Xanthan Sulfuric Acid as an Efficient Biodegradable and Recyclable Catalyst for the One-pot Synthesis of α-Amino Phosphonates

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A convenient and efficient procedure for the synthesis of α-amino phosphonates by a one-pot, three-component condensation of aldehydes, amine, and diethyl phosphite in the presence of xanthan sulfuric acid as a bio-supported catalyst under solvent-free conditions has been developed. A wide range of α-amino phosphonates have been obtained in high to excellent yields. Furthermore, the catalyst can be recovered simply and reused several times in subsequent reactions.

Keywords: Xanthan sulfuric acid; α-Aminophosphonates; One-pot synthesis; Aldehyde; Amine; Diethylphosphite; Solvent-free.

INTRODUCTION

The great importance of α-amino phosphonates is based on their structural analogues of the corresponding α-amino acids and their presence in a number of biologically active compounds.[1-3] Furthermore, it has been reported that these compounds are used as enzyme inhibitors, herbicids, insecticides, fungicides, antibiotics, pharmacological agents.[4,5] Therefore it is not surprising that research on their synthesis has received special attention.[6-9] The known method of their synthesis includes a two-step reaction: the formation of imines from aldehydes and amines (first step) and the nucleophilic addition of phosphites with imines (second step), which obtains the desired α-amino phosphonates.[10,11]

Currently, multicomponent reactions (MCRs) have been rapidly developed because such reactions offer a wide range of possibilities for the efficient construction of highly complex molecules in a single procedural step, and make the synthesis simpler and more environmentally friendly.[12-21] Recently, the synthesis of α-amino phosphonates by three-component coupling of aldehydes, amine, and diethyl phosphite in the presence of an acid or a base catalyst has been developed. A variety of catalysts that include $In(OTf)_3$,[22] $InCl_3$,[23] $Al(H_2PO_4)_3$,[24] $LiClO_4$,[25] $Mg(ClO_4)_2$,[26] $ZrOCl_2 \cdot 8H_2O$,[27] $SnCl_2$,[28] $BiCl_3$,[29] TiO_2,[30] ZnO,[31] NBS,[32] PPh_3,[33] metallotetrapyridinoporphyrazine,[34] β-cyclodextrin,[35] mesoporous aluminosilicate nanocage,[36] silica sulphuric acid[37] Amberlite-IR 120[38] as well as heteropolyacids[39] have been reported to promote this transformation. However, these approaches have some disadvantages such as the use of expensive, moisture sensitive and toxic catalysts, relatively long reaction times and the use of harmful volatile organic solvent. Thus, there is still the need to develop an efficient, mild and environmentally benign protocol for the synthesis of α-amino phosphonates.

Recently, several biopolymers have been utilized as a support for catalytic applications in organic synthesis as they are biodegradable materials and renewable resources.[40-42] Among the various biopolymers, particularly, xanthan has received much attention because it is the most abundant bacterial exopolysaccharide in the world, which is produced through fermentation. Unlike other gums, it is very stable under a wide range of temperatures and pH values. Xanthan sulfuric acid can be easily prepared by the reaction of xanthan with chlorosulfonic acid and it has been reported as an efficient catalyst for the synthesis of α-amino nitriles.[43] In continuation of our work on the development of new synthetic methods,[44-47] we report for the first time a facile and efficient synthetic strategy for the preparation of α-amino phosphonates using xanthan sulfuric acid as a biodegradable and recyclable solid acid catalyst under solvent-free conditions (Scheme I).

