Supporting Information

Iodine as a New Catalyst for the Condensation of 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone with Cyclic Enaminones: Synthesis of Spiro Dihydropyridines Derivatives in Acid Free Condition

Firouz Matloubi Moghaddam*, Vahid Saberi, Seyedmahmoudreza Keshavarz

Laboratory of Organic Synthesis and Natural Products, Department of Chemistry, Sharif University of Technology, Azadi Street, PO Box 111559516 Tehran, Iran

E-mail Address: matloubi@sharif.edu

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General information:
All chemicals were purchased from Merck or Aldrich and used without any additional purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker (Avance DRX-500) spectrometer using D$_2$O and DMSO-$d_6$ as solvent at room temperature. Chemical shifts $\delta$ were reported in ppm relative to tetramethylsilane as an internal standard. FTIR spectra of samples were taken using an ABB Bomem MB-100 FTIR spectrophotometer. CHN analysis was done by LECO Truspec and High-resolution mass spectra were obtained with a Waters Micromass Q-Tof Micro instrument using the ESI technique.

The structures of all of the products 3a-j (Figure 1) were deduced from their IR, $^1$H NMR, and $^{13}$C NMR spectra.
Figure 1. Structure of all products 3a-j
Experimental section:

**Typical procedure for the synthesis of 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone 1:** a mixture of 1,3-indandione (10 mmol), ninhydrin (10 mmol) and triethylamine (1mmol) in EtOH (50 ml) was stirred at room temperature for 5 h. the precipitates were filtrated and wash with EtOH (2× 5 ml) to give product 1.

2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone (I): Yellow powder, mp 187-190 °C, 1H NMR (500 MHz, CDCl₃): δ 8.00-7.93 (m, 2H, Ar), 7.92-7.83 (m, 6H, Ar), 5.47 (s, 1H, OH), 3.96 (s, 1H, CH) 13C NMR (125 MHz, CDCl₃): δ 197, 196, 142, 141, 137, 136, 124, 124, 76, 53.

**Typical procedure for the synthesis of Spiro Dihydropyridines 3a-j:** a mixture of 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone 1 (1 mmol), cyclic enaminone 2a-j (1mmol) and molecular iodine (20 mol%) in DMSO (4 ml) was stirred at 100 °C for 4 h. After completion of the reaction (monitored by TLC, ethylacetate/n-hexane, 1:2) the reaction mixture was allowed to cool to room temperature, then add water into and the precipitates were filtered and washed with acetone to give product 3a-j in high yield.
Spectroscopic characterization of the products

\( \text{spiro[indene-2,5'-indenophi}[2',1':5,6]\text{pyrido}[2,3-d]\text{pyrimidine}-1,2',3,4',6'(1'H,3'H,11'H)-pentaone (3a):} \) Red Powder, 0.361 g, Yield: 91%, mp 212 °C (dec.); IR (KBr) Cm\(^{-1}\): 3249, 2917, 1710, 1690, and 1666. \(^{1}\)H NMR (500 MHz, D\(_2\)O): \( \delta \) 7.89 – 7.85 (m, 4H, Ar-H), 7.36 (d, J = 6.9 Hz, 1H, Ar-H), 7.24 – 7.17 (m, 2H, Ar-H), 7.00 (d, J = 6.9 Hz, 1H, Ar-H) \(^{13}\)C NMR (125 MHz, D\(_2\)O) \( \delta \) 209, 187, 173, 170, 165, 162, 141, 138, 137, 136, 131, 130, 122, 119, 119, 100, 92, 56. Anal. Calcd for C\(_{22}\)H\(_{11}\)N\(_3\)O\(_5\): C, 66.50; H, 2.79; N, 10.58. Found: C, 65.90; H, 2.81; N, 10.61. HRMS Calcd for C\(_{22}\)H\(_{11}\)N\(_3\)O\(_5\)[M+H]\(^{+}\) 398.0777, found 398.0775

\( \text{3'-methylspiro[indene-2,5'-indenophi}[2',1':5,6]\text{pyrido}[2,3-d]\text{pyrimidine}-1,2',3,4',6'(1'H,3'H,11'H)-pentaone (3b):} \) Yellow Powder, 0.361 g, Yield: 88%, mp 188 °C (dec.); IR (KBr) Cm\(^{-1}\): 3280, 2998, 1710, 1689, and 1665. \(^{1}\)H NMR (500 MHz, DMSO-d\(_6\)): \( \delta \) 7.97 – 7.96 (m, 2H, Ar-H), 7.84 – 7.77 (m, 2H, Ar-H), 7.62 – 7.50 (m, 2H, Ar-H), 7.45 – 7.38 (m, 2H, Ar-H), 3.64 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (125 MHz, DMSO) \( \delta \) 206, 189, 175, 172, 168, 161, 152, 141, 138, 138, 136, 135, 129, 123, 133, 103, 93, 54, 26. Anal. Calcd for C\(_{23}\)H\(_{13}\)N\(_3\)O\(_5\): C, 67.15; H, 3.19; N, 10.21. Found: C, 68.11; H, 3.16; N, 10.15.

