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Graphical Abstract

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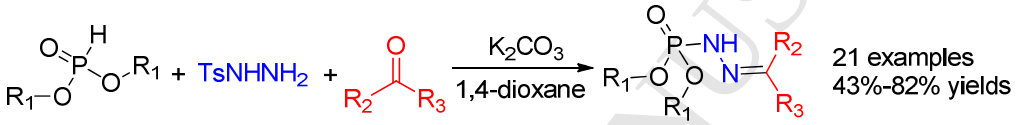

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Tel & Fax: + 86 816 2484289; E-mail: *xlwang@caep.ac.cn*

Abstract: A simple and efficient three-component coupling reaction for the synthesis of phosphorohydrazones was developed. Both aldehydes and ketones participated in the reaction to afford the corresponding phosphorohydrazones in moderate-to-good yields. Moreover, a novel P–N ligand was synthesized by this method, which can act as a fluorescent sensor for iron ion.

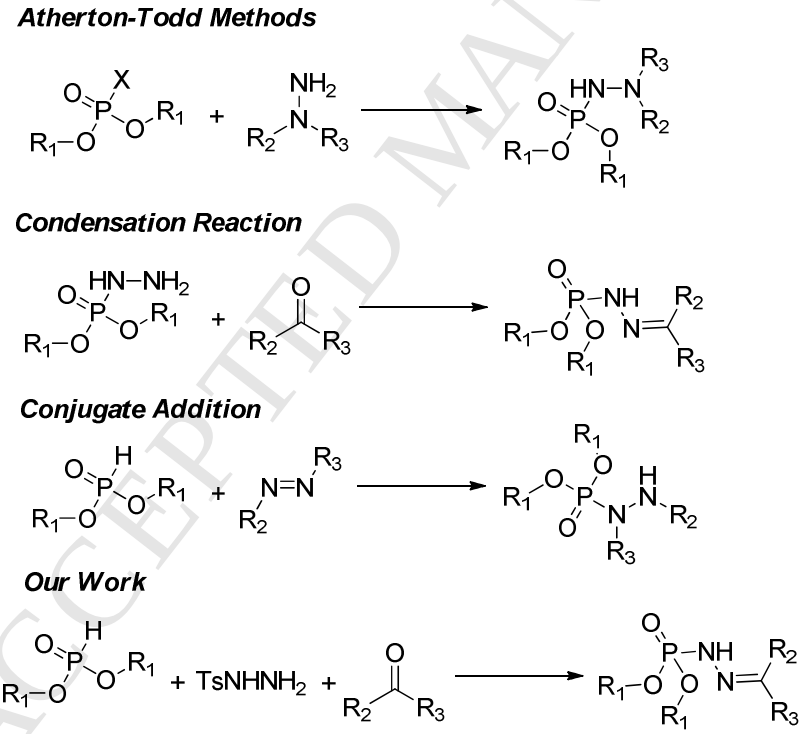
Key Words: *phosphorohydrazones, three-component, P–N ligand, fluorescent sensor*

1. Introduction

Heteroatom compounds containing P–N bonds are well known to be chemically stable and hence are widely used in catalysis [1], metal extraction, bio-organic chemistry [2], and so on. Further, highly efficient methods for synthesizing these compounds have been reported [3]. In particular, phosphorohydrazones possess a diverse range of bioactivities such as antitumor, antibacterial, and antiangiogenic activity [4] and are valuable intermediates for building blocks in natural products [5]. However, there are very few reported methods for the synthesis of phosphorohydrazones. The Atherton–Todd reaction (Scheme 1) is used as a major strategy for the synthesis of phosphorohydrazones [6], but a mixed product is often obtained because of the presence of two N–H bonds in the hydrazine group. Condensation of phosphorohydrazidates with carbonyl compounds [7] and conjugate addition of dialkyl phosphites with diazenes can also afford phosphorohydrazones [8],

but the practical applicability of these methods is severely restricted because of the need for special substrate sources.

Sulfonylhydrazones are valuable intermediates for organic synthesis; they are used as an *in situ* source of diazo compounds in many types of transition-metal-catalyzed reactions [9]. Nevertheless, such heavy metals are toxic and contamination of the final product by the metal catalysts is undesirable, which calls for the development of transition-metal-free reactions. We have recently reported an effective method for the synthesis of pyrazoles by the one-pot condensation of α,β-unsaturated carbonyl compounds with tosylhydrazide in the absence of any transition-metal catalyst [10]. Herein, we report a base-mediated three-component coupling reaction of dialkyl phosphites, tosylhydrazide, and carbonyl compounds (Scheme 1) that affords a wide variety of substituted phosphorohydrazones in moderate-to-good yields.



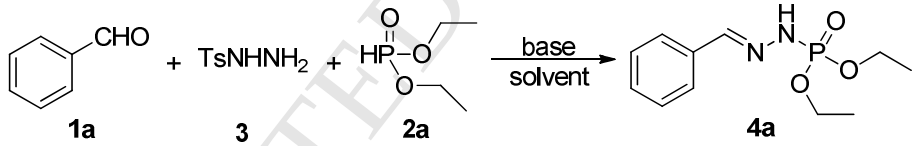
Scheme 1. Methods for the preparation of phosphorohydrazones

2. Results and discussion

For the initial optimization of the reaction conditions, the condensation of benzaldehyde **1a**, tosylhydrazide **3**, and diethyl phosphite **2a** was selected as a model

reaction system. The results are listed in Table 1. When the reaction was carried out in *N*,*N*-dimethylformamide (DMF) with K_2CO_3 as the base, the desired product **4a** was isolated in 46% yield (entry 1). A similar yield was obtained in the reaction carried out with K_3PO_4 as the base (entry 2). Other bases such as NaOH, Cs_2CO_3, and MeONa (entries 3–5), however, gave only trace amounts of the desired product, and no product was detected in the absence of the base (entry 6). These results implied that the presence of a base is crucial for the success of the reaction. Screening of solvents (entries 7–10) revealed that 1,4-dioxane was the most suitable for the reaction, affording the desired product in 76% yield. Screening of base amounts on a small scale (entries 8, 11–13) indicated that 3 equiv of K_2CO_3 was the optimal amount for the reaction, in which case 76% product yield was obtained (entry 8). Increasing the reaction temperature dramatically increased the product yield, with 60 °C being the optimal temperature. Higher temperatures were unfavorable because of the greater amount of by-products formed (entries 14–16).

Table 1 Optimization of reaction conditions [a]



1a **3** **2a** **4a**

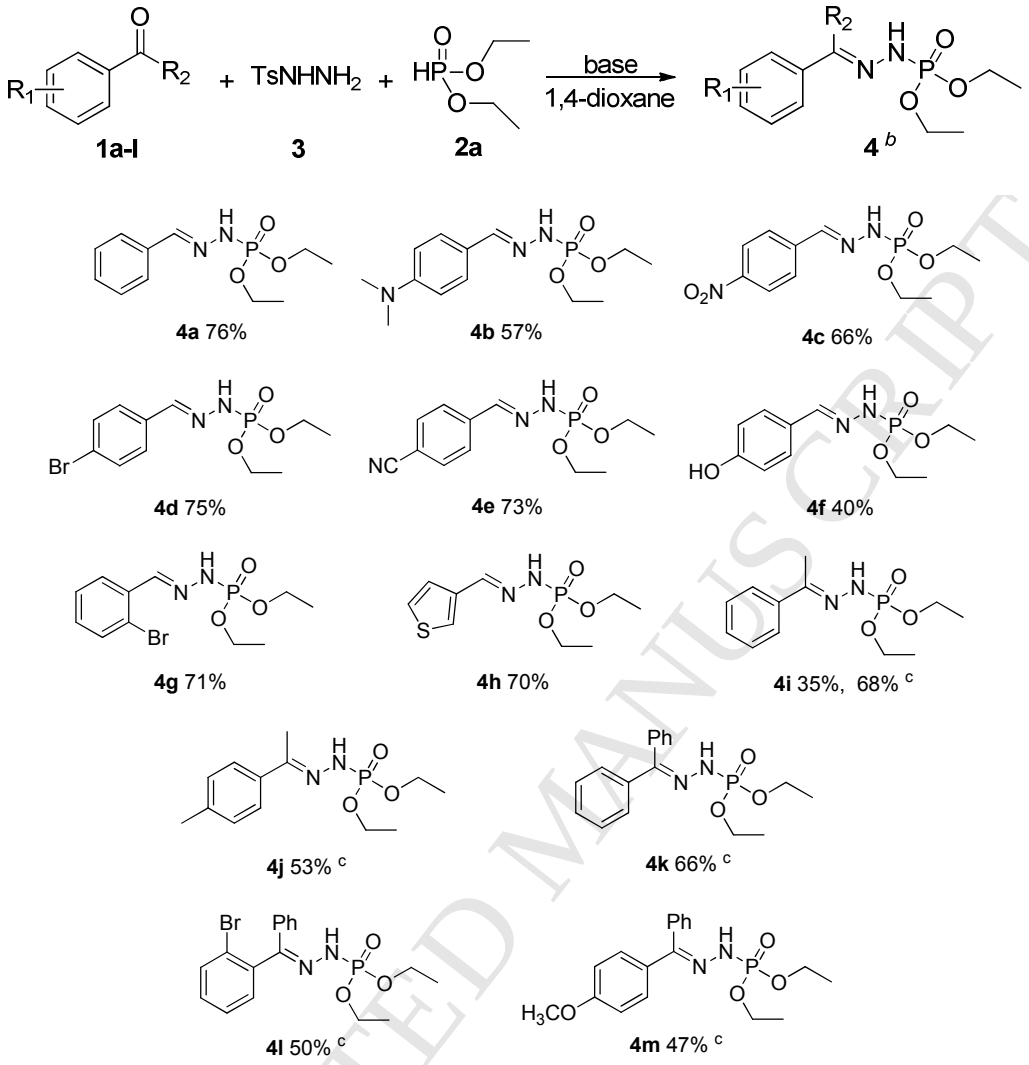
Entry	Base	Base amount (equiv.)	Solvent	Temp (^oC)	Yield (%)[b]
1	K_2CO_3	3	DMF	60	46
2	K_3PO_4	3	DMF	60	41
3	NaOH	3	DMF	60	trace
4	Cs_2CO_3	3	DMF	60	trace
5	MeONa	3	DMF	60	trace
6	-	-	DMF	60	NR
7	K_2CO_3	3	DMSO	60	trace
8	K_2CO_3	3	1,4-dioxane	60	76
9	K_2CO_3	3	toluene	60	23
10	K_2CO_3	3	EtOH	60	11

11	K_2CO_3	1	1,4-dioxane	60	14
12	K_2CO_3	1.5	1,4-dioxane	60	22
13	K_2CO_3	2	1,4-dioxane	60	51
14	K_2CO_3	3	1,4-dioxane	r.t.	NR
15	K_2CO_3	3	1,4-dioxane	40	25
16	K_2CO_3	3	1,4-dioxane	80	66

[a] Reaction conditions: 1a (0.5 mmol), 2a (0.75 mmol)), 3 (0.625 mmol), base (3.0 equiv), solvent (2 mL), 24 h, in air. [b] Isolated yield.

Under the optimized conditions, we next evaluated the substrate scope by extending the reaction to various carbonyl compounds. The results of the coupling reactions of diethyl phosphite, tosylhydrazide, and carbonyl compounds mediated by a base are summarized in Table 2. Benzaldehydes with electron-rich and electron-deficient substituents afforded the corresponding phosphorohydrazones **4a–g** in moderate-to-good yields. The results indicated that benzaldehydes with electron-withdrawing substituents can give the corresponding products in better yields. The sterically hindered 2-bromobenzaldehyde did not affect the result and gave the desired product **4g** in 71% yield. A heteroarene carbaldehyde such as thiophene-3-carbaldehyde also gave the desired product **4h** in 70% yield. When acetophenone was used as the substrate under the optimized conditions, the product **4i** was obtained but in poor yield (35%). Therefore, we optimized the reaction conditions, including the type of base and temperature, and obtained **4i** in fairly good (68%) yield when the reaction was performed at 80 ^{o}C using K_3PO_4 as the base. Under these conditions, substituted acetophenone and benzophenone could afford the corresponding phosphorohydrazones **4j–l** in moderate yields.

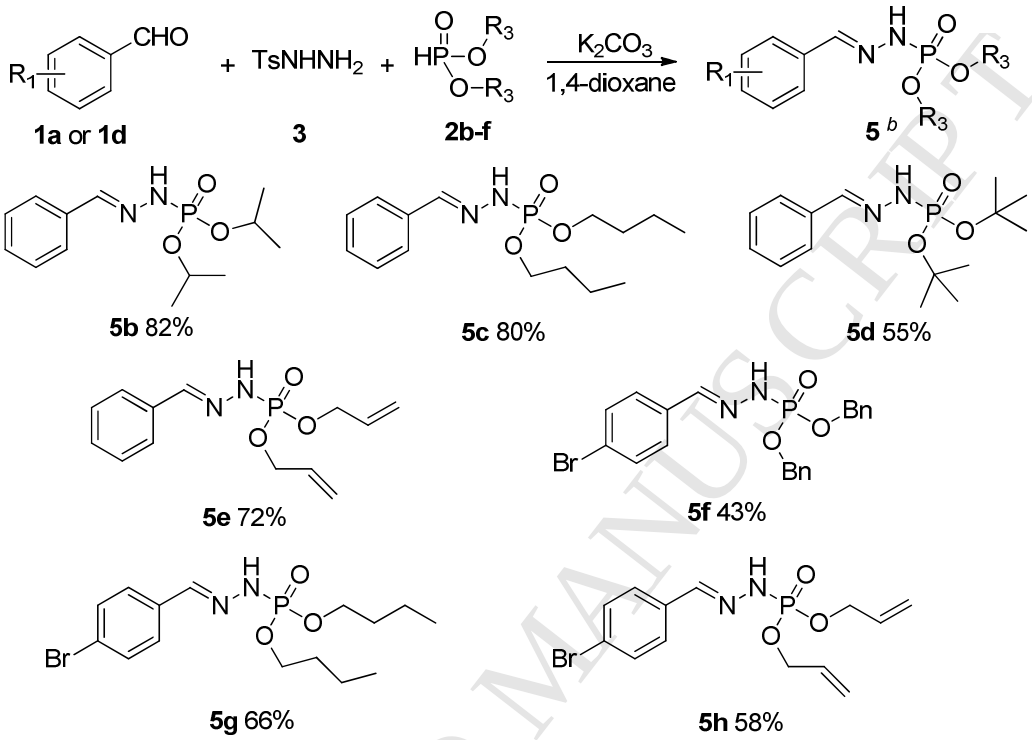
Table 2. Base-mediated three-component coupling of diethyl phosphite, tosylhydrazide, and carbonyl compounds [a]



[a] Reaction conditions: 1 (0.5 mmol), 2a (0.75 mmol)), 3 (0.625 mmol), K_2CO_3 (3.0 equiv), 1,4-dioxane (2 mL), 60 °C, 24 h, in air. [b] Isolated yield. [c] K_3PO_4 (3.0 equiv), 80 °C.

Reactions employing various dialkyl phosphites with substituted benzaldehydes and tosylhydrazide were also investigated; the results are summarized in Table 3. H-phosphite diesters bearing different alkyl groups could react smoothly under the optimized reaction conditions to afford the products **5**. Di-*t*-butyl phosphite gave the corresponding product **5d** in relatively lower yield (55%) than that with the other dialkyl phosphites, probably because of the steric effect. Dibenzyl or diallyl phosphite, too, gave the desired products **5e** and **5f** in 72% and 43% yields, respectively.

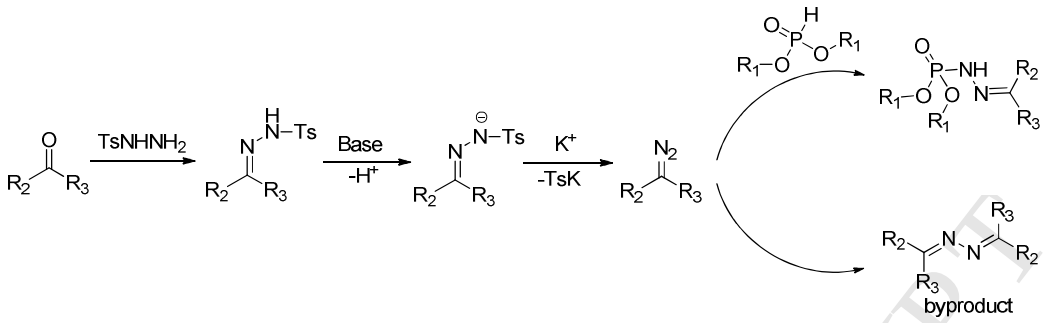
Table 3. K_2CO_3-mediated three-component coupling reactions of dialkyl phosphites, tosylhydrazide, and carbonyl compounds [a]



[a] Reaction conditions: 1 (0.5 mmol), 2 (0.75 mmol)), 3 (0.625 mmol), K_2CO_3 (3.0 equiv), 1,4-dioxane (2 mL), 60 ^{o}C, 24 h, in air. [b] Isolated yield.

We speculated that the reaction started with the condensation of tosylhydrazide with the carbonyl compound to form the tosylhydrazone, Base will deprotonate the proton of -NHTs and then kick out Tosyl group to form the diazo compound [11]. Thereafter, the intermediate diazo compound was trapped by a dialkyl phosphate to give the final product. The main byproduct is *N*,*N'*-dialkenylhydrazine, which is formed via self-coupling of the diazo compound (Scheme 2) [12].

Scheme 2. Proposed mechanism for the reaction.



Phosphorohydrazones may find application in coordination chemistry and metal extraction as well. Thus, to expand the practical utility of this synthetic method, we applied the coupling reaction to the preparation of a novel 1,1'-bi-2-naphthol (BINOL) ligand **7**. As depicted in Scheme 3, **7** was prepared in 53% yield by the reaction of binaphthalene dialdehyde **6** with tosylhydrazide and diisopropyl phosphite under the optimized conditions. The fluorescence spectra of **7** in DMF exhibited a broad emission peak, with λ_{max} at 408 nm (Figure 1). We then tested the fluorescence response of **7** toward a series of metal ions. As shown in this figure, the fluorescence of **7** was clearly quenched upon the addition of 10 equiv of Fe^{2+}, while the addition of other metal ions such as K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Al^{3+}, and Zn^{2+} had no influence on the fluorescence. Fluorescence titration with Fe^{2+} ions in varying concentrations was performed. As shown in Figure 2, the addition of increasing concentrations of Fe^{2+} ions led to a gradual diminished intensity, and the fluorescence of compound **7** was essentially quenched by 15 equiv of Fe^{2+} ions. In addition, Fe^{3+} has the same phenomenon of fluorescence quenching when add it to the solution of compound **7**. This result indicated the formation of a well-defined complex between **7** and iron ion, thus confirming the potential application of **7** as a fluorescent sensor for iron ion detection, which has received great attention because of the simplicity of operation as well as high selectivity and sensitivity [13].

Scheme 3. Preparation of binol-based P-N ligand **7.**

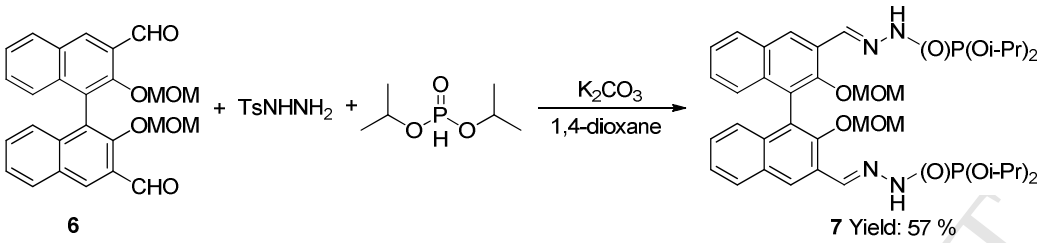


Figure 1: Fluorescence response of **7** (2.0×10^{-5} M in DMF) toward various (10 equiv) metal ions (λ_{exc} = 300 nm, slits: 5 nm/5 nm).

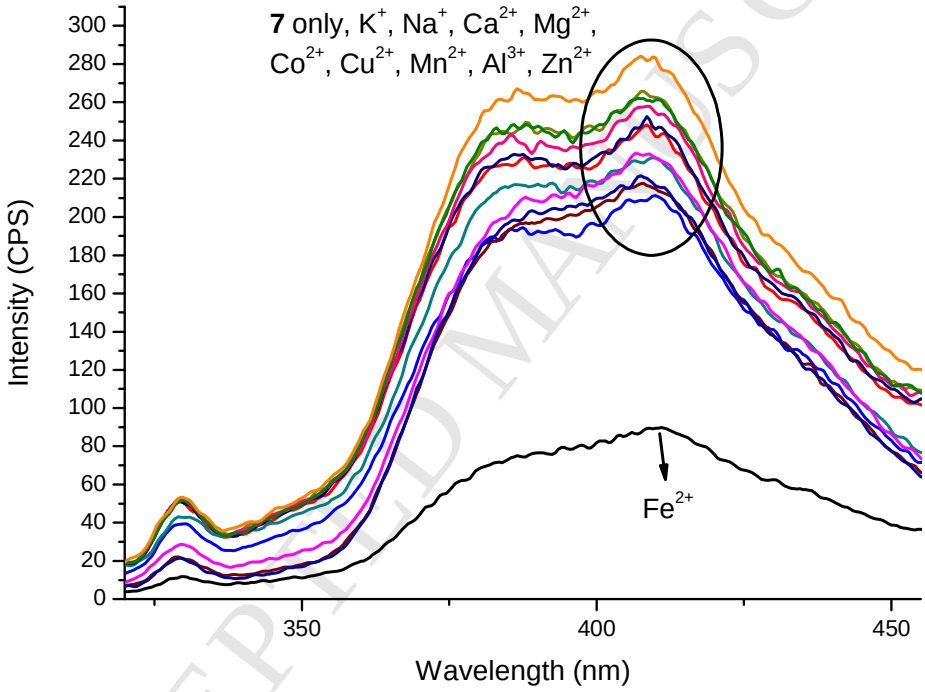
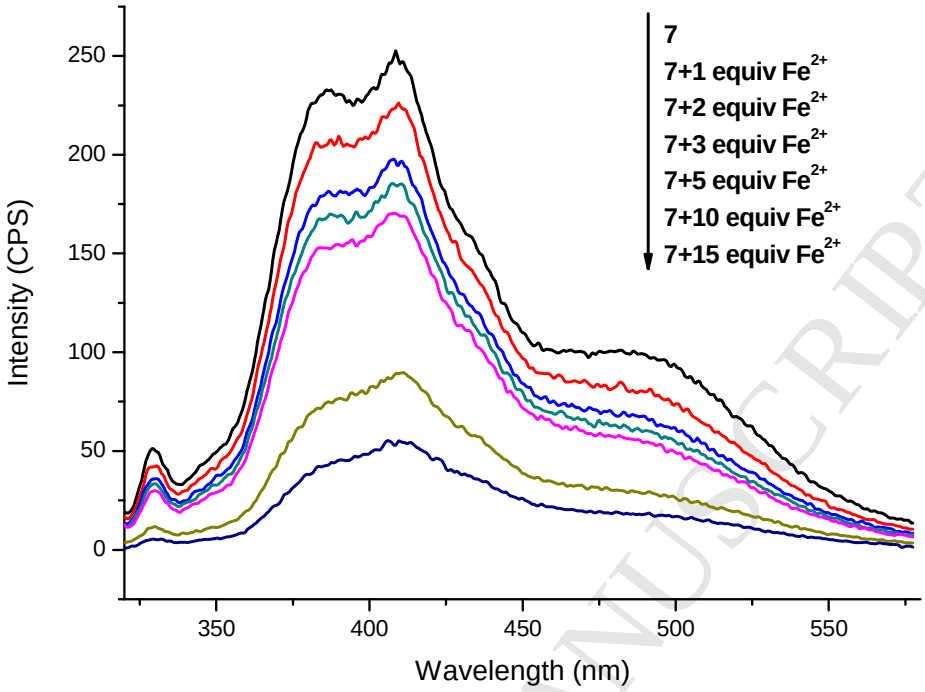


Figure 2: Fluorescence titration of **7** (2.0×10^{-5} M in DMF) with Fe^{2+} (λ_{exc} = 300 nm, slits: 5 nm/5 nm)



3. Conclusion

In conclusion, we have developed a simple and efficient method—a base-mediated three-component coupling reaction of dialkyl phosphites, tosylhydrazide, and carbonyl compounds—for the synthesis of phosphorohydrazones. Both aldehydes and ketones participated in the reaction to afford the corresponding phosphorohydrazones in moderate-to-good yields. Moreover, a novel P–N ligand that can act as a fluorescent sensor for iron ion was synthesized by this method; further studies to explore the properties of this ligand are underway. The developed reaction is expected to be a powerful tool for the synthesis of compounds containing P–N bonds.

4. Experimental

4.1 General

^{1}H-NMR, ^{13}C-NMR spectra were measured on a Bruker AM400 NMR spectrometer (400 MHz or 100MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ESI-MS spectral data were recorded on a Finnigan LCQDECA mass

spectrometer. Fluorescence spectra were recorded in the front face mode at 298 K. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Solvents were freshly distilled prior to use.

