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Three-Component Reaction of Triphenylphosphine, Acetylenic Esters and 4-(Arylideneamino)-3-ethyl-1*H*-1,2,4-triazole-5(4*H*)-thiones for the Synthesis of Phosphorus Ylides

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Abstract: Triphenylphosphine reacts with 4-(arylideneamino)-3-ethyl-1*H*-1,2,4-triazole-5(4*H*)-thiones in the presence of dialkyl acetylenedicarboxylates to produce highly functionalized, salt-free phosphorus ylides in excellent yields.

Keywords: Dialkyl acetylenedicarboxylates, Phosphorus ylides, Triphenylphosphine, NH-acid, Addition reaction

Introduction

Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis[1-3]. Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of an appropriate phosphonium salt with a base; the corresponding phosphonium salts are usually obtained from the phosphine and an alkyl halide. Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins[4,5]. Reaction of acetylenic esters with triphenylphosphine in the presence of an organic compound possessing an acidic-hydrogen has been recently reported to produce phosphorus ylides[6-16]. In continuation of our previous works on the reaction between triphenylphosphine and acetylene esters in the presence of organic N-H, O-H or C-H acids[17-23], we herein report an efficient synthetic route to stable phosphorus ylides using three-component condensation reaction.

Experimental

Melting points were determined with an electrothermal 9100 apparatus. Elemental analyses were performed at Analytical Laboratory of Islamic Azad University, Yazd Branch using a Costech ECS 4010 CHNS-O analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on BRUKER DRX-500 AVANCE spectrometer at 500, 128.5 and 202.5 MHz, respectively. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained on solution in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. The chemicals used in this work purchased from Fluka (Buchs, Switzerland) and were used without further purification.

*General procedure for preparation of compounds (**4a-f**)*

To a magnetically stirred solution of triphenylphosphine (2 mmol) and 4-(arylideneamino) -3-ethyl-1*H*-1,2,4-triazole-5(4*H*)-thione (2 mmol) in dichloromethane (10 mL) a mixture of dialkyl acetylenedicarboxylate (2 mmol) in dichloromethane (3 mL) was added drop wise at room temperature over 2 min. The reaction mixture was then stirred for 3 h (the progress of reaction was monitored by TLC). After completion of reaction, the solvent was evaporated at reduced pressure. The residue was precipitated in a mixture of diethyl ether-hexane. The solid was filtered and washed with diethyl ether to give the pure product.

*Di-t-butyl 2-[4-(benzylidene-amino)-5-ethyl -4H -1,2,4-triazol -3 -yl sulfanyl] -3-(triphenyl-λ^5–phosphanylidene)-succinate (**4a**)*

Yellow powder; m.p. 129-131 °C. IR (KBr) (ν_{max}, cm^{-1}): 1753 (C=O). ^{1}H NMR (500.1 MH_Z, $CDCl_3$): δ 0.95 (9 H, s, *t*-Bu), 1.20 (3 H, t, $^{3}J_{HH}$ = 7 H_Z, CH_3), 1.54 (9 H, s, *t*-Bu), 3.47 (2 H, q, $^{3}J_{HH}$ = 7 H_Z, CH_2), 5.24 (1 H, d, $^{3}J_{PH}$ = 16 H_Z), 7.39 -7.79 (20H, m, aromatic). 10.52 (1H, s, CH=N). ^{13}C NMR (125.8 MH_Z, $CDCl_3$): δ 10.5 (CH_3), 19.4 (CH_2), 28.6 and 28.7 (6 CH_3 of 2 *t*-Bu), 38.8 (d, $^{1}J_{PC}$ = 130 H_Z, C=P), 63.0 (d, $^{2}J_{PC}$ = 16 H_Z, CH), 81.2 and 81.3 (2 O-C$(CH_3)_3$), 128.0 (d, $^{1}J_{PC}$ = 92 H_Z), 129.0 (d, $^{2}J_{PC}$ = 12 H_Z), 132.3 (d, $^{4}J_{PC}$ = 2 H_Z), 134.2 (d, $^{3}J_{PC}$ = 10 H_Z), 126.9, 128.8, 129.1, 132.0 (ph), 151.1 (CH=N), 159.5 (SC=N), 160.8 (NC=N), 168.6 (d, $^{2}J_{PC}$ = 12 H_Z, C=O), 168.7 (d, $^{3}J_{PC}$ = 17 H_Z, C=O). ^{31}P NMR (202.5 MH_Z, $CDCl_3$): δ 30.04. Analyses: Calcd. for $C_{41}H_{45}N_4O_4PS$: C, 68.31; H, 6.29; N,7.77. Found: C, 68.5; H, 6.1; N,7.9. MS (*m/z*, %): 720 (M^+, 7); 262 (PPh_3, 85), 77 (Ph, 40), Yield: 93%.

