenol (4i)



(4i)

Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.54 (s, 1 H), 7.70 (t, *J*= 12.0 Hz, 1 H), 7.51 (d, *J*= 12.0 Hz, 1 H), 7.27 (t, *J*= 6.0 Hz, 2 H), 7.14 (t, *J*= 6.0 Hz, 1 H), 7.00 (d, *J*= 12.0 Hz, 1 H), 6.90 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.9, 149.1, 142.7, 137.1, 129.5, 127.7, 123.5, 123.1, 122.4, 118.9, 117.5, 91.1 and 86.8.

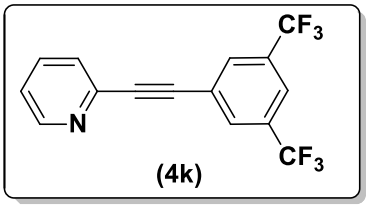
2-((2-(trifluoromethyl)phenyl)ethynyl)pyridine (4j)



(4j)

Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.59 (s, 1 H), 7.71 (d, *J*= 12.0 Hz, 1 H), 7.65 (t, *J*= 6.0 Hz, 2 H), 7.49 (t, *J*= 6.0 Hz, 2 H), 7.41 (t, *J*= 6.0 Hz, 1 H), 7.22 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.0, 142.9, 136.1, 134.2, 131.9, 131.4, 128.6, 127.6, 125.6, 125.9, 125.8, 125.80, 124.5, 123.1, 122.3, 120.4, 93.6 and 84.8; **ESI-MS** calcd for $C_{14}H_8F_3N$ (M+H): 247.0609, found: 248.06878.

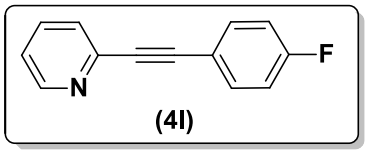
2-((3,5-bis(trifluoromethyl)phenyl)ethynyl)pyridine (4k)



(4k)

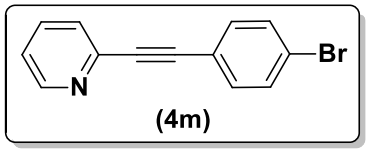
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.57 (s, 1 H), 7.95 (s, 2 H), 7.77 (s, 1 H), 7.64 (t, *J*= 12.0 Hz, 1 H), 7.49 (d, *J*= 12.0 Hz, 1 H), 7.22 (t, *J*= 6.0 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.2, 142.1, 136.2, 132.1, 131.8, 131.7, 127.3, 124.6, 123.8, 123.5, 122.1, 121.6, 119.5, 91.4 and 85.3; **ESI-MS** calcd for $C_{15}H_7F_6N$ (M+H): 315.0483, found: 316.05629.

2-((4-fluorophenyl)ethynyl)pyridine (4l)



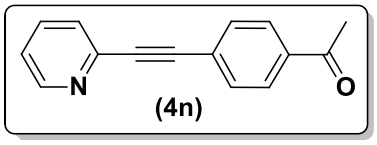
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.59 (s, 1 H), 7.65(t, J= 6.0 Hz, 1 H), 7.55 (t, J= 6.0 Hz, 2 H), 7.48 (d, J= 6.0 Hz, 1 H), 7.21 (t, J= 6.0 Hz, 1 H), 7.02 (t, J= 12.0 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.7, 162.0, 150.0, 143.2, 136.1, 134.0, 133.9, 127.0, 122.7, 118.3, 115.7, 115.6, 88.2 and 88.0; **ESI-MS** calcd for $C_{13}H_8FN$ (M+H): 197.0641, found: 198.07149.

2-((4-bromophenyl)ethynyl)pyridine (4m)



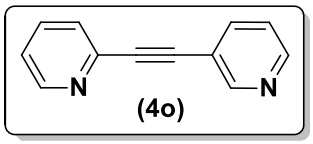
Pale yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.58 (s, 1 H), 7.65 (t, *J*= 6.0 Hz, 1 H), 7.49-7.41 (m, 5 H), 7.22 (d, *J*= 6.0 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.0, 143.0, 136.1, 133.3, 131.6, 127.1, 123.3, 122.9, 121.1, 89.5 and 88.0; **ESI-MS** calcd for $C_{13}H_8BrN$ (M+H): 256.9840, found: 257.99266.

1-(4-(pyridin-2-ylethynyl)phenyl)ethanone (4n)



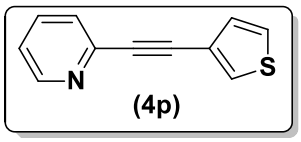
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.55 (s, 1 H), 7.86 (d, *J*= 6.0 Hz, 2 H), 7.61-7.58 (m, 5 H), 7.46 (d, *J*= 12.0 Hz, 1 H), 7.19 (d, *J*= 6.0 Hz, 1 H), 2.52 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 197.0, 150.0, 142.6, 136.5, 136.1, 131.9, 128.0, 127.2, 126.8, 123.0, 91.3, 87.9 and 26.4; **ESI-MS** calcd for $C_{15}H_{11}NO$ (M+H): 221.0841, found: 222.09179.

2-(pyridin-3-ylethynyl)pyridine (4o)



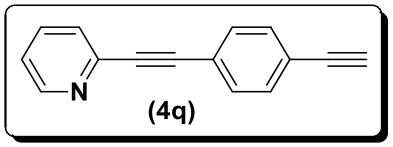
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.79 (s, 1 H), 8.61 (d, *J*= 6.0 Hz, 1 H), 8.55 (s, 1 H), 7.84 (d, *J*= 12.0 Hz, 1 H), 7.67 (t, *J*= 6.0 Hz, 1 H), 7.51 (d, *J*= 6.0 Hz, 1 H), 7.28-7.23 (m, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 152.5, 150.1, 149.1, 142.7, 138.8, 136.2, 127.2, 123.2, 123.0, 119.4, 91.6 and 85.5; **ESI-MS** calcd for $C_{12}H_8N_2$ (M+H): 180.0687, found: 181.07633.

2-(thiophen-3-ylethynyl)pyridine (4p)



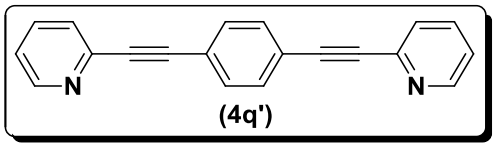
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.57 (d, *J*= 6.0 Hz, 1 H), 7.65-7.59 (m, 2 H), 7.47 (d, *J*= 6.0 Hz, 1 H), 7.27 (t, *J*= 6.0 Hz, 1 H), 7.22-7.18 (m, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.0, 143.4, 136.1, 130.1, 129.9, 126.9, 125.4, 122.6, 121.3, 88.2 and 84.4; **ESI-MS** calcd for $C_{11}H_7NS$ (M+H): 185.0299, found: 186.03747.

2-((4-ethynylphenyl)ethynyl)pyridine (4q)



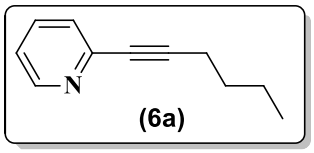
Yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.58 (d, *J*= 6.0Hz, 1 H), 7.65-7.61 (m, 1 H), 7.52-7.42 (m, 5 H), 7.22-7.18 (m, 1 H), 3.16 (s, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.8, 142.9, 135.9, 131.8, 131.6, 127.0, 122.7, 122.5, 122.4, 90.2, 88.3, 83.0 and 79.24; ESI-MS (M+H) calcd for $C_{15}H_9N$ (M+H):203.0735, found: 204.0806.

1,4-bis(pyridin-2-ylethynyl)benzene (4q')



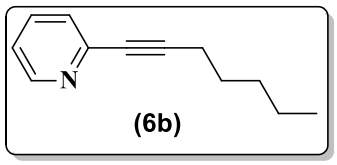
Yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.60 (d, *J*= 6.0Hz, 2 H), 7.67-7.62 (m, 2 H), 7.55 (s, 4 H), 7.50 (d, *J*= 12.0Hz, 2 H), 7.23-7.20 (m, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.9, 142.9, 136.0, 131.8, 131.7, 127.1, 122.8, 122.6, 90.5 and 88.55; ESI-MS (M+H) calcd for $C_{20}H_{12}N_2$ (M+H): 280.1000, found: 281.1069.

2-(hex-1-yn-1-yl)pyridine (6a)



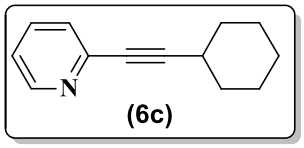
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.49 (s, 1 H), 7.55 (t, *J*= 6.0 Hz, 1 H), 7.31 (d, *J*= 6.0 Hz, 1 H), 7.12 (t, *J*= 6.0 Hz, 1 H), 2.39 (t, *J*= 12.0 Hz, 2 H), 1.59-1.54 (m, 2 H), 1.47-1.43 (m, 2 H), 0.91 (t, *J*= 6.0 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.7, 143.9, 135.9, 126.6, 122.1, 91.0, 80.2, 30.3, 21.9, 18.9 and13.5; **ESI-MS** calcd for $C_{11}H_{13}N$ (M+H): 159.1048, found: 160.11290.

2-(hept-1-yn-1-yl)pyridine (6b)



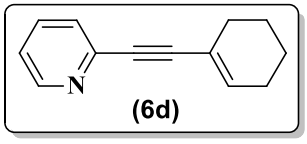
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.47 (s, 1 H), 7.53 (t, *J*= 6.0 Hz, 1 H), 7.30 (d, *J*= 6.0 Hz, 1 H), 7.10 (t, *J*= 6.0 Hz, 1 H), 2.37 (t, *J*= 6.0 Hz, 2 H), 1.60-1.55 (m, 2 H), 1.40-1.36 (m, 2 H), 1.31-1.27 (m, 3 H), 0.85 (t, *J*= 6.0 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.6, 143.9, 135.8, 126.6, 122.0, 91.0, 80.2, 31.0, 27.9, 22.1, 19.1 and 13.5; **ESI-MS** calcd for $C_{12}H_{15}N$ (M+H): 173.1204, found: 174.12758.

2-(cyclohexylethynyl)pyridine (6c)



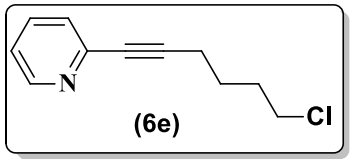
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.49 (s, 1 H), 7.55 (t, *J*= 6.0 Hz, 1 H), 7.32 (d, *J*= 12.0 Hz, 1 H), 7.11 (t, *J*= 6.0 Hz, 1 H), 2.59-2.55 (m, 1 H), 1.86 (t, *J*= 6.0 Hz, 2 H) 1.73-1.71 (m, 2 H), 1.54-1.30 (m, 6 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.6, 144.0, 135.8, 126.8, 122.0, 94.8, 80.2, 32.5, 29.5, 25.7 and 24.8; **ESI-MS** calcd for $C_{13}H_{15}N$ (M+H): 185.1204, found: 186.12837.

2-(cyclohex-1-en-1-ylethynyl)pyridine (6d)



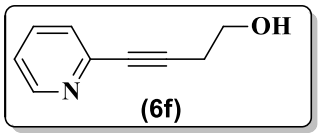
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.51 (s, 1 H), 7.57 (t, *J*= 6.0 Hz, 1 H), 7.35 (d, *J*= 12.0 Hz, 1 H), 7.14-7.11 (m, 1 H), 6.28 (t, *J*= 6.0 Hz, 1 H), 2.22-2.08 (m, 4 H), 1.64-1.56 (m, 4 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.8, 143.8, 137.1, 135.9, 126.7, 122.1, 120.0, 91.2, 86.1, 28.8, 25.7, 22.1 and 21.3; **ESI-MS** calcd for $C_{13}H_{13}N$ (M+H): 183.1048, found:184.11227.

2-(6-chlorohex-1-yn-1-yl)pyridine (6e)



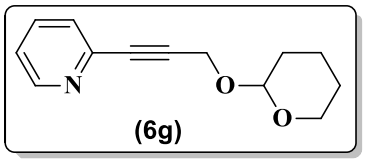
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.50 (d, *J*= 6.0 Hz, 1 H), 7.57 (t, *J*= 6.0 Hz, 1 H), 7.33 (d, *J*= 6.0 Hz, 1 H), 7.14 (t, *J*= 6.0 Hz, 1 H), 3.55 (t, *J*= 6.0 Hz, 2 H), 2.46 (t, *J*= 6.0 Hz, 2 H) 1.96-1.90 (m, 2 H), 1.78-1.72 (m, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.7, 143.6, 136.0, 126.7, 122.3, 89.8, 80.9, 44.4, 31.5, 25.4 and 18.5; **ESI-MS** calcd for $C_{11}H_{12}ClN$ (M+H): 193.0658, found: 194.07415.

4-(pyridin-2-yl)but-3-yn-1-ol (6f)



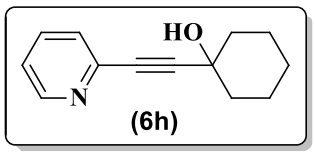
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.49 (s, 1 H), 7.60 (t, *J*= 12.0 Hz, 1 H), 7.35 (d, *J*= 6.0 Hz, 1 H), 7.18-7.15 (m, 1 H), 3.83 (t, *J*= 6.0 Hz, 2 H), 2.68 (t, *J*= 6.0 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.5, 143.2, 136.3, 126.7, 122.6, 88.1, 81.5, 60.6 and 23.7; **ESI-MS** calcd for C_9H_9NO (M+H): 147.0684, found: 170.05847.

2-(3-((tetrahydro-2H-pyran-2-yl)oxy)prop-1-yn-1-yl)pyridine (6g)



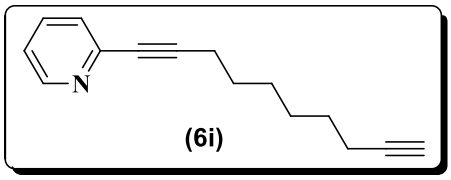
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.51 (s, 1 H), 7.57 (t, *J*= 12.0 Hz, 1 H), 7.37 (d, *J*= 12.0 Hz, 1 H), 7.16 (t, *J*= 6.0 Hz, 1 H), 4.84 (t, *J*= 6.0 Hz, 1 H), 4.49-4.40 (m, 2 H), 3.83-3.79 (m, 1 H), 3.51-3.48 (m, 1 H), 1.79-1.67 (m, 1 H), 1.61-1.54 (m, 5 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.8, 142.7, 136.0, 127.0, 122.8, 96.8, 85.3, 84.3, 61.9, 54.3, 30.1, 25.2 and 18.9; **ESI-MS** calcd for $C_{13}H_{15}NO_2$ (M+H): 217.1103, found: 218.11849.

1-(pyridin-2-ylethynyl)cyclohexanol (6h)



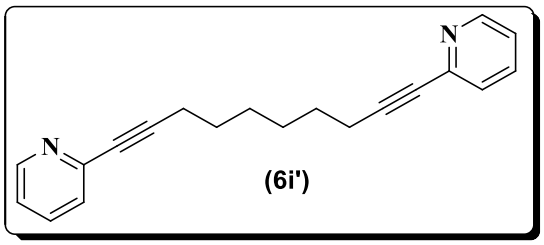
Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.52 (s, 1 H), 7.58 (t, *J*= 6.0 Hz, 1 H), 7.37 (d, *J*= 6.0 Hz, 1 H), 7.17 (t, *J*= 6.0 Hz, 1 H), 2.02 (t, *J*= 6.0 Hz, 2 H), 1.71-1.56 (m, 8 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.6, 143.0, 136.1, 127.1, 122.7, 93.6, 83.2, 68.6, 39.6, 25.1 and 23.2; **ESI-MS** calcd for $C_{13}H_{15}NO$ (M+H): 201.1154, found: 202.12285.

2-(deca-1,9-diynyl)pyridine (6i)



Pale yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.45-8.44 (m, 1 H), 7.54-7.49 (m, 1 H), 7.29-7.26 (m, 1 H), 7.10-7.07 (m, 1 H), 2.36 (t, *J*= 12.0 Hz, 2 H), 2.13-2.09 (m, 2 H), 1.86 (s, 1 H), 1.58-1.35 (m, 8 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.5, 143.5, 135.6, 126.4, 121.9, 90.6, 84.3, 80.3, 68.1, 28.3, 28.2, 28.1, 28.1, 19.2 and 18.3; **ESI-MS** calcd for $C_{15}H_{17}N$ (M+H): 211.1361, found: 212.1439.

1,10-di(pyridin-2-yl)deca-1,9-diyne (6i')



Colorless semisolid; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.46 (s, 2 H), 7.54-7.49 (m, 2 H), 7.26 (d, *J*= 12.0 Hz, 2 H), 7.10-7.07 (m, 2 H), 2.37 (t, *J*= 12.0 Hz, 4 H), 1.59-1.56 (m, 4 H), 1.44-1.42 (m, 4 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.3, 143.4, 135.6, 126.4, 121.9, 90.6, 80.2, 28.3, 28.0 and 19.1; **ESI-MS** calcd for $C_{20}H_{20}N_2$ (M+H): 288.1626, found: 289.1701.

References:

S1. GMBH; YU, Henry; DONNELLY, Marianne; NGUYEN, Ngan; JIANG, Xuliang – MERCK patent (WO2014/209980, 2014, A1)

S2. W.Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang and A. Lei, *J. Am. Chem. Soc.* 2008, **130**, 14713.

S3. Y. Okamoto and S. K. Kundu, *J. Phys. Chem.* 1973, **77**, 2677.

S4. Y. Zhao and Q. Song, *Chem. Commun.*, 2015, **51**, 13272.

S5. M. Liu, M. Ye, Y. Xue, G. Yin, D. Wang and J. Huang, *Tetrahedron. Lett*., 2016, **57**, 3137.


8.575
8.566
7.627
7.624
7.611
7.608
7.596
7.593
7.571
7.566
7.559
7.551
7.479
7.463
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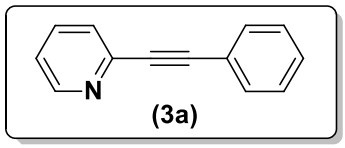
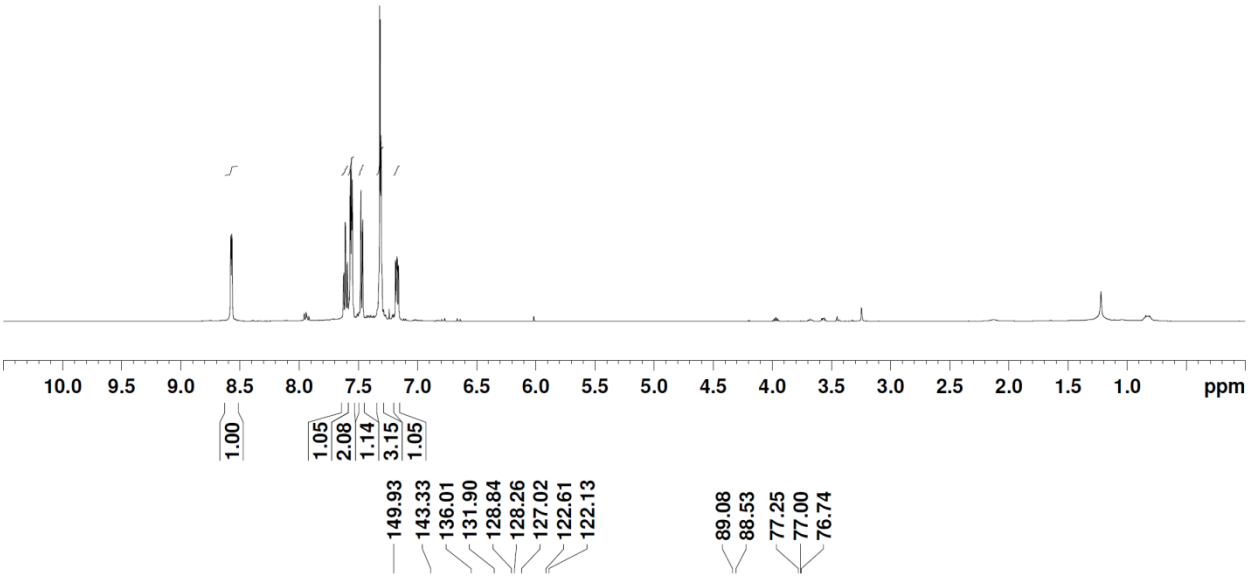
7.176
7.175
7.172
7.170
7.162
7.160


N
(3a)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1.00
1.05
2.08
1.14
3.15
1.05
149.93
143.33
136.01
131.90
128.84
128.26
127.02
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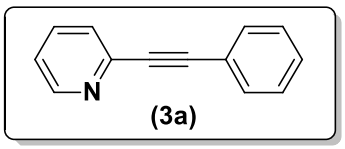
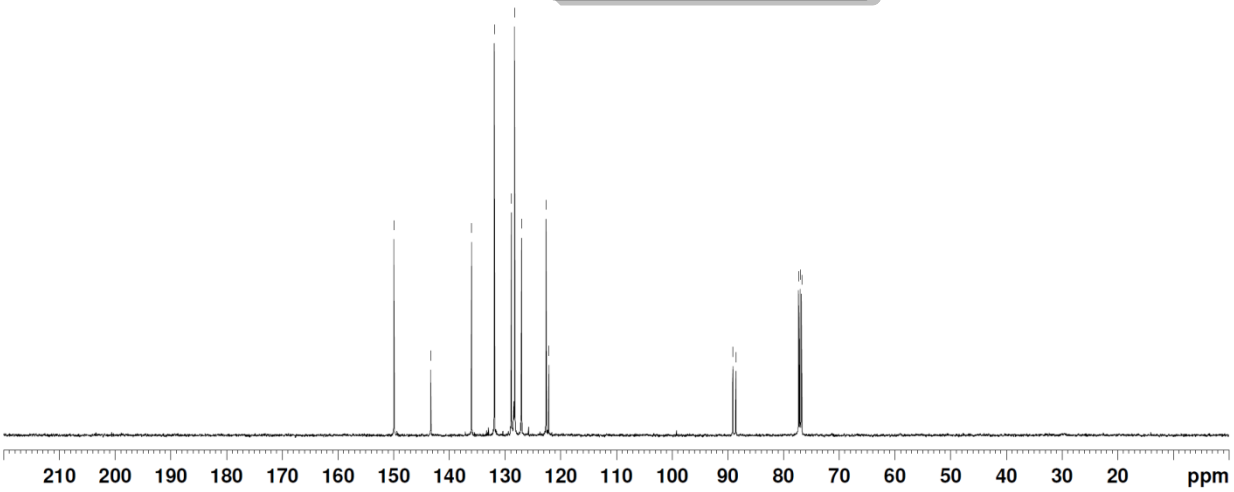
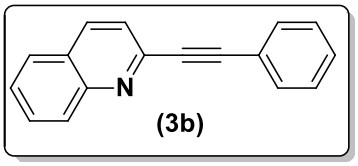
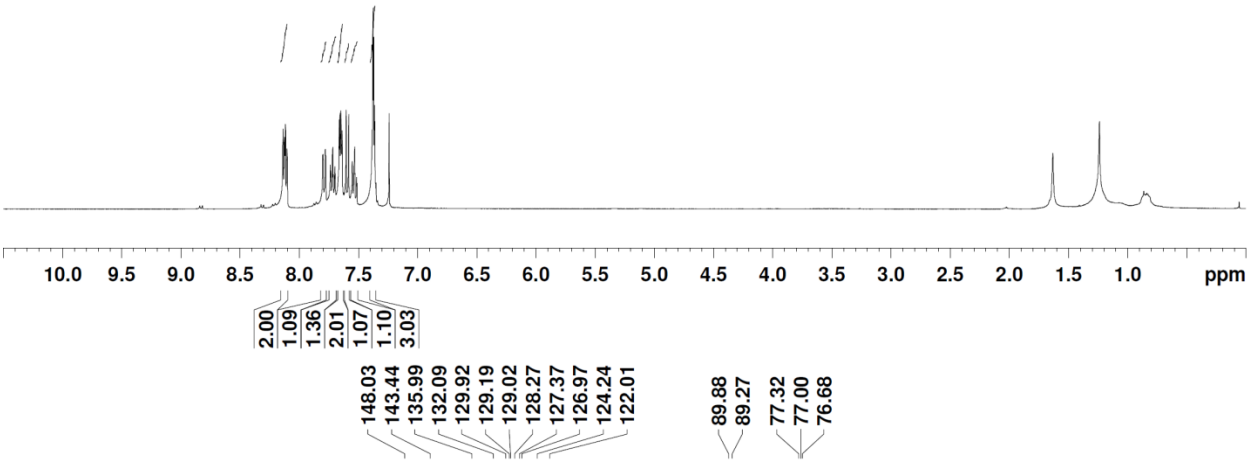
122.13
89.08
88.53
77.25
77.00
76.74


N
(3a)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.138
8.126
8.117
8.104
7.801
7.781
7.738
7.735
7.721
7.718
7.714
7.700
7.696
7.662
7.657
7.649
7.644
7.641
7.638
7.604
7.583
7.553
7.551
7.536
7.533
7.530
7.516
7.378
7.373
7.365
7.365
7.240


N
(3b)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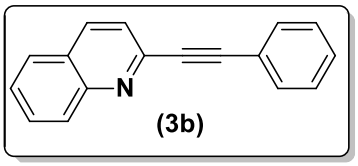
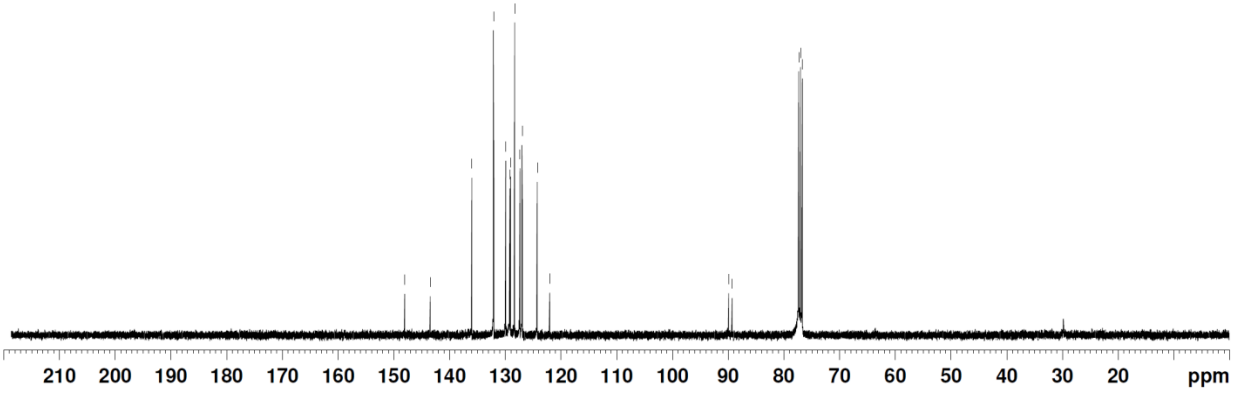
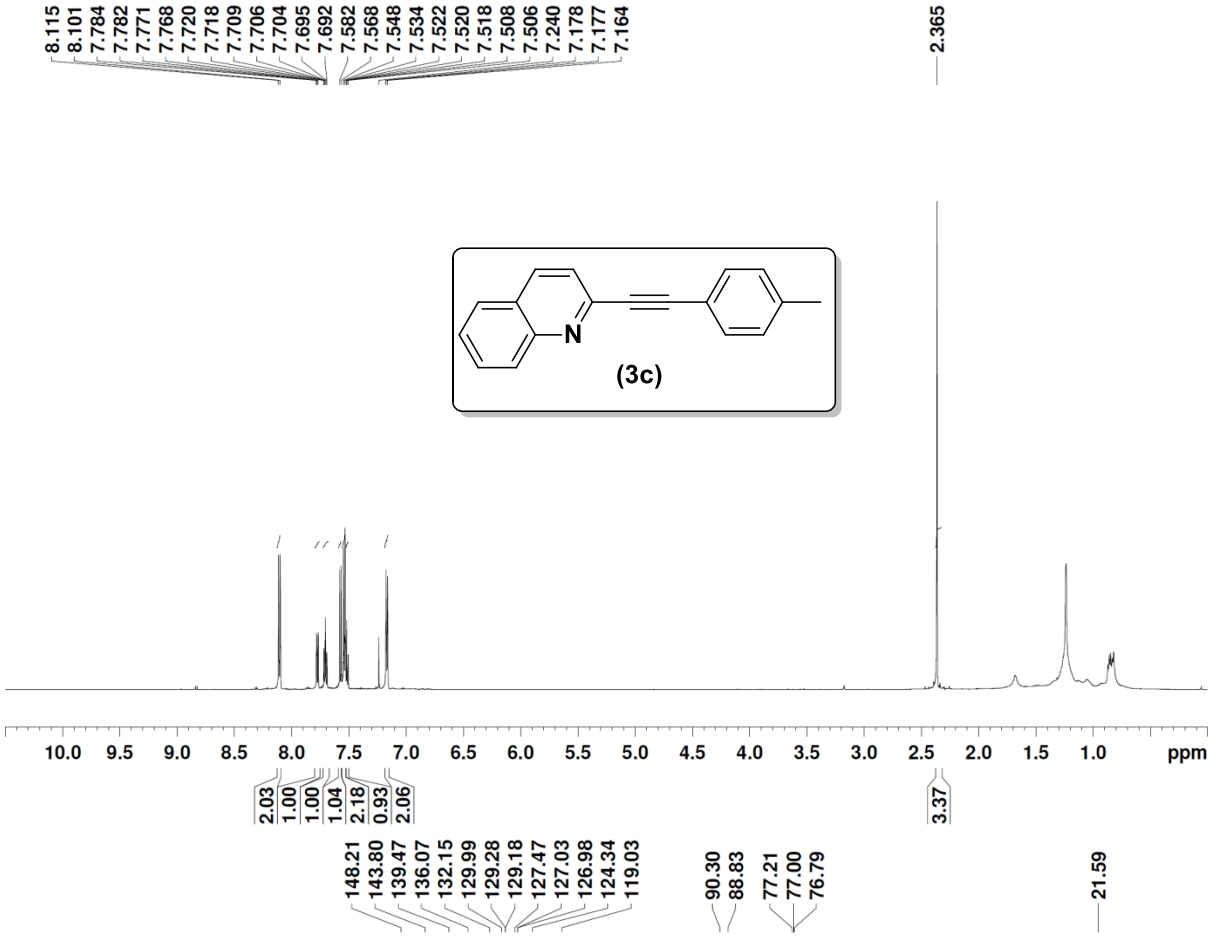
2.00
1.09
1.36
2.01
1.07
1.10
3.03
148.03
143.44
135.99
132.09
129.92
129.19
129.02
128.27
127.37
126.97
124.24
122.01
89.88
89.27
77.32
77.00
76.68


N
(3b)


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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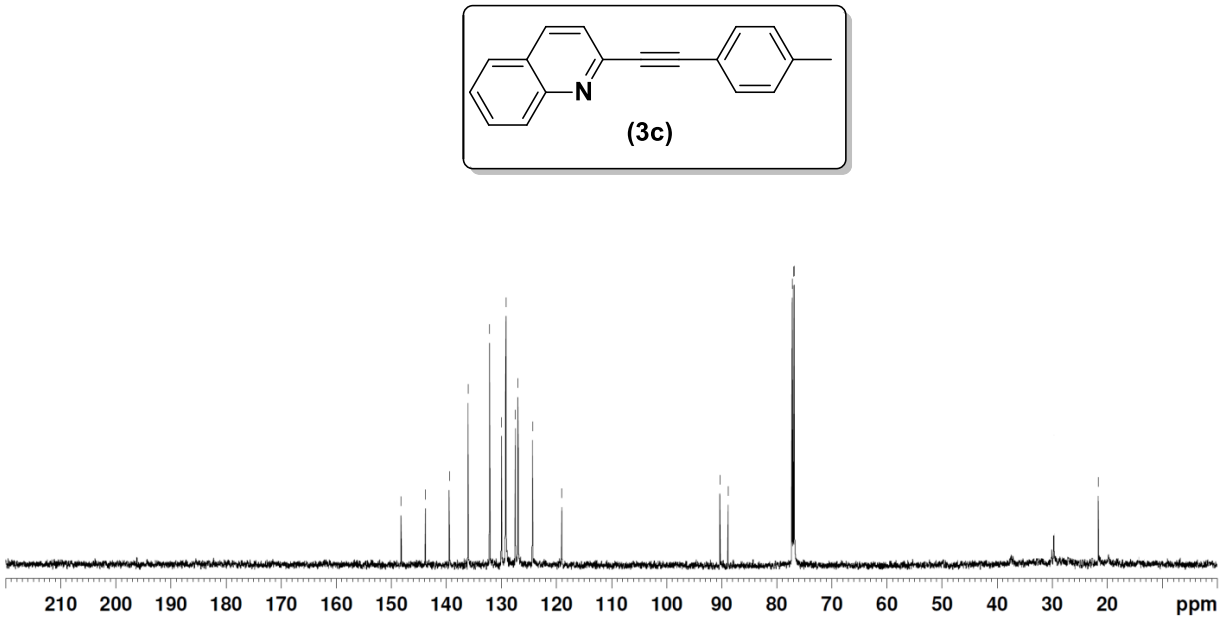
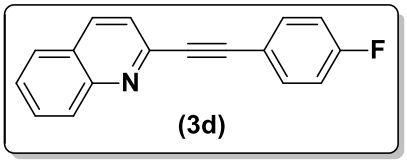
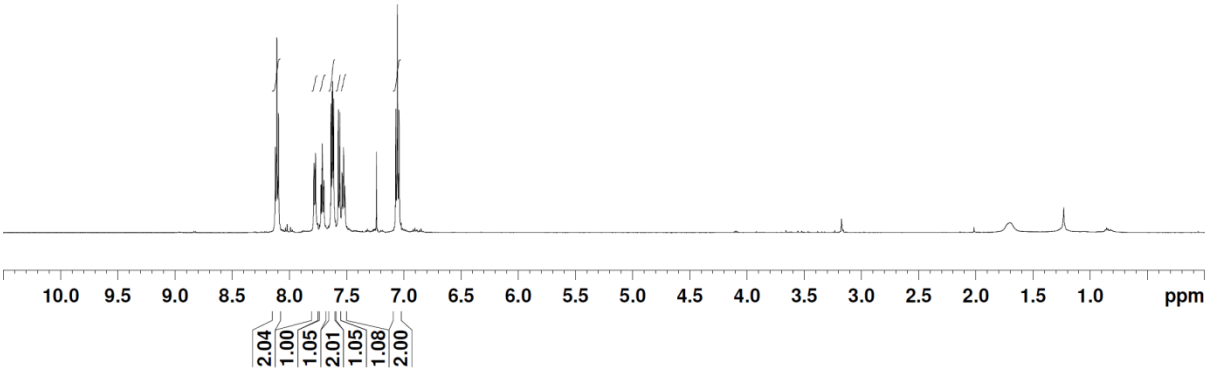
8.101
7.784
7.782
7.771
7.768
7.720
7.718
7.709
7.706
7.704
7.695
7.692
7.582
7.568
7.548
7.534
7.522
7.520
7.518
7.508
7.506
7.240
7.178
7.177
7.164
2.365
N
(3c)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.03
1.00
1.00
1.04
2.18
0.93
2.06
3.37
148.21
143.80
139.47
136.07
132.15
129.99
129.28
129.18
127.47
127.03
126.98
124.34
119.03
90.30
88.83
77.21
77.00
76.79
21.59

