Mo-Catalyzed Regio-, Diastereo-, and Enantioselective Allylic Allylation of 3-aryl oxindoles

Supplementary Information (45 pages)

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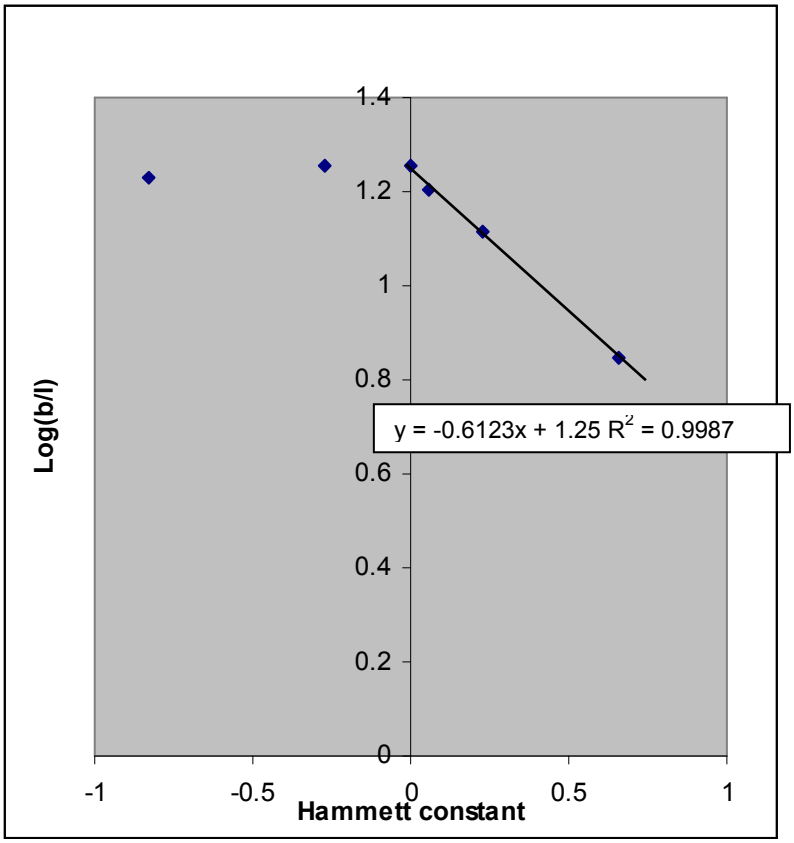


Figure 1. Hammett plot of log(b/l) data vs σ_p for substrates **1d-1i.** Substrate with electron-withdrawing *para*-substituent is approximately a perfect fit for σ_p (R^2=0.9987).

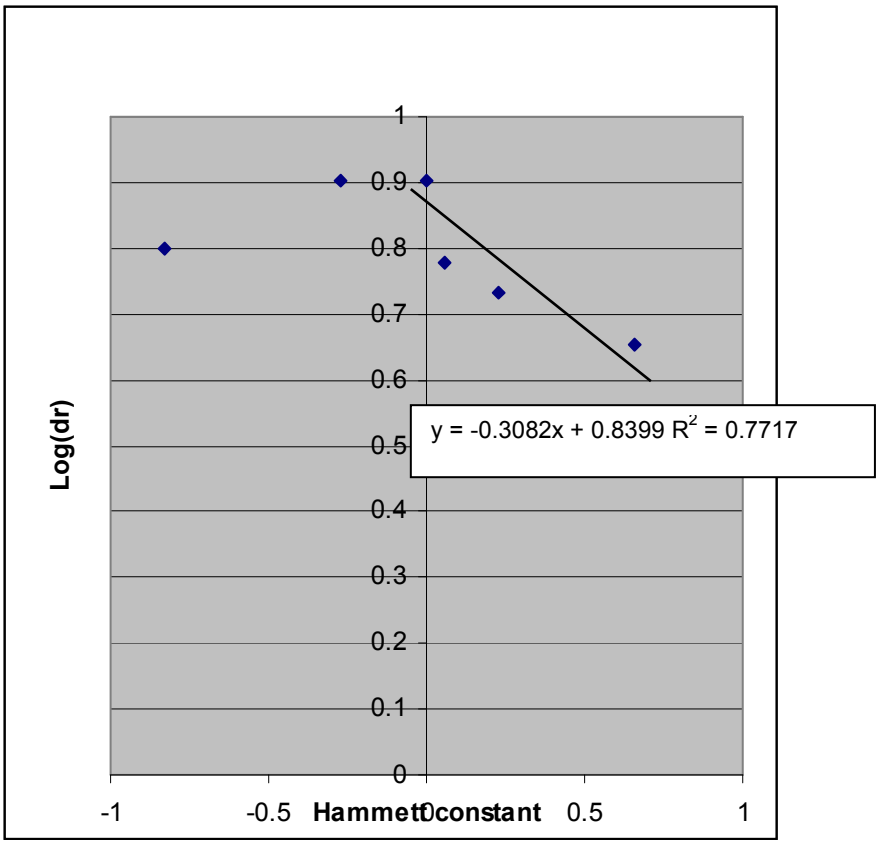


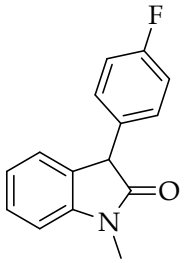
Figure 2. Hammett plot of log(dr) data vs σ_p for substrates **1d-1i.**

Experimental section

All reactions were carried out in oven-dried flasks or pyrex test tubes under a positive pressure of nitrogen, argon for Mo-catalyzed AAA. Anhydrous solvents were obtained from elution through alumina column, except for THF, which was distilled from Na-benzophenone ketyl. All reagents were purchased commercially and used without further purification unless stated otherwise. TLC was performed on precoated glass plates (Merck), flash chromatography with silica gel 60, 230-400 mesh. Enantiomeric excesses were determined by HPLC on Tsp Spectra series P100/UV100 apparatus with a chiral stationary phase (see details where applies). Melting points (uncorrected) were determined in open capillary tubes using a Thomas-Hoover apparatus. 1H-NMR (0 ppm as internal standard) and 13C- NMR (77 ppm as internal standard) spectra were recorded on Varian Mercury 400 (400 MHz for 1H-NMR) and on Unity Inova 500 (500 MHz for 1H-NMR). IR spectra (cm-1) were obtained with a Perkin-Elmer FT-IR Paragon 500 spectrometer, either using neat sample on NaCl pad (for oils and liquids), or preparing a KBr pellet.

Oxindoles 1a[1], 1b[2], 1c[3], 1d[3] 1m[3] 1n[8] were prepared according to literature procedures. Oxindoles 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1m, 1l, 1o, 1p, 1r, 1s, and 1t were prepared according to the following general procedure.

General procedure: 1-Methyl-3-(*p*-fluorophenyl)oxindole (1e)

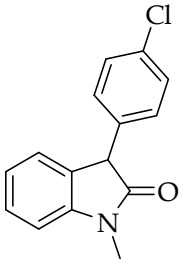


Isatin (450 mg, 3 mmol) was dissolved in anhydrous DMF (15 mL), and the resultant solution was cooled to 0°C, whereupon sodium hydride (60% dispersion in oil, 140mg, 3.5 mmol) was added in one portion and stirred for 5 minutes. Iodomethane(3.5 mmol) was added and the reaction was stirred at 0°C for 30min. The reaction mixture was then poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic portions were washed with water and brine, dried ($MgSO_4$), filtered, and concentrated to give the crude product (100% yield), which was used without further purification.

The 1-methylisatin was dissolved in anhydrous THF (15 mL) and cooled to 0°C. In a separate round-bottom flask, 4-flurobromobenzene (3.5mmol) was dissolved in 5 mL anhydrous THF. Mg tuning (91 mg, 3.75mmol) was added, and the reaction flask was briefly heated to initiate the reaction. The reaction was then stirred under N_2 until Mg tuning disappeared. The resulting Grignard solution was cooled to 0°C and added dropwise to the 1-methylisatin solution. The resulting solution was stirred at 0°C for 1h, at which point TLC indicates complete conversion and the reaction mixture was quenched with addition of 5 mL MeOH, poured into saturated aqueous NH_4Cl, and extracted with ethyl acetate. The combined organic fractions were dried ($MgSO_4$), filtered, and concentrated to give the crude alcohol.

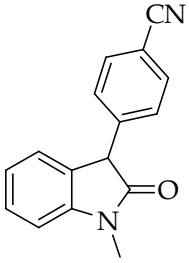
The crude alcohol was dissolved in 8mL of glacial acetic acid and $SnCl_2$ (1.15 g, 2 eq.) was added. The reaction mixture was stirred at 80 °C for 2h and then cooled to room temperature and diluted with water. The product was extracted with ethyl acetate. The organic layer was washed with 1N NaOH, dried with MgSO4, and then concentrated to afford a fluffy yellow solid which was recrystallized with ethyl acetate/ cyclohexane to give a pale-yellow solid in 54% overall yield (390 mg).

The spectroscopic properties is identical to that reported in the literature.[2] mp 138-139°C (lit[2]. 138-139°C) ; IR (KBr)ν_{max}/cm^{-1}: 1692, 1604, 1510, 1468, 1347, 1224, 1088, 827, 752; ^{1}H NMR (400 MHz, d_6-PhH): δ 7.04 (dd, J = 8.0, 7.0, 1H), 6.95 – 6.91 (m, 2H), 6.83 – 6.78 (m, 2H), 6.74 (dd, J = 9.0, 8.5, 2H), 6.31 (d, J = 8.0, 1H), 4.13 (s, 1H), 2.68 (s, 3H); ^{13}C NMR (125 MHz, d_6-PhH) δ 174.7, 163.5, 161.5, 144.9, 133.0, 130.4, 125.1, 122.3, 115.7, 115.5, 108.0, 50.9, 25.7



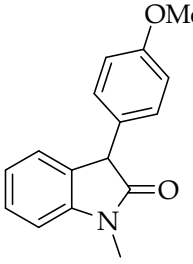
1-Methyl-3-(*p*-chlorophenyl)oxindole (1f)

Prepared according to the general procedure. white solid. 50% yield. The spectroscopic properties is identical to that reported in the literature.[2] mp 161-162°C (lit[3]. 164-165°C) ; IR (KBr)ν_{max}/cm^{-1}: 3054, 3026, 2935, 2906, 1693, 1608, 1492, 1468, 1374, 1347, 1256, 1173, 1126, 1087, 1017, 932, 815, 752, 678, 633. 1H NMR (500 MHz, $CDCl_3$): δ = 7.34 (t, J = 10, 1H), 7.29 (m, 3H), 7.14 (d, J = 8.5, 2H), 7.07 (t, J = 7.5, 1H), 6.90 (d, J = 10, 1H), 4.57 (s, 1H), 3.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 175.8, 144.7, 135.3, 133.8, 130.1, 129.3, 129.0, 128.5, 125.3, 123.1, 108.6, 51.6.



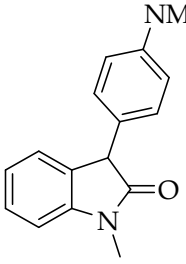
4-(1-methyl-2-oxoindolin-3-yl)benzonitrile (1g)

Prepared according to the general procedure. Grignard reagent was prepared according to Knochel's protocol.[6] The de-oxygenation step was conducted at 100 °C for 3h. white solid. 33% yield mp 163-164°C IR (KBr) ν_{max}/cm^{-1}: 3090, 3057, 2964, 2911, 2227, 1714, 1614, 1494, 1470, 1415, 1371, 1347, 1252, 1179, 1125, 1086, 1020, 924, 753; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0, 2H), 7.40 – 7.25 (m, 3H), 7.17 – 7.01 (m, 2H), 6.93 (dd, J = 8.0, 1H), 4.67 (s, 1H), 3.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 174.6, 144.4, 141.8, 132.5, 129.2, 128.9, 1271.124.9, 123.0, 118.6, 111.4, 108.5, 51.7, 26.5



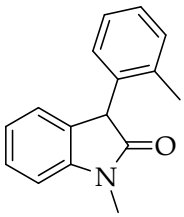
3-(4-methoxyphenyl)-1-methylindolin-2-one(1h)

Prepared according to the general procedure. 46% yield The spectroscopic properties is identical to that reported in the literature.[1] mp 92-93°C (lit[5]. 90-91°C)IR (KBr) ν_{max}/cm^{-1}: 3090, 3057, 2964, 2911, 2227, 1714, 1614, 1494, 1470, 1415, 1371, 1347, 1252, 1179, 1125, 1086, 1020, 924, 753; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (t, J = 8.0, 7.0, 1H), 7.18 (d, J = 7.5, 1H), 7.15 – 7.12 (m, 2H), 7.08 (t, J = 7.5, 1H), 6.76-6.86 (m, 3H), 4.58 (s, 1H), 3.80 (s, 3H), 3.27 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 176.2, 158.9, 144.4, 129.4, 128.6, 124.9, 122.6, 114.2, 108.1, 55.2, 51.2, 26.4



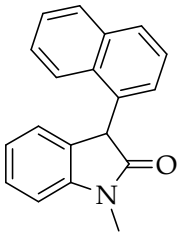
3-(4-(dimethylamino)phenyl)-1-methylindolin-2-one (1i)

Prepared according to the general procedure. 38% yield mp= 84-86 °C IR (KBr) ν_{max}/cm^{-1}: 3090, 3057, 2964, 2911, 2227, 1714, 1614, 1494, 1470, 1415, 1371, 1347, 1252, 1179, 1125, 1086, 1020, 924, 753; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (t, J = 8.0, 1H), 7.21 (dm, J = 6.0, 1H), 7.10 – 7.05 (m, 3H), 6.91 (d, J = 8.0, 1H), 6.74-6.70 (m, 2H), 4.56 (s, 1H), 3.27 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 176.2, 158.9, 144.4, 129.4, 128.6, 124.9, 122.6, 114.2, 108.1, 55.2, 51.2, 26.4



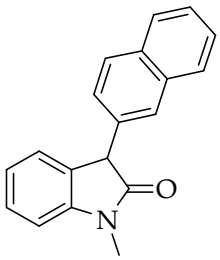
1-Methyl-3-(*o*-tolyl)oxindole (1j)

Prepared according to the general procedure 62% yield The spectroscopic properties is identical to that reported in the literature.[7]mp 130-133 °C (lit[6] 131-132°C) ^{1}H NMR (500 MHz, $CDCl_3$): 7.24 (m, 1H), 7.17-6.93 (m, 6H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.76 (br s, 1H), 3.19 (s, 3H), 2.29 (br s, 3H); ^{13}C NMR (125 MHz, CDCl3); □ = 176.6, 144.7, 137.6, 135.8, 131.4, 129.6, 128.6 (2C), 128.1, 126.71, 124.91, 123.2, 108.5, 50.6, 26.8, 20.2.



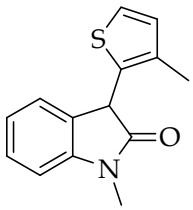
1-methyl-3-(naphthalen-1-yl)indolin-2-one(1k)

Prepared according to the general procedure 65% yield mp 144-145 °C ^{1}H NMR (500 MHz, DMSO, 100 °C): 7.97-7.85 (m, 3H), 7.55-7.48 (m, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.37-7.32(m, 1H), 7.22(br, s, 1H), 7.12 (d, *J*= 8 Hz, 1H), 7.01-6.95 (m, 2H), 5.51 (s, 1H), 3.29 (s, 3H),; ^{13}C NMR (125 MHz, DMSO, 100 °C): = HRMS—EI (m/z): calcd for $C_{19}H_{15}NO$: 273.1153; found: 277.1147



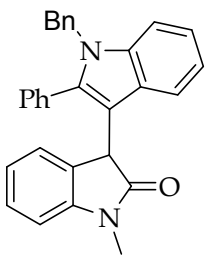
1-methyl-3-(naphthalen-2-yl)indolin-2-one (1l)

Prepared according to the general procedure 60% yield mp 87-88 °C IR (KBr) □$_{max}$/cm^{-1}: 3054, 3022, 2959, 2935, 2887, 1712, 1611, 1493, 1469, 1419, 1372, 1344, 1305, 1257, 1176, 1124, 1086, 1018, 927, 808, 748, 691. ^{1}H NMR (500 MHz, $CDCl_3$): □ = 7.83-7.77 (m, 3H), 7.72-7.71 (m, 1H), 7.49-7.44 (m, 2H), 7.37 (td, *J* = 8,1 Hz, 1H), 7.27 (dd, *J* = 8,1.5 Hz, 1H), 7.21-7.18 (m, 1H), 7.08 (dt, *J* = 7.5,1 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 4.79 (s, 1H), 3.30 (s, 3H), ; ^{13}C NMR (125 MHz, CDCl3):□ = 175.9, 144.5, 134.0, 133.5, 132.8, 128.9, 128.7, 128.5, 127.8, 127.6, 127.5, 126.2, 126.1, 125.9, 125.1, 122.8, 108.2, 52.2, 26.5 HRMS—EI (m/z): calcd for $C_{19}H_{15}NO$: 273.1153; found: 273.1185



1-methyl-3-(3-methylthiophen-2-yl)indolin-2-one (1p)

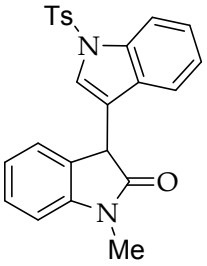
Prepared according to the general procedure 59% yield mp 201- 202°C IR (KBr) □$_{max}$/cm^{-1}: 3056, 2918, 2850, 1712, 1610, 1493, 1469, 1418, 1371, 1342, 1304, 1249, 1162, 1123, 1084, 1019, 750, 709, 690. ^{1}H NMR (500 MHz, $CDCl_3$): □ = 7.32 (t, *J* = 3 Hz, 1H), 7.20 (d, *J* = 7.5Hz, 1H), 7.09-7.02 (m, *2*H), 6.89-6.83 (m, *2*H), 4.89 (s, 1H), 3.23 (s, 3H), 2.27 (s, 3H), ; ^{13}C NMR (100 MHz, CDCl3):□ =174.9, 144.0, 136.1, 131.4, 130.4, 128.6, 128.5, 124.8, 123.0, 122.6, 108.1, 45.6, 26.4, 14.1, HRMS—EI (m/z): calcd for $C_{24}H_{18}N_2O_2$: 366.1368; found: 366.1372



1'-benzyl-1-methyl-2'-phenyl-3,3'-biindolin-2-one(1q)

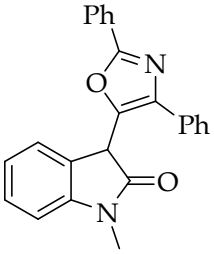
Prepared according to Muthusamy's procedure.[8] mp 101-103°C IR(KBr) 2932, 2889, 2822, 1710, 1674,k 1609, 1552, 1531, 1517, 1487, 1465, 1414, 1347,k 1303, 1280, 1254, 1216, 1180, 1157, 1120, 1083, 1027. ^{1}H NMR (500 MHz, DMSO, 100 °C): □ = 7.48-7.39 (m, 5H), 7.34 (d, *J* = 8 Hz, 1H), 7.28 (t, *J* = 8Hz, 1H), 7.24-7.15 (m, 3H), 7.09 (t, *J* = 8Hz, 1H), 7.00 (t, *J* = 8Hz, 2H), 6.96-6.85 (m, *5*H), 5.31 (s, 2H), 4.73 (s, 1H), 3.15 (s, 3H), ^{13}C NMR (100 MHz, DMSO, 100 °C):□ 175.0, 143.4, 139.6, 137.4, 135.9,

130.0, 129.9, 128.9, 127.9, 127.7, 127.6, 127.2, 126.3, 125.8, 125.5, 123.2, 121.4, 121.2, 119.0, 117.7, 110.0, 108.1, 107.5, 46.4, 42.9, 25.4, HRMS—EI (m/z): calcd for $C_{30}H_{24}N_2O$: 428.1889; found: 428.1893



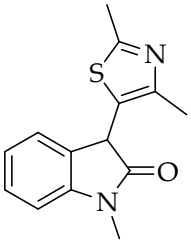
1-methyl-1'-tosyl-3,3'-biindolin-2-one (1t)

