

# Pyridine-functionalized carbazole donor and benzophenone acceptor design for thermally activated delayed fluorescence emitters in blue organic light emitting diodes

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**Abstract.** In this paper we report a new molecular design approach for blue emitting thermally activated delayed fluorescence (TADF) molecules. The two novel TADF emitters, (4-(3,6-di(pyridin-3-yl)-9H-carbazol-9-yl)phenyl)(phenyl)methanone (**3PyCzBP**), and (4-(3,6-diphenyl-9H-carbazol-9-yl)phenyl)(phenyl)methanone (**4PyCzBP**) possess a pyridine-functionalized carbazole donor and a benzophenone acceptor. Both compounds shows broad charge-transfer emission in DCM with a  $\lambda_{\text{max}}$  at 497 nm and a photoluminescence quantum yield,  $\Phi_{\text{PL}}$  of 56% for **3PyCzBP** and a  $\lambda_{\text{max}}$  at 477 nm and a  $\Phi_{\text{PL}}$  of 52% for **4PyCzBP**. The  $\Phi_{\text{PL}}$  decreased to 18% and 10%, respectively for **3PyCzBP** and **4PyCzBP** in the presence of  $\text{O}_2$  confirming that triplet states involved in emission. The PMMA doped (10 wt%) films show blue-shifted emission with  $\lambda_{\text{max}}$  at 450 and 449 nm for **3PyCzBP** and **4PyCzBP**, respectively. The maximum  $\Phi_{\text{PL}}$  of 23.4% is achieved for these compounds in PMMA doped film. Difference in energy between the singlet and triplet excited states ( $\Delta E_{\text{ST}}$ ) is very small at 0.06 eV and 0.07 eV for **3PyCzBP** and **4PyCzBP**, respectively. Multilayer organic light emitting diode devices fabricated using these molecules as emitters show that the maximum efficiency ( $\text{EQE}_{\text{max}}$ ) of the blue devices is 5.0%.

**Keywords:** TADF, OLEDs, benzophenone, blue emitter, delayed fluorescence.

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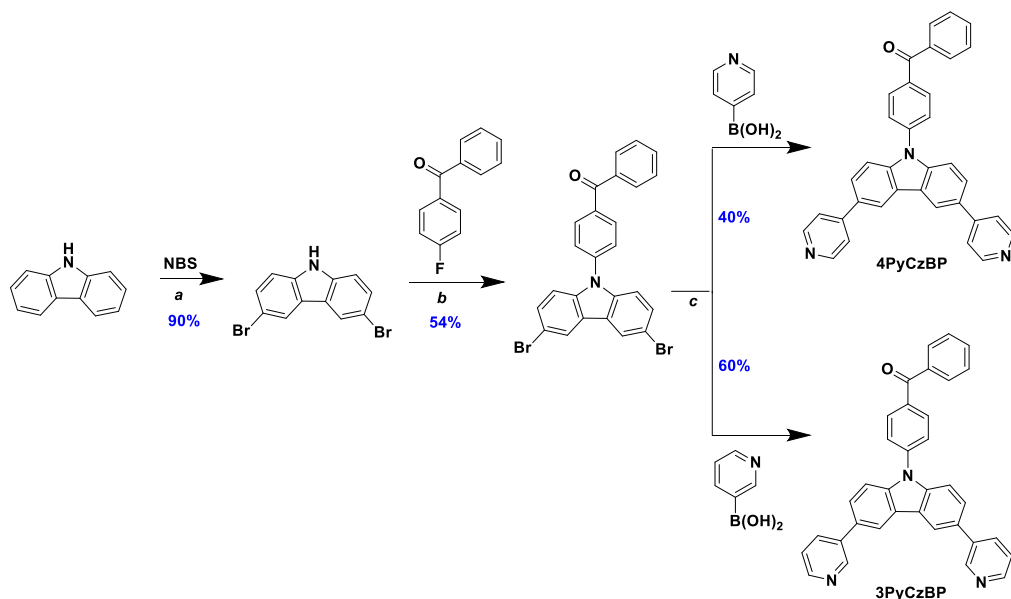
## Introduction

Organic light-emitting diodes (OLEDs) are acquiring significant and increasing attention as a technology in flat panel displays, smart watches, smart phones and large-screen televisions.(1, 2) The maximum internal quantum efficiency (IQE) is typically 25% for OLEDs using conventional fluorescent dopants.(3) The IQE can be increased from 25% to 100% by harvesting triplet excitons using phosphorescent emitters.(4-6) However, phosphorescent emitters almost always are organometallic complexes based on noble metals such as Ir or Pt. These metals are some of the rarest naturally occurring elements on Earth and the environmental sustainability and toxicity remain detracting features of these materials. Further, although many blue

35 phosphorescent materials have been developed, the OLEDs employing these materials as  
36 emissive dopants have short device operational lifetimes and show red-shifted Commission  
37 Internationale de l'Éclairage (CIE) coordinates ( $y$  coordinate is  $>0.25$ ), which precludes them  
38 from commercial use.(7-9) Thus, the development of highly efficient blue-emitting materials is  
39 desired to overcome these problems. Triplet–triplet annihilation TTA material-based devices are  
40 limited to maximum 62.5%.(10, 11) Unlike TTA, thermally activated delayed fluorescence,  
41 TADF, or E-type fluorescence materials in OLEDs can reach an internal quantum efficiency of  
42 100% by harvesting both singlet and triplet excitons.(12) In 2012, Adachi *et al*(13) demonstrated  
43 that OLED external quantum efficiency, EQE, based on organic TADF emitters could reach  
44 beyond the theoretical maximum 5%, assuming a light outcoupling efficiency of 20%. Since this  
45 seminal report, over 400 distinct TADF emitters have been developed for high performance  
46 OLEDs.(14) The TADF mechanism requires a small singlet–triplet energy gap ( $\Delta E_{ST}$ ) in order to  
47 thermally up-convert the triplet excitons to the singlet excited state *via* a reverse intersystem  
48 crossing (RISC). In terms of a molecular design this is achieved by reduced the overlap integral  
49 of the frontier molecular orbitals (i.e. the highest occupied molecular orbital, HOMO, and the  
50 lowest unoccupied molecular orbital, LUMO) in the molecule. This HOMO and LUMO  
51 separation is frequently achieved by combining the donor and acceptors counterpart in the  
52 molecule such that they are electronically decoupled. However, a reduction in  $\Delta E_{ST}$  is  
53 accompanied by a low oscillator strength,  $f$ , for the charge transfer transition, which inevitably  
54 reduces the quantum efficiency of the device. Therefore, there is a tradeoff between the  $\Delta E_{ST}$  and  
55  $f$  in order to optimize the photoluminescence quantum yield of the emitter and therefore the  
56 efficiency of the device. It now becomes evident that TADF emitter design is a critical factor to  
57 achieve high-efficiency TADF OLEDs. Although various red, green, and blue TADF emitters

58 had been developed,(14-16) the optimum molecular design for blue-emitting TADF compounds  
59 is not well understood, and guidelines for the rational molecular design are highly desired. One  
60 strategy for HOMO localization, and by extension small  $\Delta E_{ST}$ , is for wide dispersion of the  
61 HOMO through the presence of multiple donor groups or extended donors. Although the EQEs  
62 of the OLEDs were found to increase, the color coordinates were red-shift significantly from  
63 blue to green, which is a detracting feature of this strategy for the development of blue TADF  
64 materials.(17-20) Typically, extended or dendronized donors are constituted of a central  
65 carbazole heterocycle decorated on the periphery with addition carbazole or diphenylamine  
66 donor units.

67         Herein, we report a new molecular design for blue TADF emitters where in contrast to  
68 the conventional strategies, we modified the carbazole donors with weak electron-withdrawing  
69 pyridine rings. Two novel TADF emitters, **4PyCzBP** and **3PyCzBP**, have been designed,  
70 synthesized and characterized and OLED devices fabricated. These emitters are composed of a  
71 dipyridyl carbazole donor moiety and a benzophenone (BP) unit as the acceptor (Fig. **1**). The  
72 presence of these additional pyridine rings on the carbazole donor weaken the electron-donating  
73 nature of the core carbazole thereby reinforcing the blue emission of the material both in solution  
74 and in thin film. The photophysical properties of these compounds have been studied and the  
75 maximum photoluminescence quantum yield 23.4% is achieved for these compounds in PMMA  
76 doped film with a  $\lambda_{max}$  around 450 nm. Multilayer OLED devices fabricated using these  
77 molecules as dopants in a high energy DPEPO host show maximum EQEs of the blue devices as  
78 high as 5.0%.



79

80 Scheme 1. Synthesis of **4PyCzBP** and **3PyCzBP**. Reagents and conditions: <sup>a</sup> MeCN, 273 to 298  
 81 K, 2 h. <sup>b</sup> DMF, KO<sup>t</sup>Bu (1 equiv.), 150 °C, 19 h. <sup>c</sup> 1,4-dioxane:H<sub>2</sub>O (4:1 v/v), Cs<sub>2</sub>CO<sub>3</sub> (6 equiv.),  
 82 Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 equiv.), 110 °C, 48 h. All reactions were conducted under an N<sub>2</sub> atmosphere.

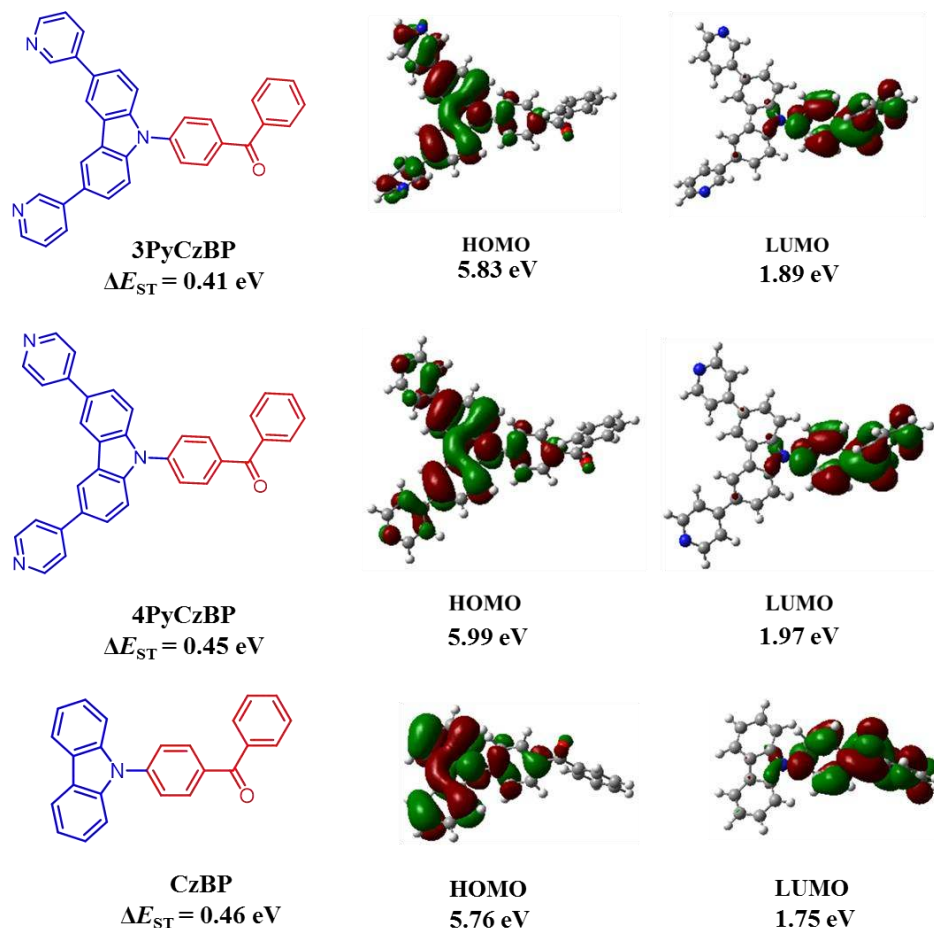
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## 84 Results and Discussion

85

86 The synthetic route for the TADF emitters **3PyCzBP** and **4PyCzBP** and are given in Scheme 1  
 87 and were synthesized with overall yields of 19% and 29%, respectively, in three steps. The  
 88 detailed synthetic procedures and characterization data are reported in the experimental section.  
 89 Density functional theory (DFT) calculations were performed for these compounds, which show  
 90 spatial separation of the HOMO and LUMO for both emitters. As illustrated in Fig. 1, the  
 91 HOMOs of **3PyCzBP** and **4PyCzBP** are mainly distributed over the dipyridylcarbazolyl donor  
 92 group and slightly extended to the bridging phenyl ring. The LUMOs are mostly localized on the  
 93 benzophenone acceptor. The small overlap between HOMO-LUMO observed, which is  
 94 important for a small  $\Delta E_{ST}$ . The time-dependent DFT (TDDFT) calculated singlet-triplet energy  
 95 gaps ( $\Delta E_{ST}$ ) are 0.45 eV and 0.41 eV, respectively, for **4PyCzBP** and **3PyCzBP**. The calculated  
 96  $\Delta E_{ST}$  values suggest that these materials may be TADF in nature.(21) In order to assess the effect

97 of the presence of the pyridine units on the optoelectronic properties of the emitters we modelled  
98 the reference compound **CzBP** and **PyCz**. This compound shows a shallower HOMO level (5.76  
99 eV) than both **3PyCzBP** (5.83 eV) and **4PyCzBP** (5.99 eV). In addition, the pyridine units on  
100 the carbazole donor increase the oscillator strength of the  $S_0$ - $S_1$  transition and slightly reduce the  
101  $\Delta E_{ST}$  values (Fig. 1 and Tables 6-13 (appendix)).



102

103 Fig. 1 Structure of TADF emitters and corresponding DFT calculated HOMO and LUMO  
104 electron density distribution.

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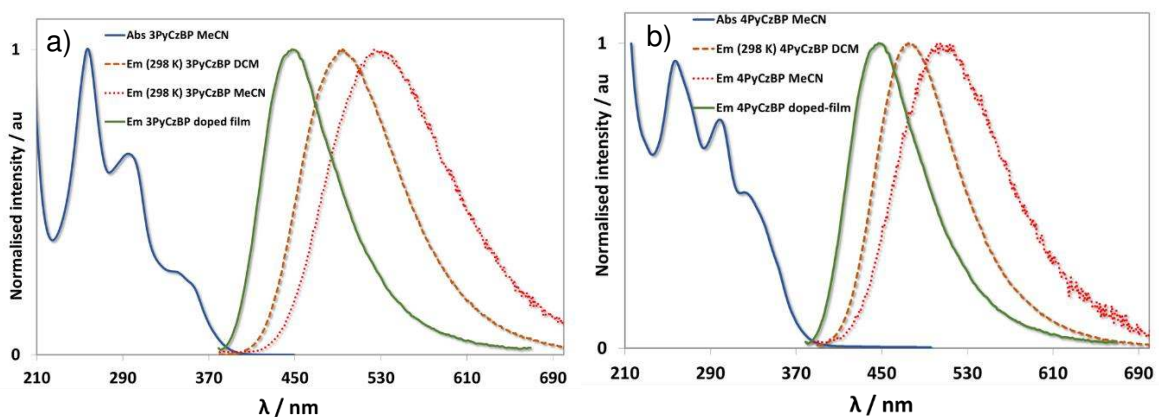
### 106 **Optoelectronic Characterization**

107 The absorption and emission spectra of **3PyCzBP** and **4PyCzBP** were measured in DCM and are  
108 shown in Fig. 2, and the data are summarized in Tables 1 and 2. Both compounds exhibit a broad

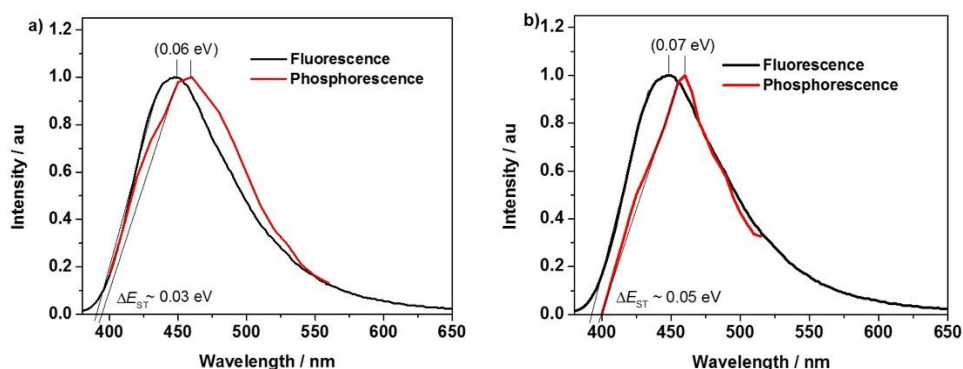
109 charge transfer (CT) absorption band at 356 and 326 nm for **3PyCzBP** and **4PyCzBP**,  
110 respectively, assigned as an intramolecular charge transfer (ICT) band from the carbazole moiety  
111 to the benzophenone based on TDDFT. The absorption bands around 300 nm are localized on the  
112 pyridylcarbazole donor, in line with the calculated absorption band found at 293 nm for **PyCz** by  
113 TDDFT (Table 8 (appendix)). Electrochemical measurements on **3PyCzBP**, and **4PyCzBP** were  
114 carried out in MeCN. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV)  
115 traces are shown in Fig. 8 (appendix). The oxidation waves are only pseudo-reversible with  
116 oxidation potentials for **3PyCzBP** of ( $E_{pa} = 1.69$  V vs SCE) and for **4PyCzBP** of ( $E_{pa} = 1.71$  V  
117 vs SCE). The calculated HOMO levels ( $E_{HOMO \text{ vs } Fc/Fc^+} = E_{pa} + 4.8$  eV) are -6.11 eV and -6.13 eV  
118 for **3PyCzBP** and **4PyCzBP**, respectively. These values are deeper than the reported values for  
119 ketone-derived carbazole-based D-A-D and D-A systems (-5.7 eV),(18, 21) demonstrating the  
120 electron-withdrawing and HOMO-stabilizing nature of the pyridine rings. This analysis is  
121 entirely consistent with the DFT calculations (Fig. 1).

122  
123 Both compounds show broad emission spectra in DCM with a  $\lambda_{max}$  at 497 nm and a  
124 photoluminescence quantum yield,  $\Phi_{PL}$ , of 56% for **3PyCzBP** and a  $\lambda_{max}$  at 477 nm and a  $\Phi_{PL}$  of  
125 52% for **4PyCzBP** (Fig. 2). Notably, the  $\Phi_{PL}$  decreased to 18% and 10%, respectively for  
126 **3PyCzBP** and **4PyCzBP** in the presence of O<sub>2</sub>, thereby confirming that triplet states are  
127 implicated in the emission, which are readily quenched in the presence of oxygen. A blue-shift of  
128 844 cm<sup>-1</sup> (20 nm) in the emission spectra of **4PyCzBP** is observed compared to **3PyCzBP** due to  
129 the greater electron-withdrawing character of the 4-pyridyl ring that is conjugated into the Cz  
130 donor system. The emission is blue-shifted when the compounds are dispersed in PMMA films  
131 (10 wt%) with  $\lambda_{max}$  at 450 and 449 nm for **3PyCzBP** and **4PyCzBP**, respectively. The  $\Phi_{PL}$

132 values under  $N_2$  are 23.4% and 21.0%, which decreased in the presence of  $O_2$  to 19.1% and  
 133 17.3% for **3PyCzBP** and **4PyCzBP**, respectively, an indication that triplet states are populated  
 134 upon photoexcitation in the film.(22) The  $\Delta E_{ST}$  values in 10 wt% doped PMMA films calculated  
 135 from the peak maxima as well as the onset of the fluorescence and phosphorescence spectra for  
 136 **3PyCzBP** and **4PyCzBP**. The  $\Delta E_{ST}$  values based on the emission maxima are 0.06 and 0.07 eV  
 137 for **3PyCzBP** and **4PyCzBP**, respectively, while the estimate of  $\Delta E_{ST}$  based on the emission  
 138 onset is even smaller at 0.03 eV and 0.05 eV, respectively (Fig. 3). The percent contribution of  
 139 the delayed fluorescence to the overall emission decay for **3PyCzBP** and **4PyCzBP** are 18.3%  
 140 and 17.7%, respectively.



141  
 142 Fig. 2 Photophysical properties of a) **3PyCzBP** and b) **4PyCzBP**, normalised UV-Vis spectrum of  
 143 collected in MeCN at 298 K (blue line) and normalised emission spectra collected in DCM at 298 K  
 144 (dashed orange line), in MeCN at 298 K (dotted red line) and as spin-coated PMMA-doped films (green)  
 145 (10 wt%) on quartz substrate.



