

# *Snapshots of Some Topics of Recent Advances in Chemistry*

- Synthesis of Angular Hetarenocoumarins
- Isolation of Ni(II) *meso*-dimesitylnorcorrole radical anion
- Synthesis of Alkyl-Co complexes containing polydentate ligands as directing groups *via* C(sp<sup>3</sup>)-H activation
- Asymmetric synthesis of chiral pyrrolidines *via* oxetane desymmetrization

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# Snapshots of some topics of interest of recent notable advances in chemistry

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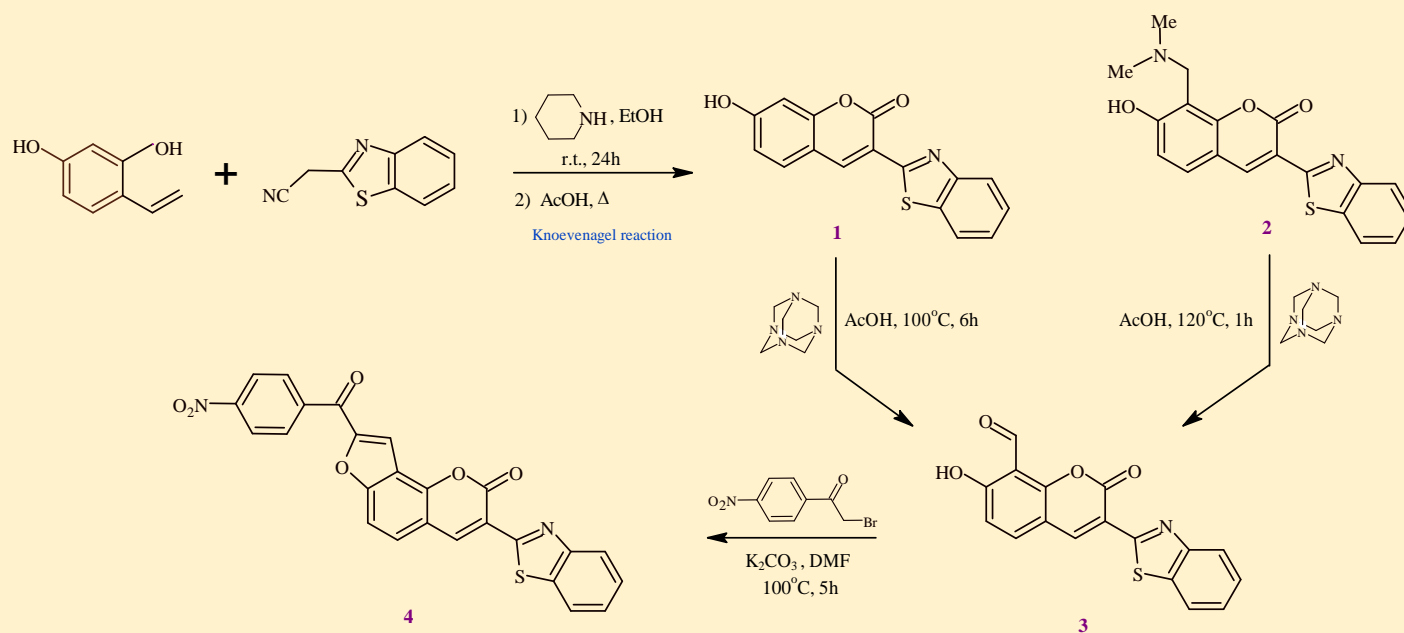
# Synthesis of Angular Hetarenocoumarins

The preparation of angular hetarenocoumarins starting from 7-hydroxy-3-(benzothiazole-2-yl)-coumarin is highlighted.

KEYWORDS: 7-hydroxy-3-benzothiazolylcoumarin, aminomethylation, formylation, cyclization, hetarenocoumarins.

Coumarins are naturally occurring active constituents of various plants and exhibit an extraordinary array of biochemical and pharmacological activity. Furthermore, this class of phenolic compounds formed by the association of  $\beta$ -pyrone rings with benzene has remarkable applications in dye industries owing to their outstanding photophysical properties. In this regard, Shokel *et al.* examined their work on 7-hydroxy-3-(benzothiazol-2-yl)coumarin **1** to synthesize angular hetarenocoumarin compounds, namely furo[2,3-*h*]chromen-2-ones.

*o*-hydroxy-formyl coumarins are considered as an appropriate substrate for the synthesis of hetarenocoumarins. Thus, targeting the preparation of 8-formylcoumarin, namely 3-(1,3-benzothiazol-2-yl)-7-hydroxy-2-oxo-2*H*-8-chromenecarbaldehyde **3** was achieved by the reaction of **1** with hexamethylenetetramine in acetic acid *via* the Duff reaction (Scheme 1). Also, 8-formylcoumarin **3** can be prepared from 3-(1,3-benzothiazol-2-yl)-8-dimethylamino-methyl-7-hydroxy-2*H*-2-chromenone **2** *via* the Duff reaction. It is worth noting that compound **2** can be prepared *via* aminomethylation under classical Mannich reaction conditions using benzylamines in dioxane. Finally, the furo[2,3-*h*]chromen-2-one system **4** was obtained from compound **3** by the reaction of **3** with 4-nitrophenacyl bromide upon heating in dimethylformamide at 100 °C in the presence of K<sub>2</sub>CO<sub>3</sub>. Ring closure is proceeded *via* alkylation of the hydroxyl group followed by the condensation of active methylene and carbonyl groups, forming the furan fragment.



**Scheme 1.** The syntheses of 3-(1,3-benzothiazol-2-yl)-8-(4-nitro-benzoyl)-2H-furo[2,3-h]chromen-2-one **4**.

#### Review

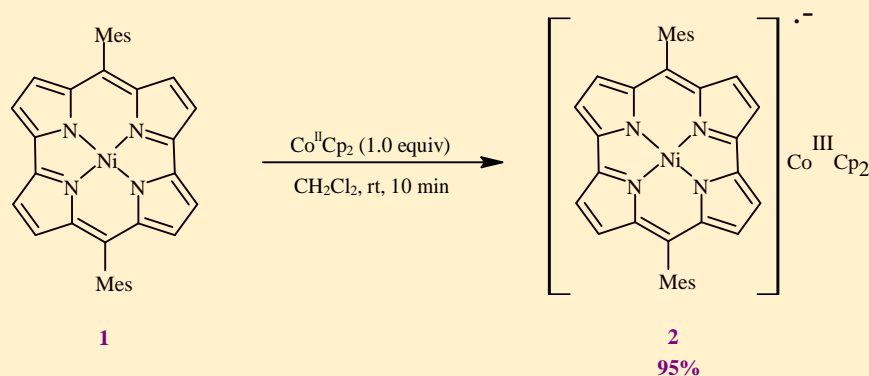
1) T. Shokol, A. Suprun, V. Moskvina, V. Khilya, *French-Ukrainian J. Chem.*, **2021**, 9.

## Isolation of Ni(II) *meso*-dimesitylnorcorrole Radical Anion

A developed n-type organic semiconductor compound is highlighted. Ni(II) *meso*-dimesitylnorcorrole radical anion was isolated upon chemical reduction of the corresponding natural species with cobaltocene ( $\text{Co}^{\text{II}}\text{Cp}_2$ ).

KEYWORDS: radical anion, porphyrinoid, antiaromatic.

n-type organic semiconductors are characterized by their high carrier mobility. To realize such a property, it is recommended to suppress structural change upon charge injection, leading to small reorganization energies. Ukai *et al.* reported a new n-type molecule, that they selected Ni(II) *meso*-dimesitylnorcorrole **1** as a stable and distinctly anti-aromatic molecule with a 16  $\pi$ -electronic system. This class of molecules is characterized by excellent reversibility of the redox process owing to their narrow HOMO-LUMO energy gap and possesses the ability to form one-dimensional  $\pi$ -stacking in the solid state, resulting in its n-type semiconducting property. They prepared and isolated compound **1** with cobaltocene ( $\text{Co}^{\text{II}}\text{Cp}_2$ ) to yield its radical anion **2** (Scheme 1).



**Scheme 1.** Chemical reduction of **1** to form radical anion **2**.

The radical anion **2** showed high stability and can be stored for long periods in the solid state. In addition, it exhibits small reorganization energy upon one-electron reduction even smaller than those of Zn(II) porphyrin and  $\text{C}_{60}$  fullerenes as revealed by DFT calculations. Besides, it features good electron-affinity as seen in its reduction potential of  $-0.92$  V (vs  $\text{Fc}/\text{Fc}^+$ ).

These properties should pave the way for designing of high-performance n-type semiconductors.

