Supporting Information

Visible Light-mediated Copper Catalyzed Regioselective Diamination of Terminal Alkynes at Room Temperature: A Facile Synthesis of Substituted Imidazo[1,2-α]pyridine

Vaibhav Pramod Charpe, Mahima Gupta, and Kuo Chu Hwang*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, R. O. C.

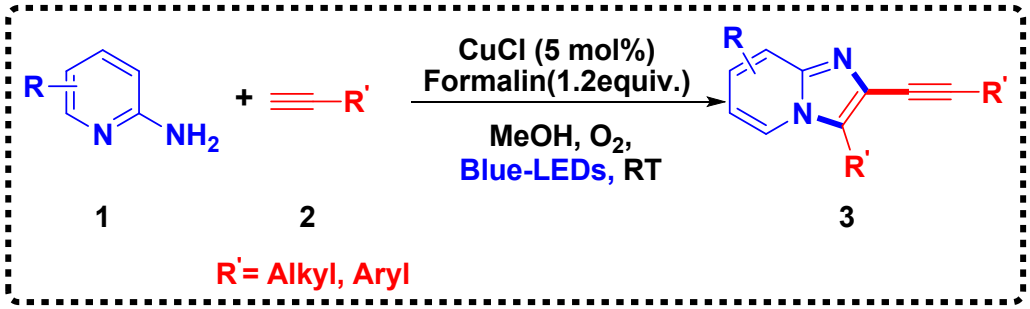
E-mail: kchwang@mx.nthu.edu.tw

Table of contents

1. Experimental section

General: All reactions were conducted in oven-dried glasswares using a blue light-emitting diode (LED) array (power density: 150 mW/cm^2 at 460 nm) as the visible-light source under an air (or O_2) atmosphere. 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 700/400 and 175/100 MHz, respectively, using deuterated $CDCl_3$ as a solvent. 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 solvent peaks (at δ 7.24 or 2.50 and δ 77.00 or 39.51 ppm, respectively) were used as the internal references.

A. ***General procedure for the synthesis of substituted imidazo[1,2-α]pyridine*:**

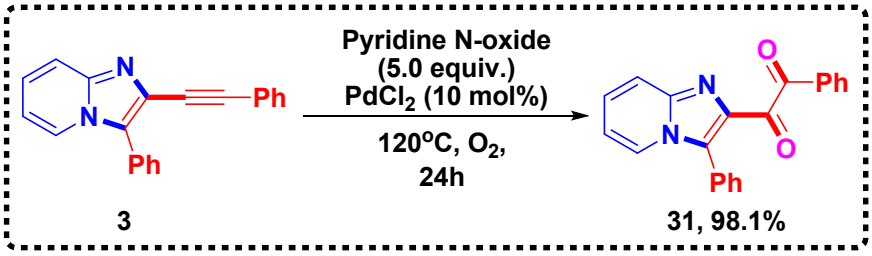


Scheme S1: Current photochemical process for the synthesis of substituted imidazo[1,2-α]pyridine.

To a dry test tube (20 mL) containing 5 mol% CuCl and 2-aminopyridine (0.5 mmol) was added 5 mL of MeOH, followed by the addition of Formalin (37% in water) (0.6 mmol). The solution was stirred for 1 min and then terminal alkyne (1.1 mmol) was added to the solution. The reaction mixture was then irradiated with blue LEDs (150 mW/cm^2 at 460 nm) under oxygen atmosphere (O_2 balloon) at room temperature (25-28 ^{o}C) until completion of the reaction (monitored by TLC). The reaction mixture was then concentrated and the residue was purified by column chromatography on silica gel.

B. Procedures for Synthetic transformations[S1]:

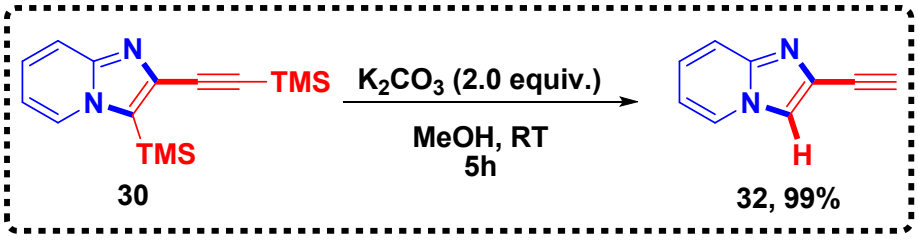
1) Synthesis of 1-phenyl-2-(3-phenylimidazo[1,2-a]pyridin-2-yl)ethane-1,2-dione



Scheme S2: Reaction scheme for the synthesis of 1-phenyl-2-(3-phenylimidazo[1,2-a]pyridin-2-yl)ethane-1,2-dione.

Procedure: A 50 mL round bottom flask was loaded with 295 mg of compound **3** (1.0 mmol). Followed by addition of 17.7 mg (10 mol%) of $PdCl_2$ and 475.5 mg of pyridine-N-oxide (5.0 equiv.). The reaction mixture was then stirred at 120°C for 24 hours under oxygen atmosphere. After completion of reaction (monitored by TLC), reaction mixture then extracted with DCM (2 x 50 mL) and the organic phase was wash with water, brine, dried over Na_2SO_4, and concentrated in vacuum to obtain the residue (product). This residue then purified by column chromatography on silica gel to collect the product **31** in 320 mg (98.1% yield).

2) Synthesis of 2-ethynylimidazo[1,2-α]pyridine



Scheme S3: Reaction scheme for the synthesis of 2-ethynylimidazo[1,2-α]pyridine.

Procedure: In a 50 mL round bottom flask, 143 mg (0.5 mmol) of compound 3**0** was dissolved in 10 mL methanol. The mixture was stirred for 5 h at room temperature. After completion of reaction (monitored by TLC), reaction mixture then extracted with EA (2 x 50 mL) and the organic phase was wash with water, brine, dried over Na_2SO_4, and concentrated in vacuum to directly afford the pure product **32** in 70.3 mg (99.02% yield).

C. Preparation of copper(I)-phenylacetylide:[S2,S3] CuI (1.0 g, 5.0 mmol) was dissolved in ammonium hydroxide to form a blue-colored solution. While stirring, phenylacetylene (0.5 g, 5.1 mmol in 50 mL ethanol) was added drop wise to the solution. The system was allowed to stand for 15 min to form a yellow precipitate suspension. The precipitate was filtered out and washed with water, ethanol, and diethyl ether, three times each. The solid was vacuum-dried, and a bright yellow solid was obtained in 64% yield. The spectroscopic data: IR (KBr, cm^{-1}) [S4] 1929 (C≡C), 1596, 1568; UV-Vis λ_{abs} = 472 nm.

The bond order in C≡C triple bond of copper phenylacetylide[S4] = 2.63, which is due to the electron-withdrawing character of Cu(I) in copper phenylacetylide and thus weakening of the adjacent C≡C triple bond.

2. Mechanistic studies

A) UV-visible spectra:

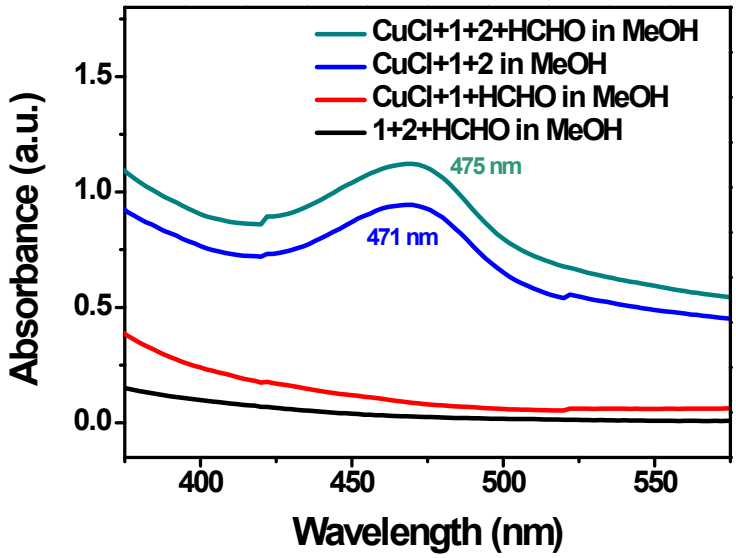


Figure S1. UV-visible absorption spectra of the reaction mixture in MeOH.

B) EPR measurements:

EPR spectra were recorded at room temperature on a Bruker ESP-300E (X band, 9.8 GHz) with parameters setting as shown below: receiver gain= 30 n; receiver phase= 0 deg; receiver harmonic=1; field modulation frequency=100000 Hz; microwave frequency[Hz]= $9.660469e^{+09}$; 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 (2-aminopyridine (**1**), Phenylacetylene (**2**), formalin, CuCl, O_2) in MeOH 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 S2** is corresponding to DMPO-OO(H). This result indicates that superoxide free radical was formed in the reaction. This result indicates that photoexcited copper(I)-phenylacetylide undergoes single electron transfer to O_2 and generates superoxide free radical upon blue LEDs irradiation.

EPR spectra of the reaction mixture after blue LEDs irradiation

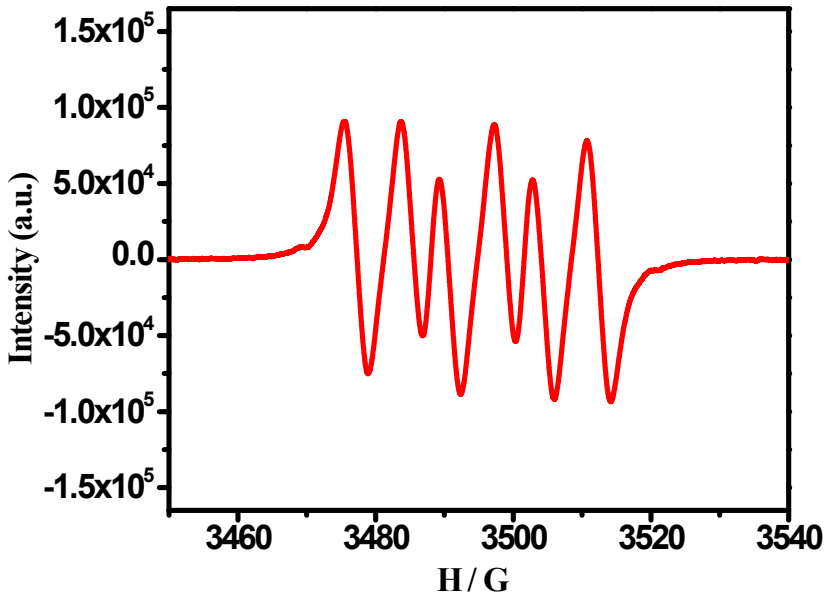
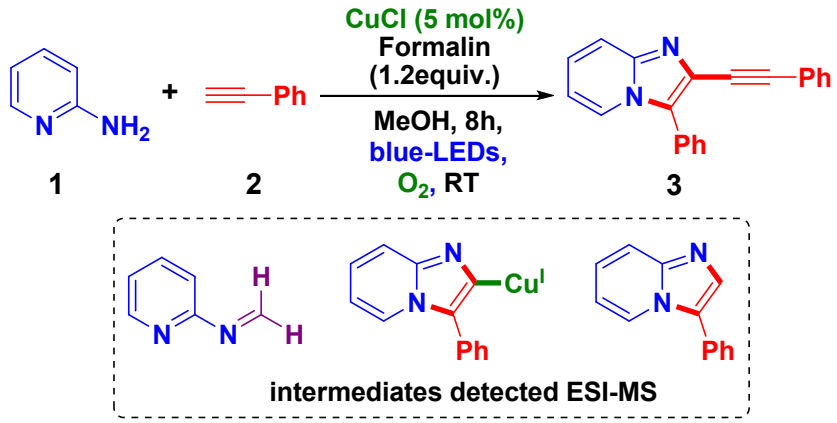


Figure S2: EPR spectra of the reaction mixture: 2-aminopyridine (**1**) (0.5 mmol), phenylacetylene (**2**) (1.1 mmol), formalin (1.2 equiv.) and 5 mol% of CuCl in MeOH (5 mL), 0.5 mL of this reaction solution was taken out into a small vial, followed by the addition of 0.01 mL of DMPO (5 x 10^{-2} M). The mixture was irradiated with blue LEDs at room temperature under an oxygen atmosphere (1 atm) for 30 minutes. The reaction mixture was then analyzed by EPR. The 6 classical peaks are corresponding to DMPO-OO(H).

C) Detection of intermediates by ESI-MS:

The standard reaction was performed for short period of 8 h to detect the reaction intermediate, and the reaction mixture was then analyzed by ESI-MS. The possible intermediates were detected by mass. The detected intermediates are shown in **Scheme S4** below.



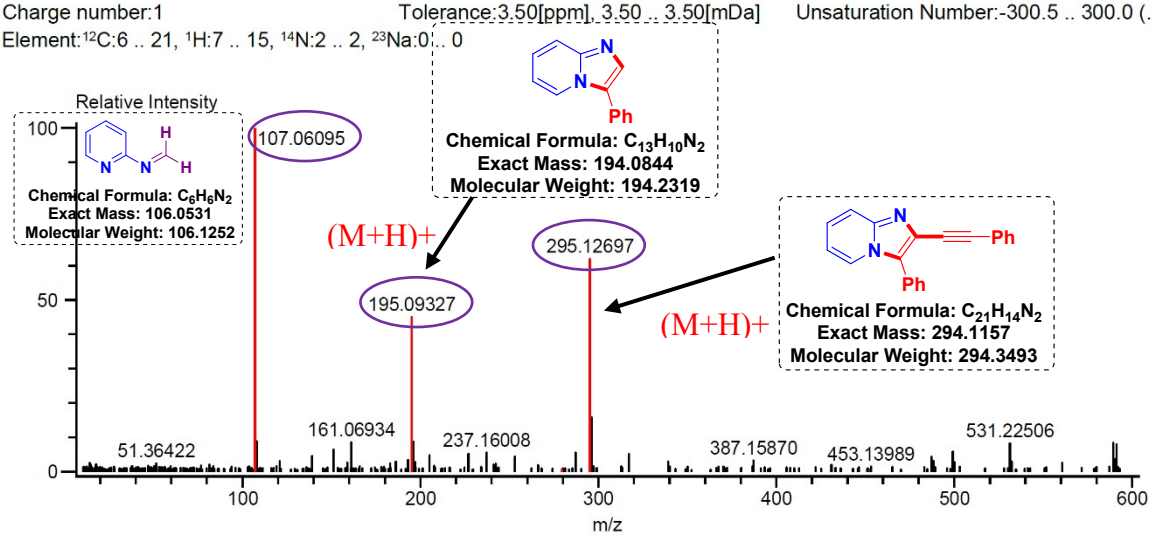
Scheme S4: Detection of intermediates by ESI-MS.

ESI Mass Data

Data:AP-65
Comment:
Description:
Ionization Mode:ESI+
History:Average(MS[1] 0.40..0.43)

Acquired:7/3/2023 4:29:03 PM
Operator:AccuTOF
m/z Calibration File:20230608-TFANa_...
Created:10/13/2023 3:17:23 PM
Created by:AccuTOF

Charge number:1
Tolerance:3.50[ppm], 3.50 .. 3.50[mDa]
Unsaturation Number:-300.5 .. 300.0 (...
Element:^{12}C:6 .. 21, ^{1}H:7 .. 15, ^{14}N:2 .. 2, ^{23}Na:0 .. 0



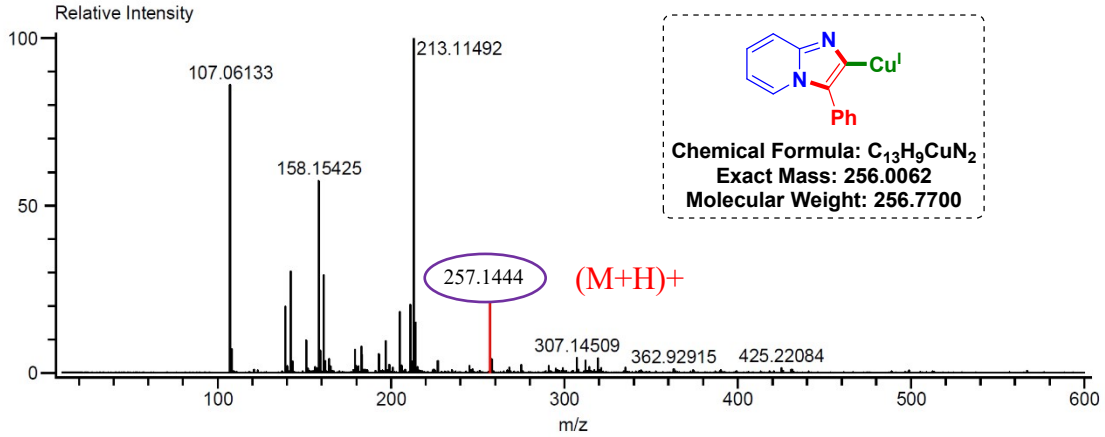
Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula
107.06095	21200.81	107.06092	0.03	0.26	$^{12}C_6{}^{1}H_7{}^{14}N_2$
195.09327	9523.02	195.09222	1.05	5.36	$^{12}C_{13}{}^{1}H_{11}{}^{14}N_2$
279.48786	135.16				
295.12697	13110.94	295.12352	3.45	11.68	$^{12}C_{21}{}^{1}H_{15}{}^{14}N_2$

ESI Mass Data

Data:AP-66R
Comment:
Description:
Ionization Mode:ESI+
History:Average(MS[1] 0.22..0.82)

Acquired:8/23/2023 5:12:01 PM
Operator:AccuTOF
m/z Calibration File:20230710-TFANa_...
Created:10/13/2023 5:07:50 PM
Created by:AccuTOF

Charge number:1 Tolerance:200.00[ppm], 200.00 .. 200.... Unsaturation Number:-300.5 .. 300.0 (...
Element:^{12}C:13 .. 13, ^{1}H:0 .. 11, ^{63}Cu:1 .. 1, ^{14}N:2 .. 2, ^{23}Na:0 .. 1

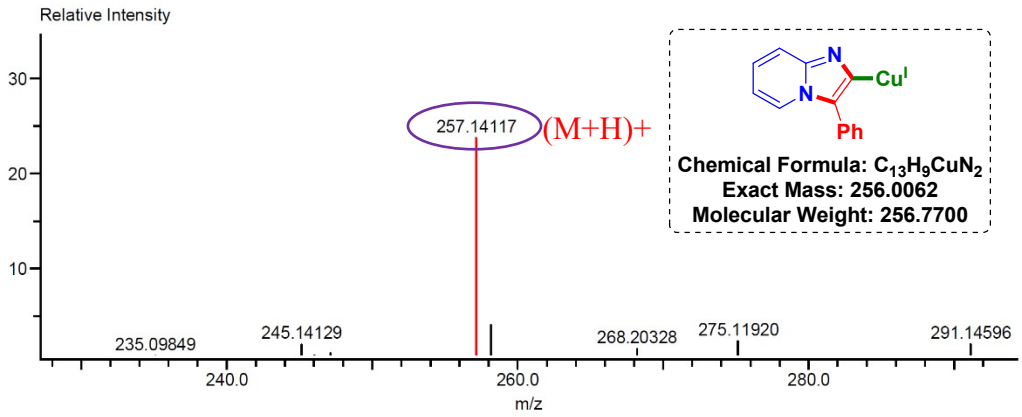


Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula
257.14117	34725.51	257.01400	127.17	494.78	$^{12}C_{13}{}^{1}H_{10}{}^{63}Cu_{1}{}^{14}N_{2}$

Data:AP-66R
Comment:
Description:
Ionization Mode:ESI+
History:Average(MS[1] 0.22..0.82)

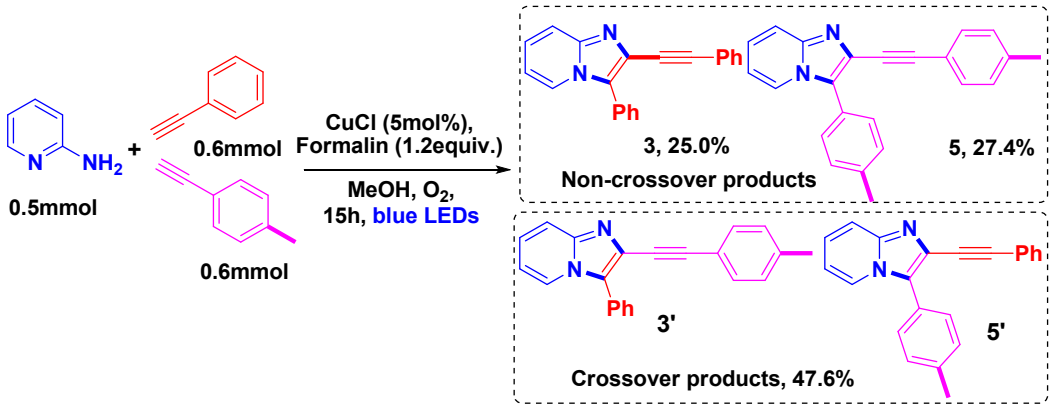
Acquired:8/23/2023 5:12:01 PM
Operator:AccuTOF
m/z Calibration File:20230710-TFANa_...
Created:10/13/2023 5:07:50 PM
Created by:AccuTOF

Charge number:1 Tolerance:200.00[ppm], 200.00 .. 200.... Unsaturation Number:-300.5 .. 300.0 (...
Element:^{12}C:13 .. 13, ^{1}H:0 .. 11, ^{63}Cu:1 .. 1, ^{14}N:2 .. 2, ^{23}Na:0 .. 1



Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula
257.14117	34725.51	257.01400	127.17	494.78	$^{12}C_{13}{}^{1}H_{10}{}^{63}Cu_{1}{}^{14}N_{2}$

D) Crossover experiment:



Scheme S5: Crossover experiment

In a crossover experiment, a mixture of alkynes, phenylacetylene (0.6 mmol) and 1-ethynyl-4-methylbenzene (0.6 mmol) was reacted with 2-aminopyridine (0.5 mmol) in the presence of formalin, CuCl and in MeOH solvent (5 mL) under visible light irradiation for 15 h. This reaction generated a mixture of non-crossover products **3** and **5** in 25% and 27.4% yields, respectively. Whereas crossover products **3'** and **5'** were obtained in an overall yield of 47.6%. Yields of these crossover experiment products were calculated based on the mass data, as the purification of this mixture of products is quite difficult.

This experiment concludes that (a) copper phenylacetylide is responsible for the formation of the desired product; (b) electron-donating terminal alkynes favours the formation of imidazopyridine product in slightly higher yield than that of electron-neutral alkynes (the product **5** was formed in slightly higher yield than that of the product **3**); and (c) we anticipate that the formation of crossover products dominate due to the electronegativity difference between terminal alkynes.

ESI Mass Data

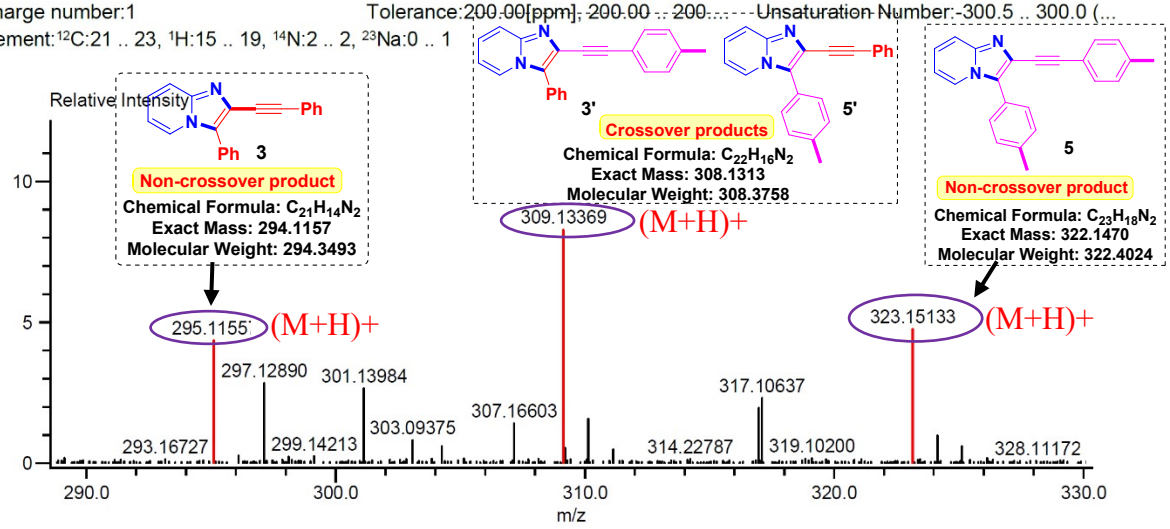
Data:AP-95
Comment:
Description:
Ionization Mode:ESI+
History:Average(MS[1] 0.23..1.01)

Acquired:10/12/2023 11:50:37 AM
Operator:AccuTOF
m/z Calibration File:20231012-TFANa_...
Created:10/13/2023 5:03:59 PM
Created by:AccuTOF

Charge number:1
Element:^{12}C:21 .. 23, ^{1}H:15 .. 19, ^{14}N:2 .. 2, ^{23}Na:0 .. 1

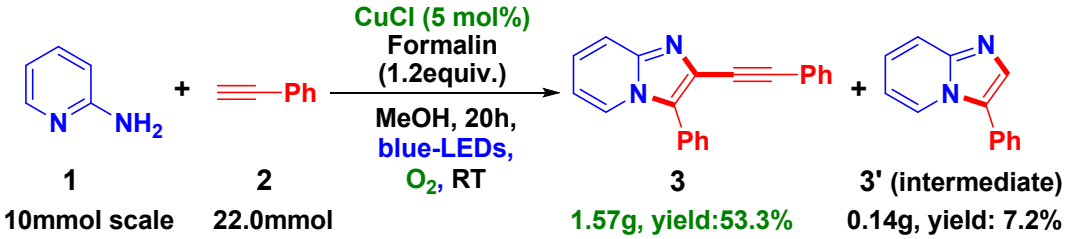
Tolerance:200.00[ppm], 200.00 .. 200....

Unsaturation Number:-300.5 .. 300.0 (...



Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula
295.11557	1016.66	295.12352	-7.95	-26.94	$^{12}C_{21}{}^{1}H_{15}{}^{14}N_2$
309.13369	1933.46	309.13917	-5.48	-17.74	$^{12}C_{22}{}^{1}H_{17}{}^{14}N_2$
323.15133	1112.12	323.15482	-3.49	-10.81	$^{12}C_{23}{}^{1}H_{19}{}^{14}N_2$

3. A gram scale reaction for the synthesis of compound 3.



Scheme S6: A gram scale reaction for the synthesis of compound **3.**

To a dry round bottom flask (50 mL, with magnetic stir bar) containing 5 mol% CuCl and 2-aminopyridine **(1)** (0.94 g, 10 mmol) was added 20 mL of MeOH, followed by the addition of Formalin (37% in water) (12.0 mmol). The solution was stirred for 1 min and then phenylacetylene **(2)** (2.25 g, 22 mmol) was added to the solution. The reaction mixture was then irradiated for 20 h (until completion of the reaction, monitored by TLC) with blue LEDs (150 mW/cm^2 at 460 nm) under oxygen atmosphere (O_2 balloon) at room temperature (25-28 ^oC). The reaction mixture was then concentrated and the residue was purified by column chromatography on silica gel. Solvent system: Ethyl acetate (EA): n-Hexane in the ratio of 1:9 to 2:8.

4. Fluorescence quantum yield calculations

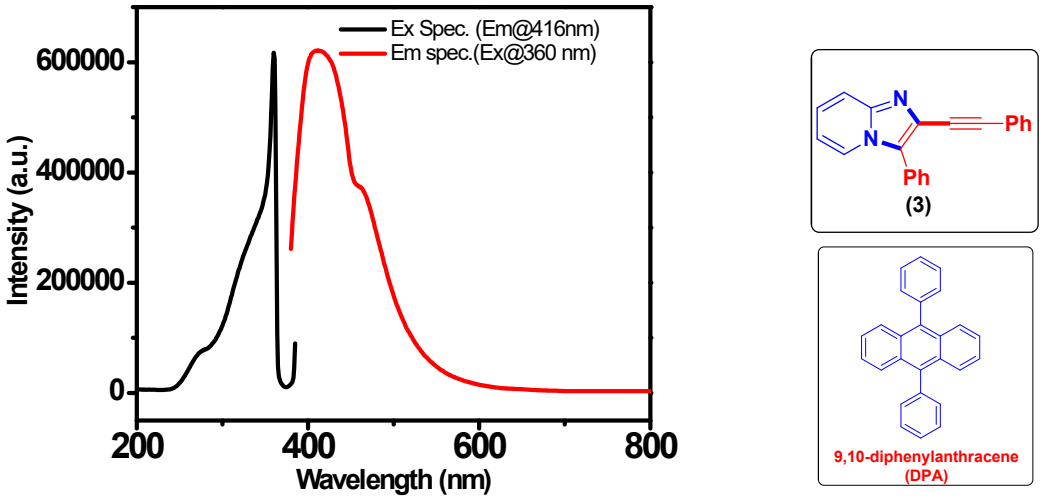


Figure S3: Emission and excitation spectra of the compound **3.**

Fluorescence quantum yield measurement

2, 3- disubstituted imidazo[1,2-α]pyridine (only aromatic substituents) compounds show blue fluorescence upon UV light photoexcitation, and thus, we have measured the fluorescence quantum yield (Φ_F) for the compound **3** (3-phenyl-2-(phenylethynyl)imidazo[1,2-α]pyridine) using 9,10- diphenylanthracene (DPA)[S5] as a fluorescence standard reference in methanol.

$$\mathbf{Area_{DPA(425\text{-}525nm)} = Ab_{DPA} \times I_{300} \times \Phi_{F,DPA}} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$Area_{DPA(425\text{-}525nm)} = 75531211$$

$$Ab_{300nn} = 0.043$$

$$I_{300nm} = 2\ mW/cm^2$$

$$\mathbf{\Phi_{F,DPA} = 0.9}$$

Similar equation can be derived for the compound **3**

$$\mathbf{Area_{Comp\ 3(425\text{-}525nm)} = Ab_{360} \times I_{360} \times \Phi_{Comp\ 3}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$Area_{\ Comp\ \mathbf{3}(425\text{-}525nm)} = 60119162.5$$

$$Ab_{360} = 0.08$$

$$I_{360} = 2\ mW/cm^2$$

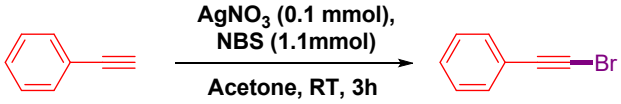
After substituting all the parameters and dividing equations (1)/(2), one can obtain the value of $\Phi_{F\ Comp\ \mathbf{3}}$ to be

$$\mathbf{\Phi_{F.Comp\ 3} = 0.385}$$

5. Evaluation of E-factor of the reported thermal method[S6]

A. Evaluation of **E-factor** of the reported thermal reaction **(Step 1)**

Reported thermal method:Step 1



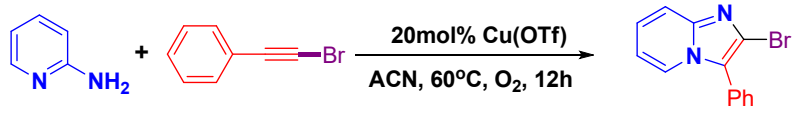
Reactant 1	**Phenylacetylene**	**0.102g**	**1.0 mmol**	**FW 102.13**
Reactant 2	**N-bromosuccinimide (NBS)**	**0.196g**	**1.1 mmol**	**FW 177.98**
Solvent	**Acetone (15mL)**	**11.76g**	**----**	**----**
Auxiliary	**----**	**----**	**----**	**----**
Product	**(bromoethynyl)benzene**	**0.179g**	**0.99 mmol**	**FW 181.02**

Product yield = 99%

$$\text{E-factor} = \frac{0.102 + 0.196 + 11.76 - 0.179}{0.179\text{g}} = 66.36 \text{ Kg waste/ 1 Kg product}$$

B. Evaluation of **E-factor** of the reported thermal reaction **(Step 2)**

Reported thermal method:Step 2



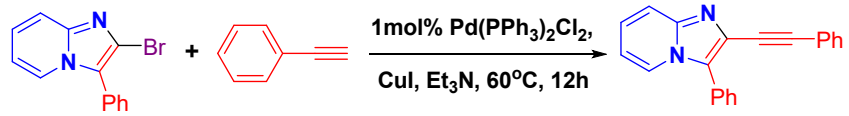
Reactant 1	**2-aminopyridine**	**0.028g**	**0.3 mmol**	**FW 94.11**
Reactant 2	**(bromoethynyl)benzene**	**0.036g**	**0.2 mmol**	**FW 181.02**
Solvent	**ACN (2mL)**	**1.57g**	**----**	**----**
Auxiliary	**----**	**----**	**----**	**----**
Product	**2-bromo-3-phenylimidazo[1,2-*a*]pyridine**	**0.0437g**	**0.16 mmol**	**FW 273.12**

Product yield = 80%

$$\text{E-factor} = \frac{0.028 + 0.036 + 1.57 - 0.0437}{0.0437\text{g}} = 36.39 \text{ Kg waste/ 1 Kg product}$$

C. Evaluation of **E-factor** of the reported thermal reaction **(Step 3)**

Reported thermal method:Step 3

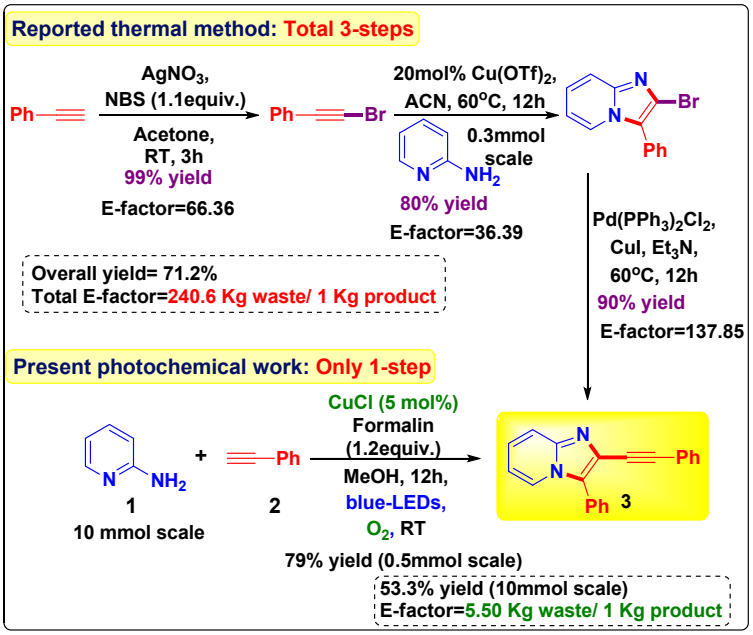


Reactant 1	**2-bromo-3-phenylimidazo [1,2-*a*]pyridine**	**0.0546g**	**0.2 mmol**	**FW 273.12**
Reactant 2	**Phenylacetylene**	**0.0306g**	**0.3 mmol**	**FW 102.13**
Solvent	**Triethylamine (10mL)**	**7.26g**	**----**	**----**
Auxiliary	**----**	**----**	**----**	**----**
Product	**3-phenyl-2-(phenylethynyl)imidazo[1,2-*a*]pyridine**	**0.0529g**	**0.18 mmol**	**FW294.34**

Product yield = 90%

$$\textbf{E-factor} = \frac{0.0546 + 0.0306 + 7.26 - 0.0529}{0.0529\text{g}} = \textbf{137.85 Kg waste/ 1 Kg product}$$

E-factor is defined as (the weight, kg, of wastes produced)/(per kg product formed). From the green organic synthetic chemistry point of view, the E-factor is the crucial parameter of the green chemistry metrics as it shows the amount of waste generated in a reaction. To get a better understanding of the importance of the current green photochemical process, we have evaluated and compared the E-factor of the reported three-step thermal method with our current single-step photochemical method for the synthesis of substituted imidazo[1,2-α]pyridine (Product 3). The detailed comparison of the reported thermal method and our current photochemical method based on the number of steps, overall yield, and E-factor is presented in the **Scheme S7.**



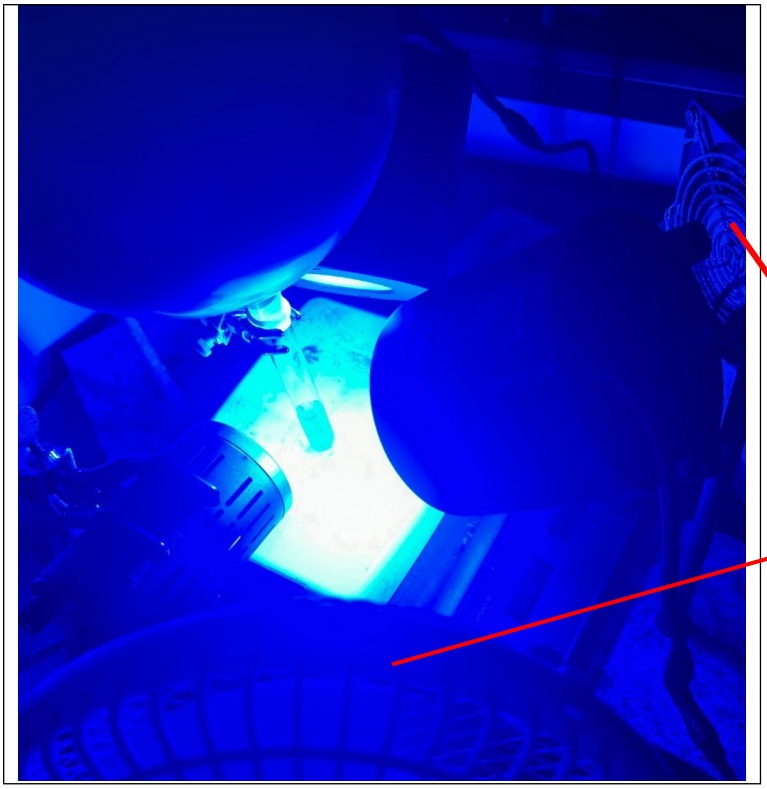
Scheme S7: Synthesis of 2, 3-disubstituted imidazo[1,2-α]pyridines by the thermal and the current photochemical process.

The results showed that the thermal process formed product **3** in three steps with an overall yield of 71.2% (0.2mmol scale) and an E-factor of 240.6. On the contrary, the current green protocol formed product 3 in only a single step with a yield of 79% on 0.5 mmol scale and 53.3% on 10.0mmol scale with an E-factor of only 5.5. The current photochemical method forms imidazo[1,2-α]pyridine product in a single step with an excellent E-factor (43.7 times better than that of the reported thermal method) (See ESI for details) and in a good yield of 79%. In addition, the thermal process uses toxic brominating reagents (NBS), toxic solvents (ACN, Et_3N), and expensive metal catalysts (Ag and Pd), which adversely affect human health and the environment. On the other hand, the present photochemical method solely uses inexpensive CuCl as a catalyst, molecular O_2 as an oxidant, formalin as an additive (which on oxidation undergoes decarboxylation), commercially available starting materials, and low-energy visible light to form substituted imidazo[1,2- a]pyridine products. Thus, in terms of the chemicals used, the easiness of operation, and friendliness to the ecosystem, our photoredox method is better than the reported thermal method.

6. Photochemical reaction setup

Light source: Kessil lights A360N/A360W (Power density: 150 mW/cm^2 at 460 nm)

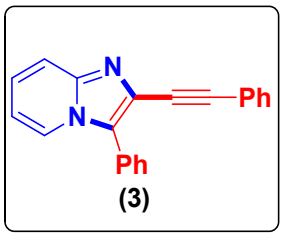
Please visit this link for more details: www.kessil.com



All light reactions were conducted in air-conditioned room with a cooling fan around blue-LED's to maintain the reaction temperature within 25-28 ^{o}C.

7. Spectroscopic Data

3-phenyl-2-(phenylethynyl)imidazo[1,2-a]pyridine (3)



(3)

The product obtained as a pale yellow oil in 79.3% (116.7 mg) yield.

