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Supporting Information

Catalytic Double Stereoinduction in Asymmetric Allylic Alkylation of Oxindoles

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Molybdenum Catalyzed Regio-, Diastereo-, and Enantioselective Allylic alkylation of 3-Alkyl oxindoles

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Supplemental Information

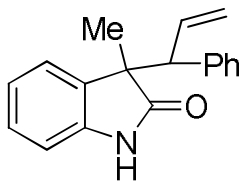
Experimental

General

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glasswares with magnetic stirring, unless otherwise indicated. Solvents were from J. C. Meyer's Solvent Purification System. All other reagents were used as obtained unless otherwise noted. Flash Chromatography was performed with EM Science silica gel (0.040-0.063)m grade). Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (E. Merck, DC-Plasrikfolien, kieselgel 60 F254). Melting points were obtained on aThomas-Hoover apparatus in open capillary tubes and are uncorrected. Proton nuclear magnetic resonance (1H-NMR) data were acquired on a Mercury 400 (400 MHz), a Varian 400 (400 MHz) or on a Varian Unity Inova-500 (500 MHz) spectrometer. Carbon-13 nuclear magnetic resonance (13C-NMR) data were acquired at 100 MHz on a Mercury 400 or at 125 MHz on a Varian Unity Inova 500 spectrometer. Infrared (IR) data were recorded as films on sodium chloride plates or a potassium bromide (KBr) pellets on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorbance requencies are reported in reciprocalcentimeters (cm-1). Elemental analyses (Anal.) were performed by M.-H.-W. Laboratories of Pheonix, AZ.

The Mo AAA reaction of oxindole were performed according to the following representative procedure.

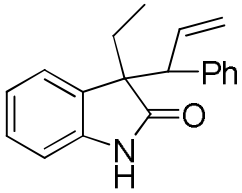
3-methyl-3-(1-phenylallyl)indolin-2-one(1b)



(*R*,*R*) Ligand **L1** (4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol) were stirred at 60 ^oC in THF (freshly distilled and degassed, 0.3 mL) in a sealed pyrex test tube under Ar atmosphere. The solution turned deep purple after 3-5 min, indicating successful generation of the active catalyst. Further heating causes black precipitation and decomposition. The active catalyst is very sensitive to oxygen and moisture and should be used immediately after generation.

A pyrex test tube containing oxindole **1a** (40 mg, 0.2 mmol) was dissolved in 1 mL dry THF and cooled to 0^oC. A solution of NaO*t*Bu (2 mg, 0.02 mmol) in 0.3 mL THF was added dropwise. The resulting solution was warmed to rt and BSA (0.24 mmol) was added via syringe. The resulting solution stirred for 5 min before the solution of the active catalyst solution was cannulated, followed by the addition of cinnamyl *tert*-Butyl carbonate (0.24 mmol) via syringe. The resulting solution was stirred at 60^oC under Ar until TLC indicates complete consumption of the starting oxindole. The reaction mixture was then cooled to 0^oC , and a solution of NaOH (0.25 mL, 1M in MeOH) was added dropwise. The resulting solution was stirred for 30 min and then quenched with H_2O (10 mL). The mixture was then extracted with EtOAc (3x10 mL), dried over sodium sulfate, concentrated, and purified through silica gel (15% EtOAc-pentane) to give **4.74** as a clear oil (50 mg, 93% yield, 98% ee, 15:1 b/l, 7:1 dr). Chiral HPLC, OD-column, flow rate 1.0 mL/min, 97:3 heptane / *i*-PrOH, t_A (minor) = 13.346 min, t_B (major) = 15.047 min. $[\alpha]_D^{24}$ = -24.7^o (*c* 1.0, CH_2Cl_2) IR (film) $?_{max}/cm^{-1}$: 3210, 3081, 3061, , 3030, 2975, 2887, 1707, 1619, 1471, 1452, 1334, 1230, 1202, 1123, 994, 917, 753, 726, 701; ^1H NMR (500 MHz, $CDCl_3$): d 8.50(s, 1H), 7.25-7.14 (m,6H), 7.04-6.97(m, 2H), 6.84(d, *J* = 7.5, 1H), 6.19-6.07 (m, 1H), 5.21 (dm, *J* =17, 1H), 5.08 (dm, *J* = 10, 1H), 3.73(d, *J* = 10, 1H), 1.38(s, 3H; ^{13}C NMR (125 MHz, $CDCl_3$) d 182.3, 140.5, 139.3, 135.7, 132.5, 129.2, 127.8, 126.8, 124.6, 121.8, 117.9, 109.5, 57.0, 52.5, 22.2. HRMS(MH^+): calcd for $C_{18}H_{18}NO$: 264.1388; found: 264.1379

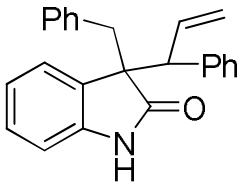
3-ethyl-3-(1-phenylallyl)indolin-2-one (2b)



Prepared according to representative procedure with **2a** (44 mg, 0.2 mmol), (*R*,*R*) Ligand **L1** (4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol)**,** NaO*t*Bu (2 mg, 0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60°C for 8h. Work-up and purification by column chromatography (15% EtOAc-pentane) afforded **2b** as a clear oil (54 mg, 90%, 99% ee, 15:1 b/l, 10:1 dr). $[\alpha]_D^{24} = -23.84^o$ (*c* = 0.9 , CH_2Cl_2)

Chiral HPLC, OD-column, flow rate 1.0 mL/min, 97:3 heptane / *i*-PrOH, t_A (major) = 10.920 min, t_B (minor) = 12.471 min. IR (film) $?_{max}/cm^{-1}$: 3205, 3078, 3030, 2968, 2880, 1704, 1619, 1469, 1341, 1295, 1229, 1189, 995, 919, 748, 727, 699; ^{1}H NMR (500 MHz, $CDCl_3$): d 8.29(s, 1H), 7.22-7.14 (m,4H), 7.13-7.09(m, 2H), 7.02-6.93 (m, 2H), 6.78 (d, *J* = 8, 1H), 6.17-6.07 (m, 1H), 5.17 (dm, *J* =17, 1H), 5.04 (dm, *J* = 10, 1H), 3.71(d, *J* = 10, 1*H*), 2.14-2.06(m, 1H), 1.66-1.58 (m, 1H), 0.53 (t, *J* = 7.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 181.4, 141.4, 139.5, 135.9, 130.3, 129.2, 127.8, 127.7, 126.8, 124.7, 121.8, 117.7, 109.3, 58.1, 57.2, 29.1, 8.6. HRMS(MH^+): calcd for $C_{19}H_{20}NO$: 278.1545; found: 278.1533

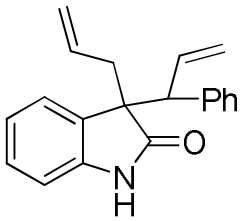
3-benzyl-3-(1-phenylallyl)indolin-2-one (3b)



Prepared according to representative procedure with **4.56** (28 mg, 0.2 mmol), (*R*,*R*) Ligand **L1** (4.8 mg, 0.015 mmol), $(C_7H_8)Mo(CO)_3$ (2.7mg, 0.01 mmol)**,** NaOtBu (2 mg,

0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60°C for 8h. Work-up and purification by column chromatography (10% EtOAc-pentane) afforded **3b** as a clear oil (61.5 mg, 85%, 98% ee, 15:1 b/l, 7:1 dr). HRMS(MH^+): calcd for $C_{21}H_{24}NO_2$: 322.1807; found: 322.1795 Chiral HPLC, OD-column, flow rate 1.0 mL/min, 99:1 heptane / *i*-PrOH, t_A (minor) = 26.827 min, t_B (major) = 31.965 min. $[\alpha]_D^{24}$ = -26.37° (*c* 1.0, CH_2Cl_2) IR (film) $?_{max}/cm^{-1}$:3207, 3061, 3030, 2918, 1710, 1619, 1491, 1471, 1453, 1344, 1231, 1174, 923, 754, 700; ^{1}H NMR (500 MHz, $CDCl_3$): d 7.98 (s, 1H), 7.25-7.17 (m, 5H),7.13-6.91 (m, 6H), 6.79 (d, *J* = 7, 2H), 6.50 (d, *J* = 8, 1H), 6.23-6.13(m, 1H), 5.21 (dm, *J* = 17, 1H), 5.04 (dm, *J* =10, 1H), 3.88 (d, *J* =10, 1H), 3.39 (d, *J* = 13, 1H), 2.85(dd, *J* = 13, *13*, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 180.5, 141.1, 139.4, 135.9, 135.8, 130.0, 129.6, 129.5, 128.0, 127.9, 127.6, 127.0, 126.3, 125.5, 121.5, 118.2, 109.3, 58.9, 57.2, 42.2. HRMS(MH^+): calcd for $C_{24}H_{21}NO$: 340.1701 found: 340.1697

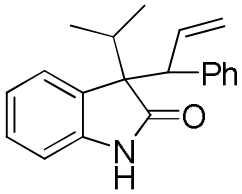
3-allyl-3-(1-phenylallyl)indolin-2-one 4b



Prepared according to representative procedure with **4a** (48 mg, 0.2 mmol), (*R*,*R*) Ligand **L1**(4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol)**,** NaOtBu (2 mg, 0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60°C for 8h. Work-up and purification by column chromatography (10% EtOAc-pentane) afforded **4b** as a clear oil (59 mg, 89%, 99% ee, 15:1 b/l, 8:1 dr). Chiral HPLC, AD-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 5.345 min, t_B (minor) = 6.968 min. $[\alpha]_D^{24}$ = -22.24° (*c* 1.01, CH_2Cl_2) IR (film) $?_{max}/cm^{-1}$: 3208, 3079, 3030, 3918, 1707, 1619, 1471, 1339, 1225, 1182, 994, 920, 730, 702, 668; ^{1}H NMR (500 MHz, $CDCl_3$): d 8.54 (s, 1H), 7.22-7.10 (m, 6H),7.02-6.98 (m, 2H), 6.77 (d, *J* =7.5, 1H), 6.19-6.11(m, 1H), 5.30-5.16 (m, 2H), 5.05 (dm, *J* = 10, 1H), 4.93 (dm, *J*

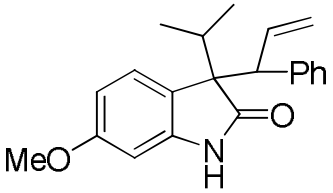
=17, 1H), 4.79 (dm, *J* =10, 1H), 3.76 (d, *J* = 10, 1H), 2.76(dd, *J = 8, 13.5,* 1H), 2.40 (dd, *J* = 7, 13.5 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 181.0, 141.2, 139.3, 135.7, 132.2, 130.1, 129.3, 128.0, 127.9, 125.0, 121.8, 118.9, 118.1, 109.5, 57.2, 56.8, 40.5. HRMS(MH^+): calcd for $C_{20}H_{20}NO$: 290.1545; found: 290.1544.