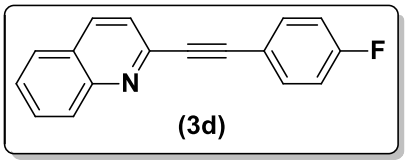

N
(3c)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

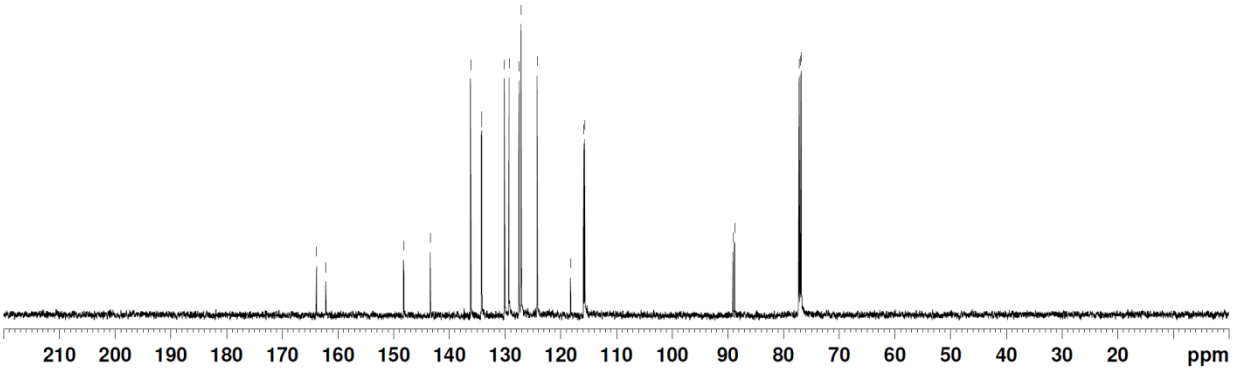

8.124
8.110
8.097
7.786
7.772
7.726
7.724
7.715
7.712
7.701
7.698
7.637
7.628
7.622
7.613
7.574
7.559
7.541
7.528
7.515
7.240
7.071
7.056
7.042

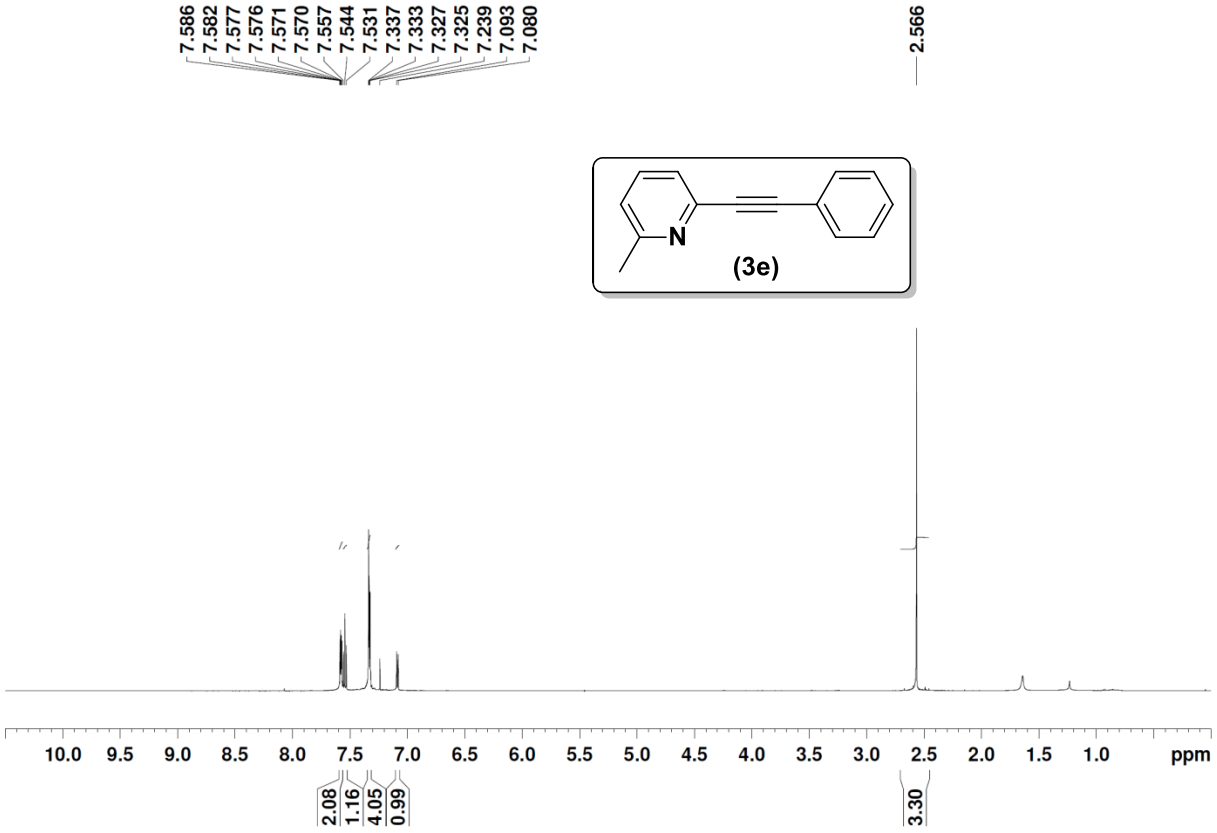

F
N
(3d)


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 ppm
2.04
1.00
1.05
2.01
1.05
1.08
2.00


163.86
162.19
148.20
143.42
136.17
134.24
134.18
130.09
129.29
127.49
127.14
124.23
118.23
115.86
115.71
89.06
88.77
77.21
77.00
76.79


F
N
(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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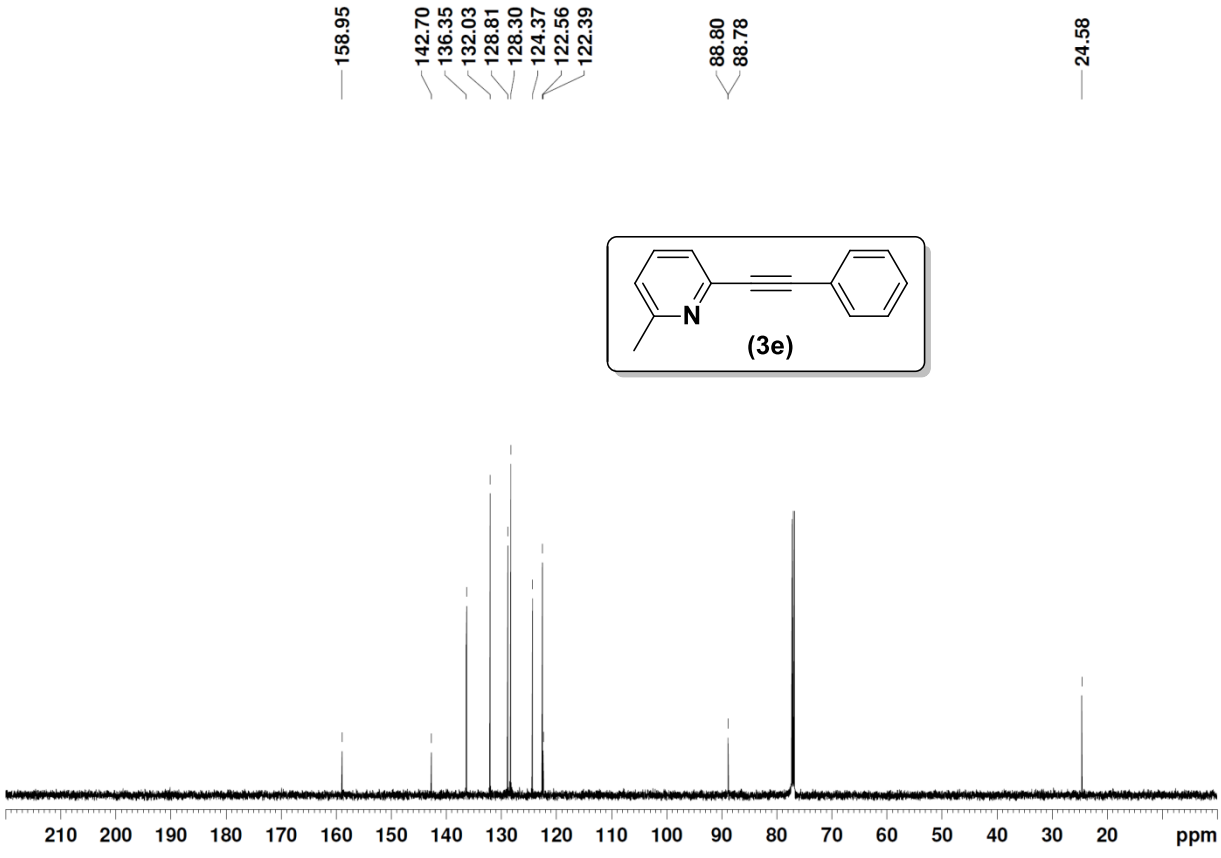
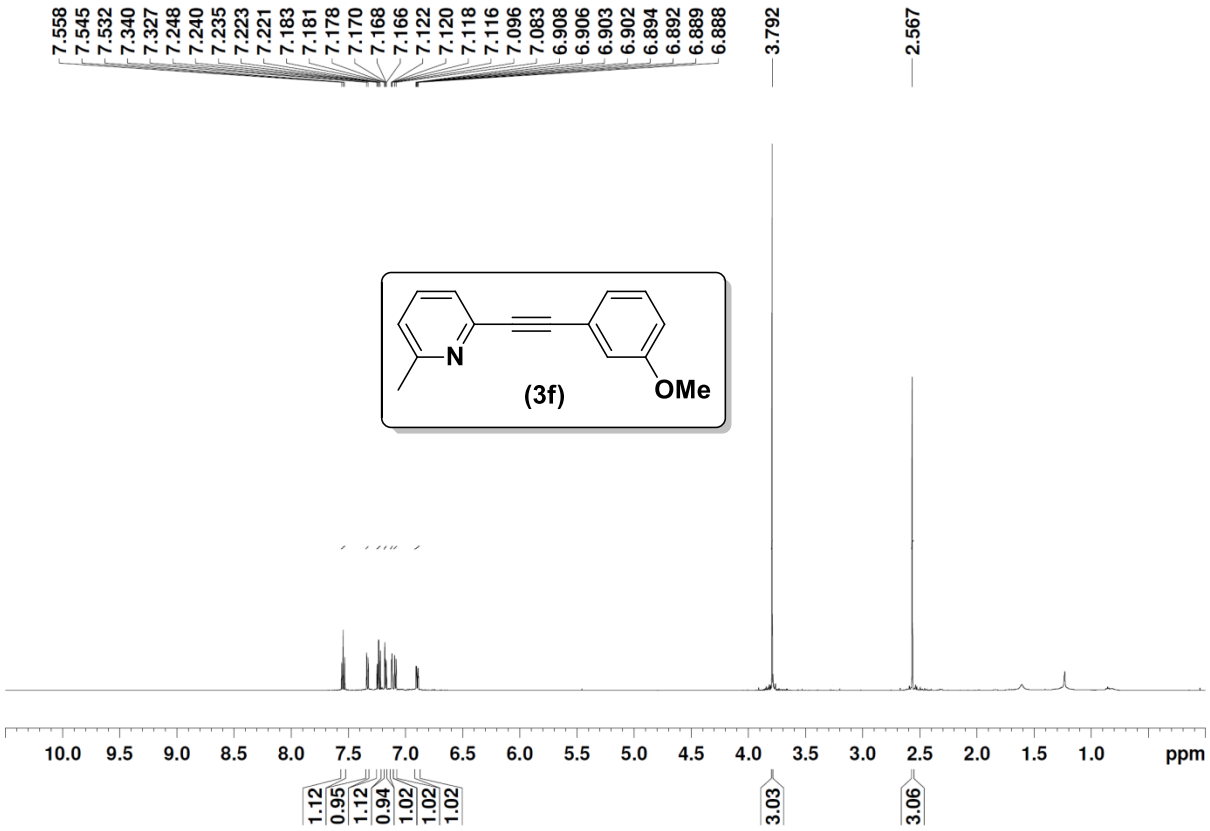
7.582
7.577
7.576
7.571
7.570
7.557
7.544
7.531
7.337
7.333
7.327
7.325
7.239
7.093
7.080
2.566
N
(3e)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.08
1.16
4.05
0.99
3.30


158.95
142.70
136.35
132.03
128.81
128.30
124.37
122.56
122.39
88.80
88.78
24.58
N
(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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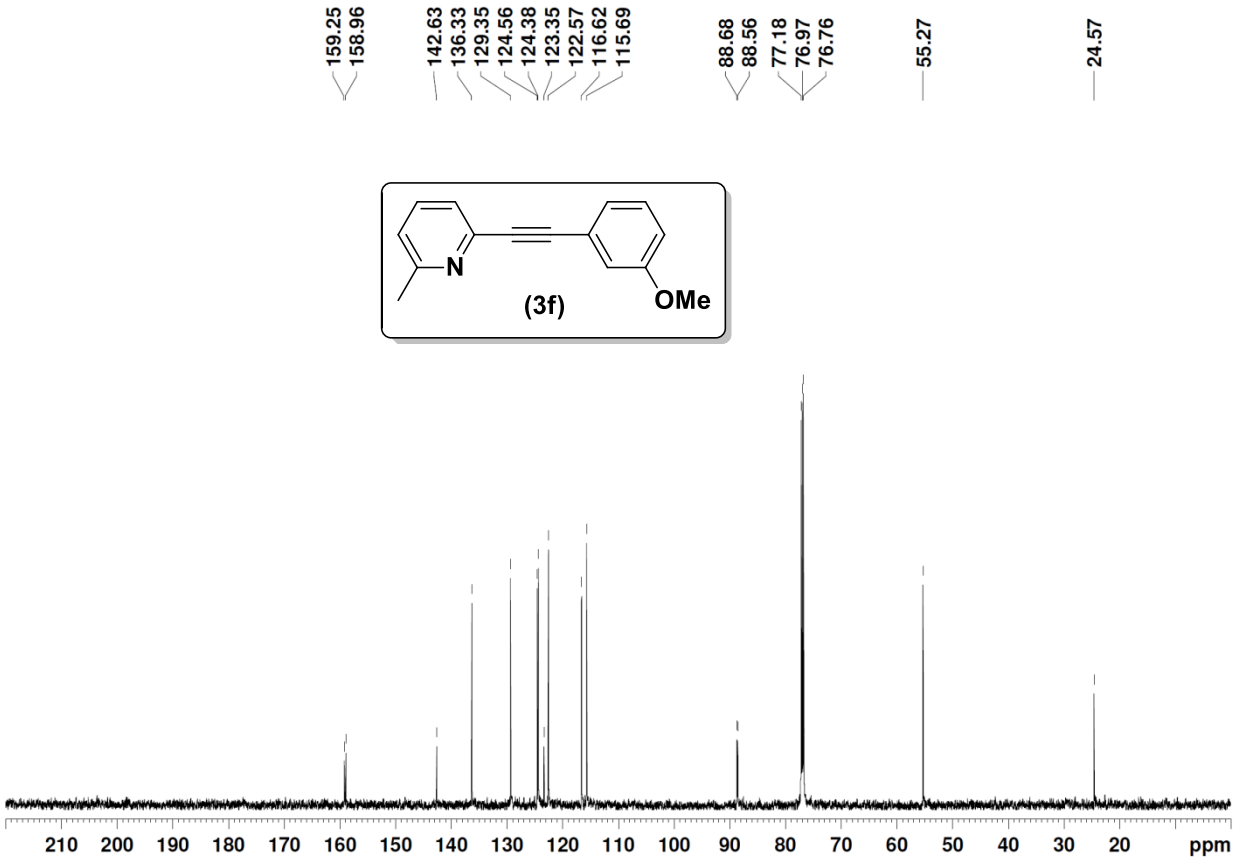
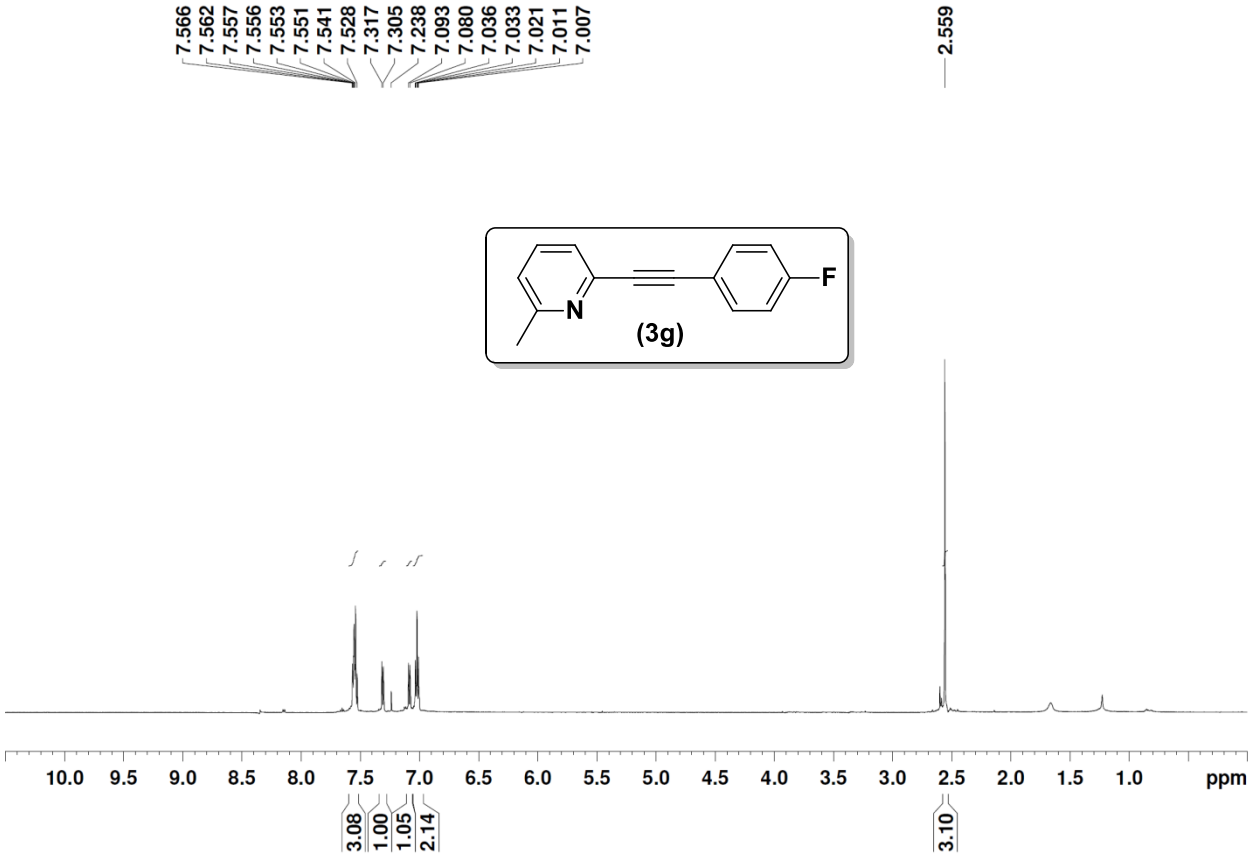
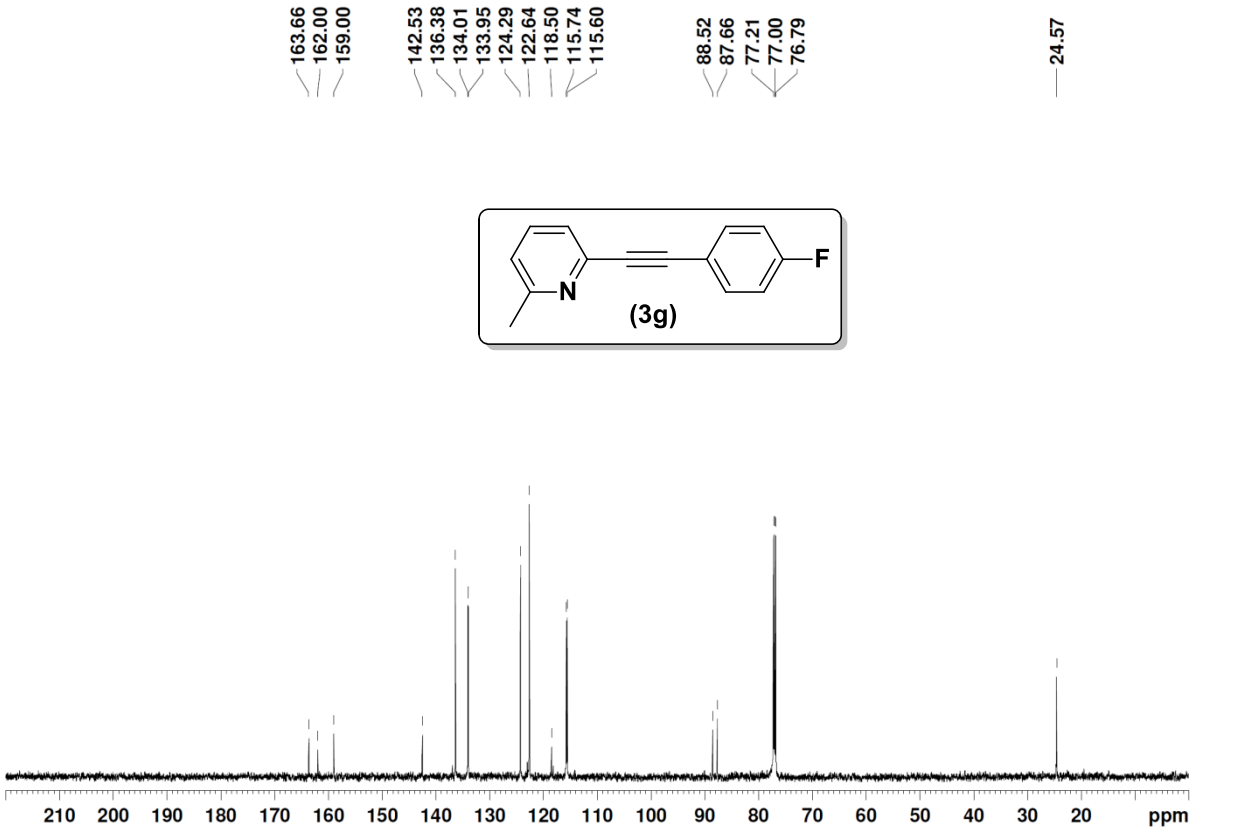
7.545
7.532
7.340
7.327
7.248
7.240
7.235
7.223
7.221
7.183
7.181
7.178
7.170
7.168
7.166
7.122
7.120
7.118
7.116
7.096
7.083
6.908
6.906
6.903
6.902
6.894
6.892
6.889
6.888
3.792
2.567
N
(3f)
OMe
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.12
0.95
1.12
0.94
1.02
1.02
1.02
3.03
3.06


159.25
158.96
142.63
136.33
129.35
124.56
124.38
123.35
122.57
116.62
115.69
88.68
88.56
77.18
76.97
76.76
55.27
24.57
N
(3f)
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.566
7.562
7.557
7.556
7.553
7.551
7.541
7.528
7.317
7.305
7.238
7.093
7.080
7.036
7.033
7.021
7.011
7.007
2.559
F
N
(3g)
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 ppm
3.08
1.00
1.05
2.14
3.10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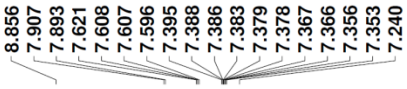
162.00
159.00
142.53
136.38
134.01
133.95
124.29
122.64
118.50
115.74
115.60
88.52
87.66
77.21
77.00
76.79
24.57
F
N
(3g)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.621
7.608
7.607
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7.388
7.386
7.383
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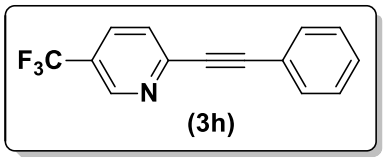
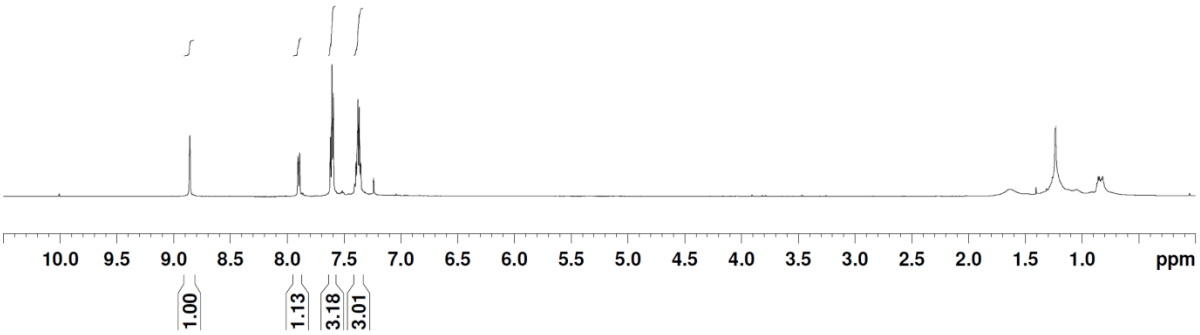
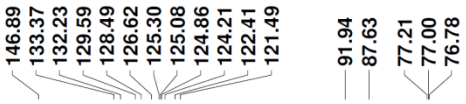
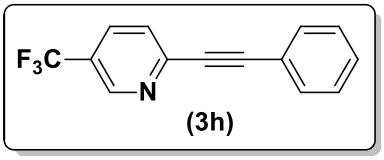
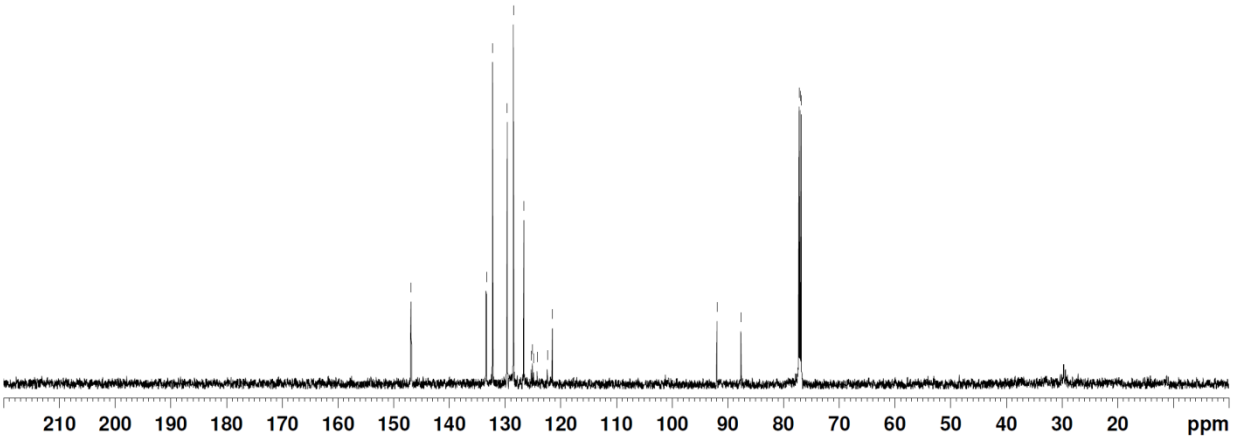
7.378
7.367
7.366
7.356
7.353
7.240

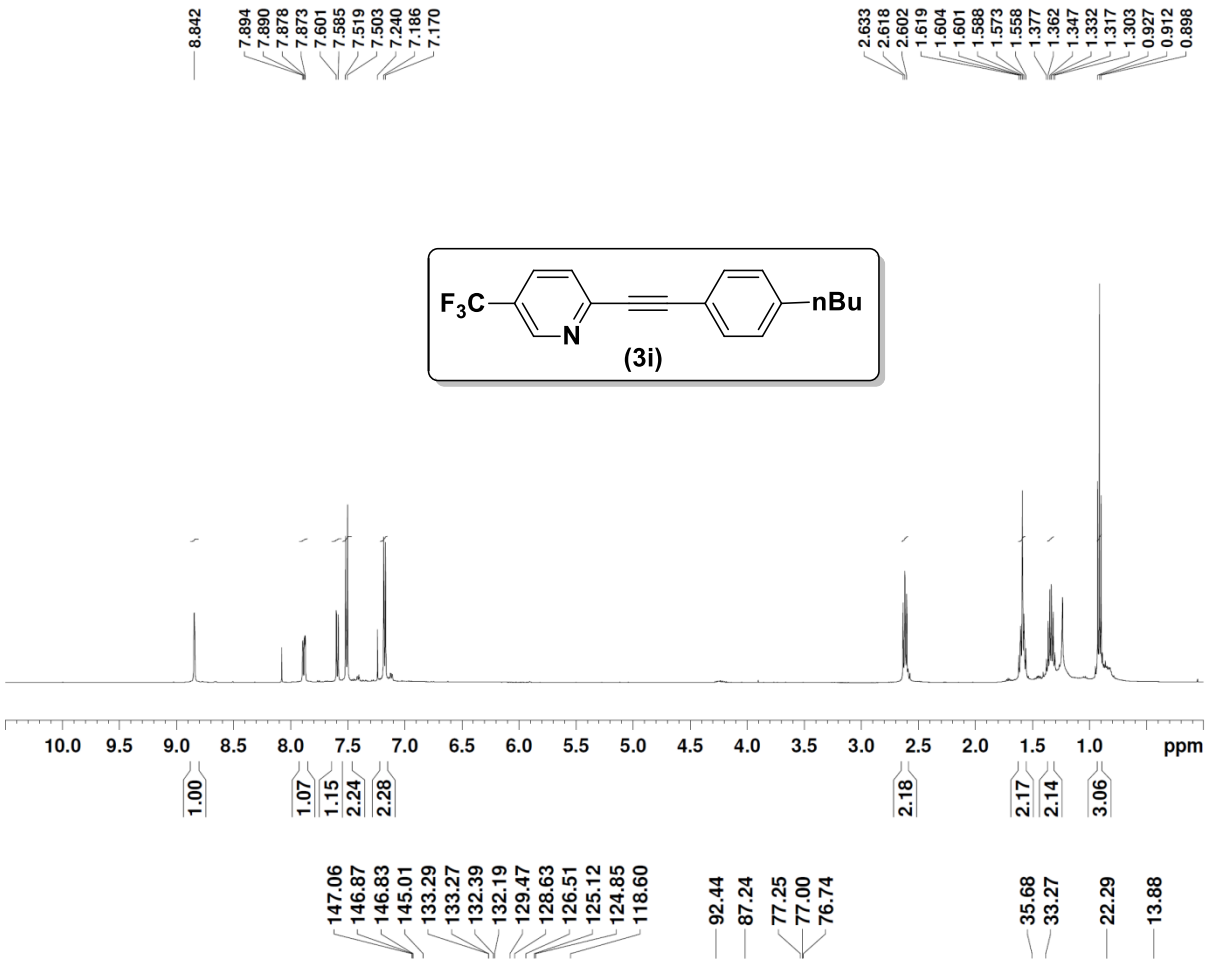

F3C
N
(3h)


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 ppm
1.00
1.13
3.18
3.01


146.89
133.37
132.23
129.59
128.49
126.62
125.30
125.08
124.86
124.21
122.41
121.49
91.94
87.63
77.21
77.00
76.78


F3C
N
(3h)


