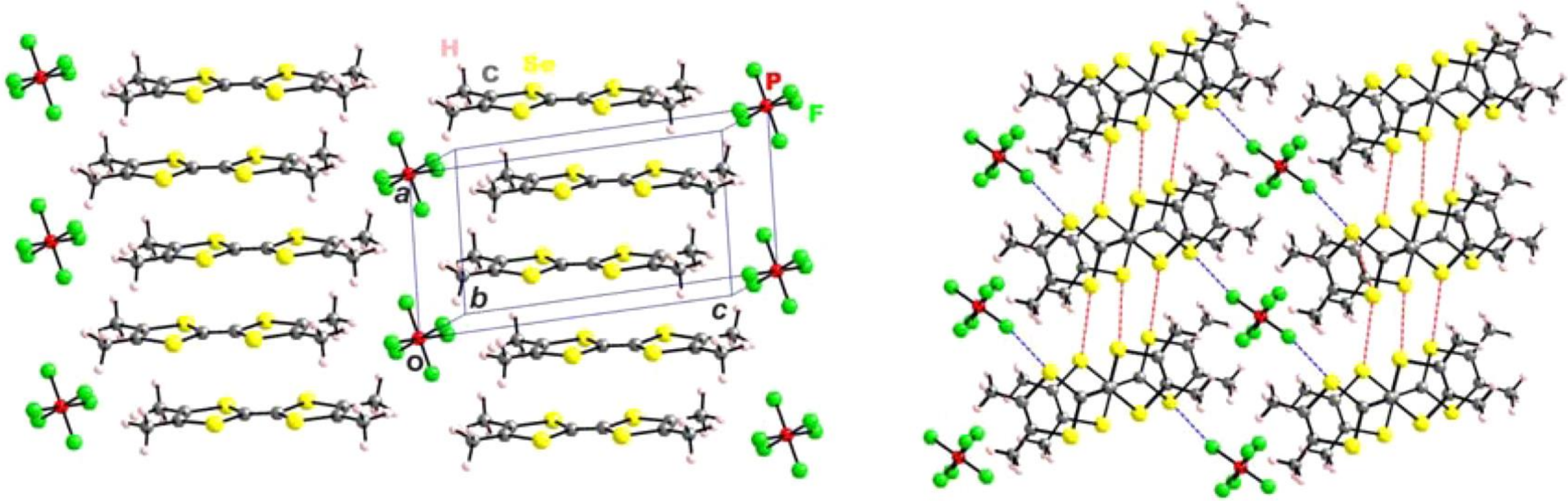
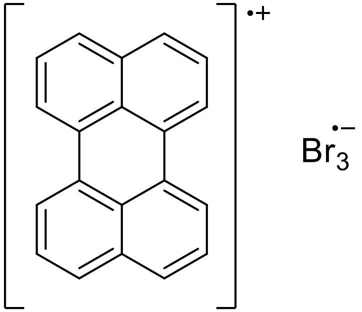
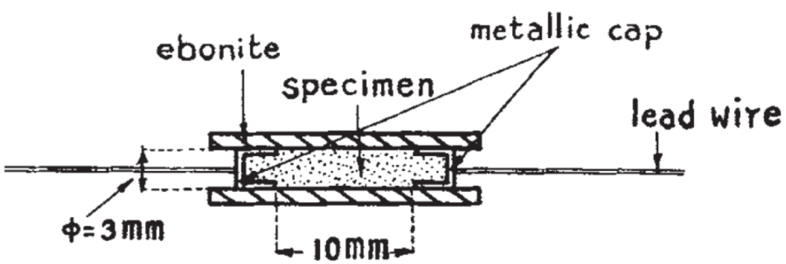
Non-polymeric Organic Conductors.



Perylene complexes

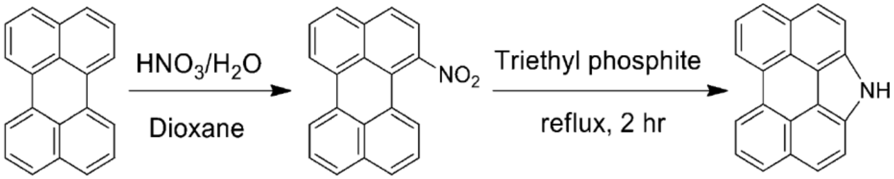


Conductivity 1-100 S/m



Specimen cell for the measurement of electrical conductivity

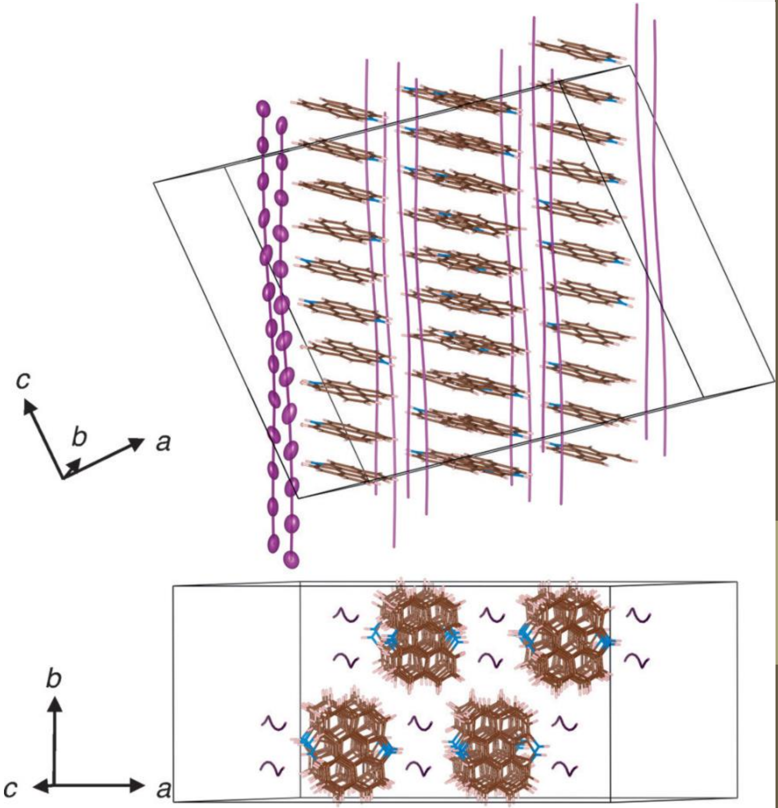
Nature **173**, 168-169 (23 January 1954)



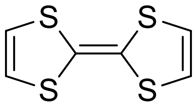
1 **2** **3**

Synthetic route for pyrroloperylene **3**.

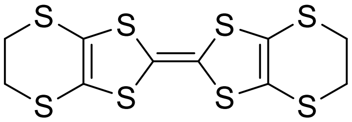
Angew. Chem. **2016**, 128, 8164 –8167



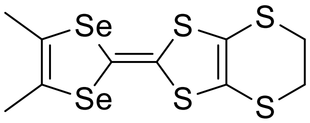
Tetrachalcogenofulvalenes



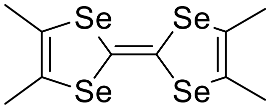
tetrathiafulvalene
TTF



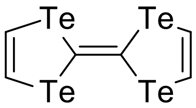
bisethylenedithiotetrathiafulvalene
BEDT-TTF



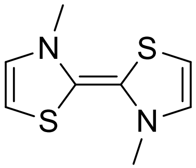
dimethyldiselenaethylenedithiodithiafulvalene
DMET



tetramethyltetraselenafulvalene
TMTSF

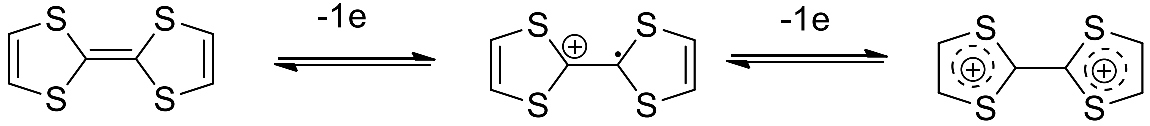


tetratellurafulvalene
TTeF



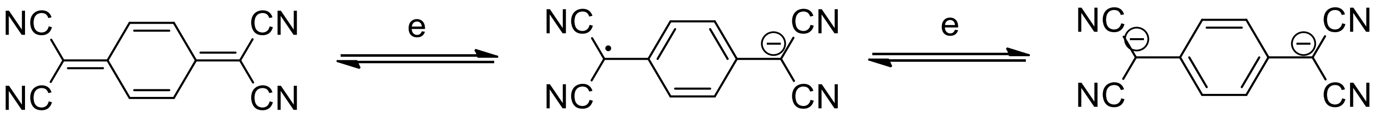
dithiadiazafulvalene
DTDAF

Tetrathiafulvalene TTF



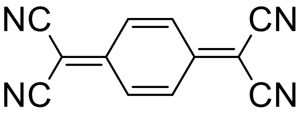
TTF

E 1 = -0.34 V, E2ox =   -0.78 V   vs Ag/AgCl in MeCN)

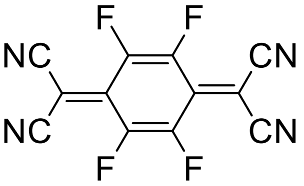


E1 = 0.12 V

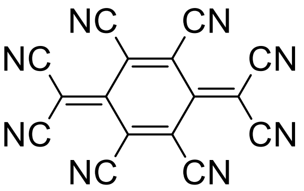
E1 = -0.13 V



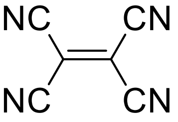
TCNQ



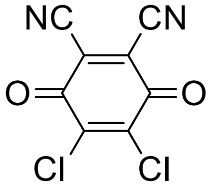
TCNQF$_4$



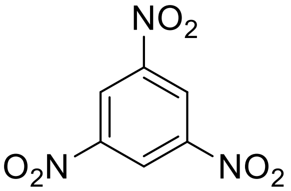
TCNQ(CN)$_4$



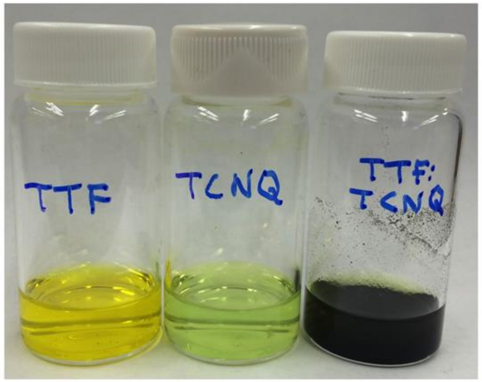
TCNE



DDQ

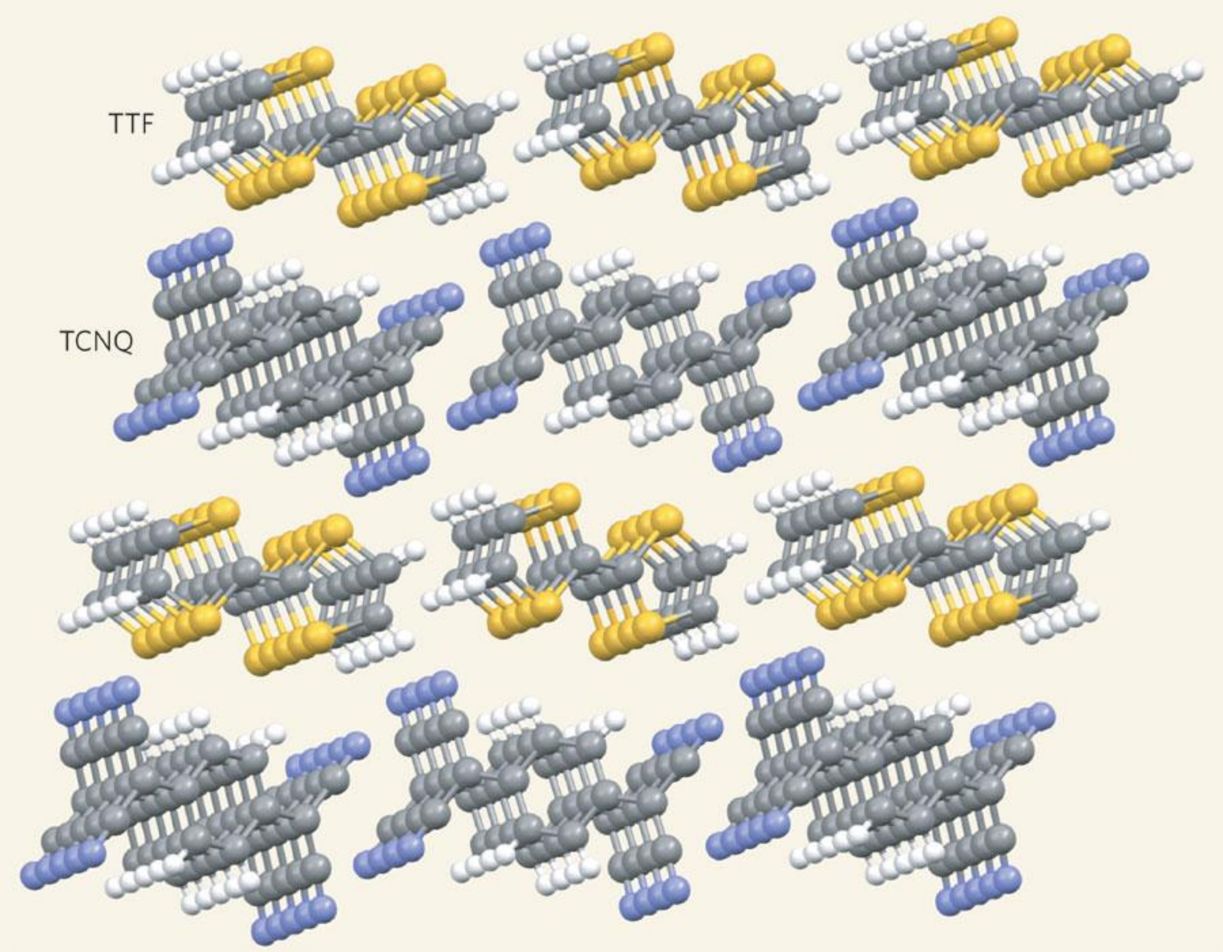


TTF-TCNQ Charge Transfer Complex



TTF
Electron donor
+
TCNQ
Electron acceptor
→
TTF–TCNQ
- Charge transfer
- Aromatic ions
- Metallic conductivity

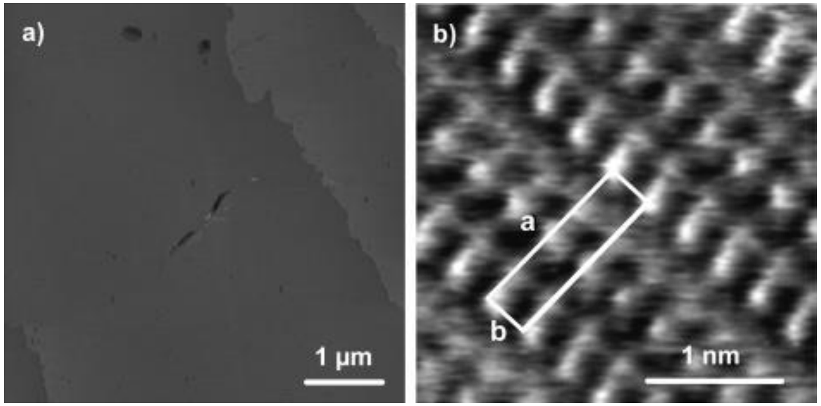
J. Chem. Educ. 2015, 92, 2134–2139



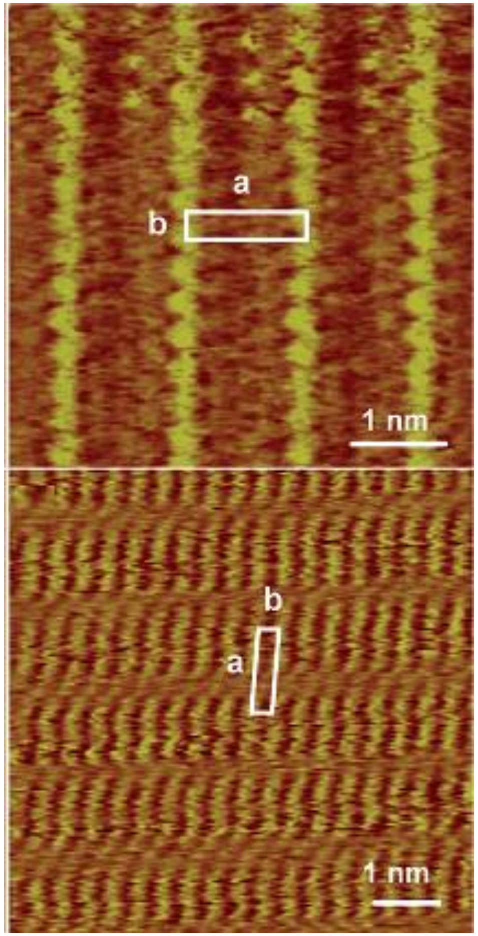
Organic crystals in chains. In a charge-transfer salt, molecules of TTF (tetrathiofulvalene) and TCNQ (7,7,8,8-tetracyanoquinodimethane) line up into orderly chains to form a crystalline structure.