3-isopropyl-3-(1-phenylallyl)indolin-2-one (5b)



Prepared according to representative procedure with **5a** (47 mg, 0.2 mmol), (*R,R*) Ligand **L1**(4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol)**,** NaOtBu (2 mg, 0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60^{o}C for 8h. Work-up and purification by column chromatography (10% EtOAc-pentane) afforded **5a** as a clear oil (56 mg, 90%, 97% ee, 15:1 b/l, 19:1 dr). Chiral HPLC, AD-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 5.345 min, t_B (minor) = 6.968 min. $[\alpha]_D^{24}$ = -25.01^o (*c* 0.9, CH_2Cl_2) IR (film) $?_{max}$/cm^{-1}: 3210, 3070, 3031, 2967, 1699, 1619, 1469, 1341, 1296, 1229, 1202, 1001, 916, 742, 699; ^{1}H NMR (500 MHz, $CDCl_3$): d 7.69(s, 1H), 7.28 (d, *J* = 7.5, 1H), 7.07 (t, *J* = 8, 1H), 7.03-6.94 (m, 6H), 6.90-6.81(m, 1H), 6.57 (d, *J* = 7.5, 1H), 5.24-5.17 (m, 2H), 3.88(d, *J* = 10, 1*H*), 2.48(hept, *J* =7, 1H), 1.17(d, *J =7,* 3H), 0.69 (d, *J* = 7, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 180.9, 140.9, 140.1, 136.2, 129.8, 128.7, 127.6, 127.5, 126.3, 125.1, 121.5, 117.1, 109.0, 60.4, 54.4, 32.1, 18.0, 16.0. HRMS(MH^+): calcd for $C_{20}H_{22}NO$: 292.1701; found: 292.1692

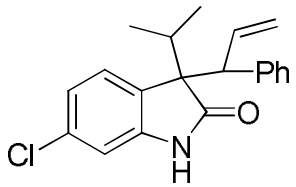
3-isopropyl-6-methoxy-3-(1-phenylallyl)indolin-2-one 6b



Prepared according to representative procedure with **6a** (51.5 mg, 0.2 mmol), (*R*,*R*) Ligand **L1** (4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol)**,** NaOtBu (2 mg, 0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60°C for 8h. Work-up and purification by column chromatography (10% EtOAc-pentane) afforded **6b** as a clear oil (61.5 mg, 90%, 96% ee, 15:1 b/l, 19:1 dr).

Chiral HPLC, AD-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 5.345 min, t_B (minor) = 6.968 min. $[\alpha]_D^{24}$ = -22.32° (*c* 1.0, CH_2Cl_2) IR (film) $?_{max}/cm^{-1}$: 3162, 2964, 2921, 2851, 1697, 1627, 1595, 1507, 1458, 1337, 1309, 1198, 1162, 1089, 1028, 912, 778; ^{1}H NMR (500 MHz, $CDCl_3$): d 7.79 (s, 1H), 7.14 (d, *J* = 8.5, 1H), 7.04-6.96 (m, 5H), 6.86-6.78 (m, 1H),6.51 (dd, *J* =8.5, 2.5, 1H), 6.17(d, *J* = 2.5, 1H), 5.22-5.15 (m, 2H), 3.85 (d, *J* = 10, 1H), 3.73 (s, 3H), 2.43(hept, *J* = *6.5*, 1H), 1.12 (d, *J* = 7, 13.5 3H), 0.69 (d, *J* = 7, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 181.7, 159.7, 142.2, 140.4, 136.5, 128.8, 127.7, 126.4, 125.7, 121.7, 117.1, 106.4, 96.3, 60.1, 55.4, 54.6, 32.2, 18.1, 16.2. HRMS(MH^+): calcd for $C_{21}H_{24}NO_2$: 322.1807; found: 322.1795

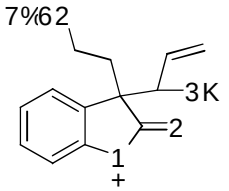
6-chloro-3-isopropyl-3-(1-phenylallyl)indolin-2-one (7b)



Prepared according to representative procedure with **7a** (53 mg, 0.2 mmol), (*R*,*R*) Ligand **L1** (4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol)**,** NaOtBu (2 mg, 0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60°C for 8h. Work-up and purification by column chromatography (10% EtOAc-pentane) afforded **7b** as a clear oil (56 mg, 90%, 98% ee, 15:1 b/l, 19:1 dr). Chiral HPLC, AD-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 6.124 min, t_B (minor) = 7.364 min. IR (film) $?_{max}/cm^{-1}$: 3230, 2967, 1705, 1613, 1485, 1454, 1334, 916, 732; ^{1}H NMR (500 MHz, $CDCl_3$): d 8.28 (s, 1H), 7.17 (d, *J* = 9, 1H), 7.06-7.01 (m, 3H), 6.99-6.95(m, 3H), 6.79 (ddd, *J* = 10, 10, 17, 1H), 6.64 (d, *J* = 2, 1H)

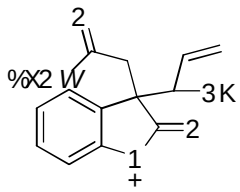
5.23-5.18 (m, 2H), 3.86 (d, *J* = 10, 1*H*), 2.46 (hept, *J* =7, 1H), 1.13(d, *J* =*7*, 3H), 0.68 (d, *J* = 7, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 181.4, 142.3, 139.9, 136.0, 133.4, 128.7, 128.4, 127.9, 126.7, 126.0, 121.6, 117.5, 109.9, 60.4, 54.4, 32.2, 18.0, 16.1 HRMS(MH^+): calcd for $C_{20}H_{20}ClNO$: 326.1312; found: 326.1317

3-(2-(*tert*-butyldimethylsilyloxy)ethyl)-3-(1-phenylallyl)indolin-2-one(8b)



Prepared according to representative procedure with **8a** (71 mg, 0.2 mmol), (*R*,*R*) Ligand **L1** (4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol)**,** NaOtBu (2 mg, 0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60^{o}C for 8h. Work-up and purification by column chromatography (10% EtOAc-pentane) afforded **8b** as a clear oil (67.5 mg, 83%, 97% ee, 15:1 b/l, 7:1 dr). Chiral HPLC, AD-column, flow rate 1.0 mL/min, 95:5 heptane / *i*-PrOH, t_A (minor) = 10.764 min, t_B (minor) = 12.587 min. $[\alpha]_D^{24}$ = -31.77^o (*c* 1.1, CH_2Cl_2) IR (film) ?$_{max}$/cm^{-1}: 3208, 3079, 3030, 3918, 1707, 1619, 1471, 1339, 1225, 1182, 994, 920, 730, 702, 668; ^{1}H NMR (500 MHz, $CDCl_3$): d 9.04 (s, 1H), 7.23-7.15 (m, 4H),7.12-7.08 (m, 2H), 7.01-6.92 (m, 2H), 6.80 (d, *J* = 8, 1H), 6..07(ddd,*J*= 10.5, 10, 16, 1H), 5.16 (dm, *J* = 16, 1H), 5.00 (dm, *J* =10.5, 1H), 3.68 (d, *J* = 10, 1H), 3.31-3.20 (m, 2H), 2.44-2.31 (m, 1H), 1.89-1.84 (m, 1H), 0.76 (s, 9H), -0.17 (s, 3H), -0.18(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 181.8, 141.6, 139.3, 135.5, 129.7, 129.4, 128.0, 127.8, 127.0, 125.0, 121.6, 118.0, 109.6, 59.5, 57.8, 55.2, 38.4, 25.9, 18.2, -5.6, -5.7. HRMS(MH^+): calcd for $C_{25}H_{33}NO_2Si$: 408.2360; found: 408.2351

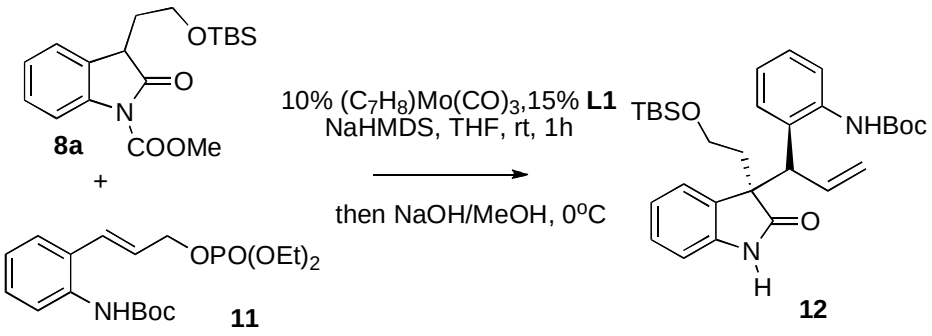
***tert*-butyl 2-(2-oxo-3-(1-phenylallyl)indolin-3-yl)acetate (9b)**



Prepared according to representative procedure with **9a** (69 mg, 0.2 mmol), (*R*,*R*) Ligand **L1** (4.8 mg, 0.15 mmol), $(C_7H_8)Mo(CO)_3$ (2.7 mg, 0.01 mmol)**,** NaOtBu (2 mg, 0.02 mmol), BSA (120 µL, 0.24 mmol), and *t*-butyl cinnamyl carbonate (56 mg, 0.24 mmol) in THF (2 mL) at 60°C for 8h. Work-up and purification by column chromatography (15% EtOAc-pentane) afforded **9b** as a clear oil (58.4 mg, 84%, 97% ee, 11:1 b/l, 4:1 dr).

Chiral HPLC, OD-column, flow rate 0.7 mL/min, 95:5 heptane / *i*-PrOH, t_A (minor) = 5.345 min, t_B (minor) = 6.968 min. $[\alpha]_D^{24}$ = -21.50° (*c* 1.10, CH_2Cl_2)IR (film) $?_{max}/cm^{-1}$: 3162, 2964, 2921, 2851, 1697, 1627, 1595, 1507, 1458, 1337, 1309, 1198, 1162, 1089, 1028, 912, 778; ^{1}H NMR (500 MHz, $CDCl_3$): d 8.70 (s, 1H), 7.24-7.13 (m, 4H), ,7.08-6.95 (m, 5H), 6.77 (d, *J* = 8, 1H), 6.13 (ddd,*J*= 10, 10, 17, 1H), 5.18 (dm, *J* = 17, 1H), 5.07 (dm, *J* =10.5, 1H), 3.65 (d, *J* = 10, 1H), 3.19 (d, *J* = 10.5, 1H), 2.60 (d, *J* = 10.5, 1H), 1.07 (s, 9H), ;^{13}C NMR (125 MHz, $CDCl_3$) d 181.0, 167.0, 141.9, 138.6, 135.0, 129.7, 129.3, 128.3, 128.0, 127.1, 124.7, 121.6, 118.4, 109.5, 81.1, 77.3, 57.4, 54.4, 41.8, 27.5. HRMS(MH^+): calcd for $C_{23}H_{25}NO_3$: 364.1913; found: 364.1901

12 *tert*-butyl2-(1-(3-(2-(*tert*-butyldimethylsilyloxy)ethyl)-2-oxoindolin-3-yl)allyl) phenylcarbamate



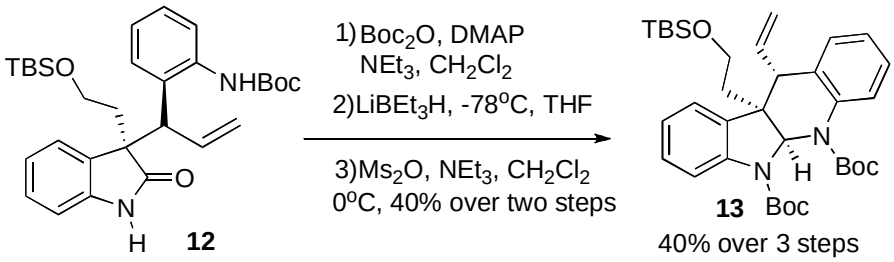
To a solution of oxindole **8a** (0.35 g, 1 mmol) in degassed THF (5 mL) was added dropwise a freshly prepared solution of NaHMDS (189 mg, 1 mmol) in degassed THF (2 mL) at 0°C. The solution was then allowed to warm to rt and stirred for 15min before a solution of premixed $Mo(C_7H_8)(CO)_3$ (27 mg, 0.1 mmol) and (*R, R*) ligand **L1** (48 mg, 0.5 mmol) in degassed THF (0.5 mL) was added, followed by dropwise addition of a solution of the phosphate **11** (385 mg, 1mmol) in degassed THF (1.5 mL) over 20 min. The reaction was stirred at rt for 1h at which point TLC indicated complete consumption of the oxindole nucleophile (Rf: 0.35, 15% ethyl acetate-pentane). The solution was cooled to 0°C and a solution of sodium hydroxide in methanol (1.2 mL, 1M) was then added dropwise. After stirring for another 30 min, the reaction was diluted with EtOAc (10 mL) and water (10 mL). The organic layer was then separated and the aqueous layer was extracted with EtOAc (2x10 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The minor and the major diastereomers were then separated on silica gel (10% ethyl acetate-pentane). Rf: minor diastereomer, 0.34; major diastereomer: 0.18, 15% ethyl acetate-pentane.

