Pyridinyl trifluoromethanesulfonates: preparation methods and use in organic synthesis

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The methods for the synthesis of pyridinyl trifluoromethanesulfonates are reviewed. Examples of their use in organic synthesis for the production of valuable products are presented.

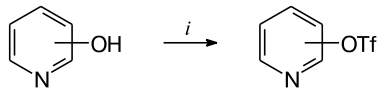
Key words: pyridinyl trifluoromethanesulfonates, diazotization, iodination, amination, Pd-catalyzed C—C cross-coupling reactions.

Methods for synthesis of pyridinyl trifluoromethanesulfonates

Acylation of hydroxypyridines by acid chlorides or anhydrides of the corresponding sulfonic acids (TfCl, Tf_2O, TsCl, MsCl) in the presence of a base has been until recently the general method for the synthesis of pyridinyl sulfonates (pyridinyl triflates, tosylates, and mesylates). This review is devoted to the methods for synthesis of pyridinyl triflates, since these derivatives find increasing use as the starting substrates for the functionalization of the pyridine cycle.

Trifluoromethanesulfonic acid anhydride is used, as a rule, as an acylating agent for the preparation of pyridinyl triflates. Several modifications of this synthetic approach were described. For example, the acylation of 2- and 3-pyridinols was carried out with trifluoromethanesulfonic acid anhydride in a pyridine medium[1] in the yields of pyridin-2-yl and pyridin-3-yl triflates **1a**,**b** higher than 80% (Scheme 1).

Scheme 1



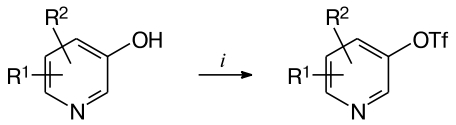
1a,b

1	Position of OTf	Yield (%)
a	2	96
b	3	87

Reagents and conditions: *i*. 1.1 equiv. Tf_2O, Py, 12 h, 0→20 °C.

It is more convenient[2,3] to synthesize pyridin-3-yl triflate (**1b**) by the acylation of 3-hydroxypyridine with trifluoromethanesulfonic acid anhydride in dichloromethane in the presence of equimolar amounts of pyridine in an inert atmosphere. Similar conditions were used[4] for the production of a series of pyridin-3-yl trifluoromethanesulfonate derivatives **1b**—**f** (Scheme 2).

Scheme 2



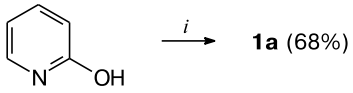
1b—f

1	R^1	R^2	Yield (%)	1	R^1	R^2	Yield (%)
b	H	H	54	**e**	5-Cl	H	67
c	6-Me	H	89	**f**	2-NO_2	6-Me	98
d	2-Cl	H	75				

Reagents and conditions: *i*. 1.1 equiv. Tf_2O, 1.5 equiv. Py, CH_2Cl_2, N_2, 12 h, 0→20 °C.

The improvement of methods for acylation of pyridinols is related to the use of inorganic bases and modified acylating agents. It was shown[5] that 2-hydroxypyridine can successfully be converted into the corresponding triflate **1a** in an aqueous-toluene solution under the action of trifluoromethanesulfonic acid anhydride in the presence of K_3PO_4 (Scheme 3).

Scheme 3

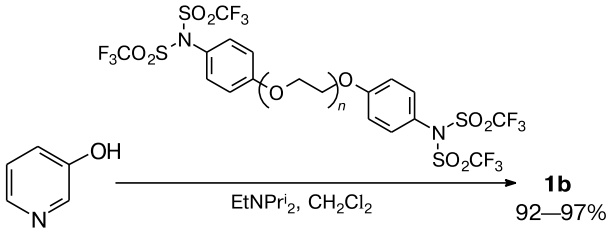


Reagents and conditions: *i*. 1.2 equiv. Tf_2O, K_3PO_4, $PhCH_3$.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2559—2567, November, 2016.

Polymeric trifluoromethanesulfimide in the presence of diisopropylethylamine was used[6] to prepare triflate **1b**, the yield of which turned out to be almost quantitative (Scheme 4).

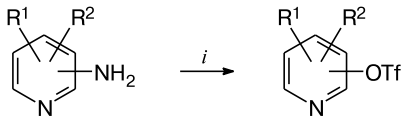
Scheme 4



It should be emphasized that predominantly 2- and 3-pyridyl triflates are obtained by the acylation of pyridinols.

It has recently been shown[7] that the diazotization of 2-, 3-, and 4-aminopyridines in the presence of TsOH in one step results in the corresponding pyridinyl tosylates. As found later,[8] the diazotization of accessible aminopyridines under the conditions of triturating of $NaNO_2$ and TfOH in a DMSO paste can serve as a new general method for synthesis of pyridinyl triflates **1a**,**b**,**g**—**o** (Scheme 5).

