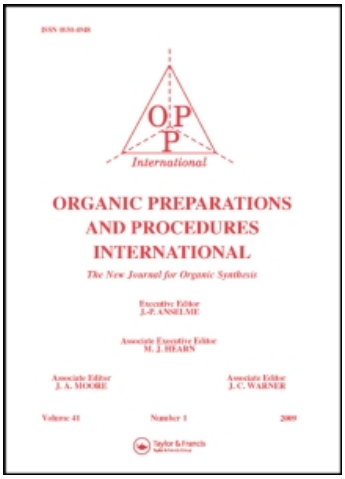


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# 2-ALKYLINDOLE-3-CARBOXYLATE ESTERS BY A TANDEM REDUCTION-ADDITION-ELIMINATION REACTION

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# OPPI BRIEFS

## 2-ALKYLINDOLE-3-CARBOXYLATE ESTERS BY A TANDEM REDUCTION-ADDITION-ELIMINATION REACTION

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(12/28/01)

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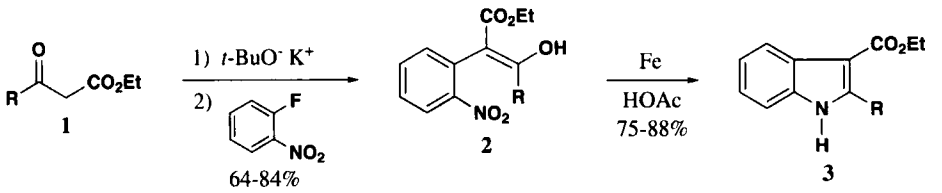
A recent study from this laboratory reported the use of mild reduction conditions (iron powder in glacial acetic acid) for a tandem reduction-Michael addition reaction to prepare tetrahydroquinoline-2-carboxylate esters.[1] We have now extended this procedure to include a reduction-addition-elimination sequence for the preparation of 2-alkylindole-3-carboxylate esters. Indole-3-carboxylic acid derivatives are known to have significant biological activity[2] and are valuable building blocks for the synthesis of other heterocycles.[3] The current procedure is simple, efficient and applicable to a wide range of substrates.

The title compounds have been prepared previously by a number of routes including: the Fischer indole synthesis;[4] reaction of indole Grignard reagents with phosgene;[5] copper(I)-promoted arylation of β-keto ester enolates with 2-iodoaniline;[6] reduction-cyclization of 2-nitrocinnamate esters using triethylphosphite;[7] and palladium-catalyzed cyclization of β-(2-halophenyl)amino-substituted α,β-unsaturated esters.[8] Ethyl 2-methylindole-3-carboxylate has also been prepared by intramolecular cyclization of an imino ether derived from 2-(2-aminophenyl)malonate.[9] Other synthetic approaches to ethyl 2-phenylindole-3-carboxylate have included hydrolysis-addition-elimination of ethyl 3-amino-3-phenyl-2-(2-acetamidophenyl)acrylate[10] and treatment of the 2-phenylindole Grignard reagent with ethyl chloroformate.[11]

The cyclization substrates were prepared by reacting two equivalents of the anion derived from β-keto ester **1** with one equivalent of 1-fluoro-2-nitrobenzene (*see Scheme*). This gave the nitroaromatic keto esters **2**, predominantly as their *Z* enols.[12] This first step also demonstrated the use of DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone) as a solvent for nucleophilic aromatic substitution reactions. Earlier reports have used DMF[13] and the more hazardous solvent HMPA.[14] In accounts using DMF, the reaction required heating at ≥ 80° for an extended period (6-16

h) and workup involved distillation or repeated washing to remove the solvent. When DMPU was employed, the reaction was complete after 30 min at 65-70°; workup was accomplished by diluting with 2.5 volumes of saturated $NH_4Cl$ and extracting with ether.




a) R = $CH_3$ b) R = $n$-$C_3H_7$ c) R = $n$-$C_5H_{11}$ d) R = $CH_2CH_2CH{=}CH_2$ ($CH_3$ ester)
e) R = $CH_2CH_2Ph$ f) R = $i$-$C_4H_9$ g) R = $i$-$C_3H_7$ h) R = $c$-$C_6H_{11}$ i) R = Ph j) R = 2-ClPh