4.2 General procedure for the preparation of phosphorohydrazones.

A Schlenk tube with a magnetic stirring bar was charged with aldehyde or ketone (0.5 mmol, 1 equiv), sulfonylhydrazide (0.625 mmol, 1.25 equiv), dialkyl phosphites (0.75 mmol, 1.5 equiv), base (1.5 mmol, 3 equiv), and 1,4-dioxane (2 mL). The reaction vessel was placed in a 60 ^{o}C oil bath, and then stirred at this temperature for 10 h. The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL) and water (15 mL). The organic layer was dried over anhydrous Na_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by ^{1}H-NMR, ^{13}C-NMR and ESI-MS.

4a: colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.57-8.49 (d, J = 28.8 Hz, 1H), 7.86 (s, 1H), 7.63-7.60 (m, 2H), 7.36-7.34 (m, 3H), 4.24-4.18 (m, 4H), 1.39-1.35 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 144.97, 144.77, 134.60, 129.30, 128.55, 126.69, 63.49, 63.43, 16.20, 16.13; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.91; HRMS (ESI): Calcd for: C11H18N2O3P, 257.1055. Found: 257.1048. IR (KBr, cm^{-1}): 3136, 2988, 2936, 1480, 1251, 1059, 1022, 985, 844, 755, 689, 560, 470.

5b: colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.61-8.53 (d, J = 28.8 Hz, 1H), 7.86 (s, 1H), 7.63-7.59 (m, 2H), 7.38-7.31 (m, 3H), 4.76-4.70 (m, 2H), 1.40-1.32 (m, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$), 144.29, 144.10, 134.86, 129.11, 128.53, 126.58, 72.08, 72.02, 23.89, 23.85, 23.64, 23.59; ^{31}P-NMR (400 MHz, $CDCl_3$), 0.08; HRMS (ESI): Calcd for: C13H22N2O3P, 285.1368. Found: 285.1372. IR (KBr, cm^{-1}): 3430, 3185, 2981, 2932, 1604, 1470, 1384, 1240, 992, 885, 834, 761, 700, 553, 480, 427.

Acknowledgments

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Supplementary data

Detailed experimental procedures and compound characterization. Supplementary data related to this article can be found in the online version.

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General information.

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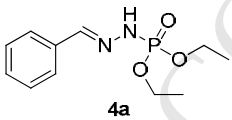
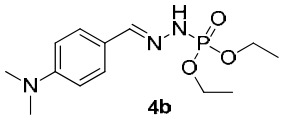
Spectroscopic data of products



4a

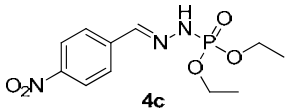
diethyl (2-benzylidenehydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.57-8.49 (d, J = 28.8 Hz, 1H), 7.86 (s, 1H), 7.63-7.60 (m, 2H), 7.36-7.34 (m, 3H), 4.24-4.18 (m, 4H), 1.39-1.35 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 144.97, 144.77, 134.60, 129.30, 128.55, 126.69, 63.49, 63.43, 16.20, 16.13; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.91; HRMS (ESI): m/z = 257.1028 $[M+H]^{+}$; IR (KBr, cm^{-1}): 3136, 2988, 2936, 1480, 1251, 1059, 1022, 985, 844, 755, 689, 560, 470.



4b

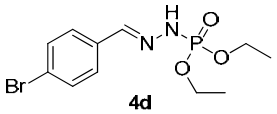
diethyl (2-(4-(dimethylamino)benzylidene)hydrazinyl)Phosphite, white crystal; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.72-7.70 (d, J = 8.0 Hz, 2H), 7.50-7.47 (d, J = 8.8 Hz, 2H), 6.69-6.66 (m, 2H),

4.23-4.16 (m, 4H), 2.98 (s, 6H), 1.38-1.34 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 151.21, 145.58, 145.39, 127.99, 122.58, 111.86, 63.28, 63.23, 40.29, 16.22, 16.15; ^{31}P-NMR (400 MHz, $CDCl_3$), 2.23; HRMS (ESI): m/z = 300.1465 $[M+H]^+$. IR (KBr, cm^{-1}): 3137, 2828, 1875, 1610, 1534, 1480, 1362, 1236, 1170, 1030, 856, 810, 548, 466.



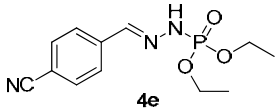
4c

diethyl (2-(4-nitrobenzylidene)hydrazinyl)Phosphite, yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 9.20-9.13 (d, J = 29.2 Hz, 1H), 8.20-8.19 (d, J = 8.4 Hz, 1H), 7.93 (s, 1H), 7.76-7.73 (d, J = 8.4 Hz, 2H), 4.24-4.17 (m, 4H), 1.39-1.35 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 147.88, 142.42, 142.22, 140.73, 127.08, 123.95, 63.80, 63.75, 16.18, 16.11; ^{31}P-NMR (400 MHz, $CDCl_3$), 0.89; HRMS (ESI): m/z = 302.0925 $[M+H]^+$. IR (KBr, cm^{-1}): 3426, 3109, 2990, 2937, 2450, 2200, 1933, 1652, 1589, 1513, 1340, 1245, 1172, 1036, 980, 865, 747, 684, 575.



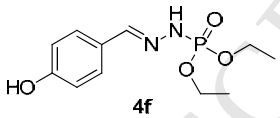
4d

diethyl (2-(4-bromobenzylidene)hydrazinyl)Phosphite, yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.88-8.80 (d, J = 28.8 Hz, 1H), 7.83 (s, 1H), 7.50-7.48 (m, 4H), 4.24-4.17 (m, 4H), 1.39-1.35 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 143.77, 143.58, 133.62, 131.73, 128.06, 123.28, 63.52, 63.47, 16.16, 16.10; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.32; HRMS (ESI): m/z = 335.0159 $[M+H]^+$. IR (KBr, cm^{-1}): 3431, 3143, 2981, 2924, 1600, 1480, 1400, 1237, 1156, 1030, 986, 820, 750, 570, 518.



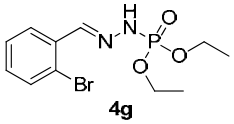
4e

diethyl (2-(4-cyanobenzylidene)hydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 9.04-8.96 (d, J = 29.2 Hz, 1H), 7.88 (s, 1H), 7.72-7.70 (d, J = 8.0 Hz, 2H) 7.65-7.63 (d, J = 8.0 Hz, 2H), 4.25-4.18 (m, 4H), 1.40-1.36 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 142.76, 142.56, 138.88, 132.39, 126.95, 118.71, 112.31, 63.74, 63.68, 16.19, 16.12; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.07; HRMS (ESI): m/z = 282.1033 $[M+H]^+$. IR (KBr, cm^{-1}): 3422, 3131, 2936, 2220, 1594, 1480, 1240, 1040, 977, 847, 798, 545.



4f

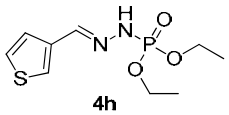
diethyl (2-(4-hydroxybenzylidene)hydrazinyl)Phosphite, white crystal; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.19 (s, 1H), 7.67 (s, 1H), 7.43-7.33 (m, 3H), 6.89-6.87 (d, J = 8.8 Hz, 2H), 4.22-4.16 (m, 4H), 1.36-1.32 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 158.30, 145.65, 145.46, 128.42, 126.10, 115.78, 63.85, 63.79, 16.16, 16.10; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.61; HRMS (ESI): m/z = 273.1021 $[M+H]^+$. IR (KBr, cm^{-1}): 3280, 3170, 2910, 2586, 2452, 1600, 1507, 1453, 1370, 1200, 1020, 833, 797, 752, 563, 527, 455.



4g

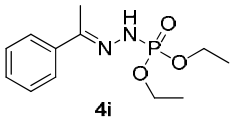
diethyl (2-(2-bromobenzylidene)hydrazinyl)Phosphite, white crystal; ^{1}H-NMR (400 MHz,

$CDCl_3$),8.73-8.66 (d, J = 28.8 Hz, 1H), 8.24 (s, 1H), 7.91-7.88 (m, 1H), 7.51-7.49 (d, J = 8.0 Hz, 1H), 7.27-7.26 (d, J = 2.0 Hz, 1H), 7.16-7.15 (d, J = 2.0 Hz, 1H), 4.21-4.18 (m, 4H), 1.38-1.34 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 143.85, 143.65, 133.50, 132.93, 130.42, 127.43, 127.35, 123.38, 63.47, 63.41, 16.22, 16.16; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.12; HRMS (ESI): m/z = 337.0155 $[M+H]^+$. IR (KBr, cm^{-1}): 3450, 3120, 2930, 1590, 1460, 1246, 1093, 1025, 977, 850, 760, 572, 545, 473.



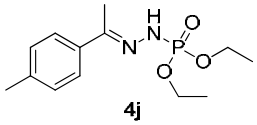
4h

diethyl (2-(thiophen-3-ylmethylene)hydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.46-8.38 (d, J = 28.0 Hz, 1H), 7.90 (s, 1H), 7.44-7.39 (m, 2H), 7.28-7.27 (m, 1H), 4.22-4.15 (m, 4H), 1.38-1.33 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 140.47, 140.28, 137.74, 126.24, 125.12, 125.08, 63.44, 63.38, 16.19, 16.12; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.78; HRMS (ESI): m/z = 263.0625 $[M+H]^+$. IR (KBr, cm^{-1}): 3341, 3060, 2981, 2930, 1630, 1460, 1390, 1230, 1165, 1040, 960, 860, 806, 713, 608, 560.



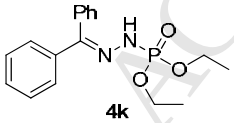
4i

diethyl (2-(1-phenylethylidene)hydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.71-7.69 (d, J = 5.2 Hz, 2H), 7.38-7.33 (m, 3H), 7.21-7.17 (d, J = 18.0 Hz, 1H), 4.23-4.19 (m, 4H), 2.19 (s, 3H), 1.38-1.35 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 148.33, 148.16, 138.43, 128.69, 128.29, 125.92, 63.49, 63.44, 16.23, 16.16, 12.29; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.29; HRMS (ESI): m/z = 271.1192 $[M+H]^+$. IR (KBr, cm^{-1}): 3359, 2981, 2657, 2406, 1969, 1606, 1440, 1390, 1360, 1205, 1040, 960, 820, 750, 690, 550.



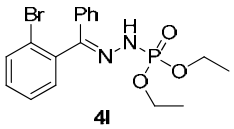
4j

diethyl (2-(1-(p-tolyl)ethylidene)hydrazinyl)Phosphite, white crystal; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.60-7.58 (d, J = 8.0 Hz, 2H), 7.17-7.15 (d, J = 8.0 Hz, 2H), 6.94-6.87 (d, J = 26.8 Hz, 1H), 4.24-4.16 (m, 4H), 2.36 (s, 3H), 2.16 (s, 3H), 1.38-1.34 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 148.24, 148.06, 138.75, 135.57, 129.01, 125.85, 63.50, 63.44, 21.22, 16.23, 16.16, 12.07; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.83; HRMS (ESI): m/z = 285.1357 $[M+H]^+$. IR (KBr, cm^{-1}): 3458, 3110, 2980, 2918, 2807, 1615, 1486, 1240, 1025, 986, 850, 806, 560, 523, 450.



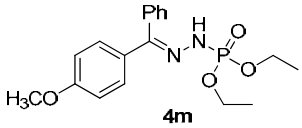
4k

diethyl (2-(diphenylmethylene)hydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.57-7.50 (m, 5H), 7.32-7.31 (m, 3H), 7.25-7.23 (m, 2H), 6.64-6.56 (d, J = 29.2 Hz, 1H), 4.24-4.18 (m, 4H), 1.41-1.37 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 151.67, 151.50, 137.25, 131.64, 129.85, 129.74, 129.10, 128.53, 128.22, 127.07, 63.53, 63.47, 16.25, 16.19; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.28; HRMS (ESI): m/z = 333.1346 $[M+H]^+$. IR (KBr, cm^{-1}): 3664, 3420, 3175, 3140, 2980, 1640, 1568, 1483, 1446, 1250, 1165, 1030, 896, 774, 688, 517.



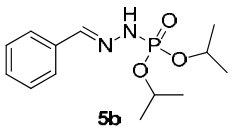
4l

diethyl (2-((2-bromophenyl)(phenyl)methylene)hydrazinyl)Phosphite, white crystal; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.79-7.76 (m, 2H), 7.51-7.47 (m, 3H), 7.41-7.38 (m, 1H), 7.34-7.32 (m, 3H), 7.20-7.17 (m, 1H), 6.40-6.34 (d, J = 19.6 Hz, 1H), 4.24-4.20 (m, 4H), 1.40-1.38 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 149.75, 149.63, 135.90, 133.90, 133.03, 131.45, 130.43, 129.22, 128.72, 128.41, 126.53, 122.53, 63.70, 63.67, 63.54, 63.51, 16.23, 16.21; ^{31}P-NMR (400 MHz, $CDCl_3$), 0.70; HRMS (ESI): m/z = 411.0457 $[M+H]^+$. IR (KBr, cm^{-1}): 3430, 3160, 3088, 2980, 2905, 2860, 1957, 1908, 1811, 1589, 1565, 1430, 1250, 1161, 1027, 978, 890, 775, 690, 545, 470.



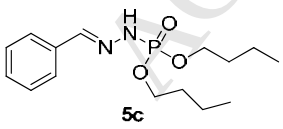
4m

diethyl (2-((4-methoxyphenyl)(phenyl)methylene)hydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.52-7.43 (m, 3H), 7.32-7.30 (m, 2H), 7.23-7.16 (m, 2H), 7.07-6.82 (m, 2H), 6.70-6.44 (m, 1H), 4.24-4.16 (m, 4H), 3.88-3.80 (d, J = 31.2 Hz, 3H), 1.41-1.36 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 160.46, 151.62, 151.45, 137.63, 131.88, 130.09, 130.02, 129.78, 129.63, 129.01, 128.50, 128.17, 127.15, 123.39, 115.25, 113.59, 63.49, 63.43, 55.44, 55.32, 16.26, 16.19; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.45; HRMS (ESI): m/z = 363.1409 $[M+H]^+$. IR (KBr, cm^{-1}): 3453, 3325, 3155, 2983, 2934, 2910, 2835, 2049, 1658, 1604, 1510, 1400, 1248, 1160, 1030, 967, 891, 837, 776, 703, 542.



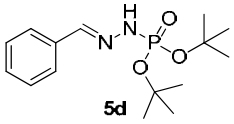
5b

diisopropyl (2-benzylidenehydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.61-8.53 (d, J = 28.8 Hz, 1H), 7.86 (s, 1H), 7.63-7.59 (m, 2H), 7.38-7.31 (m, 3H), 4.76-4.70 (m, 2H), 1.40-1.32 (m, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$), 144.29, 144.10, 134.86, 129.11, 128.53, 126.58, 72.08, 72.02, 23.89, 23.85, 23.64, 23.59; ^{31}P-NMR (400 MHz, $CDCl_3$), 0.08; HRMS (ESI): m/z = 285.1392 $[M+H]^+$. IR (KBr, cm^{-1}): 3430, 3185, 2981, 2932, 1604, 1470, 1384, 1240, 992, 885, 834, 761, 700, 553, 480, 427.



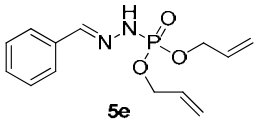
5c

dibutyl (2-benzylidenehydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.59-8.52 (d, J = 29.2 Hz, 1H), 7.86 (s, 1H), 7.62-7.59 (m, 2H), 7.36-7.34 (m, 3H), 4.16-4.11 (m, 4H), 1.73-1.65 (m, 4H), 1.48-1.38 (m, 4H), 0.92-0.88 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 144.76, 144.56, 134.69, 129.21, 128.52, 126.63, 67.13, 67.07, 32.29, 32.22, 18.70, 13.55; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.64; HRMS (ESI): m/z = 313.1699 $[M+H]^+$. IR (KBr, cm^{-1}): 3400, 3172, 2965, 2867, 1604, 1474, 1390, 1241, 1033, 860, 762, 700, 554, 453.



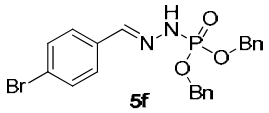
5d

di-tert-butyl (2-benzylidenehydrazinyl)Phosphite, white crystal; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.76 (s, 1H), 7.63-7.60 (m, 2H), 7.58-7.51 (d, J = 28.8 Hz, 1H), 7.38-7.31 (m, 3H), 1.53 (s, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$), 143.04, 142.85, 135.09, 128.93, 128.52, 126.55, 82.85, 82.78, 30.16, 30.12; ^{31}P-NMR (400 MHz, $CDCl_3$), 0.13; HRMS (ESI): m/z = 313.1671 $[M+H]^+$. IR (KBr, cm^{-1}): 3360, 2962, 2926, 2840, 2356, 1624, 1447, 1374, 1006, 960, 860, 752, 684, 500.



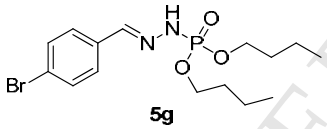
5e

diallyl (2-benzylidenehydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.48-8.40 (d, J = 28.8 Hz, 1H), 7.84 (s, 1H), 7.62-7.59 (m, 2H), 7.37-7.34 (m, 3H), 6.01-5.94 （m, 2H），5.42-5.36 (m, 2H), 5.25-5.21 (m, 2H), 4.69-4.63 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$), 145.33, 145.14, 134.45, 132.68, 132.61, 129.41, 128.57, 126.74, 118.10, 67.95, 67.90; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.81; HRMS (ESI): m/z = 281.1050 $[M+H]^+$. IR (KBr, cm^{-1}): 3430, 3147, 2932, 1650, 1451, 1225, 1025, 937, 848, 756, 690, 630, 560, 515.



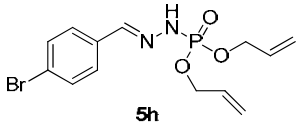
5f

dibenzyl (2-(4-bromobenzylidene)hydrazinyl)Phosphite, white crystal; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.56-8.48 (d, J = 28.8 Hz, 1H), 7.59 (s, 1H), 7.40-7.37 (m, 2H), 7.31-7.28 (m, 6H), 7.23-7.17 （m, 6H），5.11-5.07 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$), 134.89, 134.82, 132.33, 130.68, 127.44, 127.35, 127.11, 126.86, 122.40, 67.99, 67.94; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.55; HRMS (ESI): m/z = 461.0471 $[M+H]^+$. IR (KBr, cm^{-1}): 3430, 3130, 2930, 1592, 1451, 1397, 1240, 1017, 853, 814, 730, 690, 570, 507.



5g

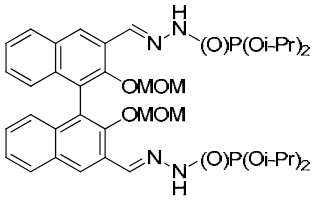
dibutyl (2-(4-bromobenzylidene)hydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.55-8.53 (d, J = 10.4 Hz, 1H), 7.79 (s, 1H), 7.47 (m, 4H), 4.15-4.09 (m, 4H), 1.71-1.66 (m, 4H), 1.45-1.39 (m, 4H), 0.92-0.88 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), 143.53, 143.33, 133.58, 131.74, 128.03, 123.29, 67.20, 67.14, 32.26, 32.20, 18.69, 13.55; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.53; HRMS (ESI): m/z = 391.0746 $[M+H]^+$. IR (KBr, cm^{-1}): 3427, 3147, 2955, 2827, 2870, 1595, 1470, 1390, 1240, 1059, 1035, 822, 730, 570, 515.



5h

diallyl (2-(4-bromobenzylidene)hydrazinyl)Phosphite, colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.60-8.52 (d, J = 29.2 Hz, 1H), 7.79 (s, 1H), 7.48-7.47 (m, 4H), 5.98-5.93 (m, 2H), 5.40-5.21 (m, 4H), 4.65-4.63 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$), 144.11, 143.91, 133.40, 132.57, 132.50,

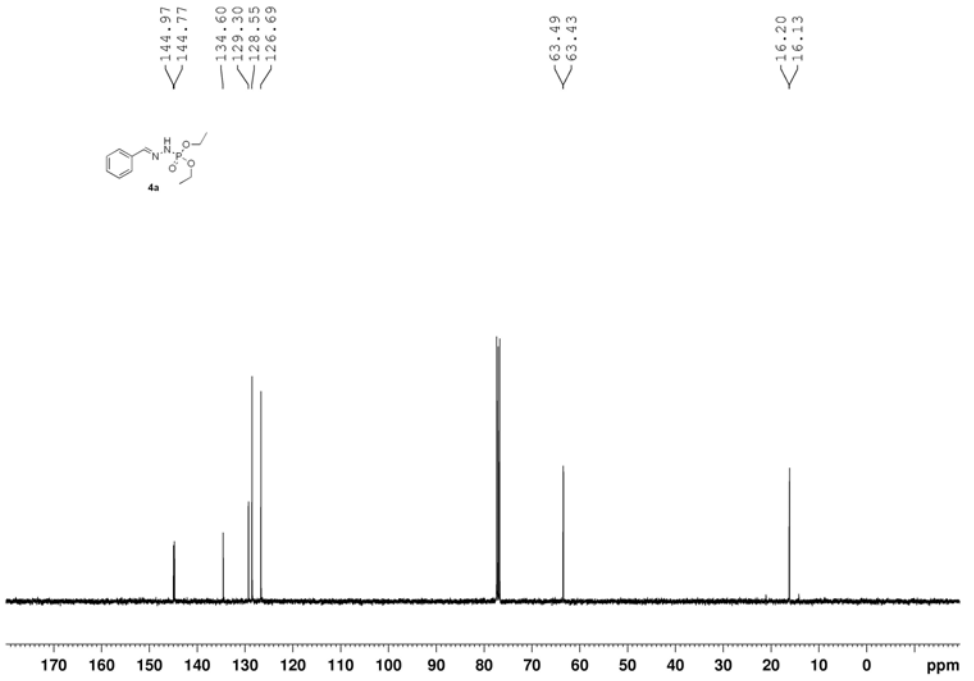
131.78, 128.12, 123.46, 118.19, 67.98, 67.93; ^{31}P-NMR (400 MHz, $CDCl_3$), 1.56; HRMS (ESI): m/z = 361.0146 $[M+H]^+$. IR (KBr, cm^{-1}): 3453, 3140, 2940, 1653, 1590, 1474, 1240, 1028, 920, 853, 814, 668, 630, 561, 522.