146

147 Fig. 3 Normalised fluorescence and phosphorescence emission spectrum of a) **3PyCzBP** and b) **4PyCzBP**  
 148 on PMMA-doped film formed (10 wt% of compound) by spin-coating deposition on quartz substrate.  
 149 Fluorescence and phosphorescence spectra measured at 293 and 77 K, respectively and phosphorescence  
 150 spectra are measured with a 10  $\mu$ s delay time.

151 **Table 1. UV-Vis absorption data of 3PyCzBP and 4PyCzBP**

Compound	$\lambda_{\max}^a$ / nm
	$[\epsilon / \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}]^b$
<b>3PyCzBP</b>	258 [54.8], 298 [47.3], 342 [24.4], 356 [23.7]
<b>4PyCzBP</b>	258 [50.8], 301 [43.9], 326 [34.2]

152  
 153  
 154 <sup>a</sup> UV-Vis absorption in DCM with a concentration on the order of  $10^{-5} - 10^{-6}$  M  
 155 collected at 298 K. <sup>b</sup> Concentration-independent molar extinction coefficients.

156 **Table 2. Photophysical properties of 3PyCzBP and 4PyCzBP**

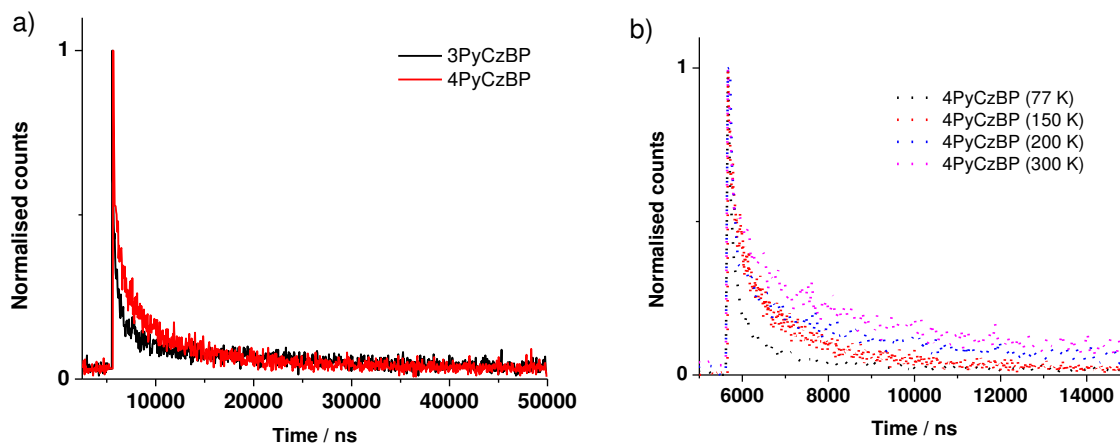
	$\lambda_{\text{em}}$ (nm)		$\Phi_{\text{PL}}$ (%)		$\tau_{\text{PL}}^d$ (ns)
	DCM <sup>a</sup>	Film <sup>b</sup>	Film <sup>b,c</sup>		Film <sup>b</sup>
			N <sub>2</sub>	O <sub>2</sub>	Vacuum
<b>3PyCzBP</b>	497	450	23.4	19.1	28 (0.71), 546.5 (0.07), 12,545 (0.22)
<b>4PyCzBP</b>	477	449	21.0	17.3	33.5 (0.75), 611.3 (0.05), 6320 (0.20)

157 <sup>a</sup> Measurements in degassed DCM at 298 K ( $\lambda_{\text{exc}} = 360$  nm). <sup>b</sup> PMMA doped thin films (10 wt%)  
 158 formed by spin-coating on a quartz substrate. <sup>c</sup> Values obtained using an integrating sphere under  
 159 nitrogen or oxygen ( $\lambda_{\text{exc}} = 360$  nm). <sup>d</sup> Values in parentheses are pre-exponential weighting  
 160 factors, in relative % intensity, of the emission decay kinetics ( $\lambda_{\text{exc}} = 378$  nm, 300 K).

161



162 The transient PL decay characteristics of **3PyCzBP** and **4PyCzBP** 10 wt% doped PMMA films  
 163 under vacuum are shown in Fig. 4 and the data are summarized in Table 2. Prompt fluorescence,  
 164  $\tau_p$ , of 28.0 ns and 33.5 ns, respectively, for **3PyCzBP** and **4PyCzBP** were determined by TCSPC  
 165 measurements. The delayed fluorescence lifetimes showed biexponential decay kinetics with  $\tau_d$ ,  
 166 of 0.55  $\mu$ s, 12.54  $\mu$ s for **3PyCzBP** and 0.61  $\mu$ s, 6.32  $\mu$ s for **4PyCzBP**, an indication of reverse  
 167 intersystem crossing (RISC) from the triplet to the singlet excited state. Variable temperature  
 168 transient PL spectra are shown in Fig. 4 and Fig. 9 (appendix) and the data summarised in Table  
 169 5 (appendix). As expected for organic materials emitting *via* a TADF mechanism,  $\tau_d$  for both  
 170 compounds gradually increased with increasing temperature due to the thermally activated RISC.  
 171 These transient PL decays corroborate the TADF assignment of the emission in doped PMMA  
 172 films.

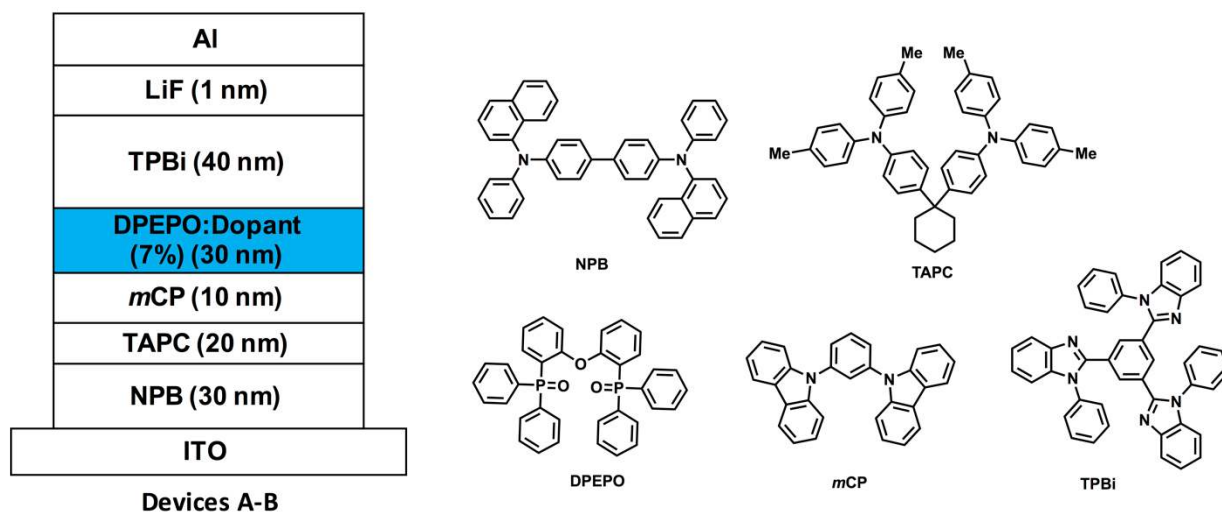


173  
 174 Fig. 4 a) Emission decay of **3PyCzBP** and **4PyCzBP** collected at 300 K ( $\lambda_{exc} = 378$  nm) in  
 175 PMMA-doped thin films (10 wt% of emitter), b) Emission decay of **4PyCzBP** ( $\lambda_{exc} = 378$  nm)  
 176 collected as PMMA-doped thin film (10 wt% of emitter) at 77 K (in blue), at 150 K (in yellow), at 200 K  
 177 (in grey) and at 300 K (in orange). Thin films are formed by spin-coating deposition on quartz substrate

## 179 Electroluminescence

180

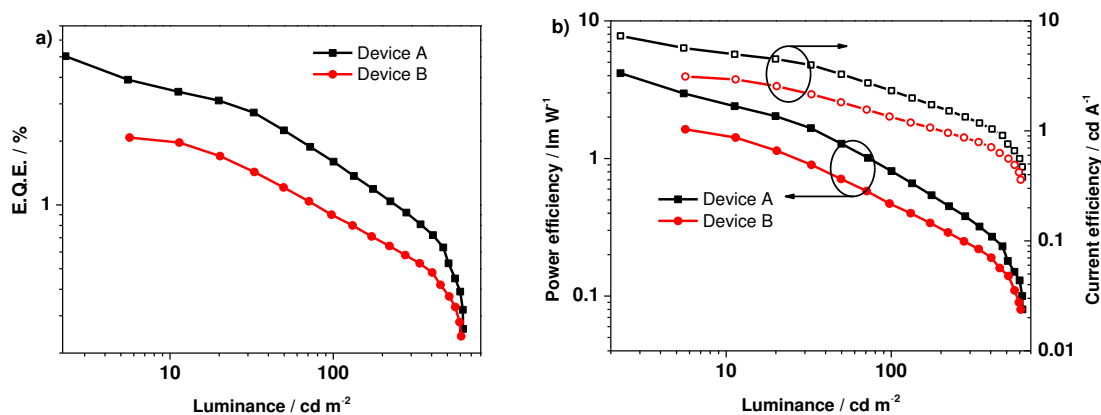
181 To evaluate the performance of **3PyCzBP** and **4PyCzBP** in OLEDs, we fabricated multilayer  
 182 devices using these dopants. The schematic representation of the device architecture and  
 183 molecular structures of the materials used in the devices are shown in Fig. 5. Devices A and B,  
 184 employing, respectively, **3PyCzBP** and **4PyCzBP** as the dopant were fabricated using the  
 185 following layers: ITO/NPB (30 nm)/TAPC (20 nm)/*m*CP (10)/DPEPO: Dopant (7 wt%) (30 nm)/  
 186 TPBi (40 nm)/LiF (0.8 nm)/Al (100 nm), respectively. In these devices, *N,N'*-bis(1-naphthyl)-  
 187 *N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) acts as the hole injection material, 1,1-bis[4-  
 188 [*N,N'*-di(*p*tolyl)amino]phenyl] cyclohexane (TAPC) is the hole transporting material, and 1,3-  
 189 bis(*N*-carbazolyl)benzene (*m*CP) is the an exciton blocking layer and 3,3-di(9*H*-carbazol-9-  
 190 yl)biphenyl (*m*CBP) is the host material, while 2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1-*H*-  
 191 benzimidazole) (TPBi) is the electron-transporting material. The electroluminescent properties of  
 192 these devices are displayed in Fig. 6 and 7, and the data are summarized in Table 3. Here,  
 193 DPEPO is used as a host as it has the most suitable HOMO level (6.1 eV) given the deep HOMO  
 194 levels of these emitters (~6.1 eV); bipolar host materials, including BCPO have too shallow  
 195 HOMO levels (~ 5.7 eV) and therefore are not suitable host materials for these emitters.



196  
 197 Fig. 5 Schematic representation of the devices A and B (left) and chemical structures of the  
 198 materials used in the devices (right).

199

200 Devices A and B show maximum EQEs of 5.0% and 2.1%, respectively. Although, these  
201 emitters show slightly lower device performances compared to benzophenone-cored dicarbazole  
202 compound (EQE  $\sim$  8.1%), device A shows a higher performance compared to the benzoyl  
203 pyridine and sulfone-based blue TADF devices (EQE  $\sim$  2.2 - 4.1%).(18, 21, 23) The current  
204 efficiencies and power efficiencies for devices A and B are 7.3, 3.1  $\text{cd A}^{-1}$ , and 4.2, 1.6  $\text{lm W}^{-1}$ ,  
205 respectively. The use of **3PyCzBP** (device A) as the dopant resulted in more than 2 times  
206 improvement of the EQE compared with **4PyCzBP** (device B) as the dopant. The higher EQE of  
207 device A can be correlated to the higher PL quantum yield of **3PyCzBP** as well as the more  
208 efficient up-conversion from the triplet to the singlet excited state as a function of the smaller  
209  $\Delta E_{\text{ST}}$ .



210

211 Fig. 6 Electroluminescent performance of devices A and B: a) EQE vs luminance, b) luminance  
212 vs current efficiency and power efficiency.

213

214 The electroluminescence spectra of both the devices are very similar to the corresponding thin  
215 film spectra, with no residual emission exhibited from other layers (Fig. 7). This observation  
216 indicates that the excitons are confined within the emission layer without leakage to the adjacent  
217 layers. Both the devices A and B gave blue electroluminescence at the  $\lambda_{\text{max}}$  457 nm and 450 nm

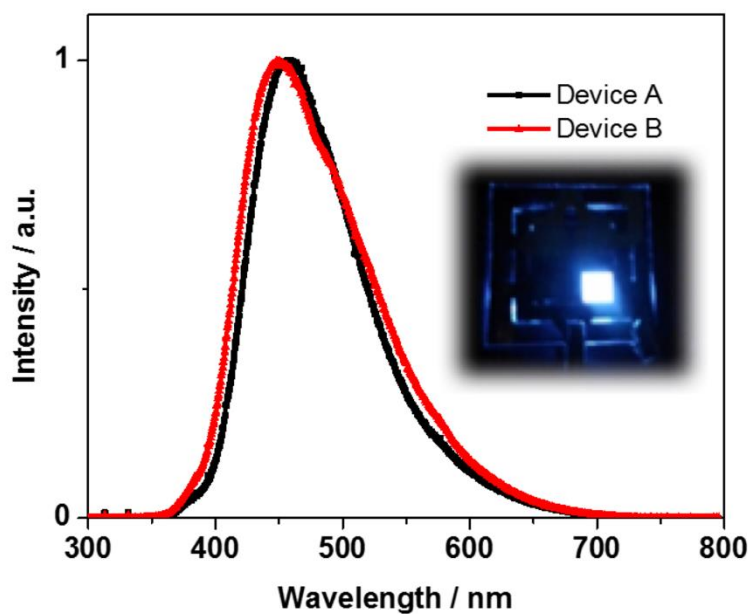
218 with color coordinates of (0.18, 0.21) and (0.19, 0.22), respectively. Although these devices do  
 219 not possess deep blue color coordinates comparable to the boron-based compounds recently  
 220 reported by Hatakeyama *et al.* (0.12, 0.13),(24) their CIE values are deeper than that reported for  
 221 similar ketone-based TADF emitters (0.17, 0.38).(23)

222

223 Table 3. The electroluminescence performances of the device A and B

Device <sup>a</sup>	Dopant	V <sub>d</sub> / V <sup>b</sup>	L / cd m <sup>-2</sup> , V	EQE / %, V	CE / cd A <sup>-1</sup> , V	PE / lm W <sup>-1</sup> , V	λ <sub>max</sub> / nm	CIE / (x,y), 8V
A	<b>3PyCzBP</b>	5.5	663 (15.0)	5.0 (5.5)	7.3 (5.5)	4.2 (5.5)	457	0.18, 0.21
B	<b>4PyCzBP</b>	6.0	605 (14.5)	2.1 (6.0)	3.1 (6.0)	1.6 (6.0)	450	0.19, 0.22

224 <sup>a</sup>Device configuration for A and B: ITO/NPB (30 nm)/TAPC (20 nm)/mCP (10 nm)/DPEPO:**3PyCzBP** or **4PyCzBP** (7 wt%) (30  
 225 nm)/ TPBi (40 nm)/LiF (1 nm)/Al (100 nm); <sup>b</sup>V<sub>d</sub>, The operating voltage at a brightness of 1 cd m<sup>-2</sup>; L, maximum luminance;  
 226 EQE, maximum external quantum efficiency; CE, maximum current efficiency; PE, maximum power efficiency; and λ<sub>max</sub>, the  
 227 wavelength where the EL spectrum has the highest intensity.



228

229 Fig. 7 Electroluminescence spectra of devices A and B measured at 10 V. The inset shows the  
 230 photograph of device A.

231

232

233 Table 4. The electroluminescence performances of the device A and B at 100 cd m<sup>-2</sup>.

Device <sup>a</sup>	Dopant	EQE / %	CE / cd A <sup>-1</sup>	PE / lm W <sup>-1</sup>
A	<b>3PyCzBP</b>	1.6	3.2	3.2
B	<b>4PyCzBP</b>	0.9	1.9	1.9

<sup>a</sup> EQE, maximum external quantum efficiency; CE, maximum current efficiency; and PE, maximum power efficiency.

234  
 235  
 236 OLED device performances at 100 cd m<sup>-2</sup> are summarized in Table 4. The EQE dropped from  
 237 5.0 to 1.6% for device A and from 2.1 to 0.9% for device B. Similarly, the current and power  
 238 efficiency also dropped from 7.3 to 3.2 cd A<sup>-1</sup>, 4.2 to 1.6 cd A<sup>-1</sup> and 4.2 to 0.79 lm W<sup>-1</sup>, 1.6 to  
 239 0.46 lm W<sup>-1</sup>, respectively, for device A and B. High turn-on voltage (Table 3) and significant  
 240 roll-off (Table 4) is observed in these devices due to non-ambipolar host materials (DPEPO).

## 241 **Experimental section**

### 242 **General Synthetic Procedures**

243 Commercial chemicals were used as supplied without further purification. All reactions were  
 244 performed using standard Schlenk techniques under inert nitrogen atmosphere with dry solvents.  
 245 Column chromatography was performed using silica gel (Silia-P from Silicycle, 60 Å, 40-63  
 246 µm). Analytical thin layer chromatography (TLC) was performed with silica plates with polymer  
 247 (250 µm with indicator F-254) and compounds were visualized under UV light. <sup>1</sup>H and <sup>13</sup>C  
 248 solution-phase NMR spectra were recorded on a Bruker Avance spectrometer operating at 11.7 T  
 249 (Larmor frequencies of 500, 126 and 471 MHz, respectively). The following abbreviations have  
 250 been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for  
 251 multiplet and “br” for broad. Melting points (Mps) were recorded using open-ended capillaries  
 252 on an Electrothermal melting point apparatus and are uncorrected. High-resolution mass spectra  
 253 of all compounds were recorded at the EPSRC UK National Mass Spectrometry Facility at

254 Swansea University on a quadrupole time-of-flight (ESI-Q-TOF), model ABSciex 5600 Triple  
255 TOF in positive electrospray or nanospray ionization mode and spectra were recorded using  
256 sodium formate solution as the calibrant.

### 257 **Synthesis of 3,6-dibromo-9H-carbazole**

258 The synthesis of this ligand is by a previously reported method.<sup>(25)</sup> 9H-carbazole (5.0 g, 0.03  
259 mol, 1 equiv.) was added to a 50 mL round bottomed flask and dissolved with 10 mL of dry  
260 acetonitrile (MeCN). The mixture was cooled to a 0 °C with an ice bath and a solution of N-  
261 bromosuccinimide (NBS) (10.7 g, 0.06 mol, 2 equiv.) in 40 mL MeCN was added dropwise  
262 using a dropping funnel. The solution was slowly allowed to come to room temperature and  
263 stirred for an additional period of 2 hours. The mixture was poured onto distilled water and  
264 extracted multiple times with ethyl acetate. The organic fractions were combined, washed with a  
265 portion of brine and dried over magnesium sulfate. Filtration and evaporation under reduced  
266 pressure gave the desired product as a white solid. **Yield:** 87%. **Mp:** 209-212°C **<sup>1</sup>H NMR (500**  
267 **MHz, CDCl<sub>3</sub>) δ (ppm):** 8.16 (d, *J* = 2.0 Hz, 2H, 7.55 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.34 (d, *J* = 8.6  
268 Hz, 2H). The characterization matches that reported.<sup>(26)</sup>

### 269 **Synthesis of (4-(3,6-dibromo-9H-carbazol-9-yl)phenyl)(phenyl)methanone**

270 3,6-dibromocarbazole (1.50 g, 4.61 mmol, 1 equiv.) and potassium *tert*-butoxide (0.52 g, 4.61  
271 mmol, 1 equiv.) were added to a 50 mL round bottomed flask and dissolved in dry DMF (25  
272 mL). The mixture was heat at 150 °C for 30 min and subsequently 4-fluorobenzophenone (0.92  
273 g, 4.61 mmol, 1 equiv.) was added. The reaction mixture was degassed by multiple vacuum and  
274 N<sub>2</sub> purging cycles it was refluxed for 18 h under inert atmosphere. The reaction mixture was  
275 cooled down and poured in distilled water. The mixture was extracted multiple times with DCM,  
276 the organic fractions were combined, washed with a portion of brine and dried over magnesium

277 sulfate. Filtration and evaporation under reduced pressure gave the crude product (3.2 g). The  
278 crude product was purified by column chromatography (silica, dichloromethane) to give 0.90 g  
279 of pure compound as a white solid. **Yield:** 54%. **R<sub>f</sub>:** 0.76 (DCM on silica). **Mp:** 226-228°C. **<sup>1</sup>H**  
280 **NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.24 (d, *J* = 1.8 Hz, 2H), 8.12 – 8.08 (m, 2H), 7.93 (dd, *J* =  
281 8.7, 1.9 Hz, 2H), 7.71 – 7.65 (m, 3H), 7.60 – 7.55 (m, 4H), 7.39 (d, *J* = 8.7 Hz, 2H). **<sup>13</sup>C NMR**  
282 **(500 MHz, CDCl<sub>3</sub>) δ (ppm):** 195.45, 140.57, 139.29, 137.18, 136.73, 132.85, 132.06, 129.68,  
283 128.53, 126.26, 124.38, 123.42, 113.71, 111.50 (Fig. **10, 11** (appendix)). **HR-MS: Calculated:**  
284 (C<sub>25</sub>H<sub>15</sub>Br<sub>2</sub>NO): 505.9573, **Found:** 505.9565.

