Supporting Information

Brønsted Acid Catalyzed Enantioselective Addition of Hydrazones to 3-Indolylmethanols

Steffen Mader,[†] Modhu Sudan Maji,[†‡] Iuliana Atodiresei[†] and Magnus Rueping *[†#]

[†]Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

[‡]Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

[#]King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC), Thuwal 23955-6900, Saudi Arabia

Table of Contents

I. General Information

Unless noted otherwise, all commercially available reagents were used without further purification. Organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon. Solvents for chromatography were technical grade and distilled prior to use. Thin layer chromatography (TLC) was carried out on Macherey-Nagel ALUGRAM Xtra SIL G/UV F_{254}, visualized by UV irradiation. Macherey-Nagel silica gel 60 (particle size 0.063-0.2 mm) was used for column chromatography. Solvent mixtures are understood as volume/volume. ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded on VNMRS-400, VNMRS-600 or Mercury 300 spectrometer in $CDCl_3$, CD_2Cl_2 and DMSO-d_6. Carbon NMR (^{13}C) spectra were recorded using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the residual proton signals in $CDCl_3$ (δ = 7.26, 77.16), DMSO-d_6 (δ = 2.50, 39.52) or CD_2Cl_2 (δ = 5.32, 54.00). Coupling constants (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010 (column: Equity®-5, length × I.D. 30 m × 0.25 mm, df 0.25 μm, lot # 28089-U, Supelco), High resolution mass spectra (HRMS-ESI) were acquired using a ThermoFisher Scientific LTQ-Orbitrap XL. Infrared Spectra were recorded on a Perkin Elmer Spektrum 100 infrared spectrometre with a Diamant/KRS5 ATR unit. For the most significant bands the wave number $\tilde{\nu}$ is given in cm^{-1}. Signals with transmissions greater than 90% were not reported. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in a 1 dm cuvette using a sodium lamp (589 nm). The optical rotation is given in degrees per mg per ml, sample concentrations are reported in g per 100 mL. Melting points (m.p.) were recorded using a Büchi SMP-20 melting point apparatus and were not corrected. High Performance Liquid Chromatography (HPLC) was carried out on a JASCO UV-2077 Plus with a PU-2080 Plus solvent pump. Operation and analysis were under control of JASCO ChromPass software. As chiral columns for determination of enantiomeric excess the following prefabricated columns from Daicel were used: Chiralpak AD-H (250 x 4.6 mm, 5 μm), Chiralpak IA (250 x 4.6 mm, 5 μm), and Chiralcel OD-H (250 x 4.6 mm, 5 μm). Supercritical Fluid Chromatography (SFC) was carried out using a (*S,S*)-Whelk-01 column. The chiral SFC methods were calibrated with the corresponding racemic mixtures. The CD-spectrum for the product **8i** was recorded on a circular dichroism spectrometer (AVIV Model 62DS) at room temperature in acetonitrile.

II. General Procedures

General Procedure A: Preparation of Hydrazones (2a-e):

A suspension of the corresponding hydrazine hydrochloride (1.47 g, 12.0 mmol) in anhydrous THF (20 mL) was treated with triethylamine (12.0 mmol, 1.21 g) for 15 min before a solution of ethyl glyoxylate (50% in toluene, 2.45 g solution, 12.0 mmol) was added dropwise into the reaction mixture at 0 °C. The mixture was stirred for 30 min at 0 °C, then for 14 h at rt. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (SiO_2 deactivated with NEt_3, *n*-pentane:ethyl acetate 9:1 to 7:3).

General Procedure B: Preparation of Alcohols (1a-r):

The corresponding bromo compound (3 equiv.) was added slowly to a suspension of magnesium (3.5 equiv.) in dry THF under vigorous stirring. The reaction mixture was stirred for 30 min, then a solution of the corresponding 1*H*-indole-3-carboxaldehyde (1 equiv.) in dry THF was added slowly to the Grignard solution at 0 °C. The resulting mixture was stirred at 0 °C for 30 min then for 14 h at rt. Water was added to quench the reaction at 0 °C. The reaction mixture was extracted with EtOAc (3x) and the combined organic layers were dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (SiO_2 deactivated with NEt_3, *n*-pentane:ethyl acetate 9:1 to 7:3).

Alcohols **1a-r** were synthesized as above, starting from the commercially available Grignard reagent and the corresponding aldehyde.

The products are not very stable at room temperature and should be stored under an atmosphere of argon in the refrigerator.

General Procedure C: Preparation of Racemic Products:

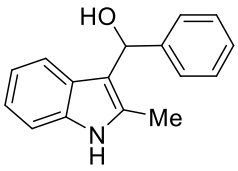
The catalyst $(PhO)_2P(O)OH$ (0.01 mmol) was added to a solution of the corresponding alcohol (0.13 mmol) and hydrazone (0.10 mmol) in dry toluene (1.5 mL). The reaction mixture was stirred for 16 h at rt. The crude product was purified by flash column chromatography (SiO_2, *n*-pentane:Et_2O 9:1 to 7:3)

General Procedure D: Preparation of Chiral Products:

A solution of catalyst **3h** (5 mol %) in toluene (1 mL) was added to a solution of the corresponding alcohol **1** (0.13 mmol) and hydrazone **2** (0.10 mmol) in toluene (1 mL) at -30 °C. The reaction mixture was stirred at -30 °C until complete conversion of the starting material (48-72 h). The crude product was purified by flash column chromatography. The enantiomeric excess was determined by HPLC or SFC analysis, using chiral stationary phases.

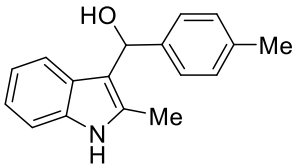
III. Characterization of Alcohols 1a-1r:

(2-Methyl-1*H*-indol-3-yl)(phenyl)methanol (1a)[1]



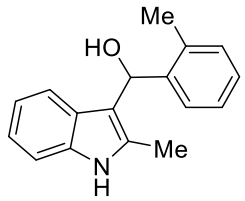
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (1.59 g, 10 mmol), bromobenzene (4.71 g, 30 mmol) and magnesium (850.5 mg, 35 mmol) using THF (100 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1a** (2.01 g, 8.45 mmol) as a yellow oil in 85% yield. **^{1}H NMR** (600 MHz, CD_2Cl_2) δ = 8.03 (s, 1H), 7.50-7.47 (m, 2H), 7.38 (dd, *J* = 7.9 Hz, 0.8, 1H), 7.34-7.31 (m, 2H), 7.27 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.24 (dd, *J* = 7.4, 0.4 Hz, 1H), 7.07 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 6.94 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.17 (s, 1H), 2.44 (s, 3H). **^{13}C NMR** (150 MHz, CD_2Cl_2) δ = 144.7, 135.8, 133.1, 128.4, 127.1, 126.2, 121.6, 119.8, 119.6, 114.6, 110.7, 69.4, 12.2. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3397, 3055, 1694, 1606, 1454, 1374, 1302, 1241, 1154, 1007, 835, 735. **EI-MS**: m/z (%) = 237.3 (M^+, 33), 220.2 (17), 159.9 (24), 131.5 (11), 117.0 (12), 105.1 (74), 82.9 (100), 77.1 (34).

(2-Methyl-1*H*-indol-3-yl)(*p*-tolyl)methanol (1b)[1a]



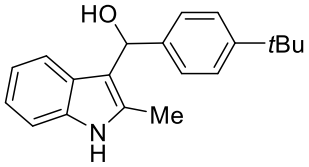
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 4-Me-phenyl bromide (2.57 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1b** (1.10 g, 4.37 mmol) as a yellow oil in 87% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.74 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.94-6.90 (m, 1H), 6.82-6.78 (m, 1H), 5.95 (d, *J* = 3.4 Hz, 1H), 5.37 (d, *J* = 3.5 Hz, 1H), 2.39 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 143.1, 135.2, 134.8, 131.8, 128.2, 126.8, 125.7, 119.8, 119.2, 118.0, 114.6, 110.2, 67.4, 20.7, 11.9. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3397, 3027, 2922, 1867, 1708, 1609, 1452, 1369, 1305, 1235, 1170, 1109, 1017, 815, 742. **EI-MS**: m/z (%) = 251.2 (M^+, 17), 234.3 (43), 232.2 (100), 217.3 (63), 188.9 (27), 157.9 (23), 146.1 (45), 119.0 (52), 90.9 (48).

(2-Methyl-1*H*-indol-3-yl)(*o*-tolyl)methanol (1c)[1a]



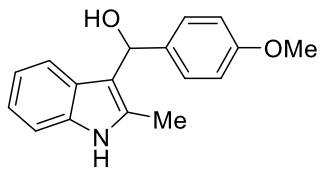
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (318.0 mg, 2.0 mmol), 2-Me-phenyl bromide (1.03 g, 6 mmol) and magnesium (170.1 mg, 7.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1c** (486 mg, 1.93 mmol) as a yellow oil in 97% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.80 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.12 (td, *J* = 7.4, 1.0 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.93-6.89 (m, 1H), 6.78-6.74 (m, 1H), 6.01 (d, *J* = 4.0 Hz, 1H), 5.28 (d, *J* = 4.0 Hz, 1H), 2.32 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 143.3, 135.1, 134.5, 133.0, 129.8, 127.1, 126.1, 126.0, 125.1, 119.7, 118.7, 118.0, 112.2, 110.3, 65.1, 18.9, 11.8. **IR** (ATR, cm^{-1}) ṽ = 3528, 3395, 3058, 2915, 1916, 1716, 1568, 1453, 1247, 992, 846, 738. **EI-MS**: m/z (%) = 251.3 (M^+, 100), 234.3 (69), 218.2 (15), 160.2 (15), 132.2 (53), 91.2 (15).

(4-(*tert*-Butyl)phenyl)(2-methyl-1*H*-indol-3-yl)methanol (1d)



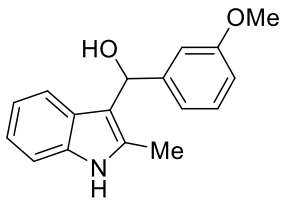
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (318.0 mg, 2.0 mmol), 4-*t*Bu-phenyl bromide (1.03 g, 6 mmol) and magnesium (170.1 mg, 7.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1d** (550 mg, 1.87 mmol) as a yellow oil in 94% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.75 (s, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.95-6.91 (m, 1H), 6.84-6.80 (m, 1H), 5.97 (d, *J* = 3.2 Hz, 1H), 5.39 (d, *J* = 3.3 Hz, 1H), 2.42 (s, 3H), 1.24 (s, 9H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 148.2, 143.2, 135.2, 131.6, 126.8, 125.5, 124.4, 119.8, 119.3, 118.0, 114.6, 110.2, 67.8, 34.1, 31.2, 11.9. **IR** (ATR, cm^{-1}) ṽ = 3502, 3397, 329, 2958, 2870, 2711, 2083, 1910, 1709, 1612, 1513, 1458, 161, 1302, 1328, 1104, 1001, 836, 741. **EI-MS**: m/z (%) = 293.3 (M^+, 93), 276.3 (100), 260.3 (40), 218.2 (15), 160.2 (20), 132.2 (17), 117.1 (12).

(4-Methoxyphenyl)(2-methyl-1*H*-indol-3-yl)methanol (1e)[1b]



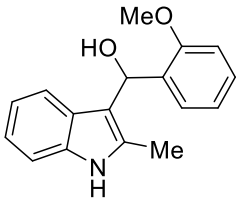
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 4-MeO-phenyl bromide (2.57 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1e** (565 mg, 2.12 mmol) as a yellow oil in 42% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.74 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.94-6.90 (m, 1H), 6.84-6.79 (m, 3H), 5.95 (d, *J* = 3.5 Hz, 1H), 5.36 (d, *J* = 3.5 Hz, 1H), 3.70 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 157.6, 138.2, 135.2, 131.8, 126.9, 126.8, 119.8, 119.2, 118.0, 114.6, 113.1, 110.2, 67.3, 55.0, 11.9. **IR** (ATR, cm^{-1}) ṽ = 3395, 2936, 1724, 1604, 1507, 1453, 1367, 1299, 1240, 1169, 1024, 831, 743. **EI-MS**: m/z (%) = 267.1 (M^+, 93), 250.3 (67), 249.3 (100), 234.2 (13), 205.3 (22), 157.9 (65), 134.9 (50), 116.9 (25), 107.9 (21), 76.8 (33).

(3-Methoxyphenyl)(2-methyl-1*H*-indol-3-yl)methanol (1f)[1b]



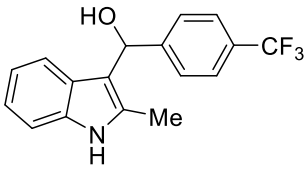
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (318.0 mg, 2.0 mmol), 3-MeO-phenyl bromide (1.03 g, 6 mmol) and magnesium (170.1 mg, 7.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1f** (501 mg, 1.87 mmol) as a yellow oil in 94% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.77 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.03 (s, 1H), 6.96-6.90 (m, 2H), 6.84-6.79 (m, 1H), 6.72 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.96 (d, *J* = 3.4 Hz, 1H), 5.45 (d, *J* = 3.5 Hz, 1H), 3.70 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 158.9, 147.9, 135.2, 132.0, 128.7, 126.8, 119.9, 119.1, 118.2, 118.1, 114.3, 111.6, 111.0, 110.3, 67.5, 54.9, 11.9. **IR** (ATR, cm^{-1}) ṽ = 3396, 2938, 2076, 1711, 1595, 1455, 1249, 1145, 1034, 862, 744, 690. **EI-MS**: m/z (%) = 267.3 (M^+, 100), 250.3 (51), 234.2 (10), 218.2 (7), 160.2 (30), 132.2 (23).

(2-Methoxyphenyl)(2-methyl-1*H*-indol-3-yl)methanol (1g)[1b]



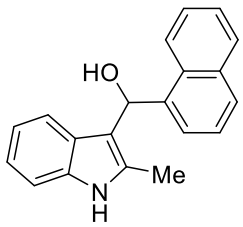
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 2-MeO-phenyl bromide (2.57 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1g** (974 mg, 3.64 mmol) as a yellow solid in 73% yield. **m.p.** 132 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.66 (s, 1H), 7.84 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.19-7.13 (m, 2H), 6.97 (td, *J* = 7.5, 0.7 Hz, 1H), 6.92-6.87 (m, 1H), 6.86-6.84 (m, 1H), 6.82-6.78 (m, 1H), 6.17 (d, *J* = 3.5 Hz, 1H), 5.21 (d, *J* = 3.5 Hz, 1H), 3.68 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 155.6, 135.0, 133.7, 132.0, 127.1, 126.9, 126.5, 119.7, 119.5, 119.3, 117.8, 113.3, 110.3, 110.2, 62.7, 55.2, 11.9. **IR** (ATR, cm^{-1}) ṽ = 3511, 3367, 1592, 1490, 1457, 1243, 998, 837, 738. **EI-MS**: m/z (%) = 267.2 (M^+, 100), 250.2 (35), 234.2 (13), 218.2 (12), 160.1 (23), 135.1 (35), 132.1 (40), 83.0 (11).

(2-Methyl-1*H*-indol-3-yl)(4-(trifluoromethyl)phenyl)methanol (1h)



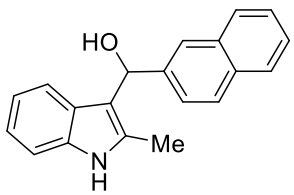
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (572.0 mg, 3.6 mmol), 4-F_3C-phenyl bromide (2.42 g, 10.8 mmol) and magnesium (305.7 mg, 12.6 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1h** (749 mg, 2.45 mmol) as a yellow solid in 68% yield. **m.p.** 82 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 10.84 (s, 1H), 7.63 (s, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.22 (dt, *J* = 8.0, 0.9 Hz, 1H), 6.93 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 6.81 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.07 (d, *J* = 3.4 Hz, 1H), 5.69 (d, *J* = 3.5 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 150.9, 135.2, 132.4, 126.5, 126.4, 124.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 271.8 Hz), 120.0, 118.8, 118.3, 113.7, 110.4, 67.1, 11.8. **^{13}C{^{19}F} NMR** (100 MHz, DMSO-d_6) δ = 150.9, 135.2, 132.4, 126.7, 126.5, 126.4, 124.6, 124.5, 120.0, 118.8, 118.3, 113.7, 110.4, 67.1, 11.8. **^{19}F NMR** (376 MHz, DMSO-d_6) δ = -60.65. **IR** (ATR, cm^{-1}) ṽ = 3394, 1703,1616, 1321,1163, 1115, 1063,1014,836, 745. **EI-MS**: m/z (%) = 305.2 (M^+, 100), 288.2 (70), 218.2 (18), 173.1 (61), 160.1 (30), 145.1 (53), 132.1 (20), 117.1 (13), 83.1 (14).

(2-Methyl-1*H*-indol-3-yl)(naphthalen-1-yl)methanol (1i)



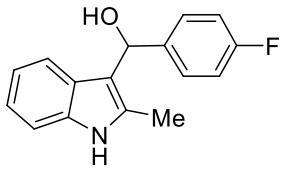
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 1-naphthyl bromide (3.11 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1i** (1.43 g, 4.99 mmol) as a yellow oil in 99% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.84 (s, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.57 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.43-7.38 (m, 1H), 7.37-7.33 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.92-6.87 (m, 1H), 6.75 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.63 (d, *J* = 4.2 Hz, 1H), 5.54 (d, *J* = 4.2 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 140.6, 135.1, 133.3, 132.8, 130.3, 128.4, 127.2, 127.0, 125.5, 125.2, 125.1, 123.7, 123.6, 119.8, 118.6, 118.2, 113.3, 110.3, 64.9, 12.0. **IR** (ATR, cm^{-1}) ṽ = 3534, 3399, 3050, 1724, 1586, 1506, 1451, 1370, 1228, 1154, 1042, 969, 864, 780, 741. **EI-MS**: m/z (%) = 287.4 (M^+, 100), 270.2 (77), 254.3 (90), 226.2 (25), 159.4 (63), 131.7 (90), 100.6 (6).

(2-Methyl-1*H*-indol-3-yl)(naphthalen-2-yl)methanol (1j)[1b]



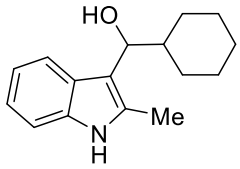
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 2-naphthyl bromide (3.11 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1j** (261 mg, 0.91 mmol) as a yellow oil in 18% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.82 (s, 1H), 8.05 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.49-7.41 (m, 3H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.93-6.89 (m, 1H), 6.79-6.75 (m, 1H), 6.17 (d, *J* = 3.1 Hz, 1H), 5.61 (d, *J* = 3.5 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 144.1, 135.6, 133.2, 132.7, 132.3, 128.2, 127.8, 127.6, 127.3, 126.3, 125.7, 125.6, 123.7, 120.3, 119.4, 118.5, 114.6, 110.7, 68.0, 12.3. **IR** (ATR, cm^{-1}) ṽ = 3542, 3394, 3050, 1687, 1611, 1455, 1363, 1304, 1227, 1153, 1116, 1010, 859, 818, 741. **EI-MS**: m/z (%) = 287.4 (M^+, 25), 269.4 (74), 253.5 (21), 226.2 (37), 157.6 (62), 146.4 (69), 131.4 (75), 127.4 (100), 116.6 (40), 77.0 (61).

(4-Fluorophenyl)(2-methyl-1*H*-indol-3-yl)methanol (1k)[1]



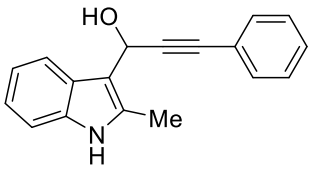
Iso-propylmagnesium chloride (2 M in hexane, 10.5 mL, 21 mmol) was added dropwise to a solution of 4-iodo-fluorobenzene (4.44 g, 20 mmol) in dry THF (15 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then 1 h at rt. A solution of 2-methyl-1*H*-indole-3-carboxaldehyde (796 mg, 5.0 mmol) in dry THF (20 mL) was added slowly to the Grignard solution at 0 °C. The resulting mixture was stirred at 0 °C for 15 min, then for 14 h at rt. Water was added to quench the reaction. The reaction mixture was extracted with Et_2O (3x25 mL) and the combined organic layer were dried over $MgSO_4$. The crude product was purified by flash chromatography (SiO_2 (NEt_3), *n*-pentane:EtOAc 8:2) to yield **1k** (1.19 g, 4.67 mmol) as a yellow solid in 93% yield. **m.p.** 137 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 10.79 (s, 1H), 7.46-7.39 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.23-7.20 (m, 1H), 7.12-7.04 (m, 2H), 6.93 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 6.81 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 5.99 (d, *J* = 3.2 Hz, 1H), 5.52 (d, *J* = 3.5 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 160.65 (d, J_{C-F} = 241.2 Hz), 142.2, 142.2, 135.2, 132.1, 127.56 (d, J_{C-F} = 7.9 Hz), 126.7, 119.9, 119.0, 118.1, 114.33 (d, J_{C-F} = 21.1 Hz), 114.2, 110.3, 67.0, 11.8. **^{19}F NMR** (376 MHz, DMSO-d_6) δ = -117.51. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3401, 3138, 3021, 1738, 1504, 1450, 1365, 1219, 1022, 831, 743. **EI-MS**: m/z (%) = 255.2 (M^+, 100), 238.2 (58), 159.6 (33), 131.7 (33), 122.9 (19), 95.1 (8), 82.9 (8).

Cyclohexyl(2-methyl-1*H*-indol-3-yl)methanol (1l)[1a]



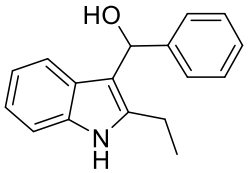
The title compound was synthesized according to general procedure B, starting from 2-methyl-1*H*-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), bromo cyclohexane (2.45 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1l** (950 mg, 3.9 mmol) as a yellow solid in 78% yield. **m.p.** 105 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.65 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.96-6.92 (m, 1H), 6.89-6.84 (m, 1H), 4.63 (d, *J* = 3.3 Hz, 1H), 4.45 (dd, *J* = 8.1, 3.3 Hz, 1H), 2.32 (s, 3H), 2.13 (d, *J* = 12.7 Hz, 1H), 1.80-1.69 (m, 2H), 1.60-1.52 (m, 2H), 1.28 (d, *J* = 12.8 Hz, 1H), 1.23-1.14 (m, 1H), 1.12-0.95 (m, 3H), 0.87-0.78 (m, 1H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 135.2, 131.7, 127.3, 119.6, 119.5, 117.8, 113.4, 110.2, 71.2, 44.3, 29.9, 29.2, 26.3, 25.8, 25.8, 12.0. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3533, 3258, 2921, 2849, 1709, 1616, 1456, 1298, 1071, 995, 889, 739, 699. **EI-MS**: m/z (%) = 243.2 (M^+, 37), 226.2 (7), 174.1 (11), 160.1 (100), 132.1 (36), 117.1 (13).

1-(2-Methyl-1*H*-indol-3-yl)-3-phenylprop-2-yn-1-ol (1m)



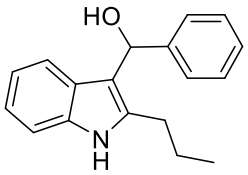
Iso-propylmagnesium chloride (2 M in hexane, 8.0 mL, 16 mmol) was added dropwise to a solution of phenyl acetylene (1.53 g, 1.65 ml, 15 mmol) in dry THF (8 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then 1 h at rt. A solution of 2-methyl-1*H*-indole-3-carboxaldehyde (796 mg, 5.0 mmol) in dry THF (20 mL) was added slowly to the Grignard solution at 0 °C. The resulting mixture was stirred at 0 °C for 15 min, then for 14 h at rt. Water was added to quench the reaction. The reaction mixture was extracted with Et_2O (3x25 mL) and the combined organic layer were dried over $MgSO_4$. The crude product was purified by flash chromatography (SiO_2 (NEt_3), *n*-pentane:EtOAc 8:2) to yield **1k** (282 mg, 1.08 mmol) as a yellow solid in 22% yield. **m.p.** 109 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 10.83 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.46-7.26 (m, 4H), 7.23 (d, J = 7.9 Hz, 1H), 6.98-6.92 (m, 1H), 6.90-6.84 (m, 1H), 5.81 (s, 1H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 134.9, 131.6, 131.0, 128.7, 127.9, 127.3, 123.4, 119.9, 118.3, 118.2, 110.4, 109.6, 92.3, 81.0, 25.1, 12.1. **IR** (ATR, cm^{-1}) ṽ = 3395, 3054, 2852, 2108, 1717, 1590, 1490, 1453, 1340, 1299, 1226, 1153, 1017, 919, 846, 744, 689. **ESI-MS**: m/z (%) = 293.2 ($[M+MeOH]^+$, 28), 244.1 ($[M-OH]^+$, 100), 214.2 (20), 202.1 (14), 102.1 (43).

(2-Ethyl-1*H*-indol-3-yl)(phenyl)methanol (1n)[1b]



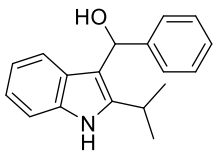
The title compound was synthesized according to general procedure B, starting from 2-ethyl-1*H*-indole-3-carboxaldehyde (600.0 mg, 3.46 mmol), bromobenzene (1.21 g, 7.71 mmol) and magnesium (218.8 mg, 9.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1n** (647 mg, 2.57 mmol) as a brown solid in 74% yield. **m.p.** 77 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.78 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.96-6.91 (m, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.01 (d, *J* = 3.3 Hz, 1H), 5.45 (d, *J* = 3.5 Hz, 1H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 146.2, 137.9, 135.4, 127.7, 126.6, 125.9, 125.8, 119.9, 119.4, 118.0, 113.6, 110.4, 67.4, 19.2, 14.6. **IR** (ATR, cm^{-1}) ṽ = 3470, 3401, 3256, 2972, 1696, 1612, 1491, 1451, 1313, 1009, 834, 730. **EI-MS**: m/z (%) = 251.3 (M^+, 100), 234.3 (58), 218.2 (22), 174.2 (53), 146.2 (34), 130.1 (10), 118.2 (12), 105.1 (25), 77.2 (14).

Phenyl(2-propyl-1*H*-indol-3-yl)methanol (1o)[1b]



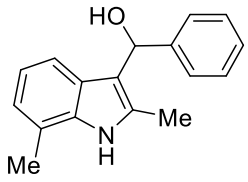
The title compound was synthesized according to general procedure B, starting from 2-propyl-1*H*-indole-3-carboxaldehyde (600.0 mg, 3.20 mmol), bromobenzene (993 mg, 6.33 mmol) and magnesium (179.7 mg, 7.39 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1o** (561 mg, 2.11 mmol) as a yellow solid in 66% yield. **m.p.** 75 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.76 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.00 (d, *J* = 3.4 Hz, 1H), 5.43 (d, *J* = 3.6 Hz, 1H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.73-1.59 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 146.1, 136.6, 135.4, 127.6, 126.6, 125.9, 125.8, 119.9, 119.4, 118.0, 114.2, 110.4, 67.4, 27.9, 22.9, 14.0. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3410, 3058, 2926, 2868, 1887, 1698, 1598, 1457, 1381, 1232, 1179, 1099, 999, 840, 742. **EI-MS**: m/z (%) = 265.3 (M^+, 100), 248.3 (56), 218.2 (39), 188.2 (53), 160.2 (27), 130.2 (13), 118.1 (13), 105.1 (26), 91.1 (11), 77.2 (15).

(2-Isopropyl-1*H*-indol-3-yl)(phenyl)methanol (1p)



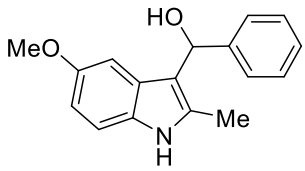
The title compound was synthesized according to general procedure B, starting from 2-isopropyl-1H-indole-3-carbaldehyde (1.59 g, 3.2 mmol), bromobenzene (1.51 g, 9.6 mmol) and magnesium (272.2 mg, 11.2 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1p** (670.0 mg, 2.525 mmol) as a yellow oil in 79% yield. **^{1}H NMR** (600MHz, DMSO-d_6): δ = 10.75 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.29-7.23 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.96-6.92 (m, 1H), 6.82-6.78 (m, 1H), 6.04 (d, *J* = 3.2 Hz, 1H), 5.45 (d, *J* =3.4 Hz, 1H), 3.44 (sept., *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 7.0 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150MHz, DMSO-d_6): δ = 146.2 (s), 141.9 (s), 135.5 (s), 127.7 (d, 2C), 126.4 (s), 125.9 (d), 125.7 (d, 2C), 119.9 (d), 119.5 (d), 118.0 (d), 112.7 (s), 110.5 (d), 67.3 (d), 25.2 (q), 22.8 (q), 22.5 (q). **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3856, 3505, 3275, 3062, 2965, 2871, 2733, 2492, 2322, 2106, 192, 1883, 1804, 1680, 1603, 1560, 1453, 1368, 1300, 1231, 1171, 1104, 1064, 1002, 917, 833, 719, 660. **EI-MS**: *m*/*z* (%) = 265.3 (M^+, 100), 250.3 (7), 249.3 (10), 248.3 (53), 232.3 (16), 222.2 (14), 188.2 (63), 160.2 (18), 144.2 (9), 118.1 (25), 105.1 (30), 77.2 (12).

(2,7-Dimethyl-1*H*-indol-3-yl)(phenyl)methanol (1q)[1a]



The title compound was synthesized according to general procedure B, starting from 2,7-dimethyl-1*H*-indole-3-carboxaldehyde (152.0 mg, 0.86 mmol), bromobenzene (254.1 mg, 1.62 mmol) and magnesium (46.0 mg, 1.89 mmol) using THF (15 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1q** (135 mg, 0.54 mmol) as a yellow oil in 61% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 10.63 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.20-7.16 (m, 1H), 7.15-7.12 (m, 1H), 6.73-6.69 (m, 2H), 5.98 (d, *J* = 3.4 Hz, 1H), 5.41 (d, *J* = 3.5 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 146.2, 134.6, 131.8, 127.7, 126.4, 125.9, 125.7, 120.5, 119.3, 118.3, 116.8, 114.8, 67.7, 16.8, 11.9. **IR** (ATR, cm^{-1}) ṽ = 3499, 3287, 1733, 1618, 1494, 1447, 1377, 1227, 1176, 1037, 997,868, 836, 784, 751, 699. **EI-MS**: m/z (%) = 251.2 (M^+, 100), 234.2 (59), 218.2 (17), 174.1 (54), 146.1 (48), 131.1 (13) 105.1 (23), 77.2 (10).

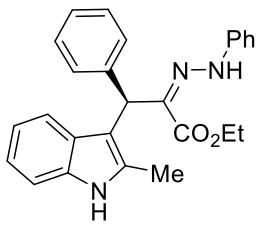
(5-Methoxy-2-methyl-1*H*-indol-3-yl)(phenyl)methanol (1r)[1b]



The title compound was synthesized according to general procedure B, starting from 5-methoxy-2-methyl-1*H*-indole-3-carboxaldehyde (193.0 mg, 1.02 mmol), bromobenzene (480.0 mg, 3.06 mmol) and magnesium (89.8 mg, 3.57 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO_2 (NEt_3), *n*-pentane:ethyl acetate 8:2) afforded **1r** (251 mg, 0.94 mmol) as a yellow oil in 92% yield. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 10.61 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.57 (dd, *J* = 8.7 Hz, 2.4, 1H), 5.97 (d, *J* = 3.5 Hz, 1H), 5.41 (d, *J* = 3.6 Hz, 1H), 3.61 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ = 152.6, 146.0, 132.9, 130.3, 127.7, 127.2, 126.0, 125.8, 114.3, 110.7, 109.2, 101.7, 67.6, 55.2, 12.0. **IR** (ATR, cm^{-1}) ṽ = 3788, 3391, 3244, 2932, 2846, 2638, 2322, 2175, 2104, 1970, 1708, 1584, 1457, 1297, 1196, 1107, 1022, 977, 918, 856, 706. **EI-MS**: m/z (%) = 267.1 (M^+, 26), 249.1 (100), 234.1 (31), 206.1 (9), 190.1 (13), 165.0 (17).

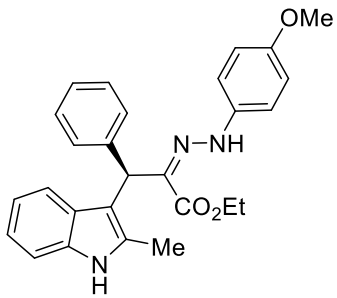
IV. Characterization of Products 4a-7a, 8a-r:

Ethyl (*R*,*Z*)-3-(2-methyl-1*H*-indol-3-yl)-3-phenyl-2-(2-phenylhydrazono)propanoate (4a)



The title compound was synthesized according to general procedure D, starting from **1a** (30.8 mg, 0.13 mmol), **2a** (19.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **4a** (28.0 mg, 0.068 mmol, 68%) as a yellow oil. 65% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 220 nm) tR = 29.1 min (minor); 35.7 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 12.16 (s, 1H), 7.79 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.34-7.31 (m, 2H), 7.29-7.25 (m, 3H), 7.23-7.18 (m, 3H), 7.10-7.06 (m, 1H), 6.99-6.93 (m, 3H), 6.92-6.88 (m, 1H), 5.81 (s, 1H), 4.21-4.15 (m, 2H), 2.37 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.9, 143.8, 142.5, 135.3, 132.4, 129.8, 129.3, 129.1, 128.7, 127.9, 125.9, 121.8, 120.9, 120.1, 119.3, 113.7, 111.8, 110.1, 60.8, 44.2, 14.2, 12.7. **IR** (ATR, cm^{-1}) ṽ = 3406, 3257, 2980, 2923, 1675, 1597, 1544, 1500, 1456, 1225, 1148, 1018, 905, 732. **EI-MS**: m/z (%) = 411.2 (M^+, 100), 319.2 (29), 281.1 (19), 245.1 (72), 220.1 (45), 131.1 (70). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{26}H_{25}O_2N_3Na]^+$: 434.1839; found 434.1839.

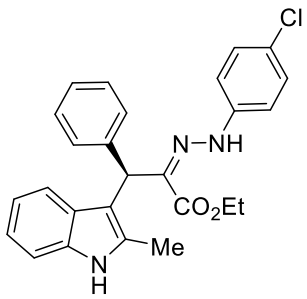
Ethyl (*R*,*Z*)-2-(2-(4-methoxyphenyl)hydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-phenylpropanoate (5a)



The title compound was synthesized according to general procedure D, starting from **1a** (30.8 mg, 0.13 mmol), **2b** (22.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **5a** (36.2 mg, 0.082 mmol, 82%) as a yellow oil. 70% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 310 nm) tR = 26.9 min (minor); 34.7 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 12.17 (s, 1H), 7.79 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.34-7.31 (m, 2H), 7.29-7.24 (m, 3H), 7.23-7.18 (m, 1H), 7.10-7.05 (m, 1H), 6.98-6.94 (m, 1H), 6.92-6.88 (m, 2H), 6.79-6.76 (m, 2H), 5.80 (s, 1H), 4.21-4.14 (m, 2H), 3.76 (s, 3H), 2.36 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 164.0, 155.0, 142.7, 137.8, 135.3, 132.3, 129.1, 128.7, 128.5, 127.9, 125.8, 120.8, 120.2, 119.3, 114.8, 114.7, 112.1, 110.1, 60.6, 55.7, 44.0, 14.2, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3404, 2935, 1739, 1671, 1510, 1453, 1366, 1217, 1149, 1025, 906, 728. **EI-**

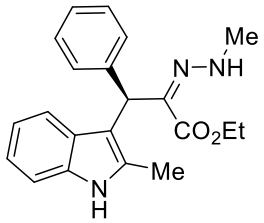
MS: m/z (%) = 441.3 (M^+, 100), 319.2 (13), 310.2 (44), 245.1 (52), 220.2 (39), 131.1 (49), 122.1 (25), 107.1 (18). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{27}H_{27}O_3N_3Na]^+$: 464.1945; found 464.1944.

Ethyl (*R*,*Z*)-2-(2-(4-chlorophenyl)hydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-phenylpropanoate (6a)



The title compound was synthesized according to general procedure D, starting from **1a** (30.8 mg, 0.13 mmol), **2c** (22.7 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **6a** (8.9 mg, 0.02 mmol, 20%) as a yellow oil. 62% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 220 nm) tR = 23.2 min (minor); 28.2 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 12.13 (s, 1H), 7.81 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.18 (m, 1H), 7.15-7.12 (m, 2H), 7.09-7.05 (m, 1H), 6.97-6.93 (m, 1H), 6.86-6.82 (m, 2H), 5.79 (s, 1H), 4.20-4.14 (m, 2H), 2.37 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.9, 142.5, 142.3, 135.4, 132.4, 130.5, 129.3, 129.1, 128.7, 127.9, 126.5, 126.0, 120.9, 120.1, 119.4, 114.8, 111.6, 110.2, 60.9, 44.2, 14.1, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3404, 2924, 1739, 1676, 1547, 1494, 1456, 1225, 1144, 1093, 1017, 822, 730. **EI-MS**: m/z (%) = 445.3 (M^+, 100), 319.2 (65), 315.2 (27), 273.2 (34), 245.2 (86), 220.2 (78), 169.1 (14), 131.1 (98). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{26}H_{24}O_2N_3ClNa]^+$: 468.1449; found 468.1454.

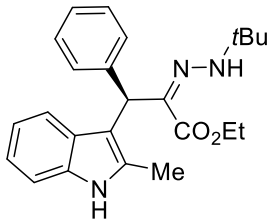
Ethyl (*R*,*Z*)-3-(2-methyl-1*H*-indol-3-yl)-2-(2-methylhydrazono)-3-phenylpropanoate (7a)



The title compound was synthesized according to general procedure D, starting from **1a** (30.8 mg, 0.13 mmol), **2d** (13.0 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, hexane / Et_2O 8: 2) afforded **7a** (14.3 mg, 0.041 mmol, 41%) as a yellow oil. 29% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, λ = 220 nm) tR = 29.4 min (minor); 37.9 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.12 (s, 1H), 7.74 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.26-7.20 (m, 5H), 7.16-7.13 (m, 1H), 7.08-7.06 (m, 1H), 6.99-6.96 (m, 1H), 5.71 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.13 (s, 3H), 2.33 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 164.0, 143.6, 135.3, 132.4, 128.9, 128.8, 127.8, 126.6, 125.5, 120.7, 120.6, 119.0,

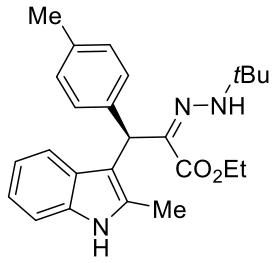
112.8, 110.0, 60.0, 43.4, 38.7, 14.3, 12.7. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3401, 3279, 2922, 1665, 1535, 1453, 1366, 1209, 1103, 1019, 908, 855, 733. **EI-MS**: m/z (%) = 349.3 (M^+, 42), 245.2 (100), 220.2 (48), 204.2 (12), 131.1 (17). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{21}H_{23}O_2N_3Na]^+$: 372.1683; found 372.1687.

Ethyl (*R*,*Z*)-2-(2-*tert*-butylhydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-phenylpropanoate (8a)



The title compound was synthesized according to general procedure D, starting from **1a** (30.8 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8a** (37.6 mg, 0.096 mmol, 96%) as a yellow oil. 93% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, λ = 220 nm) tR = 9.1 min (minor); 10.4 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.16 (s, 1H), 7.74 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.25-7.24 (m, 3H), 7.22-7.19 (m, 2H), 7.15-7.12 (m, 1H), 7.07-7.04 (m, 1H), 6.96-6.93 (m, 1H), 5.71 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.8, 143.4, 135.4, 132.2, 129.2, 128.9, 127.6, 125.8, 125.4, 120.6, 118.9, 112.9, 109.9, 59.9, 54.7, 43.7, 28.9, 14.3, 12.6. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3405, 2974, 2248, 1670, 1531, 1459, 1365, 1201, 1129, 1023, 910, 735. **EI-MS**: m/z (%) = 391.3 (M^+, 84), 334.2 (5), 261.3 (59), 245.2 (100), 220.2 (38), 131.1 (9), 57.3 (16). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{24}H_{29}O_2N_3Na]^+$: 414.2152; found 414.2158.

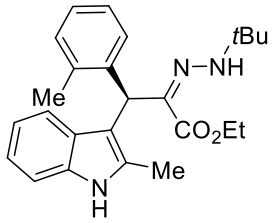
Ethyl (*R*,*Z*)-ethyl 2-(2-(*tert*-butyl)hydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-(p-tolyl)propanoate (8b)



The title compound was synthesized according to general procedure D, starting from **1b** (32.7 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8b** (40.2 mg, 0.099 mmol, 99%) as a yellow oil. 93% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 17.5 min (minor); 20.6 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.18 (s, 1H), 7.72 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97-6.93 (m, 1H), 5.69 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.18 (t, *J* =

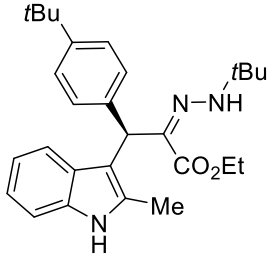
7.1 Hz, 3H), 1.15 (s, 9H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.9, 140.3, 135.3, 134.7, 132.1, 129.0, 128.9, 128.3, 125.9, 120.7, 120.6, 118.9, 113.1, 109.9, 59.8, 54.7, 43.1, 29.0, 21.1, 14.3, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3404, 2972, 2926, 1670, 1525, 1459, 1207, 1129, 1024, 754. **EI-MS**: m/z (%) = 405.2 (M^+, 100), 274.2 (23), 259.1 (70), 234.9 (7). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{25}H_{31}O_2N_3Na]^+$: 428.2309; found 428.2296. **$[\alpha]_D^{rt}$**: -29.2 (*c* 1.5, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-*tert*-butylhydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-o-tolylpropanoate (8c)



The title compound was synthesized according to general procedure D, starting from **1c** (32.7 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8c** (34.1 mg, 0.084 mmol, 84%) as a yellow oil. 97% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 8.0 min (minor); 9.7 min (major). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.03 (s, 1H), 7.73 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.14-6.95 (m, 5H), 5.71 (s, 1H), 4.08 (qd, *J* = 7.1, 1.6 Hz, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.5, 141.6, 136.2, 135.3, 132.2, 129.8, 129.5, 129.0, 125.7, 125.4, 125.2, 120.5, 120.2, 119.0, 111.9, 109.9, 59.8, 54.6, 41.8, 28.8, 19.9, 14.2, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3405, 2970, 2249, 1669, 1536, 1458, 1368, 1299, 1201, 1129, 1025, 909, 736, 625. **EI-MS**: m/z (%) = 405.2 (M^+, 100), 348.2 (5), 274.4 (16), 259.0 (72), 234.1 (12), 216.8 (11). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{25}H_{31}O_2N_3Na]^+$: 428.2309; found 428.2294. **$[\alpha]_D^{rt}$**: -64.2 (*c* 2.04, $CHCl_3$).

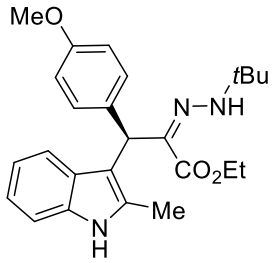
Ethyl (*R*,*Z*)-2-(2-*tert*-butylhydrazono)-3-(4-*tert*-butylphenyl)-3-(2-methyl-1*H*-indol-3-yl)propanoate (8d)



The title compound was synthesized according to general procedure D, starting from **1d** (38.1 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8d** (34.2 mg, 0.076 mmol, 76%) as a yellow oil. 95% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) tR = 16.2 min (major); 20.5 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.14 (s, 1H), 7.71 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.25-7.22 (m, 3H), 7.18-7.16 (m, 2H), 7.07-7.04 (m, 1H), 6.97-6.93 (m, 1H), 5.69 (s, 1H), 4.10

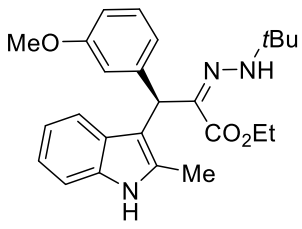
(q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.29 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.8, 148.1, 140.3, 135.4, 132.1, 128.9, 128.7, 125.9, 124.4, 120.8, 120.6, 118.8, 113.2, 109.9, 59.8, 54.7, 43.2, 34.4, 31.6, 28.9, 14.3, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3403, 2964, 1669, 1527, 1459, 1364, 1299, 1192, 1126, 1022, 910, 791, 736. **EI-MS**: m/z (%) = 447.5 (M^+, 42), 317.4 (44), 301.3 (100), 276.3 (21), 246.2 (9), 57.3 (14). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+$ = $[C_{28}H_{37}O_2N_3Na]^+$: 470.2778; found 470.2782. **$[\alpha]_D^{rt}$**: -33.6 (*c* 1.50, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(4-methoxyphenyl)-3-(2-methyl-1*H*-indol-3-yl)propanoate (8e)



The title compound was synthesized according to general procedure D, starting from **1e** (34.8 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8e** (33.7 mg, 0.080 mmol, 80%) as a yellow oil. 90% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 23.0 min (minor); 32.6 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.16 (s, 1H), 7.74 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08-7.04 (m, 1H), 6.97-6.93 (m, 1H), 6.79-6.75 (m, 2H), 5.66 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.33 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.15 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.8, 157.5, 135.6, 135.3, 132.1, 130.0, 128.8, 126.0, 120.6, 120.6, 118.9, 113.1, 112.9, 109.9, 59.8, 55.3, 54.7, 42.8, 28.9, 14.3, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3402, 3266, 2970, 1883, 1670, 1610, 1517, 1458, 1367, 1299, 1179, 1030, 753. **EI-MS**: m/z (%) = 421.2 (M^+, 100), 291.8 (9), 274.7 (74), 250.0 (10). **HRMS (ESI)**: m/z: calcd. for $[M+H]^+$ = $[C_{25}H_{32}O_3N_3]^+$: 422.2438; found 422.2427. **$[\alpha]_D^{rt}$**: -42.2 (*c* 1.18, $CHCl_3$).

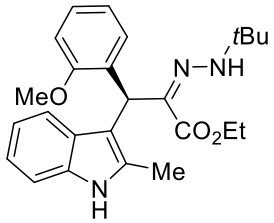
Ethyl (*R*,*Z*)-2-(2-*tert*-butylhydrazono)-3-(3-methoxyphenyl)-3-(2-methyl-1*H*-indol-3-yl)propanoate (8f)



The title compound was synthesized according to general procedure D, starting from **1f** (34.8 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8f** (35.9 mg, 0.085 mmol, 85%) as a yellow oil. 96% ee. **HPLC** (OD-H, *n*-

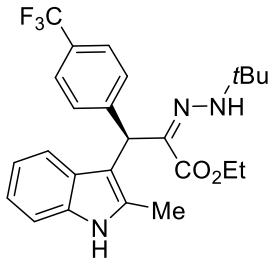
hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm) tR = 11.8 min (major); 15.6 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.19 (br s, 1H), 7.73 (br s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.23 (dt, *J* =8.0 & 0.8 Hz, 1H), 7.13 (t, *J* = 8.1 Hz, 1H), 7.07-7.03 (m, 1H), 6.97-6.93 (m, 1H), 6.86-6.83 (m, 2H), 6.72-6.69 (m, 1H), 5.70 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 2.33 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.8, 159.2, 145.2, 135.3, 132.2, 128.9, 128.4, 125.6, 121.8, 120.6, 120.6, 118.9, 115.0, 112.9, 111.0, 109.9, 59.9, 55.3, 54.7, 43.6, 29.0, 14.3, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3402, 2970, 1668, 1597, 1530, 1457, 1194, 1040, 909, 736. **EI-MS**: m/z (%) = 421.4 (M^+, 54), 291.3 (39), 275.2 (100), 250.2 (29), 131.2 (6), 57.3 (7). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+$ = $[C_{25}H_{31}O_3N_3Na]^+$: 444.2258; found 444.2265. **$[\alpha]_D^{rt}$**: -26.3 (*c* 1.50, $CHCl_3$).

Ethyl (*S*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(2-methoxyphenyl)-3-(2-methyl-1*H*-indol-3-yl)propanoate (8g)



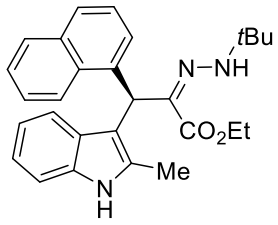
The title compound was synthesized according to general procedure D, starting from **1g** (34.8 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8g** (26.5 mg, 0.063 mmol, 63%) as a yellow solid. **m.p.** 106 °C. 84% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 14.2 min (minor); 18.8 min (major).**^{1}H NMR** (600 MHz, $CDCl_3$) δ = 9.89 (s, 1H), 7.78 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.30-7.25 (m, 1H), 7.20-7.16 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.02-6.98 (m, 1H), 6.88-6.84 (m, 1H), 6.80 (td, *J* = 7.5, 1.0 Hz, 1H), 5.89 (s, 1H), 4.09 (qq, *J* = 10.9, 7.1 Hz, 2H), 3.82 (s, 3H), 2.38 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.7, 156.8, 135.3, 132.2, 131.9, 130.0, 129.5, 126.7, 126.4, 120.7, 120.4, 119.8, 118.9, 111.7, 109.9, 109.8, 59.6, 55.7, 54.3, 38.7, 28.8, 14.2, 12.5. **IR** (ATR, cm^{-1}) ṽ = 3401, 2968, 1669, 1538, 1457, 1184, 1123, 1026, 742. **EI-MS**: m/z (%) = 421.6 (M^+, 87), 348.8 (6), 290.7 (34), 274.5 (72), 216.4 (14). **HRMS (ESI)**: m/z: calcd. for $[M+H]^+$ = $[C_{25}H_{32}O_3N_3]^+$: 422.2438; found 422.2426. **$[\alpha]_D^{rt}$**: -142.6 (*c* 1.29, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-(4-(trifluoro-methyl)phenyl)propanoate (8h)



The title compound was synthesized according to general procedure D, starting from **1h** (39.7 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8h** (43.0 mg, 0.094 mmol, 94%) as a yellow oil. 90% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm) tR = 12.7 min (minor); 13.9 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.21 (s, 1H), 7.80 (s, 1H), 7.49-7.44 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.25-7.28 (m, 1H), 7.11-7.07 (m, 1H), 6.99-6.95 (m, 1H), 5.73 (s, 1H), 4.16-4.06 (m, 2H), 2.35 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.6, 147.6, 135.4, 132.4, 129.5, 128.6, 127.7 (q, J_{C-F} = 32.0 Hz), 125.0, 124.4 (q, J_{C-F} = 3.6 Hz), 120.9, 120.4, 119.2, 111.9, 110.1, 60.0, 54.8, 43.7, 28.9, 14.3, 12.5. **^{19}F NMR** (564 MHz, $CDCl_3$) δ = -62.12. **IR** (ATR, cm^{-1}) ṽ = 3400, 2973, 1736, 1669, 1531, 1459, 1320, 1117, 1019, 909, 736. **EI-MS**: m/z (%) = 458.9 (M^+, 100), 328.5 (24), 313.6 (40), 286.8 (20). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+$ = $[C_{25}H_{28}O_2N_3F_3Na]^+$: 482.2026; found 482.2017. **$[\alpha]_D^{rt}$**: -61.9 (*c* 1.68, $CHCl_3$).

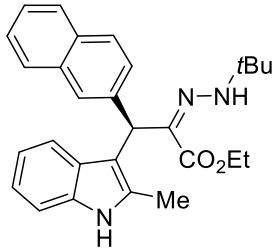
Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-(naphthalen-1-yl) propanoate (8i)



The title compound was synthesized according to general procedure D, starting from **1i** (37.4 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8i** (28.2 mg, 0.064 mmol, 64%) as a yellow oil. 98% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 13.7 min (minor); 16.9 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 9.93 (s, 1H), 7.96-7.91 (m, 1H), 7.82-7.78 (m, 1H), 7.74 (s, 1H), 7.67-7.63 (m, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.41-7.35 (m, 2H), 7.27-7.22 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.27 (s, 1H), 4.13-4.05 (m, 2H), 2.22 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.80 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.4, 139.1, 135.3, 133.9, 132.5, 132.1, 129.5, 128.6, 126.6, 126.5, 125.7, 125.5, 125.2, 124.8, 124.8, 120.6, 120.1, 119.2, 112.1, 110.0, 59.9, 54.5, 41.3, 28.6, 14.3, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3406, 2970, 1669, 1534, 1457, 1300, 1203, 1129, 1026, 755. **EI-MS**: m/z (%) = 441.3 (M^+, 100), 311.4

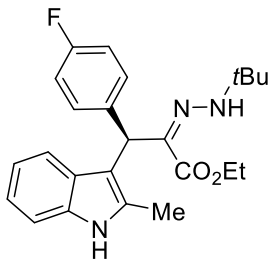
(60) 294.9 (90), 279.8 (25), 268.8 (31), 254.9 (46), 226.0 (9). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{28}H_{31}O_2N_3Na]^+$: 464.2309; found 464.2296. **$[\alpha]_D^{rt}$**: -149.6 (*c* 1.38, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(2-methyl-1*H*-indol-3-yl)-3-(naphthalen-2-yl) propanoate (8j)



The title compound was synthesized according to general procedure D, starting from **1j** (37.4 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8j** (40.3 mg, 0.091 mmol, 91%) as a yellow oil. 96% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 24.0 min (minor); 32.9 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.24 (s, 1H), 7.80-7.76 (m, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.69-7.66 (m, 1H), 7.63 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.41-7.37 (m, 2H), 7.28-7.25 (m, 1H), 7.10-7.05 (m, 1H), 6.96-6.92 (m, 1H), 5.87 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.9, 141.1, 135.4, 133.4, 132.4, 132.0, 128.9, 128.8, 128.0, 127.5, 126.8, 126.7, 125.6, 125.5, 125.0, 120.7, 120.5, 119.0, 112.7, 110.0, 59.9, 54.7, 43.7, 29.0, 14.4, 12.7. **IR** (ATR, cm^{-1}) ṽ = 3405, 3265, 3052, 2973, 1670, 1530, 1459, 1367, 1205, 1024, 753. **EI-MS**: m/z (%) = 441.3 (M^+, 72), 310.4 (13), 295.2 (100), 270.8 (7). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{28}H_{31}O_2N_3Na]^+$: 464.2309; found 464.2295. **$[\alpha]_D^{rt}$**: -14.8 (*c* 1.13, $CHCl_3$).