Ring closure to the 2-alkylindole-3-carboxylate esters **3** was effected by direct treatment of the enol mixture with six equivalents of iron powder in glacial acetic acid at 115°. This treatment resulted in reduction of the nitroarene to the aniline, Michael addition to the unsaturated ester, and finally, elimination of water. The mild conditions permitted the synthesis of indole targets bearing substitution that would not tolerate more vigorous reduction conditions (*e.g.* **3d** and **3j**). Final purification of the products was generally achieved by recrystallization; in two cases, **3f** and **3h,** chromatographic purification was required. Overall yields were 50-60%.

In conclusion, we have developed a two-step method for the efficient synthesis of 2-alkylindole-3-carboxylate esters. The procedure involves (1) nucleophilic substitution of 1-fluoro-2-nitrobenzene with a stabilized β-keto ester anion followed by (2) tandem reduction-addition-elimination using iron powder in glacial acetic acid. The final cyclization is particularly mild, allowing ring closure of substrates incorporating functional groups incompatible with many other reducing agents.



## EXPERIMENTAL SECTION

All reactions were run under dry nitrogen in oven-dried glassware. Commercial reagents and solvents were used as received. DMPU from a freshly opened bottle was stored over 4Å molecular sieves and transferred by syringe into the reaction flask. The $NH_4Cl$, $NaHCO_3$ and NaCl used in various workup procedures refer to saturated aqueous solutions. Reactions were monitored by thin layer chromatography on silica gel GF plates. Preparative separations were performed using flash column chromatography[15] on silica gel (grade 62, 60-200 mesh) mixed with Sorbent Technologies no. 5 UV-active phosphor; band elution was monitored using a hand-held ultraviolet lamp. Melting points were uncorrected. Infrared spectra were run as thin films on NaCl disks and were referenced to polystyrene. $^1H$ and $^{13}C$ nuclear magnetic resonance spectra were measured in $CDCl_3$ at 300 MHz and 75 MHz, respectively, and were referenced to internal tetramethylsilane. HRMS (EI) were obtained at 70 eV.

**Representative Procedure for Nucleophilic Aromatic Substitution. Ethyl (2Z)-3-Hydroxy-2-(2-nitrophenyl)-2-butenoate (2a).**- To a solution of 2.24 g (20.0 mmol) of potassium *tert*-butoxide in 20 mL of DMPU was added 2.60 g (20.0 mmol) of ethyl acetoacetate dropwise with stirring. The reaction became warm and was stirred for 10 min. To this solution was then added 1.41 g (10.0 mmole) of

1-fluoro-2-nitrobenzene dropwise with continued stirring. The reaction again became warm and the solution turned a dark brown color. The mixture was heated in an oil bath at 65-70° until TLC showed complete consumption of the 1-fluoro-2-nitrobenzene (*ca* 30 min), then cooled, quenched with 50 mL of $NH_4Cl$ and extracted with ether (2x). The combined ether layers were washed with NaCl (1x), then dried ($MgSO_4$) and concentrated under vacuum. The resulting yellow oil was flash chromatographed on a 50 cm x 2.5 cm silica gel column eluted with 5% ether in hexanes. Band 2 afforded 3.86 g (15.4 mmol, 77%) of enol **2a** as a yellow oil, *ca.* 90:10 *Z:E*. The spectra for the *Z* enol were as follows: IR: 1652, 1618, 1530, 1356 $cm^{-1}$; $^1H$ NMR: δ 13.02 (s, 1 H), 8.00 (d, *J* = 7.8 Hz, 1 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 4.21 (m, 1 H), 4.04 (m, 1 H), 1.86 (s, 3 H), 1.12 (t, *J* = 7.2 Hz, 3 H); $^{13}C$ NMR: δ 173.2, 171.0, 149.6, 133.9, 132.7, 130.0, 128.5, 124.4, 100.9, 60.9, 19.8, 13.8; HRMS *m/z*: Calcd for $C_{12}H_{13}NO_5$: 251.0793. Found: 251.0791.