Scheme 5



1a,b,g—o

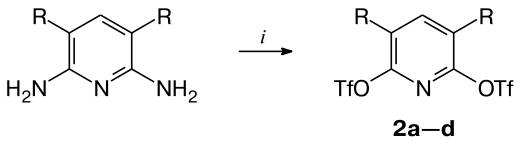
1	R^1	R^2	Position of OTf	Yield (%)
a	H	H	2	65
b	H	H	3	70
g	2-Cl	H	3	75
h	5-Cl	H	2	89
i	5-Br	H	2	70
j	5-I	H	2	78
k	5-NO_2	H	2	86
l	4-Me	H	2	90
m	6-Me	H	2	80
n	3-Br	5-Br	2	56
o	H	H	4	60

Reagents and conditions: *i.* 2.5 equiv. $NaNO_2$, 3 equiv. TfOH, DMSO, ~20 °C.

Among advantages of the method are[8] a high accessibility of the starting aminopyridines compared to pyridinols, the possibility to obtain not only 2- and 3- but also 4-pyridyl triflate (**1o**), and mild reaction conditions. At the same time, it is difficult to scale the process of triturating in paste and the trituration is very long (up to 36 h) and cannot be used in combinatory chemistry and under conditions of flow reactor. For these reasons, a method for the preparation of pyridinyl triflates **1a**,**b**,**g**—**o** in 75—96% yields has recently been developed[9] by the diazotization of aminopyridines $NaNO_2$ and TfOH in a hexane solution with DMSO additives at room temperature. In this variant, the process is much faster than in a DMSO paste (to 1 h) and can be implemented successfully using 10 mmoles of the starting aminopyridine.

It is important that this method[9] made it possible for the first time to obtain pyridyl-2,6-ditriflates **2a**—**d** (Scheme 6).

Scheme 6



2a—d

2	R	Yield (%)	**2**	R	Yield (%)
a	H	61	**c**	Br	45
b	F	45	**d**	I	56

Reagents and conditions: *i.* 5 equiv. $NaNO_2$, 6 equiv. TfOH, DMSO, ~20 °C.

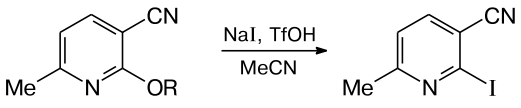
2-Aminoquinoline was transformed into quinolin-2-yl triflate in a yield of 83% using the same approach.[9]

The formation of pyridinyl triflates and tosylates by the diazotization of aminopyridines in the presence of TfOH and TsOH (see Refs 7—9) drastically distinguishes aminopyridines from anilines, which, under similar conditions, give relatively stable diazonium salts, for example, tosylates $ArN_2^+TsO^-$, but not aryl sulfonates.[10]

Pyridinyl trifluoromethanesulfonates as valuable building blocks in organic synthesis

As shown previously,[11] the triflate group has a better leaving ability than other sulfonate groups (OTs, OMs), which allows rather easy further functionalization of the pyridine cycle to perform. For example, the conversion of 3-cyano-6-methylpyridinyl sulfonates (triflate, tosylate, and mesylate) was determined in the nucleophilic substitution of the sulfonate group (OTf, OTs, OMs) by the iodide ion in an acetonitrile solution in the presence of trifluoromethanesulfonic acid (Scheme 7).

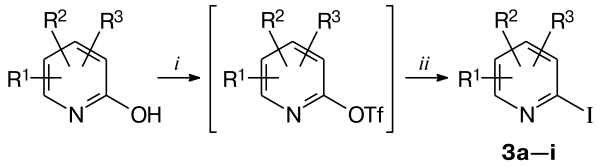
Scheme 7



R	Tf	Ts	Ms
Conversion (%)	100 (10 min)	<5	<5

The results obtained made it possible to develop the one-step synthesis of various iodopyridines **3a—i** from hydroxypyridines *via* the intermediate formation of pyridinyl triflates (Scheme 8).

Scheme 8



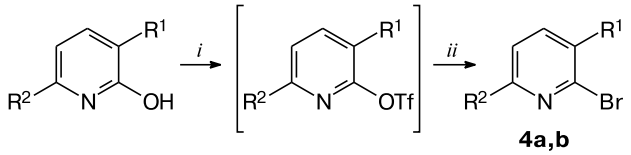
3a—i

3	R^1	R^2	R^3	Yield (%)
a	H	H	H	90
b	3-CN	4-Me	6-Me	94
c	3-CN	5-Cl	6-Me	95
d	3-CN	5-Br	6-Me	98
e	3-NO_2	4-Me	H	92
f	5-CO_2Me	H	H	97
g	3-Me	H	H	95
h	5-Cl	H	H	94
i	3-OMe	H	H	90

Reagents and conditions: *i*. 1.1 equiv. Tf_2O, 1.15 equiv. Py, MeCN or $PhCH_3$, 2 h, ~20 °C. *ii*. 1.1 equiv. HCl or TfOH, 5 equiv. NaI, 2 h, ~20 °C.

