Supporting Information

Rational molecular design of phenanthroimidazole-azine derivatives for efficient non-doped blue organic light-emitting diodes with low-efficiency roll-off

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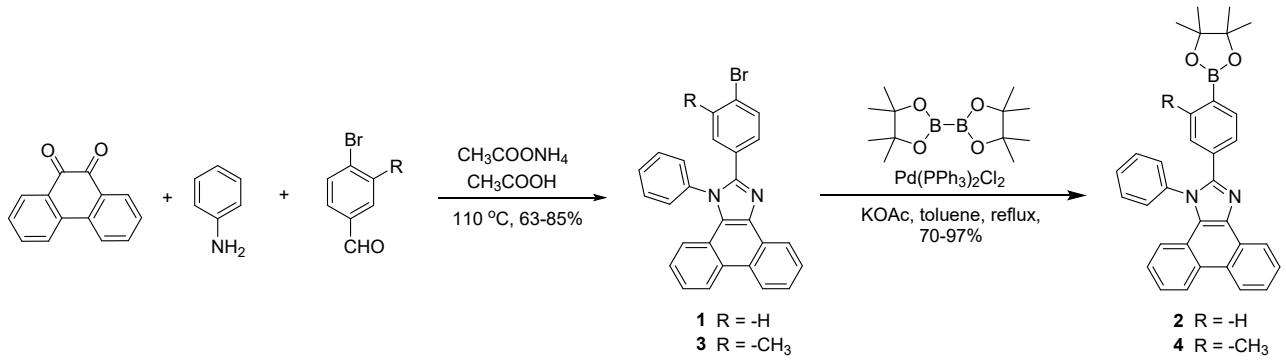
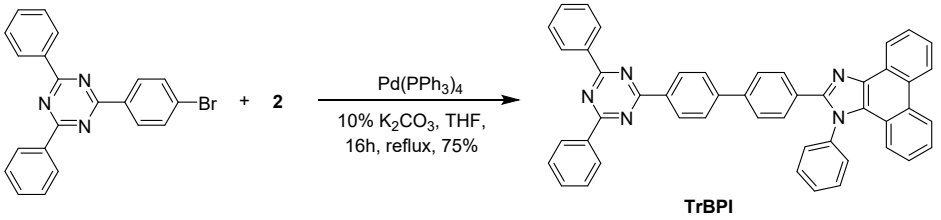
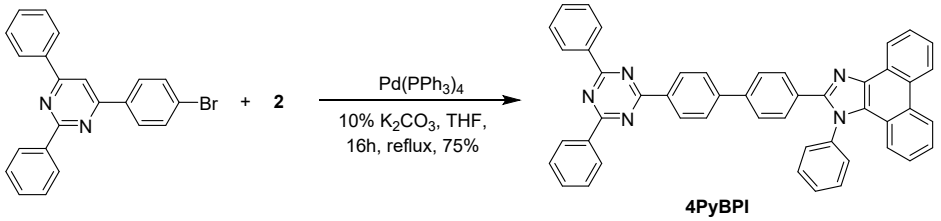
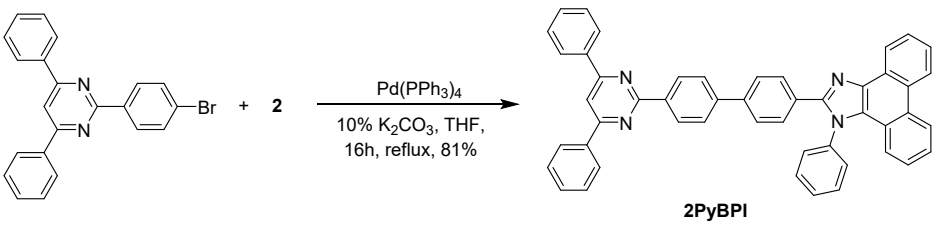
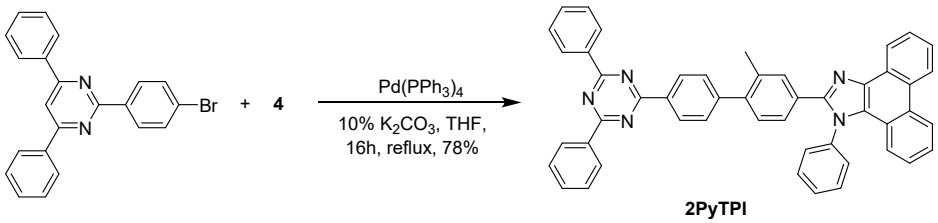
Synthesis and characterization











Scheme 1 Synthesis pathway

*2-(4-Bromophenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (**1**)*

A mixture of phenanthrene-9,10-dione (2.00 g, 9.60 mmol), aniline (1.30 ml, 14.40 mmol), 4-bromobenzaldehyde (1.78 g, 9.60 mmol), ammonium acetate (3.70 g 48.02 mmol), and acetic acid (50 mL) was refluxed at 110°C for 12 h. The mixture was cooled to room temperature and then poured into ice cold water. The solid product was separated by filtration and washed with water. The crude solid was dissolved in DCM and washed with water and brine, dried over anhydrous Na_2SO_4 and removed organic solvent, respectively. The crude product was purified by recrystallization from DCM/MeOH mixture solvent to give white solids (2.71 g, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, *J* = 7.9 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.69 – 7.58 (m, 4H), 7.55 – 7.48 (m, 3H), 7.44 (q, *J* = 8.5 Hz, 4H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.72, 138.58, 137.47, 131.44, 130.80, 130.30, 129.99, 129.50, 129.37, 129.03, 128.32, 128.30, 127.35, 127.13, 126.32, 125.73, 125.04, 124.14, 123.35, 123.14, 122.95, 122.70, 120.84. HRMS APCI/Q-TOF (m/z): calcd for $C_{27}H_{17}BrN_2$ 448.0575, found 448.6108 [M^+].

*1-Phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-phenanthro[9,10-d]imidazole (**2**)*

Compound **1** (1.0 g, 2.2 mmol), bispinacolatodiboron (1.7 g, 6.7 mmol) and potassium acetate (2.7 g, 27.0 mmol) were suspended in dried toluene (60 ml) under nitrogen atmosphere. Bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) (78 mg, 0.1 mmol) was added and degassed for 15 minutes. The reaction mixture was stirred for 16 hours under reflux, cooled to room temperature. The resulting mixture was filtered through Celite pad, washed by dichloromethane (250 ml) and concentrated *in vacuo*. The product was purified by recrystallization from dichloromethane and hexane to give grey solids (0.77 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.69 (m, 3H), 7.67 – 7.64 (m, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.63 – 7.56 (m, 5H), 7.53 – 7.48 (m, 3H), 7.28 – 7.24 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 130.5, 129.2, 128.9, 128.7, 126.7, 124.3, 123.1, 121.0, 84.1, 24.9. HRMS APCI/Q-TOF (m/z): calcd for $C_{33}H_{29}BN_2O_2$ 497.2396; found: 497.1836 [M^+].

*2-(4-Bromo-3-methylphenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (**3**)*

Phenanthrenequinone (1.0 g, 4.8 mmol), 4-bromo-3-methylbenzaldehyde (0.96 g, 4.8 mmol) were dissolved in acetic acid (25 ml), stirred at room temperature. Aniline (0.66 ml, 7.2 mmol) was added as dropwise and ammonium acetate (1.85 g, 24.0 mmol) was then added to reaction mixture, followed with heat to 110°C for 12 hours. After completion reaction was allowed to room temperature and pour into ice bath. The crude solid was filtered and washed with water. Filtered solid was dissolved in dichloromethane, washed with water (4 x 30 ml), dried (Na_2SO_4) and concentrated *in vacuo*. The product was purified by recrystallization in dichloromethane/methanol to give grey solids (1.89 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, *J* = 7.2 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.67 – 7.58 (m, 5H),

7.50 (m, 3H), 7.38 (d, J = 8.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.18 (dd, J = 8.4, 1.2 Hz, 1H), 7.08 (dd, J = 8.3, 2.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 138.5, 136.9, 134.3, 131.3, 131.2, 131.1, 130.5, 130.3, 129.5, 129.2, 128.5, 128.4, 128.2, 128.1, 127.4, 126.7, 122.6. HRMS APCI/Q-TOF (m/z): calcd for $C_{28}H_{19}BrN_2$ 463.3780; found: 463.0142 $[M]^+$.

*2-(3-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (**4**)*

Compound **3** (1.0 g, 2.2 mmol), bispinacolatodiboron (1.6 g, 6.5 mmol) and potassium acetate (2.7 g, 27.0 mmol) were suspended in dried toluene (50 ml) under nitrogen atmosphere. Bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) (76 mg, 0.1 mmol) was added and degassed for 15 minutes. The reaction mixture was stirred for 16 hours under reflux, cooled to room temperature. The resulting mixture was filtered through Celite pad, washed by dichloromethane (250 ml) and concentrated *in vacuo*. The product was purified by column chromatography on silica gel eluting with hexane:dichloromethane (3:2) to give white solids (1.10 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.89 (dd, J = 8.0, 1.4 Hz, 1H), 8.77 (dd, J = 8.5, 1.3 Hz, 1H), 8.70 (dd, J = 8.1, 1.1 Hz, 1H), 7.74 (td, J = 8.0, 1.1 Hz, 1H), 7.67 - 7.57 (m, 6H), 7.53 - 7.48 (m, 3H), 7.28 - 7.24 (m, 1H), 7.20 - 7.17 (m, 2H), 2.49 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ δ 150.9, 144.8, 138.9, 137.5, 135.8, 132.4, 130.8, 130.1, 129.7, 129.3, 129.1, 128.3, 128.2, 127.3, 127.3, 126.2, 125.6, 125.2, 124.8, 124.1, 123.1, 122.8, 120.9, 83.6, 24.9, 22.2. HRMS APCI/Q-TOF (m/z): calcd for $C_{34}H_{31}BN_2O_2$ 511.2512; found: 511.2681 $[M^+]$.

