**Supporting Information**

# One-pot Synthesis of Imidazoles from Aromatic Nitriles with Nickel Catalysts.

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**Experimental Section.**

Unless otherwise noted, all manipulations were performed using standard Schlenk and glovebox techniques under high purity argon (Praxair, 99.998 %) using an MBraun glovebox (< 1 ppm, $H_2O$ and $O_2$). Stainless steel autoclaves (T316SS) Parr Series 4590, 4561M, Bench Top Mini Reactors (100, 300 mL) and 4750 Parr vessels (125 mL) were used for catalysis experiments. **BN** was purchased from Aldrich in reagent grade and was degassed using the freeze-pump-thaw method prior to its use. *p*-substituted benzo-nitriles ($R_p$-$C_6H_4$-CN; $R_p$ = -Me, -MeO, -F) and 4-cyanopyridine were purchased from Aldrich and used without further purification. THF and *n*-hexanes (J.T. Baker) were dried and distilled from dark purple solutions of sodium/benzophenone ketyl. EtOH (Aldrich) was dried and distilled from the corresponding Grignard reagent. Deuterated solvents were dried and distilled before use from sodium/benzophenone ketyl. NMR spectra of complexes and products in this work were recorded at ambient temperature either using 300 MHz Varian Unity or 400 MHz Varian INOVA spectrometers. $^{1}H$, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of nickel(0) complexes were obtained at room temperature from concentrated THF–$d_8$ and benzene–$d_6$ solutions (100 mg) of the pure compounds under inert atmosphere, using thin wall (0.38 mm) WILMAD NMR tubes equipped with J Young valves. The $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of purified hydrogenation products were obtained from concentrated $CDCl_3$ or DMSO–$d_6$ solutions. $^{1}H$ and $^{13}C\{^{1}H\}$ chemical shifts ($\delta$, ppm) are reported relative to the corresponding residual proton or deuterium resonances in the deuterated solvent and $^{31}P\{^{1}H\}$ NMR spectra are reported relative to external 85% $H_3PO_4$. Commercially available standards for the produced imidazoles were purchased from Aldrich. Elemental analyses and mass spectra (MS-$EI^{+}$) of the purified organics were carried out by USAI-UNAM using a Perkin Elmer microanalyzer 2400 and a Jeol SX-102A mass spectrometer, respectively. GC-MS determinations were performed using an Agilent GC-MS 5975C equipped with a 30m DB-5MS capillary (0.32 mm ID) column.

Infrared spectra of pure organics were obtained using a Perkin-Elmer 1600 FT spectrophotometer. The syntheses of [(dippe)$NiCl_2$][1] and [(dippe)NiH]$_2$[2] were carried out following the reported procedures.

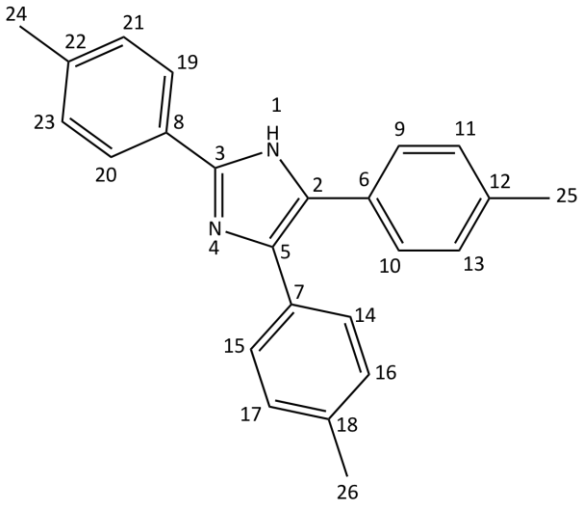
**Typical procedure for the cyclization of BN and related aromatic nitriles.**

Reactions were performed in a stainless steel mini-reactor Parr charged in the glovebox. A typical experiment is described as follows: [Ni(dippe)H]$_2$ (0.66g, 1.024 mmol) was mixed with **BN** (20 mL, 205.6 mmol) in the reactor vessel, a color change to yellow-brown was immediately observed. The reactor vessel was closed, taken out from the glovebox and then purged in a well vented fume-hood with $H_2$. The autoclave was then pressurized with $H_2$ to the corresponding pressure (as indicated in Table 1 and 2) and heated to the desired temperature under constant stirring. After 48h, heating was stopped and the reactor was allowed to cool down to room temperature at which temperature the remaining $H_2$ was released to the fume hood. The vessel was opened to air and an aliquot of the reaction mixture was immediately injected into the GC-MS. A second aliquot of the same mixture was also analyzed by $^1$H and $^{13}$C{$^1$H} NMR. All experiments were run by triplicate and the average of the product ratios obtained for each run then reported. Internal standards were used to calculate yields by GC-MS and $^1$H NMR.

For full analytical and spectroscopic details for all isolated imidazoles *vide infra*.

*Mercury drop experiment.* Homogeneity tests were performed by triplicate following the above described procedure for **TPI** while, in addition to the reactants, also adding two drops of elemental mercury to the mixture. After reaction completion, the solution was filtered and analyzed by GC-MS and $^1$H-NMR. No significant difference in conversion between these experiments and those in the absence of mercury were observed between runs and therefore suggest that no heterogeneous Nickel(0) is involved in the processes. Mercury was always visible immersed in the corresponding solution at the end of every experiment.

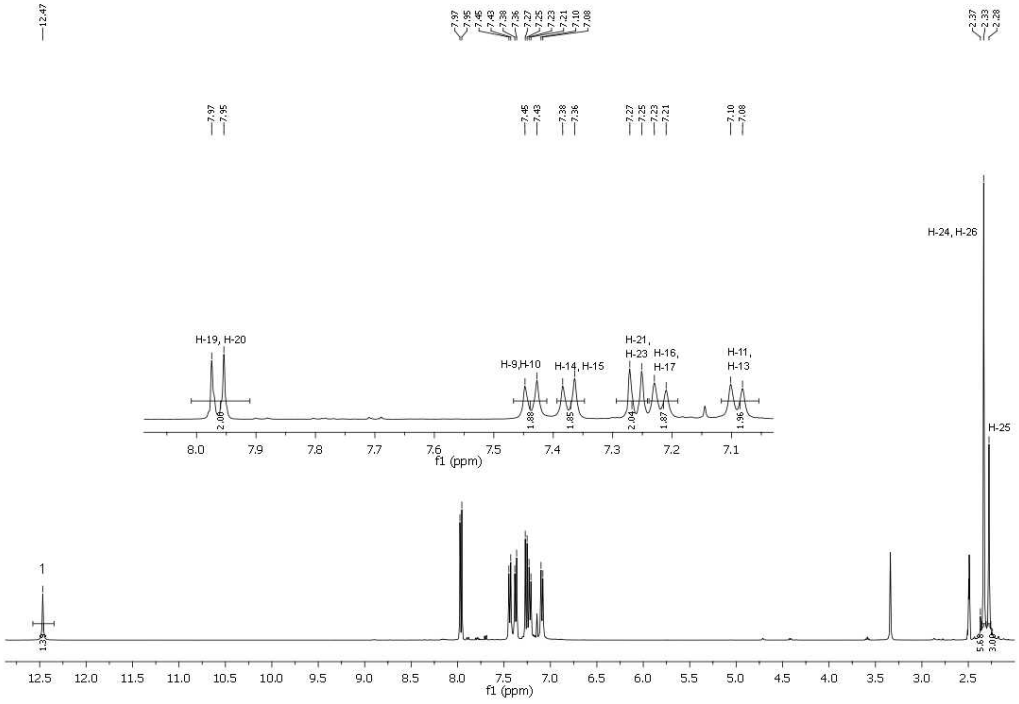
**2,4,5-tri-*p*-methylphenylimidazole.**



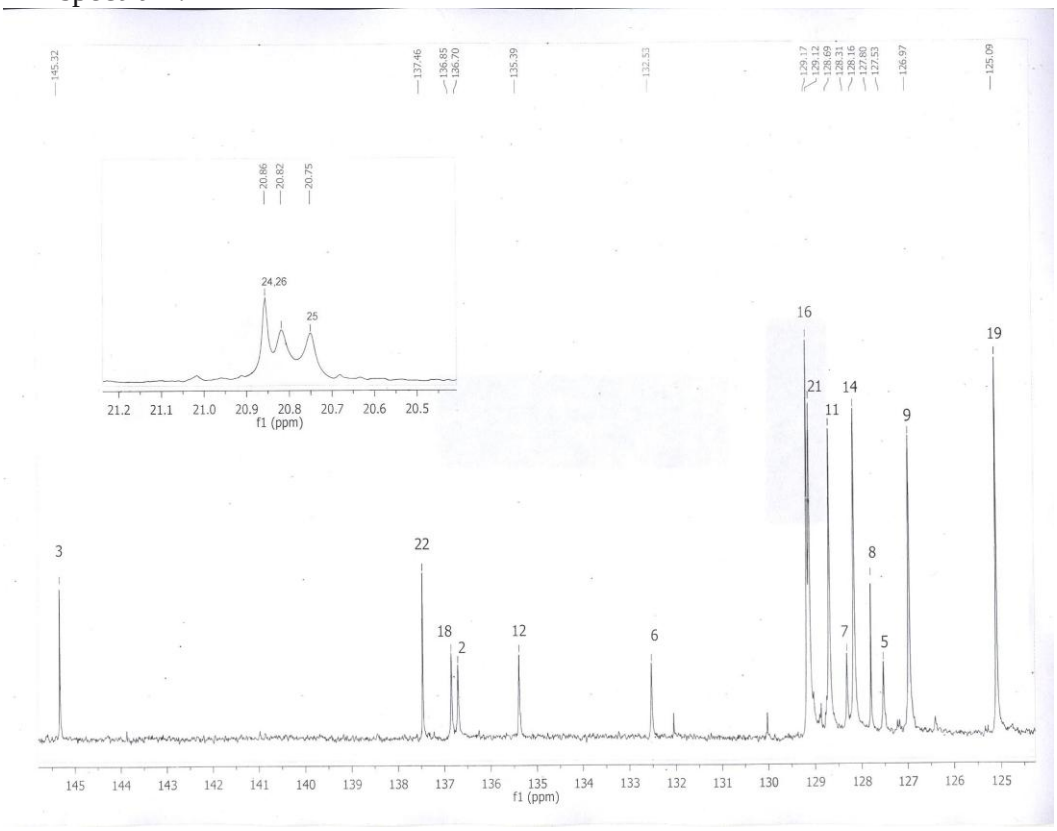

Purification by recrystallization solvent pair (THF/Hexane) as a pale yellow solid.
$^{1}$H NMR (400 MHz, DMSO-$d_6$): 12.47 (s, 1H, H-1), 7.97 (d, *J=8* Hz, 2H, H-19 y H-20), 7.45 (d, *J=8* Hz, 2H, H-9 y H-10), 7.38 (d, *J=8* Hz, 2H, H-14 y H-15), 7.27 (d, *J*= 8 Hz, 2H, H-21 y H-23), 7.23 (d, *J=8* Hz, 2H, H-16 y H-17), 7.10 (d, *J=8* Hz, 2H, H-11 y H-13), 2.33 (s, 6H, H-24 y H-26), 2.28 (s, 3H, H-25). $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$): 145.32 (C-3), 137.46 (C-22), 136.85 (C-18), 136.70 (C-2), 135.39 (C-12), 132.53 (C-6), 129.17 (C-16, C-17), 129.12 (C-21 y C-23), 128.69 (C-11 y C-13), 128.35 (C-7), 128.16 (C-14 y C-15), 127.80 (C-8), 127.53 (C-5), 126.97 (C-9 y C-10), 125.09 (C-19 y C-20), 20.86 (C-24), 20.82 (C-26), 20.75 (C-25)

Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.30; H, 6.705; N, 8.21.

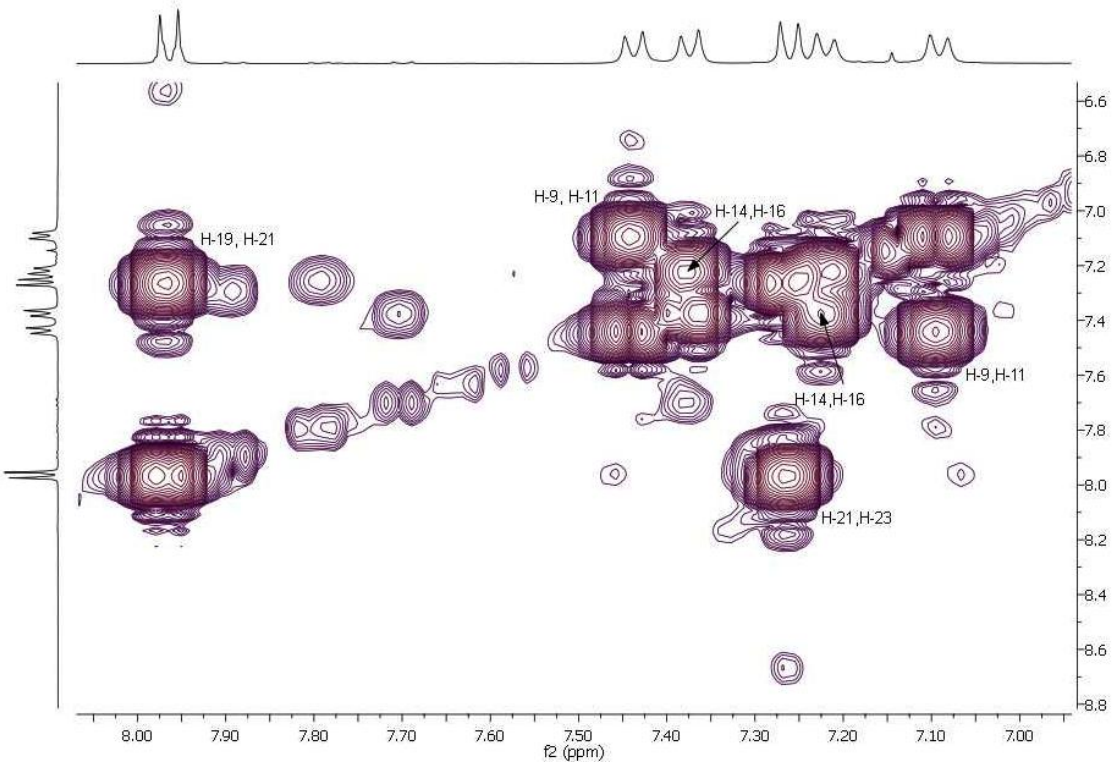
$^{1}$H-NMR spectrum.