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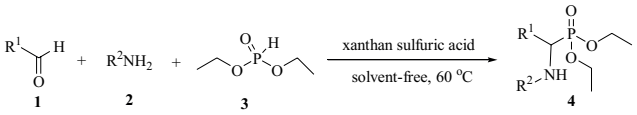
Scheme I



1 2 3 4

RESULTS AND DISCUSSION

In the initial experiments, in order to evaluate the catalytic efficiency of xanthan sulfuric acid in this three-component reaction, reaction of 2-methoxybenzaldehyde, aniline and diethyl phosphate was selected as model. It showed that only 30% of product could be obtained when a mixture of 2-methoxybenzaldehyde, aniline and diethyl phosphate was heated at 60 °C for 1 h in absence of catalyst, which indicated that the catalyst should be necessary for this transformation. The effect of amount of catalyst on the yield and rate was also investigated. It was found that the use of 0.04 g catalyst is sufficient to promote the reaction. The fewer amounts gave a low yield even after long reaction time, and the more amounts did not affect the efficiency of this transformation. Meanwhile, we also tested the effect of reaction temperature on this reaction. When the reaction was carried out at room temperature, only trace product was obtained (Table 1, entry 7). When the temperature was increased to 60 °C, the reaction proceeded smoothly and maximum yield was obtained.

After optimization of the conditions, to delineate this approach, we carried out this three-component coupling reaction of a series of aldehydes, aromatic amines and diethyl phosphate under solvent-free conditions at 60 °C in the presence of xanthan sulfuric acid. The reactions were completed after 40-60 min affording corresponding α-aminophosphonates in good to excellent yields. No competitive side reactions such as aromatic nucleophilic substitution of halogen atom, nucleophilic cleavage of the O-Me group, or decomposition of acid sensitive substrates were observed.

Table 1. Optimization of reaction conditions for the synthesis of **4g**

Entry	Amount of catalyst (g)	Temperature (°C)	Time (min)	Yield (%)[a]
1	no	60	60	30
2	0.02	60	80	45
3	0.04	60	60	95
4	0.06	60	60	95
5	0.08	60	60	95
6	0.10	60	50	95
7	0.04	25	120	5
8	0.04	40	60	50
9	0.04	50	60	93

[a] Isolated yields.

Encouraged by the above interesting results, we also attempted to synthesis bis(α-aminophosphonate) to further broaden the scope of this three-component reaction. To our delight, the reactions of isophthalaldehyde with two equivalents of 4-bromoaniline or benzene-1,4-diamine with two equivalents of benzaldehyde resulted in formation of the desired bis(α-aminophosphonates) (Scheme II) in high yields under similar condition.

Finally, the recyclability of the catalyst was investigated. After reaction, the catalyst can be easily separated by simple filtration, washing with ethyl acetate, and drying in a vacuum oven at 60 °C for 3 h. The recovered catalyst can

Scheme II

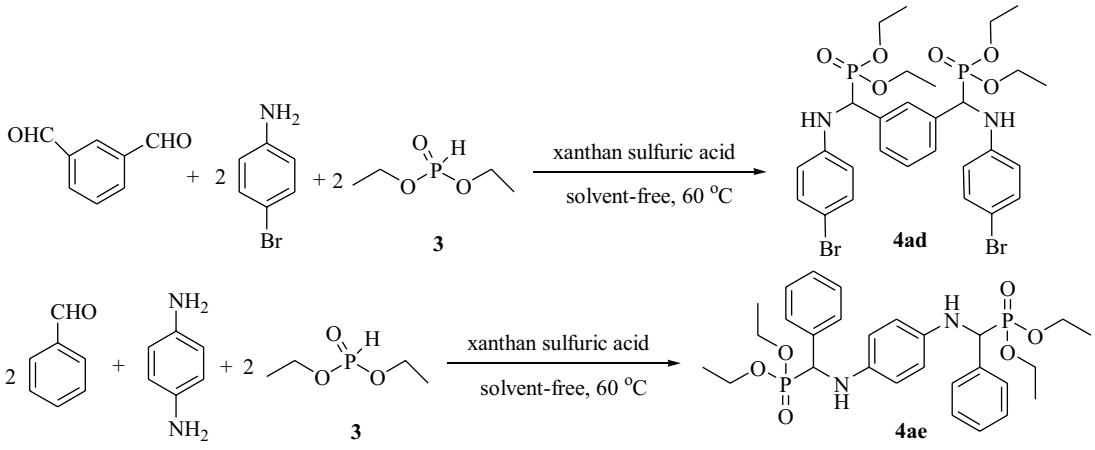
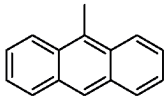
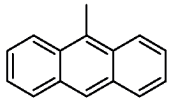
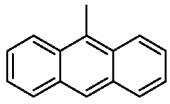
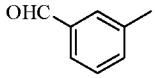