Single-crystal X-ray diffraction

Table S1. Crystallographic data of **TrBPI**, **2PyBPI** and **2PyTPI**

compound	**TrBPI**	**2PyBPI**	**2PyTPI**
CCDC deposition number	2281463	2059962	2281464
Empirical formula	$C_{48}H_{31}N_5$	$C_{49}H_{32}N_4$	$C_{50}H_{34}N_4$
Formula weight	677.78	676.78	690.81
Temperature/K	100.00	100.0	100.00
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1/n$
a/Å	8.8289(10)	8.8710(8)	15.5261(12)
b/Å	9.4225(10)	41.168(4)	11.0720(9)
c/Å	21.063(2)	9.5464(8)	23.3012(18)
α/°	80.889(4)	90	90
β/°	83.911(4)	101.567(3)	100.221(3)
γ/°	78.595(4)	90	90
Volume/Å^3	1690.9(3)	3415.6(5)	3942.0(5)
Z	2	4	4
ρ_{calc}g/cm^3	1.331	1.316	1.164
μ/mm^{-1}	0.079	0.078	0.068
F(000)	708.0	1416.0	1448.0

Crystal size/mm^3	0.28 × 0.14 × 0.08	0.253 × 0.214 × 0.134	0.274 × 0.26 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.928 to 52.776	4.466 to 55.754	3.552 to 50.146
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -26 ≤ l ≤ 26	-11 ≤ h ≤ 11, -54 ≤ k ≤ 54, -10 ≤ l ≤ 12	-18 ≤ h ≤ 18, -13 ≤ k ≤ 13, -27 ≤ l ≤ 27
Reflections collected	61351	52950	238086
Independent reflections	6905 [R_{int} = 0.0384, R_{sigma} = 0.0223]	8161 [R_{int} = 0.0611, R_{sigma} = 0.0488]	6990 [R_{int} = 0.1058, R_{sigma} = 0.0239]
Data/restraints/parameters	6905/0/478	8161/0/479	6990/0/488
Goodness-of-fit on F^2	1.054	1.027	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0952	R_1 = 0.0494, wR_2 = 0.1076	R_1 = 0.0616, wR_2 = 0.1245
Final R indexes [all data]	R_1 = 0.0454, wR_2 = 0.1042	R_1 = 0.0731, wR_2 = 0.1172	R_1 = 0.0986, wR_2 = 0.1619
Largest diff. peak/hole / e Å^{-3}	0.26/-0.27	0.33/-0.29	0.41/-0.38

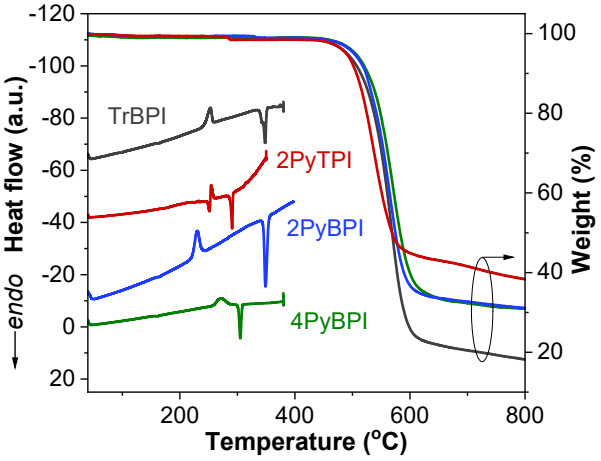


Fig. S1 DSC (2nd scan) and TGA thermograms measured at a heating rate of 10 °C/min under N_2 flow.

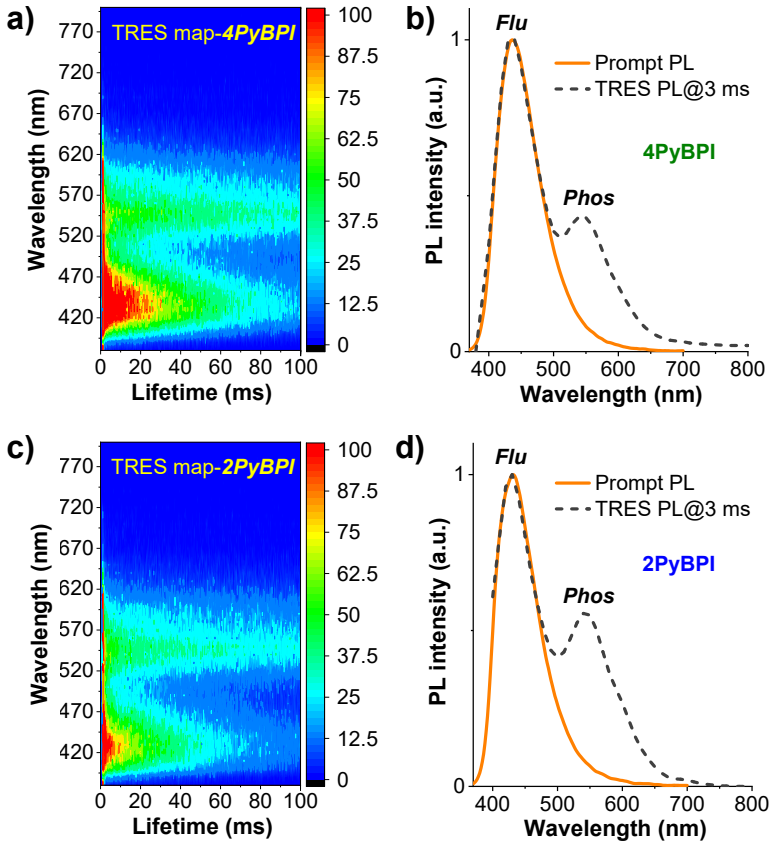


Fig. S2 a), c) TRES maps and b), d) integrated TRES slices of prompt PL and TRES PL @3 ms spectra of the neat films and 2wt% doped poly(4-bromostyrene) films covered by EXCEVAL™ film coated on fused silica substrate

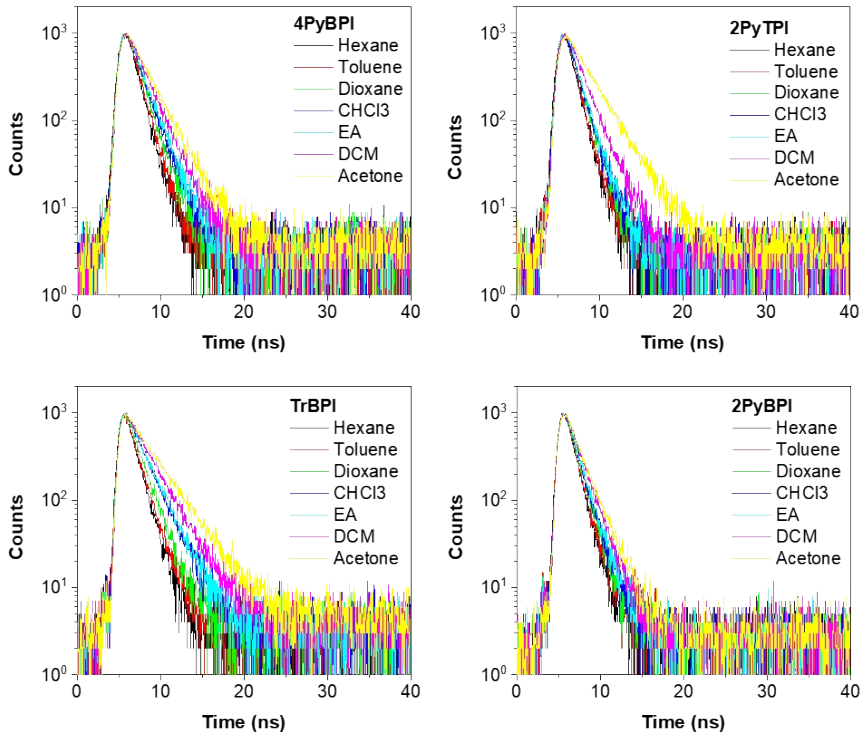


Fig. S3 Transient PL decay spectra in different solvents.

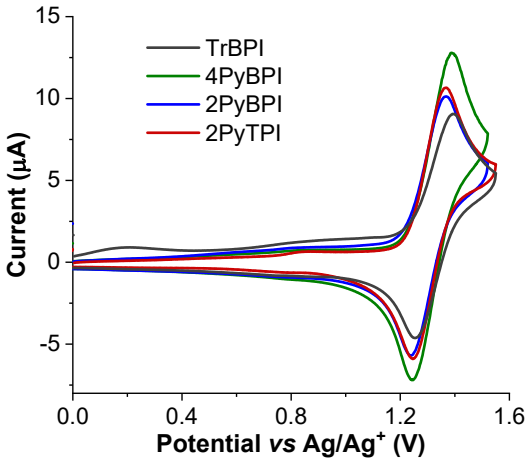


Fig. S4 Cyclic voltammograms measured in CH_2Cl_2 containing *n*-Bu_4NPF_6 at a scan rate of 50 mV/s under Ar atmosphere.