Major Diastereomer (355 mg, 68%, 96% ee):

Chiral HPLC, AD-column, flow rate 1.0 mL/min, 95:5 heptane / *i*-PrOH, t_A (major) = 12.485 min, t_B (minor) = 20.172 min. IR (film) cm^{-1}:3259, 2954, 2929, 2856, 1708, 1619, 1516, 1471, 1390, 1365, 1291, 1251, 1162, 1108, 1050, 1022, 836, 776, 751; ^1H NMR (50°C, 500 MHz, $CDCl_3$): d 7.93 (s, 1H), 7.42 (d, *J* = 7.5, 1H), 7.23-7.11 (m, 3H), 7.08 (d, *J* = 7.5, 1H), 7.05-6.98 (m, 2H), 6.72 (d, *J* = 8, 1H), 6.30-6.21 (m, 2H), 5.18 (dm, *J* = 17, 1H), 5.11 (dm, *J* =10, 1H), 4.00 (d, *J* = 10, 1H), 3.30 (dd, *J* = 5.5, 8, 2H), 2.50 (td, *J* =14, 5.5, 1H); 1.94 (td, *J* = 14,8, 1H), 1.56 (s, 9H), 0.78 (s, 9H), -0,14 (s, 3H), -0.17 (s, 3H). ^{13}C NMR (50°C, 125 MHz, $CDCl_3$) d 180.9, 153.8, 141.5, 135.6, 132.8, 130.0,

129.6, 129.1, 128.3, 127.4, 125.4, 124.8, 124.8, 121.7, 118.2, 109.577, 80.4, 59.5, 55.4, 51.5, 38.0, 28.5, 25.9, 18.3, -5.7. HRMS (M H^+): calcd for $C_{30}H_{43}N_2O_4Si$ 523.2961, found 523.2968.

13 di-*tert*-butyl 10b-(2-(*tert*-butyldimethylsilyloxy)ethyl)-11-vinyl-10b,11-dihydro-5*H*-indolo[2,3-b]quinoline-5,6(5a*H*)-dicarboxylate

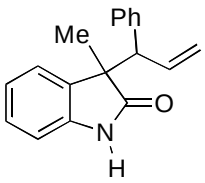


To a solution of oxindole **12** (2.09 g, 4 mmol) in CH_2Cl_2 (20 mL) was added DMAP (50 mg, 0.4 mmol) and NEt_3 (1 mL). The solution was cooled to -10 ^oC and Boc anhydride (1.01g, 4.4 mmol) was added in several portions. The reaction was then stirred at -10^oC for 1h and was then diluted with CH_2Cl_2 (50 mL). The solution was then washed with water (2x10 mL), dried over sodium sulfate, and concentrated in *vacuuo*. The product was then purified by passing it through a 3 in. column (silica gel) using ether to afford the bis-Boc compound (2.46 g, 100% yield). IR (film) $?_{max}/cm^{-1}$: 3366, 2929, 2858, 1730, 1512, 1470, 1349, 1251, 1157, 1108, 838; ^1H NMR (50^oC , 500 MHz, $CDCl_3$): d 7.65 (d, *J* = 3, 1H), 7.42 (s, br, 1H), 7.32 (dt, *J* = 1.5, 7.5, 1H), 7.27 (dd, *J* = 1, 7.5, 1H), 7.22 (dt, *J* = 7.5, 1, 1H), 7.07-7.00 (m, 2H), 6.65 (t, *J* = 7.5, 1H), 6.09 (ddd, *J* = 10, 10.5, 16, 1H), 5.99 (d, *J* = 8, 1H), 5.31-5.23 (m, 2H), 3.99(d, *J* = 10, 1H), 3.54-3.48 (m, 1H), 3.29-3.19 (m, 1H), 2.63-2.53 (m, 1H), 2.40-2.29 (m, 1H), 1.52 (s, 9H), 1.40 (s, 9H), 0.67(s, 9H), -0.03(s, 3H), -0.4(s, 3H); ^{13}C NMR (50^oC, 125 MHz, $CDCl_3$) d 179.5, 154.3, 148.4, 141.0, 135.3, 135.0, 131.4, 128.4, 127.0, 126.7, 126.4, 124.2, 123.5, 119.6, 115.0, 83.1, 79.6, 59.1, 54.9, 50.4, 37.0, 28.4, 27.7, 27.5, 25.6, 18.0, -6.3, -6.4

To a solution of the crude bis-Boc compound (2.46, 4 mmol) in THF (20 mL) was added a solution of lithium triethylborohydride (10 mL, 1M in THF) at -78^oC. The resulting solution was stirred at that temperature for 1h and was then quenched with methanol (2 mL). The mixture was then poured into 1:1 brine/water (30 mL) and extracted with EtOAc (3x30 mL). The combined organic layers were dried over $MgSO_4$

and concentrated in *vacuo*. The residue was then dissolved in CH_2Cl_2 (10 mL) and was cooled to 0°C before NEt_3 (5 mL) and Ms_2O (700 mg, 4 mmol) was added sequentially. The resulting solution was stirred for 2h at 0°C and was then diluted with CH_2Cl_2 (100 mL), washed with saturated aq. sodium bicarbonate (30 mL), dried with sodium sulfate, and concentrated in *vacuo*. Purification by flash column chromatography (5% ethyl acetate/pentane) then afforded **13** (812 mg, 40% from **12**).

IR (film) cm^{-1}:3207, 3061, 3030, 2918, 1710, 1619, 1491, 1471, 1453, 1344, 1231, 1174, 923, 754, 700; ^{1}H NMR (50°C, 500 MHz, $CDCl_3$): d 7.52 (d, 1H, *J* = 8), 7.14 (d, 1H, *J* = 7.5), 7.03 (dt, *J* = 7.5, 1.5, 1H), 7.00-6.94 (m, 2H), 6.89 (dt, *J* = 7.5, 1, 1H), 6.83 (dt, *J* = 7.5, 1, 1H), 6.78 (dt, *J* = 7.5, 1.5, 1H), 6.72 (S, 1H), 6.02 (ddd, *J* = 8, 10, 17, 1H), 5.09 (dm, *J* = 10, 1H), 5.06 (dm, *J* =17, 1H), 3.56 (d, *J* = 7.5, 1H), 3.53-3.42 (m, 2H), 2.31 - 2.25 (m, 1H), 2.08-2.02 (m, *1H*), 1.60 (s, 9H), 1.45 (s, 9H), 0.83 (s, 9H), -0,05 (s, 3H), -0.06 (s, 3H). ^{13}C NMR (50°C, 125 MHz, $CDCl_3$) d 152.8, 152.1, 143.0, 136.4, 136.1, 133.6, 127.9, 127.8, 127.7, 126.8, 126.2, 122.3, 117.6, 114.4, 81.4, 80.7, 76.3, 59.8, 55.3, 54.7, 41.5, 28.7, 28.5, 26.1, 18.4, -5.3, -5.4. HRMS (MH^+): calcd for $C_{35}H_{50}N_2O_5Si$ 607.3568, found 607.3570.



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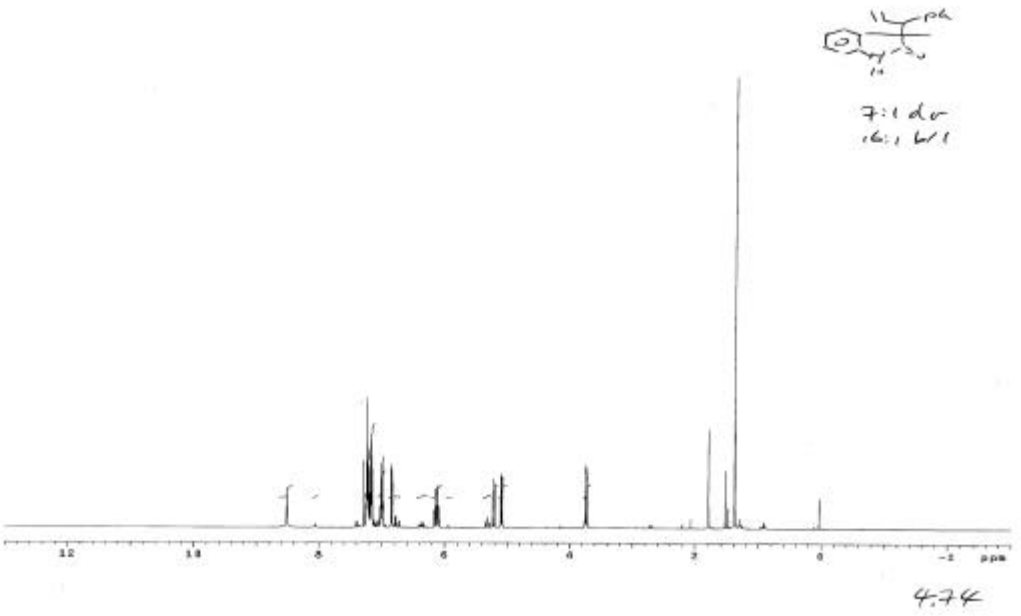

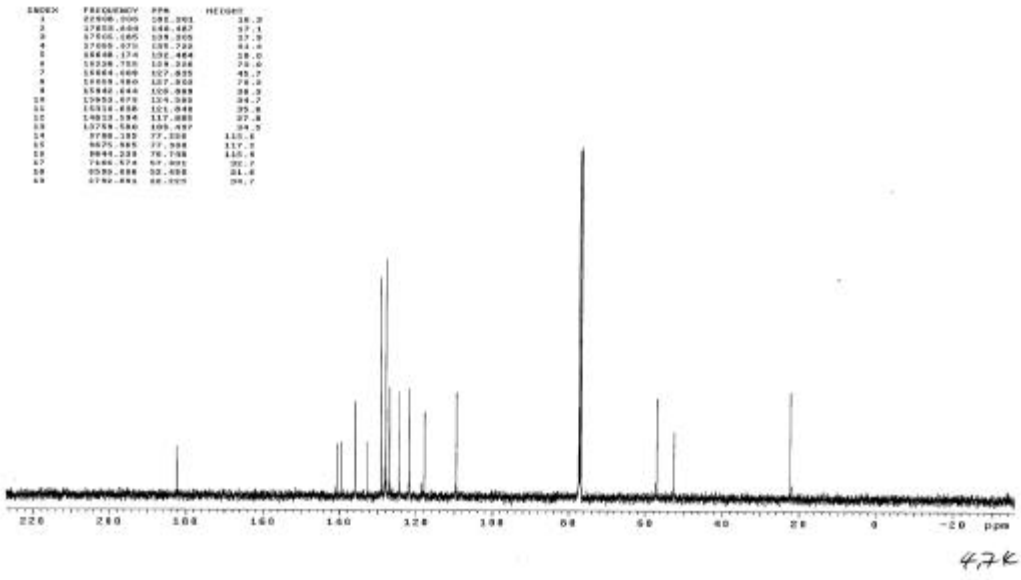

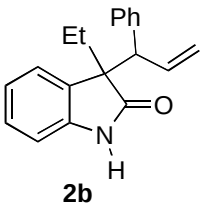

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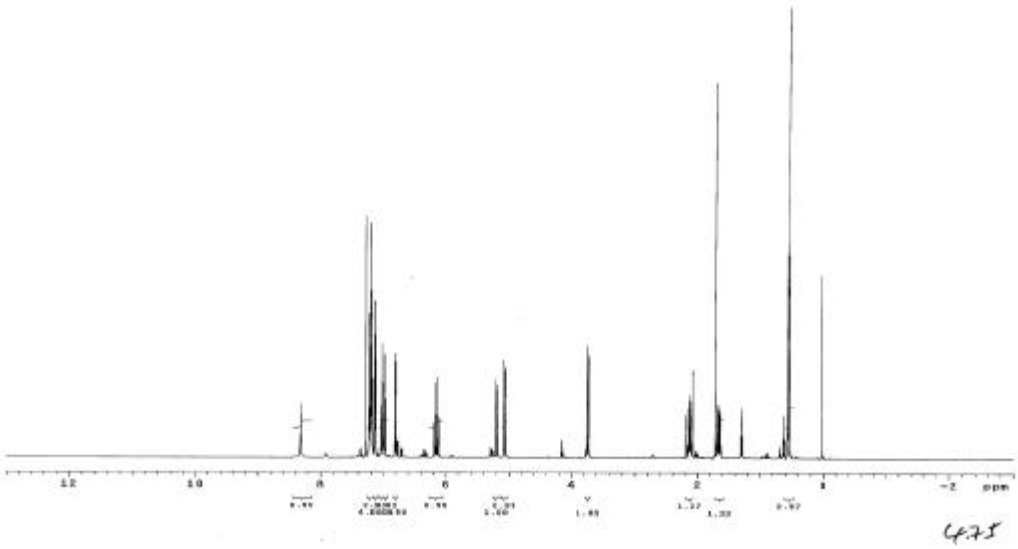

