Supporting Information

Preparation and Properties of Phosphaethynes Bearing Bulky Aryl Groups with Electron-donating Substituents at the para-Position

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CONTENTS

Preparation of 4-bromo-3,5-xylidine. To a solution of 3,5-xylidine (50 g, 0.41 mol) in $CHCl_3$ (500 mL) was added 90 mL (0.64 mol) of NEt_3. Acetic anhydride (20 ml x 3 times, total 0.64 mol) was then added at 0 °C, and the mixture was warmed to room temperature. After being stirred for 4 h, the mixture was washed with 1 M hydrochloric acid, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, and concentrated. The residue was dissolved in acetonitrile (1.5 L) and NBS (71 g, 0.40 mol) was slowly added at room temperature. After 12 h-stirring, precipitates were collected and the solvent was removed under reduced pressure. The residue and the precipitates were combined, and to this mixture were added EtOH (300 mL), water (400 mL), and conc. hydrochloric acid (125 mL). The resulting mixture was refluxed for 6 h. After cooling to room temperature, NaOH was added until pH of the solution became higher than 12. The precipitates were collected and dried to give 79.9 g (98% yield) of 4-bromo-3,5-xylidine.

Preparation of 2,5-dibromo-1,3-dimethylbenzene (3). $NaNO_2$ (17.6 g, 0.26 mol) was added to conc. sulfuric acid (130 mL) at 0 °C. To the resulting mixture was added acetic acid (100 mL), and then **2** (17 g x 3 times, total 0.26 mol) portionwise. The mixture was stirred at 0–10 °C for 1 h and 100 mL of acetic acid was added to the mixture. Then the resulting solution was poured into a mixture of CuBr (45 g, 0.31 mol) and 48% hydrobromic acid (130 mL). The resulting mixture was allowed to warm to 70 °C and vigorously stirred for 2 h. The solution was diluted with hexane and water. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2 / hexane) of the residue provided 25.4 g (38% yield) of **3**.

Crystal data for 2-[2,6-di-*t*-butyl-4-(dimethylamino)phenyl]-1-phosphaethyne (2c). $C_{17}H_{26}NP$, monoclinic, space group $P2_1/n$ (#14), a = 10.230(4), b = 11.190(6), c = 14.989(5) Å, β = 93.24(1)°, V = 1713(1) Å^3, Z = 4, D_{calc} = 1.068 gcm^{-1}, μ (Mo Kα) = 1.50 cm^{-1}. 2446 Unique reflections with $2\theta \leq 50.0°$ were collected at 203 K. Of these 2176 with $I > 2.0\sigma(I)$ were used for $R1$

calculation. The structure was solved by direct method. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. $R1 = 0.075$, $R = 0.139$, $R_w = 0.165$. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-227150).

