SUPPORTING INFORMATION

Iodonium-Induced Cyclization of N-Allenylindoles and N-Allenylpyrroles: an Access to Iododihydropyrido[1,2-a]indoles and dihydroindolizines

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**General informations**

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AV 300 instrument. All signals were expressed as ppm (δ) and internally referenced to residual protio solvent signals. Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. Mass spectrometry analyses (direct introduction by chemical ionization with ammoniac or electrospray) were performed at the Ecole Nationale Supérieure de Chimie de Paris.

**Substrates synthesis**

**Preparation of substrates 1a, 1e-f, 1h-j**

![Reaction Scheme](image)

The corresponding heterocycle (1 equiv.) was dissolved in dry THF (0.5M) under inert atmosphere. Potassium hydroxide (2 equiv.), nBu4NHSO4 (0.4 equiv.) and sodium iodide (0.1 equiv.) were subsequently added. Finally the allenylbromide (2 equiv) was added drop wise and the reaction mixture was stirred overnight at room temperature. Then the reaction mixture was diluted with water and extracted three times with ethyl acetate. After drying with MgSO4, the organic phase was filtered and concentrated under reduced pressure to afford the crude mixture, which was then purified by column chromatography.

**Preparation of substrates 1b-d, 1g**

![Reaction Scheme](image)

Tetrabutylammonium bromide (5 mol%) and 50% aqueous NaOH (1.6 M) were added to a toluene solution (0.38 M), containing the indole (1 equiv.) and propargyl bromide (1.5 equiv, 80% solution in toluene). The resulting two-phase mixture was vigorously stirred at room temperature for 1.5 hours. Then, further toluene was added and the organic layer was collected, washed with water, dried over MgSO4, filtered and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography using Petroleum ether / DCM (80:20) as eluent, to furnish the corresponding propargylated heterocycle.

The appropriate propargylated heterocycle (1 equiv.) was dissolved in distilled THF (0.3 M) and the solution was cooled to -78°C. At this temperature, nBuLi (1.3 equiv.) was added dropwise and then the reaction mixture was stirred for one hour before addition of the aldehyde or ketone (1 equiv). The reaction mixture was then stirred at room temperature overnight. The reaction was quenched with a saturated aqueous ammonium chloride solution and extracted three times with ethyl acetate. The combined organic phases were dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford the crude compound, which was then purified by flash chromatography to give the desired propargylic alcohol.

nBuLi (1.05 equiv.) was added to a solution of the propargylic alcohol (1 equiv.) in THF at -78°C. After stirring for 5 minutes, methanesulfonyl chloride (1.1 equiv.) was added at -78°C and the reaction mixture was stirred for 15 minutes. The solution of Li2CuCl4 (0.1 equiv) and the corresponding Grignard reagent (1.5 equiv.)
Typical procedure for iodocarbocyclization of N-allenylindoles and N-allenylpyrroles

The appropriate N-allenyl-heterocycle (0.2 mmol, 1 equiv.) was dissolved in acetonitrile (5 mL) and a solution of N-iodosuccinimide (0.24 mmol, 1.2 equiv.) in acetonitrile (5 mL) was added. After 10 minutes of stirring at room temperature, the TLC showed complete conversion of the substrate and the reaction mixture was quenched with 5 mL of a saturated solution of sodium thiosulfate. After two extractions with ethyl acetate, the combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford the crude product which was then purified by flash chromatography to give the desired cyclized compound.
**Characterization data of substrates 1a-k**

3-Methyl-1-(4-methylpenta-2,3-dien-1-yl)-1H-indole (1a)

![Chemical structure of 1a](image)

Colorless oil, 49%, 104 mg, \( R_f = 0.35 \) (Petroleum Ether / Dichloromethane 90/10)

\(^1\text{H NMR (300 MHz, CDCl}_3\) \( \delta \) 7.57 (ddd, \( J = 7.8, 1.2, 0.8 \) Hz, 1H), 7.38 – 7.28 (m, 1H), 7.20 (ddd, \( J = 8.0, 7.0, 1.2 \) Hz, 1H), 7.10 (ddd, \( J = 8.0, 7.0, 1.0 \) Hz, 1H), 6.89 (d, \( J = 1.0 \) Hz, 1H), 5.13 – 5.07 (m, 1H), 4.61 (d, \( J = 6.5 \) Hz, 2H), 2.33 (d, \( J = 1.1 \) Hz, 3H), 1.66 (d, \( J = 2.8 \) Hz, 6H).

