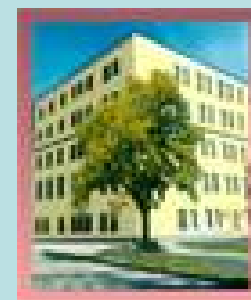


FLUORINATED LITHIUM 1,3-DIKETONATES – VALUABLE, CONVENIENT AND ACCESSIBLE SYNTHONS

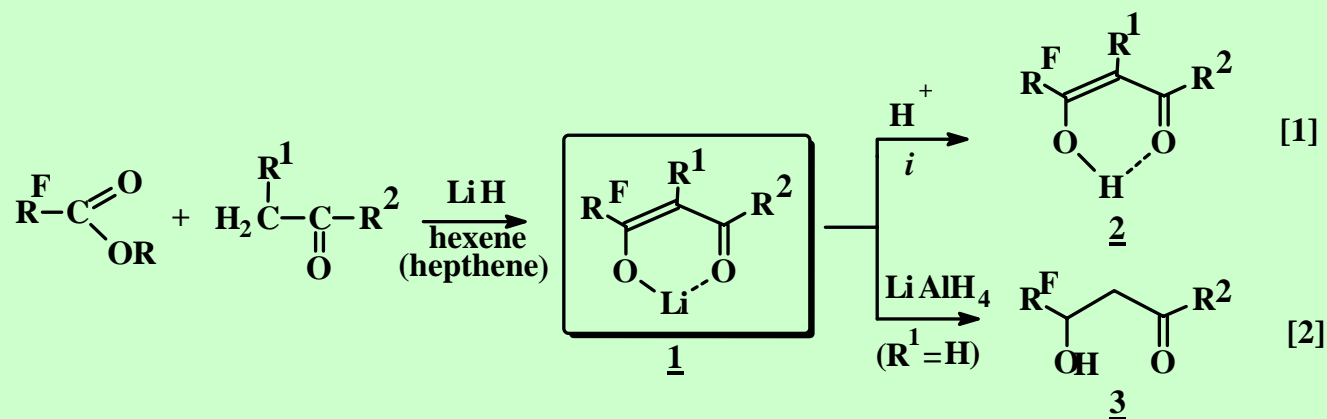
V.I. Filyakova, N.S. Boltacheva,

O.A. Kuznetsova, P.A. Slepukhin, V.N. Charushin

*Institute of Organic Synthesis named after I.Y. Postovsky, Ural Branch of the Russian
Academy of Sciences, 620219, Yekaterinburg, S. Kovalevskoy st., 22*



Synthesis of Lithium 1,3-Diketonates, 1,3-Diketones and 1,3-Hydroxyketones

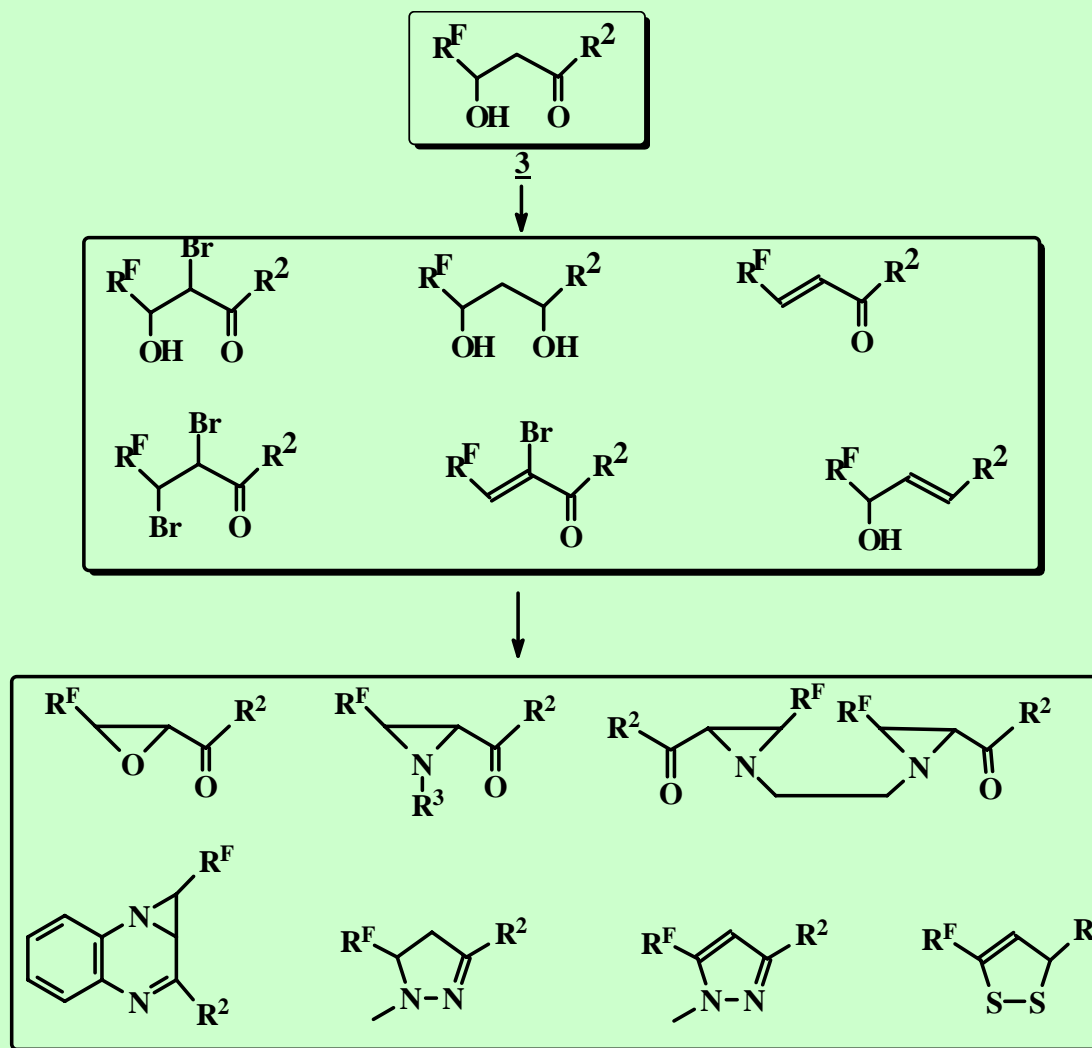


i. operations: extraction, drying, removing of solvent, vacuum destillation or recrystallization

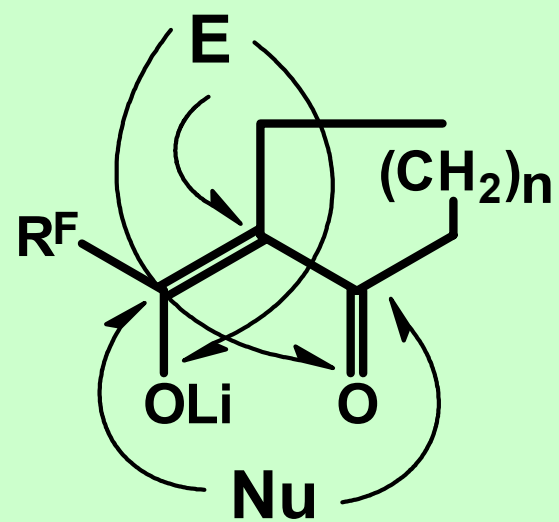
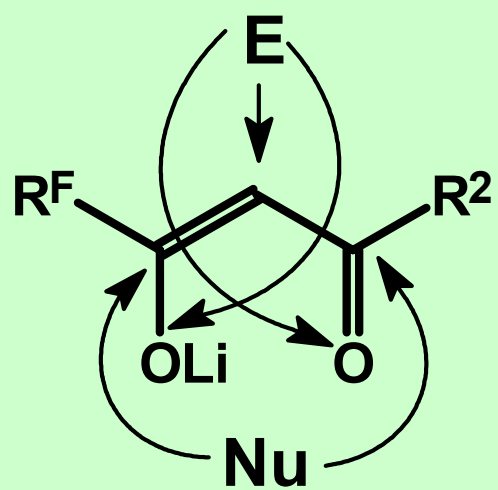
[1]. Patent Rus. Fed. 2100345 (V.I. Filyakova, V.G. Ratner, O.G. Khomutov, N.S. Karpenko, K.I.Pashkevich)

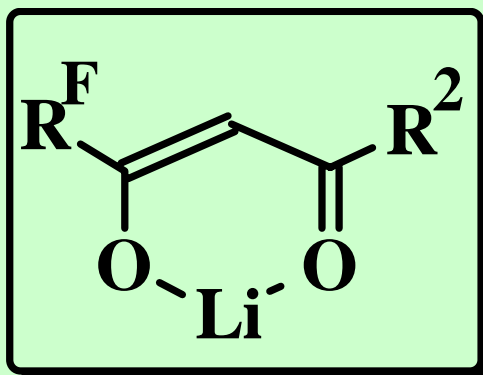
[2]. K.I.Pashkevich, V.G. Ratner, O.G. Khomutov, V.B. Korolev, V.I. Filyakova, Izv. AN SSSR. Ser. Khim. (199 1493. Chem. Bull. V.45 N6 (1996) 1423 (Engl.)

