Supporting Information

Phosphine-Mediated Reaction of 3-Methyl Allenoate and Isatins: A Protocol for the Synthesis of Spirofuran Oxindoles

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1. General

Melting points were recorded on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded at 500 (¹H) and 126 (¹³C) MHz on Bruker Avance DPX-500S MHz NMR spectrometer. Chemical shifts (δ) are reported relative to TMS (¹H) and CDCl₃ (¹³C) as the internal standards. Coupling constant (*J*) is reported in Hertz (Hz). Mass spectra were recorded under HRMS (ESI) using Thermo Scientific Exactive Orbitrap mass spectrometer. IR spectra were recorded on a Bruker Alpha-T FT-IR spectrophotometer. Allenoates were prepared using known literature procedures.¹ Isatins were purchased from Sigma-Aldrich and the *N*-protection was carried out using known procedures.² Gravity column chromatography was performed using silica gel and mixtures of petroleum ether-ethyl acetate were used for elution.

2. General experimental procedure for the synthesis of spiro tetrahydrofuran oxindole derivatives

A solution of the isatin (0.5 mmol) and the allenoate (0.75 mmol) in dry THF (5 ml) was taken in a round bottom flask under argon atmosphere. To this solution triphenylphosphine (0.75 mmol) was added and stirred for 30 min. The crude product after

¹Lang, R. W.; Hansen, H.-J. Org. Synth. Coll. Vol. 1990, 7, 232; 1984, 62, 202.

² Shmidt, M. S.; Reverdito, A. M.; Kremenchuzky, L.; Perillo, I. A.; Blanco, M. M. *Molecules* **2008**, *13*, 831

removal of the solvent was purified by column chromatography using 100-200 silica gel and 85:15 hexane: ethyl acetate as the eluent afforded spirotetrahydrofuran oxindole derivative.

3. Characterization data for compounds

(E)-Ethyl 2-(1'-methyl-2'-oxo-3H-spiro[furan-2,3'-indoline]-5(4H)-ylidene)acetate (8)

0 OEt	Yield: 126 mg (88%), pale yellow oil.
	IR (film) v _{max} : 1721, 1701, 1643, 1614, 1112, 1054 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.36 (t, <i>J</i> = 7.5 Hz, 1H), 7.29 (d,
	J = 7.5 Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 1H),
⊃	5.41 (s, 1H), 4.14 (q, J = 7.0 Hz, 2H), 3.56 – 3.52 (m, 2H), 3.18
	(d, $J = 1.5$ Hz, 3H), $2.52 - 2.47$ (m, 1H), $2.33 - 2.27$ (m, 1H),
	1.27 (t, J = 7.0 Hz, 3H) ppm.
	¹³ C NMR (126 MHz, CDCl ₃): δ 175.0, 174.1, 167.8, 143.9,
	130.8, 126.9, 123.9, 123.3, 108.6, 91.7, 85.5, 59.3, 33.0, 30.3,
	26.2, 14.5 ppm.
	HRMS (ESI-MS) calcd for $C_{16}H_{17}NO_4Na^+310.10553$; Found:
	310.10452.

(E)-Tert-butyl 2-(1'-methyl-2'-oxo-3H-spiro[furan-2,3'-indoline]-5(4H)-ylidene)acetate

0,O ^t Bu	Yield: 129 mg (82%), pale yellow oil.
	IR (film) v_{max} : 1726, 1698, 1644, 1615, 1109, 1057 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.36 (t, <i>J</i> = 7.5 Hz, 1H), 7.28 (d,
	J = 7.5 Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 8.0$ Hz, 1H),
[] >=0	5.35 (s, 1H), 3.53 - 3.49 (m, 2H), 3.19 (s, 3H), 2.52 - 2.46 (m,
N N	1H), 2.32 – 2.25 (m, 1H), 1.48 (s, 9H) ppm.
	¹³ C NMR (126 MHz, CDCl ₃): δ 174.3, 173.9, 167.3, 143.9,
	130.8, 127.1, 123.9, 123.3, 108.6, 93.5, 85.1, 79.1, 33.15, 30.0,
	28.4, 26.2 ppm.
	HRMS (ESI-MS) calcd for $C_{18}H_{21}NO_4Na^+338.13683$; Found:
	338.13568.
(E)-Ethyl 2-(1'-benzyl-2	
0, OEt	Yield: 131 mg (72%), pale yellow oil.
	IR (film) v _{max} : 1718 (broad), 1647, 1614, 1113, 1053 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.31 – 7.20 (m, 7H), 7.03 (t, <i>J</i> =
	7.5 Hz, 1H), 6.70 (d, $J = 8.0$ Hz, 1H), 5.45 (s, 1H), 4.84 (q, $J =$
	16.0 Hz, 2H), 4.15 (q, $J = 7.0$ Hz, 2H), 3.58 (t, $J = 7.5$ Hz, 2H),
	2.58 – 2.53 (m, 1H), 2.36 – 2.30 (m, 1H), 1.27 (t, <i>J</i> = 7.0 Hz, 3H
-Ph) ppm.
	¹³ C NMR (126 MHz, CDCl ₃): δ 175.0, 174.4, 167.8, 143.1,
	135.1, 130.7, 128.9, 127.8, 127.2, 127.0, 124.1, 123.4, 109.7,
	91.9, 85.5, 59.3, 43.8, 33.4, 30.3, 14.5ppm.
	HRMS (ESI-MS) calcd for $C_{22}H_{21}NO_4Na^+386.13683$; Found:
	386.13594.