\(^{13}\text{C NMR (75 MHz, CDCl}_3\) \( \delta \) 202.4 (Cq), 136.4 (Cq), 129.0 (Cq), 125.3 (CH), 121.2 (CH), 118.9 (CH), 118.5 (CH), 110.4 (Cq), 109.6 (CH), 97.6 (Cq), 86.0 (CH), 46.1 (CH\(_2\)), 20.3 (2CH\(_3\)), 9.6 (CH\(_3\)).

CI-MS (NH\(_3\)) \( m/z \) , 212 [M+H]\(^{+}\)

1-(2,4-Dimethylpenta-2,3-dien-1-yl)-3-methyl-1H-indole (1b)

![Chemical structure of 1b](image)

Pale yellow oil, 19%, 114 mg, \( R_f = 0.33 \) (Petroleum Ether / Dichloromethane 95/5)

\(^1\text{H NMR (300 MHz, CDCl}_3\) \( \delta \) 7.55 (d, \( J = 8.0 \) Hz, 1H), 7.30 (d, \( J = 8.0 \) Hz, 1H), 7.18 (t, \( J = 7.5 \) Hz, 1H), 7.08 (t, \( J = 7.5 \) Hz, 1H), 6.85 (s, 1H), 4.55 (s, 2H), 2.32 (s, 3H), 1.60 (s, 6H), 1.52 (s, 3H).

\(^{13}\text{C NMR (75 MHz, CDCl}_3\) \( \delta \) 199.8 (Cq), 136.7 (Cq), 129.0 (Cq), 126.0 (CH), 121.2 (CH), 118.8 (CH), 118.4 (CH), 110.1 (Cq), 109.8 (CH), 96.0 (Cq), 94.0 (Cq), 50.7 (CH\(_2\)), 20.5 (2CH\(_3\)), 16.6 (CH\(_3\)), 9.6 (CH\(_3\)).

APCI-MS \( m/z \) : 226 [M+H]\(^{+}\)
1-(4-Cyclopropyl-2-ethylpenta-2,3-dien-1-yl)-3-methyl-1H-indole (1c)

Pale yellow oil, 24%, 109 mg, R<sub>f</sub> = 0.2 (Petroleum Ether)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.60 (m, 1H), 7.43 – 7.35 (m, 1H), 7.30 – 7.22 (m, 1H), 7.21 – 7.12 (m, 1H), 6.90 (s, 1H), 4.64 (s, 2H), 2.40 (s, 3H), 1.88 (q, J = 7.3 Hz, 2H), 1.72 (s, 3H), 1.21 – 1.12 (m, 1H), 0.96 (t, J = 7.3 Hz, 3H), 0.71 – 0.56 (m, 2H), 0.38 – 0.21 (m, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.7 (Cq), 136.8 (Cq), 129.0 (Cq), 125.9 (CH), 121.2 (CH), 118.9 (CH), 118.5(CH), 110.1 (Cq), 109.8 (CH), 105.7 (Cq), 104.0 (Cq), 49.5 (CH<sub>2</sub>), 23.2 (CH<sub>2</sub>), 18.5 (CH), 13.8 (CH<sub>3</sub>), 12.2 (CH<sub>3</sub>), 9.6 (CH<sub>3</sub>), 6.2 (CH<sub>2</sub>), 5.9 (CH<sub>2</sub>).

CI-MS (NH<sub>3</sub>) m/z , 266 [M+H]+

3-Methyl-1-(2-methyl-3-(tetrahydro-4H-pyran-4-ylidene)allyl)-1H-indole (1d)

Colorless oil, 21%, 200 mg, R<sub>f</sub> = 0.13 (Toluene)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54 (d, J = 7.9 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.15 – 7.07 (m, 2H), 6.83 (s, 1H), 4.57 (s, 2H), 3.58 – 3.51 (m, 2H), 2.86 – 2.78 (m, 2H), 2.32 (d, J = 0.9 Hz, 3H), 2.09 – 2.00 (m, 2H), 1.81 – 1.74 (m, 2H), 1.67 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.6 (Cq), 136.6 (Cq), 128.9 (Cq), 125.9 (CH), 121.2 (CH), 119.0 (CH), 118.5 (CH), 110.0 (Cq), 109.5 (CH), 100.1 (Cq), 95.8 (Cq), 68.0 (2CH<sub>2</sub>), 49.9(CH<sub>2</sub>), 31.7 (2CH<sub>2</sub>), 16.8 (CH<sub>3</sub>), 9.6 (CH<sub>3</sub>).