**Ethyl (2Z)-3-Hydroxy-2-(2-nitrophenyl)-2-hexenoate (2b)**: 83%; yellow oil; IR: 1654, 1615, 1530, 1355 $cm^{-1}$; $^1H$ NMR: δ 13.08 (s, 1 H), 8.01 (d, *J* = 7.8 Hz, 1 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.28 (d, *J* = 7.8 Hz, 1 H), 4.20 (m, 1 H), 4.02 (m, 1 H), 2.06 (m, 2 H), 1.56 (sextet, *J* = 7.4 Hz, 2 H), 1.12 (t, *J* = 7.1 Hz, 3 H), 0.83 (t, *J* = 7.4 Hz, 3 H); $^{13}C$ NMR: δ 176.0, 171.2, 149.8, 134.0, 132.7, 130.1, 128.5, 124.5, 100.8, 60.9, 34.8, 19.7, 13.9, 13.7; HRMS *m/z*: Calcd for $C_{14}H_{17}NO_5$: 279.1106. Found: 279.1104.

**Ethyl (2Z)-3-Hydroxy-2-(2-nitrophenyl)-2-octenoate (2c)**: 82%; yellow oil; IR: 1654, 1615, 1530, 1356 $cm^{-1}$; $^1H$ NMR: δ 13.08 (s, 1 H), 8.01 (d, *J* = 7.6 Hz, 1 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.28 (d, *J* = 7.5 Hz, 1 H), 4.20 (m, 1 H), 4.03 (m, 1 H), 2.06 (m, 2 H), 1.52 (m, 2 H), 1.18 (complex, 4 H), 1.12 (t, *J* = 7.1 Hz, 3 H), 0.81 (t, *J* = 6.4 Hz, 3 H); $^{13}C$ NMR: δ 176.3, 171.2, 149.7, 134.0, 132.7, 130.1, 128.5, 124.5, 100.6, 60.9, 32.9, 31.2, 25.9, 22.2, 13.8 (2); HRMS *m/z*: Calcd for $C_{16}H_{21}NO_5$: 307.1419. Found: 307.1420.

**Methyl (2Z)-3-Hydroxy-2-(2-nitrophenyl)-2,6-heptadienoate (2d)**: 77%; yellow oil; IR: 1654, 1615, 1530, 1355, 982, 913 $cm^{-1}$; $^1H$ NMR: δ 12.98 (s, 1 H), 8.02 (d, *J* = 7.6 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 1 H), 5.67 (ddt, *J* = 17.1, 10.1, 6.7 Hz, 1 H), 4.96 (d, *J* = 17.1 Hz, 1 H), 4.93 (d, *J* = 10.1 Hz, 1 H), 3.64 (s, 3 H), 2.28 (m, 2 H), 2.17 (m, 2 H); $^{13}C$ NMR: δ 175.1, 171.7, 149.9, 136.5, 134.0, 132.8, 130.0, 128.7, 124.6, 115.6, 100.7, 51.9, 32.4, 30.1; HRMS *m/z*: Calcd for $C_{14}H_{15}NO_5$: 277.0950. Found: 277.0947.

**Ethyl (2Z)-3-Hydroxy-2-(2-nitrophenyl)-5-phenyl-2-pentenoate (2e)**: 73%; yellow oil; IR: 1654, 1615, 1530, 1355 $cm^{-1}$; $^1H$ NMR: δ 13.12 (s, 1 H), 7.97, (m, 1 H), 7.45 (m, 2 H), 7.28-7.17 (complex, 4 H), 7.04 (d, *J* = 7.6 Hz, 2 H), 4.21 (m, 1 H), 4.00 (m, 1 H), 2.96 (m, 1 H), 2.91 (m, 1 H), 2.42 (m, 1 H), 2.33 (m, 1 H), 1.10 (t, *J* = 7.1 Hz, 3 H); $^{13}C$ NMR: δ 174.5, 171.2, 149.8, 140.6, 134.0, 132.7, 129.6, 128.5, 128.4 (2), 126.2, 124.3, 101.3, 61.0, 35.0, 32.2, 13.8; HRMS *m/z*: Calcd for $C_{19}H_{19}NO_5$: 341.1263. Found: 341.1261.