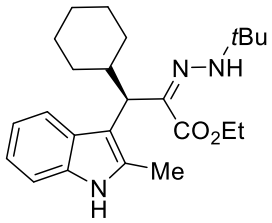
Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(4-fluorophenyl)-3-(2-methyl-1*H*-indol-3-yl) propanoate (8k)



The title compound was synthesized according to general procedure D, starting from **1k** (33.2 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8k** (31.1 mg, 0.076 mmol, 76%) as a yellow oil. 95% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 17.6 min (minor); 20.0 min (major). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.16 (s, 1H), 7.76 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.22-7.16 (m, 2H), 7.07 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 6.96 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.93-6.86 (m, 2H), 5.66 (s, 1H), 4.14-4.05 (m, 2H), 2.34 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.7, 161.1 (d, J_{C-F} = 242.7 Hz),

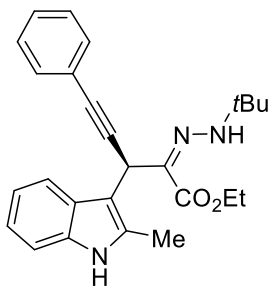
139.0, 135.4, 132.1, 130.6 (d, J_{C-F} = 5.0 Hz), 128.7, 125.6, 120.8, 120.4, 119.0, 114.2 (d, J_{C-F} = 21.0 Hz), 112.7, 110.0, 59.9, 54.7, 43.1, 28.9, 14.3, 12.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -118.83. **IR** (ATR, cm^{-1}) ṽ = 3401, 3266, 2971, 2250, 1887, 1668, 1603, 1514, 1457, 1369, 1210, 1024, 910, 738, 606. **EI-MS**: m/z (%) = 409.1 (M^+, 87), 278.5 (17), 263.0 (100), 236.6 (13). **HRMS (ESI)**: m/z: calcd. for $[M+H]^+ = [C_{24}H_{29}O_2N_3F]^+$: 410.2238; found 410.2228. **$[\alpha]_D^{rt}$**: -72.1 (*c* 1.17, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-cyclohexyl-3-(2-methyl-1*H*-indol-3-yl)propanoate (8l)



The title compound was synthesized according to general procedure D, starting from **1l** (31.6 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8l** (37.3 mg, 0.094 mmol, 94%) as a yellow oil. 93 % ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 7.7 min (minor); 8.3 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.08 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.65 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 4.13-4.01 (m, 2H), 3.82 (d, *J* = 10.9 Hz, 1H), 2.51 (ddd, *J* = 19.0, 10.9, 3.0 Hz, 1H), 2.43 (s, 3H), 2.14-2.07 (m, 1H), 1.77-1.71 (m, 1H), 1.67-1.60 (m, 1H), 1.60-1.52 (m, 1H), 1.36 (s, 9H), 1.34-1.26 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.18-1.10 (m, 2H), 0.97-0.88 (m, 1H), 0.80-0.72 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 164.2, 135.4, 131.7, 128.5, 125.0, 120.8, 120.5, 118.5, 112.8, 109.9, 59.7, 54.5, 44.6, 38.6, 33.0, 31.6, 29.2, 27.0, 26.8, 26.6, 14.4, 12.4. **IR** (ATR, cm^{-1}) ṽ = 3402, 2922, 2850, 1666, 1528, 1455, 1363, 1299, 1263, 1194, 1142, 1023, 909, 801, 735. **EI-MS**: m/z (%) = 397.4 (M^+, 58), 314.3 (100), 267.3 (11), 241.2 (9), 195.2 (16), 184.2 (19), 169.2 (16), 144.2 (16), 86.3 (13), 57.3 (24). **HRMS (ESI)**: m/z: calcd. for $[M+H]^+ = [C_{24}H_{36}O_2N_3]^+$: 398.2802; found 398.2798. **$[\alpha]_D^{rt}$**: -75.4 (*c* 1.40, $CHCl_3$).

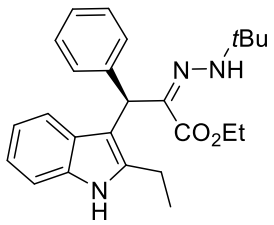
Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(2-methyl-1*H*-indol-3-yl)-5-phenylpent-4-ynoate (8m)



The title compound was synthesized according to general procedure D, starting from **1m** (34.0 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8m** (9.0 mg,

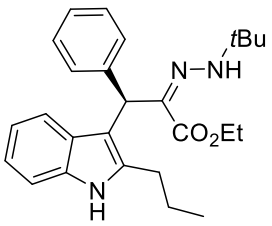
0.022 mmol, 22%) as a yellow oil. 86% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 33.6 min (major); 36.5 min (minor). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.15 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.73 (s, 1H), 7.43-7.40 (m, 2H), 7.28-7.22 (m, 3H), 7.10-7.03 (m, 2H), 5.47 (s, 1H), 4.21-4.10 (m, 2H), 2.55 (s, 3H), 1.33 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.0, 135.2, 131.9, 131.7, 128.2, 128.0, 127.5, 124.6, 123.0, 121.0, 120.3, 119.2, 110.4, 110.0, 90.4, 82.3, 60.1, 55.0, 32.2, 29.0, 14.6, 12.6. **IR** (ATR, cm^{-1}) ṽ = 3399, 3262, 3054, 2969, 2242, 1886, 1671, 1531, 1455, 1373, 1191, 1026, 911, 742, 611. **EI-MS**: m/z (%) = 415.5 (M^+, 75), 358.3 (13), 312.7 (22), 284.9 (27), 268.1 (100), 243.8 (85). **HRMS (ESI)**: m/z: calcd. for $[M+H]^+ = [C_{26}H_{30}O_2N_3]^+$: 416.2333; found 416.2329. **$[\alpha]_D^{rt}$**: -7.9 (*c* 0.45, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(2-ethyl-1*H*-indol-3-yl)-3-phenylpropanoate (8n)



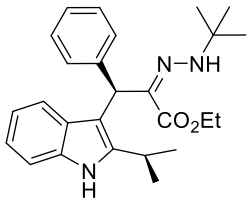
The title compound was synthesized according to general procedure D, starting from **1n** (32.7 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8n** (40.5 mg, 0.10 mmol, 99%) as a yellow oil. 98% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 9.7 min (minor); 11.8 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.17 (s, 1H), 7.81 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.28-7.23 (m, 3H), 7.23-7.19 (m, 2H), 7.16-7.12 (m, 1H), 7.09-7.05 (m, 1H), 6.97-6.93 (m, 1H), 5.73 (s, 1H), 4.15-4.05 (m, 2H), 2.82 (dq, *J* = 15.2, 7.6 Hz, 1H), 2.75 (dq, *J* = 15.2, 7.6 Hz, 1H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.8, 143.6, 137.9, 135.4, 129.1, 128.8, 127.5, 125.8, 125.4, 120.9, 120.6, 118.9, 112.0, 110.0, 59.9, 54.7, 43.6, 28.9, 19.8, 14.3, 14.2. **IR** (ATR, cm^{-1}) ṽ = 3405, 3266, 3056, 2971, 2248, 1883, 1668, 1534, 1455, 1369, 1314, 1201, 1128, 1023, 910, 735, 629. **EI-MS**: m/z (%) = 405.4 (M^+, 37), 259.2 (100), 234.2 (34), 218.2 (18), 145.1 (15), 57.2 (13). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{25}H_{31}O_2N_3Na]^+$: 428.2309; found 428.2299. **$[\alpha]_D^{rt}$**: -57.5 (*c* 1.74, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-phenyl-3-(2-propyl-1*H*-indol-3-yl)propanoate (8o)



The title compound was synthesized according to general procedure D, starting from **1o** (34.5 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8o** (41.2 mg, 0.098 mmol, 98%) as a yellow oil. 96% ee. **HPLC** (AD-H, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 9.7 min (minor); 13.6 min (major). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.17 (s, 1H), 7.79 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.28-7.23 (m, 3H), 7.23-7.19 (m, 2H), 7.16-7.12 (m, 1H), 7.09-7.05 (m, 1H), 6.96-6.92 (m, 1H), 5.72 (s, 1H), 4.15-4.06 (m, 2H), 2.79 (dt, *J* = 15.5, 7.7 Hz, 1H), 2.69 (dt, *J* = 14.9, 7.4 Hz, 1H), 1.65-1.56 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.8, 143.6, 136.6, 135.4, 129.1, 128.8, 127.5, 125.8, 125.4, 121.0, 120.6, 118.8, 112.6, 110.0, 59.8, 54.7, 43.7, 28.9, 28.7, 23.1, 14.3, 14.2. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3406, 2967, 2872, 2249, 1728, 1668, 1532, 1457, 1369, 1201, 1128, 1024, 910, 735, 627. **EI-MS**: m/z (%) = 419.5 (M^+, 45), 273.3 (100), 261.3 (78), 248.3 (34), 218.2 (27), 159.2 (15), 57.2 (16). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+$ = $[C_{26}H_{33}O_2N_3Na]^+$: 442.2465; found 442.2462. **$[\alpha]_D^{rt}$**: -42.6 (*c* 1.86, $CHCl_3$).

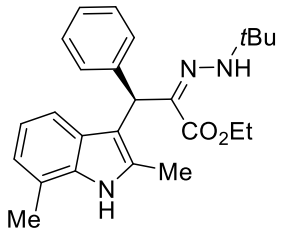
Ethyl (*R*,*Z*)-2-(2-(*tert*-Butyl)hydrazinyliden)-3-(2-isopropyl-1*H*-indol-3-yl)-3-phenyl propanoat (8p)



The title compound was synthesized according to general procedure D, starting from **1p** (34.5 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 7: 3) afforded **8p** (41.5 mg, 0.099 mmol, 99%) as a yellow oil. 70% ee. **HPLC** (IA, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 7.3 min (minor); 10.2 min (major). **^{1}H NMR** (600MHz, $CDCl_3$): *δ* = 10.17 (s, 1H), 7.84 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.25-7.18 (m, 4H), 7.15-7.11 (m, 1H), 7.09-7.04 (m, 1H), 6.95-6.91 (m, 1H), 5.75 (s, 1H), 4.16-4.04 (m, 2H), 3.40 (sept., *J* = 7.0 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.13 (s, 9H). **^{13}C NMR** (151MHz, $CDCl_3$): *δ* = 163.8, 143.6, 141.6, 135.3, 129.2, 128.7, 127.5, 125.8, 125.4, 121.2, 120.6, 118.9, 111.0, 110.1, 59.9, 54.7, 43.6, 28.9, 25.4, 23.4, 22.2, 14.3. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3414, 3270, 3056, 2969, 2248, 1882,

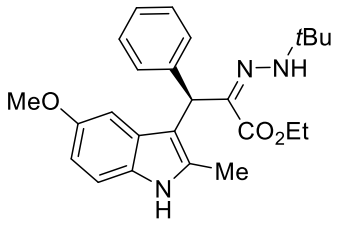
1666, 1532, 1458, 1370, 1300, 1204, 1130, 1024, 910, 733, 639. **EI-MS:** *m*/*z* (%) = 419.5 (M^+, 84), 330.3 (33), 273.3 (100), 261.3 (76), 248.3 (68), 232.2 (24), 218.2 (23), 158.2 (22), 57.2 (24). **HRMS (ESI):** *m*/*z*: calcd. for $[M+Na]^+ = [C_{26}H_{33}N_3NaO_2]^+$: 442.2465; found: 442.2466. **[*α*]$_D^{rt}$**: −44.2 (*c* 1.87, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(2,7-dimethyl-1*H*-indol-3-yl)-3-phenylpropanoate (8q)



The title compound was synthesized according to general procedure D, starting from **1q** (32.7 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8q** (32.1 mg, 0.079 mmol, 79%) as a yellow oil. 89% ee. **SFC** (WHELK-01 column, 5% MeOH/CO_2, flow rate = 4 mL/min, λ = 250 nm) tR = 7.5 min (major); 8.9 min (minor). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.17 (s, 1H), 7.67 (s, 1H), 7.39-7.33 (m, 1H), 7.26-7.18 (m, 4H), 7.16-7.10 (m, 1H), 6.90-6.96 (m, 2H), 5.72 (s, 1H), 4.11 (qd, *J* = 7.1, 1.9 Hz, 2H), 2.47 (s, 3H), 2.37 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.8, 143.5, 134.8, 131.9, 129.2, 128.4, 127.5, 125.8, 125.4, 121.4, 119.1, 119.0, 118.5, 113.4, 59.9, 54.7, 43.7, 29.0, 16.7, 14.4, 12.7. **IR** (ATR, cm^{-1}) ṽ = 3378, 2963, 2925, 2322, 1891, 1647, 1524, 1453, 1366, 1198, 1022, 784, 739, 702. **EI-MS**: m/z (%) = 405.4 (M^+, 36), 259.2 (100), 234.2 (26), 145.1 (18). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+ = [C_{25}H_{31}O_2N_3Na]^+$: 428.2309; found 428.2308. **[*α*]$_D^{rt}$**: -55.2 (*c* 1.36, $CHCl_3$).

Ethyl (*R*,*Z*)-2-(2-(*tert*-butyl)hydrazono)-3-(5-methoxy-2-methyl-1*H*-indol-3-yl)-3-phenylpropanoate (8r)



The title compound was synthesized according to general procedure D, starting from **1r** (34.8 mg, 0.13 mmol), **2e** (17.2 mg, 0.10 mmol) and **3h** (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et_2O 8: 2) afforded **8r** (41.8 mg, 0.099 mmol, 99%) as a yellow oil. 90% ee. **SFC** (WHELK-01 column, 5% MeOH/CO_2, flow rate = 4 mL/min, λ = 250 nm) tR = 10.7 min (major); 12.0 min (minor). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.15 (s, 1H), 7.63 (s, 1H), 7.26-7.20 (m, 4H), 7.16-7.10 (m, 2H), 6.91 (d, *J* = 2.2 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.2 Hz, 1H), 5.66 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 2.30 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H),

1.11 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 163.8, 153.6, 143.3, 133.1, 130.5, 129.5, 129.2, 127.6, 126.0, 125.5, 112.8, 110.5, 110.3, 103.1, 59.9, 56.1, 54.7, 43.9, 28.9, 14.3, 12.7. **IR** (ATR, cm^{-1}) $\tilde{\nu}$ = 3403, 2970, 1669, 1449, 1205, 1123, 1028, 910, 720. **EI-MS**: m/z (%) = 421.3 (M^+, 54), 275.2 (100), 261.3 (37), 250.2 (34), 218.2 (11), 161.2 (21). **HRMS (ESI)**: m/z: calcd. for $[M+Na]^+$ = $[C_{25}H_{31}O_3N_3Na]^+$: 444.2258; found 444.2254. **$[\alpha]_D^{rt}$**: -39.4 (*c* 1.71, $CHCl_3$).

V. Determination of the absolute configuration

The structure of product **8i** was confirmed by single-crystal X-ray analysis. However, the values of the Flack parameter and standard uncertainty did not allow an unambiguous determination of the absolute configuration. As an alternative, CD-spectroscopy was considered and the recorded and theoretically calculated (TD-DFT/B3LYP/6-31G*//B3LYP/6-31G*) CD-spectra of compound **8i** were analyzed (Figure 1).[2,3] Since the measured spectrum resembles the spectrum calculated for the (*R*)-enantiomer, we conclude that the absolute configuration of the compound present in our sample is (*R*).

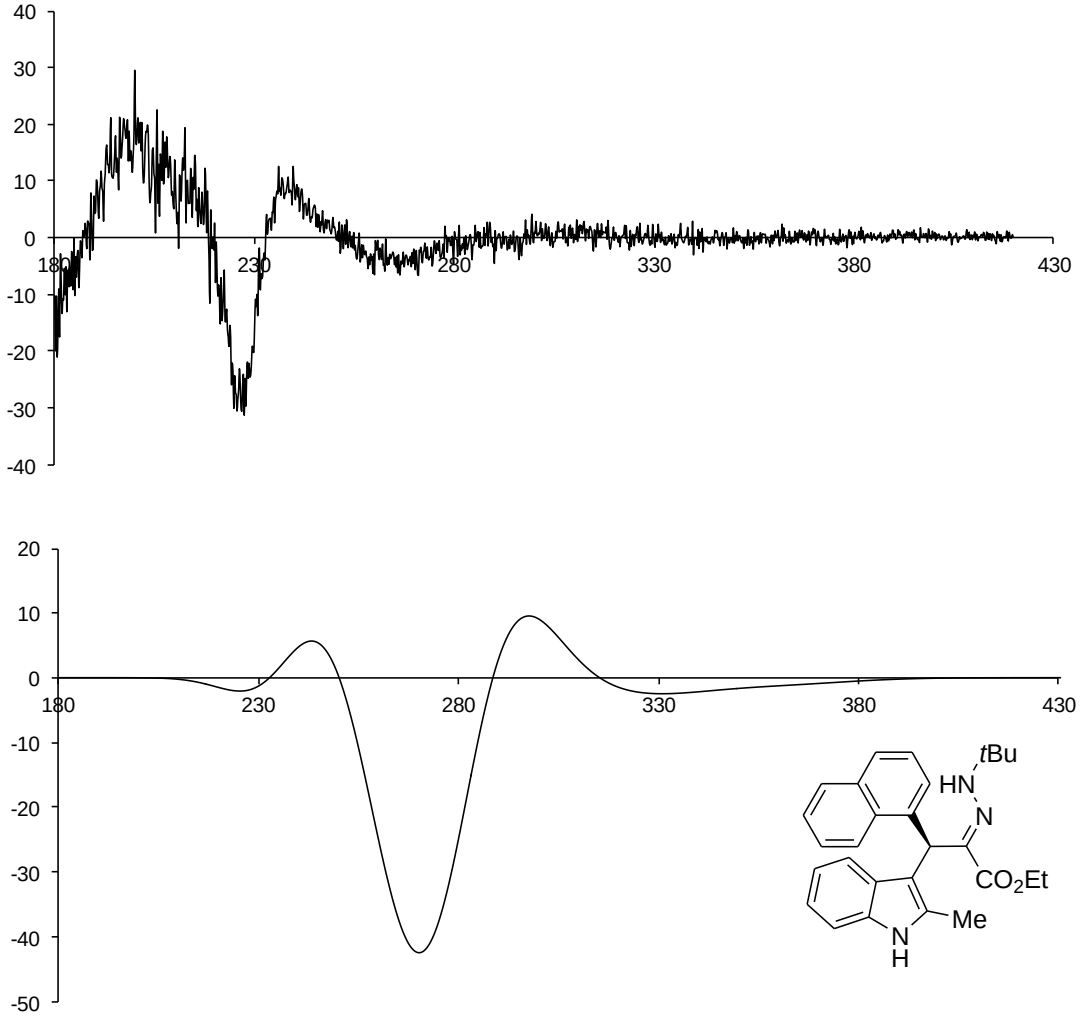


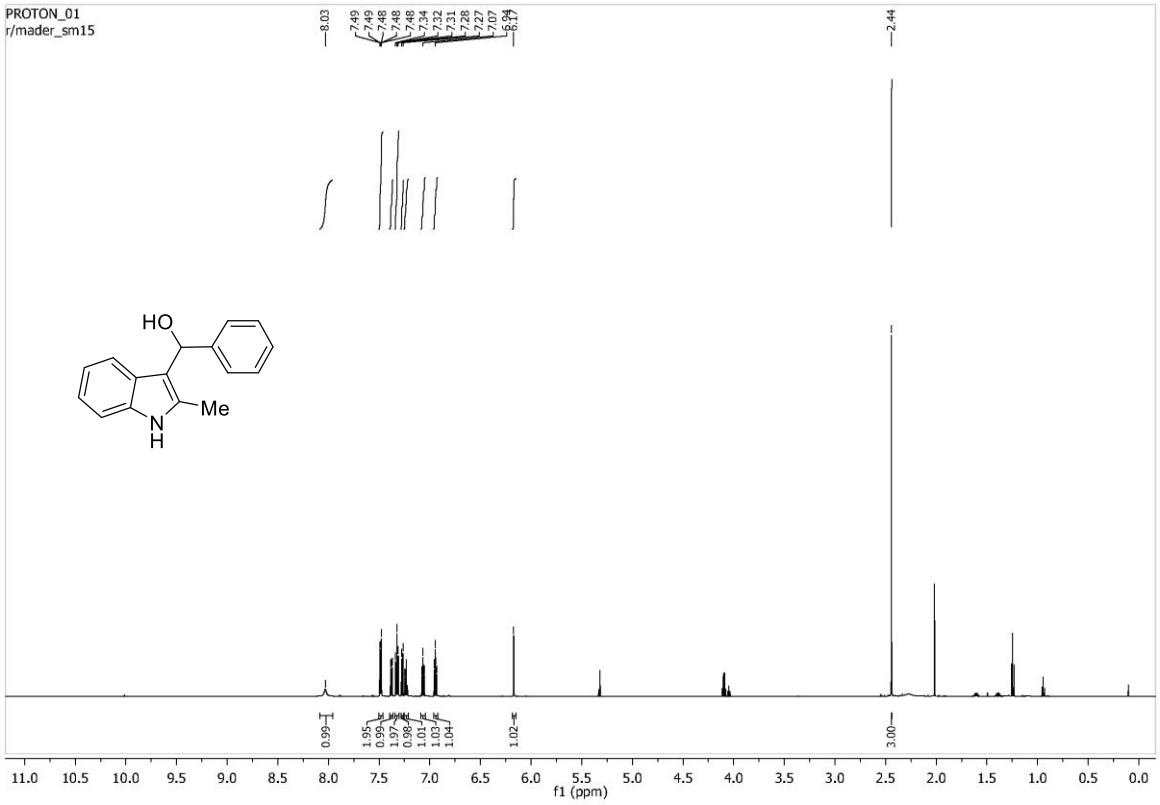
Figure 1. Recorded and calculated CD-spectra for **8i**.

VI. References:

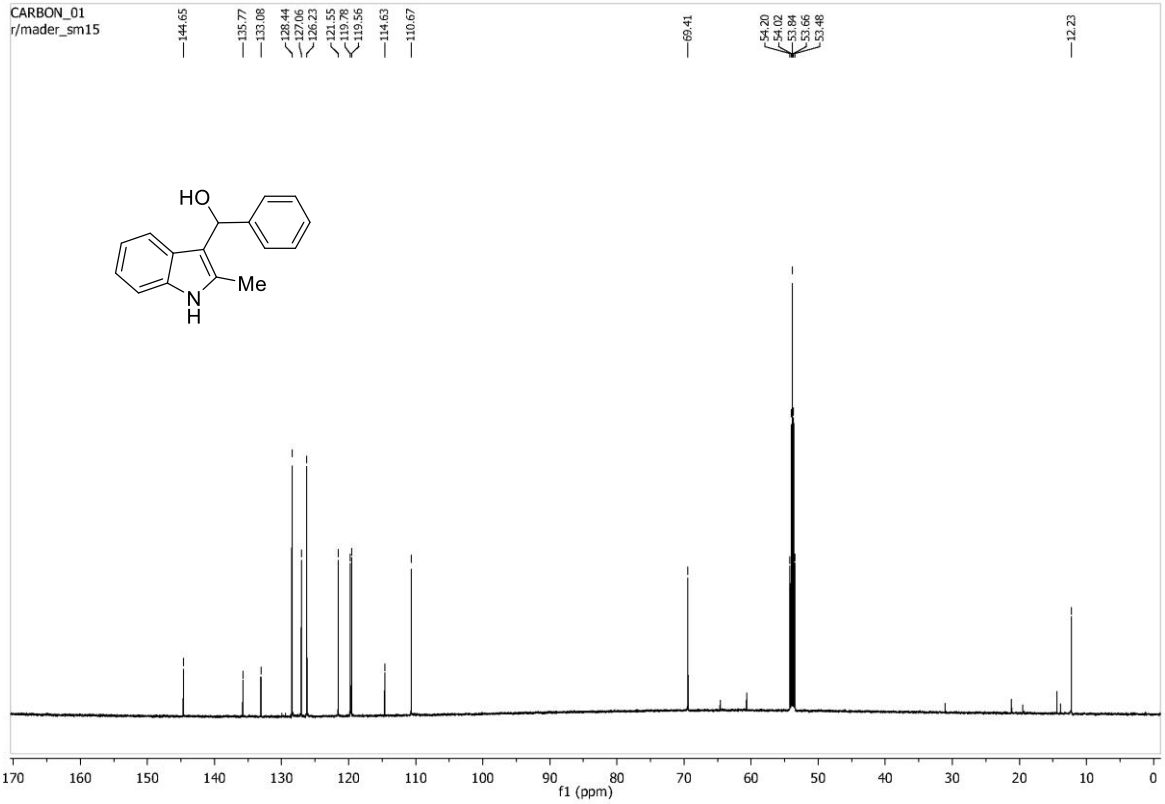
1. (a) D.-S. Wang, J. Tang, Y.-G. Zhou, M.-W. Chen, C.-B. Yu, Y. Duan and G.-F. Jiang, Dehydration triggered asymmetric hydrogenation of 3-(α-hydroxyalkyl)indoles. *Chem. Sci.* 2011, **2**, 803-806. (b) T. Varlet, M. Matišić, E. Van Elslande, L. Neuville, V. Gandon and G. Masson, Enantioselective and Diastereodivergent Synthesis of Spiroindolenines via Chiral Phosphoric Acid-Catalyzed Cycloaddition. *J. Am. Chem. Soc*. 2021, **143**, 11611-11619.
2. The calculations have been performed by using the facilities and computing resources offered by the Center for Computing and Communication of the RWTH Aachen University.
3. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

VII. Copies of ^{1}H, ^{13}C, HPLC and SFC Spectra of the Reported Compounds

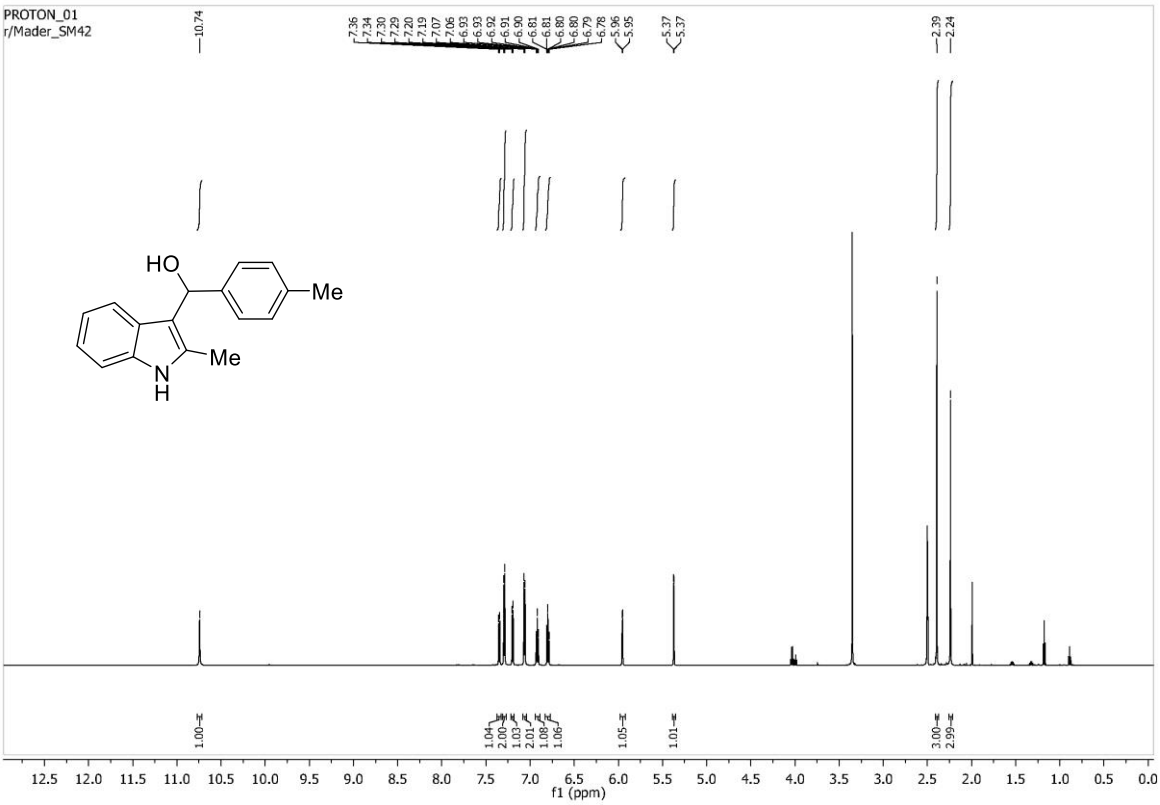
^{1}H NMR (600 MHz, CD_2Cl_2) for **1a**



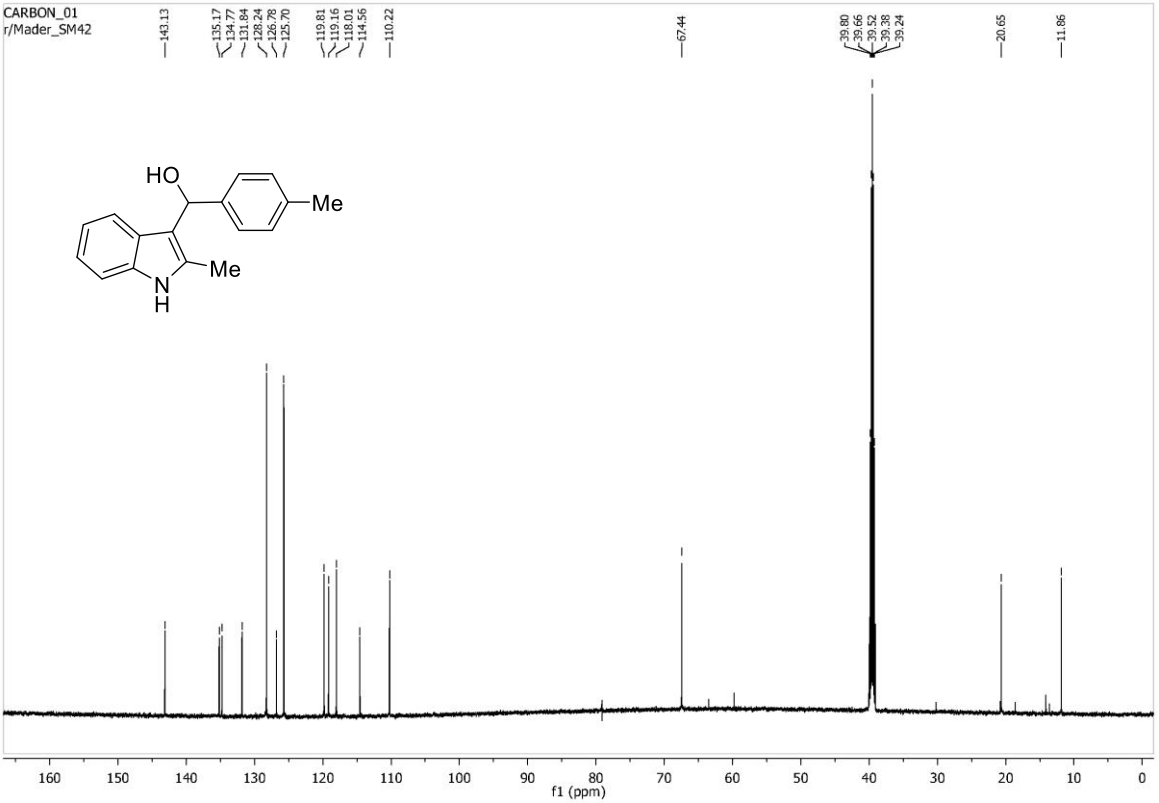
^{13}C NMR (150 MHz, CD_2Cl_2) for **1a**



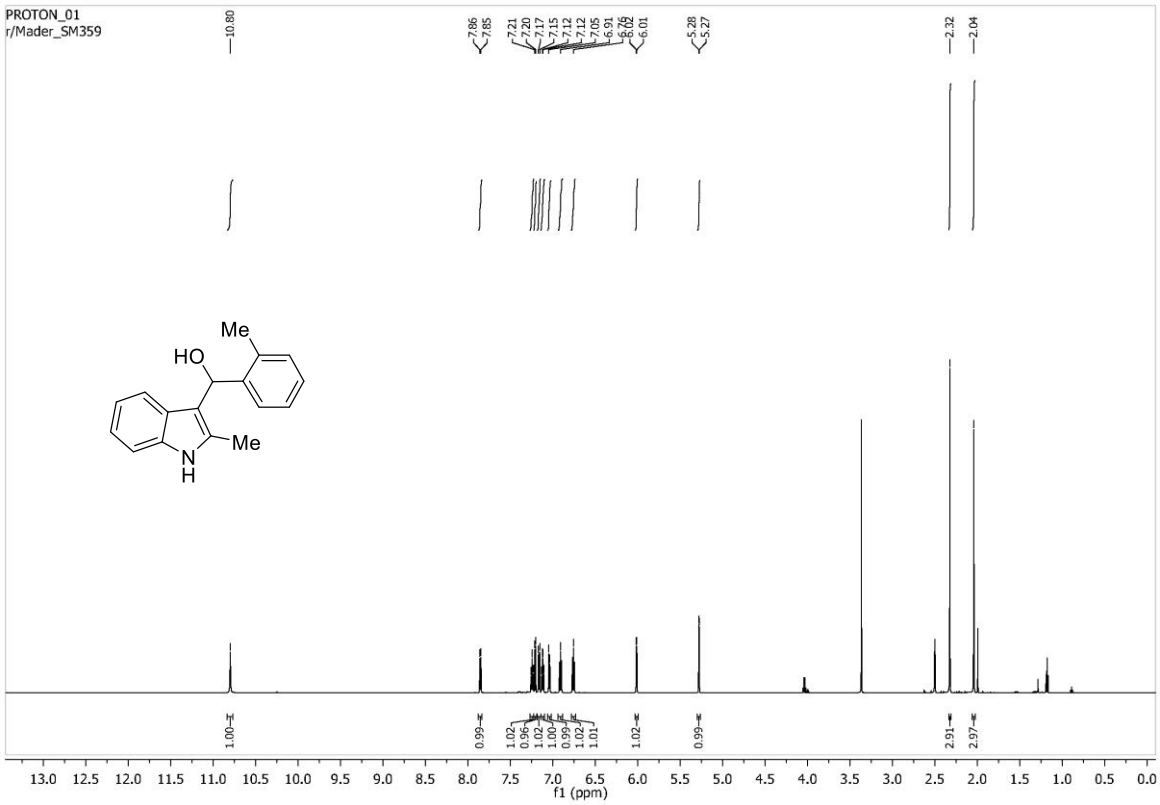
^{1}H NMR (600 MHz, DMSO-d_6) for **1b**



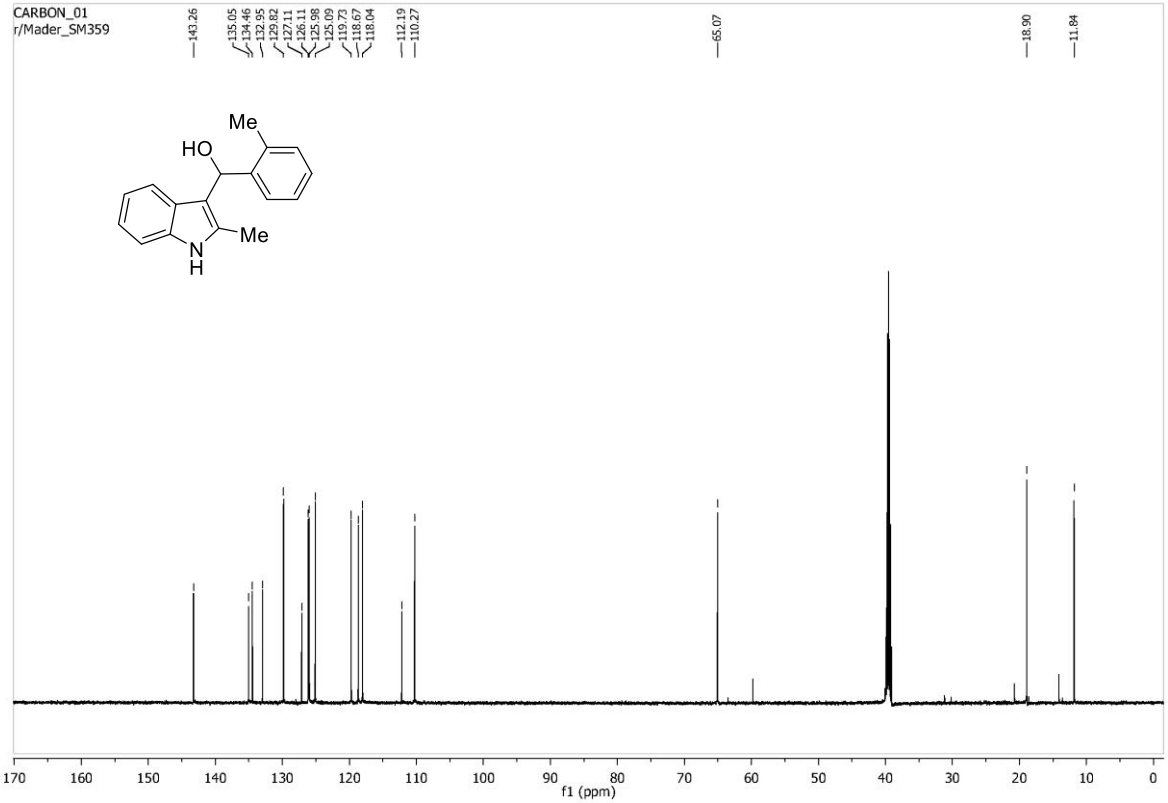
^{13}C NMR (150 MHz, DMSO-d_6) for **1b**



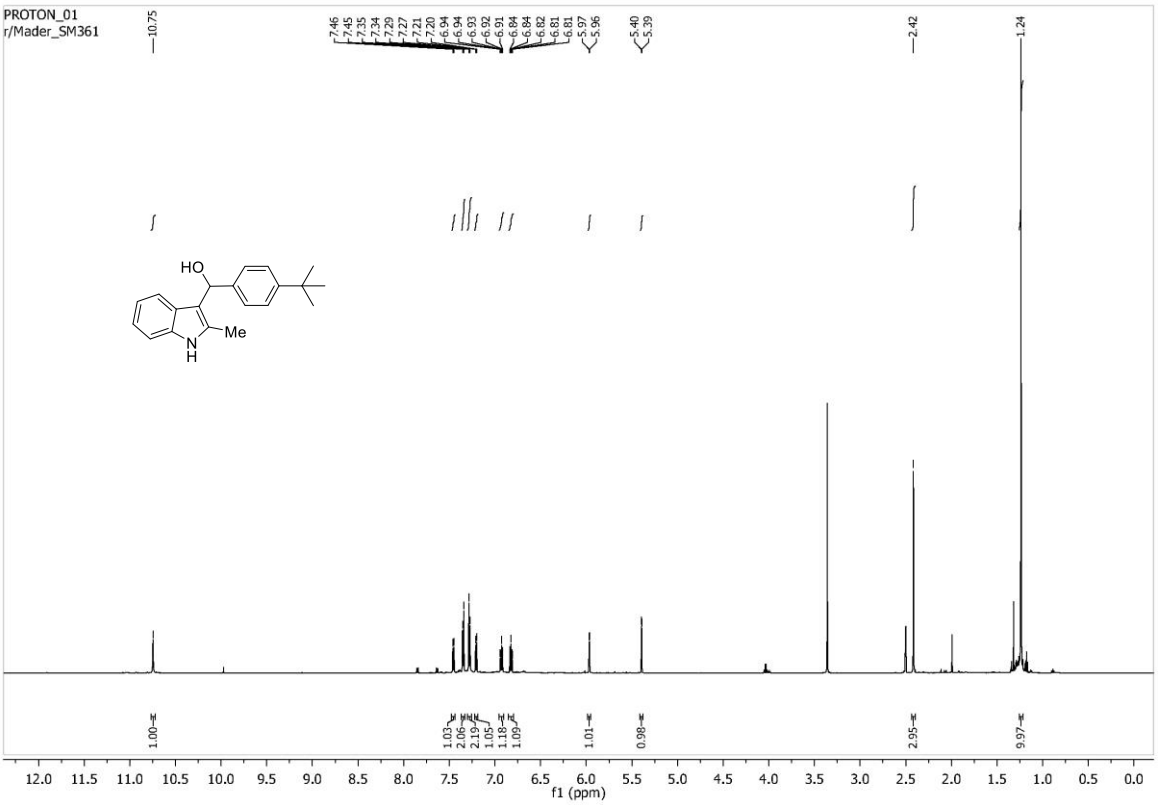
^{1}H NMR (600 MHz, DMSO-d_6) for **1c**



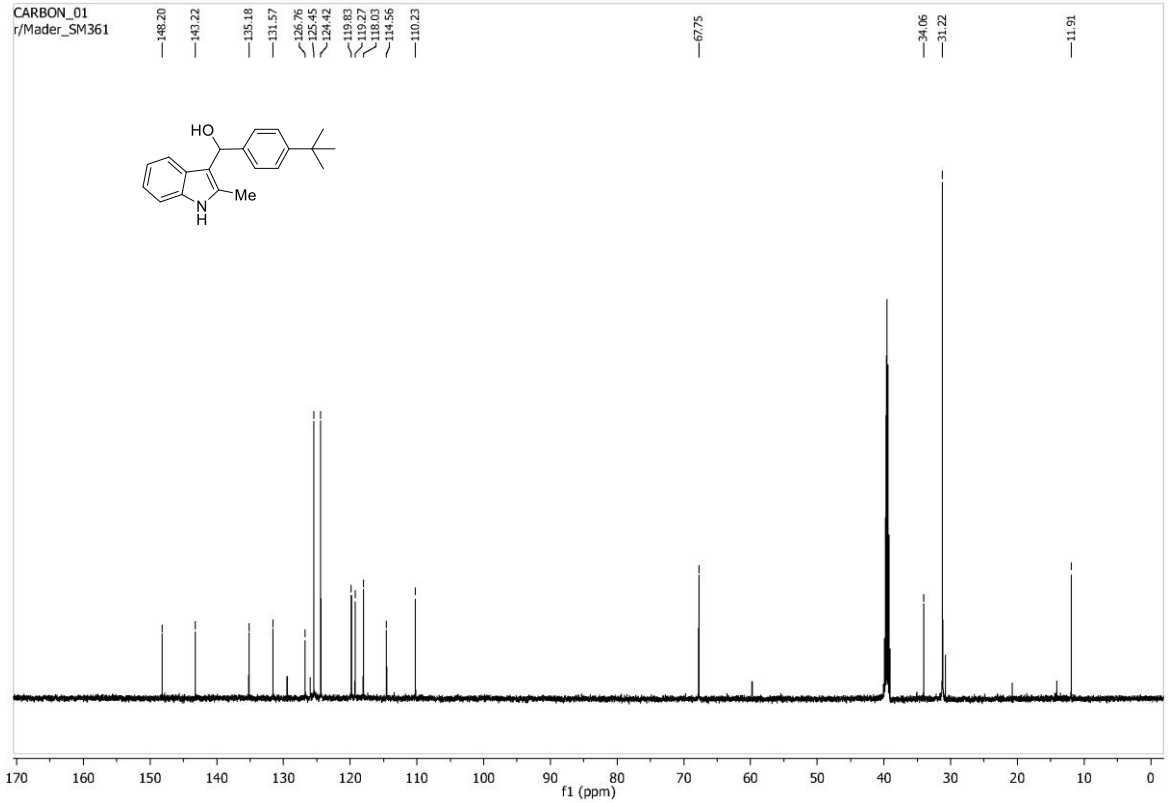
^{13}C NMR (150 MHz, DMSO-d_6) for **1c**



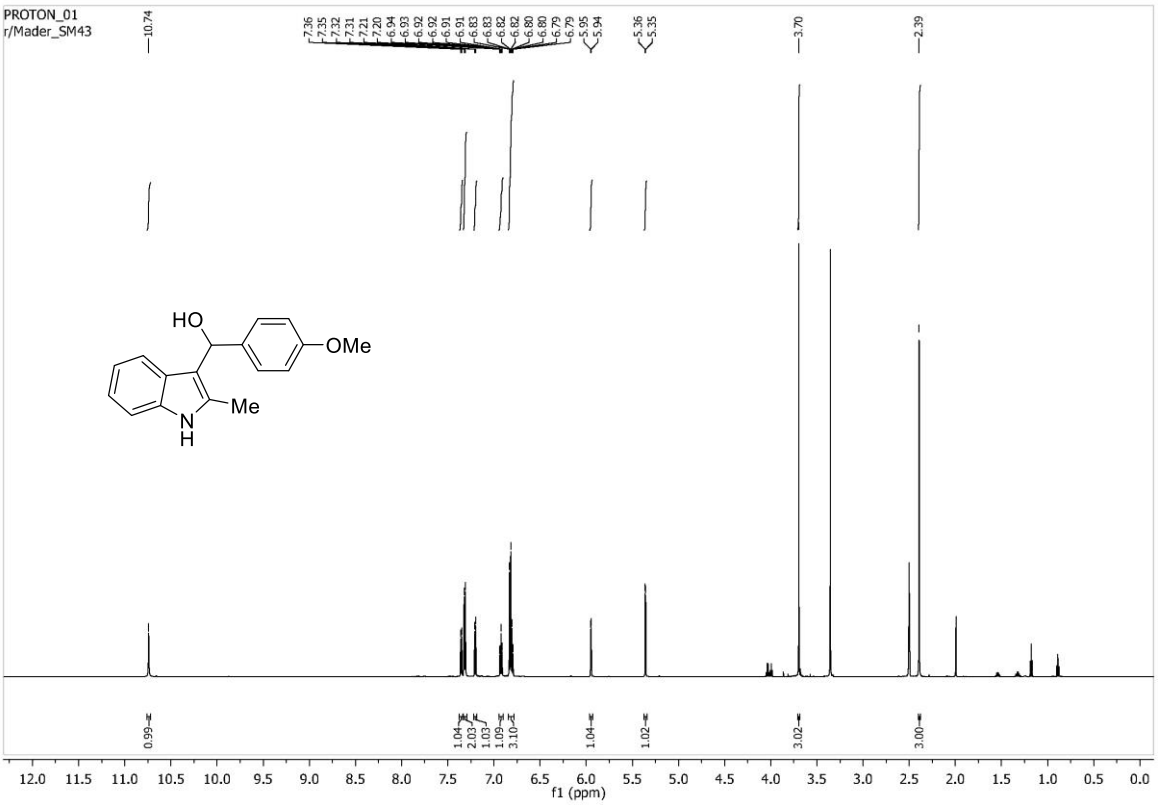
^{1}H NMR (600 MHz, DMSO-d_6) for **1d**



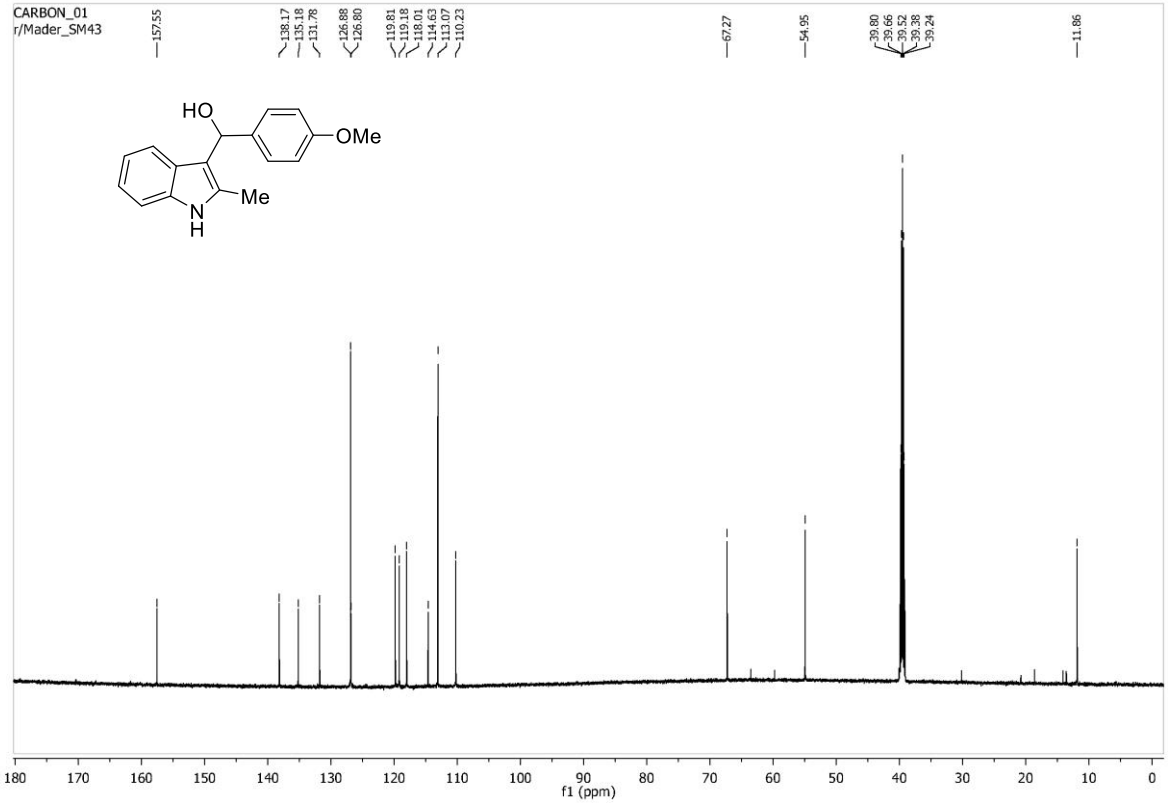
^{13}C NMR (150 MHz, DMSO-d_6) for **1d**



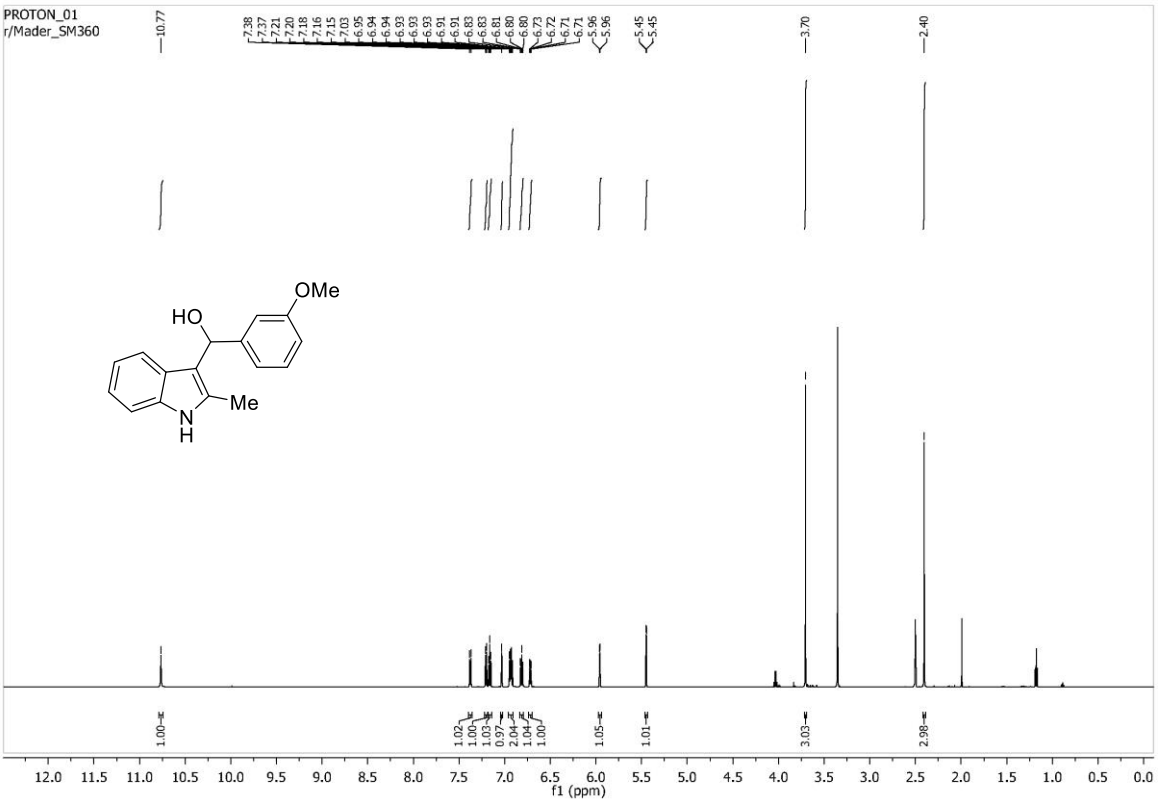
^{1}H NMR (600 MHz, DMSO-d_6) for **1e**



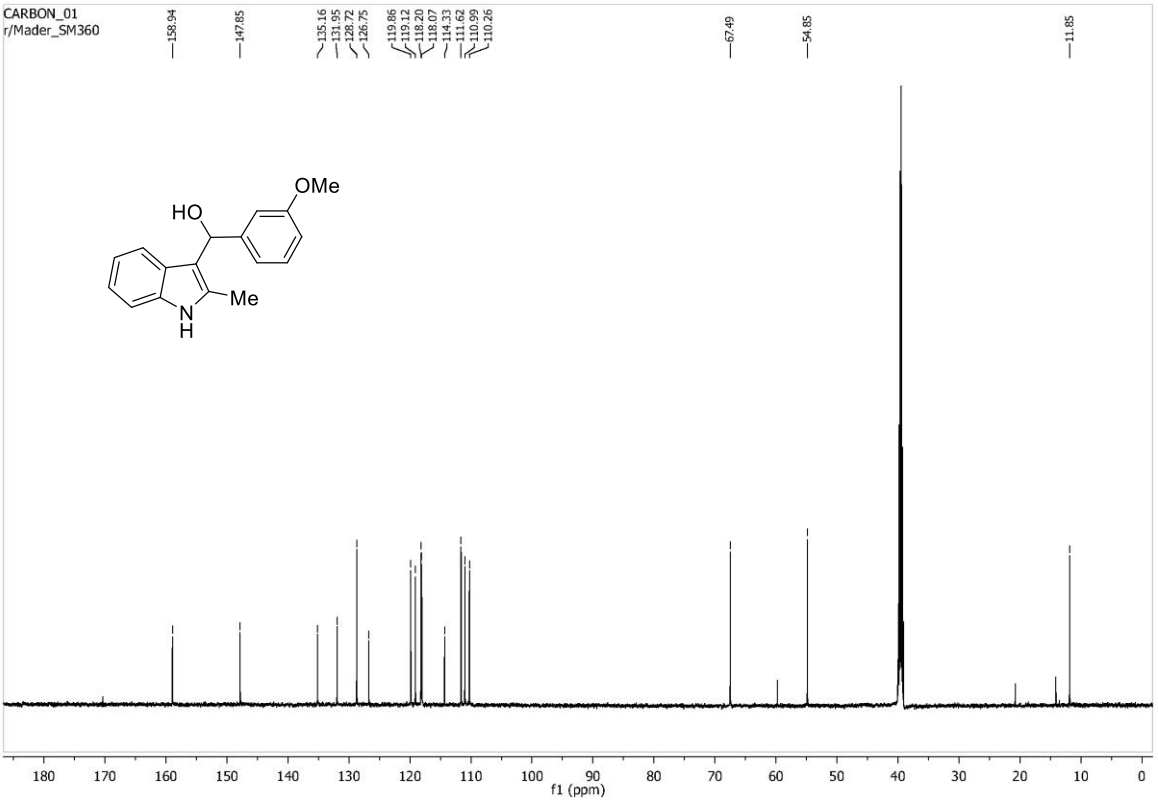
^{13}C NMR (150 MHz, DMSO-d_6) for **1e**



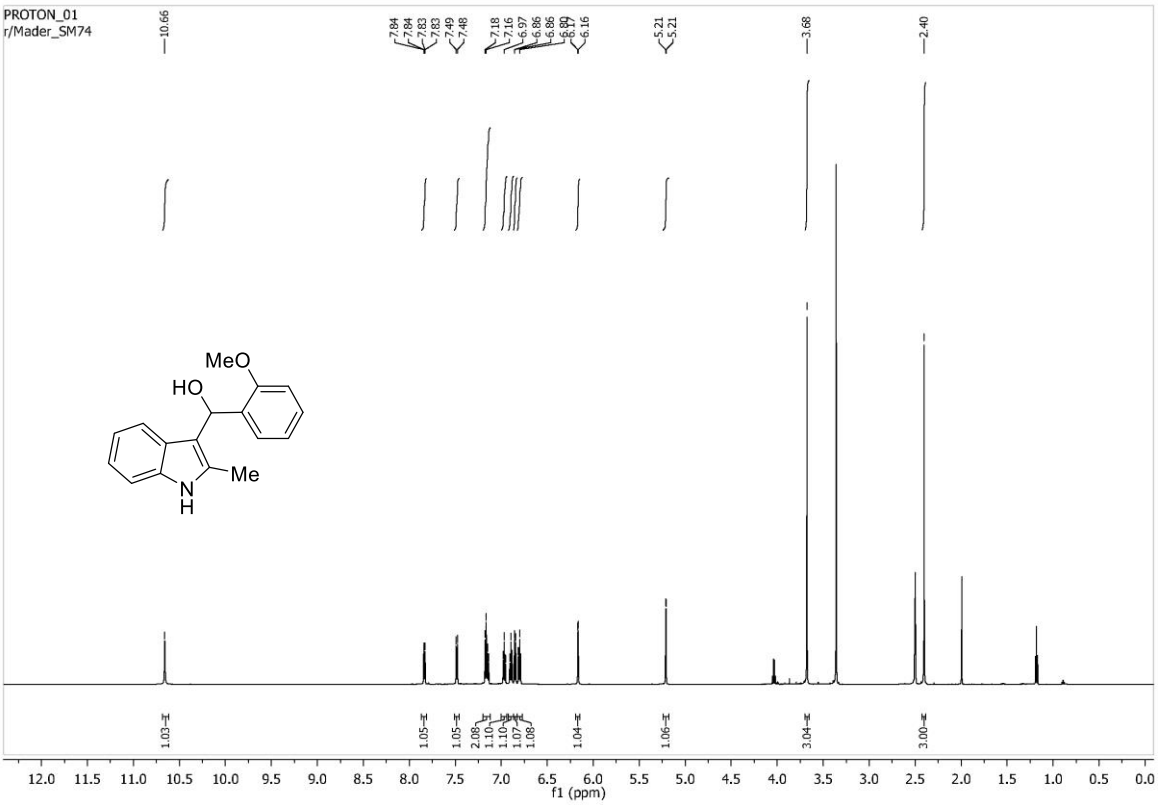
^{1}H NMR (600 MHz, DMSO-d_6) for **1f**



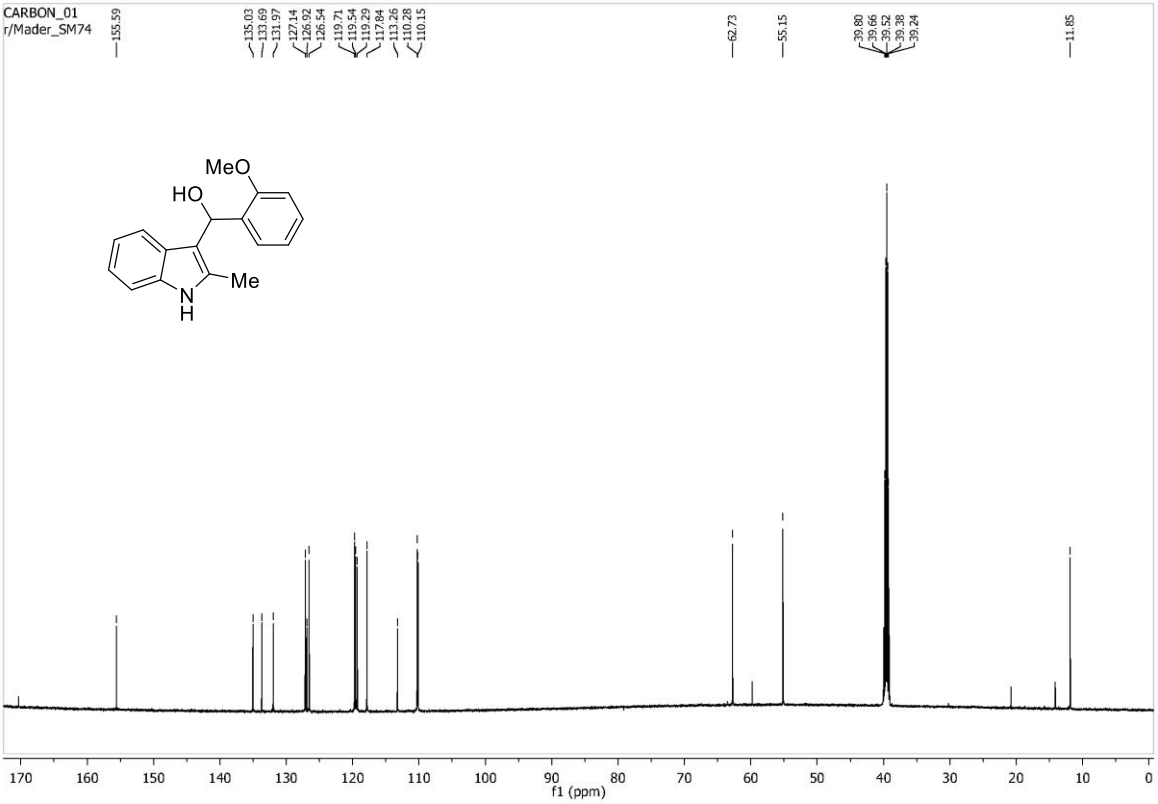
^{13}C NMR (150 MHz, DMSO-d_6) for **1f**



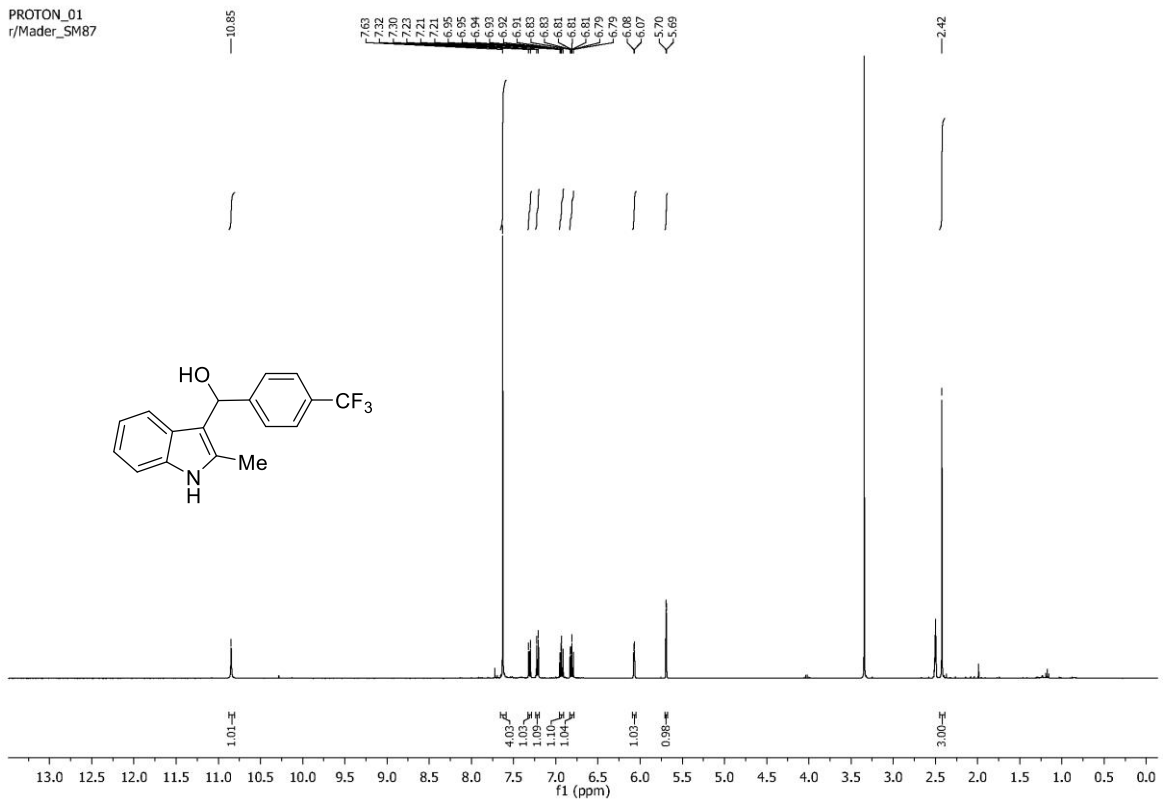
^{1}H NMR (600 MHz, DMSO-d_6) for **1g**



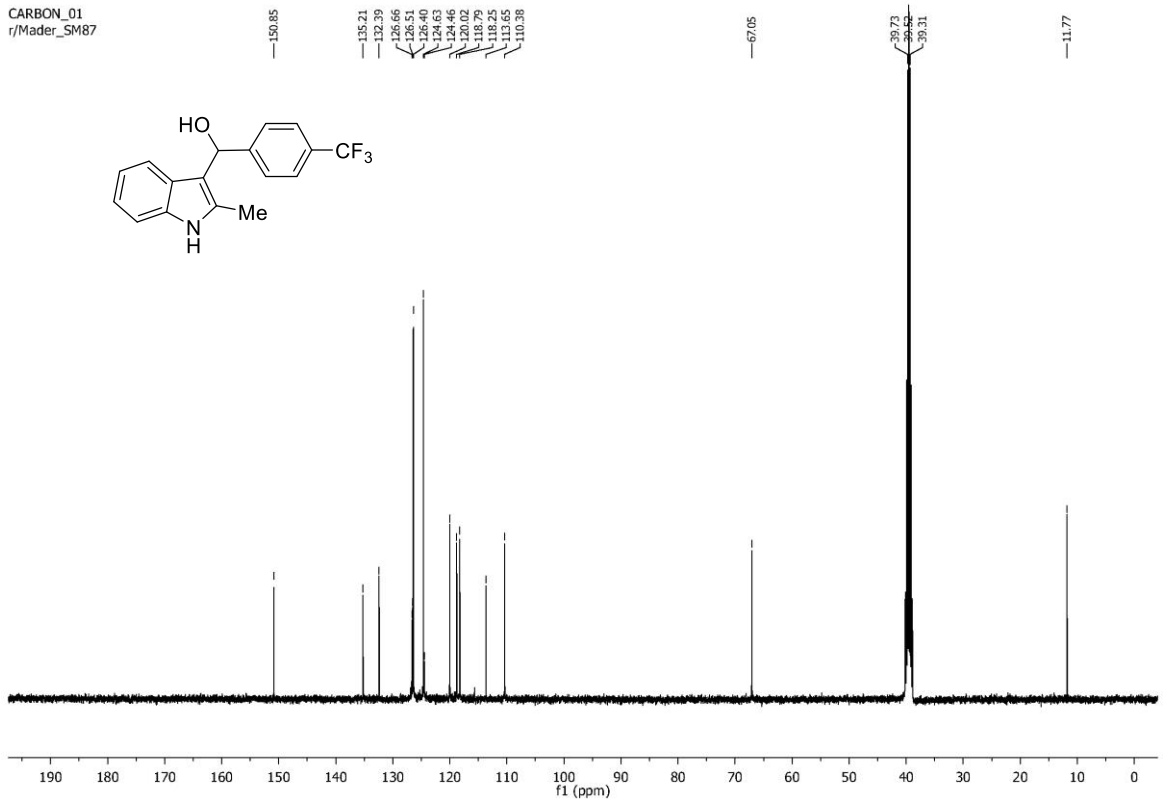
^{13}C NMR (150 MHz, DMSO-d_6) for **1g**



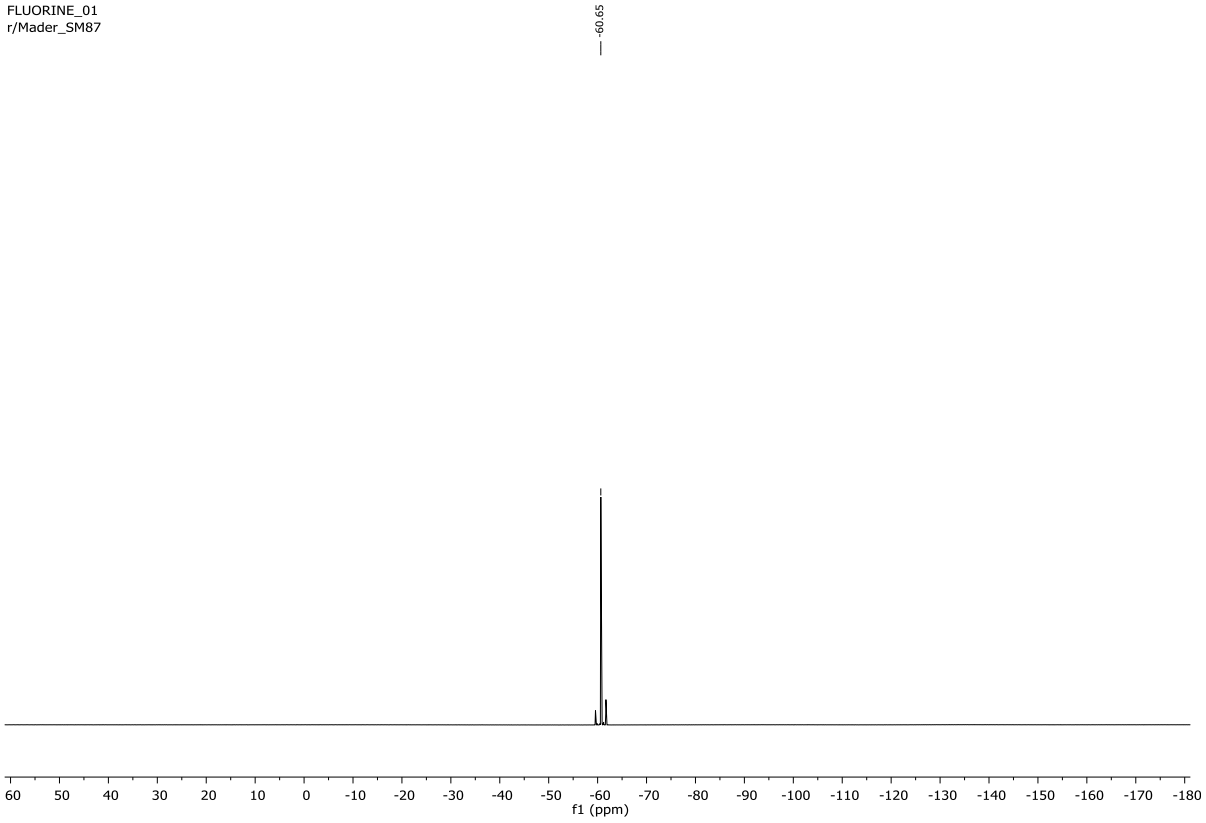
^{1}H NMR (400 MHz, DMSO-d_6) for **1h**



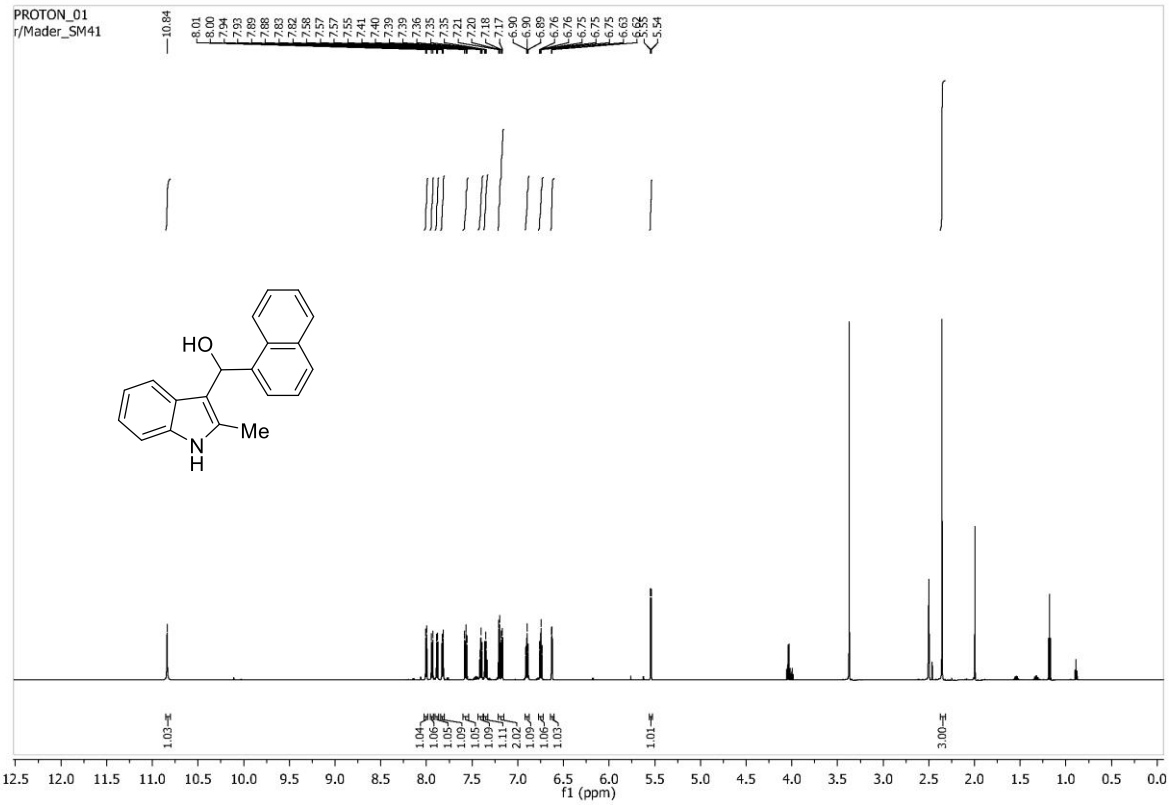
^{13}C NMR (100 MHz, DMSO-d_6) for **1h**



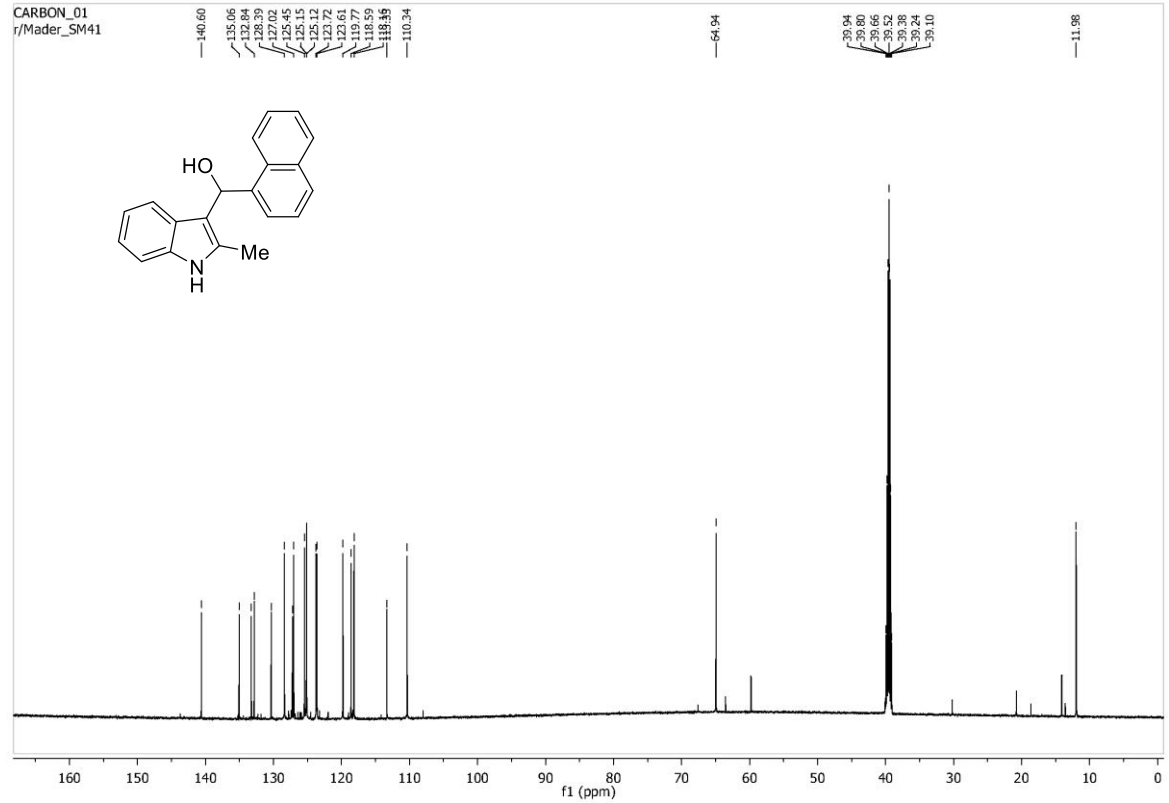
^{19}F NMR (376 MHz, DMSO-d_6) for **1h**



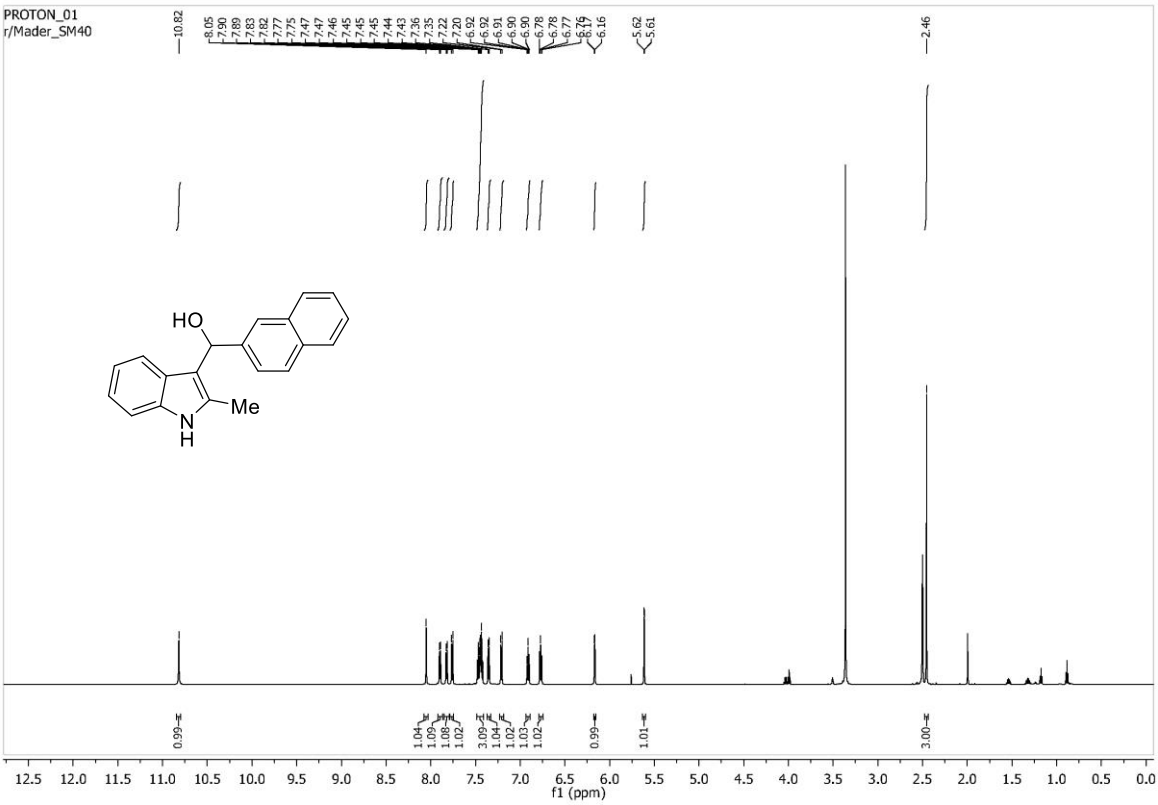
^{1}H NMR (600 MHz, DMSO-d_6) for **1i**



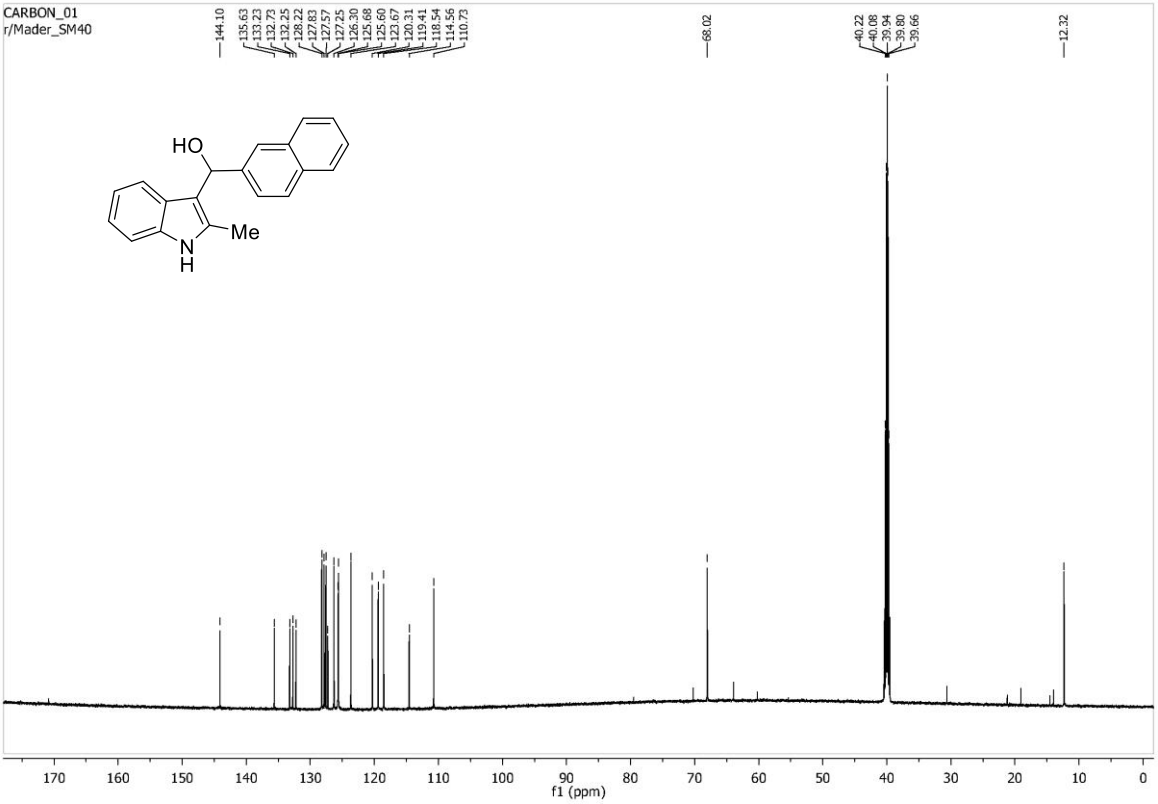
^{13}C NMR (150 MHz, DMSO-d_6) for **1i**



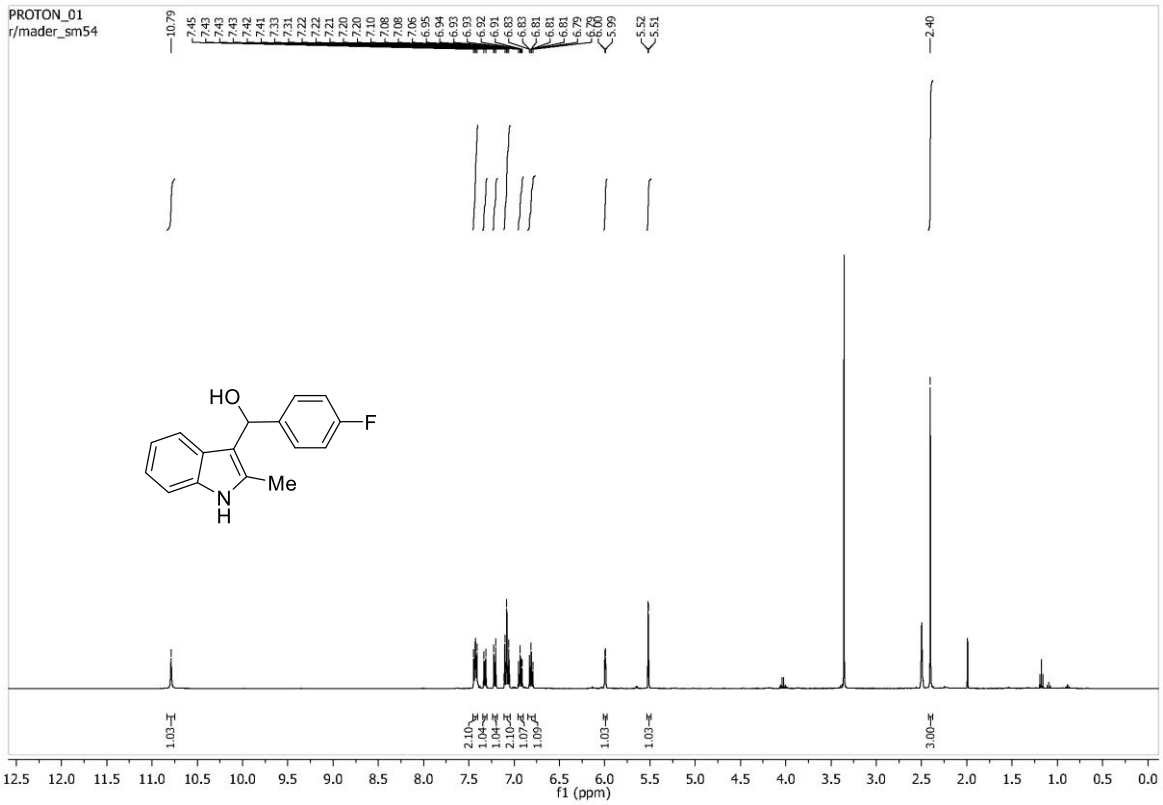
^{1}H NMR (600 MHz, DMSO-d_6) for **1j**



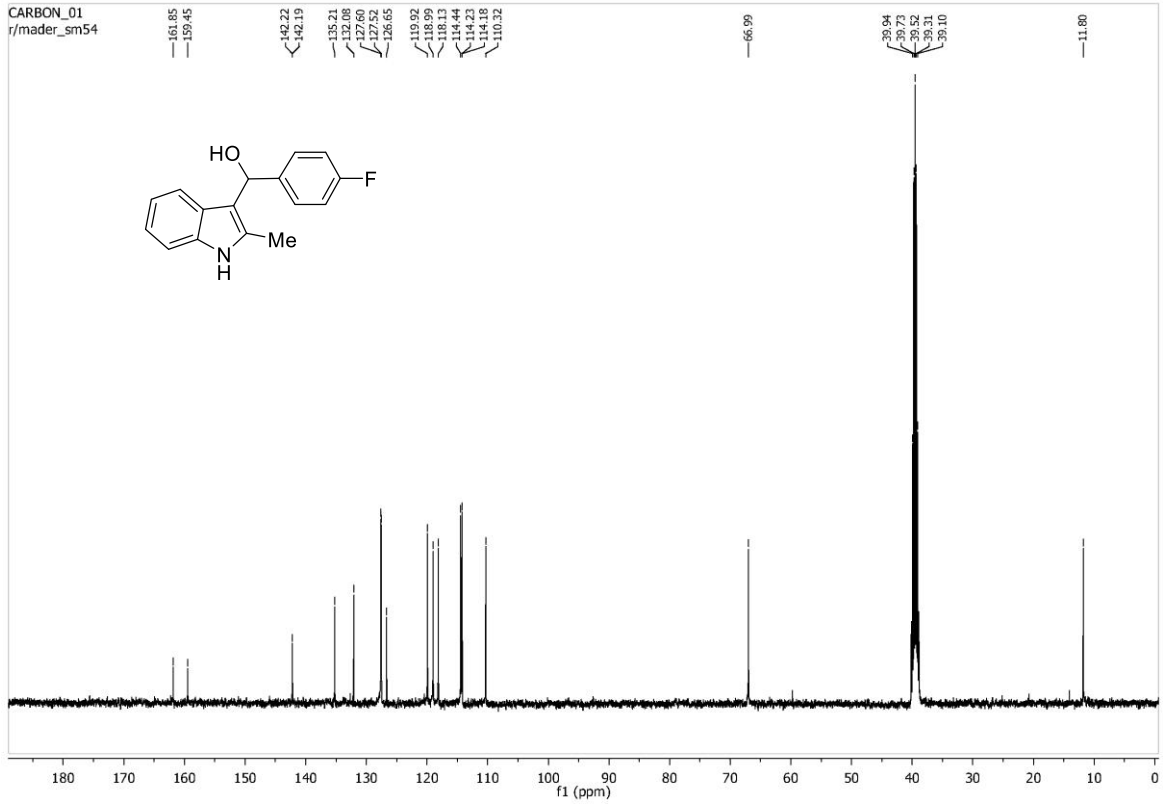
^{13}C NMR (150 MHz, DMSO-d_6) for **1j**



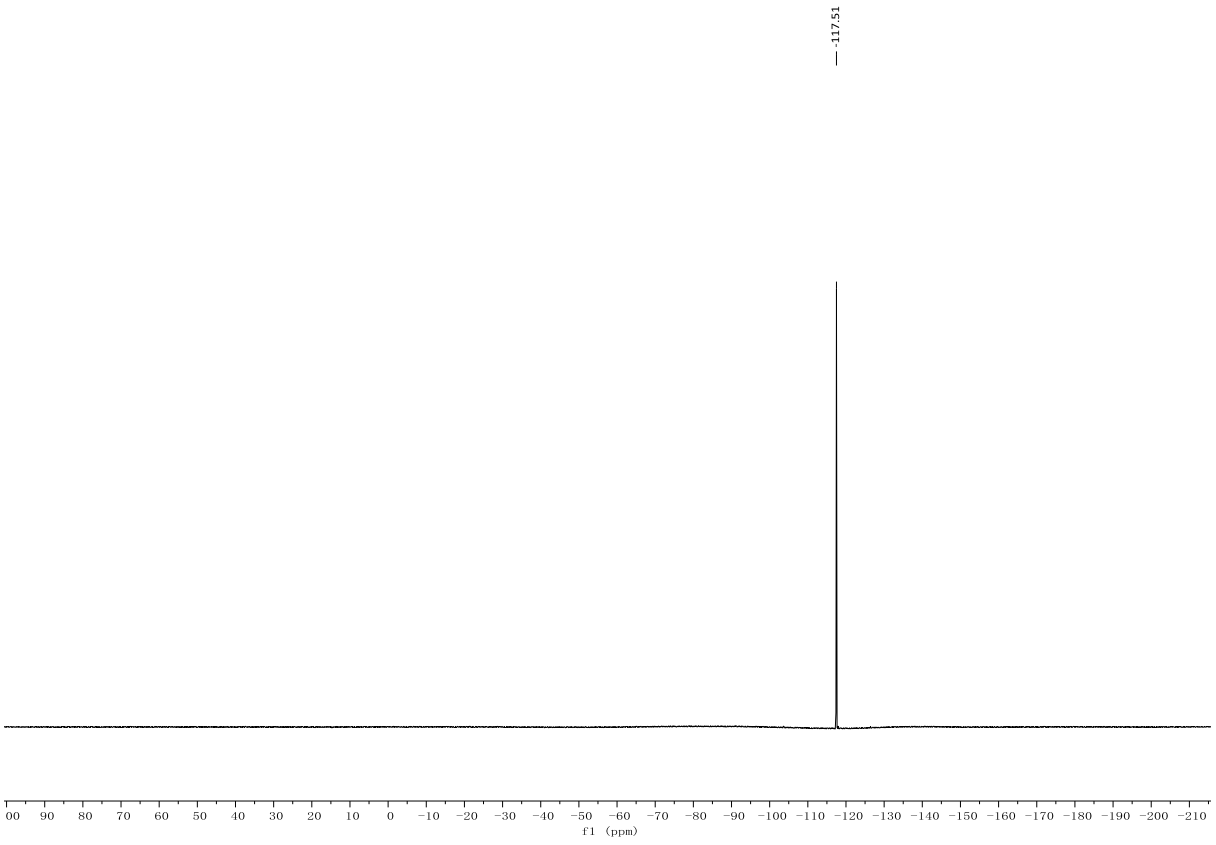
^{1}H NMR (400 MHz, DMSO-d_6) for **1k**



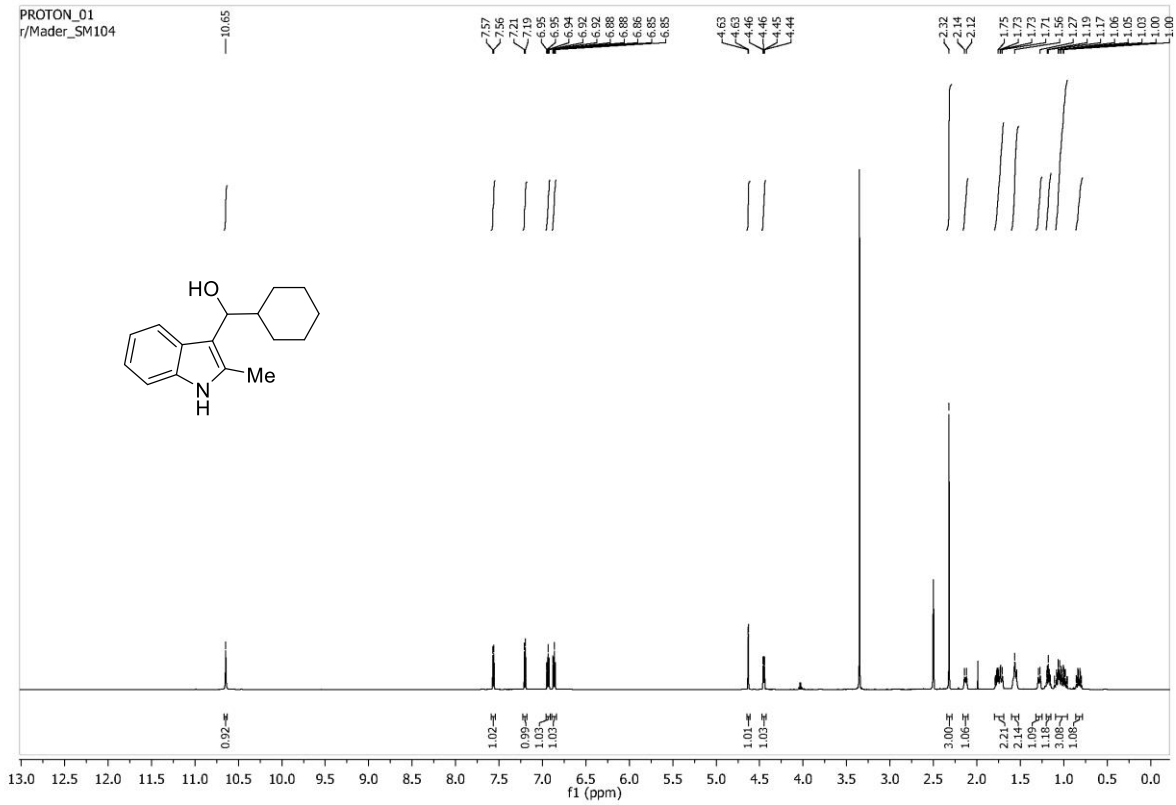
^{13}C NMR (100 MHz, DMSO-d_6) for **1k**



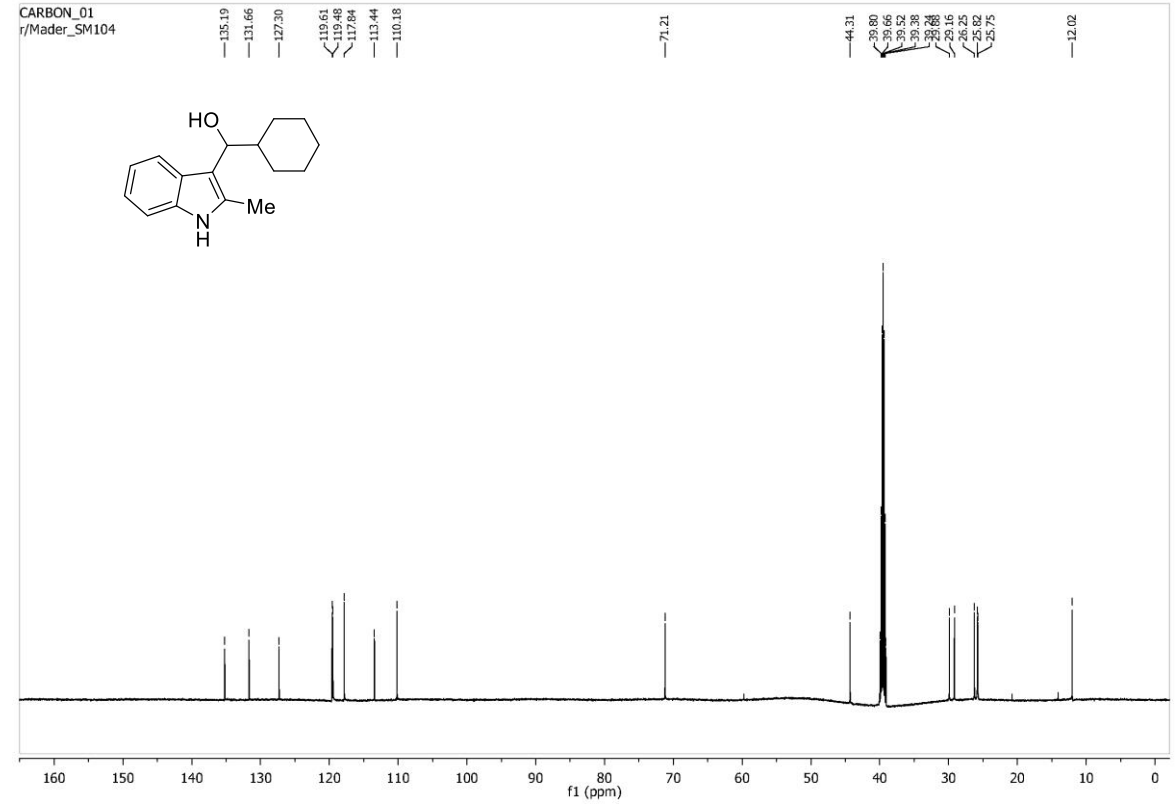
^{19}F NMR (376 MHz, DMSO-d_6) for **1k**



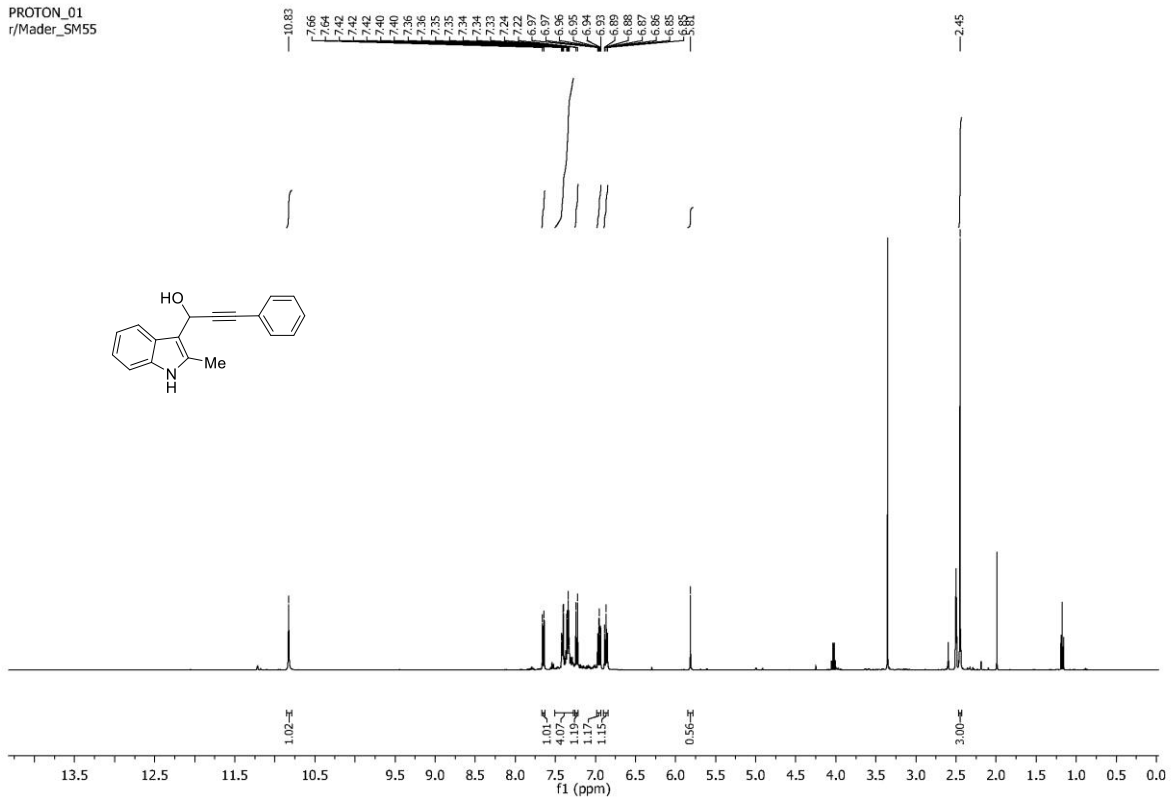
^{1}H NMR (600 MHz, DMSO-d_6) for **1l**



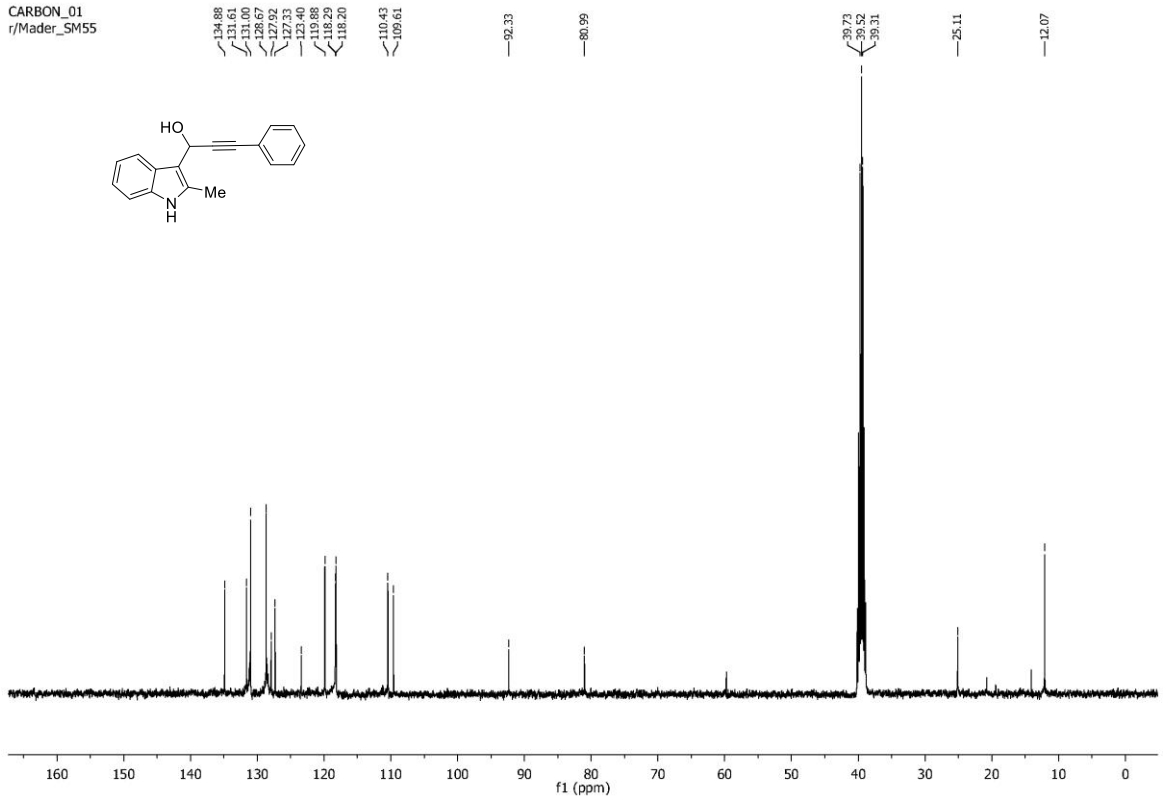
^{13}C NMR (150 MHz, DMSO-d_6) for **1l**