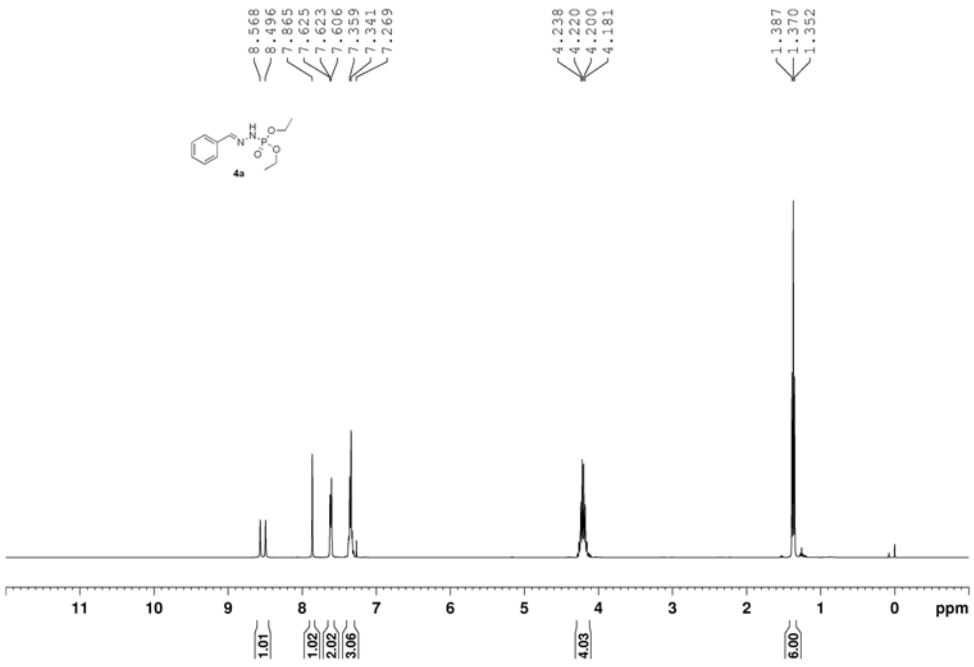


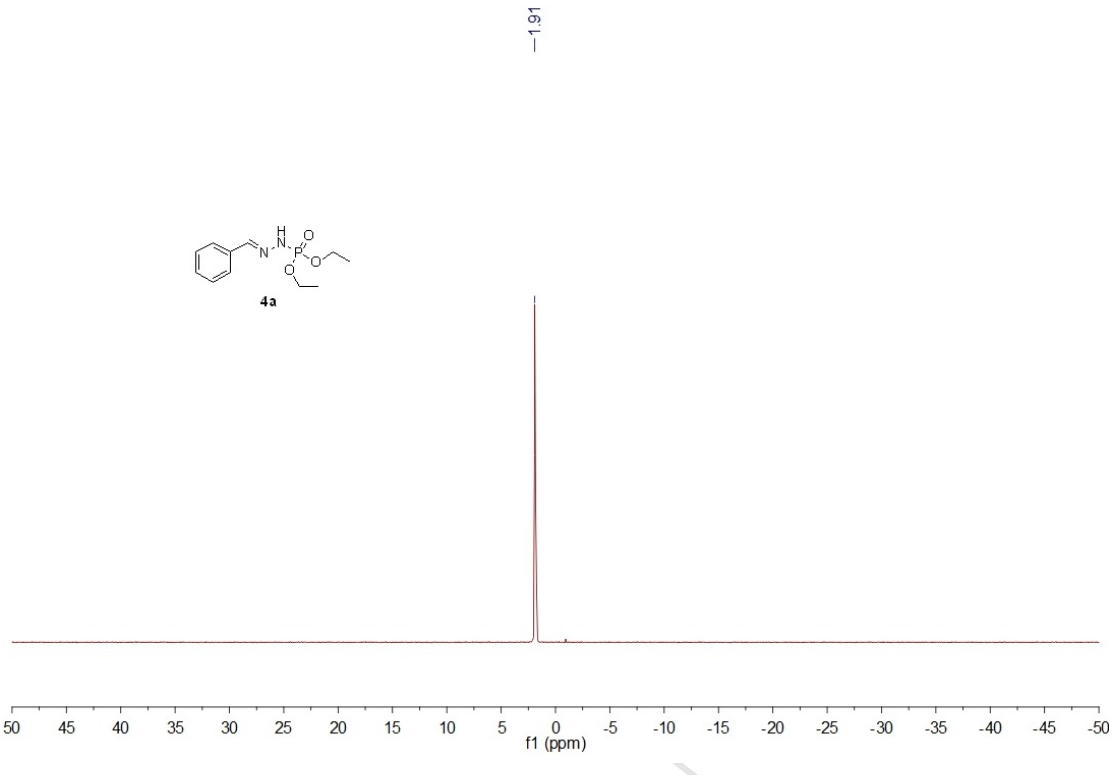
7

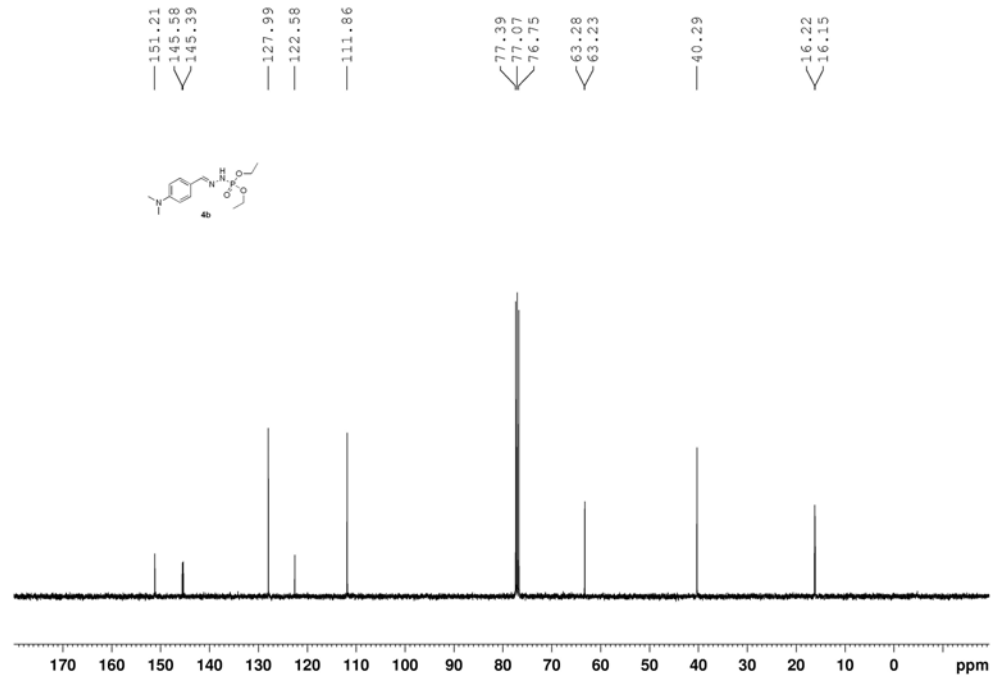
Binol P-N ligand **7**, white crystal; ^{1}H-NMR (400 MHz, $CDCl_3$), 8.54 (s, 2H), 8.31 (s, 2H), 7.95-7.92 (m, 4H), 7.42-7.40 (m, 2H), 7.27-7.16 (m, 4H), 4.82-4.77 （m, 4H），4.59-4.52 (m, 4H), 2.84 (s, 6H), 1.46-1.38 (m, 24H); ^{13}C-NMR (100 MHz, $CDCl_3$), 151.92, 141.04, 140.85, 134.27, 130.71, 128.80, 127.70, 127.14, 126.85, 126.05, 125.55, 125.37, 99.79, 56.94, 23.94, 23.92, 23.73, 23.70; ^{31}P-NMR (400 MHz, $CDCl_3$), 0.43; HRMS (ESI): m/z = 787.3158 $[M+H]^+$. IR (KBr, cm^{-1}): 3480, 3130, 2970, 2829, 1604, 1494, 1380, 1354, 1230, 1156, 1121, 1075, 980, 760, 570, 475, 415.

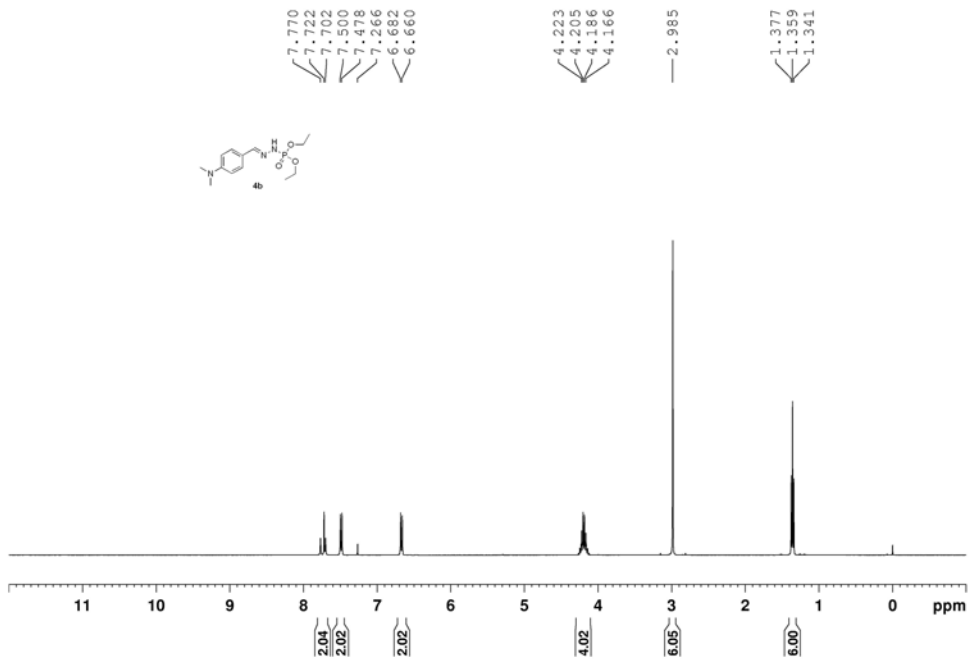
[1] H-NMR, [13] C-NMR spectra and [31]P-NMR:

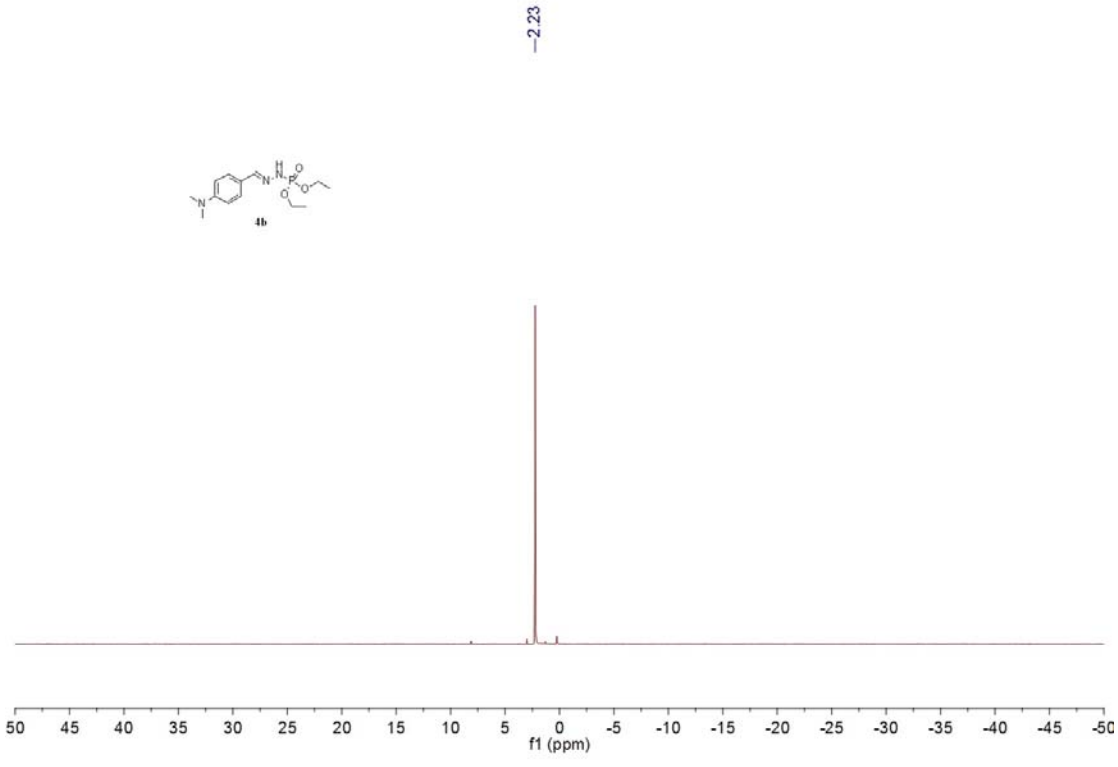


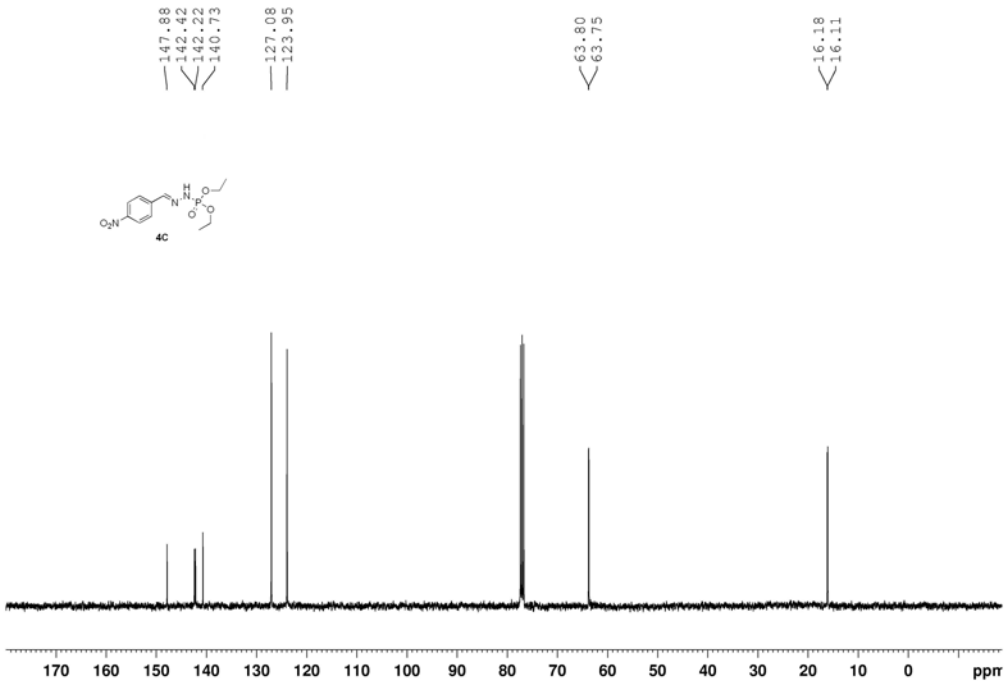


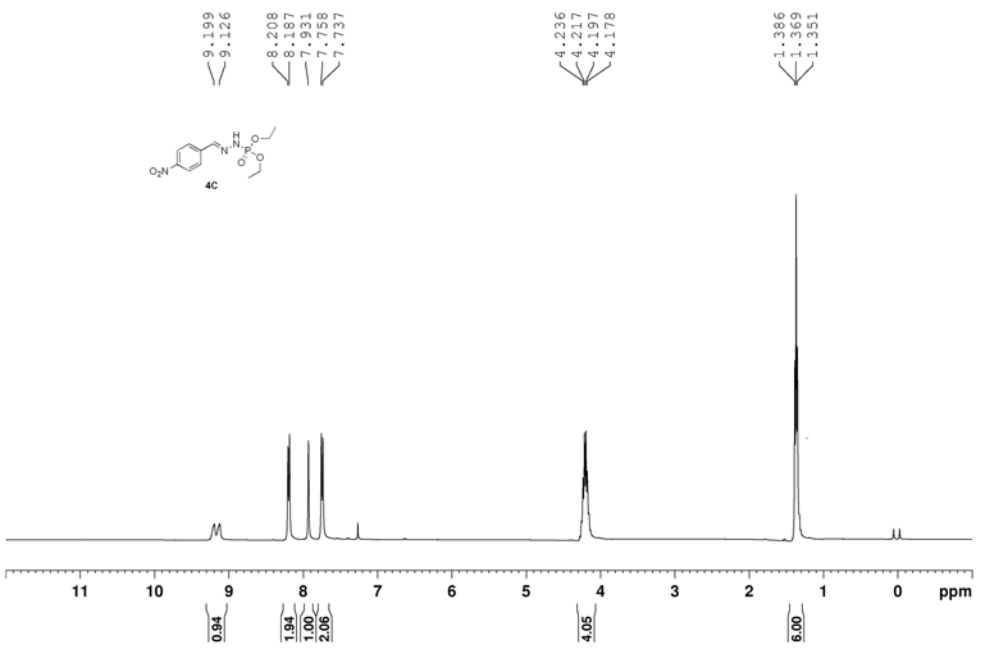

1.91
4a
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

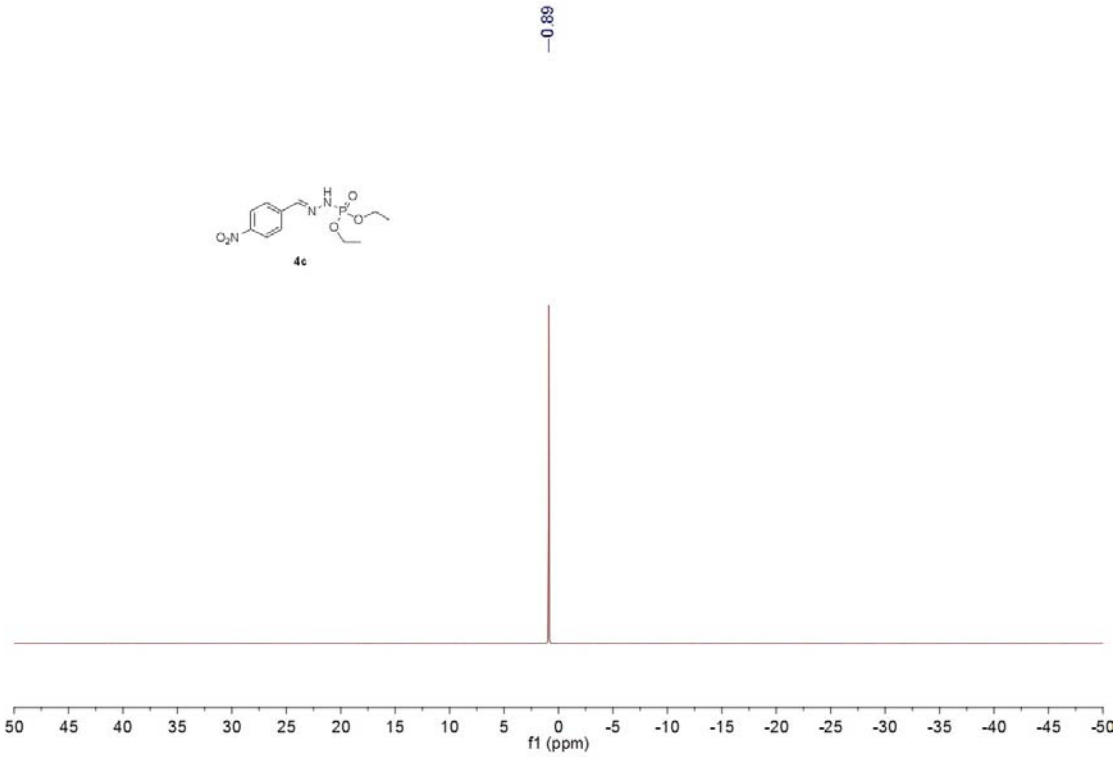

151.21
145.58
145.39
127.99
122.58
111.86
77.39
77.07
76.75
63.28
63.23
40.29
16.22
16.15
4b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

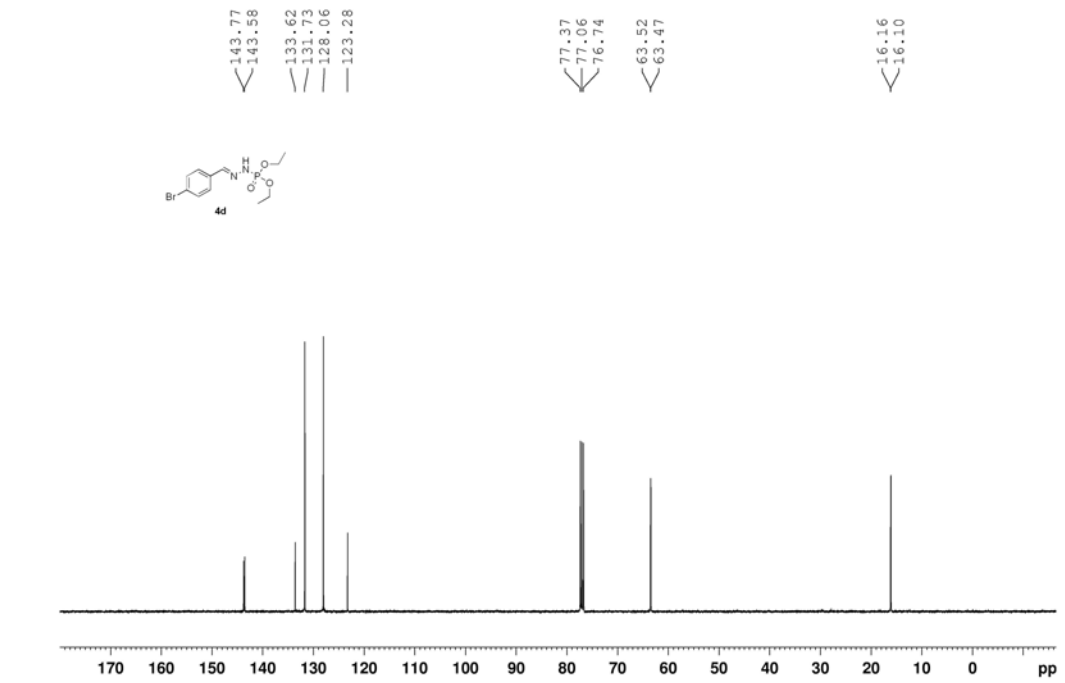

7.770
7.722
7.702
7.500
7.478
7.266
6.682
6.660
4.223
4.205
4.186
4.166
2.985
1.377
1.359
1.341
4b
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.04
2.02
2.02
4.02
6.05
6.00

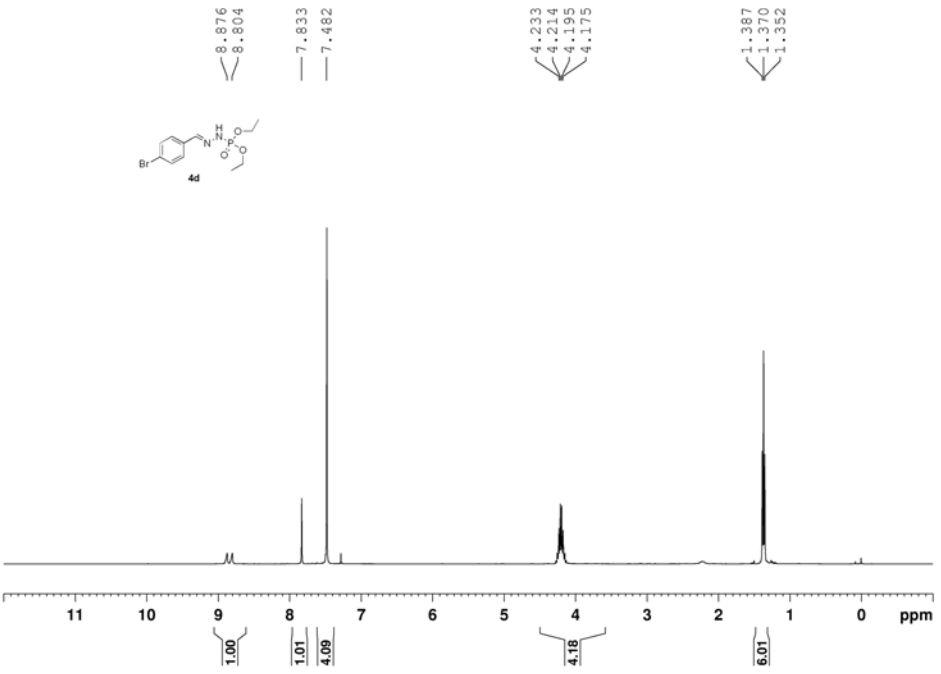

-2.23
4b
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

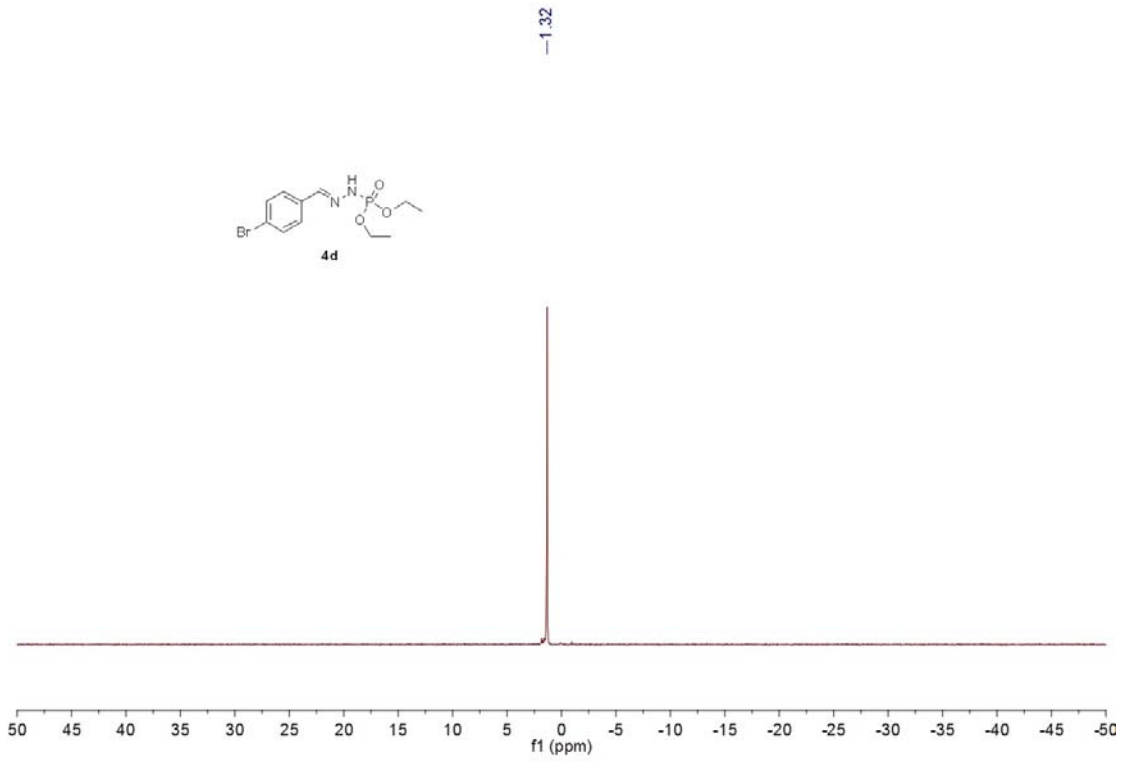

147.88
142.42
142.22
140.73
127.08
123.95
63.80
63.75
16.18
16.11
4C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

