Advances in the synthesis and application of isoindigo derivatives

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Dedicated to the memory of Professor Boris I. Buzykin late Professor of Chemistry, A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan

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Abstract
Synthetic approaches towards isoindigo derivatives and their application in medicinal chemistry as well as in the chemistry of materials are reviewed. The literature data up to 2014 are covered.

Keywords: Isatin, oxindole, isoindigo, photovoltaics, anti-cancer agents, low-band-gap polymers

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1. Introduction

Isoindigo along with indigo and indirubin is a representative of indigoid bis-indoles which in the last decade have attracted great attention as pharmaceuticals and as the components of functional materials. The isoindigo core was recently introduced as an acceptor unit for designing molecular and polymeric semiconductors for applications in organic electronics. Recent data show that numerous substances bearing the indolin-3-yliden-2-one motif possess strong potency in anti-cancer drug design[1] as well as in the search of effective antimicrobial agents. As regards this aspect, the most interesting compounds are indirubin[2-7] and isoindigo derivatives such as *Meisoindigo* and *Natura* which are already used in leukemia treatment[8-11] (Figure1).

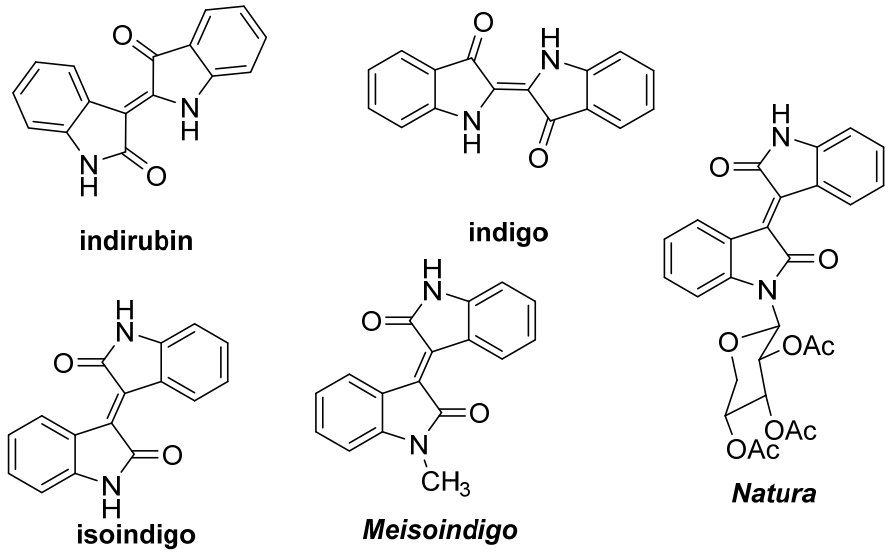


Figure 1. Representatives of isoindigo derivatives.

The goal of this review is to describe the chemistry of isoindigo, synthetic approaches to the 3,3′-biindolinylidene framework, and their application as biologically active compounds and the chemistry of functional materials. In this review we cover the available literature data from the beginning of the 20th century to the present time.

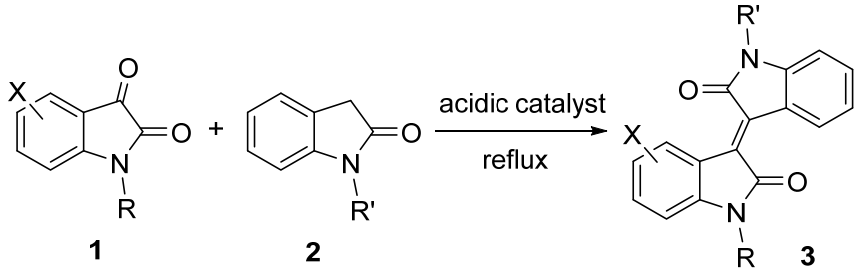
2. Synthetic Pathways for Isoindigo Scaffold Creation

The chemistry of isoindigo is inseparably connected with the fascinating synthetic potency of the nitrogen heterocycles indole, oxindole (indolin-2-one), and isatin (indoline-2,3-dione). In this

regard the vast majority of approaches to 3,3′-biindolinylidene fragment creation are based on the high reactivity of the ketone carbonyl of isatin and the methylene group of oxindole.

2.1 Isoindigo from oxindoles

A general approach to the synthesis of isoindigo derivatives (**3**) is bases by the acid-catalysed condensation of isatins (**1**) with oxindole (**2**) (Scheme 1). Generally, the reaction proceeds under reflux in an appropriate solvent for some hours in the presence of HCl/acetic acid or *p*-toluenesulfonic acid (Table 1).[12-24]



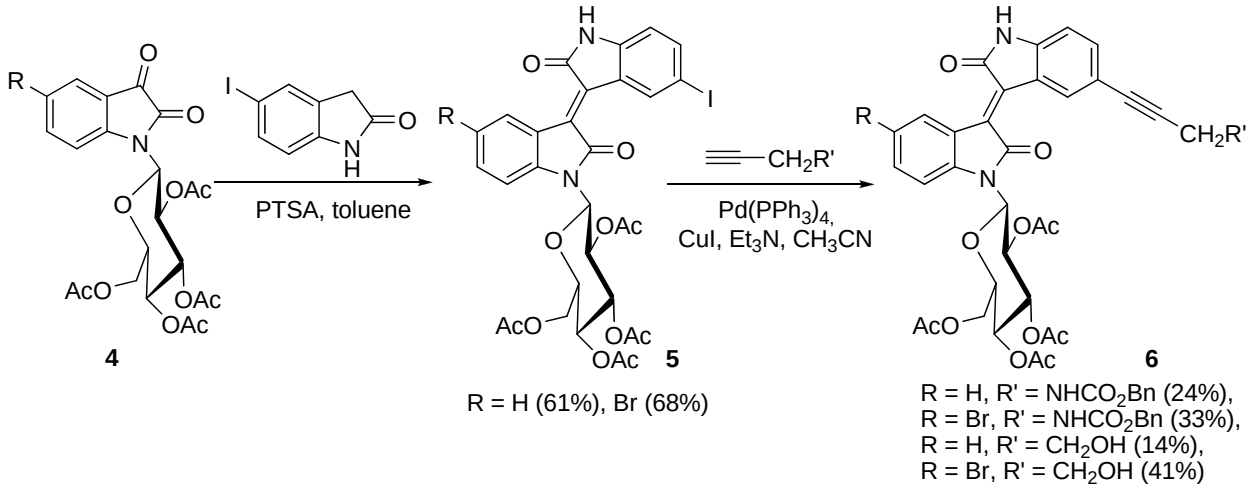
Scheme 1

Table 1. Syntheses of substituted isoindigos from isatins and oxindoles

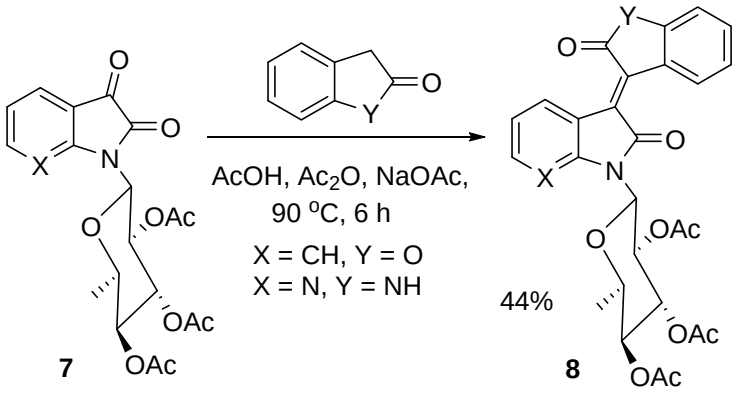
Entry	R/X	R′	Acid catalyst	Time (h)	Yield (%)
1[12]	H/H	H	AcOH/HCl	12	87
2[13]	H/H	H	AcOH/HCl	8	quantitative
3[14]	H/H	Ph	AcOH/HCl	4	*a*
4[15]	H/H	Me	AcOH/HCl	*a*	*a*
5[16,17,21]	Bn/H	H	AcOH/HCl	*a*	75
6[18,24]	H/H	H	AcOH/HCl	16	a
7[19]	R = H, Me, Bn, Ph, $(CH_2)_2Ar$; X = H	H	AcOH/HCl[b]	0.5	34-91
8[20]	H/5-NO_2, H/5-NH_2	H	AcOH/PTSA[b]	*a*	61-85
9[22]	R = Me, Bn, SEM[c], X = H	Me, Bn, SEM	HCl	*a*	52-87
10[23]	Ph/H	Ph	AcOH/HCl	*a*	*a*
11[25-27]	2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl/H	H	PTSA	24-48	23-61

[a] Not reported. [b] μW, sealed vessel, 200 °C. [c] SEM = 2-(trimethylsilyl)ethoxymethyl

This procedure can be extended to isatins bearing a carbohydrate substituent (**4**).[25-27] Furthermore, use of iodo-derivatives (**5**) allowed to introduce of an alkyne function into the isoindigo scaffold (**6**) by Sonogashira coupling (Scheme 2).[28] Under similar conditions, using benzofuran-2(3*H*)-one or benzothiophen-2(3*H*)-one instead of oxindole, and the pyrrolo[2,3-*b*]-pyridine-2,3(1*H*)-dione (7-azaisatin) derivative **7** instead of the glycosylisatin yielded oxa- and aza-analogues (**8**) of isoindigo-*N*-glycosides (Scheme 3).[29-31]