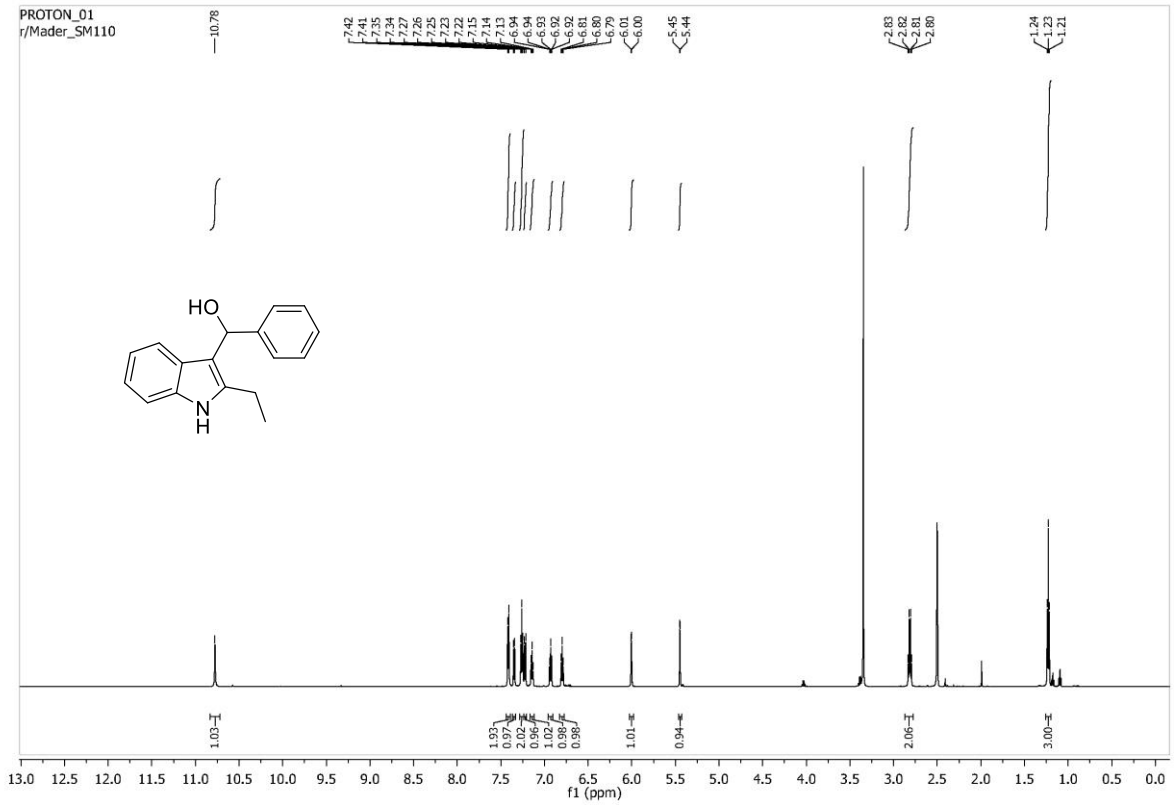
^{1}H NMR (400 MHz, DMSO-d_6) for **1m**



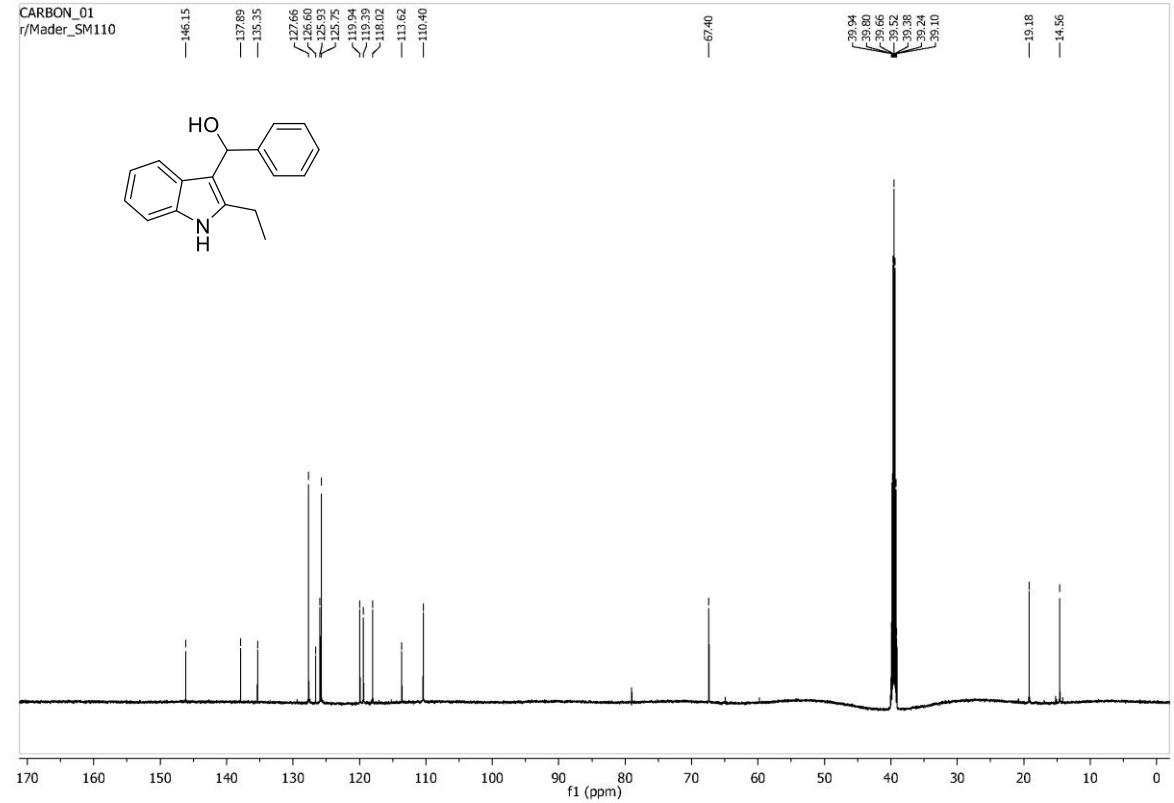
^{13}C NMR (100 MHz, DMSO-d_6) for **1m**



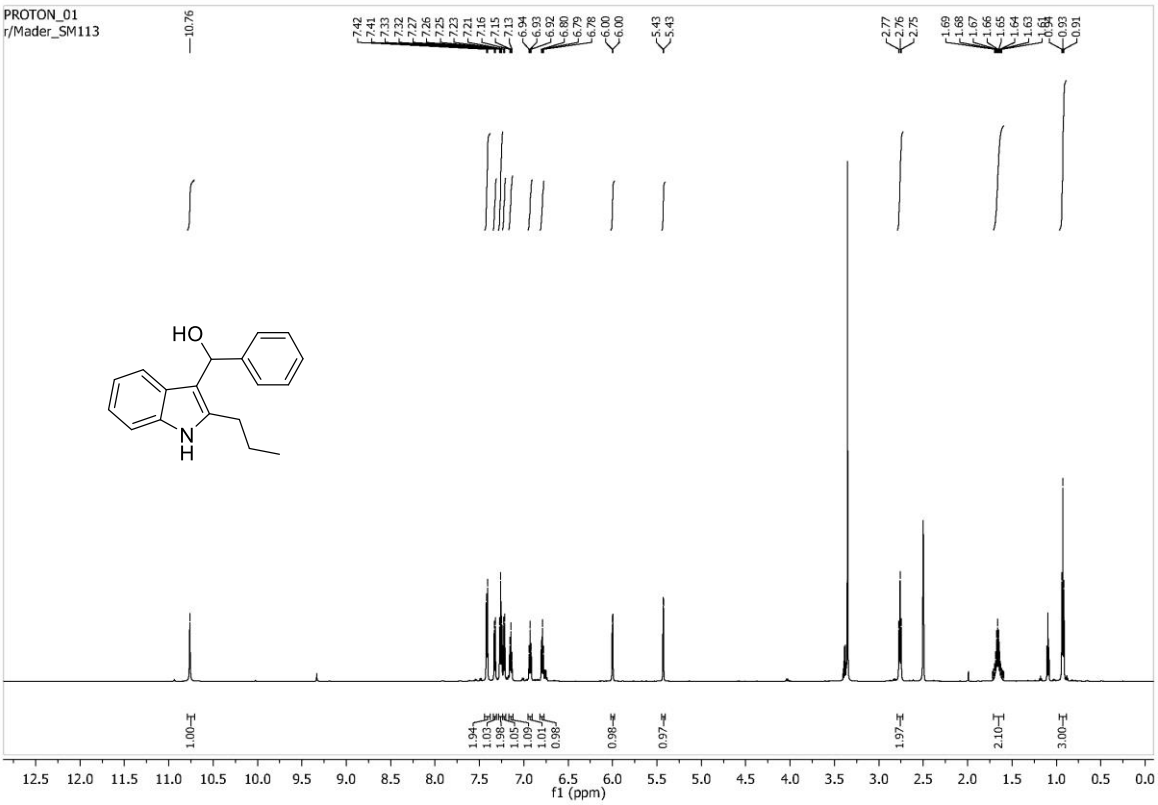
^{1}H NMR (600 MHz, DMSO-d_6) for **1n**



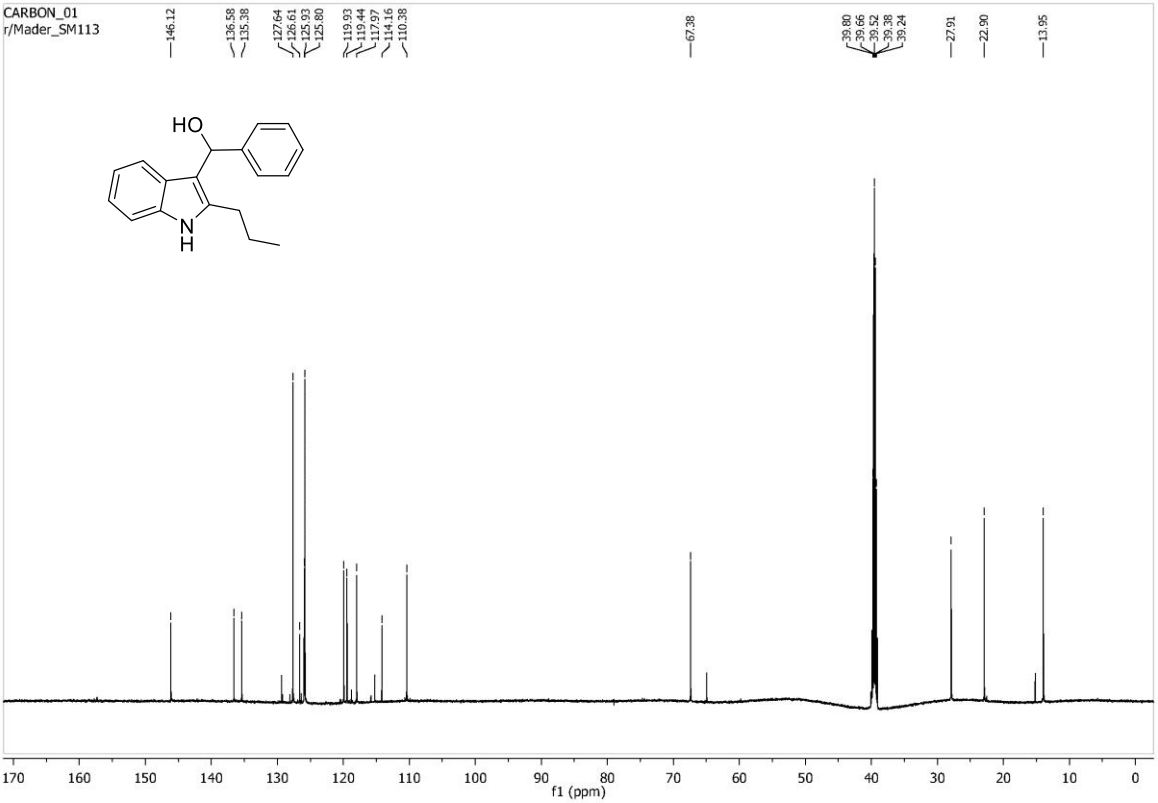
^{13}C NMR (150 MHz, DMSO-d_6) for **1n**



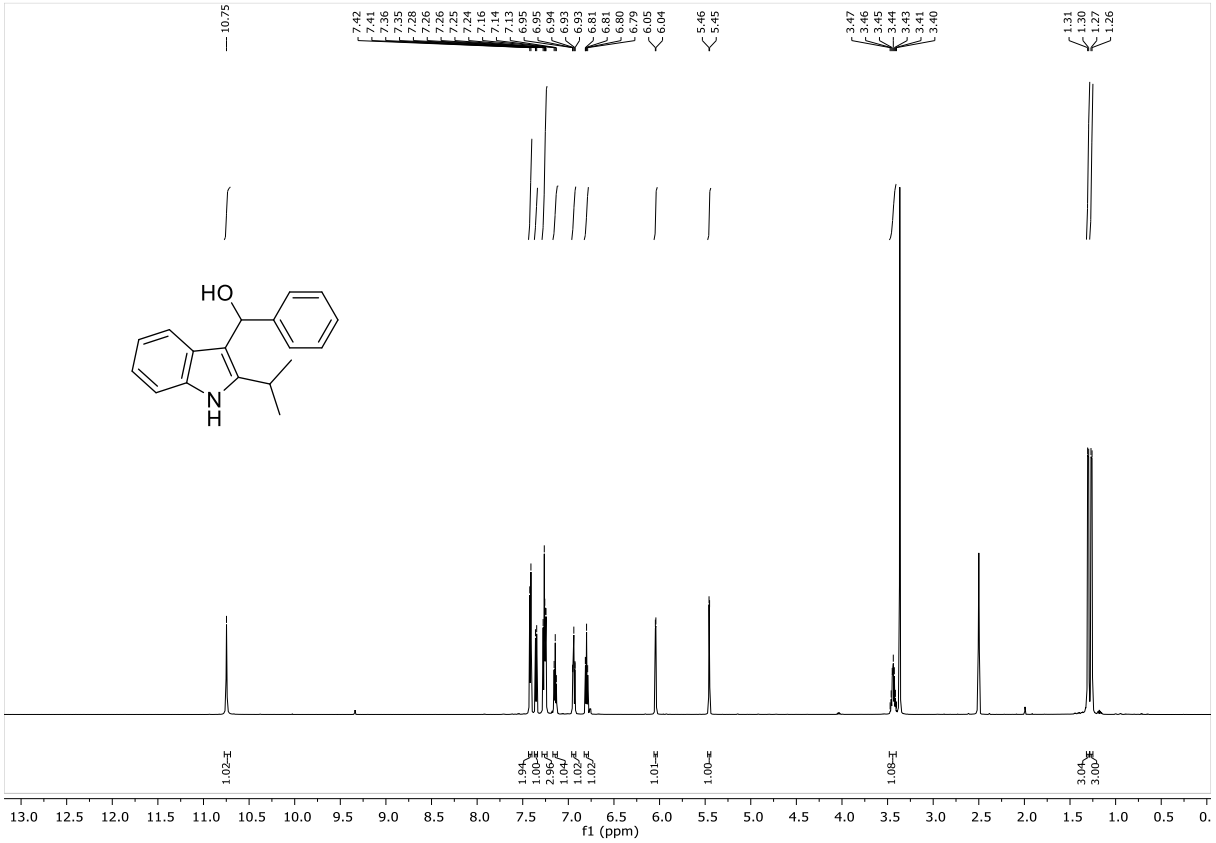
^{1}H NMR (600 MHz, DMSO-d_6) for **1o**



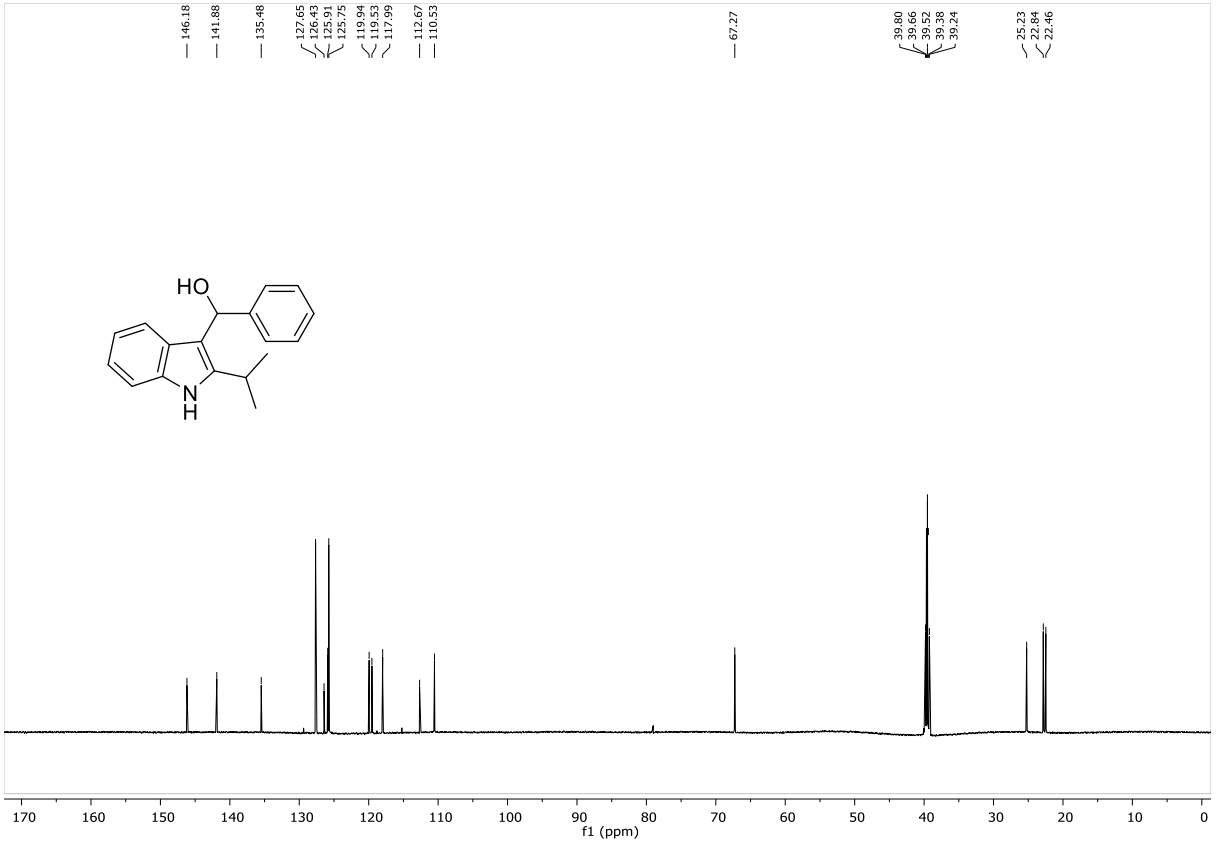
^{13}C NMR (150 MHz, DMSO-d_6) for **1o**



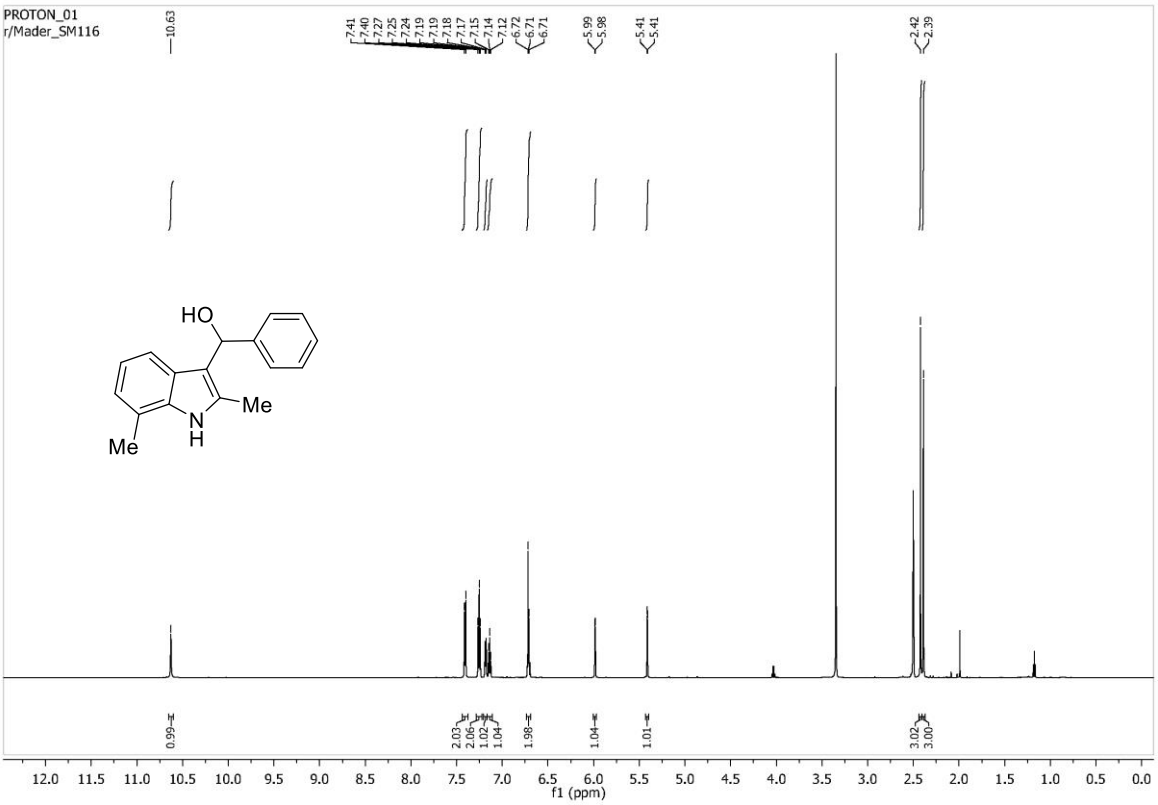
^{1}H NMR (600 MHz, DMSO-d_6) for **1p**



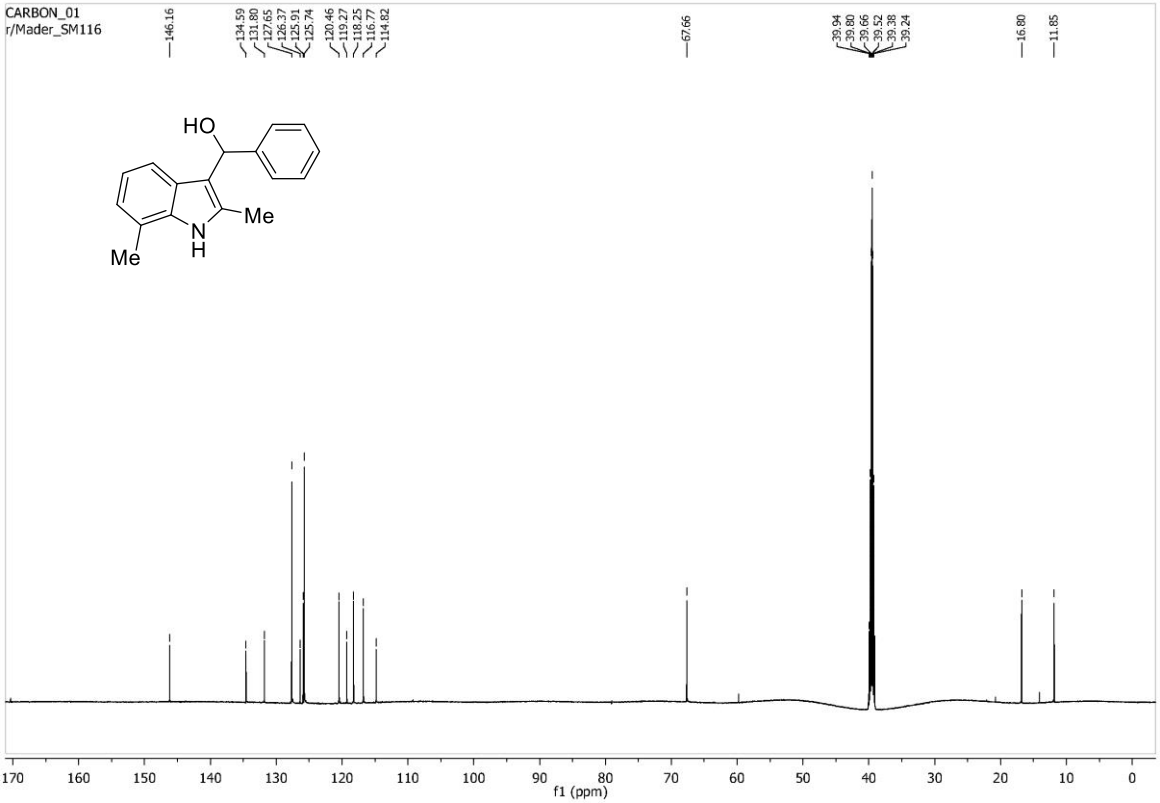
^{13}C NMR (150 MHz, DMSO-d_6) for **1p**



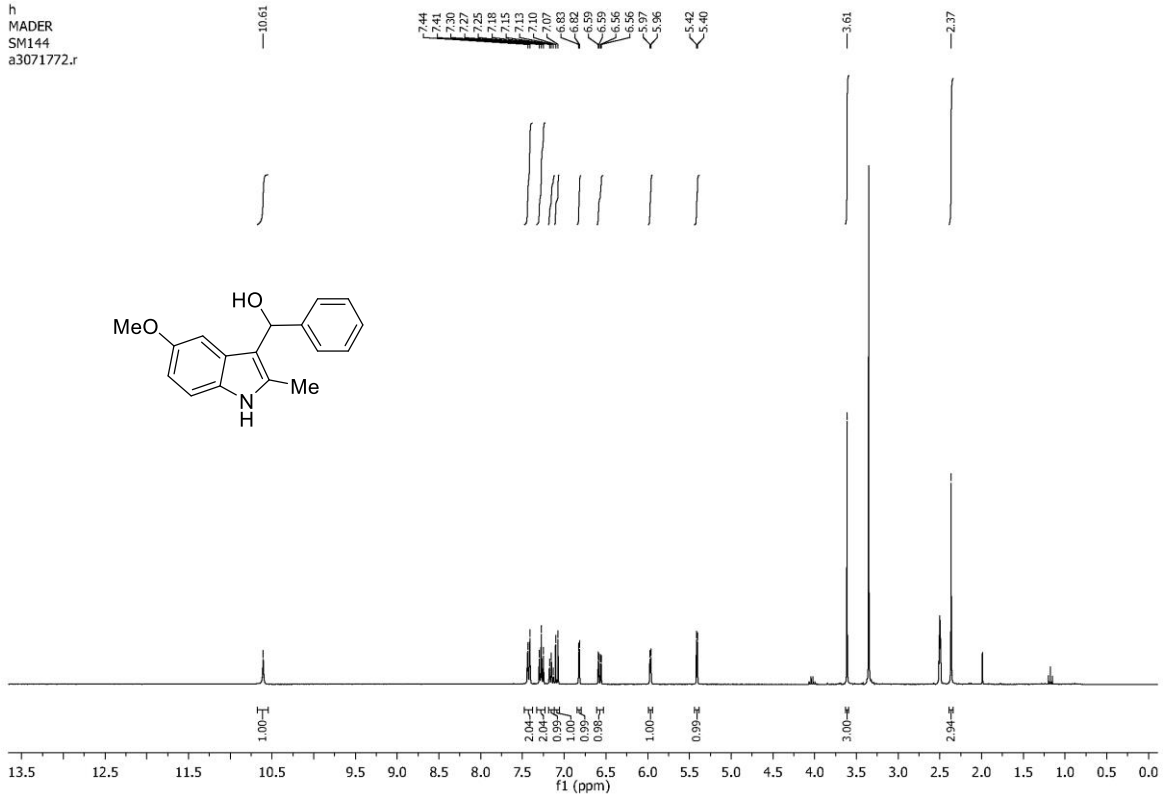
^{1}H NMR (600 MHz, DMSO-d_6) for **1q**



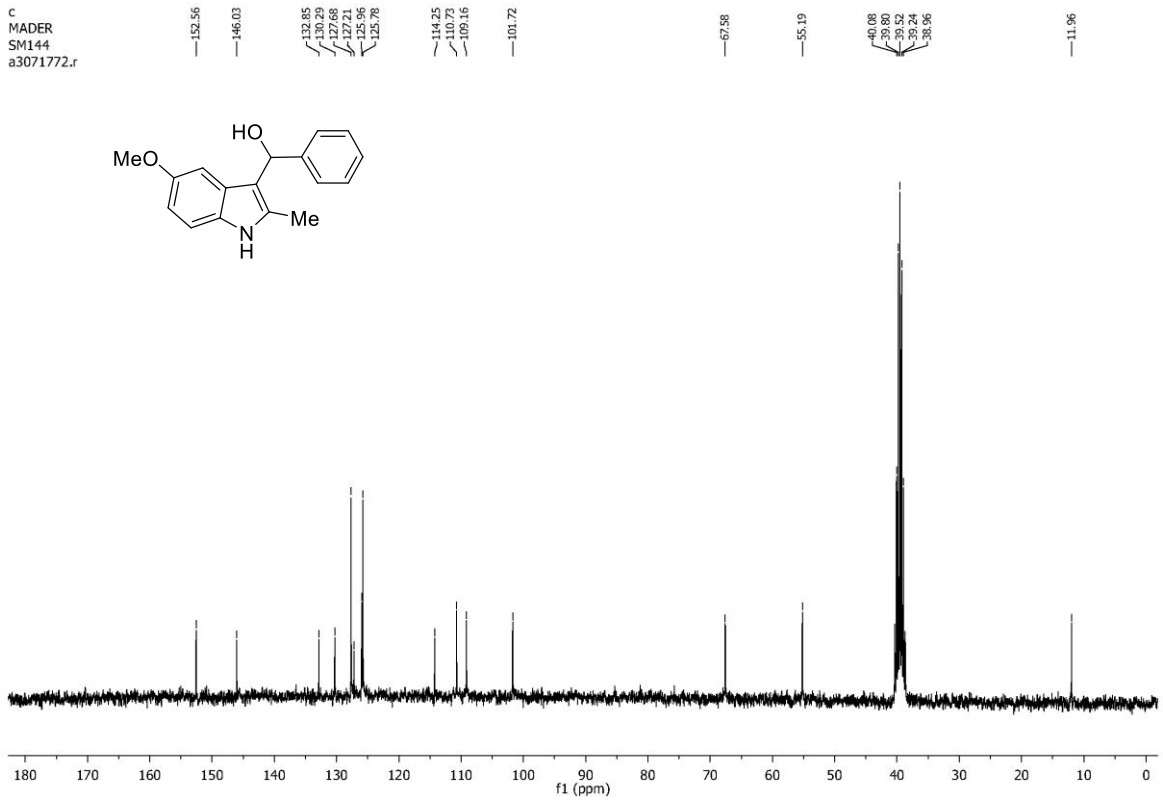
^{13}C NMR (150 MHz, DMSO-d_6) for **1q**



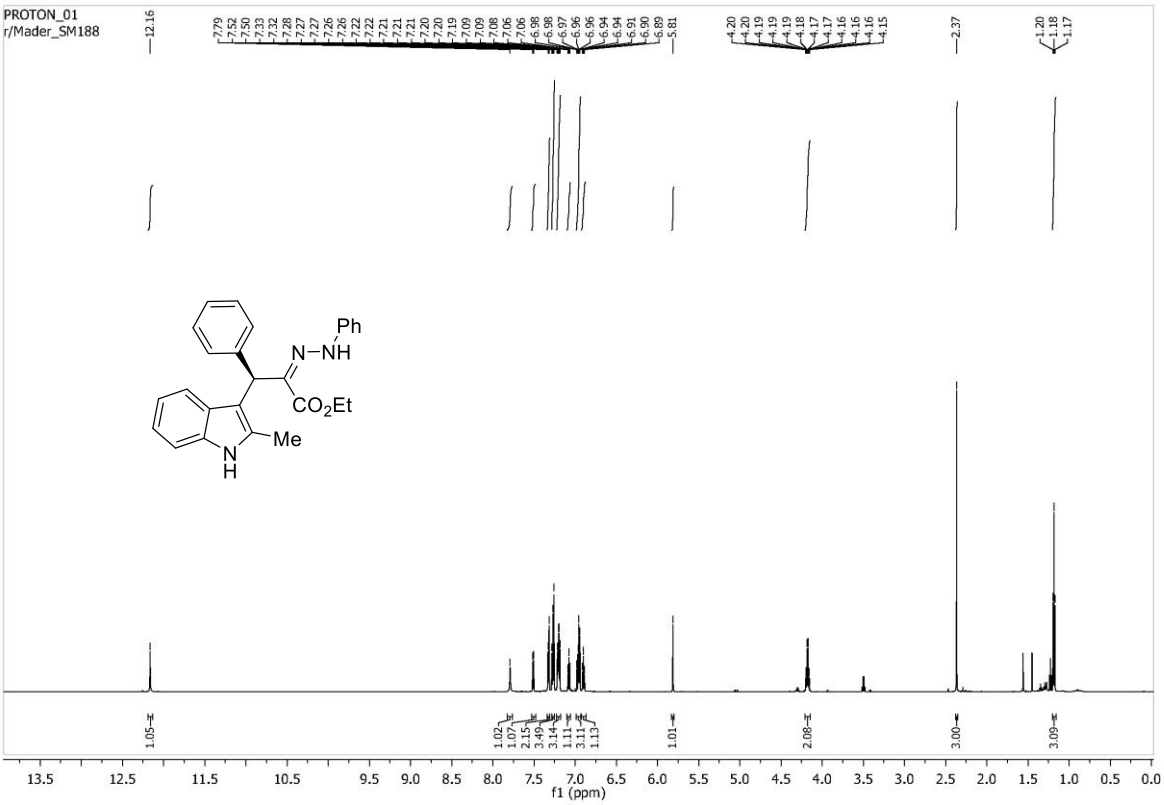
^{1}H NMR (300 MHz, DMSO-d_6) for **1r**



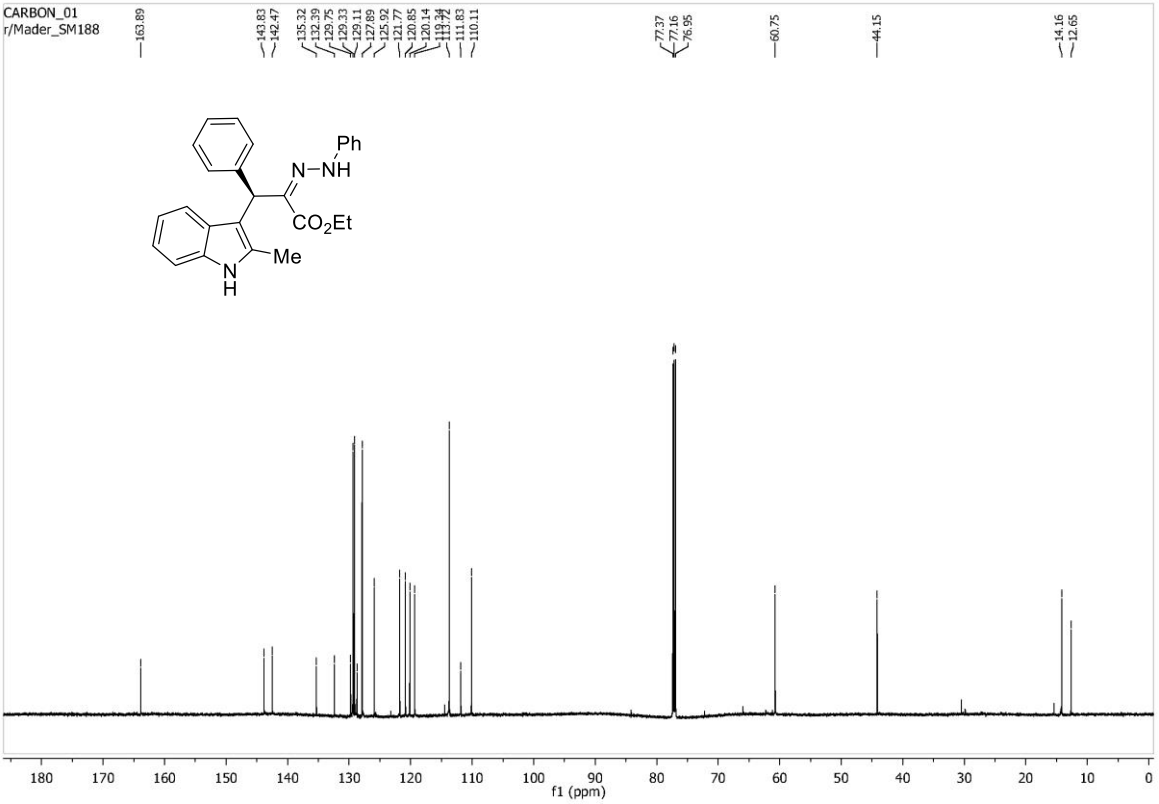
^{13}C NMR (75 MHz, DMSO-d_6) for **1r**



^{1}H NMR (600 MHz, $CDCl_3$) for **4a**

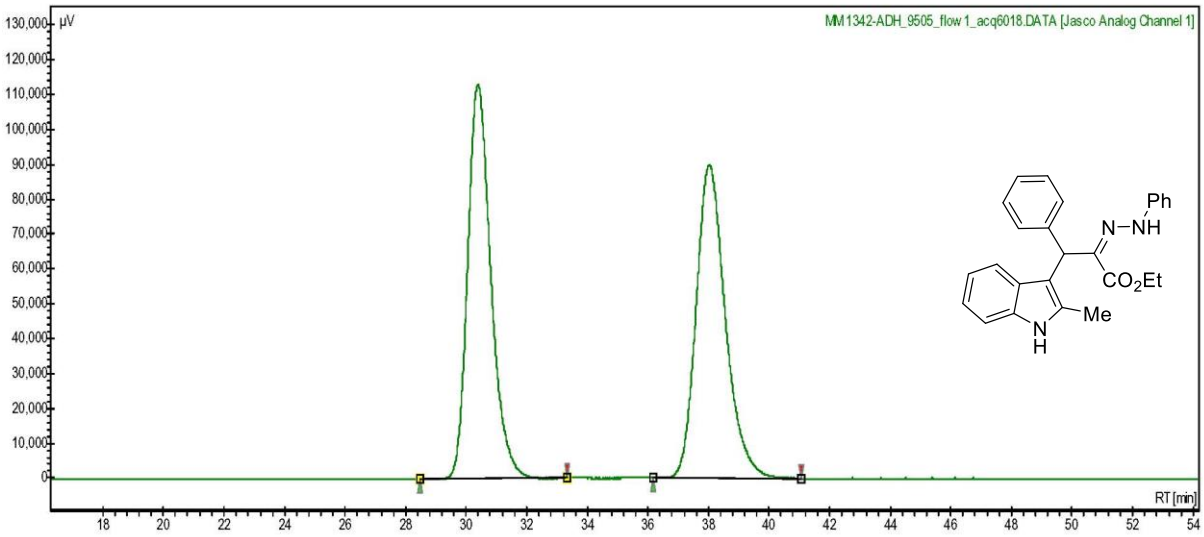


^{13}C NMR (150 MHz, $CDCl_3$) for **4a**



Chromatogram : MM 1342-ADH_9505_flow1_acq6018

Data file: MM 1342-ADH_9505_flow1_acq6018.DATA
Method: HPLC2_ADH_9505_flow1_acq60
Date: 29.01.2013 15:43:00

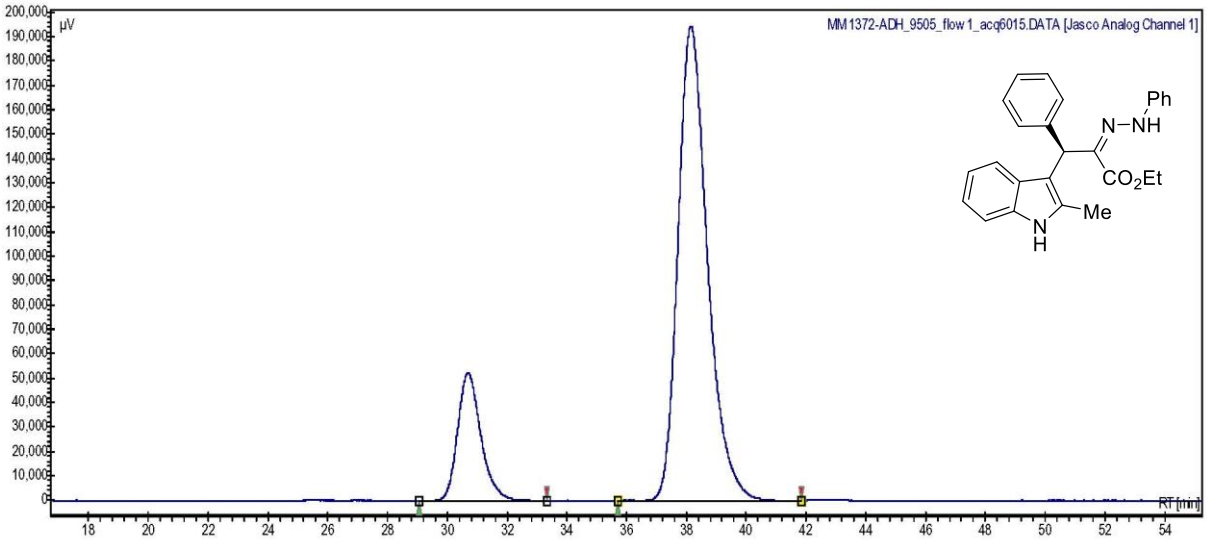


MM 1342-ADH_9505_flow1_acq6018.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	28.469	30.383	33.335	49.914
2	36.188	38.025	41.054	50.086
Total				100.000

Chromatogram : MM 1372-ADH_9505_flow1_acq6015

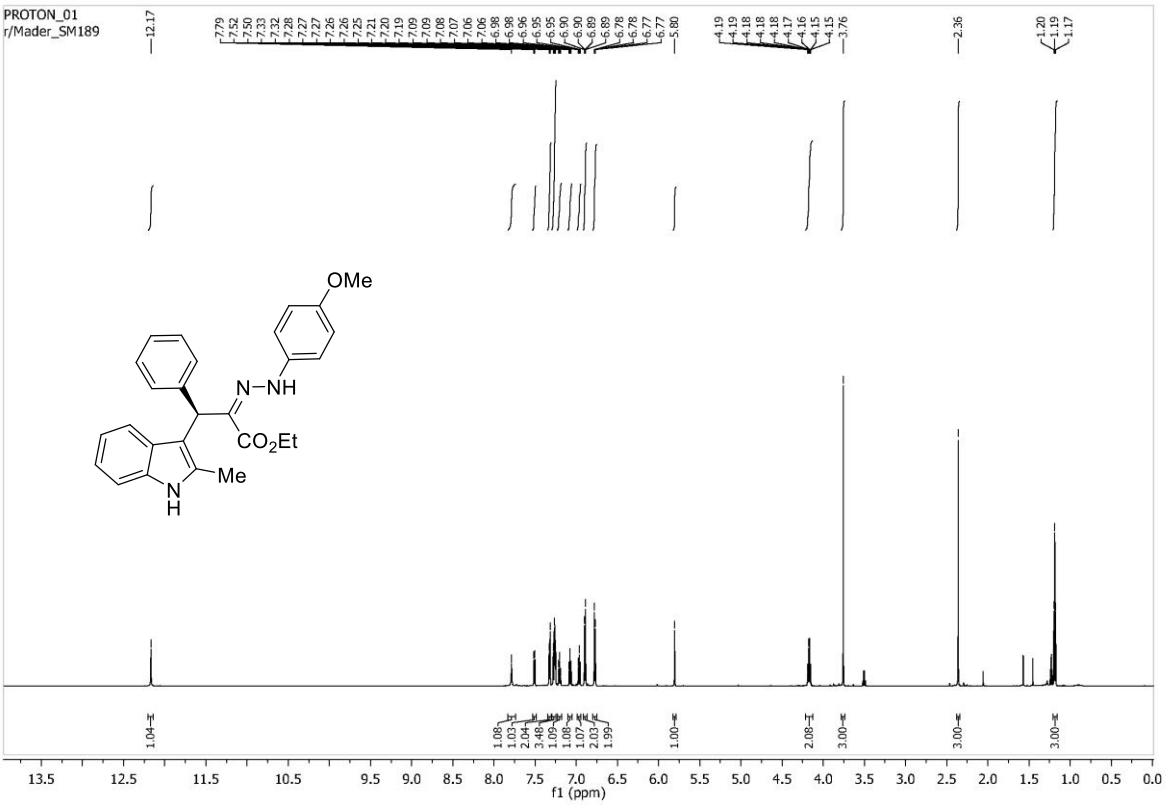
Data file: MM 1372-ADH_9505_flow1_acq6015.DATA
Method: HPLC2_ADH_9505_flow1_acq60
Date: 08.03.2013 21:51:07



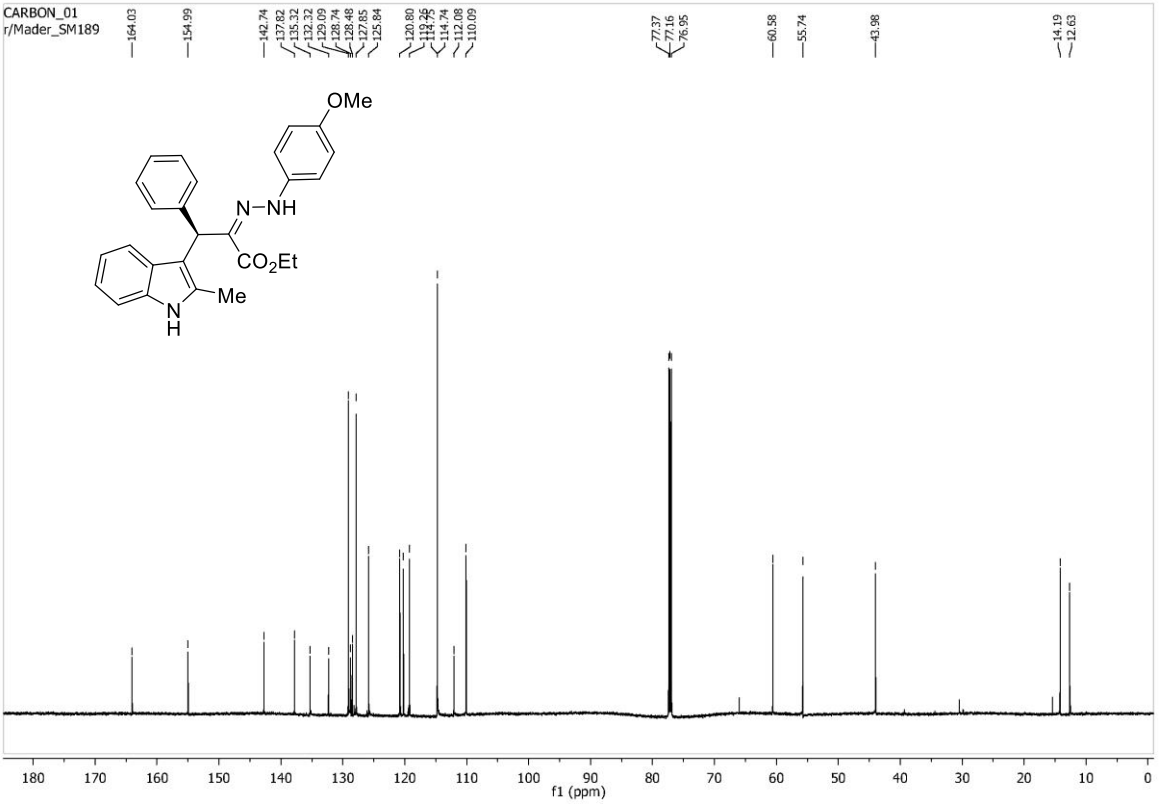
MM 1372-ADH_9505_flow1_acq6015.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	29.070	30.700	33.347	17.468
2	35.702	38.150	41.839	82.532
Total				100.000

^{1}H NMR (600 MHz, $CDCl_3$) for **5a**

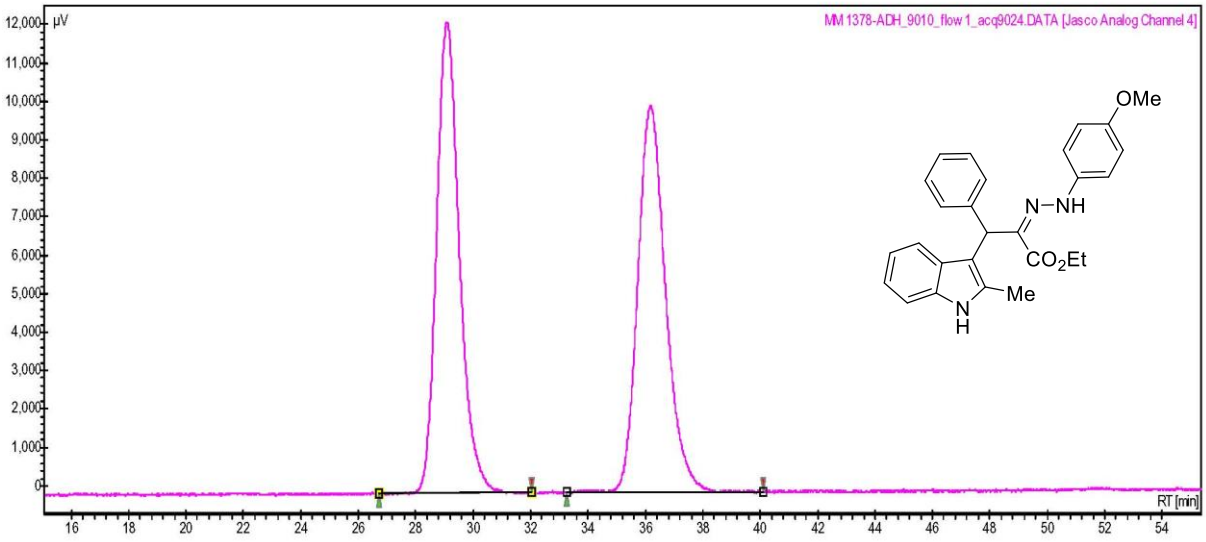


^{13}C NMR (150 MHz, $CDCl_3$) for **5a**



Chromatogram : MM 1378-ADH_9010_flow1_acq9024

Data file: MM 1378-ADH_9010_flow1_acq9024.DATA
Method: HPLC2_ADH_9010_flow1_acq90
Date: 19-Mar-13 4:04:41 PM

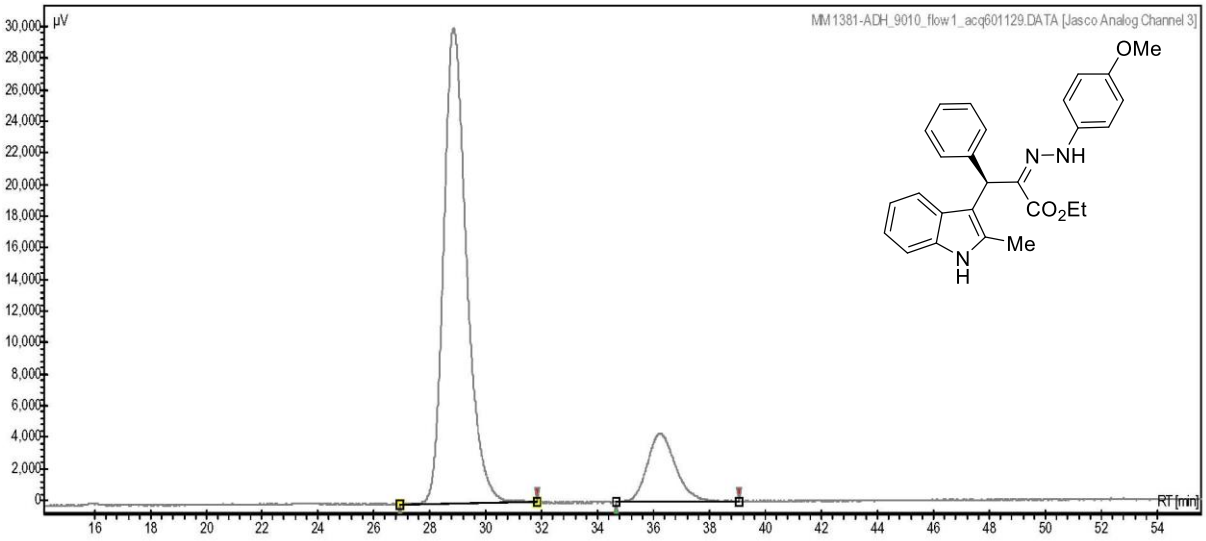


MM 1378-ADH_9010_flow1_acq9024.DATA [Jasco Analog Channel 4]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	26.725	29.092	32.040	49.951
2	33.263	36.175	40.107	50.049
Total				100.000