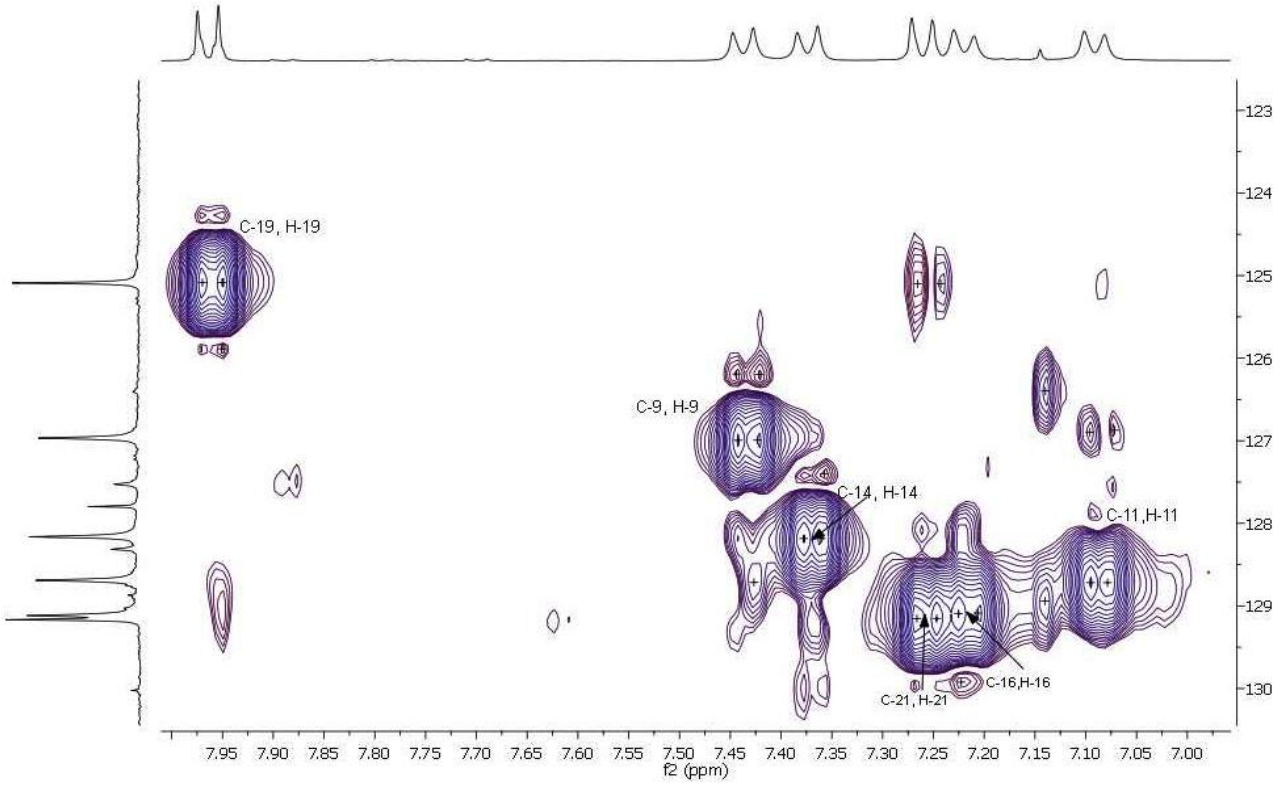
$^{13}C\{^{1}H\}$ NMR spectrum.



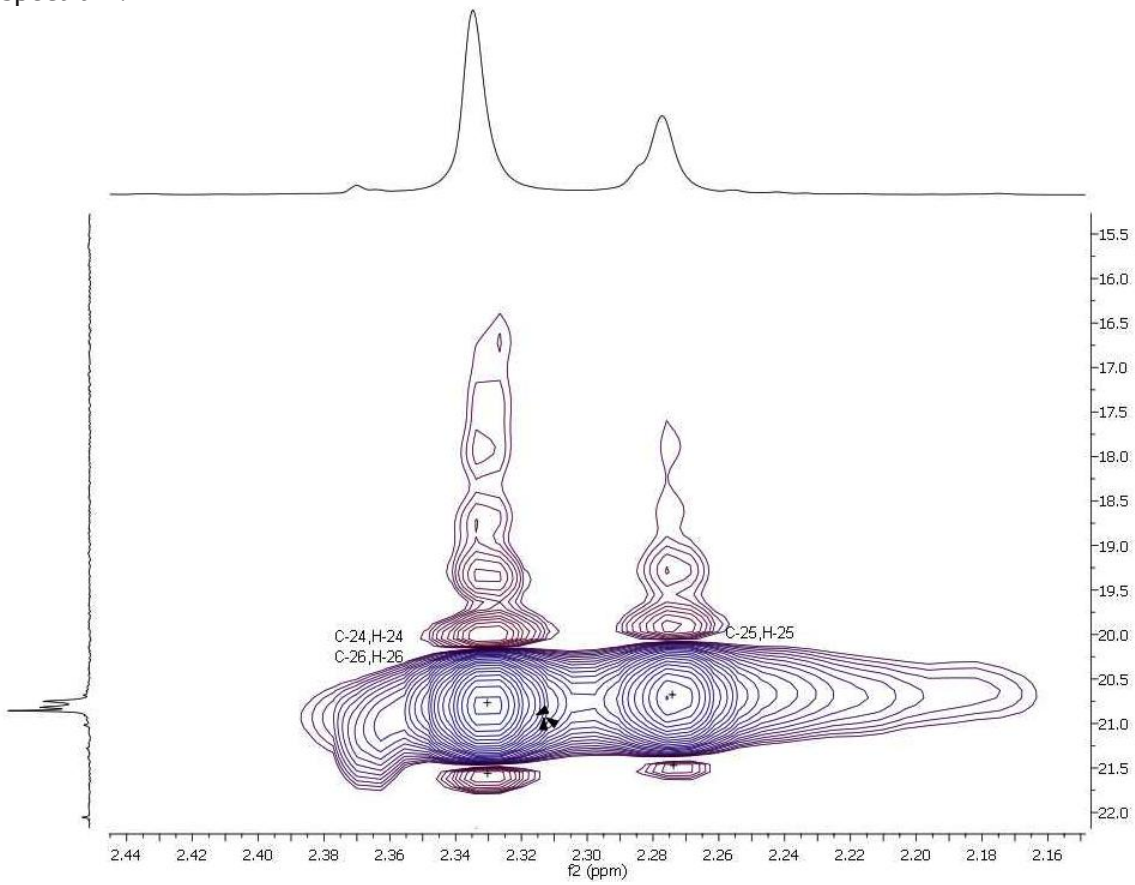

COSY spectrum.



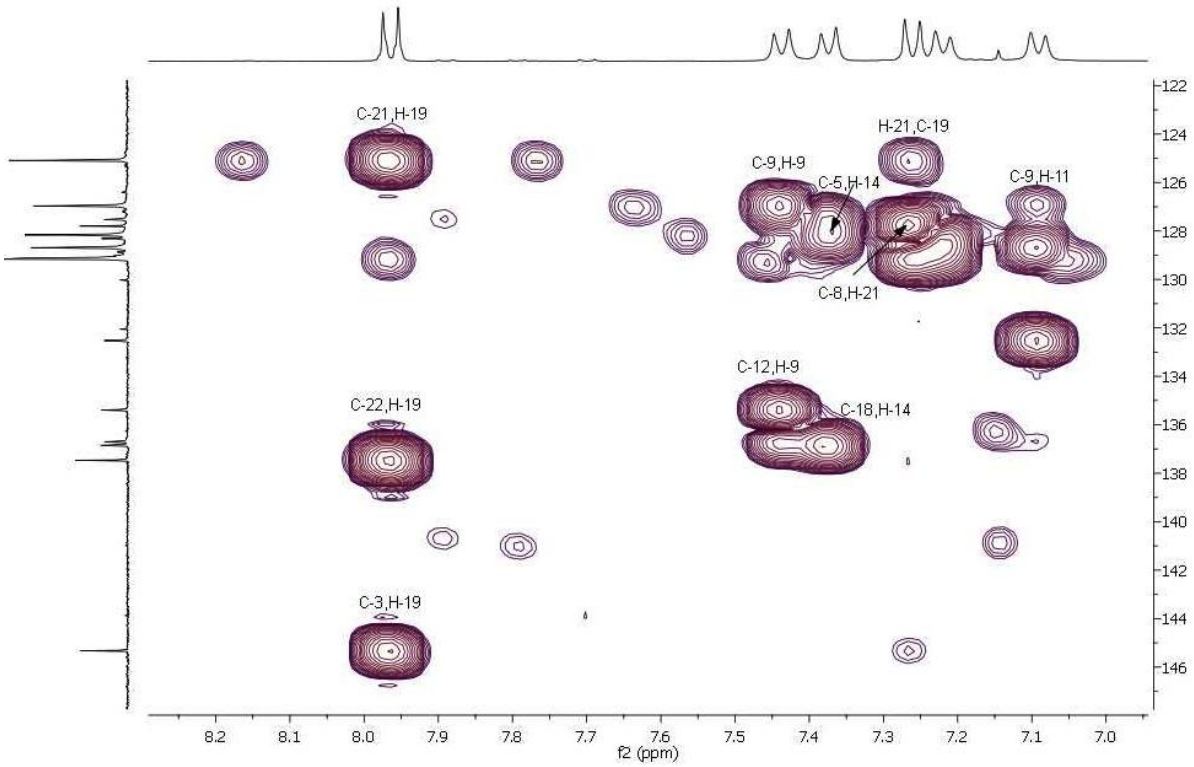
HSQC-1 spectrum.



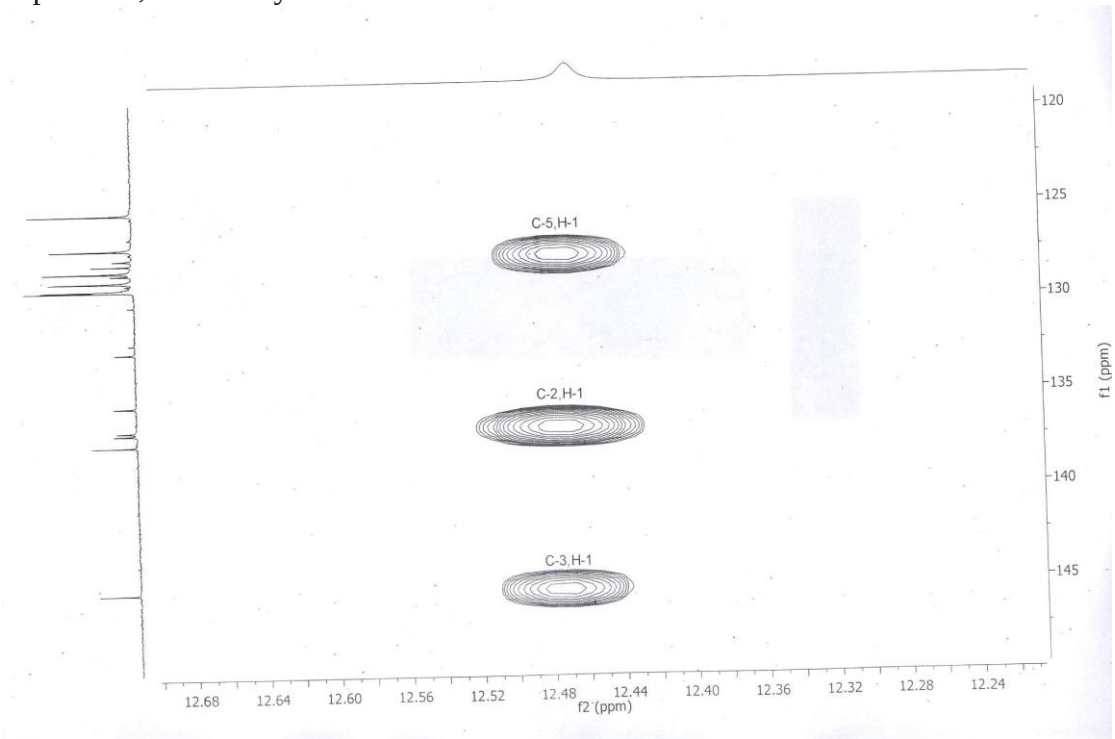

HSQC-2 spectrum.



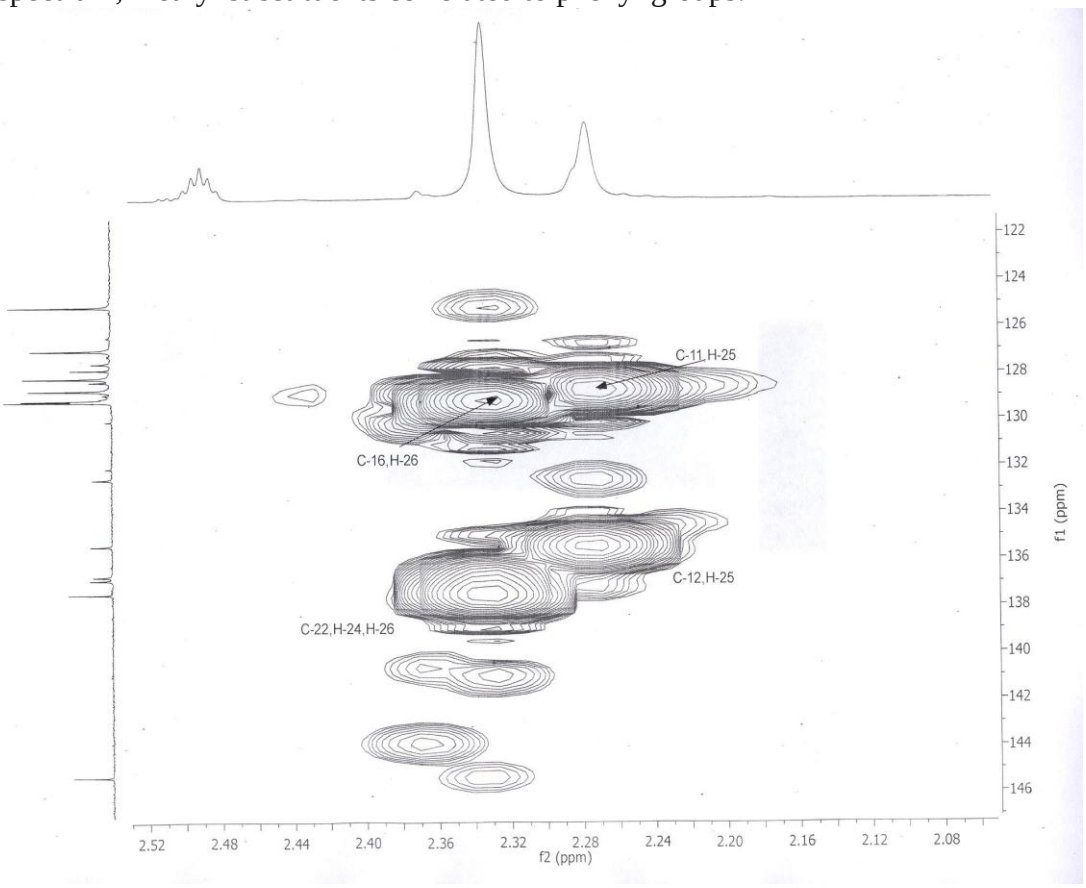
HMBC-1 spectrum, aromatic region.