Synthesis based on 1,3-Hydroxyketones



Pashkevich K.I., Filyakova V.I., Ratner V.G., Khomutov O.G. New Polyfunctional Fluoroalkyl-containing Reagents. (Review). *Bashkirskii Khim. Zhurn.* 1996. 3. 93-106





1

$R^F = \text{HCF}_2$, $R^1 = \text{H}$, $R^2 = \text{Me}$ (*a*);

$R^F = \text{H}(\text{CF}_2)_2$, $R^1 = \text{H}$, $R^2 = \text{Me}$ (*c*);

$R^F = \text{H}(\text{CF}_2)_2$, $R^1 = \text{H}$, $R^2 = \text{Ph}$ (*e*);

$R^F = \text{CF}_3$, $R^1 = \text{H}$, $R^2 = \text{Me}$ (*g*);

$R^F = \text{C}_4\text{F}_9$, $R^1 = \text{H}$, $R^2 = \text{Me}$ (*i*);

$R^F = \text{C}_6\text{F}_{13}$, $R^1 = \text{H}$, $R^2 = \text{Bu}$ (*k*);

$R^F = \text{CF}_3$, $R^1 = \text{H}$, $R^2 = \text{Ph}$ (*m*);

$R^F = \text{CF}_3$, $R^1 = \text{H}$, $R^2 = 4\text{-CH}_3\text{-C}_6\text{H}_4$ (*o*);

$R^F = \text{C}_6\text{F}_{13}$, $R^1 = \text{H}$, $R^2 = \text{Ph}$ (*q*);

$R^F = \text{HCF}_2$, $R^1 + R^2 = (\text{CH}_2)_3$ (*s*);

$R^F = \text{HCF}_2$, $R^1 + R^2 = (\text{CH}_2)_4$ (*u*);

$R^F = \text{HCF}_2$, $R^1 = \text{H}$, $R^2 = t\text{-Bu}$ (*b*);

$R^F = \text{HCF}_2$, $R^1 = \text{H}$, $R^2 = \text{Ph}$ (*d*);

$R^F = \text{H}(\text{CF}_2)_4$, $R^1 = \text{H}$, $R^2 = \text{Ph}$ (*f*);

$R^F = \text{C}_4\text{F}_9$, $R^1 = \text{H}$, $R^2 = \text{Ph}$ (*p*);

$R^F = \text{C}_4\text{F}_9$, $R^1 = \text{H}$, $R^2 = \text{Bu}$ (*j*);

$R^F = \text{C}_8\text{F}_{17}$, $R^1 = \text{H}$, $R^2 = \text{Bu}$ (*l*);

$R^F = \text{CF}_3$, $R^1 = \text{H}$, $R^2 = 4\text{-Cl-C}_6\text{H}_4$ (*n*);

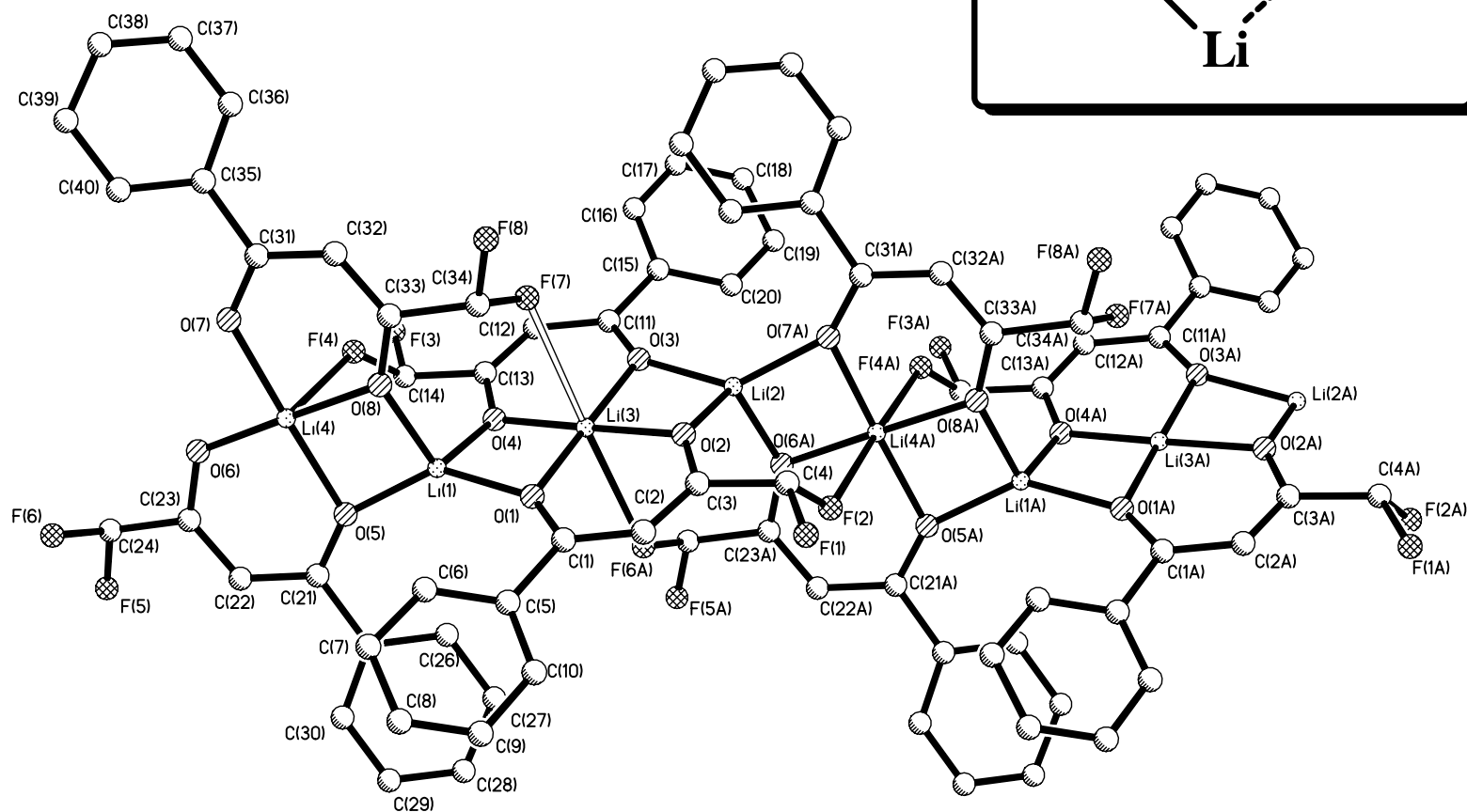
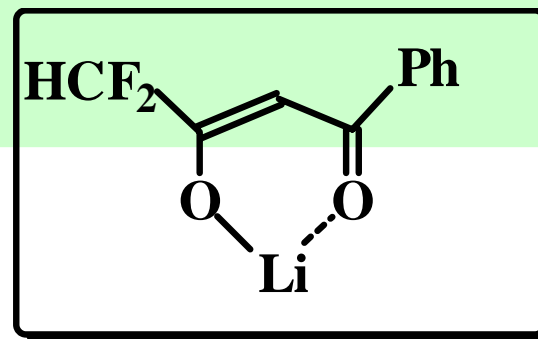
$R^F = \text{C}_4\text{F}_9$, $R^1 = \text{H}$, $R^2 = \text{Ph}$ (*p*);

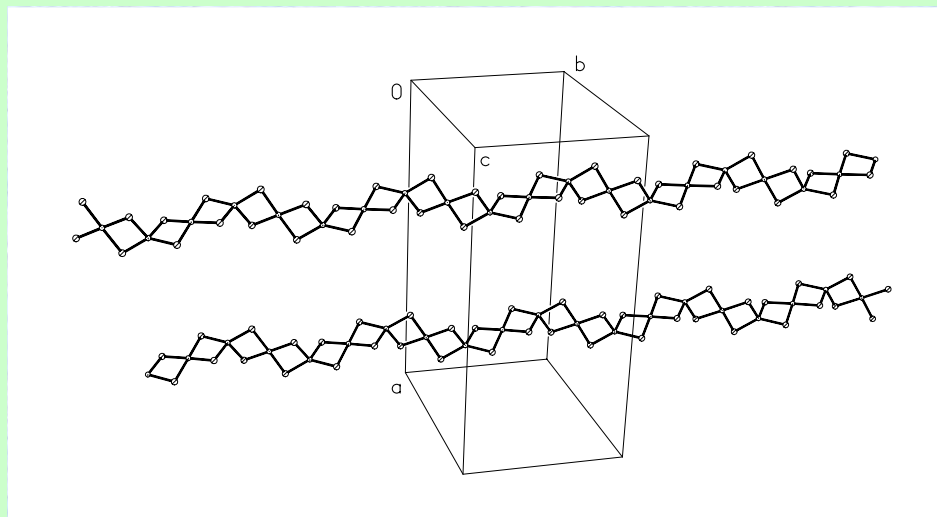
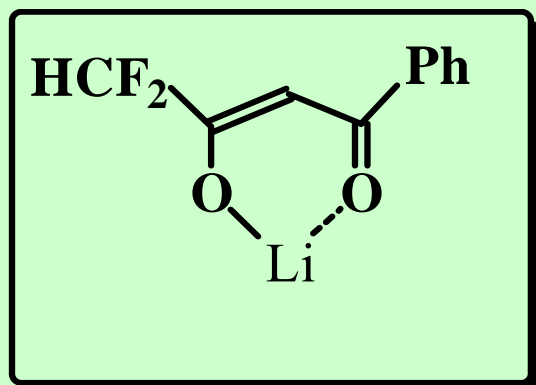
$R^F = \text{CF}_3$, $R^1 = \text{H}$, $R^2 = \text{CF}_3$ (*r*);

$R^F = \text{CF}_3$, $R^1 + R^2 = (\text{CH}_2)_3$ (*t*);

$R^F = \text{CF}_3$, $R^1 + R^2 = (\text{CH}_2)_4$ (*v*);

