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A Tandem "On-Palladium" Heck–Jeffery Amination Route Toward the Synthesis of Functionalized Indole-2-carboxylates

James McNulty*[a] and Kunal Keskar[a]

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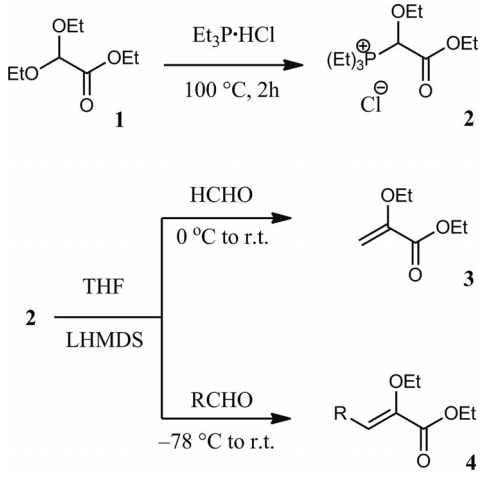
A direct synthesis of functionalized indole-2-carboxylates involving a Pd^{II}-catalyzed annulation of *ortho*-iodoanilines onto a vinyl ether is described. The reaction mechanism is shown to be distinct from a stepwise Heck, intramolecular amination pathway, likely involving a tandem "on-palladium" Heck–Jeffery amination process incorporating a novel intramolecular amination step.

Introduction

The indole nucleus occupies a privileged position amongst the nitrogen heterocycles, a consequence of its occurrence in the amino acid tryptophan. Indole derivatives are significant in terms of the varied structures and wide ranging biological activities demonstrated by both indole-containing secondary metabolites and wholly synthetic derivatives. The provenance of the indole nucleus in many of the classic alkaloid skeletons (aspidospermae, corynanthe, iboga, ergot etc) and simpler trypthophan degradation products (gramine, serotonin etc.) inspired an early interest in both the structure and synthesis of indole derivatives,[1] a trend that continues unabated.[2] Recent approaches towards indole synthesis are for the most part based on transition-metal promoted routes,[3] some of which converge on intermediates common to the classic syntheses.[1] The myriad of biological activities documented for both natural and synthetic indole derivatives continues to expand and includes toxicity, anticancer, antiviral, antimicrobial, neurological, and hormonal (plant and mammalian) activities.[4] These factors have assured a continued focus on the synthesis of functionalized indoles and their biological evaluation. The recent interest in indole-2-carboxylic acid derivatives as non-nucleoside reverse transcriptase[5a] and integrase[5b] inhibitors for HIV treatment, in conjunction with a report from our group[6] relating to the synthesis of vinyl ethers prompted us to investigate a possible tandem Pd-mediated Heck–Jeffery amination process as a direct route to such indole derivatives. In this communication we report the successful annulation of 2-iodoanilines onto an alkoxyacrylate yielding functionalized indole-2-carboxylates via an on-palladium tandem Heck–Jeffery amination (HJA) process.

We recently described a general route towards the synthesis of vinyl ethers involving the reaction of α-alkoxy-functionalized ylides with carbonyl compounds.[6] Therein it was shown that the reaction of a dialkyl acetal with a trialkylphosphane hydrobromide yielded the α-alkoxyphosphonium salt derived of the acetal. Ylide generation and olefination allowed access to a wide range of functionalized vinyl ethers and alkoxy-1,3-dienes. As an extension of this work, we have now successfully converted ethyl glyoxylate diethyl acetal (**1**, Scheme 1) into the functionalized phosphonium salt **2**. Salt **2** was also obtainable from the corresponding chloroacetal. Ylide generation from **2** and trapping with formaldehyde allowed us to access the α-alkoxy acrylate **3** as well as various α-alkoxycinnamates **4** through trapping of the ylide with aromatic aldehydes.



Scheme 1. Synthesis of α-alkoxyacrylates and cinnamates using functionalized ylides.

