Supporting Information for

Desymmetrization of Cyclohexadienones via D-Camphor-derived Triazolium Salts Catalyzed Intramolecular Stetter Reaction

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**General methods.** Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

$^1$H and $^{13}$C NMR spectra were recorded on Varian instruments (300 MHz and 75 MHz or 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for $^1$H NMR are recorded as follows: chemical shift ($\delta$, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for $^{13}$C NMR are reported in terms of chemical shift ($\delta$, ppm).

The D-camphor-derived triazolium salt$^1$, compound 3b$^2$ and 3-substituted-prop-2-ynoic acid$^{3,4}$ were prepared according to the reported procedures, compound 3a is commercially available.

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Substrate synthesis

General procedure for the synthesis of substrates 1a-l

When \( R^1 = H, R^2 = n\text{-Pr} \), the substrate was synthesized as follows:

1: General procedure for the synthesis of 3-substituted-prop-2-ynoic amide (5)

To a solution of 3-substituted-prop-2-ynoic acid (1.1 eq) in CH\(_2\)Cl\(_2\) (0.2 mol/L), DMAP (0.1 eq) was added, then the solution was cooled to 0 °C. (\( N\)-4,4-Diethoxyalkyl)-4-methoxaniline (1 eq) and DCC (1.2 eq) were added sequentially. The resulting solution was stirred at room temperature until completion. The precipitated urea was then filtered off by celite and the filtrate was concentrated.
in vacuo. The residue was purified by column chromatography on silica gel to afford the desired compounds.

2: General procedure for dearomatization

ICl (2 eq) in CH$_2$Cl$_2$ (0.1 mol/L) was added to a solution of the diethoxyacetal (1 eq) (method A) or the corresponding aldehyde (1 eq) (method B) in CH$_2$Cl$_2$ (0.03 mol/L) at -78 °C over a period of 30-60 minutes. The resulting solution was stirred for another 10-60 minutes. After the reaction was complete (monitored by TLC), it was quenched with saturated aqueous Na$_2$SO$_3$ solution. The reaction mixture was allowed to warm up to room temperature and extracted three times with CH$_2$Cl$_2$. The combined organic layers were dried over Na$_2$SO$_4$, concentrated in vacuo, the residue was purified by column chromatography on silica gel to afford the corresponding iodo cyclohexadienone.

3: General procedure for acetal removal

To the solution of acetal (1 eq) in acetone (0.04 mol/L), iodine (10 mol%) was added. The resulting solution was stirred at room temperature until completion. The solution was concentrated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired compounds.

\[
\text{OMe} \\
\text{HN} \\
\text{O} \\
\text{O} \\
\text{4a}
\]

\text{N-}(2,2-\text{Diethoxyethyl})-4-\text{methoxyaniline}

DMSO (15 mL) was added to a mixture of 4-iodoanisole (2.0 g, 8.55 mmol), CuI (163 mg, 0.85 mmol), L-proline (197 mg, 1.71 mmol) and K$_2$CO$_3$ (powdered) (2.38 g, 17.1 mmol) in a round bottom flask under argon, then 2,2-diethoxyethanamine (1.86 mL, 12.83 mmol) was added. The reaction mixture was stirred under argon at 80 °C for
40 h, diluted with water and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with water and brine, dried over Na₂SO₄, concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:PE = 1:10) to afford the product as a pale yellow oil (1.67 g, 82% yield); 

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl３)} \delta \]

6.77 (d, \( J = 9.0 \) Hz, 2H), 6.61 (d, \( J = 8.7 \) Hz, 2H), 4.67 (t, \( J = 5.4 \) Hz, 1H), 3.77-3.67 (m, 5H), 3.61-3.51 (m, 2H), 3.20 (d, \( J = 5.7 \) Hz, 2H), 1.23 (t, \( J = 7.2 \) Hz, 6H); 

\[ \text{\textsuperscript{13}C NMR (75 MHz, CDCl３)} \delta \]

152.2, 142.0, 114.7, 114.4, 100.9, 62.2, 55.6, 47.3, 15.3; MS (ESI) 240 ([M+H]+); HRMS (ESI) mass calcd. For C₁₃H₂₂NO₃ ([M+H]+): 240.1594. Found 240.1598.

\[ \text{OMe} \]

\[ \text{HN} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{4b} \]

\[ \text{N-(2,2-Diethoxyethyl)-4-methoxy-3,5-dimethylaniline} \]

Pale yellow oil (97% yield), following the procedure for 4a; 

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl３)} \delta \]

6.28 (s, 2H), 4.63 (t, \( J = 4.6 \) Hz, 1H), 3.72-3.66 (m, 3H), 3.61 (d, \( J = 1.8 \) Hz, 3H), 3.55-3.50 (m, 2H), 3.17 (d, \( J = 5.4 \) Hz, 2H), 2.20 (s, 6H), 1.23 (t, \( J = 6.9 \) Hz, 6H); 

\[ \text{\textsuperscript{13}C NMR (75 MHz, CDCl３)} \delta \]

148.5, 143.6, 130.7, 112.7, 100.5, 61.6, 59.3, 46.4, 15.7, 14.9; MS (EI, \( m/z \), rel. intensity) 267 ([M]+, 34), 164 (98), 103 (100); HRMS (EI) mass calcd. For C₁₅H₂₅NO₃ ([M]+): 267.1834. Found 267.1833.

\[ \text{OMe} \]

\[ \text{N} \]

\[ \text{OEt} \]

\[ \text{OEt} \]

\[ \text{Ph} \]

\[ \text{5a} \]

\[ \text{N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)-3-phenylpropiolamide} \]

Pale yellow solid, following general procedure 1 (93% yield). M.p. 64-66 °C. 

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl３)} \delta \]

7.29-7.23 (m, 3H), 7.17 (t, \( J = 7.2 \) Hz, 2H), 7.10 (d, \( J =
7.2 Hz, 2H), 6.88 (d, \( J = 9.0 \) Hz, 2H), 4.79 (t, \( J = 5.4 \) Hz, 1H), 3.84 (d, \( J = 5.4 \) Hz, 2H), 3.76 (s, 3H), 3.68-3.56 (m, 2H), 3.53-3.43 (m, 2H), 1.13 (t, \( J = 7.2 \) Hz, 6H); \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)) \( \delta \) 158.8, 154.4, 134.9, 132.0, 129.6, 129.3, 128.0, 120.0, 113.6, 98.9, 90.8, 82.4, 61.7, 55.1, 50.8, 14.9; MS (ESI) 368 ([M+H]\(^+\)); HRMS (ESI) mass calcd. For C\(_{22}\)H\(_{25}\)NaNO\(_4\) ([M+Na]\(^+\)): 390.1676. Found 390.1683.

\[ \text{N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)-3-(p-tolyl)propiolamide} \]

Pale yellow solid (80% yield), following general procedure 1. M.p. 54-56 °C. \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.32 (d, \( J = 9.0 \) Hz, 2H), 7.05 (s, 4H), 6.92 (d, \( J = 9.0 \) Hz, 2H), 4.84 (t, \( J = 5.7 \) Hz, 1H), 3.88-3.84 (m, 4H), 3.72-3.61 (m, 2H), 3.59-3.47 (m, 2H), 2.31 (s, 3H), 1.19 (t, \( J = 7.2 \) Hz, 6H); \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)) \( \delta \) 158.9, 154.9, 140.4, 135.4, 132.4, 129.6, 129.0, 117.3, 113.9, 99.2, 91.6, 82.3, 62.0, 55.5, 51.1, 21.5, 15.2; MS (ESI) 382 ([M+H]\(^+\)); HRMS (ESI) mass calcd. For C\(_{23}\)H\(_{27}\)NaNO\(_4\) ([M+Na]\(^+\)): 404.1832. Found 404.1840.

\[ \text{N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)-3-(m-tolyl)propiolamide} \]

Pale yellow oil (95% yield), following general procedure 1. \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.32 (d, \( J = 9.3 \) Hz, 2H), 7.11 (d, \( J = 4.5 \) Hz, 2H), 6.95-6.92 (m, 4H), 4.84 (t, \( J = 5.4 \) Hz, 1H), 3.88 (d, \( J = 6.0 \) Hz, 2H), 3.82 (s, 3H), 3.71-3.61 (m, 2H), 3.59-3.49 (m, 2H), 2.23 (s, 3H), 1.18 (t, \( J = 7.2 \) Hz, 6H); \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)) \( \delta \) 158.8,
154.5, 137.7, 135.1, 132.7, 129.4, 129.2, 127.9, 119.9, 113.7, 99.0, 91.2, 82.2, 61.7, 55.2, 50.8, 20.8, 15.0; MS (ESI) 382 ([M+H]^+); HRMS (MALDI) mass calcd. For C_{23}H_{27}NaNO_4 ([M+Na]^+): 404.1832. Found 404.1843.

\[
\text{5d}
\]

\textit{N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)-3-(o-tolyl)propiolamide}

Pale yellow oil (98% yield), following general procedure 1. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.22 (d, \(J = 8.4\) Hz, 2H), 7.14 (d, \(J = 7.5\) Hz, 1H), 7.07 (d, \(J = 7.5\) Hz, 1H), 6.95 (d, \(J = 7.5\) Hz, 2H), 6.81 (d, \(J = 8.7\) Hz, 2H), 4.75 (t, \(J = 5.7\) Hz, 1H), 3.78 (d, \(J = 5.4\) Hz, 2H), 3.69 (s, 3H), 3.61-3.51 (m, 2H), 3.49-3.38 (m, 2H), 1.84 (s, 3H), 1.08 (t, \(J = 7.2\) Hz, 6H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 159.0, 154.8, 141.2, 135.3, 133.0, 129.8, 129.6, 129.3, 125.4, 120.2, 114.1, 99.2, 99.0, 86.3, 61.9, 55.4, 51.2, 19.8, 15.1; MS (ESI) 404 ([M+Na]^+); HRMS (MALDI) mass calcd. For C_{23}H_{27}NaNO_4 ([M+Na]^+): 404.1832. Found 404.1840.

\[
\text{5e}
\]

\textit{N-(2,2-Diethoxyethyl)-3-(4-fluorophenyl)-N-(4-methoxyphenyl)propiolamide}

Yellow oil (84% yield), following general procedure 1. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.33 (d, \(J = 9.0\) Hz, 2H), 7.15 (dd, \(J = 9.0, 5.4\) Hz, 2H), 6.97-6.91 (m, 4H), 4.84 (t, \(J = 5.7\) Hz, 1H), 3.88 (d, \(J = 6.0\) Hz, 2H), 3.84 (s, 3H), 3.72-3.62 (m, 2H), 3.60-3.50 (m, 2H), 1.19 (t, \(J = 7.2\) Hz, 6H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 163.2 (d, \(J = 250.7\) Hz),
158.9, 154.5, 135.1, 134.4 (d, J = 9.1 Hz), 129.5, 116.3 (d, J = 3.4 Hz), 115.6 (d, J = 22.1 Hz), 113.8, 99.0, 90.0, 82.3, 61.9, 55.3, 50.9, 15.1; MS (ESI) 386 ([M+H]\(^+\)); HRMS (ESI) mass calcd. For C\(_{22}\)H\(_{24}\)FN\(_4\)N\(_4\) ([M+Na]\(^+\))\): 408.1582. Found 408.1583.

![5f](image)

3-(4-Chlorophenyl)-N-(2,2-diethoxyethyl)-N-(4-methoxyphenyl)propiolamide

Orange oil (82% yield), following general procedure 1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.34 (d, J = 9.0 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 4.84 (t, J = 5.7 Hz, 1H), 3.89 (d, J = 5.7 Hz, 2H), 3.82 (s, 3H), 3.71-3.61 (m, 2H), 3.59-3.48 (m, 2H), 1.18 (t, J = 7.2 Hz, 6H); \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 158.6, 153.9, 135.9, 134.5, 134.4, 133.0, 129.2, 128.2, 118.4, 113.5, 98.7, 89.3, 83.1, 61.4, 54.9, 50.6, 14.8; MS (ESI) 424 ([M+Na]\(^+\)); HRMS (MALDI) mass calcd. For C\(_{22}\)H\(_{24}\)ClNaNO\(_4\) ([M+Na]\(^+\))\): 424.1286. Found 424.1283.

![5g](image)

\(\text{N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)-3-(thiophen-2-yl)propiolamide}\)

Yellow oil (86% yield), following general procedure 1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.32-7.29 (m, 3H), 7.04 (d, J = 3.3 Hz, 1H), 6.95-6.87 (m, 3H), 4.84 (t, J = 5.7 Hz, 1H), 3.88 (d, J = 5.7 Hz, 2H), 3.82 (s, 3H), 3.70-3.60 (m, 2H), 3.57-3.478 (m, 2H), 1.17 (t, J = 6.9 Hz, 6H); \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 158.7, 154.0, 134.5, 134.4, 129.9, 129.1, 126.8, 119.6, 113.5, 98.7, 86.4, 84.5, 61.5, 55.0, 50.5, 14.8; MS (ESI)
396 ([M+Na]⁺); HRMS (MALDI) mass calcd. For C₂₀H₂₃NaNO₄S ([M+Na]⁺): 396.1240. Found 396.1243.

\[ \text{OMe} \]  \[ \text{N} \]  \[ \text{OEt} \]  \[ \text{OEt} \]  \[ \text{Me} \]  \[ \text{N} \]  \[ \text{OEt} \]  \[ \text{OEt} \]  \[ 5h \]

**N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)but-2-ynamide**

Pale yellow solid (87% yield), following general procedure 1. M.p. 54-56 °C. \(^1\)H NMR (300 MHz, CDCl₃) δ 7.23 (d, \(J = 9.0\) Hz, 2H), 6.88 (d, \(J = 9.0\) Hz, 2H), 4.78 (t, \(J = 5.7\) Hz, 1H), 3.83 (s, 3H), 3.79 (d, \(J = 6.0\) Hz, 2H), 3.68-3.58 (m, 2H), 3.56-3.46 (m, 2H), 1.74 (s, 3H), 1.16 (t, \(J = 6.9\) Hz, 6H); \(^{13}\)C NMR (75 MHz, CDCl₃) δ 158.6, 154.6, 135.2, 129.2, 113.7, 99.1, 90.0, 74.0, 61.9, 55.2, 51.0, 15.1, 3.7; MS (ESI) 328 ([M+Na]⁺); HRMS (MALDI) mass calcd. For C₁₇H₂₃NaNO₄ ([M+Na]⁺): 328.1519. Found 328.1526.

\[ \text{OMe} \]  \[ \text{N} \]  \[ \text{OEt} \]  \[ \text{OEt} \]  \[ \text{5i} \]

**N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)hex-2-ynamide**

Pale yellow oil (84% yield), following general procedure 1. \(^1\)H NMR (300 MHz, CDCl₃) δ 6.96 (dd, \(J = 9.0, 2.4\) Hz, 2H), 6.61 (dd, \(J = 9.0, 2.4\) Hz, 2H), 4.51-4.48 (m, 1H), 3.53-3.52 (m, 5H), 3.40-3.30 (m, 2H), 3.28-3.17 (m, 2H), 1.81-1.76 (m, 3H), 1.06-0.94 (m, 2H), 0.91-0.85 (m, 6H), 0.46-0.40 (m, 3H); \(^{13}\)C NMR (75 MHz, CDCl₃) δ 158.3, 154.0, 134.7, 128.8, 113.2, 98.5, 93.1, 74.5, 61.9, 54.6, 50.2, 20.2, 19.8, 14.5, 12.3; MS (ESI) 356 ([M+Na]⁺); HRMS (MALDI) mass calcd. For C₁₉H₂₇NaNO₄ ([M+Na]⁺): 356.1832. Found 356.1842.
3-Cyclopropyl-N-(2,2-diethoxyethyl)-N-(4-methoxyphenyl)propiolamide

Pale yellow oil (81% yield), following general procedure 1. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.03 (d, $J = 8.7$ Hz, 2H), 6.70 (d, $J = 8.7$ Hz, 2H), 4.57 (t, $J = 5.7$ Hz, 1H), 3.64 (s, 3H), 3.60 (d, $J = 5.4$ Hz, 2H), 3.49-3.39 (m, 2H), 3.37-3.27 (m, 2H), 0.98 (t, $J = 6.9$ Hz, 6H), 0.79-0.73 (m, 1H), 0.57-0.51 (m, 2H), 0.28-0.23 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.5, 154.2, 135.0, 129.0, 113.3, 98.8, 97.5, 69.6, 61.4, 54.9, 50.4, 14.7, 8.5, -1.1; MS (ESI) 354 ([M+Na]$^+$); HRMS (MALDI) mass calcd. For C$_{19}$H$_{25}$NaNO$_4$ ([M+Na]$^+$): 354.1676. Found 354.1680.

N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)-4,4-dimethylpent-2-ynamide

Pale yellow oil (96% yield), following general procedure 1. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 4.78 (t, $J = 5.7$ Hz, 1H), 3.81 (s, 3H), 3.80 (d, $J = 6.3$ Hz, 2H), 3.69-3.58 (m, 2H), 3.57-3.47 (m, 2H), 1.17 (t, $J = 7.2$ Hz, 6H), 0.97 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.7, 154.9, 135.5, 129.0, 113.6, 101.1, 99.1, 73.4, 61.6, 55.3, 50.7, 29.5, 27.1, 15.0; MS (ESI) 370 ([M+Na]$^+$); HRMS (MALDI) mass calcd. For C$_{20}$H$_{29}$NaNO$_4$ ([M+Na]$^+$): 370.1989. Found 370.1998.
**N-(2,2-Diethoxyethyl)-N-(4-methoxy-3,5-dimethylphenyl)-3-phenylpropiolamide**

Pale yellow solid (94% yield), following general procedure \textit{1}. M.p. 64-66 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.32-7.28 (m, 1 H), 7.28 (t, \(J = 7.5\) Hz, 2H), 7.09-7.13 (m, 4 H), 4.86 (t, \(J = 5.7\) Hz, 1H), 3.89 (d, \(J = 5.7\) Hz, 2H), 3.73 (s, 3H), 3.70-3.62 (m, 2H), 3.59-3.49 (m, 2H), 2.30 (s, 6H), 1.18 (t, \(J = 6.9\) Hz, 6H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 156.0, 153.9, 137.4, 131.8, 130.7, 129.4, 128.1, 127.8, 120.0, 98.8, 90.3, 82.4, 61.5, 59.1, 50.5, 15.5, 14.7; MS (ESI) 418 ([M+Na]\textsuperscript{+}); HRMS (MALDI) mass calcd. For C\textsubscript{24}H\textsubscript{29}NaNO\textsubscript{4} ([M+Na]\textsuperscript{+}): 419.1989. Found 418.1997.

**1-(2,2-Diethoxyethyl)-3-iodo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione**

Pale yellow solid (54% yield), following general procedure \textit{2}, method \textit{A}. M.p. 140-142 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.43-7.34 (m, 3H), 7.25 (d, \(J = 7.2\) Hz, 2H), 6.57 (d, \(J = 9.6\) Hz, 2H), 6.38 (d, \(J = 10.2\) Hz, 2H), 4.89 (t, \(J = 5.4\) Hz, 1H), 3.79-3.69 (m, 2H), 3.60-3.50 (m, 2H), 3.40 (d, \(J = 5.4\) Hz, 2H), 1.20 (t, \(J = 6.9\) Hz, 6H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 183.8, 167.8, 158.8, 144.1, 132.4, 131.7, 129.9, 128.4, 127.6, 99.1, 97.9, 71.0, 63.0, 45.1, 15.2; MS (ESI) 502 ([M+Na]\textsuperscript{+}); HRMS (MALDI) mass calcd. For C\textsubscript{21}H\textsubscript{22}INaNO\textsubscript{4} ([M+Na]\textsuperscript{+}): 502.0486. Found 502.0496.
1-(2,2-Diethoxyethyl)-3-iodo-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Pale yellow solid (45% yield), following general procedure 2, method A. M.p. 138-140 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.16 (s, 4H), 6.53 (d, $J = 10.2$ Hz, 2H), 6.38 (d, $J = 10.2$ Hz, 2H), 4.89 (t, $J = 5.7$ Hz, 1H), 3.79-3.69 (m, 2H), 3.60-3.50 (m, 2H), 3.38 (d, $J = 5.7$ Hz, 2H), 2.35 (s, 3H), 1.20 (t, $J = 6.9$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 183.8, 167.8, 158.7, 144.3, 140.0, 132.2, 129.0, 128.7, 127.4, 99.0, 97.3, 70.9, 62.9, 45.0, 21.2, 15.1; MS (ESI) 516 ([M+Na]$^+$); HRMS (ESI) mass calcd. For C$_{22}$H$_{24}$INaNO$_4$ ([M+Na]$^+$): 516.0642. Found 516.0651.

1-(2,2-Diethoxyethyl)-3-iodo-4-(m-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Yellow solid (41% yield), following general procedure 2, method A. M.p. 128-130 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.12-7.04 (m, 2H), 6.92-6.90 (m, 2H), 6.48 (d, $J = 9.9$ Hz, 2H), 6.24 (d, $J = 9.6$ Hz, 2H), 4.76 (t, $J = 5.4$ Hz, 1H), 3.65-3.55 (m, 2H), 3.46-3.36 (m, 2H), 3.27 (d, $J = 5.1$ Hz, 2H), 2.19 (s, 3H), 1.06 (t, $J = 6.9$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 183.8, 167.8, 159.0, 144.2, 138.1, 132.2, 131.7, 130.6, 128.3, 128.1, 124.5, 99.0, 97.6, 71.0, 62.9, 45.1, 21.2, 15.1; MS (ESI) 516 ([M+Na]$^+$); HRMS (MALDI) mass calcd. For C$_{22}$H$_{24}$INaNO$_4$ ([M+Na]$^+$): 516.0642. Found 516.0660.
1-(2,2-Diethoxyethyl)-3-iodo-4-(o-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

White solid (61% yield), following general procedure 2, method A. M.p. 123-124 °C. 

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.28-7.20 (m, 2H), 7.12 (t, $J = 7.2$ Hz, 1H), 6.87 (d, $J = 7.2$ Hz, 1H), 6.71 (dd, $J = 9.6$ Hz, 2.7 Hz, 1H), 6.63 (dd, $J = 9.6$ Hz, 2.7 Hz, 1H), 6.42 (d, $J = 9.9$ Hz, 1H), 6.22 (d, $J = 10.2$ Hz, 1H), 4.90 (t, $J = 5.4$ Hz, 1H), 3.79-3.69 (m, 2H), 3.60-3.50 (m, 2H), 3.47-3.37 (m, 2H), 2.21 (s, 3H), 1.22-1.17 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 183.3, 167.2, 159.8, 143.6, 143.5, 135.1, 132.3, 131.5, 130.22, 130.17, 129.2, 127.8, 124.9, 99.8, 98.8, 72.3, 62.6, 45.1, 19.7, 14.9; MS (ESI) 516 ([M+Na]$^+$); HRMS (MALDI) mass calcd. For C$_{22}$H$_{24}$INaNO$_4$ ([M+Na]$^+$): 516.0642. Found [(M+Na)$^+$] 516.0653.

1-(2,2-Diethoxyethyl)-4-(4-fluorophenyl)-3-iodo-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

White solid (51% yield), following general procedure 2, method A. M.p. 143-145 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29-7.24 (m, 2H), 7.07 (t, $J = 8.4$ Hz, 2H), 6.54 (d, $J = 10.2$ Hz, 2H), 6.39 (d, $J = 9.9$ Hz, 2H), 4.89 (t, $J = 5.7$ Hz, 1H), 3.77-3.69 (m, 2H), 3.60-3.52 (m, 2H), 3.39 (d, $J = 5.4$ Hz, 2H), 1.20 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 183.8, 167.8, 163.4 (d, $J = 250.1$ Hz), 157.9, 144.2, 132.6, 129.9 (d, $J = 8.5$ Hz), 127.9 (d, $J = 3.4$ Hz), 116.0 (d, $J = 22.1$ Hz), 99.2, 98.6, 71.1, 63.2, 45.3,
4-(4-Chlorophenyl)-1-(2,2-Diethoxyethyl)-3-iodo-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

White solid (53% yield), following general procedure 2, method A. M.p. 176-178 °C.

\[
\begin{align*}
\delta & \quad 7.36 \ (d, J = 8.4 \text{ Hz}, 2H), 7.22 \ (d, J = 8.9 \text{ Hz}, 2H), 6.55 \ (d, J = 10.2 \text{ Hz}, 2H), 6.40 \ (d, J = 9.9 \text{ Hz}, 2H), 4.89 \ (t, J = 5.4 \text{ Hz}, 1H), 3.79-3.69 \ (m, 2H), 3.60-3.49 \ (m, 2H), 3.39 \ (d, J = 5.4 \text{ Hz}, 2H), 1.20 \ (t, J = 7.2 \text{ Hz}, 6H); \\
\end{align*}
\]

\[\text{13C NMR (100 MHz, CDCl}_{3}^{3} \delta 183.7, 167.6, 157.6, 144.0, 136.2, 132.6, 130.2, 129.1, 129.0, 99.1, 98.7, 71.0, 63.1, 45.2, 15.2; MS (ESI) 536 ([M+Na]^+); HRMS (MALDI) mass calcd. For C}_{21}H_{21}ClINaNO_{4} ([M+Na]^+): 536.0096. Found 536.0105.}

1-(2,2-Diethoxyethyl)-3-iodo-4-(thiophen-2-yl)-1-azaspiro[4,5]deca-3,6,9-triene-2,8-dione

Yellow solid (51% yield), following general procedure 2, method A. M.p. 89-91 °C.

\[
\begin{align*}
\delta & \quad 7.69 \ (d, J = 3.9 \text{ Hz}, 1H), 7.54 \ (d, J = 8.1 \text{ Hz}, 1H), 7.11 \ (t, J = 4.5 \text{ Hz}, 1H), 6.60 \ (d, J = 9.9 \text{ Hz}, 2H), 6.53 \ (d, J = 10.5 \text{ Hz}, 2H), 4.92 \ (t, J = 5.4 \text{ Hz}, 1H), 3.79-3.69 \ (m, 2H), 3.59-3.49 \ (m, 2H), 3.34 \ (d, J = 5.4 \text{ Hz}, 2H), 1.19 \ (t, J = 7.2 \text{ Hz}, 6H); \\
\end{align*}
\]

\[\text{13C NMR (100 MHz, CDCl}_{3}^{3} \delta 184.2, 168.0, 150.2, 145.2, 132.6, 132.4, 132.4,}

S14
129.8, 129.5, 127.4, 99.2, 93.5, 69.7, 63.4, 44.7, 15.2; MS (ESI) 508 ([M+Na]$^+$); HRMS (MALDI) mass calcd. For C$_{19}$H$_{20}$INaNO$_4$S ([M+Na]$^+$): 508.0050. Found 508.0056.

![Chemical structure of 1-(2,2-Diethoxyethyl)-3-iodo-4-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione](image)

1-(2,2-Diethoxyethyl)-3-iodo-4-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Pale yellow solid (47% yield), following general procedure 2, method A. M.p. 94-96 $^\circ$C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.50 (d, $J$ = 10.5 Hz, 2H), 6.45 (d, $J$ = 10.5 Hz, 2H), 4.82 (t, $J$ = 5.4 Hz, 1H), 3.78-3.67 (m, 2H), 3.58-3.48 (m, 2H), 3.37 (d, $J$ = 5.7 Hz, 2H), 1.89 (s, 3H), 1.19 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 183.9, 167.7, 156.9, 145.0, 132.1, 99.0, 95.8, 70.8, 62.8, 45.1, 15.2, 15.0; MS (ESI) 440 ([M+Na]$^+$); HRMS (MALDI) mass calcd. For C$_{16}$H$_{20}$INaNO$_4$ ([M+Na]$^+$): 440.0329. Found 440.0341.

![Chemical structure of N-(4-Methoxyphenyl)-N-(2-oxoethyl)hex-2-ynamide](image)

N-(4-Methoxyphenyl)-N-(2-oxoethyl)hex-2-ynamide

Pale yellow oil (79% yield), following general procedure 3. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.61 (s, 1H), 7.27 (d, $J$ = 8.7 Hz, 2H), 6.90 (d, $J$ = 8.7 Hz, 2H), 4.48 (s, 2H), 3.81 (s, 3H), 2.09 (t, $J$ = 6.9 Hz, 2H), 1.37-1.25 (m, 2H), 0.72 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 196.1, 159.3, 155.0, 134.8, 129.2, 114.3, 95.4, 74.3, 58.8, 55.5, 20.9, 20.7, 13.1; MS (ESI) 260 ([M+H]$^+$); HRMS (MALDI) mass calcd. For

4-Cyclopropyl-1-(2,2-diethoxyethyl)-3-iodo-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Pale yellow solid (35% yield), following general procedure 2, method A. M.p. 72-74 °C. ¹H NMR (300 MHz, CDCl₃) δ 6.50 (s, 4H), 4.82 (t, J = 5.7 Hz, 1H), 3.76-3.66 (m, 2H), 3.57-3.47 (m, 2H), 3.31 (d, J = 5.4 Hz, 2H), 1.38-1.26 (m, 3H), 1.18 (t, J = 7.2 Hz, 6H), 0.99-0.94 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 184.1, 167.9, 158.9, 145.1, 132.0, 99.0, 88.0, 71.4, 62.8, 44.8, 15.0, 11.1, 7.6; MS (ESI) 466 ([M+Na]⁺); HRMS (MALDI) mass calcd. For C₁₈H₂₂INaNO₄ ([M+Na]⁺): 466.0486. Found 466.0490.

4-(tert-Butyl)-1-(2,2-diethoxyethyl)-3-iodo-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Modified general procedure 2, method A, N-(2,2-Diethoxyethyl)-N-(4-methoxyphenyl)-4,4-dimethylpent-2-ynamide (1.39 g, 4.0 mmol), CH₂Cl₂ 135 mL, ICl (408 uL, 8.0 mmol) in 80 mL CH₂Cl₂, stirred for 30 min, then the solution was slowly warmed to room temperature for 12h, quenched with saturated aqueous Na₂SO₃ solution and extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄, concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:PE, 1:3) to afford the product as a pale yellow
solid (380 mg, 28% yield); M.p. 148-150 °C. ¹H NMR (300 MHz, CDCl₃) δ 6.50 (s, 4H), 4.82 (t, J = 5.4 Hz, 1H), 3.76-3.66 (m, 2H), 3.55-3.45 (m, 2H), 3.15 (d, J = 5.7 Hz, 2H), 1.40 (s, 9H), 1.18 (t, J = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 184.2, 168.2, 166.1, 145.0, 132.2, 99.1, 96.1, 70.5, 63.3, 43.9, 36.0, 28.4, 15.2; MS (ESI) 482 ([M+Na]+); HRMS (MALDI) mass calcd. For C₁₉H₂₆INaNO₄ ([M+Na]+): 482.0799. Found 482.0801.

O

N

Ph

I

OEt

OEt

Me

Me

61

1-(2,2-Diethoxyethyl)-3-iodo-7,9-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Pale yellow solid (54% yield), following general procedure 2, method A. M.p. 153-155 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.27-7.21 (m, 3H), 7.13-7.10 (m, 2H), 6.22 (s, 2H), 4.80 (t, J = 5.7 Hz, 1H), 3.71-3.60 (m, 2H), 3.51-3.41 (m, 2H), 3.26 (d, J = 5.4 Hz, 2H), 1.77 (s, 3H), 1.12 (t, J = 6.9 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 185.3, 167.8, 160.0, 139.0, 138.8, 132.2, 129.6, 128.3, 127.5, 99.4, 96.9, 71.5, 63.0, 45.1, 16.0, 15.3; MS (ESI) 530 ([M+Na]+); HRMS (MALDI) mass calcd. For C₂₃H₂₆INaNO₄ ([M+Na]+): 530.0799. Found 530.0798.

O

N

Ph

I

O

1a

2-(3-Iodo-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

Pale yellow solid (86% yield), following general procedure 3. M.p. 93-95 °C. ¹H NMR (300 MHz, CDCl₃) δ 9.85 (s, 1H), 7.43-7.37 (m, 3H), 7.31 (d, J = 6.9 Hz, 2H), 6.64 (d, J = 9.6 Hz, 2H), 6.39 (d, J = 9.9 Hz, 2H), 4.21 (s, 2H); ¹³C NMR (75 MHz,
CDCl$_3$) $\delta$ 194.9, 183.5, 167.5, 159.3, 143.1, 133.0, 131.6, 130.2, 128.6, 127.5, 96.9, 70.1, 50.5; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2919, 1694, 1667, 1628, 1383, 1112, 1059, 724, 698; MS (ESI) 406 ([M+H]$^+$); HRMS (ESI) mass calcd. For C$_{17}$H$_{13}$INO$_3$ ([M+H]$^+$): 405.9935. Found 405.9939.

![1b](image)

2-(3-Iodo-2,8-dioxo-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

White solid (96% yield), following general procedure 3. M.p. 163-164 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.58 (s, 1H), 7.21 (m, 4H), 6.63 (d, $J$ = 9.6 Hz, 2H), 6.40 (d, $J$ = 9.6 Hz, 2H), 4.21 (s, 2H), 2.36 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 195.0, 183.6, 167.6, 159.2, 143.3, 140.5, 132.9, 129.3, 128.6, 127.4, 96.3, 70.0, 50.5, 21.3; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2921, 2854, 1733, 1699, 1667, 1627, 1507, 1386, 1060, 998, 873, 823, 749; MS (ESI) 420 ([M+H]$^+$); HRMS (ESI) mass calcd. For C$_{18}$H$_{15}$INO$_3$ 420.0091 ([M+H]$^+$). Found 420.0083.

![1c](image)

2-(3-Iodo-2,8-dioxo-4-(m-tolyl)-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

White solid (72% yield), following general procedure 3. M.p. 80-82 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.58 (s, 1H), 7.27-7.25 (m, 2H), 7.09-7.06 (m, 2H), 6.60 (d, $J$ = 9.9 Hz, 2H), 6.40 (d, $J$ = 10.2 Hz, 2H), 4.19 (s, 2H), 2.36 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.9, 183.6, 167.6, 159.6, 143.2, 138.4, 132.9, 131.5, 131.0, 128.5, 128.1, 124.5, 96.7, 70.1, 50.5, 21.3; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2922, 2854, 1733, 1700, 1668, 1629, 1507, 1385, 1061, 874, 823, 750; MS (ESI) 420 ([M+H]$^+$); HRMS
(MALDI) mass calcd. For C\textsubscript{18}H\textsubscript{15}INO\textsubscript{3} ([M+H]\textsuperscript{+}): 420.0091. Found 420.0105.

White solid (67% yield), following general procedure 3. M.p. 210-211 °C. \textsuperscript{1}H NMR (300 MHz, d\textsubscript{6}-DMSO) \(\delta\) 9.51 (s, 1H), 7.26 (s, 2H), 7.15 (s, 1H), 6.99 (d, \(J = 8.1\) Hz, 2H), 6.87 (d, \(J = 9.9\) Hz, 2H), 6.35 (d, \(J = 9.6\) Hz, 1H), 6.21(d, \(J = 9.6\) Hz, 1H), 4.20 (s, 2H), 2.19 (s, 3H); \textsuperscript{13}C NMR (75 MHz, d\textsubscript{6}-DMSO) \(\delta\) 198.3, 183.8, 167.4, 160.0, 144.2, 144.0, 135.5, 132.5, 132.0, 130.1, 130.4, 129.4, 128.4, 125.2, 100.8, 71.7, 50.9, 19.7; IR (thin film): \(\nu_{\text{max}}\) (cm\textsuperscript{-1}) = 2921, 1738, 1700, 1663, 1626, 1423, 1381, 1115, 1059, 741, 700; MS (ESI) 420 ([M+H]\textsuperscript{+}); HRMS (MALDI) mass calcd. For C\textsubscript{18}H\textsubscript{15}INO\textsubscript{3} ([M+H]\textsuperscript{+}): 420.0091. Found 420.0101.

White solid (96% yield), following general procedure 3. M.p. 186-188 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 9.56 (s, 1H), 7.33-7.29 (m, 2H), 7.07 (t, \(J = 8.4\) Hz, 2H), 6.59 (d, \(J = 9.6\) Hz, 2H), 6.38 (d, \(J = 10.2\) Hz, 2H), 4.18 (s, 2H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 194.7, 183.4, 167.4, 163.5 (d, \(J = 250.7\) Hz), 158.3, 143.1, 133.1, 129.8 (d, \(J = 8.6\) Hz), 127.6 (d, \(J = 4.0\) Hz), 116.1 (d, \(J = 22.1\) Hz), 97.5, 70.1, 50.6; IR (thin film): \(\nu_{\text{max}}\) (cm\textsuperscript{-1}) = 2920, 2127, 1706, 1663, 1627, 1503, 1383, 1231, 1159, 1062, 843; MS (ESI) 478 ([M+CH\textsubscript{3}OH+Na]\textsuperscript{+}); HRMS (ESI) mass calcd. For C\textsubscript{18}H\textsubscript{15}FI\textsubscript{2}NO\textsubscript{4} ([M+CH\textsubscript{3}OH+Na]\textsuperscript{+}): 478.0386. Found 478.0389.
2-(4-(4-Chlorophenyl)-3-iodo-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

White solid (82% yield), following general procedure 3. M.p. 180-181 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.58 (s, 1H), 7.38 (d, $J$ = 8.7 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 6.64 (d, $J$ = 10.2 Hz, 2H), 6.41 (d, $J$ = 9.9 Hz, 2H), 4.23 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.9, 182.3, 167.2, 158.0, 142.9, 136.2, 133.0, 129.9, 129.0, 128.9, 97.6, 69.9, 50.5; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2912, 1704, 1668, 1626, 1385, 1091; MS (ESI) 440 ([M+H]$^+$); HRMS (MALDI) mass calcd. For C$_{17}$H$_{12}$ClINO$_3$ ([M+H]$^+$): 439.9567. Found 439.9562.

2-(3-Iodo-2,8-dioxo-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

Yellow solid (81% yield), following general procedure 3. M.p. 165-167 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.56 (s, 1H), 7.69 (d, $J$ = 3.6 Hz, 1H), 7.57 (d, $J$ = 5.1 Hz, 1H), 7.12 (t, $J$ = 5.2 Hz, 1H), 6.69 (d, $J$ = 9.6 Hz, 2H), 6.53 (d, $J$ = 9.6 Hz, 2H), 4.20 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 195.2, 183.6, 167.4, 150.3, 144.2, 132.6, 132.1, 129.8, 129.6, 127.4, 91.8, 68.6, 49.7; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2919, 1665, 1628, 1383, 1062, 711; MS (ESI) 410 ([M-H]$^-$); HRMS (MALDI) mass calcd. For C$_{15}$H$_{11}$INO$_3$S ([M+H]$^+$): 411.9499. Found 411.9514.
2-(3-Iodo-4-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

Pale yellow solid (96% yield), following general procedure 3. M.p. 92-94 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.56 (s, 1H), 6.51 (s, 4H), 4.20 (s, 2H), 1.94 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 195.3, 183.5, 167.4, 157.8, 143.7, 132.8, 94.9, 70.0, 50.6, 15.3; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2923, 1733, 1690, 1665, 1626, 1387, 1063; MS (ESI) 344 ([M+H]$^+$); HRMS (ESI) mass calcd. For C$_{12}$H$_{11}$INO$_3$ 343.9778 ([M+H]$^+$). Found 343.9785.

2-(3-Iodo-2,8-dioxo-4-propyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

White solid (54% yield), following general procedure 2, method B. M.p. 150-152 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.55 (s, 1H), 6.53-6.45 (m, 4H), 4.16 (s, 2H), 2.18 (t, $J$ = 7.8 Hz, 2H), 1.59-1.48 (m, 2H), 0.97 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 195.1, 183.8, 167.6, 161.2, 143.6, 132.9, 95.4, 70.2, 50.6, 31.5, 21.6, 14.2; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2926, 2853, 1699, 1667, 1626, 1414, 1385, 1307, 1058, 850; MS (ESI) 372 ([M+H]$^+$); HRMS (MALDI) mass calcd. For C$_{14}$H$_{15}$INO$_3$ ([M+H]$^+$): 372.0091. Found 372.0103.
2-(4-Cyclopropyl-3-iodo-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

Yellow solid (81% yield), following general procedure 3. M.p. 166-168 °C. \(^\text{1}^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.53 (s, 1H), 6.55-6.48 (m, 4H), 4.12 (s, 2H), 1.38-1.36 (m, 3H), 1.02-0.98 (m, 2H); \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 195.2, 183.9, 167.8, 160.2, 144.1, 132.9, 88.0, 70.5, 50.4, 11.9, 8.0; IR (thin film): \(v_{\text{max}}\) (cm\(^{-1}\)) = 2921, 2857, 1737, 1699, 1666, 1627, 1414, 1384, 1308, 1058, 1110; MS (ESI) 368 ([M-H]\(^-\)); HRMS (MALDI) mass calcd. For C\(_{14}\)H\(_{13}\)INO\(_3\) ([M+H]\(^+\)): 369.9935. Found 369.9938.

2-(4-(tert-Butyl)-3-iodo-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-1-yl)acetaldehyde

Pale yellow solid (67% yield), following general procedure 3. M.p. 187-189 °C. \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.48 (s, 1H), 6.59 (d, \(J = 10.2\) Hz, 2H), 6.48 (d, \(J = 9.9\) Hz, 2H), 4.00 (s, 2H), 1.42 (s, 9H); \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 195.0, 183.8, 167.8, 166.9, 144.3, 132.2, 95.2, 69.6, 49.2, 36.0, 28.4; IR (thin film): \(v_{\text{max}}\) (cm\(^{-1}\)) = 2944, 2866, 1723, 1694, 1664, 1625, 1417, 1390, 1307, 1052, 1009, 878, 850, 796, 750; MS (ESI) 384 ([M-H]\(^-\)); HRMS (MALDI) mass calcd. For C\(_{15}\)H\(_{17}\)INO\(_3\) ([M+H]\(^+\)): 386.0248. Found 386.0256.
2-(3-Iodo-7,9-dimethyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-1-yl) acetaldehyde

Off white solid (96% yield), following general procedure 3. M.p. 214-216 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.56 (s, 1H), 7.42-7.34 (m, 3H), 7.26-7.24 (m, 2H), 6.32 (s, 2H), 4.13 (s, 2H), 1.85 (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 195.2, 184.9, 167.3, 160.3, 140.0, 137.5, 131.8, 129.8, 128.4, 127.3, 95.8, 70.5, 50.3, 15.8; IR (thin film): \(\nu_{\text{max}}\) (cm\(^{-1}\)) = 2920, 2838, 1729, 1692, 1668, 1638, 1388, 1037, 913, 756, 699; MS (ESI) 434 ([M+H]\(^+\)); HRMS (MALDI) mass calcd. For C\(_{19}\)H\(_{17}\)INO\(_3\) ([M+H]\(^+\)): 434.0248. Found 434.0255.

**General procedure for desymmetrization of cyclohexadienones via intramolecular Stetter reaction**

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added triazolium salt \(E\) (9.7 mg, 0.02 mmol, 10 mol%), \(o\)-xylene (2.0 mL), DIEA (3.3 \(uL\), 0.02 mmol, 10 mol%). The reaction mixture was stirred at 25°C for 20 minutes. The substrate (0.2 mmol) was then added. After the reaction was complete (monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product.
(6aS,10aR)-2-Iodo-1-phenyl-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 81% yield, 91% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, v = 0.7 mL min⁻¹, λ = 254 nm, t (major) = 22.9 min, t (minor) = 30.4 min]; [α]D²⁰ = +94 (c = 0.1, CHCl₃). M.p. 225 °C (decomposed). ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.44 (m, 3H), 7.30-7.29 (m, 2H), 6.62 (d, J = 10.2 Hz, 2H), 6.20 (d, J = 9.9 Hz, 2H), 4.45 (d, J = 18.9 Hz, 1H), 3.63 (d, J = 18.9 Hz, 1H), 2.96-2.87 (m, 2H), 2.12 (dd, J = 18.0, 6.6 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 208.8, 192.5, 169.5, 164.4, 143.2, 133.7, 132.4, 130.2, 129.1, 127.1, 97.5, 72.4, 50.9, 50.1, 32.7; IR (thin film): νmax (cm⁻¹) = 2922, 1765, 1707, 1682, 1632, 1382, 1346, 1255, 1098, 765, 696; MS (ESI) 406 ([M+H]+); HRMS (MALDI) calcd for C₁₇H₁₃INO₃ ([M+H]+): 405.9935. Found: 405.9947.

(6aS,10aR)-2-Iodo-1-(p-tolyl)-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 55% yield, 80% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, v = 0.8 mL min⁻¹, λ = 254 nm, t (major) = 26.4 min, t (minor) = 34.9 min]; [α]D²⁰ = +62 (c = 0.2, CHCl₃). M.p. 174-176 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.26 (d, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 6.63 (d, J = 10.2 Hz, 2H), 6.24 (d, J = 9.9 Hz, 2H), 4.47 (d, J = 19.2 Hz, 1H), 3.64 (d, J = 18.6 Hz, 2H), 2.96 (d, J = 17.7 Hz, 1H), 2.86 (d, J = 5.7 Hz, 1H), 2.40 (s, 3H), 2.16 (dd, J = 18.0, 6.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 208.9, 192.6, 169.7, 164.6, 143.4, 140.6, 133.7, 129.8, 129.4,
127.0, 97.0, 72.5, 51.2, 50.2, 32.8, 21.4; IR (thin film): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 2921, 1766, 1633, 1381, 1078, 778, 694; \) MS (ESI) 420 ([M+H]⁺); HRMS (MALDI) calcd for C₁₈H₁₅INO₃ ([M+H]⁺): 420.0091. Found: ([M+H]⁺) 420.0103.

![Chemical Structure](image)

(6aS,10aR)-2-Iodo-1-(o-tolyl)-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

Pale yellow solid, 60% yield, 71% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, \( v = 0.8 \text{ mL} \cdot \text{min}^{-1}, \lambda = 254 \text{ nm}, t_{(\text{major})} = 24.7 \text{ min}, t_{(\text{minor})} = 30.1 \text{ min}]; [\alpha]_{D}^{20} = +75 (c = 0.2, \text{CHCl}_3). \text{M.p.} 176-178 \text{oC.} \text{^1H NMR (300 MHz, CDCl3)} \delta 7.38-7.28 (m, 2H), 7.10-7.08 (m, 2H), 6.62 (d, \( J = 10.5 \text{ Hz} \), 2H), 6.22 (d, \( J = 10.2 \text{ Hz} \), 2H), 4.47 (d, \( J = 19.2 \text{ Hz} \), 1H), 3.64 (d, \( J = 19.2 \text{ Hz} \), 2H), 2.97 (d, \( J = 18.6 \text{ Hz} \), 1H), 2.87 (d, \( J = 6.9 \text{ Hz} \), 1H), 2.39 (s, 3H), 2.17 (dd, \( J = 18.0, 6.9 \text{ Hz} \), 1H); \text{^13C NMR (75 MHz, CDCl3)} \delta 208.8, 192.6, 169.7, 164.8, 143.3, 139.0, 133.7, 132.4, 131.1, 129.1, 127.6, 124.1, 97.3, 72.5, 51.1, 50.2, 32.8, 21.4; IR (thin film): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 2922, 2853, 1768, 1672, 1634, 1382, 1256, 1092, 777, 691; \) MS (ESI) 420 ([M+H]⁺); HRMS (MALDI) calcd for C₁₈H₁₅INO₃ ([M+H]⁺): 420.0091. Found: 420.0106.

![Chemical Structure](image)

(6aS,10aR)-2-Iodo-1-(o-tolyl)-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 52% yield, 89% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, \( v = 0.8 \text{ mL} \cdot \text{min}^{-1}, \lambda = 254 \text{ nm}, t_{R} \text{ (major)} = 22.8, 27.7 \text{ min}, t_{R} \text{ (minor)} = 34.9, 39.3 \text{ min}]; [\alpha]_{D}^{20} = +110 (c = 0.2, \text{CH}_2\text{Cl}_2). \text{M.p.} 227-229 \text{oC.} \text{^1H NMR (300 MHz,}
CDCl₃ δ 7.41-7.20 (m, 6H), 7.07 (d, J = 7.5 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 10.2 Hz, 1H), 6.54 (d, J = 9.9 Hz, 1H), 6.19 (d, J = 10.2 Hz, 1H), 6.06 (d, J = 10.2 Hz, 1H), 4.53 (d, J = 6.9 Hz, 1H), 4.46 (d, J = 7.2 Hz, 1H), 3.66 (d, J = 19.2 Hz, 2H), 3.10-3.04 (m, 2H), 2.98-2.87 (m, 2H), 2.49 (dd, J = 18.3, 7.5 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 2.02 (dd, J = 17.7, 7.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 208.65, 208.64, 208.37, 192.3, 192.2, 169.29, 169.27, 165.9, 164.9, 143.1, 135.3, 134.3, 133.8, 133.3, 131.8, 131.3, 131.2, 131.0, 130.2, 129.9, 127.6, 126.3, 126.2, 126.0, 99.65, 99.55, 73.4, 73.1, 51.3, 51.0, 50.2, 50.1, 32.9, 32.1, 20.0, 19.8; IR (thin film): ν max (cm⁻¹) = 2922, 2167, 1685, 1623, 1363, 1255, 1083, 986, 765, 693; MS (ESI) 420 ([M+H⁺]); HRMS (MALDI) calcd for C₁₈H₁₅INO₃ ([M+H⁺]): 420.0091. Found: 420.0102.

(6aS,10aR)-1-(4-Fluorophenyl)-2-iodo-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 55% yield, 84% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, v = 0.8 mL min⁻¹, λ = 254 nm, t (major) = 30.3 min, t (minor) = 38.6 min]; [α]D²⁰ = +128 (c = 0.1, CHCl₃). M.p. 195-197 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.33 (m, 2H), 7.18 (t, J = 8.4 Hz, 2H), 6.63 (dd, J = 9.9, 1.2 Hz, 2H), 6.26 (d, J = 10.2 Hz, 2H), 4.48 (dd, J = 18.9, 1.5 Hz, 1H), 3.66 (d, J = 18.9 Hz, 2H), 2.99 (d, J = 18.0 Hz, 1H), 2.86 (d, J = 6.9 Hz, 1H), 2.15 (ddd, J = 18.0, 7.2, 1.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 208.5, 192.2, 169.4, 163.5 (d, J = 251.0 Hz), 162.3, 143.1, 134.0, 129.4 (d, J = 8.6 Hz), 128.4 (d, J = 3.4 Hz), 116.6 (d, J = 21.9 Hz), 98.2 (d, J = 0.7 Hz), 72.4 (d, J = 0.8 Hz), 51.1, 50.2, 32.7, 25.3; IR (thin film): ν max (cm⁻¹) = 2921, 2853, 1765, 1707, 1638, 1504, 1382, 1346, 1232, 1160, 1099, 985, 848, 784, 697; MS (ESI) 424 ([M+H⁺]); HRMS (MALDI) calcd for C₁₇H₁₂FINO₃ ([M+H⁺]): 423.9840.
Found: 423.9848.

(6aS,10aR)-1-(4-Chlorophenyl)-2-iodo-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

Pale yellow solid, 54% yield, 86% ee [Daicel Chiralcel OD-H, n-hexane /2-propanol = 60/40, v = 0.8 mL min⁻¹, λ = 254 nm, t (major) = 33.8 min, t (minor) = 42.3 min]; [α]D²⁰ = +105 (c = 0.1, CHCl₃). M.p. 107-109 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 6.62 (d, J = 10.2 Hz, 1H), 6.26 (d, J = 9.9 Hz, 1H), 4.48 (d, J = 18.6 Hz, 1H), 3.66 (d, J = 18.9 Hz, 1H), 3.00 (d, J = 17.7 Hz, 1H), 2.84 (d, J = 6.0 Hz, 1H), 2.16 (dd, J = 18.0, 6.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 208.4, 192.1, 169.3, 163.1, 142.9, 136.7, 134.1, 130.8, 129.7, 128.6, 98.4, 72.4, 51.2, 50.2, 32.7; IR (thin film): νmax (cm⁻¹) = 2920, 1767, 1683, 1633, 1428, 1380, 1092, 876, 615; MS (ESI) 440 ([M+H]⁺); HRMS (MALDI) calcd for C₁₇H₁₂ClINO₃ ([M+H]⁺): 439.9545. Found: 439.9557.

(6aS,10aR)-2-Iodo-1-(thiophen-2-yl)-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

Yellow solid, 54% yield, 75% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, v = 0.8 mL min⁻¹, λ = 254 nm, t (major) = 39.1 min, t (minor) = 64.9 min]; [α]D²⁰ = +70 (c = 0.1, CHCl₃). M.p. 201-202 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80
(d, J = 4.0 Hz, 1H), 7.61 (d, J = 4.8 Hz, 1H), 7.20 (t, J = 4.8 Hz, 1H), 6.69 (dd, J = 10.0, 0.8 Hz, 1H), 6.40 (d, J = 10.4 Hz, 1H), 4.49 (dd, J = 19.2, 4.0 Hz, 1H), 3.63 (d, J = 18.8 Hz, 1H), 3.13 (d, J = 18.0 Hz, 1H), 2.91 (d, J = 7.6 Hz, 1H), 2.73 (dd, J = 18.4, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 209.2, 192.9, 170.0, 155.6, 144.1, 134.6, 133.0, 130.2, 127.9, 93.9, 72.2, 51.2, 50.0, 33.4; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2920, 2850, 1766, 1692, 1675, 1631, 1384, 1254, 1096, 712; MS (ESI) 412 ([M+H]$^+$); HRMS (MALDI) calcd for C$_{15}$H$_{11}$INO$_3$S ([M+H]$^+$): 410.9499. Found: 411.9510.

![2h](image)

(6aS,10aR)-2-Iodo-1-methyl-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 58% yield, 86% ee [Daicel Chiralpak IC, n-hexane/2-propanol = 60/40, $v$ = 0.8 mL min$^{-1}$, $\lambda$ = 254 nm, t (major) = 50.3 min, t (minor) = 69.9 min]; $[\alpha]_D^{20} = +182$ (c = 0.2, CHCl$_3$). M.p. 83-85 $^\circ$C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.42 (dd, J = 10.5, 0.9 Hz, 1H), 6.29 (d, J = 10.5 Hz, 1H), 4.42 (d, J = 18.9 Hz, 1H), 3.59 (d, J = 19.2 Hz, 1H), 3.21 (dt, J = 17.1, 4.5 Hz, 1H), 2.74-2.67 (m, 2H), 2.19 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.8, 192.4, 170.0, 163.0, 144.2, 133.8, 96.0, 71.8, 50.8, 50.2, 32.6, 17.1; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$): 2921, 2848, 1766, 1683, 1633, 1383, 1259, 1104; MS (ESI) 365 ([M+Na]$^+$); HRMS (MALDI) calcd for C$_{12}$H$_{10}$INaNO$_3$ ([M+Na]$^+$): 365.9598. Found: 365.9603.

![2i](image)

(6aS,10aR)-2-Iodo-1-propyl-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione
Pale yellow solid, 60% yield, 85% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, \( v = 0.8 \text{ mL} \cdot \text{min}^{-1}, \lambda = 254 \text{ nm}, \text{t (major)} = 19.4 \text{ min}, \text{t (minor)} = 23.7 \text{ min}]; [\alpha]_{D}^{20} = +236 (c = 0.1, \text{CHCl}_3). \text{M.p. 186-187} ^\circ \text{C.} ^1\text{H NMR (400 MHz, CDCl}_3) \delta 6.41 (dd, J = 10.4, 1.2 \text{ Hz}, 1H), 6.28 (d, J = 10.4 \text{ Hz}, 1H), 4.41 (d, J = 18.8 \text{ Hz}, 1H), 3.58 (d, J = 19.2 \text{ Hz}, 1H), 3.21 (dt, J = 16.8, 4.8 \text{ Hz}, 1H), 2.77-2.70 (m, 2H), 2.48-2.40 (m, 2H), 1.68-1.59 (m, 2H), 1.05 (t, J = 7.2 \text{ Hz}, 3H); ^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 208.9, 192.5, 169.9, 166.4, 144.2, 133.5, 96.2, 71.9, 50.7, 49.9, 32.84, 32.83, 21.7, 14.4; IR (thin film): \nu_{\text{max}} (\text{cm}^{-1}) = 2924, 1768, 1696, 1634, 1260, 1079, 778, 693; \text{MS (ESI) 372 ([M+H]}^+); \text{HRMS (MALDI) calcd for C}_{14}\text{H}_{15}\text{INO}_3 ([M+H]}^+): 372.0091. \text{Found: 372.0105.}

(6aS,10aR)-1-Cyclopropyl-2-iodo-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 85% yield, 88% ee [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, \( v = 0.8 \text{ mL} \cdot \text{min}^{-1}, \lambda = 254 \text{ nm}, \text{t (major)} = 25.2 \text{ min}, \text{t (minor)} = 33.1 \text{ min}]; [\alpha]_{D}^{20} = +177 (c = 0.1, \text{CHCl}_3). \text{M.p. 201-203} ^\circ \text{C.} ^1\text{H NMR (300 MHz, CDCl}_3) \delta 6.47 (d, J = 10.2 \text{ Hz}, 1H), 6.31 (d, J = 10.2 \text{ Hz}, 1H), 4.41 (d, J = 18.9 \text{ Hz}, 1H), 3.57 (d, J = 19.2 \text{ Hz}, 1H), 3.23 (d, J = 17.4 \text{ Hz}, 1H), 2.89-2.77 (m, 2H), 1.66-1.49 (m, 2H), 1.44-1.36 (m, 2H), 1.20-1.05 (m, 2H); ^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 209.1, 192.8, 170.3, 164.9, 144.6, 133.6, 87.6, 72.9, 51.0, 50.1, 32.8, 11.9, 8.2, 7.7; IR (thin film): \nu_{\text{max}} (\text{cm}^{-1}) = 2921, 1763, 1698, 1677, 1638, 1382, 1355, 1258, 1208, 1099, 1029, 779, 761, 714; \text{MS (ESI) 370 ([M+H]}^+); \text{HRMS (MALDI) calcd for C}_{14}\text{H}_{13}\text{INO}_3 ([M+H]}^+): 369.9935. \text{Found: 369.9942.}
(6aS,10aR)-1-(tert-Butyl)-2-iodo-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 75% yield, 94% ee [Daicel Chiralcel OD-H, \( n \)-hexane/2-propanol = 60/40, \( v \) = 0.8 mL \( \cdot \) min\(^{-1} \), \( \lambda \) = 254 nm, t (major) = 23.4 min, t (minor) = 30.8 min]; \([\alpha]_D^{20} = +153 \) (c = 0.2, CHCl\(_3\)). M.p. 203-205 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 6.50 (dd, \( J = 10.5, \ 1.2 \) Hz, 1H), 6.27 (d, \( J = 10.2 \) Hz, 1H), 4.44 (dd, \( J = 19.2, \ 0.9 \) Hz, 1H), 3.50 (d, \( J = 19.2 \) Hz, 1H), 3.23 (d, \( J = 18.3 \) Hz, 1H), 3.09-3.00 (m, 1H), 2.88 (d, \( J = 7.5 \) Hz, 2H), 1.50 (s, 9H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 210.1, 192.9, 171.5, 169.8, 145.5, 132.9, 96.3, 73.3, 49.6, 48.8, 35.9, 35.0, 29.6; IR (thin film): \( \nu_{\text{max}} \) (cm\(^{-1}\)): 2921, 1744, 1676, 1512, 1460, 1382, 1250, 1088, 776, 694; MS (ESI) 386 ([M+H\(^+\)]\(^+\)); HRMS (MALDI) calcd for C\(_{15}\)H\(_{17}\)INO\(_3\) ([M+H\(^+\)]\(^+\)): 386.0248. Found: 386.0260.

(6aS,7S,10aR)-2-Iodo-7,9-dimethyl-1-phenyl-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

White solid, 9% yield, 99% ee [Daicel Chiralcel OD-H, \( n \)-hexane/2-propanol = 60/40, \( v \) = 0.8 mL \( \cdot \) min\(^{-1} \), \( \lambda \) = 254 nm, t (major) = 22.0 min, t (minor) = 70.4 min]; M.p. 215-217 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.47-7.45 (m, 3H), 7.27-7.23 (m, 2H), 6.49 (s, 1H), 4.49 (d, \( J = 18.9 \) Hz, 1H), 3.64 (d, \( J = 18.9 \) Hz, 1H), 1.91 (s, 3H); \(^1\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 209.5, 196.6, 169.4, 165.1, 140.5, 137.5, 133.4, 130.2, 129.0, 127.9, 98.4, 73.6, 57.6,
49.8, 37.9, 17.7, 16.7; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2922, 1764, 1704, 1679, 1625, 1368, 1119, 758, 697; MS (ESI) 434 ([M+H$^+$]); HRMS (MALDI) calcd for C$_{19}$H$_{17}$INO$_3$ ([M+H$^+$]): 434.0248. Found: 434.0256.