Prepared according to the general procedure Grignard reagent prepared according to Knochel's protocol[6] from 3-bromo-1-tosyl-1H-indole[9]. mp 91-93 °C IR (KBr) ν_{max}/cm^{-1}: 3056, 2918, 2850, 1712, 1610, 1493, 1469, 1418, 1371, 1342, 1304, 1249, 1162, 1123, 1084, 1019, 750, 709, 690. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8Hz, 2H), 7.47 (s, 1H), 7.40-7.16 (m, 8H), 7.08 (t, *J* =7.5, 1H), 6.96 (d, *J* =8, *I*H), 4.84 (s, 1H), 3.30 (s, 3H), 2.36 (s, 3H), ; ^{13}C NMR (100 MHz, CDCl3): δ =174.8, 144.9, 144.2, 135.3, 135.0, 129.9, 129.4, 128.7, 127.2, 126.8, 124.9, 124.6, 123.2, 122.8, 120.2, 117.6, 113.5, 108.3, 43.8, 26.4, 21.5 HRMS—EI (m/z): calcd for $C_{24}H_{18}N_2O_2$: 366.1368; found: 366.1372



3-(2,5-diphenyloxazol-4-yl)-1-methylindolin-2-one(1s)

mp 201- 202°C IR (KBr) ν_{max}/cm^{-1}:.3059, 3005, 2925, 1710, 1611, 1559, 1491, 1472, 1373, 1349, 1258, 1174, 1125, 1088, 1022, 953, 924, 884, 752, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.97 (m, 2H), 7.83-7.79 (m, 2H), 7.51-7.44 (m, 2H), 7.43-7.37 (m, 4H), 7.33 (t, *J* = 8 Hz, 1H), 7.15 (d, *J* = 8Hz, 1H), 7.04 (t, *J* = 8Hz, 1H), 6.92 (d, *J* = 8 Hz, 1H), 4.99 (s, 1H), 3.31 (s, 3H), ; ^{13}C NMR (100 MHz, CDCl3): δ = 174.7, 160.4, 149.1, 144.4, 132.2, 130.3, 128.9, 128.8, 128.5, 128.2, 128.1, 127.6, 127.2, 126.5, 126.4, 124.5, 122.7, 108.4, 44.8, 26.6, HRMS—EI (m/z): calcd for $C_{24}H_{18}N_2O_2$: 366.1368; found: 366.1372



3-(2,4-dimethylthiazol-5-yl)-1-methylindolin-2-one(1r)

Prepared according to the general procedure Grignard reagent prepared according to Knochel's protocol[6]. mp 97-98°C IR (KBr) ν_{max}/cm^{-1}: 3057, 3021, 2927, 2884, 1711, 1609, 1552, 1490, 1466, 1366, 1347, 1303, 1251, 1176, 1122, 1084, 1022, 934, 864, 749. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (t, *J* = 7.5, 1H), 7.12 (d, *J* = 7.5, 1H), 7.02 (t, *J* = 7.5, 1H), 6.84 (d, *J* = 7.5, 1H), 4.79 (s, 1H), 3.20 (s, 3H), 2.54 (s, 3H), 2.40 (s, 3H), ; ^{13}C NMR (125 MHz, CDCl3): δ = 174.6, 163, 6, 150.5, 143.7, 128.8, 128.3, 125.1, 124.5, 122.8, 108.3, 44.1, 26.4, 19.0, 15.3. Anal Calcd $C_{14}H_{14}N_2OS$: C, 65.09, H, 5.46, N, 10.84; found: C, 65.26, H, 5.45, N, 10.88.

General procedure for Mo catalyzed AAA reactions.

Preparation of the active catalyst solution

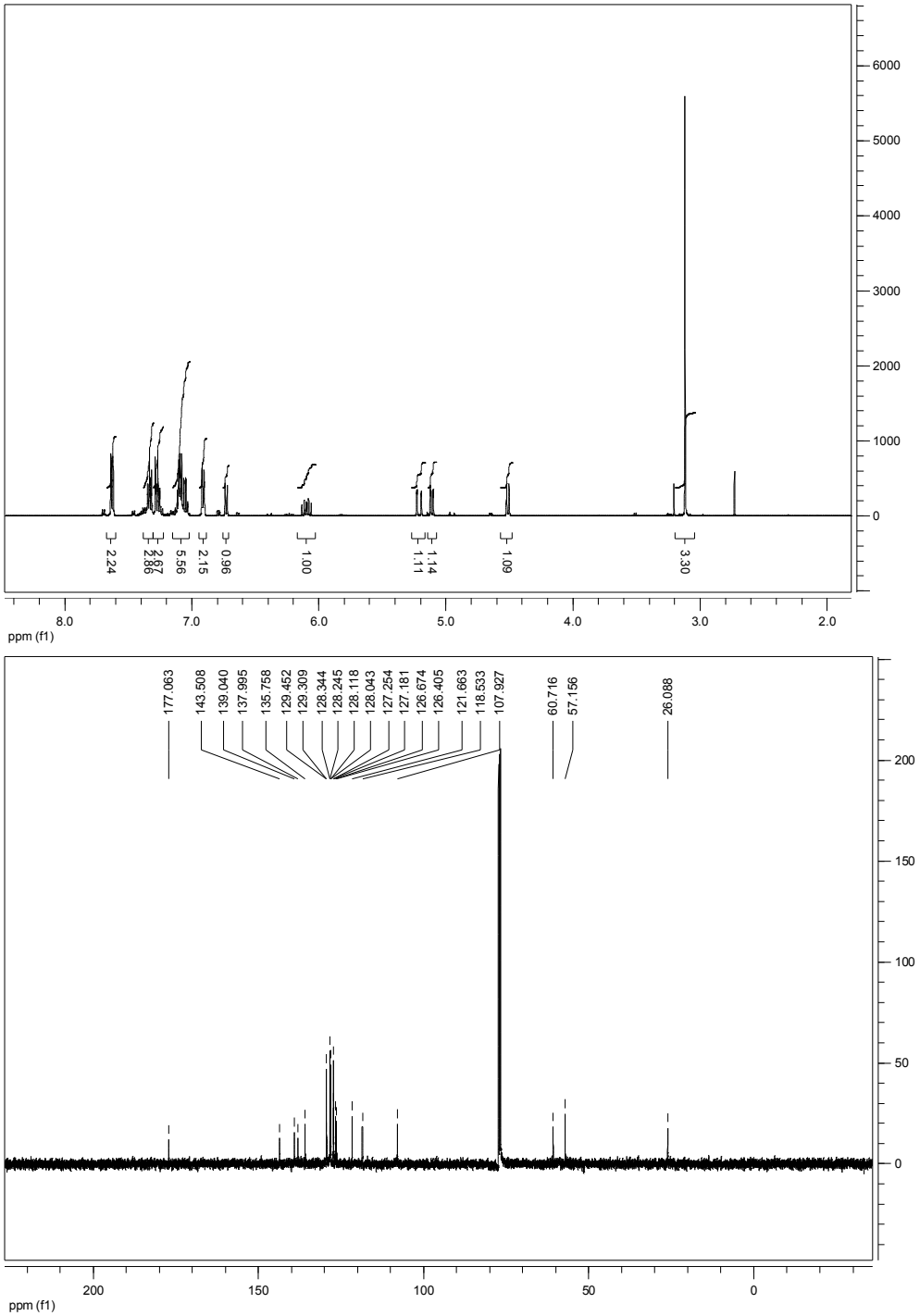
(*R,R*) ligand **L1** (2.4 mg, 0.015 mmol) and [(η^3-C_7H_8)$Mo(CO)_3$ (1.4mg, 0.01 mmol) was stirred at 60 ^oC in THF (freshly distilled and degassed, 0.3 mL) of in a sealed pyrex test tube under Ar. The solution turned deep purple after 3-5 min, indicating successful generation of the active catalyst. Further heating causes black precipitation and decomposition. The active catalyst is very sensitive to oxygen and moisture and should be used immediately after generation.

Preparation of nucleophile

A pyrex test tube containing 0.1 mmol of oxindole was transferred to the dry box and to it NaOtBu (0.11mmol , 11mg) was added. The test tube was sealed, taken out of the dry box, and to it was added 0.7 mL of degassed THF at room temperature unless indicated otherwise. The resulting solution was cooled to 0^oC and a solution of the active catalyst was added via cannula, followed by the addition of cinnamyl tert-Butyl carbonate (0.12 mmol) via syringe. The resulting solution was stirred at 60^oC under Ar for 2-16 h until TLC indicates complete consumption of the starting oxindole. The reaction mixture was then concentrated and purified through silica gel to give the desired product as a mixture of regio- and diastereomers.

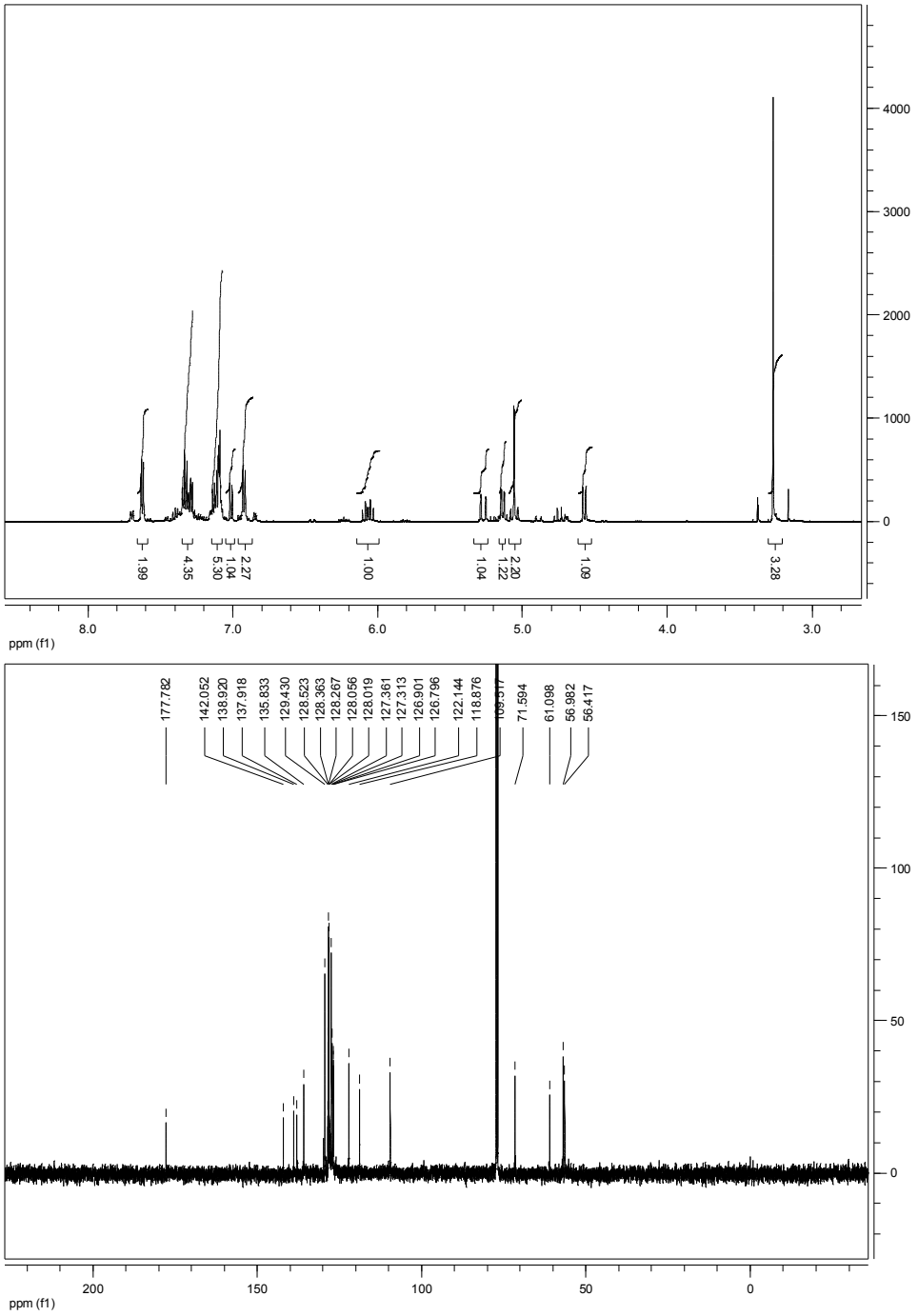
1-methyl-3-phenyl-3-(1-phenylallyl)indolin-2-one (3d)

Isolated as white solid Chiral HPLC, AD-column, flow rate 0.7 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 8.387 min, t_B (major) = 9.556 min. IR (film) ν_{max}/cm^{-1}: 3058, 2926, 1708, 1610, 1493, 1470, 1373, 1349, 1255, 1131, 1089, 1025, 923, 757, 689. ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 7.61-7.58 (m, 2H), 7.34-7.27 (m, 2H), 7.26-7.21 (m, 2H), 7.08-6.98 (m, 5H), 6.89-6.87 (m, 2H), 6.69(d, *J*=7.5, 1H), 6.06 (ddd, *J*= 9.5, 10, 17, 1H), 5.18 (dm, *J* = 17, 1H), 5.08 (dd, *J* = 1.5, 10, 1H), 4.48(d, *J*= 9.5, 1H), 3.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: δ 177.1, 143.5, 139.0, 138.0, 135.8, 129.5, 129.3, 128.2, 128.1, 128.0, 127.3, 127.2, 126.7, 126.4, 121.7, 118.5, 107.9, 60.7, 57.2, 26.1 HRMS—EI (m/z): calcd for $C_{24}H_{21}NO$: 339.1623; found: 339.1629



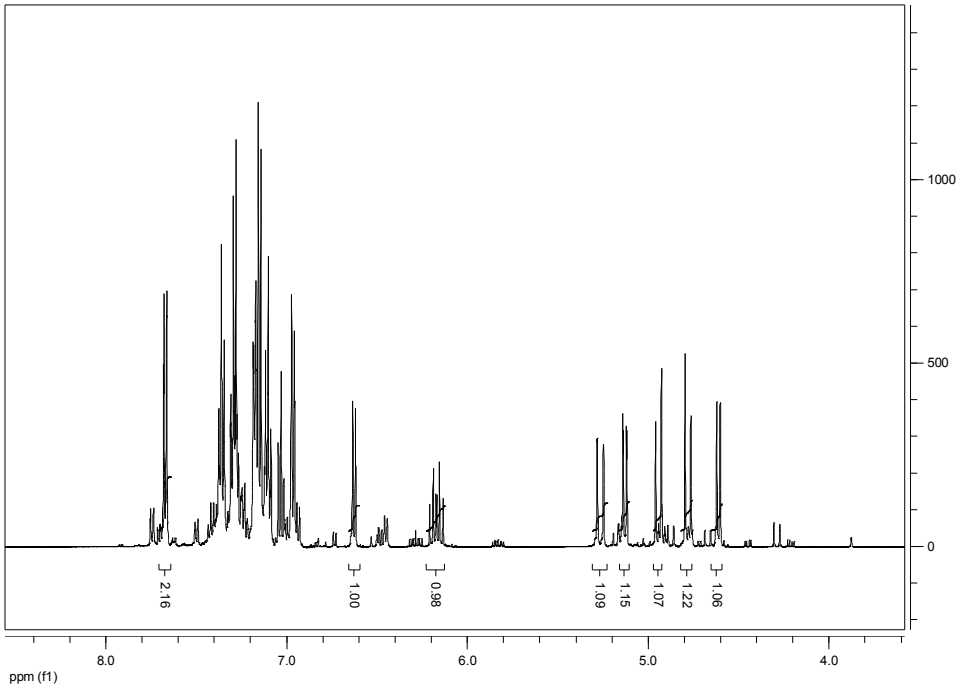
1-(methoxymethyl)-3-phenyl-3-(1-phenylallyl)indolin-2-one (3b)

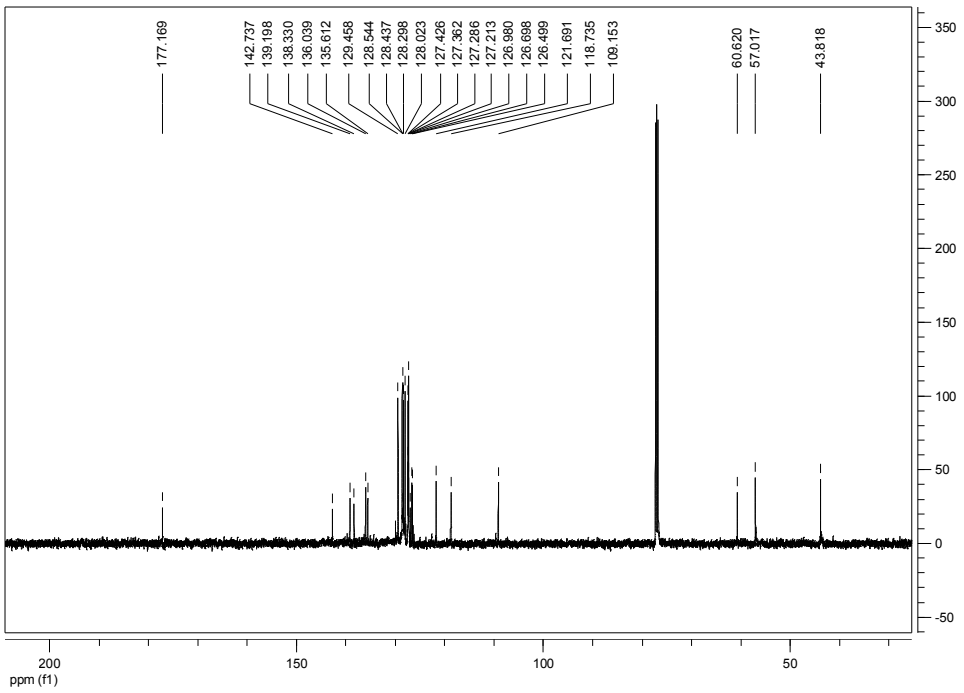
Isolated as yellow oil Chiral HPLC, OD-column, flow rate 0.8 mL/min, 99:1 heptane / *i*-PrOH, t_A (minor) = 11.825 min, t_B (major) = 16.628 min. IR (film) ν_{max}/cm^{-1}: 3058, 3031, 2936, 1716, 1610, 1487, 1467, 1453, 1365, 1344, 1299, 1237, 1189, 1124, 1092, 1072, 916, 759, 701. ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 7.61-7.56 (m, 2H), 7.31-7.23 (m, 4H), 7.09-7.02 (m, 5H), 6.97 (d, *J*=7.5, 1H), 6.90-6.87 (m, 2H), 6.03 (ddd, *J*= 9.5, 10, 17, 1H), 5.23 (dm, *J* = 17, 1H), 5.10 (dd, *J* = 1.5, 9.5, 1H), 5.02(d, *J*= 2.2, 1H), 4.53 (d, *J* = 10, 1H), 3.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: δ 177.8, 142.1, 138.9, 137.9, 135.8, 129.4, 128.5, 128.4, 128.3, 128.0, 127.4, 127.3, 127.3, 126.9, 126.8, 122.1, 118.9, 109.5, 71.6, 61.1, 57.0, 56.4 HRMS—EI (m/z): calcd for $C_{25}H_{23}NO_2$: 369.1729; found: 369.1737



1-benzyl-3-phenyl-3-(1-phenylallyl)indolin-2-one (3c)