[a] Department of Chemistry and Chemical Biology, McMaster University,
1280 Main Street West, Hamilton, ON, L8S 4M1, Canada
Fax: +1-905-522-2509
E-mail: jmcnult@mcmaster.ca

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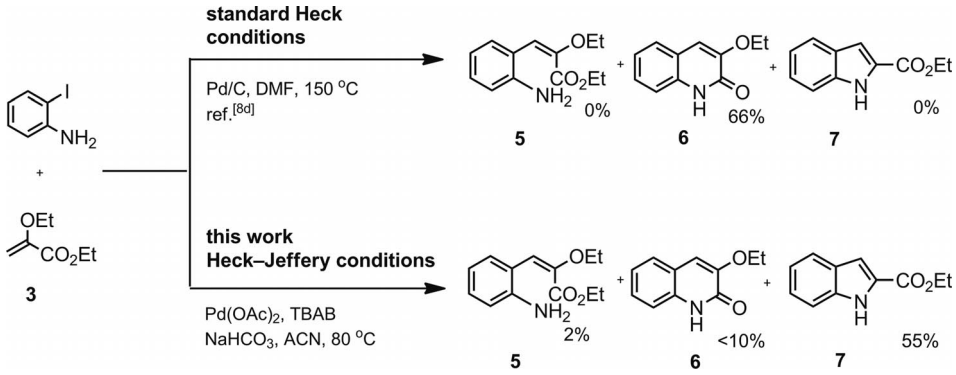
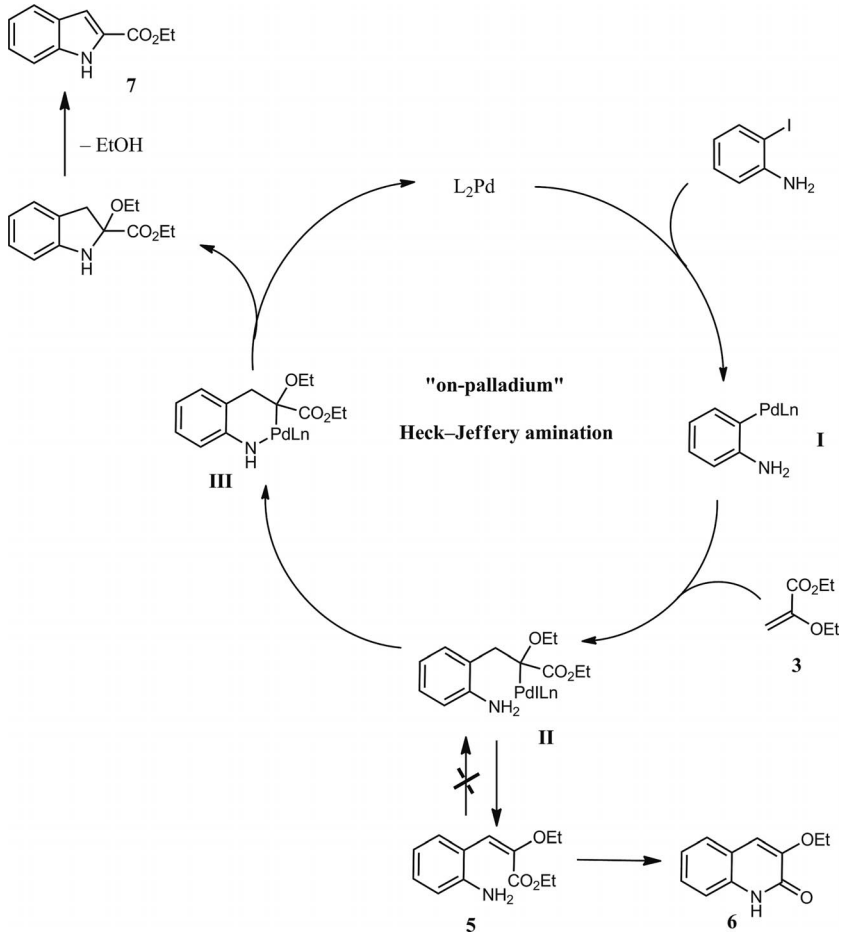
While the Heck reaction of *ortho*-haloanilines and acrylate esters is known to provide acceess to *ortho*-aminocinnamates in moderate yield,[7] it is well known that nucleophilic[8a] and Pd-mediated[8c–8d] Heck-type addition to α-alkoxyacrylates such as **3** is sluggish due to electronic deactivation of the olefin. The only report of such a process using an *ortho*-iodo aniline[8d] was shown to yield a quinolinone **6** (Scheme 2) through intramolecular *N*-acylation of the intermediate Heck adduct **5**. This result and others[7] demonstrate that under normal Heck conditions reductive elimination to yield the cinnamate precedes a possible intramolecular *N*-insertion, thus precluding a direct indole synthesis. These results led us to postulate a catalytic cycle as depicted in Scheme 3, in which, under Jeffery-type conditions (Pd^{II} precursor, no ligand, TBAB etc),[7a] an intramolecular ligand exchange (**II** to **III**), followed by reductive elimination (loss of HI/base not shown) and elimination of ethanol would deliver the indole **7** directly. The develop-



Scheme 2. Annulation of *ortho*-iodoanilines with alkoxy acrylate **3** via a standard Heck and the tandem "on-palladium" Heck–Jeffery amination process (isolated yields given).



