New Synthetic Applications of Indium Organometallics in Cross-Coupling Reactions

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Dedicated to Professor Amos B. Smith, III on the occasion of his 60th birthday.

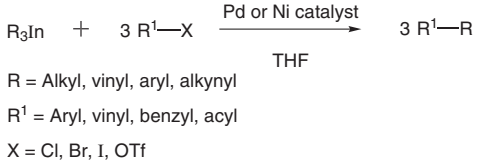
Abstract: The use of indium organometallics in multifold and sequential cross-coupling reactions is reported. Triorganoindium reagents (R_3In) react, under palladium catalysis, with oligohaloarenes affording the multiple cross-coupling products in a single operation. In the reaction, the three organic groups (alkyl, aryl, alkenyl or alkynyl) attached to indium are efficiently transferred to the electrophile, with only a slight excess of organometallic reagent. We demonstrate that indium organometallics are useful reagents for sequential cross-coupling reactions. This reaction illustrates the high chemoselectivity of R_3In.

Key words: atom economy, indium, organometallic reagents, multifold and sequential cross-coupling, palladium catalysis

1 Introduction

Over the past decade, indium has received a great deal of attention from organic chemists due to its location in the periodic table and the interesting chemical properties associated with it.[1] Indium is today recognized as a useful metal in organic synthesis and several synthetic applications, such as the allylation of carbonyls[2] or triple bonds[3] in anhydrous or aqueous media, can be performed efficiently under simple reaction conditions. Furthermore, indium organometallics have been shown to be useful reagents in several fundamental organic transformations, such as conjugate addition,[4] cross-coupling[5,6] and allylic subtitution reactions.[7]

In 1999, we discovered the metal-catalyzed cross-coupling reaction of triorganoindium compounds (R_3In) with organic halides.[5a] In this reaction, R_3In showed interesting chemical properties including high reactivity, efficiency, versatility and chemoselectivity – all three organic groups attached to the metal are efficiently transferred to the electrophile and a wide variety of carbon types (sp^3, sp^2, sp) can be bound to the metal (Scheme 1). Soon after our discovery, this reaction drew the attention of various research groups and the synthetic scope was quickly extended to include other indium reagents, such as tetraorganoindates,[6k] different reaction conditions (aqueous media),[6b] and carbonylative cross-coupling reactions.[5d,6i] We describe here a full account of the use of triorganoindium compounds in multifold and sequential cross-coupling reactions.[8]



Scheme 1

Efficiency and economy are major goals in any chemical transformation. In the field of organic synthesis, one important way to achieve efficiency in a reaction is through a high level of conversion of the reagent into the reaction product (atom economy). Another possibility is to perform more than one reaction type, or several different reactions, in a single pot. The high conversion of R_3In in the metal-catalyzed cross-coupling reaction prompted us to explore its application to efficient reactions in which more than one bond is formed in one step. For this purpose, oligohaloarenes are useful partners to perform both multifold cross-coupling reactions (multiple similar bonds formed in one step) or sequential cross-coupling reactions (multiple different bonds formed in one step).

2 Results and Discussion

2.1 Multifold Cross-Coupling Reactions

This particular type of reaction has been performed using different organometallics and allows the synthesis of highly unsaturated, conjugated π-systems, which are compounds of particular interest in materials science.[9] Among the wide variety of conjugated architectures, polyphenylene and polyphenylacetylene structures, as well as derivatives bearing a heterocyclic unit in their structure, are of particular interest. The utility of such compounds as liquid crystals,[10] core structures for dendrimers,[11] building blocks for two-dimensional carbon networks,[12] electronic

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devices[13] and molecular wires[9b] is a topic of current research.

Despite the fact that various synthetic procedures have been developed to prepare these interesting systems, metal-catalyzed cross-coupling reactions still represent the most useful and straightforward methodology.[9a,14] The cross-coupling reactions are usually performed between an organometallic or acetylenic partner and an oligohaloarene to afford the desired multifold cross-coupling products in one step. Typically, an efficient transformation requires a large excess of the organometallic reagent and harsh reaction conditions (high temperatures and pressure, long reaction times), and even in these cases the yields are sometimes low.[15] In an attempt to overcome the drawbacks outlined above, and encouraged by the particular advantages of triorganoindium compounds and the potential uses of the final products, we developed a novel multiple palladium-catalyzed cross-coupling reaction using triorganoindium compounds.

For our initial studies, we chose aryl and alkynyl triorganoindium reagents and dihalobenzenes as organic electrophiles. In our first attempt, we studied the palladium-catalyzed cross-coupling reaction of 1,4-dibromobenzene (**1a**) with Ph_3In. After some experimentation, we found that the double cross-coupling reaction product can be obtained in good yield when 100 mol% of Ph_3In is used in THF (reflux for two hours) in the presence of 4 mol% of $Pd(dppf)Cl_2$ (Table 1, entry 1). Following the same experimental procedure, the reaction of tri(phenylethynyl)indium or tris[(trimethylsilyl)ethynyl]indium with **1a** afforded the double cross-coupling products **2b** or **2c** in 84% and 60% yield, respectively (Table 1, entries 2 and 3). The transfer of an alkyl group was also effective, using only 70 mol% of *n*-Bu_3In (Table 1, entry 4).