*Dimethyl 2-[4-(benzylidene-amino)-5-ethyl -4H -1,2,4 -triazol-3-yl sulfanyl]-3-(triphenyl-λ^5–phosphanylidene)-succinate (**4b**)*

Yellow powder; m.p. 102-104 °C. IR (KBr) (ν_{max}, cm^{-1}): 1751 (C=O). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.20 (3 H, t, $^{3}J_{HH}$ = 7 H_Z, CH_3), 3.14 (3 H , s, OCH_3), 3.52 (2H, q, $^{3}J_{HH}$ = 7 H_Z, CH_2), 3.79 (3 H, s, OCH_3), 5.58 (1 H , d, $^{3}J_{PH}$ = 16 H_Z,), 7.43-7.85 (20 H, m, aromatic), 10.49 (1H, s, CH=N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 11.0 (CH_3), 19.4 (CH_2), 38.9 (d, $^{1}J_{PC}$ = 130 H_Z, C=P), 49.7 (OCH_3), 53.1 (OCH_3), 62.4 (d, $^{2}J_{PC}$ = 16 H_Z, CH), 127.1 (d, $^{1}J_{PC}$ = 92 H_Z), 129.2 (d, $^{2}J_{PC}$ = 12 H_Z), 132.4 (d, $^{4}J_{PC}$ = 2 H_Z), 134.2 (d, $^{3}J_{PC}$ = 10 H_Z), 126.1, 128.9, 129.3, 132.3 (ph), 151.2 (CH=N), 159.6 (SC=N), 161.1 (NC=N), 168.5 (d, $^{2}J_{PC}$ = 12 H_Z C=O), 170.8 (d, $^{3}J_{PC}$ = 17 H_Z C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 30.07. Analyses: Calcd. for $C_{35}H_{33}N_4O_4PS$: C, 66.02; H, 5.22; N, 8.80. Found: C, 66.1; H, 5.3; N, 8.9. MS (*m/z*, %): 636 (M^+, 5); 262 (PPh_3, 80), 77 (Ph, 55), Yield: 91%.

*Diethyl 2-[4-(benzylidene - amino) - 5- ethyl-4H-1,2,4 –triazol -3-yl sulfanyl] - 3-(triphenyl-λ^5–phosphanylidene)-succinate (**4c**)*

