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# SYNTHESIS OF NEW FUNCTIONALIZED ARYL AND HETARYL AMINOMETHYLENEBISPHOSPHONIC ACIDS VIA SILICON-ASSISTED METHODOLOGY

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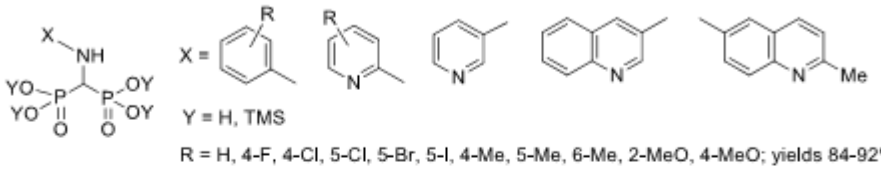
Functionalized methylenediphosphonic acids and their derivatives with aromatic and heterocyclic moieties are well-known biomimetics of hydroxy- or aminocarboxylic acids and natural pyrophosphates, and some of them such as zoledronic, risedronic, and minodronic acids are widely used in medicine. These substances demonstrate the properties of herbicides, pesticides, antibiotics, antiviral and antitumor agents and enzyme inhibitors.

The organosilicon applied synthesis of functionalized organophosphorus acids is a convenient method for creating P-C bonds; recently this methodology has been successfully developed and became modern trend in organophosphorus chemistry.[1-3]

The convenient synthesis of new functionalized aryl and hetaryl amino-methylenebisphosphonic acids has been developed *via* silicon-assisted methodology. New functionalized aminomethylenebisphosphonic acids containing aryl, pyridine and quinoline moieties were obtained using unique reaction of tris(trimethylsilyl) phosphite with *N*-formyl derivatives of corresponding (het)arylamines and trimethylsilyl triflate as a catalyst under mild conditions. Intermediates – tetra(trimethylsilyl) aminomethylenebisphosphonates formed, were converted to the target acids by further treatment with methanol excess. The catalytic schemes of target substances formation are proposed.




R = H, 4-F, 4-Cl, 5-Cl, 5-Br, 5-I, 4-Me, 5-Me, 6-Me, 2-MeO, 4-MeO; yields 84-92%.

**Figure 1**. New functionalized aryl and hetaryl aminomethylenebisphosphonic acids and their derivatives.

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## References

1. A.A. Prishchenko, R.S. Alekseyev, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *J. Organomet. Chem.*, **2018**, *867*, 149.
2. A.A. Prishchenko, R.S. Alekseyev, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *J. Organomet. Chem.*, **2018**, *871*, 36.
3. A.A. Prishchenko, R.S. Alekseyev, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *Inorg. Chim. Acta*, **2019**, *484*, 319.