Supporting Information

Catalytic Enantioselective Friedel-Crafts/Michael Addition Reactions of Indoles to Ethenetricarboxylates

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Additional experimental procedures and spectral data

General Methods. Melting points are uncorrected. IR spectra were recorded in the FT-mode. ^1H NMR spectra were recorded at 400 MHz. ^{13}C NMR spectra were recorded at 100.6 MHz. Chemical shifts are reported in ppm relative to Me_4Si or residual nondeuterated solvent. ^{13}C multiplicities were determined by DEPT and HSQC. Mass spectra were recorded at an ionizing voltage of 70 eV by EI or FAB. HPLC analysis was performed with a UN detector (detection, 254 nm light) and flow rate of 1.0 mL/min using a CHIRALPAK AS-H or AD-H (0.46 cm $\times$ 250 mm) column at 30 °C. Optical rotations were measured with a 1 cm i.d. $\times$ 10 cm cell. All reactions were carried out under a nitrogen atmosphere.

3a and **3c-d** were purchased from Tokyo Kasei or Aldrich. **3b** was prepared according to the literature.^{4c} **1a-1d**, **1f** and **1i-1l** were prepared by the reaction of the corresponding ketomalonate with the corresponding (triphenylphosphoranylidene)acetate according to the literature.⁶ **1h** and **1m** were prepared by the reaction of 1,1-diethyl 2-hydrogen ethenetricarboxylate with the corresponding amines according to the literature procedure.⁶ **1e**, **1g** and **1n** were prepared by the reaction of 1,1-diethyl 2-hydrogen ethenetricarboxylate with the corresponding alcohols in the presence of PPh_3 , DEAD (diethyl azodicarboxylate), according to the literature procedure.^{6c}

1-(4-Bromobenzyl) 2,2-diethyl ethene-1,2,2-tricarboxylate (1e) (R_f = 0.4 (hexane-ether = 1:1)): Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.29 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 4.28 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 5.16 (s, 2H), 6.90 (s, 1H), 7.24 (d-like, J = 8.4 Hz, 2H), 7.51 (d-like, J = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.9 (q), 14.0 (q), 62.2 (t), 62.7 (t), 66.7 (t), 122.8 (s), 129.4 (d), 130.2 (d), 131.9 (d), 133.8 (s), 139.6 (s), 162.2 (s), 163.3 (s), 164.2 (s); IR (neat) 2983, 1733, 1490, 1371, 1345, 1260, 1175, 1070, 1013 cm^{-1} ; MS (EI) m/z 384 (M^+), 386 (M^+); exact mass M^+ 384.0210 (calcd for $\text{C}_{16}\text{H}_{17}^{79}\text{BrO}_6$ 384.0209), 384.0195 (calcd for $\text{C}_{16}\text{H}_{17}^{81}\text{BrO}_6$ 386.0188).

Diethyl 2-(2-oxo-2-(pyrrolidin-1-yl)ethylidene)malonate (1m) (R_f = 0.1 (hexane-ether = 1:2)): Colorless crystals; mp 26-27 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.32 (t, J = 7.1

Hz, 3H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.86-1.94 (m, 2H), 1.96-2.03 (m, 2H), 3.54 (t, $J = 7.0$ Hz, 2H), 3.57 (t, $J = 6.9$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 4.38 (q, $J = 7.1$ Hz, 2H), 7.20 (s, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 14.1 (q), 24.3 (t), 26.1 (t), 46.1 (t), 47.1 (t), 61.9 (t), 62.3 (t), 132.4 (d), 135.9 (s), 161.5 (s), 163.1 (s), 165.2 (s); IR (neat) 2982, 2880, 1732, 1651, 1632, 1442, 1250, 1218, 1069 cm^{-1} ; MS (FAB) m/z 270 ($\text{M}+\text{H}^+$); exact mass ($\text{M}+\text{H}^+$) 270.1340 (calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_5$ 270.1341).

1-(3-(Dimethylamino)benzyl) 2,2-diethyl ethene-1,2,2-tricarboxylate (1n) ($R_f = 0.1$ (hexane-ether = 4:1)): Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.28 (t, $J = 7.1$ Hz, 3H), 1.31 (t, $J = 7.1$ Hz, 3H), 2.96 (s, 6H), 4.26 (q, $J = 7.1$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 5.16 (s, 2H), 6.68-6.72 (m, 3H), 6.91 (s, 1H), 7.20-7.25 (m, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.9 (q), 14.0 (q), 40.6 (q), 62.1 (t), 62.5 (t), 68.3 (t), 112.5 (d), 112.8 (d), 116.6 (d), 129.4 (d), 129.9 (d), 135.5 (s), 139.1 (s), 150.8 (s), 162.3 (s), 163.5 (s), 164.2 (s); IR (neat) 2983, 1726, 1607, 1502, 1371, 1348, 1258, 1178, 1066 cm^{-1} ; MS (EI) m/z 349 (M^+ , 100%), 134 (99%); exact mass M^+ 349.1531 (calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_6$ 349.1525).

(R)-2,2-Diethyl 1-isopropyl 1-(1H-indol-3-yl)ethane-1,2,2-tricarboxylate (4b) (Table 2, Entry 1) ($R_f = 0.2$ (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane- i PrOH = 9:1) minor peak t_{R1} 9.1 min, major peak t_{R2} 10.1 min, 74% ee; $[\alpha]_D^{30} = -92^\circ$ (c 0.93, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.855 (t, $J = 7.1$ Hz, 3H), 1.05 (d, $J = 6.2$ Hz, 3H), 1.25 (d, $J = 6.2$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 3.79-3.91 (m, 2H), 4.20-4.28 (m, 2H), 4.36 (d, $J = 11.7$ Hz, 1H), 4.61 (dd, $J = 11.7, 0.4$ Hz, 1H), 4.93-5.02 (m, 1H), 7.10-7.19 (m, 3H), 7.32 (d-like, $J = 7.9$ Hz, 1H), 7.74 (d-like, $J = 7.9$ Hz, 1H), 8.27 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 21.5 (q), 21.7 (q), 42.7 (d), 55.1 (d), 61.4 (t), 61.9 (t), 68.8 (d), 109.8 (s), 111.2 (d), 119.6 (d), 119.8 (d), 122.3 (d), 123.3 (d), 126.4 (s), 136.1 (s), 167.7 (s), 168.2 (s), 171.8 (s); IR (neat) 3401, 2982, 1728, 1458, 1370, 1297, 1174, 1106 cm^{-1} ; MS (EI) m/z 375 (M^+ , 47%), 315 (26%), 287 (92%), 170 (100%); exact mass M^+ 375.1689 (calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_6$ 375.1682).

(R)-1-tert-Butyl 2,2-diethyl 1-(1H-indol-3-yl)ethane-1,2,2-tricarboxylate (4c) (Table 2, Entry 2) ($R_f = 0.1$ (CH_2Cl_2)): Pale brown oil; HPLC (AD-H, hexane- i PrOH = 9:1) major peak

t_{R1} 11.6 min, minor peak t_{R2} 13.1 min, 73% ee; $[\alpha]^{28}_D = -82^\circ$ (c 1.23, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.847 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.37 (s, 9H), 3.78-3.90 (m, 2H), 4.21-4.28 (m, 2H), 4.30 (d, $J = 11.7$ Hz, 1H), 4.56 (dd, $J = 11.7, 0.5$ Hz, 1H), 7.08-7.18 (m, 3H), 7.31 (d-like, $J = 8.1$ Hz, 1H), 7.74 (d-like, $J = 7.9$ Hz, 1H), 8.35 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 27.9 (q), 43.5 (d), 55.1 (d), 61.4 (t), 61.8 (t), 81.5 (s), 110.0 (s), 111.2 (d), 119.5 (d), 119.7 (d), 122.2 (d), 123.2 (d), 126.4 (s), 136.2 (s), 167.8 (s), 168.3 (s), 171.5 (s); IR (neat) 3399, 2980, 1733, 1458, 1369, 1303, 1153, 1033 cm^{-1} ; MS (EI) m/z 389 (M^+ , 47%), 315 (24%), 288 (100%); exact mass M^+ 389.1831 (calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_6$ 389.1838).

(R)-1-Benzyl 2,2-diethyl 1-(1H-indol-3-yl)ethane-1,2,2-tricarboxylate (4d) (Table 2, Entry 3) ($R_f = 0.1$ (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane- i PrOH = 9:1) minor peak t_{R1} 21.5 min, major peak t_{R2} 23.6 min, 84% ee; $[\alpha]^{22}_D = -105^\circ$ (c 1.35, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.818 (t, $J = 7.1$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 3H), 3.77-3.89 (m, 2H), 4.15-4.23 (m, 2H), 4.41 (d, $J = 11.7$ Hz, 1H), 4.74 (dd, $J = 11.7, 0.4$ Hz, 1H), 5.01 (d, $J = 12.5$ Hz, 1H), 5.14 (d, $J = 12.5$ Hz, 1H), 7.02 (d, $J = 2.4$ Hz, 1H), 7.07-7.22 (m, 7H), 7.27 (d, $J = 8.1$ Hz, 1H), 7.71 (d, $J = 7.9$ Hz, 1H), 8.43 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.5 (q), 14.0 (q), 42.5 (d), 54.9 (d), 61.5 (t), 61.9 (t), 66.9 (t), 109.0 (s), 111.3 (d), 119.3 (d), 119.8 (d), 122.3 (d), 123.5 (d), 126.2 (s), 127.9 (d), 128.0 (d), 128.3 (d), 135.6 (s), 136.1 (s), 167.5 (s), 168.1 (s), 172.2 (s); IR (neat) 3404, 2982, 1733, 1458, 1370, 1297, 1161, 1030 cm^{-1} ; MS (EI) m/z 423 (M^+ , 11%), 287 (17%), 170 (26%), 130 (41%), 91 (100%); exact mass M^+ 423.1685 (calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_6$ 423.1682).

(R)-1-(4-Bromobenzyl) 2,2-diethyl 1-(1H-indol-3-yl)ethane-1,2,2-tricarboxylate (4e) (Table 2, Entry 4) ($R_f = 0.1$ (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane- i PrOH = 9:1) minor peak t_{R1} 18.2 min, major peak t_{R2} 20.1 min, 82% ee; $[\alpha]^{19}_D = -61^\circ$ (c 0.81, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.850 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.1$ Hz, 3H), 3.80-3.92 (m, 2H), 4.15-4.27 (m, 2H), 4.38 (d, $J = 11.7$ Hz, 1H), 4.71 (d, $J = 11.7$ Hz, 1H), 5.00 (d, $J = 12.7$ Hz, 1H), 5.08 (d, $J = 12.7$ Hz, 1H), 7.03 (d-like, $J = 8.6$ Hz, 2H), 7.09-7.13 (m, 2H), 7.18-7.22 (m, 1H), 7.33-7.36 (m, 3H), 7.69 (d, $J = 7.1$ Hz, 1H), 8.16 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 42.4 (d), 54.8 (d), 61.5 (t), 62.0 (t), 66.1 (t), 109.4 (s),

111.3 (d), 119.4 (d), 120.1 (d), 122.1 (s), 122.6 (d), 123.4 (d), 126.3 (s), 129.5 (d), 131.5 (d), 134.8 (s), 136.1 (s), 167.4 (s), 168.2 (s), 172.1 (s); IR (neat) 3404, 2981, 1732, 1489, 1458, 1370, 1297, 1161 cm^{-1} ; MS (EI) m/z 503 (M^+ , 16%), 501 (M^+ , 15%), 332 (46%), 287 (36%), 171 (64%), 170 (63%), 169 (66%), 83 (100%); exact mass M^+ 501.0784 (calcd for $\text{C}_{24}\text{H}_{24}^{79}\text{BrNO}_6$ 501.0787), 503.0757 (calcd for $\text{C}_{24}\text{H}_{24}^{80}\text{BrNO}_6$ 503.0767).