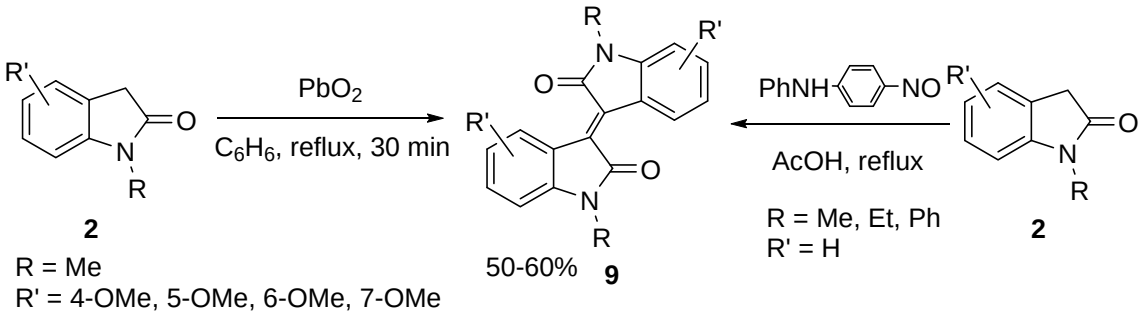


Scheme 2



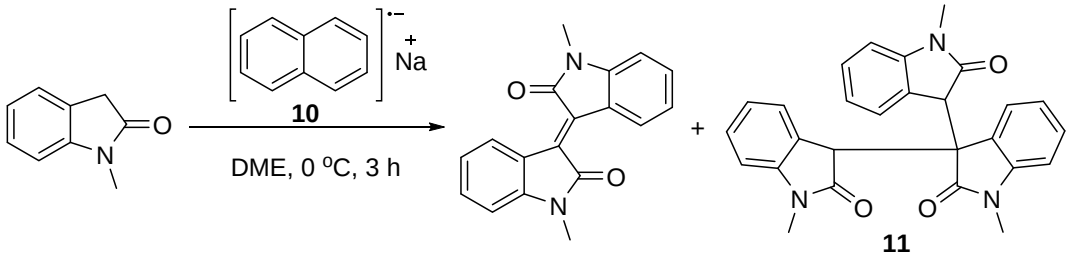
Scheme 3

Some synthetic pathways to isoindigo derivatives are based on oxidative C-C coupling of oxindoles. Thus, several alkyl or alkoxy-substituted isoindigo (**9**) have been obtained by the action of 4-nitrosodiphenylamine[15] or lead dioxide[32] on the corresponding alkyl- or alkoxy-indolin-2-ones (**2**) (Scheme 4).



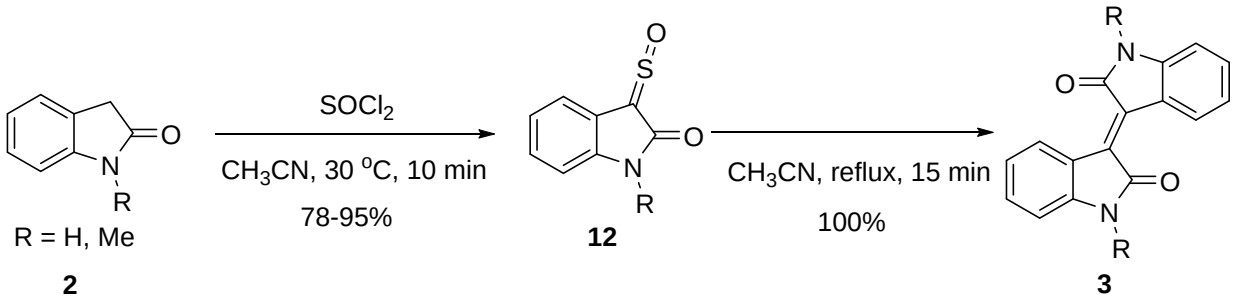
Scheme 4

The reaction of the single-electron transfer reagent sodium naphthalenide (**10**) with *N*-methyloxindole furnishes 1,1′-dimethylisoindigo in 19% yield along with the trimeric structure **11** (Scheme 5).[33]



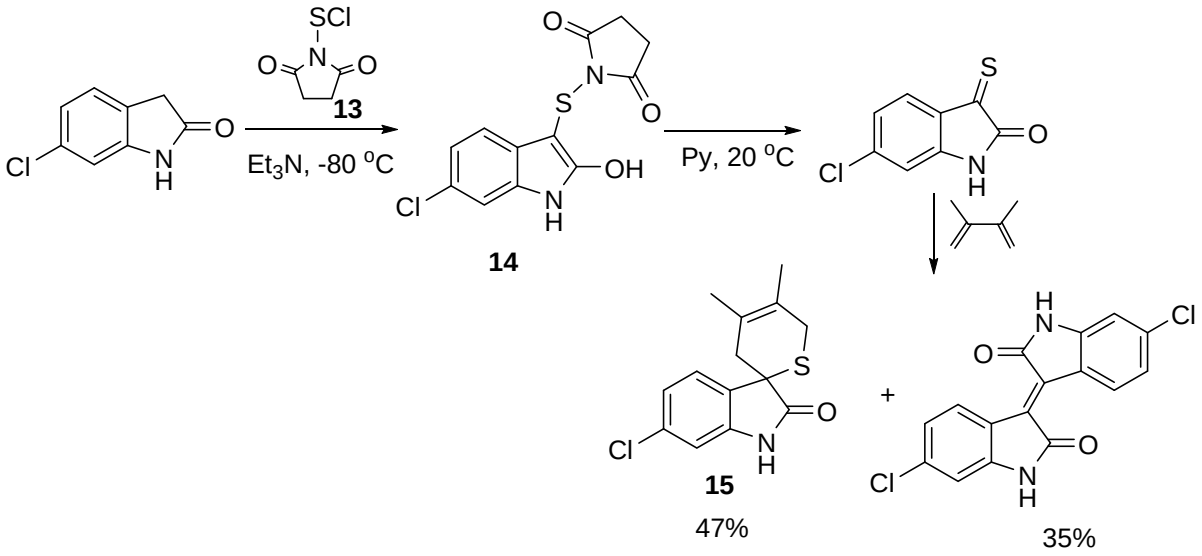
Scheme 5

Recently, Bergman and Romero have described the synthesis of isoindigo and its dimethyl derivative using readily available starting compounds (oxindole and thionyl chloride).[34] It was shown that the first stage of the reaction results in the formation of the corresponding α-oxo-sulfine (**12**) which further produces isoindigo in almost quantitative yield (Scheme 6). But this approach was limited and can't be applied on $SOCl_2$ sensitive groups such as hydroxyl, acid and amine scaffolds.



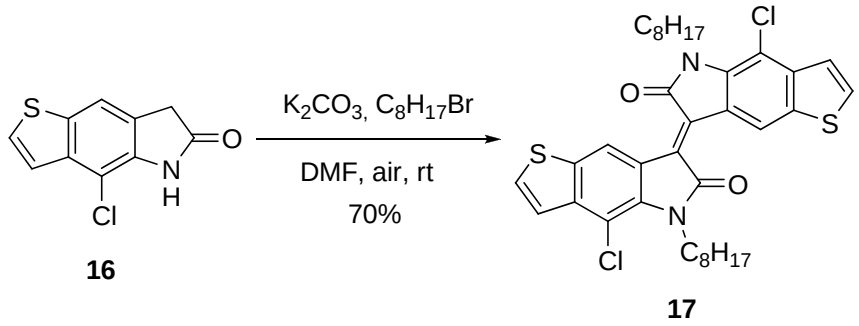
Scheme 6

Shermolovich and co-workers studied an interaction of 6-chlorooxindole with *N*-(chlorosulfenyl)succinimide (**13**) and found that the intermediate sulfenylimide (**14**) readily decomposes in pyridine in the presence of 2,3-dimethylbutadiene to form the six-membered spirocycle (**15**) along with 6,6′-dichloroisoindigo (Scheme 7).[35]



Scheme 7

Recent report showed that in the presence of alkylating agent, thiophene-fused oxindole (**16**) can be air-oxidized to alkylated thiophene-fused isoindigo (**17**) in 70% yield (Scheme 8).[36]

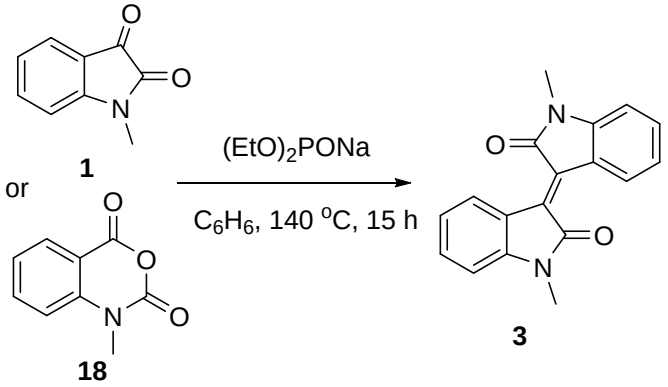


Scheme 8

2.2 Phosphorus compounds in the synthesis of isoindigo

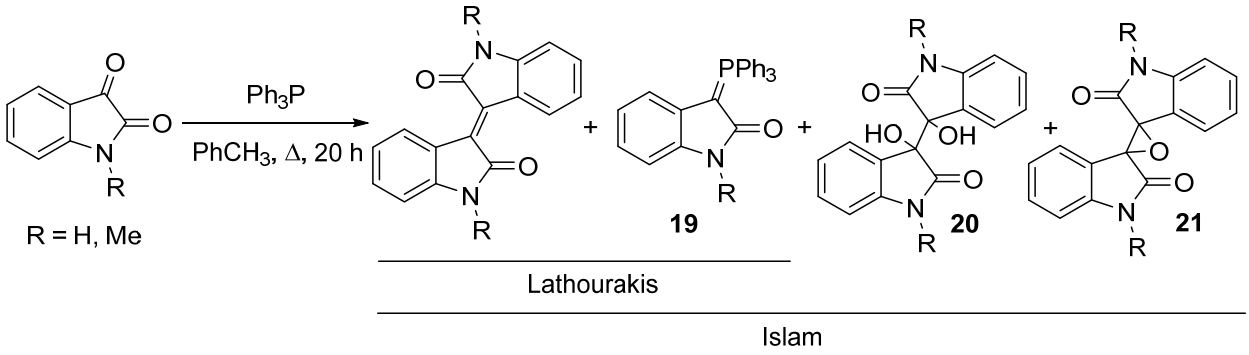
The first example of the use of organophosphorus compounds in the synthesis of isoindigo derivatives was described in Minami's work.[37,38] It was found that 1-methylisatin or 1-methylisatoic anhydride (**18**) by the action of sodium diethylphosphite under harsh conditions

(15 h, 140 ºC, C_6H_6, sealed tube) afford 1,1′-dimethylisoindigo in 37 and 79% yields respectively (Scheme 9).