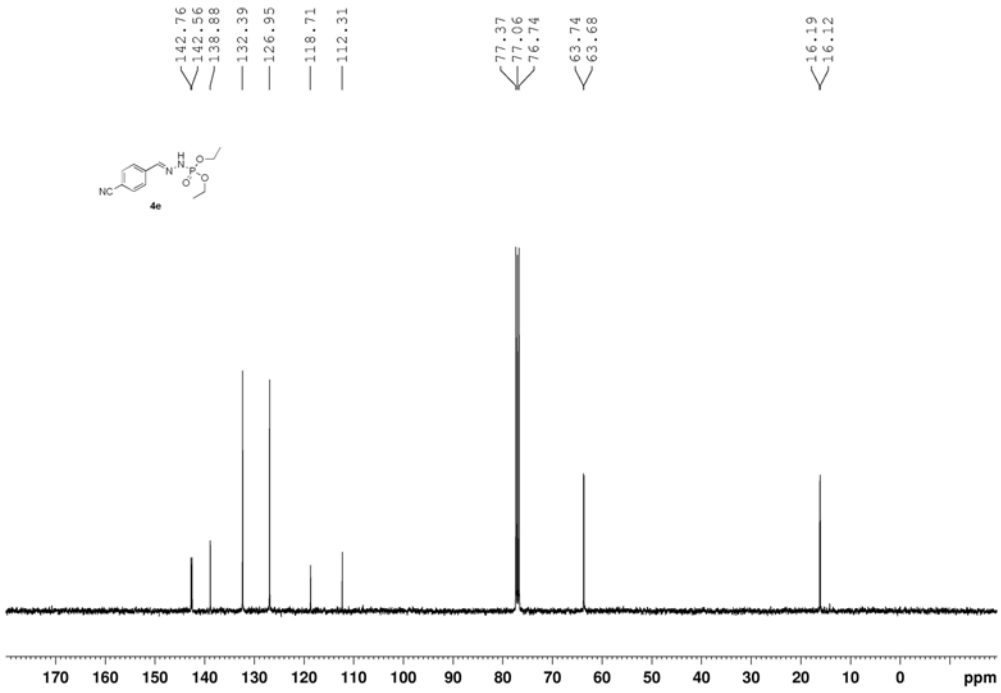

9.199
9.126
8.208
8.187
7.931
7.758
7.737
4.236
4.217
4.197
4.178
1.386
1.369
1.351
4C
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.94
1.94
1.00
2.06
4.05
6.00

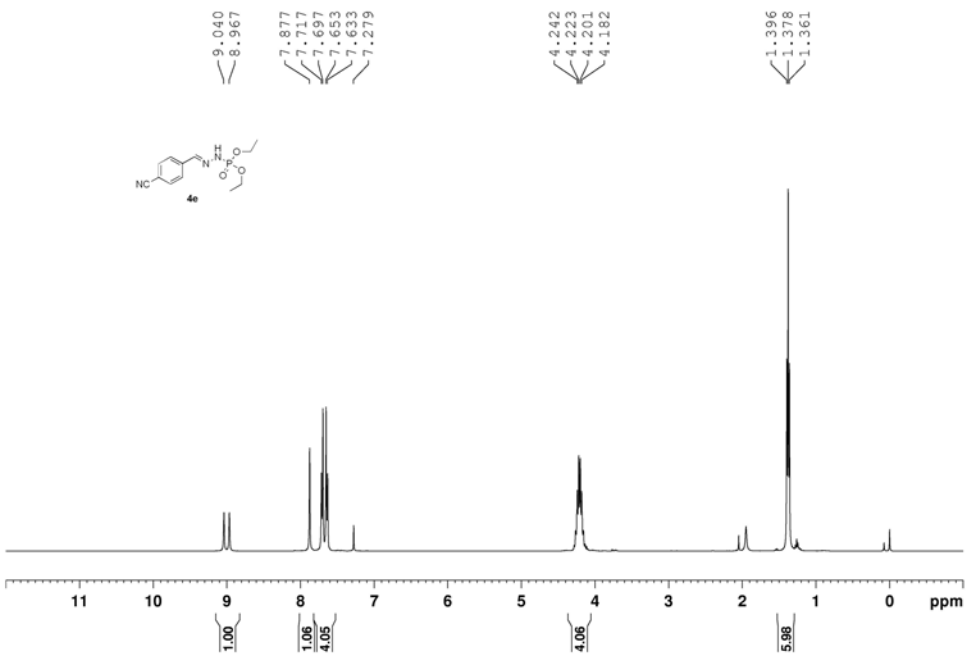

0.89
4c
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

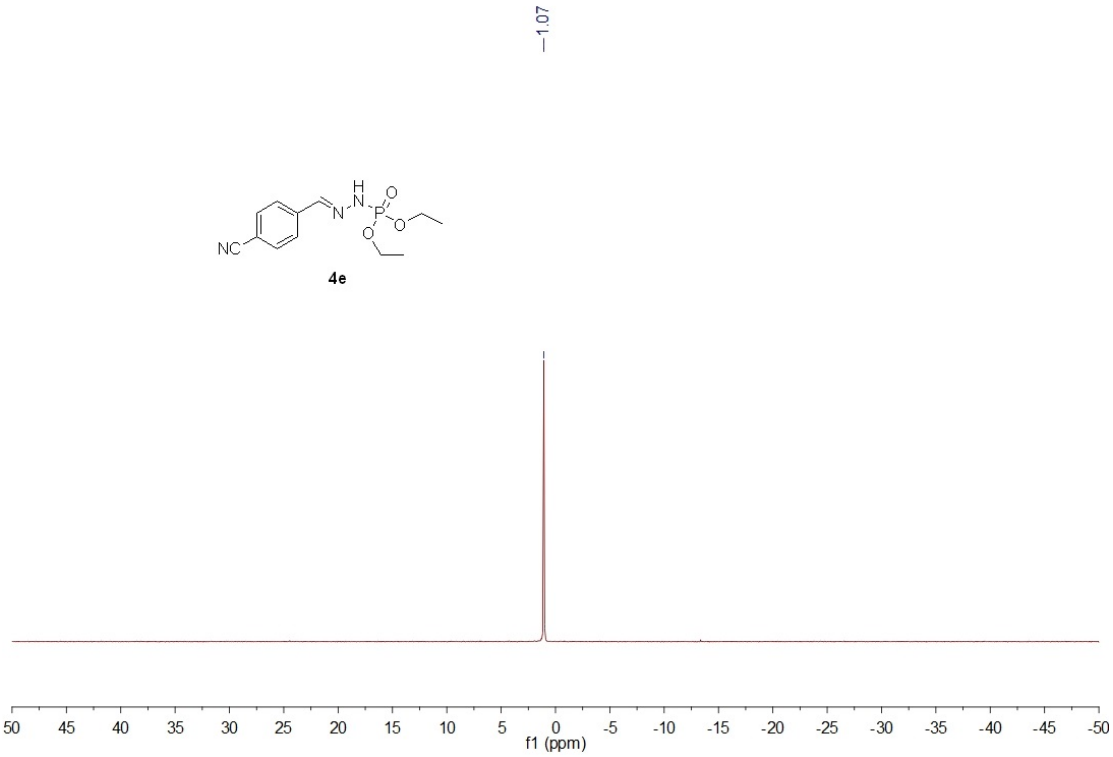

143.77
143.58
133.62
131.73
128.06
123.28
77.37
77.06
76.74
63.52
63.47
16.16
16.10
4d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 pp

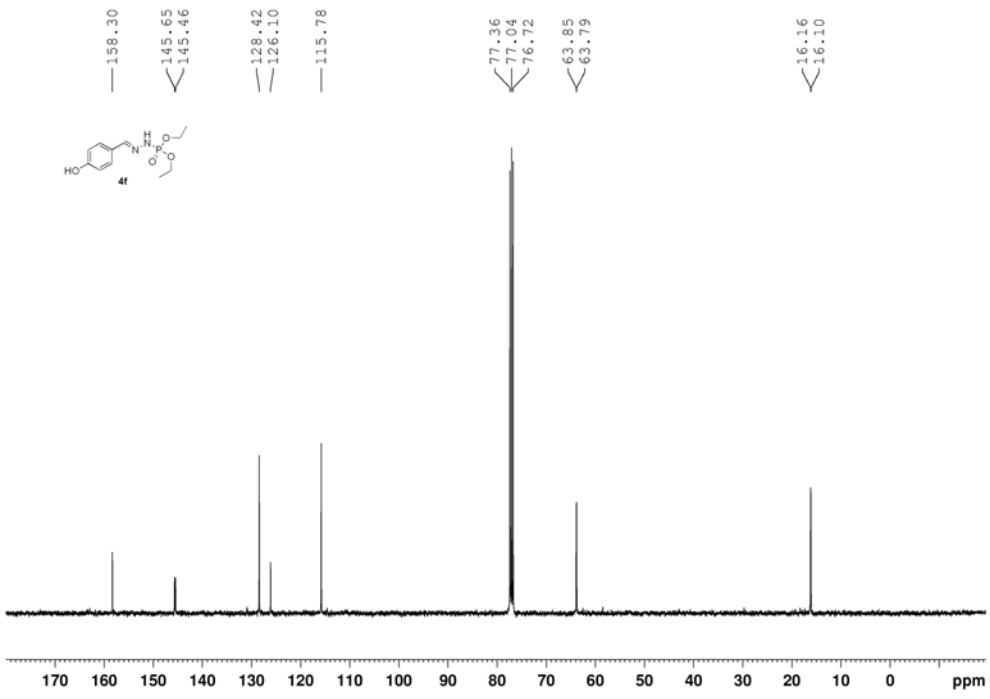

8.876
8.804
7.833
7.482
4.233
4.214
4.195
4.175
1.387
1.370
1.352
Br
4d
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
4.09
4.18
6.01

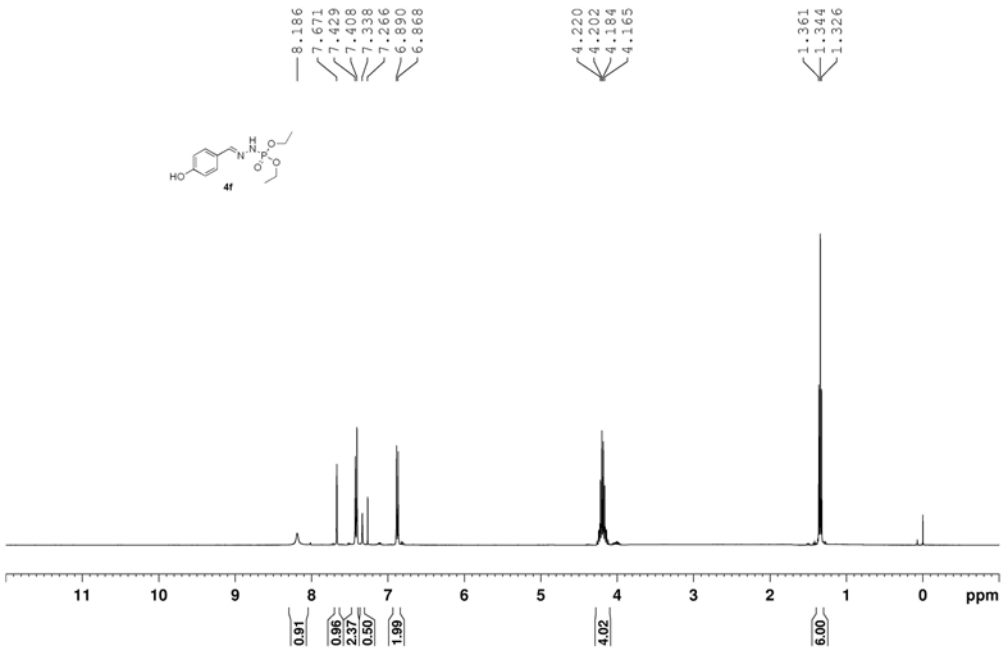

1.32
Br
4d
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

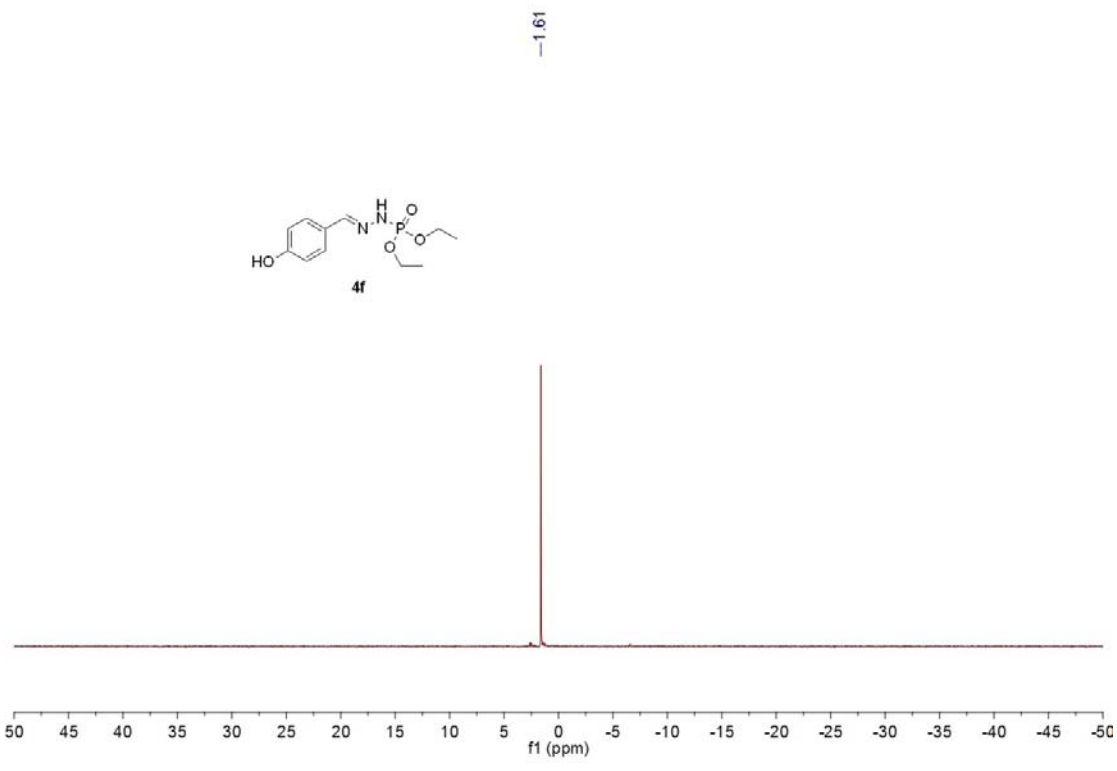

142.76
142.56
138.88
132.39
126.95
118.71
112.31
77.37
77.06
76.74
63.74
63.68
16.19
16.12
4e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

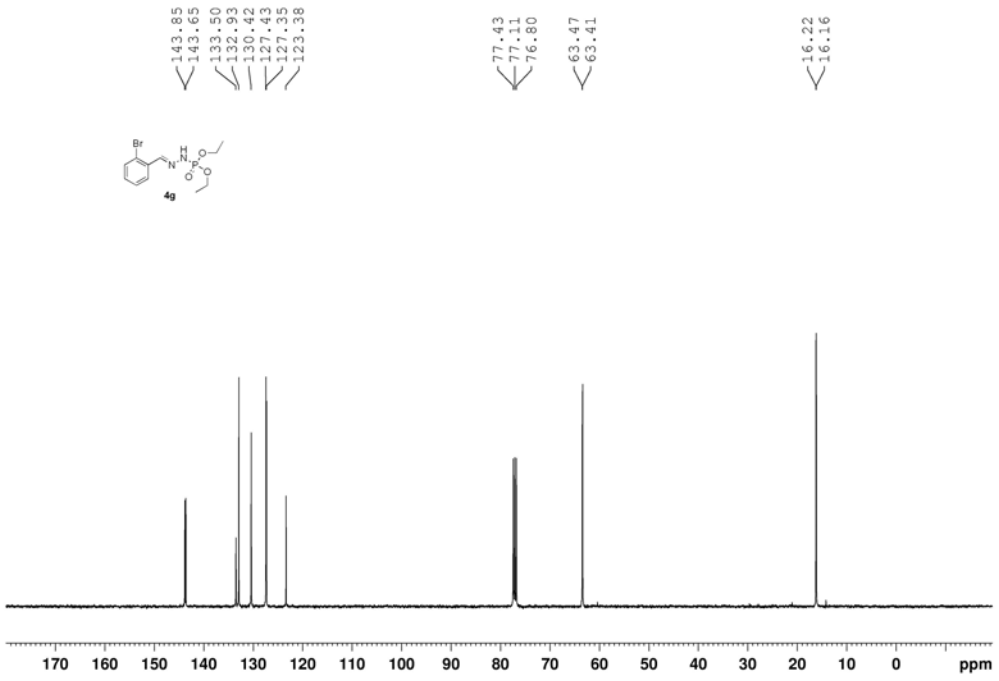

9.040
8.967
7.877
7.717
7.697
7.653
7.633
7.279
4.242
4.223
4.201
4.182
1.396
1.378
1.361
4e
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.06
4.05
4.06
5.98

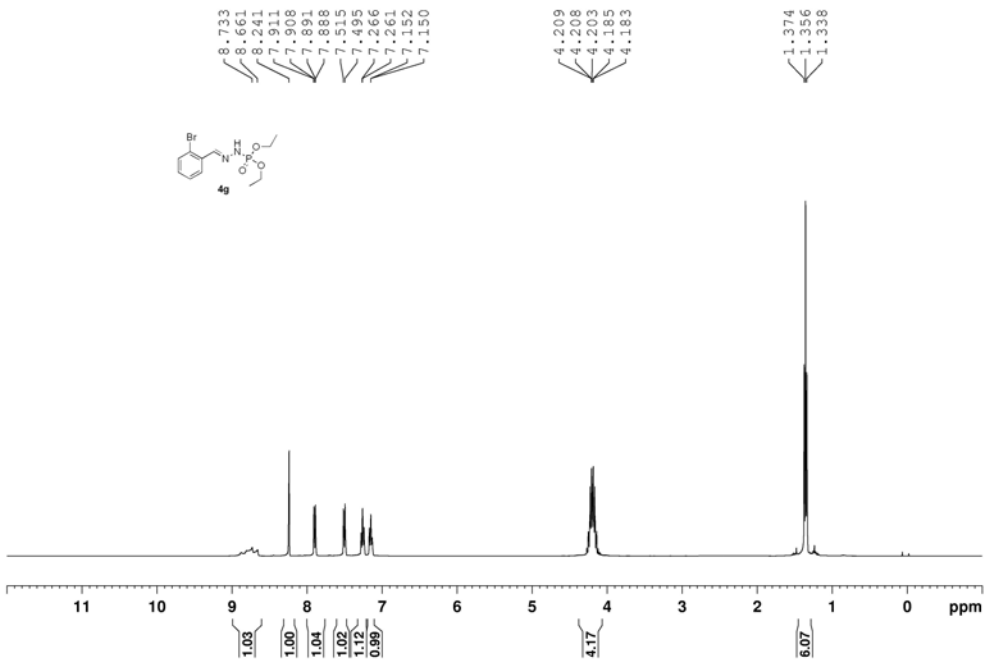

1.07
NC
4e
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

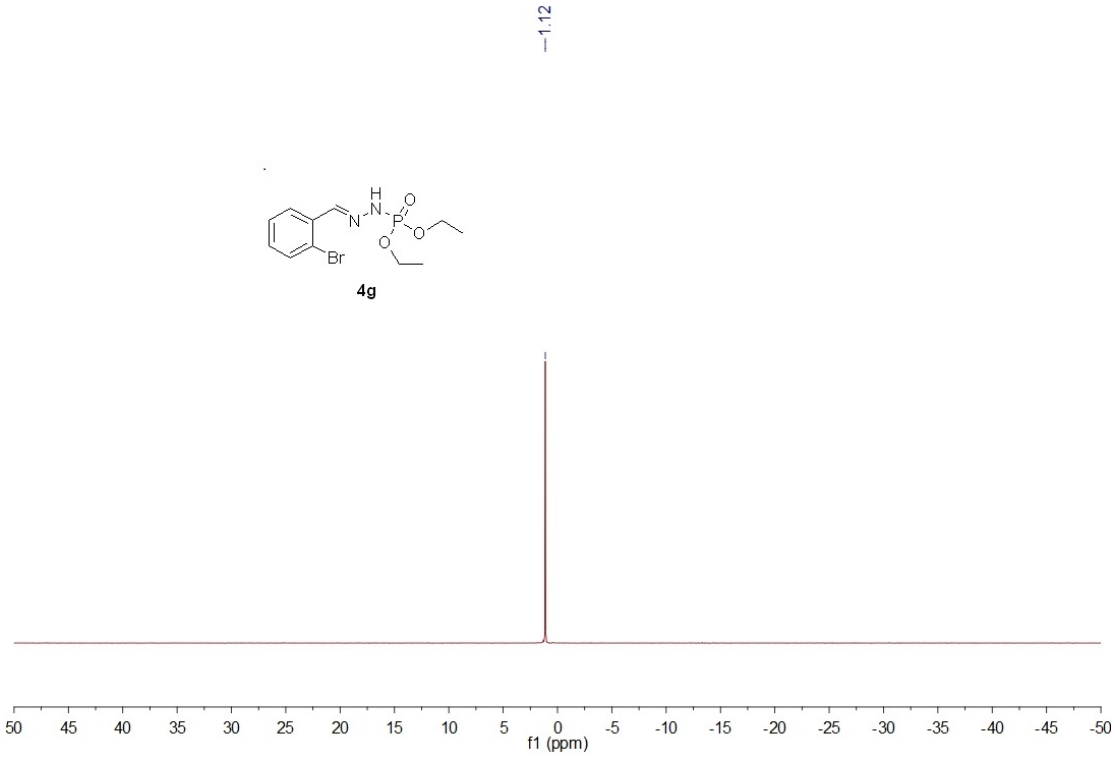

158.30
145.65
145.46
128.42
126.10
115.78
77.36
77.04
76.72
63.85
63.79
16.16
16.10
HO
4f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

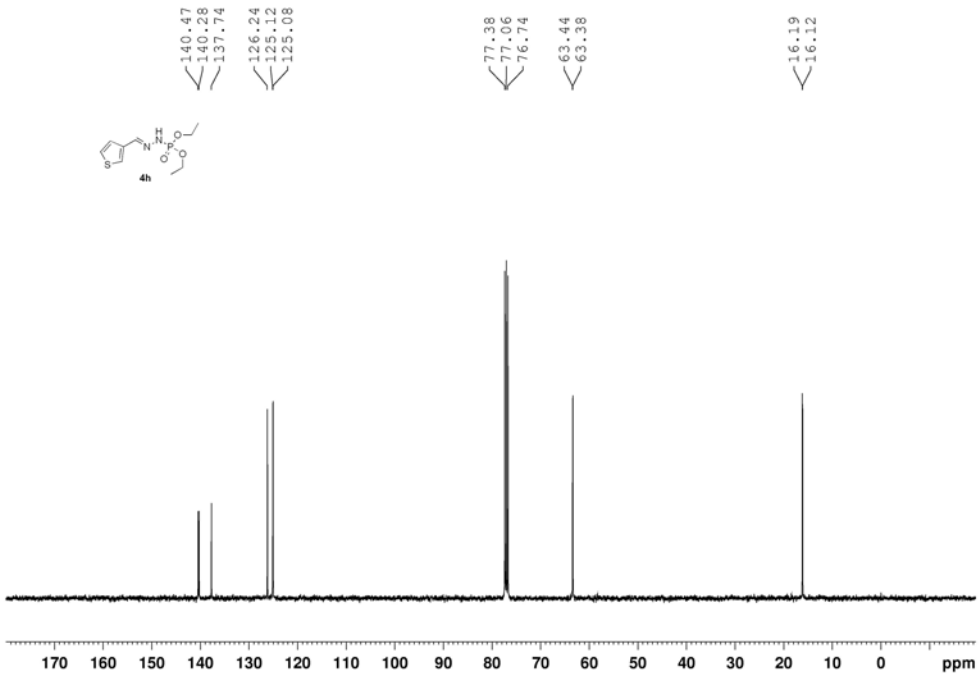

8.186
7.671
7.429
7.408
7.338
7.266
6.890
6.868
4.220
4.202
4.184
4.165
1.361
1.344
1.326
HO
4f
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
0.96
2.37
0.50
1.99
4.02
6.00