Table 2. One-pot three-component synthesis of α-aminophosphonates

Entry	R^1	R^2	Time (min)	Yield (%)[a]	m.p. (°C)	Lit. m.p. (°C)
a	Ph	Ph	60	93	90-91	89-90[6]
b	Ph	4-Me-C_6H_4	60	94	116-118	117-118[39]
c	Ph	4-MeO-C_6H_4	60	92	72-73	70-73[6]
d	Ph	4-Cl-C_6H_4	50	95	112-113	112-113[39]
e	Ph	4-NO_2-C_6H_4	50	90	143-145	145-147[33]
f	4-Me-C_6H_4	Ph	60	93	64-65	63-65[9]
g	2-MeO-C_6H_4	Ph	60	95	99-100	98-99[38]
h	4-MeO-C_6H_4	Ph	60	92	102-103	102-103[9]
i	3,4,5-$(MeO)_3$-C_6H_2	Ph	60	89	108-109	107-109[33]
j	4-OH-C_6H_4	Ph	60	91	oil	oil[33]
k	2-Cl-C_6H_4	Ph	45	90	88-89	88[30]
l	3-Cl-C_6H_4	Ph	40	92	89-91	88-90[33]
m	4-ClC_6H_4	Ph	40	95	59-60	59-60[31]
n	3-NO_2-C_6H_4	Ph	45	93	96-97	95-97[37]
o	4-$NO_2C_6H_4$	Ph	45	95	120-121	120[30]
p	3,4-(OCH_2O)-C_6H_3	4-Me-C_6H_4	60	93	103-104	102-104[10]
q	4-MeO-C_6H_4	4-Br-C_6H_4	50	94	106-108	108-109[7]
r	3-NO_2-C_6H_4	3-NO_2-C_6H_4	50	90	158-159	158[22]
s	3-Cl-C_6H_4	3-NO_2-C_6H_4	50	91	114-115	114[22]
t	4-ClC_6H_4	4-NO_2-C_6H_4	50	92	131-132	131[22]
u	4-OMe-C_6H_4	4-NO_2-C_6H_4	45	90	112-113	112[30]
v	2-NO_2-C_6H_4	4-NO_2-C_6H_4	60	90	177-178	
w	2-NO_2-C_6H_4	2-NO_2-4-OEt-C_6H_4	60	93	147-148	
x	C_6H_{11}	Ph	60	90	oil	oil[29]
y	PhCH=CH	Ph	60	85	104-105	104[30]
z		Ph	60	88	51-52	50-52[9]
aa		4-Br-C_6H_4	50	95	192-193	
ab		4-NO_2-C_6H_4	50	93	224-226	
ac		2-NO_2-4-OEt-C_6H_4	50	92	111-112	
ad[b]		4-Br-C_6H_4	60	94	184-186	
ae[c]	Ph	4-NH_2-C_6H_4	60	93	201-202	199-200[50]

[a] Isolated yield. [b] Two equivalents of 4-bromoaniline were used. [c] Two equivalents of benzaldehyde were used.

be reused for model reaction at least three additional times in subsequent reaction without significant decrease in product yields (95%, 94%, and 90%).

In conclusion, we have developed a new one-pot synthesis of α-amino phosphonates by the reaction of aldehydes, amine, and diethyl phosphate using xanthan sulfuric acid as an efficient, eco-friendly, reusable and biodegradable catalyst. The advantages of the present procedure are relatively short reaction times, high yields, mild reaction conditions and the absence of organic solvent, which make it a useful alternative to existing methods.

EXPERIMENTAL SECTION

Melting points were obtained with an X-4 apparatus. IR spectra were recorded on a Shimadzu FTIR-8900 spectrometer. NMR spectra were taken with a Bruker DRX-500

spectrometer at 500 MHz (^{1}H) and 125 MHz (^{13}C) using $CDCl_3$ as the solvent. Elemental analysis was determined on a Vario EL III CHNOS elemental analyzer.

Preparation of xanthan sulfuric acid

The preparation of xanthan sulfuric acid was carried out following a reported procedure.[43] To a magnetically stirred suspension of xanthan (5.0 g) in $CHCl_3$ (15 mL), chlorosulfonic acid (1.00 g) was added dropwise at 0 °C during 2 h. HCl gas was removed from the reaction vessel immediately. After completion of the addition, the mixture was stirred for 3 h. Then, the mixture was filtered and washed with methanol (25 mL) and dried at room temperature to obtain xanthan sulfuric acid as white powder (5.30 g).

General procedure for the preparation of α-aminophosphonates

To a mixture of aldehyde (1 mmol), amine (1 mmol), and diethylphosphite (1 mmol), xanthan sulfuric acid (0.04 g) was added and the mixture was heated at 60 °C for an appropriate time as indicated by TLC. The mixture was cooled to room temperature and ethyl acetate (15 mL) was added. The catalyst was filtered and washed with ethyl acetate. The solvent was evaporated to give the crude product. The crude product was purified by flash chromatography (ethyl acetate/petroleum ether, 1:20) to afford the pure product.

[(2-Nitrophenyl)-(4-nitrophenylamino)-methyl]-phosphonic acid diethyl ester (4v)

Yellow crystals; IR (KBr): 3269, 1600, 1533, 1508, 1488, 1315, 1284, 1234, 1112, 1018, 950, 858 cm^{-1}; δ_H 1.13 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.0 Hz, 3H), 3.79-3.87 (m, 1H), 3.94-4.02 (m, 1H), 4.17-4.25 (m, 2H), 6.25 (dd, J = 26.0, 8.5 Hz, 1H), 6.41 (t, J = 8.5 Hz, 1H), 6.72 (d, J = 9.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 8.03 (d, J = 9.5 Hz, 2H), 8.05 (d, J = 7.5 Hz, 1H); δ_C 15.9 (d, $^3J_{PC}$ = 5.5 Hz), 16.4 (d, $^3J_{PC}$ = 5.6 Hz), 49.7 (d, $^1J_{PC}$ = 151.1 Hz), 63.9 (d, $^2J_{PC}$ = 7.3 Hz), 64.1 (d, $^2J_{PC}$ = 7.1 Hz), 112.5, 125.4 (d, J_{PC} = 2.1 Hz), 126.2, 128.7 (d, J_{PC} = 4.5 Hz), 129.1 (d, J_{PC} = 3.1 Hz), 130.6, 133.6, 139.4, 149.3 (d, J_{PC} = 5.3 Hz), 151.4 (d, J_{PC} = 13.5 Hz); Anal. calcd. For $C_{17}H_{20}N_3O_7P$: C, 49.88; H, 4.92; N, 10.27. Found: C, 50.02; H, 5.15; N, 10.08.

[(4-Ethoxy-3-nitrophenylamino)-(2-nitrophenyl)-methyl]-phosphonic acid diethyl ester (4w)

Red-brown crystals; IR (KBr): 3355, 2977, 1616, 1569, 1525, 1475, 1425, 1357, 1263, 1217, 1184, 1112, 1045, 1020, 983, 873 cm^{-1}; δ_H 1.28 (t, J = 7.0 Hz, 3H), 1.22 (t, J = 7.0 Hz, 3H), 1.38 (t, J = 7.0 Hz, 3H), 3.96-4.19 (m, 6H), 6.32 (dd, J = 27.0 , 7.5 Hz, 1H), 6.77 (d, J = 9.0 Hz, 1H), 7.06 (dd, J = 9.0, 2.5 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 2.5 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.82 (dd, J = 10.5, 7.5 Hz, 1H); δ_C 14.6, 16.1 (d, $^3J_{PC}$ = 5.5 Hz), 16.3 (d, $^3J_{PC}$ = 5.5 Hz), 50.1 (d, $^1J_{PC}$ = 150.2 Hz), 63.6 (d, $^2J_{PC}$ = 7.0 Hz), 63.9 (d, $^2J_{PC}$ = 6.9 Hz), 64.2, 108.8, 115.8, 125.4, 127.0, 128.5 (d, J_{PC} = 4.5 Hz), 128.9 (d, J_{PC} = 4.0 Hz), 130.9 (d, J_{PC} = 3.3 Hz), 133.0, 138.5 (d, J_{PC} = 13.6 Hz), 149.1 (d, J_{PC} = 5.2 Hz), 150.2; Anal. calcd. For $C_{19}H_{24}N_3O_8P$: C, 50.33; H, 5.34; N, 9.27. Found: C, 50.15; H, 5.60; N, 9.09.

[Anthracen-9-yl-(4-bromophenylamino)-methyl]-phosphonic acid diethyl ester (4aa)

Yellow crystals; IR (KBr): 3323, 1593, 1508, 1487, 1242, 1070, 954, 862, 779 cm^{-1}; δ_H 0.62 (t, J = 7.0 Hz, 3H), 1.35 (t, J = 7.0 Hz, 3H), 3.21-3.29 (m, 1H), 3.67-3.74 (m, 1H), 4.20-4.26 (m, 2H), 5.21 (br s, 1H), 6.27 (d, J = 27.0 Hz, 1H), 6.33 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 9.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 8.41 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.98 (d, J = 9.0 Hz, 1H); δ_C 15.8 (d, $^3J_{PC}$ = 5.8 Hz), 16.6 (d, $^3J_{PC}$ = 5.6 Hz), 52.9 (d, $^1J_{PC}$ = 152.3 Hz), 63.1 (d, $^2J_{PC}$ = 7.0 Hz), 63.5 (d, $^2J_{PC}$ = 6.9 Hz), 109.8, 114.9, 122.5, 124.8, 125.2, 126.1, 126.2, 127.1, 129.2 (d, J_{PC} = 4.5 Hz), 129.3, 129.9, 130.3 (d, J_{PC} = 4.1 Hz), 130.6 (d, J_{PC} = 8.5 Hz), 131.2 (d, J_{PC} = 1.8 Hz), 131.8, 131.9, 145.9 (d, J_{PC} = 13.4 Hz); Anal. calcd. For $C_{25}H_{25}BrNO_3P$: C, 60.25; H, 5.06; N, 2.81. Found: C, 60.06; H, 4.92; N, 3.00.

[Anthracen-9-yl-(4-nitrophenylamino)-methyl]-phosphonic acid diethyl ester (4ab)

Yellow crystals; IR (KBr): 3313, 1596, 1508, 1477, 1311, 1286, 1228, 1112, 954, 864, 783 cm^{-1}; δ_H 0.88 (t, J = 7.5 Hz, 3H), 1.25 (t, J = 7.5 Hz, 3H), 1.27 (t, J = 7.5 Hz, 3H), 3.51-3.59 (m, 1H), 3.78-3.94 (m, 3H), 4.07-4.18 (m, 2H), 6.38 (dd, J = 9.5 Hz, 1H), 6.45 (dd, J = 27.0, 6.0 Hz, 1H), 6.69 (dd, J = 9.0, 2.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.51-7.55 (m, 3H), 7.68 (t, J = 9.0 Hz, 1H), 7.95 (t, J = 8.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 8.46 (s, 1H), 8.47 (d, J = 8.0 Hz, 1H), 8.93 (d, J = 8.0 Hz, 1H), 9.41 (d, J = 9.0 Hz, 1H); δ_C 15.9 (d, $^3J_{PC}$ = 5.5 Hz), 16.4 (d, $^3J_{PC}$ = 5.4 Hz), 49.7 (d, $^1J_{PC}$ = 151.1 Hz), 63.9 (d, $^2J_{PC}$ = 7.2 Hz), 64.1 (d, $^2J_{PC}$ = 7.1 Hz), 112.4, 125.4, 125.5, 126.2, 128.7 (d, J_{PC} = 4.5 Hz), 129.2 (d, J_{PC} = 3.1 Hz), 130.6, 130.7, 133.6, 139.4, 149.3 (d, J_{PC} = 5.3 Hz), 151.4 (d, J_{PC} = 13.5 Hz); For $C_{25}H_{25}N_2O_5P$: C, 64.65; H, 5.43; N, 6.03. Found: C, 64.48;

H, 5.61; N, 5.86.