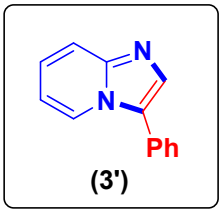
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J*= 7.2 Hz, 1H), 7.68-7.67 (m, 2H), 7.57-7.49 (m, 3H), 7.46-7.38 (m, 3H), 7.28-7.24 (m, 3H), 7.18-7.14 (m, 1H), 6.76-6.72 (m, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.8, 131.5, 128.9, 128.6, 128.5, 128.2, 128.1, 127.7, 126.6, 125.3, 123.1, 122.8, 117.7, 112.9, 91.7 and 83.5;

ESI-MS calcd for $C_{21}H_{14}N_2$ (M+H)+: 294.1157, found: 295.1239.

IR (KBr): ν = 3057, 2929, 2852, 2216, 1954, 1887, 1735, 1674, 1633, 1598, 1574, 1525, 1493, 1444, 1396, 1352, 1311, 1273, 1251, 1223, 1189, 1157, 1072, 1017, 988, 914, 878, 829, 776, 737, 694, 574, 499 cm^{-1}.

3-phenylimidazo[1,2-a]pyridine (3')



(3')

The product obtained as a pale yellow oil.

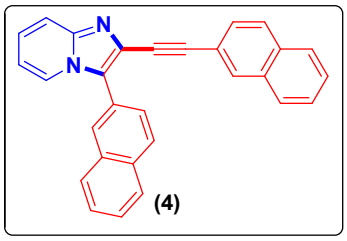
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33-8.31 (m, 1H), 7.67 (d, *J*= 11.6 Hz, 2H), 7.55-7.47 (m, 4H), 7.42-7.37 (m, 1H), 7.20-7.15 (m, 1H), 6.80-6.77 (m, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 132.5, 129.3, 129.2, 128.2, 128.0, 124.2, 123.3, 118.2 and 112.5;

ESI-MS calcd for $C_{13}H_{10}N_2$ (M+H)+: 194.0844, found: 195.0923.

IR (KBr): ν = 3367, 3054, 3031, 2922, 2851, 1731, 1679, 1634, 1602, 1574, 1522, 1499, 1480, 1446, 1352, 1297, 1263, 1175, 1149, 1073, 1009, 963, 914, 894, 858, 829, 780, 752, 736, 698, 660, 579, 529 cm^{-1}.

3-(naphthalen-2-yl)-2-(naphthalen-2-ylethynyl)imidazo[1,2-a]pyridine (4)



The product obtained as a pale yellow oil in 73.2% (144.3 mg) yield.

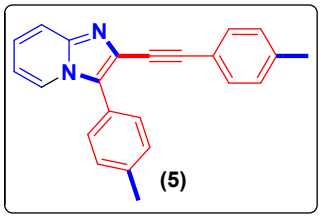
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J*= 8.4 Hz, 1H), 8.03 (d, *J*= 8.4 Hz, 1H), 7.95 (d, *J*= 8.4 Hz, 1H), 7.82 (d, *J*= 6 Hz, 1H), 7.72-7.65 (m, 6H), 7.61-7.50 (m, 3H), 7.48-7.41 (m, 1H), 7.39-7.33 (m, 1H), 7.31-7.24 (m, 1H), 7.19-7.16 (m, 1H), 6.76-6.70 (m, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 134.1, 133.9, 133.0, 132.9, 132.1, 131.8, 130.3, 130.1, 129.8, 129.6, 129.2, 128.7, 128.0, 127.1, 127.0, 126.5, 126.4, 126.3, 126.2, 126.1, 125.7, 125.6, 125.5, 125.4, 125.2, 125.1, 124.1, 120.4, 117.8, 112.9, 112.3, 90.9 and 88.1.

ESI-MS calcd for $C_{29}H_{18}N_2$ (M+H)+: 394.1470, found: 395.1552.

IR (KBr): ν = 3047, 2955, 2923, 2851, 2210, 1926, 1733, 1633, 1585, 1500, 1462, 1416, 1376, 1350, 1293, 1276, 1245, 1214, 1177, 1143, 1054, 1016, 958, 863, 800, 774, 753, 737, 667, 618, 566, 479 cm^{-1}.

3-(p-tolyl)-2-(p-tolylethynyl)imidazo[1,2-a]pyridine (5)



The product obtained as a Colourless solid in 76.0% (122.5 mg) yield.

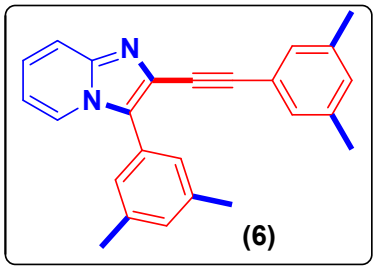
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J*= 7.2 Hz, 1H), 7.62-7.57 (m, 3H), 7.38-7.33 (m, 4H), 7.24-7.17 (m, 1H), 7.11 (d, *J*= 8 Hz, 2H), 6.79-6.75 (m, 1H), 2.43 (s, 3H), 2.32 (s, 3H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.7, 138.6, 138.5, 131.5, 129.7, 129.0, 128.6, 127.6, 126.5, 125.3, 125.2, 123.3, 120.0, 117.8, 112.9, 92.1, 82.9, 21.5 and 21.4;

ESI-MS calcd for $C_{23}H_{18}N_2$ (M+Na): 322.1470, found: 345.1368.

IR (KBr): ν = 3026, 2954, 2922, 2852, 2213, 1903, 1786, 1728, 1631, 1604, 1570, 1543, 1515, 1464, 1446, 1396, 1378, 1347, 1309, 1272, 1250, 1210, 1187, 1177, 1139, 1029, 1015, 991, 946, 877, 815, 751, 737, 668, 623, 569, 527, 504, 474 cm^{-1}.

3-(3,5-dimethylphenyl)-2-((3,5-dimethylphenyl)ethynyl)imidazo[1,2-a]pyridine (6)



The product obtained as a Pale yellow oil in 64.3% (112.6 mg) yield.

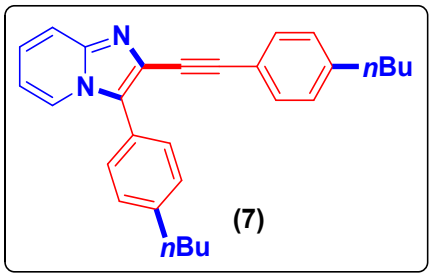
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J*= 6.8 Hz, 1H), 7.59 (d, *J*= 9.2 Hz, 1H), 7.36 (s, 2H), 7.24-7.17 (m, 1H), 7.10-7.09 (m, 3H), 6.92 (s, 1H), 6.80-6.77 (m, 1H), 2.41 (s, 6H), 2.26 (s, 6H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.8, 138.6, 137.7, 130.3, 130.2, 129.2, 128.1, 127.9, 126.7, 126.3, 125.3, 123.4, 122.7, 117.8, 112.8, 92.3, 83.1, 21.4 and 21.1;

ESI-MS calcd for $C_{25}H_{22}N_2$ (M+Na): 350.1783, found: 373.1682.

IR (KBr): ν = 2954, 2915, 2850, 2219, 1735, 1635, 1600, 1501, 1468, 1400, 1377, 1346, 1277, 1236, 1186, 1165, 1143, 1039, 941, 898, 850, 753, 716, 688, 575, 538 cm^{-1}.

3-(4-butylphenyl)-2-((4-butylphenyl)ethynyl)imidazo[1,2-a]pyridine (7)



The product obtained as a Yellow oil in 70.1% (142.5 mg) yield.

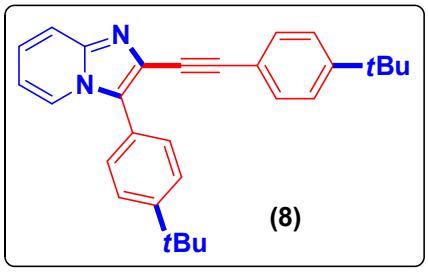
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J*= 6.8 Hz, 1H), 7.64-7.59 (m, 3H), 7.36-7.21 (m, 4H), 7.20-7.17 (m, 1H), 7.10 (d, *J*= 8 Hz, 2H), 6.79-6.75 (m, 1H), 2.68 (t, *J*= 7.6 Hz, 2H), 2.57 (t, *J*= 7.6 Hz, 2H), 1.67-1.61 (m, 2H), 1.57-1.51 (m, 2H), 1.43-1.37 (m, 2H), 1.34-1.23 (m, 2H), 0.95 (t, *J*= 7.2 Hz, 3H), 0.89 (t, *J*= 7.2 Hz, 3H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.8, 143.6, 143.4, 131.5, 129.0, 128.6, 128.3, 127.7, 126.6, 125.4, 125.2, 123.3, 120.1, 117.9, 112.9, 92.1, 83.0, 46.1, 35.6, 35.5, 33.5, 33.3, 22.4, 22.3 and 13.9;

EI-HRMS calcd for $C_{29}H_{30}N_2$ (M+Na): 406.2409, found: 429.2308.

IR (KBr): ν = 3359, 3191, 2955, 2922, 2851, 2216, 1908, 1735, 1657, 1647, 1633, 1542, 1515, 1502, 1399, 1377, 1350, 1272, 1250, 1221, 1179, 1118, 1015, 881, 833, 752, 736, 644, 611, 533 cm^{-1}.

3-(4-(tert-butyl)phenyl)-2-((4-(tert-butyl)phenyl)ethynyl)imidazo[1,2-a]pyridine (8)



The product obtained as a Pale yellow oil in 73.9% (150.2 mg) yield.

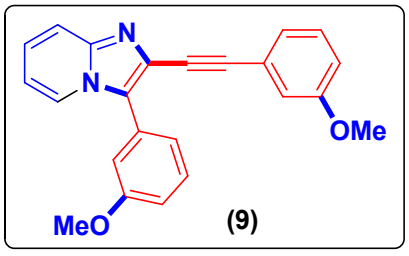
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J*= 7.2 Hz, 1H), 7.67-7.57 (m, 3H), 7.56 (d, *J*= 7.6 Hz, 2H), 7.44-7.42 (m, 2H), 7.34-7.32 (m, 2H), 7.24-7.20 (m, 1H), 6.79 (t, *J*= 6.8 Hz, 1H), 1.38 (s, 9H), 1.29 (s, 9H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 151.8, 151.7, 131.4, 128.4, 127.6, 126.0, 125.5, 125.3, 125.2, 123.5, 120.0, 117.7, 113.0, 106.5, 92.3, 34.9, 34.8, 31.3 and 31.1;

EI-HRMS calcd for $C_{29}H_{30}N_2$ (M+Na): 406.2409, found: 429.2303.

IR (KBr): ν = 3081, 3036, 2958, 2925, 2855, 2215, 1912, 1664, 1633, 1604, 1539, 1516, 1501, 1463, 1396, 1361, 1347, 1270, 1252, 1226, 1200, 1141, 1108, 1014, 1108, 1014, 963, 880, 833, 751, 735, 618, 559 cm^{-1}.

3-(3-methoxyphenyl)-2-((3-methoxyphenyl)ethynyl)imidazo[1,2-a]pyridine (9)



The product obtained as a Colourless oil in 71.4% (126.5 mg) yield.

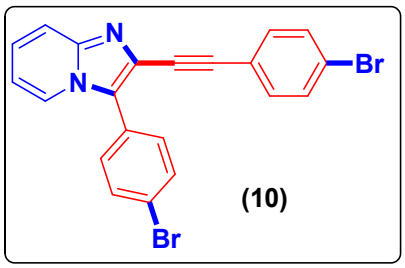
^{1}H NMR (700 MHz, $CDCl_3$): δ 8.32 (d, *J*= 9.1 Hz, 1H), 7.64 (d, *J*= 9.1 Hz, 1H), 7.48 (t, *J*= 8.4 Hz, 1H), 7.32-7.30 (m, 2H), 7.26-7.21 (m, 2H), 7.10 (d, *J*= 7.7 Hz, 1H), 7.05 (s, 1H), 7.01-7.0 (m, 1H), 6.88 (dd, *J*= 8.4 Hz, 1H), 6.83 (t, *J*= 7 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 160.1, 159.2, 144.9, 130.1, 129.3, 127.7, 126.4, 125.7, 124.1, 123.9, 123.5, 120.9, 117.9, 116.3, 115.2, 114.5, 114.3, 113.2, 92.2, 83.1, 55.4 and 55.2;

ESI-MS calcd for $C_{23}H_{18}N_2O_2$ (M+H)+: 354.1368, found: 355.1440.

IR (KBr): ν = 3067, 2955, 2922, 2851, 2213, 1732, 1686, 1633, 1597, 1574, 1487, 1462, 1426, 1387, 1345, 1315, 1283, 1252, 1200, 1153, 1138, 1082, 1042, 1024, 993, 962, 854, 780, 751, 736, 698, 685, 561, 533, 516, 486 cm^{-1}.

3-(4-bromophenyl)-2-((4-bromophenyl)ethynyl)imidazo[1,2-a]pyridine (10)



The product obtained as a Colourless Solid in 74.1% (167.5 mg) yield.

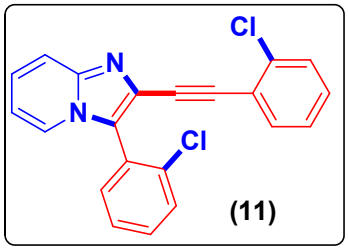
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-8.16 (m, 1H), 7.97-7.65 (m, 2H), 7.65-7.54 (m, 3H), 7.42 (d, *J*= 8.8 Hz, 2H), 7.30 (d, *J*= 8.4 Hz, 2H), 7.22-7.20 (m, 1H), 6.80 (t, *J*= 6.8 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 145.1, 133.0, 132.4, 131.6, 130.2, 127.0, 126.7, 126.6, 125.8, 123.0, 122.8, 121.6, 118.0, 113.4, 91.1 and 84.2;

ESI-MS calcd for $C_{21}H_{12}Br_2N_2$ (M+H)+: 449.9367, found: 450.9444.

IR (KBr): ν = 3326, 2955, 2918, 2851, 1735, 1649, 1586, 1489, 1466, 1395, 1377, 1309, 1274, 1249, 1218, 1191, 1157, 1123, 1089, 1071, 1024, 952, 889, 855, 823, 758, 721, 498 cm^{-1}.

3-(2-chlorophenyl)-2-((2-chlorophenyl)ethynyl)imidazo[1,2-a]pyridine (11)



The product obtained as a Yellow oil in 67.9% (123.3 mg) yield.

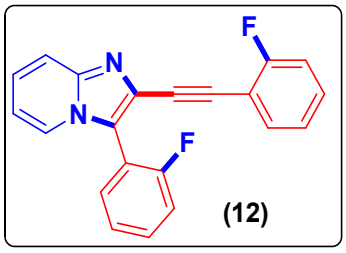
^{1}H NMR (700 MHz, $CDCl_3$): δ 7.70 (d, *J*= 7 Hz, 1H), 7.66-7.62 (m, 2H), 7.55 (d, *J*= 7.7 Hz, 1H), 7.47-7.44 (m, 1H), 7.43-7.40 (m, 2H), 7.30 (d, *J*= 7.7 Hz, 1H), 7.26-7.18 (m, 1H), 7.18-7.13 (m, 2H), 6.81-6.79 (m, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 145.0, 135.9, 134.6, 133.9, 133.3, 130.8, 130.1, 129.3, 129.1, 127.4, 127.2, 127.0, 126.3, 126.2, 125.7, 124.6, 122.8, 117.7, 112.8, 89.0 and 88.0;

ESI-MS calcd for $C_{21}H_{12}Cl_2N_2$ (M+Na): 362.0378, found: 385.0278.

IR (KBr): ν = 3060, 2954, 2925, 2852, 2219, 1922, 1801, 1733, 1679, 1634, 1591, 1564, 1502, 1480, 1434, 1392, 1351, 1280, 1246, 1221, 1194, 1128, 1070, 1057, 1018, 991, 948, 881, 829, 788, 753, 689, 668, 616, 549, 488, 453 cm^{-1}.

3-(2-fluorophenyl)-2-((2-fluorophenyl)ethynyl)imidazo[1,2-a]pyridine (12)



The product obtained as a Pale yellow oil in 66.4% (109.7 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.81 (m, 1H), 7.77-7.71 (m, 1H), 7.65 (d, *J*= 8.8 Hz, 1H), 7.48-7.42 (m, 1H), 7.30-7.25 (m, 2H), 7.11-7.0 (m, 3H), 6.88-6.78 (m, 3H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 163.6, 163.0, 162.5, 162.4, 162.2, 162.1, 160.9, 160.8, 159.4, 159.3, 145.3, 134.3, 134.2, 133.6, 133.5, 127.4, 126.0, 124.4, 122.3, 117.8, 113.3, 112.4, 112.3, 111.7, 111.6, 107.7, 107.6, 105.0, 104.8, 104.7, 104.4, 104.3, 104.1, 87.4 and 84.9;

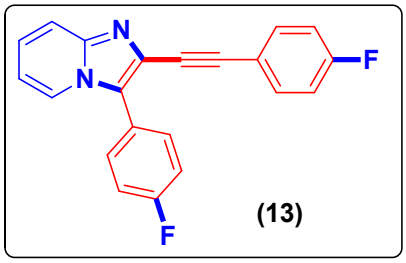
^{13}C NMR (175 MHz, $CDCl_3$): δ 163.9 (J_{C-F}= 49.1 Hz), 163.8 (J_{C-F}= 48.3 Hz), 163.0 (J_{C-F}= 97.8 Hz), 162.9 (J_{C-F}= 98.1 Hz), 162.2 (J_{C-F}= 11.2 Hz), 160.8 (J_{C-F}= 251.1 Hz), 160.7 (J_{C-F}= 250.9 Hz), 145.3, 134.2 (J_{C-F}= 9.8 Hz, 9.6 Hz), 133.5 (J_{C-F}= 9.8 Hz, 9.6 Hz), 127.3, 125.9, 124.4 (J_{C-F}= 5.2 Hz), 122.3, 117.8, 113.2, 112.4 (J_{C-F}= 21.1 Hz), 111.7 (J_{C-F}= 21.8 Hz), 111.6 (J_{C-F}= 21.7 Hz), 107.7 (J_{C-F}= 15.9 Hz), 104.9 (J_{C-F}= 50.5 Hz), 104.4 (J_{C-F}= 25.7 Hz), 104.2 (J_{C-F}= 25.9 Hz), 87.4 and 84.8;

^{19}F NMR (470 MHz, CCl_3F): δ -61.2 (s), -62.9 (s).

ESI-MS calcd for $C_{21}H_{12}F_2N_2$ (M-H): 330.0969, found: 329.0004.

IR (KBr): ν = 3077, 2953, 2920, 2850, 2222, 1733, 1615, 1588, 1543, 1511, 1502, 1476, 1455, 1423, 1398, 1377, 1354, 1293, 1265, 1247, 1182, 1142, 1097, 1021, 995, 963, 842, 812, 748, 731, 671, 606, 565, 509, 489 cm^{-1}.

3-(4-fluorophenyl)-2-((4-fluorophenyl)ethynyl)imidazo[1,2-a]pyridine (13)



(13)

The product obtained as a Pale yellow solid in 72.3% (119.4 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J*= 6.8 Hz, 1H), 7.69-7.66 (m, 2H), 7.60 (d, *J*= 9.2 Hz, 1H), 7.45-7.41 (m, 2H), 7.28-7.20 (m, 3H), 6.99 (t, *J*= 8.8 Hz, 2H), 6.81 (t, *J*= 6.8 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 163.4, 163.3, 162.0, 161.9, 145.0, 133.5, 130.8, 126.8, 126.7, 125.5, 124.2, 123.0, 118.9, 118.0, 116.4, 116.2, 115.7, 115.6, 113.2, 90.8 and 83.0;

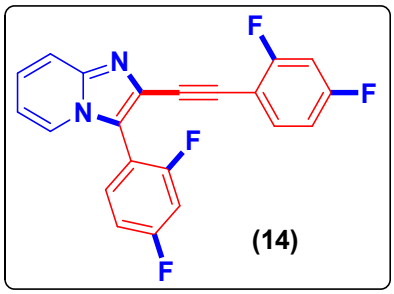
^{13}C NMR (175 MHz, $CDCl_3$): δ 163.4 (J_{C-F}= 248.1 Hz), 162.0 (J_{C-F}= 248.8 Hz), 144.9, 133.5 (J_{C-F}= 8.4 Hz), 130.8 (J_{C-F}= 8.2 Hz), 126.7 (J_{C-F}= 12.4 Hz), 125.5, 124.2, 123.0, 118.9 (J_{C-F}= 3.5 Hz), 118.0, 116.3 (J_{C-F}= 21.5 Hz), 115.7 (J_{C-F}= 22.0 Hz), 113.2, 90.8 and 82.9;

^{19}F NMR (470 MHz, CCl_3F): δ -110.2 (s), -111.3 (s).

ESI-MS calcd for $C_{21}H_{12}F_2N_2$ (M+Na): 330.0969, found: 353.0850.

IR (KBr): ν = 3359, 3190, 2955, 2920, 2850, 2217, 1728, 1647, 1633, 1601, 1543, 1515, 1502, 1468, 1413, 1377, 1346, 1275, 1228, 1157, 1094, 1014, 880, 831, 815, 750, 737, 721, 640, 606, 569, 525 cm^{-1}.

3-(2,4-difluorophenyl)-2-((2,4-difluorophenyl)ethynyl)imidazo[1,2-a]pyridine (14)



The product obtained as a solid in 63.1% (115.6 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 1H), 7.75 (q, *J*= 8.4 Hz, 1H), 7.64 (d, *J*= 9.2 Hz, 1H), 7.44-7.39 (m, 1H), 7.28-7.24 (m, 1H), 7.09-6.79 (m, 2H), 6.86-6.76 (m, 3H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 162.4, 162.3, 162.2, 162.1, 160.8, 160.7, 159.3, 145.1, 134.2, 134.1, 133.5, 133.4, 127.0, 126.1, 124.4, 124.3, 122.3, 117.6, 113.3, 112.4, 112.3, 112.2, 111.9, 111.8, 111.7, 111.6, 111.5, 107.6, 107.5, 105.0, 104.8, 104.6, 104.3, 104.2, 104.0, 87.1 and 85.1;

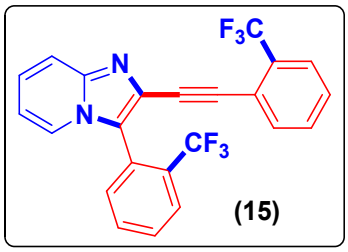
^{13}C NMR (175 MHz, $CDCl_3$): δ 163.7 ($J_{C\text{-}F}$= 43.2 Hz), 162.6 ($J_{C\text{-}F}$= 104.4Hz), 162.9 ($J_{C\text{-}F}$= 103.6 Hz), 162.4 ($J_{C\text{-}F}$= 42.0 Hz), 160.8 ($J_{C\text{-}F}$= 251.1 Hz), 159.3 ($J_{C\text{-}F}$= 251.1 Hz), 145.0, 134.2 ($J_{C\text{-}F}$= 9.8 Hz), 134.2 ($J_{C\text{-}F}$= 9.8 Hz), 133.5 ($J_{C\text{-}F}$= 9.6 Hz), 133.4 ($J_{C\text{-}F}$= 9.8 Hz), 126.9, 126.1, 124.3 ($J_{C\text{-}F}$= 5.0 Hz), 122.2 , 117.5, 113.3, 112.4 ($J_{C\text{-}F}$= 21.3 Hz), 112.3 ($J_{C\text{-}F}$= 21.3 Hz), 111.8 ($J_{C\text{-}F}$= 15.0 Hz), 111.7 ($J_{C\text{-}F}$= 15.0 Hz), 111.6 ($J_{C\text{-}F}$= 21.8 Hz, 21.7 Hz), 107.6 ($J_{C\text{-}F}$= 15.7 Hz), 107.5 ($J_{C\text{-}F}$= 15.7 Hz), 104.9 ($J_{C\text{-}F}$= 50.5 Hz), 104.7 ($J_{C\text{-}F}$= 74.3 Hz), 104.1 ($J_{C\text{-}F}$= 25.7 Hz), 87.1 and 85.0;

^{19}F NMR (470 MHz, CCl_3F): δ -104.7 (d), -105.3 (d), -106.0 (s), -106.8 (s).

EI-HRMS calcd for $C_{21}H_{10}F_4N_2$ (M+H): 366.0780, found: 367.0857.

IR (KBr): ν = 3078, 2953, 2918, 2850, 2220, 1733, 1615, 1588, 1542, 1501, 1455, 1424, 1399, 1354, 1293, 1264, 1142, 1097, 1020, 995, 963, 937, 842, 811, 748, 731, 672, 633, 565, 509, 488, 429 cm^{-1}.

3-(2-(trifluoromethyl)phenyl)-2-((2-(trifluoromethyl)phenyl)ethynyl)imidazo[1,2-a]pyridine (15)



The product obtained as a Pale yellow oil in 61.4% (132.1 mg) yield.

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.88 (d, *J*= 7.7 Hz, 1H), 7.71-7.65 (m, 2H), 7.61-7.58 (m, 2H), 7.51 (dd, *J*= 7.7 Hz, 3H), 7.41 (t, *J*= 7.7 Hz, 1H), 7.30 (t, *J*= 7.0 Hz, 1H), 7.22 (t, *J*= 7.7 Hz, 1H), 6.74 (t, *J*= 7.0 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.8, 134.2, 133.9, 132.3, 131.9, 131.7, 131.3, 131.2, 131.1, 130.3, 127.9, 127.8, 126.8, 126.7, 126.0, 125.6, 125.5, 125.1, 124.2, 124.0, 123.8, 122.7, 122.2, 121.0, 117.6, 113.0, 88.1 and 88.0;

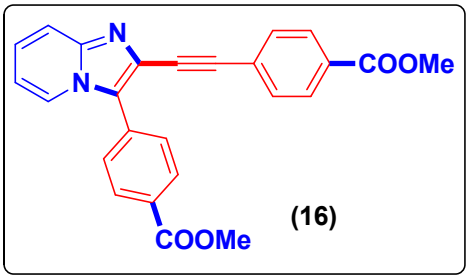
^{13}C NMR (175 MHz, $CDCl_3$): δ 144.8, 134.2, 133.9, 132.3, 132.0 (q, $J_{C\text{-}F}$= 30.2 Hz, 30.3 Hz), 131.4 (q, $J_{C\text{-}F}$= 30.5 Hz, 30.4 Hz), 131.2, 130.2, 129.1 ($J_{C\text{-}F}$= 227.3 Hz), 127.9, 127.8 ($J_{C\text{-}F}$= 319.3 Hz), 126.0 (q, $J_{C\text{-}F}$= 5.0 Hz, 4.9 Hz), 125.6 (q, $J_{C\text{-}F}$= 5.0 Hz, 5.2 Hz), 125.1, 124.2, 123.9, 123.8, 122.6, 122.2, 120.9, 117.5, 112.9, 88.1 and 88.0;

^{19}F NMR (470 MHz, CCl_3F): δ -104.7 (d), -105.3 (d), -106.1 (d), -107.0 (d).

EI-HRFD calcd for $C_{23}H_{12}F_6N_2$ (M+Na): 430.0905, found: 453.0798.

IR (KBr): ν = 3360, 3188, 3074, 2955, 2921, 2851, 2222, 1943, 1838, 1734, 1699, 1658, 1603, 1574, 1493, 1469, 1449, 1393, 1351, 1316, 1263, 1219, 1169, 1128, 1110, 1057, 1033, 1018, 991, 959, 877, 830, 800, 766, 751, 719, 653, 612, 595, 537 cm^{-1}.

Methyl 4-(2-((4-(methoxycarbonyl)phenyl)ethynyl)imidazo[1,2-a]pyridin-3-yl)benzoate (16)



The product obtained as a Pale yellow powder in 60.3% (123.7 mg) yield.

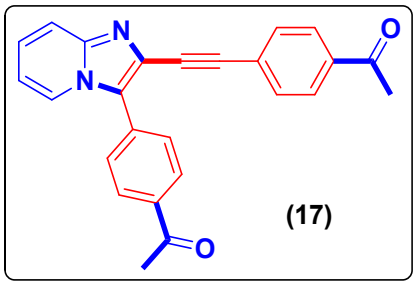
^{1}H NMR (700 MHz, $CDCl_3$): δ 8.28 (d, *J*= 7.0 Hz, 1H), 8.22 (d, *J*= 8.4 Hz, 2H), 7.97 (d, *J*= 8.4 Hz, 2H), 7.82 (d, *J*= 8.4 Hz, 2H), 7.65 (d, *J*= 9.1 Hz, 1H), 7.51 (d, *J*= 7.7 Hz, 2H), 7.28 (t, *J*= 7.7 Hz, 1H), 6.88-6.86 (m, 1H), 3.95 (s, 3H), 3.88 (s, 3H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 166.4, 145.3, 132.4, 131.5, 130.3, 130.1, 129.8, 128.3, 127.2, 126.7, 126.4, 123.3, 118.1, 113.8, 91.8, 85.8, 52.3 and 52.2;

EI-HRFD calcd for $C_{25}H_{18}N_2O_4$ (M+Na): 410.1267, found: 433.1164.

IR (KBr): ν = 3307, 2955, 2921, 2851, 2216, 1722, 1606, 1497, 1464, 1403, 1377, 1311, 1280, 1190, 1107, 1018, 968, 854, 826, 764, 751, 731, 695 cm^{-1}.

1-(4-(2-((4-acetylphenyl)ethynyl)imidazo[1,2-a]pyridin-3-yl)phenyl)ethan-1-one (17)



The product obtained as a white powder in 54.8% (103.7 mg) yield.

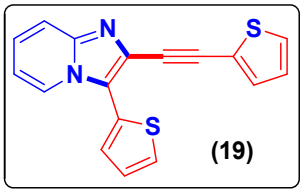
^{1}H NMR (700 MHz, $CDCl_3$): δ 8.26 (d, *J*= 11.9 Hz, 1H), 8.12 (d, *J*= 3.5 Hz, 2H), 7.87-7.81 (m, 4H), 7.61-7.57 (m, 1H), 7.52-7.49 (m, 2H), 7.26-7.22 (m, 1H), 6.86-6.82 (m, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 197.1, 145.5, 136.7, 136.3, 132.6, 131.6, 129.2, 129.0, 128.4, 128.2, 127.3, 127.2, 127.1, 127.0, 126.2, 123.2, 118.1, 113.7, 91.5 and 86.4;

EI-HRFD calcd for $C_{25}H_{18}N_2O_2$ (M+Na): 378.1368, found: 401.1271.

IR (KBr): ν = 3340, 2955, 2918, 2851, 2214, 1735, 1682, 1602, 1559, 1497, 1463, 1403, 1377, 1360, 1309, 1267, 1187, 1156, 1124, 1089, 1024, 955, 889, 829, 755, 593 cm^{-1}.

3-(thiophen-2-yl)-2-(thiophen-2-ylethynyl)imidazo[1,2-a]pyridine (19)



The product obtained as a Pale yellow oil in 64.1% (98.2 mg) yield.

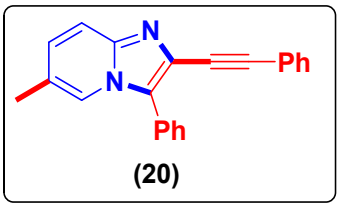
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43-8.41 (m, 1H), 7.62-7.59 (m, 1H), 7.51-7.49 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.21 (m, 2H), 7.0-6.98 (m, 1H), 6.89-6.86 (m, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 145.1, 132.5, 128.7, 127.8, 127.6, 127.1, 126.6, 125.8, 123.8, 122.9, 122.0, 118.8, 117.9, 113.5, 86.9 and 86.8;

ESI-MS calcd for $C_{17}H_{10}N_2S_2$ (M+H)+: 306.0285, found: 307.0373.

IR (KBr): ν = 3339, 2956, 2920, 2851, 2210, 1737, 1635, 1565, 1464, 1413, 1378, 1247, 1234, 1162, 1088, 1020, 951, 890, 850, 825, 752, 720, 699 cm^{-1}.

6-methyl-3-phenyl-2-(phenylethynyl)imidazo[1,2-a]pyridine (20)



(20)

The product obtained as a Pale yellow powder in 43.4% (66.9 mg) yield.

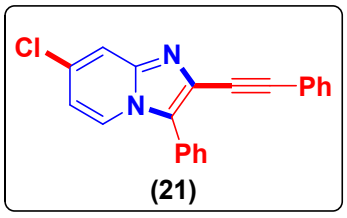
^{1}H NMR (700 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.27 (d, J= 7.7 Hz, 2H), 7.60-7.55 (m, 3H), 7.47-7.45 (m, 3H), 7.29-7.28 (m, 3H), 7.13 (d, J= 8.4 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.0, 131.5, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.4, 126.3, 123.0, 122.7, 120.7, 117.1, 91.5, 83.6 and 18.3;

ESI-MS calcd for $C_{22}H_{16}N_2$ (M+H)+: 308.1313, found: 309.1398.

IR (KBr): ν = 3339, 2955, 2922, 2852, 1737, 1669, 1600, 1538, 1495, 1378, 1341, 1276, 1163, 1123, 1089, 972, 951, 889, 852, 758, 721, 694, 577, 529 cm^{-1}.

7-Chloro-3-phenyl-2-(phenylethynyl)imidazo[1,2-a]pyridine (21)



(21)

The product obtained as a Pale yellow oil in 36.4% (59.8 mg) yield.

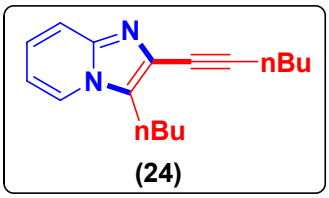
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J*= 7.2 Hz, 1H), 7.70-7.68 (m, 3H), 7.65-7.54 (m, 2H), 7.49-7.45 (m, 3H), 7.30-7.29 (m, 3H), 6.82 (dd, *J*= 7.6 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.4, 132.6, 132.4, 131.7, 129.2, 129.1, 128.9, 128.8, 128.6, 128.3, 128.0, 127.5, 127.2, 123.7, 122.6, 116.4, 115.0, 92.8 and 82.6;

ESI-MS calcd for $C_{21}H_{13}ClN_2$ (M+Na): 328.0767, found: 351.0664.

IR (KBr): ν = 3280, 3060, 2954, 2923, 2851, 2220, 1953, 1734, 1680, 1627, 1597, 1565, 1492, 1442, 1399, 1377, 1350, 1283, 1251, 1220, 1188, 1125, 1092, 1065, 1027, 995, 948, 896, 853, 819, 780, 732, 698, 671, 529, 451 cm^{-1}.

3-Butyl-2-(hex-1-ynyl)imidazo[1,2-a]pyridine (24)



The product obtained as a Yellow oil in 77.3% (98.3 mg) yield.

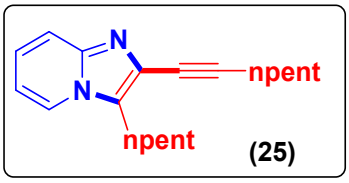
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (t, *J*= 6.8 Hz, 1H), 7.50 (q, *J*= 9.2 Hz, 1H), 7.12-7.08 (m, 1H), 6.78-6.74 (m, 1H), 2.92 (t, *J*= 7.2 Hz, 2H), 2.44 (t, *J*= 6.8 Hz, 3H), 1.66-1.22 (m, 9H), 0.93-0.89 (m, 6H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 143.8, 127.0, 126.6, 123.9, 122.7, 117.5, 112.3, 93.9, 73.9, 30.6, 29.3, 23.1, 22.2, 21.9, 19.2, 13.7 and 13.6;

ESI-HRMS calcd for $C_{17}H_{22}N_2$ (M+Na): 254.1783, found: 277.1679.

IR (KBr): ν = 3272, 3021, 2957, 2930, 2871, 2860, 2234, 1748, 1632, 1599, 1569, 1486, 1440, 1406, 1379, 1364, 1287, 1271, 1246, 1168, 1151, 1128, 1081, 1018, 981, 953, 854, 826, 774, 751, 736, 622, 522, 485 cm^{-1}.

2-(Hept-1-yn-1-yl)-3-pentylimidazo[1,2-a]pyridine (25)



The product obtained as a Pale yellow oil in 79.2% (111.8 mg) yield.

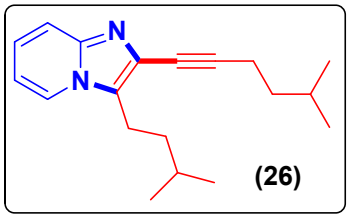
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J*= 6.8 Hz, 1H), 7.49 (d, *J*= 8.8 Hz, 1H), 7.12 (t, *J*= 7.6 Hz, 1H), 6.76 (t, *J*= 6.8 Hz, 1H), 2.93 (t, *J*= 7.6 Hz, 2H), 2.44 (t, *J*= 7.6 Hz, 2H), 1.68-1.60 (m, 4H), 1.36-1.31 (m, 7H), 0.91-0.85 (m, 7H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 149.6, 148.1, 143.9, 138.5, 138.2, 127.1, 123.8, 122.7, 117.6, 112.3, 93.9, 73.9, 71.6, 31.3, 31.1, 28.3, 26.9, 23.3, 22.3, 22.2, 19.5, 14.0 and 13.9;

ESI-HRMS calcd for $C_{19}H_{26}N_2$ (M+Na): 282.2096, found: 305.1996.

IR (KBr): ν = 3357, 3190, 2956, 2924, 2853, 2236, 1747, 1679, 1659, 1599, 1505, 1467, 1435, 1377, 1365, 1299, 1245, 1144, 965, 738, 669, 484 cm^{-1}.

3-isopentyl-2-(5-methylhex-1-yn-1-yl)imidazo[1,2-a]pyridine (26)



The product obtained as a Pale yellow oil 73.2% (103.4 mg) yield.

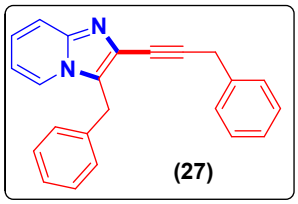
^{1}H NMR (700 MHz, $CDCl_3$): δ 7.79 (d, *J*= 7.0 Hz, 1H), 7.46 (d, *J*= 9.1 Hz, 1H), 7.09-7.06 (m, 1H), 6.74 (t, *J*= 7.0 Hz, 1H), 2.91 (t, *J*= 7.7 Hz, 2H), 2.44 (t, *J*= 7.7 Hz, 2H), 1.79-1.77 (m, 1H), 1.58 (t, *J*= 6.3 Hz, 1H), 1.52-1.47 (m, 2H), 0.94 (d, *J*= 6.3 Hz, 6H), 0.93 (d, *J*= 6.3 Hz, 6H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 143.9, 127.1, 126.6, 123.7, 122.6, 121.5, 117.5, 114.3, 112.2, 93.8, 73.9, 37.4, 35.9, 27.6, 27.0, 22.3, 22.2, 22.1, 21.3 and 17.5;

ESI-HRMS calcd for $C_{19}H_{26}N_2$ (M+H)+: 282.2096, found: 283.2176.

IR (KBr): ν = 3079, 2955, 2928, 2869, 2235, 1748, 1680, 1633, 1590, 1545, 1467, 1401, 1385, 1366, 1269, 1245, 1204, 1168, 1132, 918, 825, 750, 735 cm^{-1}.

3-benzyl-2-(3-phenylprop-1-yn-1-yl)imidazo[1,2-a]pyridine (27)



The product obtained as a Pale yellow oil 67.9% (109.5 mg) yield.