Chromatogram : MM 1381-ADH_9010_flow1_acq601129

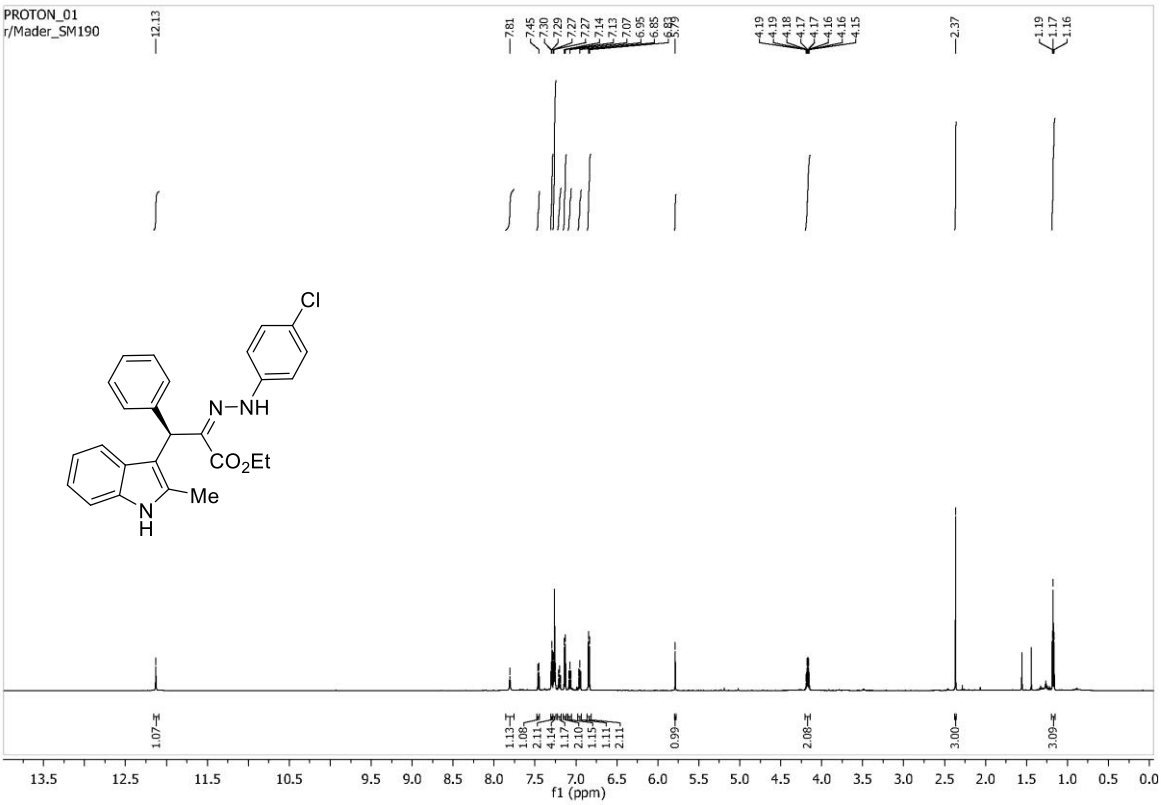
Data file: MM 1381-ADH_9010_flow1_acq601129.DATA
Method: HPLC2_ADH_9010_flow1_acq60
Date: 22-Mar-13 3:33:05 AM



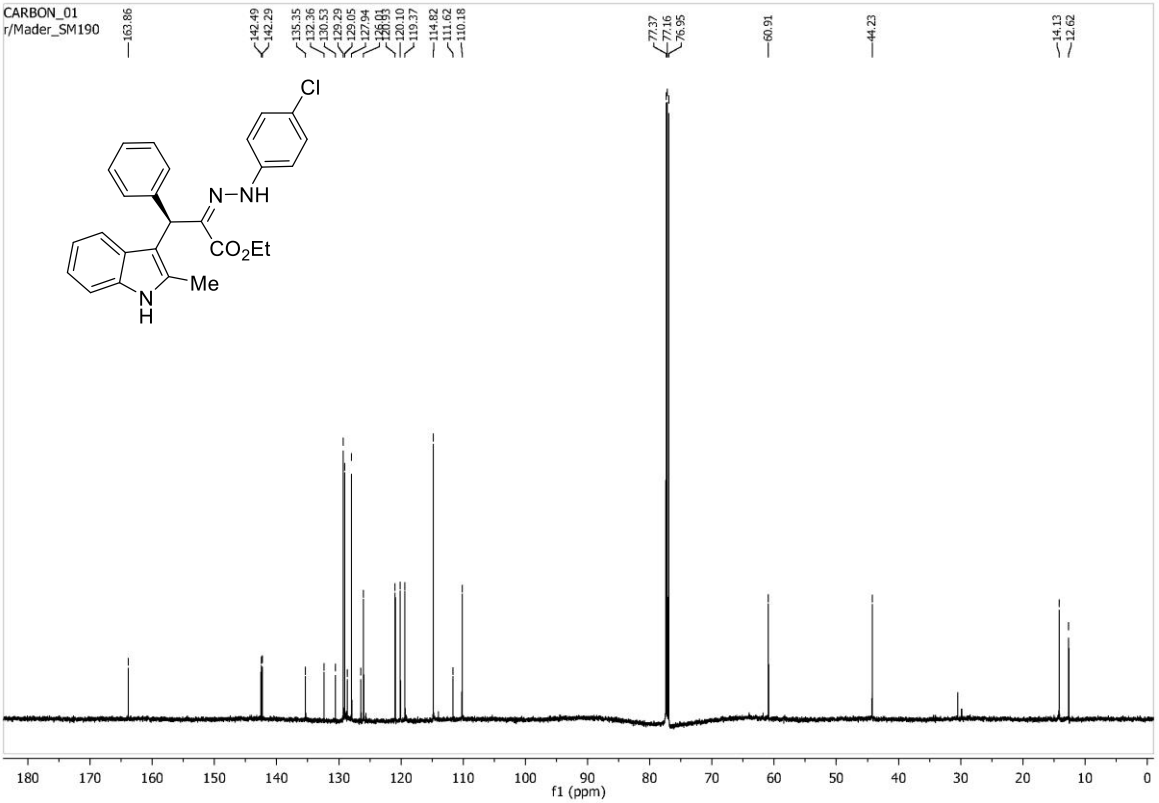
MM 1381-ADH_9010_flow1_acq601129.DATA [Jasco Analog Channel 3]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	26.926	28.850	31.825	85.012
2	34.661	36.258	39.045	14.988
Total				100.000

^{1}H NMR (600 MHz, $CDCl_3$) for **6a**

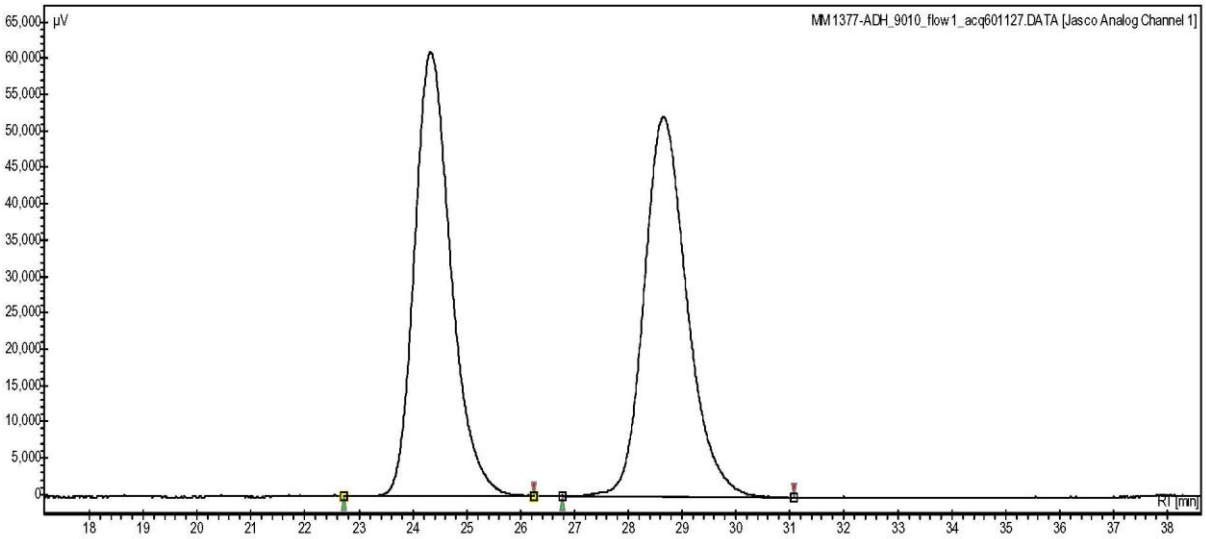


^{13}C NMR (150 MHz, $CDCl_3$) for **6a**



Chromatogram : MM 1377-ADH_9010_flow1_acq601127

Data file: MM 1377-ADH_9010_flow1_acq601127.DATA
Method: HPLC2_ADH_9010_flow1_acq60
Date: 22.03.2013 04:35:39

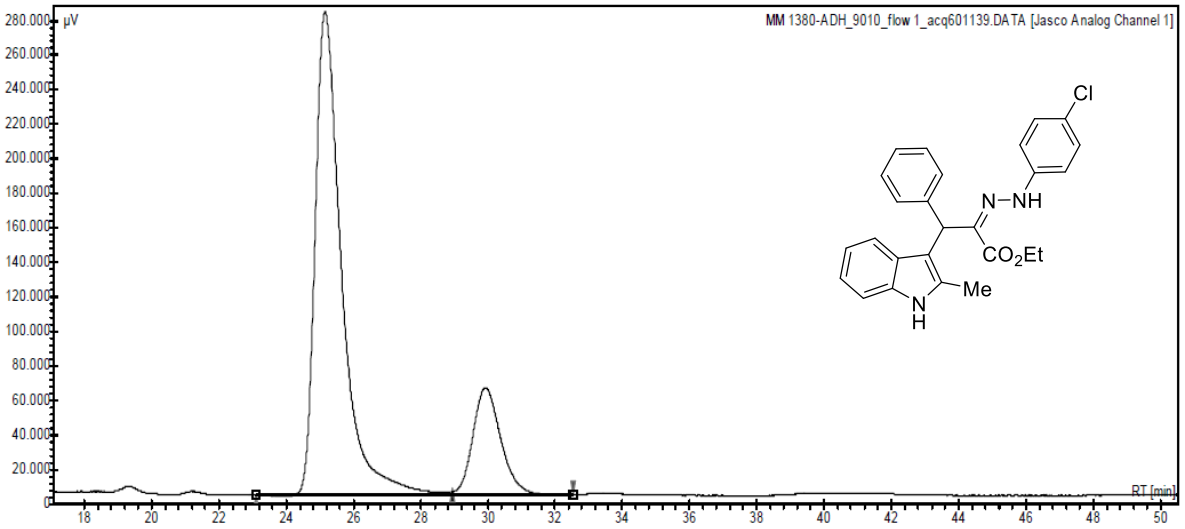


MM 1377-ADH_9010_flow1_acq601127.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	22.726	24.333	26.253	49.855
2	26.779	28.658	31.078	50.145
Total				100.000

Chromatogram : MM 1380-ADH_9010_flow1_acq601139

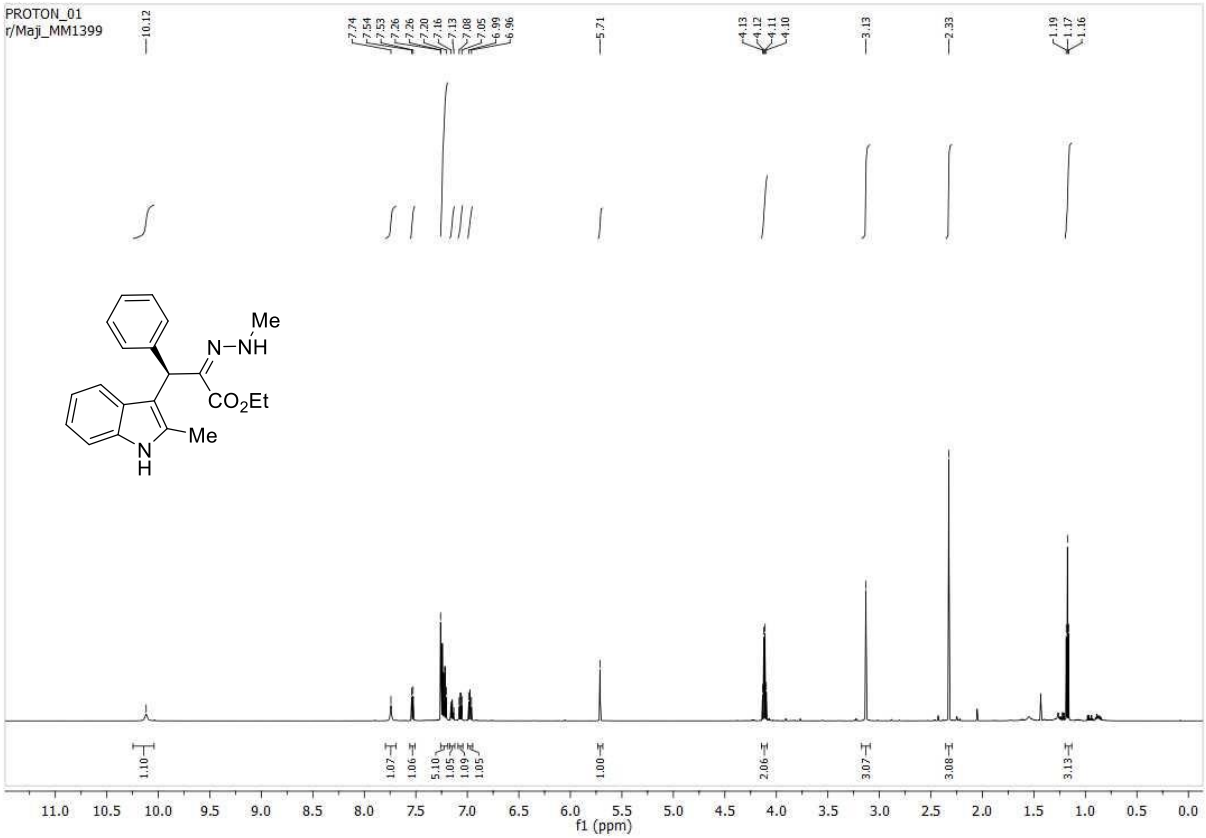
Data file: MM 1380-ADH_9010_flow1_acq601139.DATA
Method: HPLC2_ADH_9010_flow1_acq60
Date: 23.03.2013 01:33:30



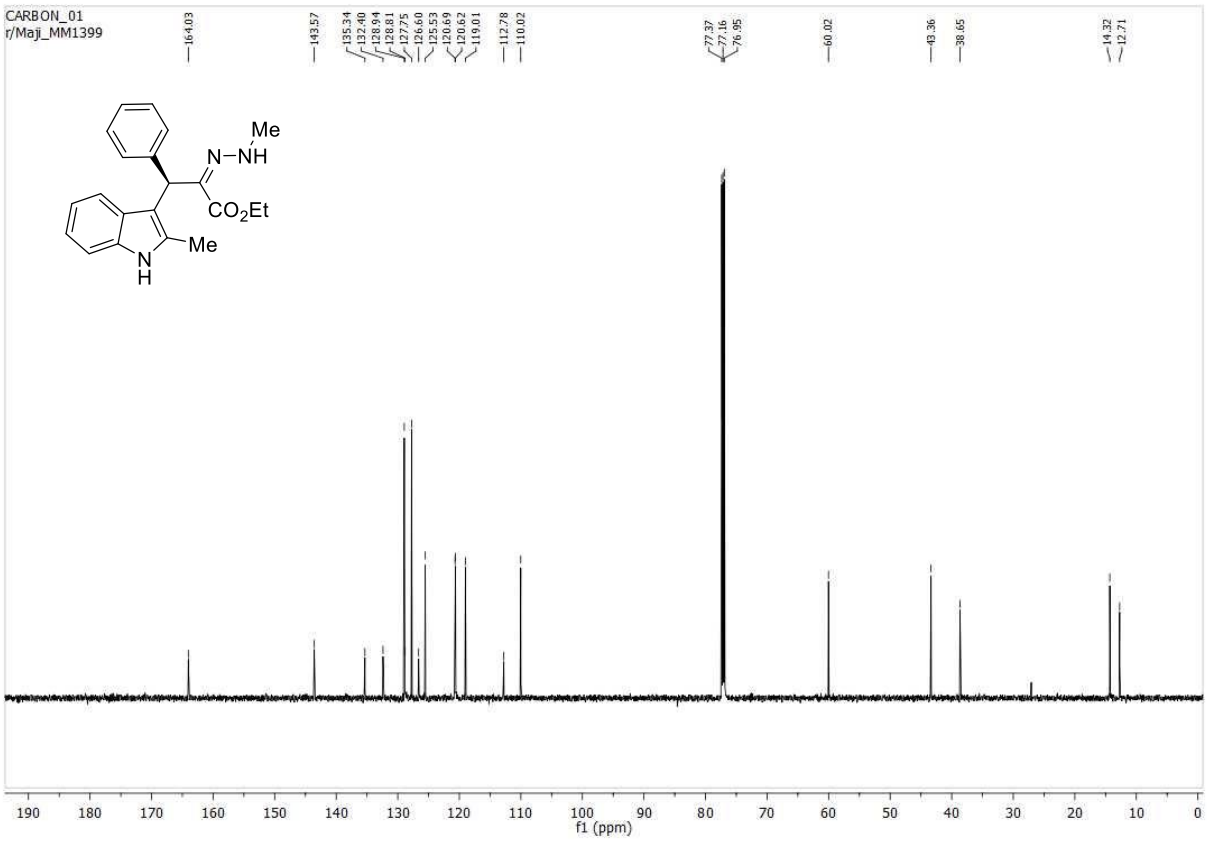
MM 1380-ADH_9010_flow1_acq601139.DATA [Jasco Analog Channel 1]

Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	23,113	25,158	28,946	0,000	80,94	280184,7	254718,1	80,945
2	UNKNOWN	28,946	29,933	32,535	0,000	19,06	62159,9	59963,6	19,055
Total						100,00	342344,6	314681,7	100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **7a**

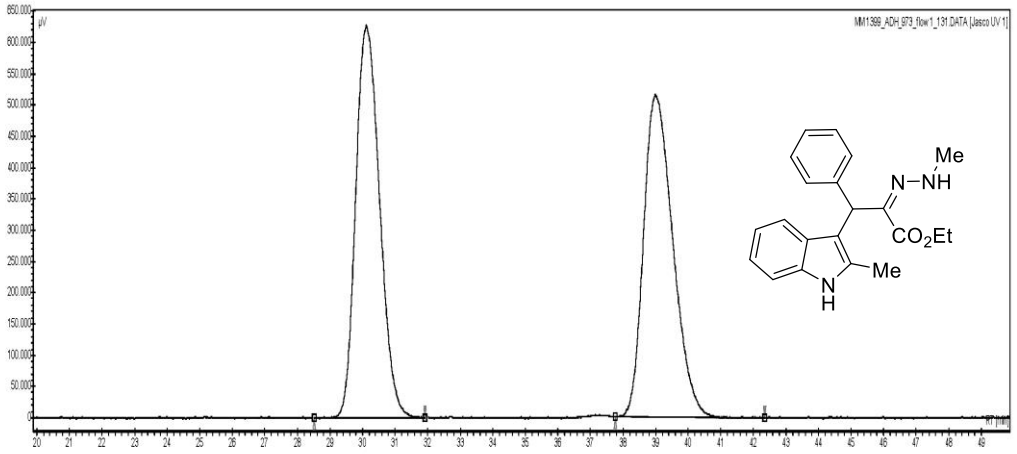


^{13}C NMR (150 MHz, $CDCl_3$) for **7a**



Chromatogram : MM 1399_ADH_973_flow1_131

Data file: MM 1399_ADH_973_flow1_131.DATA
Method: HPLC1_ADH_973_flow1_acq_50
Date: 04.04.2013 15:52:48

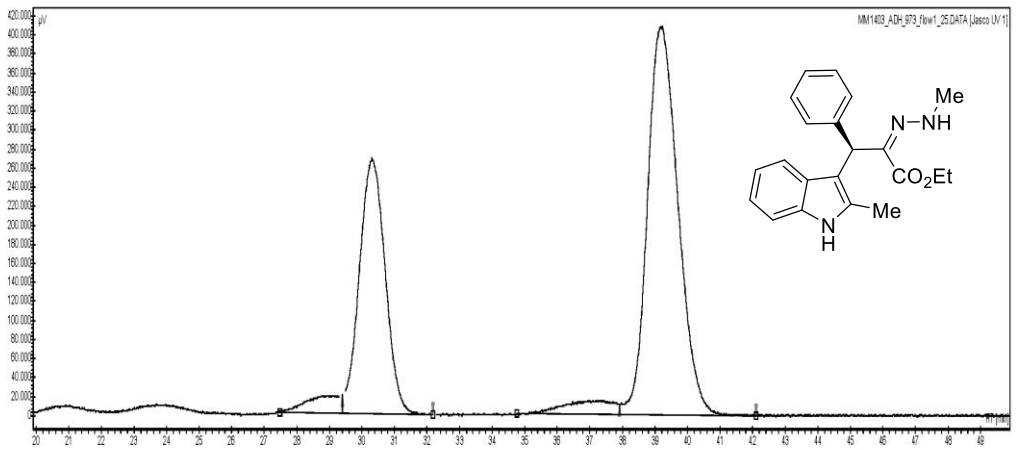


MM 1399_ADH_973_flow1_131.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	28,512	30,117	31,921	49,983
2	37,758	38,992	42,355	50,017
Total				100,000

Chromatogram : MM 1403_ADH_973_flow1_25

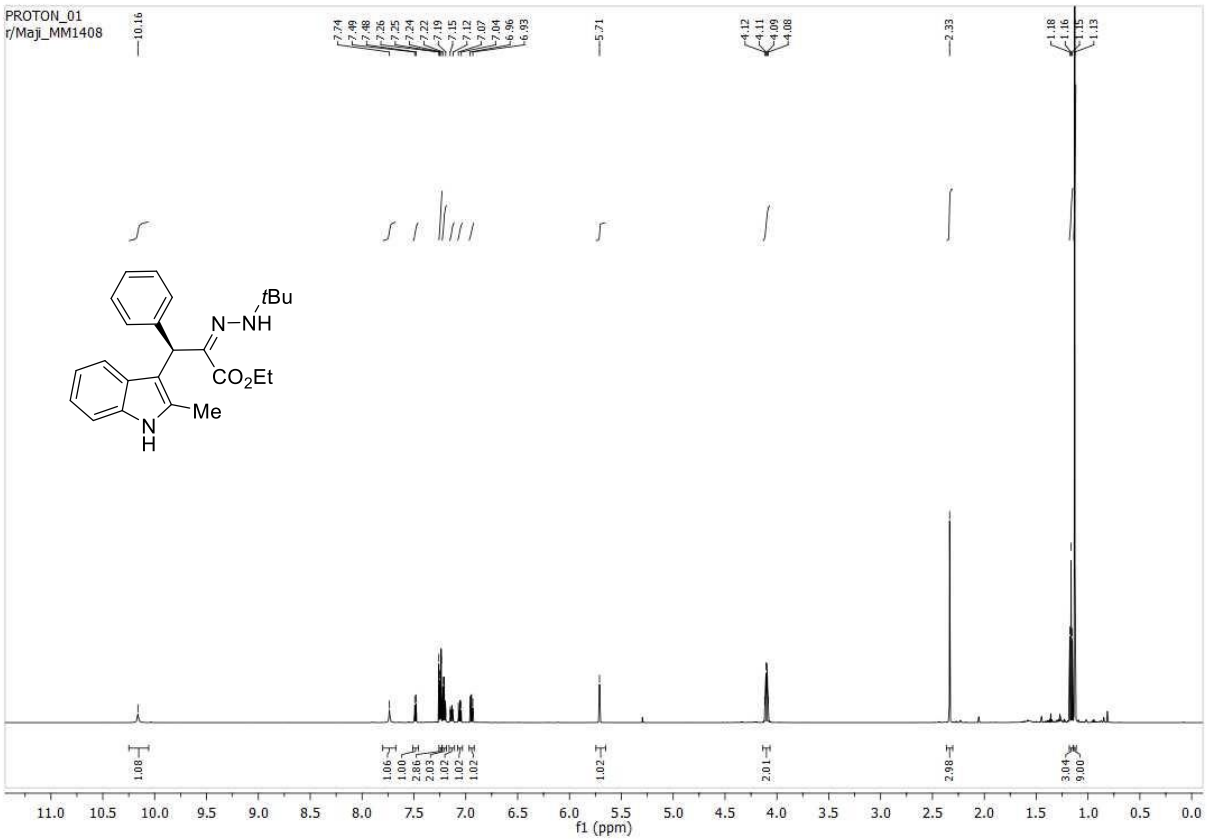
Data file: MM 1403_ADH_973_flow1_25.DATA
Method: HPLC1_ADH_973_flow1_acq_50
Date: 04.04.2013 17:20:08



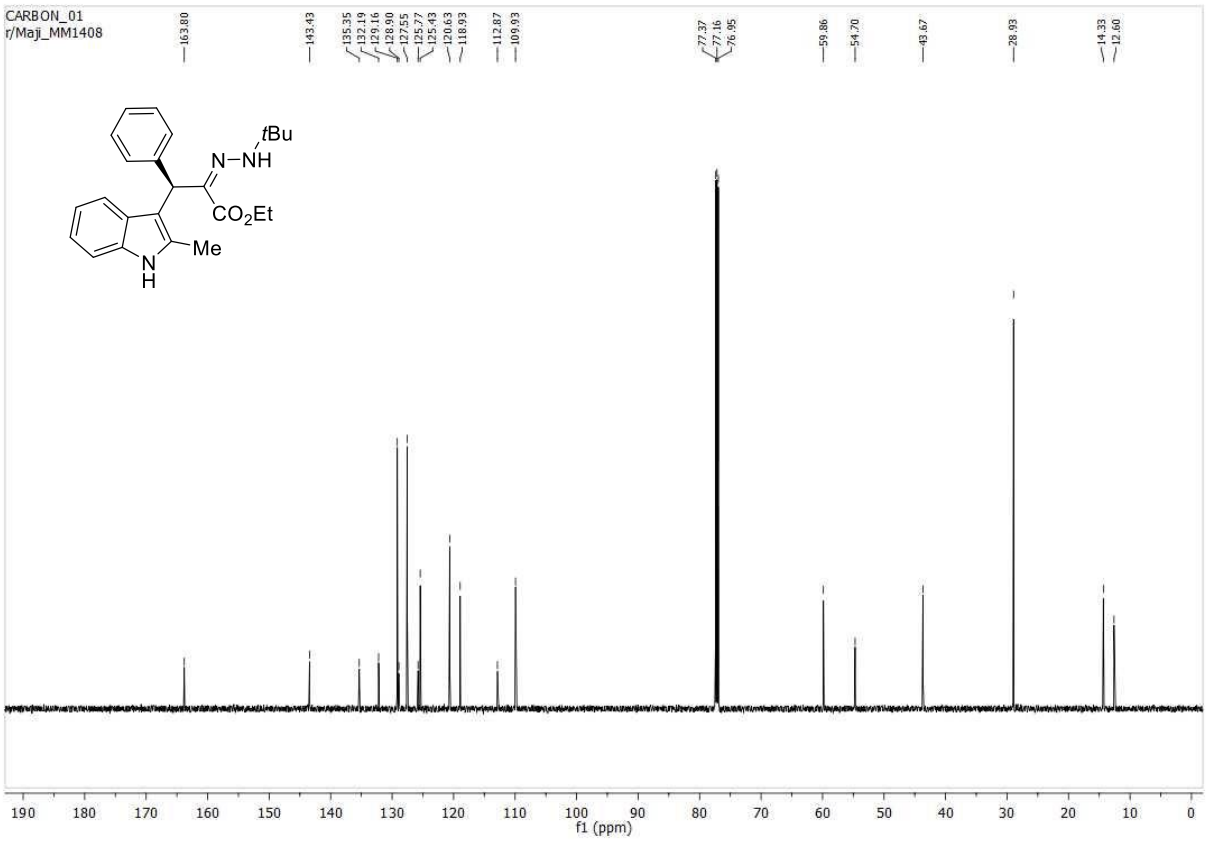
MM 1403_ADH_973_flow1_25.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	29,390	30,308	32,180	35,707
2	37,913	39,225	42,097	64,293
Total				100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **8a**

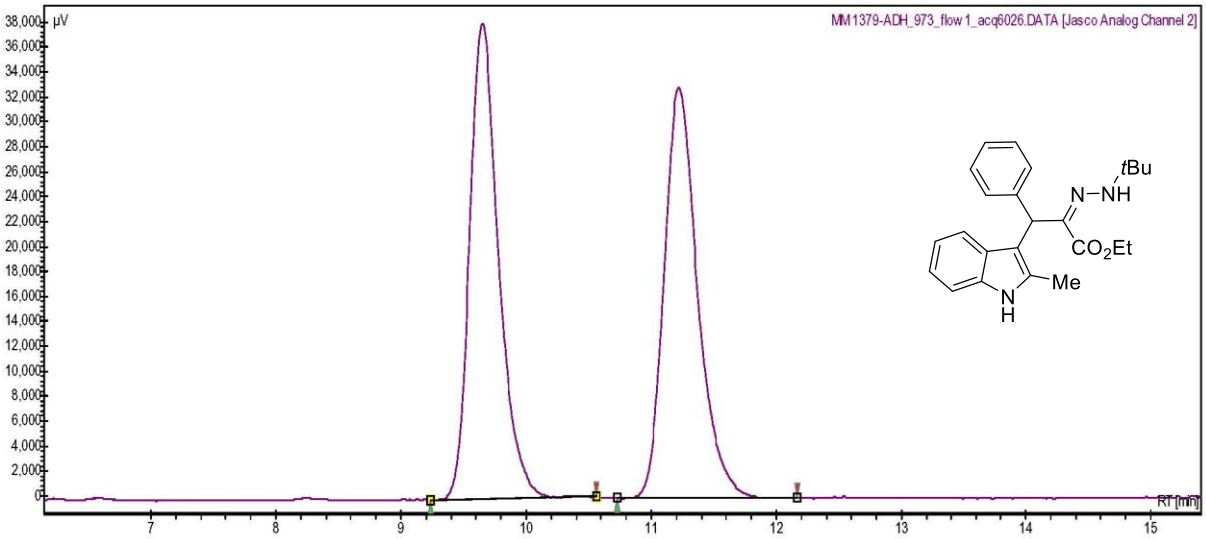


^{13}C NMR (150 MHz, $CDCl_3$) for **8a**



Chromatogram : MM 1379-ADH_973_flow1_acq6026

Data file: MM 1379-ADH_973_flow1_acq6026.DATA
Method: HPLC2_ADH_973_flow1_acq60
Date: 19-Mar-13 5:49:25 PM

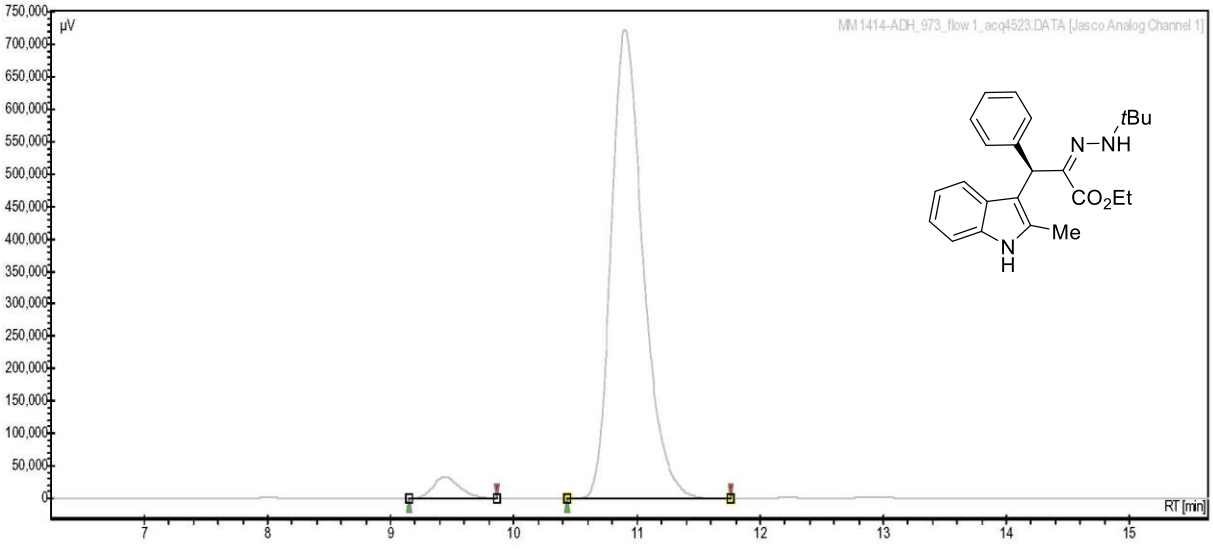


MM 1379-ADH_973_flow1_acq6026.DATA [Jasco Analog Channel 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9.236	9.650	10.562	50.164
2	10.730	11.225	12.168	49.836
Total				100.000

Chromatogram : MM 1414-ADH_973_flow1_acq4523

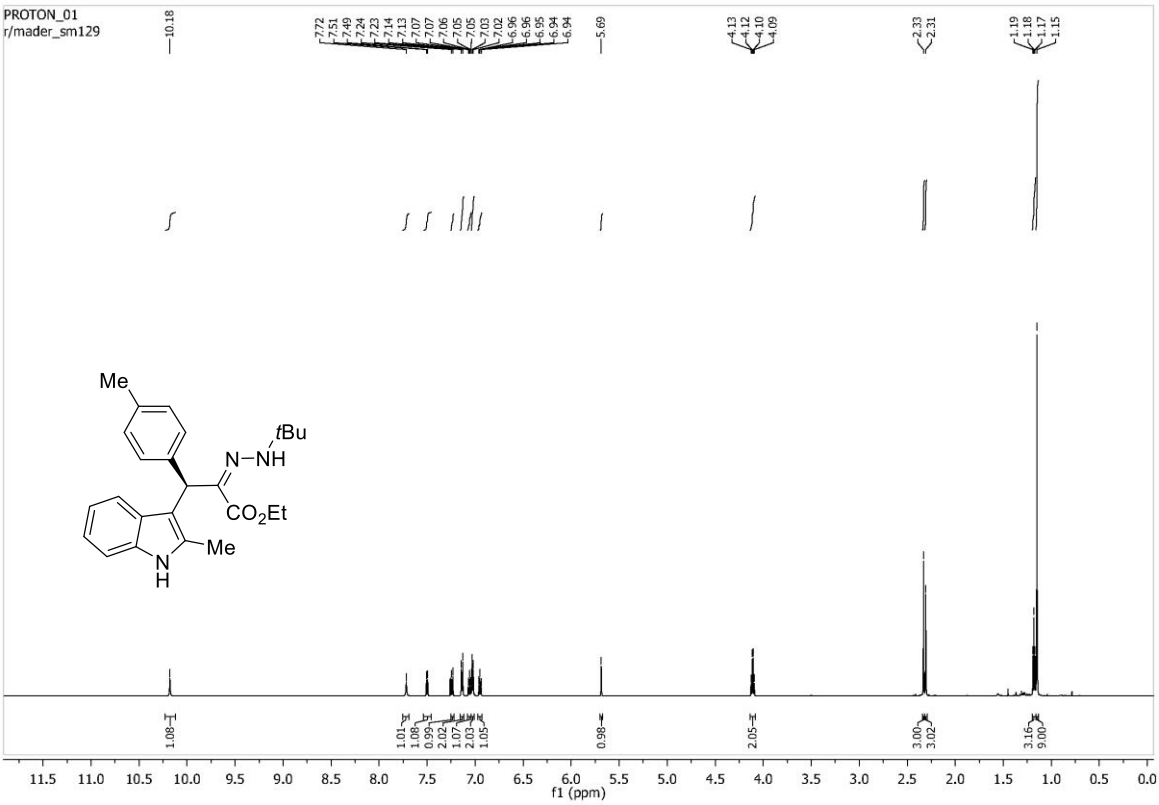
Data file: MM 1414-ADH_973_flow1_acq4523.DATA
Method: HPLC2_ADH_973_flow1_acq45
Date: 11-Apr-13 5:44:03 PM



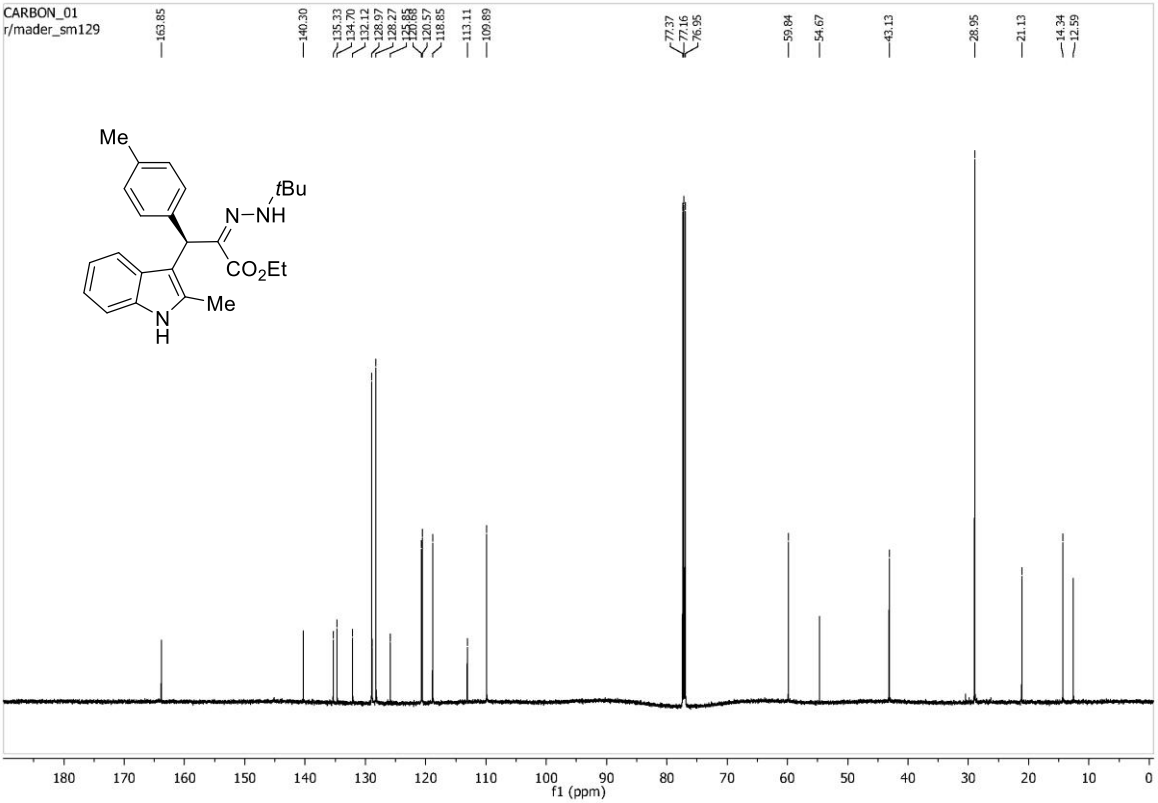
MM 1414-ADH_973_flow1_acq4523.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9.146	9.442	9.863	3.685
2	10.431	10.900	11.764	96.315
Total				100.000

^{1}H NMR (600 MHz, $CDCl_3$) for **8b**

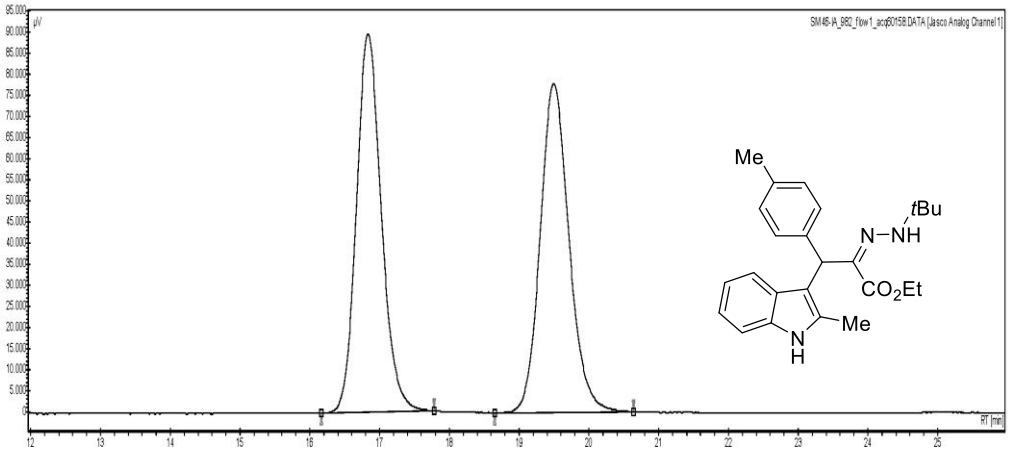


^{13}C NMR (150 MHz, $CDCl_3$) for **8b**



Chromatogram : SM 46-IA_982_flow1_acq60158

Data file: SM 46-IA_982_flow1_acq60158.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 20.04.2013 01:45:47

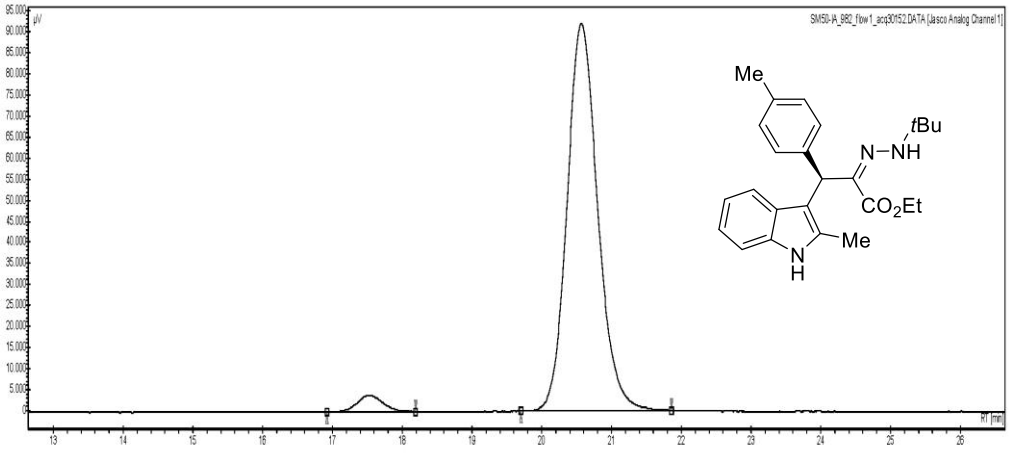


SM 46-IA_982_flow1_acq60158.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16,165	16,833	17,782	49,879
2	18,647	19,492	20,639	50,121
Total				100,000

Chromatogram : SM 50-IA_982_flow1_acq30152

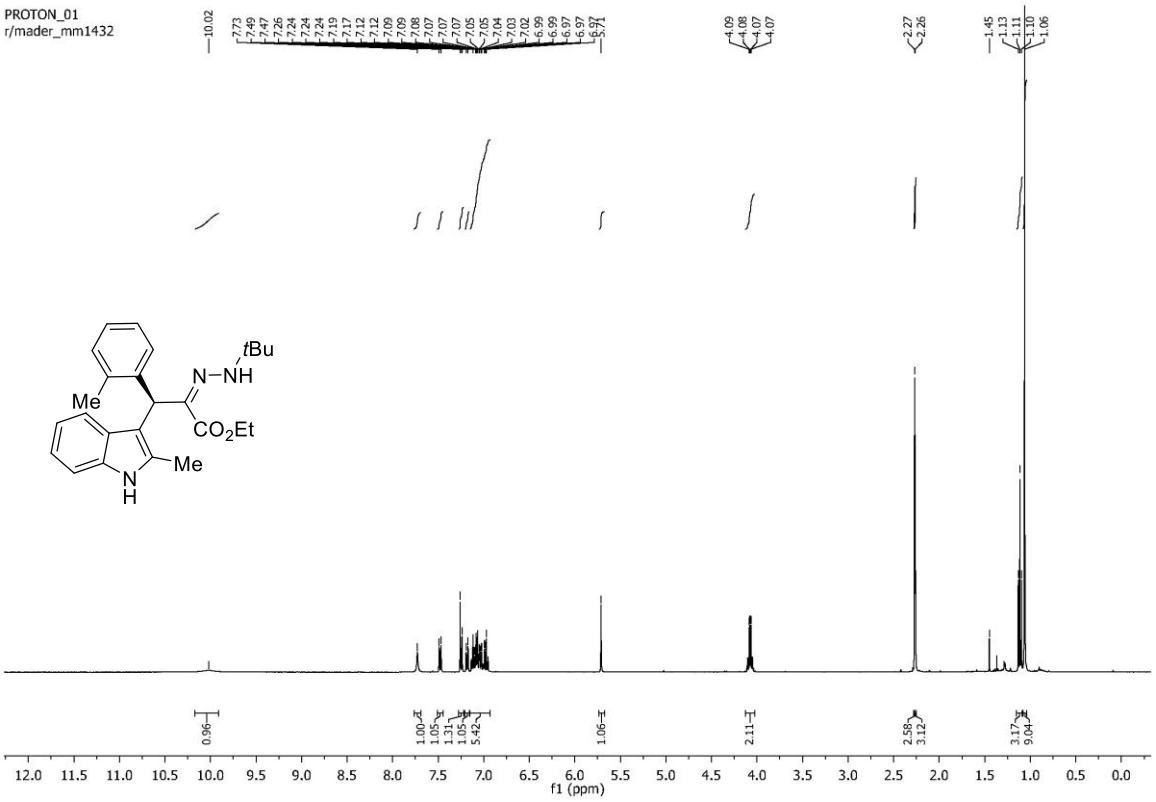
Data file: SM 50-IA_982_flow1_acq30152.DATA
Method: HPLC2_IA_982_flow1_acq30
Date: 22.04.2013 23:14:55



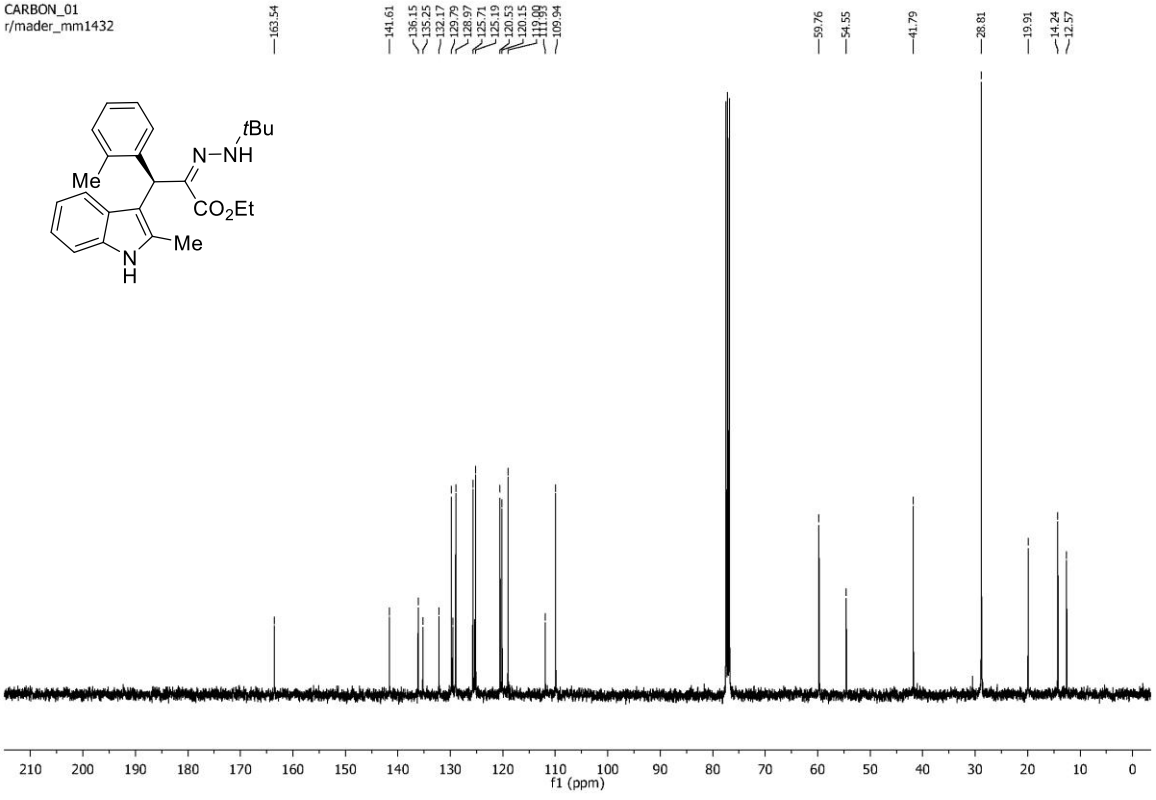
SM 50-IA_982_flow1_acq30152.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16,917	17,508	18,195	3,564
2	19,699	20,567	21,861	96,436
Total				100,000

^{1}H NMR (400 MHz, $CDCl_3$) for **8c**

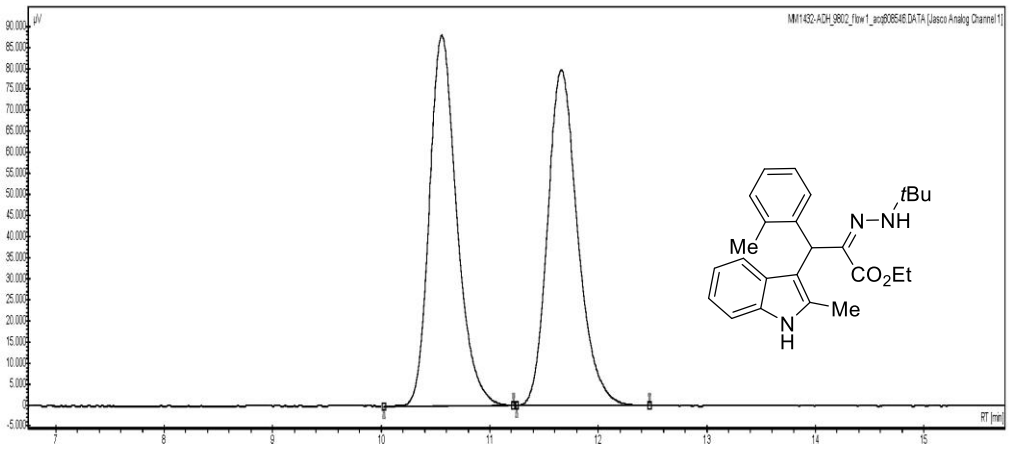


^{13}C NMR (100 MHz, $CDCl_3$) for **8c**



Chromatogram : MM 1432-ADH_9802_flow1_acq608546

Data file: MM 1432-ADH_9802_flow1_acq608546.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 25.04.2013 02:07:57

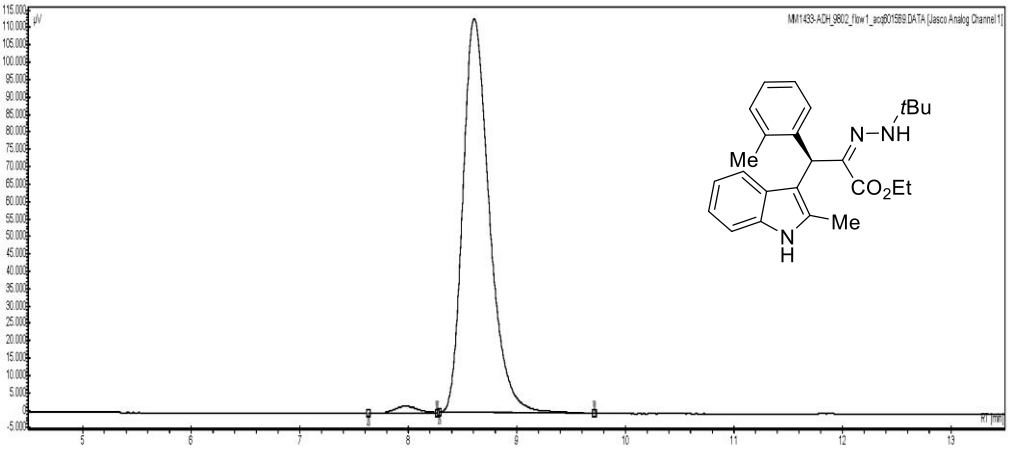


MM 1432-ADH_9802_flow1_acq608546.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	10,024	10,558	11,218	50,079
2	11,246	11,658	12,472	49,921
Total				100,000

Chromatogram : MM 1433-ADH_9802_flow1_acq601569

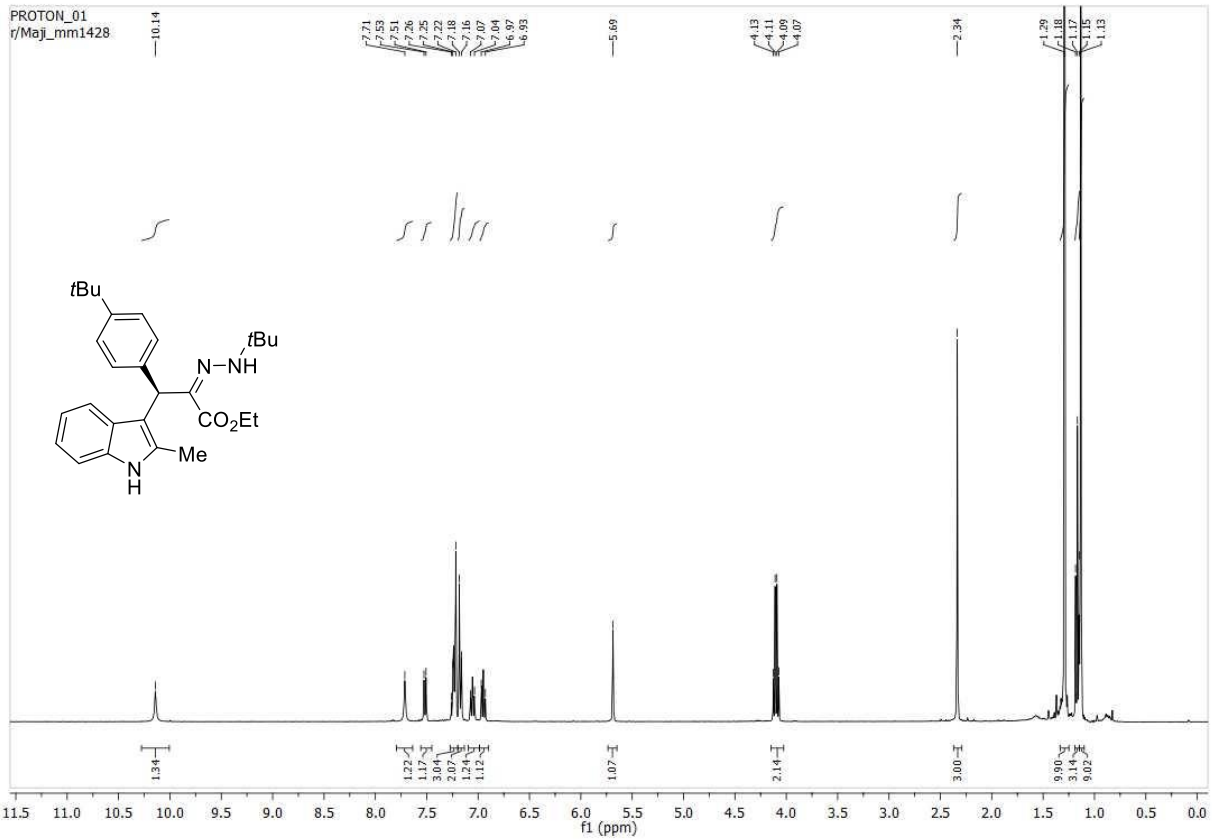
Data file: MM 1433-ADH_9802_flow1_acq601569.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 25.04.2013 22:29:40



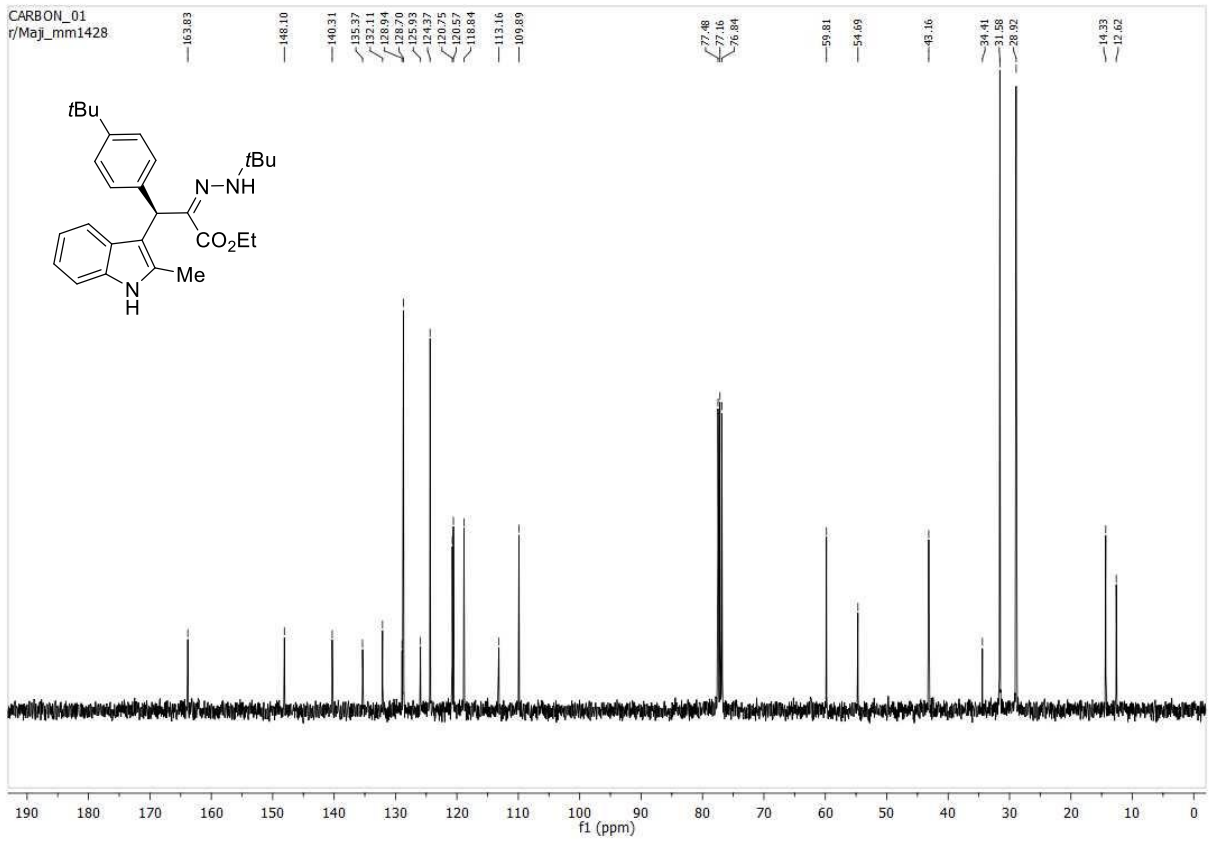
MM 1433-ADH_9802_flow1_acq601569.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	7,636	7,967	8,267	1,500
2	8,290	8,608	9,717	98,500
Total				100,000

^{1}H NMR (400 MHz, $CDCl_3$) for **8d**

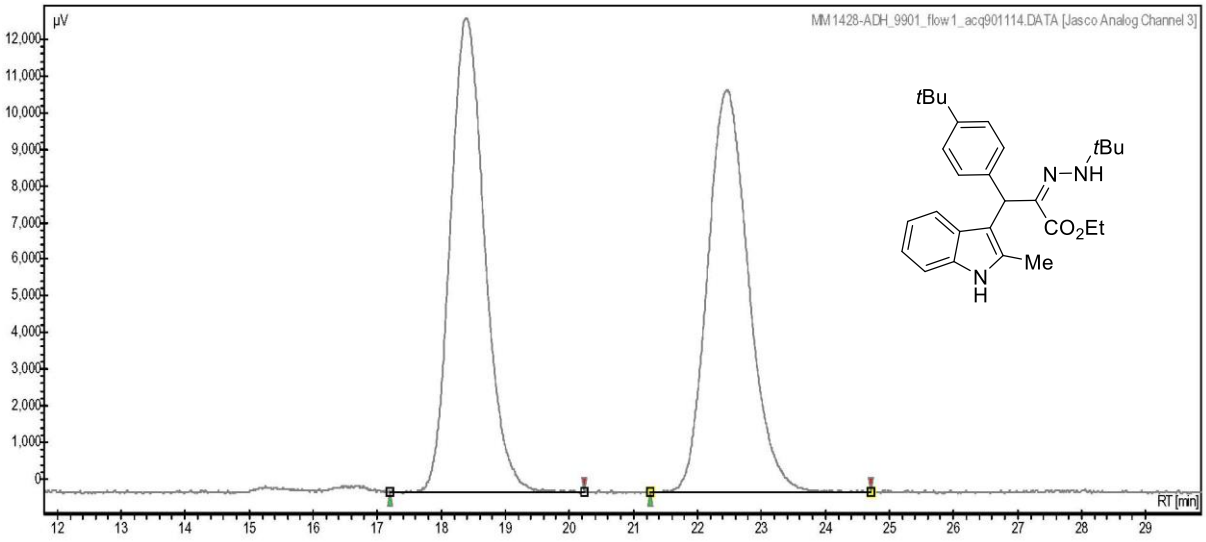


^{13}C NMR (100 MHz, $CDCl_3$) for **8d**



Chromatogram : MM 1428-ADH_9901_flow1_acq901114

Data file: MM 1428-ADH_9901_flow1_acq901114.DATA
Method: HPLC2_ADH_9901_flow1_acq90
Date: 23-Apr-13 12:52:43 AM

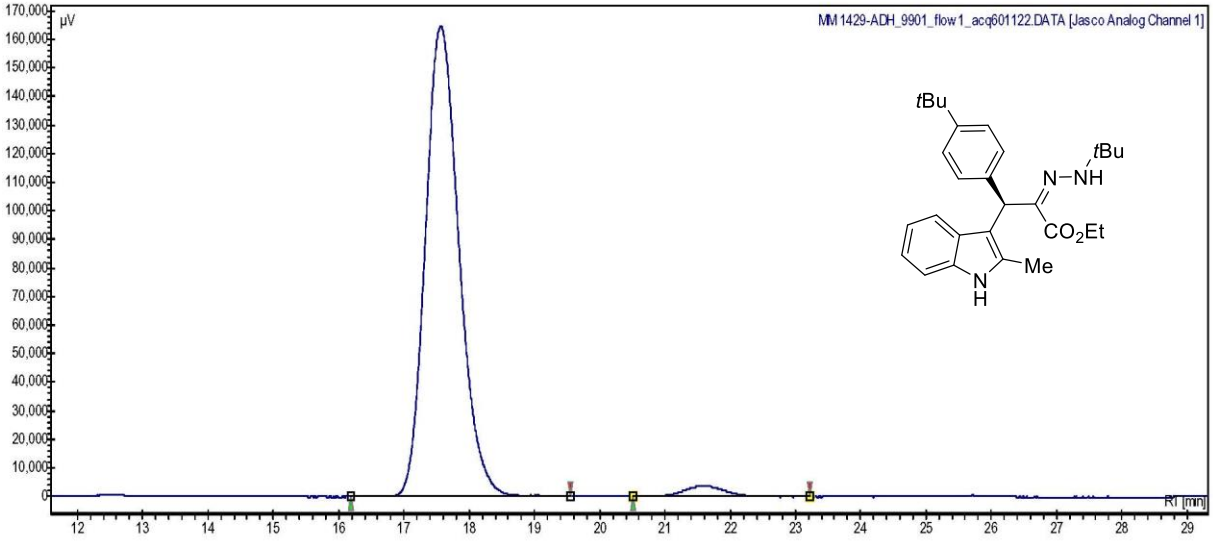


MM 1428-ADH_9901_flow1_acq901114.DATA [Jasco Analog Channel 3]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17.205	18.392	20.239	49.557
2	21.265	22.458	24.718	50.443
Total				100.000

Chromatogram : MM 1429-ADH_9901_flow1_acq601122

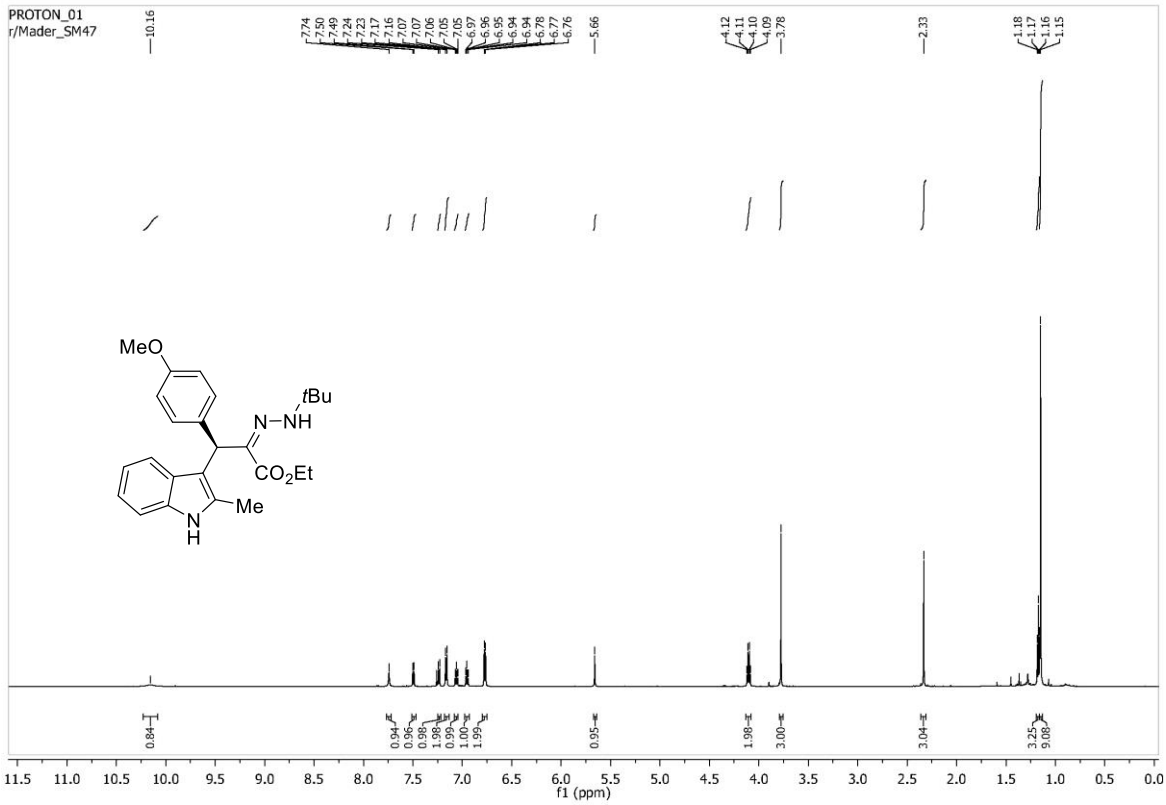
Data file: MM 1429-ADH_9901_flow1_acq601122.DATA
Method: HPLC2_ADH_9901_flow1_acq60
Date: 23-Apr-13 10:08:30 AM



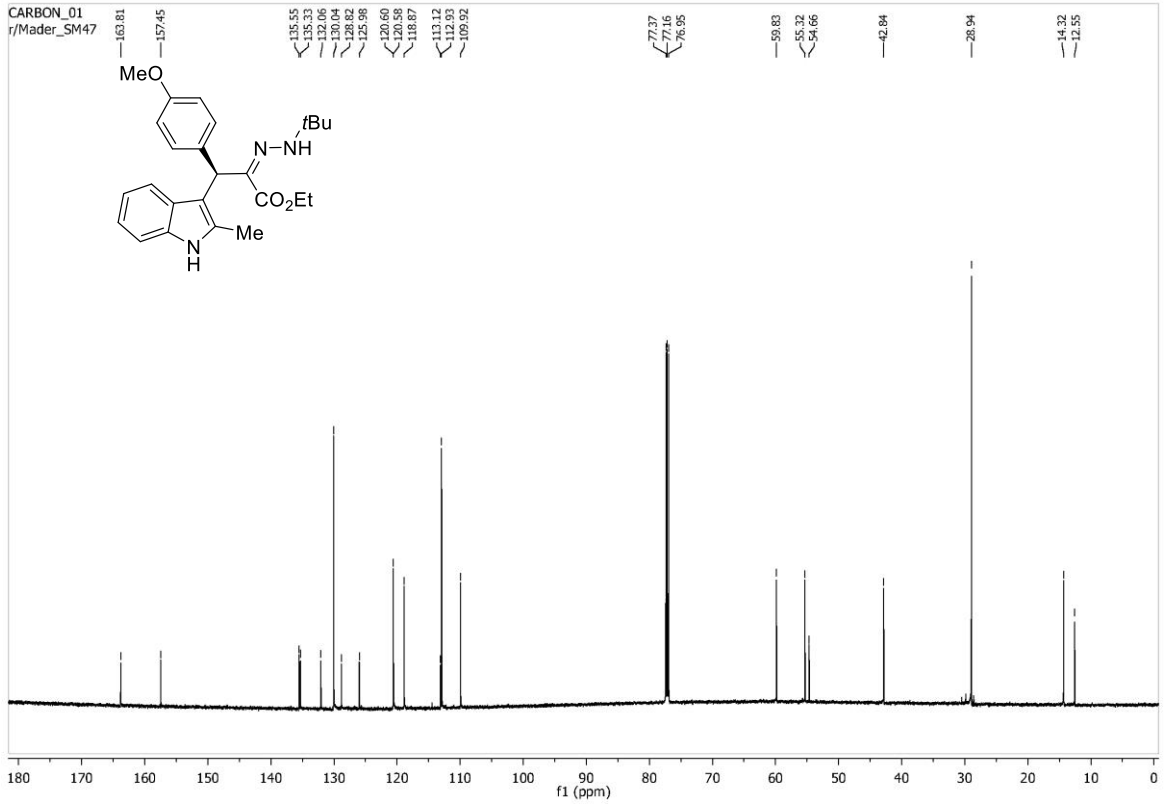
MM 1429-ADH_9901_flow1_acq601122.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16.184	17.567	19.552	97.546
2	20.516	21.567	23.219	2.454
Total				100.000

^{1}H NMR (600 MHz, $CDCl_3$) for **8e**

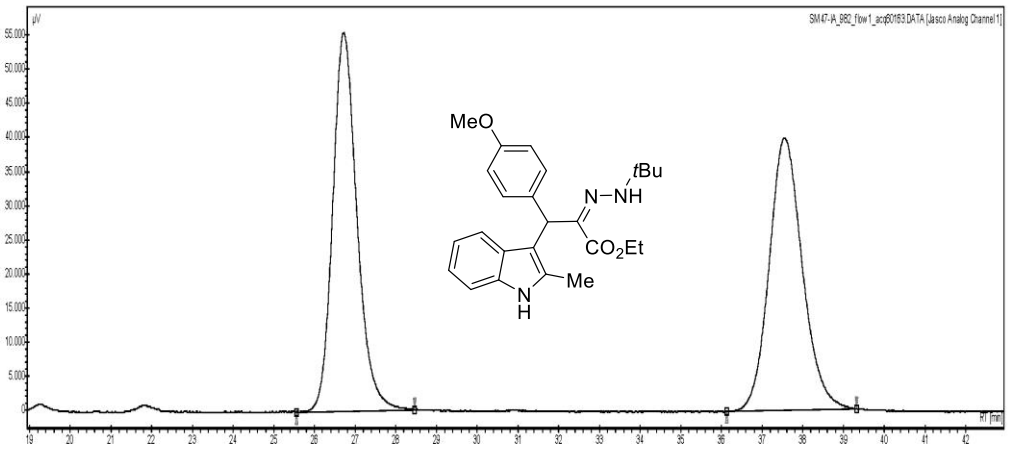


^{13}C NMR (150 MHz, $CDCl_3$) for **8e**



Chromatogram : SM 47-IA_982_flow1_acq60163

Data file: SM 47-IA_982_flow1_acq60163.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 20.04.2013 02:48:23

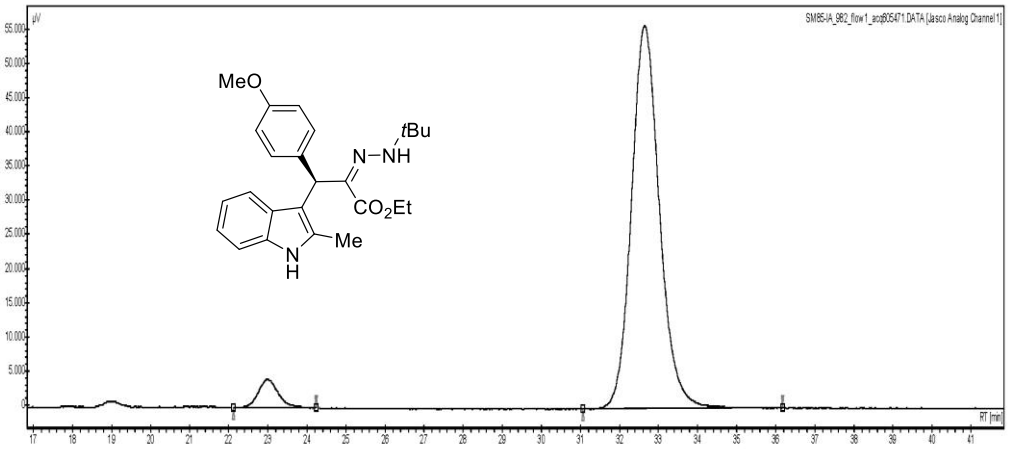


SM 47-IA_982_flow1_acq60163.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	25,564	26,717	28,459	50,356
2	36,128	37,550	39,323	49,644
Total				100,000

Chromatogram : SM 85-IA_982_flow1_acq605471

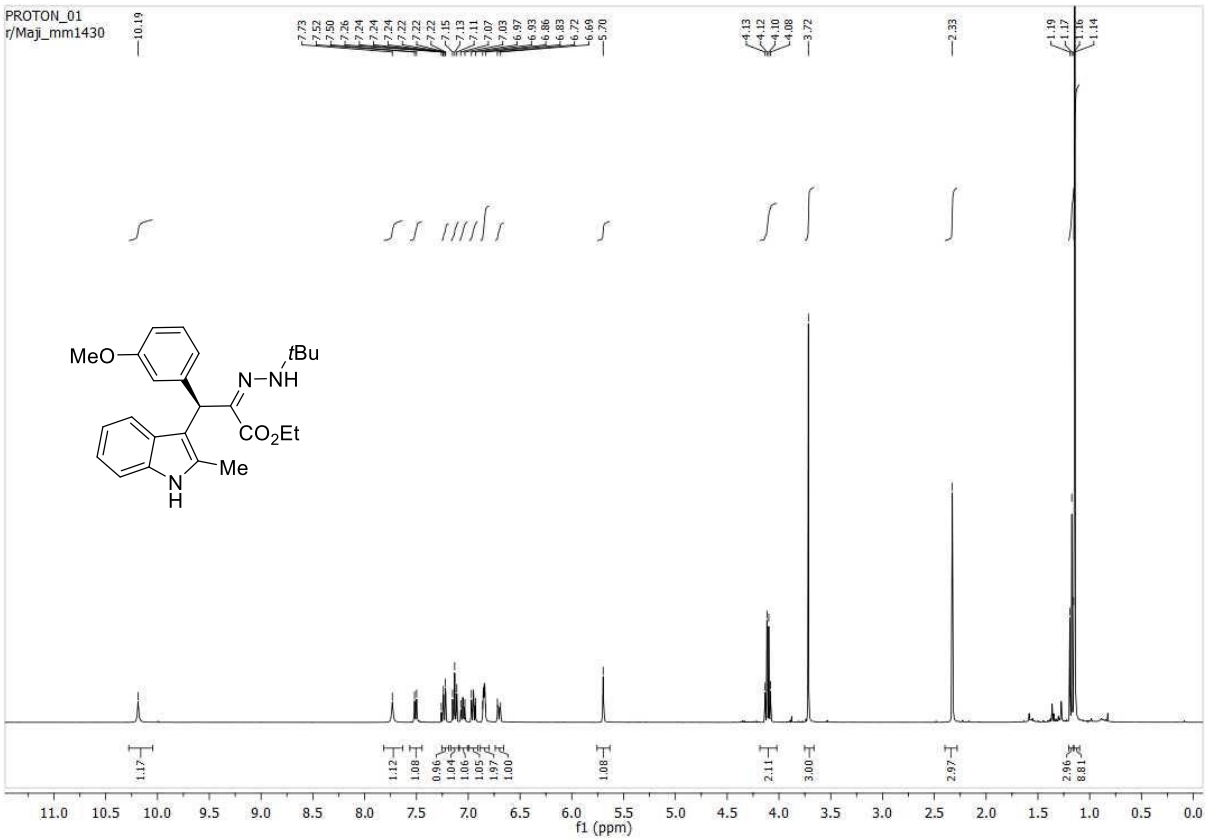
Data file: SM 85-IA_982_flow1_acq605471.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 31.05.2013 05:53:29



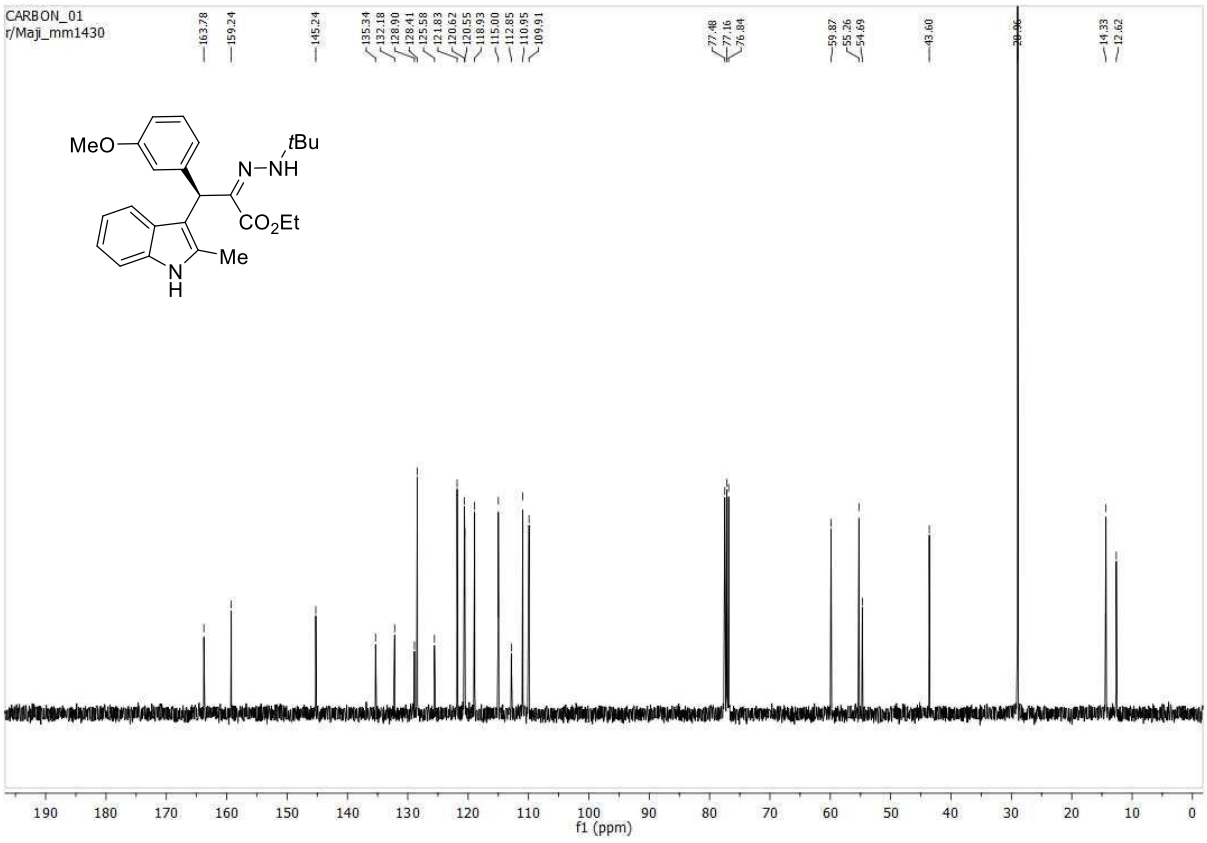
SM 85-IA_982_flow1_acq605471.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	22,115	22,983	24,233	4,973
2	31,069	32,642	36,178	95,027
Total				100,000

^{1}H NMR (400 MHz, $CDCl_3$) for **8f**

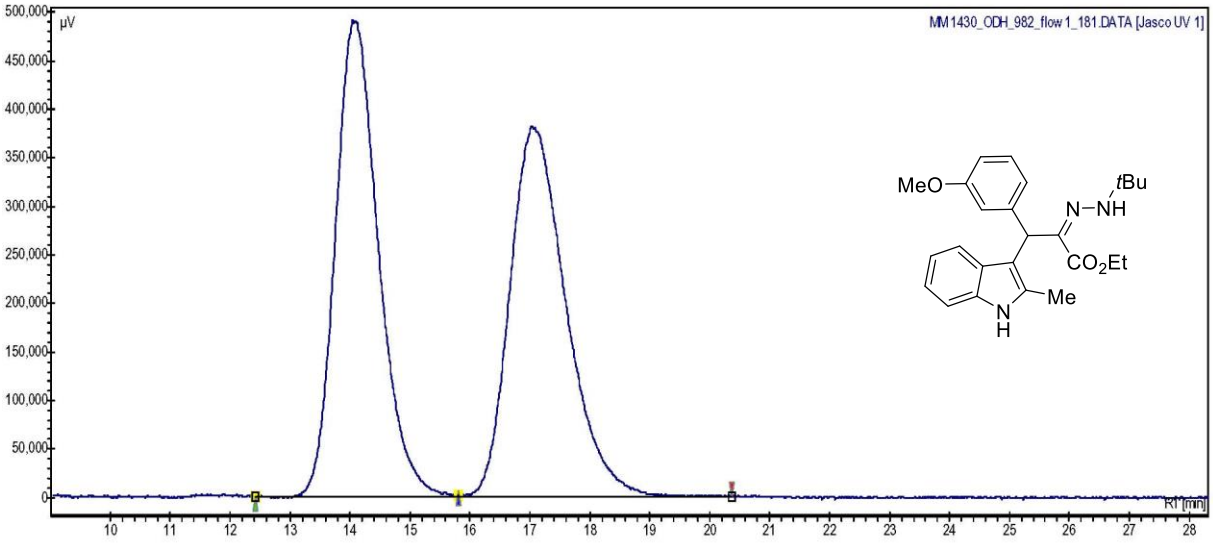


^{13}C NMR (100 MHz, $CDCl_3$) for **8f**



Chromatogram : MM 1430_ODH_982_flow1_181

Data file: MM 1430_ODH_982_flow1_181.DATA
Method: HPLC1_ODH_982_flow1_acq_90
Date: 18.04.2013 21:28:56

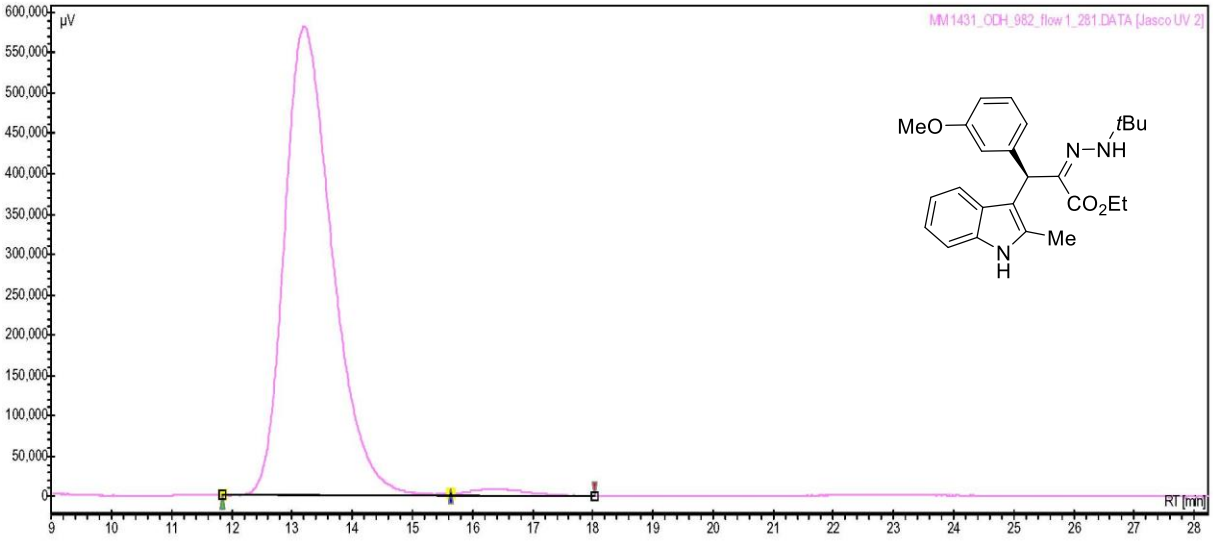


MM 1430_ODH_982_flow1_181.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	12.428	14.042	15.805	49.789
2	15.805	17.042	20.362	50.211
Total				100.000

Chromatogram : MM 1431_ODH_982_flow1_281

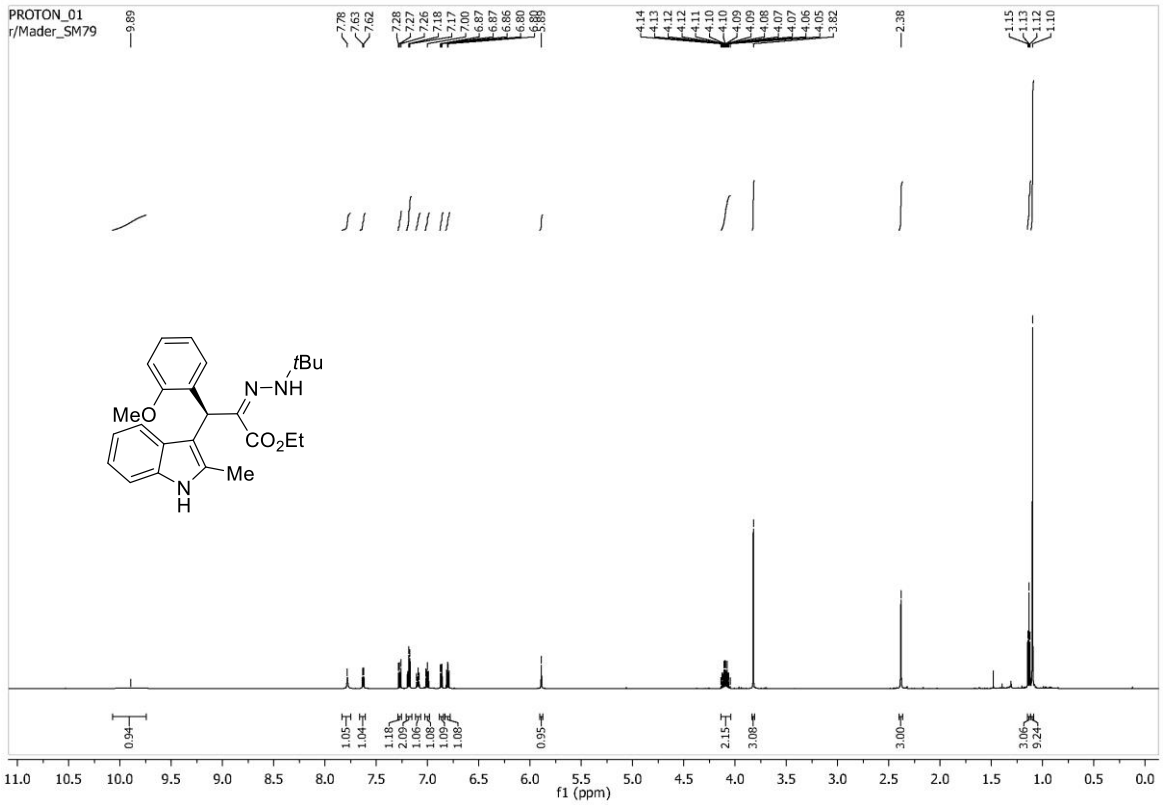
Data file: MM 1431_ODH_982_flow1_281.DATA
Method: HPLC1_ODH_982_flow1_acq_30
Date: 19-Apr-13 1:08:03 PM



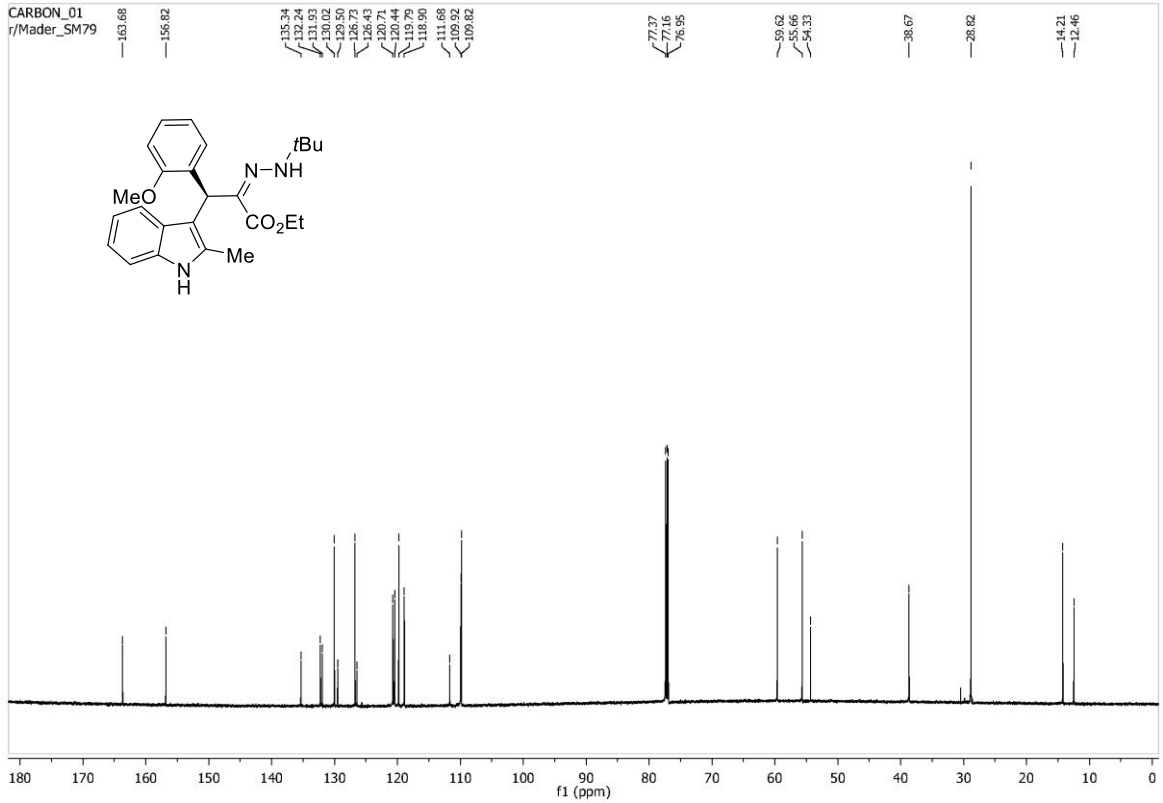
MM 1431_ODH_982_flow1_281.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	11.839	13.200	15.639	98.220
2	15.639	16.400	18.037	1.780
Total				100.000

^{1}H NMR (600 MHz, $CDCl_3$) for **8g**

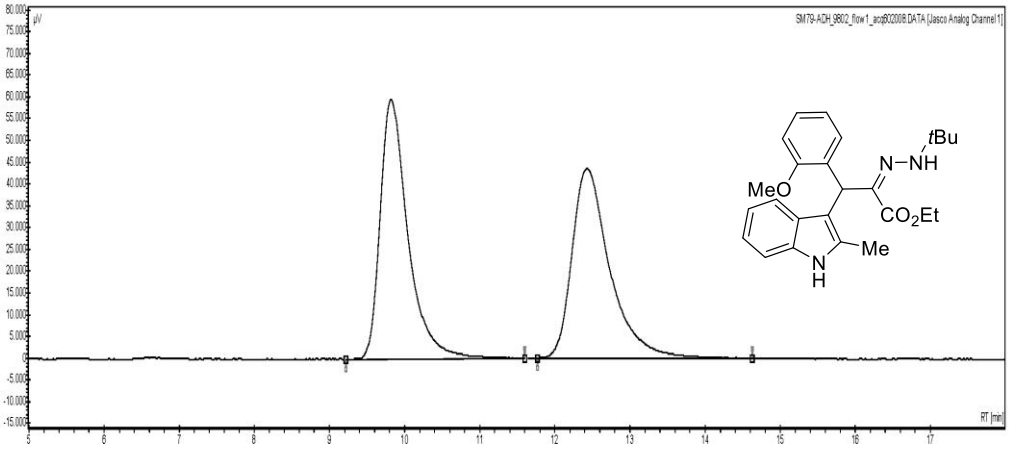


^{13}C NMR (150 MHz, $CDCl_3$) for **8g**



Chromatogram : SM 79-ADH_9802_flow1_acq602008

Data file: SM 79-ADH_9802_flow1_acq602008.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 25.05.2013 05:22:30

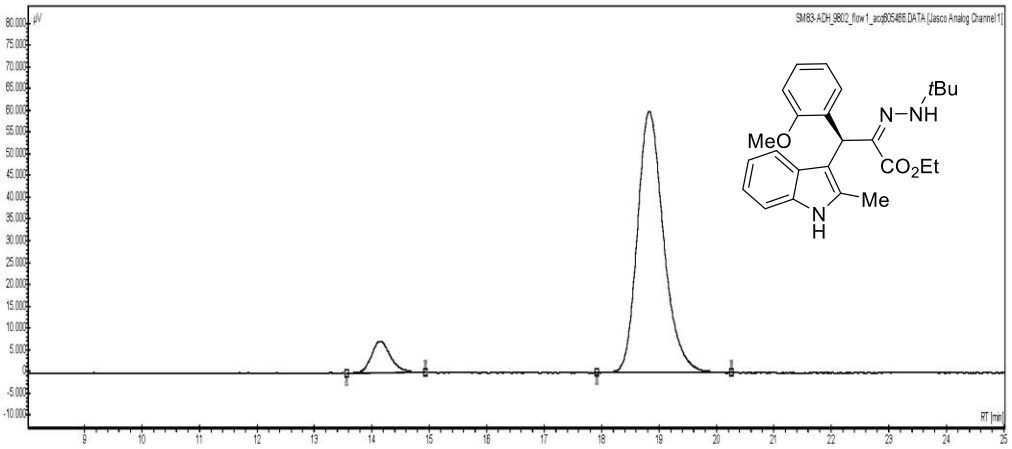


SM 79-ADH_9802_flow1_acq602008.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9,221	9,825	11,594	50,179
2	11,769	12,425	14,624	49,821
Total				100,000

Chromatogram : SM 83-ADH_9802_flow1_acq605466

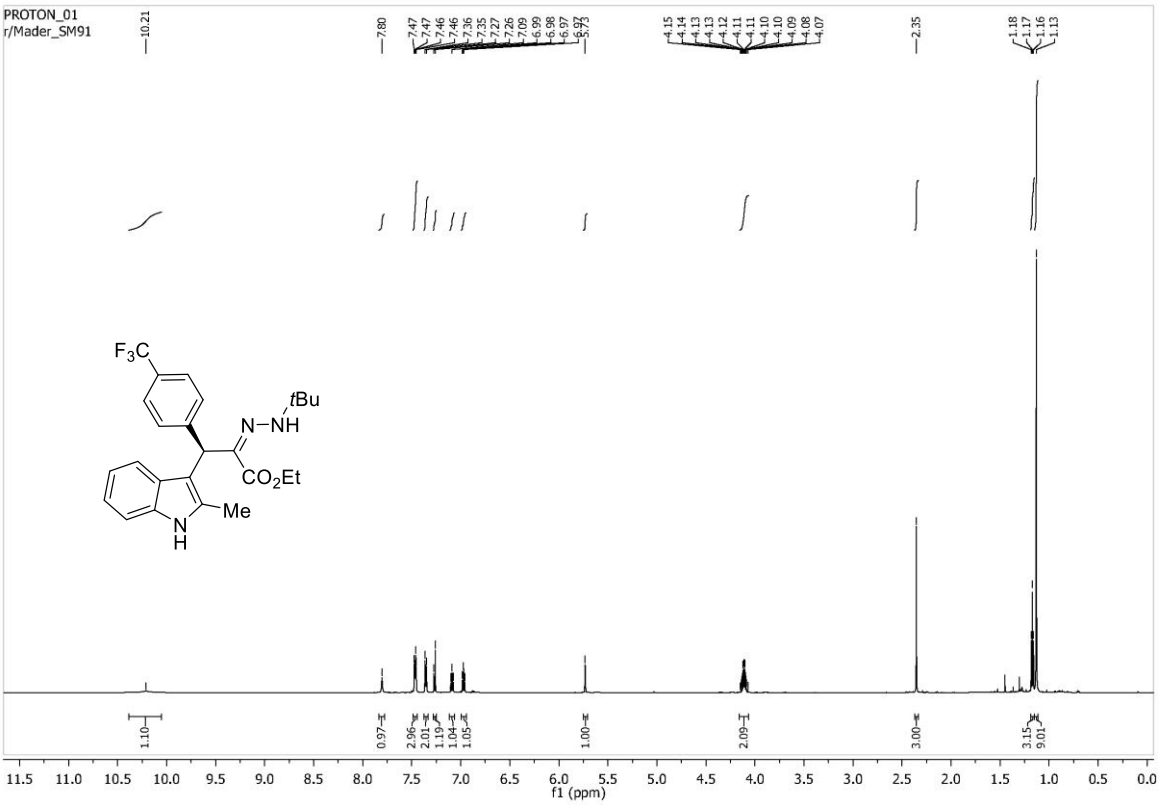
Data file: SM 83-ADH_9802_flow1_acq605466.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 31.05.2013 01:10:23



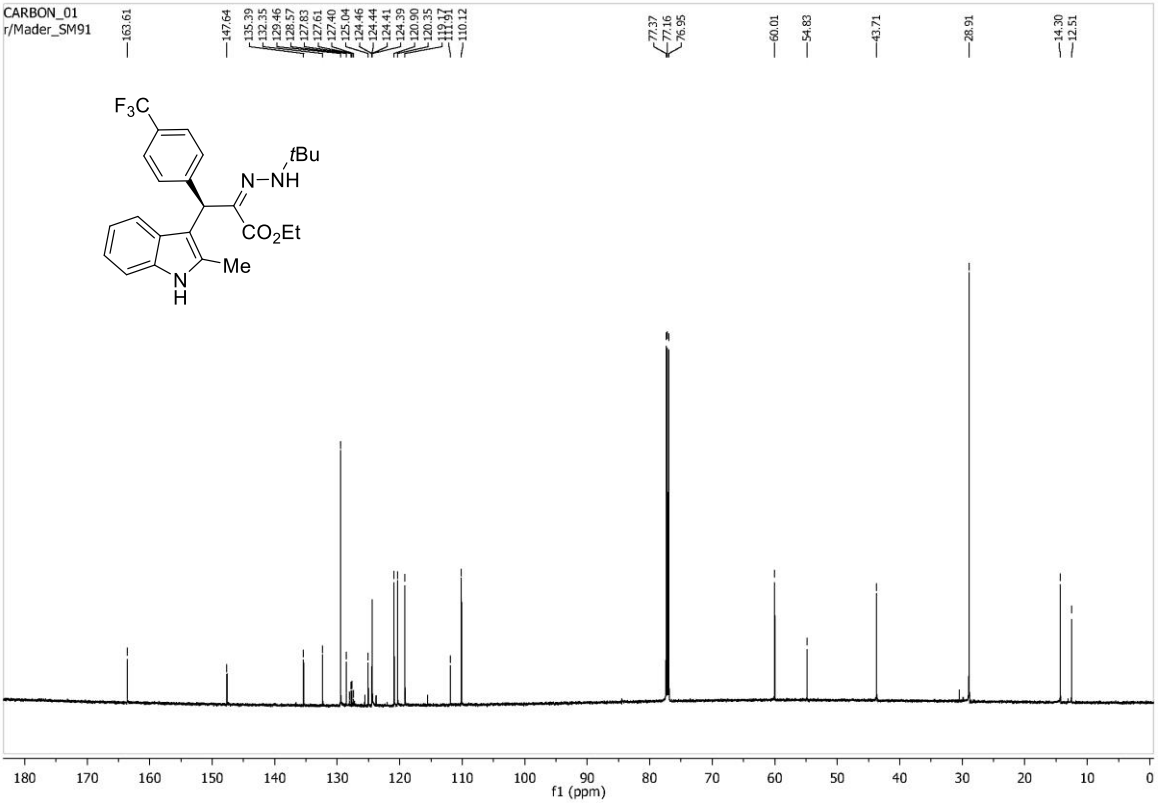
SM 83-ADH_9802_flow1_acq605466.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	13,561	14,150	14,930	8,238
2	17,917	18,833	20,262	91,762
Total				100,000

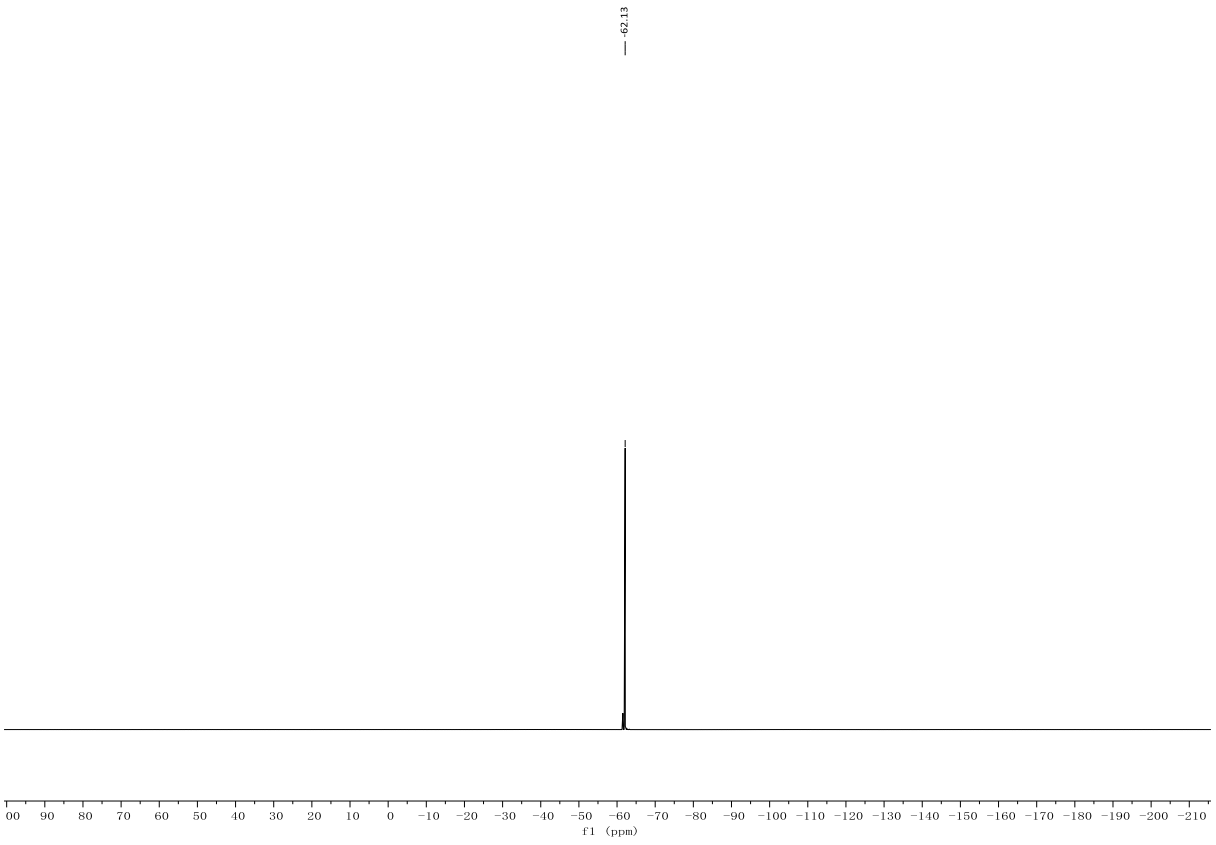
^{1}H NMR (600 MHz, $CDCl_3$) for **8h**



^{13}C NMR (150 MHz, $CDCl_3$) for **8h**

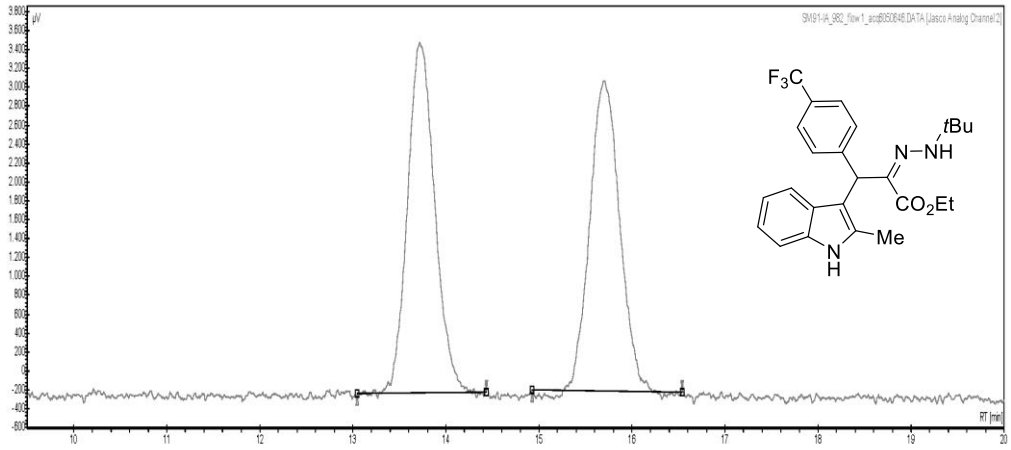


^{19}F NMR (564 MHz, $CDCl_3$) for **8h**



Chromatogram : SM 91-IA_982_flow1_acq6050646

Data file: SM 91-IA_982_flow1_acq6050646.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 28.05.2013 19:12:25

