Supporting Information

Asymmetric Indoline Synthesis via Intramolecular Aza-Michael Addition Mediated by Bifunctional Organocatalysts

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Contents

Instrumentation and Chemicals

^{1}H and ^{13}C Nuclear magnetic resonance spectra were taken on a Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane as an internal standard for ^{1}H NMR (δ = 0 ppm) and $CDCl_3$ as an internal standard for ^{13}C NMR (δ = 77.0 ppm). When a ^{13}C NMR spectrum was measured using C_6D_6 as a solvent, C_6D_6 was used as an internal standard (δ = 128.06 ppm). ^{1}HNMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration. ^{19}F NMR spectra were measured on a Varian Mercury 200 (^{19}F, 188 MHz) spectrometer with hexafluorobenzene as an internal standard (δ = 0 ppm). GC-MS analyses and High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. High performance liquid chromatography (HPLC) was performed with a SHIMADZU Prominence. Infrared (IR) spectra were determined on a SHIMADZU IR Affinity-1 spectrometer. Melting points were determined using a YANAKO MP-500D. Optical rotations were measured on a HORIBA SEPA-200. X-ray data were taken on a Bruker Smart APEX X-Ray diffractometer equipped with a large area CCD detector. The structures were solved with the program system SHELXS-97 and refined with SHELXL-97 package from Bruker. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or such as an aqueous alkaline $KMnO_4$ solution followed by heating.

Flash column chromatography was carried outusing Kanto Chemical silica gel (spherical, 40–50 μm). Unless otherwise noted, commercially available reagents were used without purification.

Experimental Procedure

General procedure for asymmetric synthesis of 2-substituted indolines 2

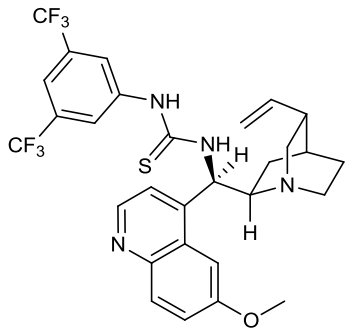
In a 5-mL vial, we sequentially added substrate **1** (0.10mmol), THF (0.8 ml), and quinidine-derived bifunctional catalyst **3a** (0.010mmol). The mixture was stirred in an oil bath maintained at 25 °C for 24 h. The reaction mixture was subsequently diluted with hexane/EtOAc (v/v = 1/1), passed through a short silica gel pad to remove **3a**, and concentrated in vacuo. Purification of the reaction mixture by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent afforded the corresponding 2-substituted indoline **2**.

Racemic compounds were prepared using *p*-toluenesulfonic acid as a catalyst.

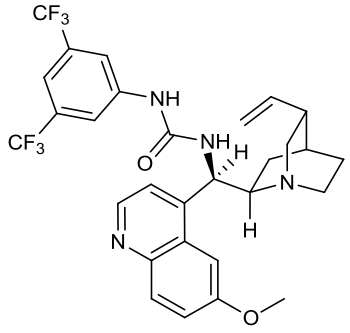
General procedure for preparation of bifunctional catalysts 3

Bifunctional organocatalysts **3** were prepared by the literature procedure.[1] A cinchona alkaloid (5 mmol) and triphenylphosphine (1.6 g, 6 mmol) were dissolved in THF (25 mL), and the solution was cooled to 0 °C. Diethyl azodicarboxylate (1.0 g, 6 mmol) was subsequently added. To the resulting solution was added dropwise the solution of diphenyl phosphoryl azide (1.3 mL, 6 mmol) in THF (10 mL) at 0 °C. The mixture was allowed to warm to ambient temperature. After being stirred for 24 h, it was heated to 50 °C and stirred for 10 h. Triphenylphosphine (1.7 g, 6.5 mmol) was added again, and the mixture was stirred at 50 °C for additional 15 h. After the solution was cooled to ambient temperature, H_2O (0.5 mL) was added, and the solution was stirred for 24 h. The solvents were removed in vacuo, and the residue was dissolved in CH_2Cl_2/10% aqueous hydrochloric acid (25 mL/25 mL). The aqueous phase was separated and washed with CH_2Cl_2 (25 mL × 4). It was subsequently made alkaline with aqueous ammonia, and the aqueous phase was extracted with CH_2Cl_2 (25 mL × 4). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using EtOAc/CH_3OH (v/v = 9/1) then $CHCl_3$/CH_3OH (v/v = 8/2) as an eluent gave the corresponding 9-amino(9-deoxy)cinchona alkaloids. Next, to the solution of the obtained 9-amino(9-deoxy)cinchona alkaloid in THF (6 mL) was slowly added a solution of 3,5-bis(trifluoromethyl)phenyl isocyanate or isothiocyanate (1 equiv) in THF (4 mL) at ambient temperature. The mixture was stirred overnight, and the solvents were removed in vacuo. Purification by flash silica gel column chromatography using EtOAc/CH_3OH (v/v = 95/5–97.5/2.5) or EtOAc as an eluent gave the corresponding bifunctional organocatalyst **3**.

The characterization results are as below.

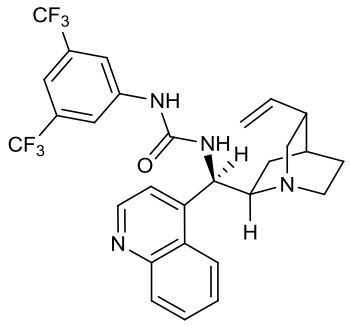


3a. White solid; 41% yield (for 2steps from quinidine). $[\alpha]_D^{23}$ +122.6 (*c* 1.33, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.65 (br s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.86 (s, 2H), 7.67 (s, 1H), 7.59 (br s, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.23 (br s, 1H), 5.86 (br s, 2H), 5.19 (br s, 1H), 5.15 (d, *J* = 9.5 Hz, 1H), 3.97 (s, 3H), 3.22 (br s, 1H), 3.10 (br s, 1H), 3.03 (m, 2H), 2.94 (m, 1H), 2.38 (m, 1H), 1.70 (s, 1H), 1.61 (m, 2H), 1.27 (br s, 1H), 1.02 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 181.0, 158.1, 147.3, 144.7, 144.5, 140.1, 139.6, 132.5 (q, *J* = 33.6 Hz), 131.6, 128.0, 123.5, 122.9 (q, *J* = 273.0 Hz), 122.3, 118.7, 115.3, 101.7, 61.4, 55.6, 48.5, 47.1, 38.7, 27.1, 26.1, 25.0. Mp. 125.0–125.2 °C. IR (KBr): 3221, 2944, 2361, 1735, 1623, 1511, 1475, 1384, 1278, 1177, 1134, 1034, 959, 916, 884, 850, 826, 682 cm^{-1}. HRMS Calcd for $C_{29}H_{29}F_6N_4OS$: $[M+H]^+$, 595.1966. Found: *m*/*z* 595.1961.

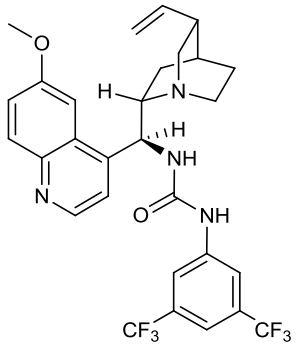


3b. White solid; 30% yield (for 2steps from quinidine). $[\alpha]_D^{18}$ +840.0 (*c* 2.00, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.76 (d, *J* = 4.5 Hz, 1H), 8.05 (d, *J* = 9.5 Hz, 1H), 7.78 (s, 2H), 7.60 (s, 1H), 7.41 (m, 3H), 6.29 (br s, 1H), 5.88 (ddd, *J* = 15.0, 10.0, 4.0 Hz, 1H), 5.33 (br s, 1H), 5.13 (m, 2H), 3.99 (s, 3H), 2.97 (d, *J* = 10.0 Hz, 3H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.23 (m, 1H), 1.82 (br s, 3H), 1.68 (br s, 1H), 1.51 (m, 1H), 1.03 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 158.4, 156.9, 156.2, 155.1, 147.7, 145.1, 140.9, 140.1, 132.3 (q, *J* = 33.2 Hz), 132.1, 128.3, 123.4 (q, *J* = 272.6 Hz), 118.5, 115.9, 115.4, 110.0, 101.7, 60.6, 55.8, 49.3, 47.2, 39.1, 32.2, 27.4, 26.6, 25.5. ^{19}F NMR ($CDCl_3$) δ 98.8. Mp. 133.0–133.5 °C. IR (KBr): 3321, 3080, 2941, 2875, 1705, 1676, 1624, 1570, 1511, 1475, 1434, 1389,

1279, 1245, 1229, 1179, 1132, 1096, 1036, 945, 917, 880, 852, 828, 703, 682 cm^{-1}. HRMS Calcd for $C_{29}H_{29}F_6N_4O_2$: $[M+H]^+$, 580.2223. Found: *m*/*z*580.2209.

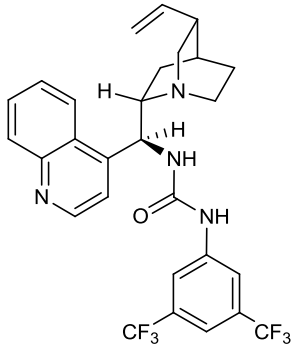


3c. White solid; 40% yield (for 2steps from cinchonine). $[\alpha]_D^{23}$ +194.9 (*c* 0.59, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.91 (d, *J* = 4.5 Hz, 1H), 8.36 (d, *J* = 7.5 Hz, 1H), 8.18 (dd, *J* = 8.3, 0.75 Hz, 1H), 7.79 (s, 2H), 7.76 (dd, *J* = 8.3, 1.3, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 4.5 Hz, 1H), 7.43 (s, 1H), 6.35 (br s, 1H), 5,87 (ddd, *J* = 18.1, 15.0, 6.0 Hz, 1H), 5.30 (br s, 1H), 5.13 (dd, *J* = 24.0, 7.5 Hz, 2H), 2.94 (m, 5H), 2.31 (m, 1H), 1.84 (br s, 1H), 1.65 (br s, 1H), 1.57 (m, 1H), 1.49 (m, 1H), 1.27 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 154.9, 150.1, 148.7, 140.7, 139.6, 132.2 (q, *J* = 33.2 Hz), 130.6, 129.4, 127.0, 123.7 (q, *J* = 273.0 Hz), 123.1, 118.26, 118.23, 115.76, 115.73, 115.70, 115.3, 61.1, 49.0, 47.0, 39.0, 29.7, 27.3, 26.3, 25.0. ^{19}F NMR ($CDCl_3$) δ 98.8. Mp. 193.5–194.0 °C. IR (KBr): 3289, 3238, 3081, 2942, 2875, 2366, 1705, 1676, 1570, 1511, 1475, 1389, 1279, 1243, 1180, 1132, 945, 916, 881, 761, 683, 624 cm^{-1}. HRMS Calcd for $C_{28}H_{27}F_6N_4O$: $[M+H]^+$, 549.2084. Found: *m*/*z* 549.2077.



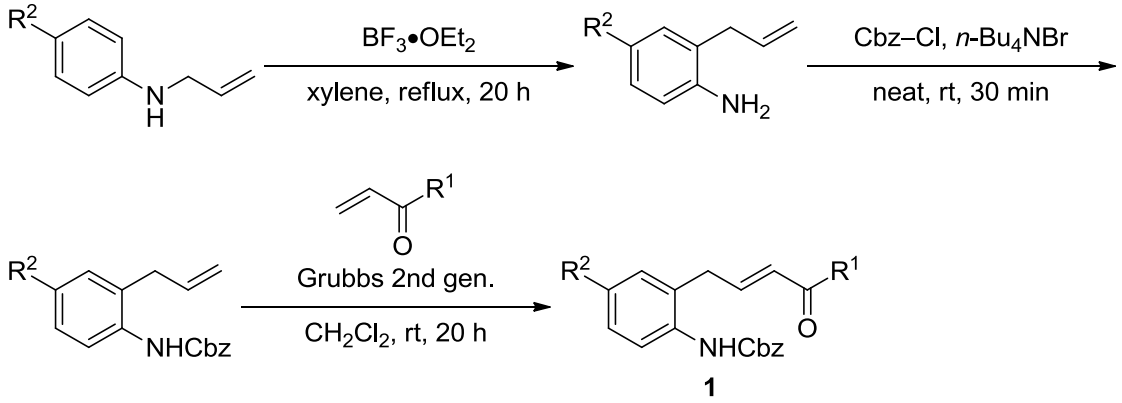
3d. White solid; 30% yield (for 2steps from quinine). $[\alpha]_D^{23}$ +20.4 (*c* 1.47, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.83 (d, *J* = 4.5 Hz, 1H), 8.06 (d, *J* = 9.5 Hz, 1H), 7.94 (br s, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 7.42 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.34 (d, *J* = 4.5 Hz, 1H), 7.32 (s, 1H), 6.13 (br s, 1H), 5.64 (ddd, *J* = 17.0, 10.3, 6.8 Hz, 2H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.84 (d, *J* = 17.0 Hz, 1H), 4.02 (s, 3H), 3.54 (br s, 1H), 3.18 (br s, 1H), 2.95 (m, 1H),

2.71 (m, 1H), 2.24 (br s, 2H), 2.11 (br s, 1H), 1.66 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 158.4, 154.6, 153.7, 147.3, 145.1, 140.5, 140.4, 131.932 (q, *J* = 33.2 Hz), 131.927, 130.2, 123.0 (q, *J* = 273.0 Hz), 118.4, 115.6, 115.1, 112.5, 109.7, 103.9, 60.1, 55.8, 55.4, 43.6, 41.4, 40.7, 38.6, 27.4, 26.9. ^{19}F NMR ($CDCl_3$) δ 98.6. Mp. 134.0–135.0 °C. IR (KBr): 3327, 3083, 2944, 2869, 2360, 1700, 1623, 1570, 1512, 1476, 1388, 1279, 1245, 1230, 1179, 1132, 1034, 881, 852, 682 cm^{-1}. HRMS Calcd for $C_{29}H_{29}F_6N_4O_2$: $[M+H]^+$, 580.2223. Found: *m*/*z* 580.2181.



3e. White solid; 40% yield (for 2steps from cinchonidine). $[\alpha]_D^{23}$ –16.3 (*c* 3.67, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.93 (d, *J* = 3.0 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.17 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.76 (m, 3H), 7.66 (m, 1H), 7.48 (d, *J* = 5.0 Hz, 1H), 7.38 (s, 1H), 6.49 (br s, 1H), 5.61 (ddd, *J* = 17.3, 10.3, 7,5 Hz, 1H), 5.44 (br s, 1H), 4.90 (m, 2H), 3.17 (br s, 1H), 2.99 (dd, *J* = 13.5, 10.0 Hz, 2H), 2.61 (m, 1H), 2.41 (m, 2H), 2.23 (m, 1H), 1.63 (m, 2H), 1.56 (m, 1H), 1.36 (m, 1H), 0.93 (dd, *J* = 13.5, 6.0 Hz 1H). ^{13}C NMR ($CDCl_3$) δ 154.8, 149.9, 148.6, 148.5, 141.5, 140.8, 140.7, 132.0 (q, *J* = 33.2 Hz), 130.3, 129.6, 127.2, 123.28, 123.11 (q, *J* = 273.0 Hz), 118.2, 115.6, 114.8, 113.0, 61.9, 55.5, 40.9, 39.1, 35.0, 27.6, 27.0, 26.0. ^{19}F NMR ($CDCl_3$) δ 98.7. Mp. 140.0–141.0 °C. IR (KBr): 3309, 3081, 2947, 2869, 2360, 1700, 1623, 1570, 1511, 1473, 1389, 1346, 1279, 1243, 1180, 1132, 882, 760, 704, 683 cm^{-1}. HRMS Calcd for $C_{28}H_{27}F_6N_4O$: $[M+H]^+$, 549.2084. Found: *m*/*z* 549.2076.

General procedure for preparation of substrates 1



1

The starting materials **1** were prepared through the synthetic route indicated above by modified procedures of the literature methods.[2–4] The characterization data of the corresponding synthetic intermediates were identical to those reported in the literatures.

To a solution of an *N*-allylaniline (3.4 mL, 20 mmol) in xylene (40 mL) was added $BF_3 \cdot OEt_2$ (3.8 mL, 20 mmol) at ambient temperature. The reaction mixture was allowed to warm to 150 °C. After being stirred for 20 h, the reaction was quenched with 20% aquous NaOH (10 mL), and the mixture was subsequently extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave the corresponding *o*-allylaniline as a pale yellow oil in 40–60% yield. *N*-allylanilines commercially unavailable were prepared by the literature procedure.[5]

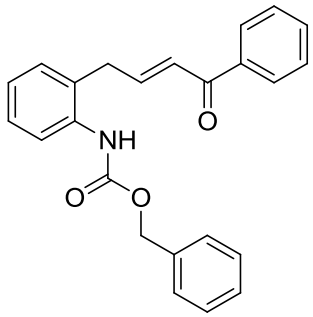
To the *o*-allylaniline (10 mmol), tetrabutylammonium bromide (161 mg, 0.5 mmol) was added. Benzyl chloroformate was added dropwise into the mixture at 0 °C, and the mixture was stirred for 30 min. Then the reaction mixture was diluted by a small amount of CH_2Cl_2, and stirred for 3 h. The reaction mixture was quenched with saturated aquous $NaHCO_3$ (10 mL), and the mixture was subsequently extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flush silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave *N*-benzyloxycarbonyl-*o*-allylaniline as a white solid in 80–100% yield.

To a solution of the *N*-benzyloxycarbonyl-*o*-allylaniline (1.0mmol) and a vinylketone (5.0 mmol) in CH_2Cl_2 (10 mL), Grubbs-catalyst-2nd-generation (26 mg, 0.03 mmol)

was added at ambient temperature. After the solution stirred for 20 h, solvents were removed in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave the corresponding *N*-benzyloxycarbonyl -(*E*)-4-(2-aminophenyl)-but-2-en-1-one (**1**). Vinyl ketones were prepared by the literature procedure.[6]

The characterization results of **1** are as below.

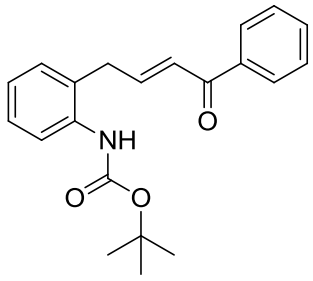
***N*-Benzyloxycarbonyl-(*E*)-4-(2-aminophenyl)-1-phenylbut-2-en-1-one (1a)**.



White solid; 40% yield (for the last step).

^{1}H NMR ($CDCl_3$) δ 7.85 (m, 2H), 7.77 (br s, 1H), 7.54 (m, 1H), 7.40 (m, 2H), 7.36 (m, 6H), 7.18 (m, 3H), 6.78 (dt, *J* = 15.0, 2.0 Hz, 1H), 6.43 (br s, 1H), 5.17 (s, 2H), 3.62 (dd, *J* = 6.0, 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 190.1, 161.5, 147.3, 145.7, 139.1, 137.5, 135.9, 135.6, 132.9, 130.3, 128.60, 128.58, 128.52, 128.4, 128.1, 126.9, 125.4, 116.6, 67.2, 35.0. Mp. 105.0–105.5 °C. TLC: R_f 0.36 (hexane/EtOAc = 3:1). IR (KBr): 3285, 3032, 2961, 2903, 1696, 1668, 1624, 1591, 1530, 1453, 1352, 1248, 1058, 987, 914, 748, 691 cm^{-1}. HRMS Calcd for $C_{24}H_{22}NO_3$: $[M+H]^+$, 372.1594. Found: *m*/*z* 372.1587.

***N*-*tert*-Butoxycarbonyl-(*E*)-4-(2-aminophenyl)-1-phenylbut-2-en-1-one (1b)**.

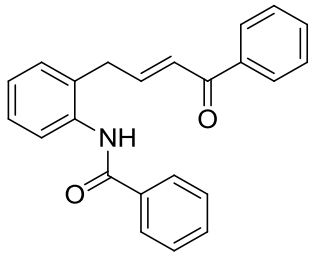


White solid; 25% yield (for the last step).

^{1}H NMR ($CDCl_3$) δ 7.87 (m, 2H), 7.74 (m, 1H), 7.55 (m, 1H), 7.45 (m, 2H), 7.29 (m, 1H), 7.19 (m, 2H), 7.12(dt, *J* = 7.5, 1.0 Hz, 1H), 6.81 (dt, 15.5, 1.5 Hz, 1H), 6.24 (br s, 1H), 3.63 (dd, *J* = 6.0, 1.5 Hz, 2H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 190.3, 153.2,

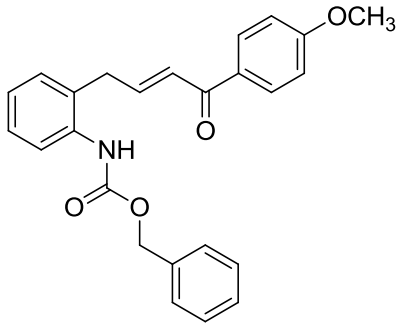
145.9, 137.6, 136.1, 132.9, 130.2, 128.6, 128.5, 128.0, 126.9, 124.8, 123.2, 109.7, 80.7, 35.1, 28.3. Mp. 91.5–92.2 °C. TLC: R_f 0.35 (hexane/EtOAc = 3:1). IR (KBr): 3295, 2983, 2963, 2917, 1722, 1666, 1614, 1596, 1579, 1513, 1490, 1452, 1366, 1250, 1168, 1052, 1021, 986, 908, 781, 758, 691 cm^{-1}. HRMS Calcd for $C_{21}H_{24}NO_3$: $[M+H]^+$, 338.1758. Found: *m*/*z* 338.1761.

***N*-Benzoyl-(*E*)-4-(2-aminophenyl)-1-phenylbut-2-en-1-one (1c)**.



White solid; 20% (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.84 (m, 1H), 7.82 (m, 3H), 7.55–7.29 (m, 10H), 7.20 (m, 2H), 6.88 (dt, *J* = 15.0, 1.5 Hz, 1H), 3.71 (dd, *J* = 6.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 189.1, 167.1, 146.5, 136.2, 136.0, 135.9, 135.6, 132.0, 131.9, 130.1, 128.6, 128.3, 128.0, 126.5, 126.4, 124.4, 115.7, 112.9, 55.5. TLC: R_f 0.37 (hexane/EtOAc = 3:1). Mp. 111.5–112.0 °C. IR (KBr): 3291, 3033, 2952, 2835, 1691, 1618, 1529, 1452, 1350, 1259, 749, 352 cm^{-1}. HRMS Calcd for $C_{23}H_{20}NO_2$: $[M+H]^+$, 342.1489. Found: *m*/*z* 342.1492.

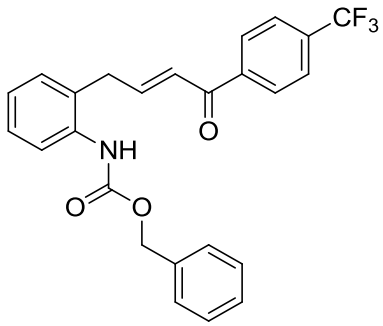
***N*-Benzyloxycarbonyl-(*E*)-4-(2-aminophenyl)-1-(4-methoxyphenyl)but-2-en-1-one (1d)**.



White solid; 25% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.86 (dt, *J* = 9.0, 2.5 Hz, 2H), 7.77 (br s, 1H), 7.34 (m, 6H), 7.21 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.14 (m, 2H), 6.89 (dt, *J* = 7.0, 2.5 Hz, 2H), 6.79 (dt, *J* = 15.0, 2.0 Hz, 1H), 6.45 (br s, 1H), 5.17 (s, 2H), 3.85 (s, 3H), 3.60 (dd, *J* = 6.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 188.3, 179.7, 164.6 163.5, 162.5, 156.4, 144.5, 136.0, 130.9, 130.4,

128.6, 128.3, 128.1, 126.8, 125.3, 120.8, 113.8, 107.1, 67.2, 55.5, 35.0. Mp. 111.5–112.0 °C. TLC: R_f 0.33 (hexane/EtOAc = 3:1). IR (KBr): 3291, 3033, 2952, 2838, 1691, 1663, 1618, 1529, 1452, 1350, 1259, 749, 352 cm^{-1}. HRMS Calcd for $C_{25}H_{24}NO_4$: $[M+H]^+$, 403.1733. Found: *m*/*z* 403.1726.

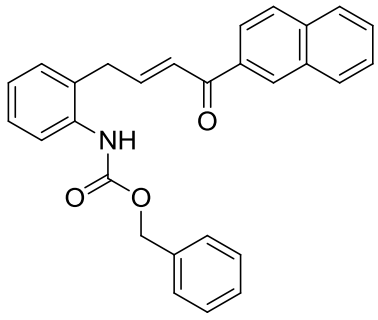
***N*-Benzyloxycarbonyl-(*E*)-4-(2-aminophenyl)-1-(4-trifluoromethylphenyl)but-2-en-1-one (1e)**.



White soild; 30% (for the last step).

^{1}H NMR ($CDCl_3$) δ 7.90 (d, *J* = 3.5 Hz, 2H), 7.73 (br s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7,34 (m, 6H), 7.19 (m, 3H), 6.74 (dt, *J* = 15.5, 1.8 Hz, 1H), 6.49 (br s, 1H), 5.17 (s, 2H), 3.63 (dd, *J* = 6.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 189.2, 162.4, 154.0, 147.2, 140.3, 135.9, 135.5, 134.0 (q, *J* = 32.6 Hz), 130.3, 128.8, 128.6, 128.4, 128.3, 126.6, 125.59, 125.57, 124.2, 123.6 (q, *J* = 272.6 Hz), 103.4, 67.3, 35.1. ^{19}F NMR ($CDCl_3$) δ 98.7. Mp. 136.0–137.0 °C. TLC: R_f 0.28 (hexane/EtOAc = 3:1). IR (KBr): 3474, 3290, 3078, 3036, 2963, 2375, 1690, 1624, 1528, 1326, 1257, 1172, 1126, 1067, 1017, 980, 750, 668 cm^{-1}. HRMS Calcd for $C_{25}H_{21}F_3NO_3$: $[M+H]^+$, 440.1468. Found: *m*/*z* 440.1463.

***N*-Benzyloxycarbonyl-(*E*)-4-(2-aminophenyl)-1-(naphthalen-2-yl)-2-en-1-one (1f)**.

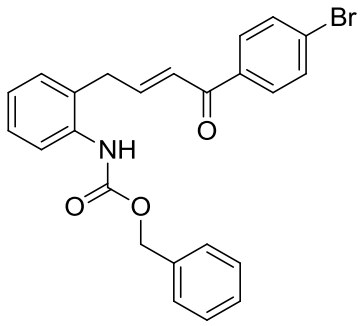


White solid; 20% yield (for the last step).

^{1}H NMR ($CDCl_3$) δ 8.35 (s, 1H), 7.96 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.78 (br s, 1H), 7.60 (ddd, *J* = 8.0, 7.5, 1.0 Hz 1H), 7.54(ddd, *J*

= 8.0, 7.5, 1.0 Hz, 1H), 7.32 (m, 6H), 7.20 (m, 3H), 6.96 (dt, *J* = 15.0, 1.8 Hz, 1H), 6.48 (br s, 1H), 5.17 (s, 2H), 3.66 (dd, *J* = 6.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 189.9, 165.2, 151.7, 145.5, 140.7, 135.6, 135.5, 134.9, 134.1, 132.5, 130.4, 130.2, 129.6, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 127.1, 126.8, 124.3, 114.7, 109.7, 67.2, 35.1. Mp. 104.5–105.0 °C. TLC: R_f 0.33 (hexane/EtOAc = 3:1). IR (KBr): 3309, 3075, 3044, 2969, 2908, 2378, 1705, 1656, 1610, 1520, 1463, 1357, 1296, 1243, 1046, 983, 808, 748, 472 cm^{-1}. HRMS Calcd for $C_{28}H_{24}NO_3$: $[M+H]^+$, 422.1743. Found: *m*/*z* 422.1751.

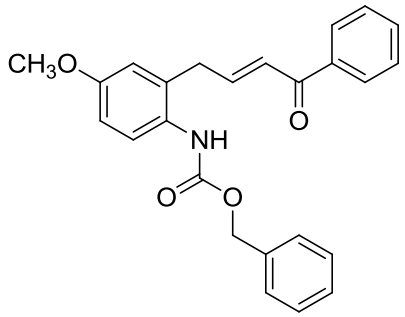
***N*-Benzyloxycarbonyl-(*E*)-4-(2-aminophenyl)-1-(4-bromophenyl)but-2-en-1-one (1g)**.



White solid; 32% yield (for the last step).

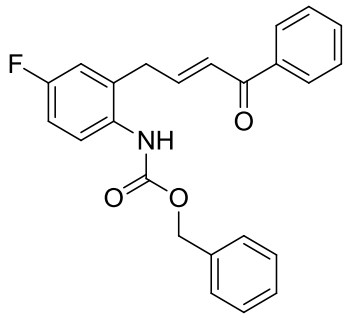
^{1}H NMR ($CDCl_3$) δ 7.70 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.54 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.32 (m, 7H), 7.17 (m, 3H), 6.72 (dt, *J* = 15.0, 2.0 Hz, 1H), 6.40 (br s, 1H), 5.17 (s, 2H), 3.62 (dd, *J* = 6.5, 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 189.0, 164.3, 146.2, 136.3, 135.9, 135.6, 131.9, 131.7, 131.5, 130.4, 130.0, 129.7, 128.6, 128.4, 128.3, 128.2, 128.0, 126.6, 67.3, 35.1. Mp. 94.0–95.0 °C. TLC: R_f 0.36 (hexane/EtOAc = 3:1). IR (KBr): 3289, 3066, 3033, 2950, 1684, 1667, 1586, 1528, 1452, 1397, 1240, 1071, 1011, 978, 836, 757, 665 cm^{-1}. HRMS Calcd for $C_{24}H_{21}BrNO_3$: $[M+H]^+$, 450.0699. Found: *m*/*z* 450.0689.

***N*-Benzyloxycarbonyl-(*E*)-4-(6-amino-3-methoxyphenyl)-1-phenylbut-2-en-1-one (1h)**.



White solid; 20% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.86 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.54 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.43 (m, 2H), 7.35 (m, 5H), 7.15 (m, 1H), 6.84 (dd, *J* = 7.5, 3.0 Hz, 1H), 6.78 (dt, *J* = 13.5, 1.5 Hz, 1H), 6.75 (d, *J* = 3.0 Hz, 1H), 6.25 (br s, 1H), 5.16 (s, 2H), 3.80 (s, 3H), 3.58 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 190.1, 145.6, 137.5, 136.0, 135.6, 132.9, 130.3, 128.62, 128.58, 128.56, 128.51, 128.31, 128.30, 128.1, 127.0, 125.4, 115.9, 111.3, 67.2, 55.7, 35.0. Mp. 124.0–125.0 °C. TLC: R_f 0.40 (hexane/EtOAc = 3:1). IR (KBr): 3291, 3034, 2968, 2331, 1952, 1808, 1692, 1666, 1622, 1587, 1532, 1452, 1352, 1243, 1059, 988, 748, 692, 577 cm^{-1}. HRMS Calcd for $C_{25}H_{23}NO_4Na$: $[M+Na]^+$, 424.1519. Found: *m*/*z* 424.1523.