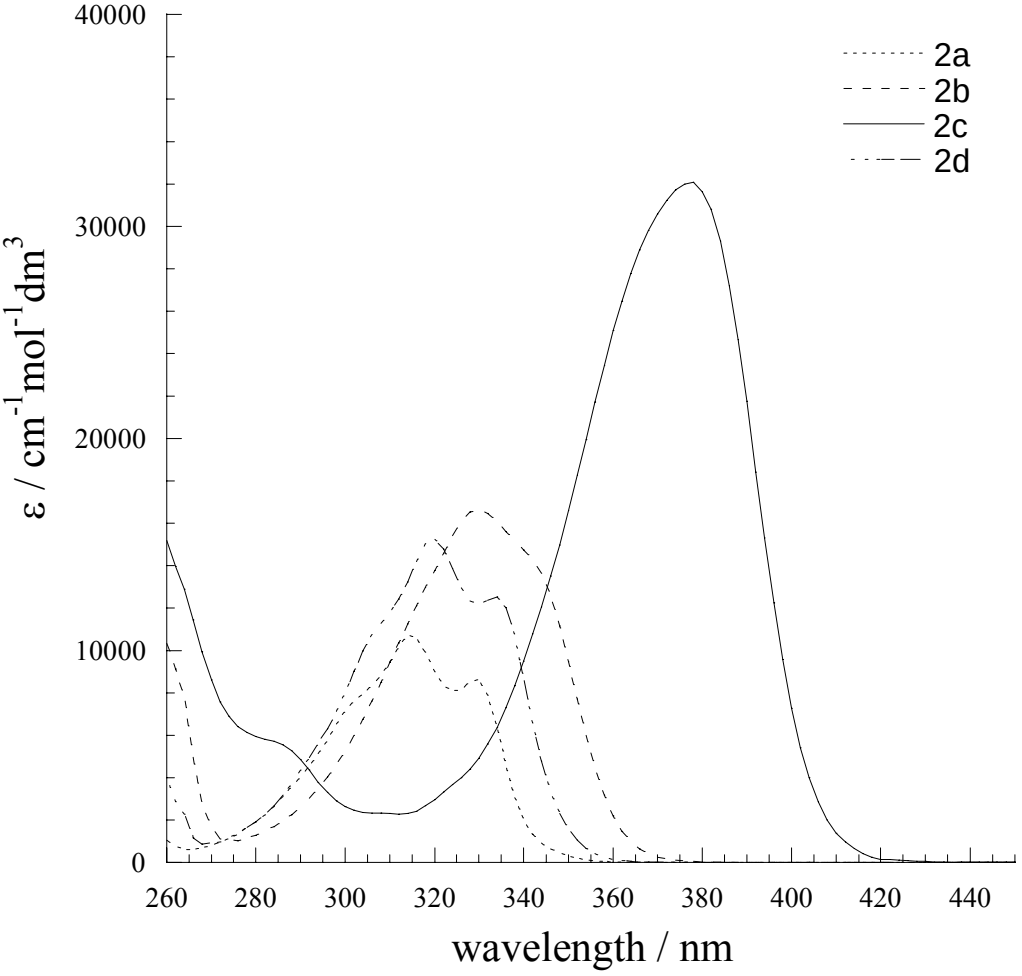

FIGURE 1. UV-vis spectra of **2a**–**d** in CH_2Cl_2.

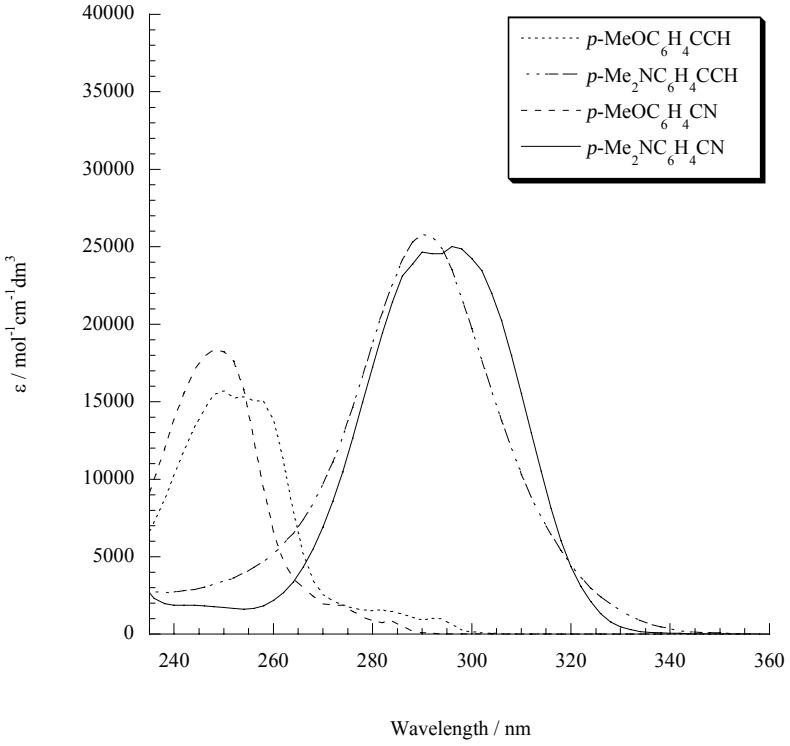

Figure 2. UV spectra of *p*-substituted phenylacetylenes and benzonitriles in CH_2Cl_2.