It is shown that the substitution of the triflate group by the iodide ion is significantly facilitated by the quaternization of the pyridine cycle with strong acids. The best yields of iodopyridines are obtained in the presence of additives of hydrochloric or trifluoromethanesulfonic acid.[11] This approach was successfully used[11] in the syntheses of 2-bromopyridine (**4a**) and 2-bromo-6-methylnicotinenitrile (**4b**) in the yields higher than 90% (Scheme 9).

Scheme 9



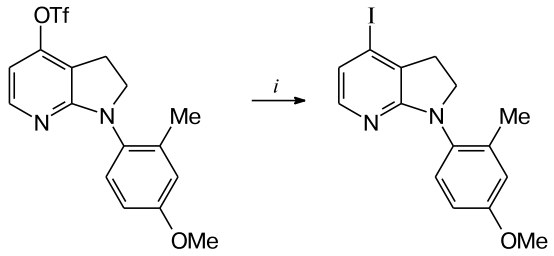
4a,b

4a: $R^1 = R^2 = H$ (90% yield); **4b:** R^1 = CN, R^2 = Me (98% yield)

Reagents and conditions: *i*. 1.1 equiv. Tf_2O, 1.15 equiv. Py, $PhCH_3$, 2 h, ~20 °C. *ii*. 1.1 equiv. TfOH, 5 equiv. LiBr, 18 h, ~20 °C.

The transformation of pyridinyl triflates into iodopyridines can also be carried out under the conditions traditional for S_N reactions: under the action of KI in DMF.[12] However, the best results are achieved in the presence of additives of the acids.[13,14] For example, 4-iododihydropyrrolopyridine **6**, which is the key intermediate in the synthesis of valuable CRF-1 antagonists, was obtained in a high yield from triflate **5** in the presence of MsOH (Scheme 10).

Scheme 10



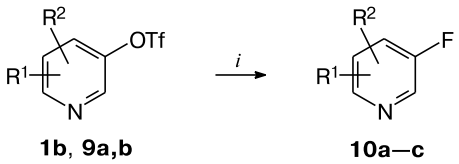
5 **6** (90%)

Reagents and conditions: *i*. KI, MsOH, DMF, 85 °C, 1.5 h.

The pyridine cycle was quaternized for the facilitation of the replacement of the triflate group in 6-methylpyridin-2-yl triflate (**7**) by the iodine atom also using acetyl chloride.[15] The reaction occurs under microwave irradiation with a low yield (33%) of 2-iodo-6-methylpyridine (**8**).

The triflate substituent in compounds **1b** and **9a**,**b** can also be substituted by the fluorine atom under the action of the palladium catalyst with the specific phosphine ligand $[(cod)(L \cdot Pd)_2]$, where cod is 1,5-cyclooctadiene and L is 2-(di-1-adamantylphosphino)-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl (AdBrettPhos), to form 3-fluoropyridines **10a—c** in moderate yields (Scheme 11).[16] This method is promising for the preparation of pyridines labeled with the ^{19}F isotope, which are used in positron emission tomography diagnostics.

Scheme 11



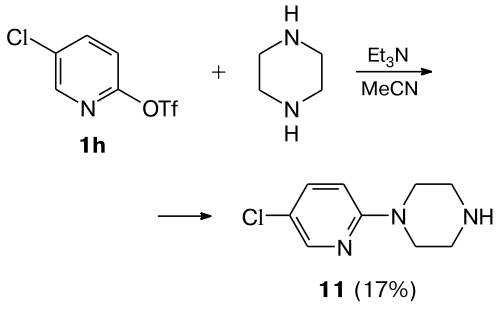
1b, **9a,b** **10a—c**

Compound	R^1	R^2	Yield **10** (%)
1b, **10a**	H	H	30
9a, **10b**	3-CO_2Me	H	44
9b, **10c**	2-Et	6-Me	64

Reagents and conditions: *i*. 3 equiv. CsF, $[(cod)(AdBrettPhos \cdot Pd)_2]$ (4%), toluene, 120—130 °C, N_2, 14 h.

Several examples were published for triflate group substitution in pyridines by the amine group for the preparation of biologically active aminopyridines or their precursors. The conversion of 5-chloropyridin-2-yl triflate (**1h**) to selective adrenoblocker **11** on heating with piperazine in acetonitrile in the presence of triethylamine in an insignificant yield was described[17] (Scheme 12).