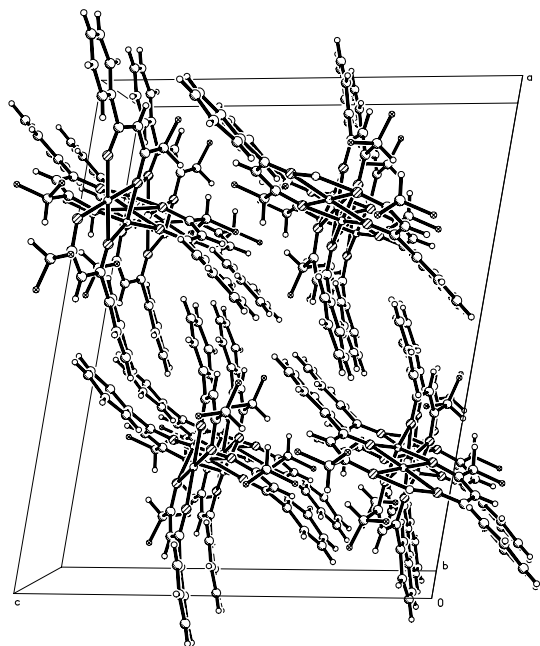
Molecular structure of lithium's 1-phenyl-4,4-difluoro-1,3-butadionate





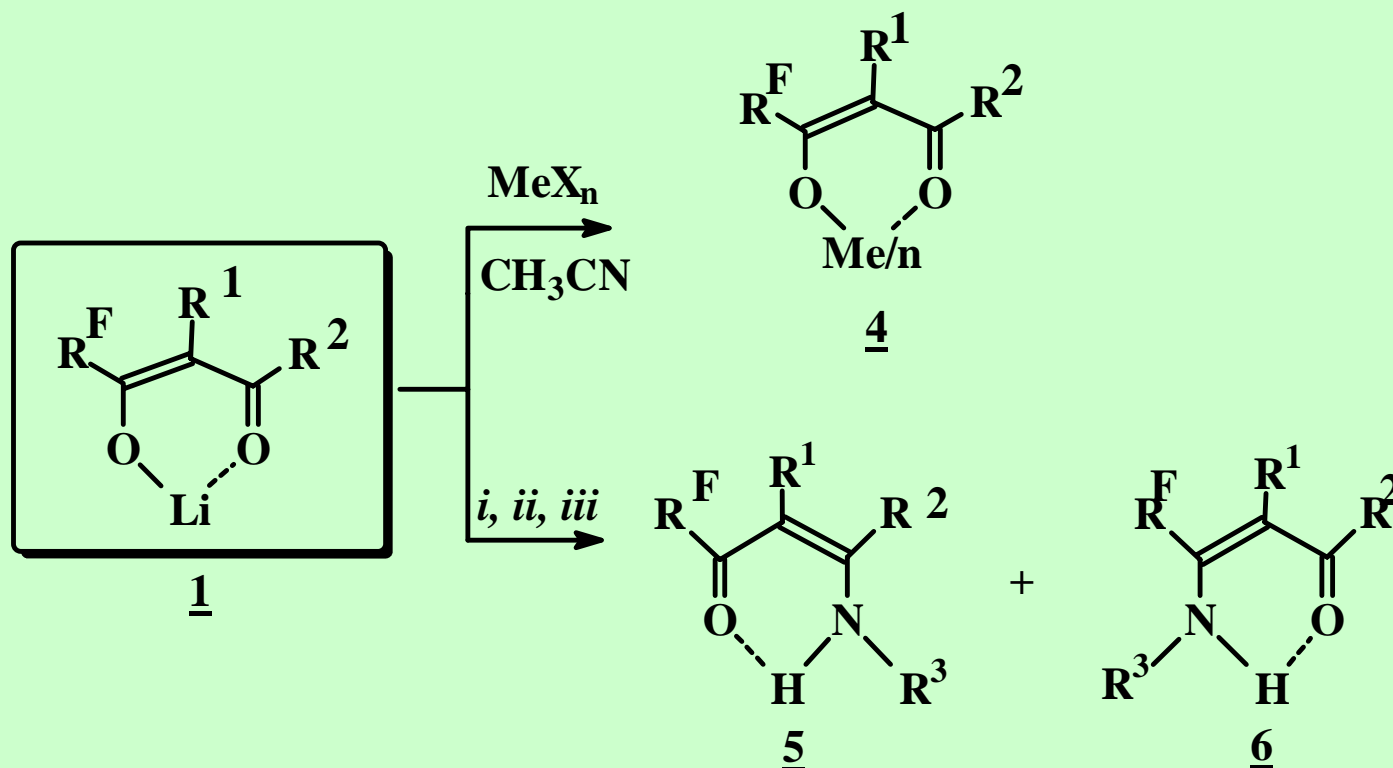
6

Chains $(\text{LiL})^\infty$ of lithium's 1-phenyl-4,4-difluoro-1,3-butadionate. (For clarity only Li and four oxygen atoms are shown)



Crystal packing diagram of lithium's 1-phenyl-4,4-difluoro-1,3-butadionate

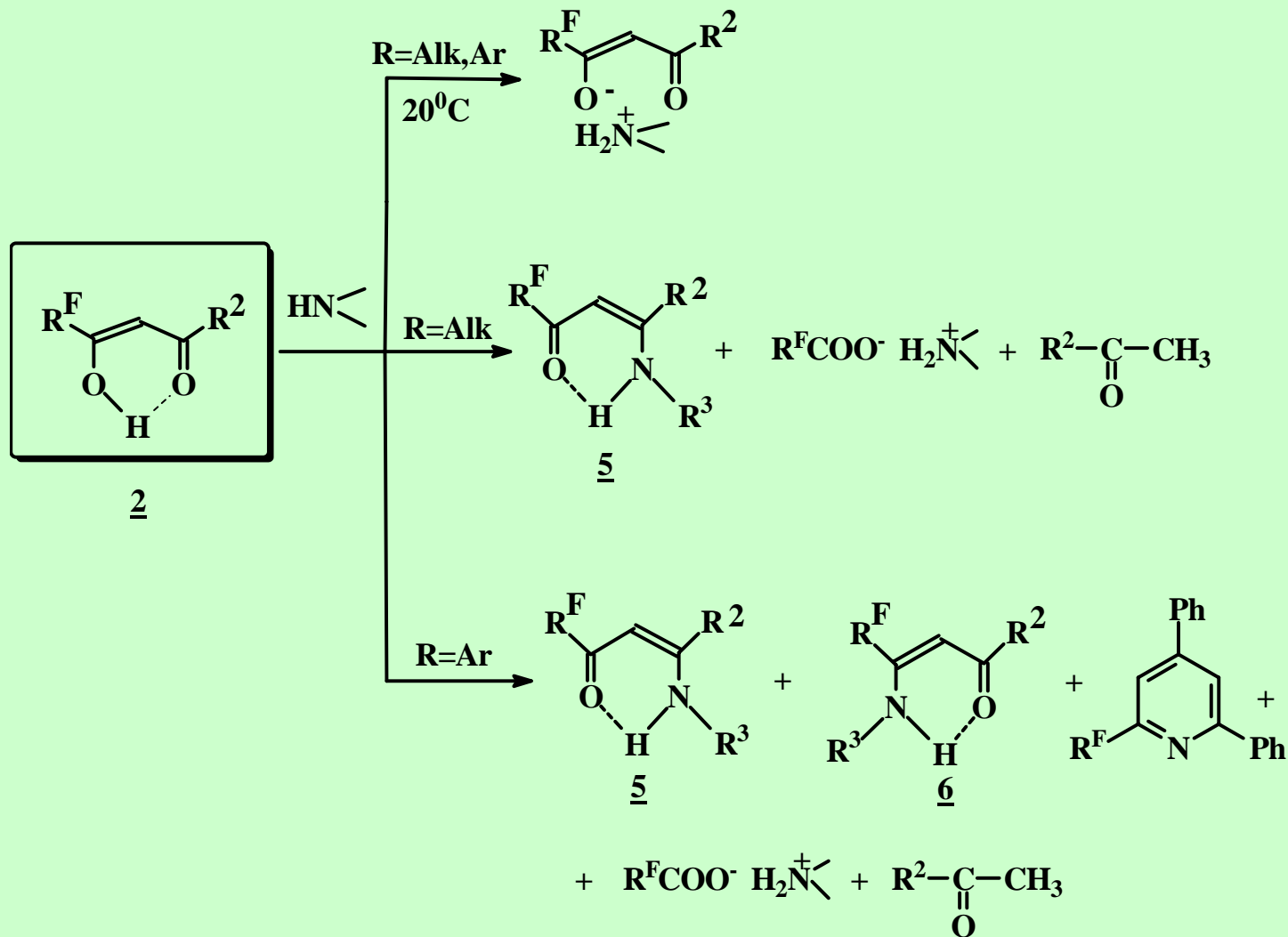
Synthesis of Metal-Chelates of 1,3-Diketones and 1,3-Enaminoketones



i: NH_4HCO_3 , MeOH *ii*: $\text{R}^3\text{NH}_2\text{HCl}$, MeOH *iii*: R^3NH_2 , AcOH