Scheme 9

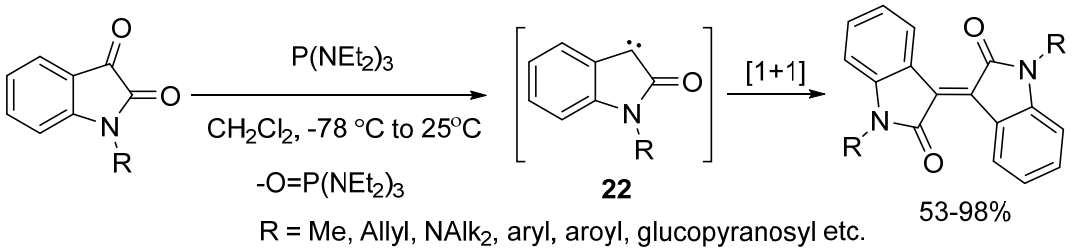
Later, 1,1′-dimethylisoindigo was obtained by the reaction of 1-methylisatin with triphenylphosphine.[39] The reaction pathway was assumed to proceed through the intermediate carbene. Phosphorus ylid (**19**) formation may be evidence for such a reaction mechanism. At the same time, Islam and coworkers found that this reaction affords the diol **20** and epoxide **21** along with the other products reported (Scheme 10).[40]



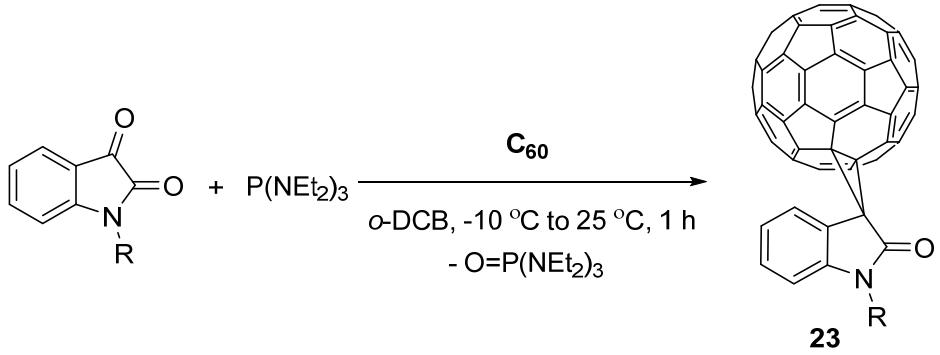
Scheme 10

Variously-substituted isoindigo derivatives can be obtained as the sole reaction products by changing triphenylphosphine to the more nucleophilic tris(diethylamino)phosphine.[41-52] In this type of 3,3′-bis-indole fragment formation a wide range of isatin derivatives including benzothiphene- or benzofuran-fused ones[53] can be used. Using this procedure the target compounds were obtained in high yields under mild reaction conditions (Scheme 11).

The assumption that the reaction proceeds *via* carbene (**22**) generation was experimentally confirmed by trapping with fullerene C_{60} to form the corresponding methanofullerenes (**23**) (Scheme 12).[54-57]

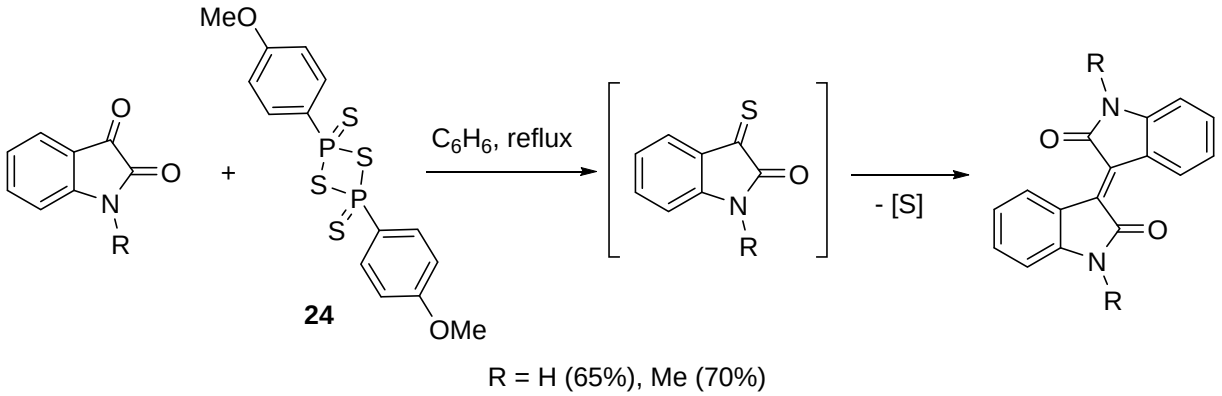


Scheme 11



Scheme 12

Lawesson's reagent (**24**) was also successfully used in the synthesis of symmetrically substituted isoindigo.[58] The authors proposed that the thiation of isatin at position 3 takes place to form 3-thioisatin which undergoes sulfur elimination to form isoindigo (Scheme 13).

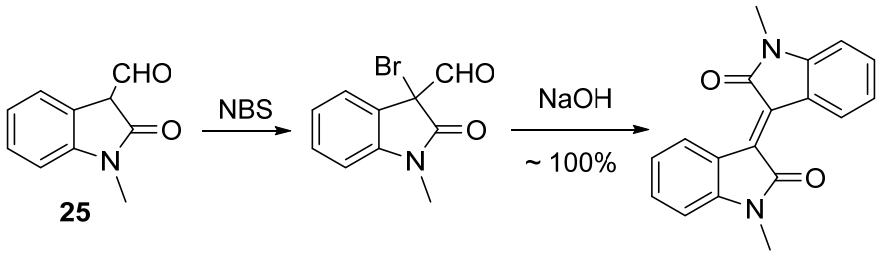


Scheme 13

2.3 Miscellaneous methods

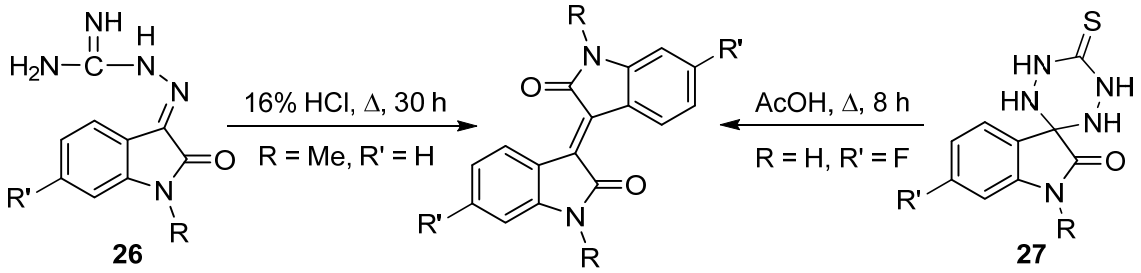
Several additional procedures which give rise to isoindigo derivatives have been reported in the literature. For example, a high-yield synthesis of 1,1′-dimethylisoindigo was developed starting

from 3-formyloxindole (**25**) using a bromination - basic decomposition sequence.[59] This approach to the synthesis of isoindigo derivatives seems to be favorable but the use of the relatively inaccessible 3-formyloxindole limits its possibilities (Scheme 14).



Scheme 14

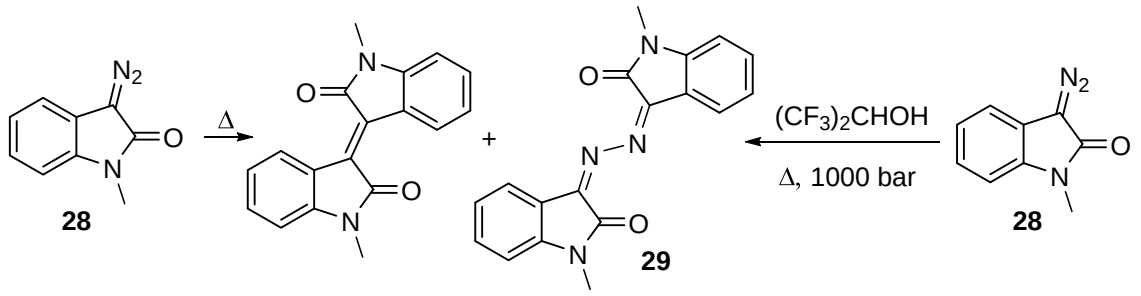
Using the high reactivity of the ketone carbonyl of isatin toward different amino-compounds, 1-methylisatin *anti*-β-guanylhydrazone (**26**) and the spirocyclic tetrazinethione (**27**) were obtained.[60,61] It was found that on prolonged heating (8-30 hours) in acidic medium these compounds give rise to 1,1′-dimethylisoindigo (37% yield) and 6,6′-difluoroisoindigo (40% yield) respectively (Scheme 15).