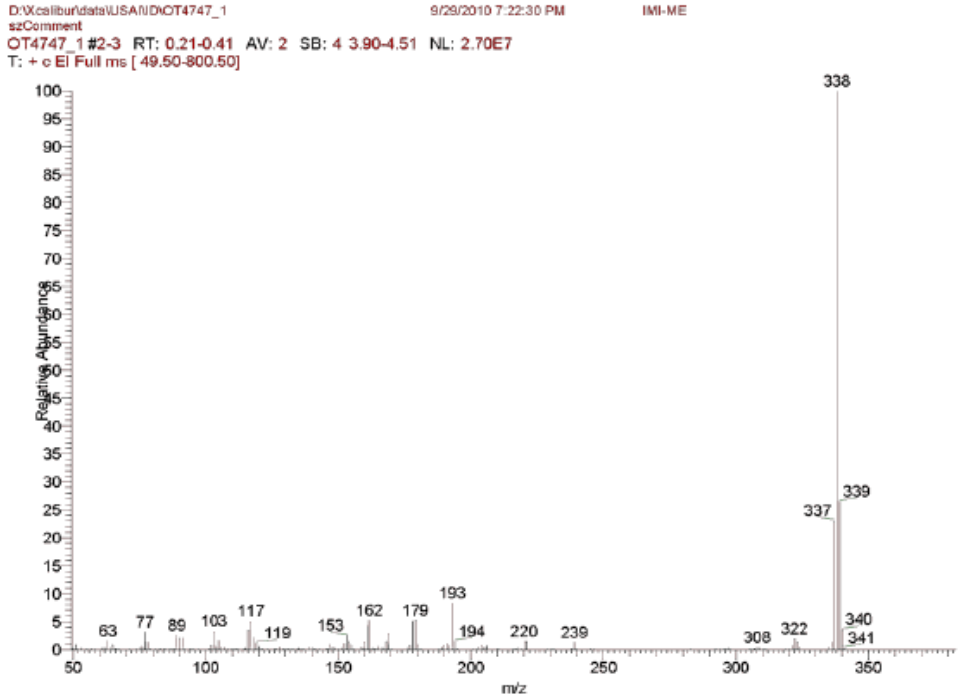

HMBC-2 spectrum, cuaternary carbons correlated to NH.



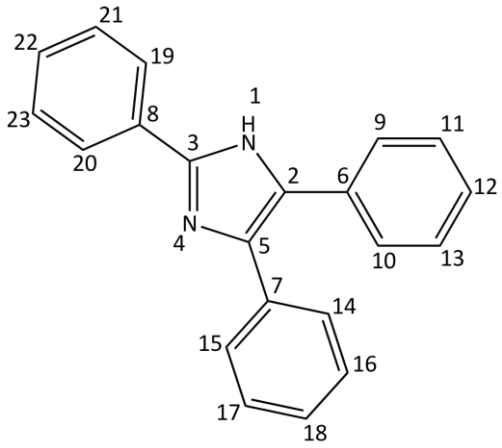
HMBC-2 spectrum, methyl substituents correlated to phenyl groups.




Mass spectrum.



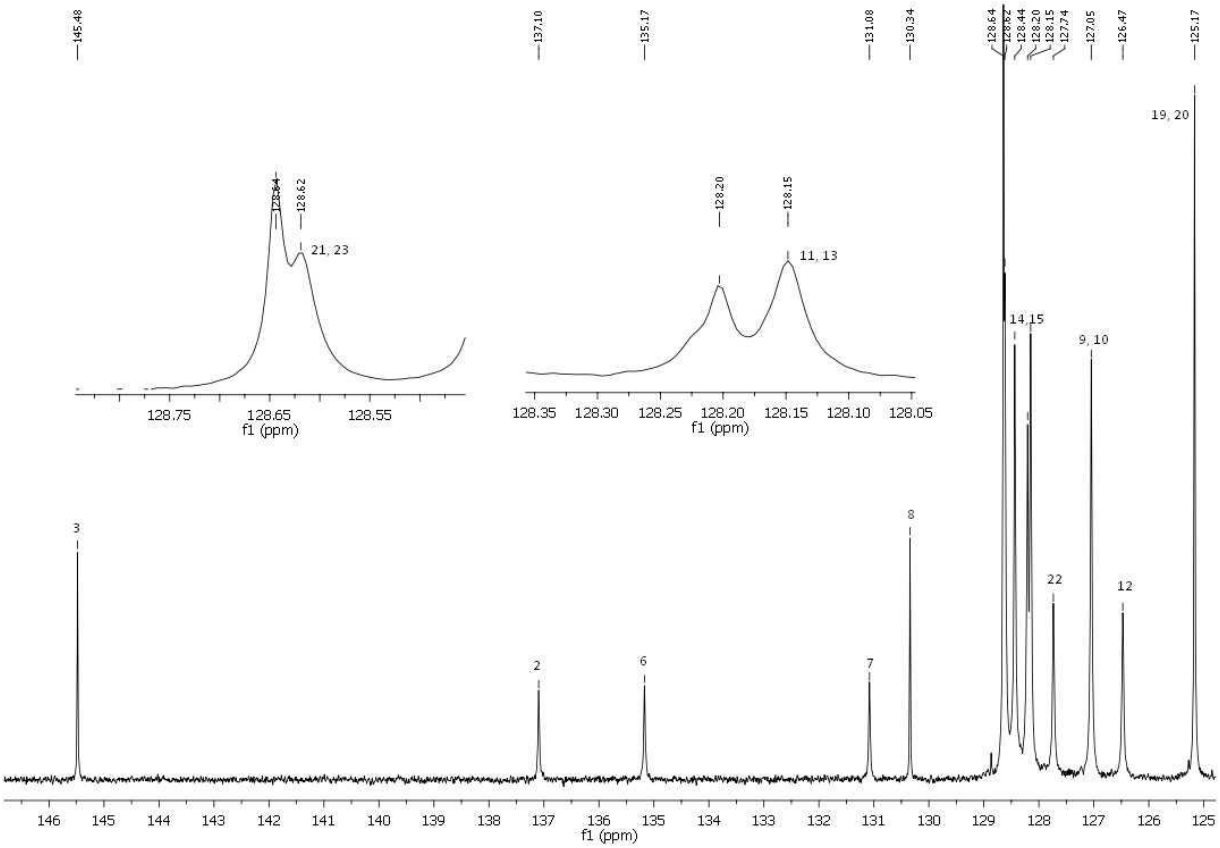
# TPI



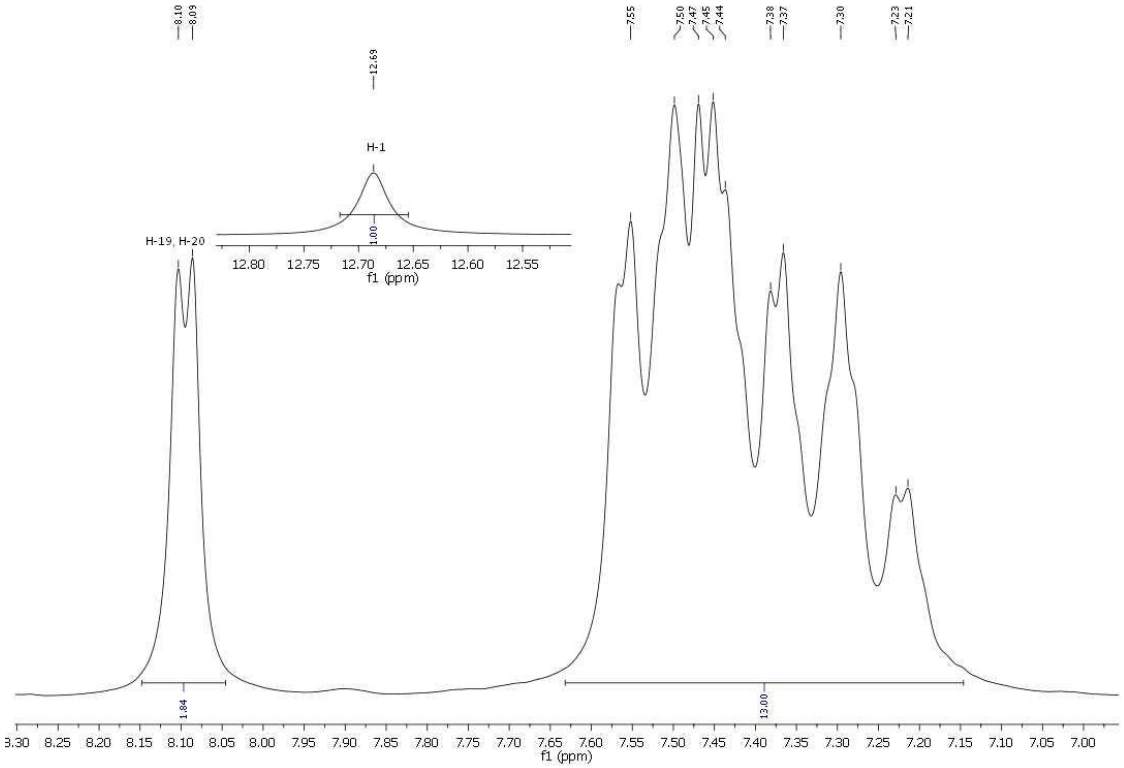

Purification by re-crystallization by solvent pair (THF/Hexane) as a colorless solid.
$^{1}$H NMR (400 MHZ, DMSO-$d_6$): 12.69 (s, 1H, H-1), 8.10 (d, 2H, H-19 y H-20), 7.55-7.21 (m, 13H, H-aromatic). $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-d6): 145.48 (C-3), 137.10 (C-2), 135.17 (C-6), 130.32 (C-8 y C-5), 131.08 (C-7), 128.64 (C-16 y C-17), 128.62 (C-21 y C-23), 128.44 (C-14 y C-15), 128.20 (C-18), 128.15 (C-11 y C-13), 127.74 (22), 127.05 (C-9 y C-10), 126.47 (C-12), 125.17 (C-19 y C-20)

Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.30; H, 6.70; N, 8.12.

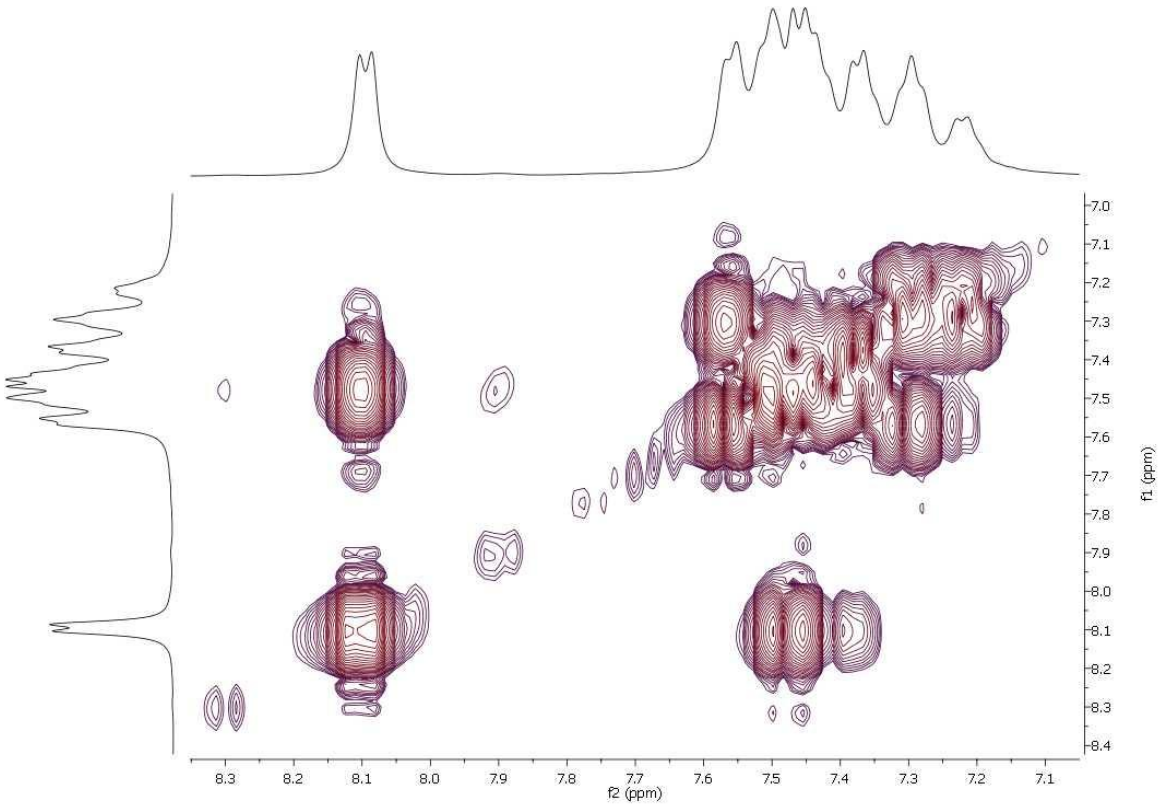
$^{13}C\{^{1}H\}$ NMR spectrum.



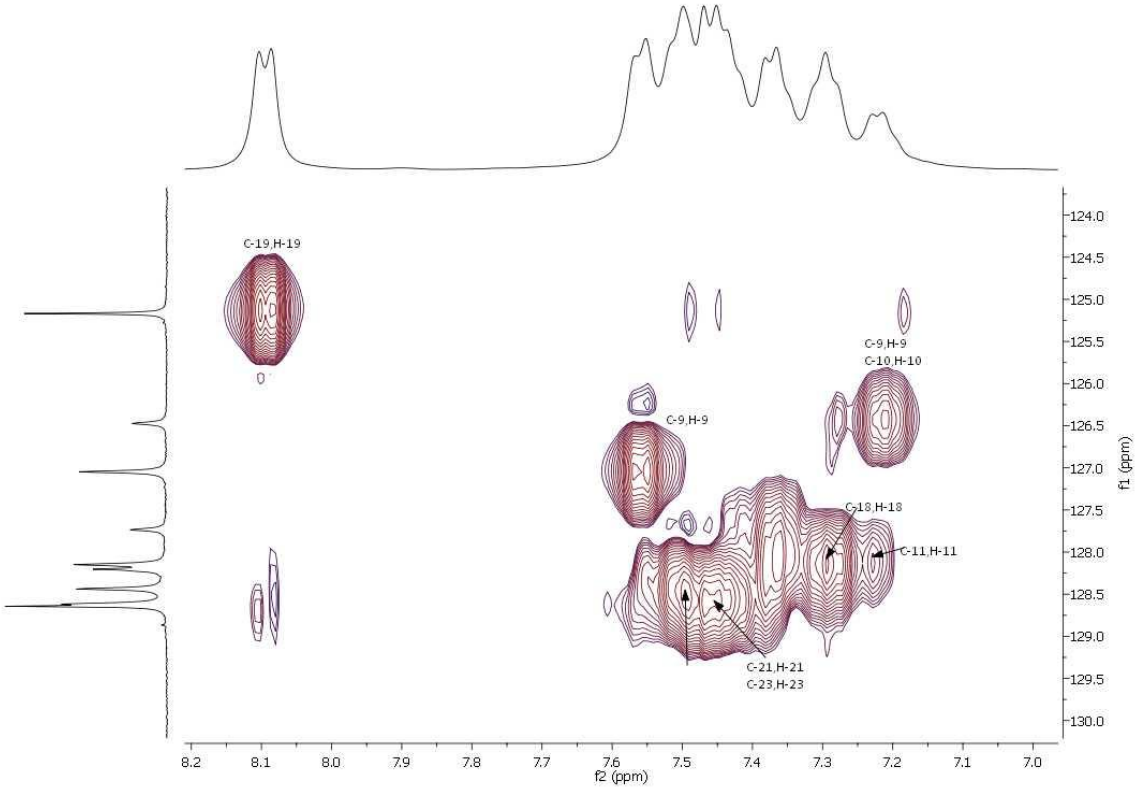

$^{1}H$ NMR spectrum.