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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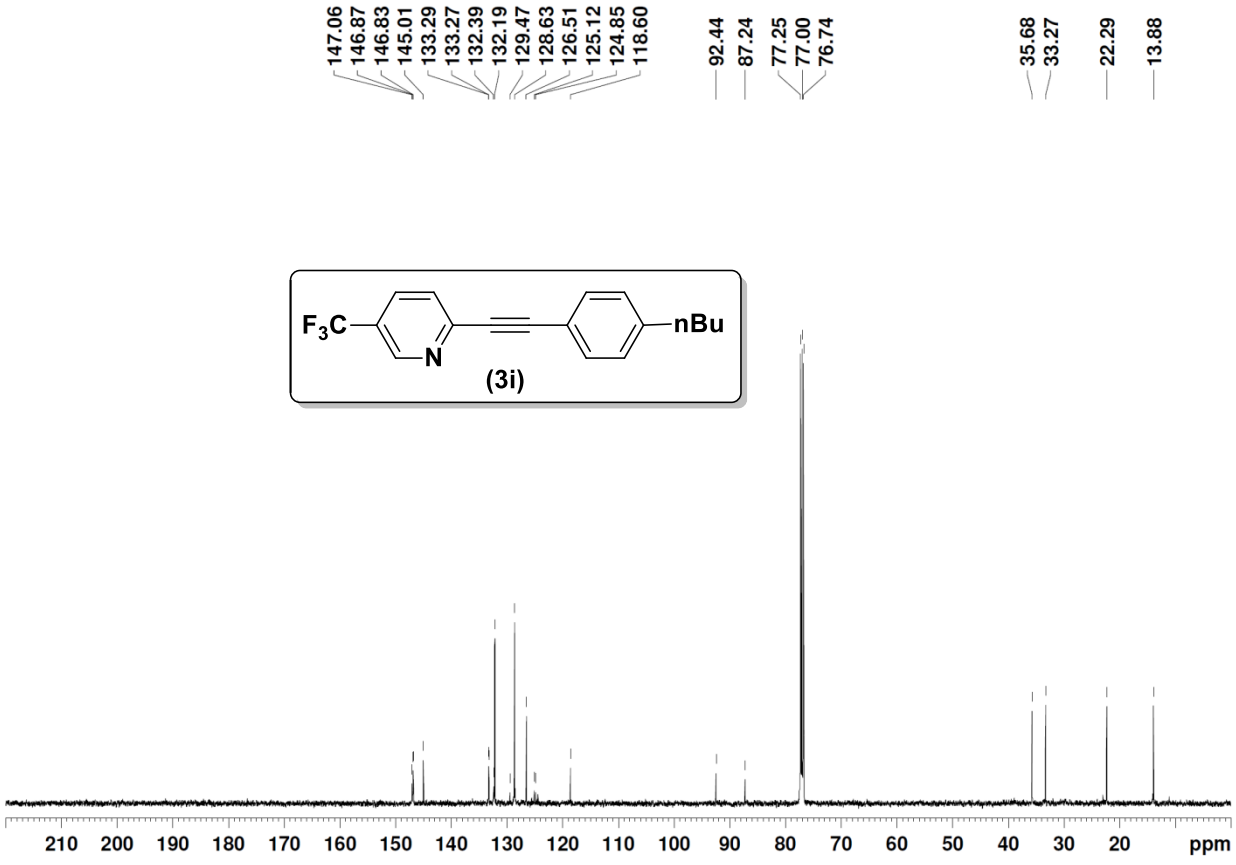
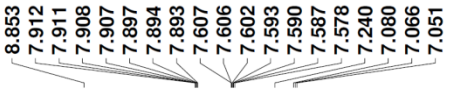
7.894
7.890
7.878
7.873
7.601
7.585
7.519
7.503
7.240
7.186
7.170
2.633
2.618
2.602
1.619
1.604
1.601
1.588
1.573
1.558
1.377
1.362
1.347
1.332
1.317
1.303
0.927
0.912
0.898
F3C
N
nBu
(3i)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.07
1.15
2.24
2.28
2.18
2.17
2.14
3.06


147.06
146.87
146.83
145.01
133.29
133.27
132.39
132.19
129.47
128.63
126.51
125.12
124.85
118.60
92.44
87.24
77.25
77.00
76.74
35.68
33.27
22.29
13.88
F3C
N
nBu
(3i)
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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7.911
7.908
7.907
7.897
7.894
7.893
7.607
7.606
7.602
7.593
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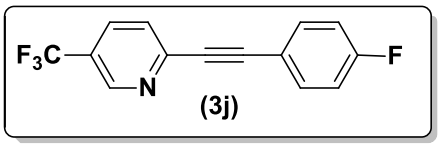
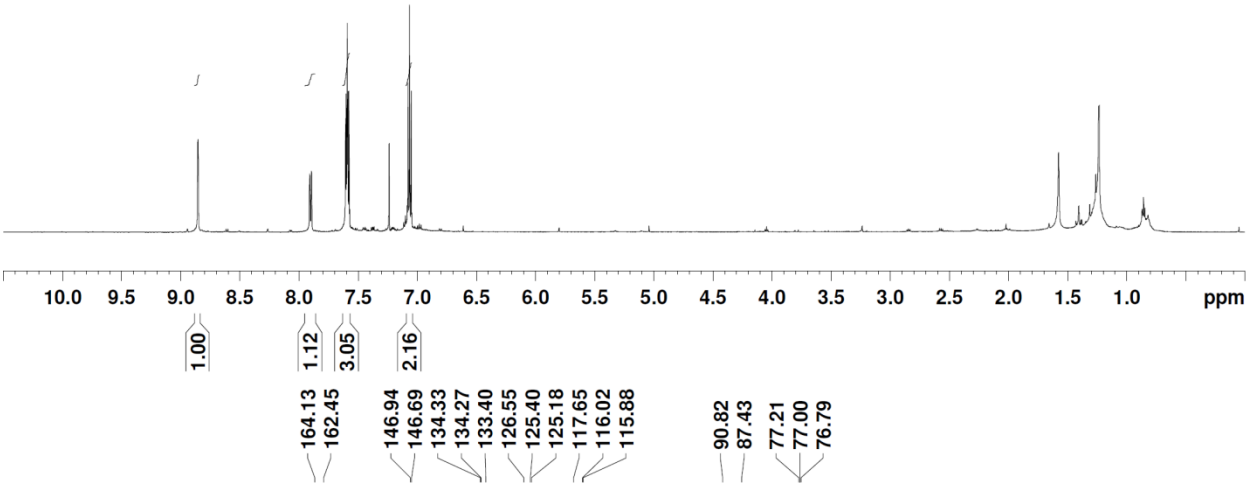
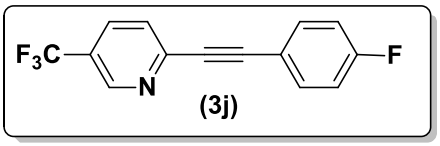
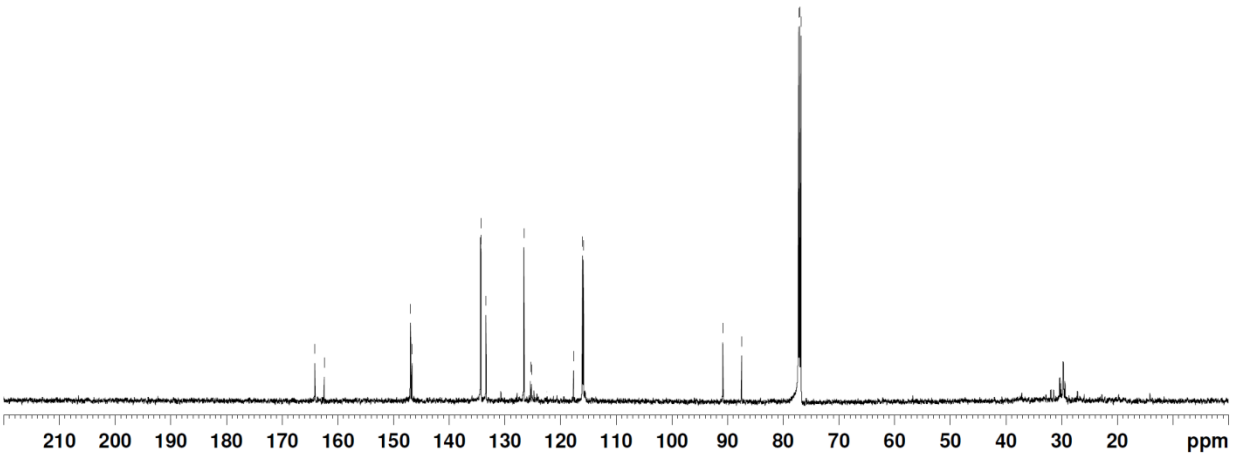
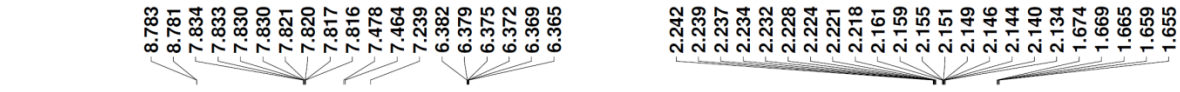
7.587
7.578
7.240
7.080
7.066
7.051

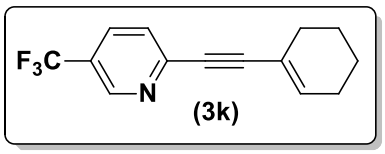

F3C
N
F
(3j)

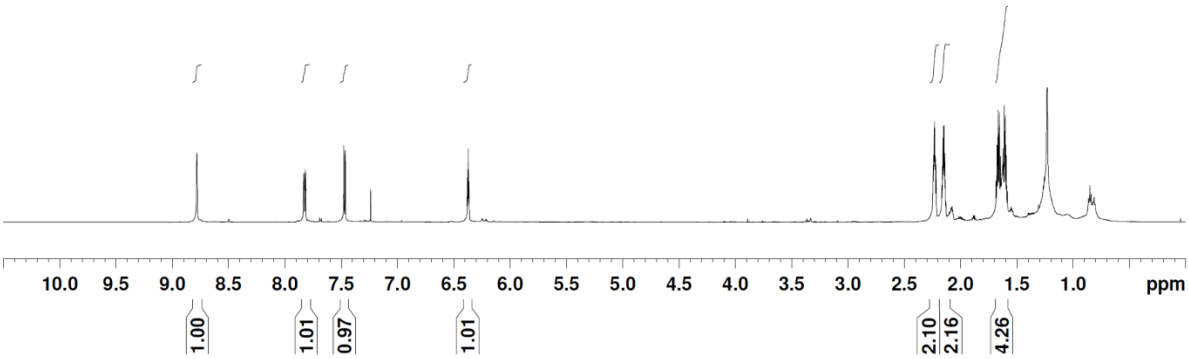

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.12
3.05
2.16
164.13
162.45
146.94
146.69
134.33
134.27
133.40
126.55
125.40
125.18
117.65
116.02
115.88
90.82
87.43
77.21
77.00
76.79

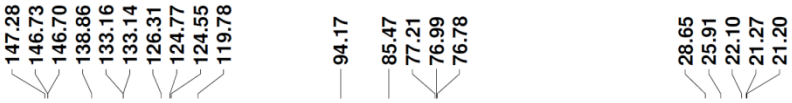

F3C
N
F
(3j)

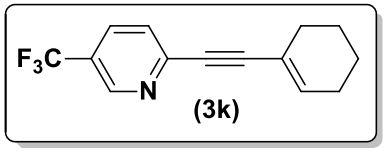

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

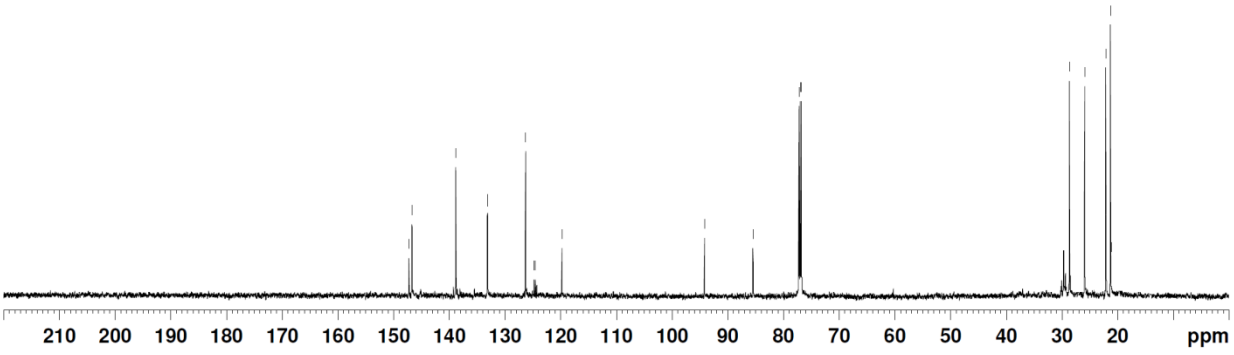

8.783
8.781
7.834
7.833
7.830
7.830
7.821
7.820
7.817
7.816
7.478
7.464
7.239
6.382
6.379
6.375
6.372
6.369
6.365
2.242
2.239
2.237
2.234
2.232
2.228
2.224
2.221
2.218
2.161
2.159
2.155
2.151
2.149
2.146
2.144
2.140
2.134
1.674
1.669
1.665
1.659
1.655


F3C
N
(3k)

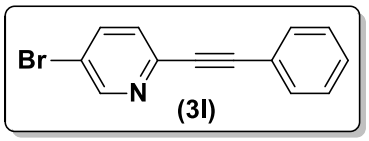

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.01
0.97
1.01
2.10
2.16
4.26

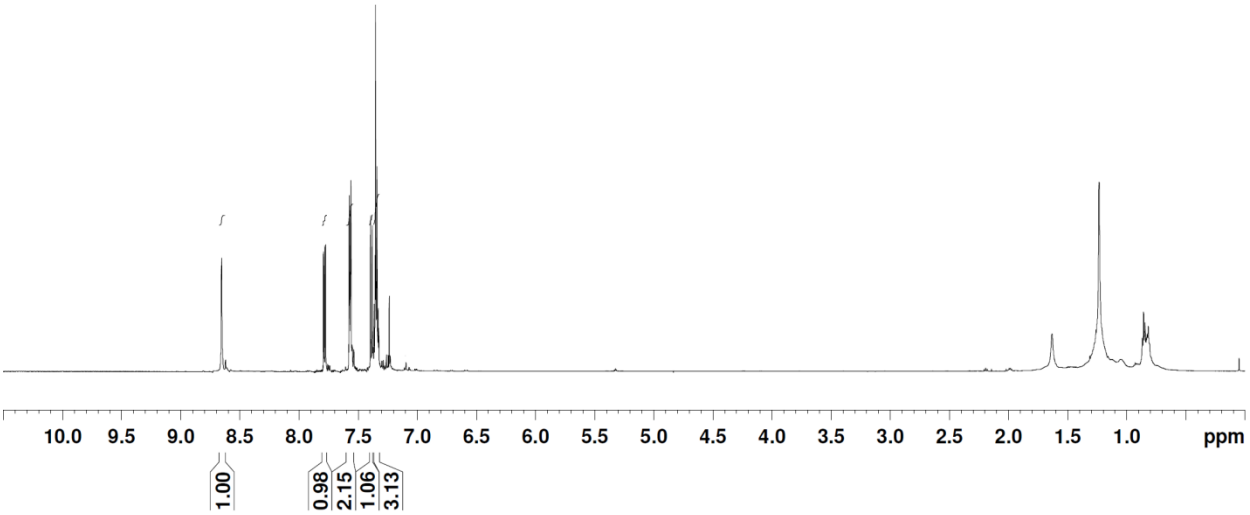

147.28
146.73
146.70
138.86
133.16
133.14
126.31
124.77
124.55
119.78
94.17
85.47
77.21
76.99
76.78
28.65
25.91
22.10
21.27
21.20

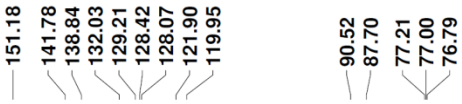

F3C
N
(3k)

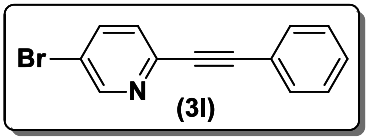

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

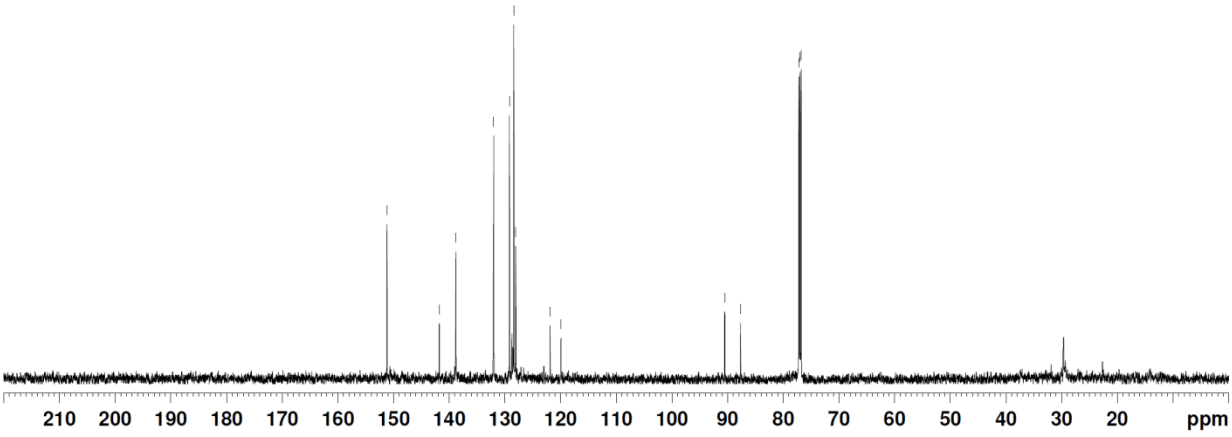

8.655
8.651
7.796
7.792
7.782
7.778
7.577
7.575
7.565
7.562
7.396
7.382
7.366
7.364
7.357
7.354
7.351
7.347
7.344
7.341
7.331
7.239

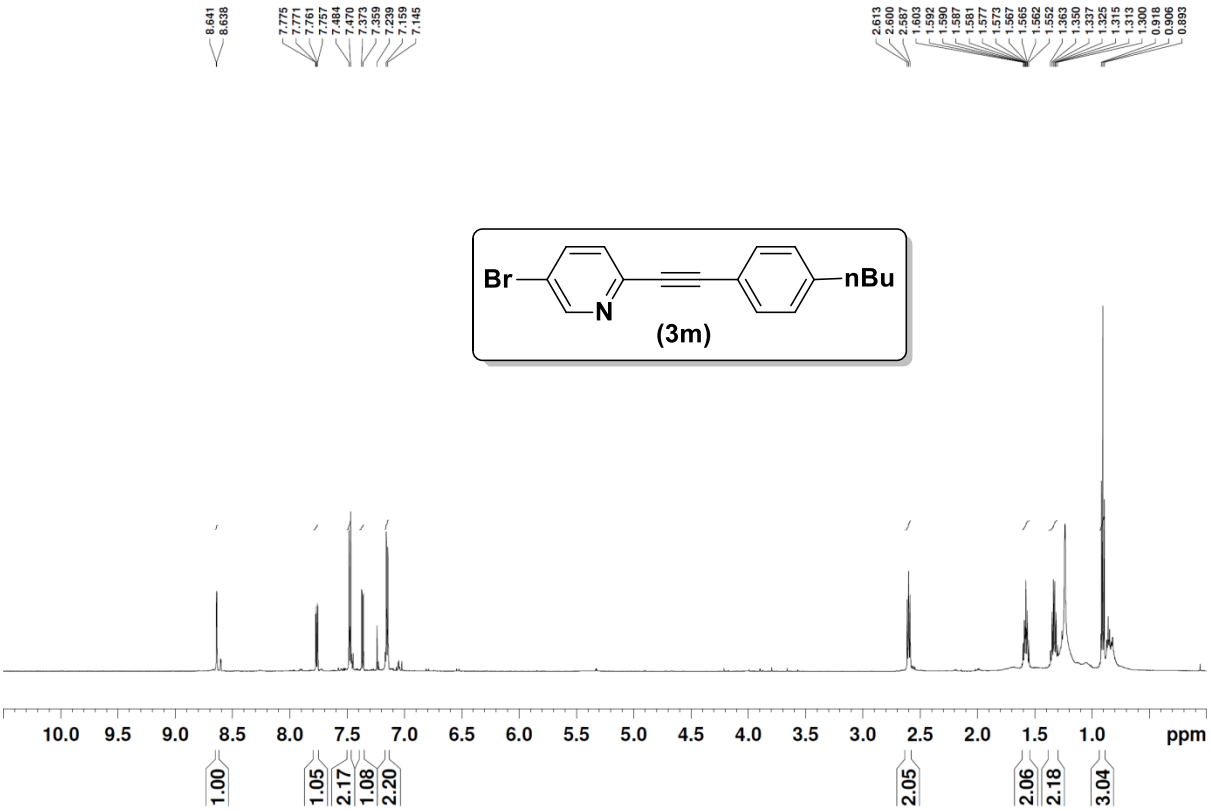

Br
N
(3l)

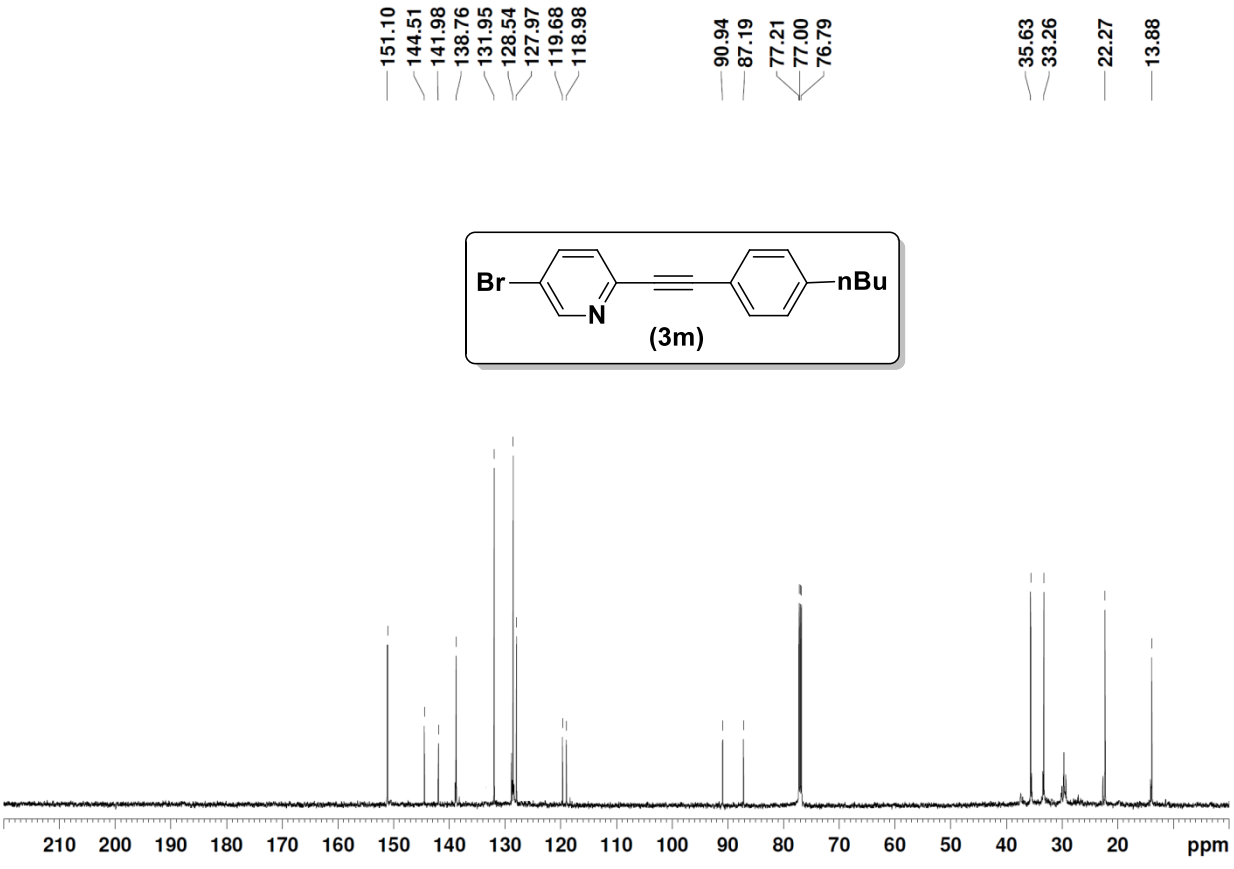

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
0.98
2.15
1.06
3.13

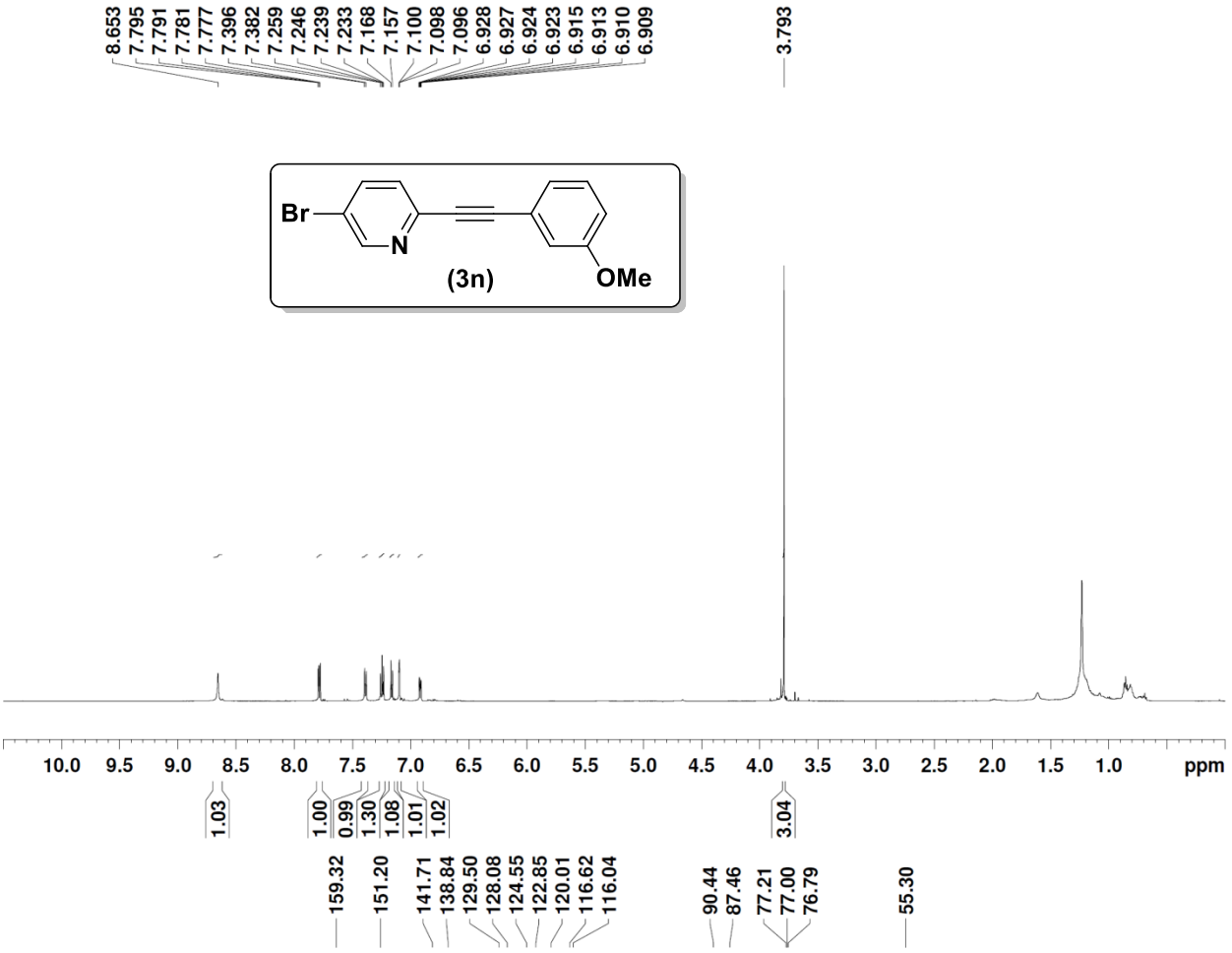

151.18
141.78
138.84
132.03
129.21
128.42
128.07
121.90
119.95
90.52
87.70
77.21
77.00
76.79

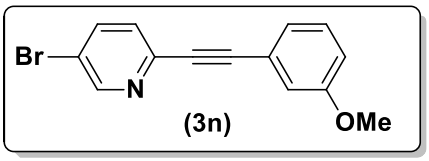

Br
N
(3l)

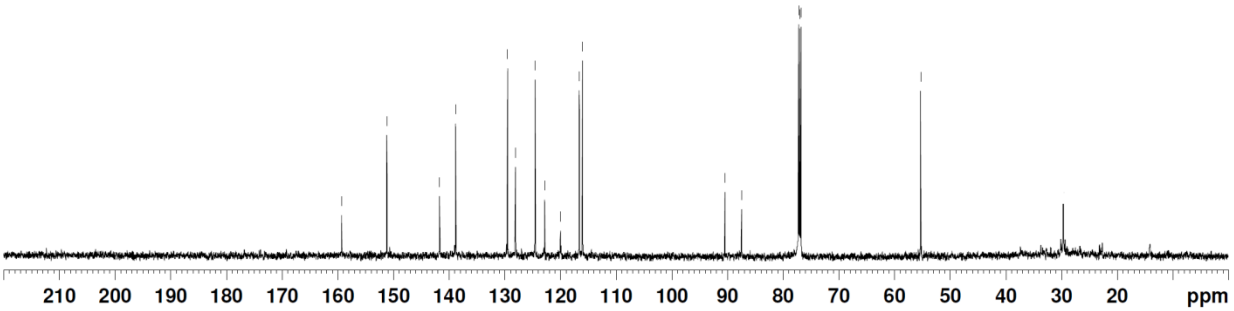

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.641
8.638
7.775
7.771
7.761
7.757
7.484
7.470
7.373
7.359
7.239
7.159
7.145
2.613
2.600
2.587
1.603
1.592
1.590
1.587
1.581
1.577
1.573
1.567
1.565
1.562
1.552
1.363
1.350
1.337
1.325
1.315
1.313
1.300
0.916
0.906
0.893
Br
N
nBu
(3m)
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 ppm
1.00
1.05
2.17
1.08
2.20
2.05
2.06
2.18
3.04

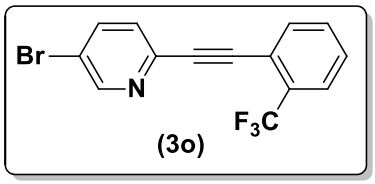

151.10
144.51
141.98
138.76
131.95
128.54
127.97
119.68
118.98
90.94
87.19
77.21
77.00
76.79
35.63
33.26
22.27
13.88
Br
N
nBu
(3m)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

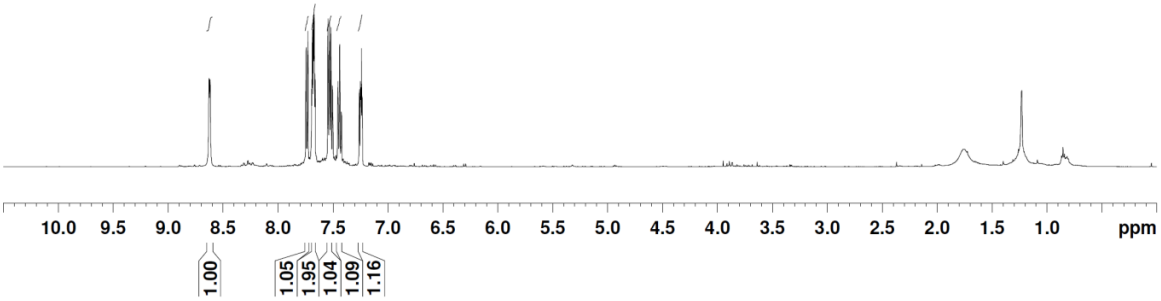

8.653
7.795
7.791
7.781
7.777
7.396
7.382
7.259
7.246
7.239
7.233
7.168
7.157
7.100
7.098
7.096
6.928
6.927
6.924
6.923
6.915
6.913
6.910
6.909
3.793
Br
N
(3n)
OMe
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.03
1.00
0.99
1.30
1.08
1.01
1.02
3.04
159.32
151.20
141.71
138.84
129.50
128.08
124.55
122.85
120.01
116.62
116.04
90.44
87.46
77.21
77.00
76.79
55.30

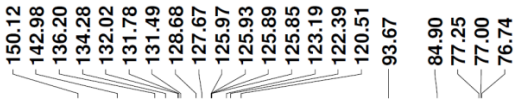

Br
N
(3n)
OMe

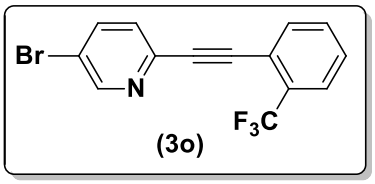

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.617
7.745
7.730
7.696
7.692
7.687
7.680
7.677
7.671
7.665
7.662
7.546
7.531
7.519
7.504
7.455
7.439
7.424
7.261
7.259
7.251
7.249
7.245
7.240
7.236