MS (ESI) m/z: 268 [M+H]+.
1-(1-(4-Methylpenta-2,3-dien-1-yl)-1H-indol-3-yl)ethan-1-one (1e)

Yellow oil, 92%, 220 mg, R_f = 0.25 (Petroleum Ether / Ethyl acetate 80/20)

^1H NMR (300 MHz, CDCl3) δ 8.51 – 8.26 (m, 1H), 7.76 (s, 1H), 7.40 – 7.33 (m, 1H), 7.31 – 7.23 (m, 2H), 5.21 – 5.11 (m, J = 8.7, 5.6, 2.8 Hz, 1H), 4.69 (d, J = 6.1 Hz, 2H), 2.53 (s, 3H), 1.60 (s, 3H), 1.59 (s, 3H).

^13C NMR (75 MHz, CDCl3) δ 202.7 (Cq), 192.9 (Cq), 136.9 (Cq), 134.6 (CH), 126.5 (Cq), 123.1 (CH), 122.6 (CH), 122.5 (Cq), 117.2 (CH), 110.2 (CH), 99.0 (Cq), 85.0 (CH), 46.8 (CH2), 27.6 (CH3), 20.1 (2CH3).

CI-MS (NH3) m/z , 240 [M+H]^+  

1-(4-Methylpenta-2,3-dien-1-yl)-1H-pyrrole (1f)

Yellow oil, 7.5%, 11 mg, R_f = 0.58 (Petroleum Ether / Dichloromethane 80/20)

^1H NMR (300 MHz, CDCl3) δ 6.70 – 6.68 (m, 2H), 6.17 – 6.15 (m, 2H), 5.18 – 5.12 (m, 1H), 4.42 (d, J = 6.7 Hz, 2H), 1.71 (d, J = 2.8 Hz, 6H).

^13C NMR (101 MHz, CDCl3) δ 202.6 (Cq), 120.4 (2CH), 108.1 (2CH), 97.4 (Cq), 86.6 (CH), 49.5 (CH2), 20.4 (2CH3).

1-(2,4-Dimethylpenta-2,3-dien-1-yl)-1H-pyrrole (1g)

Yellow oil, 26%, 80 mg, R_f = 0.41 (Petroleum Ether / Dichloromethane 95/5)

^1H NMR (300 MHz, CDCl3) δ 6.67 – 6.65 (m, 2H), 6.16 – 6.14 (m, 2H), 4.35 (s, 2H), 1.68 (s, 6H), 1.56 (s, 3H).

^13C NMR (75 MHz, CDCl3) δ 200.1 (Cq), 120.9 (2CH), 107.8 (2CH), 95.7 (Cq), 94.6 (Cq), 54.1 (CH2), 20.6 (2CH3), 16.5 (CH3).

CI-MS (NH3) m/z , 162 [M+H]^+  

1-(4-Methylpenta-2,3-dien-1-yl)-1H-indole (1h)

Colorless oil, 67%, 132 mg, R\textsubscript{f} = 0.3 (Petroleum Ether / Dichloromethane 90/10)

\textit{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3})} \delta 7.67 – 7.64 (m, 1H), 7.40 – 7.37 (m, 1H), 7.26 – 7.20 (m, 1H), 7.17 – 7.10 (m, 2H), 6.52 (dd, J = 3.1, 0.8 Hz, 1H), 5.20 – 5.10 (m, 1H), 4.69 (d, J = 6.3 Hz, 2H), 1.66 (d, J = 2.8 Hz, 6H).

\textit{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3})} \delta 202.5 (C\textsubscript{q}), 136.1 (C\textsubscript{q}), 128.9 (C\textsubscript{q}), 127.6 (CH), 121.3 (CH), 120.9 (CH), 119.3(CH), 109.8 (CH) 101.2 (CH), 97.9 (C\textsubscript{q}), 85.9 (CH), 46.3 (CH\textsubscript{2}), 20.2 (2CH\textsubscript{3}).

