New Three-Component Glyoxylation–Decarbonylative Stille Coupling Sequence to Acyl Heterocycles under Mild Conditions

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Received 15 April 2010

Dedicated to Prof. Dr. Dr. h.c. mult. Rolf Huisgen on the occasion of his 90th birthday

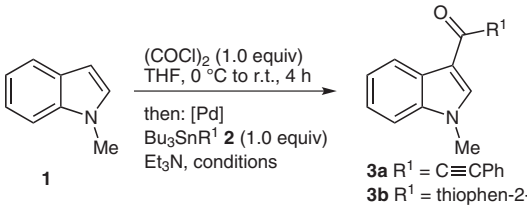
Abstract: A consecutive sequence of glyoxylation of 1-methyl-1*H*-indole, 1-(4-methoxybenzyl)-1*H*-pyrrolo[2,3-*b*]pyridine or N-substituted pyrroles with oxalyl chloride and subsequent decarbonylative Stille coupling under very mild, Lewis acid free conditions using all reactants in equimolar quantities is reported. As an illustration, this glyoxylation–decarbonylative coupling sequence was elaborated into a consecutive, four-component synthesis of 1-methyl-3-(1-methyl-4,5-dihydro-1*H*-pyrazol-3-yl)-1*H*-indole.

Key words: glyoxylation, decarbonylative Stille reaction, multicomponent reaction, C–C coupling, acyl heterocycles

The selective formation of unsymmetrical ketones by cross-coupling reactions is of significant interest in organic chemistry.[1] Therefore, many different ways to introduce the carbonyl group have been developed. Besides the well-established Friedel–Crafts-type acylations,[2] cross-coupling reactions have been introduced as catalytic alternatives. Most of the methods directly start from acid chlorides due to their easy availability. In cases where the acid chlorides are either not readily available or difficult to handle, cross coupling cannot prevail. An obvious solution to this problem are carbonylative cross-coupling reactions starting from aryl halides and carbon monoxide[3] or other carbon monoxide sources such as molybdenum hexacarbonyl.[4] Although mild carbonylations utilizing carbon monoxide at ambient pressure have been reported, the effective concentration of carbon monoxide in the reaction mixture is of crucial importance for full conversion and still represents a limitation of the method. Alternatively, decarbonylative cross coupling of α-dicarbonyl compounds can be considered. In particular, catalytic decarbonylations are highly desirable and have recently received considerable attention. For instance, palladium-catalyzed decarbonylative carbostannylations under mild conditions[5] and decarbonylative Heck reactions[6] at high temperatures and long reaction times have been reported. Recently, we established a new decarbonylative Sonogashira coupling of glyoxylyl chlorides,[7] which are in situ generated at room temperature from oxalyl chloride as an easy-to-handle carbon monoxide surrogate. In a one-pot sequence of Friedel–Crafts acylation of electron-rich heterocycles with oxalyl chloride (glyoxylation), followed by decarbonylative Sonogashira coupling, alkynones are obtained in good to excellent yields under mild conditions.

The Stille reaction is known to proceed under mild reaction conditions with high tolerance for many functional groups. Moreover, Stille couplings of acid chlorides are well precedented.[8] In addition, α-oxo acid chlorides have been successfully applied in the synthesis of 1,2-diketones.[9] Here, we report an extension of the glyoxylation–decarbonylative coupling methodology in which we have devised a consecutive three-component synthesis of ketones by a glyoxylation–decarbonylative Stille coupling sequence using electron-rich heterocycles, oxalyl chloride and organostannanes.

First, we tested the glyoxylation–decarbonylative Stille coupling of 1-methyl-1*H*-indole (**1**) with tributyl(phenylethynyl)stannane (**2a**) and tributyl(thiophen-2-yl)stannane (**2b**) via the in situ generated indole-3-glyoxylyl chloride, which gives rise to the formation of the *N*-methylindolyl ketones **3** (Scheme 1, Table 1).



Scheme 1 Optimization of the glyoxylation–decarbonylative Stille coupling of 1-methyl-1*H*-indole (**1**) with stannanes **2**

By applying 1 mol% of the air-stable precatalyst $PdCl_2(PPh_3)_2$, a 36% yield of the desired product **3a** could be isolated (Table 1, entry 1). One equivalent of triethylamine is stoichiometrically necessary to scavenge the hydrochloric acid generated in the glyoxylation step. Interestingly, addition of a second equivalent of triethylamine suppresses the formation of the non-decarbonylated byproduct (as detected by TLC) and also leads to an increase in the overall yield (Table 1, entries 2 and 3). In

SYNTHESIS 2010, No. 13, pp 2139–2146
Advanced online publication: 27.05.2010
DOI: 10.1055/s-0029-1218802; Art ID: C01410SS

the absence of triethylamine, the formation of the desired product **3b** cannot be detected by TLC (Table 1, entry 8). It is known that the addition of copper iodide often increases the yield in Stille coupling reactions ('copper effect').[10] Indeed, with stannane **2a** as a substrate, the 'copper effect' could be confirmed (Table 1, entry 4); however, with tributyl(thiophen-2-yl)stannane (**2b**), the addition of copper iodide did not exert any effect (Table 1, entries 5 and 6). Presumably, in the case of the coupling with tributyl(phenylethynyl)stannane (**2a**) in the presence of copper iodide, transmetalation produces a copper acetylide for a terminating Sonogashira coupling. As a consequence, tributyl(thiophen-2-yl)stannane (**2b**) was chosen as the model stannane for further optimization of the decarbonylative Stille coupling (Table 1, entries 7–15). After 20 hours at room temperature, the decarbonylative Stille coupling was essentially complete (Table 1, entry 7). A rapid precatalyst screening revealed that none of the other precursors gave a higher yield of **3b** than $PdCl_2(PPh_3)_2$ (Table 1, entries 9–12). Upon stirring the mixture at 60 °C, complete conversion was achieved within one hour (Table 1, entry 13). The coupling without decarbonylation[9] was attempted under palladium-free conditions (Table 1, entry 14) and with copper iodide (Table 1, entry 15), but the TLC control showed no conversion, even after 20 hours.