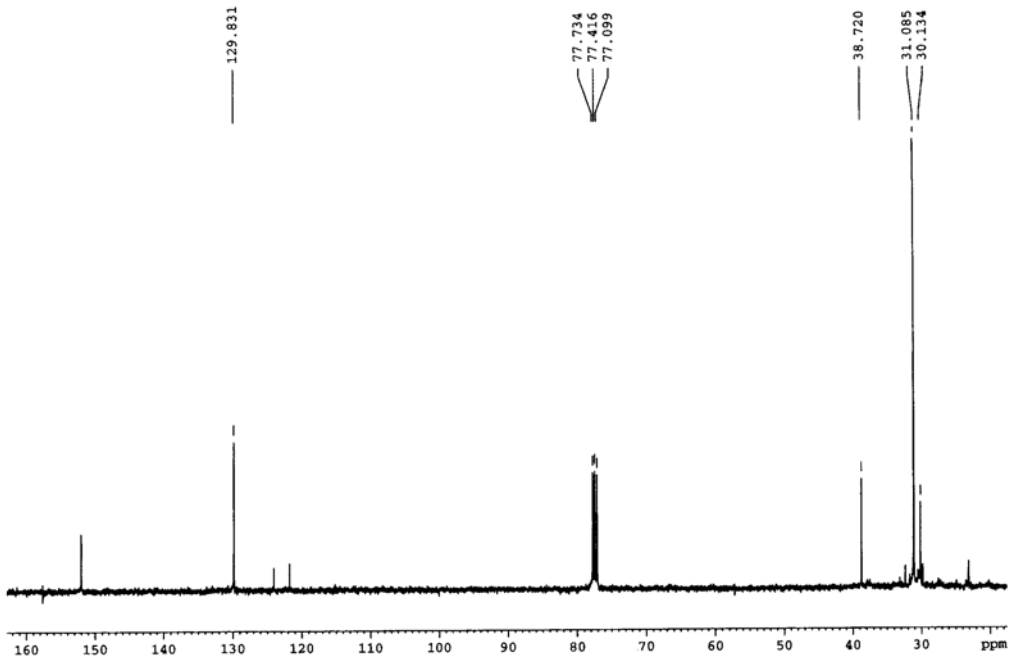

Figure 3. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2,5-dibromo-1,3-di-*t*-butylbenzene (**1e**). Trace of hexane was included in the spectrum.

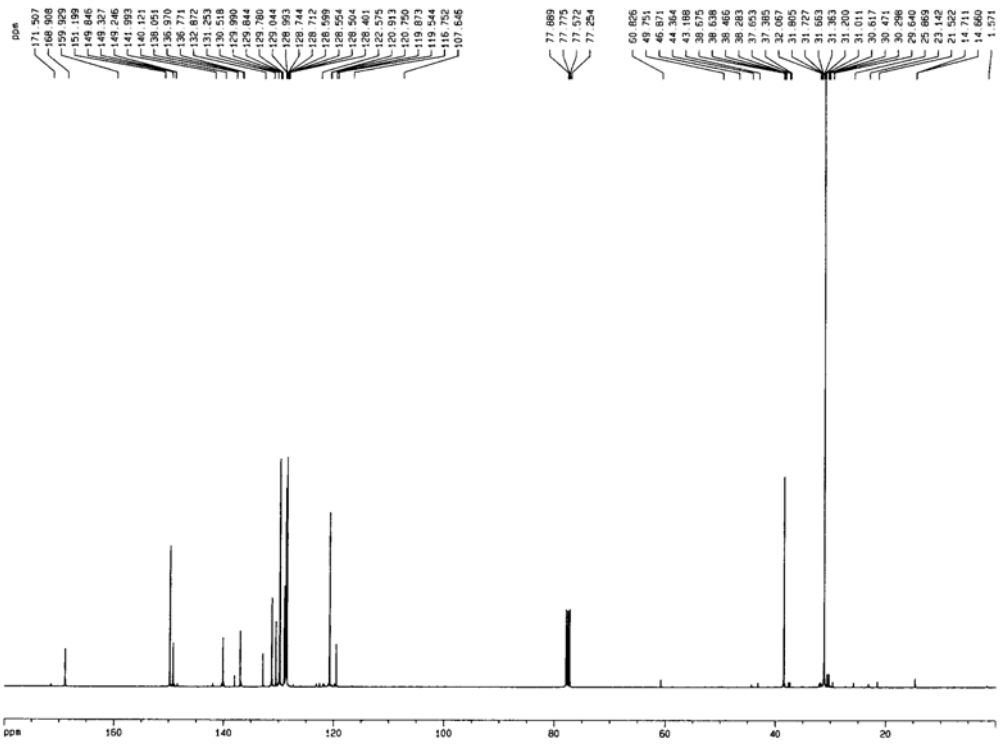

Figure 4. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (4-bromo-3,5-di-*t*-butylphenyl)(diphenyl-methylene)amine (**1f**).