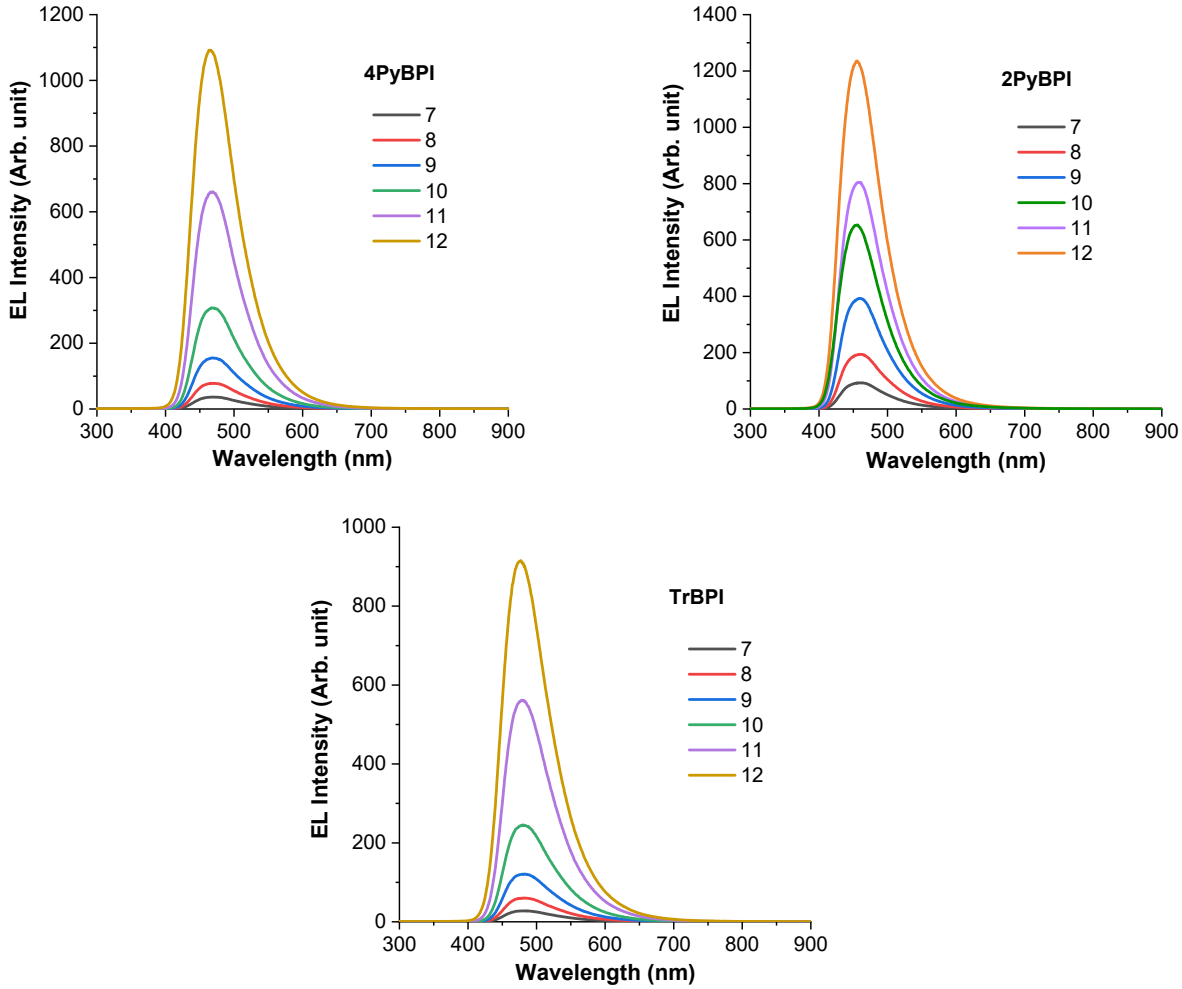
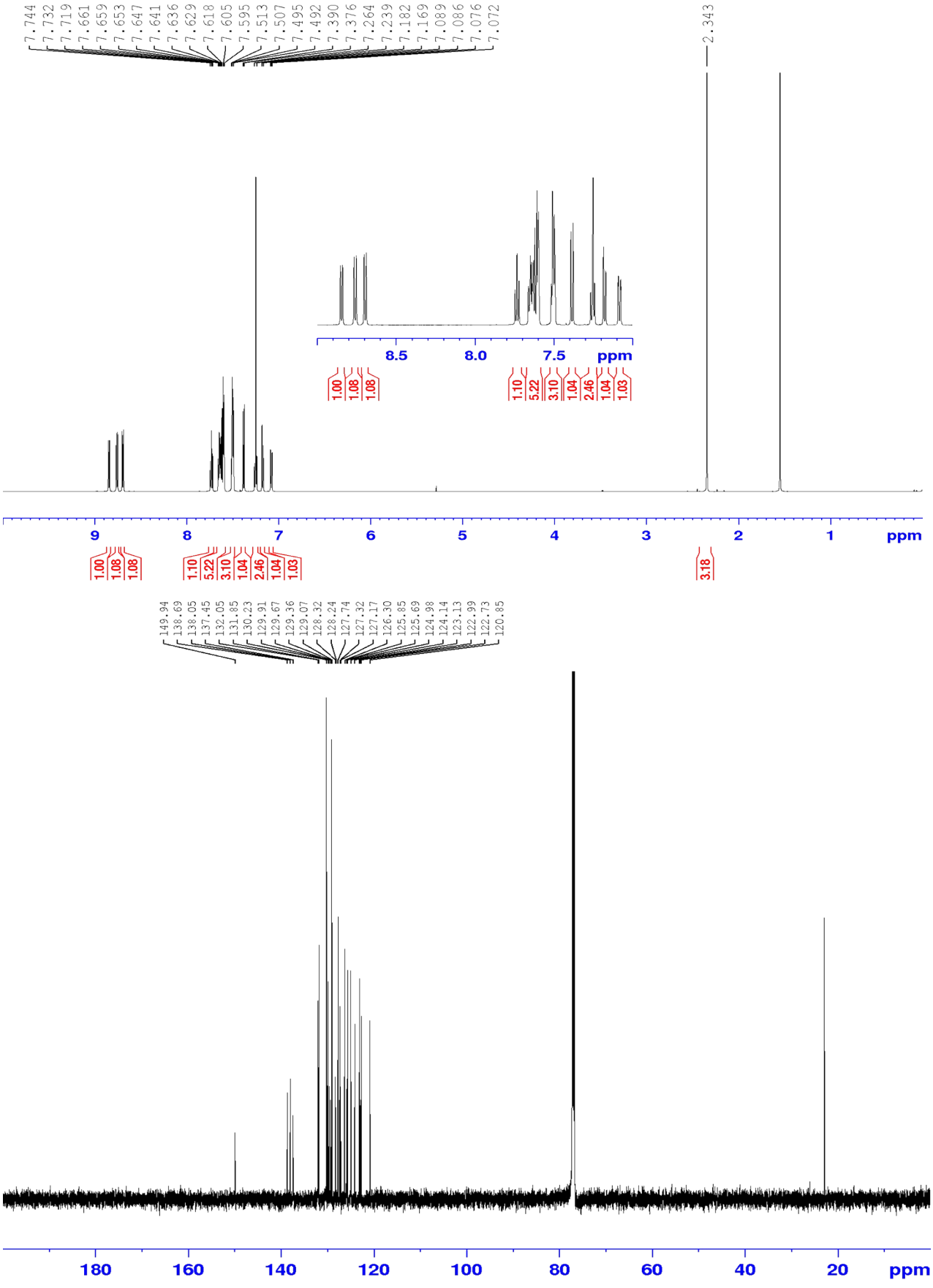


Fig. S5 EL spectra at different applied voltages.

Fig. S6 Copies of ^{1}H-NMR (600 MHz, $CDCl_3$), ^{13}C-NMR (151 MHz, $CDCl_3$) and HRMS mass spectra.