Despite the general smoothness of the Stille reaction, the separation of organotin residues during workup has occasionally been known to hamper the isolation of pure reaction products. Besides trituration of the flash-chromatographed product in *n*-pentane under sonication in an ultrasound bath, neither removal of tin residues by fluoridation with aqueous potassium fluoride solution or tetrabutylammonium fluoride,[11] nor flash chromatography on silica gel containing potassium fluoride (10:1),[12] furnished completely organotin-free products. The best workup protocol is to stir the reaction mixture after the decarbonylative Stille coupling step with an excess of potassium hydroxide in methanol[13] overnight at room temperature, followed by aqueous workup, to obtain an essentially tin-free product.

With this convenient method in hand and starting from 1-methyl-1*H*-indole (**1**), 1-(4-methoxybenzyl)-1*H*-pyrrolo[2,3-*b*]pyridine (**4**) or the N-substituted pyrroles **6** and **8**, the glyoxylation–decarbonylative Stille coupling sequence furnished various acyl heterocycles **3**, **5**, **7** and **9** in moderate to good yields (Scheme 2, Table 2).

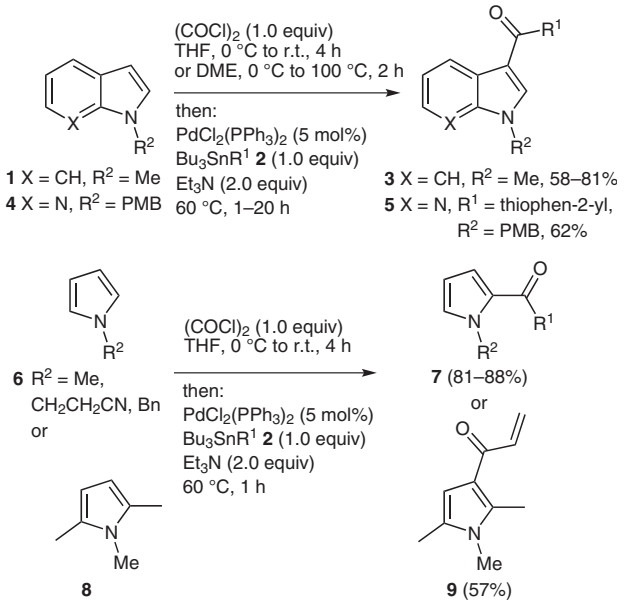
The structures of compounds **3**, **5**, **7** and **9** were unambiguously supported by NMR spectroscopy, mass spectrometry and combustion analysis, and later corroborated by an X-ray crystal structure analysis of compound **3b** (Figure 1).[14]

For the indole derivatives, 1-methyl-1*H*-indole (**1**) and 7-azaindole **4**, the glyoxylation occurs at the most electron-rich 3-position (Table 2, entries 1–7). The N-substituted

Table 1 Optimization of the Decarbonylative Stille Coupling Step of 1-Methyl-1*H*-indole (**1**) with Stannanes **2a** and **2b**[a]

Entry	Catalyst system	Conditions	Ketone **3** (% isolated yield)
1	$PdCl_2(PPh_3)_2$ (1 mol%)	**2a** (1.0 equiv), Et_3N (1.0 equiv), r.t., 1 h	**3a** (36[b])
2	$PdCl_2(PPh_3)_2$ (5 mol%)	**2a** (1.0 equiv), Et_3N (1.0 equiv), r.t., 1 h	**3a** (43[b])
3	$PdCl_2(PPh_3)_2$ (5 mol%)	**2a** (1.0 equiv), Et_3N (2.0 equiv), r.t., 1 h	**3a** (52)
4	$PdCl_2(PPh_3)_2$ (5 mol%), CuI (5 mol%)	**2a** (1.0 equiv), Et_3N (2.0 equiv), r.t., 1 h	**3a** (67)
5	$PdCl_2(PPh_3)_2$ (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), r.t., 1 h	**3b** (15)
6	$PdCl_2(PPh_3)_2$ (5 mol%), CuI (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), r.t., 1 h	**3b** (16)
7	$PdCl_2(PPh_3)_2$ (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), r.t., 20 h	**3b** (69)
8	$PdCl_2(PPh_3)_2$ (5 mol%)	**2b** (1.0 equiv), r.t., 20 h	**3b** (–[c])
9	$PdCl_2$ (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), r.t., 20 h	**3b** (77[d])
10	Pd/C (5 mol%), Ph_3P (10 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), r.t., 20 h	**3b** (–[c])
11	$Pd(PPh_3)_4$ (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), r.t., 20 h	**3b** (23)
12	$PdCl_2$dppf (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), 60 °C, 1 h	**3b** (–[c])
13	$PdCl_2(PPh_3)_2$ (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), 60 °C, 1 h	**3b** (81)
14	–	**2b** (1.0 equiv), Et_3N (2.0 equiv), 60 °C, 20 h	**3b** (–[c])
15	CuI (5 mol%)	**2b** (1.0 equiv), Et_3N (2.0 equiv), 60 °C, 20 h	**3b** (–[c])

[a] See Scheme 1. The reactions were performed on a 5.00 mmol scale in THF [*c*(**1**) = 0.2 M].
[b] TLC indicated the formation of the non-decarbonylated product as a byproduct.
[c] The formation of the desired product could not be detected by TLC.
[d] The crude reaction mixture was contaminated with a polar byproduct.