Yellow powder; m.p. 116-118 ˚C. IR (KBr) (ν_{max}, cm^{-1}): 1748 (C=O). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.17 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 1.24 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 1.36 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.47 (2 H, q, $^3J_{HH}$ = 7 H_Z, CH_2), 4.07 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 4.25 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.75 (1 H, d, $^3J_{PH}$ = 16 H_Z, CH), 7.45 -7.87 (20H, m, aromatic), 10.50 (1H, s, CH=N) . ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 10.9 (CH_3), 14.6 and 14.7 (2 CH_3), 19.4 (CH_2), 40.4 (d, $^1J_{PC}$ = 130 H_Z, C=P), 61.7 (d, $^2J_{PC}$ = 16 H_Z, CH), 58.2 and 58.9 (2 OCH_2), 126.9 (d, $^1J_{PC}$ = 92 H_Z), 128.9 (d, $^2J_{PC}$ = 12 H_Z), 132.4 (d, $^4J_{PC}$ = 2 H_Z), 134.2 (d, $^3J_{PC}$ = 10 H_Z), 126.1, 128.8, 129.2, 132.2 (ph), 151.2 (CH=N), 159.6 (SC=N), 161.0 (NC=N), 169.7 (d, $^2J_{PC}$ = 12 H_Z, C=O), 170.0 (d, $^3J_{PC}$ = 17 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 29.98. Analyses: Calcd. for $C_{37}H_{37}N_4O_4PS$: C, 66.85; H, 5.61; N,8.43. Found: C, 66.9; H, 5.5; N,8.5. MS (*m/z*, %): 664 (M^+,8); 262 (PPh_3, 87), 77 (Ph, 55), Yield: 89%.

*Dimethyl 2-{4 - [(4- chloro-benzylidene) -amino] -5- ethyl- 4H- 1,2,4 -triazol -3-yl sulfanyl}- 3-(triphenyl- λ^5–phosphanylidene)-succinate (**4d**)*

Yellow powder; m.p. 195-197 ˚C. IR (KBr) (ν_{max}, cm^{-1}): 1745 (C=O). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.19 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.24 (3 H , s, OCH_3), 3.50 (2H, q, $^3J_{HH}$ = 7 H_Z, CH_2), 3.75 (3 H, s, OCH_3), 5.52 (1 H , d, $^3J_{PH}$ = 16 H_Z), 7.59 -7.95 (19H, m, aromatic), 10.05 (1H, s, CH=N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 9.5 (CH_3), 17.8 (CH_2), 38.8 (d, $^1J_{PC}$ = 130 H_Z, C=P), 51.3 (OCH_3), 51.7 (OCH_3), 61.9 (d, $^2J_{PC}$ = 16 H_Z, CH), 127.9 (d, $^1J_{PC}$ = 92 H_Z), 129.2 (d, $^2J_{PC}$ = 12 H_Z), 132.5 (d, $^4J_{PC}$ = 2 H_Z), 133.9 (d, $^3J_{PC}$ = 10 H_Z), 128.8, 129.6, 132.2, 136.7 (ph), 151.8 (CH=N), 160.8 (SC=N), 161.1 (NC=N), 168.9 (d, $^2J_{PC}$ = 12 H_Z C=O), 170.2 (d, $^3J_{PC}$ = 17 H_Z C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 29.92. Analyses: Calcd. for $C_{35}H_{32}ClN_4O_4PS$: C, 62.64; H, 4.81; N, 8.35. Found: C, 62.7; H, 4.9; N, 8.4. MS (*m/z*, %): 670 (M^+, 7); 262 (PPh_3, 88), 77 (Ph, 48), Yield: 90%.

*Diethyl 2-{4-[(4-chloro-benzylidene) - amino] -5 -ethyl- 4H- 1,2,4-triazol -3- yl sulfanyl}-3-(triphenyl-λ^5–phosphanylidene)-succinate (**4e**)*