285

286

#### 287 **General syntheses of 3PyCzBP and 4PyCzBP**

288 The (4-(3,6-dibromo-9H-carbazol-9-yl)phenyl)(phenyl)methanone (0.40 g, 0.79 mmol, 1.0  
289 equiv.), 3-pyridinylboronic acid or 4-pyridinylboronic acid (0.24 g, 1.99 mmol, 2.5 equiv.) and  
290 cesium carbonate (1.55 g, 4.75 mmol, 6.0 equiv.) were added to a round-bottomed flask  
291 containing 50 mL of a mixture of 1,4-dioxane and distilled water (4:1 v/v). The reaction mixture  
292 was degassed by multiple vacuum and N<sub>2</sub> purging cycles, and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.91 g, 0.079 mmol,  
293 0.1 equiv.) was added to the flask under positive nitrogen pressure. The mixture was refluxed  
294 under nitrogen atmosphere for 48 h and then cooled to room temperature. The mixture was  
295 poured into distilled water and extracted multiple times with DCM. The organic fractions were  
296 combined, washed with a portion of brine and dried over magnesium sulfate. Filtration and  
297 evaporation under reduced pressure gave the crude products (1.0 g). The crude products were  
298 purified by flash column chromatography (2.5% MeOH/DCM on silica) to give 0.3 g and 0.2 g,  
299 respectively for **3PyCzBP** and **4PyCzBP**, of pure compounds as white solids. Characterisation

300 of **3PyCzBP**. **Yield:** 60%. **R<sub>f</sub>** = 0.45 (2.5% MeOH/DCM). **Mp:** 199-200°C. **<sup>1</sup>H NMR (500**  
301 **MHz, CDCl<sub>3</sub>) δ (ppm):** 9.10 – 8.90 (m, 2H), 8.64 (dd, *J* = 4.8, 1.6 Hz, 2H), 8.44 (d, *J* = 1.6 Hz,  
302 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.09 – 8.02 (m, 2H), 7.98 – 7.91 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 2H),  
303 7.74 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.70 – 7.65 (m, 3H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.49 (s, 0H), 7.47 –  
304 7.42 (m, 2H). **<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm):** 195.40, 148.33, 147.97, 134.24, 131.91,  
305 129.97, 128.44, 126.23, 125.86, 123.60, 119.08, 110.75 **HR-MS: Calculated:** (C<sub>35</sub>H<sub>24</sub>N<sub>3</sub>O):  
306 502.1914, **Found:** 502.1902 (Fig. **12-14**, (appendix)). CHN calculated for C<sub>35</sub>H<sub>23</sub>N<sub>3</sub>O · 1/3  
307 CH<sub>2</sub>Cl<sub>2</sub>: C, 80.09; H, 4.50; N, 7.93. Found: C, 80.05, H, 4.08; N, 8.24. Characterisation of  
308 **4PyCzBP**. **Yield:** 40%. **R<sub>f</sub>** = 0.34 (2.5% MeOH/DCM). **Mp:** 200-202°C. **<sup>1</sup>H NMR (500 MHz,**  
309 **CDCl<sub>3</sub>) δ (ppm):** 8.74 – 8.70 (dd, 4H), 8.55 – 8.52 (d, *J* = 1.7 Hz, 2H), 8.18 – 8.13 (m, 2H), 7.98  
310 – 7.93 (dd, 2H), 7.82 – 7.77 (m, 4H), 7.72 – 7.7 (m, 4H), 7.68-7.67 (t, 1H), 7.67-7.64 (2H, m),  
311 7.62 – 7.57 (m, 2H). **<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm):** 195.52, 150.25, 148.64, 141.30,  
312 140.77, 137.20, 136.77, 132.88, 132.09, 131.17, 130.09, 128.56, 126.33, 125.84, 124.39, 121.72,  
313 119.23, 110.79. **HR-MS: Calculated:** (C<sub>35</sub>H<sub>24</sub>N<sub>3</sub>O): 502.1914, **Found:** 502.1902 (Fig. **15-17**  
314 (appendix)). CHN calculated for C<sub>35</sub>H<sub>23</sub>N<sub>3</sub>O · 1/3 CH<sub>2</sub>Cl<sub>2</sub>: C, 80.09; H, 4.50; N, 7.93. Found: C,  
315 79.92, H, 4.16; N, 8.12

## 316 **Conclusion**

317 We have designed two TADF emitters bearing a benzophenone core as the electron accepting  
318 unit and 3-pyridyl- and 4-pyridyl-decorated carbazole as the electron-donating unit. The  
319 photophysical properties were studied for these compounds in solution and thin film. A  
320 comparison of these materials shows that **3PyCzBP** compound shows the highest  
321 photoluminescence quantum yield and smallest  $\Delta E_{ST}$ . The photoluminescence quantum yield  
322 reaches 23.4% in the PMMA film and the EQE of the blue-emitting OLED using **3PyCzBP** as



323 the dopant reached 5.0%. This molecular design opens up a new approach to the design blue  
324 TADF emitters for blue OLEDs.

### 325 *Acknowledgments*

326 We thank the Marie Skłodowska-Curie Individual Fellowship (MCIF, no 749557), the  
327 Leverhulme Trust (RPG-2016-047) and EPSRC (EP/P010482/1) for financial support. We thank  
328 the EPSRC UK National Mass Spectrometry Facility at Swansea University for analytical  
329 services.

### 330 *Appendix*

331

332

## 333 **Optoelectronic Characterization**

### 334 **Photophysical measurements**

335 All samples were prepared in HPLC grade  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  with varying concentrations on the  
336 order of  $10^{-3} - 10^{-5}$  M. Absorption spectra were recorded at room temperature using a Shimadzu  
337 UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by  
338 linear least-squares fit of the values obtained from at least four independent solutions at varying  
339 concentrations with absorbance ranging from  $6.05 \times 10^{-5}$  to  $2.07 \times 10^{-5}$  M.

340 The sample solutions for the emission spectra were prepared in HPLC-grade DCM or  
341  $\text{CH}_3\text{CN}$  and degassed *via* three freeze-pump-thaw cycles using a quartz cuvette designed in-  
342 house. Steady-state emission and excitation spectra and time-resolved emission spectra were

343 recorded at 298 K using an Edinburgh Instruments F980. All samples for steady-state  
344 measurements were excited at 360 nm using a xenon lamp, while samples for time-resolved  
345 measurements were excited at 378 nm using a PDL 800-D pulsed diode laser.  
346 Photoluminescence quantum yields were determined using the optically dilute method.(27) A  
347 stock solution with absorbance of *ca.* 0.5 was prepared and then four dilutions were prepared  
348 with dilution factors between 2 and 20 to obtain solutions with absorbances of *ca.* 0.095 0.065,  
349 0.05 and 0.018, respectively. The Beer-Lambert law was found to be linear at the concentrations  
350 of these solutions. The emission spectra were then measured after the solutions were rigorously  
351 degassed *via* three freeze-pump-thaw cycles prior to spectrum acquisition. For each sample,  
352 linearity between absorption and emission intensity was verified through linear regression  
353 analysis and additional measurements were acquired until the Pearson regression factor ( $R^2$ ) for  
354 the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were  
355 calculated for each solution and the values reported represent the slope value. The equation  $\Phi_s =$   
356  $\Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$  was used to calculate the relative quantum yield of each of the sample,  
357 where  $\Phi_r$  is the absolute quantum yield of the reference,  $n$  is the refractive index of the solvent,  $A$   
358 is the absorbance at the excitation wavelength, and  $I$  is the integrated area under the corrected  
359 emission curve. The subscripts  $s$  and  $r$  refer to the sample and reference, respectively. A solution  
360 of quinine sulfate in 0.5 M  $H_2SO_4$  ( $\Phi_r = 54.6\%$ )(28) was used as external reference.(29)

361 PMMA-doped thin films were prepared by spin coating the samples from a solution of 2-  
362 methoxyethanol (HPLC grade)  $10^{-2}$  M containing 10% w/w of the desired sample on a quartz  
363 substrate. Each sample was spin-coated three times from two different solutions following  
364 identical conditions and reproducible results were obtained. Steady-state emission and excitation  
365 spectra and time-resolved emission spectra of neat films were recorded at 298 K using an

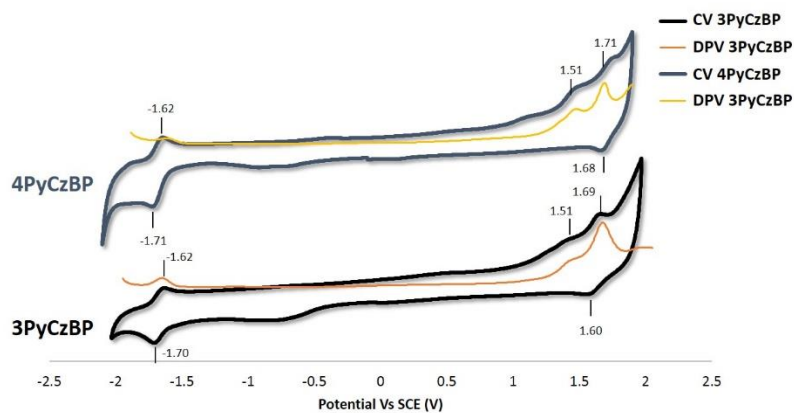
366 Edinburgh Instruments F980. Solid-state PLQY measurements of thin films were performed in  
 367 an integrating sphere under a nitrogen purge in a Hamamatsu C9920-02 luminescence  
 368 measurement system.(30)

369 Table 5. Temperature-dependent emission decays of **3PyCzBP** and **4PyCzBP**

	$\tau_e$ (ns) <sup>a</sup>			
	77 K <sup>a</sup>	150 K <sup>b</sup>	200 K <sup>c</sup>	300 K <sup>b,d</sup>
<b>3PyCzBP</b>	25.1 (0.82), 160.0 (0.01), 1573.2 (0.17)	27.6 (0.84), 243.1 (0.1), 3639.0 (0.05)	24.7 (0.81), 567.5 (0.02), 9513 (0.17)	28 (0.71), 546.5 (0.07), 12545 (0.22)
<b>4PyCzBP</b>	31.1 (0.9), 631.2 (0.1)	32.3 (0.84), 713 (0.5), 2864.0 (0.11)	34.5 (0.76), 713.4 (0.07), 5876.7 (0.15)	33.5 (0.75), 611.3 (0.05), 6320 (0.20)

<sup>a</sup> Measurements under vacuum on PMMA doped thin films (10 w/w % of compound) formed by spin-coating on a quartz substrate. Values in parentheses are pre-exponential weighting factor, in relative % intensity, of the emission decay kinetics ( $\lambda_{exc} = 378$  nm).

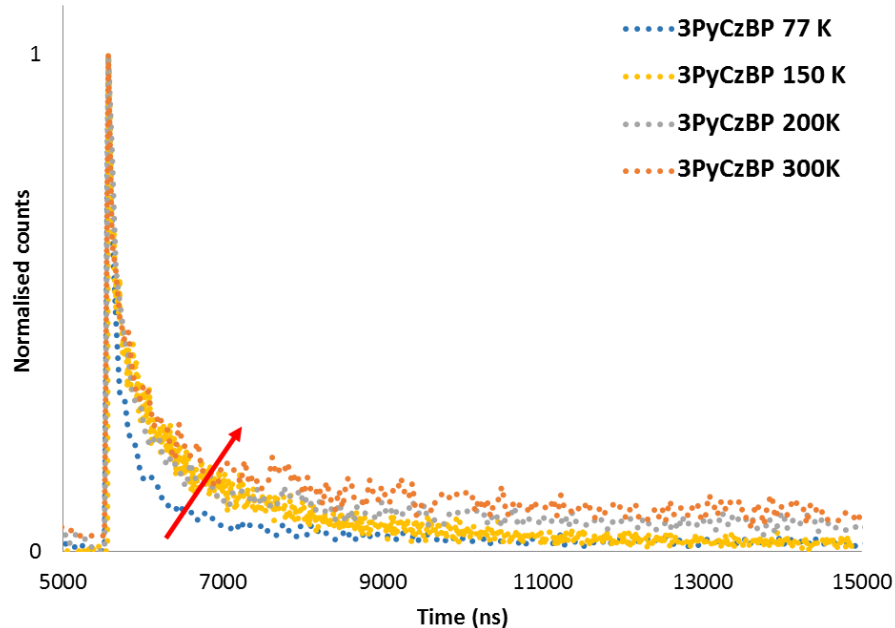
370



371

372 Fig. 8 Cyclic voltammogram (CV), black, and differential pulse voltammogram (DPV), yellow,  
 373 of **3PyCzBP** and **4PyCzBP** in MeCN solution, reported versus SCE ( $Fc/Fc^+ = 0.38$  V in  
 374 MeCN).

375



376

377 Fig. 9 Emission decay of **3PyCzBP** ( $\lambda_{\text{exc}} = 378 \text{ nm}$ ) collected on PMMA-doped thin film (10  
378 w/w % of compound) formed by spin-coating deposition on quartz substrate at 77 K (in blue), at  
379 150 K (in yellow), at 200 K (in grey) and at 300 K (in orange).

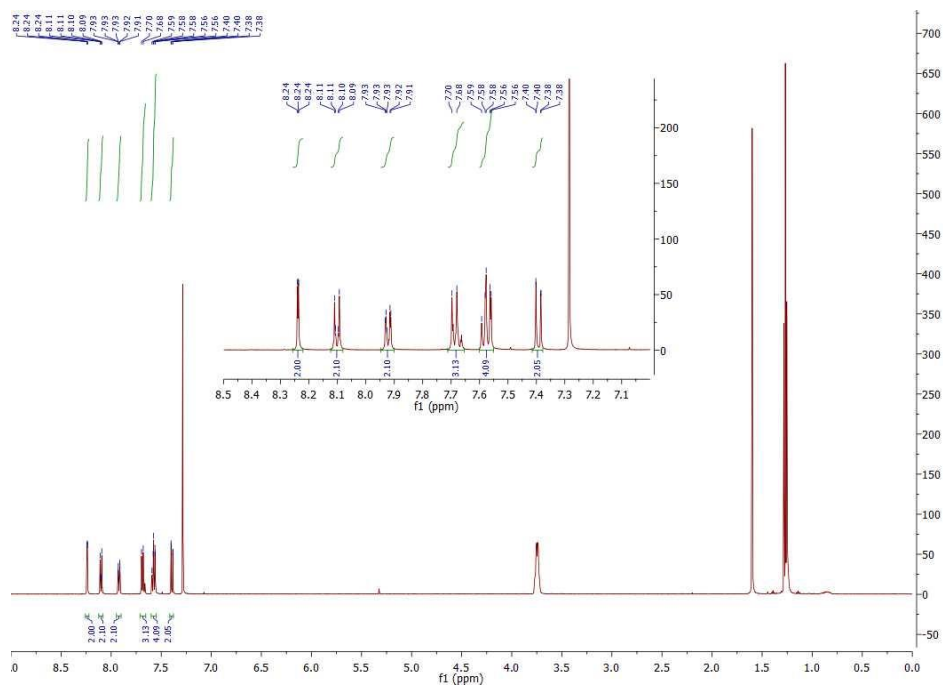
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381

382

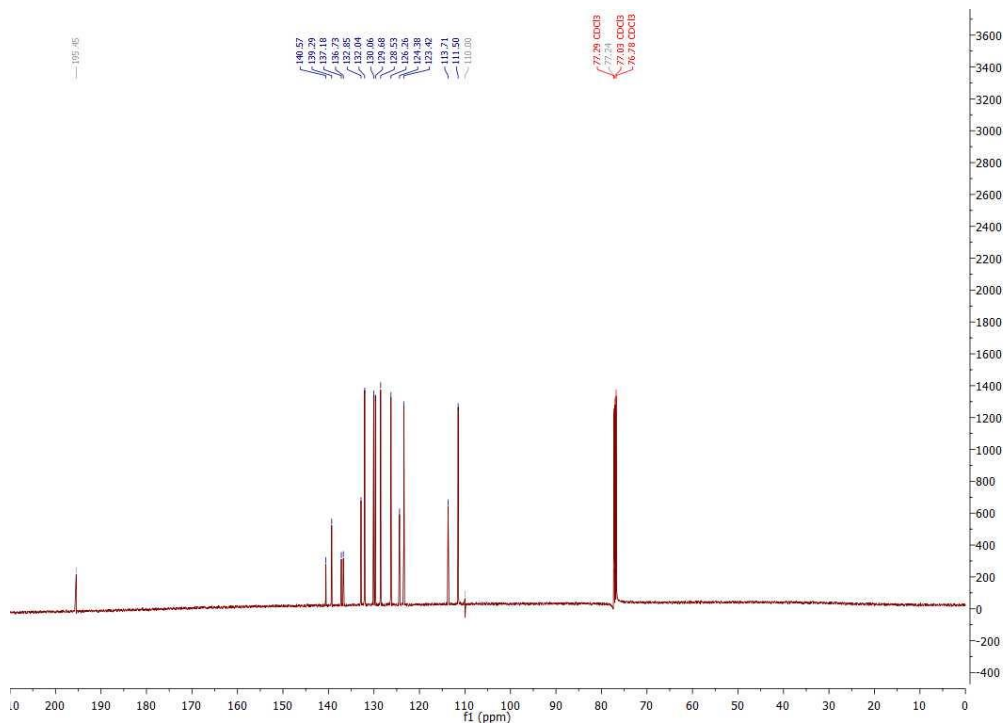
383

384 **Characterization**



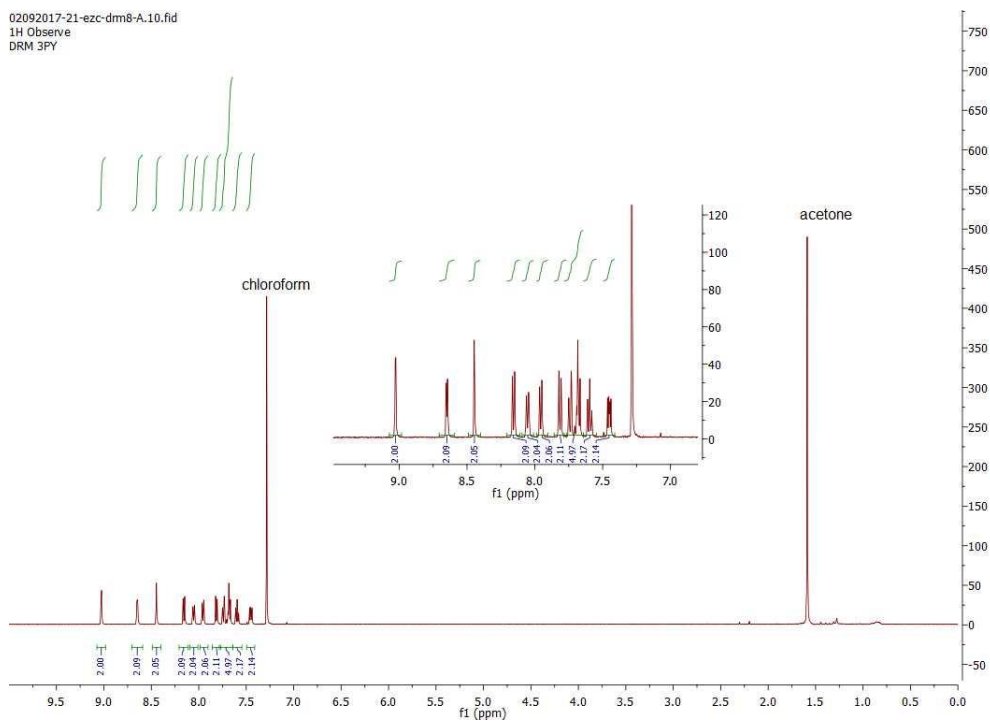
385

386 Fig. 10  $^1\text{H}$  NMR spectrum of (4-(3,6-dibromo-9H-carbazol-9-yl)phenyl)(phenyl)methanone in  
 387  $\text{CDCl}_3$ .



