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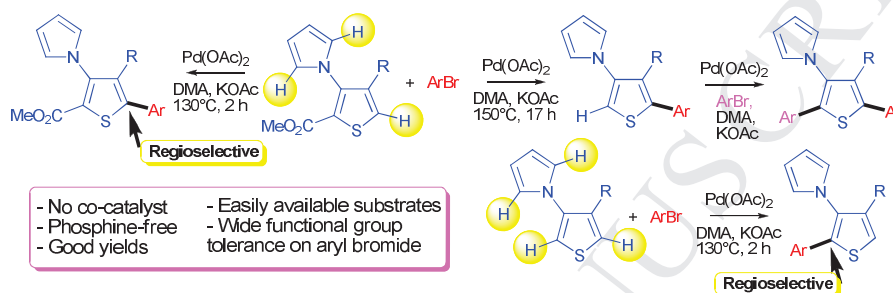
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Reactivity of 3-(Pyrrol-1-yl)thiophenes in Pd-Catalysed Direct Arylations

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Reactivity of 3-(Pyrrol-1-yl)thiophenes in Pd-Catalysed Direct Arylations

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Abstract— The regioselectivity of the Pd-catalysed direct arylation of 3-(pyrrol-1-yl)thiophene derivatives was investigated. Conditions allowing either the regioselective arylation at C2 or at C5 of the thiophene ring are reported. From methyl 3-(pyrrol-1-yl)thiophene-2-carboxylate using KOAc as the base, DMA as the solvent and only 1 mol% Pd(OAc)₂ catalyst, the target 5-arylated thiophenes were obtained in moderate to good yields with a wide variety of aryl halides; whereas the use of 1-(4-methylthiophen-3-yl)-pyrrole affords the C2-arylated thiophenes. The sequential palladium catalysed 2,5-diheteroarylation of such 3-(pyrrol-1-yl)thiophene is also reported allowing the access to thiophenes bearing two different aryl units at C2 and C5. A pyrazole bearing an ester substituent at C4 and a pyrrole substituent at C5 was only aryalted at C2 on the pyrrole ring.

1. Introduction

Both thiophene and pyrrole derivatives represent important structures due to their biological and/or physical properties. For example, Motapizone^{1a} is used against platelet aggregation, Saviprazole^{1b} is a gastric proton pump inhibitor and Tiflucarbine^{1c} displays antidepressant properties (Fig. 1). Due to these properties, the discovery of simple accesses to a variety of thiophene or pyrrole derivatives remains an important challenge for organic chemists.

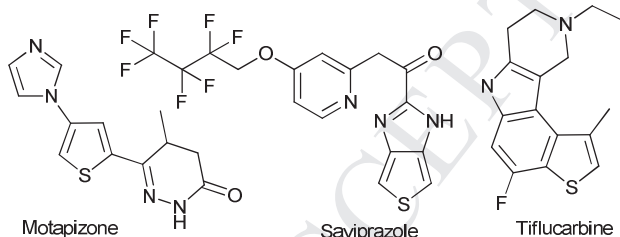


Figure 1. Examples of bioactive thiophene derivatives

As early as in 1985-1992, Ohta et al. reported the direct arylation of heteroaromatics with aryl halides via a C–H bond activation using Pd(PPh₃)₄ catalyst.² Since these results, the Pd-catalysed direct arylation of several heteroaryls using aryl halides as the coupling partners has proved to be a very powerful method for a simpler and greener access to a wide variety of arylated heterocycles.^{3,4} This method is very attractive as it avoids the preparation of an organometallic derivative and as the

major by-products of the reaction are a base associated to HX, instead of metallic salts.⁵

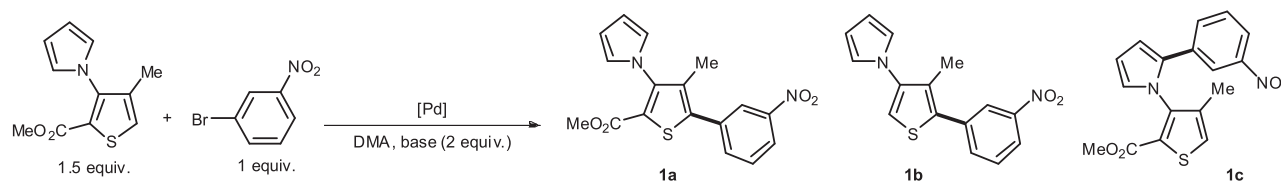
The direct arylation of a variety of thiophene and pyrrole derivatives has been reported in recent years.^{6,7} However, to our knowledge, the reactivity of a thiophene substituted by a pyrrole unit at C3 and also of a 5-pyrrolylpyrazole for Pd-catalysed direct arylations has not been described. Therefore, the reactivity for direct arylation of such substrates needed to be investigated.

Here, we wish to report (i) conditions allowing a regioselective arylation of a 3-(pyrrol-1-yl)thiophene derivative, (ii) a one pot procedure with arylation at C5 of the thiophene derivative followed by decarboxylation at C2 and (iii) the sequential arylation to prepare 2,5-diarylated thiophenes with two different aryl units.

2. Results and discussion

Based on previous results, for this study DMA was initially chosen as the solvent and KOAc as the base.⁸ The reactions were performed at 130-150 °C under argon in the presence of Pd(OAc)₂ or PdCl(C₃H₅)(dppb) catalysts. First, using only 1 mol% Pd(OAc)₂, the reaction of 1 equiv. of 3-bromonitrobenzene with 1.5 equiv. of methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate as the coupling partners at 150 °C during 17 h affords selectively the *in situ* decarboxylated C5-arylation product **1b** in 78% yield (Table 1, entry 1). On the other hand, the reaction performed under the same reaction conditions, but after only 2 h affords a mixture of **1a** and **1b** in a 83:17 ratio (Table 1, entry 2).

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Scheme 2. Regioselectivity of the palladium catalysed direct arylation using methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate and 3-bromonitrobenzene as the coupling partners

Table 1. Influence of the reaction conditions for the palladium catalysed direct arylation using methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate and 3-bromonitrobenzene as the coupling partners (Scheme 2)

Entry	Catalyst (mol%)	Base	Time (h)	Temp (°C)	Ratio 1a : 1b : 1c	Yield in 1a or 1b (%)
1	Pd(OAc) ₂ (1)	KOAc	17	150	0:100:0	76 of 1b
2	Pd(OAc) ₂ (1)	KOAc	2	150	83:17:0	-
3	Pd(OAc) ₂ (1)	KOAc	2	130	93:7:0	78 of 1a
4	Pd(OAc) ₂ (1)	CsOAc	17	150	49:51:0	-
5	Pd(OAc) ₂ (1)	CsOAc	2	130	94:6:0	78 of 1a
6	Pd(OAc) ₂ (1)	NaOAc	17	150	23:77:0	-
7	Pd(OAc) ₂ (1)	NaOAc	2	130	69:31:0	-
8	Pd(OAc) ₂ (1)	Cs ₂ CO ₃	17	150	0:100:0	77 of 1b
9	PdCl(C ₃ H ₅)(dppb) (2)	KOAc	17	150	14:86:0	70 of 1b

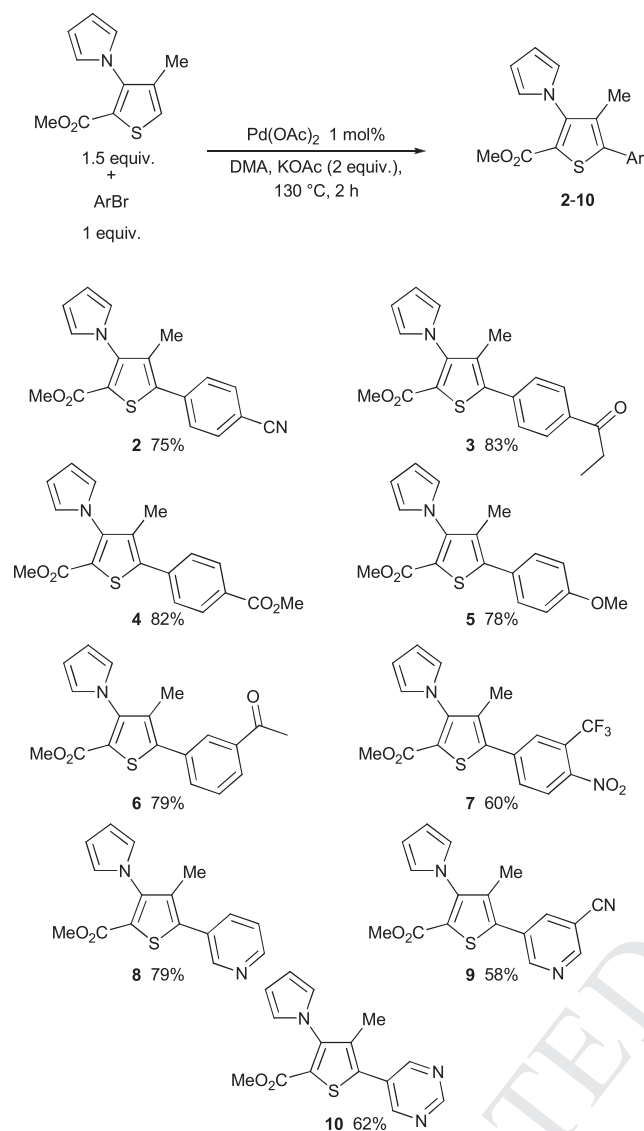
Conditions: 3-bromonitrobenzene (1 equiv.), 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (1.5 equiv.), base (2 equiv.), DMA, isolated yields, complete conversion of 3-bromonitrobenzene was observed in all cases.

It should be noted that in both cases no arylation at the pyrrole ring to afford **1c** was observed by GC/MS analysis of the crude mixture. A lower temperature led to an increase in the selectivity for **1a**, as at 130 °C ratio **1a**:**1b** was 93:7 and **1a** was isolated in 78% yield (Table 1, entry 3). Then, we examined the influence of the nature of the base for this reaction. The use of CsOAc instead of KOAc at 150 °C afforded lower amounts of decarboxylated product **1b**, and at 130 °C a 94:6 ratio (**1a**:**1b**) was obtained, with 78% isolated yield of **1a** (Table 1, entries 4 and 5). NaOAc led to mixtures of products **1a** and **1b**, whereas Cs₂CO₃ afforded exclusively **1b** (Table 1, entries 6-8). The use of 2 mol% PdCl(C₃H₅)(dppb) catalyst^{8b} instead of 1 mol% Pd(OAc)₂, also affords **1b** although in slightly lower yield (Table 1, entry 9).

Then, using the most effective reaction conditions for coupling with and without decarboxylation (DMA, KOAc, Pd(OAc)₂, 130 °C 2 h or 150 °C 17 h), we explored the scope of this reaction using a variety of aryl bromides as the coupling partner (Schemes 3 and 4).

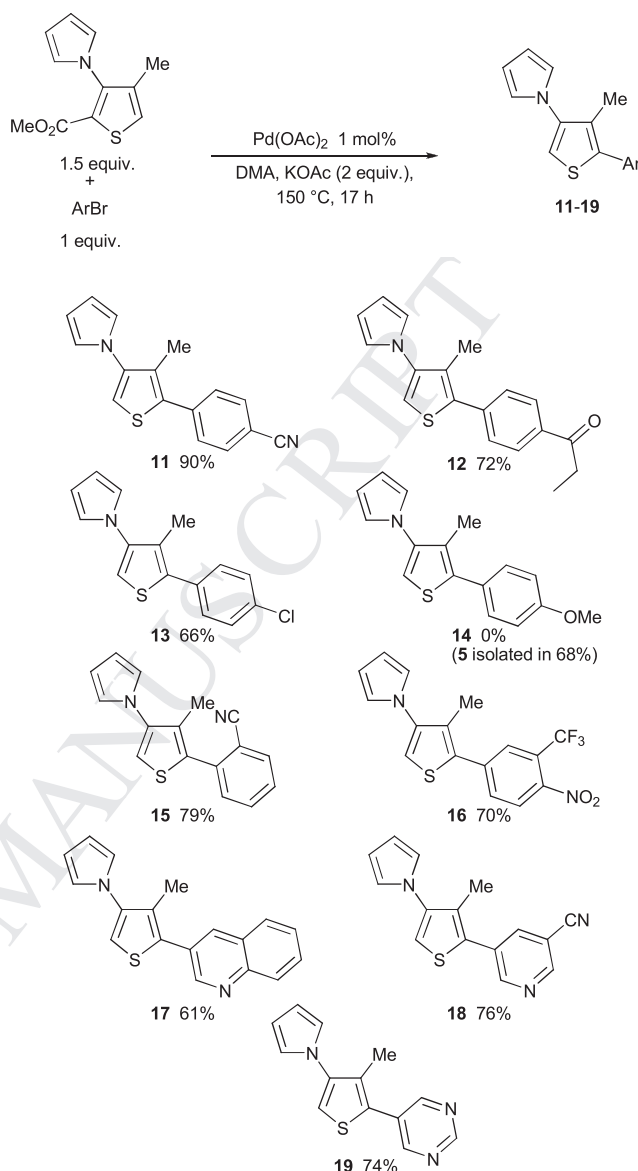
First, we investigated the reaction of methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate using 1 mol% Pd(OAc)₂ catalyst with a set of aryl bromides at 130 °C during 2 h in order to obtain the non-decarboxylated products (Scheme 3). The reaction with the *para*-substituted aryl bromides, 4-bromobenzonitrile, 4-bromopropiophenone or 4-bromoanisole proceeds very smoothly to afford the target products **2-5** in 75-83% yields. *Meta*-substituted 3-bromoacetophenone and also 4-bromo-1-nitro-2-(trifluoromethyl)benzene also react nicely to give **6** and **7** in 79% and 60% yields, respectively. 3-Bromopyridine, 5-bromonicotinonitrile

and 5-bromopyrimidine were also successfully coupled with methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate, without decarboxylation, to afford **8-10** in 58-79% yields.



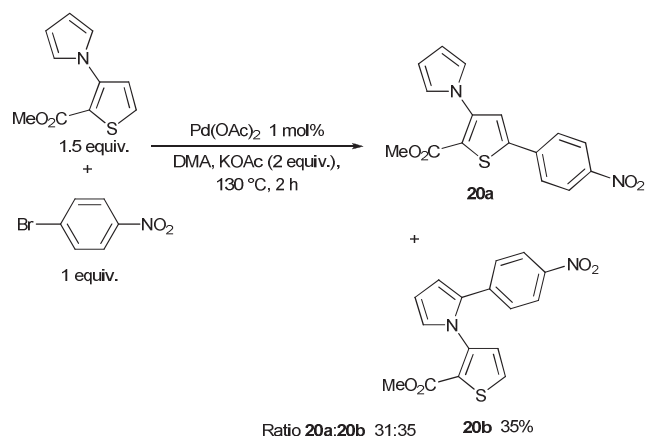
Scheme 3. Scope of the C5-arylation of methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate

The scope of the C5-arylation with *in situ* decarboxylation was also studied (Scheme 4). From 4-cyano-, 4-propionyl- and 4-chlorobromobenzene, after 17 h at 150 °C, the decarboxylated C5-arylated thiophenes **11–13** were obtained in good yields. On the other hand, no formation of the desired decarboxylated product **14** was observed in the presence of the electron-rich 4-bromoanisole as only product **5** was formed (68%). The decarboxylation step appears to be favoured by the presence of electron-withdrawing substituents on the arene. In the presence of 2-bromobenzonitrile and 4-bromo-1-nitro-2-(trifluoromethyl)benzene, **15** and **16** were obtained in 79% and 70% yields, respectively. Then, three heteroarenes were employed. 3-Bromopyridine, 5-bromonicotinonitrile and 5-bromopyrimidine also afforded the desired decarboxylated products **17–19** in good yields.



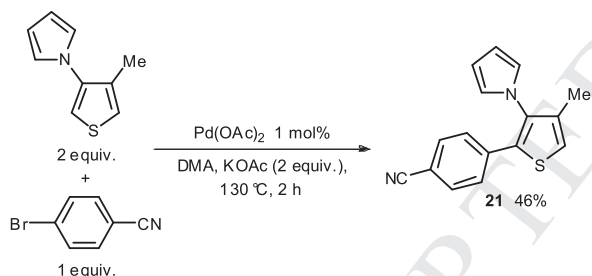
Scheme 4. Scope of the C5-arylation of methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate with *in-situ* decarboxylation

The selectivity of the arylation of 3-(pyrrol-1-yl)thiophene derivatives appears to be very sensitive to the steric hindrance of the pyrrolyl moiety. The presence of a substituent at C4 on the thienyl ring seems to be crucial to control the selectivity. Indeed, in the presence of methyl 3-(pyrrol-1-yl)thiophene-2-carboxylate and 4-bromobenzonitrile as coupling partner, the formation of a mixture of the 5-arylated thiophene **20a** and 2-arylated pyrrole **20b** in a 31:35 ratio was observed under the same reaction conditions (Scheme 5).



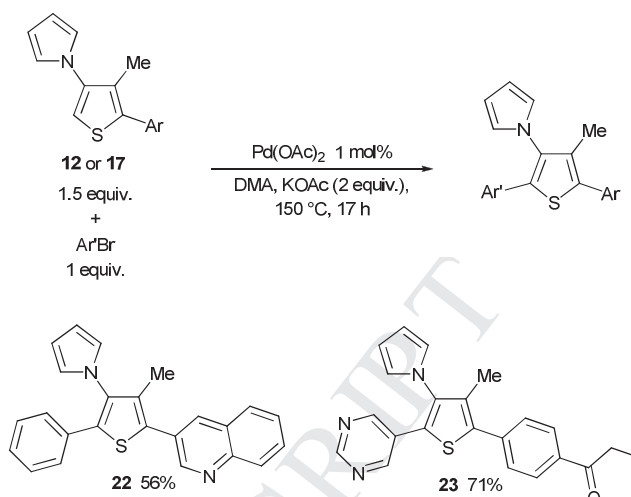
Scheme 5. Regioselectivity of the arylation of methyl 3-(pyrrol-1-yl)thiophene-2-carboxylate

The regioselectivity of the arylation of 1-(4-methylthiophen-3-yl)pyrrole was also investigated (Scheme 6). In the presence of 4-bromobenzonitrile and 1 mol% Pd(OAc)₂ catalyst, the regiospecific formation of the C2-arylated product **21** was observed which indicates that the most reactive position of a 3-pyrrolylthiophene is the carbon C2 of the thienyl ring. Therefore, this result confirms that an ester substituent at C2 on the thienyl ring acts as a blocking group, allowing for selective arylation at C5 position. A similar regioselectivity trend for direct arylations had been previously observed using 3-aminothiophene derivatives.⁹



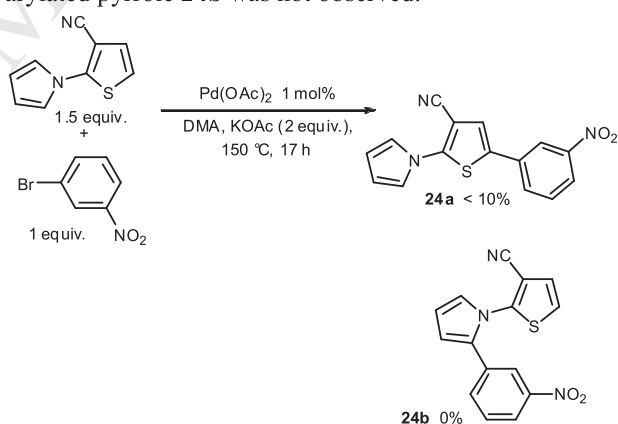
Scheme 6. Regioselectivity of the arylation of 1-(4-methylthiophen-3-yl)pyrrole

The reactivity of the arylated thiophene derivatives **12** and **17** for C5 arylation was then evaluated (Scheme 7). Such arylations would allow the preparation of non-symmetrically 2,5-diarylated thiophene derivatives. From **17** and bromobenzene the desired product **22** was obtained in 56% yield. **12** reacted with 5-bromopyridine also affords the desired 2,5-diarylated thiophene **23** in good yield.



Scheme 7. C5-arylation of 2-aryl-3-methyl-4-(pyrrol-1-yl)thiophenes

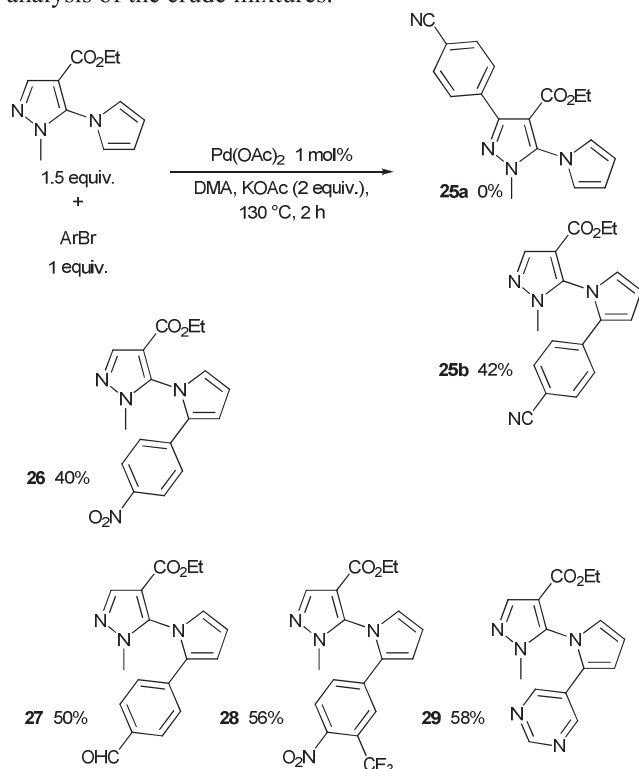
The reactivity of 2-(pyrrol-1-yl)thiophene-3-carbonitrile in the presence of 3-bromonitrobenzene was also investigated (Scheme 8). A permutation of the electron-withdrawing (pyrrolyl) and electron-donating (ester or cyano) substituents on the thiophene was found to drastically modify the reactivity. In the presence of 1 mol% Pd(OAc)₂ catalyst and KOAc as base, the expected product **24a** was obtained in a very low yield and the C2-arylated pyrrole **24b** was not observed.



Scheme 8. Reactivity of 2-(pyrrol-1-yl)thiophene-3-carbonitrile

We also explored the reactivity of a pyrazole bearing a pyrrole substituent at C5 and an ester at C4 (Scheme 9). As the position C3 of pyrazoles derivatives generally exhibits a poor reactivity, the formation of product **25b** was expected. Indeed, 4-bromobenzonitrile and this 5-(pyrrol-1-yl)pyrazole in the presence of 1 mol% Pd(OAc)₂ and KOAc in DMA at 130 °C, 2 or 17 h affords the C2-arylated pyrrole **25b** in 42% yield. No formation of **25a** was observed. A similar regioselectivity was observed in the presence of 4-bromonitrobenzene, 4-bromobenzaldehyde, 4-bromo-1-nitro-2-(trifluoromethyl)benzene and 5-bromopyrimidine as the coupling partners, and products **26-29** were obtained in

40–58% yields, respectively. The formation of diarylation products in trace amounts was also observed by GC/MS analysis of the crude mixtures.



Scheme 9. Arylation of ethyl 1-methyl-5-(pyrrol-1-yl)-pyrazole-4-carboxylate

In conclusion, thiophenes bearing a pyrrole unit at C3 and a methyl at C4 were found to react exclusively at the thienyl ring. We established that 1 mol% of air stable palladium $\text{Pd}(\text{OAc})_2$ catalyst and KOAc as base at 130 °C promotes 5-arylation of methyl 3-(pyrrol-1-yl)thiophene-2-carboxylate without decarboxylation; whereas, at 150 °C a C5 arylation followed by an in situ decarboxylation was observed. On the other hand, 1-(4-methylthiophen-3-yl)-pyrrole was selectively arylated at carbon C2 of the thienyl ring. From the decarboxylated 5-arylated thiophenes, the direct arylation at C2 position of thiophene was also found to be possible, and affords 2,5-diheteroarylated thiophenes bearing two different aryl units. A pyrazole bearing an ester substituent at C4 and a pyrrole substituent at C5 was only arylated at C2 on the pyrrole ring.

Acknowledgments

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Experimental section

General Remarks

All reactions were run under argon in Schlenk tubes using vacuum lines. DMA analytical grade was not distilled before use. KOAc (99%) was used. Commercial heteroarenes and aryl bromides were used without purification. The reactions were followed by GC and NMR. ^1H and ^{13}C spectra were recorded with a Bruker 400 MHz spectrometer in CDCl_3 solutions. Chemical shifts are reported in ppm relative to CDCl_3 (7.25 for ^1H NMR and 77.0 for ^{13}C NMR). Flash chromatography was performed on silica gel (230–400 mesh).

General procedure

In a typical experiment, the thiophene derivative (1.5 mmol), aryl bromide (1 mmol), KOAc (0.196 g, 2 mmol) and $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol) or $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$ (12.1 mg, 0.02 mmol), were dissolved in DMA (5 mL) under an argon atmosphere. The reaction mixture was stirred at 130 or 150 °C for 2 or 17 h (see schemes). Then, the reaction was stirred at 30–40 °C in vacuum (0.4 mbar) to remove the solvent, and the product was purified by silica gel column chromatography.

Preparation of the $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$ catalyst:¹⁰ An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, CDCl_3) δ = 19.3 (s).

Methyl 4-methyl-5-(3-nitrophenyl)-3-(pyrrol-1-yl)thiophene-2-carboxylate (**1a**)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 3-bromonitrobenzene (0.202 g, 1 mmol) at 130 °C during 2 h product **1a** was obtained in 78% (0.267 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 6.76 (t, J = 2.0 Hz, 2H), 6.37 (t, J = 2.0 Hz, 2H), 3.78 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.5, 148.5, 143.8, 139.8, 135.1, 134.7, 134.2, 130.0, 125.2, 123.7, 123.3, 121.9, 109.3, 52.3, 12.8.

$\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ (342.37): Calcd C 59.64, H 4.12; Found C 59.41, H 4.27.

1-(4-Methyl-5-(3-nitrophenyl)thiophen-3-yl)-pyrrole (**1b**)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 3-bromonitrobenzene (0.202 g, 1 mmol) at 150 °C during 17 h product **1b** was obtained in 76% (0.216 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.26 (s, 1H), 6.88 (t, J = 2.0 Hz, 2H), 6.36 (t, J = 2.0 Hz, 2H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 148.5, 141.0, 136.3, 134.7, 135.7, 130.8, 129.7, 123.7, 122.4, 121.9, 117.9, 109.3, 13.1. $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ (284.33): Calcd C 63.36, H 4.25; Found C 63.50, H 4.37.

Methyl 5-(4-cyanophenyl)-4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (2)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromobenzonitrile (0.182 g, 1 mmol) at 130 °C during 2 h product **2** was obtained in 75% (0.241 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 6.74 (t, J = 2.0 Hz, 2H), 6.36 (t, J = 2.0 Hz, 2H), 3.78 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 139.2, 136.4, 132.5, 130.8, 129.3, 121.9, 118.6, 118.2, 111.2, 109.3, 13.3.

$\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ (322.38): Calcd C 67.06, H 4.38; Found C 67.24, H 4.27.

Methyl 4-methyl-5-(4-propionylphenyl)-3-(pyrrol-1-yl)thiophene-2-carboxylate (3)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromopropiophenone (0.213 g, 1 mmol) at 130 °C during 2 h product **3** was obtained in 83% (0.293 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 6.75 (t, J = 2.0 Hz, 2H), 6.36 (t, J = 2.0 Hz, 2H), 3.77 (s, 3H), 3.04 (q, J = 7.6 Hz, 2H), 2.06 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 199.8, 160.6, 143.7, 141.5, 137.7, 136.5, 133.6, 128.9, 128.3, 127.2, 121.8, 109.0, 52.0, 31.7, 12.7, 8.0.

$\text{C}_{20}\text{H}_{19}\text{NO}_3\text{S}$ (353.43): Calcd C 67.97, H 5.42; Found C 67.87, H 5.34.

Methyl 5-(4-(methoxycarbonyl)phenyl)-4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (4)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and methyl 4-bromobenzoate (0.215 g, 1 mmol) at 130 °C during 2 h product **4** was obtained in 82% (0.291 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 6.75 (t, J = 2.0 Hz, 2H), 6.36 (t, J = 2.0 Hz, 2H), 3.95 (s, 3H), 3.77 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 160.7, 143.9, 141.7, 137.9, 133.7, 130.1, 128.9, 127.2, 122.0, 109.3, 109.2, 52.3, 52.1, 12.8.

$\text{C}_{19}\text{H}_{17}\text{NO}_4\text{S}$ (355.41): Calcd C 64.21, H 4.82; Found C 64.02, H 4.99.

Methyl 5-(4-methoxyphenyl)-4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (5)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromoanisole (0.187 g, 1 mmol) at 130 °C during 2 h product **5** was obtained in 78% (0.255 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.75 (t, J = 2.0 Hz, 2H), 6.35 (t, J = 2.0 Hz, 2H), 3.96 (s, 3H), 3.76 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 161.2, 160.2, 144.0, 143.5, 132.3, 130.4, 126.0, 123.2, 122.1, 114.5, 109.1, 55.5, 52.2, 12.9.

$\text{C}_{18}\text{H}_{17}\text{NO}_3\text{S}$ (327.40): Calcd C 66.03, H 5.23; Found C 65.89, H 5.07.

Methyl 5-(3-acetylphenyl)-4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (6)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 3-bromoacetophenone (0.199 g, 1 mmol) at 130 °C during 2 h product **6** was obtained in 79% (0.268 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 6.75 (t, J = 2.0 Hz, 2H), 6.35 (t, J = 2.0 Hz, 2H), 3.76 (s, 3H), 2.65 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 197.2, 160.7, 143.7, 141.7, 137.6, 133.9, 133.4, 133.2, 129.2, 128.6, 128.4, 124.3, 121.9, 109.0, 52.1, 26.6, 12.6.

$\text{C}_{19}\text{H}_{17}\text{NO}_3\text{S}$ (339.41): Calcd C 67.24, H 5.05; Found C 67.02, H 5.30.

Methyl 4-methyl-5-(4-nitro-3-(trifluoromethyl)phenyl)-3-(pyrrol-1-yl)thiophene-2-carboxylate (7)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromo-1-nitro-2-(trifluoromethyl)benzene (0.270 g, 1 mmol) at 130 °C during 2 h product **7** was obtained in 60% (0.246 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.0 Hz, 1H), 7.95 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 6.75 (t, J = 2.0 Hz, 2H), 6.38 (t, J = 2.0 Hz, 2H), 3.79 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.3, 144.0, 138.5, 138.1, 135.2, 133.0, 128.2 (q, J = 5.3 Hz), 126.4, 125.9, 124.5 (q, J = 34.4 Hz), 121.8 (q, J = 273.9 Hz), 121.9, 109.5, 52.4, 12.9.

$\text{C}_{18}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_4\text{S}$ (410.37): Calcd C 52.68, H 3.19; Found C 52.74, H 3.04.

Methyl 4-methyl-5-(pyridin-3-yl)-3-(pyrrol-1-yl)thiophene-2-carboxylate (8)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 3-bromopyridine (0.158 g, 1 mmol) at 130 °C during 2 h product **8** was obtained in 79% (0.235 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.77 (s, 1H), 8.66 (d, J = 4.2 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.41 (dd, J = 7.9, 4.2 Hz, 1H), 6.75 (s, 2H), 6.36 (s, 2H), 3.77 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 149.7, 149.5, 143.9, 138.9, 136.2, 134.1, 129.7, 125.1, 123.6, 122.0, 109.2, 52.2, 12.7.

$\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ (298.36): Calcd C 64.41, H 4.73; Found C 64.55, H 4.58.

Methyl 5-(5-cyanopyridin-3-yl)-4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (9)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 5-bromonicotinonitrile (0.183 g, 1 mmol) at 130 °C during 2 h product **9** was obtained in 58% (0.187 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 1H), 8.89 (s, 2H), 6.74 (t, J = 2.0 Hz, 2H), 6.37 (t, J = 2.0 Hz, 2H), 3.79 (s, 3H), 2.07 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 160.4, 158.2, 156.2, 143.9, 135.2, 134.5, 128.2, 126.2, 121.9, 109.4, 52.3, 12.7.

C₁₇H₁₃N₃O₂S (323.37): Calcd C 63.14, H 4.05; Found C 63.00, H 4.24.

Methyl 4-methyl-5-(pyrimidin-5-yl)-3-(pyrrol-1-yl)thiophene-2-carboxylate (10)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 5-bromopyrimidine (0.159 g, 1 mmol) at 130 °C during 2 h product **10** was obtained in 62% (0.185 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 1H), 8.86 (s, 2H), 6.75 (t, J = 2.0 Hz, 2H), 6.37 (t, J = 2.0 Hz, 2H), 3.79 (s, 3H), 2.07 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 160.3, 158.2, 156.2, 143.9, 135.2, 134.5, 128.2, 126.2, 121.9, 109.4, 52.4, 12.7.

C₁₅H₁₃N₃O₂S (299.35): Calcd C 60.18, H 4.38; Found C 60.01, H 4.24.

4-(3-Methyl-4-(pyrrol-1-yl)thiophen-2-yl)benzonitrile (11)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromobenzonitrile (0.182 g, 1 mmol) at 150 °C during 17 h product **11** was obtained in 90% (0.238 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.26 (s, 1H), 6.86 (t, J = 2.0 Hz, 2H), 6.34 (t, J = 2.0 Hz, 2H), 2.20 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 141.2, 139.2, 136.5, 132.5, 130.8, 129.4, 121.9, 118.5, 118.2, 111.3, 109.3, 13.2.

C₁₆H₁₂N₂S (264.34): Calcd C 72.70, H 4.58; Found C 72.49, H 4.37.

1-(4-(3-Methyl-4-(pyrrol-1-yl)thiophen-2-yl)phenyl)propan-1-one (12)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromopropiophenone (0.213 g, 1 mmol) at 150 °C during 17 h product **12** was obtained in 72% (0.212 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H), 7.21 (s, 1H), 6.86 (t, J = 2.0 Hz, 2H), 6.33 (t, J = 2.0 Hz, 2H), 3.04 (q, J = 7.6 Hz, 2H), 2.20 (s, 3H), 1.26 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 200.1, 141.0, 139.0, 137.4, 135.8, 130.2, 128.9, 128.4, 121.9, 117.6, 109.1, 31.8, 13.3, 8.2.

C₁₈H₁₇NOS (295.40): Calcd C 73.19, H 5.80; Found C 73.00, H 5.89.

1-(5-(4-Chlorophenyl)-4-methylthiophen-3-yl)-pyrrole (13)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromochlorobenzene (0.191 g, 1 mmol) at 150 °C during 17 h product **13** was obtained in 66% (0.180 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 7.42 (s, 4H), 7.16 (s, 1H), 6.85 (t, J = 2.0 Hz, 2H), 6.33 (t, J = 2.0 Hz, 2H), 2.15 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 140.7, 137.3, 133.8, 133.0, 130.2, 129.5, 128.9, 121.9, 116.8, 109.1, 13.1.

C₁₅H₁₂ClNS (273.78): Calcd C 65.80, H 4.42; Found C 65.88, H 4.28.

2-(3-Methyl-4-(pyrrol-1-yl)thiophen-2-yl)benzonitrile (15)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 2-bromobenzonitrile (0.182 g, 1 mmol) at 150 °C during 17 h product **15** was obtained in 79% (0.208 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.2 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.60-7.47 (m, 2H), 6.91 (t, J = 2.0 Hz, 2H), 6.35 (t, J = 2.0 Hz, 2H), 2.12 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 140.3, 138.0, 133.8, 133.4, 132.7, 132.3, 131.8, 128.6, 121.9, 118.3, 117.9, 113.6, 109.2, 13.2.

C₁₆H₁₂N₂S (264.34): Calcd C 72.70, H 4.58; Found C 72.54, H 4.33.

1-(4-Methyl-5-(4-nitro-3-(trifluoromethyl)phenyl)thiophen-3-yl)-pyrrole (16)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 4-bromo-1-nitro-2-(trifluoromethyl)benzene (0.270 g, 1 mmol) at 150 °C during 17 h product **16** was obtained in 70% (0.246 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 8.0 Hz, 1H), 7.93 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.31 (s, 1H), 6.84 (t, J = 2.0 Hz, 2H), 6.34 (t, J = 2.0 Hz, 2H), 2.21 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 146.6, 141.4, 139.7, 134.5, 132.6, 131.9, 128.0 (q, J = 5.5 Hz), 125.8, 124.2 (q, J = 34.0 Hz), 121.7 (q, J = 272.5 Hz), 121.9, 119.1, 109.5, 13.3.

C₁₆H₁₁F₃N₂O₂S (352.33): Calcd C 54.54, H 3.15; Found C 54.47, H 3.07.

3-(3-Methyl-4-(pyrrol-1-yl)thiophen-2-yl)quinoline (17)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 3-bromoquinoline (0.208 g, 1 mmol) at 150 °C during 17 h product **17** was obtained in 61% (0.177 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 9.07 (s, 1H), 8.22 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 6.89 (t, J = 2.0 Hz, 2H), 6.35 (t, J = 2.0 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 150.5, 147.2, 141.0, 135.2, 134.7, 130.6, 129.8, 129.3, 127.9, 127.8, 127.6, 127.2, 121.8, 117.7, 109.2, 13.1.

$\text{C}_{18}\text{H}_{14}\text{N}_2\text{S}$ (290.38): Calcd C 74.45, H 4.86; Found C 74.67, H 5.01.

5-(3-Methyl-4-(pyrrol-1-yl)thiophen-2-yl)nicotinonitrile (18)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 5-bromonicotinonitrile (0.183 g, 1 mmol) at 150 °C during 17 h product **18** was obtained in 76% (0.201 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 8.94 (s, 1H), 8.87 (s, 1H), 8.04 (s, 1H), 7.31 (s, 1H), 6.85 (t, J = 3.1 Hz, 2H), 6.34 (t, J = 3.1 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 150.8, 141.2, 138.7, 131.9, 131.8, 131.2, 121.9, 119.0, 116.1, 109.5, 13.1.

$\text{C}_{15}\text{H}_{11}\text{N}_3\text{S}$ (265.33): Calcd C 67.90, H 4.18; Found C 68.06, H 4.29.

5-(3-methyl-4-(pyrrol-1-yl)thiophen-2-yl)pyrimidine (19)

From methyl 4-methyl-3-(pyrrol-1-yl)thiophene-2-carboxylate (0.318 g, 1.5 mmol) and 5-bromopyrimidine (0.159 g, 1 mmol) at 150 °C during 17 h product **19** was obtained in 74% (0.178 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 9.20 (s, 1H), 8.87 (s, 2H), 7.30 (s, 1H), 6.85 (t, J = 3.1 Hz, 2H), 6.34 (t, J = 3.1 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 157.6, 156.3, 141.3, 131.9, 130.7, 129.2, 122.0, 118.9, 109.6, 13.1.

$\text{C}_{13}\text{H}_{11}\text{N}_3\text{S}$ (241.31): Calcd C 64.70, H 4.59; Found C 64.41, H 4.38.

Methyl 5-(4-nitrophenyl)-3-(pyrrol-1-yl)thiophene-2-carboxylate (20a) and Methyl 3-(2-(4-nitrophenyl)-pyrrol-1-yl)thiophene-2-carboxylate (20b)

From methyl 3-(pyrrol-1-yl)thiophene-2-carboxylate (0.310 g, 1.5 mmol) and 4-bromonitrobenzene (0.202 g, 1 mmol) at 130 °C during 2 h a mixture of **20a** and **20b** was obtained in a 31:35 ratio. After column chromatography, product **20b** was obtained in 35% (0.115 g) yield, and product **20a** was isolated in low yield.

20a: ^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.44 (s, 1H), 7.09-7.06 (m, 2H), 6.39-6.35 (m, 2H), 3.89 (s, 3H).

20b: ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 5.2 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 1.3 Hz, 1H), 6.91 (d, J = 5.2 Hz, 1H), 6.64 (dd, J = 3.6, 1.6 Hz, 1H), 6.43 (t, J = 3.3 Hz, 1H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 145.7, 142.1, 139.1, 132.9, 130.6, 128.4, 127.1, 127.0, 125.0, 123.6, 112.5, 110.2, 52.2.

$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4\text{S}$ (328.34): Calcd C 58.53, H 3.68; Found C 59.01, H 3.55.

4-(4-Methyl-3-(pyrrol-1-yl)thiophen-2-yl)benzonitrile (21)

From 1-(4-methylthiophen-3-yl)-pyrrole (0.326 g, 2 mmol) and 4-bromobenzonitrile (0.182 g, 1 mmol) at 130 °C during 2 h product **21** was obtained in 46% (0.121 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, J = 8.0 Hz, 2H), 7.07 (s, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.59 (t, J = 2.0 Hz, 2H), 6.33 (t, J = 2.0 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.8, 136.7, 136.6, 134.8, 132.4, 127.2, 121.3, 120.8, 118.6, 111.0, 110.1, 13.6.

$\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}$ (264.34): Calcd C 72.70, H 4.58; Found C 72.78, H 4.79.

3-(3-Methyl-5-phenyl-4-(pyrrol-1-yl)thiophen-2-yl)quinoline (22)

From 3-(3-methyl-4-(pyrrol-1-yl)thiophen-2-yl)quinoline **17** (0.435 g, 1.5 mmol) and bromobenzene (0.157 g, 1 mmol) at 150 °C during 17 h product **22** was obtained in 56% (0.205 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 9.11 (s, 1H), 8.27 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.30-7.24 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), 6.71 (t, J = 2.0 Hz, 2H), 6.33 (t, J = 2.0 Hz, 2H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 150.5, 137.5, 135.8, 135.0, 133.7, 131.8, 129.9, 129.4, 128.8, 128.1, 127.9, 127.7, 127.3, 127.1, 121.7, 109.7, 12.9.

$\text{C}_{24}\text{H}_{18}\text{N}_2\text{S}$ (366.48): Calcd C 78.66, H 4.95; Found C 78.54, H 5.11.

1-(4-(3-Methyl-5-(pyrimidin-5-yl)-4-(pyrrol-1-yl)thiophen-2-yl)phenyl)propan-1-one (23)

From methyl 4-methyl-5-(4-propionylphenyl)-3-(pyrrol-1-yl)thiophene-2-carboxylate **3** (0.529 g, 1.5 mmol) 5-bromopyrimidine (0.159 g, 1 mmol) at 150 °C during 17 h product **23** was obtained in 71% (0.264 g) yield.

^1H NMR (400 MHz, CDCl_3) δ 9.05 (s, 1H), 8.26 (s, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 6.68 (t, J = 2.0 Hz, 2H), 6.39 (t, J = 2.0 Hz, 2H), 3.05 (q, J = 7.6 Hz, 2H), 2.16 (s, 3H), 1.27 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 200.0, 157.4, 154.2, 138.0, 137.1, 136.3, 133.5, 129.3, 128.8, 128.6, 126.8, 121.2, 110.9, 31.9, 12.9, 8.2.

$\text{C}_{22}\text{H}_{19}\text{N}_3\text{OS}$ (373.47): Calcd C 70.75, H 5.13; Found C 70.82, H 5.01.

5-(3-Nitrophenyl)-2-(pyrrol-1-yl)thiophene-3-carbonitrile (24a)

From 2-(pyrrol-1-yl)thiophene-3-carbonitrile (0.261 g, 1.5 mmol) and 3-bromonitrobenzene (0.202 g, 1 mmol) at 150 °C during 17 h product **24a** was obtained in <10% (0.029 g) yield. This compound was not isolated in pure form.

^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 2.0 Hz, 2H), 6.44 (t, J = 2.0 Hz, 2H).

Ethyl 5-(2-(4-cyanophenyl)-pyrrol-1-yl)-1-methylpyrazole-4-carboxylate (25b)

From ethyl 1-methyl-5-(pyrrol-1-yl)-pyrazole-4-carboxylate (0.328 g, 1.5 mmol) and 4-bromobenzonitrile (0.182 g, 1 mmol) at 130 °C during 2 h product **25b** was obtained in 42% (0.134 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.88-6.80 (m, 1H), 6.69-6.66 (m, 1H), 6.49 (t, J = 3.1 Hz, 1H), 4.14 (q, J = 7.6 Hz, 2H), 3.40 (s, 3H), 1.17 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 161.3, 141.1, 139.6, 136.1, 133.3, 132.5, 126.4, 126.2, 118.6, 112.4, 111.7, 110.2, 110.1, 60.4, 35.7, 14.1.

C₁₈H₁₆N₄O₂ (320.35): Calcd C 67.49, H 5.03; Found C 67.66, H 4.78.

Ethyl 1-methyl-5-(2-(4-nitrophenyl)-pyrrol-1-yl)-pyrazole-4-carboxylate (26)

From ethyl 1-methyl-5-(pyrrol-1-yl)-pyrazole-4-carboxylate (0.328 g, 1.5 mmol) and 4-bromonitrobenzene (0.202 g, 1 mmol) at 130 °C during 2 h product **26** was obtained in 40% (0.136 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 8.0 Hz, 2H), 8.02 (s, 1H), 7.21 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 3.1 Hz, 1H), 6.79-6.75 (m, 1H), 6.54 (t, J = 3.1 Hz, 1H), 4.18 (q, J = 7.6 Hz, 2H), 3.46 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 161.3, 146.1, 141.1, 138.0, 133.1, 126.6, 126.3, 124.1, 113.0, 111.9, 110.2, 60.4, 35.7, 14.1.

C₁₇H₁₆N₄O₄ (340.33): Calcd C 59.99, H 4.74; Found C 60.11, H 4.59.

Ethyl 5-(2-(4-formylphenyl)-pyrrol-1-yl)-1-methylpyrazole-4-carboxylate (27)

From ethyl 1-methyl-5-(pyrrol-1-yl)-pyrazole-4-carboxylate (0.328 g, 1.5 mmol) and 4-bromobenzaldehyde (0.185 g, 1 mmol) at 130 °C during 2 h product **27** was obtained in 50% (0.161 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.99 (s, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 3.1 Hz, 1H), 6.74-6.70 (m, 1H), 6.50 (t, J = 3.1 Hz, 1H), 4.16 (q, J = 7.6 Hz, 2H), 3.40 (s, 3H), 1.17 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.4, 161.4, 141.1, 139.8, 137.5, 134.5, 133.9, 130.2, 126.4, 126.2, 112.3, 111.6, 110.1, 60.3, 35.7, 14.1.

C₁₈H₁₇N₃O₃ (323.34): Calcd C 66.86, H 5.30; Found C 67.04, H 5.07.

Ethyl 1-methyl-5-(2-(4-nitro-3-(trifluoromethyl)phenyl)-pyrrol-1-yl)-pyrazole-4-carboxylate (28)

From ethyl 1-methyl-5-(pyrrol-1-yl)-pyrazole-4-carboxylate (0.328 g, 1.5 mmol) and 4-bromo-1-nitro-2-(trifluoromethyl)benzene (0.270 g, 1 mmol) at 130 °C during 2 h product **28** was obtained in 56% (0.228 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.25 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 3.1 Hz, 1H), 6.80-6.75 (m, 1H), 6.54 (t, J = 3.1 Hz, 1H), 4.16 (q, J = 7.6 Hz, 2H), 3.48 (s, 3H), 1.18 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 161.1, 141.1, 139.0, 136.6, 131.9, 129.0, 127.1, 126.0, 125.4 (q, J = 5.6 Hz), 124.5 (q, J = 34.0 Hz), 121.6 (q, J = 273.7 Hz), 113.6, 112.2, 110.5, 60.5, 35.7, 14.0.

C₁₈H₁₅F₃N₄O₄ (408.33): Calcd C 52.95, H 3.70; Found C 52.79, H 3.89.

Ethyl 1-methyl-5-(2-(pyrimidin-5-yl)-pyrrol-1-yl)-pyrazole-4-carboxylate (29)

From ethyl 1-methyl-5-(pyrrol-1-yl)-pyrazole-4-carboxylate (0.328 g, 1.5 mmol) and 5-bromopyrimidine (0.159 g, 1 mmol) at 130 °C during 2 h product **29** was obtained in 58% (0.172 g) yield.

¹H NMR (400 MHz, CDCl₃) δ 9.02 (s, 1H), 8.45 (s, 2H), 7.96 (s, 1H), 6.87 (t, J = 3.1 Hz, 1H), 6.75-6.70 (m, 1H), 6.53 (t, J = 3.1 Hz, 1H), 4.13 (q, J = 7.6 Hz, 2H), 3.48 (s, 3H), 1.18 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 160.8, 156.5, 153.7, 140.8, 138.7, 128.3, 125.9, 125.7, 111.9, 111.7, 110.2, 60.1, 35.3, 13.7.

C₁₅H₁₅N₅O₂ (297.31): Calcd C 60.60, H 5.09; Found C 60.41, H 5.27.

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