Scheme 2 Three-component glyoxylation–decarbonylative Stille coupling synthesis of ketones **3**, **5**, **7** and **9**

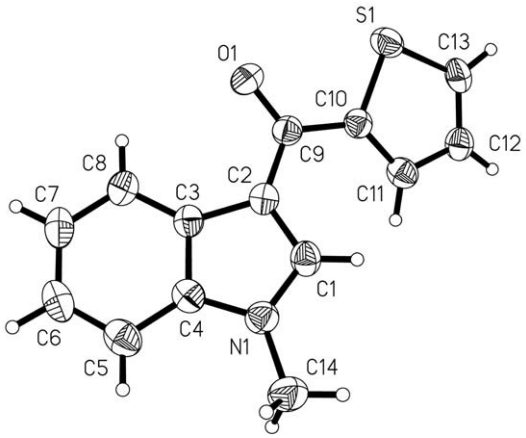
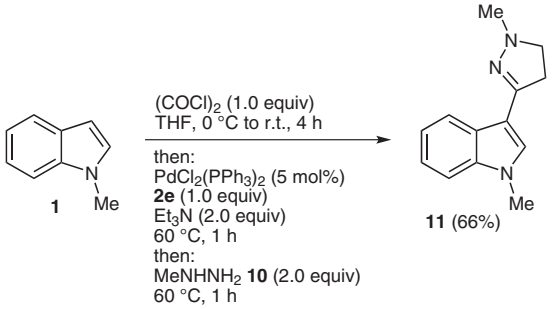


Figure 1 Molecular structure of compound **3b** in the crystal; 30% probability ellipsoids; only one orientation of the disordered thiophenyl group is shown[14]

pyrroles **6** are regioselectively glyoxylated at the 2-position (Table 2, entries 8–11). If the 2- and 5-positions are blocked, as in the case of 1,2,5-trimethyl-1*H*-pyrrole (**8**), expectedly, the glyoxylation occurs at the 3-position (Table 2, entry 12). The application of the N-substituted indole **1**, the 7-azaindole **4** and the pyrrole derivatives **6** and **8** supports the tolerance of the glyoxylation–decarbonylative Stille coupling sequence for a variety of *N*-heterocycles as substrates. In contrast to findings by Milstein and Stille,[8b] the decarbonylative Stille coupling is not inhibited by the formation of unreactive palladium carbonyl complexes but rather proceeds smoothly under mild conditions. Upon application of a wide range of unsaturated, aromatic and even heterocyclic stannanes **2**, the glyoxylation–decarbonylative Stille coupling sequence furnishes various acyl heterocycles **3**, **5**, **7** and **9**. Tributyl(phenylethynyl)stannane (**2a**) gives rise to the alkynones **3a** and **7a** (Table 2, entries 1 and 8). Interestingly, with tributyl(vinyl)stannane (**2e**), enones such as **3e** and **9** can be prepared in a one-pot fashion as highly reactive Michael systems (Table 2, entries 5 and 12). Upon extending the reaction time to 20 hours, the yield for the sequence with 1-methyl-1*H*-indole (**1**) and tributyl(phenyl)stannane (**2f**) could be increased from 16% to 68% of **3f** (Table 2, entry 6); however, in the case of stannane **2e**, an extension of the reaction time to 20 hours brought no significant increase in the yield (Table 2, entry 5).

Encouraged by the ease and broad versatility of the sequence, we probed the extension to a consecutive four-component pyrazoline synthesis (Scheme 3). Starting from 1-methyl-1*H*-indole (**1**), the glyoxylation–decarbonylative Stille coupling sequence with vinylstannane **2e** furnishes enone **3e**, which was reacted in situ with methylhydrazine (**10**) to give the pyrazoline **11** in 66% yield. Indeed, the isolated yield of **11** was higher than the isolated yield of **3e**, emphasizing the advantage of the one-pot sequence over a stepwise protocol with isolation of reactive, intermediate products.



Scheme 3 An illustrative, consecutive four-component synthesis of pyrazoline **11** by the glyoxylation–decarbonylative Stille coupling–cyclocondensation sequence

The structure of the pyrazoline **11** was unambiguously supported by NMR spectroscopy, mass spectrometry and combustion analysis.

In conclusion, we have developed a straightforward, novel, one-pot three-component synthesis of unsymmetrical heterocyclic ketones by glyoxylation of 1-methyl-1*H*-indole (**1**), the 7-azaindole **4** or the N-substituted pyrrole derivatives **6** and **8** with oxalyl chloride and subsequent decarbonylative Stille coupling of the in situ generated heteroareneglyoxylyl chlorides with various stannanes including vinyl and alkynyl, as well as *N*- and *S*-heterocyclic derivatives. As already demonstrated for glyoxylation–decarbonylative alkynylation,[7] this sequence can be performed on a 5 mmol scale under mild conditions and with only equimolar quantities of reagents and a high tolerance for various substituents. In addition, our consecutive, four-component synthesis of 1-methyl-3-(1-methyl-4,5-dihydro-1*H*-pyrazol-3-yl)-1*H*-indole (**11**) illustrates the conceptual versatility of the glyoxylation–decarbonylative cross-coupling methodology as an entry to multicomponent syntheses of densely functionalized heterocycles.

Table 2 Three-Component Glyoxylation–Decarbonylative Stille Coupling Synthesis of Ketones **3**, **5**, **7** and **9**[a]

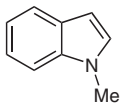
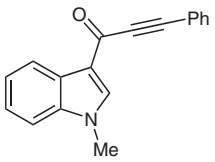
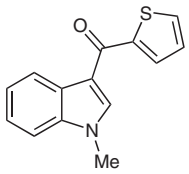
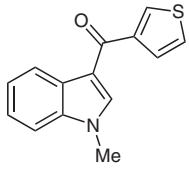
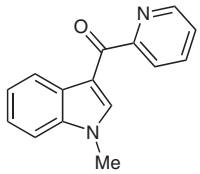
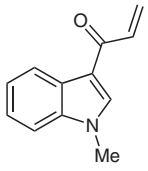
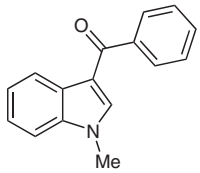
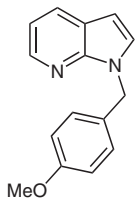
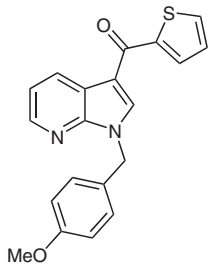
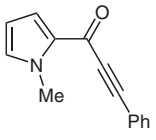
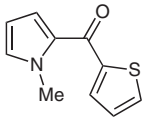
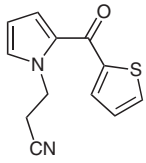
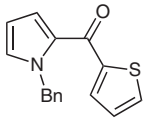
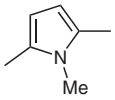
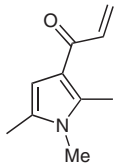
Entry	Starting electron-rich heterocycle	Stannane **2**	Reaction time (decarbonylative Stille coupling step)	Ketone product	Isolated yield (%)
1	 **1**	**2a**: R^1 = C≡CPh	1 h	 **3a**	81
2	**1**	**2b**: R^1 = thiophen-2-yl	1 h	 **3b**	81
3	**1**	**2c**: R^1 = thiophen-3-yl	1 h	 **3c**	66
4	**1**	**2d**: R^1 = pyridin-2-yl	1 h	 **3d**	75
5	**1**	**2e**: R^1 = CH=CH_2	20 h[b]	 **3e**	58
6	**1**	**2f**: R^1 = Ph	20 h	 **3f**	68
7	 **4**	**2b**: R^1 = thiophen-2-yl	1 h	 **5**	62[c]
8	**6a**: R^2 = Me	**2a**: R^1 = C≡CPh	1 h	 **7a**	82

Table 2 Three-Component Glyoxylation–Decarbonylative Stille Coupling Synthesis of Ketones **3**, **5**, **7** and **9**[a] (continued)

Entry	Starting electron-rich heterocycle	Stannane **2**	Reaction time (decarbonylative Stille coupling step)	Ketone product	Isolated yield (%)
9	**6a**: R^2 = Me	**2b**: R^1 = thiophen-2-yl	1 h	 **7b**	88
10	**6b**: R^2 = CH_2CH_2CN	**2b**: R^1 = thiophen-2-yl	1 h	 **7c**	85
11	**6c**: R^2 = Bn	**2b**: R^1 = thiophen-2-yl	1 h	 **7d**	81
12	 **8**	**2e**: R^1 = CH=CH_2	1 h	 **9**	57

[a] See Scheme 2. The reactions were performed in THF [*c*(**1**, **6** or **8**) = 0.2 M] using 5.00 mmol of 1-methyl-1*H*-indole (**1**) or N-substituted pyrroles **6** or **8** under the optimized reaction conditions.
[b] After 1 h (for the decarbonylative Stille coupling step), ketone **3e** could be isolated in 52% yield.
[c] The glyoxylation step was performed in DME [*c*(**4**) = 0.2 M] using 5.00 mmol of 7-azaindole **4** at 100 °C for 2 h.

All reactions were carried out in oven-dried Schlenk glassware using septa and syringes under argon atmosphere. THF was dried using an MBraun MB SPS-800 system. Et_3N was refluxed under argon over ketyl sodium, distilled and stored in a Schlenk flask over KOH pellets under argon atmosphere. 1-Methyl-1*H*-indole (**1**), 1-methyl-1*H*-pyrrole (**6a**), 3-(1*H*-pyrrol-1-yl)propanenitrile (**6b**), 1-benzyl-1*H*-pyrrole (**6c**), 1,2,5-trimethyl-1*H*-pyrrole (**8**), tributyl(phenylethynyl)stannane (**2a**), tributyl(thiophen-2-yl)stannane (**2b**), tributyl(pyridin-2-yl)stannane (**2d**), tributyl(vinyl)stannane (**2e**) and tributyl(phenyl)stannane (**2f**) are commercially available and were purchased from Acros Organics N. V., Aldrich Chemie GmbH, Fluka AG, ABCR GmbH & Co. KG, and Merck Serono KGaA. Oxalyl chloride was purchased from Merck Serono KGaA. All commercial grade reagents were used as supplied without further purification. Tributyl(thiophen-3-yl)stannane (**2c**) was prepared according to literature procedures.[15] MeOH (p.a.) and KOH (p.a.) used for the removal of tin residues were purchased from Aldrich Chemie GmbH and Roth GmbH & Co. KG. The purification of products was performed on silica gel 60 (0.015–0.040 mm) from Merck Serono KGaA using a Biotage SP1 Flash Purification System (SP-SNAP 340-g cartridges) and petroleum ether (boiling range 40–60 °C)–EtOAc as eluent (isocratic or gradient). The crude mixtures were adsorbed onto Celite® 545 (0.02–0.10 mm) from Merck Serono KGaA before chromatographic purification. The reaction progress was monitored qualitatively using TLC silica gel 60 F_{254} aluminum sheets (5 × 7.5 cm) obtained from Merck Serono KGaA. The spots were detected with UV light at 254 nm and using aq $KMnO_4$ soln. ^1H, ^{13}C and 135-DEPT NMR spectra were recorded on a Bruker DRX 500 spectrometer; $CDCl_3$ was used as solvent and TMS was used as reference (δ = 0.0). The type of carbon atoms was determined on the basis of the 135-DEPT NMR spectra. EI mass spectra were measured on Varian MAT 311A and Finnigan MAT 8200 spectrometers. IR spectra were obtained on a Bruker Vector 22 FT-IR instrument; solids were measured as KBr pellets and oils as films on KBr plates. Melting points (uncorrected) were measured on a Reichert-Jung Thermovar apparatus. Elemental analyses were carried out in the microanalytical laboratory of the Institut für Pharmazeutische Chemie in Düsseldorf. The X-ray crystal structure was measured on a Stoe IPDS diffractometer.

Glyoxylation–Decarbonylative Stille Coupling Sequence; General Procedure

1-Methyl-1*H*-indole (**1**), 7-azaindole **4** (see analytical data for **5**) or N-substituted pyrroles **6** or **8** (5.00 mmol) in anhyd THF (25 mL) was placed under argon atmosphere in a screw-cap vessel with a septum, and the mixture was degassed with argon for 5 min and cooled to 0 °C (ice water). After 15 min, oxalyl chloride (0.44 mL, 5.00 mmol) was added dropwise to the mixture at 0 °C. The mixture was allowed to warm to r.t. (water bath) and was stirred for 4 h. Then, $PdCl_2(PPh_3)_2$ (177 mg, 0.25 mmol), anhyd Et_3N (1.39 mL, 10.0 mmol) and a stannane **2** (5.00 mmol) were successively added to the mixture which was stirred at 60 °C for 1 h. The evolution of carbon monoxide was observed. After complete conversion (the product formation was monitored by TLC), the mixture was allowed to cool to r.t. and MeOH (25 mL) and KOH (0.66 g, 10.0 mmol) were added. The mixture was stirred at r.t. for 20 h. Then, H_2O (25 mL) was added and the mixture was extracted with CH_2Cl_2 (4 × 50 mL, monitored by TLC). The combined organic layers were dried (anhyd Na_2SO_4). The solvents were removed under reduced pressure, and the residue was absorbed onto Celite® and purified by

chromatography on silica gel [petroleum ether (40–60 °C)–EtOAc] to give the ketones **3**, **5**, **7** or **9** after drying under reduced pressure. In some cases, it was necessary to additionally purify the product by suspending it in *n*-pentane, sonication in an ultrasound bath, filtration and drying under reduced pressure.

1-(1-Methyl-1*H*-indol-3-yl)-3-phenylprop-2-yn-1-one (3a)
According to the standard procedure, the reaction with stannane **2a** (1.84 mL, 5.00 mmol) gave **3a** as a yellow solid; yield: 1.05 g (81%); mp 111–113 °C.

IR (KBr): 3053, 2204, 1593, 1525, 1490, 1469, 1398, 1377, 1339, 1272, 1250, 1198, 1149, 1123, 1088, 1049, 1011, 950, 794, 769, 751, 689, 567, 529, 430 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 7.31–7.46 (m, 6 H), 7.63–7.66 (m, 2 H), 7.93 (s, 1 H), 8.40–8.44 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.7 (CH_3), 87.6 (C_q), 87.9 (C_q), 109.9 (CH), 118.4 (C_q), 120.8 (C_q), 122.5 (CH), 123.1 (CH), 123.9 (CH), 125.8 (C_q), 128.6 (CH), 130.1 (CH), 132.7 (CH), 137.7 (C_q), 138.9 (CH), 171.1 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 260 (21), 259 (100) $[M]^+$, 232 (14), 231 (69), 230 (14), 216 (11), 158 (16) $[M - C_8H_5]^+$, 129 (7) $[C_9H_5O]^+$, 116 (18) $[C_8H_6N]^+$.

Anal. Calcd for $C_{18}H_{13}NO$ (259.3): C, 83.37; H, 5.05; N, 5.40. Found: C, 83.57; H, 4.97; N, 5.41.

(1-Methyl-1*H*-indol-3-yl)(thiophen-2-yl)methanone (3b)
According to the standard procedure, the reaction with stannane **2b** (1.64 mL, 5.00 mmol) gave **3b** as a yellow solid; yield: 981 mg (81%); mp 243–246 °C. Crystallization (CH_2Cl_2–*n*-pentane) gave yellow crystals.

IR (KBr): 3110, 2930, 1686, 1586, 1572, 1522, 1465, 1421, 1388, 1370, 1266, 1238, 1186, 1156, 1125, 1086, 1063, 1011, 934, 868, 846, 811, 771, 750, 735, 670, 568 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.30–7.38 (m, 3 H), 7.59 (dd, *J* = 5.0, 1.1 Hz, 1 H), 7.72 (dd, *J* = 3.7, 1.1 Hz, 1 H), 7.77 (s, 1 H), 8.39–8.43 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.0 (CH_3), 110.1 (CH), 115.9 (C_q), 123.0 (CH), 123.0 (CH), 124.1 (CH), 127.7 (C_q), 127.9 (CH), 131.4 (CH), 131.7 (CH), 136.5 (CH), 137.8 (C_q), 145.8 (C_q), 181.8 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 242 (18), 241 (100) $[M]^+$, 240 (20), 159 (10), 158 (90) $[M - C_4H_3S]^+$, 149 (11), 130 (8) $[C_9H_8N]^+$, 111 (4) $[C_5H_3OS]^+$, 71 (11), 57 (15), 43 (15).

Anal. Calcd for $C_{14}H_{11}NOS$ (241.3): C, 69.68; H, 4.59; N, 5.80. Found: C, 69.66; H, 4.72; N, 5.55.

(1-Methyl-1*H*-indol-3-yl)(thiophen-3-yl)methanone (3c)
According to the standard procedure, the reaction with stannane **2c** (1.86 g, 5.00 mmol) gave **3c** as a yellow solid; yield: 802 mg (66%); mp 115 °C.

IR (KBr): 3129, 3096, 3050, 2910, 1799, 1686, 1606, 1573, 1526, 1463, 1413, 1376, 1359, 1339, 1262, 1238, 1200, 1178, 1151, 1128, 1080, 1040, 1009, 936, 866, 839, 820, 800, 756, 646, 619, 591, 579, 562 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 7.30–7.37 (m, 4 H), 7.56 (m, 1 H), 7.63 (s, 1 H), 7.86 (m, 1 H), 8.40–8.43 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.5 (CH_3), 109.6 (CH), 116.3 (C_q), 122.6 (CH), 122.6 (CH), 123.6 (CH), 125.9 (CH), 127.1 (C_q), 128.1 (CH), 129.6 (CH), 136.8 (CH), 137.5 (C_q), 143.7 (C_q), 184.2 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 242 (10), 241 (58) $[M]^+$, 159 (11), 158 (100) $[M - C_4H_3S]^+$, 130 (9) $[C_9H_8N]^+$, 111 (6) $[C_5H_3OS]^+$, 103 (9), 77 (11).

Anal. Calcd for $C_{14}H_{11}NOS$ (241.3): C, 69.68; H, 4.59; N, 5.80. Found: C, 69.51; H, 4.42; N, 5.80.

(1-Methyl-1*H*-indol-3-yl)(pyridin-2-yl)methanone (3d)
According to the standard procedure, the reaction with stannane **2d** (1.70 mL, 5.00 mmol) gave **3d** as a yellow solid; yield: 882 mg (75%); mp 103–105 °C.

IR (KBr): 3139, 3050, 1736, 1686, 1617, 1578, 1563, 1511, 1460, 1365, 1270, 1230, 1156, 1123, 1074, 1033, 1012, 872, 748, 692, 624, 574, 428 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 7.28–7.38 (m, 3 H), 7.42 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1 H), 7.86 (td, *J* = 7.8, 1.8 Hz, 1 H), 8.14–8.17 (m, 1 H), 8.61 (dt, *J* = 7.2, 1.5 Hz, 1 H), 8.68–8.70 (m, 1 H), 8.71 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.0 (CH_3), 110.0 (CH), 114.2 (C_q), 123.3 (CH), 123.4 (CH), 123.8 (CH), 124.0 (CH), 126.1 (CH), 128.6 (C_q), 137.4 (C_q), 137.5 (CH), 141.0 (CH), 148.5 (CH), 157.2 (C_q), 186.7 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 237 (13), 236 (67) $[M]^+$, 235 (16), 159 (12), 158 (100) $[M - C_5H_4N]^+$, 130 (5) $[C_9H_8N]^+$, 118 (10), 103 (10), 77 (8) $[C_5H_3N]^+$, 43 (11).

Anal. Calcd for $C_{15}H_{12}N_2O$ (236.3): C, 76.25; H, 5.12; N, 11.86. Found: C, 76.00; H, 5.29; N, 11.72.

1-(1-Methyl-1*H*-indol-3-yl)prop-2-en-1-one (3e)
According to the standard procedure (20 h for the Stille coupling step), the reaction with stannane **2e** (1.54 mL, 5.00 mmol) gave **3e** as a yellow solid; yield: 534 mg (58%); mp 101–104 °C.

IR (KBr): 3107, 1645, 1588, 1574, 1530, 1468, 1414, 1371, 1335, 1299, 1233, 1146, 1125, 1089, 1011, 983, 956, 924, 801, 753, 695, 571, 428 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.75–3.79 (m, 3 H), 5.70–5.74 (m, 1 H), 6.39–6.44 (m, 1 H), 6.93–7.01 (m, 1 H), 7.27–7.35 (m, 3 H), 7.66–7.68 (m, 1 H), 8.45–8.49 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.5 (CH_3), 109.7 (CH), 116.7 (C_q), 122.7 (CH), 122.9 (CH), 123.7 (CH), 126.3 (CH_2), 126.7 (C_q), 133.7 (CH), 135.9 (CH), 137.6 (C_q), 184.7 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 186 (10), 185 (80) $[M]^+$, 159 (12), 158 (100) $[M - C_2H_3]^+$, 130 (9) $[C_9H_8N]^+$, 77 (12).

Anal. Calcd for $C_{12}H_{11}NO$ (185.2): C, 77.81; H, 5.99; N, 7.59. Found: C, 77.59; H, 6.27; N, 7.48.

(1-Methyl-1*H*-indol-3-yl)(phenyl)methanone (3f)
According to the standard procedure (20 h for the Stille coupling step), the reaction with stannane **2f** (1.68 mL, 5.00 mmol) gave **3f** as a yellow solid; yield: 800 mg (68%); mp 111–113 °C.

IR (KBr): 3051, 1619, 1574, 1524, 1471, 1372, 1267, 1233, 1126, 1077, 1025, 875, 751, 719, 697, 669, 573, 435 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 7.31–7.37 (m, 3 H), 7.44–7.56 (m, 4 H), 7.72–7.78 (m, 2 H), 8.41–8.45 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.5 (CH_3), 109.6 (CH), 115.6 (C_q), 122.7 (CH), 122.7 (CH), 123.6 (CH), 127.2 (C_q), 128.3 (CH), 128.6 (CH), 131.0 (CH), 137.5 (C_q), 137.9 (CH), 140.9 (C_q), 190.8 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 236 (16), 235 (86) $[M]^+$, 159 (11), 158 (100) $[M - C_6H_5]^+$, 130 (5) $[C_9H_8N]^+$, 77 (11), 71 (10), 57 (23), 43 (10), 43 (18).

Anal. Calcd for $C_{16}H_{13}NO$ (235.3): C, 81.68; H, 5.57; N, 5.95. Found: C, 81.39; H, 5.73; N, 5.74.

[1-(4-Methoxybenzyl)-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl](thiophen-2-yl)methanone (5)

The sequence was performed according to the standard procedure, but in DME (25 mL) at 100 °C for 2 h for the glyoxylation step. The reaction with stannane **2b** (1.64 mL, 5.00 mmol) gave **5** as a colorless solid; yield: 1.09 g (62%); mp 106 °C.