**Ethyl (2Z)-3-Hydroxy-5-methyl-2-(2-nitrophenyl)-2-hexenoate (2f)**: 74%; yellow oil; IR: 1654, 1618, 1530, 1355 $cm^{-1}$; $^1H$ NMR: δ 13.12 (s, 1 H), 8.03 (d, *J* = 7.6 Hz, 1 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.27 (d, *J* = 7.6 Hz, 1 H), 4.24 (m, 1 H), 4.04 (m, 1 H), 2.03 (m, 1 H), 1.99

(d, $J$ = 6.3 Hz, 2 H), 1.12 (t, $J$ = 7.2 Hz, 3 H), 0.85 (d, $J$ = 6.3 Hz, 3 H), 0.78 (d, $J$ = 6.3 Hz, 3 H); $^{13}$C NMR: δ 175.4, 171.3, 149.8, 134.2, 132.7, 130.1, 128.5, 124.6, 101.4, 60.9, 41.7, 26.1, 22.5, 22.0, 13.9; HRMS *m/z*: Calcd for $C_{15}H_{19}NO_5$: 291.1106. Found: 291.1105.

**Ethyl (2*Z*)-3-Hydroxy-4-methyl-2-(2-nitrophenyl)-2-pentenoate (2g)**: 84%; yellow oil; IR: 1654, 1615, 1530, 1354 cm$^{-1}$; $^1$H NMR: δ 13.09 (s, 1 H), 7.99 (d, $J$ = 7.8 Hz, 1 H), 7.60 (t, $J$ = 7.5 Hz, 1 H), 7.48 (t, $J$ = 7.5 Hz, 1 H), 7.28 (d, $J$ = 7.7 Hz, 1 H), 4.22 (m, 1 H), 4.02 (m, 1 H), 2.34 (septet, $J$ = 6.9 Hz, 1 H), 1.14 (t, $J$ = 7.2 Hz, 3 H), 1.12 (d, $J$ = 6.9 Hz, 3 H), 1.03 (d, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR: δ 180.0, 171.4, 149.8, 133.8, 132.7, 130.0, 128.5, 124.4, 98.9, 60.9, 31.5, 19.4, 19.3, 13.8; HRMS *m/z*: Calcd for $C_{14}H_{17}NO_5$: 279.1106. Found: 279.1108.

**Ethyl (2*Z*)-3-Cyclohexyl-3-hydroxy-2-(2-nitrophenyl)-2-propenoate (2h)**: 79%; yellow solid; mp 69-71°; IR: 1650, 1609, 1530, 1355 cm$^{-1}$; $^1$H NMR: δ 13.13 (s, 1 H), 7.99 (d, $J$ = 7.8 Hz, 1 H), 7.59 (t, $J$ = 7.5 Hz, 1 H), 7.49 (t, $J$ = 7.5 Hz, 1 H), 7.26 (d, $J$ = 7.7 Hz, 1 H), 4.20 (m, 1 H), 4.04 (m, 1 H), 1.98 (m, 1 H), 1.79-1.46 (complex, 7 H), 1.32-0.90 (complex, 3 H), 1.11 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR: δ 179.5, 171.5, 149.8, 133.8, 132.6, 130.0, 128.5, 124.4, 99.1, 60.9, 41.8, 41.7, 29.4, 29.0, 25.6, 25.5, 13.9; HRMS *m/z*: Calcd for $C_{17}H_{21}NO_5$: 319.1419. Found: 319.1420.

**Ethyl (2*Z*)-3-Hydroxy-2-(2-nitrophenyl)-3-phenyl-2-propenoate (2i)**: 66%; yellow oil; IR: 1650, 1615, 1530, 1354 cm$^{-1}$; $^1$H NMR: δ 13.45 (s, 1 H), 7.97 (d, $J$ = 7.8 Hz, 1 H), 7.42-7.22 (complex, 5 H), 7.17 (t, $J$ = 7.5 Hz, 2 H), 6.95 (d, $J$ = 7.8 Hz, 1 H), 4.26 (m, 1 H), 4.07 (m, 1 H), 1.17 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR: δ 171.3, 171.1, 149.2, 134.9, 132.6, 130.6, 130.1, 128.8 (2), 128.1, 127.9, 124.3, 101.6, 61.5, 13.7; HRMS *m/z*: Calcd for $C_{17}H_{15}NO_5$: 313.0950. Found: 313.0950.