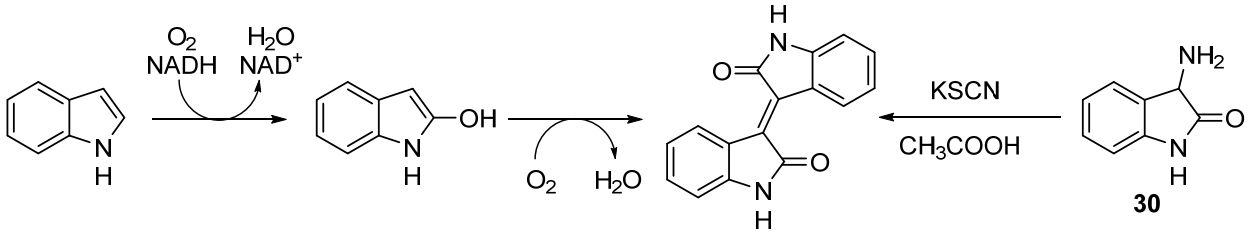
Scheme 15

One approach leading to isoindigo formation is based on the decomposition of 3-diazo-oxindole, which proceeds under various reaction conditions.[62-65] However, such methods do not afford isoindigos as the sole products. Thus, 1,1′-dimethylisoindigo can be obtained by the thermolysis of 1-methyl-3-diazooxindole (**28**), but the corresponding azine (**29**) is formed as a by-product (Scheme 16). At the same time, the desired compound was obtained in 86% yield by decomposition of isatin 3-tosylhydrazone in the presence of sodium metal.[59]

Other approaches to isoindigo formation can be noted here. They include, for example, the treatment of 3-aminooxindole (**30**) with potassium thiocyanate and the enzymatic oxidation of indole (Scheme 17).[66,67]



Scheme 16



Scheme 17

3. Properties of Isoindigo Derivatives

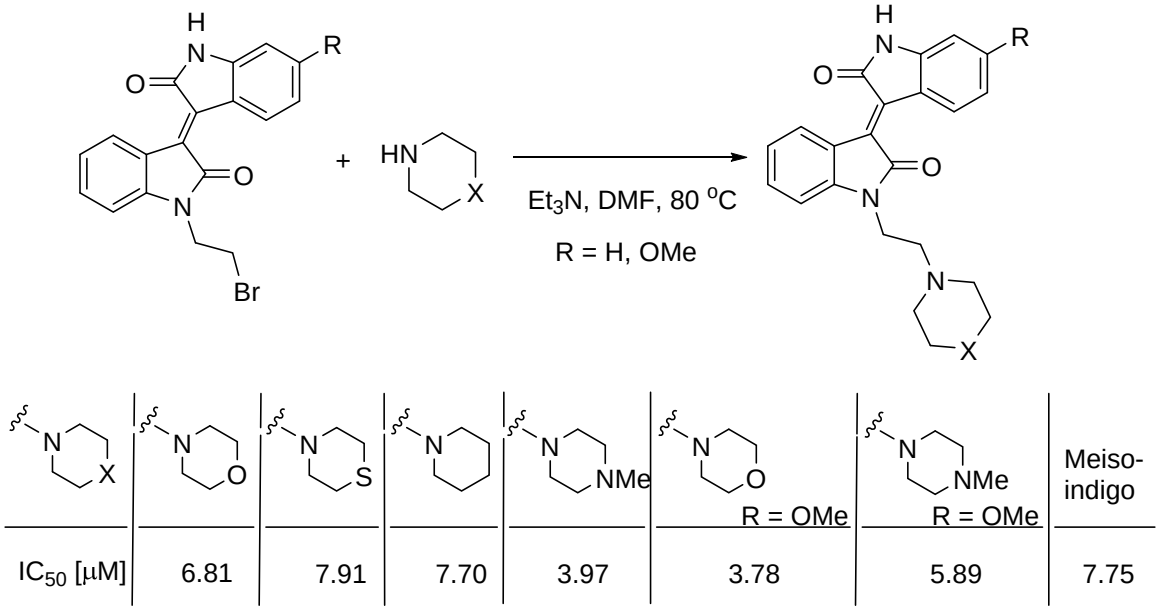
Since it is well known that 1-methylisoindigo possesses significant anti-cancer activity, a number of studies involve the functionalization of this heterocycle to find novel effective pharmaceutical agents. On the other hand, a presence of two lactam rings joined by double carbon-carbon bond implies high electron deficiency in the isoindigo molecule. These features have led to two main trends of the studies of these bis-indoles.

3.1 The biological activity of isoindigos

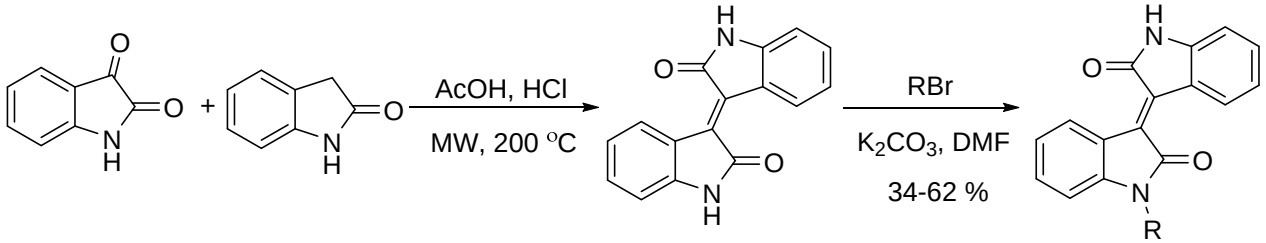
1-Methylisoindigo is the most studied isoindigo derivative and is used in the treatment of chronic myeloid leukemia (CML).[68-73] The poor solubility of this compound encouraged researchers to design analogs with improved physico-chemical characteristics. Indeed, it was found that appending a basic heterocycle side chain onto the lactam nitrogen resulted in significantly better solubility than Meisoindigo while retaining good activity against leukemia K562.[74] As can be seen from the data obtained, the most active are the *N*-methylpiperazino- and 6′-methoxy-1-(2-morpholinoethyl) derivatives (Scheme 18).

Assuming that the activity of an isoindigo depends on the presence of at least one lactam NH-moiety and a conjugated C=C bond, the methyl group of Meisoindigo was replaced with a phenyl, benzyl, phenethyl or phenpropyl side chain (compounds **31-34** respectively). However, these changes led to small increases in activity except for (**32**) (inactive against leukemic cell

lines) and (**34**) (2–3 times more potent than Meisoindigo). Introducing substituents of different polarities and electronic effects to the phenyl ring of the phenethyl analogue (**33**) did not yield compounds with improved activities. A notable exception was the *p*-methoxy analogue (**35**) which was more active on the leukemic K562 cells (IC_{50} K562 1.4 μM) and hepatoma HuH7 cells (IC_{50} K562 7.5 μM) (Scheme 19).[75]



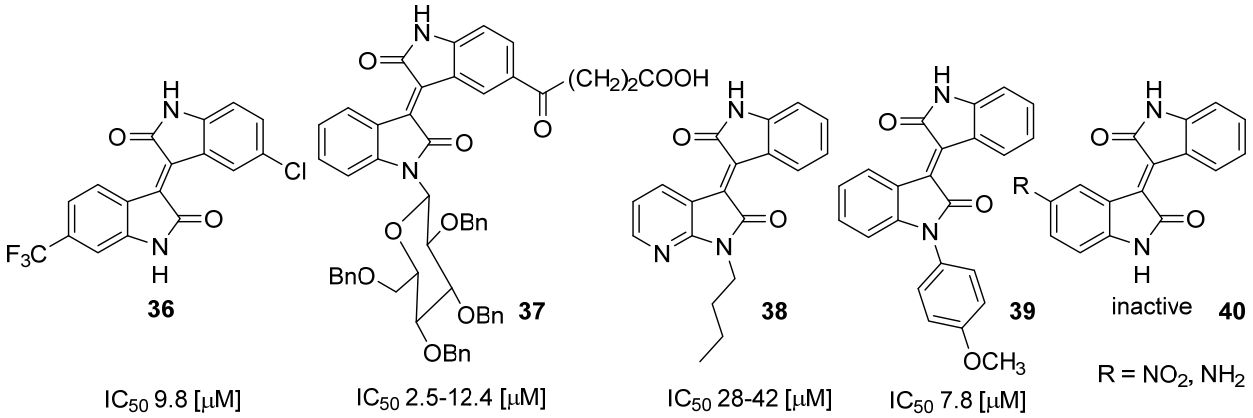
Scheme 18



R = Ph (**31**), $PhCH_2$ (**32**), $PhCH_2CH_2$ (**33**), $PhCH_2CH_2CH_2$ (**34**), *p*-$CH_3OC_6H_4CH_2CH_2$ (**35**)

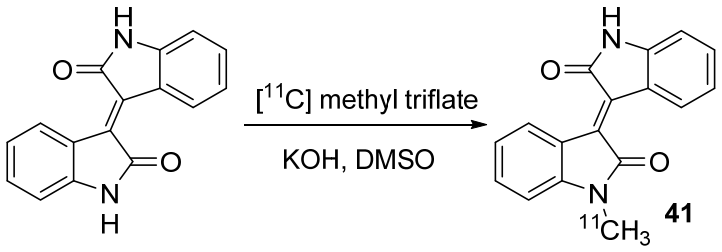
Scheme 19

The glycosyl-substituted isoindigo (**37**)**,** containing additional carboxylic group to increase water solubility, showed high anti-cancer properties.[76] Moderate activity of 6-trifluoromethyl-5′-chloroisoindigo[77] (**36**), 7-aza-1-butylisoindigo[78] (**38**) and 1-(4-methoxyphenyl)isoindigo[79] (**39**) against different cancer cell lines (PC3, DLD-1, MCF-7, M4Beu, A549, K562) was also found; 5-nitro- and 5-amino-derivatives (**40**) were inactive (Scheme 20).[20]