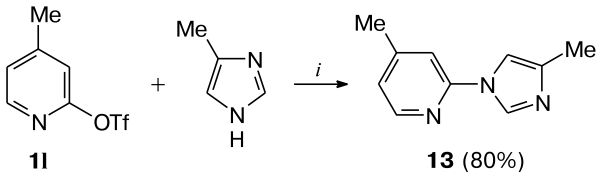
Scheme 12



11 (17%)

The amination of pyridinyl triflate **1a** by morpholine occurs more successfully on heating in DMSO,[18] and the yield of 4-(pyridin-2-yl)morpholine (**12**) is 70%. The use of palladium catalysis and 2-di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropyl-1,1′-biphenyl (Me_4Bu^tXPhos) as a ligand is needed for the amination of triflate **1l** with 4-methylimidazole to form compound **13** (Scheme 13).[19]

Scheme 13

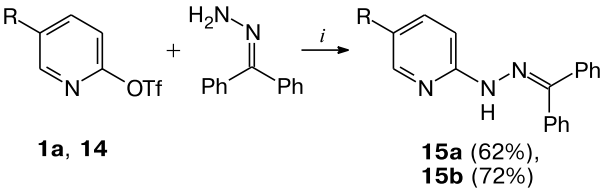


1l **13** (80%)

Reagents and conditions: *i*. $Pd_2(dba)_3/Me_4Bu^tXPhos/K_3PO_4$, toluene—dioxane (5 : 1), 120 °C, 5 h.

The substitution of the triflate group in pyridines **1a** and **14** by (diphenylmethylene)hydrazine under the action of $Pd(OAc)_2$ in the presence of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) was used for the synthesis of hydrazinopyridines **15a**,**b** (Scheme 14). It is important[20] that the corresponding 2-bromopyridines turned out to be more reactive in the described transformations than triflates **1a** and **14**.

Scheme 14



1a, **14** **15a** (62%), **15b** (72%)

R = H (**1a**, **15a**), CO_2Et (**14**, **15b**)

Reagents and conditions: *i*. $Pd(OAc)_2$/BINAP, $NaOBu^t$, toluene, 100 °C.

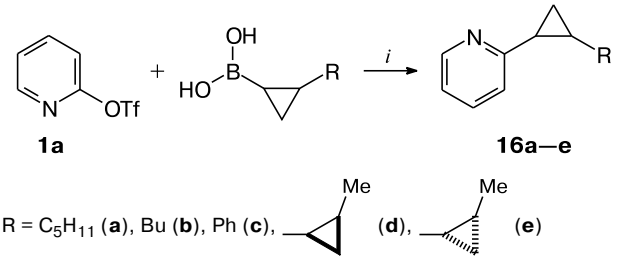
The higher reactivity of 2-bromopyridine compared to that of triflate **1a** appeared in the amination of by protected guanidine ($H_2N(NH)CNHCH_2C_6H_4OMe$-4) in the presence of the copper complexes[21]: the yields of the substitution products were 91 and 45% for 2-bromopyridine and triflate **1a**, respectively.

Pyridinyl triflates along with the pyridine haloderivatives are used in the C—C cross-coupling reactions catalyzed by transition metals.

The highly functionalized pyridines, many of which have biological activity,[22,23] are obtained by the reactions of pyridinyl triflates with boronic acids[22—27] (Suzuki reaction and its modification).

The C—C cross-coupling of triflate **1a** with cyclopropylboronic acids[22] catalyzed by the palladium—phosphine complex resulted in cyclopropylpyridines **16a—e** in 71—77% yields (Scheme 15).

Scheme 15

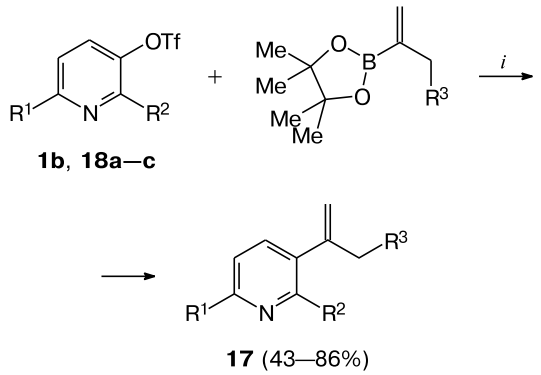


1a **16a—e**

Reagents and conditions: *i*. $Pd(PPh_3)_4$ (0.03 mol.%), 3.3 equiv. $KF \cdot 2H_2O$, 1 equiv. NaBr, toluene, 100 °C.

