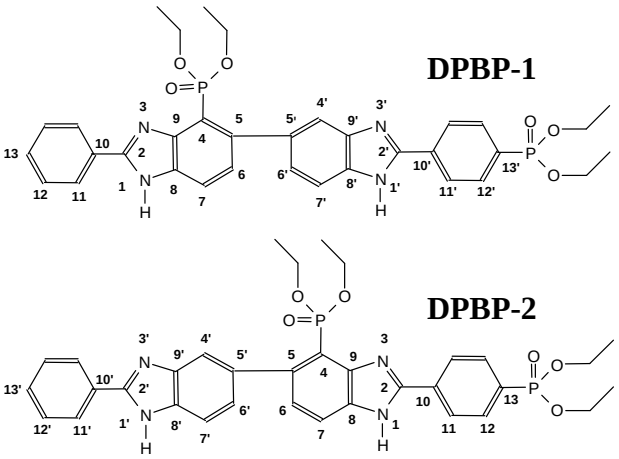
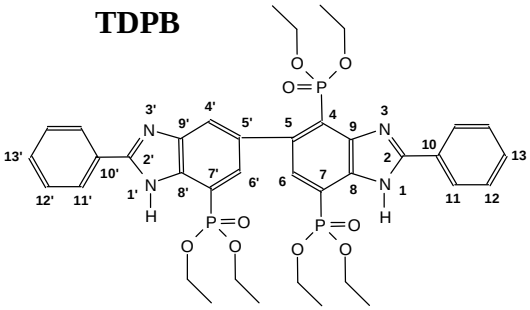
Supporting Information

Comparison of the ^{1}H NMR spectra of DPB and PBI (Figure S1A and S1B) shows the benzimidazole ring protons $\mathbf{H_4}$ and $\mathbf{H_7}$ at 7.9 and 7.7 ppm in both structures, though DPB contains two unsubstituted benzimidazole rings as evidenced by the peaks at 7.5-7.6 ppm and 8.3 ppm. Peak assignments for the benzimidazole ring protons of PBI have already been reported.[1] The ^{1}H NMR spectrum of oligomeric PBI synthesized with a 1.35 : 1 molar excess of isophthalic acid shows an additional minor peak at 8.9 ppm, likely resulting from isophthaloyl end groups (Figure S1C). The ^{1}H spectrum of isophthalic acid is also shown for comparison (Figure S1D), the isolated proton flanked by the two carboxyl groups occurring at 8.5 ppm. The $^{1}H^{13}C$ HMQC spectrum of PBI (Figure S2) reveals that the broadened carbon peaks at ~113 and ~116 ppm are $\mathbf{C_4}$ and $\mathbf{C_7}$ respectively. ^{13}C NMR spectra of PBI and $PBIP_{Et}1$ are displayed in Figure S3. The aromatic carbon region shows broadening upon phosphonylation with a noticeable shoulder at ~142 ppm corresponding to aromatic ring carbon atoms substituted with phosphorus. In Figure S4 the $^{1}H^{1}H$ COSY spectrum of $PBIP_{Et}$ (DS ~ 1) shows the protons at ~8.1 ppm and ~8.5 ppm corresponding to $\mathbf{H_{12}}$ and $\mathbf{H_{13}}$ protons of a m-phenylene ring phosphonylated at $\mathbf{C_{12}}$ to be coupled confirming their proximity. The $^{1}H^{1}H$ COSY and $^{1}H^{13}C$ HMBC spectra of DPBP are shown in Figure S5. Correlation occurs between $\mathbf{H_{11}}$ and $\mathbf{H_{12}}$ and between $\mathbf{H_6}$ and $\mathbf{H_7}$ confirming the proximity of these protons. The HMBC spectrum shows long range correlation between $\mathbf{H_6}$ and carbon at ~141 ppm, supporting a $\mathbf{C_4}$ substituted benzimidazole ring with adjacent $\mathbf{H_6}$ and $\mathbf{H_7}$ protons. TDPB with two unsubstituted phenyl rings shows long range correlation of two $\mathbf{C_{13}}$ atoms with $\mathbf{H_{11}}$ in the $^{1}H^{13}C$ HMBC spectrum (Figure S6), while DPBP shows only one such correlation. The $^{1}H^{13}C$ HMQC spectra of TDPB and DPBP (Figure S7) show that in the case of TDPB, the carbon atoms at 129 ppm ($\mathbf{C_{6'}}$) and 118 ppm ($\mathbf{C_{4'}}$) bear the protons at 7.7 ppm ($\mathbf{H_{6'}}$) and 7.9 ppm ($\mathbf{H_{4'}}$) respectively. The $^{1}H^{13}C$ HMBC spectrum shows that $\mathbf{C_{6'}}$ is coupled long range to $\mathbf{H_{4'}}$ supporting

a structure in which $\mathbf{H_6}$, and $\mathbf{H_4}$, are positioned meta to each other. Additionally, the $^{1}H,^{13}C$ HMQC and HMBC spectra of DPBP also show that the carbon resonating at 125 ppm ($\mathbf{C_6}$) bears $\mathbf{H_6}$ at 7.3 ppm (Figure S7A) and couples long range with $\mathbf{H_7}$ (7.7 ppm), Figure S5B.

Pyrolysis mass spectra of $PBIP_{Et}$ (DS ~ 3) and TDPB are displayed in Figures S8 and S9 with possible fragment structures given in Table S1. Pyrolysis of $PBIP_{Et}$ gave several large mass fragments corresponding to phosphonylated benzimidazole, phenyl benzimidazole, bibenzimidazole and diphenyl bibenzimidazole ring systems. The Pyrolysis mass spectrum of TDPB (Figure S9) shows *m/z* = 794 corresponding to the molecular ion, as well as *m/z* = 658 and 686 corresponding to diphosphonylated and diphosphonylated, ethylated DPB structures. Minor fragments, *m/z* = 640, 641 may arise from a triphosphonylated bibenzimidazole fragment. Figure S10 displays the HPLC/MS data for DPBP. The mass spectrum shows *m/z* = 659 indicating a diphosphonylated DPB structure. The fragment *m/z* = 330 could be the result of fragmentation into a monophosphonylated phenyl benzimidazole structure supporting DPBP-1 or possibly diprotonation of the DPBP structure.