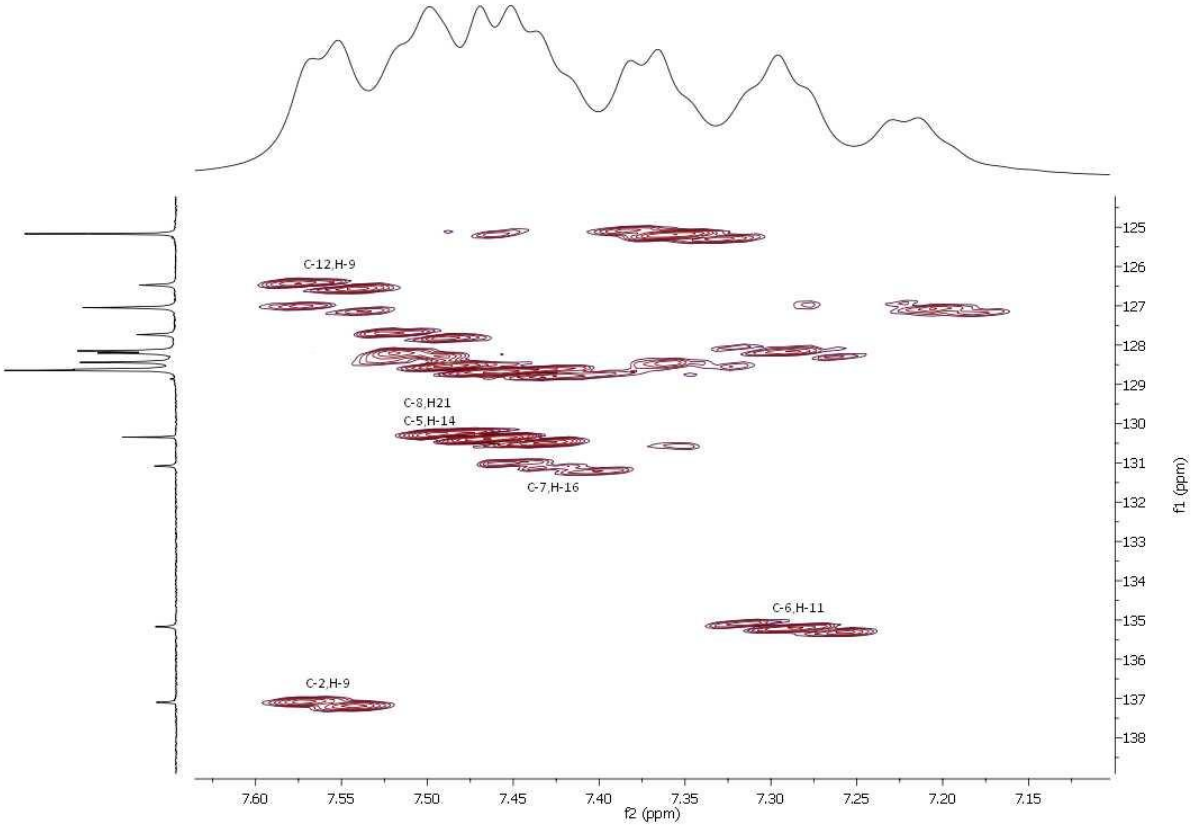
COSY spectrum.



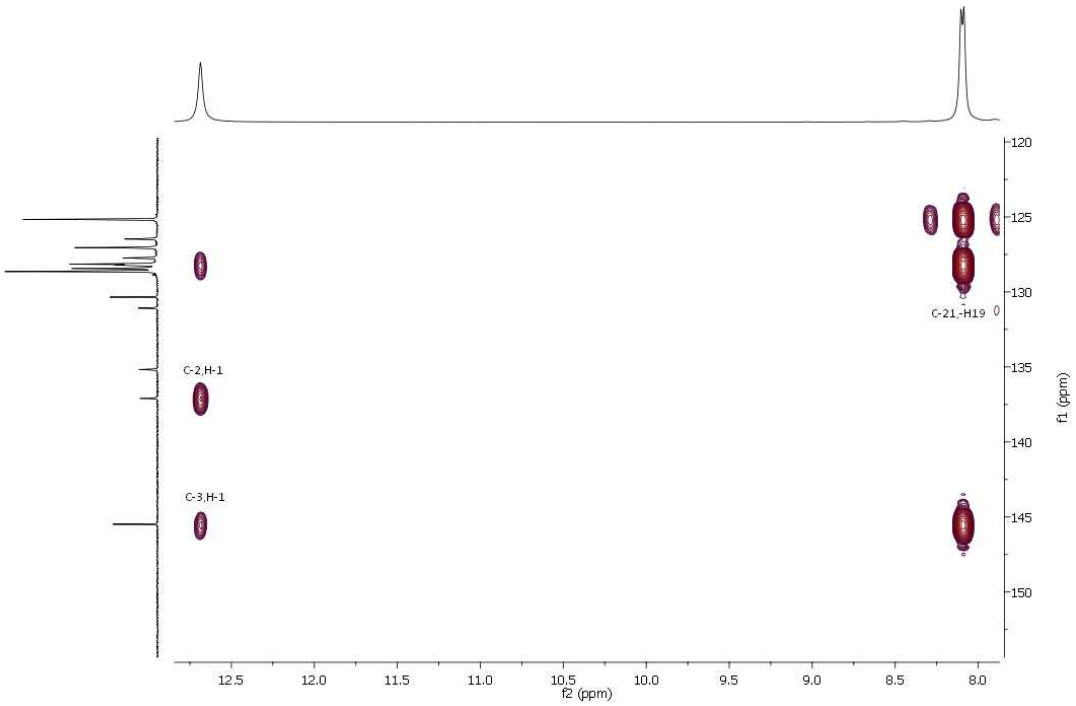

HSQC spectrum.



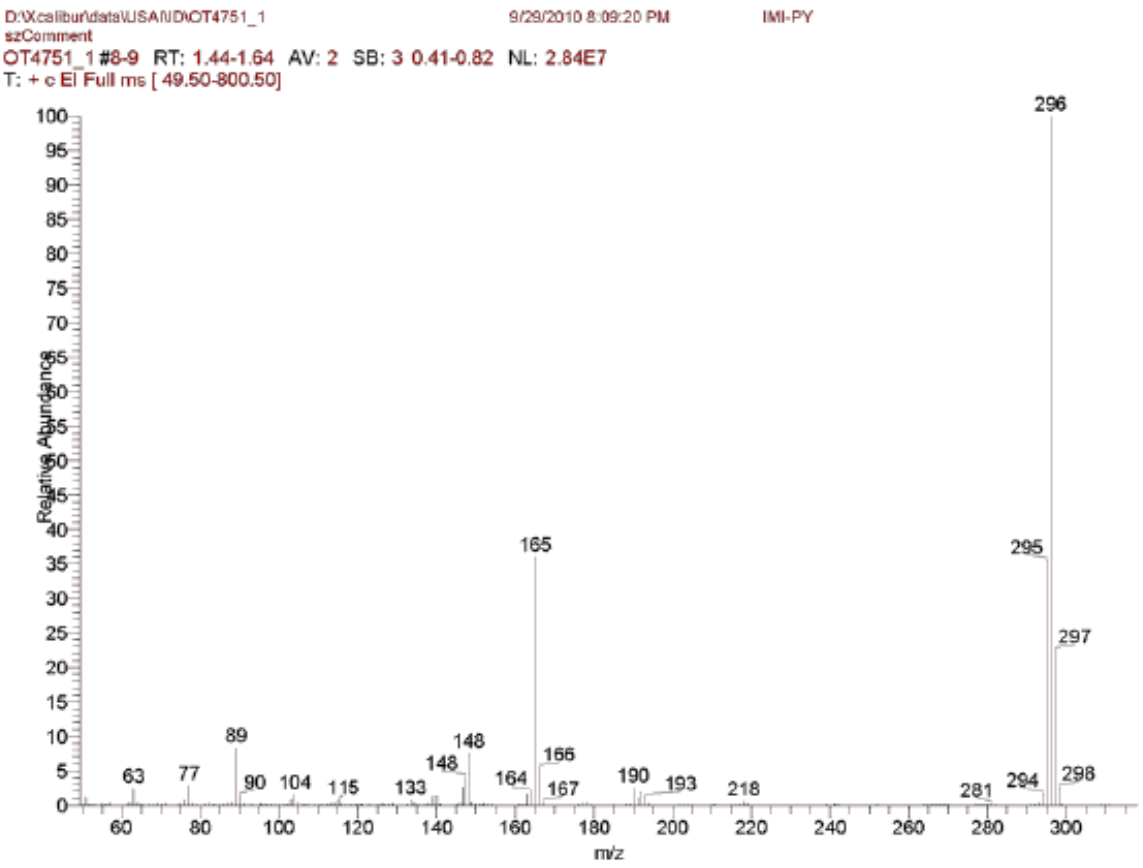
HMBC-1 spectrum.



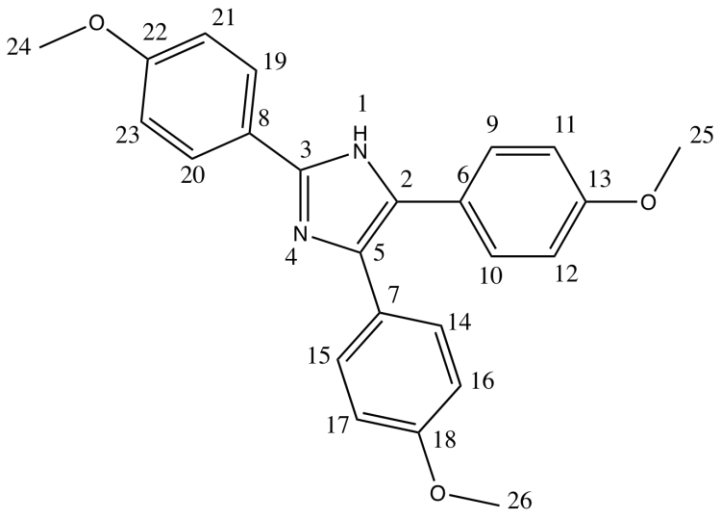

HMBC-2 spectrum.



Mass spectrum.



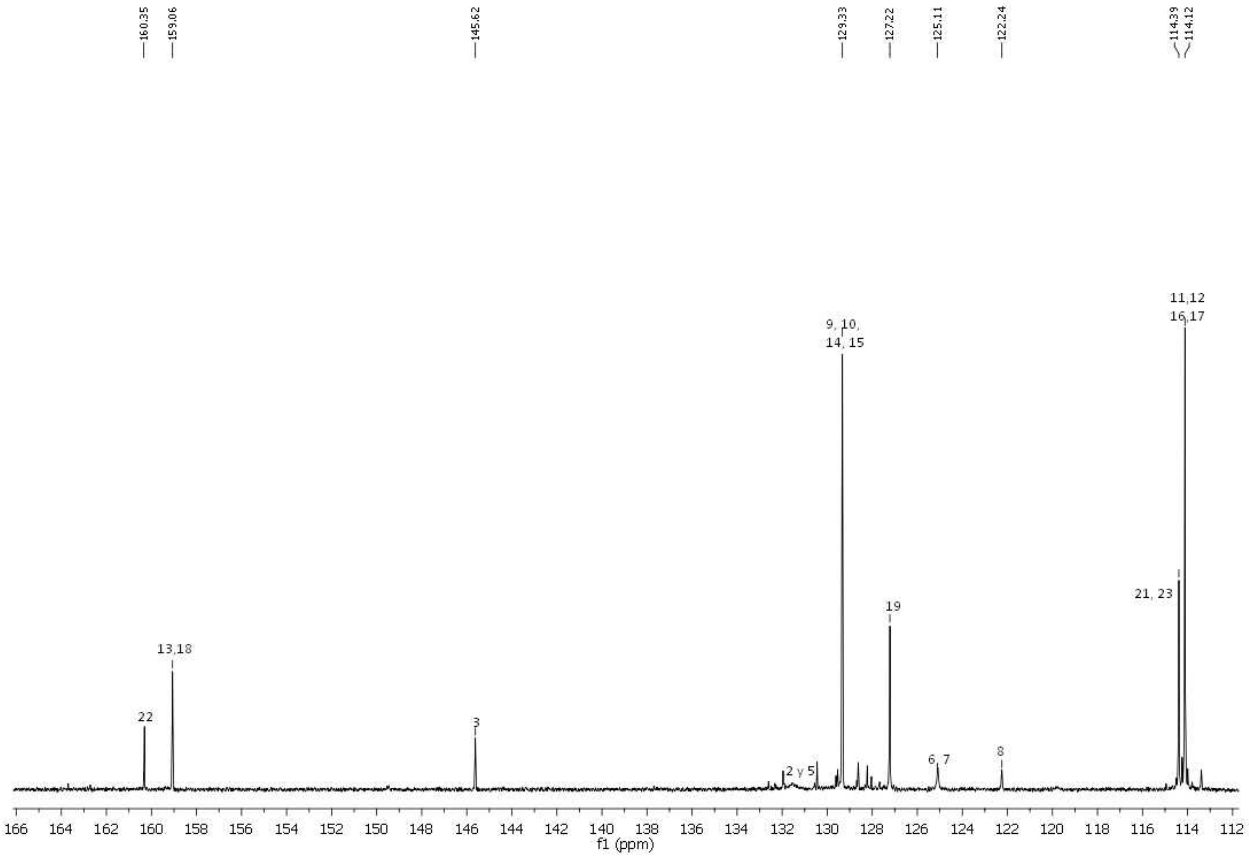
**2,4,5-tri-*p*-methoxyphenylimidazole.**