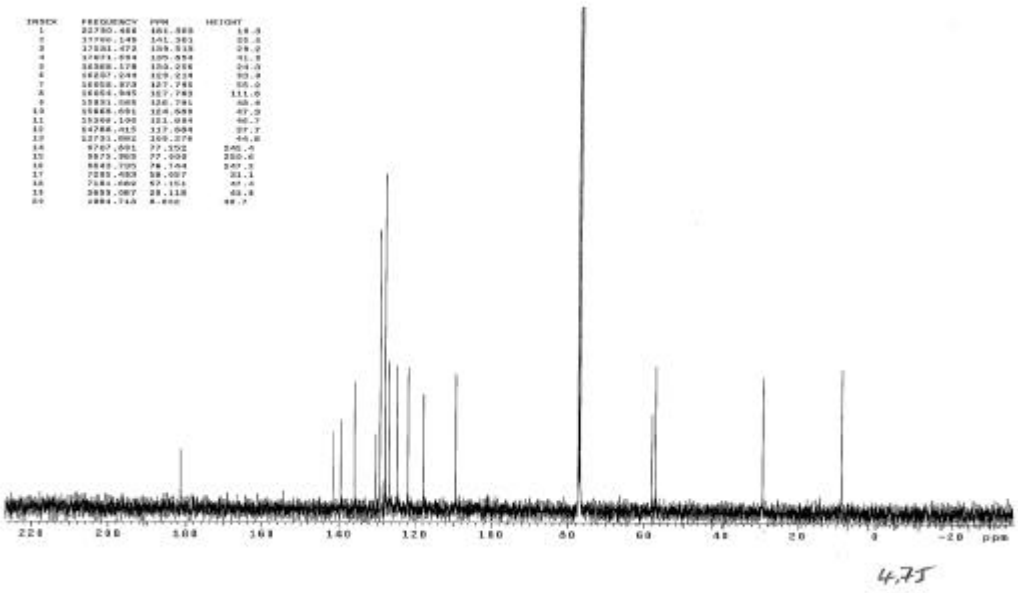

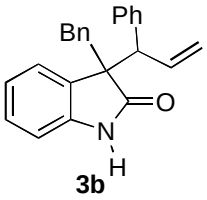
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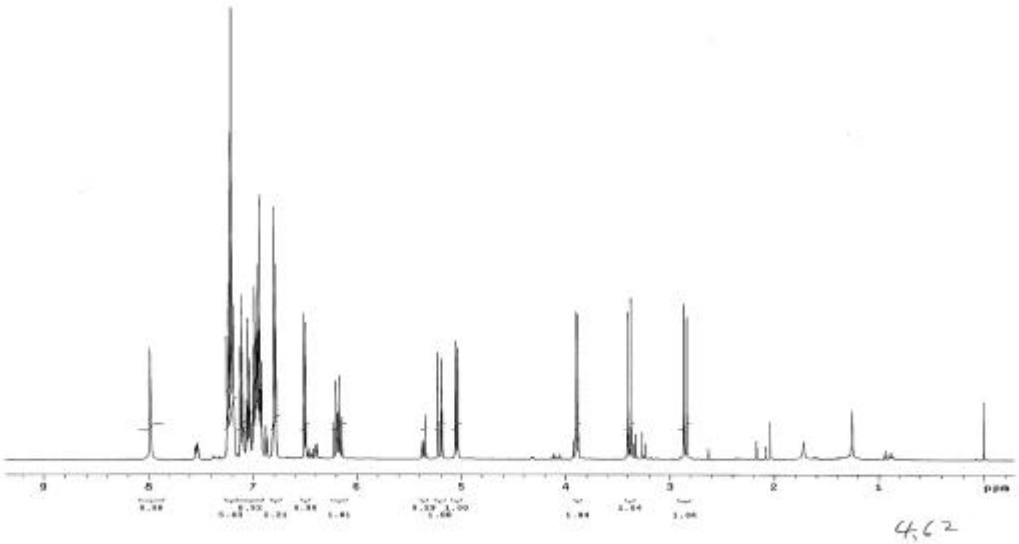
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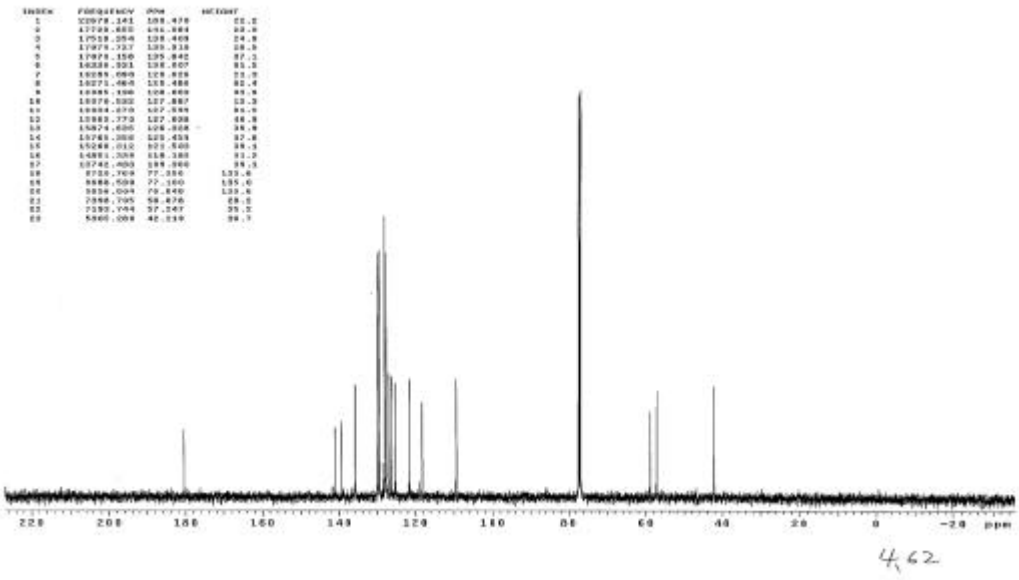
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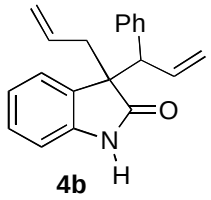

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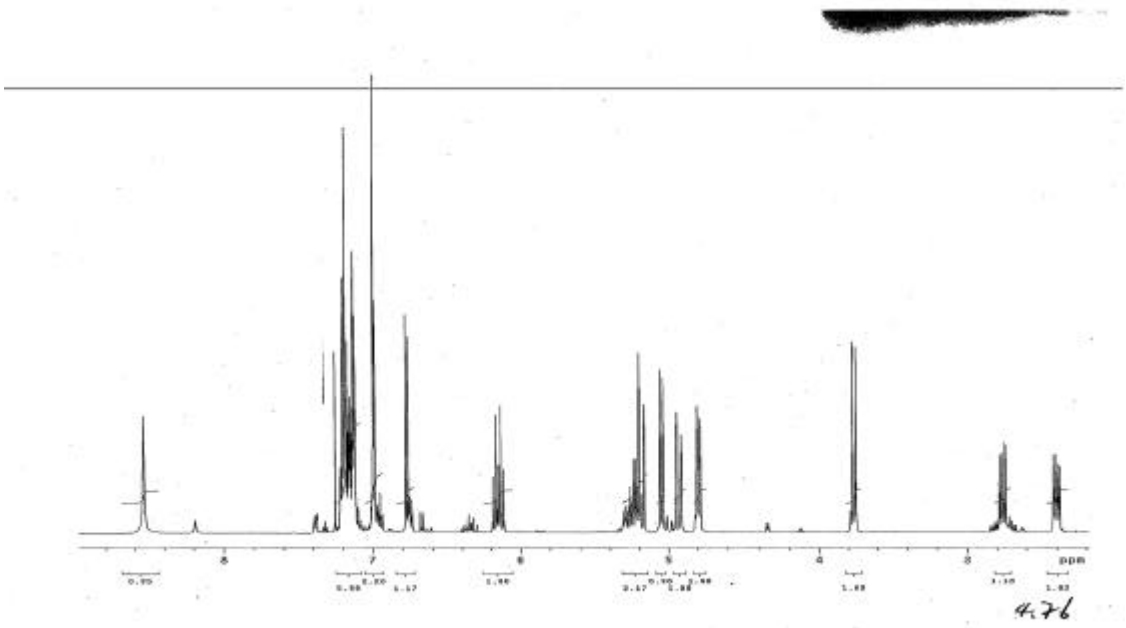

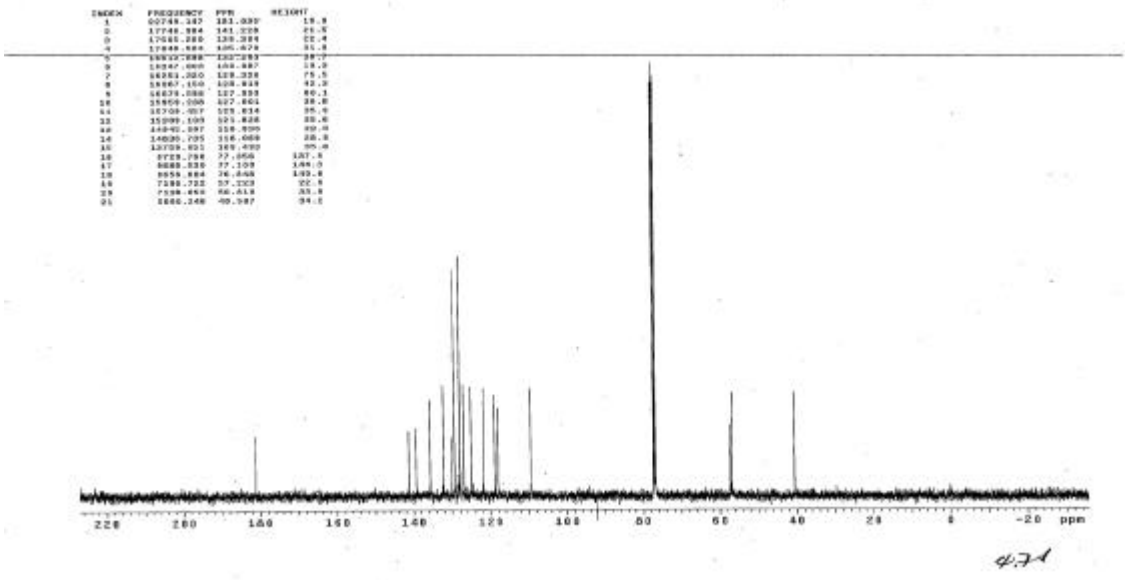

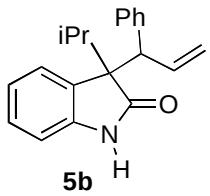

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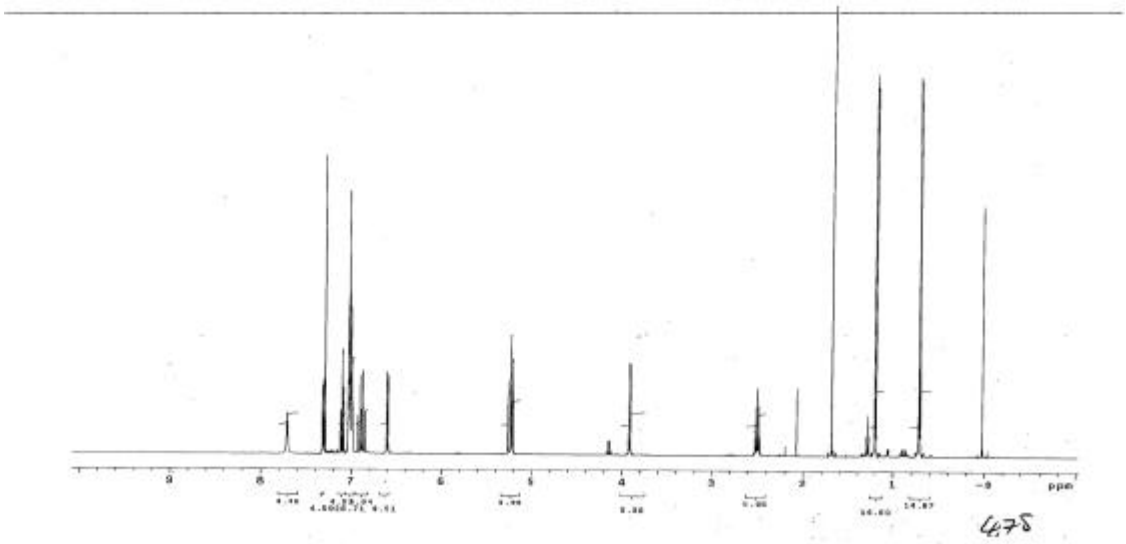