Reference

(1) Kojima, T. *J. Polym. Sci. Polym. Phys.* **1980**, *18*, 1791-1800.

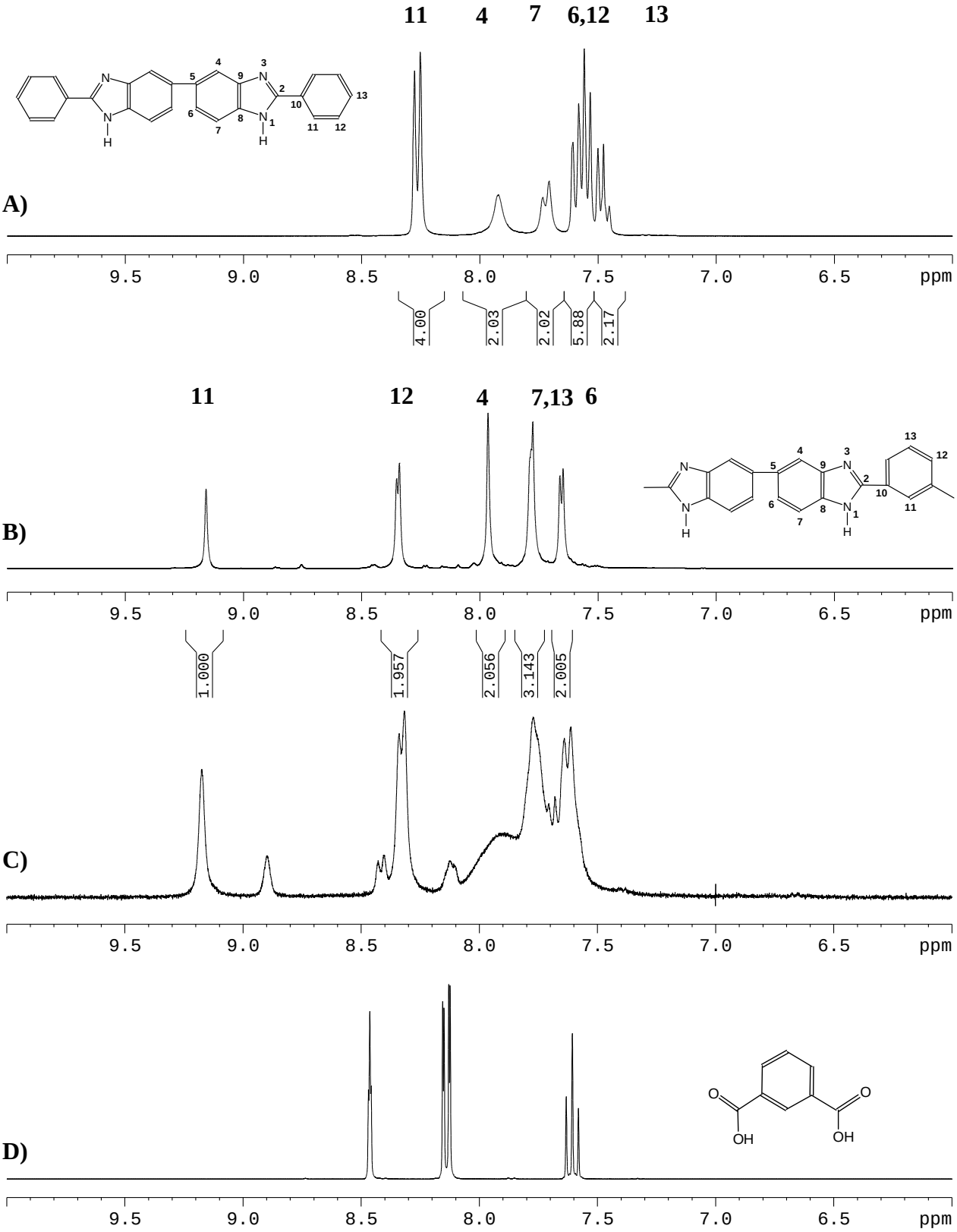


Figure S1. ^{1}H NMR spectra of A) DPB (300 MHz), B) PBI (600 MHz), C) oligomeric PBI (300 MHz), D) isophthalic acid (300 MHz), d^{6}-DMSO.