Yellow powder; m.p. 103-105 ˚C. IR (KBr) (ν_{max}, cm^{-1}): 1741 (C=O). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.05 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 1.21 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 1.39 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.49 (2 H, q, $^3J_{HH}$ = 7 H_Z, CH_2), 3.94 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 4.18 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.71 (1 H, d, $^3J_{PH}$ = 16 H_Z, CH), 7.57 -7.95 (19H, m, aromatic), 9.96 (1H, s, CH=N) . ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 9.5 (CH_3), 13.3 and 13.4 (2 CH_3), 17.7 (CH_2), 40.2 (d, $^1J_{PC}$ = 130 H_Z, C=P), 61.6 (d, $^2J_{PC}$ = 16 H_Z, CH), 58.1 and 58.9 (2 OCH_2), 127.9 (d, $^1J_{PC}$ = 92 H_Z), 128.9 (d, $^2J_{PC}$ = 12 H_Z), 132.3 (d, $^4J_{PC}$ = 2 H_Z), 134.2 (d, $^3J_{PC}$ = 10 H_Z), 128.8, 129.7, 132.1, 136.8 (ph), 151.8 (CH=N) 161.0 (SC=N), 161.3 (NC=N), 169.6 (d, $^2J_{PC}$ = 12 H_Z, C=O), 169.9 (d, $^3J_{PC}$ = 17 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 29.95. Analyses: Calcd. for $C_{37}H_{36}ClN_4O_4PS$: C, 63.56; H, 5.19; N, 8.01. Found: C, 63.6; H, 5.1; N, 8.1. MS (*m/z*, %): 698 (M^+, 6); 262 (PPh_3, 80), 77 (Ph, 50), Yield: 87%.

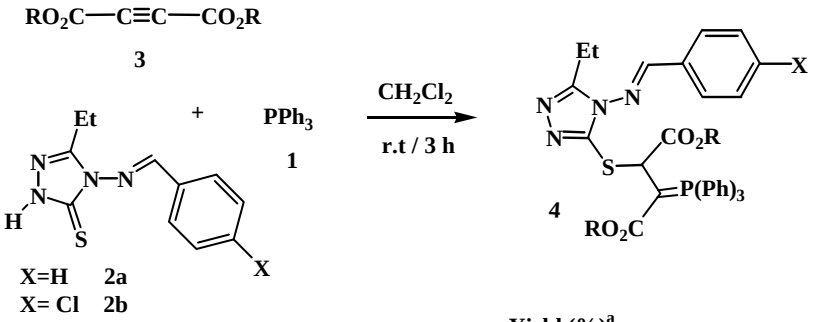
*Di-t-butyl 2-{4 -[(4 -chloro - benzylidene) -amino] -5- ethyl -4H- 1,2,4 - triazol-3-yl sulfanyl} -3-(triphenyl -λ^5–phosphanylidene) -succinate (**4f**)*

Yellow powder; m.p. 151-153 ˚C. IR (KBr) (ν_{max}, cm^{-1}): 1743 (C=O). ^{1}H NMR (500.1 MH_Z, $CDCl_3$): δ 0.94 (9 H, s, *t*-Bu), 1.20 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 1.54 (9 H, s, *t*-Bu), 3.48 (2 H, q, $^3J_{HH}$ = 7 H_Z, CH_2), 5.22 (1 H, d, $^3J_{PH}$ = 16 H_Z), 7.38 -7.80 (19H, m, aromatic).10.62 (1H, s, CH=N). ^{13}C NMR (125.8 MH_Z, $CDCl_3$): δ 10.5 (CH_3), 19.4 (CH_2), 28.6 and 28.7 (6 CH_3 of 2 *t*-Bu), 38.7 (d, $^1J_{PC}$ = 130 H_Z, C=P), 63.0 (d, $^2J_{PC}$ = 16 H_Z, CH), 81.2 and 81.3 (2 O- C

$(CH_3)_3$), 127.9 (d, $^1J_{PC}$ = 92 H_Z), 128.9 (d, $^2J_{PC}$ = 12 H_Z), 132.3 (d, $^4J_{PC}$ = 2 H_Z), 134.2 (d, $^3J_{PC}$ = 10 H_Z), 129.5, 129.9, 132.2, 138.0 (ph), 151.0 (CH=N), 159.5 (SC=N), 160.8 (NC=N), 168.5 (d, $^2J_{PC}$ = 12 H_Z, C=O), 168.7 (d, $^3J_{PC}$ = 17 H_Z, C=O). ^{31}P NMR (202.5 MH_Z, $CDCl_3$): δ 29.88. Analyses: Calcd. for $C_{41}H_{44}ClN_4O_4PS$: C, 65.20; H, 5.87; N, 7.42. Found: C, 65.3; H, 5.9; N, 7.5. MS (*m/z*, %): 754 (M^+, 8); 262 (PPh_3, 90), 77 (Ph, 42), Yield: 90%.