Nature, Vol 453, 19 June 2008, 996

TTF-TCNQ Charge Transfer Complex



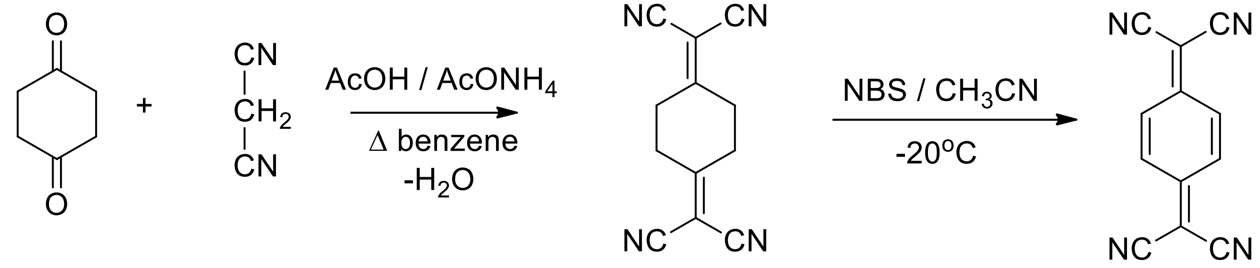
STM (Scanning tunneling microscopy) images of the *ab* plane of TTF-TCNQ single crystal.
(a) An area of 5.36 *í*m 5.36 *í*m. (b) A 3 nm 3 nm image showing molecular resolution. Imaging conditions: *I*t) 0.10 nA, *V*b) 0.10 V, constant-current mode.



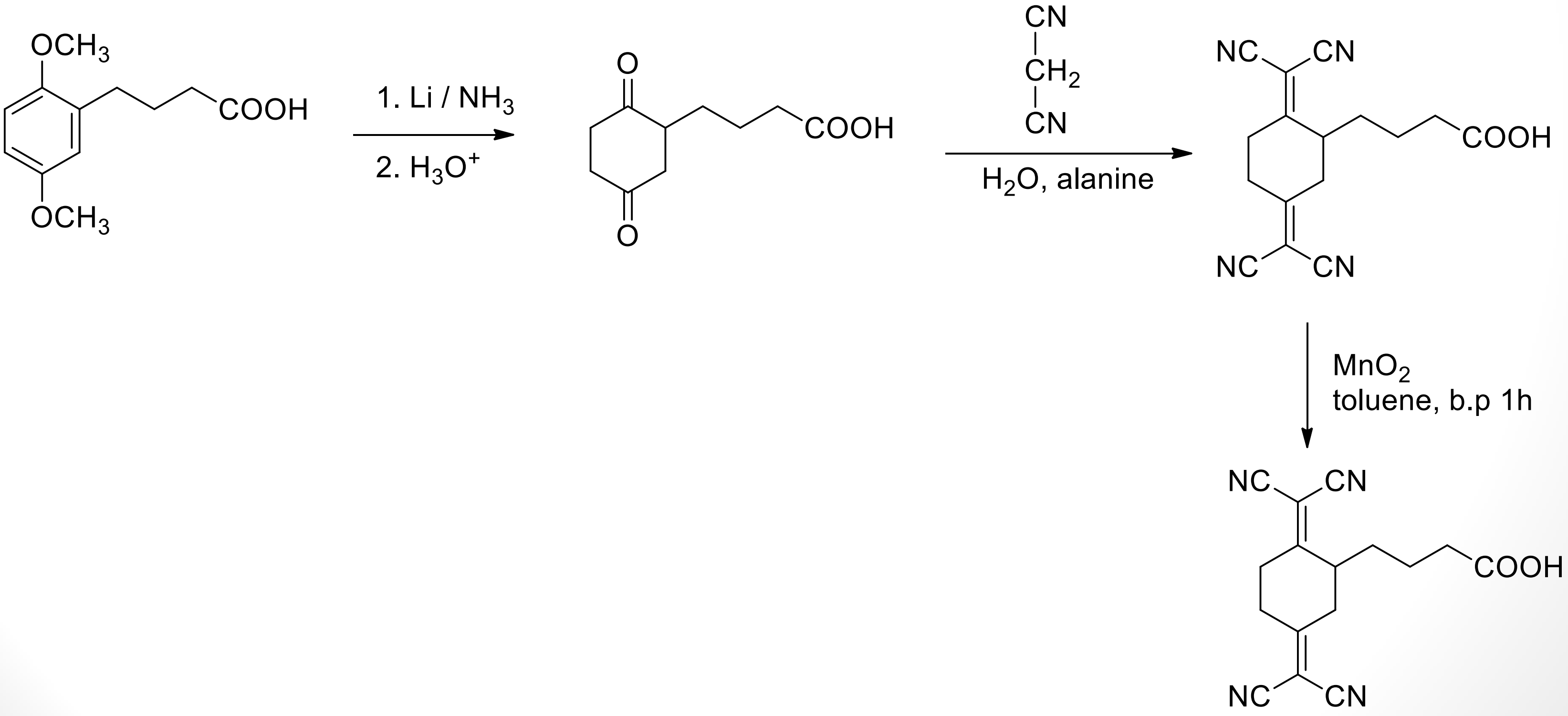
TTF- TCNQ single crystal before (a) and after (c) 90^{o} rotation. Imaging conditions: *I*t) 0.10 nA, *V*b) 0.10 V, constantcurrent mode.

J. Phys. Chem. C **2007,** *111,* 631-635

TCNQ preparation

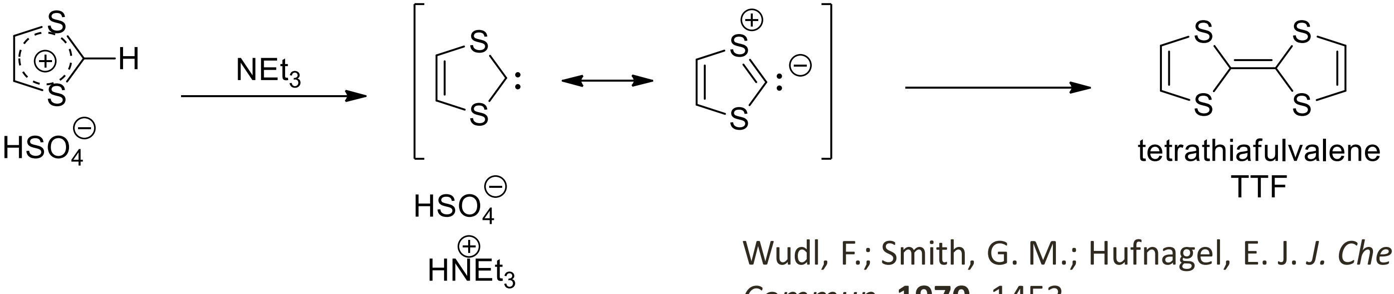


JACS, 1962, 84, 3370



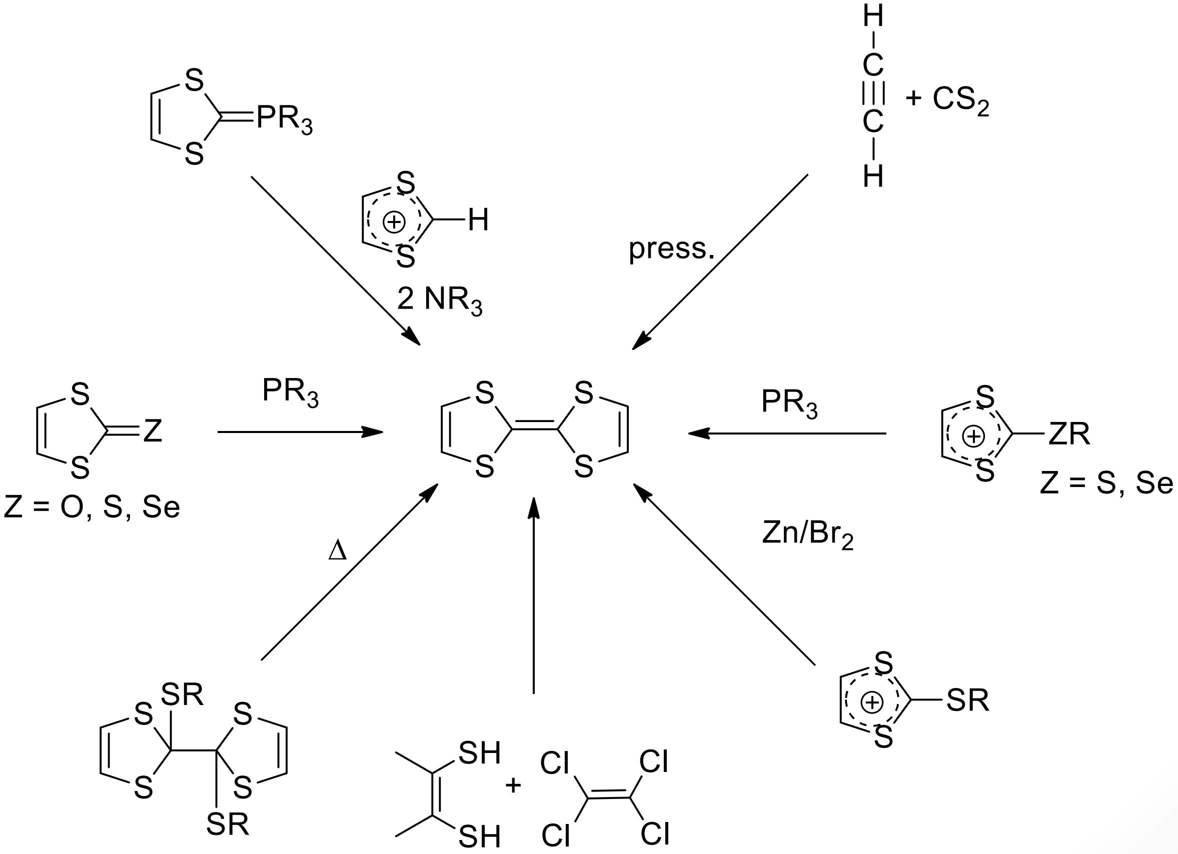
J. Org. Chem. **1983,** *48,* 3852-3854

Synthetic routes to TTF

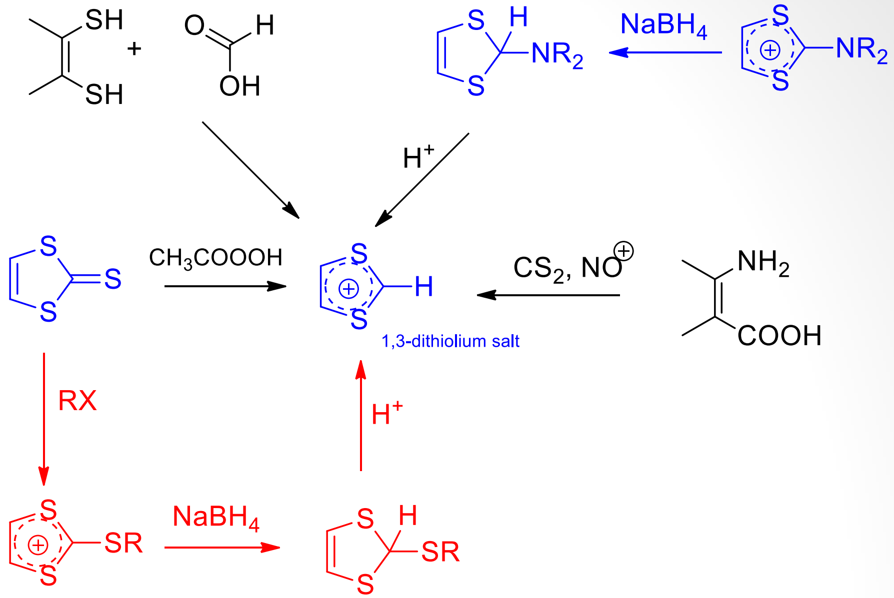


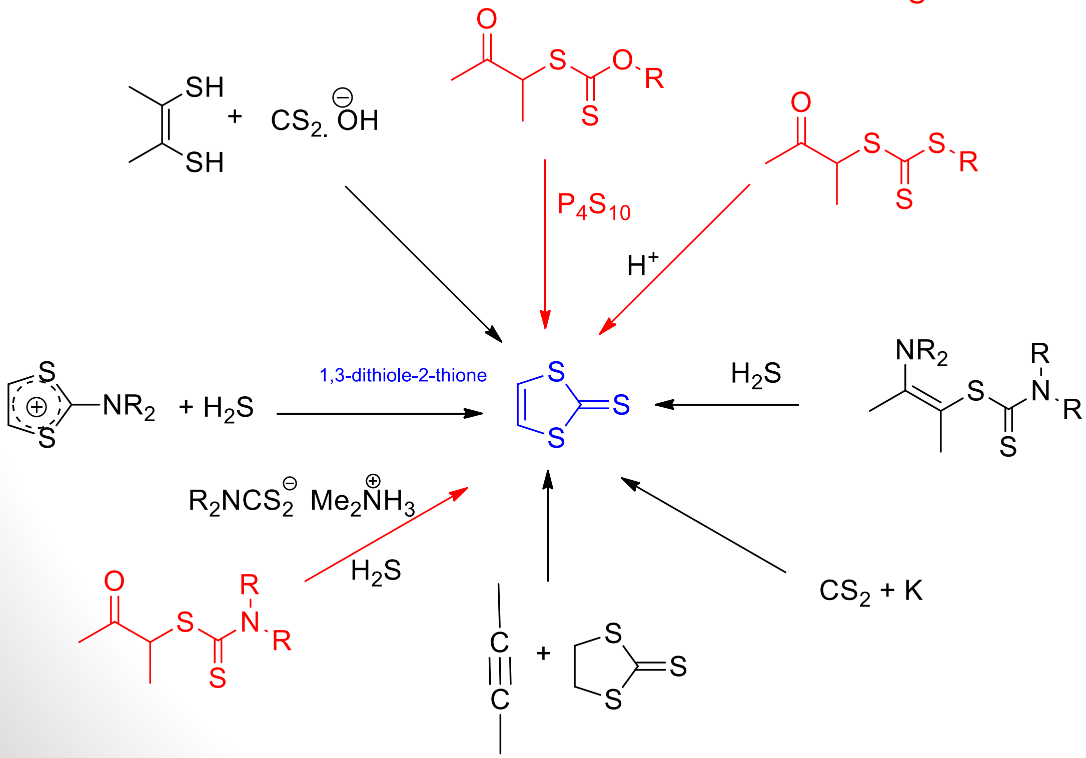
tetrathiafulvalene
TTF

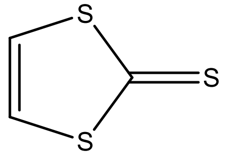
Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453.