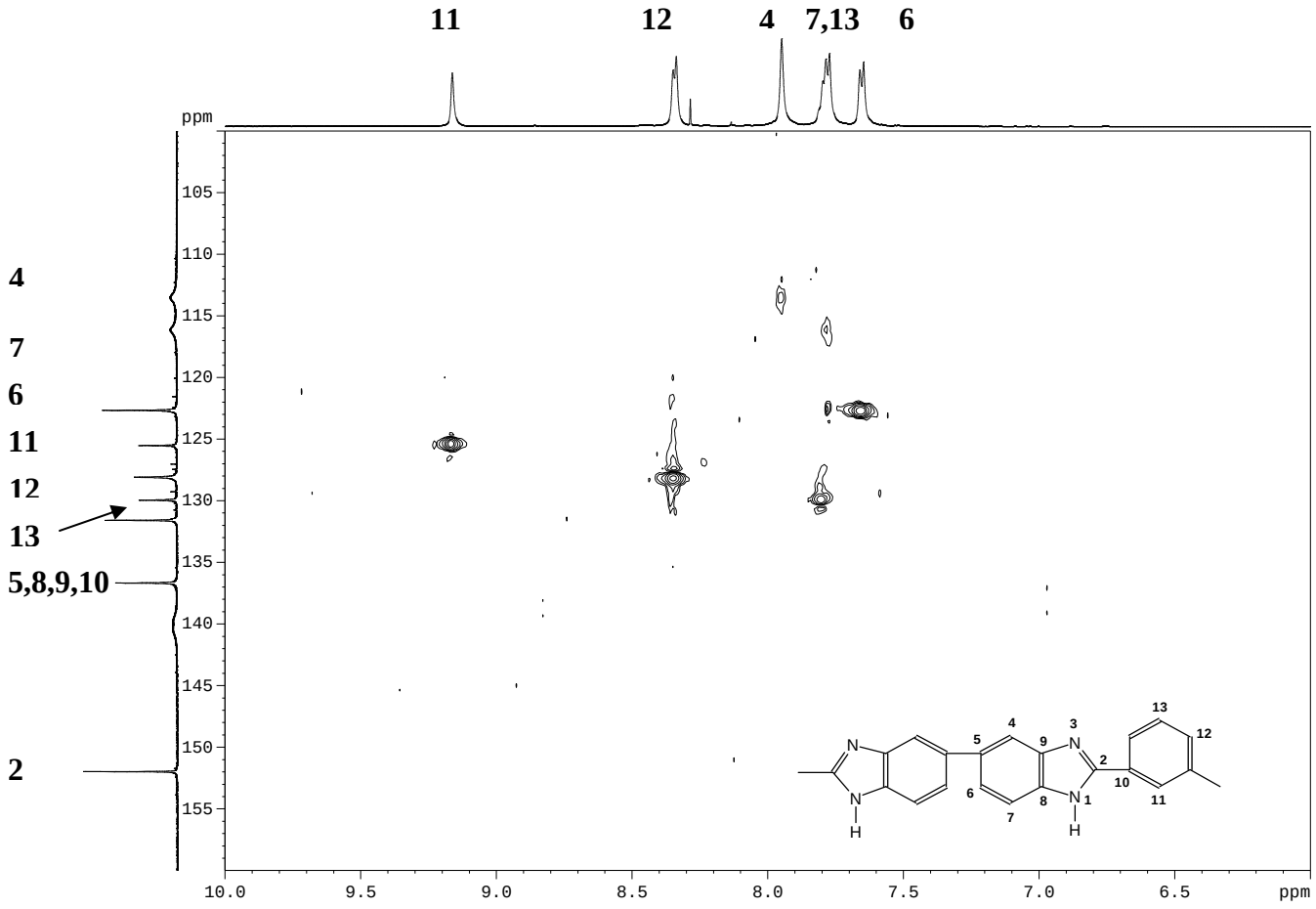


Figure S2. $^{1}H^{13}C$ HMQC (600 MHz) spectrum of PBI, 3% in d^{6}-DMSO.

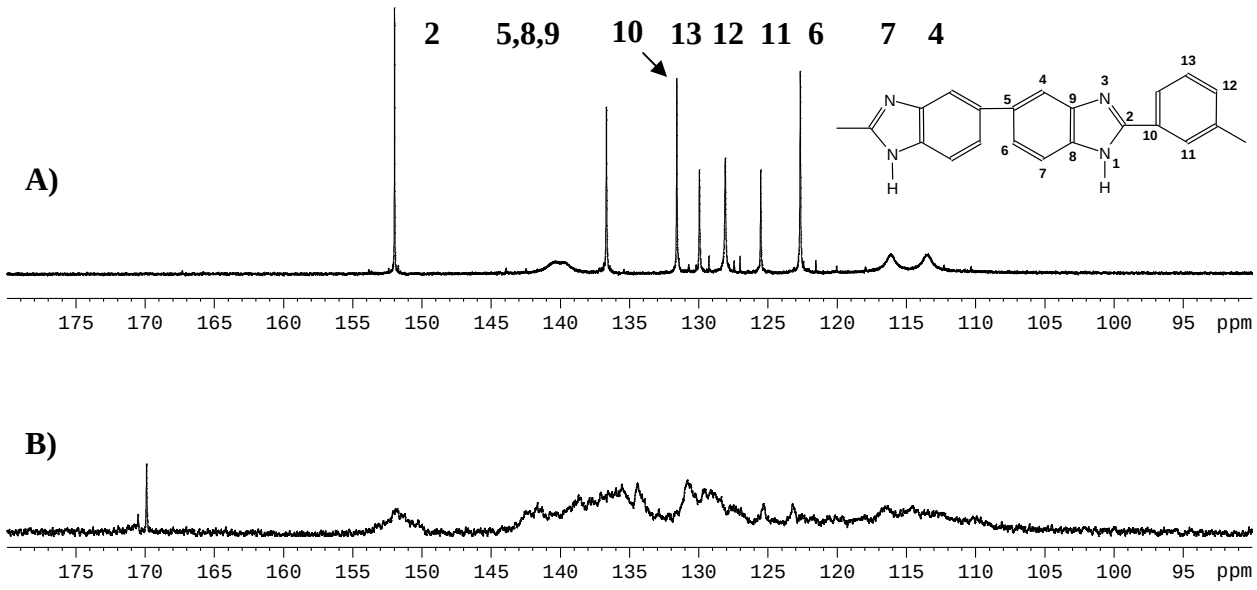


Figure S3. ^{13}C NMR (150 MHz) spectra of A) PBI and B) $PBIP_{Et}1$ in d^{6}-DMSO.