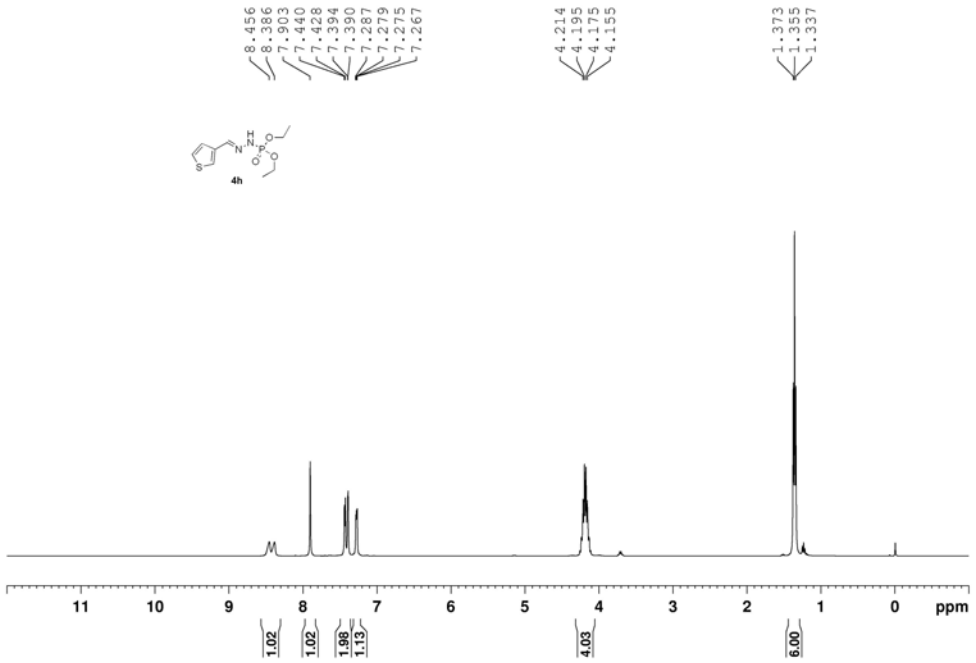

1.61
HO
4f
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

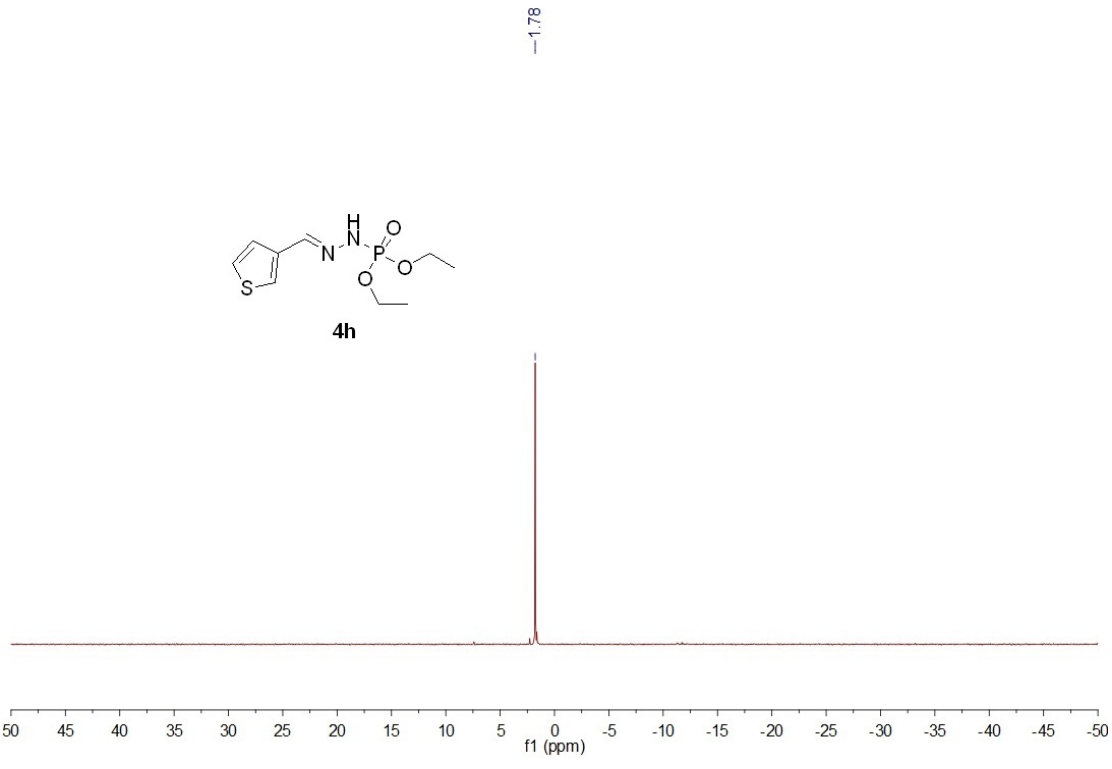

143.85
143.65
133.50
132.93
130.42
127.43
127.35
123.38
77.43
77.11
76.80
63.47
63.41
16.22
16.16
Br
N
H
P
O
O
O
4g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

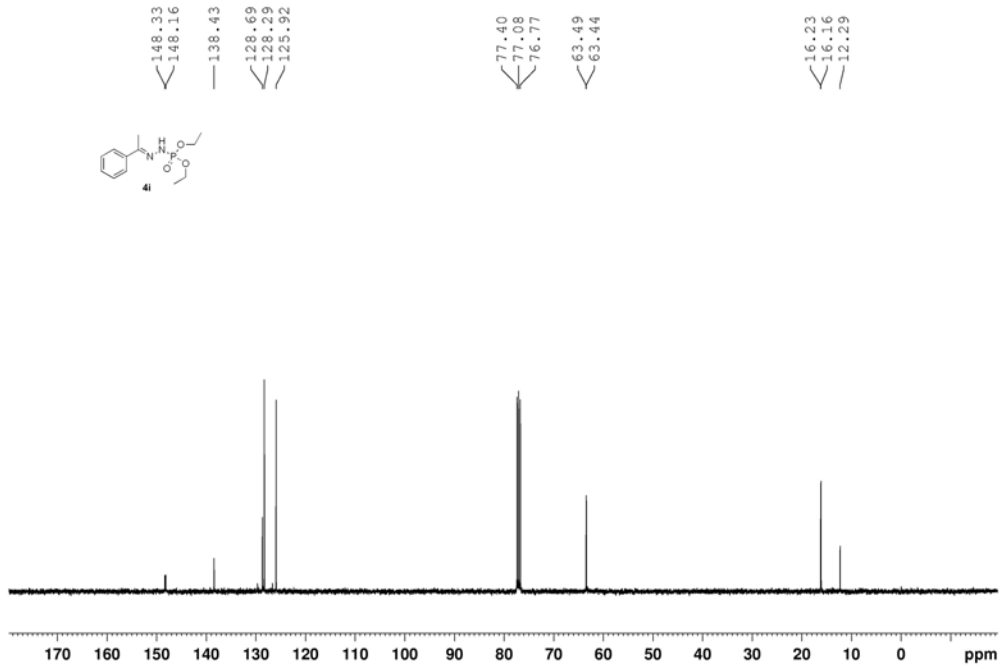

8.733
8.661
8.241
7.911
7.908
7.891
7.888
7.515
7.495
7.266
7.261
7.152
7.150
4.209
4.208
4.203
4.185
4.183
1.374
1.356
1.338
Br
N
H
P
O
O
O
4g
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.03
1.00
1.04
1.02
1.12
0.99
4.17
6.07

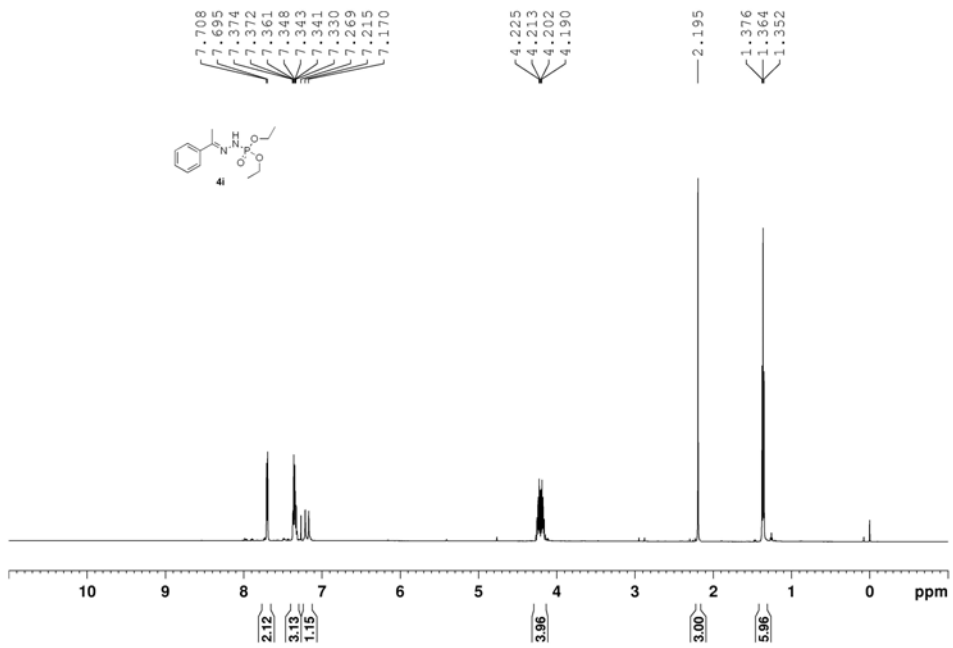

1.12
Br
4g
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

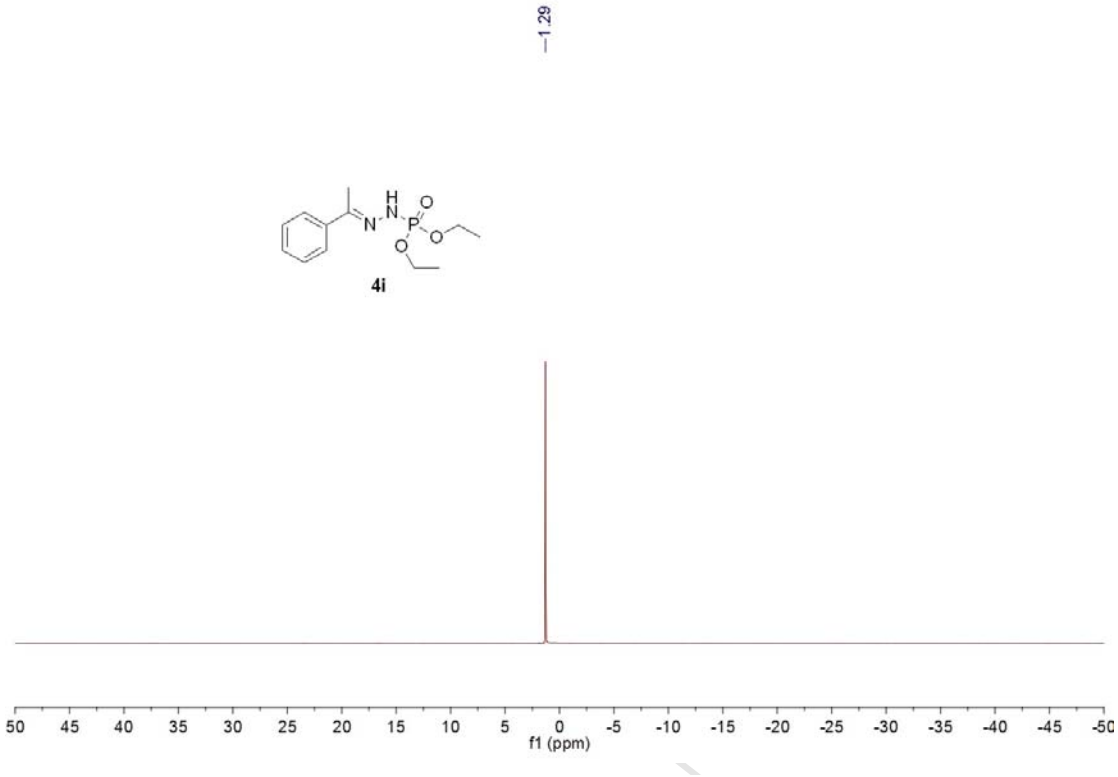

140.47
140.28
137.74
126.24
125.12
125.08
77.38
77.06
76.74
63.44
63.38
16.19
16.12
4h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

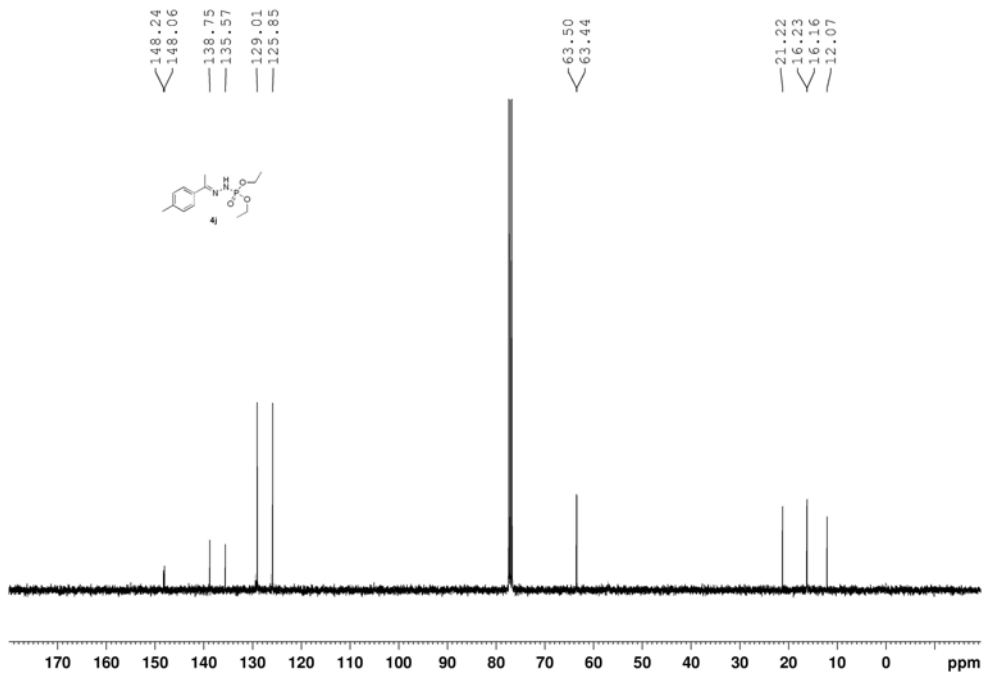

8.456
8.386
7.903
7.440
7.428
7.394
7.390
7.287
7.279
7.275
7.267
4.214
4.195
4.175
4.155
1.373
1.355
1.337
4h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.02
1.98
1.13
4.03
6.00

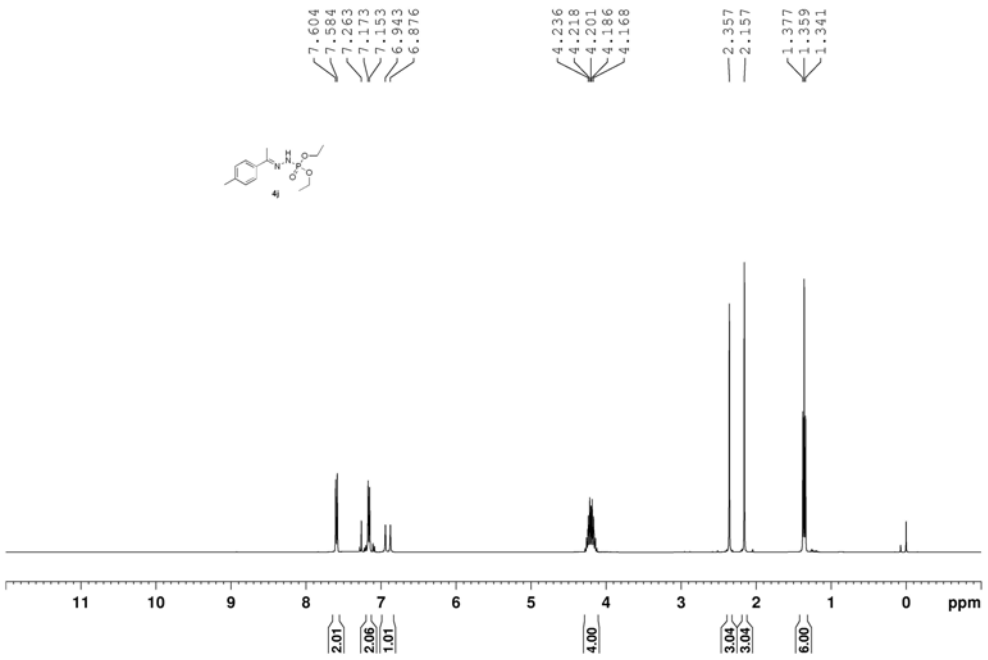

1.78
4h
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

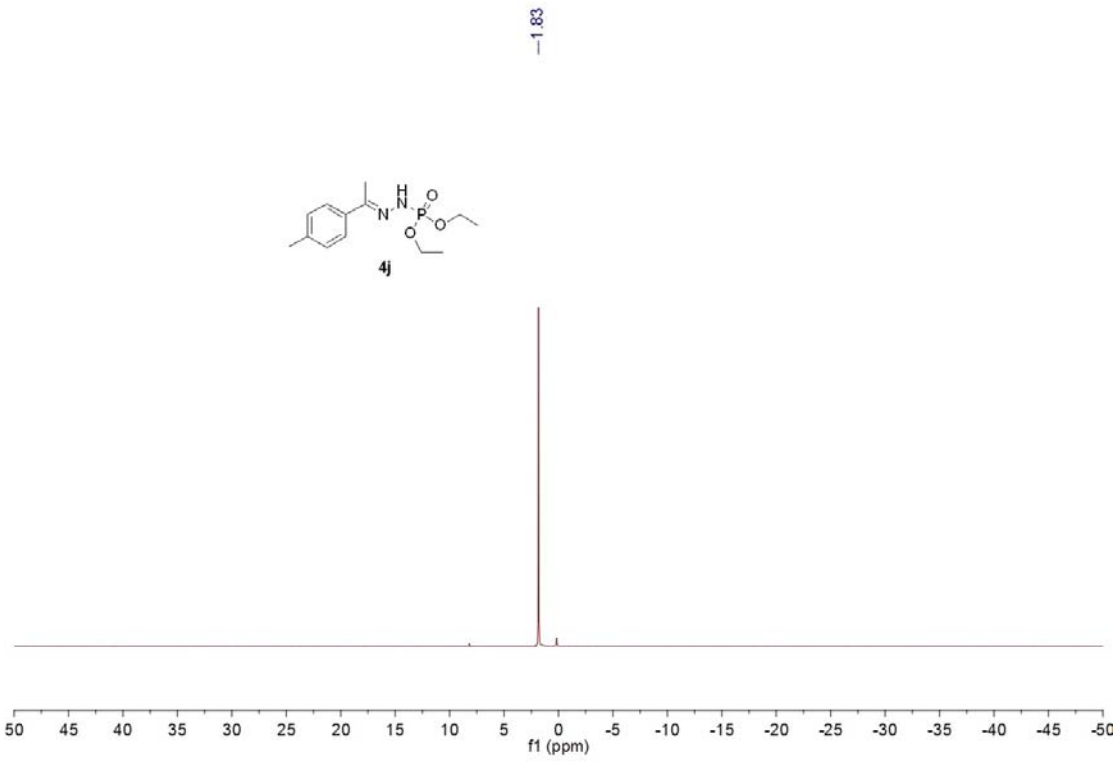

148.33
148.16
138.43
128.69
128.29
125.92
77.40
77.08
76.77
63.49
63.44
16.23
16.16
12.29
4i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

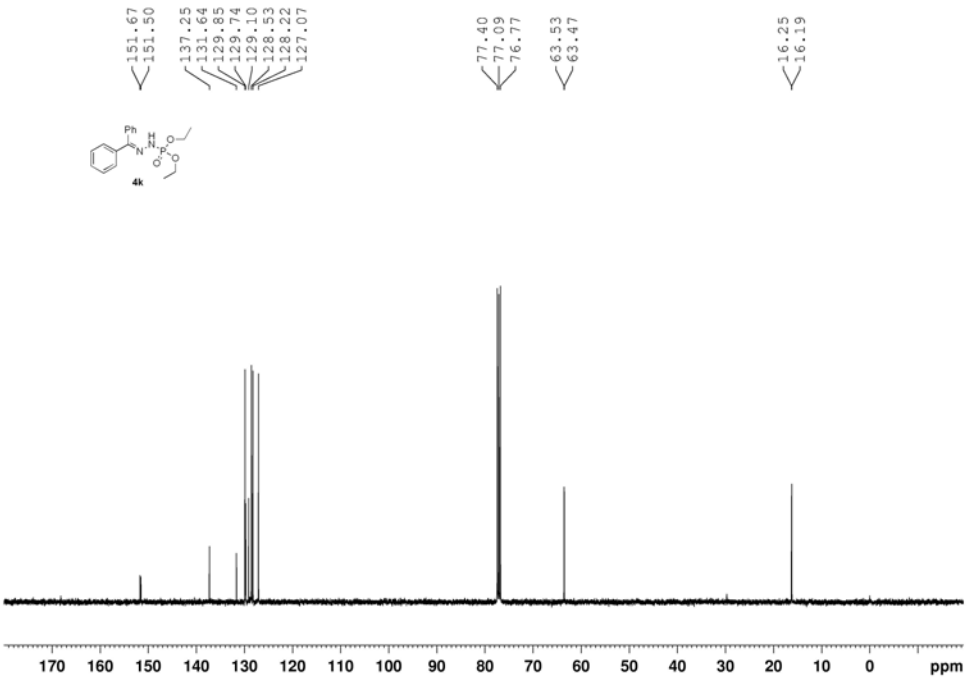

7.708
7.695
7.374
7.372
7.361
7.348
7.343
7.341
7.330
7.269
7.215
7.170
4.225
4.213
4.202
4.190
2.195
1.376
1.364
1.352
4i
10 9 8 7 6 5 4 3 2 1 0 ppm
2.12
3.13
1.15
3.96
3.00
5.96

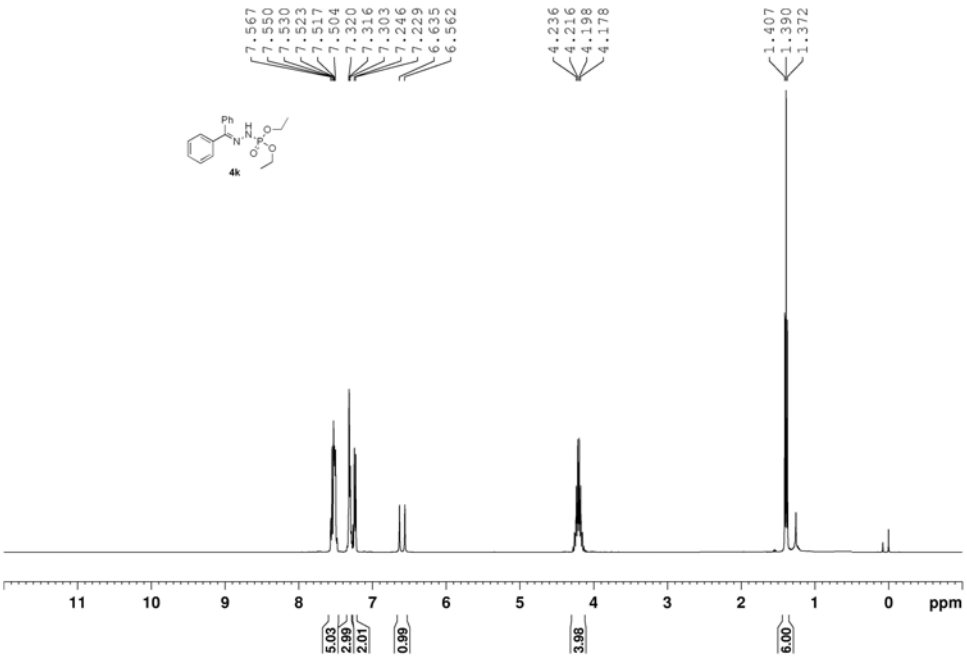

1.29
4i
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

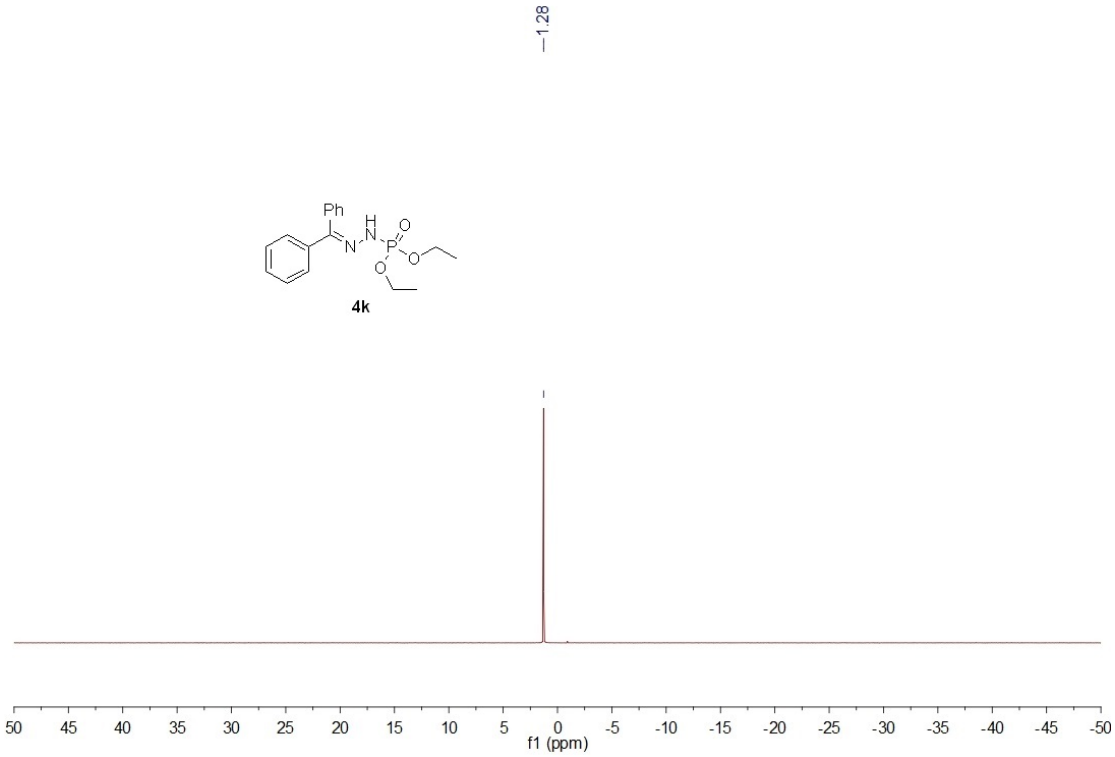

148.24
148.06
138.75
135.57
129.01
125.85
63.50
63.44
21.22
16.23
16.16
12.07
4j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