**Ethyl (2*Z*)-3-(2-Chlorophenyl)-3-hydroxy-2-(2-nitrophenyl)-2-propenoate (2j)**: 64%; yellow oil; IR: 1654, 1626, 1530, 1355 cm$^{-1}$; $^1$H NMR: δ 13.15 (s, 1 H), 7.93 (m, 1 H), 7.39-7.22 (complex, 3 H), 7.21-7.11 (complex, 2 H), 7.10-6.99 (complex, 2 H), 4.32 (m, 1 H), 4.09 (m, 1 H), 1.17 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR: δ 170.9, 169.2, 149.1, 133.9, 133.7, 132.7, 132.5, 130.6. 130.0, 129.6, 129.5, 128.3, 126.6, 124.3, 104.3, 61.6, 13.7; HRMS *m/z*: Calcd for $C_{17}H_{14}ClNO_5$: 347.0561. Found: 347.0560.

**Representative Procedure for the Tandem Reduction-Addition-Elimination Reaction. Ethyl 2-Methylindole-3-carboxylate (3a)**.- A 50-mL three-necked round-bottomed flask, equipped with a reflux condenser ($N_2$ inlet) and a magnetic stirrer, was charged with 10.0 mL of acetic acid, 502 mg (2.00 mmol) of **2a** and 670 mg (12.0 mmol) of iron powder (>100 mesh). The reaction was heated with stirring at 115° (oil bath temperature 120°) until complete by TLC and then cooled. The crude reaction mixture was transferred to a separatory funnel with 50-75 mL of ether, washed with $H_2O$ (2x), $NaHCO_3$ (3x) and NaCl (1x), then dried ($MgSO_4$), and concentrated under vacuum. The resulting yellow oil was purified by flash chromatography on a 30 cm x 2 cm silica gel column using 10% ether in hexanes to give 345 mg (1.70 mmol, 85%) of **3a** as a colorless oil that crystallized on standing at 0°. Recrystallization from ether-hexane afforded **3a** as white crystals, mp 131-133°, lit.[6] mp 133-135°. The spectral data matched those reported previously.[6]

**Ethyl 2-Propylindole-3-carboxylate (3b)**: 87%; white crystals; mp 113-114°; IR: 3293, 1662 cm$^{-1}$; $^1$H NMR: δ 8.45 (br s, 1 H), 8.11 (m, 1 H), 7.30 (m, 1 H), 7.20 (m, 2 H), 4.35 (q, $J$ = 7.1 Hz, 2 H),

3.09 (t, $J$ = 7.6 Hz, 2 H), 1.73 (sextet, $J$ = 7.6 Hz, 2 H), 1.42 (t, $J$ = 7.1 Hz, 3 H), 0.98 (t, $J$ = 7.3 Hz, 3 H); $^{13}$C NMR: δ 166.2, 148.4, 134.4, 127.2, 122.3, 121.7, 121.4, 110.6, 104.0, 59.6, 29.9, 22.5, 14.5, 13.9; HRMS *m/z*: Calcd for $C_{14}H_{17}NO_2$: 231.1259. Found: 231.1257.

*Anal.* Calcd for $C_{14}H_{17}NO_2$: C, 72.73; H, 7.63; N, 6.06. Found: C, 72.65; H, 7.67; N, 5.99.

**Ethyl 2-Pentylindole-3-carboxylate (3c)**: 78%; white crystals; mp 55-56°; IR: 3293, 1665 cm$^{-1}$; $^1$H NMR: δ 8.61 (br s, 1 H), 8.08 (m, 1 H), 7.28 (m, 1 H), 7.19 (m, 2 H), 4.33 (q, $J$ = 7.1 Hz, 2 H), 3.07 (t, $J$ = 7.6 Hz, 2 H), 1.66 (m, 2 H), 1.40 (t, $J$ = 7.1 Hz, 3 H), 1.38-1.22 (complex, 4 H), 0.86 (t, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR: δ 166.4, 148.8, 134.5, 127.2, 122.3, 121.7, 121.3, 110.6, 103.7, 59.6, 31.6, 28.9, 28.0, 22.4, 14.4, 13.9; HRMS *m/z*: Calcd for $C_{16}H_{21}NO_2$: 259.1572. Found: 259.1573.