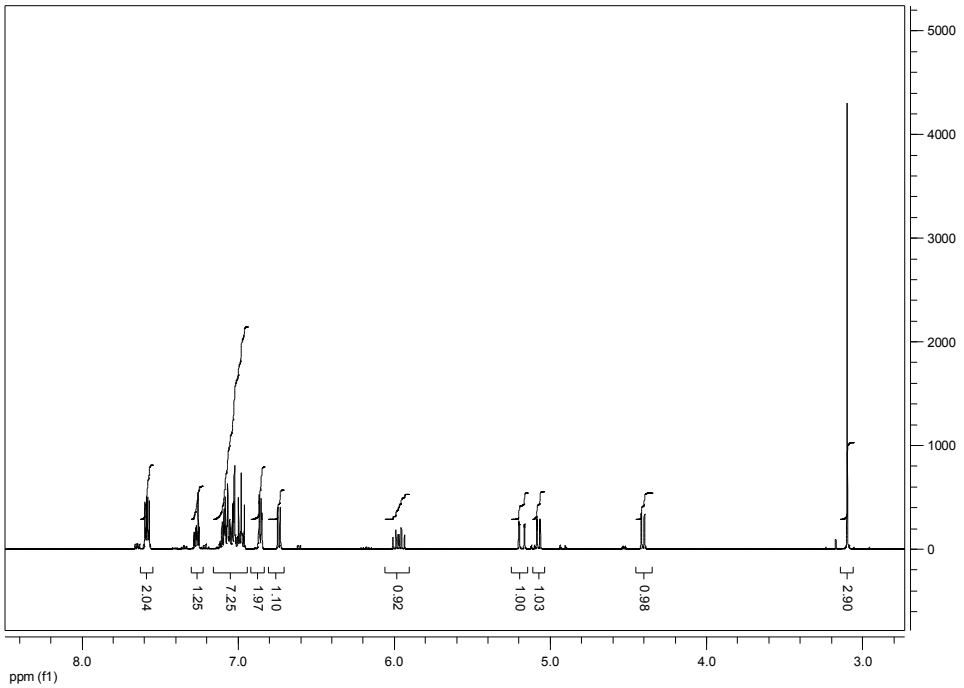
Isolated as yellow oil Chiral HPLC, OD-column, flow rate 0.8 mL/min, 99:1 heptane / *i*-PrOH, t_A (minor) = 11.825 min, t_B (major) = 16.628 min. IR (film) ν_{max}/cm^{-1}: 3058, 3031, 2936, 1716, 1610, 1487, 1467, 1453, 1365, 1344, 1299, 1237, 1189, 1124, 1092, 1072, 916, 759, 701. ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 7.63-7.61 (m, 2H), 7.35-6.88 (m, 14H), 6.58 (d, *J*=7.5, 1H), 6.12 (ddd, *J*= 10, 10, 17, 1H), 5.21 (dm, *J* = 17, 1H), 5.07 (dd, *J* = 1.5, 10, 1H), 4.88 (d, *J* = 16.8, 1H), 4.73 (d, *J* = 16.8, 1H), 4.55(d, *J*= 10, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: δ 177.2, 142.7, 139.2, 138.3, 136.0, 135.6, 129.5, 128.5, 128.4, 128.3, 128.0, 127.4, 127.4, 127.3, 127.2, 127.0, 126.7, 126.5, 121.7, 118.7, 109.1, 60.6, 57.0, 43.8. HRMS—EI (m/z): calcd for $C_{30}H_{25}NO$: 415.1936; found: 415.1935

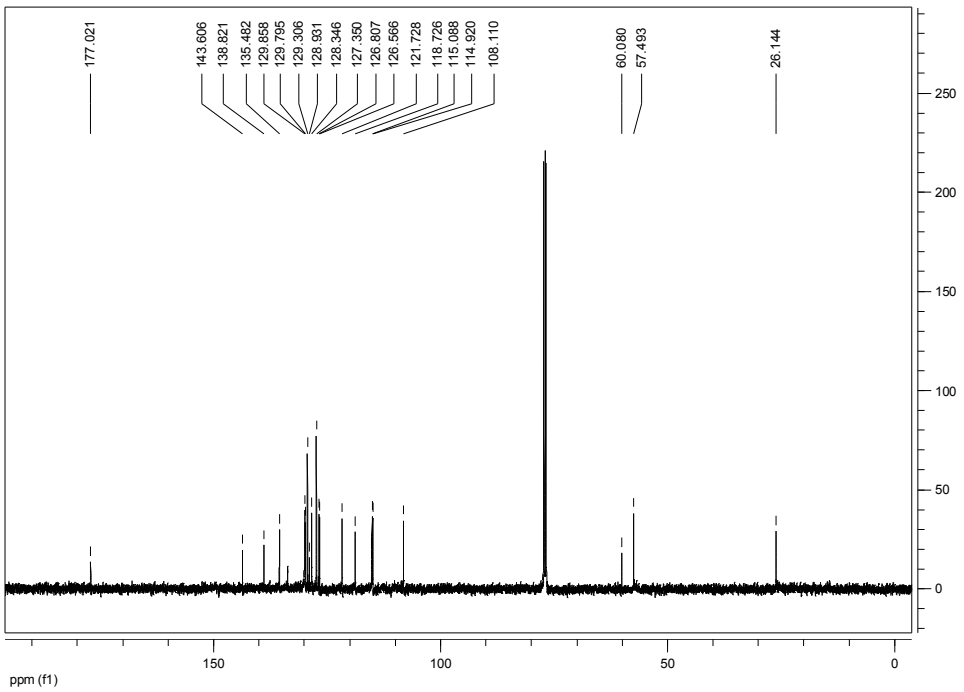




3-(4-fluorophenyl)-1-methyl-3-(1-phenylallyl)indolin-2-one (3e)

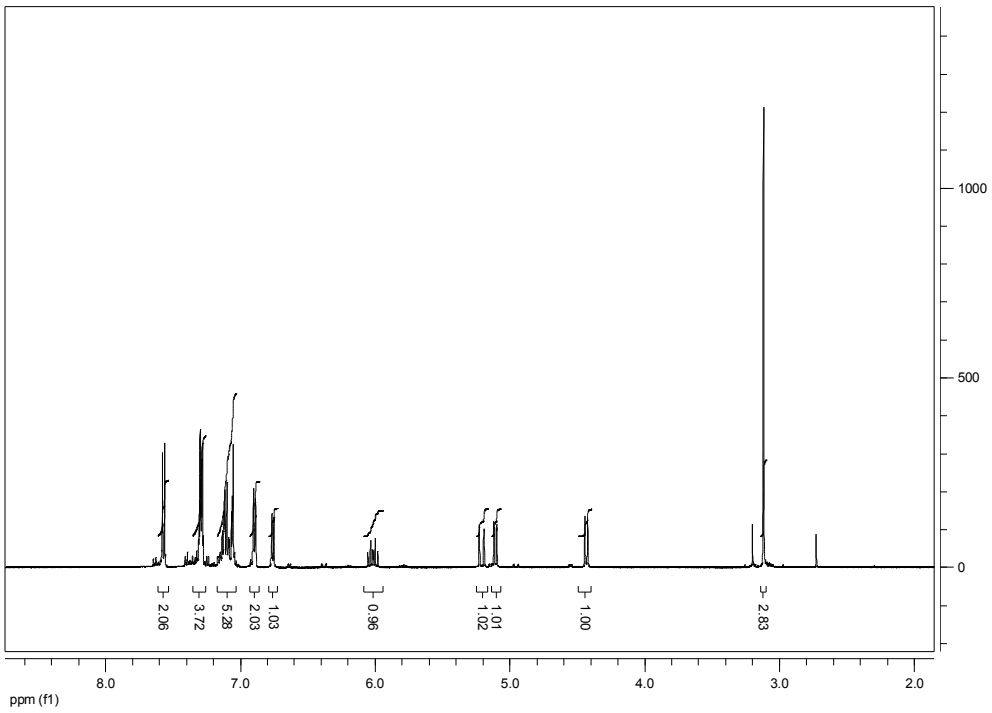
Isolated as clear oil Chiral HPLC, AD-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 5.724 min, t_B (major) = 6.889 min. IR (film) $_{max}$/cm^{-1}: 3054, 2904, 1691, 1608, 1510, 1469, 1375, 1347, 1252, 1220, 1172, 1160, 1126, 1088, 1021, 826, 813, 751, 692. ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.60-7.55 (m, 2H), 7.28-7.24 (m, 1H), 7.10-6.96 (m, 7H), 6.87-6.84 (m, 2H), 6.74(d, *J*=7.5, 1H), 5.97 (ddd, *J*= 9.5, 10, 17, 1H), 5.18 (dm, *J* = 17, 1H), 5.07 (dd, *J* = 1.5, 10, 1H), 4.40(d, *J*= 9.5, 1H), 3.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: 177.0, 143.6, 138.8, 135.5, 129.9, 129.8, 129.3, 128.9, 128.3, 127.4, 126.8, 126.6, 121.7, 118.7, 115.1, 114.9, 108.1, 60.1, 57.5, 26.1. HRMS—EI (m/z): calcd for $C_{24}H_{20}FNO$: 357.1529; found: 357.1515

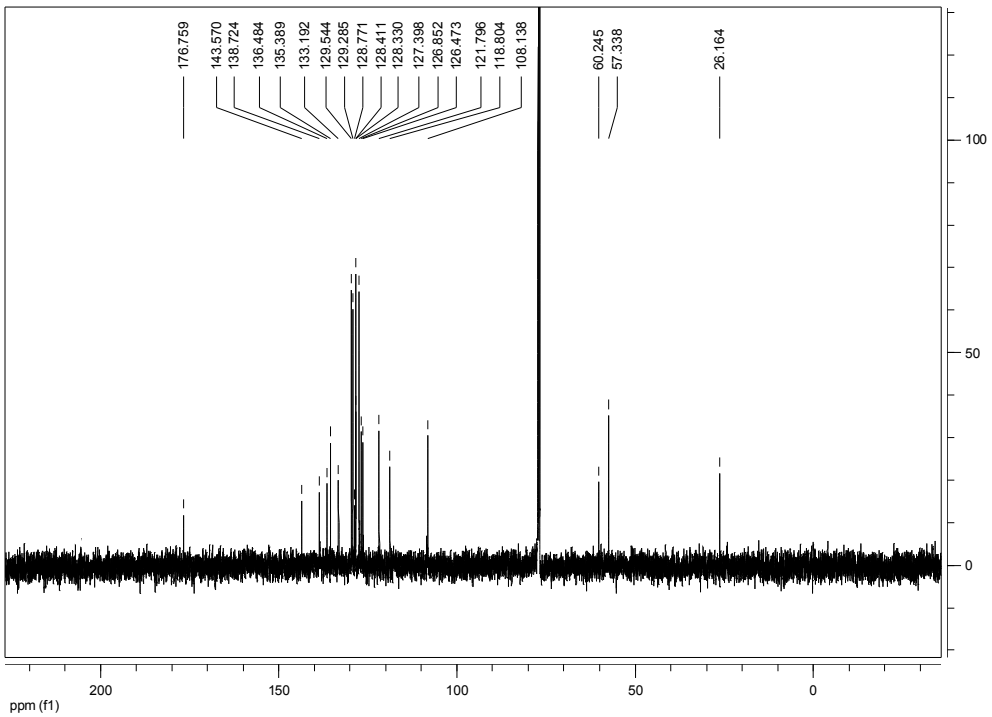




3-(4-chlorophenyl)-1-methyl-3-(1-phenylallyl)indolin-2-one (3f)

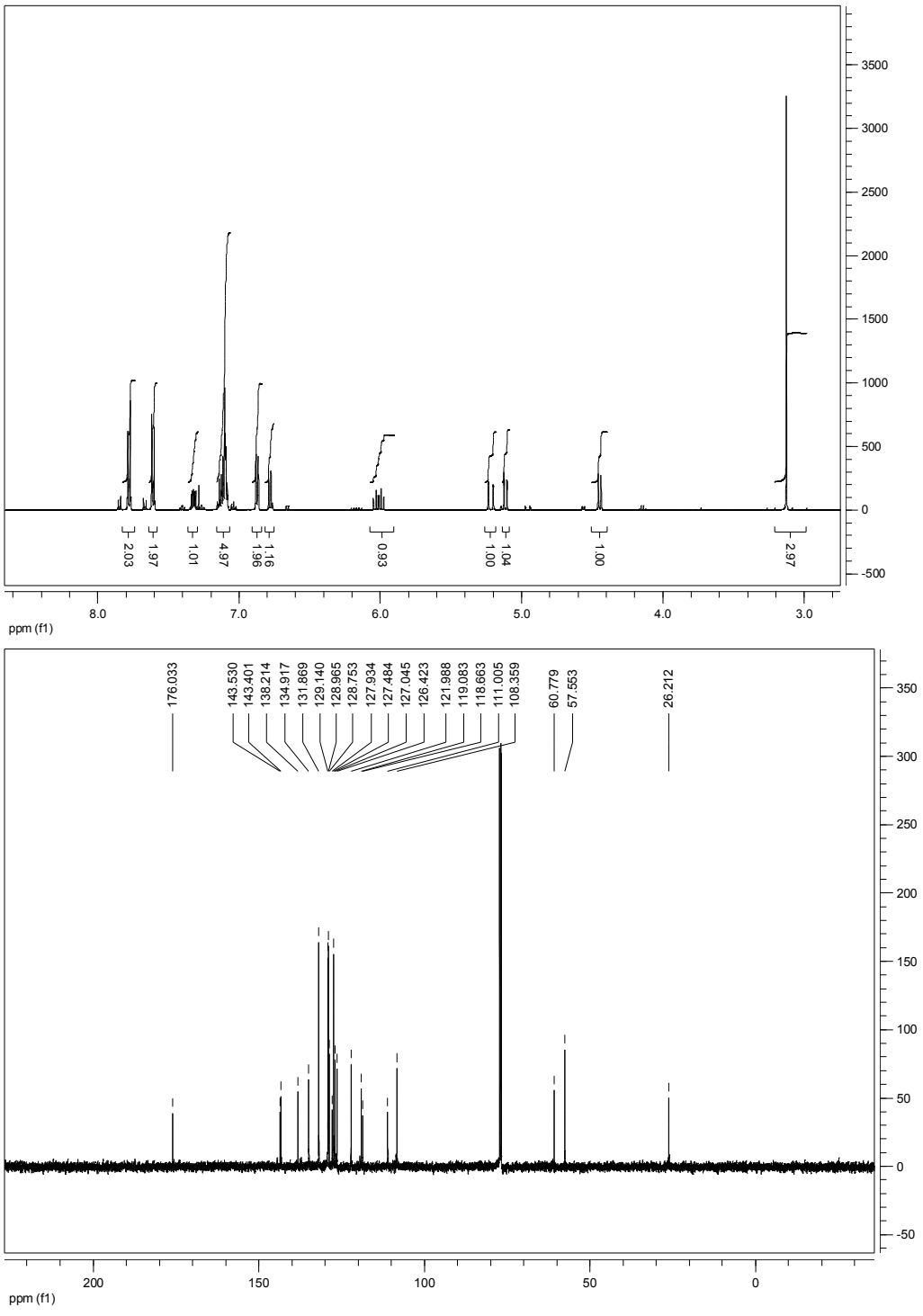
Isolated as white solid Chiral HPLC, AD-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 6.344 min, t_B (major) = 9.162 min. IR (film) ν_{max}/cm^{-1}: 3058, 2921, 1708, 1609, 1491, 1459, 1372, 1351, 1092, 1014 ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.55-7.53 (m, 2H), 7.28-7.24 (m, 3H), 7.11-7.02 (m, 5H), 6.89-6.85 (m, 2H), 6.73(d, *J*=7.5, 1H), 5.99 (ddd, *J*= 9.5, 10, 17, 1H), 5.18 (dm, *J* = 17, 1H), 5.09 (dd, *J* = 1.5, 10, 1H), 4.41(d, *J*= 9.5, 1H), 3.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: 176.7, 143.5, 138.7, 136.5, 135.4, 133.2, 129.5, 129.3, 128.8, 128.4, 128.3, 127.4, 126.8, 126.5, 121.8, 118.8, 108.1, 60.2, 57.3, 26.2, HRMS—EI (m/z): calcd for $C_{24}H_{20}ClNO$: 373.1233; found: 373.1224





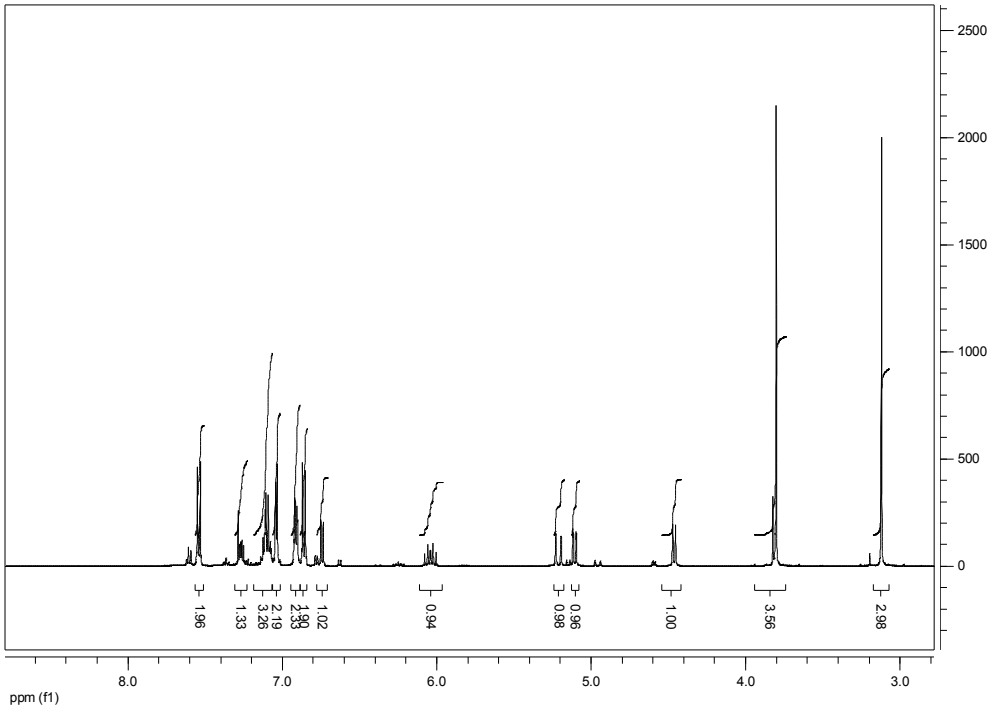
3-(4-cyanophenyl)-1-methyl-3-(1-phenylallyl)indolin-2-one (3g)

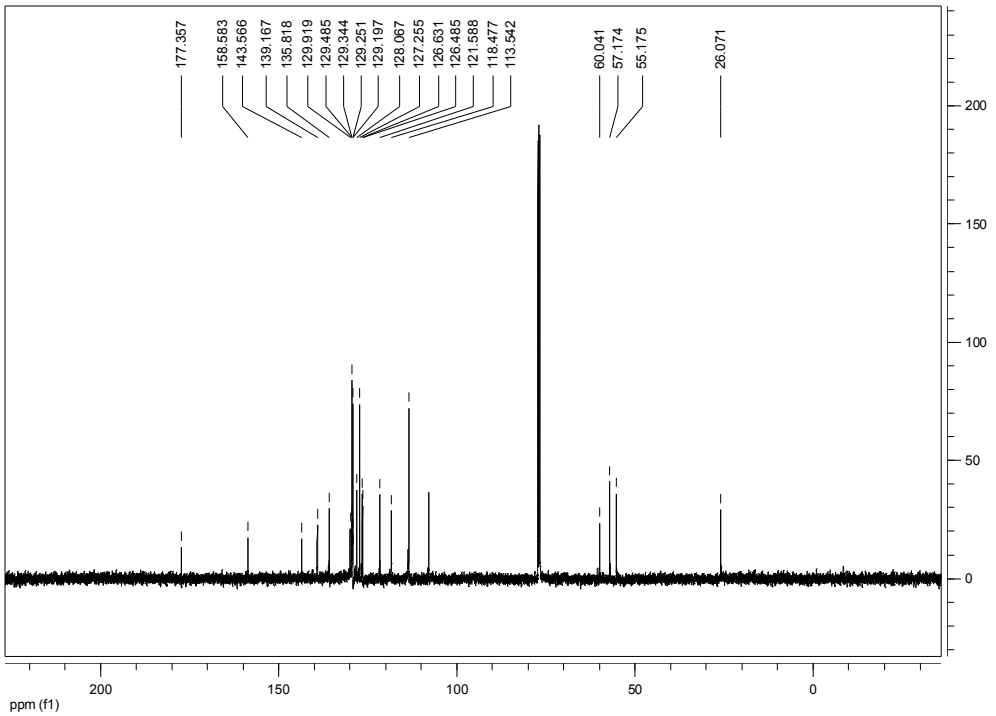
Isolated as white solid Chiral HPLC, IA-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 13.751 min, t_B (major) = 14.892 min. IR (film) ν_{max}/cm^{-1}: 3064, 3030, 2934, 2228, 1711, 1611, 1493, 1471, 1373, 1352, 1257, 1132, 1089, 916, 758, 732 ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.78-7.76 (m, 2H), 7.63-7.59 (m, 2H), 7.35-7.30 (m, 1H), 7.18-7.02 (m, 5H), 6.89-6.85 (m, 2H), 6.75(d, *J*=7.5, 1H), 6.01 (ddd, *J*= 9.5, 10, 17, 1H), 5.21 (dm, *J* = 17, 1H), 5.12 (dd, *J* = 1.5, 10, 1H), 4.44(d, *J*= 9.5, 1H), 3.13 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer176.0, 143.5, 143.4, 138.2, 134.9, 131.9, 129.2, 128.9, 128.7, 127.9, 127.5, 127.1, 126.4, 122.0, 119.1, 118.7, 111.0, 108.4. 60.8, 57.6, 26.2.