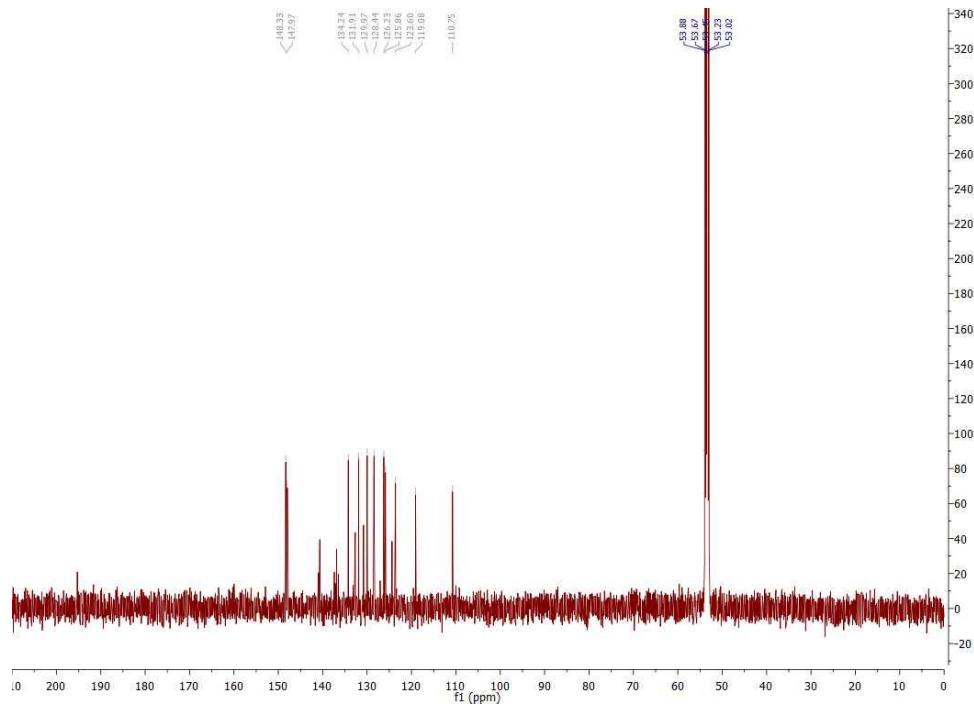
388

389 Fig. 11  $^{13}\text{C}$  NMR spectrum of (4-(3,6-dibromo-9H-carbazol-9-yl)phenyl)(phenyl)methanone in  
 390  $\text{CDCl}_3$ .



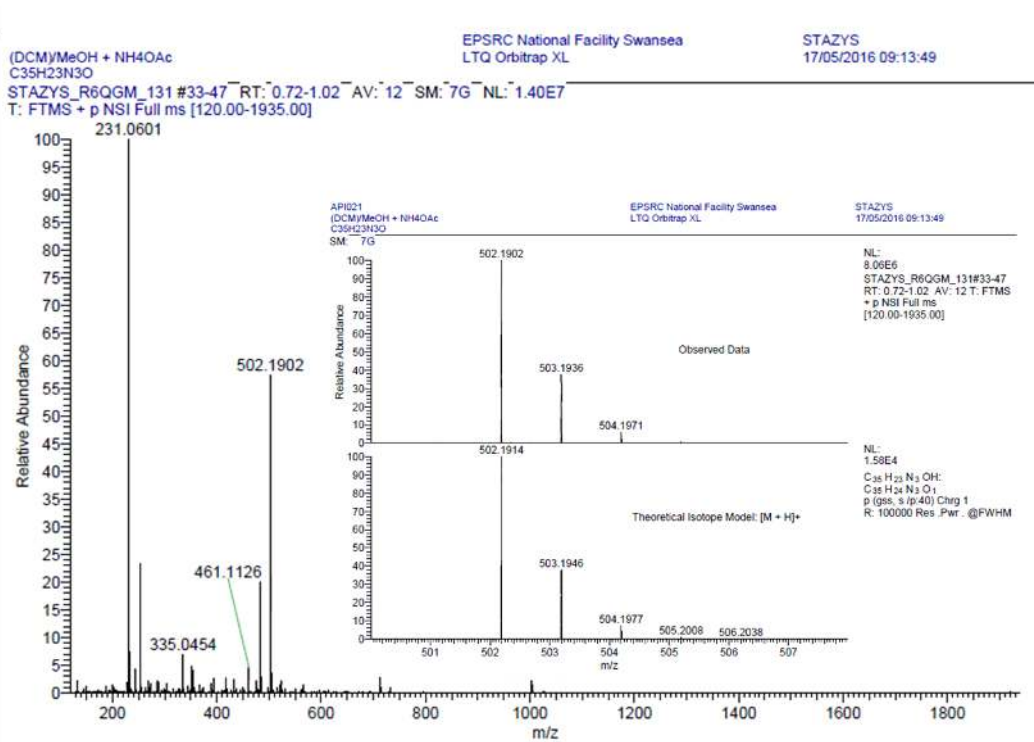
391

392 Fig. 12  $^1\text{H}$  NMR spectrum of **3PyCzBP** in  $\text{CDCl}_3$ .



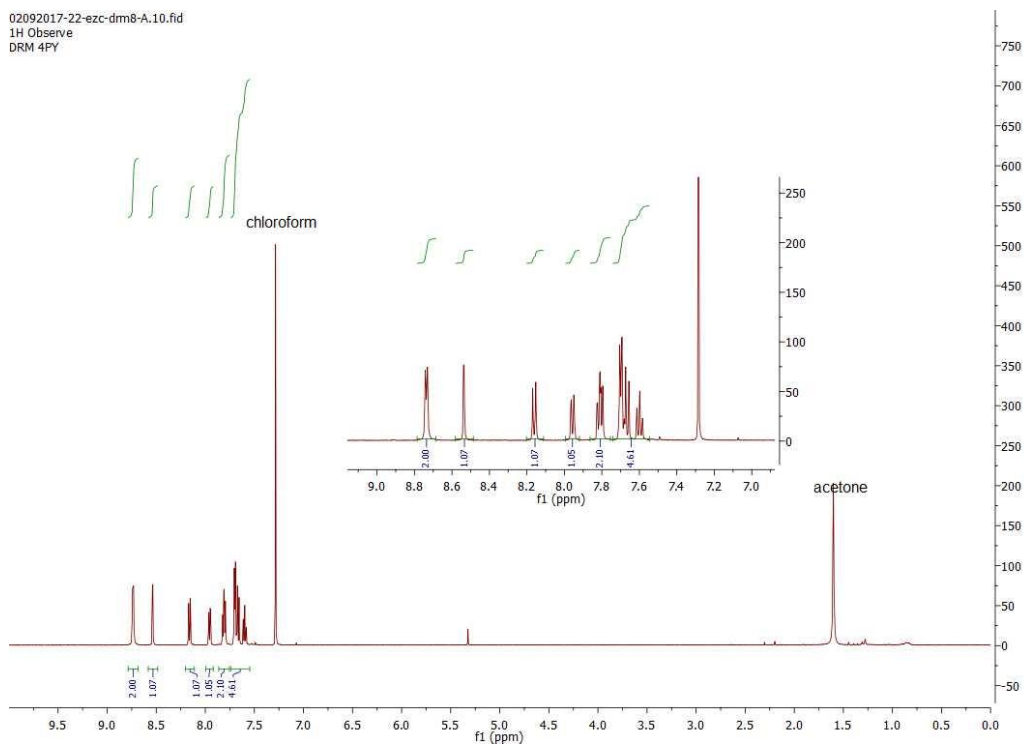
393

394 Fig. 13  $^{13}\text{C}$  NMR spectrum of **3PyCzBP** in  $\text{CDCl}_3$ .



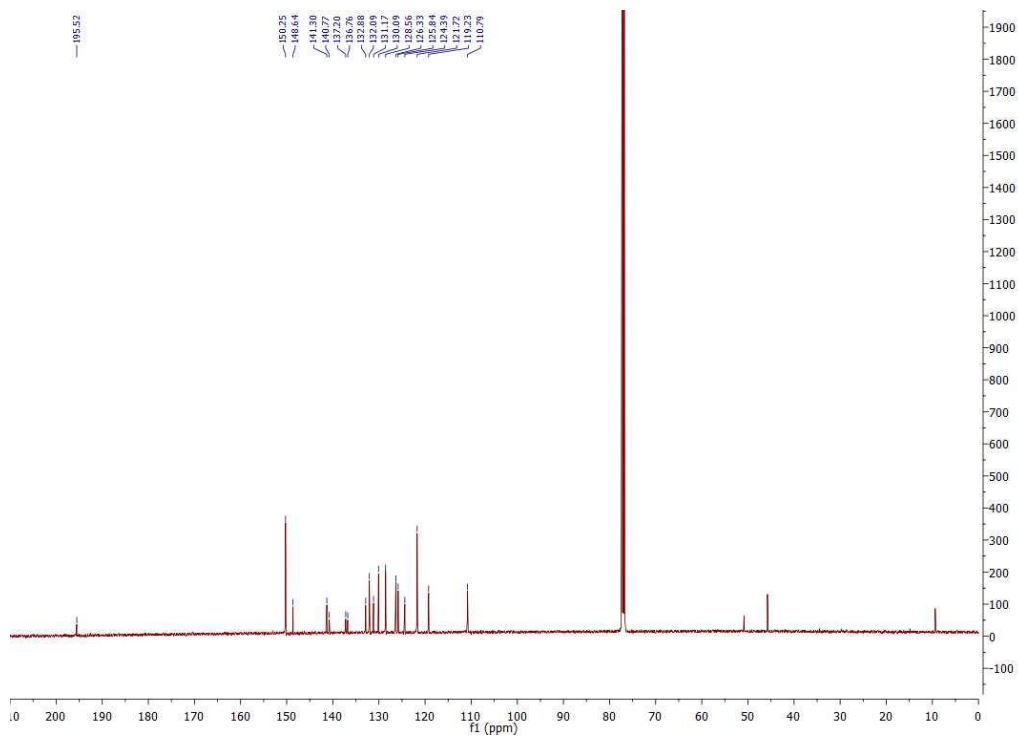
395

396 Fig. 14 HR-MS spectra of **3PyCzBP**.



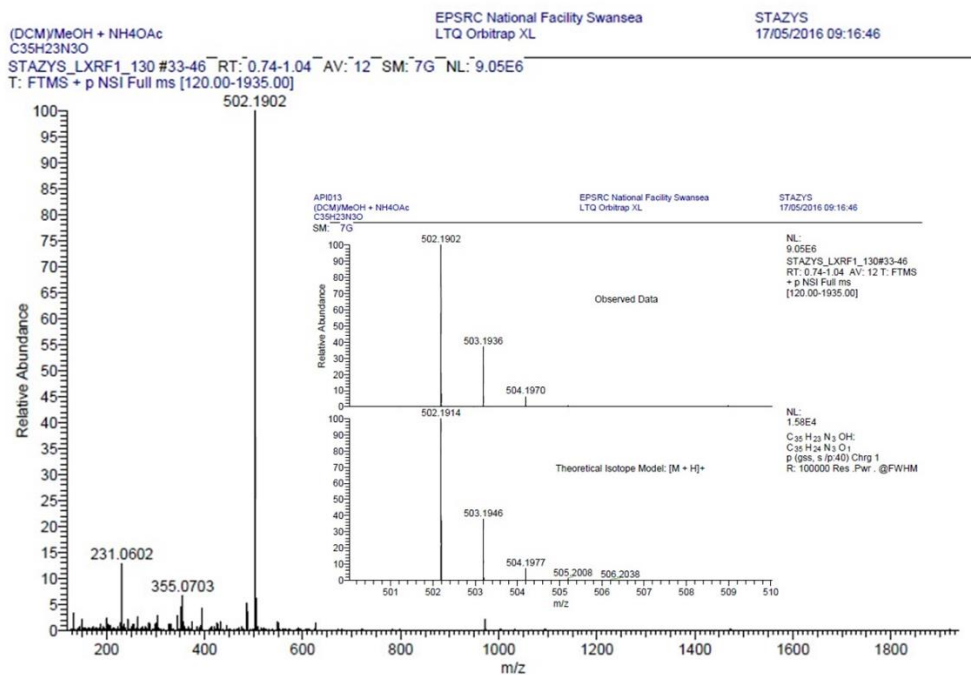
397

398 Fig. 15 <sup>1</sup>H NMR spectrum of **4PyCzBP** in CDCl<sub>3</sub>.



399

400 Fig. 16  $^{13}\text{C}$  NMR spectrum of **4PyCzBP** in  $\text{CDCl}_3$ .



401

402 Fig. 17 HR-MS spectra of **4PyCzBP**.



403

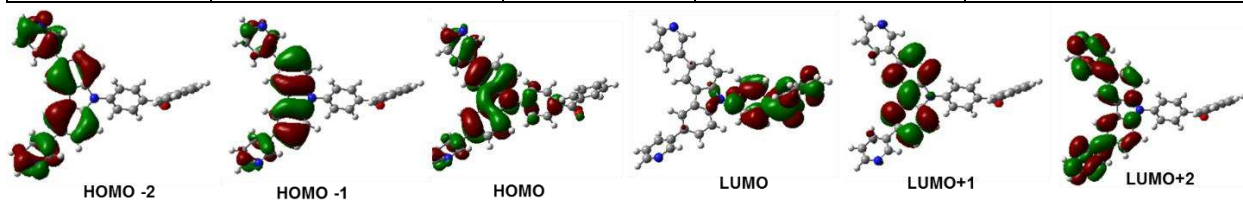
## DFT Calculations

404 The calculations were performed with the Gaussian 09,(31) revision D.018 suite of  
 405 programs. Initially the geometries of **3PyCzBP** and **4PyCzBP** were fully optimized using a DFT  
 406 methodology employing the PBE0(32) functional with the standard Pople(33) 6-31G(d,p) basis  
 407 set and Tamm–Dancoff approximation (TDA) was treated as a variant of Time-dependent  
 408 density functional theory (TD-DFT).(34) The molecular orbitals were visualized using  
 409 GaussView 5.0 software.(35)

410

411 Table 6. Main transitions and electron contour plots of molecular orbitals of **3PyCzBP**.

Transition (Wavelength)	Orbitals	Probabilities	Oscillator strength ( <i>f</i> )	Character
$S_0 \rightarrow S_1$ (366 nm)	HOMO $\rightarrow$ LUMO	97%	0.31	3Pyrdine (3Py) and carbazole (Cz) to benzophenone (BP) (CT)
$S_0 \rightarrow S_5$ (293 nm)	HOMO-1 $\rightarrow$ LUMO+1	13%	0.25	3PyCz to Cz (CT + ( $\pi$ - $\pi^*$ ))
	HOMO $\rightarrow$ LUMO+2	84%		3PyCz to 3PyCz ( $\pi$ - $\pi^*$ )
$S_0 \rightarrow S_8$ (271 nm)	HOMO-2 $\rightarrow$ LUMO	37%	0.24	3PyCz to BP (CT + ( $\pi$ - $\pi^*$ ))
	HOMO-1 $\rightarrow$ LUMO+1	31%		3PyCz to Cz (CT + ( $\pi$ - $\pi^*$ ))



412

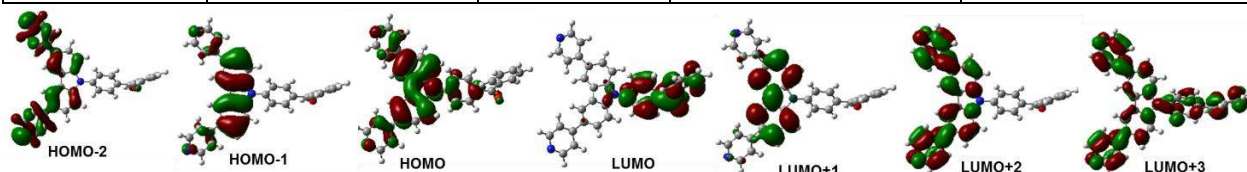
413

414

415 Table 7. Main transitions and electron contour plots of molecular orbitals of **4PyCzBP**.

Transition (Wavelength)	Orbitals	Probabilities	Oscillator strength ( <i>f</i> )	Character
$S_0 \rightarrow S_1$ (359 nm)	HOMO $\rightarrow$ LUMO	97%	0.33	4Pyrdine (4Py) and carbazole (Cz) to

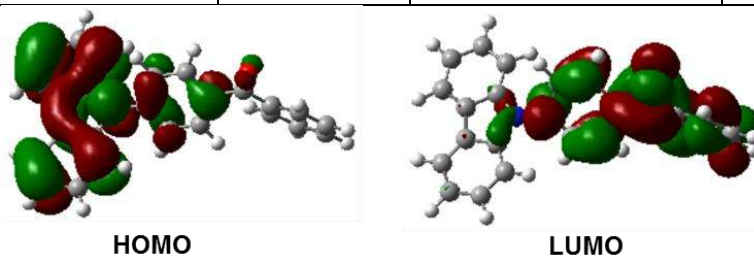
				benzophenone (BP) (CT)
$S_0 \rightarrow S_4$ (297 nm)	HOMO-1 $\rightarrow$ LUMO+1	11%	0.29	4PyCz to Cz ( $\pi$ - $\pi^*$ + CT)
	HOMO $\rightarrow$ LUMO+2	86%		4PyCz to 4PyCz ( $\pi$ - $\pi^*$ )
$S_0 \rightarrow S_7$ (266 nm)	HOMO-2 $\rightarrow$ LUMO	12%	0.45	4PyCz to BP (CT)
	HOMO-1 $\rightarrow$ LUMO+1	40%		4PyCz to Cz ( $\pi$ - $\pi^*$ + CT)
	HOMO-1 $\rightarrow$ LUMO+3	16%		4PyCz to BP (CT + $\pi$ - $\pi^*$ )



416  
417  
418

Table 8. Main transitions and electron contour plots of molecular orbitals of **CzBP**.

Transition (Wavelength)	Orbitals	Probabilities	Oscillator strength ( $f$ )	Character
$S_0 \rightarrow S_1$ (361)	HOMO $\rightarrow$ LUMO	97%	0.26	Carbazole (Cz) to benzophenone (BP) (CT)

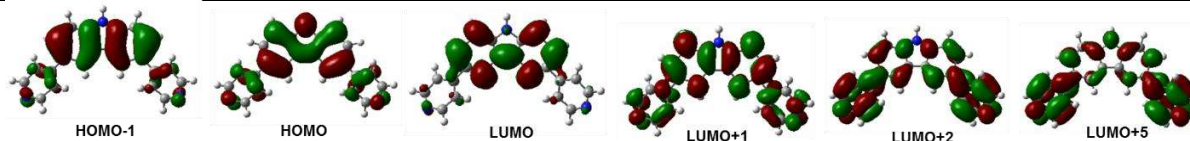


419  
420

Table 9. Main transitions and electron contour plots of molecular orbitals of **PyCz**.

