Asymmetric [3+2] Annulations Catalyzed by a Planar-Chiral Derivative of DMAP

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SUPPORTING INFORMATION

I. General

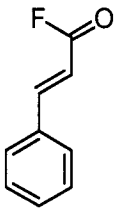
General. Anhydrous solvents were obtained by passage through drying columns of a GlassContour system (Irvine, CA). Melting points were measured on a Hoover melting point apparatus using open glass capillaries; the values are uncorrected. Infrared spectra were recorded as thin films on a Perkin Elmer Spectrum 2000 FTIR spectrophotometer.

Materials. Cinnamic acid, 3-fluorocinnamic acid, 2-methylcinnamic acid, 4-bromocinnamic acid, and 3-furan-3-ylacrylic acid were purchased from the Aldrich Chemical Company. 3,5-Dimethoxycinnamic acid was purchased from Acros Organics, 3-naphthalen-1-ylacrylic acid was purchased from Avocado, and 3-furan-2-ylacrylic acid was purchased from Alfa Aesar. DAST [(diethylamino)sulfur trifluoride] and deoxofluor [bis(2-methoxyethyl)aminosulfur trifluoride] were purchased from the Aldrich Chemical Company. The silylated 1,3-dimethylindene was prepared based on a previously reported procedure.[1] Cinnamic anhydride was prepared according to a literature procedure.[2]

II. Synthesis of Acid Fluorides

General Procedure. A Schlenk tube was charged with the acrylic acid and placed under an argon atmosphere. Dry CH_2Cl_2 (10-20 mL) was added, and the solution was cooled to 0 °C. DAST or deoxofluor (1.05-1.10 equivalents) was added in one portion by syringe. The solution was allowed to warm to room temperature overnight, and then the solvent was removed under vacuum. The residue was dissolved in the minimum amount of solvent (5-20% Et_2O/pentane), and a small amount of silica gel (~100 mg) was added. The solution was quickly passed through a short (10-15 cm) column of silica gel (5-20% Et_2O/pentane), and the solvent was removed under vacuum.[3] Caution: We recommend that a rotary evaporator NOT be used for this procedure, since some of the acid fluorides are very volatile.

The yields have not been optimized



[351-59-7] This compound was prepared according to the General Procedure using cinnamic acid (4.00 g, 27.0 mmol) and DAST (3.72 mL, 4.56 g, 28.4 mmol) in CH_2Cl_2 (40 mL). The product was obtained as a clear, colorless oil which solidified in the freezer (2.28 g, 56%).

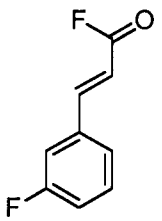
Mp 30 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 16.0 Hz, 1H), 7.52-7.59 (m, 2H), 7.43-7.51 (m, 3H), 6.39 (dd, J = 16.0 Hz, J = 7.4 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4 (d, J = 338 Hz), 151.7 (d, J = 5.8 Hz), 133.4, 132.1, 129.4, 129.0, 112.3 (d, J = 66.8 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ –135.9 (s);

GCMS: calcd for $C_9H_7F_1O_1$: 150; found: m/z: 150 [M^+].



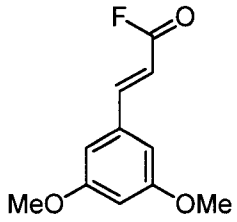
This compound was prepared according to the General Procedure using 3-fluorocinnamic acid (558 mg, 3.63 mmol) and DAST (0.53 mL, 0.64 g, 4.0 mmol) in CH_2Cl_2 (10 mL). The product was obtained as a clear, colorless oil (239 mg, 39%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.9 Hz, 1H), 7.45 (ddd, *J* = 8.0 Hz, *J* = 7.9 Hz, *J* = 5.6 Hz, 1H), 7.37 (d (br), *J* = 7.7, 1H), 7.27-7.31 (m, 1H), 7.20 (tdd, *J* = 8.3 Hz, *J* = 2.5 Hz, *J* = 1.0 Hz, 1H), 6.39 (dd, *J* = 16.0 Hz, *J* = 7.2 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248 Hz), 156.9 (d, *J* = 339 Hz), 150.0, 135 (d, *J* = 7.8 Hz), 131.1 (d, *J* = 8.0 Hz), 124.9 (d, *J* = 3.0 Hz), 119.0 (d, *J* = 21.3 Hz), 115.1 (d, *J* = 22.1 Hz), 113.8 (d, *J* = 67.6 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ –112.3 to –112.2 (m), –135.3 (s);

GCMS: calcd for $C_9H_6F_2O_1$: 168; found: m/z: 168 [M^+].



This compound was prepared according to the General Procedure using 3,5-dimethoxycinnamic acid (545 mg, 2.62 mmol) and DAST (0.38 mL, 0.46 g, 2.88 mmol) in CH_2Cl_2 (20 mL). The product was obtained as thin yellow needles (390 mg, 71%).

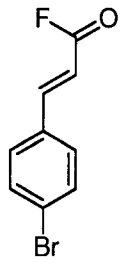
Mp 101-103 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 15.9 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 2H), 6.57 (t, *J* = 2.2 Hz, 1H), 6.34 (dd, *J* = 15.9 Hz, *J* = 7.5 Hz, 1H), 3.83 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 157.3 (d, *J* = 338 Hz), 151.7, 135.1, 112.8 (d, *J* = 66.8 Hz), 106.8, 104.2, 55.8;

^{19}F NMR (282 MHz, $CDCl_3$) δ –135.8 (s);

GCMS: calcd for $C_{11}H_{11}F_1O_3$: 210; found: m/z: 210 [M^+].



This compound was prepared according to the General Procedure using 4-bromocinnamic acid (1.00 g, 4.40 mmol) and DAST (0.61 mL, 0.74 g, 4.63 mmol) in CH_2Cl_2 (10 mL). The product was obtained as yellow needles (582 mg, 58%).

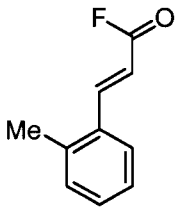
Mp 112-113 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.59 (dt, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H), 7.39 (dt, *J* = 8.4 Hz, *J* = 2.4 Hz, 2H), 6.37 (dd, *J* = 16.0 Hz, *J* = 7.2 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (d, *J* = 339 Hz), 150.2 (d, *J* = 6.0 Hz), 132.7, 132.2, 130.2, 126.7, 113.0 (d, *J* = 67.7 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ –135.5 (s);

GCMS: calcd for $C_9H_6Br_1F_1O_1$: 230/228; found: m/z: 230 [M^+], 228 [M^+].



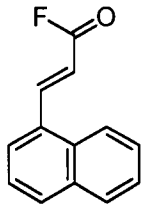
This compound was prepared according to the General Procedure using 2-methylcinnamic acid (839 mg, 5.18 mmol) and DAST (0.72 mL, 0.88 g, 5.44 mmol) in CH_2Cl_2 (15 mL). The product was obtained as a clear, colorless oil (672 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 15.9 Hz, 1H), 7.61 (dd, *J* = 9.2 Hz, *J* = 1.5 Hz, 1H), 7.39 (td, *J* = 7.6 Hz, *J* = 1.3 Hz, 1H), 7.26-7.30 (m, 2H), 6.33 (dd, *J* = 15.9 Hz, *J* = 6.9 Hz, 1H), 2.49 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4 (d, *J* = 339 Hz), 149.1 (d, *J* = 6.6 Hz), 138.7, 132.2, 131.8, 131.3, 127.0, 126.8, 113.0 (d, *J* = 66.8 Hz), 19.9;

^{19}F NMR (282 MHz, $CDCl_3$) δ –135.7 (s);

GCMS: calcd for $C_{10}H_9F_1O_1$: 164; found: m/z: 164 [M^+].



This compound was prepared according to the General Procedure using 3-naphthalen-1-ylacrylic acid (1.00 g, 5.05 mmol) and DAST (0.74 mL, 0.90 g, 5.56 mmol) in CH_2Cl_2 (10 mL). The product was obtained as yellow needles (0.86 g, 85%).

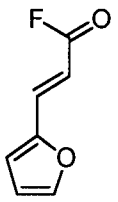
Mp 55-56 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 15.8 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 (dd, *J* = 8.3 Hz, *J* = 1.0 Hz, 1H), 7.82 (d, *J* = 7.22 Hz, 1H), 7.25-7.66 (m, 3H), 6.49 (dd, *J* = 15.7 Hz, *J* = 7.1 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (d, *J* = 339 Hz), 148.4 (d, *J* = 6.4 Hz), 133.9, 132.4, 131.5, 130.4, 129.2, 127.7, 126.8, 126.1, 125.6, 123.0, 114.5 (d, *J* = 66.9 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ –135.7 (s);

GCMS: calcd for $C_{13}H_9F_1O_1$: 200; found: m/z: 200 [M^+].



This compound was prepared according to the General Procedure using 3-furan-2-ylacrylic acid (1.00 g, 7.25 mmol) and DAST (1.01 mL, 1.23 g, 7.60 mmol) in CH_2Cl_2 (10 mL). The product was obtained as colorless needles (0.66 g, 65%).

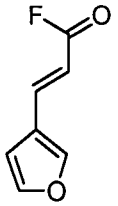
Mp 44-45 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 0.6 Hz, 1H), 7.55 (d, J = 15.6 Hz, 1H), 6.80 (d, J = 3.5 Hz, 1H), 6.55 (dd, J = 3.5 Hz, J = 1.8 Hz, 1H), 6.23 (dd, J = 15.6 Hz, J = 8.1 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5 (d, J = 336 Hz), 150.1, 146.7, 136.8 (d, J = 6.3 Hz), 118.3, 113.2, 109.4 (d, J = 68.8 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ –137.5 (s);

GCMS: calcd for $C_7H_5F_1O_2$: 140; found: m/z: 140 [M^+].



This compound was prepared according to the General Procedure using 3-furan-3-ylacrylic acid (1.00 g, 7.25 mmol) and deoxofluor (1.40 mL, 1.68 g, 7.60 mmol) in CH_2Cl_2 (10 mL). The product was obtained as yellow needles (0.67 g, 66%).

Mp 59-60 °C;

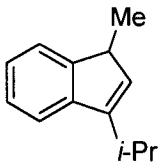
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.77 (m, 2H), 7.49-7.51 (m, 1H), 6.64 (d, J = 2.0 Hz, 1H), 6.08 (dd, J = 16.0 Hz, J = 7.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3 (d, J = 337 Hz), 146.5, 145.3, 141.6 (d, J = 6.3 Hz), 122.3, 111.9 (d, J = 67.6 Hz), 107.4;

^{19}F NMR (282 MHz, $CDCl_3$) δ –137.4 (s);

GCMS: calcd for $C_7H_5F_1O_2$: 140; found: m/z: 140 [M^+].

III. Synthesis of Indenes



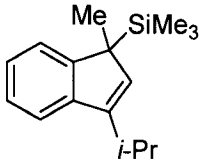
A Schlenk flask was charged with magnesium tunings (1.24 g, 51.0 mmol) and placed under an argon atmosphere. Dry Et_2O (30 mL) was added, and the solution was treated with *i*-propyl bromide (4.88 mL, 6.40 g, 51.6 mmol). After 1 h, almost all of the magnesium had been consumed, and the yellow solution was transferred to another Schlenk flask via cannula. 3-Methyl-indan-1-one (1.96 g, 13.4 mmol) was added slowly, and the yellow reaction mixture was allowed to stir for two days at room temperature. A saturated solution of NH_4Cl (50 mL) was added, followed by 1 M HCl (20 mL), in order to dissolve all of the salts. The mixture was extracted with pentane (2 x 200 mL). The organic layer was passed through a short plug of silica gel (Et_2O) and concentrated. The oily residue was dissolved in MeOH (100 mL), and 1 M HCl (10 mL) was added. The solution was allowed to stir overnight. Water (300 mL) was added, and the mixture was extracted with pentane (2 x 200 mL). The organic layer was dried over $MgSO_4$, filtered through a short plug of silica gel, and concentrated. The product was obtained as a clear, colorless oil (1.20 g, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) (contains 7% of the isomer formed by dehydration via loss of the methine proton of the *i*-Pr group) δ 7.42 (dd, J = 7.6 Hz, J = 0.4 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.30 (td, J = 7.6 Hz, J = 0.8 Hz, 1H), 7.22 (td, J = 7.2 Hz, J = 0.8 Hz, 1H), 6.14 (s, 1H), 3.43 (q, J = 7.6 Hz, 1H), 2.92 (sept (br), J = 7.2 Hz, 1H), 1.28-1.32 (m, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.4, 132.8, 126.3, 124.8, 122.8, 119.6, 43.6, 27.0, 22.1 (2), 16.6;

IR (film) v 3649, 3629, 2961, 1653, 1635, 1559, 1540, 1457, 769, 746, 668 cm^{-1};

GCMS: major isomer: calcd for $C_{13}H_{16}$: 172; found: m/z: 172 [M$^+$]; minor isomer: calcd for $C_{13}H_{16}$: 172; found: m/z: 172 [M$^+$].