3-(4-methoxyphenyl)-1-methyl-3-(1-phenylallyl)indolin-2-one (3h)

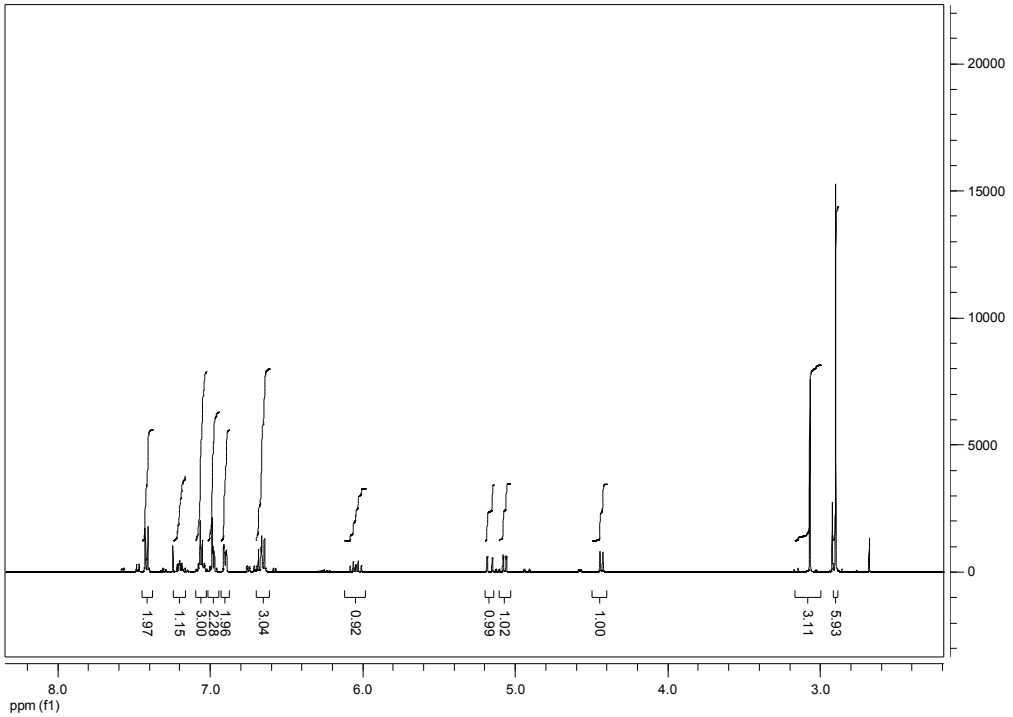
Isolated as clear oil Chiral HPLC, AD-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 7.591 min, t_B (major) = 10.162 min. IR (film) ν_{max}/cm^{-1}: 3058, 2955, 2923, 2836, 1709, 1609, 1511, 1493, 1469, 1418, 1373, 1439, 1295, 1251, 1185, 1131, 1088, 1131, 1088, 1033, 923, 756, 701. ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.52-7.49 (m, 2H), 7.25-7.21 (m, 2H), 7.10-7.04 (m, 3H), 7.01-6.98 (m, 2H), 6.89-6.85 (m, 2H), 6.83-6.80 (m, 2H), 6.71(d, *J*=7.5, 1H), 6.00 (ddd, *J*= 9.5, 10, 17, 1H), 5.18 (dm, *J* = 17, 1H), 5.07 (dd, *J* = 1.5, 10, 1H), 4.43(d, *J*= 9.5, 1H), 3.77 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: 177.4, 158.6, 143.6, 139.2, 135.8, 129.9, 129.5, 129.3, 129.2, 128.1, 127.3, 126.6, 126.5, 121.6, 118.5, 113.5, 107.9, 60.0, 57.2, 55.2, 26.1 HRMS—EI (m/z): calcd for $C_{25}H_{23}NO_2$: 369.1869; found: 369.1729

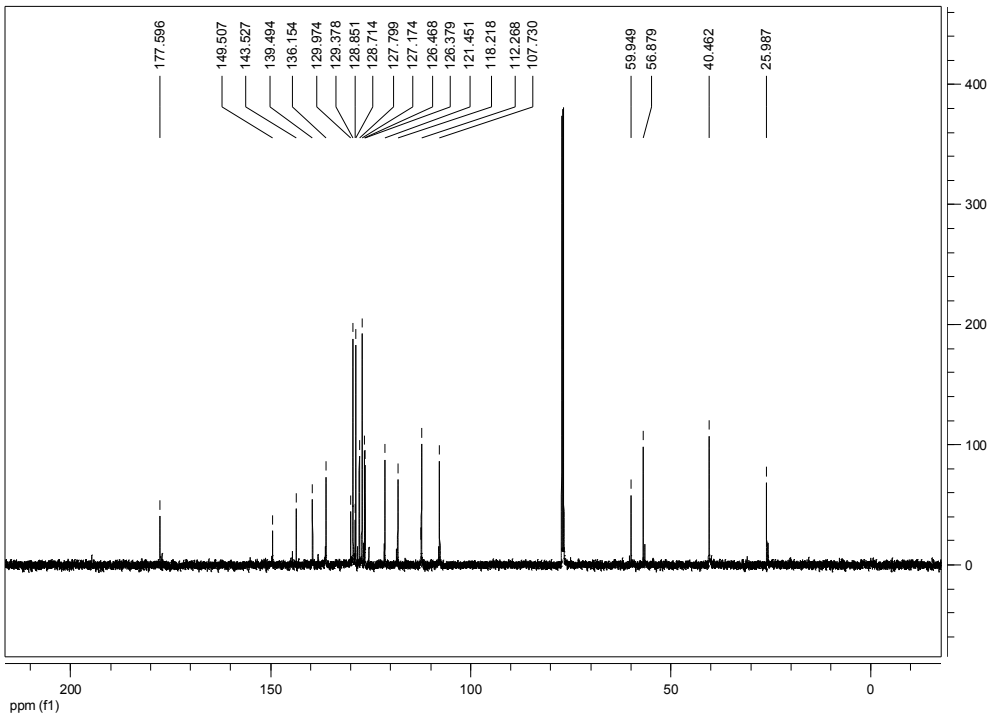




3-(4-(dimethylamino)phenyl)-1-methyl-3-(1-phenylallyl)indolin-2-one (3i)

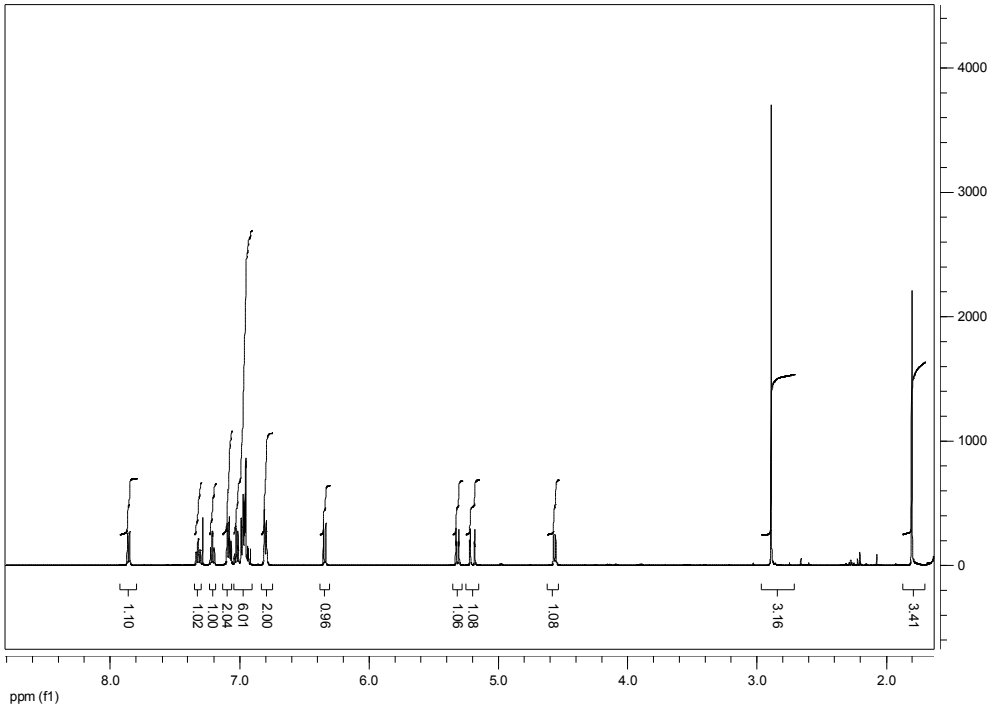
Isolated as clear oil Chiral HPLC, IA-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 8.218 min, t_B (major) = 10.932 min. IR (film) ν_{max}/cm^{-1}: 3055, 3028, 2974, 2884, 2802, 1707, 1609, 1520, 1493, 1470, 1451, 1373, 1349, 1264, 1208, 1160, 1128, 1088, 920, 756, 701. ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 7.44-7.39 (m, 2H), 7.23-7.17 (m, 1H), 7.09-7.02 (m, 3H), 7.01-6.96 (m, 2H), 6.92-6.87 (m, 2H), 6.69-6.62 (m, 3H), 6.04(ddd, *J*= 9.5, 10, 17, 1H), 5.16 (dm, *J* = 17, 1H), 5.06 (dd, *J* = 1.5, 10, 1H), 4.43(d, *J*= 9.5, 1H), 3.07 (s, 3H), 2.90 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer 177.6, 149.5, 143.5, 139.5, 136.2, 129.9, 129.4, 128.8, 128.7, 127.8, 127.2, 126.5, 126.4, 121.5, 118.2, 112.3, 107.7, 59.9, 56.9, 40.5, 26.0

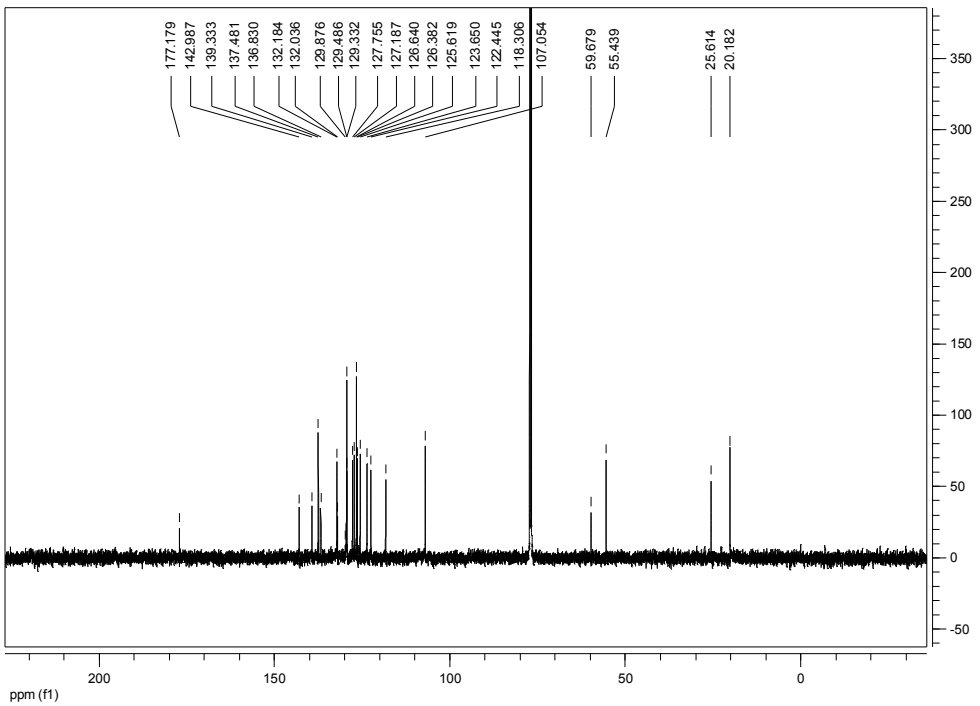




1-methyl-3-(1-phenylallyl)-3-o-tolylindolin-2-one (3j)

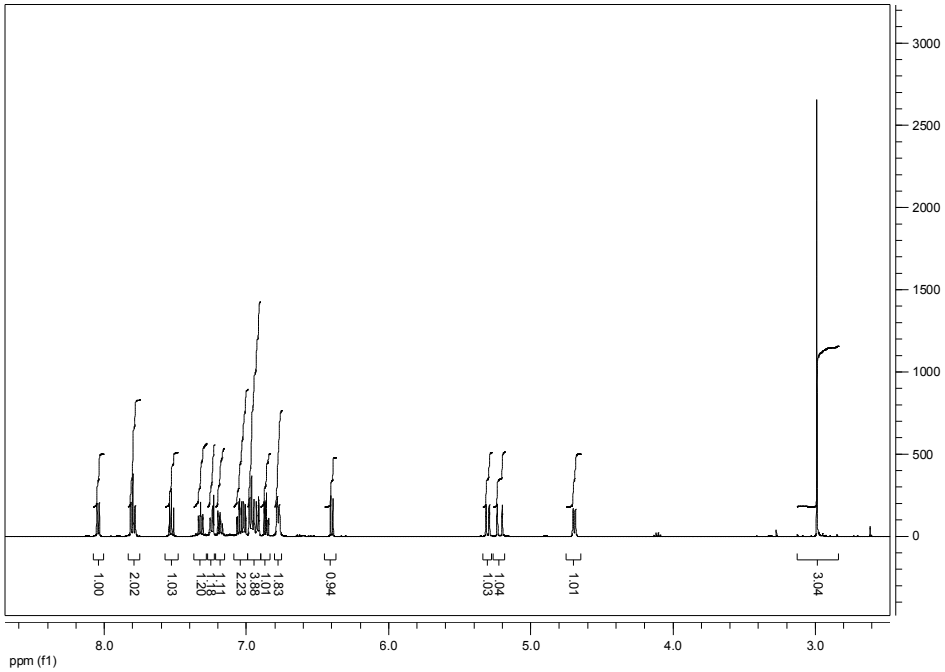
Isolated as clear oil Chiral HPLC, AD-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 5.622 min, t_B (major) = 6.433 min. IR (film) ν_{max}/cm^{-1}: 3059, 3028, 2972, 2931, 2880, 1710, 1611, 1493, 1470, 1417, 1373, 1346, 1305, 1249, 1125, 1085, 1020, 999, 916, 750, 701. ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.83(d, *J*=7.5, 1H), 7.29 (dt, *J*=7.5, 1, 1H), 7.18 (dt, *J*=7.5, 1, 1H), 7.08-7.04 (m, 2H), 7.02-6.88 (m, 6H), 6.79-6.75 (m, 2H), 6.31 (d, *J* = 7.5, 1H), 5.29 (dm, *J* = 10.5, 1H), 5.18 (dm, *J* = 17.5, 1H), 4.53(d, *J*= 8, 1H), 2.86 (s, 3H), 1.78 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: 177.2, 143.0, 139.3, 137.5, 136.8, 132.2, 132.0, 129.9, 129.5, 129.3, 127.8, 127.2, 126.7, 126.4, 125.6, 123.7, 122.5, 118.3, 107.0, 59.7, 55.4, 25.6, 20.2. HRMS—EI (m/z): calcd for $C_{25}H_{23}NO$: 353.1780; found: 353.1791

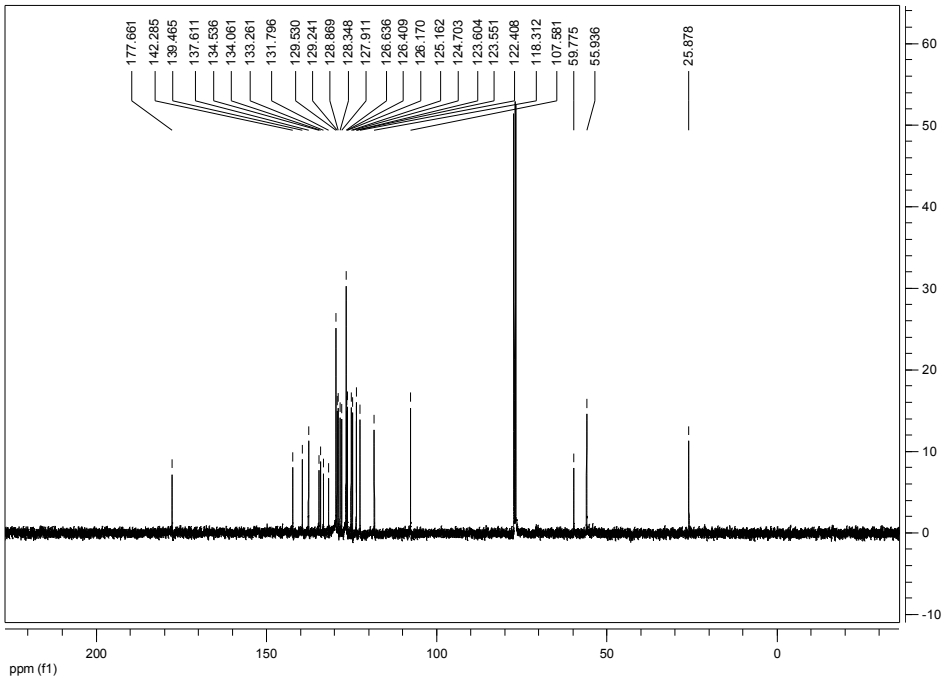




1-methyl-3-(naphthalen-1-yl)-3-(1-phenylallyl)indolin-2-one (3k)

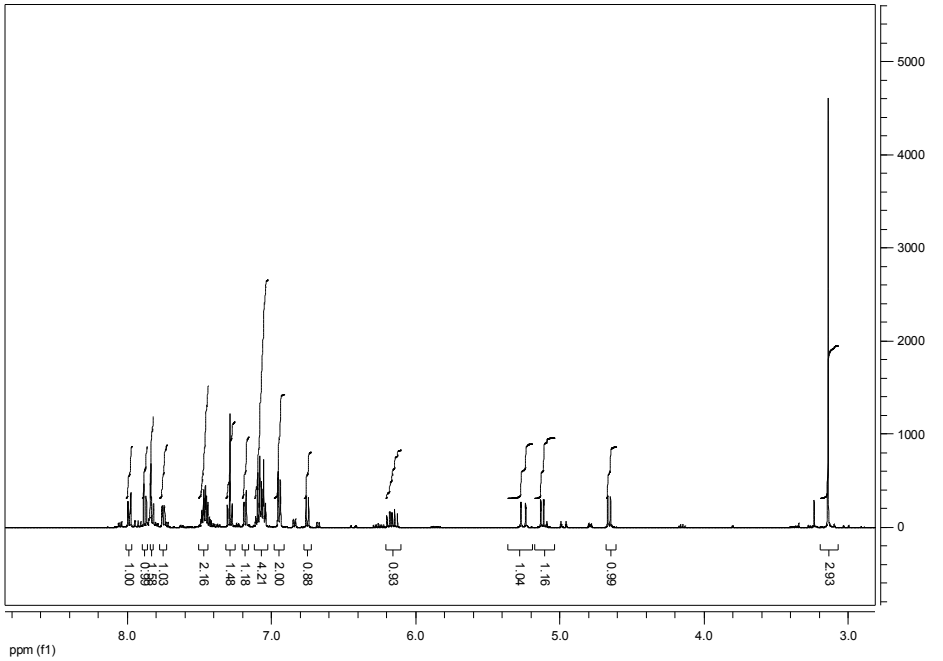
Isolated as clear oil Chiral HPLC AD-column, flow rate 1.0 ml/min, 90:10 heptane/I-PrOH, t_A (major) = 8.174 min, t_B (minor) = 11.321 min IR (film) ν_{max}/cm^{-1}: 3051, 3029, 2930, 1709, 1611, 1490, 1469, 1417, 1402, 1371, 1347, 1303, 1248, 1220, 1125, 1081, 1020, 999, 919, 851, 777, 744, 702. . ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 8.04 (d, *J* = 7.5, 1H), 7.80 (d, *J* =7.5, 1H), 7.51 (t, *J* =7.5, 1H), 7.32 (t, *J* = 7.5, 1H), 7.26-7.24 (m, 1H), 7.21-7.16(m, 1H), 7.08-7.00(m, 2H), 6.98-6.91 (m, 4H), 6.80(d, *J* = 7.0, 1H), 6.40(d, *J* = 8.0), 5.30 (dm, *J* = 10, 1H), 5.22 (d, *J* = 17.5, 1H), 4.69 (d, *J* = 8.0, 1H), 3.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: δ 177.7, 142.3, 139.5, 137.6, 134.5, 134.1, 133.3, 131.8, 129.5, 129.2, 128.9, 128.3, 127.9, 126.6, 126.4, 126.2, 125.2, 124.7, 123.6, 123.6, 122.4, 118.3, 107.6, 59.8, 55.9, 25.9, HRMS—EI (m/z): calcd for $C_{28}H_{23}NO$: 389.1780; found: 389.1785