3-Alkenylpyridines **17**, *viz.*, precursors of alkaloids cananodine and xestamine C, were obtained in good yields by the reactions of unsaturated boronic acid esters and pyridin-3-yl triflates **1b** and **18a—c** (Scheme 16).[23]

Scheme 16



1b, **18a—c** **17** (43—86%)

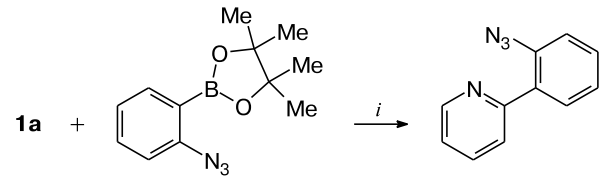
18: R^1 = H, R^2 = Me (**a**); R^1 = Me, R^2 = H (**b**); R^1 = Me, R^2 = $CH_2OC(O)Bu^t$ (**c**)

R^3 = prenyl, All, Pr, (2,2,5,5-tetramethyl-1,3-dioxolan-4-yl)methyl

Reagents and conditions: *i*. $Pd(PPh_3)_4$ (10 mol.%) or $Pd(dppf)Cl_2$ (10 mol.%), 3 equiv. K_3PO_4, dioxane, 80—100 °C.

The Suzuki reaction was used for the preparation of azidophenylpyridine **19** (Scheme 17) in an inert atmosphere.[24]

Scheme 17

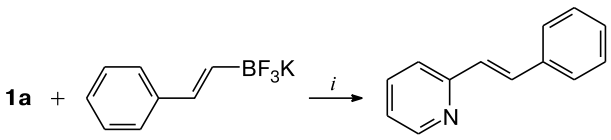


19 (40%)

Reagents and conditions: *i.* $PdCl_2(PPh_3)_2$, $NaHCO_3$, THF, 80 °C.

The cross-coupling of potassium trifluoro(hex-1-yn-1-yl)borate with triflate **1a** (Suzuki—Miyaura reaction) under the action of $PdCl_2(dppf)$[25] (dppf is 1,1′-bis(diphenylphosphino)ferrocene) gives a moderate yield of 2-(hex-1-ynyl)pyridine (**20**). It was shown[26] that the condensation of triflate **1a** with potassium styryl trifluoroborate in the presence of $PdCl_2(dppf)$ afforded 2-styrylpyridine (**21**) in a yield of 41% (Scheme 18), whereas 2-bromopyridine, under the same conditions, provides 70% yield of compound **21**.

Scheme 18



21 (41%)

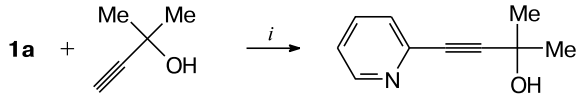
Reagents and conditions: *i.* $PdCl_2(dppf) \cdot CH_2Cl_2$, Bu^tNH_2, $Pr^iOH—H_2O$ (2 : 1), Δ.

In the condensation with derivative 9-BBN under the action of $Pd(PPh_3)_4$, triflate **1b** is also inferior in reactivity to 3-bromo- and 3-iodopyridine.[27]

Pyridinyl triflates are used rather frequently in the Pd-catalyzed cross-coupling with alkynes under the conditions of the Sonogashira reaction. Triflate **1a** was successfully applied for the synthesis of ethynylpyridine **22** at one of the steps of complete synthesis of selective ionic blocker of neuron acetylcholine: (*S*)-(−)-5-ethynyl-3-(1-methyl-2-pyrrolidinyl)pyridine[28] (Scheme 19).

It was shown[29] that triflate **1a** and quinolin-2-yl and isoquinolin-1-yl triflates easily reacted with trimethylsilylacetylene under the action of $Pd_2(dba)_3/P(o\text{-}Tol)_3$ in DMF or THF to give the corresponding alkynyl derivatives in 52—92% yields. The synthesis of compound **23** as a precursor of antitumor drug dinemicyn A(1) was synthesized under the determined conditions[29] (Scheme 20).

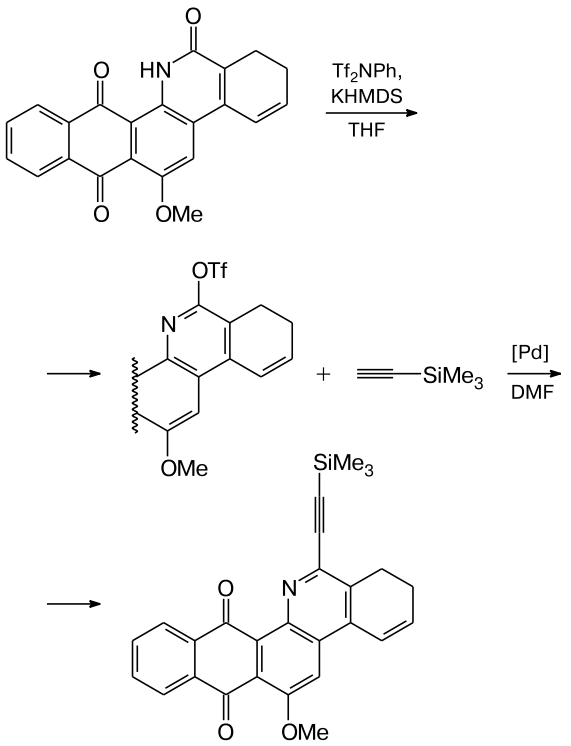
Scheme 19



22 (95%)