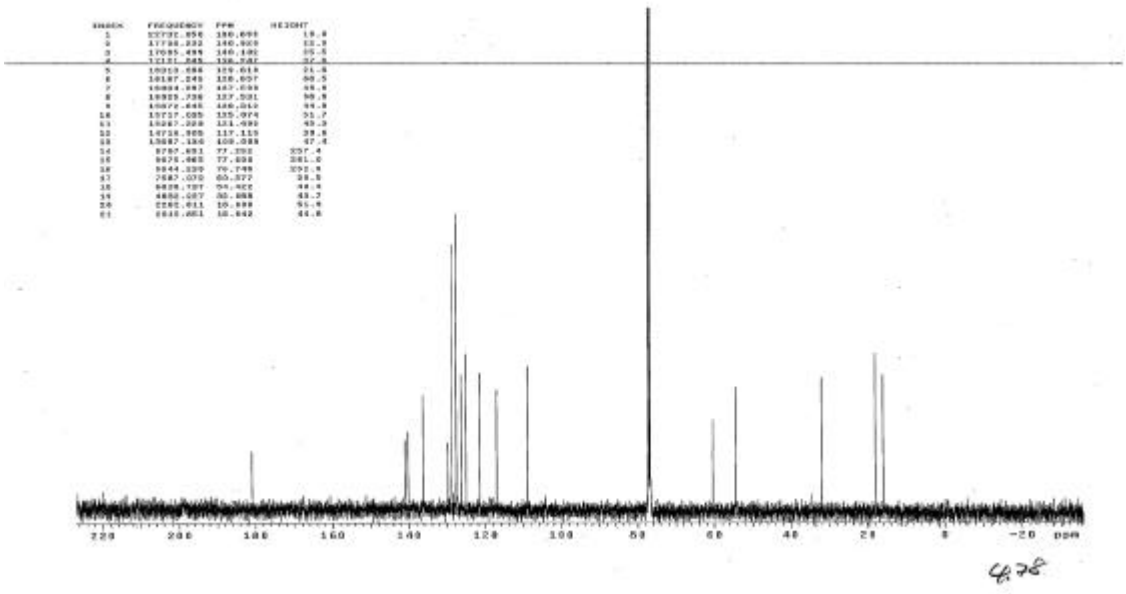

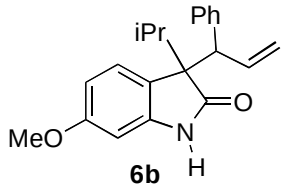

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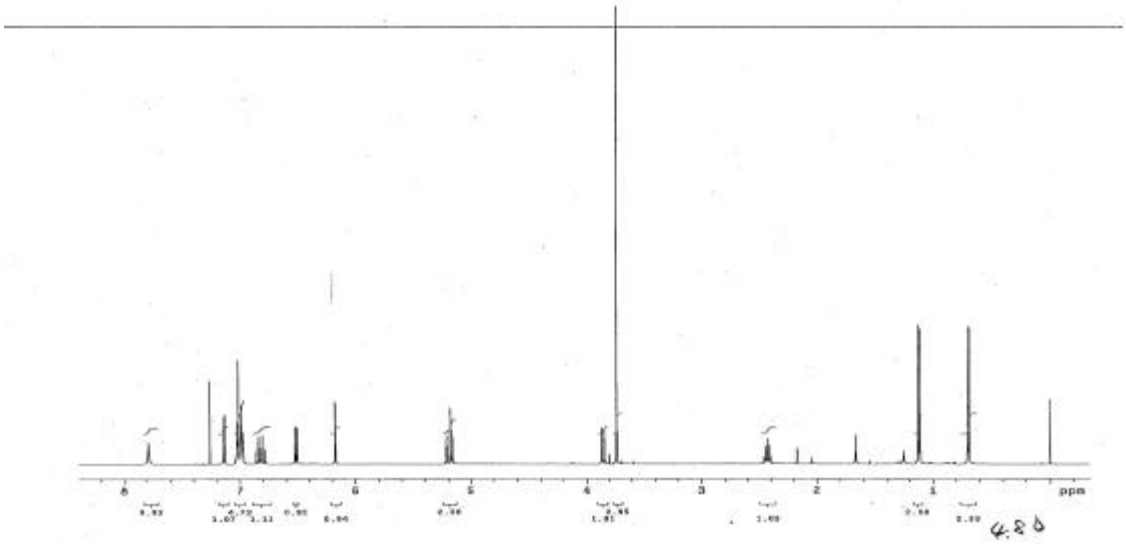

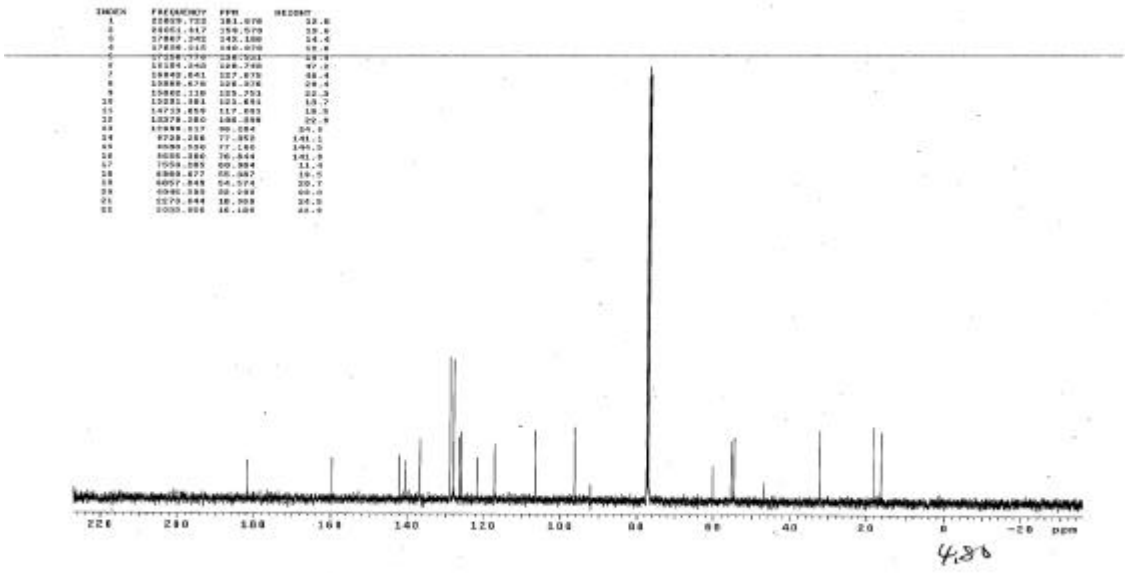

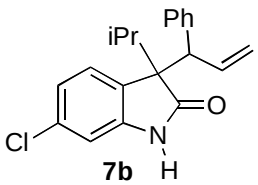

7b

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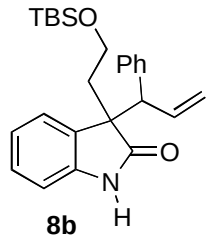

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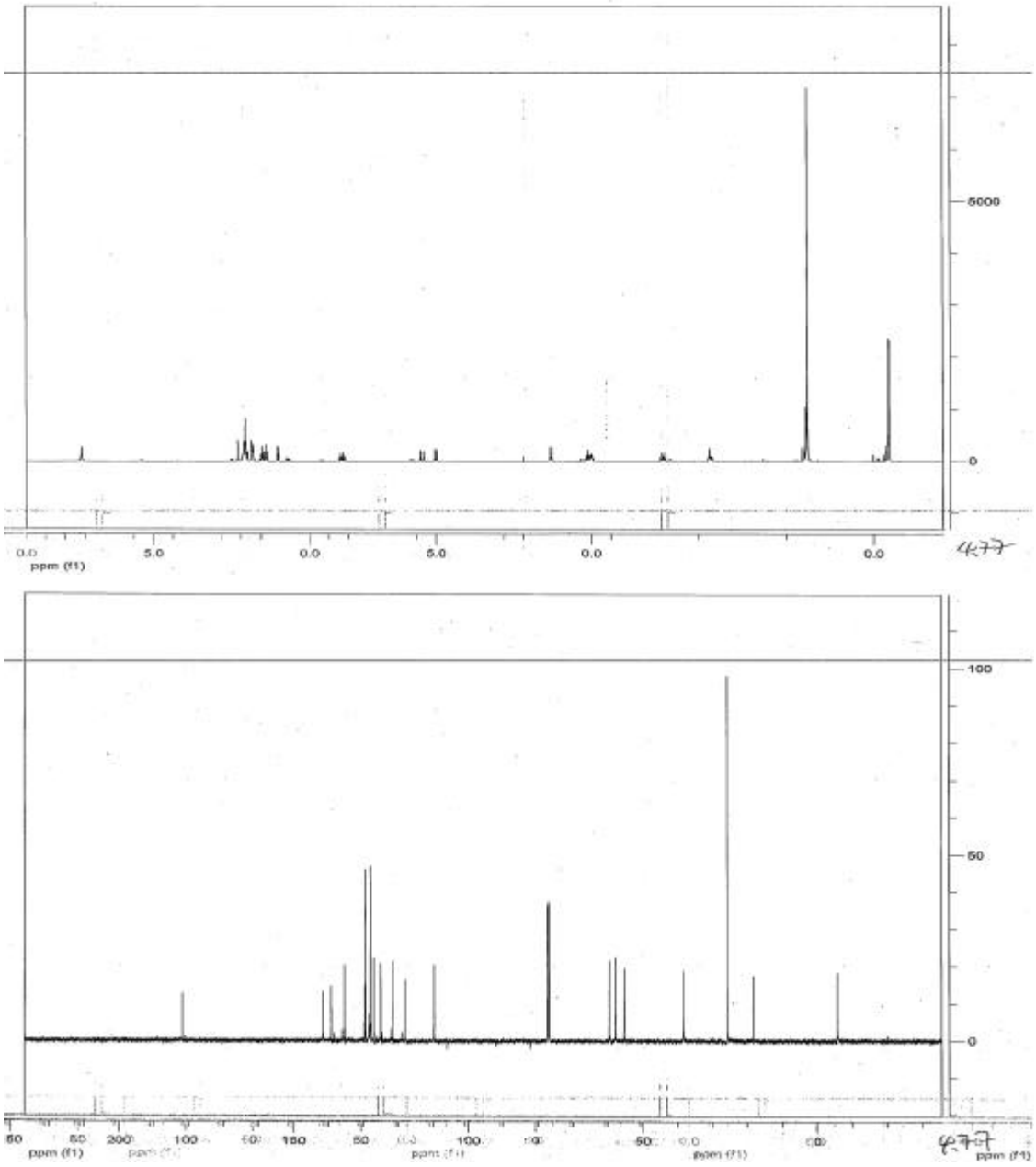