As demonstrated above, triorganoindium compounds are able to transfer efficiently all three aryl, alkynyl or alkyl groups. These results can be improved using 1,4-diiodobenzene (**1b**) as the electrophile. In this case, the cross-coupling reactions proceed in good yields using just 80 mol% of R_3In. The reaction proceeds with triphenylindium, tri(phenylethynyl)indium or tris[(trimethylsilyl)ethynyl]indium to give the twofold cross-coupling products **2a**–**2c** in 60–76% yields. These yields can be further increased to quantitative upon using 100 mol% of the trior-

Biographical Sketches

Miguel A. Pena was born in Ferrol, Spain, in 1978. He studied chemistry at the Universidade da Coruña, Spain, where he obtained his B.S. degree in 2001 and his M.S. degree in 2003. He is currently working on his Ph.D. thesis, as FPU fellow, on new developments of cross-coupling reactions with indium organometallics under the supervision of Profs. L. A. Sarandeses and J. Pérez Sestelo. He spent a predoctoral training period at the Max-Planck Institut für Kohlenforschung in Mülheim an der Ruhr, Germany, under the supervision of Prof. A. Fürstner.

José Pérez Sestelo was born in Vigo (Spain) in 1966. He studied chemistry at the Universidade de Santiago de Compostela (B.S. degree in 1989) where he got his Ph.D. in 1994 under the supervision of Profs. Antonio Mouriño and Luis Castedo. After postdoctoral studies with Prof. Amos B. Smith III at the University of Pennsylvania (1994–95) and Prof. T. Ross Kelly at Boston College (1996) he joined the Universidade da Coruña (1997). After a period as assistant professor (1998–2003) in the same institution, he became associate professor. His main research topics are focused on the development of novel metal-promoted organic reactions and their application to the synthesis of biologically active natural products.

Luis A. Sarandeses was born in Lugo, Spain, in 1963. He studied chemistry at the Universidade de Santiago de Compostela, Spain, (B.S. degree in 1985) and obtained his Ph.D. in 1989 under the supervision of Profs. L. Castedo and A. Mouriño. He spent two years (1990–1991) as a NATO postdoctoral researcher at the Université Joseph Fourier de Grenoble, France, working with Dr. J.-L. Luche on the applications of ultrasound in organic synthesis. In 1992, he joined the Universidade da Coruña, Spain, as assistant professor, and became associate professor in 1994. His research interests are focused on the utilization of transition metals in organic synthesis and in the synthesis of natural products and pharmacologically active compounds.

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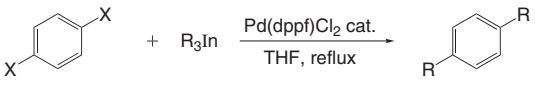
Table 1 Palladium-Catalyzed Twofold Cross-Coupling Reactions with Triorganoindium Reagents[a]



1a, X = Br
1b, X = I

2a–e

Entry	X	R	R_3In (mol%)	Product	Yield (%)[b]
1	Br (**1a**)	Ph	100	**2a**	70
2		PhC≡C	100	**2b**	84
3		$Me_3SiC{\equiv}C$	100	**2c**	60
4		*n*-Bu	70	**2d**	83
5	I (**1b**)	Ph	80	**2a**	72
6		PhC≡C	80	**2b**	76 (99)[c]
7		$Me_3SiC{\equiv}C$	80	**2c**	60 (92)[c]
8		*n*-Bu	70	**2d**	70
9		CH_2=CH	80	**2e**	96

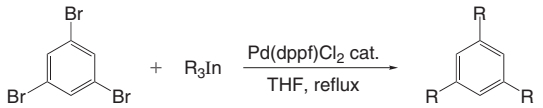
[a] Reactions were carried out in refluxing THF for 2 h using 4 mol% of $Pd(dppf)Cl_2$ as catalyst.
[b] Isolated yield.
[c] The yield obtained using 100 mol% of R_3In is shown in parentheses.

ganoindium reagents (Table 1, entries 6 and 7). The reaction of **1b** with tributylindium afforded a similar result to that obtained previously (Table 1, entry 8), while the reaction of trivinylindium (80 mol%) gave an excellent yield of **2e** (96%) after just two hours of reaction (Table 1, entry 9). As previously reported,[5b] these results are in accordance with the higher reactivity of aryl iodides than bromides towards triorganoindium reagents.