A Schlenk flask was charged with the indene prepared above (480 mg, 2.79 mmol) and placed under an argon atmosphere. Dry pentane (40 mL) was added, and the solution was treated with TMEDA (0.46 mL, 3.07 mmol) and *n*-butyllithium (1.92 mL, 3.07 mmol; 1.6 M in hexanes). The solution was stirred at room temperature overnight. A grainy yellow precipitate formed in the orange solution. The Schlenk flask was transferred into a glove box, and the solution was decanted. The precipitate was

dissolved in dry THF (10 mL), and Me_3SiCl (0.39 mL, 3.07 mmol) was added. After 10 minutes, the reaction mixture was concentrated to dryness. Column chromatography on silica gel (pentane) afforded the product as a clear, colorless oil (255 mg, 38%).

^1H NMR (400 MHz, $CDCl_3$) (contains 5% of the isomer with the TMS group adjacent to the *i*-Pr group) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.28 (td, *J* = 7.4 Hz, *J* = 1.2 Hz, 1H), 7.22 (td, *J* = 7.4 Hz, *J* = 1.2 Hz, 1H), 6.20 (d, *J* = 0.9 Hz, 1H), 3.04 (septd, *J* = 6.8 Hz, *J* = 1.1 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.49 (s, 3H), –0.11 (s, 9H);

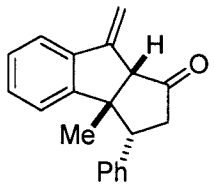
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 147.4, 143.6, 134.4, 124.8, 123.8, 122.1, 119.6, 46.0, 27.1, 23.0, 22.2, 16.3, –3.3;

IR (film) *v* 3064, 2958, 2867, 1456, 1381, 1248, 1078, 1020, 936, 838, 749, 668 cm^{-1};

GCMS: calcd for $C_{16}H_{24}Si_1$: 244; found: m/z: 244 [M^+].

IV. Catalytic Asymmetric [3+2] Annulations

General Procedure. Catalyst **2** (9.2 mg/vial; total: 18.4 mg, 0.050 mmol, 10 mol%) was weighed into two 1.5-mL vials in a glove box. One batch of the catalyst was dissolved in anhydrous CH_2Cl_2 (2.0 mL) and added to the acid fluoride (0.50 mmol, 1.0 equiv) in a dry 25-mL vial. CH_2Cl_2 (0.5 mL) was used to rinse the vial that contained the catalyst, and this solution was also added to the 25-mL vial. A solution of the silylated indene (0.650 mmol, 1.3 equiv) in anhydrous CH_2Cl_2 (2.0 mL) was added in one portion to the vial that contained the catalyst and the acid fluoride. CH_2Cl_2 (0.5 mL) was used to rinse the vial that contained the silylated indene, and this solution was added to the reaction vessel. The reaction vessel was capped with a septum cap and stirred for 7 h at ~40 °C. Then, the second batch of catalyst was added as a solution in CH_2Cl_2 (0.2 mL). The reaction mixture was stirred for an additional 15 h at ~40 °C, then it was passed through a short plug of silica gel (Et_2O) and concentrated. The diastereomeric ratio of the unpurified mixture was determined ^1H NMR analysis. The desired product was then purified by column chromatography on silica gel using 5-20% Et_2O/pentane as the eluent.



Eq 1. (3*R*,3a*R*,8a*S*)-3a-Methyl-8-methylene-3-phenyl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as white needles: run 1: 79.5 mg (58%; 77% ee, 93:7 dr); run 2: 84.0 mg (61%; 78% ee, 92:8 dr).

Mp 108-109 °C;

^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.7 Hz, 1H), 7.33-7.35 (m, 3H), 7.19 (t, J = 7.4 Hz, 1H), 7.12 (d (br), J = 3.2 Hz, 2H), 6.94 (t, J = 7.5 Hz, 1H), 5.89 (d, J = 7.8 Hz, 1H), 5.60 (d, J = 1.6 Hz, 1H), 5.38 (d, J = 1.4 Hz, 1H), 3.61 (dd, J = 14.5 Hz, J = 6.4 Hz, 1H), 3.30 (d, J = 1.3 Hz, 1H), 2.68 (dd, J = 16.5 Hz, J = 14.6 Hz, 1H), 2.49 (ddd, J = 16.6 Hz, J = 6.4 Hz, J = 1.4 Hz, 1H), 1.57 (s, 3H);

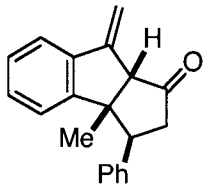
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 147.6, 145.6, 140.2, 137.6, 129.1, 128.2, 128.2, 127.8, 127.6, 127.0, 120.6, 106.3, 66.4, 55.3, 51.8, 42.8, 28.1;

IR (film) v 3467, 3030, 2958, 2924, 2867, 1745 (C=O), 1638, 1497, 1453, 1185, 881, 768, 702 cm^{-1};

LCMS (ES^+): calcd for $C_{20}H_{18}O_1$ [M^+]: 274; found [$M+H^+$]: 275.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 13.8 min; (3*R*,3a*R*,8a*S*): t_r: 17.1 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +38° (c = 0.50, $CHCl_3$).



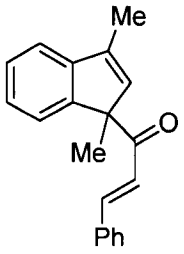
3a-Methyl-8-methylene-3-phenyl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as a resinous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.54 (m, 1H), 7.28-7.40 (m, 5H), 7.15-7.21 (m, 3H), 5.67 (d, J = 2.3 Hz, 1H), 5.47 (d, J = 2.1 Hz, 1H), 3.51 (t, J = 7.6 Hz, 1H), 3.37 (d, J = 1.8 Hz, 1H), 2.82 (ddd, J = 17.9 Hz, J = 7.3 Hz, J = 1.7 Hz, 1H), 2.66 (dd, J = 17.9 Hz, J = 8.0 Hz, 1H), 1.11 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 152.3, 144.9, 140.4, 138.7, 129.3, 128.6, 128.4, 128.0, 127.3, 123.6, 121.3, 106.8, 65.2, 55.6, 50.9, 45.3, 23.0;

IR (film) v 3061, 2973, 2929, 2863, 1726, 1683 (C=O), 1609, 1576, 1449, 1057, 1031, 752 cm^{-1};

LCMS (ES$^+$): calcd for $C_{20}H_{18}O_1$ [M$^+$]: 274; found [M+H$^+$]: 275.



1-(1,3-Dimethyl-1*H*-inden-1-yl)-3-phenyl-propenone. Isolated as a resinous solid: run 1: 25.1 mg (18%; 11% ee); run 2: 24.2 mg (18%; 14% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 15.7 Hz, 1H), 7.41-7.45 (m, 2H), 7.26-7.32 (m, 7H), 6.09 (d, J = 1.4 Hz, 1H), 6.04 (d, J = 15.7 Hz, 1H), 2.30 (d, J = 1.5 Hz, 3H), 1.56 (s, 3H);

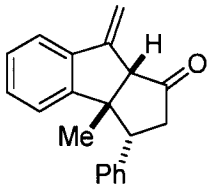
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 147.7, 146.3, 143.2, 141.8, 135.0, 134.9, 130.2, 128.9, 128.4, 127.9, 126.6, 123.1, 121.9, 119.9, 64.5, 17.9, 13.4;

IR (film) v 3030, 2960, 2924, 1740 (C=O), 1497, 1462, 1453, 1408, 1204, 1157, 886, 765, 701 cm^{-1};

LCMS (ES$^+$): calcd for $C_{20}H_{18}O_1$ [M$^+$] 274; found [M+H$^+$] 275.

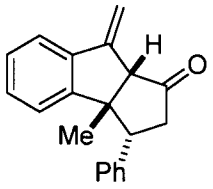
The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AD-H, 1.0% *i*-PrOH:hexanes, 1.0 mL/min, t_r: 13.3 min; t_r: 25.6 min.

Using catalyst (–)-**2**, $[\alpha]^{22}_D$ –9.2° (c = 0.50, $CHCl_3$).



Eq 2 (cinnamic anhydride). (3*R*,3a*R*,8a*S*)-3a-Methyl-8-methylene-3-phenyl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. The General Procedure was followed, except that cinnamic anhydride (139 mg, 0.50 mmol) was used instead of an acid fluoride.

Isolated as white needles: run 1: 37.6 mg (29%; 77% ee, 89:11 dr); run 2: 43.3 mg (32%; 79% ee, 90:10 dr).



Eq 2 (cinnamoyl chloride/[Ph_3SiF_2]NBu_4). (3*R*,3a*R*,8a*S*)-3a-Methyl-8-methylene-3-phenyl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. The General Procedure was followed, except that cinnamoyl chloride (83.3 mg, 0.50 mmol) and TBAT (269 mg, 0.50 mmol) were used instead of an acid fluoride. (Note: We have established through a separate NMR study that cinnamoyl chloride reacts rapidly with TBAT to form cinnamoyl fluoride)

Isolated as white needles: run 1: 75.3 mg (55%; 72% ee, 92:8 dr); run 2: 72.1 mg (53%; 75% ee, 93:7 dr).

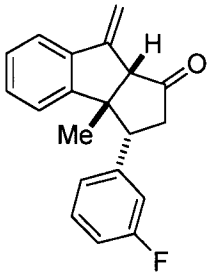


Table 1, entry 2. (3*R*,3a*R*,8a*S*)-3-(3-Fluoro-phenyl)-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as a yellow microcrystalline solid: run 1: 76.8 mg (53%; 58% ee, 88:12 dr); run 2: 70.9 mg (49%; 58% ee, 88:12 dr).

Mp 88-91 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.27-7.34 (m, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.97-7.07 (m, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 10.0 Hz, 1H), 5.97 (d, *J* = 7.8 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 5.40 (d, *J* = 1.3 Hz, 1H), 3.61 (dd, *J* = 14.2 Hz, *J* = 6.6

Hz, 1H), 3.32 (d, J = 1.2 Hz, 1H), 2.63 (dd, J = 16.5 Hz, J = 14.3 Hz, 1H), 2.50 (ddd, J = 16.6 Hz, J = 6.6 Hz, J = 1.1 Hz, 1H), 1.59 (s, 3H);

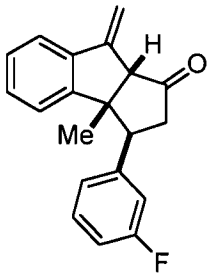
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 162.7 (d, J = 246 Hz), 147.2, 145.3, 140.5 (d, J = 7.2 Hz), 140.1, 129.6 (d, J = 8.3 Hz), 128.3, 128.0, 126.7, 124.8, 120.7, 116.0 (d, J = 21.4 Hz), 114.4 (d, J = 21.1 Hz), 106.4, 66.3, 55.2, 51.7, 42.8, 28.0;

IR (film) v 3068, 2960, 2925, 1746 (C=O), 1613, 1588, 1489, 14448, 1256, 1219, 1161, 876, 785, 765, 708 cm^{-1};

LCMS (ES$^+$): calcd for $C_{20}H_{17}F_1O_1$ [M$^+$] 292; found [M+H$^+$] 293.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 15.4 min; (3*R*,3a*R*,8a*S*): t_r: 17.1 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +29° (c = 0.50, $CHCl_3$).



3-(3-Fluoro-phenyl)-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. The minor diastereomer was isolated as a white microcrystalline solid.

Mp 114-116 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.53 (m, 1H), 7.29-7.35 (m, 3H), 7.17-7.19 (m, 1H), 7.00 (tdd, J = 8.5 Hz, J = 2.5 Hz, J = 0.8 Hz, 1H), 6.91 (d (br), J = 7.7 Hz, 1H), 6.86 (dt, J = 10.0 Hz, J = 2.1 Hz, 1H), 5.66 (d, J = 2.3 Hz, 1H), 5.45 (d, J = 2.1 Hz, 1H), 3.48 (t, J = 7.7 Hz, 1H), 3.36 (d, J = 1.8 Hz, 1H), 2.77 (ddd, J = 18.0 Hz, J = 7.4 Hz, J = 1.6 Hz, 1H), 2.65 (dd, J = 17.9 Hz, J = 8.0 Hz, 1H), 1.12 (s, 3H).

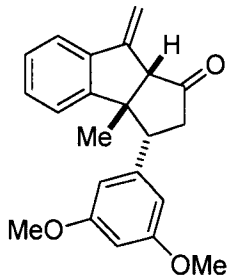


Table 1, entry 3. (3*R*,3a*R*,8a*S*)-3-(3,5-Dimethoxy-phenyl)-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as a colorless resinous oil: run 1: 103 mg (62%; 71% ee, 89:11 dr); run 2: 100 mg (60%; 69% ee, 89:11 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.7 Hz, 1H), 7.19 (td, J = 8.0 Hz, J = 0.8 Hz, 1H), 6.99 (td, J = 8.0 Hz, J = 0.8 Hz, 1H), 6.43 (t, J = 2.2 Hz, 1H), 6.24 (s (br), 2H), 6.12 (d, J

= 7.8 Hz, 1H), 5.59 (d, *J* = 1.9 Hz, 1H), 5.36 (d, *J* = 1.7 Hz, 1H), 3.74 (s, 6H), 3.52 (dd, *J* = 14.2 Hz, *J* = 6.7 Hz, 1H), 3.28 (d, *J* = 1.7 Hz, 1H), 2.60 (dd, *J* = 16.6 Hz, *J* = 14.3 Hz, 1H), 2.47 (ddd, *J* = 16.6 Hz, *J* = 6.7 Hz, *J* = 1.6 Hz, 1H), 1.58 (s, 3H);

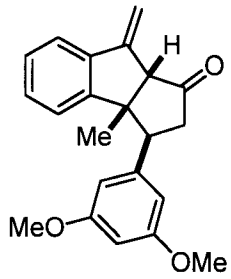
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8, 160.5, 147.6, 145.6, 140.0, 140.0, 128.2, 127.9, 127.1, 120.5, 107.4, 106.2, 99.3, 66.3, 55.5, 55.2, 52.1, 43.0, 28.1;

IR (film) *v* 2958, 2838, 1744 (C=O), 1596, 1461, 1430, 1357, 1205, 1155, 1066, 836, 758 cm^{-1};

LCMS (ES^+): calcd for $C_{22}H_{22}O_3$ [M^+] 334; found [$M+H^+$] 335.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 25.9 min; (3*R*,3a*R*,8a*S*): t_r: 28.7 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +44° (*c* = 0.50, $CHCl_3$).