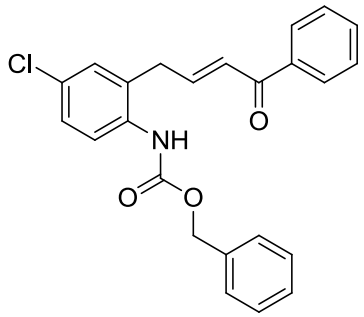
***N*-Benzyloxycarbonyl-(*E*)-4-(2-amino-5-fluorophenyl)-1-phenylbut-2-en-1-one (1i)**.



White solid; 20% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.86 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.55 (tt, *J* = 4.5, 1.3 Hz, 1H), 7.44 (m, 2H), 7.34 (m, 6H), 7.12 (dt, *J* = 15.0, 6.0 Hz, 1H), 7.01 (dt, *J* = 3.0, 8.0 Hz, 1H), 6.94 (dd, *J* = 9.0, 8.0 Hz, 1H), 6.80 (dt, *J* = 15.0, 1.5 Hz, 1H), 6.33 (br s, 1H), 5.16 (s, 2H), 3.59 (dd, *J* = 6.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 189,8 153.7, 144.5, 141.1, 137.3, 135.7, 134.2, 133.0, 131.6, 129.1 (d, *J* = 246.7 Hz), 128.6, 128.53, 128.46, 128.4, 127.3, 124.3, 118.3, 105.4, 67.2, 35.0. ^{19}F NMR ($CDCl_3$) δ 77.1. Mp. 106.0–107.0 °C. TLC: R_f 0.23 (hexane/EtOAc = 3:1). IR (KBr): 3293, 3034, 2939, 2375, 1699, 1620,

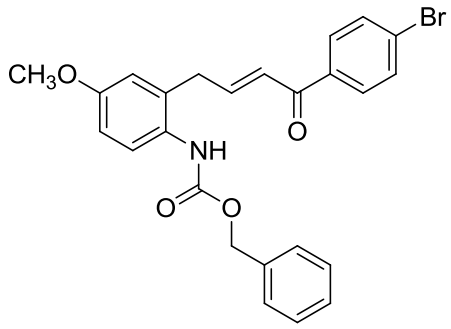
1530, 1453, 1248, 1063, 986, 755, 694, 498 cm^{-1}. HRMS Calcd for $C_{24}H_{20}FNO_3Na$: $[M+Na]^+$, 412.1319. Found: *m*/*z* 412.1327.

_N_-Benzyloxycarbonyl-(_E_)-4-(2-amino-5-chlorophenyl)-1-phenyl)but-2-en-1-one (1j).



White solid; 15% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.86(m, 2H), 7.73 (br s, 1H), 7.56 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.43 (tt, *J* = 7.5, 2.0Hz, 2H), 7.34 (m, 5H), 7.28 (dd, *J* = 8.5, 2.5Hz, 1H), 7.19 (d, *J* = 2.5 Hz, 1H) 7.13 (dt, *J* = 15.0, 6.0 Hz, 1H), 6.79 (dt, *J* = 15.0, 2.0 Hz, 1H), 6.41 (br s, 1H), 5.17 (s, 2H), 3.57 (d, *J* = 3.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 189.9, 157.6, 156.6, 145.1, 144.4, 137.4, 135.7, 134.3, 133.0, 130.1, 128.6, 128.5, 128.44, 128.37, 128.1, 127.4, 124.8, 122.3, 67.4, 34.7. Mp. 132.5–132.0 °C. TLC: R_f 0.30 (hexane/EtOAc = 3:1). IR (KBr): 3264, 3047, 2939, 2354, 1696, 1620, 1526, 1403, 1349, 1259, 1102, 1063, 990, 904, 697, 531 cm^{-1}. HRMS Calcd for $C_{24}H_{21}ClNO_3$: $[M+H]^+$, 406.1204. Found: *m*/*z* 406.1212.

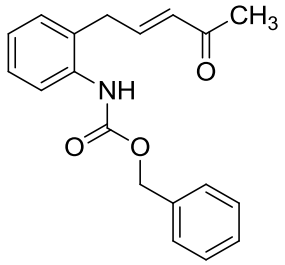
_N_-Benzyloxycarbonyl-(_E_)-4-(6-amino-3-methoxyphenyl)-1-(4-bromophenyl)but-2-en-1-one (1k).



White solid; 20% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.71 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.54 (dt, *J* = 7.5, 2.0 Hz, 2H), 7.47 (br s, 1H), 7.34 (m, 5H), 7.15 (m, 1H), 6.84 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.74 (d, *J* = 3.0 Hz, 1H) 6.72 (dt, *J* = 15.5, 2.0 Hz, 1H), 6.23 (br s, 1H), 5.15 (s, 2H), 3.80 (s, 3H), 3.58

(dd, *J* = 6.0, 1.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 188.8, 178.7, 164.2, 157.8, 151.7, 150.1, 143.4, 141.8, 138.2, 135.7, 131.9, 130.1, 127.7, 123.8, 118.1, 113.0, 111.7, 106.8, 67.2, 55.5, 35.3. Mp. 130.5–131.0 °C. TLC: R_f 0.37 (hexane/EtOAc = 3:1). IR (KBr): 3234, 3035, 2965, 2365, 1685, 1669, 1624, 1585, 1534, 1266, 1253, 1071, 1028, 861, 743, 697, 492 cm^{-1}. HRMS Calcd for $C_{25}H_{22}BrNO_4Na$: $[M+Na]^+$, 502.0624. Found: *m*/*z* 502.0634.

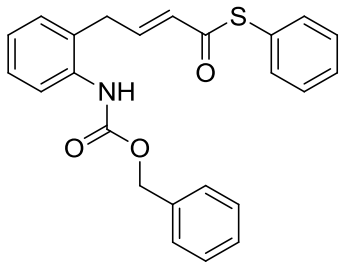
***N*-Benzyloxycarbonyl-(*E*)-5-(2-aminophenyl)-pent-3-en-2-one (1l)**.



Whitie solid; 50% yield (for the last step).

^{1}H NMR ($CDCl_3$) δ 7.57 (br s, 1H), 7.26–7.20 (m, 5H), 7.15 (m, 1H), 7.01 (m, 2H), 6.74 (dt, *J* = 16.0, 6.0 Hz, 1H), 6.35 (br s, 1H), 5.85 (dt, *J* = 6.0, 2.0 Hz, 1H), 5.05 (s, 2H), 3.38 (dd, *J* = 6.0, 2.0 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 198.2, 154.0, 144.6, 135.9, 135.4, 132.0, 130.2, 129.9, 128.6, 128.3, 128.0, 127.5, 125.4, 123.5, 67.2, 34.5, 27.1. TLC: R_f 0.25 (hexane/EtOAc). The characterization data were identical to those reported in the literature.[6]

(*E*)-*S*-Phenyl 4-(2-(((benzyloxy)carbonyl)amino)phenyl)but-2-enethioate (1m).

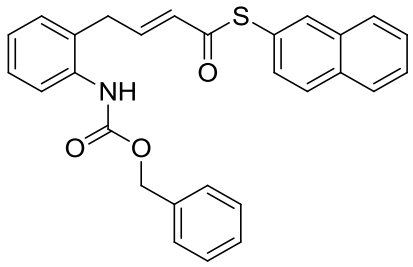


White solid; 34% (for the last step).

^{1}H NMR ($CDCl_3$) δ 7.72 (br s, 1H), 7.41 (m, 7H), 7.37 (m, 3H), 7.31 (m, 1H), 7.16 (m, 2H), 7.09 (dt, *J* = 15.5, 1.0 Hz, 1H), 6.35 (br s, 1H), 6.05 (dt, *J* = 15.5, 2.0 Hz, 1H), 5.21 (s, 2H), 3.74 (dd, *J* = 6.0, 1.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 195.4, 183.3, 176.2, 175.3, 162.4, 153.9, 142.9, 136.0, 134.6, 130.3, 129.5, 129.2, 129.0, 128.6, 128.4, 128.2, 109.7, 102.5, 67.3, 34.4. Mp. 88.5–89.5 °C. TLC: R_f 0.37 (hexane/EtOAc = 3:1). IR (KBr): 3313, 3001, 2939, 2361, 1693, 1641, 1540, 1451, 1306, 1234, 1059, 1016, 918,

752, 694, 651 cm^{-1}. HRMS Calcd for $C_{24}H_{22}NO_3S$: $[M+H]^+$, 404.1315. Found: *m*/*z* 404.1320.

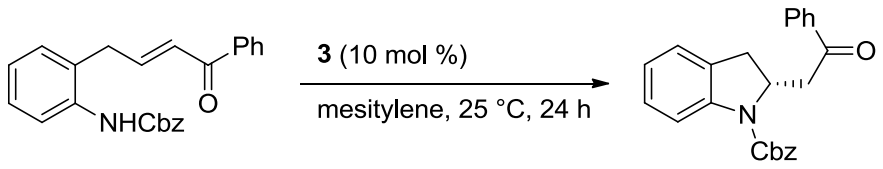
(*E*)-*S*-Naphthyl -4-(2-(((benzyloxy)carbonyl)amino)phenyl)but-2-enethioate (1n).



Pale yellow solid; 25% (for the last step).

^{1}H NMR ($CDCl_3$) δ 8.62 (m, 1H), 7.95 (m, 1H), 7.86 (m, 2H), 7.82 (d, *J* = 7.0, 1.5 Hz, 1H), 7.71 (br s, 1H), 7.68 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.53 (m, 2H), 7.44 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.42–7.34 (m, 3H), 7.29 (m, 1H), 7.16 (m, 2H), 7.11 (dt, *J* = 16.0, 6.0 Hz, 1H), 6.39 (br s, 1H), 6.08 (dt, *J* = 16.0, 1.5 Hz, 1H), 5.22 (s, 2H), 3.54 (dd, *J* = 6.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 187.9, 169.4, 153.9, 149.8, 143.0, 136.0, 135.5, 134.5, 133.5, 133.4, 130.9, 130.3, 129.0, 128.8, 128.64, 128.57, 128.4, 128.2, 128.0, 127.8, 127.2, 126.6, 124.7, 123.7, 67.3, 34.4. Mp. 128.5–129.5 °C. TLC: R_f 0.38 (hexane/EtOAc = 3:1). IR (KBr): 3286, 3057, 2926, 2373, 1734, 1700, 1628, 1587, 1529, 1465, 1294, 1243, 1217, 1056, 976, 814, 745, 696, 473 cm^{-1}. HRMS Calcd for $C_{28}H_{24}NO_3S$: $[M+H]^+$, 455.1505. Found: *m*/*z* 455.1511.

Table S1. Screening of Catalysts[a]



1a **2a**

entry	catalyst (**3**)	yield (%)[b]	*ee* (%)
1	**3a**	73	81
2	**3b**	99	87
3	**3c**	59	76
4	**3d**	66	–84
5	**3e**	53	–78
6	**3f**	16	79
7	**3g**	81	–75
8	**3h**	67	–75
9	**3i**	62	78
10	**3j**	36	69
11	**3k**	36	62
12	**3l**	12	32
13	**3m**	95	44
14	**3n**	<1	—
15	**3o**	29	21

[a] Reactions were run using **1a** (0.1 mmol) and the catalyst (0.01 mmol) in mesitylene (0.8 mL). [b] Isolated yields.

(Table S1)

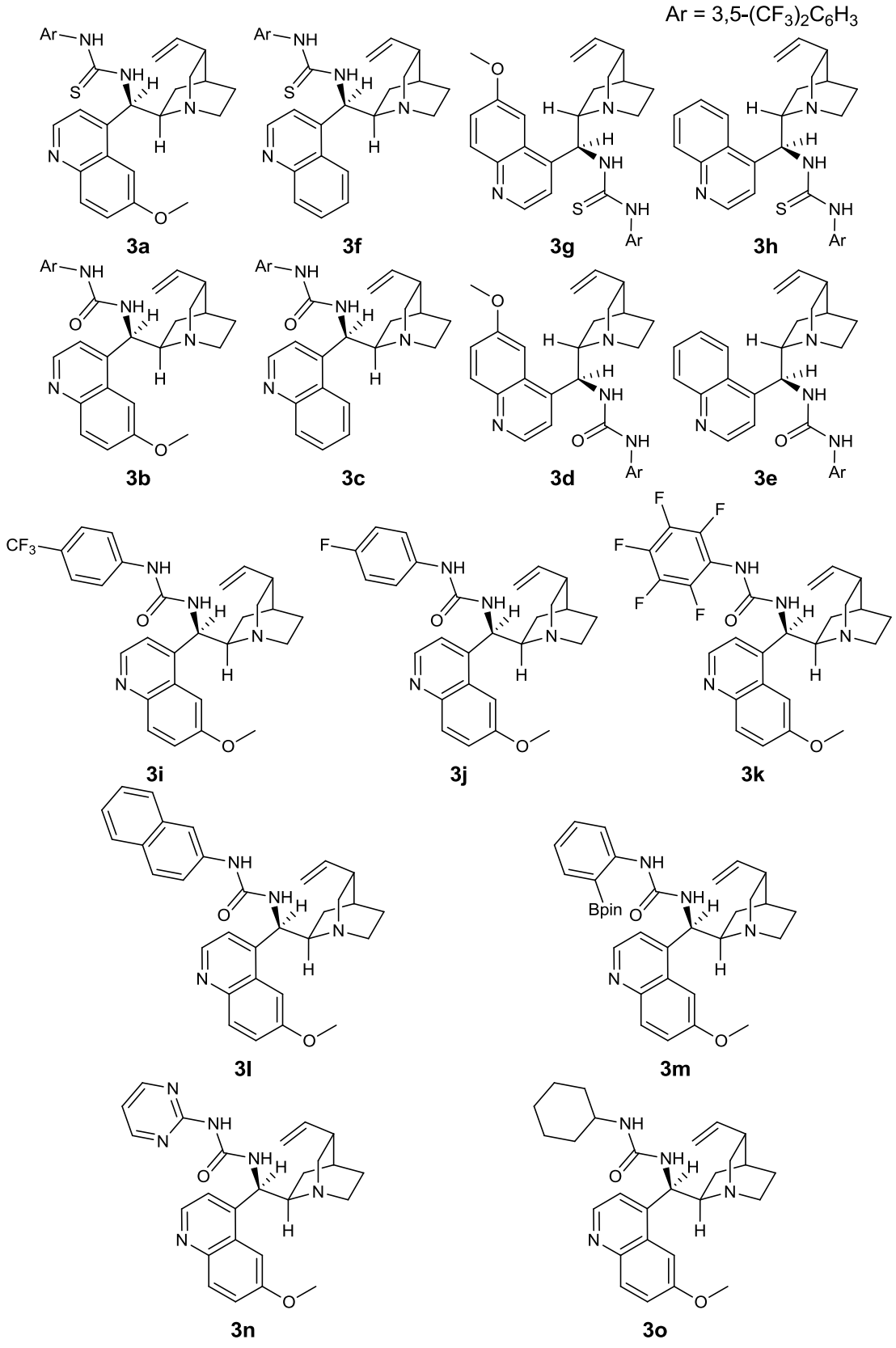
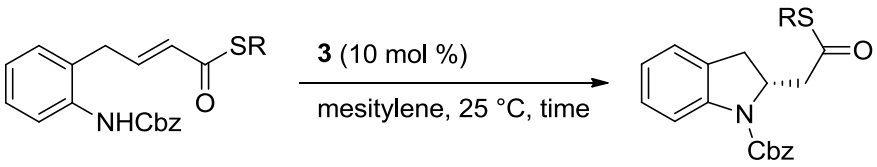


Table S2. Investigations on Reactions from α,β-Unsaturated Thioesters [a]



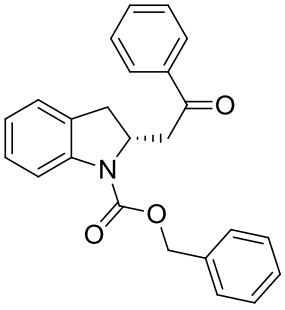
entry	R	catalyst	time (h)	yield (%)[b]	*ee* (%)
1	Ph	**3b**	24	55	52
2	Ph	**3b**	90	80	55
3	2-naphthyl	**3b**	24	40	51
4	2-naphthyl	**3a**	24	32	69
5	4-$CH_3C_6H_4$	**3b**	24	27	54
6	4-BrC_6H_4	**3b**	24	69	57
7	2,4,6-$(CH_3)_3C_6H_4$	**3b**	24	35	57
8	Bn	**3b**	24	19	76

[a] Reactions were run using **1** (0.1 mmol) and **3b** (0.01 mmol) in mesitylene (0.8 mL).

[b] Isolated yields.

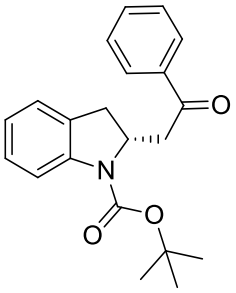
Characterization Data of Products

1-Phenyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2a).



Yield: 99%, 87% *ee*, white solid. $[\alpha]_D^{25}$ +74.7 (*c* 2.81, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.86 (br s, 1H), 7.47–7.31 (m, 10H), 7.21 (br s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.32 (s, 2H), 4.93 (br s, 1H), 3.41 (dd, *J* = 16.5, 4.5 Hz, 1H), 3.27 (br s, 1H), 2.93 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 194.9, 141.9, 136.0, 134.4, 129.5, 129.2, 128.7, 128.5, 128.4, 128.3, 128.2, 127.7, 127.3, 125.1, 123.2, 115.5, 67.4, 56.5, 47.8, 33.8. Mp. 106.0–107.0 °C. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (KBr): 3056, 2955, 2910, 2374, 1701, 1598, 1493, 1408, 1327, 1288, 1203, 1128, 1038, 994, 759, 697, 593 cm^{-1}. HRMS Calcd for $C_{24}H_{22}NO_3$: $[M+H]^+$, 372.1594. Found: *m*/*z* 372.1599. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98.0/2.0, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 11.1 min, t_{major} = 16.3 min.

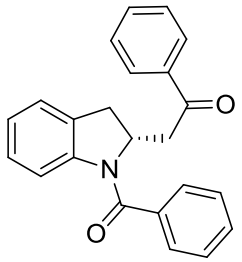
1-Phenyl-2-(*N*-*tert*-butoxycarbonylindolin-2-yl)ethanone (2b).



Yield: 46%, 75% *ee*, pale yellow oil. $[\alpha]_D^{25}$ +66.5 (*c* 2.03, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.80 (br s, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 7.5, 0.50 Hz, 1H), 6.95 (t, 7.5 Hz, 1H), 5.00 (t, *J* = 4.5 Hz, 1H), 3.60 (br s, 1H), 3.46 (dd, *J* = 16.5, 9.0 Hz, 1H), 3.14, (br s, 1H), 2.77 (d, *J* = 16.5, 1H), 1.56 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 198,3, 152.1, 136.8, 133.3, 128.92, 128.86, 128.6, 128.1, 127.5, 125.1, 122.6, 115.4, 81.3, 56.3, 43.4, 34.2, 28.5. TLC: R_f 0.48 (hexane/EtOAc = 3:1). IR (neat): 3249, 3059, 1650, 1523, 1485, 1307, 997, 734, 717, 597, 470 cm^{-1}. HRMS Calcd for $C_{21}H_{24}NO_3$: $[M+H]^+$, 338.1751.

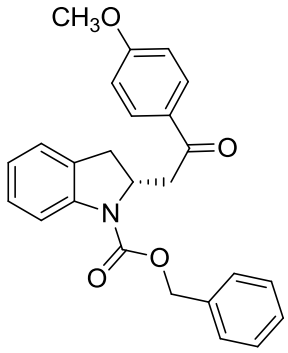
Found: *m*/*z* 338.1747. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98.0/2.0, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 3.77 min, t_{major} = 4.40 min.

1-Phenyl-2-(*N*-benzoylindolin-2-yl)ethanone (2c).



Yield: 48%, 1% *ee*, white solid. $[\alpha]_D^{25}$ +1.2 (*c* 2.01, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.95 (br s, 2H), 7.57–7.44 (m, 9H), 7.20 (d, *J* = 12.5 Hz, 1H), 6.97 (m, 2H), 5.26 (br s, 1H), 3.82 (br s, 1H), 3.49 (dd, *J* = 16.0, 7.5 Hz, 1H), 3.10 (dd, *J* = 16.0, 12.5 Hz, 1H), 2.89 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 198.0, 168.7, 141.4, 136.5, 136.3, 133.4, 131.6, 130.6, 128.8, 128.7, 128.2, 127.4, 127.0, 125.8, 123.8, 116.3, 58.2, 42.4, 33.7. Mp. 106.0–107.0 °C. TLC: R_f 0.45 (hexane/EtOAc = 3:1). IR (KBr): 3056, 2955, 2910, 2374, 1701, 1598, 1493, 1408, 1327, 1288, 1203, 1128, 1038, 994, 759, 697, 593 cm^{-1}. HRMS Calcd for $C_{23}H_{19}NO_2Na$: $[M+Na]^+$, 364.1308. Found: *m*/*z* 364.1297. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90.0/10.0, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 9.16 min, t_{major} = 19.4 min.

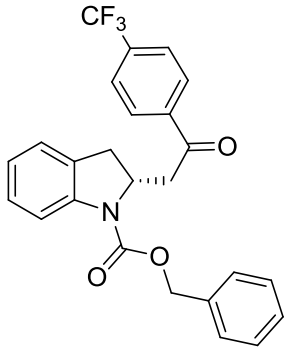
1-(4-Methoxyphenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2d).



Yield: 73%, 84% *ee*, white solid. $[\alpha]_D^{18}$ +31.0 (*c* 1.05, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.10–7.70 (m, 3H), 7.60–7.29 (m, 5H), 7.20 (br s, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.90 (br s, 1H), 6.82 (br s, 1H), 5.28 (br s, 2H), 5.02 (t, *J* = 9.0 Hz, 1H), 3.86 (s, 3H), 3.49 (br s, 1H), 3.43 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.02 (dd, *J* = 16.0, 10.5 Hz, 1H), 2.84 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 196.5, 163.7, 136.1, 130.5, 129.8, 128.7, 128.6, 128.34, 128.31, 128.3, 127.6, 125.2, 123.1, 115.4, 114.2, 113.8, 67.3, 56.5,

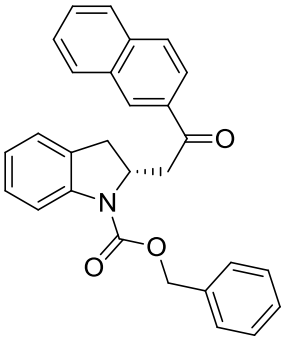
55.5, 43.3, 34.3. Mp. 94.2–94.5 °C. TLC: R_f 0.52 (hexane/EtOAc = 3:1). IR (KBr): 3073, 2965, 2840, 1711, 1664, 1512, 1489, 1399, 1365, 1281, 1262, 1172, 1138, 1022, 751, 697 cm^{-1}. HRMS Calcd for $C_{25}H_{24}NO_4$: $[M+H]^+$, 402.1700. Found: *m*/*z* 402.1692. HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98.0/2.0, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 22.7 min, t_{major} = 24.5 min.

1-(4-Trifluoromethylphenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2e).



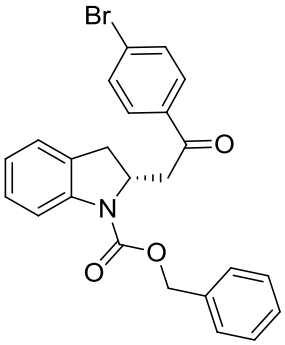
Yield: 79%, 88% *ee*, white solid. $[\alpha]_D^{18}$ +75.0 (*c* 1.00, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.20–7.50 (m, 5H), 7.50–7.30 (m, 5H), 7.22 (br s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.01 (m, 1H), 5.31 (m, 2H), 5.04 (m, 1H), 3.56 (br s, 1H), 3.49 (dd, *J* = 16.0, 9.5 Hz, 1H), 3.14 (dd, *J* = 16.0, 10.5 Hz, 1H), 2.85 (d, *J* = 17.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 197.1, 158.2, 139.1, 135.9, 135.0, 134.6 (q, *J* = 32.7 Hz), 128.7, 128.4, 127.71, 125.70, 125.68, 125.65, 125.2, 123.4 (q, *J* = 272.5 Hz), 123.2, 122.4, 115.4, 67.5, 56.1, 43.9, 34.3. ^{19}F NMR ($CDCl_3$) δ 98.7. Mp. 141.0–142.0 °C. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (KBr): 3066, 3036, 2915, 2369, 1710, 1684, 1487, 1413, 1366, 1331, 1286, 1159, 1123, 1070, 911, 758, 600, 567 cm^{-1}. HRMS Calcd for $C_{25}H_{21}F_3NO_3$: $[M+H]^+$, 440.1468. Found: *m*/*z*440.1462. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 5.1 min, t_{major} = 9.5 min.

1-Naphthyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2f).



Yield: 83%, 88% *ee*, white solid. $[\alpha]_D^{18}$ +5.8 (*c* 0.43, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.35 (br s, 1H), 7.97–7.76 (m, 5H), 7.61 (dt, *J* = 1.5, 7.0 Hz, 1H), 7.53 (dt, *J* = 1.5, 7.0 Hz, 1H), 7.50–7.38 (m, 5H), 7.23 (br s, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.99 (m, 1H), 5.30 (m, 2H), 5.13 (t, *J* = 10.0 Hz, 1H), 3.65 (br s, 1H), 3.52 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.28 (br s, 1H), 2.86 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 198.0, 159.3, 146.3, 136.1, 135.7, 134.0, 132.5, 130.1, 129.6, 128.7, 128.6, 128.5, 128.31, 128,25, 127.8, 127.6, 126.8, 125.2, 123.6, 123.1, 120.9, 115.5, 56.5, 43.7, 34.7, 30.9. Mp. 95.0–96.0 °C. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (KBr): 3067, 3032, 2976, 2938, 2363, 2325, 1705, 1686, 1493, 1410, 1278, 1123, 1013, 824, 755, 699, 483 cm^{-1}. HRMS Calcd for $C_{28}H_{23}NO_3Na$: $[M+Na]^+$, 444.1570. Found: *m*/*z* 444.1567. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 16.8 min, t_{minor} = 20.3 min.

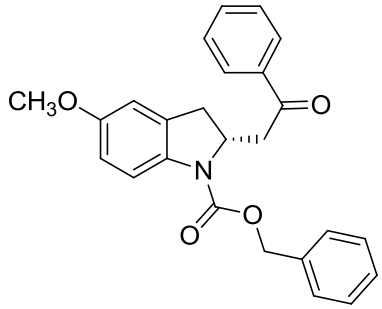
(*R*)-1-(4-Bromophenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2g).



Yield: 75%, 91% *ee*, white solid. $[\alpha]_D^{23}$ +63.9 (*c* 1.80, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.00–7.30 (m, 10H), 7.22 (br s, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.99 (m, 1H), 5.28 (br s, 2H), 5.01 (m, 1H), 3.75 (br s, 1H), 3.46 (dd, *J* = 16.5, 9.5 Hz, 1H), 3.06 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.82 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 197.1, 176.4, 152.2, 144.6, 136.0, 135.2, 132.0, 129.6, 128.7, 128.6, 128.41, 128.35, 127.7, 125.2, 123.2,

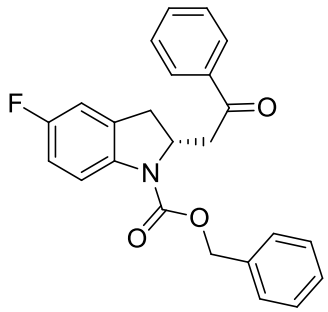
115.5, 67.4, 56.3, 43.7, 34.2. Mp. 106.0–107.0 °C. TLC: R_f 0.49 (hexane/EtOAc = 3:1). IR (KBr): 3035, 2949, 2368, 1710, 1671, 1586, 1528, 1487, 1414, 1369, 1286, 1210, 1147, 1047, 991, 816, 749, 694, 609, 576 cm^{-1}. HRMS Calcd for $C_{24}H_{21}BrNO_3$: $[M+H]^+$, 450.0699. Found: *m*/*z* 450.0713. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 24.1 min, t_{minor} = 49.2 min.

1-Phenyl-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2h).



Yield: 82%, 83% *ee*, white solid. $[\alpha]_D^{18}$ +65.4 (*c* 2.98, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.88 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.47–7.34 (m, 8H), 6.75 (m, 2H), 5.26 (m, 2H), 5.03 (br s, 1H), 3.76 (s, 3H), 3.54 (m, 1H), 3.44 (dd, *J* = 12.5, 9.5 Hz, 1H), 3.10 (dd, *J* = 16.0, 11.0 Hz, 1H), 2.79 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 198.2, 159.9, 156.1, 152.3, 136.6, 136.2, 133.4, 131.1, 128.7, 128.6, 128.3, 128.1, 120.1, 115.9, 112.4, 111.4, 67.1, 56.4, 55.7, 43.7, 34.7. Mp. 115.0–116.0 °C. TLC: R_f 0.45 (hexane/EtOAc = 3:1). IR (KBr): 3234, 3035, 2965, 2365, 1685, 1669, 1624, 1585, 1534, 1266, 1253, 1071, 1028, 861, 743, 697, 492 cm^{-1}. HRMS Calcd for $C_{25}H_{24}NO_4$: $[M+H]^+$, 402.1700. Found: *m*/*z* 402.1695. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 10.0 min, t_{major} = 24.0 min.

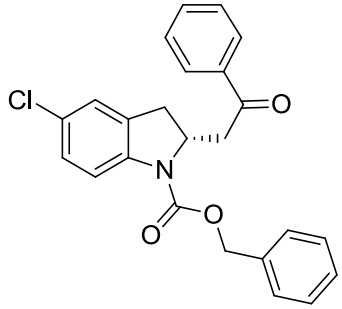
1-Phenyl-2-(*N*-benzyloxycarbony-5-fluorolindolin-2-yl)ethanone (2i).



Yield: 69%, 82% *ee*, white solid. $[\alpha]_D^{18}$ +23.3 (*c* 0.43, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.86 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.39 (m, 7H), 7.23 (br s, 1H), 7.16 (d, *J* = 7.0,

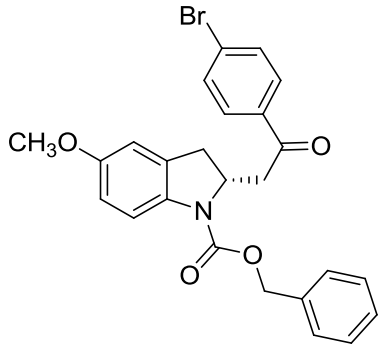
1H), 6.99 (t, *J* = 7.0 Hz, 1H), 5.29 (br s, 2H), 5.06 (t, *J* = 9.0 Hz, 1H), 3.53 (br s, 1H), 3.48 (dd, *J* = 16.5, 9.5 Hz, 1H), 3.12 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.84 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 198.1, 152.2, 141.6, 136.6, 136.05, 135.99, 135.5, 133.3, 128.65, 128.62, 128.56 (d, *J* = 242.9 Hz), 128.28, 128.1, 125.2, 123.1, 115.4, 67.2, 56.3, 43.6, 31.7. ^{19}F NMR ($CDCl_3$) δ 77.1. Mp. 110.0–111.0 °C. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (KBr): 3054, 2932, 2857, 2354, 1905, 1712, 1672, 1600, 1486, 1450, 1406, 1368, 1283, 1213, 1145, 1047, 1020, 995, 867, 755, 730, 690, 605 cm^{-1}. HRMS Calcd for $C_{24}H_{19}FNO_4$: $[M+O-H]^-$, 404.1304. Found: *m*/*z* 404.1286. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 4.6 min, t_{major} = 6.4 min.