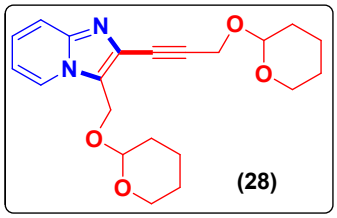
^{1}H NMR (700 MHz, $CDCl_3$): δ 7.63 (d, *J*= 7.0 Hz, 1H), 7.51 (d, *J*= 9.1 Hz, 1H), 7.42 (d, *J*= 7.7 Hz, 2H), 7.28 (t, *J*= 7.7 Hz, 2H), 7.24 (t, *J*= 7.7 Hz, 2H), 7.21-7.18 (m, 2H), 7.16 (d, *J*= 7.0 Hz, 2H), 7.09 (t, *J*= 8.4 Hz, 1H), 6.30 (t, *J*= 6.3 Hz, 1H), 4.33 (s, 2H), 3.88 (s, 2H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.3, 136.4, 136.2, 128.7, 128.4, 128.1, 127.9, 127.6, 126.7, 126.5, 125.3, 124.4, 123.1, 117.4, 112.4, 91.0, 76.0, 29.6 and 25.8;

EI-HRMS calcd for $C_{23}H_{18}N_2$ (M+H): 322.1470, found: 323.1547.

IR (KBr): ν = 3360, 3182, 3137, 3084, 3061, 2923, 2852, 2238, 1950, 1747, 1660, 1603, 1584, 1547, 1495, 1422, 1364, 1270, 1249, 1186, 1136, 1116, 1075, 1029, 1003, 940, 889, 824, 748, 722, 696, 615, 594, 586, 489 cm^{-1}.

3-(((tetrahydro-2H-pyran-2-yl)oxy)methyl)-2-(3-((tetrahydro-2H-pyran-2-yl)oxy)prop-1-yn-1-yl)imidazo[1,2-a]pyridine (28)



The product obtained as a Yellow oil 58.2% (107.8 mg) yield.

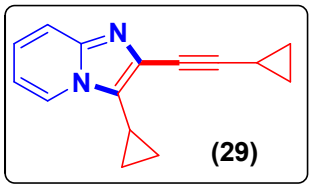
^{1}H NMR (700 MHz, $CDCl_3$): δ 8.13 (d, *J*= 7.0 Hz, 1H), 7.48 (d, *J*= 9.1 Hz, 1H), 7.17 (t, *J*= 8.4 Hz, 1H), 6.79 (t, *J*= 7.0 Hz, 1H), 5.00 (dd, *J*= 2.3, 13.3 Hz, 1H), 4.90 (dd, *J*= 3.5, 14.0 Hz, 2H), 4.61 (s, 1H), 4.50 (s, 2H), 3.89-3.81 (m, 2H), 3.52-3.49 (m, 2H), 1.78-1.69 (m, 3H), 1.62-1.44 (m, 9H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 145.05, 128.0, 125.5, 124.3, 123.8, 117.5, 112.8, 98.0, 96.6, 88.9, 78.4, 62.9, 62.0, 57.3, 54.5, 30.3, 30.2, 30.2, 25.3, 25.2, 19.6 and 19.0;

EI-HRMS calcd for $C_{21}H_{26}N_2O_4$ (M+Na): 370.1893, found: 393.1789.

IR (KBr): ν = 3081, 2940, 2867, 2851, 2234, 1684, 1634, 1554, 1501, 1453, 1389, 1364, 1352, 1272, 1201, 1182, 1152, 1118, 1076, 1024, 969, 945, 902, 870, 815, 754, 737, 480 cm^{-1}.

3-cyclopropyl-2-(cyclopropylethynyl)imidazo[1,2-a]pyridine (29)



The product obtained as a Pale yellow oil 66.1% (73.5 mg) yield.

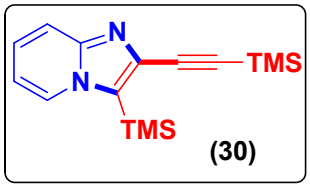
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (m, 1H), 7.45-7.43(m, 1H), 7.15-7.11 (m, 1H), 6.81-6.77 (m, 1H), 1.80-1.75 (m, 2H), 1.50-1.47 (m, 1H), 1.22 (s, 1H), 1.07-1.02 (m, 2H), 0.93 (m, 2H), 0.87-0.84 (m, 2H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 143.6, 127.0, 126.6, 124.5, 123.1, 117.2, 112.3, 97.2, 69.4, 8.6, 5.1, 3.9, and 0.3;

EI-HRMS calcd for $C_{15}H_{14}N_2$ (M+H): 222.1157, found: 223.1234.

IR (KBr): ν = 3088, 3008, 2955, 2923, 2851, 2233, 1732, 1662, 1632, 1594, 1551, 1463, 1418, 1378, 1341, 1270, 1237, 1198, 1168, 1144, 1118, 1051, 1026, 989, 926, 879, 854, 812, 752, 738, 516, 464 cm^{-1}.

3-(trimethylsilyl)-2-((trimethylsilyl)ethynyl)imidazo[1,2-a]pyridine (30)



The product obtained as a Light brown liquid 69.8% (100.0 mg) yield.

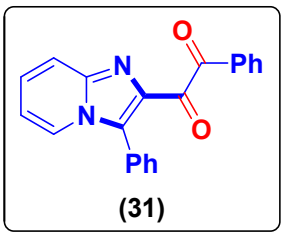
^{1}H NMR (700 MHz, $CDCl_3$): δ 8.10 (d, *J*= 6.3 Hz, 1H), 7.54 (d, *J*= 9.1 Hz, 1H), 7.17-7.15 (m, 1H), 6.76-6.74 (m, 1H), 0.46 (s, 9H), 0.22 (s, 9H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 147.6, 136.2, 126.5, 125.9, 125.5, 125.4, 117.9, 117.8, 112.9, 112.7, 100.4, 97.4, 80.1, -0.4 and -0.8;

EI-HRMS calcd for $C_{15}H_{22}N_2Si_2$ (M+H): 286.1322, found: 287.1398.

IR (KBr): ν = 3310, 2957, 2926, 2854, 2161, 1735, 1634, 1600, 1501, 1458, 1437, 1377, 1341, 1299, 1251, 1150, 1074, 1003, 932, 881, 842, 760, 736, 720, 698, 655, 628, 570 cm^{-1}.

1-phenyl-2-(3-phenylimidazo[1,2-a]pyridin-2-yl)ethane-1,2-dione (31)



The product obtained as a pale yellow oil 98.1% (320.1 mg) yield.

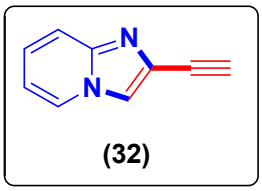
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, *J*= 6.0, 7.6 Hz, 1H), 7.92-7.90 (m, 2H), 7.66 (d, *J*= 9.2, 1H), 7.59-7.55 (m, 1H), 7.54-7.50 (m, 2H), 7.49-7.47 (m, 3H), 7.26-7.21 (m, 1H), 6.83-6.79 (m, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 194.1, 191.1, 146.3, 145.0, 136.7, 134.3, 133.0, 130.4, 130.2, 129.9, 129.0, 128.7, 126.8, 126.6, 124.1, 119.6 and 114.4;

ESI-MS calcd for $C_{21}H_{14}N_2O_2$ (M+Na): 326.1055, found: 349.0953.

IR (KBr): ν = 3359, 3188, 3061, 2921, 2851, 1734, 1684, 1636, 1596, 1580, 1545, 1480, 1449, 1376, 1359, 1343, 1315, 1265, 1216, 1179, 1143, 1074, 1010, 983, 940, 881, 754, 742, 726, 699, 672, 568, 483 cm^{-1}.

2-ethynylimidazo[1,2-a]pyridine (32)



(32)

The product obtained as a Light brown liquid 99.0% (70.3 mg) yield.

^{1}H NMR (700 MHz, $CDCl_3$): δ 8.03 (d, *J*= 6.3 Hz, 1H), 7.7 (s, 1H), 7.54 (d, *J*= 9.1 Hz, 1H), 7.18 (t, *J*= 7.7 Hz, 1H), 6.79 (t, *J*= 6.3 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$): δ 144.8, 127.3, 125.5, 125.4, 117.8, 116.2, 113.2 and 79.0;

EI-HRMS calcd for $C_9H_6N_2$ (M+H): 142.0531, found: 143.0610.

IR (KBr): ν = 3287, 3198, 3139, 3109, 3051, 2957, 2914, 2849, 2113, 1734, 1636, 1532, 1485, 1361, 1307, 1240, 1160, 1126, 1013, 976, 917, 831, 811, 752, 665, 558 cm^{-1}.

6. Supporting references

S1. Y. Sawama, M. Takubo, S. Mori, Y. Monguchi and H. Sajiki, *Eur. J. Org. Chem.,* 2011, **18**, 3361–3367.

S2. W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang and A. Lei, *J. Am. Chem. Soc.,* 2008, **130**, 14713-14720.

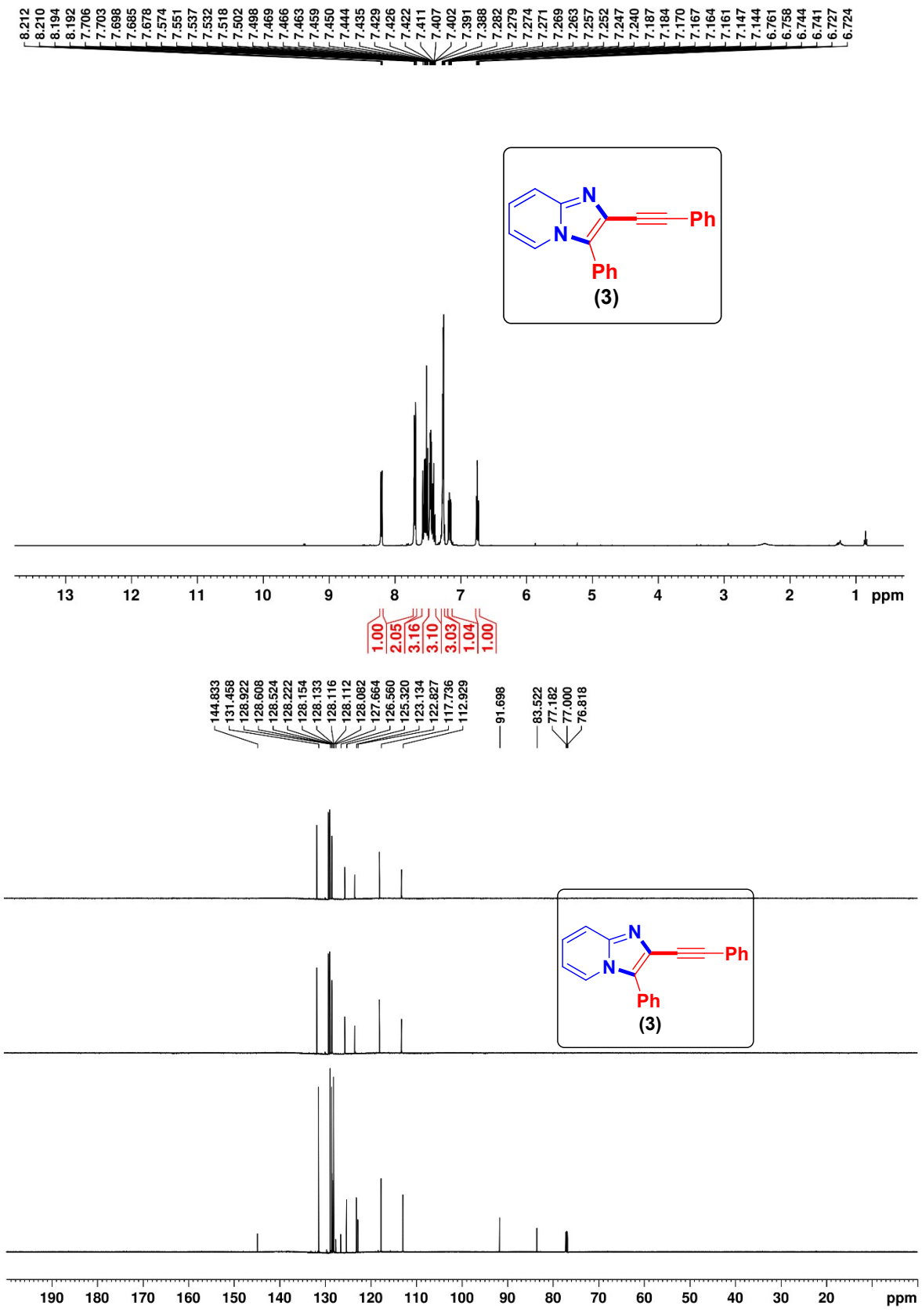
S3. Y. Okamoto and S. K. Kundu, *J. Phys. Chem.,* 1973, **77**, 2677.

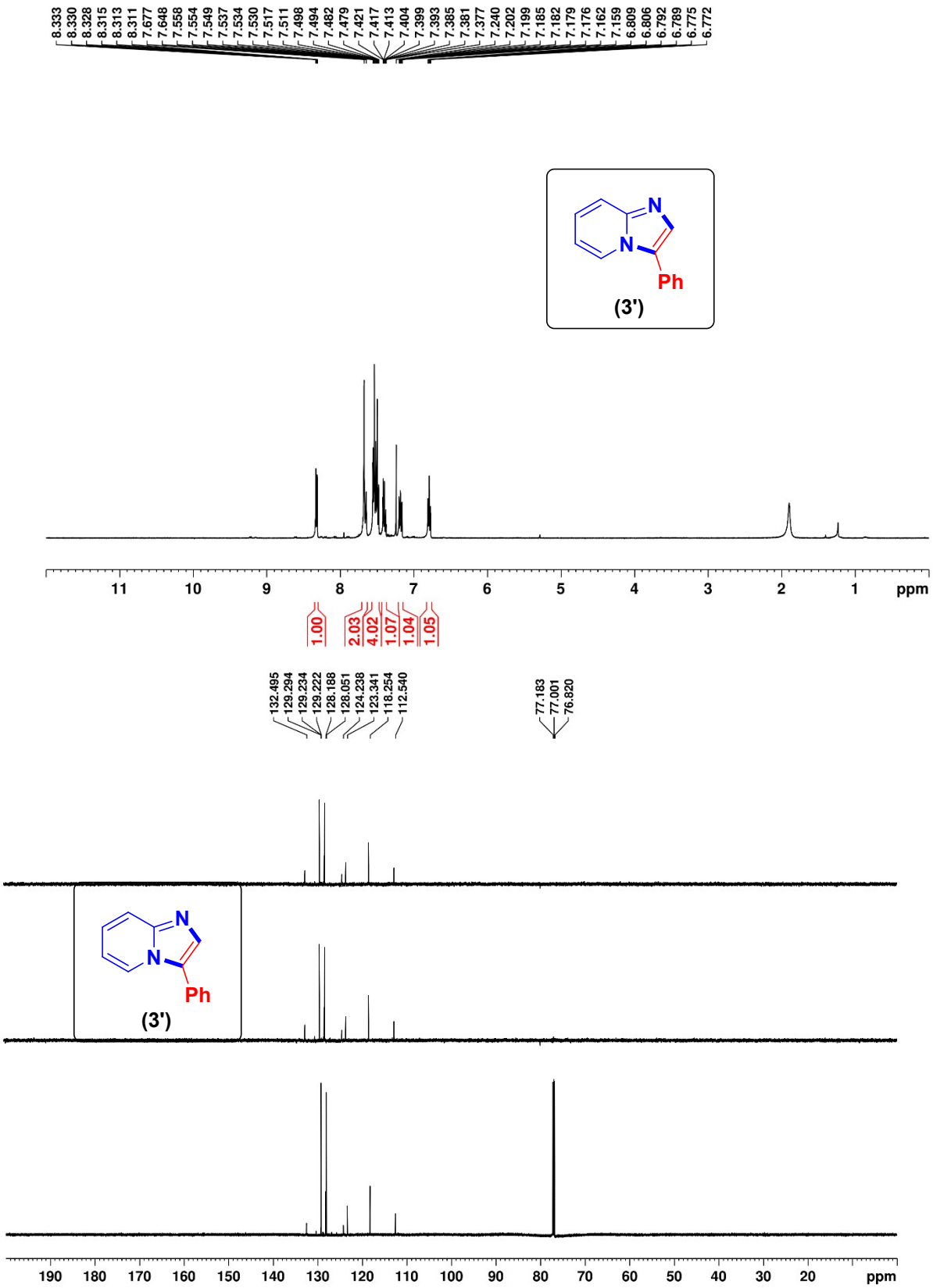
S4. V. P. Charpe, A. A. Hande, A. Sagadevan and K. C. Hwang, *Green Chem.,* 2018, **20**, 4859.

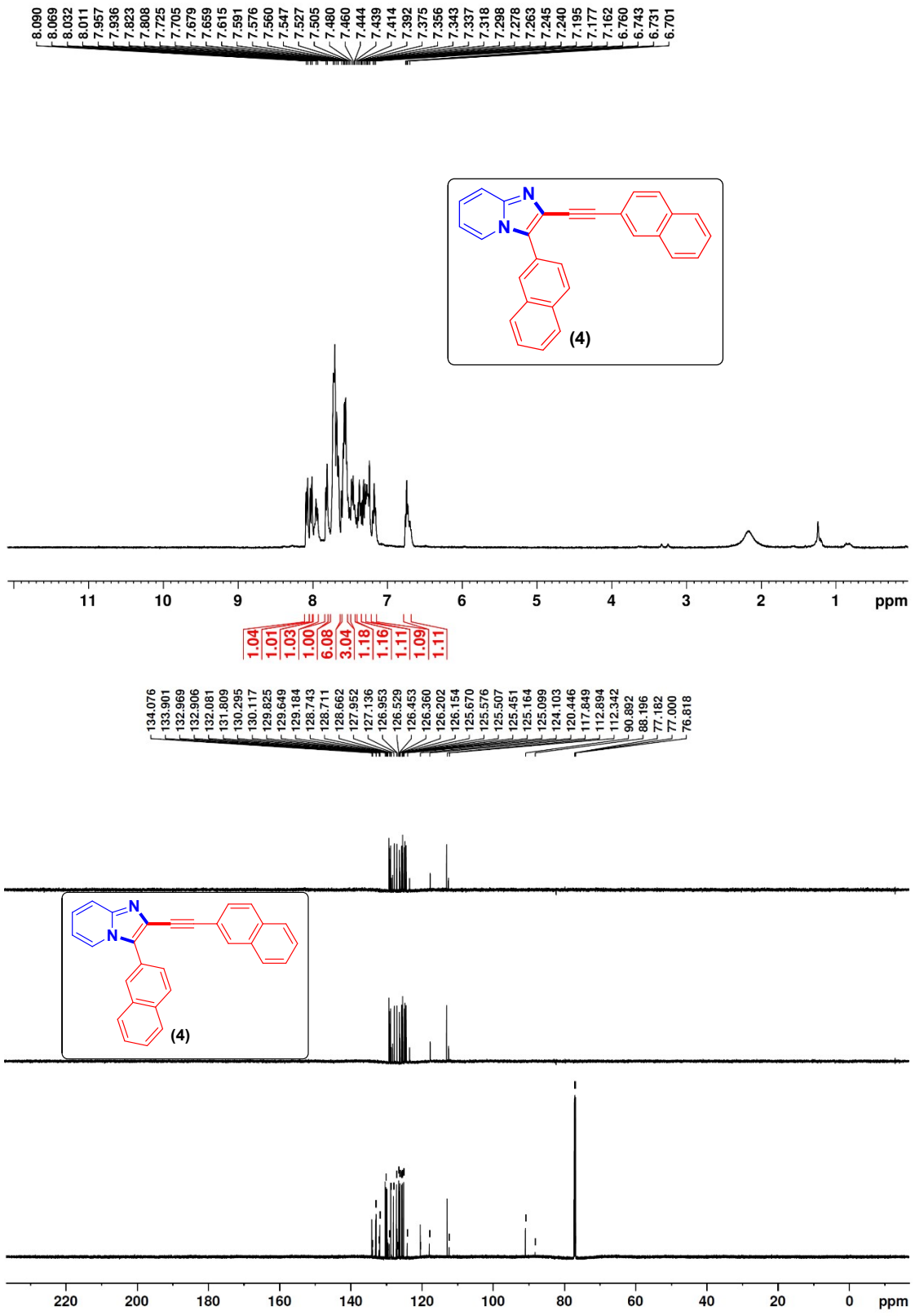
S5. J. V. Morris, M. A. Mahaney and J. R. Huber, *J. Phys. Chem.,* 1976, **80**, 969-974.

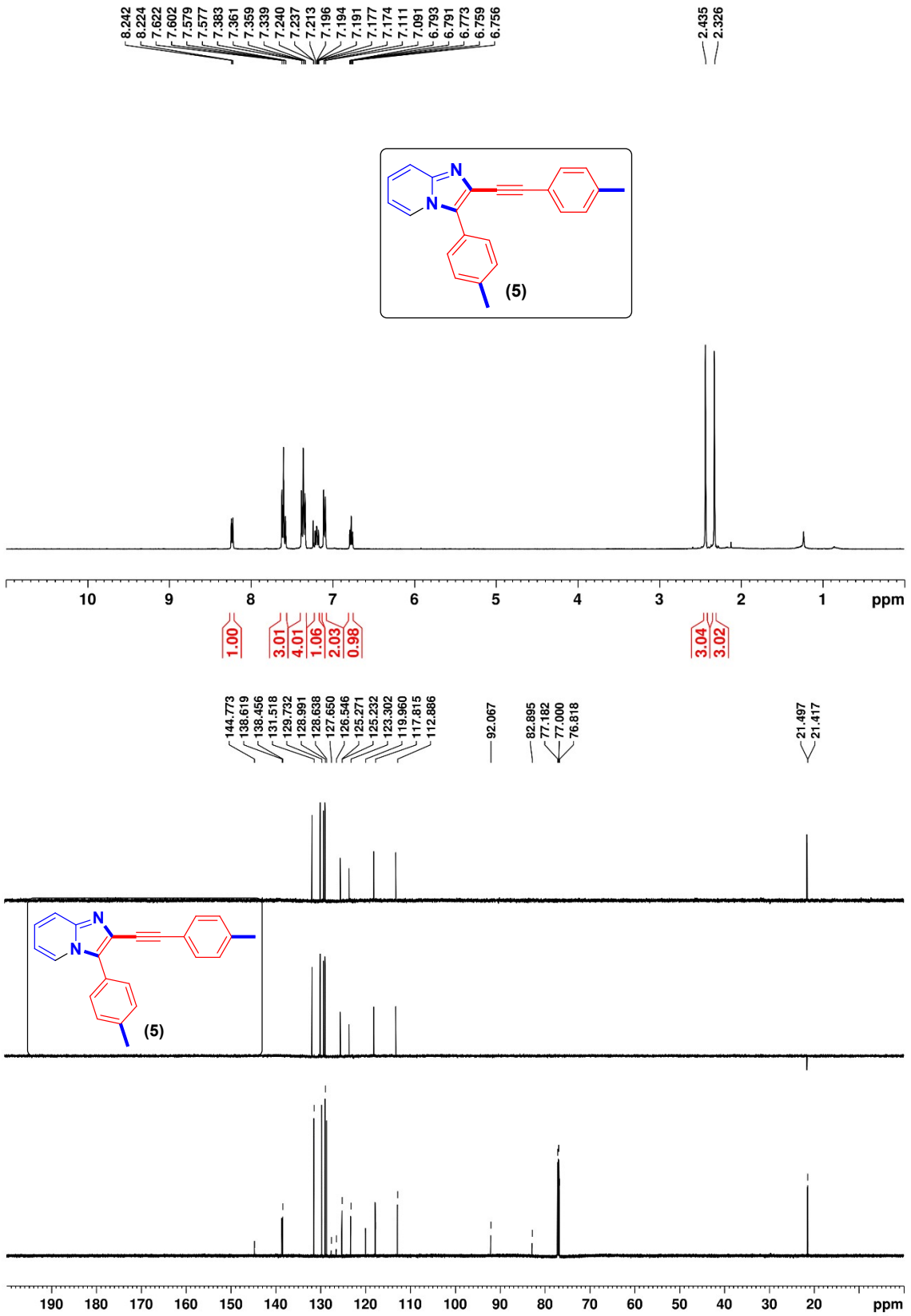
S6. Y. Gao, M. Yin, W. Wu, H. Huang and H. Jiang, *Adv. Synth. Catal.,* 2013, **355**, 2263;

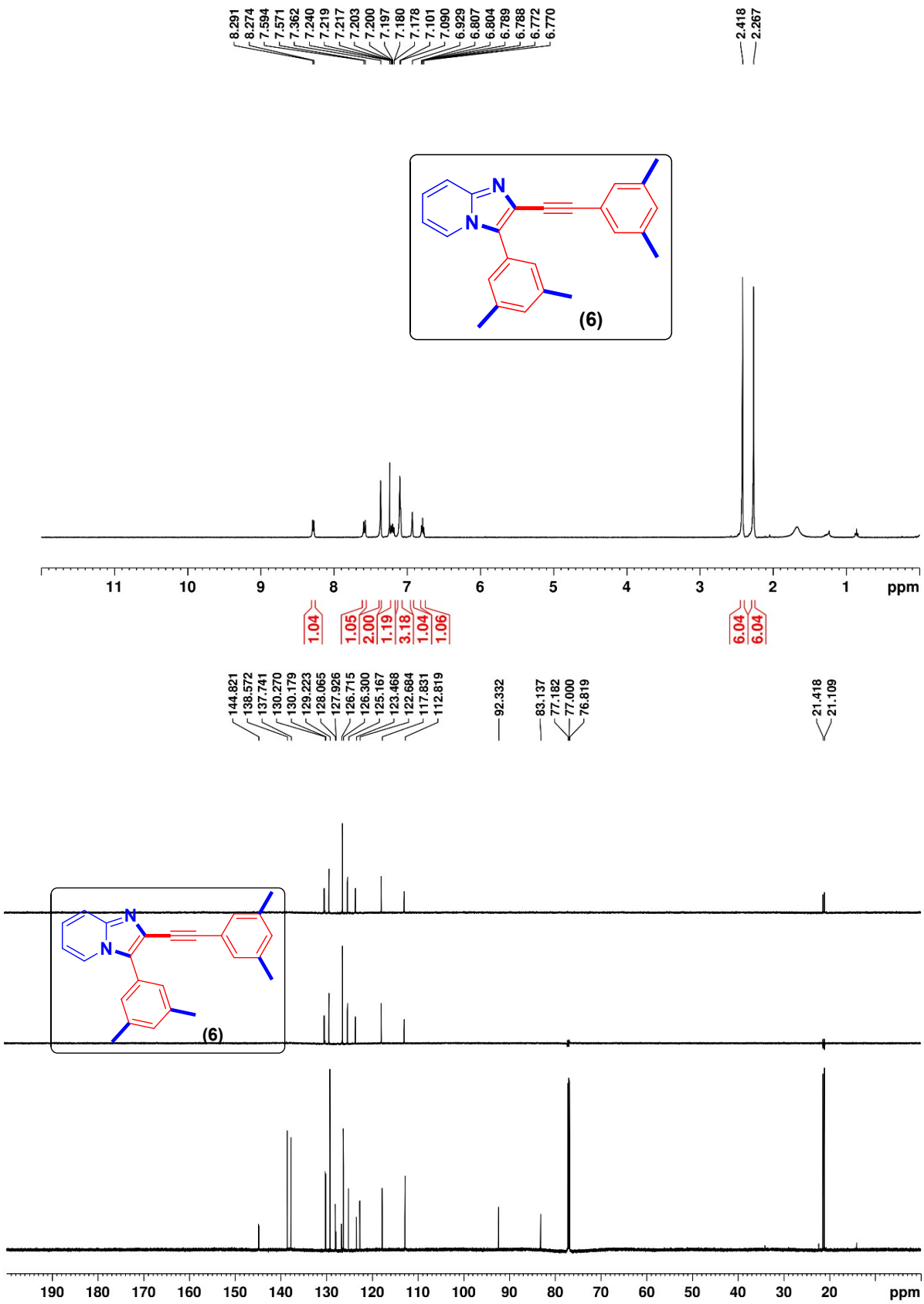
1. ^{1}H NMR, ^{13}C NMR, and ^{19}F-NMR spectra

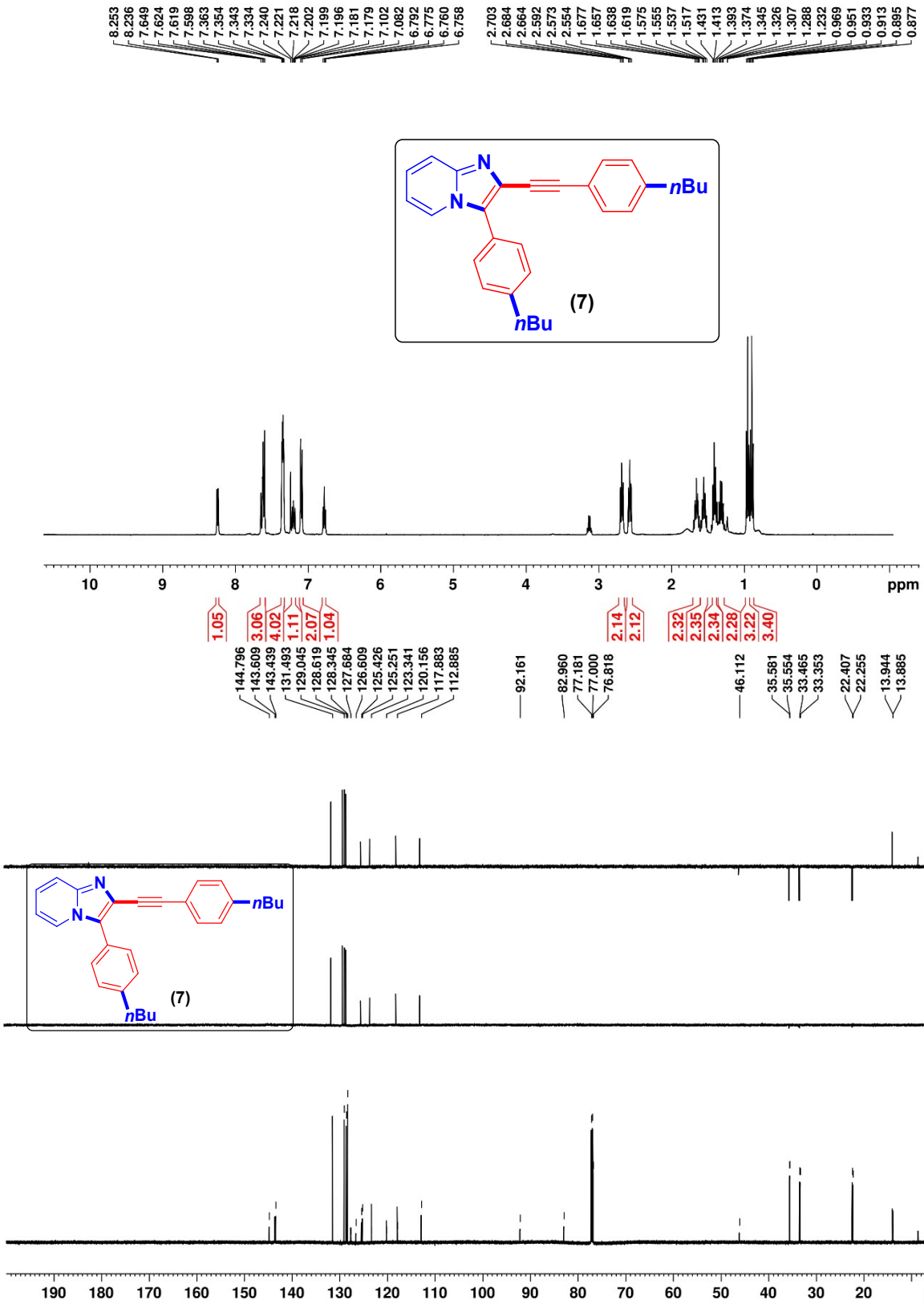

8.212
8.210
8.194
8.192
7.706
7.703
7.698
7.685
7.678
7.574
7.551
7.537
7.532
7.518
7.502
7.498
7.469
7.466
7.463
7.459
7.450
7.444
7.435
7.429
7.426
7.422
7.411
7.407
7.402
7.391
7.388
7.282
7.279
7.274
7.271
7.269
7.263
7.257
7.252
7.247
7.240
7.187
7.184
7.170
7.167
7.164
7.161
7.147
7.144
6.761
6.758
6.744
6.741
6.727
6.724
N
N
Ph
Ph
(3)
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.05
3.16
3.10
3.03
1.04
1.00
144.833
131.458
128.922
128.608
128.524
128.222
128.154
128.133
128.116
128.112
128.082
127.664
126.560
125.320
123.134
122.827
117.736
112.929
91.698
83.522
77.182
77.000
76.818
N
N
Ph
Ph
(3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

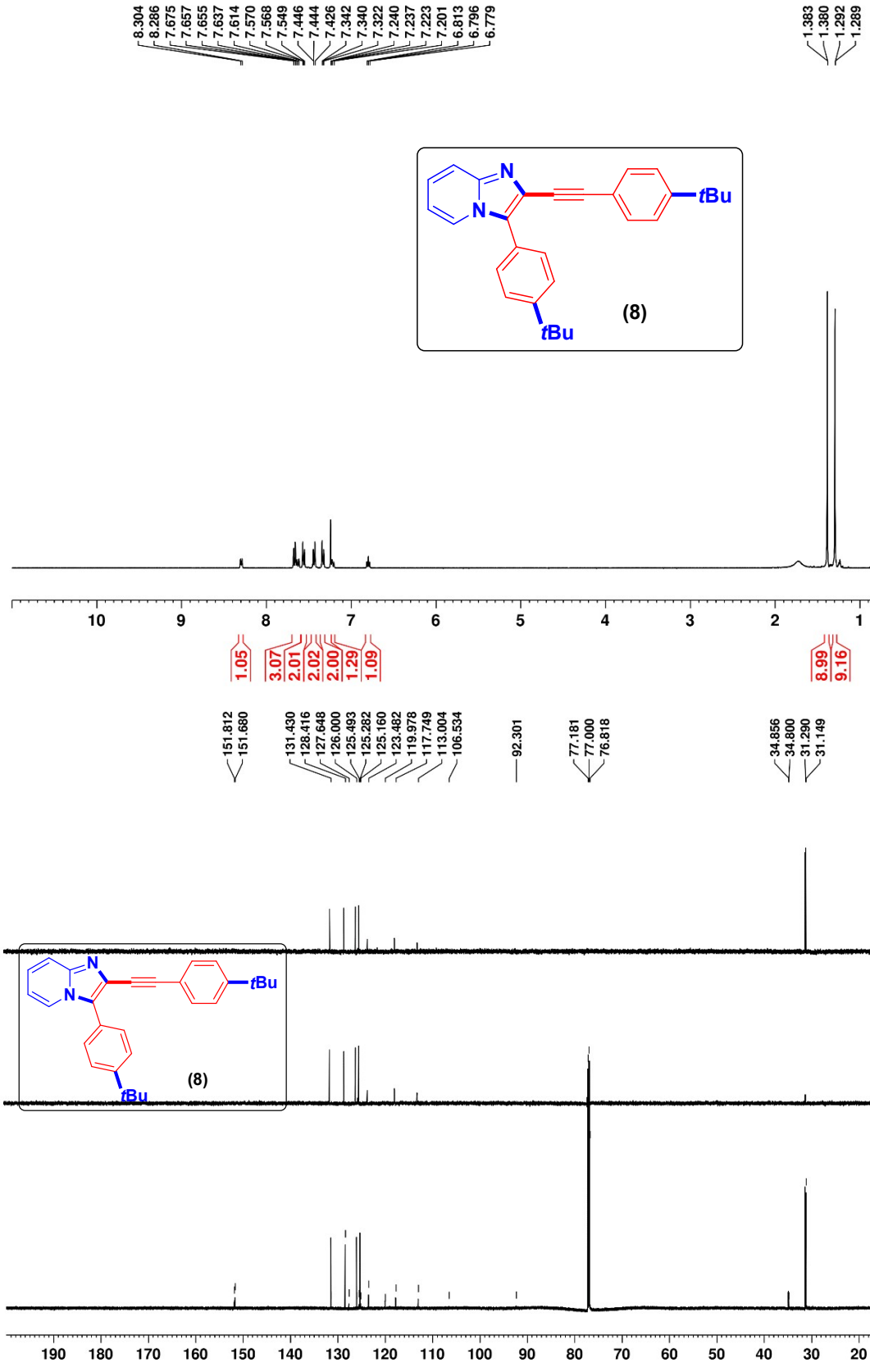

8.333
8.330
8.328
8.315
8.313
8.311
7.677
7.648
7.558
7.554
7.549
7.537
7.534
7.530
7.517
7.511
7.498
7.494
7.482
7.479
7.421
7.417
7.413
7.404
7.399
7.393
7.385
7.381
7.377
7.240
7.202
7.199
7.185
7.182
7.179
7.176
7.162
7.159
6.809
6.806
6.792
6.789
6.775
6.772
N
N
Ph
(3')
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.03
4.02
1.07
1.04
1.05
132.495
129.294
129.234
129.222
128.188
128.051
124.238
123.341
118.254
112.540
77.183
77.001
76.820
N
N
Ph
(3')
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

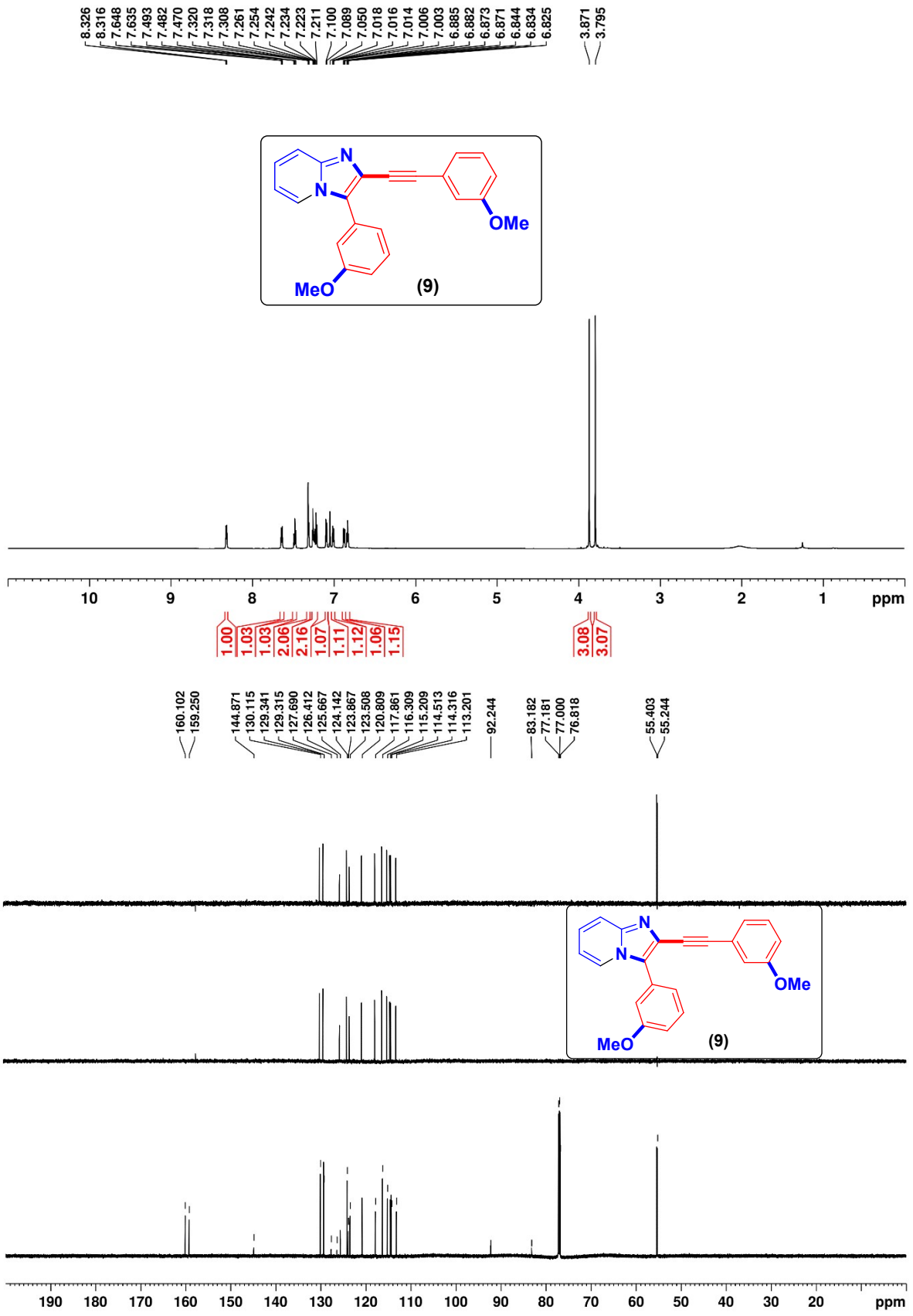

8.090
8.069
8.032
8.011
7.957
7.936
7.823
7.808
7.725
7.705
7.679
7.659
7.615
7.591
7.576
7.560
7.547
7.527
7.505
7.480
7.460
7.444
7.439
7.414
7.392
7.375
7.356
7.343
7.337
7.318
7.298
7.278
7.263
7.245
7.240
7.195
7.177
7.162
6.760
6.743
6.731
6.701
(4)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.04
1.01
1.03
1.00
6.08
3.04
1.18
1.16
1.11
1.09
1.11
134.076
133.901
132.969
132.906
132.081
131.809
130.295
130.117
129.825
129.649
129.184
128.743
128.711
128.662
127.952
127.136
126.953
126.529
126.453
126.360
126.202
126.154
125.670
125.576
125.507
125.451
125.164
125.099
124.103
120.446
117.849
112.894
112.342
90.892
88.196
77.182
77.000
76.818
(4)
220
200
180
160
140
120
100
80
60
40
20
0
ppm