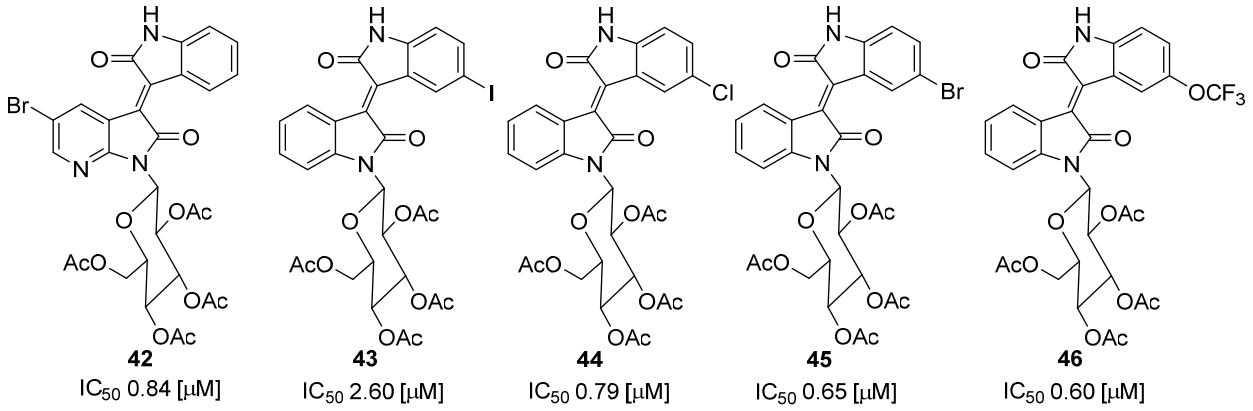


Scheme 20

Recently, radiolabelled 1-methylisoindigo (**41**) was synthesized for use in positron emission tomography to obtain understanding of the physiological action of Meisoindigo (Scheme 21).[80]



Scheme 21



Scheme 22

The biological activity of substituted glycosyl-isoindigo derivatives against the causative agents of tropical diseases (malaria, Chagas disease, leishmaniasis and human African

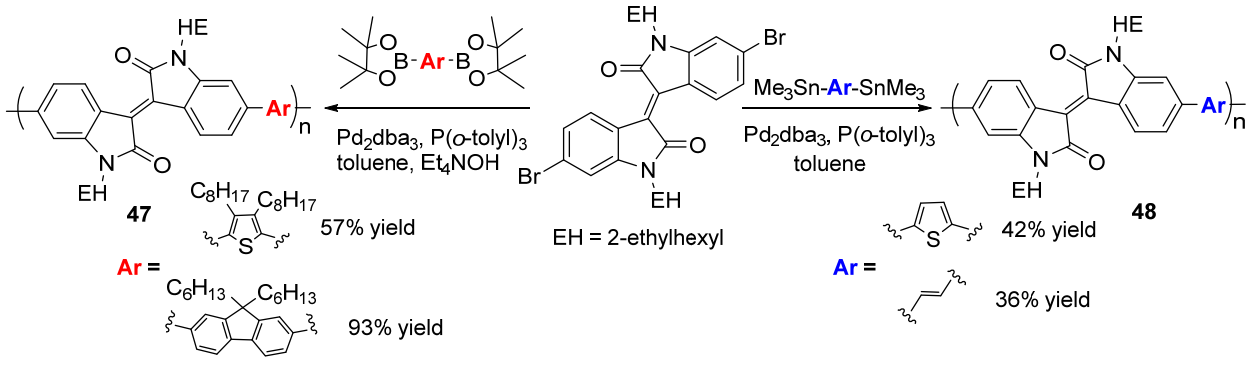
trypanosomiasis) was reported. Various authors have found a selective activity toward those or other pathogens. Thus, compound (**42**) possessed high activity against *L. donovani* (leishmaniasis), whereas structures (**43**, **44**) and (**45**, **46**) were effective against *P. falciparum* (malaria) and *T. cruzi* (trypanosomiasis) respectively (Scheme 22).[81]

3.2 Isoindigo in organic electronics

Being a bis-heterocycle incorporating two lactams moieties connected by a double carbon-carbon bond, isoindigo represents highly reactive conjugated system. Such a structure gives rise to the application of these molecules as electron-acceptor materials in organic electronics, focusing on organic photovoltaics (OPVs) and organic field effect transistors (OFETs).[82-84] In these studies the high reactivity of bromine atoms in the 6- and 6′-positions of the arene moiety has been widely applied.

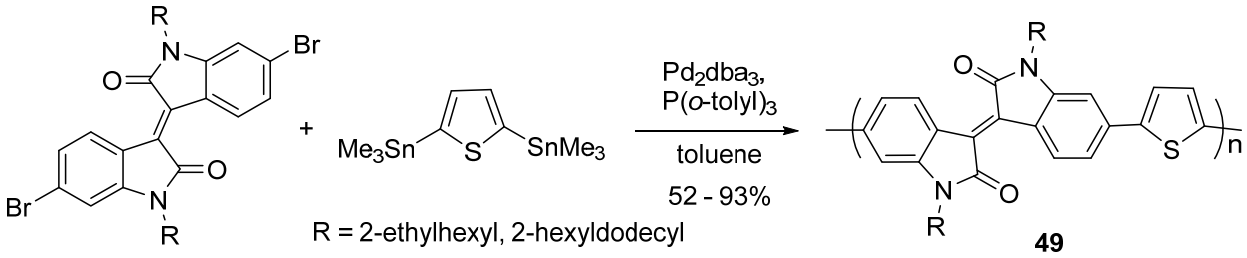
3.2.1 Isoindigo in organic solar cell production. In recent years, organic solar cells (OSC) have attracted much attention as one of the more promising solutions for generation of renewable clean energy.[85] Reynolds's group was the first to report the use of isoindigo in OSC.[86,87] High photophysical data (short current J_{sc}, open-circuit voltage V_{oc}, fill-factor *FF* and power conversion efficiency *PCE*) show that isoindigo is perspective acceptor group for photovoltaics application. Some aspects of these isoindigo properties were briefly discussed in some reviews.[88-92]

Synthetic applications of isoindigo are mainly based on the creation of polymeric structures. Variation of substituents both at the nitrogen atom and the side chain is directed towards improving the physical and chemical characteristics of the target compounds: solubility, UV-visible absorption, electron affinity and others. These factors, in turn, directly influence the PCE value. Reynolds *et al.* were the first to use Suzuki or Stille cross-coupling reactions to create polymers (**47, 48**) with the isoindigo subunit (Scheme 23).[86,87]



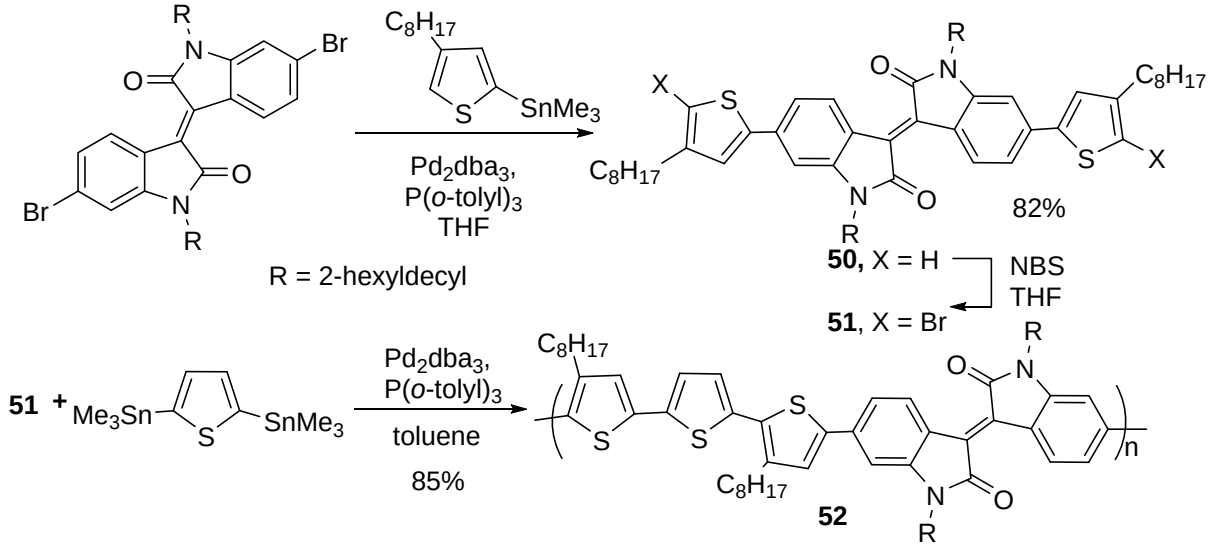
Scheme 23

The first studies of isoindigo-based polymers (IBP) were devoted to increasing their solubility in organic solvents. It was achieved by introduction of branched alkyl substituents (2-ethylhexyl, 2-hexyldecyl or 2-octyldodecyl) at a nitrogen atom. At present, the vast majority of the reports relate to the preparation of thiophene-containing polymers. In these, the structure of the monomer unit can contain from one to several thienyl,[93-99] isomeric benzodifuran[100] or naphthodifuran[101] substituents. A general approach to the synthesis of thienyl-isoindigo copolymers (**49**) is presented here (Scheme 24).