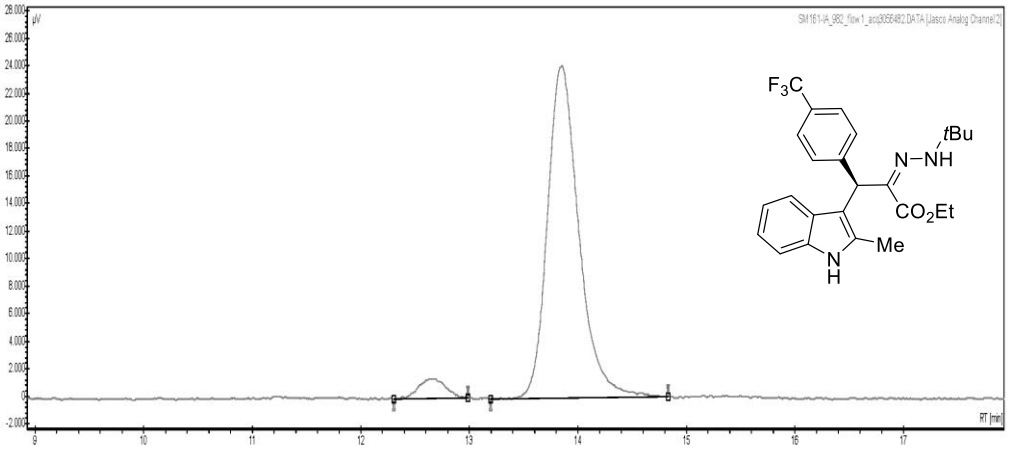


SM 91-IA_982_flow1_acq6050646.DATA [Jasco Analog Channel 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	13,045	13,717	14,436	51,224
2	14,925	15,700	16,541	48,776
Total				100,000

Chromatogram : SM 161-IA_982_flow1_acq3056482

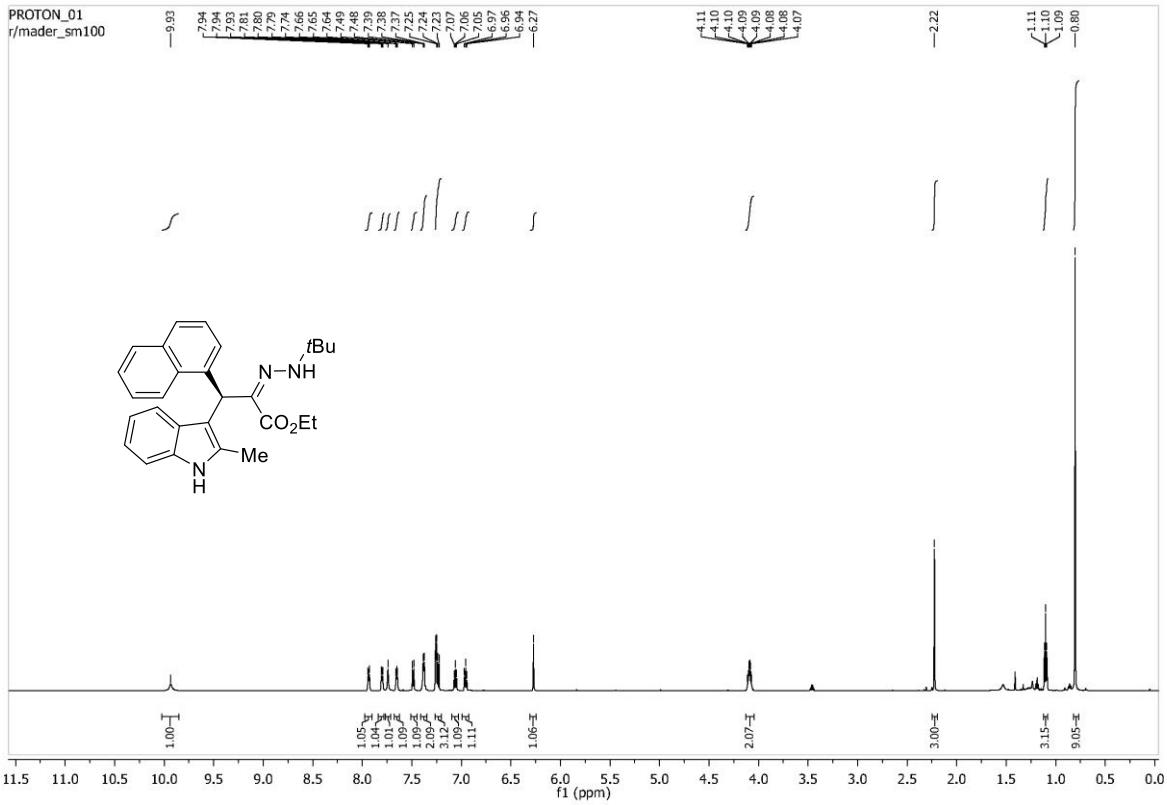
Data file: SM 161-IA_982_flow1_acq3056482.DATA
Method: HPLC2_IA_982_flow1_acq30
Date: 02.08.2013 00:02:41



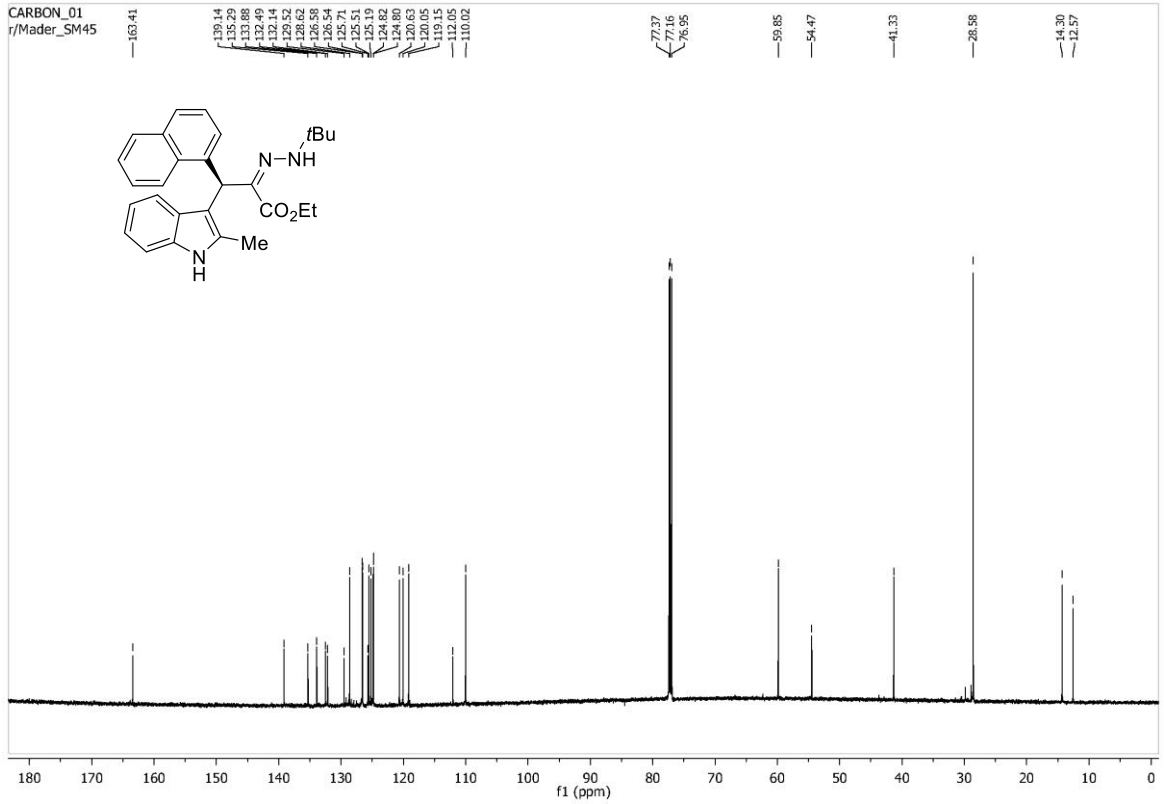
SM 161-IA_982_flow1_acq3056482.DATA [Jasco Analog Channel 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	12,302	12,658	12,986	4,899
2	13,194	13,850	14,828	95,101
Total				100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **8i**

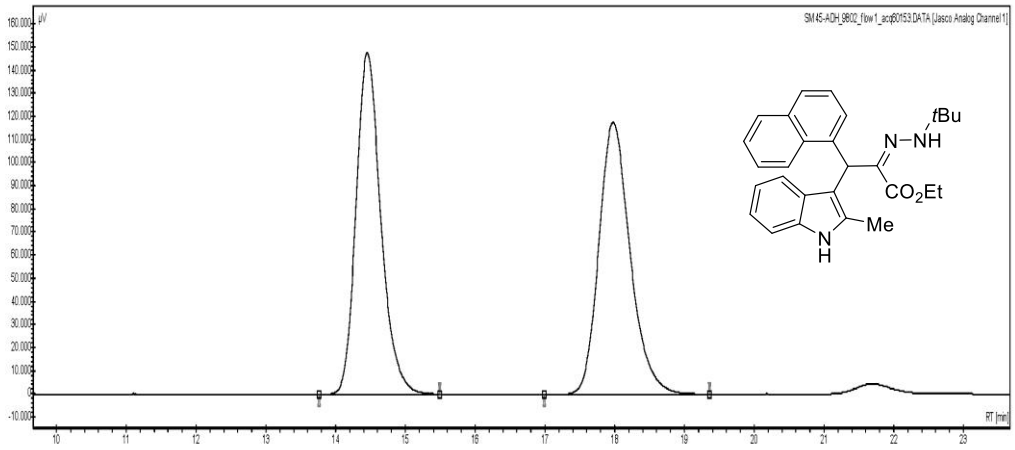


^{13}C NMR (150 MHz, $CDCl_3$) for **8i**



Chromatogram : SM 45-ADH_9802_flow1_acq60153

Data file: SM 45-ADH_9802_flow1_acq60153.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 19.04.2013 21:02:32

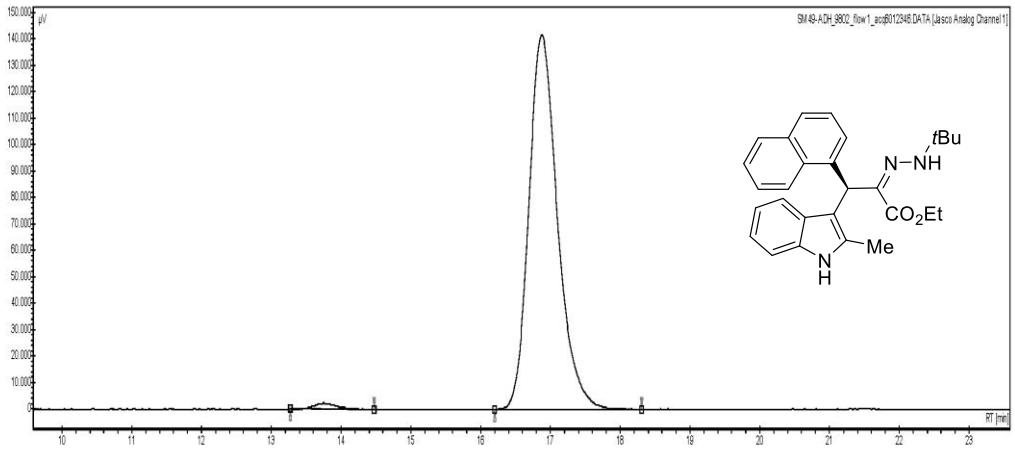


SM 45-ADH_9802_flow1_acq60153.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	13,759	14,458	15,489	49,874
2	16,992	17,975	19,361	50,126
Total				100,000

Chromatogram : SM 49-ADH_9802_flow1_acq6012346

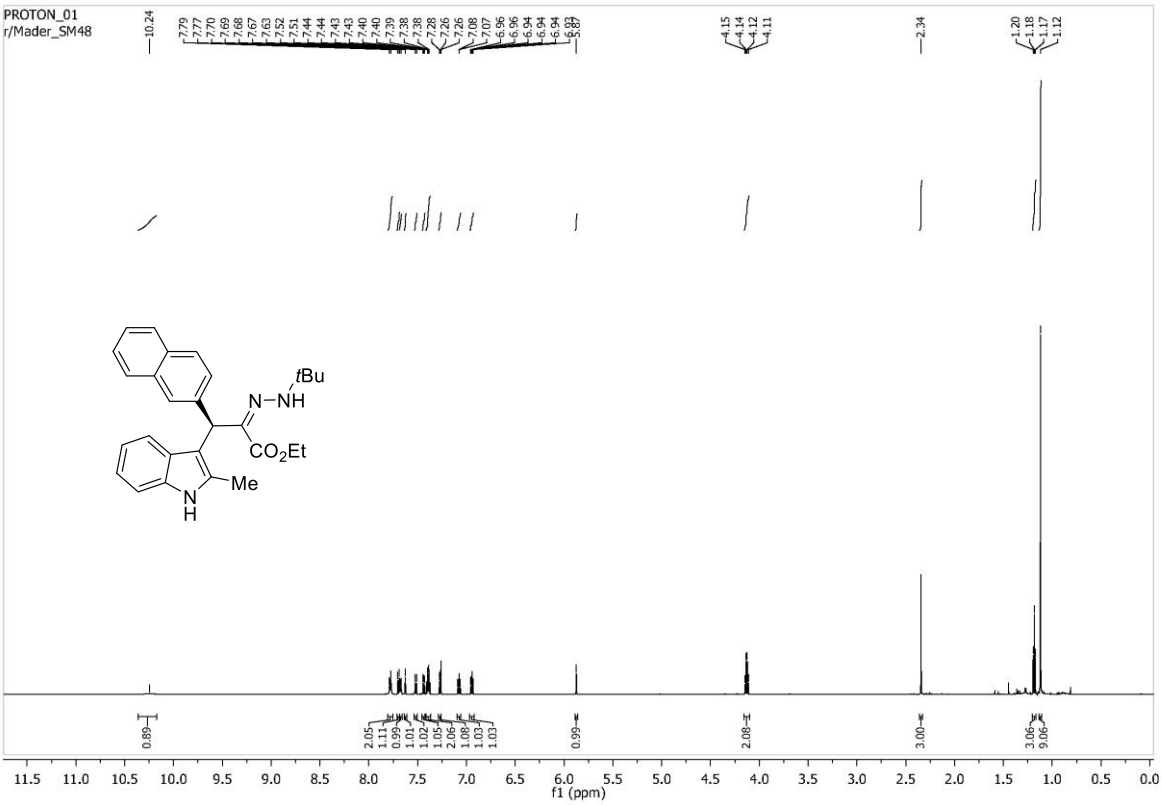
Data file: SM 49-ADH_9802_flow1_acq6012346.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 04.07.2013 18:46:59



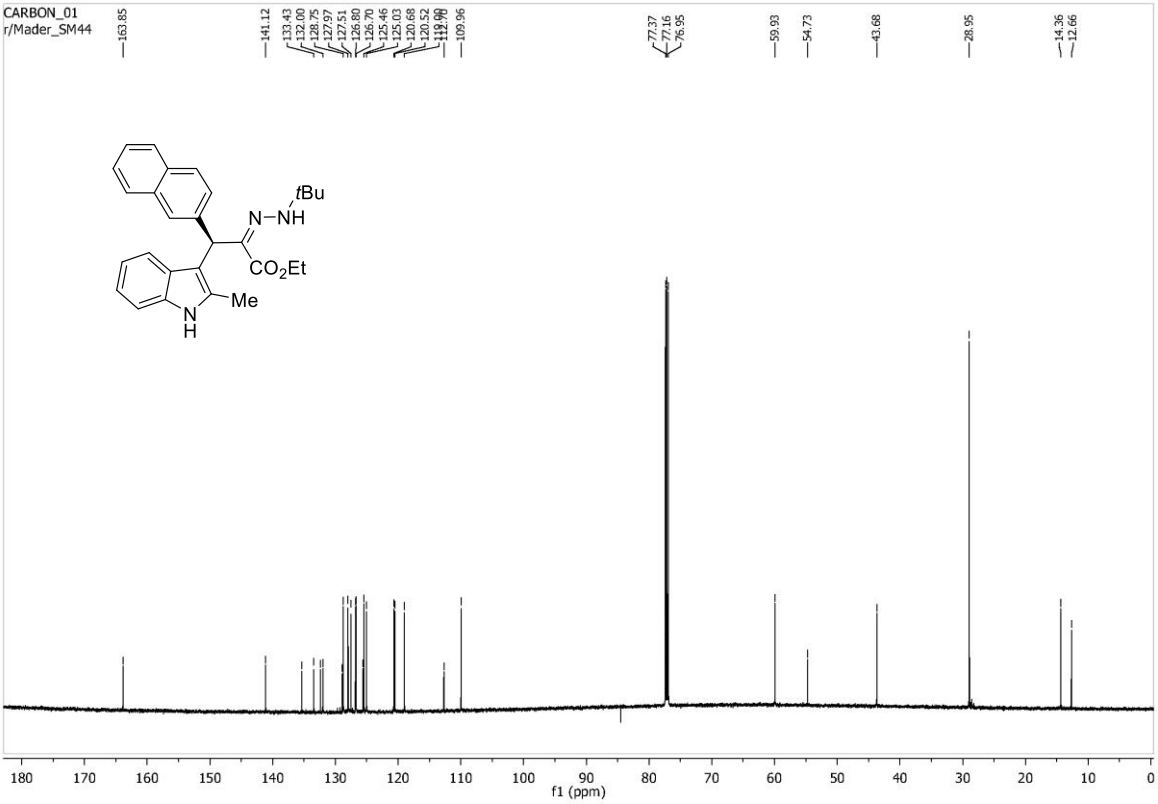
SM 49-ADH_9802_flow1_acq6012346.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	13,271	13,742	14,474	1,198
2	16,203	16,875	18,308	98,802
Total				100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **8j**

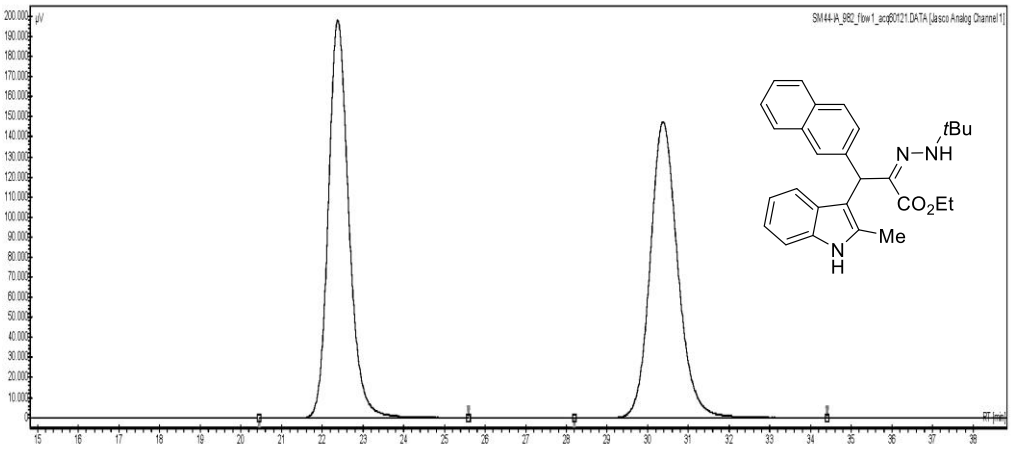


^{13}C NMR (150 MHz, $CDCl_3$) for **8j**



Chromatogram : SM 44-IA_982_flow1_acq60121

Data file: SM 44-IA_982_flow1_acq60121.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 19.04.2013 12:11:42

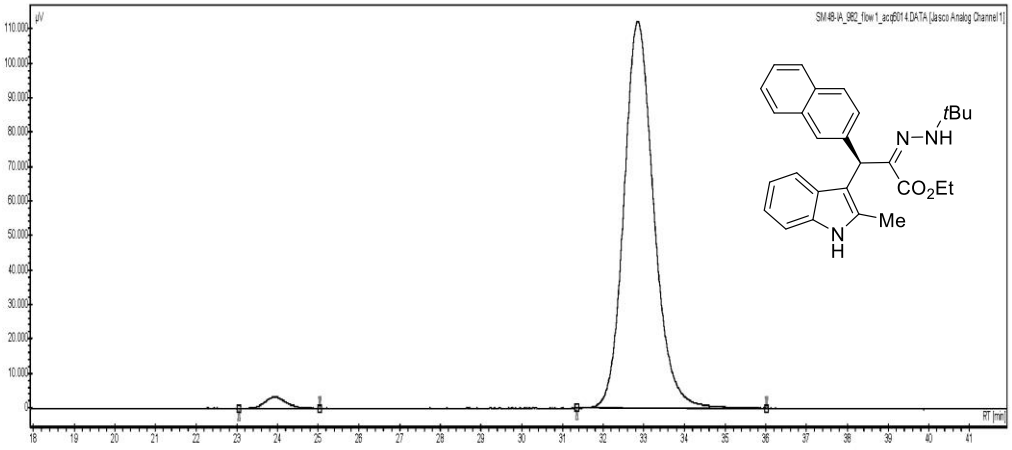


SM 44-IA_982_flow1_acq60121.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	20,455	22,383	25,599	50,076
2	28,202	30,375	34,401	49,924
Total				100,000

Chromatogram : SM 48-IA_982_flow1_acq6014

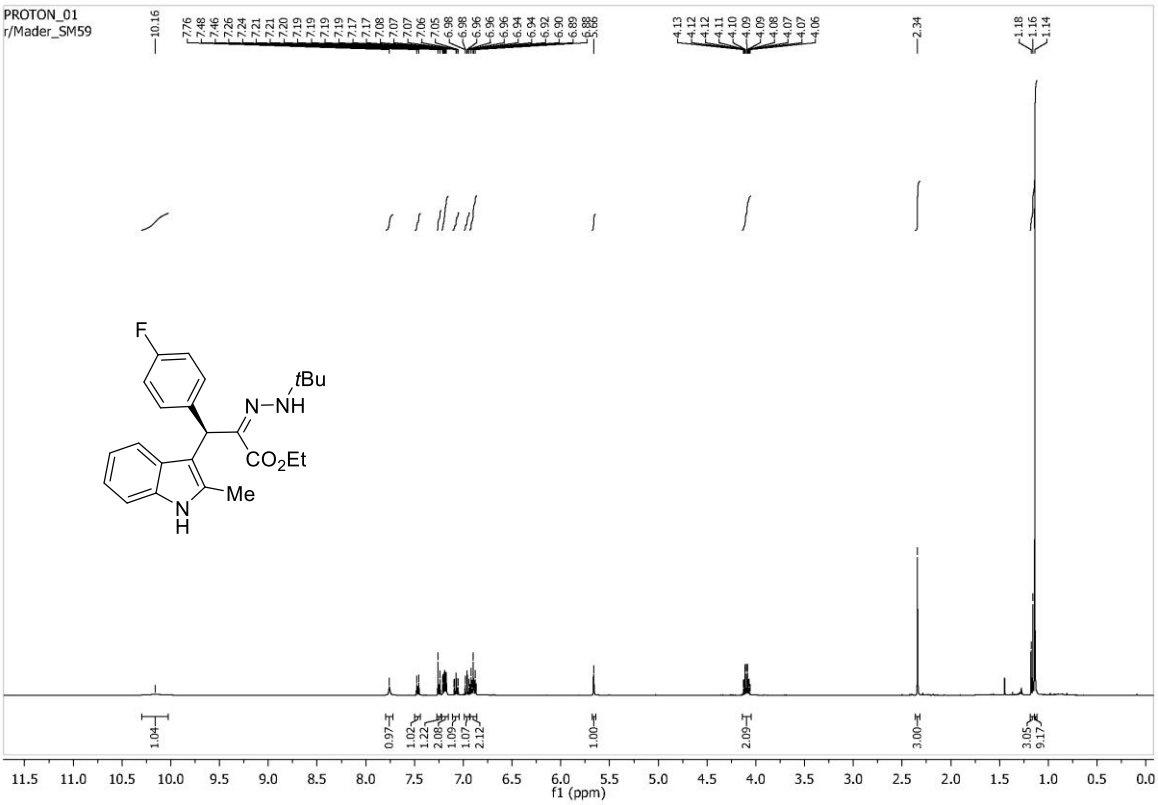
Data file: SM 48-IA_982_flow1_acq6014.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 22.04.2013 21:09:37



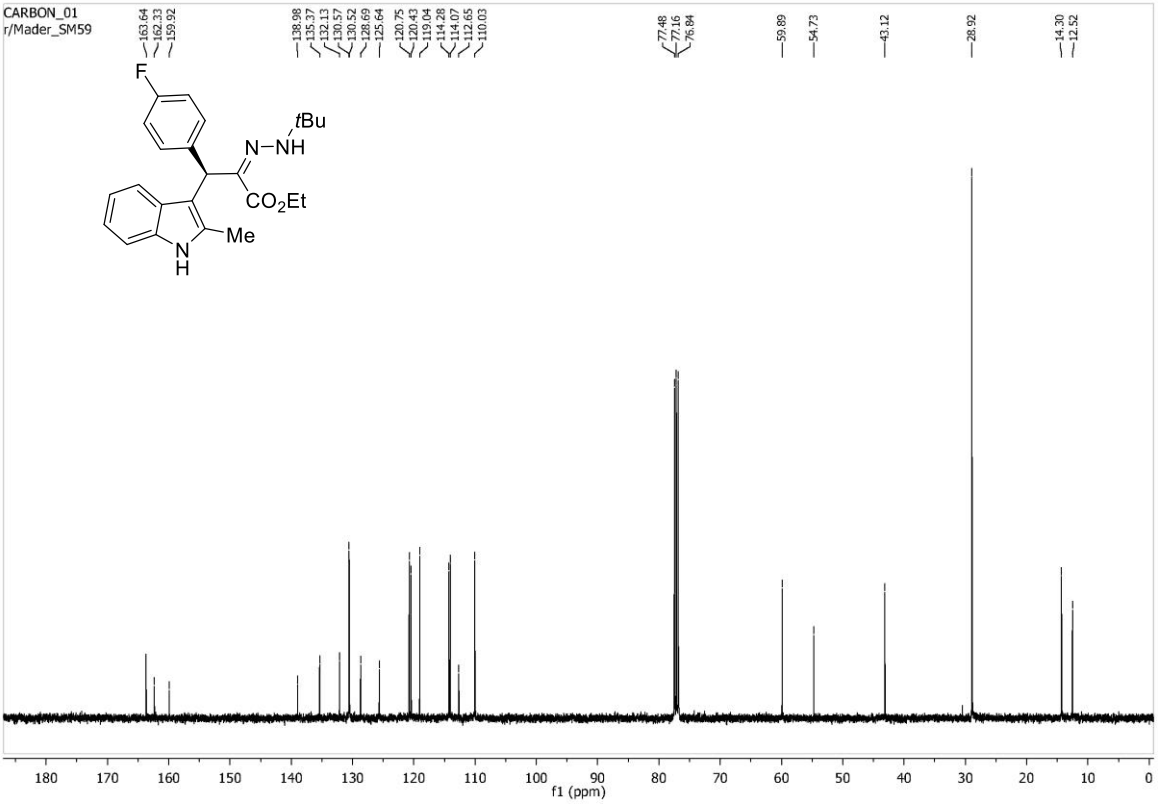
SM 48-IA_982_flow1_acq6014.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	23,045	23,950	25,038	2,104
2	31,353	32,850	36,015	97,896
Total				100,000

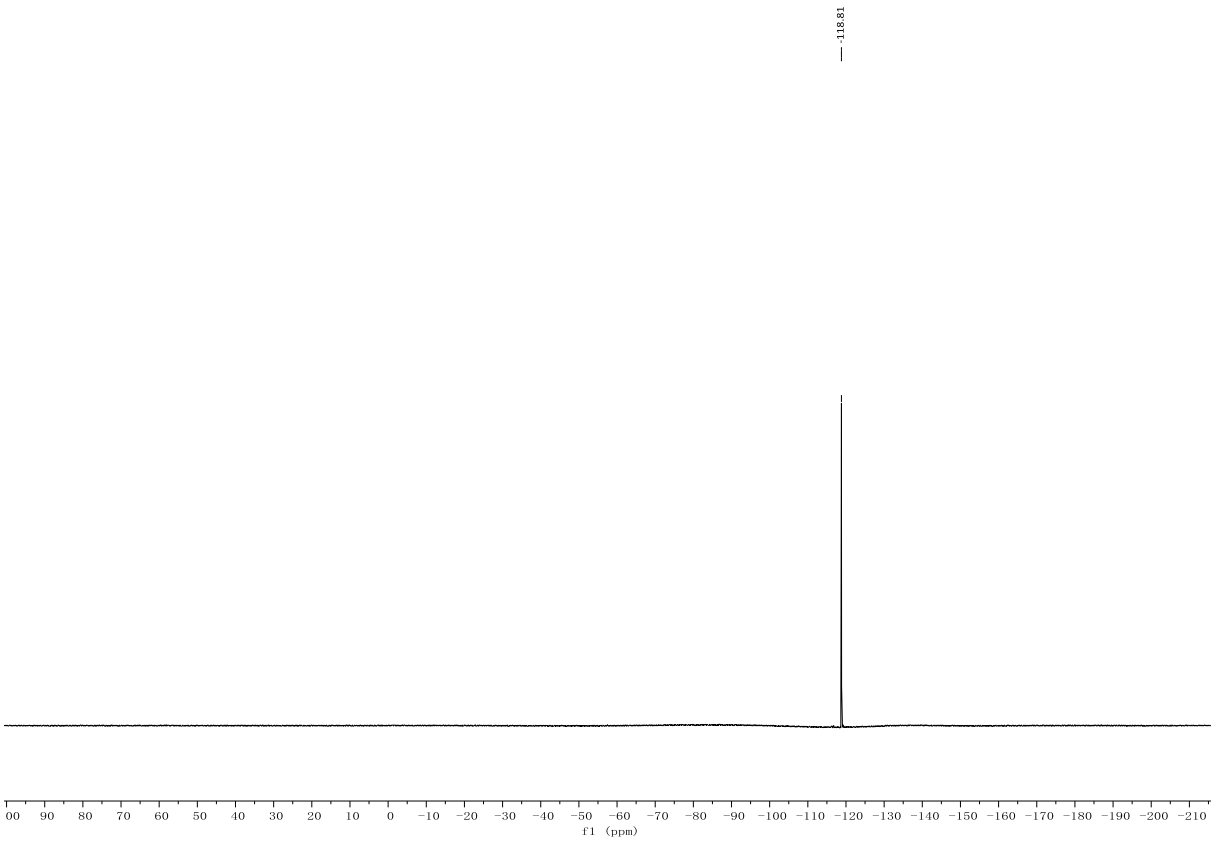
^{1}H NMR (400 MHz, $CDCl_3$) for **8k**



^{13}C NMR (100 MHz, $CDCl_3$) for **8k**

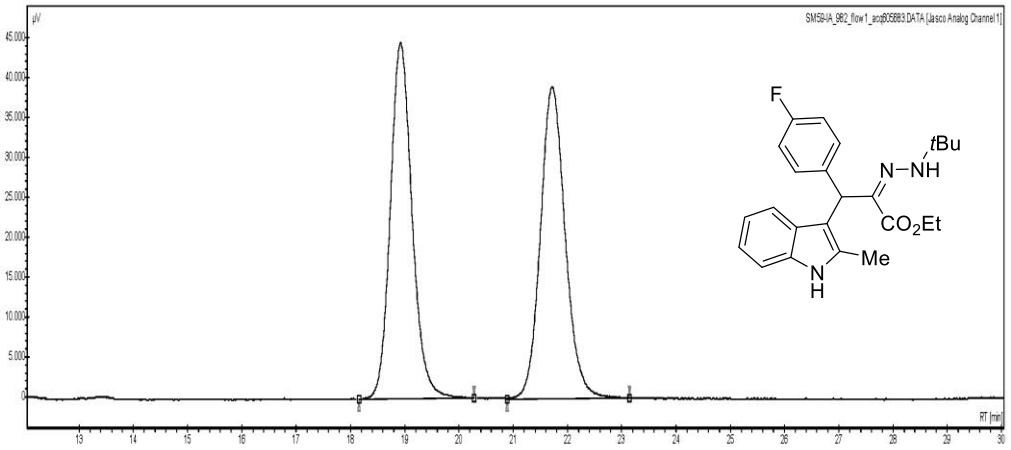


^{19}F NMR (376 MHz, $CDCl_3$) for **8k**



Chromatogram : SM 59-IA_982_flow1_acq605683

Data file: SM 59-IA_982_flow1_acq605683.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 25.04.2013 04:45:53

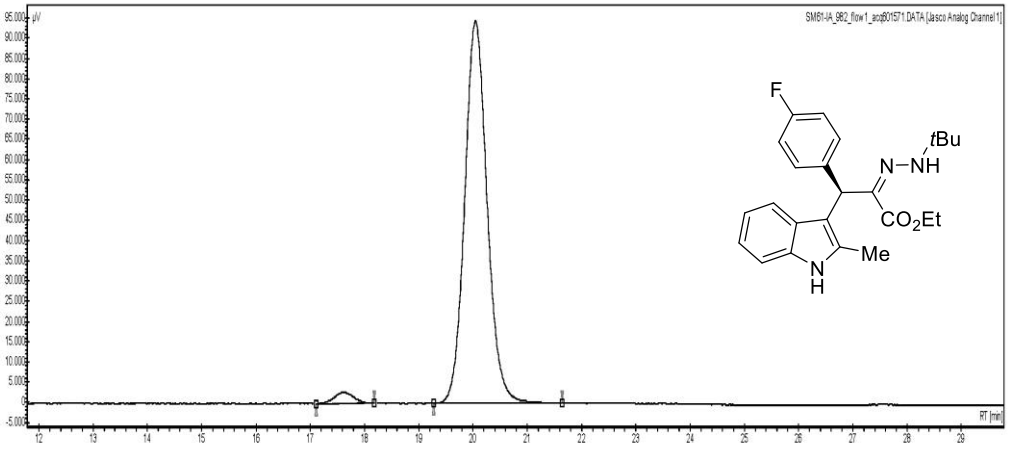


SM 59-IA_982_flow1_acq605683.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	18,156	18,925	20,278	50,129
2	20,885	21,717	23,139	49,871
Total				100,000

Chromatogram : SM 61-IA_982_flow1_acq601571

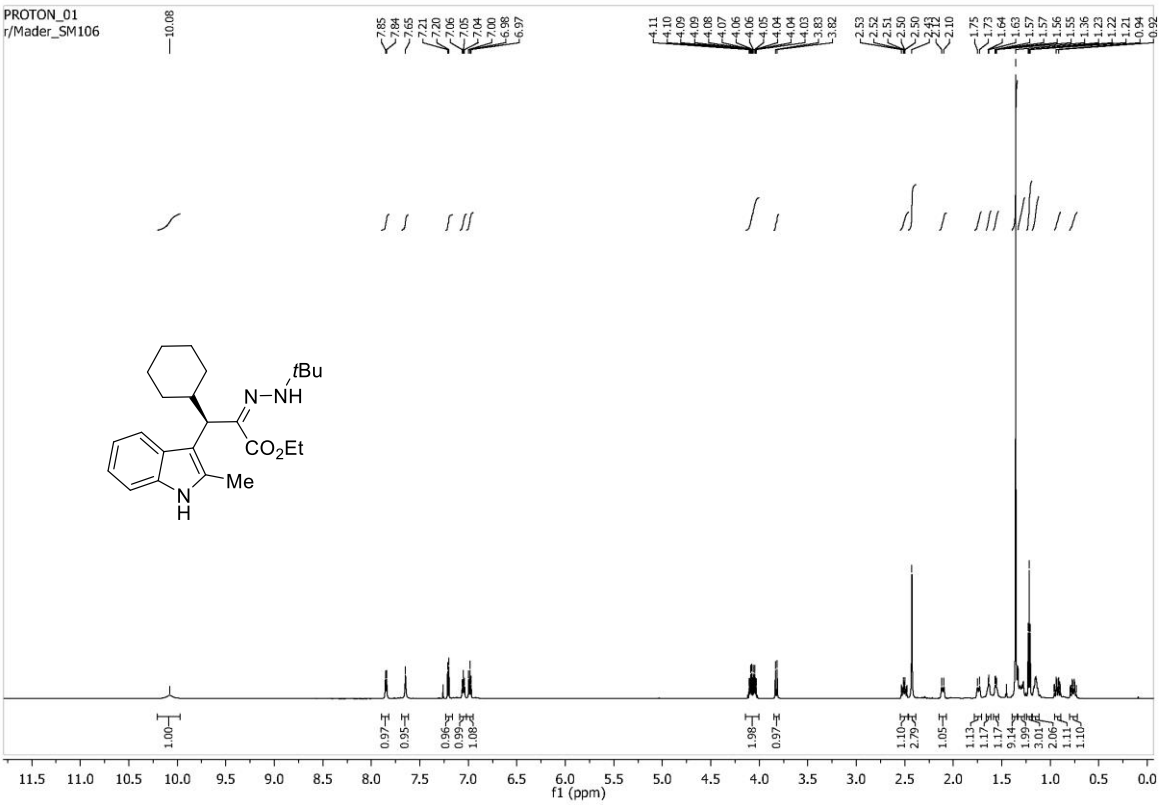
Data file: SM 61-IA_982_flow1_acq601571.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 26.04.2013 01:07:36



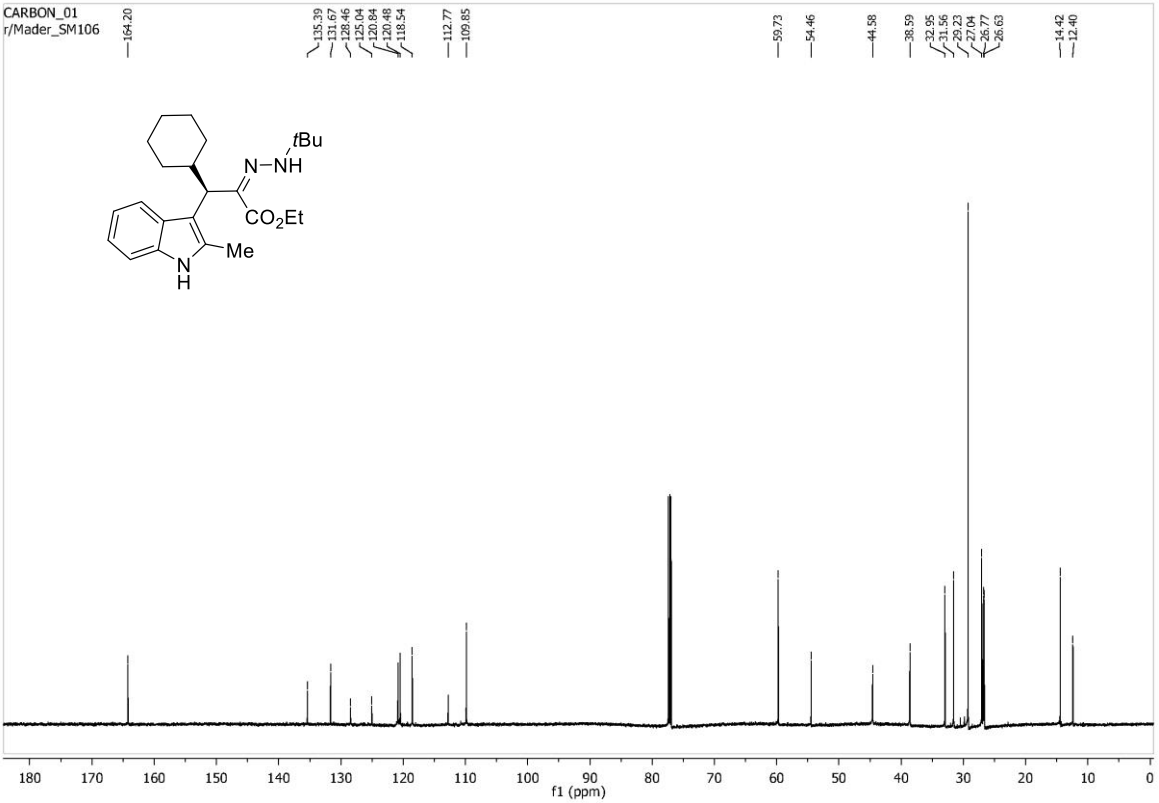
SM 61-IA_982_flow1_acq601571.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17,112	17,617	18,185	2,458
2	19,273	20,042	21,638	97,542
Total				100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **8l**

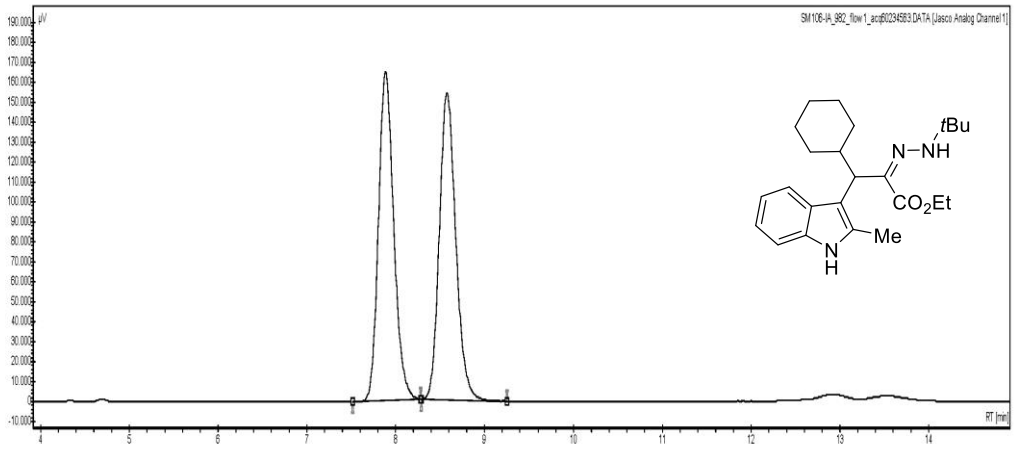


^{13}C NMR (150 MHz, $CDCl_3$) for **8l**



Chromatogram : SM 106-IA_982_flow1_acq60234563

Data file: SM 106-IA_982_flow1_acq60234563.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 18.06.2013 13:53:06

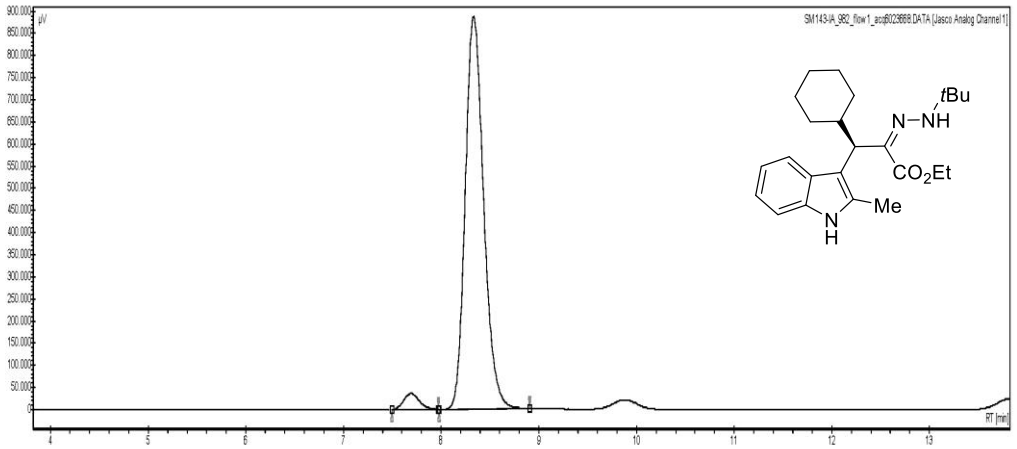


SM 106-IA_982_flow1_acq60234563.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	7,518	7,883	8,281	49,909
2	8,290	8,575	9,255	50,091
Total				100,000

Chromatogram : SM 143-IA_982_flow1_acq6023668

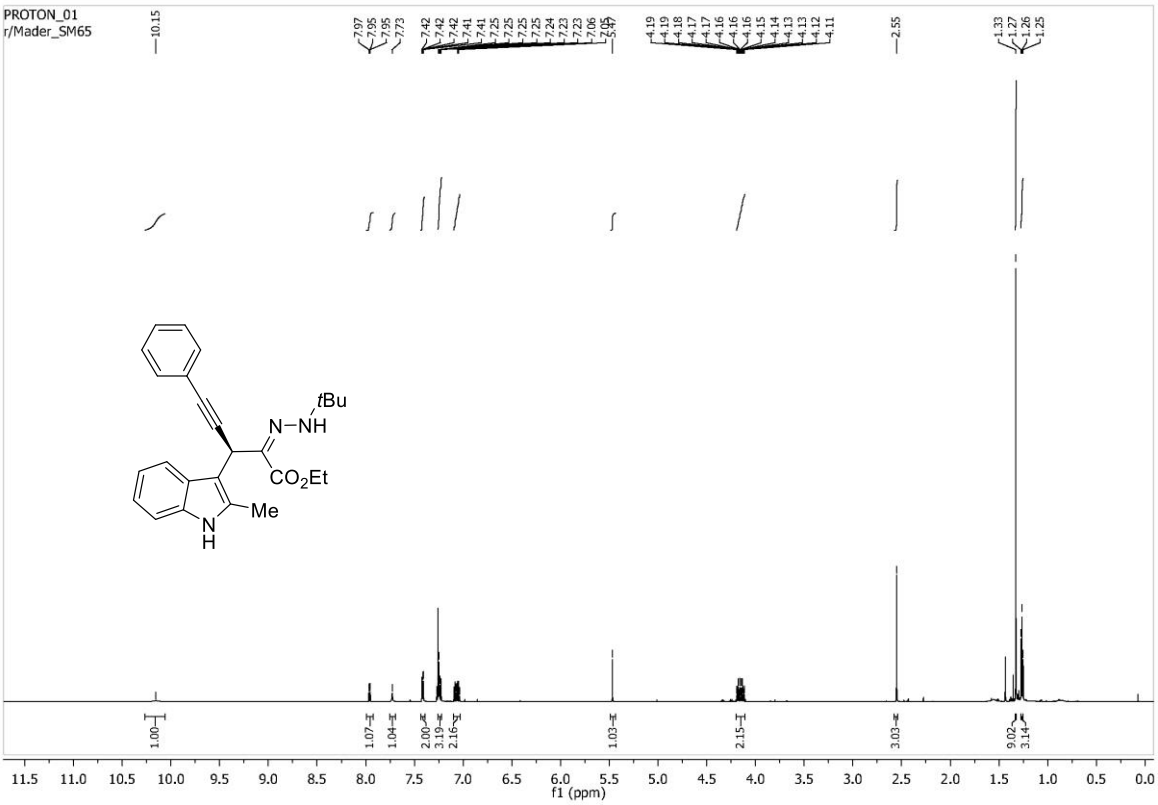
Data file: SM 143-IA_982_flow1_acq6023668.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 09.07.2013 10:21:51



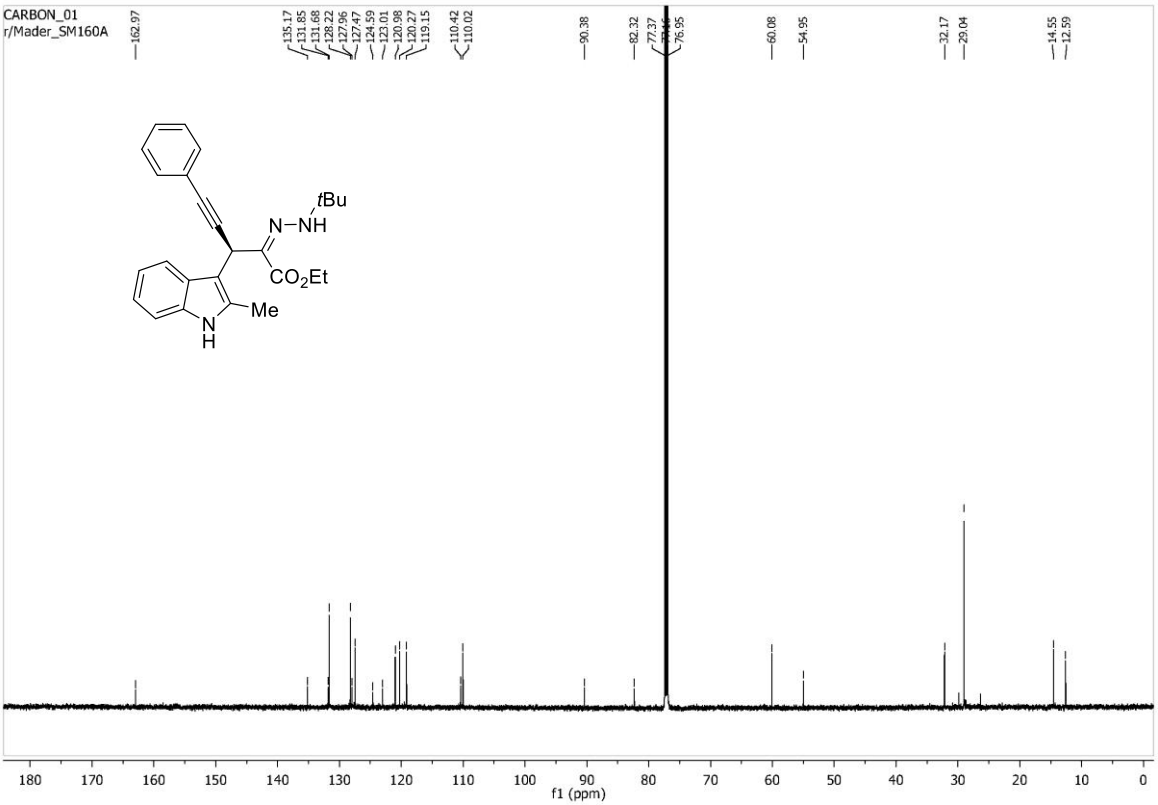
SM 143-IA_982_flow1_acq6023668.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	7,498	7,692	7,973	3,326
2	7,981	8,333	8,906	96,674
Total				100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **8m**

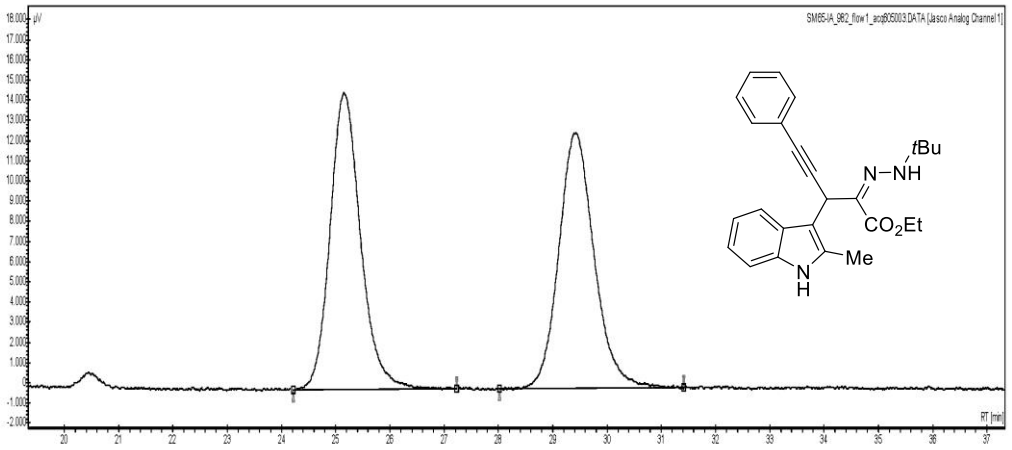


^{13}C NMR (150 MHz, $CDCl_3$) for **8m**



Chromatogram : SM 65-IA_982_flow1_acq605003

Data file: SM 65-IA_982_flow1_acq605003.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 07.05.2013 20:39:50

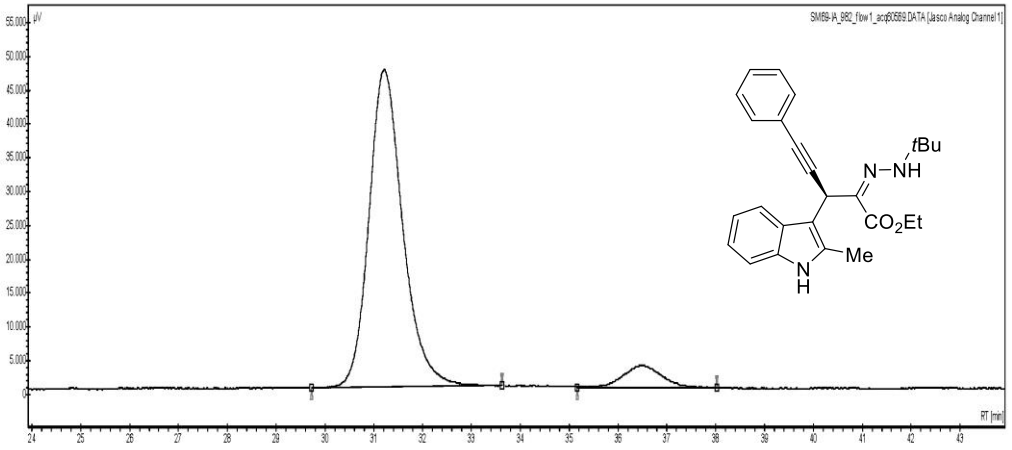


SM 65-IA_982_flow1_acq605003.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	24,214	25,150	27,226	49,951
2	28,017	29,392	31,415	50,049
Total				100,000