8.242
8.224
7.622
7.602
7.579
7.577
7.383
7.361
7.359
7.339
7.240
7.237
7.213
7.196
7.194
7.191
7.177
7.174
7.111
7.091
6.793
6.791
6.773
6.759
6.756
2.435
2.326
(5)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.01
4.01
1.06
2.03
0.98
3.04
3.02
144.773
138.619
138.456
131.518
129.732
128.991
128.638
127.650
126.546
125.271
125.232
123.302
119.960
117.815
112.886
92.067
82.895
77.182
77.000
76.818
21.497
21.417
(5)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

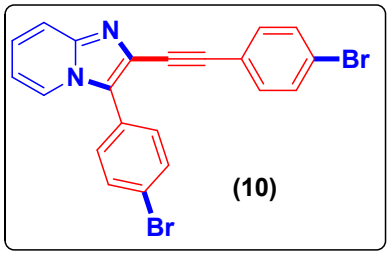

8.291
8.274
7.594
7.571
7.362
7.240
7.219
7.217
7.203
7.200
7.197
7.180
7.178
7.101
7.090
6.929
6.807
6.804
6.789
6.788
6.772
6.770
2.418
2.267
(6)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.04
1.05
2.00
1.19
3.18
1.04
1.06
6.04
6.04
144.821
138.572
137.741
130.270
130.179
129.223
128.065
127.926
126.715
126.300
125.167
123.468
122.684
117.831
112.819
92.332
83.137
77.182
77.000
76.819
21.418
21.109
(6)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

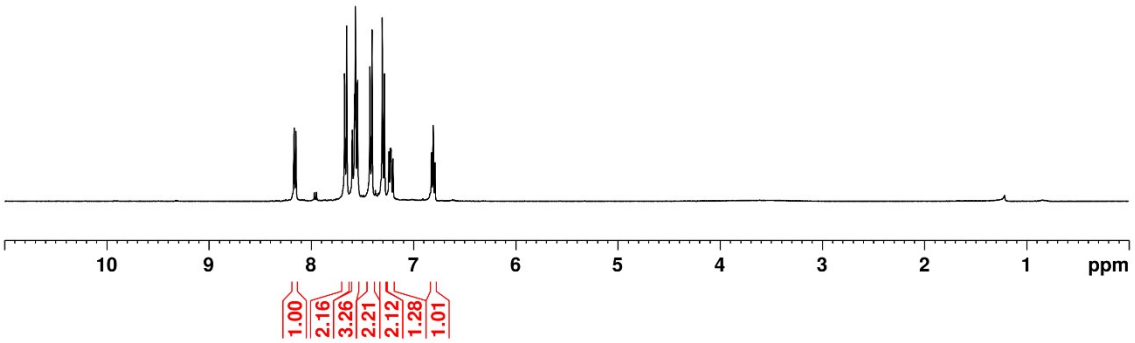

8.253
8.236
7.649
7.624
7.619
7.598
7.363
7.354
7.343
7.334
7.240
7.221
7.218
7.202
7.199
7.196
7.181
7.179
7.102
7.082
6.792
6.775
6.760
6.758
2.703
2.684
2.664
2.592
2.573
2.554
1.677
1.657
1.638
1.619
1.575
1.555
1.537
1.517
1.431
1.413
1.393
1.374
1.345
1.326
1.307
1.288
1.232
0.969
0.951
0.933
0.913
0.895
0.877
N
N
nBu
nBu
(7)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
3.06
4.02
1.11
2.07
1.04
2.14
2.12
2.32
2.35
2.34
2.28
3.22
3.40
144.796
143.609
143.439
131.493
129.045
128.619
128.345
127.684
126.609
125.426
125.251
123.341
120.156
117.883
112.885
92.161
82.960
77.181
77.000
76.818
46.112
35.581
35.554
33.465
33.353
22.407
22.255
13.944
13.885
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

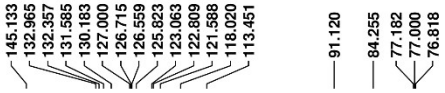

8.304
8.286
7.675
7.657
7.655
7.637
7.614
7.570
7.568
7.549
7.446
7.444
7.426
7.342
7.340
7.322
7.240
7.237
7.223
7.201
6.813
6.796
6.779
1.383
1.380
1.292
1.289
N
N
tBu
tBu
(8)
10
9
8
7
6
5
4
3
2
1
ppm
1.05
3.07
2.01
2.02
2.00
1.29
1.09
8.99
9.16
151.812
151.680
131.430
128.416
127.648
126.000
125.493
125.282
125.160
123.482
119.978
117.749
113.004
106.534
92.301
77.181
77.000
76.818
34.856
34.800
31.290
31.149
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

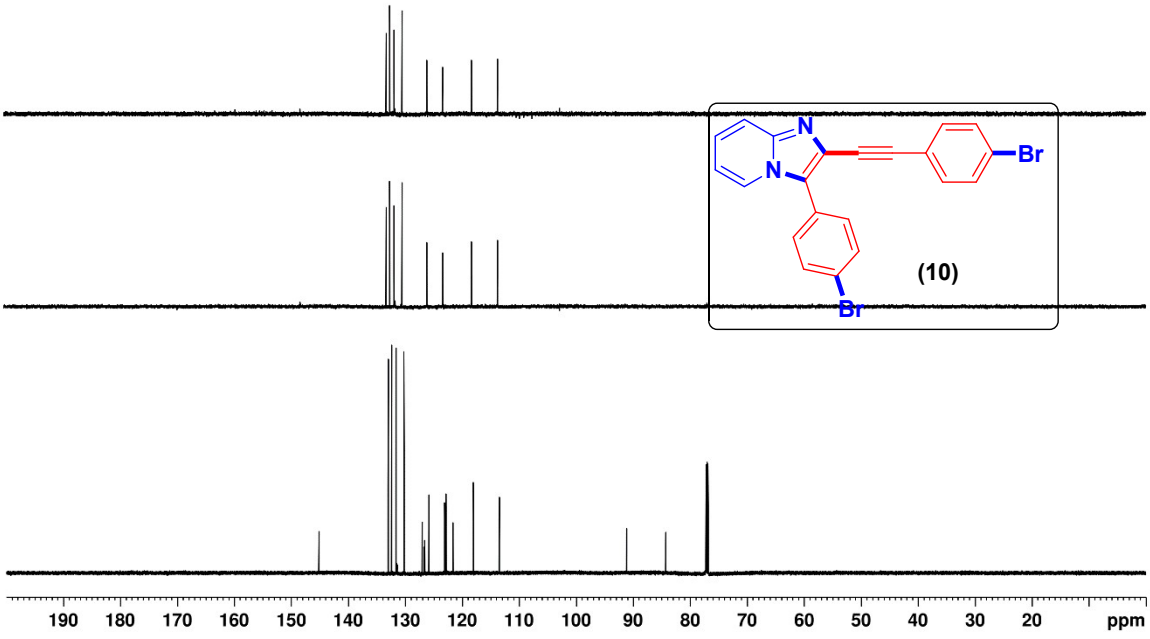

8.326
8.316
7.648
7.635
7.493
7.482
7.470
7.320
7.318
7.308
7.261
7.254
7.242
7.234
7.223
7.211
7.100
7.089
7.050
7.018
7.016
7.014
7.006
7.003
6.885
6.882
6.873
6.871
6.844
6.834
6.825
3.871
3.795
N
N
OMe
MeO
(9)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.03
2.06
2.16
1.07
1.11
1.12
1.06
1.15
3.08
3.07
160.102
159.250
144.871
130.115
129.341
129.315
127.690
126.412
125.667
124.142
123.867
123.508
120.809
117.861
116.309
115.209
114.513
114.316
113.201
92.244
83.182
77.181
77.000
76.818
55.403
55.244
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

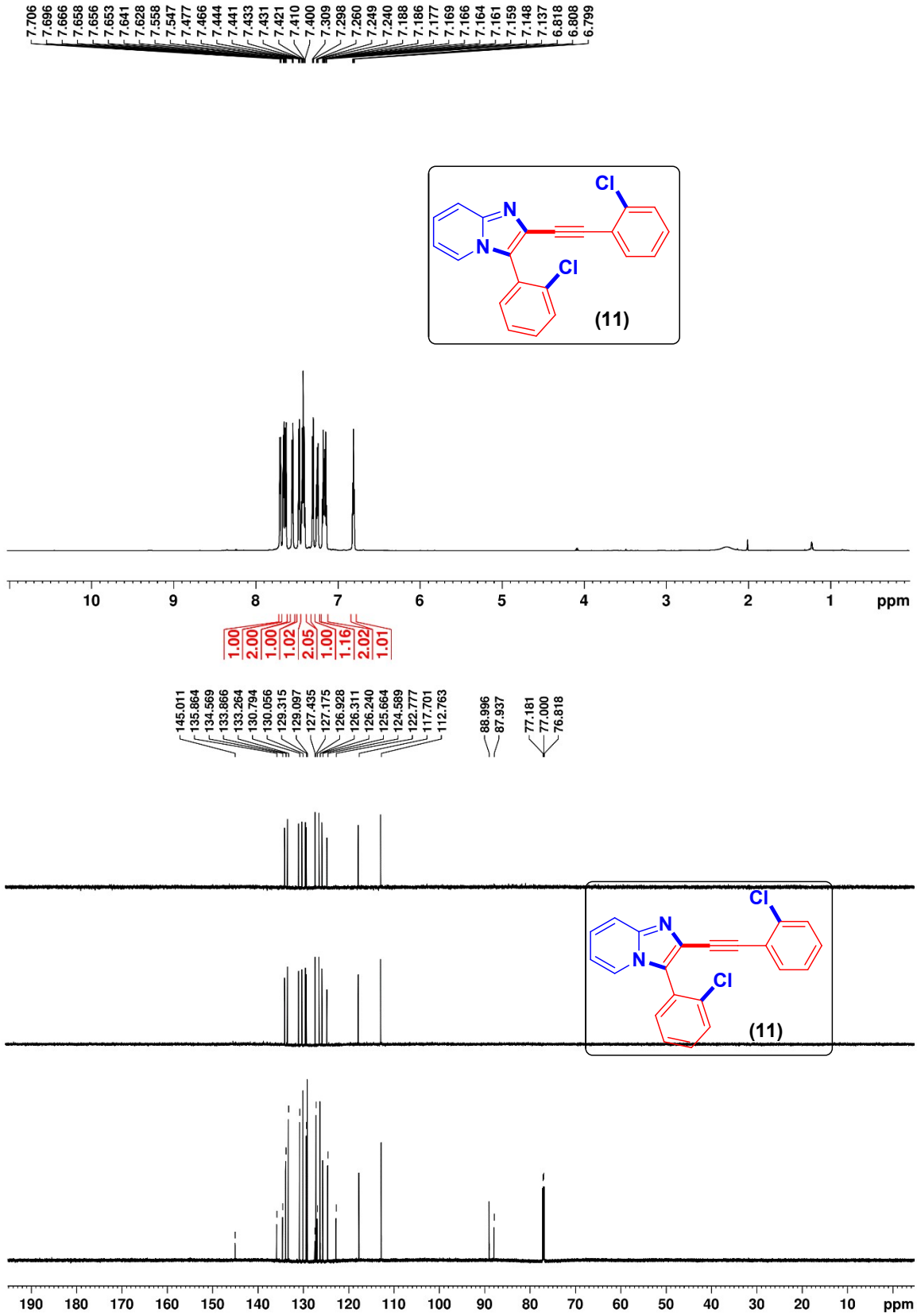

8.170
8.168
8.153
8.150
7.970
7.949
7.674
7.654
7.653
7.600
7.599
7.578
7.575
7.568
7.553
7.547
7.427
7.407
7.405
7.305
7.284
7.240
7.229
7.226
7.223
7.220
7.218
7.203
7.201
6.824
6.807
6.790

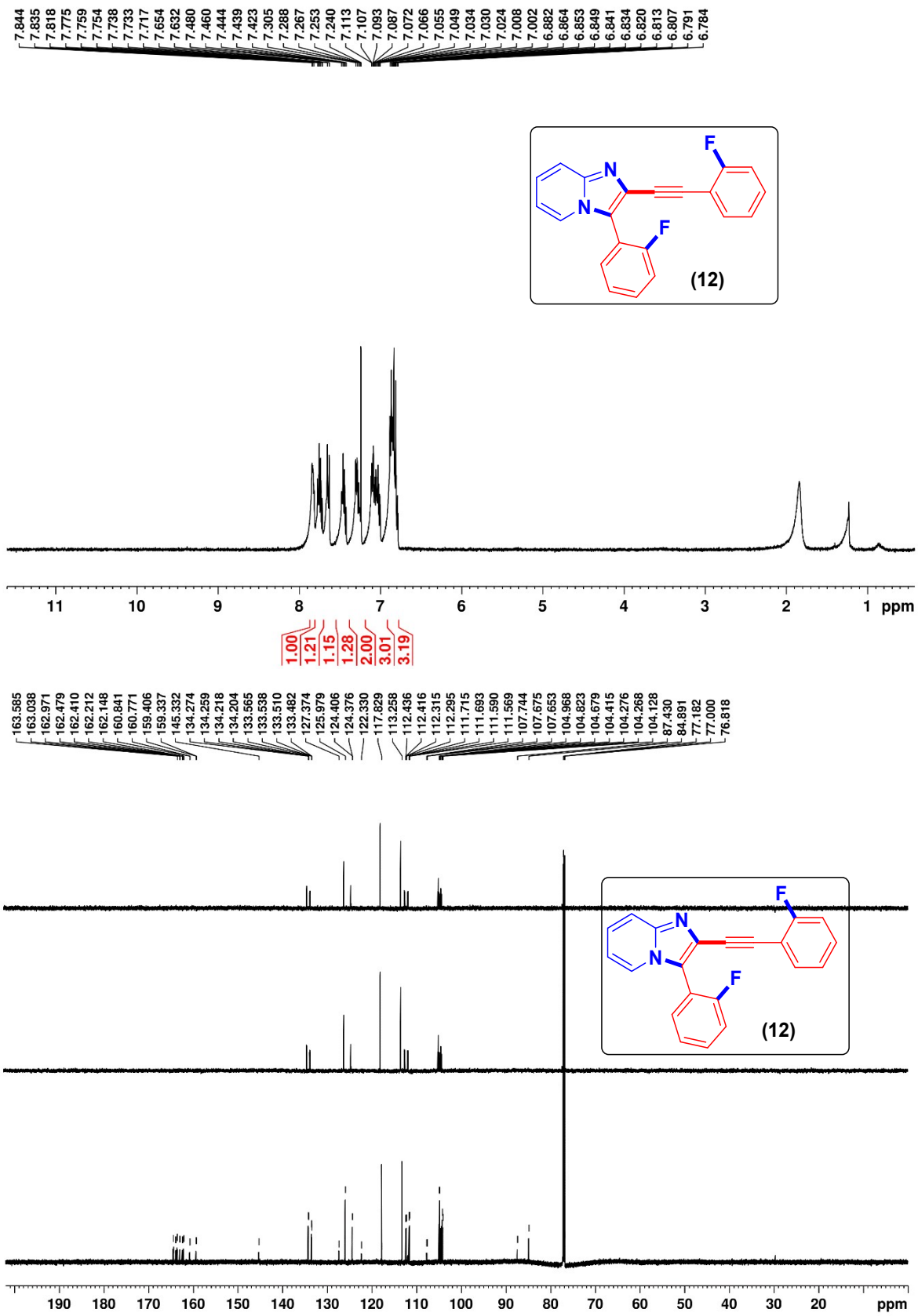

N
N
Br
Br
(10)


10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.16
3.26
2.21
2.12
1.28
1.01

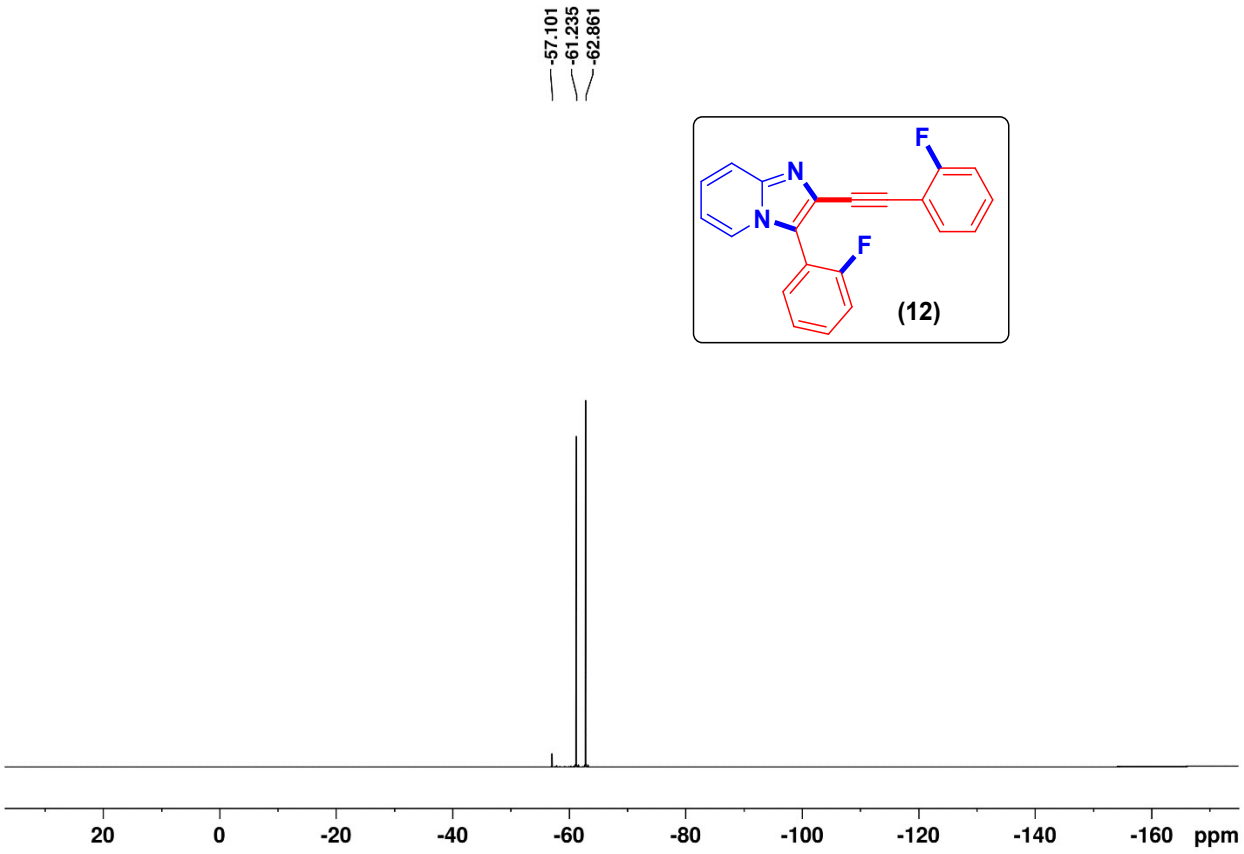

145.133
132.965
132.357
131.585
130.183
127.000
126.715
126.559
125.823
123.063
122.809
121.588
118.020
113.451
91.120
84.255
77.182
77.000
76.818

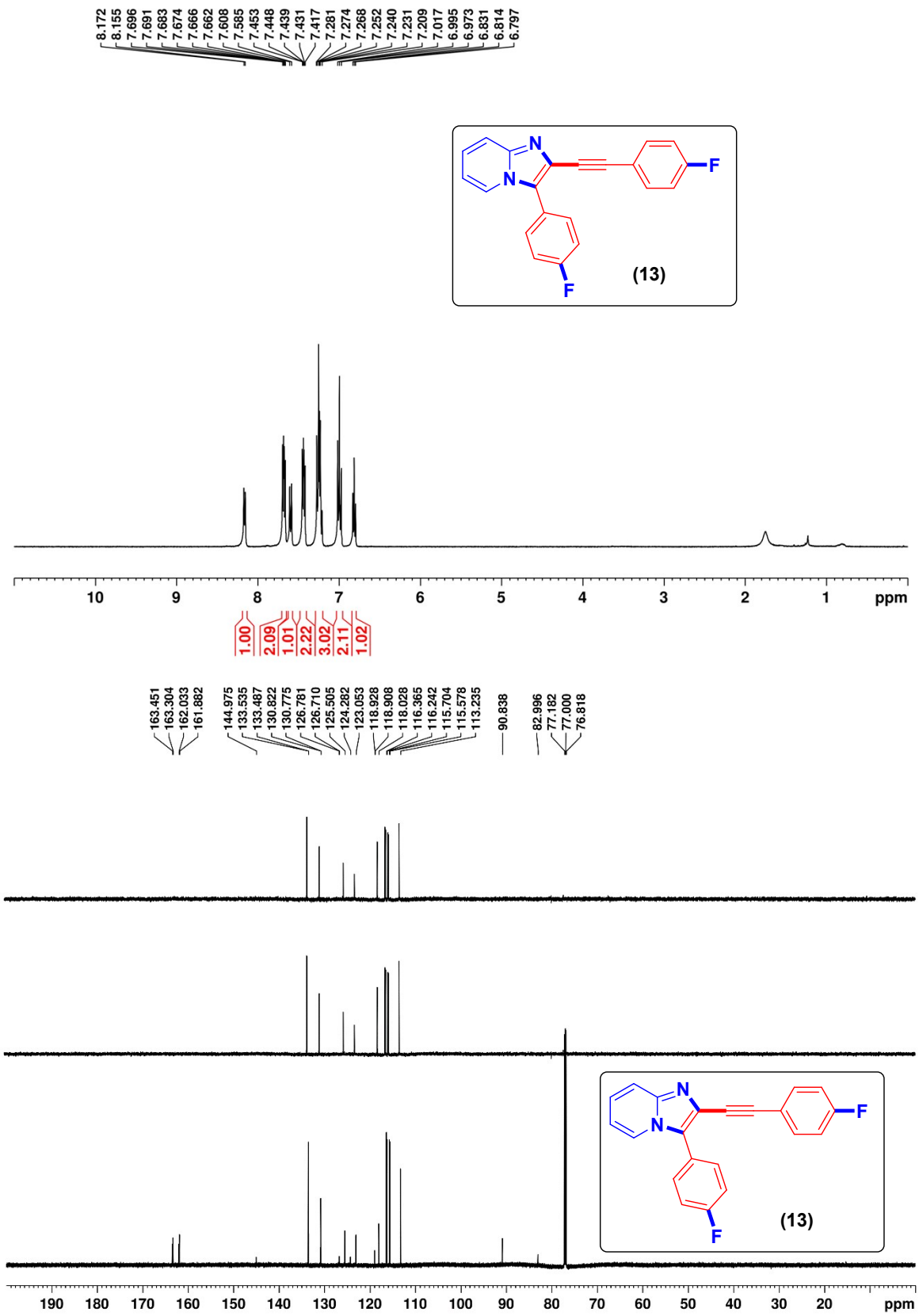

N
N
Br
Br
(10)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.706
7.696
7.666
7.658
7.656
7.653
7.641
7.628
7.558
7.547
7.477
7.466
7.444
7.441
7.433
7.431
7.421
7.410
7.400
7.309
7.298
7.260
7.249
7.240
7.188
7.186
7.177
7.169
7.166
7.164
7.161
7.159
7.148
7.137
6.818
6.808
6.799
Cl
N
N
Cl
(11)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.00
1.00
1.02
2.05
1.00
1.16
2.02
1.01
145.011
135.864
134.569
133.866
133.264
130.794
130.056
129.315
129.097
127.435
127.175
126.928
126.311
126.240
125.664
124.589
122.777
117.701
112.763
88.996
87.937
77.181
77.000
76.818
Cl
N
N
Cl
(11)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

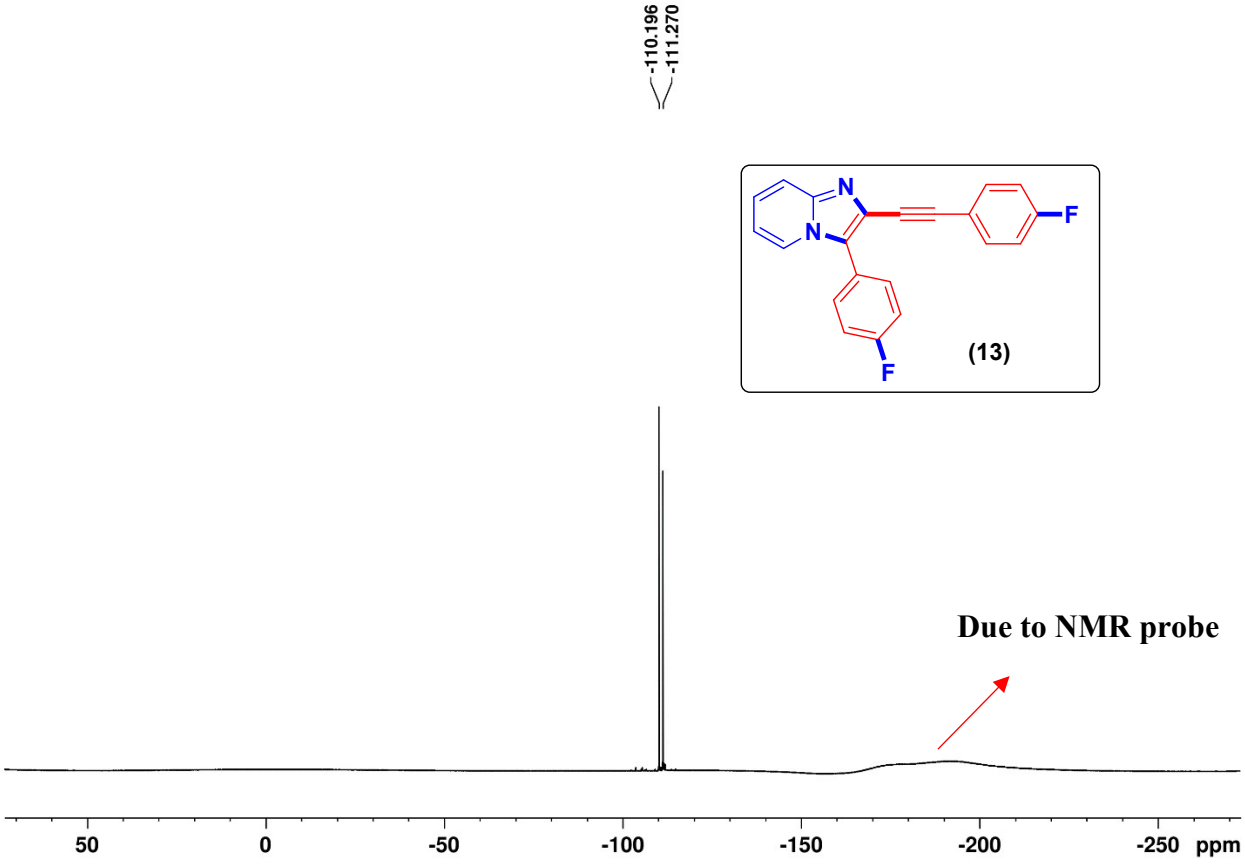

7.844
7.835
7.818
7.775
7.759
7.754
7.738
7.733
7.717
7.654
7.632
7.480
7.460
7.444
7.439
7.423
7.305
7.288
7.267
7.253
7.240
7.113
7.107
7.093
7.087
7.072
7.066
7.055
7.049
7.034
7.030
7.024
7.008
7.002
6.882
6.864
6.853
6.849
6.841
6.834
6.820
6.813
6.807
6.791
6.784
F
N
N
F
(12)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.21
1.15
1.28
2.00
3.01
3.19
163.585
163.038
162.971
162.479
162.410
162.212
162.148
160.841
160.771
159.406
159.337
145.332
134.274
134.259
134.218
134.204
133.565
133.538
133.510
133.482
127.374
125.979
124.406
124.376
122.330
117.829
113.258
112.436
112.416
112.315
112.295
111.715
111.693
111.590
111.569
107.744
107.675
107.653
104.968
104.823
104.679
104.415
104.276
104.268
104.128
87.430
84.891
77.182
77.000
76.818
F
N
N
F
(12)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

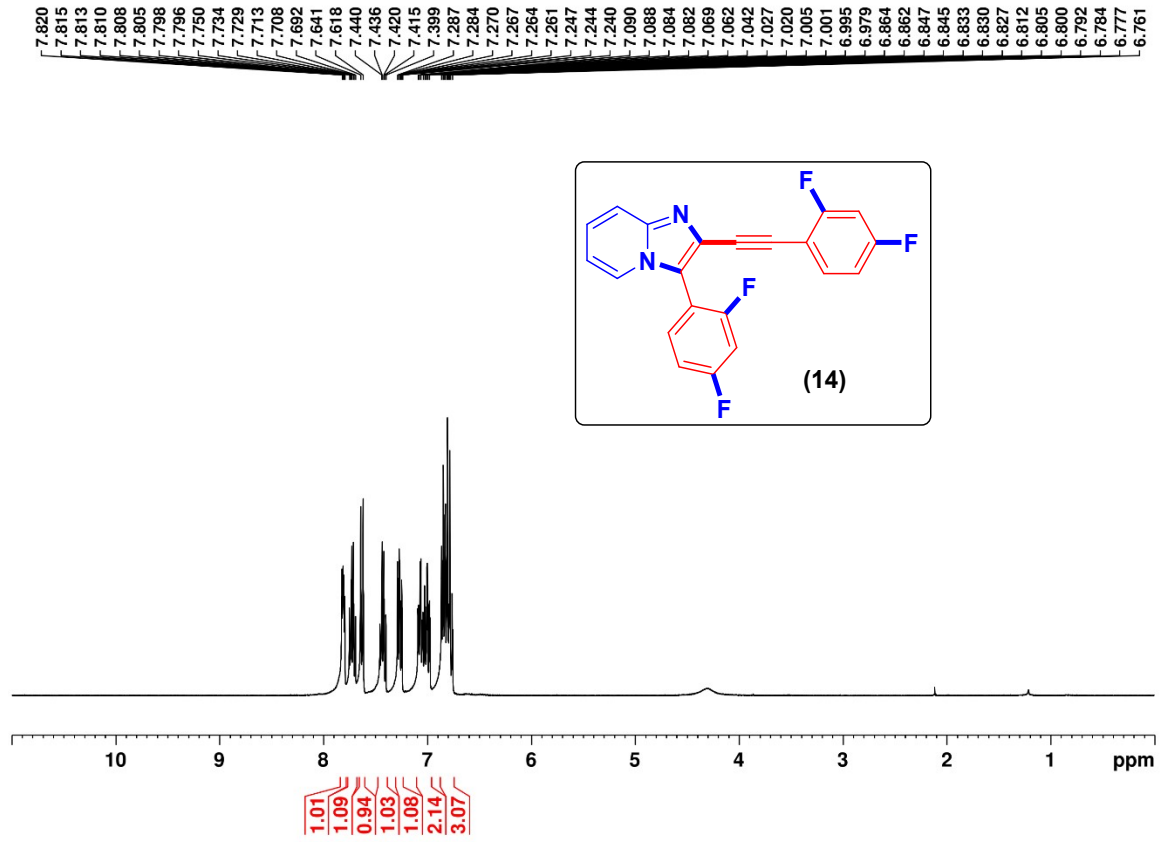
^{19}F-NMR

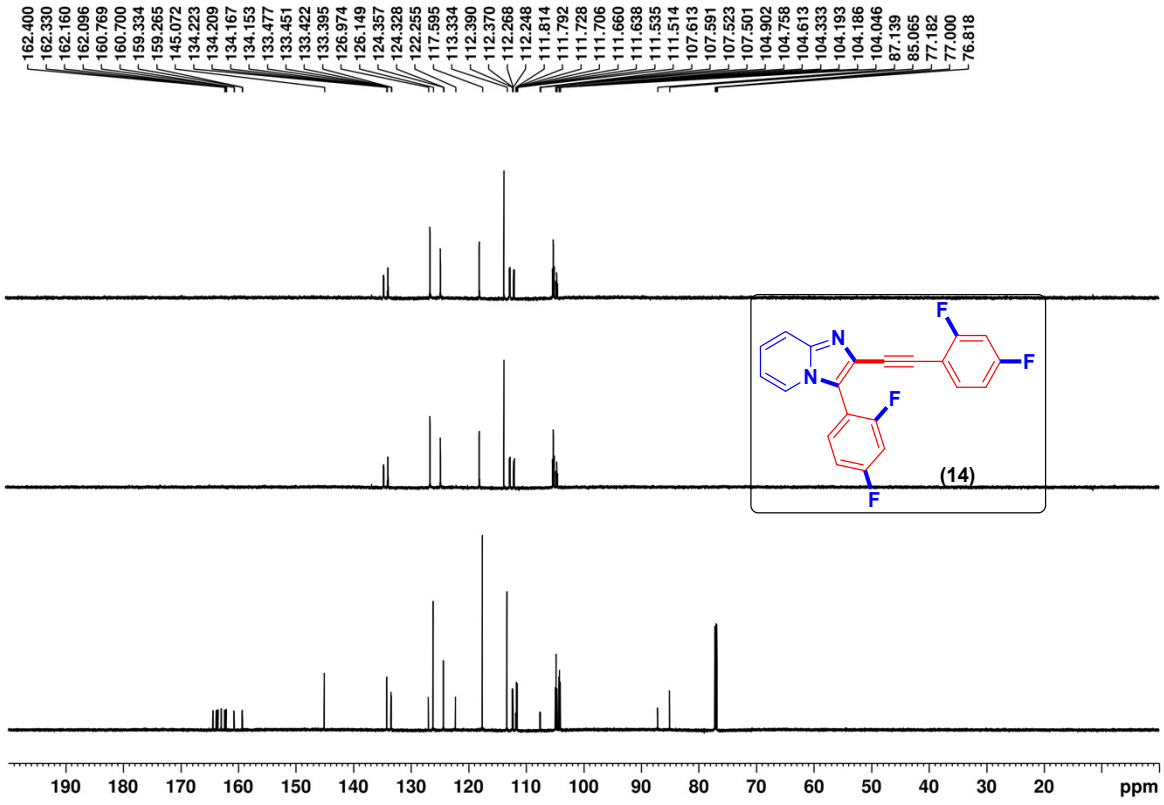



8.172
8.155
7.696
7.691
7.683
7.674
7.666
7.662
7.608
7.585
7.453
7.448
7.439
7.431
7.417
7.281
7.274
7.268
7.252
7.240
7.231
7.209
7.017
6.995
6.973
6.831
6.814
6.797
N
N
F
F
(13)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.09
1.01
2.22
3.02
2.11
1.02
163.451
163.304
162.033
161.882
144.975
133.535
133.487
130.822
130.775
126.781
126.710
125.505
124.282
123.053
118.928
118.908
118.028
116.365
116.242
115.704
115.578
113.235
90.838
82.996
77.182
77.000
76.818
N
N
F
F
(13)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