Synthetic routes to TTF

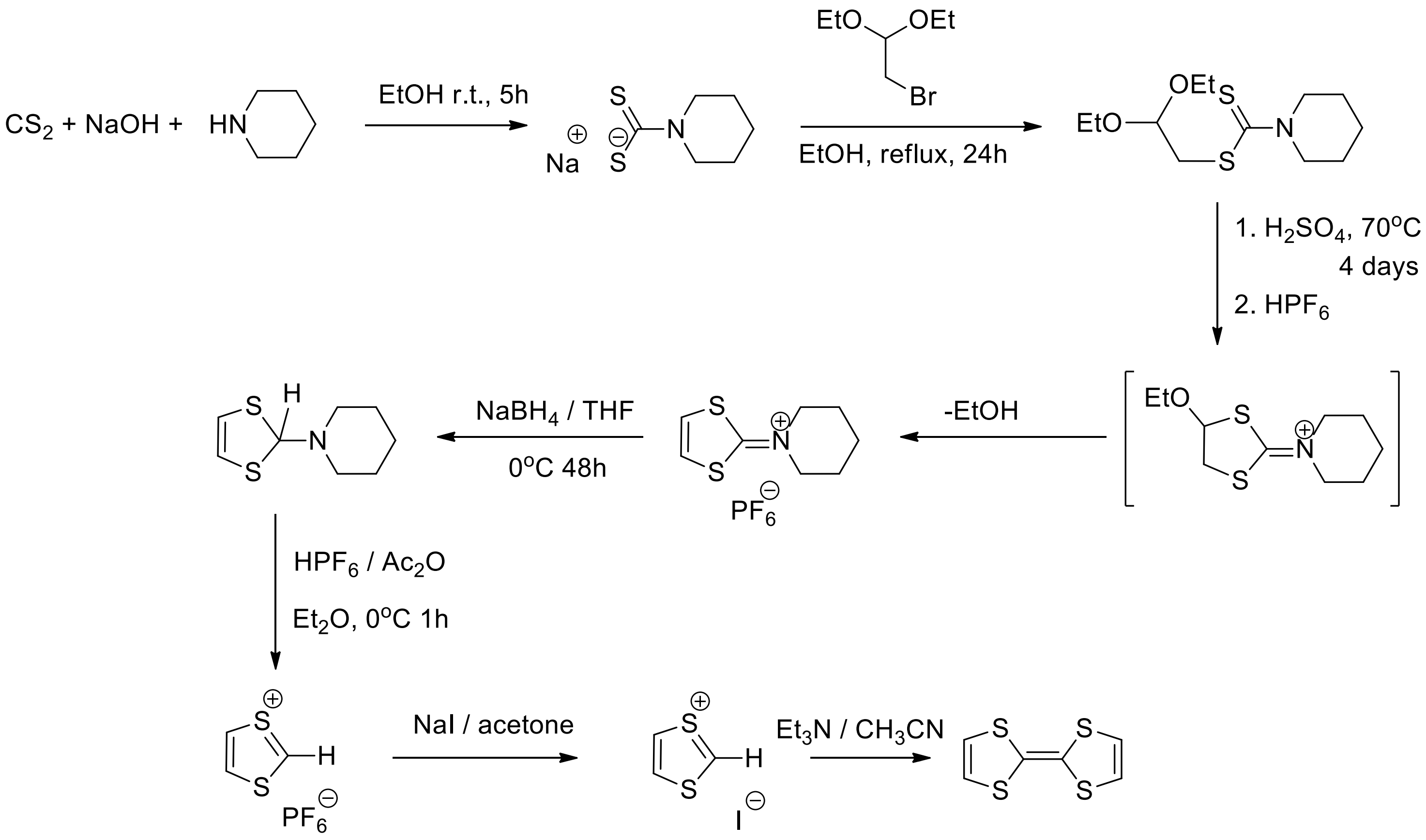






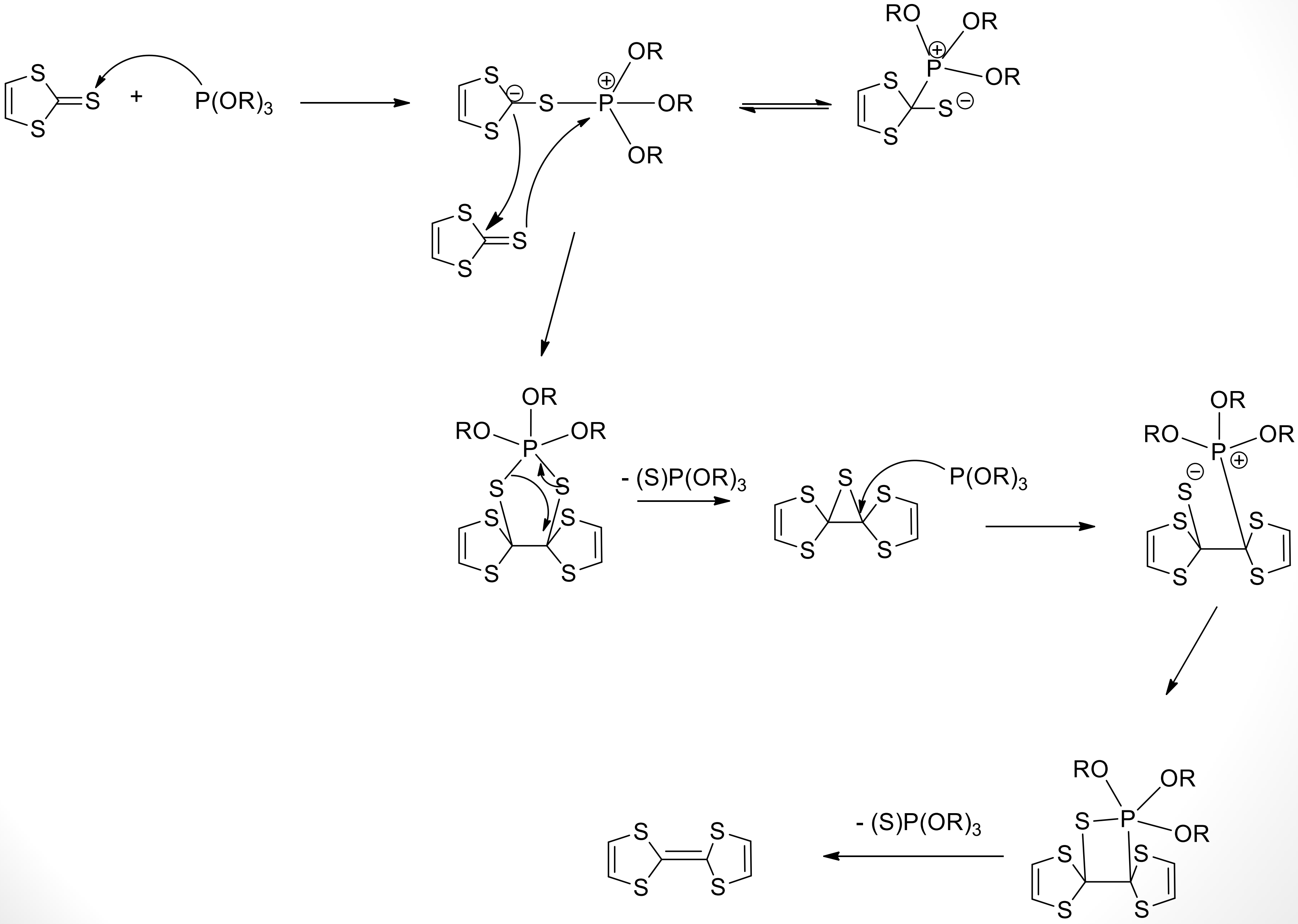
1,3-dithiole-2-thione

TTF via dithiolium salt



Syntesis, **1998**, 4515

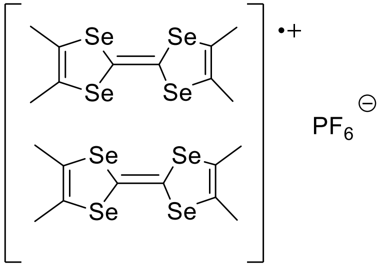
Coupling of 1,3-dichalcogenole-2-chalcogenones



Organic Superconductors

$(TMTSF)_2PF_6$

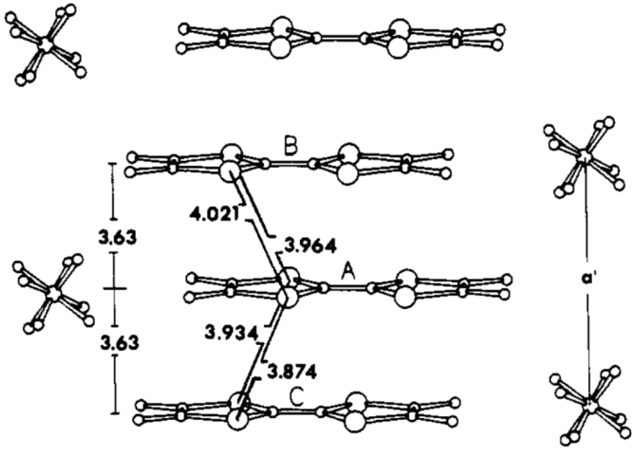
Bechgaard salt



Superconductor with a transition temperature of T_C = 1.1 K, and external pressure of 1.2 GPa.

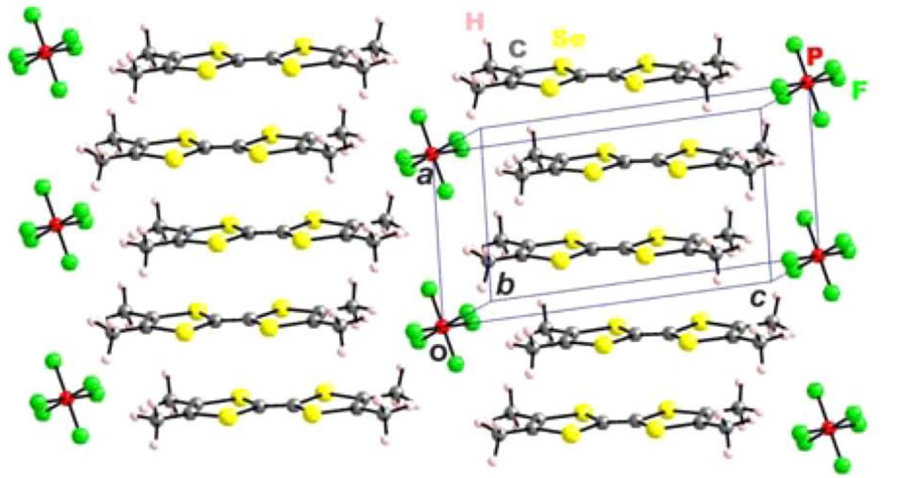
$(TMTSF)_2X$, X = $SbF_6^{\ominus}$ $AsF_6^{\ominus}$ $ClO_4^{\ominus}$ $ReO_4^{\ominus}$

1. Bechgaard, K.; Jacobsen, C. **S.;** Mortensen, K.; Pedersen, H. J.; Thorup, N. ***Solid State Commun.*** **1980, *33,*** 1119
2. Jerome, D.: Mazaud, A.; Ribault, M.: Bechgaard, K. ***J. Phys. Letf.*** **1980, *41,*** L-95.



Side view of the stacks in $(TMTSF)_2ClO_4$ (tilted 10°).

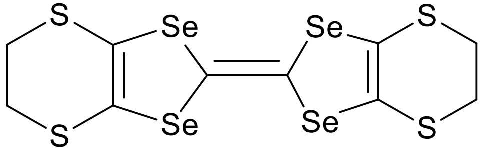
J. Am. Chem. SOC. **1981, *103,*** 2440-2442



Structure of $(TMTSF)_2PF_6$.