CI-MS (NH\textsubscript{3}) m/z , 198 [M+H]+

5-Fluoro-1-(4-methylpenta-2,3-dien-1-yl)-1H-indole (1i)

Pale yellow oil, 64%, 139 mg, R\textsubscript{f} = 0.35 (Petroleum Ether / Dichloromethane 90/10)

\textit{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3})} \delta 7.34 – 7.21 (m, 2H), 7.14 (d, J = 3.1 Hz, 1H), 7.05 – 6.84 (m, 1H), 6.45 (dd, J = 3.1, 0.8 Hz, 1H), 5.12 (ddd, J = 8.9, 6.2, 2.8 Hz, 1H), 4.65 (d, J = 6.2 Hz, 2H), 1.62 (d, J = 2.8 Hz, 6H).

\textit{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3})} \delta 202.4 (C\textsubscript{q}), 157.8 (d, J = 234 Hz, C\textsubscript{q}F), 132.8 (C\textsubscript{q}), 129.2 (CH), 129.0 (d, J = 10.3 Hz, C\textsubscript{q}), 110.4 (d, J = 9.7 Hz, CH), 109.7 (d, J = 26.4 Hz, CH), 105.5 (d, J = 23.3 Hz, CH), 101.1 (d, J = 4.6 Hz, CH), 98.1 (C\textsubscript{q}), 85.7 (CH), 46.6 (CH\textsubscript{2}), 20.2 (2CH\textsubscript{3}).

\textit{\textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3})} \delta -126.77.

CI-MS (NH\textsubscript{3}) m/z , 216 [M+H]+

5-Methoxy-1-(4-methylpenta-2,3-dien-1-yl)-1H-indole (1j)

Colorless oil, 46%, 104 mg, R\textsubscript{f} = 0.3 (Petroleum Ether / Dichloromethane 70/30)

\textit{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3})} \delta 7.29 – 7.22 (m, 1H), 7.15 – 7.05 (m, 2H), 6.88 (dd, J = 8.9, 2.5 Hz, 1H), 6.41 (dd, J = 3.1, 0.7 Hz, 1H), 5.19 – 5.05 (m, 1H), 4.63 (d, J = 6.4 Hz, 2H), 3.86 (s, 3H), 1.66 (d, J = 2.8 Hz, 6H).

\textit{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3})} \delta 202.5 (C\textsubscript{q}), 154.0 (C\textsubscript{q}), 131.5 (C\textsubscript{q}), 129.2 (C\textsubscript{q}), 128.1 (CH), 111.7 (CH), 110.5(CH), 102.7 (CH), 100.7 (CH), 97.8 (C\textsubscript{q}), 85.9 (CH), 55.9 (CH\textsubscript{3}), 46.5 (CH\textsubscript{2}), 20.3 (2CH\textsubscript{3}).

CI-MS (NH\textsubscript{3}) m/z , 228 [M+H]+
1-(Buta-2,3-dien-1-yl)-3-methyl-1H-indole (1k)

Pale yellow oil, 48%, 400 mg, R_f = 0.45 (Petroleum Ether / AcOEt 40/1)

Spectral data were in accordance with those from the literature.¹

**Characterization data of products 2a-j, 5a-b**

8-Iodo-9,9,10-trimethyl-6,9-dihydropyrido[1,2-a]indole (2a)

Pale yellow oil, 60%, 40.4 mg, R_f = 0.4 (Petroleum Ether / Dichloromethane 90/10)

^1^H NMR (300 MHz, CDCl₃) δ 7.57 (dd, J = 6.7, 1.5 Hz, 1H), 7.24 – 7.05 (m, 3H), 6.68 (t, J = 3.4 Hz, 1H), 4.55 (d, J = 3.4 Hz, 2H), 2.44 (s, 3H), 1.59 (s, 6H).

^13^C NMR (75 MHz, CDCl₃) δ 134.5 (Cq), 134.0 (Cq), 130.0 (Cq), 129.1 (CH), 121.2 (CH), 119.6 (CH), 117.9 (CH), 113.5 (Cq), 108.6 (CH), 105.2 (Cq), 44.8 (CH₂), 39.8(Cq), 29.7 (2CH₃), 10.9 (CH₃).

APCI-MS m/z: 352 [M+H]^+  

8-Iodo-7,9,9,10-tetramethyl-6,9-dihydropyrido[1,2-a]indole (2b)

Colorless oil, 75%, 53.4 mg, R_f = 0.38 (Petroleum Ether / Dichloromethane 95/5)

^1^H NMR (300 MHz, CDCl₃) δ 7.57 (dd, J = 6.7, 1.5 Hz, 1H), 7.26 – 7.09 (m, 3H), 4.57 (s, 2H), 2.44 (s, 3H), 2.14 (s, 3H), 1.62 (s, 6H).

^13^C NMR (75 MHz, CDCl₃) δ 134.7 (Cq), 133.6 (Cq), 130.2 (Cq), 129.5 (Cq), 120.9 (CH), 119.5 (CH), 117.9 (CH), 115.9 (Cq), 108.6 (CH), 104.5 (Cq), 46.8 (CH₂), 40.7 (Cq), 30.5 (2CH₃), 28.5 (CH₃), 10.9 (CH₃).

APCI-MS m/z: 352 [M+H]^+

8'-Iodo-7',10'-dimethyl-2,3,5,6-tetrahydro-6'H-spiro[pyran-4,9'-pyrido[1,2-a]indole] (2c)

Pale yellow oil, 38%, 30 mg, R<sub>f</sub> = 0.3 (Petroleum Ether / Dichloromethane 95/5)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.57 (m, 1H), 7.26 – 7.03 (m, 1H), 4.60 (d, J = 16.9 Hz, 1H), 4.53 (d, J = 16.9 Hz, 1H), 2.65 – 2.32 (m, 5H), 1.86 (s, 3H), 1.17 (t, J = 7.5 Hz, 3H), 0.87-0.75 (m, 1H), 0.66-0.58 (m, 1H), 0.42 – 0.30 (m, 2H), -0.23– -0.30 (m, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 135.3 (Cq), 134.1 (Cq), 131.6 (Cq), 129.4 (Cq), 121.0 (CH), 119.4 (CH), 118.1 (CH), 114.6 (Cq), 108.5 (CH), 106.1 (Cq), 45.3(CH<sub>2</sub>), 44.1(Cq), 35.1(CH<sub>2</sub>), 30.8 (CH<sub>3</sub>), 23.6 (CH<sub>3</sub>), 12.1 (CH<sub>3</sub>), 11.6 (CH), 6.2 (CH<sub>2</sub>), 2.8 (CH<sub>2</sub>).

CI-MS (NH<sub>3</sub>) m/z , 392 [M+H]<sup>+</sup>, 266 [M-I]<sup>+</sup>

8'-Iodo-7',10'-dimethyl-2,3,5,6-tetrahydro-6'H-spiro[pyran-4,9'-pyrido[1,2-a]indole] (2d)

White solid, 69%, 54 mg, R<sub>f</sub> = 0.2 (Toluene)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.59 (d, J = 7.6 Hz, 1H), 7.33 – 7.05 (m, 3H), 4.61 (s, 2H), 4.23 (ddd, J = 11.7, 7.6, 4.6 Hz, 2H), 3.88 (ddd, J = 11.7, 6.7, 4.9 Hz, 2H), 2.55 (s, 3H), 2.41 (ddd, J = 14.7, 7.6, 4.9 Hz, 2H), 2.21 (ddd, J = 14.7, 6.7, 4.6 Hz, 2H), 2.12 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 136.6 (Cq), 135.4 (Cq), 133.9 (Cq), 130.1 (Cq), 121.6 (CH), 119.6 (CH), 118.5 (CH), 111.9 (Cq), 108.5 (CH), 105.1 (Cq), 64.2 (2CH<sub>2</sub>), 47.9 (CH<sub>2</sub>), 40.6 (Cq), 37.2 (2CH<sub>2</sub>), 28.7 (CH<sub>3</sub>), 11.1 (CH<sub>3</sub>).

APCI-MS m/z: 394 [M+H]<sup>+</sup>
3,7-Diiodo-8,8-dimethyl-5,8-dihydroindolizine (2f)

3,7-Diiodo-8,8-dimethyl-5,8-dihydroindolizine (2f)

Yellow solid, 37%, 11.2 mg, R$_f$ = 0.65 (Petroleum Ether / Dichloromethane 80/20)

$^1$H NMR (300 MHz, CDCl$_3$) δ 6.51 (t, $J$ = 3.7 Hz, 1H), 6.38 (d, $J$ = 3.6 Hz, 1H), 6.08 (d, $J$ = 3.7 Hz, 1H), 4.29 (d, $J$ = 3.6 Hz, 2H), 1.41 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.6 (Cq), 130.3 (CH), 118.3 (CH), 111.6 (Cq), 106.7 (CH), 64.3 (Cq), 49.6 (CH$_2$), 40.4 (Cq), 32.6 (2CH$_3$).