Chromatogram : SM 69-IA_982_flow1_acq60569

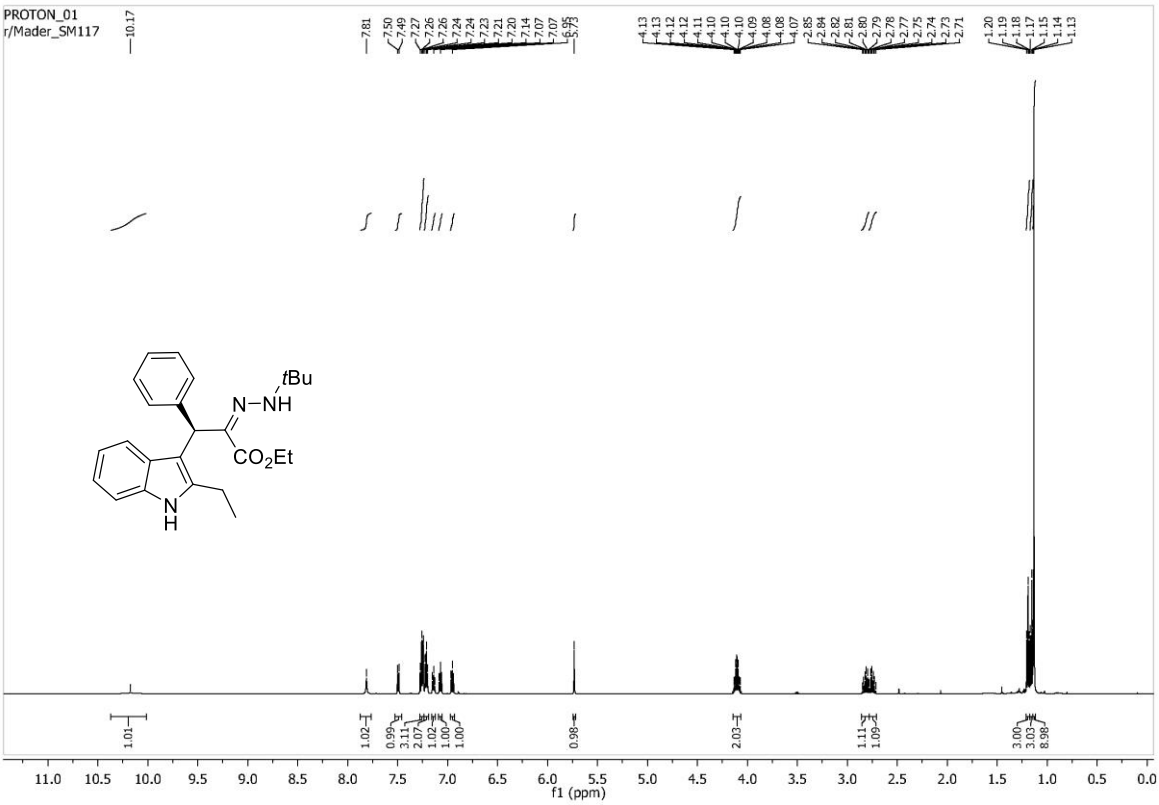
Data file: SM 69-IA_982_flow1_acq60569.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 13.05.2013 10:01:11



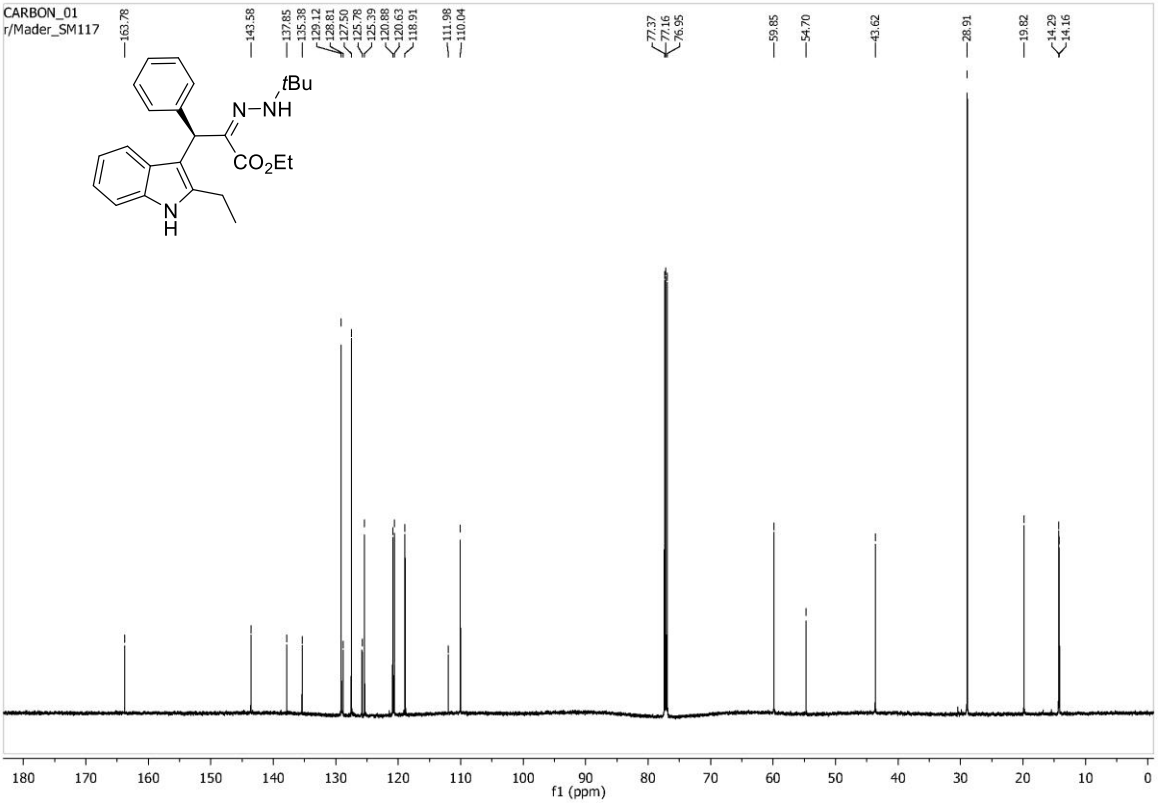
SM 69-IA_982_flow1_acq60569.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	29,723	31,217	33,630	92,794
2	35,167	36,508	38,024	7,206
Total				100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **8n**

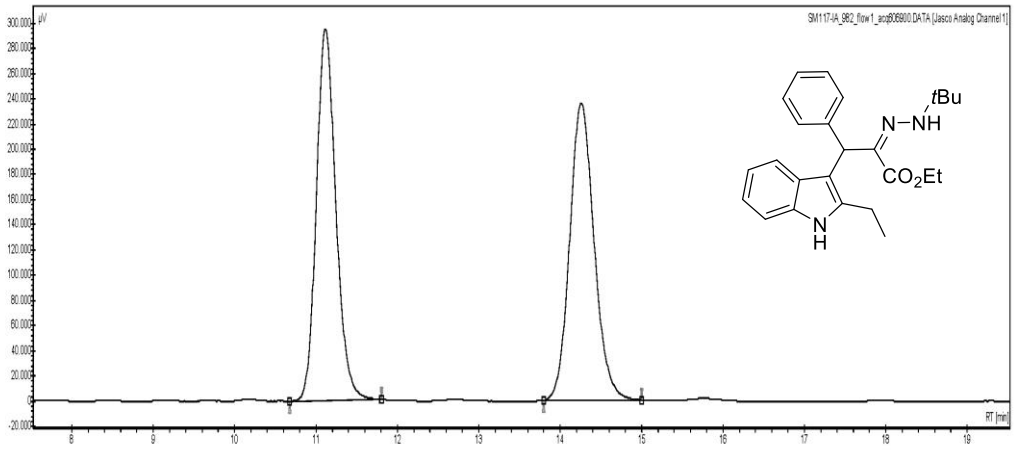


^{13}C NMR (150 MHz, $CDCl_3$) for **8n**



Chromatogram : SM 117-IA_982_flow1_acq606900

Data file: SM 117-IA_982_flow1_acq606900.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 25.06.2013 01:54:09

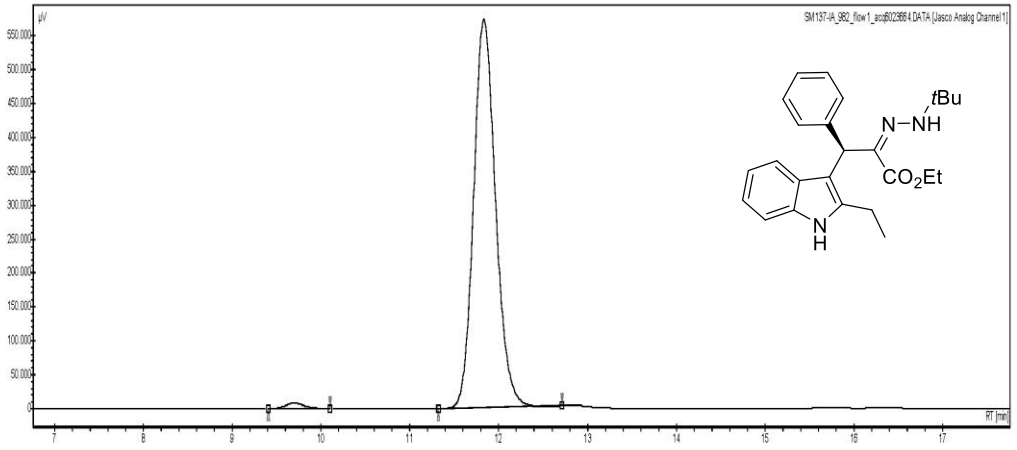


SM 117-IA_982_flow1_acq606900.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	10,677	11,117	11,805	50,014
2	13,797	14,258	15,000	49,986
Total				100,000

Chromatogram : SM 137-IA_982_flow1_acq6023664

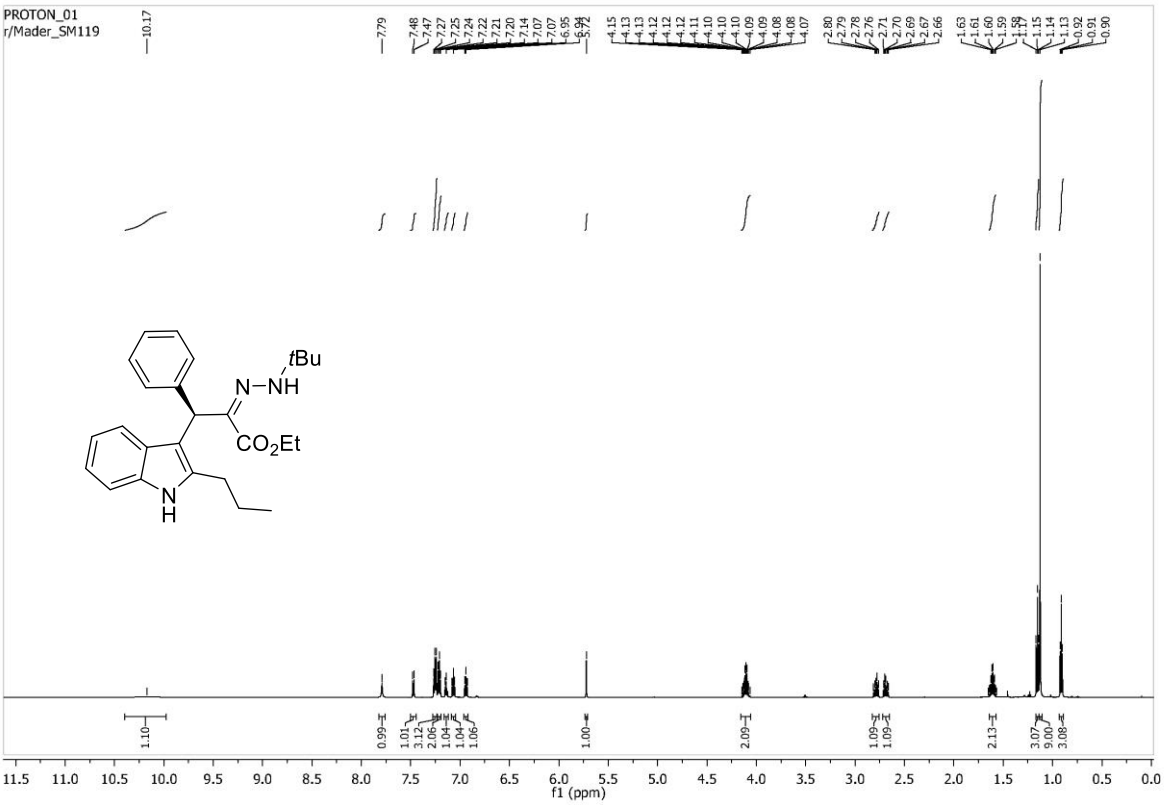
Data file: SM 137-IA_982_flow1_acq6023664.DATA
Method: HPLC2_IA_982_flow1_acq60
Date: 09.07.2013 08:56:43



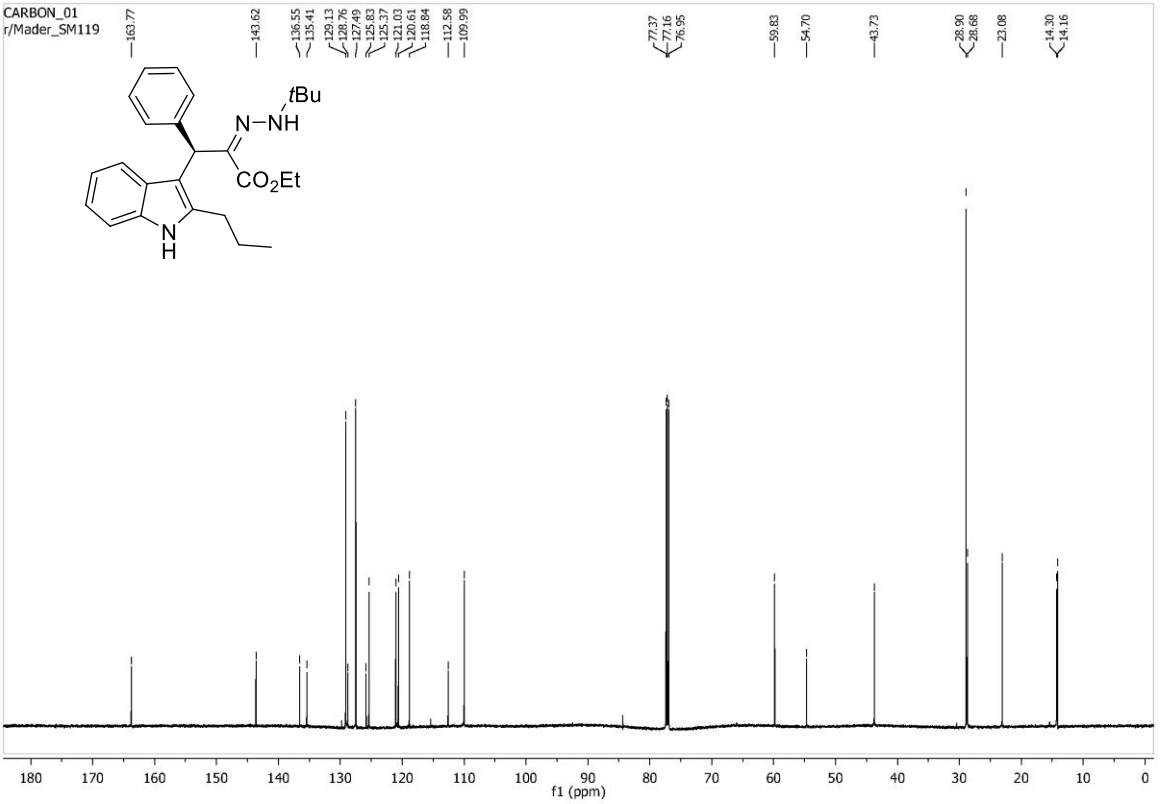
SM 137-IA_982_flow1_acq6023664.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9,407	9,700	10,103	1,235
2	11,319	11,833	12,712	98,765
Total				100,000

^{1}H NMR (600 MHz, $CDCl_3$) for **8o**

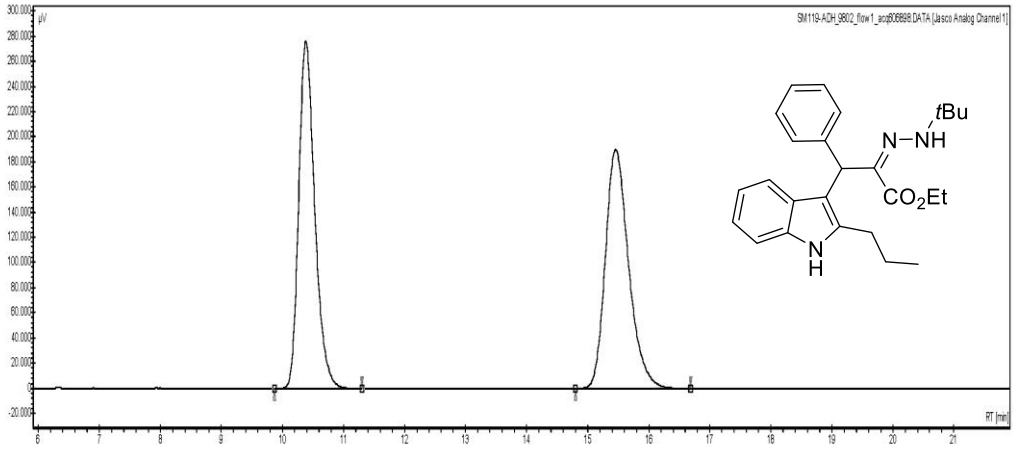


^{13}C NMR (150 MHz, $CDCl_3$) for **8o**



Chromatogram : SM 119-ADH_9802_flow1_acq606898

Data file: SM 119-ADH_9802_flow1_acq606898.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 25.06.2013 00:18:52

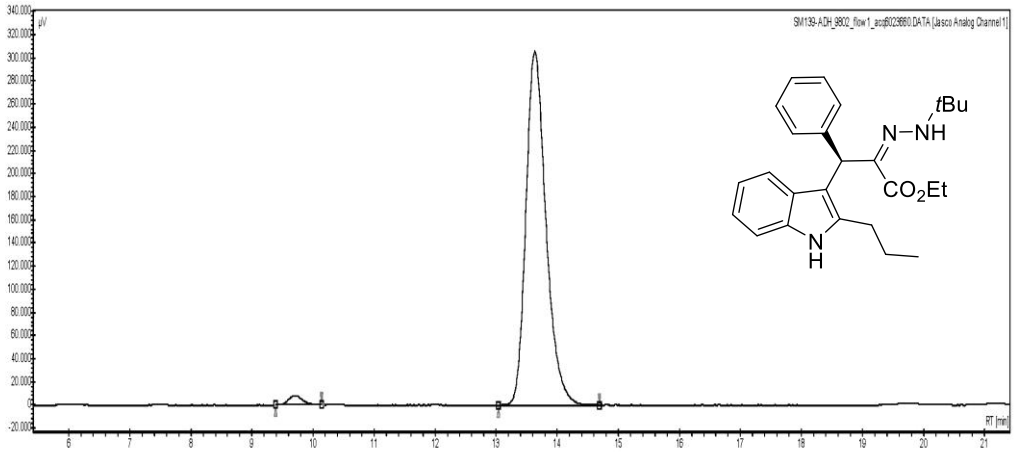


SM 119-ADH_9802_flow1_acq606898.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9,874	10,383	11,300	49,900
2	14,797	15,458	16,688	50,100
Total				100,000

Chromatogram : SM 139-ADH_9802_flow1_acq6023660

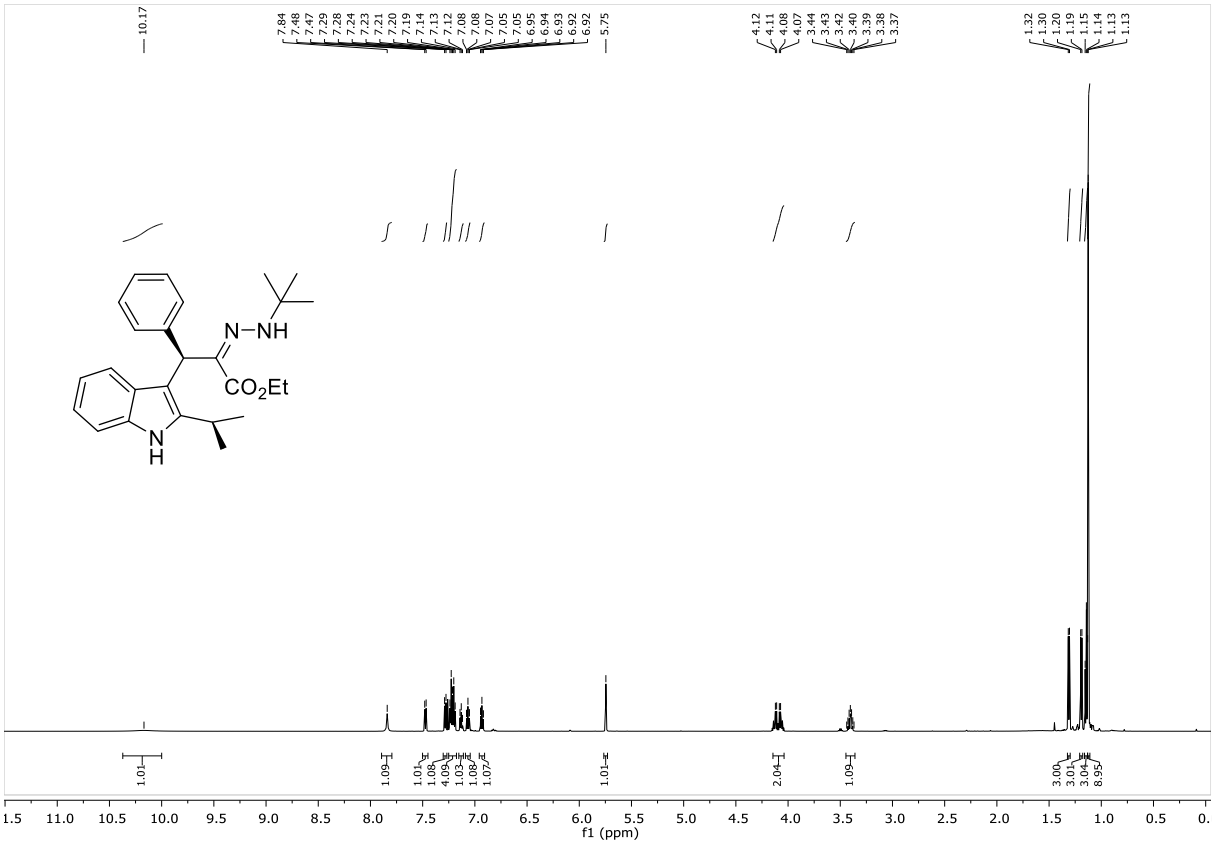
Data file: SM 139-ADH_9802_flow1_acq6023660.DATA
Method: HPLC2_ADH_9802_flow1_acq60
Date: 09.07.2013 06:18:46



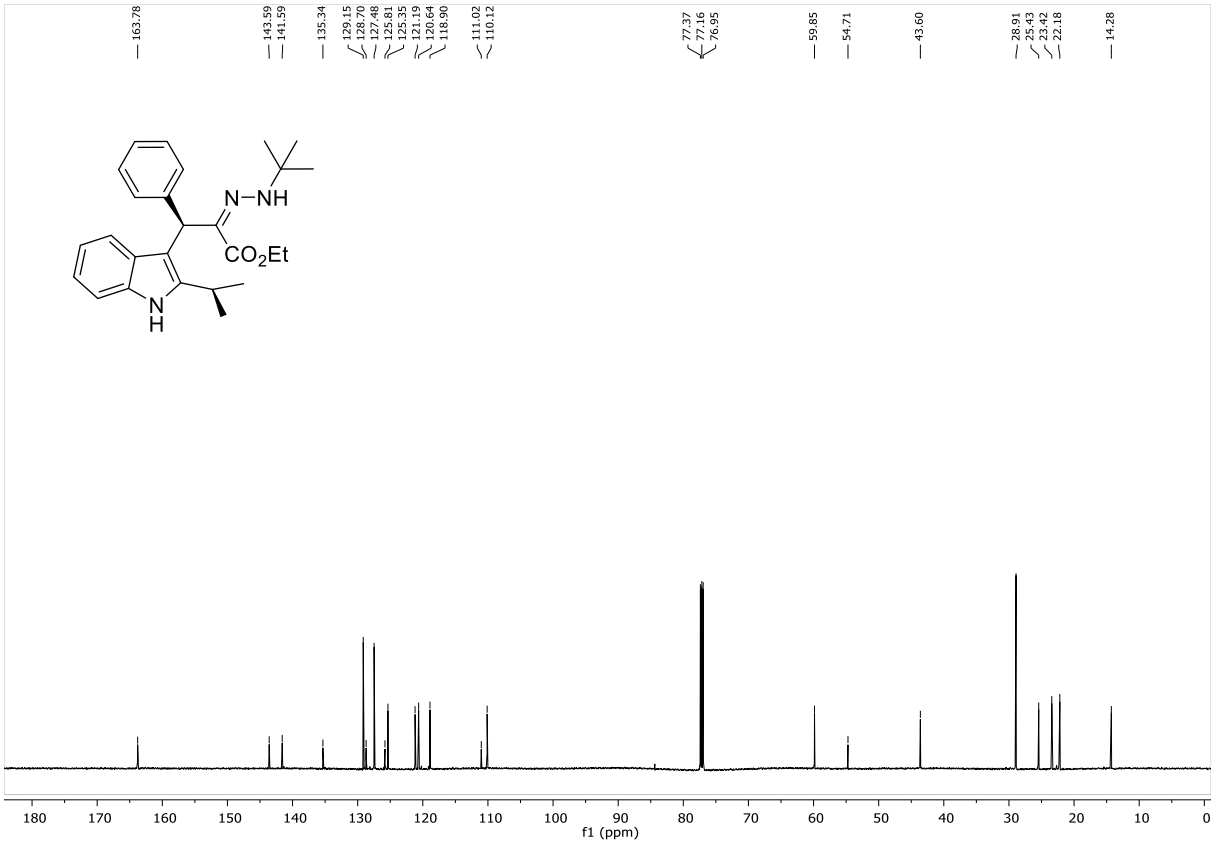
SM 139-ADH_9802_flow1_acq6023660.DATA [Jasco Analog Channel 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9,387	9,708	10,137	1,848
2	13,041	13,633	14,695	98,152
Total				100,000

^{1}H NMR (400 MHz, $CDCl_3$) for **8p**

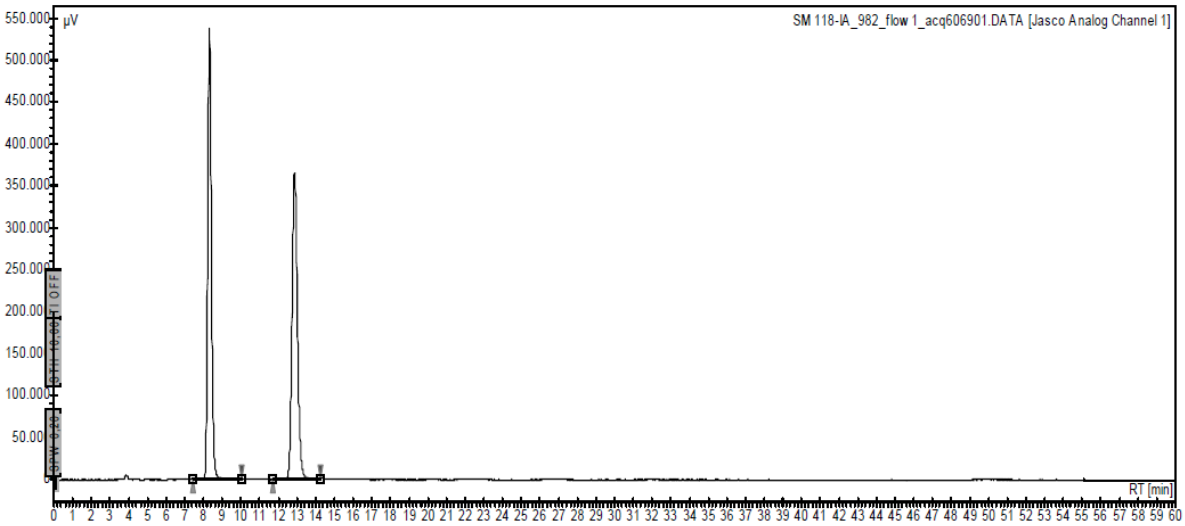


^{13}C NMR (100 MHz, $CDCl_3$) for **8p**



Chromatogram : SM 118-IA_982_flow1_acq606901

Data file: SM 118-IA_982_flow1_acq606901.DATA
Method: HPLC2_IA_982_flow1_acq60

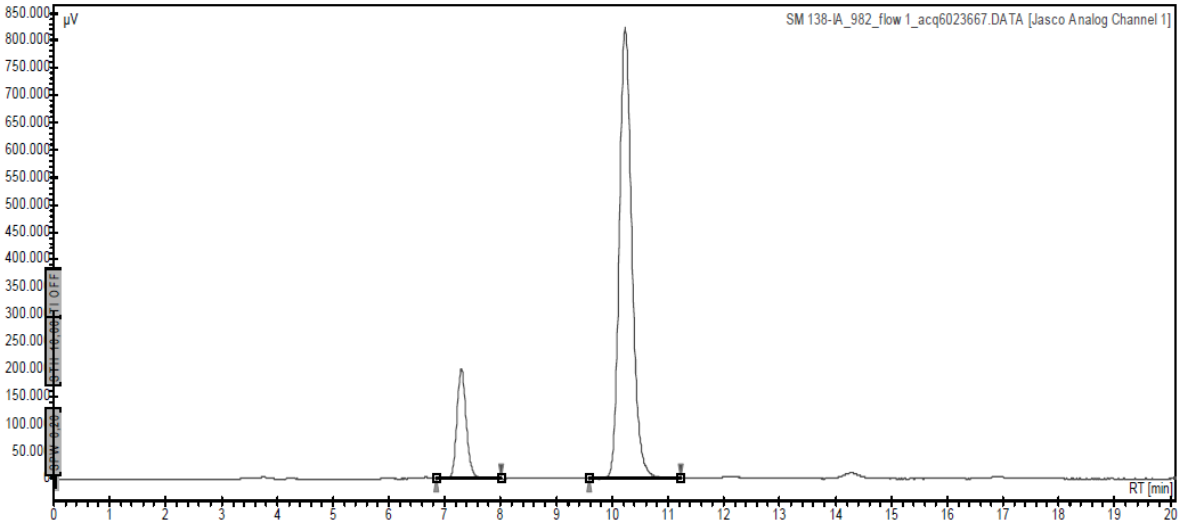


SM 118-IA_982_flow1_acq606901.DATA [Jasco Analog Channel 1]

Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7,438	8,317	10,041	0,000	49,77	537120,9	118896,8	49,772
2	UNKNOWN	11,715	12,875	14,256	0,000	50,23	365615,0	119986,0	50,228
Total						100,00	902735,9	238882,8	100,000

Chromatogram : SM 138-IA_982_flow1_acq6023667

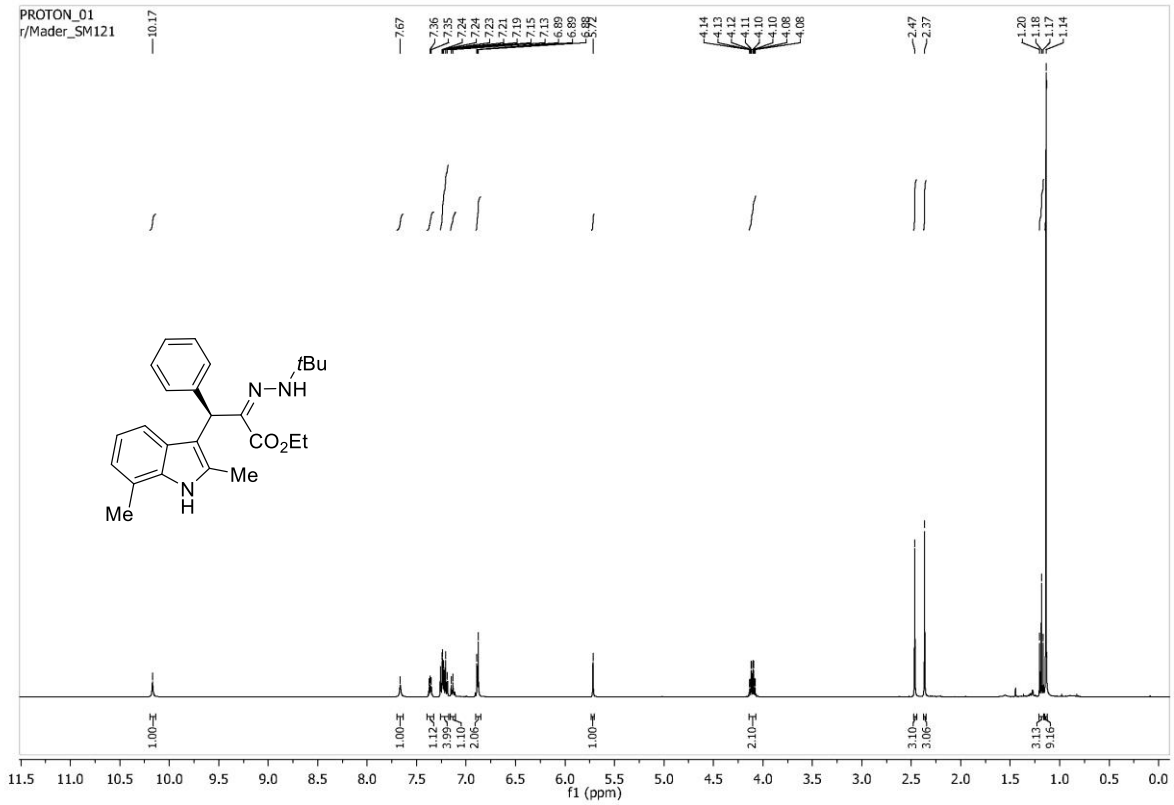
Data file: SM 138-IA_982_flow1_acq6023667.DATA
Method: HPLC2_IA_982_flow1_acq60



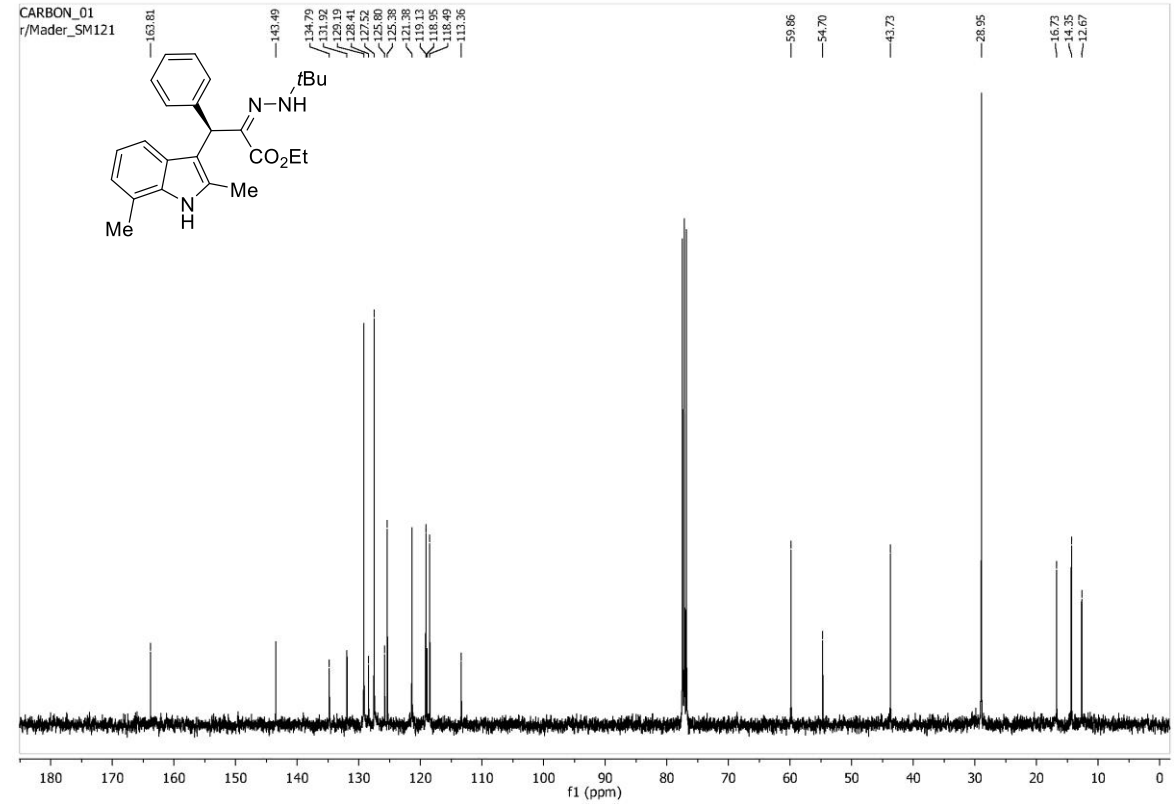
SM 138-IA_982_flow1_acq6023667.DATA [Jasco Analog Channel 1]

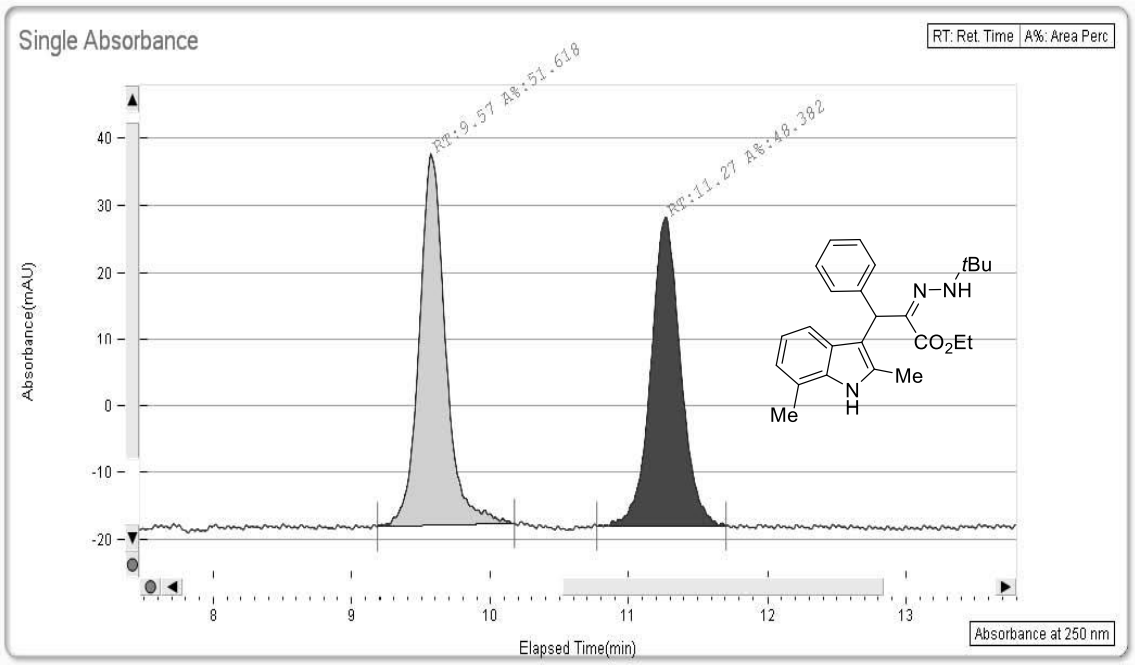
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6,849	7,300	8,012	0,000	15,02	200281,5	38137,5	15,025
2	UNKNOWN	9,589	10,233	11,229	0,000	84,98	822543,1	215691,9	84,975
Total						100,00	1022824,6	253829,4	100,000

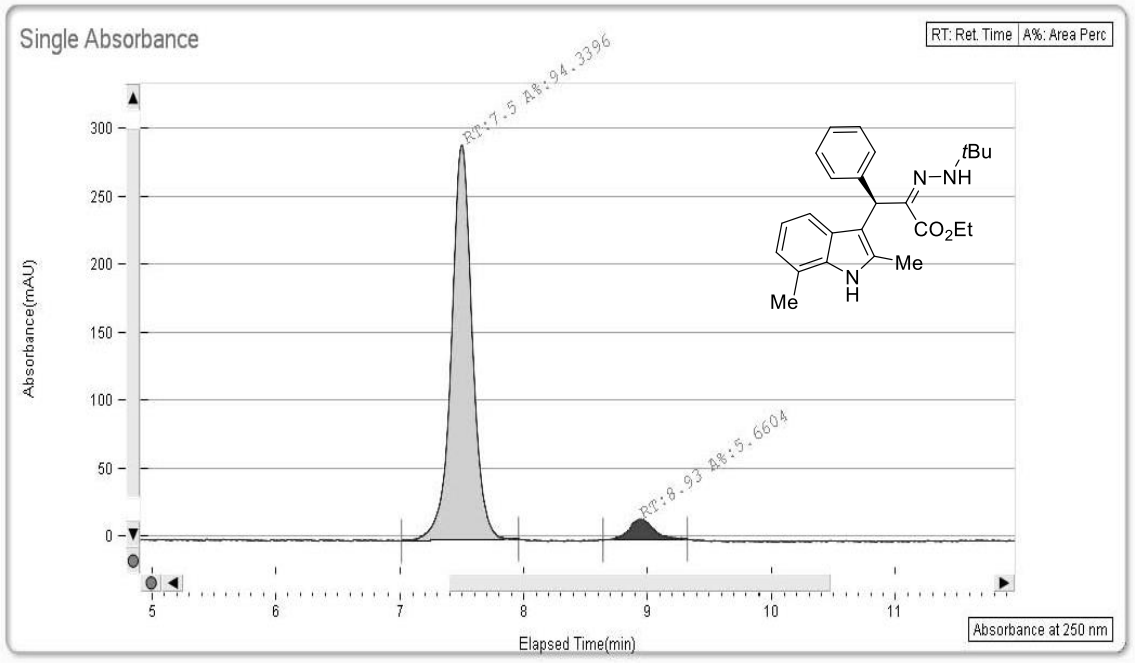
^{1}H NMR (400 MHz, $CDCl_3$) for **8q**



^{13}C NMR (100 MHz, $CDCl_3$) for **8q**



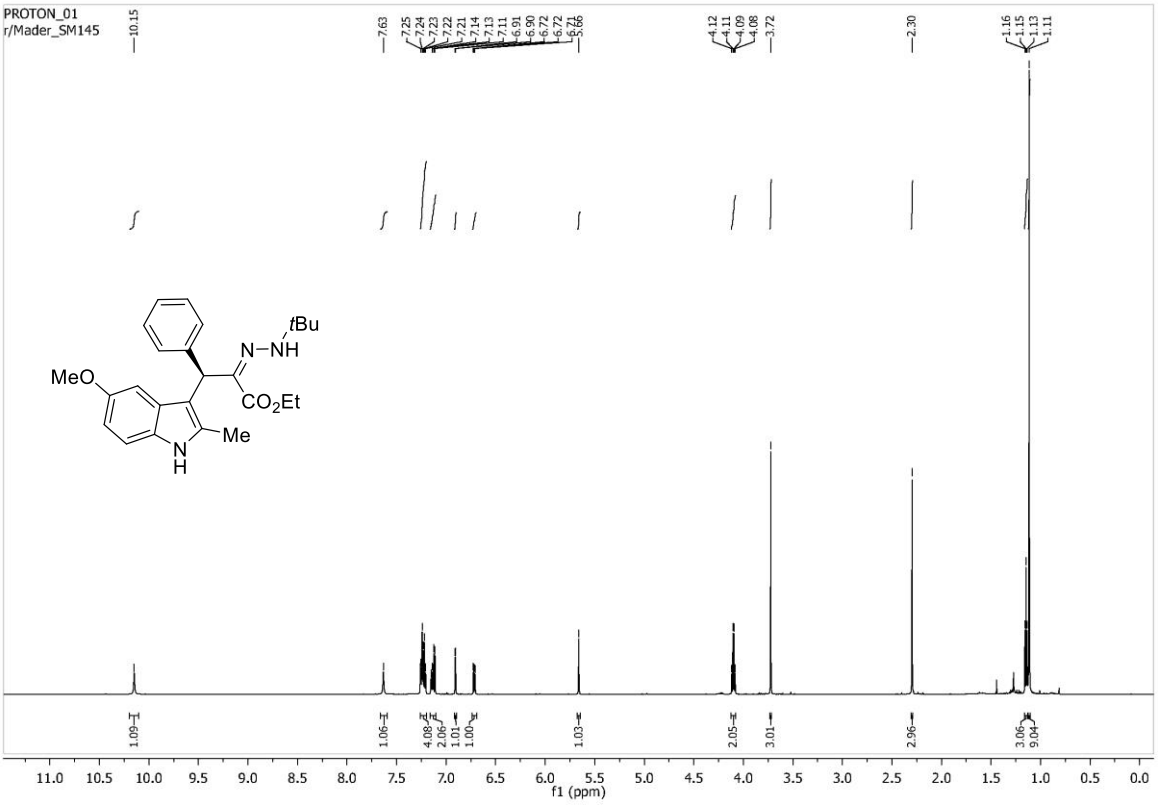




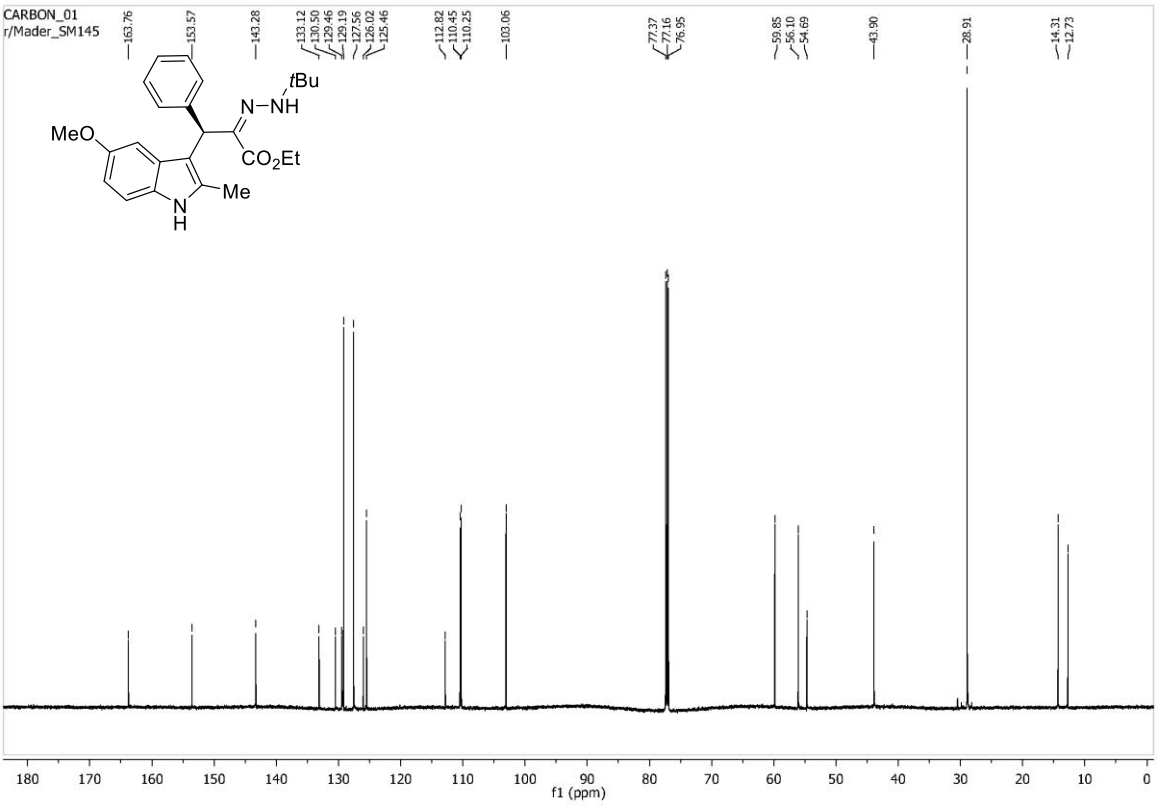
Peak Info

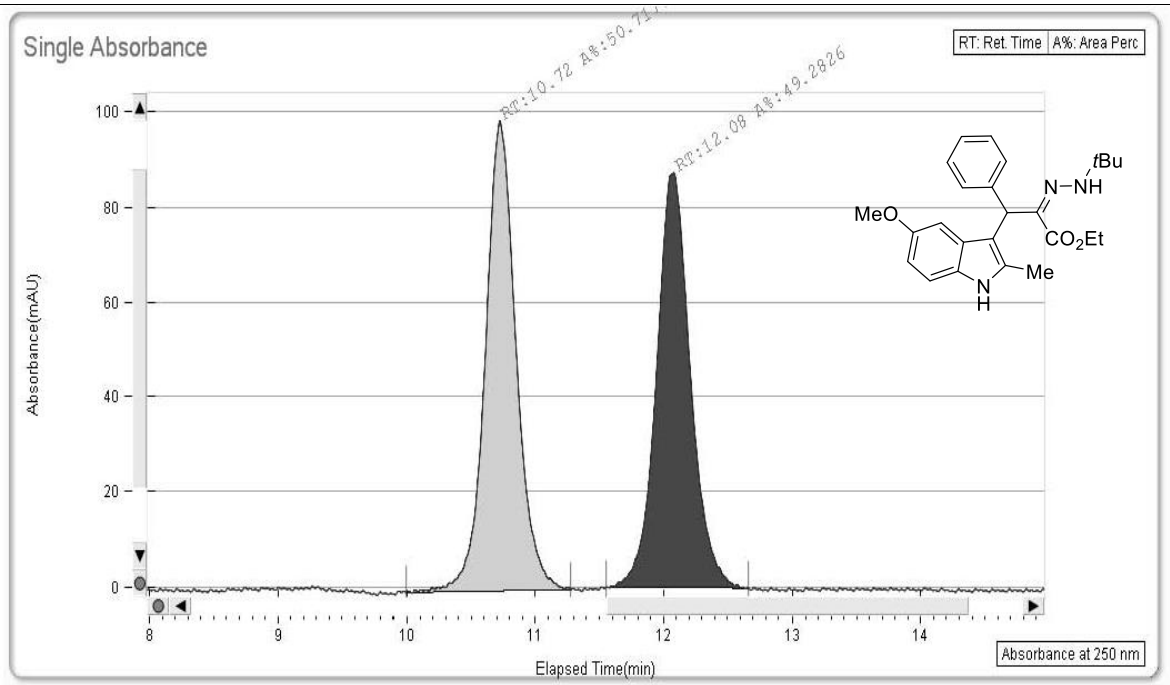
Number	Area %	Area	RT (min)	St. (min)	End (min)
1	94.3396	3385.9288	7.5	7.0078	7.9544
2	5.6604	203.155	8.93	8.6395	9.3214

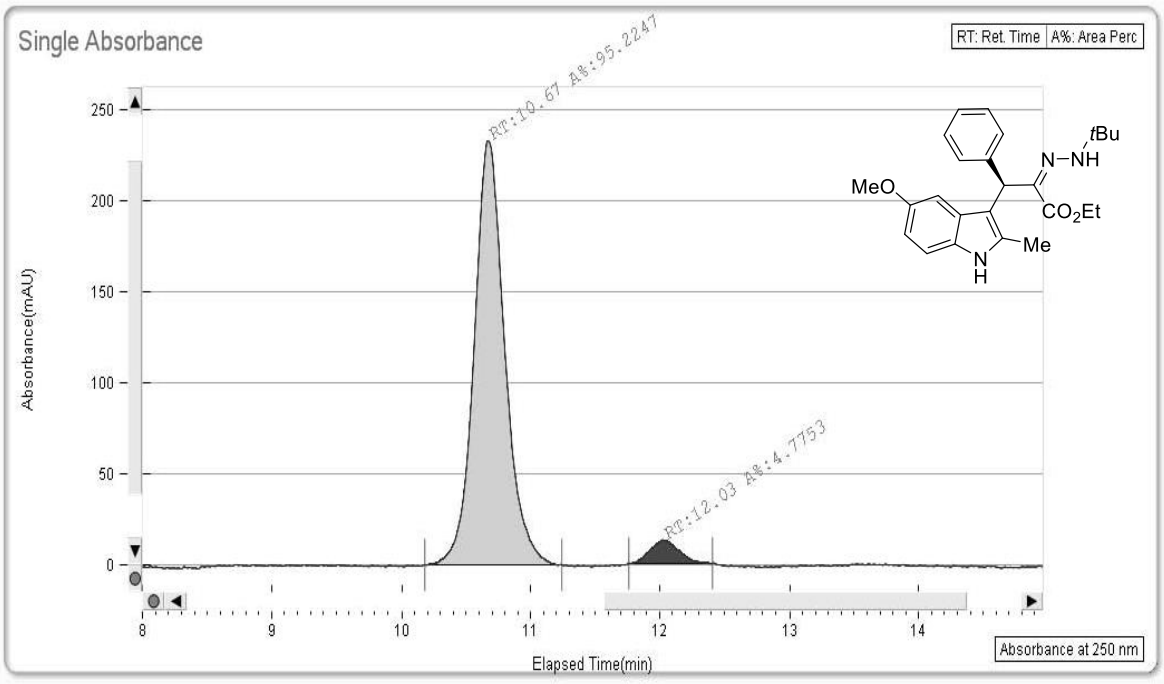
^{1}H NMR (600 MHz, $CDCl_3$) for **8r**



^{13}C NMR (150 MHz, $CDCl_3$) for **8r**







Peak Info

Number	Area %	Area	RT (min)	St. (min)	End (min)
1	95.2247	3823.7489	10.67	10.1782	11.2384
2	4.7753	191.751	12.03	11.7602	12.407