Reagents and conditions: *i.* Pd/C (2 mol.%), PPh_3 (8 mol.%), CuI (4 mol.%), 2.5 equiv. K_2CO_3, H_2O—DME (1 : 1), 80 °C, 16 h.

Scheme 20



23 (61%)

KHMDS is potassium hexamethyldisilazide.

The use of triflate **1a** in the Sonogashira—Hagihara condensation[30] with trimethyl(phenylethynyl)silane catalyzed by $Pd(PPh_3)_4$/CuCl in DMF provides 2-(phenylethynyl)pyridine in 68% yield.

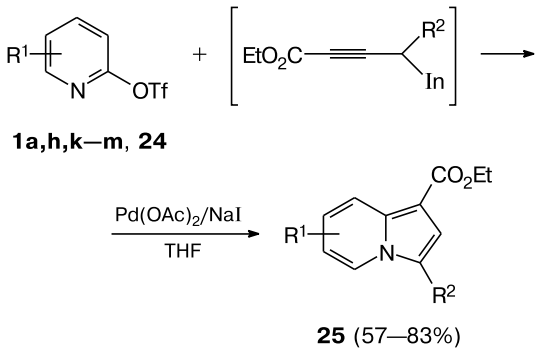
The Pd-catalyzed tandem reaction[31] of pyridin-2-yl triflates **1a**,**h**,**k**—**m** and **24** with *in situ* generated In derivatives of acetylenecarboxylates affords highly functionalyzed indolizines **25** in good yields (Scheme 21).

It is noteworthy that the reactivity of pyridyl triflates in this reaction is almost the same as that of iodopyridines.[31]

The condensation of triflate **1b** with styrene under the conditions of the Heck reaction ($Pd(OAc)_2$, K_2CO_3, KI, DMF, 80 °C)[32] provides a quantitative yield of 3-styrylpyridine (**26**).

Aromatic triflates ArOTf are very frequently used in the Stille C—C cross-coupling reactions. Pyridyl triflates

Scheme 21

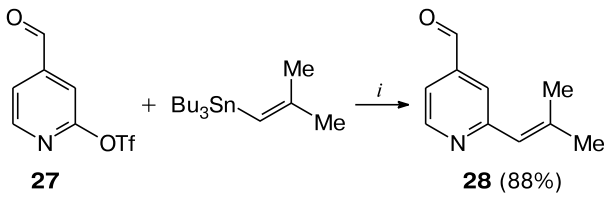


R^1 = 5-Me (**24**); R^2 = Me, Et, Pr, $PhCH_2CH_2$

along with bromopyridines are also used in this reaction.[1,33—40] The main advantage of the Stille reaction is tolerance to the most part of functional groups, which allows one to synthesize complicated molecular structures. 4-Formylpyridin-2-yl triflate (**27**) was used[34,35] in the full synthesis of pigment A2E. One of the key steps of this synthesis, namely, C—C cross-coupling with the formation of unsaturated isonicotinealdehyde **28** in a high yield, is shown in Scheme 22.

The use of highly functionalized pyridin-2-yl triflate **29** in the convergent method of synthesis of alkaloid strepto-

Scheme 22



Reagents and conditions: *i.* $Pd(PPh_3)_4$, LiCl, CuI, dioxane, Δ.

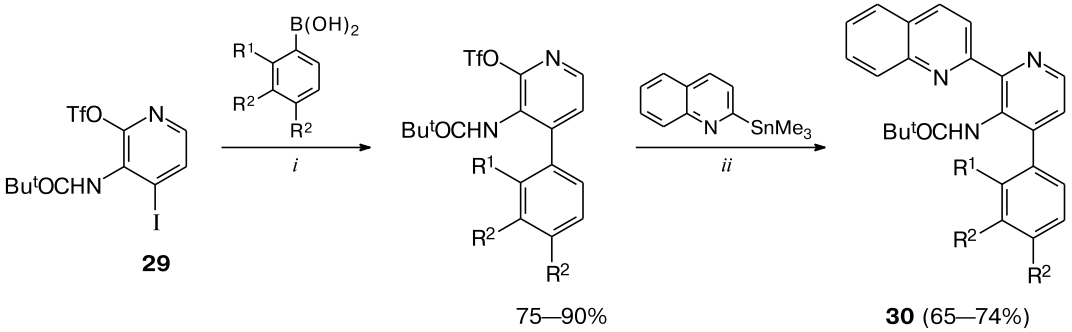
nigrin[36] made it possible to obtain 2-[2-(4-phenyl-3-pivaloylamino)pyridinyl]quinolines **30** (Scheme 23). The selective substitution of the iodine atom in substrate **29** occurs in the first step, and further the Stille C—C cross-coupling provides the functionalization of the pyridine fragment at the triflate group.