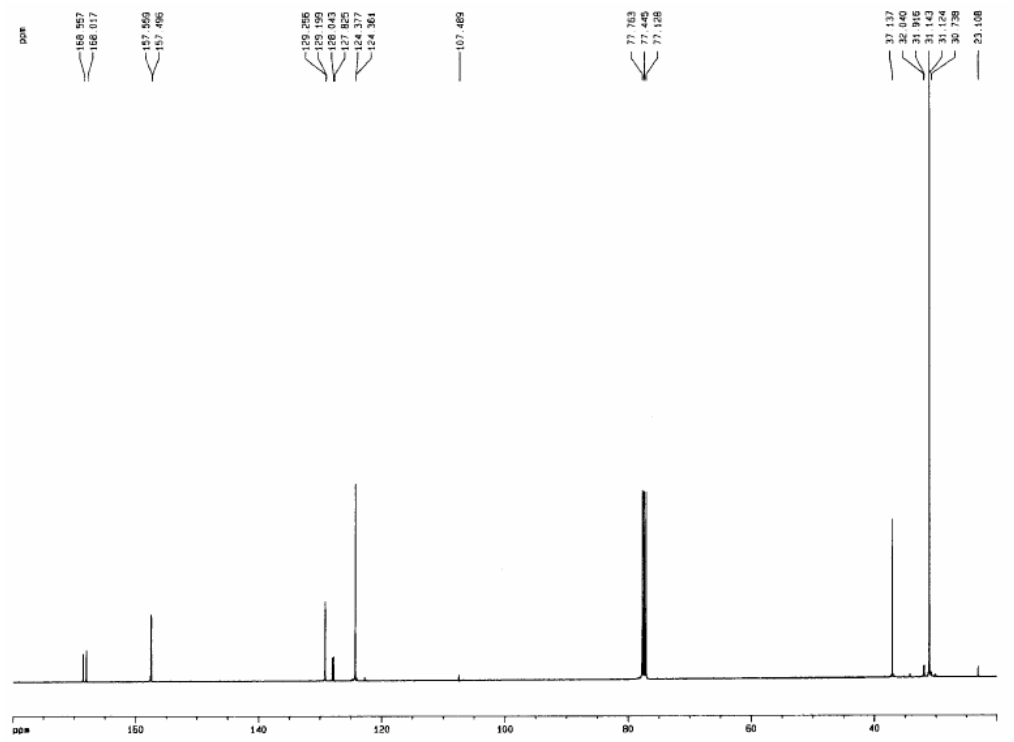

Figure 5. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (2,6-di-*t*-butylphenyl)-1-phosphaethyne (**2a**).