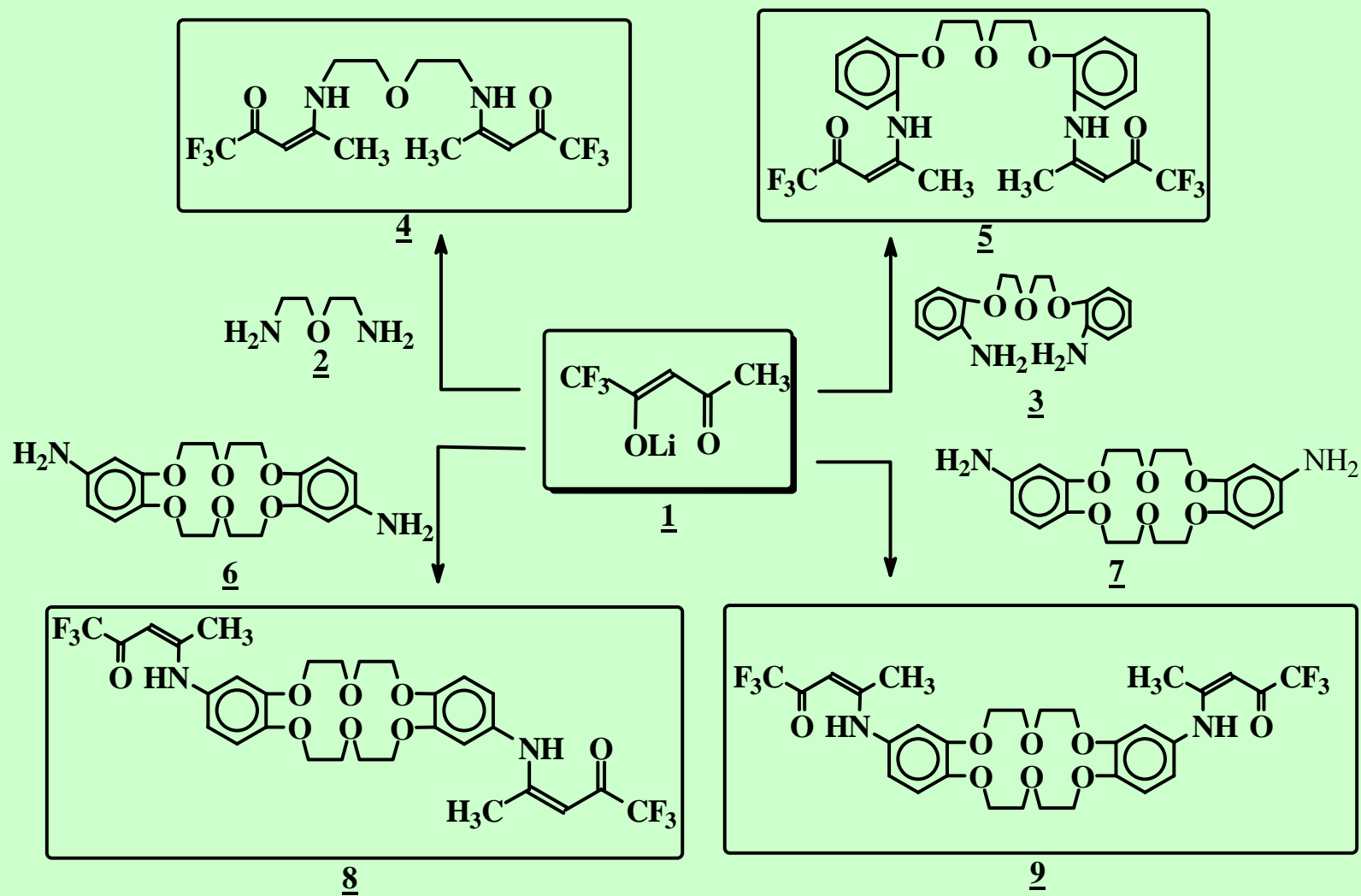
V.I. Filyakova, N.S. Karpenko, O.A.Kuznetsova, K.I. Pashkevich, Zh. Org. Khim 1998, N3,411. [J.Org.Chem.,1998, 34(3), 381 (Engl.Transl.)]

Reactions of fluoroalkyl-containing 1,3-diketones with amines

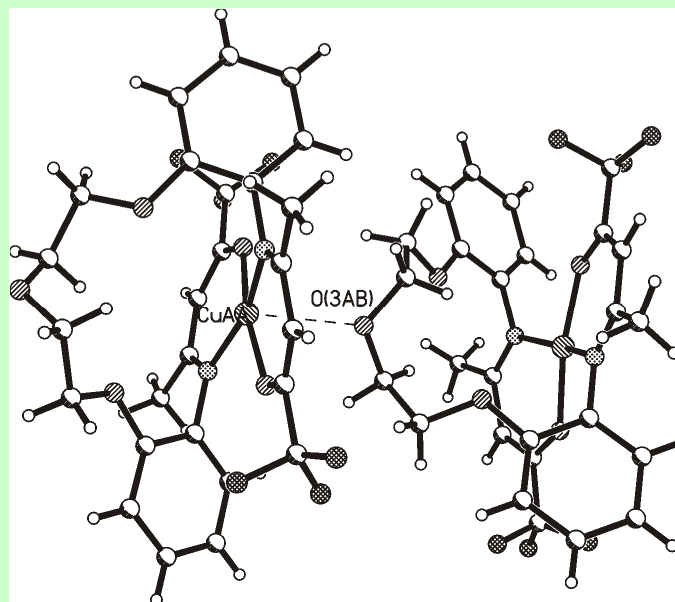
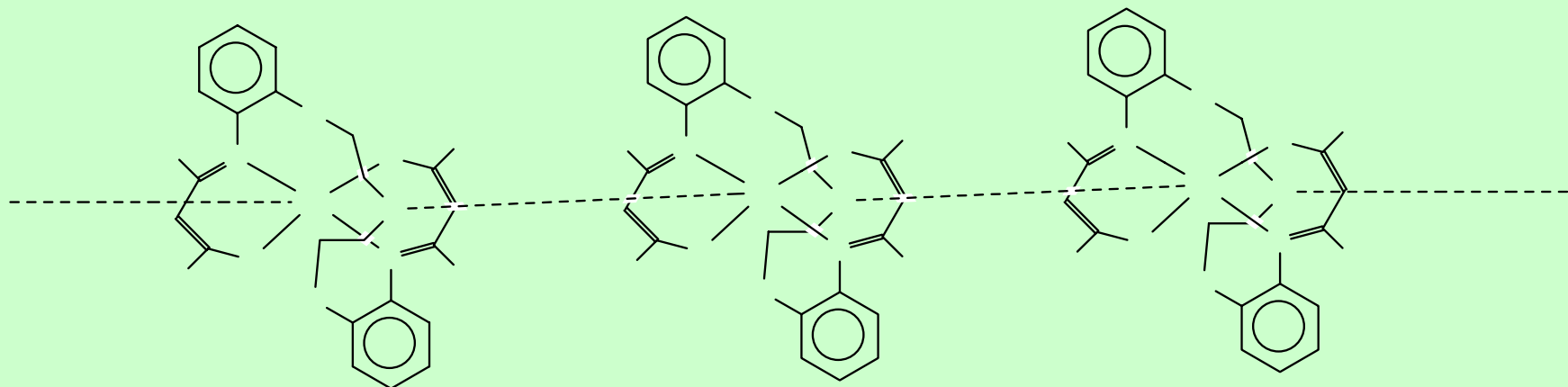


V.I. Filyakova, Ratner V.G., N.S. Karpenko, K.I. Pashkevich,
Izv. AN SSSR. Ser. Khim. (1996) 2278.

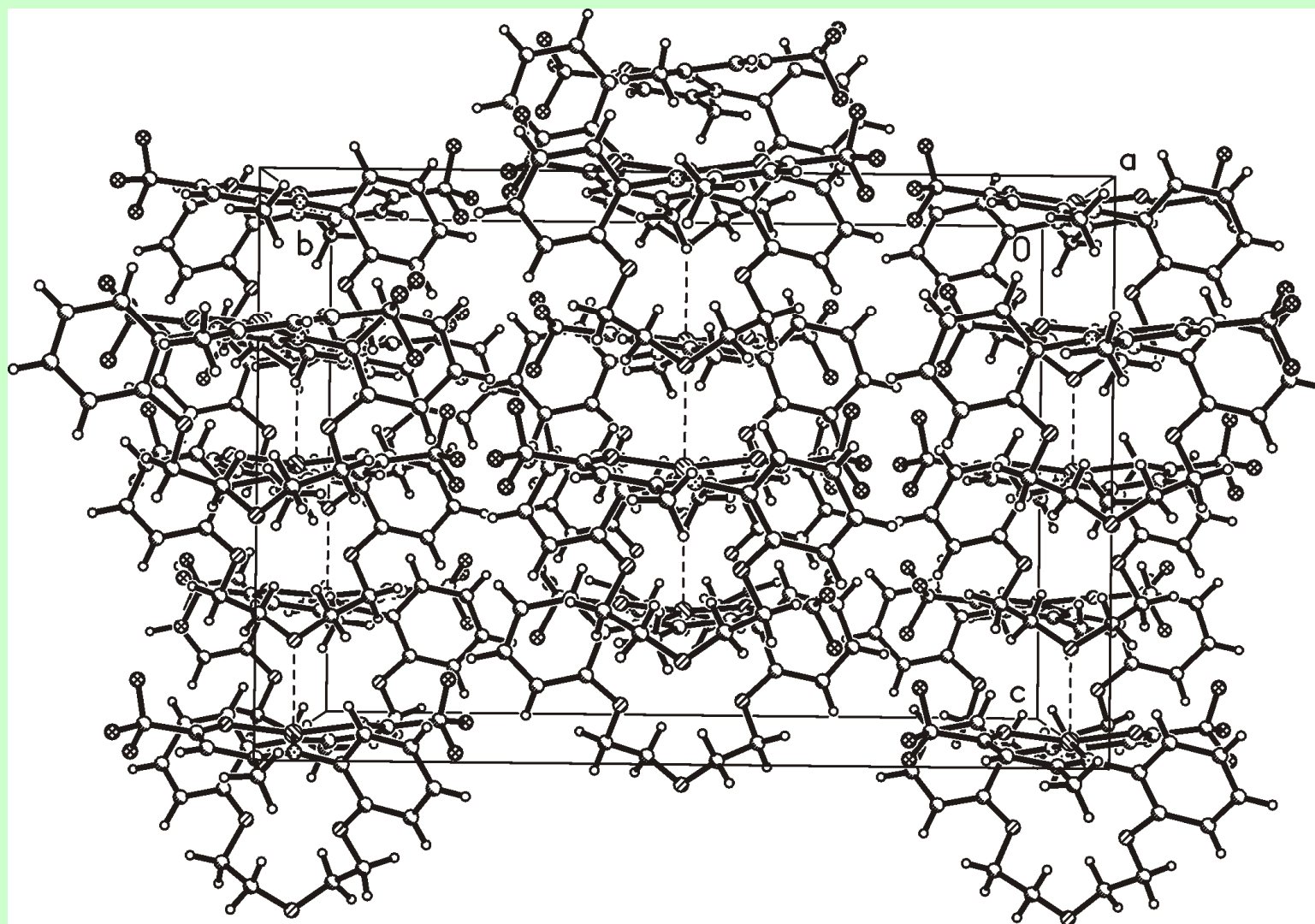
FLUORINATED LITHIUM 1,3-DIKETONATES AS REAGENTS TO MODIFY PODANDES AND CROWN-ETHERS



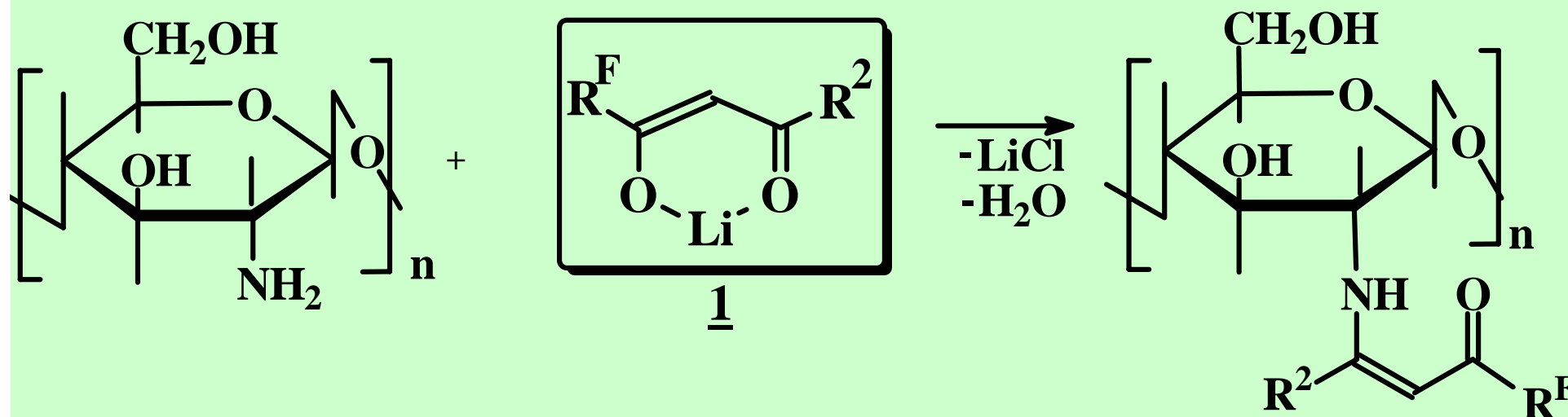
Intermolecular Cu-O interactions between molecules



Packing of the $\text{C}_{26}\text{H}_{24}\text{CuF}_6\text{N}_2\text{O}_5$ in crystal



APPLICATION OF FLUORINATED LITHIUM 1,3-DIKETONATES TO MODIFY OF NATURE POLYMERS



$\text{R}^{\text{F}} = \text{CF}_3$, $\text{R}^2 = \text{C}_6\text{H}_5$, (Sorbent 1)

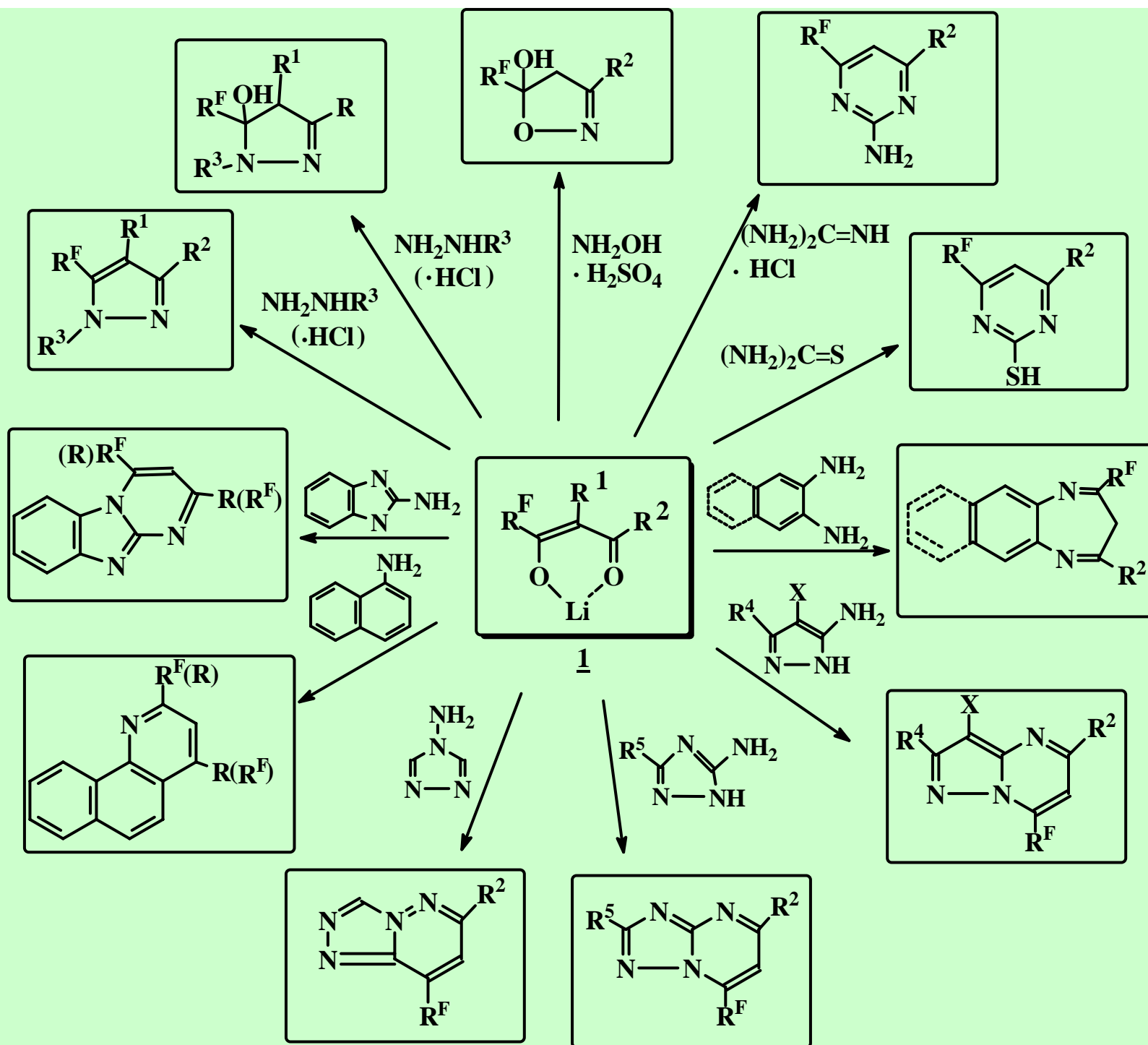
$\text{R}^{\text{F}} = \text{CF}_3$, $\text{R}^2 = 4\text{-CH}_3\text{-C}_6\text{H}_4$ (Sorbent 2)

$\text{R}^{\text{F}} = \text{H}(\text{CF}_2)_4$; $\text{R}^2 = \text{C}_6\text{H}_5$, (Sorbent 1)

Sorption of metals from the solution containing Cu (II), Ni (II) and Zn (II) acetates (C = 0.025 mole/l, pH = 6.5, ammonium-acetate buffer solution)

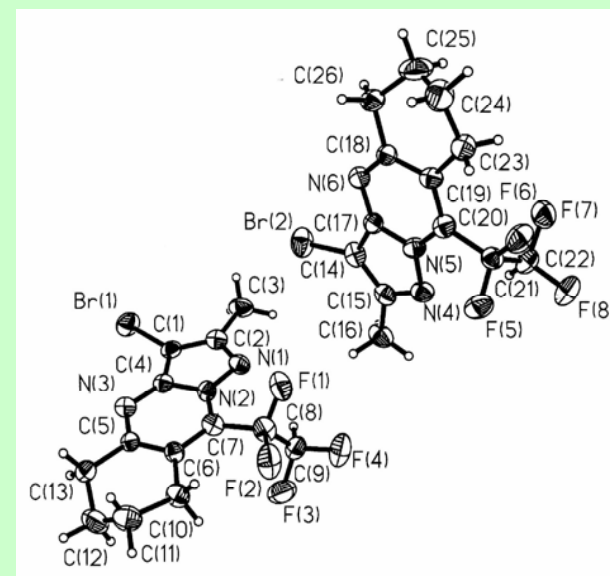
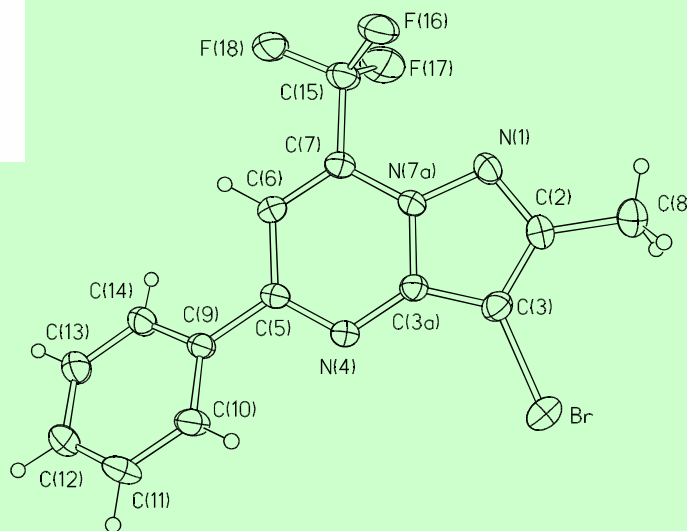
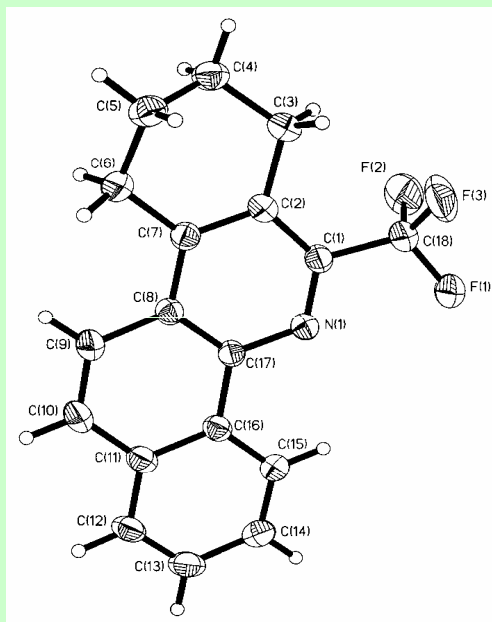
13

Sample	mole/g			
	Ni²⁺	Cu²⁺	Zn²⁺	Σ
Sorbent 1	0	1,51	0	1,51
Sorbent 2	0	1,46	0	1,46
Sorbent 3	0	1,50	0	1,50
Chitosan	0	1,26	0	1,26

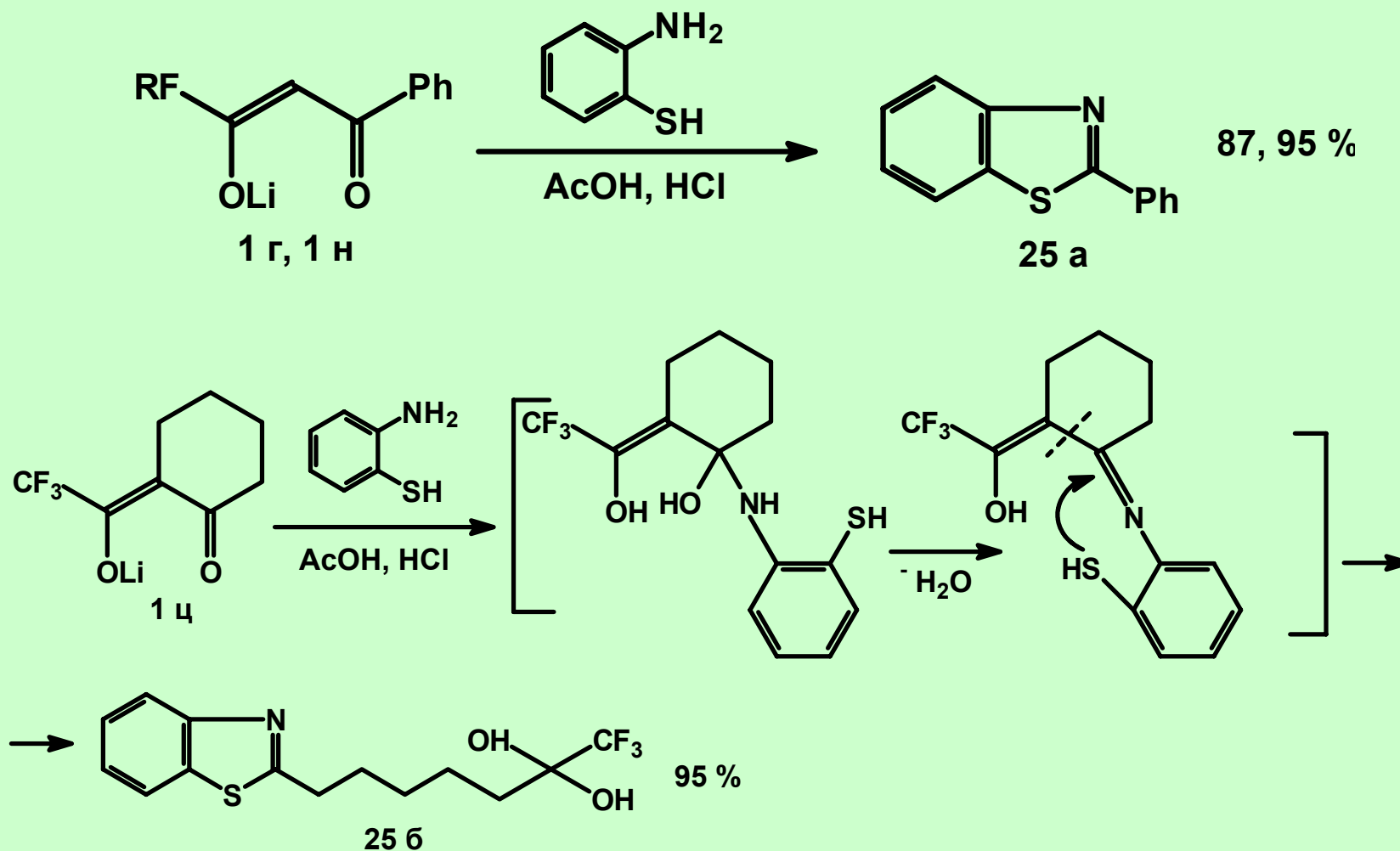


Geometry of molecules of 6-Trifluoromethyl-7,8,9,10-tetrahydrobenzo[*c*] phenanthridine, 3-bromo-2-methyl-7-trifluoromethyl-5-phenyl-1,2-pyrazolo[1,5-*a*] pyrimidine and 3-bromo-5,6,7,8-tetrahydro-2-methyl-9-(1,1,2,2-tetrafluoroethyl)-pyrazolo [3,4-*b*]chinazoline

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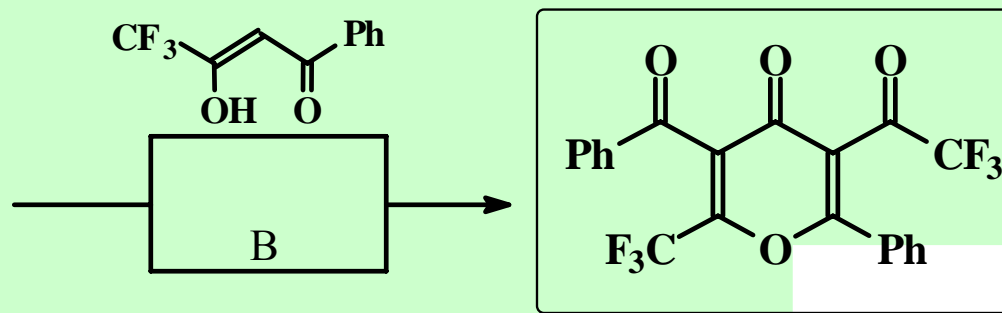
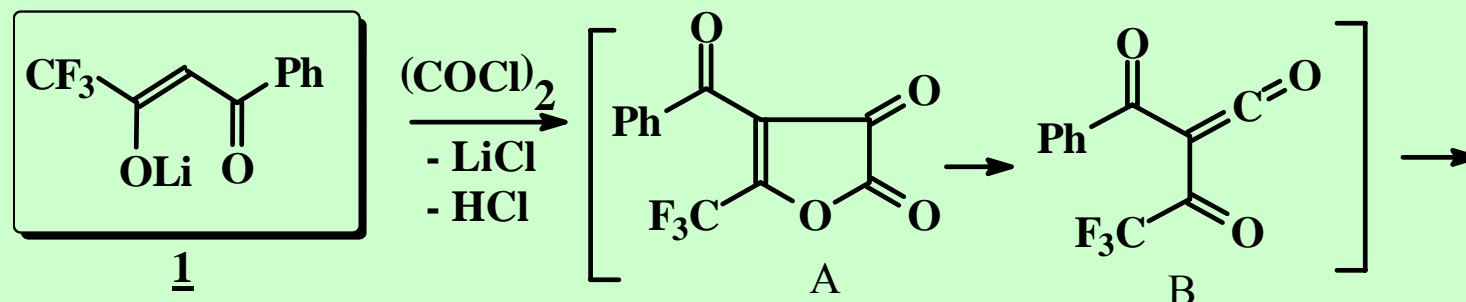
Reactions of fluoroalkyl-containing lithium 1,3-diketonates with 1,2-aminothiophenol