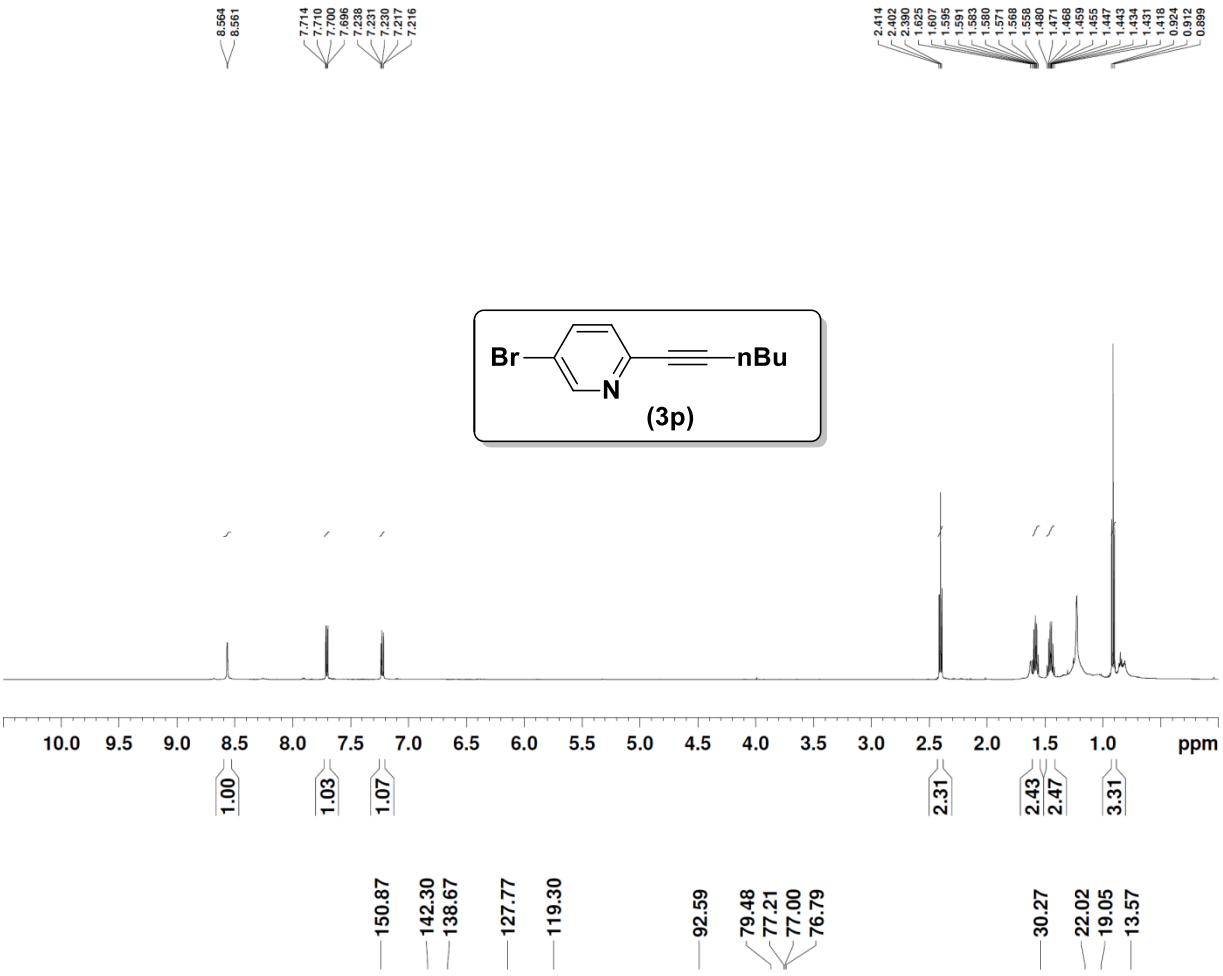

Br
N
F3C
(3o)

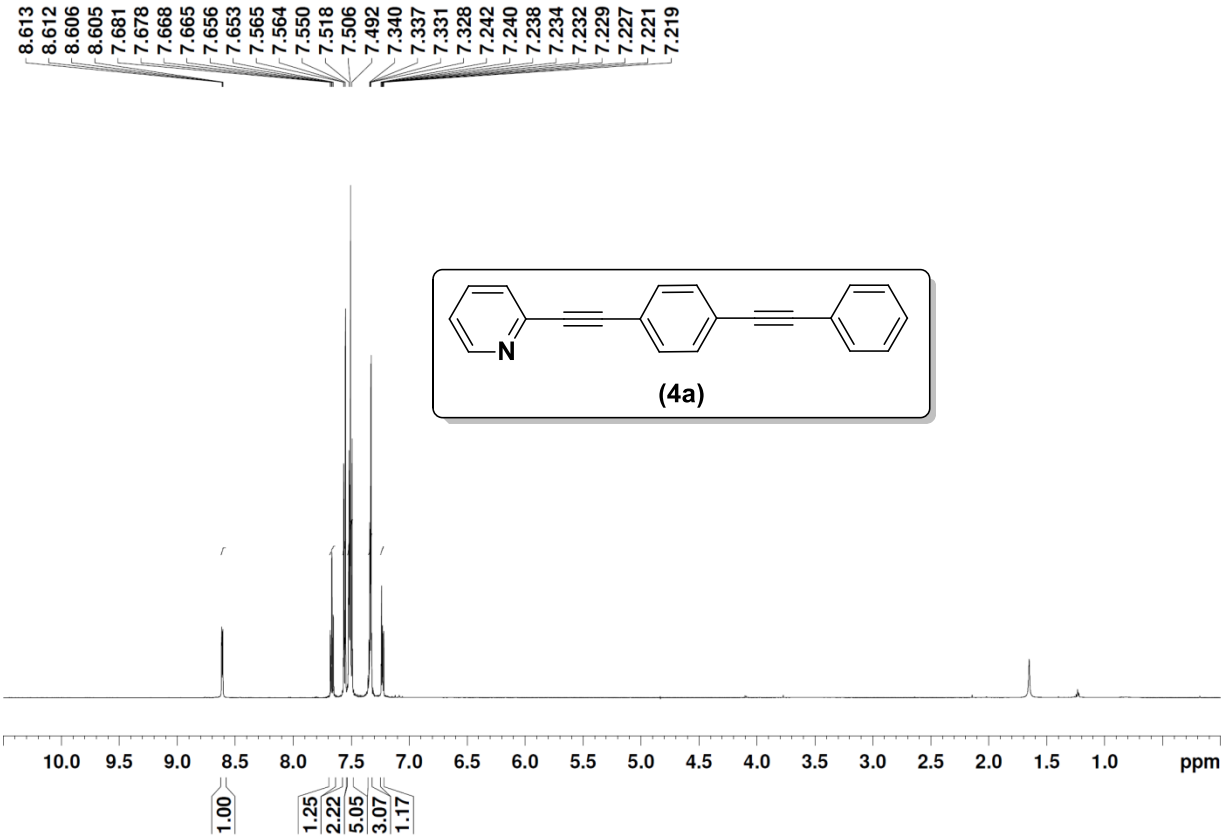

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.05
1.95
1.04
1.09
1.16

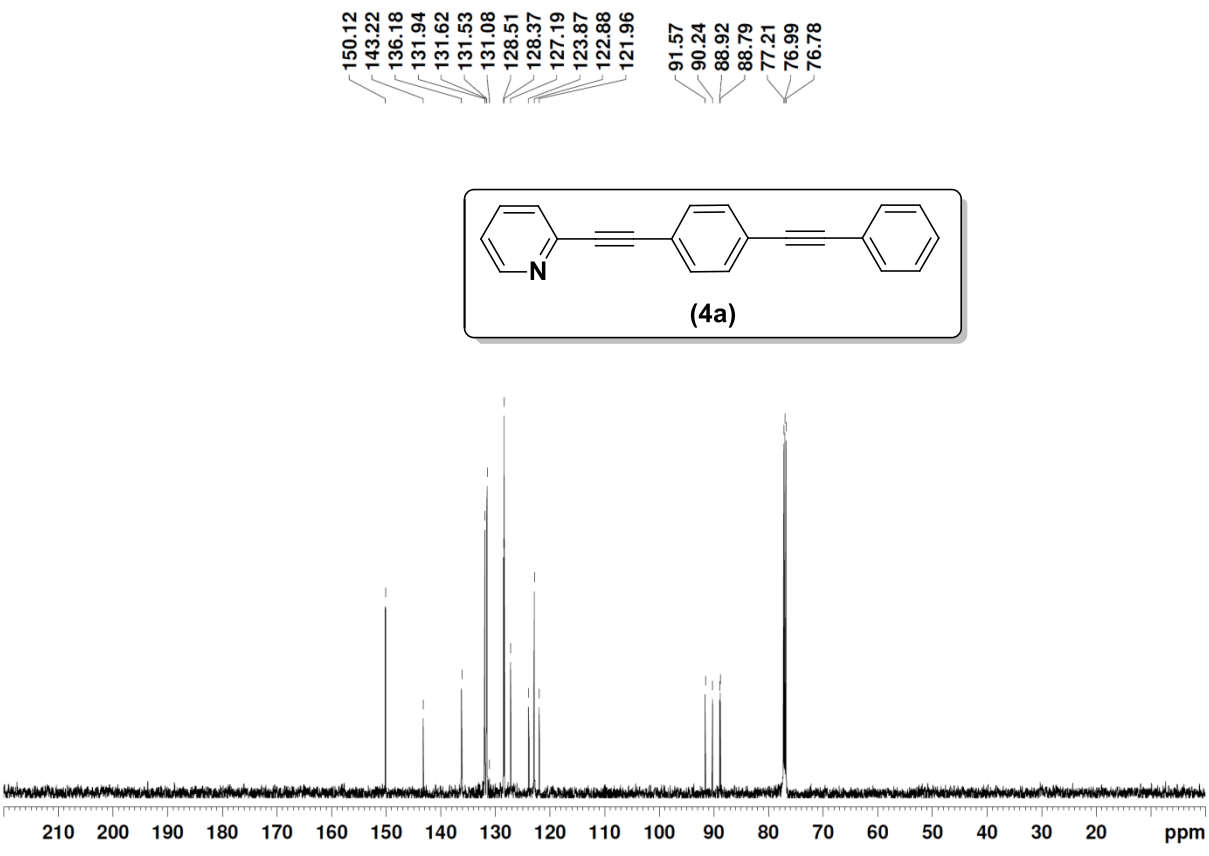

150.12
142.98
136.20
134.28
132.02
131.78
131.49
128.68
127.67
125.97
125.93
125.89
125.85
123.19
122.39
120.51
93.67
84.90
77.25
77.00
76.74

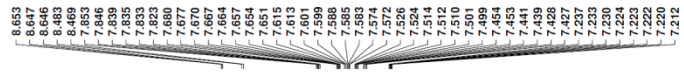

Br
N
F3C
(3o)

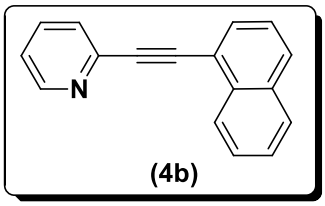
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

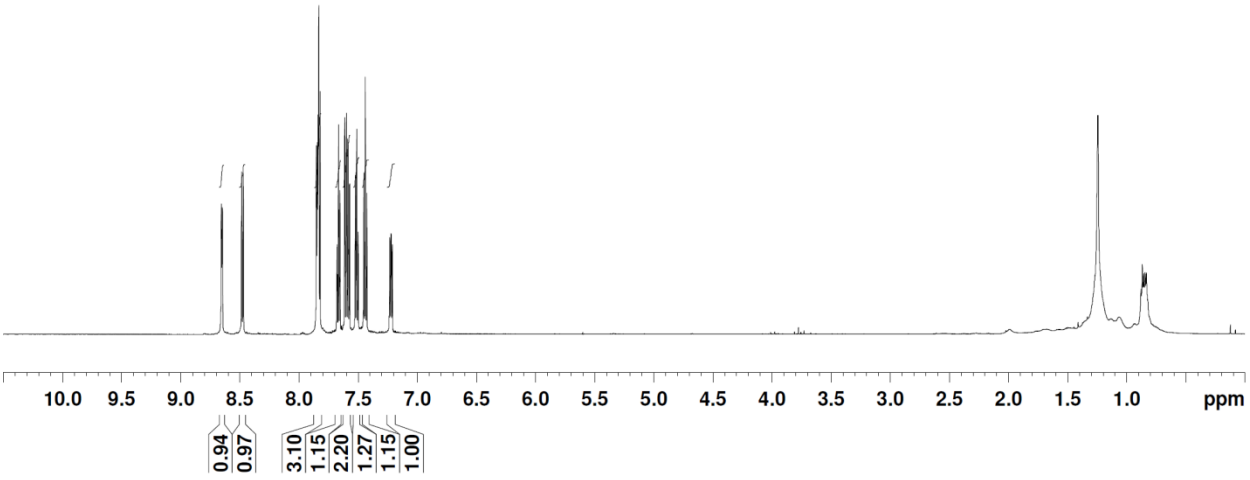

8.564
8.561
7.714
7.710
7.700
7.696
7.238
7.231
7.230
7.217
7.216
2.414
2.402
2.390
1.625
1.607
1.595
1.581
1.563
1.560
1.571
1.568
1.558
1.480
1.471
1.468
1.459
1.455
1.447
1.443
1.434
1.431
1.418
0.924
0.912
0.899
Br
N
nBu
(3p)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.03
1.07
2.31
2.43
2.47
3.31
150.87
142.30
138.67
127.77
119.30
92.59
79.48
77.21
77.00
76.79
30.27
22.02
19.05
13.57
Br
N
nBu
(3p)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

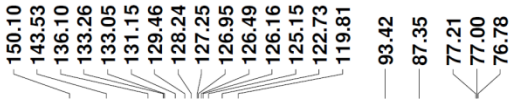

8.613
8.612
8.606
8.605
7.681
7.678
7.668
7.665
7.656
7.653
7.565
7.564
7.550
7.518
7.506
7.492
7.340
7.337
7.331
7.328
7.242
7.240
7.238
7.234
7.232
7.229
7.227
7.221
7.219
N
(4a)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.25
2.22
5.05
3.07
1.17

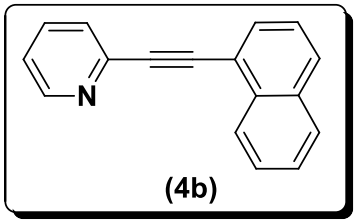

150.12
143.22
136.18
131.94
131.62
131.53
131.08
128.51
128.37
127.19
123.87
122.88
121.96
91.57
90.24
88.92
88.79
77.21
76.99
76.78
N
(4a)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

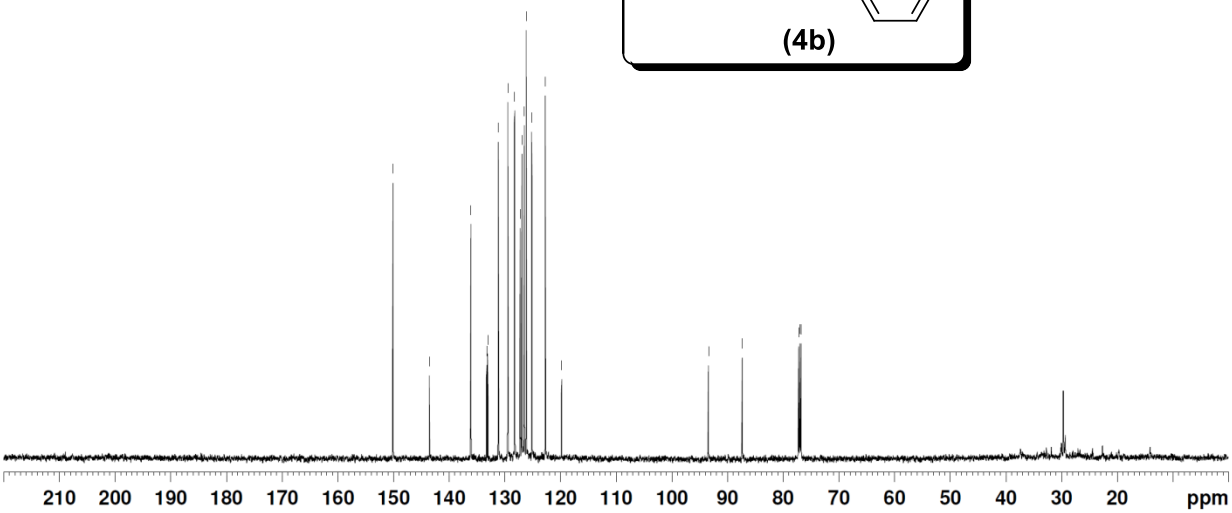

8.653
8.647
8.646
8.483
8.469
7.853
7.846
7.839
7.835
7.833
7.823
7.680
7.677
7.670
7.667
7.664
7.657
7.654
7.651
7.615
7.613
7.601
7.599
7.588
7.585
7.583
7.574
7.572
7.526
7.524
7.514
7.512
7.510
7.501
7.499
7.454
7.453
7.441
7.439
7.428
7.427
7.237
7.233
7.230
7.224
7.223
7.222
7.220
7.212

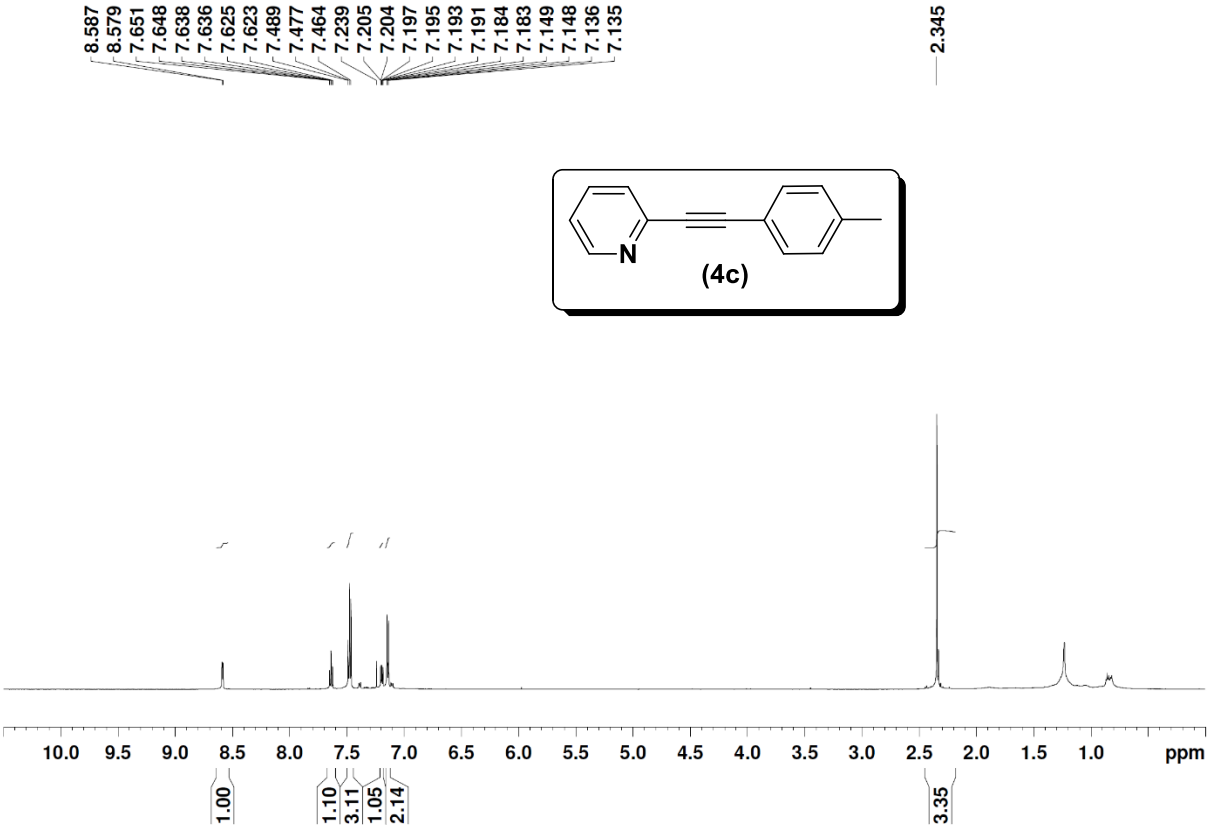

N
(4b)

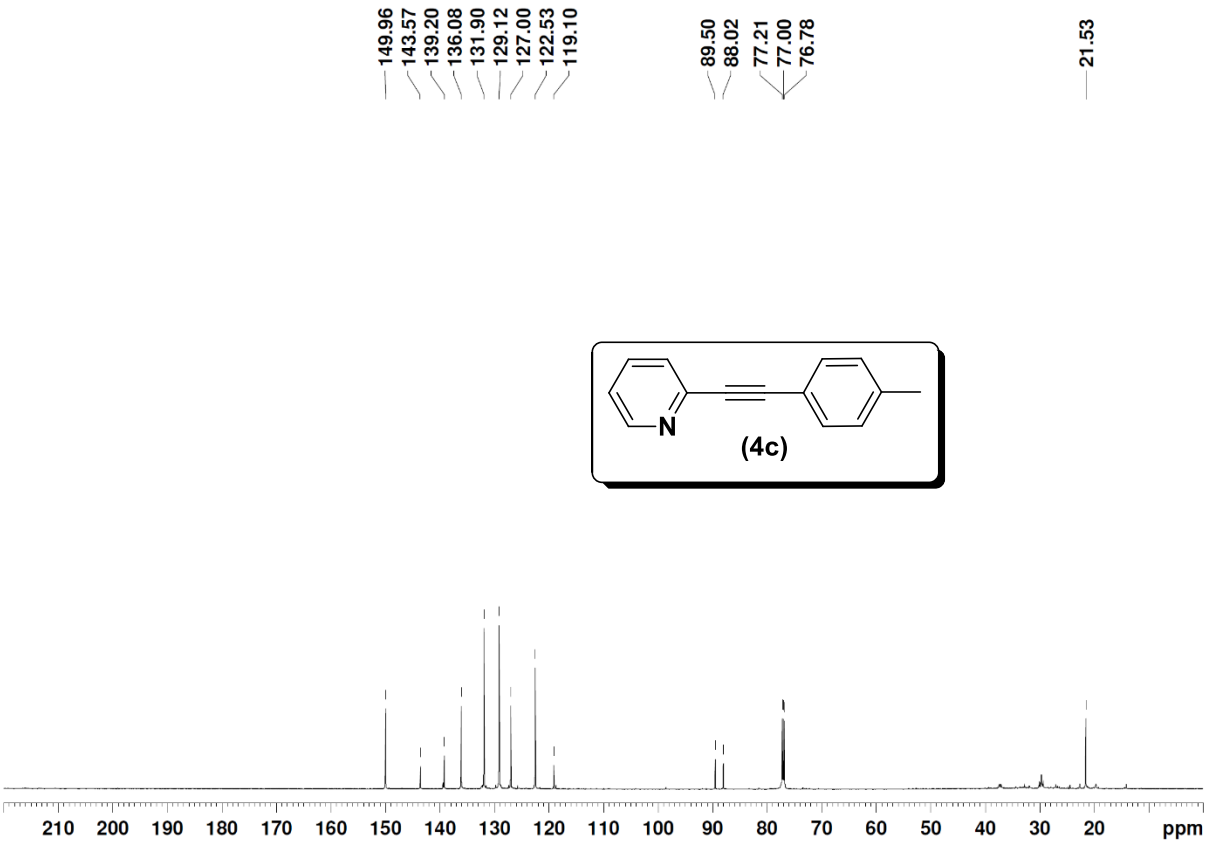

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.94
0.97
3.10
1.15
2.20
1.27
1.15
1.00

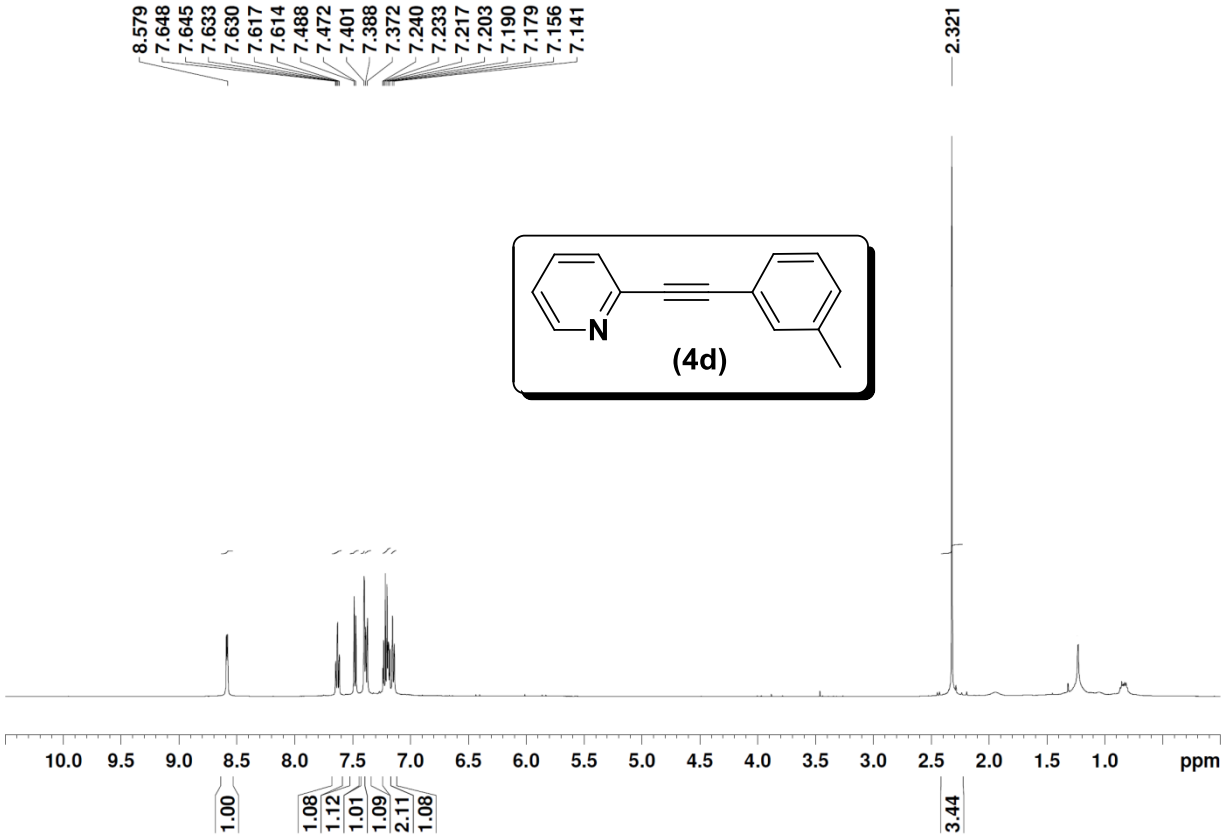

150.10
143.53
136.10
133.26
133.05
131.15
129.46
128.24
127.25
126.95
126.49
126.16
125.15
122.73
119.81
93.42
87.35
77.21
77.00
76.78

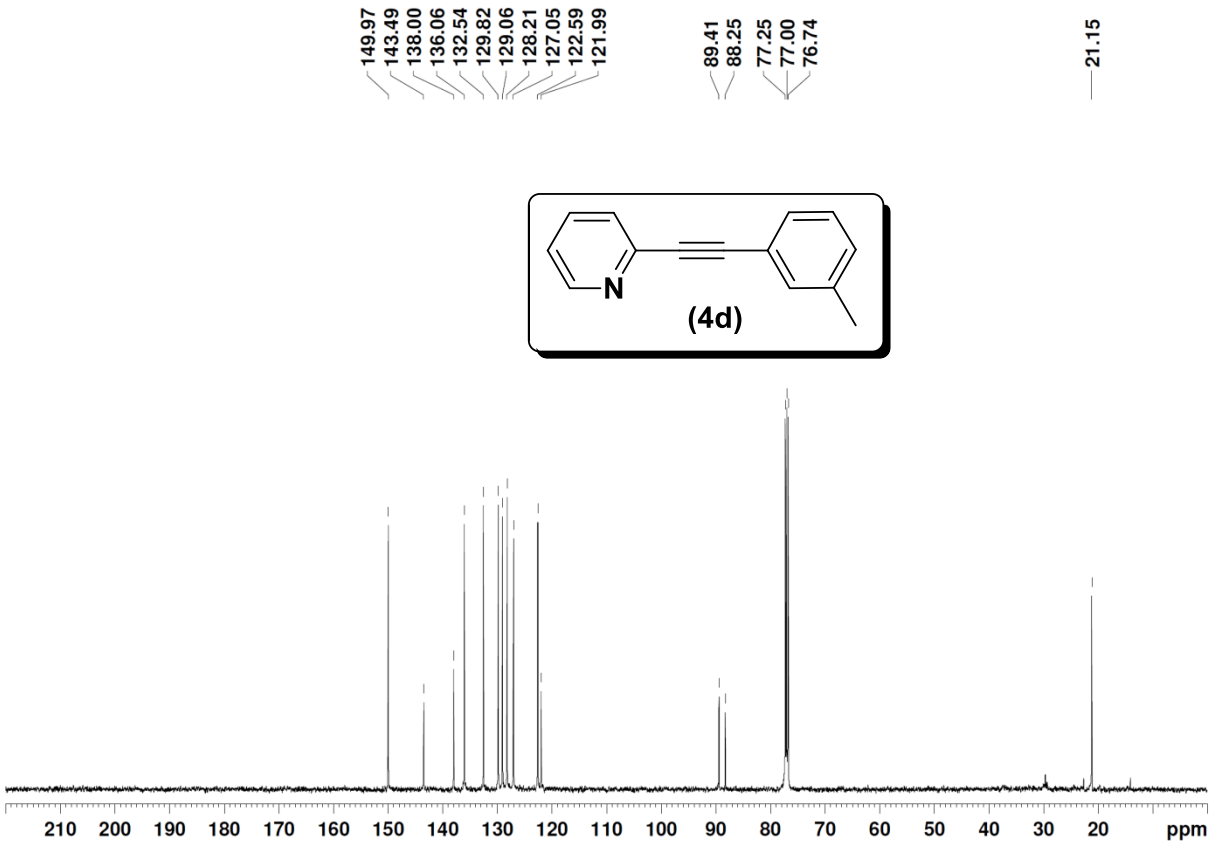

N
(4b)

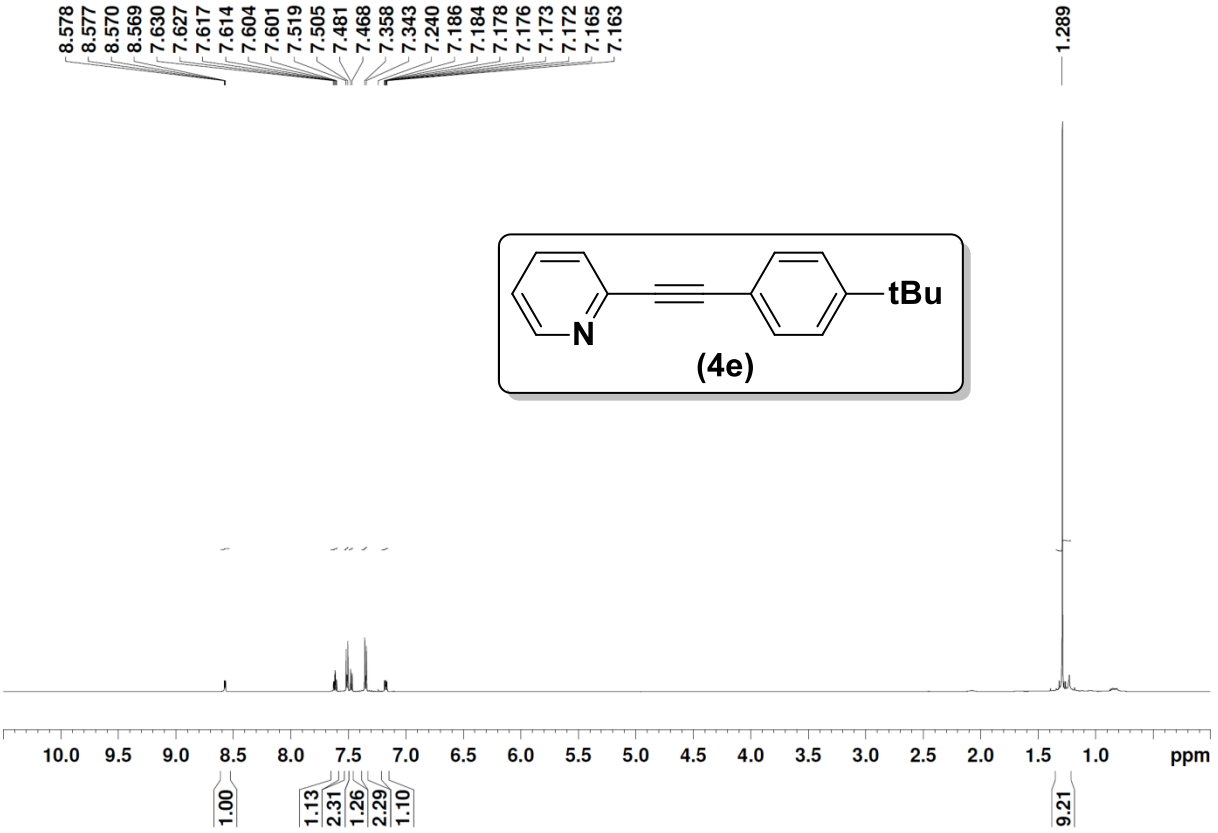

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

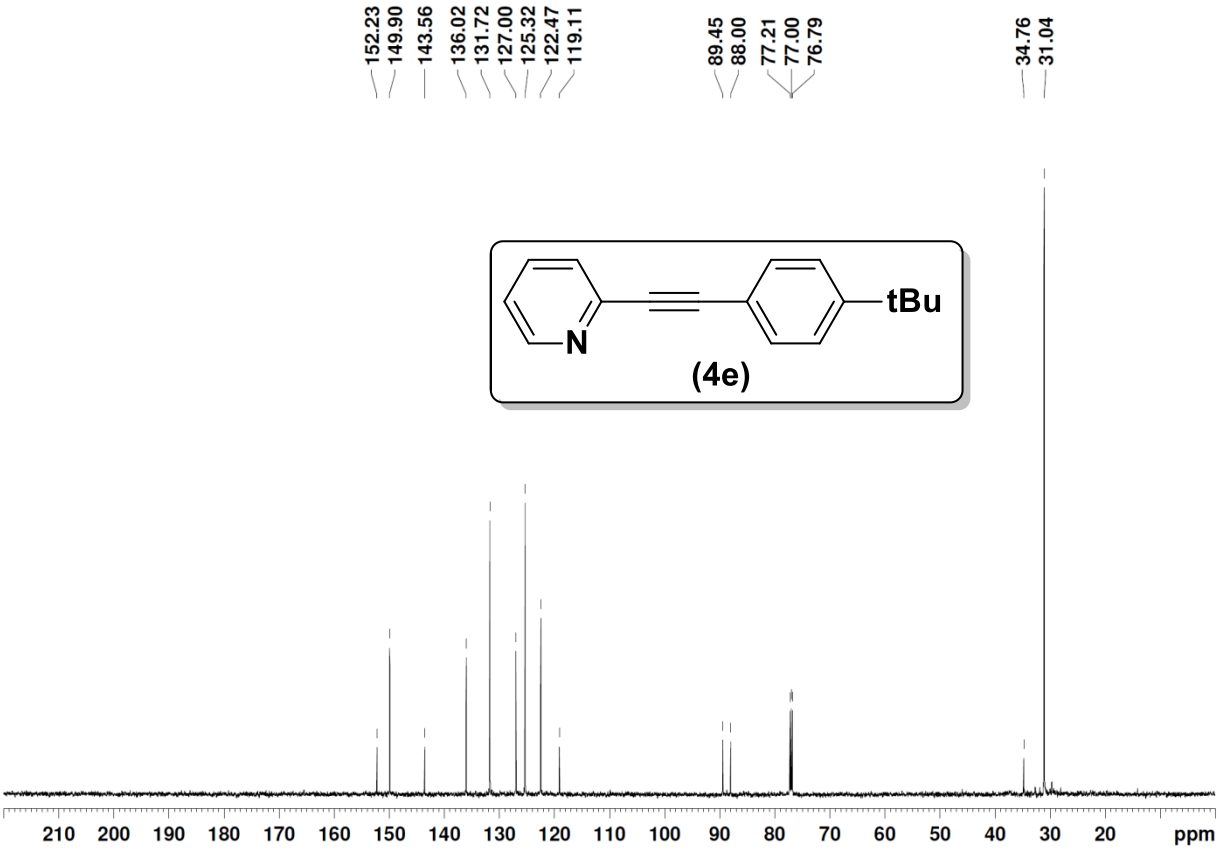

8.587
8.579
7.651
7.648
7.638
7.636
7.625
7.623
7.489
7.477
7.464
7.239
7.205
7.204
7.197
7.195
7.193
7.191
7.184
7.183
7.149
7.148
7.136
7.135
2.345
N
(4c)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.10
3.11
1.05
2.14
3.35