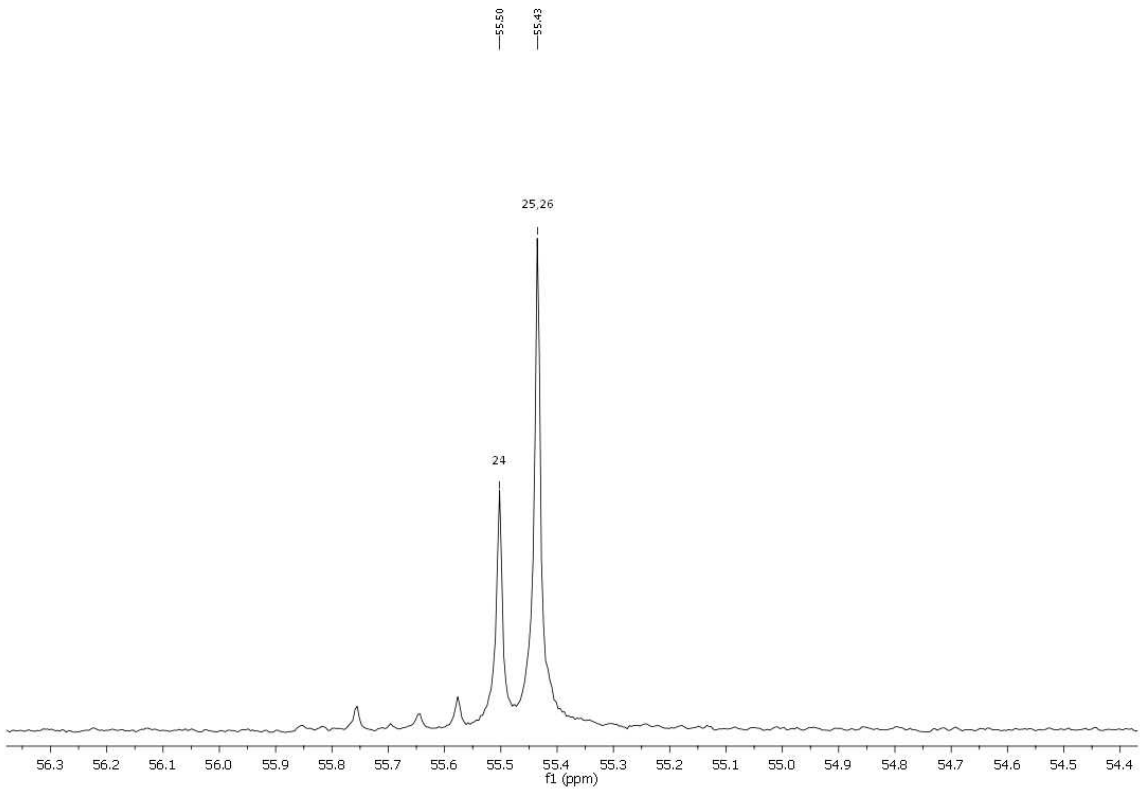



Purification by chromatographic column eluting with THF/hexane (1:1) and recrystallization THF/hexane to yield a pale yellow solid.
$^{1}$H NMR (400 MHz, $CDCl_3$) 7.82 (d, 2H, *J=8 Hz*, H-19 y H-20), 7.39 (d, 4H, *J=8 Hz*, H-9, H-10, H-14 y H-15) 6.86 (d, 2H, *J=8 Hz*, H-21 y H-23), 6.80 (d, 4H, *J=8 Hz*, H-11, H-12, H-16 y H-17), 3.77 (s, 9H, H-24, H-25 y H-26). $^{13}$C{$^{1}$H} NMR( 100 MHz, $CDCl_3$): 160.35 (C-22), 159.06 (C-13 y C-18), 145.62 (C-3), 131.58 (C-2 y C-5), 129.33 (C-9,C-10, C-14 y C-15), 127.22 (C-19 y C-20), 125.11 (C-6 y C-7), 122.24 (C-8), 114.39 (C-21 y C-23), 114.12 (C-11, C-12, C-16 y C-17), 55.50 (C-24), 55.48 (C-25 y C-26)

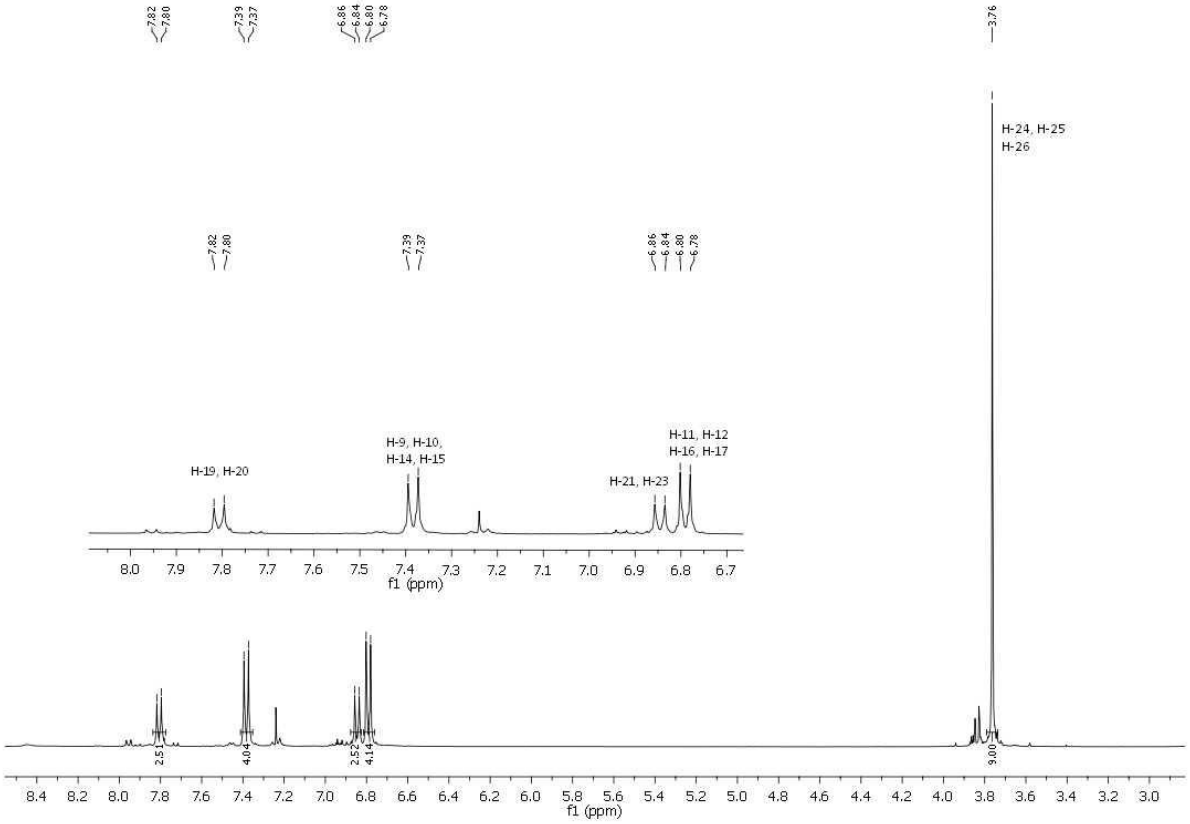
Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.27; H, 5.60; N, 7.21.

$^{13}C\{^{1}H\}$ spectra.

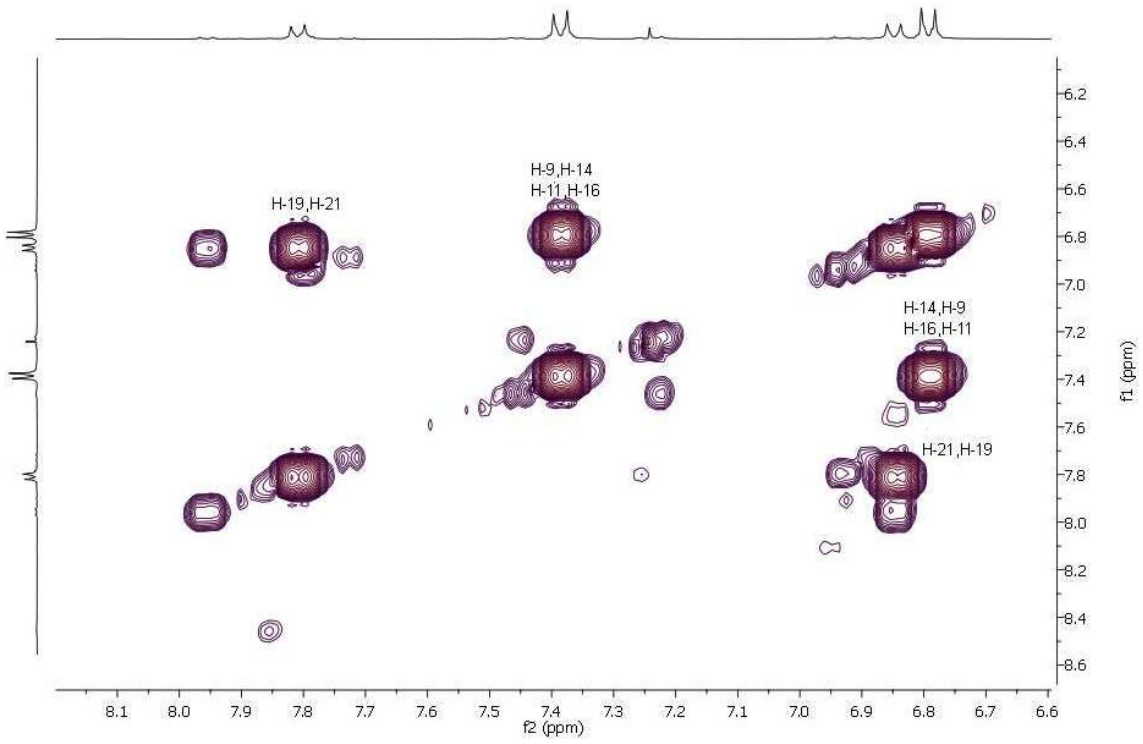


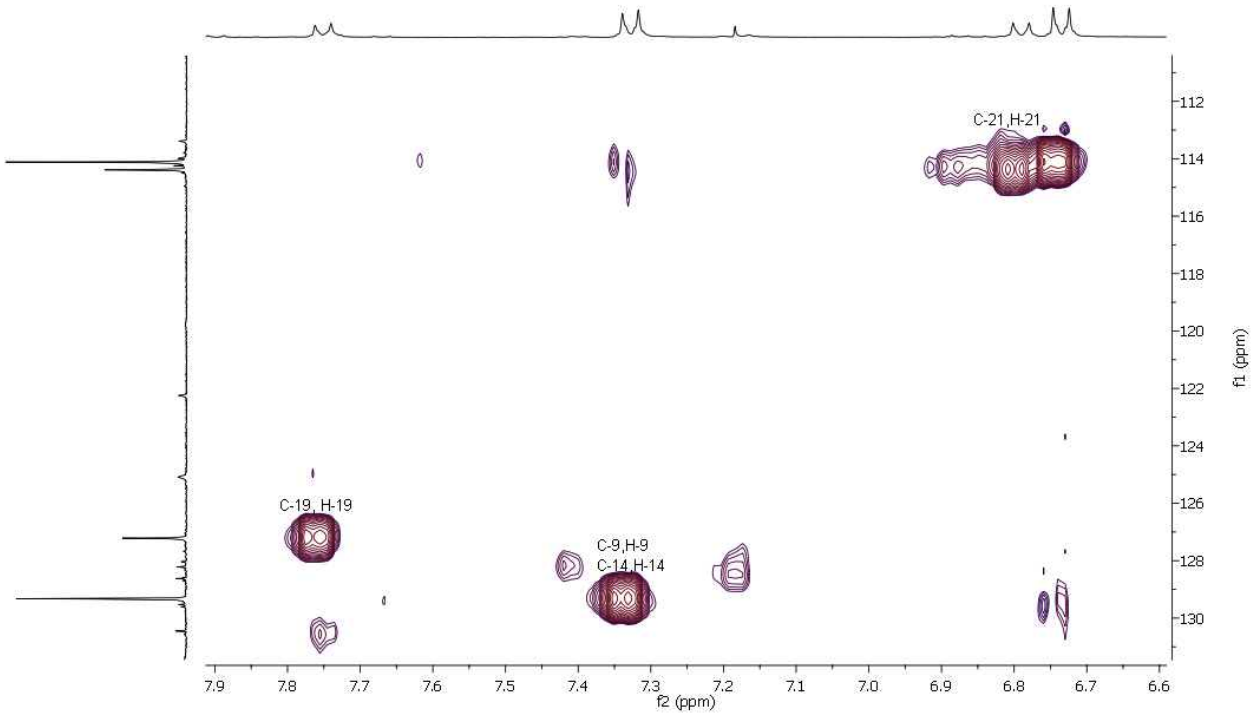
$^1$H NMR spectrum.



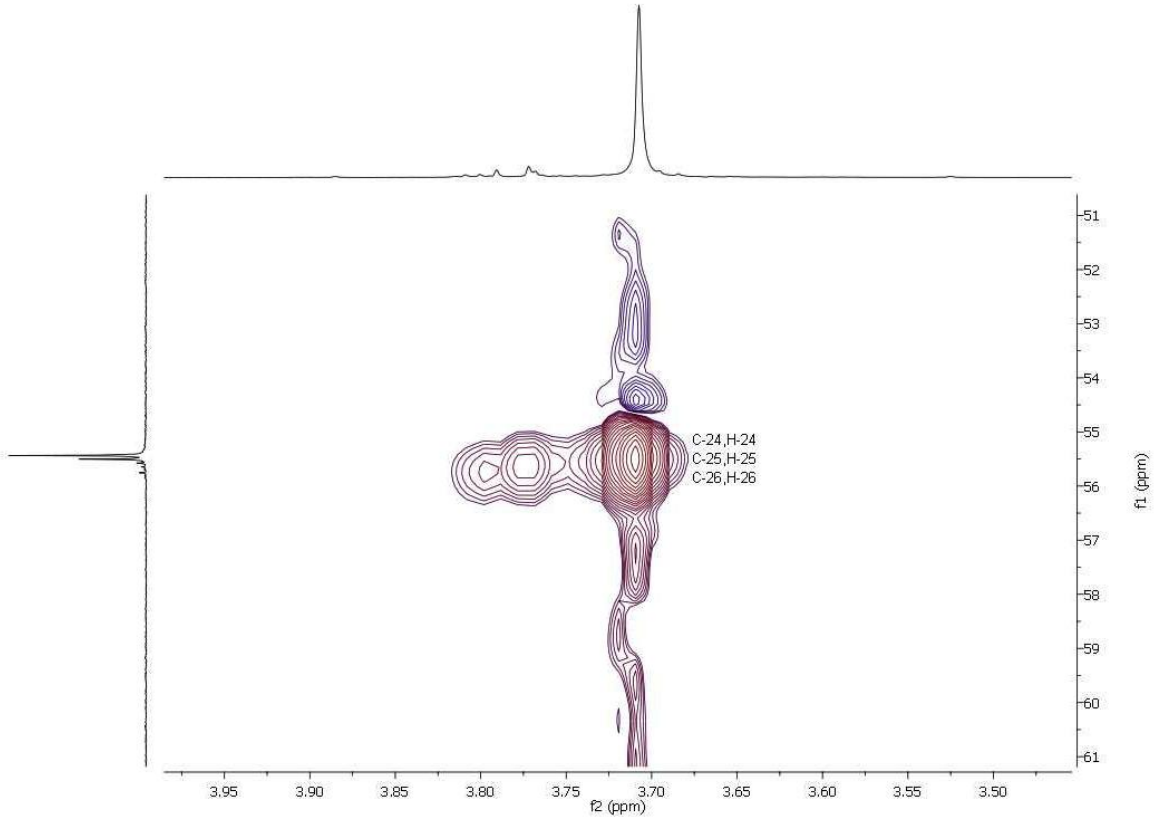

COSY spectrum.