Compound 1



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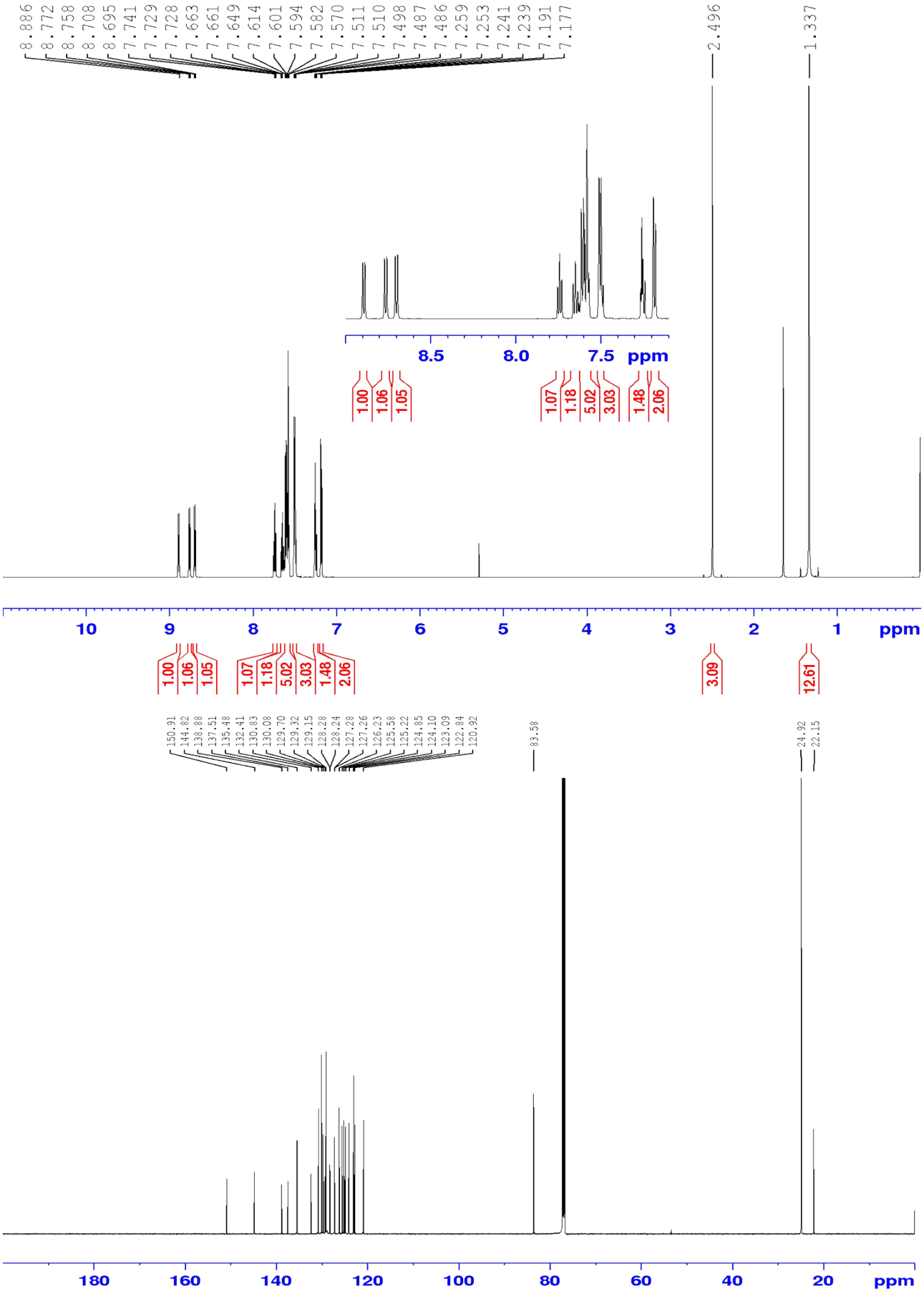
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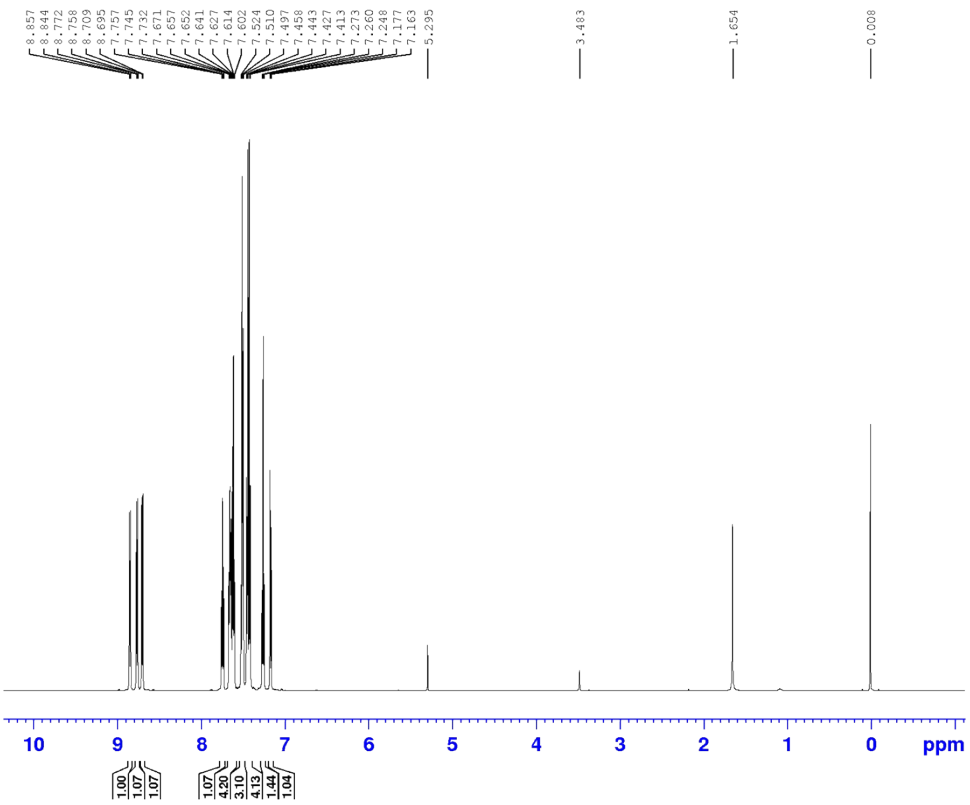

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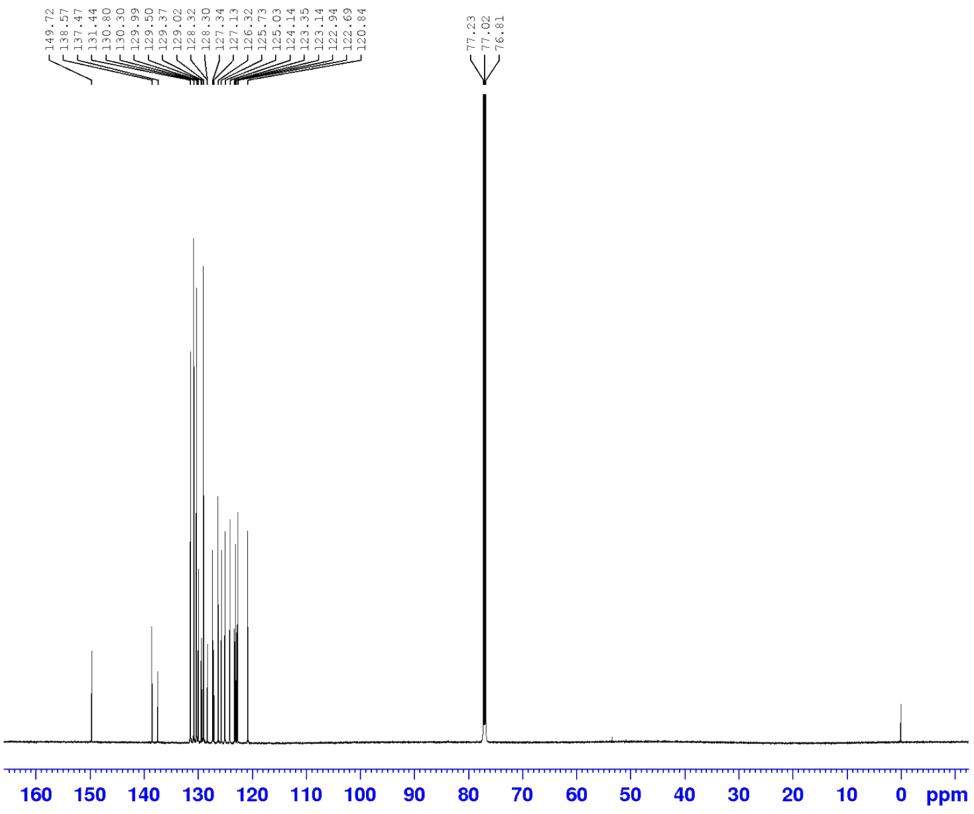