(E)-Ethyl 2-(1'-ethyl-2'-oxo-3H-spiro[furan-2,3'-indoline]-5(4H)-ylidene)acetate (11)

0 _√ OEt	Yield: 117 mg (78%), pale yellow oil.
	IR (film) v_{max} : 1722 (broad), 1648, 1615, 1117, 1059 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.34 (t, <i>J</i> = 7.5 Hz, 1H), 7.29 (d, <i>J</i>
	= 7.5 Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 1H),
	5.42 (s, 1H), 4.15 (q, J = 7.0 Hz, 2H), 3.73 (q, J = 7.0 Hz, 2H), 3.56
	-3.53 (m, 2H), 2.53 - 2.48 (m, 1H), 2.32 - 2.26 (m, 1H), 1.30 -
	1.25 (m, 6H) ppm.
	¹³ C NMR (126 MHz, CDCl ₃): δ 175.0, 173.8, 167.8, 143.0, 130.7,
	127.2, 124.2, 123.1, 108.7, 91.7, 85.4, 59.2, 34.8, 33.1, 30.3, 14.5,
	12.5 ppm.
	HRMS (ESI-MS) calcd for $C_{17}H_{19}NO_4Na^+324.12118$; Found:
	324,11960.

(*E*)-Ethyl 2-(2'-oxo-1'-(prop-2-ynyl)-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene)acetate (12)

0 _≫ ∕ ^{OEt}	Yield: 106 mg (68%), colourless oil.
	IR (film) v _{max} : 1719 (broad), 1648, 1614, 1112, 1055 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.38 (t, <i>J</i> = 8.0 Hz, 1H), 7.30 (d, <i>J</i> =
	7.5 Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 5.35
	(s, 1H), 4.55 (dd, J_1 = 17.5 Hz, J_2 = 1.5 Hz, 1H), 4.36 (dd, J_1 = 18.0
	Hz, $J_2 = 2.0$ Hz, 1H), $3.52 - 3.49$ (m, 2H), $2.54 - 2.49$ (m, 1H), 2.33
	- 2.23 (m, 2H), 1.48 (s, 9H) ppm.
	¹³ C NMR (126 MHz, CDCl ₃): δ 173.7, 173.4, 167.2, 142.0, 130.7,
	127.1, 124.0, 123.7, 109.7, 93.7, 85.1, 79.1, 76.3, 72.9, 33.4, 29.9,
	29.3, 28.4 ppm.

(*E*)-Ethyl 2-(5'-bromo-1'-methyl-2'-oxo-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene) acetate (13)

0 OEt	Yield: 99 mg (54%), pale yellow oil.
	IR (film) v_{max} : 1729, 1705, 1650, 1612, 1118, 1059 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.48 (d, <i>J</i> = 8.5 Hz, 1H), 7.40 (s,
Br	1H), 6.71 (t, $J = 8.0$ Hz, 1H), 5.41 (s, 1H), 4.15 (q, $J = 7.0$ Hz,
	2H), 3.55 – 3.52 (m, 2H), 3.18 (s, 3H), 2.53 – 2.48 (m, 1H), 2.32 –
	2.26 (m, 1H), 1.29 (t, <i>J</i> = 7.5 Hz, 3H) ppm.
	¹³ C NMR (126 MHz, CDCl ₃) δ 174.4, 173.6, 167.6, 142.9, 133.5,
	129.1, 127.3, 115.9, 109.9, 92.2, 84.9, 59.4, 33.2, 30.1, 26.3, 14.5
	ppm.
	HRMS (ESI-MS) calcd for $C_{16}H_{16}BrNO_4Na^+$ 388.01604; Found:
	388.01486.