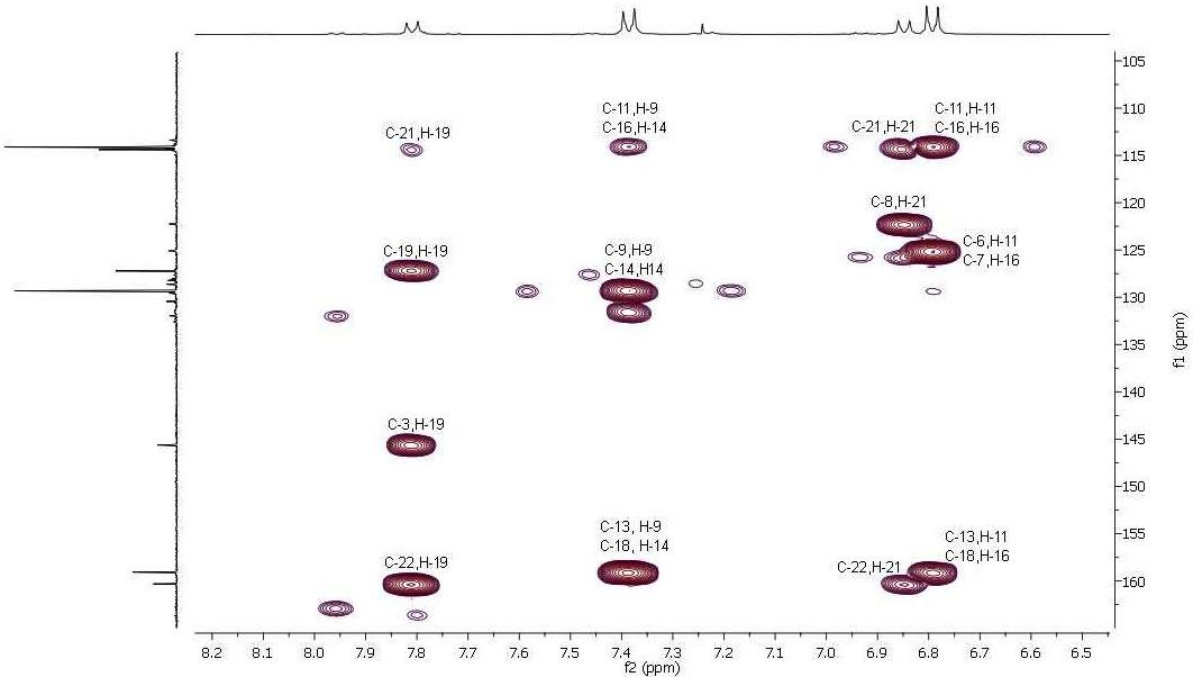
HSQC-1 spectrum.



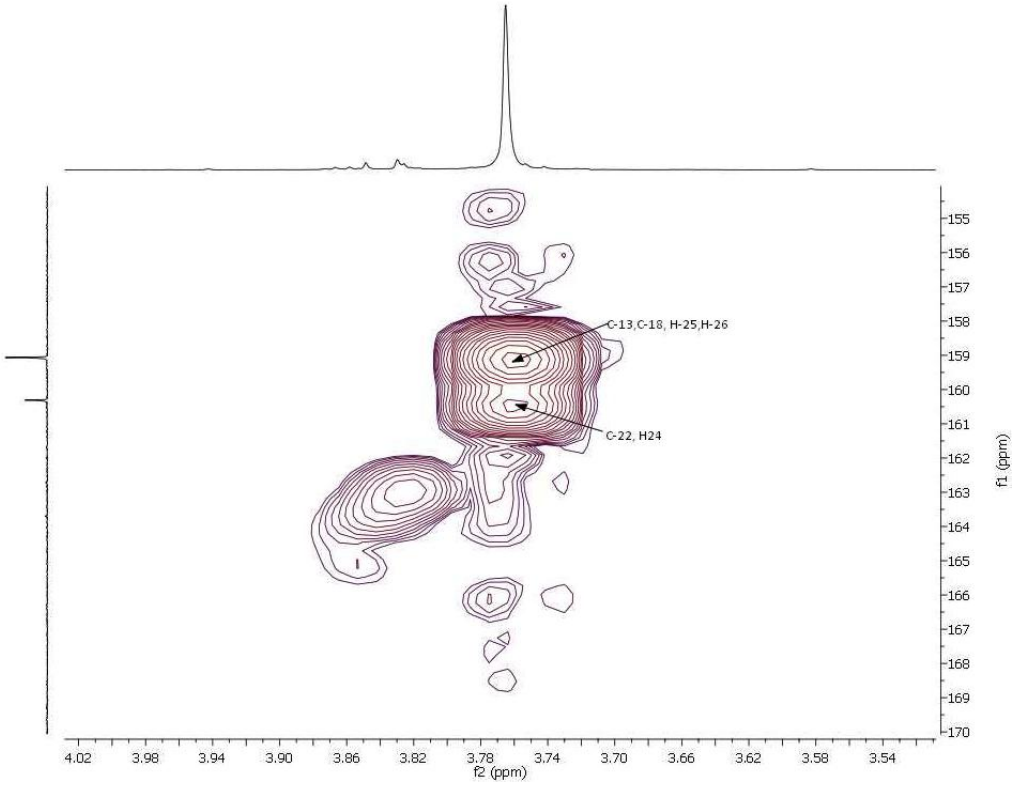

HSQC-2 spectrum.



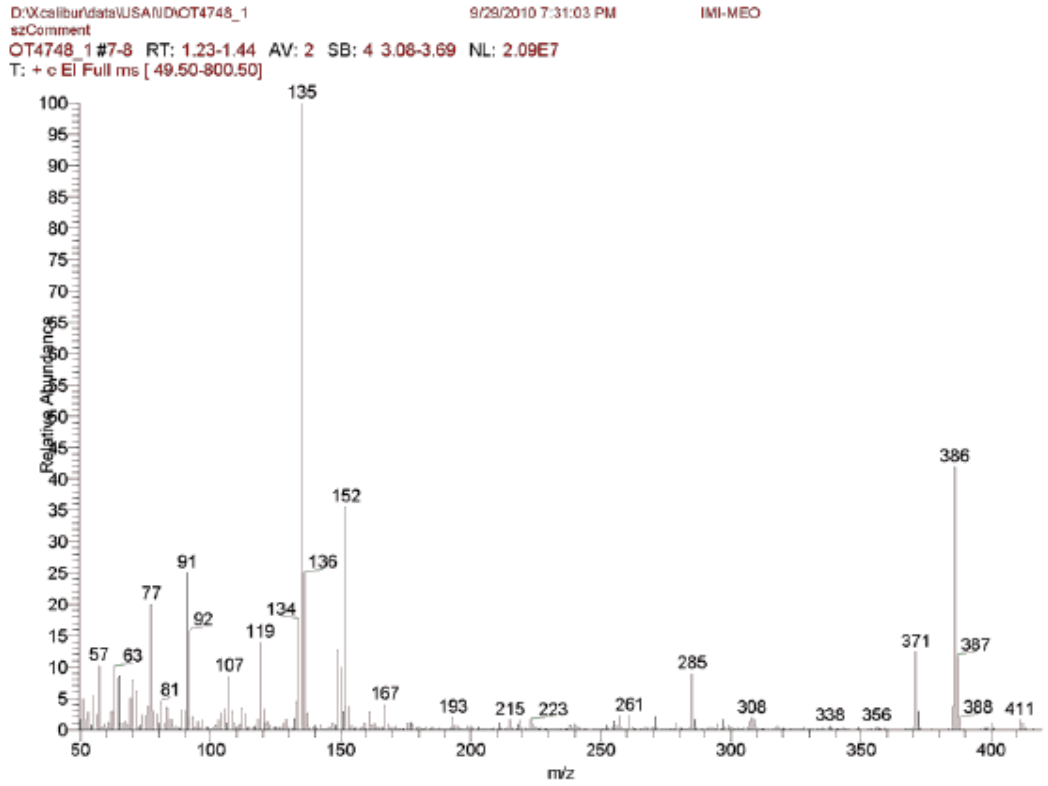
HMBC-1 spectrum.



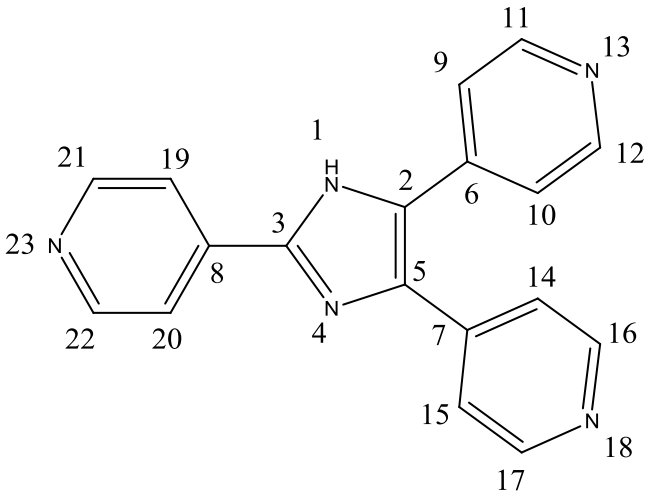

HMBC-2 spectrum.



Mass spectrum.