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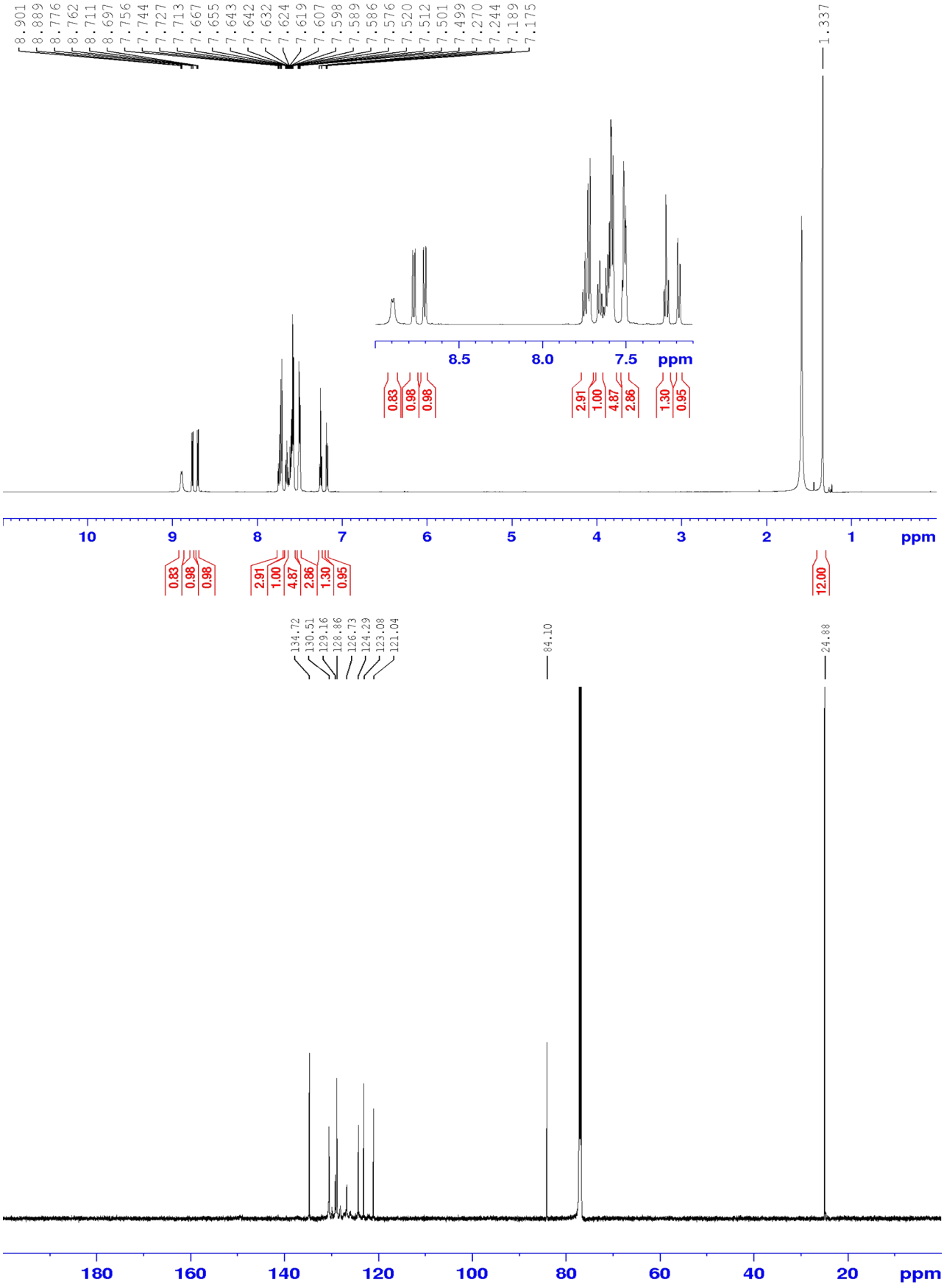
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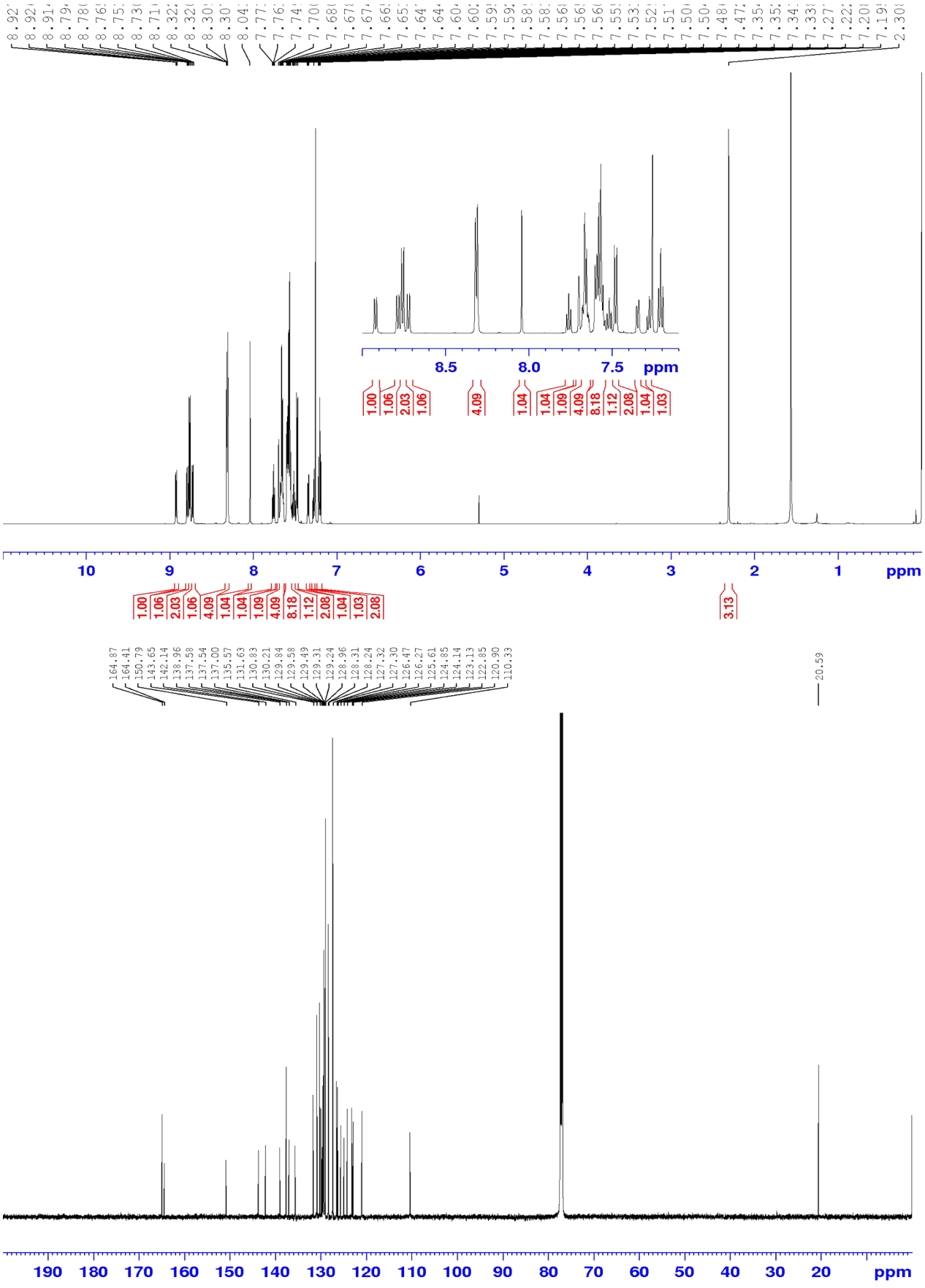
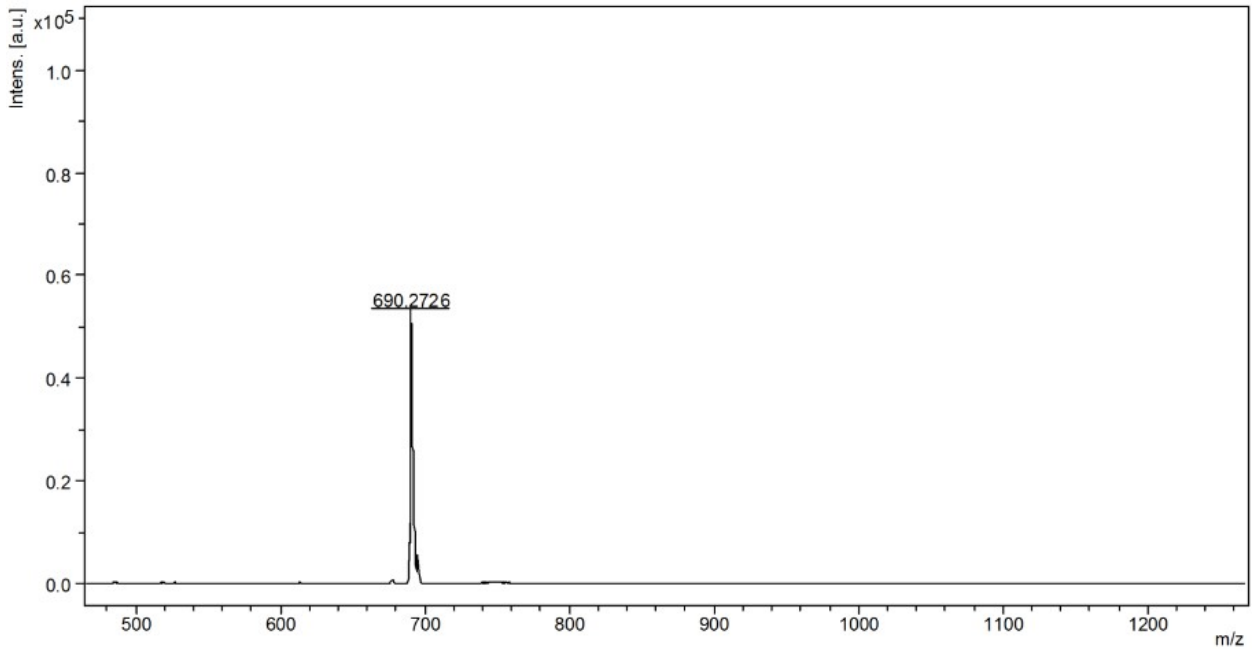
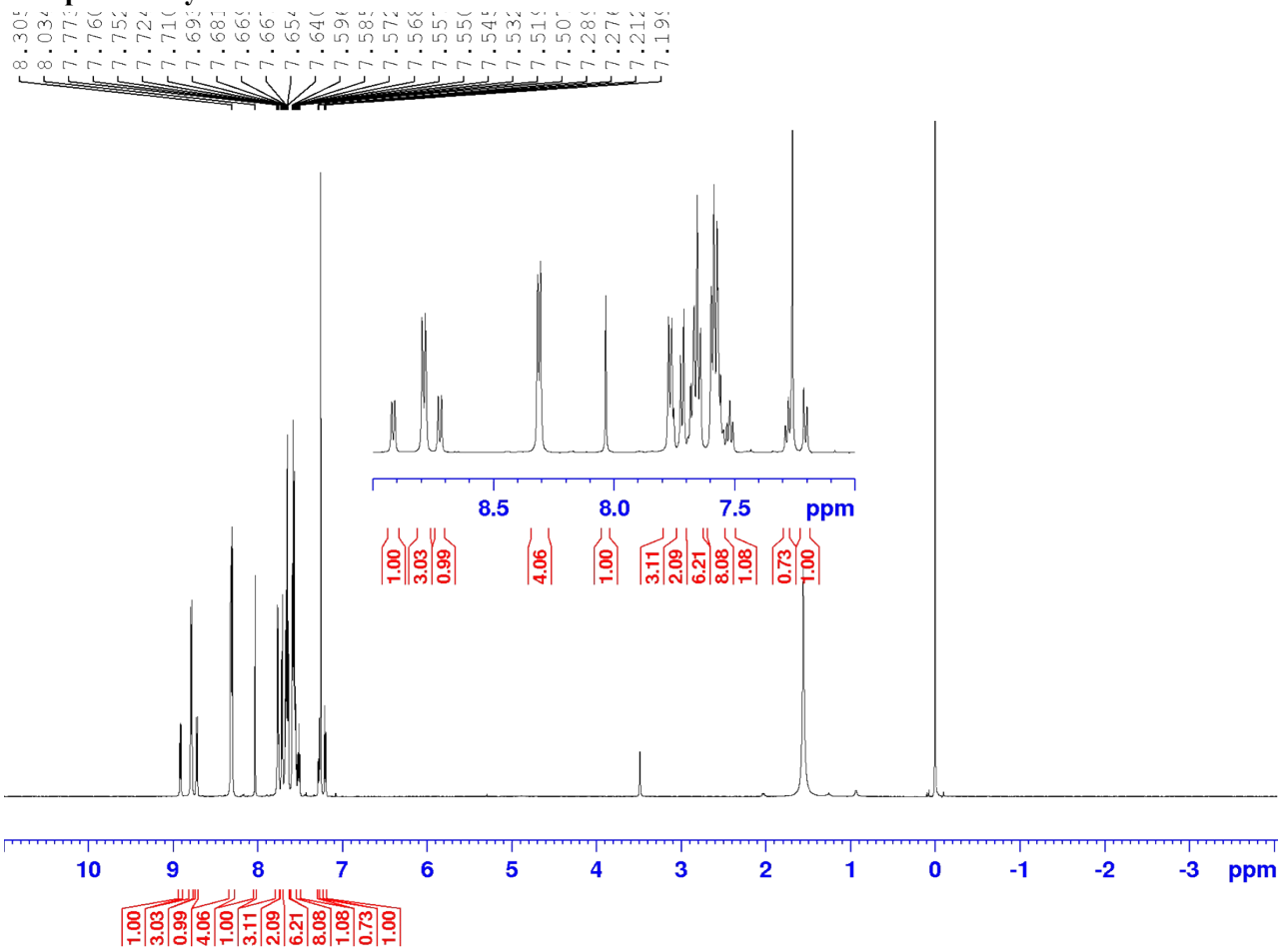
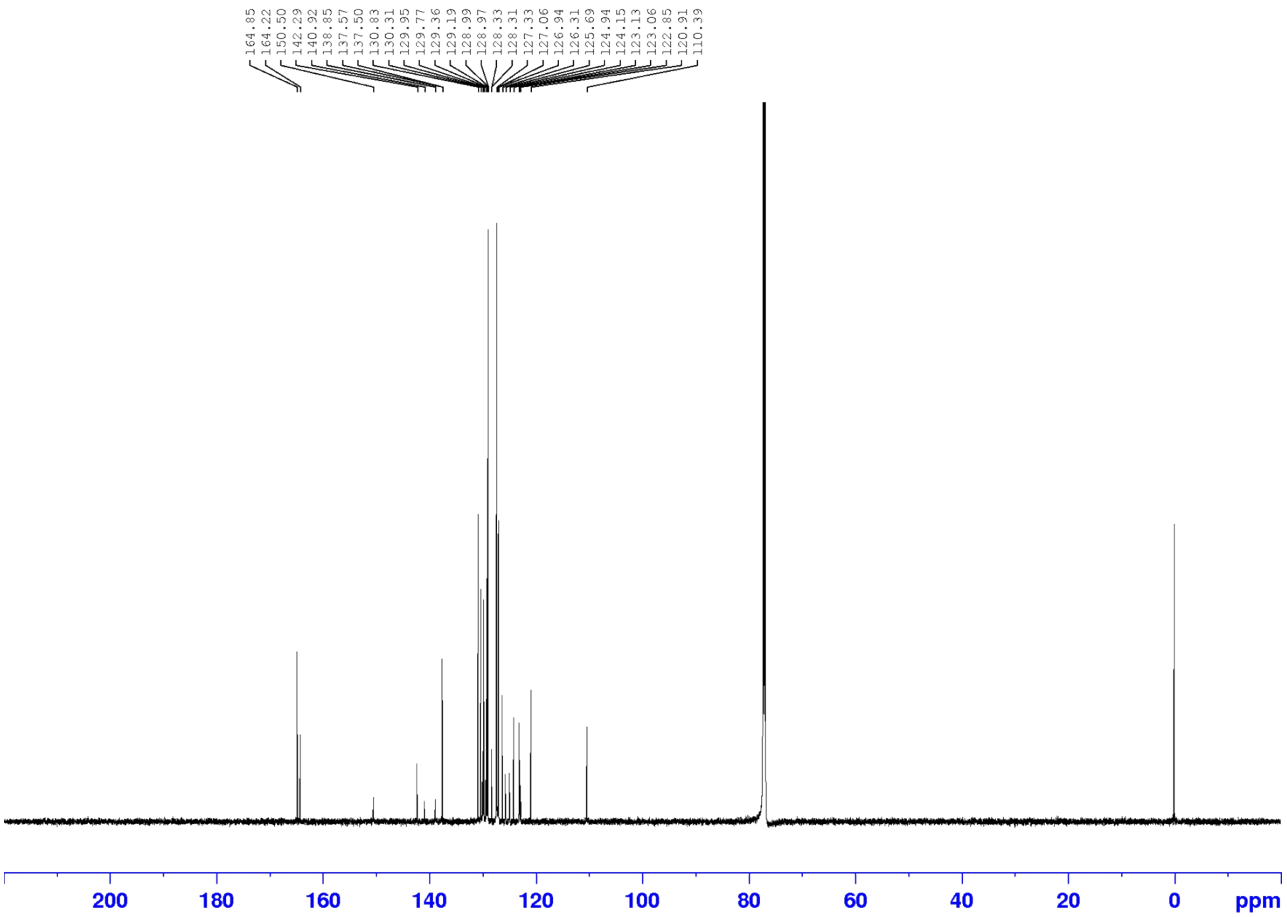
Compound 2PyTPI