Review

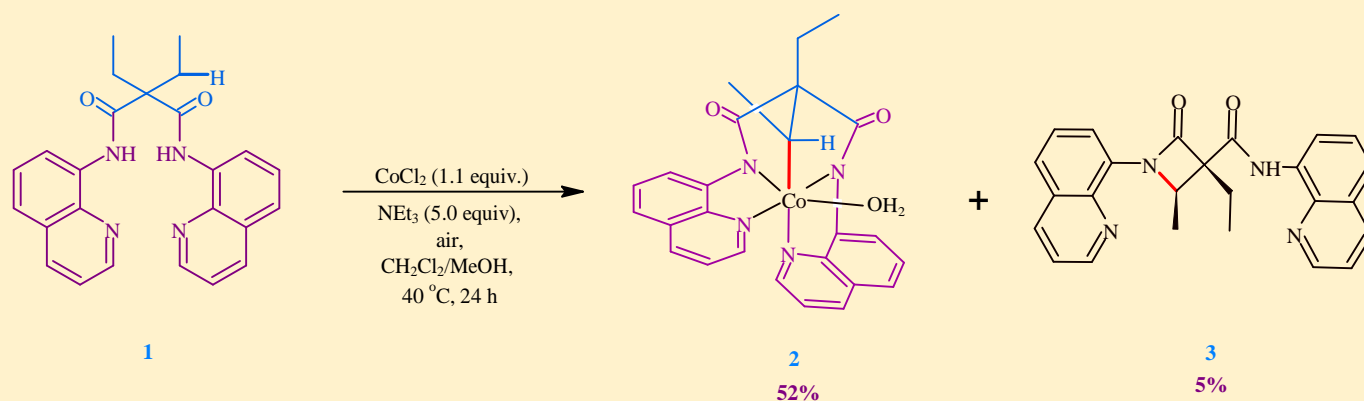
2) S. Ukai, N. Fukui, T. Akeue, H. Shinokubo, *Chem. Lett.*, **2022**, *51*, 182-184.

# Synthesis of Alkyl-Co Complexes Containing Polydentate Ligands as Directing Groups *via* C(sp<sup>3</sup>)-H Activation

The synthesis of an alkyl-Co(III) complex from *N,N'*-bis(8-quinolyl)malonamide derivative through selective  $\beta$ -C(sp<sup>3</sup>)-H activation is highlighted. The malonamide substrate was shown to be converted into a pentadentate ligand with an N<sub>4</sub>C set, acquiring a helical configuration around the Co(III) center.

KEYWORDS: C-H bond activation, alkyl-cobalt complex, C-N bond reductive elimination.

Cobalt mediated carbon-hydrogen functionalization plays an important role in the direct formation of carbon-carbon and carbon-heteroatom bonds from C-H bonds. In this context, Tahara *et al.* reported the preparation of alkyl-Co(III) complex possessing a polydentate ligand as a directing group *via* C(sp<sup>3</sup>)-H activation. Their strategy is based on enhancing the stability of the complex through polydentate ligation. So, *N,N'*-bis(8-quinolyl)malonamide derivative **1** was employed in order to disubstituted of two ethyl groups in the malonyl fragment containing the C(sp<sup>3</sup>)-H bonds. The preparation of alkyl-Co(III) complex **2** was accomplished by the stoichiometric reaction of CoCl<sub>2</sub> with **1** in a mixture of MeOH and CH<sub>2</sub>Cl<sub>2</sub> in the presence of NEt<sub>3</sub> under aerobic oxidation of the Co(II) salt at 40 °C for 24 h to afford a mixture of the cobaltacycle **2** as a dark brown solid in 52% yield and a C(sp<sup>3</sup>)-H aminated product **3** in 5% yield with conversion of **1** occurring in 98% (Scheme 1). Taking into consideration that the soft base (NEt<sub>3</sub>) is effective in deprotonating an *N,N'*-bis(8-quinolyl) malonamide derivative lacking two alkyl groups to provide a four-coordinated Co(II) complex with *N,N,N,N*-tetradentate ligand. The relative configuration of the  $\beta$ -lactam **3** was determined as the *cis* configuration between the methyl and ethyl groups by differential NOE analysis.



Scheme 1. Stoichiometric reaction of **1** with Co(II) compound.

The combined NMR spectroscopic and X-ray crystal structural analyses of the resulting cobaltacycle revealed that the substrate was converted into a pentadentate ligand with an N<sub>4</sub>C set, yielding a helical configuration around the Co(III) center. The defined coordination geometry around the Co(III) center allowed the direct observation of reductive elimination of C(sp<sup>3</sup>)-N from an isolated Co(III) complex. These findings reflect important facts regarding the synthesis and reactivity of metallacycles toward designing elaborate C(sp<sup>3</sup>)-H functionalization systems.

Review

- 1) K. Tahara, S. Takezaki, Y. Ozawa, M. Abe, *Bull. Chem. Soc. Jpn.*, **2022**, 95, 400-409.



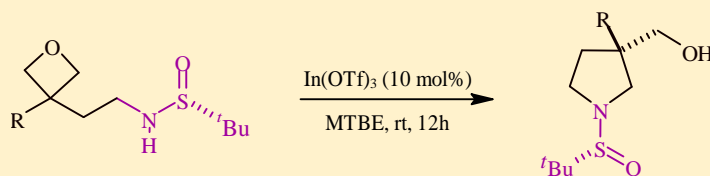
# Asymmetric Synthesis of Chiral Pyrrolidines *via* Oxetane Desymmetrization

Two novel protocols for efficient asymmetric synthesis of chiral pyrrolidines bearing an all-carbon quaternary stereocenter in the 3-position through oxetane desymmetrization are outlined. They employed a readily available *tert*-butylsulfinamide chiral auxiliary and a catalytic system with chiral phosphoric acid as the source of chirality, respectively.

KEYWORDS: pyrrolidines, oxetane, *tert*-butylsulfinamide.

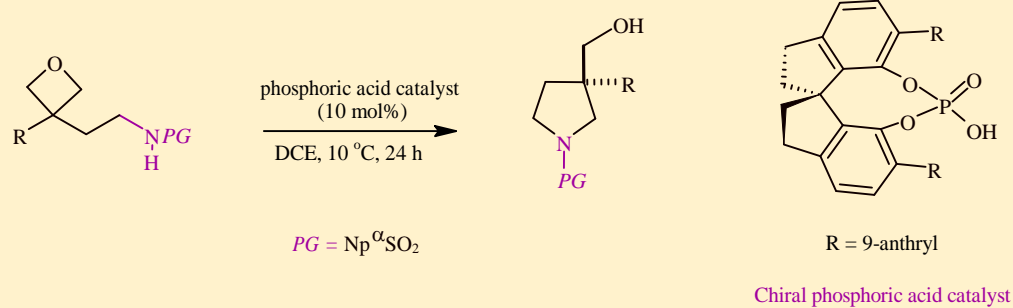
Pyrrolidines have received considerable attention because of their ubiquity in both medicinal chemistry and organic synthesis. Thus, the construction of enantioenriched pyrrolidines has been extensively studied, but remains a challenge to establish a stereogenic center in the relatively remote 3-position. Addressing this challenge, Zhang *et al.* reported two novel asymmetric synthetic approaches for chiral pyrrolidines bearing an all carbon quaternary stereocenter in the 3-position based on oxetane desymmetrization, which provide rapid access to the target pyrrolidines.

In the first protocol, the cyclization of a 3,3-disubstituted oxetane tethered with *tert*-butylsulfinamide as chiral auxiliary and  $\text{In}(\text{OTf})_3$  as catalyst, featuring mild conditions and remarkable diastereocontrol (Scheme 1). Using benzoic acid as cocatalyst and toluene as solvent, a range of oxetanes reacted smoothly to form the corresponding pyrrolidines. Alternatively, methyl *tert*-butyl ether (MTBE) was used as solvent in the case of the presence of electron-withdrawing groups, which they exhibited a deceleration under the former conditions.



**Scheme 1.** 3,3-disubstituted oxetane tethered with (*R*) *tert*-butylsulfinamide to provide pyrrolidines.

Further improvement by chiral phosphoric acid catalysis was achieved (Scheme 2). The use of a 2-naphthalenesulfonyl group for amine protection is crucial for the achieved excellent efficiency and enantioselectivity.



**Scheme 2.** Synthesis chiral pyrrolidines bearing an all carbon quaternary stereocenter in the 3-position.

Both protocols exhibited good substrate scope with excellent functional group compatibility.

Review

- 1) R. Zhang, M. Sun, Q. Yan, X. Lin, X. Li, X. Fang, H. H. Y. Sung, I. D. Williams, J. Sun, *Org. Lett.*, **2022**, *24*, 2359-2364.