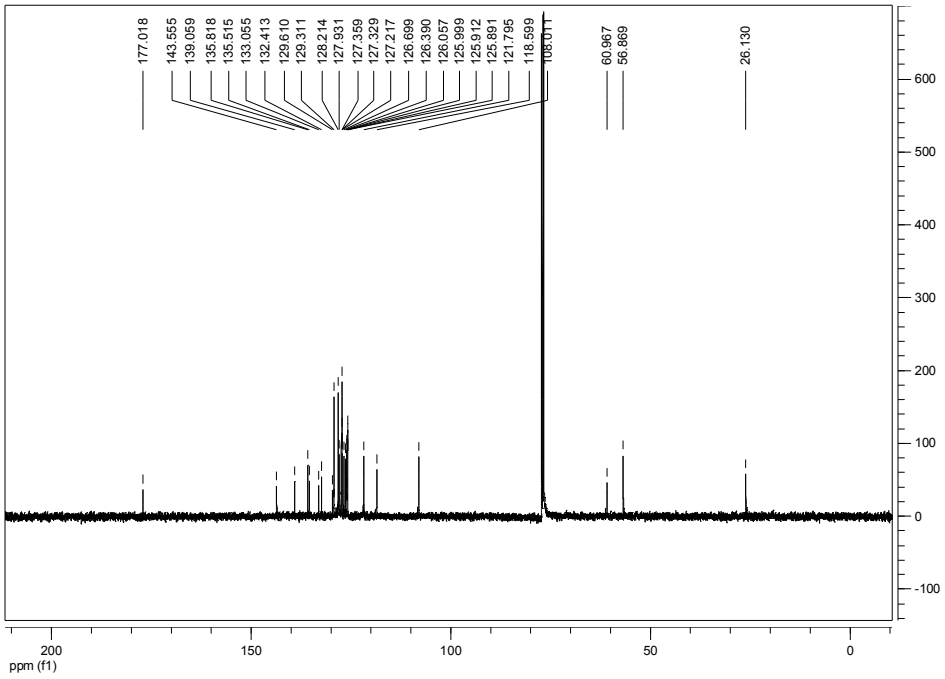




1-methyl-3-(naphthalen-2-yl)-3-(1-phenylallyl)indolin-2-one (3l)

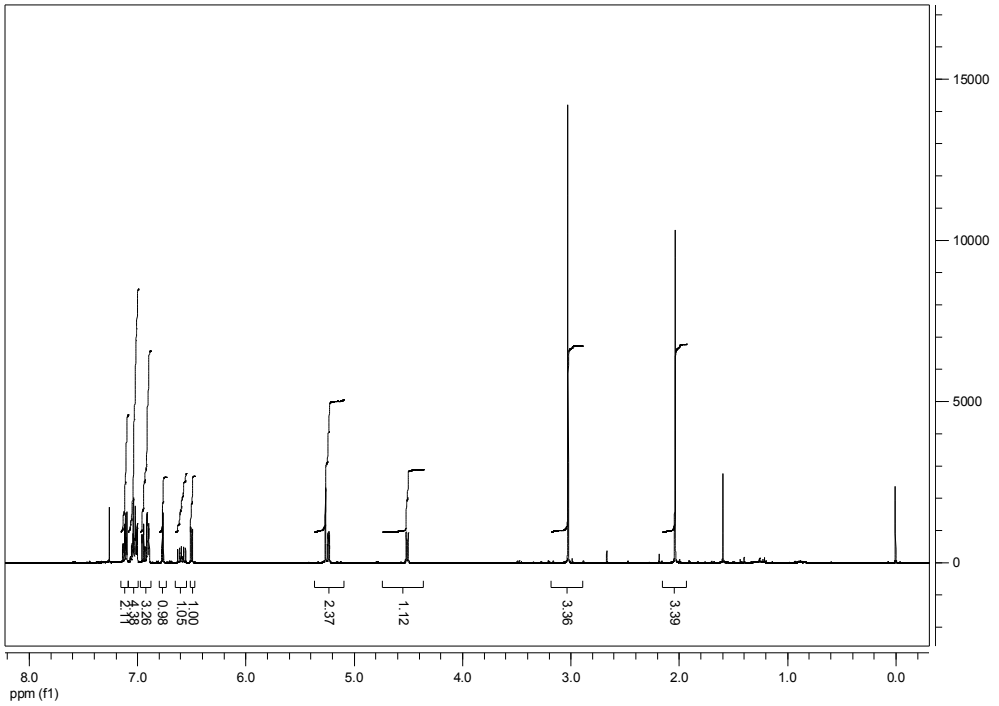
Isolated as clear oil Chiral HPLC AD-column, flow rate 1.0 ml/min, 90:10 heptane/I-PrOH, t_A (minor) = 8.545 min, t_B (minor) = 13.950 min IR (film) ν_{max}/cm^{-1}: 3051, 3029, 2930, 1709, 1611, 1490, 1469, 1417, 1402, 1371, 1347, 1303, 1248, 1220, 1125, 1081, 1020, 999, 919, 851, 777, 744, 702. . ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.96(dd, *J*=8.8,2, 1H), 7.86-7.78 (m, 3H), 7.74-7.71 (m, 1H), 7.46-7.40 (m, 2H), 7.26 (dt, *J* = 7.8, 1, 1H), 7.13 (d, *J* = 7.5, 1H), 7.09-7.0 (m, 4H), 6.93-6.90 (m, 2H), 6.72 (d, *J* = 7.5, 1H), 6.13 (ddd, *J*= 9.5, 10, 17, 1H), 5.23 (dm, *J* = 17.5, 1H), 5.09 (dm, *J* = 10, 1H), 4.63(d, *J*= 9.5, 1H), 3.11 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer 177.0 143.6,139.1, 135.8, 135.5, 133.1, 132.4, 129.6, 129.3, 128.2, 127.9, 127.4, 127.3, 127.2, 126.7, 126.4, 126.1, 126.0, 125.9, 125.8, 121.8, 118.6, 108.0, 61.0, 56.9, 26.1 HRMS—EI (m/z): calcd for $C_{28}H_{23}NO$: 389.1780; found: 389.1783

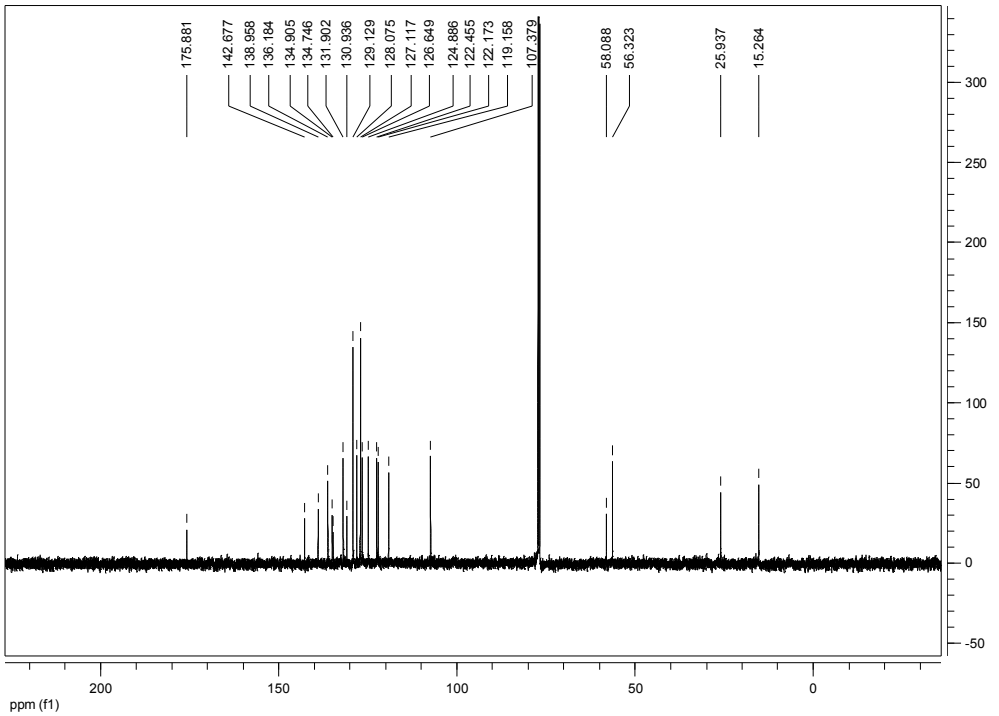




1-methyl-3-(3-methylthiophen-2-yl)-3-(1-phenylallyl)indolin-2-one (3p)

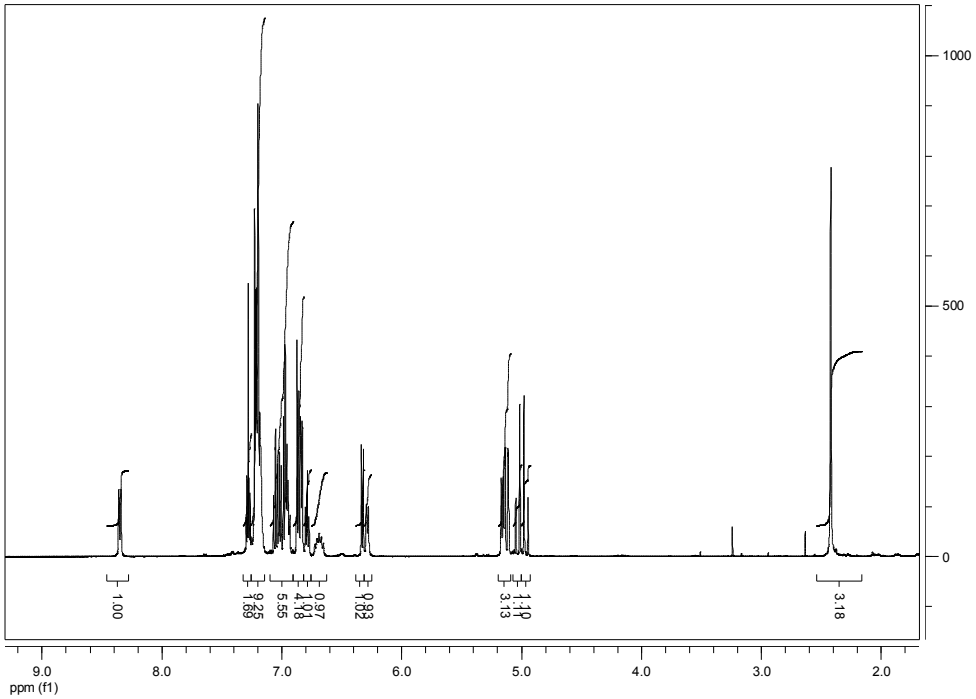
Isolated as white solid Chiral HPLC, AD-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 5.025 min, t_B (major) = 6.005 min. IR (film) ν_{max}/cm^{-1}: 3056, 2961, 2918, 2848, 1712, 1609, 1538, 1493, 1470, 1453, 1417, 1372, 1347, 1301, 1257, 1156, 1127, 1084, 1028, 919, 843, 799, 755, 701. ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer; 7.14-7.08 (m, 2H), 7.05-6.98 (m, 4H), 6.96-6.87 (m, *3*H), 6.76 (d, *J* =5, 1H), 6.63-6.53 (m, *1H*), 6.49 (d, *J*= 7.5, 1H), 5.26-5.20 (m, 2H), 4.51(d, *J*= 8.5, 1H), 3.03 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer:175.9, 142.7, 138.9, 136.2, 134.9, 134.8, 131.9, 131.0, 129.1, 128.1, 127.1, 126.7, 124.9, 122.5, 122.2, 119.1, 107.4, 58.1, 56.3, 25.9, 15.3, HRMS—EI (m/z): calcd for $C_{23}H_{21}NOS$: 359.1344; found: 359.1334.

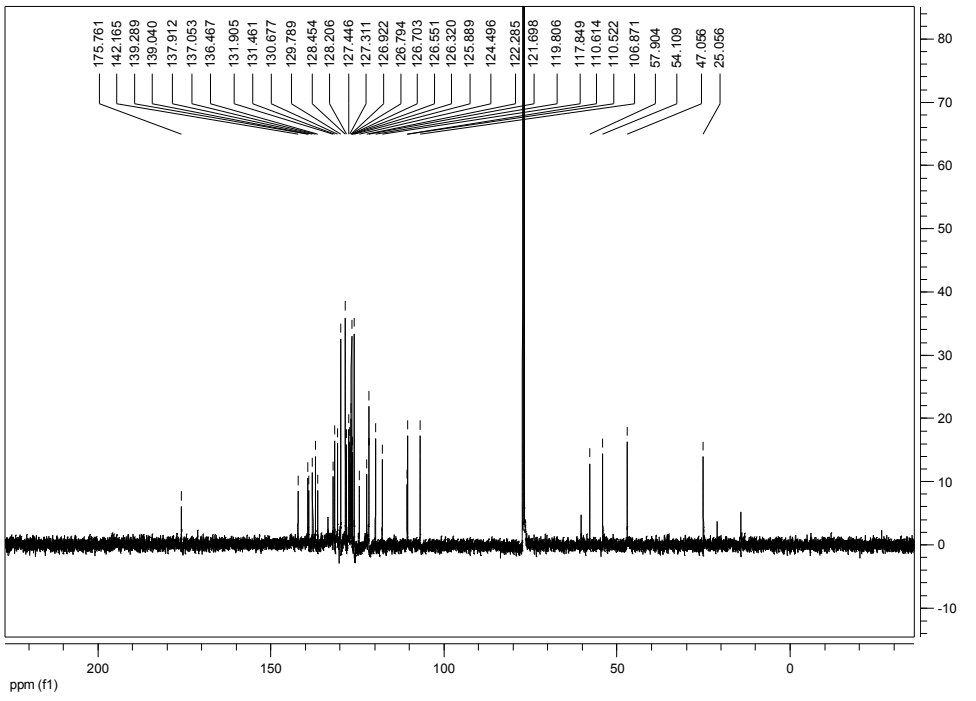




1'-benzyl-1-methyl-2'-phenyl-3-(1-phenylallyl)-3,3'-biindolin-2-one(3q)

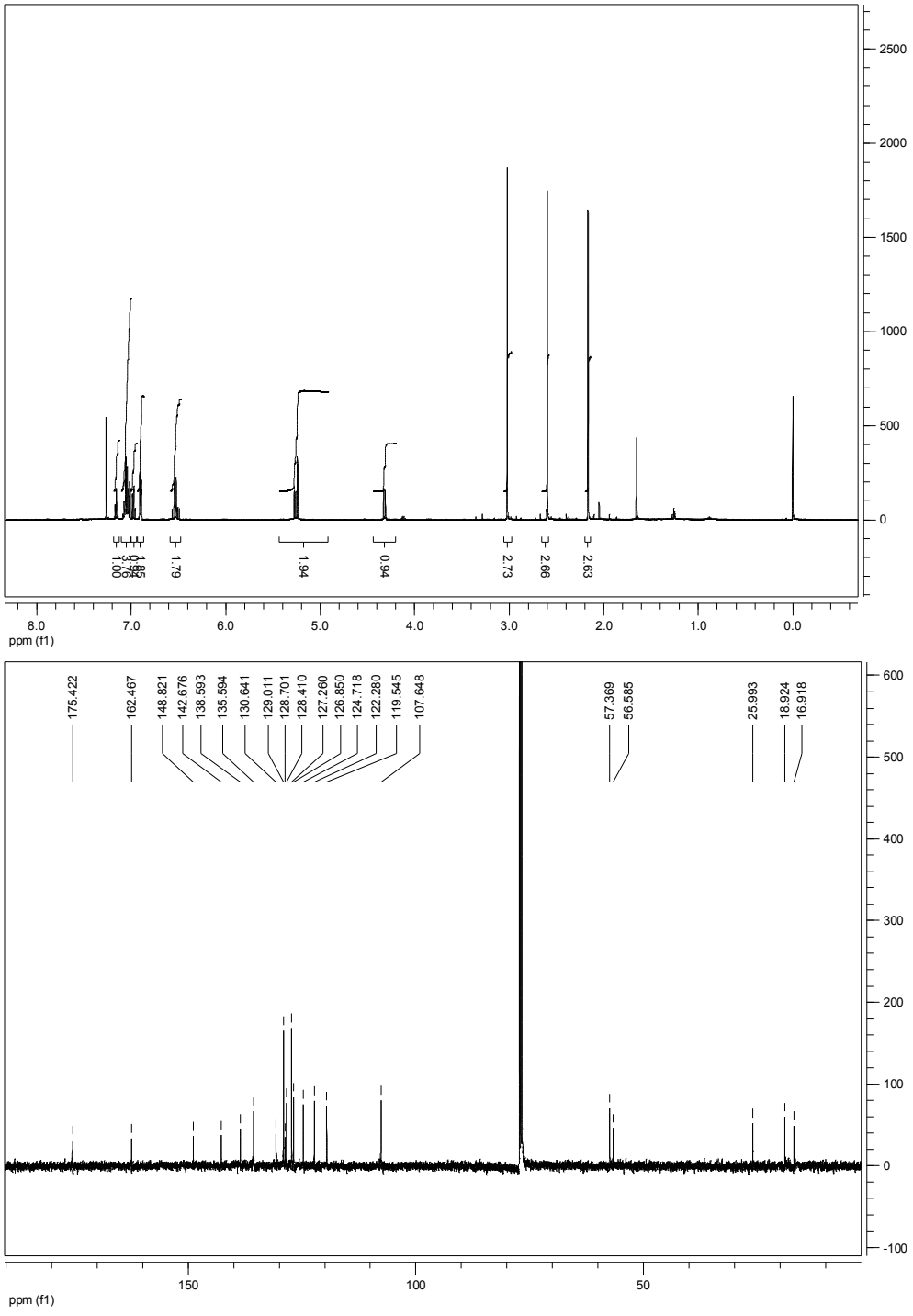
Isolated as yellow oil Chiral HPLC, ODH-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH, t_A (major) = 9.261 min, t_B (minor) 14.766 min. IR (film) ν_{max}/cm^{-1}: 3058, 3029, 2950, 2930, 1711, 1610, 1493, 1463, 1374, 1350, 1304, 1259, 1186, 1157, 1128, 1086, 1028, 1001, 909, 733, 701. ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer; 8.35 (d, *J* = 8, 1H), 7.30-7.25 (m, 1H), 7.24-7.14 (m, 9H), 7.17-6.92 (m, 5H), 6.88-6.82 (m, 4H), 6.78 (t, *J* =7.5, 1H), 6.74-6.65 (m, *1H*), 6.33 (d, *J*= 8, 1H), 6.28 (d, *J* = 7.5, 1H), 5.17-5.09 (m, 3H), 5.03(d, *J*= 17, 1H), 4.97(d, *J*= 17, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: 175.8, 142.2, 139.3, 139.0, 137.9, 137.1, 136.5, 131.9, 131.5, 130.7, 129.8, 128.5, 128.2, 127.4, 127.3, 126.9, 126.8, 126.7, 126.6, 126.3, 125.9, 124.5, 122.3, 121.7, 119.8, 117.8, 110.6, 110.5, 106.9, 57.9, 54.1, 47.1, 25.1,