(R)-1-(3,5-Dimethoxybenzyl) 2,2-diethyl 1-(1H-indol-3-yl)ethane-1,2,2-tricarboxylate (4f) (Table 2, Entry 5) (R_f = 0.1 (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane- i PrOH = 19:1) minor peak t_{R1} 71.1 min, major peak t_{R2} 76.0 min, 87% ee; $[\alpha]_D^{24}$ = -94° (c 1.79, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.827 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 3.58 (s, 6H), 3.78-3.90 (m, 2H), 4.16-4.28 (m, 2H), 4.42 (d, J = 11.7 Hz, 1H), 4.75 (d, J = 11.7 Hz, 1H), 5.04 (d, J = 12.6 Hz, 1H), 5.07 (d, J = 12.6 Hz, 1H), 6.29 (d, J = 2.3 Hz, 2H), 6.31 (t, J = 2.3 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 7.07-7.17 (m, 2H), 7.27 (d-like, J = 7.7 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 8.44 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.5 (q), 14.0 (q), 42.4 (d), 54.8 (d), 55.1 (q), 61.5 (t), 62.0 (t), 66.6 (t), 100.4 (d), 104.9 (d), 109.0 (s), 111.3 (d), 119.2 (d), 119.9 (d), 122.3 (d), 123.6 (d), 126.2 (s), 136.1 (s), 138.1 (s), 160.7 (s), 167.5 (s), 168.2 (s), 172.2 (s); IR (neat) 3400, 2980, 1733, 1599, 1459, 1299, 1206, 1157 cm^{-1} ; MS (EI) m/z 483 (M^+ , 9%), 289 (14%), 151 (61%), 130 (49%), 84 (100%); exact mass M^+ 483.1895 (calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_8$ 489.1893).

(R)-2,2-Diethyl 1-phenyl 1-(1H-indol-3-yl)ethane-1,2,2-tricarboxylate (4g) (Table 2, Entry 6) (R_f = 0.4 (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane- i PrOH = 9:1) minor peak t_{R1} 13.4 min, major peak t_{R2} 21.3 min, 50% ee; $[\alpha]_D^{26}$ = -72° (c 0.62, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.874 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 3.83-3.95 (m, 2H), 4.21-4.34 (m, 2H), 4.45 (d, J = 11.7 Hz, 1H), 4.90 (d, J = 11.7 Hz, 1H), 6.94-6.98 (m, 2H), 7.13-7.21 (m, 4H), 7.25-7.33 (m, 3H), 7.80 (d-like, J = 8.0 Hz, 1H), 8.37 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 42.5 (d), 55.1 (d), 61.6 (t), 62.1 (t), 108.8 (s), 111.4 (d), 119.3 (d), 120.1 (d), 121.4 (d), 122.5 (d), 123.7 (d), 125.9 (d), 126.3 (s), 129.4 (d), 136.2 (s), 150.8 (s), 167.5 (s), 168.2 (s), 171.3 (s); IR (neat) 3399, 2983, 1738, 1492, 1458, 1370, 1193, 1162 cm^{-1} ; MS (EI) m/z 409 (M^+ , 24%), 288 (100%); exact mass M^+ 409.1521 (calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_6$ 409.1525).

Diethyl 2-((*R*)-1-(1*H*-indol-3-yl)-2-oxo-2-(piperidin-1-yl)ethyl)malonate (4h) (Table 2, Entry 7) (R_f = 0.5 (CH₂Cl₂-ether = 9:1)): Colorless crystals; mp 147-149 °C; HPLC (AD-H, hexane-ⁱPrOH = 9:1) minor peak t_{R1} 16.3 min, major peak t_{R2} 18.6 min, 53% ee; $[\alpha]_D^{22}$ = -193° (c 3.14, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.781 (t, J = 7.1 Hz, 3H), 0.873-0.943 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.30-1.61 (m, 5H), 3.28-3.34 (m, 1H), 3.40-3.60 (m, 3H), 3.70-3.81 (m, 2H), 4.14-4.29 (m, 2H), 4.44 (d, J = 11.2 Hz, 1H), 4.90 (d, J = 11.2 Hz, 1H), 7.07-7.17 (m, 3H), 7.35 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 7.9 Hz, 1H), 8.94 (bs, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ (ppm) 13.5 (q), 14.0 (q), 24.5 (t), 25.5 (t), 25.7 (t), 40.0 (d), 43.6 (t), 46.9 (t), 56.5 (d), 61.2 (t), 61.5 (t), 109.9 (s), 111.4 (d), 118.8 (d), 119.7 (d), 122.0 (d), 123.7 (d), 126.1 (s), 136.1 (s), 168.7 (s), 168.8 (s), 169.9 (s); IR (neat) 3249, 2937, 2860, 1746, 1726, 1615, 1463, 1273, 1195, 1147 cm⁻¹; MS (EI) m/z 400 (M⁺, 2.0%), 361 (4.1%), 238 (32%), 200 (32%), 154 (46%), 84 (100%); exact mass M⁺ 400.2000 (calcd for C₂₂H₂₈N₂O₅ 400.1998).

Diethyl 2-((*R*)-1-(1*H*-indol-3-yl)-2-oxopropyl)malonate (4i) (Table 2, Entry 8) (R_f = 0.1 (CH₂Cl₂)): Pale brown oil; HPLC (AS-H, hexane-ⁱPrOH = 9:1) minor peak t_{R1} 9.5 min, major peak t_{R2} 19.8 min, 38% ee; $[\alpha]_D^{27}$ = -124° (c 1.07, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.783 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H), 2.17 (s, 3H), 3.73-3.86 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 4.35 (d, J = 11.4 Hz, 1H), 4.78 (d, J = 11.4 Hz, 1H), 7.09 (d, J = 2.6 Hz, 1H), 7.12-7.16 (m, 1H), 7.18-7.22 (m, 1H), 7.35 (d-like, J = 7.9 Hz, 1H), 7.64 (d-like, J = 7.0 Hz, 1H), 8.30 (bs, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ (ppm) 13.6 (q), 14.1 (q), 28.7 (q), 49.2 (d), 54.4 (d), 61.3 (t), 61.9 (t), 108.7 (s), 111.4 (d), 119.1 (d), 120.3 (d), 122.7 (d), 124.0 (d), 126.6 (s), 136.3 (s), 168.3 (s), 168.6 (s), 206.0 (s); IR (neat) 3400, 2981, 1748, 1732, 1716, 1458, 1369, 1278, 1223, 1161, 1098, 1033 cm⁻¹; MS (EI) m/z 331 (M⁺, 12%), 288 (49%), 215 (23%), 170 (100%); exact mass M⁺ 331.1416 (calcd for C₁₈H₂₁NO₅ 331.1420).

Diethyl 2-((*R*)-1-(1*H*-indol-3-yl)-2-oxo-2-phenylethyl)malonate (4j) (Table 2, Entry 9) (R_f = 0.2 (CH₂Cl₂)): Colorless crystals; mp 103-106 °C; HPLC (AS-H, hexane-ⁱPrOH = 9:1) minor peak t_{R1} 13.1 min, major peak t_{R2} 16.7 min, 69% ee; $[\alpha]_D^{28}$ = -302° (c 1.66, CHCl₃); 100% ee (by HPLC) after recrystallization (EtOH); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.796 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H), 3.72-3.86 (m, 2H), 4.11-4.24 (m, 2H), 4.55 (d, J = 11.3 Hz, 1H), 5.65 (d, J = 11.3 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 7.13-7.16 (m, 2H), 7.23-7.31

(m, 3H), 7.38-7.42 (m, 1H), 7.75-7.79 (m, 1H), 7.97-8.00 (m, 2H), 8.39 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.5 (q), 14.0 (q), 44.2 (d), 55.8 (d), 61.4 (t), 61.8 (t), 109.1 (s), 111.5 (d), 118.9 (d), 120.1 (d), 122.4 (d), 124.2 (d), 126.1 (s), 128.5 (d), 128.7 (d), 133.0 (d), 136.0 (s), 136.3 (s), 168.6 (s), 197.3 (s); IR (KBr) 3342, 2992, 1750, 1660, 1595, 1309, 1295, 1183, 1151 cm^{-1} ; MS (EI) m/z 393 (M^+ , 39%), 288 (100%); exact mass M^+ 393.1584 (calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_5$ 393.1576); Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_5$: C, 70.21; H, 5.89; N, 3.56. Found: C, 70.24; H, 5.84; N, 3.58.

(*R*)-1-*tert*-Butyl 2,2-dimethyl 1-(1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4k) (Table 2, Entry 10) (R_f = 0.1 (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane-*i*PrOH = 9:1) major peak t_{R1} 9.6 min, minor peak t_{R2} 10.5 min, 68% ee; $[\alpha]_D^{31}$ = -99° (c 0.60, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.37 (s, 9H), 3.40 (s, 3H), 3.78 (s, 3H), 4.31 (d, J = 11.7 Hz, 1H), 4.58 (d, J = 11.7 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 7.09-7.18 (m, 2H), 7.30 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 8.41 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 27.6 (q), 43.5 (d), 52.5 (q), 52.8 (q), 54.9 (d), 81.6 (s), 109.9 (s), 111.3 (d), 119.4 (d), 119.7 (d), 122.2 (d), 123.1 (d), 126.3 (s), 136.2 (s), 168.2 (s), 168.6 (s), 171.4 (s); IR (neat) 3406, 2979, 1716-1758, 1456, 1435, 1369, 1303, 1159 cm^{-1} ; MS (EI) m/z 361 (M^+ , 6.8%), 260 (24%), 84 (100%); exact mass M^+ 361.1527 (calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_6$ 361.1525).

(*R*)-1-*tert*-Butyl 2,2-diisopropyl 1-(1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4l) (Table 2, Entry 11) (R_f = 0.1 (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane-*i*PrOH = 19:1) minor peak t_{R1} 7.9 min, major peak t_{R2} 8.9 min, 44% ee; $[\alpha]_D^{26}$ = -58° (c 0.85, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.799 (d, J = 6.2 Hz, 3H), 0.914 (d, J = 6.2 Hz, 3H), 1.24 (d, J = 6.2 Hz, 3H), 1.29 (d, J = 6.2 Hz, 3H), 1.36 (s, 9H), 4.26 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.8 Hz, 1H), 4.69 (septet, J = 6.2 Hz, 1H), 5.10 (septet, J = 6.2 Hz, 1H), 7.09-7.18 (m, 3H), 7.31 (d-like, J = 7.9 Hz, 1H), 7.75 (d-like, J = 7.9 Hz, 1H), 8.23 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 21.1 (q), 21.3 (q), 21.6 (q), 21.8 (q), 27.9 (q), 43.4 (d), 55.3 (d), 68.8 (d), 69.4 (d), 81.3 (s), 110.4 (s), 111.1 (d), 119.7 (d), 119.8 (d), 122.2 (d), 123.1 (d), 126.6 (s), 136.1 (s), 167.3 (s), 167.9 (s), 171.5 (s); IR (neat) 3390, 2981, 1728, 1458, 1369, 1299, 1155, 1103 cm^{-1} ; MS (EI) m/z 417 (M^+ , 39%), 316 (52%), 188 (60%), 170 (100%); exact mass M^+ 417.2155 (calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_6$ 417.2151).