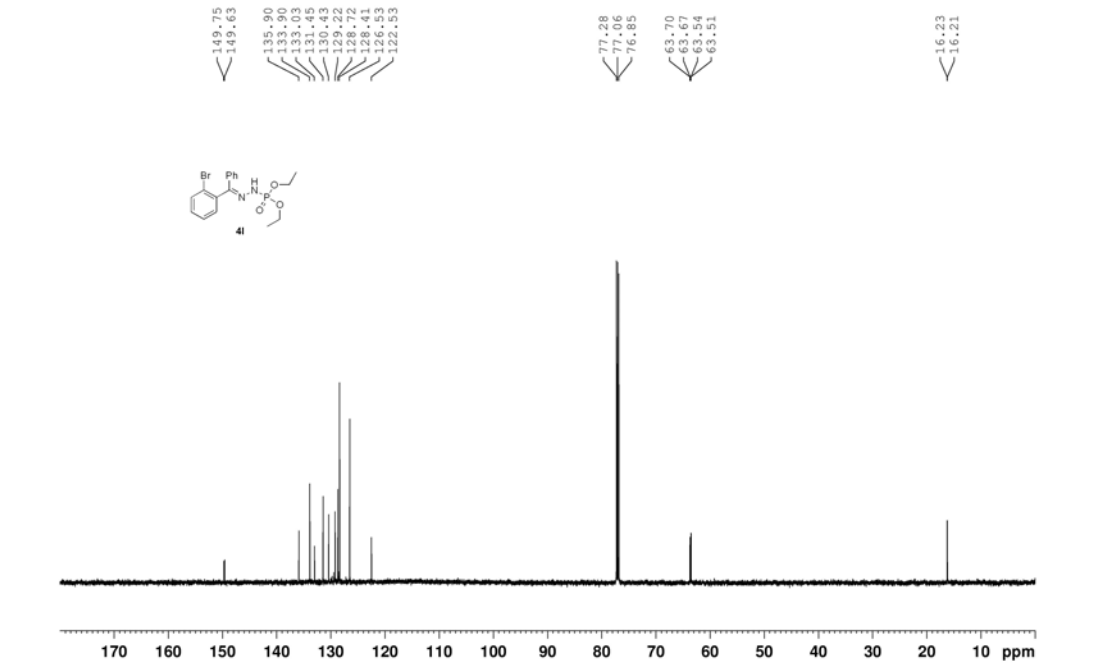

7.604
7.584
7.263
7.173
7.153
6.943
6.876
4.236
4.218
4.201
4.186
4.168
2.357
2.157
1.377
1.359
1.341
4j
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.06
1.01
4.00
3.04
3.04
6.00

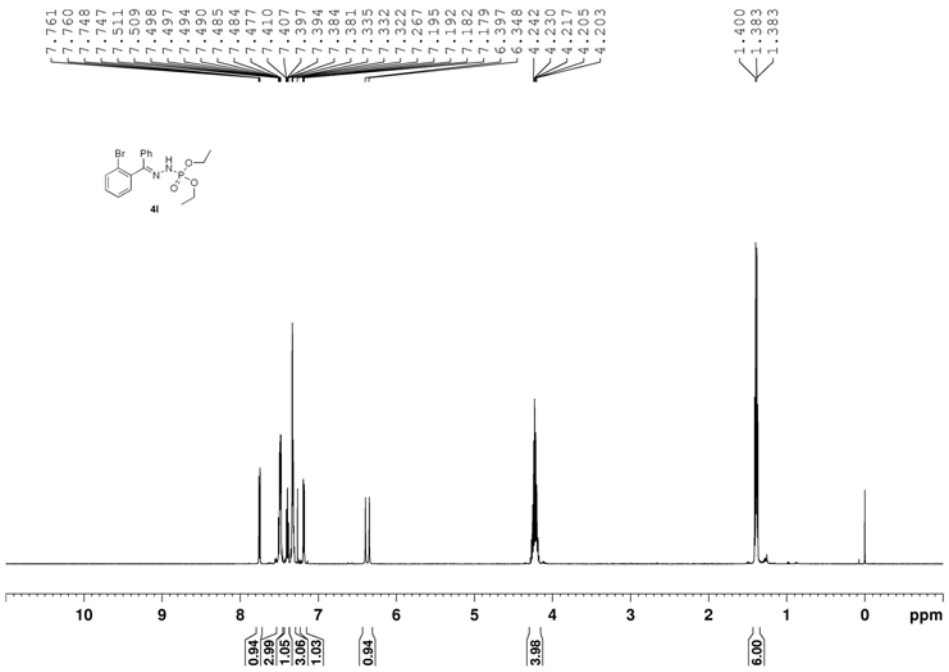

1.83
4j
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

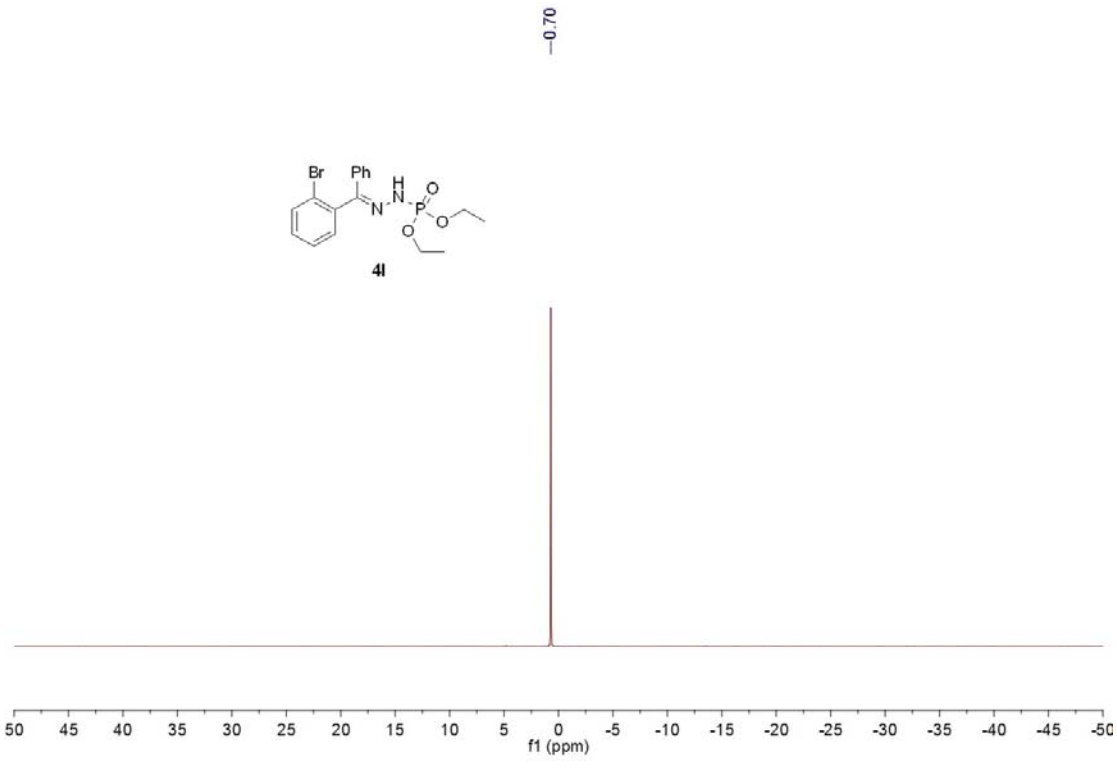

151.67
151.50
137.25
131.64
129.85
129.74
129.10
128.53
128.22
127.07
77.40
77.09
76.77
63.53
63.47
16.25
16.19
4k
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

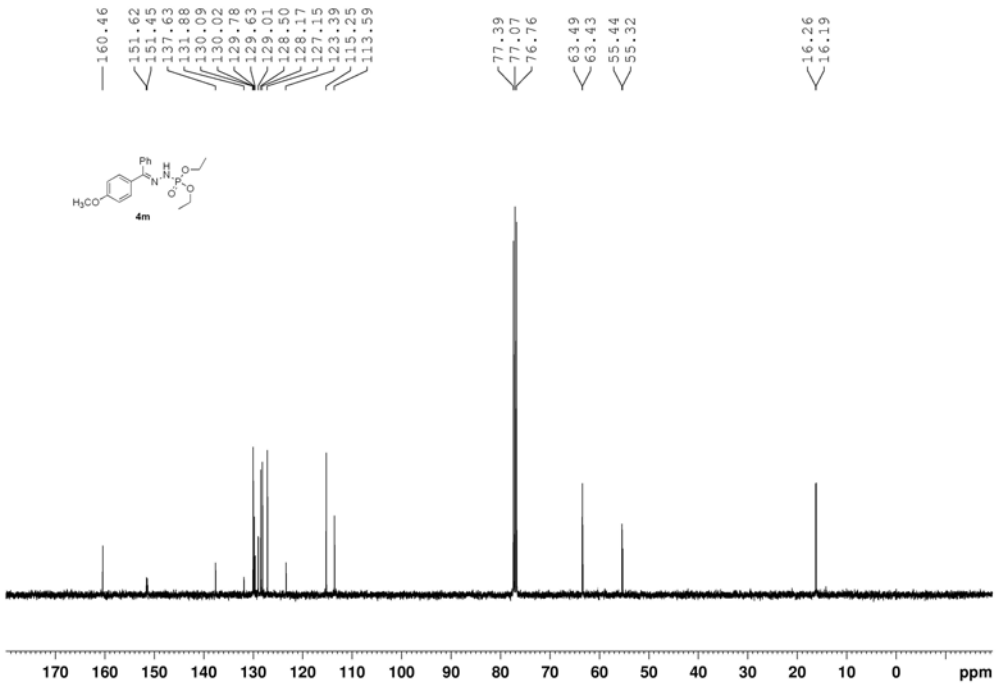

7.567
7.550
7.530
7.523
7.517
7.504
7.320
7.316
7.303
7.246
7.229
6.635
6.562
4.236
4.216
4.198
4.178
1.407
1.390
1.372
4k
11 10 9 8 7 6 5 4 3 2 1 0 ppm
5.03
2.99
2.01
0.99
3.98
5.00

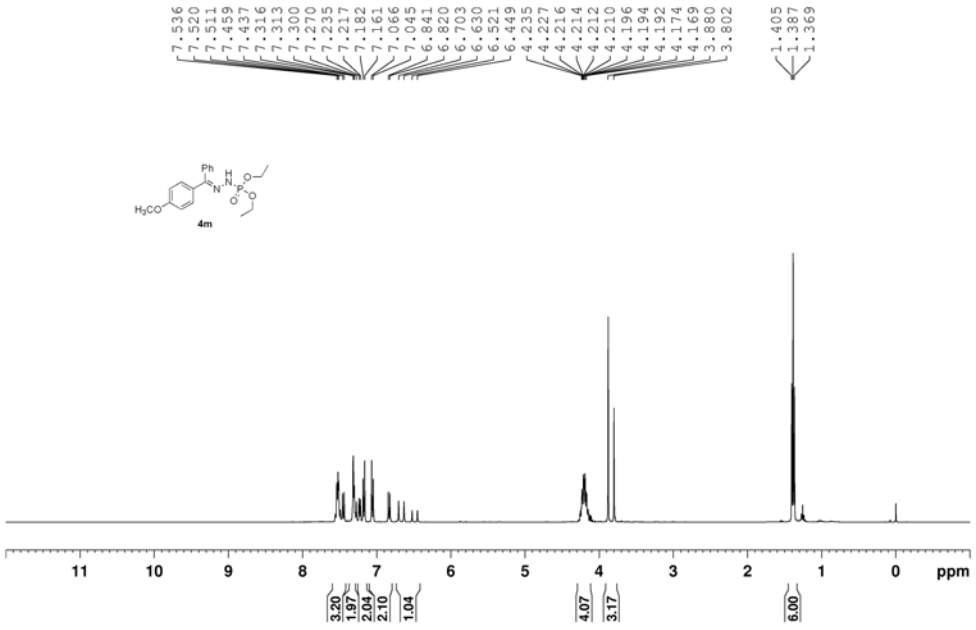

1.28
Ph
N
H
N
P
O
O
O
4k
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

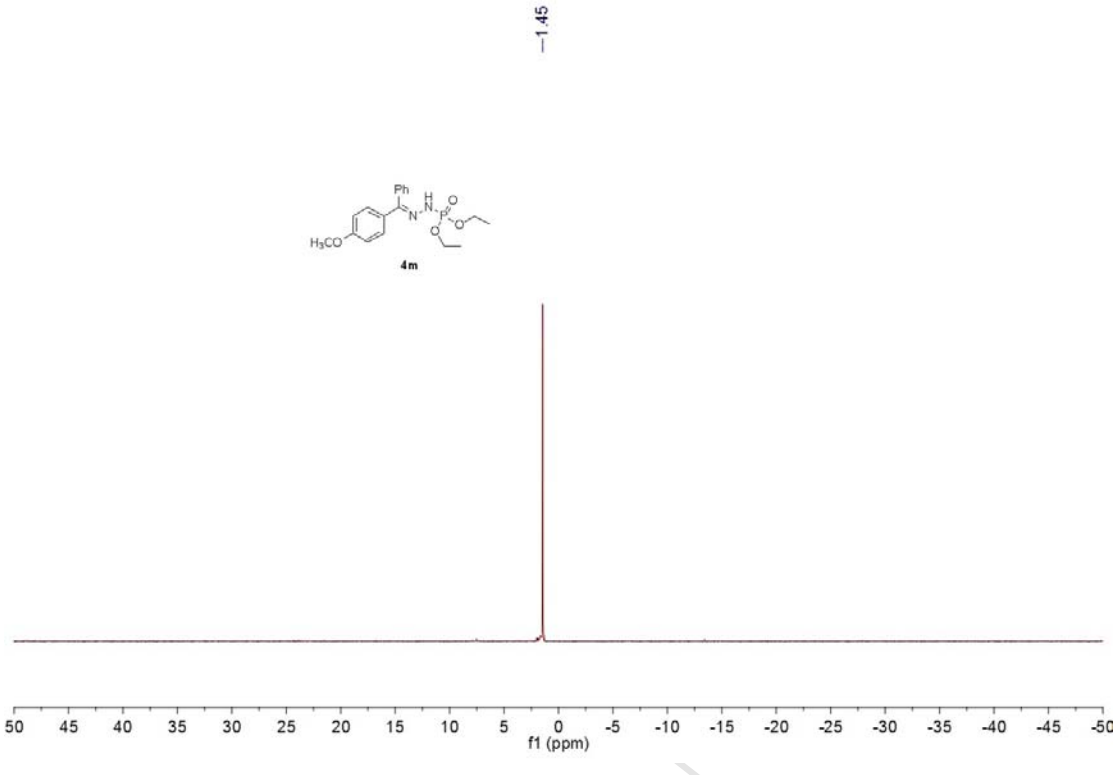

149.75
149.63
135.90
133.90
133.03
131.45
130.43
129.22
128.72
128.41
126.53
122.53
77.28
77.06
76.85
63.70
63.67
63.54
63.51
16.23
16.21
Br
Ph
N
H
N
P
O
O
O
4l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

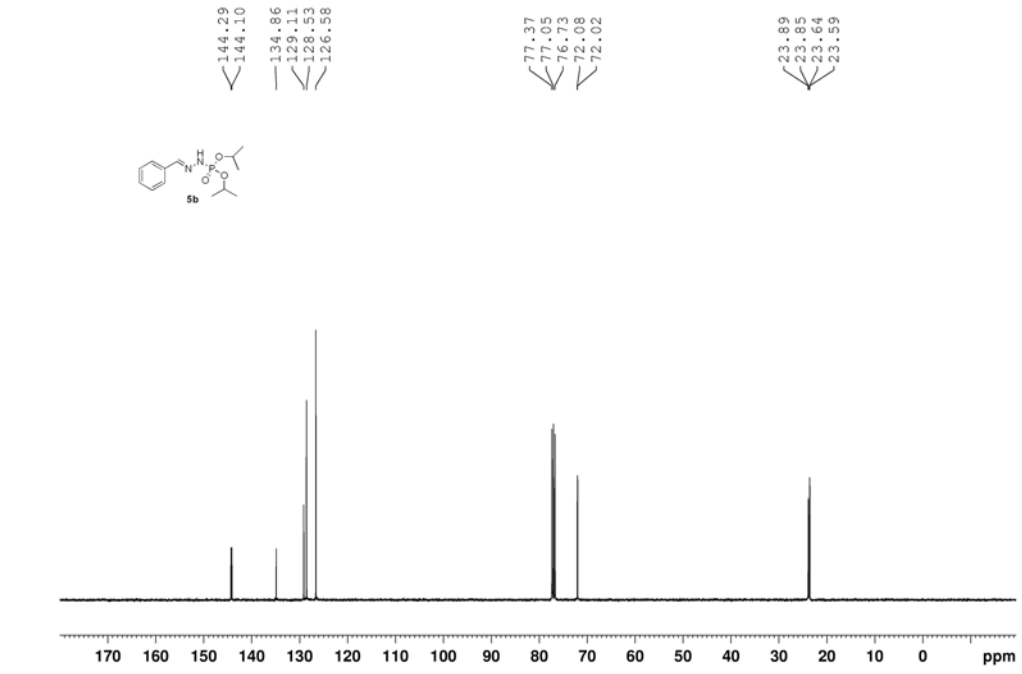

7.761
7.760
7.748
7.747
7.511
7.509
7.498
7.497
7.494
7.490
7.485
7.484
7.477
7.410
7.407
7.397
7.394
7.384
7.381
7.335
7.332
7.267
7.195
7.192
7.182
7.179
6.397
6.348
4.242
4.230
4.217
4.205
4.203
1.400
1.383
1.383
Br
Ph
4l
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
2.99
1.05
3.06
1.03
0.94
3.98
6.00

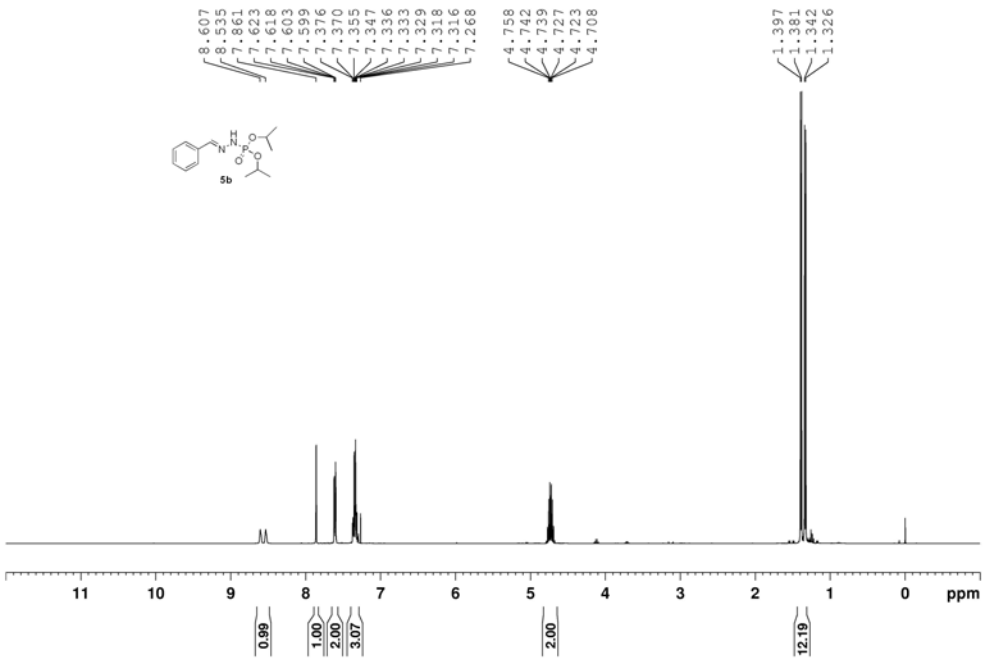

-0.70
Br
Ph
4l
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

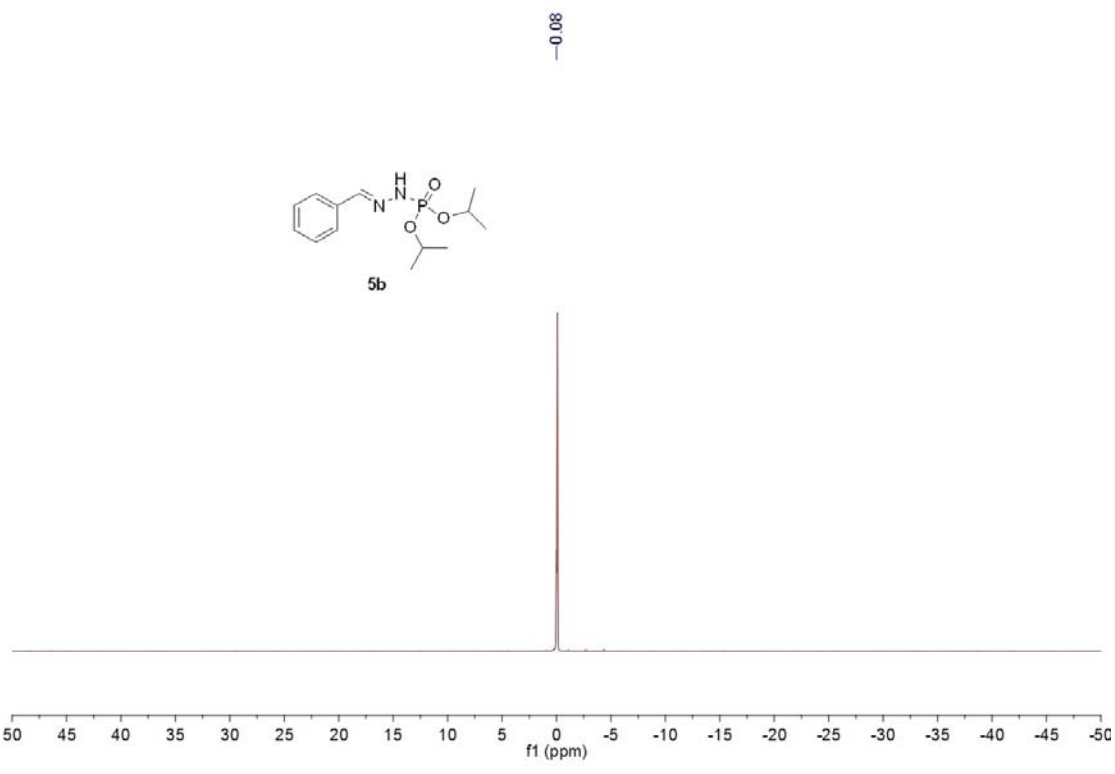

160.46
151.62
151.45
137.63
131.88
130.09
130.02
129.78
129.63
129.01
128.50
128.17
127.15
123.39
115.25
113.59
77.39
77.07
76.76
63.49
63.43
55.44
55.32
16.26
16.19
Ph
H
N
O
P
O
O
H3CO
4m
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

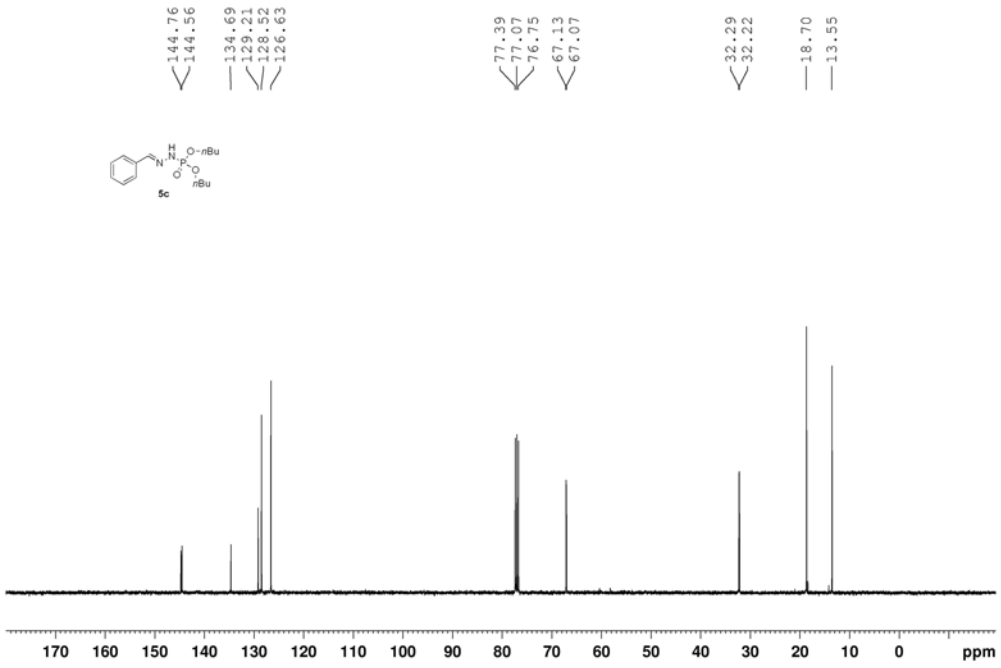

7.536
7.520
7.511
7.459
7.437
7.316
7.313
7.300
7.270
7.235
7.217
7.182
7.161
7.066
7.045
6.841
6.820
6.703
6.630
6.521
6.449
4.235
4.227
4.216
4.214
4.212
4.210
4.196
4.194
4.192
4.174
4.169
3.880
3.802
1.405
1.387
1.369
Ph
H
N
O
P
O
O
H3CO
4m
11 10 9 8 7 6 5 4 3 2 1 0 ppm
3.20
1.97
2.04
2.10
1.04
4.07
3.17
6.00