Scheme 3. Proposed catalytic cycle for annulation of *ortho*-iodoanilines with alkoxy acrylate **3** via the tandem "on-palladium" Heck–Jeffery amination process.

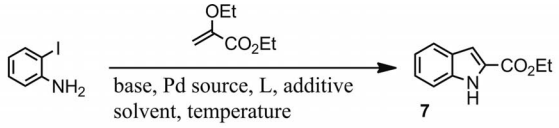
ment of such a tandem HJA process to functionalized *ortho*-iodo anilines and vinyl ethers would allow for a direct "on-palladium" route to indole-2-carboxylates. A Heck–Jeffery route to indoles has been reported from *N*-acyl enamines, involving a subsequent enamine hydrolysis and Reissert-type ring closure.[9a] This process does not involve an intramolecuar ligand exchange. The intramolecular trapping of Heck-type intermediates via aminopalladation is a known process in the synthesis of pyrrolidines, but to the best of our knowledge has not been applied towards the synthesis of indoles.[9b]

Results and Discussion

The reaction of *ortho*-iodoaniline with α-ethoxyacrylate **3**, investigated under standard Heck conditions (Scheme 2) furnished only the quinolinone **6**, with no trace of the corresponding indole-2-carboxylate ester, as previously reported.[8d] We experimented with various parameters of the reaction under Jeffery-type conditions[7a] and determined that the desired indole-2-carboxylate derivative was formed under a narrow subset of conditions. A summary of various conditions attempted is reported in Table 1. For comparison, these reactions were stopped after 24 h and the isolated yield of ethyl indole-2-carboxylate determined. Although the reaction was sluggish, it was found best performed in dipolar aprotic solvents using $Pd(OAc)_2$ as catalyst. The reaction requires base and sodium hydrogen carbonate proved most effective, although is perhaps not critical (entries 1–3).

No reaction occurs at room temperature while heating in acetonitrile at 80 °C as solvent proved slightly superior to

Table 1. Optimization of the Heck–Jeffery amination process for the synthesis of indole-2-carboxylate **7**. General reaction screening conditions: iodoaniline (0.18 mmol), ethyl 2-ethoxyacrylate (0.27 mmol), TBAB (0.36 mmol), Pd-source (0.018 mmol), ligand (0.009 mmol), base (0.54 mmol), solvent (1.5 mL).



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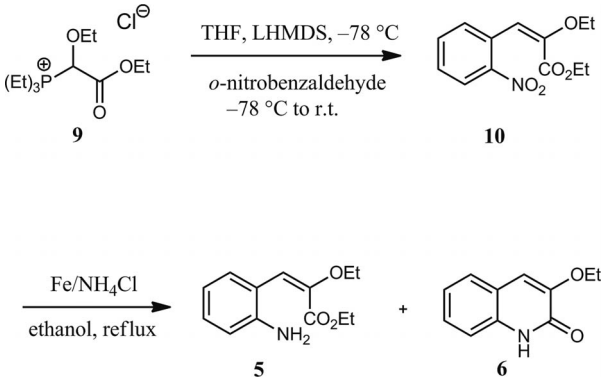
Entry	Base	Pd-Source	Ligand	Additive	Solvent	Temperature	Yield (%)
1	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB	DMF	95	29
2	K_2CO_3	$Pd(OAc)_2$	none	TBAB	DMF	95	20
3	Cs_2CO_3	$Pd(OAc)_2$	none	TBAB	DMF	95	trace
4	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB	ACN	80	30
5	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB, 5 Å MS	ACN	80	<10
6	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB	ACN	r.t.	n.r.
7	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB	DMF	150	17
8	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB, $AgSO_4$	ACN	80	<10
9	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB	ACN	80	38[a]
10	$NaHCO_3$	$Pd(OAc)_2$	none	TBAB	CYPHOS IL-109	120	n.r.
11	$NaHCO_3$	$Pd(OAc)_2$	none	none	CYPHOS IL-109	120	n.r.
12	$NaHCO_3$	$Pd(OAc)_2$	CYTOP 292	TBAB	ACN	80	<5
13	$NaHCO_3$	$Pd(OAc)_2$	CYTOP 292	TBAB	DMF	150	trace
14	Et_3N	$Pd(OAc)_2$	CYTOP 292	TBAB	DMF	150	n.r.
15	Et_3N	$Pd(OAc)_2$	PPh_3	TBAB	DMF	150	n.r.
16	Et_3N	$Pd(OAc)_2$	bidentate ligand[b]	TBAB	DMF	150	n.r.
17	$NaHCO_3$	Pd_2dba_3	none	TBAB	DMF	95	trace