The utility of indium organometallics in multifold coupling reactions was explored further by attempting to form three bonds in one step. 1,3,5-Triarylbenzenes and 1,3,5-triethynylbenzenes display interesting physical properties as liquid crystals or non-linear optical materials and these were chosen as our first targets.[16] The reaction of 1,3,5-tribromobenzene (**3**) with Ph_3In (130 mol%) in the presence of catalytic amounts of $Pd(dppf)Cl_2$ (4 mol%) under reflux in THF afforded 1,3,5-triphenylbenzene (**4a**) in 97% yield (Table 2, entry 1). This result demonstrates the feasibility of using this type of organometallic reagent to form three C–C bonds on the same substrate in one pot, and the efficient transfer of all three organic groups attached to indium(III).

Under the same experimental conditions, the reaction of **3** with tri(phenylethynyl)indium gave the threefold cross-coupling product **4b** in quantitative yield (Table 2, entry 2). When the reaction was performed with tris[(trimethylsilyl)ethynyl]indium, 150 mol% was needed to optimize the yield (80%, Table 2, entry 3). Functionalized triarylindium reagents can also be efficiently used (Table 2, entries 4 and 5) and the cross-coupling products should allow the synthesis of more complex compounds such as

Table 2 Threefold Cross-Coupling Reactions of 1,3,5-Tribromobenzene (**3**) with Indium(III) Organometallics[a]



3

4a–f

Entry	R	R_3In (mol%)	Product	Yield (%)[b]
1	Ph	130	**4a**	97
2	PhC≡C	130	**4b**	99
3	$Me_3SiC{\equiv}C$	150	**4c**	80
4	*p*-$MeOC_6H_4$	130	**4d**	90
5	*m*-$MeOC_6H_4$	130	**4e**	70
6	*n*-Bu	130	**4f**	76

[a] Reactions were performed with 4 mol% of $Pd(dppf)Cl_2$ as catalyst in refluxing THF for 2–4 h.
[b] Isolated yield.

dendrimers.[5c] The reaction with a trialkylindium species also afforded the desired product in good yield (76%, Table 1, entry 6). In all cases, the small excesses of triorganoindium compound used and the short reaction times required to construct three C–C bonds in a one-step, high yielding sequence should be highlighted.

At this point, we became interested in extending the scope of the multifold cross-coupling reactions to include aromatic compounds other than benzene. For this purpose, we selected an electron-deficient heteroaromatic compound, 2,6-dibromopyridine (**5**), and an electron-rich heteroaromatic compound, 2,5-dibromothiophene (**7**).

Aryl- and ethynyl-substituted pyridines have important applications as fluorescent chemosensors,[17] as chelating agents in coordination chemistry,[18] and as building blocks in supramolecular structures.[19] These compounds are usually obtained in step-by-step cross-coupling reactions, but these processes are associated with some synthetic difficulties.[20] Following our methodology, we found that the reaction of 2,6-dibromopyridine (**5**) with just 80 mol% of triphenylindium in the presence of catalytic amounts of $Pd(dppf)Cl_2$ (4 mol%) afforded the twofold cross-coupling product **6a** in 91% yield (Table 3, entry 1). In the same way, the reaction using tri(phenylethynyl)indium (80 mol%) as the organometallic component afforded the desired product, 2,6-bis(phenylethynyl)pyridine (**6b**), in 90% yield (Table 3, entry 2). Other acetylenic, vinylic or alkyl derivatives can also be efficiently synthesized using the same experimental procedure, although larger amounts of triorganoindium species were required (100 mol%, Table 3, entries 3–5). In particular, the lower reactivity of the trialkylindium organometallics with respect to the other compounds is evident in the reaction of *n*-Bu_3In with **5**, which affords the cross-coupling product in only 50% yield. In addition, in this reaction the use of $Pd(Ph_3P)_4$ as the catalyst gave the best results.

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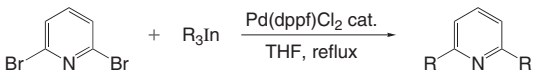
Table 3 Synthesis of Disubstituted Pyridines Using Triorganoindium Reagents[a]



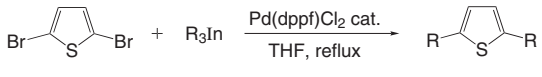
5 6a–e

Entry	R	R_3In (mol%)	Product	Yield (%)[b]
1	Ph	80	**6a**	91
2	PhC≡C	80	**6b**	90 (99)[c]
3	$Me_3SiC≡C$	100	**6c**	82
4	CH_2=CH	100	**6d**	90
5	*n*-Bu	100	**6e**	50[d]

[a] Reactions were carried out in refluxing THF with Pd(dppf)Cl_2 (4 mol%).
[b] Isolated yield.
[c] The yield obtained by on using 100 mol% of R_3In is shown in parentheses.
[d] Reaction performed with Pd(Ph_3P)$_4$ (4 mol%) as catalyst.