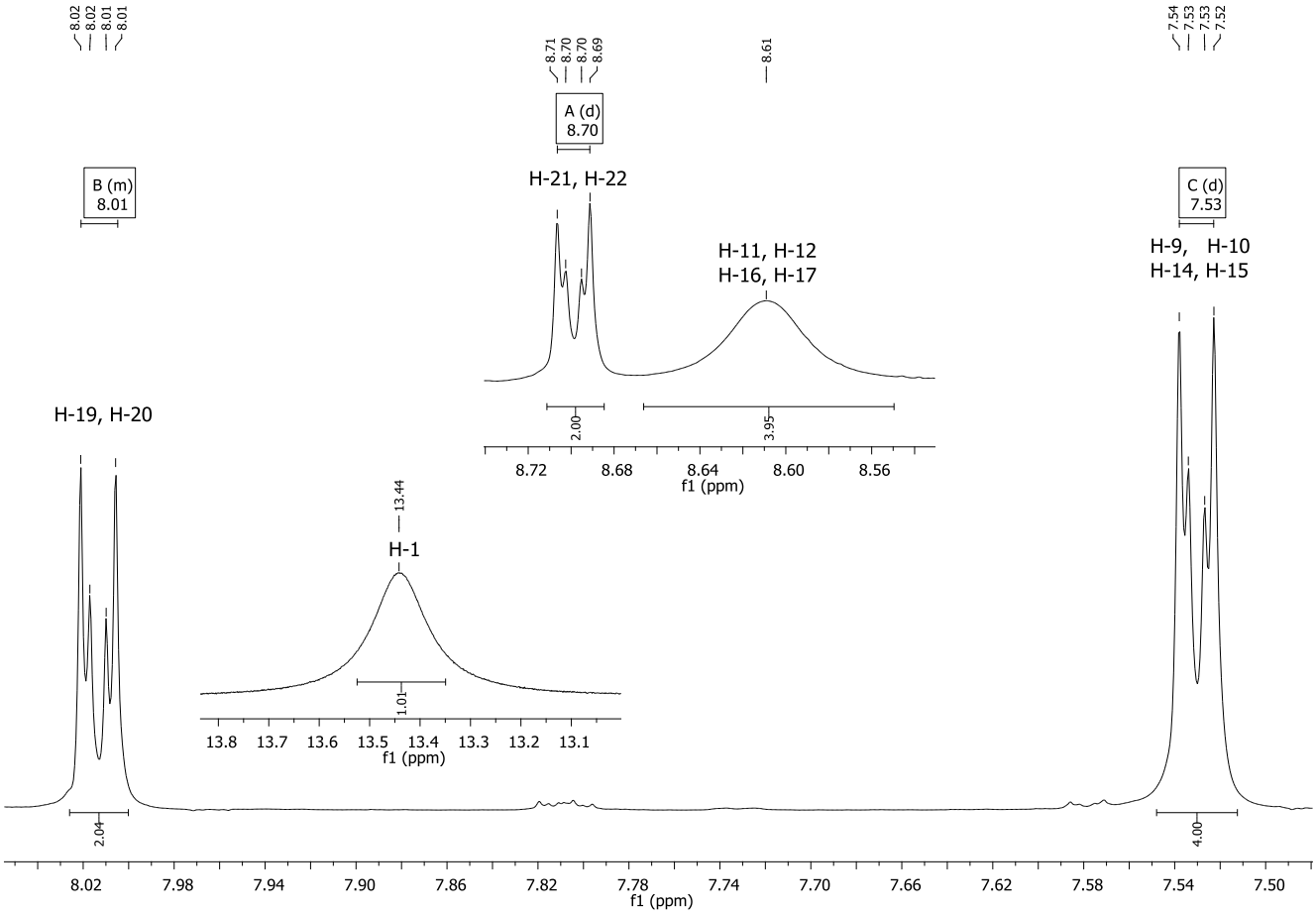
**TPyI**



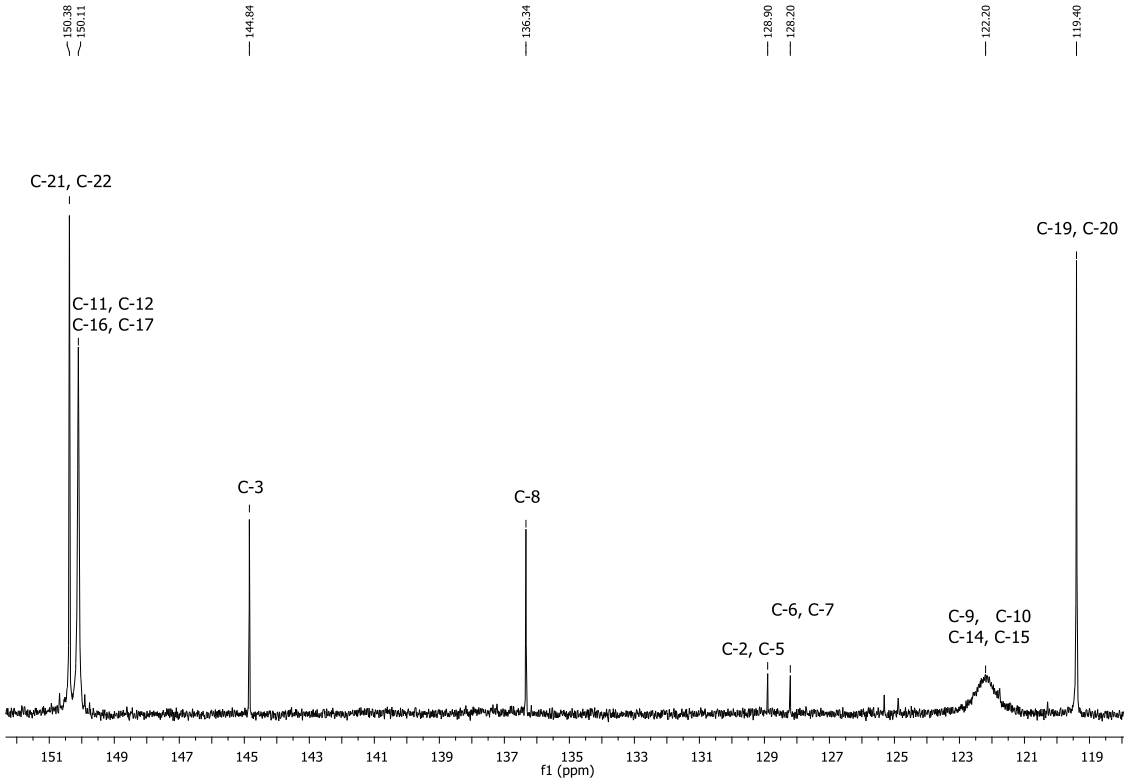

Purification by chromatographic column eluting with THF/hexane (1:1) and recrystallization THF/water to yield a pale yellow solid.
$^{1}$H NMR (400 MHz, DMSO-$d_6$): 13.44 (s, 1H, H-1), 8.70 (dd, *J=6* Hz, 2H, H-21, H-22), 8.61 (br s, 4H, H-11, H-12, H-16, H-17), 8.01 (dd, *J=6* Hz, 2H, H-19, H-20), 7.53 (dd, *J=6* Hz, 4H, H-9, H-10, H-14, H-15). $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$): 150.38 (C-21, C-22), 150.11 (C-11, C-12, C-16, C-17), 144.84 (C-3), 136.34 (C-8), 128.90 (C-2, C-5), 128.20 (C-6, C-7), 122.20 (C-9, C-10, C-14, C-15), 119.40 (C-19, C-20).

Anal. Calcd for $C_{21}H_{19}N_5$: C, 73.87; H, 5. 60; N, 20.51. Found: C, 73.90; H, 6.70; N, 20.55.

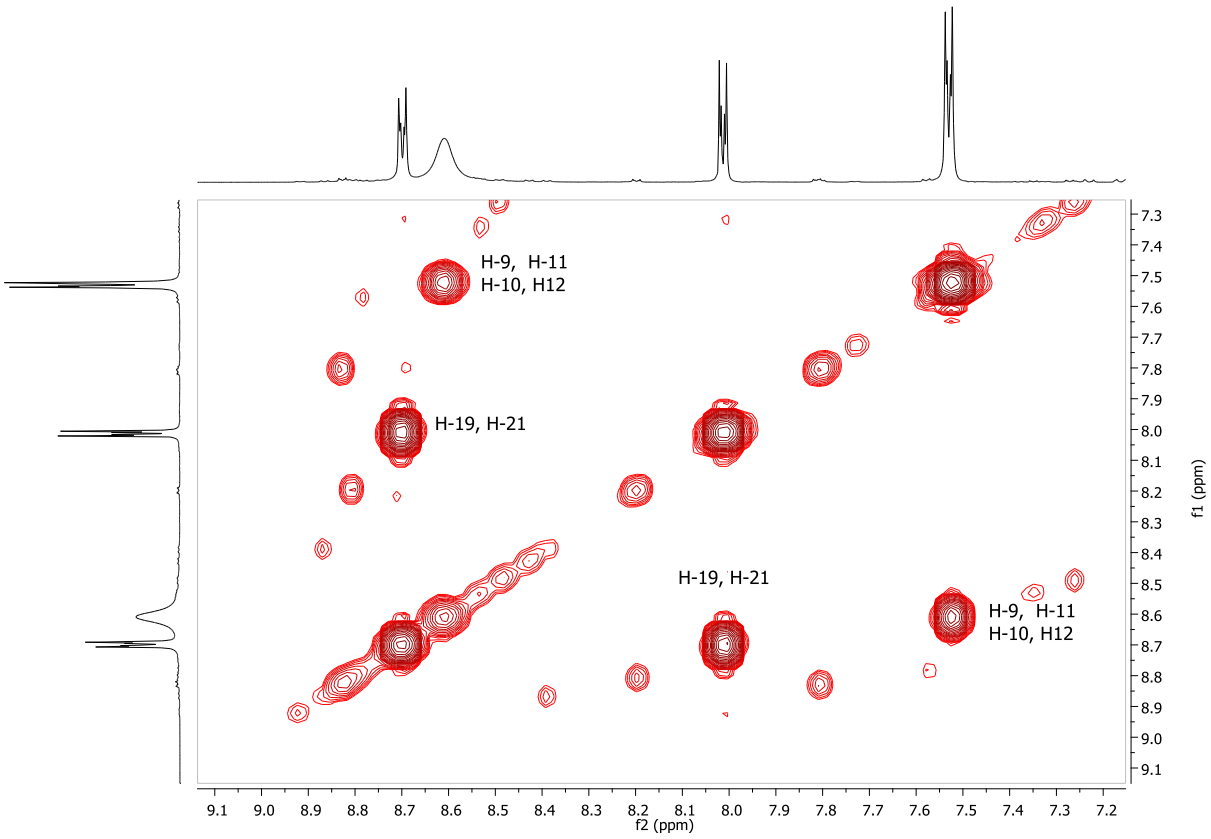
$^{1}$H NMR spectrum.



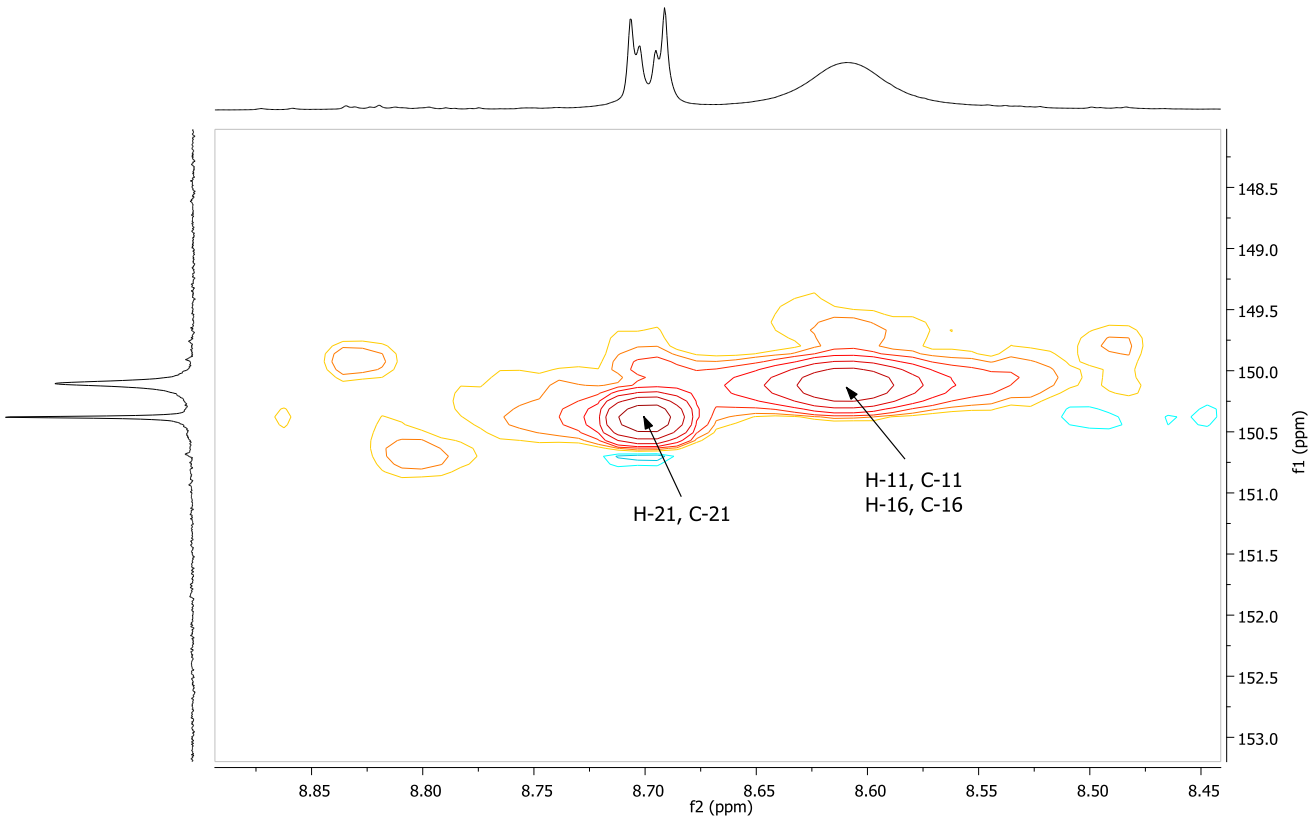
$^{13}C\{^{1}H\}$ NMR spectrum.



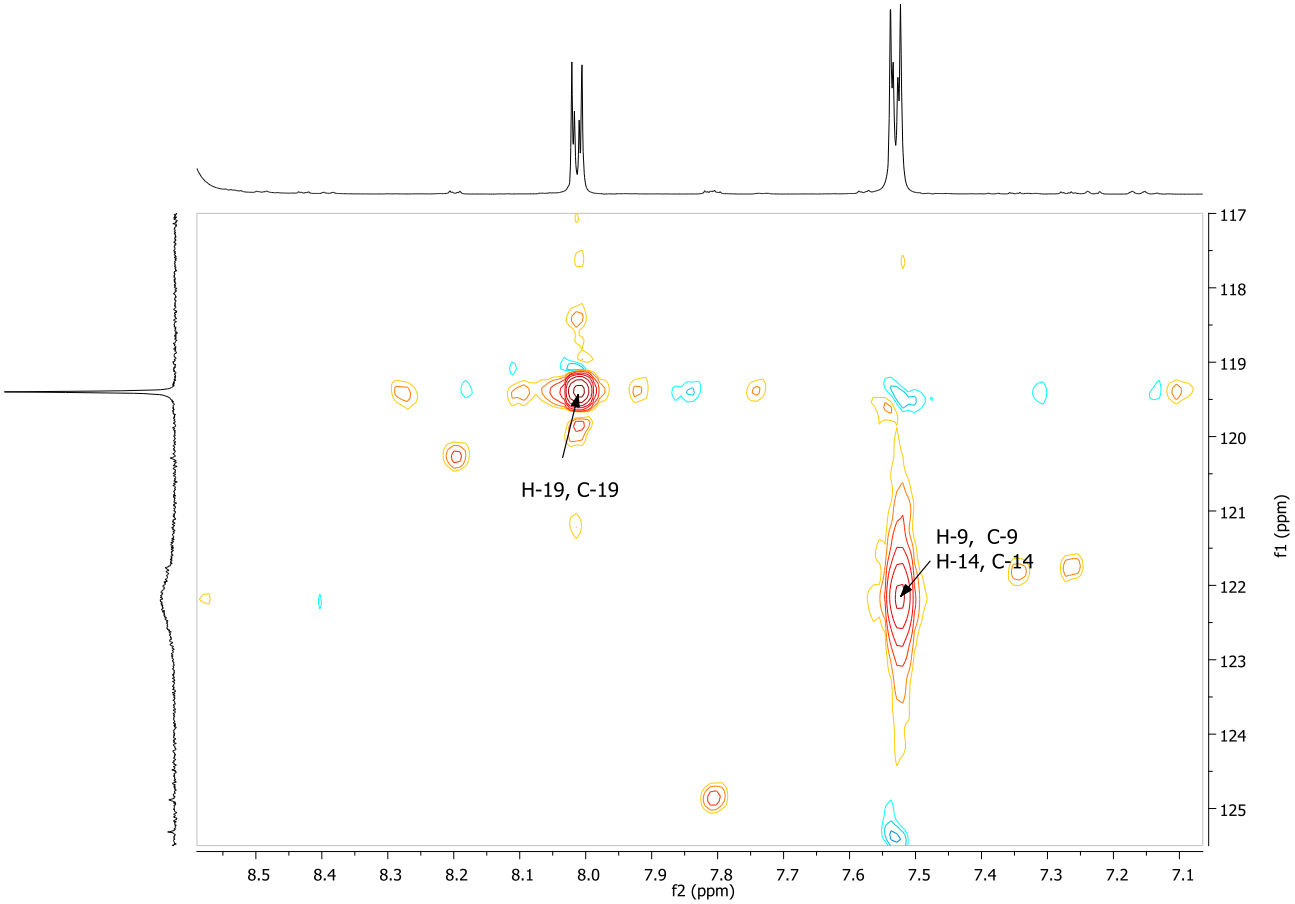

COSY spectrum.