[a] 24 h reaction with 2.8 equiv. of acrylate. [b] 1,2-Bis(di-*tert*-butylphosphanylmethyl)benzene.

DMF. Further experiments (entries 4–9) allowed us to identify satisfactory conditions (entry 9). Several failed optimization attempts provided circumstantial evidence indicating the lack of involvement of a Pd^0-species as the active catalyst, differing from a straightforward Heck reaction.[7c] For example, the reaction failed completely when conducted in an ionic liquid solvent [entries 10 and 11, IL-109 = trihexyl(tetradecyl)phosphonium bistriflimide], a media known to be highly effective in Pd^0-mediated amination[6b] and Heck processes.[6e] Furthermore, the addition of ligands including *P*-phenylphosphadamantane (Cytop 292),[6c] triphenylphosphane or bidentate bis(di-*tert*-butylphosphanyl)-*o*-xylene[6d] with $Pd(OAc)_2$ (entries 12–16) proved to shut down the catalytic cycle completely. The direct use of Pd^0 catalyst precursors proved also to be ineffective.

Extension of the reaction time of the optimized protocol (Table 1, entry 9) to 96 h gave maximum yield of ethyl indole-2-carboxylate **7a** as shown in Scheme 2, bottom. Under these conditions, annulation of 2-iodoaniline onto the alkoxyacrylate occurred yielding indole-2-carboxylate **7a** as the major product, contrasting sharply to the Heck process[8d] (Scheme 2, top) that yields the quinolinone. Formation of a small amount of the quinolinone **6** and a trace amount of the cinnamate **5** under the HJA conditions most likely represents "leakage" from the catalytic cycle via Heck-type β-hydride elimination from intermediate **II**. This step could potentially be reversible via an aminopalladation process. In order to test this hypothesis, we desired to investigate the reversibility of this elimination step and show that **5** is not converted into the indole under these conditions through re-entry to the catalytic cycle or by other means. To this end, we synthesized the *ortho*-aminocinnamate **5** independently through the route shown in Scheme 4. Olefination of 2-nitrobenzaldehyde **8** with the functionalized ylide **9** (derived from **2**) yielded the 2-nitrocinnamate **10**. Dissolving metal reduction (Fe, NH_4Cl) of **10** gave the aniline **5** (12%) as well as quinolinone **6** (48%). Compounds **5** and **6** were readily separated by silica-gel chromatography. Compound **5** was treated under standard Heck conditions

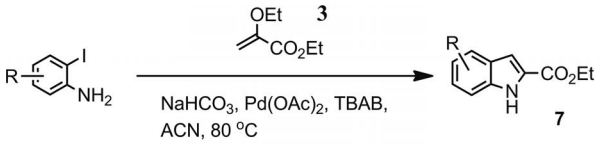


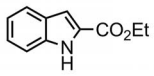
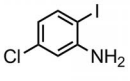
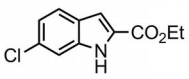
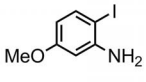
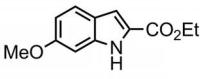
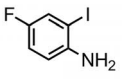
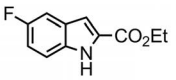
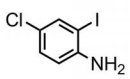
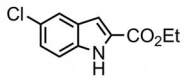
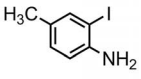
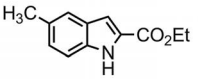
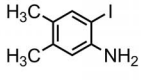
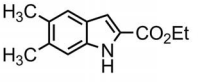
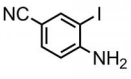
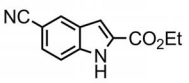
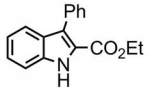
Scheme 4. Independent synthesis of the α-ethoxycinnamate **5** and conversion to **6** thermally and under Heck–Jeffery amination conditions.