3,7-Diiodo-6,8,8-trimethyl-5,8-dihydroindolizine (2g)

3,7-Diiodo-6,8,8-trimethyl-5,8-dihydroindolizine (2g)

Yellow solid, 94%, 78 mg, R$_f$ = 0.7 (Petroleum Ether / Dichloromethane 95/5)

$^1$H NMR (300 MHz, CDCl$_3$) δ 6.42 (d, $J$ = 3.7 Hz, 1H), 6.08 (d, $J$ = 3.7 Hz, 1H), 4.32 (d, $J$ = 0.7 Hz, 2H), 2.06 (t, $J$ = 0.7 Hz, 3H), 1.44 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.8 (Cq), 131.0 (Cq), 118.4 (CH), 113.6(Cq), 106.2 (CH), 63.3 (Cq), 51.4 (CH$_2$), 41.3 (Cq), 33.4 (2CH$_3$), 28.1 (CH$_3$).

APCI-MS m/z: 414 [M+H]$^+$

8,10-Diiodo-9,9-dimethyl-6,9-dihydropyrido[1,2-a]indole (2h)

8,10-Diiodo-9,9-dimethyl-6,9-dihydropyrido[1,2-a]indole (2h)

Yellow oil, 58%, 52 mg, R$_f$ = 0.28 (Petroleum Ether / Dichloromethane 90/10)

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.53 – 7.49 (m, 1H), 7.35 – 7.21 (m, 3H), 6.70 (t, $J$ = 3.4 Hz, 1H), 4.60 (d, $J$ = 3.4 Hz, 2H), 1.77 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.0 (Cq), 134.8 (Cq), 131.0 (Cq), 128.9 (CH), 122.6 (CH), 121.2 (CH), 121.0 (CH), 112.5 (Cq), 109.1 (CH), 54.7 (Cq), 45.2 (CH$_2$), 40.0 (Cq), 29.3 (2CH$_3$).

CI-MS (NH$_3$) m/z , 450 [M+H]$^+$, 324 [M-I]$^+$, 198 [M-2I]$^+$
2-Fluoro-8,10-diiodo-9,9-dimethyl-6,9-dihydropyrido[1,2-a]indole (2i)

Yellow solid, 38%, 35.5 mg, Rf = 0.22 (Petroleum Ether)

1H NMR (300 MHz, CDCl3) δ 7.21 – 7.11 (m, 2H), 6.99 (td, J = 9.0, 2.5 Hz, 1H), 6.69 (t, J = 3.4 Hz, 1H), 4.58 (d, J = 3.4 Hz, 2H), 1.75 (s, 6H).

13C NMR (75 MHz, CDCl3) δ 159.1 (d, J = 237 Hz, CqF), 138.7 (Cq), 131.8 (d, J = 11 Hz, Cq), 131.4 (Cq), 128.7 (CH), 112.2 (Cq), 111.0 (d, J = 26 Hz, CH), 110.8 (d, J = 10 Hz, CH), 110.0 (d, J = 25 Hz, CH), 45.3 (Cq), 40.0 (CH2), 29.2 (2CH3).

19F NMR (282 MHz, CDCl3) δ -123.3.

CI-MS (NH3) m/z , 468 [M+H]+, 342 [M-I]+, 216 [M-2I]+

8,10-Diiodo-2-methoxy-9,9-dimethyl-6,9-dihydropyrido[1,2-a]indole (2j)

Yellow solid, 23%, 20 mg, Rf = 0.2 (Petroleum Ether / Dichloromethane 70/30)

1H NMR (300 MHz, CDCl3) δ 7.12 (d, J = 8.7 Hz, 1H), 7.03 – 6.81 (m, 2H), 6.68 (t, J = 3.4 Hz, 1H), 4.57 (d, J = 3.4 Hz, 2H), 3.91 (s, 3H), 1.75 (s, 6H).

13C NMR (75 MHz, CDCl3) δ 155.6 (Cq), 137.4 (Cq), 131.6 (Cq), 129.9 (Cq), 128.9 (CH), 113.0 (CH), 112.5 (Cq), 110.0 (CH), 102.7 (CH), 56.0 (CH3), 54.1 (Cq), 45.3 (CH2), 40.0 (Cq), 29.3 (2CH3).