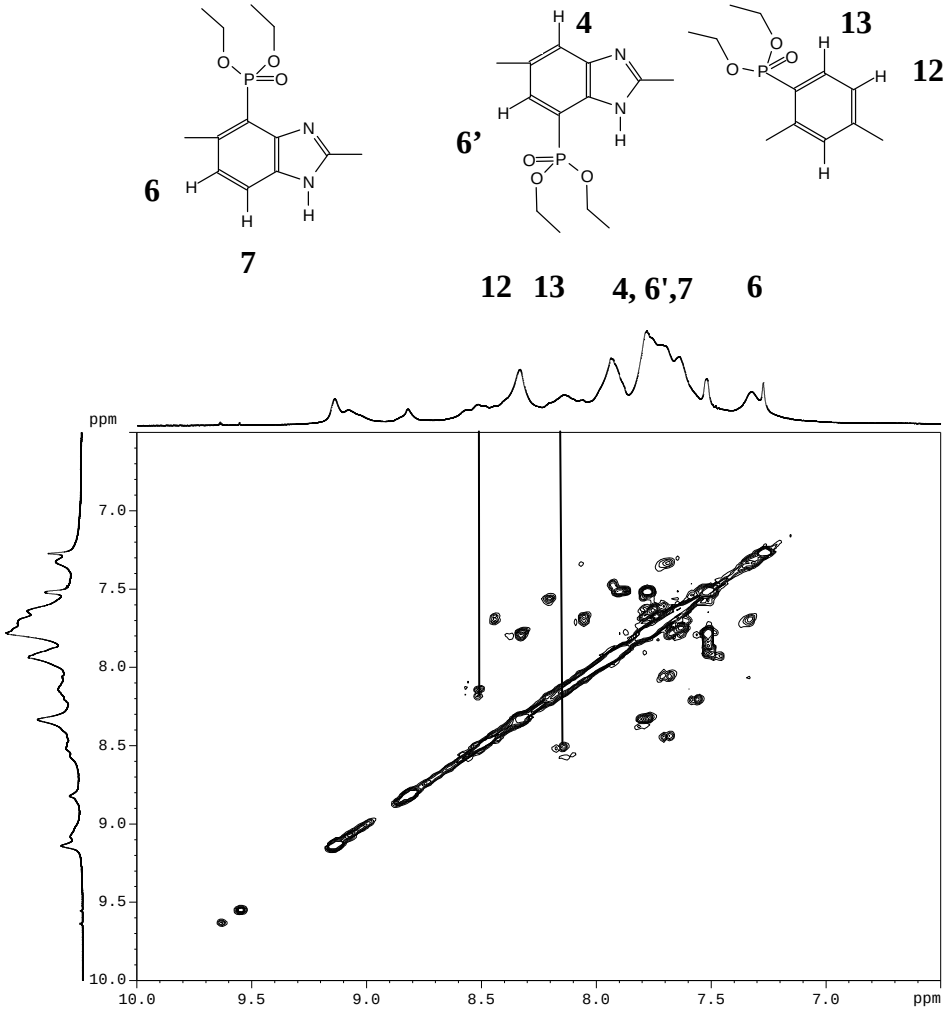


Figure S4. $^{1}H^{1}H$ COSY (600 MHz) spectrum of $PBIP_{Et}$ (DS ~ 1) in Φ-H region, d^{6}-DMSO.

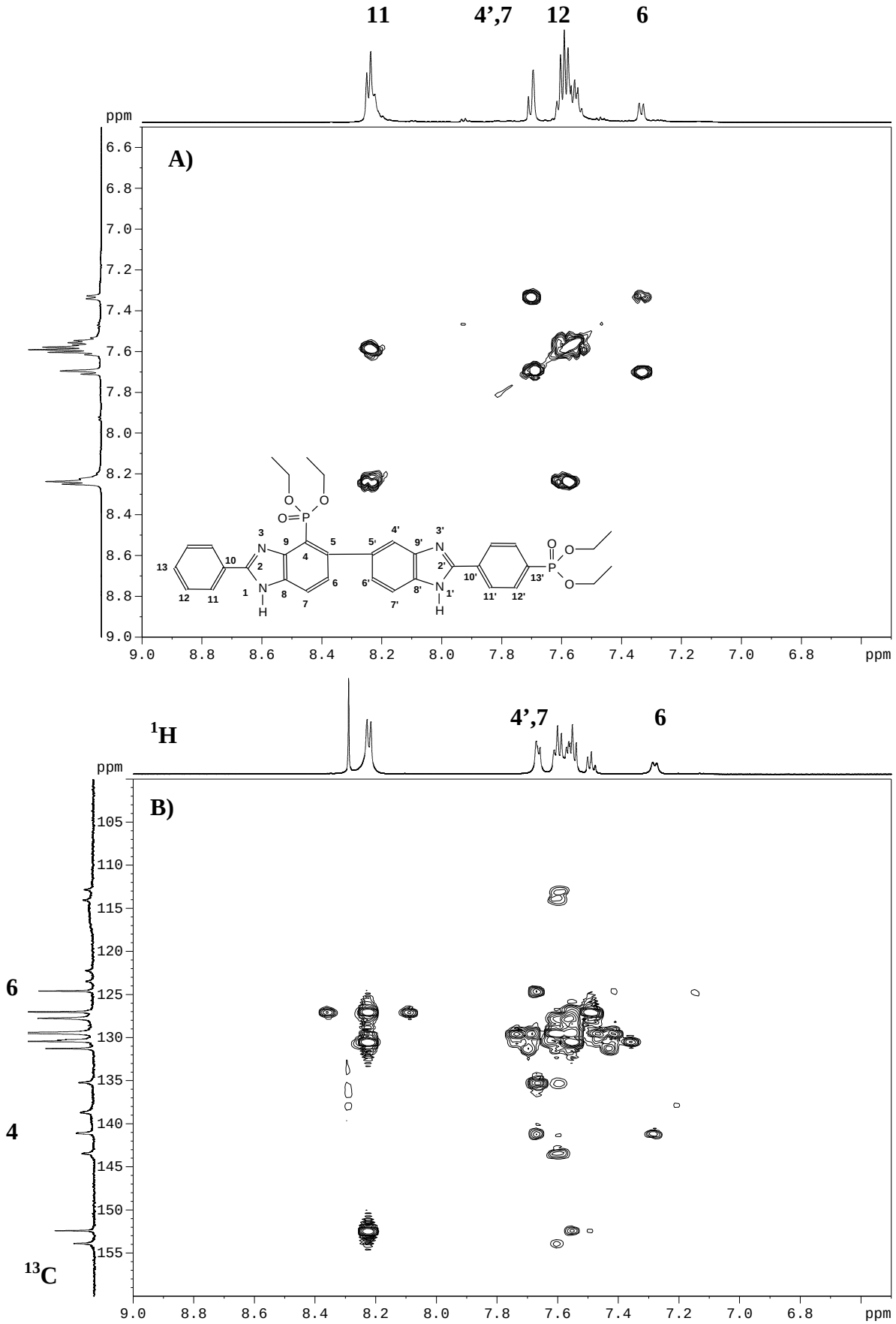


Figure S5. A) ^{1}H COSY (600 MHz) spectrum and B) ^{1}H^{13}C HMBC (600 MHz) spectrum of DPBP in d^{6}-DMSO.