\( \text{1',3'-dimethylspiro[indene-2,5'-indenophi}[2',1':5,6]\text{pyrido}[2,3-d]\text{pyrimidine}-1,2',3,4',6'(1'H,3'H,11'H)-pentaone (3c):} \) Yellow Powder, 0.365 g, Yield: 85%, mp 185 – 187 °C; IR (KBr) Cm\(^{-1}\): 3273, 1701, 1690, and 1669. \(^{1}\)H NMR (500 MHz, DMSO-d\(_6\)): \( \delta \) 8.31 – 8.30 (d, 1H, Ar-H), 8.13 – 8.11 (d, 1H, Ar-H), 8.05 – 7.99 (m, 2H, Ar-H), 7.34 – 7.32 (d, 1H, Ar-H), 7.19 – 7.18 (d, 1H, Ar-H), 7.13 – 7.05 (2H, m, Ar-H), 3.85 (s, 3H, CH\(_3\)), 3.65 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (125 MHz, DMSO) \( \delta \) 197, 197, 196, 157, 154, 152, 141, 141, 135, 135, 135, 132, 129, 123, 123, 103, 93, 54, 26. Anal. Calcd for C\(_{24}\)H\(_{15}\)N\(_3\)O\(_5\): C, 67.76; H, 3.55; N, 9.88. Found: C, 67.12; H, 3.61; N, 9.85.

\( \text{2'-thioxo-2',3'-dihydrospiro[indene-2,5'-indenophi}[2',1':5,6]\text{pyrido}[2,3-d]\text{pyrimidine}-1,3,4',6'(1'H,11'H)-tetaone(3d):} \) Red Powder, 0.380 g, Yield: 92%, mp 218 °C (dec.); IR (KBr) Cm\(^{-1}\): 3251, 3020, 1715, 1690, and 1664. \(^{1}\)H NMR (500 MHz, D\(_2\)O): \( \delta \) 7.90 (s, 4H, Ar-H), 7.35 – 7.34 (d, 1H, Ar-H), 7.19 – 7.14 (m, 2H, Ar-H), 6.95 – 6.94 (d, 1H, Ar-H). \(^{13}\)C NMR (125 MHz, D\(_2\)O) \( \delta \) 209, 187, 179, 173, 165, 162, 141, 137, 136, 131, 130, 122, 119, 119, 100, 92,
56. Anal. Calcd for C_{22}H_{11}N_{3}O_{4}: C, 63.92; H, 2.68; N, 10.16. Found: C, 63.94; H, 2.69; N, 10.14.

1',3'-dimethyl-2'-thioxo-2',3'-dihydrospiro[indene-2,5'-indeno[2',1':5,6]pyrido[2,3-d]pyrimidine]-1,3,4',6'(1'H,11'H)-tetaone (3e): Yellow Powder, 0.379 g, Yield: 86%, mp 187-190 °C; IR (KBr) Cm⁻¹: 3263, 3015, 1715, 1690, and 1658. ¹H NMR (500 MHz, DMSO-d₆): δ 7.81 – 7.73 (m, 7H, Ar-H), 7.52 (b, 1H), 7.42 (s, 1H, Ar-H), 3.07(s, 3H, CH₃). ¹³C NMR (125 MHz, DMSO) δ 1716, 1699, 1695. Anal. Calcd for C_{125}H_{26}N_{13}O_{4}S: C, 64.63; H, 3.05; N, 9.78. Found: C, 64.71; H, 3.05; N, 9.78.

3'-methyl-2'-thioxo-2',3'-dihydrospiro[indene-2,5'-indeno[2',1':5,6]pyrido[2,3-d]pyrimidine]-1,3,4',6'(1'H,11'H)-tetaone (3f): Yellow Powder, 0.341 g, Yield: 80%, mp 174-177 °C; IR (KBr) Cm⁻¹: 3310, 3005, 1708, 1699, and 1668. ¹H NMR (500 MHz, DMSO-d₆): δ 8.06-7.96 (m, 4H, Ar-H), 7.48-7.41 (m, 4H, Ar-H), 4.15(s, 3H, CH₃), 3.17(s, 3H, CH₃). ¹³C NMR (125 MHz, DMSO) δ 198, 197, 196, 187, 163, 155, 151, 142, 140, 136, 135, 134, 129, 124, 122, 122, 101, 95, 65, 33, 27. Anal. Calcd for C_{24}H_{13}N_{3}O_{4}S: C, 65.30; H, 3.42; N, 9.52. Found: C, 65.41; H, 3.41; N, 9.81.

2'-phenyl-1',2'-dihydro-3'H-spiro[indene-2,4'-indeno[1,2-b]pyrazolo[4,3-e]pyridine]-1,3,3',5'(10'H)-tetaone (3g): Red Powder, 0.324 g, Yield: 73%, mp 271 °C (dec.), IR (KBr) Cm⁻¹: 3315, 3001, 1712, 1700, and 1669. ¹H NMR (500 MHz, DMSO-d₆): δ 12.0 (s, 1H), 10.9 (s, 1H), 8.07-8.00 (m, 4H, Ar-H), 7.74-7.40 (m, 7H, Ar-H), 7.26-7.23 (m, 2H, Ar-H). ¹³C NMR (125 MHz, DMSO) δ 201, 189, 142, 138, 137, 136, 132, 131, 130, 124, 121, 120, 90, 52. Anal. Calcd for C_{27}H_{15}N_{3}O_{4}: C, 72.8; H, 3.39; N, 9.43. Found: C, 73.1; H, 3.39; N, 9.71.

7',7'-dimethyl-7',8'-dihydrospiro[indene-2,10'-indeno[1,2-b]quinoline]-1,3,9',11'(5'H,6'H)-tetaone (3h): Red Powder, 0.339 g, Yield: 83%, mp 190 °C (dec.), IR (KBr) Cm⁻¹: 3310, 1716, 1699, 1695. ¹H NMR (500 MHz, DMSO-d₆): δ 9.3 (s, 1H), 7.87-7.86 (m, 2H, Ar-H), 7.84-7.76 (m, 4H, Ar-H), 7.73-7.72 (m, 1H, Ar-H), 7.68-7.67 (m, 1H, Ar-H), 2.55 (4H, 2CH₂), 1.29 (3H, s, Me), 0.96 (3H, s, Me). ¹³C NMR (125 MHz, DMSO) δ 202, 199, 198, 197, 154, 151, 142, 141, 136, 135, 130, 125, 124, 123, 96, 52, 50, 37, 34, 30, 28. Anal. Calcd for C_{26}H_{15}NO_{4}: C, 76.27; H, 4.68; N, 3.42. Found: C, 76.87; H, 4.60; N, 3.48.
13-phenyl-6H-spiro[chromeno[4,3-b]indeno[2,1-e]pyridine-7,2'-indene]-1',3',6,8(13H)tetraone (3i): Yellow Powder, 0.309 g, Yield: 63%, mp 217 °C (dec.), IR (KBr) Cm\(^{-\text{1}}\): 1715, 1701, 1696, 1690. \(^1\)H NMR (500 MHz, DMSO): \(\delta\) 8.26-8.25 (d, 1H, Ar-H), 7.96 (m, 3H, Ar-H), 7.92 (m, 2H, Ar-H), 7.69-7.66, (m, 2H, Ar-H), 7.52-7.50 (m, 3H, Ar-H), 7.40-7.38 (m, 5H, Ar-H), 7.32-7.31 (m, 1H, Ar-H). \(^13\)C NMR (125 MHz, DMSO-d\(_6\)) \(\delta\) 200, 192, 180, 162, 158, 153, 143, 134, 133, 130, 126, 125, 123, 122, 120, 119, 117, 115, 107, 94, 85, 80, 76, 51. Anal. Calcd for C\(_{33}\)H\(_{17}\)NO\(_5\): C, 78.10; H, 3.38; N, 2.76. Found: C, 78.23; H, 3.34; N, 2.75.

13-benzyl-6H-spiro[chromeno[4,3-b]indeno[2,1-e]pyridine-7,2'-indene]-1',3',6,8(13H)tetraone (3j): Yellow Powder, 0.297 g, Yield: 57%, mp 221 °C (dec.), IR (KBr) Cm\(^{-\text{1}}\): 1712, 1700, 1693, 1591. \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \(\delta\) 8.38 (s, 1H, Ar-H), 7.93-7.92 (m, 3H, Ar-H), 7.87-7.85 (m, 1H, Ar-H), 7.78-7.7 (m, 2H, Ar-H), 7.62-7.59 (m, 2H, Ar-H), 7.49-7.48 (m, 1H, Ar-H), 7.37-7.33 (m, 3H, Ar-H), 7.20-7.19 (m, 2H, Ar-H), 7.08-7.07 (m, 1H, Ar-H), 7.97-7.96 (m, 1H, Ar-H). \(^13\)C NMR (125 MHz, DMSO) \(\delta\) 201, 198, 183, 171, 160, 158, 155, 153, 148, 144, 142, 138, 136, 129, 129, 127, 126, 125, 123, 123, 121, 118, 112, 99, 96, 93, 62, 52. Anal. Calcd for C\(_{34}\)H\(_{19}\)NO\(_5\): C, 78.30; H, 3.67; N, 2.69. Found: C, 78.31; H, 3.61; N, 2.70.
$^1$H-NMR and $^{13}$C-NMR spectra of the products

$^1$H NMR 3a
$^{13}$CNMR of 3a
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**HRMS of 3a**

![HRMS Graph](image-url)
$^1$H NMR 3b
$^{13}$CNMR of 3b
$^1$H NMR 3e
$^{13}$CNMR of 3c
$^1$H NMR 3d
$^{13}$CNMR of 3d
$^{1} \text{H NMR 3e}$
$^{13}$CNMR of $3e$
$^{1}H$ NMR 3f
15CNMR of 3f
$^1$H NMR 3g

$^{13}$CNMR of 3g
**1H NMR 3h**
$^{13}$CNMR of 3h

$^1$H NMR 3i
13CNMR of 3i
$^1$H NMR 3j

$^{13}$CNMR of 3j