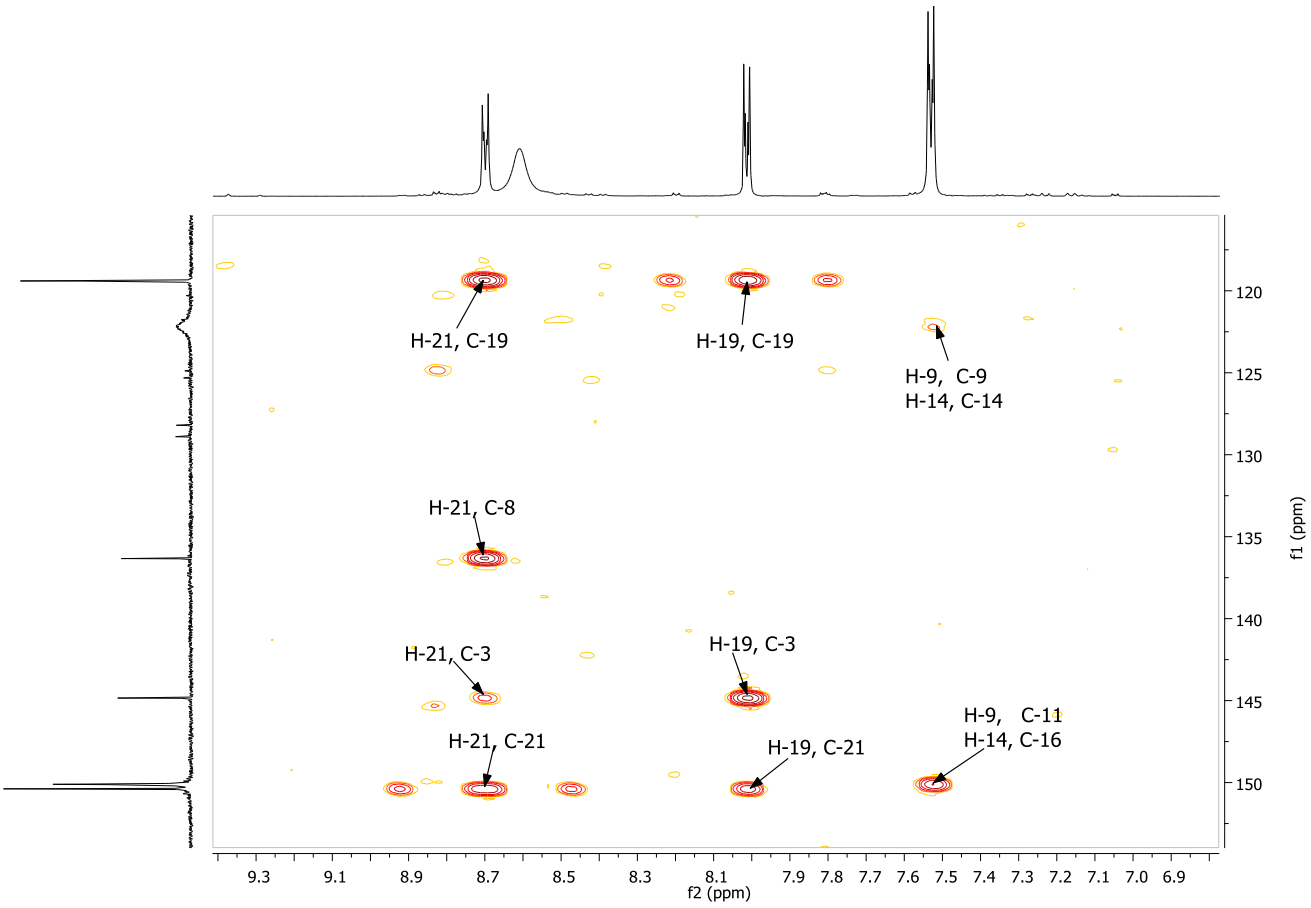
HSQC (1) spectrum.



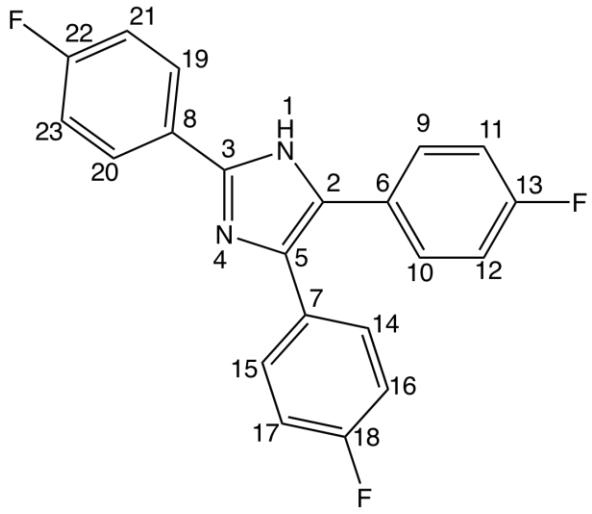
HSQC (2) spectrum.



HMBC spectrum.



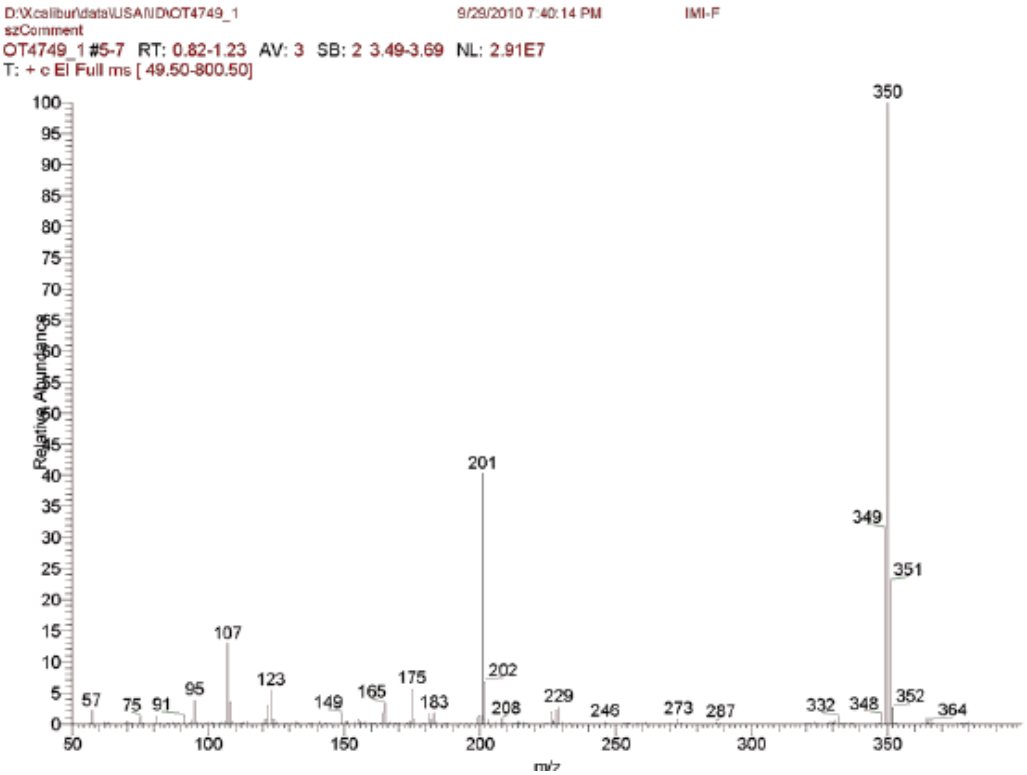
**2,4,5-tri-*p*-fluorophenylimidazole.**



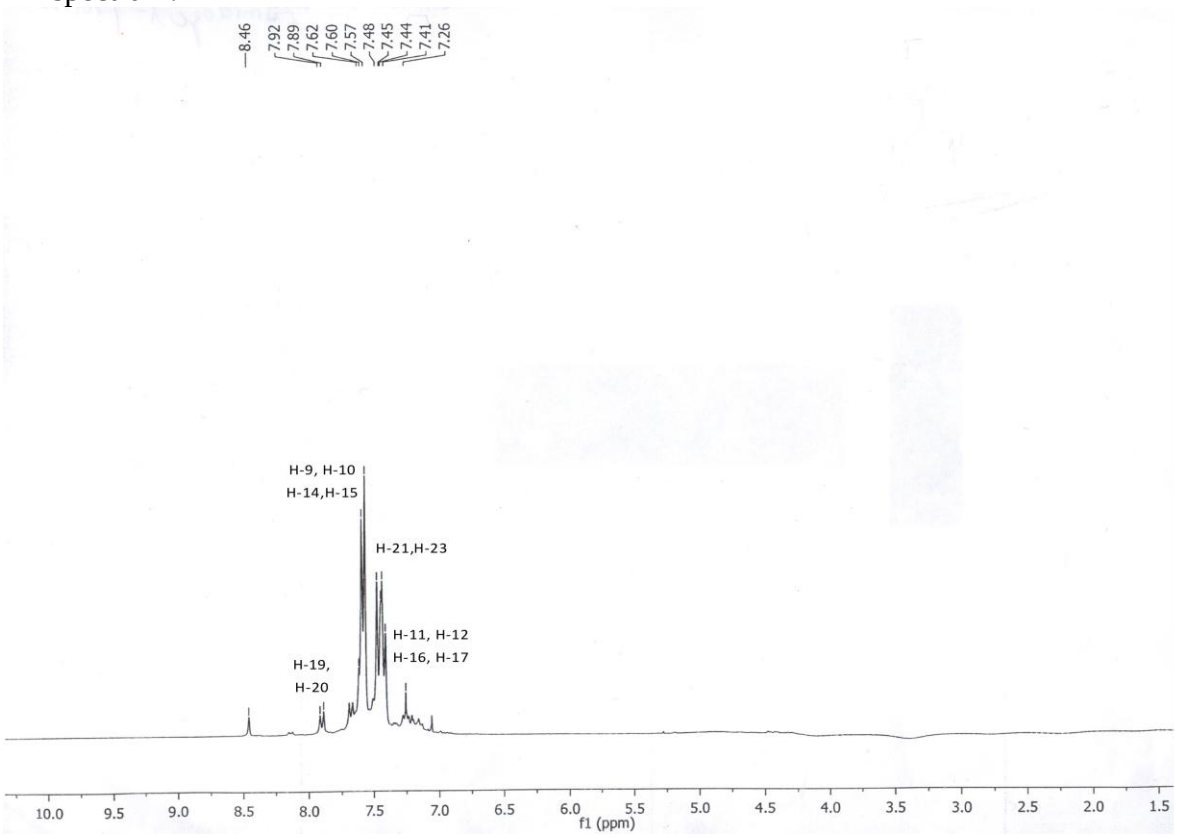

Purification by chromatographic column eluting with THF/hexane (1:1) and recrystallization THF/hexane to produce a pale yellow solid.
$^{1}$H NMR (300 MHz, $CDCl_3$): 7.92 (d, 2H, *J=9 Hz*, H-19 y H-20), 7.60 (d, 4H, *J=9 Hz*, H-9, H-10, H-14 y H-15), 7.48 (d, 2H, *J=9 Hz*, H-21 y H-23), 7.44 (d, 4H, *J=9 Hz*, H-11, H-12, H-16 y H-17). $^{13}$C{$^{1}$H} NMR (75.36 MHz, $CDCl_3$): 170.374 (C-22), 168.55-165.32 ($^{1}J_{C-F}$*=259 Hz*, C-18), 158.42 (C-13) 149.559 (C-3 y C-8), 133.05-132.92 (d, $^{3}J_{C-F}$*=9.8 Hz*, C-19 y C-20), 129.605 (C-2 y C-5), 129.52 (d, $^{3}J_{C-F}$*=4 Hz*, C-14 Y C-15), 129.48 (C-9 y C-10), 116.79 (d, $^{2}J_{C-F}$*=21.85 Hz*, C-21 y C-23), 115.98 (d, $^{2}J_{C-F}$*=21.85* Hz, C-11 y C-12), 110.39 (d, $^{2}J_{C-F}$*=21.47 Hz*, C-16 y C-17), 108.70 (C-6 y C-7)

Anal. Calcd for $C_{21}H_{13}F_3N_2$: C, 71.99; H, 3.74; N, 7.99. Found: C, 71.92; H, 3.77; N, 7.92.

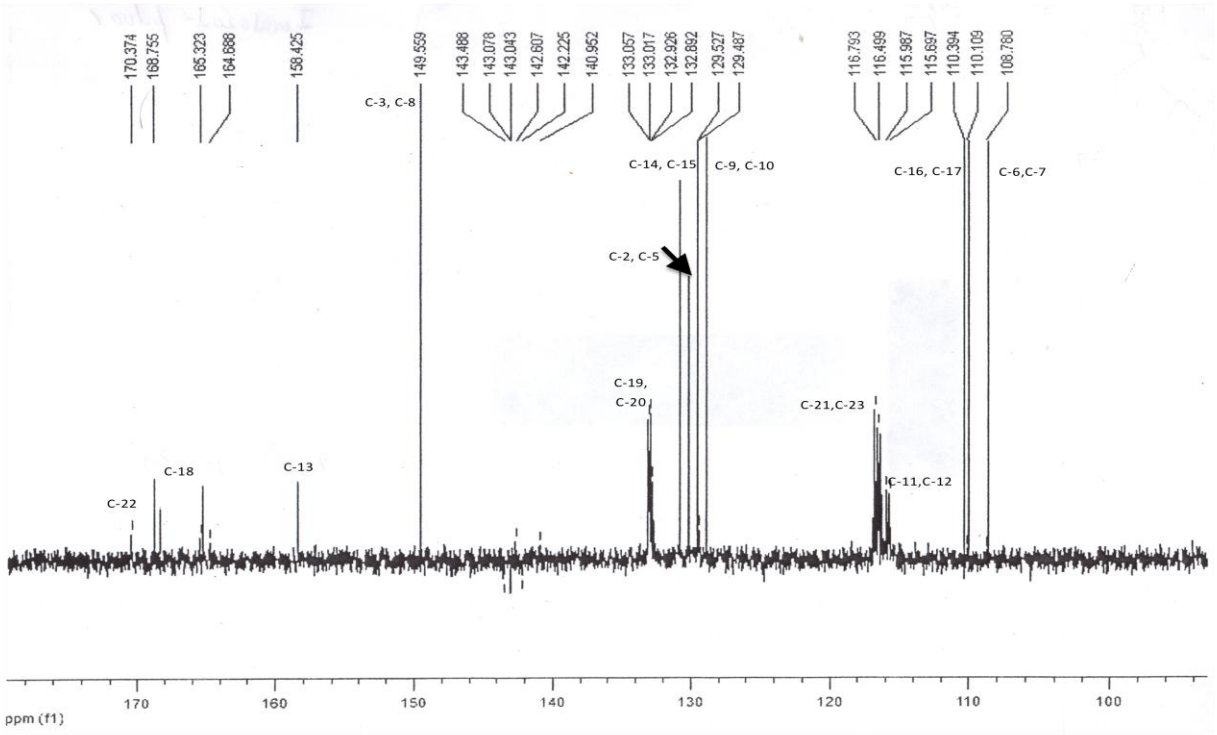
Mass spectrum




$^{1}$H NMR spectrum.



$^{13}C\{^{1}H\}$ NMR spectrum.




(1) F. Scott, C. Krüger, P. Betz, *J. Organomet. Chem.* **1990**, 387, 113.

(2) D. A. Vicic, W.D. Jones, *J. Am. Chem. Soc.* **1997**, 119, 10855.