(*E*)-Ethyl 2-(1'-benzyl-5'-bromo-2'-oxo-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene) acetate (14)



(*E*)-*Tert*-butyl 2-(1'-benzyl-5'-bromo-2'-oxo-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene) acetate (15)



(*E*)-*Tert*-butyl 2-(5'-bromo-2'-oxo-1'-(prop-2-ynyl)-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene)acetate (16)



(*E*)-Ethyl 2-(5'-chloro-1'-methyl-2'-oxo-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene) acetate (17)

0 _√ ∕OEt	Yield: 122 mg (76%), colourless oil.
	IR (film) v_{max} : 1726, 1701, 1646, 1613, 1113, 1056 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.34 (d, <i>J</i> = 8.5 Hz, 1H), 7.28 (s,
CI	1H), 6.77 (t, $J = 8.0$ Hz, 1H), 5.42 (s, 1H), 4.16 (q, $J = 8.0$ Hz,
	2H), 3.55 – 3.52 (m, 2H), 3.18 (s, 3H), 2.54 – 2.49 (m, 1H), 2.33
	-2.26 (m, 1H), 1.28 (t, $J = 7.0$ Hz, 3H) ppm.
	¹³ C NMR (126 MHz, CDCl ₃): δ 174.5, 173.8, 167.7, 142.4,
	130.7, 128.8, 128.6, 124.6, 109.6, 92.2, 85.1, 59.4, 33.2, 30.1,
	26.4, 14.5ppm.
	HRMS (ESI-MS) calcd for $C_{16}H_{16}CINO_4Na^+344.06656$; Found:
	344.06512.

(*E*)-*Tert*-butyl 2-(5'-chloro-1'-methyl-2'-oxo-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene)acetate (18)

O _√ O ^t Bu	Yield: 126 mg (72%), colourless oil.
	IR (film) v _{max} : 1728, 1702, 1648, 1613, 1110, 1059 cm ⁻¹ .
	¹ H NMR (500 MHz, CDCl ₃): δ 7.33 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.0$
CI	Hz, 1H), 7.26 (s, 1H), 6.76 (d, <i>J</i> = 8.5 Hz, 1H), 5.34 (s, 1H), 3.52
0=()	-3.48 (m, 2H),3.18 (s, 3H), 2.52 - 2.47 (m, 1H), 2.30 - 2.24 (m,
	1H), 1.48 (s, 9H) ppm.
·	¹³ C NMR (126 MHz, CDCl ₃): δ 173.9, 173.4, 167.1, 142.4,
	130.5, 129.0, 128.8, 124.6, 109.5, 93.9, 84.7, 79.2, 33.3, 29.8,
	28.4, 26.3ppm.
	HRMS (ESI-MS) calcd for $C_{18}H_{20}CINO_4Na^+372.09786$; Found:
	372.09601.

(*E*)-Ethyl 2-(1'-benzyl-5'-chloro-2'-oxo-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene) acetate (19)



(*E*)-Ethyl 2-(5'-chloro-2'-oxo-1'-(prop-2-ynyl)-3H-spiro[furan-2,3'-indoline]-5(4H)-ylidene)acetate (20)



(*E*)-*Tert*-butyl 2-(5'-chloro-2'-oxo-1'-(prop-2-ynyl)-3H-spiro[furan-2,3'-indoline]-5(4H)-ylidene)acetate (21)

0, ∠O ^t Bu	Yield: 60 mg (32%), colourless oil.
	IR (film) v _{max} : 1732, 1699, 1649, 1255, 1111 cm ⁻¹ .
\sim	¹ H NMR (500 MHz, CDCl ₃): δ 7.36 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.0$
Cl	Hz, 1H),7.29 (d, $J = 2.0$ Hz, 1H), 7.01 (d, $J = 8.5$ Hz, 1H), 5.36
[])=0	(t, $J = 1.5$ Hz, 1H), 4.54 (dd, $J_1 = 17.5$ Hz, $J_2 = 2.5$ Hz, 1H), 4.36
N N	(dd, $J_1 = 17.5$ Hz, $J_2 = 2.5$ Hz, 1H), $3.52 - 3.48$ (m, 2H), $2.55 - 3.48$
	2.50 (m, 1H),2.32 – 2.25 (m, 2H), 1.49 (s, 1H) ppm.
111	¹³ C NMR (126 MHz, CDCl ₃): δ173.2, 173.0, 167.1, 140.4,
	130.6, 129.3, 128.8, 124.6, 110.8, 94.1, 84.7, 79.3, 75.9, 73.3,
	33.5, 29.7, 29.5, 28.4.
	HRMS (ESI-MS) calcd for $C_{20}H_{20}CINO_4Na^+$ 396.09786; Found:
	396.09694.

(*E*)-Ethyl 2-(1'-methyl-5'-nitro-2'-oxo-3*H*-spiro[furan-2,3'-indoline]-5(4*H*)-ylidene) acetate (22)



4. ¹H and ¹³C NMR spectra of compounds

















ppm




















S21

5. ORTEP of compound 14



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