3-(3,5-Dimethoxy-phenyl)-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. The minor diastereomer was isolated as a yellow resinous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.52 (m, 1H), 7.25-7.34 (m, 3H), 6.41-6.44 (m, 1H), 6.29 (d, *J* = 2.2 Hz, 2H), 5.66 (d, *J* = 2.3 Hz, 1H), 5.45 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 6H), 3.44 (dd, *J* = 7.6 Hz, *J* = 7.5 Hz, 1H), 3.36 (d, *J* = 1.7 Hz, 1H), 2.77 (ddd, *J* = 17.9 Hz, *J* = 7.1 Hz, *J* = 1.6 Hz, 1H), 2.62 (dd, *J* = 17.9 Hz, *J* = 8.0 Hz, 1H), 1.15 (s, 3H).

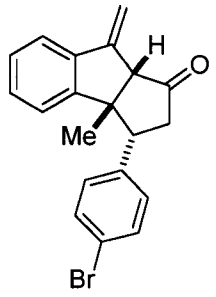


Table 1, entry 4. (3*R*,3a*R*,8a*S*)-3-(4-Bromo-phenyl)-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2H-cyclopenta[a]inden-1-one. Isolated as white prisms: run 1: 89.4 mg (51%; 69% ee, 90:10 dr); run 2: 92.0 mg (52%; 70% ee, 89:11 dr).

Mp 135-137 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.47 (m, 3H), 7.19-7.22 (m, 1H), 6.97-7.01 (m, 3H), 5.97 (d, *J* = 7.8 Hz, 1H), 5.60 (d, *J* = 1.9 Hz, 1H), 5.37 (d, *J* = 1.7 Hz, 1H), 3.55 (dd, *J* = 14.3

Hz, J = 6.6 Hz, 1H), 3.30 (d, J = 1.7 Hz, 1H), 2.61 (dd, J = 16.5 Hz, J = 14.3 Hz, 1H), 2.47 (ddd, J = 16.5 Hz, J = 6.6 Hz, J = 1.6 Hz, 1H), 1.55 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 147.2, 145.3, 140.1, 136.7, 131.3, 130.8, 128.4, 128.0, 126.8, 121.4, 120.7, 106.4, 66.2, 55.1, 51.4, 42.8, 27.9;

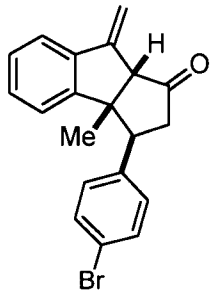
IR (film) v 3066, 2959, 2920, 1746 (C=O), 1694, 1489, 1411, 1186, 1074, 1010, 821, 769, 755 cm^{-1};

LCMS (ES$^+$): calcd for $C_{20}H_{17}Br_1O_1$ [M$^+$] 352/354; found [M+H$^+$] 353/355.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*R*,3a*R*,8a*S*): t_r: 17.1 min; (3*S*,3a*S*,8a*R*): t_r: 18.1 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +1.5° (c = 0.50, $CHCl_3$).

Crystals (from the reaction catalyzed by (+)-**2**) suitable for X-ray crystallographic analysis were obtained through crystallization from CH_2Cl_2/pentane.



3-(4-Bromo-phenyl)-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2H-cyclopenta[a]inden-1-one. The minor diastereomer was isolated as a resinous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.53 (m, 3H), 7.29-7.34 (m, 2H), 7.12-7.16 (m, 1H), 6.99-7.03 (m, 2H), 5.66 (d, J = 2.4 Hz, 1H), 5.45 (d, J = 2.2 Hz, 1H), 3.43 (dd, J = 7.9 Hz, J = 7.8 Hz, 1H), 3.36 (d, J = 1.8 Hz, 1H), 2.76 (ddd, J = 17.9 Hz, J = 7.9 Hz, J = 1.6 Hz, 1H), 2.64 (dd, J = 17.9 Hz, J = 7.9 Hz, 1H), 1.11 (s, 3H).

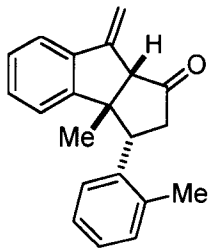


Table 1, entry 5. (3*R*,3a*R*,8a*S*)-3a-Methyl-8-methylene-3-o-tolyl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as white needles: run 1: 57.8 mg (40%; 65% ee, 88:12 dr); run 2: 59.4 mg (41%; 66% ee, 87:13 dr).

Mp 102-104 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.8 Hz, 1H), 7.16-7.28 (m, 3H), 7.00-7.04 (m, 2H), 6.61 (d, J = 7.7 Hz, 1H), 6.21 (d, J = 7.8 Hz, 1H), 5.64 (d, J = 2.1 Hz, 1H), 5.42 (d, J = 1.9 Hz, 1H), 3.97 (dd, J = 13.6 Hz, J = 7.0 Hz, 1H), 3.36 (d, J = 1.9 Hz, 1H), 2.68 (dd, J =

16.8 Hz, J = 13.6 Hz, 1H), 2.56 (s, 3H), 2.53 (ddd, J = 16.8 Hz, J = 7.0 Hz, J = 1.7 Hz, 1H), 1.57 (s, 3H);

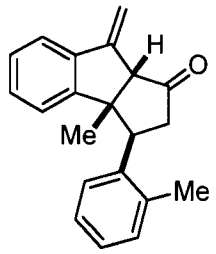
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 147.9, 145.6, 140.1, 137.0, 136.3, 130.8, 129.3, 128.0, 127.8, 127.6, 127.0, 125.2, 120.5, 106.0, 66.4, 56.2, 46.7, 45.1, 29.1, 20.9;

IR (film) v 3065, 3024, 2925, 2958, 1743 (C=O), 1637, 1463, 1408, 1218, 1182, 1025, 881, 766, 730 cm^{-1};

LCMS (ES$^+$): calcd for $C_{21}H_{20}O_1$ [M$^+$] 288; found [M+H$^+$] 289.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 11.4 min; (3*R*,3a*R*,8a*S*): t_r: 18.4 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +58° (c = 0.50, $CHCl_3$).



3a-Methyl-8-methylene-3-o-tolyl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. The minor diastereomer was isolated as a white microcrystalline solid.

Mp 95-96 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.52 (m, 1H), 7.18-7.34 (m, 6H), 7.05 (d, J = 7.6 Hz, 1H), 5.65 (d, J = 1.9 Hz, 1H), 5.44 (d, J = 1.8 Hz, 1H), 3.94 (dd, J = 6.6 Hz, J = 6.5 Hz, 1H), 3.32 (s, 1H), 2.63 (d, J = 6.8 Hz, 2H), 2.33 (s, 3H), 1.09 (s, 3H).

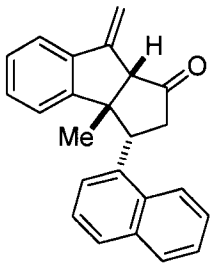


Table 1, entry 6. (3*R*,3a*R*,8a*S*)-3a-Methyl-8-methylene-3-naphthalen-1-yl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as a white microcrystalline solid: run 1: 69.3 mg (43%; 67% ee, 90:10 dr); run 2: 65.1 mg (40%; 73% ee, 90:10 dr).

Mp 142-143 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.54-7.64 (m, 2H), 7.47 (d, J = 7.7 Hz, 1H), 7.32 (dd, J = 7.8 Hz, J = 7.7 Hz, 1H), 7.18 (dd, J = 7.6 Hz, J = 7.4 Hz, 1H), 6.85-6.87 (m, 2H), 5.82 (d, J = 7.8 Hz, 1H), 5.65 (d, J = 1.9 Hz, 1H), 5.45 (dd, J = 1.7 Hz, 1H), 4.62 (dd, J = 13.6 Hz, J = 6.6 Hz, 1H), 3.44 (d, J = 1.6 Hz, 1H), 2.88 (dd, J = 16.6 Hz, J = 13.8 Hz, 1H), 2.61 (ddd, J = 16.6 Hz, J = 6.6 Hz, J = 1.6 Hz, 1H), 1.61 (s, 3H);

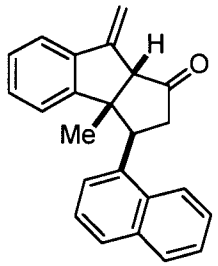
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 147.9, 145.7, 140.0, 134.2, 134.1, 133.1, 129.2, 127.9, 127.8 (2), 127.5, 126.5, 126.1, 125.7, 124.8, 124.1, 120.5, 106.1, 66.7, 56.4, 45.3, 44.8, 29.1;

IR (film) *v* 3049, 2958, 1741 (C=O), 1639, 1598, 1512, 1462, 1408, 1264, 1220, 1189, 882, 778, 760, 736 cm^{-1};

LCMS (ES^+): calcd for $C_{24}H_{20}O_1$ [M^+] 324; found [$M+H^+$] 325;

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 15.3 min; (3*R*,3a*R*,8a*S*): t_r: 24.7 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +27° (*c* = 0.50, $CHCl_3$).



3a-Methyl-8-methylene-3-naphthalen-1-yl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. The minor diastereomer was isolated as a yellow microcrystalline solid.

Mp 161-164 °C (dec.);

^{1}H NMR (400 MHz, $CDCl_3$) 8.08-8.10 (m, 1H), 7.90-7.93 (m, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.48-7.57 (m, 4H), 7.39-7.41 (m, 1H), 7.31-7.36 (m, 2H), 7.26-7.29 (m, 1H), 5.68 (d, *J* = 1.8 Hz, 1H), 5.47 (d, *J* = 1.7 Hz, 1H), 4.62 (dd, *J* = 7.5 Hz, *J* = 5.1 Hz, 1H), 3.35 (d, *J* = 1.1 Hz, 1H), 2.74-2.86 (m, 2H), 1.02 (s, 3H).

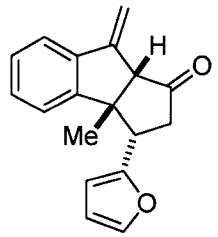


Table 1, entry 7. (3*R*,3a*R*,8a*S*)-3-Furan-2-yl-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as a yellow resinous solid: run 1: 63.8 mg (48%; 74% ee, 87:13 dr); run 2: 59.2 mg (45%; 76% ee, 83:17 dr);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.46 (m, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.20 (ddd, *J* = 7.8 Hz, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 7.02-7.06 (m, 1H), 6.39 (dd, *J* = 3.2 Hz, *J* = 1.9 Hz, 1H), 6.02-6.05 (m, 2H), 5.59 (d, *J* = 1.7 Hz, 1H), 5.35 (d, *J* = 1.6 Hz, 1H), 3.62 (dd, *J* = 10.6 Hz, *J* = 10.3 Hz, 1H), 3.24 (s, 1H), 2.55 (d (br), *J* = 10.8 Hz, 2H), 1.65 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.6, 153.5, 147.8, 145.4, 141.6, 139.8, 128.8, 127.9, 125.4, 120.5, 110.7, 107.6, 106.4, 66.3, 55.5, 45.0, 41.5, 28.1;

IR (film) v 3471, 3117, 3068, 2959, 2925, 2868, 1746 (C=O), 1638, 1505, 1463, 1321, 1219, 1183, 1157, 1010, 885, 764, 737 cm^{-1};

LCMS (ES^+): calcd for $C_{18}H_{16}O_2$ [M^+] 264; found [$M+H^+$] 265.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AS-H, 5.0% *i*-PrOH:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 10.5 min; (3*R*,3a*R*,8a*S*): t_r: 14.8 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +32° (c = 0.50, $CHCl_3$).

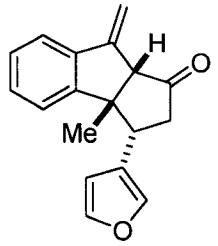


Table 1, entry 8. (3*R*,3a*R*,8a*S*)-3-Furan-3-yl-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as a yellow microcrystalline solid: run 1: 62.3 mg (47%; 77% ee, 88:12 dr); run 2: 65.0 mg (49%; 77% ee, 92:8 dr).