J. Phys. Chem. A 2016, 120, 8574–8583

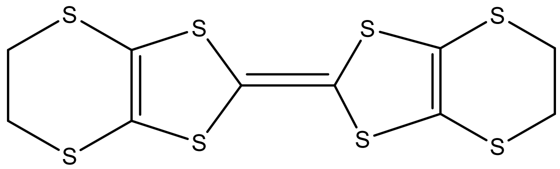
Organic Superconductors



BETS

Tc of $(BETS)_2GaCl_4$ is 6 K

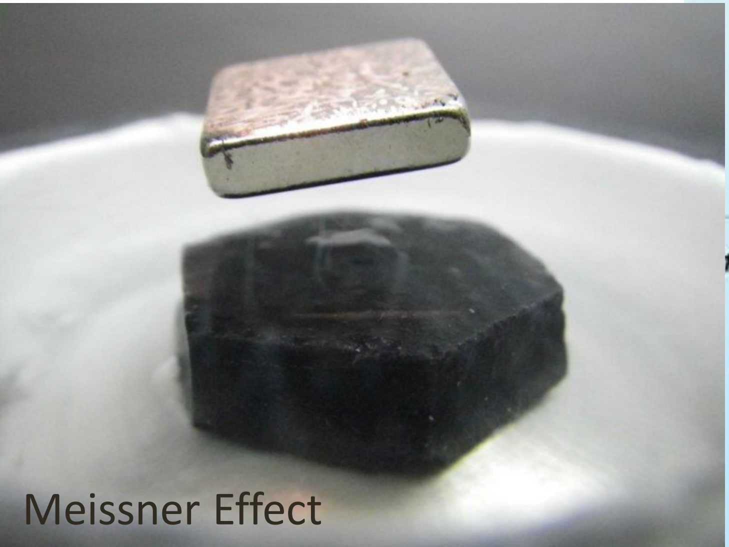
J. Am. Chem. Soc. **1999,** *121,* 760-768



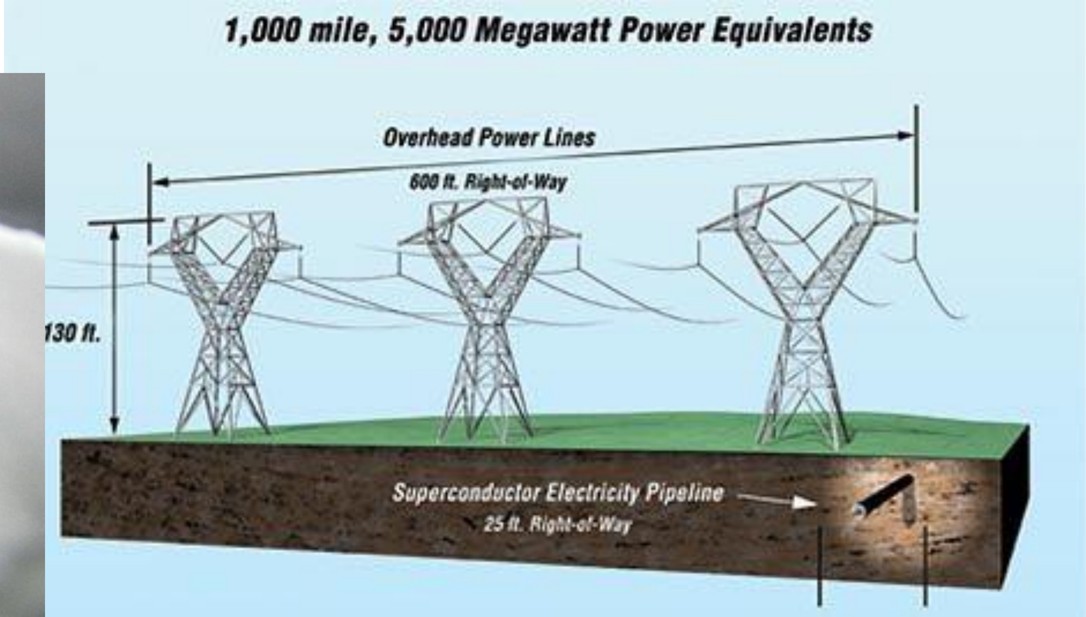
BEDT-TTF

$(ET)_2Cu[N(CN)_2]Br$ superconducting at T_C = 12.5 K at ambient pressure,

Inorg. Chem., 1990, 29 (14), pp 2555–2557

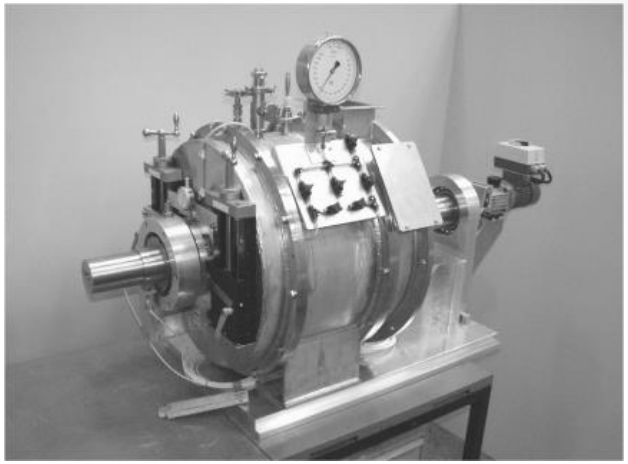


Meissner Effect

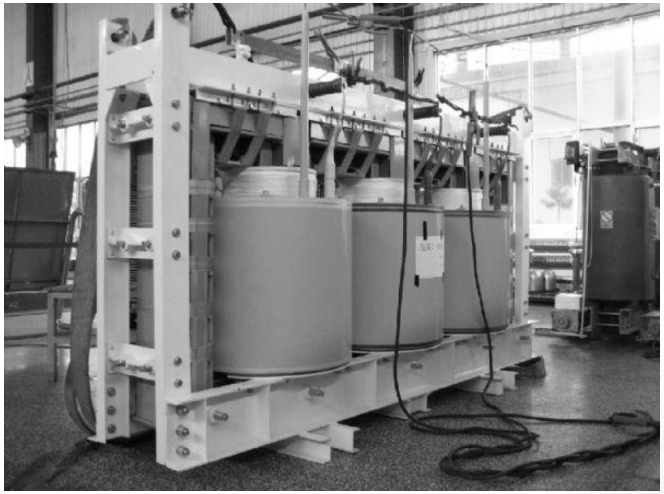


Superconductors applications

138kV HTS cable system installed in Long Island, NY

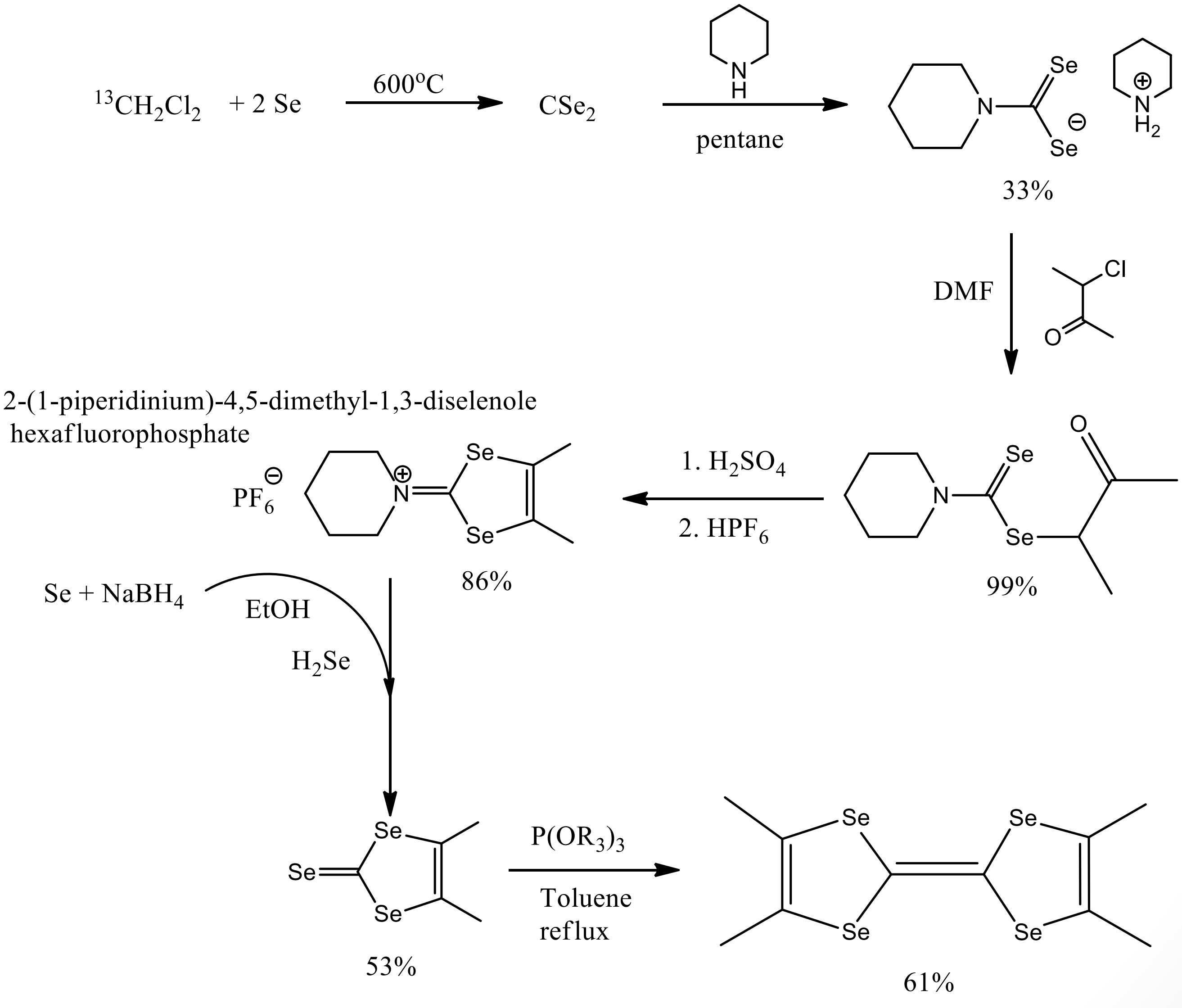


Superconducting bearing
Superconductor Science and Technology, 2004, 17, 5



Frontiers of Electrical and Electronic Engineering, 2009, 4, 1, 104

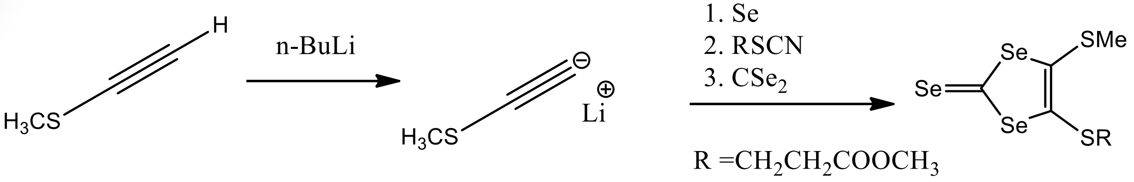
Tetramethyltetraselenafulvalene TMTSF

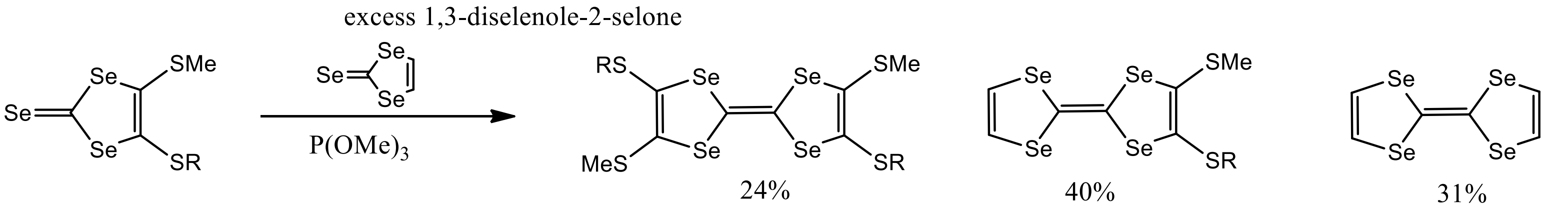


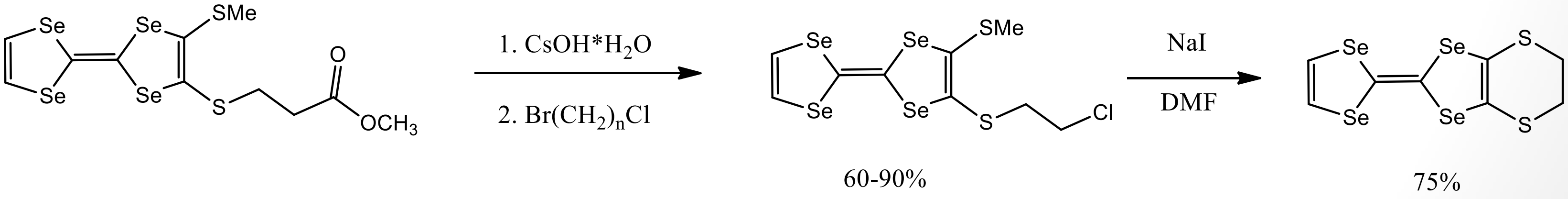
overall yield 9%

J. Labelled Cpd. Radiiopharm, ***2001***, 44, 1035-1041

Alkylenedithio- and bis(alkylenedithio) TSF



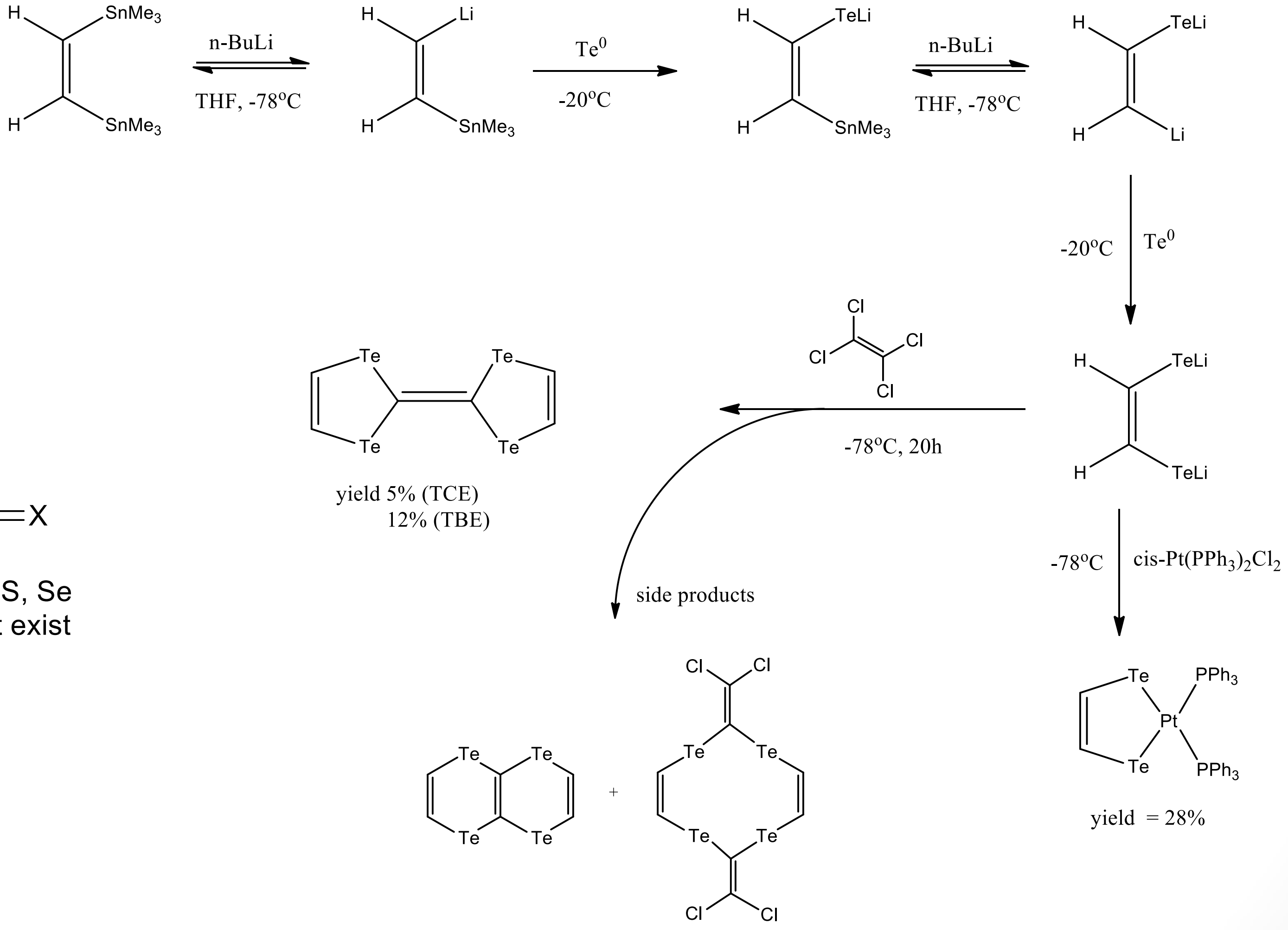




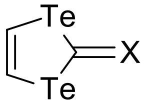
J. Org. Chem. *2003*, 68, 5217-5224

Synthesis of tetratellurafulvalene

stepwise approach



!