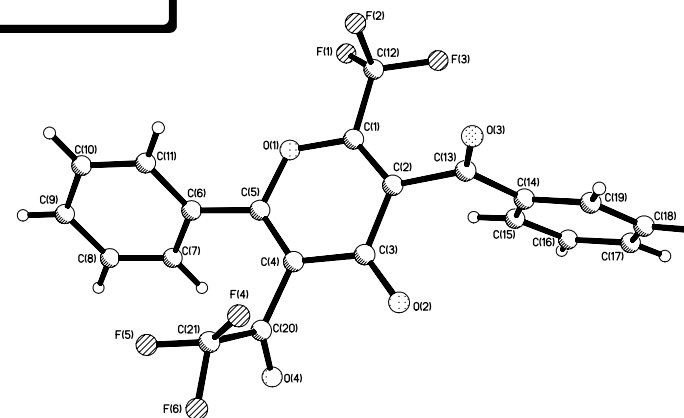
We have developed two universal methods of preparation of above mentioned heterocycles:

- **Method 1. Condensation of 1,3-diketonates with hydrochlorides of nucleophiles in boiling methanol or ethanol**
- **Method 2. Condensation of 1,3-diketonates with free nucleophilic bases in glacial acetic acid at 20-118⁰C**

Reactions of fluoroalkyl-containing lithium's 1,3-diketonates with oxalylchloride

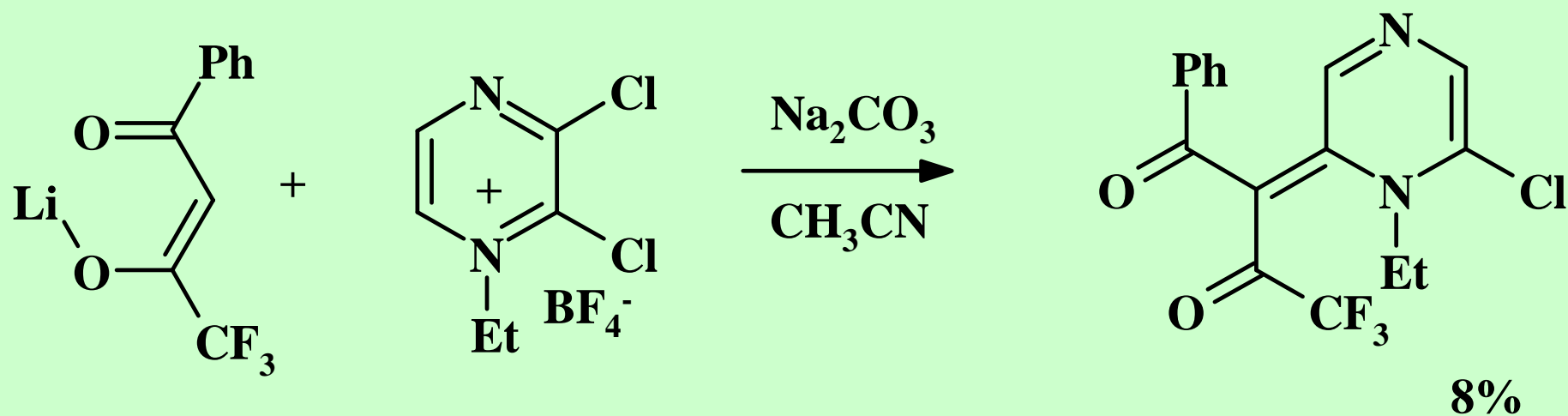


Structure of 3-Benzoyl-6-phenyl-5-(2,2,2-trifluoroacetyl)-2-(trifluoromethyl)-4 *H*-pyrane-4-one

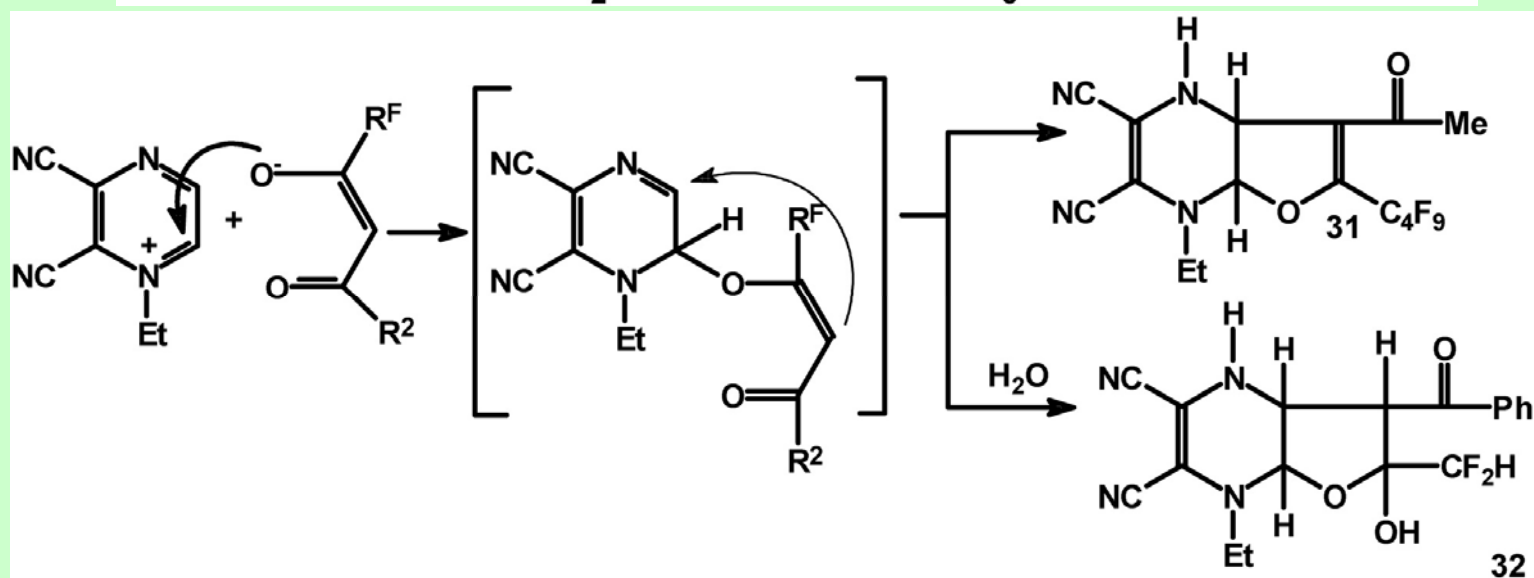
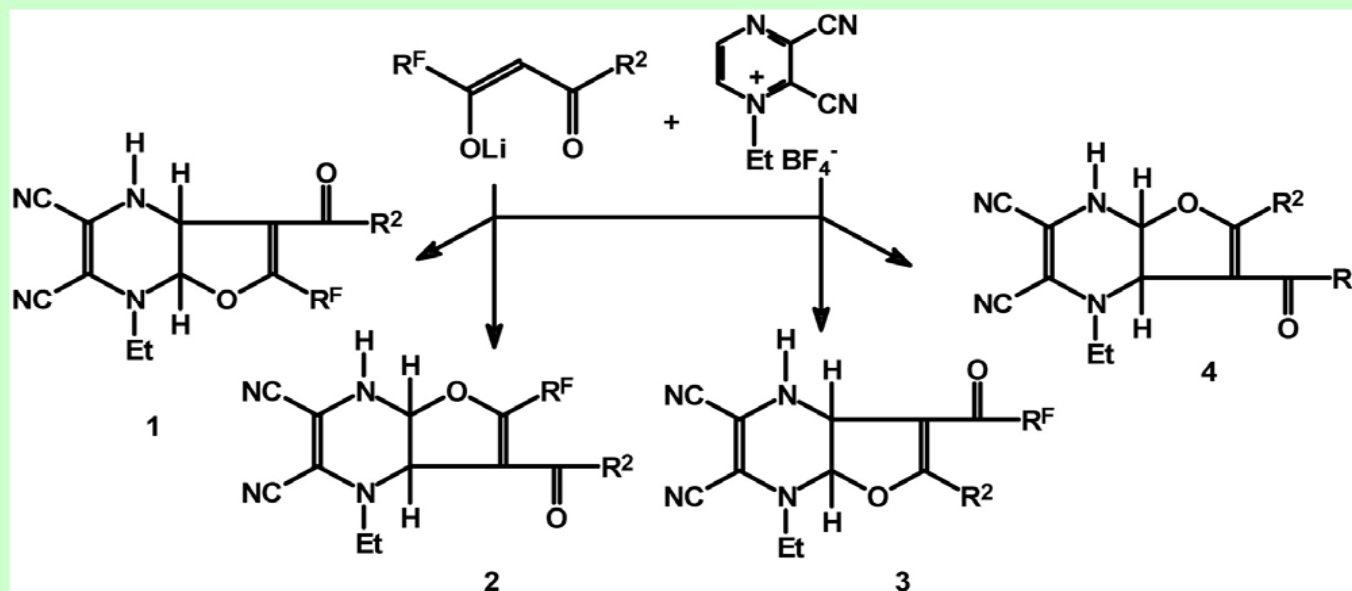