Mp 96-98 °C;

^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.47 (m, 2H), 7.20-7.23 (m, 2H), 7.07 (t, J = 7.5 Hz, 1H), 6.47 (d, J = 7.8 Hz, 1H), 6.29 (s, 1H), 5.59 (d, J = 1.6 Hz, 1H), 5.36 (d, J = 1.4 Hz, 1H), 3.44 (dd, J = 14.1 Hz, J = 6.6 Hz, 1H), 3.25 (d, J = 1.3 Hz, 1H), 2.50 (ddd, J = 16.7 Hz, J = 6.6 Hz, J = 1.3 Hz, 1H), 2.38 (dd, J = 16.6 Hz, J = 14.1 Hz, 1H), 1.57 (s, 3H);

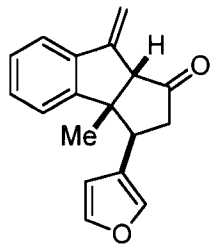
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 147.8, 145.4, 143.1, 140.2, 140.1, 128.5, 127.9, 126.5, 122.7, 120.6, 111.4, 106.4, 66.4, 54.7, 43.2, 42.9, 27.8;

IR (film) v 3132, 3070, 2924, 2959, 2867, 1745 (C=O), 1639, 1503, 1463, 1184, 1163, 1037, 1024, 874, 785, 764 cm^{-1};

LCMS (ES^+): calcd for $C_{18}H_{16}O_2$ [M^+] 264; found [$M+H^+$] 265.

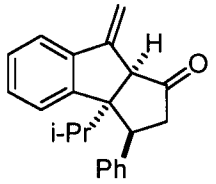
The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 14.8 min; (3*R*,3a*R*,8a*S*): t_r: 20.4 min.

(3*R*,3a*R*,8a*S*): Using catalyst (–)-**2**, $[\alpha]^{22}_D$ +77° (c = 0.50, $CHCl_3$).



3-Furan-3-yl-3a-methyl-8-methylene-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. The minor diastereomer was isolated as a yellow resinous solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.03 (m, 1H), 7.45-7.46 (m, 1H), 7.25-7.35 (m, 4H), 6.32 (s (br), 1H), 5.65 (d, J = 2.0 Hz, 1H), 5.44 (d, J = 2.0 Hz, 1H), 3.38 (dd, J = 8.0 Hz, J = 7.6 Hz, 1H), 3.32 (t, J = 2.0 Hz, 1H), 2.61 (d, J = 7.6 Hz, 2H), 1.25 (s, 3H).



Eq 3. (3*S*,3a*S*,8a*R*)-3a-Isopropyl-8-methylene-3-phenyl-3,3a,8,8a-tetrahydro-2*H*-cyclopenta[*a*]inden-1-one. Isolated as a yellow resinous oil: run 1: 65.7 mg (44%; 81% ee, **D**:**E** = 87:13); run 2: 63.1 mg (42%; 81% ee, **D**:**E** = 86:14). The diastereomer of **D** could not be detected.

^{1}H NMR (400 MHz, $CDCl_3$) (contains 6% of **E**) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.27-7.31 (m, 3H), 7.17 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 7.00-7.06 (m, 2H), 6.89 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 5.80 (d, *J* = 7.8 Hz, 1H), 5.55 (d, *J* = 1.9 Hz, 1H), 5.36 (d, *J* = 1.8 Hz, 1H), 3.96 (dd, *J* = 14.1 Hz, *J* = 6.6 Hz, 1H), 3.44 (d, *J* = 1.7 Hz, 1H), 2.67 (dd, *J* = 16.2 Hz, *J* = 14.2 Hz, 1H), 2.43 (ddd, *J* = 16.2 Hz, *J* = 6.6 Hz, *J* = 1.8 Hz, 1H), 2.32 (sept, *J* = 6.8 Hz, 1H), 1.29 (d, *J* = 6.7 Hz, 3H), 0.44 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 146.9, 146.9, 140.9, 138.4, 129.2, 128.1, 127.9, 127.7, 127.3, 127.2, 120.3, 105.2, 63.2, 58.9, 45.6, 42.8, 33.3, 19.0, 18.7;

IR (film) *v* 3064, 3030, 2962, 2875, 1744 (C=O), 1637, 1498, 1470, 1453, 1390, 1311, 1185, 1147, 1129, 880, 769, 701 cm^{-1};

LCMS (ES^+): calcd for $C_{22}H_{22}O_1$ [M^+] 302; found [$M+H^+$] 303.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak IA, 10.0% CH_2Cl_2:hexanes, 1.0 mL/min, (3*S*,3a*S*,8a*R*): t_r: 10.5 min; (3*R*,3a*R*,8a*S*): t_r: 11.6 min.

(3*S*,3a*S*,8a*R*): Using catalyst (+)-**2**, $[\alpha]^{22}_D$ –57° (*c* = 0.50, $CHCl_3$).

References

(1) Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1999**, *583*, 11-27.

(2) Plusquellec, D.; Roulleau, F.; Lefeuvre, M.; Brown, E. *Tetrahedron* **1988**, *44*, 2471-2476.

(3) This is based on a literature procedure: Biesalski, H.-K.; Doepner, G.; Kunz, H.; Paust, J.; John, M. *Liebigs Ann. Chem.* **1995**, *4*, 717-20.

V. X-Ray Crystal Structures

Both crystals were prepared with (+)-**2**.

***N*-Cinnamoylated catalyst (Figure 2).** In a glove box, a solution of cinnamoyl chloride (18.1 mg, 109 μmol) in dry CH_2Cl_2 (2.0 mL) was added to (+)-**2** (40.0 mg, 109 μmol). The resulting dark-green solution was stirred for 20 minutes, and then a solution of $AgPF_6$ (28.1 mg, 111 μmol) in dry acetonitrile (1.4 mL) was added. The reaction mixture was stirred for 30 minutes, and then the gray precipitate was removed by filtration through an acrodisc (rinsed with dry CH_2Cl_2 (2.0 mL)). The resulting clear, dark-green solution was concentrated under reduced pressure. The green oil was dissolved in dry THF, and then pentane was added. The solvent was removed, furnishing a green amorphous powder (65.2 mg, 93%). Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/pentane.

Mp 225-227 °C (dec.);

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.31 (s (br), 1H), 8.02 (d, J = 14.2 Hz, 1H), 7.72 (s (br), 2H), 7.49 (s (br), 3H), 7.24 (d, J = 15.0 Hz, 1H), 6.18 (s (br), 1H), 5.78 (d, J = 2.0 Hz, 1H), 4.57 (s, 1H), 4.39 (s, 1H), 3.68-3.87 (m, 4H), 2.20-2.28 (m, 4H), 1.57 (s, 15H);

^{13}C NMR (100 MHz, CD_2Cl_2) δ 166.3, 165.6, 150.5, 140.1, 134.3, 132.2, 130.3, 129.7, 116.0, 99.6, 98.1, 82.7, 79.7, 69.7, 68.5, 68.1, 26.5, 24.9, 10.1;

IR (film) υ 2972, 2909, 1701, 1608 (C=O), 1576, 1505, 1452, 1327, 1238, 1199, 1159, 1115, 1065, 840, 765 cm^{-1};

MS (ESI$^+$) calcd for $C_{31}H_{35}Fe_1N_2O_1$ [M$^+$] 507, found: 507.

A colorless plate of dimensions 0.20 x 0.20 x 0.05 mm^3 was mounted under oil and transferred to a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Apex CCD detector and equipped with an Oxford Cryostream low-temperature device. Diffraction data were collected with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073Å), performing ϕ- and ω-scans. The unit cell parameters were determined with the diffractometer control software SMART[1], and the raw data were integrated and reduced using the program SAINT,[2] version 7.23. Semi-empirical absorption correction was performed with SADABS.[3] The structure was solved by direct methods using SHELXS[4] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[5]

The structure was solved and refined in the tetragonal space group $P4_32_12$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters for the hydrogen atoms were constrained to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). The Flack-x parameter[6] refined to -0.008(14), confirming the absolute stereochemistry.

Table 1 gives details about unit cell, data quality, and the residual values of the refinement.

References

(1) SMART *Software for the CCD Detector System*; Bruker AXS, Madison, WI (2003).
(2) SAINT *Software for the CCD Detector System*; Bruker AXS, Madison, WI (2003).
(3) SADABS *Program for absorption (and other) corrections*; Bruker AXS, Madison, WI (2005).
(4) Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467-473.
(5) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
(6) Flack, H. D. *Acta Cryst.* **1983**, *A39*, 876-881.

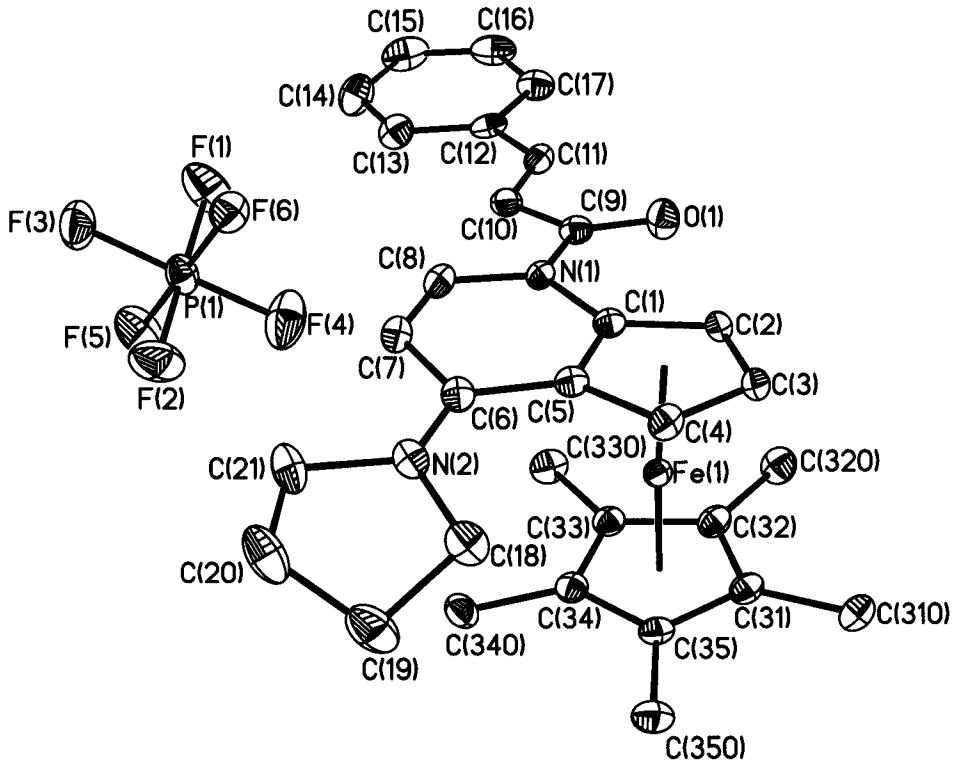

C(15)
C(16)
C(14)
C(17)
C(13)
C(12)
C(11)
F(1)
F(3)
F(6)
C(10)
C(9)
O(1)
C(8)
N(1)
P(1)
C(1)
C(2)
F(5)
F(4)
C(7)
C(3)
F(2)
C(6)
C(5)
C(4)
C(330)
C(21)
N(2)
Fe(1)
C(320)
C(33)
C(32)
C(18)
C(20)
C(34)
C(31)
C(310)
C(340)
C(35)
C(19)
C(350)

Table 1. Crystal data and structure refinement for 05261.

Identification code	05261	
Empirical formula	C31 H35 F6 Fe N2 O P	
Formula weight	652.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(3)2(1)2	
Unit cell dimensions	a = 11.9811(3) Å	α= 90°.
	b = 11.9811(3) Å	β= 90°.
	c = 40.4968(19) Å	γ = 90°.
Volume	5813.2(3) $Å^3$	
Z	8	
Density (calculated)	1.491 Mg/m^3	
Absorption coefficient	0.641 mm^{-1}	
F(000)	2704	
Crystal size	0.20 x 0.20 x 0.05 mm^3	
Theta range for data collection	1.77 to 28.70°.	
Index ranges	-16<=h<=16, -16<=k<=16, -54<=l<=54	
Reflections collected	124357	
Independent reflections	7504 [R(int) = 0.0955]	
Completeness to theta = 28.70°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9686 and 0.8825	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7504 / 0 / 384	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.0862	
R indices (all data)	R1 = 0.0501, wR2 = 0.0904	
Absolute structure parameter	-0.008(14)	
Largest diff. peak and hole	0.542 and -0.335 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 05261. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	213(1)	9834(1)	829(1)	14(1)
O(1)	-1468(2)	7362(2)	387(1)	27(1)
N(1)	-1767(2)	9238(2)	366(1)	16(1)
N(2)	-782(2)	12607(2)	424(1)	19(1)
C(1)	-616(2)	9491(2)	401(1)	16(1)
C(2)	324(2)	8781(2)	431(1)	17(1)
C(3)	1284(2)	9468(2)	445(1)	18(1)
C(4)	965(2)	10607(2)	433(1)	18(1)
C(5)	-232(2)	10644(2)	404(1)	16(1)
C(6)	-1035(2)	11543(2)	391(1)	17(1)
C(7)	-2167(2)	11201(2)	336(1)	20(1)
C(8)	-2477(2)	10123(2)	325(1)	19(1)
C(9)	-2148(2)	8116(2)	385(1)	19(1)
C(10)	-3363(2)	7904(2)	408(1)	20(1)
C(11)	-3709(2)	6849(2)	401(1)	20(1)
C(12)	-4855(2)	6427(2)	412(1)	20(1)
C(13)	-5782(2)	7128(2)	418(1)	26(1)
C(14)	-6849(2)	6677(2)	405(1)	32(1)
C(15)	-7001(2)	5532(3)	387(1)	34(1)
C(16)	-6091(2)	4827(3)	392(1)	31(1)
C(17)	-5023(2)	5277(2)	404(1)	25(1)
C(18)	318(2)	13063(2)	523(1)	25(1)
C(19)	12(2)	14204(2)	666(1)	36(1)
C(20)	-952(2)	14578(2)	447(1)	34(1)
C(21)	-1626(2)	13511(2)	401(1)	26(1)
C(31)	1083(2)	9472(2)	1248(1)	19(1)
C(32)	138(2)	8749(2)	1215(1)	19(1)
C(33)	-845(2)	9435(2)	1208(1)	18(1)
C(34)	-501(2)	10570(2)	1238(1)	18(1)
C(35)	686(2)	10600(2)	1262(1)	18(1)
C(310)	2283(2)	9115(2)	1265(1)	23(1)

C(320)	160(2)	7496(2)	1198(1)	25(1)
C(330)	-2028(2)	9037(2)	1184(1)	24(1)
C(340)	-1278(2)	11557(2)	1250(1)	23(1)
C(350)	1389(2)	11623(2)	1316(1)	24(1)
P(1)	-5624(1)	11081(1)	450(1)	25(1)
F(1)	-6222(2)	9967(1)	315(1)	48(1)
F(2)	-5004(2)	12179(1)	568(1)	46(1)
F(3)	-6452(1)	11803(2)	227(1)	42(1)
F(4)	-4801(2)	10329(2)	665(1)	52(1)
F(5)	-6481(2)	11146(2)	748(1)	46(1)
F(6)	-4769(1)	10994(1)	143(1)	29(1)

Table 3. Bond lengths [Å] and angles [°] for 05261.