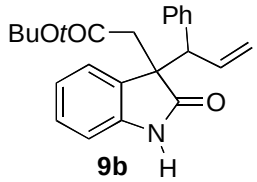

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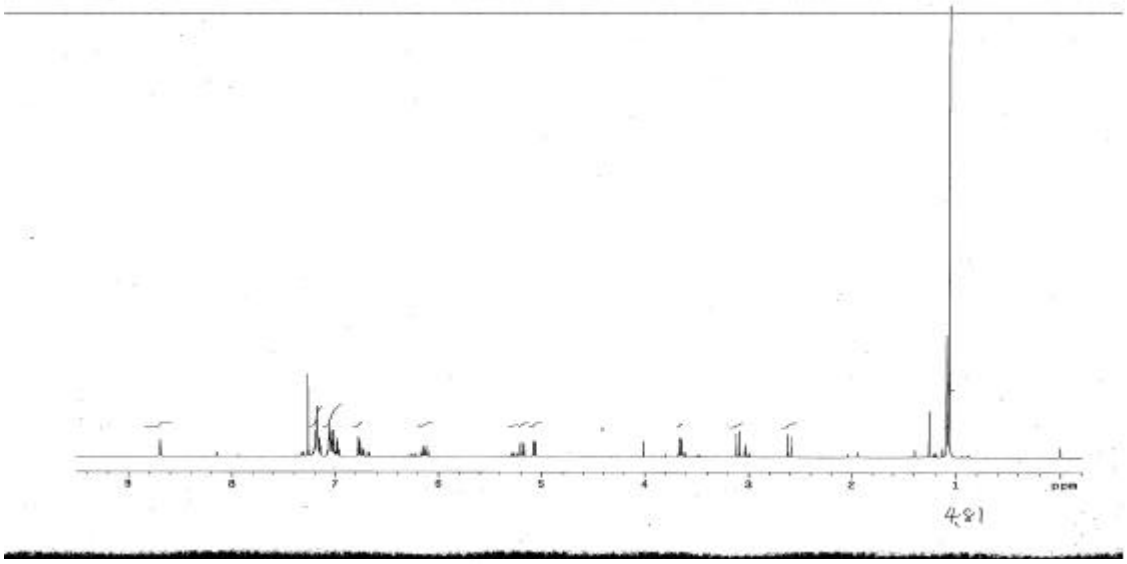

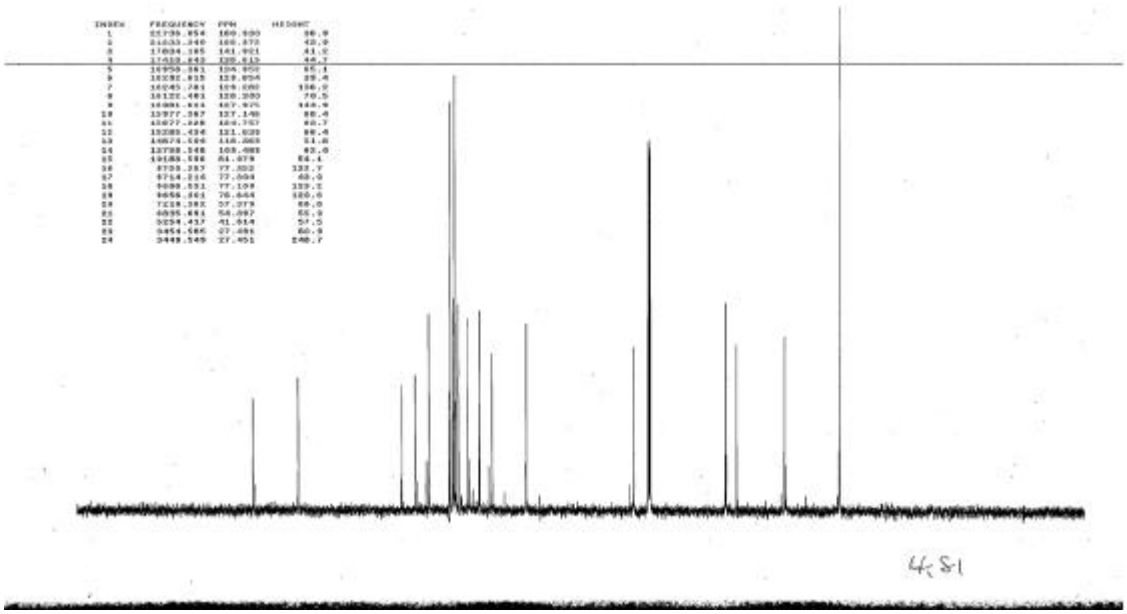

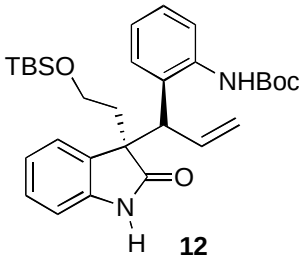

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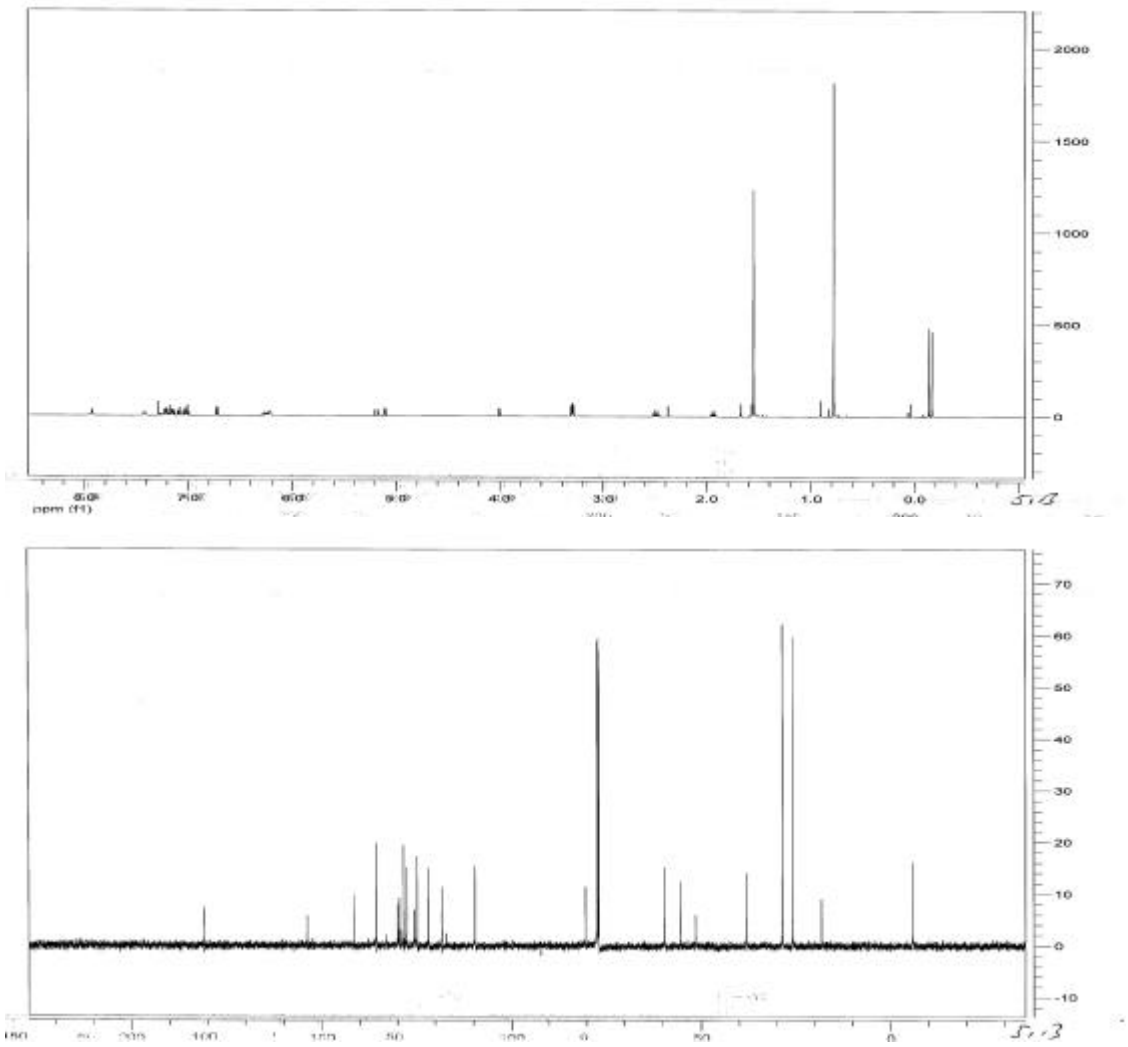

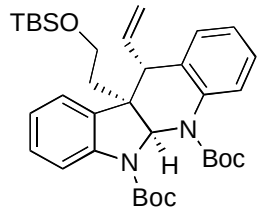
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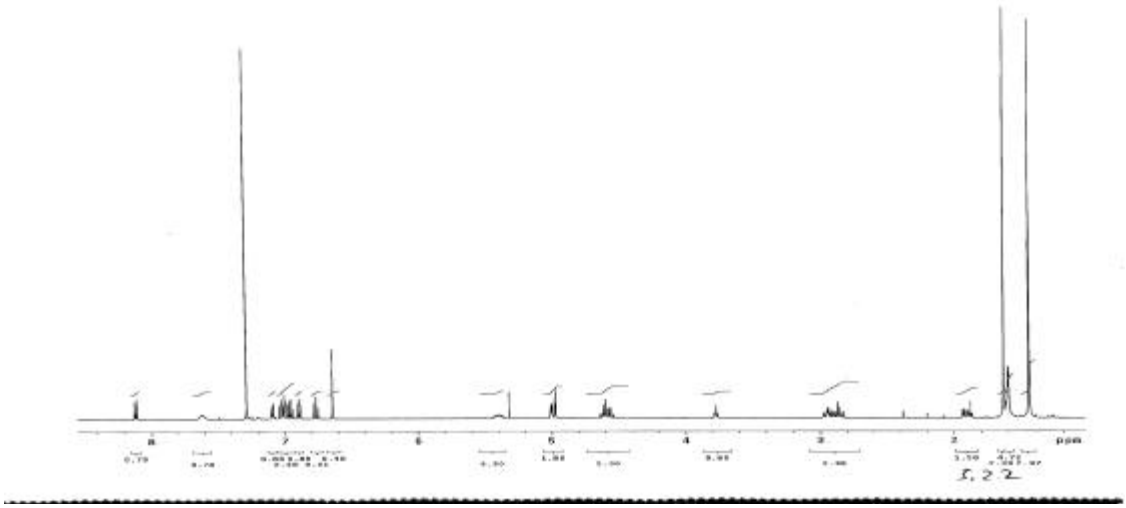

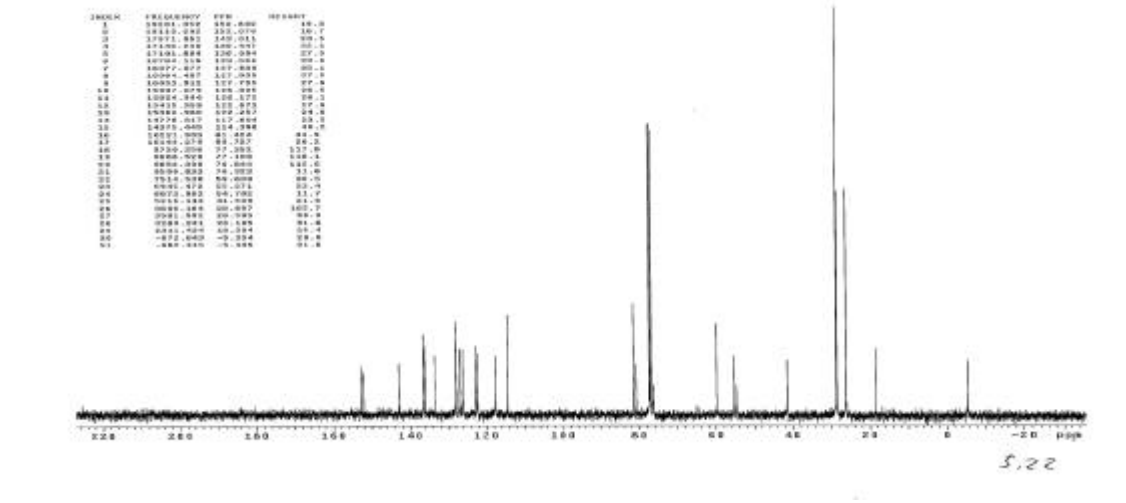

X-ray Crystallography Data for Compound **1b**

Discussion

The compound crystallizes as colorless block-like crystals from an isopropanol / heptane solution. There are two crystallographically independent yet, chemically identical molecules in the asymmetric unit. This leads to a sum of eight molecules in the unit cell of the primitive, acentric, orthorhombic space group $P2_12_12_1$. The absolute configuration could not be determined accurately. The anomalous dispersion signal does not appear for light atom structures using Mo radiation. Indeed, it appears that the two molecules differ in the configuration at C2 / C2A and in the orientation of the phenyl ring with respect to the indolinone moiety (see Figures).