Transition (Wavelength)	Orbitals	Probabilities	Oscillator strength ( $f$ )	Character
$S_0 \rightarrow S_2$ (293 nm)	HOMO-1 $\rightarrow$ LUMO	14%	0.28	Pyrdine carbazole (PyCz) to Pyrdine carbazole (PyCz) ( $\pi$ - $\pi^*$ )
	HOMO $\rightarrow$ LUMO+1	83%		PyCz to PyCz ( $\pi$ - $\pi^*$ )
$S_0 \rightarrow S_4$ (264 nm)	HOMO-1 $\rightarrow$ LUMO	50%	0.85	PyCz to PyCz ( $\pi$ - $\pi^*$ )
	HOMO-1 $\rightarrow$ LUMO+2	26%		PyCz to PyCz ( $\pi$ - $\pi^*$ )
	HOMO $\rightarrow$ LUMO+1	10%		PyCz to PyCz ( $\pi$ - $\pi^*$ )
$S_0 \rightarrow S_7$	HOMO-	56%	0.45	PyCz to PyCz ( $\pi$ - $\pi^*$ )

(247 nm)	1→LUMO+1		0.45	
	HOMO → LUMO+2	23%		PyCz to PyCz ( $\pi$ - $\pi^*$ )
$S_0 \rightarrow S_{10}$ (239 nm)	HOMO-1→LUMO	19%	0.45	PyCz to PyCz ( $\pi$ - $\pi^*$ )
	HOMO-1→LUMO+2	59%		PyCz to PyCz ( $\pi$ - $\pi^*$ )
	HOMO→LUMO+5	10%		PyCz to PyCz ( $\pi$ - $\pi^*$ )



421

422

423 Table 10. Optimized Atomic coordinates of **3PyCzBP** obtained from DFT calculations.

424 Center Atomic Atomic Coordinates (Angstroms)  
425 Number Number Type X Y Z  
426 -----

427	1	6	0	8.370275	0.517539	-0.149998
428	2	6	0	7.410758	-0.283577	-0.768893
429	3	6	0	6.351926	-0.804268	-0.024977
430	4	6	0	6.252753	-0.523914	1.337765
431	5	6	0	7.212301	0.277109	1.956677
432	6	6	0	8.271101	0.797893	1.212745
433	7	6	0	3.121177	-2.074858	-1.146026
434	8	6	0	1.768527	-1.751968	-1.038469
435	9	6	0	1.375510	-0.627885	-0.312089
436	10	6	0	2.335135	0.173138	0.306768
437	11	6	0	3.687758	-0.149792	0.199299
438	12	6	0	4.080801	-1.273834	-0.527169
439	13	6	0	5.409376	-1.591045	-0.632827
440	14	8	0	5.749755	-2.564490	-1.261964

441	15	7	0	0.134221	-0.331457	-0.213441
442	16	6	0	-0.359965	0.951518	-0.193917
443	17	6	0	-1.745846	0.853110	-0.076595
444	18	6	0	-2.074374	-0.539606	-0.025535
445	19	6	0	-0.880257	-1.254141	-0.113068
446	20	6	0	-3.282256	-1.259160	0.087535
447	21	6	0	-3.251264	-2.658374	0.108660
448	22	6	0	-2.041321	-3.342592	0.019156
449	23	6	0	-0.830299	-2.653216	-0.093570
450	24	6	0	0.309538	2.178753	-0.270682
451	25	6	0	-0.464467	3.342145	-0.225914
452	26	6	0	-1.850934	3.277920	-0.109109
453	27	6	0	-2.503580	2.041970	-0.033595
454	28	6	0	-4.413401	-3.356350	0.217596
455	29	6	0	-2.577405	4.426900	-0.068044
456	30	6	0	-3.924143	4.432935	-0.415899
457	31	6	0	-4.636131	5.626750	-0.362135
458	32	6	0	-3.966878	6.771682	0.039848
459	33	7	0	-2.660658	6.796982	0.383500
460	34	6	0	-1.995616	5.622786	0.321471
461	35	6	0	-4.414345	-4.673509	0.648238
462	36	7	0	-5.532192	-5.420867	0.777939
463	37	6	0	-6.700939	-4.821649	0.461973

464	38	6	0	-6.801432	-3.511083	0.023041
465	39	6	0	-5.632695	-2.767051	-0.100304
466	40	1	0	9.205234	0.928251	-0.736648
467	41	1	0	7.489044	-0.504740	-1.843583
468	42	1	0	5.417751	-0.934566	1.924396
469	43	1	0	7.134090	0.498142	3.031399
470	44	1	0	9.027849	1.429673	1.700788
471	45	1	0	3.431149	-2.961257	-1.718927
472	46	1	0	1.011744	-2.383753	-1.526451
473	47	1	0	2.025165	1.059578	0.879605
474	48	1	0	4.444524	0.481914	0.687410
475	49	1	0	-4.241149	-0.724857	0.158562
476	50	1	0	-2.038604	-4.442437	0.037452
477	51	1	0	0.126971	-3.190450	-0.164370
478	52	1	0	1.404656	2.225874	-0.362858
479	53	1	0	0.029154	4.323461	-0.283836
480	54	1	0	-3.598838	1.998193	0.058561
481	55	1	0	-4.421029	3.503269	-0.730261
482	56	1	0	-5.702077	5.661046	-0.631550
483	57	1	0	-4.531978	7.714511	0.081523
484	58	1	0	-0.930471	5.615508	0.596086
485	59	1	0	-3.448960	-5.137360	0.898982
486	60	1	0	-7.626564	-5.408043	0.558714

487            61        1        0    -7.779445 -3.070888 -0.221328

488            62        1        0    -5.672203 -1.723422 -0.445670

489

490    Table **11**. Optimized Atomic coordinates of **4PyCzBP** obtained from DFT calculations.

491	Center	Atomic	Atomic	Coordinates (Angstroms)		
492	Number	Number	Type	X	Y	Z
493	-----					
494	1	6	0	8.935797	0.176230	0.173023
495	2	6	0	7.921793	-0.486484	-0.417081
496	3	6	0	6.637730	-0.383452	0.018998
497	4	6	0	6.453030	0.362537	1.123804
498	5	6	0	7.460057	1.029058	1.725814
499	6	6	0	8.706723	0.947419	1.242279
500	7	6	0	3.390065	-1.745322	-0.900608
501	8	6	0	2.066084	-1.543286	-0.793193
502	9	6	0	1.498594	-0.416507	-0.314076
503	10	6	0	2.427113	0.501328	0.026500
504	11	6	0	3.755472	0.314597	-0.060108
505	12	6	0	4.298261	-0.835756	-0.496983
506	13	6	0	5.644122	-1.085555	-0.621801
507	14	8	0	5.980451	-1.998454	-1.357066
508	15	6	0	-0.431329	0.888225	-0.201751
509	16	6	0	-1.743346	0.701348	-0.089552
510	17	6	0	-1.927017	-0.620108	-0.050930

511	18	6	0	-0.694697	-1.153186	-0.124173
512	19	7	0	0.214593	-0.235533	-0.221390
513	20	6	0	-3.065213	-1.338990	0.050153
514	21	6	0	-3.047909	-2.682516	0.118077
515	22	6	0	-1.807569	-3.215292	0.119050
516	23	6	0	-0.668143	-2.481151	0.019789
517	24	6	0	-0.076859	2.180408	-0.369580
518	25	6	0	-0.972513	3.172596	-0.317894
519	26	6	0	-2.306826	2.990200	-0.130395
520	27	6	0	-2.665789	1.698668	-0.038026
521	28	6	0	-4.178483	-3.433765	0.211789
522	29	6	0	-3.202193	4.013179	-0.074174
523	30	6	0	-4.180235	-4.777507	0.282360
524	31	6	0	-5.339210	-5.483215	0.373758
525	32	7	0	-6.481592	-4.956465	0.398843
526	33	6	0	-6.520639	-3.695957	0.331124
527	34	6	0	-5.442689	-2.907181	0.238566
528	35	6	0	-2.856576	5.315258	-0.167360
529	36	6	0	-3.783416	6.294807	-0.104497
530	37	7	0	-5.018979	6.090106	0.043405
531	38	6	0	-5.377231	4.882697	0.137234
532	39	6	0	-4.533291	3.838458	0.086892
533	40	1	0	9.961741	0.083047	-0.222422

534	41	1	0	8.202593	-1.091850	-1.295642
535	42	1	0	5.492434	0.412272	1.656727
536	43	1	0	7.269750	1.616658	2.640396
537	44	1	0	9.535576	1.480993	1.736036
538	45	1	0	3.693608	-2.712863	-1.337043
539	46	1	0	1.462479	-2.350366	-1.230163
540	47	1	0	2.152048	1.462078	0.479845
541	48	1	0	4.365563	1.192703	0.198393
542	49	1	0	-3.997451	-0.763055	0.080033
543	50	1	0	-1.633217	-4.295839	0.233281
544	51	1	0	0.262620	-3.055679	0.121676
545	52	1	0	0.946583	2.495660	-0.611742
546	53	1	0	-0.539073	4.172127	-0.473200
547	54	1	0	-3.710784	1.387842	0.076382
548	55	1	0	-3.268524	-5.391546	0.268870
549	56	1	0	-5.314500	-6.585563	0.430294
550	57	1	0	-7.529517	-3.247901	0.352007
551	58	1	0	-5.658458	-1.830402	0.187826
552	59	1	0	-1.823504	5.668663	-0.294994
553	60	1	0	-3.478767	7.353129	-0.182747
554	61	1	0	-6.460608	4.715112	0.268430
555	62	1	0	-5.014377	2.854964	0.186099

556 Table 12. Optimized Atomic coordinates of **CzBP** obtained from DFT calculations.



557	Center	Atomic	Atomic	Coordinates (Angstroms)		
558	Number	Number	Type	X	Y	Z
559	-----					
560	1	6	0	-6.806531	5.381945	0.549127
561	2	6	0	-7.240051	6.204869	1.527717
562	3	6	0	-7.620160	5.666917	2.690682
563	4	6	0	-7.548093	4.339833	2.882538
564	5	6	0	-7.071003	3.494632	1.940694
565	6	6	0	-6.739447	4.060500	0.760709
566	7	6	0	-5.237999	1.526821	0.683593
567	8	6	0	-6.289332	1.232183	1.477562
568	9	6	0	-6.533457	-0.087429	1.588786
569	10	6	0	-5.838582	-1.016002	0.899228
570	11	6	0	-4.814741	-0.740997	0.063747
571	12	6	0	-4.549622	0.580035	0.015038
572	13	7	0	-4.152251	-1.649217	-0.589125
573	14	6	0	-2.936987	-1.569768	-1.029736
574	15	6	0	-2.582871	-2.699325	-1.666962
575	16	6	0	-3.636085	-3.507321	-1.593689
576	17	6	0	-4.581436	-2.823261	-0.934923
577	18	6	0	-1.953167	-0.657879	-0.894929
578	19	6	0	-0.740523	-0.835580	-1.454214
579	20	6	0	-0.448708	-1.955693	-2.141214
580	21	6	0	-1.384677	-2.923727	-2.238016

581	22	6	0	-3.777958	-4.755151	-2.077537
582	23	6	0	-4.971007	-5.360330	-1.919870
583	24	6	0	-5.971933	-4.683105	-1.323149
584	25	6	0	-5.783265	-3.431584	-0.858587
585	26	6	0	-7.024622	2.144321	2.196352
586	27	8	0	-7.684406	1.722791	3.131292
587	28	1	0	-6.542678	5.804246	-0.435772
588	29	1	0	-7.308895	7.292158	1.358785
589	30	1	0	-7.997240	6.324386	3.492679
590	31	1	0	-7.877230	3.991443	3.876267
591	32	1	0	-6.473369	3.473088	-0.129998
592	33	1	0	-4.845079	2.549037	0.579770
593	34	1	0	-7.326267	-0.476091	2.251473
594	35	1	0	-6.112219	-2.048956	1.154959
595	36	1	0	-3.780855	0.992130	-0.651258
596	37	1	0	-2.039466	0.252338	-0.288040
597	38	1	0	0.044957	-0.070941	-1.323956
598	39	1	0	0.551416	-2.101477	-2.581962
599	40	1	0	-1.148361	-3.864256	-2.759351
600	41	1	0	-2.964171	-5.278697	-2.602782
601	42	1	0	-5.137262	-6.377113	-2.312620
602	43	1	0	-6.966857	-5.155490	-1.248822
603	44	1	0	-6.692029	-2.949819	-0.474342

604

605 Table 13. Optimized Atomic coordinates of **PyCz** obtained from DFT calculations.

606	Center	Atomic	Atomic	Coordinates (Angstroms)		
607	Number	Number	Type	X	Y	Z
608	-----					
609	1	6	0	-1.132907	3.309931	0.989010
610	2	6	0	-0.655795	2.169817	0.300516
611	3	6	0	-1.541423	1.103501	0.094593
612	4	6	0	-2.853511	1.174308	0.559164
613	5	6	0	-3.296282	2.336435	1.246672
614	6	6	0	-2.432505	3.411854	1.464012
615	7	6	0	-3.982869	0.273862	0.510661
616	8	6	0	-5.052507	0.936126	1.171461
617	9	7	0	-4.609907	2.161577	1.597299
618	10	6	0	-4.180125	-1.000204	-0.018671
619	11	6	0	-5.425483	-1.632713	0.096045
620	12	6	0	-6.466094	-0.942018	0.760600
621	13	6	0	-6.302345	0.326423	1.298302
622	14	6	0	-5.648513	-2.975639	-0.457018
623	15	6	0	0.730677	2.109039	-0.183751
624	16	6	0	-6.885930	-3.632467	-0.359667
625	17	6	0	-7.041952	-4.905564	-0.902121
626	18	7	0	-6.079167	-5.580511	-1.530631

627	19	6	0	-4.902484	-4.961028	-1.625583
628	20	6	0	-4.638163	-3.690840	-1.119746
629	21	6	0	1.641746	3.159489	0.009832
630	22	6	0	2.945038	3.047571	-0.471015
631	23	7	0	3.418342	1.988699	-1.123482
632	24	6	0	2.557867	0.989035	-1.309855
633	25	6	0	1.235334	0.995131	-0.872404
634	26	1	0	-0.466605	4.144756	1.158857
635	27	1	0	-1.215297	0.212218	-0.427952
636	28	1	0	-2.753132	4.304059	1.985469
637	29	1	0	-5.162088	2.827647	2.089560
638	30	1	0	-3.357373	-1.495129	-0.520503
639	31	1	0	-7.435207	-1.411655	0.860665
640	32	1	0	-7.127344	0.816445	1.798297
641	33	1	0	-7.731589	-3.169727	0.131466
642	34	1	0	-8.004436	-5.399414	-0.818514
643	35	1	0	-4.110573	-5.500169	-2.135007
644	36	1	0	-3.647365	-3.275355	-1.248869
645	37	1	0	1.355809	4.064480	0.528795
646	38	1	0	3.635920	3.869143	-0.312434
647	39	1	0	2.932000	0.120000	-1.840713
648	40	1	0	0.616746	0.130765	-1.075073
649						
650						

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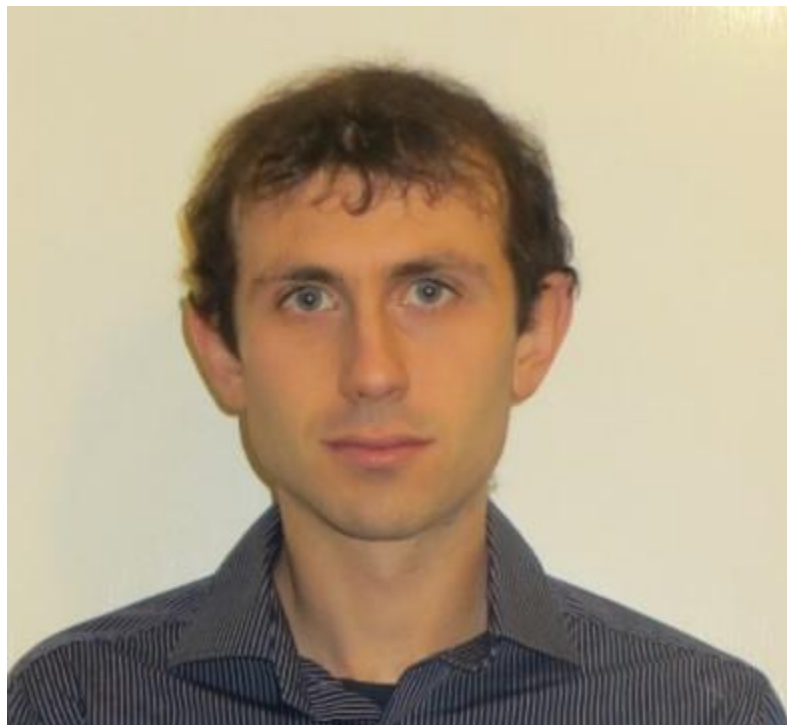
725

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732

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737

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739 supervision of Prof. David N. Harpp as an FCAR scholar where he conducting research in  
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747 design of: (I) luminophores for energy-efficient visual displays and flat panel lighting based on  
748 organic light emitting diode (OLED) and light-emitting electrochemical cell (LEEC) device  
749 architectures; (II) light harvesting dyes for dye-sensitized solar cells (DSSCs) and organic  
750 photovoltaics; (III) sensing materials employed in electrochemiluminescence; and (IV)  
751 photoredox catalysts for organic reactions.



752  
753 **Caption List**

754  
755 Scheme 1. Synthesis of **4PyCzBP** and **3PyCzBP**. Reagents and conditions: <sup>a</sup> MeCN, 273 to 298  
756 K, 2 h. <sup>b</sup> DMF, KO<sup>t</sup>Bu (1 equiv.), 150 °C, 19 h. <sup>c</sup> 1,4-dioxane:H<sub>2</sub>O (4:1 v/v), Cs<sub>2</sub>CO<sub>3</sub> (6 equiv.),  
757 Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 equiv.), 110 °C, 48 h. All reactions were conducted under an N<sub>2</sub> atmosphere.

758  
759 Fig. 1 Structure of TADF emitters and corresponding DFT calculated HOMO and LUMO  
760 electron density distribution.

761  
762 Fig. 2 Photophysical properties of a) **3PyCzBP** and b) **4PyCzBP**, normalised UV-Vis spectrum  
763 of collected in MeCN at 298 K (blue line) and normalised emission spectra collected in DCM at



764 298 K (dashed orange line), in MeCN at 298 K (dotted red line) and as spin-coated PMMA-  
765 doped films (green) (10 wt%) on quartz substrate.

766 Fig. 3 Normalised fluorescence and phosphorescence emission spectrum of a) **3PyCzBP** and b)  
767 **4PyCzBP** on PMMA-doped film formed (10 wt % of compound) by spin-coating deposition on  
768 quartz substrate. Fluorescence and phosphorescence spectra measured at 293 and 77 K,  
769 respectively and phosphorescence spectra are measured with a 10  $\mu$ s delay time.

770 Fig. 4 a) Emission decay of **3PyCzBP** and **4PyCzBP** collected at 300 K ( $\lambda_{exc} = 378$  nm) in  
771 PMMA-doped thin films (10 wt% of emitter), b) Emission decay of **4PyCzBP** ( $\lambda_{exc} = 378$  nm)  
772 collected as PMMA-doped thin film (10 wt% of emitter) at 77 K (in blue), at 150 K (in yellow),  
773 at 200 K (in grey) and at 300 K (in orange). Thin films are formed by spin-coating deposition on  
774 quartz substrate.

775 Fig. 5 Schematic representation of the devices A and B (left) and chemical structures of the  
776 materials used in the devices (right).

777 Fig. 6 Electroluminescent performance of devices A and B: a) EQE vs luminance, b) luminance  
778 vs current efficiency and power efficiency.

779 Fig. 7 Electroluminescence spectra of devices A and B measured at 10 V. The inset shows the  
780 photograph of device A.

781 Fig. 8 Cyclic voltammogram (CV), black, and differential pulse voltammogram (DPV), yellow,  
782 of **3PyCzBP** and **4PyCzBP** in MeCN solution, reported versus SCE ( $Fc/Fc^+ = 0.38$  V in  
783 MeCN).

784 Fig. 9 Emission decay of **3PyCzBP** ( $\lambda_{exc} = 378$  nm) collected on PMMA-doped thin film (10  
785 w/w % of compound) formed by spin-coating deposition on quartz substrate at 77 K (in blue), at  
786 150 K (in yellow), at 200 K (in grey) and at 300 K (in orange).