CI-MS (NH3) m/z , 480 [M+H]+, 354 [M-I]+, 228 [M-2I]+

2-Bromo-1-(buta-2,3-dien-1-yl)-3-methyl-1H-indole (5a)

Yellow oil, 72%, 37.8 mg, Rf=0.33 (Petroleum Ether / Dichloromethane 90/10)

1H NMR (300 MHz, CDCl3) δ 7.51 (ddd, J = 7.8, 1.2, 0.8 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.19 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 7.11 (ddd, J = 7.8, 7.1, 1.2 Hz, 1H), 5.27 – 5.16 (m, 1H), 4.88 – 4.68 (m, 4H), 2.29 (s, 3H).

13C NMR (75 MHz, CDCl3) δ 208.9 (Cq), 136.2 (Cq), 128.1 (Cq), 121.8 (CH), 119.6 (CH), 118.3 (CH), 112.2 (Cq), 110.9 (Cq), 109.5 (CH), 87.0 (CH), 43.6 (CH2), 9.9 (CH3).

CI-MS (NH3) m/z , 264 [M+H]+
2,6-Dibromo-1-(buta-2,3-dien-1-yl)-3-methyl-1H-indole (5b)

![Chemical structure](image)

Yellow solid, 17%, 11.6 mg, R_f=0.4 (Petroleum Ether / Dichloromethane 90/10)

^1H NMR (300 MHz, CDCl3) δ 7.44 (d, J = 1.7 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 8.4, 1.7 Hz, 1H), 5.19 (p, J = 6.3 Hz, 1H), 4.85 – 4.70 (m, 4H), 2.25 (s, 3H).

^13C NMR (75 MHz, CDCl3) δ 208.9 (Cq), 136.8 (Cq), 127.0 (Cq), 123.0 (Cq), 122.8 (CH), 119.5 (CH), 115.5 (Cq), 112.6 (CH), 111.6 (Cq), 86.7(CH), 43.7 (CH2), 9.9 (CH3).

Cl-MS (NH3) m/z, 342 [M+H]^+. 
NMR Spectra

3-methyl-1-(4-methylpenta-2,3-dien-1-yl)-1H-indole (1a)

1-(2,4-dimethylpenta-2,3-dien-1-yl)-3-methyl-1H-indole (1b)
1-(4-cyclopropyl-2-ethylpenta-2,3-dien-1-yl)-3-methyl-1H-indole (1c)
3-methyl-1-(2-methyl-3-(tetrahydro-4H-pyran-4-ylidene)allyl)-$IH$-indole (1d)
1-(1-(4-methylpenta-2,3-dien-1-yl)-1H-indol-3-yl)ethan-1-one (1e)
1-(4-methylpenta-2,3-dien-1-yl)-1H-pyrrole (1f)
1-(2,4-dimethylpenta-2,3-dien-1-yl)-1H-pyrrole (1g)
1-(4-methylpenta-2,3-dien-1-yl)-1H-indole (Ih)
5-fluoro-1-(4-methylpenta-2,3-dien-1-yl)-1H-indole (1i)
5-methoxy-1-(4-methylpenta-2,3-dien-1-yl)-1H-indole (1j)
1-(buta-2,3-dien-1-yl)-3-methyl-1H-indole (1k)
8-iodo-9,9,10-trimethyl-6,9-dihydropyrido[1,2-a]indole (2a)
8-iodo-7,9,9,10-tetramethyl-6,9-dihydropyrido[1,2-a]indole (2b)
8'-iodo-7',10'-dimethyl-2,3,5,6-tetrahydro-6'H-spiro[pyran-4,9'-pyrido[1,2-a]indole] (2c)
8'-ido-7',10'-dimethyl-2,3,5,6-tetrahydro-6'H-spiro[pyran-4,9'-pyrido[1,2-ajindole] (2d)
3,7-diido-8,8-dimethyl-5,8-dihydroindolizine (2f)
3,7-diido-6,8,8-trimethyl-5,8-dihydroindolizine (2g)
8,10-diiodo-9,9-dimethyl-6,9-dihydropyrido[1,2-a]indole (2h)
2-fluoro-8,10-diiodo-9,9-dimethyl-6,9-dihydropyrido[1,2-a]indole (2i)
8,10-diiodo-2-methoxy-9,9-dimethyl-6,9-dihydropyrido[1,2-a]indole (2j)
2-bromo-1-(buta-2,3-dien-1-yl)-3-methyl-1H-indole (5a)
2,6-dibromo-1-(buta-2,3-dien-1-yl)-3-methyl-1H-indole (5b)