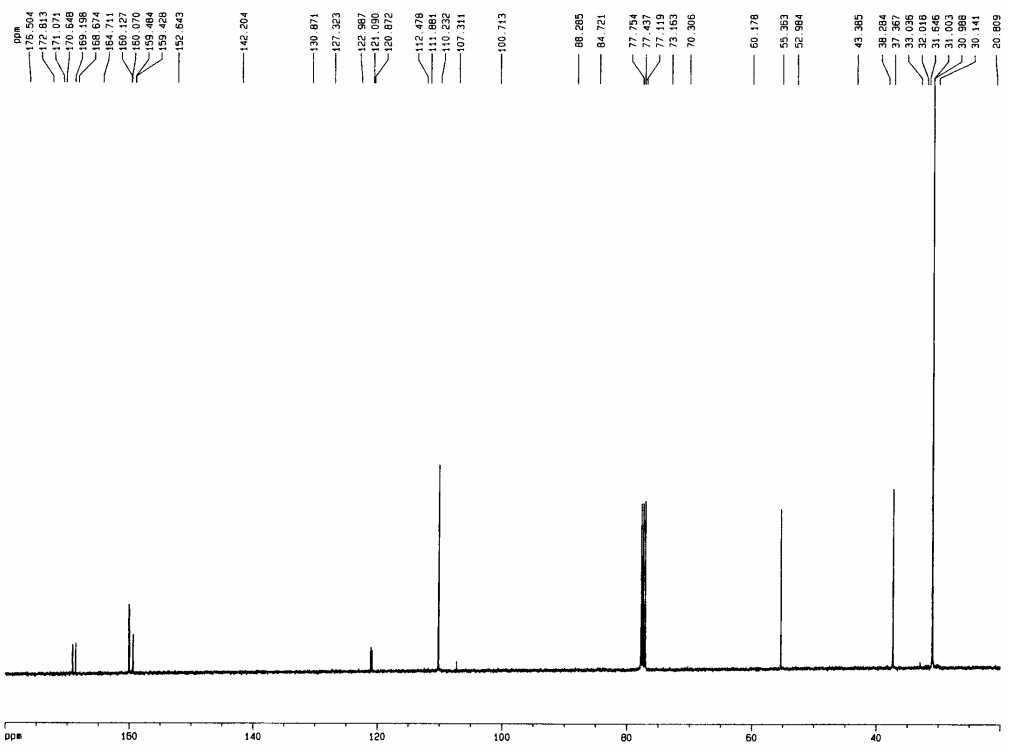

Figure 6. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (2,6-di-*t*-butyl-4-methoxyphenyl)-1-phosphaethyne (**2b**).

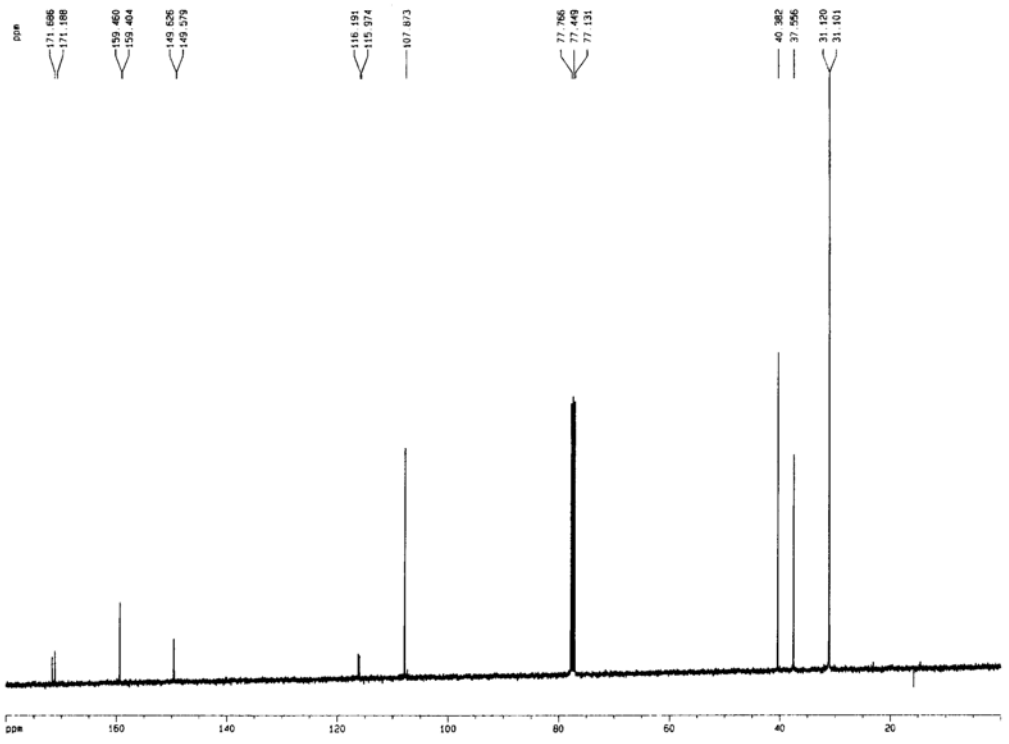

Figure 7. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of [2,6-di-*t*-butyl-4-(dimethylamino)phenyl]-1-phosphaethyne (**2c**).