*Anal.* Calcd for $C_{16}H_{21}NO_2$: C, 74.13; H, 8.11; N, 5.41. Found: C, 73.98; H, 8.02; N, 5.48

**Methyl 2-(3-Butenyl)indole-3-carboxylate (3d)**: 75%; white crystals; mp 77-78°; IR: 3293, 1665 cm$^{-1}$; $^1$H NMR: δ 8.53 (br s, 1 H), 8.08 (m, 1 H), 7.30 (m, 1 H), 7.21 (m, 2 H), 5.87 (ddt, $J$ = 17.1, 10.1, 6.6 Hz, 1 H), 5.09 (d, $J$ = 17.1 Hz, 1 H), 5.03 (d, $J$ = 10.2 Hz, 1 H), 3.91 (s, 3 H), 3.24 (t, $J$ = 7.3 Hz, 2 H), 2.49 (q, $J$ = 7.2 Hz, 2 H); $^{13}$C NMR: δ 166.5, 147.7, 137.3, 134.4, 126.9, 122.5, 121.8, 121.4, 116.1, 110.6, 103.9, 50.9, 32.9, 27.3; HRMS *m/z*: Calcd for $C_{14}H_{15}NO_2$: 229.1103. Found: 229.1103.

*Anal.* Calcd for $C_{14}H_{15}NO_2$: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.19; H, 6.63; N, 5.99

**Ethyl 2-(2-Phenylethyl)indole-3-carboxylate (3e)**: 77%; white crystals; mp 86-87°; IR: 3293, 1665 cm$^{-1}$; $^1$H NMR: δ 8.24 (br s, 1 H), 8.11 (d, $J$ = 7.8 Hz, 1 H), 7.54-7.08 (complex, 8 H), 4.38 (q, $J$ = 7.1 Hz, 2 H), 3.40 (t, $J$ = 7.3 Hz, 2 H), 3.00 (t, $J$= 7.3 Hz, 2 H), 1.43 (t, $J$ = 7.1 Hz, 3 H); $^{13}$C NMR: δ 166.1, 147.3, 140.8, 134.4, 128.6, 128.5, 128.4, 126.3, 122.4, 121.7, 121.4, 110.6, 104.1, 59.7, 35.4, 30.1, 14.5; HRMS *m/z*: Calcd for $C_{19}H_{19}NO_2$: 293.1416. Found: 293.1413.

*Anal.* Calcd for $C_{19}H_{19}NO_2$: C, 77.82; H, 6.48; N, 4.78. Found: C, 77.54; H, 6.55; N, 4.67

**Ethyl 2-Isobutylindole-3-carboxylate (3f)**: 83%; light yellow oil; IR: 3293, 1659 cm$^{-1}$; $^1$H NMR: δ 8.51 (br s, 1 H), 8.08 (m, 1 H), 7.29 (m, 1 H), 7.19 (m, 2 H), 4.31 (q, $J$ = 7.2 Hz, 2 H), 2.95 (d, $J$ = 7.2 Hz, 2 H), 2.08 (nonet, $J$ = 6.7 Hz, 1 H), 1.40 (t, $J$ = 7.2 Hz, 3 H), 0.93 (d, $J$ = 6.6 Hz, 3 H), 0.91 (d, $J$ = 6.6 Hz, 3 H); $^{13}$C NMR: δ 166.4, 147.8, 134.5, 127.2, 122.4, 121.7, 121.4, 110.6, 104.3, 59.6, 36.9, 29.1, 22.5, 22.4, 14.4; HRMS *m/z*: Calcd for $C_{15}H_{19}NO_2$: 245.1416. Found: 245.1414.

*Anal.* Calcd for $C_{15}H_{19}NO_2$: C, 77.82; H, 6.48; N, 4.78. Found: C, 77.75; H, 6.53; N, 4.69.