Results and Discussion

After some preliminary experiments, it was found that a mixture of triphenylphosphine (**1**), 4-(arylideneamino)-3-ethyl-1*H*-1,2,4-triazole-5(4*H*)-thiones **(2a,b)** and dialkyl acetylenedicarboxylates (DAAD) (**3a-c)** afforded corresponding products (**4a-f)** in good yields (Figure 1).



4	X	R	Yield (%)[a]
a	H	t-Butyl	93
b	H	Methyl	91
c	H	Ethyl	89
d	Cl	Methyl	90
e	Cl	Ethyl	87
f	Cl	t-Butyl	90

[a] Isolated yields

Figure 1. Three-component reaction between dialkyl acetylenedicarboxylate, triphenylphosphine and 4-(arylideneamino)-3-ethyl-1*H*- 1,2,4-triazole-5(4*H*)-thiones

The nature of these compounds as 1:1:1 adducts was apparent from their mass spectra, which displayed, in each case, the molecular ion peak at appropriate *m/z* values. The ^{1}H NMR spectrum of compound **4a** displays two sharp lines (δ 0.95, 1.54 ppm) for the protons of two t-butyl groups, a doubled signal for the methine proton at 5.24 ppm ($^3J_{HP}$ = 16 H_Z), a single signal at 10.52 ppm for the C*H*=N proton and multiplets for aromatic protons (δ 7.39-7.79 ppm). ^{13}C NMR spectrum of compound **4a** showed twenty one distinct signals, which is consistent with the proposed structure. The ^{31}P NMR spectrum of compound **4a** consists of one signal at 30.04 ppm. This shift is similar to those observed for other stable phosphorus compounds[24]. The structural assignments made on the basis of the NMR spectra of compounds **4a-f** are supported by their IR spectra. The carbonyl region of the spectrum exhibits absorption bands at 1753 cm^{-1} for the ester groups.

It is reasonable to assume that formation of **4** results from the initial addition of triphenylphosphine (**1)** to DAAD (**3)** and subsequent protonation of the 1:1 adduct by the NH-acidic triazole. The positively charged ion **5** is then attacked by the triazole anion **6** to form the phosphorane **4** (Figure 2).

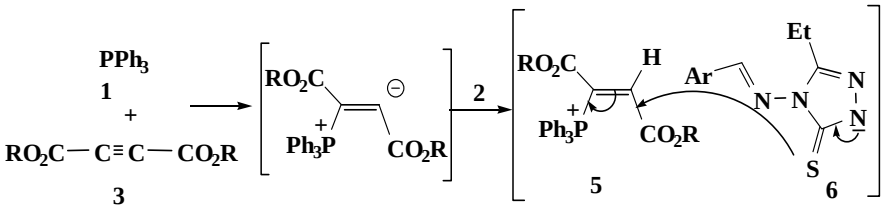


Figure 2. Suggested mechanism for formation of ylides (**4)**

Conclusion

We have described a simple, and one-pot, three-component reaction between dialkyl acetylenedicarboxylate, triphenylphosphine and 4-(arylideneamino)-3-ethyl-1*H*-1,2,4-triazole-5(4*H*)-thiones for the preparation of functionalized phosphoranes in good yields. The advantages of the reported method are simple available starting materials, short reaction time, simple work-up, neutral reaction conditions and high yields.