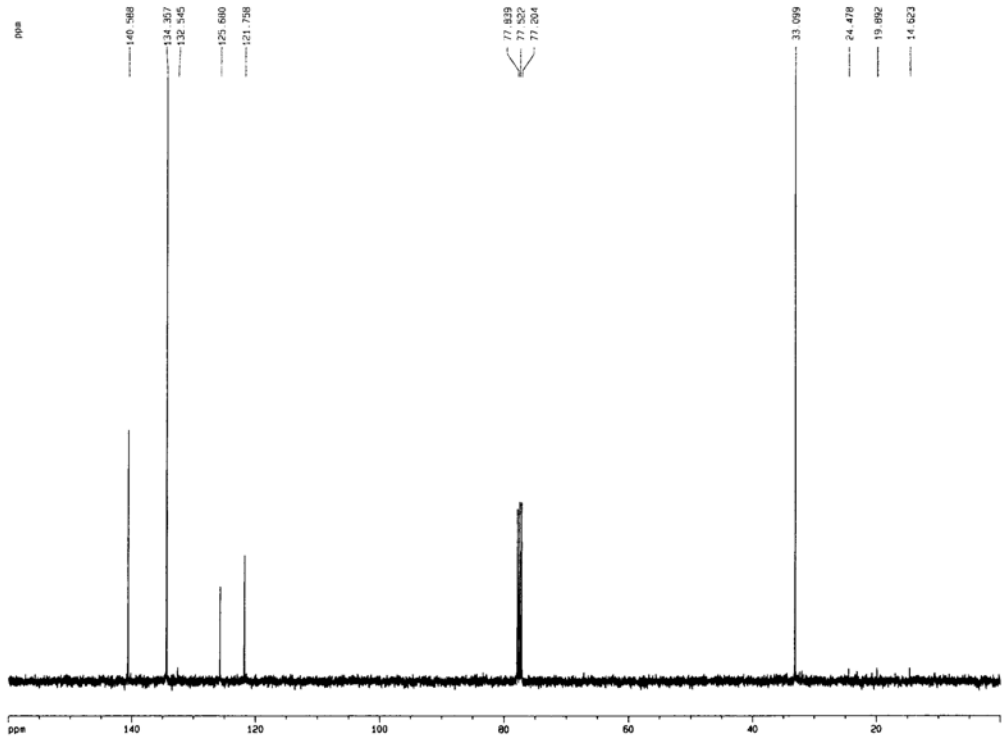

Figure 8. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2,5-dibromo-1,3-bis(bromomethyl)benzene (**4**).