Compound 2PyBPI

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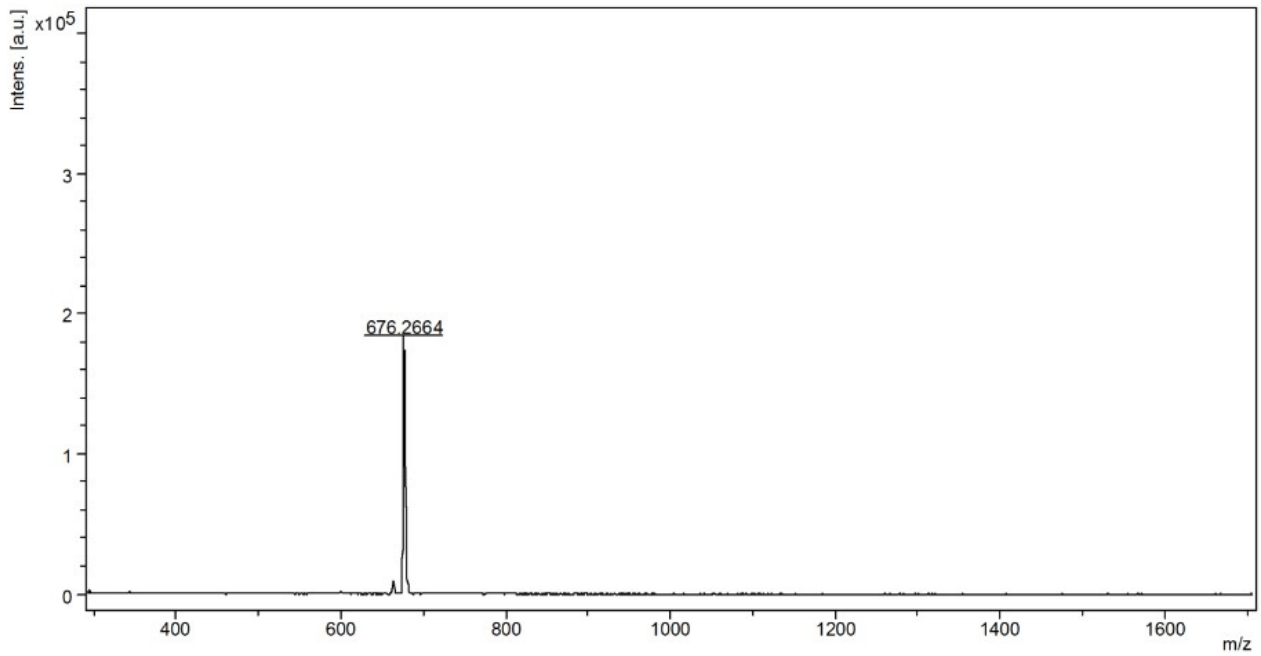
20
0
ppm