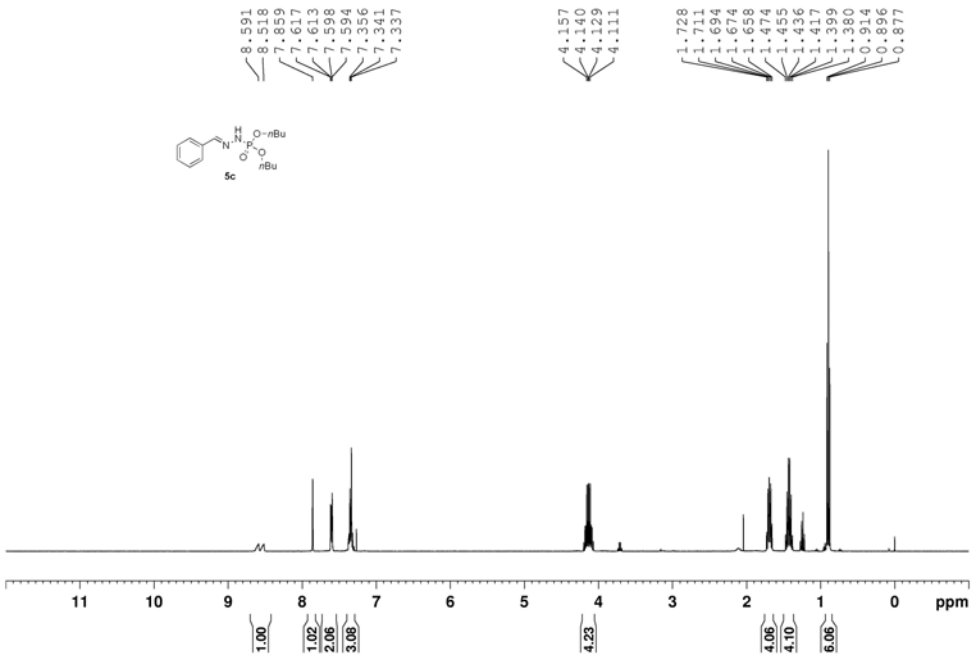

1.45
Ph
H
N
N
P
O
O
O
H3CO
4m
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

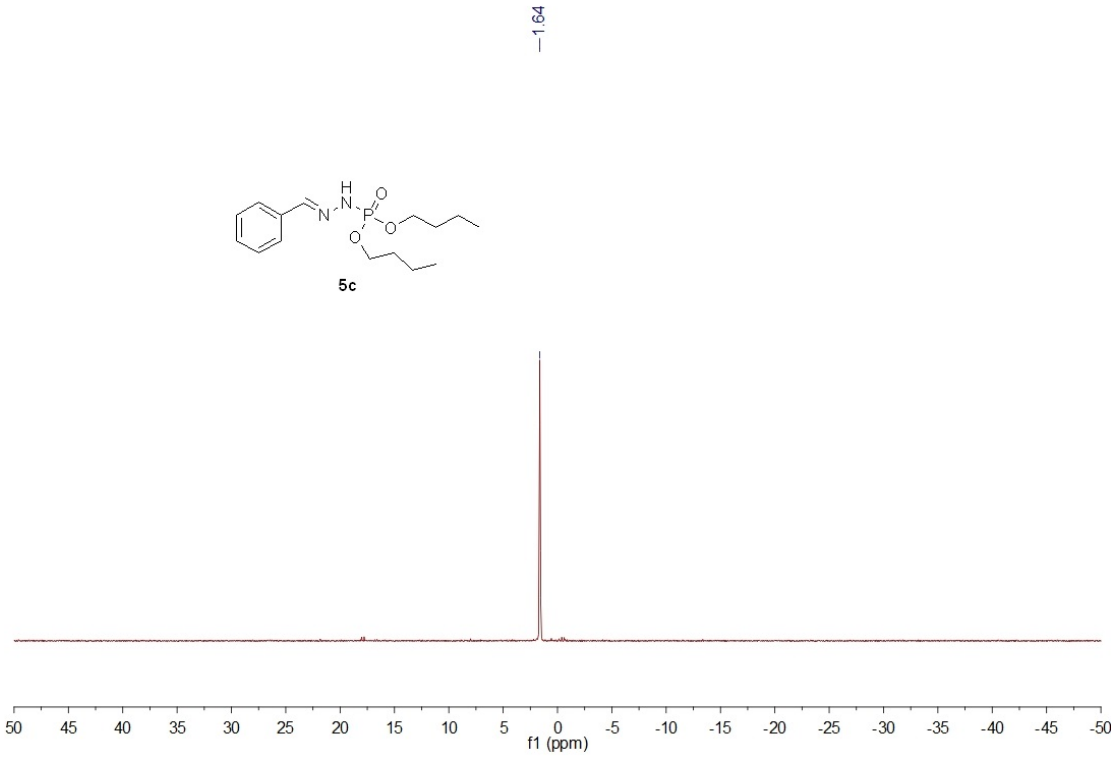

144.29
144.10
134.86
129.11
128.53
126.58
77.37
77.05
76.73
72.08
72.02
23.89
23.85
23.64
23.59
5b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

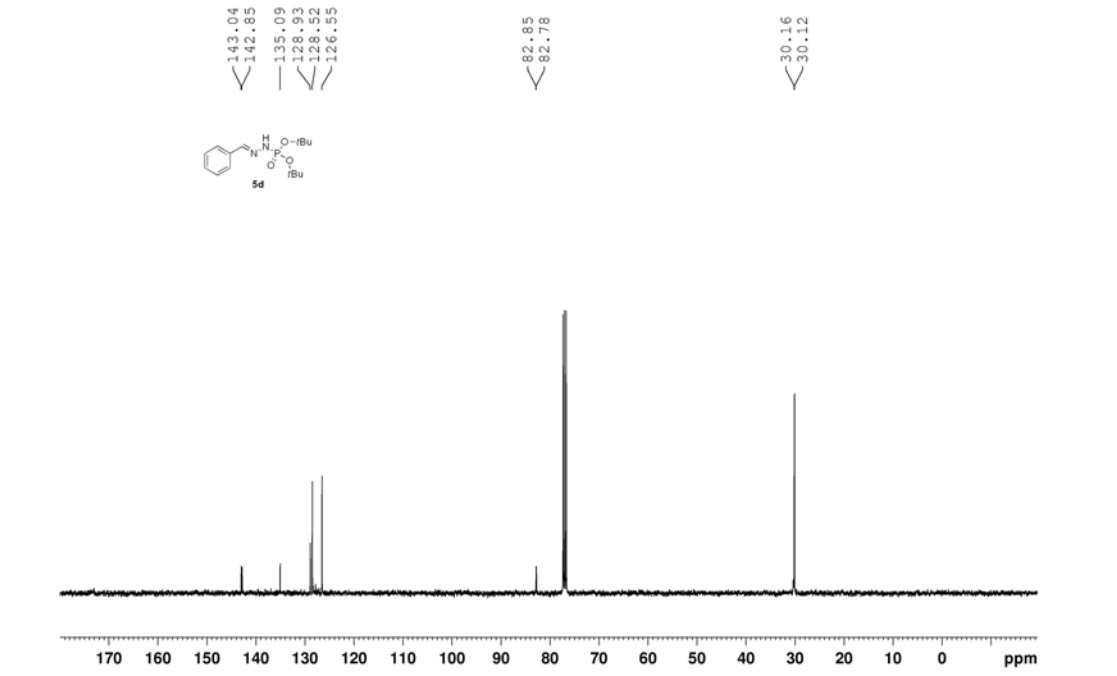

8.607
8.535
7.861
7.623
7.618
7.603
7.599
7.376
7.370
7.355
7.347
7.336
7.333
7.329
7.318
7.316
7.268
4.758
4.742
4.739
4.727
4.723
4.708
1.397
1.381
1.342
1.326
5b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.00
2.00
3.07
2.00
12.19

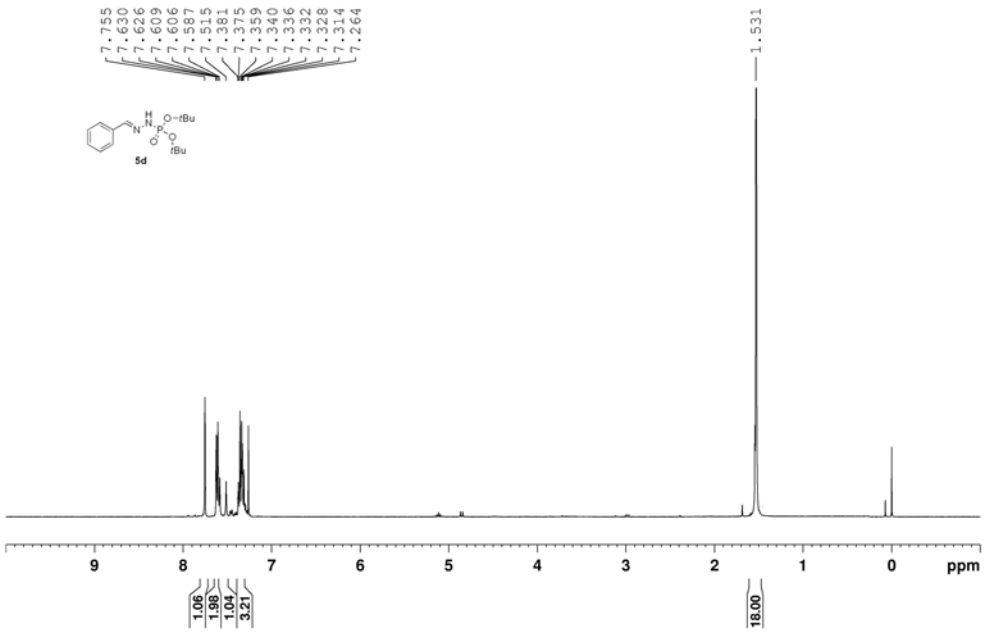

0.08
5b
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

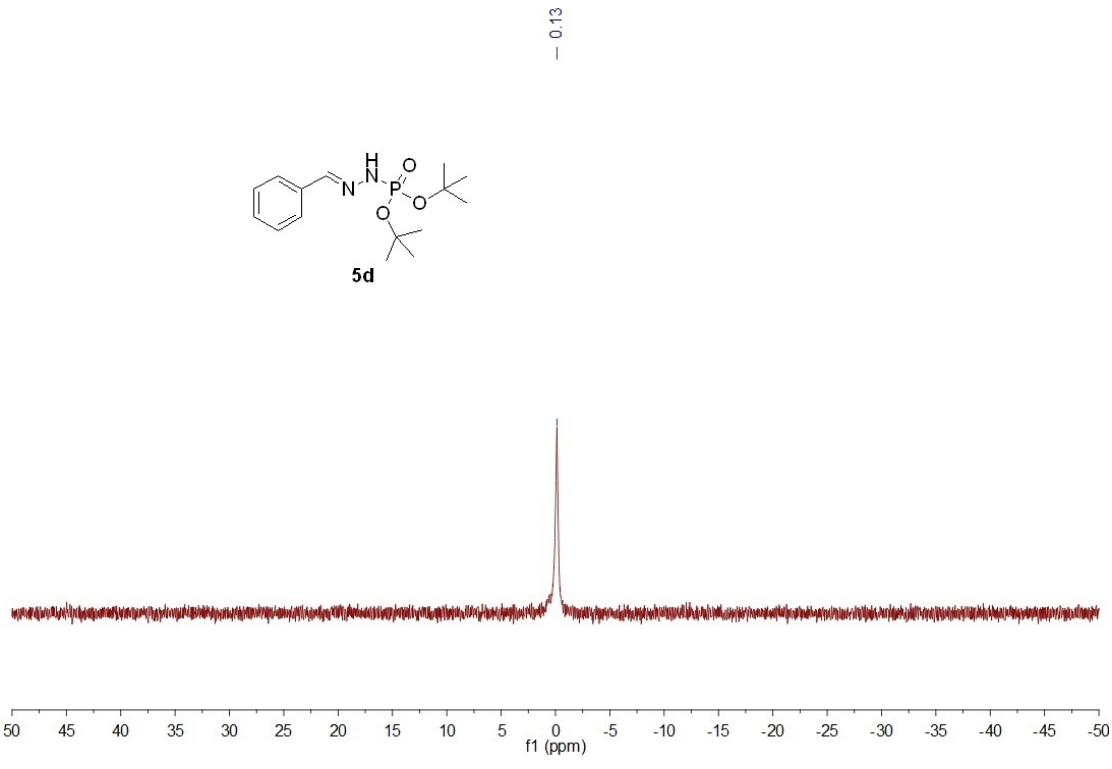

144.76
144.56
134.69
129.21
128.52
126.63
77.39
77.07
76.75
67.13
67.07
32.29
32.22
18.70
13.55
5c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

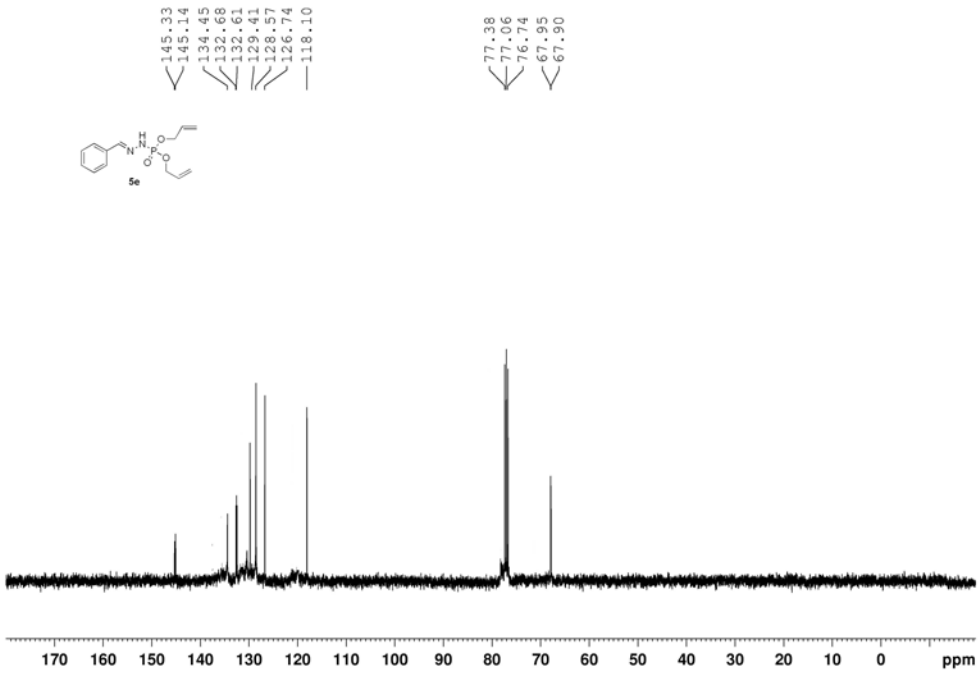

8.591
8.518
7.859
7.617
7.613
7.598
7.594
7.356
7.341
7.337
4.157
4.140
4.129
4.111
1.728
1.711
1.694
1.674
1.658
1.474
1.455
1.436
1.417
1.399
1.380
0.914
0.896
0.877
5c
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
2.06
3.08
4.23
4.06
4.10
6.06

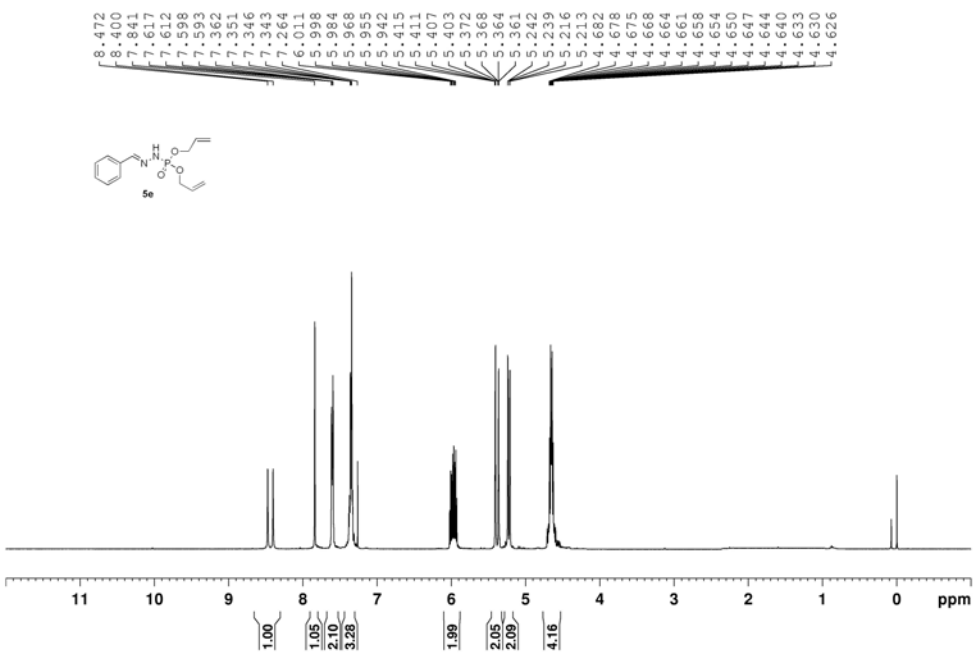

1.64
5c
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

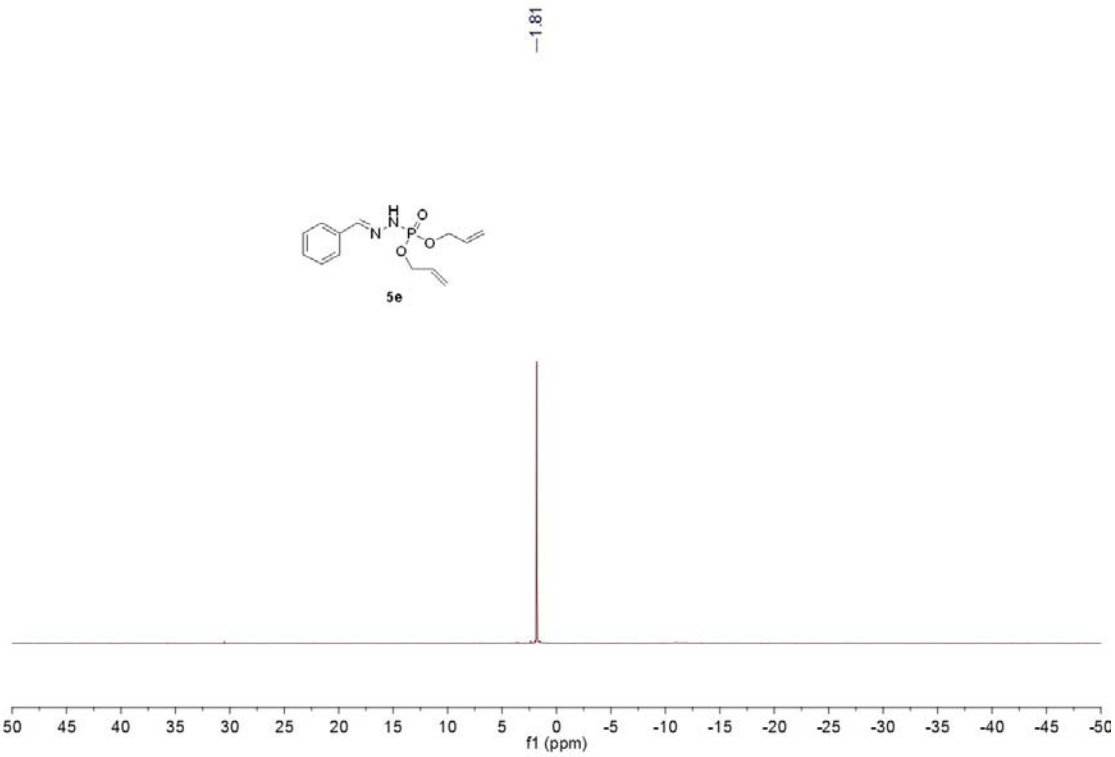

143.04
142.85
135.09
128.93
128.52
126.55
82.85
82.78
30.16
30.12
5d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

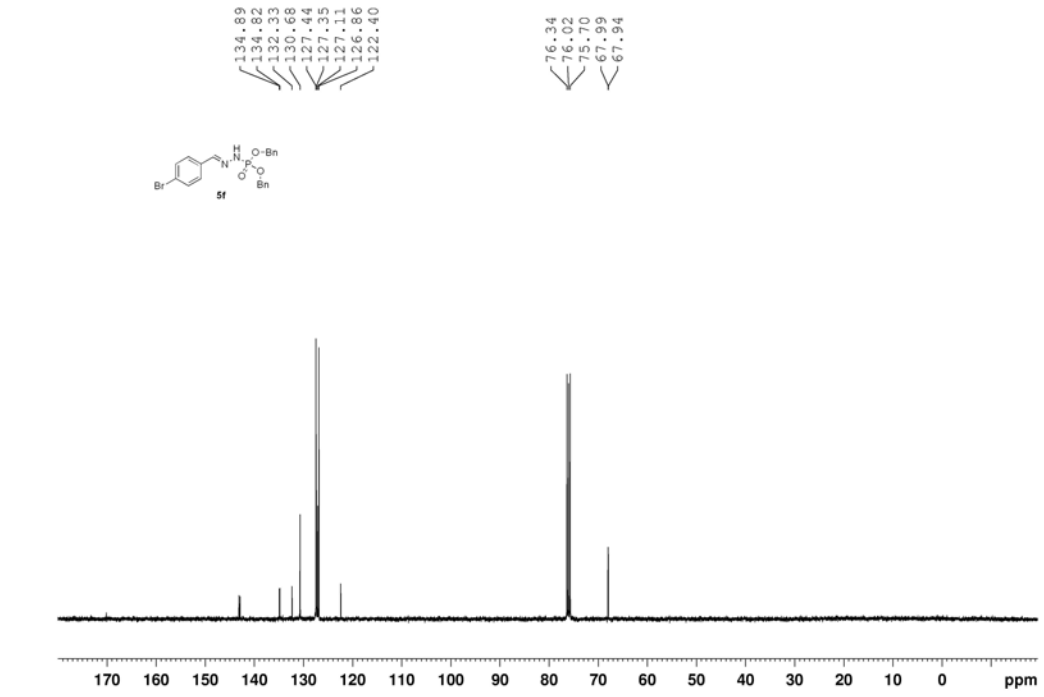

7.755
7.630
7.626
7.609
7.606
7.587
7.515
7.381
7.375
7.359
7.340
7.336
7.332
7.328
7.314
7.264
1.531
5d
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.98
1.04
3.21
18.00

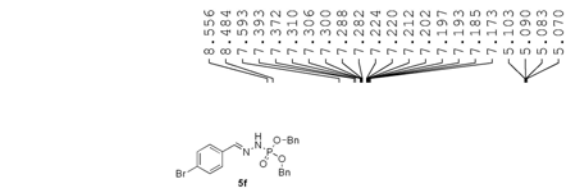

0.13
5d
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

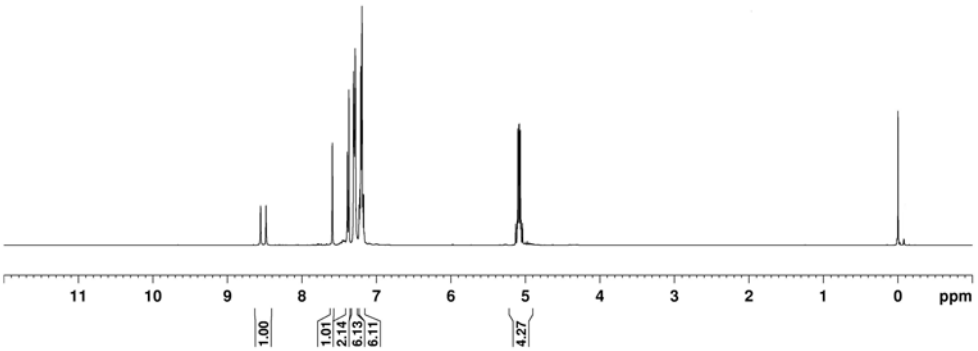

145.33
145.14
134.45
132.68
132.61
129.41
128.57
126.74
118.10
77.38
77.06
76.74
67.95
67.90
5e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