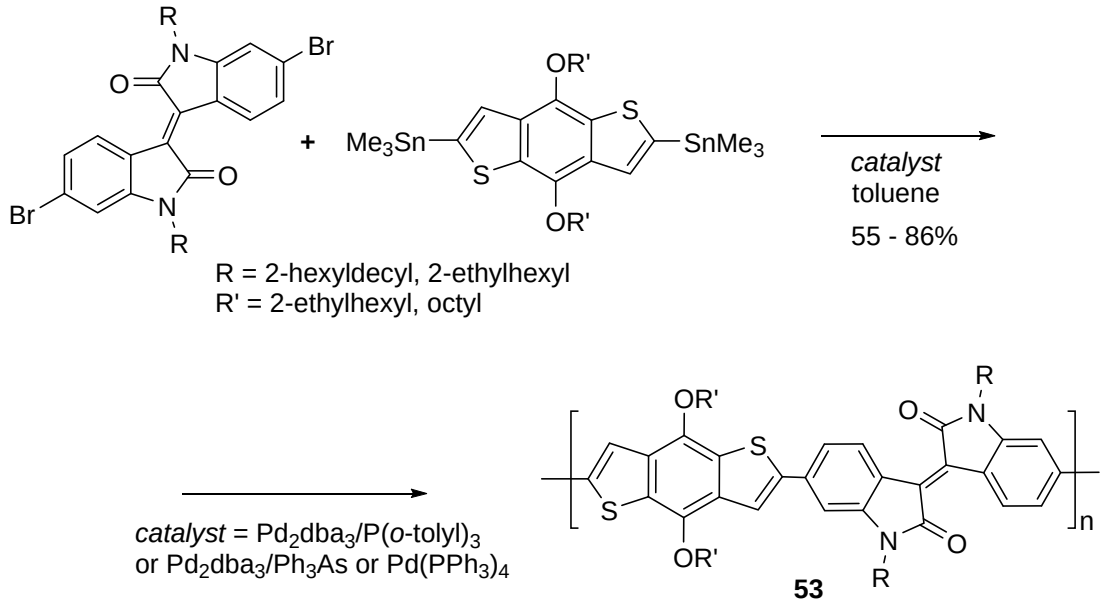
Scheme 24

A solar cell composed of this polymer as electron rich donor and $PC_{71}BM$ as electron acceptor shows 2.0-3.0% PCE values. A low-band-gap alternating copolymer (**52**) consisting of di- or terthiophene and isoindigo has been synthesized via Stille cross-coupling (Scheme 25). Solar cells based on this polymer and $PC_{71}BM$ show a power conversion efficiency of 6.3%.[94,102-104]



Scheme 25

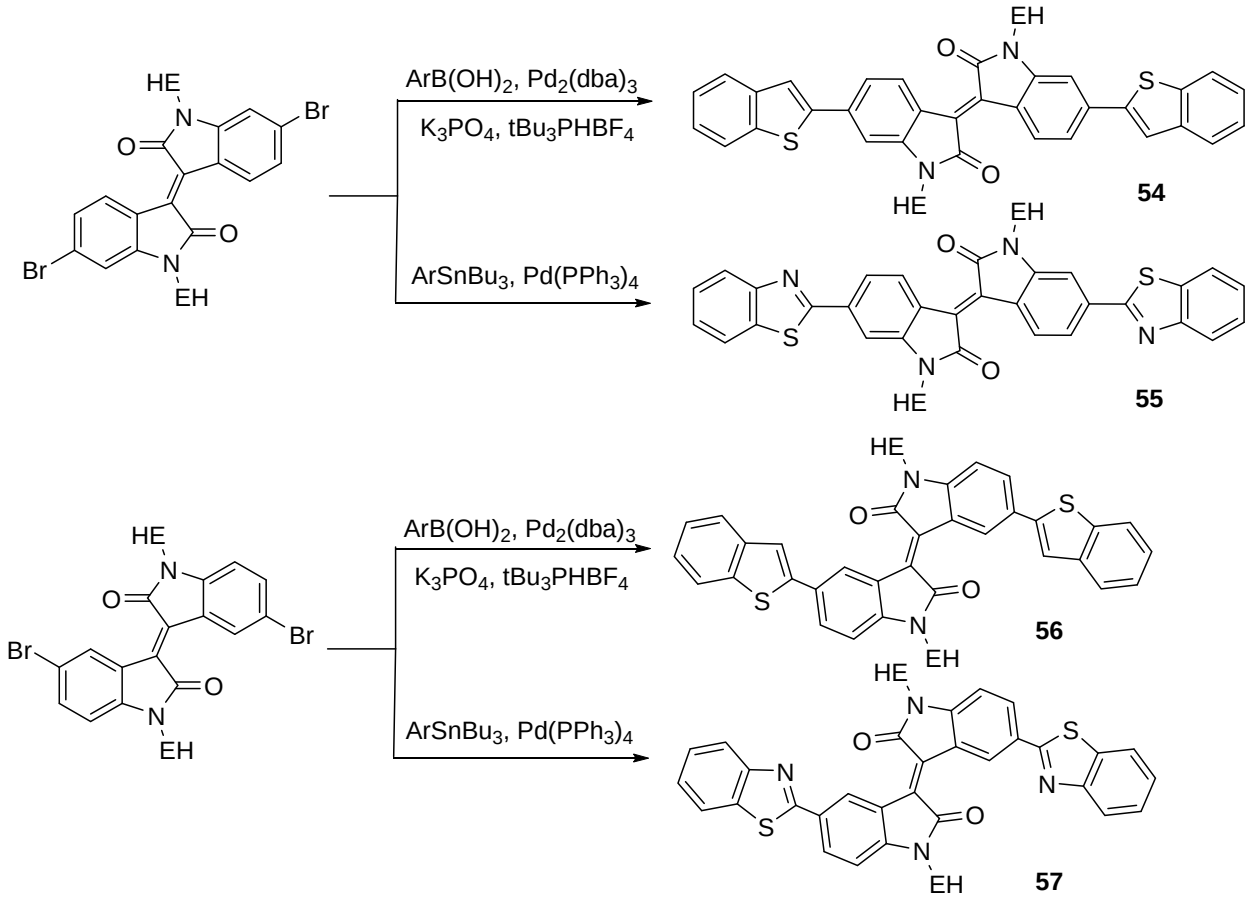
One way to increase the PCE of the solar cells on the base of IBP involves the introduction of a benzodithiophene moiety into the polymer structure (Scheme 26).[105,106] The best PCE value of solar cells made from IBP/PCBM blend was 4.22%. Catalyst variation showed that the use of $Pd(PPh_3)_4$ provides a better yield of desired polymer (**53**).[107]



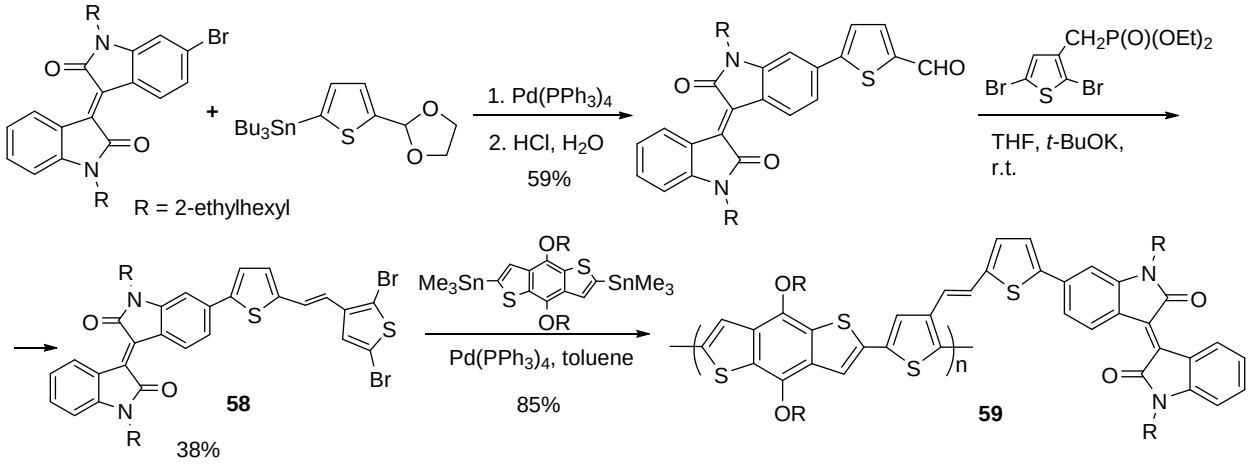
Scheme 26

Very recently a series of 6,6′- and 5,5′-substituted isoindigo (**54-57**) bearing the benzothiophene or benzothiazole moieties as model compounds were synthesized to elucidate the effects of the electronic nature of the substituent and its position on the physical properties and solid-state organization.[107] These studies show that both the placement and the electronic nature of the substituent affect on the molecular properties and corresponding device performance of solar cells containing these materials (Scheme 27).

Using monobrominated derivatives allows polymers bearing the isoindigo moiety in the side chain to be prepared (Scheme 28). Thus, the isoindigo core was modified with a thiophene-carbaldehyde fragment using Stille coupling followed by Horner-Wadsworth-Emmons reaction to give corresponding monomer (**58**).[109] Then repeated Stille polycondensation afforded the desired polymeric compound (**59**) in 85% yield. BHJ solar cells based on these polymers show an enhanced PCE of 5.3%.