**Ethyl 2-Isopropylindole-3-carboxylate (3g)**: 84%; white crystals; mp 104-105°; IR: 3315, 1665 cm$^{-1}$; $^1$H NMR: δ 8.70 (br s, 1 H), 8.10 (m, 1 H), 7.32 (m, 1 H), 7.19 (m, 2 H), 4.37 (q, $J$ = 7.1 Hz, 2 H), 4.09 (septet, $J$ = 7.1 Hz, 1 H), 1.42 (t, $J$ = 7.1 Hz, 3 H), 1.33 (d, $J$ = 6.9 Hz, 6 H); $^{13}$C NMR: δ 166.2, 153.7, 134.4, 127.1, 122.3, 121.7, 121.5, 110.8, 102.8, 59.6, 26.3, 21.7 (2), 14.5; HRMS *m/z*: Calcd for $C_{14}H_{17}NO_2$: 231.1259. Found: 231.1259.

*Anal.* Calcd for $C_{14}H_{17}NO_2$: C, 72.73; H, 7.36; N, 6.06. Found: C, 73.01; H, 7.46; N, 5.94

**Ethyl 2-Cyclohexylindole-3-carboxylate (3h)**: 85%; white crystals; mp. 103-105°; IR: 3315, 1665 cm$^{-1}$; $^1$H NMR: δ 8.52 (br s, 1 H), 8.11 (m, 1 H), 7.32 (m, 2 H), 4.36 (q, $J$ = 7.2 Hz, 2 H), 3.76 (tt, $J$ = 11.7, 3.2 Hz, 1 H), 2.08 (m, 2 H), 1.84 (m, 3 H), 1.50-1.10 (complex, 6 H), 1.43 (t, $J$ = 7.2 Hz, 3 H);

$^{13}$C NMR: δ 166.1, 152.9, 134.3, 127.1, 122.3, 121.7, 121.5, 110.7, 102.9, 59.5, 36.3, 32.4, 26.4, 26.0, 14.5; HRMS *m/z*: Calcd for $C_{17}H_{21}NO_2$: 271.1572. Found: 271.1569.

*Anal.* Calcd for $C_{17}H_{21}NO_2$: C, 75.28; H, 7.75; N, 5.17. Found: C, 75.35; H. 7.69; N, 5.08

**Ethyl 2-Phenylindole-3-carboxylate (3i)**: 88%; white crystals; mp 152-154°, lit.[9] mp 153-155°. The spectral data matched those reported previously.[10]

**Ethyl 2-(2-Chlorophenyl)indole-3-carboxylate (3j)**: 89%; light gray crystals; mp 152-153°; IR: 3275, 1672 cm$^{-1}$; $^1$H NMR: δ 8.69 (br s, 1 H), 8.23 (m, 1 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 7.38-7.24 (complex, 5 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 1.18 (t, *J* = 7.2 Hz, 3 H); $^{13}$C NMR: δ 164.9, 140.8, 135.1, 133.9, 132.0, 131.6, 130.3, 129.5, 126.7, 126.3, 123.3, 122.0 (2), 111.6, 106.7, 59.6, 14.1; HRMS *m/z*: Calcd for $C_{17}H_{14}{}^{35}ClNO_2$: 299.0714. Found: 299.0715.

*Anal.* Calcd for $C_{17}H_{14}ClNO_2$: C, 68.23; H, 4.68; N, 4.68. Found: C, 68.44; H, 4.99; N, 4.52

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## ONE-POT SYNTHESIS OF SELENOESTERS FROM ALKYNYL ARYL SELENIDES

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Organoselenium compounds have attracted considerable interest as reagents and intermediates in organic synthesis.[1] Selenoesters, a class of useful intermediates in the synthesis of natural compounds,[2] are commonly prepared by the reaction of acyl halides with selenols,[2,3] or by the alkylation of the selenolate ion.[4] Recently, other methods from arylselenotrimethyl-silane[5] and diselenides[6-8] have also been reported. However, most of these preparations are limited to alkyl esters, or involve difficult removal of by-products such as diaryl diselenides, harsh reaction conditions, laborious manipulation, low yields, or in some cases, reagents are not readily available. Herein, we report a one-pot, two-step synthesis of selenoesters **(3)** from alkynyl aryl selenides **(1),** which are treated succes-