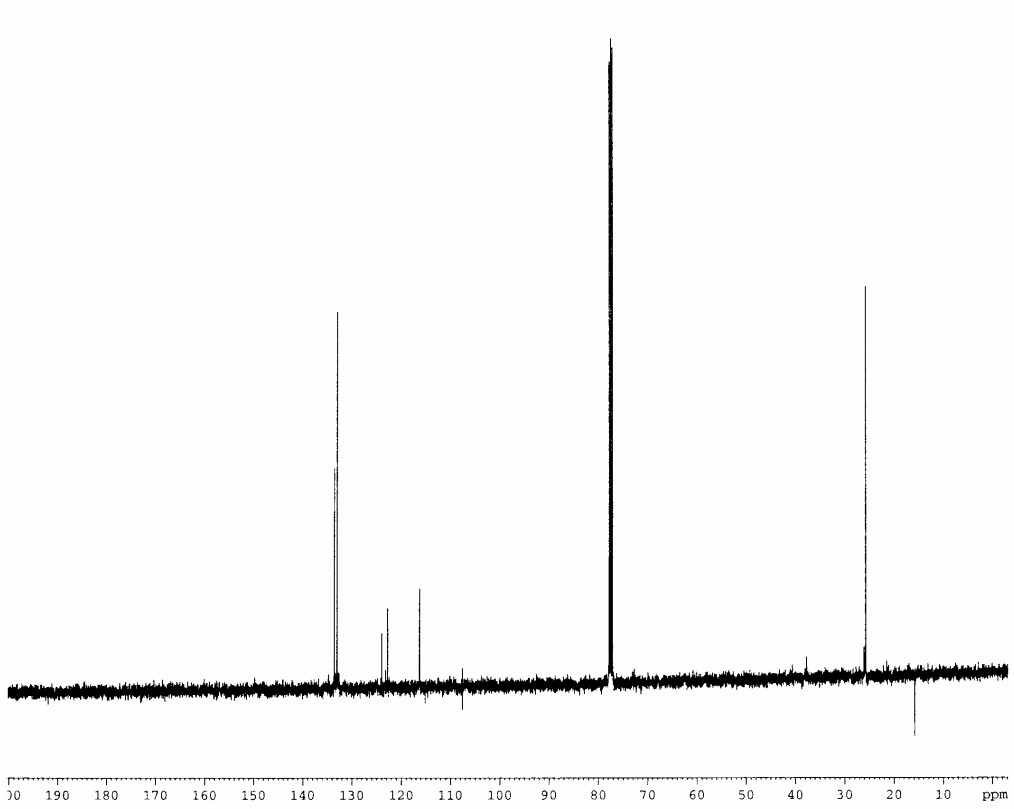

Figure 9. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2,5-dibromo-1,3-bis(cyanomethyl)benzene (**5**).

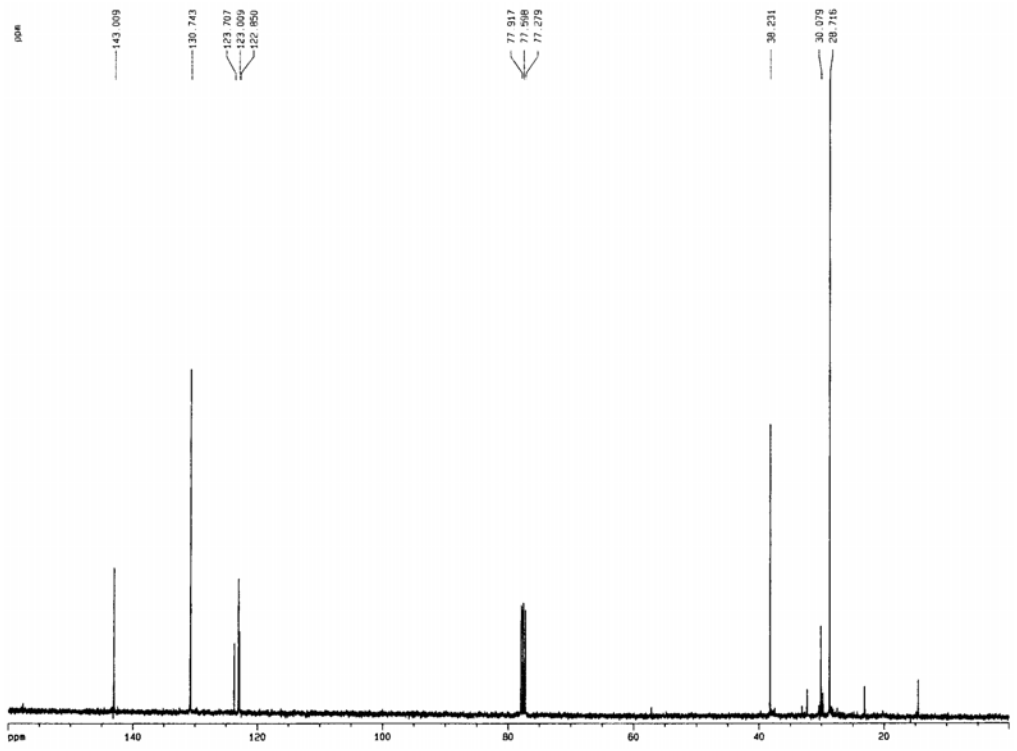

Figure 10. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2,5-dibromo-1,3-bis(1-cyano-1-methylethyl)benzene (**6**). Trace of hexane was included in the spectrum.