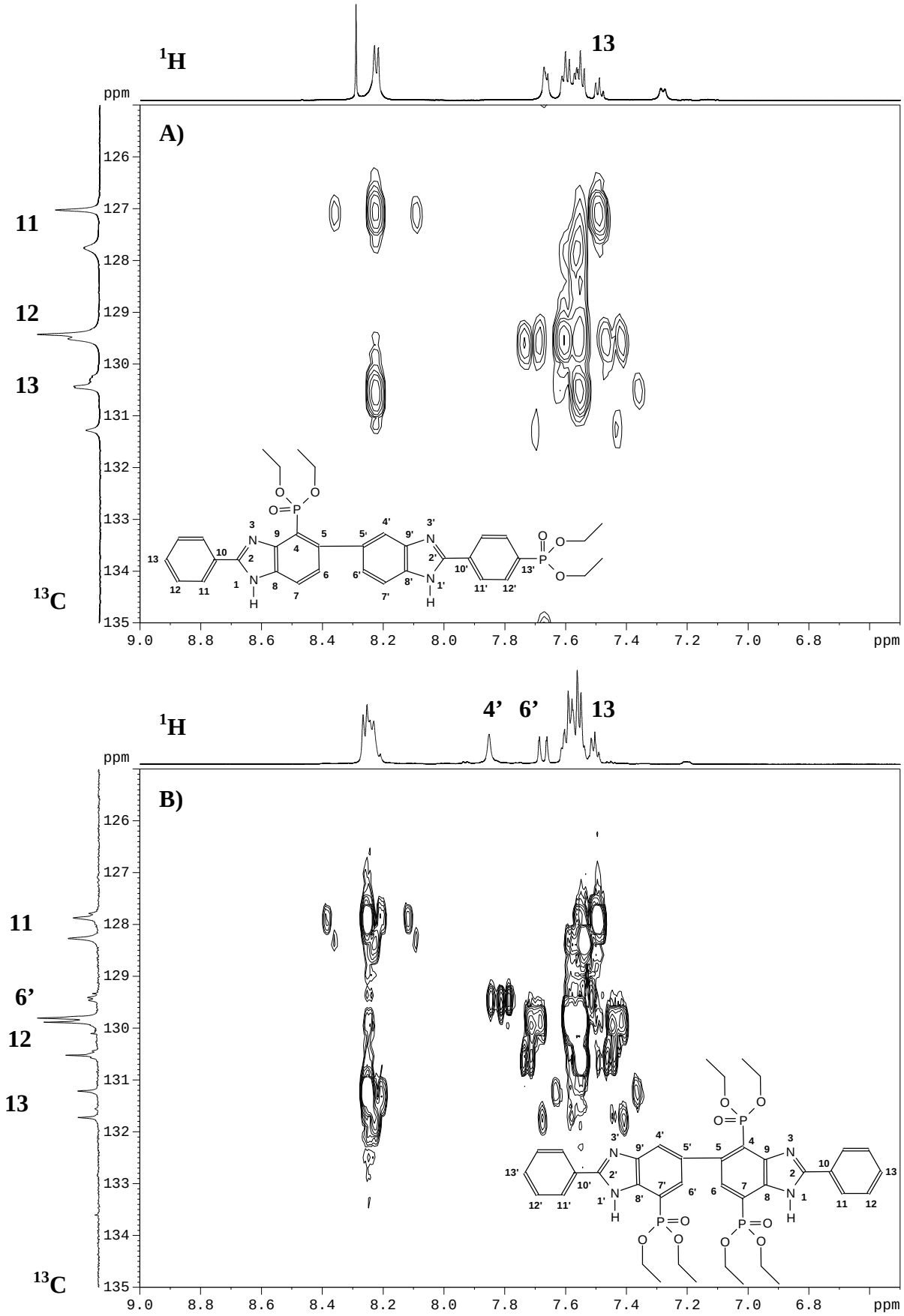


Figure S6. $^1H^{13}C$ HMBC (600 MHz) spectra of A) DPBP and B) TDPB in d^6-DMSO.