787 Fig. 10  $^1H$  NMR spectrum of (4-(3,6-dibromo-9H-carbazol-9-yl)phenyl)(phenyl)methanone in  
788  $CDCl_3$ .

789 Fig. 11  $^{13}C$  NMR spectrum of (4-(3,6-dibromo-9H-carbazol-9-yl)phenyl)(phenyl)methanone in  
790  $CDCl_3$ .

791 Fig. **12**  $^1\text{H}$  NMR spectrum of **3PyCzBP** in  $\text{CDCl}_3$ .

792 Fig. **13**  $^{13}\text{C}$  NMR spectrum of **3PyCzBP** in  $\text{CDCl}_3$ .

793 Fig. **14** HR-MS spectra of **3PyCzBP**.

794 Fig. **15**  $^1\text{H}$  NMR spectrum of **4PyCzBP** in  $\text{CDCl}_3$ .

795 Fig. **16**  $^{13}\text{C}$  NMR spectrum of **4PyCzBP** in  $\text{CDCl}_3$ .

796 Fig. **17** HR-MS spectra of **4PyCzBP**.

797 Table **1**. UV-Vis absorption data of **3PyCzBP** and **4PyCzBP**.

798 Table **2**. Photophysical properties of **3PyCzBP** and **4PyCzBP**.

799 Table **3**. The electroluminescence performances of the device A and B.

800 Table **4**. The electroluminescence performances of the device A and B at  $100 \text{ cd m}^{-2}$ .

801 Table **5**. Temperature-dependent emission decays of **3PyCzBP** and **4PyCzBP**.

802 Table **6**. Main transitions and electron contour plots of molecular orbitals of **3PyCzBP**.

803 Table **7**. Main transitions and electron contour plots of molecular orbitals of **4PyCzBP**.

804 Table **8**. Main transitions and electron contour plots of molecular orbitals of **CzBP**.

805 Table **9**. Main transitions and electron contour plots of molecular orbitals of **PyCz**.

806 Table **10**. Optimized Atomic coordinates of **3PyCzBP** obtained from DFT calculations.

807 Table **11**. Optimized Atomic coordinates of **4PyCzBP** obtained from DFT calculations.

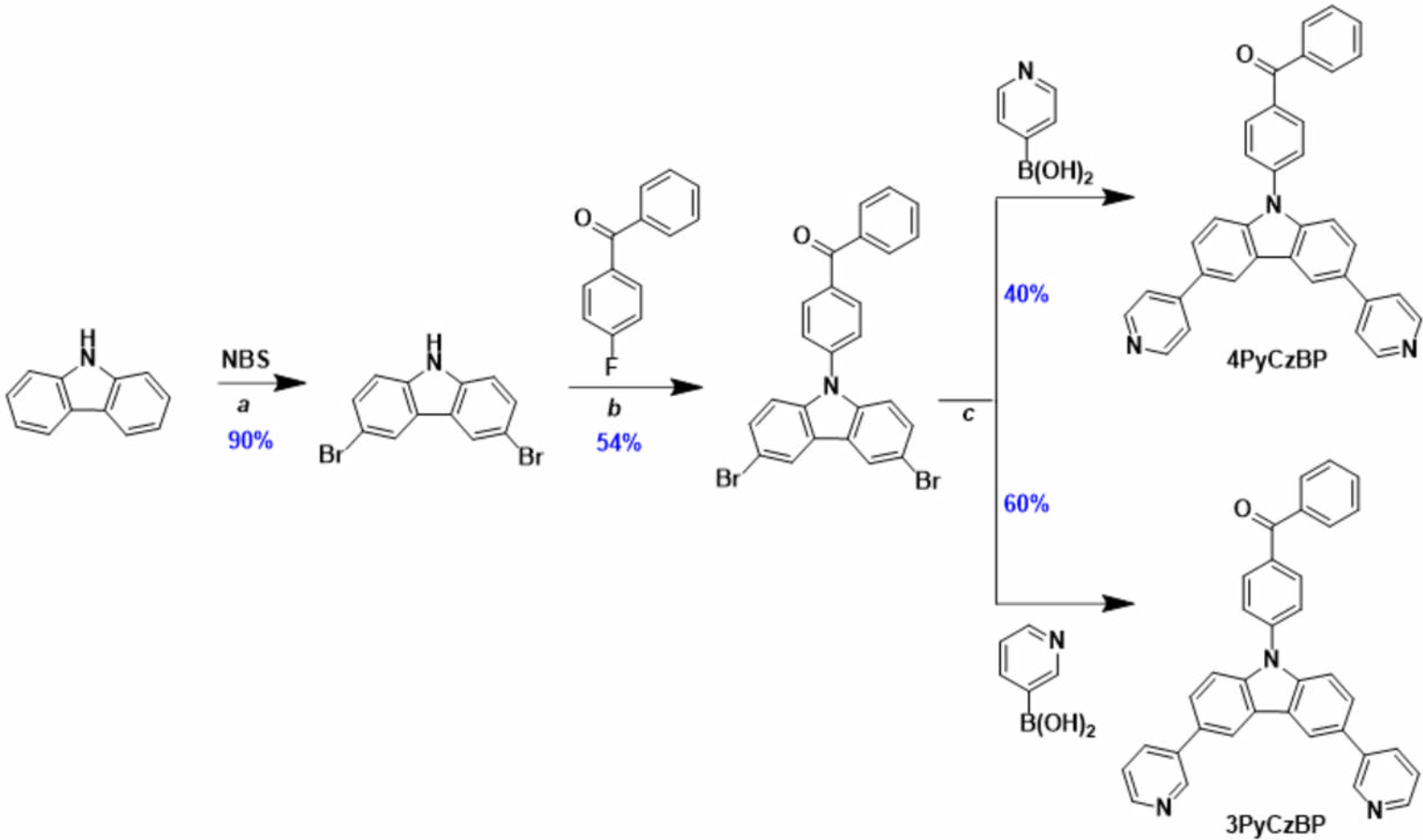
808 Table **12**. Optimized Atomic coordinates of **CzBP** obtained from DFT calculations.

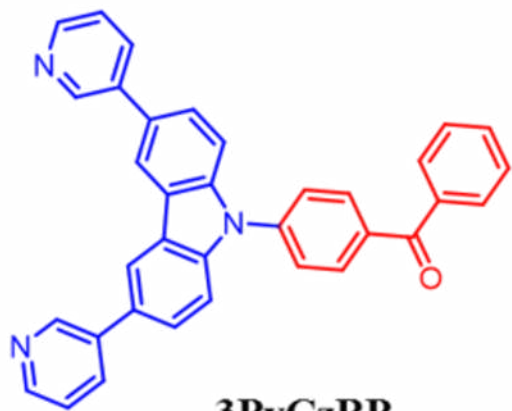
809 Table **13**. Optimized Atomic coordinates of **PyCz** obtained from DFT calculations.

810

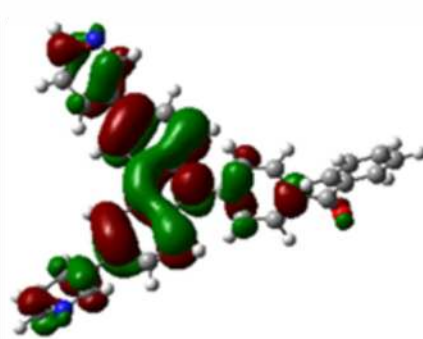
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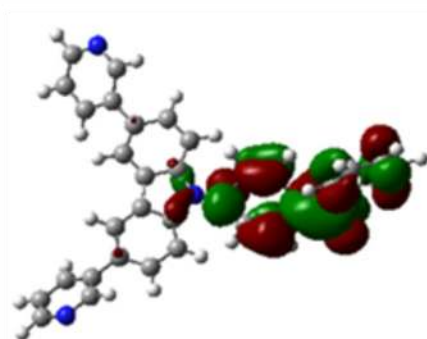




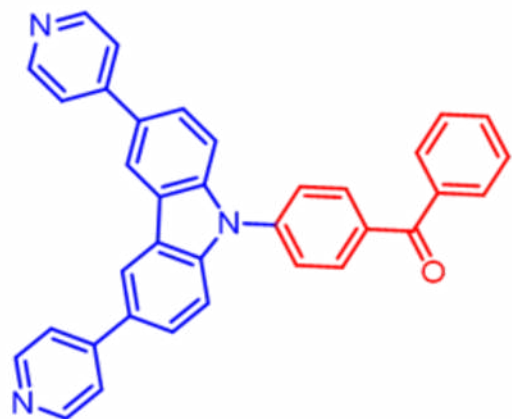
**3PyCzBP**  
 $\Delta E_{ST} = 0.41 \text{ eV}$



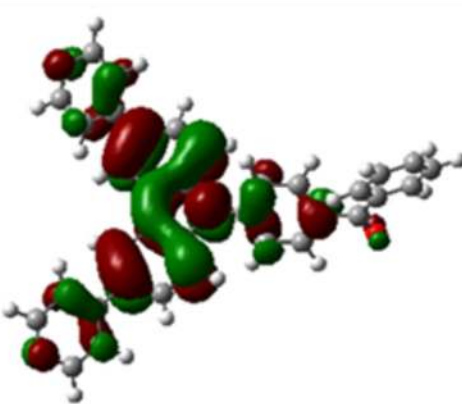
**HOMO**  
5.83 eV



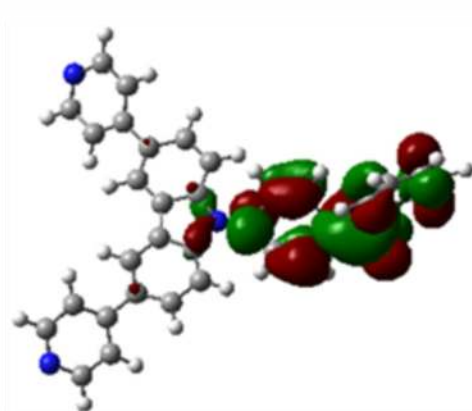
**LUMO**  
1.89 eV



**4PyCzBP**  
 $\Delta E_{ST} = 0.45 \text{ eV}$



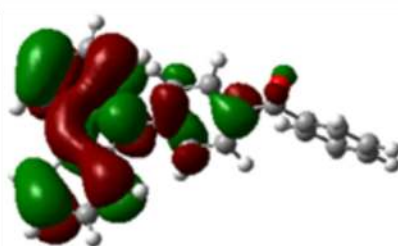
**HOMO**  
5.99 eV



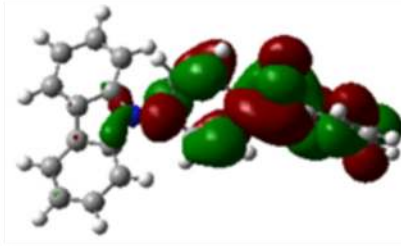
**LUMO**  
1.97 eV



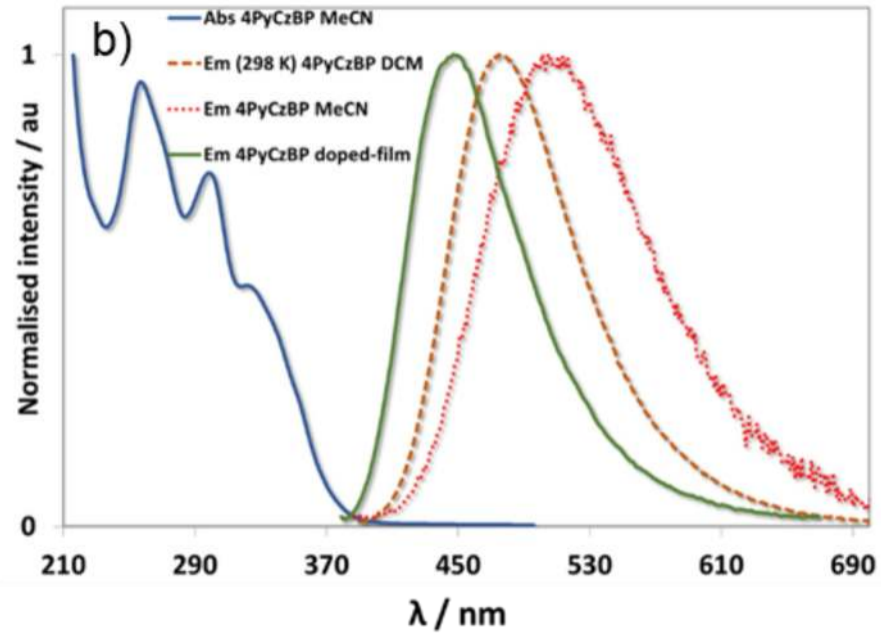
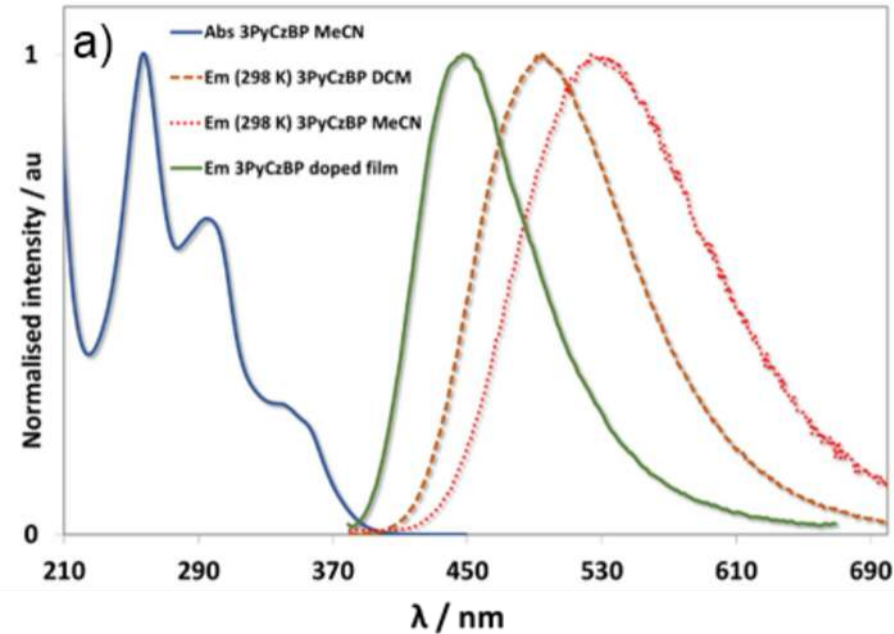
**CzBP**  
 $\Delta E_{ST} = 0.46 \text{ eV}$

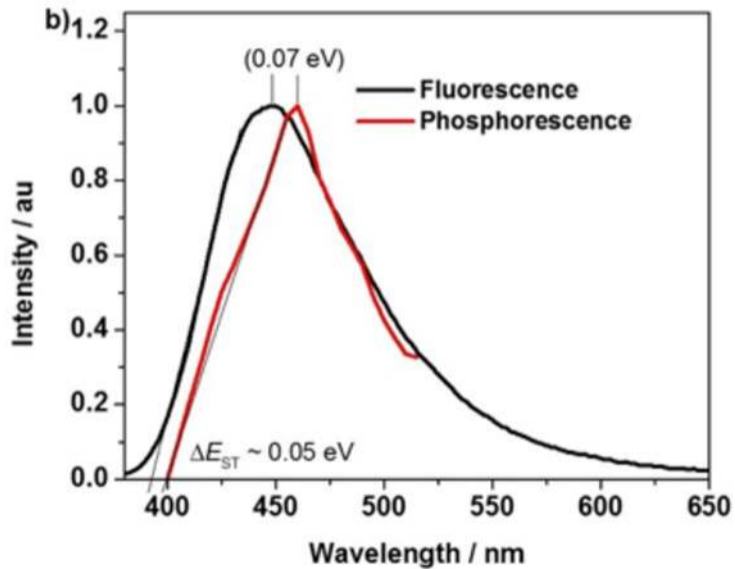
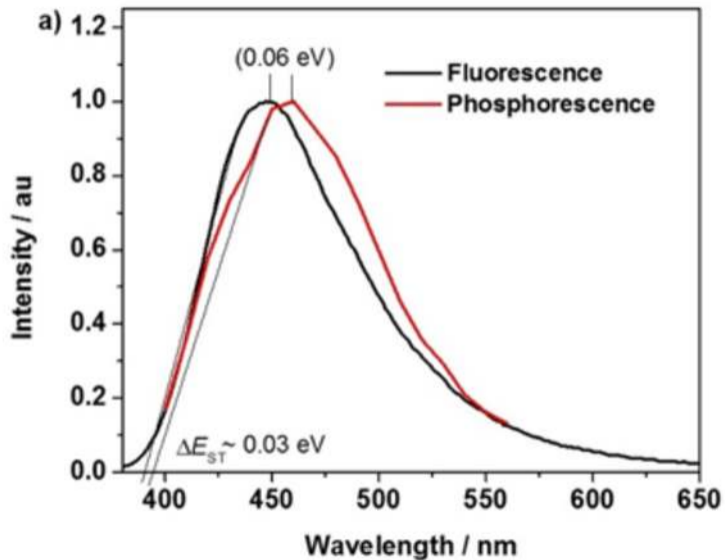


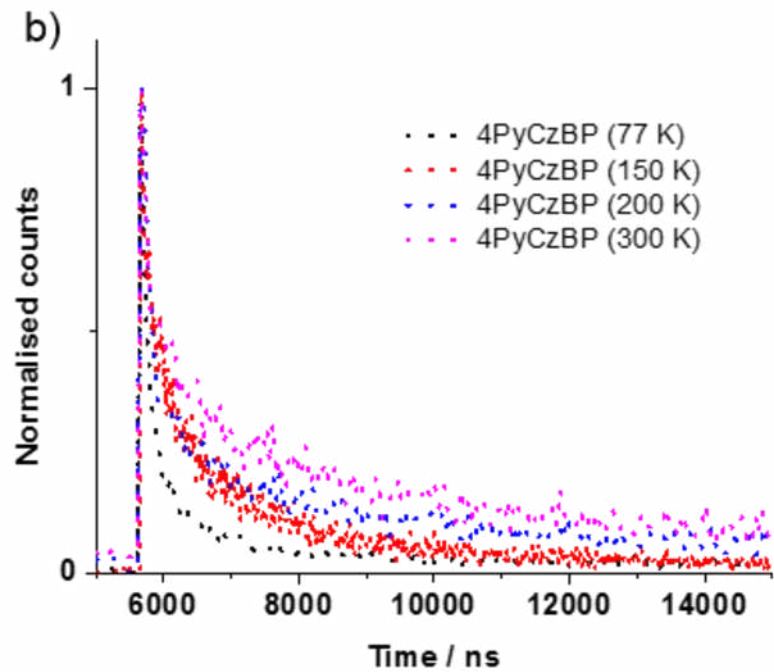
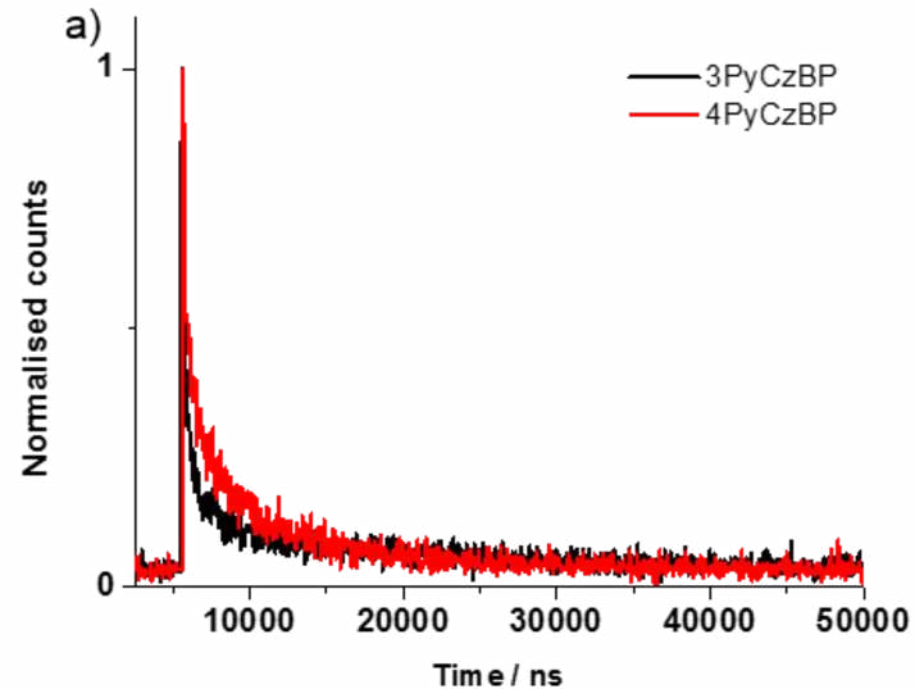
**HOMO**  
5.76 eV