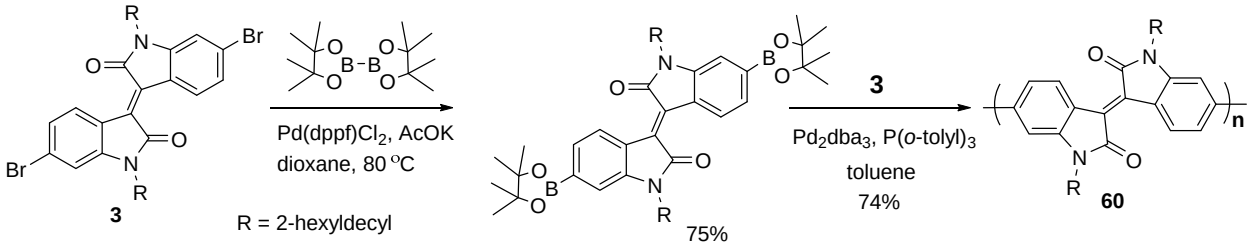


Scheme 27



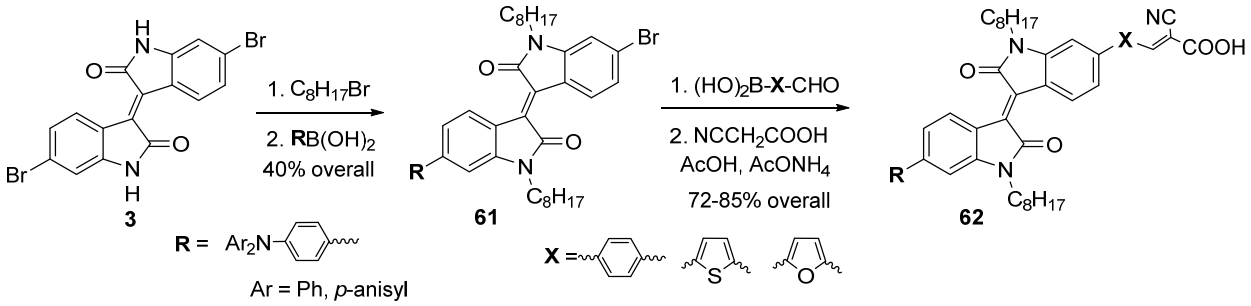
Scheme 28

The electron acceptor isoindigo was used to synthesize conjugated polymer with backbones composed exclusively of electron-deficient units (Scheme 29). Suzuki-Miyaura polycondensation afforded the homopolymer of isoindigo (**60**) which is thermally stable up to 380 °C, has a good solubility in organic solvents, and absorbs light over a wide range of the visible spectrum.[110]



Scheme 29

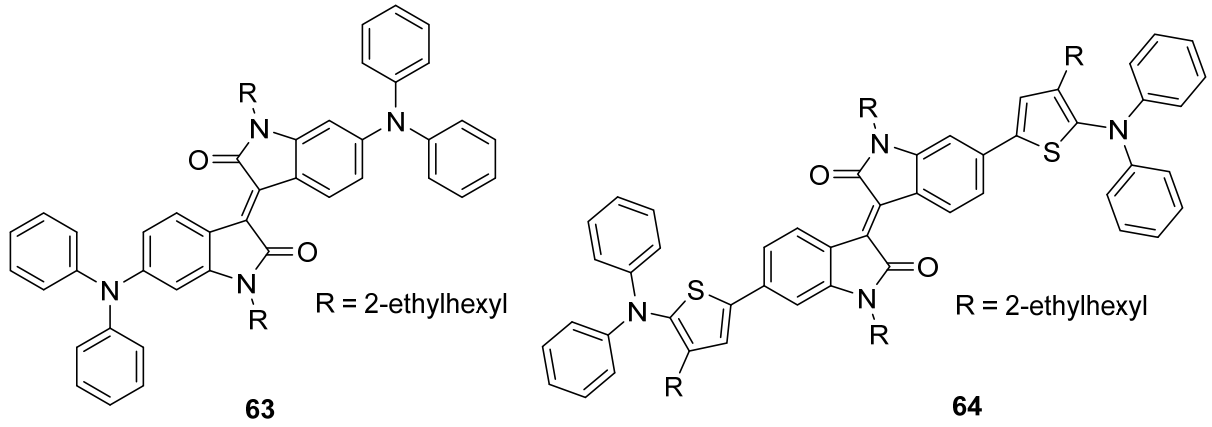
However, despite the variety of the obtained isoindigo-based polymers, it was shown that small molecule analogues may compete with them, particularly in terms of PCE. Thus, isoindigo (**3**) was transformed to the corresponding triarylamino derivatives (**61**) with retention of one bromine atom that in the next step was used in the synthesis of corresponding carbaldehydes. The last were finally converted to the target dyes (**62**) with α-cyanoacrylate fragment as anchoring group.[111] The best PCE of 5.98% was obtained for solar cells based on these isoindigo derivatives as acceptor material in active layers (Scheme 30).



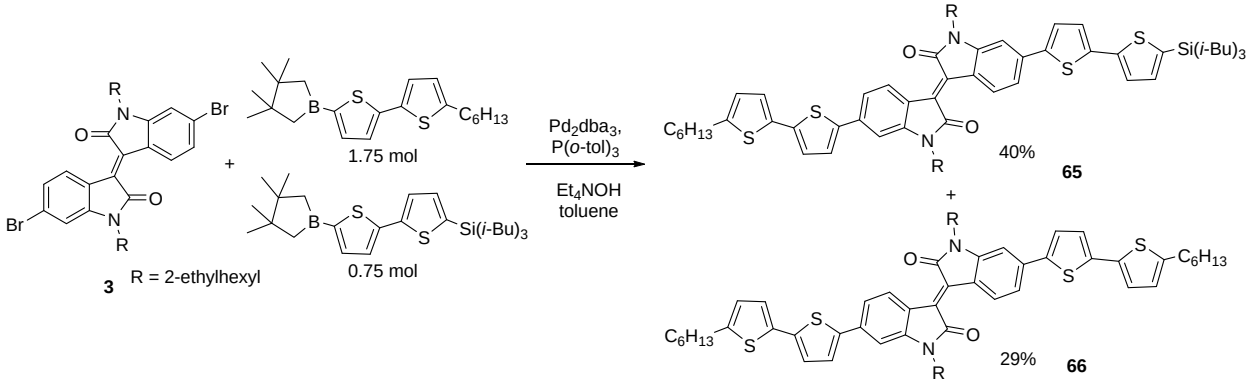
Scheme 30

A symmetrically substituted isoindigo with two electron donating groups either bonded directly to an arene fragment (**63**) or through a thienylene spacer (**64**) were synthesized and used in OSC creation. However, in both cases a PCE of these samples was less than 1% (Scheme 31).[112,113]

Utilization of monofunctional organotin or organoboron compounds in Stille or Suzuki reactions conditions allowed the preparation of the corresponding isoindigos (**65, 66**) with dithiophene groups in moderate yields (Scheme 32).[114,115]



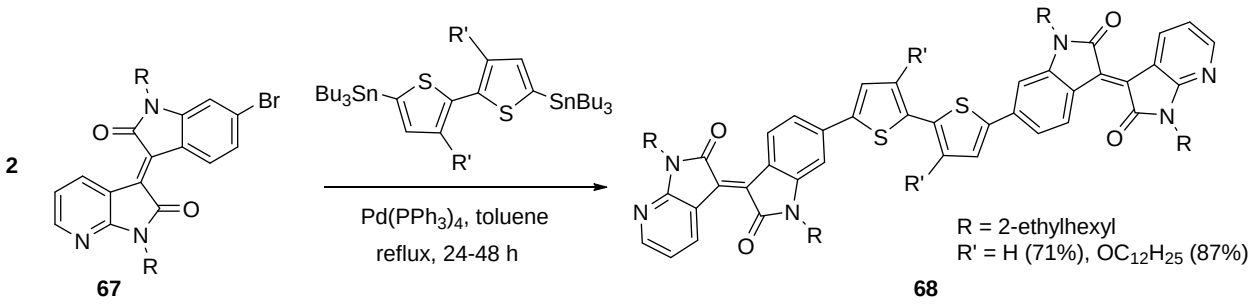
Scheme 31



Scheme 32

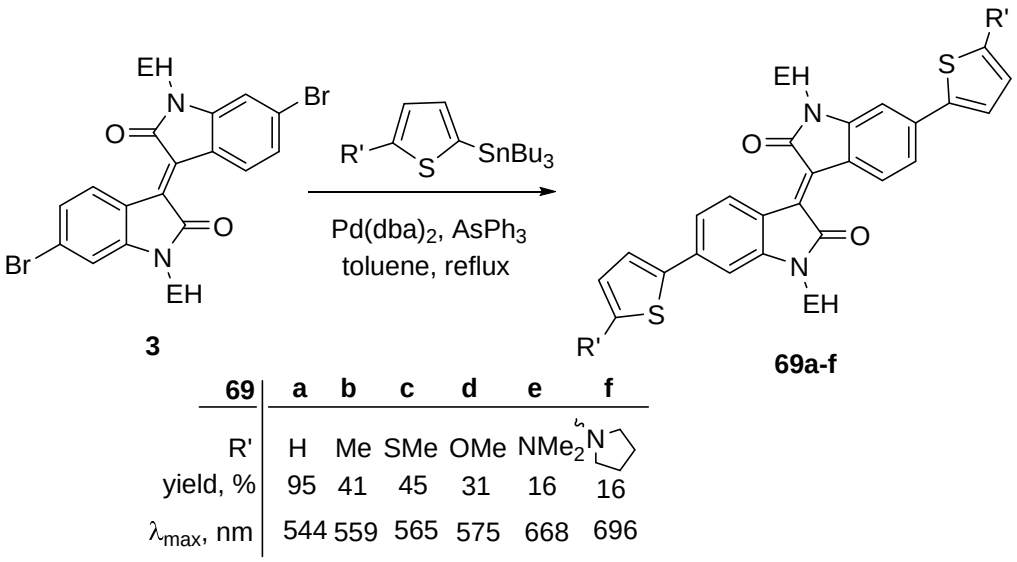
PCE of the solar cells based on these compounds varied in the range 1.3-2.2%.

Recently, the 7-azaisoindigo (**67**) was for the first time utilized in the synthesis of the highly conjugated chromophore (**68**) the structure of which contains two 7-azaisoindigo moieties separated by a dithiophene bridge. Then these electron acceptor compounds were used in OSC creation but last performed with very low PCE values (Scheme 33).[116]



Scheme 33

Detailed investigations of diversely substituted isoindigos revealed a strong dependence of their optical properties on the structures of substituents distanced from the heterocyclic core. A series of highly soluble *N*,*N*′-dialkylated isoindigo derivatives (**69a-f**) bearing different electron donating thiophene units at the 6,6′-positions were synthesized by Stille cross-coupling reactions. The optical and electrochemical properties of these dyes were studied by UV-vis spectroscopy and cyclic voltammetry, revealing a dependence of their electronic properties on the peripheral substituents, leading to strong absorption as far as the near infra-red region (Scheme 34).[117] These findings can be significant in the further use of these compounds in the creation of OSC.