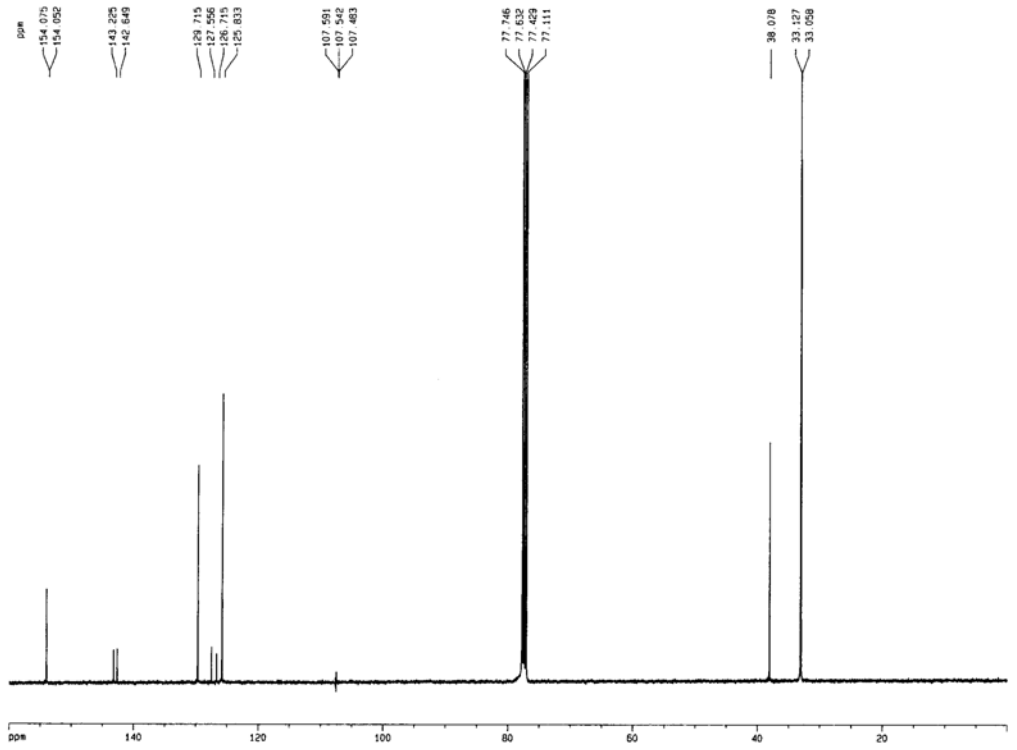

Figure 11. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (dibromomethylene)(2,6-di-*t*-butyl-phenyl)phosphine (**9a**).

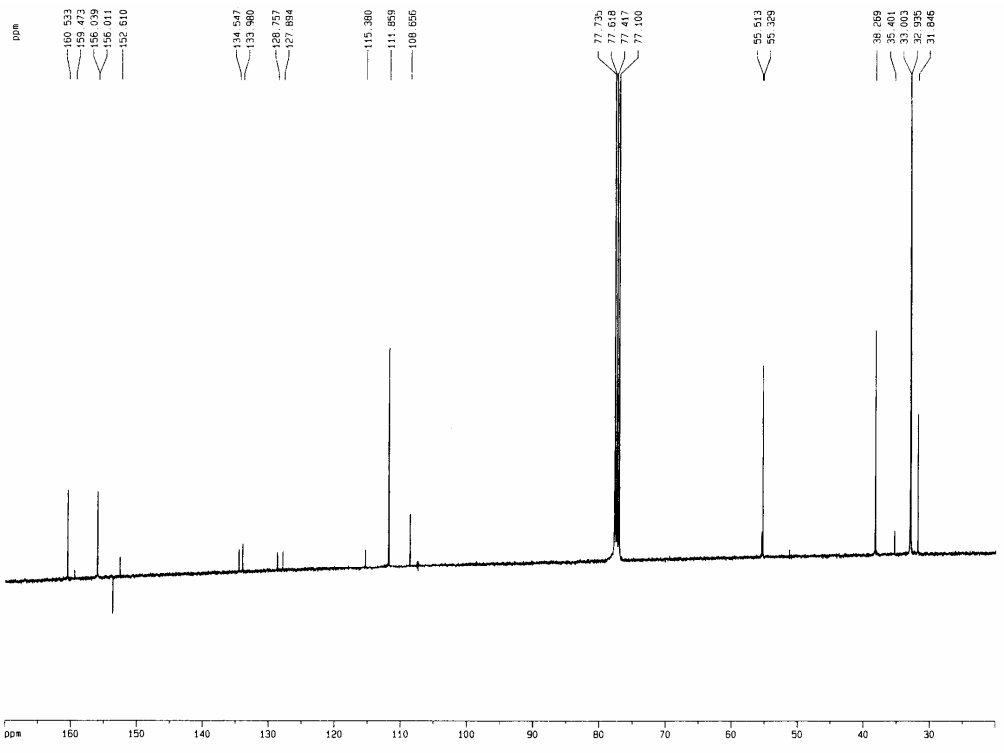

Figure 12. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (dibromomethylene)(2,6-di-*t*-butyl-4-methoxyphenyl)phosphine (**9b**). Partial decomposition of **9b** occurred during the measurement.