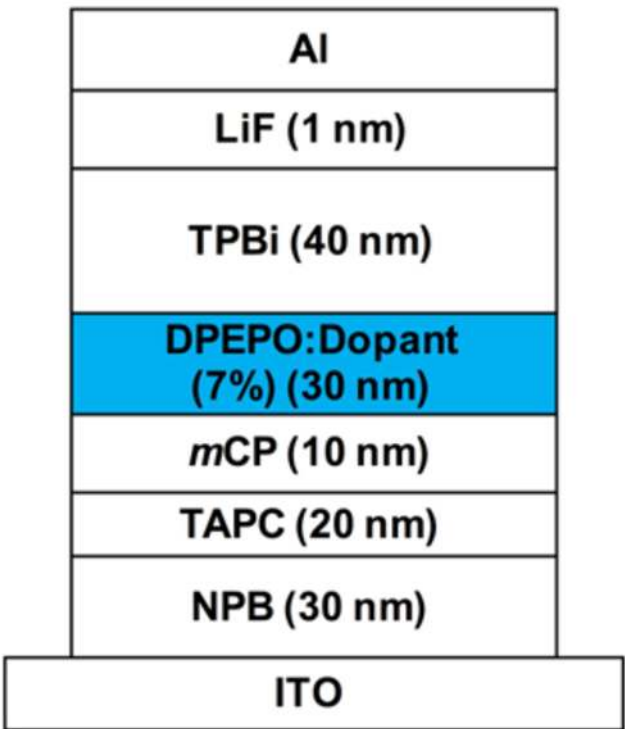
**LUMO**  
1.75 eV



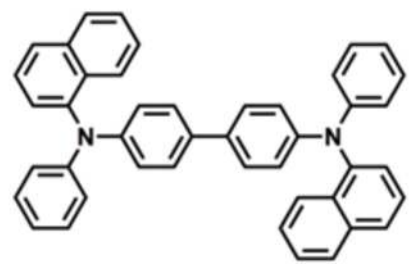




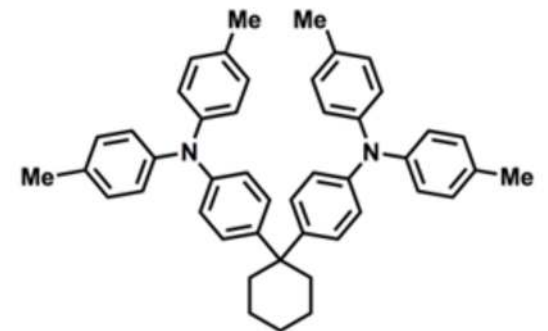




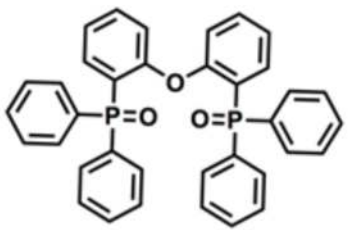
Devices A-B



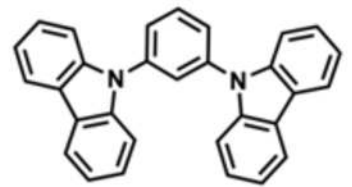
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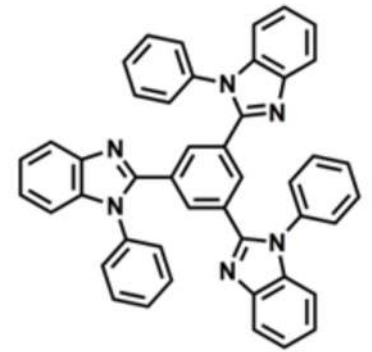
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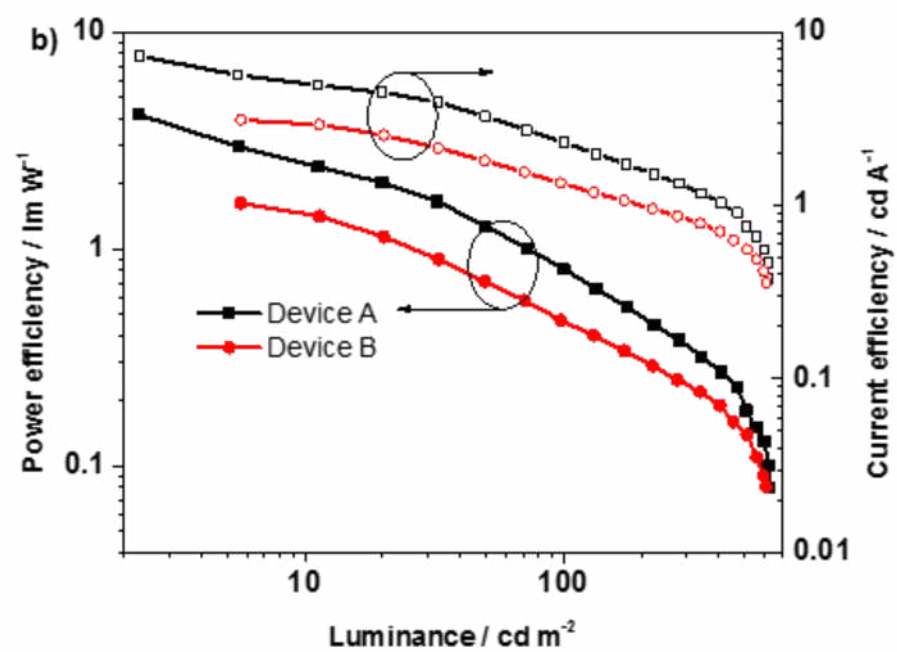
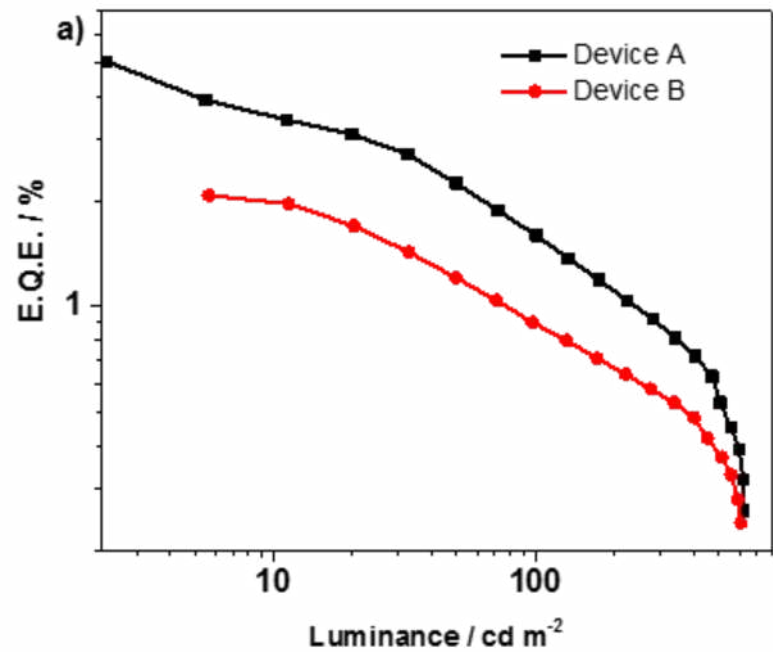
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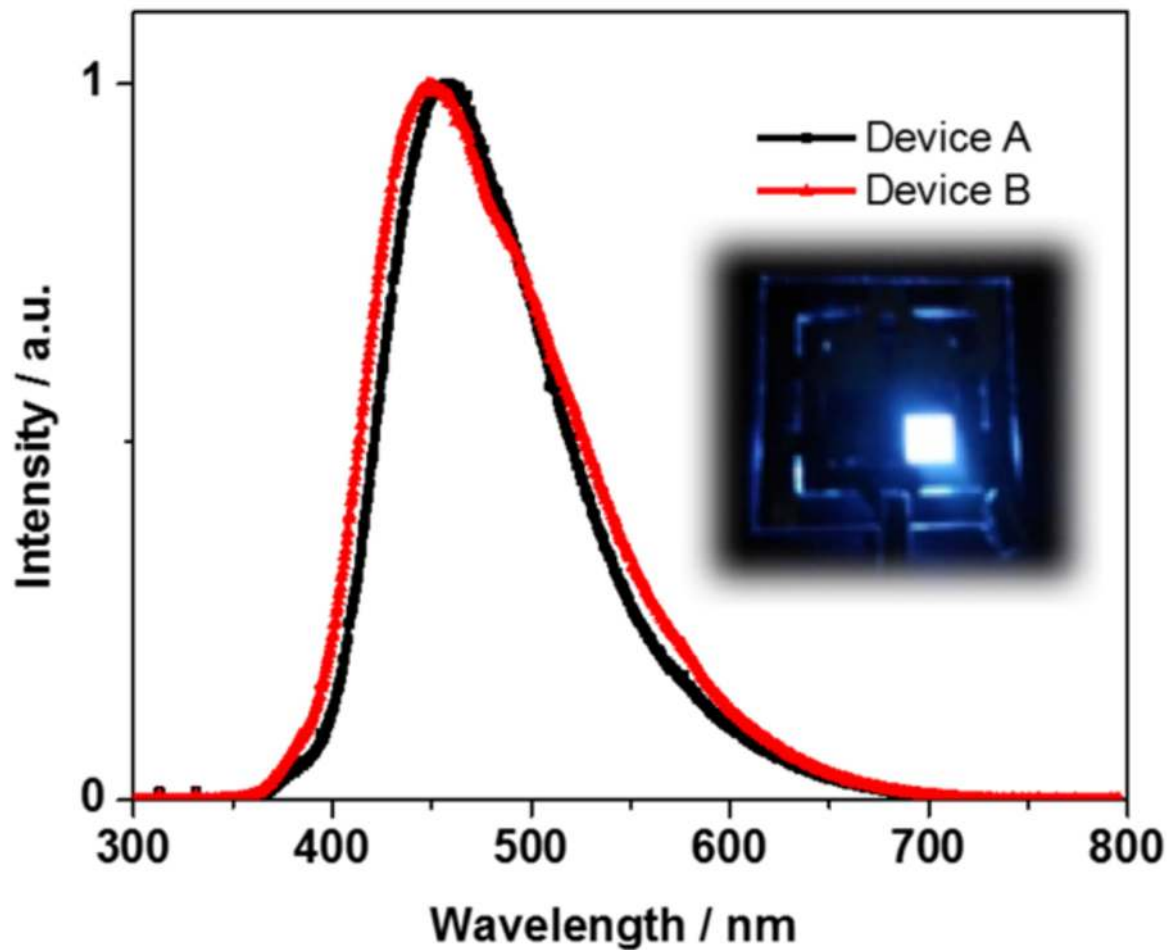


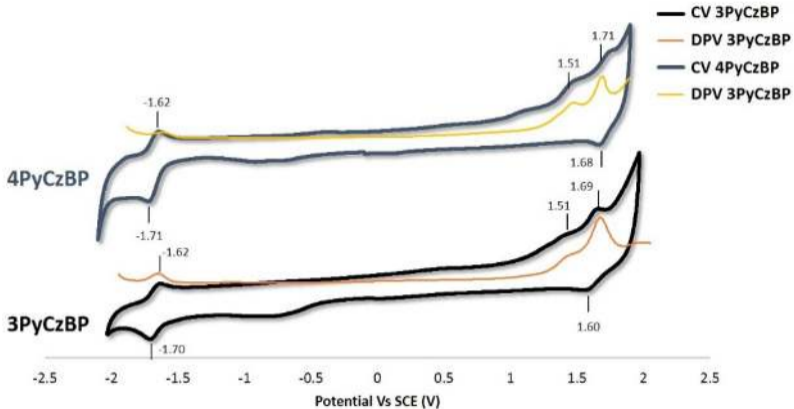
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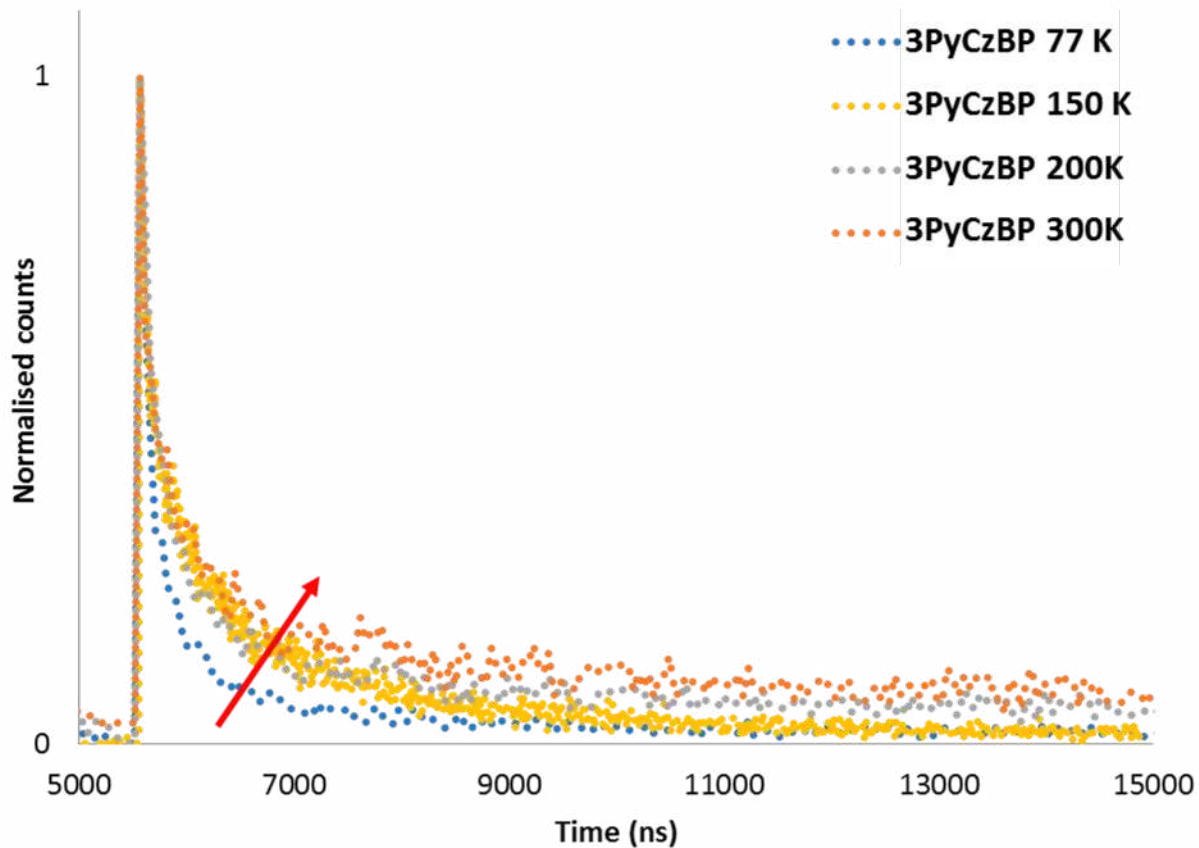


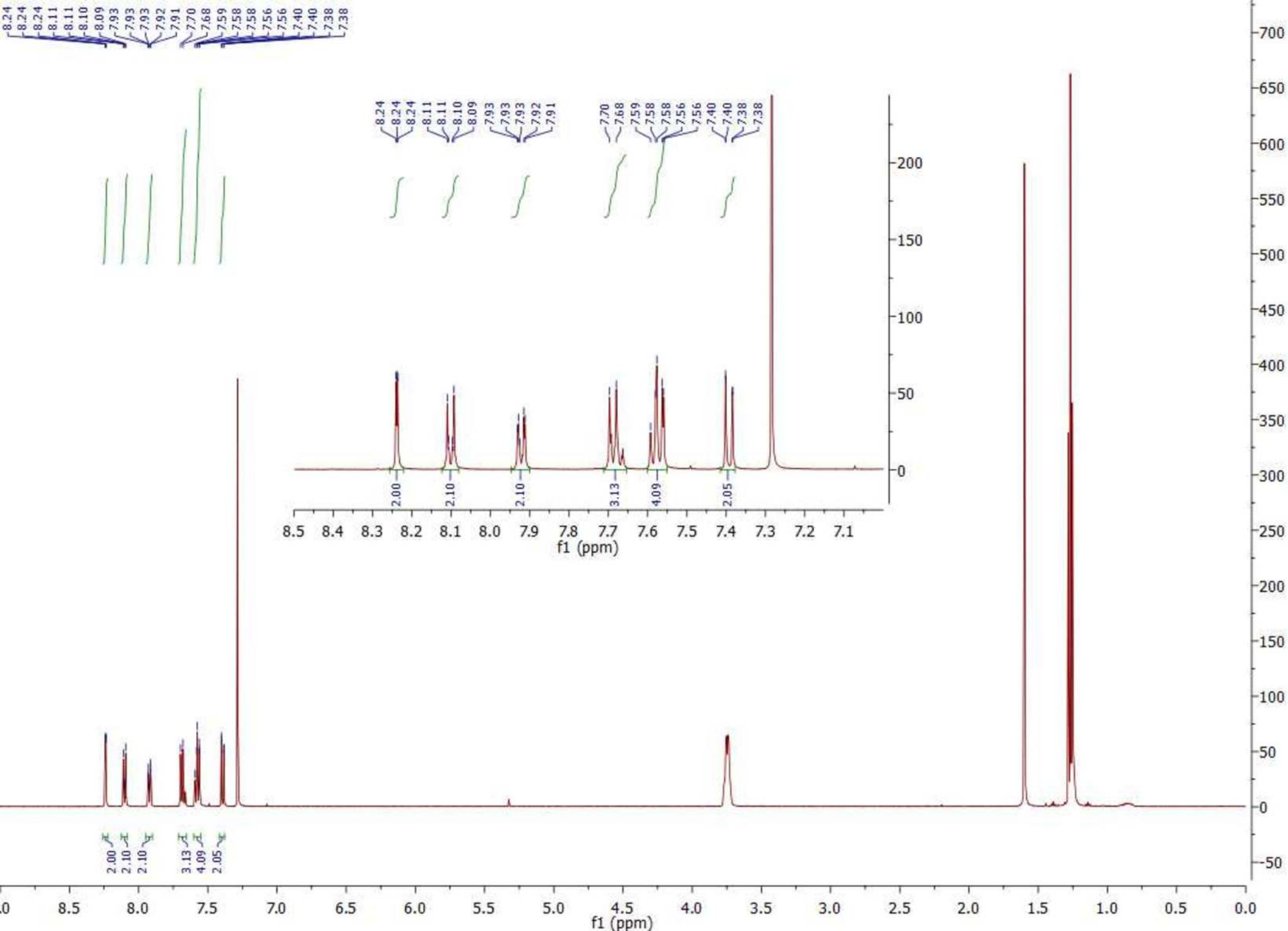
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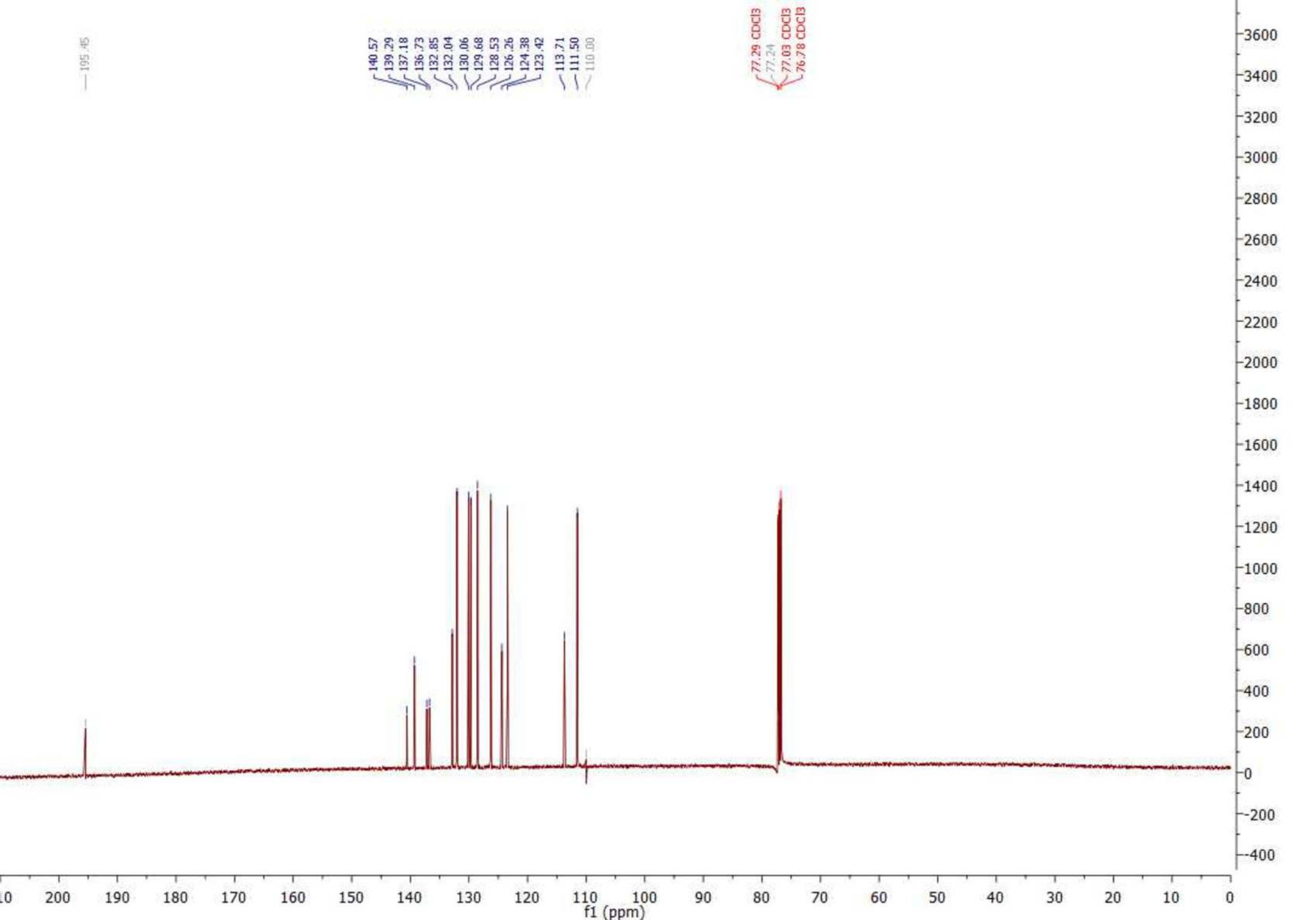