Fe(1)-C(32)	2.034(2)
Fe(1)-C(31)	2.035(2)
Fe(1)-C(1)	2.040(2)
Fe(1)-C(33)	2.045(2)
Fe(1)-C(5)	2.046(2)
Fe(1)-C(2)	2.052(2)
Fe(1)-C(35)	2.059(2)
Fe(1)-C(34)	2.060(2)
Fe(1)-C(4)	2.060(2)
Fe(1)-C(3)	2.063(2)
O(1)-C(9)	1.217(3)
N(1)-C(8)	1.369(3)
N(1)-C(1)	1.419(3)
N(1)-C(9)	1.422(3)
N(2)-C(6)	1.317(3)
N(2)-C(18)	1.481(3)
N(2)-C(21)	1.485(3)
C(1)-C(2)	1.416(3)
C(1)-C(5)	1.456(3)
C(2)-C(3)	1.416(3)
C(3)-C(4)	1.418(3)
C(4)-C(5)	1.439(3)
C(5)-C(6)	1.445(3)
C(6)-C(7)	1.435(3)
C(7)-C(8)	1.344(3)
C(9)-C(10)	1.480(3)
C(10)-C(11)	1.330(3)
C(11)-C(12)	1.464(3)
C(12)-C(17)	1.392(3)
C(12)-C(13)	1.394(4)
C(13)-C(14)	1.389(4)
C(14)-C(15)	1.386(4)
C(15)-C(16)	1.380(4)
C(16)-C(17)	1.390(3)

C(18)-C(19)	1.528(3)
C(19)-C(20)	1.524(4)
C(20)-C(21)	1.523(4)
C(31)-C(32)	1.432(3)
C(31)-C(35)	1.434(3)
C(31)-C(310)	1.502(3)
C(32)-C(33)	1.436(3)
C(32)-C(320)	1.503(3)
C(33)-C(34)	1.426(3)
C(33)-C(330)	1.499(3)
C(34)-C(35)	1.426(3)
C(34)-C(340)	1.506(3)
C(35)-C(350)	1.503(3)
P(1)-F(2)	1.5850(17)
P(1)-F(5)	1.5884(17)
P(1)-F(4)	1.5942(18)
P(1)-F(3)	1.5954(18)
P(1)-F(1)	1.6101(18)
P(1)-F(6)	1.6133(16)

C(32)-Fe(1)-C(31)	41.20(10)
C(32)-Fe(1)-C(1)	120.17(9)
C(31)-Fe(1)-C(1)	156.03(10)
C(32)-Fe(1)-C(33)	41.21(10)
C(31)-Fe(1)-C(33)	69.13(9)
C(1)-Fe(1)-C(33)	106.76(9)
C(32)-Fe(1)-C(5)	159.60(10)
C(31)-Fe(1)-C(5)	159.09(10)
C(1)-Fe(1)-C(5)	41.75(9)
C(33)-Fe(1)-C(5)	125.41(9)
C(32)-Fe(1)-C(2)	102.37(9)
C(31)-Fe(1)-C(2)	119.37(9)
C(1)-Fe(1)-C(2)	40.49(9)
C(33)-Fe(1)-C(2)	119.06(9)
C(5)-Fe(1)-C(2)	69.35(9)
C(32)-Fe(1)-C(35)	69.08(9)

C(31)-Fe(1)-C(35)	40.99(10)
C(1)-Fe(1)-C(35)	161.38(10)
C(33)-Fe(1)-C(35)	68.67(9)
C(5)-Fe(1)-C(35)	125.19(9)
C(2)-Fe(1)-C(35)	157.81(10)
C(32)-Fe(1)-C(34)	68.81(9)
C(31)-Fe(1)-C(34)	68.64(9)
C(1)-Fe(1)-C(34)	124.49(9)
C(33)-Fe(1)-C(34)	40.64(9)
C(5)-Fe(1)-C(34)	111.32(9)
C(2)-Fe(1)-C(34)	157.08(10)
C(35)-Fe(1)-C(34)	40.50(9)
C(32)-Fe(1)-C(4)	154.81(10)
C(31)-Fe(1)-C(4)	121.34(9)
C(1)-Fe(1)-C(4)	68.97(9)
C(33)-Fe(1)-C(4)	163.66(10)
C(5)-Fe(1)-C(4)	41.03(9)
C(2)-Fe(1)-C(4)	68.62(9)
C(35)-Fe(1)-C(4)	110.05(9)
C(34)-Fe(1)-C(4)	127.90(10)
C(32)-Fe(1)-C(3)	118.07(10)
C(31)-Fe(1)-C(3)	105.27(9)
C(1)-Fe(1)-C(3)	67.64(9)
C(33)-Fe(1)-C(3)	154.22(10)
C(5)-Fe(1)-C(3)	68.25(9)
C(2)-Fe(1)-C(3)	40.24(9)
C(35)-Fe(1)-C(3)	124.44(9)
C(34)-Fe(1)-C(3)	162.59(10)
C(4)-Fe(1)-C(3)	40.23(9)
C(8)-N(1)-C(1)	116.76(19)
C(8)-N(1)-C(9)	122.63(19)
C(1)-N(1)-C(9)	120.57(19)
C(6)-N(2)-C(18)	126.1(2)
C(6)-N(2)-C(21)	122.8(2)
C(18)-N(2)-C(21)	110.70(19)
C(2)-C(1)-N(1)	130.8(2)

C(2)-C(1)-C(5)	108.54(19)
N(1)-C(1)-C(5)	120.7(2)
C(2)-C(1)-Fe(1)	70.22(12)
N(1)-C(1)-Fe(1)	126.94(15)
C(5)-C(1)-Fe(1)	69.35(11)
C(3)-C(2)-C(1)	107.5(2)
C(3)-C(2)-Fe(1)	70.28(13)
C(1)-C(2)-Fe(1)	69.29(12)
C(2)-C(3)-C(4)	109.8(2)
C(2)-C(3)-Fe(1)	69.48(13)
C(4)-C(3)-Fe(1)	69.78(13)
C(3)-C(4)-C(5)	107.6(2)
C(3)-C(4)-Fe(1)	69.98(13)
C(5)-C(4)-Fe(1)	68.97(12)
C(4)-C(5)-C(6)	133.6(2)
C(4)-C(5)-C(1)	106.61(19)
C(6)-C(5)-C(1)	119.8(2)
C(4)-C(5)-Fe(1)	70.00(12)
C(6)-C(5)-Fe(1)	123.94(15)
C(1)-C(5)-Fe(1)	68.90(11)
N(2)-C(6)-C(7)	120.7(2)
N(2)-C(6)-C(5)	124.3(2)
C(7)-C(6)-C(5)	115.0(2)
C(8)-C(7)-C(6)	122.7(2)
C(7)-C(8)-N(1)	124.7(2)
O(1)-C(9)-N(1)	119.2(2)
O(1)-C(9)-C(10)	122.0(2)
N(1)-C(9)-C(10)	118.8(2)
C(11)-C(10)-C(9)	117.9(2)
C(10)-C(11)-C(12)	128.3(2)
C(17)-C(12)-C(13)	118.8(2)
C(17)-C(12)-C(11)	118.5(2)
C(13)-C(12)-C(11)	122.7(2)
C(14)-C(13)-C(12)	119.9(2)
C(15)-C(14)-C(13)	120.6(3)
C(16)-C(15)-C(14)	120.1(3)

C(15)-C(16)-C(17)	119.4(3)
C(16)-C(17)-C(12)	121.2(2)
N(2)-C(18)-C(19)	102.7(2)
C(20)-C(19)-C(18)	103.0(2)
C(21)-C(20)-C(19)	103.1(2)
N(2)-C(21)-C(20)	104.1(2)
C(32)-C(31)-C(35)	108.2(2)
C(32)-C(31)-C(310)	126.1(2)
C(35)-C(31)-C(310)	125.7(2)
C(32)-C(31)-Fe(1)	69.35(13)
C(35)-C(31)-Fe(1)	70.38(12)
C(310)-C(31)-Fe(1)	126.17(16)
C(31)-C(32)-C(33)	107.7(2)
C(31)-C(32)-C(320)	126.5(2)
C(33)-C(32)-C(320)	125.8(2)
C(31)-C(32)-Fe(1)	69.45(13)
C(33)-C(32)-Fe(1)	69.81(12)
C(320)-C(32)-Fe(1)	127.00(16)
C(34)-C(33)-C(32)	107.9(2)
C(34)-C(33)-C(330)	125.6(2)
C(32)-C(33)-C(330)	126.5(2)
C(34)-C(33)-Fe(1)	70.22(12)
C(32)-C(33)-Fe(1)	68.98(13)
C(330)-C(33)-Fe(1)	127.69(16)
C(35)-C(34)-C(33)	108.6(2)
C(35)-C(34)-C(340)	126.4(2)
C(33)-C(34)-C(340)	125.0(2)
C(35)-C(34)-Fe(1)	69.73(12)
C(33)-C(34)-Fe(1)	69.14(12)
C(340)-C(34)-Fe(1)	128.33(15)
C(34)-C(35)-C(31)	107.7(2)
C(34)-C(35)-C(350)	126.2(2)
C(31)-C(35)-C(350)	126.0(2)
C(34)-C(35)-Fe(1)	69.77(12)
C(31)-C(35)-Fe(1)	68.62(12)
C(350)-C(35)-Fe(1)	129.88(16)

F(2)-P(1)-F(5)	91.85(10)
F(2)-P(1)-F(4)	90.81(11)
F(5)-P(1)-F(4)	90.68(10)
F(2)-P(1)-F(3)	90.74(10)
F(5)-P(1)-F(3)	90.12(10)
F(4)-P(1)-F(3)	178.23(11)
F(2)-P(1)-F(1)	177.55(10)
F(5)-P(1)-F(1)	90.58(10)
F(4)-P(1)-F(1)	89.51(12)
F(3)-P(1)-F(1)	88.91(11)
F(2)-P(1)-F(6)	89.38(9)
F(5)-P(1)-F(6)	178.75(10)
F(4)-P(1)-F(6)	89.50(9)
F(3)-P(1)-F(6)	89.67(9)
F(1)-P(1)-F(6)	88.18(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for 05261. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	13(1)	15(1)	13(1)	0(1)	0(1)	0(1)
O(1)	22(1)	17(1)	41(1)	-1(1)	-3(1)	-1(1)
N(1)	13(1)	17(1)	18(1)	-1(1)	-3(1)	0(1)
N(2)	23(1)	17(1)	18(1)	3(1)	5(1)	0(1)
C(1)	17(1)	17(1)	14(1)	1(1)	0(1)	-1(1)
C(2)	17(1)	18(1)	17(1)	-2(1)	0(1)	5(1)
C(3)	15(1)	20(1)	17(1)	-3(1)	0(1)	4(1)
C(4)	14(1)	23(1)	17(1)	2(1)	2(1)	-3(1)
C(5)	17(1)	17(1)	13(1)	1(1)	1(1)	-3(1)
C(6)	19(1)	19(1)	14(1)	3(1)	3(1)	1(1)
C(7)	17(1)	20(1)	21(1)	3(1)	0(1)	2(1)
C(8)	15(1)	23(1)	18(1)	3(1)	-2(1)	0(1)
C(9)	21(1)	17(1)	17(1)	0(1)	-2(1)	-2(1)
C(10)	21(1)	20(1)	18(1)	-1(1)	-2(1)	-1(1)
C(11)	19(1)	22(1)	19(1)	1(1)	-3(1)	1(1)
C(12)	25(1)	24(1)	13(1)	2(1)	-4(1)	-7(1)
C(13)	28(1)	22(1)	27(1)	5(1)	-3(1)	-3(1)
C(14)	22(1)	36(2)	38(2)	7(1)	-2(1)	-2(1)
C(15)	26(1)	49(2)	28(1)	1(1)	0(1)	-20(1)
C(16)	41(2)	29(1)	22(1)	-1(1)	1(1)	-16(1)
C(17)	32(2)	23(1)	20(1)	1(1)	0(1)	-5(1)
C(18)	23(1)	21(1)	30(1)	0(1)	6(1)	-5(1)
C(19)	36(2)	25(1)	47(2)	-10(1)	10(1)	-7(1)
C(20)	39(2)	17(1)	46(2)	2(1)	18(1)	1(1)
C(21)	29(1)	18(1)	32(1)	4(1)	8(1)	5(1)
C(31)	19(1)	23(1)	15(1)	3(1)	-2(1)	-2(1)
C(32)	19(1)	23(1)	16(1)	3(1)	-1(1)	-1(1)
C(33)	20(1)	21(1)	14(1)	1(1)	0(1)	0(1)
C(34)	19(1)	21(1)	14(1)	1(1)	1(1)	1(1)
C(35)	20(1)	22(1)	14(1)	-2(1)	-1(1)	-2(1)
C(310)	21(1)	26(1)	23(1)	3(1)	-5(1)	0(1)

C(320)	26(1)	22(1)	26(1)	4(1)	-2(1)	-1(1)
C(330)	20(1)	29(1)	22(1)	1(1)	2(1)	-6(1)
C(340)	25(1)	23(1)	21(1)	-3(1)	3(1)	5(1)
C(350)	26(1)	24(1)	23(1)	-5(1)	-2(1)	-6(1)
P(1)	18(1)	24(1)	33(1)	-2(1)	5(1)	1(1)
F(1)	43(1)	30(1)	73(1)	-13(1)	22(1)	-12(1)
F(2)	42(1)	45(1)	51(1)	-17(1)	-2(1)	-13(1)
F(3)	29(1)	40(1)	58(1)	-3(1)	-8(1)	11(1)
F(4)	46(1)	74(1)	37(1)	22(1)	12(1)	25(1)
F(5)	37(1)	51(1)	50(1)	-9(1)	23(1)	3(1)
F(6)	23(1)	36(1)	30(1)	3(1)	3(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 05261.

	x	y	z	U(eq)
H(2)	312	7989	439	21
H(3)	2030	9206	461	21
H(4)	1452	11232	442	22
H(7)	-2721	11759	305	23
H(8)	-3242	9964	286	22
H(10)	-3879	8502	427	23
H(11)	-3139	6300	387	24
H(13)	-5685	7914	430	31
H(14)	-7480	7158	409	38
H(15)	-7734	5233	372	41
H(16)	-6194	4041	388	37
H(17)	-4396	4792	407	30
H(18A)	821	13138	331	30
H(18B)	679	12585	692	30
H(19A)	-225	14141	899	43
H(19B)	648	14729	651	43
H(20A)	-1402	15164	556	41
H(20B)	-678	14865	233	41
H(21A)	-2197	13434	576	31
H(21B)	-2000	13503	183	31
H(31A)	2462	8889	1491	35
H(31B)	2764	9739	1200	35
H(31C)	2405	8485	1115	35
H(32A)	67	7187	1420	37
H(32B)	875	7251	1106	37
H(32C)	-450	7235	1056	37
H(33A)	-2045	8305	1076	35
H(33B)	-2465	9570	1053	35
H(33C)	-2348	8977	1406	35
H(34A)	-1539	11665	1477	34

H(34B)	-1918	11421	1105	34
H(34C)	-881	12227	1176	34
H(35A)	1012	12274	1221	36
H(35B)	2116	11522	1209	36
H(35C)	1497	11740	1554	36

Structural Data

Date: December 15, 2005

Submitter: Erhard Bappert

Sample Reference Number:

X-ray Number: gf106

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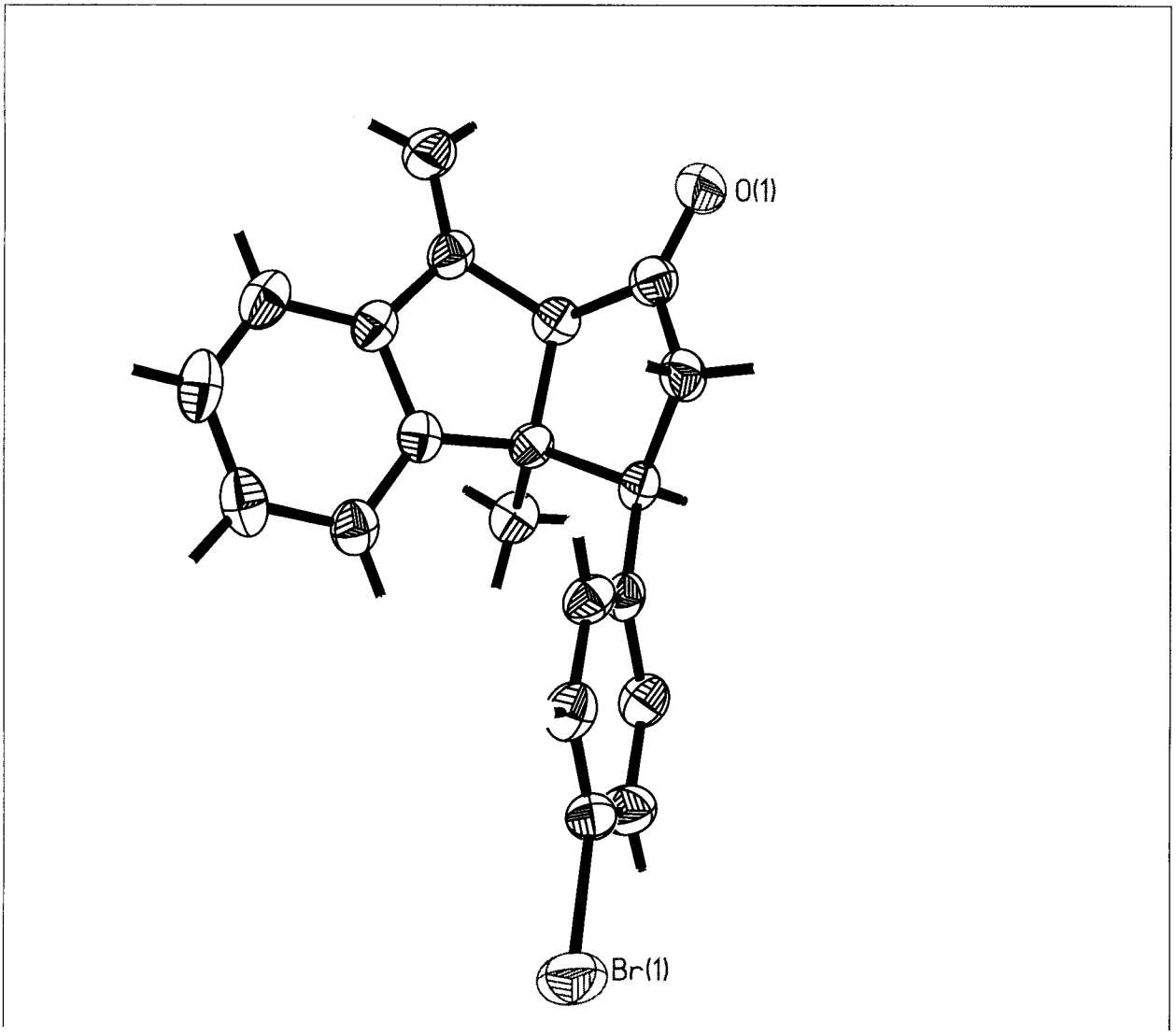


Introduction:

Single crystal study to confirm the identity of the sample submitted. Chirality was determined.

Experimental Section:

A colorless block crystal with dimensions 0.12 x 0.10 x 0.10 mm was mounted on a glass fiber using very small amount of paratone oil.

Data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 193 K. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.76 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[1] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[2] which corrects for Lp and decay. Absorption corrections were applied using SADABS[6] multiscan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97[3] program and refined by least squares method on F^2, SHELXL-97,[4] incorporated in SHELXTL-PC V 6.10.[5]

The structure was solved in the space group $P2_12_12_1$ (# 19) by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically. Hydrogens were found by difference fourier methods and refined isotropically. The Flack[7] parameter is used to determine chirality of the crystal studied, the value should be near zero, a value of one is the other enantiomer and a value of 0.5 is racemic. The Flack parameter was refined to 0.015(9), confirming the absolute stereochemistry. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 50% ellipsoids.

Acknowledgement. The CCD based x-ray diffractometer at Harvard University was purchased through NIH grant (1S10RR11937-01).

References

1. SMART V 5.625 (NT) *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (2001).

2. SAINT V 6.22 (NT) *Software for the CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (2001).

3. Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1990.

4. Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure,* University of Göttingen, Germany, 1997.

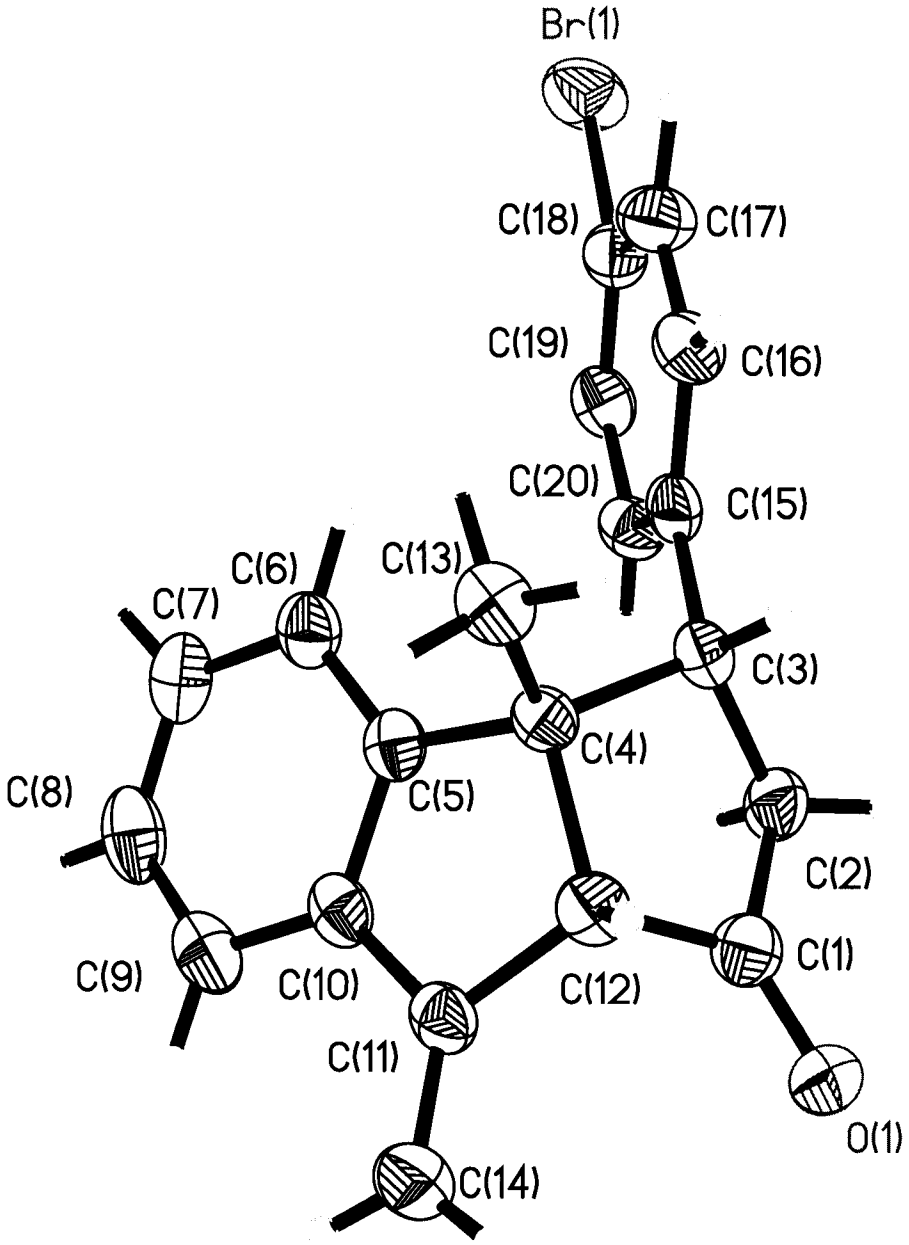
5. SHELXTL 6.1 (PC-Version), *Program library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems, Madison, WI (2000).

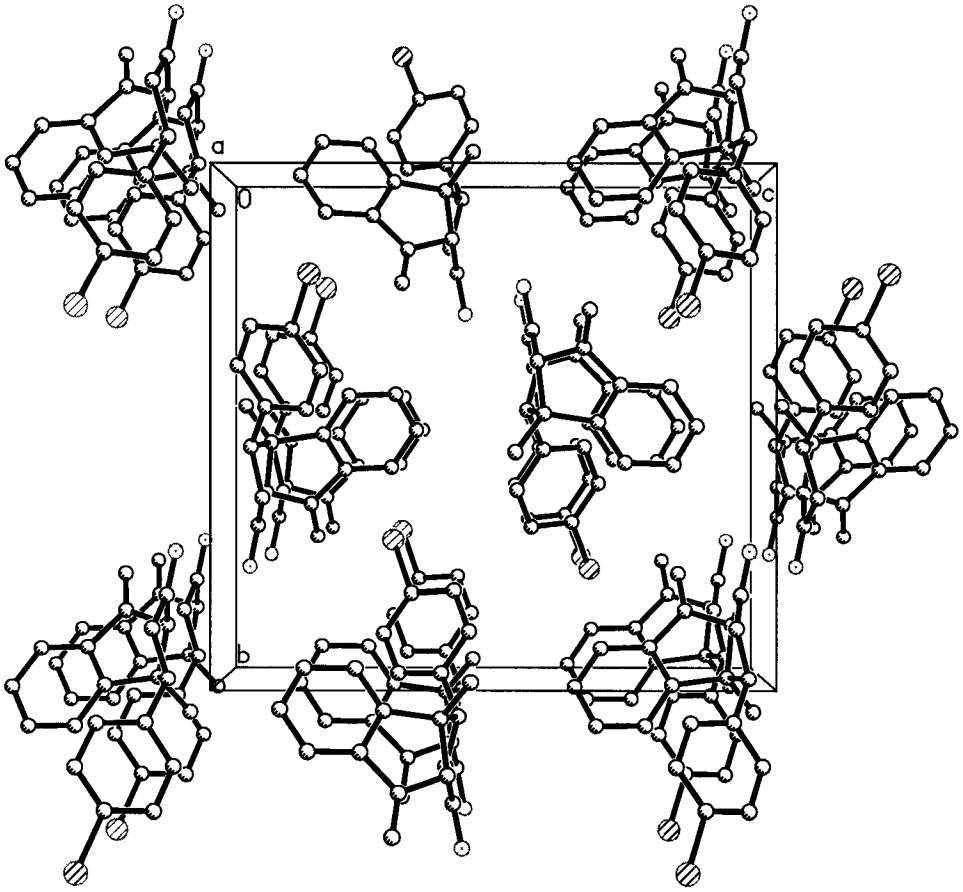
6. SADABS. Program for absorption corrections using Siemens CCD based on the method of Robert Blessing; Blessing, R.H. *Acta Cryst. A51* **1995**, 33-38.

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

[a] Obtained with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation.
[b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\{\Sigma[w(F_o^2)^2]\}^{1/2}$.

The following are 50% thermal ellipsoidal drawings of the molecule in the asymmetric cell with various amount of labeling.


Br(1)
C(18)
C(17)
C(19)
C(16)
C(20)
C(15)
C(6)
C(13)
C(7)
C(3)
C(4)
C(8)
C(5)
C(2)
C(9)
C(10)
C(12)
C(1)
C(11)
O(1)
C(14)



This is a drawing of the packing along the a-axis.

Table 1. Crystal data and structure refinement for gf106t.

Identification code	gf106t	
Empirical formula	C20 H17 Br O	
Formula weight	353.25	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.2277(14) Å	α= 90°.
	b = 14.583(3) Å	β= 90°.
	c = 15.656(3) Å	γ = 90°.
Volume	1650.2(5) $Å^3$	
Z	4	
Density (calculated)	1.422 Mg/m^3	
Absorption coefficient	2.490 mm^{-1}	
F(000)	720	
Crystal size	0.20 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.91 to 27.88°.	
Index ranges	-9<=h<=9, -18<=k<=18, -20<=l<=12	
Reflections collected	9518	
Independent reflections	3593 [R(int) = 0.0238]	
Completeness to theta = 27.88°	94.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7888 and 0.6358	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3593 / 0 / 267	
Goodness-of-fit on F^2	0.971	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0694	
R indices (all data)	R1 = 0.0437, wR2 = 0.0728	
Absolute structure parameter	0.015(9)	
Largest diff. peak and hole	0.492 and -0.365 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for gf106t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	7460(1)	2843(1)	8184(1)	53(1)
O(1)	1265(3)	-2701(1)	9463(1)	44(1)
C(1)	1321(4)	-1890(2)	9310(2)	35(1)
C(2)	3044(4)	-1329(2)	9164(2)	35(1)
C(3)	2457(4)	-354(2)	9395(2)	29(1)
C(4)	386(3)	-280(2)	9106(2)	28(1)
C(5)	101(3)	-120(2)	8152(2)	28(1)
C(6)	597(3)	642(2)	7666(2)	35(1)
C(7)	112(4)	673(2)	6815(2)	42(1)
C(8)	-865(4)	-39(2)	6447(2)	44(1)
C(9)	-1422(4)	-776(2)	6921(2)	41(1)
C(10)	-939(3)	-818(2)	7781(2)	30(1)
C(11)	-1452(3)	-1508(2)	8430(2)	33(1)
C(12)	-378(4)	-1270(2)	9226(2)	31(1)
C(13)	-656(4)	441(2)	9618(2)	36(1)
C(14)	-2643(4)	-2192(2)	8344(2)	44(1)
C(15)	3713(3)	408(2)	9086(2)	29(1)
C(16)	3889(4)	1204(2)	9570(2)	35(1)
C(17)	4961(4)	1941(2)	9300(2)	41(1)
C(18)	5898(3)	1863(2)	8537(2)	35(1)
C(19)	5791(3)	1090(2)	8045(2)	34(1)
C(20)	4695(3)	362(2)	8324(2)	32(1)

Table 3. Bond lengths [Å] and angles [°] for gf106t.

Br(1)-C(18)	1.903(2)	O(1)-C(1)	1.208(3)
C(1)-C(2)	1.507(4)	C(1)-C(12)	1.531(4)
C(2)-C(3)	1.527(3)	C(2)-H(2)	0.92(3)
C(2)-H(1)	1.02(3)	C(3)-C(15)	1.514(4)
C(3)-C(4)	1.567(4)	C(3)-H(3)	0.96(2)
C(4)-C(13)	1.521(4)	C(4)-C(5)	1.526(4)
C(4)-C(12)	1.556(3)	C(5)-C(10)	1.392(3)
C(5)-C(6)	1.394(4)	C(6)-C(7)	1.378(4)
C(6)-H(4)	0.97(3)	C(7)-C(8)	1.381(5)
C(7)-H(5)	1.03(3)	C(8)-C(9)	1.367(4)
C(8)-H(6)	0.94(3)	C(9)-C(10)	1.392(4)
C(9)-H(7)	0.93(3)	C(10)-C(11)	1.477(4)
C(11)-C(14)	1.324(4)	C(11)-C(12)	1.510(4)
C(12)-H(8)	0.87(3)	C(13)-H(10)	1.02(3)
C(13)-H(9)	0.91(3)	C(13)-H(11)	0.95(3)
C(14)-H(12)	0.91(3)	C(14)-H(13)	0.90(3)
C(15)-C(20)	1.390(4)	C(15)-C(16)	1.393(4)
C(16)-C(17)	1.390(4)	C(16)-H(14)	0.91(3)
C(17)-C(18)	1.379(4)	C(17)-H(15)	0.95(3)
C(18)-C(19)	1.368(4)	C(19)-C(20)	1.394(4)
C(19)-H(16)	0.89(3)	C(20)-H(17)	0.91(3)

O(1)-C(1)-C(2)	126.1(3)	O(1)-C(1)-C(12)	124.7(3)
C(2)-C(1)-C(12)	109.2(2)	C(1)-C(2)-C(3)	103.9(2)
C(1)-C(2)-H(2)	106.8(17)	C(3)-C(2)-H(2)	119.8(17)
C(1)-C(2)-H(1)	110.7(18)	C(3)-C(2)-H(1)	109.8(17)
H(2)-C(2)-H(1)	106(3)	C(15)-C(3)-C(2)	116.2(2)
C(15)-C(3)-C(4)	115.4(2)	C(2)-C(3)-C(4)	105.1(2)
C(15)-C(3)-H(3)	107.5(14)	C(2)-C(3)-H(3)	109.3(13)
C(4)-C(3)-H(3)	102.4(17)	C(13)-C(4)-C(5)	110.1(2)
C(13)-C(4)-C(12)	113.7(2)	C(5)-C(4)-C(12)	102.3(2)
C(13)-C(4)-C(3)	111.6(2)	C(5)-C(4)-C(3)	115.0(2)
C(12)-C(4)-C(3)	103.90(19)	C(10)-C(5)-C(6)	119.6(3)
C(10)-C(5)-C(4)	111.7(2)	C(6)-C(5)-C(4)	128.5(2)

C(7)-C(6)-C(5)	119.3(3)	C(7)-C(6)-H(4)	121.1(16)
C(5)-C(6)-H(4)	119.6(16)	C(6)-C(7)-C(8)	120.6(3)
C(6)-C(7)-H(5)	123.8(17)	C(8)-C(7)-H(5)	115.7(16)
C(9)-C(8)-C(7)	121.0(3)	C(9)-C(8)-H(6)	118.9(18)
C(7)-C(8)-H(6)	120.1(18)	C(8)-C(9)-C(10)	119.1(3)
C(8)-C(9)-H(7)	120.6(16)	C(10)-C(9)-H(7)	120.2(16)
C(9)-C(10)-C(5)	120.4(3)	C(9)-C(10)-C(11)	129.2(2)
C(5)-C(10)-C(11)	110.3(2)	C(14)-C(11)-C(10)	127.4(3)
C(14)-C(11)-C(12)	126.3(3)	C(10)-C(11)-C(12)	106.4(2)
C(11)-C(12)-C(1)	110.3(2)	C(11)-C(12)-C(4)	107.2(2)
C(1)-C(12)-C(4)	105.9(2)	C(11)-C(12)-H(8)	114.6(16)
C(1)-C(12)-H(8)	107.6(16)	C(4)-C(12)-H(8)	110.9(16)
C(4)-C(13)-H(10)	111.5(18)	C(4)-C(13)-H(9)	109.9(16)
H(10)-C(13)-H(9)	107(2)	C(4)-C(13)-H(11)	108.5(17)
H(10)-C(13)-H(11)	110(2)	H(9)-C(13)-H(11)	110(2)
C(11)-C(14)-H(12)	117.3(19)	C(11)-C(14)-H(13)	119.4(16)
H(12)-C(14)-H(13)	123(2)	C(20)-C(15)-C(16)	117.4(2)
C(20)-C(15)-C(3)	123.1(2)	C(16)-C(15)-C(3)	119.5(2)
C(17)-C(16)-C(15)	122.0(3)	C(17)-C(16)-H(14)	119.9(16)
C(15)-C(16)-H(14)	117.9(16)	C(18)-C(17)-C(16)	118.3(3)
C(18)-C(17)-H(15)	121.0(17)	C(16)-C(17)-H(15)	120.6(17)
C(19)-C(18)-C(17)	121.9(2)	C(19)-C(18)-Br(1)	119.3(2)
C(17)-C(18)-Br(1)	118.8(2)	C(18)-C(19)-C(20)	118.9(3)
C(18)-C(19)-H(16)	121.4(18)	C(20)-C(19)-H(16)	119.7(18)
C(15)-C(20)-C(19)	121.5(3)	C(15)-C(20)-H(17)	120.7(15)
C(19)-C(20)-H(17)	117.8(15)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for gf106t. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	61(1)	50(1)	47(1)	5(1)	-3(1)	-26(1)
O(1)	44(1)	34(1)	53(1)	10(1)	-11(1)	-7(1)
C(1)	40(1)	37(2)	29(1)	3(1)	-1(1)	-4(1)
C(2)	27(1)	34(1)	44(2)	4(1)	-4(1)	3(1)
C(3)	26(1)	35(1)	24(1)	1(1)	-3(1)	-1(1)
C(4)	24(1)	31(1)	29(1)	-1(1)	1(1)	-1(1)
C(5)	22(1)	34(1)	29(1)	-1(1)	2(1)	6(1)
C(6)	25(1)	42(2)	38(2)	3(1)	-1(1)	2(1)
C(7)	32(1)	55(2)	38(2)	14(2)	2(2)	8(1)
C(8)	40(2)	67(2)	25(2)	2(2)	-3(1)	11(2)
C(9)	32(1)	52(2)	38(2)	-10(1)	-6(1)	6(1)
C(10)	21(1)	38(2)	32(1)	-5(1)	0(1)	5(1)
C(11)	24(1)	36(1)	39(2)	-4(1)	-4(1)	4(1)
C(12)	29(1)	36(2)	29(1)	2(1)	5(1)	-4(1)
C(13)	31(2)	44(2)	32(2)	-6(1)	4(1)	2(1)
C(14)	35(1)	42(1)	55(2)	-2(2)	-8(2)	-4(1)
C(15)	21(1)	33(1)	32(1)	1(1)	-6(1)	3(1)
C(16)	35(2)	42(2)	29(1)	-3(1)	1(1)	-1(1)
C(17)	47(2)	37(2)	40(2)	-6(1)	-1(1)	-5(1)
C(18)	31(1)	35(1)	40(2)	7(1)	-4(1)	-9(1)
C(19)	25(1)	45(2)	34(2)	0(1)	1(1)	-1(1)
C(20)	25(1)	34(1)	35(2)	-7(1)	-1(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for gf106t.

	x	y	z	U(eq)
H(2)	3980(40)	-1609(18)	9463(19)	34(7)
H(1)	3430(40)	-1350(20)	8530(20)	56(9)
H(3)	2370(40)	-301(14)	10002(15)	21(5)
H(4)	1260(40)	1145(19)	7932(17)	38(8)
H(5)	410(40)	1220(20)	6419(19)	49(9)
H(6)	-1130(40)	-30(18)	5860(20)	46(9)
H(7)	-2100(40)	-1249(18)	6672(16)	39(8)
H(8)	-1010(30)	-1314(16)	9698(17)	24(7)
H(10)	-160(40)	1090(20)	9500(20)	49(9)
H(9)	-500(30)	336(16)	10186(18)	21(6)
H(11)	-1930(40)	406(18)	9472(18)	41(8)
H(12)	-3160(40)	-2280(20)	7820(20)	44(8)
H(13)	-2860(40)	-2564(19)	8792(17)	31(7)
H(14)	3200(40)	1253(17)	10056(17)	32(7)
H(15)	5100(40)	2469(19)	9651(17)	43(8)
H(16)	6400(40)	1043(18)	7553(17)	31(7)
H(17)	4660(30)	-152(17)	7994(16)	19(7)

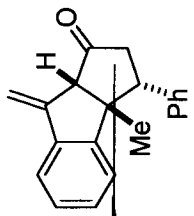
Table 6. Torsion angles [°] for gf106t.

O(1)-C(1)-C(2)-C(3)	-155.6(3)
C(12)-C(1)-C(2)-C(3)	24.9(3)
C(1)-C(2)-C(3)-C(15)	-163.7(2)
C(1)-C(2)-C(3)-C(4)	-34.7(3)
C(15)-C(3)-C(4)-C(13)	-76.2(3)
C(2)-C(3)-C(4)-C(13)	154.4(2)
C(15)-C(3)-C(4)-C(5)	50.0(3)
C(2)-C(3)-C(4)-C(5)	-79.3(3)
C(15)-C(3)-C(4)-C(12)	160.9(2)
C(2)-C(3)-C(4)-C(12)	31.6(3)
C(13)-C(4)-C(5)-C(10)	-112.2(2)
C(12)-C(4)-C(5)-C(10)	8.8(3)
C(3)-C(4)-C(5)-C(10)	120.7(2)
C(13)-C(4)-C(5)-C(6)	61.7(3)
C(12)-C(4)-C(5)-C(6)	-177.3(2)
C(3)-C(4)-C(5)-C(6)	-65.4(3)
C(10)-C(5)-C(6)-C(7)	-2.6(4)
C(4)-C(5)-C(6)-C(7)	-176.1(2)
C(5)-C(6)-C(7)-C(8)	0.4(4)
C(6)-C(7)-C(8)-C(9)	2.1(4)
C(7)-C(8)-C(9)-C(10)	-2.2(4)
C(8)-C(9)-C(10)-C(5)	-0.1(4)
C(8)-C(9)-C(10)-C(11)	176.4(3)
C(6)-C(5)-C(10)-C(9)	2.5(3)
C(4)-C(5)-C(10)-C(9)	177.1(2)
C(6)-C(5)-C(10)-C(11)	-174.6(2)
C(4)-C(5)-C(10)-C(11)	-0.1(3)
C(9)-C(10)-C(11)-C(14)	-7.2(4)
C(5)-C(10)-C(11)-C(14)	169.6(3)
C(9)-C(10)-C(11)-C(12)	174.0(2)
C(5)-C(10)-C(11)-C(12)	-9.1(3)
C(14)-C(11)-C(12)-C(1)	80.8(3)
C(10)-C(11)-C(12)-C(1)	-100.4(2)
C(14)-C(11)-C(12)-C(4)	-164.3(3)

C(10)-C(11)-C(12)-C(4)	14.5(3)
O(1)-C(1)-C(12)-C(11)	-69.0(4)
C(2)-C(1)-C(12)-C(11)	110.5(3)
O(1)-C(1)-C(12)-C(4)	175.3(3)
C(2)-C(1)-C(12)-C(4)	-5.2(3)
C(13)-C(4)-C(12)-C(11)	104.6(3)
C(5)-C(4)-C(12)-C(11)	-14.0(2)
C(3)-C(4)-C(12)-C(11)	-133.9(2)
C(13)-C(4)-C(12)-C(1)	-137.6(2)
C(5)-C(4)-C(12)-C(1)	103.8(2)
C(3)-C(4)-C(12)-C(1)	-16.1(3)
C(2)-C(3)-C(15)-C(20)	33.1(3)
C(4)-C(3)-C(15)-C(20)	-90.7(3)
C(2)-C(3)-C(15)-C(16)	-148.1(2)
C(4)-C(3)-C(15)-C(16)	88.2(3)
C(20)-C(15)-C(16)-C(17)	1.6(4)
C(3)-C(15)-C(16)-C(17)	-177.3(3)
C(15)-C(16)-C(17)-C(18)	-1.3(4)
C(16)-C(17)-C(18)-C(19)	0.3(4)
C(16)-C(17)-C(18)-Br(1)	-177.1(2)
C(17)-C(18)-C(19)-C(20)	0.3(4)
Br(1)-C(18)-C(19)-C(20)	177.68(19)
C(16)-C(15)-C(20)-C(19)	-1.1(4)
C(3)-C(15)-C(20)-C(19)	177.8(2)
C(18)-C(19)-C(20)-C(15)	0.1(4)

Symmetry transformations used to generate equivalent atoms:

Table 1, entry 1



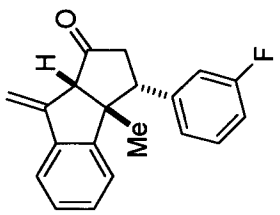

```
Current Data Parameters
NAME       Eb2-186A-Prod
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20051225
Time              19.11
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   9
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ           3.9584243 sec
RG                 128
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =========
NUC1                1H
P1                7.90 usec
PL1               0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300051 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

Table 1, entry 2



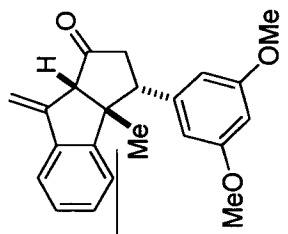

```
Current Data Parameters
NAME      EB2-202A-23-35
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051221
Time               18.49
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    6
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                   57
DW                60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ===========
NUC1                1H
P1                7.90 usec
PL1               0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Table 1, entry 3



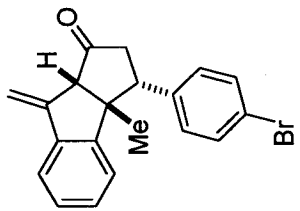

```
Current Data Parameters
NAME      EB2-198B-40-46
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051225
Time               19.17
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    7
DS                    2
SWH          8278.146 Hz
FIDRES       0.126314 Hz
AQ           3.9584243 sec
RG                  256
DW             60.400 usec
DE              6.00 usec
TE              300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ==========
NUC1                1H
P1               7.90 usec
PL1              0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300051 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

Table 1, entry 4



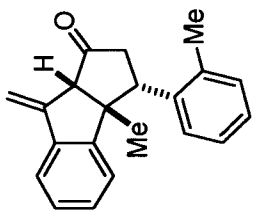

```
Current Data Parameters
NAME       EB2-178-28-44
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051223
Time                0.36
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   11
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                287.4
DW               60.400 usec
DE                6.00 usec
TE               300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 7.90 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300054 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

Table 1, entry 5



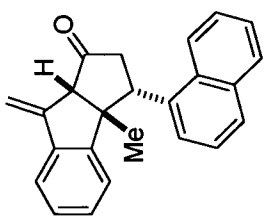

```
Current Data Parameters
NAME      EB2-196A-20-28
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051220
Time               21.29
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    6
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                   57
DW                60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 7.90 usec
PL1                0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF         400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Table 1, entry 6



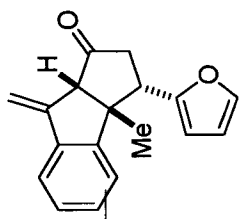

```
Current Data Parameters
NAME      EB2-182A-24-38
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051214
Time               18.12
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                   64
DW               60.400 usec
DE                6.00 usec
TE               300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 7.90 usec
PL1                0.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF         400.1300049 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Table 1, entry 7



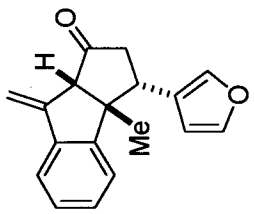

```
Current Data Parameters
NAME       eb2-204-19-31
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20051223
Time               1.08
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  11
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 362
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ==========
NUC1                1H
P1               7.90 usec
PL1              0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300056 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

Table 1, entry 8



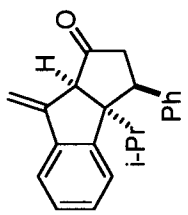

```
Current Data Parameters
NAME      EB2-176Bfr37-4
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051211
Time               16.17
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    4
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                   57
DW               60.400 usec
DE                6.00 usec
TE               300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ==========
NUC1                1H
P1               7.90 usec
PL1              0.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF         400.1300051 MHz
WDW                   EM
SSB                    0
LB               0.30 Hz
GB                     0
PC                  1.00
```

Eq 8



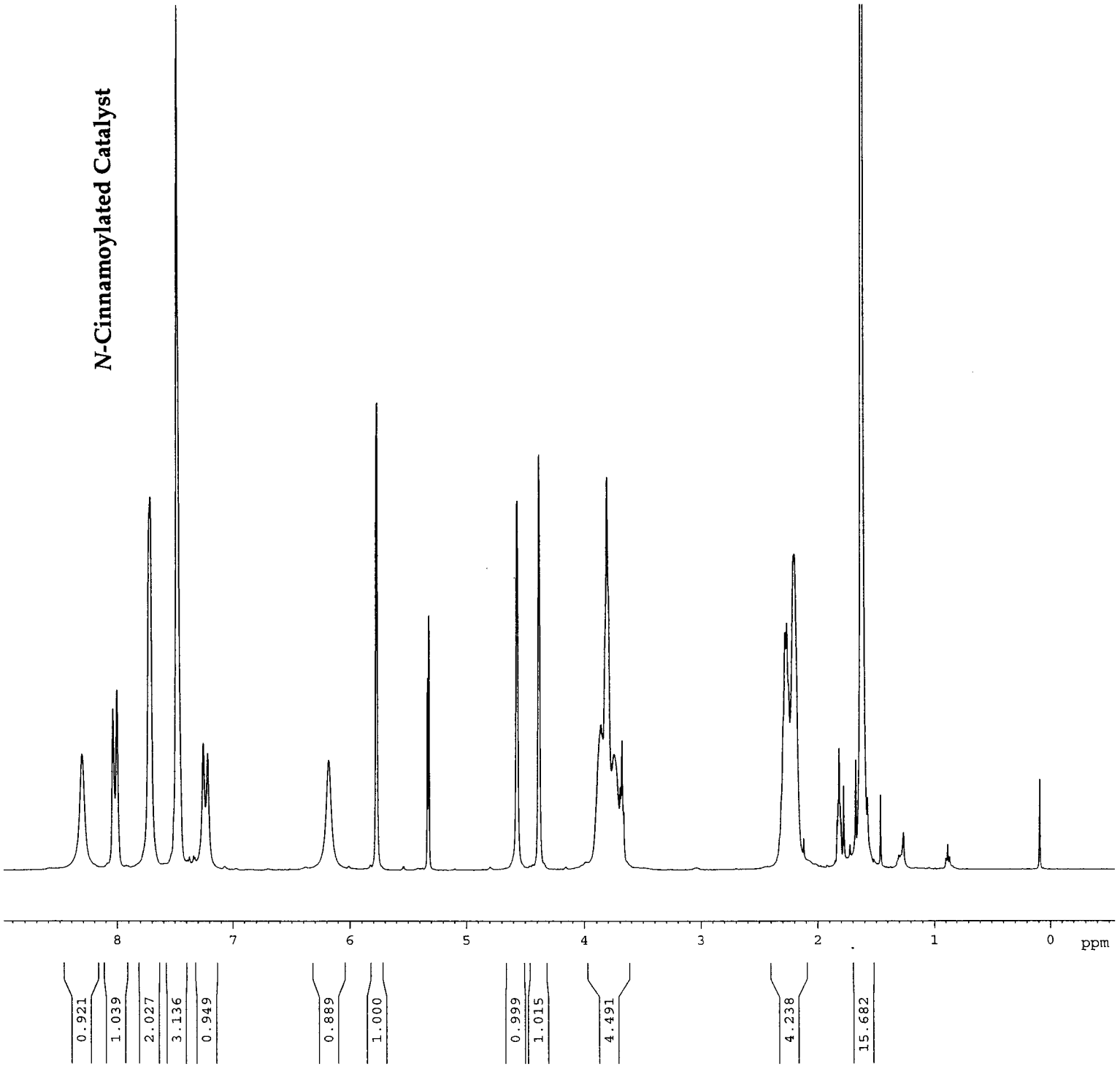

```
Current Data Parameters
NAME        EB2-210A2col
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051228
Time               18.25
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   11
DS                    2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ           3.9584243 sec
RG               322.5
DW            60.400 usec
DE             6.00 usec
TE             294.8 K
D1          1.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1              9.88 usec
PL1             3.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                32768
SF         400.1300059 MHz
WDW                  EM
SSB                   0
LB             0.30 Hz
GB                    0
PC                 1.00
```

N-Cinnamoylated Catalyst



Current Data Parameters

NAME	eb2-190
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20051217	
Time	18.16	
INSTRUM	spect	
PROBHD	5 mm QNP 1H/1	
PULPROG	zg30	
TD	65536	
SOLVENT	CD2Cl2	
NS	32	
DS	2	
SWH	8278.146	Hz
FIDRES	0.126314	Hz
AQ	3.9584243	sec
RG	101.6	
DW	60.400	usec
DE	6.00	usec
TE	293.7	K
D1	1.00000000	sec
MCREST	0.00000000	sec
MCWRK	0.01500000	sec

======== CHANNEL f1 ========

NUC1	1H	
P1	9.88	usec
PL1	3.00	dB
SFO1	400.1324710	MHz

F2 - Processing parameters

SI	32768	
SF	400.1300146	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	