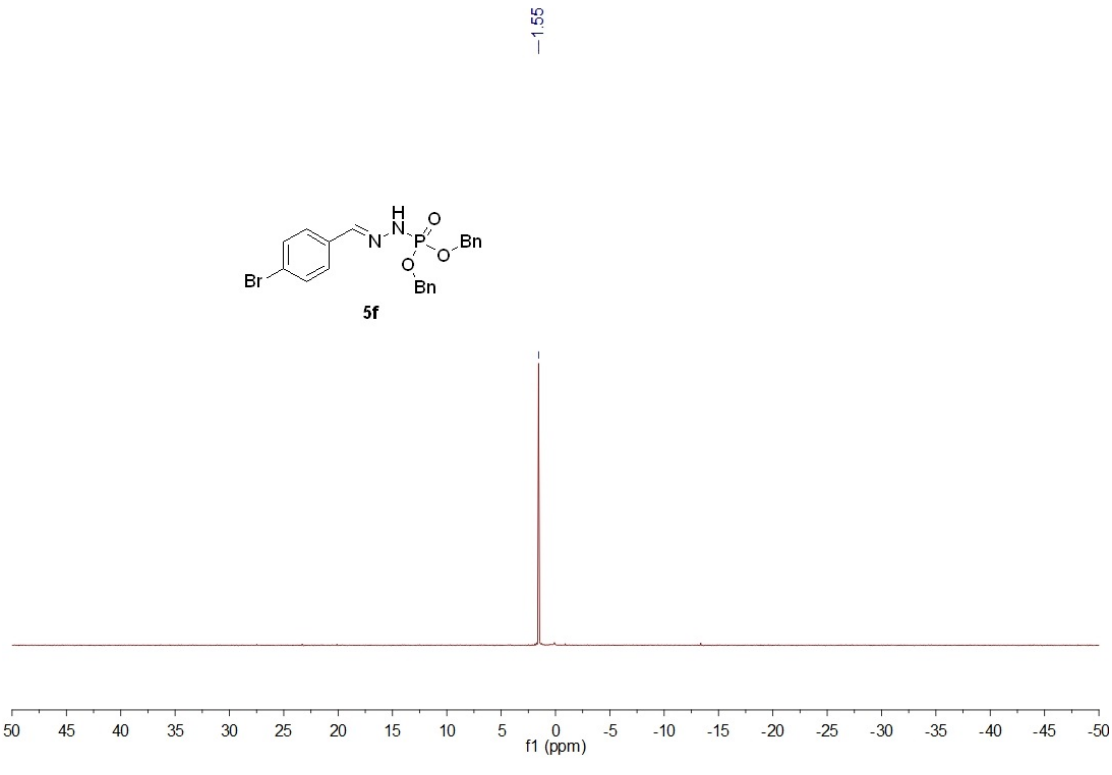

8.472
8.400
7.841
7.617
7.612
7.598
7.593
7.362
7.351
7.346
7.343
7.264
6.011
5.998
5.984
5.968
5.955
5.942
5.415
5.411
5.407
5.403
5.372
5.368
5.364
5.361
5.242
5.239
5.216
5.213
4.682
4.678
4.675
4.668
4.664
4.661
4.658
4.654
4.650
4.647
4.644
4.640
4.633
4.630
4.626
5e
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.05
2.10
3.28
1.99
2.05
2.09
4.16

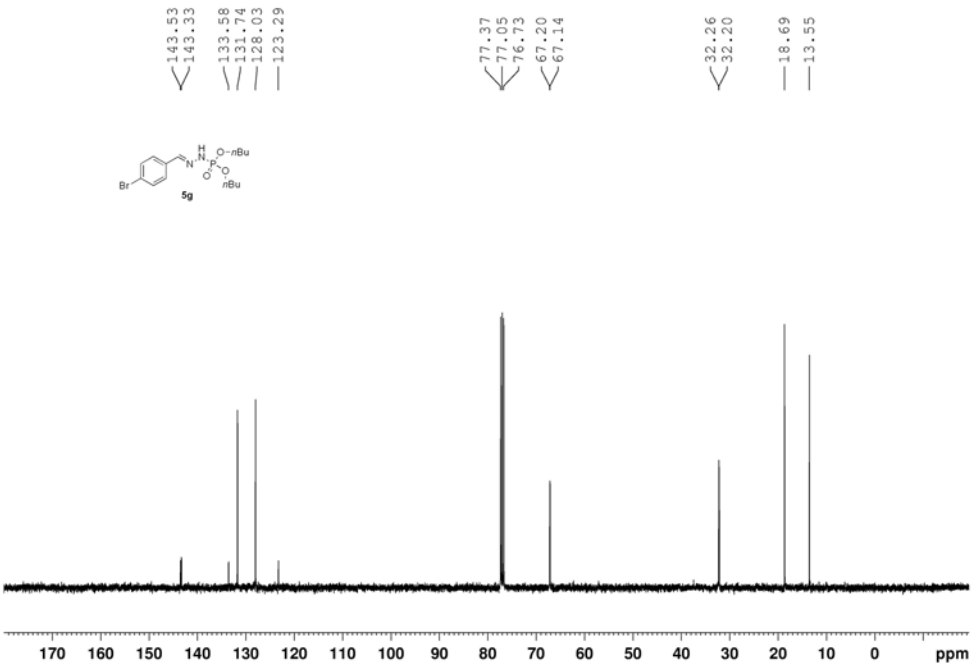

-1.81
5e
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

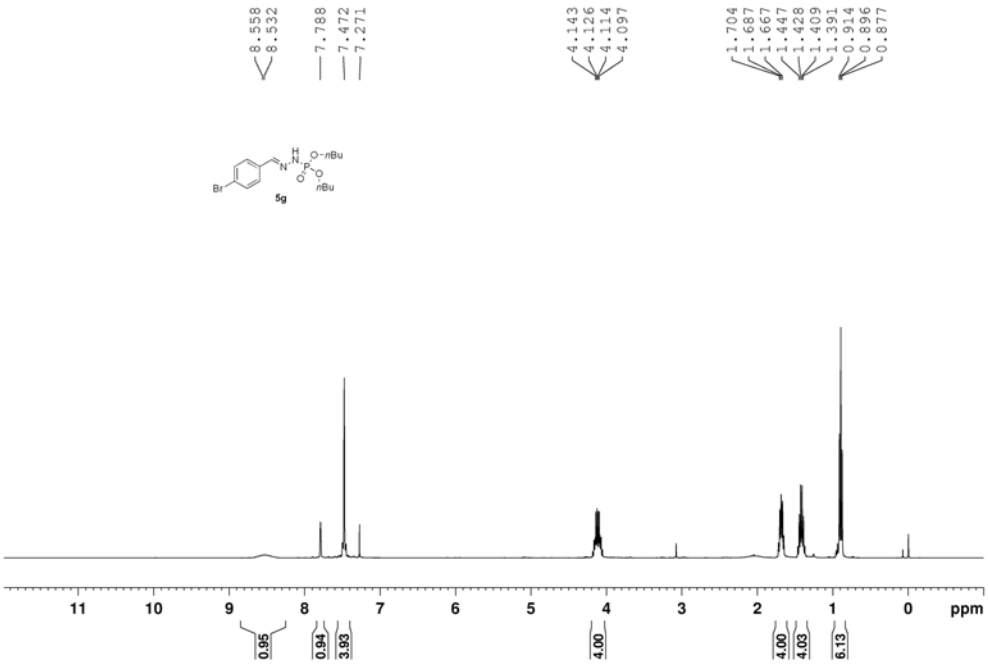

134.89
134.82
132.33
130.68
127.44
127.35
127.11
126.86
122.40
76.34
76.02
75.70
67.99
67.94
5f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

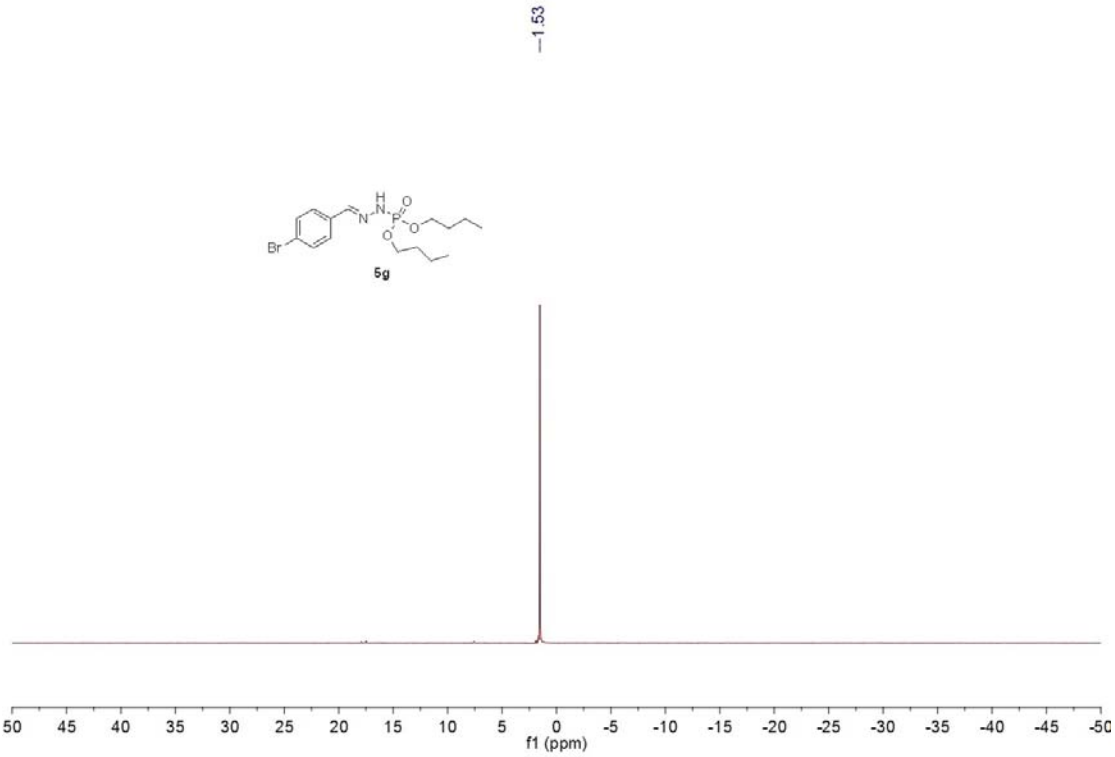

8.556
8.484
7.593
7.393
7.372
7.310
7.306
7.300
7.288
7.282
7.224
7.220
7.212
7.202
7.197
7.193
7.185
7.173
5.103
5.090
5.083
5.070
5f

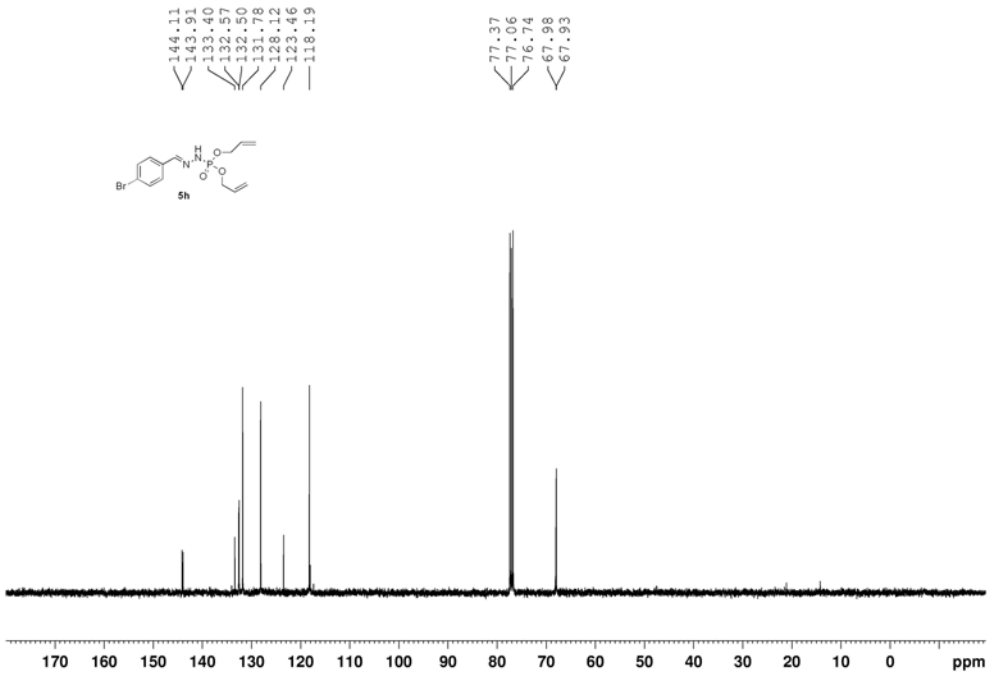

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.14
6.13
6.11
4.27

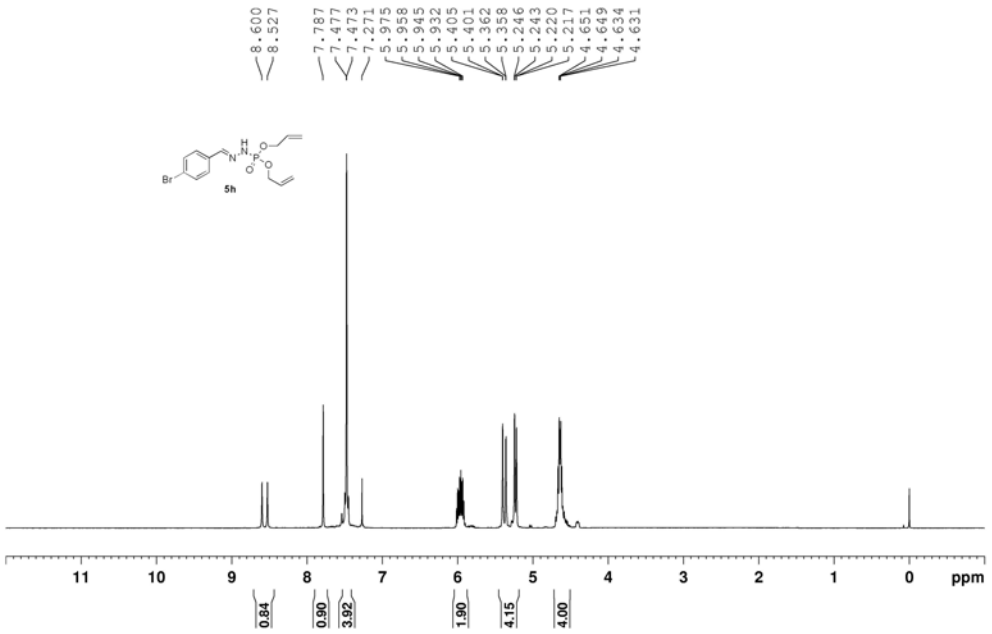

1.55
Br
N
H
O
P
O
Bn
O
Bn
5f
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

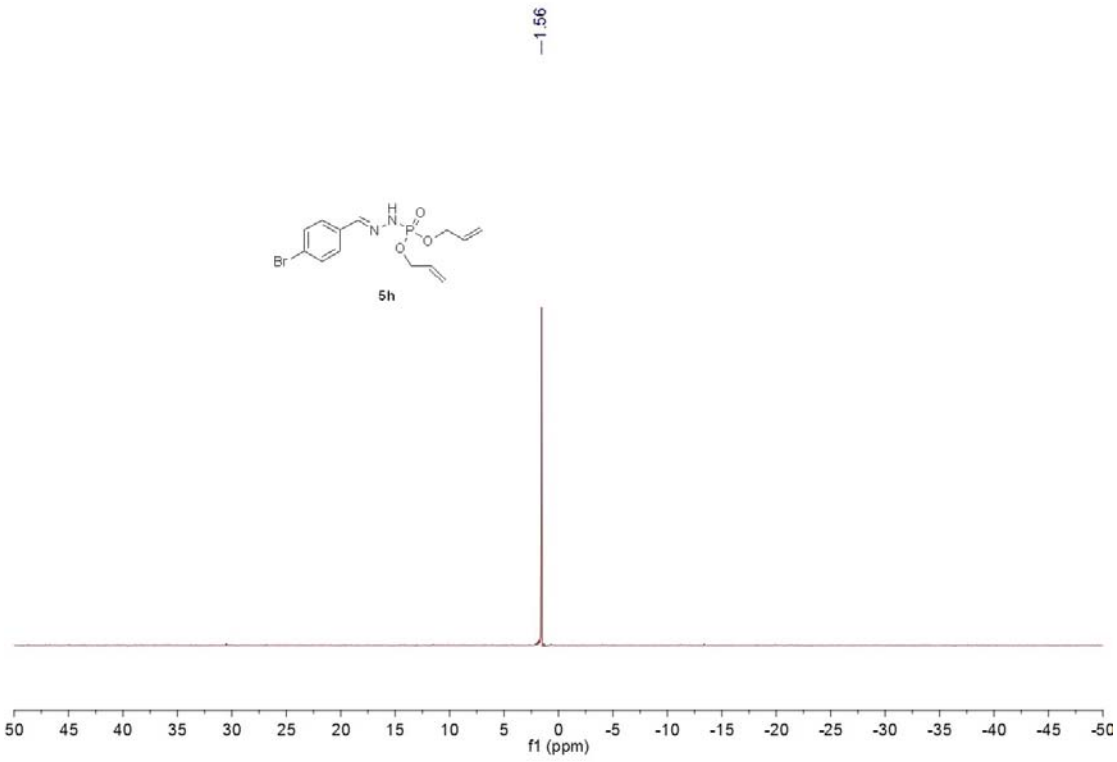

143.53
143.33
133.58
131.74
128.03
123.29
77.37
77.05
76.73
67.20
67.14
32.26
32.20
18.69
13.55
5g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

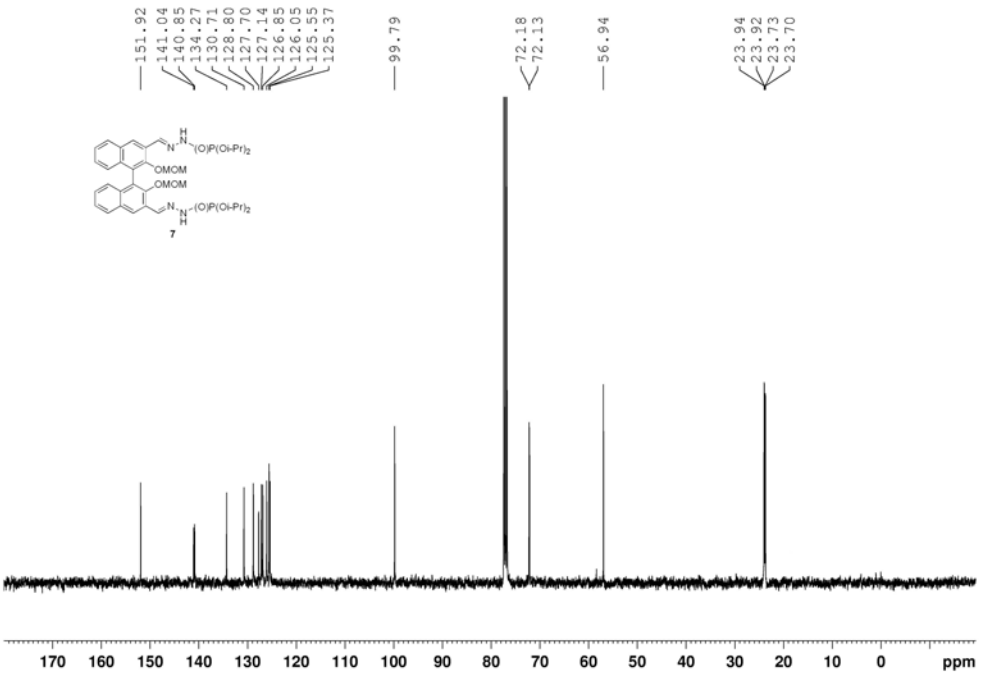

8.558
8.532
7.788
7.472
7.271
4.143
4.126
4.114
4.097
1.704
1.687
1.667
1.447
1.428
1.409
1.391
0.914
0.896
0.877
5g
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.95
0.94
3.93
4.00
4.00
4.03
6.13

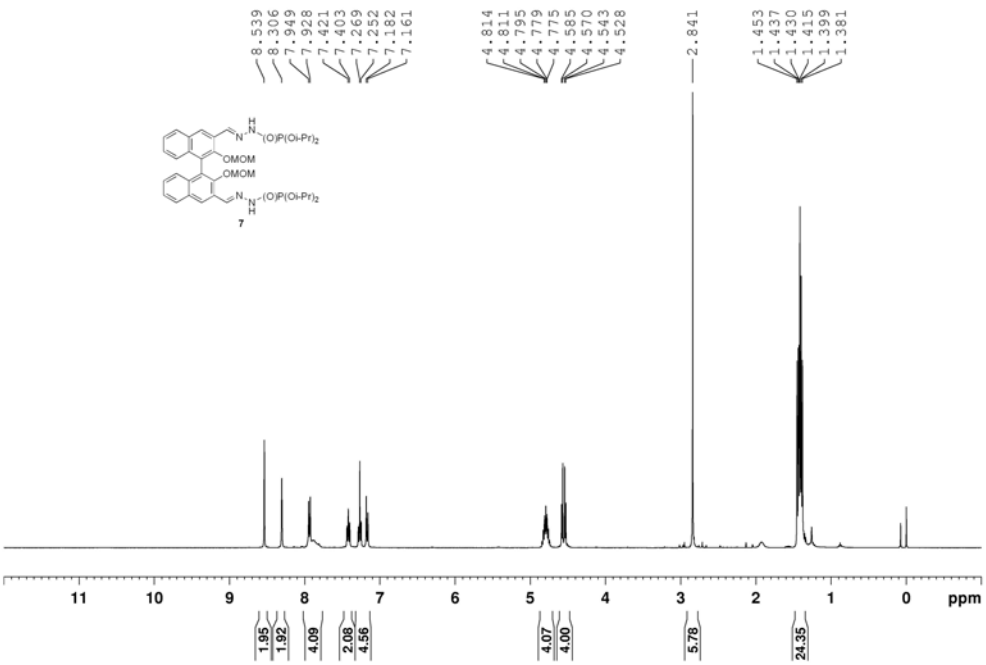

1.53
5g
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

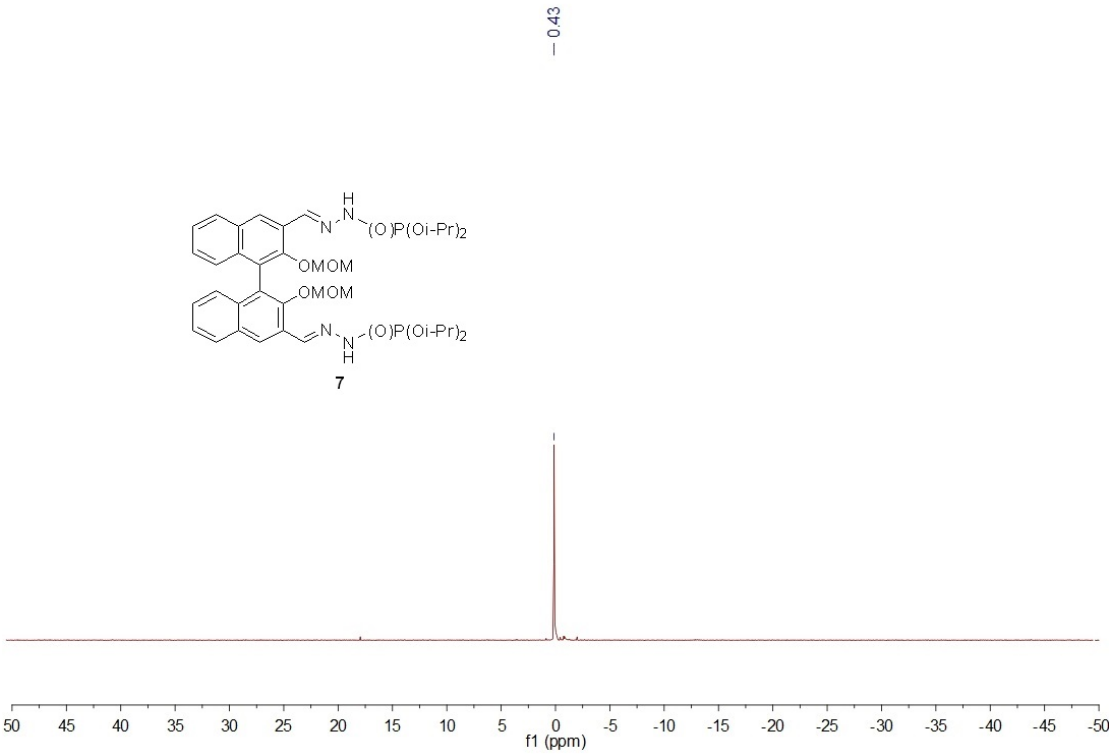

144.11
143.91
133.40
132.57
132.50
131.78
128.12
123.46
118.19
77.37
77.06
76.74
67.98
67.93
5h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.600
8.527
7.787
7.477
7.473
7.271
5.975
5.958
5.945
5.932
5.405
5.401
5.362
5.358
5.246
5.243
5.220
5.217
4.651
4.649
4.634
4.631
5h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.84
0.90
3.92
1.90
4.15
4.00


1.56
5h
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


151.92
141.04
140.85
134.27
130.71
128.80
127.70
127.14
126.85
126.05
125.55
125.37
99.79
72.18
72.13
56.94
23.94
23.92
23.73
23.70
OMOM
OMOM
7
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.539
8.306
7.949
7.928
7.421
7.403
7.269
7.252
7.182
7.161
4.814
4.811
4.795
4.779
4.775
4.585
4.570
4.543
4.528
2.841
1.453
1.437
1.430
1.415
1.399
1.381
OMOM
OMOM
7
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.95
1.92
4.09
2.08
4.56
4.07
4.00
5.78
24.35



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