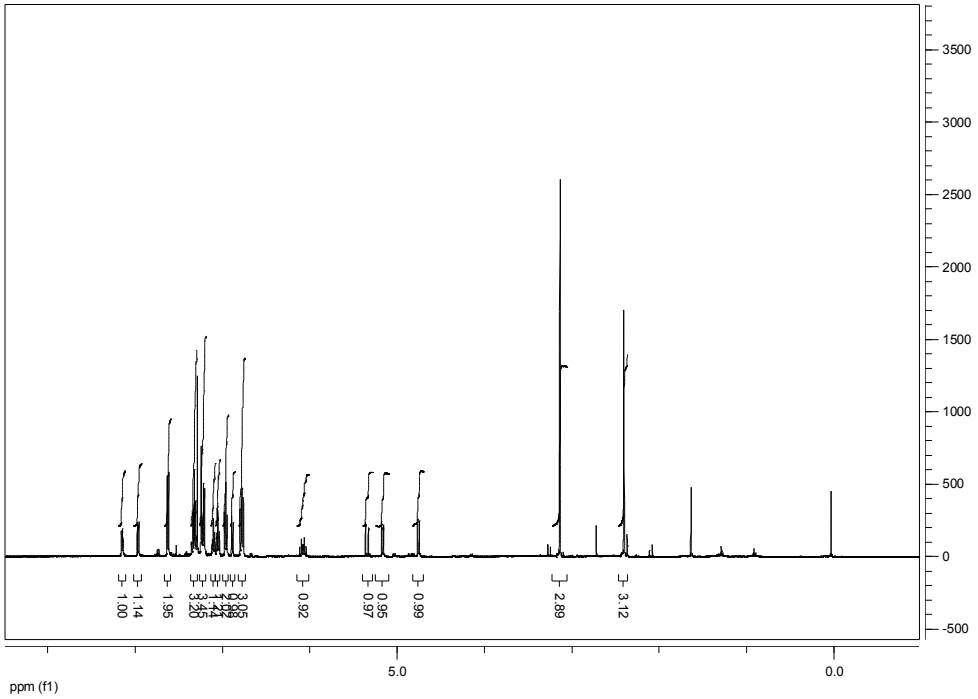
3-(2,4-dimethylthiazol-5-yl)-1-methyl-3-(1-phenylallyl)indolin-2-one (3r)

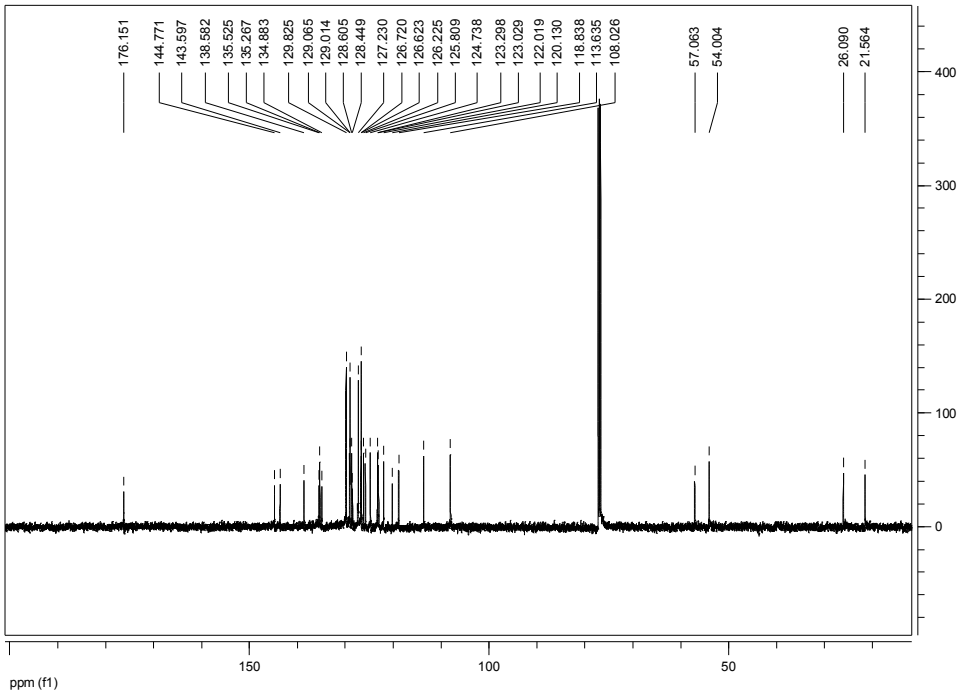
Isolated as clear oil Chiral HPLC AD-column, flow rate 1.0 ml/min, 90:10 heptane/I-PrOH, t_A (major) = 8.174 min, t_B (minor) = 11.321 min IR (film) ν_{max}/cm^{-1}: 3051, 3029, 2930, 1709, 1611, 1490, 1469, 1417, 1402, 1371, 1347, 1303, 1248, 1220, 1125, 1081, 1020, 999, 919, 851, 777, 744, 702. . ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.16 (dt, *J* = 8, 1.5, 1H), 7.19-7.00 (m, 4H), 6.97(dt, *J* = 7.5, 1, 1H), 6.92-6.88 (m, 2H), 6.57-6.48 (m, 2H), 5.27-5.23 (m, 2H), 4.32 (d, *J* = 9.0, 1H), 3.02 (s, 3H), 2.60 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer 175.4, 162.5, 148.8, 142.7, 138.6, 135.6, 130.6, 129.0, 128.7, 128.4, 127.3, 126.9, 124.7, 122.3, 119.6, 107.6, 57.4, 56.6, 26.0, 18.9, 16.9, HRMS—EI (m/z): calcd for $C_{23}H_{21}N_2OS$ (M-H): 373.1374; found: 373.1393.



1-methyl-3-(1-phenylallyl)-1'-tosyl-3,3'-biindolin-2-one (3t)

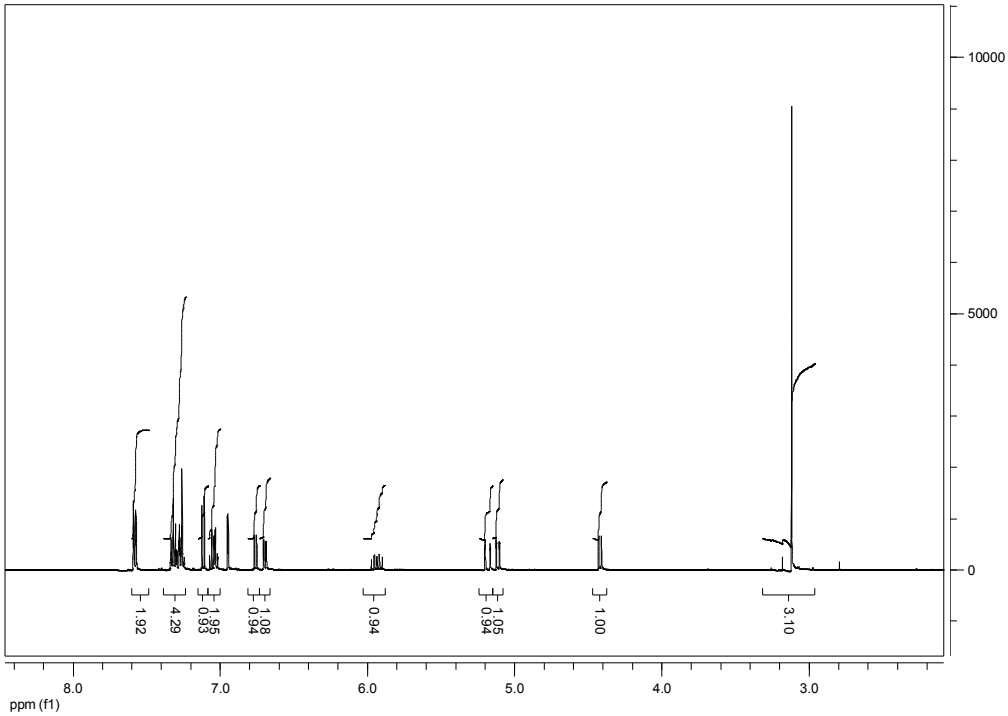
Isolated as yellow oil Chiral HPLC, AD-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH, t_A (major) = 11.954 min, t_B (minor)= 13.851 min. IR (film) ν_{max}/cm^{-1}: 3059, 3030, 2974, 2927, 2867, 1711, 1610, 1492, 1470, 1448, 1371, 1303, 1278, 1174, 1141, 1125, 1089, 987, 747, 704. ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer; 8.12 (d, *J* = 7.5, 1H), 7.93 (dd, *J* = 7.0, 1, 1H), 7.59 (d, *J* = 8.5, 1H), 7.33-7.28 (m, 3H), 7.26 (s, 1H), 7.23-7.17 (m, 3H), 7.07 (t, *J* = 7.5, 1H), 7.02 (t, *J* = 8, 1H), 6.93 (t, *J* = 7.5, 2H), 6.85 (d, *J* = 7.5, 1H), 6.77-6.72 (m, 3H), 6.09-6.00 (m, *1H*), 5.33 (d, *J*= 18, 1H), 5.13 (d, *J* = 10, 1H), 4.72(d, *J*= 10, 1H), 3.11 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: 176.2, 144.8, 143.6, 138.6, 135.5, 135.3, 134.9, 129.8, 129.1, 129.0, 128.6, 128.4, 127.2, 126.7, 126.6, 126.2, 125.8, 124.7, 123.3, 123.0, 122.0, 120.1, 118.8, 113.6, 108.0, 57.1, 54.0, 26.1, 21.6, HRMS—EI (m/z): calcd for $C_{33}H_{28}N_2O_3S$: 532.1821; found: 532.1821

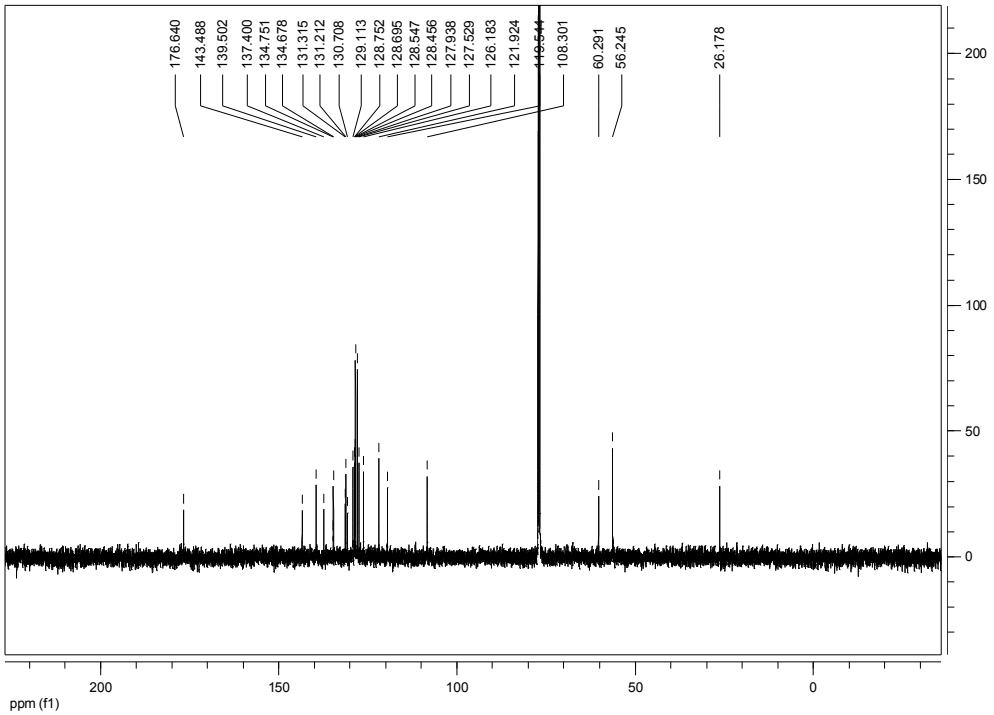




3-(1-(3,4-dichlorophenyl)allyl)-1-methyl-3-phenylindolin-2-one (5a)

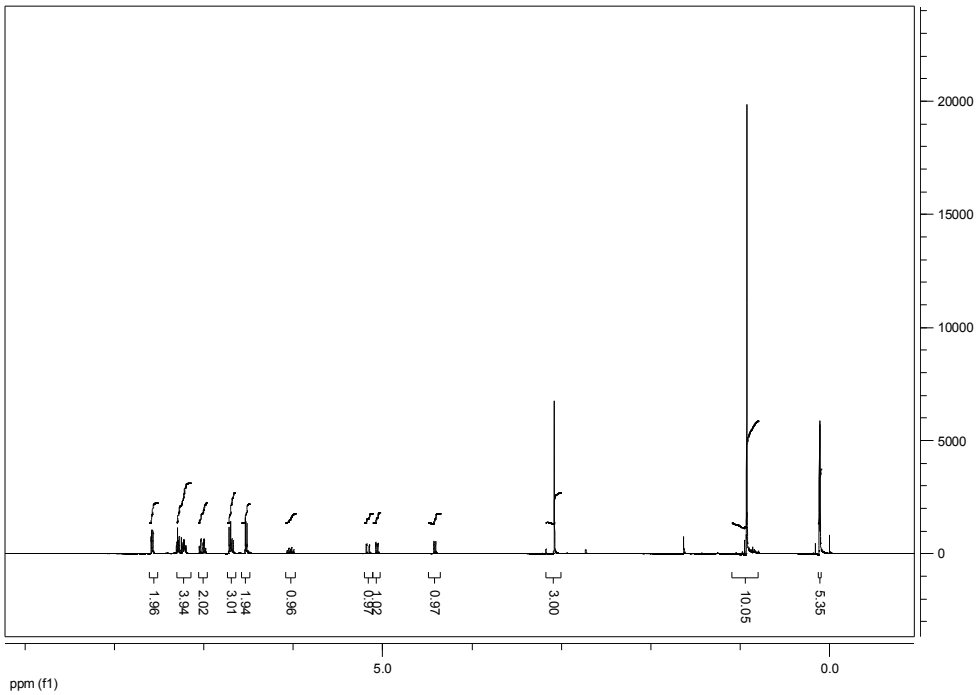
Isolated as clear oil Chiral HPLC, OD-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 6.307 min, t_B (major) = 7.840 min. IR (film) ν_{max}/cm^{-1}: 3059, 2926, 1706, 1611, 1492, 1471, 1373, 1349, 1257, 1133, 1088, 1029, 924, 821, 748. ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.60-7.57 (m, 2H), 7.35-7.26 (m, 4H), 7.12 (d, *J* =8, 1H), 7.08-7.01 (m, 2H), 6.95 (d, *J* =2, 1H), 6.76 (d, *J* =8, 1H), 6.70 (d, *J* =2, 1H), 5.94 (ddd, *J*= 9.5, 10, 17, 1H), 5.18 (dm, *J* = 17, 1H), 5.11 (dm, *J* = 10, 1H), 4.42(d, *J*= 9.5, 1H), 3.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: 176.6, 143.5, 139.5, 137.4, 134.7, 131.3, 131.2, 130.7, 129.1, 128.8, 128.7, 128.5, 128.4, 128.0, 127.5, 126.2, 121.9, 119.5, 108.3, 60.3, 56.2, 26.2 HRMS—EI (m/z): calcd for $C_{24}H_{19}Cl_2NO$: 409.0814; found: 409.0806

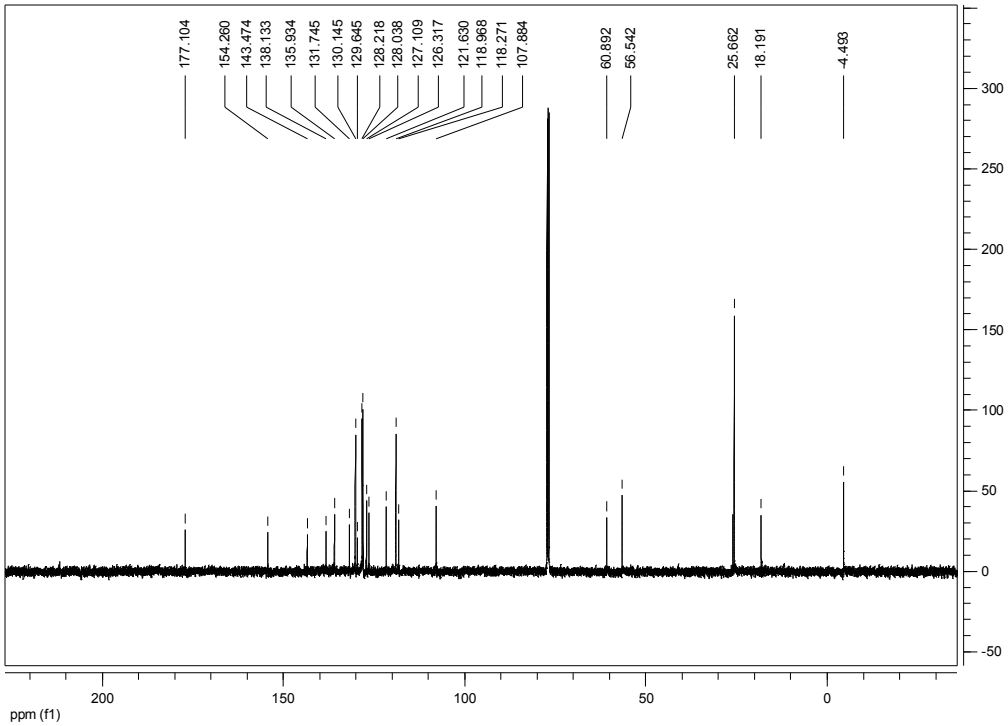




3-(1-(4-(tert-butyldimethylsilyloxy)phenyl)allyl)-1-methyl-3-phenylindolin-2-one (5b)

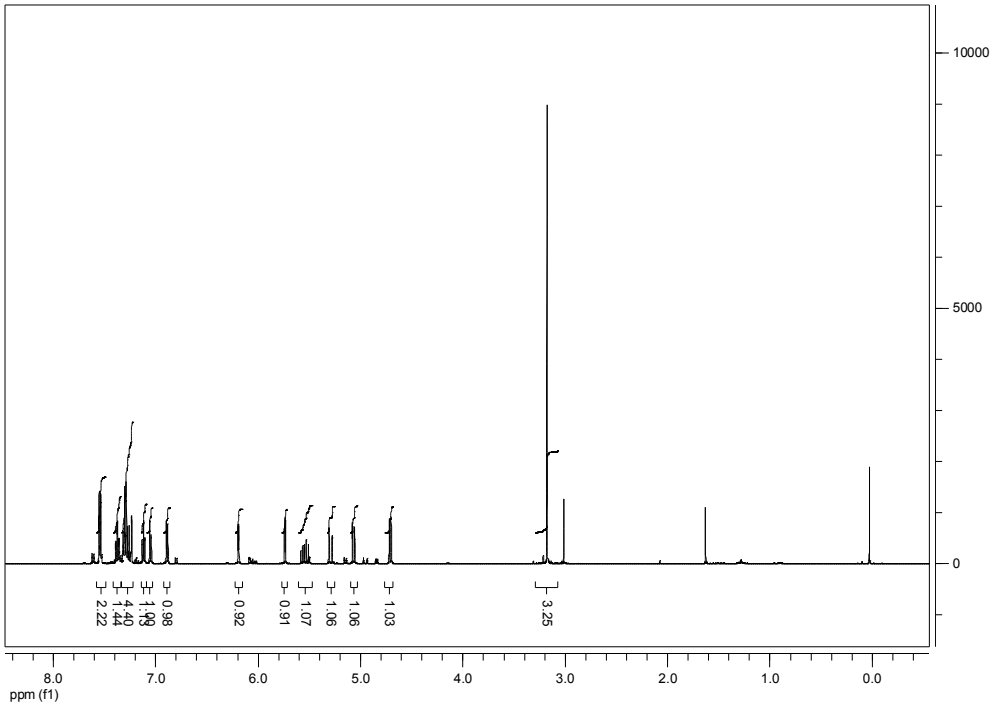
Isolated as white solid Chiral HPLC, OD-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 6.292 min, t_B (major) = 7.265 min. IR (film) ν_{max}/cm^{-1}: 3036, 2956, 2938, 2858, 1710, 1509, 1493, 1471, 1419, 1374, 1349, 1258, 1174, 1131, 1088, 1004, 915, 840, 781, 748, 697 ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 7.60-7.56 (m, 2H), 7.32-7.20 (m, 4H), 7.06-6.97 (m, 2H), 6.74-6.66 (m, 3H), 6.54-6.51 (m, 2H), 6.03 (ddd, *J*= 9.5, 10, 17, 1H), 5.17 (dm, *J* = 17, 1H), 5.06 (dd, *J* = 1.5 10, 1H), 4.41(d, *J*= 9.5, 1H), 3.08 (s, 3H), 0.93 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer: δ 177.1, 154.3, 143.5, 138.1, 135.9, 131.8, 130.1, 129.6, 128.2, 128.0, 127.1, 126.3, 121.6, 121.6, 118.9, 119.3, 107.9, 60.9, 56.5, 26.1, 25.7, 18.2, -4.5. HRMS—EI (m/z): calcd for $C_{30}H_{35}SiNO_2$: 469.2437; found: 469.2447