with $Pd(OAc)_2$ and found to slowly convert to **6**, with no trace of the indole-2-carboxylate being observed. Treatment of **5** under the Heck–Jeffery conditions described (Scheme 2) slowly (over 48 h) yielded quinolinone **6** (60%), unreacted cinnamate **5** (30%) and a trace of the indole **7** observed only by thin-layer chromatography. We attribute the trace indole formation to hydrolysis of the enol ether in **10** followed by Reissert-type closure. These results indicate that under the Heck–Jeffery conditions, elimination from intermediate **II** to give **5** is essentially irreversible and that indole formation is in accord with the "on-palladium" catalytic cycle indicated in Scheme 3.

The scope of this new route to valuable indole-2-carboxylate derivatives[5] was investigated with a mini-panel of readily available *ortho*-iodoanilines and is summarized in Table 2. The HJA process allowed general conversion to the corresponding indole-2-carboxylate derivative in 48 to 77%

Table 2. Synthesis of functionalized indole-2-carboxylates.



Entry	Iodoaniline	Indole-2-carboxylates	Isolated yield (%)
1. (**7a**)			55%
2. (**7b**)			54%
3. (**7c**)			57%
4. (**7d**)			48%
5. (**7e**)			77%
6. (**7f**)			52%
7. (**7g**)			63%
8. (**7h**)			50%[a]
9.			trace[b]

[a] Based on recovered starting iodoaniline. [b] Ethyl 2-ethoxy-3-phenylacrylate was used as the acrylate source.

isolated yields, always accompanied by 5 to 10% of the corresponding quinolinone, produced via the "leakage" pathway. The indole-2-carboxylate derivatives were easily separable from the quinolinones on silica gel and the numbers reported in Table 1 are final isolated yields. The annulation also proved chemoselective in the presence of lesser reactive aryl halides, allowing access to useful chloro- and fluoro-functionalized indole-2-carboxylates.

Lastly, several of our results have brought into question the accepted mechanism of the Heck–Jeffery reaction. The dichotomy (see Scheme 2) between the standard Pd^0-mediated Heck reaction of vinyl ethers such as **3** and that described herein under the "on-palladium" Heck–Jeffery amination process is indicative of the involvement of a distinct catalytic species for the HJA process. Proposed catalytic cycles involving Jeffery conditions typically invoke Pd^0/Pd^{II} intermediates,[7a] although they invariably require Pd^{II} precursors. The present HJA process requires a Pd^{II} precursor, Pd^0 pre-catalysts and/or addition of ligands do not promote this direct indole formation, but instead result in exit from the catalytic cycle via intermediate **II** giving quinolinone **6**.[8d] The HJA process proceeds slowly under conditions where typical Pd^0-mediated pathways would be expected to be rapid and the normal Heck-type adducts should be formed. The present results also show that the normal Heck adducts do not re-enter the catalytic cycle, indole formation likely occurs via an independent on-palladium route. One explanation may be that excess halide anion present during the HJA process (requires TBAB) hinders β-hydride elimination (Scheme 3, **II** to **5**) on the standard Pd^{II} intermediate, a process known in the Heck reaction itself,[10e] leaving little option but intramolecular ligand exchange, leading to the indole-2-carboxylate. However this explanation does not account for the lack of reactivity under conditions of low halide concentration (Table 1, entry 8), or in ionic liquids containing non-nucleophilic counter anions (Table 1, entries 10 and 11). Additionally, this does not satisfactorily account for the inability of direct Pd^0 sources to promote the HJA process as described nor why Pd^0 sources under standard Pd^0/Pd^{II} Heck conditions gives only quinolinones (Scheme 2, top),[8d] not indole-2-carboxylates. Another possible explanation for this dichotomy is that while the standard Heck process proceeds via Pd^0/Pd^{II} intermediates, the on-palladium HJA reaction proceeds via a different cycle possibly involving Pd^{II}/Pd^{IV} intermediates, Scheme 3 (L = AcO^-). Such catalytic cycles have been proposed and deemed to be "unlikely" in the Heck reaction.[7c] The increased electrophilicity of the Pd-centre on intermediate **II** under such conditions, may be expected to favour intramolecular ligand exchange onto the appended *ortho*-amino group, and thus account for the successful direct annulation to the indole derivatives. Known catalytic processes involving Pd^{II}/Pd^{IV} intermediates typically proceed under oxidative conditions,[10] at least one report on the intramolecular trapping of Heck adducts on-Pd via a Pd^{II}/Pd^{IV} pathway is known.[10d] The present HJA process would require a direct oxidative addition of an aryl iodide to a Pd^{II} catalyst to access the Pd^{IV} intermediate.