It should also be mentioned that pyridinyl triflates were used for the synthesis of organostannates for the Stille reactions[37] and, in addition, their use as ligands of the palladium—phosphine complexes was described.[38—40]

The C—C cross-coupling of 2- and 3-pyridyl triflates **1a**,**b** with organosilicon reagent **31**, which is an alternative for Sn reagents, was carried out[1] to form 2- and 3-phenylpyridines **32a**,**b** (Scheme 24).

It was found[41] that methylpyridin-2-yl triflates **1l**,**m** and **24** can enter into the Negishi reaction with pyridin-2-

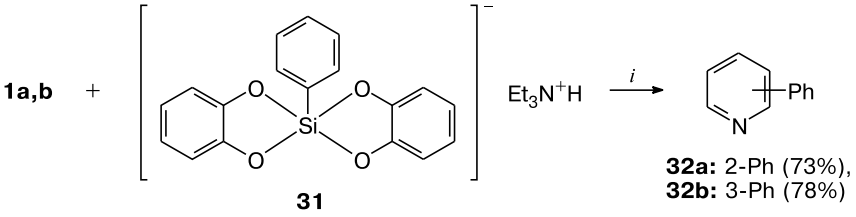
Scheme 23



R^1, R^2 = H, OMe, $CONPr^i_2$

Reagents and conditions: *i.* $Pd(PPh_3)_4$ (2.5 mol.%), 2 equiv. Na_2CO_3, argon, EtOH/toluene, Δ, 12 h. *ii.* 3 equiv. LiCl, $Pd(PPh_3)_4$ (3 mol.%), dioxane, Δ, 15—36 h.

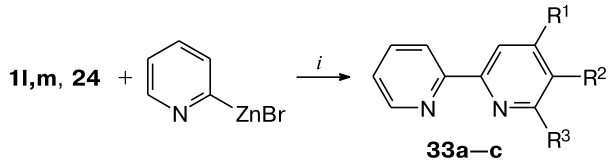
Scheme 24



Reagents and conditions: *i.* $Pd(dba)_2$ (5 mol.%), Buchwald phosphine (5 mol.%), 1.5 equiv. Bu_4NF, dioxane, Δ, 6 h.

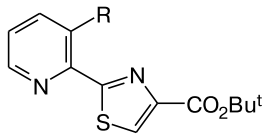
ylzinc bromide to give nonsymmetric 2,2′-bipyridyls **33a—c** in very high yields (Scheme 25).

Scheme 25

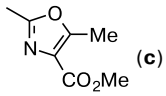


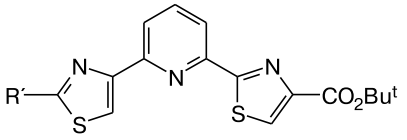
33	R^1	R^2	R^3	Yield (%)
a	Me	H	H	94
b	H	Me	H	90
c	H	H	Me	95

Reagents and conditions: *i*. $Pd_2(dba)_3$, PPh_3, LiCl, THF.

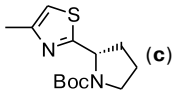


34a—c

R = H (**a**), CO_2H (**b**),  (**c**)



35a—c

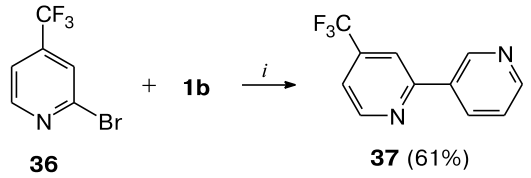
R′ = CO_2Me (**a**), COMe (**b**),  (**c**)

The substitution of the triflate group in pyridines in thiazolyl-2-zinc(II) bromide in the Negishi reaction was used in the syntheses of pyridinylthiazoles **34a—c** and **35a—c** exhibiting biological activity.[42]

In addition to the presented above Stille[36,37] and Negishi[41,42] cross-coupling reactions, the arylation of pyridinyl triflates are carried out using various catalytic systems based on palladium,[43—45] bismuth,[46] and indium[47] to give, as a rule, arylpyridines in good yields. This can be exemplified by the work[48] where two catalysts based on nickel and palladium provide a unique possibility of selective C—C condensation of bromopyridine **36** with triflate **1b** (Scheme 26).