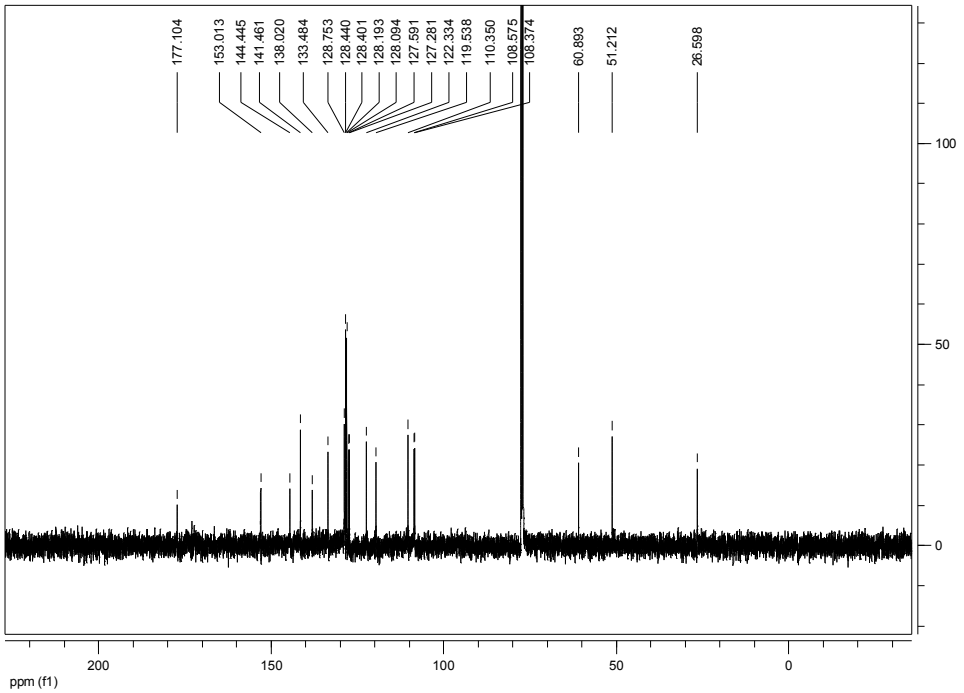




3-(1-(furan-2-yl)allyl)-1-methyl-3-phenylindolin-2-one(5c)

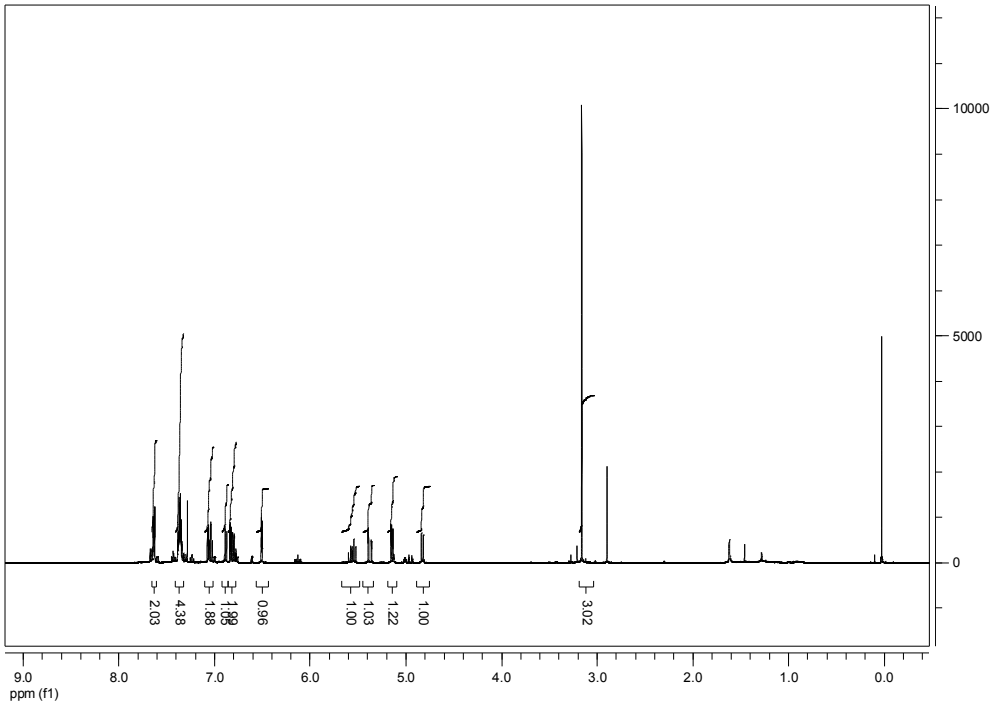
Isolated as clear oil Chiral HPLC, OD-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH, t_A (minor) = 6.292 min, t_B (major) = 7.265 min. IR (film) ν_{max}/cm^{-1}: 3056, 3024, 2933, 1714, 1611, 1494, 1471, 1446, 1418, 1371, 1350, 1253, 1221, 1148, 1131, 1092, 1079, 1025, 1014, 995, 932, 741, 696. ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 7.53-7.50 (m, 2H), 7.35 (dt, *J* = 1, 7.5, 1H), 7.29-7.20 (m, 4H), 7.09 (dt, *J* = 1, 7.5, 1H), 7.02 (d, *J* = 7.5, 1H), 6.86 (d, *J* = 7.5, 1H), 6.16 (dd, *J* = 1.7, 3.2, 1H), 5.71 (d, *J* = 3.5, 1H), 5.52 (ddd, *J*= 9.5, 10, 17, 1H), 5.26 (dm, *J* = 17, 1H), 5.04 (dd, *J* = 1.5 10, 1H), 4.69(d, *J*= 9.5, 1H), 3.15 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer δ 176.8, 152.7, 144.2, 141.2, 137.7, 133.2, 128.5, 128.1, 127.8, 127.3, 127.0, 122.0, 119.2, 110.0, 108.3, 108.1, 60.6, 50.9, 26.3. HRMS—EI (m/z): calcd for $C_{22}H_{19}NO$: 329.1416; found: 329.1429

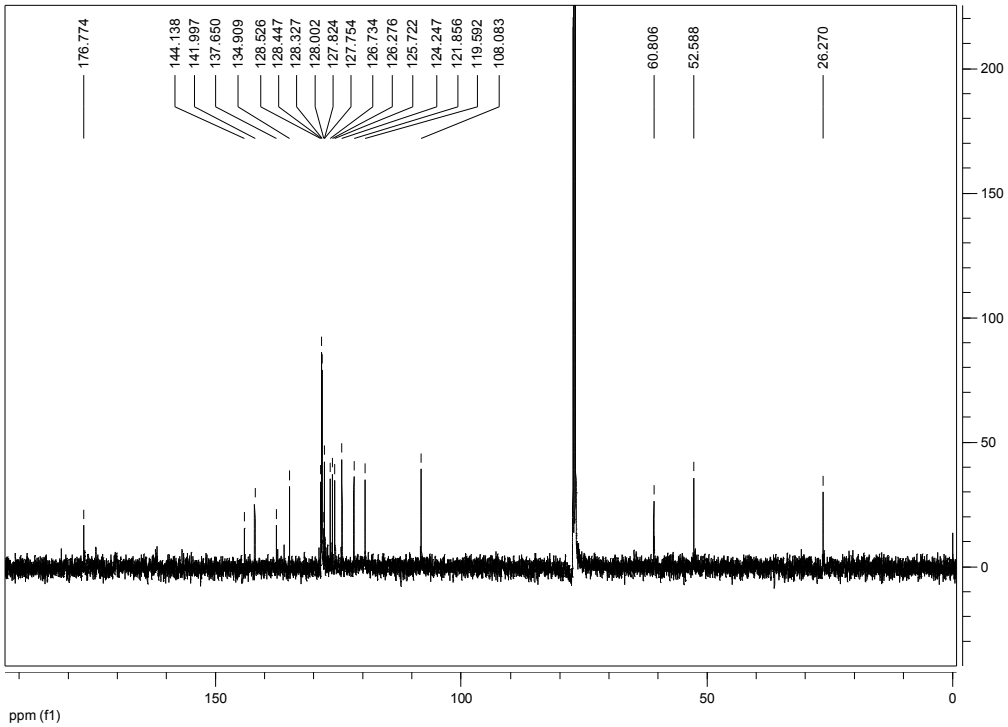




1-methyl-3-phenyl-3-(1-(thiophen-2-yl)allyl)indolin-2-one (5d)

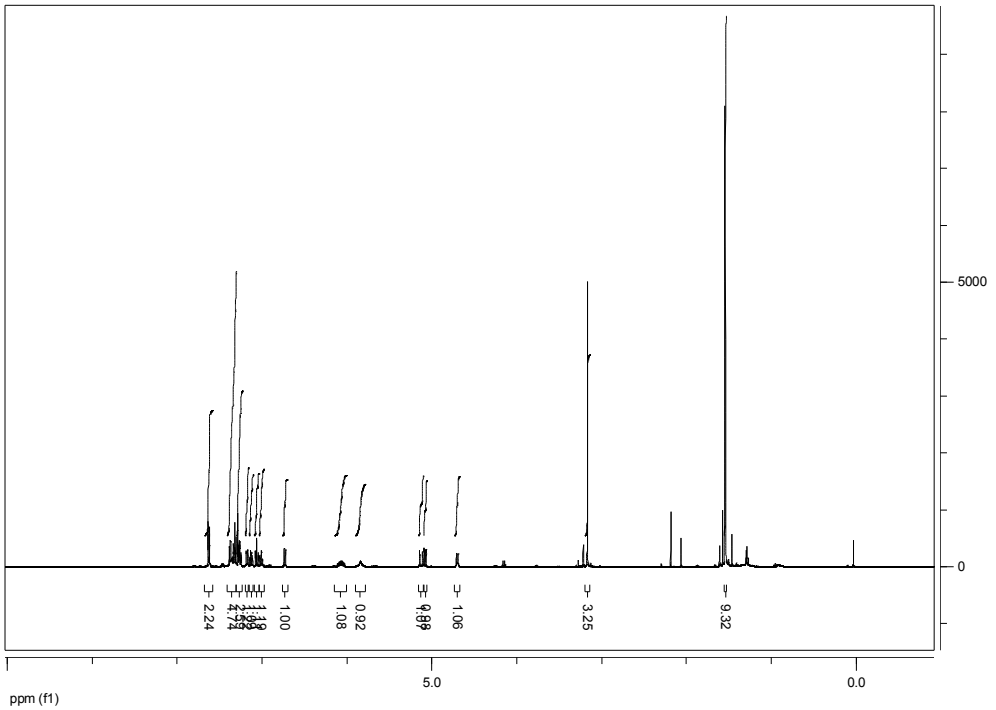
Isolated as clear oil Chiral HPLC, AD-column, flow rate 0.8 mL/min, 90:10 heptane / *i*-PrOH t_A (minor) = 5.724 min, t_B (major) = 6.889 min IR (film) ν_{max}/cm^{-1}: 3056, 2918, 2849, 1713, 1610, 1493, 1470, 1446, 1418, 1371, 1348, 1251, 1233, 1158, 1130, 1091, 1077, 1024, 996, 926, 751, 725, 695. ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: 7.65-7.62 (m, 2H), 7.39-7.33 (m, 4H), 7.08-7.03 (m, 2H), 6.87 (d, *J* = 7.5, 1H), 6.84-6.76 (m, 2H), 6.51 (dt, *J* =3.5,1 1H), 5.562 (ddd, *J*= 7.5, 10, 17, 1H), 5.37 (dm, *J* = 17, 1H), 5.14 (dd, *J* = 1.5, 10, 1H), 4.82(d, *J*= 7.5, 1H), 3.16 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer176.8, 144.2, 142.0, 137.7, 134.9, 128.5, 128.4, 128.3, 127.8, 127.7, 126.7, 126.3, 125.7, 124.3, 121.9, 119.6, 108.1, 60.8, 52.6, 26.3 HRMS—EI (m/z): calcd for $C_{22}H_{19}NOS$: 345.1107; found: 345.1191

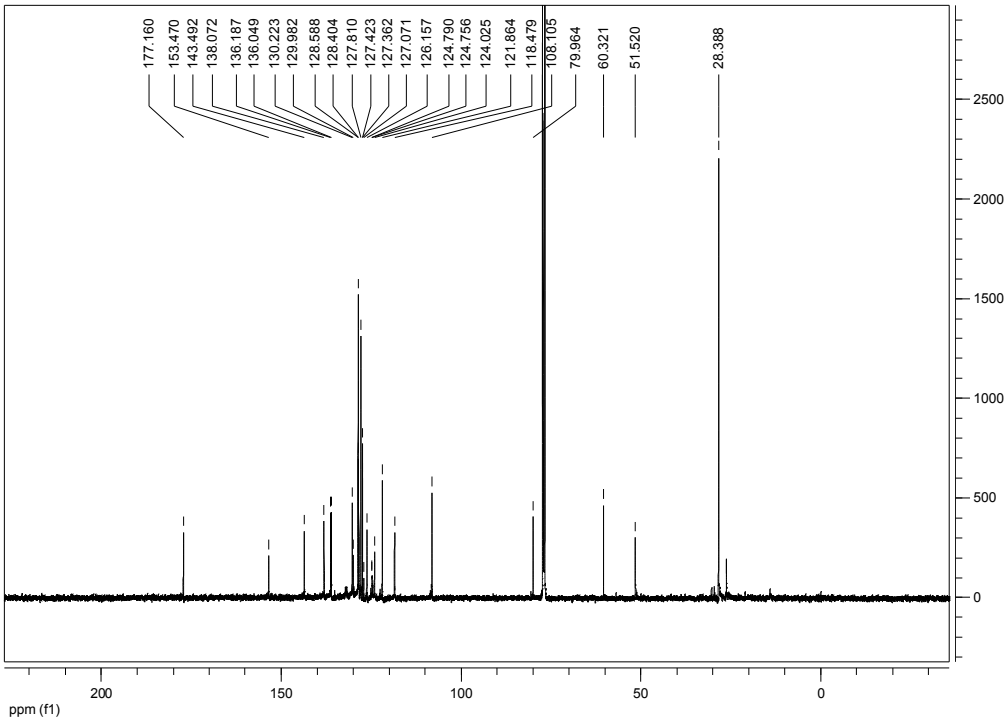




tert-butyl 2-(1-(1-methyl-2-oxo-3-phenylindolin-3-yl)allyl)phenylcarbamate (5e)

Isolated as clear oil Chiral HPLC, IA-column, flow rate 1.0 mL/min, 90:10 heptane / *i*-PrOH t_A (minor) = 7.567 min, t_B (major) = 8.467 min IR (film) ν_{max}/cm^{-1}: 3397, 3330, 3061, 2978, 2932, 1713, 1612, 1585, 1518, 1495, 1471, 1448, 1368, 1352, 1296, 1232, 1158, 1090, 1048, 1025, 912, 734, 698. ^1H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 7.64-7.61 (m, 2H), 7.39-7.24 (m, 6H), 7.17 (dd, *J* = 7.5 1, 1H), 7.13 (dd, *J* = 7.5 1, 1H), 7.06 (dd, *J* = 7.5 1, 1H), 7.01 (dd, *J* = 7.5 1, 1H), 6.73 (d, *J* = 8, 1H), 6.11-6.03 (m, 1H), 5.84 (b, s, 1H), 5.13 (d, *J* = 17, 1H), 5.08 (d, *J* = 10, 1H), 4.70(d, *J*= 8.5, 1H), 3.17 (s, 3H), 1.54 (s, 9H) ^{13}C NMR (125 MHz, $CDCl_3$) major 177.2 153.5, 143.5, 138.1, 136.2, 136.0, 130.2, 130.0, 128.6, 128.4, 127.8, 127.4, 127.4, 127.1, 126.2, 124.8, 124.8, 124.0, 121.9, 118.5, 108.1, 79.9, 60.3, 51.5, 28.4,





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REFERENCE NUMBER: 06275

CRYSTAL STRUCTURE REPORT

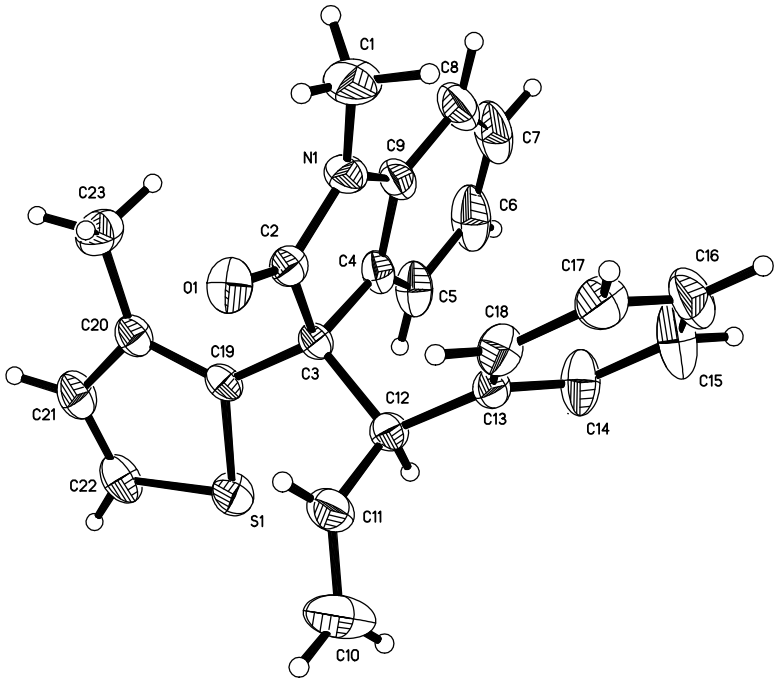
$C_{23}\ H_{21}\ N\ O\ S$

Report prepared for:

Yong Zhang

Prof. Barry Trost

November 22, 2006



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Data collection

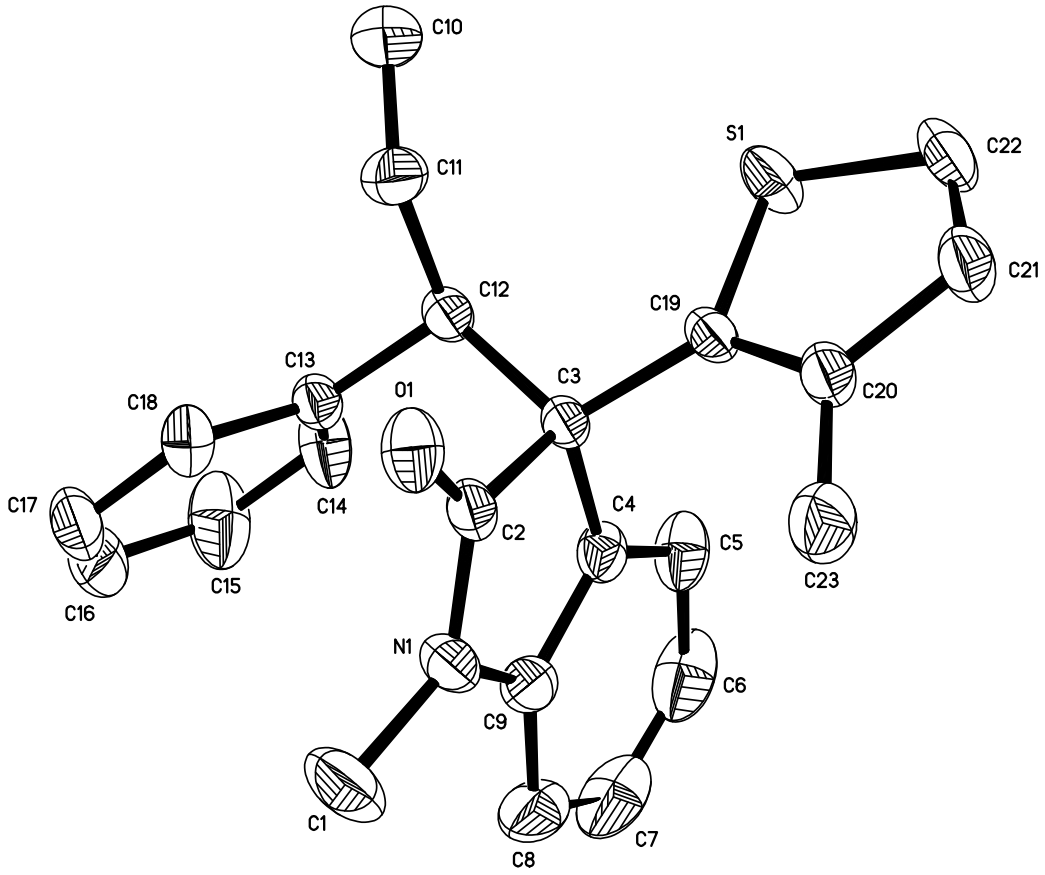
A crystal (approximate dimensions 0.50 x 0.40 x 0.30 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 124 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 45 seconds and a detector distance of 3.86 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.70 Å. Two major sections of frames were collected with 0.30º steps in ω at two different ϕ settings and a detector position of -33º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from the xyz centroids of 3893 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

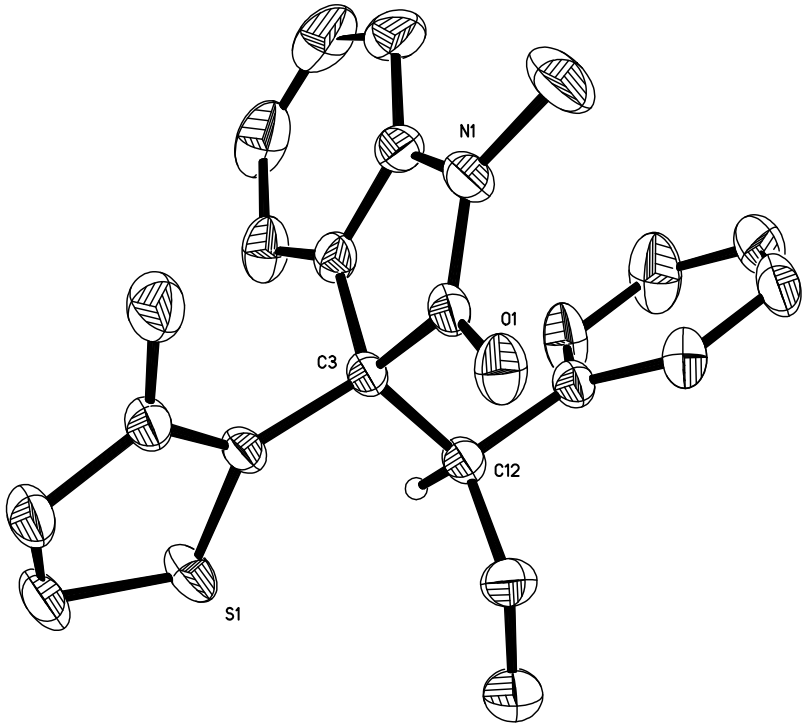
Structure solution and refinement

The structure was solved using SHELXS-97 [4] and refined using SHELXL-97.[4] The space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0367$ and $wR2 = 0.1003$ (F^2, all data).

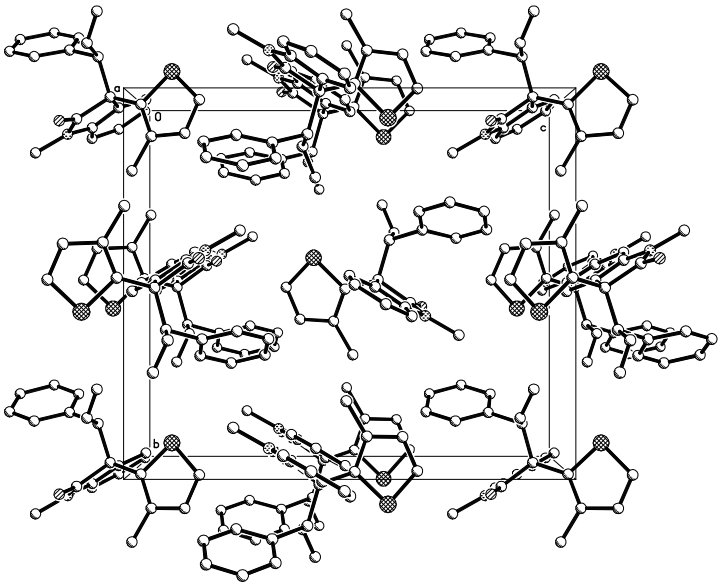
Structure description

The structure is the one suggested. The crystal diffracted well enough at higher angles that the detector was brought in to 3.85 cm (normally it is set at 4.9 cm). This allowed the collection of the high angle data (out to 0.70 Å; 0.77 Å - 0.84 Å is the usual range) necessary to achieve absolute stereochemistry (aided by the anomalous dispersion of the sulfur atom). Based on the flack parameter close to zero (0.04(5)) the stereochemistry around C3 is assigned "S" and the stereochemistry around C12 is assigned "R".





Picture of the stereocenters (other hydrogen atoms omitted for clarity)



Matrix Packing Plot (looking down the a-axis, hydrogen atoms omitted for clarity)

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed

using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1)include Benjamin E. Kucera as a coauthor or 2)acknowledge Benjamin E. Kucera, Victor G. Young, Jr., and the X-Ray Crystallographic Laboratory.

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1 SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI (2001).

2 An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38 (1995).

3 SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI (2003).

4 SHELXTL V6.14, Bruker Analytical X-Ray Systems, Madison, WI (2000).

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 06275.

Identification code	06275	
Empirical formula	C_{23} H_{21} N O S	
Formula weight	359.47	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.4847(4) Å	α = 90°
	b = 13.9643(7) Å	β = 90°
	c = 16.1353(8) Å	γ = 90°
Volume	1911.76(16) Å^3	
Z	4	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.180 mm^{-1}	
F(000)	760	
Crystal color, morphology	colorless, block	
Crystal size	0.50 x 0.40 x 0.30 mm^3	
Theta range for data collection	1.93 to 30.53°	
Index ranges	$-11 \le h \le 12$, $-19 \le k \le 19$, $-13 \le l \le 23$	
Reflections collected	15748	
Independent reflections	5789 [R(int) = 0.0252]	
Observed reflections	5306	
Completeness to theta = 30.53°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9479 and 0.9153	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5789 / 0 / 237	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0953	
R indices (all data)	R1 = 0.0423, wR2 = 0.1003	
Absolute structure parameter	0.04(5)	
Largest diff. peak and hole	0.290 and -0.191 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 06275. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S1	4057(1)	4289(1)	4141(1)	36(1)
O1	3581(1)	5638(1)	6726(1)	34(1)
N1	6256(1)	5865(1)	6753(1)	31(1)
C1	6337(3)	6380(1)	7530(1)	50(1)
C2	4882(2)	5519(1)	6428(1)	25(1)
C3	5307(1)	4896(1)	5667(1)	21(1)
C4	7058(1)	5086(1)	5585(1)	27(1)
C5	8124(2)	4794(1)	4992(1)	38(1)
C6	9721(2)	5024(1)	5110(1)	54(1)
C7	10196(2)	5525(1)	5796(1)	57(1)
C8	9136(2)	5844(1)	6388(1)	47(1)
C9	7554(2)	5622(1)	6263(1)	31(1)
C10	2646(3)	2798(1)	5786(1)	59(1)
C11	3318(2)	3584(1)	6065(1)	38(1)
C12	5045(1)	3816(1)	5935(1)	26(1)
C13	6032(2)	3556(1)	6690(1)	25(1)
C14	7467(2)	3099(1)	6586(1)	43(1)
C15	8415(2)	2880(2)	7262(1)	58(1)
C16	7931(2)	3108(1)	8051(1)	48(1)
C17	6493(2)	3556(1)	8166(1)	40(1)
C18	5547(2)	3770(1)	7490(1)	32(1)
C19	4407(1)	5151(1)	4889(1)	24(1)
C20	3934(2)	6039(1)	4616(1)	28(1)
C21	3255(2)	5991(1)	3804(1)	36(1)
C22	3262(2)	5100(1)	3471(1)	39(1)
C23	4113(2)	6962(1)	5076(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for 06275.

S(1)-C(22)	1.7056(15)
S(1)-C(19)	1.7307(12)
O(1)-C(2)	1.2155(16)
N(1)-C(2)	1.3661(16)
N(1)-C(9)	1.3977(18)
N(1)-C(1)	1.4476(18)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.5481(16)
C(3)-C(19)	1.5121(15)
C(3)-C(4)	1.5155(16)
C(3)-C(12)	1.5839(15)
C(4)-C(5)	1.3776(18)
C(4)-C(9)	1.3908(19)
C(5)-C(6)	1.406(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.371(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.386(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.3920(18)
C(8)-H(8)	0.9500
C(10)-C(11)	1.316(2)
C(10)-H(10A)	0.9500
C(10)-H(10B)	0.9500
C(11)-C(12)	1.5158(19)
C(11)-H(11)	0.9500
C(12)-C(13)	1.5216(16)
C(12)-H(12)	1.0000
C(13)-C(14)	1.3853(19)
C(13)-C(18)	1.3886(17)
C(14)-C(15)	1.389(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.376(3)

C(15)-H(15)	0.9500
C(16)-C(17)	1.383(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.386(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.3752(17)
C(20)-C(21)	1.4319(18)
C(20)-C(23)	1.4949(19)
C(21)-C(22)	1.355(2)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

C(22)-S(1)-C(19)	92.71(7)
C(2)-N(1)-C(9)	111.70(10)
C(2)-N(1)-C(1)	123.28(13)
C(9)-N(1)-C(1)	124.96(13)
N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-N(1)	125.11(12)
O(1)-C(2)-C(3)	127.00(11)
N(1)-C(2)-C(3)	107.74(10)
C(19)-C(3)-C(4)	112.40(10)
C(19)-C(3)-C(2)	114.12(9)
C(4)-C(3)-C(2)	101.46(10)
C(19)-C(3)-C(12)	112.40(9)
C(4)-C(3)-C(12)	109.17(9)
C(2)-C(3)-C(12)	106.58(9)
C(5)-C(4)-C(9)	120.46(12)
C(5)-C(4)-C(3)	130.68(13)

C(9)-C(4)-C(3)	108.82(11)
C(4)-C(5)-C(6)	118.14(16)
C(4)-C(5)-H(5)	120.9
C(6)-C(5)-H(5)	120.9
C(7)-C(6)-C(5)	120.58(16)
C(7)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(6)-C(7)-C(8)	122.04(14)
C(6)-C(7)-H(7)	119.0
C(8)-C(7)-H(7)	119.0
C(7)-C(8)-C(9)	116.99(16)
C(7)-C(8)-H(8)	121.5
C(9)-C(8)-H(8)	121.5
C(4)-C(9)-C(8)	121.73(14)
C(4)-C(9)-N(1)	109.69(11)
C(8)-C(9)-N(1)	128.58(14)
C(11)-C(10)-H(10A)	120.0
C(11)-C(10)-H(10B)	120.0
H(10A)-C(10)-H(10B)	120.0
C(10)-C(11)-C(12)	123.39(18)
C(10)-C(11)-H(11)	118.3
C(12)-C(11)-H(11)	118.3
C(11)-C(12)-C(13)	111.75(11)
C(11)-C(12)-C(3)	112.17(10)
C(13)-C(12)-C(3)	111.64(9)
C(11)-C(12)-H(12)	107.0
C(13)-C(12)-H(12)	107.0
C(3)-C(12)-H(12)	107.0
C(14)-C(13)-C(18)	118.16(12)
C(14)-C(13)-C(12)	119.83(11)
C(18)-C(13)-C(12)	122.01(12)
C(13)-C(14)-C(15)	121.05(14)
C(13)-C(14)-H(14)	119.5
C(15)-C(14)-H(14)	119.5
C(16)-C(15)-C(14)	120.18(16)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9

C(15)-C(16)-C(17)	119.45(15)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-H(16)	120.3
C(16)-C(17)-C(18)	120.22(14)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(13)	120.93(13)
C(17)-C(18)-H(18)	119.5
C(13)-C(18)-H(18)	119.5
C(20)-C(19)-C(3)	128.79(11)
C(20)-C(19)-S(1)	110.72(9)
C(3)-C(19)-S(1)	120.06(9)
C(19)-C(20)-C(21)	111.61(12)
C(19)-C(20)-C(23)	126.02(11)
C(21)-C(20)-C(23)	122.36(12)
C(22)-C(21)-C(20)	113.84(12)
C(22)-C(21)-H(21)	123.1
C(20)-C(21)-H(21)	123.1
C(21)-C(22)-S(1)	111.09(10)
C(21)-C(22)-H(22)	124.5
S(1)-C(22)-H(22)	124.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 06275. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	45(1)	39(1)	23(1)	-5(1)	-11(1)	4(1)
O1	35(1)	40(1)	26(1)	2(1)	8(1)	8(1)
N1	38(1)	30(1)	24(1)	-2(1)	-9(1)	-3(1)
C1	73(1)	44(1)	32(1)	-11(1)	-17(1)	-1(1)
C2	30(1)	25(1)	18(1)	2(1)	-2(1)	1(1)
C3	21(1)	26(1)	17(1)	1(1)	-2(1)	0(1)
C4	21(1)	32(1)	26(1)	8(1)	-1(1)	2(1)
C5	31(1)	49(1)	35(1)	13(1)	8(1)	11(1)
C6	27(1)	71(1)	64(1)	31(1)	12(1)	11(1)
C7	21(1)	68(1)	83(1)	38(1)	-8(1)	-6(1)
C8	34(1)	47(1)	59(1)	20(1)	-21(1)	-14(1)
C9	27(1)	32(1)	33(1)	9(1)	-9(1)	-5(1)
C10	72(1)	62(1)	43(1)	8(1)	-14(1)	-37(1)
C11	35(1)	39(1)	42(1)	11(1)	-11(1)	-11(1)
C12	30(1)	26(1)	21(1)	1(1)	-4(1)	-1(1)
C13	30(1)	25(1)	21(1)	2(1)	-3(1)	1(1)
C14	46(1)	55(1)	28(1)	9(1)	5(1)	22(1)
C15	41(1)	87(1)	46(1)	24(1)	1(1)	25(1)
C16	45(1)	64(1)	35(1)	15(1)	-16(1)	-3(1)
C17	60(1)	39(1)	21(1)	1(1)	-3(1)	0(1)
C18	39(1)	33(1)	24(1)	4(1)	4(1)	4(1)
C19	23(1)	32(1)	17(1)	-2(1)	-2(1)	-1(1)
C20	27(1)	35(1)	22(1)	4(1)	-3(1)	-1(1)
C21	36(1)	46(1)	27(1)	10(1)	-7(1)	2(1)
C22	39(1)	55(1)	22(1)	3(1)	-11(1)	2(1)
C23	58(1)	30(1)	35(1)	5(1)	-6(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 06275.

	x	y	z	U(eq)
H1A	5268	6496	7737	74
H1B	6874	6993	7444	74
H1C	6925	5999	7936	74
H5	7788	4446	4518	46
H6	10478	4830	4709	65
H7	11286	5657	5868	69
H8	9473	6198	6859	56
H10A	3250	2341	5486	70
H10B	1557	2687	5885	70
H11	2687	4028	6363	46
H12	5423	3407	5467	31
H14	7809	2932	6044	52
H15	9401	2571	7179	69
H16	8579	2960	8514	58
H17	6154	3718	8709	48
H18	4553	4066	7577	38
H21	2837	6533	3525	43
H22	2875	4948	2934	46
H23A	5218	7047	5236	62
H23B	3451	6949	5573	62
H23C	3786	7494	4719	62

Table 6. Torsion angles [°] for 06275.

C9-N1-C2-O1	-179.03(12)
C1-N1-C2-O1	3.6(2)
C9-N1-C2-C3	5.26(13)
C1-N1-C2-C3	-172.12(12)
O1-C2-C3-C19	55.90(16)
N1-C2-C3-C19	-128.49(10)
O1-C2-C3-C4	177.01(12)
N1-C2-C3-C4	-7.38(12)
O1-C2-C3-C12	-68.78(15)
N1-C2-C3-C12	106.83(10)
C19-C3-C4-C5	-52.84(18)
C2-C3-C4-C5	-175.16(13)
C12-C3-C4-C5	72.58(16)
C19-C3-C4-C9	129.42(11)
C2-C3-C4-C9	7.10(12)
C12-C3-C4-C9	-105.15(11)
C9-C4-C5-C6	2.2(2)
C3-C4-C5-C6	-175.33(13)
C4-C5-C6-C7	0.0(2)
C5-C6-C7-C8	-1.6(3)
C6-C7-C8-C9	0.9(2)
C5-C4-C9-C8	-3.0(2)
C3-C4-C9-C8	175.02(13)
C5-C4-C9-N1	177.46(12)
C3-C4-C9-N1	-4.54(13)
C7-C8-C9-C4	1.4(2)
C7-C8-C9-N1	-179.11(14)
C2-N1-C9-C4	-0.55(14)
C1-N1-C9-C4	176.78(12)
C2-N1-C9-C8	179.94(14)
C1-N1-C9-C8	-2.7(2)
C10-C11-C12-C13	-98.05(17)
C10-C11-C12-C3	135.70(15)
C19-C3-C12-C11	-56.99(14)
C4-C3-C12-C11	177.58(11)
C2-C3-C12-C11	68.74(13)
C19-C3-C12-C13	176.71(10)

C4-C3-C12-C13	51.28(13)
C2-C3-C12-C13	-57.57(12)
C11-C12-C13-C14	136.42(14)
C3-C12-C13-C14	-97.05(14)
C11-C12-C13-C18	-44.12(16)
C3-C12-C13-C18	82.41(14)
C18-C13-C14-C15	-1.5(3)
C12-C13-C14-C15	177.96(16)
C13-C14-C15-C16	0.6(3)
C14-C15-C16-C17	0.1(3)
C15-C16-C17-C18	0.2(3)
C16-C17-C18-C13	-1.2(2)
C14-C13-C18-C17	1.8(2)
C12-C13-C18-C17	-177.63(12)
C4-C3-C19-C20	-78.92(16)
C2-C3-C19-C20	35.91(17)
C12-C3-C19-C20	157.43(13)
C4-C3-C19-S1	92.82(11)
C2-C3-C19-S1	-152.35(9)
C12-C3-C19-S1	-30.83(13)
C22-S1-C19-C20	-0.65(11)
C22-S1-C19-C3	-173.77(10)
C3-C19-C20-C21	173.80(12)
S1-C19-C20-C21	1.44(14)
C3-C19-C20-C23	-4.9(2)
S1-C19-C20-C23	-177.25(12)
C19-C20-C21-C22	-1.77(18)
C23-C20-C21-C22	176.97(15)
C20-C21-C22-S1	1.26(18)
C19-S1-C22-C21	-0.36(13)

Symmetry transformations used to generate equivalent atoms: