# Stereoselective Copper-Catalyzed Heteroarene C–H Functionalization/Michael-Type Annulation Cascade With α-Diazocarbonyls

## Supporting Information

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#### **General Procedures**

Unless stated otherwise, all reactions were performed in oven- or flame-dried glassware under an atmosphere of dry nitrogen. Dry acetonitrile (CH<sub>3</sub>CN), dichloromethane, and toluene were by passing previously-degassed solvents through activated alumina columns. these N,Ndimethylformamide (DMF) was obtained from Sigma Aldrich SureSeal<sup>TM</sup> bottles. All other reagents were used as received from commercial sources, unless stated otherwise. Silicon oil bath was used as the heat source for the reactions performing above room temperature. Reactions were monitored by thin layer chromatography (TLC) on Silicycle Siliaplate<sup>TM</sup> glass-backed TLC plates (250 µm thickness, 60 Å porosity, F254 indicator) and visualized by UV irradiation or development with anisaldehyde stain. Volatile solvents were removed under reduced pressure with a rotary evaporator. All flash column chromatography was performed using Silicycle SiliaFlash® F60, 230-400 mesh silica gel (40-63 µm). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with Bruker AV, spectrometers operating at 300 or 500 MHz for <sup>1</sup>H (75, and 125 MHz for <sup>13</sup>C) in chloroform-d (CDCl<sub>3</sub>). Chemical shifts for <sup>1</sup>H NMR are reported relative to the signal of tetramethylsilane (TMS) at  $\delta = 0$  ppm (internal standard). Chemical shifts for <sup>13</sup>C NMR are reported relative to the center line of residual solvent signal (CDCl<sub>3</sub>) at  $\delta$  = 77.16 ppm. NMR data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Splitting is reported with the following symbols: s = singlet, bs = broad singlet, d = doublet, t = triplet, app t = apparent triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublets, m = multiplet. Note; unless otherwise stated, for simplicity AA'BB' systems are reported as pseudo doublets. Infrared (IR) spectra were recorded on Bruker Alpha and Bruker Tensor 27 FT-IR spectrometers. High resolution mass spectrometry (HRMS) data were obtained using an Agilent 6200 series instrument, employing a TOF mass analyzer. Melting Points (M.P.) were obtained in open glass capillaries on an OptiMelt instrument (a digital apparatus) produced by Stanford Research Systems by scanning temperature ranges from 40 - 150 °C at a rate of 3 °C/s.

#### Synthesis and Characterization of Indole Starting Materials:



Figure S1: General Synthetic Scheme for the Synthesis of Alkynyl-Ester Substituted Indoles



Substituted indole S1-S4 (1.0 equiv) was added to a round-bottom flask equipped with a magnetic stir bar and dissolved in THF (0.2 M) under an N<sub>2</sub> atmosphere. The solution was cooled to -78 °C on acetone/dry ice cooling bath, and *n*-BuLi (2.5 M in hexanes, 1.5 equiv) was slowly added dropwise using a syringe on the side of RBF. The resulting reaction mixture was stirred for 30 min at the same temperature, before dropwise addition of the desired chloroformate (1.5 equiv) at -78 °C. The reaction mixture was stirred for another 1.5 h, during which temperature reached -20 °C. The reaction was quenched with sat. aq. NH<sub>4</sub>Cl and allowed to warm to room temperature. The mixture was extracted twice with Et<sub>2</sub>O. The organic layers were then combined and washed with water, then brine, and then dried over MgSO<sub>4</sub>. The solution was concentrated in vacuo, and the resulting crude material was purified by flash chromatography to yield **1a-g and S5**.



1a was prepared using General Experimental Procedure A. Reagents employed: 5-methoxy *N*-Propargyl skatole S1 (1.60 g, 8.03 mmol), *n*-BuLi (4.81 mL, 12.1 mmol), Methyl chloroformate (0.930 mL, 12.1 mmol). 1a (1.30 g, 5.05 mmol, 63%) was obtained as thick light brown color oil:

 $\mathbf{R_f} = 0.30, 20\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta = \delta$  7.20 (d, J = 8.8 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.91 (dd, J = 8.8, 2.4 Hz, 1H), 6.88 (s, 1H), 4.90 (s, 2H), 3.87 (s, 3H), 3.74 (s, 3H), 2.28 (s, 2H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 153.9$ , 153.8, 131.1, 129.4, 125.9, 111.9, 110.7, 109.6, 101.1, 85.8, 75.9, 55.9, 52.7, 20.7, 9.6 ppm; IR (neat):  $v_{max} = 2951$ , 2836, 2240, 1711, 1485, 1389, 1250, 1224, 1039, 748 cm<sup>-1</sup>;

**HRMS (APPI+)**: calc'd for C<sub>15</sub>H<sub>16</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 258.1125, found 258.1124.



**1b** was prepared using General Experimental Procedure A. Reagents employed: *N*-Propargyl skatole **S2** (0.800 g, 4.73 mmol), *n*-BuLi (2.80 mL, 7.10 mmol), Methyl chloroformate (0.550 mL, 7.10 mmol). **1b** (579 mg, 2.55 mmol, 54%) was obtained as thick light brown color oil:

**R**<sub>f</sub> = 0.35, 20% EtOAc in hexanes; <sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.57 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.32 – 7.22 (m, 2H), 7.17 – 7.12 (m, 1H), 6.89 (d, *J* = 1.2 Hz, 1H), 4.91 (s, 2H), 3.73 (s, 3H), 2.31 (d, *J* = 1.1 Hz, 3H) ppm; <sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  = 153.5, 136.3, 129.4, 124.8, 122.3, 119.6, 119.4, 112.2, 109.0, 81.8, 76.2, 53.0, 35.5, 9.7 ppm; **IR (neat)**: v<sub>max</sub> = 2919, 2241, 1711, 1462, 1250, 1034, 879, 738 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub> [M]<sup>+</sup> 227.0946, found 227.0948



1c was prepared using General Experimental Procedure A. Reagents employed: 5-methoxy-*N*-Propargyl skatole S1 (0.500 g, 2.51 mmol), *n*-BuLi (1.50 mL, 3.76 mmol), ethyl chloroformate (0.360 mL, 3.76 mmol). 1c (339 mg, 1.25 mmol, 50%) was obtained as a thick light brown oil:

 $\mathbf{R}_{\mathbf{f}} = 0.46, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.22 (dd, *J* = 8.8, 0.6 Hz, 1H,), 7.00 (dd, *J* = 2.5, 0.6 Hz, 1H), 6.94 – 6.90 (m, 1H), 6.89 (s, 1H), 4.91 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.29 (d, *J* = 1.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.3, 153.2, 131.6, 129.8, 125.7, 112.3, 111.7, 109.9, 101.4, 81.4, 76.5, 62.4, 56.1, 35.7, 14.1, 9.8 ppm;

**IR (neat)**:  $v_{max} = 2926, 2239, 1707, 1486, 1248, 1179, 1040, 749 cm<sup>-1</sup>;$ **HRMS (APPI+)**: calc'd for C<sub>16</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 272.1278, found 272.1273.



1d was prepared using General Experimental Procedure A. Reagents employed: 5-methoxy *N*-Propargyl skatole S1 (0.500 g, 2.51 mmol), *n*-BuLi (1.50 mL, 3.77 mmol), Phenyl chloroformate (0.475 mL, 3.77 mmol). 1d (402 mg, 1.26 mmol, 50%) was obtained as a thick light brown oil:

 $\mathbf{R}_{\mathbf{f}} = 0.40, 20\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.35 (td, *J* = 7.8, 1.8 Hz, 2H), 7.28 – 7.16 (m, 2H), 7.08 (dt, *J* = 8.1, 1.5 Hz, 2H), 7.01 (q, *J* = 1.7 Hz, 1H), 6.92 (dt, *J* = 8.8, 2.3 Hz, 1H), 6.87 (d, *J* = 1.4 Hz, 1H), 4.93 (d, *J* = 2.1 Hz, 2H), 3.86 (d, *J* = 1.6 Hz, 3H), 2.32 – 2.22 (m, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.3, 151.4, 149.9, 131.5, 129.8, 129.7, 126.6, 125.6, 121.4, 112.4, 111.9, 109.9, 101.4, 84.1, 75.9, 56.0, 35.7, 9.7 ppm;

**IR (neat)**:  $v_{max} = 2923, 2231, 1729, 1486, 1223, 1183, 999, 743, 687 cm<sup>-1</sup>;$ 

HRMS (APPI+): calc'd for C<sub>20</sub>H<sub>17</sub>NO<sub>3</sub> [M]<sup>+</sup> 319.1208, found 319.1209.



**1e** was prepared using General Experimental Procedure A. Reagents employed: 5-methoxy *N*-Propargyl skatole **S1** (0.500 g, 2.51 mmol), *n*-BuLi (1.50 mL, 3.77 mmol), benzyl chloroformate (0.538 mL, 3.77 mmol). **1e** (451 mg, 1.35 mmol, 54%) was obtained as a thick light brown oil:

 $\mathbf{R}_{\mathbf{f}} = 0.40, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.39 – 7.31 (m, 5H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.85 (d, *J* = 1.2 Hz, 1H), 5.15 (s, 2H), 4.87 (s, 2H), 3.86 (s, 3H), 2.27 (d, *J* = 1.1 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.3, 153.0, 134.7, 131.5, 129.7, 128.80, 128.77, 128.7, 125.6, 112.3, 111.7, 109.9, 101.4, 82.1, 76.2, 68.0, 56.1, 35.7, 9.7 ppm; IR (neat): v<sub>max</sub> = 2921, 2238, 1707, 1486, 1453, 1226, 1039, 835, 697 cm<sup>-1</sup>; HDMS (APPL 1): cala<sup>2</sup>d for C. H. NO. [M]<sup>+</sup>222, 1265, found 222, 1268

**HRMS (APPI+)**: calc'd for C<sub>21</sub>H<sub>19</sub>NO<sub>3</sub> [M]<sup>+</sup> 333.1365, found 333.1368.



**1f** was prepared using General Experimental Procedure A. Reagents employed: 5-methoxy-*N*-Propargyl skatole **S1** (0.500 g, 2.51 mmol), *n*-BuLi (1.50 mL, 3.77 mmol), benzyl chloroformate (0.492 mL, 3.76 mmol). **1f** (421 mg, 1.41 mmol, 56%) was obtained as a thick brown oil:

 $\mathbf{R}_{\mathbf{f}} = 0.40, 40\%$  DCM in hexanes;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.20 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.86 (d, *J* = 1.2 Hz, 1H), 4.86 (s, 2H), 3.92 (d, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 2.27 (d, *J* = 1.1 Hz, 3H), 1.93 (dt, *J* = 13.4, 6.7 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 6H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.3, 153.3, 131.6, 129.7, 125.7, 112.3, 111.7, 109.9, 101.4,

81.5, 76.5, 72.3, 56.1, 35.7, 27.7, 19.1, 9.7 ppm;

**IR (neat)**:  $v_{\text{max}} = 2962, 2240, 1707, 1487, 1248, 749 \text{ cm}^{-1}$ ;

HRMS (APPI+): calc'd for C<sub>18</sub>H<sub>21</sub>NO<sub>3</sub> [M]<sup>+</sup> 299.1521, found 299.1520.



1g was prepared using General Experimental Procedure A. Reagents employed: Substituted indole S3 (0.730 g, 3.42 mmol), *n*-BuLi (2.05 mL, 5.13 mmol), Methyl chloroformate (0.396 mL, 5.13 mmol). 1g (586 mg, 2.16 mmol, 63%) was obtained as thick light brown color oil:

 $\mathbf{R}_{\mathbf{f}} = 0.35, 20\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.14 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (d, *J* = 1.3 Hz, 1H), 4.20 (t, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.74 (s, 3H), 2.70 (t, *J* = 7.1 Hz, 2H), 2.26 (t, *J* = 1.4 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 153.9, 153.8, 131.1, 129.4, 125.9, 111.9, 110.7, 109.6, 101.1, 85.8, 74.7, 55.9, 52.7, 44.1, 20.7, 9.6 ppm;

**IR (neat)**:  $v_{max} = 3398$ , 2916, 2235, 1712, 1491, 1435, 1234, 1071, 1046, 896, 792 cm<sup>-1</sup>; **HRMS (APPI+)** calc'd for C<sub>16</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 272.1278, found 272.1283.



S5 was prepared using General Experimental Procedure A. Reagents employed: substituted S4 (0.357 g, 1.57 mmol), n-BuLi (1.00 mL, 2.35 mmol), Methyl chloroformate (183 uL, 2.36 mmol). S5 (313 mg, 1.10 mmol, 70%) was obtained as thick light brown color oil:

 $\mathbf{R}_{\mathbf{f}} = 0.25, 20\%$  Et<sub>2</sub>O in hexanes;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.18 (d, J = 8.8 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.84 (d, J = J = 1.1 Hz, 3H), 2.23 (t, J = 6.9 Hz, 2H), 2.04 (q, J = 6.6 Hz, 2H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.1, 153.8, 131.5, 129.2, 126.2, 111.9, 110.2, 109.9, 101.0, 88.1, 73.9, 56.0, 52.8, 44.5, 28.1, 16.1, 9.7 ppm; **IR (neat)**:  $v_{max} = 2923$ , 1730, 1449, 1217, 1033, 796 cm<sup>-1</sup>;



S6 was prepared by the following procedure: Substituted indole S1 (0.400 g, 2.01 mmol) was added to a round-bottom flask equipped with a magnetic stir bar and dissolved in THF (0.2 M) under an N<sub>2</sub> atmosphere. The solution was cooled to -78 °C on acetone/dry ice cooling bath, and *n*-BuLi (2.5 M in hexanes, 1.20 mL, 3.01 mmol) was slowly added dropwise using a syringe on the side of RBF. The resulting reaction mixture was stirred for 30 min at the same temperature, before dropwise addition of the iodomethane (0.187 mL, 3.01 mmol) at -78 °C. The reaction mixture was stirred for another 1.5 h, during which temperature reached -20 °C. The reaction was quenched with sat. aq. NH<sub>4</sub>Cl and allowed to warm to room temperature. The mixture was extracted twice with Et<sub>2</sub>O. The organic layers were then combined and washed with water, then brine, and then dried over MgSO<sub>4</sub>. The solution was concentrated in vacuo, and the resulting crude material was purified by flash chromatography to yield S6 (279 mg, 1.31 mmol, 65%) as a light brown oil

 $\mathbf{R}_{\mathbf{f}} = 0.35, 20\%$  EtOAc in hexanes;

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.25 (s, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.95 (s, 1H), 6.88 (dd, J = 8.8, 2.4 Hz, 1H), 4.72 (d, J = 2.4 Hz, 2H), 3.87 (s, 3H), 2.29 (d, J = 0.8 Hz, 3H), 1.81 (t, J = 2.4Hz. 3H) ppm: <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 154.0, 131.6, 129.5, 125.8, 111.9, 110.5, 110.2, 101.2, 81.0, 73.7, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5, 10.5,$ 56.1, 36.2, 9.8, 3.7 ppm; **IR (neat)**:  $v_{\text{max}} = 2918$ , 1489, 1443, 1220, 1035, 890, 779 cm<sup>-1</sup>;

**HRMS (APPI+)**: calc'd for C<sub>14</sub>H<sub>16</sub>NO [M+H]<sup>+</sup> 214.1224, found 214.1233.

Figure S3: Synthesis of Indole Starting Material 5



**5** was prepared by the following two-step procedure:

Step 1:

Aldehyde S7 (370 mg, 1.70 mmol, 1.0 equiv), Dimethyl (1-Diazo-2-oxopropyl)phosphonate (490 mg, 2.55 mmol, 1.5 equiv) and  $K_2CO_3$  (352 mg, 2.55 mmol, 1.5 equiv) were suspended in MeOH–THF (1:1, 9 mL) under an N<sub>2</sub> atmosphere. The reaction mixture was stirred at r.t. for 12 hours. Upon completion, the reaction mixture was concentrated in *vacuo* and purified by column chromatography (10-12 % EtOAc in hexanes) to give intermediate alkyne (272 mg, 1.28 mmol) as a white fluffy solid in 75% yield which was used directly in the next step.

Step 2:

To a solution of the alkyne (192 mg, 0.900 mmol, 1.0 equiv) in THF (4.5 mL) was slowly added *n*-BuLi (0.800 mL, 1.35 mmol, 1.5 equiv) at -78 °C under the N<sub>2</sub> atmosphere. The resulting reaction mixture was stirred for 30 min at the same temperature before the dropwise addition of Methyl chloroformate (104 uL, 1.35 mmol, 1.5 equiv) at -78 °C. The reaction mixture was then allowed to stir for another 1.5 hours, during which temperature reached -20 °C. The reaction was quenched with sat. aq. NH<sub>4</sub>Cl and allowed to warm to room temperature. The mixture was extracted with Et<sub>2</sub>O, washed with brine, and then dried over MgSO<sub>4</sub> and concentrated *in vacuo* to yield a crude reaction mixture. The resulting material was purified by column chromatography (12-18% EtOAc in hexanes) to obtain 5 (209 mg, 0.770 mmol) as light green foam in 86% yield.

 $R_f = 0.35, 20\%$  Et<sub>2</sub>O in hexanes;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.16 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.26 – 6.20 (m, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.65 (s, 3H), 3.08 – 2.97 (m, 2H), 2.88 – 2.63 (m, 2H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.2, 154.2, 138.8, 132.9, 128.0, 111.3, 109.7, 102.2, 99.0, 88.2,

73.7, 56.0, 52.8, 29.8, 25.4, 18.6 ppm;

**IR (neat)**:  $v_{max} = 2924$ , 2235, 1742, 1488, 1253, 1215, 1069, 776 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>16</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 272.1278, found 272.1300. Figure S4: Synthesis of Indole Starting Material 6



**6** was prepared by the following two-step procedure:

Step 1:

Aldehyde **S8** (500 mg, 2.30 mmol, 1.0 equiv), Dimethyl (1-Diazo-2-oxopropyl)phosphonate (477 mg, 3.45 mmol, 1.5 equiv) and  $K_2CO_3$  (633 mg, 3.45 mmol, 1.5 equiv) were suspended in MeOH–THF (1:1; 12 mL) under an N2 atmosphere. The reaction mixture was stirred at r.t. for 12 hours. Upon completion, the reaction mixture was concentrated in *vacuo* and purified by column chromatography (8-10 % EtOAc in hexanes) to give intermediate alkyne (374 mg, 1.75 mmol) as a thick greenish oil in 76% yield and was used in the next step.

Step 2:

To a solution of the alkyne (374 mg, 1.75 mmol, 1.0 equiv) in THF (9 mL) was slowly added *n*-BuLi (1.00 mL, 2.63 mmol, 1.5 equiv) at -78 °C under the N<sub>2</sub> atmosphere. The resulting reaction mixture was stirred for 30 min at the same temperature before the dropwise addition of Methyl chloroformate (204 uL, 2.63 mmol, 1.5 equiv) at -78 °C. The reaction mixture was then allowed to stir for another 1.5 hours, during which temperature reached -20 °C. The reaction was quenched with sat. aq. NH<sub>4</sub>Cl and allowed to warm to room temperature. The mixture was extracted with Et<sub>2</sub>O, washed with brine, and then dried over MgSO<sub>4</sub> and concentrated in *vacuo* to yield a crude reaction mixture. The resulting material was purified by column chromatography (10-15% EtOAc in hexanes) to obtain **6** (408 mg, 1.50 mmol) as white solid in 86% yield.

 $\mathbf{R}_{\mathbf{f}} = 0.35, 20\%$  Et<sub>2</sub>O in hexanes;

**M.P.** = 125-128 °C

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.18 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.94 – 6.85 (m, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.4, 153.9, 132.5, 127.7, 127.2, 112.2, 112.1, 110.2, 100.6, 89.9, 73.4, 56.1, 52.7, 32.9, 23.8, 20.4 ppm;

**IR (neat)**:  $v_{max} = 2925$ , 2334, 1749, 1494, 1255, 1033, 787 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>16</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 272.1278, found 272.1297. Figure S5: Synthesis of Indole Starting Material 11a



**11a** was prepared by the following procedure: Substituted indole **S1** (0.500 mg, 2.51 mmol), CuI (4.78 mg, 1.00 mol%), and  $PdCl_2(PPh_3)_2$  (87.7 mg, 5.00 mol%) was added to a flame dried round bottom flask equipped with a magnetic stir bar and dissolved in CH<sub>3</sub>CN (0.6 M) under a N<sub>2</sub> atmosphere. Next, Et<sub>3</sub>N (1.05 mL, 7.53 mmol) and iodobenzene (0.337 mL, 3.01 mmol) were added, and the reaction mixture was allowed to stir at room temperature for approximately 12 hr. Upon completion of the reaction as determined by TLC analysis, the reaction mixture was filtered through Celite, washed with sat. aq. NH<sub>4</sub>Cl, dried over MgSO<sub>4</sub>, and concentrated in *vacuo* to yield a crude reaction mixture. The resulting material was purified by column chromatography (5-25 % EtOAc in hexanes) to yield 11a (531 mg, 1.93 mmol, 77%) as a beige solid.

**R**<sub>f</sub> = 0.61, 25% EtOAc in hexanes; **M.P.** = 68-69 °C <sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)** δ = 7.41 – 7.37 (m, 2H), 7.31 – 7.24 (m, 4H), 7.02 (d, J = 2.1 Hz, 2H), 6.90 (dd, J = 8.8, 2.5 Hz, 1H), 5.00 (s, 2H), 3.87 (s, 3H), 2.29 (bs, J = 1.0 Hz, 3H) ppm; <sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>)** δ = 154.1, 131.8, 131.6, 129.6, 128.6, 128.3, 125.8, 122.5, 111.9, 110.6, 110.2, 101.2, 84.8, 83.7, 56.0, 36.5, 9.7 ppm; **IR (neat)**: v<sub>max</sub> = 2911, 1703, 1579, 1487, 1369, 1178, 1124, 1102, 890, 753 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>19</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 276.1381 found 276.1390. Figure S6: Synthesis of Indole Starting Material 11b



**11b** was prepared by the following procedure: Substituted indole **S1** (447 mg, 2.24 mmol), CuI (4.27 mg, 1.00 mol%), and  $PdCl_2(PPh_3)_2$  (78.5 mg, 5.00 mol%) was added to a flame dried round bottom flask equipped with a magnetic stir bar and dissolved in CH<sub>3</sub>CN (0.6 M) under a N<sub>2</sub> atmosphere. Next, Et<sub>3</sub>N (0.937 mL, 6.72 mmol) and iodobenzene (0.452 mL, 2.69 mmol) were added, and the reaction mixture was allowed to stir at room temperature for approximately 12 hr. Upon completion of the reaction as determined by TLC analysis, the reaction mixture was filtered through Celite, washed with sat. aq. NH<sub>4</sub>Cl, dried over MgSO<sub>4</sub>, and concentrated in *vacuo* to yield a crude reaction mixture. The resulting material was purified by column chromatography (5-25 % EtOAc in hexanes) to yield **11a** (602 mg, 1.73 mmol, 77%) as a beige solid.

 $\mathbf{R_f} = 0.54, 25\%$  EtOAc in hexanes;

**M.P.** = 86-87 °C

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.91 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.9 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.92 – 6.87 (m, 2H), 4.88 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.27 (d, *J* = 0.9 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.0, 154.1, 131.7, 131.6, 130.3, 129.6, 129.5, 127.0, 125.8, 112.0, 110.9, 110.1, 101.3, 86.7, 84.1, 61.2, 56.0, 36.5, 14.4, 9.7 ppm; IR (neat): v<sub>max</sub> = 2913, 1703, 1451, 1283, 1227, 1102, 764 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>22</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 348.1594, found 348.1595.



14 was prepared by the following three-step procedure:

#### Step 1:

To a stirred solution of **S9** (1.2 g, 7.4 mmol, 1.0 equiv) in acetic acid (30 mL) was added NaBH<sub>3</sub>CN (1.20 g, 18.5 mmol, 2.5 equiv) at 0 °C. The reaction was allowed to stir at room temperature for 4 hrs. The reaction mixture was diluted with H<sub>2</sub>O, brought to pH ~9 with NaOH pellets and extracted with EtOAc (15 mL 3x). The combined organic layers were washed with H<sub>2</sub>O, brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (18-20 % EtOAc in hexanes) to obtain **S10** (745 mg, 4.56 mmol) as light-yellow color oil in 62% yield.

## Step 2:

Methyl 4-bromocrotonate (643 uL, 5.47 mmol, 1.2 equiv) was added to a solution of KI (908 mg, 5.47 mmol, 1.2 equiv) in DMF (1 mL/mmol of KI) under an N<sub>2</sub> atmosphere. The solution was heated to 100 °C for 30 minutes then cooled to room temperature.  $K_2CO_3$  (945 mg, 6.84 mmol, 1.5 equiv) was then added to the reaction mixture, followed by the addition of a pre-dissolved solution of S10 (745 mg, 4.56 mmol, 1.0 equiv) in DMF (0.4 mL/mmol). The reaction mixture was then heated to 100 °C for ~12 hours (overnight), then cooled to room temperature, and H<sub>2</sub>O was added. The mixture was extracted three times with diethyl ether, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated in *vacuo*. The resulting residue was passed through a short silica gel plug using 2% EtOAc in hexanes as eluent. **S11** (661 mg, 2.53 mmol) was obtained as brown oil in 55% yield.

## Step 3:

DDQ (651 mg, 2.87 mmol, 1.5 equiv) was added to a solution of **S11** (0.500 g, 1.91 mmol, 1.0 equiv) in  $CH_2Cl_2$  (10 mL) at 0 °C. The reaction mixture was stirred for 2 hours at room temperature. When the reaction was considered complete as determined by TLC analysis, the mixture was filtered through a pad of Celite® and washed with  $CH_2Cl_2$ . The resulting liquid was concentrated in *vacuo* and the corresponding residue was purified by silica gel flash column chromatography (8-10 % EtOAc in hexanes) to give **14** (198 mg, 0.764 mmol) as thick brown color oil in 40% yield.

**R**<sub>f</sub> = 0.54, 25% EtOAc in hexanes; <sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)** δ = 7.08 – 6.98 (m, 3H), 6.85 (dd, J = 8.9, 2.4 Hz, 1H), 6.80 – 6.78 (m, 1H), 5.58 (dt, J = 15.6, 2.0 Hz, 1H), 4.76 (dd, J = 4.6, 2.0 Hz, 2H), 3.87 (s, 3H), 3.67 (s, 3H), 2.29 (d, J = 1.1 Hz, 3H) ppm; <sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>)** δ = 166.4, 154.0, 143.8, 131.7, 129.3, 126.2, 122.0, 112.1, 111.0, 110.0, 101.1, 56.0, 51.7, 47.0, 9.8 ppm; **IR (neat)**:  $v_{max}$  = 2928, 2238, 1723, 1488, 1274, 1226, 1042, 784 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>15</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 260.1278, found 260.1295.

Figure S8: Synthesis of Indole Starting Material 15



**15** was prepared by the following procedure: To a\_solution of triethyl phosphonoacetate reagent (386 mg, 1.72 mmol, 1.2 equiv) in THF (9 mL) was added NaH (740 mg, 1.86 mmol, 1.3 equiv) in one portion at 0 °C. The reaction was then stirred for 30 min at the same temperature before the addition of a pre-dissolved solution of S7 (311 mg, 1.43 mmol, 1.0 equiv) in THF. The mixture was stirred at room temperature for another 2 hours before quenching with water. The mixture was extracted with EtOAc ( $\times$ 2). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub> and concentrated in *vacuo*. The residue was purified by a flash column chromatography (8-10 % EtOAc in hexanes) to afford **15** (169 mg, 0.588 mmol, 41%) as light brown solid:

 $\mathbf{R_f} = 0.30, 20\%$  EtOAc in hexanes;

**M.P.** = 68-70 °C

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.11 (d, *J* = 8.8 Hz, 1H), 7.08 – 6.98 (m, 2H), 6.80 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.16 (d, *J* = 1.0 Hz, 1H), 5.90 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.55 (s, 3H), 2.83 – 2.78 (m, 2H), 2.63 – 2.54 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.4, 154.0, 147.5, 140.0, 132.7, 128.0, 122.2, 110.7, 109.4, 102.0, 98.6, 60.3, 55.9, 30.9, 29.5, 25.4, 14.3 ppm; IR (neat): v<sub>max</sub> = 2981, 1726, 1486, 1257, 1188, 1153, 1071, 746 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>17</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 288.1591, found 288.1605. Figure S9: Synthesis of Indole Starting Material 16



16 was prepared by the following procedure: To a solution of triethyl phosphonoacetate reagent (682 mg, 3.04 mmol, 1.2 equiv) in THF (15 mL) was added NaH (132 mg, 3.29 mmol, 1.3 equiv) in one portion at 0 °C. The reaction was then stirred for 30 min at the same temperature before the addition of a pre-dissolved solution of S8 (550 mg, 2.53 mmol, 1.0 equiv) in THF. The mixture was stirred at room temperature for another 2 hours before quenching with water. The mixture was extracted with EtOAc ( $\times$ 2). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub> and concentrated in *vacuo*. The residue was purified by a flash column chromatography (8-10 % EtOAc in hexanes) to afford 16 (327 mg, 1.14 mmol, 45%) as light brown solid:

 $\mathbf{R}_{\mathbf{f}} = 0.30, 20\%$  EtOAc in hexanes;

**M.P.** = 47-49 °C

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.18 (d, *J* = 8.8 Hz, 1H), 7.08 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (s, 1H), 5.89 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.71 (s, 3H), 2.88 (dd, *J* = 8.6, 6.5 Hz, 2H), 2.64 – 2.56 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 166.8, 153.8, 149.0, 132.6, 128.0, 126.9, 121.7, 113.2, 111.9, 110.1, 100.9, 60.3, 56.1, 32.9, 32.9, 23.9, 14.4 ppm;

**IR (neat)**:  $v_{max} = 2920$ , 1708, 1649, 1492, 1175, 1032, 857, 799 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>17</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 288.1591, found 288.1606.

 Table S1: Cascade Optimization Experiments

	Ме				Ме
MeO.	$\sim$			MeO	CO <sub>2</sub> Et
	1	(	CO <sub>2</sub> Et		
		N2			
	10	°CO <sub>2</sub> Me	20	20	/ MeO <sub>2</sub> C
Entwy	id Catalvat	Looding	Za Salwant	Jd	- Viald
Entry	Catalyst	Loauing	Solvent	(Time)	1 leiu
1	Rh <sub>2</sub> (OAc) <sub>4</sub> / ZnBr <sub>2</sub>	2 mol% / 10 mol%	$C_6H_6$	80 °C (12 h)	26%
2	Cu(acac) <sub>2</sub>	10 mol%	$C_6H_6$	80 °C (12 h)	70%
3	Cu(OAc) <sub>2</sub>	10 mol%	C <sub>6</sub> H <sub>6</sub>	80 °C (12 h)	58%
4	Cu(OTf) <sub>2</sub>	10 mol%	C <sub>6</sub> H <sub>6</sub>	80 °C (12 h)	65%
5	Cu(BF <sub>4</sub> ) <sub>2</sub> ·XH <sub>2</sub> O	10 mol%	$C_6H_6$	80 °C (12 h)	12%
6	CuCl <sub>2</sub>	10 mol%	$C_6H_6$	80 °C (12 h)	42%
7	CuBr·S(CH <sub>3</sub> ) <sub>2</sub>	10 mol%	C <sub>6</sub> H <sub>6</sub>	80 °C (12 h)	41%
8	Cu(OTf)·C <sub>6</sub> H <sub>6</sub>	10 mol%	C <sub>6</sub> H <sub>6</sub>	80 °C (12 h)	61%
9	CuCl	10 mol%	C <sub>6</sub> H <sub>6</sub>	80 °C (12 h)	50%
10	Cu(ClO <sub>4</sub> ) <sub>2</sub>	10 mol%	$C_6H_6$	80 °C (12 h)	21%
11	CuI	10 mol%	$C_6H_6$	80 °C (12 h)	41%
12	Cu(CN)4(BF4)	10 mol%	$C_6H_6$	80 °C (12 h)	Decomposition <sup>b</sup>
13	Cu(tfacac) <sub>2</sub>	10 mol%	C <sub>6</sub> H <sub>6</sub>	80 °C (12 h)	79%
14	Cu(tfacac) <sub>2</sub>	10 mol%	$C_6H_6$	140 °C, (20 mins)	69% <sup>c</sup>
15	Cu(tfacac) <sub>2</sub>	10 mol%	Hexanes	60 °C (12 hr)	36%
16	Cu(tfacac) <sub>2</sub>	10 mol%	$CH_2Cl_2$	40 °C (120 hr)	67%
17	Cu(tfacac) <sub>2</sub>	10 mol%	ClCH <sub>2</sub> CH <sub>2</sub> Cl	80 °C (12 hr)	52%
18	Cu(tfacac) <sub>2</sub>	10 mol%	THF	80 °C (12 hr)	No reaction
19	Cu(tfacac) <sub>2</sub>	10 mol%	PhCH <sub>3</sub>	80 °C (12 hr)	59%
20	Cu(tfacac) <sub>2</sub>	10 mol%	PhCF <sub>3</sub>	80 °C (12 hr)	48%
21	Cu(tfacac) <sub>2</sub>	10 mol%	$C_6F_6$	80 °C (12 hr)	63%
22	Cu(tfacac) <sub>2</sub>	10 mol%	Mesitylene	80 °C (12 hr)	49%
23	Cu(tfacac) <sub>2</sub>	0.5 mol%	C <sub>6</sub> H <sub>6</sub>	80 °C (12 h)	59%
24	Cu(tfacac) <sub>2</sub>	1 mol%	$C_6H_6$	80 °C (12 h)	65%
25	Cu(tfacac) <sub>2</sub>	5 mol%	$C_6H_6$	80 °C (12 h)	79%
26	Cu(tfacac) <sub>2</sub>	5 mol%	$C_6H_6$	80 °C (12 h)	78% <sup>d</sup>
27 <sup>e</sup>	Cu(tfacac) <sub>2</sub>	5 mol%	$C_6H_6$	80 °C (12 h)	complex mixture

<sup>a</sup> Reaction conditions: indole **1a** (1.2 equiv), diazo **2a** (1.0 equiv, 0.14 mmol), cat. (loading as indicated in table), in 1.0 M (solvent). <sup>b</sup> no product observed by <sup>1</sup>H NMR of crude reaction mixture. <sup>c</sup> Microwave heating. <sup>d</sup> 1.0 mmol scale of **2a**. <sup>e</sup> Ethyl diazoacetate was used in place of **2a**.

#### **Synthesis and Characterization of Annulation Products:**

Figure S10: Copper-Catalyzed Cascade Reaction with  $\alpha$ -Diazo Carbonyl Compounds



Figure S11: Synthesis of Tetrahydrocarbazole 7 via a Copper-Catalyzed Cascade Reaction



Figure S12: Synthesis of Tetrahydrocarbazole 8 via a Copper-Catalyzed Cascade Reaction



#### **General Experimental Procedure B**:

Indole starting material (1a-g, S5, S6, 5 and 6, 1.2 equiv) was added to a reaction vessel equipped with a stir bar, and the vessel was then evacuated and backfilled with N<sub>2</sub>. This cycle was repeated two additional times, followed by the addition of Benzene (5 mL/mmol of indole) under an N<sub>2</sub> atmosphere. Cu(tfacac)2 (5 mol %) was then added to the reaction vessel, and again, the vessel was evacuated (quickly) and backfilled with N<sub>2</sub>. Diazo reagent **2a-g** (1.0 equiv) was added to a separate reaction vessel, and the vessel was then evacuated and backfilled with N<sub>2</sub>. This cycle was repeated two additional times. The diazo reagent was then dissolved in Benzene (3 mL/mmol of diazo) under an N<sub>2</sub> atmosphere and transferred dropwise by syringe to the solution of indole starting material. Two sequential rinses and transfers using small quantities of Benzene were then conducted to ensure complete transfer of the diazo reagent. The reaction mixture was then heated to 80 °C and stirred at this temperature for 12 hours. The reaction progress was monitored by TLC analysis and considered complete upon consumption of diazo reagent. Upon completion, the reaction mixture was concentrated in *vacuo* and purified by silica gel flash column chromatography (hexanes/EtOAc gradient) to yield annulation products **3a-m**, **7** and **8**.



**3a** was prepared using General Experimental Procedure B. Reagents employed: Indole **1a** (309 mg, 1.20 mmol), diethyl diazomalonate **2a** (187 mg, 1.00 mmol), Cu(tfacac)<sub>2</sub> (18.5 mg, 0.0500 mmol). **3a** (322 mg, 0.775 mmol, 78%) was obtained as a brown oil:

Me X-ray quality crystal prepared by vapor diffusion in ether with pentane.

 $\mathbf{R_f} = 0.47, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = \delta$  7.19 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 2.2 Hz, 1H), 6.88 (dd, J = 8.8, 2.4 Hz, 1H), 6.49 (t, J = 2.6 Hz, 1H), 5.22 (d, J = 2.6 Hz, 2H), 4.32 – 4.19 (m, 4H), 3.87 (s, 3H), 3.81 (s, 3H), 2.30 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 166.9$ , 166.0, 156.3, 154.1, 133.6, 133.0, 127.6, 119.1, 112.3, 110.6, 105.6, 101.3, 64.3, 62.8, 56.0, 51.8, 48.9, 14.0, 9.1 ppm; IR (neat):  $v_{max} = 2981$ , 2361, 1722, 1484, 1351, 1213, 1043, 795 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>22</sub>H<sub>25</sub>NO<sub>7</sub> [M]<sup>+</sup> 415.1631, found 415.1631.



**3b** was prepared using General Experimental Procedure B. Reagents employed: Substituted Indole **1b** (146 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). **3b** (143 mg, 0.371 mmol, 69%) was obtained as a dark yellow oil:

 $R_f = 0.50, 60\%$  CH<sub>2</sub>Cl<sub>2</sub> in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta = \delta$  7.60 (d, J = 7.9 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.16 – 7.11 (m, 1H), 6.51 (t, J = 2.6 Hz, 1H), 5.26 (d, J = 2.7 Hz, 2H), 4.35 – 4.18 (m, 4H), 3.82 (s, 3H), 2.34 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.0, 166.1, 156.4, 133.0, 132.8, 132.3, 122.1, 119.6, 119.4, 119.3, 109.9, 106.2, 64.2, 63.0, 52.0, 48.8, 14.1, 9.1 ppm;

**IR (neat)**:  $v_{max} = 2979, 2360, 1732, 1454, 1365, 1215, 743 \text{ cm}^{-1}$ ;

HRMS (APPI+): calc'd for C<sub>21</sub>H<sub>24</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 386.1595, found 386.1621.



**3c** was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **1c** (175 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). **3c** (179 mg, 0.417 mmol, 78%) was obtained as a dark brown oil:

 $R_f = 0.60, 50\%$  CH<sub>2</sub>Cl<sub>2</sub> in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = \delta$  7.19 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.48 (t, *J* = 2.6 Hz, 1H), 5.23 (d, *J* = 2.6 Hz, 2H), 4.36 – 4.18 (m, 6H), 3.87 (s, 3H), 2.31 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 167.0$ , 165.7, 156.1, 154.2, 133.7, 133.1, 127.7, 119.6, 112.4, 110.6, 105.6, 101.4, 64.4, 62.9, 60.9, 56.1, 49.0, 14.3, 14.1, 9.2 ppm; IR (neat): v<sub>max</sub> = 2978, 1731, 1473,1443, 1261, 1253, 1216, 1024, 855, 808 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>23</sub>H<sub>28</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 430.1858, found 430.1872.



**3d** was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **1d** (206 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). **3d** (201 mg, 0.421 mmol, 78%) was obtained as a dark brown oil:

**R**<sub>f</sub> = 0.60, 40% CH<sub>2</sub>Cl<sub>2</sub> in hexanes; <sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.45 – 7.39 (m, 2H), 7.30 – 7.24 (m, 1H), 7.19 – 7.14 (m, 3H), 7.03 (d, *J* = 2.1 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.73 (t, *J* = 2.6 Hz, 1H), 5.27 (d, *J* = 2.6 Hz, 2H), 4.40 – 4.22 (m, 4H), 3.87 (s, 3H), 2.33 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  = 166.9, 164.1, 158.7, 154.3, 150.5, 133.5, 133.1, 129.6, 127.7, 126.2, 121.6, 118.8, 112.5, 110.6, 105.8, 101.5, 64.6, 63.1, 56.1, 49.2, 14.2, 9.2 ppm; **IR (neat)**: v<sub>max</sub> = 2972, 2928, 1732, 1484, 1185, 1161, 1041, 688 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>27</sub>H<sub>28</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 478.1858, found 478.1878.



3e was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole 1e (215 mg, 0.644 mmol), diethyl diazomalonate 2a (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). 3e (192 mg, 0.391 mmol, 73%) was obtained as a pale-yellow solid:

 $\mathbf{R}_{\mathbf{f}} = 0.50, 60\% \text{ CH}_2\text{Cl}_2 \text{ in hexanes;}$ 

**M.P.** = 107-109 °C

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.43 – 7.33 (m, 5H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.53 (t, *J* = 2.6 Hz, 1H), 5.23 (bs, 4H), 4.34 – 4.17 (m, 4H), 3.87 (s, 3H), 2.30 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.9, 165.5, 156.8, 154.1, 135.7, 133.7, 133.1, 128.8, 128.6, 128.6, 127.8, 119.3, 112.5, 110.6, 105.7, 101.4, 66.8, 64.4, 63.0, 56.1, 49.1, 14.1, 9.2 ppm; IR (neat): v<sub>max</sub> = 2969, 2360, 1736, 1238, 1191, 1162, 1028, 846, 748 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>28</sub>H<sub>30</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 492.2014, found 492.2011.



**3f** was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **1f** (193 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). **3f** (198 mg, 0.433 mmol, 81%) was obtained as a yellow oil:

 $R_f = 0.60, 40\%$  CH<sub>2</sub>Cl<sub>2</sub> in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.19 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.50 (t, *J* = 2.6 Hz, 1H), 5.23 (d, *J* = 2.7 Hz, 2H), 4.37 – 4.16 (m, 4H), 3.98 (d, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 2.31 (s, 3H), 2.09 – 1.94 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 6H), 0.99 (d, *J* = 6.7 Hz, 6H) ppm;

<sup>13</sup>**C** NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.1, 165.8, 156.1, 154.2, 133.7, 133.1, 127.7, 119.6, 112.4, 110.6, 105.6, 101.4, 71.1, 64.4, 62.9, 56.1, 49.0, 27.9, 19.3, 14.1, 9.2 ppm;

**IR (neat)**:  $v_{\text{max}} = 2964$ , 1726, 1477, 1214, 1040, 795 cm<sup>-1</sup>;

HRMS (APPI+): calc'd for C<sub>25</sub>H<sub>32</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 458.2171, found 458.2195.



**3g** was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **1g** (175 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). **3g** (158 mg, 0.368 mmol, 68%) was obtained as a pale-yellow crystal: X-ray quality crystal prepared by slow evaporation from

X-ray quality crystal prepared by slow evaporation from ethanol.

 $\mathbf{R}_{\mathbf{f}} = 0.45, 30\%$  EtOAc in hexanes;

**M.P.** = 115-118 °C

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.17 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.97 (s, 1H), 4.30 – 4.20 (m, 4H), 4.13 (t, *J* = 6.2 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 3.54 (t, *J* = 6.1 Hz, 2H), 2.21 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.0, 166.2, 154.2, 151.7, 130.5, 129.0, 127.4, 119.5, 112.2,

109.7, 109.6, 100.6, 63.7, 62.7, 56.0, 51.6, 41.6, 26.1, 14.0, 9.6 ppm;

**IR (neat)**:  $v_{max} = 2926, 1728, 1255, 1162, 1068, 1023, 743 \text{ cm}^{-1}$ ;

**HRMS (APPI+)**: calc'd for C<sub>23</sub>H<sub>28</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 430.1858, found 430.1875.



**S12** was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **S5** (184 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). **S12** (0.170 g, 0.383 mmol, 71%) was obtained as a light green oil:

**NOTE:** Additional attempts to promote the C–H functionalization/annulation cascade including (i) increased reaction times (48 h), (ii) elevated temperatures (reflux in toluene instead of benzene), and (iii) addition of base (Cs<sub>2</sub>CO<sub>3</sub>) provided **S12** with no indication of the desired cyclized product.

 $\mathbf{R}_{\mathbf{f}} = 0.50, 30\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.22 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.3 Hz, 1H), 4.96 (s, 1H), 4.32 – 4.16 (m, 6H), 3.86 (s, 3H), 3.78 (s, 3H), 2.35 (t, *J* = 6.9 Hz, 2H), 2.27 (s, 3H), 2.05 – 1.96 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  = 167.2, 154.1, 154.1, 131.6, 128.7, 127.0, 112.7, 111.2, 110.4, 100.9, 88.1, 73.8, 62.2, 56.0, 52.8, 49.6, 42.8, 27.9, 16.2, 14.1, 9.3 ppm; **IR (neat)**: v<sub>max</sub> = 2971, 2236, 1707, 1494, 1256, 1163, 1033, 751 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>24</sub>H<sub>30</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 444.2017, found 444.2054.



4 was prepared using General Experimental Procedure B. Reagents
cO<sub>2</sub>Et employed: Substituted *N*-propargylindole S6 (137 mg, 0.644 mmol), diethyl diazomalonate 2a (0.100 g, 0.537 mmol),
cO<sub>2</sub>Et Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). 4 (104 mg, 0.280 mmol, 52%) was obtained as a yellow solid:

**NOTE:** An attempt to promote the C–H functionalization/annulation cascade using  $Rh_2(OAc)_4$  (2 mol%) and ZnBr<sub>2</sub> (10 mol%) in place of Cu(tfacac)<sub>2</sub> provided only insertion product **4** with no indication of the desired cyclized product.

 $\mathbf{R}_{\mathbf{f}} = 0.50, 20\%$  Acetone in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.32 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.07 (s, 1H), 4.86 (q, *J* = 2.4 Hz, 2H), 4.36 – 4.16 (m, 4H), 3.87 (s, 3H), 2.28 (s, 3H), 1.73 (t, *J* = 2.4 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  = 167.4, 154.2, 131.9, 128.6, 126.9, 112.7, 111.3, 110.8, 101.1, 80.1, 74.1, 62.3, 56.1, 49.7, 34.5, 14.2, 9.3, 3.7 ppm; **IR (neat)**: v<sub>max</sub> = 2933, 1729, 1306, 1207, 1163, 1030, 831 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>21</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 372.1803, found 372.1786.



7 was prepared using General Experimental Procedure B. Reagents employed: Substituted indole S7 (175 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). 7 (180 mg, 0.42 mmol, 78%) was obtained as yellow crystals:

X-ray quality crystal prepared by slow evaporation from ethanol.

 $\mathbf{R}_{\mathbf{f}} = 0.50, 40\%$  Acetone in hexanes;

**M.P.** = 161-163 °C

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.13 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.87 (s, 1H), 4.34 – 4.15 (m, 4H), 3.81 (s, 3H), 3.73 (s, 3H), 3.57 (s, 3H), 3.44 (t, *J* = 6.4 Hz, 2H), 2.91 (t, *J* = 6.4 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.9, 166.6, 155.0, 154.0, 137.5, 132.9, 126.2, 118.1, 111.2, 109.6, 105.4, 102.7, 63.8, 62.1, 55.9, 51.4, 29.4, 24.9, 23.2, 14.2 ppm; IR (neat): v<sub>max</sub> = 2926, 1728, 1649, 1487, 1255, 1162, 1068, 802 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>23</sub>H<sub>28</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 430.1858, found 430.1875.



**8** was prepared using General Experimental Procedure B. Reagents employed: Substituted indole **S8** (175 mg, 0.644 mmol), diethyl diazomalonate **2a** (0.100 g, 0.537 mmol), Cu(tfacac)<sub>2</sub> (0.010 mg, 0.027 mmol). **8** (164 mg, 0.382 mmol, 71%) was obtained as a light green oil:

 $\mathbf{R}_{\mathbf{f}} = 0.40, 20\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.20 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 2.3 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.78 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.86 (s, 3H), 3.75 (s, 3H), 3.64 (s, 3H), 3.30 (t, *J* = 6.3 Hz, 2H), 2.91 (t, *J* = 6.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.6, 166.3, 155.5, 154.0, 133.7, 129.8, 125.6, 118.0, 112.7, 112.5, 110.1, 100.6, 64.6, 62.7, 56.0, 51.4, 31.3, 25.9, 21.7, 13.9 ppm; IR (neat): v<sub>max</sub> = 2932, 1728, 1663, 1487, 1250, 1162, 1068, 779 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>23</sub>H<sub>28</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 430.1858, found 430.1875.



**3h** was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **1a** (154 mg, 0.600 mmol), dimethyl diazomalonate **2b** (79 mg, 0.50 mmol), Cu(tfacac)<sub>2</sub> (9.2 mg, 0.025 mmol). **3h** (144 mg, 0.372 mmol, 74%) was obtained as a dark brown oil:

 $\mathbf{R}_{\mathbf{f}} = 0.47, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.19 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.48 (t, 2.3 Hz, 1H), 5.23 (d, *J* = 2.5 Hz, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 3.79 (s, 6H), 2.28 (s, 3H) ppm; <sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  = 167.4, 165.9, 156.2, 154.3, 133.4, 132.9, 127.7, 119.3, 112.6, 110.7, 105.7, 101.4, 63.9, 56.1, 53.7, 51.9, 48.9, 8.8 ppm; **IR (neat)**: v<sub>max</sub> = 2951, 2361, 1716, 1435, 1231, 1211, 1046, 904, 785 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>20</sub>H<sub>22</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 388.1391, found 388.1406.



**3i** was prepared using General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **1a** (154 mg, 0.600 mmol), Methyl 2-diazoacetoacetate **2c** (71 mg, 0.50 mmol), Cu(tfacac)<sub>2</sub> (9.2 mg, 0.025 mmol). **3i** (70 mg, 0.19 mmol, 38%) was obtained as a brown oil:

 $\mathbf{R}_{\mathbf{f}} = 0.47, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.23 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.34 (t, *J* = 2.6 Hz, 1H), 5.35 – 5.19 (m, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 2.28 (s, 3H), 2.05 (s, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 199.1, 167.6, 165.9, 155.8, 154.4, 134.0, 133.1, 128.0, 120.1, 112.9, 110.8, 105.9, 101.4, 70.9, 56.1, 53.5, 52.0, 49.1, 26.7, 9.1 ppm;

**IR (neat)**:  $v_{max} = 2952, 2360, 2191, 1715, 1485, 1349, 1218, 1162, 1041, 792 cm<sup>-1</sup>;$ **HRMS (APPI+)**: calc'd for C<sub>20</sub>H<sub>21</sub>NO<sub>6</sub> [M]<sup>+</sup> 371.1369, found 371.1373.



Product 9j, 3j-(Z), and 3j-(E) were prepared following General Experimental Procedure B. Reagents employed: Substituted N-propargylindole 1a (154 mg, 0.600 mmol), ethyl 2phenyldiazoacetate 2d (95 mg, 0.50 mmol), Cu(tfacac)<sub>2</sub> (9.2 mg, 0.025 mmol). 9j (65 mg, 0.16 mmol, 32%) was obtained as a brown oil, 3j-(Z) (43 mg, 0.10 mmol, 20%) was obtained as a brown oil, and 3j-(E) (9 mg, 0.02 mmol, 4%) was obtained as a brown oil:

**NOTE:** Diagnostic <sup>1</sup>H NMR signals between Z and E isomers; **3j-(Z)**  $H_a \delta = 5.92$  (t, J = 2.5 Hz, 1H),  $H_b \delta = 5.45 - 5.12$  (m, 2H). **3j-(E)**  $H_a \delta = 6.11$  (t, J = 1.9 Hz, 1H),  $H_b \delta = 4.97$  (d, J = 1.5 Hz, 2H)

Compound **9j**:  $\mathbf{R}_{f} = 0.50, 25\%$  EtOAc in hexanes; <sup>1</sup>H NMR (**300 MHz, CDCl<sub>3</sub>**)  $\delta = 7.35 - 7.14$  (m, 6H), 7.03 (d, J = 2.4 Hz, 1H), 6.92 (dd, J = 8.8, 2.5 Hz, 1H), 5.50 (s, 1H), 4.97 - 4.76 (m, 2H), 4.37 - 4.20 (m, 2H), 3.89 (s, 3H), 3.68 (s, 3H), 2.30 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm; <sup>13</sup>C NMR (**75 MHz, CDCl<sub>3</sub>**)  $\delta = 171.3, 154.6, 153.5, 136.3, 131.9, 131.4, 129.0, 128.9, 127.9,$ 

127.5, 112.6, 111.5, 110.2, 101.3, 82.4, 75.3, 61.9, 56.2, 52.7, 48.0, 34.5, 14.3, 9.2 ppm;

**IR (neat)**:  $v_{max} = 2945, 2327, 2240, 1716, 1483, 1253, 1158, 1034, 734 cm<sup>-1</sup>;$ 

**HRMS (APPI+)**: calc'd for C<sub>25</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 420.1803, found 420.1825.

Compound **3j**-(**Z**):

 $\mathbf{R_f} = 0.59, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.37 – 7.30 (m, 3H), 7.27 – 7.18 (m, 3H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.93 (t, *J* = 2.5 Hz, 1H), 5.40 – 5.19 (m, 2H), 4.33 – 4.12 (m, 2H), 3.88 (s, 3H), 3.73 (s, 3H), 2.06 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 170.3, 166.4, 163.2, 154.2, 139.5, 138.0, 133.2, 128.8, 127.9, 127.7, 127.5, 119.0, 112.0, 110.6, 104.8, 101.3, 63.5, 62.5, 56.1, 51.7, 49.1, 14.1, 9.0 ppm;

**IR (neat)**:  $v_{max} = 2922$ , 1730, 1438, 1305, 1212, 1024, 806, 703 cm<sup>-1</sup>;

**HRMS (APPI+)**: calc'd for C<sub>25</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 420.1803, found 420.1829.

Compound **3j-**(*E*):

 $\mathbf{R}_{\mathbf{f}} = 0.50, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.45 – 7.42 (m, 2H), 7.23 – 7.16 (m, 4H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.11 (t, *J* = 1.9 Hz, 1H), 4.97 (d, *J* = 1.5 Hz, 2H), 4.35 – 4.11 (m, 2H), 3.87 (s, 3H), 3.64 (s, 3H), 2.04 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.8, 164.9, 161.1, 154.3, 139.5, 133.5, 128.5, 127.9, 127.3, 127.1, 116.1, 111.9, 110.4, 103.8, 101.5, 61.7, 56.1, 51.6, 50.3, 14.2, 8.0 (Note: two carbon signals are missing presumably due to overlap with the signals at 139.5 and 61.7 ppm)

**IR (neat)**:  $v_{\text{max}} = 2941, 1730, 1582, 1480, 1350, 1216, 1116, 1033, 855 \text{ cm}^{-1}$ ;

**HRMS (APPI+)**: calc'd for  $C_{25}H_{26}NO_5 [M+H]^+ 420.1803$ , found 420.1832.



Product 9k, 3k-(Z), and 3k-(E) were prepared following General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole 1a (154 mg, 0.600 mmol), ethyl 2-(4-methoxyphenyl) diazoacetate 2e (110 mg, 0.50 mmol), Cu(tfacac)<sub>2</sub> (9.2 mg, 0.025 mmol). 9k (72

mg, 0.16 mmol, 32%) was obtained as a brown oil,  $3\mathbf{k}$ -(Z) (58 mg, 0.13 mmol, 26%) was obtained as a brown oil, and  $3\mathbf{k}$ -(E) (17 mg, 0.038 mmol, 8%) was obtained as a brown oil:

**NOTE:** Diagnostic <sup>1</sup>H NMR signals between Z and E isomers; **3k-(Z)**  $H_a \delta = 5.91$  (t, J = 2.5 Hz, 1H),  $H_b \delta = 5.39 - 5.17$  (m, 2H). **3k-(E)**  $H_a \delta = 6.07$  (t, J = 1.9 Hz, 1H),  $H_b \delta = 4.94$  (d, J = 1.5 Hz, 2H)

Compound **9k**:

 $\mathbf{R}_{\mathbf{f}} = 0.49, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.21 (d, *J* = 8.8 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.43 (s, 1H), 5.01 – 4.76 (m, 2H), 4.34 – 4.21 (m, 2H), 3.88 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 2.30 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 171.6, 159.0, 154.6, 153.5, 131.9, 131.8, 129.1, 128.2, 114.3, 113.8, 112.6, 111.2, 110.2, 101.4, 82.5, 75.2, 61.9, 56.2, 55.4, 52.7, 47.3, 34.4, 14.3, 9.2 ppm; **IR (neat)**: v<sub>max</sub> = 2928, 2247, 1715, 1444, 1260, 1169 1026, 810 cm<sup>-1</sup>;

**HRMS (APPI+)**: calc'd for C<sub>26</sub>H<sub>28</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 450.1917, found 450.1955.

Compound **3k**-(**Z**):

 $\mathbf{R}_{\mathbf{f}} = 0.49, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.24 (d, *J* = 8.8 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.91 (t, *J* = 2.5 Hz, 1H), 5.39 - 5.17 (m, 2H), 4.29 - 4.12 (m, 2H), 3.88 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 2.07 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 170.5, 166.5, 163.7, 159.2, 154.2, 138.2, 133.2, 131.5, 128.7, 127.8, 118.7, 114.2, 112.0, 110.6, 104.7, 101.3, 62.9, 62.5, 56.2, 55.4, 51.7, 49.1, 14.2, 9.0 ppm; **IR (neat)**: v<sub>max</sub> = 2923, 2855, 2242 1721, 1453, 1249, 1175, 1026, 803 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>26</sub>H<sub>28</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 450.1917, found 450.1964.

Compound **3k**-(*E*):

 $\mathbf{R}_{\mathbf{f}} = 0.41, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.34 (d, *J*= 8.9 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.07 (t, *J* = 1.9 Hz, 1H), 4.94 (d, *J* = 1.9 Hz, 2H), 4.28 – 4.12 (m, 2H), 3.87 (s, 3H), 3.75 (s, 3H), 3.66 (s, 3H), 2.05 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.0, 165.0, 161.4, 158.7, 154.3, 142.5, 133.5, 131.6, 129.8, 127.2, 115.6, 113.2, 111.9, 110.4, 103.6, 101.5, 61.7, 60.0, 56.1, 55.3, 51.6, 50.3, 14.2, 8.0. ppm; **IR (neat)**: v<sub>max</sub> = 2943, 1730, 1607, 1447, 1349, 1215, 1178, 1033, 730 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>26</sub>H<sub>28</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 450.1917, found 450.1941.



Product 91, 31-(Z), and 31-(E) were prepared following General Experimental Procedure B. Reagents employed: Substituted N-propargylindole 1a (155 mg, 0.602 mmol), ethyl 2-(4-bromophenyl)diazoacetate 2f (135 mg, 0.502 mmol), Cu(tfacac)<sub>2</sub> (9.2 mg, 0.025 mmol). 91 (46 mg, 0.092 mmol, 18%) was obtained as a brown oil, 31-(Z) (79 mg, 0.16 mmol, 32%) was obtained as a brown oil, and 31-(E) (33 mg, 0.066 mmol, 13%) was obtained as a brown oil:

**NOTE:** Diagnostic <sup>1</sup>H NMR signals between Z and E isomers; **31-(Z)**  $H_a \delta = 5.88$  (t, J = 2.5 Hz, 1H),  $H_b \delta = 5.40 - 5.18$  (m, 2H). **31-(E)**  $H_a \delta = 6.10$  (t, J = 1.9 Hz, 1H),  $H_b \delta = 4.97$  (d, J = 2.1 Hz, 2H)

Compound 91:

 $\mathbf{R_f} = 0.54, 25\%$  EtOAc in hexanes;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.44 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.07 – 6.91 (m, 3H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.40 (s, 1H), 5.02 – 4.74 (m, 2H), 4.37-4.19 (m, 2H), 3.89 (s, 3H), 3.70 (s, 3H), 2.29 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 170.9$ , 154.7, 153.4, 135.3, 132.0, 131.9, 130.9, 129.8, 129.0, 121.7, 112.9, 111.7, 110.2, 101.4, 82.0, 75.4, 62.1, 56.2, 52.9, 47.4, 34.3, 14.3, 9.3, ppm; IR (neat):  $v_{max} = 2971$ , 2925, 2361, 1716, 1484, 1436, 1300, 1158, 1035, 798 cm<sup>-1</sup>;

HRMS (APPI+): calc'd for  $C_{25}H_{25}^{79}BrNO_5$  [M+H]<sup>+</sup> 498.0908, found 498.0929.

Compound **3l-**(*Z*):

 $\mathbf{R_f} = 0.66, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.47 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.88 (t, *J* = 2.5 Hz, 1H), 5.40 – 5.18 (m, 2H), 4.29 – 4.11 (m, 2H), 3.88 (s, 3H), 3.74 (s, 3H), 2.05 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.9, 166.2, 162.8, 154.3, 138.6, 137.5, 133.1, 132.0, 129.3, 127.8, 122.1, 119.0, 112.3, 110.7, 104.8, 101.3, 62.9, 62.7, 56.1, 51.8, 49.1, 14.1, 9.0 ppm; IR (neat): ν<sub>max</sub> = 2923, 1718, 1482, 1298, 1204, 1014, 798 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>25</sub>H<sub>25</sub><sup>79</sup>BrNO<sub>5</sub> [M+H]<sup>+</sup> 498.0908, found 498.0932.

Compound **3l**-*(E)*:

 $\mathbf{R}_{\mathbf{f}} = 0.51, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.33 (apt s, (AA' BB') 4H), 7.18 (d, *J* = 8.7 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.10 (t, *J* = 1.9 Hz, 1H), 4.97 (t, *J* = 2.1 Hz, 2H), 4.31 – 4.09 (m, 2H), 3.87 (s, 3H), 3.65 (s, 3H), 2.02 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.4, 164.8, 161.0, 154.4, 141.8, 138.7, 133.4, 130.9, 130.4, 127.2, 121.5, 116.2, 112.2, 110.5, 103.9, 101.5, 61.9, 59.9, 56.1, 51.8, 50.2, 14.1, 8.0 ppm;



Product 3m-(Z) and 3m-(E) were prepared following General Experimental Procedure B. Reagents employed: Substituted *N*-propargylindole **1a** (155 mg, 0.602 mmol), ethyl 2-(4nitrophenyl)diazoacetate **2g** (118 mg, 0.502 mmol), Cu(tfacac)<sub>2</sub> (9.2 mg, 0.025 mmol). **3m-(Z)** (90.0 mg, 0.194 mmol, 39%) was obtained as a brown oil and **3m-(E)** (60.0 mg, 0.129 mmol, 26%) was obtained as a brown oil:

**NOTE:** Diagnostic <sup>1</sup>H NMR signals between Z and E isomers; **3m-(Z)**  $H_a \delta = 5.87$  (t, J = 2.5 Hz, 1H),  $H_b \delta = 5.42 - 5.22$  (m, 2H). **3m-(E)**  $H_a \delta = 6.17$  (t, J = 2.0 Hz, 1H),  $H_b \delta = 5.04$  (d, J = 1.9 Hz, 2H)

Compound **3m-(***Z***)**:

 $\mathbf{R_f} = 0.51, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 8.21 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.87 (t, *J* = 2.5 Hz, 1H), 5.42 – 5.22 (m, 2H), 4.30 – 4.19 (m, 2H), 3.89 (s, 3H), 3.75 (s, 3H), 2.03 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.4, 165.9, 162.1, 154.4, 147.5, 146.6, 136.9, 133.1, 128.8, 127.8, 124.1, 119.5, 112.7, 110.8, 105.0, 101.4, 62.99, 62.96, 56.1, 51.9, 49.2, 14.1, 9.0 ppm; **IR (neat)**: ν<sub>max</sub> = 2936, 1726, 1606, 1521, 1445, 1349, 1219, 1028, 733 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>25</sub>H<sub>25</sub>N<sub>2</sub>O<sub>7</sub> [M+H]<sup>+</sup> 465.1656, found 465.1666.

Compound **3m-(***E***)**:

 $\mathbf{R_f} = 0.38, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 8.07$  (d, J = 9.0 Hz, 2H), 7.69 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.7 Hz, 1H), 6.98 (d, J = 2.3 Hz, 1H), 6.91 (dd, J = 8.8, 2.4 Hz, 1H), 6.17 (t, J = 2.0 Hz, 1H), 5.04 (t, J = 1.9 Hz, 2H), 4.34 – 4.10 (m, 2H), 3.86 (s, 3H), 3.64 (s, 3H), 2.00 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.8, 164.7, 160.8, 154.5, 146.9, 146.8, 141.2, 133.5, 129.7, 127.3, 122.8, 116.8, 112.6, 110.6, 104.3, 101.5, 62.1, 59.9, 56.1, 51.9, 50.3, 14.1, 7.9 ppm; IR (neat): v<sub>max</sub> = 2958, 1729, 1519, 1445, 1346, 1218, 1111, 1031, 802, 731 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>25</sub>H<sub>25</sub>N<sub>2</sub>O<sub>7</sub> [M]<sup>+</sup> 464.1584, found 464.1615.

 Figure S13: One-Pot Copper/Cesium Telescope Reactions with α-Diazo Carbonyl Compounds

 MeO

 MeO



Figure S14: : One-Pot Copper/Cesium Annulation Reactions with Alkenyl-Ester Electrophiles



#### **General Experimental Procedure C**:

Indole starting material (1a, 11a-b, and 14-16, 1.2 equiv) was added to a reaction vessel equipped with a stir bar, and the vessel was then evacuated and backfilled with N<sub>2</sub>. This cycle was repeated two additional times, followed by the addition of Benzene (5 mL/mmol of indole) under an N<sub>2</sub> atmosphere. Cu(tfacac)2 (5 mol %) was then added to the reaction vessel, and again, the vessel was evacuated (quickly) and backfilled with  $N_2$ . Diazo reagent **2a,d** (1.0 equiv) was added to a separate reaction vessel, and the vessel was then evacuated and backfilled with N<sub>2</sub>. This cycle was repeated two additional times. The diazo reagent was then dissolved in Benzene (3 mL/mmol of diazo) under an  $N_2$  atmosphere and transferred dropwise by syringe to the solution of indole starting material. Two sequential rinses and transfers using small quantities of Benzene were then conducted to ensure complete transfer of the diazo reagent. The reaction mixture was then heated to 80 °C and stirred at this temperature for 12 hours. The reaction progress was monitored by TLC analysis and considered complete upon consumption of diazo reagent. Upon completion, Cs<sub>2</sub>CO<sub>3</sub> (1.2 equiv) was added and allowed to stir for an additional 12 hours. After 12 hours had elapsed, the reaction mixture was filtered through Celite, concentrated in vacuo, and purified by silica gel flash column chromatography (hexanes/EtOAc gradient) to yield annulation products 10, 12, 13a**b**, and **17-19**.



**10** was prepared using General Experimental Procedure C. Reagents employed: Substituted *N*-propargylindole **1a** (50.0 mg, 0.194 mmol), ethyl 2-phenyldiazoacetate **2d** (31 mg, 0.16 mmol), Cu(tfacac)<sub>2</sub> (4.0 mg, 0.0097 mmol), Cs<sub>2</sub>CO<sub>3</sub> (63 mg, 0.19 mmol). **10** (43 mg, 0.10 mmol, 63%) was obtained as a brown oil: X-ray quality crystal prepared by vapor diffusion in ether with

 $\mathbf{R}_{\mathbf{f}} = 0.44, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.31 – 7.26 (m, 5H), 7.13 – 7.00 (m, 2H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.58 (s, 3H), 3.50 – 3.12 (m, 2H), 2.14 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; <sup>13</sup>**C** NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 171.5, 170.6, 154.1, 140.0, 137.2, 132.7, 128.8, 127.8, 127.1, 125.6, 124.4, 123.0, 112.2, 110.2, 109.4, 101.8, 64.2, 62.1, 56.1, 52.0, 31.9, 14.3, 9.2 ppm; IR (neat):  $v_{max}$  = 2948, 2361, 1727, 1483, 1446, 1365, 1231, 1043, 796 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>25</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 420.1806, found 420.1838.



12 was prepared using General Experimental Procedure C. Reagents employed: Substituted *N*-propargylindole 1a (154 mg, 0.600 mmol), diethyl diazomalonate 2a (93 mg, 0.50 mmol), Cu(tfacac)<sub>2</sub> (9.0 mg, 0.025 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.600 mmol). 12 (118 mg, 0.284 mmol, 57%) was obtained as a brown oil:

 $\mathbf{R_f} = 0.32, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.31 (t, *J* = 1.4 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 4H), 3.86 (s, 3H), 3.72 (s, 3H), 3.56 (d, *J* = 1.4 Hz, 2H), 2.36 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 171.6, 166.9, 154.2, 134.6, 132.8, 127.5, 125.7, 117.0, 112.7, 110.8, 110.2, 102.0, 65.1, 62.5, 56.1, 52.2, 32.0, 14.2, 9.2 ppm;

**IR (neat)**:  $v_{max} = 2983$ , 1732, 1484, 1447, 1366, 1234, 1157, 1044, 799 cm<sup>-1</sup>;

HRMS (APPI+): calc'd for C<sub>22</sub>H<sub>26</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 416.1704, found 416.1738.



Product 13a-(Z) and 13a-(E) were prepared following General Experimental Procedure C. Reagents employed: Substituted *N*-propargylindole 11a (154 mg, 0.600 mmol), diethyl diazomalonate 2a (93 mg, 0.50 mmol), Cu(tfacac)<sub>2</sub> (9.2 mg, 0.025 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.600 mmol). 13a-(Z) (67 mg, 0.15 mmol, 30%) was obtained as a brown oil and 13a-(E) (62 mg, 0.14 mmol, 28%) was obtained as a brown oil:

Compound **13a-(***Z***)**:

 $\mathbf{R}_{\mathbf{f}} = 0.63, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.47 – 7.30 (m, 5H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 2.6 Hz, 2H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.03 (d, *J* = 2.5 Hz, 2H), 4.37 – 4.20 (m, 4H), 3.88 (s, 3H), 2.32 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H) ppm;

<sup>13</sup>**C** NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.2, 154.1, 137.1, 136.1, 135.1, 133.1, 129.1, 128.8, 128.1, 127.9, 112.1, 110.5, 105.3, 101.5, 64.2, 62.5, 56.1, 47.7, 14.2, 9.2 ppm;

(Note: one carbon signal is missing presumably due to overlap with the signal at 128.8 ppm) **IR (neat)**:  $v_{max} = 2927, 2361, 1730, 1485, 1388, 1241, 1161, 1035, 767 cm<sup>-1</sup>;$ 

**HRMS (APPI+)**: calc'd for  $C_{26}H_{28}NO_5 [M+H]^+ 434.1962$ , found 434.1981.

Compound **13a-(***E***)**:

 $\mathbf{R}_{\mathbf{f}} = 0.63, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  = 7.42 – 7.24 (m, 5H), 7.16 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.94 (bs, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.89 (d, *J* = 1.9 Hz, 2H), 4.00 – 3.85 (m, 4H), 3.87 (s, 3H), 2.21 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 6H) ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 167.6, 154.0, 137.9, 137.7, 135.0, 132.6, 129.0, 128.9, 128.1, 128.0, 127.5, 112.0, 110.5, 104.5, 101.4, 62.5, 62.3, 56.1, 50.7, 13.9, 8.6 ppm;

**IR (neat)**:  $v_{max} = 2961$ , 2924, 2361, 1730, 1482, 1368, 1231, 1161, 1043, 759 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>26</sub>H<sub>28</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 434.1962, found 434.1993.



Product 13b-(Z) and 13b-(E) were prepared following General Experimental Procedure C. Reagents employed: Substituted *N*-propargylindole 11b (154 mg, 0.600 mmol), diethyl diazomalonate 2a (93.1 mg, 0.500 mmol), Cu(tfacac)<sub>2</sub> (9.25 mg, 0.0500 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.600 mmol). 13b-(Z) (129 mg, 0.255 mmol, 51%) was obtained as a brown oil and 13b-(E) (35 mg, 0.069 mmol, 14%) was obtained as a brown oil:

#### Compound **13b-(***Z***)**:

 $\mathbf{R}_{\mathbf{f}} = 0.47, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.11 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.08 (t, *J* = 2.6 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.04 (d, *J* = 2.5 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 4.38 – 4.20 (m, 4H), 3.88 (s, 3H), 2.33 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 6H). ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.0, 166.3, 154.2, 140.3, 139.5, 134.7, 133.1, 130.0, 129.8, 128.7, 128.4, 127.8, 112.2, 110.5, 105.5, 101.5, 64.3, 62.6, 61.3, 56.1, 47.7, 14.5, 14.2, 9.2 ppm; **IR (neat)**: v<sub>max</sub> = 2984, 2853, 2361, 1716, 1607, 1485, 1366, 1241, 1101, 1026, 764 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>29</sub>H<sub>32</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 506.2175, found 506.2178.

Compound **13b-(***E***)**:

 $\mathbf{R_f} = 0.47, 25\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.01 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.95 (t, *J* = 2.0 Hz, 1H), 6.87 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.91 (d, *J* = 1.9 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 4.03 – 3.85 (m, 4H), 2.21 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.09 (s, 6H). ppm;

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.4, 166.5, 154.1, 139.6, 139.5, 137.5, 132.7, 129.8, 129.4, 128.9, 128.2, 127.5, 112.2, 110.5, 104.7, 101.4, 62.7, 62.4, 61.2, 56.1, 50.7, 14.5, 13.9, 8.6 ppm; **IR (neat)**: ν<sub>max</sub> = 2981, 2928, 2361, 1718, 1608, 1483, 1390, 1274, 1228, 1045, 768 cm<sup>-1</sup>; **HRMS (APPI+)**: calc'd for C<sub>29</sub>H<sub>32</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 506.2175, found 506.2204.



17 was prepared using General Experimental Procedure C. Reagents employed: 14 (84 mg, 0.32 mmol), diethyl diazomalonate (0.050 mg, 0.27 mmol), Cu(tfacac)<sub>2</sub> (5.0 mg, 0.014 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (9.0 mg, 0.027 mmol). 17 (45 mg, 0.11 mmol, 41%) was obtained as a brown oil: (Note: 10 mol% of Cs<sub>2</sub>CO<sub>3</sub> was used)

 $\mathbf{R_f} = 0.50, 20\%$  EtOAc in hexanes;

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.11 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.49 – 4.42 (m, 1H), 4.36 – 4.13 (m, 4H), 3.89 – 3.80 (m, 5H), 3.73 (s, 3H), 2.93 – 2.74 (m, 2H), 2.30 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.5, 168.5, 167.8, 154.0, 135.0, 133.1, 128.2, 112.2, 110.5, 105.9, 101.4, 62.3, 62.1, 56.1, 52.1, 48.2, 45.9, 34.2, 14.24, 14.17, 9.3 ppm; (Note: one carbon signal is missing presumably due to overlap with the signal at 62.09) IR (neat): v<sub>max</sub> = 2933, 2361, 1732, 1444, 1370, 1256, 1160, 1038, 795 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>22</sub>H<sub>28</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 418.1858, found 418.1873.



CO<sub>2</sub>Et 18 was prepared using General Experimental Procedure C. Reagents employed: 15 (92 mg, 0.32 mmol), diethyl diazomalonate (0.050 g, 0.27 mmol), Cu(tfacac)<sub>2</sub> (5.0 mg, 0.014 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (9.0 mg, 0.027 mmol). 18 (86 mg, 0.19 mmol, 70%) was obtained as yellow crystals: (Note: 10 mol% of Cs<sub>2</sub>CO<sub>3</sub> was used)

MP: 161-163 °C

 $\mathbf{R}_{\mathbf{f}} = 0.40, 25\%$  Acetone in hexanes;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.14 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.29 – 4.09 (m, 6H), 3.82 (s, 3H), 3.59 (s, 3H), 3.08 – 2.93 (m, 1H), 2.76 (t, *J* = 6.5 Hz, 2H), 2.69 – 2.52 (m, 2H), 2.30 – 2.08 (m, 2H), 1.30 – 1.22 (m, 9H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.9, 171.2, 170.1, 153.7, 137.5, 132.6, 126.7, 110.8, 109.3, 105.1, 103.7, 61.6, 61.3, 60.5, 58.1, 55.9, 37.0, 35.3, 29.3, 24.6, 20.3, 14.34, 14.28, 14.25 ppm; IR (neat): v<sub>max</sub> = 2981, 1726, 1621, 1486, 1371, 1251, 1188, 1071, 798 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>24</sub>H<sub>32</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 445.2178, found 446.2207.



CO<sub>2</sub>Et 17 was prepared using General Experimental Procedure C. Reagents employed: 16 (92 mg, 0.32 mmol), diethyl diazomalonate (0.050 g, 0.27 mmol), Cu(tfacac)<sub>2</sub> (5.0 mg, 0.014 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (9.0 mg, 0.027 mmol). 19 (82 mg, 0.18 mmol, 67%) was obtained as light green oil: (Note: 10 mol% of Cs<sub>2</sub>CO<sub>3</sub> was used)

 $\mathbf{R}_{\mathbf{f}} = 0.40, 20\%$  Acetone in hexanes;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.19 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.28 – 4.10 (m, 6H), 3.86 (s, 3H), 3.63 (s, 3H), 3.20 – 3.12 (m, 1H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.73 – 2.57 (m, 2H), 2.11 – 1.96 (m, 2H), 1.29 – 1.23 (m, 9H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.9, 170.2, 169.1, 154.0, 133.5, 130.6, 126.0, 112.6, 111.5, 110.1, 100.6, 62.3, 62.1, 60.6, 59.2, 56.2, 38.9, 35.6, 31.8, 25.8, 19.4, 14.4, 14.12, 14.08 ppm; IR (neat):  $v_{max}$  = 2975, 2935, 2360, 1738, 1489, 1273, 1162, 1035, 798 cm<sup>-1</sup>; HRMS (APPI+): calc'd for C<sub>24</sub>H<sub>32</sub>NO<sub>7</sub> [M+H]<sup>+</sup> 445.2178 found 446.2193.

## **Experimental details**

Single-crystal X-ray diffraction data was collected at 173(2) K on a XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5406$  Å). Crystal was mounted on nylon CryoLoops with Paraton-N. The data collection and reduction were processed within *CrysAlisPro* (Rigaku OD, 2019). A multi-scan absorption correction was applied to the collected reflections. Using Olex<sup>2</sup> [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically.

<sup>1.</sup> Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

<sup>2.</sup> Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

<sup>3.</sup> Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.



**Figure S15** X-ray crystal structure of **3a** (Only one orientation of the disordered ethyl group is shown for clarity. Non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level.)

<b>Fable S2</b> Crystal data and structure refinement			
Empirical formula	C <sub>22</sub> H <sub>25</sub> NO <sub>7</sub>		
Formula weight	415.43		
Temperature/K	173(2)		
Crystal system	triclinic		
Space group	<i>P</i> -1		
a/Å	8.1806(3)		
<i>b</i> /Å	11.5207(3)		
c/Å	12.2742(2)		
$\alpha^{\prime \circ}$	70.006(2)		
$\beta^{\prime}$	77.003(2)		
$\gamma^{\prime \circ}$	88.377(3)		
Volume/Å <sup>3</sup>	1057.73(5)		
Ζ	2		
$ ho_{ m calc} { m g/cm^3}$	1.304		
$\mu/\mathrm{mm}^{-1}$	0.812		
F(000)	440.0		
Crystal size/mm <sup>3</sup>	0.18  imes 0.13  imes 0.1		
Radiation	$Cu K\alpha (\lambda = 1.54184)$		
$2\theta$ range for data collection/°	7.874 to 154.884		
Index ranges	$-10 \le h \le 10, -14 \le k \le 14, -13 \le l \le 15$		
Reflections collected	26839		
Independent reflections	4446 [ $R_{\text{int}} = 0.0554, R_{\text{sigma}} = 0.0298$ ]		
Data/restraints/parameters	4446/1/287		
Goodness-of-fit on F <sup>2</sup>	1.079		
Final <i>R</i> indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0402, wR_2 = 0.1089$		
Final R indexes [all data]	$R_1 = 0.0434, wR_2 = 0.1122$		
Largest diff. peak/hole / e Å <sup>-3</sup>	0.17/-0.24		

Parameters (Å <sup>2</sup> ×10 <sup>3</sup> ). U <sub>eq</sub> is defined as 1/3 of the trace of the orthogonalised U <sub>IJ</sub> tensor.				
Atom	x	у	Z	U(eq)
O1	759.6(13)	1385.7(9)	10042.9(8)	46.7(2)
O2	4883.3(12)	1884.2(9)	3192.3(8)	42.5(2)
O3	7138.2(11)	1318.9(8)	3968.8(8)	38.1(2)
O4	8738.1(11)	3740.5(8)	4371.4(8)	38.1(2)
05	8693.5(11)	3755.2(9)	2535.7(8)	39.6(2)
06	3093.9(11)	6177.1(9)	2054.9(7)	39.6(2)
07	5114.8(12)	6431.6(10)	405.6(8)	46.7(2)
N1	3736.0(12)	3502.0(9)	5298.2(8)	28.9(2)
C1	2819.8(14)	3090.9(10)	6455.2(9)	28.1(2)
C2	1182.2(15)	3311.6(11)	6951.1(10)	32.0(2)
C3	581.0(15)	2713.9(11)	8156.0(11)	35.9(3)
C4	1567.6(16)	1908.7(11)	8858.1(10)	35.0(3)
C5	3176.3(15)	1672.5(11)	8374.2(10)	32.9(2)
C6	3826.3(14)	2272.1(10)	7138.8(10)	28.9(2)
C7	5380.5(14)	2187.7(10)	6353.4(10)	29.3(2)
C8	5248.5(14)	2949.6(10)	5241.2(10)	28.3(2)
C9	6132.2(14)	3255.4(10)	3950.0(10)	29.2(2)
C10	5068.8(14)	4272.1(10)	3307.6(10)	30.1(2)
C11	3453.5(14)	4332.5(11)	4173.3(9)	31.0(2)
C12	1616(2)	478.2(15)	10784.1(12)	53.8(4)
C13	6798.3(16)	1412.6(12)	6712.0(11)	37.9(3)
C14	5965.5(14)	2085.7(11)	3630.3(10)	31.0(2)
C15	7169.1(18)	168.1(12)	3718.0(14)	44.4(3)
C16	8499(2)	-565.7(14)	4249.6(18)	57.1(4)
C17	8006.7(14)	3623.1(10)	3669.2(10)	31.4(2)
C18	10509.5(16)	4002.7(16)	2141.6(14)	49.3(3)
C19	11053(4)	4194(5)	907(3)	67.4(12)
C19A	11319(4)	2944(4)	2201(4)	69.8(12)
C20	5517.1(15)	4971.2(12)	2159.1(10)	35.0(3)
C21	4430.7(15)	5907.4(11)	1578.0(10)	33.7(3)
C22	4129(2)	7353.3(16)	-248.2(12)	56.0(4)

**Table S3**Fractional Atomic Coordinates (×10<sup>4</sup>) and Equivalent Isotropic Displacement

Table S4	Selected	Bond Distances (Å)					
Atom	Atom	Length/Å	Atom	Atom	Length/Å		
01	C4	1.3805(14)	C3	C4	1.4066(17)		
01	C12	1.4166(17)	C4	C5	1.3775(17)		
O2	C14	1.1991(14)	C5	C6	1.4146(16)		
O3	C14	1.3243(14)	C6	C7	1.4356(16)		
O3	C15	1.4583(14)	C7	C8	1.3738(16)		
O4	C17	1.1981(14)	C7	C13	1.4962(15)		
05	C17	1.3352(14)	C8	C9	1.5085(15)		
05	C18	1.4590(15)	C9	C10	1.5394(15)		
O6	C21	1.2051(16)	C9	C14	1.5442(15)		
07	C21	1.3458(14)	C9	C17	1.5326(15)		
07	C22	1.4426(17)	C10	C11	1.5145(16)		
N1	C1	1.3727(14)	C10	C20	1.3335(16)		
N1	C8	1.3740(14)	C15	C16	1.488(2)		
N1	C11	1.4502(14)	C18	C19	1.420(4)		
C1	C2	1.3962(16)	C18	C19A	1.359(4)		
C1	C6	1.4133(15)	C20	C21	1.4720(17)		
C2	C3	1.3780(16)					
Table S	5	Selected	Dolla Aligles				
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Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	O1	C12	116.87(11)	C7	C8	C9	140.03(10)
C14	O3	C15	116.83(10)	C8	C9	C10	102.46(9)
C17	05	C18	116.69(10)	C8	C9	C14	107.16(9)
C21	07	C22	114.97(11)	C8	C9	C17	114.38(9)
C1	N1	C8	109.17(9)	C10	C9	C14	110.04(9)
C1	N1	C11	135.14(9)	C17	C9	C10	114.60(9)
C8	N1	C11	115.68(9)	C17	C9	C14	107.90(9)
N1	C1	C2	130.90(10)	C11	C10	C9	109.57(9)
N1	C1	C6	106.71(10)	C20	C10	C9	124.32(11)
C2	C1	C6	122.29(10)	C20	C10	C11	126.11(11)
C3	C2	C1	117.18(10)	N1	C11	C10	102.14(9)
C2	C3	C4	121.57(11)	O2	C14	O3	125.45(11)
O1	C4	C3	113.66(11)	O2	C14	C9	124.65(11)
C5	C4	01	124.65(11)	O3	C14	C9	109.82(9)
C5	C4	C3	121.68(11)	O3	C15	C16	106.81(11)
C4	C5	C6	118.01(10)	O4	C17	05	125.78(11)
C1	C6	C5	119.27(10)	O4	C17	C9	124.90(10)
C1	C6	C7	108.33(10)	05	C17	C9	109.29(9)
C5	C6	C7	132.34(10)	C19	C18	O5	110.63(17)
C6	C7	C13	125.78(10)	C19A	C18	O5	111.17(19)
C8	C7	C6	105.12(9)	C10	C20	C21	122.19(11)
C8	C7	C13	129.10(11)	O6	C21	O7	123.07(11)
N1	C8	C9	108.70(9)	O6	C21	C20	126.17(11)
C7	C8	N1	110.66(10)	07	C21	C20	110.76(10)

Table S5Selected Bond Angles

Tabl	le S6	S	elected	Torsion Angles					
Α	В	С	D	Angle/°	Α	В	С	D	Angle/°
01	C4	C5	C6	179.37(11)	C8	C9	C17	05	174.01(9)
N1	C1	C2	C3	177.20(11)	C9	C10	C11	N1	7.97(11)
N1	C1	C6	C5	-178.18(9)	C9	C10	C20	C21	178.15(10)
N1	C1	C6	C7	-0.71(12)	C10	C9	C14	O2	-16.54(15)
N1	C8	C9	C10	11.29(11)	C10	C9	C14	O3	166.69(9)
N1	C8	C9	C14	-104.52(10)	C10	C9	C17	O4	113.66(13)
N1	C8	C9	C17	135.92(10)	C10	C9	C17	05	-68.08(12)
C1	N1	C8	C7	-1.29(13)	C10	C20	C21	O6	2.8(2)
C1	N1	C8	C9	171.60(9)	C10	C20	C21	07	-176.10(11)
C1	N1	C11	C10	-178.94(11)	C11	N1	C1	C2	3.3(2)
C1	C2	C3	C4	-0.40(18)	C11	N1	C1	C6	179.67(11)
C1	C6	C7	C8	-0.05(12)	C11	N1	C8	C7	179.91(9)
C1	C6	C7	C13	-179.56(11)	C11	N1	C8	C9	-7.20(13)
C2	C1	C6	C5	-1.46(17)	C11	C10	C20	C21	-0.94(19)
C2	C1	C6	C7	176.01(10)	C12	01	C4	C3	174.38(12)
C2	C3	C4	01	-179.56(11)	C12	01	C4	C5	-4.7(2)
C2	C3	C4	C5	-0.5(2)	C13	C7	C8	N1	-179.70(11)
C3	C4	C5	C6	0.36(18)	C13	C7	C8	C9	10.8(2)
C4	C5	C6	C1	0.56(17)	C14	03	C15	C16	-176.18(12)
C4	C5	C6	C7	-176.19(12)	C14	C9	C10	C11	101.90(10)
C5	C6	C7	C8	176.97(12)	C14	C9	C10	C20	-77.32(14)
C5	C6	C7	C13	-2.5(2)	C14	C9	C17	O4	-123.38(12)
C6	C1	C2	C3	1.36(17)	C14	C9	C17	05	54.88(12)
C6	C7	C8	N1	0.80(12)	C15	03	C14	O2	3.97(17)
C6	C7	C8	C9	-168.68(13)	C15	03	C14	C9	-179.29(10)
C7	C8	C9	C10	-179.10(14)	C17	05	C18	C19	-176.6(2)
C7	C8	C9	C14	65.08(17)	C17	05	C18	C19A	96.1(2)
C7	C8	C9	C17	-54.47(18)	C17	C9	C10	C11	-136.30(10)
C8	N1	C1	C2	-175.12(11)	C17	C9	C10	C20	44.48(15)
C8	N1	C1	C6	1.20(12)	C17	C9	C14	O2	-142.24(12)
C8	N1	C11	C10	-0.55(12)	C17	C9	C14	03	40.99(12)
C8	C9	C10	C11	-11.82(11)	C18	05	C17	O4	3.29(18)
C8	C9	C10	C20	168.97(11)	C18	05	C17	C9	-174.96(11)
C8	C9	C14	O2	94.13(13)	C20	C10	C11	N1	-172.83(11)
C8	C9	C14	O3	-82.64(11)	C22	O7	C21	06	0.25(19)
C8	C9	C17	O4	-4.25(16)	C22	O7	C21	C20	179.20(12)

# X-ray Crystallographic Analysis of 3g

# **Experimental details**

Single-crystal X-ray diffraction data was collected at 100(2) K on a XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5406$  Å). Crystal was mounted on nylon CryoLoops with Paraton-N. The data collection and reduction were processed within *CrysAlisPro* (Rigaku OD, 2019). A multi-scan absorption correction was applied to the collected reflections. Using Olex<sup>2</sup> [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically.

<sup>1.</sup> Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

<sup>2.</sup> Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

<sup>3.</sup> Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.



**Figure S16** X-ray crystal structure of **3g** (Non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level)

Table S7Crystal data and structure it	refinement					
Empirical formula	C <sub>23</sub> H <sub>27</sub> NO <sub>7</sub>					
Formula weight	429.45					
Temperature/K	100(2)					
Crystal system	triclinic					
Space group	<i>P</i> -1					
a/Å	8.24253(9)					
b/Å	10.98466(11)					
c/Å	12.92511(13)					
$\alpha/^{\circ}$	111.4045(10)					
$\beta^{\prime}$	93.4027(8)					
$\gamma/^{\circ}$	104.9018(9)					
Volume/Å <sup>3</sup>	1037.52(2)					
Ζ	2					
$ ho_{ m calc} g/{ m cm}^3$	1.375					
$\mu/\text{mm}^{-1}$	0.846					
F(000)	456.0					
Crystal size/mm <sup>3</sup>	0.23  imes 0.17  imes 0.07					
Radiation	$Cu K\alpha (\lambda = 1.54184)$					
$2\theta$ range for data collection/°	7.456 to 154.448					
Index ranges	$-10 \le h \le 10, -13 \le k \le 13, -16 \le l \le 16$					
Reflections collected	50608					
Independent reflections	4341 [ $R_{\text{int}} = 0.0396, R_{\text{sigma}} = 0.0148$ ]					
Data/restraints/parameters	4341/0/285					
Goodness-of-fit on F <sup>2</sup>	1.037					
Final <i>R</i> indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0324, wR_2 = 0.0818$					
Final <i>R</i> indexes [all data]	$R_1 = 0.0333, wR_2 = 0.0825$					
Largest diff. peak/hole / e Å <sup>-3</sup>	0.32/-0.29					

Atom	<i>x</i>	у	z	U(eq)
01	7298.4(9)	2147.8(8)	2002.9(6)	17.61(16)
O2	4980.1(9)	4356.3(7)	8264.9(6)	19.32(17)
O3	3746.8(9)	2303.7(7)	8305.9(6)	16.08(16)
O4	1672.3(9)	269.4(7)	5878.6(6)	17.68(16)
05	135.2(9)	1328.8(7)	7088.5(6)	17.34(16)
O6	-850.1(10)	5499.5(8)	7510.6(7)	23.08(18)
O7	212.0(10)	6030.4(8)	9313.7(6)	20.54(17)
N1	3035.3(11)	3306.6(8)	5082.5(7)	13.90(17)
C1	4068.6(13)	3158.5(10)	4277.1(8)	14.1(2)
C2	4062.1(13)	3534.0(10)	3350.5(8)	15.5(2)
C3	5190.7(13)	3180.3(10)	2634.5(8)	15.9(2)
C4	6304.7(13)	2469.7(10)	2826.8(8)	14.7(2)
C5	6364.5(13)	2142.2(10)	3763.5(8)	14.6(2)
C6	5226.4(13)	2509.6(10)	4513.6(8)	14.0(2)
C7	4899.2(13)	2305.1(10)	5524.9(8)	14.1(2)
C8	3554.1(13)	2797.5(10)	5837.7(8)	13.36(19)
C9	2591.9(12)	2780.1(10)	6801.9(8)	13.3(2)
C10	1431.2(12)	3702.8(10)	6958.6(8)	13.8(2)
C11	444.6(13)	3465.3(10)	5847.0(8)	15.8(2)
C12	1703.8(13)	3973.9(10)	5167.2(8)	15.2(2)
C13	8518.6(14)	1504.5(11)	2178.5(9)	19.7(2)
C14	5885.0(13)	1694.8(11)	6109.5(9)	17.1(2)
C15	3914.9(13)	3255.6(10)	7873.9(8)	13.71(19)
C16	5055.4(14)	2648.9(11)	9271.1(9)	18.4(2)
C17	4759.4(15)	1412.6(12)	9565.3(9)	23.1(2)
C18	1427.1(12)	1290.5(10)	6519.2(8)	13.55(19)
C19	-1159.7(13)	30.6(10)	6870.4(9)	16.7(2)
C20	-1973.3(16)	231.2(12)	7903.5(10)	26.7(3)
C21	1334.9(13)	4584.4(10)	7970.0(9)	15.3(2)
C22	122.7(13)	5400.7(10)	8189.7(9)	16.6(2)
C23	-1057.0(15)	6722.3(12)	9644.3(10)	24.3(2)

**Table S8**Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic DisplacementParameters (Å<sup>2</sup> $\times 10^3$ ). U<sub>eq</sub> is defined as 1/3 of the trace of the orthogonalised U<sub>IJ</sub> tensor.

Table S9	Selected	Bond Distances (Å)			
Atom	Atom	Length/Å	Atom	Atom	Length/Å
01	C4	1.3811(12)	C3	C4	1.4133(14)
01	C13	1.4206(13)	C4	C5	1.3847(14)
O2	C15	1.2014(13)	C5	C6	1.4141(14)
O3	C15	1.3361(12)	C6	C7	1.4342(14)
O3	C16	1.4656(12)	C7	C8	1.3738(14)
O4	C18	1.2013(13)	C7	C14	1.5025(13)
05	C18	1.3306(12)	C8	С9	1.5196(13)
05	C19	1.4630(12)	C9	C10	1.5348(13)
O6	C22	1.2065(13)	C9	C15	1.5432(13)
07	C22	1.3499(13)	C9	C18	1.5642(13)
07	C23	1.4420(13)	C10	C11	1.5074(13)
N1	C1	1.3742(13)	C10	C21	1.3345(14)
N1	C8	1.3857(12)	C11	C12	1.5263(14)
N1	C12	1.4571(13)	C16	C17	1.5053(15)
C1	C2	1.4020(14)	C19	C20	1.4995(15)
C1	C6	1.4095(14)	C21	C22	1.4804(14)
C2	C3	1.3778(15)			

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	01	C13	116.63(8)	C7	C8	С9	129.76(9)
C15	03	C16	114.99(8)	C8	C9	C10	110.44(8)
C18	05	C19	117.75(8)	C8	C9	C15	107.90(8)
C22	07	C23	114.87(9)	C8	С9	C18	109.53(8)
C1	N1	C8	108.30(8)	C10	С9	C15	111.67(8)
C1	N1	C12	125.50(8)	C10	C9	C18	107.44(8)
C8	N1	C12	126.07(9)	C15	C9	C18	109.87(8)
N1	C1	C2	129.69(9)	C11	C10	C9	111.53(8)
N1	C1	C6	107.97(9)	C21	C10	C9	122.53(9)
C2	C1	C6	122.34(9)	C21	C10	C11	125.93(9)
C3	C2	C1	117.08(9)	C10	C11	C12	108.09(8)
C2	C3	C4	121.39(9)	N1	C12	C11	108.76(8)
O1	C4	C3	113.74(9)	02	C15	O3	124.23(9)
O1	C4	C5	124.41(9)	O2	C15	C9	123.36(9)
C5	C4	C3	121.85(9)	O3	C15	C9	112.40(8)
C4	C5	C6	117.50(9)	O3	C16	C17	107.30(8)
C1	C6	C5	119.72(9)	O4	C18	05	125.50(9)
C1	C6	C7	107.39(9)	O4	C18	C9	124.53(9)
C5	C6	C7	132.82(9)	O5	C18	C9	109.97(8)
C6	C7	C14	125.47(9)	O5	C19	C20	106.71(8)
C8	C7	C6	106.11(9)	C10	C21	C22	125.13(9)
C8	C7	C14	128.41(9)	O6	C22	07	122.77(10)
N1	C8	C9	119.96(9)	06	C22	C21	127.99(10)
C7	C8	N1	110.20(9)	<b>O</b> 7	C22	C21	109.21(9)

Table S10Selected Bond Angles

Tabl	e S11	Se	elected	Torsion Angles					
Α	B	С	D	Angle/°	Α	B	С	D	Angle/°
01	C4	C5	C6	-178.18(9)	C8	C9	C18	05	-155.71(8)
N1	C1	C2	C3	-176.03(10)	C9	C10	C11	C12	-67.77(10)
N1	C1	C6	C5	175.48(9)	C9	C10	C21	C22	-173.65(9)
N1	C1	C6	C7	-1.92(11)	C10	C9	C15	O2	-61.97(13)
N1	C8	C9	C10	-15.03(12)	C10	C9	C15	O3	118.57(9)
N1	C8	C9	C15	-137.33(9)	C10	C9	C18	O4	144.09(10)
N1	C8	C9	C18	103.10(10)	C10	C9	C18	05	-35.72(10)
C1	N1	C8	C7	-0.73(11)	C10	C11	C12	N1	54.46(10)
C1	N1	C8	C9	-177.75(8)	C10	C21	C22	06	-6.84(18)
C1	N1	C12	C11	158.64(9)	C10	C21	C22	07	171.37(10)
C1	C2	C3	C4	0.02(14)	C11	C10	C21	C22	5.76(16)
C1	C6	C7	C8	1.46(11)	C12	N1	C1	C2	-3.04(16)
C1	C6	C7	C14	-177.48(9)	C12	N1	C1	C6	177.69(9)
C2	C1	C6	C5	-3.87(15)	C12	N1	C8	C7	-176.74(9)
C2	C1	C6	C7	178.73(9)	C12	N1	C8	C9	6.23(14)
C2	C3	C4	O1	177.47(9)	C13	01	C4	C3	176.40(8)
C2	C3	C4	C5	-2.56(15)	C13	01	C4	C5	-3.57(14)
C3	C4	C5	C6	1.85(14)	C14	C7	C8	N1	178.43(9)
C4	C5	C6	C1	1.25(14)	C14	C7	C8	C9	-4.92(17)
C4	C5	C6	C7	177.87(10)	C15	03	C16	C17	-174.54(9)
C5	C6	C7	C8	-175.46(10)	C15	C9	C10	C11	165.93(8)
C5	C6	C7	C14	5.60(17)	C15	C9	C10	C21	-14.59(13)
C6	C1	C2	C3	3.16(14)	C15	C9	C18	O4	-94.24(11)
C6	C7	C8	N1	-0.47(11)	C15	C9	C18	05	85.94(9)
C6	C7	C8	C9	176.18(9)	C16	03	C15	O2	-4.31(14)
C7	C8	C9	C10	168.60(10)	C16	03	C15	C9	175.15(8)
C7	C8	C9	C15	46.30(13)	C18	05	C19	C20	155.61(9)
C7	C8	C9	C18	-73.27(13)	C18	C9	C10	C11	-73.54(10)
C8	N1	C1	C2	-179.08(10)	C18	C9	C10	C21	105.95(10)
C8	N1	C1	C6	1.65(11)	C18	C9	C15	O2	178.93(9)
C8	N1	C12	C11	-26.01(13)	C18	C9	C15	O3	-0.53(11)
C8	C9	C10	C11	45.87(10)	C19	05	C18	O4	-4.01(14)
C8	C9	C10	C21	-134.65(10)	C19	05	C18	C9	175.80(8)
C8	C9	C15	O2	59.58(12)	C21	C10	C11	C12	112.76(11)
C8	C9	C15	03	-119.88(9)	C23	<b>O</b> 7	C22	06	5.78(14)
C8	C9	C18	04	24.11(13)	C23	<b>O</b> 7	C22	C21	-172.54(8)

### **Experimental details**

Single-crystal X-ray diffraction data was collected at 100(2) K on a XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5406$  Å). Crystal was mounted on nylon CryoLoops with Paraton-N. The data collection and reduction were processed within *CrysAlisPro* (Rigaku OD, 2019). A multi-scan absorption correction was applied to the collected reflections. Using Olex<sup>2</sup> [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
- 3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.



Figure S17 X-ray crystal structure of 7 (Non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level).

refinement				
AHB-A-106				
$C_{23}H_{27}NO_7$				
429.45				
100(2)				
monoclinic				
$P2_{1}/c$				
13.27378(13)				
17.12971(15)				
9.94500(9)				
104.3152(10)				
2191.04(4)				
4				
1.302				
0.801				
912.0				
$0.199 \times 0.136 \times 0.074$				
6.872 to 154.686°				
$-15 \le h \le 16, -21 \le k \le 21, -10 \le l \le 12$				
19064				
4580 [R(int) = 0.0550]				
4580/0/286				
1.060				
$R_1 = 0.0402, wR_2 = 0.1027$				
$R_1 = 0.0461, wR_2 = 0.1069$				
0.25/-0.21				

Atom	x	у	z	U(eq)
01	3799.3(8)	6228.6(6)	8214.9(9)	25.6(2)
O2	3940.5(7)	4509.9(5)	3899.1(9)	20.4(2)
O3	3788.9(7)	5496.4(5)	2363.7(9)	20.2(2)
O4	1436.0(7)	5882.2(6)	871.7(9)	21.8(2)
05	2027.5(7)	6312.7(5)	3060.1(9)	19.2(2)
O6	1375.3(9)	3025.2(6)	-539.1(11)	31.3(2)
O7	3114.7(9)	2941.1(6)	-46.1(13)	37.0(3)
N1	902.8(9)	4168.5(7)	5272.1(11)	21.1(2)
C1	1579.5(10)	4667.5(8)	6152.1(13)	19.5(3)
C2	1725.4(11)	4796.9(8)	7573.3(14)	22.6(3)
C3	2472.2(11)	5327.4(8)	8207.2(13)	23.0(3)
C4	3068.6(10)	5730.9(8)	7437.4(13)	20.3(3)
C5	2918.6(10)	5615.7(7)	6022.7(13)	17.8(3)
C6	2169.6(10)	5068.4(7)	5368.2(13)	16.7(3)
C7	1818.5(10)	4785.9(7)	3972.9(12)	16.7(3)
C8	2221.7(10)	4964.7(7)	2706.1(12)	16.0(3)
C9	1822.4(10)	4320.2(7)	1627.0(12)	18.0(3)
C10	682.1(10)	4148.3(8)	1413.7(14)	22.3(3)
C11	454.6(10)	3801.1(8)	2735.3(14)	23.0(3)
C12	1049.0(10)	4249.7(7)	3958.6(13)	19.0(3)
C13	163.1(11)	3646.2(9)	5667.0(16)	27.4(3)
C14	4369.8(11)	6705.2(8)	7492.0(15)	26.4(3)
C15	3418.1(10)	4962.5(7)	3092.5(12)	16.1(2)
C16	4916.2(10)	5480.3(9)	2534.9(15)	25.4(3)
C17	5210.6(13)	6174.6(11)	1812(2)	38.8(4)
C18	1841.2(10)	5764.6(7)	2074.4(12)	16.4(2)
C19	1749.4(11)	7107.9(7)	2608.6(13)	20.8(3)
C20	1963.7(12)	7603.9(8)	3891.1(14)	25.3(3)
C21	2475.2(11)	3941.4(8)	1026.1(13)	19.3(3)
C22	2219.1(11)	3267.8(8)	66.6(13)	22.1(3)
C23	3008.3(17)	2265.0(12)	-941(3)	62.5(7)

**Table S13**Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic DisplacementParameters (Å<sup>2</sup> $\times 10^3$ ). U<sub>eq</sub> is defined as 1/3 of the trace of the orthogonalised U<sub>IJ</sub> tensor.

Table S14	Selected Bo	ond Distances (Å)			
Atom	Atom	Length/Å	Atom	Atom	Length/Å
01	C4	1.3764(17)	C3	C4	1.4108(19)
01	C14	1.4234(18)	C4	C5	1.3854(18)
O2	C15	1.2042(16)	C5	C6	1.4040(18)
O3	C15	1.3343(15)	C6	C7	1.4343(17)
O3	C16	1.4638(15)	C7	C8	1.5168(16)
O4	C18	1.2010(15)	C7	C12	1.3711(18)
05	C18	1.3355(15)	C8	C9	1.5396(17)
05	C19	1.4530(15)	C8	C15	1.5388(17)
O6	C22	1.2068(18)	C8	C18	1.5397(17)
07	C22	1.3435(18)	C9	C10	1.5046(18)
07	C23	1.4459(19)	C9	C21	1.3360(19)
N1	C1	1.3837(18)	C10	C11	1.5390(19)
N1	C12	1.3744(17)	C11	C12	1.4894(19)
N1	C13	1.4524(17)	C16	C17	1.491(2)
C1	C2	1.3960(19)	C19	C20	1.5001(19)
C1	C6	1.4123(18)	C21	C22	1.4823(18)
C2	C3	1.377(2)			

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	01	C14	117.42(10)	C7	C8	C18	111.78(10)
C15	O3	C16	115.32(10)	C9	C8	C18	109.39(10)
C18	05	C19	116.45(9)	C15	C8	C9	109.18(10)
C22	07	C23	115.54(13)	C15	C8	C18	108.56(10)
C1	N1	C13	125.88(11)	C10	C9	C8	113.55(11)
C12	N1	C1	108.45(11)	C21	C9	C8	120.69(12)
C12	N1	C13	125.67(12)	C21	C9	C10	125.66(12)
N1	C1	C2	130.11(12)	C9	C10	C11	110.99(11)
N1	C1	C6	108.25(11)	C12	C11	C10	108.79(11)
C2	C1	C6	121.64(12)	N1	C12	C11	123.60(12)
C3	C2	C1	118.17(12)	C7	C12	N1	109.74(11)
C2	C3	C4	120.79(12)	C7	C12	C11	126.65(12)
01	C4	C3	114.24(11)	O2	C15	O3	125.04(12)
01	C4	C5	124.27(12)	O2	C15	C8	123.82(11)
C5	C4	C3	121.48(13)	O3	C15	C8	111.05(10)
C4	C5	C6	118.26(12)	O3	C16	C17	108.13(12)
C1	C6	C7	106.15(11)	O4	C18	05	124.69(12)
C5	C6	C1	119.64(11)	O4	C18	C8	125.21(11)
C5	C6	C7	134.21(11)	05	C18	C8	110.09(10)
C6	C7	C8	129.68(11)	05	C19	C20	106.74(10)
C12	C7	C6	107.40(11)	C9	C21	C22	126.52(12)
C12	C7	C8	122.79(11)	O6	C22	O7	123.11(12)
C7	C8	C9	107.63(10)	O6	C22	C21	128.76(13)
C7	C8	C15	110.27(10)	07	C22	C21	108.13(11)

Table S15Selected Bond Angles

e S16	Sele	ected To	rsion Angles					
В	С	D	Angle/°	Α	В	С	D	Angle/°
C4	C5	C6	177.71(11)	C9	C8	C18	O4	-10.53(17)
C1	C2	C3	179.17(13)	C9	C8	C18	05	169.51(10)
C1	C6	C5	179.88(11)	C9	C10	C11	C12	43.36(14)
C1	C6	C7	-0.15(14)	C9	C21	C22	06	14.5(2)
N1	C12	C7	0.76(15)	C9	C21	C22	O7	-165.55(13)
N1	C12	C11	179.86(12)	C10	C9	C21	C22	-1.8(2)
C2	C3	C4	0.3(2)	C10	C11	C12	N1	169.88(12)
C6	C7	C8	-175.26(12)	C10	C11	C12	C7	-11.18(18)
C6	C7	C12	0.60(14)	C12	N1	C1	C2	180.00(13)
C1	C6	C5	-0.45(19)	C12	N1	C1	C6	-0.36(14)
C1	C6	C7	179.53(12)	C12	C7	C8	C9	-13.57(16)
C3	C4	O1	-178.63(12)	C12	C7	C8	C15	-132.57(12)
C3	C4	C5	0.7(2)	C12	C7	C8	C18	106.57(13)
C4	C5	C6	-1.57(19)	C13	N1	C1	C2	-0.1(2)
C5	C6	C1	1.42(18)	C13	N1	C1	C6	179.59(12)
C5	C6	C7	-178.55(13)	C13	N1	C12	C7	-179.19(12)
C6	C7	C8	4.7(2)	C13	N1	C12	C11	-0.1(2)
C6	C7	C12	-179.43(14)	C14	01	C4	C3	-174.77(12)
C1	C2	C3	-0.43(19)	C14	01	C4	C5	5.90(19)
C7	C8	C9	161.73(12)	C15	03	C16	C17	-172.38(12)
C7	C8	C15	42.73(17)	C15	C8	C9	C10	166.98(10)
C7	C8	C18	-78.13(16)	C15	C8	C9	C21	-9.68(16)
C7	C12	N1	-0.84(14)	C15	C8	C18	04	108.52(14)
C7	C12	C11	-179.91(12)	C15	C8	C18	05	-71.44(12)
C8	C9	C10	47.28(13)	C16	03	C15	O2	3.47(18)
C8	C9	C21	-129.38(12)	C16	03	C15	C8	-173.17(10)
C8	C15	O2	38.17(16)	C18	05	C19	C20	176.46(11)
C8	C15	O3	-145.14(10)	C18	C8	C9	C10	-74.36(13)
C8	C18	O4	-129.63(13)	C18	C8	C9	C21	108.98(13)
C8	C18	05	50.41(13)	C18	C8	C15	O2	160.93(11)
C7	C12	N1	175.37(11)	C18	C8	C15	03	-22.38(13)
C7	C12	C11	-3.7(2)	C19	05	C18	04	-2.48(18)
C9	C10	C11	-65.50(14)	C19	05	C18	C8	177.48(10)
С9	C21	C22	174.46(12)	C21	C9	C10	C11	110.96(14)
C8	C15	O2	-79.88(14)	C23	07	C22	06	-0.6(2)
C8	C15	03	96.81(12)	C23	07	C22	C21	179.43(16)
	<b>B</b> C4         C1         C2         C6         C1         C3         C3         C4         C5         C6         C1         C7         C7 <td>B       C         C4       C5         C1       C2         C1       C6         C1       C6         N1       C12         C2       C3         C6       C7         C1       C6         C3       C4         C3       C4         C3       C4         C3       C4         C4       C5         C5       C6         C5       C6         C5       C6         C7       C8         C7       C12         C8       C15         C8       C15<td>B         C         D           C4         C5         C6           C1         C2         C3           C1         C6         C7           N1         C12         C1           C2         C3         C4           C6         C7         N1           C12         C1         C6           N1         C12         C11           C2         C3         C4           C6         C7         C8           C6         C7         C12           C1         C6         C7           C3         C4         O1           C3         C4         C5           C4         C5         C6           C5         C6         C7           C6         C7         C8           C4         C5         C6           C5         C6         C7           C6         C7         C8           C6         C7         C8           C7         C8         C15           C7         C8         C15           C7         C8         C12           C8         C15         O2</td><td>BCDAngle/°C4C5C6<math>177.71(11)</math>C1C2C3<math>179.17(13)</math>C1C6C5<math>179.88(11)</math>C1C6C7<math>-0.15(14)</math>N1C12C11<math>179.86(12)</math>C2C3C4<math>0.3(2)</math>C6C7C12<math>0.60(14)</math>C1C6C5<math>-0.45(19)</math>C1C6C7<math>179.53(12)</math>C3C4C1<math>-178.63(12)</math>C3C4C5<math>0.7(2)</math>C4C5C6<math>-1.57(19)</math>C5C6C1<math>1.42(18)</math>C5C6C7<math>-178.55(13)</math>C6C7C12<math>-179.43(14)</math>C1C2C3<math>-0.43(19)</math>C7C8C15<math>42.73(17)</math>C7C8C15<math>42.73(17)</math>C7C8C18<math>-78.13(16)</math>C7C12C11<math>-179.91(12)</math>C8C9C10<math>47.28(13)</math>C8C15O2<math>38.17(16)</math>C8C15O3<math>-145.14(10)</math>C8C18O4<math>-129.63(13)</math>C7C12C11<math>-3.7(2)</math>C9C10C11<math>-65.50(14)</math>C9C21C22<math>174.46(12)</math>C8C15O2<math>-79.88(14)</math>C7C12C11<math>-3.7(2)</math>C9C10C11<math>-65.50(14)</math>C9C21C22<math>-79.88(14)</math>C8C15&lt;</td><td>B         C         D         Angle/°         A           C4         C5         C6         177.71(1)         C9           C1         C2         C3         179.17(13)         C9           C1         C6         C5         179.88(11)         C9           C1         C6         C7         -0.15(14)         C9           N1         C12         C7         0.76(15)         C9           N1         C12         C11         179.86(12)         C10           C2         C3         C4         0.3(2)         C10           C6         C7         C12         0.60(14)         C12           C1         C6         C5         -0.45(19)         C12           C3         C4         O1         -178.63(12)         C12           C3         C4         C5         0.7(2)         C12           C3         C4         C5         0.7(2)         C13           C5         C6         C1         1.42(18)         C13           C5         C6         C7         -178.55(13)         C13           C6         C7         C12         -179.43(14)         C14           C</td><td>B         C         D         Angle/°         A         B           C4         C5         C6         177.71(1)         C9         C8           C1         C2         C3         179.17(13)         C9         C8           C1         C6         C5         179.88(11)         C9         C10           C1         C6         C7         -0.15(14)         C9         C21           N1         C12         C1         179.86(12)         C10         C9         C22           N1         C12         C11         179.86(12)         C10         C11         C6           C6         C7         C8         -175.26(12)         C10         C11         C6           C6         C7         C12         0.60(14)         C12         N1         C1         C6         C5         -0.45(19)         C12         N1           C1         C6         C7         179.53(12)         C12         C7         C3         C4         O1         -178.63(12)         C12         C7           C3         C4         C5         0.7(2)         C12         C7         C4         C5         C6         C1         1.42(18)         N</td><td>B         C         D         Angle/°         A         B         C           C4         C5         C6         177.71(11)         C9         C8         C18           C1         C2         C3         179.17(13)         C9         C8         C18           C1         C6         C5         179.88(11)         C9         C10         C11           C1         C6         C7         -0.15(14)         C9         C21         C22           N1         C12         C11         179.86(12)         C10         C9         C21           C2         C3         C4         0.3(2)         C10         C11         C12           C6         C7         C12         0.60(14)         C12         N1         C1           C6         C7         179.53(12)         C12         C1         C1           C6         C7         179.53(12)         C12         C7         C8           C3         C4         C5         0.7(2)         C12         C7         C8           C3         C4         C5         0.6         -1.57(19)         C13         N1         C1           C5         C6</td><td>B         C         D         Angle/°         A         B         C         D           C4         C5         C6         177.71(11)         C9         C8         C18         O4           C1         C2         C3         179.17(13)         C9         C8         C18         O5           C1         C6         C5         179.88(11)         C9         C10         C11         C12           C1         C6         C7         -0.15(14)         C9         C21         C22         O7           N1         C12         C11         179.86(12)         C10         C11         C12         C7           C6         C7         C8         -175.26(12)         C10         C11         C12         C7           C6         C7         C12         0.60(14)         C12         N1         C1         C2           C1         C6         C7         179.53(12)         C12         C7         C8         C15           C3         C4         C5         0.7(2)         C12         C7         C8         C15           C3         C4         C5         0.7(2)         C12         C7         C8         C18</td></td>	B       C         C4       C5         C1       C2         C1       C6         C1       C6         N1       C12         C2       C3         C6       C7         C1       C6         C3       C4         C3       C4         C3       C4         C3       C4         C4       C5         C5       C6         C5       C6         C5       C6         C7       C8         C7       C12         C8       C15         C8       C15 <td>B         C         D           C4         C5         C6           C1         C2         C3           C1         C6         C7           N1         C12         C1           C2         C3         C4           C6         C7         N1           C12         C1         C6           N1         C12         C11           C2         C3         C4           C6         C7         C8           C6         C7         C12           C1         C6         C7           C3         C4         O1           C3         C4         C5           C4         C5         C6           C5         C6         C7           C6         C7         C8           C4         C5         C6           C5         C6         C7           C6         C7         C8           C6         C7         C8           C7         C8         C15           C7         C8         C15           C7         C8         C12           C8         C15         O2</td> <td>BCDAngle/°C4C5C6<math>177.71(11)</math>C1C2C3<math>179.17(13)</math>C1C6C5<math>179.88(11)</math>C1C6C7<math>-0.15(14)</math>N1C12C11<math>179.86(12)</math>C2C3C4<math>0.3(2)</math>C6C7C12<math>0.60(14)</math>C1C6C5<math>-0.45(19)</math>C1C6C7<math>179.53(12)</math>C3C4C1<math>-178.63(12)</math>C3C4C5<math>0.7(2)</math>C4C5C6<math>-1.57(19)</math>C5C6C1<math>1.42(18)</math>C5C6C7<math>-178.55(13)</math>C6C7C12<math>-179.43(14)</math>C1C2C3<math>-0.43(19)</math>C7C8C15<math>42.73(17)</math>C7C8C15<math>42.73(17)</math>C7C8C18<math>-78.13(16)</math>C7C12C11<math>-179.91(12)</math>C8C9C10<math>47.28(13)</math>C8C15O2<math>38.17(16)</math>C8C15O3<math>-145.14(10)</math>C8C18O4<math>-129.63(13)</math>C7C12C11<math>-3.7(2)</math>C9C10C11<math>-65.50(14)</math>C9C21C22<math>174.46(12)</math>C8C15O2<math>-79.88(14)</math>C7C12C11<math>-3.7(2)</math>C9C10C11<math>-65.50(14)</math>C9C21C22<math>-79.88(14)</math>C8C15&lt;</td> <td>B         C         D         Angle/°         A           C4         C5         C6         177.71(1)         C9           C1         C2         C3         179.17(13)         C9           C1         C6         C5         179.88(11)         C9           C1         C6         C7         -0.15(14)         C9           N1         C12         C7         0.76(15)         C9           N1         C12         C11         179.86(12)         C10           C2         C3         C4         0.3(2)         C10           C6         C7         C12         0.60(14)         C12           C1         C6         C5         -0.45(19)         C12           C3         C4         O1         -178.63(12)         C12           C3         C4         C5         0.7(2)         C12           C3         C4         C5         0.7(2)         C13           C5         C6         C1         1.42(18)         C13           C5         C6         C7         -178.55(13)         C13           C6         C7         C12         -179.43(14)         C14           C</td> <td>B         C         D         Angle/°         A         B           C4         C5         C6         177.71(1)         C9         C8           C1         C2         C3         179.17(13)         C9         C8           C1         C6         C5         179.88(11)         C9         C10           C1         C6         C7         -0.15(14)         C9         C21           N1         C12         C1         179.86(12)         C10         C9         C22           N1         C12         C11         179.86(12)         C10         C11         C6           C6         C7         C8         -175.26(12)         C10         C11         C6           C6         C7         C12         0.60(14)         C12         N1         C1         C6         C5         -0.45(19)         C12         N1           C1         C6         C7         179.53(12)         C12         C7         C3         C4         O1         -178.63(12)         C12         C7           C3         C4         C5         0.7(2)         C12         C7         C4         C5         C6         C1         1.42(18)         N</td> <td>B         C         D         Angle/°         A         B         C           C4         C5         C6         177.71(11)         C9         C8         C18           C1         C2         C3         179.17(13)         C9         C8         C18           C1         C6         C5         179.88(11)         C9         C10         C11           C1         C6         C7         -0.15(14)         C9         C21         C22           N1         C12         C11         179.86(12)         C10         C9         C21           C2         C3         C4         0.3(2)         C10         C11         C12           C6         C7         C12         0.60(14)         C12         N1         C1           C6         C7         179.53(12)         C12         C1         C1           C6         C7         179.53(12)         C12         C7         C8           C3         C4         C5         0.7(2)         C12         C7         C8           C3         C4         C5         0.6         -1.57(19)         C13         N1         C1           C5         C6</td> <td>B         C         D         Angle/°         A         B         C         D           C4         C5         C6         177.71(11)         C9         C8         C18         O4           C1         C2         C3         179.17(13)         C9         C8         C18         O5           C1         C6         C5         179.88(11)         C9         C10         C11         C12           C1         C6         C7         -0.15(14)         C9         C21         C22         O7           N1         C12         C11         179.86(12)         C10         C11         C12         C7           C6         C7         C8         -175.26(12)         C10         C11         C12         C7           C6         C7         C12         0.60(14)         C12         N1         C1         C2           C1         C6         C7         179.53(12)         C12         C7         C8         C15           C3         C4         C5         0.7(2)         C12         C7         C8         C15           C3         C4         C5         0.7(2)         C12         C7         C8         C18</td>	B         C         D           C4         C5         C6           C1         C2         C3           C1         C6         C7           N1         C12         C1           C2         C3         C4           C6         C7         N1           C12         C1         C6           N1         C12         C11           C2         C3         C4           C6         C7         C8           C6         C7         C12           C1         C6         C7           C3         C4         O1           C3         C4         C5           C4         C5         C6           C5         C6         C7           C6         C7         C8           C4         C5         C6           C5         C6         C7           C6         C7         C8           C6         C7         C8           C7         C8         C15           C7         C8         C15           C7         C8         C12           C8         C15         O2	BCDAngle/°C4C5C6 $177.71(11)$ C1C2C3 $179.17(13)$ C1C6C5 $179.88(11)$ C1C6C7 $-0.15(14)$ N1C12C11 $179.86(12)$ C2C3C4 $0.3(2)$ C6C7C12 $0.60(14)$ C1C6C5 $-0.45(19)$ C1C6C7 $179.53(12)$ C3C4C1 $-178.63(12)$ C3C4C5 $0.7(2)$ C4C5C6 $-1.57(19)$ C5C6C1 $1.42(18)$ C5C6C7 $-178.55(13)$ C6C7C12 $-179.43(14)$ C1C2C3 $-0.43(19)$ C7C8C15 $42.73(17)$ C7C8C15 $42.73(17)$ C7C8C18 $-78.13(16)$ C7C12C11 $-179.91(12)$ C8C9C10 $47.28(13)$ C8C15O2 $38.17(16)$ C8C15O3 $-145.14(10)$ C8C18O4 $-129.63(13)$ C7C12C11 $-3.7(2)$ C9C10C11 $-65.50(14)$ C9C21C22 $174.46(12)$ C8C15O2 $-79.88(14)$ C7C12C11 $-3.7(2)$ C9C10C11 $-65.50(14)$ C9C21C22 $-79.88(14)$ C8C15<	B         C         D         Angle/°         A           C4         C5         C6         177.71(1)         C9           C1         C2         C3         179.17(13)         C9           C1         C6         C5         179.88(11)         C9           C1         C6         C7         -0.15(14)         C9           N1         C12         C7         0.76(15)         C9           N1         C12         C11         179.86(12)         C10           C2         C3         C4         0.3(2)         C10           C6         C7         C12         0.60(14)         C12           C1         C6         C5         -0.45(19)         C12           C3         C4         O1         -178.63(12)         C12           C3         C4         C5         0.7(2)         C12           C3         C4         C5         0.7(2)         C13           C5         C6         C1         1.42(18)         C13           C5         C6         C7         -178.55(13)         C13           C6         C7         C12         -179.43(14)         C14           C	B         C         D         Angle/°         A         B           C4         C5         C6         177.71(1)         C9         C8           C1         C2         C3         179.17(13)         C9         C8           C1         C6         C5         179.88(11)         C9         C10           C1         C6         C7         -0.15(14)         C9         C21           N1         C12         C1         179.86(12)         C10         C9         C22           N1         C12         C11         179.86(12)         C10         C11         C6           C6         C7         C8         -175.26(12)         C10         C11         C6           C6         C7         C12         0.60(14)         C12         N1         C1         C6         C5         -0.45(19)         C12         N1           C1         C6         C7         179.53(12)         C12         C7         C3         C4         O1         -178.63(12)         C12         C7           C3         C4         C5         0.7(2)         C12         C7         C4         C5         C6         C1         1.42(18)         N	B         C         D         Angle/°         A         B         C           C4         C5         C6         177.71(11)         C9         C8         C18           C1         C2         C3         179.17(13)         C9         C8         C18           C1         C6         C5         179.88(11)         C9         C10         C11           C1         C6         C7         -0.15(14)         C9         C21         C22           N1         C12         C11         179.86(12)         C10         C9         C21           C2         C3         C4         0.3(2)         C10         C11         C12           C6         C7         C12         0.60(14)         C12         N1         C1           C6         C7         179.53(12)         C12         C1         C1           C6         C7         179.53(12)         C12         C7         C8           C3         C4         C5         0.7(2)         C12         C7         C8           C3         C4         C5         0.6         -1.57(19)         C13         N1         C1           C5         C6	B         C         D         Angle/°         A         B         C         D           C4         C5         C6         177.71(11)         C9         C8         C18         O4           C1         C2         C3         179.17(13)         C9         C8         C18         O5           C1         C6         C5         179.88(11)         C9         C10         C11         C12           C1         C6         C7         -0.15(14)         C9         C21         C22         O7           N1         C12         C11         179.86(12)         C10         C11         C12         C7           C6         C7         C8         -175.26(12)         C10         C11         C12         C7           C6         C7         C12         0.60(14)         C12         N1         C1         C2           C1         C6         C7         179.53(12)         C12         C7         C8         C15           C3         C4         C5         0.7(2)         C12         C7         C8         C15           C3         C4         C5         0.7(2)         C12         C7         C8         C18

### X-ray Crystallographic Analysis of 10

#### **Experimental details**

Single-crystal X-ray diffraction data was collected at 100(2) K on a XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5406$  Å). Crystal was mounted on nylon CryoLoops with Paraton-N. The data collection and reduction were processed within *CrysAlisPro* (Rigaku OD, 2019). A multi-scan absorption correction was applied to the collected reflections. Using Olex<sup>2</sup> [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
- 3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.



**Figure S18** X-ray crystal structure of **10** (Non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level).

Table S17Crystal data and structure a	refinement				
Empirical formula	C <sub>25</sub> H <sub>25</sub> NO <sub>5</sub>				
Formula weight	419.46				
Temperature/K	100(2)				
Crystal system	triclinic				
Space group	<i>P</i> -1				
a/Å	9.2549(5)				
<i>b</i> /Å	10.9358(4)				
c/Å	11.8353(5)				
$\alpha$ /°	70.812(4)				
$\beta^{\prime \circ}$	83.459(4)				
$\gamma^{\prime \circ}$	69.525(4)				
Volume/Å <sup>3</sup>	1059.84(9)				
Ζ	2				
$ ho_{ m calc} mg/mm^3$	1.314				
$\mu/\text{mm}^{-1}$	0.747				
<i>F</i> (000)	444.0				
Crystal size/mm <sup>3</sup>	$0.264 \times 0.147 \times 0.1$				
$2\theta$ range for data collection	7.91 to 154.704°				
Index ranges	$-11 \le h \le 11, -13 \le k \le 13, -14 \le l \le 14$				
Reflections collected	17518				
Independent reflections	4403[R(int) = 0.0522]				
Data/restraints/parameters	4403/0/285				
Goodness-of-fit on $F^2$	1.074				
Final <i>R</i> indexes [ $I \ge 2\sigma$ (I)]	$R_1 = 0.0436, wR_2 = 0.1161$				
Final <i>R</i> indexes [all data]	$R_1 = 0.0504, wR_2 = 0.1217$				
Largest diff. peak/hole / e Å <sup>-3</sup>	0.25/-0.23				

Atom	x	у	Z	U(eq)
01	4980.7(13)	6614.1(12)	6436.3(9)	35.8(3)
O2	3274.1(13)	5834.9(11)	7700.2(9)	32.9(3)
O3	1922.2(12)	4757.6(11)	4554.6(9)	31.7(2)
O4	1409.0(12)	5600.5(10)	2588.2(9)	30.0(2)
05	7097.9(12)	8942.5(12)	-1706.3(9)	33.6(3)
N1	4484.1(13)	7220.0(12)	2675.3(10)	24.6(3)
C1	4551.7(16)	6922.9(14)	3921.4(12)	25.6(3)
C2	3211.7(16)	6802.1(14)	4416.9(12)	25.2(3)
C3	2102.4(15)	7007.5(14)	3436.8(12)	24.1(3)
C4	3037.1(15)	7379.7(14)	2320.8(12)	23.6(3)
C5	2906.5(16)	7867.9(14)	1107.4(12)	23.9(3)
C6	4371.1(16)	8028.2(14)	672.1(12)	24.0(3)
C7	4923.0(16)	8484.2(14)	-492.2(12)	25.7(3)
C8	6413.0(17)	8518.5(15)	-617.3(13)	27.5(3)
C9	7354.9(17)	8117.5(16)	380.8(13)	29.7(3)
C10	6836.0(16)	7666.6(15)	1535.3(13)	28.6(3)
C11	5333.6(16)	7630.0(14)	1666.6(12)	24.3(3)
C12	2702.2(17)	6509.8(16)	5689.4(12)	29.5(3)
C13	3808.9(17)	6336.9(14)	6607.9(12)	27.2(3)
C14	4238(2)	5569.5(17)	8685.6(13)	37.1(4)
C15	1828.4(15)	5647.4(14)	3606.8(12)	25.2(3)
C16	1073(2)	4366.3(17)	2680.4(14)	35.0(3)
C17	703(2)	4461.9(19)	1448.7(16)	42.6(4)
C18	536.3(15)	8119.6(14)	3473.0(11)	24.6(3)
C19	-701.3(16)	7768.0(15)	4104.1(12)	27.2(3)
C20	-2084.5(17)	8786.2(17)	4191.7(13)	32.3(3)
C21	-2248.3(18)	10153.2(17)	3655.4(14)	34.8(3)
C22	-1019.1(19)	10511.1(16)	3016.2(13)	33.0(3)
C23	366.2(17)	9497.4(15)	2923.7(12)	28.7(3)
C24	1546.8(16)	8195.3(16)	357.0(12)	28.9(3)
C25	6205.0(19)	9345.9(18)	-2747.1(13)	34.8(3)

**Table S18**Fractional Atomic Coordinates (×104) and Equivalent Isotropic DisplacementParameters (Å2×103). Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Table S19	Selected Bo	ond Distances (Å)			
Atom	Atom	Length/Å	Atom	Atom	Length/Å
01	C13	1.2036(19)	C4	C5	1.3610(19)
O2	C13	1.3399(17)	C5	C6	1.4425(18)
O2	C14	1.4398(18)	C5	C24	1.4936(19)
O3	C15	1.2076(17)	C6	C7	1.4052(18)
O4	C15	1.3296(17)	C6	C11	1.4139(19)
O4	C16	1.4560(18)	C7	C8	1.382(2)
05	C8	1.3801(16)	C8	C9	1.405(2)
05	C25	1.419(2)	C9	C10	1.384(2)
N1	C1	1.4058(17)	C10	C11	1.394(2)
N1	C4	1.3843(18)	C12	C13	1.500(2)
N1	C11	1.3876(17)	C16	C17	1.497(2)
C1	C2	1.3406(19)	C18	C19	1.3936(19)
C2	C3	1.5456(19)	C18	C23	1.390(2)
C2	C12	1.4899(18)	C19	C20	1.392(2)
C3	C4	1.5137(18)	C20	C21	1.379(2)
C3	C15	1.540(2)	C21	C22	1.393(2)
C3	C18	1.5391(19)	C22	C23	1.392(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	O2	C14	115.69(12)	C8	C7	C6	117.87(13)
C15	O4	C16	115.00(11)	05	C8	C7	123.85(14)
C8	05	C25	117.02(12)	05	C8	C9	114.56(13)
C4	N1	C1	111.14(11)	C7	C8	C9	121.59(13)
C4	N1	C11	108.88(11)	C10	C9	C8	121.57(13)
C11	N1	C1	138.82(12)	С9	C10	C11	117.08(13)
C2	C1	N1	109.77(12)	N1	C11	C6	106.32(12)
C1	C2	C3	109.81(11)	N1	C11	C10	131.58(13)
C1	C2	C12	130.59(13)	C10	C11	C6	122.09(12)
C12	C2	C3	119.60(12)	C2	C12	C13	117.76(12)
C4	C3	C2	100.96(11)	01	C13	O2	123.49(14)
C4	C3	C15	111.28(11)	01	C13	C12	127.58(13)
C4	C3	C18	114.16(11)	O2	C13	C12	108.91(12)
C15	C3	C2	109.61(11)	O3	C15	O4	124.11(13)
C18	C3	C2	111.89(11)	O3	C15	C3	124.33(13)
C18	C3	C15	108.74(11)	O4	C15	C3	111.50(11)
N1	C4	C3	107.86(11)	O4	C16	C17	107.47(13)
C5	C4	N1	110.80(12)	C19	C18	C3	120.74(12)
C5	C4	C3	141.26(13)	C23	C18	C3	120.01(12)
C4	C5	C6	105.59(12)	C23	C18	C19	119.16(13)
C4	C5	C24	128.36(12)	C20	C19	C18	120.32(14)
C6	C5	C24	126.05(12)	C21	C20	C19	120.49(14)
C7	C6	C5	131.79(13)	C20	C21	C22	119.46(14)
C7	C6	C11	119.81(13)	C23	C22	C21	120.31(14)
C11	C6	C5	108.41(11)	C18	C23	C22	120.24(13)

Table S20Selected Bond Angles

Table	ble S21 Selected Torsion Angles								
A	В	С	D	Angle/°	Α	В	С	D	Angle/°
05	C8	C9	C10	179.99(13)	C6	C7	C8	05	179.96(13)
N1	C1	C2	C3	1.06(16)	C6	C7	C8	C9	-0.2(2)
N1	C1	C2	C12	-179.38(14)	C7	C6	C11	N1	-179.24(12)
N1	C4	C5	C6	-0.15(15)	C7	C6	C11	C10	-0.3(2)
N1	C4	C5	C24	-179.50(13)	C7	C8	C9	C10	0.2(2)
C1	N1	C4	C3	-6.57(15)	C8	C9	C10	C11	-0.2(2)
C1	N1	C4	C5	170.82(12)	С9	C10	C11	N1	178.86(14)
C1	N1	C11	C6	-166.87(15)	C9	C10	C11	C6	0.2(2)
C1	N1	C11	C10	14.3(3)	C11	N1	C1	C2	169.22(16)
C1	C2	C3	C4	-4.65(15)	C11	N1	C4	C3	-176.67(11)
C1	C2	C3	C15	112.83(13)	C11	N1	C4	C5	0.71(16)
C1	C2	C3	C18	-126.46(13)	C11	C6	C7	C8	0.3(2)
C1	C2	C12	C13	1.3(2)	C12	C2	C3	C4	175.73(12)
C2	C3	C4	N1	6.56(14)	C12	C2	C3	C15	-66.79(16)
C2	C3	C4	C5	-169.53(18)	C12	C2	C3	C18	53.92(16)
C2	C3	C15	O3	26.90(18)	C14	O2	C13	01	-3.2(2)
C2	C3	C15	O4	-155.85(11)	C14	O2	C13	C12	178.15(12)
C2	C3	C18	C19	-94.22(15)	C15	O4	C16	C17	-177.19(13)
C2	C3	C18	C23	82.49(15)	C15	C3	C4	N1	-109.70(13)
C2	C12	C13	O1	12.7(2)	C15	C3	C4	C5	74.2(2)
C2	C12	C13	O2	-168.63(12)	C15	C3	C18	C19	26.99(17)
C3	C2	C12	C13	-179.19(12)	C15	C3	C18	C23	-156.29(12)
C3	C4	C5	C6	175.87(17)	C16	O4	C15	03	-0.6(2)
C3	C4	C5	C24	-3.5(3)	C16	O4	C15	C3	-177.89(11)
C3	C18	C19	C20	176.13(13)	C18	C3	C4	N1	126.76(12)
C3	C18	C23	C22	-176.04(13)	C18	C3	C4	C5	-49.3(2)
C4	N1	C1	C2	3.52(16)	C18	C3	C15	03	-95.70(15)
C4	N1	C11	C6	-0.96(15)	C18	C3	C15	04	81.55(13)
C4	N1	C11	C10	-179.76(15)	C18	C19	C20	C21	0.1(2)
C4	C3	C15	O3	137.72(14)	C19	C18	C23	C22	0.7(2)
C4	C3	C15	O4	-45.03(15)	C19	C20	C21	C22	0.4(2)
C4	C3	C18	C19	151.90(13)	C20	C21	C22	C23	-0.3(2)
C4	C3	C18	C23	-31.39(18)	C21	C22	C23	C18	-0.3(2)
C4	C5	C6	C7	179.68(14)	C23	C18	C19	C20	-0.6(2)
C4	C5	C6	C11	-0.46(15)	C24	C5	C6	C7	-1.0(2)
C5	C6	C7	C8	-179.85(14)	C24	C5	C6	C11	178.92(13)
C5	C6	C11	N1	0.87(15)	C25	05	C8	C7	-0.8(2)

Α	В	С	D	Angle/°	Α	В	С	D	Angle/°
C5	C6	C11	C10	179.81(13)	C25	05	C8	C9	179.35(13)



S61

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)







<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

Me







Me









9.0



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)








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Ŧ - 0 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) -9 15'6-E1.41 ---12.01 -----2 06'22 ---8 - 6 45'22 20-15'6t-22'29-H0'95~ - 6 22.23 ----2 #8'82~ #2'92~ 91'22 J - 8 06 (mdd) 80.88-100 06'001-110 110.36 111.20 120 -CO<sub>2</sub>Me 126.921 130 +9.151 ----140 `co₂Et <sup>co2</sup>Et 150 01.421 24.10 Me 7 160 S12 170 MeO. 180

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<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 68,8 -86.84 ----C6'IS~ S6'89 -₩2'92 91'22 85'22 75,101-8Z'S01-02'611-127.72 C135.95 ĊO₂Me Me Z Зh 

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96'8

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195'9#1 19'2#1

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S156

·CO<sub>2</sub>Et