IR (KBr): 2926, 2833, 1609, 1572, 1524, 1509, 1448, 1428, 1416, 1396, 1349, 1306, 1252, 1245, 1190, 1175, 1107, 1036, 871, 828, 809, 769, 735, 710, 648, 584, 537, 510 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 5.50 (s, 2 H), 6.84–6.89 (m, 2 H), 7.12–7.15 (m, 1 H), 7.22–7.31 (m, 3 H), 7.57–7.70 (m, 2 H), 7.92 (s, 1 H), 8.45–8.47 (m, 1 H), 8.64–8.67 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 48.4 (CH_2), 55.7 (CH_3), 114.7 (C_q), 114.8 (CH), 119.2 (CH), 120.2 (C_q), 128.1 (CH), 128.7 (C_q), 129.7 (CH), 131.5 (CH), 131.7 (CH), 132.3 (CH), 134.7 (CH), 145.1 (C_q), 145.4 (CH), 148.6 (C_q), 159.9 (C_q), 181.6 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 349 (2), 348 (11) $[M]^+$, 237 (9) $[M - C_5H_3OS]^+$, 122 (9), 121 (100) $[C_8H_9O]^+$.

Anal. Calcd for $C_{20}H_{16}N_2O_2S$ (348.4): C, 68.94; H, 4.63; N, 8.04. Found: C, 68.71; H, 4.57; N, 8.07.

1-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylprop-2-yn-1-one (7a)

According to the standard procedure, the reaction with stannane **2a** (1.84 mL, 5.00 mmol) gave **7a** as a dark yellow oil; yield: 855 mg (82%).

IR (film): 3108, 3060, 2997, 2951, 2459, 2202, 1608, 1524, 1489, 1465, 1443, 1401, 1330, 1270, 1234, 1206, 1177, 1159, 1090, 1058, 984, 920, 884, 791, 757, 734, 690, 632, 603, 548 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.97 (s, 3 H), 6.19 (dd, *J* = 4.1, 2.4 Hz, 1 H), 6.87–6.88 (m, 1 H), 7.29 (dd, *J* = 4.1, 1.7 Hz, 1 H), 7.35–7.45 (m, 3 H), 7.59–7.63 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 37.8 (CH_3), 88.0 (C_q), 88.1 (C_q), 109.5 (CH), 121.1 (C_q), 124.2 (CH), 129.0 (CH), 130.6 (CH), 132.7 (C_q), 133.0 (CH), 133.2 (CH), 167.3 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 210 (18), 209 (100) $[M]^+$, 208 (71), 181 (29), 180 (45), 129 (11) $[C_9H_5O]^+$, 115 (17).

Anal. Calcd for $C_{14}H_{11}NO$ (209.2): C, 80.36; H, 5.30; N, 6.69. Found: C, 80.10; H, 5.13; N, 6.71.

(1-Methyl-1*H*-pyrrol-2-yl)(thiophen-2-yl)methanone (7b)

According to the standard procedure, the reaction with stannane **2b** (1.64 mL, 5.00 mmol) gave **7b** as a yellow oil; yield: 843 mg (88%).

IR (film): 3106, 2950, 2464, 1614, 1525, 1463, 1417, 1379, 1329, 1254, 1141, 1094, 1049, 904, 869, 853, 816, 785, 739, 666, 606, 566 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.97 (s, 3 H), 6.18 (dd, *J* = 4.1, 2.5 Hz, 1 H), 6.89–6.92 (m, 1 H), 7.03 (dd, *J* = 4.1, 1.7 Hz, 1 H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.60 (dd, *J* = 5.0, 1.2 Hz, 1 H), 7.75 (dd, *J* = 3.7, 1.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 37.6 (CH_3), 108.7 (CH), 121.3 (CH), 128.0 (CH), 130.6 (C_q), 131.8 (CH), 132.4 (CH), 132.7 (CH), 145.2 (C_q), 177.6 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 192 (17), 191 (100) $[M]^+$, 190 (51), 158 (20), 111 (20), 108 (25) $[M - C_4H_3S]^+$, 94 (15), 53 (14), 39 (16).

Anal. Calcd for $C_{10}H_9NOS$ (191.3): C, 62.80; H, 4.74; N, 7.32. Found: C, 62.51; H, 4.79; N, 7.06.

3-[2-(Thiophen-2-ylcarbonyl)-1*H*-pyrrol-1-yl]propanenitrile (7c)

According to the standard procedure, the reaction with stannane **2b** (1.64 mL, 5.00 mmol) gave **7c** as a yellow oil; yield: 977 mg (85%).

IR (film): 3108, 2961, 2251, 1732, 1601, 1527, 1466, 1416, 1354, 1337, 1257, 1180, 1133, 1089, 1048, 889, 868, 853, 813, 740, 663, 611 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.00 (t, *J* = 6.3 Hz, 2 H), 4.55 (t, *J* = 6.3 Hz, 2 H), 6.28 (dd, *J* = 3.8, 2.7 Hz, 1 H), 7.08–7.18 (m, 3 H), 7.64 (d, *J* = 5.0 Hz, 1 H), 7.76 (d, *J* = 3.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9 (CH_2), 45.8 (CH_2), 109.9 (CH), 118.1 (C_q), 122.6 (CH), 128.0 (CH), 129.7 (C_q), 131.7 (CH), 132.94 (CH), 133.0 (CH), 144.6 (C_q), 177.6 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 231 (13), 230 (100) $[M]^+$, 197 (32), 190 (42) $[C_{10}H_8NOS]^+$, 189 (21), 157 (10), 147 (8) $[C_8H_7N_2O]^+$, 111 (35) $[C_5H_3OS]^+$, 97 (20).

Anal. Calcd for $C_{12}H_{10}N_2OS$ (230.3): C, 62.59; H, 4.38; N, 12.16. Found: C, 62.49; H, 4.17; N, 11.87.

(1-Benzyl-1*H*-pyrrol-2-yl)(thiophen-2-yl)methanone (7d)

According to the standard procedure, the reaction with stannane **2b** (1.64 mL, 5.00 mmol) gave **7d** as a milky, colorless oil; yield: 1.08 g (81%).