We next explored the reactivity of 2,5-dibromothiophene (**7**). Aryl and alkynyl thiophene derivatives have interesting properties as electronic devices and molecular wires.[9b] Following our previously developed methodology, triorganoindium reagents were able to efficiently transfer aryl, alkenyl and alkynyl groups, although in this case it was necessary to increase the ratio of indium organometallic employed in order to optimize the yields (Table 4).

Table 4 Synthesis of Disubstituted Thiophenes Using Triorganoindium Reagents[a]

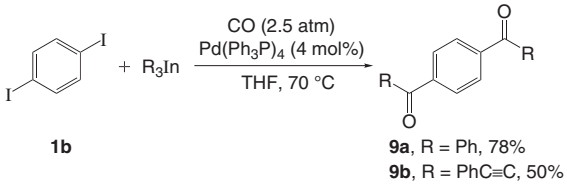


7 8a–d

Entry	R	R_3In (mol%)	Product	Yield (%)[b]
1	Ph	200	**8a**	84 (40)[c]
2	PhC≡C	150	**8b**	91 (50)[c]
3	$Me_3SiC≡C$	150	**8c**	77
4	CH_2=CH	150	**8d**	77

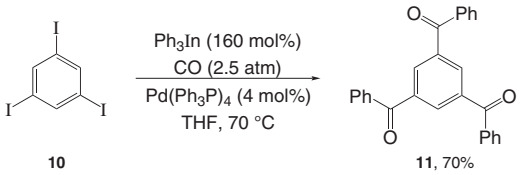
[a] Reactions were carried out in refluxing THF using 4 mol% of Pd(dppf)Cl_2.
[b] Isolated yield.
[c] The yield obtained on using 80 mol% of R_3In is shown in parentheses.

Having demonstrated the utility of indium organometallics in multifold cross-coupling reactions with oligohaloarenes under palladium catalysis, we proceeded to study the application of this methodology in carbonylative multifold coupling. The carbonylative coupling using triorganoindium compounds has proven to be an efficient method to synthesize unsymmetrical ketones with high atom efficiency, with the three organic groups attached to the metal transferred to the electrophile.[5d,6i] In our case, under the reaction conditions previously reported[5d] [2.5 atm CO, 4 mol% of Pd(Ph_3P)$_4$ in THF at 70 °C], 1,4-diiodobenzene (**1b**) reacted with triphenylindium (100 mol%) or tri(phenylethynyl)indium (80 mol%) to afford the corresponding 1,4-diacylbenzene derivatives (**9a** or **9b**) in moderate to good yields (78% and 50%, respectively, Scheme 2).



Scheme 2

A threefold carbonylative coupling was also achieved by reaction of 1,3,5-triiodobenzene (**10**) with Ph_3In (160 mol%), under 2.5 atm of CO in the presence of 4 mol% of Pd(Ph_3P)$_4$ in THF at 70 °C, to afford the triacylbenzene **11** in 70% yield (Scheme 3). These reactions demonstrate the utility of indium organometallics in multifold cross-carbonylative coupling processes.



Scheme 3

2.2 Sequential Cross-Coupling Reactions

Once the behavior of indium organometallics in multifold cross-coupling reactions was established, we decided to explore the use of these reagents in sequential one-pot metal-catalyzed cross-coupling reactions. The combination of several steps into a single-pot operation constitutes an important way to improve the efficiency of a synthetic methodology – an aspect also relevant from an economic and environmental point of view. This methodology requires high chemoselectivity, high levels of reagent conversion, and the minimization of reaction byproducts. Sequential cross-coupling reactions have already been performed using different types of organometallics,[21] and some examples can be found based on bis-Suzuki[22] couplings or on a combination of two reaction types.[23] In our case, the efficiency of the cross-coupling reaction with indium organometallics can be studied in the construction of different C–C bonds in a one-step sequence by successive addition of different triorganoindium reagents to a substituted oligohaloarene with different halogen atoms.

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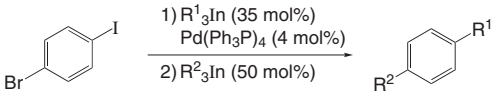
According to our previous studies, the aryl–iodide bond is more reactive than the aryl–bromide bond in cross-coupling reactions with triorganoindium compounds.[5c] Therefore, we selected 1-bromo-4-iodobenzene (**12**) as the first electrophile to study in sequential cross-coupling reactions. A refluxing solution of **12** and $Pd(Ph_3P)_4$ (4 mol%) was treated successively with triphenylindium (35 mol%) and tributylindium (50 mol%) and the sequential cross-coupling product, 4-butylbiphenyl (**13a**, Table 5, entry 1), was obtained in 76% yield. This result illustrates the chemoselectivity of the reaction and the utility of indium organometallics in the one-pot preparation of unsymmetrically substituted aromatic compounds. In an effort to extend the scope of the reaction, different organic groups were used as nucleophiles in this reaction. Aryl, alkynyl and alkyl groups could all be accommodated as organometallic counterparts, affording the corresponding 1,4-unsymmetrically substituted arenes **13b–h** in good yields (40–95%, Table 5, entries 2–8).

Table 5 Sequential Cross-Coupling Reactions with Indium(III) Organometallics[a]



12 **13a–h**

Entry	R^1	R^2	Product	Yield (%)[b]
1	Ph	*n*-Bu	**13a**	76
2		Me	**13b**	95
3	PhC≡C	Ph	**13c**	81
4		*n*-Bu	**13d**	75
5		Me	**13e**	80
6	$Me_3SiC{\equiv}C$	Ph	**13f**	56
7		*n*-Bu	**13g**	82
8	*n*-Bu	Ph	**13a**	73
9	Me	*n*-Bu	**13h**	40

[a] All reactions were carried out with 35 mol% of $R^1{}_3In$ followed by 50 mol% of $R^2{}_3In$ in the presence of 4 mol% of $Pd(Ph_3P)_4$ in refluxing THF.
[b] Isolated yield.

3 Conclusions

Triorganoindium compounds can be efficiently employed in multifold cross-coupling reactions using oligohaloarenes and polyhalogenated aromatic heterocyclic compounds. This methodology provides the possibility of building several C–C bonds in a single operation. The multifold cross-coupling reaction can be performed under a carbon monoxide atmosphere giving di- or triacylbenzene derivatives in one pot. Furthermore, the high chemoselectivity and atom efficiency in metal-catalyzed cross-coupling processes involving triorganoindium compounds allow the development of sequential cross-coupling reactions that afford unsymmetrical alkyl-, aryl- and alkynyl-substituted aromatic compounds in one pot. In all cases, the reaction proceeds in good yields with low catalyst loading and short reaction times. The small excess of reagent employed shows that triorganoindium reagents transfer their three organic groups to the electrophile with high atom efficiency. These novel features make indium organometallics useful alternatives to other organometallic reagents in organic synthesis and reveal them to be an important tool in modern organic synthesis.

All reactions were conducted in flame-dried glassware in a well ventilated hood. Reaction temperatures refer to external bath temperatures. NMR spectra were obtained with a Bruker AC-200F (200 MHz for ^1H NMR and 50 MHz for ^{13}C NMR) spectrometer in $CDCl_3$ using the residual solvent signal at $\delta = 7.26$ ppm (^1H NMR) or $\delta = 77.0$ ppm (^{13}C NMR) as internal standard. DEPT was used to assign carbon types. The electron-impact mass spectra were measured on a Fisons VG-Quattro spectrometer at 70 eV. Compounds **2a**, **2c**, **2d**, **2e**, **4a**, **4b**, **4d**, **6a**, **9a**, and **13b** are commercially available and were identified by comparison of their spectral data (^1H NMR, ^{13}C NMR, IR, MS) and physical properties with authentic samples.

Triorganoindium Reagents; General Procedure

A 25 mL round-bottomed flask containing a stir bar was charged with $InCl_3$ (0.40 mmol) and dried under vacuum with a heat gun. The mixture was cooled, a positive argon pressure was established, and anhydrous THF (4 mL) was added. The resulting solution was cooled to –78 °C and a solution of RLi or RMgBr (1.1 mmol, 1.0–2.5 M in hexanes, THF, or Et_2O) was slowly added (15–30 min). The mixture was stirred for 30 min, the cooling bath was removed, and the reaction mixture was warmed to r.t.

Palladium-Catalyzed Multifold Cross-Coupling Reaction; General Procedure

A solution of R_3In (0.80 to 2.00 mmol, ca. 0.1 M in anhydrous THF) was added to a refluxing mixture of the electrophile (**1**, **3**, **5** or **7**, 1 mmol) and $Pd(dppf)Cl_2$ (0.04 mmol) in anhydrous THF (4 mL). The mixture was heated under reflux until the starting material had been consumed (2–4 h, TLC monitoring) and the reaction was quenched by the addition of few drops of MeOH. The mixture was concentrated in vacuo and Et_2O (30 mL) was added. The organic phase was washed with sat. aq NH_4Cl (15 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by flash chromatography to afford, after concentration and high-vacuum drying, the multifold cross-coupling product.

Palladium-Catalyzed Multifold Carbonylative Cross-Coupling Reaction; General Procedure

In a Schlenk tube, a solution of R_3In (0.80 to 1.35 mmol, ca. 0.1 M in anhydrous THF) was added to a mixture of the electrophile (**1b** or **12**, 1 mmol) and $Pd(Ph_3P)_4$ (0.05 mmol) in anhydrous THF (5 mL). The tube was charged with CO (2.5 atm) and the resulting mixture was heated at 70 °C for 6 h. The mixture was cooled, the pressure was released and the reaction was quenched by the addition of a few drops of MeOH. The mixture was concentrated in vacuo and Et_2O (20 mL) was added. The organic phase was washed with sat. aq NH_4Cl (15 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by flash chromatography (15% EtOAc–hexanes) to afford, after concentration and high-vacuum drying, the multifold carbonylative cross-coupling product.

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Palladium-Catalyzed Sequential Cross-Coupling Reactions; General Procedure

A solution of $R^1{}_3In$ (0.35 mmol, ca. 0.1 M in anhydrous THF) was added to a refluxing mixture of **9** (1 mmol) and $Pd(Ph_3P)_4$ (0.04 mmol) in anhydrous THF (4 mL). After refluxing the mixture until the starting material had been consumed (2–4 h, TLC monitoring), a solution of $R^2{}_3In$ (0.50 mmol, ca. 0.1 M in anhydrous THF) was added. The resulting mixture was refluxed under the same conditions until the intermediate product had been consumed (2–4 h) and the reaction was quenched with a few drops of MeOH. The mixture was concentrated in vacuo, Et_2O (30 mL) was added and the organic phase was washed with sat. aq NaCl (15 mL), dried (Na_2SO_4), filtered and concentrated under vacuum. The residue was purified by flash chromatography (hexanes) to afford, after concentration and high-vacuum drying, the sequential cross-coupling product.

1,4-Bis(phenylethynyl)benzene (2b)[24]

^{1}H NMR ($CDCl_3$): δ = 7.33–7.40 (m, 6 H), 7.51–7.58 (m, 8 H).

^{13}C NMR ($CDCl_3$): δ = 89.1 (2 × C), 91.2 (2 × C), 123.0 (2 × C), 123.1 (2 × C), 128.37 (2 × CH), 128.43 (2 × CH), 131.5 (4 × CH), 131.6 (4 × CH).

MS (EI): *m/z* (%) = 278 (M^+, 100), 139 (19).

1,3,5-Tris[(trimethylsilyl)ethynyl]benzene (4c)[25]

^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 27 H), 7.50 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = –10.9 (9 × CH_3), 95.6 (3 × C), 103.1 (3 × C), 123.6 (3 × C), 134.9 (3 × CH).

MS (EI): *m/z* (%) = 366 (M^+, 32), 351 [($M^+ - CH_3$), 100].

1,3,5-Tris(3-methoxyphenyl)benzene (4e)[26]

^{1}H NMR ($CDCl_3$): δ = 3.91 (s, 9 H), 6.98 (br d, *J* = 7.9 Hz, 3 H), 7.28 (br s, 3 H), 7.32 (d, *J* = 7.6 Hz, 3 H), 7.44 (dd, *J* = 7.9, 7.6 Hz, 3 H), 7.82 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 55.4 (3 × CH_3), 113.0 (3 × CH), 113.1 (3 × CH), 119.9 (3 × CH), 125.4 (3 × CH), 129.9 (3 × CH), 142.2 (3 × C), 142.6 (3 × C), 160.0 (3 × C).

MS (EI): *m/z* (%) = 396 (M^+, 100).

1,3,5-Tributylbenzene (4f)[27]

^{1}H NMR ($CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 9 H), 1.28–1.47 (m, 6 H), 1.54–1.69 (m, 6 H), 2.57 (t, *J* = 7.3 Hz, 6 H), 6.83 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 14.0 (3 × CH_3), 22.5 (3 × CH_2), 33.8 (3 × CH_2), 35.7 (3 × CH_2), 125.8 (3 × CH), 142.6 (3 × C).

MS (EI): *m/z* (%) = 246 (M^+, 43), 204 (100), 147 (77).

2,6-Bis(phenylethynyl)pyridine (6b)[28]

^{1}H NMR ($CDCl_3$): δ = 7.35–7.41 (m, 6 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.59–7.64 (m, 4 H), 7.70 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 88.3 (2 × C), 89.6 (2 × C), 122.1 (2 × C), 126.2 (2 × CH), 128.4 (4 × CH), 129.1 (2 × CH), 132.1 (4 × CH), 136.4 (CH), 143.8 (2 × C).

MS (EI): *m/z* (%) = 279 (M^+, 100), 278 [($M^+ - 1$), 43], 178 [($M^+ - C_8H_5$), 6].

2,6-Bis[(trimethylsilyl)ethynyl]pyridine (6c)[29]

^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 18 H), 7.38 (d, *J* = 7.9 Hz, 2 H), 7.59 (t, *J* = 7.9 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = –0.4 (6 × CH_3), 95.3 (2 × C), 103.1 (2 × C), 126.6 (2 × CH), 136.2 (CH), 143.3 (2 × C).

MS (EI): *m/z* (%) = 271 (M^+, 38), 256 [($M^+ - CH_3$), 100], 226 [($M^+ - C_2H_6$), 5].