The two molecules are identical in connectivity and are the expected compound. The indolinone nitrogen forms a hydrogen bond to a neighboring indolinone oxygen of the partner molecule; thus N1 forms an H-bond to O1A of a nearby molecule and N1A to O1 of a molecule related by translation along the *a*-axis. (see Table of Hydrogen-bonds for details). The hydrogens on the indolinone nitrogens were located from a difference Fourier map and included in their observed positions and allowed to refine. The resulting one-dimensional chains run through the lattice parallel to the crystallographic *a*-axis.

The bond distances and angles within the molecules are as expected.

Data Collection

A fragment of a colorless block-like crystal of $C_{18}H_{18}NO$ having approximate dimensions of 0.15 × 0.11 × 0.08 mm was mounted on a Kapton loop using Paratone N hydrocarbon oil. All measurements were made on a Bruker APEX-II[1] CCD area detector with graphite monochromated Mo-Ka radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 3065 centered reflections with I > 10s(I) in the range 2.25 < ? < 20.47° corresponded to a Orthorhombic cell with dimensions:

a = 8.6112(12) Å	a = 90°
b = 14.640(2) Å	ß = 90°

c = 23.051(3) Å ? = 90°
V = 2906.0(7) Å^3

For Z = 8 and F.W. = 264.33, the calculated density is 1.208 g.cm^{-3}.

Analysis of the systematic absences allowed the space group to be uniquely determined to be:

$P2_12_12_1$

The data were collected at a temperature of 150(2) K. Frames corresponding to an arbitrary sphere of data were collected using ?-scans of 0.3° counted for a total of 30 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[2] to a maximum ?-value of 26.39°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP[3]. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[4]. (Tmax = 0.9941, Tmin = 0.9889). Of the 28686 reflections that were collected, 5943 were unique (R_{int} = 0.0784); equivalent reflections were merged. No decay correction was applied.

Structure Solution and Refinement

The structure was solved by direct methods[5] and expanded using Fourier techniques[6]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[7] was based on 5943 reflections (all data) and 371 variable parameters and converged (largest parameter shift was 0.193 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = S||Fo| - |Fc|| / S|Fo| = 0.0520 \text{ for 3907 data with } I > 2s(I)$$

$$wR_2 = [(Sw (|Fo|^2 - |Fc|^2)^2 / Sw |Fo|^2)]^{1/2} = 0.1101$$

The standard deviation of an observation of unit weight[8] was 1.018. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.234 and -0.305 e$^-$.Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[9]. Anomalous dispersion effects were included in Fcalc[2]; the values for ? f' and ? f'' were those of

Creagh and McAuley[10]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[11]. All calculations were performed using the SHELXTL[1-6] crystallographic software package of Bruker Analytical X-ray Systems Inc.

References

(1)APEX-II: Area-Detector Software Package v2.1, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (2006)

(2)SAINT: SAX Area-Dectector Integration Program, 7.34A; Siemens Industrial Automation, Inc.: Madison, WI, (2006)

(3)XPREP:(v 6.14) Part of the SHELXTL Crystal Structure Determination Package, Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(4)SADABS: Siemens Area Detector ABSorption correction program v.2.10, George Sheldrick, (2005).

(5) XS: Program for the Solution of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)

(6) XL: Program for the Refinement of X-ray Crystal Structure Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)

(7) Least-Squares:

Function minimized: $S w (|Fo|^2 - |Fc|^2)^2$

(8) Standard deviation of an observation of unit weight:

$[S w(|Fo|^2 - |Fc|^2)^2/(N_o - N_v)]^{1/2}$
where: N_o = number of observations
N_v = number of variables

(9) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(10) Creagh, D. C. & McAuley, W. J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(11) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C,

(A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

Crystal data for $C_{18}H_{18}NO$; M_r = 264.33; Orthorhombic; space group $P2_12_12_1$; *a* = 8.6112(12) Å; *b* = 14.640(2) Å; *c* = 23.051(3) Å; a = 90°; ß = 90°; ? = 90°; V = 2906.0(7) $Å^3$; Z = 8; T = 150(2) K; ?(Mo-Ka) = 0.71073 Å; µ(Mo-Ka) = 0.074 mm^{-1}; d_{calc} = 1.208g.cm^{-3}; 28686 reflections collected; 5943 unique (R_{int} = 0.0784); giving R_1 = 0.0520, wR_2 = 0.1101 for 3907 data with [I>2s (I)] and R_1 = 0.0962, wR_2 = 0.1290 for all 5943 data. Residual electron density ($e^-.Å^{-3}$) max/min: 0.234/-0.305. An arbitrary sphere of data were collected on a colorless block-like crystal, having approximate dimensions of 0.15 × 0.11 × 0.08 mm, on a Bruker APEX-II diffractometer using a combination of ? - and f -scans of 0.3°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 X for methyl, 1.2 for all others).

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Table 1. Crystal data and structure refinement for stanu001.

Identification code	stanu001
Empirical formula	C18 H18 N O
Formula weight	264.33
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	*a* = 8.6112(12) Å a = 90°
	b = 14.640(2) Å ß = 90°
	c = 23.051(3) Å ? = 90°
Volume	2906.0(7) $Å^3$
Z	8
Density (calculated)	1.208 $g.cm^{-3}$
Absorption coefficient (µ)	0.074 mm^{-1}
F(000)	1128
Crystal size	0.15 × 0.11 × 0.08 mm^3
? range for data collection	2.25 to 26.39°
Index ranges	-10 = h =0, -18 = k = 18, -28 = l = 28
Reflections collected	28686
Independent reflections	5943 [R_{int} = 0.0784]
Completeness to ? = 26.39°	99.8 %
Absorption correction	Numerical
Max. and min. transmission	0.9941 and 0.9889
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5943 / 0 / 371
Goodness-of-fit on F^2	1.018
Final R indices [I>2s (I)]	R_1 = 0.0520, wR_2 = 0.1101
R indices (all data)	R_1 = 0.0962, wR_2 = 0.1290
Absolute structure parameter	-2(2)
Largest diff. peak and hole	0.234 and -0.305 $e^-.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for stanu001. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	0.0292(2)	0.49792(16)	0.18304(9)	0.047(1)
N(1)	0.2359(3)	0.54598(16)	0.12863(9)	0.031(1)
C(1)	0.0851(3)	0.5258(2)	0.13723(13)	0.035(1)
C(2)	-0.0037(3)	0.54015(19)	0.08008(11)	0.029(1)
C(3)	0.1218(3)	0.58216(18)	0.04264(12)	0.029(1)
C(4)	0.1139(3)	0.62108(19)	-0.01178(11)	0.032(1)
C(5)	0.2491(4)	0.65828(19)	-0.03545(12)	0.038(1)
C(6)	0.3876(3)	0.6557(2)	-0.00489(13)	0.038(1)
C(7)	0.3954(3)	0.61695(19)	0.04975(12)	0.032(1)
C(8)	0.2604(3)	0.58176(17)	0.07282(11)	0.029(1)
C(9)	-0.1427(3)	0.6033(2)	0.08947(13)	0.036(1)
C(10)	-0.0532(3)	0.44078(19)	0.05938(12)	0.034(1)
C(11)	-0.1522(3)	0.44308(18)	0.00455(13)	0.034(1)
C(12)	-0.3128(3)	0.4526(2)	0.00957(14)	0.042(1)
C(13)	-0.4070(4)	0.4534(2)	-0.03931(16)	0.052(1)
C(14)	-0.3432(4)	0.4434(2)	-0.09369(16)	0.053(1)
C(15)	-0.1865(4)	0.4335(2)	-0.09915(15)	0.053(1)
C(16)	-0.0905(4)	0.4340(2)	-0.05108(14)	0.043(1)
C(17)	0.0865(3)	0.3801(2)	0.05331(15)	0.045(1)
C(18)	0.1161(4)	0.3103(2)	0.08726(18)	0.067(1)
O(1A)	0.5197(2)	0.50245(14)	0.17977(9)	0.041(1)
N(1A)	0.7352(3)	0.45134(16)	0.22784(9)	0.031(1)
C(1A)	0.5814(3)	0.45611(19)	0.21808(12)	0.031(1)
C(2A)	0.4979(3)	0.3927(2)	0.26096(12)	0.031(1)
C(3A)	0.6309(3)	0.36422(18)	0.30006(12)	0.029(1)
C(4A)	0.6356(3)	0.3152(2)	0.35125(12)	0.036(1)
C(5A)	0.7797(4)	0.3005(2)	0.37755(13)	0.042(1)
C(6A)	0.9146(3)	0.3328(2)	0.35238(13)	0.039(1)
C(7A)	0.9122(3)	0.3825(2)	0.30151(12)	0.034(1)
C(8A)	0.7674(3)	0.39845(18)	0.27713(11)	0.028(1)
C(9A)	0.3674(3)	0.4428(2)	0.29224(13)	0.041(1)

C(10A)	0.4309(3)	0.3109(2)	0.22392(12)	0.033(1)
C(11A)	0.5532(3)	0.2671(2)	0.18612(13)	0.040(1)
C(12A)	0.6630(4)	0.2063(2)	0.20797(16)	0.049(1)
C(13A)	0.7742(4)	0.1675(2)	0.17181(19)	0.062(1)
C(14A)	0.7759(5)	0.1885(3)	0.1143(2)	0.067(1)
C(15A)	0.6699(5)	0.2484(2)	0.09138(17)	0.061(1)
C(16A)	0.5577(4)	0.2874(2)	0.12711(13)	0.044(1)
C(17A)	0.3473(4)	0.2407(2)	0.25998(14)	0.040(1)
C(18A)	0.1984(4)	0.2212(2)	0.25380(15)	0.051(1)
H(1Y)	0.315(3)	0.5315(19)	0.1543(12)	0.037
H(4A)	0.0188	0.6225	-0.0326	0.038
H(5A)	0.2461	0.6856	-0.0728	0.045
H(6A)	0.4787	0.6809	-0.0218	0.046
H(7A)	0.4904	0.6147	0.0706	0.039
H(9A)	-0.1075	0.6603	0.1075	0.053
H(9B)	-0.2183	0.5733	0.1149	0.053
H(9C)	-0.1914	0.6169	0.0520	0.053
H(10A)	-0.1191	0.4141	0.0908	0.041
H(12A)	-0.3583	0.4586	0.0469	0.050
H(13A)	-0.5161	0.4609	-0.0352	0.062
H(14A)	-0.4078	0.4434	-0.1271	0.063
H(15A)	-0.1424	0.4261	-0.1366	0.063
H(16A)	0.0186	0.4280	-0.0560	0.052
H(17A)	0.1579	0.3930	0.0230	0.053
H(18A)	0.2262	0.2940	0.0842	0.100
H(18B)	0.0523	0.2580	0.0755	0.100
H(18C)	0.0920	0.3266	0.1275	0.100
H(1Z)	0.811(3)	0.4772(19)	0.2044(12)	0.037
H(4AA)	0.5430	0.2921	0.3682	0.044
H(5AA)	0.7850	0.2679	0.4131	0.050
H(6AA)	1.0114	0.3206	0.3706	0.047
H(7AA)	1.0048	0.4046	0.2841	0.041
H(9AA)	0.4104	0.4949	0.3135	0.061
H(9AB)	0.3166	0.4010	0.3195	0.061
H(9AC)	0.2914	0.4645	0.2638	0.061
H(10B)	0.3519	0.3378	0.1971	0.040