Intens. [a.u.]
x10^5
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2
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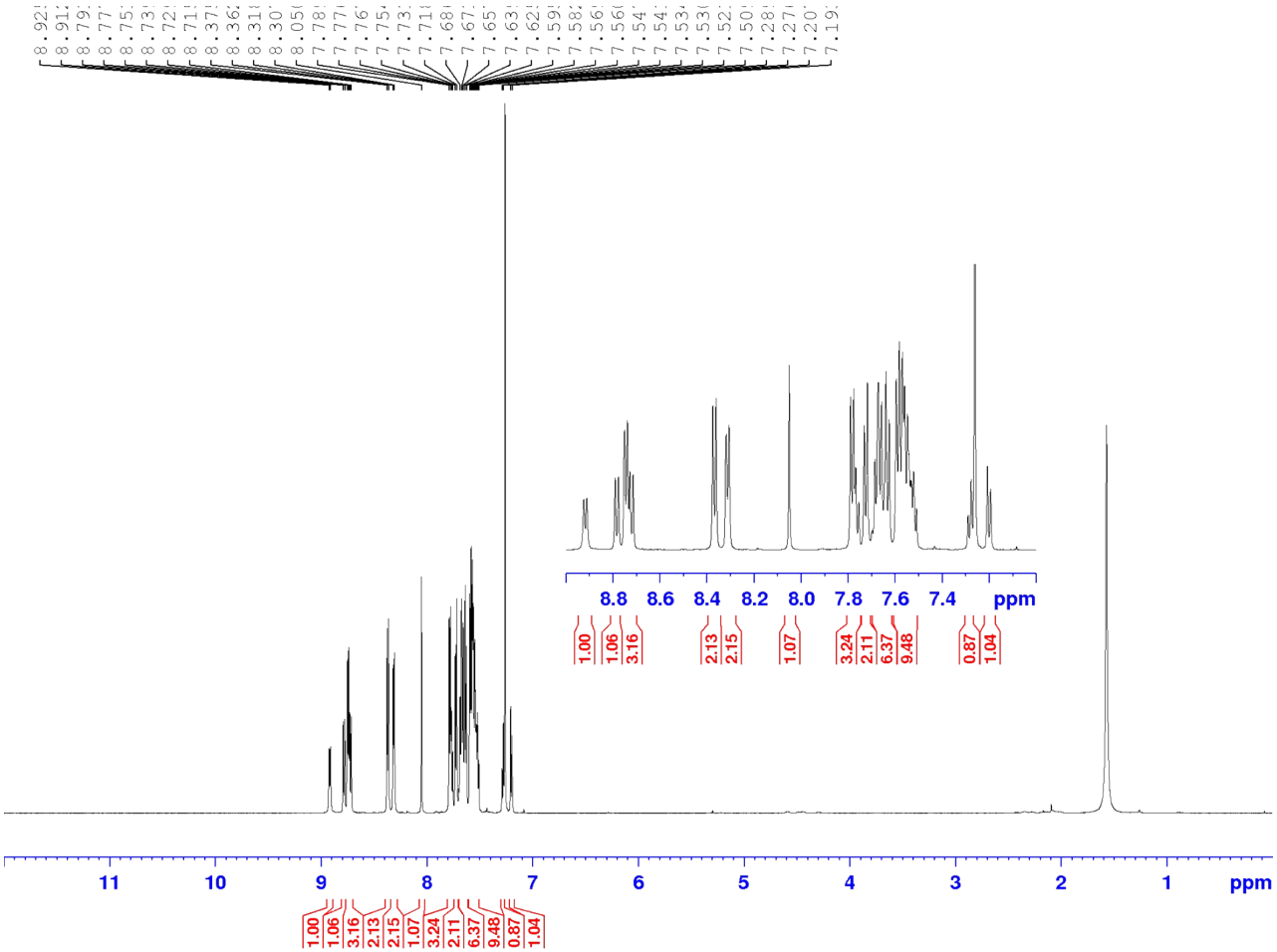
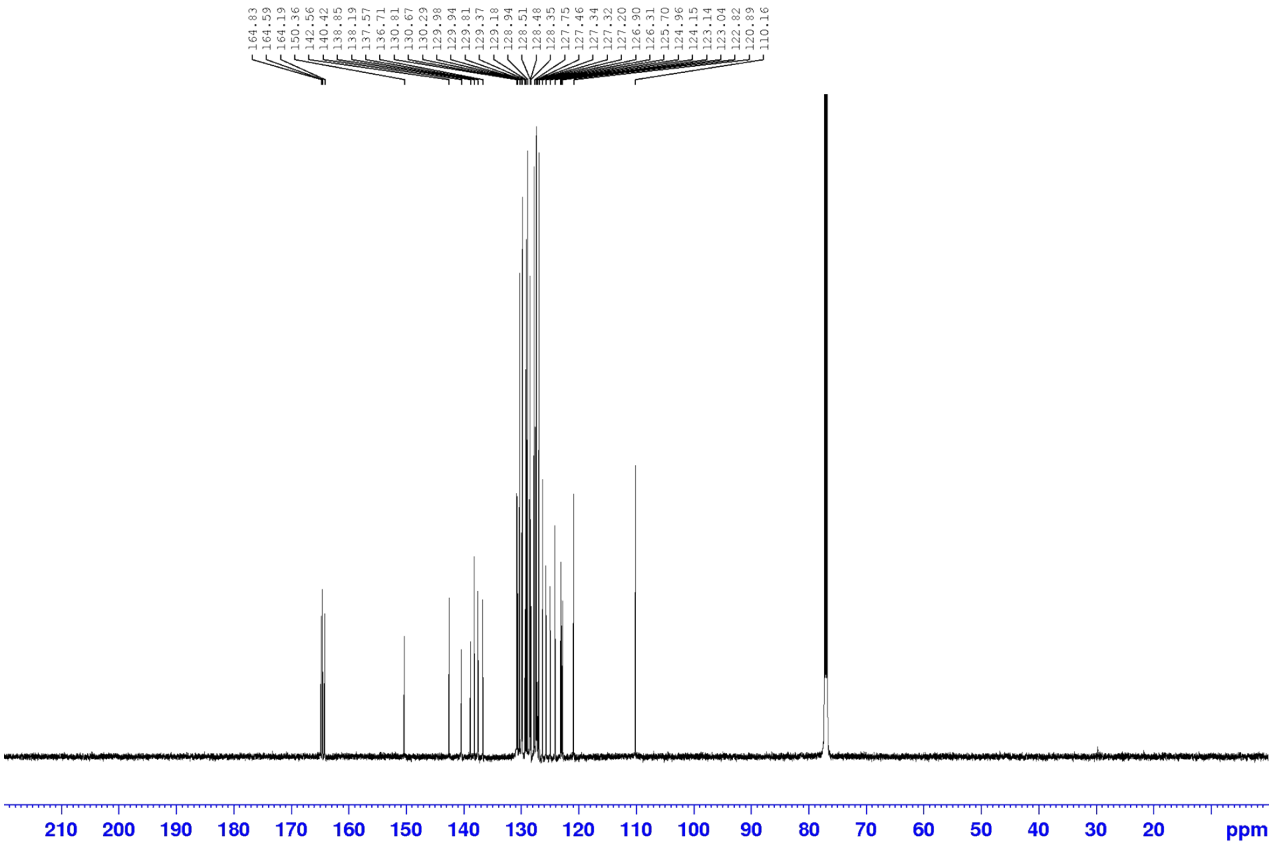
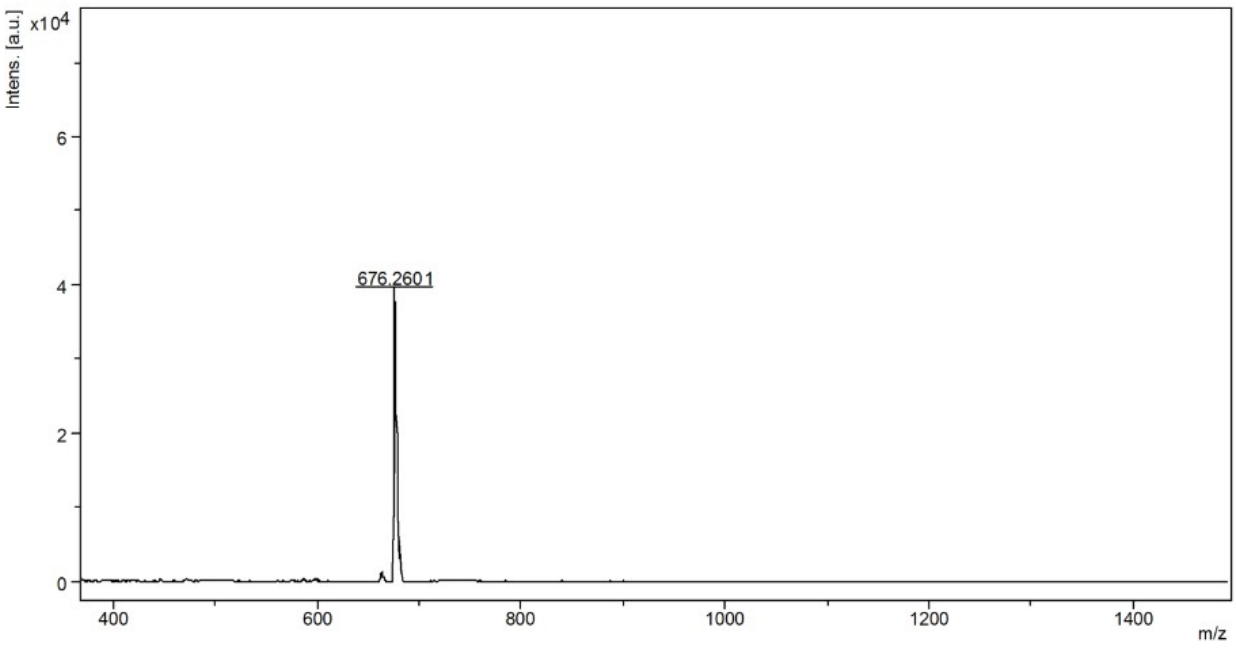
400
600
800
1000
1200
1400
1600
m/z