1-Phenyl-2-(*N*-benzyloxycarbony-5-chlorolindolin-2-yl)ethanone (2j).



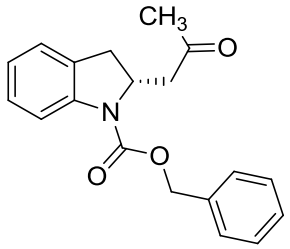
Yield: 82%, 84% *ee*, white solid. $[\alpha]_D^{18}$ +6.2 (*c* 0.65, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.80 (m, 3H), 7.56 (m, 1H), 7.36 (m, 7H), 7.17 (br s, 1H), 7.11 (m, 1H), 5.27 (br s, 2H), 5.05 (t, *J* = 9.5 Hz, 1H), 3.53 (br s, 1H), 3.45 (dd, *J* = 16.5, 9.5 Hz, 1H), 3.11 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.81 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 197.8, 166.0, 136.5, 135.8, 134.4, 133.5, 131.5, 129.5, 128.71, 128.68, 128.45, 128.35, 128.1, 127.6, 125.3, 116.3, 67.8, 56.6, 43.5, 31.2. Mp. 122.0–123.0 °C. TLC: R_f 0.52 (hexane/EtOAc = 3:1). IR (KBr): 3066, 3032, 2928, 2354, 1700, 1666, 1595, 1486, 1399, 1359, 1293, 1227, 1144, 1025, 812, 766, 751, 694, 686, 615, 589 cm^{-1}. HRMS Calcd for $C_{24}H_{19}ClNO_4$: $[M+O-H]^-$, 420.1008. Found: *m*/*z* 420.1008. HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 5.8 min, t_{major} = 9.9 min.

1-(4-Bromophenyl)-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2k).



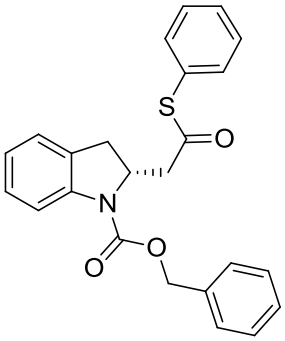
Yield: 53%, 93% *ee*, white solid. $[\alpha]_D^{18}$ +36.8 (*c* 3.53, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.90–7.50 (m, 3H), 7.48–7.26 (m, 7H), 6.74 (br s, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 5.25 (m, 2H), 4.99 (br s, 1H), 3.76 (s, 3H), 3.48 (br s, 1H), 3.43 (dd, *J* = 16.5, 9.0 Hz, 1H), 3.05 (dd, *J* = 16.5, 10.0, 1H), 2.79 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 197.1, 156.1, 142.6, 138.1, 136.1, 135.2, 131.94, 131.90, 129.6, 128.7, 128.6, 128.4, 115.9, 112.5, 111.4, 109.7, 67.2, 56.3, 55.7, 43.6, 34.6. Mp. 118.0–119.0 °C. TLC: R_f 0.51 (hexane/EtOAc = 3:1). IR (KBr): 3461, 3033, 2954, 2854, 1685, 1586, 1493, 1455, 1399, 1364, 1327, 1274, 1208, 1126, 1071, 1024, 990, 813, 742, 698, 572, 511 cm^{-1}. HRMS Calcd for $C_{25}H_{23}BrNO_4$: $[M+H]^+$, 480.0805. Found: *m*/*z* 480.0813. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 10.0 min, t_{major} = 14.3 min.

1-Methyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2l).



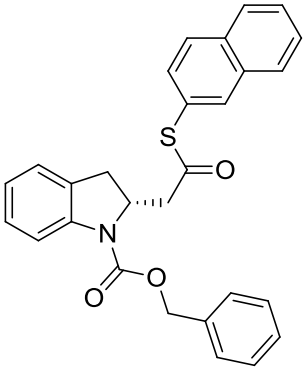
Yield: 18%, 74% *ee*, white solid. ^{1}H NMR ($CDCl_3$) δ (19H)7.84 (br s, 1H), 7.34 (m, 5H), 7.18 (br s, 1H), 7.14 (dd, *J* = 7.0, 1.0 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 5.28 (m, 2H), 4.86 (t, *J* = 10.0 Hz, 1H), 3.45 (dd, *J* = 16.5, 9.5 Hz, 1H), 2.97 (br s, 1H), 2.67 (m, 2H), 2.10 (br s, 3H). ^{13}C NMR ($CDCl_3$) δ 181.5, 165.1, 161.2, 146.1, 141.4, 130.5, 128.9, 128.6, 128.4, 127.9, 123.3, 115.7, 68.1, 58.0, 46.3, 36.4, 30.7. TLC: R_f 0.40 (hexane/EtOAc = 3:1). HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98.0/2.0, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 10.2 min, t_{minor} = 11.7 min. The characterization data were identical to those reported in the literature.[7]

1-Phenylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2m).



Yield: 55%, 52% *ee*, white solid. $[\alpha]_D^{18}$ +39.3 (*c* 1.78, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ (21H)7.86 (br s, 1H), 7.46–7.27 (m, 10H), 7.23 (br s, 1H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.00 (t, *J* = 7.0 Hz, 1H), 5.32 (br s, 2H), 4.92 (br s, 1H), 3.41 (dd, *J* = 16.5, 9.5 Hz, 1H), 3.15 (br s, 1H), 2.96 (dd, *J* = 16.5, 2.0 Hz, 1H), 2.91 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 194.9, 158.3, 143.5, 137.3, 136.0, 134.4, 129.5, 129.2, 128.7, 128.3, 128.2, 127.7, 127.3, 125.2, 123.2, 115.5, 67.4, 56.5 47.8, 33.9. Mp. 88.5–89.5 °C. TLC: R_f 0.45 (hexane/EtOAc = 3:1). IR (KBr): 3473, 3313, 3001, 2939, 2361, 1693, 1641, 1540, 1451, 1306, 1234, 1059, 1016, 918, 752, 694, 651 cm^{-1}. HRMS Calcd for $C_{24}H_{22}NO_3S$: $[M+H]^+$, 404.1315. Found: *m*/*z* 404.1308. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 8.7 min, t_{major} = 12.1 min.

1-Naphthalen-2-ylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2n).



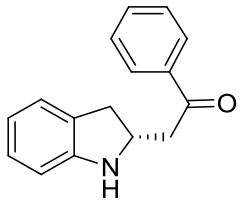
Yield: 32%, 69% *ee*, white solid. $[\alpha]_D^{18}$ +38.0 (*c* 1.95, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ (23H) 8.10–7.80 (m, 3H), 7.55 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.46–7.30 (m, 9H), 7.20 (br s, 1H), 7.15 (dt, *J* = 7.5, 0.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.29 (br s, 2H), 5.05 (m, 1H), 3.80 (br s, 1H), 3.47 (dd, *J* = 16.5, 9.5 Hz, 1H), 3.11 (dd, *J* = 16.5, 10.0 Hz, 1H), 2.83 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 198.1, 163.1, 152.5, 141.6, 136.7, 136.1, 133.3, 133.1, 129.9, 128.7, 128.6, 128.33, 128.30, 128.1, 127.6, 125.2, 123.1, 122.0, 115.5, 114.0, 111.5, 67.4, 56.4, 43.5, 34.4. Mp. 125.0–125.5 °C. TLC: R_f 0.50

(hexane/EtOAc = 3:1). IR (KBr): 3049, 2957, 2373, 1707, 1672, 1597, 1485, 1454, 1405, 1364, 1281, 1211, 1140, 1040, 976, 754, 697, 604, 576 cm^{-1}. HRMS Calcd for $C_{28}H_{24}NO_3S$: $[M+H]^+$, 455.1505. Found: *m*/*z* 455.1513. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 15.4 min, t_{major} = 22.0 min.

Procedure for deprotection of 2b

After Pd/C (0.010 g, 10%, 10 mol %) in a 20mL flask was degassed under reduced pressure, H_2 gas (balloon) was introduced into the flask, and EtOH (0.15 mL) was added. To the mixture, a solution of **2a** (0.037 mg, 0.10 mmol) in CH_2Cl_2 (0.2 mL) and EtOH (0.45mL) was added. After being stirred for 6 h, the reaction mixuture was diluted with hexane/EtOAc (v/v = 1/1), passed through a short celite pad to remove Pd/C, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 2/1) as an eluent gave (*R*)-1-phenyl 2-(idolin-2-yl)acetate (**4**).

(*R*)-1-Phenyl-2-(indolin-2-yl)ethanone (4).



Yield: 80%, 87% *ee*, colorless oil.

$[\alpha]_D^{18}$ +24.4 (*c* 2.08, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ (14H.NH が出ていない？)7.84 (br s, 1H), 7.47 (br s, 1H), 7.36 (m, 3H), 7.31 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 5.32 (m, 1H), 5.23 (m, 1H), 4.82 (m, 2H), 3.37 (dd, *J* = 16.5, 10.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 194.6, 144.3, 128.6, 128.5, 128.24, 128.20, 127.5, 125.5, 125.0, 123.0, 115.6, 67.1, 57.1, 33.9. TLC: R_f 0.48 (hexane/EtOAc = 2:1). IR (neat): 3442, 3064, 2923, 2362, 2331, 1688, 1603, 1486, 1465, 1419, 1368, 1126, 1042, 668, 461 cm^{-1}. HRMS Calcd for $C_{16}H_{16}NO$: $[M+H]^+$, 238.1226. Found: *m*/*z* 238.1225. HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 7.7 min, t_{minor} = 20.3 min.

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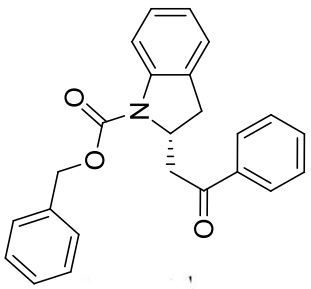
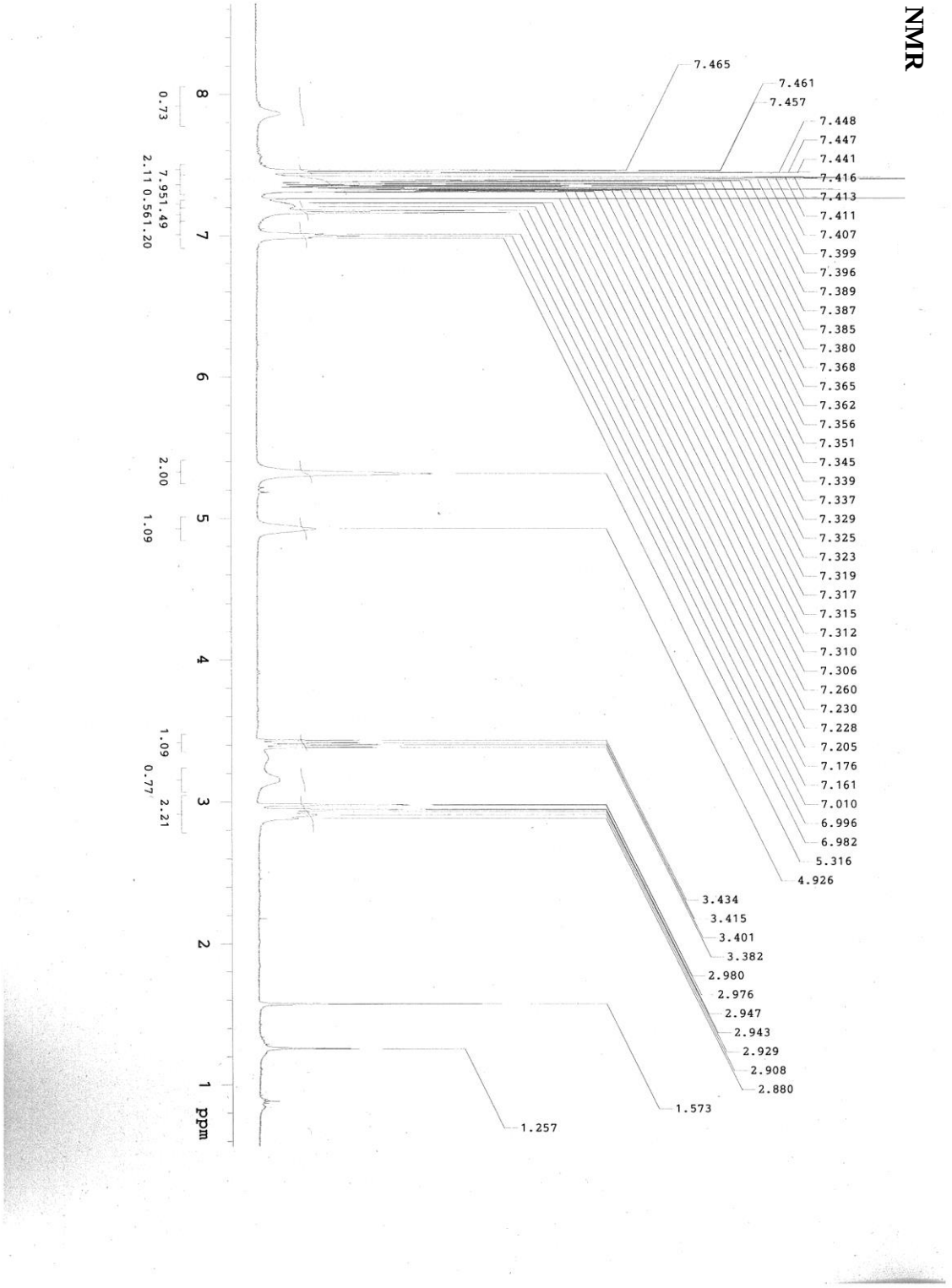
NMRSpectra (^{1}H, ^{13}C) of Products

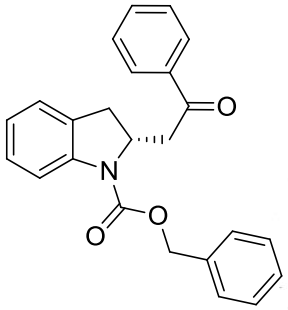
1-Phenyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2a)



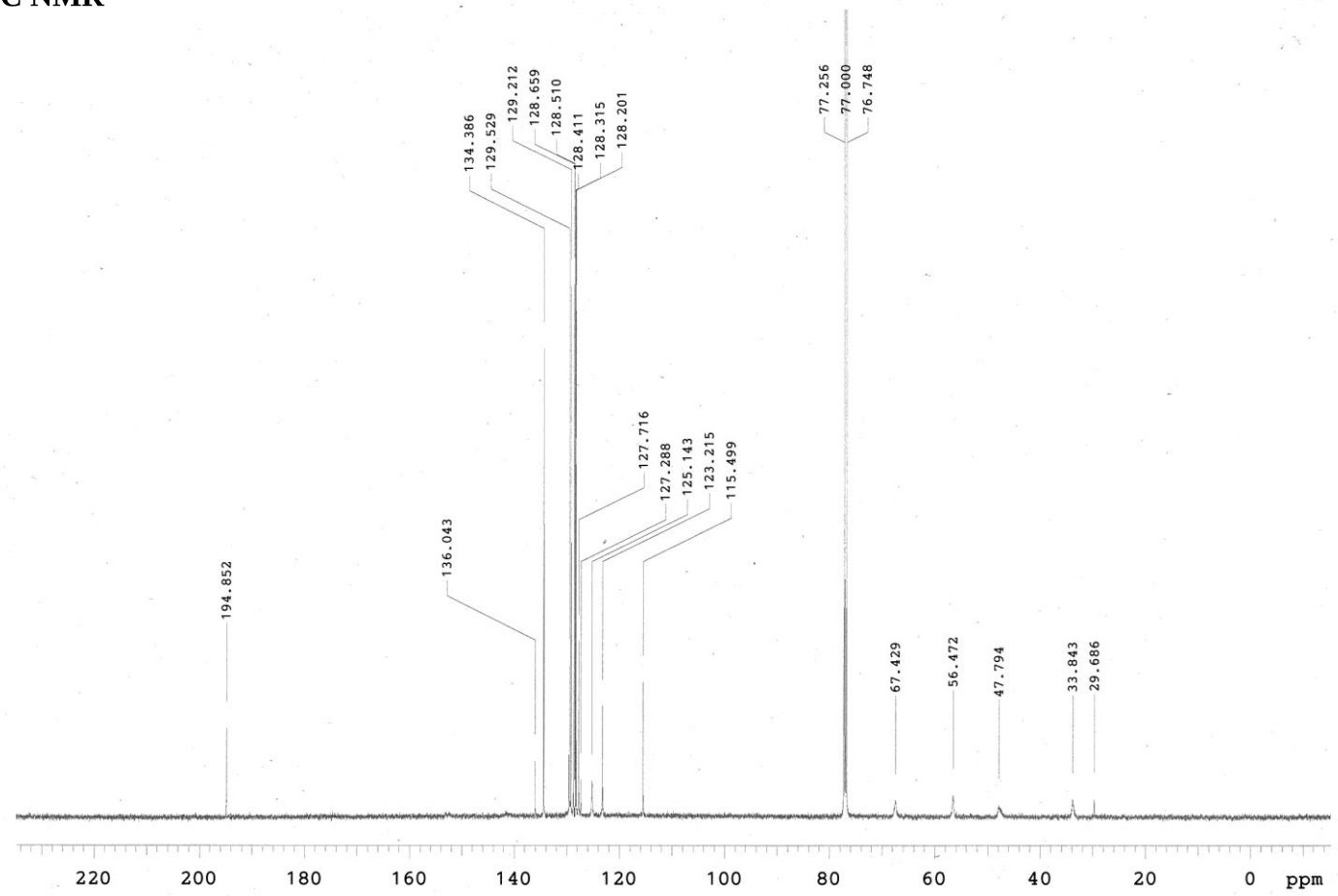
^{1}H NMR



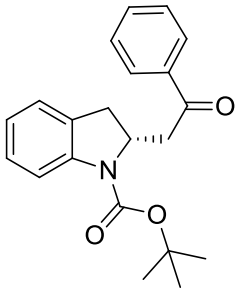
1-Phenyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2a)



^{13}C NMR



1-Phenyl-2-(*N*-*tert*-butoxycarbonylindolin-2-yl)ethanone (2b)



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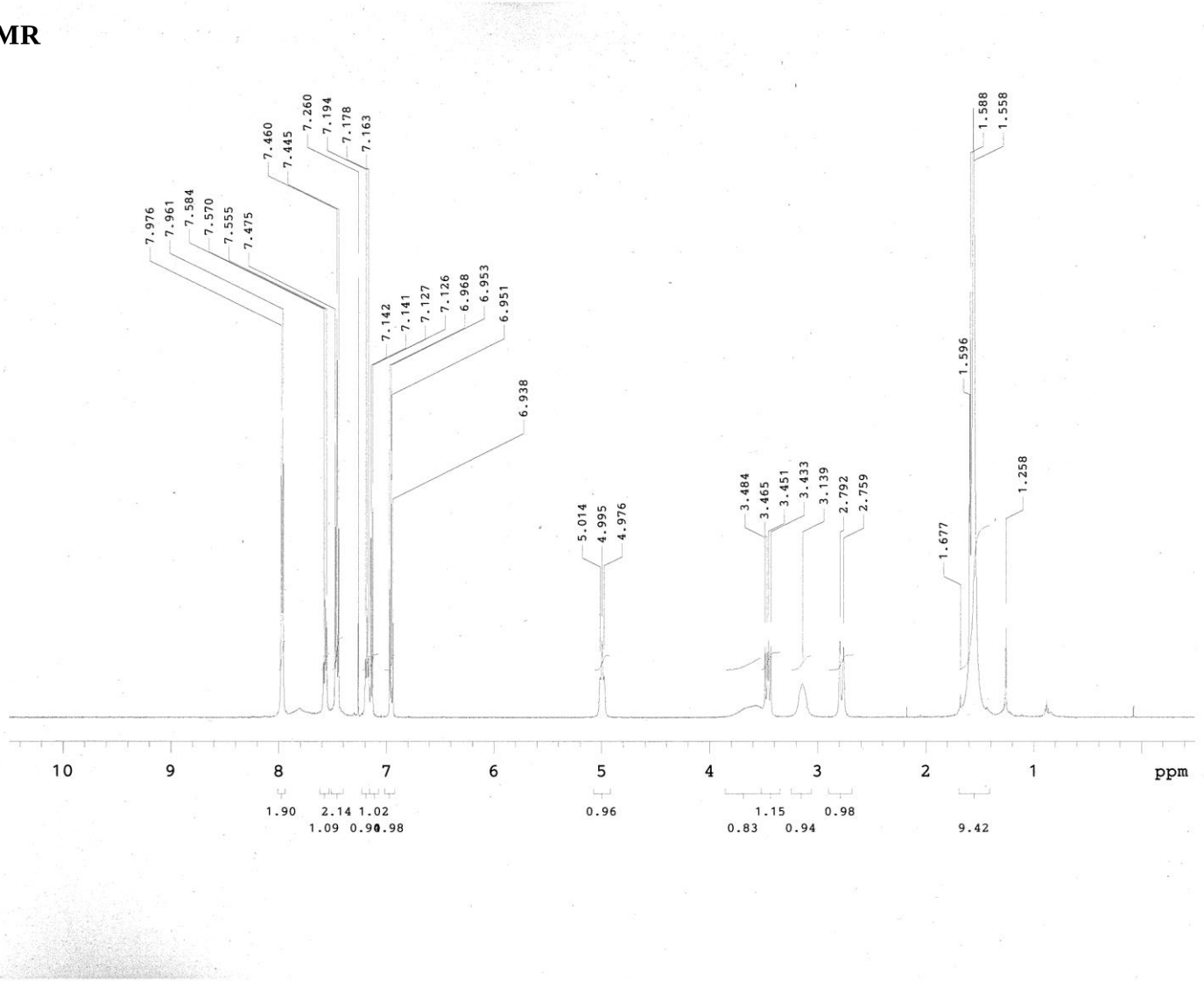
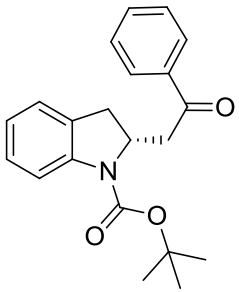


1-Phenyl-2-(*N*-*tert*-butoxycarbonylindolin-2-yl)ethanone (2b)



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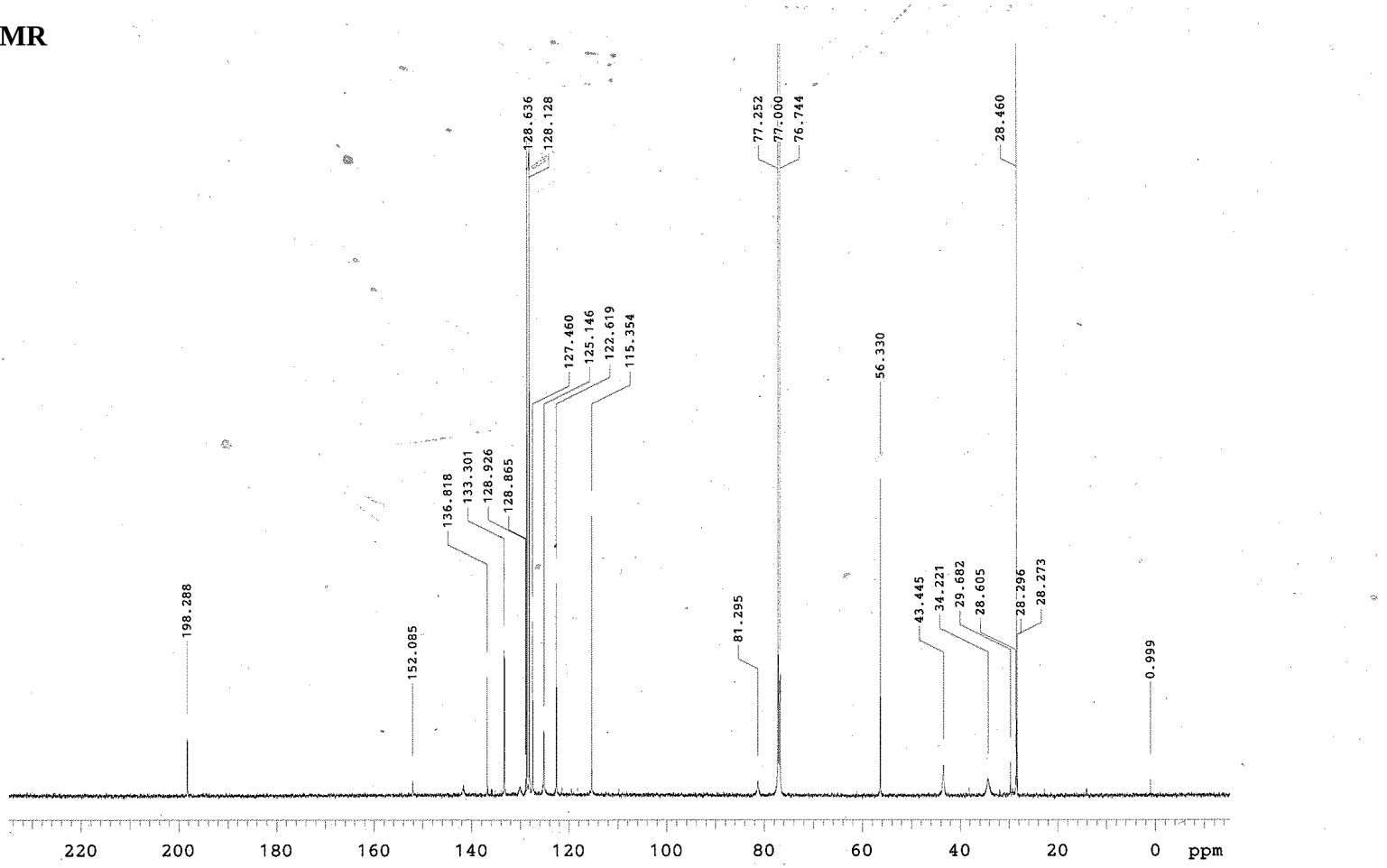
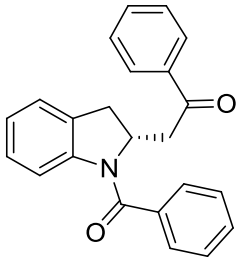


1-Phenyl-2-(*N*-benzoylindolin-2-yl)ethanone (2c)



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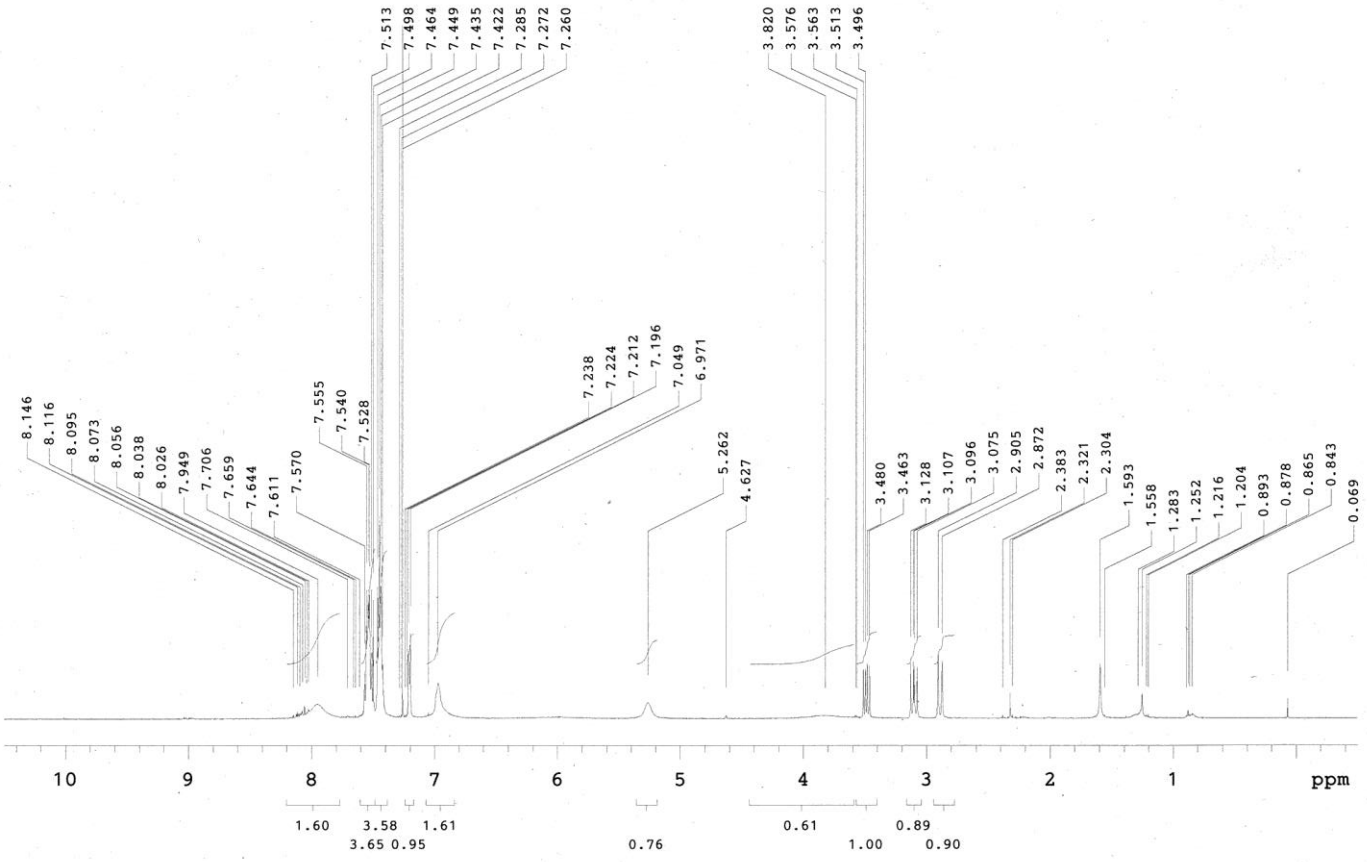
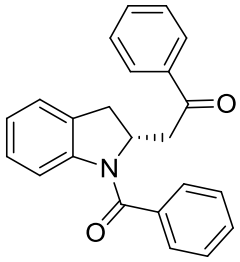
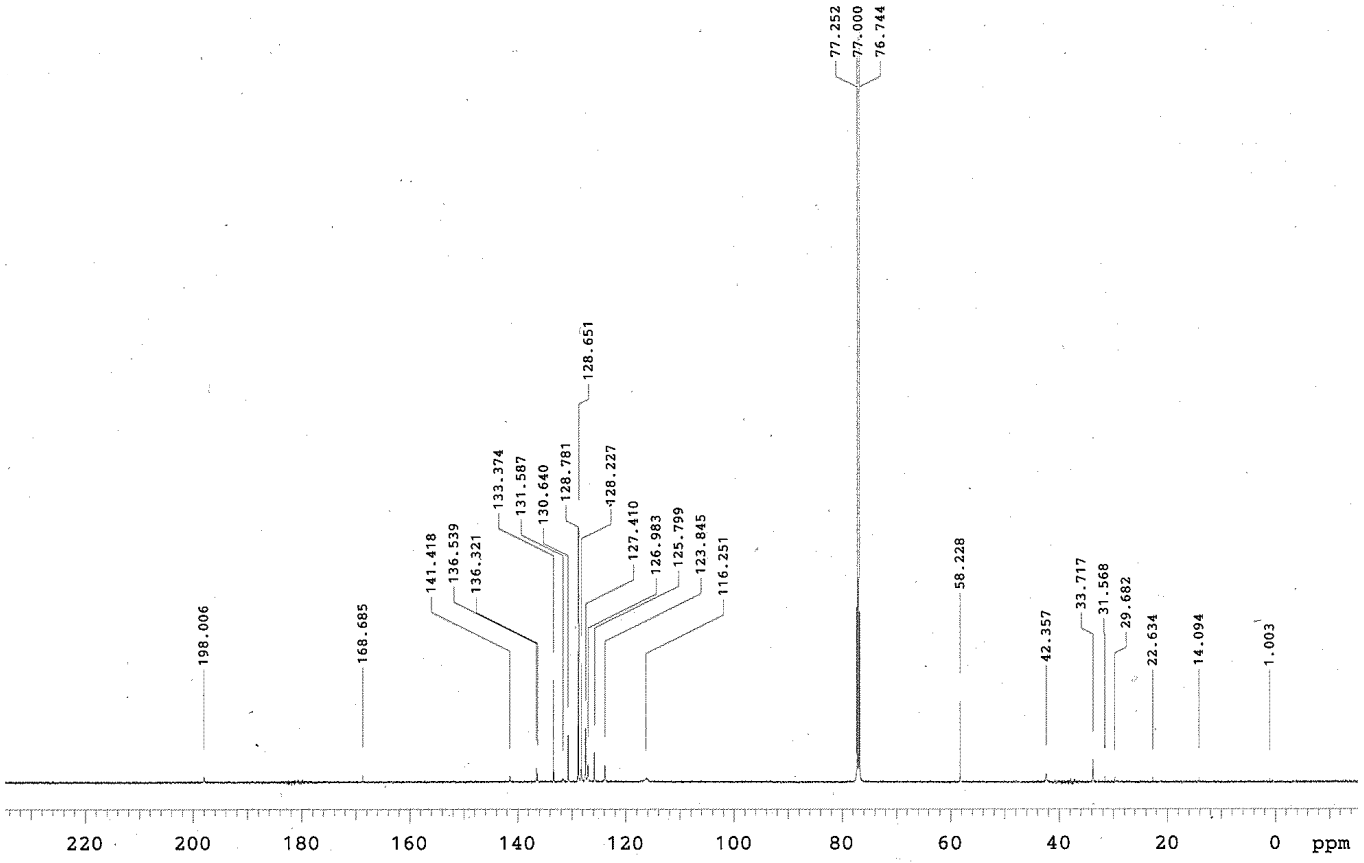


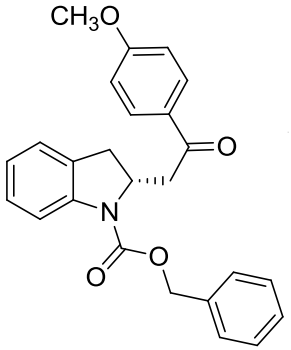
1-Phenyl-2-(*N*-benzoylindolin-2-yl)ethanone (2c)



^{13}C NMR



1-(4-Methoxyphenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2d)



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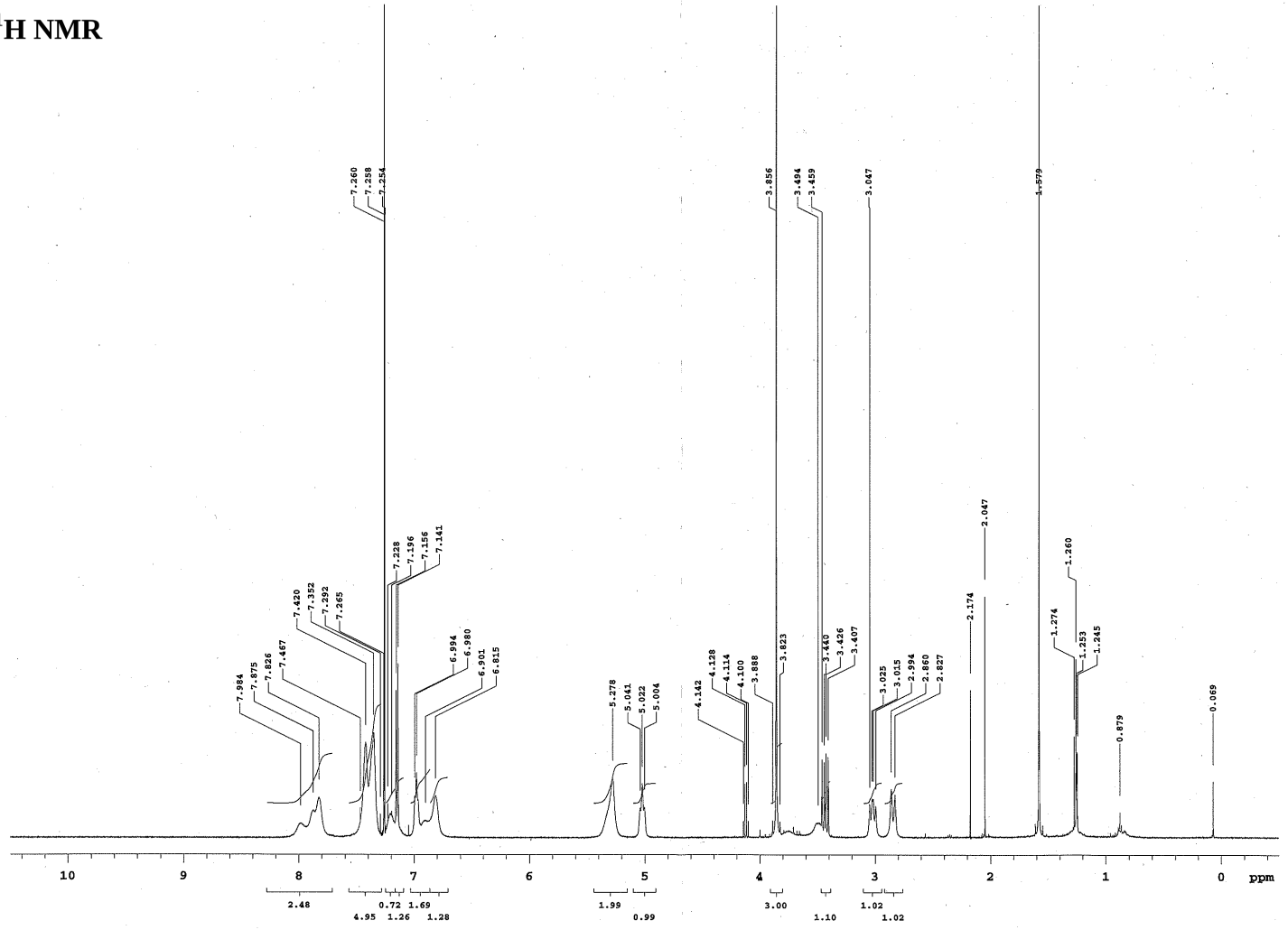

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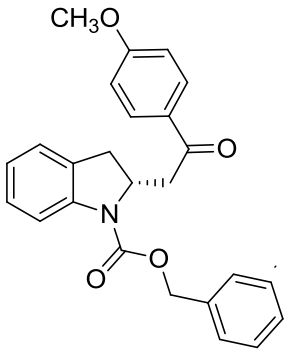
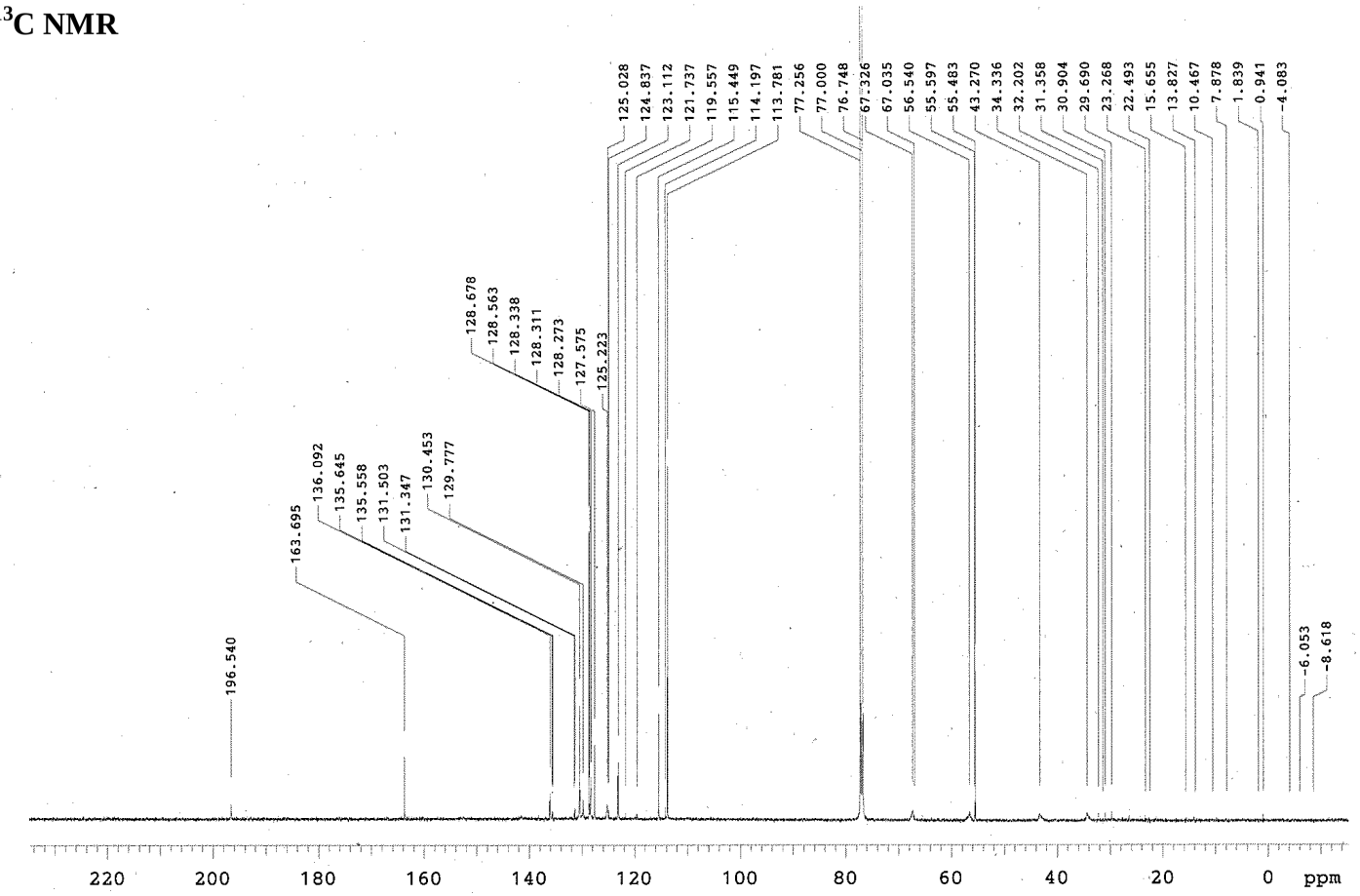
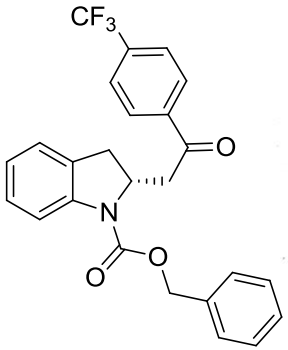


^{13}C NMR



1-(4-Trifluoromethylphenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2e)



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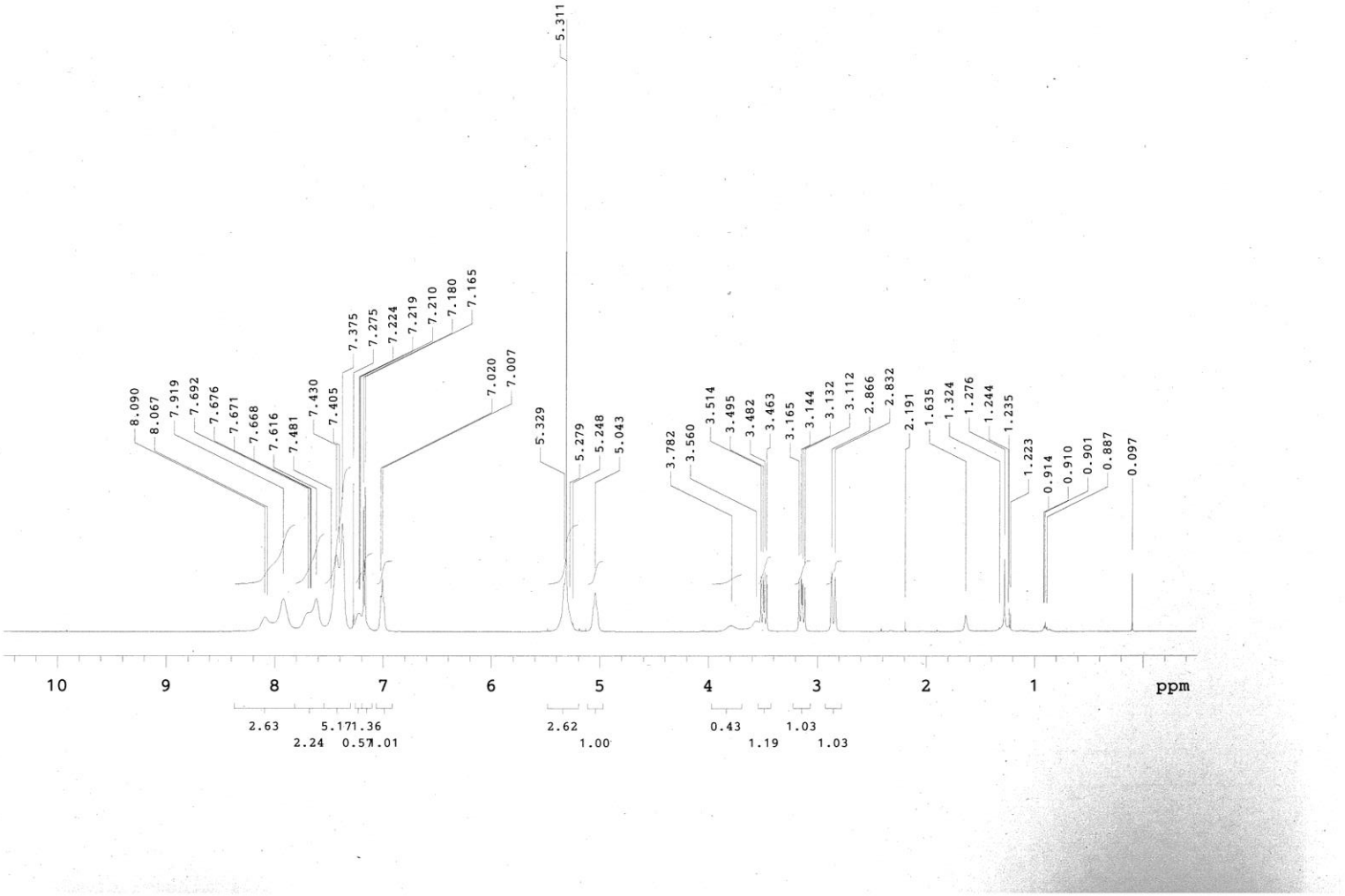
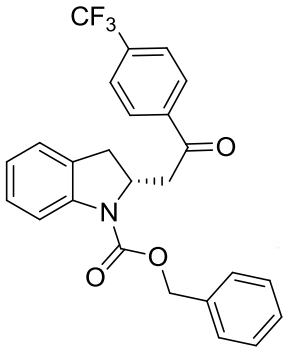


1-(4-Trifluoromethylphenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2e)



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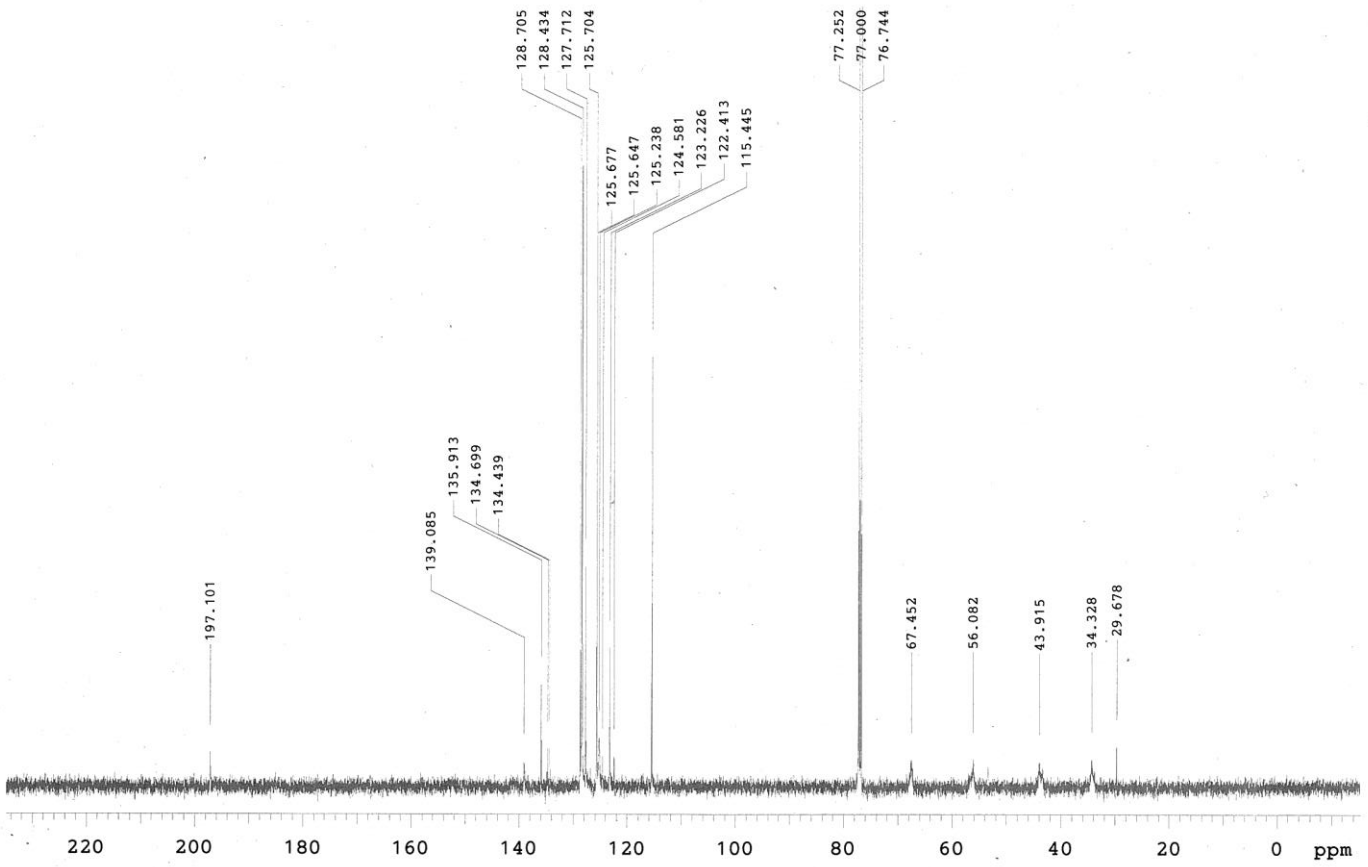
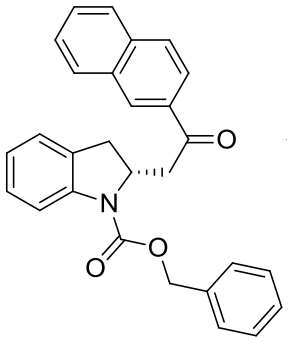


1-Naphthyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2f)



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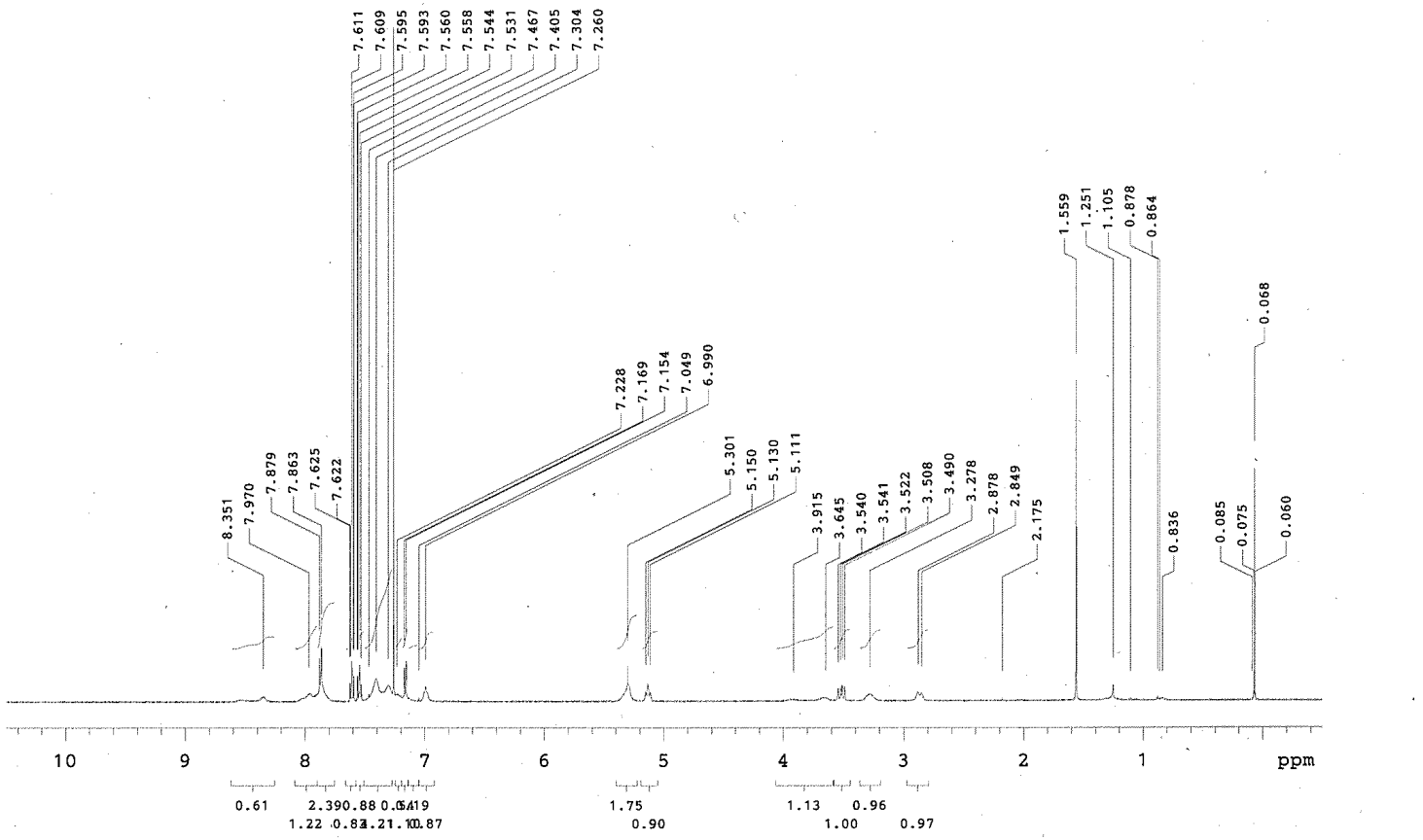
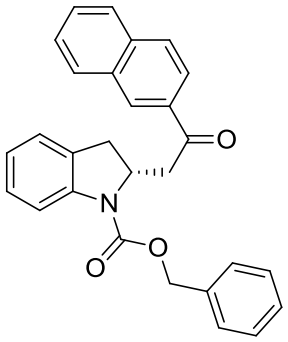


1-Naphthyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2f)



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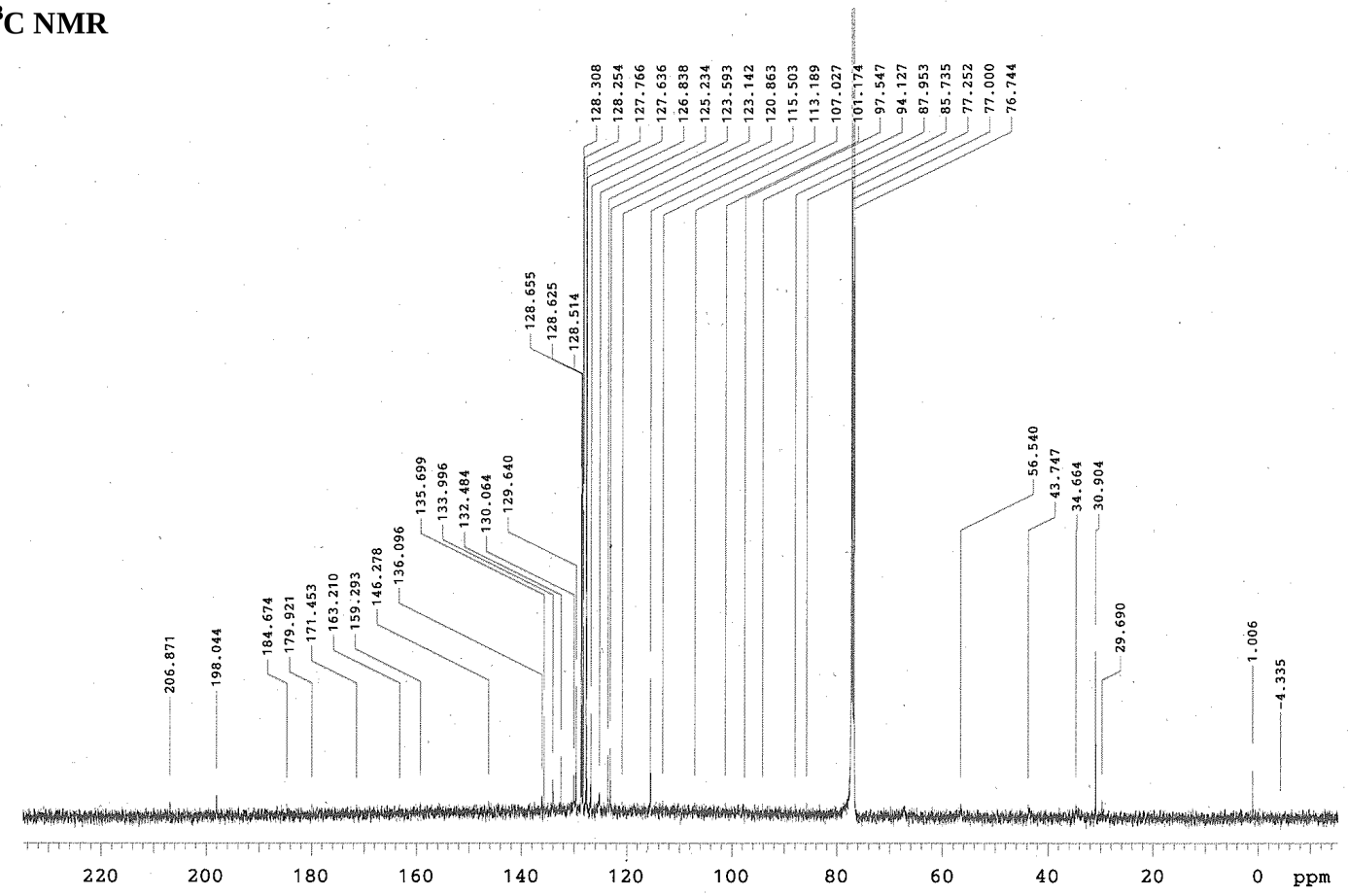
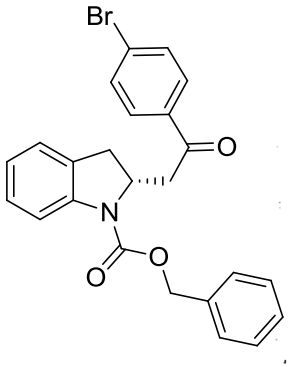


(*R*)-1-(4-Bromophenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2g)



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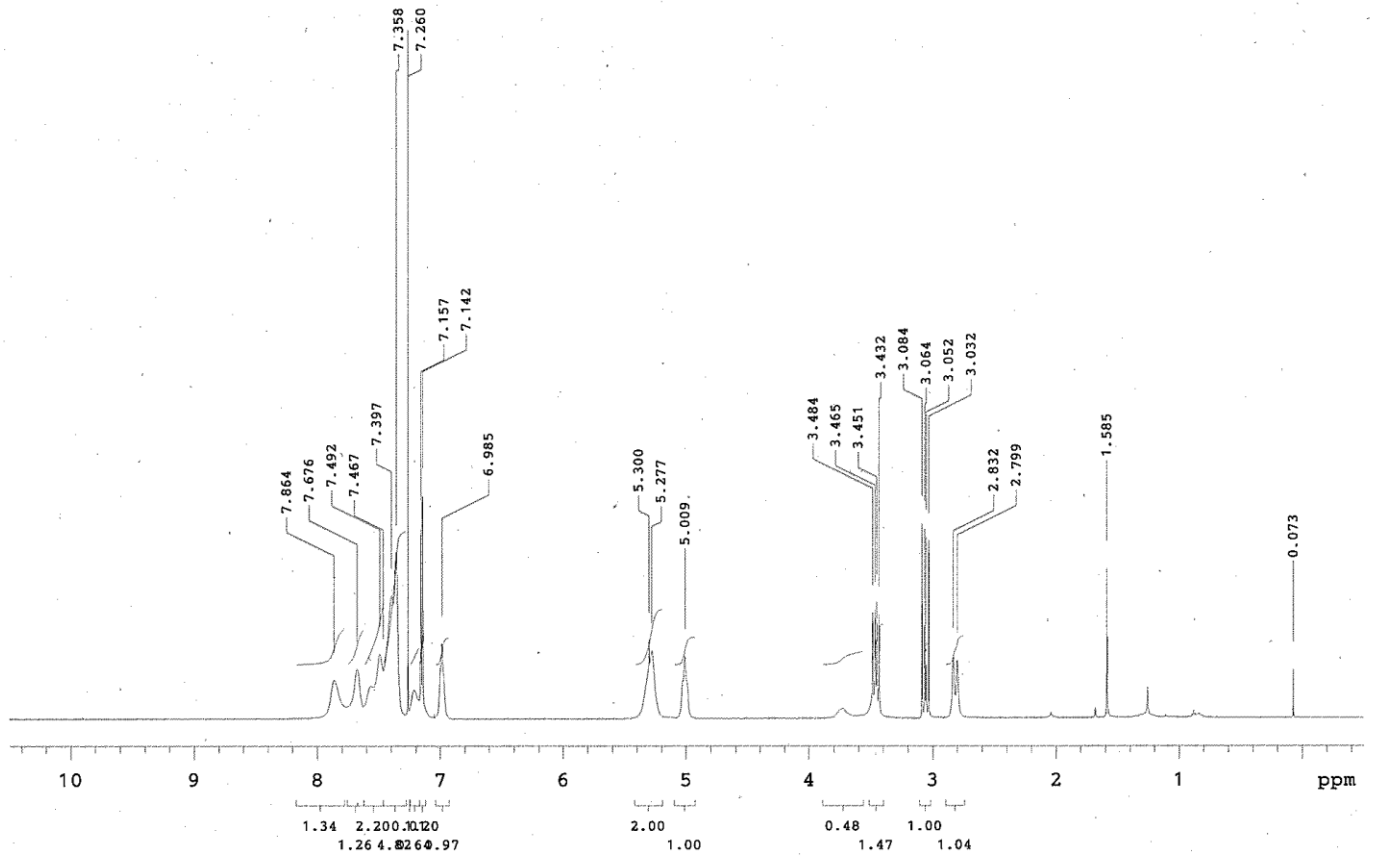
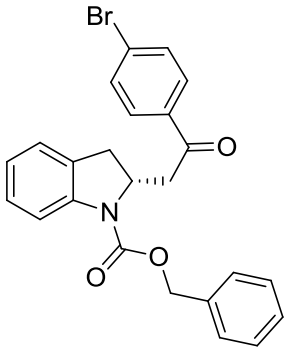


(*R*)-1-(4-Bromophenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2g)



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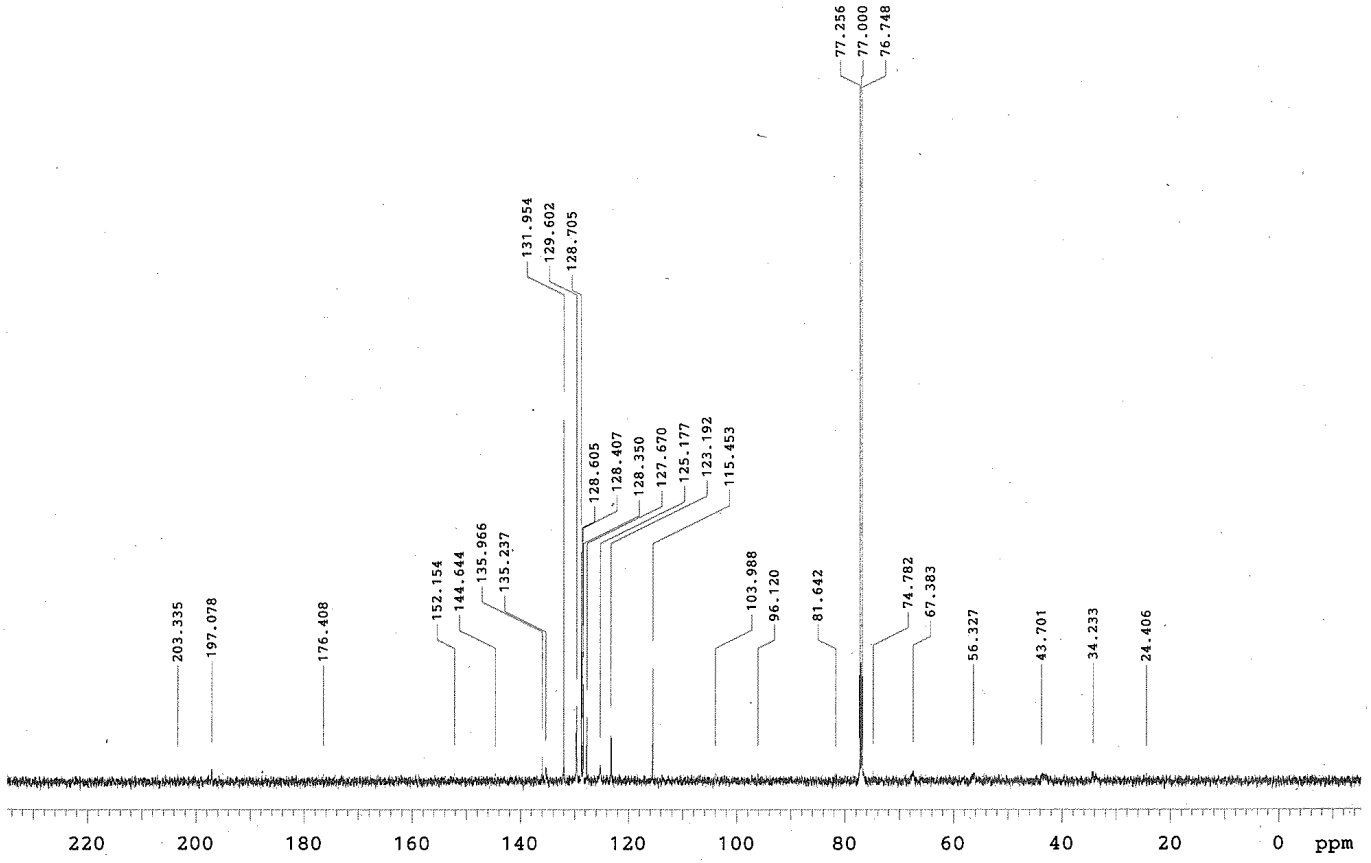
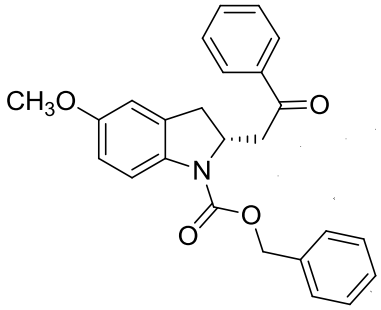


1-Phenyl-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2h)



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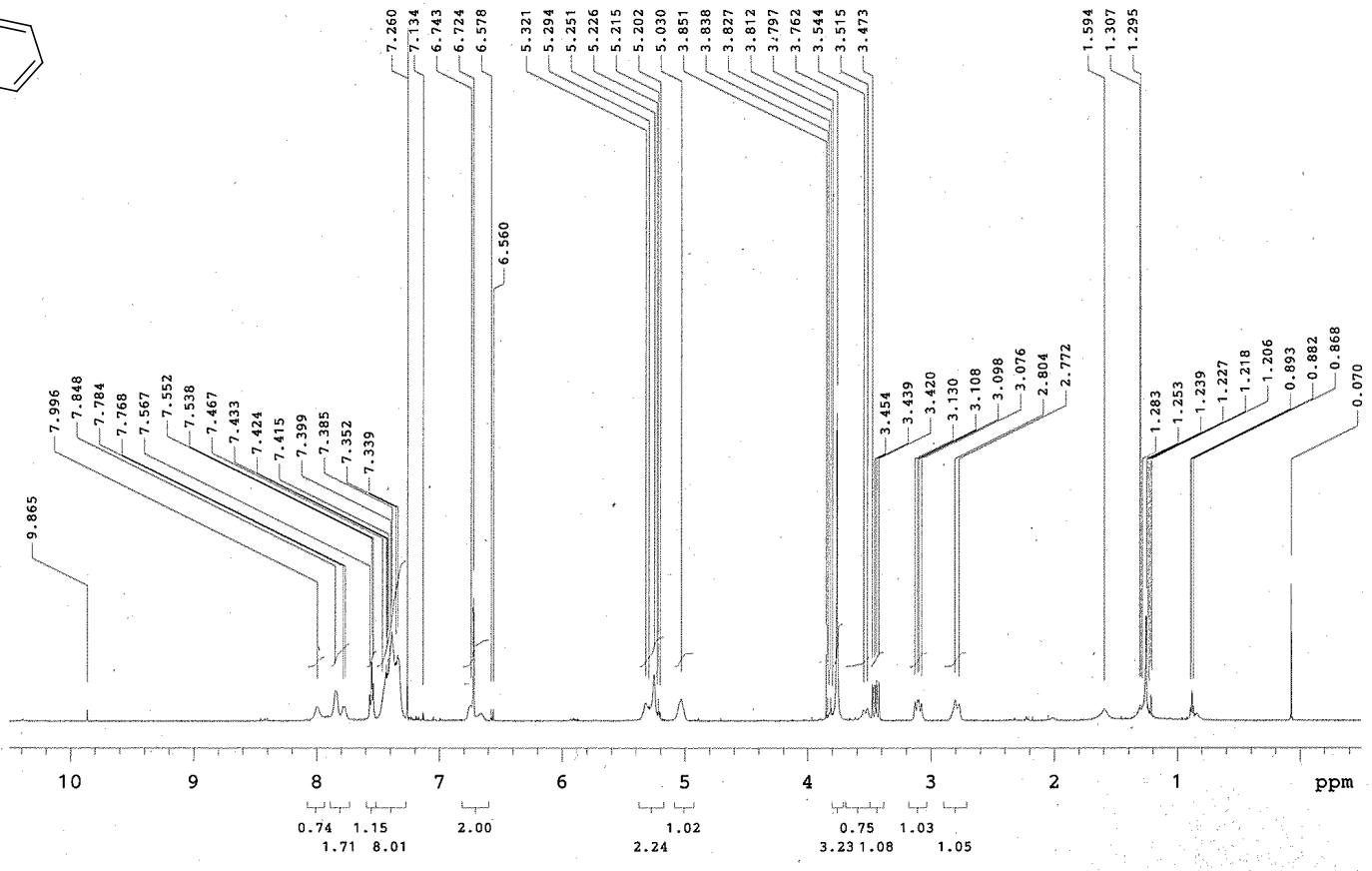
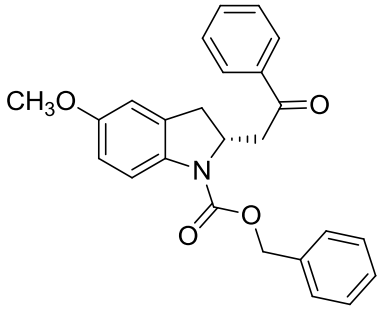


1-Phenyl-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2h)



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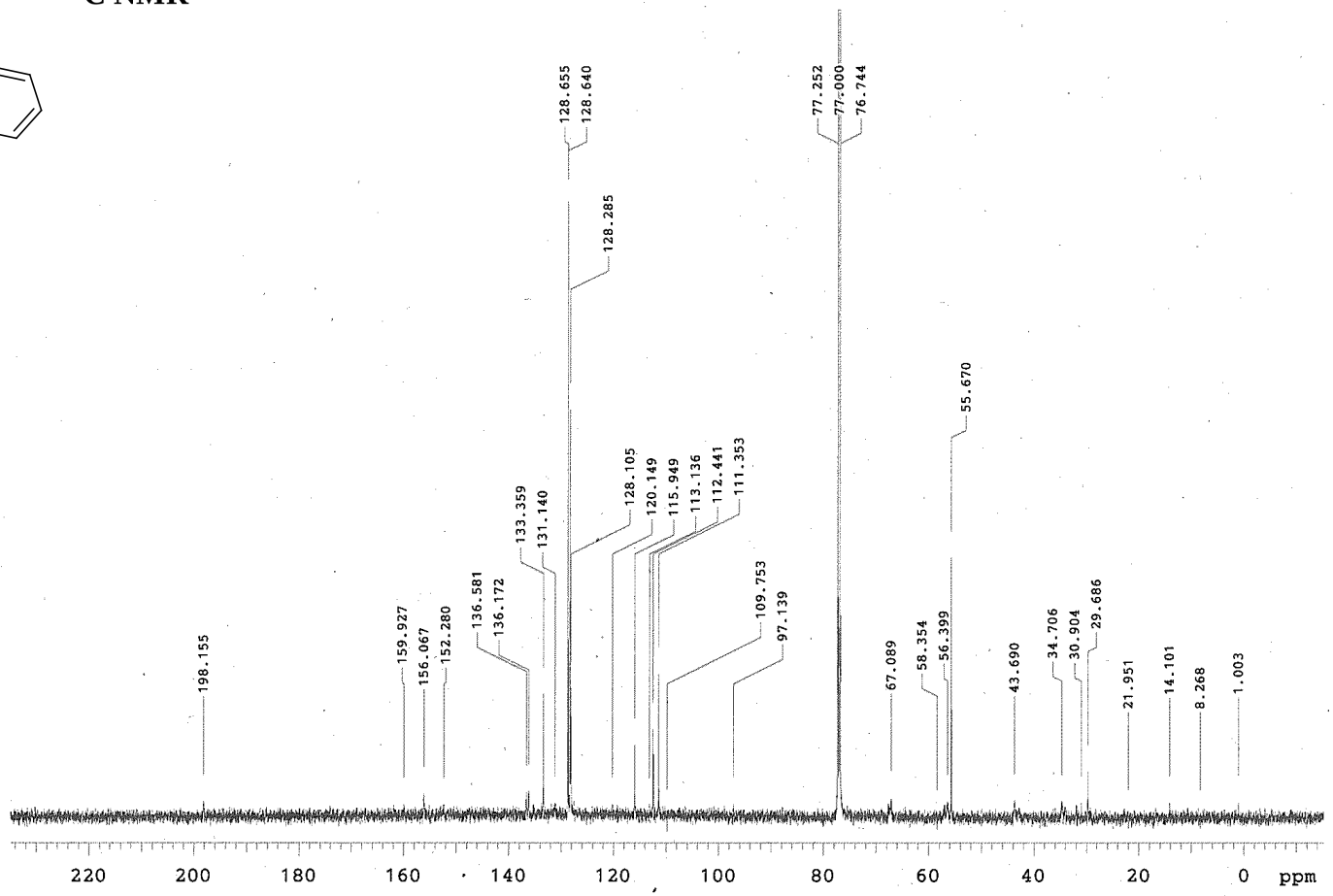
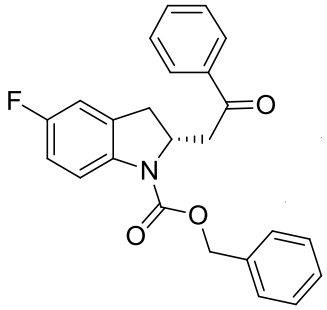


1-Phenyl-2-(*N*-benzyloxycarbony-5-fluorolindolin-2-yl)ethanone (2i)



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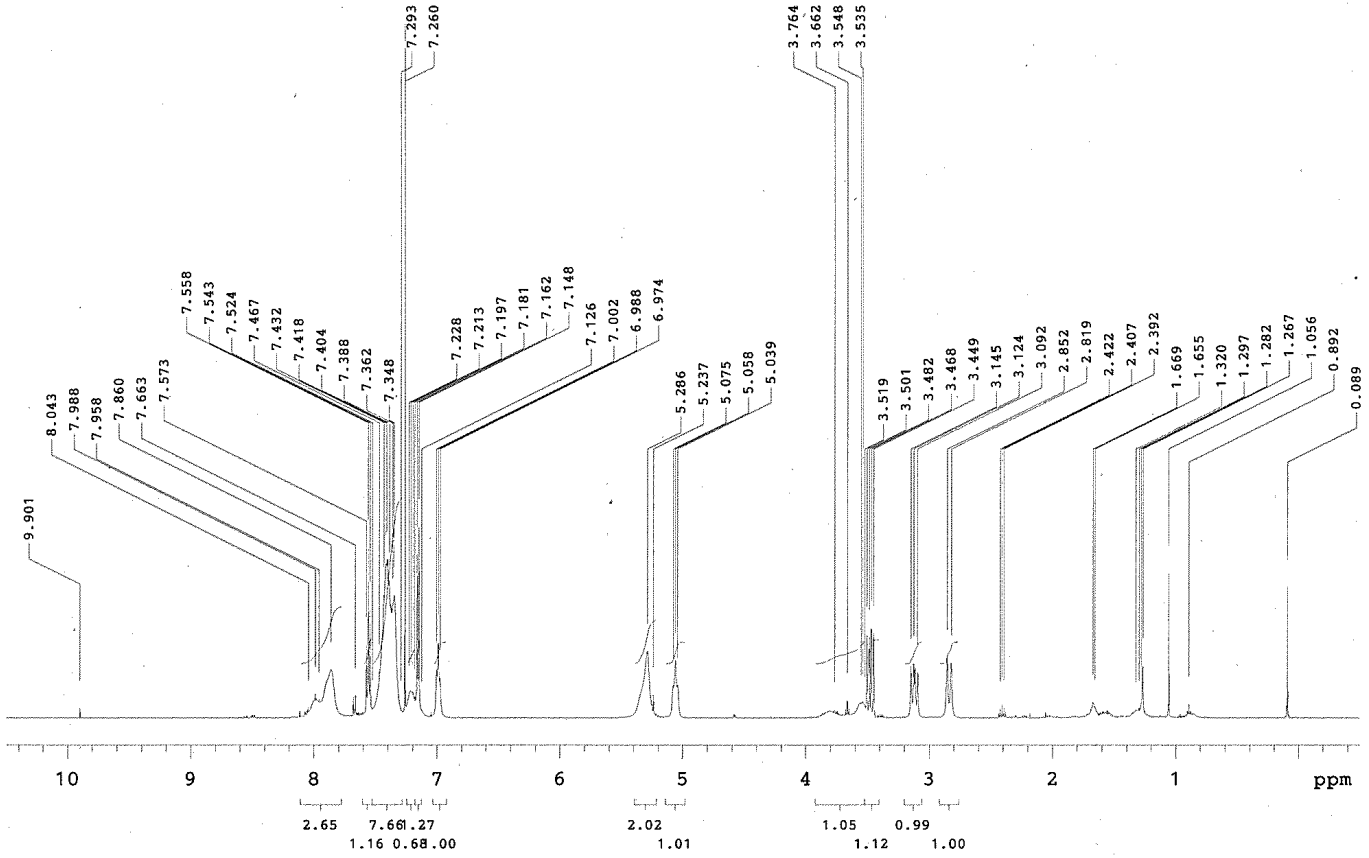
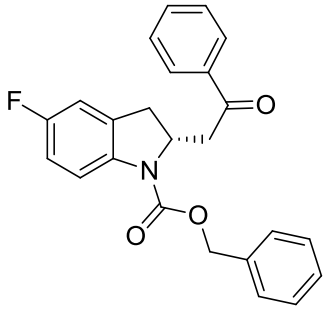


1-Phenyl-2-(*N*-benzyloxycarbony-5-fluorolindolin-2-yl)ethanone (2i)



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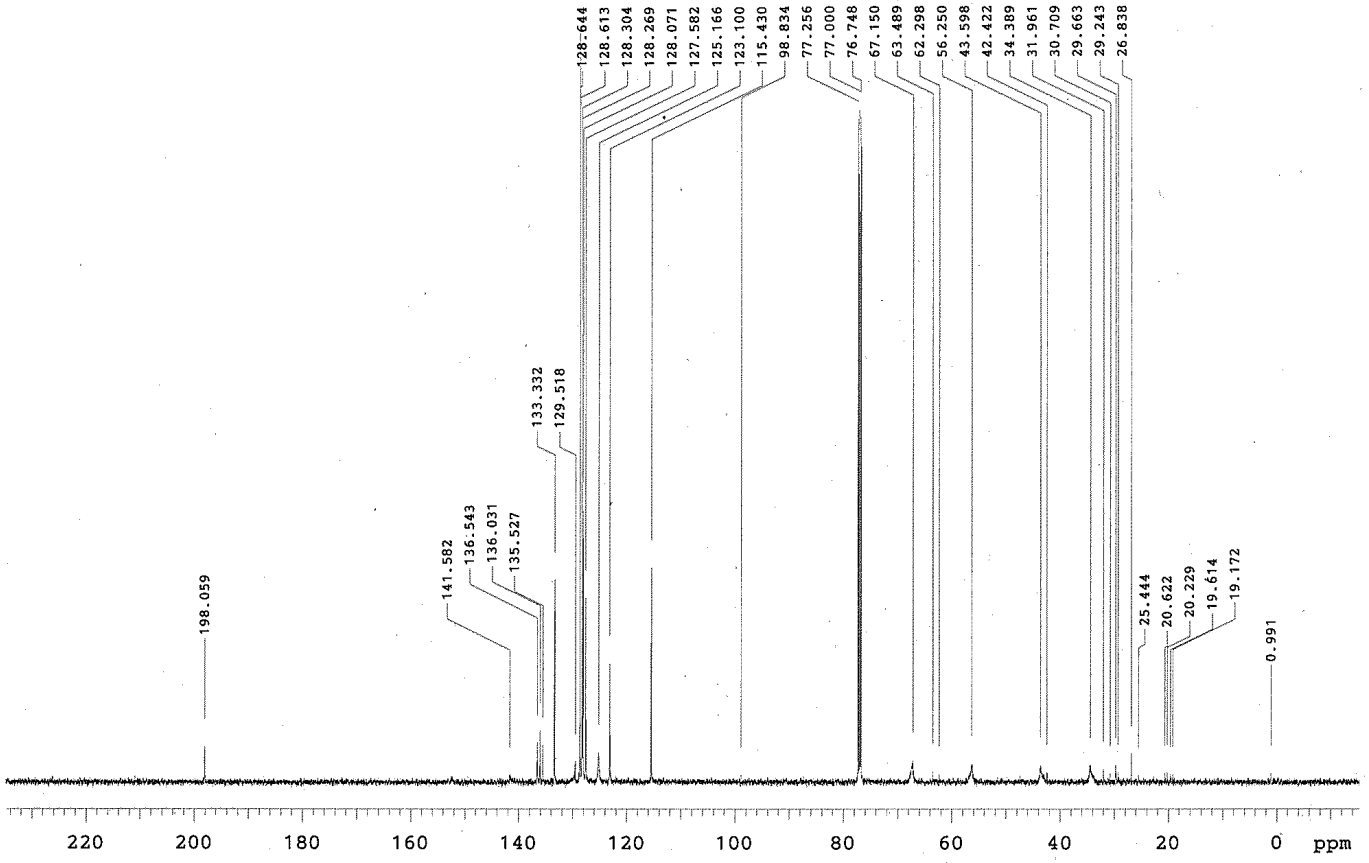

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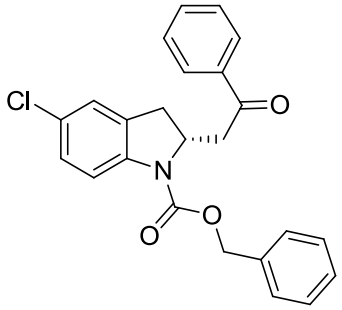

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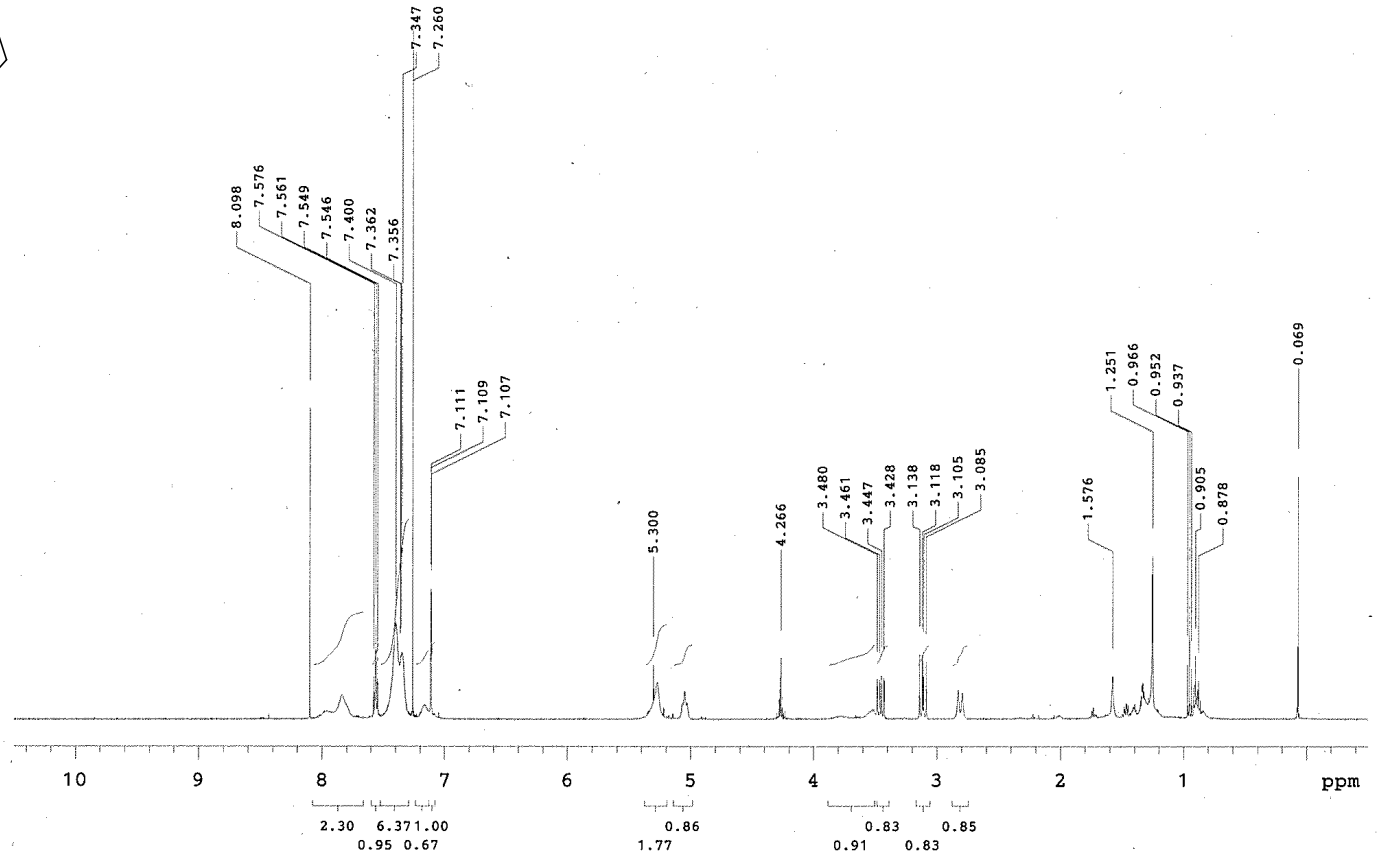

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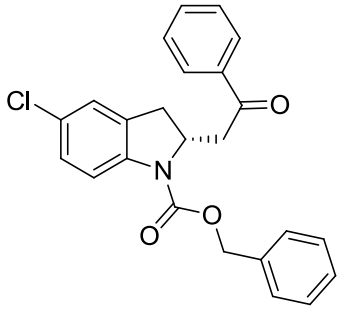
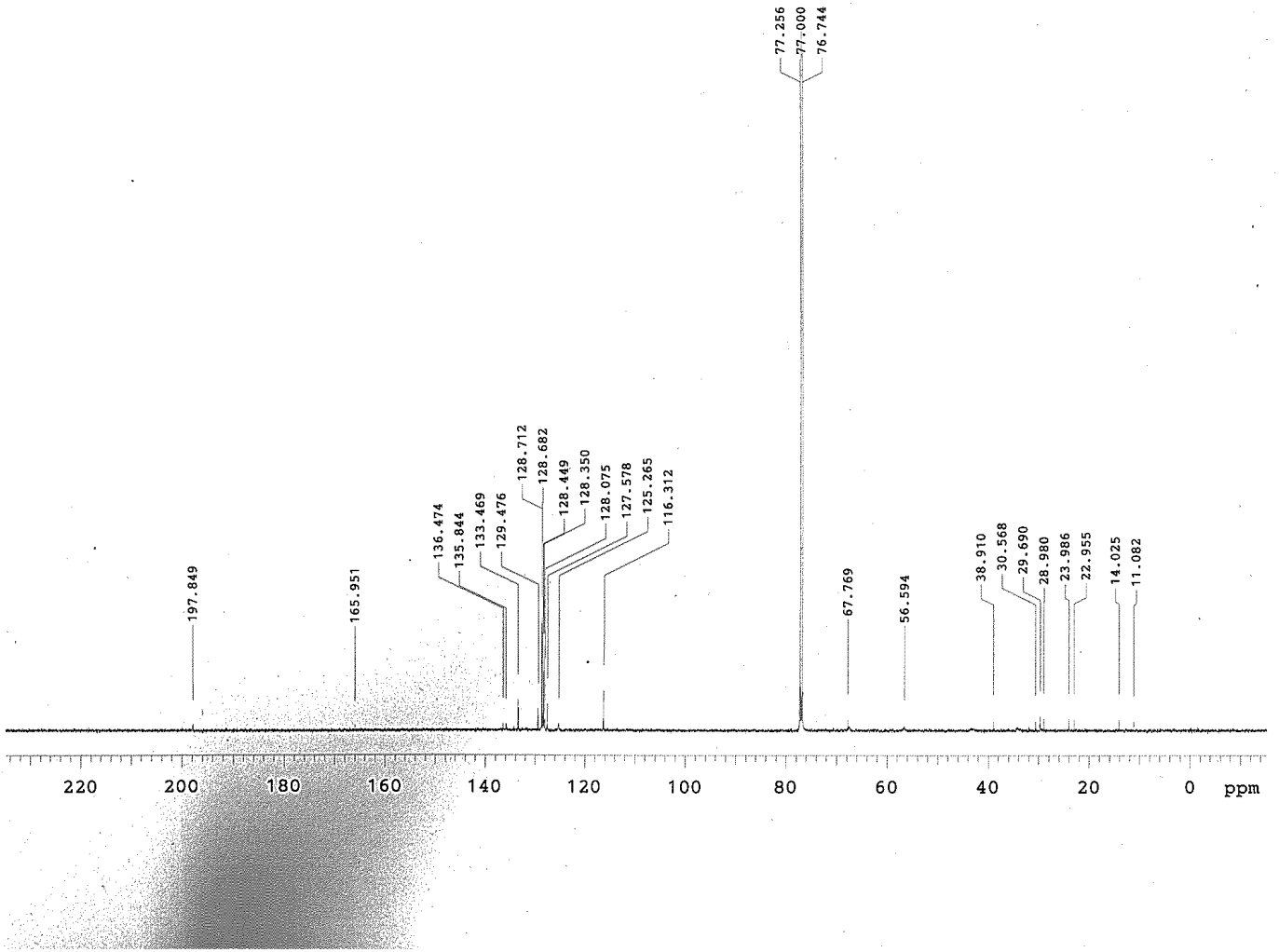
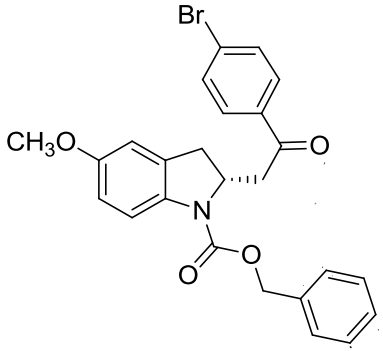


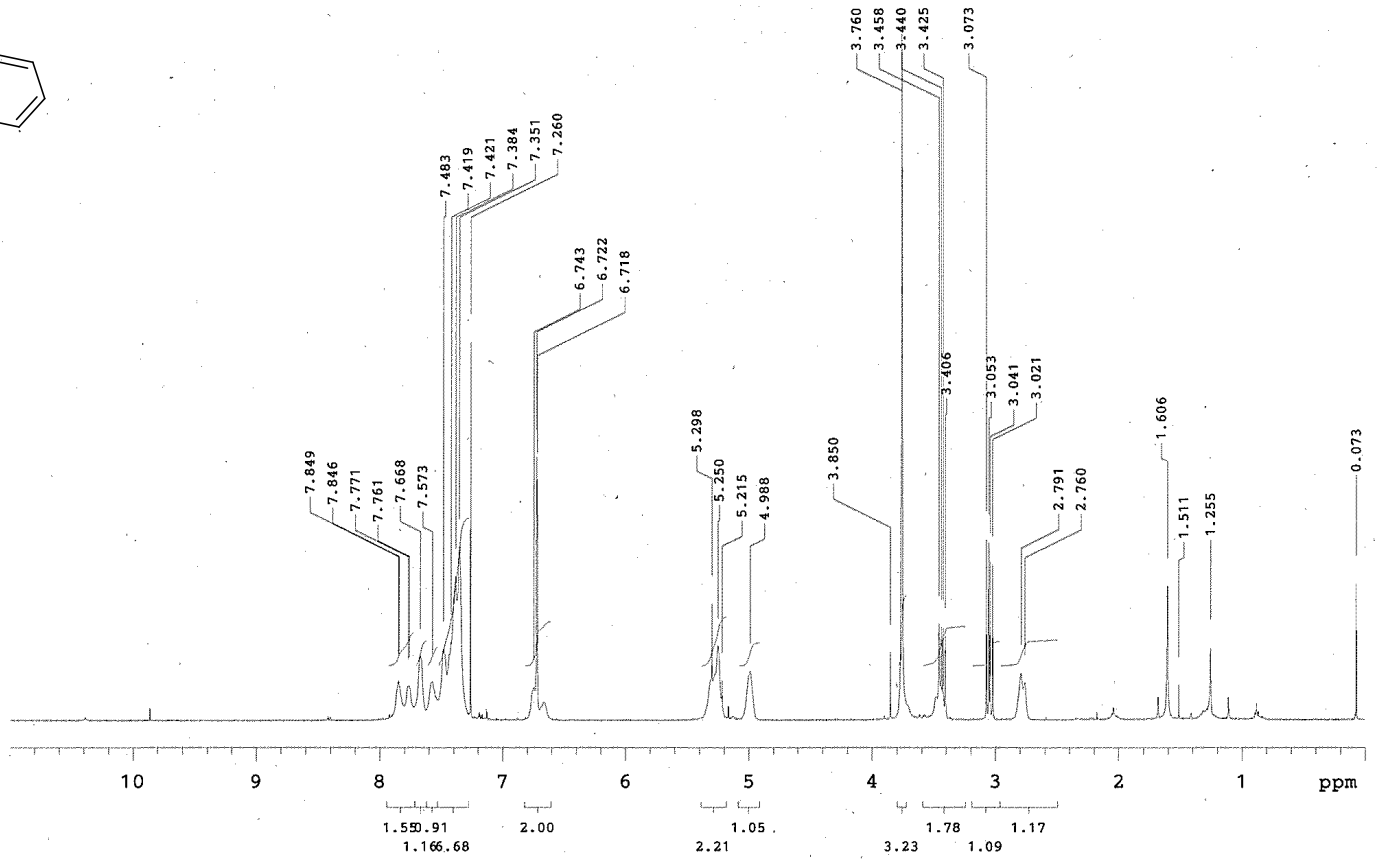
^{13}C NMR



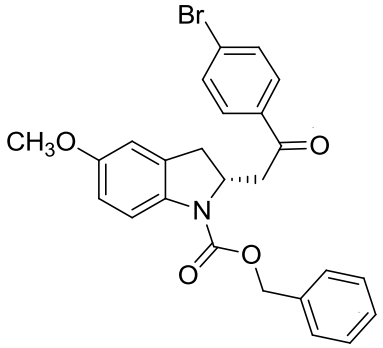
1-(4-Bromophenyl)-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2k)



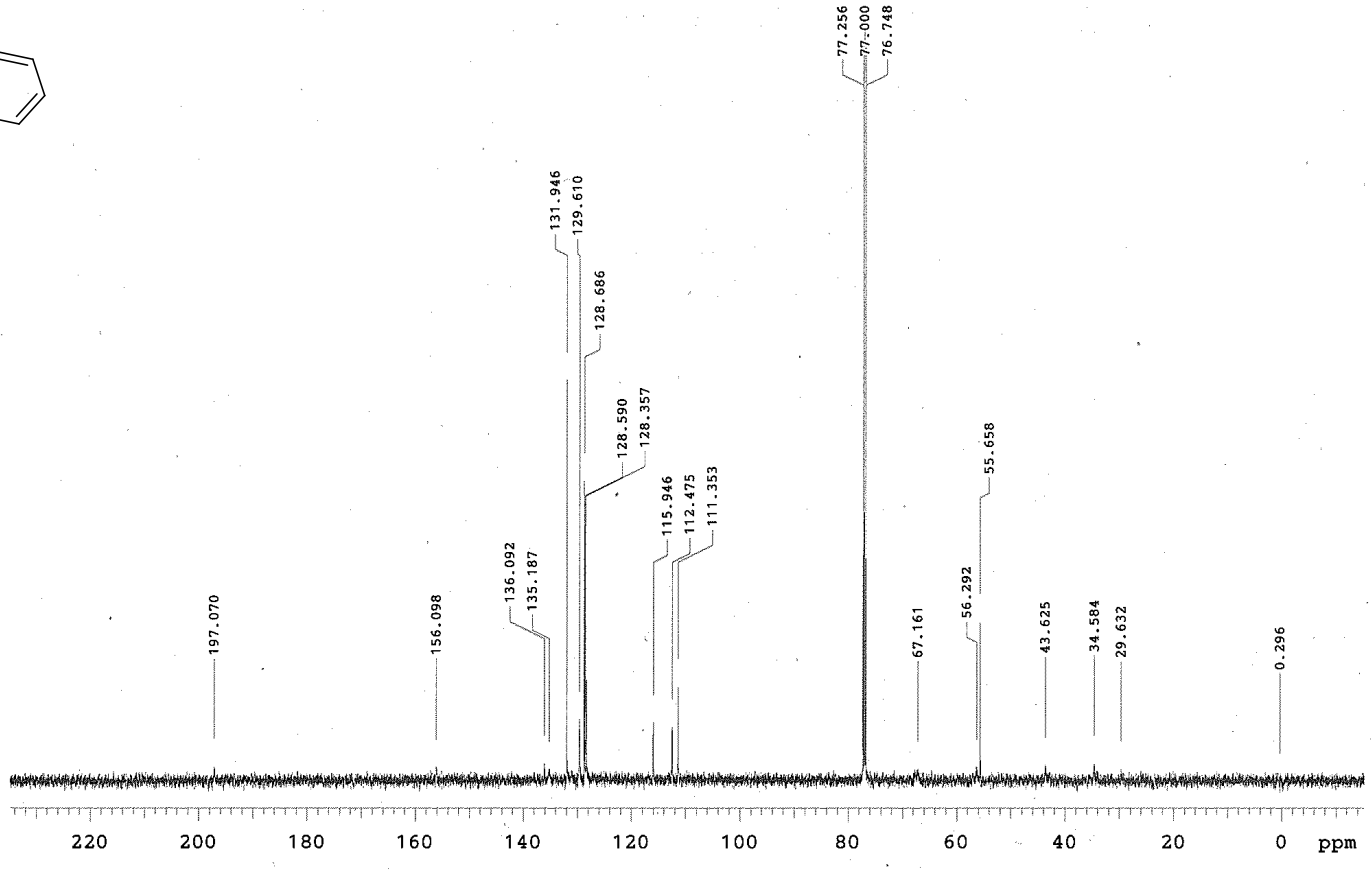
^{1}H NMR



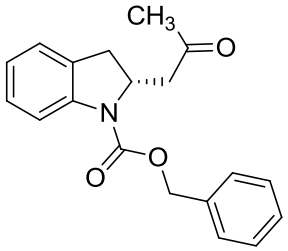
1-(4-Bromophenyl)-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2k)



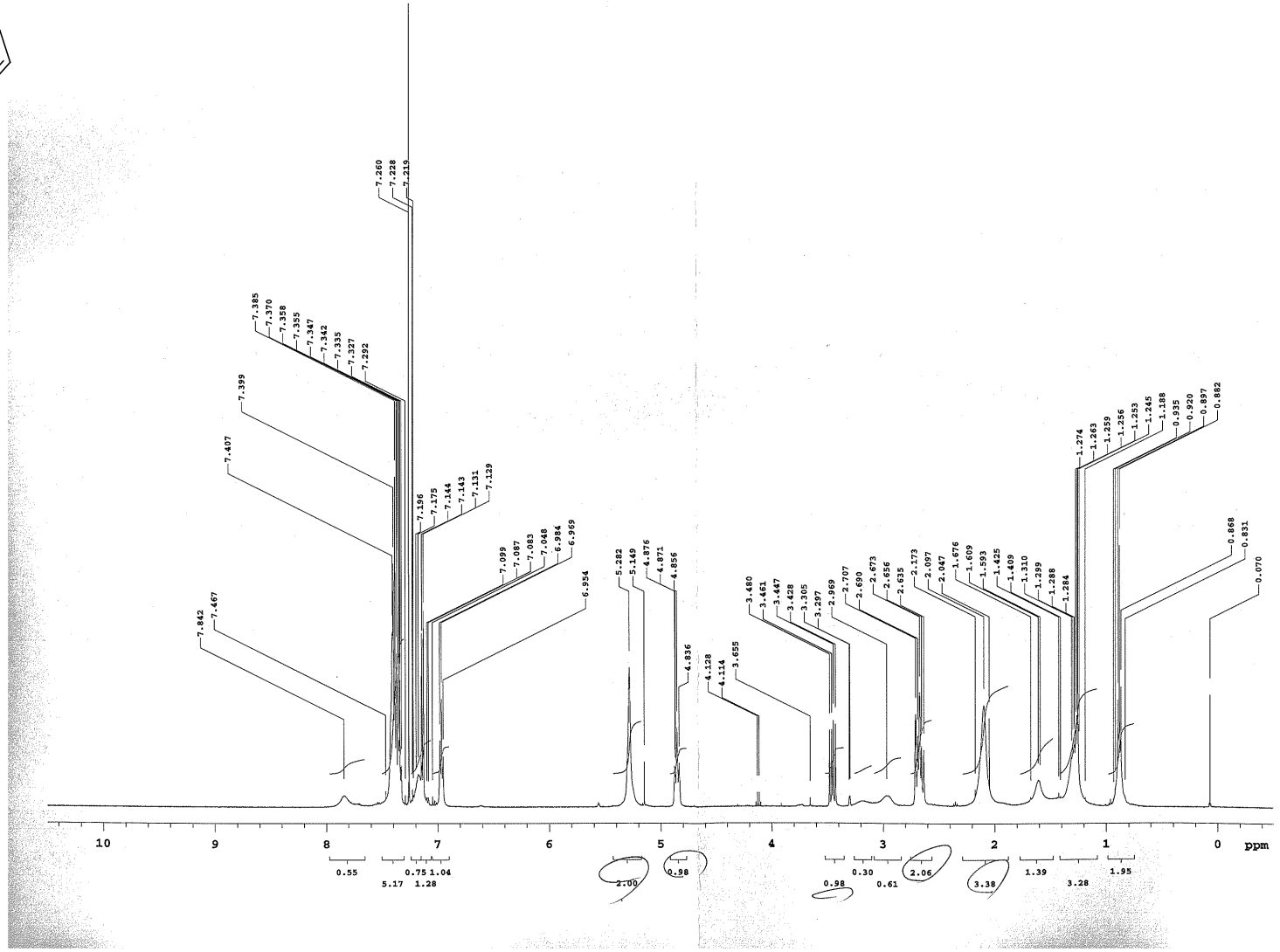
^{13}C NMR



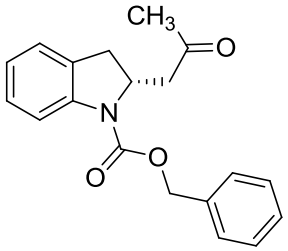
1-Methyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2l)



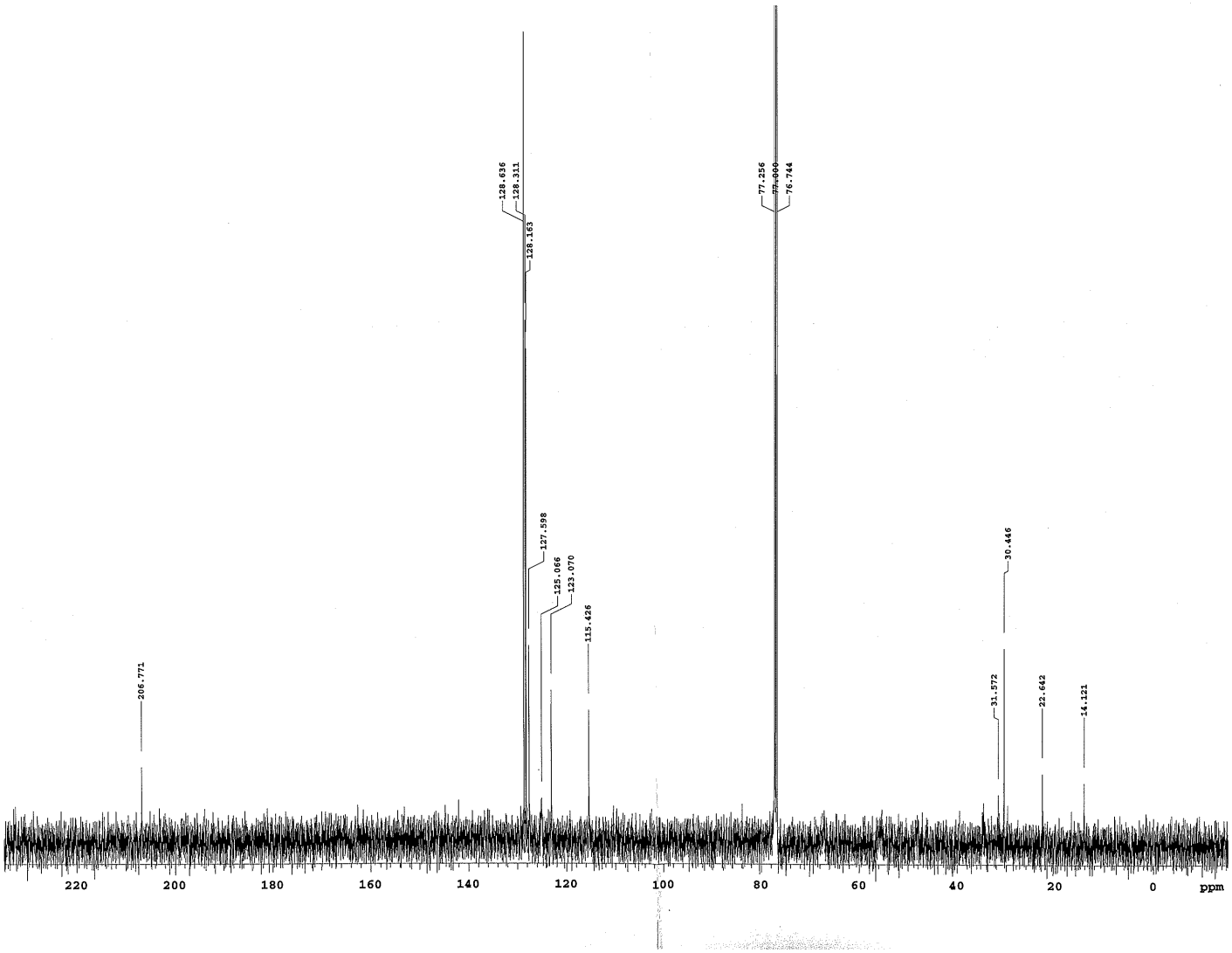
^{1}H NMR



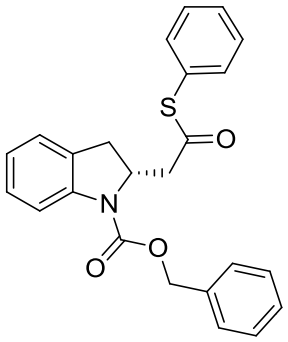
1-Methyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2l)



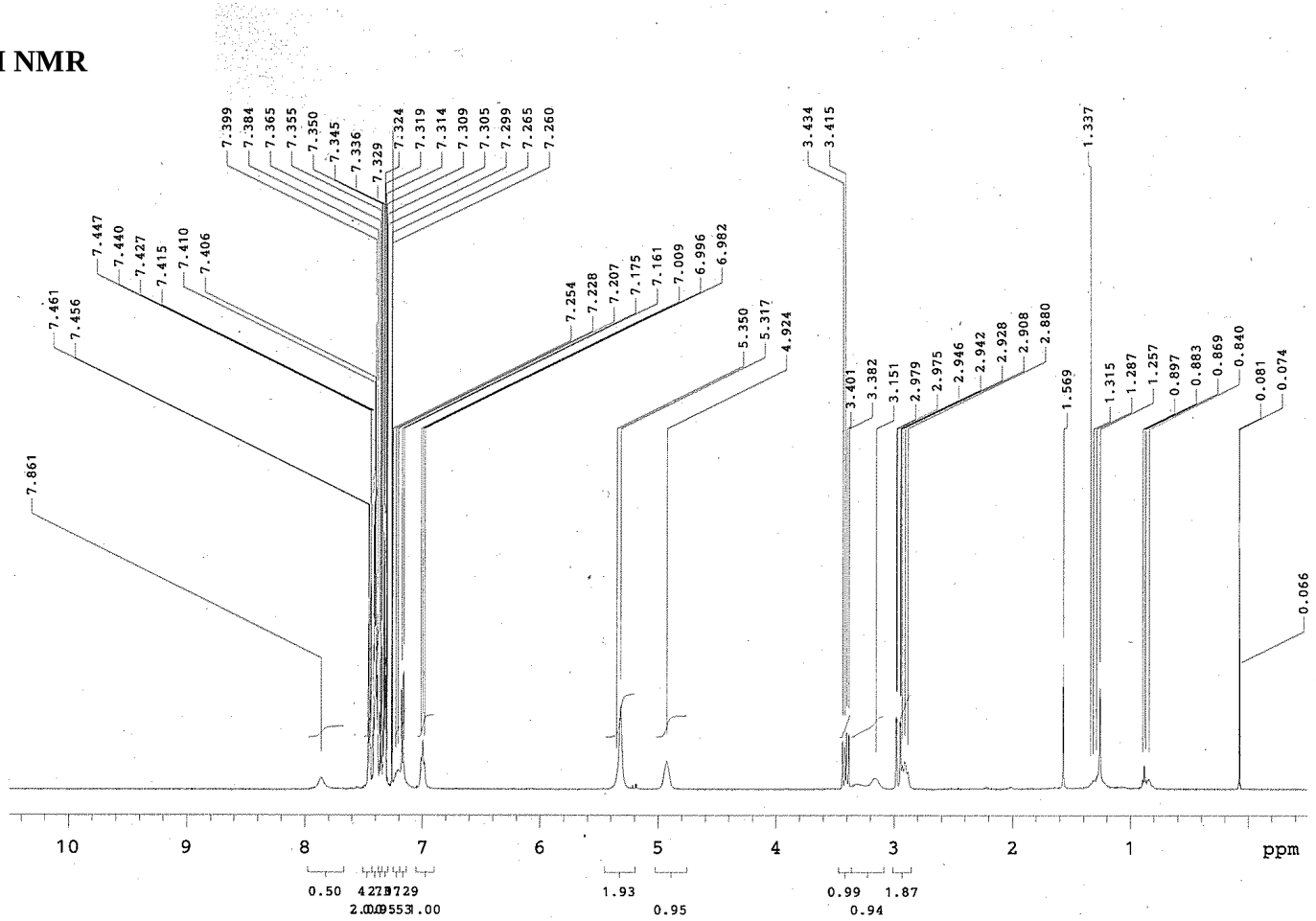
^{13}C NMR



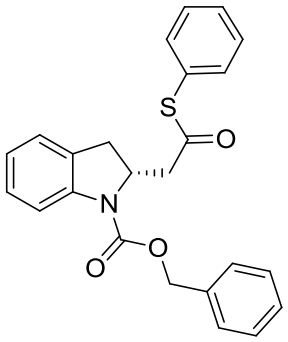
1-Phenylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2m)



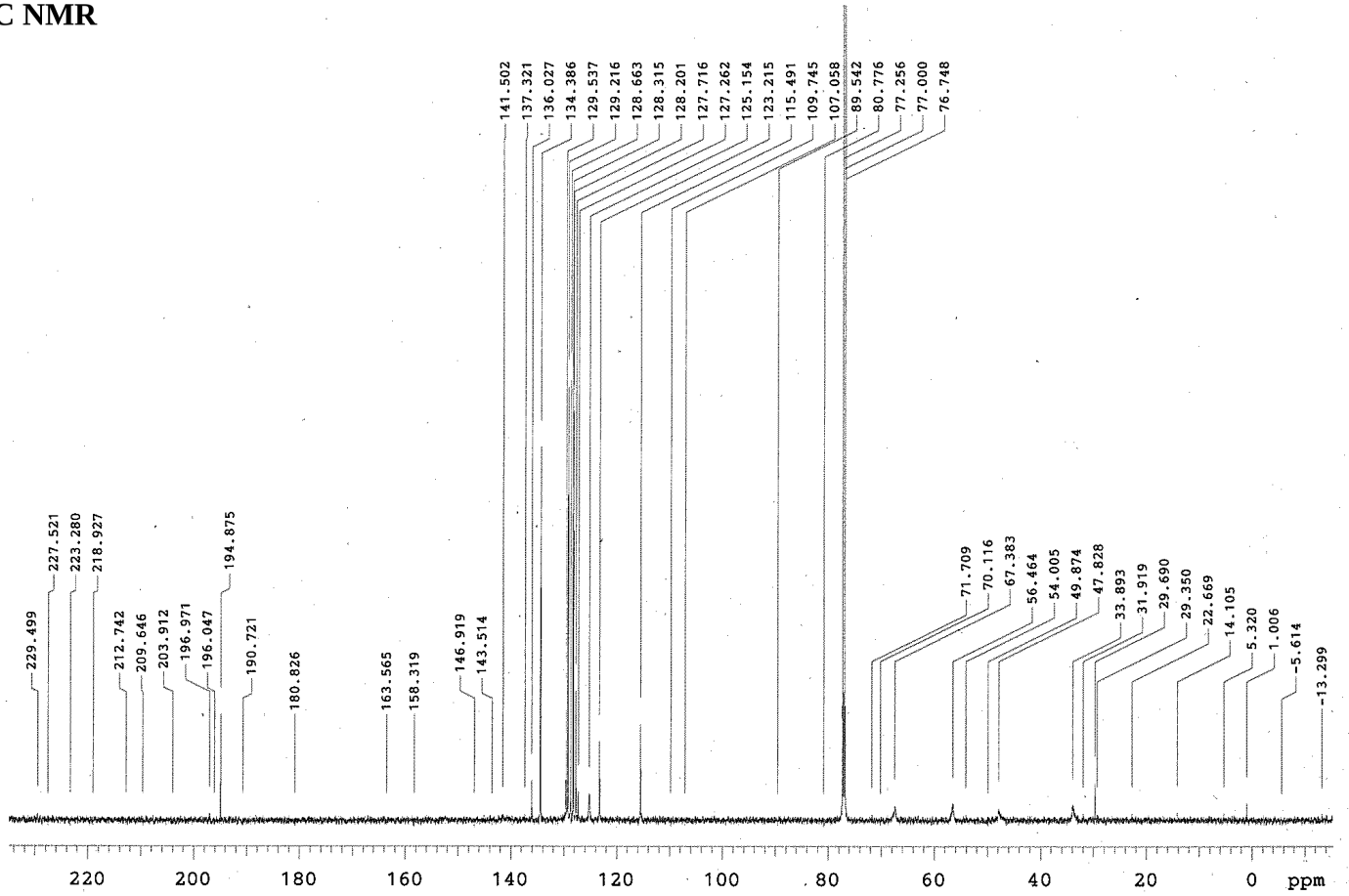
^{1}H NMR



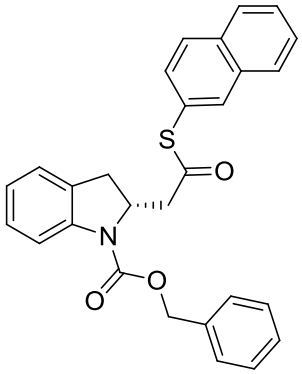
1-Phenylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2m)



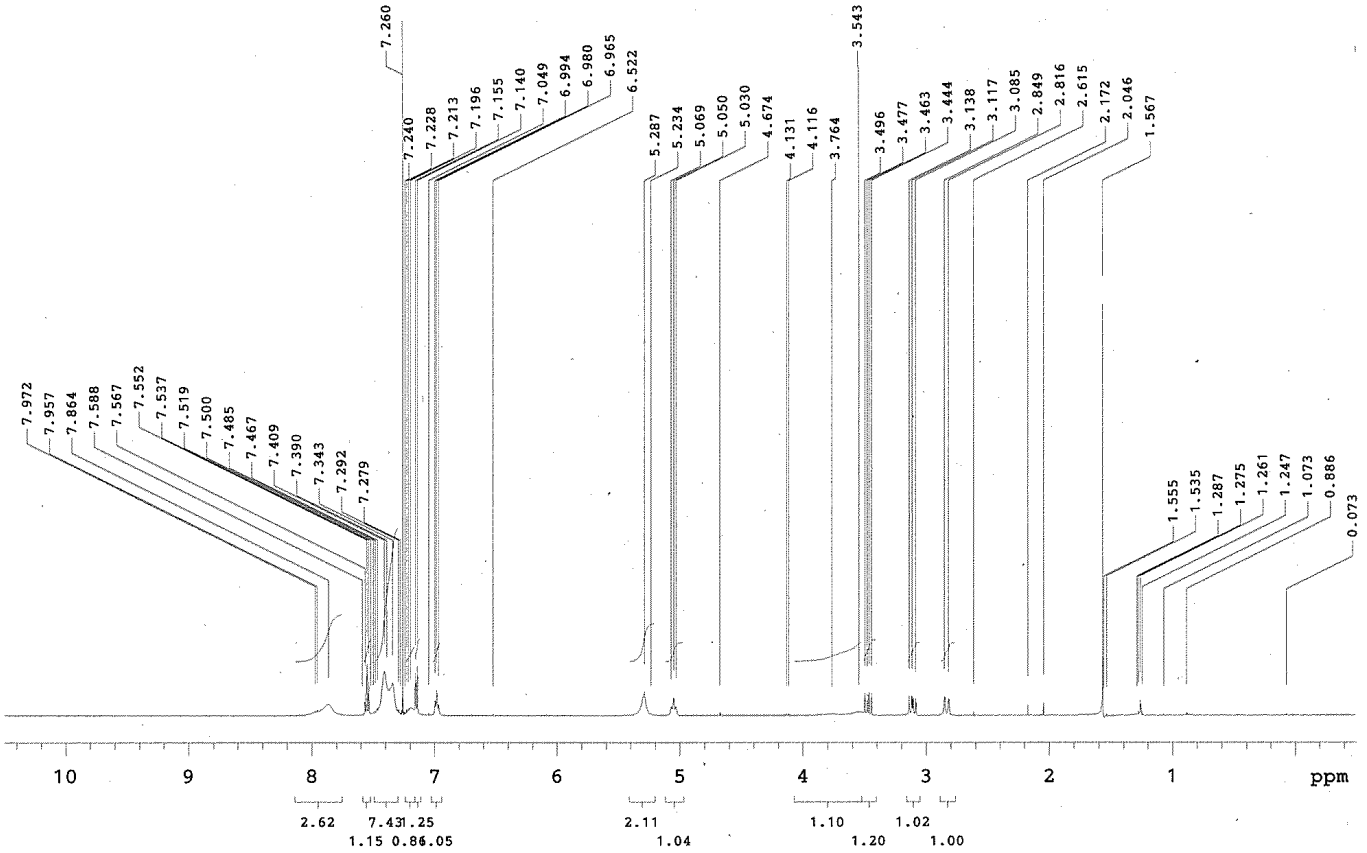
^{13}C NMR



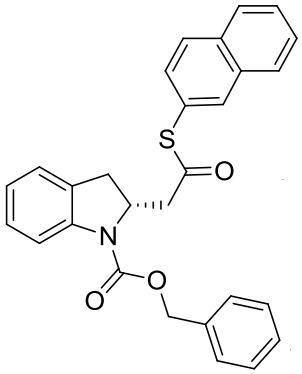
1-Naphthalen-2-ylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2n)



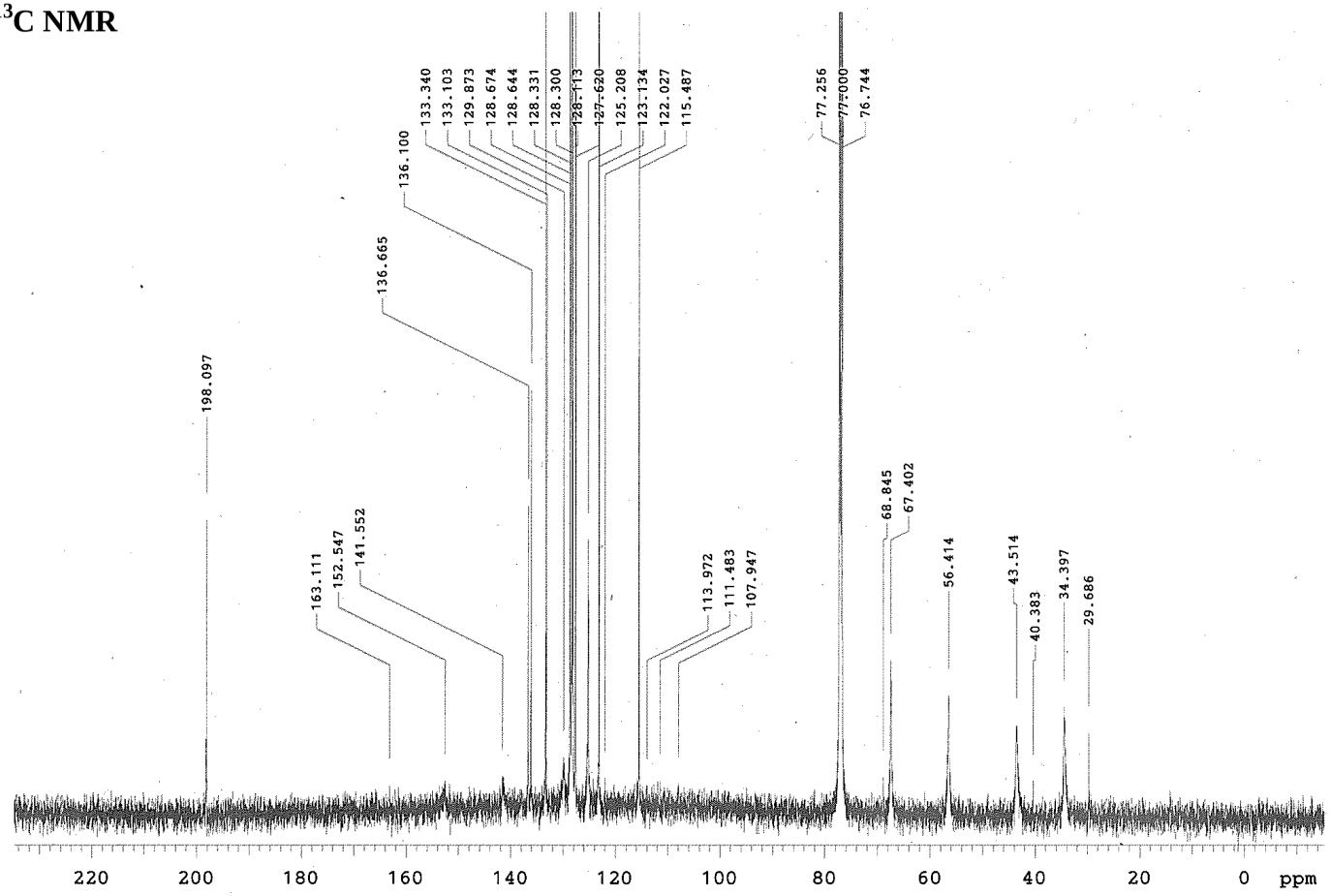
^{1}H NMR



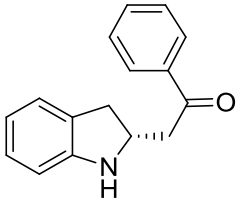
1-Naphthalen-2-ylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2n)



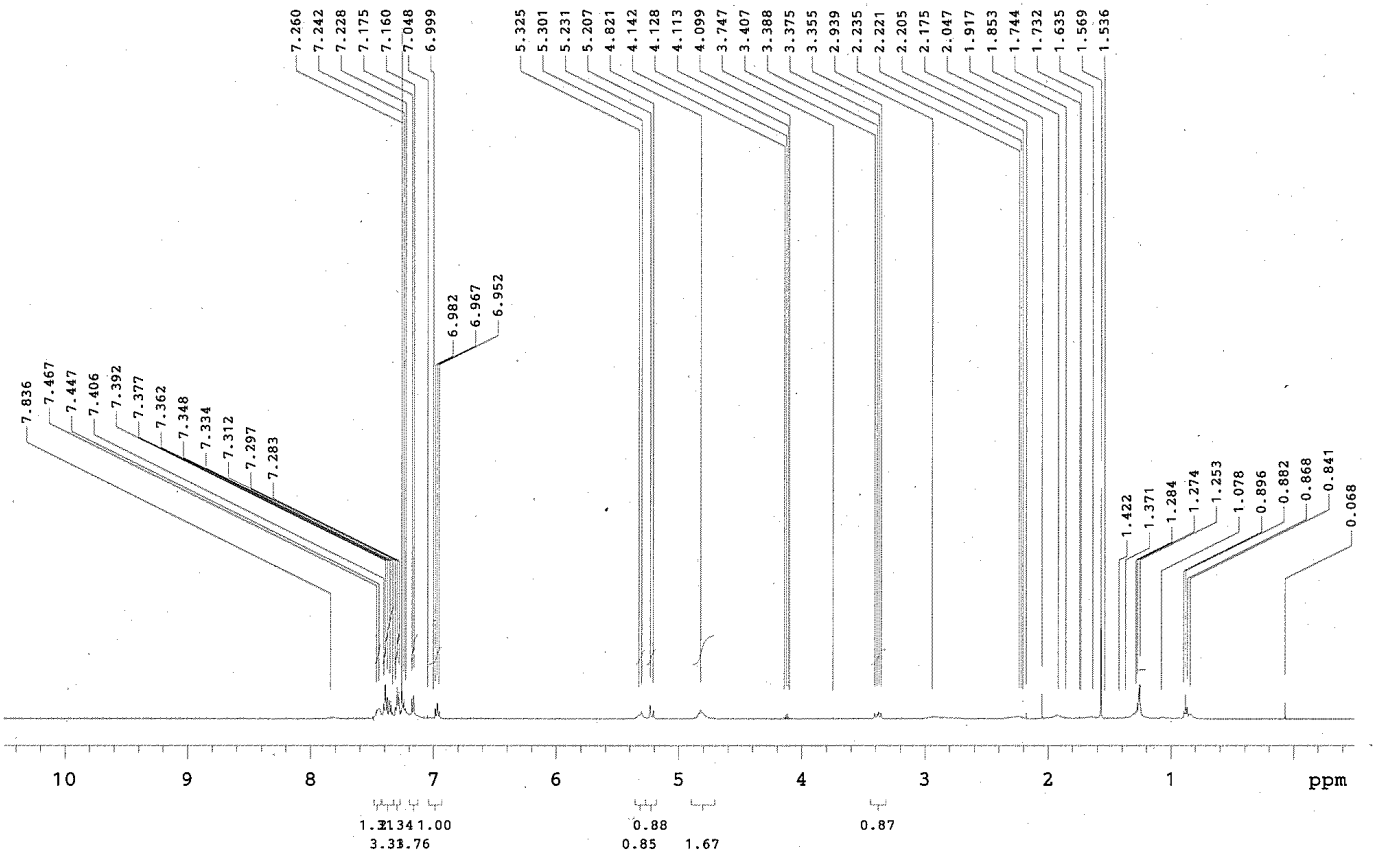
^{13}C NMR



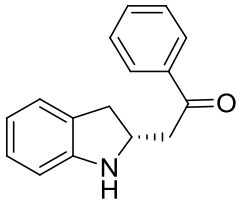
(*R*)-1-Phenyl-2-(indolin-2-yl)ethanone (4)



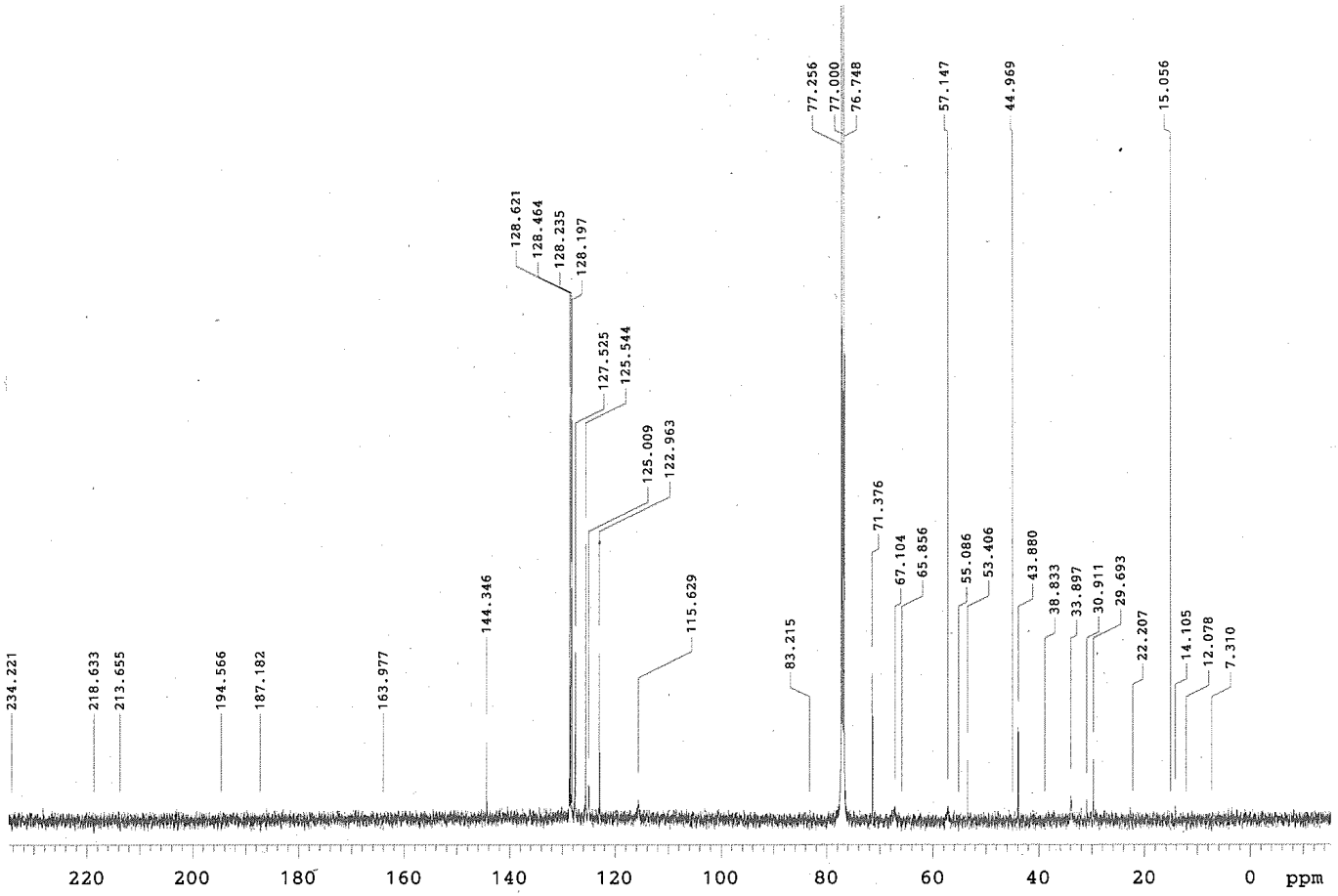
^{1}H NMR



(*R*)-1-Phenyl-2-(indolin-2-yl)ethanone (4)



^{13}C NMR



HPLC Chromatogram Profiles

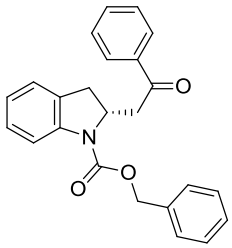
Tables for each HPLC analysis are given as follows:

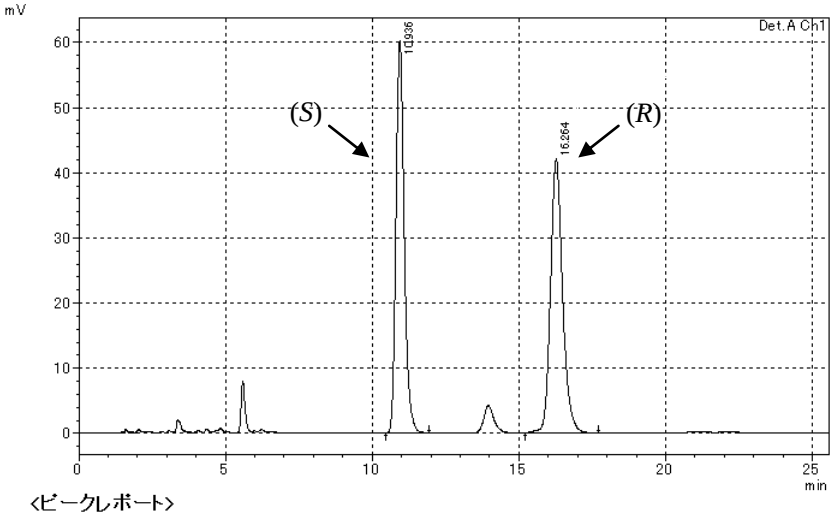
<peak report>

detector A Ch1 254 nm

peak#	retention time	area	height	area %	height %	mark
1	##	##	##	##	##	
2	##	##	##	##	##	
total		##	##	100.000	100.000	

1-Phenyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2a)

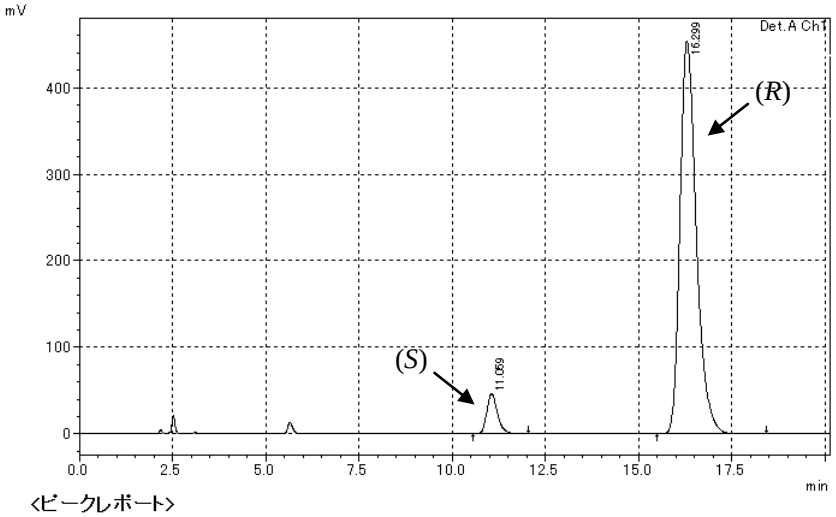




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.936	1169161	60251	49.329	58.912	
2	16.264	1200967	42022	50.671	41.088	
合計		2370128	102274	100.000	100.000	

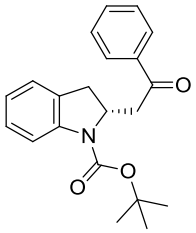


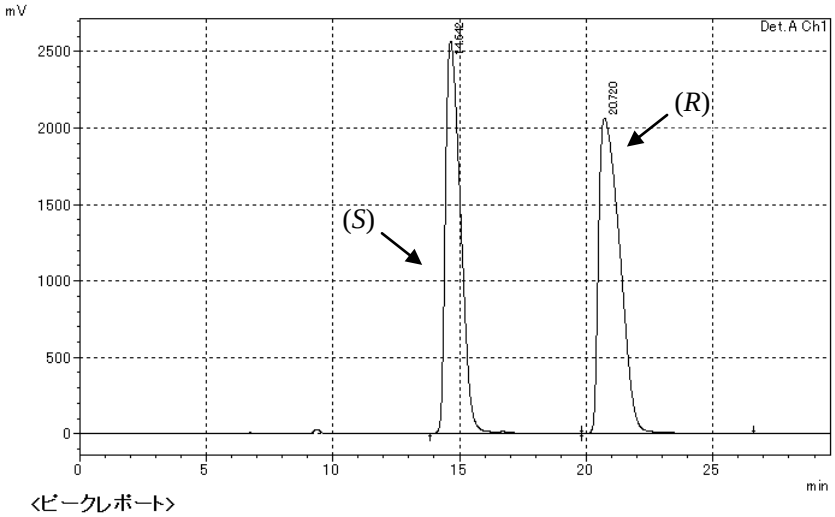
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	11.059	923802	46808	6.276	9.345	
2	16.299	13794954	454070	93.724	90.655	
合計		14718756	500879	100.000	100.000	

1-Phenyl-2-(*N*-*tert*-butoxycarbonylindolin-2-yl)ethanone (2b)

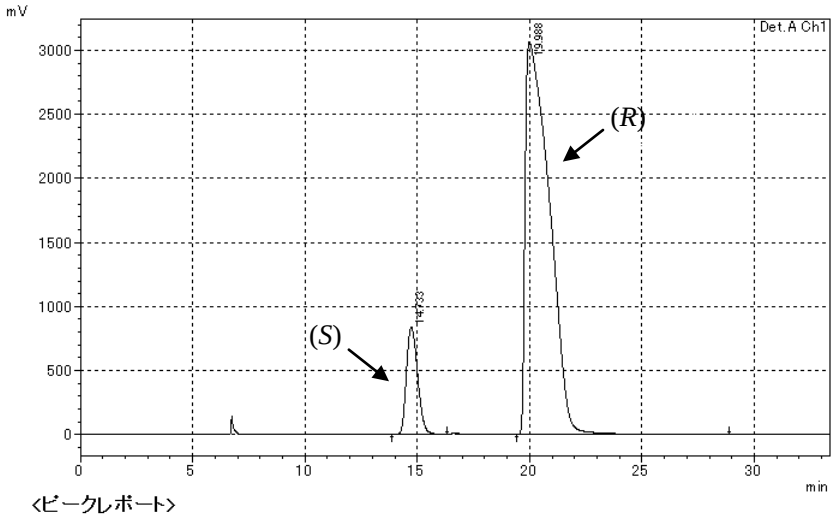




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	14.642	106916152	2569343	47.260	55.431	
2	20.720	119312358	2065870	52.740	44.569	
合計		226228510	4635213	100.000	100.000	

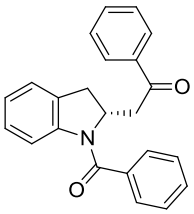


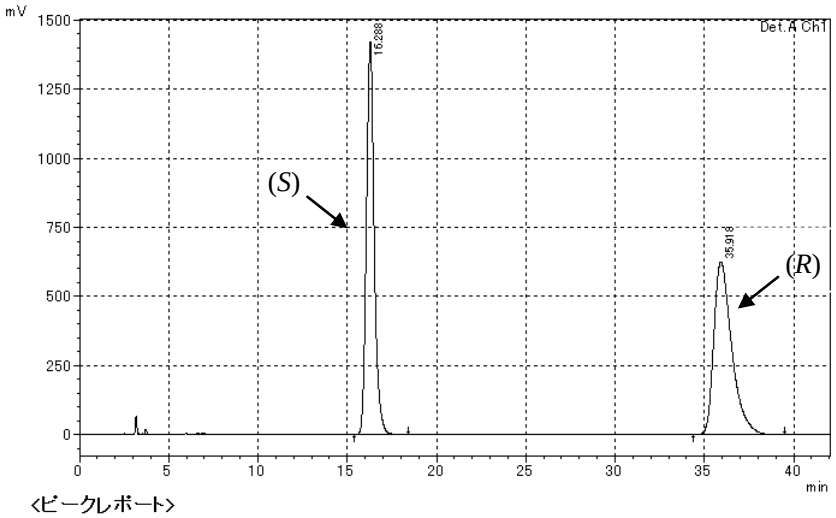
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	14.733	29110804	836406	11.330	21.424	
2	19.988	227831882	3067604	88.670	78.576	
合計		256942686	3904009	100.000	100.000	

1-Phenyl-2-(*N*-benzoylindolin-2-yl)ethanone (2c)

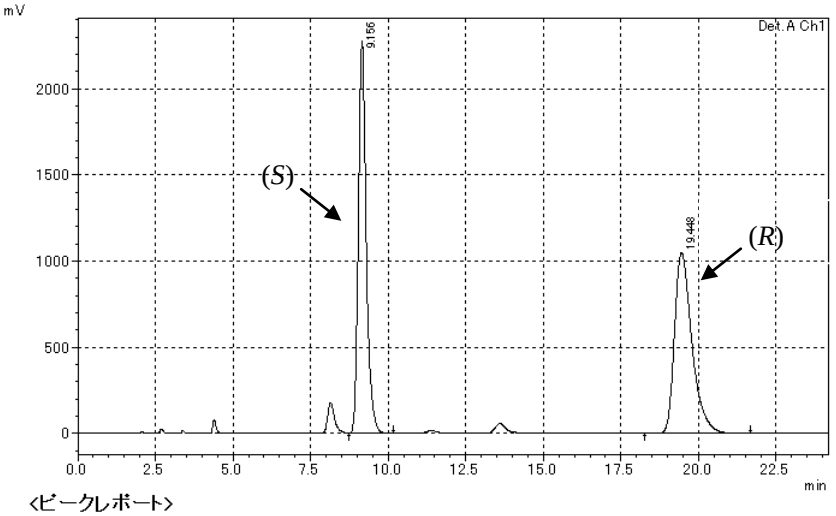




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	16.288	42967825	1421252	49.600	69.486	
2	35.918	43661570	624132	50.400	30.514	
合計		86629395	2045384	100.000	100.000	

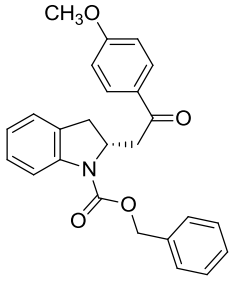


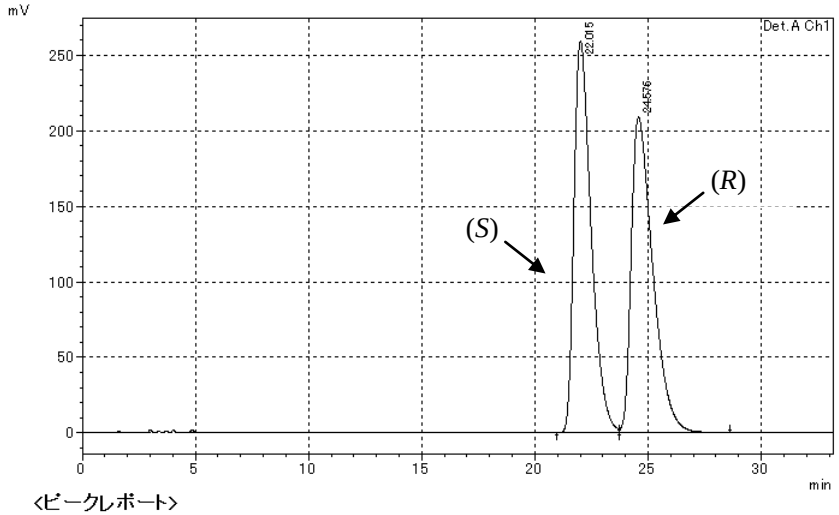
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.156	40054012	2275998	49.528	68.497	
2	19.448	40817509	1046762	50.472	31.503	
合計		80871521	3322760	100.000	100.000	

1-(4-Methoxyphenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2d)

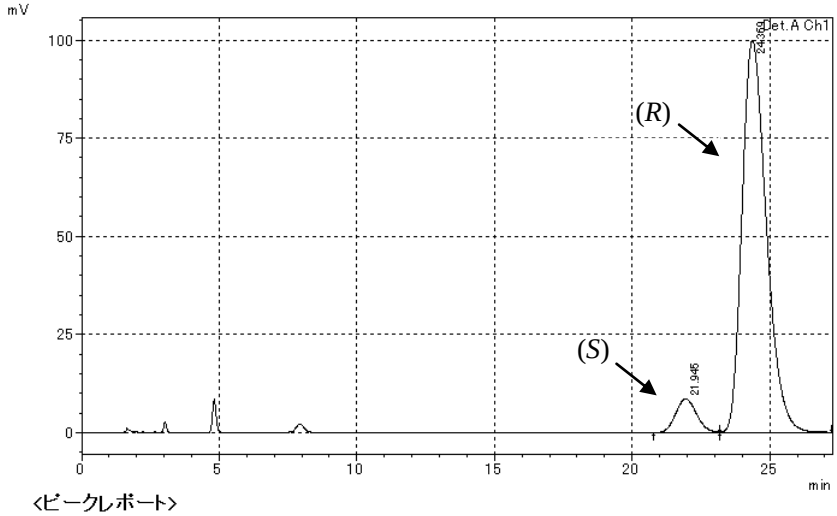




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	22.015	13732935	259567	49.836	55.413	
2	24.576	13823157	208856	50.164	44.587	V
合計		27556092	468423	100.000	100.000	

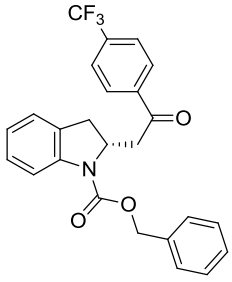


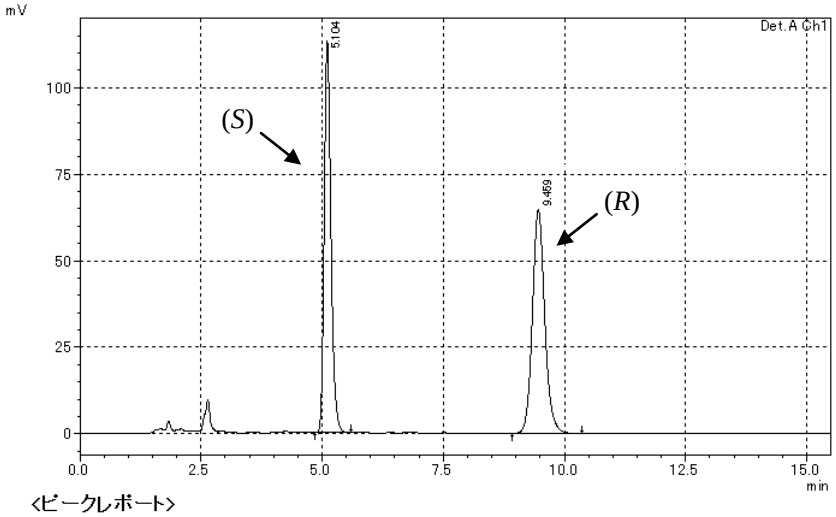
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	21.945	454134	8576	6.891	7.905	
2	24.369	6136107	99909	93.109	92.095	V
合計		6590241	108485	100.000	100.000	

1-(4-Trifluoromethylphenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2e)

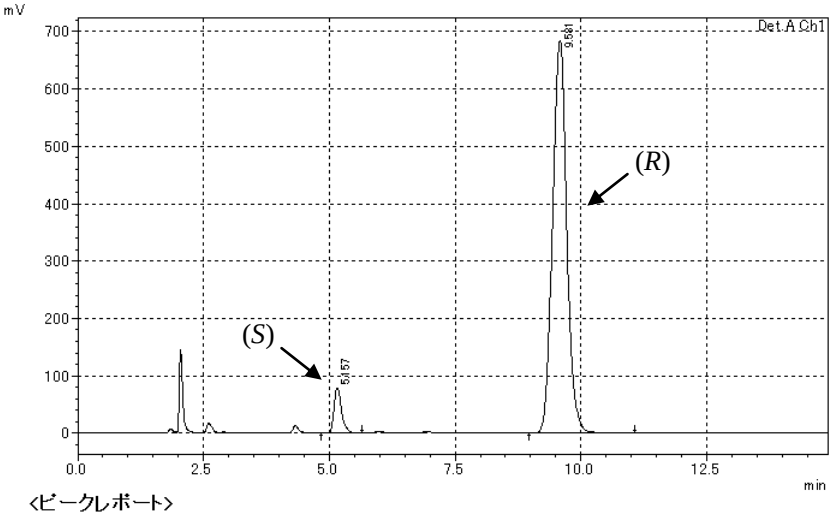




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.104	1105972	113312	48.987	63.679	
2	9.459	1151713	64629	51.013	36.321	
合計		2257684	177941	100.000	100.000	

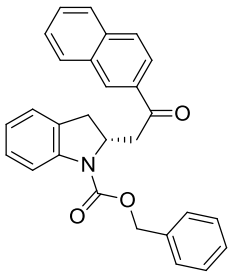


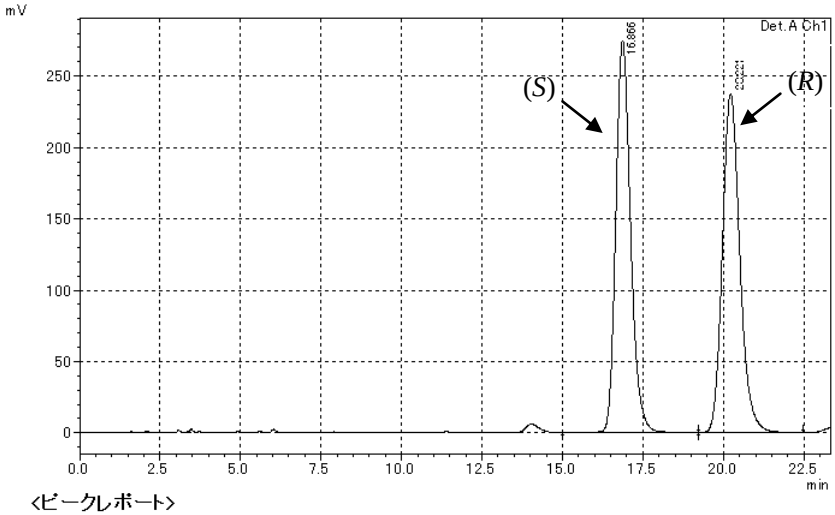
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.157	816565	78917	5.735	10.334	
2	9.581	13422756	684744	94.265	89.666	
合計		14239321	763660	100.000	100.000	

1-Naphthyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2f)





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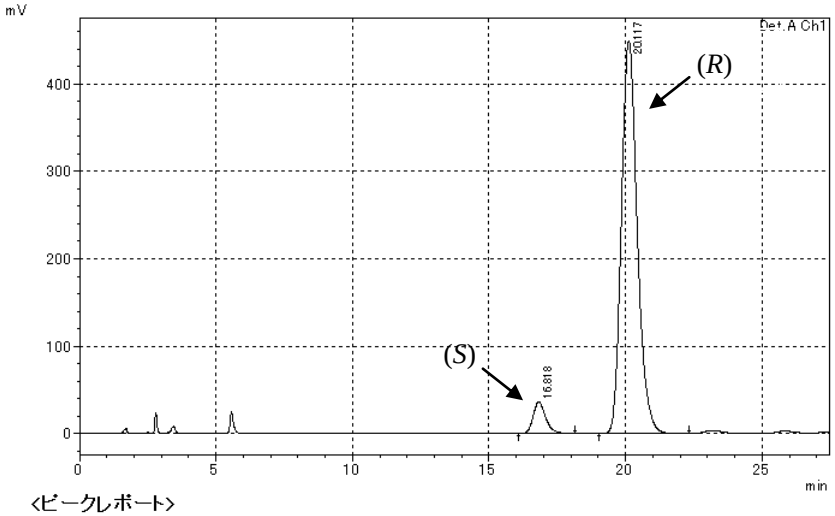
検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	16.866	8814520	274726	49.598	53.633	
2	20.221	8957369	237509	50.402	46.367	V
合計		17771889	512234	100.000	100.000	



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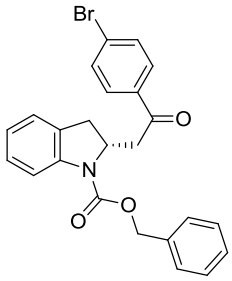
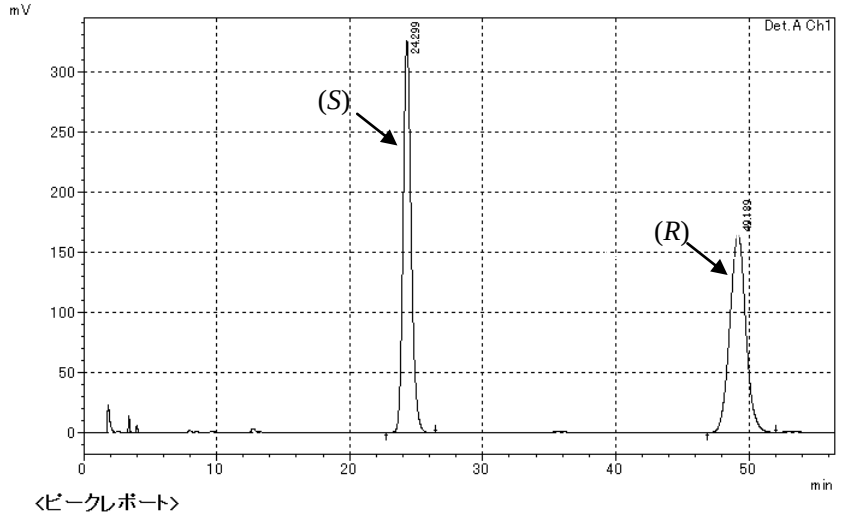
検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	16.818	1139384	36234	5.936	7.464	
2	20.117	18054296	449209	94.064	92.536	
合計		19193680	485444	100.000	100.000	

(*R*)-1-(4-Bromophenyl)-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2g)

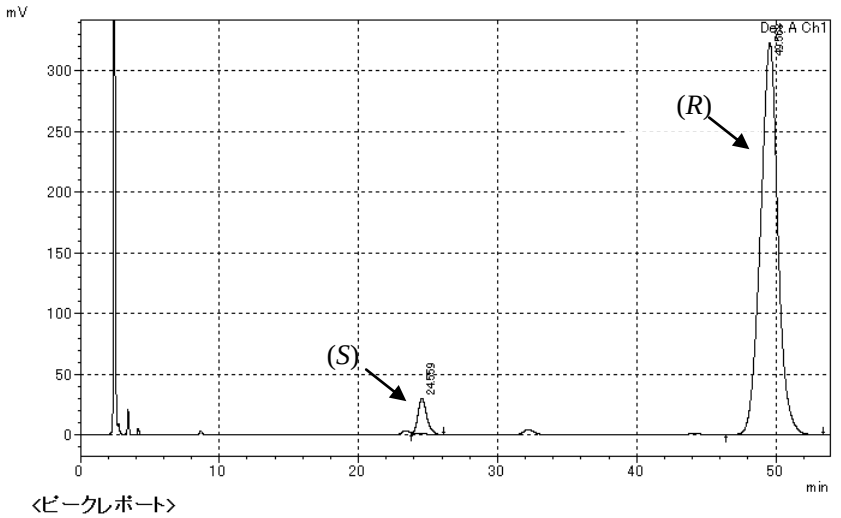




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	24.299	13734195	325670	50.029	66.524	
2	49.189	13718406	163880	49.971	33.476	
合計		27452601	489550	100.000	100.000	

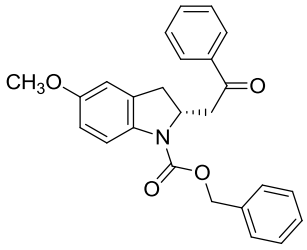


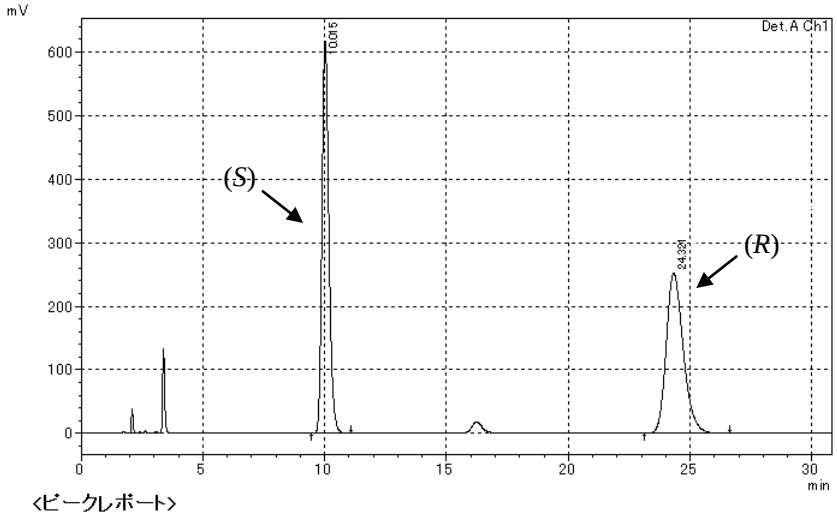
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	24.559	1249218	29038	4.254	8.237	
2	49.568	28115716	323507	95.746	91.763	
合計		29364935	352545	100.000	100.000	

1-Phenyl-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2h)

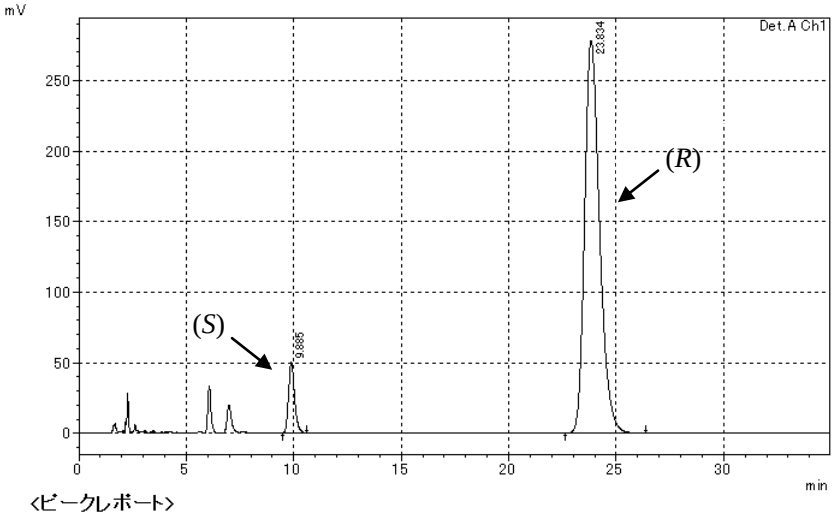




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.015	12033381	617593	49.599	71.023	
2	24.321	12228192	251976	50.401	28.977	
合計		24261573	869569	100.000	100.000	

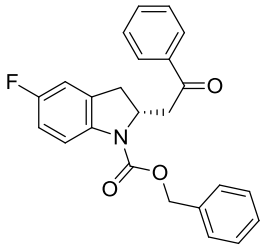


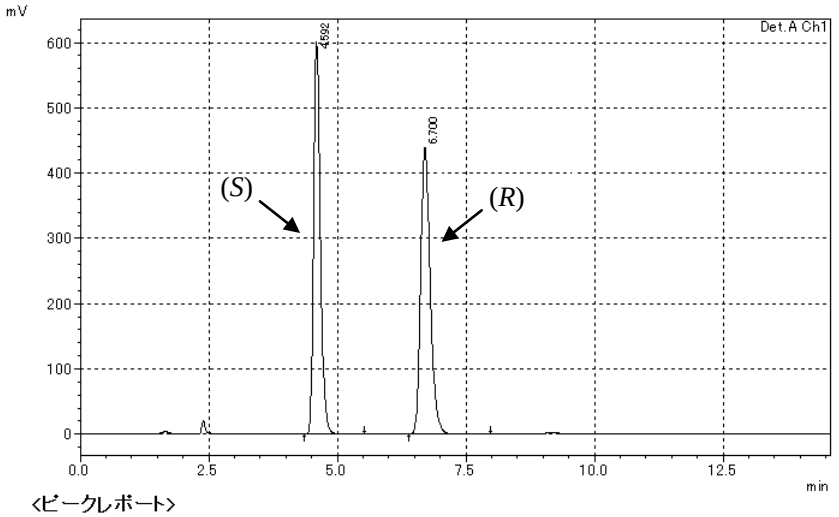
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.885	957747	49863	6.657	15.214	
2	23.834	13430107	277881	93.343	84.786	
合計		14387855	327744	100.000	100.000	

1-Phenyl-2-(*N*-benzyloxycarbony-5-fluorolindolin-2-yl)ethanone (2i)

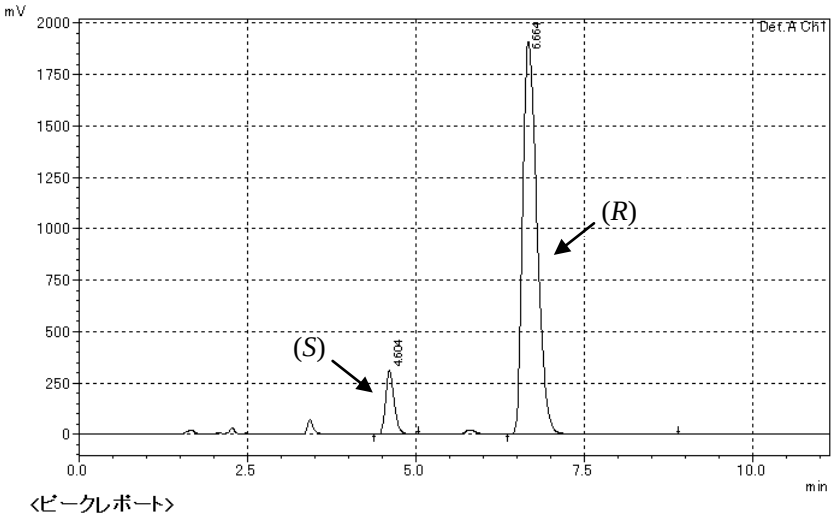




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	4.592	5459771	601516	49.090	57.806	V
2	6.700	5662249	439059	50.910	42.194	
合計		11122020	1040574	100.000	100.000	

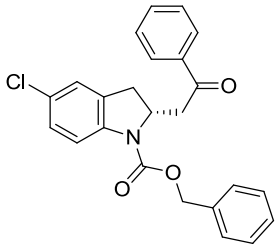


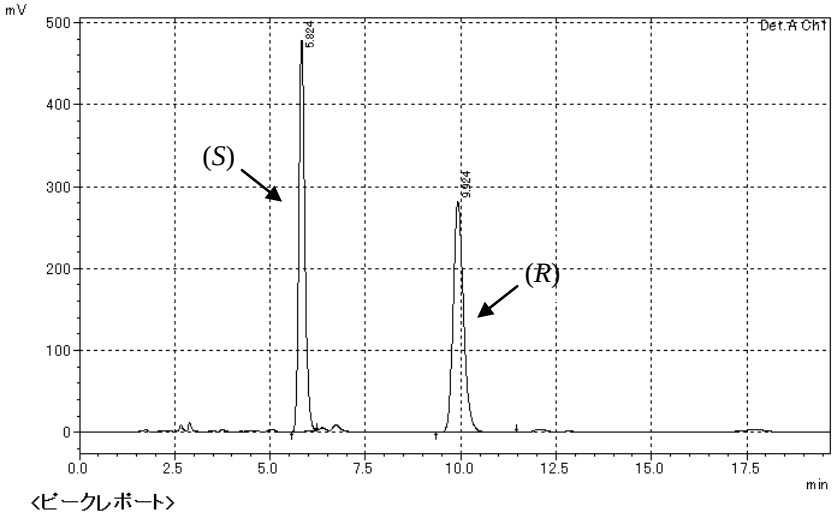
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	4.604	2725163	313606	8.830	14.103	
2	6.664	28138250	1910123	91.170	85.897	S
合計		30863413	2223729	100.000	100.000	

1-Phenyl-2-(*N*-benzyloxycarbony-5-chlorolindolin-2-yl)ethanone (2j)

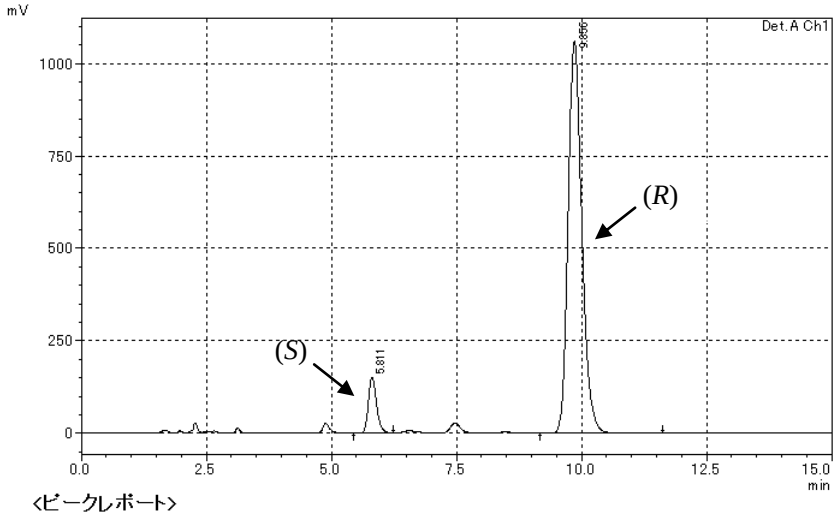




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.824	5197503	477353	49.623	62.941	
2	9.924	5276494	281061	50.377	37.059	
合計		10473997	758414	100.000	100.000	

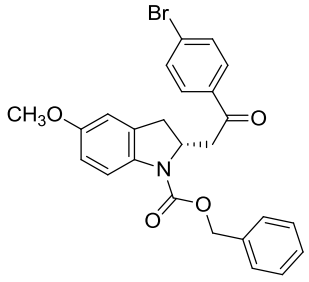


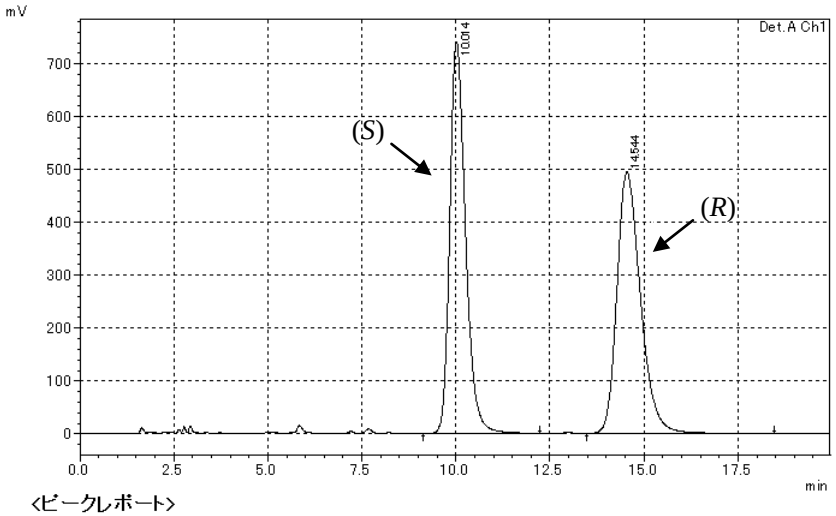
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.811	1693837	149825	7.726	12.373	
2	9.856	20231395	1061109	92.274	87.627	
合計		21925232	1210935	100.000	100.000	

1-(4-Bromophenyl)-2-(*N*-benzyloxycarbony-5-methoxylindolin-2-yl)ethanone (2k)

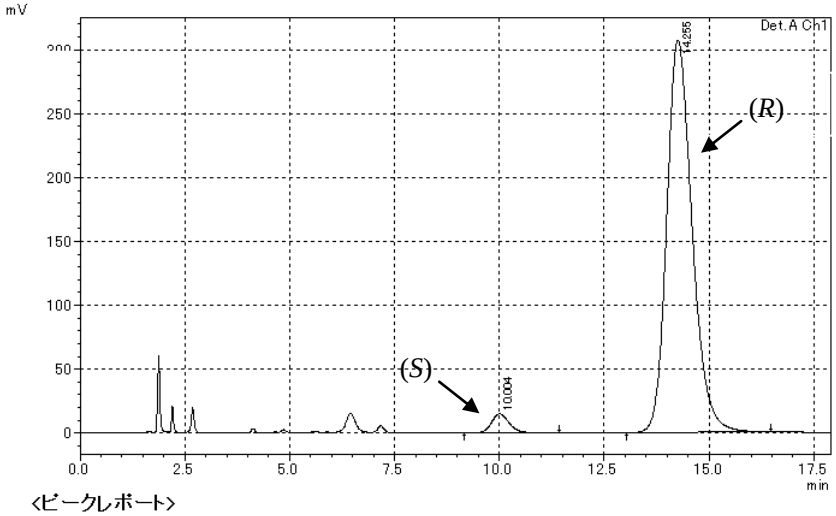




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.014	21570662	741266	50.042	59.982	
2	14.544	21534634	494543	49.958	40.018	
合計		43105296	1235809	100.000	100.000	

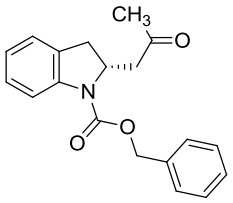


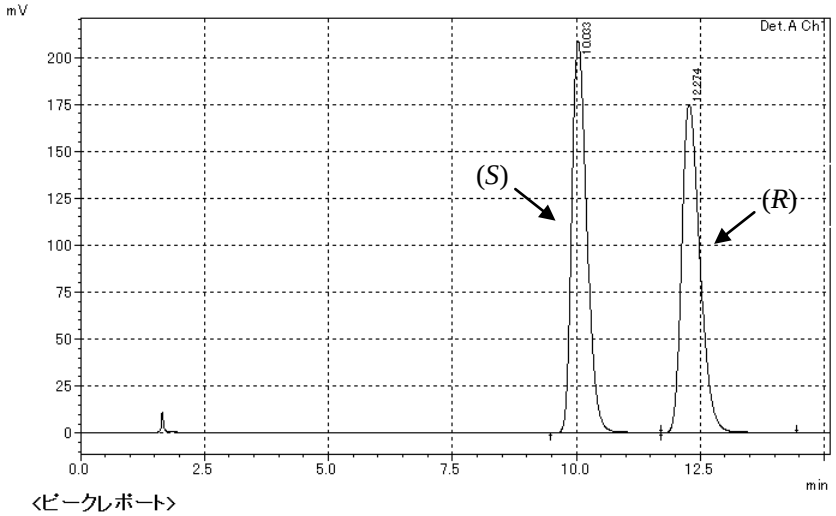
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.004	443218	15011	3.313	4.660	
2	14.255	12933075	307099	96.687	95.340	
合計		13376293	322111	100.000	100.000	

1-Methyl-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2l)





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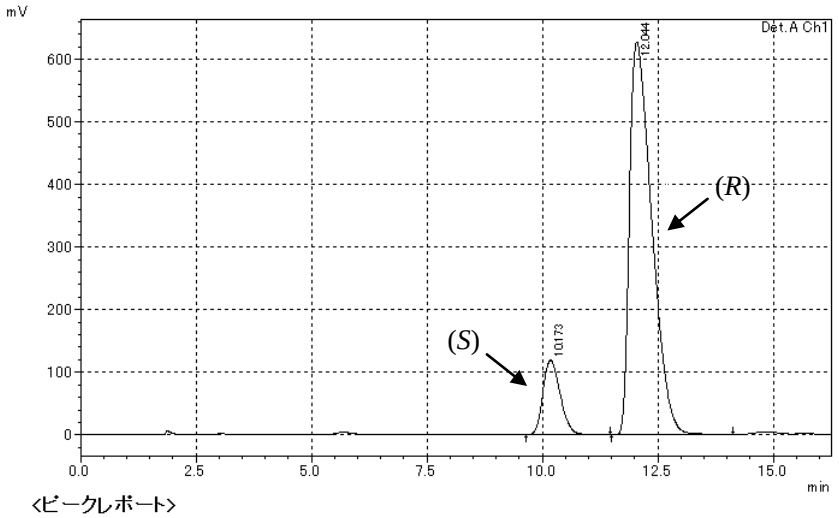
検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.033	4433232	208792	49.799	54.439	
2	12.274	4469026	174740	50.201	45.561	V
合計		8902258	383531	100.000	100.000	

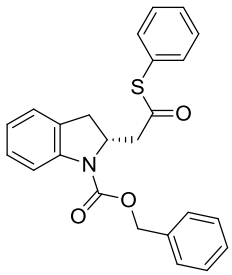


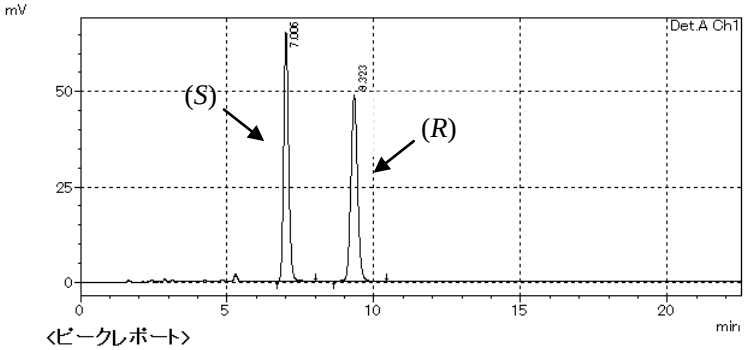
<ピークレポート>

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.173	3073706	118615	12.762	15.906	
2	12.044	21011705	627119	87.238	84.094	
合計		24085411	745734	100.000	100.000	

1-Phenylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2m)

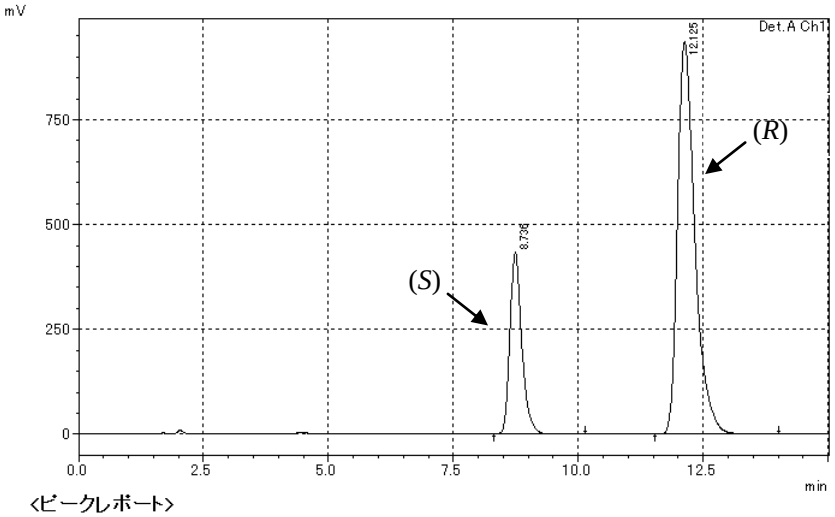




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%
1	7.006	769542	65301	49.821	57.160
2	9.323	775060	48942	50.179	42.840
合計		1544602	114243	100.000	100.000

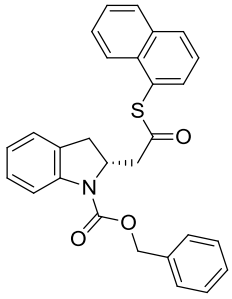


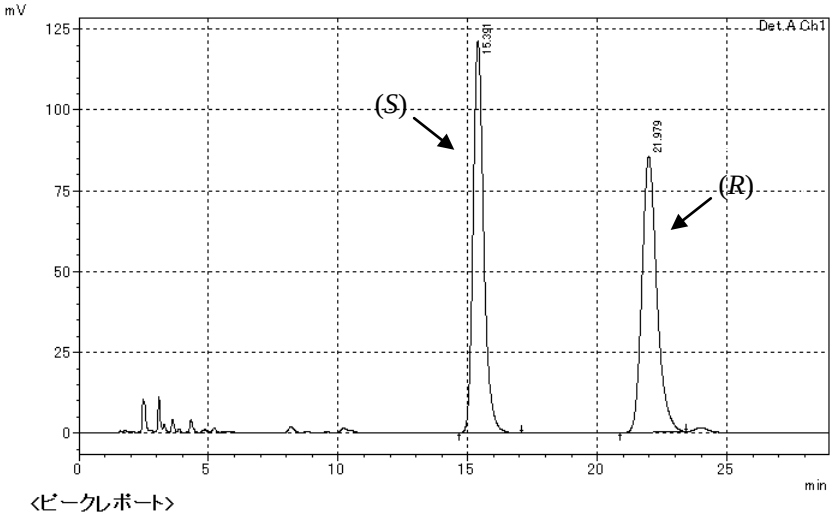
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	8.736	7180564	433293	24.110	31.611	
2	12.125	22602344	937402	75.890	68.389	
合計		29782909	1370695	100.000	100.000	

1-Naphthalen-2-ylthio-2-(*N*-benzyloxycarbonylindolin-2-yl)ethanone (2n)

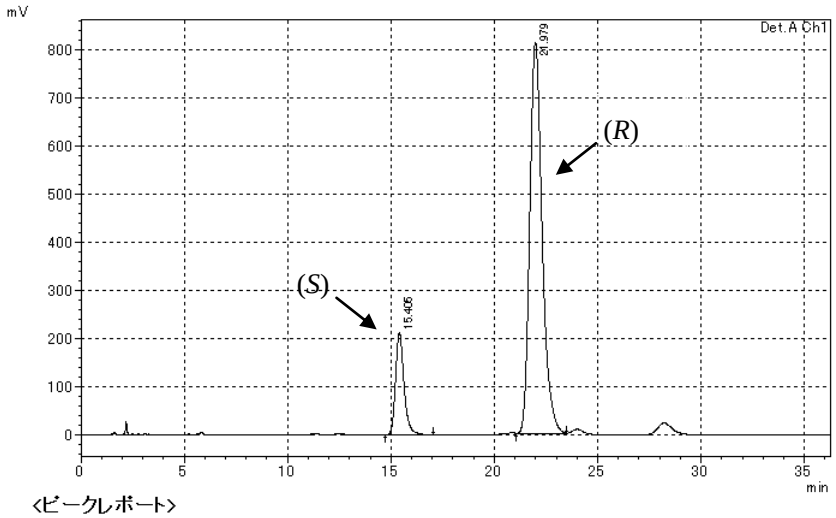




〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	15.391	3440079	121374	50.172	58.731	
2	21.979	3416531	85288	49.828	41.269	
合計		6856610	206661	100.000	100.000	

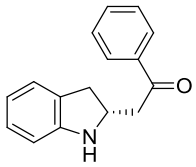


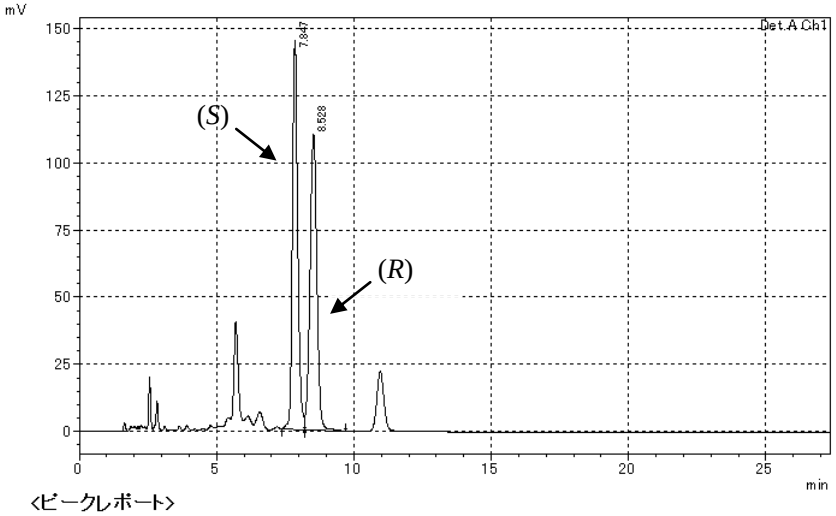
〈ピークレポート〉

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	15.405	6099232	212260	15.350	20.716	
2	21.979	33635520	812369	84.650	79.284	
合計		39734752	1024628	100.000	100.000	

(*R*)-1-Phenyl-2-(indolin-2-yl)ethanone (4)





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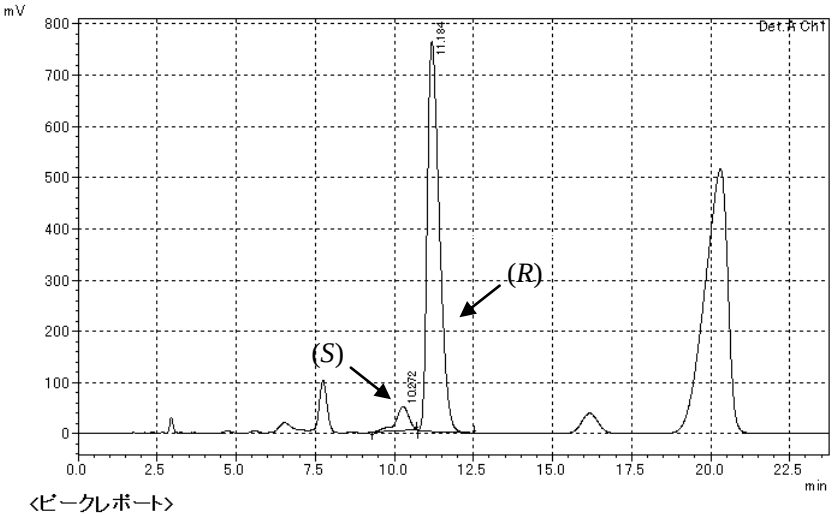
検出器A Ch1 250nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	7.847	1938868	144909	50.294	56.884	
2	8.528	1916200	109838	49.706	43.116	V
合計		3855068	254747	100.000	100.000	

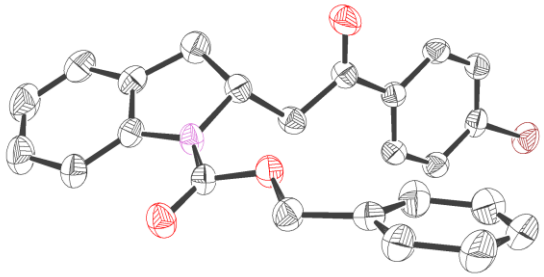


<ピークレポート>

検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.272	1371610	47294	6.375	5.849	
2	11.184	20143232	761263	93.625	94.151	
合計		21514841	808557	100.000	100.000	

ORTEP Drawing of 2g



Identification code	**2g**	
Empirical formula	$C_{24}H_{20}BrNO_3$	
Formula weight	450.32	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 4.8951(6) Å	α= 90°
	b = 18.566(2) Å	β= 96.116(2)°
	c = 11.3888(14) Å	γ = 90°
Volume 1029.2(2) $Å^3$		
Z	2	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	2.022 mm^{-1}	
F(000)	460	
Crystal size	0.50 x 0.30 x 0.30 mm^3	
Theta range for data collection	1.80 to 27.02°.	
Index ranges	-4<=h<=6, -23<=k<=23, -11<=l<=14	
Reflections collected	6282	
Independent reflections	4166 [R(int) = 0.0211]	
Completeness to theta = 27.02°	99.6 %	
Absorption correction	None	
Max. and min. transmission	0.5822 and 0.4313	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4166 / 1 / 214	
Goodness-of-fit on F^2	0.981	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0953	
R indices (all data)	R1 = 0.0579, wR2 = 0.1022	
Absolute structure parameter	0.014(10)	
Largest diff. peak and hole	0.523 and -0.166 e.$Å^{-3}$	