NOE experiment of 2l:

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{Ph} & \quad \text{O} \\
\text{Tol} & \quad 2\text{a} \\
\end{align*}
\]

(6aS,10aR)-1-Phenyl-2-(p-tolylethynyl)-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5 H)-trione

Under argon, compound 2a (40.5 mg, 0.1 mmol), CuI (5.7 mg, 0.03 mmol) and PdCl$_2$(PPh$_3$)$_2$ (21.0 mg, 0.03 mmol) were placed in a Schlenk tube equipped with a stir bar. Then Et$_3$N/toluene (2mL/2mL) and 4-ethynyltoluene (116.0 mg, 1.0 mmol) were added. The reaction was stirred at room temperature for 48h. After the reaction was complete, the reaction mixture was filtrated over a pad of celite, and extracted with CH$_2$Cl$_2$. The combined organic layers were dried over Na$_2$SO$_4$. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc:PE, 1:2) affording compound 2aa as a white solid (30 mg, 76% yield, 98% ee). [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, $v$ = 0.8 mL·min$^{-1}$, $\lambda$ = 254 nm, t (major) = 20.6 min, t (minor) = 28.0 min]; $[\alpha]_D^{20} = +200$ (c = 0.1, CHCl$_3$). M.p. 186-188 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.76
(d, J = 6.3 Hz, 2H), 7.51-7.43 (m, 3H), 7.35 (d, J = 7.2 Hz, 2H), 7.14 (d, J = 7.2 Hz, 2H), 6.75 (d, J = 9.9 Hz, 1H), 6.34 (d, J = 9.9 Hz, 1H), 4.50 (d, J = 19.2 Hz, 1H), 3.60 (d, J = 19.2 Hz, 1H), 3.04 (d, J = 19.2 Hz, 1H), 2.87 (d, J = 6.6 Hz, 3H), 2.41-2.36 (m, 4H); 13C NMR (75 MHz, CDCl3) δ 209.5, 193.0, 169.9, 159.2, 145.0, 139.9, 133.6, 132.0, 131.8, 130.7, 129.2, 129.0, 127.6, 120.1, 118.7, 99.9, 80.0, 69.3, 51.3, 49.6, 33.3, 21.6; IR (thin film): νmax (cm⁻¹) = 2918, 2850, 1767, 1717, 1693, 1637, 1413, 1385, 1342, 1211, 816, 767, 693; MS (ESI) 394 ([M+H]+); HRMS (MALDI) calcd for C26H20NO3 ([M+H]+): 394.1438. Found: 394.1447.

(6aS,10aR)-1-Phenyl-2-(p-tolyl)-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

Under argon, Pd(OAc)2 (4.8 mg, 0.02 mmol), PPh3 (12.8 mg, 0.04 mmol), 4-tolylboronic acid (20.4 mg, 0.15 mmol), compound 2a (40.5 mg, 0.1 mmol) and K2CO3 (27.8 mg, 0.2 mmol) were placed in a Schlenk tube equipped with a stir bar. Benzene/H2O (5/1, 4.8 mL) was added, and the resulting heterogeneous reaction mixture was stirred vigorously for 48 hours at 60 °C. The reaction mixture was then filtered through a short pad of celite and concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (EtOAc:PE, 1:2) to afford compound 2ab as a white solid (36.0 mg, 97% yield, 98% ee). [Daicel Chiralcel OD-H, n-hexane/2-propanol = 60/40, ν = 0.8 mL.min⁻¹, λ = 254 nm, t (major) = 21.2 min, t (minor) = 29.0 min]; [α]D²⁰ = +193 (c = 0.1, CHCl3). M.p. >250 °C. 1H NMR (300 MHz, CDCl3) δ 7.35 (m, 5H), 7.17 (d, J = 5.7 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.67 (d, J = 9.9 Hz, 1H), 6.21 (d, J = 10.5 Hz, 1H), 4.54 (d, J = 18.6 Hz, 1H), 3.64 (d, J = 18.9 Hz, 1H), 2.99 (d, J = 18.0 Hz, 1H), 2.88 (d, J = 7.2 Hz, 1H), 2.31 (s, 3H), 2.20 (dd, J = 18.0, 7.2 Hz, 1H); 13C NMR (75 MHz, CDCl3) δ 210.0,
193.0, 172.0, 154.7, 145.0, 138.9, 134.1, 133.6, 132.7, 129.4, 129.19, 129.16, 129.0, 127.9, 126.8, 68.9, 51.3, 49.8, 33.0, 21.3; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$): 2922, 2852, 1769, 1696, 1696, 1635, 1378, 1333, 1085, 775, 696; MS (EI, m/z, rel. intensity) 369 ($[M]^+\,$, 100), 312 (56); HRMS (EI) calcd for C$_{24}$H$_{19}$NO$_3$ ($[M]^+$): 369.1365. Found: 369.1364.

(6aS,10aR)-1-Phenyl-6a,7-dihydropyrrolo[2,1-i]indole-3,6,8(5H)-trione

CH$_3$OH/CH$_2$Cl$_2$ (4 mL/1 mL) was added to a Schlenk tube containing compound 2a (40.5 mg, 0.1 mmol) equipped with a stir bar, then 10% Pd/C (20 mg, 50% wt) was added. The vial was sealed up, and then it was evacuated and filled with hydrogen (three cycles). The reaction was stirred at room temperature for 120h. After the reaction was complete, the reaction mixture was filtrated over a pad of celite and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc:PE, 1:2) to afford compound 2ac as a white solid (26.0 mg, 64% yield, 99% ee). \([\alpha]_D^{20} = +92 \text{ (c = 0.1, CHCl}_3\text{). M.p. 183-185 °C.}^{1}$ H NMR (300 MHz, CDCl$_3$) $\delta$ 7.54-7.43 (m, 5H), 6.75 (d, $J = 9.9$ Hz, 1H), 6.54 (s, 1H), 6.35 (d, $J = 10.2$ Hz, 1H), 4.45 (d, $J = 18.6$ Hz, 1H), 3.56 (d, $J = 19.2$ Hz, 1H), 3.10 (d, $J = 19.3$ Hz, 1H), 2.82 (d, $J = 6.6$ Hz, 1H), 2.55 (dd, $J = 18.0$, 7.2 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 210.1, 193.1, 172.4, 162.4, 145.3, 133.4, 131.7, 130.9, 129.3, 126.8, 124.1, 70.1, 51.1, 49.2, 33.4; IR (thin film): $\nu_{\text{max}}$ (cm$^{-1}$) = 2920, 2852, 1762, 1634, 1444, 1380, 768, 694; MS (EI, m/z, rel. intensity) 279 ($[M]^+$, 22), 251 (100), 223 (33), 167 (57); HRMS (EI) calcd for C$_{17}$H$_{13}$NO$_3$ ($[M]^+$): 279.0895. Found: 279.0901.

X-ray of enantiopure (6aS,10aR)-2a
Table 1. Crystal data and structure refinement for cd211527.

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<th>Value</th>
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<td>Wavelength</td>
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<td>Volume</td>
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<td>Z, Calculated density</td>
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<td>F(000)</td>
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<td>Full-matrix least-squares on F²</td>
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<td>Largest diff. peak and hole</td>
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NMR and HPLC Spectra

[Image of NMR spectra and molecular structure]
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2a

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<th>Peak Area</th>
<th>Percent</th>
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<table>
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<th>R. Time</th>
<th>Peak Height</th>
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<th>Percent</th>
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**2d**

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Peak No.</th>
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<th>Peak Area (a.u.)</th>
<th>Percent</th>
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![Graph with Data](image)

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**Figure 1**

![Diagram of molecule 2e](image)

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**Figure 2**

![Graph of chromatogram](image)

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### Table 1: Peak Analysis

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### Table 2: Peak Analysis

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### Table 1: Peak Data

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![Chemical Structure](image1.png)

2j

![Graph](image2.png)

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![Graph](image3.png)

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2k

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<table>
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<table>
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<td>2</td>
<td>66.183</td>
<td>91.556</td>
<td>22356.002</td>
<td>0.6109</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>42670.615</strong></td>
<td><strong>3659591.252</strong></td>
<td><strong>100.0000</strong></td>
<td><strong>100.0000</strong></td>
</tr>
</tbody>
</table>
### Peak No. | R. Time | Peak Height | Peak Area | Percent
--- | --- | --- | --- | ---
1 | 43.558 | 97660.727 | 13425020.000 | 99.2866
2 | 76.732 | 578.410 | 96467.695 | 0.7134
**Total** | | 98239.137 | 13521487.695 | 100.0000

2ac