EurJOC
European Journal of Organic Chemistry

Research Article
doi.org/10.1002/ejoc.202301007

Chemistry Europe
European Chemical Societies Publishing

www.eurjoc.org

Highly Versatile Preparation of Imidazo[1,5-a]quinolines and Characterization of Their Photoluminescent Properties

Niclas Kulhanek,[a] Niklas Martin,[a] and Richard Göttlich*[a]

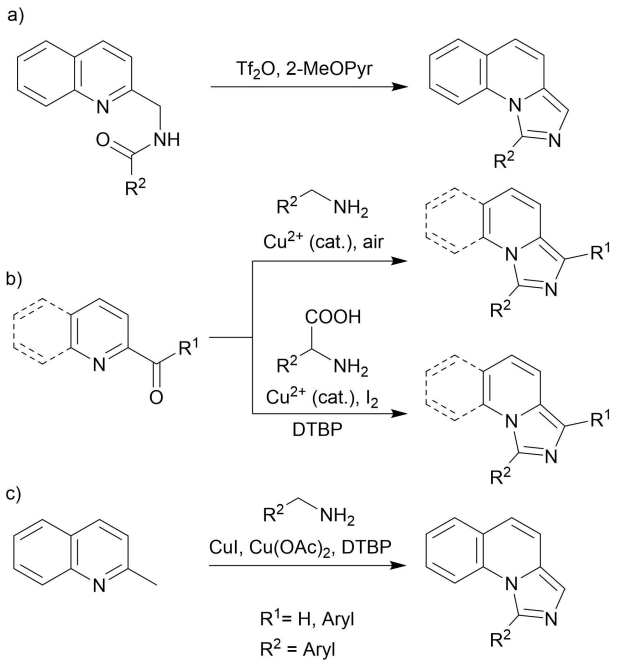
In this work, we describe a simple and robust synthetic approach for the formation of 1,3-substituted imidazo[1,5-*a*]quinolines. This was achieved by developing a mild and selective bromination with N-bromosuccinimide (NBS) in 3-position of the imidazole ring. This was followed by a Negishi coupling, which we performed with various coupling partners, resulting in a wide range of different combinations, usually unattainable by other approaches and similar coupling reactions. Fluorescence measurements identified beneficial substitution patterns for the future use of imidazo[1,5-*a*]quinolines in optical applications, such as organic light-emitting diodes (OLEDs).

Introduction

Since their introduction in 1987 by Tang and VanSlyke, organic light-emitting diodes (OLEDs) have become a fundamental part of the modern lighting industry.[1] To this day, there have been several OLED generations produced utilizing different strategies to improve the internal quantum efficiency (IQE).[2] Regardless of the generation, blue OLED emitter materials are particularly challenging, due to a band gap of around 3 eV and long exciton lifetime (μs), which are higher than for green or red OLED emitter materials. The interaction of excitons and polarons creates hot exciton states that can lead to decomposition of the material. This means that the lifetime of blue emitters is more limited, which makes materials with blue emission and high stability very important.[3]

Imidazo[1,5-*a*]*N*-heteroaromatic ring systems are a common structural motif in pharmacologically and biologically active agents.[4] This important class also includes imidazo[1,5-*a*]pyridines and imidazo[1,5-*a*]quinolines, which are of particular interest because these compounds possess interesting photophysical properties. The simple and small imidazo[1,5-*a*]pyridines show blue emission with good quantum yields (QYs) in combination with a large Stokes shift, qualifying them as emitter materials for OLED application.[5] They can also be used as ligands with various central atoms, without losing their characteristic photoluminescent properties.[6] Weber *et al.* successfully implemented an imidazo[1,5-*a*]pyridine complex into an optical device.[7]

While the synthesis of imidazo[1,5-*a*]pyridines and recently imidazo[5,1-*a*]isoquinolines were the main topic of many studies, imidazo[1,5-*a*]quinolines have been examined less.[8,9] Classically, approaches to the preparation of imidazo[1,5-*a*]quinolines involve ring closure of a carbonyl species. This could be achieved *via* a Vilsmeier-type reaction starting from an amide, but in the modern variant by Pelletier *et al.*, the cyclization can occur under milder conditions (Scheme 1a).[10,11] Wang and Xu *et al.* prepared imidazo[1,5-*a*]quinolines using a copper-catalyzed decarboxylative cyclization of ketones or aldehydes with primary amines and amino acids (Scheme 1b).[12] Wu *et al.* formed the carbonyl species *in situ*, using a copper-promoted oxidative amination (Scheme 1c).[13]



Scheme 1. Known strategies for direct formation of imidazo[1,5-*a*]quinolines using various carbonyl compounds. Di-*t*-butyl peroxide (DTBP).

[a] *N. Kulhanek, N. Martin, Prof. Dr. R. Göttlich*
Institute of Organic Chemistry
Justus-Liebig-University
Heinrich-Buff-Ring 17
35392 Giessen, Germany
E-mail: Richard.Goettlich@org.chemie.uni-giessen.de

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202301007

Research Article
doi.org/10.1002/ejoc.202301007

In our group we have already characterized some imidazo[1,5-*a*]quinoline derivatives and they possessed similar photophysical characteristics as imidazo[1,5-*a*]pyridines, but with higher QY and better stability.[14] We observed that the QY of imidazo[1,5-*a*]quinolines was dependent on the residues R^1 and R^2 (Figure 1), but we were not able to identify a clear trend.[15] In addition, we were able to successfully construct an OLED with **PCIC** as the dopant, in order to show that these compounds could be used as blue light-emitting materials (Figure 1).[16] Since imidazo[1,5-*a*]quinolines are suitable as blue OLED emitters, and showed interesting properties in complexes, we wanted to investigate this system further.

The focus of this study is to examine the effects of R^1 and R^2 residues on the emission, especially the impact of electron-rich, electron-poor, and sterically demanding residues in these positions. Thus, the goal is to develop a synthesis that allows the simple preparation of imidazo[1,5-*a*]quinolines with different residues R^1 and R^2.

Results and Discussion

Synthesis of the imidazo[1,5-a]quinolines

To achieve maximum flexibility we decided to close the imidazole ring with a suitable amide of R^2 and introduce R^1 separately, using a cross-coupling reaction (Scheme 2).

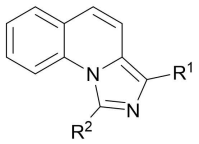
To obtain the required amine **3**, we reduced quinolin-2-carbonitrile **2**, which was excessed from quinoline *N*-oxide **1**, with conditions described in literature.[17]

We utilized an Einhorn acylation with an excess of triethylamine (TEA) to introduce R^2, using a variety of acid chlorides to form the amides **4**. To study the effect of R^2, the chosen residues used were a basic system with phenyl **4a**, an electron-rich aromatic group **4b**, an electron-poor aromatic group **4c** and a sterically demanding group **4d**. Purification of these compounds proved to be difficult. Therefore, we used the crude amides **4**. For the ring closure, we chose the Pelletier approach because it proved to be particularly reliable.[11] Following the procedure, we obtained the desired imidazo[1,5-*a*]quinolines **5** in excellent yields (Scheme 3). Initially we wanted to perform a halogenation with bromine in the 3-position of the imidazole ring system as reported by Shibahara *et al.*[18] However, this approach led to undesired side products, so we performed the bromination at −20 °C with NBS. This granted us the bromide **6** in excellent yields for all compounds (Scheme 3). It must be noted that such bromides can also be accessed directly, as shown by Sandeep and Tan *et al.*[19] These procedures were not used because they lacked the scalability needed for our project.

2-Boronic acids of *N*-heteroaromatics are known to be unstable and the boronic acid of **6** could not be isolated, making a Suzuki coupling not possible.[20] Therefore, we chose a Negishi coupling as our final reaction. Synthesis with **6** as the metallo-organic component resulted in better yields. Thus, in all experiments, bromide **6** was lithiated at −78 °C and transmetalated using an excess of $ZnCl_2$ in THF. We screened for a suitable Pd catalyst (Table 1). Pd(II) catalysts (entry 1–5) showed similar activity to Pd(0) (entry 6–10). However, the yields with Pd(II) did not improve with the addition of ligands, while the Pd(0) complexes led to higher yields in combination with an electron-rich and sterically demanding ligand. The best reactivity in this cross-coupling reaction was obtained with 3 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 6 mol% $P(t\text{-}Bu)_3$ (entry 10). Therefore, the conditions of entry 10 were adapted for all of the following experiments.

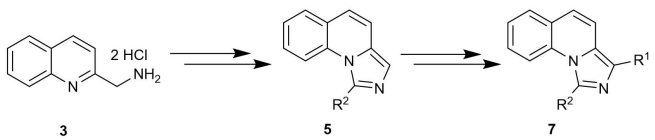
It should be noted that we applied two different workups in the following procedures. The presence of $ZnCl_2$ during the coupling reaction led to the formation of Zn complexes for all chelating compounds **7**–**10a**–**f**, which could be simply filtered off then treated with conc. NH_3 solution to isolate the products directly. The other compounds **g**–**p** were purified by liquid column chromatography.

We started with the coupling of **6a** and the electron-poor substrates and obtained them in very good yields (Table 2). The only exception is **7e**, which was formed in only 13% yield, a sterically demanding substrates can be problematic for the Negishi reaction.[21] This trend continued with the *ortho*-substituted aryl bromides. Thus, **7j** and **7n** were formed in lower yields than their *para*-substituted equivalents. Surpris-

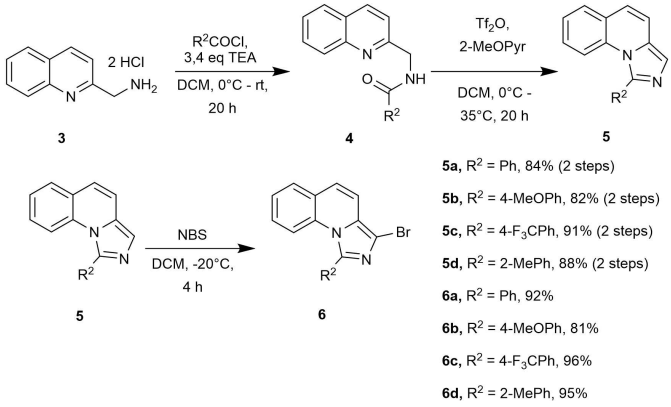


PCIC, R^2 = 2-Pyridyl, R^1 = 2-Quinolyl

Figure 1. General structure and example for imidazo[1,5-*a*]quinoline from our group.



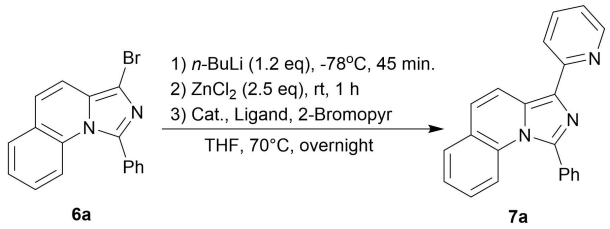
Scheme 2. General approach to the synthesis.



Scheme 3. Introduction of the first selectable residue R^2 using an Einhorn acylation. The crude amides **4** were then cyclized using triflic anhydride (Tf_2O) and 2-MeO-pyridine. After bromination with NBS the first coupling component was obtained.

Research Article
doi.org/10.1002/ejoc.202301007

Table 1. Screening results for the desired Negishi coupling.



6a **7a**

Entry	Cat.	Ligand	Yield/%
1[a]	$Pd(OAc)_2$	PPh_3	69
2[a]	$Pd(OAc)_2$	$P(t\text{-}Bu)_3$	71
3[b]	$[PdCl_2COD]$	–	66
4[b]	$[PdCl_2(MeCN)_2]$	–	61
5[b]	$[PdCl_2(PPh_3)_2]$	–	61
6[b]	$[Pd(PCy_3)_2]$	–	50
7[b]	$[Pd(PPh_3)_4]$	–	69
8[c]	$[Pd_2(dba)_3]\cdot CHCl_3$	PPh_3	72
9[c]	$[Pd_2(dba)_3]\cdot CHCl_3$	dppf	77
10[c]	$[Pd_2(dba)_3]\cdot CHCl_3$	$P(t\text{-}Bu)_3$	83

Reaction conditions: [a] 6 mol% cat., 12 mol% ligand. [b] 6 mol% cat. [c] 3 mol% cat., 6 mol% ligand.

Table 2. Isolated products for the couplings with **6a**, using the conditions of entry 10[c] (Table 1).

Nr.	R^2	R^1	Yield/%
7a	Ph	2-Pyridinyl	73
7b	Ph	2-Pyrimidinyl	60
7c	Ph	2-(5-Ph-Pyridinyl)	70
7d	Ph	2-Quinolinyl	79
7e	Ph	1-Isoquinolinyl	13
7f	Ph	3-Isoquinolinyl	79
7g	Ph	2-Thiophenyl	58
7h	Ph	4-F3 C-Ph	77
7i	Ph	Ph	84
7j	Ph	2-Me-Ph	52
7k	Ph	4-Me-Ph	78
7l	Ph	2-MeO-Ph	84
7m	Ph	4-MeO-Ph	61
7n	Ph	2-Me_2N-Ph	40
7o	Ph	4-Me_2N-Ph	68
7p	Ph	Allyl	47

ingly **7l** opposes this trend. It could be possible that the methoxy group stabilizes the intermediate by coordination to the Pd. This chelation would be stronger for a dimethylamine group which could inhibit the reductive elimination and hinder the coupling reaction, resulting in lower yield for **7n**. The coupling with allylic bromide was also successful, but the obtained mixture contained a large amount of various undefined side products. Purification was therefore challenging and only 47% of **7p** could be isolated.

The general trends observed for the phenyl system **7** largely followed the other coupling systems (Table 3). The 1-isoquinoline substrate could only be isolated in two cases and in low yields. The sterically demanding products **7**–**10j** and **7**–**10n** were formed in lower yields, and **7**–**10l** in higher yield than their equivalents. The allylic product was not formed for **9p** and the other products **7p**, **8p** and **10p** were isolated in lower yields. Surprisingly, the products **10a**–**f** were isolated in lower yields. The Zn complexes for these systems are presumably more soluble in THF and could not be isolated by filtration in the same amount as the other products.

Photophysical measurements

Optical measurements were conducted using a 0.1 mM chloroform solution at room temperature. A 0.1 mM solution of quinine sulfate in 0.5 M H_2SO_4 was used as the reference.[22] The fluorescence QY was calculated as described in the literature.[23] All measurements were performed under non-inert conditions. The extinction and emission spectra of all measured compounds are provided in the supporting information.

The measurements showed that no strong deviation of the extinction in the individual systems occurred. No major shift in the extinction maxima was observed, staying in a range of 350–390 nm (Table 4). In addition, the molar extinction coefficient log ε varied at approximately 4 $L\cdot mol^{-1}\cdot cm^{-1}$ (Table 5) and matches the findings of Volpi *et al.* with a similar system.[9]

Table 3. Isolated products in % for all performed coupling reactions using the conditions of entry 10[c] (Table 1).

	R^1	R^2			
		Ph **7**	4-MeO-Ph **8**	4-F_3C-Ph **9**	2-Me-Ph **10**
a	2-Pyridinyl	73	76	61	52
b	2-Pyrimidinyl	60	73	65	25
c	2-(5-Ph-Pyridinyl)	70	89	88	45
d	2-Quinolinyl	79	91	76	46
e	1-Isoquinolinyl	13	–	–	17
f	3-Isoquinolinyl	79	95	75	12
g	2-Thiophenyl	58	88	98	61
h	4-F_3C-Ph	77	51	53	96
i	Ph	84	95	68	84
j	2-Me-Ph	52	52	27	44
k	4-Me-Ph	78	69	49	56
l	2-MeO-Ph	84	97	77	77
m	4-MeO-Ph	61	75	71	66
n	2-Me_2N-Ph	40	25	62	67
o	4-Me_2N-Ph	68	84	76	74
p	Allyl	47	35	–	48

Research Article
doi.org/10.1002/ejoc.202301007

Table 4. Measured extinction maxima in nm for all isolated products. Every measurement was performed using a 1 μM solution of the compound in chloroform at 25 °C in air.

	R^1	R^2			
		Ph **7**	4-MeO-Ph **8**	4-F_3C-Ph **9**	2-Me-Ph **10**
a	2-Pyridinyl	373	374	360	373
b	2-Pyrimidinyl	369	369	364	369
c	2-(5-Ph-Pyridinyl)	383	385	368	383
d	2-Quinolinyl	390	392	386	389
e	1-Isoquinolinyl	380	–	–	377
f	3-Isoquinolinyl	367	368	365	368
g	2-Thiophenyl	375	374	368	375
h	4-F_3C-Ph	359	361	354	363
i	Ph	361	362	359	360
j	2-Me-Ph	355	354	350	352
k	4-Me-Ph	364	364	362	364
l	2-MeO-Ph	355	355	356	359
m	4-MeO-Ph	364	368	365	366
n	2-Me_2N-Ph	360	339	357	362
o	4-Me_2N-Ph	377	377	378	381
p	Allyl	349	348	–	344

Table 5. Calculated molar extinction coefficient log ε in $L \cdot mol^{-1} \cdot cm^{-1}$ for all isolated products in 1 μM solution with 1 cm cuvette length.

	R^1	R^2			
		Ph **7**	4-MeO-Ph **8**	4-F_3C-Ph **9**	2-Me-Ph **10**
a	2-Pyridinyl	4.20	4.11	4.26	4.26
b	2-Pyrimidinyl	4.27	4.20	4.32	4.41
c	2-(5-Ph-Pyridinyl)	4.18	4.23	4.41	4.38
d	2-Quinolinyl	4.34	4.11	4.34	4.40
e	1-Isoquinolinyl	4.08	–	–	4.23
f	3-Isoquinolinyl	4.15	4.36	4.36	4.41
g	2-Thiophenyl	4.04	4.08	3.90	4.18
h	4-F_3C-Ph	4.15	4.08	4.20	4.26
i	Ph	4.08	4.04	4.08	4.08
j	2-Me-Ph	4.08	4.04	4.04	4.04
k	4-Me-Ph	4.00	4.04	4.04	4.04
l	2-MeO-Ph	4.04	4.08	4.08	4.15
m	4-MeO-Ph	3.95	4.08	4.08	4.15
n	2-Me_2N-Ph	3.95	3.78	3.95	4.04
o	4-Me_2N-Ph	4.00	4.11	4.11	4.15
p	Allyl	3.85	3.95	–	3.95

The measured emission data for the base system **7** showed minor red shifts for **7e**, **7g** and **7o** compared to **7i** (Table 6, Figure 2). Lower emission wavelengths were observed for **7b** and **7p**. Electron-rich and -poor systems in position R^1 seem to have only small effects on the emission wavelength. Therefore,

Table 6. Measured emission maxima for the base system **7**. Every measurement was performed using a 1 μM solution of the compound in chloroform at 25 °C in air. The extinction maxima of the specific compound was chosen as the excitation wavelength.

Nr.	R^2	R^1	Emission/nm	QY / %
7a	Ph	2-Pyridinyl	455	28.35
7b	Ph	2-Pyrimidinyl	447	33.23
7c	Ph	2-(5-Ph-Pyridinyl)	462	38.27
7d	Ph	2-Quinolinyl	463	34.24
7e	Ph	1-Isoquinolinyl	475	32.35
7f	Ph	3-Isoquinolinyl	462	35.83
7g	Ph	2-Thiophenyl	483	24.16
7h	Ph	4-F3 C-Ph	460	33.64
7i	Ph	Ph	464	36.16
7j	Ph	2-Me-Ph	462	20.58
7k	Ph	4-Me-Ph	465	33.07
7l	Ph	2-MeO-Ph	452	26.10
7m	Ph	4-MeO-Ph	467	33.58
7n	Ph	2-Me_2N-Ph	456	26.73
7o	Ph	4-Me_2N-Ph	475	33.94
7p	Ph	Allyl	430	27.31

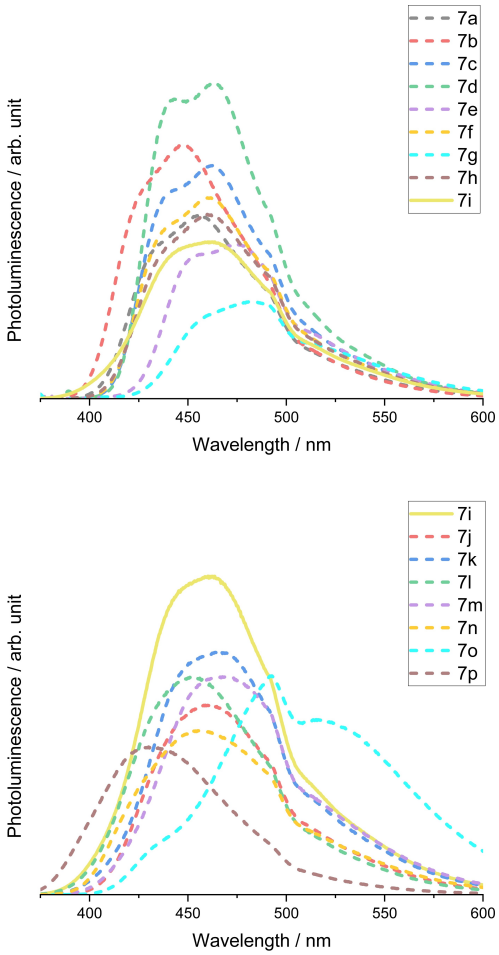


Figure 2. Photoluminescence spectra as 0.1 mM chloroform solution of electron-poor (top) and electron-rich substituted (bottom) base system **7**.

Research Article
doi.org/10.1002/ejoc.202301007

all of **7** displayed a strong blue emission around 450 nm. The QY of **7** was negatively affected by more sterically demanding substituents R^1. Compared to **7i** and their *para*-substituted equivalents, the *ortho*-substituted systems **7j**, **7l** and **7n** showed much lower QYs (Table 6). *N*-heteroaromatic substituents showed higher QYs, which could be increased by extension of their π-system (compare **7a** to **7c**) or introduction of more nitrogen centers (compare **7a** to **7b**). This presumably countered the negative steric effect of the R^1-substituent in **7d**, **7e** and **7f**. Thiophen **7g** and the non-conjugated allyl in **7p** decreased the QY significantly.

Table 7. Measured emission maxima in nm for all isolated products. Every measurement was performed using a 1 μM solution of the compound in chloroform at 25 °C in air. The extinction maxima of the specific compound was chosen as the excitation wavelength.

	R^1	R^2			
		Ph **7**	4-MeO-Ph **8**	4-F_3C-Ph **9**	2-Me-Ph **10**
a	2-Pyridinyl	455	462	457	441
b	2-Pyrimidinyl	447	458	445	428
c	2-(5-Ph-Pyridinyl)	462	468	461	449
d	2-Quinolinyl	463	456	461	452
e	1-Isoquinolinyl	475	–	–	466
f	3-Isoquinolinyl	462	464	463	448
g	2-Thiophenyl	483	477	485	473
h	4-F_3C-Ph	460	470	460	448
i	Ph	464	459	465	456
j	2-Me-Ph	462	453	459	454
k	4-Me-Ph	465	464	470	460
l	2-MeO-Ph	452	457	458	451
m	4-MeO-Ph	467	467	479	466
n	2-Me_2N-Ph	456	459	486	470
o	4-Me_2N-Ph	475	493	493	482
p	Allyl	430	437	–	442

Table 8. Calculated QYs in % for all measured systems.

	R^1	R^2			
		Ph **7**	4-MeO-Ph **8**	4-F_3C-Ph **9**	2-Me-Ph **10**
a	2-Pyridinyl	28.35	26.36	25.14	43.83
b	2-Pyrimidinyl	33.23	27.06	32.64	52.76
c	2-(5-Ph-Pyridinyl)	38.27	35.05	31.48	52.04
d	2-Quinolinyl	34.24	29.85	30.94	47.06
e	1-Isoquinolinyl	32.35	–	–	42.43
f	3-Isoquinolinyl	35.83	27.00	28.55	46.91
g	2-Thiophenyl	24.16	28.36	17.88	38.05
h	4-F_3C-Ph	33.64	31.92	23.19	47.41
i	Ph	36.16	37.82	19.47	41.58
j	2-Me-Ph	20.58	30.43	14.43	25.50
k	4-Me-Ph	33.07	37.67	17.38	46.43
l	2-MeO-Ph	26.10	27.89	15.54	28.89
m	4-MeO-Ph	33.58	35.83	16.19	41.63
n	2-Me_2N-Ph	26.73	18.25	15.27	33.17
o	4-Me_2N-Ph	33.94	23.02	16.40	27.69
p	Allyl	27.31	33.79	–	15.51

The trends of the base system **7** persisted for **8**–**10** (Table 7) and no radical changes of the spectra (Figure 2) could be observed. Comparing **7**–**9**, the measured emission wavelengths were similar. Only **10** showed slightly lower emission wavelengths. The R^2 substituent seems to have only a limited effect on the emission. In general, it is notable that the imidazo[1,5-*a*]quinolines maintained their blue luminescence. We expected a wide range of emission colors, as observed for the imidazo[1,5-*a*]pyridines measured by Shibahara *et al.*[18]

The trends for substitution in R^1 observed for the base system **7** were also observed for the other compounds (Table 8). The more electron-rich system **8** showed a slight reduction in QY for all substitutions. While the electron-poor system **9** also reduced the QY slightly for all electron-poor residues **9a**–**h**, it showed a significant decrease for the more electron-rich residues **9i**–**o**. The introduction of a sterically demanding group R^2 for system **10** led to a strong increase in QY, especially in combination with electron-poor residues **10a**–**h**. The nitrogen-rich pyrimidyl **10b** and the substituted pyridyl **10c** showed a very high QY of around 52%. **10o** underwent slow decomposition in solution. In addition, we obtained a much lower QY for this compound. Substitution with an electron-poor or -rich aromatic group in R^2 led to no significant impact. But the introduction of a sterically demanding group showed an impact on the photoluminescent properties. The combination with *N*-heteroaromatics or electron-poor substituents in R^1 increased the QY even further (Figure 3). *N*-heteroaromatic compounds have already shown this effect earlier.[14] We suspect that the planar orientation of all the π-systems leads to more orbital overlap and therefore better QYs. The substitution of a phenyl at R^1 for pyridinyl or pyrimidyl removes hydrogen in the *ortho* positions and could create more overlap with the aromatic core.

Conclusions

We were successful in designing an easy and reliable synthesis to obtain large numbers of imidazo[1,5-*a*]quinoline derivatives.

Figure 3. Demonstration of QY increase of compounds as 0.02 M DCM solution (left to right: **9j**, **7j**, **8d**, **7i**, **7c**, **10h**, **10b**).

The developed Negishi coupling conditions are widely applicable for various coupling partners. Optical measurements have identified that a combination of a sterically demanding group in R^2 and an electron-withdrawing group in R^1 is beneficial for the emission; especially electron-poor *N*-heteroaromatics improved the QY significantly, with **10b** showing a QY of 53% in solution. Electron-rich residues as R^1 lowered the emission, apart from dimethylamine-substituted residues. In addition, we showed that *ortho*-substituted residues as R^1 reduce the QY considerably.

Experimental Section

All solvents were purified by distillation prior to use. Anhydrous solvents were used from ACROS Organics™ as AcroSeal™ bottles. Commercially available chemicals were used as obtained from the supplier, unless otherwise stated. Syntheses prepared under anhydrous conditions were generally performed using standard Schlenk technique in nitrogen atmosphere. For purification by column chromatography, silica gel 60 (Merck) was used. ^{1}H and ^{13}C NMR spectra were recorded on the Bruker Avance II 400, the Bruker Avance III 400 and the Bruker Avance II 200 "Microbay" spectrometers in deuterated solvents. ^{1}H and ^{13}C chemical shifts were determined by reference to the residual solvent signals. High-resolution ESI mass spectra were recorded in methanol with an ESImicroTOF spectrometer from Bruker Daltonics in positive ion mode, unless otherwise stated. As a power supply, the Sky Toppower PS1110 was used. UV-Vis extinction was measured with an Analytik Jena Specord 200 Plus spectrometer and fluorescence emission data were obtained from a Jasco Germany FP 8300 spectrometer. Melting points were determined with a Gallenkamp Melting Point Apparatus.

General procedure for imidazole ring closure adapted from Pelletier et al.[11]

60 mL of dry DCM was added to 2-(aminomethyl)quinoline dihydrochloride **3** (1 eq) under N_2 atmosphere. The suspension was cooled to 0 °C and dry TEA (3.4 eq) was added. The yellow solution was kept at 0 °C for 30 min. Acid chloride R^2COCl (1.1 eq) was added, and the solution was stirred for 20 h at room temperature. Finally, 60 mL sat. Na_2CO_3 solution was added, and the aqueous phase was extracted twice with 60 mL DCM. The combined organic phases were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. The crude quinoline amide **4** (1 eq) was placed in 60 mL of dry DCM under N_2 atmosphere and cooled to 0 °C. The solution was first treated with 2-methoxypyridine (1.1 eq), followed by slow addition of Tf_2O (1.2 eq). The reaction solution was stirred at 35 °C for 20 h. Then, 20 mL sat. Na_2CO_3 solution was added slowly, and the aqueous phase was extracted twice with 60 mL DCM. The combined organic phases were dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. Purification was carried out by silica chromatography.

General procedure for bromination

The imidazo[1,5-*a*]quinoline **5** was placed in 60 mL dry DCM under N_2 atmosphere and cooled to −20 °C. 1.1 eq NBS was slowly added to the solution. The reaction solution was stirred at −20 °C for 4 h. Then, 20 ml sat. $Na_2S_2O_3$ solution was added and the aqueous phase extracted twice with 40 mL DCM. The combined organic phases were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. Purification was carried out by silica chromatography.

General procedure methods for the Negishi coupling

0.400 g (1 eq) 3-bromoimidazo[1,5-*a*]quinoline **6** was dissolved in 10 mL dry THF under N_2 atmosphere and cooled to −78 °C. 1.2 eq of *n*-BuLi (1.6 M) were slowly added dropwise and the solution was kept at −78 °C for 30 min. 2.5 eq $ZnCl_2$ in dry THF (1 M) were added at −78 °C and then stirred at room temperature for 1 h. 3 mol% of $[Pd_2(dba)_3]\cdot CHCl_3$, 6 mol% of P(t-Bu)$_3$ and 2 eq of the chosen coupling bromide were added and the reaction solution was stirred at 70 °C for 20 h. Depending on the compound, two different methods for workup were applied.

Method A for **7**–**10a**–**f**:

The precipitate was filtered off and washed first with THF, then with H_2O and again with THF. The solid was treated with 15 mL conc. $NH_{3(aq)}$ solution and the aqueous phase was extracted three times with 20 mL DCM. The pure product was obtained after concentration *in vacuo* of the combined organic phases.

Method B for **7**–**10g**–**p**:

15 mL conc. $NH_{3(aq)}$ solution was added and the aqueous phase was extracted three times with 20 mL DCM. The combined organic phases were concentrated *in vacuo* and the impure product was purified by silica chromatography.

Supporting Information

Experimental procedures, optical values and spectra for all measured compounds and analytical data of all compounds are provided in the online Supporting Information. Additional references cited within the Supporting Information (Ref. [24]).

Acknowledgements

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: emitter material · imidazo[1,5-*a*]quinolines · Negishi coupling · nitrogen heterocycles · photoluminescence

[1] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913–915.
[2] a) C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, R. C. Kwong, *Appl. Phys. Lett.* **2001**, *78*, 1622–1624; b) C.-L. Ho, H. Li, W.-Y. Wong, *J. Organomet. Chem.* **2014**, *751*, 261–285; c) H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda, C. Adachi, *Nat. Commun.* **2014**, *5*, 4016.
[3] N. C. Giebink, B. W. D'Andrade, M. S. Weaver, P. B. Mackenzie, J. J. Brown, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* **2008**, *103*, 44509.

[4] a) M. S. Malamas, Y. Ni, J. Erdei, H. Stange, R. Schindler, H.-J. Lankau, C. Grunwald, K. Y. Fan, K. Parris, B. Langen, U. Egerland, T. Hage, K. L. Marquis, S. Grauer, J. Brennan, R. Navarra, R. Graf, B. L. Harrison, A. Robichaud, T. Kronbach, M. N. Pangalos, N. Hoefgen, N. J. Brandon, *J. Med. Chem.* **2011**, *54*, 7621–7638; b) A. Kamal, G. Ramakrishna, P. Raju, A. V. S. Rao, A. Viswanath, V. L. Nayak, S. Ramakrishna, *Eur. J. Med. Chem.* **2011**, *46*, 2427–2435; c) D. Kim, L. Wang, J. J. Hale, C. L. Lynch, R. J. Budhu, M. Maccoss, S. G. Mills, L. Malkowitz, S. L. Gould, J. A. DeMartino, M. S. Springer, D. Hazuda, M. Miller, J. Kessler, R. C. Hrin, G. Carver, A. Carella, K. Henry, J. Lineberger, W. A. Schleif, E. A. Emini, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 2129–2134.

[5] a) F. Shibahara, R. Sugiura, E. Yamaguchi, A. Kitagawa, T. Murai, *J. Org. Chem.* **2009**, *74*, 3566–3568; b) G. Volpi, G. Magnano, I. Benesperi, D. Saccone, E. Priola, V. Gianotti, M. Milanesio, E. Conterosito, C. Barolo, G. Viscardi, *Dyes Pigm.* **2017**, *137*, 152–164; c) E. Yamaguchi, F. Shibahara, T. Murai, *J. Org. Chem.* **2011**, *76*, 6146–6158; d) G. Volpi, B. Lace, C. Garino, E. Priola, E. Artuso, P. Cerreia Vioglio, C. Barolo, A. Fin, A. Genre, C. Prandi, *Dyes Pigm.* **2018**, *157*, 298–304.

[6] a) F. Yagishita, T. Kinouchi, K. Hoshi, Y. Tezuka, Y. Jibu, T. Karatsu, N. Uemura, Y. Yoshida, T. Mino, M. Sakamoto, Y. Kawamura, *Tetrahedron* **2018**, *74*, 3728–3733; b) G. A. Ardizzoia, G. Colombo, B. Therrien, S. Brenna, *Ber. Dtsch. Chem. Ges. A* **2019**, *2019*, 1825–1831; c) S. Durini, G. A. Ardizzoia, B. Therrien, S. Brenna, *New J. Chem.* **2017**, *41*, 3006–3014; d) C. Garino, T. Ruiu, L. Salassa, A. Albertino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Ber. Dtsch. Chem. Ges. A* **2008**, *2008*, 3587–3591; e) L. Salassa, C. Garino, A. Albertino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Organometallics* **2008**, *27*, 1427–1435.

[7] M. D. Weber, C. Garino, G. Volpi, E. Casamassa, M. Milanesio, C. Barolo, R. D. Costa, *Dalton Trans.* **2016**, *45*, 8984–8993.

[8] a) J. Wang, L. Dyers, R. Mason, P. Amoyaw, X. R. Bu, *J. Org. Chem.* **2005**, *70*, 2353–2356; b) M. Li, Y. Xie, Y. Ye, Y. Zou, H. Jiang, W. Zeng, *Org. Lett.* **2014**, *16*, 6232–6235; c) Z. Hu, J. Hou, J. Liu, W. Yu, J. Chang, *Org. Biomol. Chem.* **2018**, *16*, 5653–5660; d) S. Chandrasekar, S. Sangeetha, G. Sekar, *ChemistrySelect* **2019**, *4*, 5651–5655; e) A. Joshi, D. C. Mohan, S. Adimurthy, *J. Org. Chem.* **2016**, *81*, 9461–9469.

[9] M. Giordano, G. Volpi, C. Garino, F. Cardano, C. Barolo, G. Viscardi, A. Fin, *Dyes Pigm.* **2023**, *218*, 111482.

[10] J. D. Bower, G. R. Ramage, *J. Chem. Soc.* **1955**, 2834.

[11] G. Pelletier, A. B. Charette, *Org. Lett.* **2013**, *15*, 2290–2293.

[12] a) H. Wang, W. Xu, L. Xin, W. Liu, Z. Wang, K. Xu, *J. Org. Chem.* **2016**, *81*, 3681–3687; b) H. Wang, W. Xu, Z. Wang, L. Yu, K. Xu, *J. Org. Chem.* **2015**, *80*, 2431–2435.

[13] Z. Li, S.-S. Wu, Z.-G. Luo, W.-K. Liu, C.-T. Feng, S.-T. Ma, *J. Org. Chem.* **2016**, *81*, 4386–4392.

[14] G. Albrecht, C. Rössiger, J. M. Herr, H. Locke, H. Yanagi, R. Göttlich, D. Schlettwein, *Phys. Status Solidi B* **2020**, *257*, 1900677.

[15] J. M. Herr, C. Rössiger, H. Locke, M. Wilhelm, J. Becker, W. Heimbrodt, D. Schlettwein, R. Göttlich, *Dyes Pigm.* **2020**, *180*, 108512.

[16] G. Albrecht, C. Geis, J. M. Herr, J. Ruhl, R. Göttlich, D. Schlettwein, *Org. Electron.* **2019**, *65*, 321–326.

[17] a) M. Henze, *Ber. Dtsch. Chem. Ges. A* **1936**, *69*, 1566–1568; b) K. C. Langry, *Org. Prep. Proced. Int.* **1994**, *26*, 429–438.

[18] F. Shibahara, E. Yamaguchi, A. Kitagawa, A. Imai, T. Murai, *Tetrahedron* **2009**, *65*, 5062–5073.

[19] a) M. Sandeep, P. Swati Dushyant, B. Sravani, K. Rajender Reddy, *Eur. J. Org. Chem.* **2018**, *2018*, 3036–3047; b) Z. Tan, H. Zhao, C. Zhou, H. Jiang, M. Zhang, *J. Org. Chem.* **2016**, *81*, 9939–9946.

[20] a) E. Tyrrell, P. Brookes, *Synthesis* **2003**, *2003*, 469–483; b) M. Hapke, L. Brandt, A. Lützen, *Chem. Soc. Rev.* **2008**, *37*, 2782–2797; c) L.-C. Campeau, K. Fagnou, *Chem. Soc. Rev.* **2007**, *36*, 1058–1068.

[21] J. E. Milne, S. L. Buchwald, *J. Am. Chem. Soc.* **2004**, *126*, 13028–13032.

[22] D. F. Eaton, *Pure Appl. Chem.* **1988**, *60*, 1107–1114.

[23] A. M. Brouwer, *Pure Appl. Chem.* **2011**, *83*, 2213–2228.

[24] a) J. R. Quinn, S. C. Zimmerman, *J. Org. Chem.* **2005**, *70*, 7459–7467; b) P. Qian, Z. Yan, Z. Zhou, K. Hu, J. Wang, Z. Li, Z. Zha, Z. Wang, *Org. Lett.* **2018**, *20*, 6359–6363.

Manuscript received: October 2, 2023
Revised manuscript received: November 21, 2023
Accepted manuscript online: November 22, 2023
Version of record online: December 19, 2023