The palladium catalyst was shown[48] to activate triflate **1b**, whereas the nickel catalyst activates bromopyridine **36**. The high selectivity of the process with the predominant formation of nonsymmetric bipyridine **37** was achieved due to the exact selection of the composition of the catalytic system.

Scheme 26



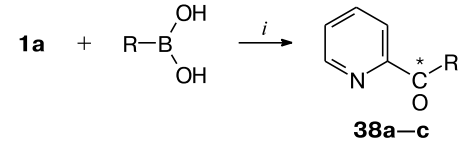
36 **37** (61%)

Reagents and conditions: *i*. $NiBr_2$ (diglyme) (5 mol.%), 2,2′-bipyridine (5 mol.%), $PdCl_2$ (5 mol.%), 1,3-bis(diphenylphosphino)propane (5 mol.%), 2 equiv. Zn, 1 equiv. KF, DMF, 40 °C.

The Pd-catalyzed reactions of carbonylation of pyridinyl triflates by CO are of interest. In these transformations, pyridinyl triflates are not inferior in reactivity to iodopyridines.

Pyridin-3-yl triflate (**1b**) can enter into the Pd-catalyzed alkoxycarbonylation[49] in methanol under a CO pressure to form 3-pyridinylethanone **38a** in 72% yield. A series of pyridinyl ketones **38a—c** containing the carbonyl carbon isotope ^{11}C was obtained[50] from triflate **1a** (Scheme 27).

Scheme 27



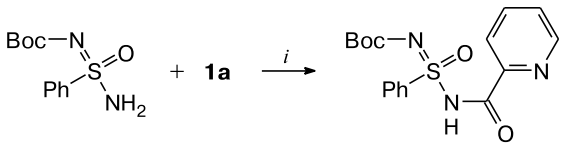
38a—c

38	R	Yield (%)	38	R	Yield (%)
a	Me	33	**c**	Ph	74
b	4-FC_6H_4	67			

Reagents and conditions: *i*. $Pd(PPh_3)_4$ (^{11}CO), THF, LiBr, 0.08 h, 150 °C.

The method of Pd-catalyzed amidocarbonylation of aromatic triflates by sulfonimidamides was proposed.[51] The use of triflate **1a** for these purposes gives picolinesulfamide (**39**) in a moderate yield (Scheme 28).

Scheme 28

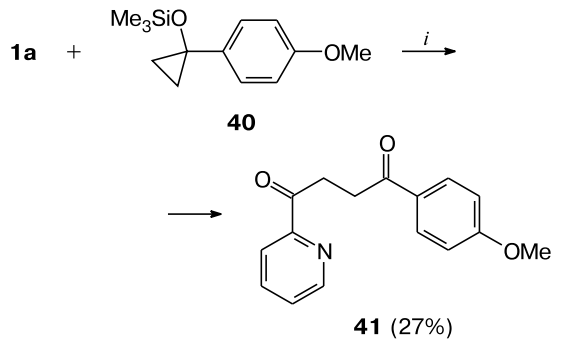


39 (46%)

Reagents and conditions: *i*. $Pd(dppf)Cl_2$, $Mo(CO)_6$, Et_3N, DBU, dioxane, 80 °C, 4 h.

1,4-Diketone **41** was obtained[52] in a low yield by the reaction of triflate **1a** with arylsiloxycyclopropane (**40**) in an atmosphere of carbon monoxide under a pressure of 10—20 bar (Scheme 29).

Scheme 29



Reagents and conditions: *i*. $Pd(PPh_3)_2$ (0.005 equiv.), CO, HMPA, 90 °C, 10 bar, 40 h.

Thus, the data presented demonstrate a wide range of synthetic transformations of pyridinyl trifluoromethanesulfonates. The best leaving ability of the triflate group in a series of other sulfonate groups (tosylate, mesylate) provides a possibility of the further functionalization of the pyridine cycle with the formation of both intermediates of organic synthesis and important biologically active substances.

A certain factor restraining a wider use of pyridinyl triflates is their high cost when preparing by the acylation of pyridinols with Tf_2O. The recently appeared methods for the synthesis of pyridinyl triflates by the diazotization of cheap aminopyridines in the presence of TfOH make these substances more available and extend possibilities of their practical use.

This work was financially supported by the Ministry of Education and Science of the Russian Federation (State Task "Nauka," Project No. 4.1991.2014K) and the Russian Science Foundation (Project No. 15-13-10023).

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Received February 11, 2016;
in revised form July 11, 2016