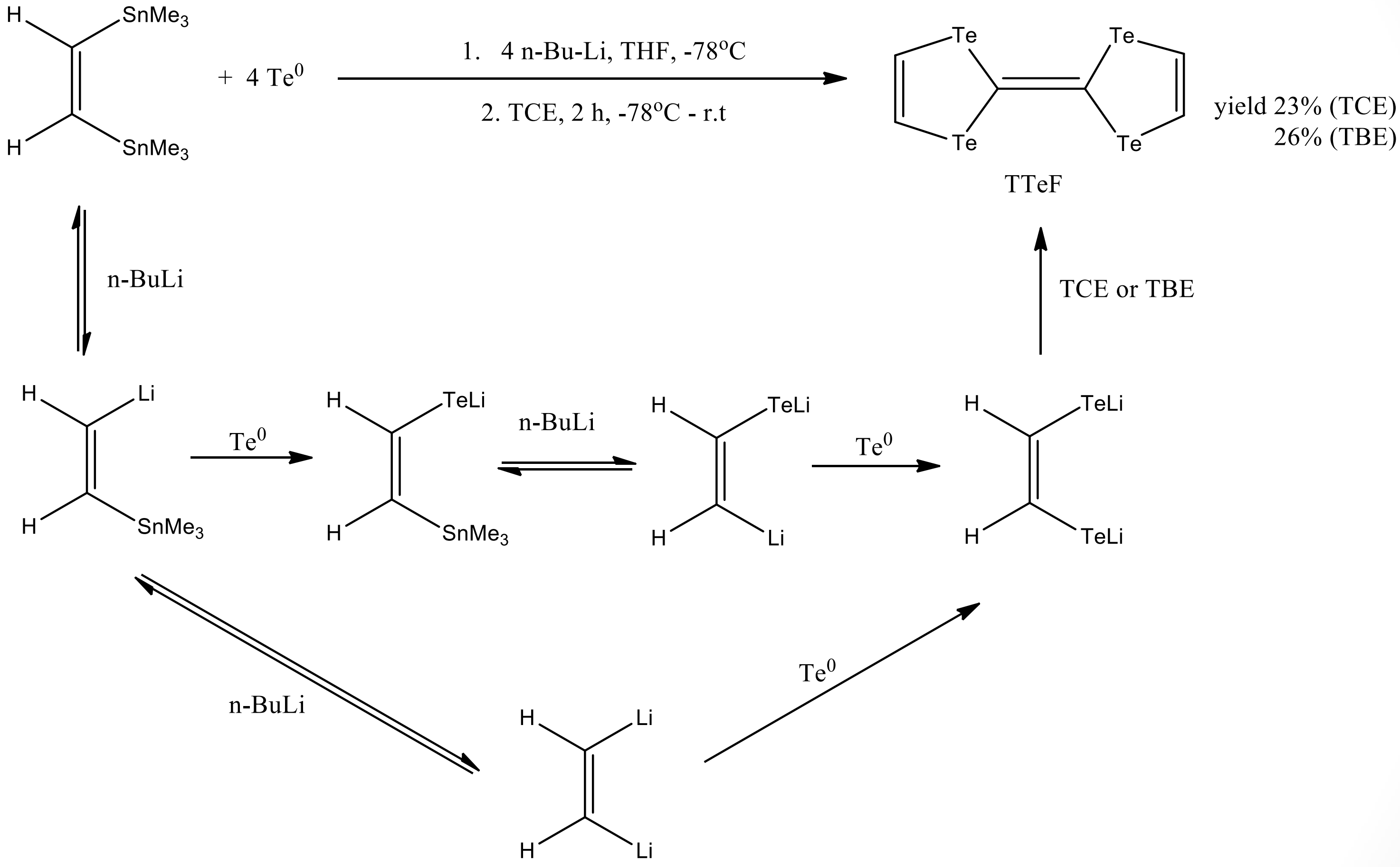


X = O, S, Se
doesn't exist

J. Org. Chem. **1996**, 61, 7006-7011

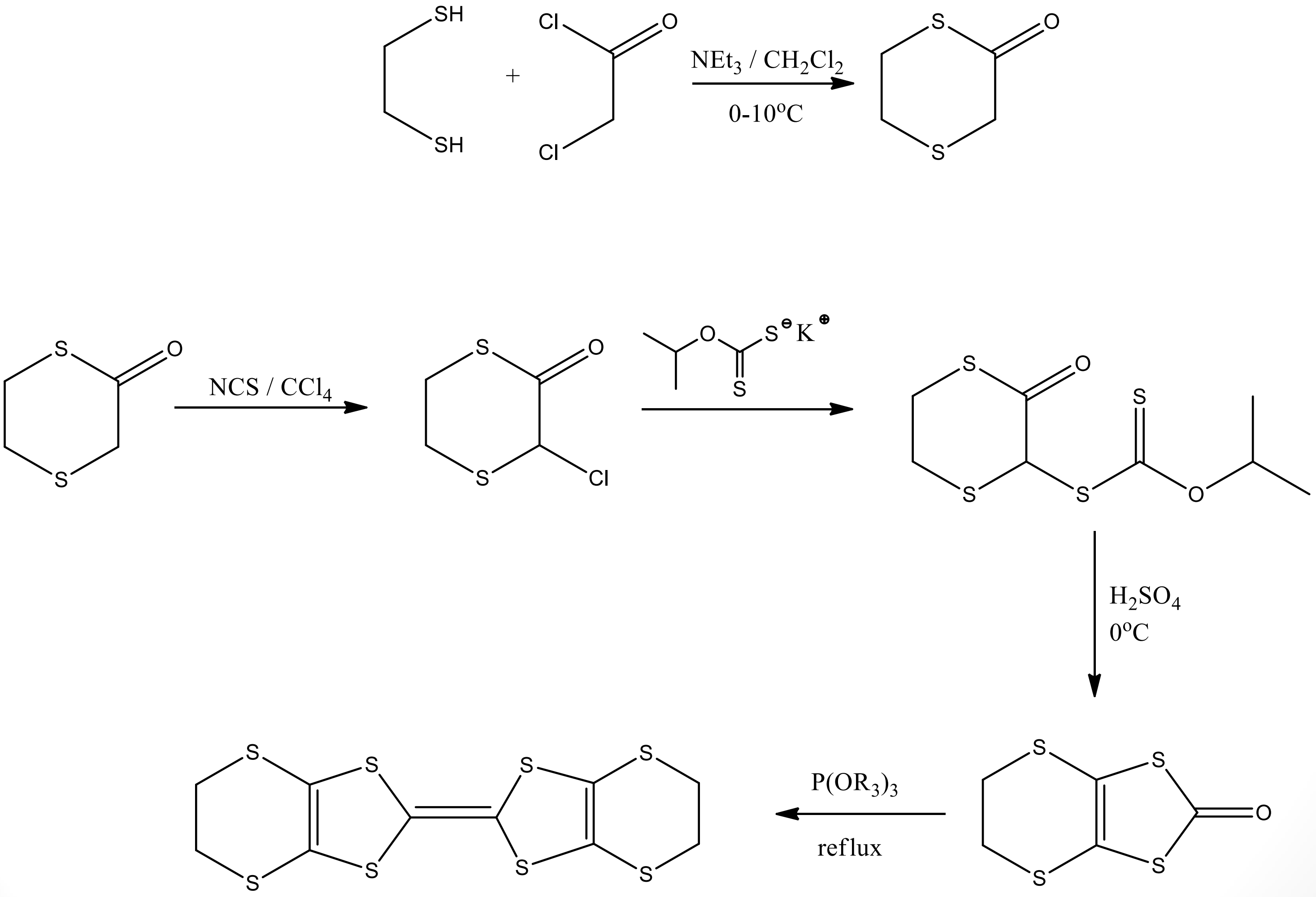
Synthesis of tetratellurafulvalene

one-step approach

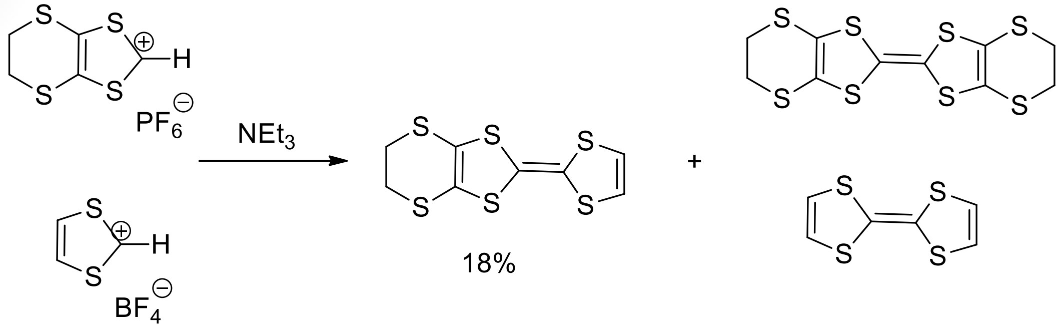


J. Org. Chem. **1996**, 61, 7006-7011

Superconductor BEDT-TTF

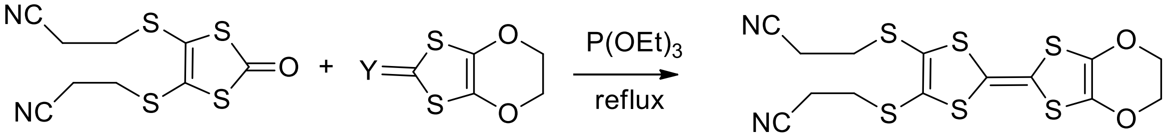


Nonsymmerticaly substituted TTF

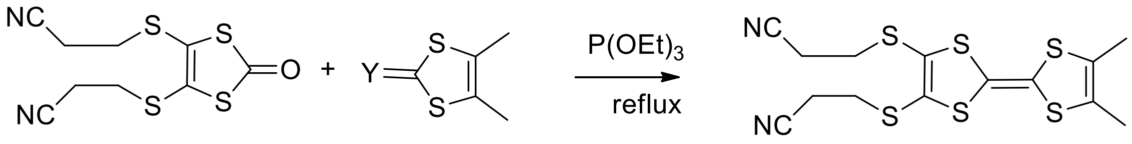


18%

J. Chem. Soc. Chem. Commun. **1985**, 106



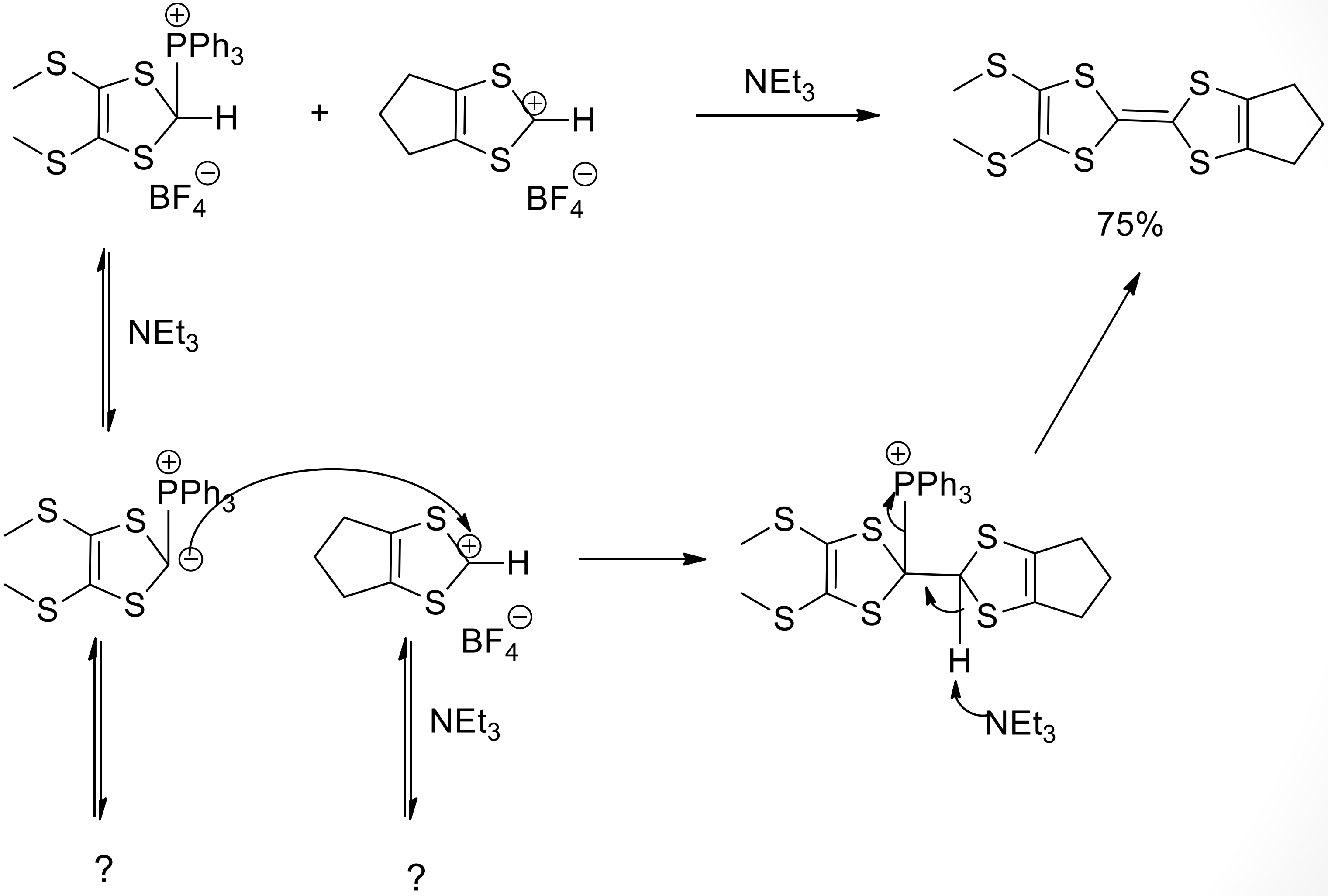
Y = S, 45%
Y = Se, 30%
Y = O, 12%



Y = S, 10%
Y = Se, 19%

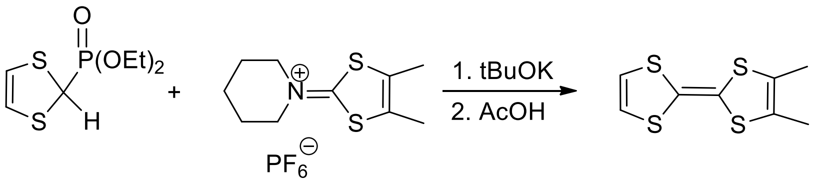
J. Chem. Soc. Perkin Tr.1 . **1996**, 783