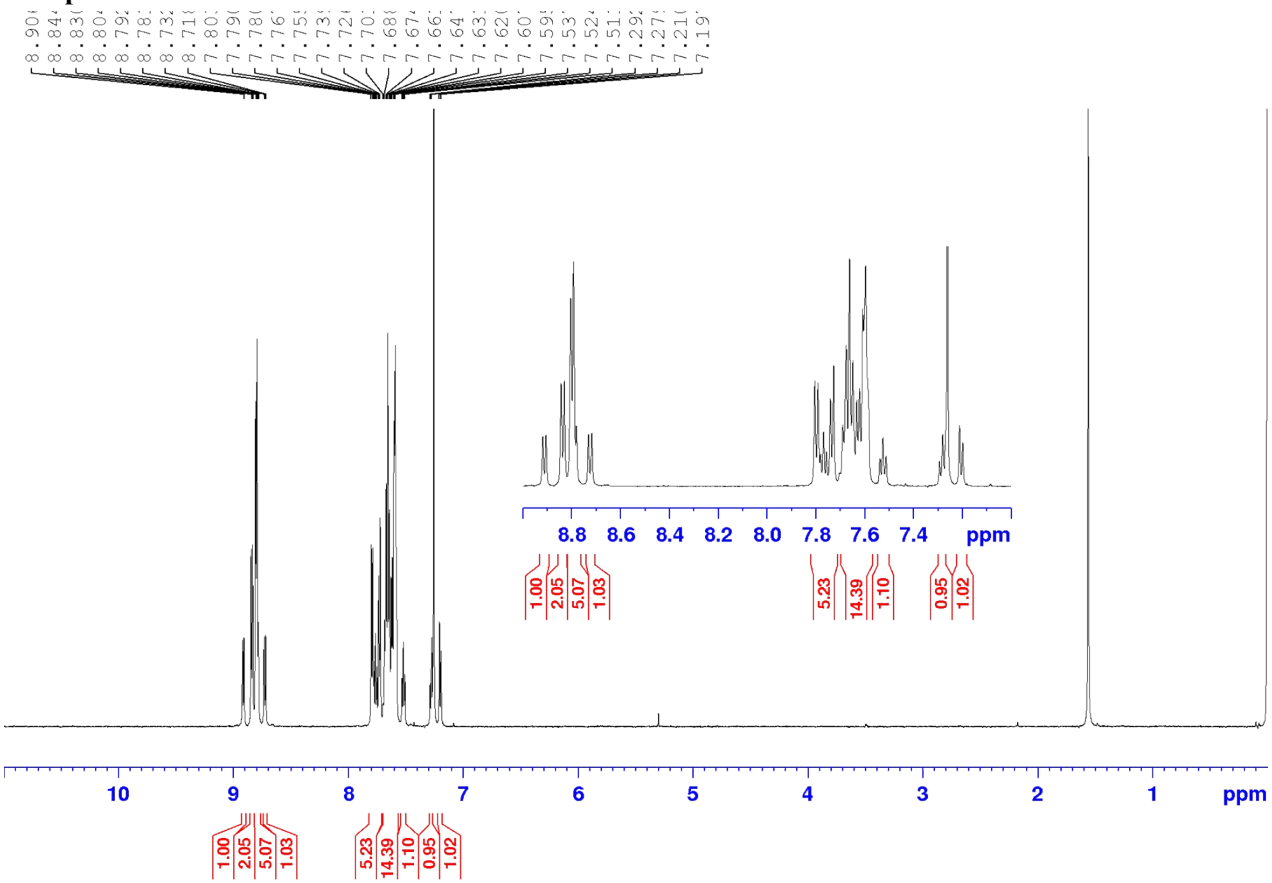
Compound 4PyBPI

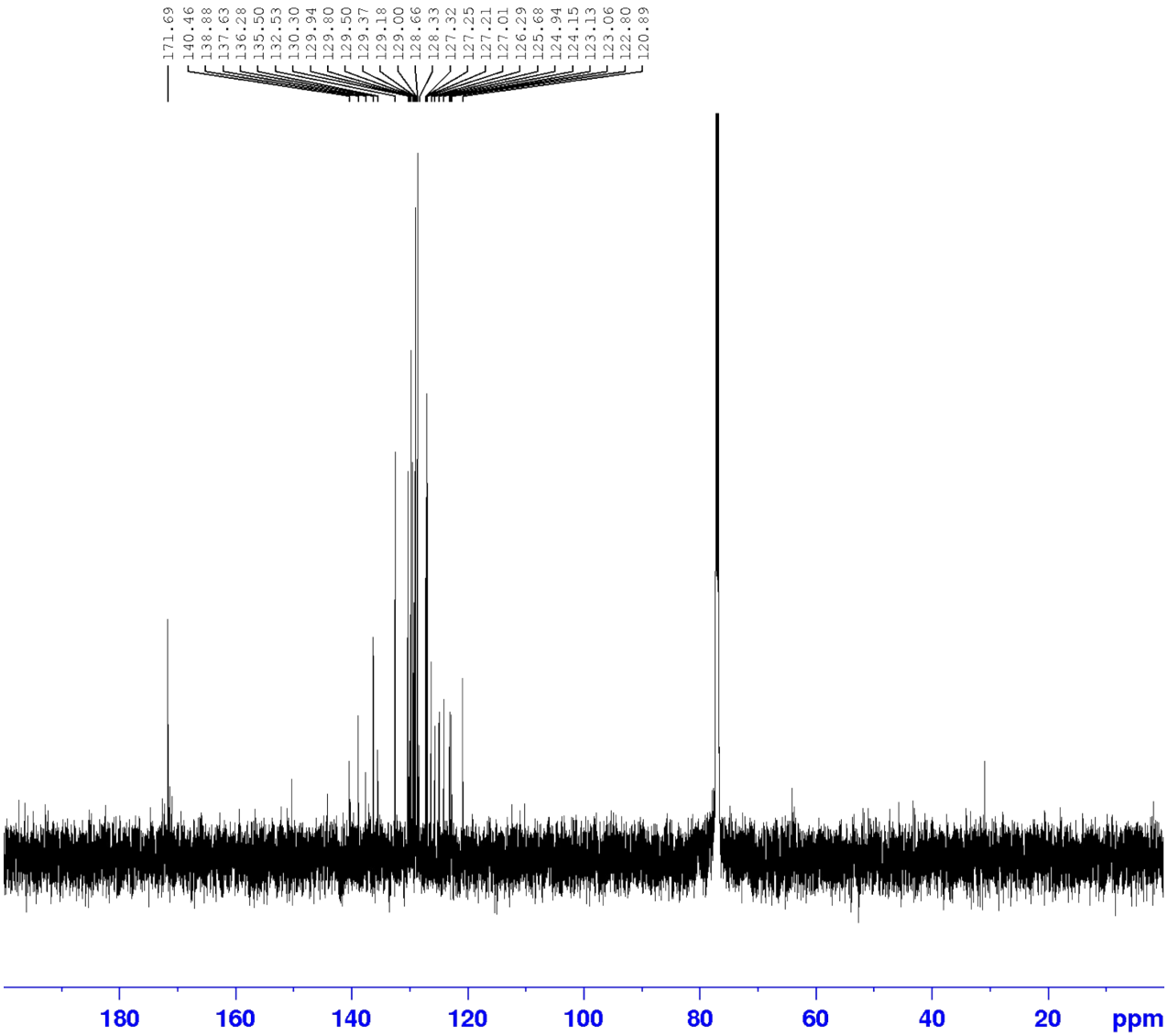






Compound TrBPI

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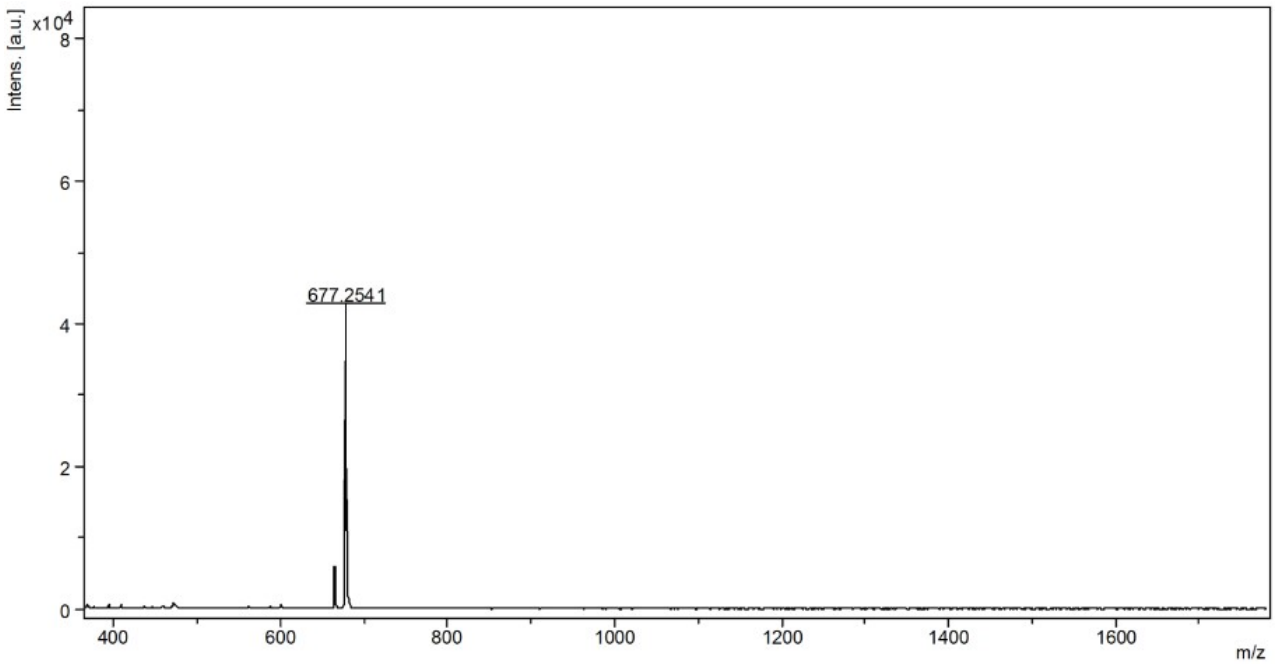
140.46
138.88
137.63
136.28
135.50
132.53
130.30
129.94
129.80
129.50
129.37
129.18
129.00
128.66
128.33
127.32
127.25
127.21
127.01
126.29
125.68
124.94
124.15
123.13
123.06
122.80
120.89
180
160
140
120
100
80
60
40
20
ppm


Intens. [a.u.]
x10^4
8
6
4
2
0
677.2541
400
600
800
1000
1200
1400
1600
m/z