(R)-Triethyl 1-(1-methyl-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4m) (Table 3, Entry 1) ($R_f = 0.4$ (CH_2Cl_2)): Colorless crystals; mp 102-104 °C; HPLC (AS-H, hexane-*i*PrOH = 19:1) major peak t_{R1} 9.4 min, minor peak t_{R2} 10.4 min, 43% ee; $[\alpha]_D^{30} = -146^\circ$ (c 0.30, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.855 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H), 1.28 (s, 9H), 3.72 (s, 3H), 3.79-3.93 (m, 2H), 4.00-4.08 (m, 1H), 4.15-4.28 (m, 3H), 4.34 (d, $J = 11.7$ Hz, 1H), 4.61 (d, $J = 11.7$ Hz, 1H), 7.03 (s, 1H), 7.09-7.13 (m, 1H), 7.18-7.22 (m, 1H), 7.25 (d-like, $J = 8.2$ Hz, 1H), 7.72 (dt, $J = 8.1, 0.9$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 32.8 (q), 42.3 (d), 55.1 (d), 61.28 (t), 61.32 (t), 61.8 (t), 108.0 (s), 109.3 (d), 119.4 (d), 119.5 (d), 121.9 (d), 126.9 (s), 127.8 (d), 136.9 (s), 167.5 (s), 168.2 (s), 172.5 (s); IR (KBr) 2979, 1728, 1305, 1228, 1161, 1036 cm^{-1} ; MS (EI) m/z 375 (M^+ , 57%), 301 (89%), 216 (100%); exact mass M^+ 375.1688 (calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_6$ 375.1682); Anal. Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_6$: C, 63.99; H, 6.71; N, 3.73. Found: C, 63.78; H, 6.65; N, 3.77.

(R)-1-*tert*-Butyl 2,2-diethyl 1-(1-methyl-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4n) (Table 3, Entry 2) ($R_f = 0.2$ (CH_2Cl_2)): Yellow crystals; mp 66-69 °C; HPLC (AS-H, hexane-*i*PrOH = 19:1) major peak t_{R1} 6.0 min, minor peak t_{R2} 6.5 min, 83% ee; $[\alpha]_D^{29} = -108^\circ$ (c 0.97, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.864 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.37 (s, 9H), 3.72 (s, 3H), 3.78-3.92 (m, 2H), 4.20-4.28 (m, 2H), 4.26 (d, $J = 11.7$ Hz, 1H), 4.52 (d, $J = 11.7$ Hz, 1H), 7.01 (s, 1H), 7.08-7.12 (m, 1H), 7.18-7.22 (m, 1H), 7.25 (d-like, $J = 8.2$ Hz, 1H), 7.72 (dt, $J = 8.1, 0.9$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 27.9 (q), 32.9 (q), 43.4 (d), 55.2 (d), 61.3 (t), 61.8 (t), 81.3 (s), 108.6 (s), 109.2 (d), 119.2 (d), 119.7 (d), 121.8 (d), 127.0 (s), 127.6 (d), 137.0 (s), 167.7 (s), 168.3 (s), 171.5 (s); IR (neat) 2980, 1733, 1475, 1369, 1301, 1150 cm^{-1} ; MS (EI) m/z 403 (M^+ , 42%), 329 (16%), 302 (100%); exact mass M^+ 403.2000 (calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_6$ 403.1995).

(R)-1-Benzyl 2,2-diethyl 1-(1-methyl-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4o) (Table 3, Entry 3) ($R_f = 0.2$ (CH_2Cl_2)): Yellow crystals; mp 65-68 °C; HPLC (AS-H, hexane-*i*PrOH = 19:1) major peak t_{R1} 13.0 min, minor peak t_{R2} 13.7 min, 86% ee; $[\alpha]_D^{29} = -103^\circ$ (c 0.65, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.854 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H), 3.70 (s, 3H), 3.79-3.92 (m, 2H), 4.15-4.23 (m, 2H), 4.36 (d, $J = 11.7$ Hz, 1H), 4.70 (dd, $J = 11.7, 0.4$ Hz, 1H), 5.02 (d, $J = 12.5$ Hz, 1H), 5.17 (d, $J = 12.5$ Hz, 1H), 6.99 (s, 1H),

7.08-7.12 (m, 1H), 7.19-7.22 (m, 3H), 7.24-7.27 (m, 4H), 7.70 (dt, $J = 8.0, 1.0$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.0 (q), 32.9 (q), 42.4 (d), 55.1 (d), 61.4 (t), 61.9 (t), 66.9 (t), 107.8 (s), 109.3 (d), 119.5 (d), 119.6 (d), 122.0 (d), 126.9 (s), 127.92 (d), 127.98 (d), 128.04 (d), 128.4 (d), 135.8 (s), 136.9 (s), 167.4 (s), 168.1 (s), 172.3 (s); IR (KBr) 2979, 1728, 1304, 1224, 1159 cm^{-1} ; MS (EI) m/z 437 (M^+ , 41%), 346 (39%), 302 (55%), 184 (92%), 144 (100%); exact mass M^+ 437.1841 (calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_6$ 437.1838); Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_6$: C, 68.63; H, 6.22; N, 3.20. Found: C, 68.77; H, 6.48; N, 3.13.

(*R*)-1-(4-Bromobenzyl) 2,2-diethyl 1-(1-methyl-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4p) (Table 3, Entry 4) ($R_f = 0.3$ (CH_2Cl_2)): Yellow crystals; mp 86-89 °C; HPLC (AD-H, hexane-*i*PrOH = 9:1) minor peak t_{R1} 23.4 min, major peak t_{R2} 27.2 min, 81% ee; $[\alpha]_D^{28} = -76^\circ$ (c 1.48, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.853 (t, $J = 7.1$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H), 3.69 (s, 3H), 3.79-3.92 (m, 2H), 4.16-4.24 (m, 2H), 4.35 (d, $J = 11.7$ Hz, 1H), 4.69 (d, $J = 11.7$ Hz, 1H), 4.97 (d, $J = 12.6$ Hz, 1H), 5.08 (d, $J = 12.6$ Hz, 1H), 6.97 (s, 1H), 7.03 (d, $J = 8.3$ Hz, 2H), 7.08-7.11 (m, 1H), 7.19-7.26 (m, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.0 (q), 32.8 (q), 42.2 (d), 54.9 (d), 61.4 (t), 61.9 (t), 66.0 (t), 107.5 (s), 109.3 (d), 119.4 (d), 119.6 (d), 121.97 (d), 122.00 (s), 126.8 (s), 127.9 (d), 129.6 (d), 131.4 (d), 134.8 (s), 136.9 (s), 167.3 (s), 168.1 (s), 172.2 (s); IR (KBr) 2983, 1727, 1168, 1154 cm^{-1} ; MS (EI) m/z 517 (M^+ , 21%), 515 (M^+ , 21%), 346 (64%), 302 (67%), 229 (55%), 184 (100%); exact mass M^+ 515.0944 (calcd for $\text{C}_{25}\text{H}_{26}^{79}\text{BrNO}_6$ 515.0944), 517.0934 (calcd for $\text{C}_{25}\text{H}_{26}^{81}\text{BrNO}_6$ 517.0923); Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{BrNO}_6$: C, 58.15; H, 5.08; N, 2.71. Found: C, 58.15; H, 5.07; N, 2.61.

Diethyl 2-((*R*)-1-(1-methyl-1*H*-indol-3-yl)-2-oxopropyl)malonate (4q) (Table 3, Entry 5) ($R_f = 0.2$ (CH_2Cl_2)): Yellow crystals; mp 110-112 °C; HPLC (AS-H, hexane-*i*PrOH = 19:1) minor peak t_{R1} 9.7 min, major peak t_{R2} 10.2 min, 27% ee; $[\alpha]_D^{29} = -75^\circ$ (c 0.62, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.791 (t, $J = 7.1$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 2.17 (s, 3H), 3.73-3.87 (m, 2H), 3.74 (s, 3H), 4.19-4.25 (m, 2H), 4.31 (d, $J = 11.5$ Hz, 1H), 4.75 (d, $J = 11.7$ Hz, 1H), 6.95 (s, 1H), 7.11-7.15 (m, 1H), 7.20-7.25 (m, 1H), 7.28 (d-like, $J = 8.1$ Hz, 1H), 7.62 (dt, $J = 8.1, 1.0$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 28.8 (q), 32.9 (q), 49.0 (d), 54.5 (d), 61.2 (t), 61.8 (t), 106.9 (s), 109.5 (d), 119.1

(d), 119.8 (d), 122.1 (d), 127.1 (s), 128.5 (d), 137.1 (s), 168.2 (s), 168.6 (s), 205.9 (s); IR (KBr) 2978, 1729, 1713, 1299, 1222, 1160, 1038 cm^{-1} ; MS (EI) m/z 345 (M^+ , 37%), 302 (100%); exact mass M^+ 345.1581 (calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_5$ 345.1576); Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 65.85; H, 6.65; N, 4.12.

Diethyl 2-((*R*)-1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)malonate (4r) (Table 3, Entry 6) (R_f = 0.4 (CH_2Cl_2)): Pale brown crystals; mp 85-88 $^\circ\text{C}$; HPLC (AS-H, hexane-*i*PrOH = 9:1) minor peak t_{R1} 8.7 min, major peak t_{R2} 9.7 min, 95% ee; $[\alpha]_D^{18} = -309^\circ$ (c 1.75, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.815 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 3.65 (s, 3H), 3.72-3.87 (m, 2H), 4.12-4.25 (m, 2H), 4.51 (d, J = 11.4 Hz, 1H), 5.63 (d, J = 11.4 Hz, 1H), 6.94 (s, 1H), 7.13-7.18 (m, 1H), 7.19-7.23 (m, 2H), 7.31-7.35 (m, 2H), 7.40-7.45 (m, 1H), 7.75-7.78 (m, 1H), 8.00-8.03 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.0 (q), 32.9 (q), 43.9 (d), 56.0 (d), 61.4 (t), 61.8 (t), 107.5 (s), 109.4 (d), 119.1 (d), 119.7 (d), 122.0 (d), 126.7 (s), 128.5 (d), 128.6 (d), 128.8 (d), 132.9 (d), 136.0 (s), 137.1 (s), 168.4 (s), 168.5 (s), 197.3 (s); IR (neat) 2975, 1747, 1732, 1682, 1370, 1287, 1181 cm^{-1} ; MS (EI) m/z 407 (M^+ , 22%), 302 (100%); exact mass M^+ 407.1733 (calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_5$ 407.1733).

(*R*)-1-*tert*-Butyl 2,2-diethyl 1-(5-methoxy-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4s) (Table 3, Entry 7) (R_f = 0.1 (CH_2Cl_2)): Colorless oil; HPLC (AS-H, hexane-*i*PrOH = 19:1) major peak t_{R1} 20.0 min, minor peak t_{R2} 21.9 min, 86% ee; $[\alpha]_D^{23} = -99^\circ$ (c 1.76, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.873 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.38 (s, 9H), 3.81-3.92 (m, 2H), 3.86 (s, 3H), 4.21-4.29 (m, 2H), 4.27 (d, J = 11.8 Hz, 1H), 4.51 (dd, J = 11.8, 0.5 Hz, 1H), 6.83 (ddd, J = 8.8, 2.5, 0.4 Hz, 1H), 7.10 (d, J = 2.7 Hz, 1H), 7.18 (d, J = 2.5 Hz, 1H), 7.20 (dd, J = 8.8, 0.5 Hz, 1H), 8.08 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.7 (q), 14.1 (q), 28.0 (q), 43.4 (d), 55.0 (d), 55.9 (q), 61.4 (t), 61.9 (t), 81.4 (s), 101.0 (d), 110.0 (s), 111.9 (d), 112.9 (d), 123.6 (d), 127.0 (s), 131.2 (s), 154.2 (s), 167.8 (s), 168.3 (s), 171.4 (s); IR (neat) 3390, 2981, 1728, 1488, 1369, 1302, 1151 cm^{-1} ; MS (EI) m/z 419 (M^+ , 48%), 345 (19%), 318 (100%); exact mass M^+ 419.1953 (calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_7$ 419.1944).

(*R*)-1-*tert*-butyl 2,2-diethyl 1-(5-chloro-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4t) (Table 3, Entry 8) (R_f = 0.1 (CH_2Cl_2)): Pale brown oil; HPLC (AS-H, hexane-*i*PrOH = 19:1) major peak t_{R1} 12.5 min, minor peak t_{R2} 13.7 min, 74% ee; $[\alpha]_D^{20} = -86^\circ$ (c 1.80, CHCl_3); ^1H

NMR (400 MHz, CDCl₃) δ (ppm) 0.920 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.39 (s, 9H), 3.82-3.96 (m, 2H), 4.21-4.29 (m, 2H), 4.26 (d, J = 11.7 Hz, 1H), 4.49 (dd, J = 11.7, 0.4 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 7.10 (dd, J = 8.7, 2.0 Hz, 1H), 7.19-7.22 (m, 1H), 7.72 (d, J = 2.0 Hz, 1H), 8.63 (bs, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ (ppm) 13.6 (q), 14.1 (q), 27.8 (q), 43.4 (d), 55.0 (d), 61.6 (t), 62.0 (t), 81.9 (s), 109.6 (s), 112.4 (d), 118.9 (d), 122.6 (d), 124.6 (d), 125.4 (s), 127.3 (s), 134.5 (s), 167.7 (s), 168.1 (s), 171.2 (s); IR (neat) 3377, 2980, 1763-1716, 1571, 1464, 1371, 1102, 1032 cm⁻¹; MS (EI) m/z 425 (M⁺, 11%), 423 (M⁺, 30%), 349 (26%), 322 (100%); exact mass M⁺ 423.1449 (calcd for C₂₁H₂₆³⁵ClNO₆ 423.1449), 425.1444 (calcd for C₂₁H₂₆³⁷ClNO₆ 425.1419).

Diethyl 2-((*R*)-1-(5-chloro-1*H*-indol-3-yl)-2-oxo-2-(pyrrolidin-1-yl)ethyl)malonate (4u) (Table 3, Entry 9) (R_f = 0.3 (CH₂Cl₂-ether = 2:1)): Pale yellow viscous oil; HPLC (AS-H, hexane-ⁱPrOH = 9:1) minor peak t_{R1} 10.5 min, major peak t_{R2} 19.2 min, 65% ee; $[\alpha]_D^{30}$ = -118° (c 0.93, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.864 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.68-1.95 (m, 4H), 3.21-3.26 (m, 1H), 3.30-3.36 (m, 1H), 3.51-3.57 (m, 1H), 3.73-3.88 (m, 3H), 4.12-4.29 (m, 2H), 4.41 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 7.10 (dd, J = 8.6, 1.9 Hz, 1H), 7.18-7.21 (m, 1H), 7.26-7.28 (m, 1H), 7.70 (d, J = 1.9 Hz, 1H), 9.38 (bs, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ (ppm) 13.5 (q), 14.0 (q), 24.2 (t), 25.9 (t), 41.1 (d), 46.2 (t), 46.4 (t), 56.30 (d), 56.34 (d), 61.4 (t), 61.7 (t), 109.0 (s), 112.6 (d), 118.2 (d), 122.4 (d), 125.4 (d), 125.5 (s), 127.6 (s), 134.4 (s), 168.3 (s), 168.6 (s), 170.1 (s); IR (neat) 3218, 2979, 2876, 1734, 1622, 1455, 1370, 1340, 1301, 1182, 1036 cm⁻¹; MS (EI) m/z 422 (M⁺, 1.4%), 420 (M⁺, 4.1%), 84 (100%); exact mass M⁺ 420.1452 (calcd for C₂₁H₂₅³⁵ClN₂O₅ 420.1452), 422.1399 (calcd for C₂₁H₂₅³⁷ClN₂O₅ 422.1422).

Diethyl 2-((*R*)-1-(5-chloro-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)malonate (4v) (Table 3, Entry 10) (R_f = 0.1 (CH₂Cl₂)): Colorless oil; HPLC (AS-H, hexane-ⁱPrOH = 9:1) minor peak t_{R1} 12.9 min, major peak t_{R2} 15.3 min, 93% ee; $[\alpha]_D^{23}$ = -318° (c 1.60, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.912 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H), 3.76-3.94 (m, 2H), 4.10-4.24 (m, 2H), 4.51 (d, J = 11.4 Hz, 1H), 5.57 (d, J = 11.4 Hz, 1H), 6.94 (d, J = 2.6 Hz, 1H), 7.07 (dd, J = 8.6, 1.8 Hz, 1H), 7.12 (d, J = 8.6 Hz, 1H), 7.29-7.32 (m, 2H), 7.39-7.44 (m, 1H), 7.74 (d, J = 1.8 Hz, 1H), 7.94-7.96 (m, 2H), 8.65 (bs, 1H); ¹³C NMR (100.6 MHz,

CDCl₃) δ (ppm) 13.6 (q), 14.0 (q), 43.9 (d), 55.8 (d), 61.7 (t), 62.0 (t), 108.6 (s), 112.6 (d), 118.2 (d), 122.8 (d), 125.6 (d), 125.9 (s), 127.0 (s), 128.6 (d), 128.7 (d), 133.2 (d), 134.6 (s), 135.7 (s), 168.4 (s), 168.5 (s), 197.1 (s); IR (neat) 3378, 2982, 1747, 1732, 1683, 1597, 1464, 1370, 1298, 1182, 1103, 1032 cm⁻¹; MS (EI) m/z 429 (M⁺, 6.7%), 427 (M⁺, 17%), 322 (70%), 204 (64%), 85 (93%), 83 (100%); exact mass M⁺ 427.1184 (calcd for C₂₃H₂₂³⁵ClNO₅ 427.1187), 429.1166 (calcd for C₂₃H₂₂³⁷ClNO₅ 429.1157).

(*R*)-1-*tert*-Butyl 2,2-diethyl 1-(5-bromo-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4w)

(Table 3, Entry 11) (R_f = 0.4 (CH₂Cl₂)): Pale brown oil; HPLC (AD-H, hexane-ⁱPrOH = 9:1) major peak t_{R1} 9.9 min, minor peak t_{R2} 11.4 min, 80% ee; [α]_D²³ = -87° (c 0.95, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.933 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.39 (s, 9H), 3.83-3.97 (m, 2H), 4.21-4.29 (m, 2H), 4.26 (d, *J* = 11.8 Hz, 1H), 4.49 (dd, *J* = 11.8, 0.5 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 7.15-7.17 (m, 1H), 7.23 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.88 (d, *J* = 1.8 Hz, 1H), 8.36 (bs, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ (ppm) 13.7 (q), 14.1 (q), 27.8 (q), 43.4 (d), 55.0 (d), 61.6 (t), 62.0 (t), 81.9 (s), 109.5 (s), 112.8 (d), 113.0 (s), 122.0 (d), 124.4 (d), 125.1 (d), 128.0 (s), 134.8 (s), 167.7 (s), 168.1 (s), 171.1 (s); IR (neat) 3378, 2980, 1733, 1463, 1370, 1301, 1155, 1032 cm⁻¹; MS (EI) m/z 469 (M⁺, 18%), 467 (M⁺, 18%), 368 (55%), 366 (55%), 84 (90%), 57 (100%); exact mass M⁺ 467.0943 (calcd for C₂₁H₂₆⁷⁹BrNO₆ 467.0944), 469.0941 (calcd for C₂₁H₂₆⁸¹BrNO₆ 469.0923).

(*R*)-1-(3-(Dimethylamino)benzyl) 2,2-diethyl 1-(5-bromo-1*H*-indol-3-yl)ethane-1,2,2-tricarboxylate (4x)

(Table 3, Entry 12) (R_f = 0.1 (CH₂Cl₂)): Pale brown oil; HPLC (AS-H, hexane-ⁱPrOH = 9:1) major peak t_{R1} 16.3 min, minor peak t_{R2} 20.6 min, 72% ee; [α]_D²⁷ = -71° (c 0.85, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.894 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 2.81 (s, 6H), 3.80-3.93 (m, 2H), 4.14-4.26 (m, 2H), 4.34 (d, *J* = 11.7 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 5.07 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 6.52 (bs, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 6.63 (dd, *J* = 7.9, 2.6 Hz, 1H), 7.04 (bs, 1H), 7.11-7.15 (m, 2H), 7.23 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 8.37 (bs, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ (ppm) 13.7 (q), 14.1 (q), 40.6 (q), 42.3 (d), 55.0 (d), 61.6 (t), 62.0 (t), 67.6 (t), 109.1 (s), 111.9 (d), 112.5 (d), 112.8 (d), 113.4 (s), 116.2 (d), 121.9 (d), 124.7 (d), 125.4 (d), 128.0 (d), 129.2 (s), 134.7 (s), 136.4 (s), 150.6 (s), 167.4 (s), 168.0 (s), 172.0 (s); IR (neat) 3391, 2981, 1733,

1606, 1501, 1463, 1296, 1160 cm^{-1} ; MS (EI) m/z 546 (M^+ , 3.4%), 544 (M^+ , 3.4%), 349 (88%), 275 (100%); exact mass M^+ 544.1207 (calcd for $\text{C}_{26}\text{H}_{29}^{79}\text{BrN}_2\text{O}_6$ 544.1209), 546.1194 (calcd for $\text{C}_{26}\text{H}_{29}^{80}\text{BrN}_2\text{O}_6$ 546.1193).

Diethyl 2-((*R*)-1-(5-bromo-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)malonate (4y) (Table 3, Entry 13) (R_f = 0.2 (CH_2Cl_2)): Pale yellow oil; HPLC (AS-H, hexane-*i*PrOH = 9:1) minor peak t_{R1} 13.7 min, major peak t_{R2} 15.7 min, 83% ee; $[\alpha]_D^{23}$ = -269° (c 1.65, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.929 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H), 3.77-3.85 (m, 1H), 3.87-3.95 (m, 1H), 4.10-4.24 (m, 2H), 4.50 (d, J = 11.2 Hz, 1H), 5.57 (d, J = 11.2 Hz, 1H), 6.91 (d, J = 2.6 Hz, 1H), 7.05-7.09 (m, 1H), 7.18-7.21 (m, 1H), 7.28-7.32 (m, 2H), 7.39-7.43 (m, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.93-7.95 (m, 2H), 8.68 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.0 (q), 43.8 (d), 55.9 (d), 61.7 (t), 62.0 (t), 108.4 (s), 113.1 (d), 113.4 (s), 121.2 (d), 125.3 (d), 125.4 (d), 127.7 (s), 128.58 (d), 128.63 (d), 133.2 (d), 134.9 (s), 135.7 (s), 168.39 (s), 168.43 (s), 197.0 (s); IR (neat) 3379, 2979, 1732, 1681, 1597, 1462, 1448, 1370, 1294, 1182, 1031 cm^{-1} ; MS (EI) m/z 473 (M^+ , 24%), 471 (M^+ , 24%), 368 (97%), 366 (100%); exact mass M^+ 471.0685 (calcd for $\text{C}_{23}\text{H}_{22}^{79}\text{BrNO}_5$ 471.0681), 473.0668 (calcd for $\text{C}_{23}\text{H}_{22}^{81}\text{BrNO}_5$ 473.0661).

Diethyl 2-((*R*)-1-(5-bromo-1*H*-indol-3-yl)-2-oxo-2-(piperidin-1-yl)ethyl)malonate (4z) (Table 3, Entry 14) (R_f = 0.5 (CH_2Cl_2 -ether = 4:1)): Colorless crystals; mp 158-160 $^\circ\text{C}$; HPLC (AS-H, hexane-*i*PrOH = 9:1) minor peak t_{R1} 10.1 min, major peak t_{R2} 16.9 min, 56% ee; $[\alpha]_D^{24}$ = -140° (c 1.05, CHCl_3); >99% ee (by HPLC) after recrystallization (MeOH); $[\alpha]_D^{30}$ = -198° (c 2.15, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.908 (t, J = 7.1 Hz, 3H), 0.90-0.98 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.34-1.56 (m, 5H), 3.26-3.32 (m, 1H), 3.43-3.52 (m, 3H), 3.74-3.91 (m, 2H), 4.13-4.30 (m, 2H), 4.38 (d, J = 11.1 Hz, 1H), 4.83 (d, J = 11.1 Hz, 1H), 7.08 (d, J = 2.6 Hz, 1H), 7.20-7.25 (m, 2H), 7.82 (bs, 1H), 8.98 (bs, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) 13.6 (q), 14.1 (q), 24.5 (t), 25.5 (t), 25.8 (t), 39.6 (d), 43.7 (t), 47.0 (t), 56.7 (d), 61.5 (t), 61.7 (t), 109.8 (s), 113.0 (d), 113.2 (s), 121.3 (d), 124.9 (d), 125.2 (d), 127.8 (s), 134.7 (s), 168.5 (s), 168.6 (s), 169.6 (s); IR (KBr) 3746, 2938, 1756, 1732, 1621, 1293, 1185, 1144, 1029 cm^{-1} ; MS (EI) m/z 480 (M^+ , 19%), 478 (M^+ , 19%), 368 (54%), 366 (54%), 112 (58%), 84 (100%); exact mass M^+ 478.1100 (calcd for $\text{C}_{22}\text{H}_{27}^{79}\text{BrN}_2\text{O}_5$ 478.1103),

480.1130 (calcd for $C_{22}H_{27}^{81}BrN_2O_5$ 480.1083); Anal. Calcd for $C_{22}H_{27}BrN_2O_5$: C, 55.12; H, 5.68; N, 5.84. Found: C, 55.15; H, 5.80; N, 5.75.

Transformation of 4w to (R)-4z (eq 2). The mixture of **4w** (770 mg, 1.6 mmol, 80% ee, prepared in Table 3, entry 11) and CF_3CO_2H (6.6 mL) was stirred at 0 °C for 1 h. The mixture was concentrated *in vacuo*. THF (2.2 mL) was added to the residue. To the solution were added HOBt (1-hydroxybenzotriazole) (443 mg, 3.3 mmol), EDCI (1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride) (328 mg, 1.7 mmol) and piperidine (0.32 mL, 279 mg, 3.3 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The mixture was concentrated *in vacuo* and diluted with CH_2Cl_2 . The organic phase was washed with saturated aqueous $NaHCO_3$ solution, 2M aqueous citric acid, saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane-ether (1 : 4) to give **4z** (572 mg, 73%). 80% ee by HPLC; (>99% ee by HPLC after recrystallization (MeOH), $[\alpha]_D^{30} = -202^\circ$ (c 1.78, $CHCl_3$)).

1-tert-Butyl 2,2-diethyl 1-(1-methyl-1H-pyrrol-2-yl)ethane-1,2,2-tricarboxylate (6) (eq 3) ($R_f = 0.5$ (CH_2Cl_2)): Pale yellow oil; ; HPLC (AS-H, hexane-*i*PrOH = 19:1) minor peak t_{R1} 3.8 min, major peak t_{R2} 4.0 min, 18% ee; $[\alpha]_D^{23} = -21^\circ$ (c 0.81, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.05 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.37 (s, 9H), 3.68 (s, 3H), 3.94-4.07 (m, 2H), 4.17 (d, $J = 11.9$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 4.32 (d, $J = 11.9$ Hz, 1H), 5.99-6.03 (m, 2H), 6.50-6.51 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 13.9 (q), 14.1 (q), 27.9 (q), 34.0 (q), 43.1 (d), 54.6 (d), 61.6 (t), 62.0 (t), 81.7 (s), 107.1 (d), 107.2 (d), 122.6 (d), 126.4 (s), 167.4 (s), 168.0 (s), 169.8 (s); IR (neat) 2980, 1733, 1489, 1369, 1304, 1155, 1033 cm^{-1} ; MS (EI) m/z 353 (M^+ , 24%), 252 (100%); exact mass M^+ 353.1838 (calcd for $C_{18}H_{27}NO_6$ 353.1838).

iwata3/IndEt
expl00 std1h

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ACQUISITION				
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tn	H1	dseq		
at	3.744	dres	1.0	
np	44928	homo	n	
sw	5999.3	PROCESSING		
fb	3000	wtfile		
bs	1	proc	ft	
tpwr	61	fn	not used	
pw	5.5	math	f	
dl	1.256			
tof	600.0	weir	react	
nt	16	wexp	procp1ot	
ct	16	wbs		
alock	n	wnt		
gain	not used			
FLAGS				
il	n			
in	n			
dp	y			
hs	nn			
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wp	4079.2			
vs	214			
sc	0			
wc	380			
hzmm	10.74			
ls	843.11			
rfl	388.5			
rfp	0			
th	2			
ins	100.000			
nm	ph			

1H NMR (CDCl3, 400 MHz) □
4a

SAMPLE

DEC. & VT

date

Sep 14 2004

dfreq

399.936

solvent

CDCl3

dn

H1

file

/export/home/~

dpwr

42

nmr1/data/iwata3/~

doe

0

IndEt_c.fid

dm

YYY

w

ACQUISITION

sfrq

100.574

dmf

11056

tn

C13

dseq

garpl

at

1.199

dres

1.0

np

59968

homo

n

sw

25000.0

PROCESSING

fb

14000

lb

1.00

bs

16

wfile

tpwr

52

proc

ft

pw

4.3

fn

not used

dl

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match

f

tof

1000.0

nt

2048

werr

react

ct

2048

wexp

procplot

alock

n

wbs

gain

not used

wnt

FLAGS

il

n

in

n

dp

y

hs

nn

DISPLAY

sp

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wp

25000.0

vs

622

sc

0

wc

380

hzmm

0.55

ls

500.00

rfl

9749.9

rfp

7753.5

th

26

ins

500.000

nm

no

ph

13C NMR (CDCl3, 100.6 MHz) □
4a

iwata4/iprInd
expl00 std1h

SAMPLE			DEC. & VT	
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solvent	CDCl3	dn	H1	
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nmr1/data/iwata4/~ dof			0	
iprInd_h.fid	dm		nmn	
ACQUISITION				
sfrq	399.937	dmf	c	200
tn	H1	dseq		
at	3.744	dres	1.0	
np	44928	homo	n	
sw	5999.3	PROCESSING		
fb	3000	wtfile		
bs	1	proc	ft	
tpwr	61	fn	not used	
pw	5.5	math	f	
dl	1.256			
tof	600.0	weir	react	
nt	16	wexp	procp1ot	
ct	16	wbs		
alock	n	wnt		
gain	not used			
FLAGS				
il	n			
in	n			
dp	Y			
hs	nm			
DISPLAY				
sp	-80.0			
wp	4079.2			
vs	214			
sc	0			
wc	380			
hzmm	10.74			
ls	618.15			
rfl	388.7			
rfp	0			
th	20			
ins	100.000			
nm	ph			

1H NMR (CDCl3, 400 MHz) □
4b

iwata4/iprInd

expl00 std13c

SAMPLE			DEC. & VT		
date	Oct 13 2004	dfreq		399.936	
solvent	CDCl3	dn		H1	
file	/export/home/~ dpwr			42	
nmr1/data/iwata4/~ dof				0	
iprInd_c.fid	dm			YYY	
ACQUISITION					
sfrq	100.574	dmf		11056	w
tn	C13	dseq		garpl	
at	1.199	dres		1.0	
np	59968	homo		n	
sw	25000.0	PROCESSING			
fb	14000	lb		1.00	
bs	16	wtfile			
tpwr	52	proc		ft	
pw	4.3	fn		not used	
dl	0.801	match		f	
tof	1000.0				
nt	2048	werf		react	
ct	2048	wexp		procplot	
alock	n	wbs			
gain	not used	wnt			
FLAGS					
il	n				
in	n				
dp	y				
hs	nn				
DISPLAY					
sp	-1397.2				
wp	25000.0				
vs	497				
sc	0				
wc	380				
hzmm	1.19				
ls	500.00				
rfl	9750.7				
rfp	7753.5				
th	20				
ins	500.000				
nm	no	ph			

13C NMR (CDCl3, 100.6 MHz) ☐
4b

iwata3/tbuidn
expl00 std1h

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vmrml/data/iwata3/~ dof			0	
tbuidn_h.fid	dm		nmn	
ACQUISITION			c	
sfrq	399.937	dmf	200	
tn	H1	dseq		
at	3.744	dres	1.0	
np	44928	homo	n	
sw	5999.3	PROCESSING		
fb	3000	wtfile		
bs	1	proc	ft	
tpwr	61	fn	not used	
pw	5.5	math	f	
dl	1.256			
tof	600.0	werr	react	
nt	16	wexp	procp1ot	
ct	16	wbs		
alock	n	wnt		
gain	not used			
FLAGS				
il	n			
in	n			
dp	y			
hs	nm			
DISPLAY				
sp	-80.0			
wp	4079.2			
vs	214			
sc	0			
wc	380			
hzmm	10.74			
ls	599.95			
rfl	390.2			
rfp	0			
th	11			
ins	100.000			
nm	ph			

1H NMR (CDCl3, 400 MHz) □
4c

iwata3/tbun

expl00 std13c

SAMPLE			DEC. & VT	
date	Oct 8 2004	dfreq	399.936	
solvent	CDCl3	dn	H1	
file	/export/home/~ dpwr		42	
vmr1/data/iwata3/~ dof			0	
tbund_c.fid	dm		YYY	
ACQUISITION				
sfrq	100.574	dmf	11056	w
tn	C13	dseq	garp1	
at	1.199	dres	1.0	
np	59968	homo	n	
sw	25000.0	PROCESSING		
fb	14000	lb	1.00	
bs	16	wtfile		
tpwr	52	proc	ft	
pw	4.3	fn	not used	
dl	0.801	match	f	
tof	1000.0			
nt	1024	werr	react	
ct	1024	wexp	procp1ot	
alock	n	wbs		
gain	not used	wnt		
FLAGS				
il	n			
in	n			
dp	y			
hs	mn			
DISPLAY				
sp	-1399.5			
wp	25000.0			
vs	214			
sc	0			
wc	380			
hzmm	0.37			
ls	500.00			
rfl	9753.0			
rfp	7753.5			
th	20			
ins	500.000			
nm	no	ph		

13C NMR (CDCl3, 100.6 MHz) □
4c

iwata5/BenzInd
expl00 std1h

SAMPLE		DEC. & VT	
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solvent	CDCl3	dn	H1
file	/export/home/~ dpwr		20
nmr1/data/iwata5/~ dof			0
BenzInd_h.fid	dm		nmn
ACQUISITION			
sfrq	399.937	dmf	c
tn	H1	dseq	200
at	3.744	dres	1.0
np	44928	homo	n
sw	5399.3	PROCESSING	
fb	3000	wtfile	
bs	1	proc	ft
tpwr	61	fn	not used
pw	5.5	math	f
dl	1.256		
tof	600.0	weir	react
nt	16	wexp	procp1ot
ct	16	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-80.0		
wp	4079.2		
vs	214		
sc	0		
wc	380		
hzmm	10.74		
ls	682.80		
rfl	403.5		
rfp	0		
th	20		
ins	100.000		
nm	ph		

¹H NMR (CDCl₃, 400 MHz) □
4d

iwata5/BenzInd
expl00 std13c

SAMPLE			DEC. & VT	
date	Mar 12 2005	dfreq	399.936	
solvent	CDCl3	dn	H1	
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nmr1/data/iwata5/~ dof			0	
BenzInd_c.fid		dm	YYY	
ACQUISITION				
sfrq	100.574	dmf	11056	w
tn	C13	dseq	garp1	
at	1.199	dres	1.0	
np	59968	homo	n	
sw	25000.0	PROCESSING		
fb	14000	lb	1.00	
bs	16	wtfile		
tpwr	52	proc	ft	
pw	4.3	fn	not used	
dl	0.801	match	f	
tof	1000.0			
nt	1024	werf	react	
ct	1024	wexp	procplot	
alock	n	wbs		
gain	not used	wnt		
FLAGS				
il	n			
in	n			
dp	y			
hs	nn			
DISPLAY				
sp	-2009.4			
wp	25000.0			
vs	214			
sc	0			
wc	380			
hzmm	0.34			
ls	500.00			
rfl	9762.9			
rfp	7753.5			
th	10			
ins	500.000			
nm	no	ph		

13C NMR (CDCl3, 100.6 MHz) □
4d

iwata4/BrBzInd

exp100 std1h

SAMPLE DEC. & VT
date Jan 8 2005 dfreq 399.936
solvent CDCl3 dn H1
file/export/home/~ dpwr 20
vnmr1/data/iwata4/~ dof 0
BrBzInd.h.fid dn nn
ACQUISITION dnm c
sfrq 399.937 dmf 200
tn H1 dseq
at 3.744 dres 1.0
np 44928 homo n
sw 5999.3 PROCESSING
fb 3000 wftile
bs 1 proc ft
tpwr 61 fn not used
pw 5.5 math f
d1 1.256
tof 6000 werr react
nt 16 wexp procpilot
ct 16 wbs
alock n wnt
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -80.0
wp 4079.2
vs 214
sc 0
wc 380
hzmh 10.74
is 912.22
rfi 389.1
rfp 0
th 20
ins 100.000
nm ph

¹H NMR (CDCl₃, 400 MHz) □
4e

SAMPLE			DEC. & VT	
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nmr1/data/iwata4/~	dof		0	
BrBzInd.c.fid	dm		yy	
ACQUISITION				
sfrq	100.574	dmf	11056	
tn	C13	dseq	gar p1	
at	1.199	dres	1.0	
np	59968	homo	n	
sw	25000.0	PROCESSING		
fb	14000	lb	1.00	
bs	16	wtfile		
tpwr	52	proc	ft	
pw	4.3	fn	not used	
d1	0.801	math	f	
tof	1000.0			
nt	5000	werr	react	
ct	4805	wexp	procpot	
alock	n	wbs		
gain	not used	wit		
FLAGS				
il	n			
in	n			
dp	y			
hs	nn			
DISPLAY				
sp	-1997.2			
wp	25000.0			
vs	869			
sc	0			
wc	380			
hzmh	8.99			
is	500.00			
rfl	9750.7			
rfp	7753.5			
th	14			
ins	500.000			
nm no	ph			

13C NMR (CDCl3, 100.6 MHz) □
4e

iwata4/dlMeOBz

exp100 std1h

SAMPLE DEC. & VT
date Jan 5 2005 dfreq 399.936
solvent CDCl3 dn H1
file/export/home/~ dpwr 20
vnmr1/data/iwata4/~ dof 0
dlMeOBz_hfid dm nm
ACQUISITION dmm c
sfrq 399.937 dmf 200
tn H1 dseq
at 3.744 dres 1.0
np 44928 homo n
sw 5999.3 PROCESSING
fb 3000 wftile
bs 1 proc ft
tpwr 61 fn not used
pw 5.5 math f
d1 1.256
tof 600.0 werr react
nt 16 wexp procpilot
ct 16 wbs
alock n wnt
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -80.0
wp 4079.2
vs 214
sc 0
wc 380
hzmh 10.74
ls 810.38
rfi 394.7
rfp 0
th 3
ins 100.000
nm ph

¹H NMR (CDCl₃, 400 MHz) □
4f

iwata4/dlMeOBz

exp100 std13c

SAMPLE DEC. & VT
date Jan 5 2005 dfreq 399.936
solvent CDCl3 dn H1
file/export/home/~ dpwr 42
vnmr1/data/iwata4/~ dof 0
dlMeOBz.cfid dm yyy
ACQUISITION dmm w
sfrq 100.574 dmf 11056
tn C13 dseq garp1
at 1.199 dres 1.0
np 59968 homo n
sw 25000.0 PROCESSING
fb 14000 lb 1.00
bs 16 wrfile
tpwr 52 proc ft
pw 4.3 fn not used
d1 0.801 math f
tof 1000.0
nt 1024 werr react
ct 1024 wexp procp1ot
alock n wbs
gain not used wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2007.1
wp 25000.0
vs 214
sc 0
wc 380
hzzmm 65.79
is 500.00
rfi 9760.6
rfp 7753.5
th 20
ins 500.000
nm no ph

13C NMR (CDCl3, 100.6 MHz) □
4f

SAMPLE

DEC. & VT

date Oct 30 2004

dfreq 399.936

solvent CDCl3

dn H1

file/export/home/~ dpwr

42

nmr1/data/iwata4/~ dof

0

PhInd2.cfid

dm

yyy

ACQUISITION

dm

mm

w

sfrq 100.574

dmf 110.56

tn C13

dseq garp1

at 1.199

dres 1.0

np 59968

homo n

sw 25000.0

PROCESSING

fb 14000

lb 1.00

bs 16

wffile

tpwr 52

proc ft

pw 4.3

fn not used

d1 0.801

math f

tof 1000.0

nt 1024

werr react

ct 1024

wexp procp1ot

alock n

wbs

gain not used

wnt

FLAGS

il n

in n

dp y

hs nn

DISPLAY

sp -2001.0

wp 25000.0

vs 214

sc 0

wc 380

hzm 0.42

is 500.00

rfl 9754.5

rfp 7753.5

th 20

ins 500.000

nm no ph

13C NMR (CDCl3, 100.6 MHz) □
4g

iwata6/PipInd
exp100 std1h

SAMPLE DEC. & VT
date Sep 8 2005 dfrq 399.936
solvent CDCl3 dn H1
file/export/home/~ dpwr 20
vnmr1/data/iwata6/~ dof 0
PipInd_h.fid dm nm
ACQUISITION dmm c
sfrq 399.937 dmf 200
tn H1 dseq
at 3.744 dres 1.0
np 44928 homo n
sw 5999.3 PROCESSING
fb 3000 wftile
bs 1 proc ft
tpwr 61 fn not used
pw 5.5 math f
d1 1.256
tof 600.0 werr react
nt 160 wexp procpot
ct 93 wbs
alock n wnt
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -80.0
wp 4079.2
vs 214
sc 0
wc 380
h2mm 10.74
is 877.72
rfi 381.6
rfp 0
th 20
ins 100.000
nm ph

1H NMR (CDCl3, 400 MHz) □
4h

iwata6/PipInd

exp100 std13c

SAMPLE DEC. & VT
date Sep 8 2005 dfreq 399.936
solvent CDCl3 dn H1
file/export/home/~ dpwr 42
vnmr1/data/iwata6/~ dof 0
PipInd_c.fid dm yy
ACQUISITION dmm w
sfrq 100.574 dmf 11056
tn C13 dseq garp1
at 1.199 dres 1.0
np 59968 homo n
sw 25000.0 PROCESSING
fb 14000 lb 1.00
bs 16 wtf file
tpwr 52 proc ft
pw 4.3 fn not used
d1 0.801 math f
tof 1000.0
nt 5000 wefr react
ct 5000 wexp procp1ot
alock n wbs
gain not used wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2003.3
wp 25000.0
vs 229
sc 0
wc 380
hzm 0.56
is 500.00
rfi 9756.8
rfp 7753.5
th 20
ins 500.000
nm no ph

13C NMR (CDCl3, 100.6 MHz) □
4h

SAMPLE DEC. & VT
date Sep 15 2004 dfreq 399.936
solvent CDCl3 dn H1
file/export/home/~ dpwr 20
vnmr1/data/iwata3/~ dof 0
indAc_h.fid dm nnn
ACQUISITION dmm c
sfreq 399.937 dmf 200
tn H1 dseq
at 3.744 dres 1.0
np 44928 homo n
sw 5999.3 PROCESSING
fb 3000 wfttle
bs 1 proc ft
tpwr 61 fn not used
pw 5.5 math f
d1 1.256
tof 6000 werr react
nt 16 wexp procplo
ct 16 wbs
alock n wnt
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -80.0
wp 4079.2
vs 214
sc 0
wc 380
hzmh 10.74
is 1566.56
rfi 388.1
rfp 0
th 20
ins 100.000
nm ph

1H NMR (CDCl3, 400 MHz) $\square$
4i

SAMPLE DEC. & VT
date Sep 24 2004 dfreq 399.936
solvent CDCl3 dn H1
file/export/home/~ dpwr 42
vnmr1/data/iwata3/~ dof 0
IndAc.c.fid dm yy
ACQUISITION dmm w
sfrq 100.574 dmf 11056
tn C13 dseq garp1
at 1.199 dres 1.0
np 59968 homo n
sw 25000.0 PROCESSING
fb 14000 lb 1.00
bs 16 wtf file
tpwr 52 proc ft
pw 4.3 fn not used
d1 0.801 math f
tof 1000.0
nt 6000 werr react
ct 5078 wexp procp1ot
alock n wbs
gain not used wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1995.7
wp 25000.0
vs 824
sc 0
wc 380
hzm 0.57
is 500.00
rfi 9749.1
rfp 7753.5
th 17
ins 500.000
nm no ph

13C NMR (CDCl3, 100.6 MHz) □
4i

Figure S1. X-ray structure of 4z (ORTEP) drawing, 50% probability ellipsoids).

Crystal and molecular structure

Abstract

We present the crystal and molecular structure of diethyl 2-((*R*)-1-(5-bromo-1*H*-indol-3-yl)-2-oxo-2-(piperidin-1-yl)ethyl)malonate (**4z**). CCDC 285373.

Comment

The study of the titled structure was undertaken to establish its three dimensional structure. Geometries are tabulated below. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan).

Experimental

Crystal data

$C_{22}H_{27}BrN_2O_5$
 $C_{22}H_{27}BrN_2O_5$
 $M_r = 479.376$
Monoclinic
 $P2_1$
 $a = 8.0060 (5) \text{ \AA}$
 $b = 11.1950 (8) \text{ \AA}$
 $c = 13.0820 (11) \text{ \AA}$
 $\alpha = 90.00^\circ$
 $\beta = 100.242 (3)^\circ$
 $\gamma = 90.00^\circ$
 $V = 1153.82 (15) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.380 \text{ Mg m}^{-3}$
Density measured by: not measured
fine-focus sealed tube
Mo $K\alpha$ radiation
 $\lambda = 0.71073$
 $\mu = 1.815 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
Cube
Colourless
Crystal source: Local laboratory

Data collection

MacScience, Japan
DIP Image plate
IP
Absorption correction: sphere
 $T_{\min} = 0.273$, $T_{\max} = 0.170$
3833 measured reflections
3210 independent reflections
2836 observed reflections
Criterion: $>2\sigma(I)$
 $\theta_{\max} = 25.66^\circ$
 $h = -9 \rightarrow 9$
 $k = -13 \rightarrow 13$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2

fullmatrix least squares refinement

R(all) = 0.0542

R(gt) = 0.0478

wR(ref) = 0.1351

wR(gt) = 0.1279

S(ref) = 1.025

3210 reflections

272 parameters

1 restraints

Only coordinates of H atoms refined

Calculated weights calc

$\Delta/\sigma_{\max} = 0.000$

$\Delta\rho_{\max} = 0.438\text{e}\text{\AA}^3$

$\Delta\rho_{\min} = -0.385\text{e}\text{\AA}^3$

Extinction correction: *SHELXL*

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient = 0.035 (4)

Atomic scattering factors from International Tables Vol C Tables 4.2.6.8 and 6.1.1.4

Flack parameter = 0.031 (13)

Flack H D (1983), *Acta Cryst.* A39, 876-881

Data collection: DIP Image plate

Cell refinement: Scalepack(HKL)

Data reduction: maXus (Mackay et al., 1999)

Program(s) used to refine structure: *SHELXL-97* (Sheldrick, 1997)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$)

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

	x	y	z	U_{eq}	Occ
Br1	0.44025 (11)	0.81040 (7)	0.52768 (6)	0.1055 (3)	1
O2	0.0889 (4)	0.2745 (3)	0.0932 (3)	0.0740 (10)	1
C3	0.2100 (6)	0.3277 (4)	0.1463 (3)	0.0554 (10)	1
C4	0.1593 (5)	0.5346 (3)	0.1988 (3)	0.0486 (8)	1
N5	0.3702 (5)	0.3213 (3)	0.1290 (3)	0.0570 (8)	1
O6	0.1388 (5)	0.1769 (3)	0.3251 (4)	0.0794 (11)	1
N7	0.0796 (6)	0.6951 (4)	0.0993 (3)	0.0679 (10)	1
C8	-0.0248 (6)	0.4402 (3)	0.3588 (4)	0.0568 (10)	1
C9	0.0123 (7)	0.2335 (4)	0.2976 (4)	0.0564 (10)	1
C10	0.1731 (5)	0.4064 (3)	0.2356 (3)	0.0479 (8)	1
C11	0.2960 (6)	0.6618 (4)	0.3598 (4)	0.0565 (9)	1
O12	-0.1460 (5)	0.1927 (3)	0.2896 (4)	0.0736 (10)	1
C13	0.0069 (5)	0.3644 (3)	0.2673 (4)	0.0500 (9)	1
O14	0.0609 (6)	0.4365 (4)	0.4433 (3)	0.0890 (12)	1
O15	-0.1497 (6)	0.5165 (3)	0.3317 (3)	0.0786 (11)	1
C16	0.1843 (8)	0.8572 (4)	0.2260 (5)	0.0704 (14)	1
C17	0.5116 (6)	0.3954 (4)	0.1786 (4)	0.0570 (10)	1
C18	0.0791 (6)	0.5742 (4)	0.1034 (4)	0.0604 (10)	1
C19	0.2122 (5)	0.6400 (3)	0.2589 (3)	0.0489 (8)	1
C20	0.3240 (7)	0.7797 (4)	0.3918 (4)	0.0681 (12)	1
C21	0.1582 (7)	0.7387 (4)	0.1924 (4)	0.0593 (11)	1
C22	0.4079 (8)	0.2498 (4)	0.0418 (4)	0.0712 (14)	1

C23	0.5672 (7)	0.4789 (4)	0.0990 (4)	0.0686 (12)	1
C24	0.4625 (9)	0.3310 (6)	-0.0392 (5)	0.0838 (16)	1
C25	0.6072 (8)	0.4109 (5)	0.0076 (5)	0.0796 (15)	1
C26	0.2679 (8)	0.8759 (4)	0.3263 (5)	0.0744 (14)	1
C27	-0.1688 (9)	0.0697 (5)	0.3180 (7)	0.092 (2)	1
C29	-0.3442 (10)	0.0379 (6)	0.2924 (9)	0.109 (3)	1
C30	-0.1860 (14)	0.6035 (7)	0.4090 (6)	0.113 (3)	1
C32	-0.1985 (18)	0.7184 (7)	0.3675 (10)	0.141 (5)	1
H7	0.0290	0.7356	0.0368	0.081	1
H10	0.2635	0.3862	0.2951	0.057	1
H11	0.3341	0.6067	0.4101	0.068	1
H13	-0.0845	0.3913	0.2120	0.060	1
H16	0.1363	0.9229	0.1786	0.084	1
H17A	0.4663	0.4092	0.2401	0.068	1
H17B	0.6004	0.3353	0.1968	0.068	1
H18	0.0387	0.5175	0.0444	0.072	1
H22A	0.5332	0.1901	0.0775	0.085	1
H22B	0.3222	0.2059	0.0088	0.085	1
H23A	0.4766	0.5334	0.0736	0.082	1
H23B	0.6656	0.5231	0.1306	0.082	1
H24A	0.4986	0.2829	-0.0919	0.101	1
H24B	0.3686	0.3801	-0.0699	0.101	1
H25A	0.6291	0.4667	-0.0442	0.096	1
H25B	0.7064	0.3630	0.0300	0.096	1
H26	0.3052	0.9645	0.3369	0.089	1
H27A	-0.1030	0.0181	0.2820	0.111	1
H27B	-0.1325	0.0607	0.3916	0.111	1
H29A	-0.3607	-0.0434	0.3116	0.131	1
H29B	-0.3803	0.0471	0.2188	0.131	1
H29C	-0.4098	0.0898	0.3283	0.131	1
H30A	-0.2886	0.5817	0.4328	0.135	1
H30B	-0.0931	0.6031	0.4666	0.135	1
H32A	-0.2206	0.7763	0.4176	0.170	1
H32B	-0.2911	0.7176	0.3097	0.170	1
H32C	-0.0956	0.7391	0.3436	0.170	1

Table 2. Anisotropic displacement parameters ($\text{\AA}^2$)

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Br1	0.1359 (6)	-0.0327 (4)	-0.0029 (3)	0.1030 (5)	-0.0294 (3)	0.0699 (4)
O2	0.071 (2)	-0.0146 (15)	0.0014 (16)	0.089 (2)	-0.0278 (16)	0.058 (2)
C3	0.065 (3)	-0.0019 (17)	0.0017 (18)	0.053 (2)	-0.0052 (16)	0.044 (2)
C4	0.055 (2)	0.0010 (15)	0.0013 (16)	0.0481 (18)	-0.0004 (14)	0.040 (2)
N5	0.064 (2)	-0.0005 (15)	0.0098 (15)	0.0507 (18)	-0.0104 (16)	0.056 (2)
O6	0.071 (2)	0.0051 (15)	0.001 (2)	0.0612 (18)	0.0165 (18)	0.101 (3)
N7	0.076 (2)	0.0021 (18)	-0.0037 (19)	0.070 (2)	0.0201 (17)	0.052 (2)
C8	0.069 (3)	-0.0005 (17)	0.014 (2)	0.051 (2)	0.0004 (16)	0.052 (3)
C9	0.065 (3)	-0.0026 (17)	0.006 (2)	0.047 (2)	0.0040 (17)	0.056 (3)
C10	0.054 (2)	-0.0015 (15)	0.0000 (15)	0.0496 (19)	-0.0005 (14)	0.037 (2)
C11	0.065 (3)	-0.0045 (17)	0.0059 (19)	0.055 (2)	-0.0015 (16)	0.048 (2)
O12	0.069 (2)	-0.0068 (14)	0.0081 (18)	0.0593 (18)	0.0136 (16)	0.090 (3)
C13	0.053 (2)	-0.0035 (14)	0.0024 (18)	0.0488 (19)	-0.0017 (15)	0.046 (2)
O14	0.107 (3)	0.022 (2)	-0.004 (2)	0.102 (3)	-0.0144 (19)	0.051 (2)
O15	0.098 (3)	0.0301 (19)	0.0121 (19)	0.078 (2)	-0.0087 (16)	0.060 (2)
C16	0.077 (3)	0.0059 (19)	0.024 (3)	0.051 (2)	0.011 (2)	0.086 (4)

C17	0.057 (3)	-0.0009 (17)	0.0068 (18)	0.062 (2)	0.0004 (17)	0.050 (2)
C18	0.069 (3)	-0.0004 (18)	-0.0040 (18)	0.068 (3)	0.0016 (17)	0.039 (2)
C19	0.053 (2)	-0.0026 (14)	0.0037 (16)	0.0475 (19)	0.0016 (15)	0.044 (2)
C20	0.077 (3)	-0.014 (2)	0.018 (2)	0.061 (3)	-0.016 (2)	0.068 (3)
C21	0.067 (3)	0.0008 (18)	0.010 (2)	0.053 (2)	0.0096 (18)	0.058 (3)
C22	0.091 (4)	0.000 (2)	0.024 (3)	0.060 (3)	-0.020 (2)	0.066 (3)
C23	0.081 (3)	-0.003 (2)	0.013 (2)	0.057 (2)	0.003 (2)	0.068 (3)
C24	0.110 (5)	0.001 (3)	0.023 (3)	0.086 (4)	-0.010 (3)	0.059 (3)
C25	0.084 (4)	0.003 (3)	0.029 (3)	0.082 (3)	0.006 (3)	0.078 (4)
C26	0.088 (4)	-0.003 (2)	0.029 (3)	0.053 (3)	-0.010 (2)	0.087 (4)
C27	0.085 (4)	-0.012 (2)	0.007 (4)	0.064 (3)	0.024 (3)	0.123 (6)
C29	0.095 (5)	-0.020 (3)	0.009 (5)	0.075 (4)	0.003 (4)	0.151 (8)
C30	0.163 (8)	0.056 (5)	0.032 (5)	0.104 (5)	-0.018 (4)	0.075 (4)
C32	0.208 (12)	0.001 (5)	0.096 (10)	0.084 (5)	-0.037 (5)	0.155 (11)

Table 3 . *Geometric parameters* (Å, °)

Br1—C20	1.886 (6)
O2—C3	1.240 (5)
C3—N5	1.343 (6)
C3—C10	1.533 (5)
C4—C18	1.371 (6)
C4—C19	1.439 (5)
C4—C10	1.512 (5)
N5—C17	1.459 (6)
N5—C22	1.468 (6)
O6—C9	1.195 (6)
N7—C18	1.355 (6)
N7—C21	1.358 (7)
C8—O14	1.193 (7)
C8—O15	1.315 (6)
C8—C13	1.525 (6)
C9—O12	1.334 (6)
C9—C13	1.516 (6)
C10—C13	1.536 (6)
C11—C20	1.390 (6)
C11—C19	1.392 (6)
O12—C27	1.445 (6)
O15—C30	1.470 (7)
C16—C26	1.379 (10)
C16—C21	1.402 (7)
C17—C23	1.524 (7)
C19—C21	1.425 (6)
C20—C26	1.399 (8)
C22—C24	1.517 (9)
C23—C25	1.499 (8)
C24—C25	1.505 (10)
C27—C29	1.430 (10)
C30—C32	1.393 (13)
N7—H7	0.9600
C10—H10	0.9900
C11—H11	0.9139
C13—H13	0.9802
C16—H16	0.9945
C17—H17A	0.9509

C17—H17B	0.9770
C18—H18	1.0067
C22—H22A	1.2271
C22—H22B	0.8907
C23—H23A	0.9600
C23—H23B	0.9600
C24—H24A	0.9601
C24—H24B	0.9600
C25—H25A	0.9599
C25—H25B	0.9600
C26—H26	1.0381
C27—H27A	0.9599
C27—H27B	0.9600
C29—H29A	0.9599
C29—H29B	0.9599
C29—H29C	0.9601
C30—H30A	0.9601
C30—H30B	0.9599
C32—H32A	0.9601
C32—H32B	0.9599
C32—H32C	0.9600
O2—C3—N5	123.7 (4)
O2—C3—C10	117.7 (4)
N5—C3—C10	118.5 (4)
C18—C4—C19	106.1 (4)
C18—C4—C10	126.3 (4)
C19—C4—C10	127.3 (4)
C3—N5—C17	125.7 (3)
C3—N5—C22	119.6 (4)
C17—N5—C22	113.9 (4)
C18—N7—C21	109.1 (4)
O14—C8—O15	123.8 (4)
O14—C8—C13	124.0 (4)
O15—C8—C13	112.0 (4)
O6—C9—O12	125.7 (4)
O6—C9—C13	125.1 (5)
O12—C9—C13	109.2 (4)
C4—C10—C3	108.4 (3)
C4—C10—C13	111.0 (3)
C3—C10—C13	108.9 (3)
C20—C11—C19	118.5 (4)
C9—O12—C27	117.9 (4)
C9—C13—C8	109.5 (4)
C9—C13—C10	112.3 (4)
C8—C13—C10	108.3 (3)
C8—O15—C30	118.6 (5)
C26—C16—C21	117.6 (5)
N5—C17—C23	110.0 (4)
N7—C18—C4	110.7 (4)
C11—C19—C21	119.1 (4)
C11—C19—C4	135.0 (4)
C21—C19—C4	105.9 (4)
C11—C20—C26	122.0 (5)
C11—C20—Br1	118.9 (4)

C26—C20—Br1	119.2 (3)
N7—C21—C16	129.9 (5)
N7—C21—C19	108.1 (4)
C16—C21—C19	122.0 (5)
N5—C22—C24	109.9 (4)
C25—C23—C17	111.3 (4)
C25—C24—C22	111.6 (6)
C23—C25—C24	111.6 (5)
C16—C26—C20	120.9 (4)
C29—C27—O12	109.9 (6)
C32—C30—O15	110.6 (7)
C18—N7—H7	120.1
C21—N7—H7	130.8
C4—C10—H10	118.0
C3—C10—H10	104.8
C13—C10—H10	105.4
C20—C11—H11	114.1
C19—C11—H11	127.4
C9—C13—H13	118.2
C8—C13—H13	101.7
C10—C13—H13	106.0
C26—C16—H16	123.3
C21—C16—H16	119.0
N5—C17—H17A	94.9
C23—C17—H17A	132.8
N5—C17—H17B	101.0
C23—C17—H17B	107.5
H17A—C17—H17B	106.0
N7—C18—H18	127.1
C4—C18—H18	121.9
N5—C22—H22A	105.6
C24—C22—H22A	105.9
N5—C22—H22B	115.5
C24—C22—H22B	106.6
H22A—C22—H22B	113.0
C25—C23—H23A	107.6
C17—C23—H23A	109.4
C25—C23—H23B	109.2
C17—C23—H23B	109.8
H23A—C23—H23B	109.5
C25—C24—H24A	108.5
C22—C24—H24A	109.1
C25—C24—H24B	108.6
C22—C24—H24B	109.5
H24A—C24—H24B	109.5
C23—C25—H25A	108.9
C24—C25—H25A	108.9
C23—C25—H25B	108.8
C24—C25—H25B	109.1
H25A—C25—H25B	109.5
C16—C26—H26	110.6
C20—C26—H26	126.9
C29—C27—H27A	109.7
O12—C27—H27A	110.0
C29—C27—H27B	108.5

O12—C27—H27B	109.2
H27A—C27—H27B	109.5
C27—C29—H29A	110.5
C27—C29—H29B	108.4
H29A—C29—H29B	109.5
C27—C29—H29C	109.5
H29A—C29—H29C	109.5
H29B—C29—H29C	109.5
C32—C30—H30A	110.8
O15—C30—H30A	109.8
C32—C30—H30B	107.6
O15—C30—H30B	108.4
H30A—C30—H30B	109.5
C30—C32—H32A	111.4
C30—C32—H32B	106.8
H32A—C32—H32B	109.5
C30—C32—H32C	110.1
H32A—C32—H32C	109.5
H32B—C32—H32C	109.5

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Figure S2. UB3LYP/LANL2MB optimized structure of (dimethyl benzilidene malonate (**7**)-Cu-**3a**)²⁺.

Scheme S1

Scheme S2

Figure 1. (1o-Cu-3a)²⁺

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.414477	-0.553320	0.577108
2	6	0	-3.071600	-0.447048	0.351701
3	6	0	-2.092986	-0.950044	1.430833
4	6	0	-2.402615	0.150236	-0.888351
5	1	0	-4.734698	-1.006396	1.534588
6	6	0	-5.576654	-0.092489	-0.297683
7	8	0	-5.523645	0.503610	-1.435124
8	8	0	-6.776837	-0.408964	0.347067
9	6	0	-7.972874	0.017661	-0.448013
10	1	0	-8.844312	-0.312245	0.147738
11	1	0	-7.981746	1.119756	-0.568683
12	1	0	-7.972158	-0.475463	-1.441046
13	8	0	-0.819874	-0.906149	1.357708
14	8	0	-1.158958	0.412602	-1.019239
15	8	0	-3.305521	0.389024	-1.922530
16	8	0	-2.759492	-1.475498	2.530510
17	29	0	0.531294	-0.037689	0.085205
18	7	0	1.651018	1.601828	-0.191244
19	6	0	2.966424	1.590150	-0.458887
20	6	0	4.010518	0.454751	-0.262351
21	6	0	3.384385	-0.909430	0.141884
22	7	0	2.098395	-1.294341	0.126694
23	8	0	4.333974	-1.855426	0.493007
24	6	0	3.561316	-3.084109	0.878156
25	1	0	4.012235	-3.937898	0.334876
26	1	0	3.695873	-3.230024	1.971040
27	6	0	2.065533	-2.795920	0.470707
28	1	0	1.392961	-2.931362	1.341787
29	6	0	1.143753	3.035750	-0.439750
30	1	0	0.309477	2.979709	-1.167666
31	6	0	2.399652	3.730989	-1.092586
32	1	0	2.278919	3.916288	-2.181023
33	1	0	2.695972	4.672806	-0.589921
34	8	0	3.535742	2.763586	-0.926374
35	6	0	4.787869	0.242607	-1.621050
36	1	0	4.099421	-0.087106	-2.415935
37	1	0	5.257980	1.192344	-1.918781
38	1	0	5.570560	-0.517907	-1.477855
39	6	0	5.010243	0.911613	0.871409
40	1	0	4.474204	1.072519	1.820635
41	1	0	5.773999	0.131933	1.013983
42	1	0	5.502003	1.848014	0.567023
43	6	0	1.524069	-3.678440	-0.737236
44	6	0	0.616882	3.731479	0.889887
45	6	0	1.533333	-5.179285	-0.278813
46	1	0	0.919091	-5.315300	0.624675
47	1	0	2.553770	-5.530896	-0.067068
48	1	0	1.117322	-5.808063	-1.080067
49	6	0	2.406553	-3.493701	-2.016739
50	1	0	2.003225	-4.112269	-2.831813
51	1	0	3.446757	-3.805070	-1.840215
52	1	0	2.400332	-2.442984	-2.348204
53	6	0	0.050273	-3.268245	-1.064198
54	1	0	0.010829	-2.245143	-1.480192
55	1	0	-0.582262	-3.327991	-0.163591
56	1	0	-0.365373	-3.949712	-1.821346
57	6	0	1.736593	3.795944	1.981415
58	1	0	2.601854	4.382819	1.639161
59	1	0	1.338303	4.278394	2.885973
60	1	0	2.076848	2.784072	2.253736
61	6	0	0.133970	5.177166	0.516943
62	1	0	0.962560	5.795410	0.141714
63	1	0	-0.653329	5.139631	-0.251798
64	1	0	-0.276682	5.667542	1.412036
65	6	0	-0.603714	2.928246	1.449492
66	1	0	-1.043550	3.465834	2.302664
67	1	0	-1.382628	2.811411	0.678179
68	1	0	-0.286366	1.933567	1.811269

69	6	0	-1.820604	-1.942453	3.595458
70	6	0	-2.669571	0.991587	-3.138319
71	1	0	-1.189789	-1.102415	3.950671
72	1	0	-1.182925	-2.765253	3.214604
73	1	0	-2.471451	-2.307814	4.411822
74	1	0	-1.930814	0.287233	-3.571650
75	1	0	-2.183231	1.954470	-2.884383
76	1	0	-3.507350	1.153692	-3.842315

Figure S2. (Dimethyl benzilidene malonate (**7**)-Cu-**3a**)²⁺

Standard orientation:					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.126013	-0.657267	0.660301
2	6	0	-2.774220	-0.433651	0.348318
3	6	0	-1.786337	-1.020714	1.328251
4	6	0	-2.130810	0.291397	-0.795550
5	6	0	-5.428207	-0.295673	0.122215
6	1	0	-4.203183	-1.258716	1.587821
7	8	0	-0.490977	-0.994379	1.267142
8	8	0	-0.863957	0.547576	-0.913601
9	8	0	-2.965307	0.704589	-1.831685
10	8	0	-2.385438	-1.657652	2.410746
11	29	0	0.763569	-0.028105	0.072546
12	7	0	1.932236	1.573515	-0.174972
13	6	0	3.252435	1.553623	-0.417501
14	6	0	4.274537	0.403259	-0.204288
15	6	0	3.604797	-0.955303	0.141226
16	7	0	2.307592	-1.299256	0.099086
17	8	0	4.517088	-1.943495	0.469007
18	6	0	3.695925	-3.153568	0.816177
19	1	0	4.139389	-4.015130	0.279589
20	1	0	3.788912	-3.312345	1.911849
21	6	0	2.224931	-2.815627	0.362306
22	1	0	1.512016	-2.981282	1.194730
23	6	0	1.446990	3.019684	-0.392572
24	1	0	0.600012	2.993654	-1.107135
25	6	0	2.708057	3.697636	-1.052130
26	1	0	2.594162	3.861137	-2.145057
27	1	0	3.006040	4.647384	-0.566220
28	8	0	3.838913	2.726587	-0.860763
29	6	0	5.107643	0.208700	-1.531868
30	1	0	4.449980	-0.089721	-2.364233
31	1	0	5.606131	1.156924	-1.785057
32	1	0	5.870408	-0.568673	-1.372622
33	6	0	5.229705	0.817889	0.983154
34	1	0	4.655048	0.965497	1.911799
35	1	0	5.974497	0.022578	1.139858
36	1	0	5.749128	1.752744	0.722995
37	6	0	1.724546	-3.622783	-0.915143
38	6	0	0.960288	3.704934	0.958781
39	6	0	1.669645	-5.142944	-0.529354
40	1	0	1.003535	-5.303801	0.332349
41	1	0	2.667517	-5.533298	-0.280807
42	1	0	1.281860	-5.721502	-1.381009
43	6	0	2.680552	-3.406329	-2.135509
44	1	0	2.302145	-3.970922	-3.000105
45	1	0	3.699294	-3.761440	-1.920627
46	1	0	2.724946	-2.341664	-2.415074
47	6	0	0.282544	-3.155946	-1.303129
48	1	0	0.290950	-2.113878	-1.671073
49	1	0	-0.403581	-3.241601	-0.444889
50	1	0	-0.105396	-3.788667	-2.115198
51	6	0	2.112589	3.762400	2.016679
52	1	0	2.965879	4.355603	1.656016
53	1	0	1.739131	4.234391	2.937204
54	1	0	2.463404	2.749291	2.270114
55	6	0	0.469331	5.153621	0.608209
56	1	0	1.286573	5.770857	0.206961

57	1	0	-0.344139	5.121634	-0.133030
58	1	0	0.091184	5.641711	1.518746
59	6	0	-0.243009	2.902024	1.555494
60	1	0	-0.656426	3.442262	2.420057
61	1	0	-1.046066	2.783631	0.809748
62	1	0	0.084102	1.908522	1.912864
63	6	0	-1.399461	-2.216967	3.384195
64	6	0	-2.225311	1.378787	-2.943553
65	1	0	-0.752859	-1.412580	3.789670
66	1	0	-0.782279	-3.002524	2.904097
67	1	0	-2.017120	-2.656004	4.190158
68	1	0	-1.473117	0.692836	-3.382361
69	1	0	-1.737079	2.305098	-2.580654
70	1	0	-3.003485	1.623251	-3.690671
71	6	0	-5.662116	0.483067	-1.060826
72	6	0	-6.968096	0.784630	-1.464441
73	6	0	-8.074608	0.317963	-0.708951
74	6	0	-7.871037	-0.457516	0.460147
75	6	0	-6.568346	-0.762117	0.873300
76	1	0	-4.787726	0.816689	-1.637730
77	1	0	-7.141387	1.379079	-2.372854
78	1	0	-9.099833	0.555936	-1.036018
79	1	0	-8.733407	-0.817178	1.039642
80	1	0	-6.405691	-1.359622	1.783132