Nonsymmerticaly substituted TTF

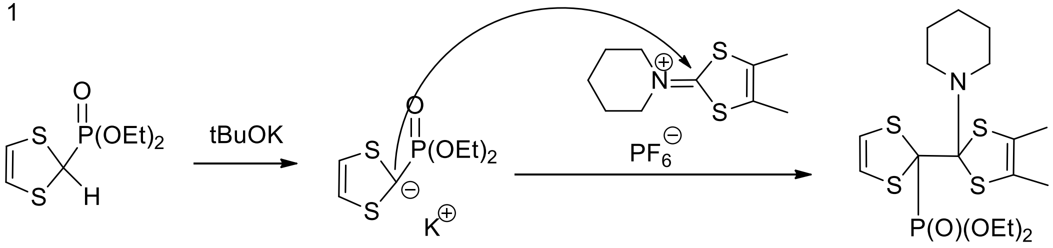


JACS, **2004**, 126, 426

Selective Horner-Wadsworth-Emmons condensation

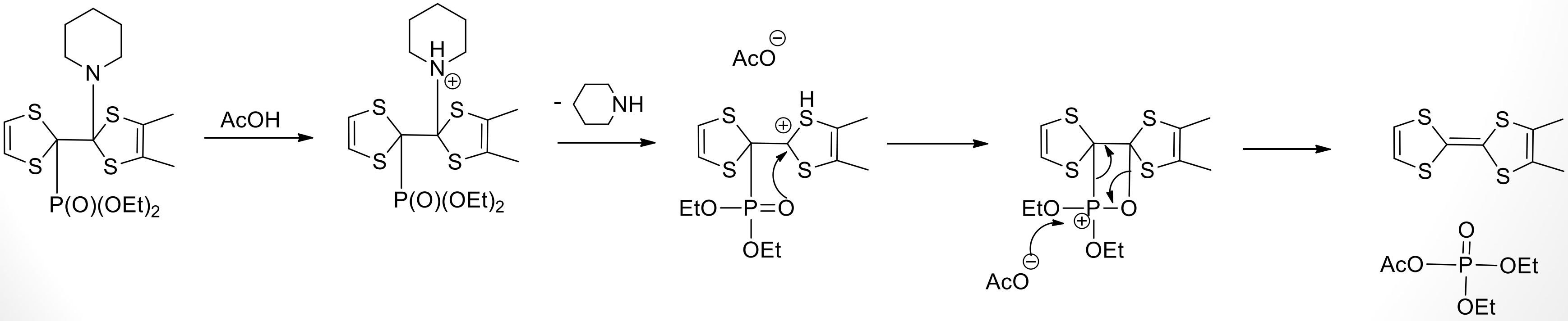


step 1



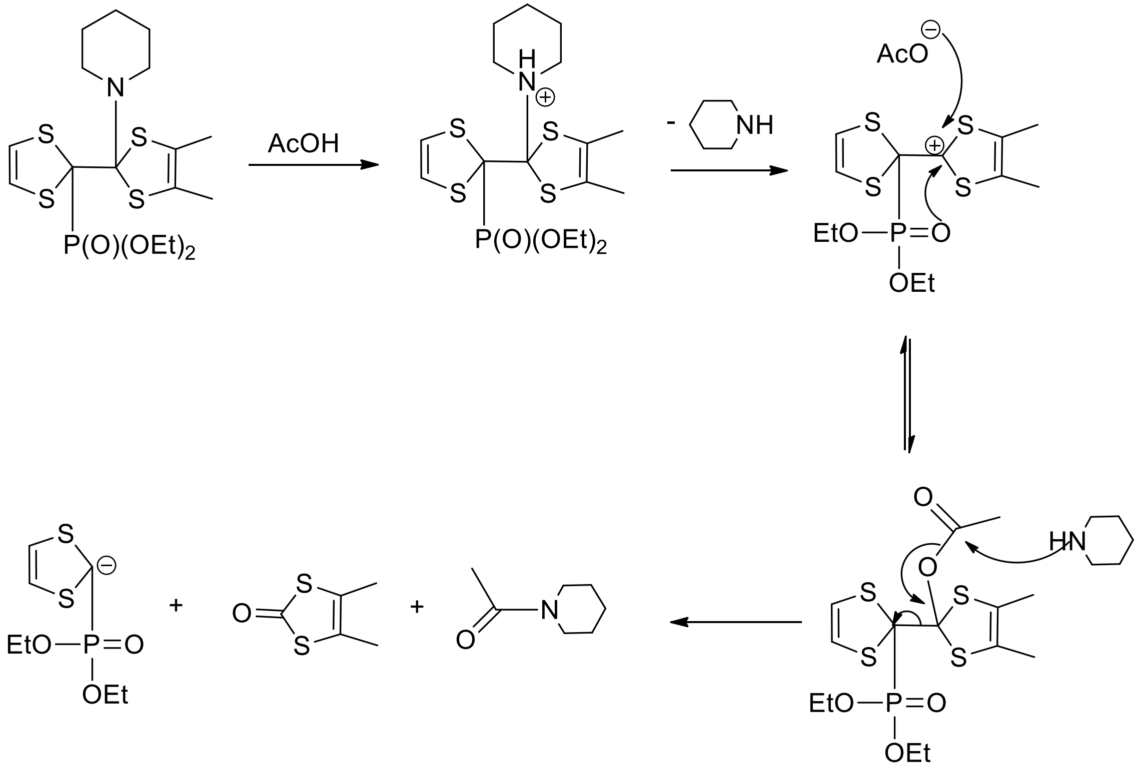
quantative yield

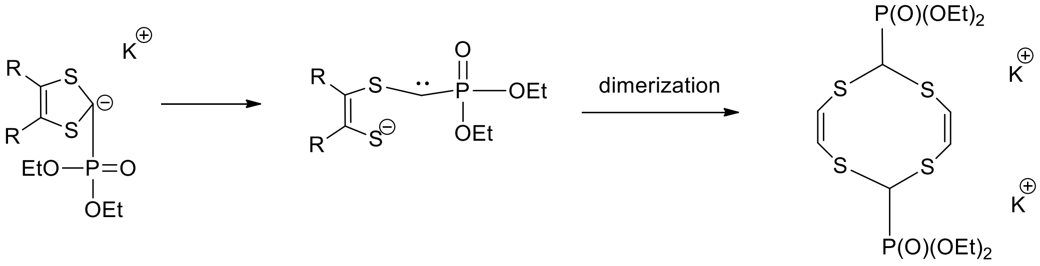
step 2



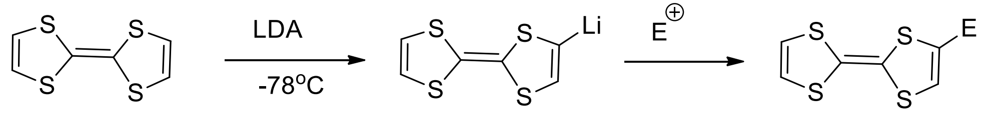
Tetrahedron Lett. **1999**, 40, 7219

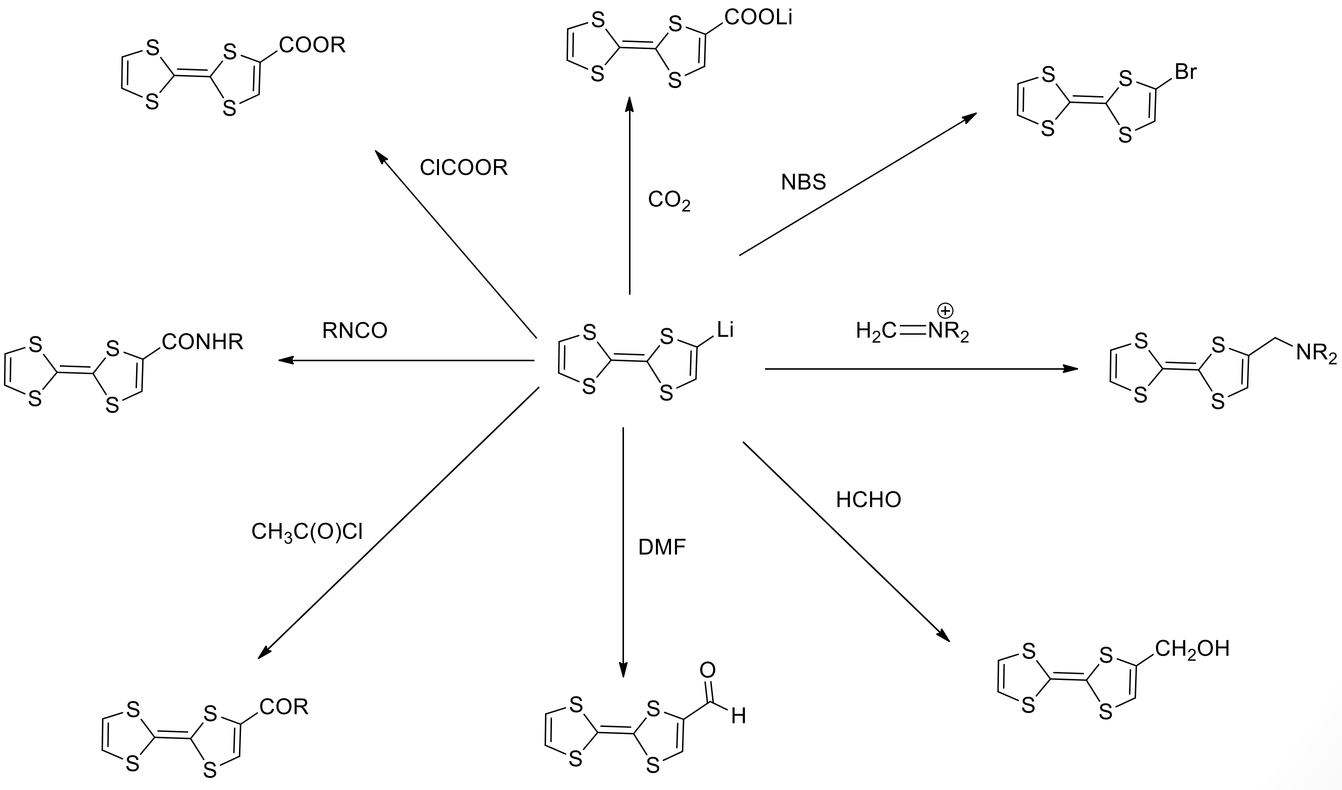
Horner-Wadsworth-Emmons side reactions



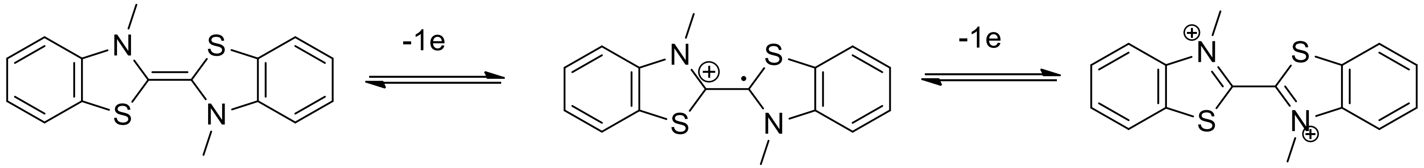


Elecrophilic substitution of metalated tetrachalcogenafulvalenes

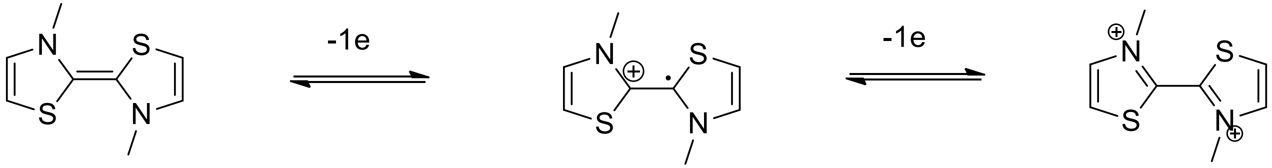




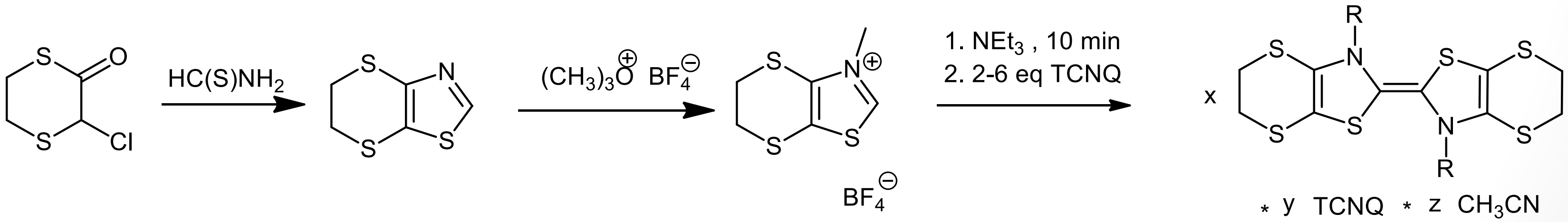
Dithiadiazafulvalenes DTDAF



(E°1ox) -0.17 V, E°2ox -0.02 V vs SCE in MeCN)

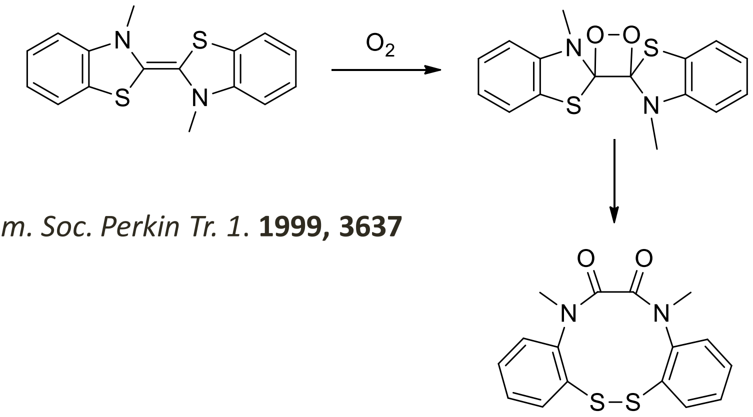


(E°1ox) -0.54 V, E°2ox -0.41 V vs SCE in MeCN)