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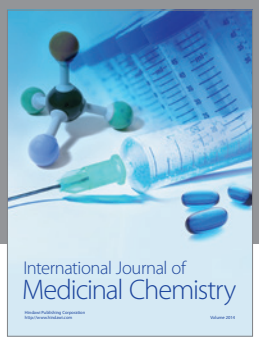

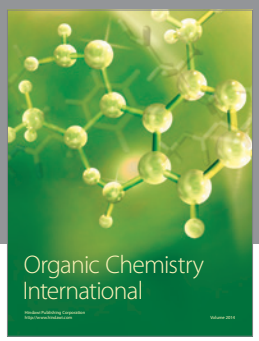

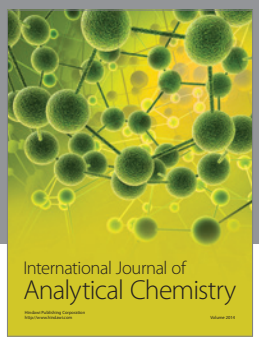

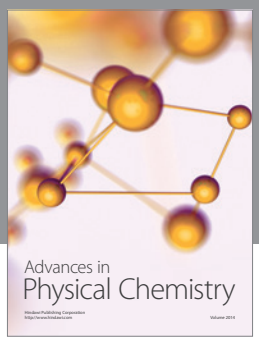

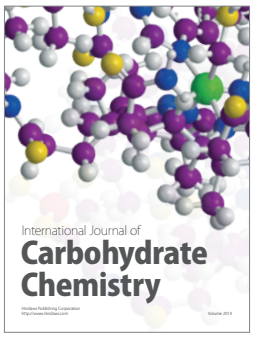

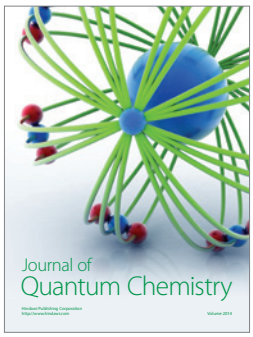

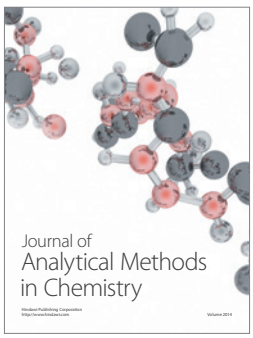

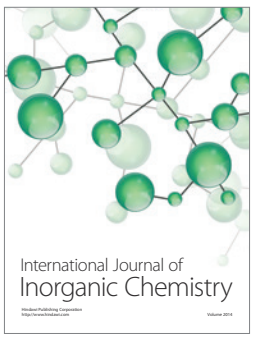

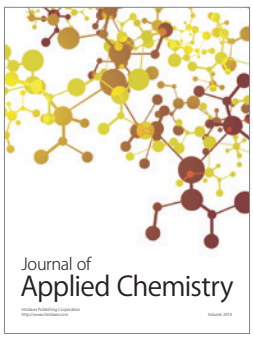

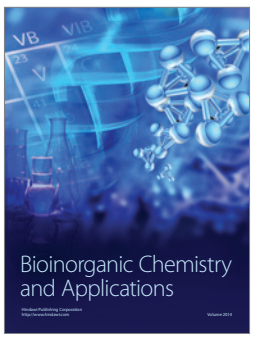

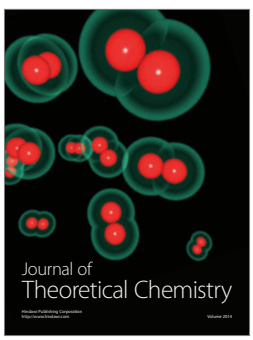

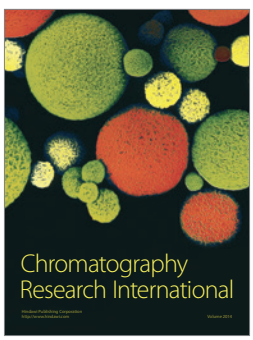

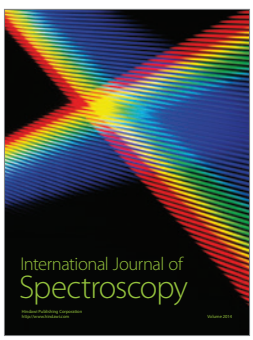

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