2,6-Divinylpyridine (6d)[30]

^{1}H NMR ($CDCl_3$): δ = 5.49 (dd, *J* = 10.7, 1.5 Hz, 2 H), 6.26 (dd, *J* = 17.6, 1.5 Hz, 2 H), 6.84 (dd, *J* = 17.6, 10.7 Hz, 2 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 7.60 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 118.2 (2 × CH_2), 119.9 (2 × CH), 136.8 (CH), 137.0 (2 × CH), 155.3 (2 × C).

MS (FAB) *m/z* (%) = 132 [(M^+ + 1), 100].

2,6-Dibutylpyridine (6e)[31]

^{1}H NMR ($CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 6 H), 1.23–1.46 (m, 4 H), 1.60–1.75 (m, 4 H), 2.74 (m, *J* = 7.8 Hz, 4 H), 6.91 (d, *J* = 7.8 Hz, 2 H), 7.45 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 13.9 (2 × CH_3), 22.5 (2 × CH_2), 32.3 (2 × CH_2), 38.3 (2 × CH_2), 119.5 (2 × CH), 136.2 (CH), 161.8 (2 × C).

MS (EI): *m/z* (%) = 191 (M^+, 4), 176 [($M^+ - CH_3$), 8], 149 (100).

2,5-Diphenylthiophene (8a)[32]

^{1}H NMR ($CDCl_3$): δ = 7.26–7.45 (m, 6 H), 7.31 (s, 2 H), 7.62–7.68 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 124.0 (2 × CH), 125.6 (4 × CH), 127.5 (2 × CH), 128.9 (4 × CH), 134.3 (2 × C), 143.6 (2 × C).

MS (EI): *m/z* (%) = 236 (M^+, 100).

2,5-Bis(phenylethynyl)thiophene (8b)[32]

^{1}H NMR ($CDCl_3$): δ = 7.17 (s, 2 H), 7.33–7.40 (m, 6 H), 7.50–7.57 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 82.2 (2 × C), 94.0 (2 × C), 122.6 (2 × C), 124.6 (2 × C), 128.4 (4 × CH), 128.6 (2 × CH), 131.5 (4 × CH), 131.8 (2 × CH).

MS (EI): *m/z* (%) = 284 (M^+, 19), 88 (100).

2,5-Bis[(trimethylsilyl)ethynyl]thiophene (8c)[33]

^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 18 H), 7.05 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –0.2 (6 × CH_3), 96.9 (2 × C), 99.9 (2 × C), 124.5 (2 × C), 132.2 (2 × CH).

MS (EI): *m/z* (%) = 276 (M^+, 47), 261 [($M^+ - CH_3$), 100].

2,5-Divinylthiophene (8d)[34]

^{1}H NMR ($CDCl_3$): δ = 5.15 (d, *J* = 10.8 Hz, 2 H), 5.55 (d, *J* = 17.1 Hz, 2 H), 6.76 (dd, *J* = 17.1, 10.8, 2 H), 6.84 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 113.4 (2 × CH_2), 126.3 (2 × CH), 130.0 (2 × CH), 141.9 (2 × C).

MS (EI): *m/z* (%) = 136 (M^+, 100).

1,1′-(1,4-Phenylene)bis[3-phenylprop-2-yn-1-one] (9b)[35]

^{1}H NMR ($CDCl_3$): δ = 7.41–7.58 (m, 6 H), 7.70–7.76 (m, 4 H), 8.36 (s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 86.8 (2 × C), 94.5 (2 × C), 119.7 (2 × C), 129.6 (4 × CH), 131.2 (2 × CH), 133.2 (4 × CH), 140.5 (2 × C), 177.0 (2 × C).

MS (EI): *m/z* (%) = 334 (M^+, 34), 306 (15), 278 (26), 183 (22), 129 (100).

1,3,5-Tribenzoylbenzene (11)[36]

^{1}H NMR ($CDCl_3$): δ = 7.48–7.68 (m, 9 H), 7.83–7.89 (m, 6 H), 8.41 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 128.6 (6 × CH), 130.1 (6 × CH), 133.2 (3 × CH), 134.0 (3 × CH), 136.4 (3 × C), 138.2 (3 × C), 194.9 (3 × C).

MS (EI): *m/z* (%) = 390 (M^+, 7), 105 (100).

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4-Butyl-1,1′-biphenyl (13a)[37]
^{1}H NMR ($CDCl_3$): δ = 0.98 (t, *J* = 7.3 Hz, 3 H), 1.30–1.54 (m, 2 H), 1.61–1.76 (m, 2 H), 2.69 (t, *J* = 7.3 Hz, 2 H), 7.29 and 7.55 (2 d, AB system, *J* = 8.3 Hz, 4 H), 7.33–7.52 (m, 3 H), 7.60–7.66 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.4 (CH_2), 33.6 (CH_2), 35.3 (CH_2), 127.0 (2 × CH), 127.16 (CH), 127.23 (CH), 128.68 (2 × CH_2), 128.74 (2 × CH), 128.8 (2 × CH), 138.5 (C), 141.2 (C), 142.0 (C).