**Reactions of fluoroalkyl-containing lithium's
1,3-diketonates with
1-ethyl-2,3-dichloro tetrafluoroborate**

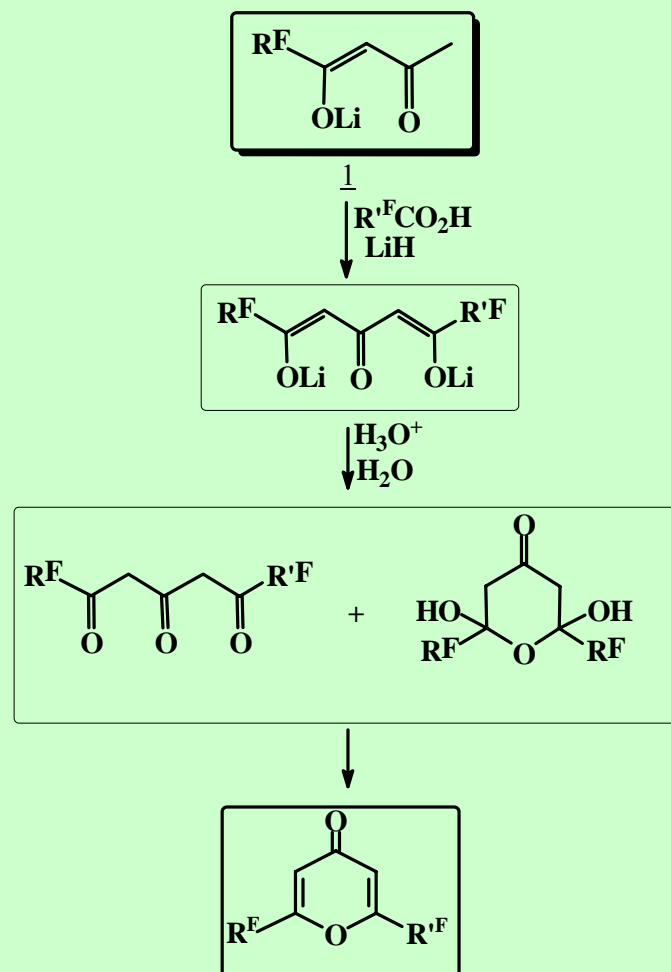
20



Reactions of fluoroalkyl-containing lithium's 1,3-diketonates with 1-ethyl-2,3-dicyanopyrazinium tetrafluoroborate



Synthesis of 1,3,5-Triketones and Pyrones



D. S. Yachevskii, D. L. Chizhov, K. I. Pashkevich, V.N. Charushin Arkivoc, v.2004, Part(xi), 71-76

D. S. Yachevskii, D. L. Chizhov, V.G.Ratner, K. I. Pashkevich, Izv.AN, Ser.Khim, 2001, 50, 1176. [Russ. Chem. Bull., 2001, 50, 1233 (Engl. Transl.)].

Lithium 1,3-diketonates as polyfunctional fluorinated synthons

23

- **They are versatile reagents for preparation of a number of fluoroalkyl-containing compounds:**
- **1,3-diketones, enaminoenones, 1,3-hydroxyketones, α,β -enones and their halogen derivatives**
- **- three-, five-, six-, seven-membered and fused heterocycles (derivatives of pyrazole, isoxazole, pyrimidine, 1,5-benzo- and 1,5-naphthodiazepines, pyrazolopyrimidines, 1,2,4-triazolo pyrimidines, 1,2,4-triazolopyridazines, pyrazoloquinazolines, benzoquinolines, tetrahydrobenzophenanthridines, benzo imidazopyrimidines, furopyrazines).**

Fluorine-containing lithium 1,3-diketonates are valuable and convenient synthons

Lithium 1,3-diketonates are more accessible, are more convenient for work and are steady at storage than appropriate 1,3-diketones.

They are:

- Readily accessible**
- Stable on storage**
- Highly reactive**
- All processes are simple and provide yields of target products from 40 up to 90%**

Acknowledgement:

- *We thank:*
- *Dr. E. Lork, Bremen University (Germany), Prof. O.A. Dyachenko, Dr. O.N. Kazheva, Dr. A.N. Chekhlov, Institute of physical chemistry problems, RAS, Chernogolovka, for X-ray diffraction analysis.*
- *Dr. G.L. Rusinov, Dr. O.V. Fedorova, I.G. Ovchinnikova, Institute of Organic Synthesis, UD of RAS, Ekaterinburg, Russia, for podandes and crown-ethers.*
- *Dr. Yu.G. Yatluk Institute of Organic Synthesis, UD of RAS, Ekaterinburg, Russia, for chitosan.*
- *Dr. O. P. Krasnykh, Perm Pharmaceutical Academy, SEC, Perm, Russia, for oxalychloride.*

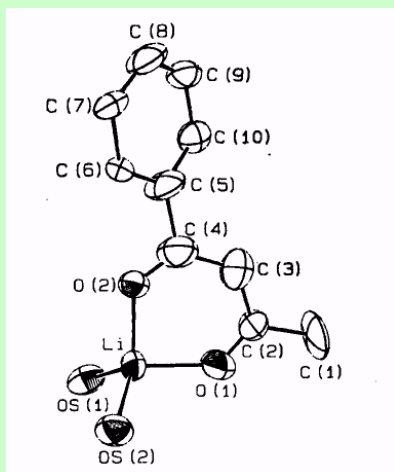


Рис. 4. Фрагмент элементарной ячейки $\text{Li}(\text{bzac})(\text{H}_2\text{O})_2$

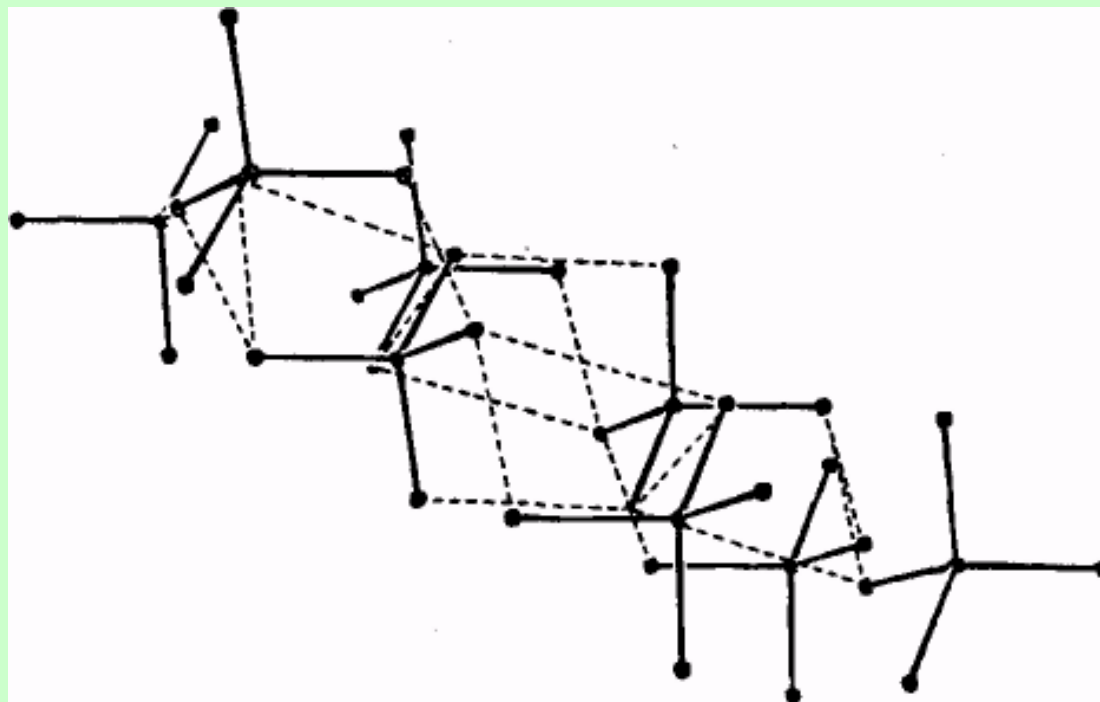


Рис. 5. Диаграмма кристаллической упаковки $\text{Li}(\text{bzac})(\text{H}_2\text{O})_2$, показывающая межмолекулярные водородные связи вдоль оси Z. Показаны только один атом лития и четыре атома кислорода.

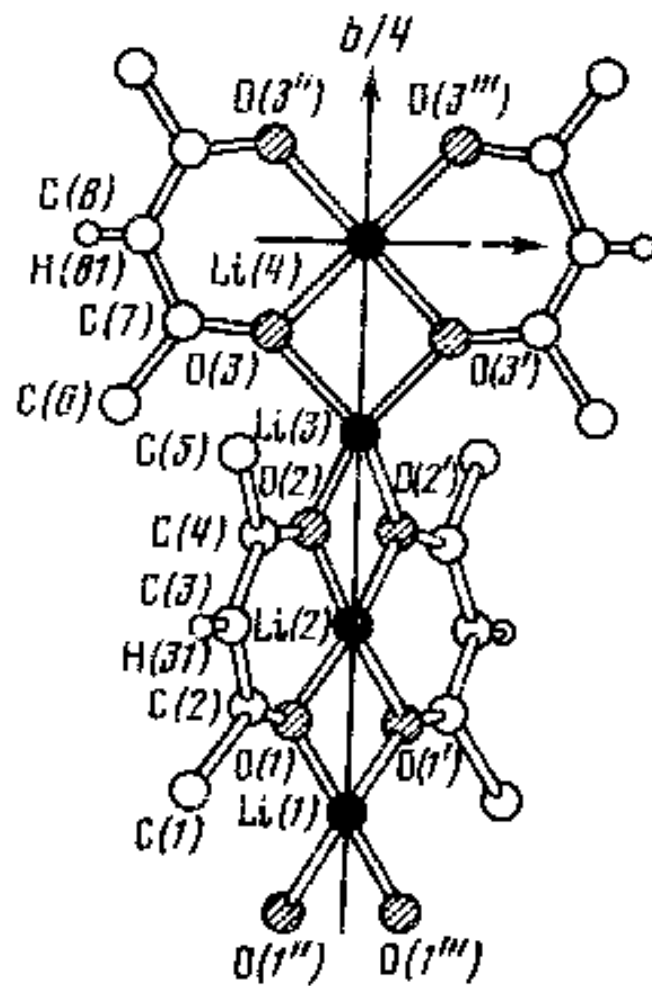


Рис.4. Молекулярная структура ацетилацетоната лития.