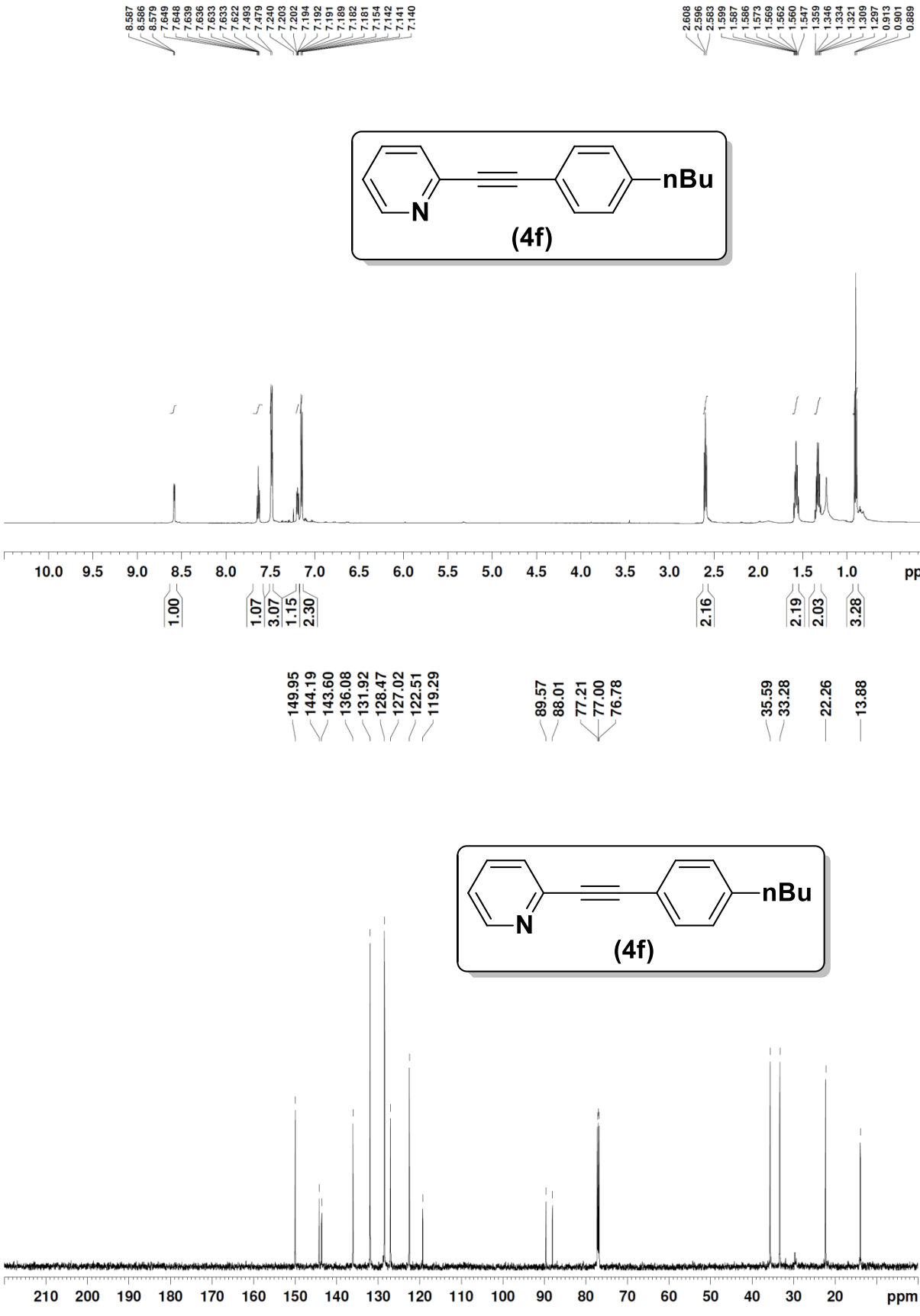

149.96
143.57
139.20
136.08
131.90
129.12
127.00
122.53
119.10
89.50
88.02
77.21
77.00
76.78
21.53
N
(4c)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

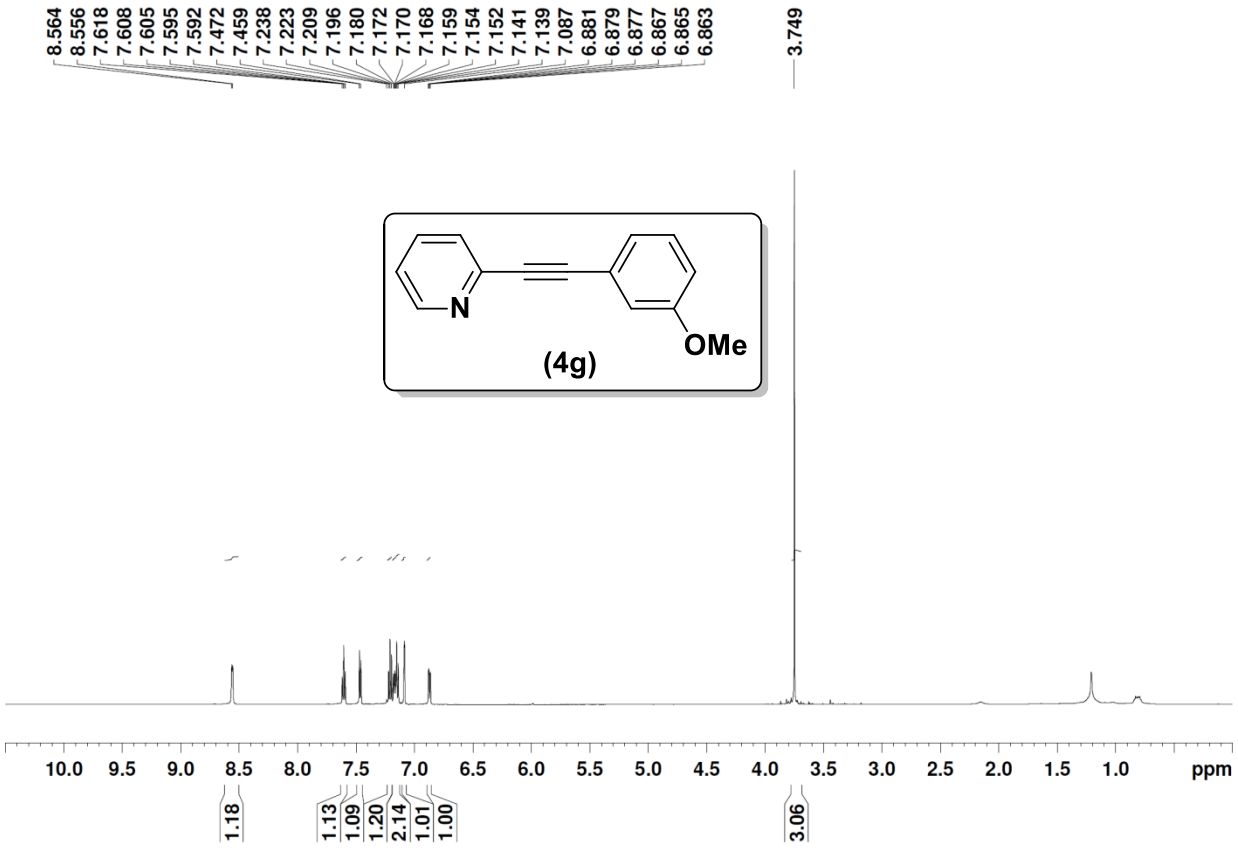

8.579
7.648
7.645
7.633
7.630
7.617
7.614
7.488
7.472
7.401
7.388
7.372
7.240
7.233
7.217
7.203
7.190
7.179
7.156
7.141
2.321
N
(4d)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.08
1.12
1.01
1.09
2.11
1.08
3.44

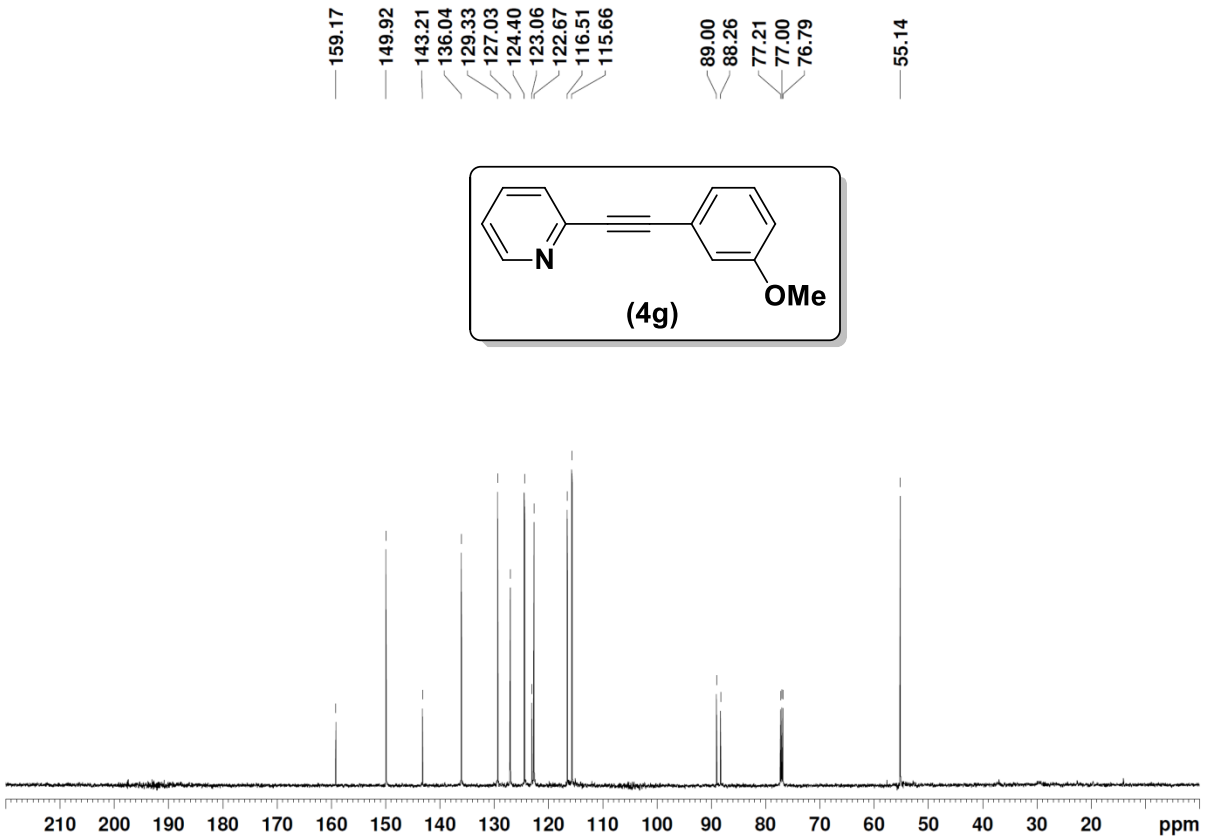

149.97
143.49
138.00
136.06
132.54
129.82
129.06
128.21
127.05
122.59
121.99
89.41
88.25
77.25
77.00
76.74
21.15
N
(4d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

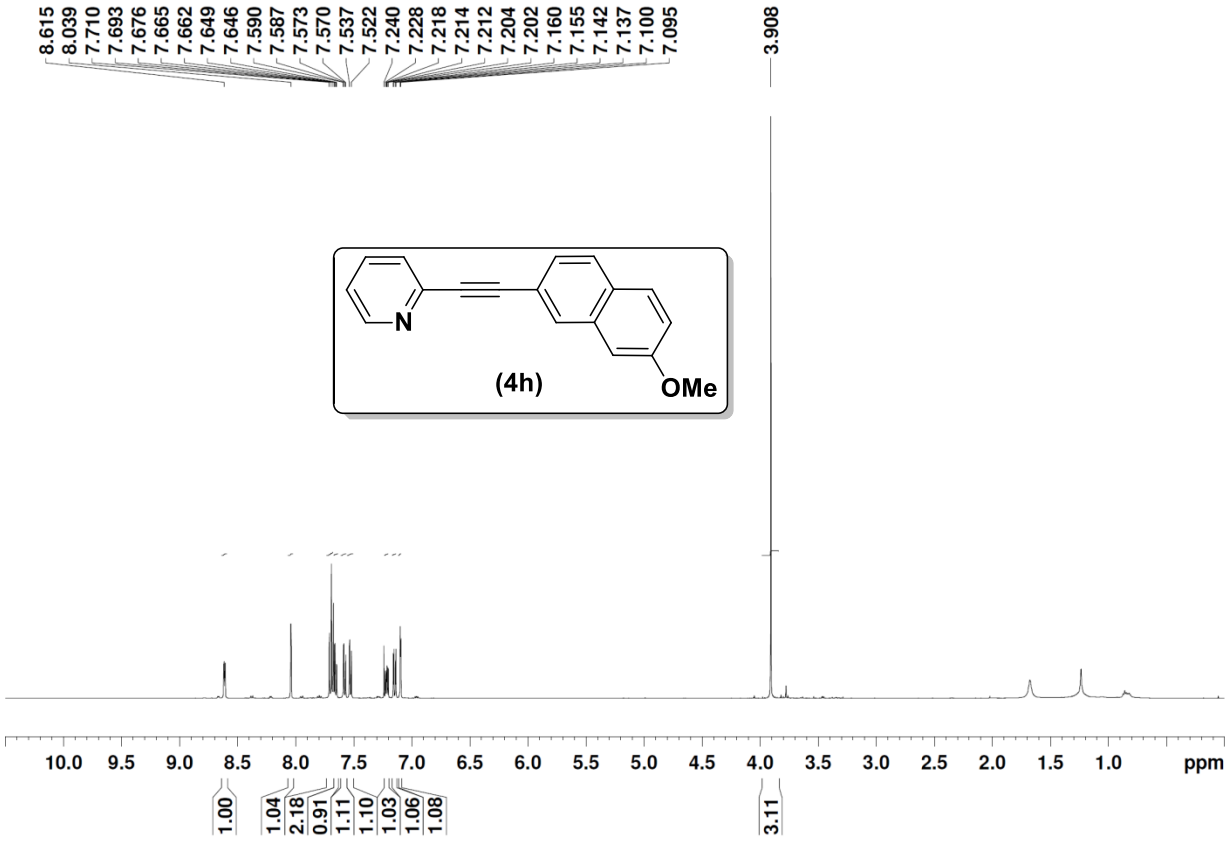

8.578
8.577
8.570
8.569
7.630
7.627
7.617
7.614
7.604
7.601
7.519
7.505
7.481
7.468
7.358
7.343
7.240
7.186
7.184
7.178
7.176
7.173
7.172
7.165
7.163
1.289
tBu
N
(4e)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.13
2.31
1.26
2.29
1.10
9.21

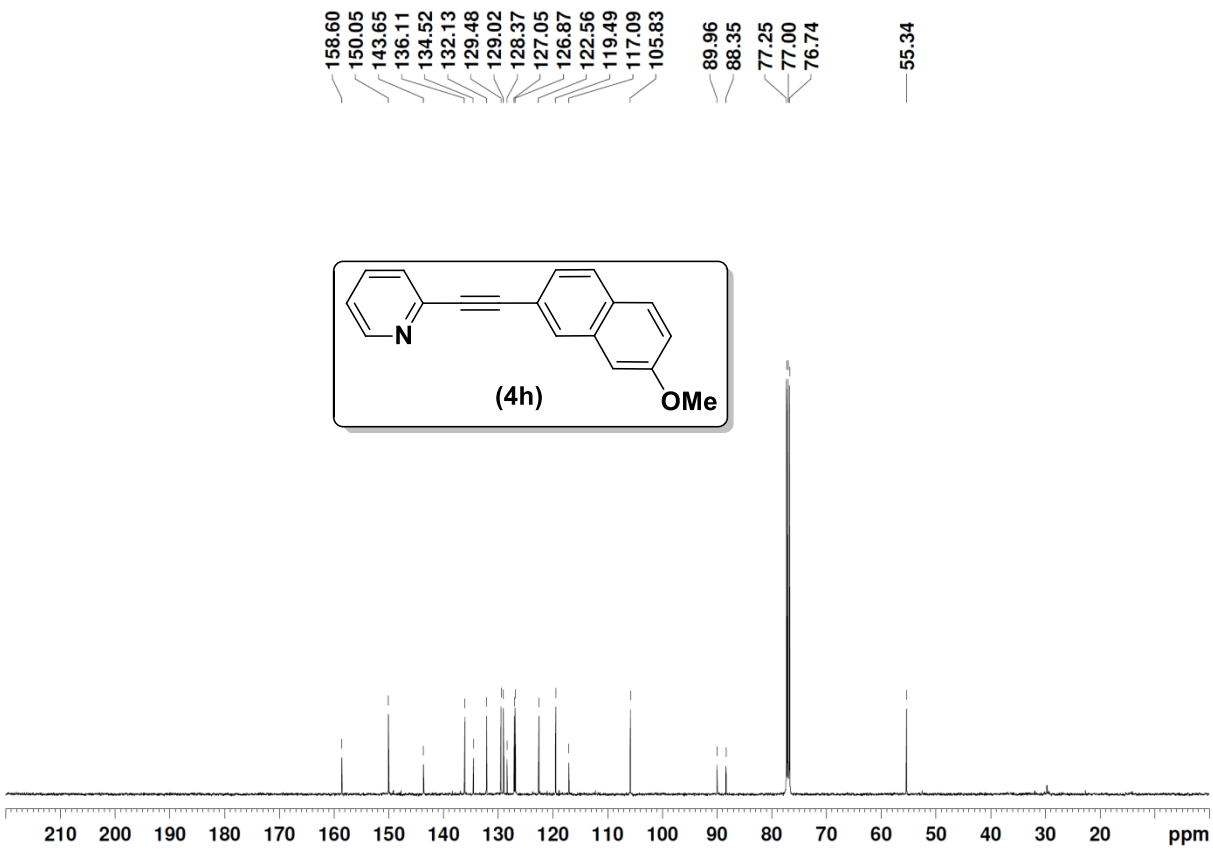

152.23
149.90
143.56
136.02
131.72
127.00
125.32
122.47
119.11
89.45
88.00
77.21
77.00
76.79
34.76
31.04
tBu
N
(4e)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.587
8.586
8.579
7.649
7.648
7.639
7.636
7.633
7.633
7.622
7.493
7.479
7.240
7.203
7.202
7.194
7.192
7.191
7.189
7.182
7.181
7.154
7.142
7.141
7.140
2.608
2.596
2.583
1.599
1.587
1.586
1.573
1.569
1.562
1.560
1.547
1.359
1.346
1.334
1.321
1.309
1.297
0.913
0.901
0.889
nBu
N
(4f)
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 ppm
1.00
1.07
3.07
1.15
2.30
2.16
2.19
2.03
3.28
149.95
144.19
143.60
136.08
131.92
128.47
127.02
122.51
119.29
89.57
88.01
77.21
77.00
76.78
35.59
33.28
22.26
13.88
nBu
N
(4f)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

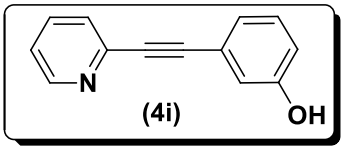

8.564
8.556
7.618
7.608
7.605
7.595
7.592
7.472
7.459
7.238
7.223
7.209
7.196
7.180
7.172
7.170
7.168
7.159
7.154
7.152
7.141
7.139
7.087
6.881
6.879
6.877
6.867
6.865
6.863
3.749
N
OMe
(4g)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.18
1.13
1.09
1.20
2.14
1.01
1.00
3.06

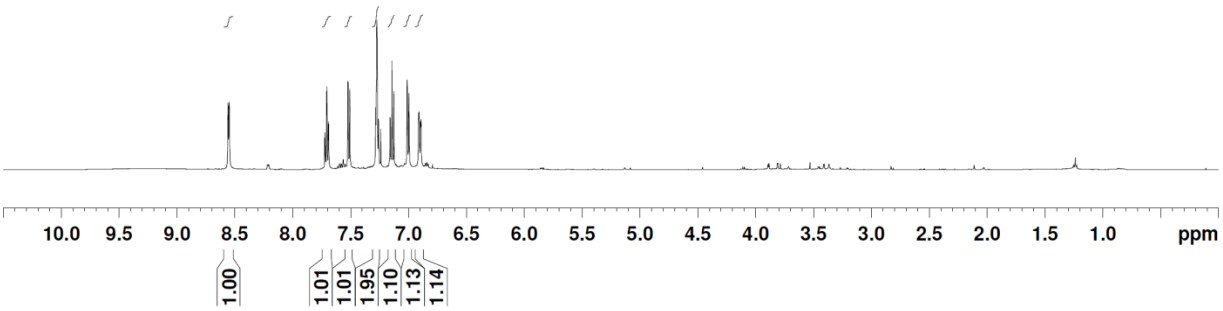

159.17
149.92
143.21
136.04
129.33
127.03
124.40
123.06
122.67
116.51
115.66
89.00
88.26
77.21
77.00
76.79
55.14
N
OMe
(4g)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

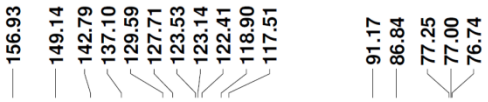

8.615
8.039
7.710
7.693
7.676
7.665
7.662
7.649
7.646
7.590
7.587
7.573
7.570
7.537
7.522
7.240
7.228
7.218
7.214
7.212
7.204
7.202
7.160
7.155
7.142
7.137
7.100
7.095
3.908
N
(4h)
OMe
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.04
2.18
0.91
1.11
1.10
1.03
1.06
1.08
3.11

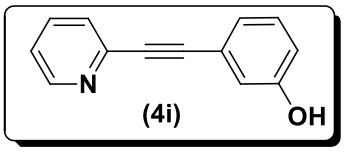

158.60
150.05
143.65
136.11
134.52
132.13
129.48
129.02
128.37
127.05
126.87
122.56
119.49
117.09
105.83
89.96
88.35
77.25
77.00
76.74
55.34
N
(4h)
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.547
7.725
7.721
7.709
7.706
7.693
7.690
7.524
7.508
7.285
7.284
7.274
7.271
7.260
7.258
7.240
7.159
7.144
7.128
7.011
6.996
6.913
6.909
6.896
6.893


N
(4i)
OH

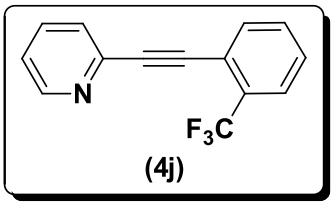

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.01
1.01
1.95
1.10
1.13
1.14

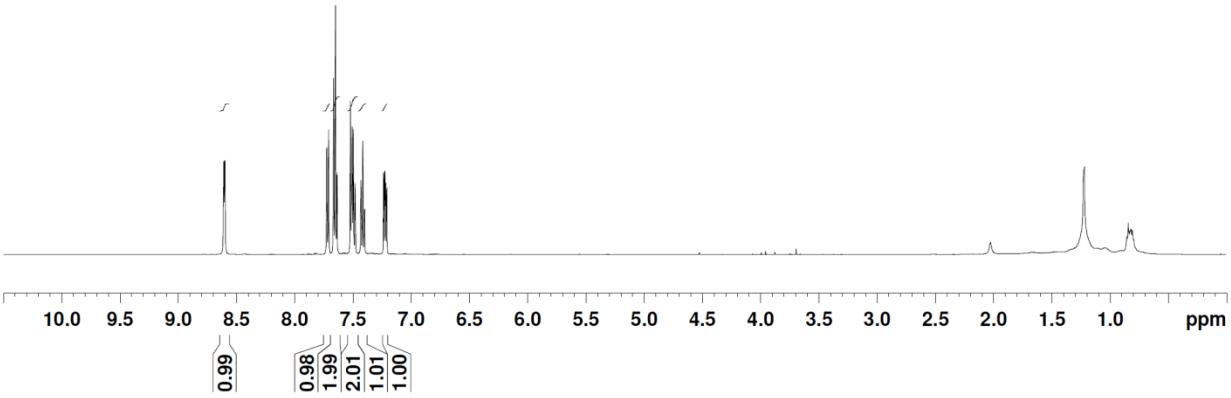

156.93
149.14
142.79
137.10
129.59
127.71
123.53
123.14
122.41
118.90
117.51
91.17
86.84
77.25
77.00
76.74

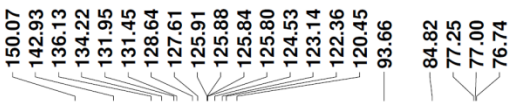

N
(4i)
OH

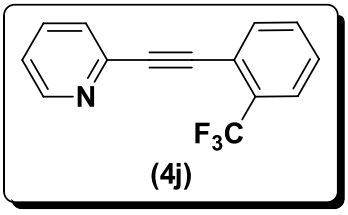
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

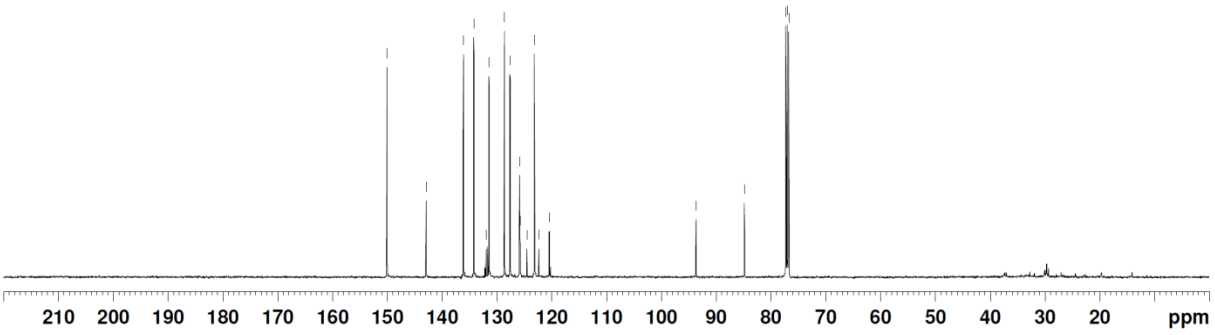

8.596
7.724
7.709
7.665
7.653
7.649
7.638
7.635
7.521
7.506
7.496
7.481
7.431
7.415
7.400
7.240
7.236
7.234
7.226
7.224
7.221
7.219
7.211
7.209

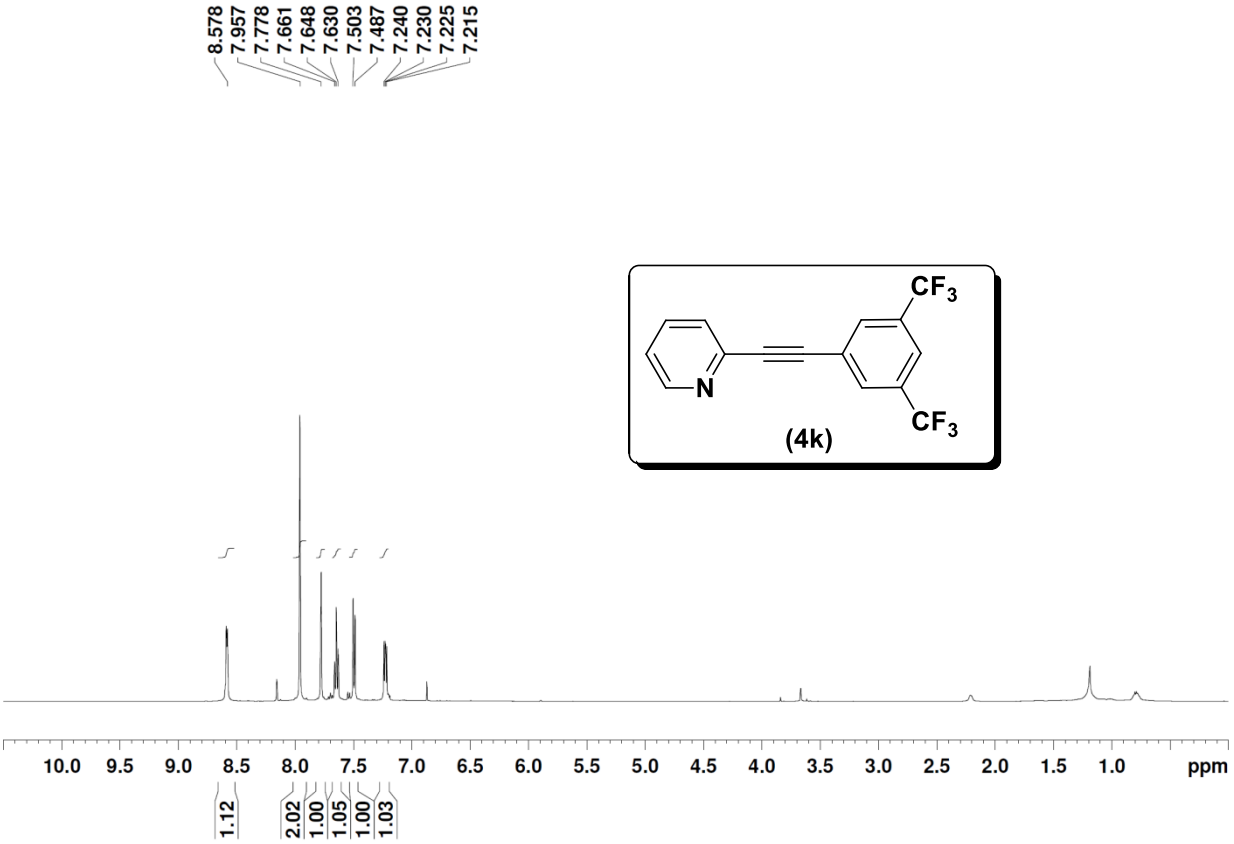

N
F3C
(4j)

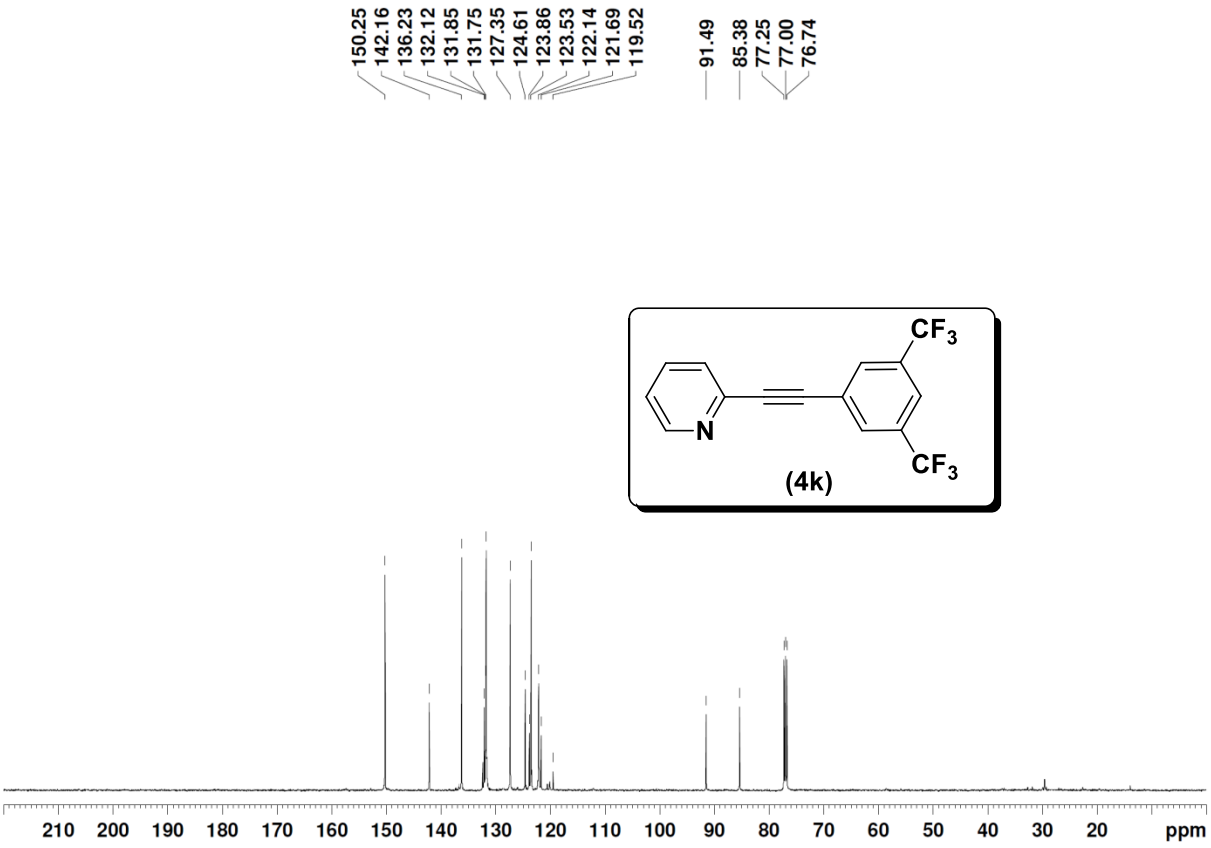

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.99
0.98
1.99
2.01
1.01
1.00