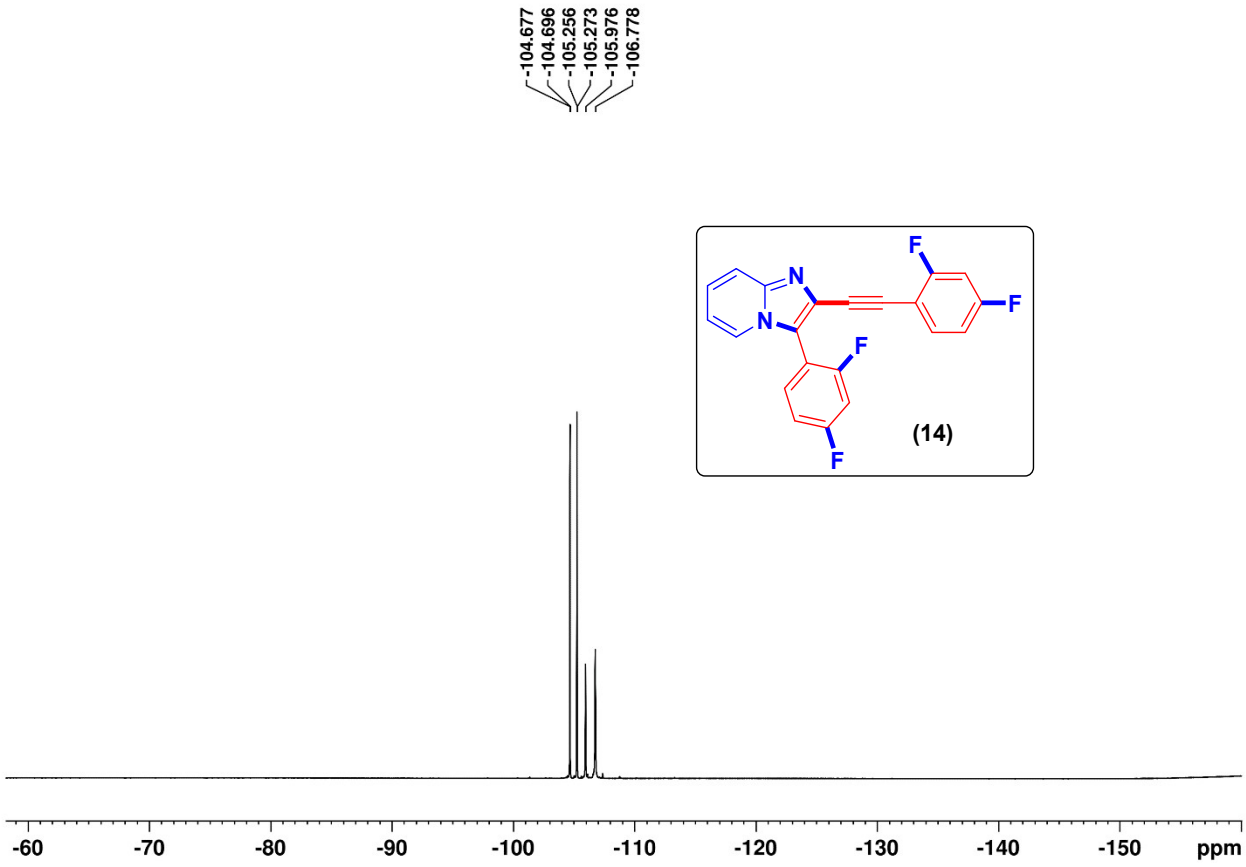
^{19}F-NMR

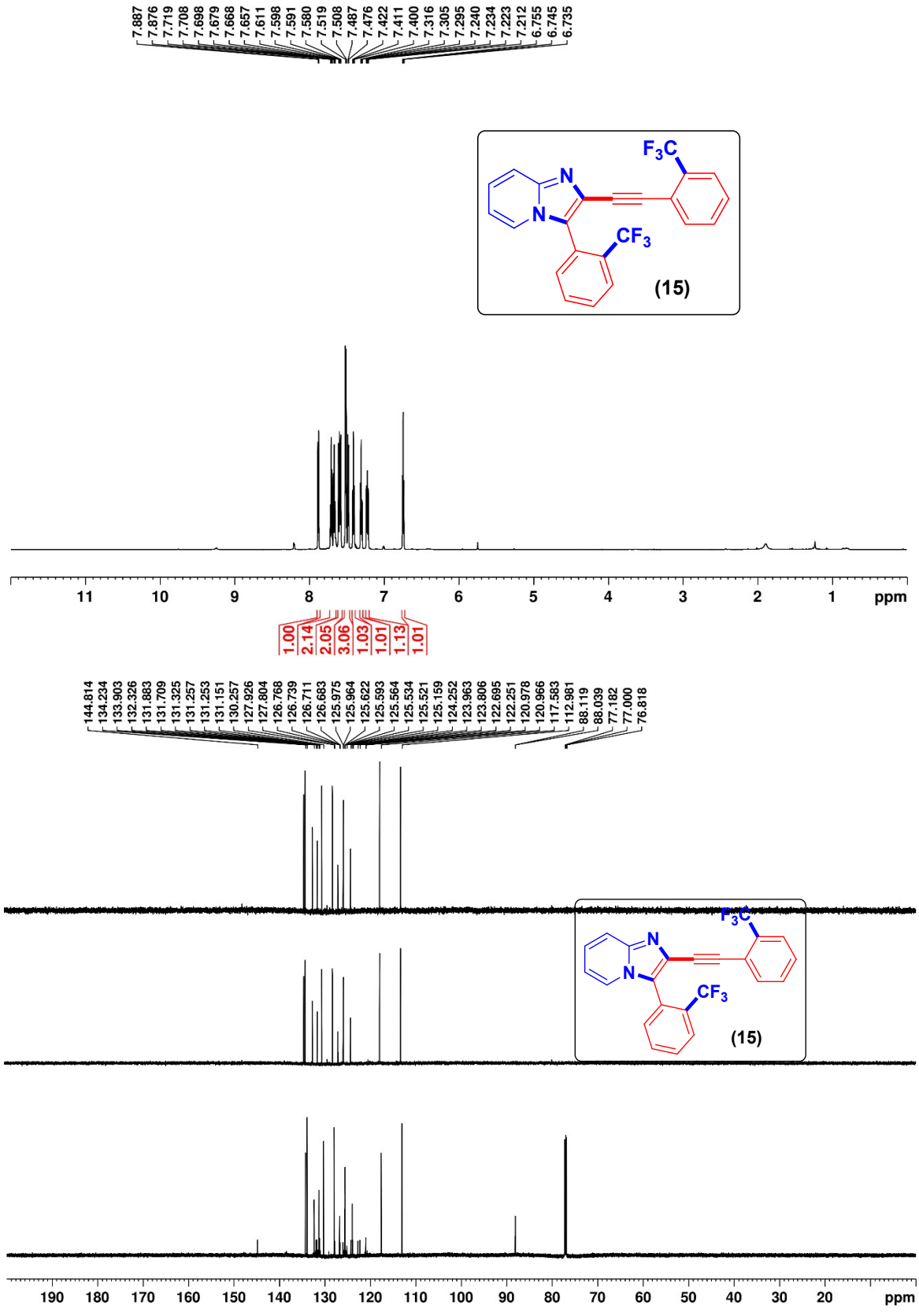

-110.196
-111.270
N
N
F
F
(13)
Due to NMR probe
50
0
-50
-100
-150
-200
-250
ppm


7.820
7.815
7.813
7.810
7.808
7.805
7.798
7.796
7.750
7.734
7.729
7.713
7.708
7.692
7.641
7.618
7.440
7.436
7.420
7.415
7.399
7.287
7.284
7.270
7.267
7.264
7.261
7.247
7.244
7.240
7.090
7.088
7.084
7.082
7.069
7.062
7.042
7.027
7.020
7.005
7.001
6.995
6.979
6.864
6.862
6.847
6.845
6.833
6.830
6.827
6.812
6.805
6.800
6.792
6.784
6.777
6.761
F
N
N
F
F
(14)
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.09
0.94
1.03
1.08
2.14
3.07

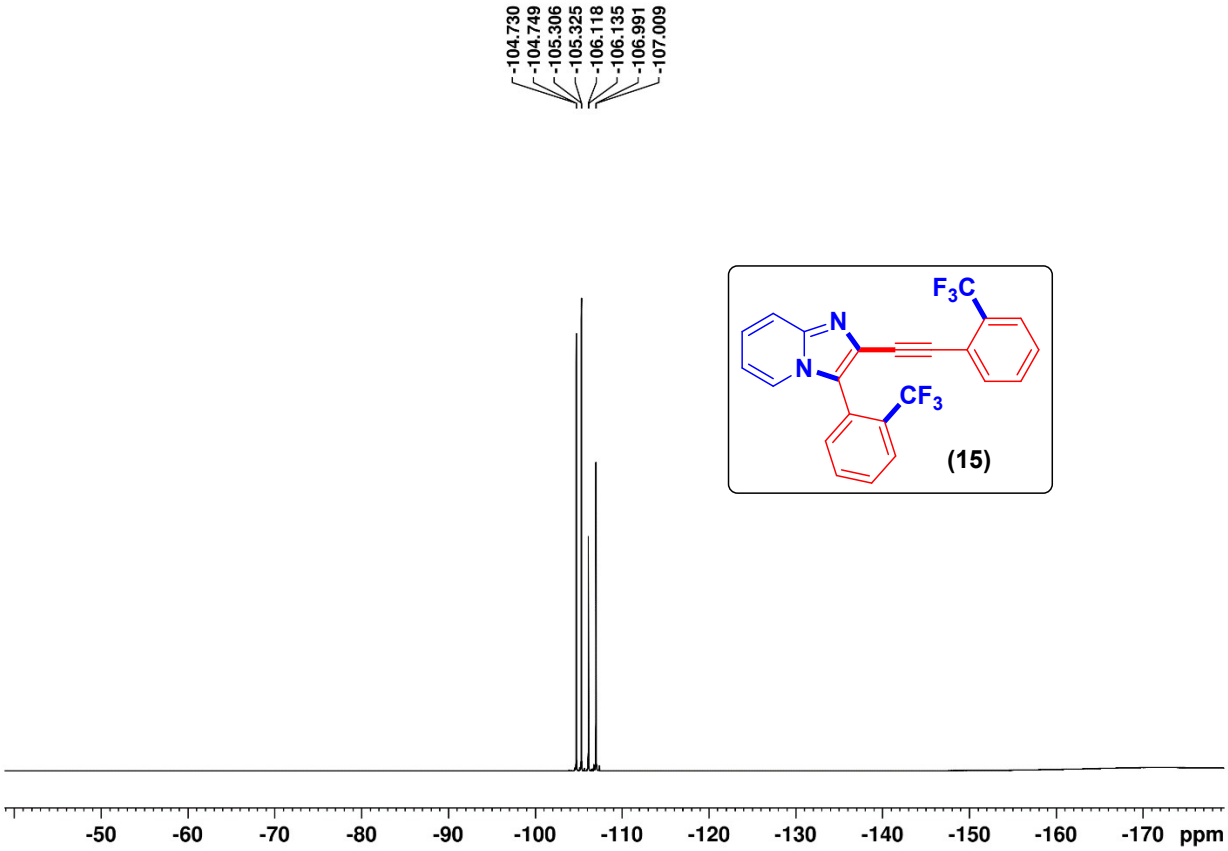

162.400
162.330
162.160
162.096
160.769
160.700
159.334
159.265
145.072
134.223
134.209
134.167
134.153
133.477
133.451
133.422
133.395
126.974
126.149
124.357
124.328
122.255
117.595
113.334
112.390
112.370
112.268
112.248
111.814
111.792
111.728
111.706
111.660
111.638
111.535
111.514
107.613
107.591
107.523
107.501
104.902
104.758
104.613
104.333
104.193
104.186
104.046
87.139
85.065
77.182
77.000
76.818
F
N
N
F
F
(14)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

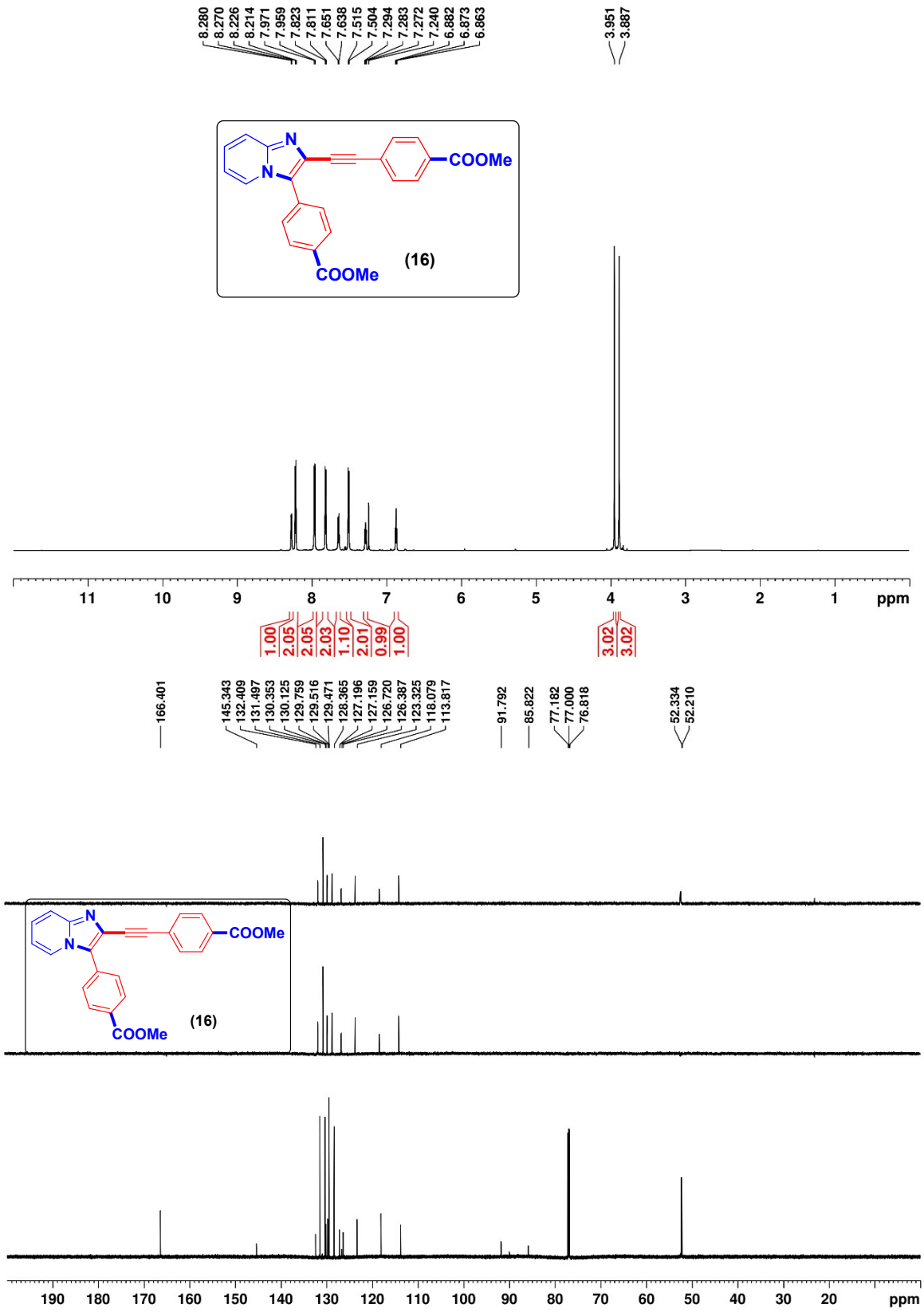
^{19}F-NMR

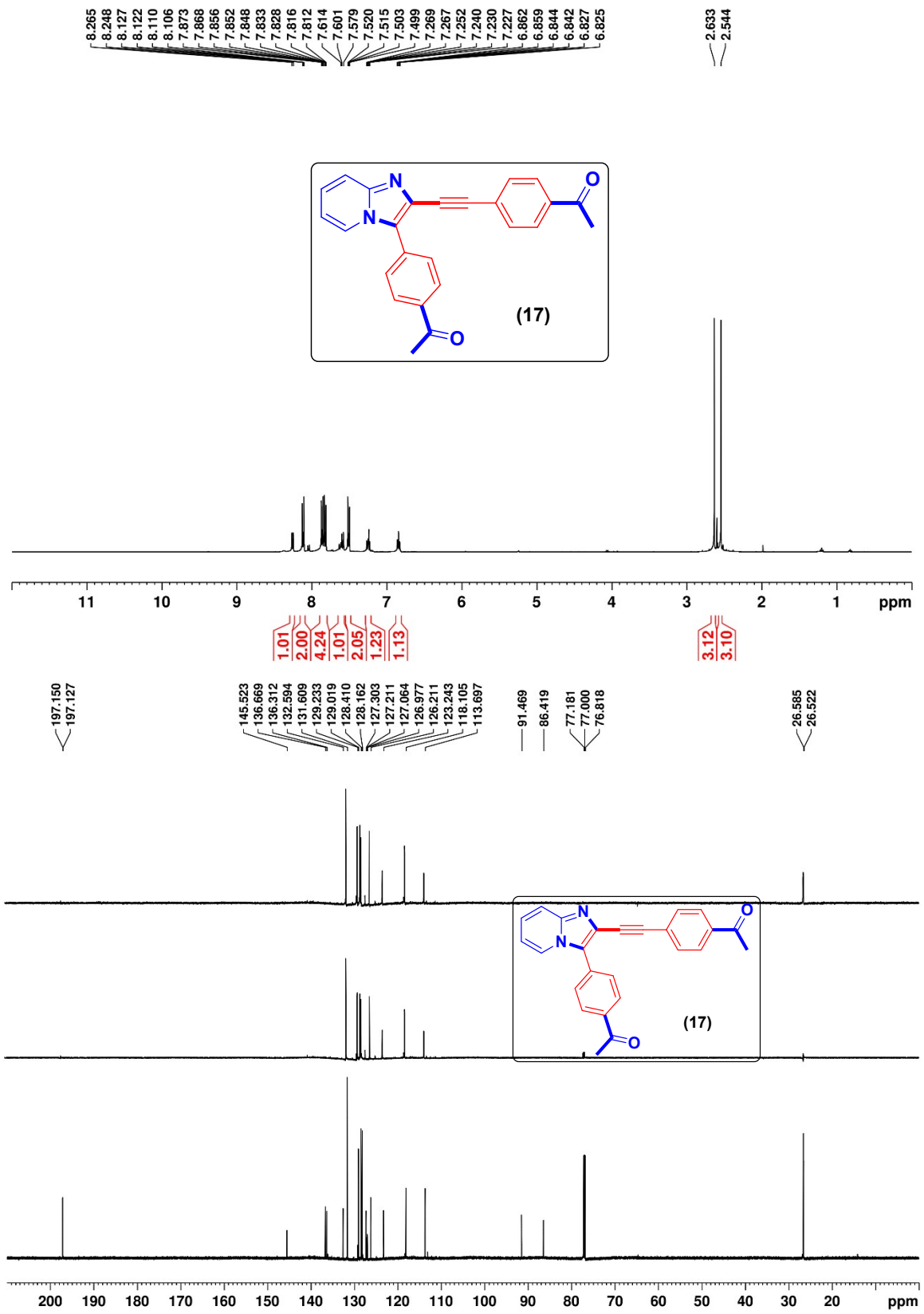

-104.677
-104.696
-105.256
-105.273
-105.976
-106.778
F
N
N
F
F
F
(14)
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm

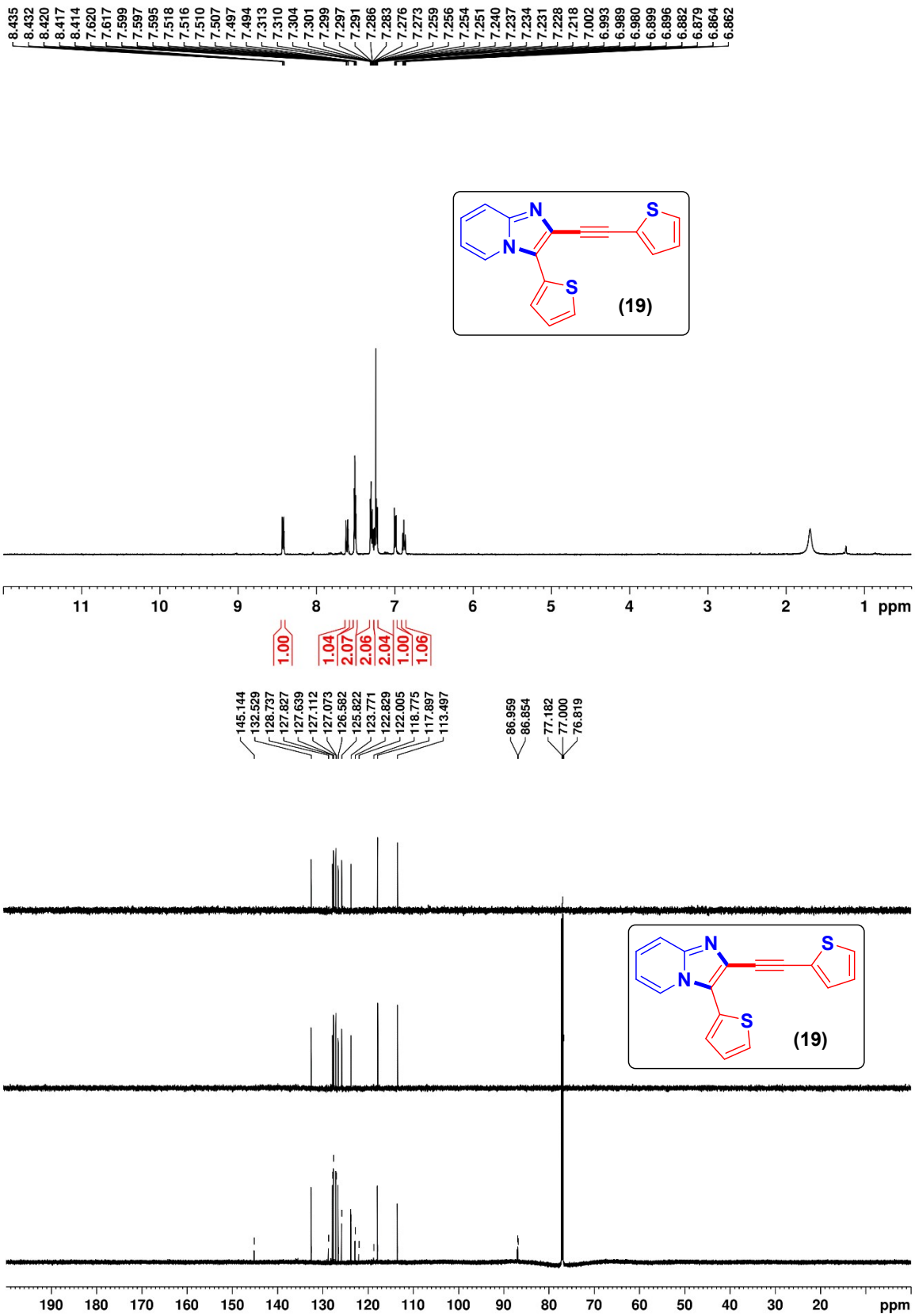

7.887
7.876
7.719
7.708
7.698
7.679
7.668
7.657
7.611
7.598
7.591
7.580
7.519
7.508
7.487
7.476
7.422
7.411
7.400
7.316
7.305
7.295
7.240
7.234
7.223
7.212
6.755
6.745
6.735
F3C
N
N
CF3
(15)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.14
2.05
3.06
1.03
1.01
1.13
1.01
144.814
134.234
133.903
132.326
131.883
131.709
131.325
131.257
131.253
131.151
130.257
127.926
127.804
126.768
126.739
126.711
126.683
125.975
125.964
125.622
125.593
125.564
125.534
125.521
125.159
124.252
123.963
123.806
122.695
122.251
120.978
120.966
117.583
112.981
88.119
88.039
77.182
77.000
76.818
F3C
N
N
CF3
(15)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

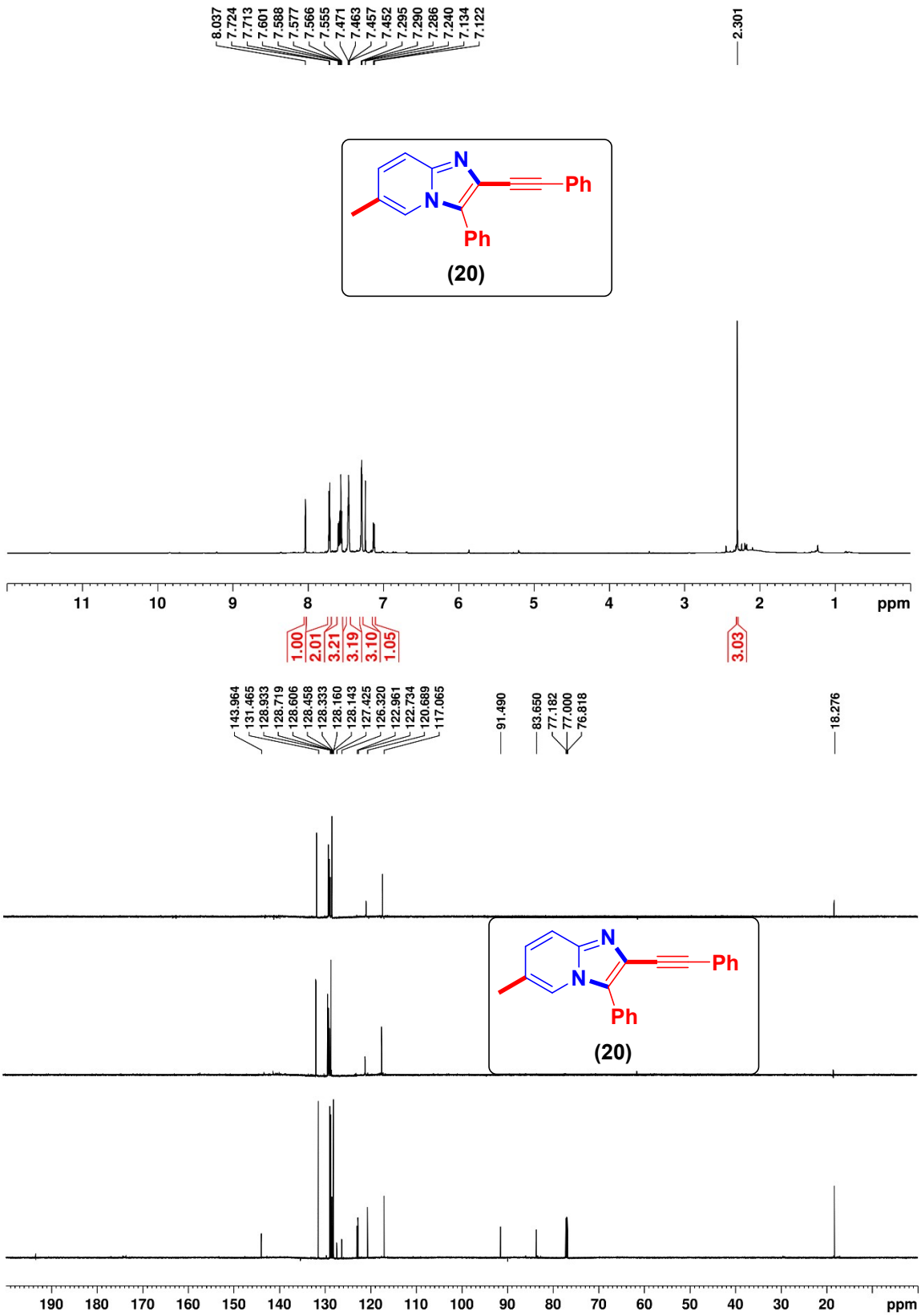
^{19}F-NMR


-104.730
-104.749
-105.306
-105.325
-106.118
-106.135
-106.991
-107.009
F3C
N
N
CF3
(15)
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
ppm

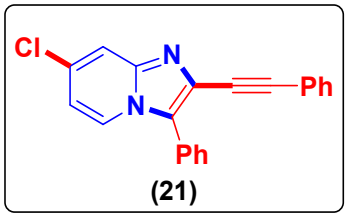

8.280
8.270
8.226
8.214
7.971
7.959
7.823
7.811
7.651
7.638
7.515
7.504
7.294
7.283
7.272
7.240
6.882
6.873
6.863
3.951
3.887
COOMe
COOMe
(16)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.05
2.05
2.03
1.10
2.01
0.99
1.00
3.02
3.02
166.401
145.343
132.409
131.497
130.353
130.125
129.759
129.516
129.471
128.365
127.196
127.159
126.720
126.387
123.325
118.079
113.817
91.792
85.822
77.182
77.000
76.818
52.334
52.210
COOMe
COOMe
(16)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.265
8.248
8.127
8.122
8.110
8.106
7.873
7.868
7.856
7.852
7.848
7.833
7.828
7.816
7.812
7.614
7.601
7.579
7.520
7.515
7.503
7.499
7.269
7.267
7.252
7.240
7.230
7.227
6.862
6.859
6.844
6.842
6.827
6.825
2.633
2.544
(17)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
2.00
4.24
1.01
2.05
1.23
1.13
3.12
3.10
197.150
197.127
145.523
136.669
136.312
132.594
131.609
129.233
129.019
128.410
128.162
127.303
127.211
127.064
126.977
126.211
123.243
118.105
113.697
91.469
86.419
77.181
77.000
76.818
26.585
26.522
(17)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

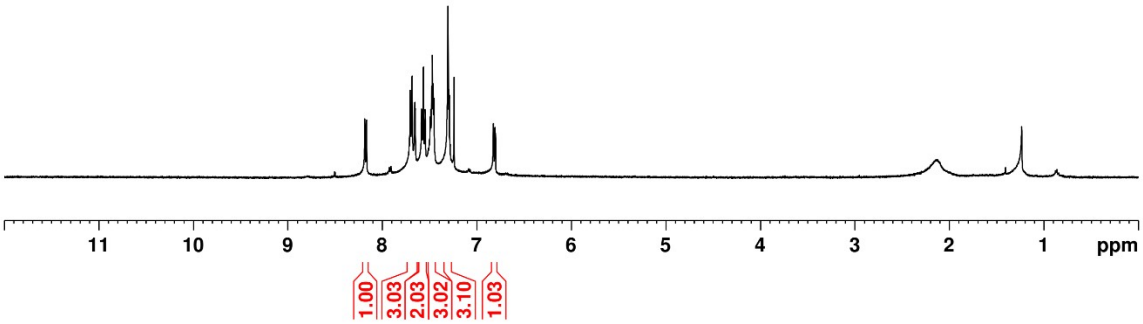

8.435
8.432
8.420
8.417
8.414
7.620
7.617
7.599
7.597
7.595
7.518
7.516
7.510
7.507
7.497
7.494
7.313
7.310
7.304
7.301
7.299
7.297
7.291
7.286
7.283
7.276
7.273
7.259
7.256
7.254
7.251
7.240
7.237
7.234
7.231
7.228
7.218
7.002
6.993
6.989
6.980
6.899
6.896
6.882
6.879
6.864
6.862
N
S
N
S
(19)
11
10
9
8
7
6
5
4
3
2
1 ppm
1.00
1.04
2.07
2.06
2.04
1.00
1.06
145.144
132.529
128.737
127.827
127.639
127.112
127.073
126.582
125.822
123.771
122.829
122.005
118.775
117.897
113.497
86.959
86.854
77.182
77.000
76.819
N
S
N
S
(19)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

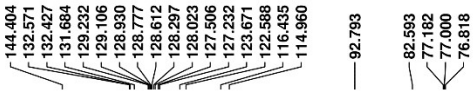

8.037
7.724
7.713
7.601
7.588
7.577
7.566
7.555
7.471
7.463
7.457
7.452
7.295
7.290
7.286
7.240
7.134
7.122
2.301
N
N
Ph
Ph
(20)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.01
3.21
3.19
3.10
1.05
3.03
143.964
131.465
128.933
128.719
128.606
128.458
128.333
128.160
128.143
127.425
126.320
122.961
122.734
120.689
117.065
91.490
83.650
77.182
77.000
76.818
18.276
N
N
Ph
Ph
(20)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

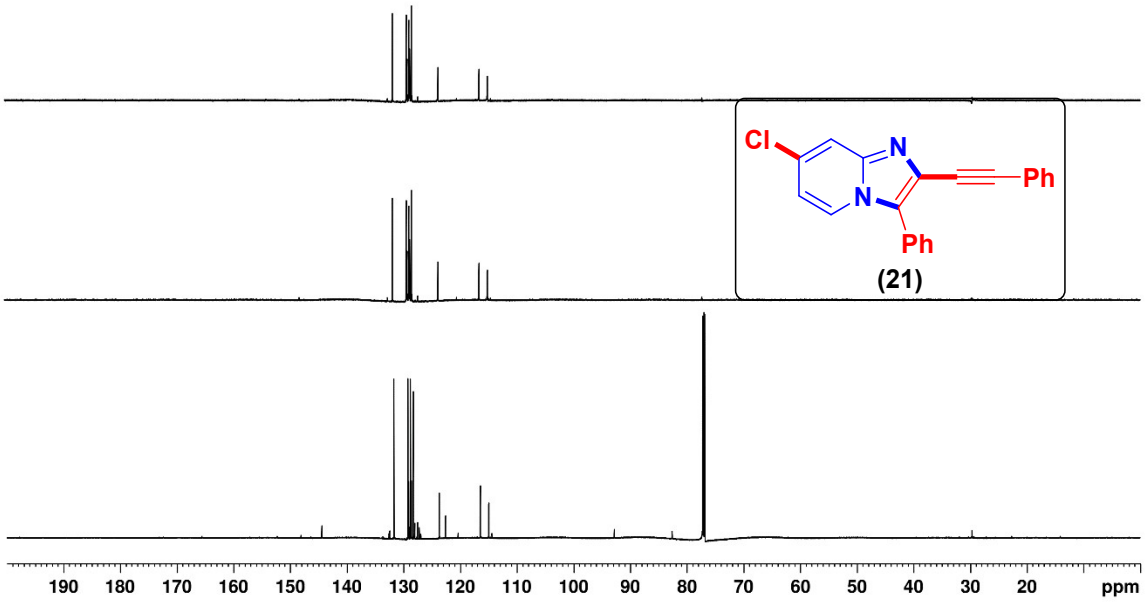

8.185
8.167
7.707
7.703
7.685
7.656
7.652
7.584
7.579
7.565
7.549
7.546
7.492
7.489
7.486
7.477
7.471
7.465
7.462
7.453
7.307
7.301
7.293
7.291
7.240
6.826
6.821
6.807
6.802


Cl
N
N
Ph
Ph

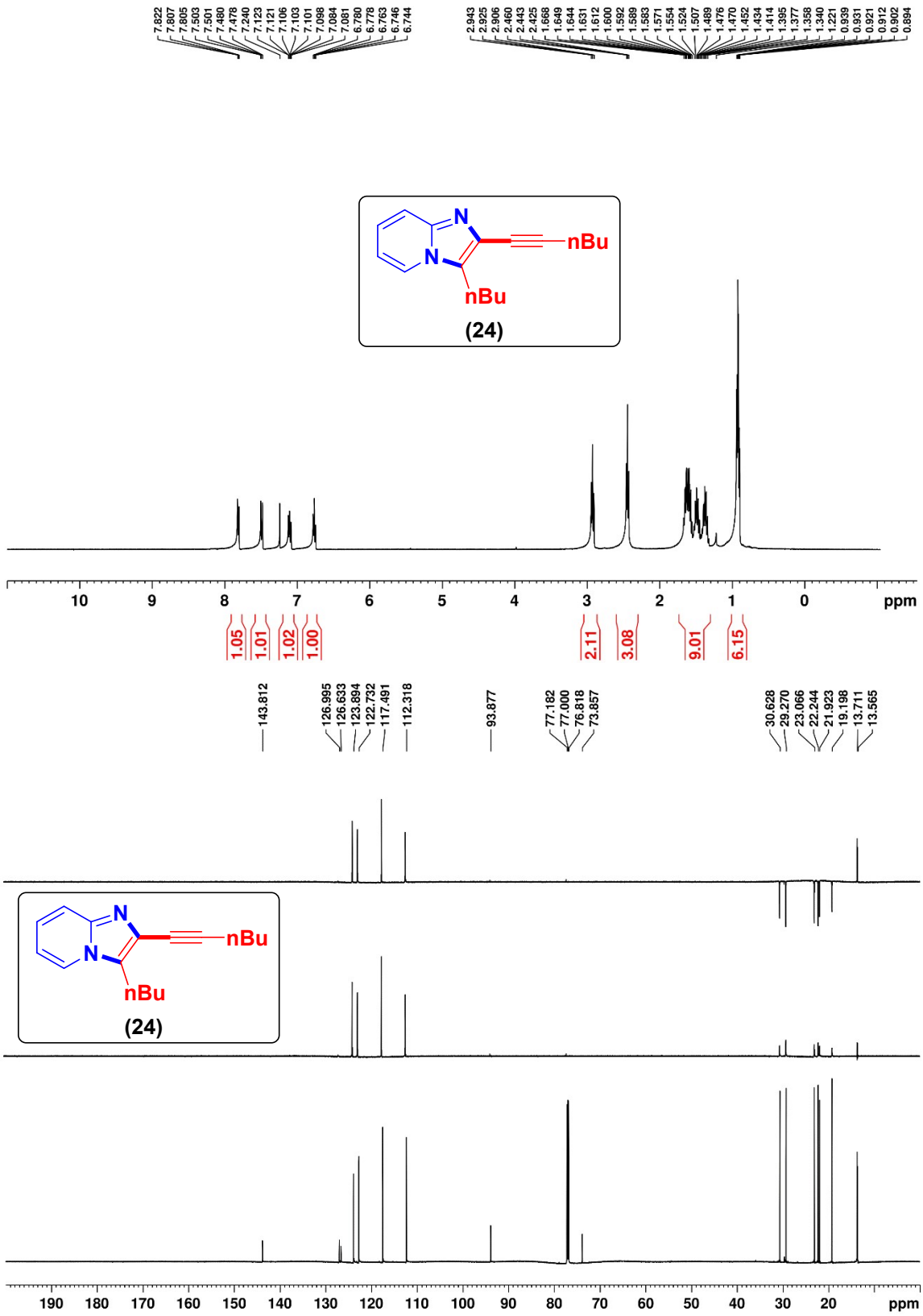
(21)

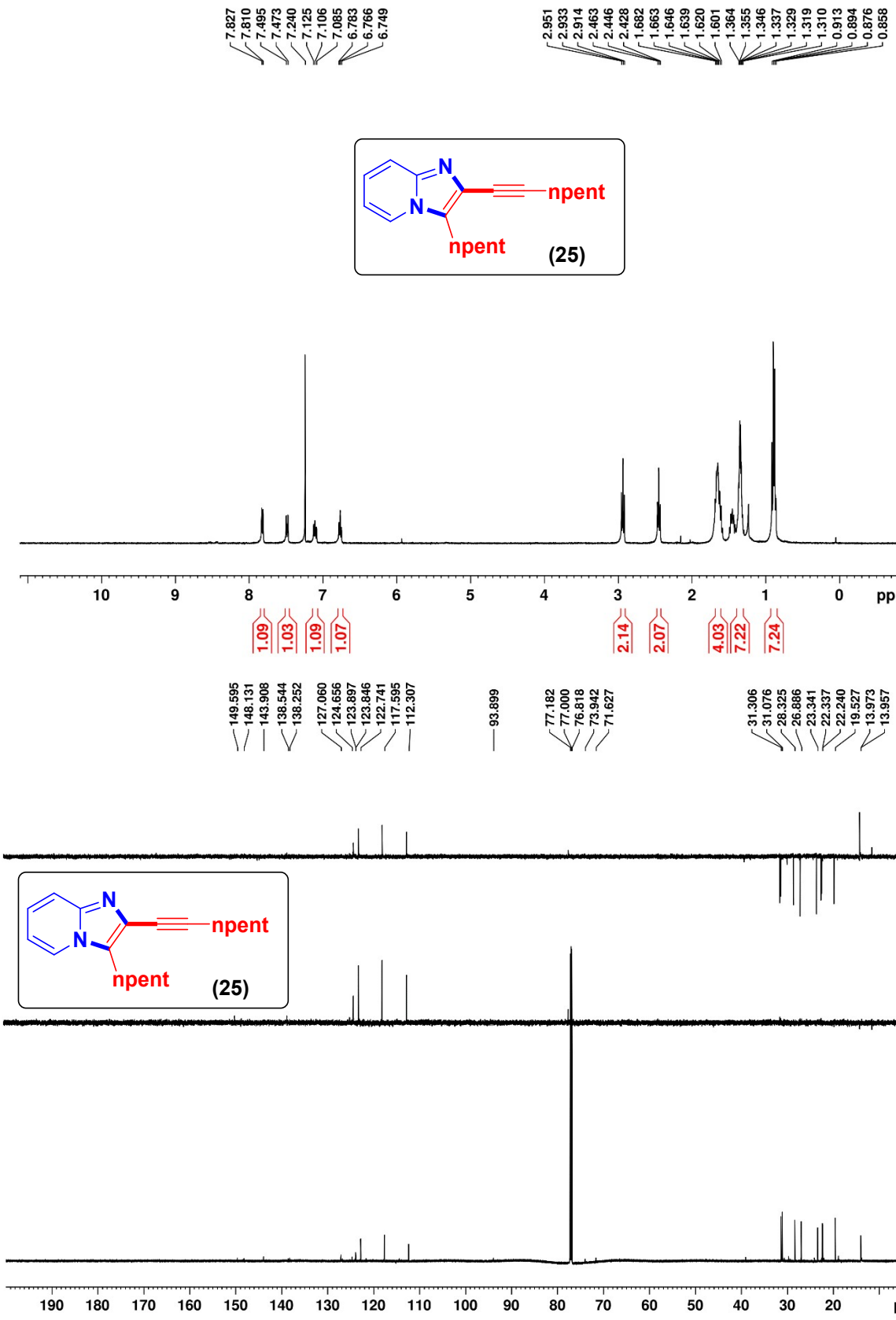

11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.03
2.03
3.02
3.10
1.03

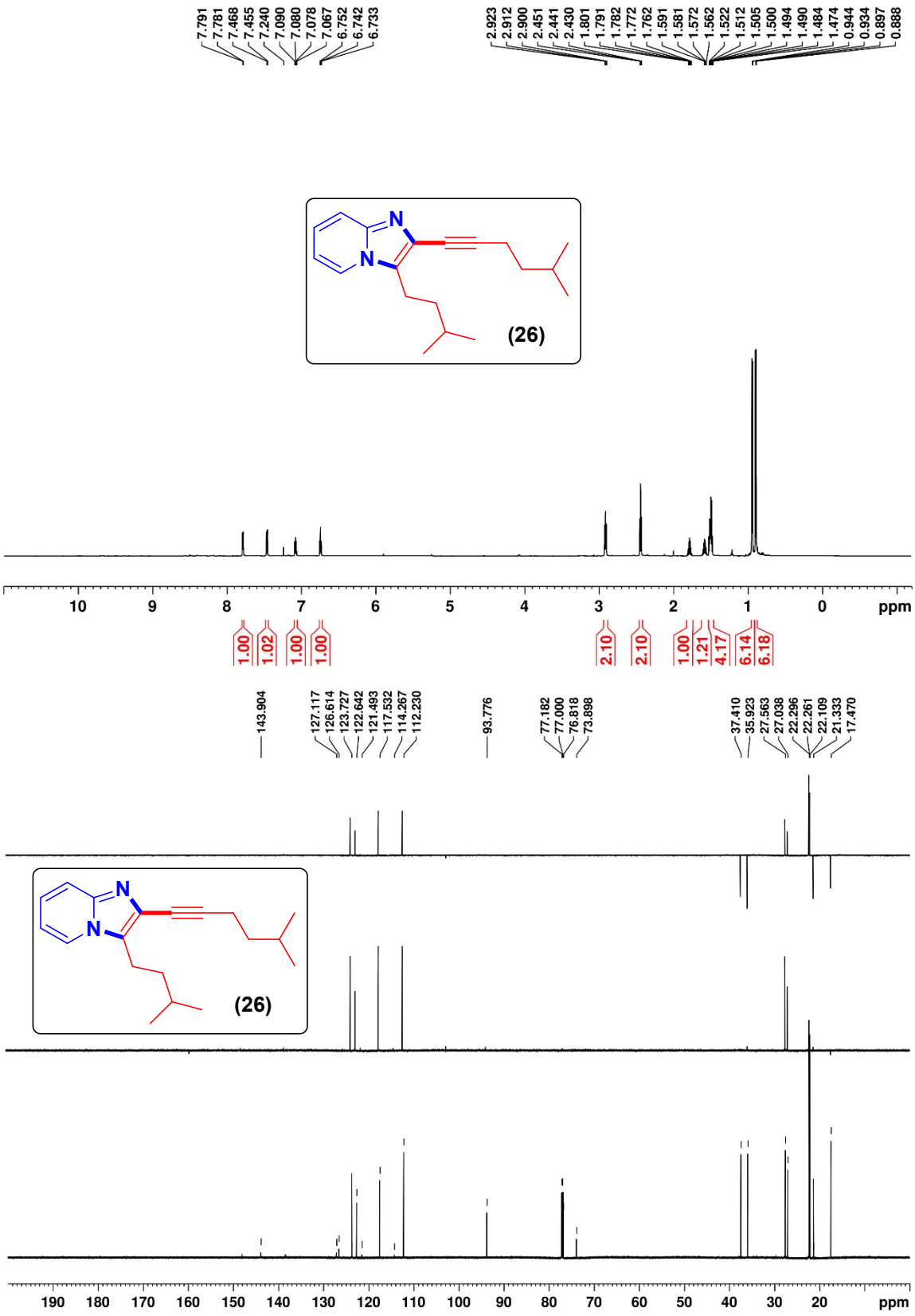

144.404
132.571
132.427
131.684
129.232
129.106
128.930
128.777
128.612
128.297
128.023
127.506
127.232
123.671
122.588
116.435
114.960
92.793
82.593
77.182
77.000
76.818