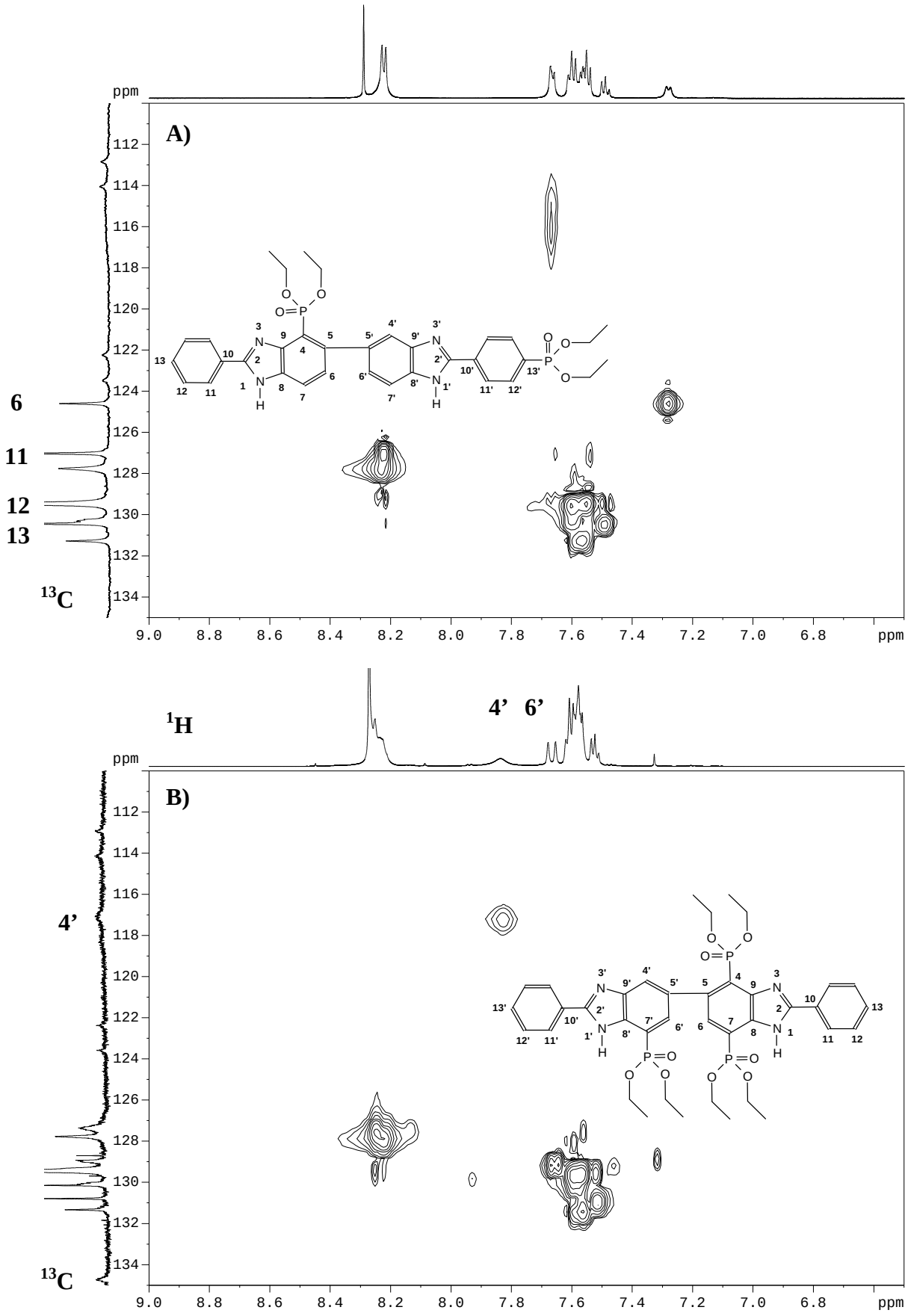
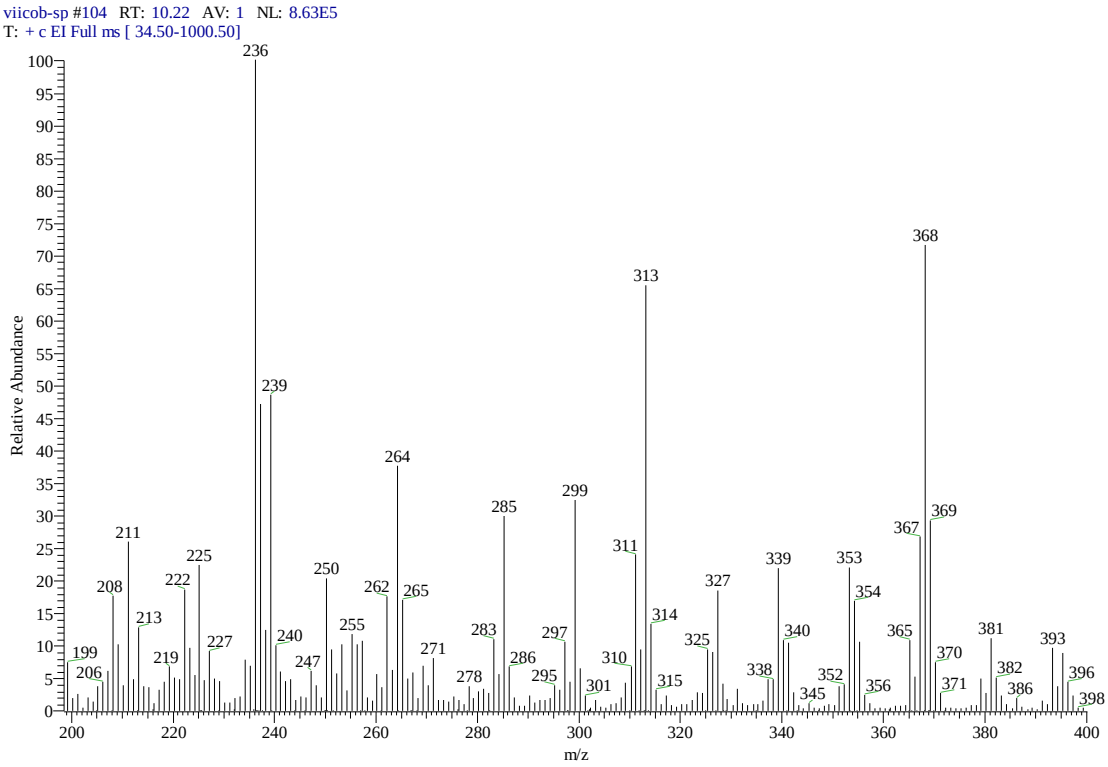


Figure S7. $^{1}H^{13}C$ HMQC (600 MHz) spectra of A) DPBP and B) TDPB in d^{6}-DMSO.

A)



B)