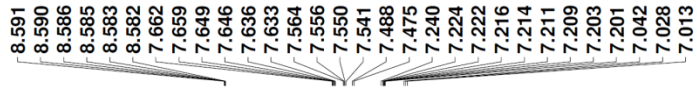

150.07
142.93
136.13
134.22
131.95
131.45
128.64
127.61
125.91
125.88
125.84
125.80
124.53
123.14
122.36
120.45
93.66
84.82
77.25
77.00
76.74

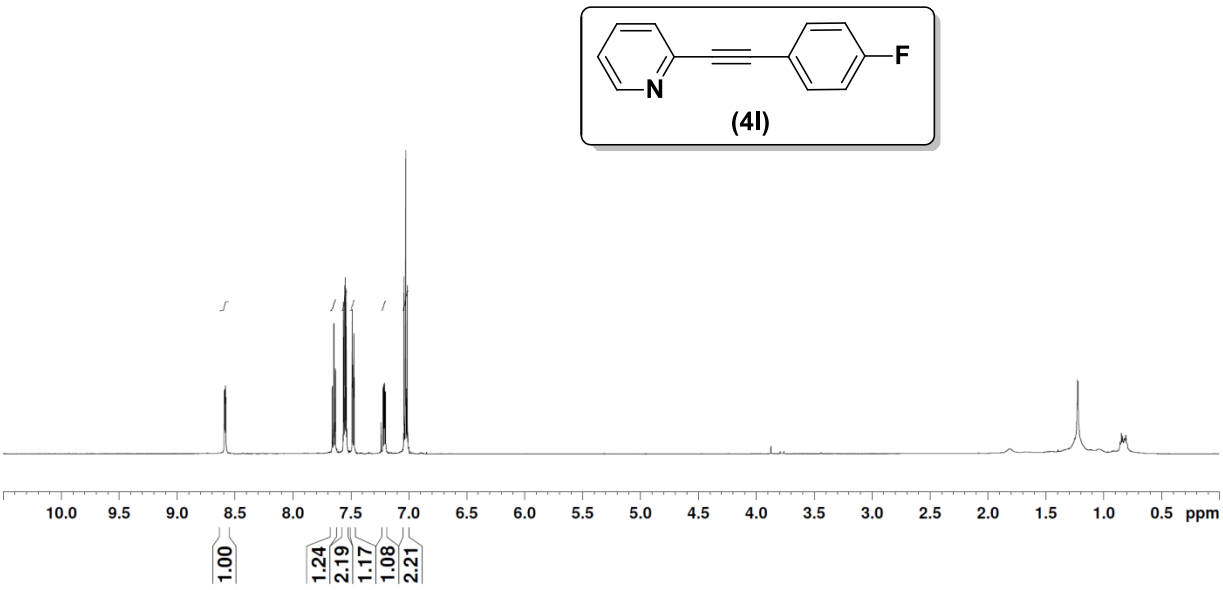

N
F3C
(4j)

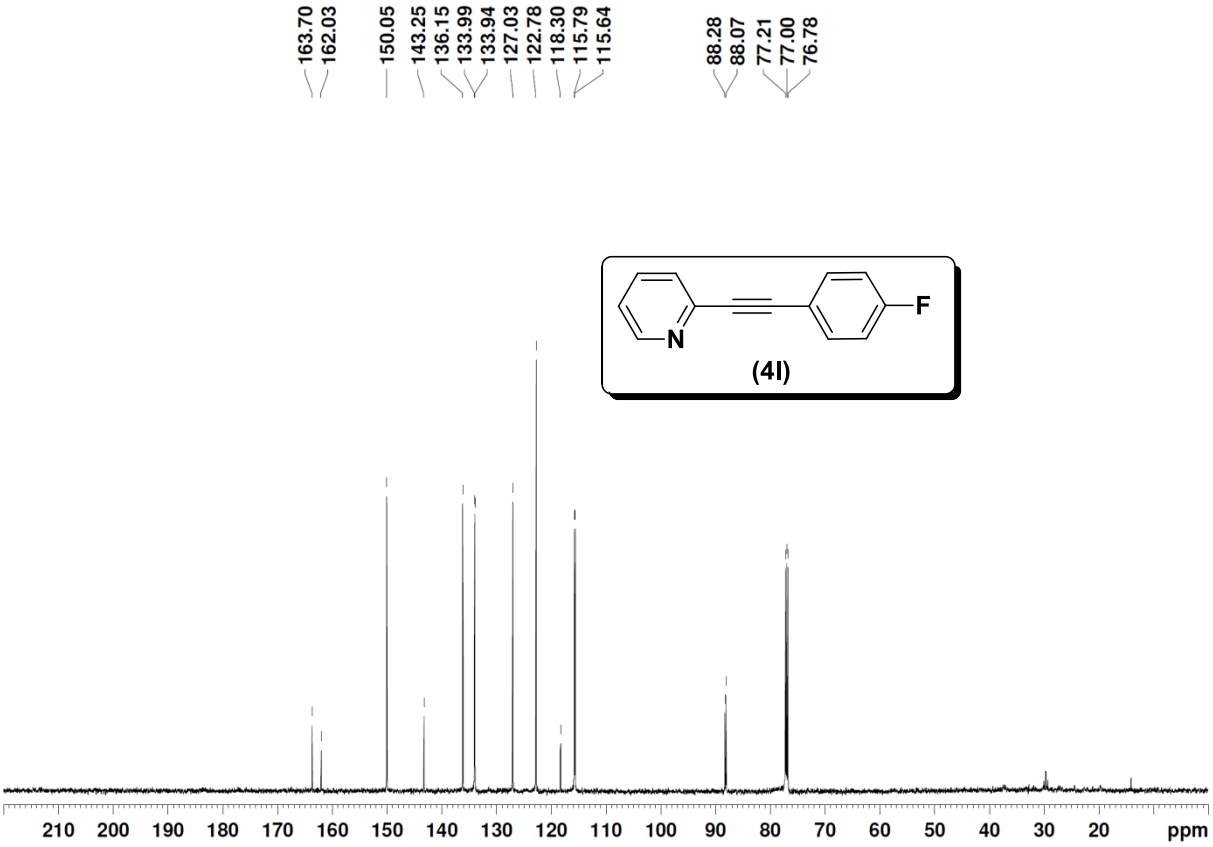

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

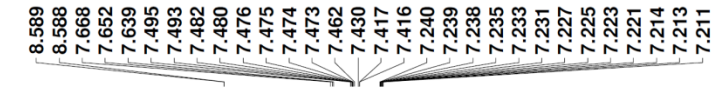

8.578
7.957
7.778
7.661
7.648
7.630
7.503
7.487
7.240
7.230
7.225
7.215
CF3
N
CF3
(4k)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.12
2.02
1.00
1.05
1.00
1.03

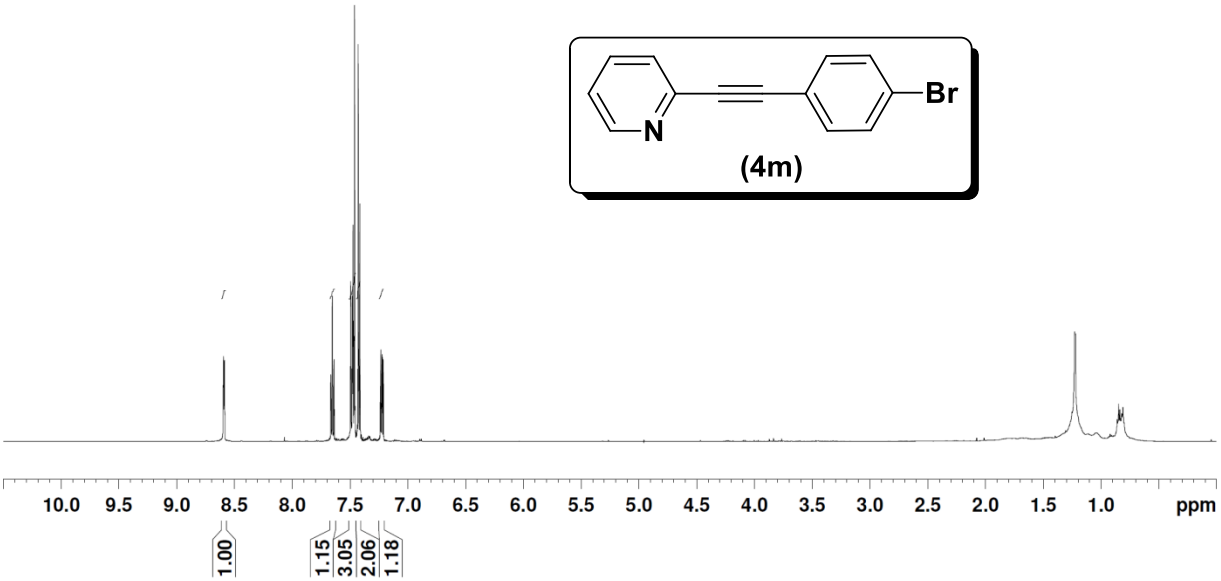

150.25
142.16
136.23
132.12
131.85
131.75
127.35
124.61
123.86
123.53
122.14
121.69
119.52
91.49
85.38
77.25
77.00
76.74
CF3
N
CF3
(4k)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

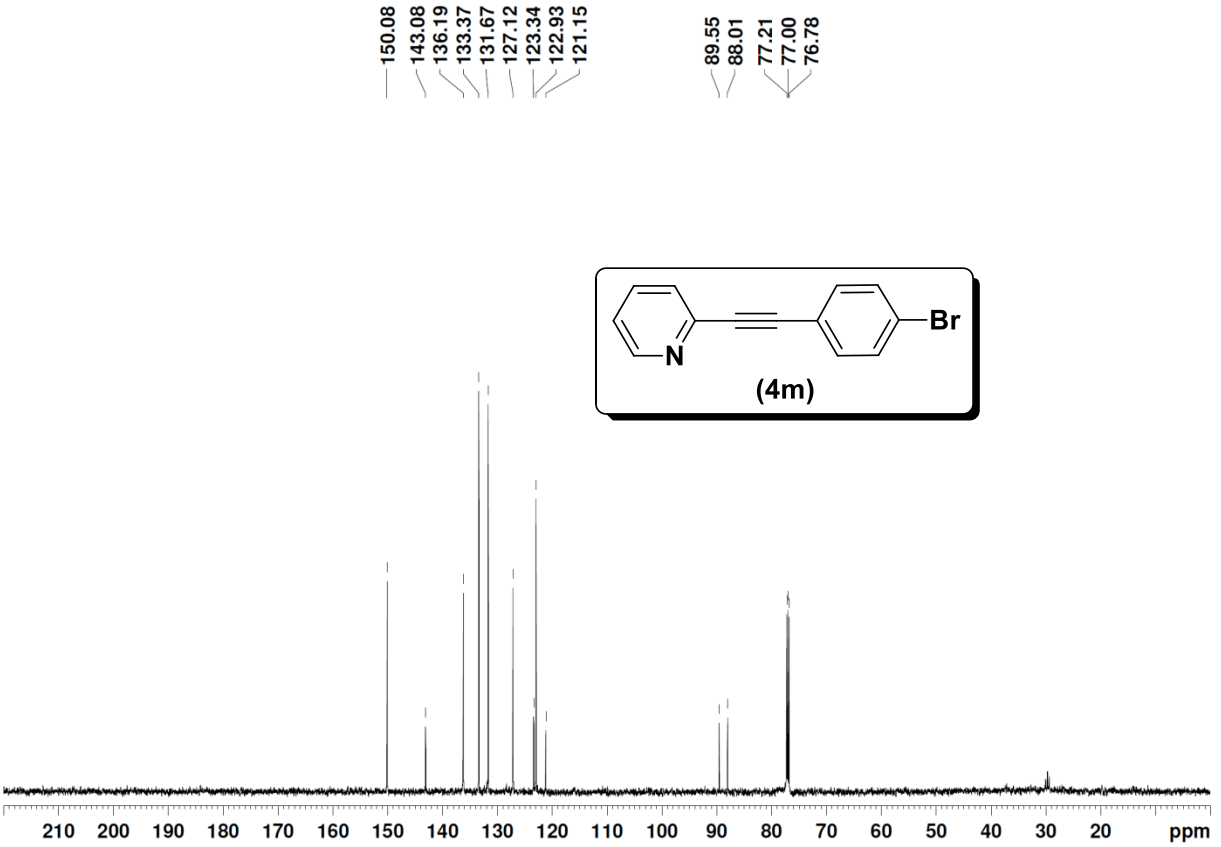

8.591
8.590
8.586
8.585
8.583
8.582
7.662
7.659
7.649
7.646
7.636
7.633
7.564
7.556
7.550
7.541
7.488
7.475
7.240
7.224
7.222
7.216
7.214
7.211
7.209
7.203
7.201
7.042
7.028
7.013

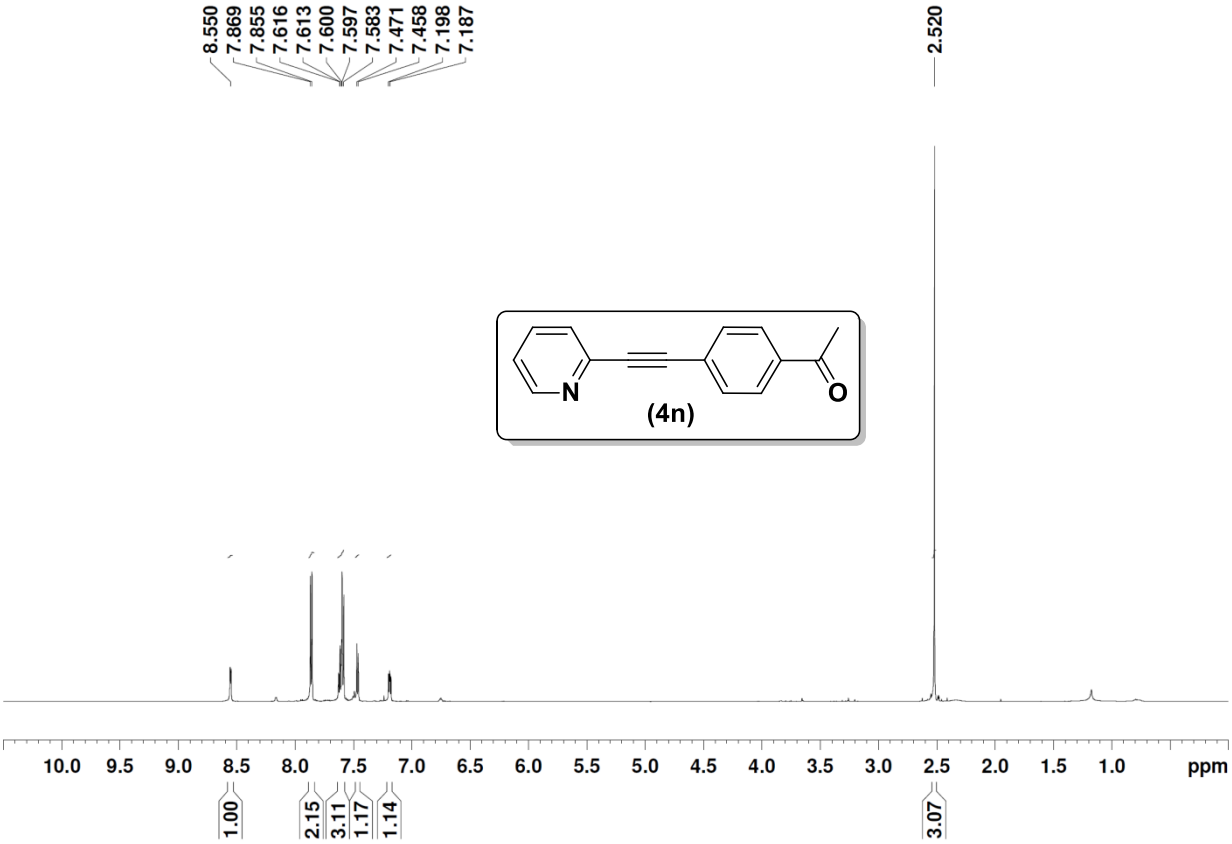

N
F
(4l)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.24
2.19
1.17
1.08
2.21

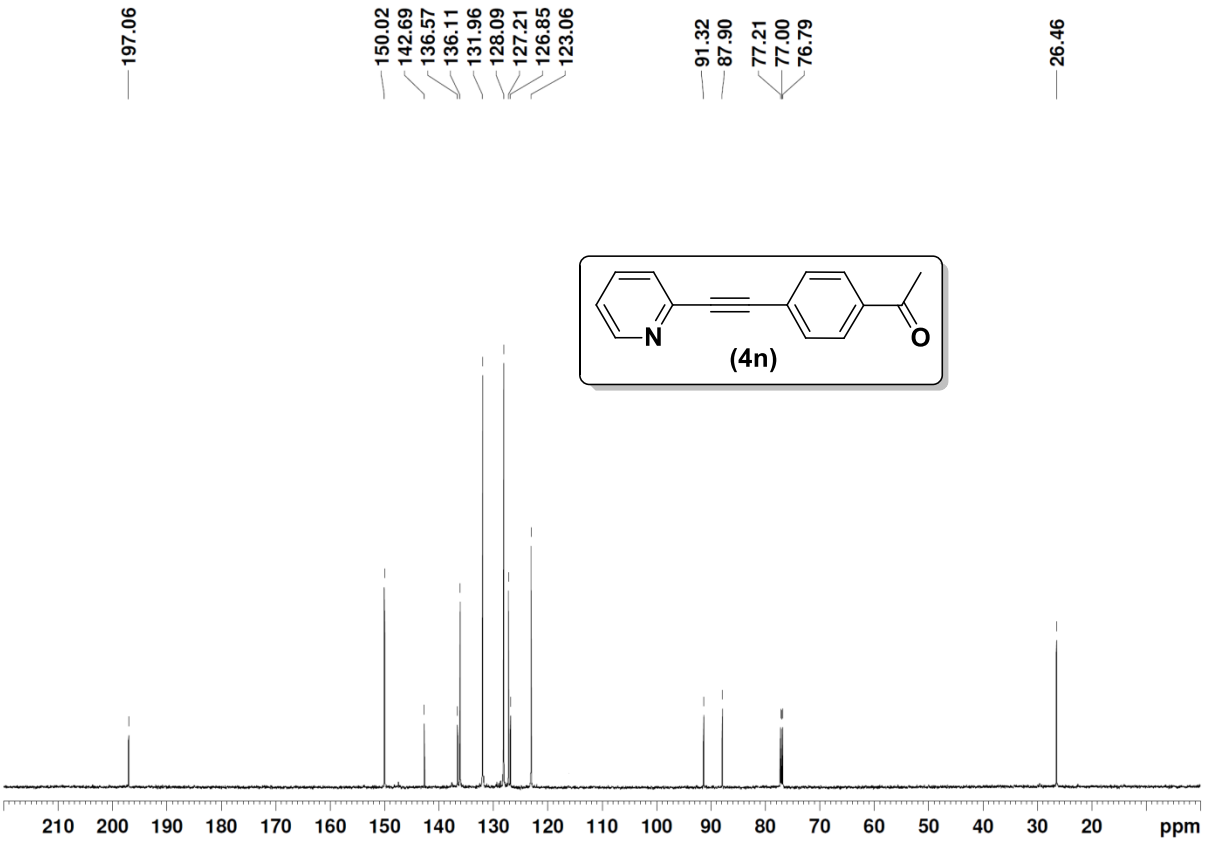

163.70
162.03
150.05
143.25
136.15
133.99
133.94
127.03
122.78
118.30
115.79
115.64
88.28
88.07
77.21
77.00
76.78
N
F
(4l)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

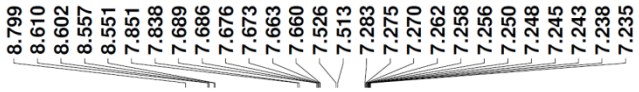

8.589
8.588
7.668
7.652
7.639
7.495
7.493
7.482
7.480
7.476
7.475
7.474
7.473
7.462
7.430
7.417
7.416
7.240
7.239
7.238
7.235
7.233
7.231
7.227
7.225
7.223
7.221
7.214
7.213
7.211


Br
N
(4m)
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
ppm
1.00
1.15
3.05
2.06
1.18


150.08
143.08
136.19
133.37
131.67
127.12
123.34
122.93
121.15
89.55
88.01
77.21
77.00
76.78
Br
N
(4m)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.550
7.869
7.855
7.616
7.613
7.600
7.597
7.583
7.471
7.458
7.198
7.187
2.520
N
O
(4n)
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 ppm
1.00
2.15
3.11
1.17
1.14
3.07


197.06
150.02
142.69
136.57
136.11
131.96
128.09
127.21
126.85
123.06
91.32
87.90
77.21
77.00
76.79
26.46
N
O
(4n)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.799
8.610
8.602
8.557
8.551
7.851
7.838
7.689
7.686
7.676
7.673
7.663
7.660
7.526
7.513
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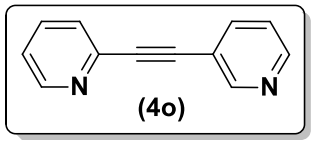
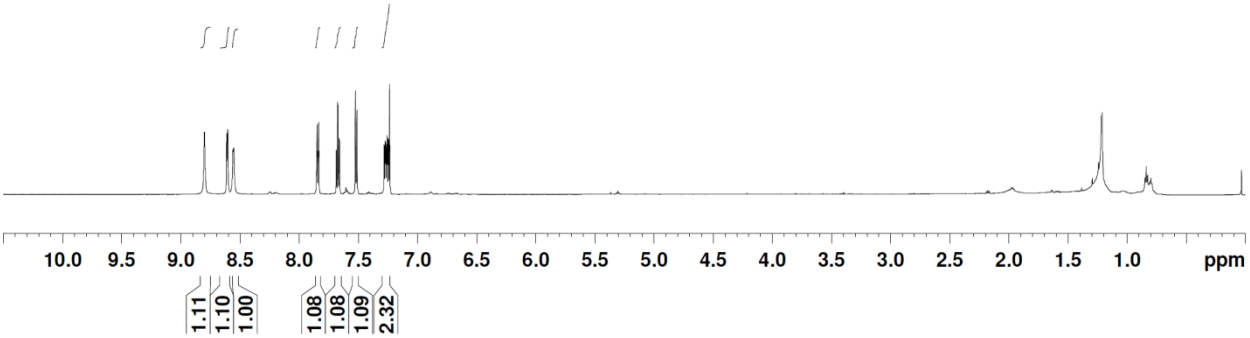
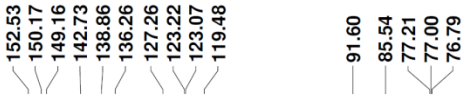
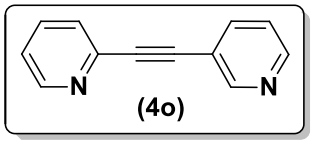
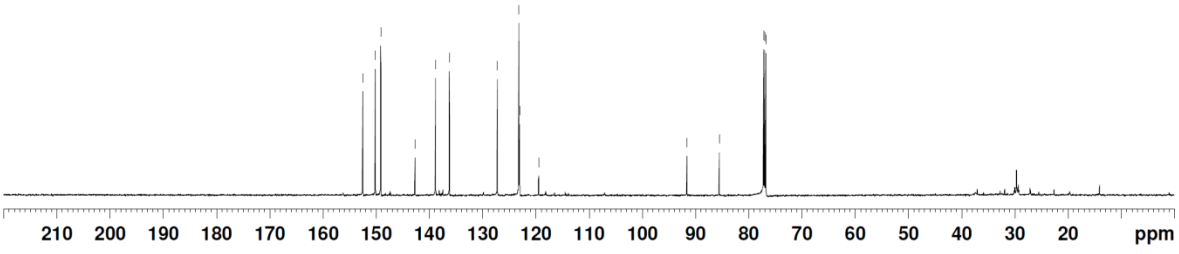
7.250
7.248
7.245
7.243
7.238
7.235

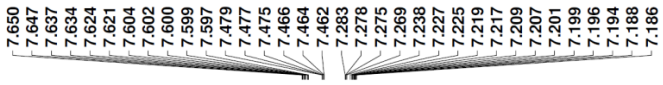

N
N
(4o)

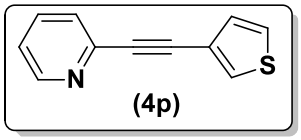

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.11
1.10
1.00
1.08
1.08
1.09
2.32

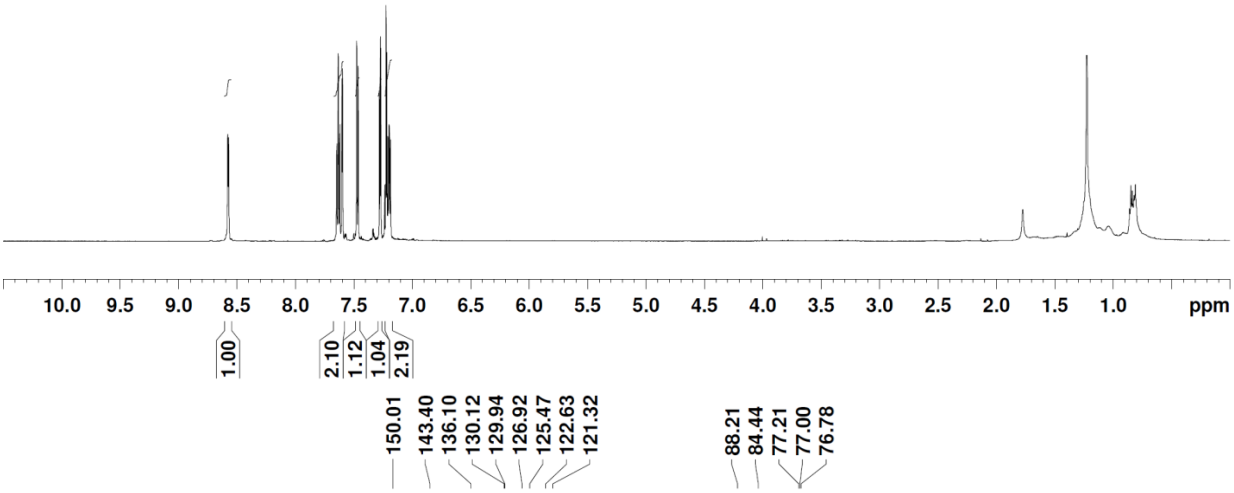

152.53
150.17
149.16
142.73
138.86
136.26
127.26
123.22
123.07
119.48
91.60
85.54
77.21
77.00
76.79


N
N
(4o)

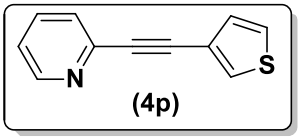

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

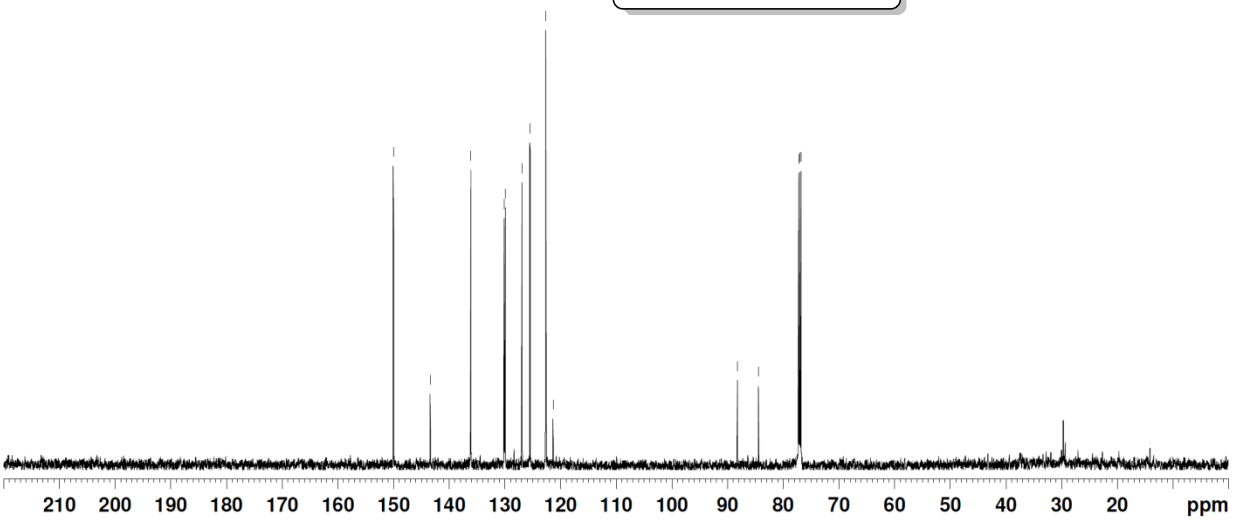

7.650
7.647
7.637
7.634
7.624
7.621
7.604
7.602
7.600
7.599
7.597
7.479
7.477
7.475
7.466
7.464
7.462
7.283
7.278
7.275
7.269
7.238
7.227
7.225
7.219
7.217
7.209
7.207
7.201
7.199
7.196
7.194
7.188
7.186

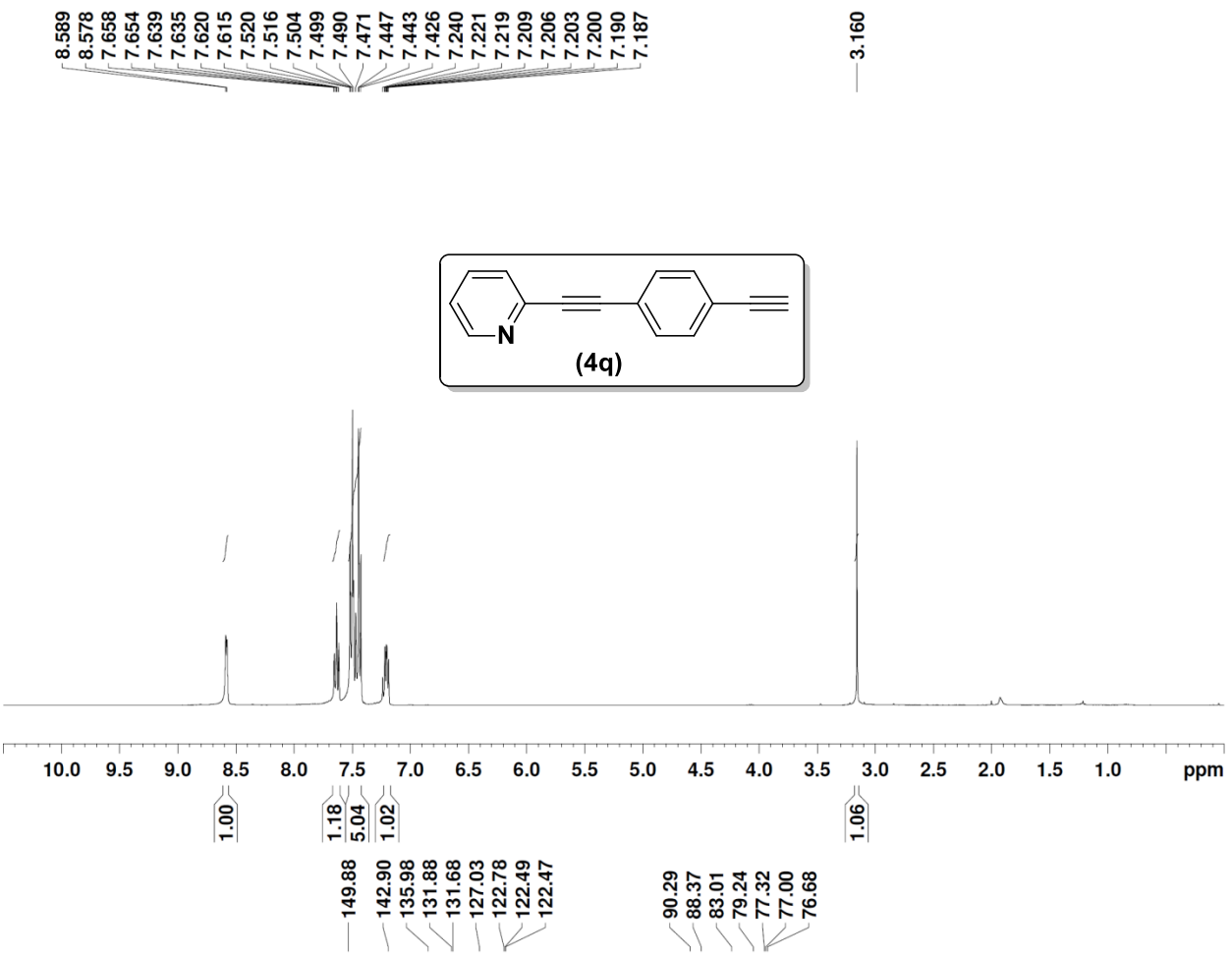

N
S
(4p)

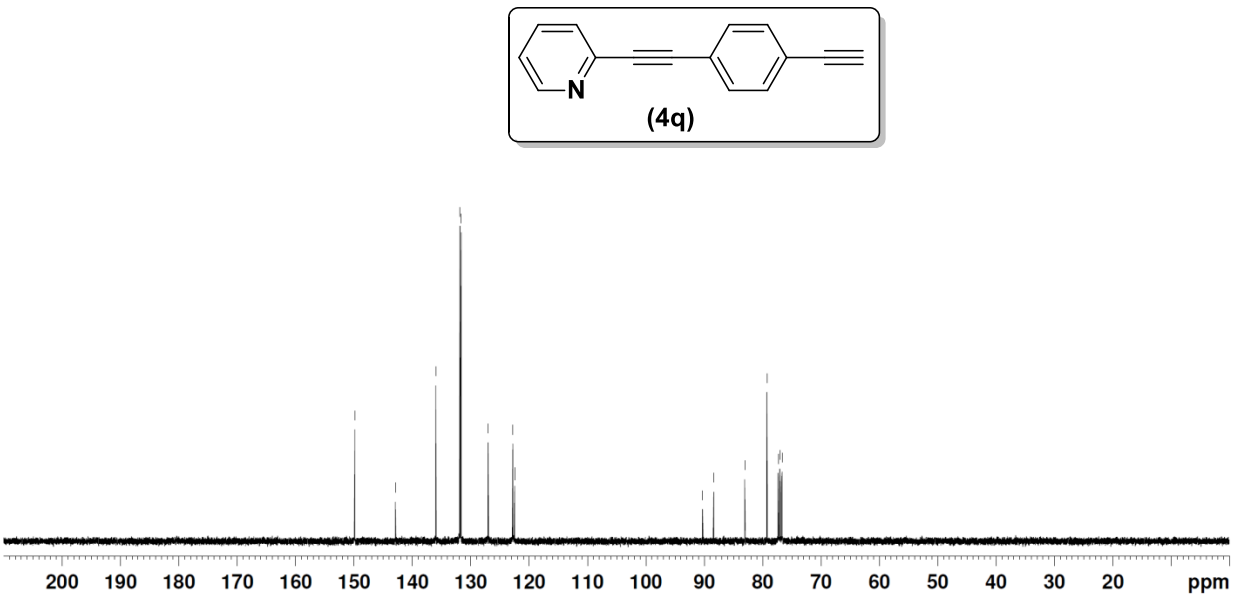

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.10
1.12
1.04
2.19

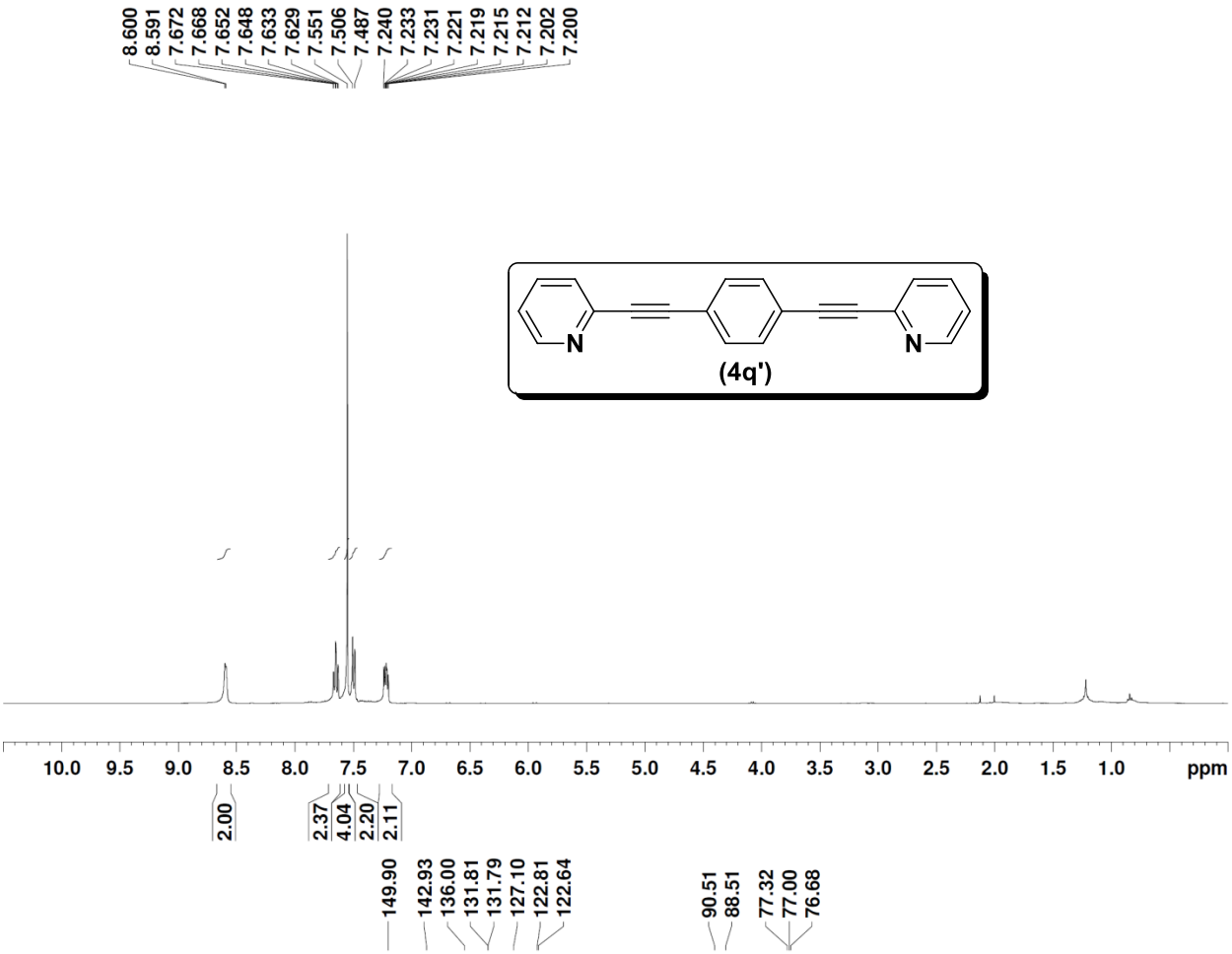
150.01
143.40
136.10
130.12
129.94
126.92
125.47
122.63
121.32
88.21
84.44
77.21
77.00
76.78

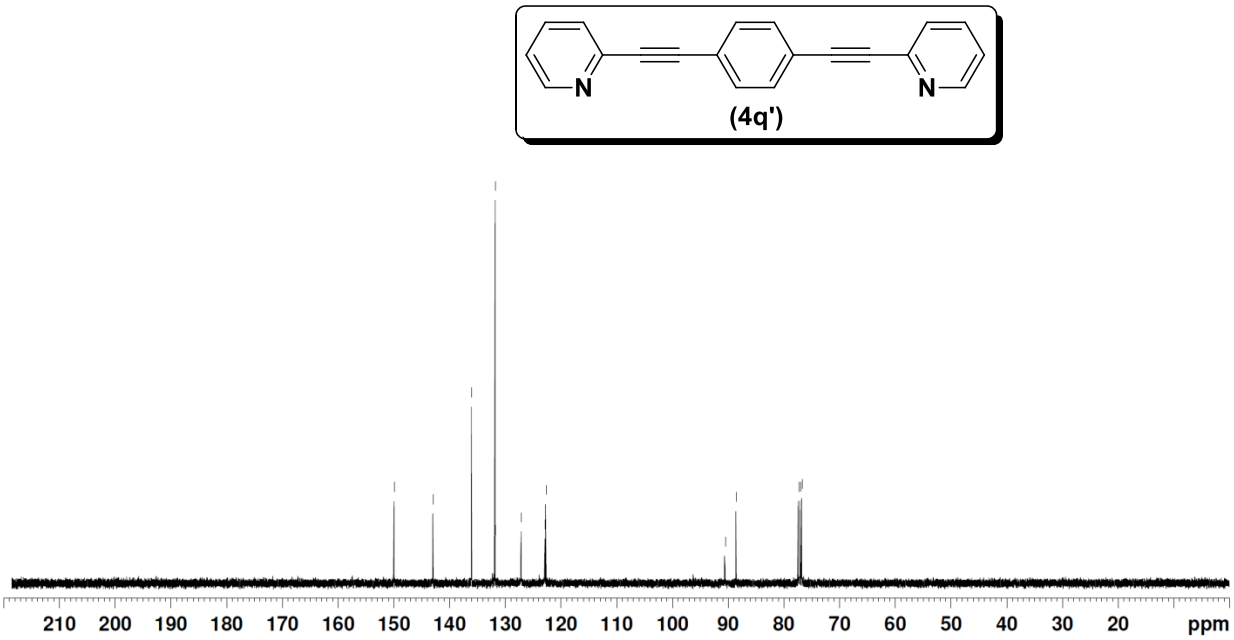

N
S
(4p)

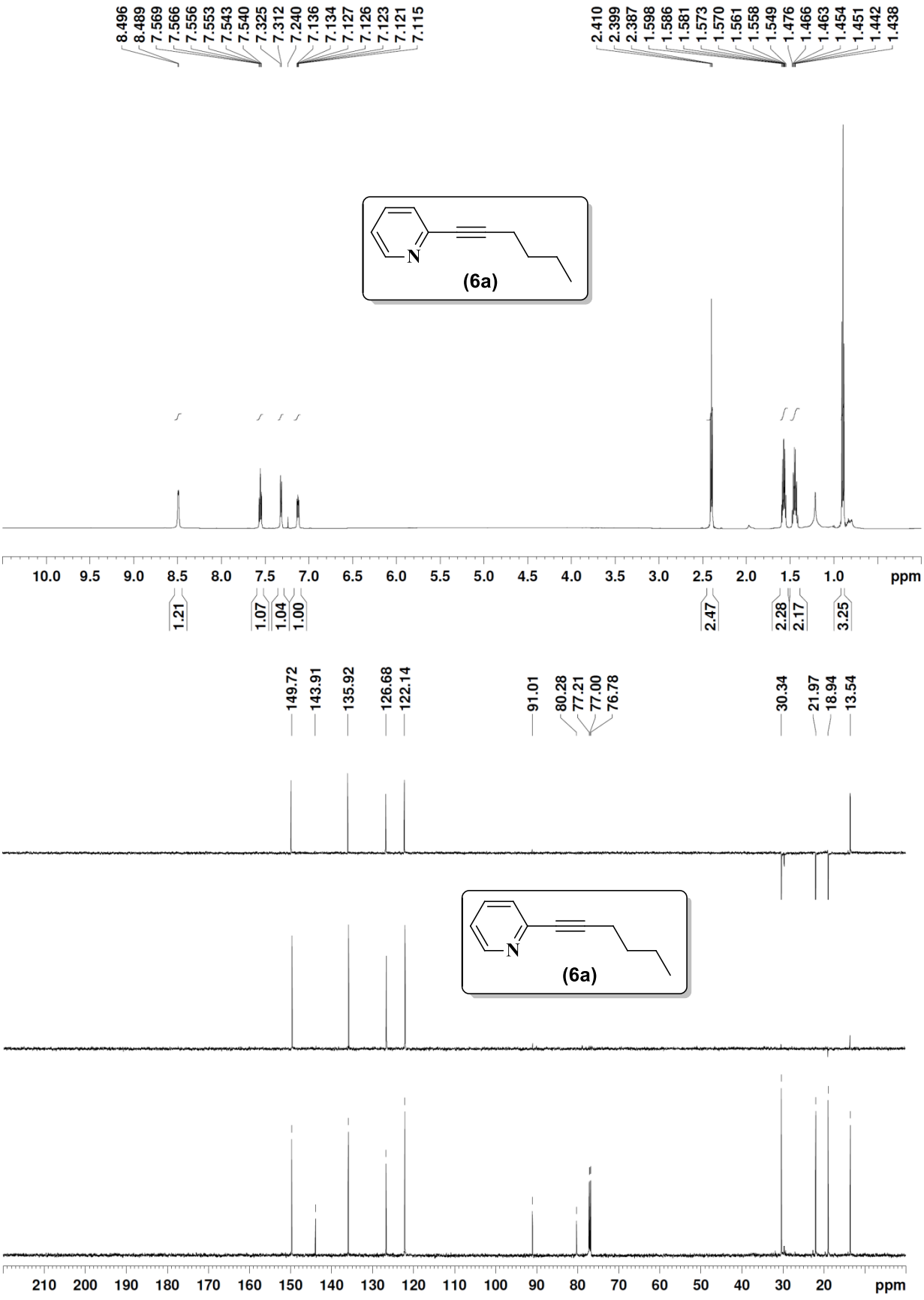

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

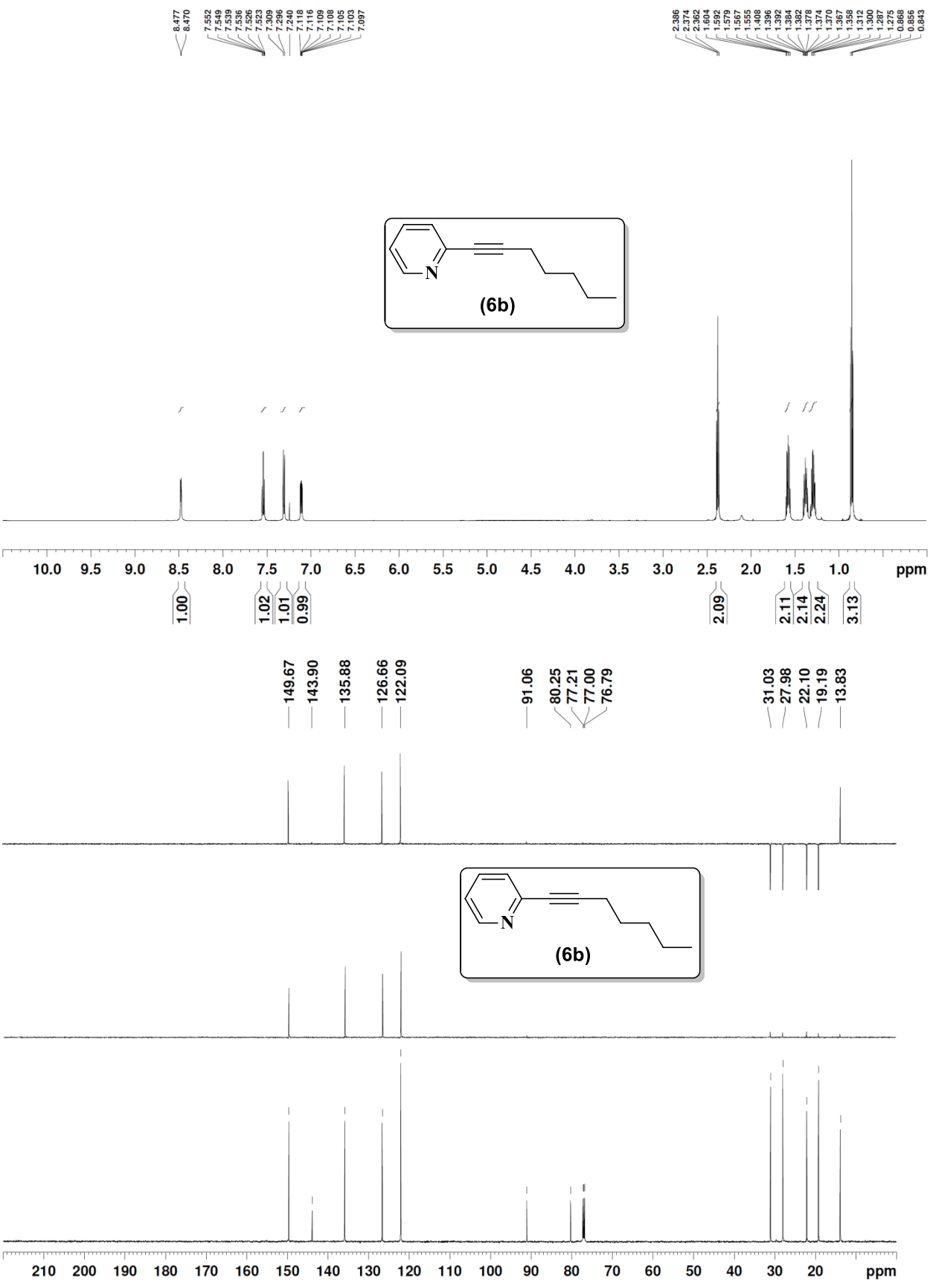

8.589
8.578
7.658
7.654
7.639
7.635
7.620
7.615
7.520
7.516
7.504
7.499
7.490
7.471
7.447
7.443
7.426
7.240
7.221
7.219
7.209
7.206
7.203
7.200
7.190
7.187
3.160
N
(4q)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.18
5.04
1.02
1.06
149.88
142.90
135.98
131.88
131.68
127.03
122.78
122.49
122.47
90.29
88.37
83.01
79.24
77.32
77.00
76.68


N
(4q)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

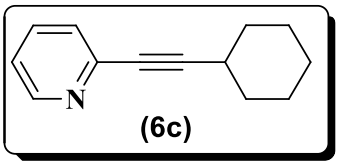

8.600
8.591
7.672
7.668
7.652
7.648
7.633
7.629
7.551
7.506
7.487
7.240
7.233
7.231
7.221
7.219
7.215
7.212
7.202
7.200
N
N
(4q')
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
2.37
4.04
2.20
2.11
149.90
142.93
136.00
131.81
131.79
127.10
122.81
122.64
90.51
88.51
77.32
77.00
76.68

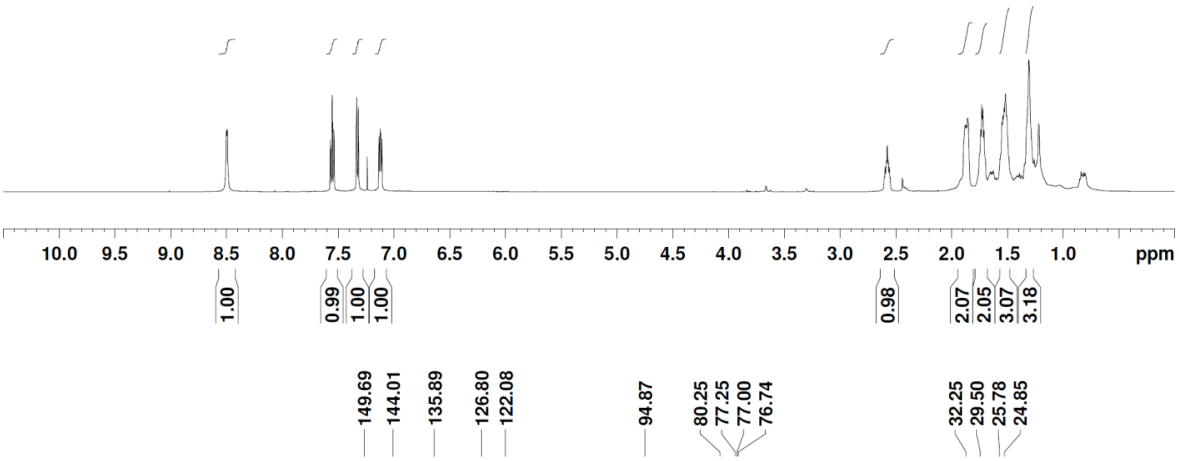

N
N
(4q')
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

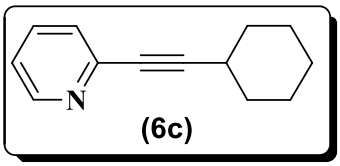

8.496
8.489
7.569
7.566
7.556
7.553
7.543
7.540
7.325
7.312
7.240
7.136
7.134
7.127
7.126
7.123
7.121
7.115
2.410
2.399
2.387
1.598
1.586
1.581
1.573
1.570
1.561
1.558
1.549
1.476
1.466
1.463
1.454
1.451
1.442
1.438
N
(6a)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.21
1.07
1.04
1.00
2.47
2.28
2.17
3.25
149.72
143.91
135.92
126.68
122.14
91.01
80.28
77.21
77.00
76.78
30.34
21.97
18.94
13.54
N
(6a)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

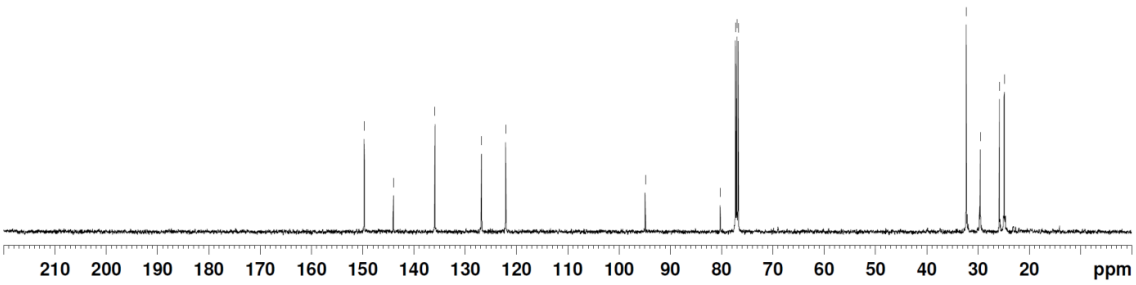

8.477
8.470
7.552
7.549
7.539
7.536
7.526
7.523
7.309
7.296
7.240
7.118
7.116
7.109
7.108
7.105
7.103
7.097
2.386
2.374
2.362
1.604
1.592
1.579
1.567
1.555
1.408
1.396
1.392
1.384
1.382
1.378
1.374
1.370
1.367
1.358
1.312
1.300
1.297
1.275
0.868
0.856
0.843
N
(6b)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.02
1.01
0.99
2.09
2.11
2.14
2.24
3.13
149.67
143.90
135.88
126.66
122.09
91.06
80.25
77.21
77.00
76.79
31.03
27.98
22.10
19.19
13.83
N
(6b)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

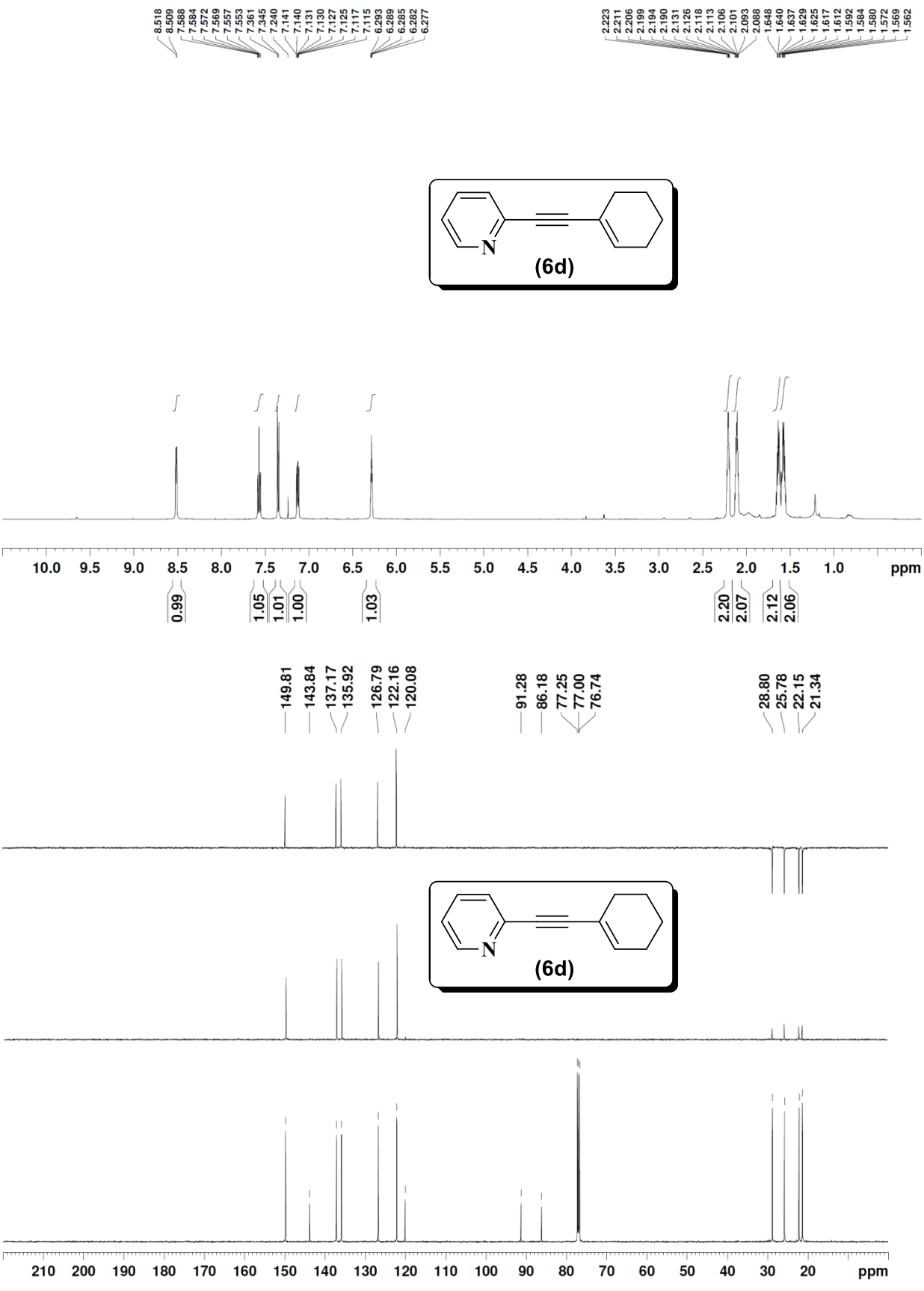

8.499
8.491
7.570
7.566
7.554
7.551
7.539
7.536
7.334
7.319
7.240
7.134
7.124
7.122
7.119
7.109
2.595
2.584
2.577
2.569
2.558
1.877
1.868
1.856
1.737
1.730
1.719
1.710
1.548
1.541
1.530
1.520
1.516
1.505
1.308
1.304

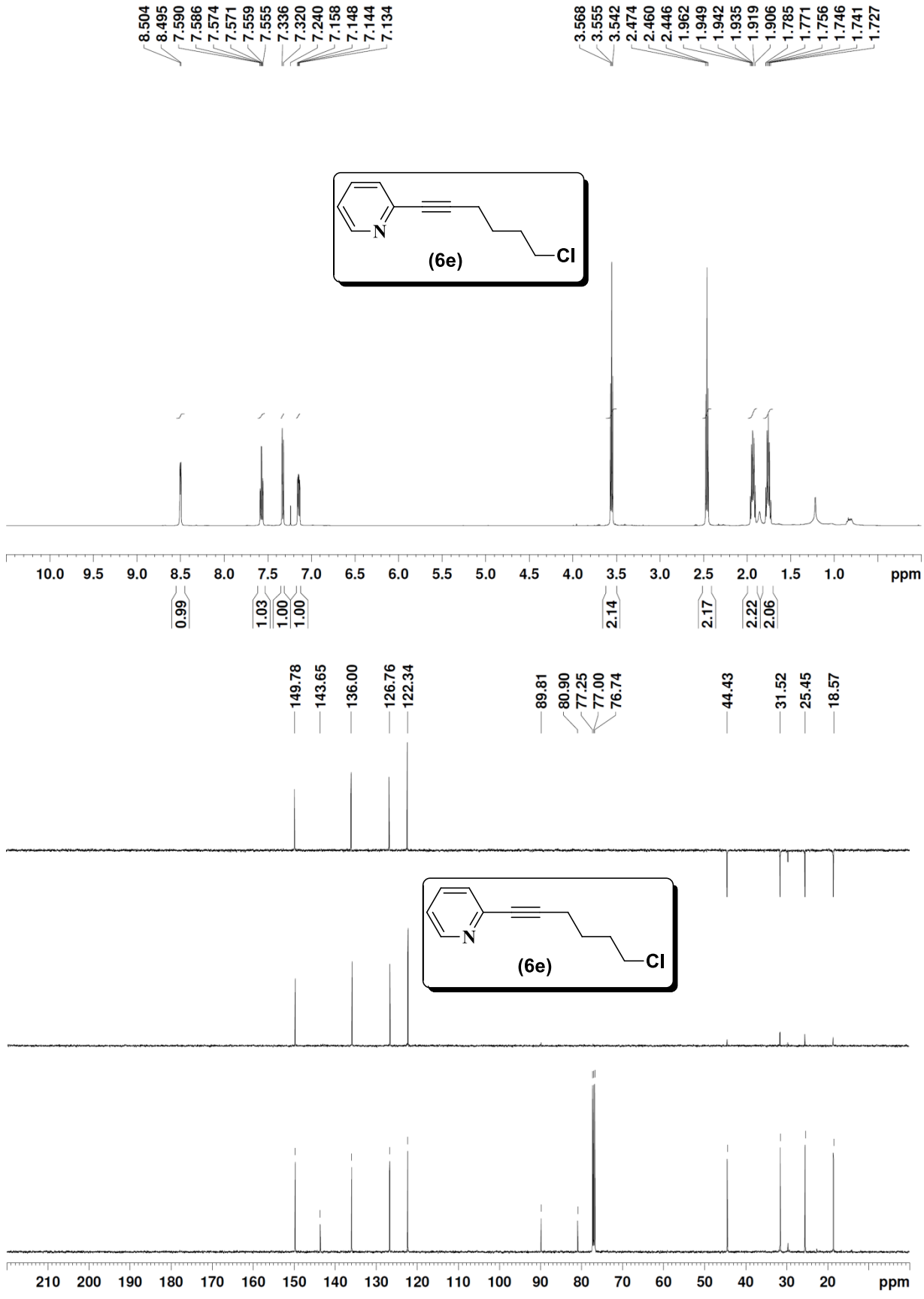

N
(6c)

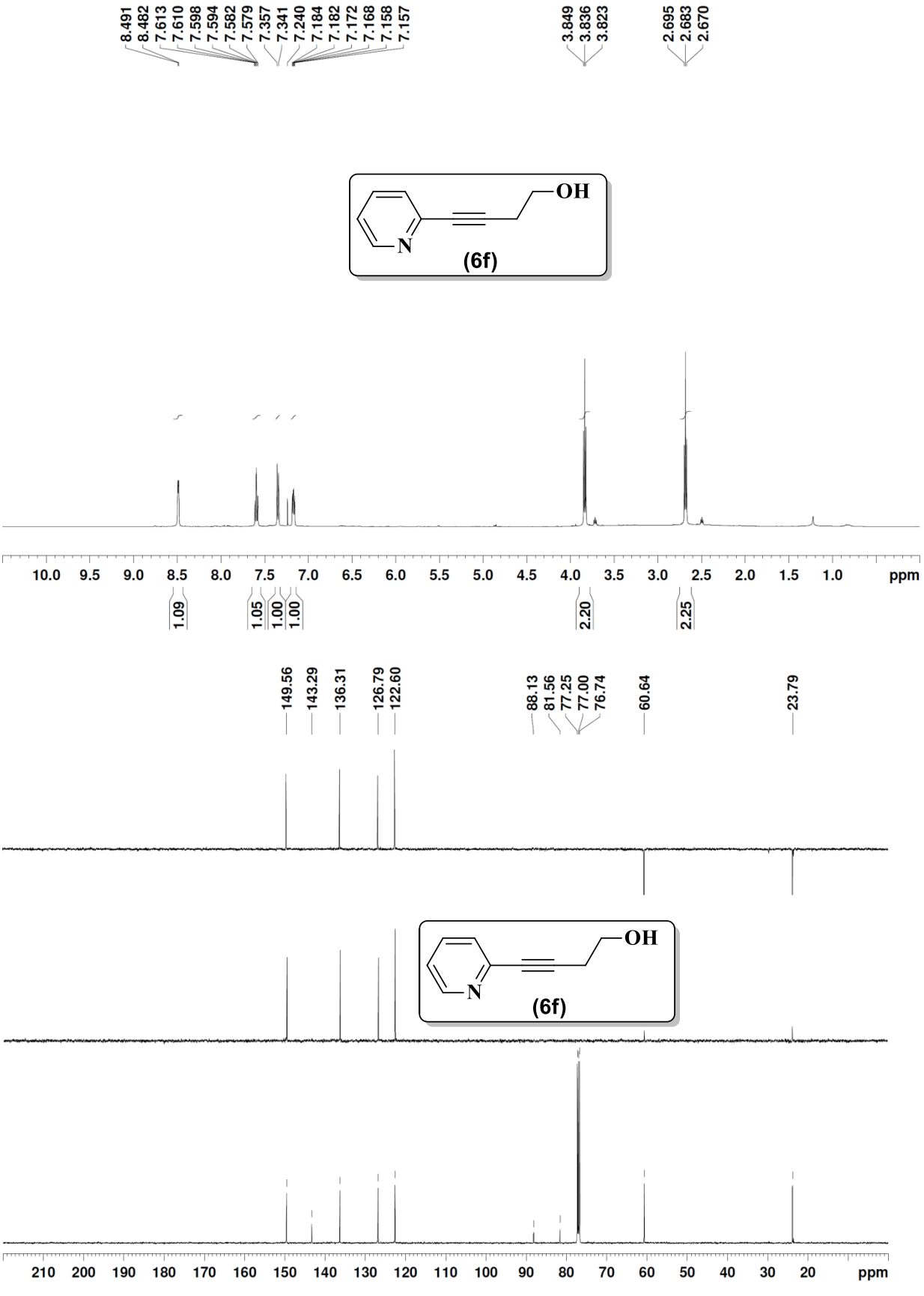

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
0.99
1.00
1.00
0.98
2.07
2.05
3.07
3.18
149.69
144.01
135.89
126.80
122.08
94.87
80.25
77.25
77.00
76.74
32.25
29.50
25.78
24.85

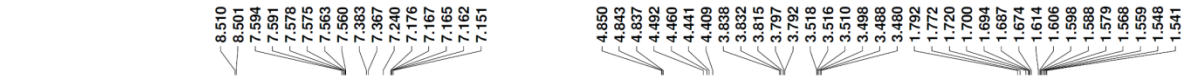

N
(6c)

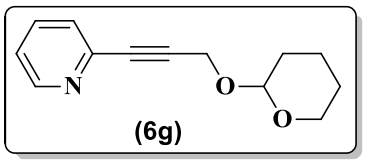

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

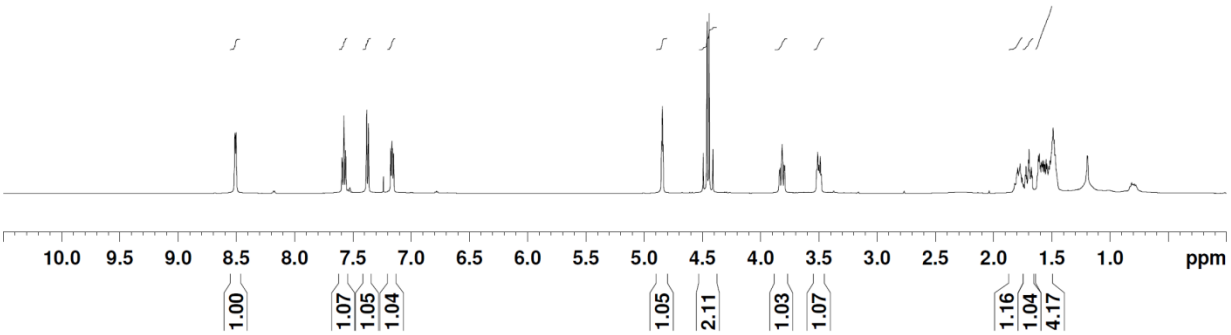

8.518
8.509
7.588
7.584
7.572
7.569
7.557
7.553
7.361
7.345
7.240
7.141
7.140
7.131
7.130
7.127
7.125
7.117
7.115
6.293
6.289
6.285
6.282
6.277
2.223
2.211
2.206
2.199
2.194
2.190
2.131
2.126
2.118
2.113
2.106
2.101
2.093
2.088
1.648
1.640
1.637
1.629
1.625
1.617
1.612
1.592
1.584
1.580
1.572
1.569
1.562
N
(6d)
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 ppm
0.99
1.05
1.01
1.00
1.03
2.20
2.07
2.12
2.06
149.81
143.84
137.17
135.92
126.79
122.16
120.08
91.28
86.18
77.25
77.00
76.74
28.80
25.78
22.15
21.34
N
(6d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

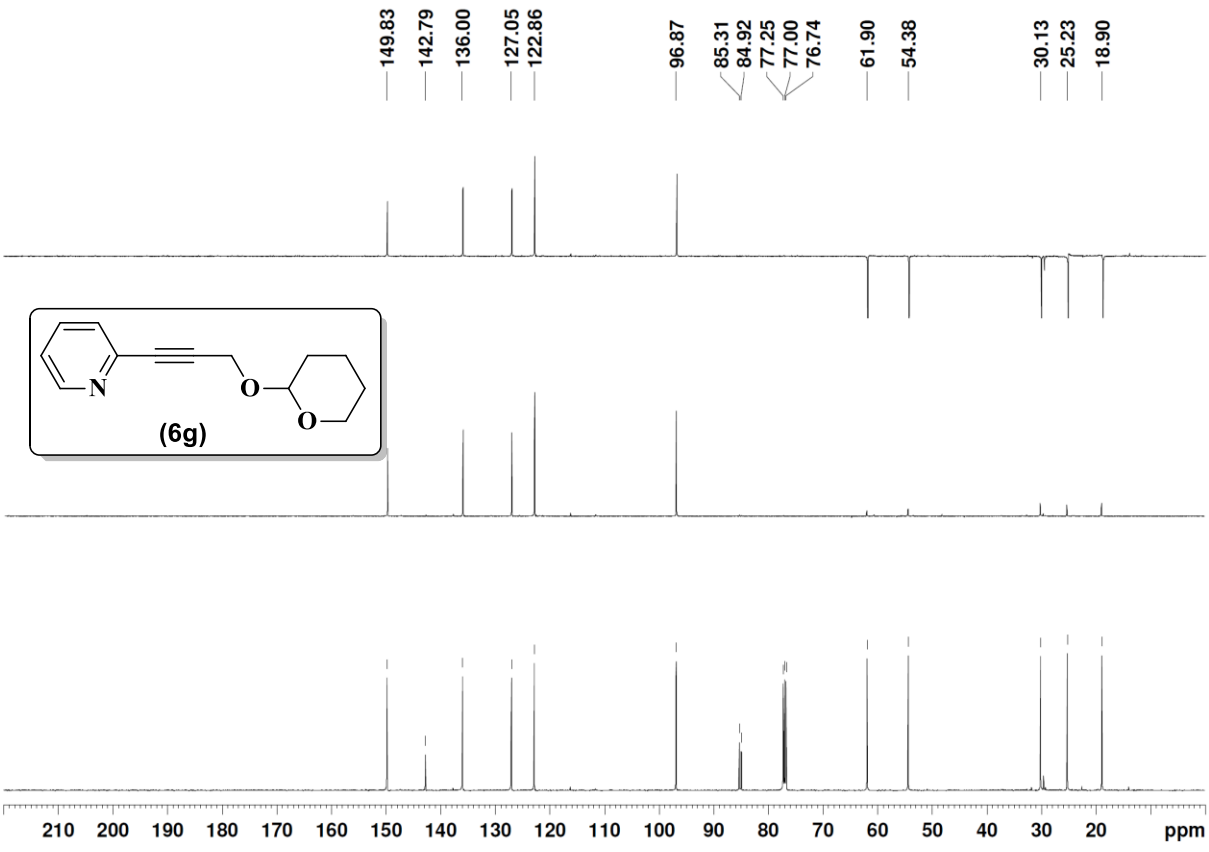

8.504
8.495
7.590
7.586
7.574
7.571
7.559
7.555
7.336
7.320
7.240
7.158
7.148
7.144
7.134
3.568
3.555
3.542
2.474
2.460
2.446
1.962
1.949
1.942
1.935
1.919
1.906
1.785
1.771
1.756
1.746
1.741
1.727
N
Cl
(6e)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.99
1.03
1.00
1.00
2.14
2.17
2.22
2.06
149.78
143.65
136.00
126.76
122.34
89.81
80.90
77.25
77.00
76.74
44.43
31.52
25.45
18.57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

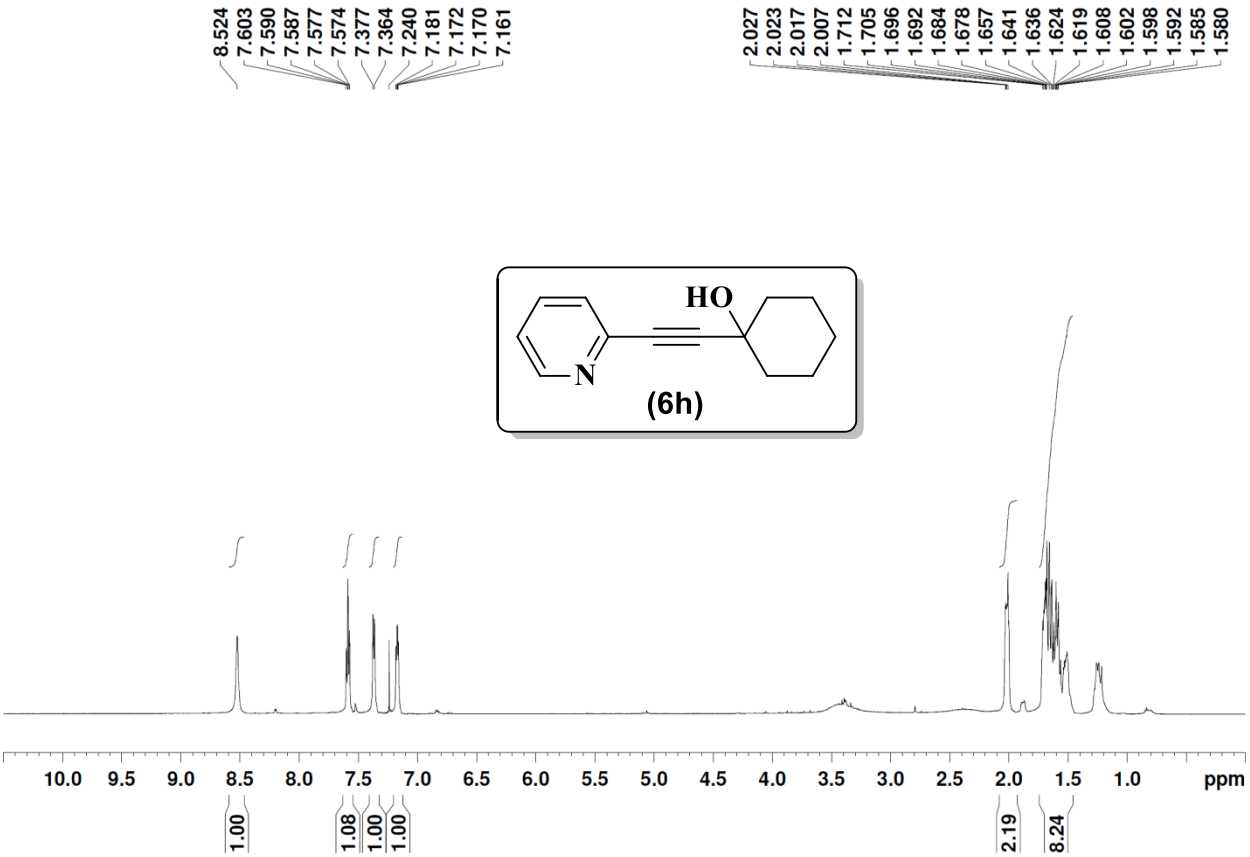

8.491
8.482
7.613
7.610
7.598
7.594
7.582
7.579
7.357
7.341
7.240
7.184
7.182
7.172
7.168
7.158
7.157
3.849
3.836
3.823
2.695
2.683
2.670
OH
N
(6f)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.09
1.05
1.00
1.00
2.20
2.25
149.56
143.29
136.31
126.79
122.60
88.13
81.56
77.25
77.00
76.74
60.64
23.79
OH
N
(6f)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

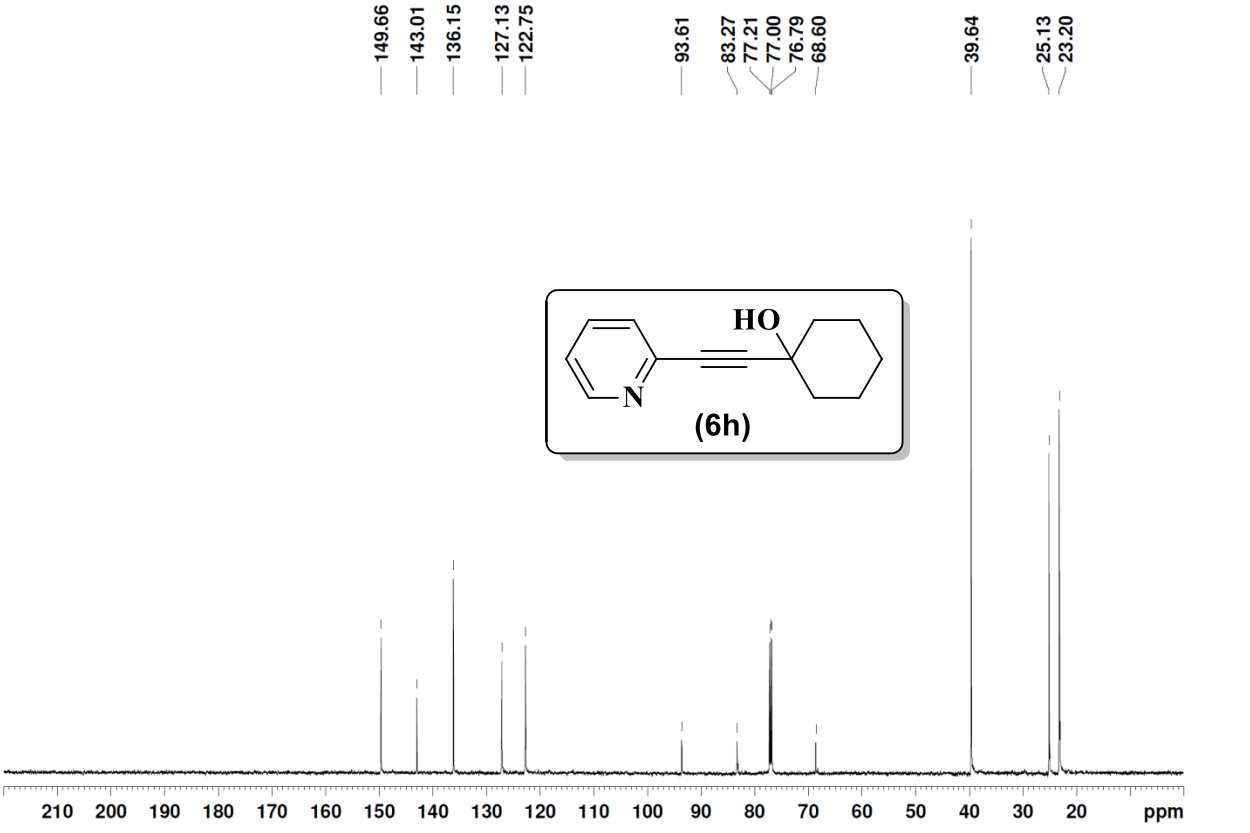

8.510
8.501
7.594
7.591
7.578
7.575
7.563
7.560
7.383
7.367
7.240
7.176
7.167
7.165
7.162
7.151
4.850
4.843
4.837
4.492
4.460
4.441
4.409
3.838
3.832
3.815
3.797
3.792
3.518
3.516
3.510
3.498
3.488
3.480
1.792
1.772
1.720
1.700
1.694
1.687
1.674
1.614
1.606
1.598
1.588
1.579
1.568
1.559
1.548
1.541

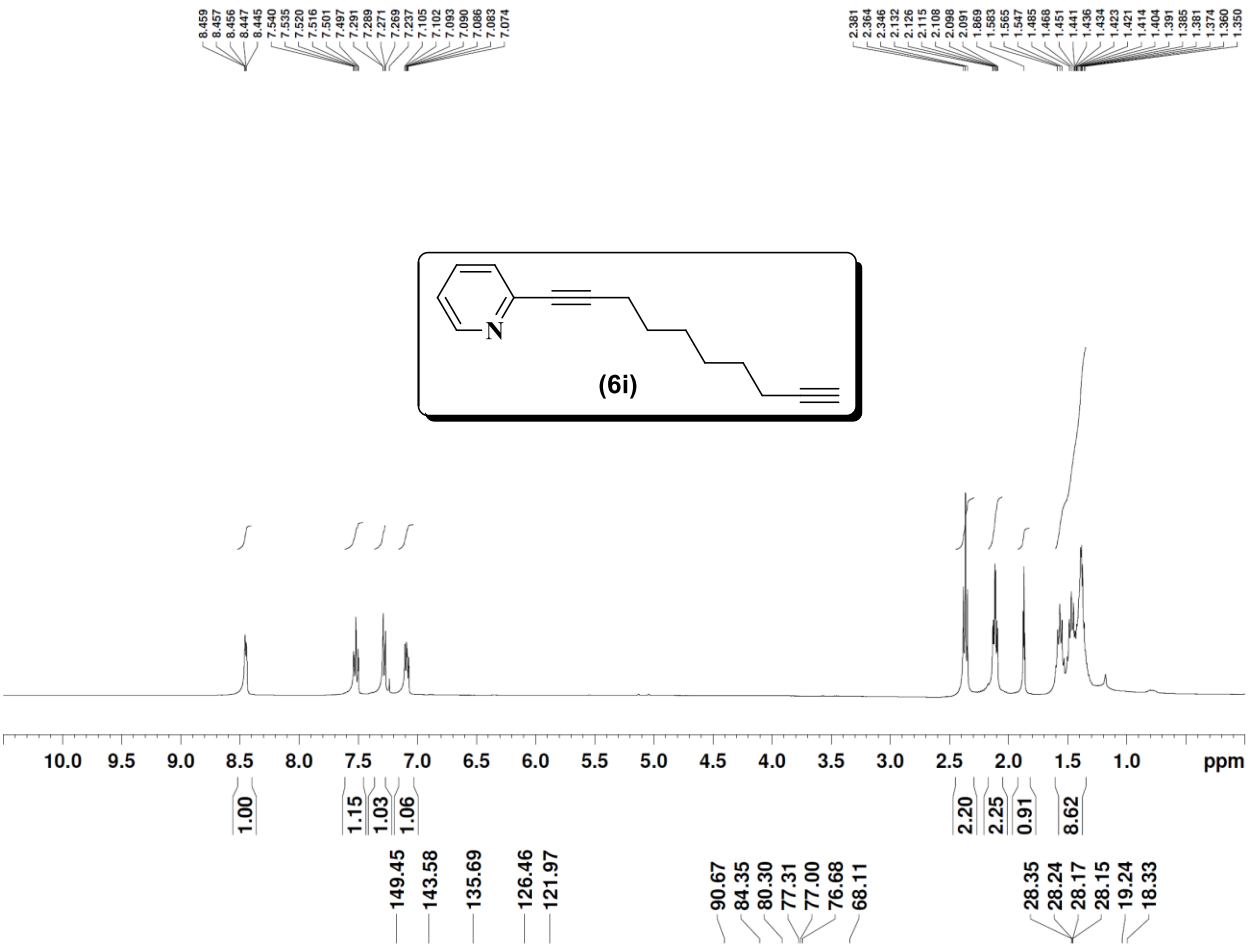

N
O
O
(6g)


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 ppm
1.00
1.07
1.05
1.04
1.05
2.11
1.03
1.07
1.16
1.04
4.17


149.83
142.79
136.00
127.05
122.86
96.87
85.31
84.92
77.25
77.00
76.74
61.90
54.38
30.13
25.23
18.90
N
O
O
(6g)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.524
7.603
7.590
7.587
7.577
7.574
7.377
7.364
7.240
7.181
7.172
7.170
7.161
2.027
2.023
2.017
2.007
1.712
1.705
1.696
1.692
1.684
1.678
1.657
1.641
1.636
1.624
1.619
1.608
1.602
1.598
1.592
1.585
1.580
HO
N
(6h)
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 ppm
1.00
1.08
1.00
1.00
2.19
8.24


149.66
143.01
136.15
127.13
122.75
93.61
83.27
77.21
77.00
76.79
68.60
39.64
25.13
23.20
HO
N
(6h)
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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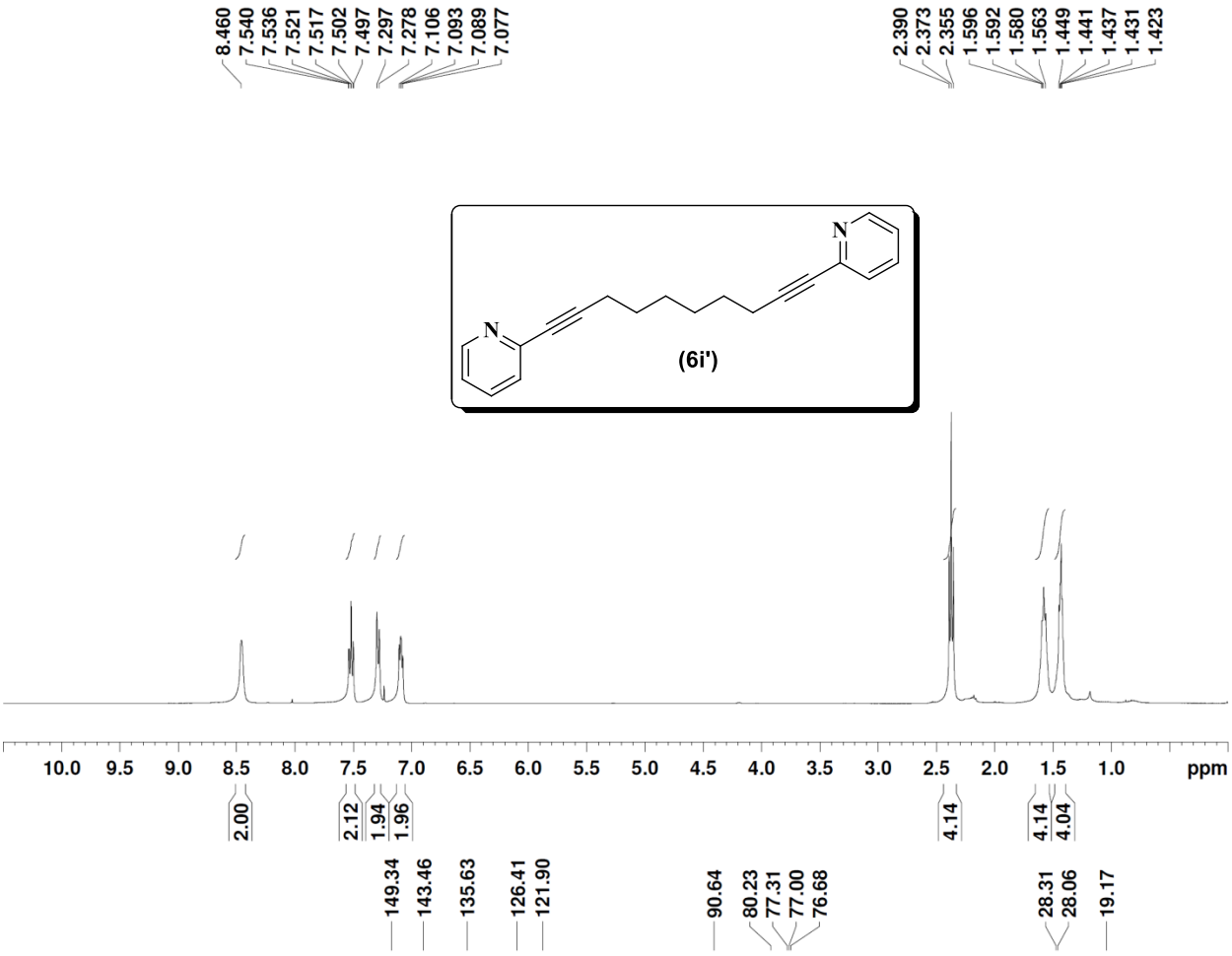
8.457
8.456
8.447
8.445
7.540
7.535
7.520
7.516
7.501
7.497
7.291
7.289
7.271
7.269
7.237
7.105
7.102
7.093
7.090
7.086
7.083
7.074
2.381
2.364
2.346
2.132
2.126
2.115
2.108
2.098
2.091
1.869
1.583
1.565
1.547
1.485
1.468
1.451
1.441
1.436
1.434
1.423
1.421
1.414
1.404
1.391
1.385
1.361
1.374
1.360
1.350
N
(6i)
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 ppm
1.00
1.15
1.03
1.06
2.20
2.25
0.91
8.62
149.45
143.58
135.69
126.46
121.97
90.67
84.35
80.30
77.31
77.00
76.68
68.11
28.35
28.24
28.17
28.15
19.24
18.33
N
(6i)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.460
7.540
7.536
7.521
7.517
7.502
7.497
7.297
7.278
7.106
7.093
7.089
7.077
2.390
2.373
2.355
1.596
1.592
1.580
1.563
1.449
1.441
1.437
1.431
1.423
N
N
(6i')
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 ppm
2.00
2.12
1.94
1.96
4.14
4.14
4.04
149.34
143.46
135.63
126.41
121.90
90.64
80.23
77.31
77.00
76.68
28.31
28.06
19.17

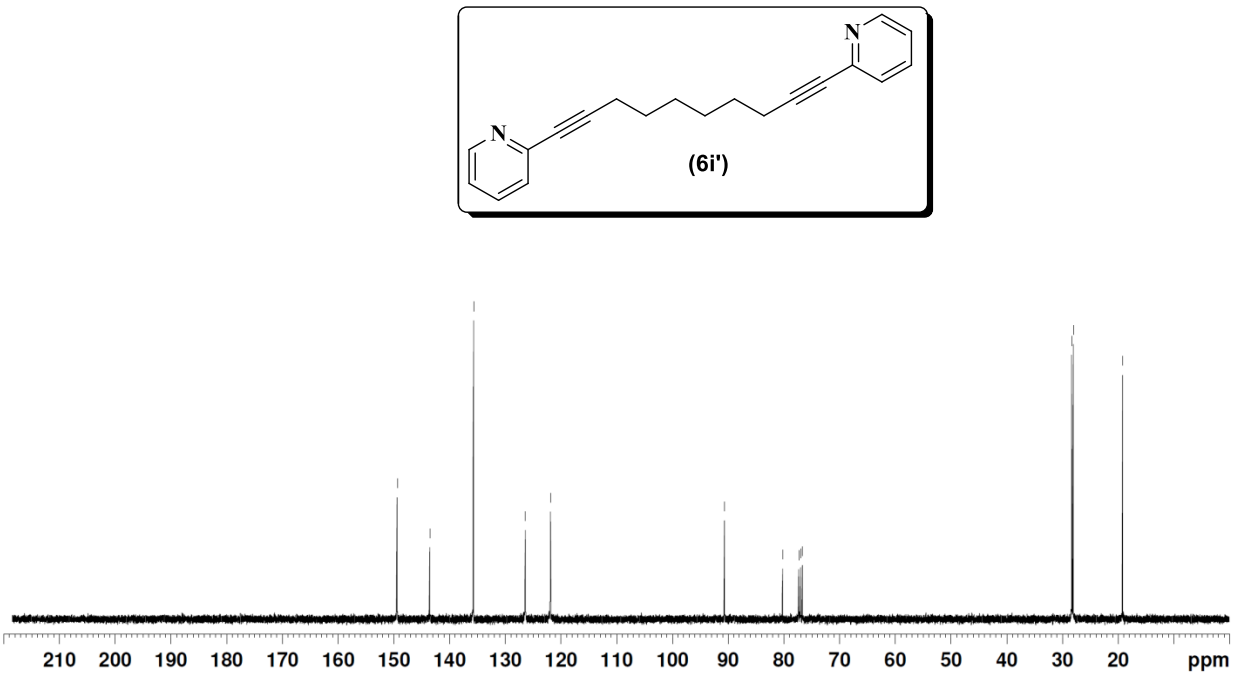

N
N
(6i')
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Figure S5: ORTEP diagram of compound **3j (CCDC No. 1813512)**

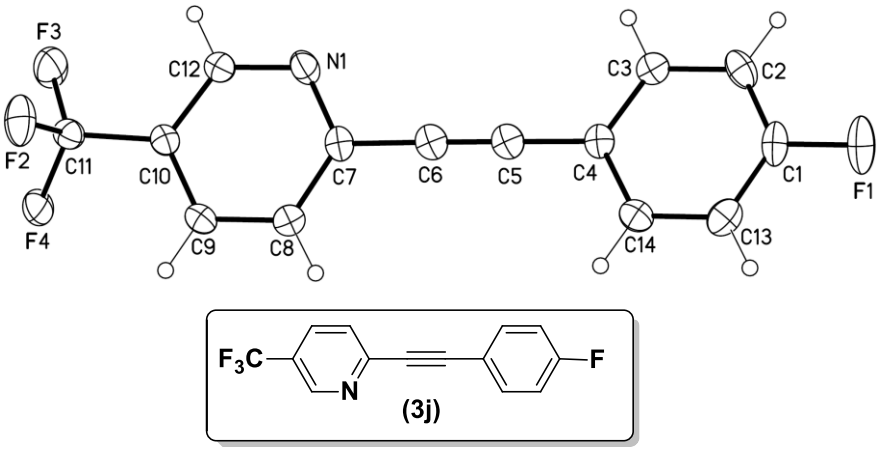


Table S1. Crystal data and structure refinement for 170634LT.

Identification code	170634LT	
Empirical formula	C14 H7 F4 N	
Formula weight	265.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.274(3) Å	a= 90°.
	b = 14.344(3) Å	b= 101.518(9)°.
	c = 6.1256(12) Å	g = 90°.
Volume	1142.8(4) $Å^3$	
Z	4	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	0.137 mm^{-1}	
F(000)	536	
Crystal size	0.15 x 0.07 x 0.02 mm^3	
Theta range for data collection	1.566 to 26.424°.	
Index ranges	-16<=h<=16, -17<=k<=17, -6<=l<=7	
Reflections collected	8087	
Independent reflections	2261 [R(int) = 0.0315]	
Completeness to theta = 25.242°	97.4 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.9485 and 0.7919
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2261 / 0 / 172
Goodness-of-fit on F^2	1.111
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1159
R indices (all data)	R1 = 0.0735, wR2 = 0.1476
Extinction coefficient	n/a
Largest diff. peak and hole	0.271 and -0.311 e.Å $^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for 170634LT. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	14098(1)	1204(1)	414(3)	46(1)
F(2)	5625(1)	2141(1)	7480(3)	40(1)
F(3)	5369(1)	706(1)	6625(3)	41(1)
F(4)	6162(1)	1087(1)	9900(2)	39(1)
N(1)	7967(1)	911(1)	4071(3)	26(1)
C(1)	13220(2)	1206(2)	1217(4)	28(1)
C(2)	12357(2)	798(2)	-31(4)	27(1)
C(3)	11463(2)	807(2)	794(4)	23(1)
C(4)	11436(2)	1218(2)	2843(4)	21(1)
C(5)	10514(2)	1217(2)	3733(4)	24(1)
C(6)	9748(2)	1215(2)	4484(4)	24(1)
C(7)	8832(2)	1229(1)	5403(4)	21(1)
C(8)	8850(2)	1565(1)	7554(4)	22(1)
C(9)	7954(2)	1579(2)	8360(4)	22(1)
C(10)	7057(2)	1267(2)	6980(4)	20(1)
C(11)	6057(2)	1297(2)	7746(4)	23(1)
C(12)	7109(2)	936(2)	4874(4)	25(1)
C(13)	13230(2)	1617(2)	3256(4)	28(1)
C(14)	12331(2)	1620(2)	4065(4)	24(1)

Table S3. Bond lengths [Å] and angles [°] for 170634LT.

F(1)-C(1)	1.352(3)
F(2)-C(11)	1.336(3)
F(3)-C(11)	1.332(3)
F(4)-C(11)	1.333(3)
N(1)-C(12)	1.328(3)
N(1)-C(7)	1.349(3)
C(1)-C(2)	1.375(3)
C(1)-C(13)	1.379(4)
C(2)-C(3)	1.379(3)
C(2)-H(4)	0.9500
C(3)-C(4)	1.393(3)
C(3)-H(7)	0.9500
C(4)-C(14)	1.396(3)
C(4)-C(5)	1.436(3)
C(5)-C(6)	1.197(3)
C(6)-C(7)	1.438(3)
C(7)-C(8)	1.398(3)
C(8)-C(9)	1.376(3)
C(8)-H(2)	0.9500
C(9)-C(10)	1.390(3)
C(9)-H(1)	0.9500
C(10)-C(12)	1.389(3)
C(10)-C(11)	1.494(3)
C(12)-H(3)	0.9500
C(13)-C(14)	1.380(3)
C(13)-H(5)	0.9500
C(14)-H(6)	0.9500
C(12)-N(1)-C(7)	117.1(2)
F(1)-C(1)-C(2)	118.7(2)
F(1)-C(1)-C(13)	118.5(2)
C(2)-C(1)-C(13)	122.9(2)
C(1)-C(2)-C(3)	118.3(2)
C(1)-C(2)-H(4)	120.9
C(3)-C(2)-H(4)	120.9

C(2)-C(3)-C(4)	120.8(2)
C(2)-C(3)-H(7)	119.6
C(4)-C(3)-H(7)	119.6
C(3)-C(4)-C(14)	119.0(2)
C(3)-C(4)-C(5)	121.2(2)
C(14)-C(4)-C(5)	119.7(2)
C(6)-C(5)-C(4)	179.7(3)
C(5)-C(6)-C(7)	178.9(2)
N(1)-C(7)-C(8)	122.6(2)
N(1)-C(7)-C(6)	116.3(2)
C(8)-C(7)-C(6)	121.1(2)
C(9)-C(8)-C(7)	119.4(2)
C(9)-C(8)-H(2)	120.3
C(7)-C(8)-H(2)	120.3
C(8)-C(9)-C(10)	118.3(2)
C(8)-C(9)-H(1)	120.9
C(10)-C(9)-H(1)	120.9
C(12)-C(10)-C(9)	118.6(2)
C(12)-C(10)-C(11)	120.9(2)
C(9)-C(10)-C(11)	120.4(2)
F(3)-C(11)-F(4)	106.96(18)
F(3)-C(11)-F(2)	106.28(18)
F(4)-C(11)-F(2)	106.41(18)
F(3)-C(11)-C(10)	112.37(18)
F(4)-C(11)-C(10)	112.41(18)
F(2)-C(11)-C(10)	111.98(18)
N(1)-C(12)-C(10)	124.0(2)
N(1)-C(12)-H(3)	118.0
C(10)-C(12)-H(3)	118.0
C(1)-C(13)-C(14)	118.2(2)
C(1)-C(13)-H(5)	120.9
C(14)-C(13)-H(5)	120.9
C(13)-C(14)-C(4)	120.7(2)
C(13)-C(14)-H(6)	119.6
C(4)-C(14)-H(6)	119.6

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x 10^3$) for 170634LT. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	36(1)	39(1)	73(1)	2(1)	36(1)	1(1)
F(2)	37(1)	32(1)	57(1)	8(1)	23(1)	13(1)
F(3)	27(1)	53(1)	45(1)	-18(1)	12(1)	-13(1)
F(4)	29(1)	69(1)	22(1)	13(1)	12(1)	9(1)
N(1)	28(1)	29(1)	23(1)	-2(1)	11(1)	-1(1)
C(1)	25(1)	22(1)	43(2)	6(1)	18(1)	4(1)
C(2)	39(1)	20(1)	28(1)	-1(1)	16(1)	4(1)
C(3)	24(1)	19(1)	26(1)	0(1)	4(1)	0(1)
C(4)	24(1)	15(1)	26(1)	4(1)	7(1)	2(1)
C(5)	29(1)	17(1)	28(1)	1(1)	7(1)	1(1)
C(6)	29(1)	18(1)	28(1)	1(1)	9(1)	0(1)
C(7)	24(1)	15(1)	26(1)	3(1)	10(1)	2(1)
C(8)	23(1)	18(1)	24(1)	1(1)	4(1)	-2(1)
C(9)	28(1)	20(1)	19(1)	-1(1)	6(1)	1(1)
C(10)	24(1)	17(1)	20(1)	4(1)	6(1)	2(1)
C(11)	25(1)	23(1)	21(1)	0(1)	5(1)	1(1)
C(12)	23(1)	30(1)	21(1)	-2(1)	5(1)	-1(1)
C(13)	24(1)	23(1)	36(2)	4(1)	4(1)	-3(1)
C(14)	30(1)	21(1)	22(1)	2(1)	6(1)	0(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2}x 10 ^{3}) for 170634LT.

	x	y	z	U(eq)
H(4)	12376	517	-1427	33
H(7)	10858	530	-45	28
H(2)	9475	1781	8449	26
H(1)	7949	1796	9823	26
H(3)	6494	714	3953	30
H(5)	13840	1891	4083	34
H(6)	12322	1898	5468	29