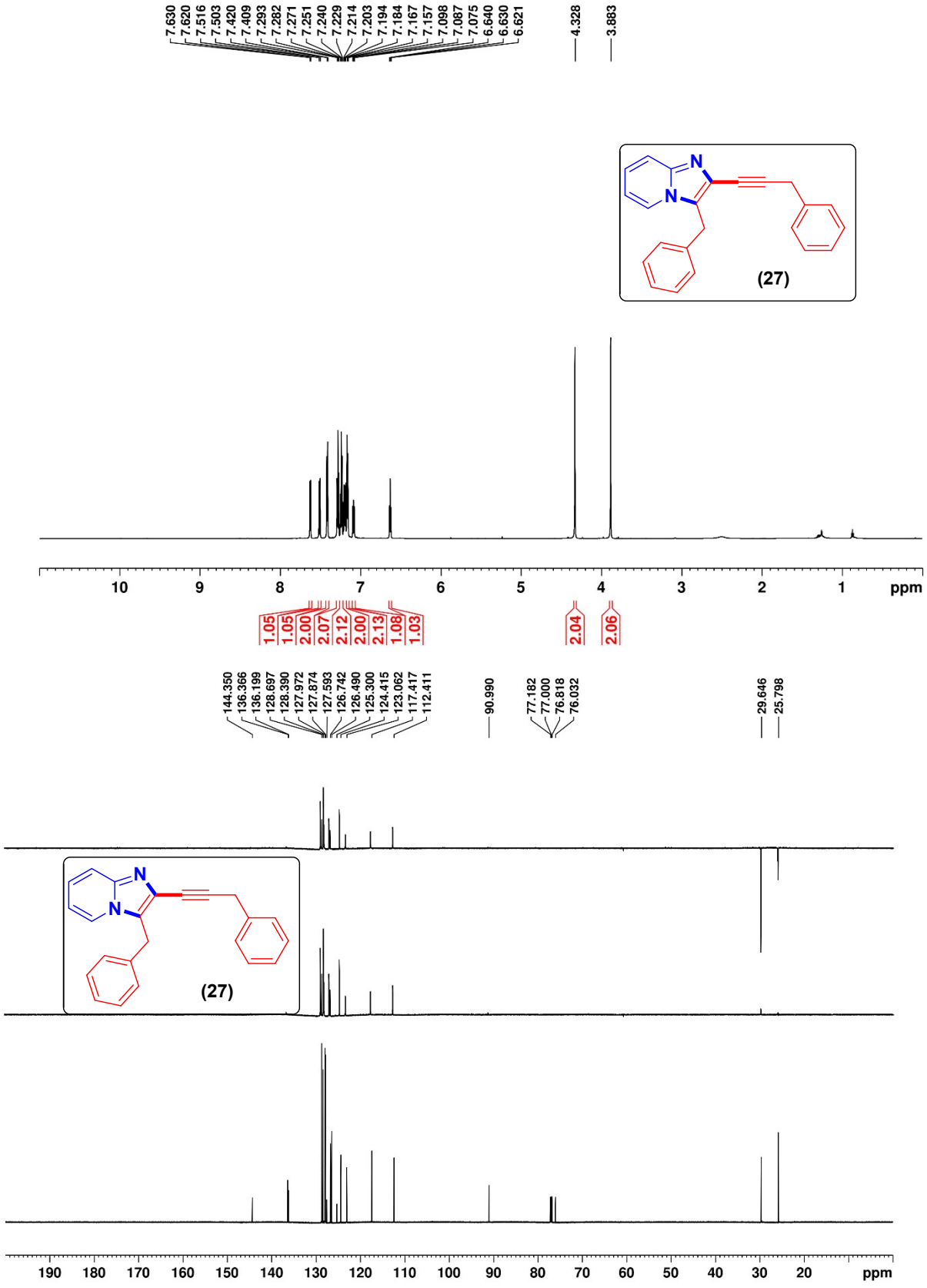

Cl
N
N
Ph
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

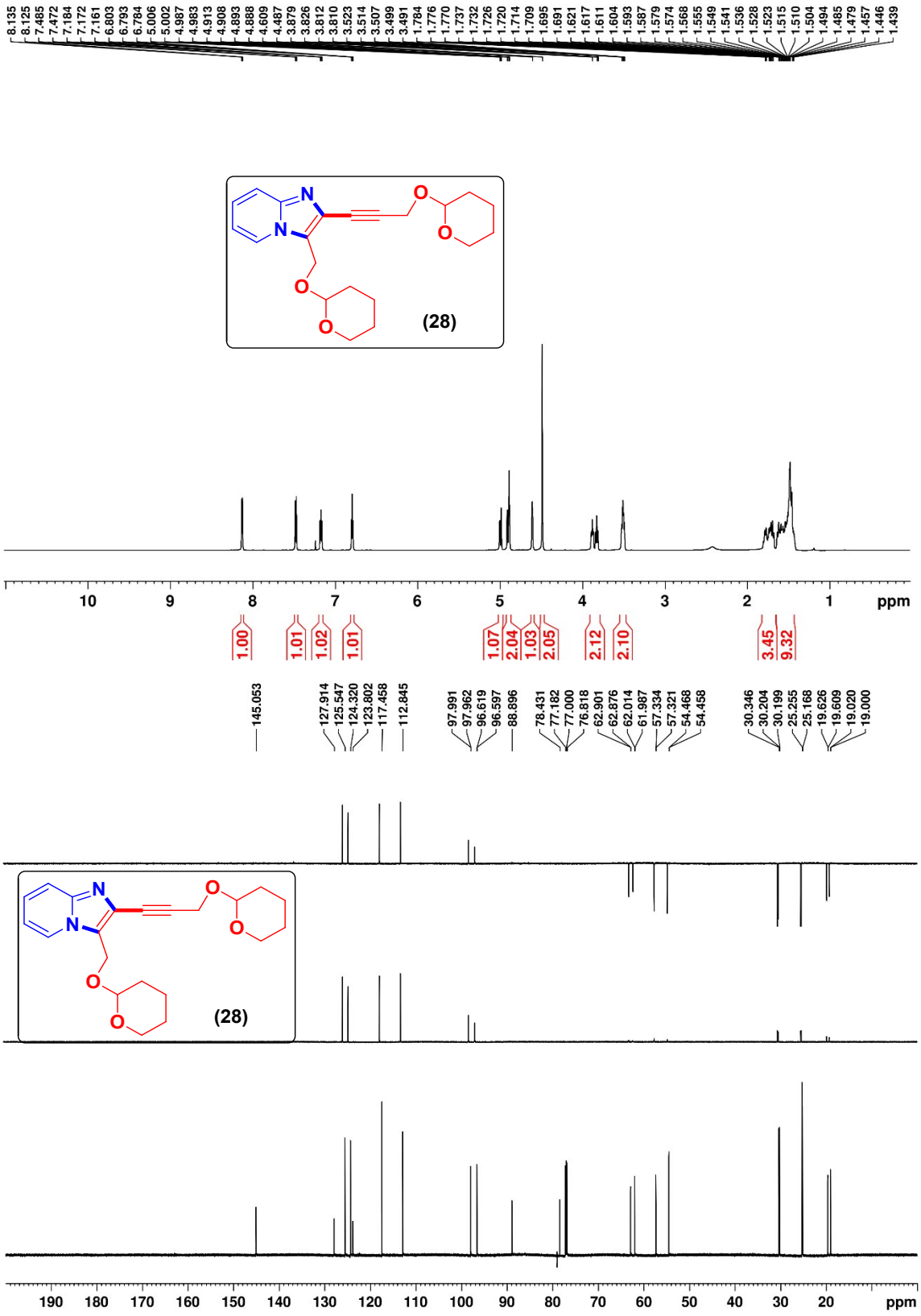
(21)


7.822
7.807
7.805
7.503
7.501
7.480
7.478
7.240
7.123
7.121
7.106
7.103
7.101
7.098
7.084
7.081
6.780
6.778
6.763
6.746
6.744
2.943
2.925
2.906
2.460
2.443
2.425
1.668
1.649
1.644
1.631
1.612
1.600
1.592
1.589
1.583
1.571
1.554
1.524
1.507
1.489
1.476
1.470
1.452
1.434
1.414
1.395
1.377
1.358
1.340
1.221
0.939
0.931
0.921
0.912
0.902
0.894
N
N
nBu
nBu
(24)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.01
1.02
1.00
2.11
3.08
9.01
6.15
143.812
126.995
126.633
123.894
122.732
117.491
112.318
93.877
77.182
77.000
76.818
73.857
30.628
29.270
23.066
22.244
21.923
19.198
13.711
13.565
N
N
nBu
nBu
(24)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

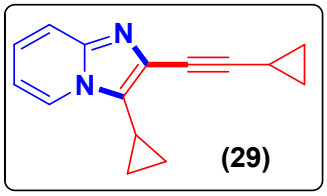

7.827
7.810
7.495
7.473
7.240
7.125
7.106
7.085
6.783
6.766
6.749
2.951
2.933
2.914
2.463
2.446
2.428
1.682
1.663
1.646
1.639
1.620
1.601
1.364
1.355
1.346
1.337
1.329
1.319
1.310
0.913
0.894
0.876
0.858
N
N
npent
npent
(25)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.09
1.03
1.09
1.07
2.14
2.07
4.03
7.22
7.24
149.595
148.131
143.908
138.544
138.252
127.060
124.656
123.897
123.846
122.741
117.595
112.307
93.899
77.182
77.000
76.818
73.942
71.627
31.306
31.076
28.325
26.886
23.341
22.337
22.240
19.527
13.973
13.957
N
N
npent
npent
(25)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

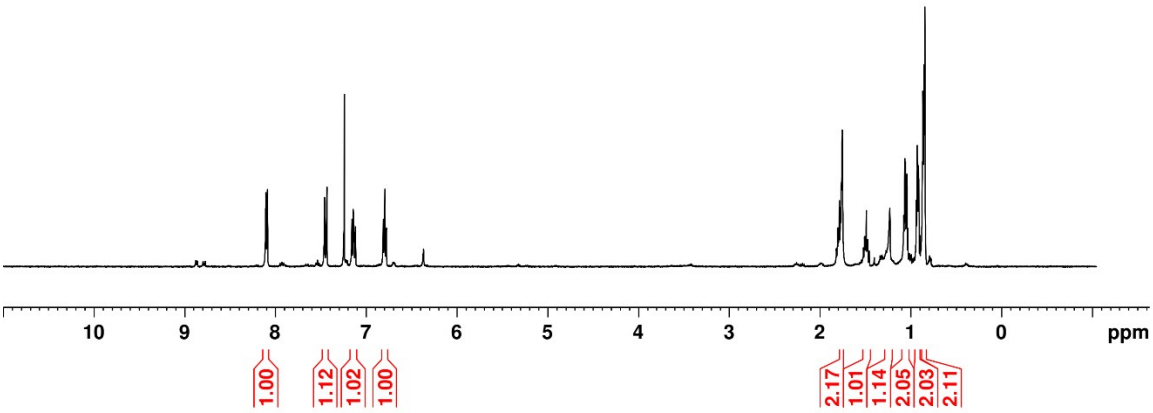

7.791
7.781
7.468
7.455
7.240
7.090
7.080
7.078
7.067
6.752
6.742
6.733
2.923
2.912
2.900
2.451
2.441
2.430
1.801
1.791
1.782
1.772
1.762
1.591
1.581
1.572
1.562
1.522
1.512
1.505
1.500
1.494
1.490
1.484
1.474
0.944
0.934
0.897
0.888
(26)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.00
1.00
2.10
2.10
1.00
1.21
4.17
6.14
6.18
143.904
127.117
126.614
123.727
122.642
121.493
117.532
114.267
112.230
93.776
77.182
77.000
76.818
73.898
37.410
35.923
27.563
27.038
22.296
22.261
22.109
21.333
17.470
(26)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

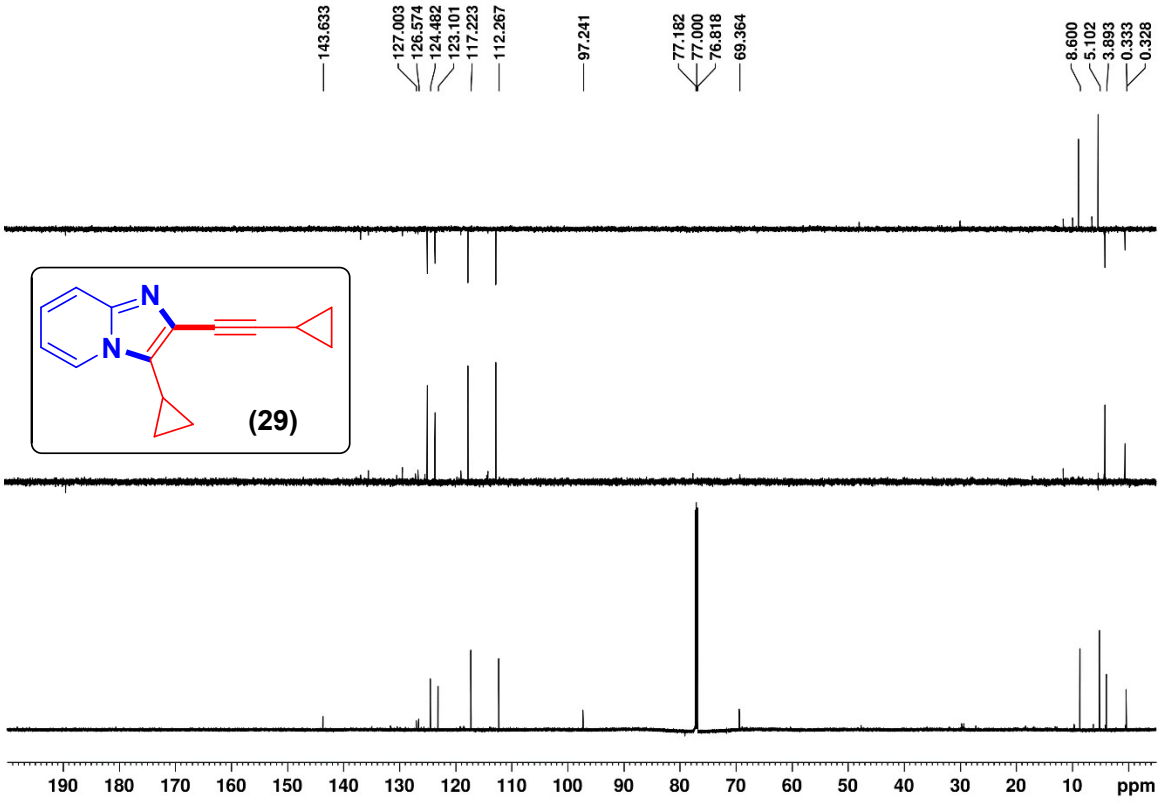

7.630
7.620
7.516
7.503
7.420
7.409
7.293
7.282
7.271
7.251
7.240
7.229
7.214
7.203
7.194
7.184
7.167
7.157
7.098
7.087
7.075
6.640
6.630
6.621
4.328
3.883
(27)
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.05
2.00
2.07
2.12
2.00
2.13
1.08
1.03
2.04
2.06
144.350
136.366
136.199
128.697
128.390
127.972
127.874
127.593
126.742
126.490
125.300
124.415
123.062
117.417
112.411
90.990
77.182
77.000
76.818
76.032
29.646
25.798
(27)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

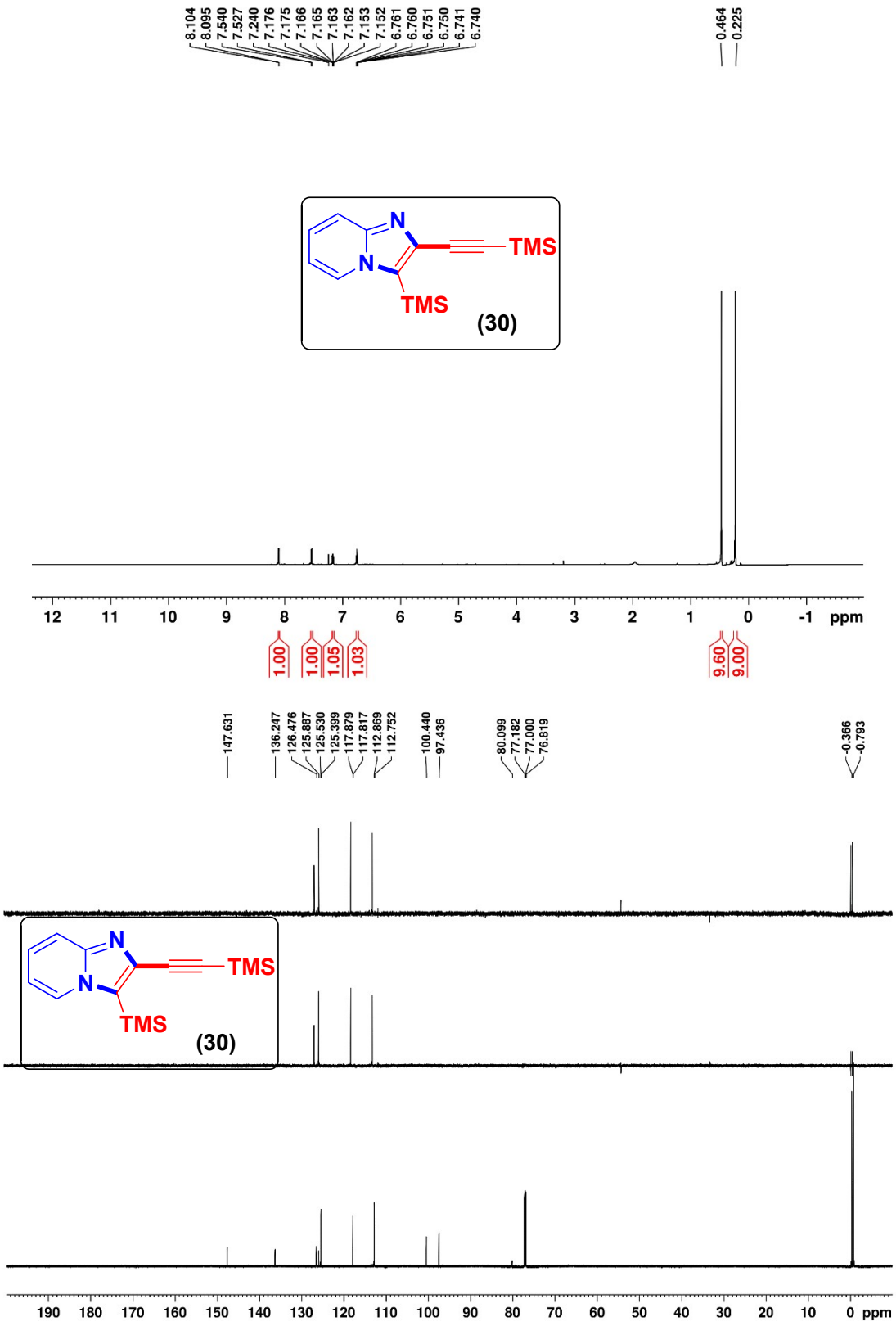

8.135
8.125
7.485
7.472
7.184
7.172
7.161
6.803
6.793
6.784
5.006
5.002
4.987
4.983
4.913
4.908
4.893
4.888
4.609
4.487
3.879
3.826
3.812
3.810
3.523
3.514
3.507
3.499
3.491
1.784
1.776
1.770
1.737
1.732
1.726
1.720
1.714
1.709
1.695
1.691
1.621
1.617
1.611
1.604
1.593
1.587
1.579
1.574
1.568
1.555
1.549
1.541
1.536
1.528
1.523
1.515
1.510
1.504
1.494
1.485
1.479
1.457
1.446
1.439
(28)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.02
1.01
1.07
2.04
1.03
2.05
2.12
2.10
3.45
9.32
145.053
127.914
125.547
124.320
123.802
117.458
112.845
97.991
97.962
96.619
96.597
88.896
78.431
77.182
77.000
76.818
62.901
62.876
62.014
61.987
57.334
57.321
54.468
54.458
30.346
30.204
30.199
25.255
25.168
19.626
19.609
19.020
19.000
(28)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

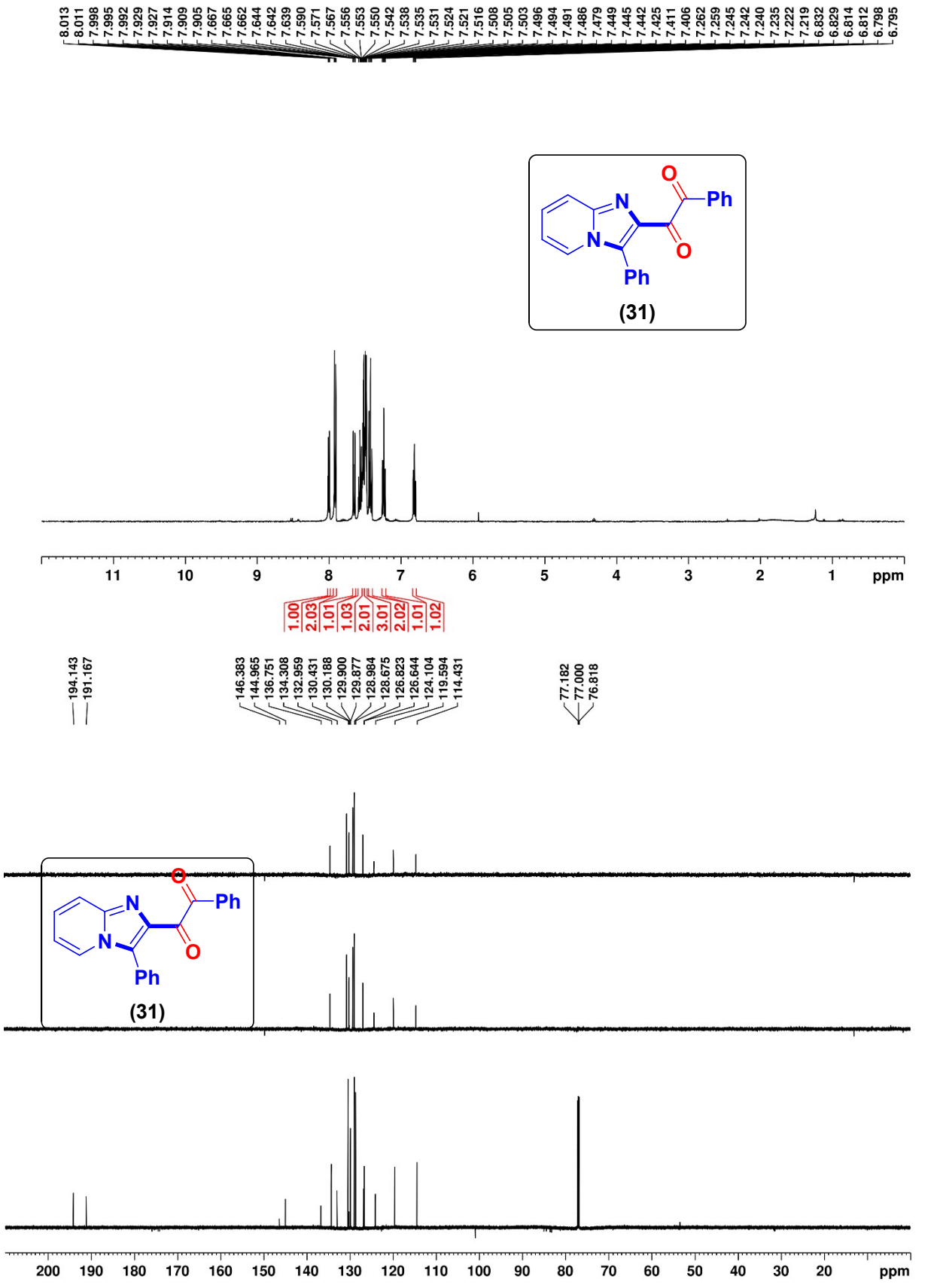

8.104
8.090
8.087
7.459
7.456
7.436
7.434
7.240
7.158
7.155
7.141
7.138
7.135
7.132
7.118
7.115
6.812
6.809
6.795
6.792
6.778
6.775
1.804
1.796
1.791
1.784
1.776
1.771
1.763
1.752
1.507
1.505
1.502
1.494
1.487
1.480
1.475
1.472
1.227
1.074
1.063
1.057
1.047
1.042
1.037
1.027
0.936
0.926
0.922
0.913
0.909
0.870
0.864
0.860
0.855
0.852
0.843


N
N
(29)


10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.12
1.02
1.00
2.17
1.01
1.14
2.05
2.03
2.11


143.633
127.003
126.574
124.482
123.101
117.223
112.267
97.241
77.182
77.000
76.818
69.364
8.600
5.102
3.893
0.333
0.328
N
N
(29)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.104
8.095
7.540
7.527
7.240
7.176
7.175
7.166
7.165
7.163
7.162
7.153
7.152
6.761
6.760
6.751
6.750
6.741
6.740
0.464
0.225
N
N
TMS
TMS
(30)
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
1.00
1.00
1.05
1.03
9.60
9.00
147.631
136.247
126.476
125.887
125.530
125.399
117.879
117.817
112.869
112.752
100.440
97.436
80.099
77.182
77.000
76.819
-0.366
-0.793
N
N
TMS
TMS
(30)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.013
8.011
7.998
7.995
7.992
7.929
7.927
7.914
7.909
7.905
7.667
7.665
7.662
7.644
7.642
7.639
7.590
7.571
7.567
7.556
7.553
7.550
7.542
7.538
7.535
7.531
7.524
7.521
7.516
7.508
7.505
7.503
7.496
7.494
7.491
7.486
7.479
7.449
7.445
7.442
7.425
7.411
7.406
7.262
7.259
7.245
7.242
7.240
7.235
7.222
7.219
6.832
6.829
6.814
6.812
6.798
6.795
O
Ph
N
N
O
Ph
(31)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.03
1.01
1.03
2.01
3.01
2.02
1.01
1.02
194.143
191.167
146.383
144.965
136.751
134.308
132.959
130.431
130.188
129.900
129.877
128.984
128.675
126.823
126.644
124.104
119.594
114.431
77.182
77.000
76.818
O
Ph
N
N
O
Ph
(31)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

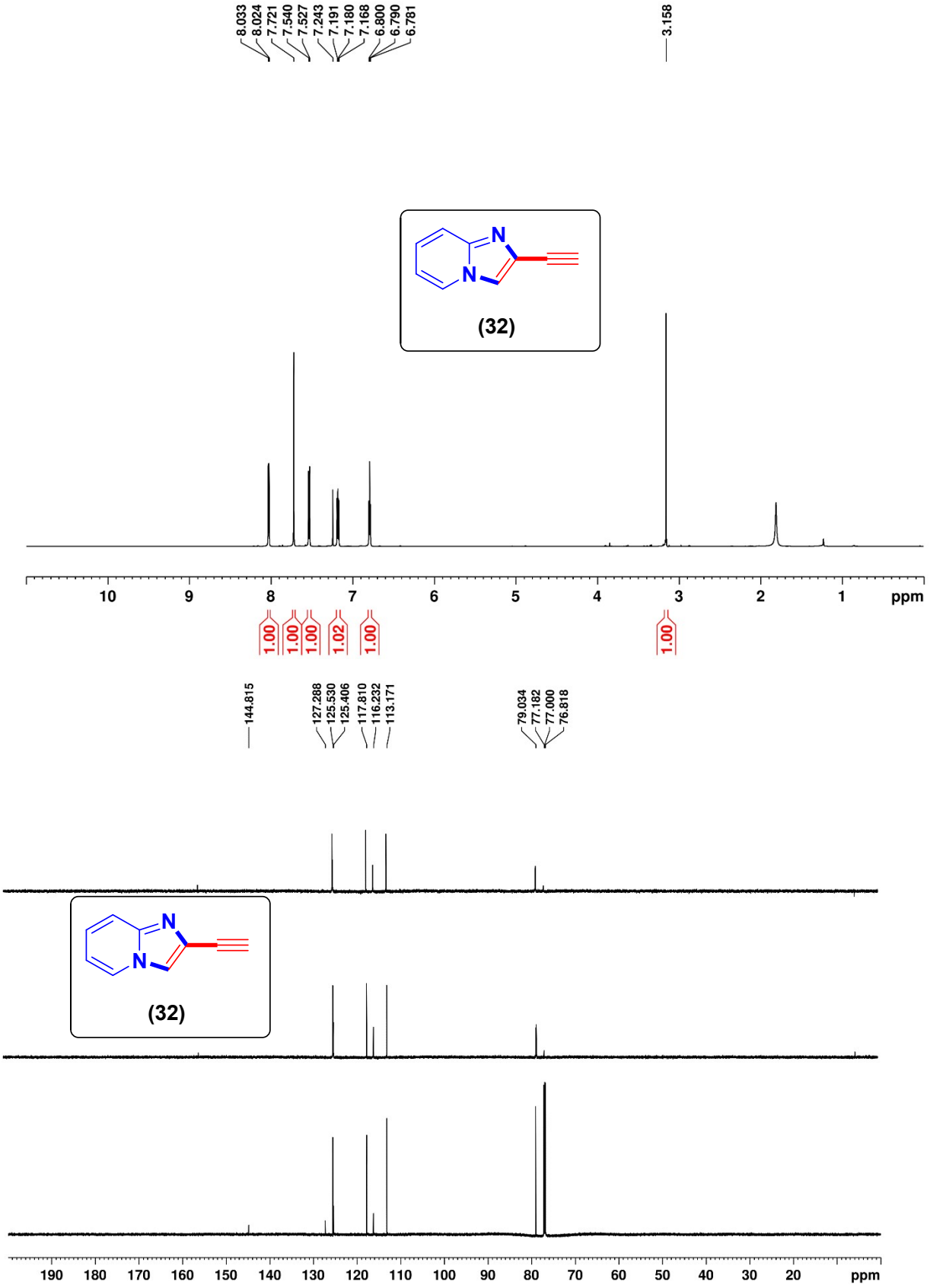
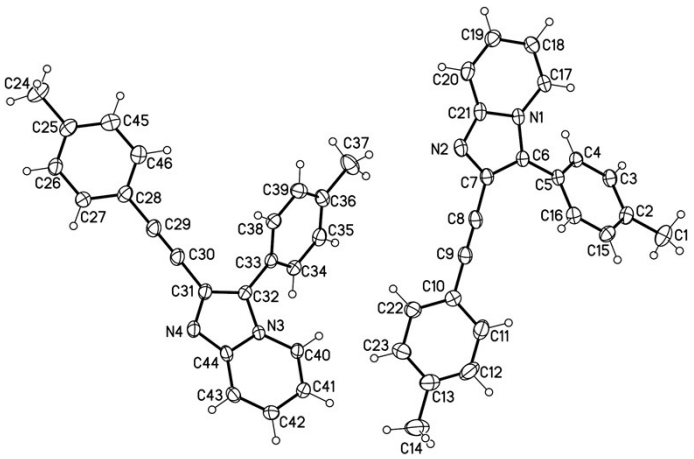
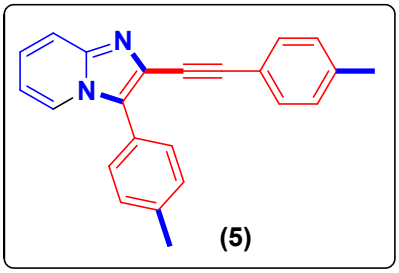

8.033
8.024
7.721
7.540
7.527
7.243
7.191
7.180
7.168
6.800
6.790
6.781
3.158
(32)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.02
1.00
1.00
144.815
127.288
125.530
125.406
117.810
116.232
113.171
79.034
77.182
77.000
76.818
(32)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

Figure S4. ORTEP diagram of compound **5 (CCDC No. 2303797)**





170449LT_0m

Table S1 Crystal data and structure refinement for 170449LT_0m.