Conclusions

In conclusion, we report the successful annulation of *ortho*-iodoanilines onto an α-ethoxy acrylate resulting in a general synthesis of indole-2-carboxylate derivatives. The reaction appears to be mechanistically distinct from a standard Heck reaction. Under Heck–Jeffery conditions, evidence is presented consistent with an all "on-palladium" mechanism, involving a critical intramolecular amination, or ligand exchange step, (**II**–**III**, Scheme 3) that intervenes and effectively competes with the standard Heck process (**II**–**5**). Further investigation into the mechanism, scope and application of the method is in progress.

Experimental Section

General: All reactions were carried out under argon atmosphere in oven dried glassware. Acetonitrile and DMF were obtained from Sigma–Aldrich. Iodoaniline derivatives were obtained from Sigma–Aldrich, AlfaAesar and AB Chem, Canada. THF was distilled from sodium/benzophenone. Melting points were recorded in open capillary tubes using a calibrated Büchi B540 apparatus. Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel $60F_{254}$ (Merck) and was visualized under 254/360 nm UV. ^1H and ^{13}C spectra were recorded on a AV 600 spectrometer in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) are reported in ppm downfield of TMS and coupling constants (J) are expressed in Hertz (Hz).

General Procedure for the Heck–Jeffery Indole-2-carboxylate Synthesis: Into a flame-dried Schlenk tube, containing a magnetic stirring bar, was weighed the corresponding 2-iodoaniline (0.040 g, 0.18 mmol 1.0 equiv.), ethyl 2-ethoxyacrylate (0.052 g, 0.36 mmol, 2.0 equiv.), TBAB (0.118 g, 0.36 mmol, 2.0 equiv.), $NaHCO_3$ (0.092 g, 1.09 mmol, 6.0 equiv.), $Pd(OAc)_2$ (0.0061 g, 15 mol-%) and dry acetonitrile (1.8–2.0 mL). The reaction mixture was stirred at 80 °C for 96 h monitored by TLC. The reaction mixture was allowed to cool to room temperature. Solvent was evaporated under vacuum and crude reaction mixture was extracted with ethyl acetate and washed with brine. The combined organic extracts were dried with sodium sulfate, filtered, and concentrated. The product was purified using silica gel column chromatography using 2–5% ethyl acetate in hexanes to yield corresponding ethyl 1*H*-indole-2-carboxylate. Data are summarized below for the entries in Table 1.

Ethyl 1*H*-Indole-2-carboxylate (7a):[11] M.p. 123–125 °C (ref.[12] m.p. 121–123 °C). ^1H NMR (600 MHz, $CDCl_3$): δ = 8.92 (br. s, 1 H), 7.69 (d, J = 8.12 Hz, 1 H), 7.42 (d, J = 8.12 Hz, 1 H), 7.32 (m, 1 H), 7.23 (m, 1 H), 7.15 (m, 1 H), 4.42 (q, J = 7.20 Hz, 2 H), 1.42 (t, J = 7.20 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.16, 136.94, 127.66, 125.49, 122.75, 120.94, 111.98, 108.79, 61.17, 14.55 ppm.

Ethyl 6-Chloro-1*H*-indole-2-carboxylate (7b):[12] M.p. 169–171 °C (ref.[12] m.p. 163–165 °C). ^1H NMR (600 MHz, $CDCl_3$): δ = 9.07 (br. s, 1 H), 7.59 (d, J = 8.50 Hz, 1 H), 7.42 (s, 1 H), 7.19 (s, 1 H), 7.12 (dd, J = 8.50, 1.8 Hz, 1 H), 4.20 (q, J = 7.10 Hz, 2 H), 1.42 (t, J = 7.10 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.95, 137.18, 131.43, 128.37, 126.17, 123.67, 122.01, 111.84, 108.75, 61.39, 14.52 ppm.