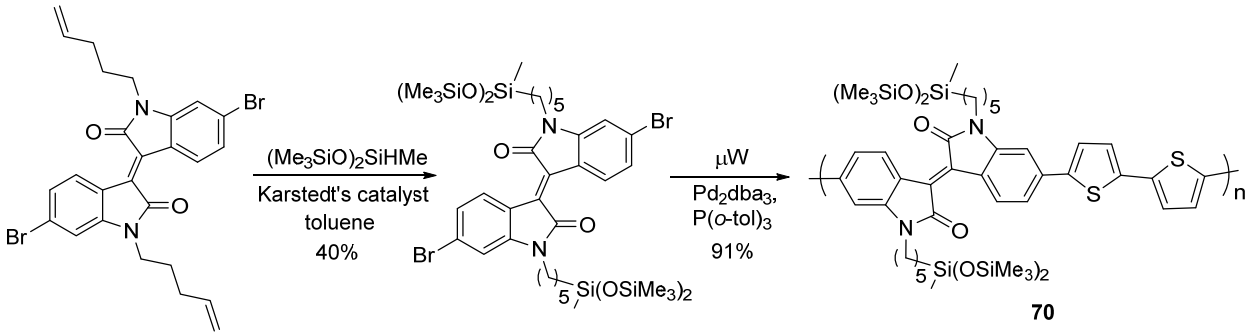
3 **69a-f**

69	a	b	c	d	e	f
R'	H	Me	SMe	OMe	NMe_2	
yield, %	95	41	45	31	16	16
λ_{max}, nm	544	559	565	575	668	696

Scheme 34

3.2.2 Organic field-effect transistors with isoindigo unit. Design strategies to improve charge carrier mobility of polythiophenes include the incorporation of electron deficient aromatic rings into the backbone. Attaching electron-withdrawing moieties lowers the HOMO level, which improves the air stability of these polymers (an important drawback of polythiophenes). It has also been reasoned that donor-acceptor interactions may help to close-pack the polymer chains, resulting in enhanced mobilities.

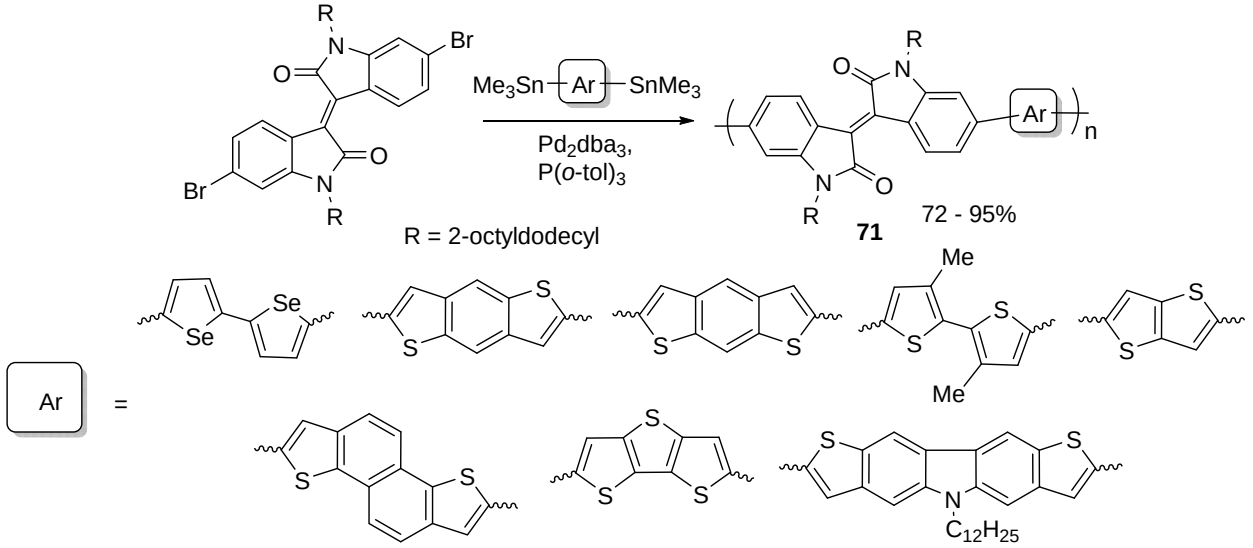
Some aspects of the utilization of isoindigo derivatives in OFETs creation have been highlighted in some brief reviews.[118-123] Mei[124] and Lei[125] were the first who offered IBP in this field of organic electronics. The synthesis of the target compounds (**70**) is also based on a sequence of Knoevenagel and Stille reactions. As reported, in the hydrosilylation reaction the central bis-indole C=C bond is not affected (Scheme 35).[125]



Scheme 35

The introduction of a siloxane fragment into the side chain of a polymer allowed increasing hole mobility, up to 2.00 $cm^2V^{-1}s^{-1}$. This was attributed to a tighter packing of the polymer in thin film that improves conductivity and ambient stability.

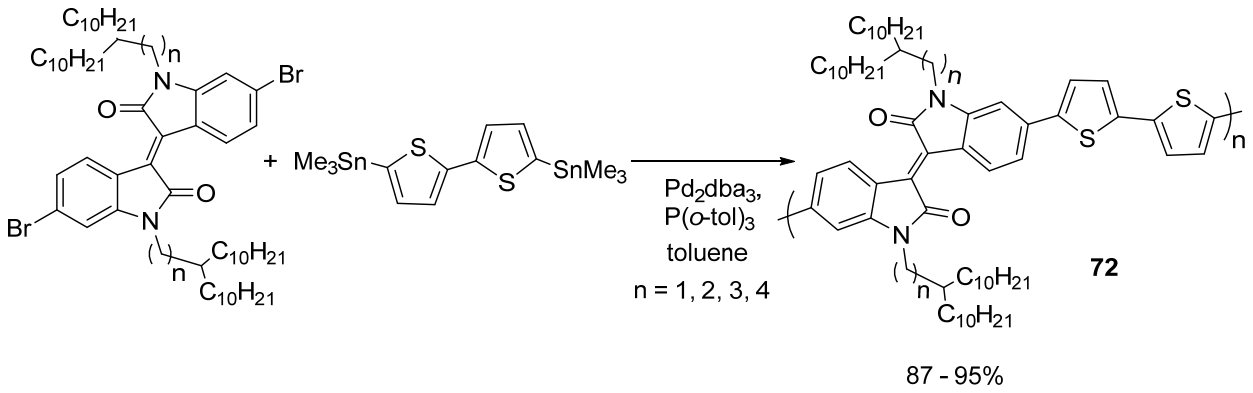
Using the highly reactive 6,6′-dibromoisoindigo in Stille couplings, a series of polymeric structures (**71**) with thiophene, selenophene or dithienocarbazole units were obtained (Scheme 36).[126,127]



Scheme 36

The hole mobilities of these polymers exceeded 0.3 $cm^2V^{-1}s^{-1}$, and the maximum reached 1.06 $cm^2V^{-1}s^{-1}$. A good stability of these copolymers upon moisture authors attribute with their low-lying HOMO levels.

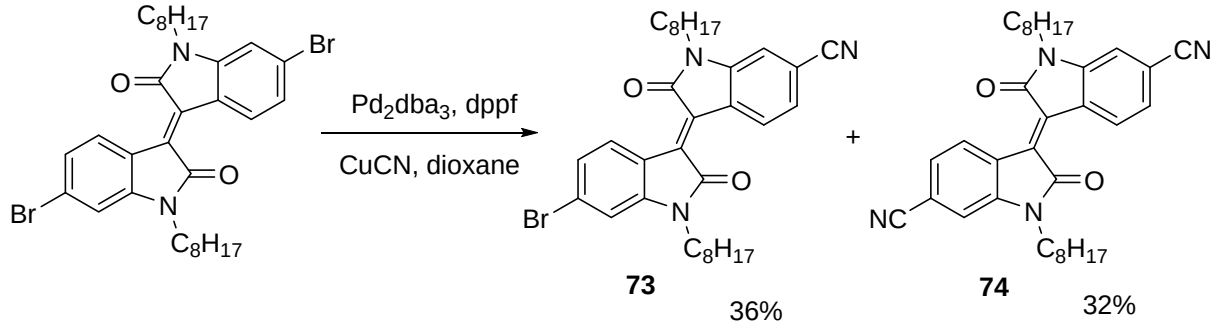
The influence of the alkyl chain branching position on the hole mobilities of isoindigo-based polymer (**72**) thin-film transistors has been studied (Scheme 37).[128] A sample with n = 3 showed the best hole mobility value (3.62 $cm^2V^{-1}s^{-1}$).



Scheme 37

An isoindigo-based polymer structures with halogen atoms either in heterocyclic core[129,130] or in arylene units[131] also found their application in OFETs creation.

A straightforward synthesis of cyanated isoindigo derivatives (**73, 74**) with moderate yields and significant impact of cyano groups on the electronic properties, i.e. LUMO levels, is also reported (Scheme 38).[132]



Scheme 38

4. Conclusions

A wide range of practically useful properties that are inherent to isoindigos indicate the urgency and the need for further development of effective and tolerant synthetic pathways toward this class of heterocycles. As can be seen from published data, some syntheses are either non-selective or proceed in strict conditions with very low yields. The most popular approach to the synthesis of isoindigo-based polymers utilizes only 6,6′-dibromoisoindigo whereas its 5,5′- or 7,7′-analogues seem to be more available and cheaper.

Thus, despite its century of history, the chemistry of isoindigo still remains a fertile field for structural, biological and synthetic studies.

Acknowledgements

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