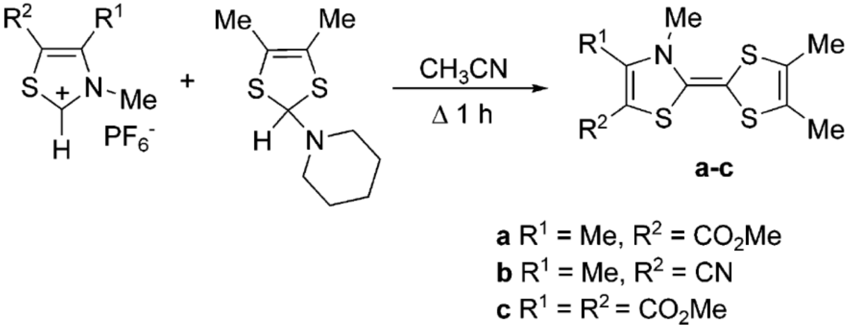


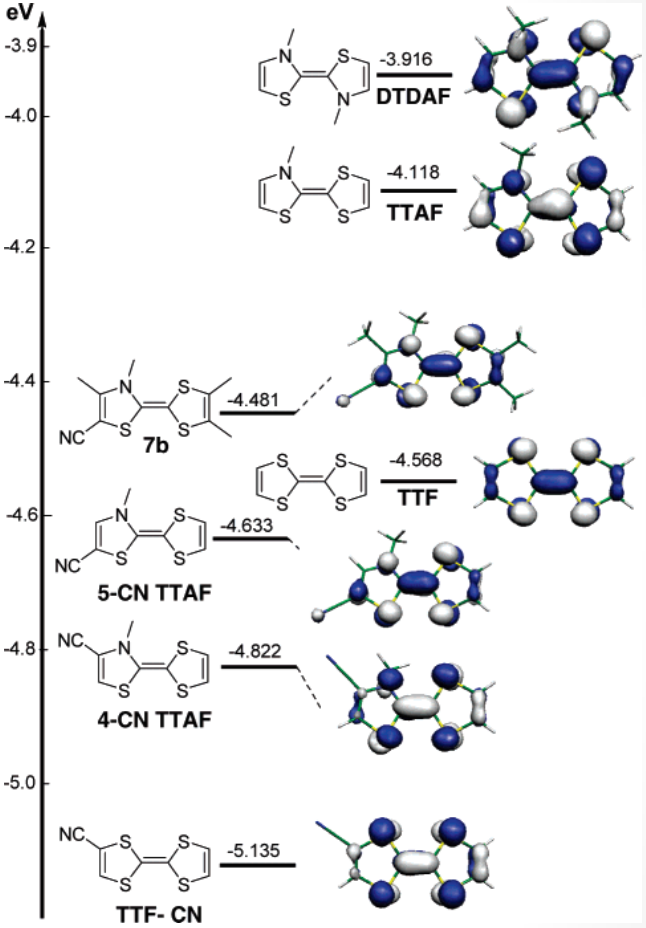
Synthesis **2008**, 5, 696-698

Trithiaazafulvalenes TTAF ver. DTDAF



J. Chem. Soc. Perkin Tr. 1. **1999, 3637**

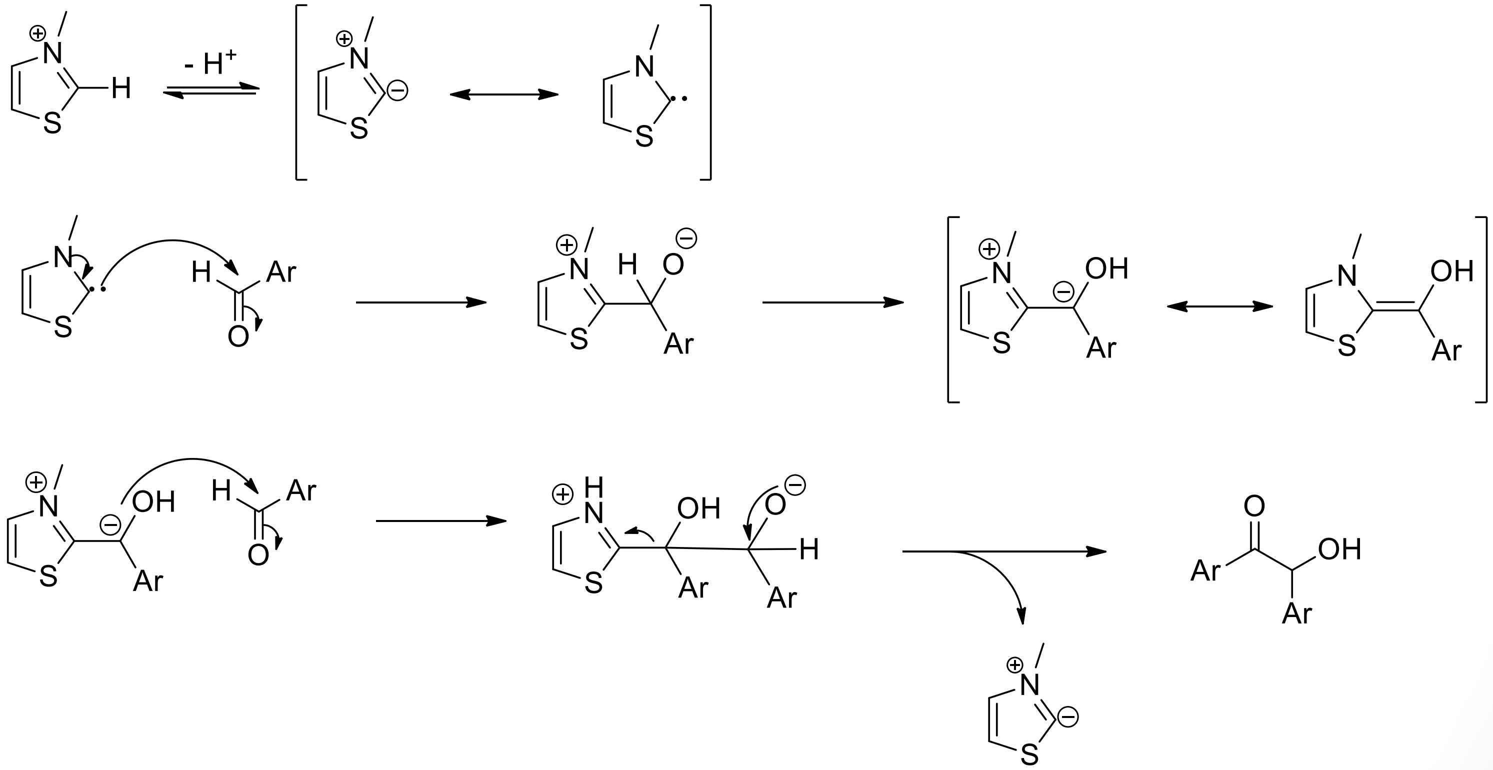




Molecular orbital surfaces and HOMO levels.

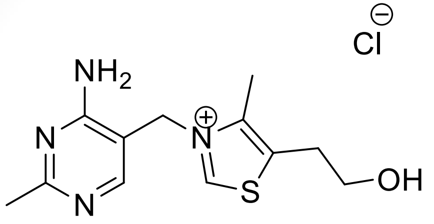
Org. Lett., **2006,** 8**,** 2377

Synthesis of DTDAF - nucleophilic carbene – benzoin condensation

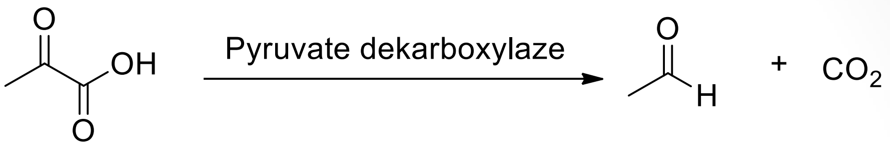


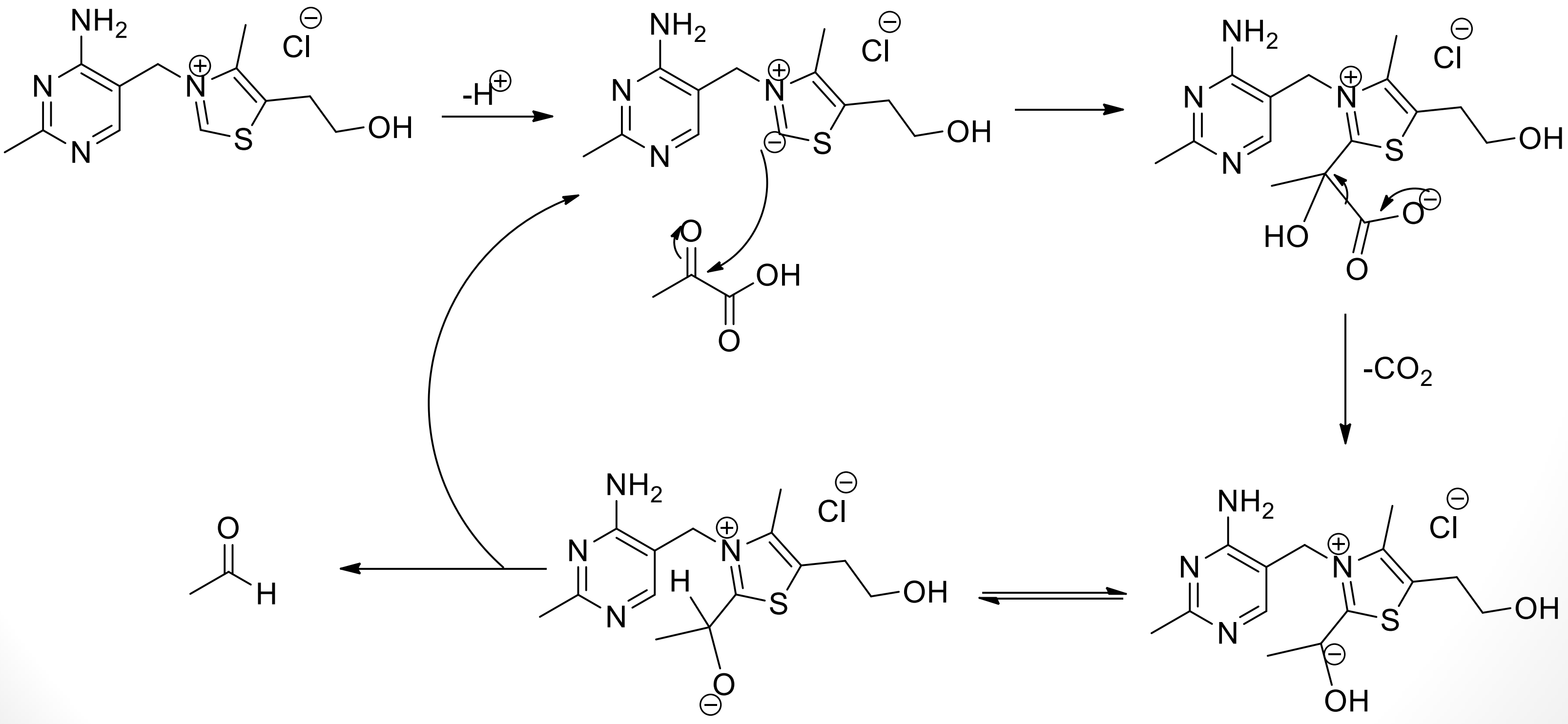
Tetrahedron Letters, Vol, 37. No. 45, pp. 8241-8242, 1996

Pyruvate decarboxylation

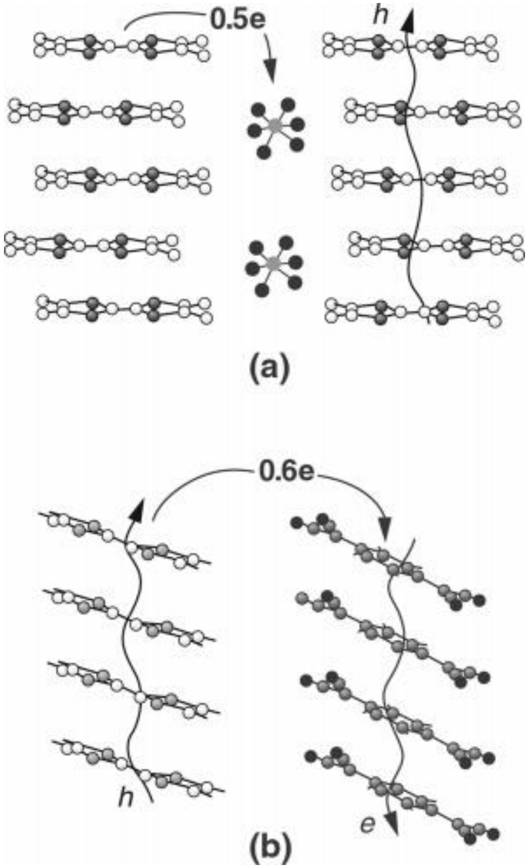


Thiamine (vitamin B_1)



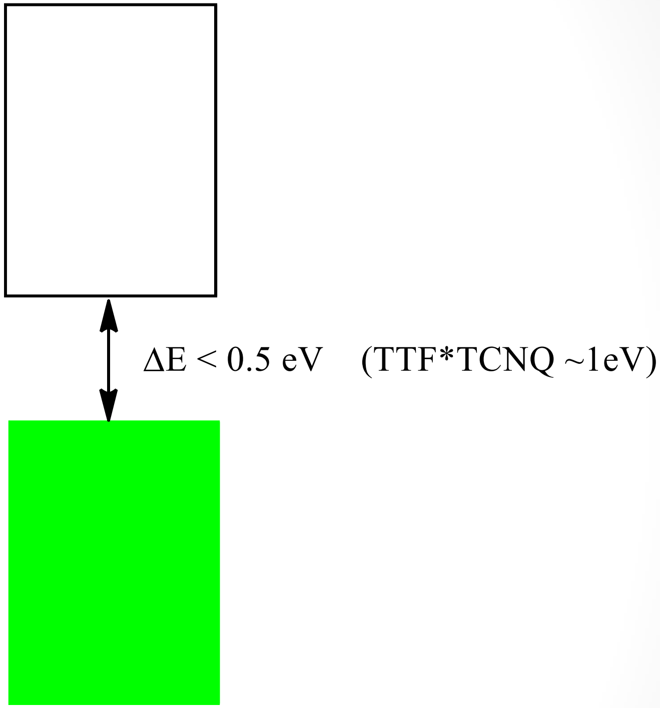


Single-Component Molecular Metals



(a) TMTSF molecule forms a conduction band, and metal electrons are generated by electron transfer between TMTSF and PF^{6-} anions.
(b) In the case of (TTF)(TCNQ), free carriers are generated in both columns by partial charge transfer between TTF and TCNQ.