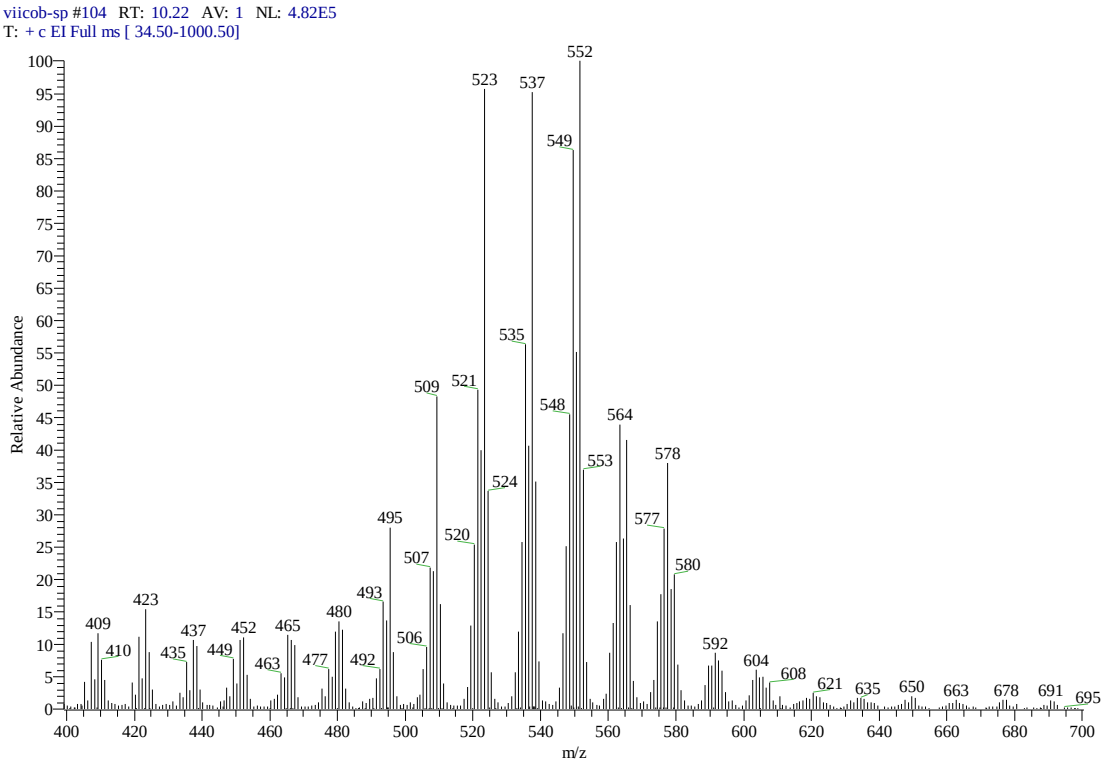


Figure S8. Pyrolysis mass spectrum of $PBIP_{Et}1$ at 234 ^{o}C, A) *m/z* = 200-400, B) *m/z* = 400-700.

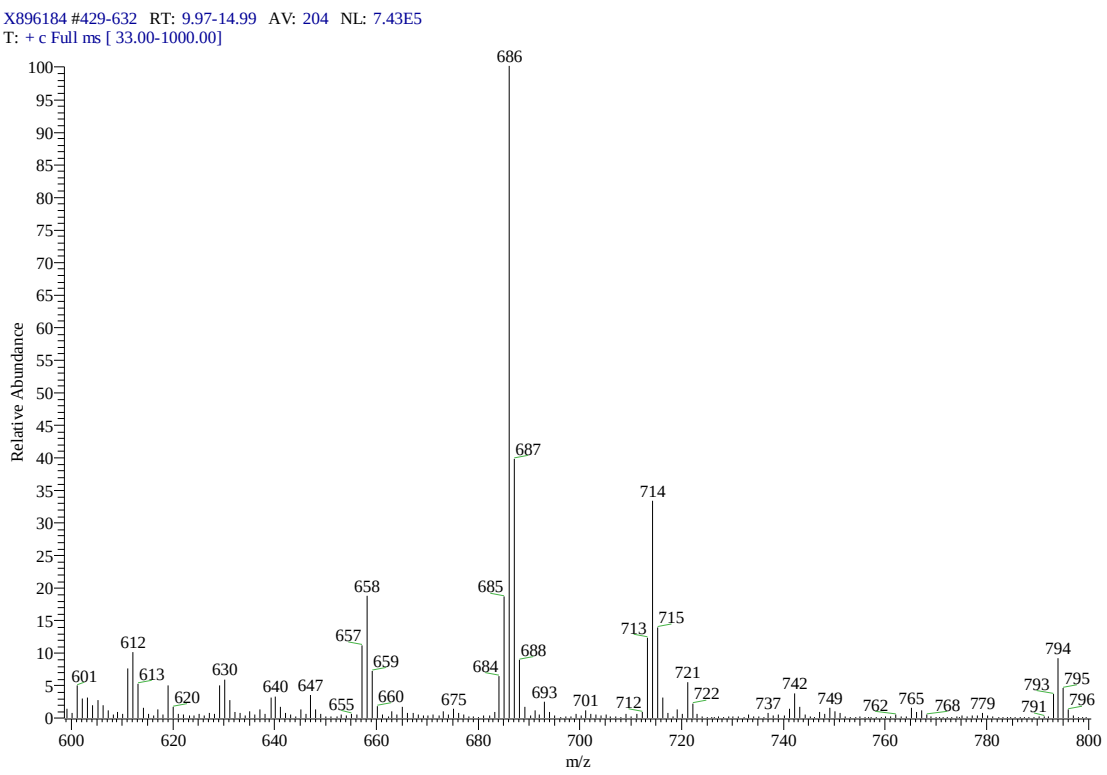
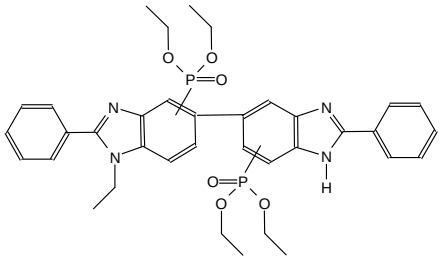
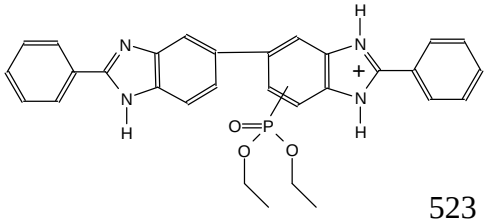
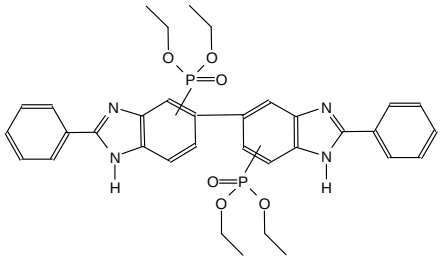
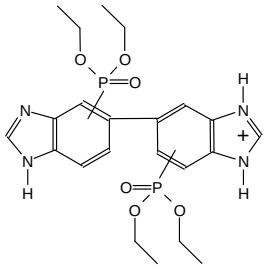
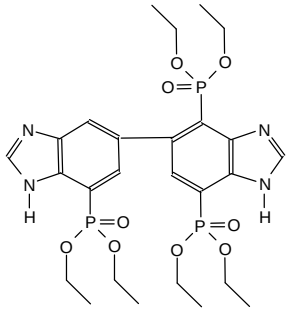
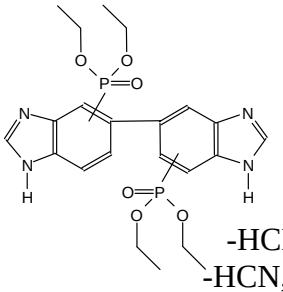
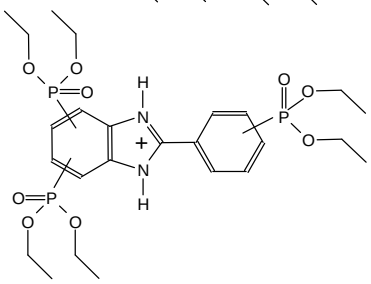
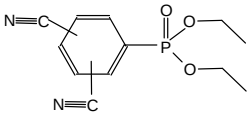
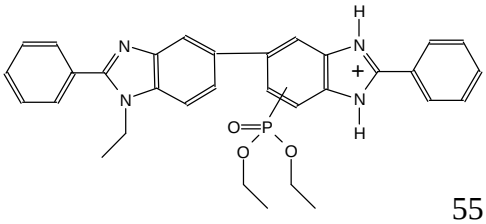
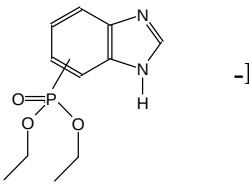
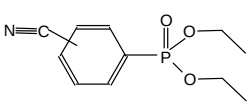