H(12B)	0.6619	0.1911	0.2480	0.058
H(13B)	0.8490	0.1264	0.1872	0.075
H(14B)	0.8515	0.1614	0.0897	0.081
H(15B)	0.6730	0.2632	0.0513	0.073
H(16B)	0.4836	0.3283	0.1111	0.052
H(17B)	0.4046	0.2087	0.2887	0.048
H(18D)	0.1674	0.1765	0.2832	0.077
H(18E)	0.1804	0.1957	0.2151	0.077
H(18F)	0.1368	0.2770	0.2585	0.077

Table 3. Anisotropic displacement parameters $(Å)^2$ for stanu001. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.0328(11)	0.0703(17)	0.0367(13)	0.0223(11)	0.0009(10)	-0.0089(11)
N(1)	0.0225(12)	0.0391(14)	0.0322(13)	0.0088(11)	-0.0022(11)	0.0007(11)
C(1)	0.0274(15)	0.0383(17)	0.0383(17)	0.0071(14)	-0.0033(13)	-0.0011(13)
C(2)	0.0209(14)	0.0342(15)	0.0325(15)	0.0070(13)	-0.0009(12)	-0.0009(12)
C(3)	0.0274(15)	0.0246(14)	0.0362(16)	0.0014(13)	0.0012(12)	-0.0031(11)
C(4)	0.0334(16)	0.0326(15)	0.0301(16)	0.0015(13)	-0.0010(12)	-0.0026(13)
C(5)	0.0428(18)	0.0378(17)	0.0326(15)	0.0029(13)	0.0060(15)	-0.0069(14)
C(6)	0.0339(17)	0.0416(17)	0.0399(18)	-0.0037(15)	0.0126(14)	-0.0065(14)
C(7)	0.0263(15)	0.0321(15)	0.0386(17)	-0.0034(14)	0.0019(12)	-0.0001(13)
C(8)	0.0264(15)	0.0265(14)	0.0334(15)	0.0011(12)	0.0000(13)	0.0015(12)
C(9)	0.0267(15)	0.0407(17)	0.0391(17)	0.0004(14)	-0.0009(13)	-0.0023(13)
C(10)	0.0268(14)	0.0332(16)	0.0431(17)	0.0109(14)	-0.0016(13)	-0.0030(13)
C(11)	0.0324(16)	0.0258(15)	0.0431(18)	-0.0007(14)	-0.0040(14)	-0.0038(12)
C(12)	0.0355(17)	0.0389(18)	0.051(2)	-0.0031(16)	-0.0106(14)	0.0028(14)
C(13)	0.047(2)	0.0387(19)	0.069(2)	-0.0094(18)	-0.0207(18)	0.0042(16)
C(14)	0.067(2)	0.0381(19)	0.053(2)	0.0019(18)	-0.024(2)	-0.0045(18)
C(15)	0.075(3)	0.040(2)	0.043(2)	-0.0004(16)	-0.0013(18)	-0.0146(18)
C(16)	0.0449(19)	0.0348(17)	0.050(2)	0.0006(15)	0.0012(16)	-0.0074(15)
C(17)	0.0348(17)	0.0340(17)	0.065(2)	0.0062(17)	-0.0087(16)	-0.0008(14)
C(18)	0.052(2)	0.037(2)	0.111(3)	0.006(2)	-0.041(2)	-0.0067(17)
O(1A)	0.0311(11)	0.0465(13)	0.0452(13)	0.0149(10)	-0.0089(10)	-0.0010(10)
N(1A)	0.0267(12)	0.0367(14)	0.0302(12)	0.0074(11)	0.0003(11)	-0.0024(11)
C(1A)	0.0265(14)	0.0319(15)	0.0332(15)	0.0006(14)	-0.0048(12)	0.0010(12)
C(2A)	0.0212(13)	0.0373(16)	0.0330(16)	0.0030(13)	-0.0013(11)	0.0011(12)
C(3A)	0.0254(14)	0.0290(15)	0.0316(16)	0.0007(13)	-0.0023(12)	0.0023(12)
C(4A)	0.0379(17)	0.0387(17)	0.0324(17)	0.0064(14)	0.0021(14)	-0.0083(14)
C(5A)	0.0474(19)	0.0416(18)	0.0363(17)	0.0118(14)	-0.0073(15)	-0.0060(16)
C(6A)	0.0335(17)	0.0432(19)	0.0413(18)	0.0058(15)	-0.0122(15)	0.0033(14)
C(7A)	0.0248(14)	0.0397(17)	0.0377(17)	0.0058(15)	-0.0015(12)	0.0016(13)
C(8A)	0.0302(14)	0.0282(15)	0.0254(14)	0.0018(12)	-0.0015(12)	0.0012(12)
C(9A)	0.0288(15)	0.0431(18)	0.0495(19)	-0.0011(15)	0.0023(14)	0.0024(14)

C(10A)	0.0254(14)	0.0390(17)	0.0355(16)	-0.0007(14)	0.0023(12)	-0.0026(13)
C(11A)	0.0333(16)	0.0372(18)	0.0482(19)	-0.0084(15)	0.0034(15)	-0.0113(13)
C(12A)	0.0403(18)	0.0392(18)	0.066(2)	-0.0032(17)	0.0066(17)	-0.0027(15)
C(13A)	0.044(2)	0.042(2)	0.100(3)	-0.015(2)	0.012(2)	-0.0002(16)
C(14A)	0.063(3)	0.046(2)	0.093(3)	-0.032(2)	0.036(2)	-0.016(2)
C(15A)	0.069(3)	0.051(2)	0.062(2)	-0.020(2)	0.027(2)	-0.023(2)
C(16A)	0.0443(18)	0.0427(18)	0.0440(19)	-0.0079(15)	0.0078(15)	-0.0127(15)
C(17A)	0.0348(17)	0.0402(18)	0.0458(19)	0.0005(15)	0.0015(15)	-0.0067(14)
C(18A)	0.052(2)	0.050(2)	0.052(2)	-0.0109(16)	0.0097(16)	-0.0142(17)

Table 4. Bond lengths [Å] for stanu001.

atom-atom	distance	atom-atom	distance	
O(1)-C(1)	1.230(3)	N(1)-C(1)	1.347(3)	N(1)-C(
1.382(4)	C(4)-C(5)	1.396(4)	C(4)-H(4A)	0.9500
0.9800	C(9)-H(9C)	0.9800	C(10)-C(17)	1.502(4)
C(13)-H(13A)	0.9500	C(14)-C(15)	1.363(5)	C(14)-H
0.9800	C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(10A)	1.580(4)	C(3A)-C(4A)	1.382(4)	C(3A)-C
C(7A)-C(8A)	1.388(4)	C(7A)-H(7AA)	0.9500	C(9A)-H
C(16A)	1.393(4)	C(11A)-C(12A)	1.393(4)	C(12A)-
C(16A)	1.392(5)	C(15A)-H(15B)	0.9500	C(16A)-

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for stanu001.

atom-atom-atom	angle	atom-atom-atom	angle	
C(1)-N(1)-C(8)	111.2(2)	C(1)-N(1)-H(1Y)	124.5(17)	C(8)-N(
C(2)-C(1)	110.5(2)	C(3)-C(2)-C(10)	113.1(2)	C(9)-C(
C(4)-H(4A)	120.8	C(5)-C(4)-H(4A)	120.8	C(6)-C(
C(7)-H(7A)	121.2	C(6)-C(7)-H(7A)	121.2	C(7)-C(
H(9A)-C(9)-H(9C)	109.5	H(9B)-C(9)-H(9C)	109.5	C(17)-C
	117.7(3)	C(12)-C(11)-C(10)	119.2(3)	C(16)-C
C(15)-C(14)-C(13)	119.4(3)	C(15)-C(14)-H(14A)	120.3	C(13)-C
C(17)-C(10)	124.1(3)	C(18)-C(17)-H(17A)	117.9	C(10)-C
C(1A)-N(1A)-C(8A)	111.0(2)	C(1A)-N(1A)-H(1Z)	124.9(17)	C(8A)-N
C(9A)-C(2A)-C(1A)	111.0(2)	C(3A)-C(2A)-C(10A)	112.9(2)	C(9A)-C
C(3A)-C(4A)-H(4AA)	120.8	C(5A)-C(4A)-H(4AA)	120.8	C(6A)-C
C(6A)-C(7A)-C(8A)	116.5(3)	C(6A)-C(7A)-H(7AA)	121.7	C(8A)-C
C(9A)-H(9AB)	109.5	C(2A)-C(9A)-H(9AC)	109.5	H(9AA)
H(10B)	106.5	C(11A)-C(10A)-H(10B)	106.5	C(2A)-C
C(12A)-H(12B)	119.6	C(11A)-C(12A)-H(12B)	119.6	C(14A)-
	119.6	C(14A)-C(15A)-C(16A)	119.8(4)	C(14A)-
	123.5(3)	C(18A)-C(17A)-H(17B)	118.2	C(10A)-
H(18E)-C(18A)-H(18F)	109.5			

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for stanu001.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle	
C(8)-N(1)-C(1)-O(1)	-176.1(3)	C(8)-N(1)-C(1)-C(2)	5.8(3)	O(1)-C(
C(2)-C(3)-C(4)	-53.3(4)	C(1)-C(2)-C(3)-C(4)	-171.5(3)	C(10)-C
	0.2(4)	C(4)-C(5)-C(6)-C(7)	-0.5(4)	C(5)-C(6
C(1)-N(1)-C(8)-C(7)	174.3(3)	C(1)-N(1)-C(8)-C(3)	-2.2(3)	C(3)-C(2
C(11)	176.4(2)	C(17)-C(10)-C(11)-C(12)	146.7(3)	C(2)-C(1
C(14)	1.0(5)	C(12)-C(13)-C(14)-C(15)	-0.6(5)	C(13)-C
	111.4(3)	C(8A)-N(1A)-C(1A)-O(1A)	175.5(3)	C(8A)-N
C(10A)	67.6(3)	N(1A)-C(1A)-C(2A)-C(10A)	-110.6(2)	C(9A)-C
C(2A)-C(3A)-C(8A)	107.0(3)	C(8A)-C(3A)-C(4A)-C(5A)	-1.2(4)	C(2A)-C
178.0(3)	C(4A)-C(3A)-C(8A)-N(1A)	-175.6(2)		C(2A)-C
C(17A)	68.7(3)	C(9A)-C(2A)-C(10A)-C(17A)	-60.5(3)	C(1A)-C
	129.9(3)	C(2A)-C(10A)-C(11A)-C(16A)	-	
102.1(3)	C(17A)-C(10A)-C(11A)-C(12A)	-50.0(4)		C(2A)-C
C(13A)-C(14A)-C(15A)-C(16A)	-0.8(5)	C(14A)-C(15A)-C(16A)-C(11A)	0.7(5)	C(12A)-

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for stanu001 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1Y)...O(1A)	0.93(3)	1.90(3)	2.787(3)	158(2)
N(1A)-H(1Z)...O(1)#1	0.93(3)	1.97(3)	2.818(3)	152(2)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z