Ethyl 6-Methoxy-1*H*-indole-2-carboxylate (7c):[13] M.p. 131–133 °C (ref.[14] m.p. 135–136 °C). ^1H NMR (600 MHz, $CDCl_3$): δ = 8.88

(br. s, 1 H), 7.54 (d, J = 8.6 Hz, 1 H), 7.16 (m, 1 H), 6.83 (s, 1 H), 6.82 (dd, J = 8.6, 2.2 Hz, 1 H), 4.39 (q, J = 7.18 Hz, 2 H), 3.86 (s, 3 H), 1.41 (t, J = 7.18 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.16, 159.01, 138.06, 126.56, 123.51, 122.00, 112.41, 109.15, 93.86, 60.93, 55.62, 14.57 ppm.

Ethyl 5-Fluoro-1*H*-indole-2-carboxylate (7d):[11] M.p. 147–149 °C (ref.[11] m.p. 147–148 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.00 (br. s, 1 H), 7.36 (dd, J = 8.9, 4.3 Hz, 1 H), 7.32 (dd, J = 9.2, 2.4 Hz, 1 H), 7.18 (m, 1 H), 7.09 (td, J = 9.02, 2.48 Hz, 1 H), 4.42 (q, J = 7.10 Hz, 2 H), 1.42 (t, J = 7.10 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.89, 158.31 (d, J = 237.59 Hz), 129.20, 127.82 (d, J = 10.4 Hz), 114.59 (d, J = 26.89 Hz), 112.91 (d, J = 9.59 Hz), 108.57 (d, J = 5.25 Hz), 106.92 (d, J = 23.26 Hz), 61.34, 14.53 ppm.

Ethyl 5-Chloro-1*H*-indole-2-carboxylate (7e):[12] M.p. 167 °C (ref.[12] m.p. 167–169 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.12 (br. s, 1 H), 7.66 (d, J = 1.83 Hz, 1 H), 7.35 (d, J = 8.35 Hz, 1 H), 7.27 (dd, J = 8.73, 1.92 Hz, 1 H), 7.15 (m, 1 H), 4.42 (q, J = 7.10 Hz, 2 H), 1.42 (t, J = 7.10 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.91, 135.22, 128.89, 128.55, 126.59, 125.97, 121.89, 113.12, 108.08, 61.42, 14.51 ppm.

Ethyl 5-Methyl-1*H*-indole-2-carboxylate (7f):[15] M.p. 161–162 °C (ref.[16] m.p. 163 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.85 (br. s, 1 H), 7.46 (d, J = Hz 0.64 H, 1 H), 7.31 (d, J = 8.46 Hz, 1 H), 7.15 (m, 2 H), 4.41 (q, J = 7.10 Hz, 2 H), 2.44 (s, 3 H), 1.42 (t, J = 7.10 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.22, 135.38, 130.23, 127.93, 127.65, 127.45, 121.98, 111.64, 108.27, 61.08, 21.55, 14.55 ppm.

Ethyl 5,6-Dimethyl-1*H*-indole-2-carboxylate (7g):[17] M.p. 162–165 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.71 (br. s, 1 H), 7.43 (s, 1 H), 7.18 (s, 1 H), 7.12 (dd, J = 2.00, 0.84 Hz, 1 H), 4.39 (q, J = 7.18 Hz, 2 H), 2.37 (s, 3 H), 2.34 (s, 3 H), 1.41 (t, J = 7.18 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.27, 136.13, 135.32, 129.99, 126.85, 126.14, 122.30, 112.30, 112.00, 108.28, 60.96, 20.91 20.22, 14.57 ppm.

Ethyl 5-Cyano-1*H*-indole-2-carboxylate (7h):[18] M.p. 179–180 °C, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.20 (s, 1 H), 8.08 (s, 1 H), 7.54 (dd, J = 8.6, 1.3 Hz, 1 H), 7.50 (d, J = 8.6 Hz, 1 H), 7.28 (d, J = 1.2 Hz, 1 H), 4.44 (q, J = 7.1 Hz, 2 H), 1.43 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.41, 138.08, 129.96, 128.68, 127.73, 127.32, 120.08, 113.07, 109.00, 104.55, 61.76, 14.49 ppm.

Supporting Information (see footnote on the first page of this article): Additional experimental procedures, compound characterization data and copies of ^{1}H and ^{13}C spectra.

Acknowledgments

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