Identification code	170449LT_0m
Empirical formula	$C_{46}H_{36}N_4$
Formula weight	644.79
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.6958(4)
b/Å	12.8863(5)
c/Å	14.1978(5)
α/°	95.348(2)
β/°	91.322(2)
γ/°	97.198(2)

Volume/Å^3	1751.19(12)
Z	2
ρ_{calc}g/cm^3	1.223
μ/mm^{-1}	0.072
F(000)	680.0
Crystal size/mm^3	0.15 × 0.14 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.096 to 52.808
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 16, -13 ≤ l ≤ 17
Reflections collected	21609
Independent reflections	6900 [R_{int} = 0.0274, R_{sigma} = 0.0320]
Data/restraints/parameters	6900/0/456
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.0989
Final R indexes [all data]	R_1 = 0.0538, wR_2 = 0.1069
Largest diff. peak/hole / e Å^{-3}	0.22/-0.21

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 170449LT_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	11217.8(11)	3863.2(8)	7154.8(8)	21.3(3)
N2	11069.1(12)	5568.5(9)	7604.1(9)	26.3(3)
N3	1185.2(12)	8804.4(8)	6762.9(8)	20.8(3)
N4	1687.0(13)	10518.6(9)	6551.6(9)	27.3(3)
C1	6999.0(17)	203.7(13)	9119.8(12)	37.4(4)
C2	7807.1(14)	1157.4(11)	8762.0(11)	26.0(3)

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 170449LT_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C3	8080.7(14)	1196.8(11)	7806.3(10)	24.4(3)
C4	8838.2(14)	2069.7(10)	7482.8(10)	21.7(3)
C5	9361.3(14)	2934.0(10)	8114.7(10)	20.6(3)
C6	10180.3(14)	3871.4(10)	7810.5(10)	21.3(3)
C7	10126.6(14)	4929.9(10)	8071.3(10)	23.1(3)
C8	9201.3(15)	5368.5(10)	8717.4(10)	25.2(3)
C9	8432.4(15)	5762.6(10)	9255.2(10)	25.6(3)
C10	7578.1(14)	6248.3(11)	9933.7(10)	25.0(3)
C11	6815.0(18)	5664.9(13)	10561.0(12)	39.3(4)
C12	6033.8(19)	6153.6(15)	11233.5(13)	46.4(5)
C13	5989.2(16)	7227.3(14)	11302.6(11)	35.3(4)
C14	5162(2)	7764.6(18)	12049.0(13)	54.9(6)
C15	8289.5(15)	2033.4(11)	9382.2(10)	26.8(3)
C16	9057.9(14)	2908.7(11)	9070.2(10)	24.7(3)
C17	11756.2(14)	3039.5(11)	6661.4(10)	23.8(3)
C18	12757.9(15)	3252.4(11)	6039.1(11)	27.3(3)
C19	13277.5(15)	4309.1(12)	5900.3(11)	30.6(3)
C20	12777.3(15)	5123.5(11)	6404.4(11)	29.1(3)
C21	11722.6(14)	4912.7(10)	7052.3(10)	24.5(3)
C22	7526.5(16)	7331.2(12)	9996.9(11)	30.8(3)
C23	6741.4(16)	7804.4(13)	10671.9(11)	34.2(4)
C24	5758.1(18)	12902.2(14)	1308.5(12)	40.9(4)
C25	5044.2(16)	12334.5(12)	2081.1(11)	29.4(3)

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 170449LT_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C26	3878.6(17)	12671.9(11)	2499.0(11)	32.5(4)
C27	3233.9(17)	12161.2(11)	3220.5(11)	31.8(4)
C28	3747.0(15)	11290.3(11)	3543.1(10)	25.7(3)
C29	3101.4(16)	10777.1(11)	4308.3(10)	28.5(3)
C30	2578.6(16)	10361.5(11)	4955.6(11)	28.1(3)
C31	1994.0(15)	9899.2(11)	5759.5(10)	25.3(3)
C32	1697.8(14)	8837.0(10)	5861.5(10)	21.5(3)
C33	1917.0(14)	7896.4(10)	5243.9(9)	21.2(3)
C34	888.2(14)	7033.2(11)	5074.8(10)	23.5(3)
C35	1141.8(15)	6144.2(11)	4506.9(10)	26.0(3)
C36	2412.8(16)	6090.0(11)	4085.0(10)	27.1(3)
C37	2692.9(18)	5123.6(13)	3471.6(12)	38.7(4)
C38	3186.7(14)	7848.8(11)	4810.4(10)	24.1(3)
C39	3422.5(15)	6959.4(12)	4242.2(10)	27.6(3)
C40	814.6(14)	7963.0(10)	7278.9(10)	22.3(3)
C41	419.8(14)	8148.9(11)	8178.8(10)	24.5(3)
C42	397.3(15)	9191.0(11)	8594.8(10)	27.1(3)
C43	791.4(15)	10026.2(11)	8096.8(10)	26.8(3)
C44	1207.9(14)	9842.8(10)	7155.4(10)	23.5(3)
C45	5539.5(15)	11454.5(12)	2398.5(11)	31.0(3)
C46	4906.7(15)	10935.9(12)	3114.6(11)	29.1(3)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 170449LT_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	22.2(6)	15.6(5)	26.2(6)	3.6(5)	-2.5(5)	2.7(4)
N2	27.8(6)	17.2(6)	34.0(7)	3.4(5)	-0.9(5)	2.4(5)
N3	24.8(6)	16.7(5)	21.5(6)	2.9(5)	1.7(5)	4.7(4)
N4	38.4(7)	18.5(6)	26.0(7)	4.8(5)	2.4(5)	5.4(5)
C1	38.1(9)	34.3(9)	39.1(10)	14.0(7)	-1.4(7)	-5.8(7)
C2	23.6(7)	24.7(7)	30.1(8)	8.4(6)	-2.8(6)	1.2(6)
C3	25.1(7)	18.7(7)	28.3(8)	0.6(6)	-4.8(6)	0.8(5)
C4	23.5(7)	20.4(7)	21.5(7)	2.8(6)	-1.3(6)	4.1(5)
C5	21.2(7)	17.3(6)	23.8(7)	3.0(5)	-2.9(5)	3.8(5)
C6	21.8(7)	18.9(7)	23.2(7)	3.4(6)	-2.8(6)	2.8(5)
C7	25.1(7)	18.1(7)	25.6(8)	1.1(6)	-3.6(6)	1.7(5)
C8	29.4(8)	16.1(7)	29.1(8)	0.7(6)	-5.0(6)	0.8(6)
C9	29.3(8)	18.1(7)	28.1(8)	1.6(6)	-2.9(6)	-0.3(6)
C10	23.5(7)	27.3(7)	23.7(8)	2.1(6)	-1.9(6)	1.5(6)
C11	41.5(9)	34.8(9)	45.0(10)	18.4(8)	7.4(8)	6.8(7)
C12	41.7(10)	63.1(12)	41.5(10)	29.9(9)	16.5(8)	12.4(9)
C13	28.1(8)	56.7(11)	24.5(8)	8.6(8)	-0.3(6)	15.6(7)
C14	50.1(11)	91.9(16)	32.7(10)	17.6(10)	11.6(8)	38.3(11)
C15	27.8(8)	31.5(8)	21.7(7)	7.0(6)	-1.1(6)	3.2(6)
C16	27.8(7)	22.1(7)	23.6(8)	0.1(6)	-5.0(6)	2.8(6)
C17	23.8(7)	18.4(7)	29.4(8)	2.4(6)	-3.1(6)	4.6(5)
C18	25.3(7)	26.5(7)	30.9(8)	2.2(6)	-0.6(6)	6.7(6)
C19	25.6(8)	33.9(8)	34.5(9)	11.7(7)	4.0(6)	5.0(6)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 170449LT_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C20	26.0(8)	24.1(7)	38.0(9)	12.3(7)	-0.5(6)	-0.1(6)
C21	24.5(7)	16.8(7)	32.2(8)	6.2(6)	-4.0(6)	0.9(5)
C22	31.1(8)	25.9(8)	35.0(9)	2.2(7)	8.2(7)	0.8(6)
C23	31.9(8)	34.6(8)	36.2(9)	-1.1(7)	5.9(7)	6.9(7)
C24	37.9(9)	48.1(10)	34.0(9)	10.9(8)	3.9(7)	-10.8(8)
C25	31.3(8)	28.1(8)	25.6(8)	2.6(6)	-0.3(6)	-8.8(6)
C26	48.1(10)	21.3(7)	29.2(8)	6.0(6)	6.5(7)	4.4(7)
C27	41.5(9)	24.8(8)	30.3(8)	4.2(6)	10.6(7)	6.2(7)
C28	33.8(8)	19.9(7)	21.2(7)	1.1(6)	-0.3(6)	-4.5(6)
C29	38.7(9)	19.3(7)	26.3(8)	1.9(6)	0.6(7)	-0.2(6)
C30	37.3(8)	19.3(7)	27.3(8)	3.3(6)	1.8(7)	1.4(6)
C31	32.0(8)	19.9(7)	24.3(8)	5.0(6)	1.4(6)	2.7(6)
C32	23.6(7)	21.3(7)	20.2(7)	4.6(6)	1.4(5)	2.8(5)
C33	26.7(7)	19.7(7)	18.0(7)	4.6(5)	-0.8(6)	4.0(5)
C34	24.6(7)	24.0(7)	22.4(7)	5.5(6)	0.8(6)	2.5(6)
C35	33.2(8)	20.7(7)	23.0(7)	3.8(6)	-5.5(6)	-0.5(6)
C36	36.2(8)	25.9(7)	20.2(7)	0.9(6)	-6.1(6)	10.4(6)
C37	49.6(10)	33.5(9)	33.2(9)	-7.9(7)	-8.2(8)	16.1(7)
C38	25.1(7)	24.8(7)	22.2(7)	3.4(6)	0.0(6)	1.7(6)
C39	26.5(8)	34.8(8)	22.7(8)	3.1(6)	0.3(6)	9.2(6)
C40	23.8(7)	17.9(7)	25.9(8)	5.4(6)	1.9(6)	2.9(5)
C41	26.4(7)	23.6(7)	24.4(8)	6.4(6)	2.4(6)	3.8(6)
C42	31.5(8)	29.0(8)	22.2(7)	2.2(6)	4.6(6)	8.2(6)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 170449LT_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C43	33.4(8)	22.3(7)	25.7(8)	-0.2(6)	1.5(6)	9.8(6)
C44	28.6(7)	16.9(6)	25.8(8)	1.8(6)	-0.6(6)	6.4(5)
C45	24.2(7)	38.7(9)	28.3(8)	1.4(7)	-0.9(6)	-0.6(6)
C46	31.5(8)	27.5(8)	27.4(8)	3.1(6)	-5.4(6)	1.6(6)

Table S4 Bond Lengths for 170449LT_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C6	1.3866(17)	C17	C18	1.348(2)
N1	C17	1.3809(17)	C18	C19	1.425(2)
N1	C21	1.4014(17)	C19	C20	1.361(2)
N2	C7	1.3760(17)	C20	C21	1.409(2)
N2	C21	1.3277(18)	C22	C23	1.382(2)
N3	C32	1.3859(17)	C24	C25	1.508(2)
N3	C40	1.3799(16)	C25	C26	1.387(2)
N3	C44	1.3980(17)	C25	C45	1.393(2)
N4	C31	1.3777(19)	C26	C27	1.388(2)
N4	C44	1.3287(17)	C27	C28	1.394(2)
C1	C2	1.5085(19)	C28	C29	1.4391(19)
C2	C3	1.393(2)	C28	C46	1.397(2)
C2	C15	1.390(2)	C29	C30	1.197(2)
C3	C4	1.3858(18)	C30	C31	1.4320(19)
C4	C5	1.3978(19)	C31	C32	1.3847(19)
C5	C6	1.4660(18)	C32	C33	1.4691(19)

Table S4 Bond Lengths for 170449LT_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5	C16	1.3972(19)	C33	C34	1.397(2)
C6	C7	1.3874(19)	C33	C38	1.3945(19)
C7	C8	1.426(2)	C34	C35	1.389(2)
C8	C9	1.202(2)	C35	C36	1.389(2)
C9	C10	1.435(2)	C36	C37	1.509(2)
C10	C11	1.386(2)	C36	C39	1.390(2)
C10	C22	1.397(2)	C38	C39	1.385(2)
C11	C12	1.387(2)	C40	C41	1.351(2)
C12	C13	1.384(3)	C41	C42	1.419(2)
C13	C14	1.512(2)	C42	C43	1.3622(19)
C13	C23	1.380(2)	C43	C44	1.413(2)
C15	C16	1.3861(19)	C45	C46	1.382(2)

Table S5 Bond Angles for 170449LT_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	N1	C21	107.21(11)	N2	C21	N1	111.30(12)
C17	N1	C6	131.05(11)	N2	C21	C20	130.10(13)
C17	N1	C21	121.73(12)	C23	C22	C10	120.66(14)
C21	N2	C7	104.87(11)	C13	C23	C22	121.33(15)
C32	N3	C44	107.35(11)	C26	C25	C24	121.18(14)
C40	N3	C32	130.56(11)	C26	C25	C45	117.94(13)
C40	N3	C44	121.85(11)	C45	C25	C24	120.88(15)
C44	N4	C31	104.78(11)	C25	C26	C27	121.27(14)

Table S5 Bond Angles for 170449LT_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C2	C1	121.54(14)	C26	C27	C28	120.45(14)
C15	C2	C1	120.55(13)	C27	C28	C29	120.49(13)
C15	C2	C3	117.90(13)	C27	C28	C46	118.57(13)
C4	C3	C2	121.31(13)	C46	C28	C29	120.94(13)
C3	C4	C5	120.50(13)	C30	C29	C28	178.90(18)
C4	C5	C6	122.65(12)	C29	C30	C31	177.32(17)
C16	C5	C4	118.33(12)	N4	C31	C30	120.84(12)
C16	C5	C6	119.00(13)	N4	C31	C32	112.34(12)
N1	C6	C5	125.08(12)	C32	C31	C30	126.80(14)
N1	C6	C7	104.28(11)	N3	C32	C33	123.59(11)
C7	C6	C5	130.63(13)	C31	C32	N3	104.26(12)
N2	C7	C6	112.34(12)	C31	C32	C33	132.02(12)
N2	C7	C8	120.77(12)	C34	C33	C32	122.01(12)
C6	C7	C8	126.85(13)	C38	C33	C32	119.78(12)
C9	C8	C7	178.36(15)	C38	C33	C34	118.21(13)
C8	C9	C10	176.85(16)	C35	C34	C33	120.58(13)
C11	C10	C9	121.15(13)	C36	C35	C34	121.27(13)
C11	C10	C22	118.17(14)	C35	C36	C37	121.37(14)
C22	C10	C9	120.65(13)	C35	C36	C39	117.82(13)
C10	C11	C12	120.34(15)	C39	C36	C37	120.80(14)
C13	C12	C11	121.62(15)	C39	C38	C33	120.57(13)
C12	C13	C14	121.67(16)	C38	C39	C36	121.53(13)
C23	C13	C12	117.88(15)	C41	C40	N3	118.96(12)
C23	C13	C14	120.44(16)	C40	C41	C42	120.84(13)

Table S5 Bond Angles for 170449LT_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	C15	C2	121.41(13)	C43	C42	C41	120.53(13)
C15	C16	C5	120.48(13)	C42	C43	C44	119.20(13)
C18	C17	N1	119.01(13)	N3	C44	C43	118.58(12)
C17	C18	C19	120.89(14)	N4	C44	N3	111.26(12)
C20	C19	C18	120.29(14)	N4	C44	C43	130.11(13)
C19	C20	C21	119.44(13)	C46	C45	C25	121.46(14)
N1	C21	C20	118.59(13)	C45	C46	C28	120.30(14)

Table S6 Torsion Angles for 170449LT_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C6	C7	N2	0.46(15)	C21	N1	C6	C7	-0.41(14)
N1	C6	C7	C8	178.38(13)	C21	N1	C17	C18	-2.5(2)
N1	C17	C18	C19	1.1(2)	C21	N2	C7	C6	-0.32(16)
N3	C32	C33	C34	49.56(19)	C21	N2	C7	C8	-178.39(13)
N3	C32	C33	C38	-130.18(14)	C22	C10	C11	C12	-0.4(2)
N3	C40	C41	C42	-0.6(2)	C24	C25	C26	C27	-178.93(15)
N4	C31	C32	N3	-0.10(16)	C24	C25	C45	C46	179.10(15)
N4	C31	C32	C33	-176.10(14)	C25	C26	C27	C28	-0.1(3)
C1	C2	C3	C4	-179.20(13)	C25	C45	C46	C28	-0.3(2)
C1	C2	C15	C16	178.67(13)	C26	C25	C45	C46	-0.8(2)
C2	C3	C4	C5	0.6(2)	C26	C27	C28	C29	178.34(15)
C2	C15	C16	C5	0.4(2)	C26	C27	C28	C46	-1.0(2)
C3	C2	C15	C16	-2.0(2)	C27	C28	C46	C45	1.2(2)

Table S6 Torsion Angles for 170449LT_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	C4	C5	C6	179.36(12)	C29	C28	C46	C45	-178.17(14)
C3	C4	C5	C16	-2.28(19)	C30	C31	C32	N3	178.65(14)
C4	C5	C6	N1	-42.2(2)	C30	C31	C32	C33	2.7(3)
C4	C5	C6	C7	137.15(15)	C31	N4	C44	N3	-0.73(16)
C4	C5	C16	C15	1.77(19)	C31	N4	C44	C43	176.83(15)
C5	C6	C7	N2	-178.95(13)	C31	C32	C33	C34	-135.10(16)
C5	C6	C7	C8	-1.0(2)	C31	C32	C33	C38	45.2(2)
C6	N1	C17	C18	178.48(13)	C32	N3	C40	C41	175.82(13)
C6	N1	C21	N2	0.24(16)	C32	N3	C44	N4	0.70(15)
C6	N1	C21	C20	-178.74(13)	C32	N3	C44	C43	-177.18(12)
C6	C5	C16	C15	-179.81(12)	C32	C33	C34	C35	-178.28(12)
C7	N2	C21	N1	0.05(15)	C32	C33	C38	C39	178.60(12)
C7	N2	C21	C20	178.88(15)	C33	C34	C35	C36	-0.6(2)
C9	C10	C11	C12	177.73(16)	C33	C38	C39	C36	0.0(2)
C9	C10	C22	C23	-177.76(15)	C34	C33	C38	C39	-1.14(19)
C10	C11	C12	C13	-0.1(3)	C34	C35	C36	C37	179.72(13)
C10	C22	C23	C13	0.1(2)	C34	C35	C36	C39	-0.6(2)
C11	C10	C22	C23	0.4(2)	C35	C36	C39	C38	0.9(2)
C11	C12	C13	C14	-178.68(17)	C37	C36	C39	C38	-179.40(13)
C11	C12	C13	C23	0.6(3)	C38	C33	C34	C35	1.46(19)
C12	C13	C23	C22	-0.6(2)	C40	N3	C32	C31	-174.69(13)
C14	C13	C23	C22	178.68(16)	C40	N3	C32	C33	1.7(2)
C15	C2	C3	C4	1.5(2)	C40	N3	C44	N4	175.65(12)
C16	C5	C6	N1	139.49(14)	C40	N3	C44	C43	-2.23(19)

Table S6 Torsion Angles for 170449LT_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C16	C5	C6	C7	-41.2(2)	C40	C41	C42	C43	-0.8(2)
C17	N1	C6	C5	-1.8(2)	C41	C42	C43	C44	0.7(2)
C17	N1	C6	C7	178.72(13)	C42	C43	C44	N3	0.7(2)
C17	N1	C21	N2	-178.99(12)	C42	C43	C44	N4	-176.69(15)
C17	N1	C21	C20	2.0(2)	C44	N3	C32	C31	-0.34(15)
C17	C18	C19	C20	0.7(2)	C44	N3	C32	C33	176.09(12)
C18	C19	C20	C21	-1.2(2)	C44	N3	C40	C41	2.18(19)
C19	C20	C21	N1	-0.2(2)	C44	N4	C31	C30	-178.32(14)
C19	C20	C21	N2	-178.92(15)	C44	N4	C31	C32	0.52(17)
C21	N1	C6	C5	179.05(12)	C45	C25	C26	C27	0.9(2)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 170449LT_0m.

Atom	*x*	*y*	*z*	U(eq)
H1A	6007.21	284.11	9117.76	56
H1B	7325.44	132.8	9766.29	56
H1C	7139.48	-425.21	8707.94	56
H3	7741.31	613.61	7367.41	29
H4	9003.19	2080.75	6826.66	26
H11	6827.24	4926.52	10529.94	47
H12	5516.44	5741.36	11657.2	56
H14A	4307.43	7303.32	12153.15	82
H14B	4923.15	8423.59	11835.83	82
H14C	5719.58	7914.99	12641.79	82

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 170449LT_0m.

Atom	*x*	*y*	*z*	U(eq)
H15	8088.3	2032.28	10033.8	32
H16	9380.67	3495.76	9509.28	30
H17	11425.59	2333.37	6759.14	29
H18	13122.16	2690.24	5688.37	33
H19	13976.26	4445.85	5453.83	37
H20	13136.12	5828.02	6320.28	35
H22	8035.99	7746.38	9571.71	37
H23	6719.12	8541.64	10702.27	41
H24A	5238.62	13473	1154.36	61
H24B	5792.94	12408.34	743.8	61
H24C	6706.45	13193.95	1525.3	61
H26	3514.74	13263.96	2287.04	39
H27	2437.29	12406.96	3496.51	38
H34	7.37	7054.2	5350.52	28
H35	432.33	5562.12	4405.18	31
H37A	2821.73	5297.11	2819.25	58
H37B	1902.54	4571.68	3486.56	58
H37C	3536.23	4874.19	3710.56	58
H38	3896.09	8431.5	4905.72	29
H39	4294.54	6943.19	3953.29	33
H40	836.74	7264.02	7005.59	27
H41	153.72	7574.47	8537.59	29
H42	105.15	9307.23	9225.78	33

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 170449LT_0m.

Atom	*x*	*y*	*z*	U(eq)
H43	786.17	10723.62	8379.21	32
H45	6329.82	11205.46	2116.24	37
H46	5261.86	10335.62	3316.4	35

Experimental

Single crystals of $C_{46}H_{36}N_4$ **[170449LT_0m]** were **[]**. A suitable crystal was selected and **[]** on a **Bruker APEX-II CCD** diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [170449LT_0m]

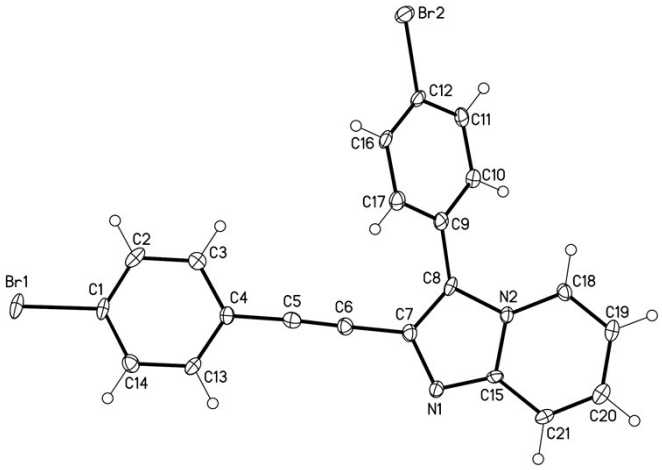
Crystal Data for $C_{46}H_{36}N_4$ (M =644.79 g/mol): triclinic, space group P-1 (no. 2), a = 9.6958(4) Å, b = 12.8863(5) Å, c = 14.1978(5) Å, α = 95.348(2)°, β = 91.322(2)°, γ = 97.198(2)°, V = 1751.19(12) Å^3, Z = 2, T = 100.15 K, μ(MoKα) = 0.072 mm^{-1}, *Dcalc* = 1.223 g/cm^3, 21609 reflections measured (4.096° ≤ 2Θ ≤ 52.808°), 6900 unique (R_{int} = 0.0274, R_{sigma} = 0.0320) which were used in all calculations. The final R_1 was 0.0416 (I > 2σ(I)) and wR_2 was 0.1069 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C3(H3), C4(H4), C11(H11), C12(H12), C15(H15), C16(H16), C17(H17), C18(H18), C19(H19), C20(H20), C22(H22), C23(H23), C26(H26), C27(H27), C34(H34), C35(H35), C38(H38), C39(H39), C40(H40), C41(H41), C42(H42), C43(H43), C45(H45), C46(H46)
2.b Idealised Me refined as rotating group:
 C1(H1A,H1B,H1C), C14(H14A,H14B,H14C), C24(H24A,H24B,H24C), C37(H37A,H37B,H37C)

This report has been created with Olex2, compiled on 2023.08.24 svn.re1ec1418 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Figure S5. ORTEP diagram of compound **10 (CCDC No. 2287150)**



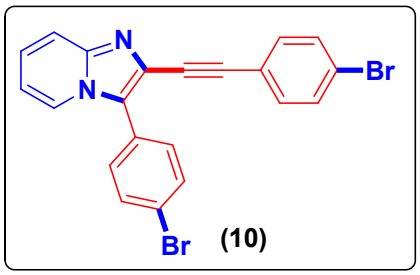


Table S8. Crystal data and structure refinement for mo_170754lt_0m.

Identification code	mo_170754LT_0m	
Empirical formula	C21 H12 Br2 N2	
Formula weight	452.15	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 3.8778(5) Å	a= 90°.
	b = 12.9392(17) Å	b= 92.968(3)°.
	c = 16.735(2) Å	g = 90°.
Volume	838.57(19) $Å^3$	
Z	2	
Density (calculated)	1.791 Mg/m^3	
Absorption coefficient	4.839 mm^{-1}	
F(000)	444	
Crystal size	0.20 x 0.18 x 0.02 mm^3	

Theta range for data collection	1.218 to 26.303°.
Index ranges	-4<=h<=4, -16<=k<=15, -20<=l<=19
Reflections collected	6578
Independent reflections	3304 [R(int) = 0.0295]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9485 and 0.7232
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3304 / 1 / 226
Goodness-of-fit on F^2	0.951
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0540
R indices (all data)	R1 = 0.0297, wR2 = 0.0549
Absolute structure parameter	0.025(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.408 and -0.479 e.$Å^{-3}$

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_170754lt_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-2478(1)	13896(1)	-83(1)	20(1)
Br(2)	6264(1)	6155(1)	1250(1)	18(1)
N(1)	6927(11)	10831(3)	4695(2)	14(1)
N(2)	8254(11)	9128(3)	4777(2)	12(1)
C(1)	-615(13)	13072(5)	782(3)	14(1)
C(2)	-840(15)	12013(5)	737(3)	18(1)
C(3)	437(14)	11434(4)	1379(3)	18(1)
C(4)	1972(13)	11915(4)	2060(3)	13(1)
C(5)	3324(13)	11325(4)	2739(3)	13(1)
C(6)	4520(13)	10879(4)	3310(3)	14(1)
C(7)	6050(14)	10332(4)	3982(3)	14(1)
C(8)	6835(13)	9297(4)	4002(3)	12(1)
C(9)	6599(13)	8521(4)	3366(3)	13(1)

C(10)	5339(13)	7517(4)	3470(3)	14(1)
C(11)	5215(13)	6821(4)	2835(3)	15(1)
C(12)	6328(13)	7128(4)	2101(3)	13(1)
C(13)	2174(13)	12986(4)	2081(3)	14(1)
C(14)	908(13)	13576(4)	1444(3)	16(1)
C(15)	8287(13)	10086(4)	5156(3)	12(1)
C(16)	7571(14)	8108(4)	1980(3)	14(1)
C(17)	7704(12)	8804(5)	2614(3)	15(1)
C(18)	9573(14)	8253(4)	5145(3)	14(1)
C(19)	10996(13)	8314(4)	5902(3)	16(1)
C(20)	11127(14)	9286(4)	6299(3)	18(1)
C(21)	9798(13)	10149(4)	5942(3)	13(1)

Table S10. Bond lengths [Å] and angles [°] for mo_170754lt_0m.

Br(1)-C(1)	1.910(5)
Br(2)-C(12)	1.900(5)
N(1)-C(15)	1.327(6)
N(1)-C(7)	1.384(6)
N(2)-C(18)	1.375(6)
N(2)-C(15)	1.391(6)
N(2)-C(8)	1.400(5)
C(1)-C(2)	1.374(7)
C(1)-C(14)	1.391(7)
C(2)-C(3)	1.380(7)
C(2)-H(12)	0.9500
C(3)-C(4)	1.403(7)
C(3)-H(1)	0.9500
C(4)-C(13)	1.389(7)
C(4)-C(5)	1.444(6)
C(5)-C(6)	1.190(6)
C(6)-C(7)	1.432(6)
C(7)-C(8)	1.374(7)
C(8)-C(9)	1.462(7)

C(9)-C(17)	1.399(7)
C(9)-C(10)	1.402(7)
C(10)-C(11)	1.392(7)
C(10)-H(4)	0.9500
C(11)-C(12)	1.381(7)
C(11)-H(7)	0.9500
C(12)-C(16)	1.375(8)
C(13)-C(14)	1.380(7)
C(13)-H(3)	0.9500
C(14)-H(2)	0.9500
C(15)-C(21)	1.413(6)
C(16)-C(17)	1.390(7)
C(16)-H(5)	0.9500
C(17)-H(6)	0.9500
C(18)-C(19)	1.359(6)
C(18)-H(11)	0.9500
C(19)-C(20)	1.421(8)
C(19)-H(10)	0.9500
C(20)-C(21)	1.355(7)
C(20)-H(8)	0.9500
C(21)-H(9)	0.9500

C(15)-N(1)-C(7)	103.6(4)
C(18)-N(2)-C(15)	122.4(4)
C(18)-N(2)-C(8)	131.5(4)
C(15)-N(2)-C(8)	106.1(4)
C(2)-C(1)-C(14)	122.3(5)
C(2)-C(1)-Br(1)	119.7(4)
C(14)-C(1)-Br(1)	118.1(4)
C(1)-C(2)-C(3)	118.6(5)
C(1)-C(2)-H(12)	120.7
C(3)-C(2)-H(12)	120.7
C(2)-C(3)-C(4)	120.8(5)
C(2)-C(3)-H(1)	119.6
C(4)-C(3)-H(1)	119.6
C(13)-C(4)-C(3)	118.9(4)

C(13)-C(4)-C(5)	119.4(4)
C(3)-C(4)-C(5)	121.7(5)
C(6)-C(5)-C(4)	176.9(5)
C(5)-C(6)-C(7)	178.2(6)
C(8)-C(7)-N(1)	113.0(4)
C(8)-C(7)-C(6)	125.7(4)
N(1)-C(7)-C(6)	121.3(5)
C(7)-C(8)-N(2)	104.5(4)
C(7)-C(8)-C(9)	130.3(4)
N(2)-C(8)-C(9)	125.1(4)
C(17)-C(9)-C(10)	118.6(5)
C(17)-C(9)-C(8)	117.7(5)
C(10)-C(9)-C(8)	123.7(5)
C(11)-C(10)-C(9)	120.3(5)
C(11)-C(10)-H(4)	119.9
C(9)-C(10)-H(4)	119.9
C(12)-C(11)-C(10)	119.5(5)
C(12)-C(11)-H(7)	120.2
C(10)-C(11)-H(7)	120.2
C(16)-C(12)-C(11)	121.6(5)
C(16)-C(12)-Br(2)	119.5(4)
C(11)-C(12)-Br(2)	118.9(4)
C(14)-C(13)-C(4)	121.0(4)
C(14)-C(13)-H(3)	119.5
C(4)-C(13)-H(3)	119.5
C(13)-C(14)-C(1)	118.4(5)
C(13)-C(14)-H(2)	120.8
C(1)-C(14)-H(2)	120.8
N(1)-C(15)-N(2)	112.8(4)
N(1)-C(15)-C(21)	129.2(5)
N(2)-C(15)-C(21)	117.9(4)
C(12)-C(16)-C(17)	119.0(5)
C(12)-C(16)-H(5)	120.5
C(17)-C(16)-H(5)	120.5
C(16)-C(17)-C(9)	121.1(5)
C(16)-C(17)-H(6)	119.5

C(9)-C(17)-H(6)	119.5
C(19)-C(18)-N(2)	119.5(5)
C(19)-C(18)-H(11)	120.2
N(2)-C(18)-H(11)	120.2
C(18)-C(19)-C(20)	119.3(5)
C(18)-C(19)-H(10)	120.3
C(20)-C(19)-H(10)	120.3
C(21)-C(20)-C(19)	121.3(4)
C(21)-C(20)-H(8)	119.4
C(19)-C(20)-H(8)	119.4
C(20)-C(21)-C(15)	119.5(5)
C(20)-C(21)-H(9)	120.2
C(15)-C(21)-H(9)	120.2

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_170754lt_0m. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

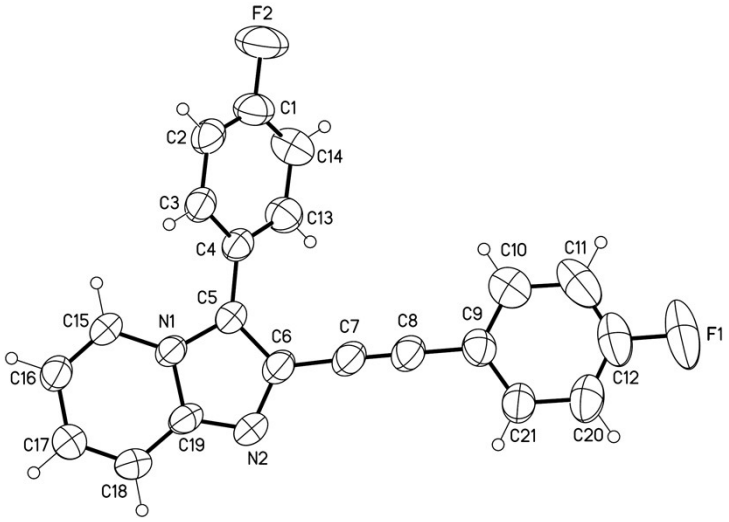
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	17(1)	32(1)	12(1)	7(1)	-2(1)	6(1)
Br(2)	20(1)	21(1)	14(1)	-4(1)	-3(1)	2(1)
N(1)	16(2)	13(2)	12(2)	2(2)	-4(2)	-1(2)
N(2)	15(2)	12(3)	10(2)	3(2)	-1(2)	0(2)
C(1)	10(3)	23(3)	9(3)	6(2)	0(2)	3(2)
C(2)	16(3)	29(4)	9(3)	-2(3)	-1(2)	-2(3)
C(3)	22(3)	14(3)	17(3)	0(2)	-1(2)	0(2)
C(4)	11(3)	15(3)	13(3)	2(2)	-1(2)	1(2)
C(5)	12(2)	12(3)	16(3)	0(2)	3(2)	-3(2)
C(6)	13(3)	14(3)	15(3)	1(2)	-1(2)	0(2)
C(7)	16(3)	13(3)	12(3)	3(2)	0(2)	0(2)
C(8)	10(3)	19(3)	7(2)	3(2)	0(2)	0(2)
C(9)	9(3)	16(3)	14(3)	1(2)	-2(2)	3(2)

C(10)	13(3)	16(3)	13(2)	3(2)	-1(2)	0(2)
C(11)	12(3)	14(3)	17(3)	4(2)	-3(2)	1(2)
C(12)	12(3)	17(3)	10(3)	-1(2)	-4(2)	1(2)
C(13)	14(3)	19(3)	9(2)	-1(2)	-2(2)	0(2)
C(14)	14(3)	14(3)	19(3)	1(2)	-1(2)	1(2)
C(15)	13(3)	11(3)	12(3)	-3(2)	-2(2)	-2(2)
C(16)	16(3)	18(3)	7(3)	2(2)	-2(2)	3(2)
C(17)	13(3)	17(3)	16(2)	2(2)	-3(2)	-1(2)
C(18)	18(3)	12(3)	12(2)	3(2)	3(2)	2(2)
C(19)	16(3)	21(3)	12(2)	6(2)	-1(2)	0(2)
C(20)	16(3)	25(3)	12(3)	1(2)	-1(2)	-1(2)
C(21)	10(3)	18(3)	11(2)	-5(2)	1(2)	0(2)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for mo_170754lt_0m.

	x	y	z	U(eq)
H(12)	-1853	11686	274	22
H(1)	274	10702	1360	21
H(4)	4566	7311	3975	17
H(7)	4372	6140	2906	18
H(3)	3199	13318	2541	17
H(2)	1072	14308	1458	19
H(5)	8328	8306	1472	17
H(6)	8559	9482	2535	18
H(11)	9490	7610	4871	17
H(10)	11894	7714	6165	20
H(8)	12166	9332	6824	21
H(9)	9882	10791	6217	16

Figure S6. ORTEP diagram of compound **13 (CCDC No. 2287146)**



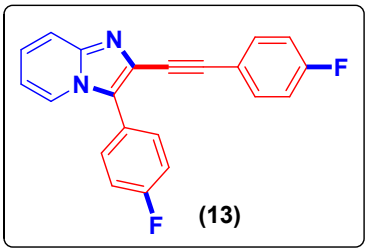


Table S13. Crystal data and structure refinement for 170613LT_0M.

Identification code	170613LT_0m	
Empirical formula	C21 H12 F2 N2	
Formula weight	330.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 14.4478(6) Å	a= 90°.
	b = 17.5319(7) Å	b= 99.180(2)°.
	c = 12.9774(4) Å	g = 90°.
Volume	3245.0(2) $Å^3$	
Z	8	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	1360	
Crystal size	0.22 x 0.20 x 0.19 mm^3	
Theta range for data collection	1.841 to 26.387°.	

Index ranges	-18<=h<=18, -21<=k<=21, -16<=l<=13
Reflections collected	12325
Independent reflections	3321 [R(int) = 0.0305]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9485 and 0.9055
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3321 / 0 / 226
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1156
R indices (all data)	R1 = 0.0681, wR2 = 0.1316
Extinction coefficient	n/a
Largest diff. peak and hole	0.245 and -0.224 e.$Å^{-3}$

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 170613LT_0M. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

F(1)	1448(1)	-314(1)	10452(2)	138(1)
F(2)	1189(1)	1643(1)	2919(1)	97(1)
N(1)	1201(1)	4558(1)	5991(1)	44(1)
N(2)	1238(1)	4340(1)	7702(1)	60(1)
C(1)	1204(1)	2166(1)	3695(1)	63(1)
C(2)	1788(1)	2778(1)	3710(1)	57(1)
C(3)	1805(1)	3310(1)	4501(1)	49(1)
C(4)	1234(1)	3224(1)	5263(1)	45(1)
C(5)	1240(1)	3775(1)	6116(1)	44(1)
C(6)	1260(1)	3663(1)	7175(1)	51(1)
C(7)	1323(1)	2953(1)	7717(1)	55(1)
C(8)	1374(1)	2368(1)	8194(1)	56(1)
C(9)	1410(1)	1668(1)	8769(1)	54(1)
C(10)	1247(2)	977(1)	8268(2)	83(1)
C(11)	1269(2)	304(1)	8846(3)	102(1)
C(12)	1443(2)	350(1)	9902(2)	87(1)

C(13)	660(1)	2587(1)	5220(1)	56(1)
C(14)	644(1)	2050(1)	4437(2)	67(1)
C(15)	1135(1)	5016(1)	5116(1)	47(1)
C(16)	1073(1)	5776(1)	5215(1)	52(1)
C(17)	1060(1)	6113(1)	6195(1)	61(1)
C(18)	1114(2)	5669(1)	7059(1)	64(1)
C(19)	1190(1)	4875(1)	6976(1)	52(1)
C(20)	1623(2)	1008(1)	10419(2)	74(1)
C(21)	1610(1)	1675(1)	9854(1)	60(1)

Table S15. Bond lengths [Å] and angles [°] for 170613LT_0M.

F(1)-C(12)	1.365(2)
F(2)-C(1)	1.361(2)
N(1)-C(15)	1.3815(19)
N(1)-C(5)	1.383(2)
N(1)-C(19)	1.3962(19)
N(2)-C(19)	1.324(2)
N(2)-C(6)	1.373(2)
C(1)-C(2)	1.362(3)
C(1)-C(14)	1.368(3)
C(2)-C(3)	1.385(2)
C(2)-H(12)	0.9500
C(3)-C(4)	1.393(2)
C(3)-H(11)	0.9500
C(4)-C(13)	1.388(2)
C(4)-C(5)	1.468(2)
C(5)-C(6)	1.384(2)
C(6)-C(7)	1.426(2)
C(7)-C(8)	1.194(2)
C(8)-C(9)	1.432(2)
C(9)-C(10)	1.377(3)
C(9)-C(21)	1.392(3)
C(10)-C(11)	1.396(3)

C(10)-H(9)	0.9500
C(11)-C(12)	1.356(4)
C(11)-H(8)	0.9500
C(12)-C(20)	1.339(3)
C(13)-C(14)	1.383(2)
C(13)-H(2)	0.9500
C(14)-H(1)	0.9500
C(15)-C(16)	1.343(2)
C(15)-H(3)	0.9500
C(16)-C(17)	1.406(2)
C(16)-H(4)	0.9500
C(17)-C(18)	1.357(3)
C(17)-H(5)	0.9500
C(18)-C(19)	1.401(3)
C(18)-H(10)	0.9500
C(20)-C(21)	1.378(3)
C(20)-H(7)	0.9500
C(21)-H(6)	0.9500

C(15)-N(1)-C(5)	132.06(13)
C(15)-N(1)-C(19)	120.78(14)
C(5)-N(1)-C(19)	107.09(12)
C(19)-N(2)-C(6)	105.09(13)
F(2)-C(1)-C(2)	118.57(18)
F(2)-C(1)-C(14)	118.59(19)
C(2)-C(1)-C(14)	122.84(17)
C(1)-C(2)-C(3)	118.58(16)
C(1)-C(2)-H(12)	120.7
C(3)-C(2)-H(12)	120.7
C(2)-C(3)-C(4)	120.72(17)
C(2)-C(3)-H(11)	119.6
C(4)-C(3)-H(11)	119.6
C(13)-C(4)-C(3)	118.44(15)
C(13)-C(4)-C(5)	119.44(14)
C(3)-C(4)-C(5)	122.11(15)
N(1)-C(5)-C(6)	104.54(14)

N(1)-C(5)-C(4)	124.70(13)
C(6)-C(5)-C(4)	130.74(15)
N(2)-C(6)-C(5)	111.99(15)
N(2)-C(6)-C(7)	120.89(14)
C(5)-C(6)-C(7)	127.09(16)
C(8)-C(7)-C(6)	178.30(18)
C(7)-C(8)-C(9)	178.48(19)
C(10)-C(9)-C(21)	118.49(18)
C(10)-C(9)-C(8)	121.23(18)
C(21)-C(9)-C(8)	120.28(17)
C(9)-C(10)-C(11)	120.2(2)
C(9)-C(10)-H(9)	119.9
C(11)-C(10)-H(9)	119.9
C(12)-C(11)-C(10)	118.5(2)
C(12)-C(11)-H(8)	120.7
C(10)-C(11)-H(8)	120.7
C(20)-C(12)-C(11)	123.2(2)
C(20)-C(12)-F(1)	119.3(3)
C(11)-C(12)-F(1)	117.6(3)
C(14)-C(13)-C(4)	121.18(16)
C(14)-C(13)-H(2)	119.4
C(4)-C(13)-H(2)	119.4
C(1)-C(14)-C(13)	118.23(18)
C(1)-C(14)-H(1)	120.9
C(13)-C(14)-H(1)	120.9
C(16)-C(15)-N(1)	119.73(14)
C(16)-C(15)-H(3)	120.1
N(1)-C(15)-H(3)	120.1
C(15)-C(16)-C(17)	120.88(15)
C(15)-C(16)-H(4)	119.6
C(17)-C(16)-H(4)	119.6
C(18)-C(17)-C(16)	119.97(18)
C(18)-C(17)-H(5)	120.0
C(16)-C(17)-H(5)	120.0
C(17)-C(18)-C(19)	120.09(16)
C(17)-C(18)-H(10)	120.0

C(19)-C(18)-H(10)	120.0
N(2)-C(19)-N(1)	111.27(15)
N(2)-C(19)-C(18)	130.17(15)
N(1)-C(19)-C(18)	118.54(15)
C(12)-C(20)-C(21)	118.7(2)
C(12)-C(20)-H(7)	120.7
C(21)-C(20)-H(7)	120.7
C(20)-C(21)-C(9)	120.9(2)
C(20)-C(21)-H(6)	119.5
C(9)-C(21)-H(6)	119.5

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 170613LT_0M. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

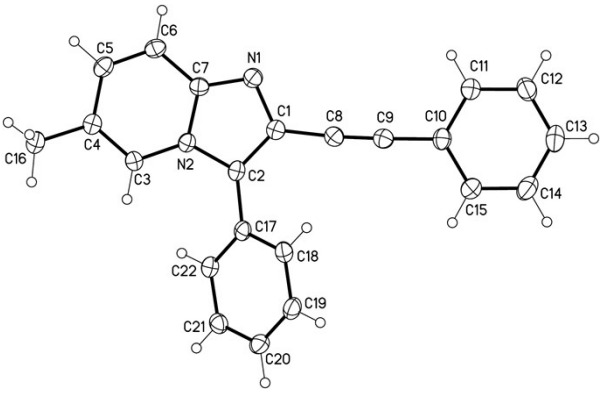
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	158(2)	70(1)	191(2)	65(1)	42(1)	19(1)
F(2)	123(1)	85(1)	84(1)	-38(1)	22(1)	13(1)
N(1)	49(1)	49(1)	33(1)	2(1)	7(1)	-2(1)
N(2)	85(1)	61(1)	34(1)	2(1)	12(1)	-1(1)
C(1)	73(1)	59(1)	55(1)	-12(1)	6(1)	16(1)
C(2)	69(1)	61(1)	46(1)	7(1)	18(1)	20(1)
C(3)	55(1)	52(1)	42(1)	8(1)	13(1)	7(1)
C(4)	46(1)	50(1)	38(1)	4(1)	7(1)	6(1)
C(5)	48(1)	50(1)	37(1)	4(1)	8(1)	1(1)
C(6)	60(1)	58(1)	37(1)	6(1)	11(1)	1(1)
C(7)	64(1)	62(1)	40(1)	5(1)	14(1)	3(1)
C(8)	64(1)	60(1)	46(1)	6(1)	18(1)	6(1)
C(9)	55(1)	51(1)	60(1)	6(1)	17(1)	8(1)
C(10)	102(2)	67(2)	79(1)	-5(1)	12(1)	-2(1)
C(11)	120(2)	48(1)	139(3)	-6(2)	26(2)	-4(1)
C(12)	88(2)	59(2)	117(2)	31(1)	25(2)	16(1)

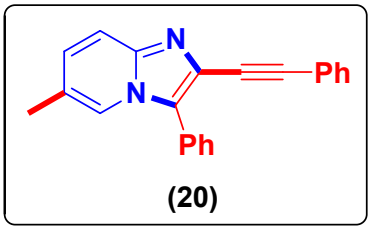
C(13)	55(1)	57(1)	58(1)	-3(1)	17(1)	-2(1)
C(14)	64(1)	58(1)	80(1)	-14(1)	13(1)	-3(1)
C(15)	53(1)	56(1)	33(1)	3(1)	9(1)	0(1)
C(16)	58(1)	54(1)	44(1)	7(1)	10(1)	-3(1)
C(17)	80(1)	50(1)	52(1)	0(1)	10(1)	-6(1)
C(18)	91(2)	58(1)	41(1)	-8(1)	11(1)	-8(1)
C(19)	65(1)	58(1)	32(1)	-2(1)	7(1)	-5(1)
C(20)	74(1)	74(2)	76(1)	27(1)	20(1)	19(1)
C(21)	67(1)	56(1)	60(1)	12(1)	19(1)	9(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 170613LT_0M.

H(12)	2175	2838	3188	69
H(11)	2210	3739	4524	59
H(9)	1120	959	7527	100
H(8)	1164	-176	8506	122
H(2)	271	2518	5738	67
H(1)	254	1612	4414	81
H(3)	1133	4795	4448	56
H(4)	1038	6091	4613	62
H(5)	1014	6651	6253	73
H(10)	1099	5896	7721	76
H(7)	1758	1015	11160	89
H(6)	1739	2145	10211	72

Figure S7. ORTEP diagram of compound **20 (CCDC No. 2303798)**





(20)

230756L3_twin1_hklf4

Table S18 Crystal data and structure refinement for 230756L3_twin1_hklf4.

Identification code	230756L3_twin1_hklf4
Empirical formula	$C_{44}H_{32}N_4$
Formula weight	616.73
Temperature/K	100.00(11)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.7695(5)
b/Å	8.6997(3)
c/Å	11.0836(3)
α/°	90
β/°	91.718(3)
γ/°	90

Volume/Å^3	1616.26(8)
Z	2
ρ_{calc}g/cm^3	1.267
μ/mm^{-1}	0.578
F(000)	648.0
Crystal size/mm^3	0.03 × 0.03 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.272 to 148.92
Index ranges	-20 ≤ h ≤ 20, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	3602
Independent reflections	3602 [R_{int} = ?, R_{sigma} = 0.0160]
Data/restraints/parameters	3602/0/219
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0835
Final R indexes [all data]	R_1 = 0.0440, wR_2 = 0.0877
Largest diff. peak/hole / e Å^{-3}	0.16/-0.22

Table S19 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 230756L3_twin1_hklf4. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	6648.1(8)	3683.4(16)	221.5(13)	21.2(3)
C2	6498.8(8)	4354.9(16)	1325.6(13)	20.2(3)
C3	5190.2(8)	4610.5(16)	2373.4(12)	20.8(3)
C4	4396.4(8)	4306.4(16)	2279.1(13)	21.5(3)
C5	4097.4(9)	3419.5(16)	1281.2(13)	23.1(3)

Table S19 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 230756L3_twin1_hklf4. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C6	4583.5(8)	2923.9(16)	405.5(13)	23.2(3)
C7	5406.4(8)	3284.2(16)	479.4(12)	20.6(3)
C8	7377.2(9)	3718.1(16)	-408.6(13)	22.3(3)
C9	7953.4(9)	3784.5(17)	-1024.2(13)	23.4(3)
C10	8610.2(8)	3921.2(17)	-1816.3(13)	23.1(3)
C11	8525.1(9)	3415.6(18)	-3013.9(14)	26.7(3)
C12	9139.8(9)	3623.3(19)	-3801.3(15)	31.0(4)
C13	9845.7(10)	4314(2)	-3408.9(15)	33.3(4)
C14	9938.2(10)	4804(2)	-2224.2(15)	33.9(4)
C15	9326.6(9)	4610.5(19)	-1430.1(15)	29.1(4)
C16	3825.2(9)	4963.5(18)	3163.9(14)	26.1(3)
C17	7029.7(8)	5205.9(16)	2165.3(13)	20.4(3)
C18	7550.7(8)	6305.1(17)	1702.9(13)	23.2(3)
C19	8079.8(9)	7089.0(18)	2465.3(14)	26.8(3)
C20	8098.3(9)	6785.0(18)	3693.5(14)	27.1(3)
C21	7587.6(8)	5695.4(18)	4159.0(13)	24.4(3)
C22	7052.9(8)	4908.8(16)	3402.9(13)	21.7(3)
N1	5978.0(7)	3005.8(13)	-295.3(11)	22.5(3)
N2	5692.3(7)	4094.9(13)	1491.8(10)	19.8(3)

Table S20 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 230756L3_twin1_hklf4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

Table S20 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 230756L3_twin1_hklf4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	21.2(7)	19.2(7)	23.3(7)	1.2(5)	1.0(6)	1.6(5)
C2	17.8(7)	19.7(7)	23.3(7)	2.0(6)	3.0(6)	1.3(5)
C3	21.1(7)	20.8(7)	20.6(7)	-0.2(6)	2.7(6)	0.9(5)
C4	20.9(7)	19.4(7)	24.4(7)	2.8(6)	1.7(6)	1.3(6)
C5	20.4(7)	19.0(7)	29.9(8)	2.1(6)	0.2(6)	-1.0(6)
C6	23.5(8)	18.8(7)	27.1(7)	-0.6(6)	-2.0(6)	-1.4(6)
C7	22.2(7)	18.2(7)	21.4(7)	-0.6(5)	-0.3(6)	0.3(5)
C8	23.6(8)	20.5(8)	22.8(7)	-0.2(6)	0.7(6)	2.1(6)
C9	23.8(8)	22.8(8)	23.5(7)	-0.2(6)	-1.0(6)	2.0(6)
C10	20.8(7)	23.0(8)	25.6(8)	2.6(6)	2.7(6)	3.5(6)
C11	23.7(8)	28.8(8)	27.6(8)	-1.6(6)	2.3(6)	0.3(6)
C12	30.8(9)	37.5(10)	24.9(8)	-1.2(7)	5.4(7)	3.0(7)
C13	25.8(9)	40.2(10)	34.4(9)	6.8(7)	9.2(7)	3.1(7)
C14	20.5(8)	41.2(10)	40.0(10)	2.3(8)	0.7(7)	-2.4(7)
C15	22.5(8)	35.7(9)	29.2(8)	-1.7(7)	-0.7(6)	0.2(6)
C16	21.3(8)	26.8(8)	30.6(9)	0.1(6)	4.4(6)	0.3(6)
C17	17.2(7)	19.5(7)	24.8(7)	-0.8(6)	2.7(6)	3.3(5)
C18	24.1(8)	23.4(8)	22.5(7)	0.1(6)	5.1(6)	-0.1(6)
C19	21.8(8)	25.8(8)	33.2(8)	-1.6(6)	6.6(6)	-4.1(6)
C20	19.3(7)	31.2(9)	30.7(8)	-6.7(6)	0.0(6)	0.5(6)
C21	22.0(7)	29.9(8)	21.4(7)	-1.3(6)	1.2(6)	5.3(6)
C22	19.2(7)	21.3(8)	24.8(7)	1.7(6)	3.4(6)	1.3(6)
N1	22.3(6)	20.7(6)	24.6(6)	-1.2(5)	1.3(5)	0.5(5)

Table S20 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230756L3_twin1_hklf4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	18.1(6)	18.5(6)	22.7(6)	0.6(5)	1.8(5)	0.3(5)

Table S21 Bond Lengths for 230756L3_twin1_hklf4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.386(2)	C9	C10	1.434(2)
C1	C8	1.427(2)	C10	C11	1.402(2)
C1	N1	1.3782(18)	C10	C15	1.398(2)
C2	C17	1.469(2)	C11	C12	1.382(2)
C2	N2	1.3890(17)	C12	C13	1.386(2)
C3	C4	1.358(2)	C13	C14	1.385(2)
C3	N2	1.3835(17)	C14	C15	1.382(2)
C4	C5	1.427(2)	C17	C18	1.403(2)
C4	C16	1.504(2)	C17	C22	1.395(2)
C5	C6	1.356(2)	C18	C19	1.386(2)
C6	C7	1.415(2)	C19	C20	1.386(2)
C7	N1	1.3281(18)	C20	C21	1.387(2)
C7	N2	1.3979(18)	C21	C22	1.389(2)
C8	C9	1.201(2)			

Table S22 Bond Angles for 230756L3_twin1_hklf4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C8	127.13(14)	C15	C10	C11	119.11(14)

Table S22 Bond Angles for 230756L3_twin1_hklf4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	112.38(12)	C12	C11	C10	120.02(15)
N1	C1	C8	120.38(13)	C11	C12	C13	120.31(15)
C1	C2	C17	130.55(13)	C14	C13	C12	120.09(15)
C1	C2	N2	104.53(12)	C15	C14	C13	120.16(15)
N2	C2	C17	124.90(12)	C14	C15	C10	120.30(15)
C4	C3	N2	119.89(13)	C18	C17	C2	118.98(13)
C3	C4	C5	119.06(13)	C22	C17	C2	121.88(13)
C3	C4	C16	121.18(13)	C22	C17	C18	119.09(13)
C5	C4	C16	119.66(13)	C19	C18	C17	120.46(14)
C6	C5	C4	121.44(13)	C20	C19	C18	119.99(14)
C5	C6	C7	119.61(14)	C19	C20	C21	119.98(14)
N1	C7	C6	130.07(13)	C20	C21	C22	120.45(14)
N1	C7	N2	111.97(12)	C21	C22	C17	120.03(13)
N2	C7	C6	117.94(12)	C7	N1	C1	104.39(11)
C9	C8	C1	174.44(16)	C2	N2	C7	106.71(11)
C8	C9	C10	176.21(16)	C3	N2	C2	131.03(12)
C11	C10	C9	119.71(14)	C3	N2	C7	121.95(12)
C15	C10	C9	121.12(14)				

Table S23 Torsion Angles for 230756L3_twin1_hklf4.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C17	C18	43.6(2)	C11	C12	C13	C14	-0.2(3)
C1	C2	C17	C22	-133.77(16)	C12	C13	C14	C15	-0.2(3)

Table S23 Torsion Angles for 230756L3_twin1_hklf4.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	N2	C3	-173.56(13)	C13	C14	C15	C10	-0.1(3)
C1	C2	N2	C7	0.01(14)	C15	C10	C11	C12	-1.0(2)
C2	C1	N1	C7	1.21(16)	C16	C4	C5	C6	174.01(14)
C2	C17	C18	C19	-177.66(13)	C17	C2	N2	C3	4.9(2)
C2	C17	C22	C21	177.31(13)	C17	C2	N2	C7	178.46(13)
C3	C4	C5	C6	-2.4(2)	C17	C18	C19	C20	0.2(2)
C4	C3	N2	C2	173.99(13)	C18	C17	C22	C21	-0.1(2)
C4	C3	N2	C7	1.2(2)	C18	C19	C20	C21	0.0(2)
C4	C5	C6	C7	0.3(2)	C19	C20	C21	C22	-0.3(2)
C5	C6	C7	N1	-175.54(14)	C20	C21	C22	C17	0.3(2)
C5	C6	C7	N2	2.5(2)	C22	C17	C18	C19	-0.2(2)
C6	C7	N1	C1	176.98(15)	N1	C1	C2	C17	-179.08(14)
C6	C7	N2	C2	-177.65(13)	N1	C1	C2	N2	-0.76(16)
C6	C7	N2	C3	-3.36(19)	N1	C7	N2	C2	0.77(16)
C8	C1	C2	C17	-2.9(3)	N1	C7	N2	C3	175.06(12)
C8	C1	C2	N2	175.40(14)	N2	C2	C17	C18	-134.40(14)
C8	C1	N1	C7	-175.24(13)	N2	C2	C17	C22	48.2(2)
C9	C10	C11	C12	176.33(14)	N2	C3	C4	C5	1.6(2)
C9	C10	C15	C14	-176.63(15)	N2	C3	C4	C16	-174.73(12)
C10	C11	C12	C13	0.8(2)	N2	C7	N1	C1	-1.19(15)
C11	C10	C15	C14	0.7(2)					

Table S24 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230756L3_twin1_hklf4.

Atom	*x*	*y*	*z*	U(eq)
H3	5400.3	5176.36	3043.51	25
H5	3545.84	3170.9	1229.04	28
H6	4372.73	2338.35	-253.49	28
H11	8044.87	2930.12	-3284.66	32
H12	9078.05	3291.03	-4615.21	37
H13	10266.78	4451.17	-3953.41	40
H14	10423.29	5274.37	-1956.86	41
H15	9393.17	4947.31	-617.94	35
H16A	3550.18	5851.77	2801.16	39
H16B	4120.8	5287.39	3896.55	39
H16C	3432.5	4179.47	3370.39	39
H18	7540.81	6513.8	861.24	28
H19	8429.73	7834.49	2146.16	32
H20	8460.61	7322.53	4216.28	32
H21	7603.66	5485.84	5000.56	29
H22	6702.94	4168.26	3728.54	26

Experimental

Single crystals of $C_{44}H_{32}N_4$ **[230756L3_twin1_hklf4]** were **[]**. A suitable crystal was selected and **[]** on a **XtaLAB Synergy R, DW system, HyPix-Arc 150** diffractometer. The crystal was kept at 100.00(11) K during data collection. Using Olex2 [1], the structure was solved with the SHELXD [2] structure solution program using Dual Space and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [230756L3_twin1_hklf4]

Crystal Data for $C_{44}H_{32}N_4$ (*M* =616.73 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 16.7695(5) Å, *b* = 8.6997(3) Å, *c* = 11.0836(3) Å, *β* = 91.718(3)°, *V* = 1616.26(8) Å^3, *Z* = 2, *T* = 100.00(11) K, μ(Cu Kα) = 0.578 mm^{-1}, *Dcalc* = 1.267 g/cm^3, 3602 reflections measured (5.272°

≤ 2Θ ≤ 148.92°), 3602 unique (R_{int} = ?, R_{sigma} = 0.0160) which were used in all calculations. The final R_1 was 0.0341 (I > 2σ(I)) and wR_2 was 0.0877 (all data).

Refinement model description

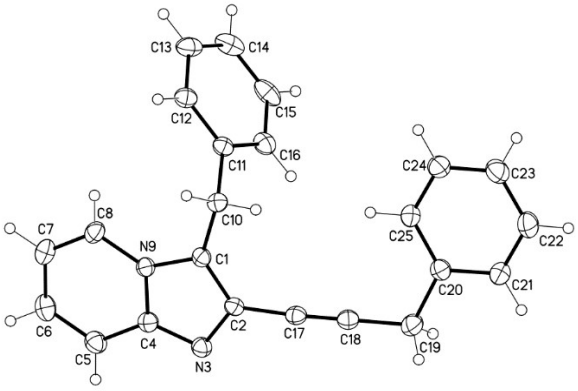
Number of restraints - 0, number of constraints - unknown.

Details:

1. Twinned data refinement
 Scales: 0.5422(12)
 0.4578(12)
2. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
3.a Aromatic/amide H refined with riding coordinates:
 C3(H3), C5(H5), C6(H6), C11(H11), C12(H12), C13(H13), C14(H14), C15(H15),
 C18(H18), C19(H19), C20(H20), C21(H21), C22(H22)
3.b Idealised Me refined as rotating group:
 C16(H16A,H16B,H16C)

This report has been created with Olex2, compiled on 2023.08.24 svn.re1ec1418 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Figure S8. ORTEP diagram of compound **27 (CCDC No. 2295775)**



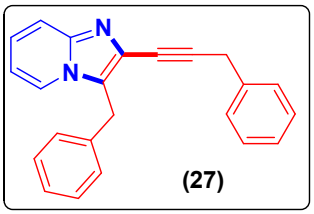


Table S25 Crystal data and structure refinement for 230885lt_auto.

Identification code	230885lt_auto
Empirical formula	$C_{46}H_{36}N_4$
Formula weight	644.79
Temperature/K	99.8(5)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.92700(10)
b/Å	11.98670(10)
c/Å	36.2753(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3446.83(6)
Z	4
ρ_{calc}g/cm^3	1.243
μ/mm^{-1}	0.563
F(000)	1360.0
Crystal size/mm^3	0.06 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.872 to 149.538
Index ranges	$-9 \le h \le 9$, $-14 \le k \le 13$, $-44 \le l \le 40$
Reflections collected	21562
Independent reflections	6582 [R_{int} = 0.0303, R_{sigma} = 0.0311]
Data/restraints/parameters	6582/0/453
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0805
Final R indexes [all data]	R_1 = 0.0370, wR_2 = 0.0830
Largest diff. peak/hole / e Å^{-3}	0.16/-0.16

Flack parameter 0.0(5)

Table S26 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 230885lt_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	6301(2)	6869.8(16)	6628.9(5)	18.8(4)
C2	6931(2)	5847.8(16)	6530.3(5)	18.9(4)
C4	6893(2)	5811.8(17)	7119.8(5)	20.9(4)
C5	6988(3)	5586.1(19)	7503.3(5)	25.7(5)
C6	6476(3)	6380.1(19)	7747.3(5)	28.9(5)
C7	5855(3)	7429.6(18)	7623.1(6)	27.2(5)
C8	5769(2)	7657.5(17)	7258.1(5)	23.5(4)
C10	5711(2)	7835.6(16)	6404.0(5)	19.2(4)
C11	3810(2)	7987.7(16)	6405.5(5)	19.8(4)
C12	3110(2)	8967.5(17)	6543.7(5)	23.2(4)
C13	1370(3)	9101.3(19)	6559.0(5)	28.4(5)
C14	318(3)	8259.2(19)	6437.2(6)	31.0(5)
C15	1004(3)	7282(2)	6296.3(6)	30.8(5)
C16	2747(3)	7148.2(18)	6278.2(5)	24.5(4)
C17	7141(2)	5473.5(16)	6157.5(5)	20.1(4)
C18	7242(2)	5188.7(17)	5842.5(5)	22.7(4)
C19	7323(3)	4808.2(18)	5459.0(6)	28.9(5)
C20	6551(2)	5603.8(16)	5179.4(5)	22.0(4)
C21	6746(3)	5361.8(17)	4805.0(5)	26.1(4)
C22	6083(3)	6064.6(18)	4537.8(6)	31.6(5)
C23	5195(3)	7011.2(18)	4641.0(6)	31.6(5)
C24	4969(3)	7247.3(17)	5010.4(6)	29.0(5)
C25	5652(3)	6550.4(16)	5278.9(5)	24.1(4)
N3	7312.1(19)	5187.8(14)	6831.1(5)	21.6(3)
N9	6274.9(19)	6849.6(13)	7010.5(4)	18.9(3)
C26	8333(2)	1856.9(16)	6624.4(5)	18.7(4)
C28	9098(2)	2622.0(17)	7245.2(5)	23.3(4)
C29	9142(3)	2376.1(18)	7610.2(5)	28.4(5)
C30	8560(3)	1327.4(19)	7741.6(5)	29.5(5)
C31	7944(3)	546.2(19)	7503.8(5)	26.6(5)
C32	7892(2)	785.8(17)	7121.5(5)	20.5(4)
C34	7640(2)	840.4(17)	6532.9(5)	18.7(4)
C35	8890(2)	2822.2(16)	6396.3(5)	19.7(4)
C36	10788(2)	2978.7(16)	6397.7(5)	19.1(4)
C37	11855(3)	2118.9(18)	6288.3(5)	23.9(4)

C38	13597(3)	2273(2)	6288.6(5)	29.2(5)
C39	14273(3)	3282(2)	6401.9(6)	32.6(5)
C40	13224(2)	4136.8(19)	6515.3(6)	28.6(5)
C41	11489(2)	3990.5(17)	6510.4(5)	23.0(4)
C42	7244(2)	477.9(16)	6166.4(5)	20.1(4)
C43	6892(2)	169.6(16)	5863.5(5)	22.6(4)
C44	6404(3)	-271.7(17)	5501.3(5)	28.5(5)
C45	6279(2)	599.6(16)	5198.4(5)	23.4(4)
C46	6942(3)	373.0(18)	4851.1(6)	28.8(5)
C47	6782(3)	1149(2)	4565.5(6)	32.8(5)
C48	5943(3)	2143.7(19)	4626.5(5)	30.5(5)
C49	5268(3)	2373.1(18)	4970.7(6)	28.1(5)
C50	5450(3)	1607.6(16)	5255.5(5)	24.7(4)
N27	8489.5(19)	1826.8(13)	7004.4(4)	19.2(3)
N33	7362.1(19)	178.0(14)	6838.8(5)	21.5(3)

Table S27 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230885lt_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	16.9(9)	19.3(10)	20.1(9)	-1.1(7)	-1.0(7)	-2.1(7)
C2	16.4(9)	20.4(10)	20.0(9)	0.7(8)	-1.0(7)	0.6(8)
C4	19.6(9)	20.1(10)	22.9(9)	-0.2(8)	-0.7(7)	-1.1(8)
C5	28.5(11)	24.4(12)	24.1(11)	3.0(8)	-2.6(8)	-0.1(9)
C6	33.2(12)	32.7(12)	20.9(10)	0.9(9)	-0.5(9)	-5.1(10)
C7	30.9(11)	25.6(12)	25.0(10)	-6.2(8)	2.6(8)	-3.0(9)
C8	24.2(10)	20.5(10)	25.9(10)	-5.4(8)	0.8(8)	-0.1(8)
C10	18.4(9)	16.5(9)	22.5(9)	0.2(8)	0.1(7)	-1.3(8)
C11	20.6(9)	19.7(10)	19.2(9)	4.7(8)	-0.3(7)	0.0(8)
C12	23.1(10)	21.9(10)	24.6(10)	3.8(8)	-0.2(8)	1.0(8)
C13	25.9(10)	31.1(11)	28.3(10)	9.6(9)	4.2(8)	8.6(9)
C14	20.2(10)	39.9(13)	32.9(11)	15.7(10)	-0.1(8)	0.5(9)
C15	25.3(11)	37.0(13)	30.1(11)	13.2(10)	-8.9(8)	-11.3(10)

C16	28.6(10)	20.4(10)	24.4(10)	4.4(8)	-3.9(8)	-2.4(9)
C17	19.3(9)	16.6(9)	24.3(10)	1.2(8)	-1.1(7)	0.1(7)
C18	24.7(10)	19.2(10)	24.1(10)	1.9(8)	-1.0(8)	2.3(8)
C19	37.4(12)	23.6(11)	25.6(10)	-1.5(9)	-0.4(9)	7.0(9)
C20	20.2(9)	22.8(10)	23.0(9)	-0.1(8)	-0.7(7)	-2.0(8)
C21	27.5(11)	26.1(11)	24.7(10)	-3.7(8)	0.5(8)	1.5(9)
C22	38.0(12)	35.7(12)	21.0(10)	-0.7(9)	-0.6(9)	1.2(10)
C23	37.4(12)	30.3(11)	27.1(10)	3.4(9)	-5.7(9)	2.2(10)
C24	31.7(11)	23.6(10)	31.7(11)	-2.8(9)	-5.8(9)	2.9(9)
C25	25.5(10)	24.4(10)	22.4(9)	-3.8(8)	-1.4(8)	0.3(8)
N3	22.5(8)	20.1(8)	22.0(8)	0.4(7)	-1.6(6)	0.4(7)
N9	18.2(7)	18.5(8)	19.8(7)	-1.3(6)	-1.2(6)	-0.9(6)
C26	16.6(9)	20.0(10)	19.5(9)	-0.2(8)	0.3(7)	2.2(8)
C28	22.7(10)	21.7(10)	25.7(10)	-4.4(8)	0.3(8)	-0.6(8)
C29	31.3(11)	30.3(12)	23.5(10)	-7.2(9)	-0.8(8)	3.1(9)
C30	34.9(12)	33.5(12)	20.0(10)	0.2(9)	1.2(9)	3.8(10)
C31	29.7(11)	28.4(12)	21.7(10)	2.8(8)	2.3(8)	1.6(9)
C32	19.8(9)	19.0(10)	22.6(9)	1.1(8)	3.0(7)	-0.2(8)
C34	16.6(9)	18.6(10)	21.0(9)	-0.2(8)	0.4(7)	1.0(7)
C35	18.2(9)	18.5(9)	22.4(9)	2.1(8)	-1.5(7)	0.3(8)
C36	19.3(9)	20.5(10)	17.4(8)	3.6(7)	-0.1(7)	0.0(8)
C37	28.9(11)	23.3(10)	19.4(9)	4.8(8)	2.4(8)	3.0(9)
C38	25.1(10)	35.1(12)	27.3(10)	9.9(9)	5.8(8)	11.7(10)
C39	19.9(10)	43.7(14)	34.3(11)	14.5(10)	0.0(9)	-1.1(10)
C40	23.8(10)	29.4(11)	32.6(11)	8.2(9)	-3.7(9)	-7.4(9)
C41	20.8(9)	21.2(10)	26.8(10)	3.5(8)	-1.0(8)	-1.6(8)
C42	20.6(9)	16.5(9)	23.3(10)	1.3(8)	-0.5(7)	-0.1(8)
C43	25.8(10)	16.2(9)	25.6(10)	0.5(8)	-1.6(8)	0.4(8)
C44	37.1(12)	21.8(10)	26.5(10)	-2.6(9)	-8.6(9)	-0.2(9)

C45	24.4(10)	23.8(10)	21.8(9)	-2.3(8)	-3.6(8)	-2.4(8)
C46	26.2(10)	30.3(11)	29.9(11)	-5.6(9)	-0.4(9)	2.0(9)
C47	32.6(12)	43.4(13)	22.4(10)	-4.1(9)	2.9(9)	-5.0(10)
C48	34.9(12)	34.4(12)	22.3(10)	6.1(9)	-1.3(8)	-6.8(10)
C49	30.3(11)	25.2(11)	28.8(10)	2.3(9)	-3.9(8)	-1.5(9)
C50	28.0(11)	24.3(10)	21.9(9)	-0.9(8)	0.0(8)	-1.5(8)
N27	18.8(8)	19.5(8)	19.2(7)	-1.3(6)	0.4(6)	1.8(7)
N33	23.9(8)	19.3(8)	21.3(8)	1.1(7)	0.7(6)	-1.3(7)

Table S28 Bond Lengths for 230885lt_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.371(3)	C26	C34	1.377(3)
C1	C10	1.491(3)	C26	C35	1.489(3)
C1	N9	1.385(2)	C26	N27	1.384(2)
C2	C17	1.434(3)	C28	C29	1.357(3)
C2	N3	1.381(2)	C28	N27	1.380(2)
C4	C5	1.419(3)	C29	C30	1.421(3)
C4	N3	1.329(2)	C30	C31	1.364(3)
C4	N9	1.395(2)	C31	C32	1.417(3)
C5	C6	1.362(3)	C32	N27	1.401(2)
C6	C7	1.424(3)	C32	N33	1.326(3)
C7	C8	1.354(3)	C34	C42	1.433(3)
C8	N9	1.380(2)	C34	N33	1.382(2)
C10	C11	1.518(3)	C35	C36	1.516(3)
C11	C12	1.393(3)	C36	C37	1.391(3)
C11	C16	1.392(3)	C36	C41	1.395(3)
C12	C13	1.390(3)	C37	C38	1.393(3)
C13	C14	1.382(3)	C38	C39	1.385(3)
C14	C15	1.389(3)	C39	C40	1.382(3)
C15	C16	1.392(3)	C40	C41	1.387(3)
C17	C18	1.195(3)	C42	C43	1.192(3)
C18	C19	1.465(3)	C43	C44	1.468(3)
C19	C20	1.521(3)	C44	C45	1.519(3)
C20	C21	1.397(3)	C45	C46	1.392(3)
C20	C25	1.387(3)	C45	C50	1.391(3)
C21	C22	1.388(3)	C46	C47	1.398(3)

Table S28 Bond Lengths for 230885lt_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C22	C23	1.387(3)	C47	C48	1.383(3)
C23	C24	1.381(3)	C48	C49	1.386(3)
C24	C25	1.393(3)	C49	C50	1.389(3)

Table S29 Bond Angles for 230885lt_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C10	131.71(17)	C34	C26	C35	132.19(17)
C2	C1	N9	104.52(16)	C34	C26	N27	104.64(16)
N9	C1	C10	123.76(17)	N27	C26	C35	123.15(17)
C1	C2	C17	124.60(17)	C29	C28	N27	118.47(19)
C1	C2	N3	112.67(16)	C28	C29	C30	120.7(2)
N3	C2	C17	122.71(18)	C31	C30	C29	120.75(19)
N3	C4	C5	130.68(19)	C30	C31	C32	119.4(2)
N3	C4	N9	111.44(16)	N27	C32	C31	117.89(18)
N9	C4	C5	117.88(17)	N33	C32	C31	130.91(19)
C6	C5	C4	119.2(2)	N33	C32	N27	111.21(16)
C5	C6	C7	120.98(19)	C26	C34	C42	125.40(18)
C8	C7	C6	120.35(19)	C26	C34	N33	112.23(16)
C7	C8	N9	118.71(19)	N33	C34	C42	122.38(18)
C1	C10	C11	113.75(16)	C26	C35	C36	112.85(16)
C12	C11	C10	119.90(18)	C37	C36	C35	120.73(18)
C16	C11	C10	120.90(18)	C37	C36	C41	119.02(18)
C16	C11	C12	119.18(18)	C41	C36	C35	120.25(17)
C13	C12	C11	120.5(2)	C36	C37	C38	120.3(2)
C14	C13	C12	120.1(2)	C39	C38	C37	119.9(2)
C13	C14	C15	119.86(19)	C40	C39	C38	120.19(19)
C14	C15	C16	120.2(2)	C39	C40	C41	119.9(2)
C11	C16	C15	120.2(2)	C40	C41	C36	120.6(2)
C18	C17	C2	176.7(2)	C43	C42	C34	179.0(2)
C17	C18	C19	178.0(2)	C42	C43	C44	176.3(2)
C18	C19	C20	114.86(17)	C43	C44	C45	114.63(17)
C21	C20	C19	118.25(17)	C46	C45	C44	119.73(18)
C25	C20	C19	123.08(17)	C50	C45	C44	121.36(17)
C25	C20	C21	118.66(18)	C50	C45	C46	118.86(18)
C22	C21	C20	120.71(19)	C45	C46	C47	120.4(2)
C23	C22	C21	120.03(19)	C48	C47	C46	119.90(19)
C24	C23	C22	119.7(2)	C47	C48	C49	120.1(2)
C23	C24	C25	120.3(2)	C48	C49	C50	119.9(2)

Table S29 Bond Angles for 230885lt_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C20	C25	C24	120.54(18)	C49	C50	C45	120.80(18)
C4	N3	C2	104.22(16)	C26	N27	C32	107.16(15)
C1	N9	C4	107.14(15)	C28	N27	C26	130.06(17)
C8	N9	C1	129.99(17)	C28	N27	C32	122.78(16)
C8	N9	C4	122.86(16)	C32	N33	C34	104.76(16)

Table S30 Torsion Angles for 230885lt_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	N3	C4	0.6(2)	C26	C34	N33	C32	-0.3(2)
C1	C10	C11	C12	118.78(19)	C26	C35	C36	C37	56.7(2)
C1	C10	C11	C16	-59.7(2)	C26	C35	C36	C41	−123.11(19)
C2	C1	C10	C11	107.2(2)	C28	C29	C30	C31	0.0(3)
C2	C1	N9	C4	0.0(2)	C29	C28	N27	C26	−178.97(19)
C2	C1	N9	C8	179.62(18)	C29	C28	N27	C32	1.1(3)
C4	C5	C6	C7	-0.2(3)	C29	C30	C31	C32	0.2(3)
C5	C4	N3	C2	179.7(2)	C30	C31	C32	N27	0.2(3)
C5	C4	N9	C1	−179.88(17)	C30	C31	C32	N33	180.0(2)
C5	C4	N9	C8	0.4(3)	C31	C32	N27	C26	179.17(17)
C5	C6	C7	C8	-0.2(3)	C31	C32	N27	C28	-0.9(3)
C6	C7	C8	N9	0.7(3)	C31	C32	N33	C34	-179.2(2)
C7	C8	N9	C1	179.53(19)	C34	C26	C35	C36	-111.0(2)
C7	C8	N9	C4	-0.9(3)	C34	C26	N27	C28	−179.52(18)
C10	C1	C2	C17	-1.0(3)	C34	C26	N27	C32	0.44(19)
C10	C1	C2	N3	−179.34(18)	C35	C26	C34	C42	-1.5(3)
C10	C1	N9	C4	179.07(16)	C35	C26	C34	N33	178.17(18)
C10	C1	N9	C8	-1.3(3)	C35	C26	N27	C28	2.0(3)
C10	C11	C12	C13	−177.67(17)	C35	C26	N27	C32	−178.05(17)
C10	C11	C16	C15	177.21(18)	C35	C36	C37	C38	179.64(17)
C11	C12	C13	C14	0.1(3)	C35	C36	C41	C40	179.48(18)
C12	C11	C16	C15	-1.2(3)	C36	C37	C38	C39	0.7(3)
C12	C13	C14	C15	-0.6(3)	C37	C36	C41	C40	-0.3(3)
C13	C14	C15	C16	0.1(3)	C37	C38	C39	C40	0.1(3)
C14	C15	C16	C11	0.8(3)	C38	C39	C40	C41	-1.0(3)

Table S30 Torsion Angles for 230885lt_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C16	C11	C12	C13	0.8(3)	C39	C40	C41	C36	1.1(3)
C17	C2	N3	C4	−177.83(18)	C41	C36	C37	C38	−0.6(3)
C18	C19	C20	C21	172.92(19)	C42	C34	N33	C32	179.44(17)
C18	C19	C20	C25	−7.6(3)	C43	C44	C45	C46	136.6(2)
C19	C20	C21	C22	−179.34(19)	C43	C44	C45	C50	−46.1(3)
C19	C20	C25	C24	−179.83(19)	C44	C45	C46	C47	177.59(19)
C20	C21	C22	C23	−0.9(3)	C44	C45	C50	C49	−176.64(18)
C21	C20	C25	C24	−0.4(3)	C45	C46	C47	C48	−0.7(3)
C21	C22	C23	C24	−0.3(3)	C46	C45	C50	C49	0.7(3)
C22	C23	C24	C25	1.1(3)	C46	C47	C48	C49	0.2(3)
C23	C24	C25	C20	−0.8(3)	C47	C48	C49	C50	0.6(3)
C25	C20	C21	C22	1.2(3)	C48	C49	C50	C45	−1.1(3)
N3	C4	C5	C6	179.8(2)	C50	C45	C46	C47	0.2(3)
N3	C4	N9	C1	0.4(2)	N27	C26	C34	C42	−179.81(17)
N3	C4	N9	C8	−179.28(17)	N27	C26	C34	N33	−0.1(2)
N9	C1	C2	C17	178.03(17)	N27	C26	C35	C36	67.0(2)
N9	C1	C2	N3	−0.3(2)	N27	C28	C29	C30	−0.6(3)
N9	C1	C10	C11	−71.6(2)	N27	C32	N33	C34	0.5(2)
N9	C4	C5	C6	0.1(3)	N33	C32	N27	C26	−0.6(2)
N9	C4	N3	C2	−0.6(2)	N33	C32	N27	C28	179.33(17)

Table S31 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230885lt_auto.

Atom	*x*	*y*	*z*	U(eq)
H5	7403.66	4889.24	7588.77	31
H6	6532.9	6231.66	8004.29	35
H7	5499.78	7972.68	7797.3	33
H8	5368.79	8359.77	7174.01	28
H10A	6093.44	7731.79	6146.5	23
H10B	6244.2	8524.51	6499.35	23
H12	3826.7	9548.79	6628.24	28
H13	902.78	9773.04	6653.31	34
H14	−871.09	8348.54	6449.83	37
H15	281.87	6702.79	6211.99	37

Table S31 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230885lt_auto.

Atom	*x*	*y*	*z*	U(eq)
H16	3210.95	6482.29	6178.84	29
H19A	6738.07	4080.75	5440.44	35
H19B	8520.66	4685.02	5393.04	35
H21	7340.11	4709.06	4732.64	31
H22	6236.8	5897.17	4284.05	38
H23	4743.87	7495.03	4458.53	38
H24	4345.03	7888.48	5081.73	35
H25	5502.03	6724.65	5532.27	29
H28	9476.44	3325.51	7157.47	28
H29	9566.94	2910.7	7779.77	34
H30	8600.2	1168.88	7998.04	35
H31	7553.62	-152.04	7593.56	32
H35A	8348.37	3509.55	6490.74	24
H35B	8504.66	2709.68	6139.37	24
H37	11394.07	1423.71	6213.11	29
H38	14320.8	1686.1	6211.25	35
H39	15460.85	3386.85	6401.53	39
H40	13691.51	4823.92	6596.5	34
H41	10771.35	4584.39	6584.52	28
H44A	5297.71	-648.12	5525.34	34
H44B	7239.09	-842.1	5426.14	34
H46	7508.25	-313.28	4807.88	35
H47	7248.14	992.97	4329.77	39
H48	5829.39	2670.15	4432.37	37
H49	4682.27	3053.16	5011.79	34
H50	5002.48	1774.6	5492.08	30

Experimental

Single crystals of $C_{46}H_{36}N_4$ **[230885lt_auto]** were **[]**. A suitable crystal was selected and **[]** on a **XtaLAB Synergy R, DW system, HyPix-Arc 150** diffractometer. The crystal was kept at 99.8(5) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [230885lt_auto]

Crystal Data for $C_{46}H_{36}N_4$ (M =644.79 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.92700(10) Å, b = 11.98670(10) Å, c = 36.2753(4) Å, V = 3446.83(6) Å^3, Z = 4, T = 99.8(5) K, μ(Cu Kα) = 0.563 mm^{-1}, $Dcalc$ = 1.243 g/cm^3, 21562 reflections measured (4.872° ≤ 2Θ ≤ 149.538°), 6582 unique (R_{int} = 0.0303, R_{sigma} = 0.0311) which were used in all calculations. The final R_1 was 0.0330 (I > 2σ(I)) and wR_2 was 0.0830 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Twinned data refinement
 Scales: 1.0(5)
 -0.0(5)
2. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
3.a Secondary CH2 refined with riding coordinates:
 C10(H10A,H10B), C19(H19A,H19B), C35(H35A,H35B), C44(H44A,H44B)
3.b Aromatic/amide H refined with riding coordinates:
 C5(H5), C6(H6), C7(H7), C8(H8), C12(H12), C13(H13), C14(H14), C15(H15),
 C16(H16), C21(H21), C22(H22), C23(H23), C24(H24), C25(H25), C28(H28), C29(H29),
  C30(H30), C31(H31), C37(H37), C38(H38), C39(H39), C40(H40), C41(H41),
 C46(H46), C47(H47), C48(H48), C49(H49), C50(H50)
```