Chem. Rev. **2004,** 104, 5243-5264

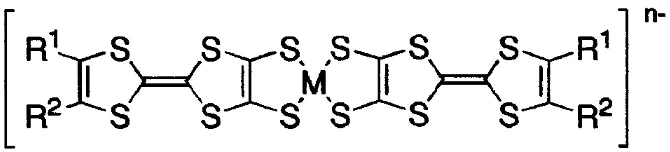


$\Delta E < 0.5$ eV (TTF*TCNQ ~1eV)

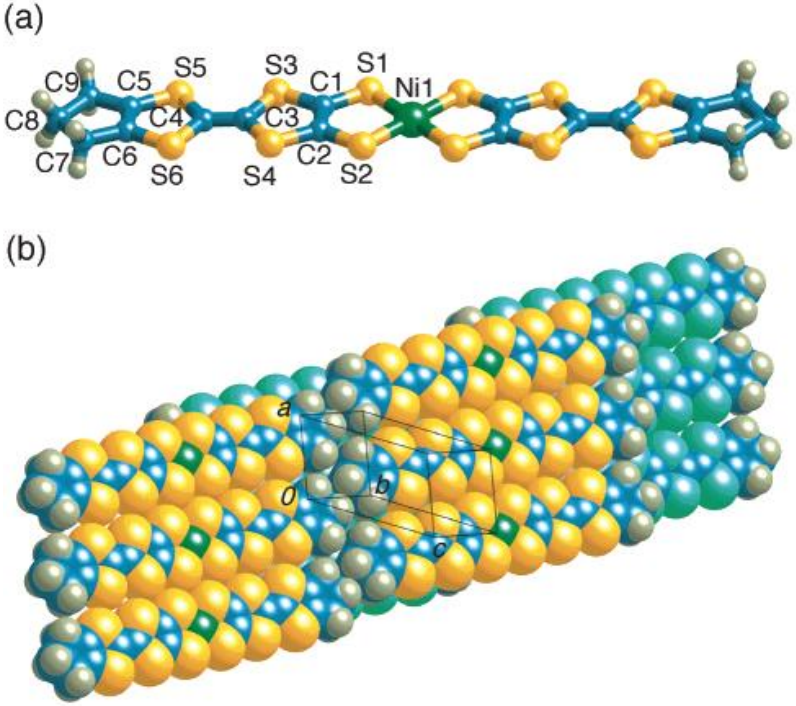
Single component
molecular metal

excitation energy ~4000cm^{-1}

Single-Component Molecular Metals



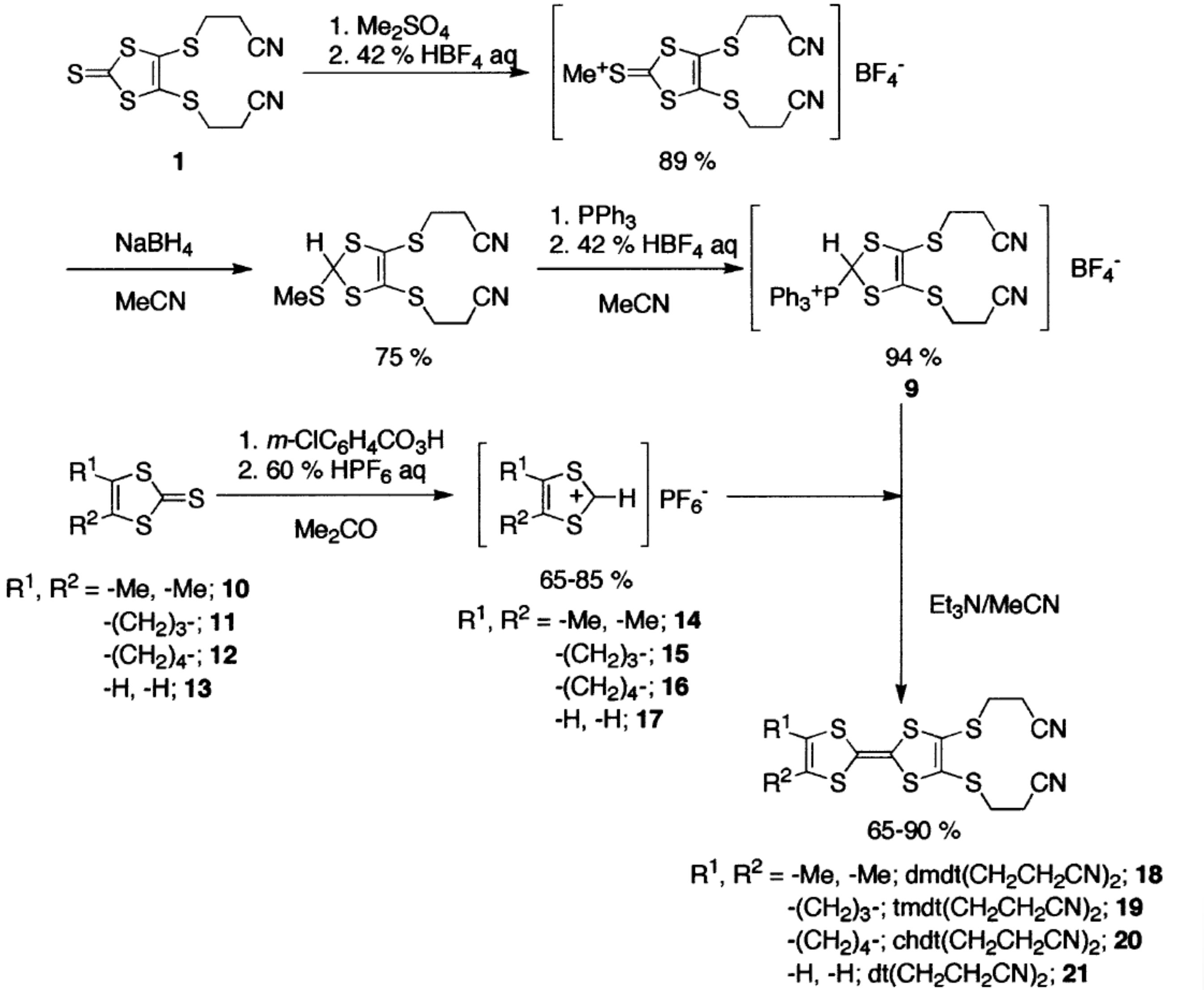
R^1, R^2 = $-CF_3$, $-CF_3$; $\mathbf{[M(hfdt)_2]^{n-}}$
R^1, R^2 = $-(CH_2)_3-$; $\mathbf{[M(tmdt)_2]^{n-}}$
R^1, R^2 = -Me, -Me; $\mathbf{[M(dmdt)_2]^{n-}}$
R^1, R^2 = $-(CH_2)_4-$; $\mathbf{[M(chdt)_2]^{n-}}$
R^1, R^2 = $-O(CH_2)_2O-$; $\mathbf{[M(eodt)_2]^{n-}}$
R^1, R^2 = $-S(CH_2)_3S-$; $\mathbf{[M(ptdt)_2]^{n-}}$
R^1, R^2 = $-S(CH_2)_2S-$; $\mathbf{[M(etdt)_2]^{n-}}$
R^1, R^2 = -SMe, -SMe
R^1, R^2 = -SEt, -SEt
R^1, R^2 = $-S^nPr$, $-S^nPr$; $\mathbf{[M(C3\text{-}tdt)_2]^{n-}}$
R^1, R^2 = $-S^nBu$, $-S^nBu$
M = Co, Ni, Cu, Pd, Pt, Au, Hg, ···



(a) Molecular structure and (b) crystal structure of [Ni(tmdt)2]. The molecule is ideally planar even in the terminal trimethylene group.

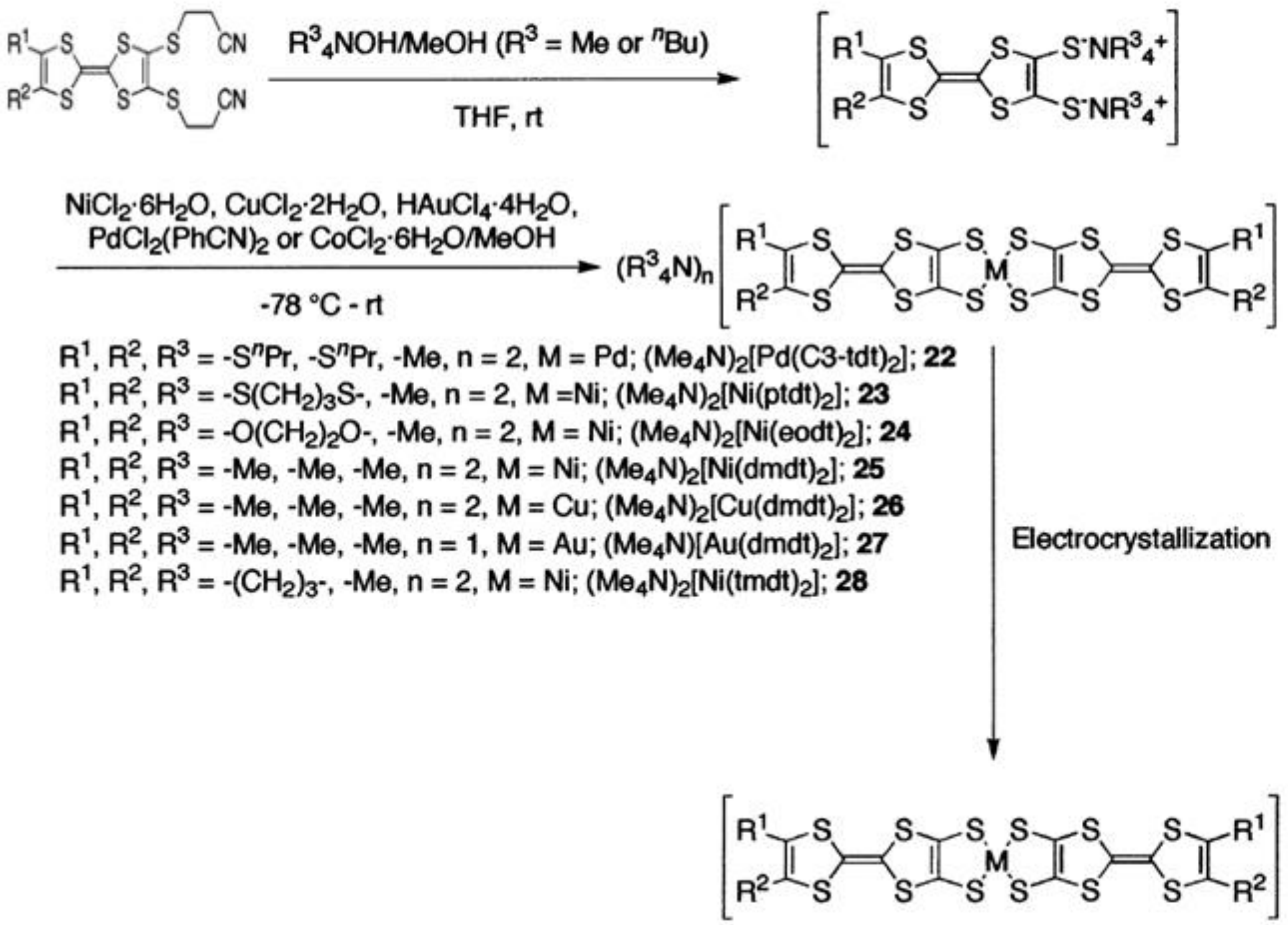
J. Mater. Chem. **2001,** 11, 2078

Single-Component Molecular Metals



Chem. Rev. **2004,** 104, 5243-5264

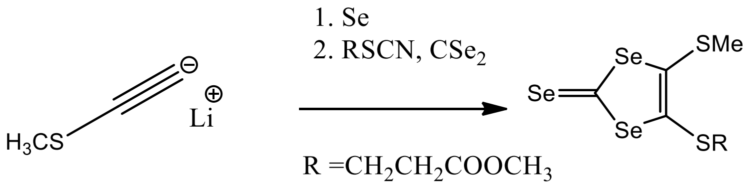
Single-Component Molecular Metals



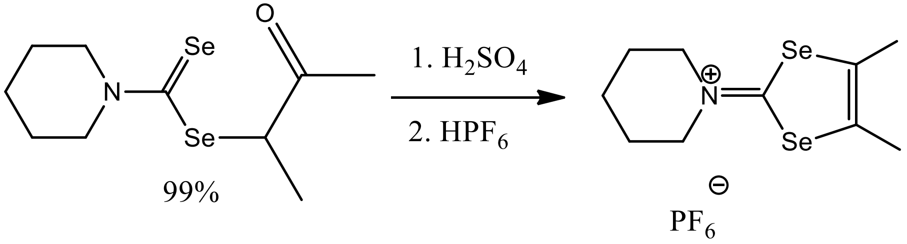
R^1, R^2, R^3 = -S^nPr, -S^nPr, -Me, n = 2, M = Pd; $(Me_4N)_2[Pd(C3\text{-}tdt)_2]$; **22**
R^1, R^2, R^3 = -$S(CH_2)_3S$-, -Me, n = 2, M =Ni; $(Me_4N)_2[Ni(ptdt)_2]$; **23**
R^1, R^2, R^3 = -$O(CH_2)_2O$-, -Me, n = 2, M = Ni; $(Me_4N)_2[Ni(eodt)_2]$; **24**
R^1, R^2, R^3 = -Me, -Me, -Me, n = 2, M = Ni; $(Me_4N)_2[Ni(dmdt)_2]$; **25**
R^1, R^2, R^3 = -Me, -Me, -Me, n = 2, M = Cu; $(Me_4N)_2[Cu(dmdt)_2]$; **26**
R^1, R^2, R^3 = -Me, -Me, -Me, n = 1, M = Au; $(Me_4N)[Au(dmdt)_2]$; **27**
R^1, R^2, R^3 = -$(CH_2)_3$-, -Me, n = 2, M = Ni; $(Me_4N)_2[Ni(tmdt)_2]$; **28**

Chem. Rev. **2004,** 104, 5243-5264

Example questions

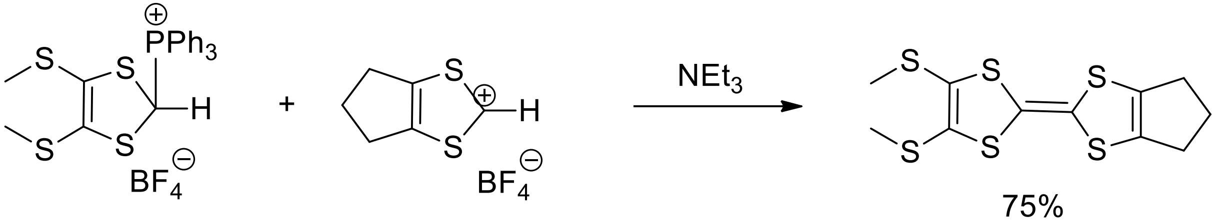


Propose reaction mechanism for the following step, where 4-methylthio-5-(2-methoxycarbonylethylthio)-1,3-diselenole-2-selone is produced.

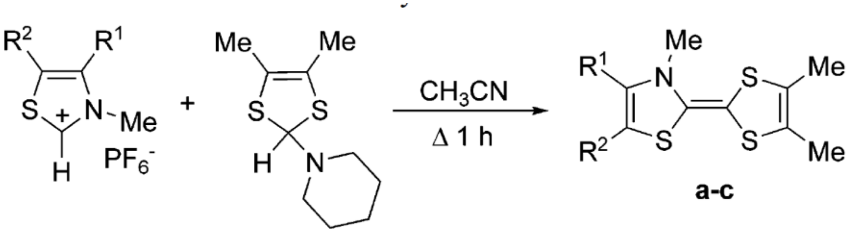


Propose reaction mechanism for the preparation of 2-(1-piperidinium)-4,5-dimethyl-1,3-diselenole hexafluorophosphate.

Example questions



Which process cause formation of symmetrical products?



a-c

a R^1 = Me, R^2 = CO_2Me
b R^1 = Me, R^2 = CN
c R^1 = R^2 = CO_2Me

Suggest possible reaction mechanism
for the following transformation.