MS (EI): *m/z* (%) = 210 (M^+, 31), 167 [($M^+ - C_3H_7$), 100], 152 [($M^+ - C_4H_9$), 19].

4-(Phenylethynyl)-1,1′-biphenyl (13c)[38]
^{1}H NMR ($CDCl_3$): δ = 7.35–7.71 (m, 14 H).

^{13}C NMR ($CDCl_3$): δ = 89.3 (C), 90.1 (C), 122.2 (C), 123.3 (C), 127.0 (2 × CH), 127.5 (CH), 127.6 (CH), 128.26 (2 × CH), 128.35 (2 × CH), 128.9 (2 × CH), 131.6 (2 × CH), 132.0 (2 × CH), 140.4 (C), 141.0 (C).

MS (EI): *m/z* (%) = 254 (M^+, 100).

1-Butyl-4-(phenylethynyl)benzene (13d)[39]
^{1}H NMR ($CDCl_3$): δ = 0.98 (t, *J* = 7.3 Hz, 3 H), 1.22–1.46 (m, 2 H), 1.51–1.70 (m, 2 H), 2.64 (t, *J* = 7.3 Hz, 2 H), 7.18 and 7.45 (2 d, AB system, *J* = 7.8 Hz, 4 H), 7.31–7.39 (m, 3 H), 7.52–7.53 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3), 22.3 (CH_2), 33.4 (CH_2), 88.7 (C), 89.6 (C), 120.6 (C), 123.5 (C), 128.0 (CH), 128.2 (CH), 128.3 (CH), 128.4 (2 × CH), 131.5 (2 × CH), 131.6 (2 × CH), 143.4 (C).

MS (EI): *m/z* (%) = 234 (M^+, 60), 191 [($M^+ - C_3H_7$), 100].

1-Methyl-4-(phenylethynyl)benzene (13e)[40]
^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3 H), 7.18 and 7.47 (2 d, AB system, *J* = 7.8 Hz, 4 H), 7.33–7.40 (m, 3 H), 7.53–7.61 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 21.5 (CH_3), 88.8 (C), 89.6 (C), 120.2 (C), 123.5 (C), 128.1 (CH), 128.3 (2 × CH), 129.1 (2 × CH), 131.5 (2 × CH), 131.6 (2 × CH), 138.4 (C).

MS (EI): *m/z* (%) = 192 (M^+, 100), 115 [($M^+ - C_6H_5$), 9].

1-Phenyl-4-[(trimethylsilyl)ethynyl]benzene (13f)[41]
^{1}H NMR ($CDCl_3$): δ = 0.30 (s, 9 H), 7.33–7.51 (m, 3 H), 7.56 (s, 4 H), 7.59–7.66 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 0.0 (3 × CH_3), 94.8 (C), 105.0 (C), 122.0 (C), 126.8 (2 × CH), 127.0 (2 × CH), 127.6 (CH), 128.8 (2 × CH), 132.4 (2 × CH), 140.3 (C), 141.2 (C).

MS (EI): *m/z* (%) = 250 (M^+, 56), 235 [($M^+ - CH_3$), 100].

1-Butyl-4-[(trimethylsilyl)ethynyl]benzene (13g)[42]
^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 9 H), 0.83–0.99 (m, 3 H), 1.24–1.46 (m, 2 H), 1.51–1.72 (m, 2 H), 2.56–2.67 (m, 2 H), 7.11 and 7.38 (2 d, AB system, *J* = 8.3 Hz, 4 H).

^{13}C NMR ($CDCl_3$): δ = 0.0 (3 × CH_3), 14.1 (CH_3), 22.2 (CH_2), 33.3 (CH_2), 35.5 (CH_2), 93.2 (C), 105.4 (C), 120.2 (C), 128.3 (2 × CH), 131.8 (2 × CH), 143.6 (C).

MS (FAB): *m/z* (%) = 230 (M^+, 17), 215 [($M^+ - CH_3$), 74], 71 (100).

1-Butyl-4-methylbenzene (13h)[43]
^{1}H NMR ($CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3 H), 1.32 (m, 2 H), 1.60 (m, 2 H), 2.34 (s, 3 H), 2.60 (t, *J* = 7.3 Hz, 2 H), 7.11 (s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 21.0 (CH_3), 22.4 (CH_2), 33.8 (CH_2), 35.2 (CH_2), 128.3 (2 × CH), 128.9 (2 × CH), 134.9 (C), 139.8 (C).

MS (EI): *m/z* (%) = 148 (M^+, 23), 105 [($M^+ - C_3H_7$), 100].

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