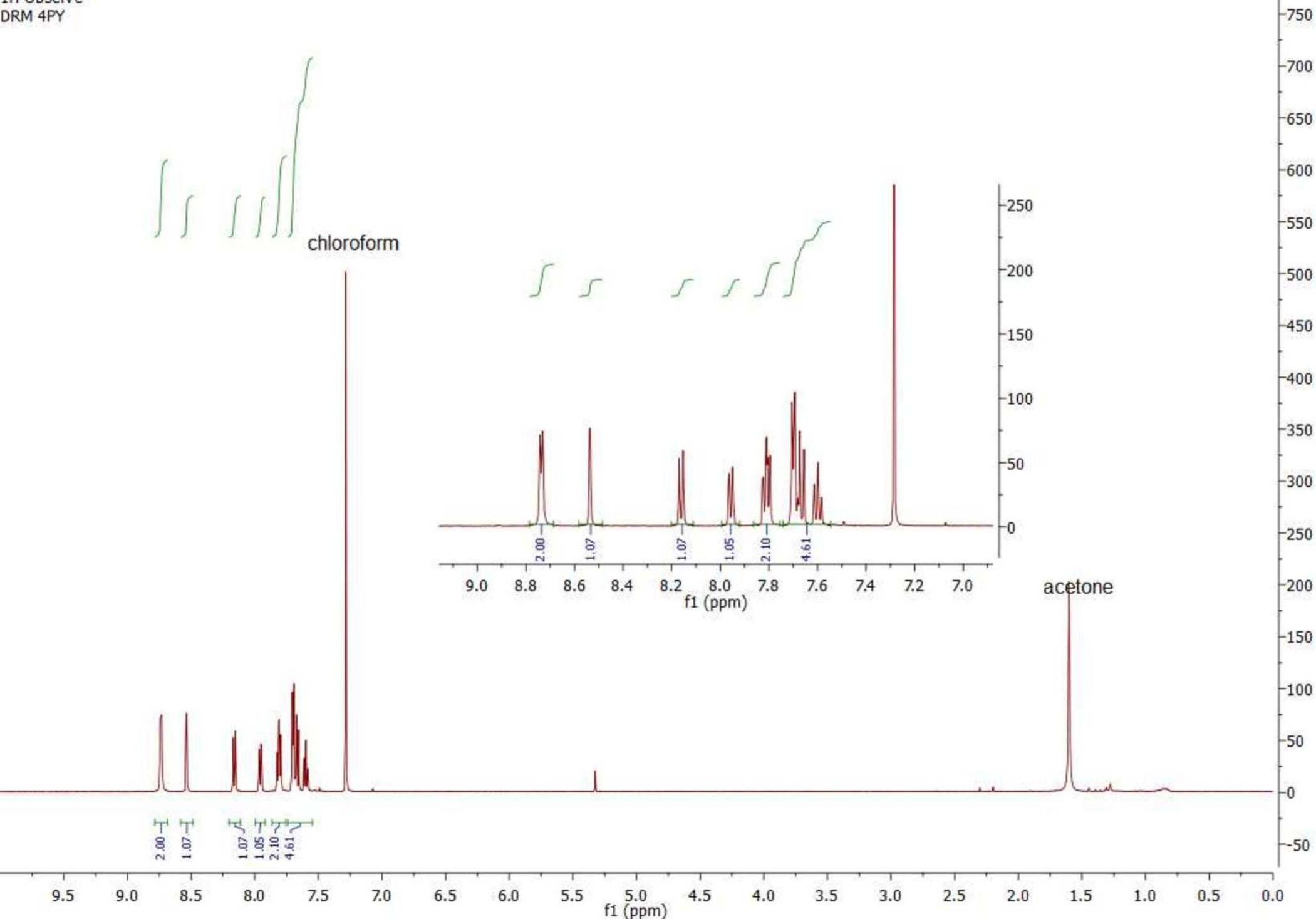




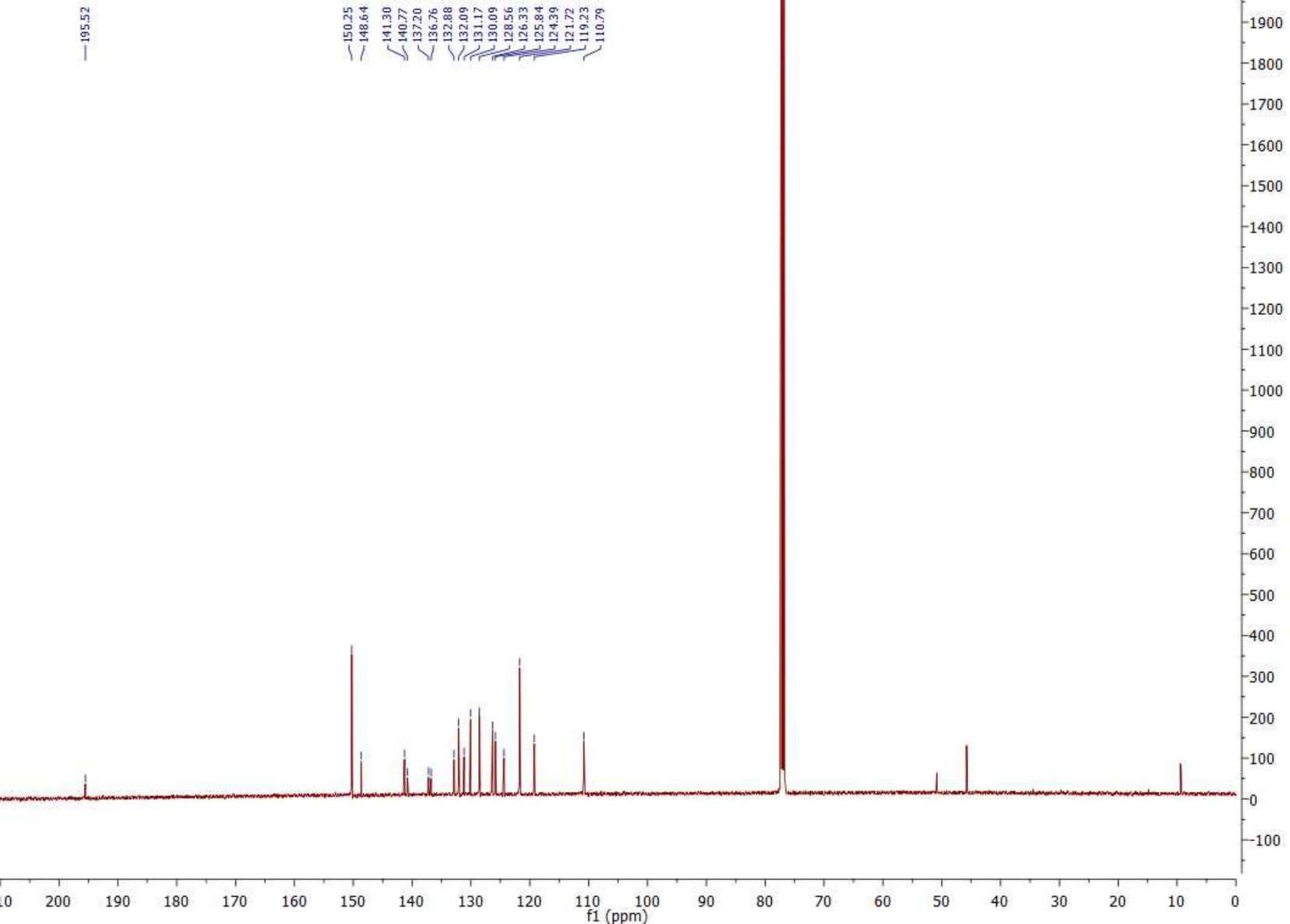


— 195 .45







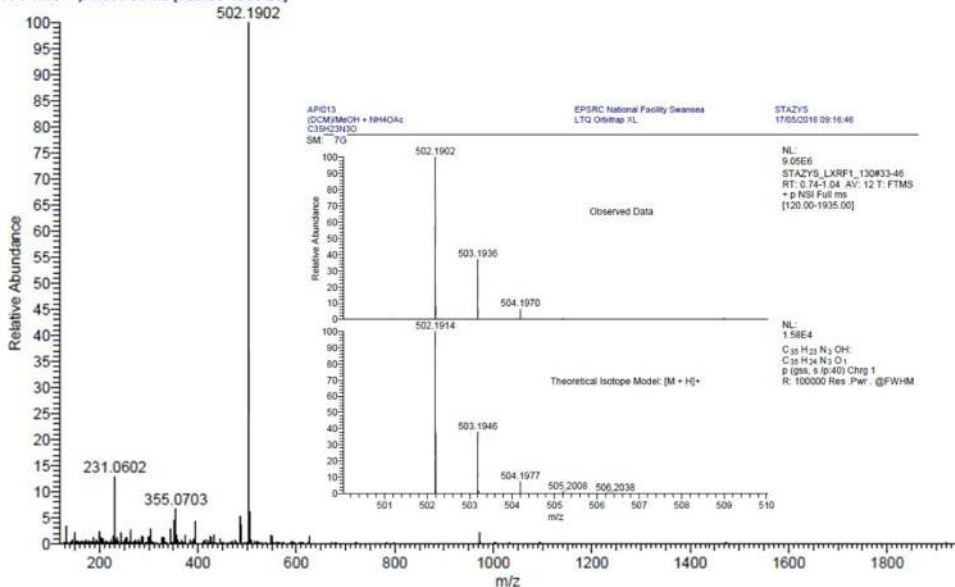


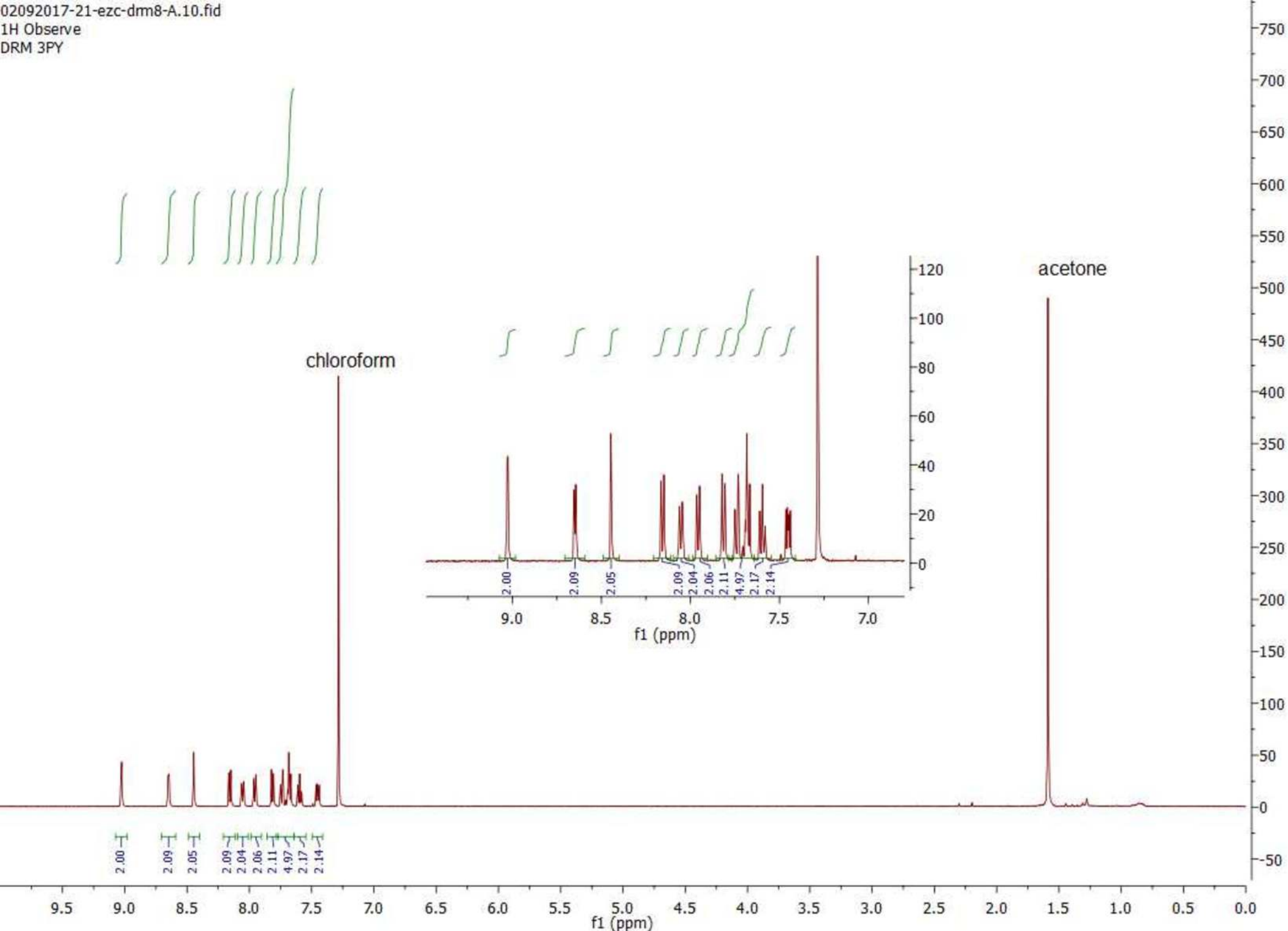
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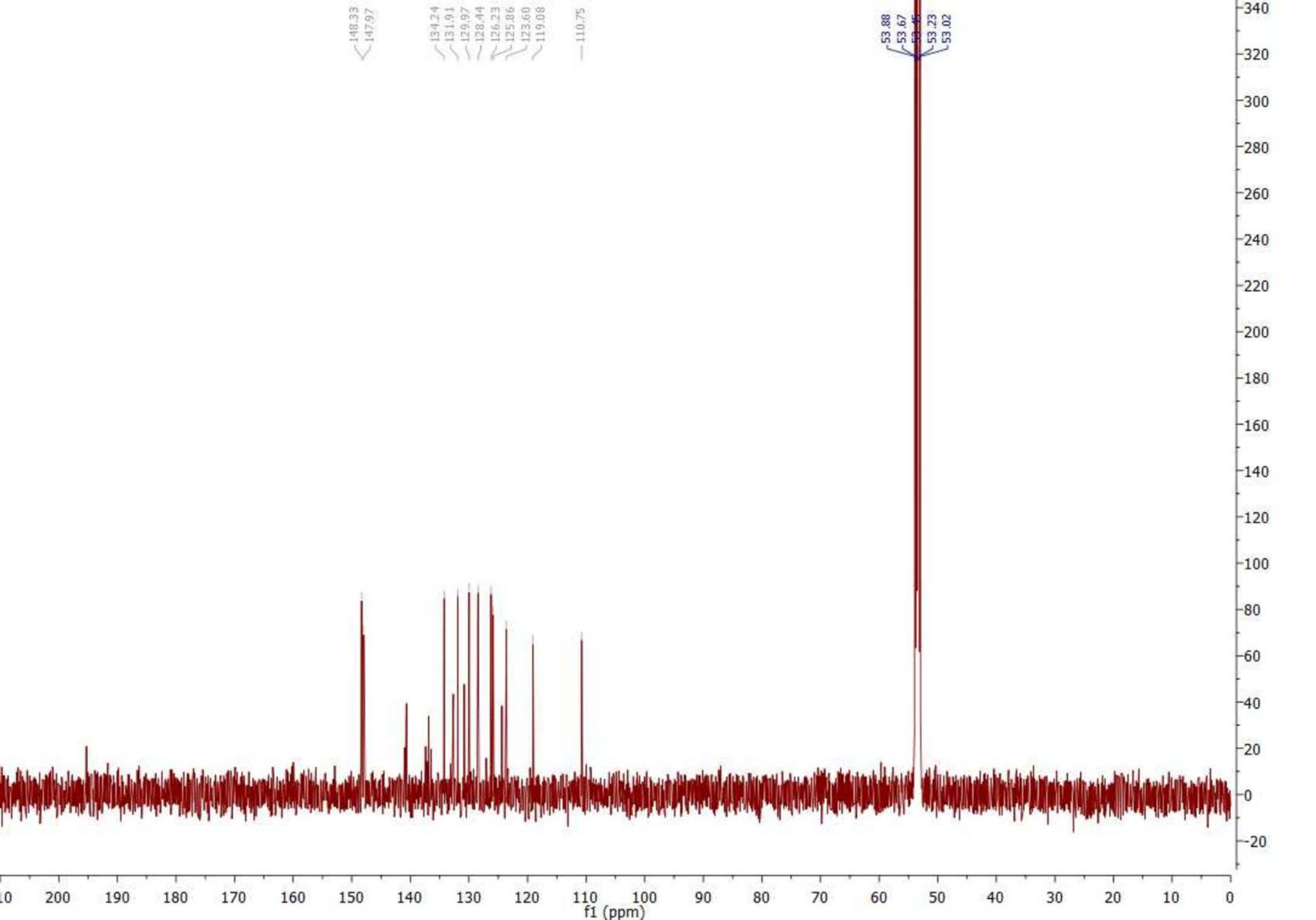
EPSRC National Facility Swansea  
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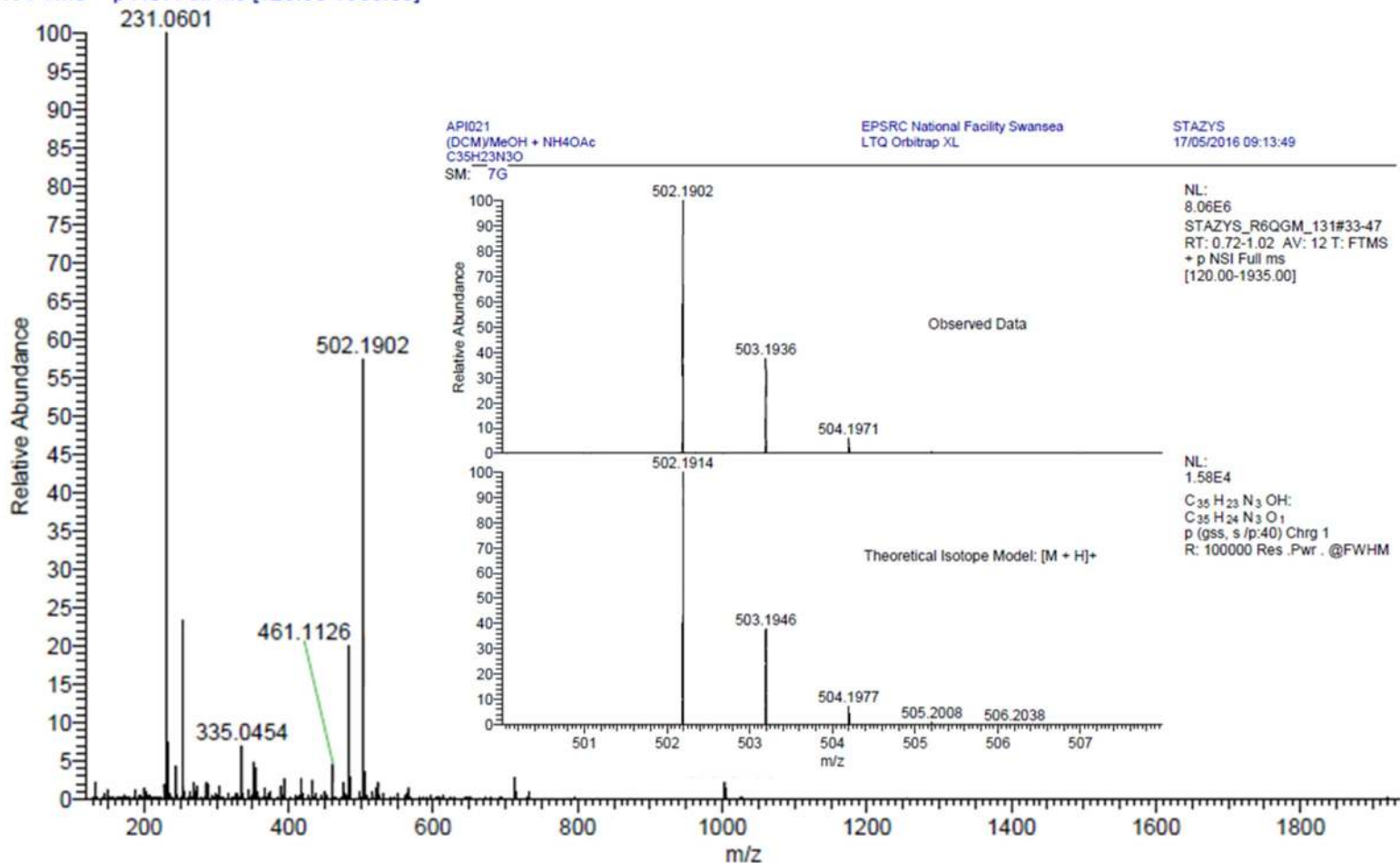




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API021  
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SM: 7G

EPSRC National Facility Swansea  
LTQ Orbitrap XL

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17/05/2016 09:13:49

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