[Anthracen-9-yl-(4-ethoxy-2-nitrophenylamino)-methyl]-phosphonic acid diethyl ester (4ac)

Red-brown crystals; IR (KBr): 3369, 2981, 1573, 1506, 1417, 1323, 1257, 1137, 1118, 1064, 952, 860, 781 cm^{-1}; δ_H 0.61 (t, J = 7.0 Hz, 3H), 1.39 (t, J = 7.0 Hz, 3H), 3.17-3.25 (m, 1H), 3.67-3.75 (m, 1H), 4.24-4.29 (m, 2H), 6.14 (dd, J = 9.5, 6.0 Hz, 1H), 6.37 (dd, J = 27.0, 6.0 Hz, 1H), 6.40 (d, J = 9.0 Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 9.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.80 (d, J = 9.0 Hz, 2H), 7.97 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.47 (s, 1H), 8.88 (d, J = 9.0 Hz, 1H); δ_C 14.6, 16.0 (d, $^3J_{PC}$ = 5.8 Hz), 16.4 (d, $^3J_{PC}$ = 5.6 Hz), 52.4 (d, $^1J_{PC}$ = 153.1 Hz), 63.5 (d, $^2J_{PC}$ = 7.0 Hz), 63.6 (d, $^2J_{PC}$ = 7.0 Hz), 64.1, 108.6, 115.6, 122.3, 124.9, 126.0 (d, J_{PC} = 4.0 Hz), 126.4, 126.9, 127.4, 129.2, 129.6 (d, J_{PC} = 4.3 Hz), 130.0, 130.2 (d, J_{PC} = 4.2 Hz), 130.4 (d, J_{PC} = 7.8 Hz), 131.1, 133.9 (d, J_{PC} = 3.9 Hz), 132.1, 139.7 (d, J_{PC} = 13.8 Hz), 149.4; Anal. calcd. For $C_{27}H_{29}N_2O_6P$: C, 63.77; H, 5.75; N, 5.51. Found: C, 63.58; H, 5.92; N, 5.35.

((4-Bromophenylamino)-{3-[(4-bromophenylamino)-(diethoxy-phosphoryl)-methyl]-phenyl}-methyl)-phosphonic acid diethyl ester (4ad)

White crystals; IR (KBr): 3300, 2977, 1589, 1517, 1487, 1444, 1367, 1317, 1236, 1031, 962, 860, 796 cm^{-1}; δ_H 0.92 (t, J = 7.5 Hz, 6H), 1.27 (t, J = 7.5 Hz, 6H), 3.31-3.39 (m, 2H), 3.69-3.77 (m, 2H), 4.12-4.14 (m, 4H), 4.67 (d, J = 24.0 Hz, 2H), 4.93 (s, 2H), 6.41 (d, J = 8.5 Hz, 4H), 7.12 (d, J = 8.5 Hz, 4H), 7.31 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 7.5 Hz, 2H), 7.51 (s, 1H); δ_C 16.1 (d, $^3J_{PC}$ = 5.5 Hz), 16.4 (d, $^3J_{PC}$ = 6.1 Hz), 55.9 (d, $^1J_{PC}$ = 150.1 Hz), 63.2 (d, $^2J_{PC}$ = 7.3 Hz), 63.6 (d, $^2J_{PC}$ = 7.3 Hz), 110.2, 115.6, 127.3 (d, J_{PC} = 5.3 Hz), 127.9 (d, J_{PC} = 3.8 Hz), 129.1, 131.8, 136.2, 145.7 (d, J_{PC} = 15.6 Hz); Anal. calcd. For $C_{28}H_{36}Br_2N_2O_8P_2$: C, 44.82; H, 4.84; N, 3.73; Found: C, 45.01; H, 5.03; N, 3.58.

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