Figure S9. Pyrolysis mass spectrum of TDPB at 270-450 ^{o}C, *m/z* = 600-800.

Table S1. Structures Corresponding to Mass Spectral Fragments

Fragment	*m/z*	Fragment	*m/z*
	686		523 -C_2H_4 = 495 -2 C_2H_4 = 467
	658		507 -C_2H_4 = 479 -2 C_2H_4 = 451 -3 C_2H_4 = 423
	642 -H = 641		506 -HCN = 479 -HCN, -C_2H_4 = 451 -HCN, -2 C_2H_4 = 423 -HCN, -3 C_2H_4 = 395 -HCN, -4 C_2H_4 = 367
	603		264 -C_2H_4 = 236
	551 -CH_2 = 537 -CH_2, -C_2H_4 = 509 -CH_2, -2 C_2H_4 = 481		254 -H, -C_2H_4 = 225
			239 -C_2H_4 = 211

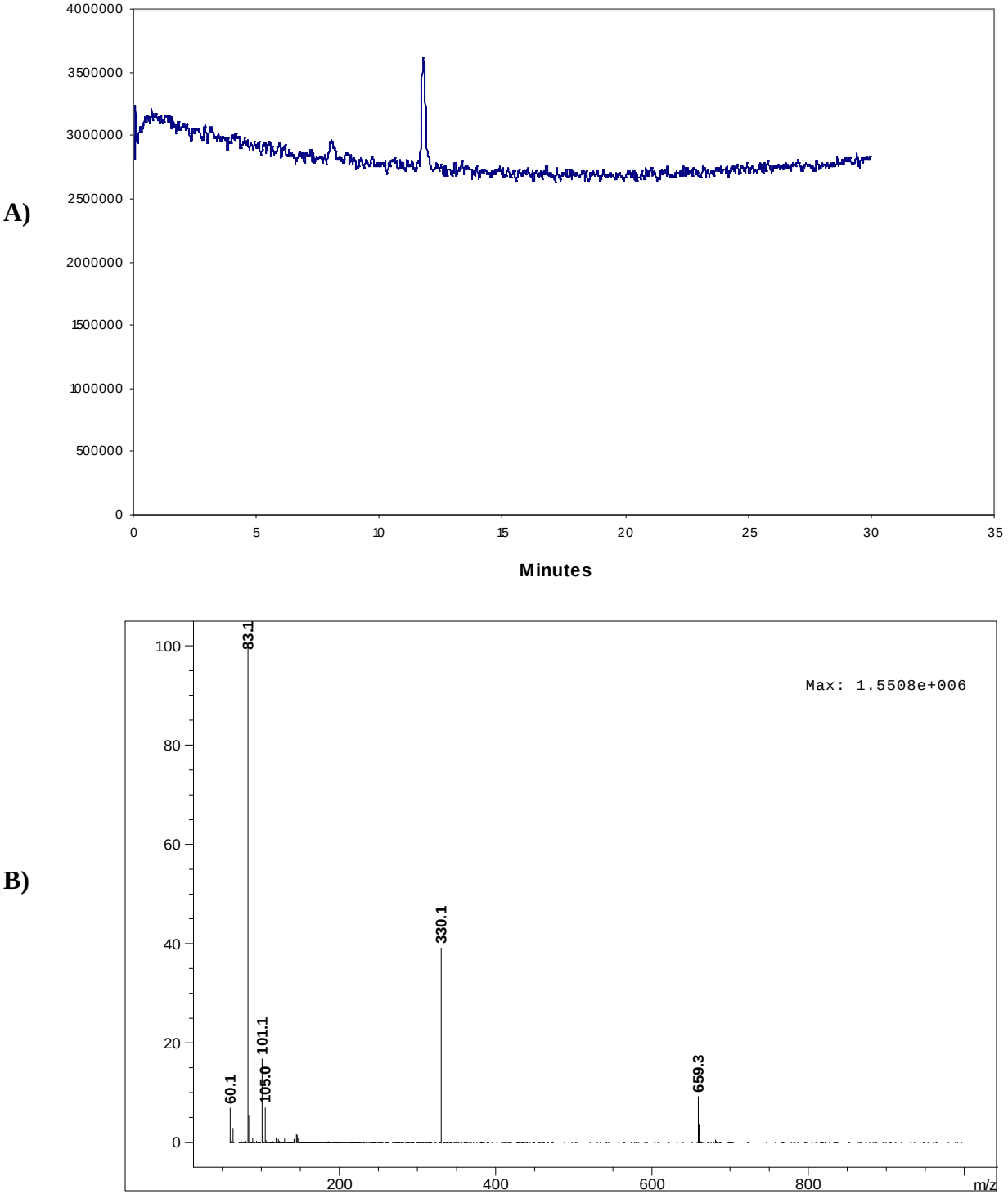


Figure S10. Isolated DPBP product A) HPLC trace, 50-100% MeCN gradient for 30 min, 1mL/min, mass spectral detector, and B) corresponding mass spectrum.