IR (film): 3105, 3031, 2927, 1605, 1524, 1496, 1462, 1415, 1354, 1332, 1246, 1130, 1085, 1048, 869, 853, 816, 716, 675, 611 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.60 (s, 2 H), 6.24 (dd, *J* = 4.0, 2.6 Hz, 1 H), 6.98–7.01 (m, 1 H), 7.08 (dd, *J* = 4.0, 1.6 Hz, 1 H), 7.11 (dd, *J* = 4.9, 3.8 Hz, 1 H), 7.14–7.17 (m, 2 H), 7.20–7.25 (m, 1 H), 7.26–7.31 (m, 2 H), 7.58 (dd, *J* = 5.0, 1.1 Hz, 1 H), 7.73 (dd, *J* = 3.7, 1.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.6 (CH_2), 109.3 (CH), 122.0 (CH), 127.6 (CH), 127.9 (CH), 128.0 (CH), 129.1 (CH), 130.3 (C_q), 131.1 (CH), 132.5 (CH), 132.9 (CH), 138.6 (C_q), 145.2 (C_q), 177.6 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 267 (23) $[M]^+$, 156 (36) $[M - C_5H_3OS]^+$, 111 (41) $[C_5H_3OS]^+$, 91 (50) $[C_7H_7]^+$, 83 (48) $[C_4H_3S]^+$, 57 (100) $[C_2HS]^+$.

Anal. Calcd for $C_{16}H_{13}NOS$ (267.3): C, 71.88; H, 4.90; N, 5.24. Found: C, 71.96; H, 5.11; N, 5.02.

1-(1,2,5-Trimethyl-1*H*-pyrrol-3-yl)prop-2-en-1-one (9)

According to the standard procedure, the reaction with stannane **2e** (1.54 mL, 5.00 mmol) gave **9** as a yellow solid; yield: 468 mg (57%); mp 73–75 °C.

IR (KBr): 3096, 2912, 1639, 1594, 1570, 1521, 1429, 1415, 1372, 1344, 1295, 1220, 1187, 1154, 1044, 1006, 989, 951, 790, 728, 691, 561 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.21 (s, 3 H), 2.58 (s, 3 H), 3.41 (s, 3 H), 5.64–5.68 (m, 1 H), 6.26–6.35 (m, 2 H), 6.97 (dd, *J* = 17.1, 10.4 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.5 (CH_3), 12.8 (CH_3), 30.5 (CH_3), 107.7 (CH), 120.0 (C_q), 126.4 (CH_2), 128.4 (C_q), 135.3 (CH), 137.2 (C_q), 186.4 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 164 (11), 163 (100) $[M]^+$, 162 (74), 147 (24) $[M - CH_4]^+$, 136 (81) $[M - C_2H_3]^+$, 134 (15), 108 (12), 67 (10), 56 (14) $[C_3H_4O]^+$.

Anal. Calcd for $C_{10}H_{13}NO$ (163.2): C, 73.59; H, 8.03; N, 8.58. Found: C, 73.45; H, 8.03; N, 8.36.

1-Methyl-3-(1-methyl-4,5-dihydro-1*H*-pyrazol-3-yl)-1*H*-indole (11)

1-Methyl-1*H*-indole (**1**; 669 mg, 5.00 mmol) in anhyd THF (25 mL) was placed under an argon atmosphere in a screw-cap vessel with a septum, and the mixture was degassed with argon for 5 min and cooled to 0 °C (ice water). After 15 min, oxalyl chloride (0.44 mL, 5.00 mmol) was added to the mixture at 0 °C. The mixture was allowed to warm to r.t. (water bath) and was stirred for 4 h. Then, $PdCl_2(PPh_3)_2$ (177 mg, 0.25 mmol), anhyd Et_3N (1.39 mL, 10.0 mmol) and tributyl(vinyl)stannane (**2e**; 1.54 mL, 5.00 mmol) were successively added to the mixture which was stirred at 60 °C for 1 h. The evolution of carbon monoxide was observed. Then, methylhydrazine (**10**; 0.54 mL, 10.0 mmol) was added and the mixture was stirred at 60 °C for 1 h. After complete conversion (the product formation was monitored by TLC), the mixture was allowed to cool to r.t. and MeOH (25 mL) and KOH (0.66 g, 10.0 mmol) were added. The mixture was stirred at r.t. for 20 h. Then, H_2O (25 mL) was added and the mixture was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were dried (anhyd Na_2SO_4). The solvents were removed under reduced pressure, and the residue was absorbed onto Celite® and purified by chromatography on silica gel [petroleum ether (40–60 °C)–EtOAc] to give the pyrazoline **11**. It was necessary to additionally purify the product by suspending it in *n*-pentane, sonication in an ultrasound bath, filtration and drying under reduced pressure.

Yield: 704 mg (66%); yellow solid; mp 110–112 °C.

IR (KBr): 3060, 2945, 2834, 2803, 2776, 1719, 1655, 1591, 1543, 1524, 1473, 1442, 1422, 1403, 1367, 1336, 1293, 1237, 1167, 1139, 1113, 1013, 956, 884, 851, 805, 768, 742, 630, 568, 528 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.94 (s, 3 H), 3.00–3.12 (m, 4 H), 3.77 (s, 3 H), 7.18–7.34 (m, 4 H), 8.27 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.0 (CH_3), 35.2 (CH_2), 44.3 (CH_3), 55.7 (CH_2), 109.1 (CH), 109.9 (C_q), 120.6 (CH), 122.6 (CH), 122.7 (CH), 125.6 (C_q), 128.9 (CH), 137.5 (C_q), 149.2 (C_q).

MS (EI, 70 eV): *m*/*z* (%) = 213 (100) $[M]^+$, 212 (37), 211 (57), 210 (12), 170 (15) $[M - C_2H_5N]^+$, 156 (13) $[M - C_2H_5N_2]^+$, 155 (17), 144 (15), 128 (12), 106 (18), 105 (15).

Anal. Calcd for $C_{13}H_{15}N_3$ (213.3): C, 73.21; H, 7.09; N, 19.70. Found: C, 73.41; H, 6.87; N, 19.53.

Acknowledgment

This work was supported by Merck Serono, Darmstadt, and the Fonds der Chemischen Industrie (scholarship to B.O.A.T.).

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